

Singlet Oxygen Responsive Small Molecules and Polymers

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Abstract

Conjugated polymers are widely used in applications for developing sensory materials. The binding of a single analyte to one of the receptors in conjugated polymer results in an amplified response due to the migration of the exciton on the polymer chain. This amplification of the signal makes the conjugated polymers more advantageous relative to small molecule sensors. This thesis describes the use of conjugated polymers as well as non-conjugated polymers, mimicking the light harvesting behavior of conjugated polymers, that response to photogenerated singlet oxygen in both organic solvent and aqueous environment.

Chapter 2 describes conjugated poly(fluorene-*co*-phenylene)s (PFs) with 2,5-diarylfuran moieties as nonconjugated pendants that respond to singlet oxygen by fluorescence quenching. By oxidizing the diarylfurans to more electron-poor moieties, singlet oxygen causes poly(fluorene-*co*-phenylene) conjugated backbones to donate excited electrons to the oxidized pendants, resulting in quenching of up to 93% of the initial fluorescence of the polymer.

Chapter 3 describes two-dimensional conjugated poly(phenylene-ethynylene)s (PPEs) linked to singlet oxygen-reactive diethynyltetracene units through phenylene-ethynylene (PE) bridges. Small molecule models of the polymers showed ratiometric responses of fluorescence upon exposure to singlet oxygen. The fluorescent responses of the tetracene-linked PPEs, however, were remarkably different: i) upon exposure to singlet oxygen, fluorescence intensity and fluorescence lifetime of the side-chain tetracenes was increased initially,

indicating an analyte-induced slowing of self-quenching due to high local acene concentration, and ii) ratiometric blue-shifted response did not occur until approximately 75% of pendant acenes were oxidized, which highlights the potential utility of analyte-induced removal of traps in light-harvesting fluorescent materials.

Chapter 4 describes the design of a system that respond singlet oxygen in water for potential use in bioanalytical applications such as protein sensing. The designed system mimics the light harvesting behavior of CPs, but is prepared with an acrylic polymer formulation that is easier to make water-soluble. The signal transduction mechanism uses $^1\text{O}_2$ to communicate the presence of dye-labeled protein to the responsive non-conjugated polymer and prevents proteins from directly interacting with the polymer.

For Ozgur

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“About 13.5 billions years ago, matter, energy, time and space came into being in what is known as the Big Bang. The story of these fundamental features of our universe is called physics.

About 300,000 years after their appearance, matter and energy started to coalesce into complex structures, called atoms, which then combined into molecules. The story of atoms, molecules and their interactions is called *chemistry*”

From *Sapiens: A Brief History of Humankind* by Yuval Noah Harari

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List of Common Abbreviations

AIBN.....	Azobisisobutyronitrile
CP.....	Conjugated Polymer
CPE.....	Conjugated polyelectrolytes
DCM.....	Dichloromethane
DFT.....	Density Functional Theory
DIPA.....	Diisopropylamine
DMAP.....	Dimethylaminopyridine
DMF.....	Dimethylformamide
DMSO.....	Dimethyl sulfoxide
DPA.....	9,10-diphenylanthracene
EPO.....	Endoperoxide
FRET.....	Fluorescence Resonance Energy Transfer
GPC.....	Gel Permeation Chromatography
HOMO.....	Highest Occupied Molecular Orbital
HRMS.....	High Resolution Mass Spectrometry
IC.....	Internal Conversion
ISC.....	Intersystem Crossing
LED.....	Light Emitting Diode
LOCI.....	Luminescent Oxygen Channeling Immunoassay
LUMO.....	Lowest Occupied Molecular Orbital
MB.....	Methylene Blue
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
nCP.....	Nonconjugated polymers
NMP.....	<i>N</i> -Methyl-2-pyrrolidone
NMR.....	Nuclear Magnetic Resonance
OD.....	Optical Density/Absorbance
OPE.....	Oligophenylene-ethynylene
PDI.....	Polydispersity Index
PET.....	Photo-induced Electron Transfer
PF.....	Poly(fluorene)
PMMA.....	Poly(methyl methacrylate)
PPE.....	Poly(phenylene ethynylene)
PPV.....	Poly(phenylene vinylene)
PTSA.....	<i>p</i> -toluenesulfonic acid
TCSPC.....	Time-correlated Single Photon Counting
THF.....	Tetrahydrofuran
TLC.....	Thin Layer Chromatography
TMS.....	Trimethylsilyl
TMT.....	Teracenomonothiophene
TTA.....	Triplet- triplet annihilation
UV.....	Ultraviolet
Φ_F	Quantum Yield of Fluorescence
τ_f	Lifetime of Fluorescence

Singlet Oxygen Responsive Small Molecules and Polymers

Chapter 1:

Introduction to Conjugated Polymers: Structures, Photophysics, and Applications

1.1 Introduction to Conjugated Polymers

Conjugated polymers (CPs) are unsaturated macromolecules with alternating single and double bonds throughout the polymer backbone. They display interesting properties due to continuous overlapping of π -orbitals along the polymer backbone.¹ Their unique semiconducting, photophysical and electronic properties make them very useful and attractive in a diverse range of applications including, light-emitting diodes (LEDs),^{2,3} solar cells,⁴ and sensors.^{5,6} Figure 1.1 shows some examples of prevalent functional CPs, including polyacetylene, poly (phenylene), poly (phenylene vinylene), poly (phenylene ethynylene), and poly (fluorene).

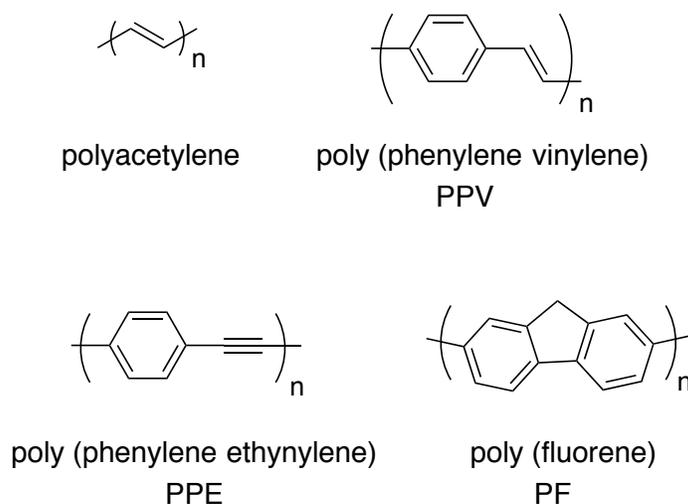


Figure 1.1. Structure of commonly seen CPs.

Metal-catalyzed C-C bond forming reactions, particularly palladium-catalyzed coupling reactions, have become very popular in the synthesis of CPs due to mild reaction conditions, a variety of compatible solvents, and tolerance to wide variety of functional groups.⁷ The synthesis of poly (fluorene)s (PFs) by Suzuki Coupling,⁸ poly(phenylene vinylene)s (PPVs) by Heck coupling,⁹ and

poly(phenylene ethynylene)s (PPEs) by Sonogashira coupling¹⁰ are some examples of palladium-catalyzed coupling reactions for the syntheses of conjugated polymers.

In recent years, the application of fluorescent conjugated polymers in the field of responsive materials for sensing chemical and biological analytes has received much attention due to facile chemical functionalization, great thermal stability and relatively easy processability. Chemical sensors based on conjugated polymers respond to various types of analytes with a similar detection mechanism. Transduction of certain analyte binding event can be shown by using changes in the fluorescence emission of a conjugated polymer, which can be in the form of reduced emission from the polymer (turn-off), the appearance of fluorescence emission (turn-on), or both.

1.1.1 Photophysical Properties of Conjugated Polymers

Conjugated polymers show interesting photophysical properties as a result of interactions with light. Once a molecule has absorbed energy in the form of electromagnetic radiation, there are number of possible pathways by which the photon-generated excited state can release its energy and return the ground state. These processes are classically presented by Jablonksi Diagram, which is shown in Figure 1.2. Ground state (S_0) is the lowest energy state, it is statistically the most common energy state for most chemical species at room temperature. Absorption of photons results in promotion to higher-energy excited states (S_1 , S_2 , S_3 ,...) depending on how much energy is absorbed. Although several processes

will occur following absorption of light, non-radiative relaxation from higher vibrational energy levels to the lowest vibrational energy level of the first excited state will be most likely first. This process is known as Internal Conversion (IC). IC occurs quite rapidly, 10^{-14} - 10^{-11} seconds after light absorption. That is significantly faster than the average fluorescence lifetime, which is typically 10^{-9} - 10^{-7} seconds. That is the reason why emission usually occurs from the lowest energy electronic excited state. If the emission occurs between the states of the same spin (S_1 to S_0), it is called "Fluorescence". Other pathways of returning to the ground state from the excited singlet state besides fluorescence emission may be the release of heat non-radiatively (IC) or intersystem crossing (ISC) to a triplet excited state (T_1). Intersystem crossing (ISC) is a non-radiative decay between different spin states. If the emission occurs after ISC between two different spin states (T_1 to S_0), it is called "Phosphorescence". The typical phosphorescence lifetimes are rather longer than that of fluorescence, which are 10^{-4} seconds to minutes or even hours. Therefore, fluorescence is statistically much more likely to occur than phosphorescence for most molecules.

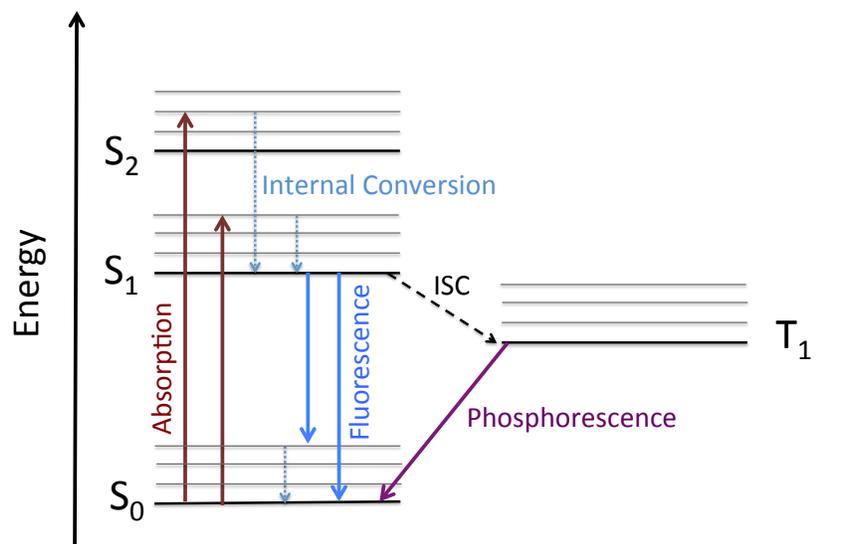


Figure 1.2. Jablonski Diagram showing the transitions between ground (S₀) and excited (S₁ and T₁) states. Solid arrows show radiative decays, whereas dashed arrows show non-radiative decays.

Fluorescent molecules, also known as fluorophores, have two important aspects: the quantum yield and lifetime. The fluorescent quantum yield (Φ_F) of a fluorophore is defined as ratio of the number of photons emitted over the number of photon absorbed. More explicitly, the quantum yield gives the probability of the excited state being deactivated by fluorescence rather than a non-radiative decay. Therefore, quantum yield can be given by,

$$\phi_F = \frac{k_r}{k_r + k_{nr}} \quad (1)$$

where k_r is the radiative rate constant and k_{nr} is non-radiative rate constant. Non-radiative decay can be in the form of different deactivation pathways, such as internal conversion, intersystem crossing, or other quenching mechanisms. Higher

quantum yields occurs with relatively fast rate of radiative decay and it is desired in sensing applications, which rely on fluorescence output.

A convenient method for the determination of quantum yield of a fluorophore is comparison with standards of known quantum yield. First, a fluorescent standard absorbing and emitting in the wavelength range of the fluorophore to be investigated should be chosen. Then, it simply requires absorbance and emission of the fluorophore and standard. The optical density (absorbance) should be kept below 0.05 to avoid inner filter effects. The quantum yield of the fluorophore is then calculated using,

$$\phi_F = \phi_S \frac{I}{I_S} \frac{OD_S}{OD} \frac{n^2}{n_S^2} \quad (2)$$

where Φ is quantum yield, I is the integrated intensity of emission, OD is the absorbance at the excitation wavelength, n is the refractive index of solvent. The subscript S refers to the standard fluorophore with known quantum yield.¹¹

The average time a molecule spends in its excited state before returning to the ground state is termed as fluorescence lifetime (τ_f), which is given by,

$$\tau_f = \frac{1}{k_r + k_{nr}} \quad (3)$$

where k_r is the radiative rate constant and k_{nr} is non-radiative rate constant. Typically, the lifetimes of fluorophores range from picoseconds to hundreds of nanoseconds. Lifetime of the fluorophore can be measured by time-correlated single-photon counting (TCSPC) method.

1.1.2 Fluorescence Quenching

There are additional pathways besides IC and ISC that result in decrease in the fluorescence quantum yield or lifetime, or both. These are referred as fluorescence quenching. There are different types of quenching processes including excited state reactions, molecular rearrangements, ground state complex formation, collisional quenching, and energy transfer.¹¹ There are two principle mechanisms of fluorescence quenching: static and dynamic quenching. In static quenching, the fluorophore and quencher bind to form a ground state complex, which is non-fluorescent; therefore, it decays non-radiatively upon photoexcitation.¹² On the other hand, dynamic quenching, also known as collisional quenching, occurs due to collisional interactions between fluorophore and quencher while the fluorophore is in the excited state.¹² In both cases, the decrease in the fluorescence intensity can be expressed by Stern-Volmer Equation,

$$\frac{F_0}{F} = 1 + K_{SV}[Q] \quad (4)$$

where F_0 is the fluorescence intensity in the absence of quencher, F is the fluorescence intensity in the presence of quencher, K_{SV} is the quenching constant, and $[Q]$ is the quencher concentration. In dynamic quenching, lifetime of fluorophore is also quenched due to the interactions in the excited state. Therefore, Stern-Volmer Equation can be rewritten by substituting fluorescence intensities with the lifetime,

$$\frac{\tau_0}{\tau} = \frac{F_0}{F} = 1 + K_D[Q] = 1 + k_q\tau_0[Q] \quad (5)$$

where τ_0 is the lifetime of fluorophore in the absence of quencher, τ is the lifetime of fluorophore in the presence of quencher, $[Q]$ is the quencher concentration, and k_q is the bimolecular quenching constant. If the quenching is dynamic, K_{SV} is given by K_D , which is equal to $k_q\tau_0$.¹¹ In static quenching, because fluorescence intensity is dependent on quencher concentration, Stern-Volmer equation can be represented by association constant for complex formation,

$$\frac{F_0}{F} = 1 + K_S[Q] \quad (6)$$

where K_S is the association constant of the ground-state complex between the fluorophore and the quencher. Both in collisional and static quenching, dependence of F_0 over F on quencher concentration is linear. Therefore, it is difficult to determine the mechanism of quenching by steady-state Stern-Volmer experiments. Time-resolved Stern-Volmer measurements need to be examined in order to be able to distinguish two mechanisms.

In many instances, two mechanisms occur at the same time.¹³ In this case, the equation below can be used to calculate the portion of static and dynamic quenching,

$$\frac{F_0}{F} = (1 + K_C[Q])(1 + K_S[Q]) = 1 + (K_C + K_S)[Q] + K_C K_S [Q]^2 \quad (7)$$

This equation is second order in $[Q]$. Therefore, upward curvature is expected when both static and collisional quenching occur. However, for low quencher concentrations and small Stern-Volmer constants, the contribution from the $[Q]^2$ term to the total quenching will be much less than from the two linear terms that will make plot appear linear.¹² Therefore, time-resolved fluorescence measurement should be done to determine the portion of collisional quenching.

1.2 Photo-induced Electron and Energy Transfer

Photo-induced electron and energy transfer are the main steps of many interesting chemical and physical processes that occur in various disciplines such as physics, chemistry, materials science, and biology.¹⁴ They are examples of processes that may result in fluorescence quenching.¹⁵ In the systems that have donor-acceptor characteristics, excited states may relax back to the ground state by photo-induced electron or energy transfer.

1.2.1 Photo-induced Electron Transfer (PET)

In photo-induced electron transfer, an electron migration occurs between two molecules or parts of the same molecule that are in ground state and photo-excited state, respectively. Figure 2 is a schematic illustration of PET. As shown in Figure 1.3, excited state molecule can be either the electron donor (D) or the electron acceptor (A). An asterisk (*) indicates an excited state.

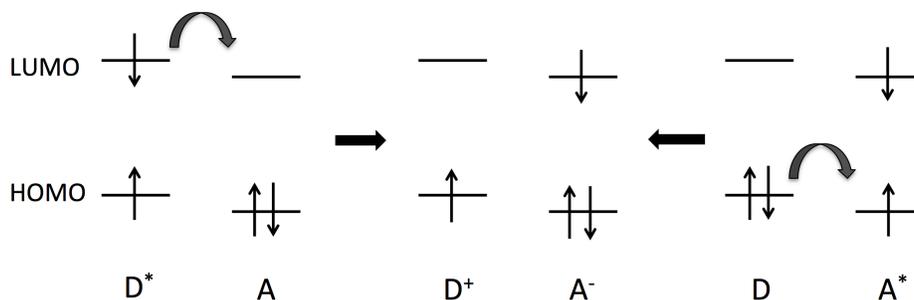


Figure 1.3. Photo-induced electron transfer processes.

Electron transfer can occur from the donor to the acceptor, depending on oxidation and reduction potential of the donor and acceptor as well as the energy of excited state. As a result, the excited state dissipates in a non-radiative way.¹⁶

The Rehm-Weller equation is used to calculate the free energy of PET from redox potentials and excitation energy,

$$\Delta G = E_{ox} - E_{red} - E_{0-0} - \frac{e^2}{\epsilon d} \quad (8)$$

where E_{ox} is the oxidation potential of donor and E_{red} is the reduction potential of acceptor in solvent. E_{0-0} is the energy of the zero-zero transition to the lowest excited singlet state (S_0 to S_1). The last term is the coulombic interaction energy; ϵ is the dielectric constant of the solvent, and d is the distance between the charges.^{11,16}

1.2.2 Photo-induced Energy Transfer

Another important process that occurs in the excited state and may lead to fluorescence quenching is energy transfer. It attracts considerable interest due to potential applications in optoelectronics as well as in biological systems. In energy transfer, the excited state is exclusively an energy donor as opposed to electron transfer. More specifically, the donor is the chromophore that initially absorbs the energy and then energy is subsequently transferred to the acceptor chromophore. The transfer of energy results in a decrease in the emission intensity of the donor (fluorescence quenching), and an increase in the emission intensity of the acceptor. It can be described by following process,



where D is the energy donor, A is the energy acceptor, and the asterisk (*) shows the excited state. For the energy transfer to be thermodynamically favorable, the excited state energy of the donor must be higher than that of acceptor. There are two types of energy transfer mechanism: Coulombic and electron exchange mechanism. The coulombic mechanism (also known as Resonance, Förster-type, dipole-dipole or through-space in the literature) involves the long-range dipole-dipole interactions.¹⁷ On the other hand, the electron exchange mechanism (also known as collisional, dexter-type, or through-bond) demands much closer contact between the donor and acceptor.¹⁸ Figure 1.4 is an illustration of both mechanisms.

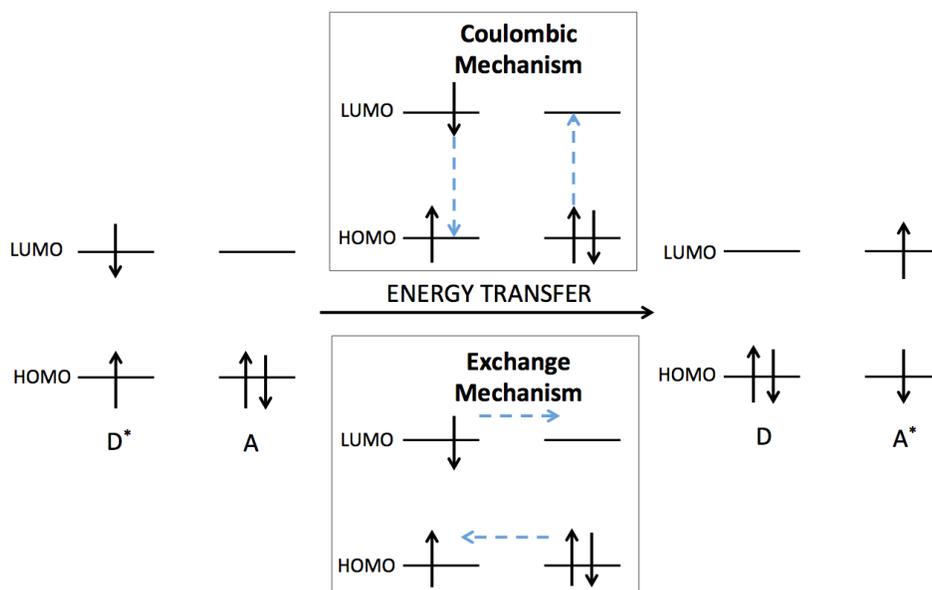


Figure 1.4. The illustration of energy transfer mechanisms: Coulombic and Exchange Mechanism.

1.2.2a Coulombic Energy Transfer

Coulombic Energy Transfer, also known as fluorescence resonance energy transfer (FRET), is a physical process, by which energy created by excitation of donor is transferred to an nearby molecule, the acceptor, by long-range dipole-dipole coupling. Therefore, excitation of the donor results in fluorescence emission of the acceptor. There are couple requirements for FRET to occur. First of all, it is highly distance-dependent. The donor and acceptor must be within a range of 1 to 10 nm of each other. According to Förster`s theory, the efficiency of the FRET depends on the inverse sixth power of the distance between the donor and acceptor (r), and rate of energy transfer is given by,

$$rate = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad (10)$$

where τ_D is the excited state lifetime of the donor in the absence of acceptor, R_0 is the critical transfer distance for which probability of energy transfer is equal to probability of spontaneous deactivation of the donor.¹⁷ Equation (10) also implies that the lifetime of the donor must be of sufficient duration to permit FRET. Another important criterion for FRET to happen is the spectral overlap between donor and acceptor. Emission spectrum of the donor must overlap with the absorption spectrum of the acceptor as shown in Figure 1.5.

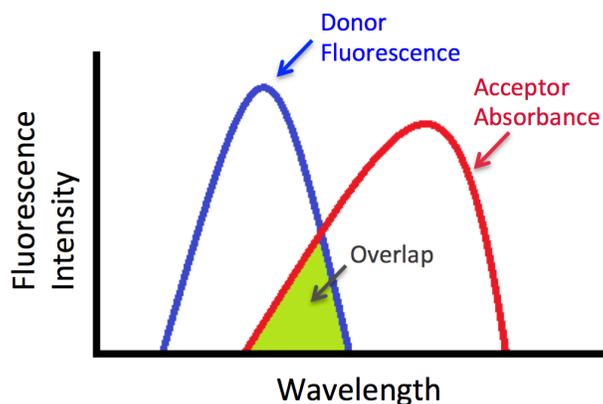


Figure 1.5. The illustration of spectral overlap between donor and acceptor.

Relative orientations and frequency of transition dipoles of donor and acceptor also affect the efficiency of energy transfer. For classical dipole-dipole energy transfer to happen, frequency of oscillating dipole of excited electrons of donor must match with natural oscillation frequency of electrons on acceptor so that it can interact with the acceptor and induce oscillation of the acceptor.¹⁹ These oscillations will lead to excitation of the electron on the acceptor with the corresponding relaxation of the excited electron on the donor. The dipole-dipole coupling mechanism is possible only in spin-allowed transitions with large transition dipoles. Therefore, only singlet –singlet energy transfer can proceed by this mechanism.¹⁹



where a singlet state produces a singlet state.

1.2.2b Electron Exchange Energy Transfer

Electron exchange (Dexter) energy transfer is a short-range process in which two molecules (intermolecular) or two parts of a single molecule (intramolecular) exchange their electrons, simultaneously. It requires much closer contact between the donor and acceptor because it occurs via collisions. It means the donor and acceptor must be sufficiently close that their electron clouds overlap significantly in space.¹⁹ The exchange mechanism typically occurs within 10 Angstroms. The rate constant of energy transfer is given by,

$$k_{ET} = KJ \exp(-2R_{DA}/R_{DA}^0) \quad (12)$$

where K is a parameter related to specific orbital interactions, J is the normalized spectral overlap integral, R_{DA} is the distance between D^* and A, and R_{DA}^0 is the distance between D^* and A when they are in van der Waals contact.¹⁹ Because efficiency of electron exchange energy transfer does not depend on the transition dipoles, triplet-triplet energy transfer and triplet-triplet annihilation is possible as well as singlet-singlet energy transfer in the exchange mechanism.^{19,20,21} Triplet-triplet annihilation (TTA) is a special case of exchange energy transfer in which two triplets interact to produce an excited singlet and a ground-state singlet.^{19,20}



The rates and efficiencies of energy transfer do not depend on only electronic factors but also depends on diffusional and structural properties. A molecular spacer generally connects the donor and acceptor in order to bring the donor and acceptor within critical distance for the energy transfer occurs. In FRET, a non-conjugated linker usually connects the donor and acceptor and the

energy transfer occurs through space.²² However, a conjugated linker in electron exchange energy transfer usually links the donor and acceptor.^{23,24} The conjugated linker must prevent the donor and acceptor fragments from becoming planar because otherwise system would behave as a single chromophore.²²⁻²⁴ Figure 1.6 visualizes the non-conjugated and conjugated linkers between the donor and acceptor.

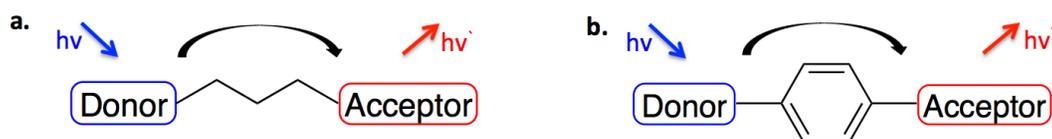


Figure 1.6. Examples of the non-conjugated and conjugated linkers between the donor and acceptor: **(a)** is FRET, **(b)** is electron exchange energy transfer.

1.3 Applications of Conjugated Polymers

The optoelectronic and semiconducting properties of conjugated polymers make them very good candidates in the diverse range of applications from organic electronic devices to biomedical applications.²⁵⁻²⁷ They also have a number of advantages in the field of developing responsive materials for detection and sensory applications.^{6,28} A key advantage of CP-based sensors over small molecule based sensors is the amplified response that is sensitive to very minor changes.⁶ Transport properties, electrical conductivity or energy migration in CPs provide amplified sensitivity.⁵ As shown in Figure 1.7, a small molecule sensor, composed of receptor and analyte, can provide a real-time response when the equilibrium between the receptor and analyte is rapid. Therefore, the detection sensitivity depends on the equilibrium constant of the receptor-analyte complex and alters with the concentration of analyte. However, a CP-based sensor, which

wires sensory molecules in series,⁵ yields enhanced sensitivity due to amplification of the signal.

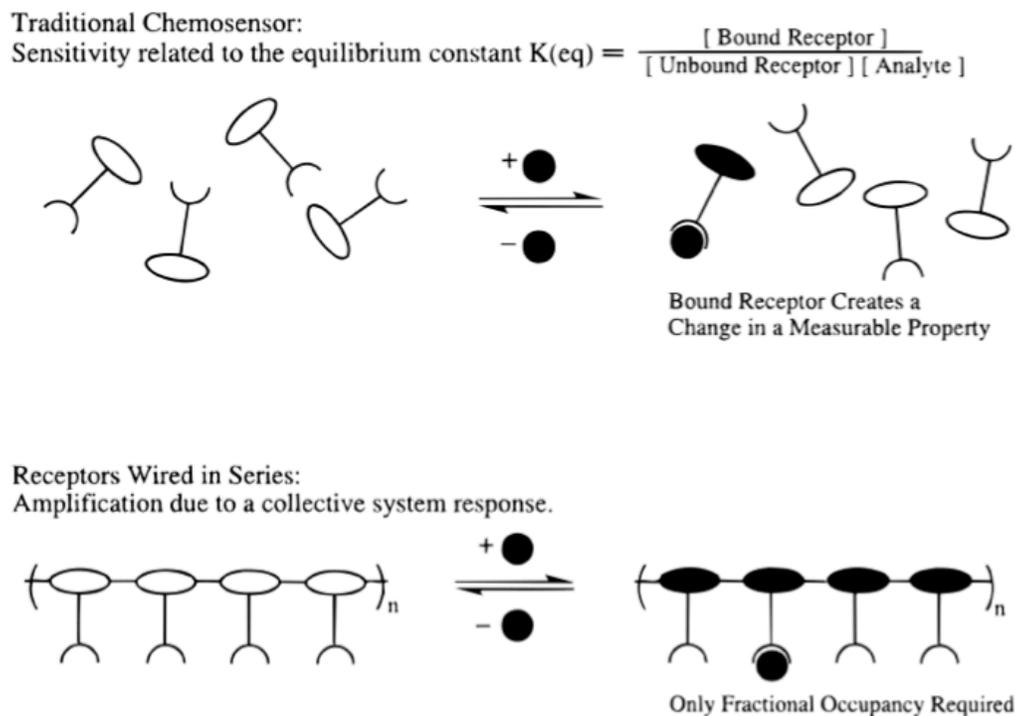


Figure 1.7. Schematic representation of sensory signal amplification in conjugated polymers (molecular wires), a concept advanced by Swager et al.^{5,6,29}

The sensors based on conjugated polymers detect various types of analytes with similar detection mechanism. Transduction of certain analyte binding event can be shown by using changes in the fluorescence of conjugated polymer, which can be either reduced emission from the polymer (turn-off) or the appearance of fluorescence emission (turn-on) or both. During the course of this thesis, you will see some examples of conjugated polymers designed for sensing singlet oxygen.

1.4 Introduction to Singlet Oxygen

Molecular oxygen, O_2 , is essential for many processes that occur on earth. Unlike most molecules, electronic ground state of molecular oxygen is a spin triplet; therefore, it often behaves like a radical in chemical reactions.³⁰ Molecular oxygen has two low-lying singlet excited states, $^1\Delta_g$ and $^1\Sigma_g^+$ above the triplet state as shown in Figure 1.8.³¹

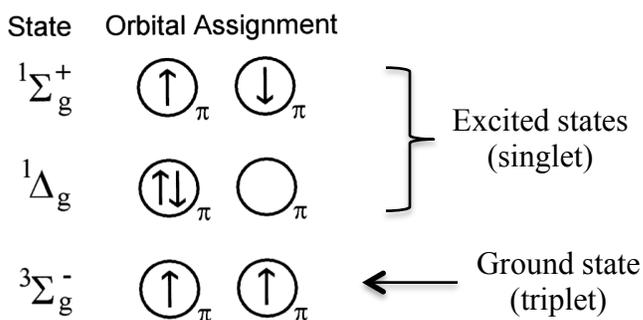


Figure 1.8. Representations of molecular oxygen lowest singlet and triplet states.³¹

The only difference in the electronic configurations of these excited states is the structure of the π -antibonding orbitals. The transition from $^1\Delta_g$ to electronic ground state is spin forbidden making $^1\Delta_g$ a relatively long-lived species. The electronically excited $^1\Sigma_g^+$, on the other hand, is a short-lived species as a result of fast, spin allowed relaxation to the $^1\Delta_g$. That is why the electronically excited $^1\Delta_g$ state is referred as singlet oxygen (1O_2).³¹

1.4.1 Generation and Applications of Singlet Oxygen

There are different methods of generation of 1O_2 , with photosensitization being the most commonly used method because of its simplicity and

controllability.³¹ The only required elements for the photosensitization are oxygen, photosensitizer, and light of appropriate wavelength. In this method, the sensitizer (in the ground state (S_0)) is excited by light to the higher excited electronic singlet states which then relaxes to the lowest excited singlet state of S_1 . Intersystem crossing converts S_1 to the sensitizer's triplet excited state (T_1). Collision with molecular oxygen results in an energy transfer, exciting oxygen to its singlet state.^{30,31}

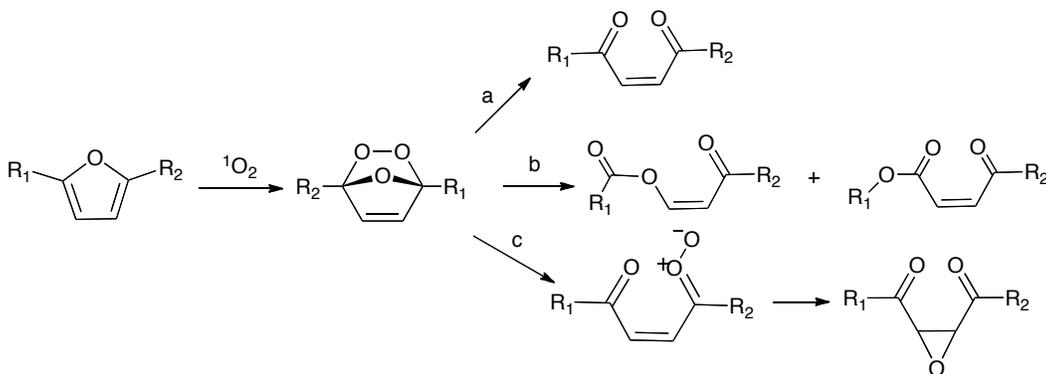
Two singlet excited states enable the molecular O_2 having unique properties by allowing rich and accessible chemistry.³² In particular, 1O_2 plays an important role in the surface patterning,³³ protein inactivation,³⁴⁻³⁶ fine chemicals synthesis,³¹ and especially in the photodynamic therapy of cancer.^{31,37} Excess 1O_2 in biological systems is believed to be toxic: 1O_2 oxidizes variety of biological molecules including DNA, protein, and lipids. On the other hand, it also has a significant place in the cell-signaling cascade and in the induction of gene expression.³⁸ Therefore, the design of stable and specific probes for 1O_2 has been increasingly important.

1.4.2 Singlet Oxygen Probes

Most of 1O_2 probes rely on the cycloaddition reaction of 1O_2 with acenes, particularly anthracenes.³⁸⁻⁴¹ Our group prepared a conjugated polymer with tetracene pendant groups that respond to 1O_2 ratiometrically with enhancement of fluorescence.⁴² To the best of our knowledge, it was the first reported CP system demonstrating a ratiometric response with fluorescence enhancement to 1O_2 .

1.4.2a Furans as Singlet Oxygen Probes

Furans undergo cycloaddition reactions with $^1\text{O}_2$ like acenes. The cycloaddition reaction of furan with $^1\text{O}_2$ forms a bicyclic endoperoxide intermediate, which is only stable at low temperatures in the absence of stabilizing substituents.⁴³ This endoperoxide intermediate breaks down to a diversity of products whose structures strongly depend on both the substituents of furan and the conditions of the reaction.⁴⁴ Some of the previously identified products of rearrangement of these endoperoxide intermediates are shown in the Scheme 1.



Scheme 1.1. Some of the possible products of endoperoxides at room temperature.⁴³⁻⁴⁵

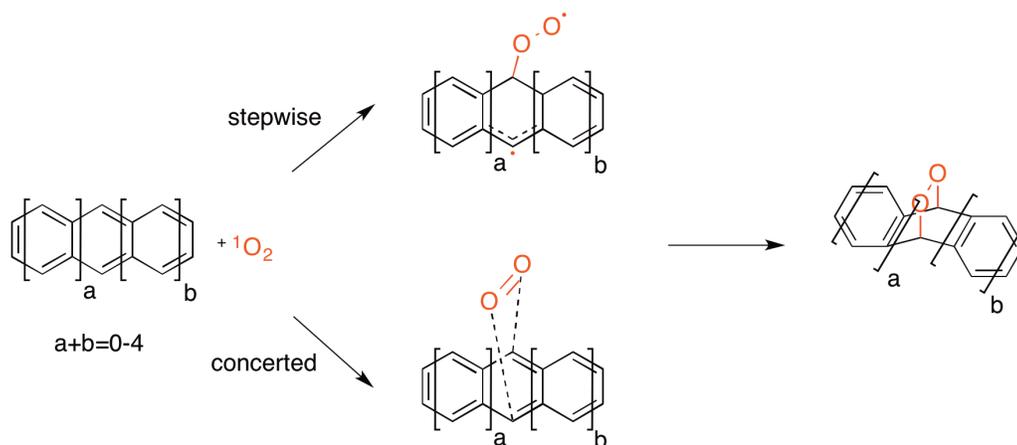
Reduction of the endoperoxide intermediate by cleavage of the O-O bond and loss of oxygen yields the diketone product shown in pathway a.⁴³ The ester products, shown in pathway b, are formed by Baeyer-Villiger like rearrangement.⁴³ Formation of epoxide, as in path c, is initiated by decomposition of endoperoxide followed by the donation of oxygen from the carbonyl oxide intermediate.⁴³ Because all of these products are oxidized and more electron poor than the furan starting material, we propose that the fluorescence of electron rich

fluorophores (in our case, conjugated polymer backbone) is likely quenched by photoinduced electron transfer.

1.4.2b Acenes as Singlet Oxygen Probes

Acenes undergo [4+2] cycloaddition (Diels-Alder Reaction) reaction with singlet oxygen that forms endoperoxides of acenes (EPOs). Many aromatic EPOs have low thermal stability, so their parent acenes can be recovered at elevated temperatures. In general, Diels-Alder reaction may take place via two different mechanisms: concerted or step-wise (Scheme 2). In the concerted mechanism, two new bonds are partially formed to the same extent in a single transition state. The stepwise mechanism involves the initial formation of single bond between singlet oxygen and acene and the subsequent formation of the second bond that yields EPO.^{46,47}

Therefore, the concerted mechanism is expected to be energetically more favorable than the stepwise mechanism.⁴⁸



Scheme 1.2. Representation of Stepwise and Concerted Mechanism.

According to the theoretical study by Reddy et al, change in the mechanism (from concerted to biradical) is observed for the reaction of acenes (benzene through pentacene) with singlet oxygen.⁴⁹ They found that only the concerted mechanism operates in the reaction of singlet oxygen with benzene and naphthalene, which is in agreement with previous studies.^{50,51} However, starting from anthracene, acenes react with singlet oxygen via the stepwise mechanism.⁴⁹

1.5 Conclusions

CPs are an important class of compounds that attracts many scientist from diverse range of areas due to their unique photophysical and optoelectronic properties. CPs are especially advantageous in the developing sensory materials due to amplification of response when they functionalized with a suitable receptor that respond to specific analyte. In this dissertation we describe a series of conjugated and non-conjugated polymers that respond to singlet oxygen in organic and aqueous solutions. The designed systems in the following work rely on changes in the emission intensity by either electron transfer or the interruption of energy transfer.

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Chapter 2:

Furan-Containing Singlet Oxygen-Responsive Conjugated Polymers

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2.1 Introduction

This chapter describes new conjugated polymers that contain 2,5-diarylfuran pendants and respond to singlet oxygen by photo-induced electron transfer resulting in fluorescence quenching. Conjugated polymers have a number of advantages for developing responsive materials for sensory applications. One of the main advantages is the intramolecular and intermolecular mobility of excitons and charge carriers. This mobility results in amplification of signal in sensing applications because one mobile exciton can probe a large number of potential trap sites. Fluorescent sensing schemes are usually intensity-based, which can use either fluorescence quenching (turn-off) or enhancement (turn-on), or a combination of both (ratiometric), although lifetime-based schemes are applicable. The systems that rely on fluorescence enhancement by removing an exciton trap have some distinct advantages over fluorescence quenching because it may prevent false positives from bleaching and fewer interferents. However, the amplification mechanism of CPs enables maximal amplification through by introduction of a trap for excitons that results in fluorescence quenching. This can be accomplished either by energy transfer or electron transfer quenching.¹ Therefore, it is advantageous to have a number of related strategies that show different types of fluorescent response that could be employed depending on the importance of different performance-related characteristics.

The development of new polymeric materials that respond to singlet oxygen (or $^1\text{O}_2$) is one of the main interest in our laboratory.² $^1\text{O}_2$ is generated readily by triplet energy transfer from the excited dye molecules to the ground

state O_2 as shown in Figure 2.1. Ambient O_2 , photosensitizer (dye), and light of appropriate wavelength are the only required elements for the photosensitization.³

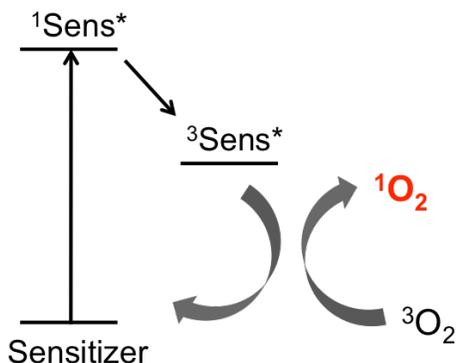


Figure 2.1. 1O_2 sensitization

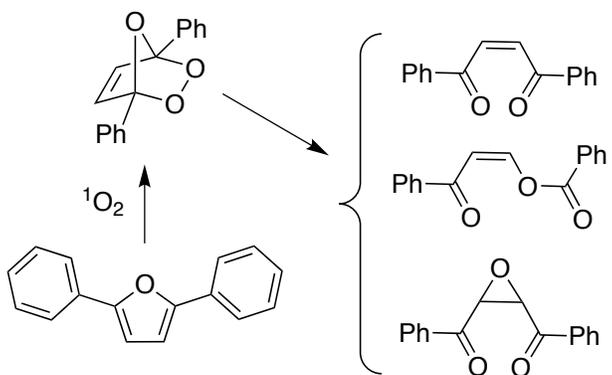
1O_2 is useful in applications such as surface patterning,⁴ photodynamic therapy,⁵ and protein inactivation.⁶⁻⁸ There are a number of known fluorescent sensing dyes that respond to 1O_2 through cycloaddition reaction between 1O_2 and acenes. These previously described dosimeters typically use anthracenes as the 1O_2 -reactive moieties;⁹⁻¹³ our group, however, has developed a tetracene-linked CP that shows a ratiometric fluorescent response to 1O_2 by interrupting energy transfer from the CP backbone to the tetracene pendant.¹⁴ Our group has also demonstrated a related approach using tetracene-doped CP thin films for responding to 1O_2 in aqueous environments.¹⁵

In addition to acenes, furans also undergo facile [4+2] cycloaddition reactions with 1O_2 ; the resulting endoperoxides, however, are only stable at low temperatures and react further at room temperature to produce other products.¹⁶ Incorporation of furan moieties is becoming an increasingly important design strategy in conjugated materials:¹⁷ Bendikov and coworkers recently prepared a

series of oligofurans with up to nine rings,¹⁸ and have also studied the semiconducting¹⁹ and Diels-Alder reactivity²⁰ of these materials. A number of groups have prepared conjugated polymers with furan rings in the main chain, generally to compare their properties to the more typical thiophene-based polymers.²¹⁻³² Diels-Alder reactions between furans and maleimides have been a design feature of functional conjugated polymers,^{26,33} including work from the group of Reynolds that used furan-substituted polyfluorenes to enable solution-processed multilayer polymer-based light-emitting devices.³⁴ We are unaware of any reported $^1\text{O}_2$ -responsive systems comprising a coupled furan derivative and fluorophore. Herein we present conjugated polymers that respond to $^1\text{O}_2$ by fluorescence quenching induced by oxidation of 2,5-diarylfuran pendant groups.

2.2 Results and Discussion

Scheme 1 shows that endoperoxide intermediates formed upon cycloaddition between $^1\text{O}_2$ and diarylfurans decompose to several products resulting from fragmentation at room temperature. There are a number of pathways resulting in different products. The distribution of these products can depend strongly on both the structure of the starting material and the conditions of the reaction; the final products, however, are generally oxidized, electron-poor molecules relative to the furan starting material. Therefore, our hypothesis was that the products of the $^1\text{O}_2$ -diarylfuran reaction would be more likely to quench the fluorescence of electron-rich fluorophores by photoinduced electron transfer than the comparatively electron-rich diarylfuran derivatives.



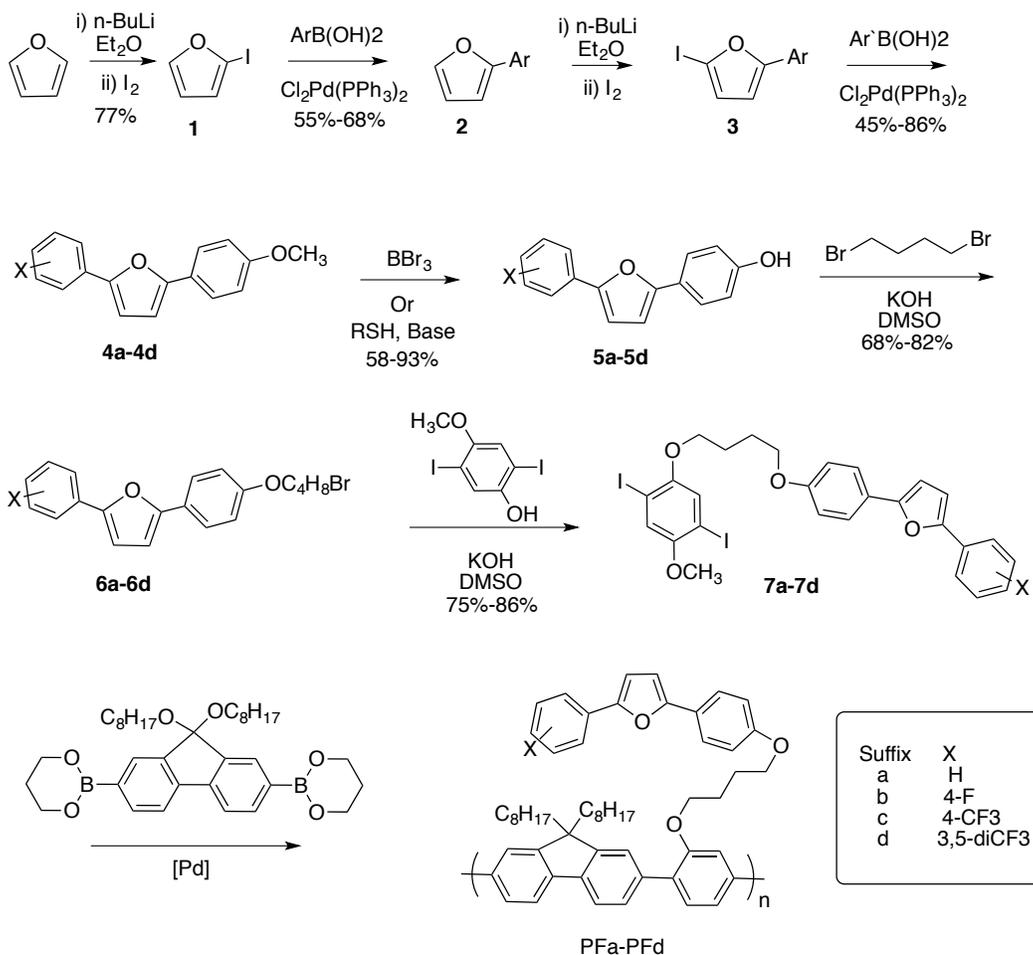
Scheme 2.1. The intermediate endoperoxide product of $^1\text{O}_2$ -diphenylfuran cycloaddition opens at room temperature to give one of several oxidized products. The oxidized products are potential fluorescence quenchers by photoinduced electron transfer.

2.2.1 Synthesis of Furan-linked Conjugated Polymers

Scheme 2.2 illustrates the modular synthetic scheme of furan-linked poly(fluorene-*co*-phenylene) (**PF**) polymers with a variety of substituents on the 4-position of the terminal aryl ring of the diarylfuran moiety. Deprotonation of furan in the 2-position with *n*-BuLi followed by quenching with molecular iodine yielded 2-iodofuran **1**. Because of the instability of this molecule, it was converted as soon as possible to a 2-arylfuran **2** by Suzuki coupling. Various conditions for bromination at the 5-position of the furan gave 2-bromo-5-arylfuran in only low yields.³⁵ We found, however, that deprotonation with *n*-BuLi followed by quenching with I_2 gave higher yields of the iodofuran **3**, a common intermediate in the syntheses of all furan-containing monomers described here. Suzuki coupling of the unstable **3** with aryl boronic acids gave unsymmetrically substituted 2,5-diarylfurans **4a-4d**,³⁵ which each had a *p*-methoxyphenyl as one aryl ring, and either a phenyl or fluorinated phenyl ring as

the other. Deprotection of the methyl ether with either BBr_3 or alkylthiolate followed by a sequence of two alkylation reactions yielded the desired monomers furan-substituted diiodide monomers **7a-7d**.

Furan-containing monomers **7a-7d** were amenable to cross-coupling polymerizations for the synthesis of conjugated polymers. We prepared **PFa-d**, which had one furan moiety per repeat unit, using Suzuki polymerizations.



Scheme 2.2. Synthesis of furan-linked poly(fluorene-*co*-phenylene)s.

A similar strategy using 2,5-diiodohydroquinone gave diiodide monomers substituted with two diarylfurans **8a** and **8c**. We prepared **PF-8a** and **PF-8c**,

Sonogashira coupling conditions. Typical number-average molecular weights of all polymers synthesized were determined by gel-permeation chromatography and are between 8,000 and 25,000 g/mol with polydispersity indices between 1.2-2.8 (Table 2.1).

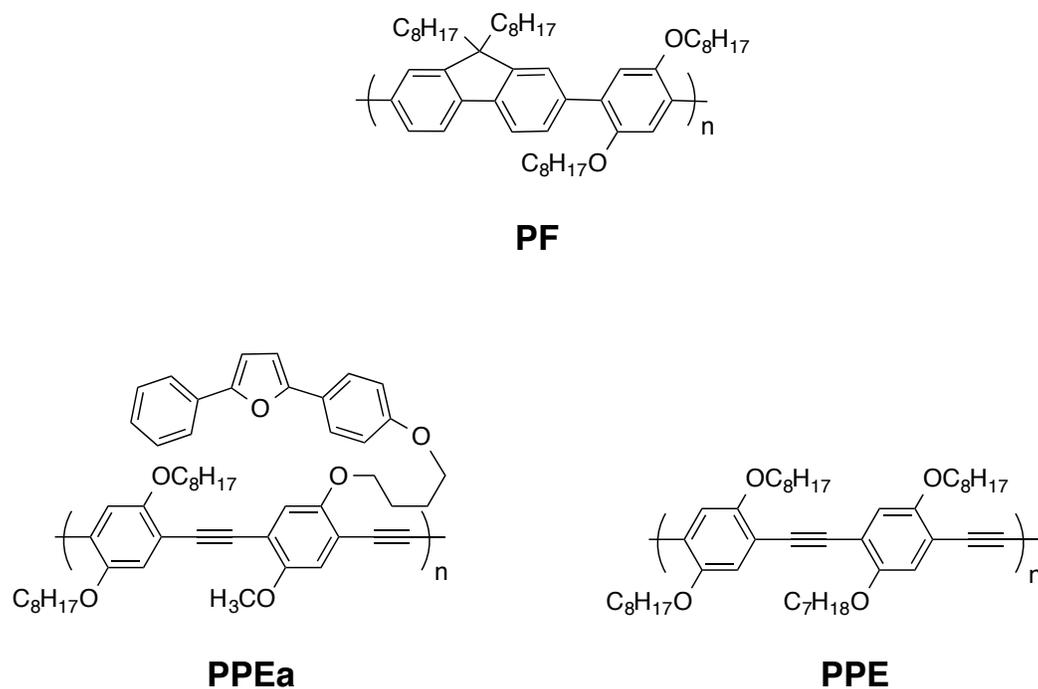


Chart 2.1. Other CPs investigated in this study

2.2.3 Spectral Properties of Synthesized Polymers

Figure 2.2 shows the normalized absorbance spectra of two furan containing conjugated polymers (**PFa** and **PPEa**), control polymers that do not have furan groups as pendants (**PF** and **PPE**), and a small molecule model of the furan pendant, compound **4a**. As Figure 2.1 and Table 2.1 illustrate, **PPE** derivatives have absorbance spectra that are red-shifted by about 70 nm from **PF** derivatives because of their more highly conjugated backbone. The shapes and spectral positions of these polymers are consistent with those reported in the

literature.³⁶ The shapes of absorbance spectra of furan-linked CPs **PFa** and **PPEa** show features attributable to both the conjugated polymer backbone and the furan pendants with no additional signals. These observations are both consistent with their chemical structures and the conclusion that no electronically significant interactions occur between the polymer chains and furan pendant groups. Diarylfuran **4a**, with a λ_{max} of 332 nm, does not absorb light at wavelengths greater than 370 nm, which enables selective irradiation of the CP backbones without the furan moieties absorbing light. Diarylfurans with donor-acceptor character due to fluorinated substituents (**4b**, **4c**, and **4d**) showed slightly red-shifted absorbance spectra, with **4d** having λ_{max} of 342 nm.

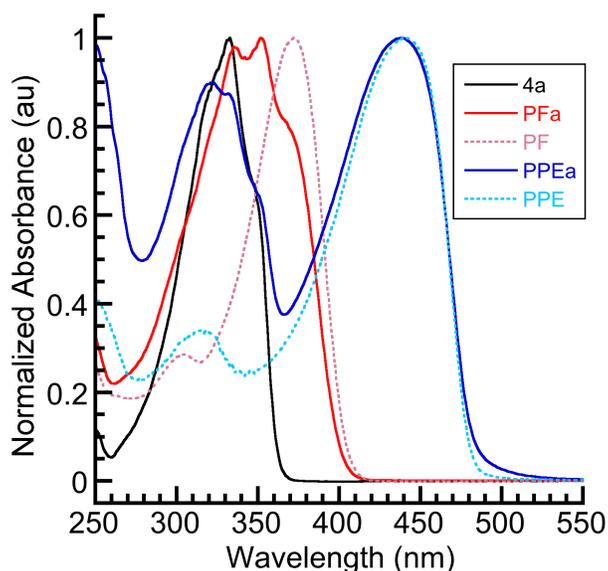


Figure 2.2. Normalized absorbance spectra (in CH_2Cl_2) of CPs with and without furan pendants, and the furan pendant model compound **4a**.

Figure 2.3 shows height-normalized emission spectra of furan-containing CPs **PFa** and **PPEa**, while Table 2.1 summarizes their emission maxima and

fluorescence quantum yields. These polymers have shapes of emission spectra that are indistinguishable from control polymers **PF** and **PPE**. Both excitation spectra and emission spectra acquired with an excitation wavelength of 320 nm revealed that excitation of the furan pendants on these polymers leads to emission from the polymer backbone. These observations are consistent with the conclusion that energy transfer from the larger band-gap furan to the smaller band-gap CP backbone, and that the presence of furan has at most a limited effect on the luminescence of the CP upon direct excitation of the polymer backbone.

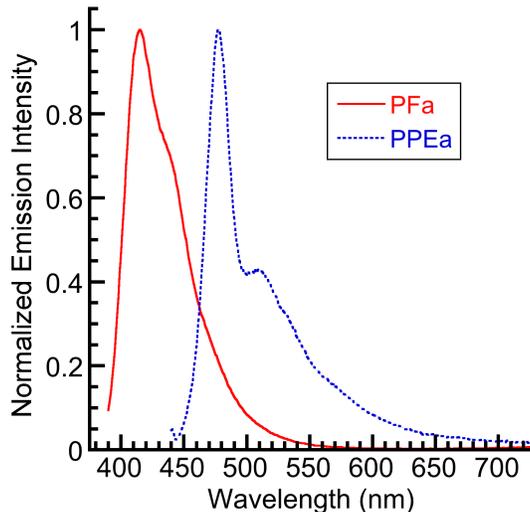


Figure 2.3. Normalized emission spectra of furan-linked CPs **PFa** and **PPEa**.

Table 2.1. Properties of 2,5-diarylfurans and furan-linked conjugated polymers.

Sample	X	M _n , [kg/mol]	PDI	λ _{max(ab)} ^a [nm]	λ _{max(em)} ^a [nm]	Φ _F ^c
4a	H	-	-	332		0.73
PFa	H	12	2.4	352	415	0.62
PF-8a	H	8.3	1.4	335	417	0.58
PPEa	H	13	2.8	440	478	0.36
4b	4-F	-	-	330		0.68
PFb	4-F	8	1.5	350	415	0.60
4c	4-CF ₃	-	-	342		0.69
PFc	4-CF ₃	25	2.3	361	416	0.59
PF-8c	4-CF ₃	8.2	1.2	346	415	0.58
4d	3,5-diCF ₃	-	-	344		0.39
PFd	3,5-diCF ₃	10.3	1.7	360	415	0.59
PF	H	28	2.1	373	417	0.76
PPE	H	9.0	1.6	440	478	0.54

^a Measured in CH₂Cl₂. ^b Determined relative to either quinine sulfate in 0.1 N H₂SO₄ (Φ_F^c = 0.54) or Coumarin 6 in ethanol (Φ_F^c = 0.78)

2.2.4 The Reactivity of Furan-linked CPs and Parent 2,5-diarylfurans with ¹O₂ as a Function of the Electronic Effect of Substituents

To understand the reactivity between ¹O₂ and the furan-linked CPs, we studied the reaction between ¹O₂ and diarylfuran derivative **4a**, the π-conjugated network of which is identical to the furan pendant bound to the **PFa** backbones, as well as the known cycloaddition reaction between 9,10-diphenylanthracene (DPA) and ¹O₂ ($k = 3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$)³⁷. We exposed **4a** to ¹O₂ by photosensitization using the dye methylene blue (MB), a sensitizer that is soluble in moderately polar organic solvents such as CH₂Cl₂. All kinetic experiments were performed under ambient conditions with identical concentrations of MB (OD = 0.87 at 653 nm) using either a combination of high-pass filters and a Hg/Xe lamp or a 4.5 mW laser diode at 630 nm to prevent direct excitation of any chromophores other

than MB. We followed the disappearance of the furan as a function of irradiation time in each experiment by absorbance spectrophotometry. Upon subtracting the absorbance due to the MB in solution, the resulting absorbance data fit semilogarithmic linear regressions versus time with correlation coefficients of $R \geq 0.99$ and yielded relative pseudo-first order rate constants. Negative control experiments in the presence of MB with no irradiation showed no change in the concentration of furan.

Figure 2.4 shows the response of the UV/vis spectra of furan **4a** and polymer **PFa** during exposure to $^1\text{O}_2$ over 5 min of irradiation of MB. The spectral responses of **4a** and **PFa** are similar, with the lowest energy band of **PFa** after the completion of the reaction resembling that of **PF** with a λ_{max} value of 367 nm. During the duration of the experiment, the absorbance features due solely to the CP backbone ($\lambda > 370$ nm) did not change, which indicates that the polymer did not degrade from exposure to $^1\text{O}_2$ under these conditions; **PPEa** showed similar resistance to degradation during the reaction between $^1\text{O}_2$ and the side-chain furan moieties.

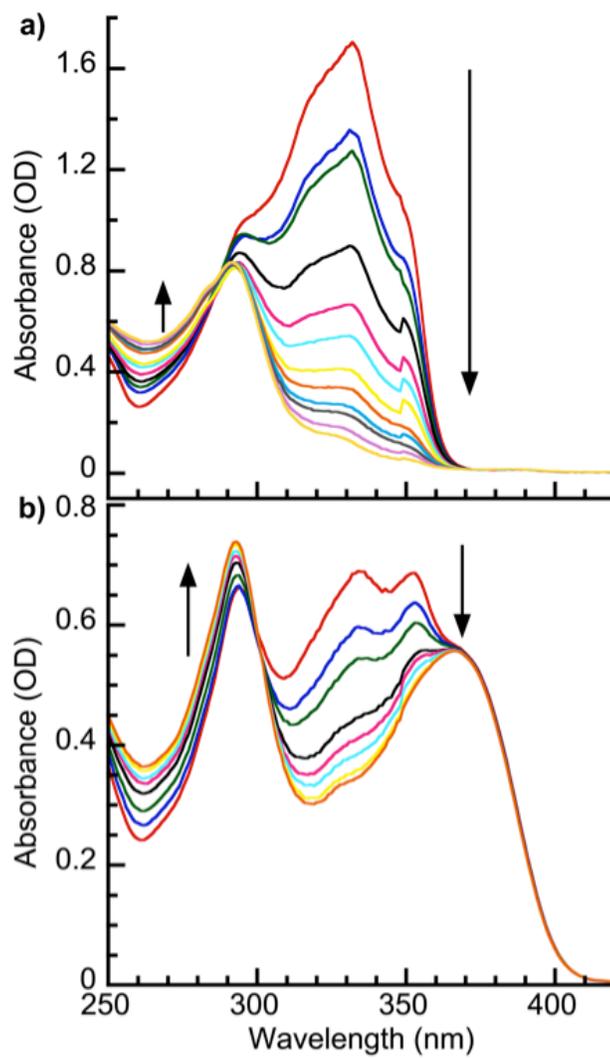


Figure 2.4. Response of UV/vis spectrum of (a) diarylfuran **4a** and (b) furan-linked **Pfa** to $^1\text{O}_2$ produced by photosensitization with MB (1.0 OD) in CH_2Cl_2 during ca. 5 min of irradiation.

Figure 2.5 shows the fits of the decrease in absorbance of the furan moiety to a pseudo-first order kinetic model. In addition, there was not a statistically significant difference between the pseudo-first order kinetics for the disappearance of the furan moieties of the small molecule **4a** and the furan side-

groups in polymer **PFa**. The rate of reaction of both furan derivatives was 56 ± 10 times higher than DPA. We therefore estimate that the bimolecular rate constant of reaction between the diarylfuran moiety **4a** and $^1\text{O}_2$ is $\sim 1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$; this value is similar to the previously published value of $8.6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$.³⁸

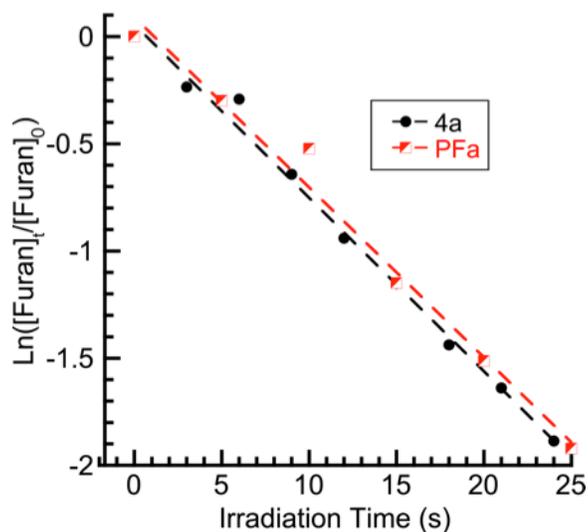


Figure 2.5. Pseudo-first order kinetics of furan disappearance in **4a** and **PFa**.

We examined the rate of $^1\text{O}_2$ -furan cycloaddition for both the parent 2,5-diarylfurans (**4a-4d**), including fluorinated electron withdrawing groups and the *p*-methoxy electron-donating group, and the furan-substituted polymers as a function of the electronic effect of substituents. In each small molecule studied, one of the aryl rings was *p*-anisyl in order to model the electronics of the furan side-chains on the polymers, which were bound to the polymer backbones through ether linkages. Data for each reaction fit a pseudo-first order model and allowed us to estimate bimolecular rate constants by comparing pseudo-first order rate constants with the DPA standard. The relative bimolecular rate constants for reaction of diarylfuran derivatives **4a-4d** were compared as determined using

absorption spectrophotometry, with $k_{\text{rel}} = 1$ for the reaction between DPA and $^1\text{O}_2$ in Figure 2.6. Heights of the bars are the average relative rate constants from three independent kinetic experiments; errors bars represent one standard deviation. As shown in Figure 2.6, increasingly strong electron withdrawing groups on the non-anisyl phenyl ring (4-fluoro, 4-trifluoromethyl, and 3,5-bis(trifluoromethyl)) slowed the cycloaddition reaction between diarylfuran and $^1\text{O}_2$, such that the most electron-poor furan we investigated, **4d**, reacted with $^1\text{O}_2$ four-times slower than **4a**. In all cases, the rates of reaction of furan moieties bound to conjugated polymers were within 15% of the rates of reaction of the analogous small molecule diarylfuran derivatives.

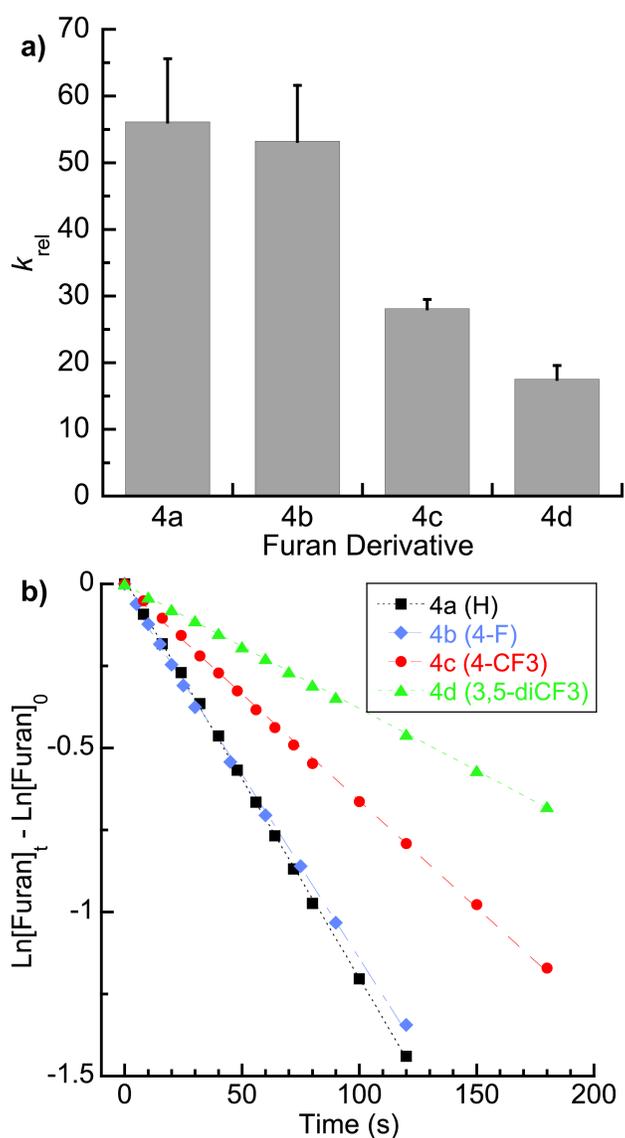


Figure 2.6. a) Comparison of the relative bimolecular rate constants ($k_{rel} = 1$ for the reaction between DPA and $^1\text{O}_2$). b) Representative pseudo first-order kinetic data for the consumption of furans **4a-4d** at steady-state [$^1\text{O}_2$].

2.2.5 Characterization of the Reaction between 2,5-diarylfurans and $^1\text{O}_2$, and Products by ^1H NMR

To establish that the reaction between the diarylfuran moieties in these materials and $^1\text{O}_2$ yielded the expected oxidized products, we followed the MB-

mediated photooxidation of **4a** by NMR in CDCl₃. After selective irradiation of methylene blue in the presence of **4a** sample in for 15 minutes, ¹H NMR revealed no remaining furan **4a**. TLC analysis indicated four major products. We identified ¹O₂-derived products through a combination of ¹H chemical shift analysis, ¹H-¹H coupling in two-dimensional NMR, and mass spectrometry. Figure 2.7 shows the ¹H NMR spectra of the isolated oxidized products of **4a** as well as **PFa** before and after exposure to ¹O₂ for 15 minutes. As shown in Figure 2.7 and Scheme 2.1, the major products identified were the *cis*-dibenzoylethylene (olefinic protons give two coupled doublets at d 7.1-7.2 ppm), its epoxidized analog (resonance at 4.5 ppm) and a mixture of the *cis*- (coupled doublets at d 6.3 and 8.0 ppm, *J* = 8 Hz) and *trans*- (coupled doublets at d 6.9 and 8.7 ppm, *J* = 12 Hz) enol esters.¹⁶ Similar to previously reported observations,¹⁶ we found that the initial enol ester product, which is nearly completely of *cis* configuration, isomerized to the *trans* configuration at room temperature within several days. Analogous photooxidation experiments using the conjugated polymers **PFa-PFd**, as well as **PPEa** showed complete disappearance of furan resonances and new signals consistent with the furan side-chains oxidized to both the *cis*-enol esters and epoxides.

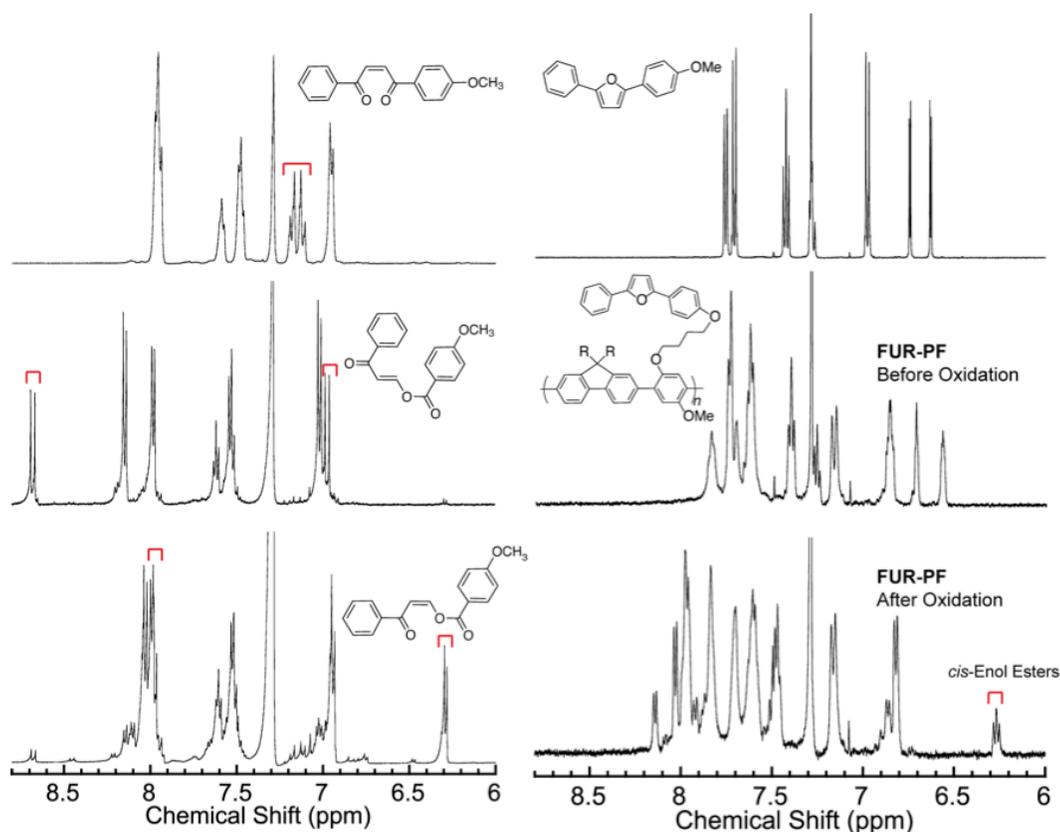


Figure 2.7. ^1H NMR spectra of the isolated $^1\text{O}_2$ -derived products of **4a** (left) and of **PFa** before and after exposure to $^1\text{O}_2$ for 15 minutes (right). Red brackets indicate resonances due to the vinylic protons.

2.2.6 Photophysical Characterization of $^1\text{O}_2$ -induced Oxidation of Pendant Furans on CPs

To test our principal hypothesis that $^1\text{O}_2$ -induced oxidation of pendant furans on CPs would cause fluorescence quenching, we monitored the fluorescence spectra of **PFa** and **PPEa** during photochemical generation of $^1\text{O}_2$ by selective irradiation of the photosensitizer MB. The observations of fluorescence response of the CPs to $^1\text{O}_2$ are consistent with quenching of CP backbone fluorescence by oxidized furan side chains *via* photoinduced electron transfer.

The polymer with the larger band gap of the two, **PFa**, showed a dramatic response to $^1\text{O}_2$, with a 12% reduction in fluorescence intensity and quantum yield after only 5 seconds of exposure to $^1\text{O}_2$ as shown in Figure 2.8. After 5 minutes of exposure to $^1\text{O}_2$, the degree of fluorescence quenching of the polymer reached a plateau of ca. 73%; additional exposure to $^1\text{O}_2$, up to 25 minutes in duration, resulted in no further change in either the fluorescence or absorbance spectra. We attribute the plateau in quenching to favorable reduction potentials of the oxidized products of the furan side-chains (enol esters and epoxides), and therefore leading to an electron transfer reaction from photoexcited CP and oxidized pendants.

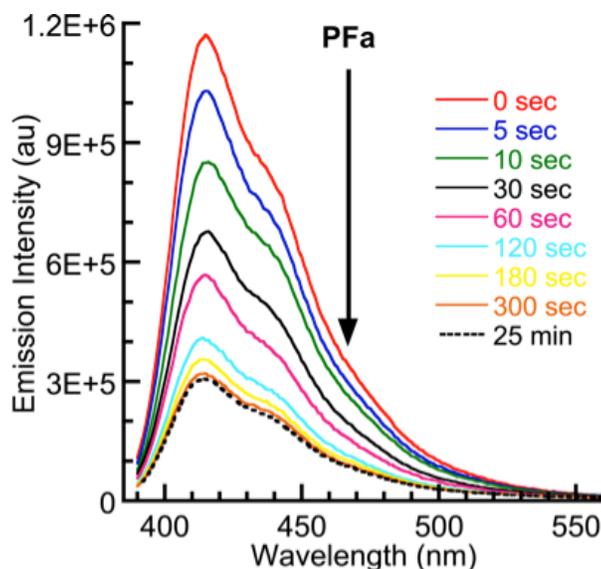


Figure 2.8. Fluorescent response of furan-linked conjugated polymer **PFa** to photogenerated $^1\text{O}_2$ in CH_2Cl_2 . The excitation wavelength was 380 nm, which the furan moieties do not absorb.

As shown in Figure 2.9, during exposure to $^1\text{O}_2$ experiment, only the intensity of the emission changed. The shapes of the emission spectra were the same at all irradiation times, although the emission intensity is decreased by about

5-fold. The normalized fluorescence spectra of **PFa** at 0 and 300 seconds of exposure to $^1\text{O}_2$ are nearly indistinguishable.

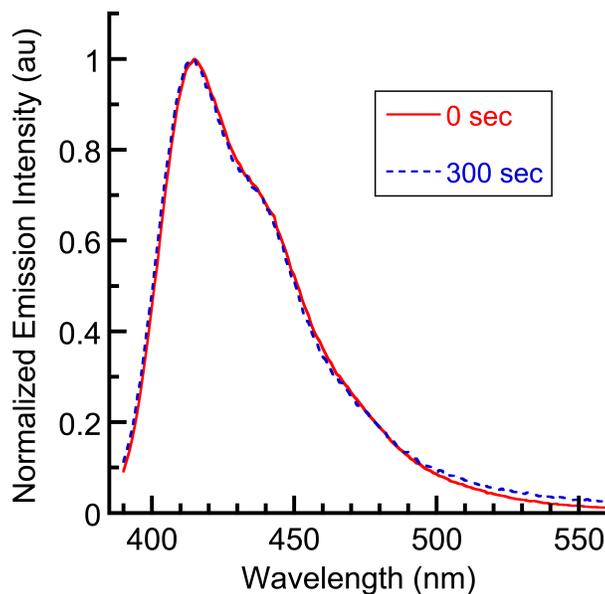


Figure 2.9. Overlaid, normalized emission spectra of **PFa** before and after reaction with $^1\text{O}_2$ for 300 seconds.

Figure 2.10 shows the response of an analogous polymer that contained only alkoxy side chains with no furan moieties (control polymer, **PF**). **PF** showed no change in fluorescence intensity upon exposure to $^1\text{O}_2$ under identical conditions. It further supports that the reduction in the emission intensity is due to the photo-induced electron transfer from CP backbone, not due to the photobleaching of the CP.

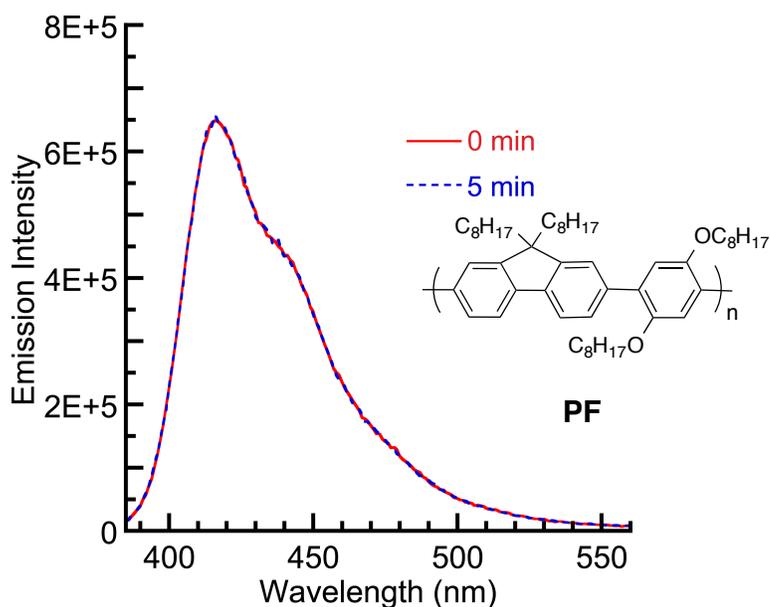


Figure 2.10. Emission spectra of **PF**, before (*red solid line*) and after (*blue dashed line*) exposure to $^1\text{O}_2$ for 5 minutes under identical conditions.

In contrast to the significant quenching of the fluorescence of **PFa**, exposure of **PPEa** to $^1\text{O}_2$ under identical conditions (using MB as a sensitizer in CH_2Cl_2) led to no significant change of either the shape or intensity of the emission spectrum of this polymer after 40 minutes, as shown in Figure 2.11 (bottom). The excitation wavelength was 380 nm, which the furan moieties do not absorb. The lack of fluorescent response is in spite of the complete reaction of the furan pendant under these conditions after about 10 minutes, as determined by absorbance spectrophotometry (Figure 2.11, top). The lack of a response from the **PPEa** derivative is also consistent with this scenario, as the smaller band gap of PPEs relative to poly(fluorene-*co*-phenylene)s has been identified as a limitation in using them for responding to weakly oxidizing potential quenchers.³⁶

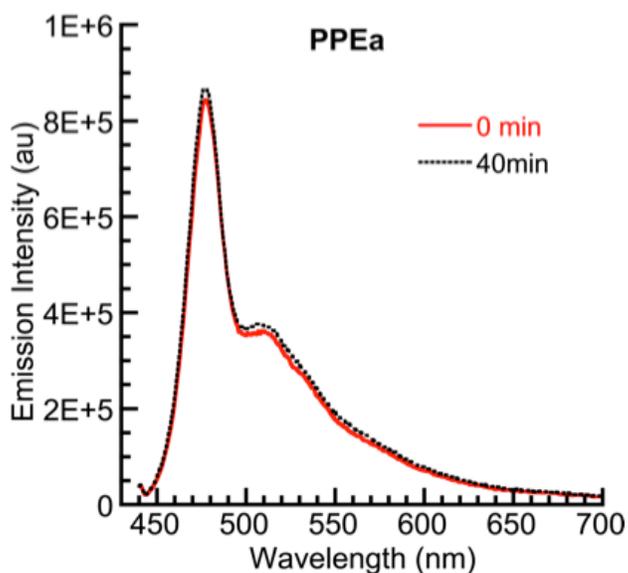
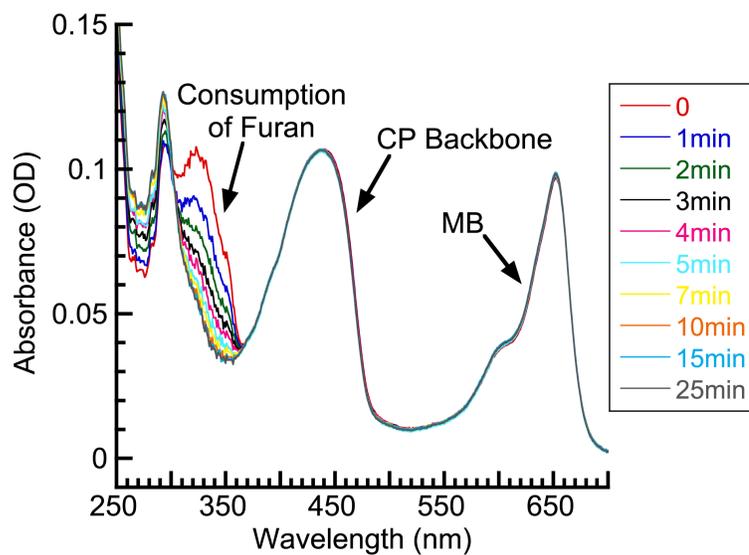


Figure 2.11. Top: Absorbance spectra showing reaction of **PPEa** with photogenerated $^1\text{O}_2$. Bottom: Fluorescent response of furan-linked conjugated polymer **PPEa** to $^1\text{O}_2$ in CH_2Cl_2 .

Substituents on the diarylfuran pendants had significant effects on the quenching of CP fluorescence. While introducing increasingly powerful fluorine-

based electron-withdrawing substituents slowed the rate of reaction between $^1\text{O}_2$ and the 2,5-diarylfuran, poly(fluorene-*co*-phenylene)s with fluorinated diarylfurans showed more efficient fluorescence quenching upon reaction with $^1\text{O}_2$ than analogous polymers with non-fluorinated diarylfurans. To illustrate this effect, Figure 2.12 shows the ratio of initial polymer fluorescence intensity to polymer fluorescence intensity after all furan pendants had reacted with $^1\text{O}_2$ (when the UV/vis and fluorescence spectra no longer changed in response to $^1\text{O}_2$). Heights of the bars represent the average result of at least three trials; errors bars represent standard deviations of those averages. For example, polymer **PFa**, which has no fluorinated substituents, showed I_0/I (ratio of fluorescence intensity before exposure to $^1\text{O}_2$ to fluorescence intensity after reaction with $^1\text{O}_2$ was complete) of 3.77 ± 0.04 upon consumption of all furan groups, while **PFc**, with a *para*-trifluoromethyl substituent on the terminal aryl ring had I_0/I of 7.57 ± 0.10 upon consumption of all furan groups. We attribute this effect to a combination of two factors: i) the electron withdrawing trifluoromethyl substituent decreasing the magnitude of the reduction potentials of the products of the $^1\text{O}_2$ -furan cycloaddition/fragmentation process, making them more powerful electron acceptors and therefore more efficient fluorescence quenchers by photoinduced electron transfer from the CP backbone to the oxidized side-chains, and ii) a potentially different distribution of products of epoxide and ester side-chains—at concentrations suitable for NMR analysis (~ 2 mg/mL), trifluoromethyl-substituted diaryl furans of **PFc** yielded a epoxide:ester ratio of 4:1, while the unsubstituted diaryl furans of **PFa** yielded a 1:2 epoxide:ester ratio. In addition,

because of an increase in the local concentration of $^1\text{O}_2$ -induced quenchers, increasing the number of furan side-chains per repeat unit also increased the efficiency of quenching: **PF-8a**, which has two diarylfurans per repeat unit, showed 1.7-fold more quenching upon consumption of all furans than **PFa**, which has one diarylfuran per repeat unit. Finally, the effect of the electron withdrawing trifluoromethyl group and increased concentration of potential quenchers with doubly-substituted monomers was roughly additive, with polymer **PF-8c** showing I_0/I_f of 12.1 ± 1.89 (90–93% quenching). **PF-8c** showed the largest amount of fluorescence quenching upon complete conversion of furans by $^1\text{O}_2$ among all polymers we studied.

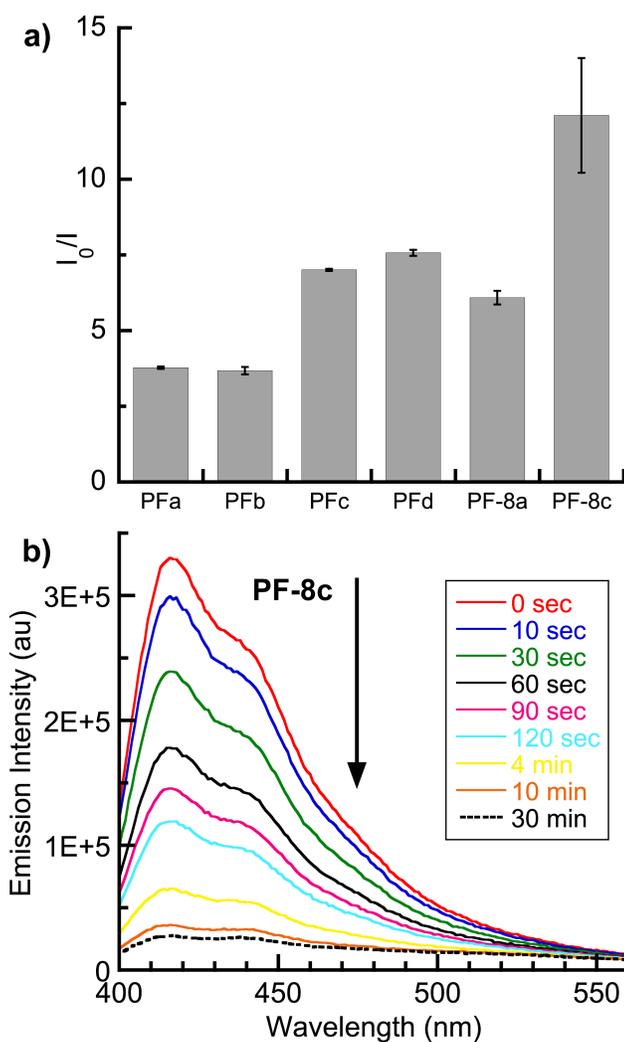


Figure 2.12. a) Ratio of fluorescence intensity of furan-substituted PFs before exposure to 1O_2 (I_0) to fluorescence intensity after all furan side chains reacted (I) as a function of polymer structure. b) Fluorescent response of **PF-8c**

2.3 Conclusion

In conclusion, we have prepared a series of new diarylfuran-linked poly(fluorene-*co*-phenylene)s that show a fluorescence quenching response to 1O_2 by photoinduced electron transfer. The rapid rate of reaction between 1O_2 and diarylfurans ($k \sim 10^8 \text{ M}^{-1}\text{s}^{-1}$) enables a fast fluorescence quenching response of

these polymers, while variations in the electronic nature of substituents on the furan moiety enables tuning both of the rates of reactions and efficiency of fluorescence quenching. Conjugated polymer backbones with a lower excited state energy (PPEs) showed no fluorescence quenching in response to oxidation of the furan side-chains. These results advance our capabilities for designing the components of luminescent $^1\text{O}_2$ -responsive materials rationally.

2.4 Experimental Section

2.4.1 General Considerations

The following chemicals were purchased from commercial sources and used as received: *n*-butyllithium (Aldrich), furan (Aldrich), iodine (Aldrich), phenylboronic acid (Strem), 4-methoxyphenylboronic acid (Strem), 4-fluorophenylboronic acid (Strem), 4-(trifluoromethyl)phenylboronic acid (Alfa Aesar), 3,5-bis(trifluoromethyl)phenylboronic acid (Aldrich), $\text{PdCl}_2(\text{PPh}_3)_2$ (Strem), BBr_3 (Aldrich), 1-dodecanethiol (Aldrich), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (Aldrich), $\text{Pd}(\text{PPh}_3)_4$ (Strem), Aliquat 336 (Aldrich), K_2CO_3 (Fisher), NaOH (Aldrich), and KOH (Fisher). Tetrahydrofuran (THF), dichloromethane (DCM), diethylether (Et_2O), and toluene were dried on an Innovative Technologies PureSolv 400 solvent purifier. Dry dimethyl sulfoxide (DMSO) was purchased from Acros (AcroSeal). Dry 1-methyl-2-pyrrolidinone (NMP) was purchased from Sigma (Sure/Seal).

All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless

otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent (7.27 ppm for CHCl_3). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. Molecular weight distribution measurements of the polymers were conducted with a Shimadzu Gel Permeation Chromatography (GPC) system equipped with a Tosoh TSKgel GMHhr-M mixed-bed column and guard column using either UV or refractive index detectors. The column was calibrated with low polydispersity poly(styrene) standards (Tosoh, PSt Quick Kit) with THF as the mobile phase eluting at 0.75 mL/min. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

2.4.2 Optical Experiments

All solution optical spectra were acquired of samples in quartz cuvettes (NSG Precision Cells). Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Fluorescence spectra were acquired

using sample absorbances less than 0.1 OD. Fluorescence quantum yields were determined relative to either quinine sulfate in 0.1 N H₂SO₄ or Coumarin 6 in ethanol. Irradiation of the methylene blue photosensitizer to generate ¹O₂ was performed with either 1) 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water, shutter, and 515 nm and 590 nm high-pass filters, or 2) a 4.5 mW 635 nm laser diode (ThorLabs).

2.4.2.a Fluorescence Response to Singlet Oxygen

A cuvette containing the test sample solution was irradiated for numerous timed intervals. Both the absorbance and fluorescence spectra were taken after each interval of irradiation. The absorbance for both methylene blue and samples was approximately 0.1 OD. The excitation wavelengths used for the fluorescence spectra are summarized in the Table 2.2.

Table 2.2 The excitation wavelengths chosen for the fluorescence spectra

Polymer	λ_{ex}
PFa	380 nm
PFb	395 nm
PFc	390 nm
PFd	395 nm
PF-8a	380 nm
PF-8c	390 nm

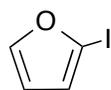
2.4.2.b Kinetics

A stock solution of methylene blue was prepared in CH₂Cl₂ to give an absorbance of ~1.0 at its peak. 2-Phenyl-5-(4-methoxyphenyl)furan (**4a**), 2-(4-fluorophenyl)-5-(4-methoxyphenyl)furan (**4b**), 2-(4-trifluorophenyl)-5-(4-

methoxyphenyl)furan (**4c**), or 2-(3,5-bis(trifluoromethyl)phenyl)-5-(4-methoxyphenyl)furan (**4d**) was dissolved in CH₂Cl₂ at a concentration of 0.005 M to give stock solutions. When 25 μ L of each stock solution was dissolved in 3.5 mL MB solution, the final concentration of the corresponding compound in the sample was 35.5 μ M. The solution was irradiated for numerous timed intervals, with acquisition of an absorbance spectrum after each interval until the spectra stopped changing between intervals of irradiation (all furan groups having reacted). This procedure was repeated several times for (**4a-4d**), 9,10-diphenylanthracene (DPA), and all conjugated polymers in CH₂Cl₂. The initial concentration of polymer was adjusted in a way that it contains the same concentration of furan moieties as the small molecule kinetics experiments. The wavelengths used for the analysis of kinetics were the peaks of the highest absorbance of small molecule furan pendants (**4a-4d**).

2.4.3 Detailed Synthetic Procedures

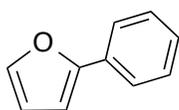
2-Iodofuran (**1**).



A solution of *n*-Butyllithium (3.28 mL, 1.6 M in hexanes, 5.25 mmol, 1.0 eq) was added dropwise to a solution of furan (0.53 mL, 7.4 mmol, 1.4 eq) in dry Et₂O (5 mL) at -78 °C under argon and stirred vigorously at -78 °C for 30 minutes. The reaction mixture was then warmed to 0 °C and stirred for 1 hour. The solution was then warmed to room temperature and stirred for 90 minutes before being cooled again to -78 °C. Iodine (1.87 g, 7.35 mmol, 1.4 eq) in 10 mL of Et₂O was slowly added to this solution, which was warmed

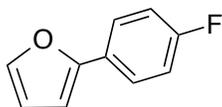
slowly to room temperature and stirred overnight. The reaction was stopped by adding $\text{Na}_2\text{S}_2\text{O}_3$ (15% aq). The mixture was extracted twice with Et_2O , and the combined organic phases were washed with brine, dried over MgSO_4 and filtered. Removal of solvent *in vacuo* yielded 0.79 g of 2-iodofuran (77%) as a brown liquid pure by NMR that was taken to the next step immediately without further purification.³⁹

2-Phenylfuran (2-H)



Phenylboronic acid (245 mg, 2.0 mmol, 1.0 eq) was suspended in 8 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of 2-iodofuran (662 mg, 3.4 mmol, 1.7 eq), $\text{PdCl}_2(\text{PPh}_3)_2$ (28 mg, 0.04 mmol, 0.02 eq), and K_2CO_3 (691 mg, 5.0 mmol, 2.5 eq) under argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and water was added. The mixture was extracted twice with Et_2O , and combined organic phases were washed with brine and dried over MgSO_4 , filtered, and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes to yield **2-H**.³⁵ Yield: 197 mg (68%).

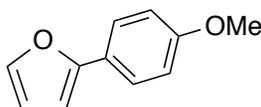
2-(4-fluorophenyl)furan (2-F)



4-fluorophenylboronic acid (848 mg, 6.1 mmol, 1.0 eq) was suspended in 24 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of 2-iodofuran (2.0 g, 0.010 mol, 1.7 eq), $\text{PdCl}_2(\text{PPh}_3)_2$ (85 mg, 0.12 mmol, 0.02 eq),

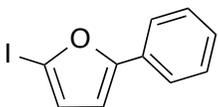
and K_2CO_3 (2.1 g, 15.3 mmol, 2.5 eq) under argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. The mixture was extracted twice with Et_2O , and combined organic phases were washed with brine and dried over $MgSO_4$, filtered, and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes to yield **2-F**.⁴⁰ Yield: 546 mg (55%).

2-(4-Methoxyphenyl)furan (2-OMe)



4-Methoxyphenylboronic acid (309 mg, 2.03 mmol, 1.0 eq) was suspended in 8 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of 2-iodofuran (670 mg, 3.45 mmol, 1.7 eq), $PdCl_2(PPh_3)_2$ (28.5 mg, 0.04 mmol, 0.02 eq), and K_2CO_3 (701 mg, 5.1 mmol, 2.5 eq) under argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. The mixture was extracted twice with Et_2O , and combined organic phases were washed with brine and dried over $MgSO_4$, filtered, and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (9.8:0.2, v/v) to yield **2-OMe**.⁴¹ Yield: 233 mg (66%).

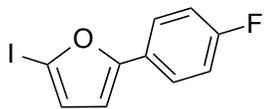
2-Phenyl-5-iodofuran (3-H).



A solution of *n*-butyllithium (0.52 mL, 1.6 M in hexanes, 0.83

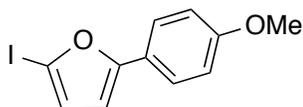
mmol, 1.4 eq) was added dropwise to a solution of 2-phenylfuran (85 mg, 0.59 mmol, 1.0 eq) in dry THF (1 mL) at -78 °C under argon. The reaction mixture was then warmed to 0 °C and stirred for 10 minutes before being cooled again to -78 °C. Iodine (162 mg, 0.64 mmol, 1.1 eq) in 0.5 mL of THF was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). The mixture was extracted twice with hexanes, and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated using rotary evaporation. Compound **3-H** was taken to the next step immediately without further purification.

2-(4-fluorophenyl-5-iodofuran) (3-F)



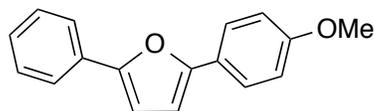
A solution of *n*-butyllithium (1.4 mL, 1.6 M in hexanes, 2.2 mmol, 1.4 eq) was added dropwise to a solution of 2-(4-fluorophenyl)furan (252 mg, 1.55 mmol, 1.0 eq) in dry THF (3.0 mL) at -78 °C under argon. The reaction mixture was then warmed to 0 °C and stirred for 20 minutes before being cooled again to -78 °C. Iodine (426 mg, 1.7 mmol, 1.1 eq) in 1.5 mL of THF was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). The mixture was extracted twice with hexanes, and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated using rotary evaporation. Compound **3-F** was taken to the next step immediately without further purification.

2-(4-methoxyphenyl-5-iodofuran) (3-OMe)



A solution of *n*-butyllithium (1.75 mL, 1.6 M in hexanes, 2.8 mmol, 1.4 eq) was added dropwise to a solution of 2-(4-methoxyphenyl)furan (85 mg, 2.0 mmol, 1.0 eq) in dry THF (3.9 mL) at -78 °C under argon. The reaction mixture was then warmed to 0 °C and stirred for 20 minutes before being cooled again to -78 °C. Iodine (551 mg, 2.2 mmol, 1.1 eq) in 1.9 mL of THF was slowly added to this solution, which was warmed slowly to room temperature and stirred overnight. The reaction was stopped by adding Na₂S₂O₃ (15% aq). The mixture was extracted twice with hexanes, and the combined organic phases were washed with brine, dried over MgSO₄, filtered, and concentrated using rotary evaporation. Compound **3-OMe** was taken to the next steps immediately without further purification.

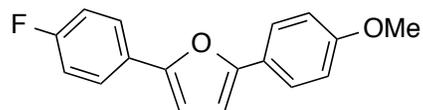
2-Phenyl-5-(4-methoxyphenyl)furan (4a)



4-methoxyphenylboronic acid (30 mg, 0.19 mmol, 1.0 eq) was suspended in 1.0 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of **3-H** (90 mg, 0.33 mmol, 1.7 eq), PdCl₂(PPh₃)₂ (2.8 mg, 0.004 mmol, 0.02 eq), and K₂CO₃ (66 mg, 0.48 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. The mixture was extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude

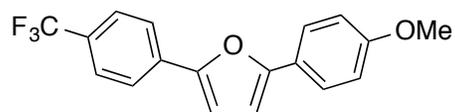
product was purified *via* flash chromatography using hexanes and EtOAc (8:1, v/v) to yield **4a**.³⁵ Yield: 42 mg (86%).

2-(4-fluorophenyl)-5-(4-methoxyphenyl)furan (**4b**)



Compound (**3-F**) (99 mg, 0.34 mmol, 1.7 eq) and 4-methoxyphenyl boronic acid (31 mg, 0.2 mmol, 1.0 eq) were suspended in 1.2 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of PdCl₂(PPh₃)₂ (3.0 mg, 4 μmol, 0.02 eq), and K₂CO₃ (70 mg, 0.5 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. The mixture was extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and CH₂Cl₂ (5:1, v/v) to yield **4b**.⁴² Yield: 29 mg (54%).

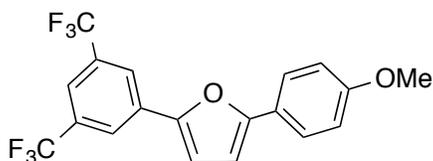
2-(4-trifluorophenyl)-5-(4-methoxyphenyl)furan (**4c**)



4-trifluorophenylboronic acid (112 mg, 0.6 mmol, 1.0 eq) was suspended in 3.7 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of **3-OMe** (301 mg, 1.0 mmol, 1.7 eq), PdCl₂(PPh₃)₂ (8.4 mg, 0.01 mmol, 0.02 eq), and K₂CO₃ (207 mg, 1.5 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture

was then cooled to room temperature and stopped by adding water. The mixture was extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (9:1, v/v) to yield **4c**. Yield: 107 mg (56%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J=8 Hz, 2H), 7.70 (d, J=8.5 Hz, 2H), 7.65 (d, J=8 Hz, 2H), 6.97 (d, J=8.5 Hz, 2H), 6.84 (d, J=3.5 Hz, 1H), 6.64 (d, J=3.5 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 159.5, 154.6, 151.2, 134, 128.6 (q, J=129 Hz), 125.7 (q, J=15 Hz), 125.4, 124.2 (q, J=1080 Hz), 123.5, 123.4, 114.3, 109.3, 105.9, 55.4. HRMS calcd for C₁₈H₁₃F₃O₂ (M+H)⁺, 319.0940, found, 319.0924.

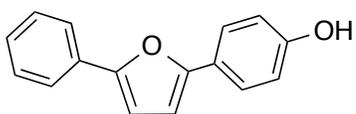
2-(3,5-Bis(trifluoromethyl)phenyl)-5-(4-methoxyphenyl)furan (4d)



Compound **3-OMe** (690 mg, 2.3 mmol, 1.7 eq) and 3,5-bis(trifluoromethyl)phenyl boronic acid (348 mg, 1.4 mmol, 1.0 eq) were suspended in 8.4 mL of a DMF/water (3:1) mixture (which was deoxygenated by sparging with argon), followed by the addition of PdCl₂(PPh₃)₂ (19 mg, 0.03 mmol, 0.02 eq), and K₂CO₃ (469 mg, 3.4 mmol, 2.5 eq) under an argon atmosphere. The mixture was heated to 80 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. The mixture was extracted twice with Et₂O, and combined organic phases were washed with brine and dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (9.5:0.5, v/v) to yield **4d**. Yield: 400 mg (45%). ¹H NMR

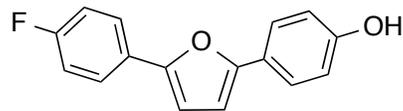
(500 MHz, CDCl₃): δ 8.09 (s, 2H), 7.72-7.70 (m, 3H), 6.99 (d, J=8.5 Hz, 2H), 6.91 (d, J=3.5 Hz, 1H), 6.66 (d, J=3 Hz, 1H), 3.88 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 159.8, 155.3, 149.6, 132.7, 132.2 (q, J=133 Hz), 125.6, 123.3 (q, J=1085 Hz), 123 (m, 2C), 119.9 (m, 1C), 114.3, 110.2, 106, 55.4. HRMS calcd for C₁₉H₁₂F₆O₂ (M+H)⁺, 387.0814, found, 387.0805.

2-Phenyl-5-(4-hydroxyphenyl)furan (5a)



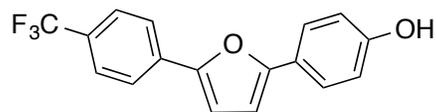
Compound **4a** (277 mg, 1.1 mmol, 1.0 eq) was suspended in 8.5 mL of dry DCM, followed by the addition of BBr₃ (2.77 mL, 1.0 M in DCM, 2.77 mmol, 2.5 eq) at -78 °C under argon and stirred for 4.5 hours. The reaction was stopped by pouring the reaction mixture onto ice. The mixture was extracted twice with DCM, and combined organic phases were washed with brine, dried over MgSO₄, and filtered. Removal of solvent *in vacuo* yielded 165 mg of **5a** (63%) that was taken to the next step immediately without further purification. ¹H NMR (500 MHz, CDCl₃): δ 7.75-7.72 (m, 2H), 7.67-7.64 (m, 2H), 7.42-7.39 (m, 2H), 7.3-7.25 (m, 1H), 6.91-6.88 (m, 2H), 6.72 (d, J=3.5 Hz, 1H), 6.61 (d, J=3 Hz, 1H), 4.74 (s, 1H). ¹³C NMR: (125 MHz, CDCl₃) δ 155, 153.4, 152.8, 130.9, 128.7, 127.1, 125.4, 124.2, 123.6, 115.7, 107.2, 105.7. HRMS calcd for C₁₆H₁₂O₂ (M+H)⁺, 237.0910, found, 237.0903.

2-(4-fluorophenyl)-5-(4-hydroxyphenyl)furan (5b).



Compound **4b** (19.4 mg, 0.07 mmol, 1.0 eq) was suspended in 0.7 mL of dry DCM, followed by the addition of BBr_3 (1.8 mL, 0.1M in DCM, 0.18 mmol, 2.5 eq) at $-78\text{ }^\circ\text{C}$ under argon and stirred overnight. The reaction was stopped by pouring the reaction mixture onto ice. The mixture was extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (3:1, v/v) to yield **5b**. Yield: 10 mg (58%). ^1H NMR (500 MHz, CDCl_3): δ 7.71-7.68 (m, 2H), 7.63 (d, $J=8.5$ Hz, 2H), 7.1 (t, $J=9$ Hz, 2H), 6.89 (d, $J=9$ Hz, 2H), 6.65 (d, $J=3.5$ Hz, 1H), 6.59 (d, $J=3.5$ Hz, 1H), 4.77 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 163, 161.1, 155.1, 153.4, 152, 127.3, 127.2, 125.4, 125.3, 125.2, 124.1, 115.8, 115.7, 115.6, 106.8, 105.7. HRMS calcd for $\text{C}_{16}\text{H}_{11}\text{FO}_2$ ($\text{M}+\text{H}$) $^+$, 255.0816, found, 255.0819.

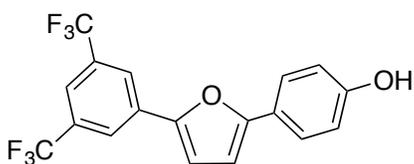
2-(4-trifluorophenyl)-5-(4-hydroxyphenyl)furan (5c).



Compound **4c** (95.3 mg, 0.3 mmol, 1.0 eq) and NaOH (36 mg, 0.9 mmol, 3.0 eq) were dissolved in 0.3 mL of dry NMP, followed by the addition of 1-dodecanethiol (108 μL , 0.45 mmol, 1.5 eq) at room temperature under argon. The mixture was heated to $135\text{ }^\circ\text{C}$ and stirred overnight. The mixture was then cooled to room temperature. The reaction was stopped by acidification with 1N HCl. The mixture was extracted twice with EtOAc, and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The

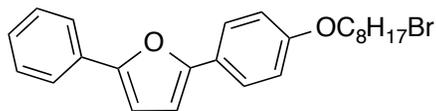
crude product was purified *via* flash chromatography using hexanes and EtOAc (3:1, v/v) to yield **5c**. Yield: 85 mg (93%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J= 8 Hz, 2H), 7.65 (t, J=8 Hz, 4H), 6.91 (d, J=8.5 Hz, 2H), 6.84 (d, J=3 Hz, 1H), 6.64 (d, J=3.5 Hz, 1H), 4.84 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 155.6, 154.6, 151.1, 134, 128.6 (q, J=129 Hz), 125.7 (m, 2C), 124.2 (q, J=1080 Hz), 123.6, 123.4, 115.8, 109.3, 105.9. HRMS calcd for C₁₇H₁₁F₃O₂ (M+H)⁺, 305.0784, found, 305.0778.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-(4-hydroxyphenyl)furan (5d).



Compound **4d** (30 mg, 0.08 mmol, 1.0 eq) was suspended in 1.1 mL of dry DCM, followed by the addition of BBr₃ (0.19 mL, 1.0 M in DCM, 0.19 mmol, 2.5 eq) at -78 °C under argon and stirred overnight. The reaction was stopped by pouring the reaction mixture onto ice. Organics were extracted twice with DCM, and combined organic phases were washed with brine, dried over MgSO₄, and filtered. Removal of solvent *in vacuo* yielded 27 mg of **5d** (93%) that was taken to the next step immediately without further purification. ¹H NMR (500 MHz, CDCl₃): δ 8.09 (s, 2H), 7.73 (s, 1H), 7.68 (d, J=8 Hz, 2H), 6.93-6.92 (m, 3H), 6.66 (d, J=3.5 Hz, 1H), 4.85 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 155.7, 155.2, 149.6, 132.2 (m, 2C), 125.9, 123.3 (q, J=1085.5 Hz), 123.3, 123 (m, 1C), 120 (m, 1C), 115.8, 110.2, 106.1. HRMS calcd for C₁₈H₁₀F₆O₂ (M+H)⁺, 373.0658, found, 373.0643.

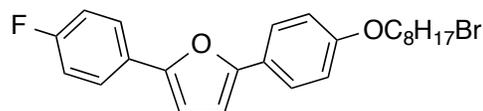
2-(4-(4-bromobutoxy)phenyl)-5-phenylfuran (6a).



Compound **5a** (159 mg, 0.67 mmol, 1.0 eq)
and KOH (75 mg, 1.34 mmol, 2.0 eq) were

dissolved in 2.5 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (0.25 mL, 2.0 mmol, 3.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (5:1, v/v) to yield **6a**. Yield: 188 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, J=8 Hz, 2H), 7.68 (d, J=8.5 Hz, 2H), 7.41 (t, J=7.5 Hz, 2H), 7.27-7.25 (m, 1H), 6.94 (d, J=8.5 Hz, 2H), 6.72 (d, J=3.5 Hz, 1H), 6.61 (d, J=3.5 Hz, 1H), 4.05 (t, J= 6 Hz, 2H), 3.52 (t, J=6.5 Hz, 2H), 2.11 (quintet, J= 7 Hz, 2H), 1.98 (quintet, J=6.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 158.4, 153.5, 152.7, 130.9, 128.7, 127.1, 125.2, 124, 123.6, 114.8, 107.2, 105.7, 67, 33.4, 29.5, 27.9. HRMS calcd for C₂₀H₁₉BrO₂ (M+H)⁺, 371.0641, found, 371.0648.

2-(4-(4-bromobutoxy)phenyl)-5-(4-fluorophenyl)furan (6b).

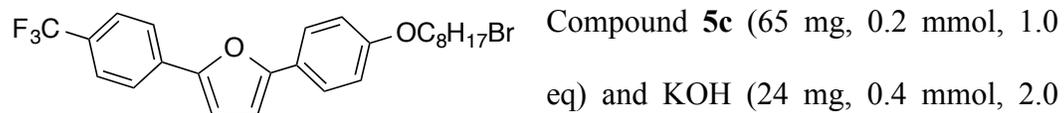


Compound **5b** (23 mg, 0.09 mmol, 1.0 eq)
and KOH (10 mg, 0.18 mmol, 2.0 eq)

were dissolved in 0.4 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (54 uL, 0.45 mmol, 5.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl.

The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (6:1, v/v) to yield **6b**. Yield: 26 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.68 (m, 2H), 7.67 (d, J=8.5 Hz, 2H), 7.11 (t, J=8.5 Hz, 2H), 6.94 (d, J=8.5 Hz, 2H), 6.65 (d, J=3 Hz, 1H), 6.60 (d, J=3 Hz, 1H), 4.05 (t, J=6 Hz, 2H), 3.52 (t, J=6.5 Hz, 2H), 2.13-2.08 (m, 2H), 2.01-1.96 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 163, 161, 158.4, 153.5, 151.9, 127.3, 127.3, 125.3, 125.2, 125.2, 123.9, 115.8, 115.6, 114.8, 106.8, 105.7, 67, 33.4, 29.5, 27.9. HRMS calcd for C₂₀H₁₈BrFO₂ (M+H)⁺, 389.0547, found, 389.0552.

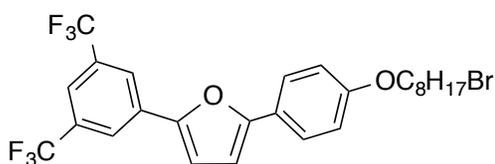
2-(4-(4-bromobutoxy)phenyl)-5-(4-trifluorophenyl)furan (6c).



eq) were dissolved in 1 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (128 uL, 1.0 mmol, 5.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (5:1, v/v) to yield **6c**. Yield: 64 mg (68%). ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, J=8 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H), 7.64 (d, J=8.5 Hz, 2H), 6.95 (d, J=8.5 Hz, 2H), 6.84

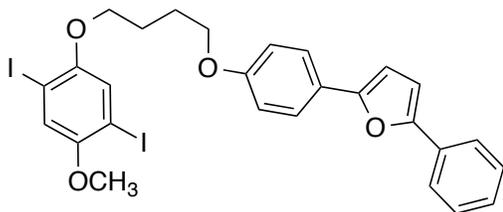
(d, J=3.5 Hz, 1H), 6.64 (d, J=3.5 Hz, 1H), 4.06 (t, J=6 Hz, 2H), 3.52 (t, J=6.5 Hz, 2H), 2.14-2.08 (m, 2H), 2.01-1.96 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.8, 154.6, 151.2, 134, 128.6 (q, J=129 Hz), 125.7 (q, J=15 Hz), 125.5, 124.2 (q, J=1080 Hz), 123.5, 123.4, 114.8, 109.3, 105.9, 66.9, 32.4, 29.5, 27.9. HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{Br}_2\text{F}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 439.0515, found, 439.0513.

2-(4-(4-bromobutoxy)phenyl)-5-(3,5-bis(trifluoromethyl)phenyl)furan (6d)



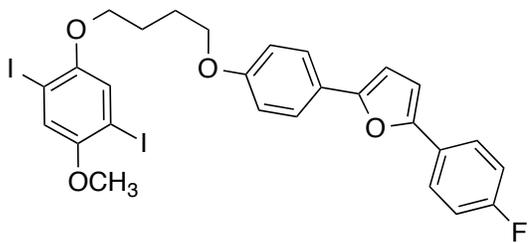
Compound **5d** (27 mg, 0.07 mmol, 1.0 eq) and KOH (8.2 mg, 0.15 mmol, 2.0 eq) were dissolved in 0.3 mL of dry DMSO, followed by the addition of 1,4-dibromobutane (26 μL , 0.2 mmol, 3.0 eq) at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was chromatographed on silica gel column using stepwise gradient elution of hexanes, and then hexanes and EtOAc (8:1, v/v) to yield **6d**. Yield: 30 mg (82%). ^1H NMR (500MHz, CDCl_3): δ 8.09 (s, 2H), 7.71-7.69 (m, 3H), 6.97 (d, J=8.5 Hz, 2H), 6.92 (d, J=3 Hz, 1H), 6.67 (d, J=2.5 Hz, 1H), 4.07 (t, J=5 Hz, 2H), 3.52 (t, J=6.5 Hz, 2H), 2.14-2.08 (m, 2H), 2.06-1.98 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 159, 155.3, 149.6, 132.7, 132.2 (q, J=132.5 Hz), 125.6, 123.3 (q, J=1084 Hz), 123 (m, 2C), 120 (m, 1C), 114.9, 110.2, 106, 67, 33.3, 29.5, 27.9. HRMS calcd for $\text{C}_{22}\text{H}_{17}\text{BrF}_6\text{O}_2$ ($\text{M}+\text{H}$) $^+$, 507.0389, found, 507.0388.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-phenylfuran (7a)



Compound **6a** (22.7 mg, 0.06 mmol, 1.0 eq), KOH (7 mg, 0.12 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (26.5 mg, 0.07 mmol, 1.2 eq) were dissolved in 0.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH, dried over MgSO₄, filtered and concentrated using rotary evaporation to yield **7a**. Yield: 35 mg (86%) ¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, J= 8 Hz, 2H), 7.68 (d, J=9 Hz, 2H), 7.41 (t, J= 8 H, 2H), 7.27-7.25 (m, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 6.96 (d, J=9 Hz, 2H), 6.73 (d, J=3 Hz, 1H), 6.61 (d, J=3.5 Hz, 1H), 4.12 (t, J=6 Hz, 2H), 4.05 (t, J= 5.5 Hz, 2H), 3.83 (s, 3H), 2.06-2.03 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 158.5, 153.5, 153.4, 152.8, 152.7, 131, 128.7, 127.1, 125.2, 123.9, 123.6, 123, 121.6, 114.8, 107.2, 105.6, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₇H₂₄I₂O₄ (M+H)⁺, 666.9837, found, 666.9859.

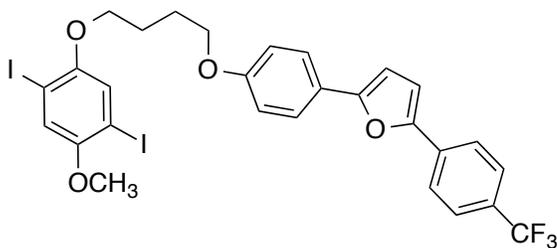
2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-(4-fluorophenyl)furan (7b)



Compound **6b** (27 mg, 0.07 mmol, 1.0 eq), KOH (8 mg, 0.14 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (52 mg, 0.14 mmol, 2.0 eq) were

dissolved in 0.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (5:1, v/v) to yield **7b**. Yield: 36 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.68 (m, 2H), 7.66 (d, J=9 Hz, 2H), 7.21 (s, 1H), 7.20 (s, 1H), 7.10 (t, J=8.5 Hz, 2H), 6.96 (d, J=8.5 Hz, 2H), 6.65 (d, J=3.5 Hz, 1H), 6.59 (d, J=3Hz, 1H), 4.12 (t, J=6 Hz, 2H), 4.04 (t, J=5.5 Hz, 2H), 3.83 (s, 1H), 2.08-2.03 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 163, 161, 158.5, 153.5, 153.4, 152.8, 151.9, 127.4, 127.3, 125.3, 125.2, 125.2, 123.7, 123, 121.6, 115.8, 115.6, 114.8, 106.8, 105.6, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₄H₂₃FI₂O₄ (M+H)⁺, 684.9742, found, 684.9742.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-(4-trifluorophenyl)furan (7c)

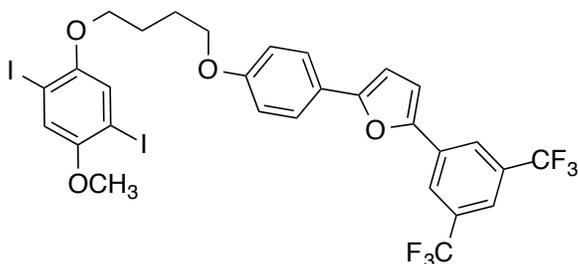


Compound **6c** (56 mg, 0.13 mmol, 1.0 eq), KOH (14 mg, 0.26 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (96 mg, 0.26 mmol,

2.0 eq) were dissolved in 0.8 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH to yield **7c**. Yield: 80 mg (86%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J=8 Hz, 2H), 7.69 (d, J=8.5 Hz, 2H), 7.65 (d, J=8 Hz, 2H), 7.22 (s, 1H), 7.20 (s, 1H), 6.97 (d, J=8.5 Hz, 1H), 6.84 (d, J=3 Hz, 1H), 6.64 (d, J=3 Hz, 1H), 4.13 (t, J=6 Hz 2H), 4.05 (t, J=6 Hz, 2H), 3.83 (s, 3H), 2.08-2.05 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 158.9, 154.7, 153.4, 152.8, 151.1, 134, 128.6 (q, J=129 Hz), 125.7 (q, J=15 Hz), 125.4, 124.2 (q, J=1080 Hz), 123.4, 123.4, 123, 121.5, 114.9, 109.3, 105.9, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₈H₂₃F₃I₂O₄ (M+H)⁺, 734.9711, found, 734.9698.

2-(4-(4-(2,5-diiodo-4-methoxyphenoxy)butoxy)phenyl)-5-(3,5-

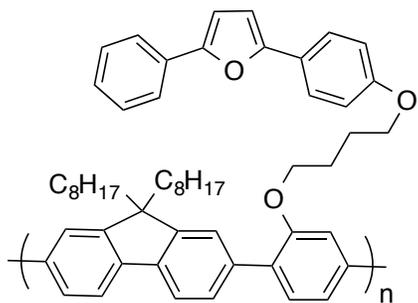
Bis(trifluoromethyl)furan (7d)



Compound **6d** (27 mg, 0.05 mmol, 1.0 eq), KOH (6 mg, 0.1 mmol, 2.0 eq) and 2,5-diiodo-4-methoxyphenol (40 mg, 0.2 mmol,

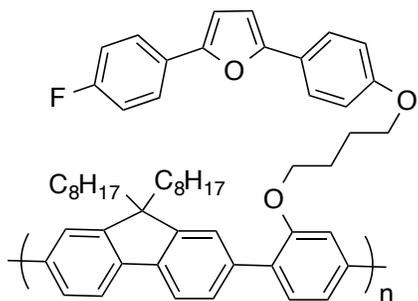
2.0 eq) were dissolved in 0.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and EtOAc (6:1, v/v) to yield **7d**. Yield: 32 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 8.1 (s, 2H), 7.72-7.69 (m, 3H) 7.22 (s, 1H), 7.20 (s, 1H), 6.99 (d, J=8.5 Hz, 2H), 6.92 (d, J=3.5 Hz, 2H), 6.66 (d, J=3.5 Hz, 1H), 4.14 (t, J=5.5 Hz), 4.05 (t, J=5 Hz), 3.84 (s, 1H), 2.10-2.04 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 159.1, 155.4, 153.4, 152.8, 149.6, 132.7, 132.2 (q, J=133 Hz), 125.6, 123.3 (q, J=1084 Hz), 123 (m, 3C), 121.5, 119.9 (m, 1C), 115, 110.2, 106, 86.3, 85.5, 69.9, 67.6, 57.2, 26.1, 26. HRMS calcd for C₂₉H₂₂F₆I₂O₄ (M+H)⁺, 802.9584, found, 802.9586.

PFa.



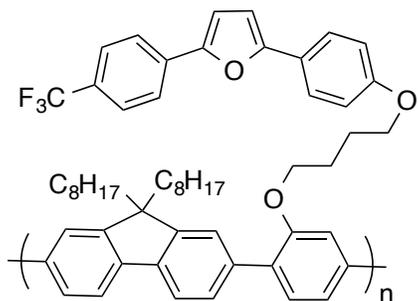
Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (25 mg, 40. μ mol) and **7a** (30. mg, 40. μ mol) were weighed into a

Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$. 1 mL of deoxygenated toluene, 1 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of diethyl ether and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. Yield: 30 mg (93%) M_n [g/mol]:12k, M_w [g/mol]: 29k. ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.61, 7.41-7.40, 7.27-7.24, 7.18-7.15, 6.88-6.84, 6.72-6.71, 6.58-6.56, 4.01, 3.99-3.96, 3.88-3.86, 2.1-1.94, 1.3-0.8.

PFb.

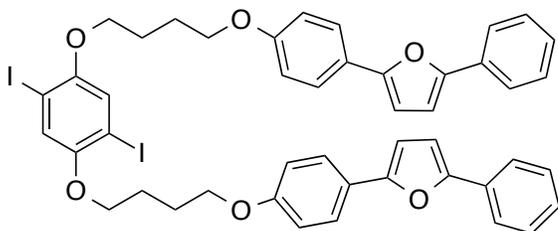
Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (21.7 mg, 32.0 μmol) and **7b** (26.5 mg, 32.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$. 0.7 mL of deoxygenated toluene, 0.7 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 8k, M_w [g/mol]: 12k. Yield: 23 mg (88%). ^1H NMR (500 MHz, CDCl_3): δ 7.83-7.6, 7.17-7.15, 7.10-7.07, 6.85, 6.63, 6.56, 4.09, 3.97-3.96, 3.86-3.83, 2.05-1.94, 1.28-0.8.

PFc.



Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (23 mg, 41.0 μmol) and **7c** (30 mg, 40.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of Pd(PPh₃)₄. 1 mL of deoxygenated toluene, 1 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 25k, M_w [g/mol]: 57k. Yield: 25 mg (70%). ¹H NMR (500 MHz, CDCl₃): δ 7.82-7.62, 7.17-7.15, 6.87-6.86, 6.82, 6.6-6.58, 4.1, 3.98, 3.86, 2.07-1.94, 1.4-0.8.

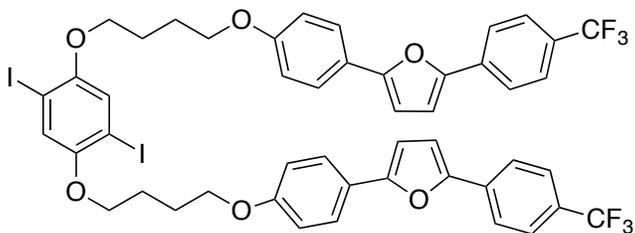
5,5'-(4,4'-(4,4'-(2,5-diiodo-1,4-phenylene)bis(oxy)bis(butane-4,1-diyl))bis(oxy)bis(4,1-phenylene))bis(2-phenylfuran) (8a)



Compound **6a** (95 mg, 0.26 mmol, 2.0 eq), KOH (29 mg, 0.5 mmol, 4.0 eq) and 1,4-diiodo-2,5-hydroquinone (47 mg, 0.13 mmol,

1.0 eq) were dissolved in 1.4 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. The mixture was extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and CH₂Cl₂ (2:1, v/v) to yield **8a**. Yield: 49 mg (40%). ¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, J=8 Hz, 4H), 7.67 (d, J=8.5 Hz, 4H), 7.40 (t, J=7.5 Hz, 4H), 7.27-7.24 (m, 2H), 7.21 (s, 2H), 6.96 (d, J=8 Hz, 4H), 6.72 (m, 2H), 6.61 (d, J= 3.5 Hz, 2H), 4.12 (t, J=6 Hz, 4H), 4.04 (t, J= 5 Hz, 4H), 2.05(m, 8H). ¹³C NMR (125 MHz, CDCl₃): δ 158.5, 153.5, 152.8, 152.7, 131, 128.7, 127.1, 125.2, 123.9, 123.6, 122.8, 114.8, 107.2, 105.6, 86.3, 69.9, 67.6, 26.1, 26. HRMS calcd for C₄₆H₄₀I₂O₆ (M+NH₄)⁺, 960.1253, found, 960.1275.

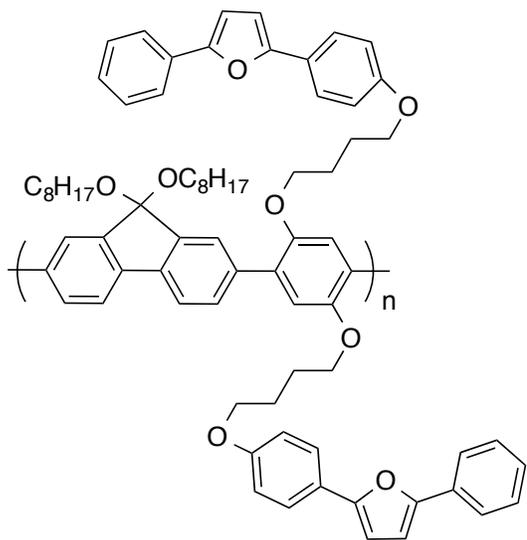
5,5'-(4,4'-(4,4'-(2,5-diiodo-1,4-phenylene)bis(oxy)bis(butane-4,1-diyl))bis(oxy)bis(4,1-phenylene))bis(2-(4-(trifluoromethyl)phenylfuran) (8c).



Compound **6c** (97 mg, 0.22 mmol, 2.0 eq), KOH (25 mg, 0.44 mmol, 4.0 eq) and 1,4-Diiodo-2,5-hydroquinone (40

mg, 0.11 mmol, 1.0 eq) were dissolved in 3.2 mL of dry DMSO at room temperature under argon and stirred overnight. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was dissolved in CH₂Cl₂ and washed with 10% aq NaOH, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was recrystallized from hexanes and CH₂Cl₂ mixture to yield **8c**. Yield: 45 mg (38%). ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, J=8 Hz, 4H), 7.69 (d, J=8.5 Hz, 4H), 7.64 (t, J=8.5 Hz, 4H), 7.21 (s, 2H), 6.97 (d, J=8.5 Hz, 4H), 6.84 (d, J=3 Hz, 2H), 6.64 (d, J= 3 Hz, 2H), 4.13 (t, J=6 Hz, 4H), 4.04 (t, J= 6 Hz, 4H), 2.07-2.03 (m, 8H). ¹³C NMR (125 MHz, CDCl₃): d 158.9, 154.7, 152.8, 151.1, 134.0, 128.6 (q, J=130 Hz), 125.7 (m, 1C), 125.4, 124.2 (J = 1080 Hz), 123.4, 123.4, 122.8, 114.9, 109.3, 105.9, 86.3, 69.9, 67.6, 26.1, 26.0. HRMS calcd for C₄₈H₃₈F₆I₂O₆ (M+NH₄)⁺, 1096.1000, found, 1096.1007.

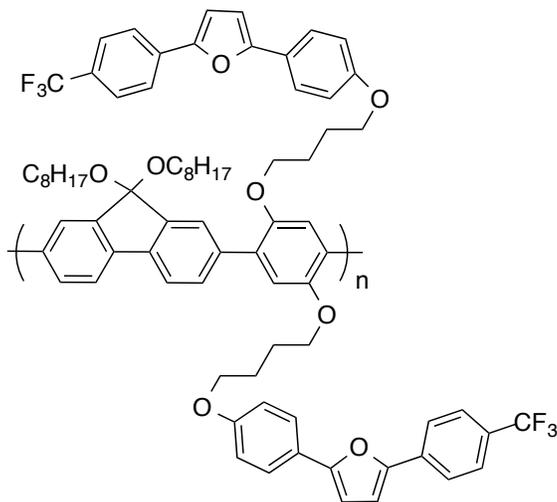
PF-8a.



Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (13.6 mg, 24.0 μ mol) and **8a** (23 mg, 24.0 μ mol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of Pd(PPh₃)₄.

0.75 mL of deoxygenated toluene, 0.75 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 1 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. Yield: 12.5 mg (50%) M_n [g/mol]: 8.3k, M_w [g/mol]: 12k. ¹H NMR (500 MHz, CDCl₃): δ 7.84-7.61, 7.4-7.38, 7.25, 7.16, 6.84, 6.73-6.7, 6.6-6.55, 4.1, 3.94, 2.07-1.93, 1.28-0.79.

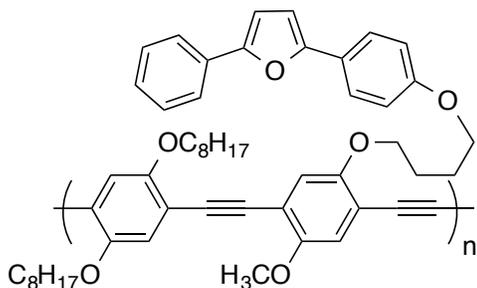
PF-8c.



Equimolar amounts of two monomers: 9,9-dioctylfluorene-2,7-diboronic acid bis (1,3-propanediol) ester (13.5 mg, 24.0 μmol) and **8c** (26 mg, 24.0 μmol) were weighed into a Schlenk tube equipped with a small magnetic stir bar. To the reaction tube was

added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$. 0.6 mL of deoxygenated toluene, 0.6 mL of deoxygenated 2M aqueous potassium carbonate solution, and several drops of Aliquat 336 were added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 90 °C for 48 hours. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated from the toluene solution into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 1 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 8.2k, M_w [g/mol]: 10k. Yield: 14.8 mg (51%). ^1H NMR (500 MHz, CDCl_3): δ 7.77-7.59, 7.16, 6.85-6.84, 6.8, 6.56, 4.08, 3.95, 2.05-1.93, 1.28-0.8.

PPEa.



Equimolar amounts of two monomers: 1,4-Diethynyl-2,5-bis(octyloxy)benzene (15 mg, 39.0 μmol) and **7a** (26.7 mg, 24.0 μmol) were weighed into a Schlenk tube

equipped with a small magnetic stir bar. To the reaction tube was added less than 0.5 mg of $\text{Pd}(\text{PPh}_3)_4$ and CuI . 6 mL of deoxygenated toluene: diisopropylamine (4:1) solution was added under a heavy argon flow. Deoxygenation of solvents was achieved by sparging with argon. The reaction mixture in the sealed tube was then stirred vigorously at 65 °C overnight. After cooling to room temperature, the aqueous layer was removed by pipette, and the organic layer was washed with several milliliters deionized water. The polymer was then precipitated into 15 mL of methanol and collected by centrifugation and decanting. The polymer was then dissolved in 1 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 15 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 12500, M_w [g/mol]: 35600. Yield: 24 mg (77%) ^1H NMR (500 MHz, CDCl_3): δ 7.77-7.69, 7.62, 7.42-7.37, 7.32-7.24, 7.09-7.05, 6.92-6.89, 6.7, 6.59, 4.14-4.00, 3.93-3.85, 2.09, 1.88-1.8, 1.6-1.47, 1.41-1.28, 0.88-0.86.

2.5 References

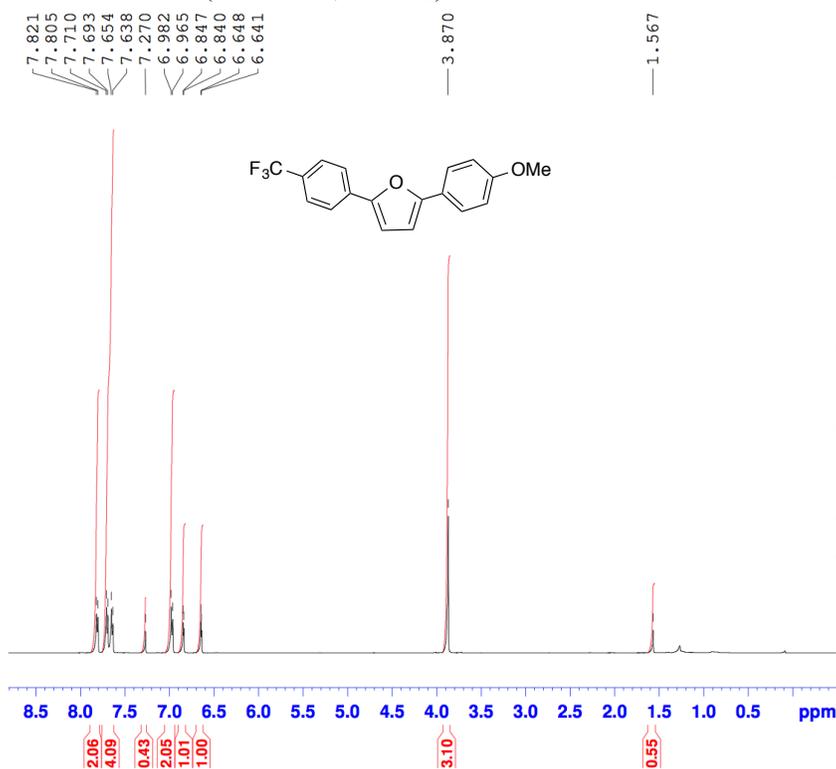
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Chapter 2 Appendix

^1H and ^{13}C NMR

¹H NMR of **4c** (500 MHz, CDCl₃)

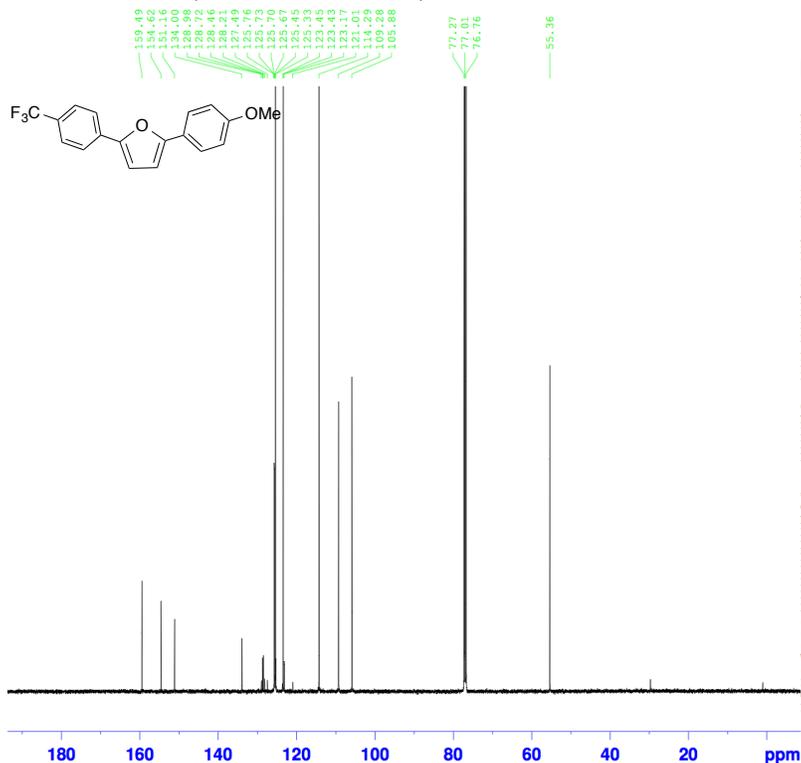


```

NAME      ek-1-158
EXPNO    1
PROCNO   1
Date_    20120711
Time     13.54
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ        3.2768500 sec
RG        203
DW        50.000 usec
DE        6.50 usec
TE        293.3 K
D1        0.50000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1     1H
P1       17.00 usec
PL1      1.00 dB
PL1W     17.75783539 W
SFO1     500.1318364 MHz
SI       65536
SF       500.13000718 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
```

¹³C NMR of **4c** (125 MHz, CDCl₃)



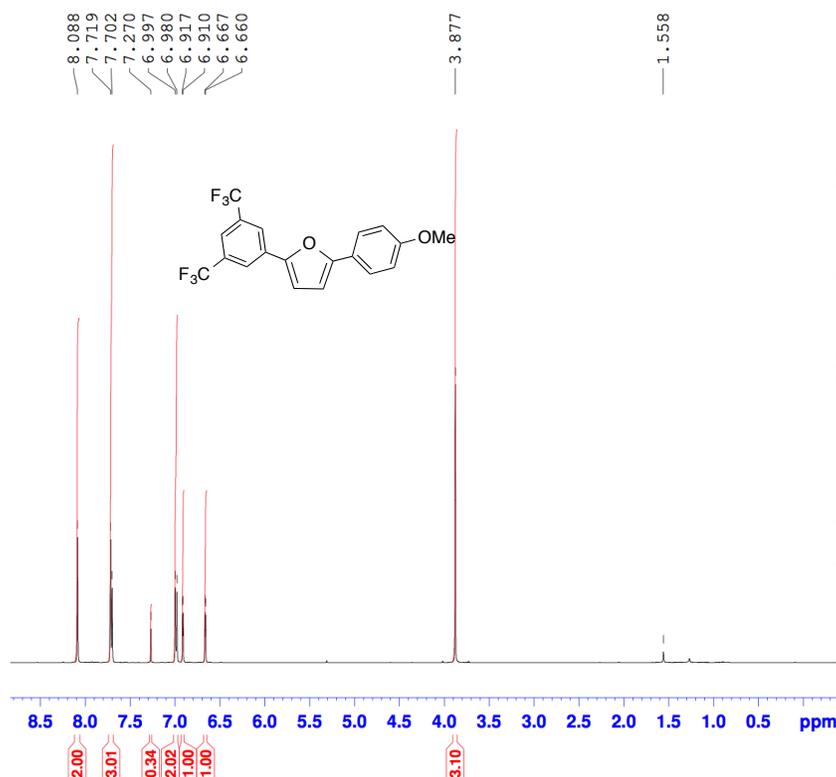
```

NAME      CF3-Pendant-13C
EXPNO    3
PROCNO   1
Date_    20121204
Time     14.30
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        5131
DS        4
SWH      29761.904 Hz
FIDRES   0.454131 Hz
AQ        1.1010548 sec
RG        203
DW        16.800 usec
DE        6.50 usec
TE        295.3 K
D1        0.50000000 sec
D11      0.03000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1     13C
P1       9.50 usec
PL1      0.00 dB
PL1W     89.92553711 W
SFO1     125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      1.00 dB
PL12     13.04 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    1.11017132 W
PL13W    0.46707872 W
SFO2     500.1320005 MHz
SI       65536
SF       125.7577890 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
    
```

¹H NMR of **4d** (500 MHz, CDCl₃)

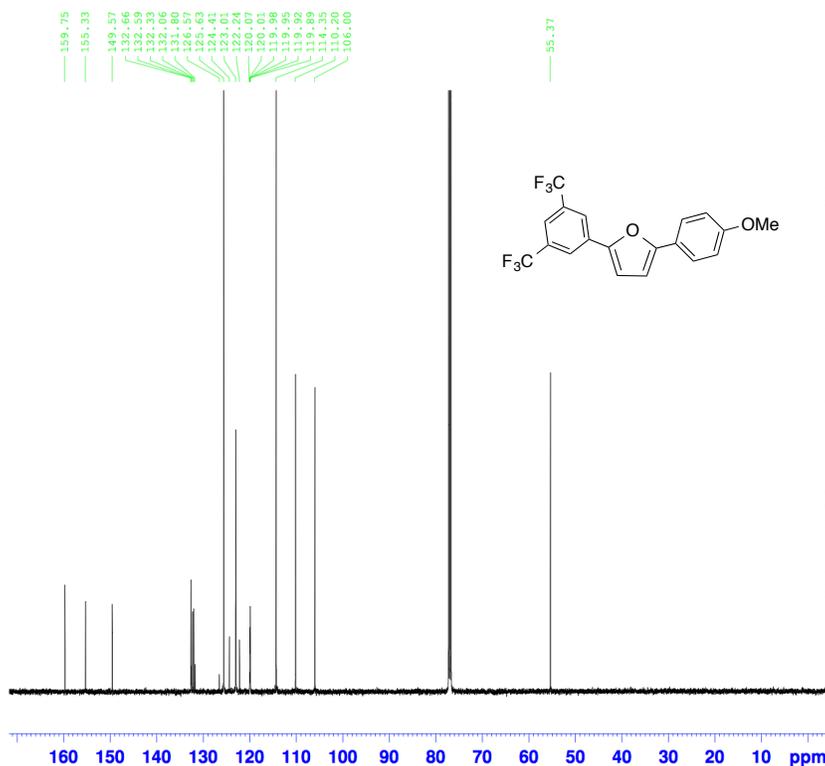


```

NAME      bisCF3-Pendant-13C
EXPNO     1
PROCNO    1
Date_     20121205
Time      9.08
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        10000.000 Hz
FIDRES     0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         294.8 K
D1         0.50000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       1H
P1         20.00 usec
PL1        1.00 dB
PL1W       17.75783539 W
SFO1       500.1318364 MHz
SI         65536
SF         500.1300078 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR of **4d** (125 MHz, CDCl₃)



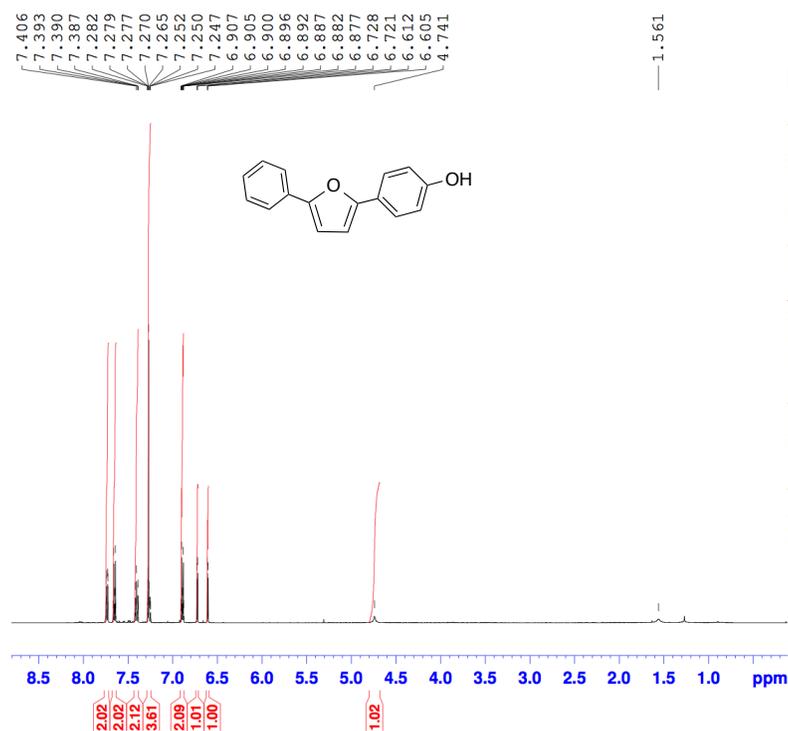
```

NAME      bisCF3-Pendant-13C
EXPNO     2
PROCNO    1
Date_     20121205
Time      9.11
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         3872
DS         4
SWH        29761.904 Hz
FIDRES     0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         295.3 K
D1         0.50000000 sec
D11        0.03000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.50 usec
PL1        0.00 dB
PL1W       89.92553711 W
SFO1       125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        1.00 dB
PL12       13.04 dB
PL13       16.80 dB
PL12W      17.75783539 W
PL12W      1.11017132 W
PL13W      0.46707872 W
SFO2       500.1320005 MHz
SI         65536
SF         125.7577890 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

¹H NMR of **5a** (500 MHz, CDCl₃)



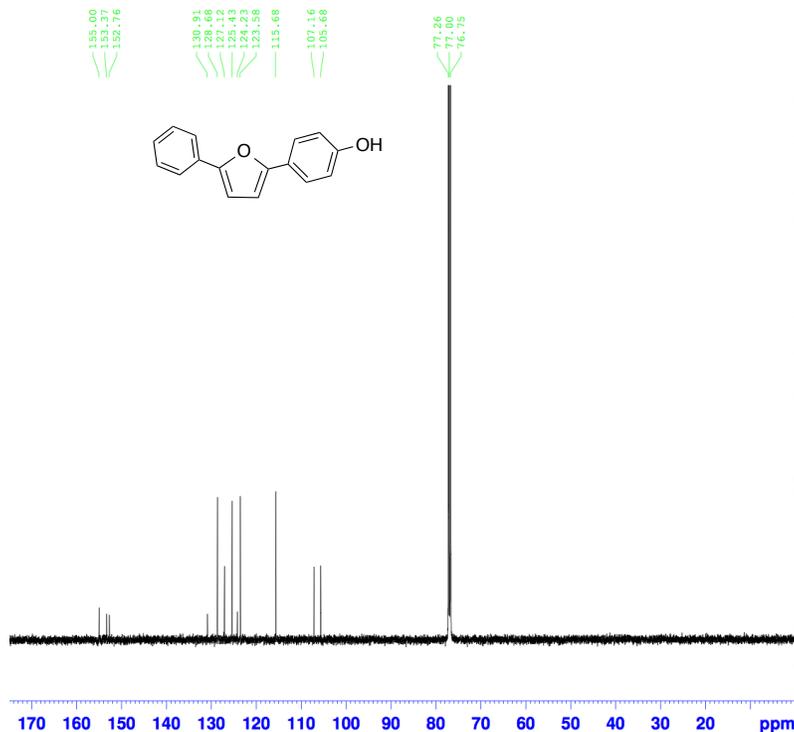
```

NAME          ek-1-031
EXPNO         12
PROCNO        1
Date_         20110823
Time          11.34
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
ID            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            203
DW            50.000 usec
DE            6.50 usec
TE            299.7 K
D1            0.50000000 sec
D10           1
  
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            14.50 usec
PL1           2.00 dB
PL1W          14.10554981 W
SFO1          500.1318364 MHz
SI            65536
SF            500.1300085 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
  
```

¹³C NMR of **5a** (125 MHz, CDCl₃)



```

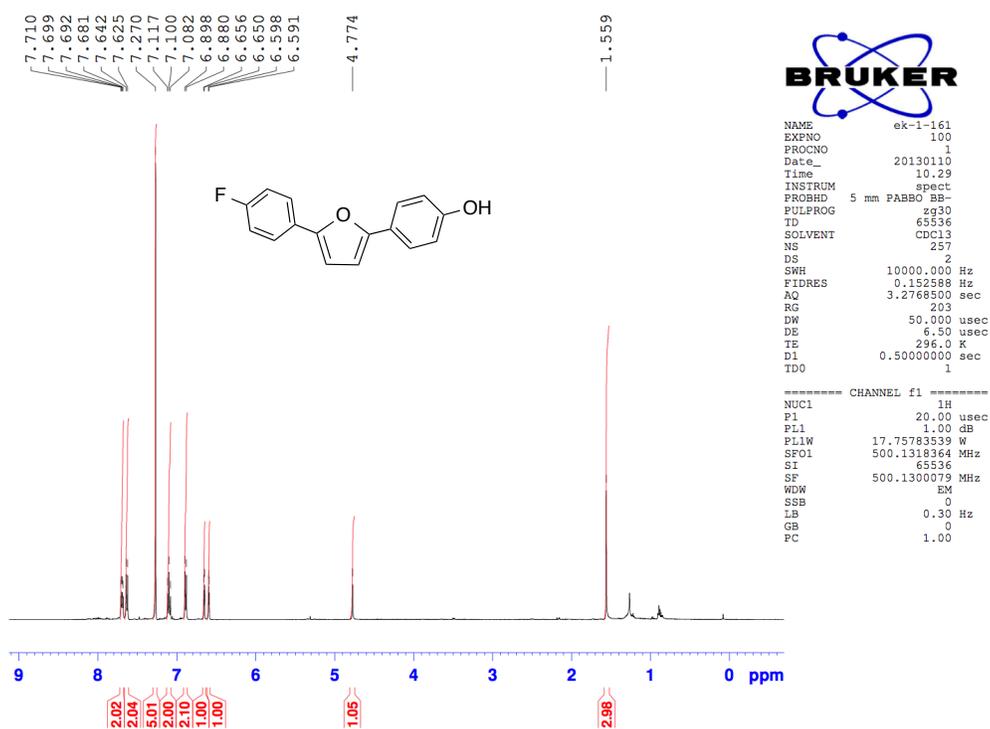
NAME          ek-1-031
EXPNO         6
PROCNO        1
Date_         20110823
Time          14.28
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
ID            65536
SOLVENT       CDCl3
NS            4
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            300.2 K
D1            0.50000000 sec
D11           0.03000000 sec
D10           1
  
```

```

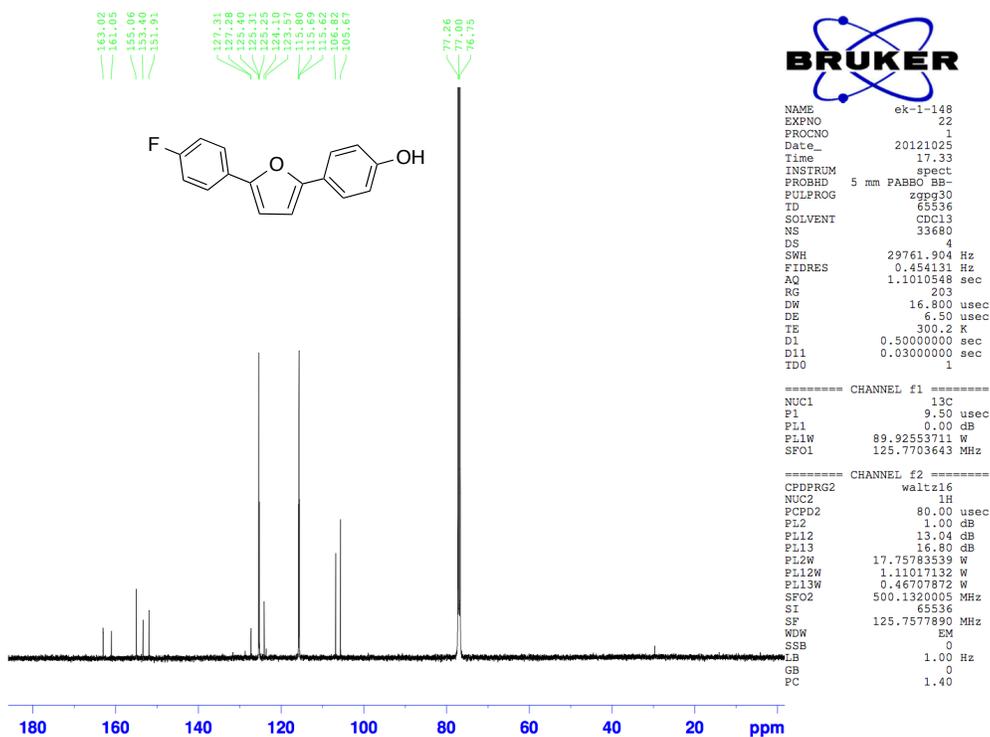
===== CHANNEL f1 =====
NUC1          13C
P1            8.50 usec
PL1           0.00 dB
PL1W          89.92553711 W
SFO1          125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           2.00 dB
PL12          16.83 dB
PL13          16.80 dB
PL2W          14.10554981 W
PL12W         0.46386331 W
PL13W         0.46707872 W
SFO2          500.1320005 MHz
SI            65536
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

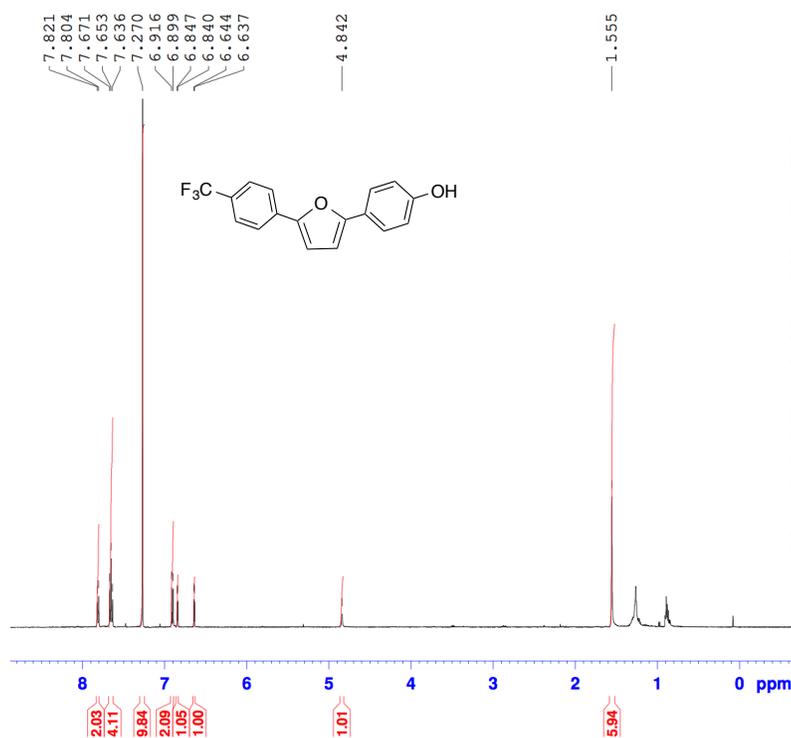
¹H NMR of **5b** (500 MHz, CDCl₃)



¹³C NMR of **5b** (125 MHz, CDCl₃)



¹H NMR of **5c** (500 MHz, CDCl₃)



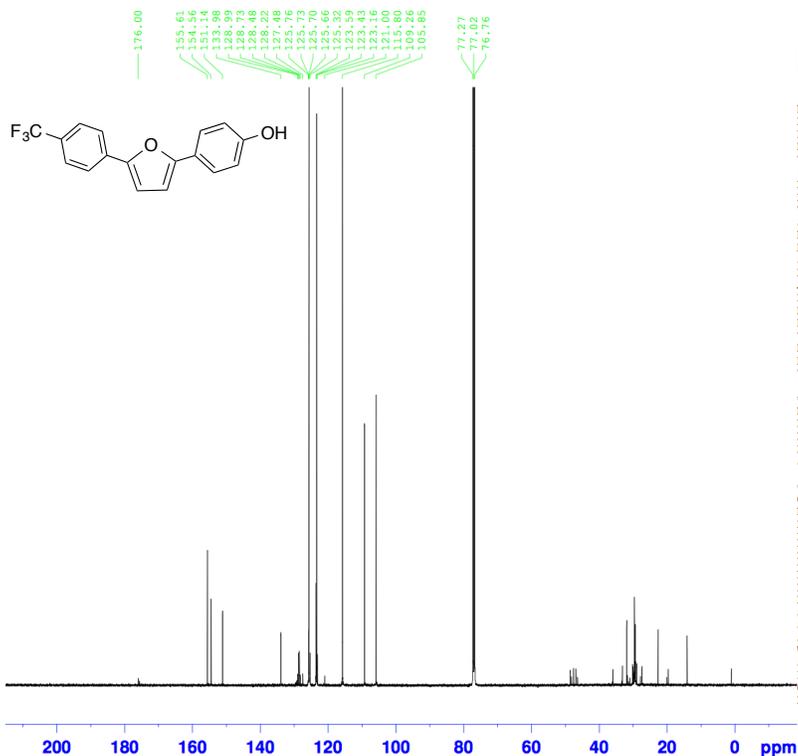
```

NAME      ek-1-161
EXPNO    22
PROCNO   1
Date_    20130110
Time     10.14
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
ID       65536
SOLVENT  CDCl3
NS       149
DS       2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ       3.2768500 sec
RG       203
DW       50.000 usec
DE       6.50 usec
TE       296.2 K
D1       0.50000000 sec
TD0      1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        20.00 usec
PL1       1.00 dB
PL1W     17.75783539 W
SFO1     500.1318364 MHz
SI       65536
SF       500.1300079 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
```

¹³C NMR of **5c** (125 MHz, CDCl₃)



```

NAME      CF3---OH-13C
EXPNO    12
PROCNO   1
Date_    20121204
Time     23.27
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
ID       65536
SOLVENT  CDCl3
NS       19650
DS       4
SWH      29761.904 Hz
FIDRES   0.454131 Hz
AQ       1.1010548 sec
RG       203
DW       16.800 usec
DE       6.50 usec
TE       296.2 K
D1       0.50000000 sec
D11     0.03000000 sec
TD0      1
    
```

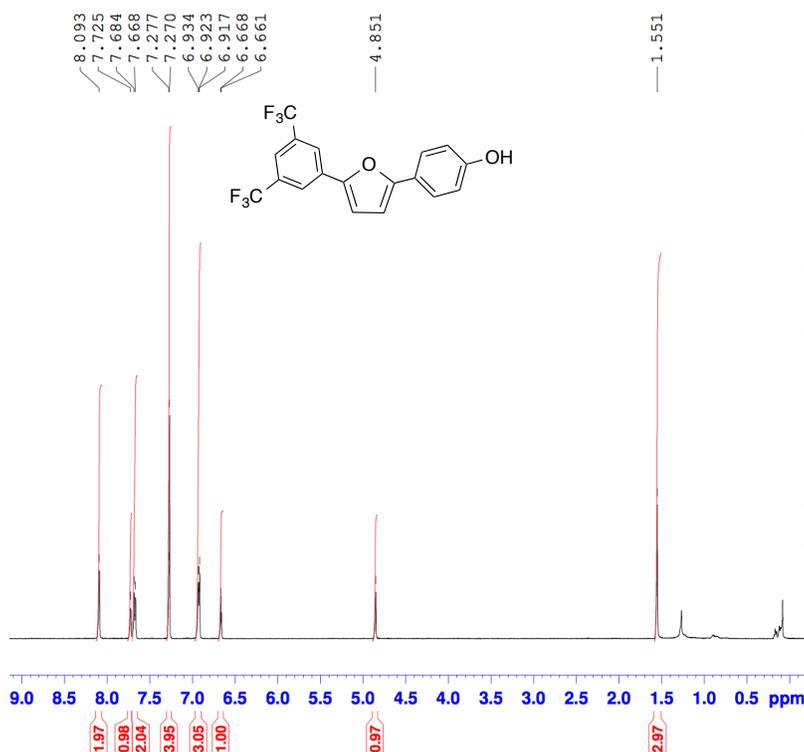
```

===== CHANNEL f1 =====
NUC1      13C
P1        9.50 usec
PL1       0.00 dB
PL1W     89.92553711 W
SFO1     125.7703643 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2      1H
PCPD2    80.00 usec
PL2       1.00 dB
PL12     13.04 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    1.11017132 W
PL13W    0.46707872 W
SFO2     500.1320005 MHz
SI       65536
SF       125.7577890 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
    
```

¹H NMR of **5d** (500MHz, CDCl₃)



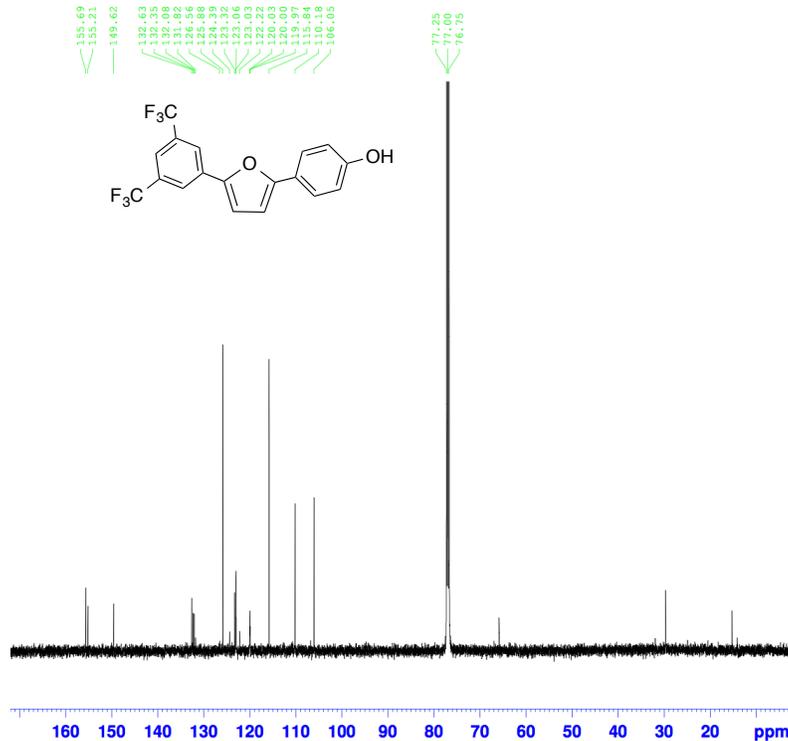
```

NAME          ek-1-182
EXPNO         1
PROCNO        1
Date_         20120918
Time          12.41
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            203
DW            50.000 usec
DE            6.50 usec
TE            300.1 K
D1            0.50000000 sec
D11           1
TD0           1
    
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            20.00 usec
PL1           1.00 dB
PL1W          17.75783539 W
SFO1          500.1318364 MHz
SI            65536
SF            500.1300075 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

¹³C NMR of **5d** (500MHz, CDCl₃)



```

NAME          bisCF3-----OH 13C
EXPNO         2
PROCNO        1
Date_         20121205
Time          23.26
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            24100
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            295.7 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1
    
```

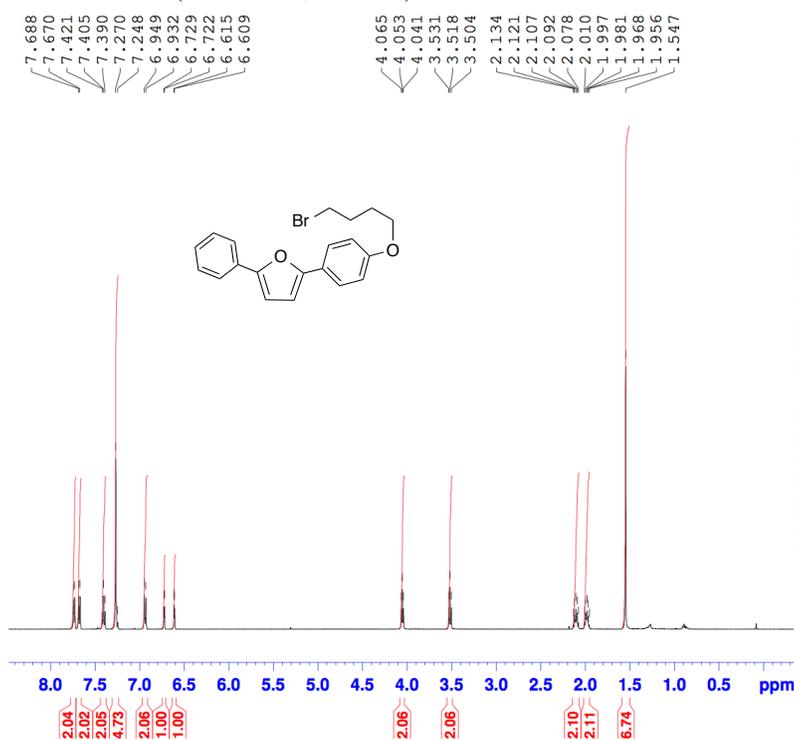
```

===== CHANNEL f1 =====
NUC1          13C
P1            9.50 usec
PL1           0.00 dB
PL1W          89.92553711 W
SFO1          125.7703643 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           1.00 dB
PL12          13.04 dB
PL13          16.80 dB
PL2W          17.75783539 W
PL12W         1.11017132 W
PL13W         0.46707872 W
SFO2          500.1320005 MHz
SI            65536
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            0.50
    
```

¹H NMR of **6a** (500 MHz, CDCl₃)



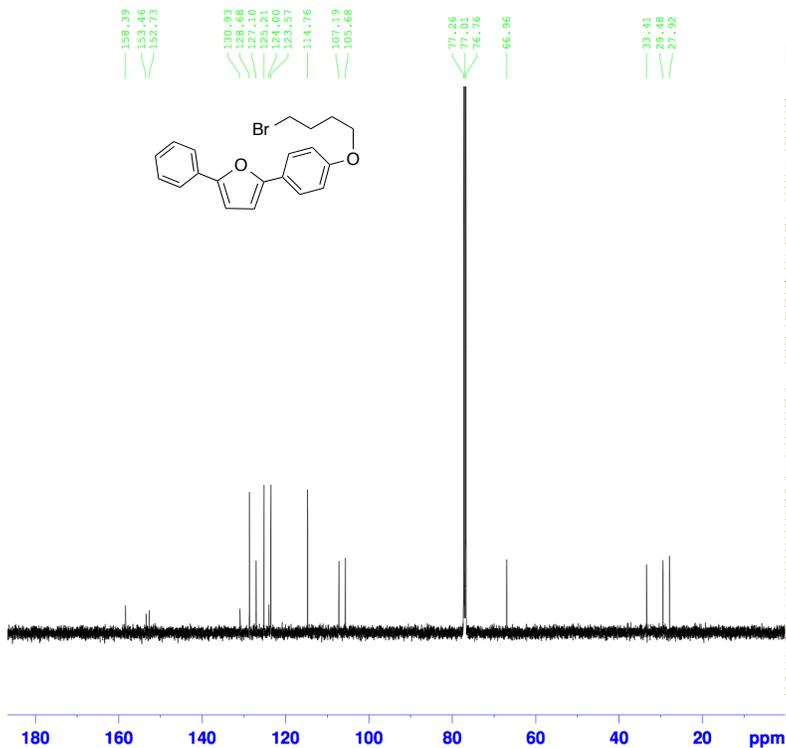
```

NAME      ek-1-165
EXPNO     4
PROCNO    1
Date_     20120806
Time      13.11
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        10000.000 Hz
FIDRES    0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         299.7 K
D1         0.50000000 sec
TDO       1
    
```

```

----- CHANNEL f1 -----
NUC1      1H
P1         20.00 usec
PL1        1.00 dB
PL1W      17.75783539 W
SFO1      500.1318364 MHz
SI         65536
SF         500.1300078 MHz
WDW        EM
SBB         0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR of **6a** (125 MHz, CDCl₃)



```

NAME      ek-1-165
EXPNO     3
PROCNO    1
Date_     20120806
Time      12.54
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         513
DS         4
SWH        29761.904 Hz
FIDRES    0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         300.3 K
D1         0.50000000 sec
D11        0.03000000 sec
TDO       1
    
```

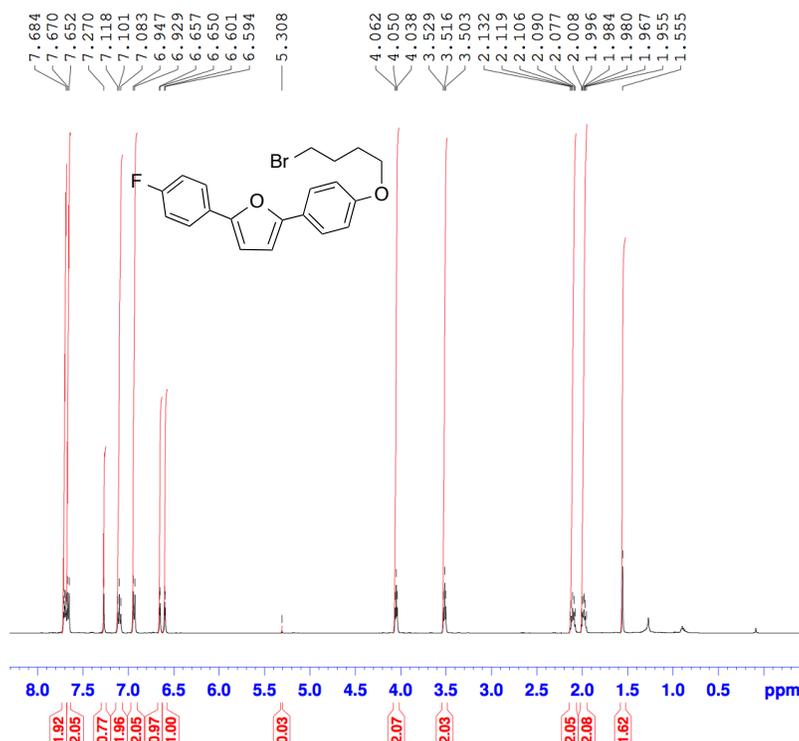
```

----- CHANNEL f1 -----
NUC1      13C
P1         9.50 usec
PL1         0.00 dB
PL1W      89.92553711 W
SFO1      125.7703643 MHz
    
```

```

----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        1.00 dB
PL12      13.04 dB
PL13      16.80 dB
PL2W      17.75783539 W
PL12W     1.11017132 W
PL13W     0.46707872 W
SFO2      500.1320005 MHz
SI         65536
SF         125.7577890 MHz
WDW        EM
SBB         0
LB         1.00 Hz
GB         0
PC         1.40
    
```

¹H NMR of **6b** (500 MHz, CDCl₃)



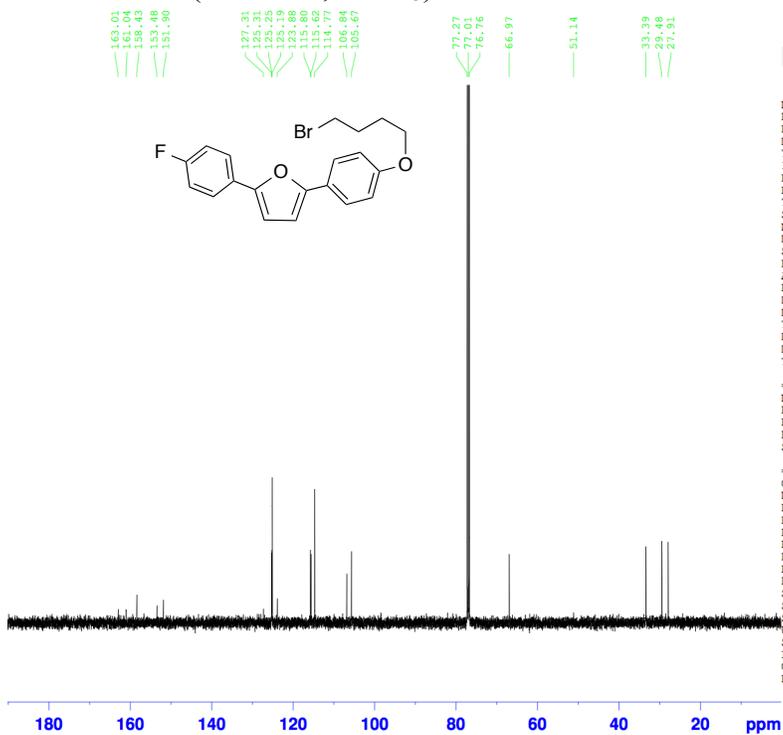
```

NAME      ek-1-149
EXPNO     1
PROCNO    1
Date_     20120625
Time      13.14
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
ID        65536
SOLVENT   CDCl3
NS        18
DS        2
SWH       10000.000 Hz
FIDRES    0.152588 Hz
AQ        3.2768500 sec
RG        203
DW        50.000 usec
DE        6.50 usec
TE        300.0 K
D1        0.50000000 sec
TD0       1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        17.00 usec
PL1       1.00 dB
PL1W      17.75783539 W
SF01      500.1318364 MHz
SI        65536
SF        500.1300084 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```

¹³C NMR of **6b** (125 MHz, CDCl₃)



```

NAME      ek-1-149
EXPNO     2
PROCNO    1
Date_     20120625
Time      13.18
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
ID        65536
SOLVENT   CDCl3
NS        273
DS        4
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ        1.1010548 sec
RG        203
DW        16.800 usec
DE        6.50 usec
TE        300.0 K
D1        0.50000000 sec
D11       0.03000000 sec
TD0       1
    
```

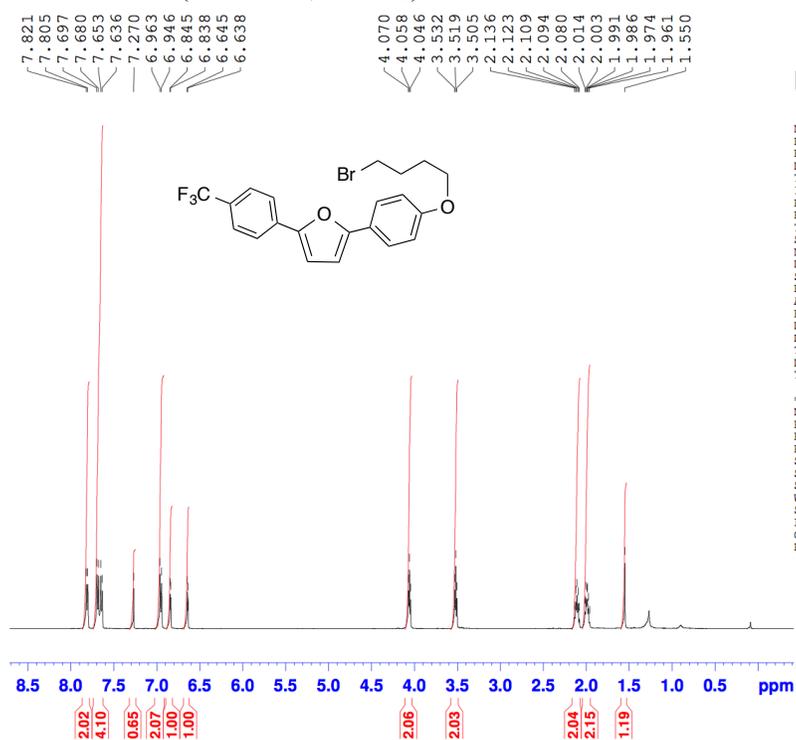
```

===== CHANNEL f1 =====
NUC1      13C
P1        9.50 usec
PL1       0.00 dB
PL1W      89.92553711 W
SF01      125.7703643 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       1.00 dB
PL12     14.45 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    0.80239832 W
PL13W    0.46707812 W
SF02     500.1320005 MHz
SI        65536
SF        125.7577890 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.00
    
```

¹H NMR of **6c** (500 MHz, CDCl₃)



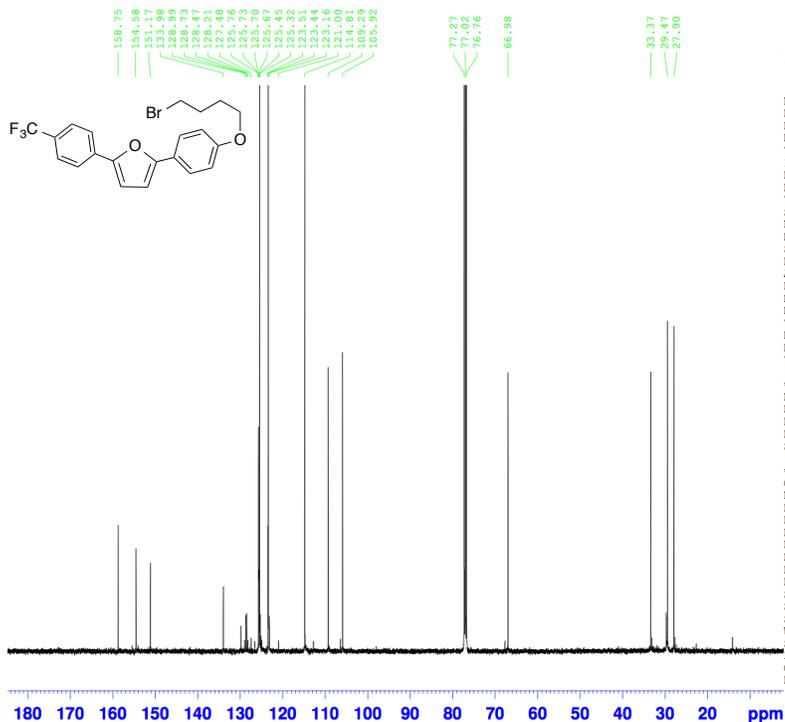
```

NAME      ek-1-162
EXPNO    1
PROCNO   1
Date_    20120801
Time     16.49
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ        3.2768500 sec
RG        203
DW        50.000 usec
DE        6.50 usec
TE        299.9 K
D1        0.5000000 sec
TD0       1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        20.00 usec
PL1       1.00 dB
PL1W     17.75783539 W
SF01     500.1318364 MHz
SI        65536
SF        500.1300075 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```

¹³C NMR of **6c** (125 MHz, CDCl₃)



```

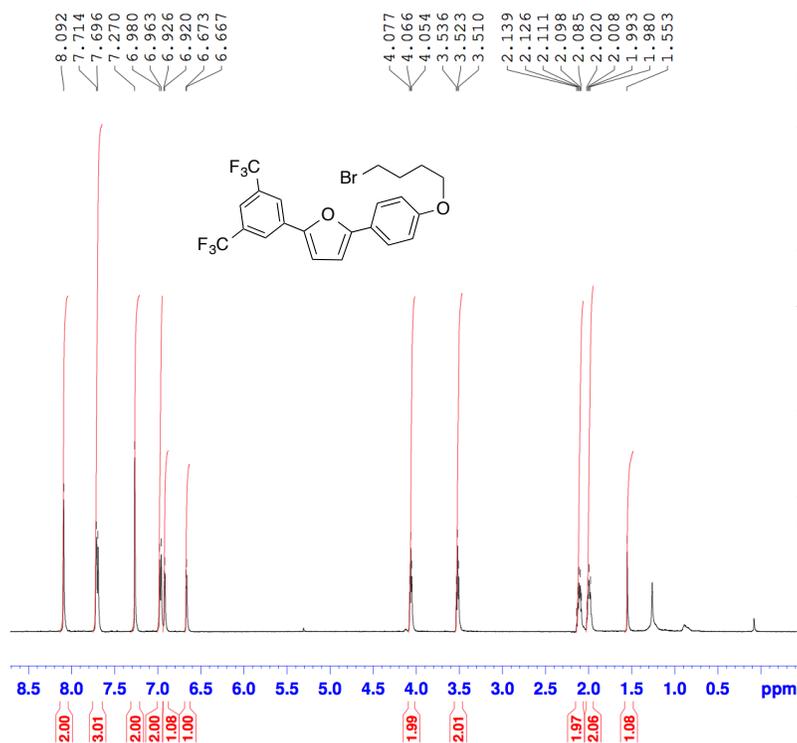
NAME      CF3---Br-13C
EXPNO    2
PROCNO   1
Date_    20121204
Time     20.43
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        5725
DS        4
SWH      29761.904 Hz
FIDRES   0.454131 Hz
AQ        1.1010548 sec
RG        203
DW        16.800 usec
DE        6.50 usec
TE        296.1 K
D1        0.5000000 sec
D11      0.0300000 sec
TD0       1
    
```

```

===== CHANNEL f1 =====
NUC1      13C
P1        9.50 usec
PL1       0.00 dB
PL1W     89.92553711 W
SF01     125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2      1H
PCPD2    80.00 usec
PL2       1.00 dB
PL12     13.04 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    1.11017132 W
PL13W    0.46707872 W
SF02     500.1320005 MHz
SI        65536
SF        125.7577890 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
    
```

¹H NMR of **6d** (500 MHz, CDCl₃)

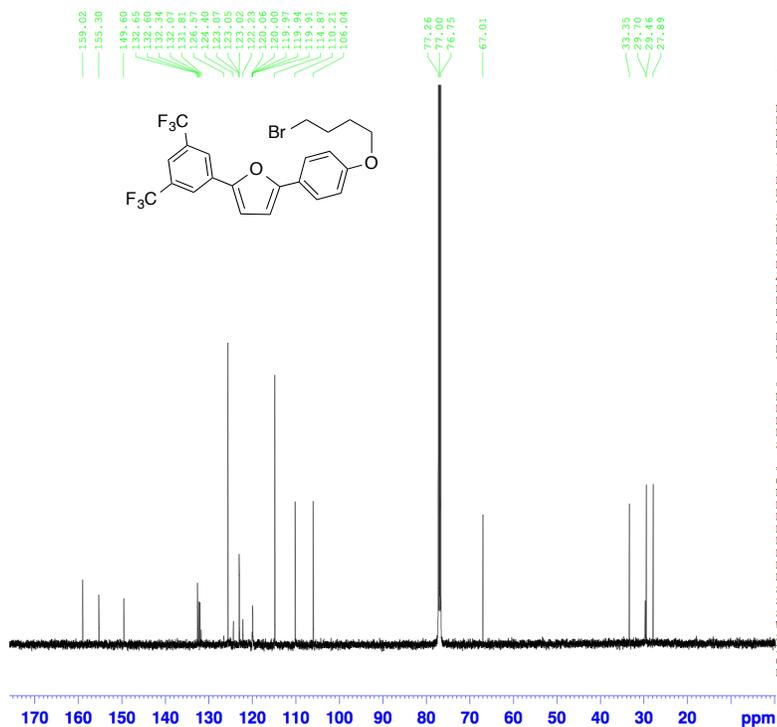


```

NAME      ek-1-183
EXPNO    3
PROCNO   1
Date_    20120920
Time     11.02
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      10000.000 Hz
FIDRES   0.152568 Hz
AQ       3.2768500 sec
RG       203
DW       50.000 usec
DE       6.50 usec
TE       294.5 K
D1       0.50000000 sec
TDO      1

===== CHANNEL f1 =====
NUC1     1H
P1       20.00 usec
PL1      1.00 dB
PL1W     17.75783539 W
SFO1     500.1318364 MHz
SI       65536
SF       500.1300085 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
```

¹³C NMR of **6d** (125 MHz, CDCl₃)



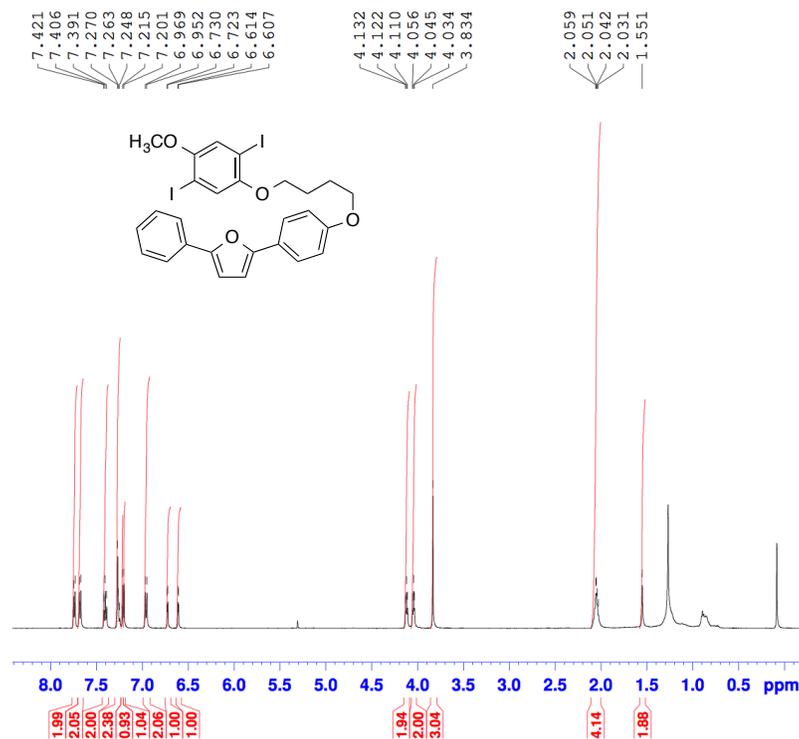
```

NAME      bisCF3----Br-13C
EXPNO    2
PROCNO   1
Date_    20121205
Time     11.04
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       12000
DS       4
SWH      29761.904 Hz
FIDRES   0.454131 Hz
AQ       1.1010548 sec
RG       203
DW       16.800 usec
DE       6.50 usec
TE       296.0 K
D1       0.50000000 sec
D11      0.03000000 sec
TDO      1

===== CHANNEL f1 =====
NUC1     13C
P1       9.50 usec
PL1      0.00 dB
PL1W     89.92553711 W
SFO1     125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      1.00 dB
PL12     13.04 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    1.11017132 W
PL13W    0.46707872 W
SFO2     500.1320005 MHz
SI       65536
SF       125.7577890 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       0.20
    
```

¹H NMR of **7a** (500 MHz, CDCl₃)



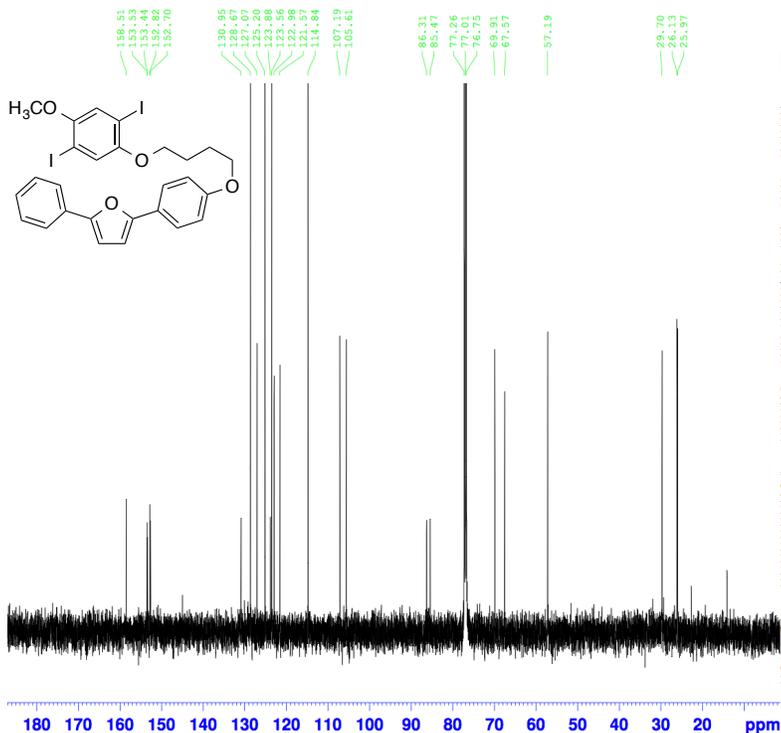
```

NAME      ek-1-210
EXPNO     2
PROCNO    1
Date_     20121101
Time      14.55
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
ID        65536
SOLVENT   CDCl3
NS        16
DS        2
SWH       10000.000 Hz
FIDRES    0.152588 Hz
AQ        3.2768500 sec
RG        203
DW        50.000 usec
DE        6.50 usec
TE        300.1 K
D1        0.50000000 sec
TDO       1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        20.00 usec
PL1       1.00 dB
PL1W     17.75783539 W
SFO1     500.1318364 MHz
SI        65536
SF        500.1300077 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```

¹³C NMR of **7a** (125 MHz, CDCl₃)



```

NAME      ek-1-210
EXPNO     3
PROCNO    1
Date_     20121101
Time      14.59
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
ID        65536
SOLVENT   CDCl3
NS        1623
DS        4
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ        1.1010548 sec
RG        203
DW        16.800 usec
DE        6.50 usec
TE        300.3 K
D1        0.50000000 sec
D11       0.03000000 sec
TDO       1
    
```

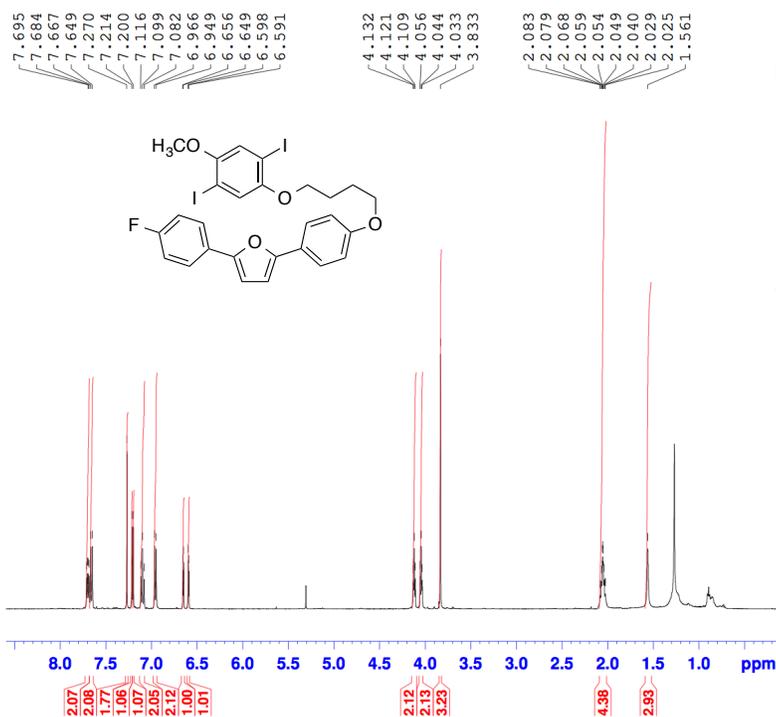
```

===== CHANNEL f1 =====
NUC1      13C
P1        9.50 usec
PL1       0.00 dB
PL1W     89.92553711 W
SFO1     125.7703643 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       1.00 dB
PL12     13.04 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    1.11017132 W
PL13W    0.46707872 W
SFO2     500.1320005 MHz
SI        65536
SF        125.7577890 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
    
```

¹H NMR of **7b** (500 MHz, CDCl₃)

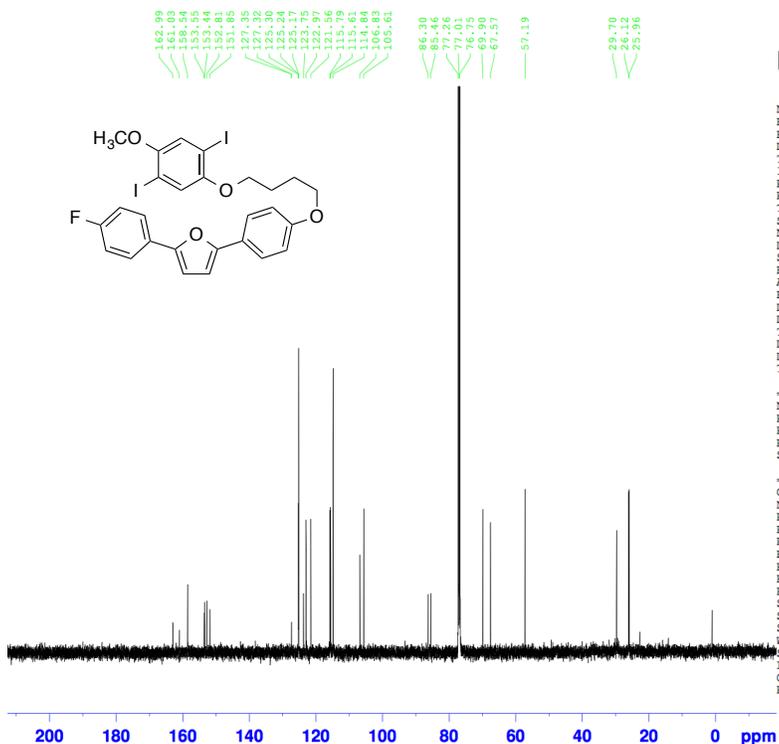


```

NAME          ek-1-150
EXPNO         2
PROCNO        1
Date_         20120627
Time         10.40
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            203
DW            50.000 usec
DE            6.50 usec
TE            299.9 K
D1            0.50000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            17.00 usec
PL1          1.00 dB
PL1W         17.75783539 W
SFO1         500.1318364 MHz
SI           65536
SF           500.1300084 MHz
WDW          EM
SSB          0
LB           0.30 Hz
GB           0
PC           1.00
    
```

¹³C NMR of **7b** (125 MHz, CDCl₃)



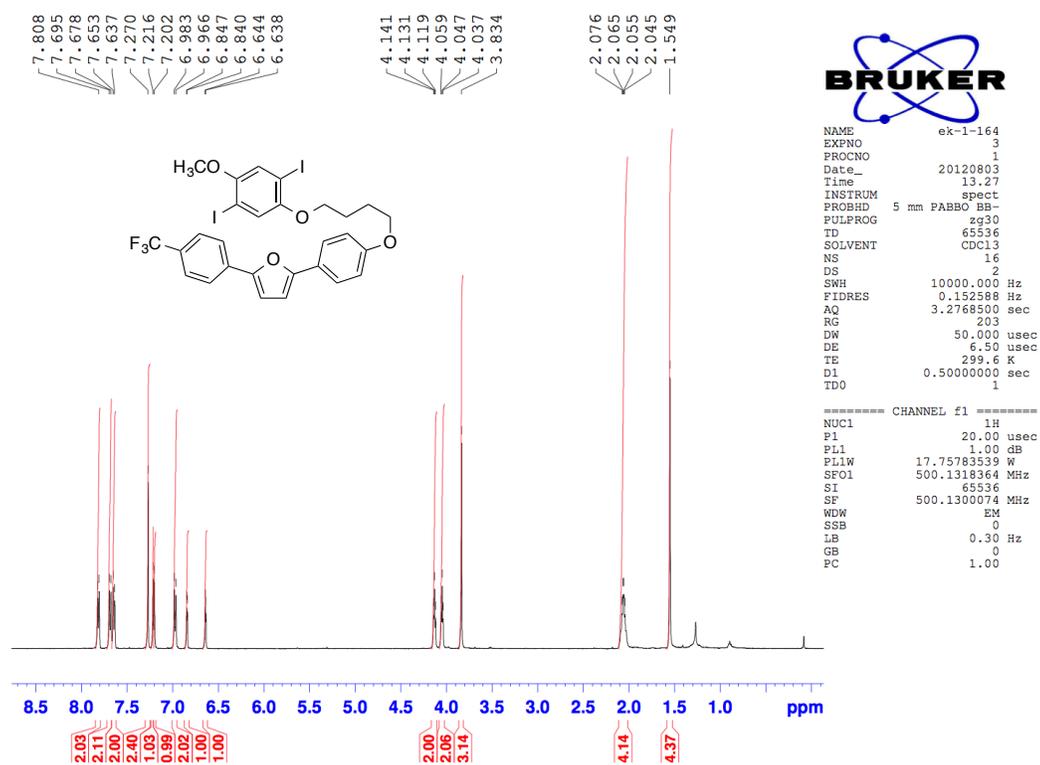
```

NAME          ek-1-150
EXPNO         56
PROCNO        1
Date_         20121203
Time         15.45
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            3367
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010348 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            296.0 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

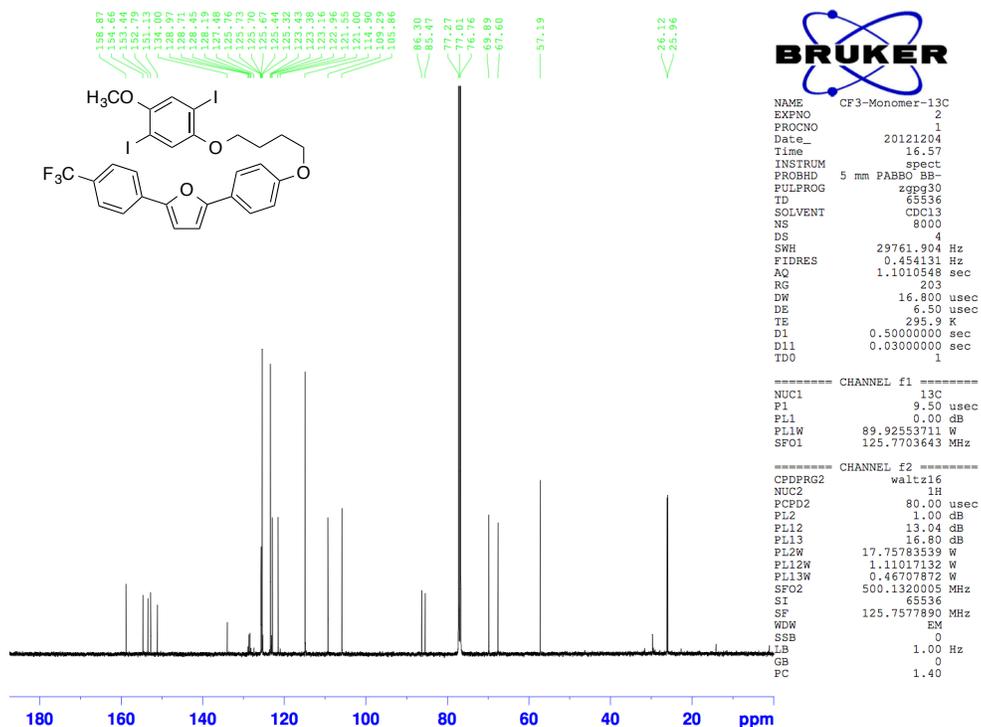
===== CHANNEL f1 =====
NUC1          13C
P1            9.50 usec
PL1          0.00 dB
PL1W         89.92553711 W
SFO1         125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2        80.00 usec
PL2          1.00 dB
PL12         13.04 dB
PL13         16.80 dB
PL2W         17.75783539 W
PL12W        1.11017132 W
PL13W        0.46707872 W
SFO2         500.1320005 MHz
SI           65536
SF           125.7577890 MHz
WDW          EM
SSB          0
LB           1.00 Hz
GB           0
PC           1.20
    
```

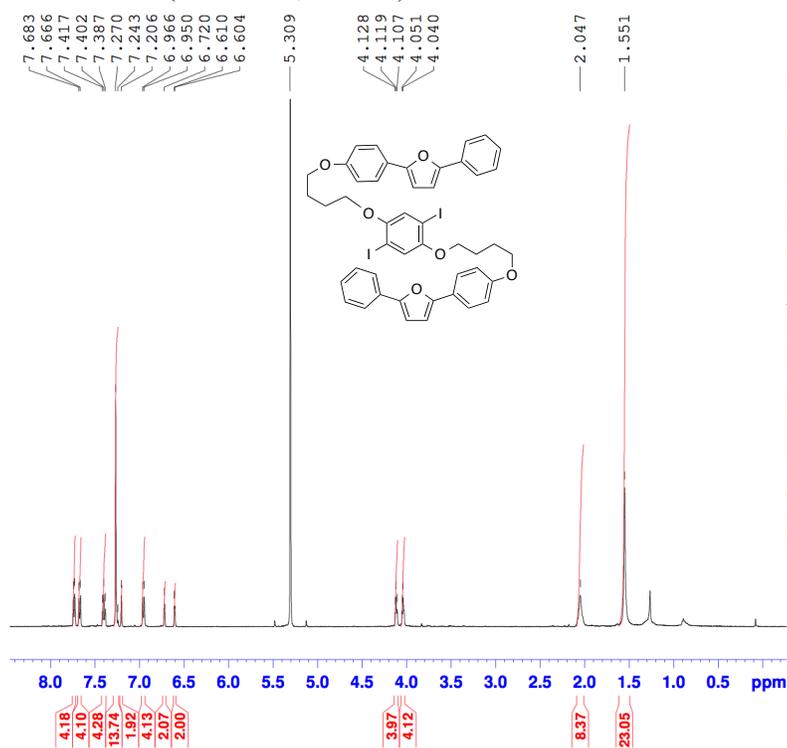
¹H NMR of 7c (500 MHz, CDCl₃)



¹³C NMR of 7c (500 MHz, CDCl₃)



¹H NMR of **8a** (500 MHz, CDCl₃)



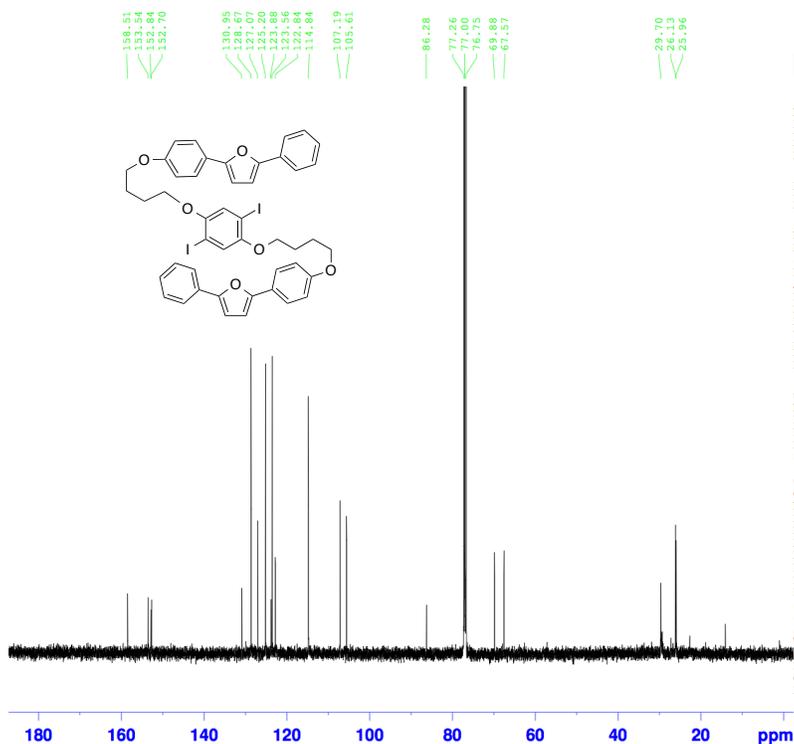
```

NAME      ek-1-167
EXPNO     5
PROCNO    1
Date_     20120808
Time      9.27
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH       10000.000 Hz
FIDRES    0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         300.1 K
D1         0.50000000 sec
TD0        1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1         20.00 usec
PL1        1.00 dB
PL1W      17.75783539 W
SFO1      500.1318364 MHz
SI         65536
SF         500.1300086 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR of **8a** (125 MHz, CDCl₃)



```

NAME      Double Monomer 13C
EXPNO     3
PROCNO    1
Date_     20121206
Time      11.29
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         2387
DS         4
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         300.0 K
D1         0.50000000 sec
D11        0.03000000 sec
TD0        1
    
```

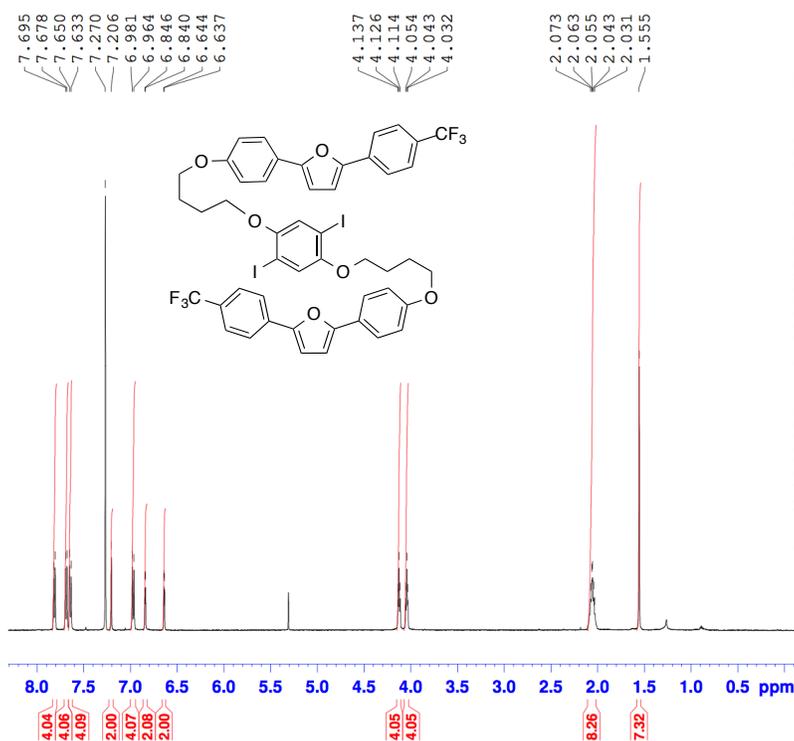
```

===== CHANNEL f1 =====
NUC1      13C
P1         9.50 usec
PL1         0.00 dB
PL1W      89.92553711 W
SFO1      125.7703643 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2        1.00 dB
PL2W      13.04 dB
PL13      16.80 dB
PL2W      17.75783539 W
PL12W     1.11017132 W
PL13W     0.46707872 W
SFO2      500.1320005 MHz
SI         65536
SF         125.7577890 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40
    
```

¹H NMR of **8c** (500 MHz, CDCl₃)

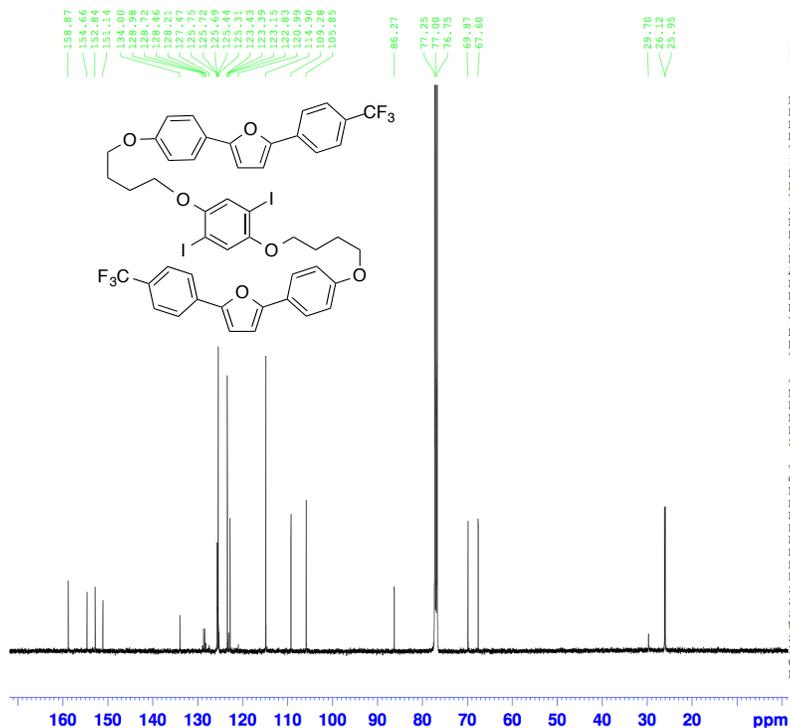


```

NAME          ek-1-203
EXPNO         7
PROCNO        1
Date_         20121019
Time          13.04
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            203
DW            50.000 usec
DE            6.50 usec
TE            293.8 K
D1            0.50000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1           1H
P1            20.00 usec
PL1           1.00 dB
PL1W          17.75783539 W
SFO1          500.1318364 MHz
SI            65536
SF            500.1300070 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

¹³C NMR of **8c** (125 MHz, CDCl₃)



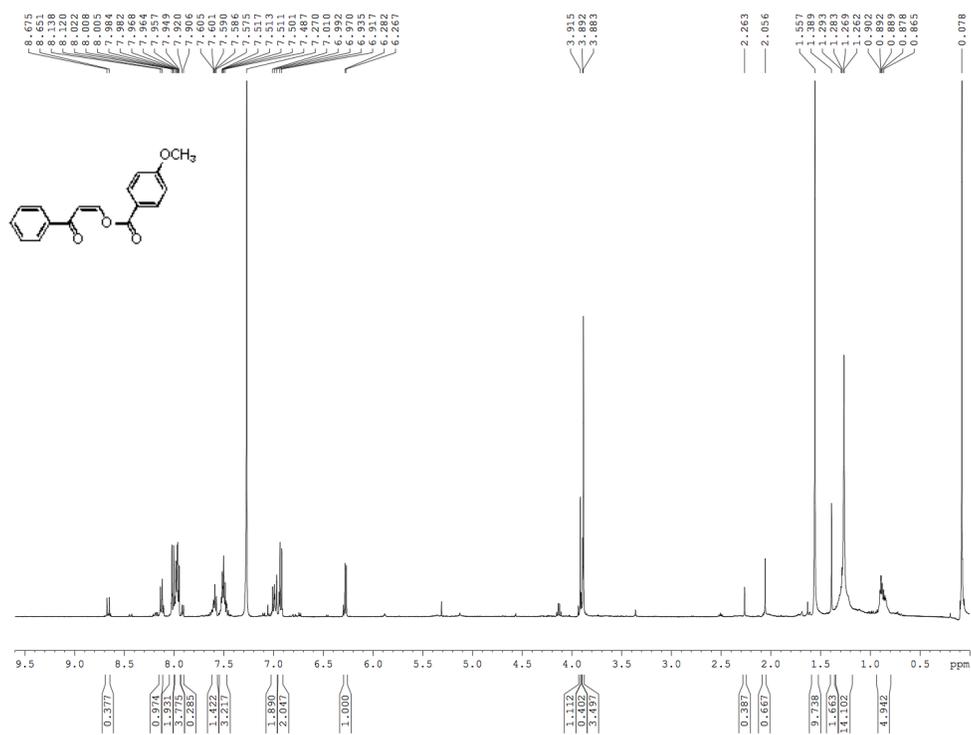
```

NAME          ek-1-203
EXPNO         11
PROCNO        1
Date_         20121210
Time          21.47
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            25000
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            300.2 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

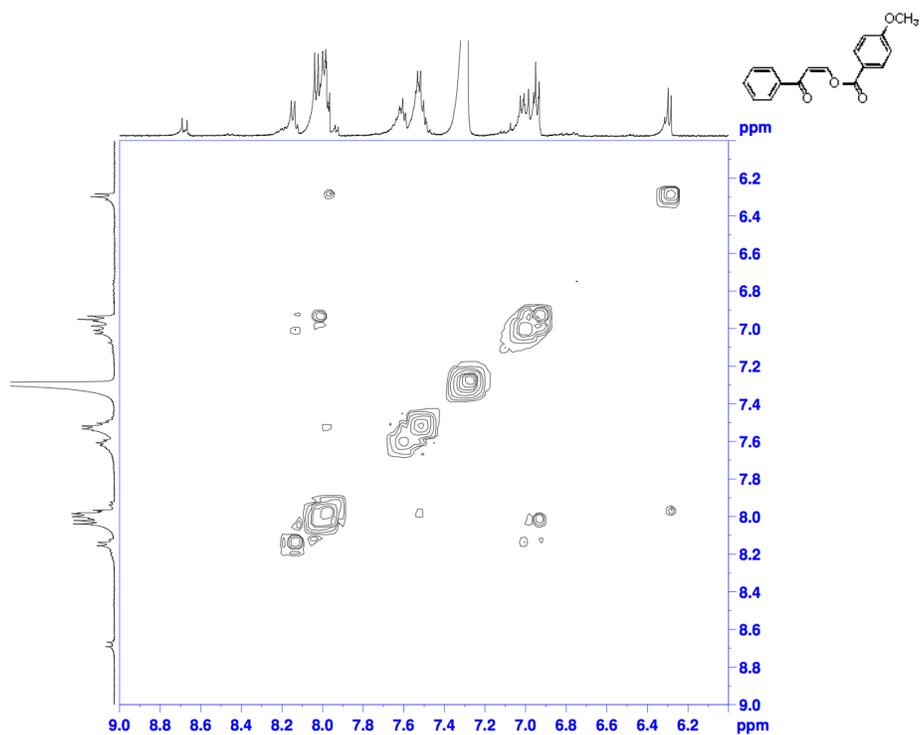
===== CHANNEL f1 =====
NUC1           13C
P1            9.50 usec
PL1           0.00 dB
PL1W          89.92553711 W
SFO1          125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2           1H
PCPD2         80.00 usec
PL2           1.00 dB
PL12          13.04 dB
PL13          16.80 dB
PL2W          17.75783539 W
PL12W         1.1101132 W
PL13W         0.46707872 W
SFO2          500.1320005 MHz
SI            65536
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            0.50
    
```

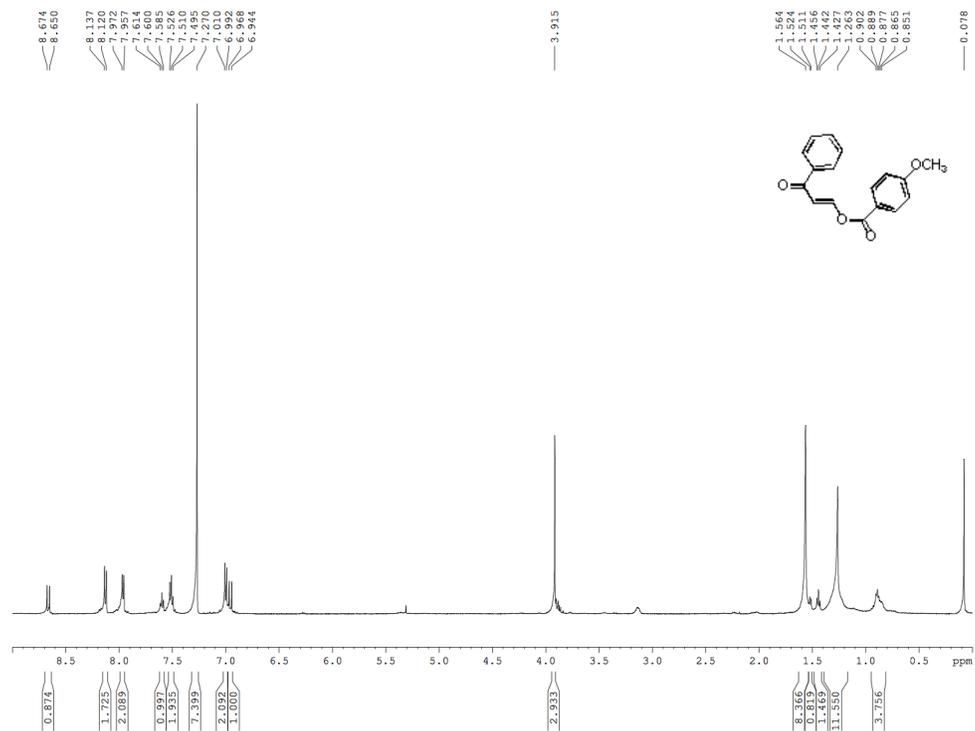
^1H NMR of *cis*-enolester (500 MHz, CDCl_3)



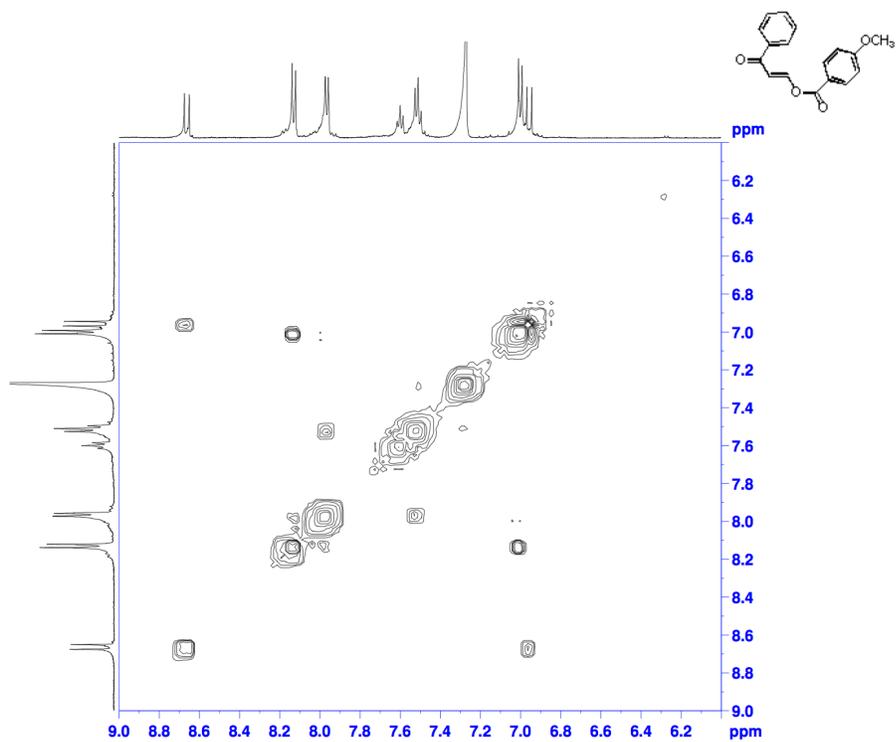
^1H - ^1H coupling in 2D NMR of *cis*-enolester (500 MHz, CDCl_3)



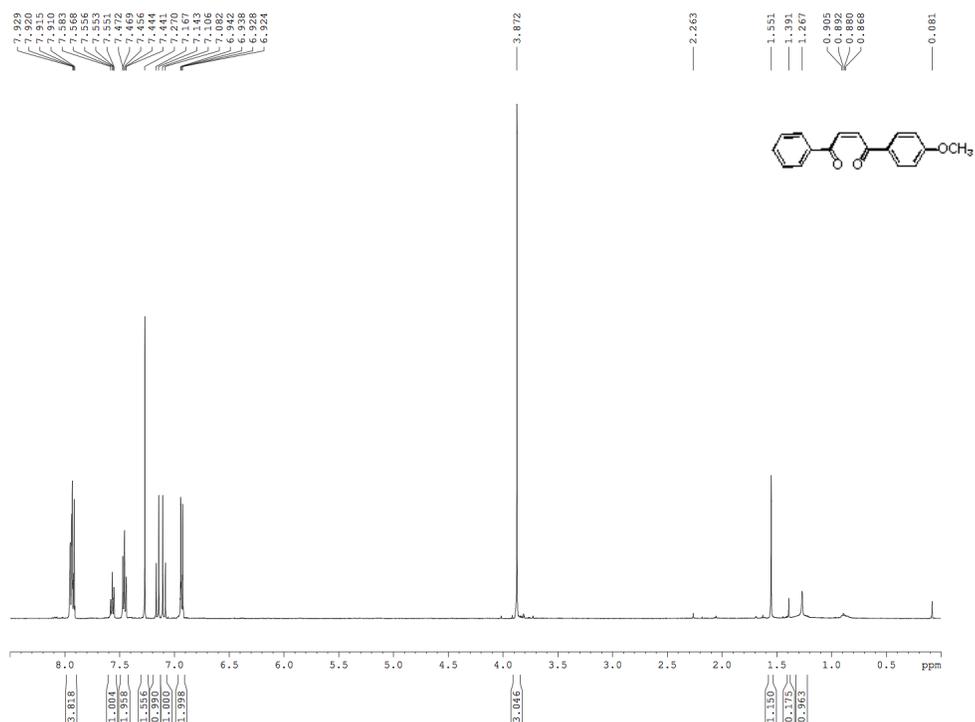
^1H NMR of *trans*-enolester (500 MHz, CDCl_3)



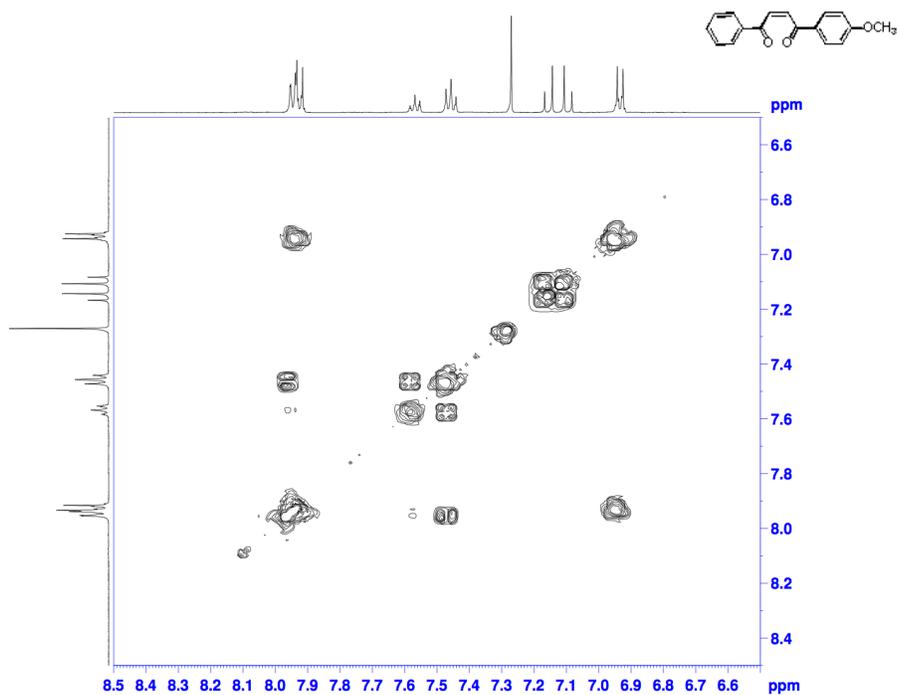
^1H - ^1H coupling in 2D NMR of *trans*-enolester (500 MHz, CDCl_3)



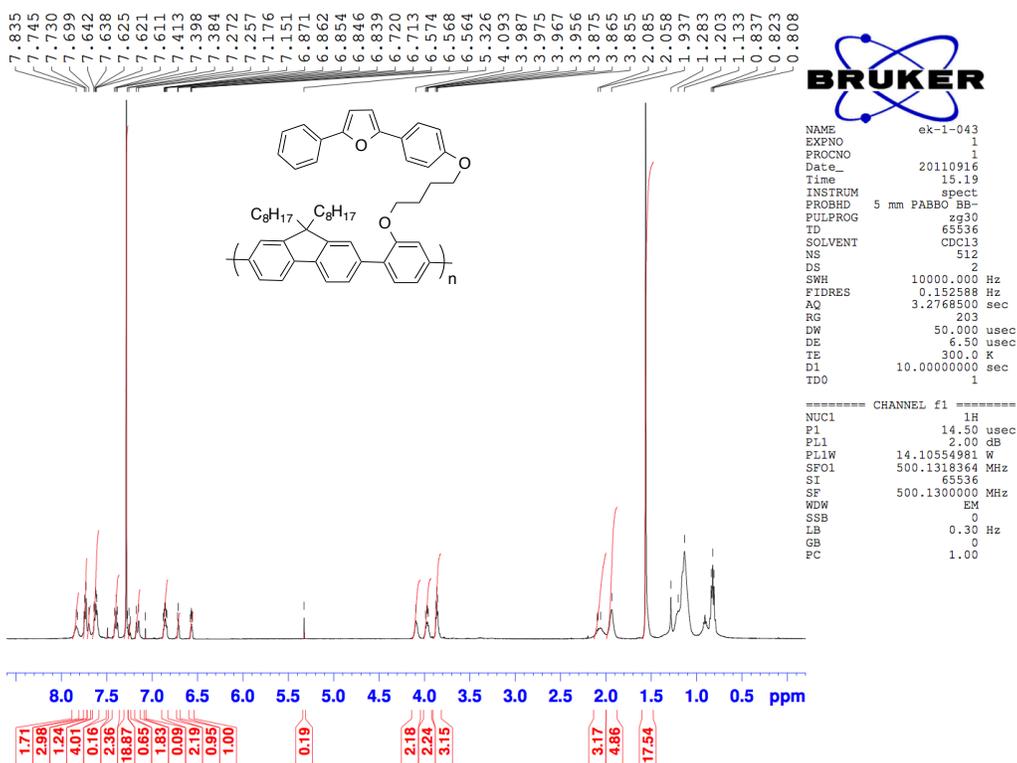
^1H NMR of **diketone** (500 MHz, CDCl_3)



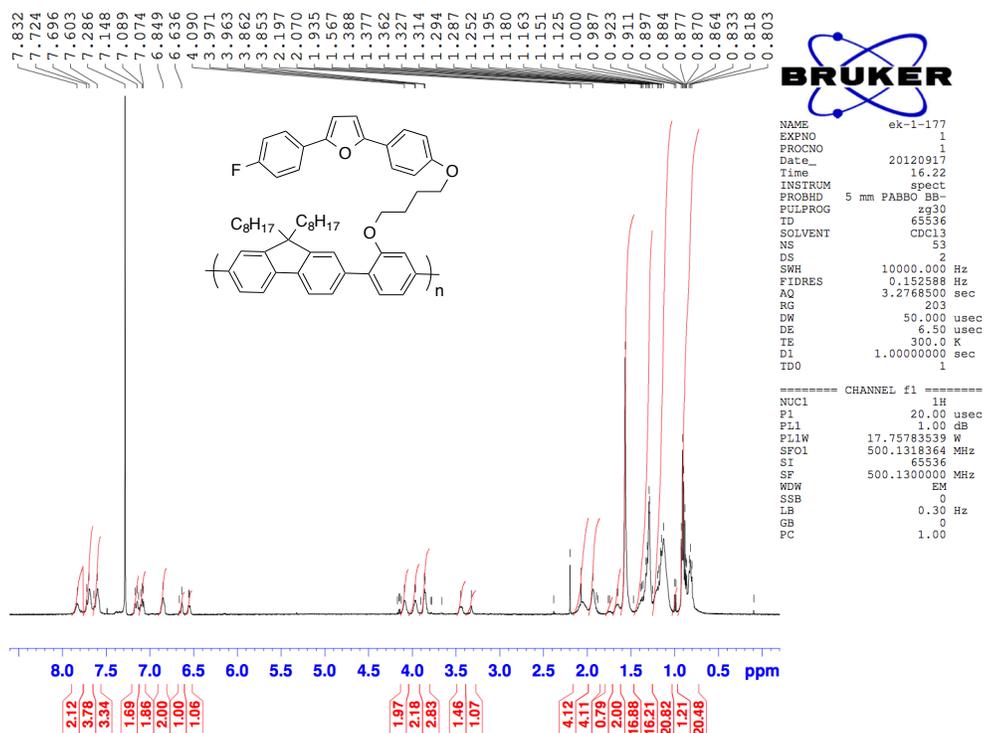
^1H - ^1H coupling in 2D NMR of **diketone** (500 MHz, CDCl_3)



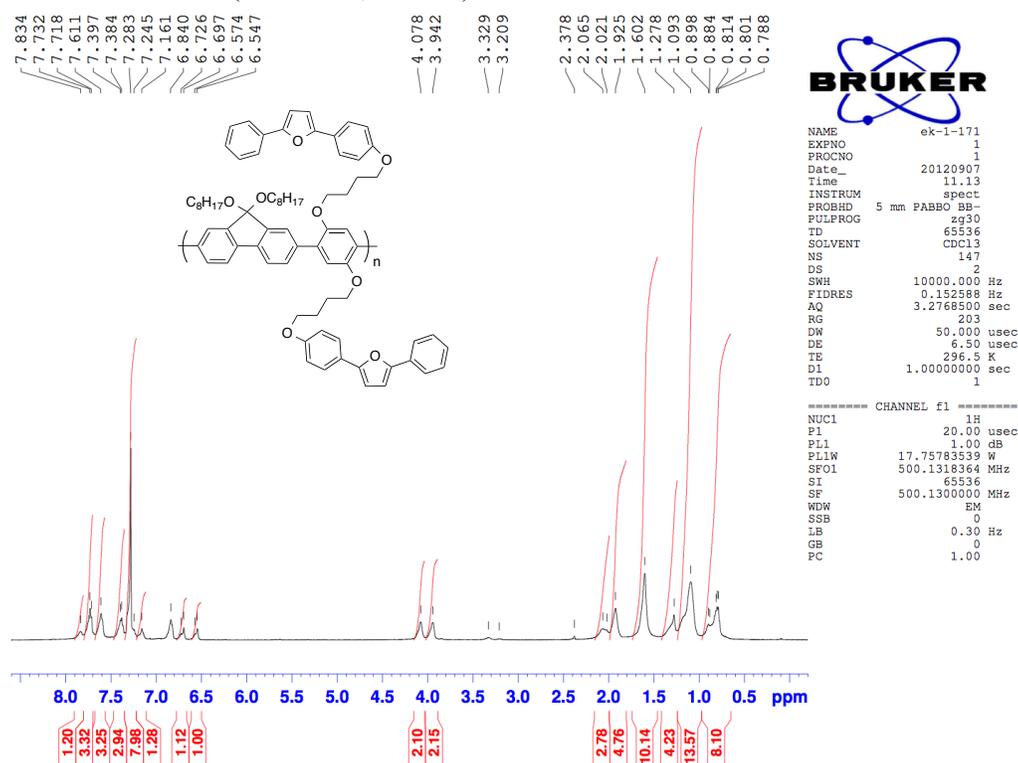
¹H NMR of PFa (500 MHz, CDCl₃)



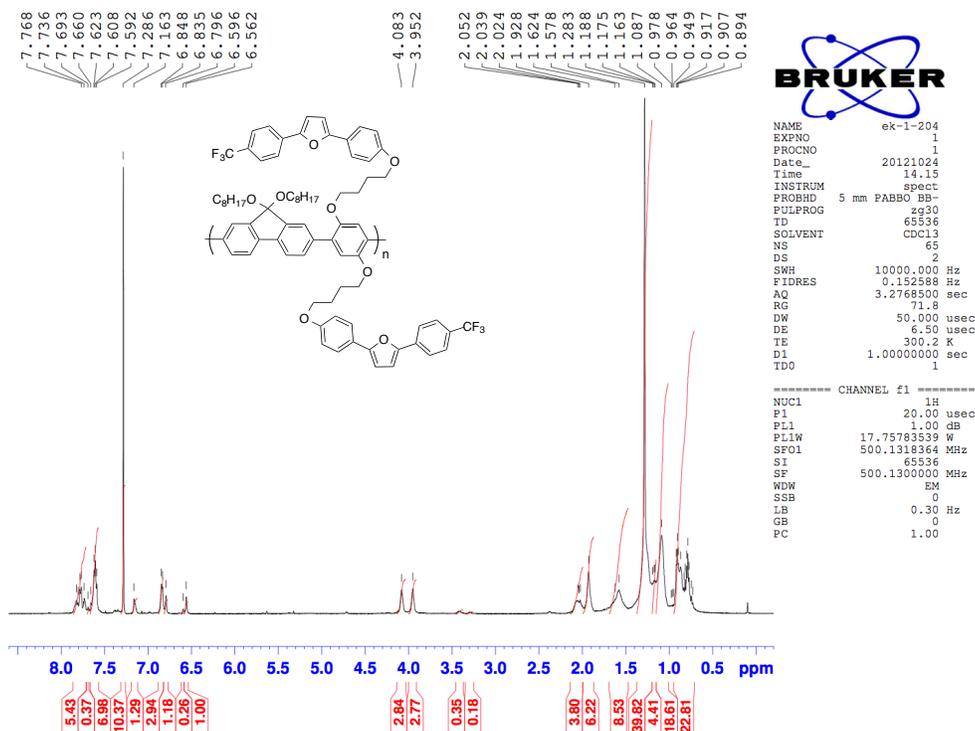
¹H NMR of PFb (500 MHz, CDCl₃)



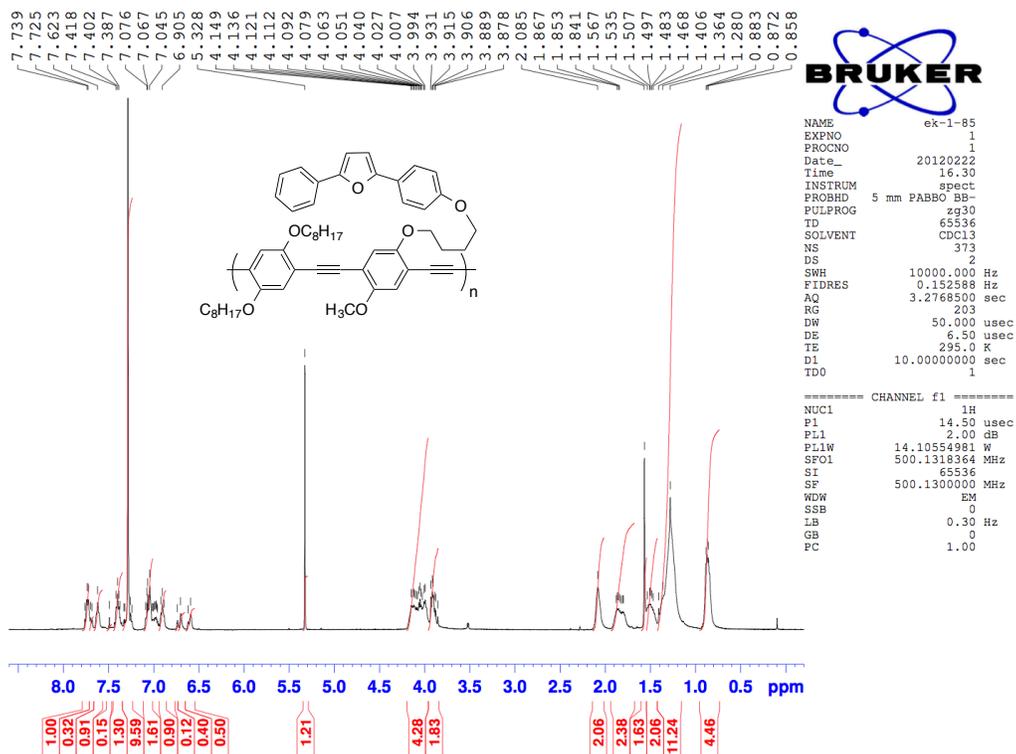
¹H NMR of PF-8a (500 MHz, CDCl₃)



¹H NMR of PF-8c (500 MHz, CDCl₃)



¹H NMR of PPEa (500 MHz, CDCl₃)



Chapter 3:

**Acene-Containing Conjugated Polymers That
Show Ratiometric Fluorescent Response To
Singlet Oxygen**

Altinok, E.; Smith, Z.C.; Thomas III, S.W.
Two-Dimensional, Acene-Containing Conjugated Polymers That Show
Ratiometric Fluorescent Response To Singlet Oxygen. *Submitted*.

3.1 Introduction

Conjugated polymers (CPs) are an important class of macromolecules that have been becoming increasingly important in a variety of applications due to their useful optoelectronic properties. They have the potential to combine the limitless tunability of organic chromophores and dyes, the processability and mechanical flexibility of polymers, and the optoelectronic properties of semiconductors. This unique combination of features makes them important candidate materials for applications such as flexible electronics and chemosensors. The vast majority of CPs has one-dimensional pathways of π -conjugation that involve the polymeric main chains. An area of interest that presents a contrast to this pattern are conjugated materials that have two-dimensional pathways of π -conjugation in two different directions. A conventional way to achieve this is to introduce the conjugated side chains to the conjugated polymer main chains. A number of groups have reported such polymers that display broadened absorbance spectra, which is important for applications in photovoltaics.¹⁻⁴ Jeffries-EL and coworkers have demonstrated impressive tunability of frontier molecular orbital energies of benzobisoxazines by structural modifications along two directions, including as part of conjugated polymer backbones.⁵⁻⁷ Specifically in the area of phenylene-ethynylene materials, Bunz and coworkers have reported phenylene-ethynylene/phenylene-vinylene cruciforms which have spatially separated frontier molecular orbitals and unique luminescence responses to metal ions and pH.⁸⁻¹⁰

Acenes are another important class of organic molecules in a variety of optoelectronics applications due to their semiconducting properties: the performance of pentacene, rubrene, and a variety of diethynylacenes and heteroacenes are benchmark materials in thin film and single crystal transistors.^{11,12} These classes of molecules have tunable optical and electrochemical properties in solution through structural modifications of both the acene core and substituents.¹²⁻¹⁴ Several groups have reported CPs that integrate linear acenes of four or more fused rings into their π -conjugated structures for use in transistors and photovoltaics,¹⁵⁻²¹ including pentacene and anthradithiophene-containing poly(arylene-ethynylene)s from the group of Bao.²²⁻²⁴

In addition to their utility in optoelectronic devices, acenes and heteroacenes can also participate in cycloaddition reactions under mild conditions, especially as dienes in [4+2] reactions with activated dieneophiles, including singlet oxygen ($^1\text{O}_2$), to form bridged bicyclic products.^{14,25-29} These facile [4+2] cycloaddition reactions of acenes and its derivatives, as well as their photochemically-allowed [4+4] “butterfly” dimerizations³⁰ present a challenge from the perspective of fabricating devices such as transistors that have long operational lifetimes; therefore, usually at least one of the several known strategies (such as increased steric bulk or the introduction of physical $^1\text{O}_2$ deactivation pathways) should be applied in order to improve their persistence under photooxidative conditions.^{13,14,31-34} In contrast, rapid cycloaddition reactions of $^1\text{O}_2$ are the basis for a number of molecules and materials that respond to $^1\text{O}_2$ through changes in the emission wavelength or intensity, including CP-based

materials that our group has reported as well as polymers studied in the first chapter of this thesis.³⁵⁻⁴⁰ In this chapter, we combine features from these areas of current interest by preparing a new type of CP with acene-containing side chains that are π -conjugated to the polymer backbone. We also demonstrate their applicability as amplified $^1\text{O}_2$ -responsive polymers.

3.2 Results and Discussion

Chart 3.1 shows the PPEs with acene-containing cross-conjugated side chains that we prepared and studied in this work. We chose PPE backbones for our polymers because of their facile synthesis via Sonogashira coupling at room temperature, their high quantum yields of fluorescence, and their well-documented strong performance in chemosensing and biosensing applications.^{41,42} Diethynylacenes are popular choices in the area of organic electronics because of their stability and efficient charge transport properties, enabled by cofacial interactions between the acene cores in the solid state. In addition, preparation of unsymmetrically substituted diethynylacenes, as we used in the synthesis of **P1** and **P2**, is straightforward.^{43,44} Also important to our decision was our observation that of six different similarly substituted diethynyl-substituted analogs with different acene or thienoacene cores, the tetracene derivative showed the fastest observed rate of cycloaddition with photogenerated singlet oxygen.¹⁴

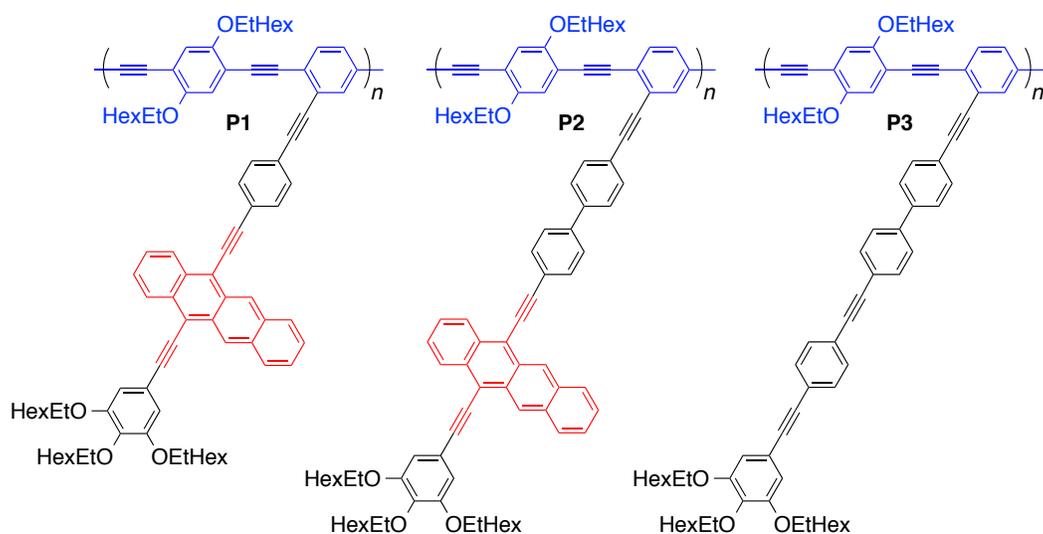


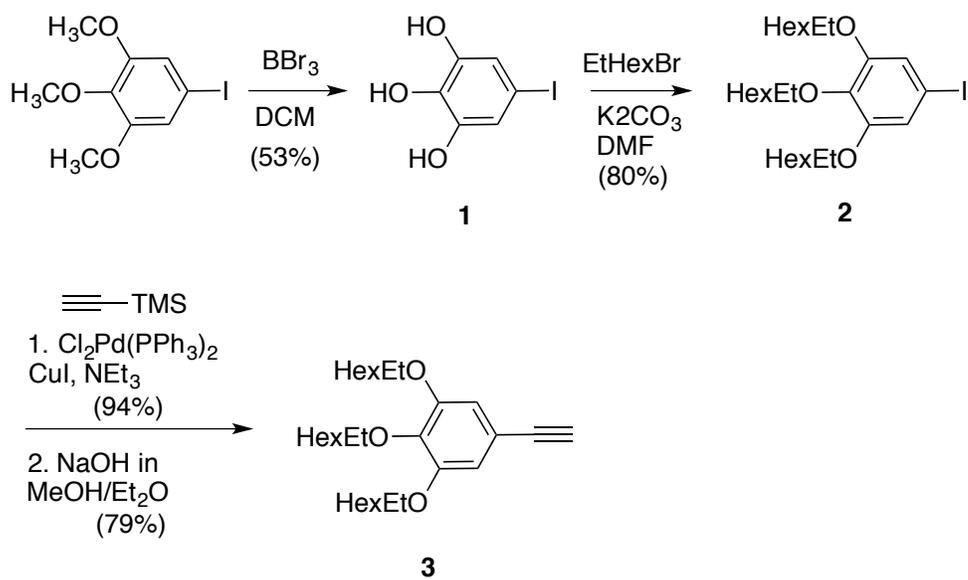
Chart 3.1. CPs **P1** and **P2** comprising PPE backbones (blue) with 5,12-diethynyltetracene pendants (red) bound through conjugated linkers. Polymer **P3** lacks the tetracene chromophore.

3.2.1 Synthesis of CPs having PPE Backbones with 5,12-diethynyltetracene Pendants and a Control Polymer that does not contain Acene Side-Chains

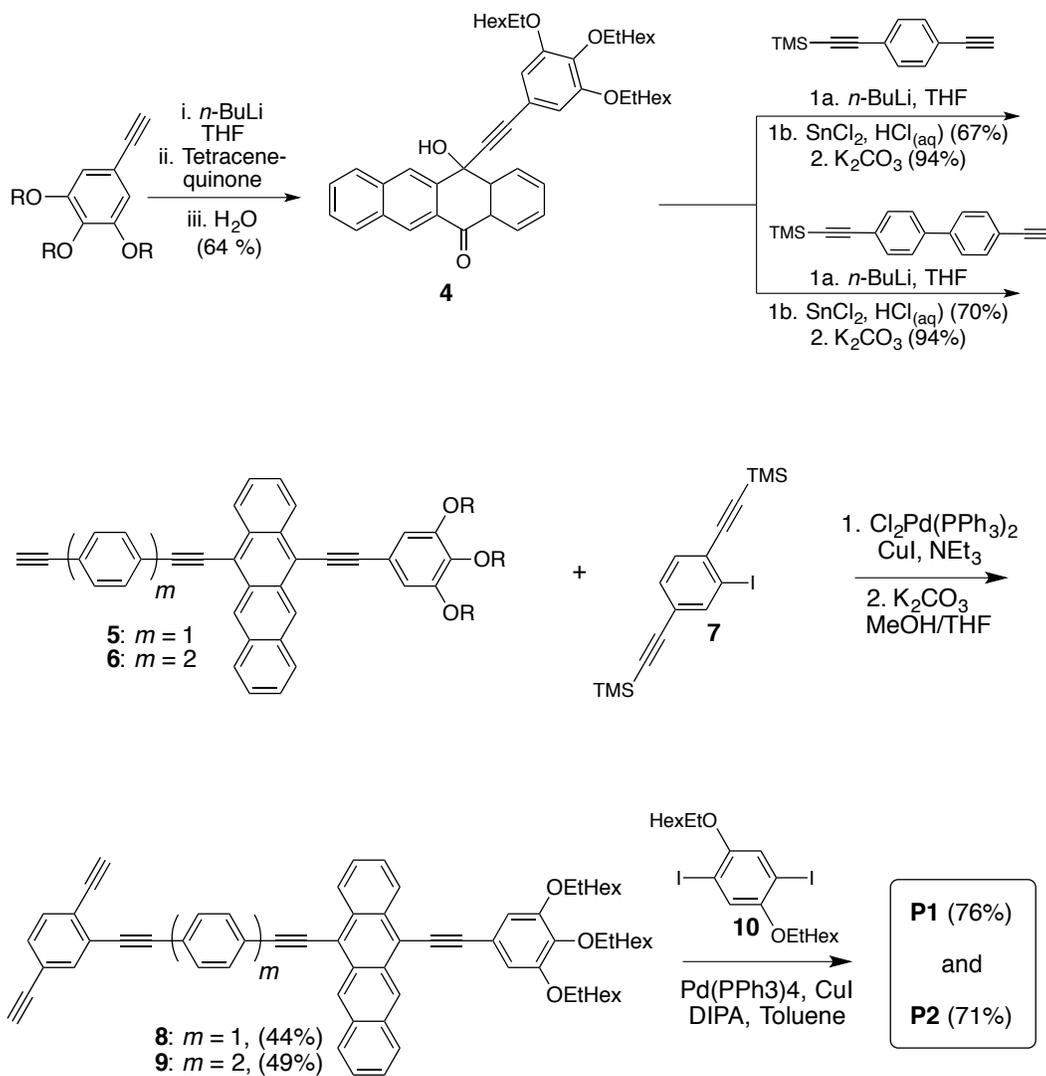
We prepared polymers **P1-P3** using Sonorashira polymerizations between the same 2,5-dialkoxy-1,4-diiodobenzene comonomer and elaborated triethynyl monomers. We started with the preparation of 3,4,5-trialkoxyethynylbenzene **3**, a common compound for all of the polymers synthesized as shown in Scheme 3.1. Deprotection of methoxy groups of commercially available 3,4,5-trimethoxy-4-iodobenzene by BBr_3 followed by alkylation with ethylhexylbromide yielded **2**. Sonogashira coupling to ethynyltrimethylsilane followed by deprotection of the silyl group yielded **3** having terminal alkyne. We prepared tetracene-linked polymers (Scheme 3.2 and 3.3) by adding one equivalent of the lithium acetylide salt of 3,4,5-trialkoxyethynylbenzene, prepared using a previously reported strategy,⁴⁵ to 5,12-tetracenequinone to yield intermediate g-hydroxyketone **4**. A

second addition of lithium acetylide derived from the known mono-protected derivatives of either 1,4-diethynylbenzene or 4,4'-diethynylbiphenyl,^{46,47} followed by standard aromatization and deprotection reactions gave ethynyl-terminated, tetracene-containing side-chains **5** and **6**. Sonogashira coupling to 2-iodo-1,4-bis(trimethylsilylethynyl)benzene (**7**) followed by deprotection of the silyl groups yielded step growth monomers **8** and **9** bearing terminal alkynes with *para* regiochemistry.⁴⁸ Other designs in which the tetracene moiety had only one solubilizing chain instead of three resulted in intermediates that were difficult to isolate in good yields due to poor solubility. A similar strategy, instead using successive Sonogashira reactions with *p*-diiodobenzene led to monomer **13**, which has a structure analogous to **9**, but does not contain a tetracene chromophore.

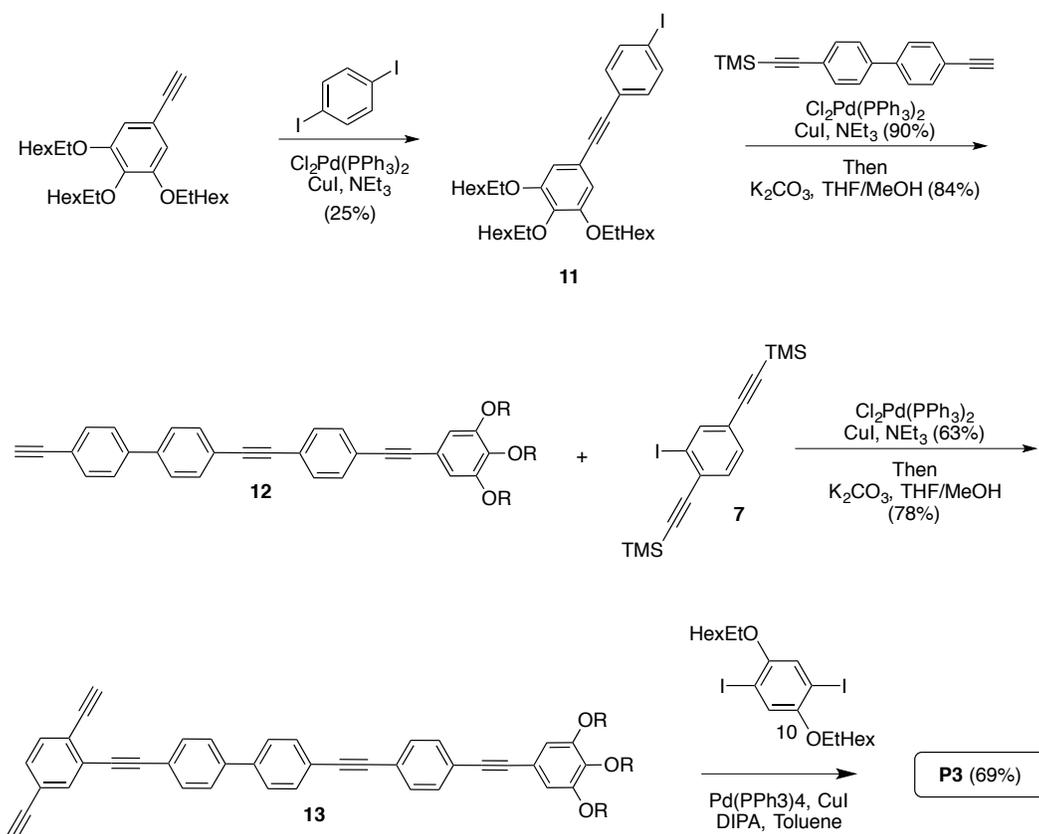
Sonogashira step-growth polymerizations of monomers **8**, **9**, and **13** with diiodo monomer **10** gave polymers **P1**, **P2**, and **P3**, respectively. Running these polymerizations at room temperature, as reported in Sonogashira polymerizations with other triethynyl cross-conjugated monomers, followed by precipitation into MeOH twice gave polymers with number-average molecular weights between 20 kDa and 31 kDa with polydispersity indices between 1.8 and 2.3 (Table 3.1). Running these polymerizations at 65° under otherwise identical conditions led to intractable gels with less than 5% isolated yields of soluble polymers.



Scheme 3.1. Synthesis of 3,4,5-trialkoxyethynylbenzene; EtHex = 2-ethylhexyl.



Scheme 3.2. Synthesis of tetracene-linked CPs **P1-P2**; EtHex = 2-ethylhexyl.

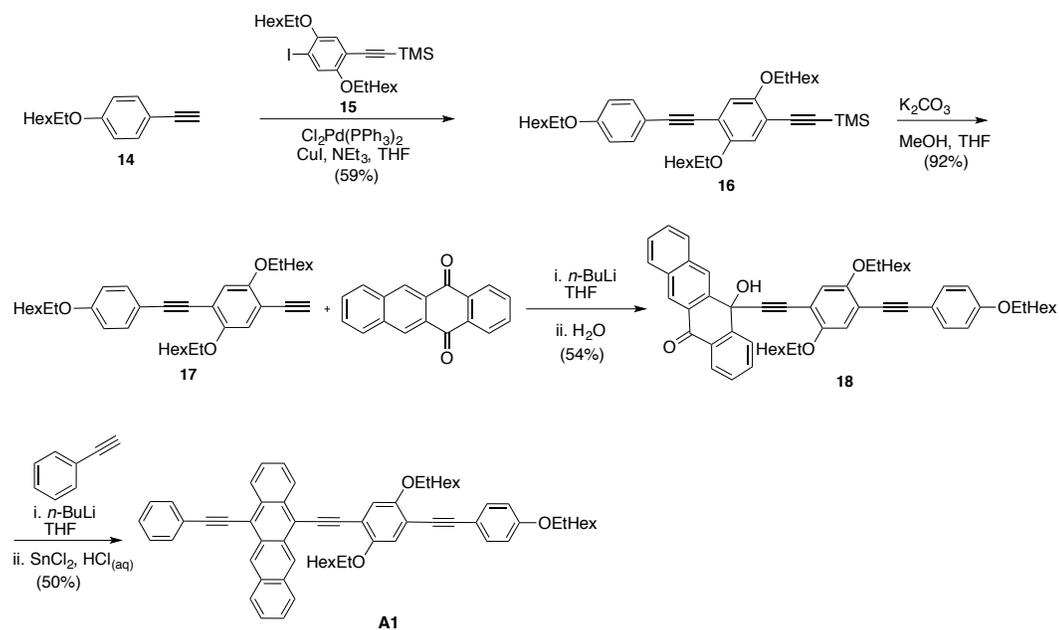


Scheme 3.3. Synthesis of tetracene-linked CPs **P3**; EtHex = 2-ethylhexyl.

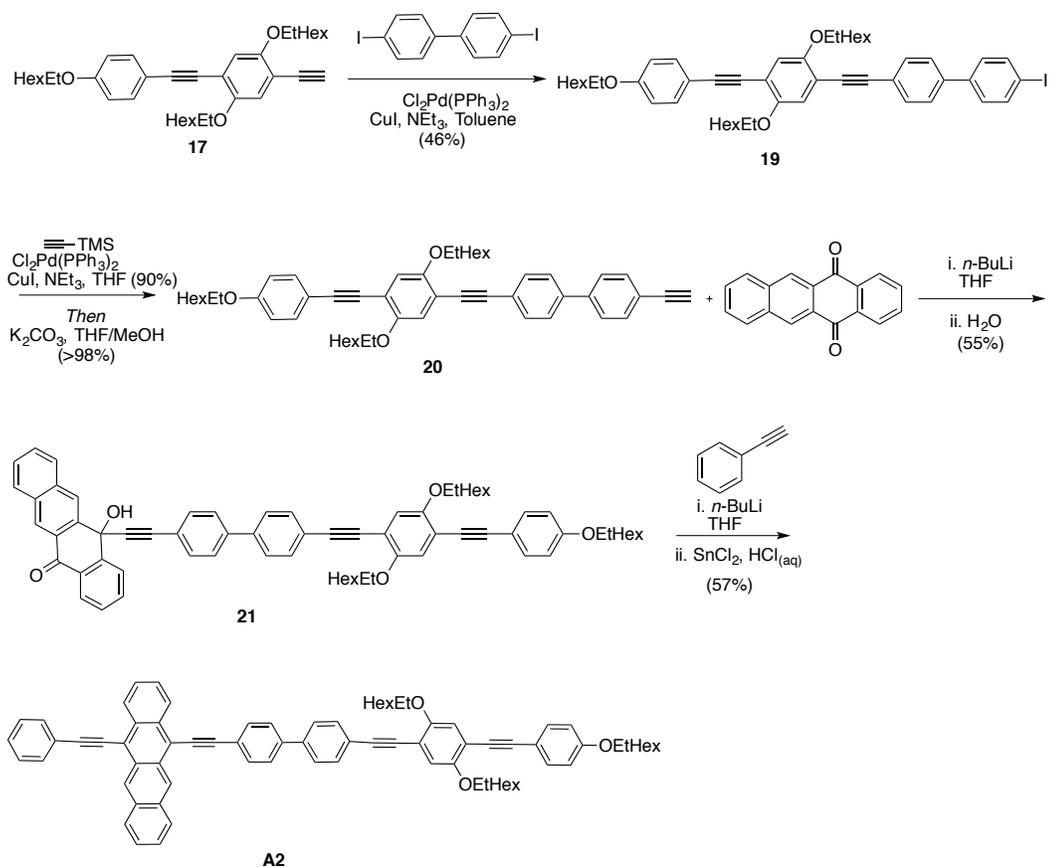
3.2.2 Synthesis of Small Molecules Bearing Tetracene

We also synthesized tetracenes **A1-A3** in an effort to develop a better understanding of the properties of **P1-P3**. Scheme 3.4, 3.5, and 3.6 shows the synthesis of these small molecules. The synthesis of molecule **A1** began with compound **14**, which was coupled with dialkoxy aryl iodide **15** under Sonogashira conditions. Then, the deprotection of the TMS group of **16** yielded compound **17**. Commercially available 4,4'-diiodobiphenyl was the starting material for the synthesis of both **A2** and **A3**: coupling with either **14** or **17** followed by two-step installation of a terminal alkyne gave compounds **20** and **23**. Finally, addition of

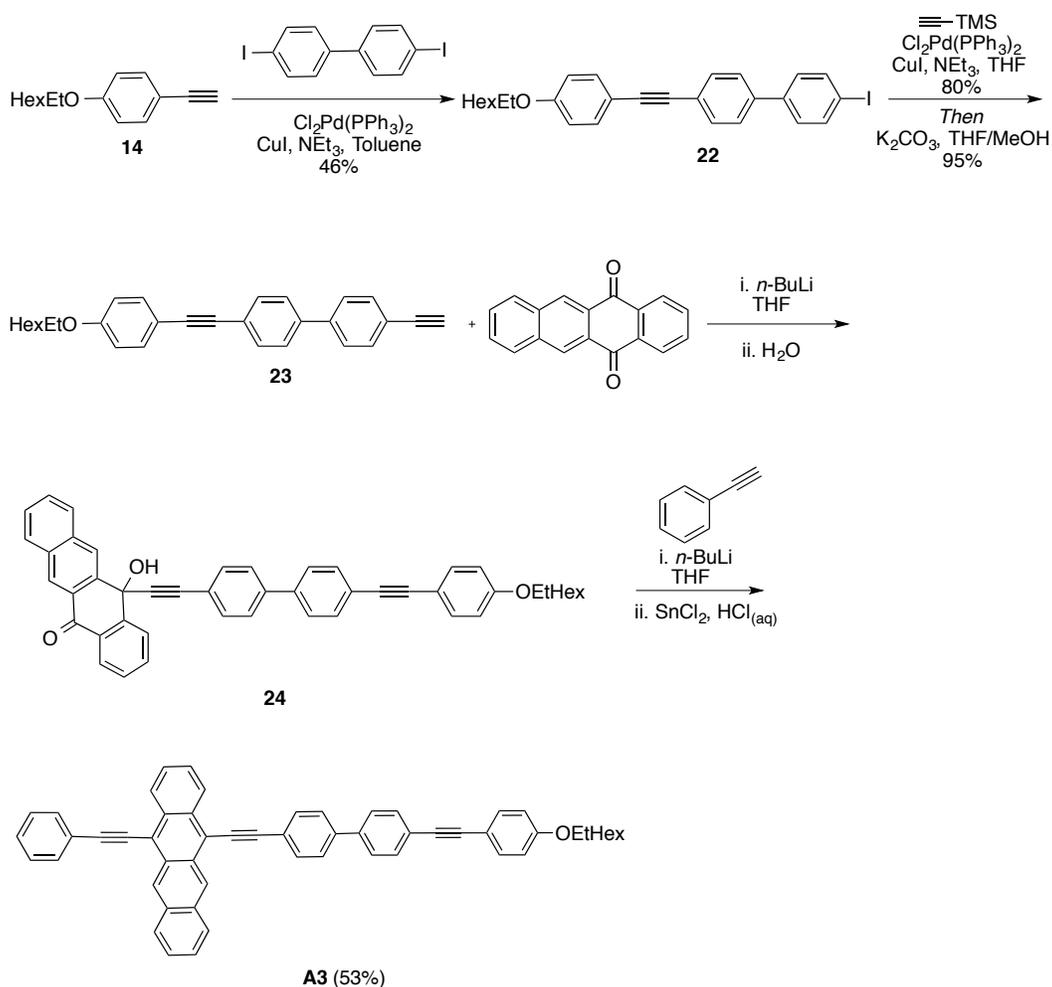
a slight excess of any of the lithiated acetylenes of **17**, **20**, or **23** to 5,12-tetracenequinone, followed by addition of lithiated phenylacetylene yielded the corresponding diols, which we reduced *in situ* with saturated SnCl₂ in aqueous HCl to give the target compounds **A1-A3**.



Scheme 3.4. Synthesis of **A1**.



Scheme 3.5. Synthesis of **A2**.



Scheme 3.6. Synthesis of **A3**.

3.2.3 Spectral Properties of CPs (P1-P3) and Small Molecules (A1-A3)

Figure 3.1 shows the normalized absorption spectra of small molecules **A1-A3** and PPEs **P1-P3**. The shapes and spectral positions of these molecules are consistent with those reported in the literature and shows characteristic bands of tetracene and oligophenylene-ethynylene (OPE). The tetracene-based long wavelength absorbance band between 500 and 600 nm that displays vibronic resolution is red shifted by 10 nm for **A1** with respect to **A2** and **A3**, consistent with the twisted nature of the biphenyl linker of **A2** and **A3** inhibiting coupling

between the tetracene and phenylene-ethynylene units. Density functional theory calculations of geometry-optimized structures of **A1-A3** (see experimental section for the results of these calculations) support significant separation of the OPE and tetracene chromophores due to the biphenyl linker. The calculated acene-based HOMO and LUMO wavefunctions of **A1** are more delocalized onto the extended phenylene-ethynylene substituent than those of **A2** and **A3**, and time-dependent DFT calculations predict the red-shifted HOMO-LUMO transition observed for **A1**. These calculations also support the conclusion that the bands of **A2** and **A3** between 300-400 nm are due in large part to localized excitations on the phenylene-ethynylene pendant from the HOMO-1 wavefunctions to the LUMO+1 wavefunctions.

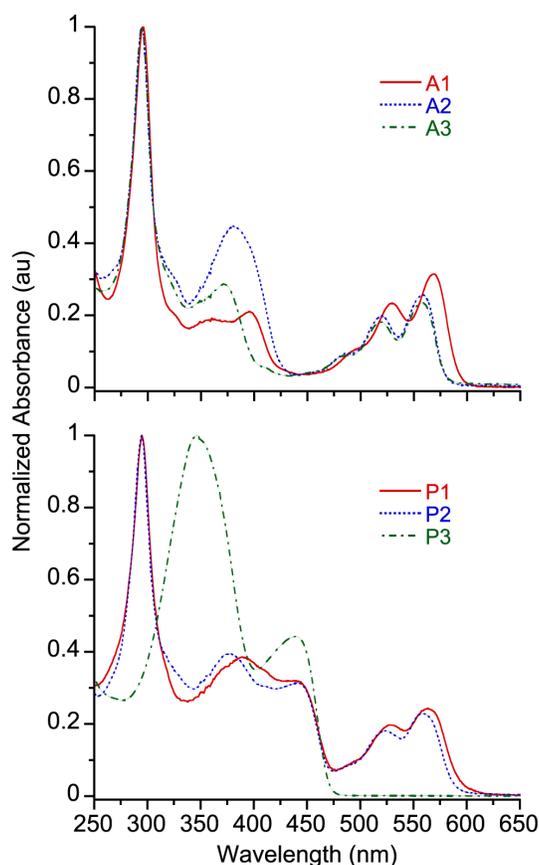


Figure 3.1. Absorbance spectra of small molecule tetracenes **A1-A3** and PPEs **P1-P3** in CHCl_3 .

In comparison, the absorbance of polymers **P1-P3** in the near-UV stretches to longer wavelengths due to the increased conjugation of the polymeric PPE backbones. In contrast to the small molecules, the presence or absence of the twisted biphenyl linker makes comparatively little difference between the absorbance spectra of **P1** and **P2**, which we attribute, at least in part, to the cross-conjugated nature of the acenes and PPE chromophores. Consistent with its chemical structure, the absorbance spectrum of **P3** lacks tetracene bands at 290 nm and between 500-600 nm.

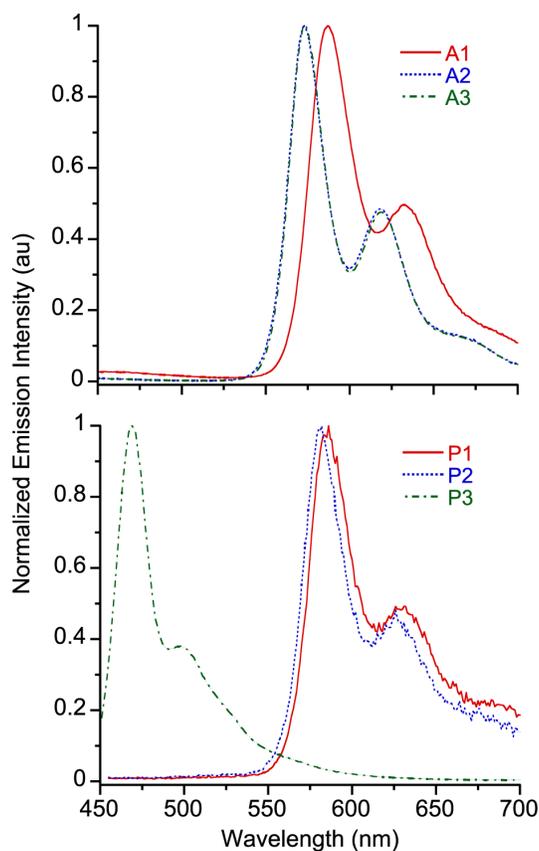


Figure 3.2. Normalized emission spectra of small molecules (**A1**-solid red, **A2**-solid blue, **A3**-solid green) and polymers (**P1**-solid red, **P2**-solid blue, **P3**-solid green) in CHCl_3 .

Figure 3.2 shows normalized emission spectra of small molecules **A1-A3** and polymers **P1-P3**. All the spectra, except for **P3** (which lacks tetracene groups) are consistent with fluorescence from the diethynyltetracene chromophore, with maxima between 575-600 nm, and show no significant signal from any isolated OPE or PPE chromophore, indicating that even in the presence of the biphenyl linkers, energy transfer from the phenylene-ethynylene chromophore to the acene is efficient. **P3** shows the emission spectrum of the cross-conjugated PPE without the low energy acene pendant, with maximum of

approximately 469 nm. The emission spectra of all molecules follows a similar pattern to that found in absorbance: The emission of **A1** is red-shifted by 14 nm from **A2** and **A3** as a result of extended conjugation due to absence of the biphenyl linker and additional electron donating alkoxy groups. All tetracenes described here are fluorescent with quantum yields of fluorescence of approximately 0.5. Absorption and emission maxima, quantum yields, and fluorescence lifetime of all molecules are summarized in Table 3.1.

Table 3.1. Optical characteristics of **P1-P3, A1-A3, P2-25 and 25** in CHCl₃.

	Mn (PDI)	λ_{\max} abs (ϵ)	λ_{\max} (em)	Φ_F	τ (ns)
P1	26 kDa (1.8)	564 nm (34k)	585 nm	0.15	2.76
P2	20 kDa (2.3)	558 nm (33 k)	582 nm	0.21	2.64
P3	31 kDa (1.9)	439 nm (55 k)	469 nm	0.32	-
A1	-	568 nm (38 k)	587 nm	0.48	4.10
A2	-	558 nm (41 k)	573 nm	0.56	5.93
A3	-	557 nm (25 k)	573 nm	0.53	5.48
P2-25	68 kDa (2.9)	558 nm (23 k)	581nm	0.64	4.67
25	-	558 nm (33 k)	581nm	0.52	5.26

3.2.4 ¹O₂ Reactivity of Synthesized Small Molecules and CPs

In the design of these molecules, we have targeted materials that show a fluorescent response to ¹O₂ for potential application of these cross-conjugated materials. In support of this goal, we determined the reactivity of the acenes **A1-A3** towards photogenerated ¹O₂ by following the kinetics of the disappearance of the acene using UV/vis spectrophotometry. The materials we synthesized does not absorb at wavelengths longer than 600 nm; therefore, we used the photosensitizer methylene blue (MB) to generate ¹O₂ due to its absorbance band with maximum at 652 nm that allows for its selective excitation. Irradiation of a solution containing

both MB (OD = 1.0 at 652 nm) and **A2** (at a concentration of 32 mM) using a 200 W Hg/Xe lamp, equipped with a 630 nm long-pass filter, resulted in conversion of the tetracene unit to a mixture of two regioisomeric endoperoxides: across either the 5,12 and 6,11 positions of the tetracene. Figure 3.3 (*top*) shows the response of absorption spectrum as evidence by the disappearance of the acene absorbance bands. This conversion was also confirmed by the ^1H NMR spectra of analogous experiments performed at higher acene concentration. Figure 3.3 (*bottom*) shows that the kinetics follows a pseudo first-order rate law, consistent with a steady-state concentration of $^1\text{O}_2$ during irradiation. The rate of reaction of all the acene small molecules and polymers in this chapter were estimated by comparing the slope of the best-fit lines of the pseudo-first order kinetic models for these compounds to that of 9,10-diphenylanthracene (DPA), which reacts with $^1\text{O}_2$ with a known rate constant of $\sim 1.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.⁴⁹ We measure that the observed rate of reaction of **A2** is 6 times faster than that of DPA; therefore, estimate that the rate constant of reaction between tetracene **A2** and $^1\text{O}_2 \sim 8 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ at room temperature. Figure 3.4 (*left column*) shows the changes in both absorbance and fluorescence spectra of **A2**. Corresponding data for **A1** and **A3** were similar as shown in Figure E1 and E2 in experimental section. Changes in both the absorbance and fluorescence spectra of tetracenes **A1-A3** upon irradiation of MB were also consistent with $^1\text{O}_2$ -induced endoperoxidation. The tetracene absorbance bands at 295 nm and between 450 nm and 575 nm decreased in intensity. We also observed a ratiometric change in the fluorescence spectra these molecules molecule upon reaction with $^1\text{O}_2$: as an example, for **A2**, while the

emission at 573 nm decreased, emission at 439 nm increased. We attribute this change in fluorescence to the mixture of new higher energy fluorophores generated upon endoperoxidation across either the 5,12 and 6,11 positions of the tetracene.

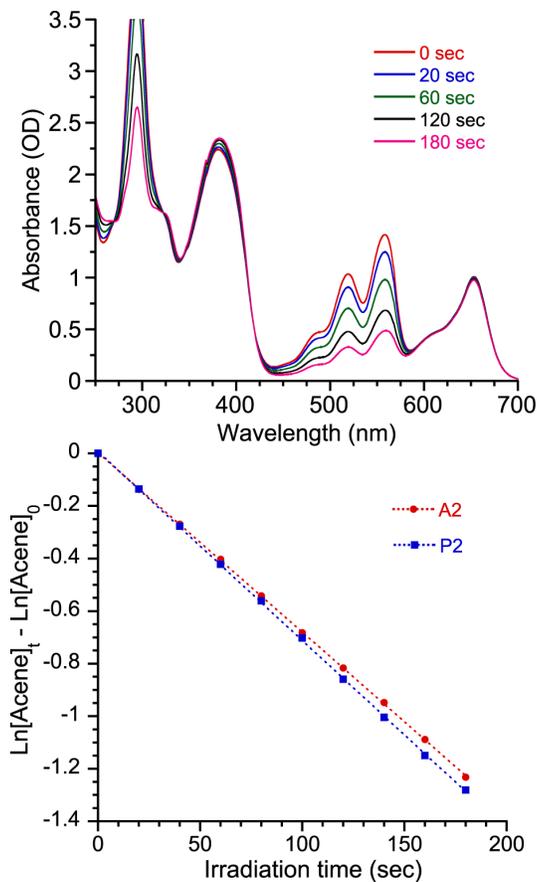


Figure 3.3. *Top:* Response of UV/vis spectrum of **A2** to $^1\text{O}_2$ produced by photosensitization with MB (1.0 OD at 652 nm) in CHCl_3 during 3 min of irradiation. *Bottom:* Pseudo-first-order kinetics of disappearance of the tetracene moiety of **A2** and **P2**.

In many respects, cross-conjugated polymer **P2** showed analogous behavior to **A2** upon exposure to photogenerated $^1\text{O}_2$. The observed rate of

tetracene consumption (5.5 times greater than DPA) was nearly identical to that observed for **A2** (6 times greater than DPA). It indicates that attaching the acene to the polymer backbone does not inhibit the reaction. The overall fluorescent response of **P2** to $^1\text{O}_2$ was also similar to that of **A2**: before exposure to $^1\text{O}_2$, only tetracene-based fluorescence at 582 nm is observable in the emission spectrum, regardless of the excitation wavelength used. The tetracene-based side-chain clearly accepts energy from excited states initially generated elsewhere on the polymer backbone due to its low excited-state energy. Upon oxidation of most of the acene (as followed by the decrease in absorbance of the tetracene bands) fluorescence at 469 nm dominates the emission spectrum, which is the emission from the conjugated polymer backbone. We attribute this change in the emission intensities by disruption of energy transfer due to the increase in excited state energies of the pendant acene groups upon oxidation. As a result of oxidation, energy transfer from CP backbone to oxidized tetracenes is no longer competitive with other excited-state processes of the CP backbone.

3.2.5 Photophysical Characterization of $^1\text{O}_2$ -induced Oxidation of Pendant Acenes on CPs

In contrast to the similarity in behavior observed of the initial reactants and the final products when comparing the fluorescent response of **A2** and **P2**, the evolution of the fluorescence emission spectrum during the oxidation reaction of **P2** is significantly different compared to that of **A2**. It shows the non-linearity of fluorescent response as shown in Figure 3.4 (*right column*), while **A2** shows a

linear ratiometric response. Initially, exposing **P2** to photogenerated $^1\text{O}_2$ did not decrease the emission intensity at 580 nm, but instead an *increased* it, which reach a plateau after approximately 15 minutes of irradiation time at $\sim 3\times$ the initial emission intensity at 580 nm. Approximately 75% of the side-chain tetracene moieties were oxidized at this time, based on the decrease in absorbance at 558 nm. Increase in emission in the blue region of the spectrum at 469 nm, attributed to the CP backbone, does not occur to significant degree until this point of $\sim 75\%$ conversion. Only at this point, additional exposure to $^1\text{O}_2$ and oxidation of side-chain tetracenes of **P2** resulted in the same type of ratiometric response in the emission spectrum that the small molecule tetracenes exhibited: decreasing red-shifted emission from tetracene and increasing blue-shifted emission from CP backbone. Figure 3.4 shows the spectra for **P2**; data for **P1** was similar (see experimental section for spectra of **P1**). An analogous polymer, which lacks tetracene moieties (**P3**) showed no change in fluorescence intensity upon exposure to $^1\text{O}_2$ under identical conditions (as shown in the Figure E4 in the experimental section)

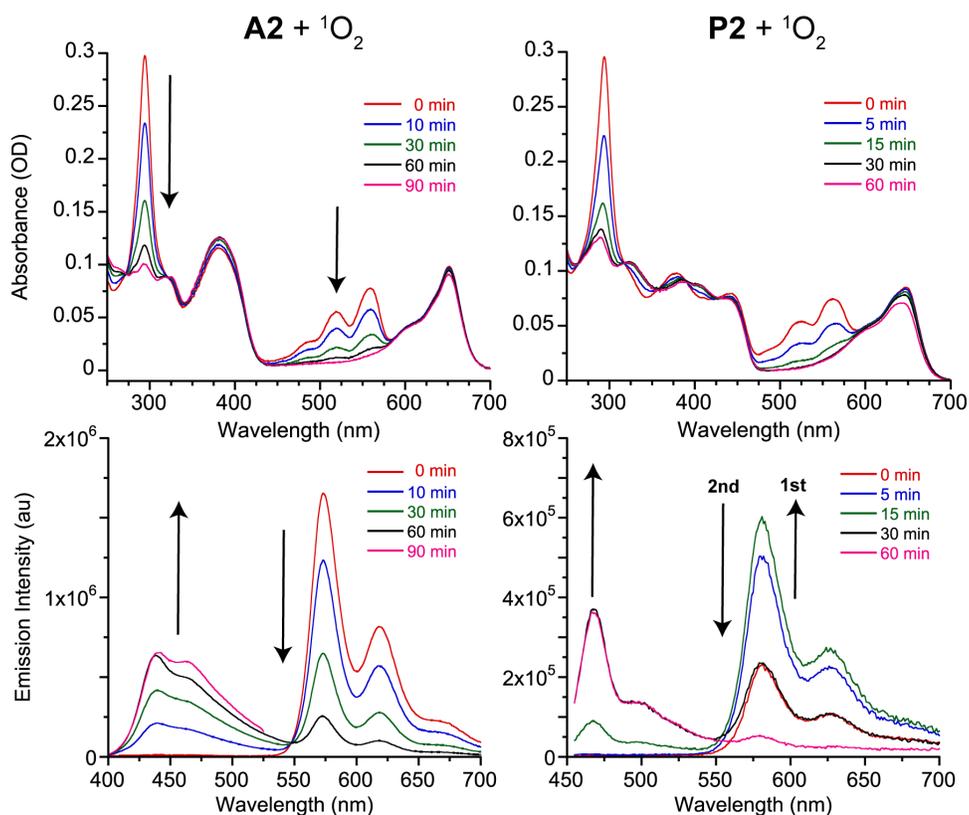


Figure 3.4. The response of absorbance spectra (top) and fluorescence spectra (bottom) of **A2** and **P2** during exposure to singlet oxygen in CHCl_3 .

To understand why tetracene oxidations initially yielded an increase in fluorescence intensity of the tetracene moieties for **P2**, we measured excited-state lifetimes at the band with emission maximum at 580 nm as a function of conversion to endoperoxides. The excited state lifetimes were measured with time-correlated single-photon counting (TCSPC) and the reported lifetimes for **P2** are the mean lifetimes determined from a double exponential fit to the TCSPC data. An analogous small molecule of **P2**, compound **25**, which contains only one tetracene capable of accepting energy from a three-ring phenylene-ethynylene

donor was also synthesized to compare with. For the preparation of **25**, monomer **9** was simply coupled with 2-iodo-1,4-bis(ethylhexyloxy)benzene under Sonogashira coupling conditions. As shown in Figure 3.5, the excited-state lifetime measured with TCSPC of **P2** was 2.65 ns, before exposure to singlet oxygen, which was about half that of **25**, a small molecule analog of **P2**. The lifetime of this emissive excited-state of **P2** increased steadily with increasing extent of tetracene oxidation. Our conclusion from the combination of steady-state and time-resolved fluorescence spectroscopy is that the close proximity of diethynyltetracene moieties substituted on every other repeat unit of the CP chains results in sufficiently high local concentrations of fluorophore (acene side-chain) that yield dynamic self-quenching of the excited states of the acene side-chains. Reduction of this local concentration through oxidation of the acene side chains results in slower rate of self-quenching, increasing the lifetime up until the point when self-quenching does not compete significantly with unimolecular relaxation processes.

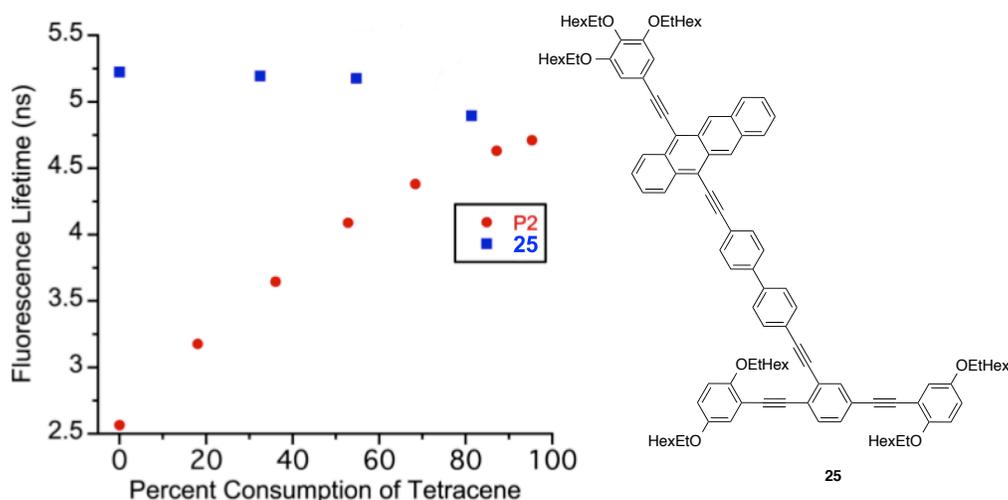


Figure 3.5. Comparison of how tetracene oxidation by $^1\text{O}_2$ influences the fluorescence lifetime of the tetracene moieties of **P2** and **25**. R = 2-ethylhexyl.

Another important feature of the response of the conjugated polymer is that the ratiometric response—increase in the blue fluorescence intensity at 469 nm—does not occur until most of the tetracenes have oxidized. In systems that have a single acceptor in dilute solution, it is expected that every reaction that removes an energy acceptor will contribute to observed emission intensity from the donor. In contrast, the conjugated polymers which we studied here has many potential energy acceptors (in each repeating unit of CP backbone); therefore, effective removal of one energy acceptor from the system does not necessarily contribute to an increase in observed emission from the donor because even after removal of some energy acceptors from the energy-donating CP backbone, some energy acceptors are still present. For the purposes of chemical sensing this type of response is not very useful because each reaction does not results in a change in the observed fluorescence. Taking this model to an extreme example, however,

one could imagine an idealized system that contains only one energy acceptor into which all excited state energy funnels. This idea can be considered like the reverse of highly amplified quenching or energy transfer with CPs. The reason behind that is that such an example would be maximally sensitive to whatever stimulus removes the acceptor, as a single reaction would result in a complete change in observed fluorescence. As a demonstration of this basic idea, we compared the ratiometric fluorescence response as a function of tetracene oxidation of **P2** to small molecule analog **25**, which contains only one tetracene capable of accepting energy from a cross-conjugated three-ring phenylene-ethynylene donor. Figure 3.6 shows that the ratiometric response of **P2**, in strong contrast to that of small molecule model **25**, only shows significant ratiometric fluorescent signal occurring when most of the acenes are oxidized. This result suggests that with this energy harvesting system composed of PPE backbone and acene side chains linked through conjugated biphenyl linker, fewer reactions are required to remove the smaller number of energy acceptors present in order to access the same range in signal, relative to corresponding small molecule energy transfer cassettes.

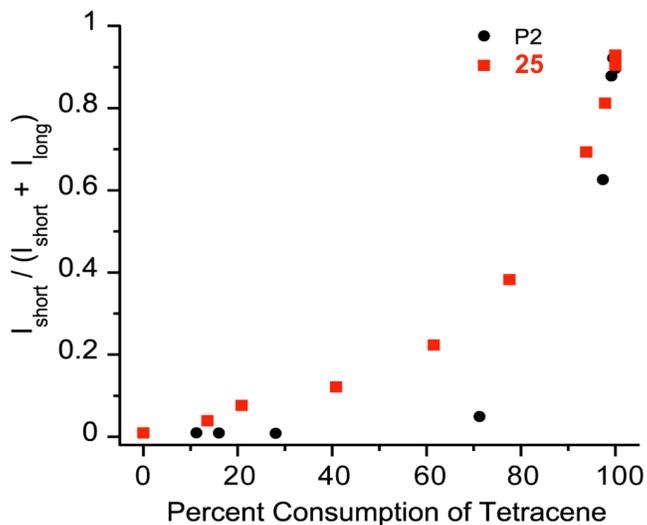


Figure 3.6. Comparison of ratiometric response of small molecule model **22** compared to that of **P2**.

To follow up on this point, we synthesized another polymer sample analogous to **P2** (**P2-25**), in which only 25% of the dialkyne monomers by mole contained acene side-chains of conjugated polymer backbone is substituted with tetracene (monomer **9**). This new polymer, which has a smaller density of tetracene side chains, also shows nearly complete energy transfer before exposure to $^1\text{O}_2$. The tetracene-based emission decreases while the blue-shifted CP backbone-based emission increases during exposure to $^1\text{O}_2$ as illustrated Figure 3.7. In addition, the fluorescence lifetime of the tetracene fluorophore measured with TCSPC did not change significantly as tetracenes were oxidized (between 4.7 and 5.0 ns). Therefore, the results of this example show that the amount of reactions required to achieve a nearly complete ratiometric response decreased by a factor of four.

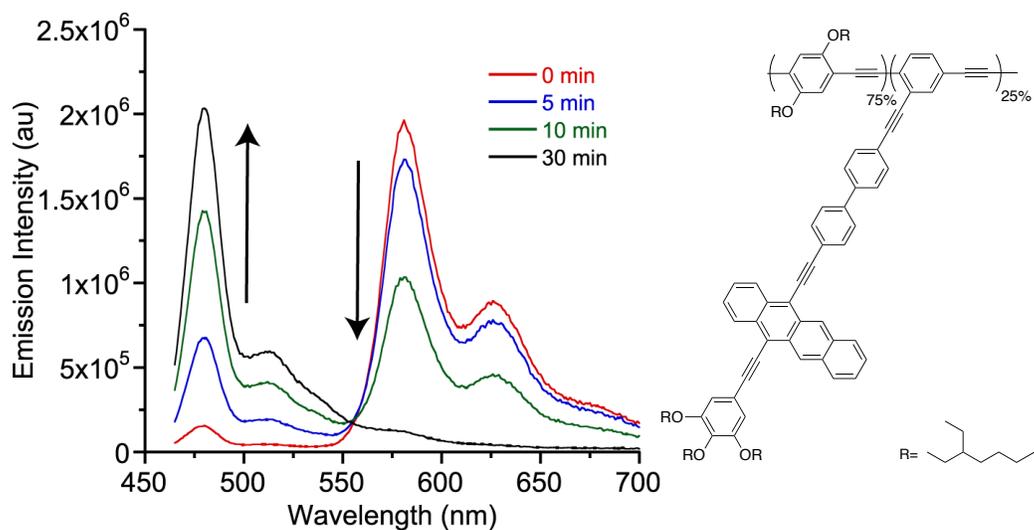


Figure 3.7. Fluorescent response and structure of the **P2** analog (**P2-25**) that has only 25% of repeat units functionalized with tetracene.

3.3 Conclusion

This chapter demonstrates the synthesis and properties of new conjugated polymers comprising PPE backbones and tetracene-based side chains that are π -conjugated to the PPE main chains. Our overall synthetic approach should be general for the preparation of fluorescent CPs with conjugated side chains, which are becoming more popular for increasing spectral coverage for applications involving light absorption. Our results illustrate how the well established amplified response of CPs to analytes that introduce new electron or energy transfer relaxation pathways can also apply to the reverse of this process—the removal of such pathways. Realization of large amplification in this type of approach requires that the efficiency of the process interrupted by the analyte—in our case energy transfer to tetracene side chains—be highly efficient. It also requires that small concentrations of these removable ‘traps’ be integrated into the

material with both accuracy and precision. Strategies under investigation in our lab to achieve these goals are the use of conjugated materials as thin films and nanoparticles, as well as the self-assembly of non-conjugated materials to control the distributions of energy donors and acceptors.

3.4 Experimental Section

3.4.1 General Considerations

All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent for CHCl_3 . High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. Molecular weight distribution measurements of the polymers were conducted with a Shimadzu Gel Permeation Chromatography (GPC) system equipped with a Tosoh TSKgel GMHhr-M mixed-bed column and guard column using either UV or refractive index detectors. The column was calibrated with low polydispersity poly(styrene) standards (Tosoh, PSt Quick Kit) with THF as the mobile phase eluting at 0.75 mL/min. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

3.4.2 Optical Experiments

All solution optical spectra were acquired of samples in quartz cuvettes (NSG Precision Cells). Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Fluorescence spectra were acquired using sample absorbances less than 0.1 OD. Fluorescence quantum yields were determined relative to either quinine sulfate in 0.1 N H₂SO₄ or Coumarin 6 in ethanol. Irradiation of the methylene blue photosensitizer to generate ¹O₂ was performed with 200W Hg/Xe lamp (Newport-Oriel) equipped with a 1) 200W Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water, shutter, and 635 nm high-pass filters, or 2) a 635 nm laser diode (4.5 mW). Time-resolved fluorescence data was collected using a time-correlated single-photon counting instrument with a pulsed LED operating at 403 nm.

3.4.2.a Fluorescence Response to Singlet Oxygen

A cuvette containing the test sample solution was irradiated for numerous timed intervals. Both the absorbance and fluorescence spectra were taken after each interval of irradiation. The absorbance for both methylene blue and samples was approximately 0.1 OD.

3.4.2.b Kinetics

A stock solution of methylene blue was prepared in CHCl_3 to give an absorbance of ~ 1.0 at its peak. 9,10-diphenylanthracene (DPA) was used as a reference. DPA, **A2**, or **P2** was dissolved in 3.5 mL MB solution; the final concentration of the corresponding compound in the sample was 32 μM . The solution was irradiated for numerous timed intervals, with acquisition of an absorbance spectrum after each interval until the spectra stopped changing between intervals of irradiation (all tetracene groups having reacted). The wavelengths used for the analysis of kinetics were the peaks of the highest absorbance of the compounds.

3.4.3 Supporting Figures

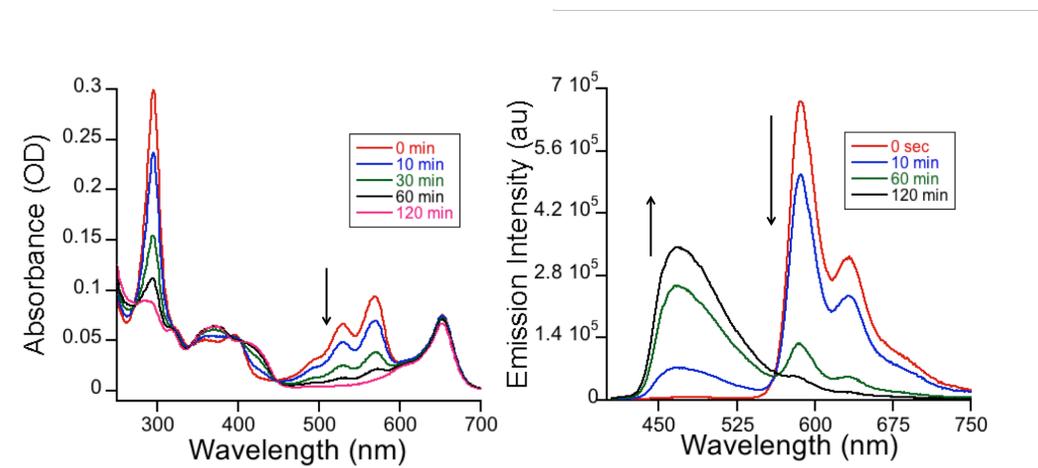


Figure E1. The absorbance and fluorescence response of **A1** (irradiated using a 635 nm laser diode (4.5 mW))

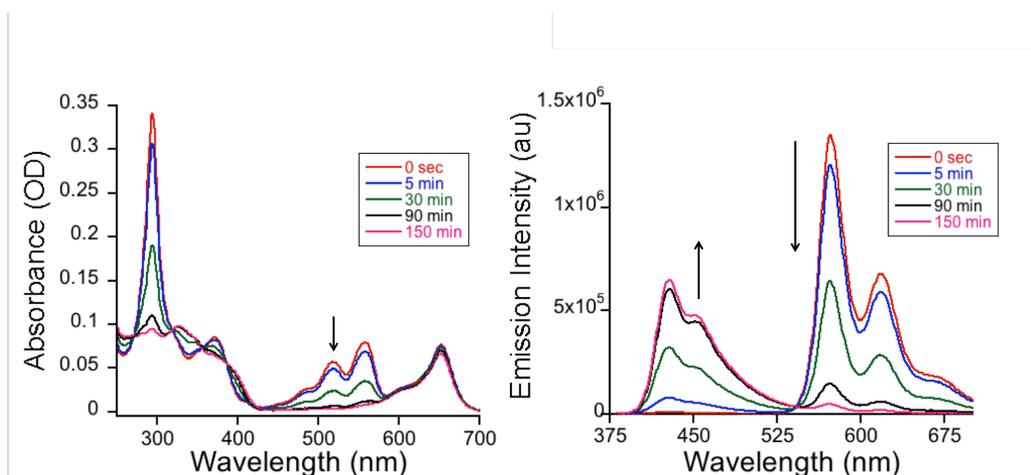


Figure E2. The absorbance and fluorescence response of **A3** (irradiated using a 635 nm laser diode (4.5 mW))

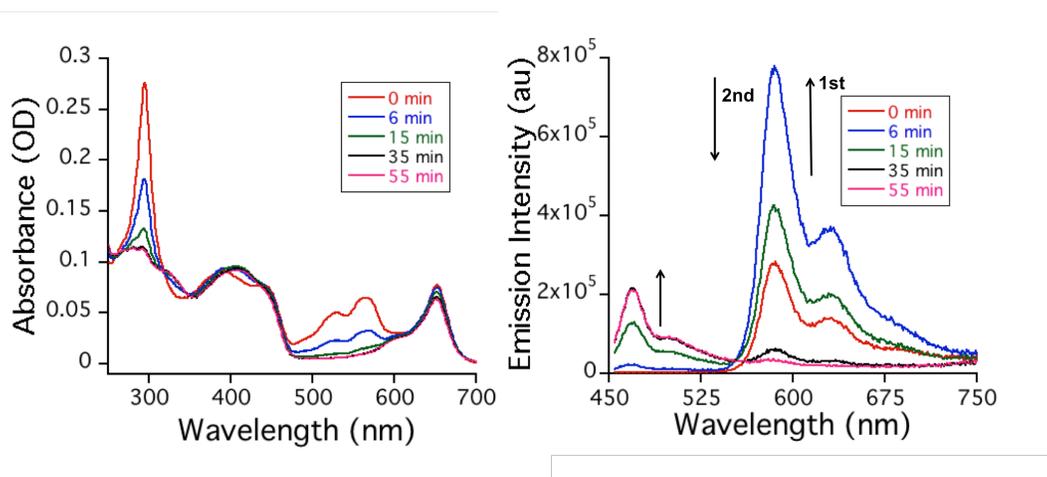


Figure E3. The absorbance and fluorescence response of **P1** with phenyl linker.

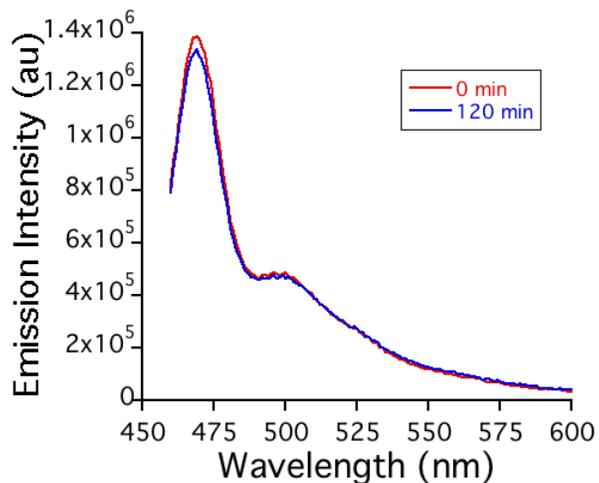
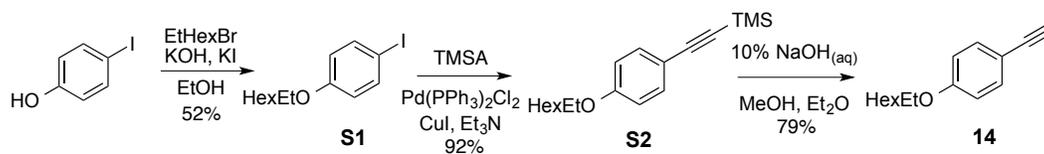
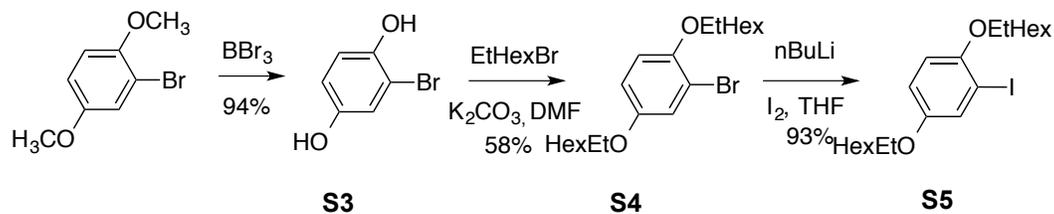


Figure E4. Fluorescence response of **P3** with no tetracene moieties.

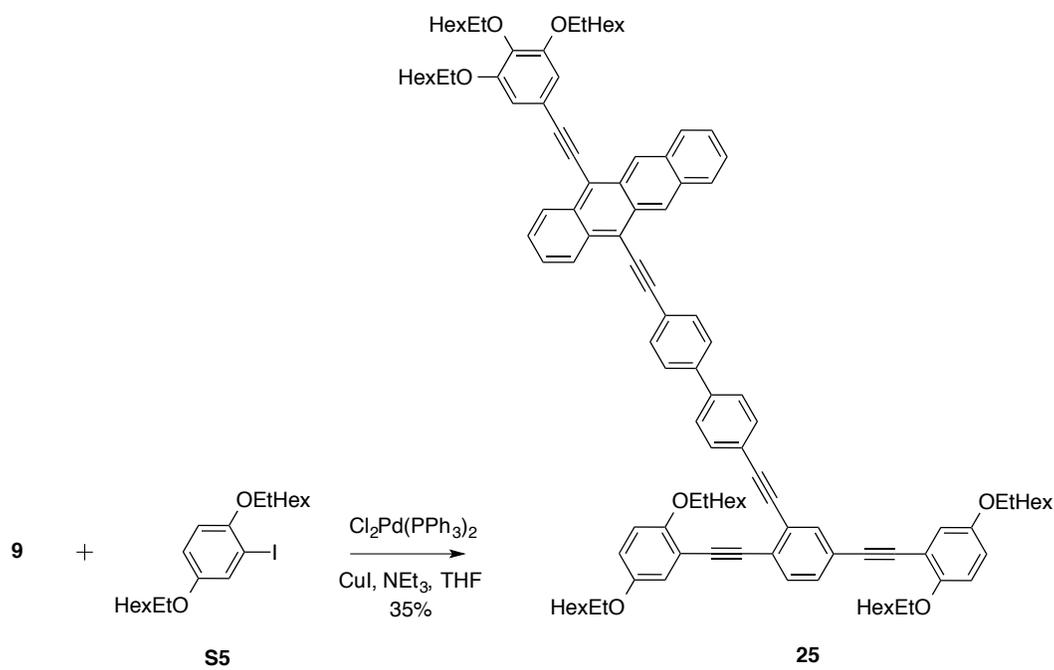
3.4.4 Detailed Synthetic Procedures



Scheme 3.7. Synthesis of 4-ethylhexyloxyethynylbenzene



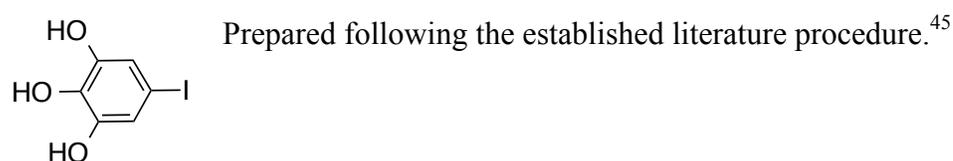
Scheme 3.8. Synthesis of 2,5-diethylhexyloxy-1-iodobenzene



Scheme 3.9. Synthesis of small molecule model of **P2**, compound **25**.

Synthesis monomers for P1 and P2:

5-iodobenzene-1,2,3-triol (1)

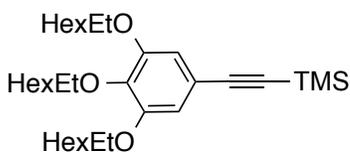


5-iodo-1,2,3-tris(ethylhexyloxy)benzene (2)

Compound **1** (562 mg, 2.23 mmol, 1.0 eq) and K_2CO_3 (2.5 g, 17.8 mmol, 8.0 eq) were dissolved in 12 mL of dry DMF at room temperature under argon. 2-ethylhexylbromide (1.8 mL, 10 mmol, 4.5 eq) was then added to this solution under an argon atmosphere. The mixture was heated to 95 °C and stirred for 4 days. The mixture was then cooled to room temperature. The reaction was stopped by quenching with 10% aq NaOH.

Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.5:1) to yield **2**. Yield: 1.05 g (%80). ¹H NMR (500 MHz, CDCl₃): δ 6.86 (s, 2H), 3.84-3.78 (m, 6H), 1.77-1.73 (m, 2H), 1.71 - 1.66 (m, 1H), 1.56-1.33 (m, 24H), 0.96-0.91 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 154.2, 138.2, 115.6, 85.6, 75.9, 71.4, 40.6, 39.6, 30.5, 29.3, 29.1, 23.8, 23.7, 23.14, 23.08, 14.14, 14.09, 11.19, 11.09.

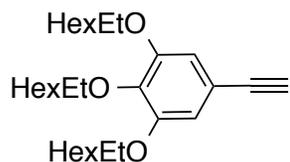
Trimethyl((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)silane (**3a**)



A round bottom flask was charged with Pd(PPh₃)₂Cl₂ (25 mg, 0.036 mmol, 0.02 eq) and CuI (14 mg, 0.072 mmol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, **2** (1.05 g, 1.8 mmol, 1 eq) was dissolved in 63 mL of Et₃N:THF(1:3, v/v) and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. While stirring, TMSA (0.31 mL, 2.16 mmol, 1.2 eq) were added dropwise to the flask. The reaction mixture was stirred for 2 days at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.5:1) to yield **3a**. Yield: 940 mg (%94). ¹H NMR (300 MHz, CDCl₃): δ 6.65 (s, 2H), 3.81 (m, 6H), 1.72-1.64 (m, 3H), 1.5-1.31 (m, 24H), 0.92-0.88 (m, 18H), 0.23 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 153.2, 139.3, 117.5, 110.1, 105.8, 92.6, 76.1, 71.3, 40.8, 39.7,

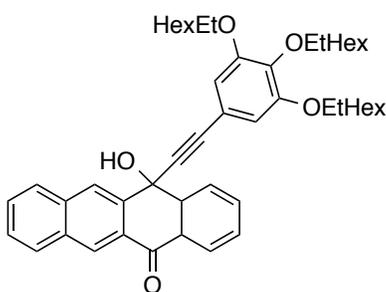
30.7, 29.48, 29.47, 29.3, 23.97, 23.9, 23.3, 23.2, 14.29, 14.25, 11.37, 11.35, 11.2, 0.20.

5-ethynyl-1,2,3-tris(ethylhexyloxy)benzene (3)



Compound **3a** (940 mg, 1.7 mmol, 1 eq) was dissolved in mixture of MeOH (17 mL), Et₂O (17 mL) and 10% NaOH_(aq) (7 mL). The reaction mixture was stirred overnight at room temperature. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.5:1) to yield **3**. Yield: 652 g (%79). ¹H NMR (500 MHz, CDCl₃): δ 6.71 (s, 2H), 3.88-3.81 (m, 6H), 3.02 (s, 1H), 1.79-1.67 (m, 3H), 1.55-1.28 (m, 24H), 0.96-0.91 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 153.2, 139.4, 116.3, 110.1, 84.2, 76, 75.7, 71.2, 40.6, 39.6, 30.5, 29.3, 29.1, 23.8, 23.7, 23.2, 23.1, 14.2, 14.1, 11.2, 11.1.

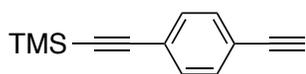
12-hydroxy-12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)-12,12a-dihydrotetracen-5(4aH)-one (4)



Compound **3** (195 mg, 0.4 mmol, 1eq) was dissolved in 2.1 mL of dry THF, followed by dropwise addition of *n*-butyllithium (0.23 mL, 0.36 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour

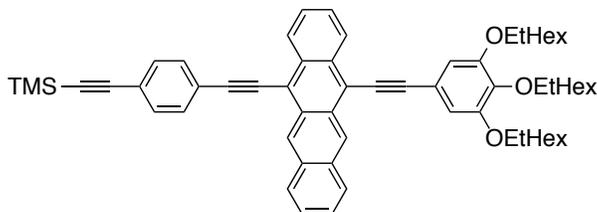
and then transferred to the flask containing 5,12- naphthacenequinone (104 mg, 0.4 mmol, 1 eq), which was dissolved in 1.8 mL of dry THF and cooled to 0 °C, dropwisely via syringe. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction was quenched by addition of 10 mL of ice cold DI H₂O and then filtered via vacuum filtration by washing about 30 mL of THF:H₂O (1:1, v/v). Saturated NH₄Cl was added to filtrate and let it stir for 30 min. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **4**. Yield: 190 mg (%63.5). ¹H NMR (500 MHz, CDCl₃): δ 8.71 (s, 1H), 8.66 (s, 1H), 8.28 (d, J=8 Hz, 1H), 8.2 (m, 1H), 7.97-7.94 (m, 2H), 7.75-7.72 (m, 1H), 7.63-7.6 (m, 1H), 7.57-7.54 (m, 1H), 7.5-7.47 (m, 1H), 6.63 (s, 2H), 3.84-3.74 (m, 6H), 1.74-1.57 (m, 3H), 1.54-1.28 (m, 24H), 0.96-0.89 (m, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 183.5, 153.1, 144.4, 139.6, 139.3, 135.9, 134.3, 132.7, 129.9, 129.8, 129.3, 129, 128.9, 128.2, 128.1, 127.7, 127.4, 127.2, 127.1, 116.2, 109.7, 89.9, 86.9, 76.1, 71.3, 67, 40.6, 39.6, 30.5, 29.31, 29.29, 29.1, 23.8, 23.7, 23.1, 23.06, 14.13, 14.1, 11.19, 11.18, 11.16, 11.07.

((4-ethynylphenyl)ethynyl)trimethylsilane (S6)



Prepared following the established literature procedure.⁴⁷

Trimethyl((4-((12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracen-5-yl)ethynyl)phenyl)ethynyl)silane (5a)

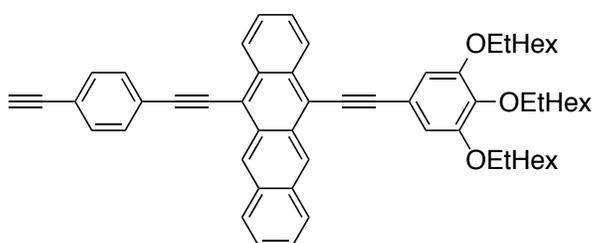


Compound **S6** (271 mg, 1.37 mmol, 4.0 eq) was dissolved in 4.3 mL of dry THF, followed by

dropwise addition of *n*-butyllithium (0.83 mL, 1.33 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 75 minutes and then transferred to the flask containing compound **4** (255 mg, 0.34 mmol, 1 eq), which was dissolved in 2.2 mL of dry THF and cooled to -78 °C, via cannula transfer. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction mixture was then treated with 10% HCl aqueous solution saturated with SnCl₂ dihydrate and left overnight stirring. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **5a**. Yield: 210 mg (%67). ¹H NMR (500 MHz, CDCl₃): δ 9.33 (s, 1H), 9.3 (s, 1H), 8.72-8.68 (m, 2H), 8.16-8.13 (m, 2H), 7.84-7.8 (m, 2H), 7.65-7.61 (m, 4H), 7.53-7.51 (m, 2H), 7.05 (s, 2H), 4.02-3.95 (m, 6H), 1.87-1.83 (m, 2H), 1.8-1.74 (m, 1H), 1.68-1.28 (m, 24H), 1.02-0.94 (m, 18H), 0.33 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 153.5, 139.6, 132.5, 132.4, 132.34, 132.28, 132.26, 132.24, 132.17, 132.14, 131.6, 131.5, 129.9, 128.6, 128.5, 127.6, 127.3, 127.2, 126.83, 126.79, 126.58, 126.24, 126.14, 126.11, 126.05, 125.96, 125.93, 123.9, 123.6, 123.4, 122.3, 119.1, 118.9,

117.7, 117.6, 117.5, 110.1, 109.8, 104.7, 104.14, 104.1, 102.9, 102.6, 96.8, 89.2, 89.1, 85.7, 83.3, 79.3, 76.2, 71.5, 40.7, 39.7, 30.6, 30.5, 29.38, 29.36, 29.35, 29.18, 23.89, 23.75, 23.19, 23.13, 14.19, 14.14, 11.27, 11.25, 11.23, 11.19.
 HRMS calcd for C₆₃H₇₆O₃Si (M+H)⁺, 909.5636, found, 909.5630.

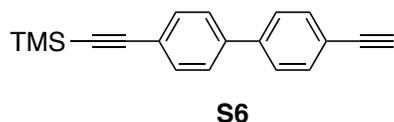
5-((4-ethynylphenyl)ethynyl)-12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracene (5)



Compound **5a** (207 mg, 0.23 mmol, 1.0 eq) and K₂CO₃ (94 mg, 0.68 mmol, 3.0 eq) were dissolved in mixture of THF (4

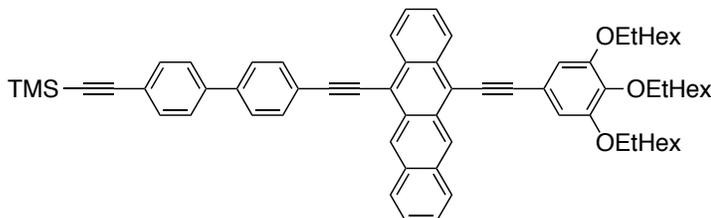
mL), and MeOH (4 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was used without further purification. Yield: 180 mg (%94). ¹H NMR (300 MHz, CDCl₃): δ 9.29 (s, 1H), 9.26 (s, 1H), 8.67 (m, 2H), 8.12 (m, 2H), 7.80-7.78 (m, 2H), 7.62-7.60 (m, 4H), 7.5 (m, 2H), 7.01 (m, 2H), 3.97-3.93 (m, 6H), 3.24 (s, 1H), 1.82-1.74 (m, 3H), 1.54-1.24 (m, 24H), 0.99-0.92 (m, 18H).

((4'-ethynyl-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane (S7)



Prepared following the established literature procedure.⁴⁶

Trimethyl((4'-((12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracen-5-yl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)silane (6a)

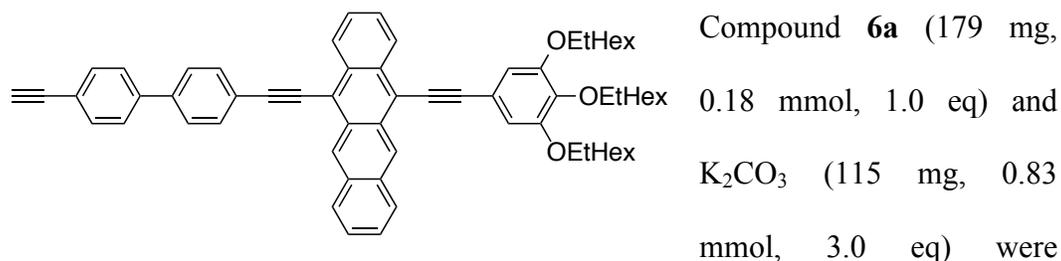


Compound **S7** (505 mg, 1.83 mmol, 7.0 eq) was dissolved in 3.2 mL of dry THF, followed by

dropwise addition of *n*-butyllithium (1.11 mL, 1.78 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 75 minutes and then transferred to the flask containing compound **4** (190 mg, 0.26 mmol, 1.0 eq), which was dissolved in 1.6 mL of dry THF and cooled to -78 °C, via cannula transfer. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction mixture was then treated with 10% HCl aqueous solution saturated with SnCl₂ dihydrate and left overnight stirring. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **6a**. Yield: 179 mg (%70). ¹H NMR (500 MHz, CDCl₃): δ 9.29 (s, 2H), 8.70-8.69 (m, 2H), 8.13-8.12 (m, 2H), 7.92 (d, J=8 Hz, 2H), 7.74 (d, J=8 Hz, 2H), 7.66-7.56 (m, 6H), 7.52-7.49 (m, 2H), 7.07 (s, 2H), 4.04-3.98 (m, 6H), 1.89-1.78 (m, 3H), 1.68-1.41 (m, 24H), 1.04-0.96 (m, 18H), 0.34 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 153.5, 140.4, 140.3, 139.7, 132.8, 132.7, 132.6, 132.4, 132.3, 132.2, 132.1, 129.99, 129.97, 128.6, 128.56, 127.5, 127.4, 127.2, 127.1, 126.9, 126.89, 126.8,

126.7, 126.6, 126.2, 126, 125.9, 122.9, 122.6, 118.7, 117.9, 117.8, 109.9, 104.9, 104, 103.1, 95.4, 88.3, 85.8, 40.7, 39.8, 30.6, 30.5, 29.4, 29.2, 23.9, 23.8, 23.2, 23.15, 14.2, 14.1, 11.3, 11.2, 0.02.

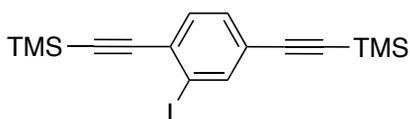
5-((4'-ethynyl-[1,1'-biphenyl]-4-yl)ethynyl)-12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracene (6)



dissolved in mixture of THF (1.5 mL), and MeOH (3 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was used without further purification. Yield: 159 mg (%94). ¹H NMR (500 MHz, CDCl₃): δ 9.34 (s, 1H), 9.33 (s, 1H), 8.75-8.71 (m, 2H), 8.18-8.14 (m, 2H), 7.95 (d, J=8.5 Hz, 2H), 7.75 (d, J=8 Hz, 2H), 7.69-7.62 (m, 6H), 7.54-7.51 (m, 2H), 7.06 (s, 2H), 3.99-3.94 (m, 6H), 3.2 (s, 1H), 1.88-1.82 (m, 2H), 1.8-1.77 (m 1H), 1.68-1.23 (m, 24H), 1.02-0.94 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 153.6, 140.8, 140.6, 139.8, 132.9, 132.6, 132.5, 132.4, 132.37, 132.3, 130.2, 128.8, 128.7, 127.7, 127.5, 127.4, 127.1, 126.9, 126.7, 126.4, 126.2, 126.19, 123.1, 121.7, 118.9, 118.1, 117.9, 109.9, 104.2, 103.2, 88.4, 85.9, 83.6, 78.3, 76.4, 71.6, 40.8, 39.8, 30.7, 30.68, 29.5, 29.3,

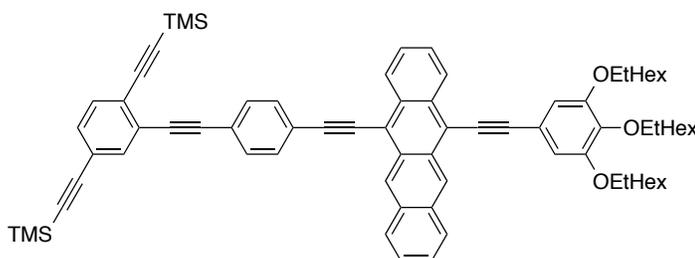
24, 23.9, 23.3, 23.28, 14.33, 14.28, 11.39, 11.37, 11.34. HRMS calcd for $C_{66}H_{72}O_3$ (M+H)⁺, 913.5554, found, 913.5566.

((2-iodo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (7)



Prepared following the established literature procedure.⁵⁰

((2-((4-((12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracen-5-yl)ethynyl)phenyl)ethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (8a)

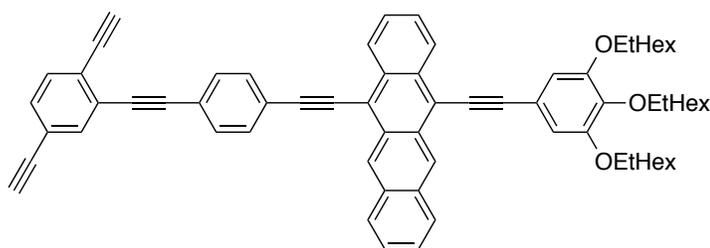


A round bottom flask was charged with **5** (180 mg, 0.22 mmol, 1.0 eq), **7** (196 mg, 0.49 mmol,

2.3 eq), $Pd(PPh_3)_2Cl_2$ (3 mg, 4.3 μ mol, 0.02 eq) and CuI (1.7 mg, 8.6 μ mol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, 11 mL of deoxygenated $Et_3N:THF$ (1:3, v/v) was transferred to reaction flask. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **8a**. Yield: 135 mg (%56). ¹H NMR (500 MHz, $CDCl_3$): δ 9.31 (s, 1H), 9.30 (s, 1H), 8.72-8.69 (m, 2H), 8.17-8.13 (m, 2H), 7.86 (d, J=8 Hz, 2H), 7.72-7.68 (m, 3H), 7.63-7.61 (m, 2H), 7.53-7.49 (m, 3H), 7.41-7.39 (m, 1H), 7.06 (s, 2H), 4.05-3.94 (m, 6H), 1.89-1.76 (m, 3H), 1.69-1.35 (m, 24H), 1.03-0.95 (m, 18H), 0.36 (s, 9H), 0.30 (s, 9H). ¹³C NMR (125

MHz, CDCl₃): δ 153.6, 141.8, 139.8, 135.3, 132.6, 132.4, 132.38, 132.28, 132.2, 132, 131.8, 131.5, 131.2, 130.1, 128.8, 128.7, 127.7, 127.5, 126.9, 126.7, 126.4, 126.3, 126.2, 126.1, 125.6, 123.8, 123.5, 123.4, 119.1, 117.9, 117.8, 109.9, 104.3, 103.8, 103.2, 103.1, 100.9, 97.2, 93.7, 89.8, 89.5, 85.9, 76.4, 71.6, 40.8, 39.8, 30.7, 30.6, 29.53, 29.51, 29.5, 29.3, 24, 23.9, 23.3, 23.28, 14.3, 14.28, 11.41, 11.40, 11.38, 11.34, 0.18, 0.02.

5-((4-((2,5-diethynylphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracene (8)

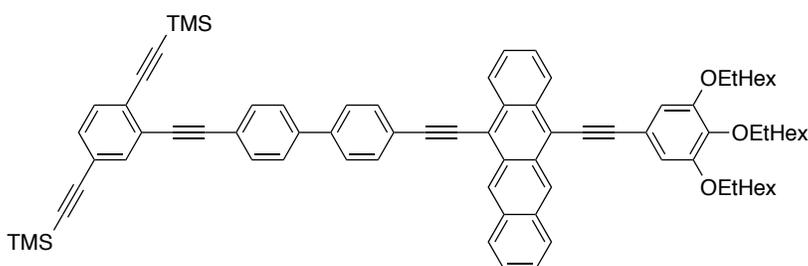


Compound **8a** (135 mg, 0.12 mmol, 1.0 eq) and K₂CO₃ (135 mg, 0.98 mmol, 8.0 eq) were

dissolved in mixture of THF (2 mL), and MeOH (4 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.25:1) to yield **8**. Yield: 80 mg (%68). ¹H NMR (500 MHz, CDCl₃): δ 9.34 (s, 1H), 9.32 (s, 1H), 8.73-8.70 (m, 2H), 8.18-8.14 (m, 2H), 7.87 (d, J=8.5 Hz, 2H), 7.74 (s, 1H), 7.71 (d, J=8.5, 2H), 7.64-7.62 (m, 2H), 7.56-7.52 (m, 3H), 7.46-7.44 (m, 1H), 7.08 (s, 2H), 4.04-3.93 (m, 6H), 3.52 (s, 1H), 3.24 (s, 1H), 1.90-1.73 (m, 3H), 1.66-1.37 (m, 24H), 1.02-0.89 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 153.5, 139.7, 135.3, 132.7, 132.5, 132.29,

132.27, 132.16, 132, 131.7, 131.6, 130, 128.6, 127.6, 127.3, 126.8, 126.6, 126.4, 126.3, 126.2, 126.1, 125.9, 124.9, 123.8, 123.1, 122.7, 119, 117.7, 117.6, 109.8, 104.2, 102.9, 93.9, 89.4, 89.1, 85.7, 83.1, 82.2, 81.7, 79.7, 76.2, 71.5, 40.7, 39.7, 30.6, 30.5, 29.4, 29.2, 23.9, 23.8, 23.2, 23.1, 14.2, 14.1, 11.25, 11.23, 11.2. HRMS calcd for C₇₀H₇₂O₃ (M+H)⁺, 961.5554, found, 961.5554.

((2-((4'-((12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracen-5-yl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (9a)

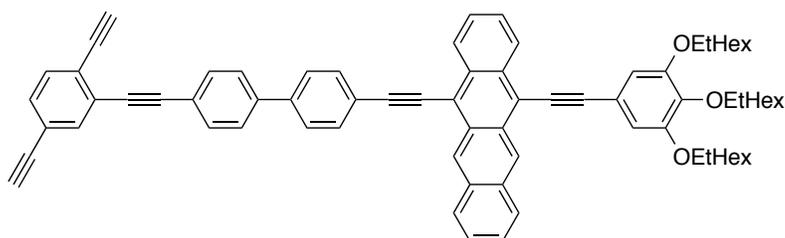


A round bottom flask was charged with **6** (159 mg, 0.17

mmol, 1.0 eq), **7** (165 mg, 0.42 mmol, 2.4 eq), Pd(PPh₃)₂Cl₂ (2.4 mg, 3.4 μmol, 0.02 eq) and CuI (1.3 mg, 6.8 μmol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, 10 mL of deoxygenated Et₃N:THF (1:3, v/v) was transferred to reaction flask. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **9a**. Yield: 110 mg (%55). ¹H NMR (500 MHz, CDCl₃): δ 9.29 (s, 2H), 8.71-8.69 (m, 2H), 8.14-8.11 (m, 2H), 7.93 (d, J=8.5 Hz, 2H), 7.77 (d, J=8.5, 2H), 7.73-7.71 (m, 5H), 7.62-7.60 (m, 2H), 7.52-7.50 (m, 3H), 7.42-7.40 (m, 1H), 7.08 (s, 2H), 4.06-3.99 (m, 6H), 1.90-1.79 (m, 2H), 1.68-1.39 (m, 24H), 1.05-0.97 (m, 18H), 0.37 (s, 9H), 0.32 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 153.6, 140.5,

140.4, 139.8, 135.2, 132.5, 132.4, 132.36, 132.3, 132.25, 131.3, 130.1, 130, 128.7, 127.2, 127.1, 126.8, 126.6, 126.3, 126.29, 126.16, 126.13, 126.10, 125.6, 123.4, 123.1, 122.7, 118.8, 118.1, 117.9, 109.9, 104, 103.9, 103.3, 103.26, 100.9, 97.1, 93.9, 88.7, 88.5, 85.9, 76.4, 71.6, 40.8, 39.9, 30.8, 30.7, 29.54, 29.53, 29.51, 29.3, 24.1, 23.9, 23.4, 23.3, 14.33, 14.28, 11.43, 11.41, 11.39, 11.35, 0.18, 0.02.

5-((4'-((2,5-diethynylphenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracene (9)

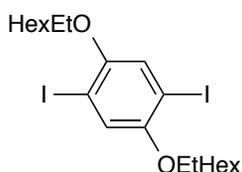


Compound **9a**
(105 mg, 0.09
mmol, 1.0 eq) and
K₂CO₃ (104 mg,

0.75 mmol, 8.4 eq) were dissolved in mixture of THF (1.5 mL), and MeOH (3 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.75:1) to yield **5**. Yield: 78 mg (%85). ¹H NMR (500 MHz, CDCl₃): δ 9.29 (s, 2H), 8.71-8.69 (m, 2H), 8.13-8.11 (m, 2H), 7.91 (d, J=8 Hz, 2H), 7.75-7.72 (m, 3H), 7.69 (s, 4H), 7.61-7.59 (m, 2H), 7.52-7.42 (m, 3H), 7.41-7.40 (m, 1H), 7.1 (s, 2H), 4.03-3.96 (m, 6H), 3.51 (s, 1H), 3.22 (s, 1H), 1.87-1.77 (m, 3H), 1.68-1.39 (m, 24H), 1.03-0.94 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 153.5, 140.5, 140.4, 139.7, 135.2, 132.6, 132.4, 132.39, 132.3, 132.25, 132.2, 132.1, 131.4, 130, 129.9, 128.6,

128.5, 127.2, 126.9, 126.7, 126.6, 126.5, 126.2, 126.04, 126, 124.9, 122.9, 122.7, 122.3, 118.7, 117.9, 117.8, 109.9, 104, 103, 94.1, 88.4, 88, 85.8, 82.9, 82.3, 81.8, 79.6, 76.3, 71.5, 40.7, 39.7, 30.62, 30.6, 29.41, 29.39, 29.38, 29.2, 23.9, 23.8, 23.2, 23.15, 14.2, 14.15, 11.29, 11.27, 11.25, 11.21. HRMS calcd for C₇₆H₇₆O₃ (M+H)⁺, 1037.5867, found, 1037.5869.

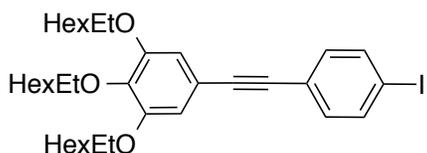
1,4-diiodo-2,5-bis(ethylhexyloxy)benzene (10)



Prepared following the established literature procedure.⁵¹

Synthesis of monomer for P3:

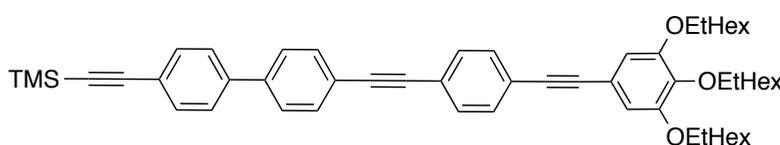
5-((4-iodophenyl)ethynyl)-1,2,3-tris(ethylhexyloxy)benzene (11)



A round bottom flask was charged with **3** (652 mg, 1.34 mmol, 1.0 eq), **1,4-diiodobenzene** (1.33 g, 4 mmol, 3 eq), Pd(PPh₃)₄ (46 mg, 0.04 mmol, 0.03 eq) and CuI (15 mg, 0.08 mmol, 0.06 eq) and evacuated and refilled with argon three times. In another flask, 51 mL of deoxygenated Et₃N:Toluene (1:5, v/v) was transferred to reaction flask. The reaction mixture was stirred for overnight at 40 °C. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.75:1) to yield **11**. Yield: 230 mg (%25). ¹H NMR (500 MHz, CDCl₃): δ 7.70 (d, J=9 Hz, 2H), 7.26 (d, J=10 Hz, 2H), 6.75 (s, 2H), 3.90-

3.84 (m, 6H), 1.80-1.69 (m, 3H), 1.60-1.41 (m, 24 H), 0.97-0.92 (m, 18 H). ¹³C NMR (125 MHz, CDCl₃): δ 153.27, 137.5, 133, 122.9, 117.1, 110.4, 109.5, 93.8, 91.4, 87.1, 76, 71.3, 40.6, 39.6, 30.5, 29.3, 29.1, 23.82, 23.79, 23.71, 23.2, 23.1, 14.15, 14.11, 11.21, 11.19, 11.10.

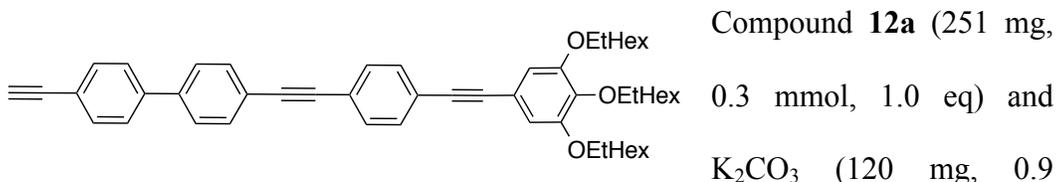
Trimethyl((4'-((4-((3,4,5-tris(octyloxy)phenyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)silane (12a)



A round bottom flask was charged with **S7** (120 mg,

0.44 mmol, 1.3 eq), Pd(PPh₃)₂Cl₂ (5 mg, 6.8 μmol, 0.02 eq) and CuI (2.6 mg, 13.6 μmol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, **11** (230 mg, 0.34 mmol, 1.0 eq) was dissolved in 20 mL of Et₃N:THF (1:3, v/v) and this solution was added to flask containing catalysts and other starting material via cannula transfer after deoxygenating for 1 hour with argon. The reaction mixture was stirred for overweekend at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.75:1) to yield **12a**. Yield: 251 mg (%90). ¹H NMR (500 MHz, CDCl₃): δ 7.62-7.54 (m, 12H), 6.78 (s, 2H), 3.93-3.84 (m, 6H), 1.82-1.70 (m, 3H), 1.61-1.35 (m, 24H), 0.99-0.93 (m, 18 H). ¹³C NMR (125 MHz, CDCl₃): δ 153.4, 140.4, 140.3, 139.4, 132.6, 132.3, 131.7, 131.6, 127.1, 126.9, 123.5, 122.9, 122.7, 122.5, 117.4, 109.8, 104.9, 95.4, 92.1, 91.2, 90.3, 87.9, 76.9, 76.2, 71.5, 40.8, 39.8, 30.7, 29.5, 29.49, 29.47, 29.3, 23.9, 23.88, 23.3, 23.2, 14.3, 14.25, 11.38, 11.37, 11.35, 11.25, 0.13.

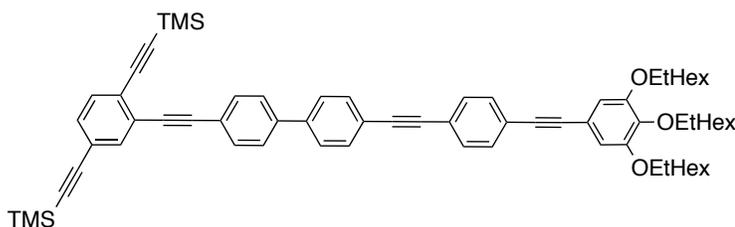
**4-ethynyl-4'-((4-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-
1,1'-biphenyl (12)**



mmol, 3.0 eq) were dissolved in mixture of THF (1.8 mL), and MeOH (3.6 mL).

The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and ethylacetate (9:1) to yield **12**. Yield: 194 mg (%84). ¹H NMR (500 MHz, CDCl₃): δ 7.65-7.62 (m, 4H), 7.60 (s, 4H), 7.56-7.52 (m, 4H), 6.77 (s, 2H), 3.92-3.86 (m, 6H), 3.17 (s, 1H), 1.81-1.70 (m, 3H), 1.60-1.35 (m, 24H), 0.98-0.92 (m, 18 H). ¹³C NMR (125 MHz, CDCl₃): δ 153.3, 140.6, 140.1, 139.2, 132.7, 132.1, 131.5, 131.4, 126.9, 126.8, 123.4, 122.8, 122.5, 121.5, 117.2, 109.6, 91.9, 90.9, 90.2, 87.8, 83.4, 78.1, 76.1, 71.3, 40.6, 39.6, 30.5, 29.34, 29.33, 29.32, 29.1, 23.8, 23.7, 23.1, 23.09, 14.13, 14.09, 11.22, 11.20, 11.1. HRMS calcd for C₅₄H₆₆O₃ (M+H)⁺, 763.5085, found, 763.5081.

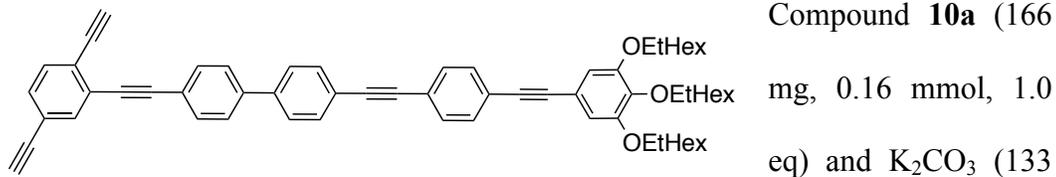
((2-((4'-((4-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (13a)



A round bottom flask was charged with **12** (194 mg, 0.25 mmol, 1.0 eq), **7** (131 mg,

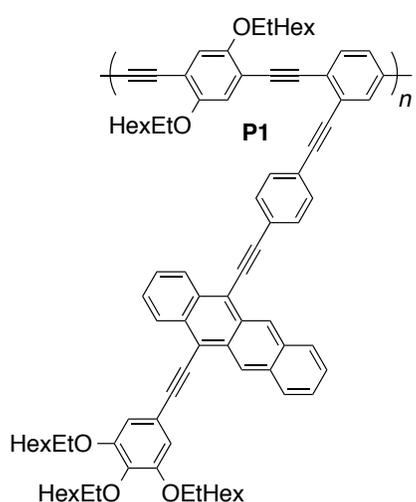
0.33 mmol, 1.3 eq), Pd(PPh₃)₂Cl₂ (3.6 mg, 5.1 μmol, 0.02 eq) and CuI (2 mg, 0.01 mmol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, 12 mL of deoxygenated Et₃N:THF (1:3, v/v) was transferred to reaction flask. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **13a**. Yield: 166 mg (%63). ¹H NMR (500 MHz, CDCl₃): δ 7.68-7.63 (m, 9H), 7.56-7.53 (m, 4H), 7.48-7.46 (m, 2H), 7.38-7.36 (m, 2H), 6.78 (s, 2H), 3.92-3.87 (m, 6H), 1.82-1.70 (m, 3H), 1.60-1.36 (m, 24H), 1.01-0.90 (m, 18 H), 0.32 (s, 9H), 0.29 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 153.4, 140.4, 140.3, 139.4, 135.2, 132.4, 132.36, 132.29, 131.7, 131.6, 131.3, 127.1, 127, 126.3, 125.6, 123.5, 123.4, 122.9, 122.6, 117.4, 109.8, 103.9, 103.3, 100.8, 97.1, 93.9, 92.1, 91.2, 90.4, 88.6, 87.9, 76.2, 71.5, 40.8, 39.8, 30.7, 29.5, 29.3, 23.99, 23.88, 23.3, 23.25, 14.3, 14.2, 11.4, 11.3, 0.15, 0.01.

4-((2,5-diethynylphenyl)ethynyl)-4'-((4-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-1,1'-biphenyl (13)



mg, 0.9 mmol, 8.4 eq) were dissolved in mixture of THF (1.8 mL), and MeOH (3.6 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was used without further purification. Yield: 111 mg (%78). ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.70 (m, 1H), 7.68-7.64 (m, 8H), 7.56-7.52 (m, 5H), 7.43-7.41 (m, 1H), 6.77 (s, 2H), 3.92-3.86 (m, 6H), 3.5 (s, 1H), 3.22 (s, 1H), 1.81-1.70 (m, 3H), 1.61-1.35 (m, 24H), 0.98-0.92 (m, 18 H). ¹³C NMR (125 MHz, CDCl₃): δ 153.3, 140.5, 140.2, 139.2, 135.2, 132.6, 132.4, 132.2, 131.6, 131.5, 131.4, 126.97, 126.94, 126.6, 124.9, 123.4, 122.8, 122.7, 122.5, 122.2, 117.2, 109.6, 94, 91.9, 91, 90.2, 87.9, 87.8, 82.9, 82.3, 81.7, 79.6, 76.1, 71.3, 40.6, 39.6, 30.5, 29.3, 29.1, 23.8, 23.7, 23.2, 23.1, 14.16, 14.12, 11.24, 11.22, 11.11. HRMS calcd for C₆₄H₇₀O₃ (M+H)⁺, 887.5398, found, 887.5418.

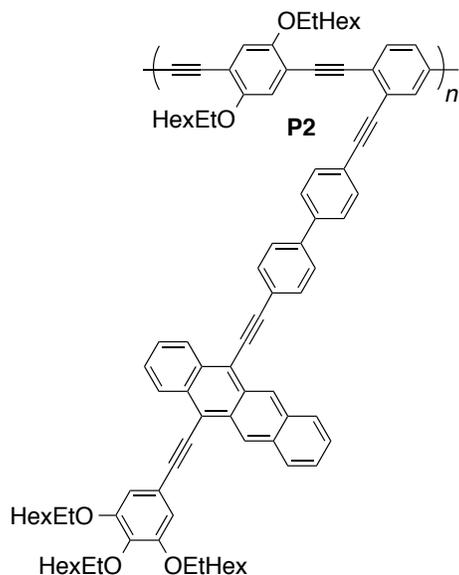
P1.



A Schlenk tube was charged with <1 mg Pd(PPh₃)₄, and <1 mg CuI, and evacuated and refilled with argon three times. **8** (19.5 mg, 0.02 mmol, 1.0 eq) and **10** (12 mg, 0.02 mmol, 1.0 eq) was dissolved in 2.5 mL 4:1 (v:v) toluene:diisopropylamine and sparged with argon for 30 minutes. The solution was added to the reaction vessel and the mixture stirred for 72

hours at room temperature. The reaction mixture was precipitated into 200 mL methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 100 mL of methanol and isolated by centrifugation and decanting. *M_n* [g/mol]: 26k, *M_w* [g/mol]: 47k. Yield: 20 mg (76%) ¹H NMR (500 MHz, CDCl₃): δ 9.34-9.32 (m, 1H), 8.95 (m, 0.5H), 8.81 (m, 0.5H), 8.72 (m, 1H), 8.46 (m, 0.5H), 8.29 (m, 0.5H), 8.16 (m, 1H), 8.00 (m, 0.5), 7.89-7.80 (m, 2H), 7.75-7.68 (m, 3H), 7.65-7.37 (m, 6H), 7.13-7.02 (m, 3H), 4.02-3.76 (m, 10H), 1.89-1.75 (m, 5H), 1.67-1.28 (m, 40H), 1.08-0.79 (m, 30H).

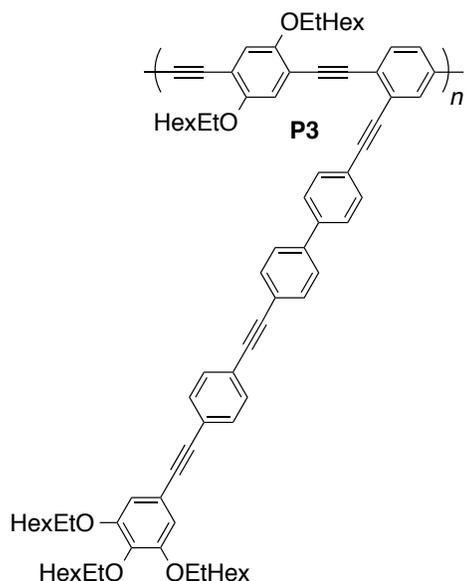
P2.



A Schlenk tube was charged with <1 mg Pd(PPh₃)₄, and <1 mg CuI, and evacuated and refilled with argon three times. **9** (18.3 mg, 0.016 mmol, 1.0 eq) and **10** (9.1 mg, 0.016 mmol, 1.0 eq) was dissolved in 2 mL 4:1 (v:v) toluene:diisopropylamine and sparged with argon for 30 minutes. The solution was added to the reaction vessel and the mixture stirred for 72 hours at room

temperature. The reaction mixture was precipitated into 200 mL methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 100 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 20k, M_w [g/mol]: 46k. Yield: 15 mg (71%) ¹H NMR (500 MHz, CDCl₃): δ 9.34-9.3 (m, 1H), 9.22-9.18 (m, 1H), 8.72 (m, 1H), 8.64 (m, 1H), 8.15-8.07 (m, 2H), 7.97-7.88 (m, 2H), 7.82-7.70 (m, 7H), 7.63-7.49 (m, 6H), 7.17-7.03 (m, 4H), 4.02-3.88 (m, 10H), 1.86-1.76 (m, 5H), 1.65-1.29 (m, 40H), 1.06-0.87 (m, 30H).

P3.



A Schlenk tube was charged with <1 mg Pd(PPh₃)₄, and <1 mg CuI, and evacuated and refilled with argon three times. **13** (26 mg, 0.03 mmol, 1.0 eq) and **10** (17 mg, 0.03 mmol, 1.0 eq) was dissolved in 3.3 mL 4:1 (v:v) toluene:diisopropylamine and sparged with argon for 30 minutes. The solution was added to the reaction vessel and the mixture stirred for 72 hours at 60 °C. The reaction mixture was precipitated into 150 mL methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove insoluble catalyst residues, reprecipitated into 100 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 31k, M_w [g/mol]: 58k. Yield: 25 mg (69%) ¹H NMR (500 MHz, CDCl₃): δ 7.74 (m, 1H), 7.64-7.4 (m, 13H), 7.05-7.00 (m, 2H), 6.73 (m, 2H), 3.85 (m, 10H), 1.75 (m, 5H), 1.52-1.20 (m, 40H), 1.03-0.79 (m, 30H).

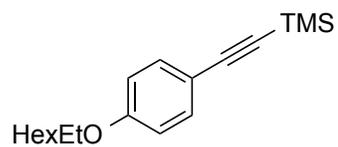
Synthesis of A1, A2 and A3

1-iodo-4-(ethylhexyloxy)benzene (S1)

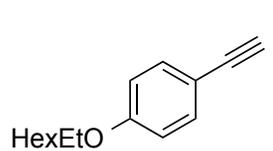
4-iodophenol (9 g, 0.04 mol, 1.0 eq), KOH (2.35 g, 0.04 mol, 1.0 eq) and KI (180 mg, 0.8 mmol, 0.02 eq) were dissolved in 102 mL of dry EtOH at room temperature under argon. 2-ethylhexylbromide (8.1

mL, 0.045 mmol, 1.1 eq) was then added to this solution under an argon atmosphere. The mixture was heated to 60 °C and stirred for overnight. The mixture was then cooled to room temperature. After precipitate (KBr) was collected, the solution was distilled off using rotavap and remaining residue was redissolved in CH₂Cl₂. Organic phase were washed with water and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was taken next step without further purification. Yield: 7.34 g (%52).

Trimethyl((4-(ethylhexyloxy)phenyl)ethynyl)silane (S2)

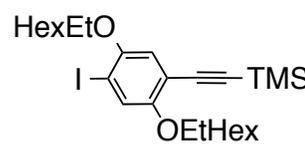
 A round bottom flask was charged with Pd(PPh₃)₂Cl₂ (404 mg, 0.6 mmol, 0.04 eq) and CuI (195 mg, 1 mmol, 0.07 eq) and evacuated and refilled with argon three times. In another flask, **S1** (5 g, 14.4 mmol, 1.0 eq) was dissolved in 77 mL of Et₃N and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. While stirring, TMSA (2.4 mL, 16.7 mmol, 1.2 eq) were added dropwise to the flask. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.5:1) to yield **S2**. Yield: 3.23 mg (%92).

1-ethynyl-4-(ethylhexyloxy)benzene (14)

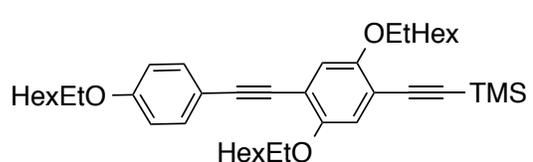
 Compound **S2** (3.2 g, 10.6 mmol, 1.0 eq) was dissolved in mixture of MeOH (106 mL), Et₂O (106 mL) and 10%

NaOH_(aq) (44 mL). The reaction mixture was stirred overnight at room temperature. The reaction was stopped by acidification with 10% aq HCl. Organics were extracted twice with Et₂O, and combined organic phases were washed with brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.5:1) to yield **14**. Yield: 1.93 g (%79). ¹H and ¹³C NMR is in good agreement with the same compound reported in the literature.⁵²

((4-iodo-2,5-bis(ethylhexyloxy)phenyl)ethynyl)trimethylsilane (15)

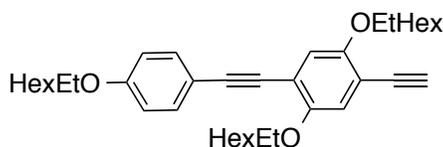

 A round bottom flask was charged with Pd(PPh₃)₂Cl₂ (39 mg, 0.06 mmol, 0.09 eq) and CuI (6 mg, 1 mmol, 0.05 eq) and evacuated and refilled with argon three times. In another flask, **10** (1.11 g, 18.8 mmol, 1.0 eq) was dissolved in 15 mL of Et₃N and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. While stirring, TMSA (0.09 mL, 0.6 mmol, 1 eq) were added dropwise to the flask. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (7.5:1) to yield **15**. Yield: 350 mg (%25). ¹H and ¹³C NMR is in good agreement with literature.⁵³

((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)trimethylsilane (16)


 A round bottom flask was charged with Pd(PPh₃)₂Cl₂ (7 mg, 0.01 mmol,

0.02 eq) and CuI (3.8 mg, 0.02 mmol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, **14** (112 mg, 0.49 mmol, 1.0 eq) and **15** (325 mg, 0.58 mmol, 1.2 eq) were dissolved in 20 mL of Et₃N:THF(1:3, v/v) and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (5:1) to yield **16**. Yield: 190 mg (%59). ¹H NMR (500 MHz, CDCl₃): δ 7.46 (d, J=10 Hz, 2H), 6.97 (s, 1H), 6.96 (s, 1H), 6.89 (d, J=8.6 Hz, 2H), 3.94-3.85 (m, 6H), 1.82-1.73 (m, 3H), 1.64-1.34 (m, 24H), 0.99-0.89 (m, 18H), 0.28 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 159.6, 154.6, 153.6, 133.1, 117.2, 116.4, 115.5, 114.9, 114.7, 113.2, 101.5, 99.7, 95.2, 84.7, 72.2, 71.9, 70.7, 39.81, 39.80, 39.5, 30.8, 30.7, 29.32, 29.28, 29.2, 24.2, 24.1, 24, 23.24, 23.22, 23.19, 14.26, 14.23, 14.21, 11.44, 11.42, 11.26, 0.13.

1-ethynyl-2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)benzene (17)

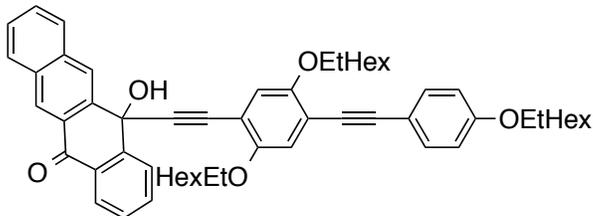


Compound **16** (190 mg, 0.3 mmol, 1 eq) and K₂CO₃ (120 mg, 0.9 mmol, 3.0 eq) were dissolved in mixture of THF (1 mL), and

MeOH (2 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product

was used without further purification. Yield: 154 mg (%92). ^1H NMR (500 MHz, CDCl_3): δ 7.45 (d, $J=8.8$ Hz, 2H), 6.98 (s, 1H), 6.97 (s, 1H), 6.88 (d, $J=8.8$ Hz, 2H), 3.91-3.84 (m, 6H), 3.31 (s, 1H), 1.80-1.72 (m, 3H), 1.62-1.32 (m, 24H), 0.98-0.88 (m, 18H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.7, 154.7, 153.7, 133.1, 117.6, 116.8, 115.4, 115.3, 114.7, 112.2, 95.3, 84.5, 82.1, 80.3, 72.3, 72.2, 70.8, 39.8, 39.6, 39.5, 30.8, 30.7, 29.3, 29.24, 29.23, 24.2, 24.1, 24, 23.22, 23.20, 23.19, 14.23, 14.22, 11.4, 11.32, 11.26. HRMS calcd for $\text{C}_{40}\text{H}_{58}\text{O}_3$ ($\text{M}+\text{H}$) $^+$, 587.4459, found, 587.4467.

12-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-12-hydroxytetracen-5(12*H*)-one (18)

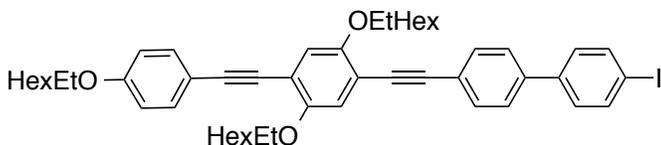


Compound **17** (149 mg, 0.25 mmol, 1.0 eq) was dissolved in 1 mL of dry THF, followed by dropwise addition of *n*-

butyllithium (0.14 mL, 0.23 mmol, 1.6 M in hexanes) at -78 $^{\circ}\text{C}$. The reaction mixture was stirred at -78 $^{\circ}\text{C}$ for 1 hour and then transferred to the flask containing 5,12- naphthacenequinone (66 mg, 0.25 mmol, 1 eq), which was dissolved in 1 mL of dry THF and cooled to 0 $^{\circ}\text{C}$, dropwisely via syringe. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction was quenched by addition of 5 mL of ice cold DI H_2O and then filtered via vacuum filtration by washing about 20 mL of $\text{THF}:\text{H}_2\text{O}$ (1:1, v/v). Saturated NH_4Cl was added to

filtrate and let it stir for 30 min. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **18**. Yield: 117 mg (%54). ¹H NMR (500 MHz, CDCl₃): δ 8.8 (s, 1H), 8.69 (s, 1H), 8.32-8.28 (m, 2H), 8.02 (d, J=8.1 Hz, 1H), 7.97 (d, J=8.2, 1H), 7.77-7.73 (m, 1H), 7.65-7.62 (m, 1H), 7.59-7.53 (m, 2H), 7.45 (d, J=8.7 Hz, 2H), 6.90-6.88 (m, 4H), 3.90-3.73 (m, 6H), 3.71 (s, 1H), 1.8-1.73 (m, 3H), 1.62-1.14 (m, 24H), 0.97-0.88 (m, 12H), 0.84-0.79 (m, 3H), 0.77-0.72 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 183.5, 159.6, 154.1, 153.4, 144.2, 139.5, 135.9, 134.2, 132.9, 132.7, 130, 129.8, 129.3, 129, 128.8, 128.3, 128.1, 127.7, 127.4, 127.3, 127.2, 116.9, 116, 115.2, 115.1, 114.6, 111.7, 96.1, 95.3, 84.5, 83.4, 72.1, 71.3, 70.6, 67.2, 39.6, 39.4, 39.33, 39.31, 30.6, 30.5, 30.2, 30.1, 29.2, 29.1, 28.9, 28.8, 23.9, 23.8, 23.7, 23.6, 23.07, 23.04, 22.94, 22.93, 14.09, 14.08, 14.06, 11.3, 11.1, 10.96, 10.92.

4-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-4'-iodo-1,1'-biphenyl (19)

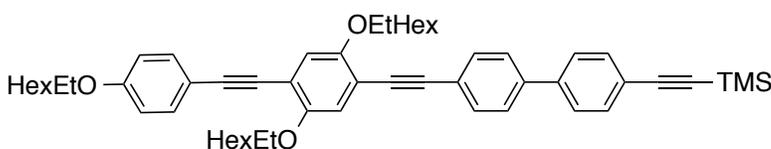


A round bottom flask was charged with Pd(PPh₃)₄ (9 mg, 7.9 μmol, 0.03 eq)

and CuI (3 mg, 15.8 μmol, 0.06 eq) and evacuated and refilled with argon three times. In another flask, **17** (154 mg, 0.26 mmol, 1.0 eq) and **4,4'-diiodophenyl** (320 mg, 0.79 mmol, 3 eq) were dissolved in 12 mL of Et₃N:Toluene(1:5, v/v) and this solution was added to flask containing catalysts via cannula transfer after

deoxygenating for 1 hour with argon. The reaction mixture was stirred for overnight at 40 °C. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (4:1) to yield **19**. Yield: 140 mg (%62). ¹H NMR (500 MHz, CDCl₃): δ 7.8 (d, J=8 Hz, 2H), 7.61 (d, J=8 Hz, 2H), 7.57 (d, J=8 Hz, 2H), 7.48 (d, J=8 Hz, 2H), 7.38 (d, J=8 Hz, 2H), 7.04 (s, 1H), 7.03 (s, 1H), 6.90 (d, J=8.5 Hz, 2H), 3.97-3.94 (m, 4H), 3.89-3.88 (m, 2H), 1.84-1.82 (m, 2H), 1.79-1.73 (m, 1H), 1.67-1.29 (m, 24H), 1.02-0.91 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 159.5, 153.9, 153.7, 139.9, 139.6, 137.9, 132.9, 132, 128.8, 126.7, 123.1, 116.7, 116.5, 115.4, 114.7, 114.6, 113.3, 95.2, 94.3, 93.4, 87.3, 84.6, 72.1, 72, 70.6, 39.7, 39.4, 30.71, 30.69, 30.53, 29.2, 29.1, 24.06, 24.04, 23.88, 23.09, 23.04, 14.09, 14.06, 11.29, 11.11.

((4'-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane (20a)

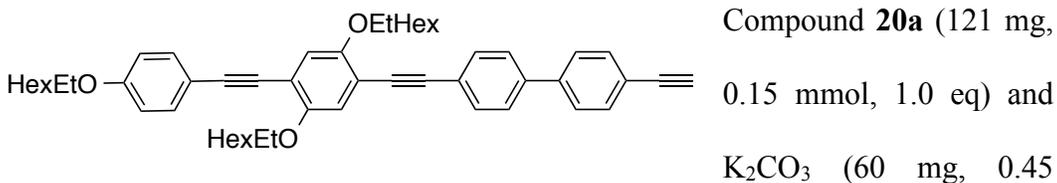


A round bottom flask was charged with Pd(PPh₃)₂Cl₂

(2 mg, 3.2 umol, 0.02 eq) and CuI (1 mg, 6.4 umol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, **19** (140 mg, 0.16 mmol, 1.0 eq) was dissolved in 6 mL of Et₃N:THF(1:3, v/v) and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. While stirring, TMSA (40 uL, 0.28 mmol, 1.8 eq) were added dropwise to the flask. The reaction mixture was stirred for 2 days at room temperature. The

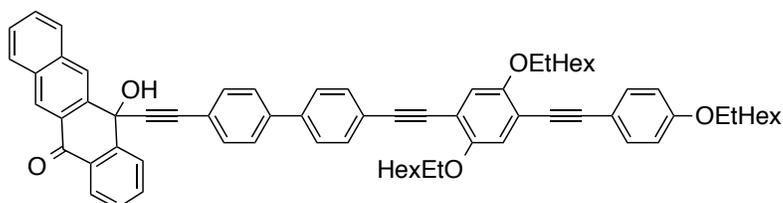
solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **20a**. Yield: 121 mg (%90). ¹H NMR (500 MHz, CDCl₃): δ 7.61-7.56 (m, 8H), 7.48 (d, J=8.7 Hz, 2H), 7.04 (s, 1H), 7.03 (s, 1H), 6.9 (d, J=8.7 Hz, 2H), 3.98-3.91 (m, 4H), 3.89-3.88 (m, 2H), 1.86-1.81 (m, 2H), 1.78-1.74 (m, 1H), 1.67-1.28 (m, 24), 1.02-0.9 (m, 18H), 0.3 (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ 159.7, 154.2, 153.9, 140.5, 140, 133.2, 132.7, 132.2, 127.1, 126.9, 123.2, 122.6, 116.8, 116.7, 115.6, 114.8, 113.5, 105.1, 95.4, 95.3, 94.6, 87.5, 84.9, 72.3, 72.2, 70.8, 39.9, 39.6, 30.9, 30.7, 29.4, 29.3, 24.27, 24.25, 24.09, 23.31, 23.26, 14.32, 14.29, 11.53, 11.52, 11.33, 0.21.

4-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-4'-ethynyl-1,1'-biphenyl (20)



1.74 (m, 1H), 1.68-1.28 (m, 24H), 1.02-0.91 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 159.7, 154.2, 153.9, 140.9, 139.9, 133.2, 132.9, 132.2, 127.1, 127.06, 123.3, 121.5, 116.8, 116.7, 115.6, 114.8, 114.77, 113.5, 95.4, 94.6, 87.5, 84.9, 83.7, 78.2, 72.3, 72.2, 70.8, 39.9, 39.6, 30.92, 30.9, 30.7, 29.4, 29.3, 24.27, 24.25, 24.1, 23.3, 23.26, 14.32, 14.29, 11.52, 11.33. HRMS calcd for C₅₄H₆₆O₃ (M+H)⁺, 763.5085, found, 763.5096.

12-((4'-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-12-hydroxytetracen-5(12*H*)-one (21)

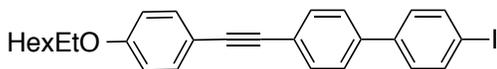


Compound **20**
(202 mg, 0.27 mmol, 1.0 eq) was

dissolved in 1.4 mL of dry THF, followed by dropwise addition of *n*-butyllithium (0.15 mL, 0.24 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred to the flask containing 5,12-naphthacenequinone (69 mg, 0.27 mmol, 1 eq), which was dissolved in 1.2 mL of dry THF and cooled to 0 °C, dropwisely via syringe. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction was quenched by addition of 5 mL of ice cold DI H₂O and then filtered via vacuum filtration by washing about 30 mL of THF:H₂O (1:1, v/v). Saturated NH₄Cl was added to filtrate and let it stir for 30 min. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated

using rotary evaporation. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **21**. Yield: 150 mg (%55). ¹H NMR (500 MHz, CDCl₃): δ 8.9 (s, 1H), 8.7 (s, 1H), 8.38-8.36 (m, 1H), 8.31-8.29 (m, 1H), 8.1-8.09 (m, 1H), 8.05-8.03 (m, 1H), 7.83-7.79 (m, 1H), 7.7-7.67 (m, 1H), 7.64-7.54 (m, 10H), 7.47 (d, J= 8.8 Hz, 2H), 7.03 (s, 1H), 7.02 (s, 1H), 6.9 (d, J=8.8 Hz, 2H), 3.98-3.91 (m, 4H), 3.89-3.86 (m, 2H), 3.18 (s, 1H), 1.85-1.80 (m, 2H), 1.78-1.73 (m, 1H), 1.66-1.35 (m, 24H), 1.01-0.89 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 183.5, 159.7, 154.1, 153.8, 144.1, 140.9, 139.8, 139.4, 136, 134.5, 133.1, 132.9, 132.4, 132.1, 130.3, 130, 129.7, 129.4, 129.1, 128.4, 128.1, 127.8, 127.7, 127.6, 127.4, 127, 126.9, 123.3, 121.3, 116.7, 116.6, 115.5, 114.8, 114.7, 113.3, 95.3, 94.5, 92.1, 87.5, 86.7, 84.8, 72.2, 72.1, 70.7, 67.4, 39.8, 39.5, 30.8, 30.7, 29.3, 29.2, 24.18, 24.16, 24, 23.23, 23.18, 14.3, 14.2, 11.4, 11.3.

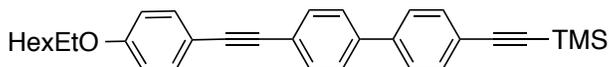
4-iodo-4'-((4-(ethylhexyloxy)phenyl)ethynyl)-1,1'-biphenyl (**22**)



A round bottom flask was charged with Pd(PPh₃)₄ (78 mg, 0.06 mmol, 0.03 eq) and CuI (26 mg, 0.12 mmol, 0.06 eq) and evacuated and refilled with argon three times. In another flask, **14** (500 mg, 2.18 mmol, 1.0 eq) and **4,4'-diiodophenyl** (2.64 g, 6.52 mmol, 3 eq) were dissolved in 80 mL of Et₃N:Toluene(1:5, v/v) and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. The reaction mixture was stirred for overnight at 40 °C. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (5:1) to

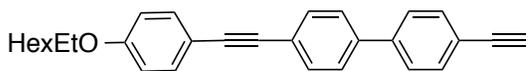
yield **22**. Yield: 506 mg (%46). ^1H NMR (500 MHz, CDCl_3): δ 7.8 (d, $J=8.3$ Hz, 2H), 7.59 (d, $J=8.5$ Hz, 2H), 7.55(d, $J=8$ Hz, 2H), 7.49 (d, $J=8.6$ Hz, 2 H), 7.37 (d, $J=8.3$ Hz, 2H), 6.91 (d, $J=8.6$ Hz, 2H), 3.91-3.86 (m, 2H), 1.79-1.74 (m, 1H), 1.55-1.33 (m, 8H), 0.98-0.92 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.6, 139.9, 139.3, 137.9, 133, 131.9, 128.8, 126.7, 123.2, 114.9, 114.6, 93.3, 90.6, 87.7, 70.7, 39.4, 30.5, 29.1, 23.9, 23, 14.1, 11.1.

Trimethyl((4'-((4-(ethylhexyloxy)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)silane (23a)



A round bottom flask was charged with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (5 mg, 0.006 mmol, 0.02 eq) and CuI (2.5 mg, 0.012 mmol, 0.04 eq) and evacuated and refilled with argon three times. In another flask, **22** (170 mg, 0.33 mmol, 1.0 eq) was dissolved in 12 mL of $\text{Et}_3\text{N}:\text{THF}$ (1:3, v/v) and this solution was added to flask containing catalysts via cannula transfer after deoxygenating for 1 hour with argon. While stirring, TMSA (57 μL , 0.4 mmol, 1.2 eq) were added dropwise to the flask. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (4:1) to yield **23a**. Yield: 160 mg (%80). ^1H NMR (300 MHz, CDCl_3): δ 7.56-7.45 (m, 8H), 7.47(d, $J=8.4$ Hz) 6.88 (d, $J=8.4$ Hz), 3.85 (d, 2H), 1.75-1.69 (m, 1H), 1.50-1.25 (m, 8H), 0.95-0.88 (m, 6H), 0.27 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ 159.7, 140.5, 139.7, 133.2, 132.6, 132.1, 126.9, 126.8, 123.2, 122.5, 115.1, 114.8, 105.1, 95.3, 90.7, 87.9, 70.8, 39.5, 30.7, 29.3, 24, 23.2, 14.2, 11.3, 0.14.

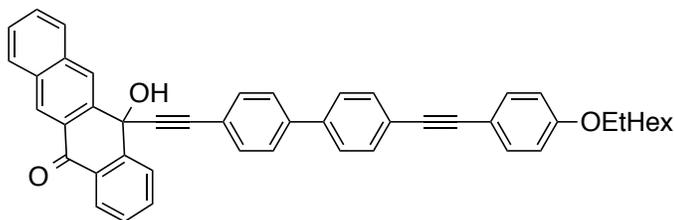
4-ethynyl-4'-((4-(ethylhexyloxy)phenyl)ethynyl)-1,1'-biphenyl (23)



Compound **23a** (129 mg, 0.26 mmol, 1.0 eq) and K_2CO_3 (106 mg, 0.77

mmol, 3 eq) were dissolved in mixture of THF (1 mL), and MeOH (2 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed *in vacuo*. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated using rotary evaporation. The crude product was used without further purification. Yield: 106 mg (%95). 1H NMR (500 MHz, $CDCl_3$): δ 7.62-7.58 (m, 8H), 7.5 (d, $J=8.6$ Hz, 2H), 6.91 (d, $J=8.6$ Hz, 2H), 3.89-3.88 (m, 2H), 3.17 (s, 1H), 1.79-1.74 (m, 1H), 1.56-1.34 (m, 8H), 0.98-0.93 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 140.8, 139.5, 133.1, 132.6, 131.9, 126.9, 126.8, 123.2, 121.3, 114.9, 114.6, 90.7, 87.8, 83.5, 77.9, 70.6, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1. HRMS calcd for $C_{30}H_{30}O$ ($M+H$) $^+$, 407.2369, found, 407.2367.

12-hydroxy-12-((4'-((4-(ethylhexyloxy)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)tetracen-5(12H)-one (24)

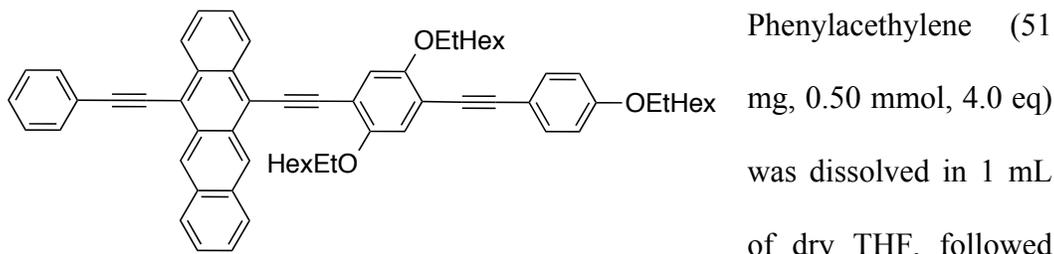


Compound **23** (135 mg, 0.33 mmol, 1.0 eq) was dissolved in 1 mL of dry THF, followed by

dropwise addition of *n*-butyllithium (0.18 mL, 0.29 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred

to the flask containing 5,12- naphthacenequinone (86 mg, 0.33 mmol, 1 eq), which was dissolved in 1.5 mL of dry THF and cooled to 0 °C, dropwisely via syringe. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction was quenched by addition of 5 mL of ice cold DI H₂O and then filtered via vacuum filtration by washing about 20 mL of THF:H₂O (1:1, v/v). Saturated NH₄Cl was added to filtrate and let it stir for 30 min. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **24**. Yield: 100 mg (%45). ¹H NMR (500 MHz, CDCl₃): δ 8.77 (s, 1H), 8.67 (s, 1H), 8.29-8.25 (m, 2H), 8.01-7.98 (m, 2H), 7.78-7.75 (m, 1H), 7.65-7.63 (m, 1H), 7.59-7.48 (m, 12H), 6.9 (d, J=8.8 Hz, 2H), 3.89-3.87 (m, 2H), 3.61 (s, 1H), 1.78-1.73 (m, 1H), 1.56-1.29 (m, 8H), 0.98-0.93 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 183.7, 159.8, 144.3, 140.9, 139.5, 136.1, 134.5, 133.2, 132.9, 132.5, 132.1, 130.2, 130, 129.7, 129.4, 129.1, 128.4, 128.3, 127.9, 127.7, 127.5, 127.4, 127, 126.9, 123.4, 121.3, 115.1, 114.8, 92.3, 90.9, 87.9, 86.6, 70.8, 67.4, 39.5, 30.7, 29.3, 24, 23.2, 14.3, 11.3.

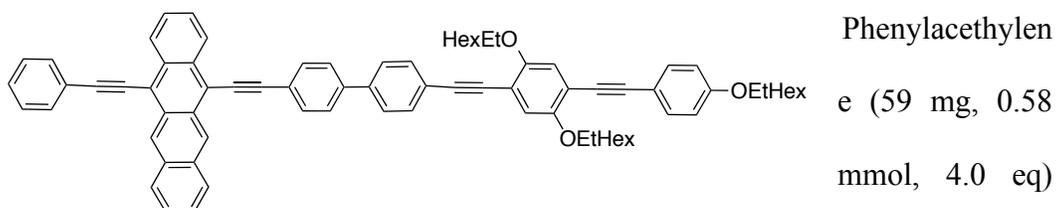
**5-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-12-(phenylethynyl)tetracene
(A1)**



by dropwise addition of *n*-butyllithium (0.3 mL, 0.48 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred to the flask containing **18** (105 mg, 0.12 mmol, 1.0 eq), which was dissolved in 0.6 mL of dry THF and cooled to -78 °C, dropwisely via cannula. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction mixture was then treated with 15 mL of 10% HCl aqueous solution saturated with SnCl₂ dihydrate and left overnight stirring. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3.5:1) to yield **A1**. Yield: 56 mg (%50). ¹H NMR (500 MHz, CDCl₃): δ 9.41 (s, 1H), 9.33 (s, 1H), 8.86-8.84 (m, 1H), 8.73-8.71 (m, 1H), 8.16-8.14 (m, 2H), 7.89-7.87 (m, 2H), 7.63-7.58 (m, 2H), 7.55-7.47 (m, 7H), 7.32 (s, 1H), 7.16 (s, 1H), 6.95-6.92 (m, 2H), 4.13-4.07 (m, 4H), 3.93-3.90 (m, 2H), 2.06-1.98 (m, 1H), 1.95-1.88 (m, 1H), 1.8-1.76 (m, 1H), 1.73-1.21 (m, 24H), 1.07 (t, 3H), 0.99-0.93 (m, 12H), 0.79

(t, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.6, 154.1, 153.8, 133, 132.4, 132.3, 132.2, 132.1, 131.8, 130.1, 129.9, 128.7, 128.6, 127.9, 127.3, 126.7, 126.5, 126.4, 126, 125.9, 125.8, 123.6, 118.9, 118.1, 116.9, 116.1, 115.3, 115.2, 114.6, 113.4, 103.3, 100.5, 95.6, 92.5, 87.3, 84.9, 72.3, 71.9, 70.6, 39.8, 39.5, 39.4, 30.8, 30.5, 30.4, 29.3, 29.1, 29, 24.1, 23.9, 23.8, 23.1, 23.06, 23, 14.2, 14.1, 13.9, 11.4, 11.1, 10.95. HRMS calcd for $\text{C}_{66}\text{H}_{72}\text{O}_3$ (M^+), 912.5476, found, 912.5493.

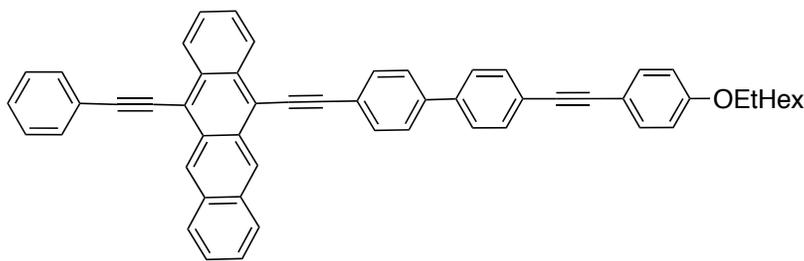
5-((4'-((2,5-bis(ethylhexyloxy)-4-((4-(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-12-(phenylethynyl)tetracene (A2)



was dissolved in 1.1 mL of dry THF, followed by dropwise addition of *n*-butyllithium (0.35 mL, 0.56 mmol, 1.6 M in hexanes) at $-78\text{ }^\circ\text{C}$. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 hour and then transferred to the flask containing **21** (148 mg, 0.15 mmol, 1.0 eq), which was dissolved in 0.5 mL of dry THF and cooled to $-78\text{ }^\circ\text{C}$, dropwisely via cannula. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction mixture was then treated with 15 mL of 10% HCl aqueous solution saturated with SnCl_2 dihydrate and left overnight stirring. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with H_2O and brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography

using hexanes and dichloromethane (2.75:1) to yield **A2**. Yield: 90 mg (%57). ^1H NMR (500 MHz, CDCl_3): δ 9.28 (s, 2H), 8.7-8.68 (m, 2H), 8.14-8.11 (m, 2H), 7.93 (d, $J=8.2$ Hz, 2H), 7.87 (d, $J=7$ Hz, 2H), 7.77 (d, $J=8.2$ Hz, 2H), 7.72-7.67 (m, 4H), 7.61-7.59 (m, 2H), 7.55-7.49 (m, 7H), 7.08 (s, 1H), 7.06 (s, 1H), 6.91 (d, $J=8.7$ Hz, 2H), 4.01-3.94 (m, 4H), 3.92-3.87 (m, 2H), 1.89-1.83 (m, 2H), 1.79-1.74 (m, 1H), 1.7-1.29 (m, 24H), 1.06-0.93 (m, 18H). HRMS calcd for $\text{C}_{80}\text{H}_{80}\text{O}_3$ ($\text{M}+\text{H}$) $^+$, 1089.6180, found, 1089.6184.

5-((4'-((4-(ethylhexyloxy)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-12-(phenylethynyl)tetracene (A3)



Phenylacetylene

(48 mg, 0.47 mmol, 4.0 eq)

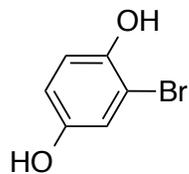
was dissolved in

1 mL of dry THF, followed by dropwise addition of *n*-butyllithium (0.29 mL, 0.45 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred to the flask containing **24** (78 mg, 0.12 mmol, 1.0 eq), which was dissolved in 0.5 mL of dry THF and cooled to -78 °C, dropwisely via cannula. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction mixture was then treated with 15 mL of 10% HCl aqueous solution saturated with SnCl_2 dihydrate and left overnight stirring. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with H_2O and brine, dried over MgSO_4 , filtered and concentrated using rotary evaporation. The

crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1) to yield **A3**. Yield: 45 mg (%53). ¹H NMR (500 MHz, CDCl₃): δ 9.35 (s, 1H), 9.34 (s, 1H), 8.75-8.72 (m, 2H), 8.18-8.15 (m, 2H), 7.95 (d, J=8.5 Hz, 2H), 7.89-7.88 (m, 2H), 7.78 (d, J=8.5 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H), 7.66 (d, J=8.4 Hz, 2H), 7.64-7.61 (m, 2H), 7.55-7.48 (m, 7H), 6.93 (d, J=8.7 Hz, 2H), 3.91-3.89 (m, 2H), 1.79-1.75 (m, 1H), 1.56-1.28 (m, 8H), 0.98-0.93 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 159.6, 140.6, 139.6, 133.1, 132.35, 132.34, 132.25, 132.2, 132, 131.8, 129.98, 129.97, 128.8, 128.7, 128.6, 127.5, 127.4, 127.1, 126.9, 126.7, 126.6, 126.1, 126.08, 123.5, 123.2, 122.7, 118.4, 118.3, 114.9, 114.6, 103.4, 103.3, 90.7, 88.2, 87.8, 87.1, 70.6, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1. HRMS calcd for C₅₆H₄₄O (M)⁺, 732.3387, found, 732.3377.

Synthesis of Compound 25

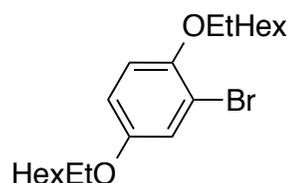
2-bromobenzene-1,4-diol (S3)



Compound **1-bromo-2,5-dimethoxybenzene** (800 mg, 3.7 mmol, 1.0 eq) was suspended in 4 mL of dry CH₂Cl₂, followed by the addition of BBr₃ (11 mL, 1.0 M in CH₂Cl₂, 11 mmol, 3.0 eq) at -78 °C under argon and stirred overnight at room temperature. The reaction was stopped by pouring the reaction mixture onto ice. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with brine, dried over MgSO₄, and filtered. Removal of solvent *in vacuo* yielded 650 mg of **S3** (94%) that was taken to the next step immediately without further purification. ¹H

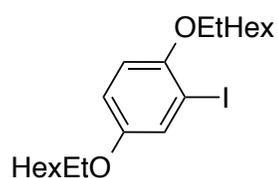
NMR (500 MHz, D-THF): δ 7.86 (s, 2H), 6.85-6.84 (m, 1H), 6.67-6.66 (m, 1H), 6.56-6.54 (m, 1H).

2-bromo-1,4-bis(ethylhexyloxy)benzene (S4)



Compound **S3** (639 mg, 3.4 mmol, 1.0 eq) and K_2CO_3 (1.9 g, 13.5 mmol, 4.0 eq) were dissolved in 22.5 mL of dry DMF at room temperature under argon. 2-ethylhexylbromide (1.3 mL, 7.4 mmol, 2.2 eq) was then added to this solution under an argon atmosphere. The mixture was heated to 70 °C and stirred for overnight. The mixture was then cooled to room temperature. The reaction was stopped by quenching with 10% aq NaOH. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (9:1) to yield **S4**. Yield: 812 mg (%58). 1H NMR (500 MHz, $CDCl_3$): δ 7.14 (m, 1H), 6.85-6.8 (m, 2H), 3.87-3.85 (m, 2H), 3.81-3.79 (m, 2H), 1.78-1.69 (m, 1H), 1.61-1.58 (m, 1H), 1.56-1.33 (m, 16H), 0.98-0.92 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8, 149.9, 119.5, 114.34, 114.29, 112.7, 72.5, 71.3, 39.5, 39.4, 30.5, 29.09, 29.08, 23.89, 23.83, 23.1, 14.1, 11.2, 11.1.

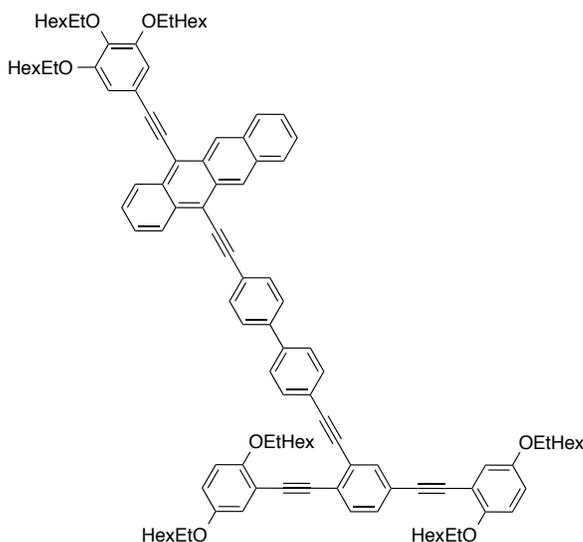
2-iodo-1,4-bis(ethylhexyloxy)benzene (S5)



Compound **S4** (658.8 mg, 1.66 mmol, 1.0 eq) was dissolved in 12 mL of dry THF, followed by dropwise

addition of *n*-butyllithium (2.6 mL, 4.2 mmol, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then I₂ (969 mg, 3.8 mmol, 2.3 eq) which was dissolved in 7 mL of dry THF was added to the solution containing **S5** via syringe. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction was quenched by addition of aqueous Na₂S₂O₃. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with H₂O and brine, dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (9:1) to yield **S5**. Yield: 714 mg (%93). ¹H NMR (500 MHz, CDCl₃): δ 7.36-7.35 (m, 1H), 6.88-6.85 (m, 1H), 6.75-6.73 (m, 1H), 3.86-3.85 (m, 2H), 3.79-3.78 (m, 2H), 1.78-1.75 (m, 1H), 1.72-1.68 (m, 1H), 1.61-1.34 (m, 16H), 0.98-0.97 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 153.9, 152.2, 125.4, 115.3, 112.6, 86.8, 72.2, 71.3, 39.5, 39.4, 30.6, 30.5, 29.11, 29.08, 23.9, 23.8, 23.1, 14.14, 14.11, 11.2, 11.1.

5-((4'-((2,5-bis((2,5-bis(ethylhexyloxy)phenyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)-12-((3,4,5-tris(ethylhexyloxy)phenyl)ethynyl)tetracene (25)



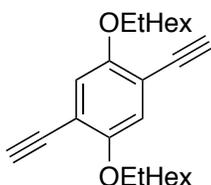
A round bottom flask was charged with Pd(PPh₃)₂Cl₂ (0.5 mg, 0.67 umol, 0.02 eq), CuI (0.3 mg, 1.4 umol, 0.04 eq) and **9** (35 mg, 33.7 umol, 1.0 eq) was placed in a 25 mL two necks flask and evacuated and refilled with argon three times. In another flask, **S5** (60 mg,

0.1 mmol, 3.9 eq) was dissolved in 1.2 mL of Et₃N:THF (1:3) mixture and this solution was added to flask containing catalysts and **6** via cannula transfer after deoxygenating for 1 hour with argon. The reaction mixture was stirred for overnight at room temperature. The solvent was removed *in vacuo*. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2.5:1) to yield **25**. Yield: 20 mg (%35). ¹H NMR (500 MHz, CDCl₃): δ 9.36 (s, 1H), 9.34 (s, 1H), 8.76-8.72 (m, 2H), 8.19-8.15 (m, 2H), 7.95 (d, J=8.3 Hz, 2H), 7.78-7.76 (m, 3H), 7.75-7.68 (m, 4H), 7.64-7.63 (m, 2H), 7.56-7.52 (m, 3H), 7.48-7.46 (m, 1H), 7.14-7.13 (m, 1H), 7.07-7.06 (m, 3H), 6.93-6.87 (m, 4H), 4.05-3.90 (m, 10H), 3.86-3.84 (m, 2H), 3.79-3.77 (m, 2H), 1.88-1.73 (m, 7H), 1.70-1.28 (m, 56 H), 1.04-0.89 (m, 42 H). ¹³C NMR (125 MHz, CDCl₃): δ 154.7, 153.7, 153.3, 153.2, 140.7, 140.3, 139.8, 134.7, 132.59, 132.56, 132.5,

132.4, 132.3, 131.8, 130.9, 130.2, 128.8, 128.7, 127.7, 127.6, 127.3, 127.1, 126.9, 126.7, 126.4, 126.23, 126.19, 125.95, 125.93, 123.6, 123, 118.9, 118.59, 118.58, 118.2, 117.9, 117.3, 117.1, 114.3, 113.9, 113.7, 113.4, 109.9, 104.2, 103.3, 93.8, 92.41, 92.38, 92.1, 89.2, 88.6, 88.4, 85.9, 76.4, 72.7, 72.4, 71.7, 71.5, 71.3, 40.9, 39.9, 39.86, 39.8, 39.7, 39.6, 30.9, 30.85, 30.75, 30.70, 29.9, 29.5, 29.39, 29.36, 29.33, 29.3, 24.2, 24.14, 24.06, 24, 23.9, 23.33, 23.28, 23.22, 23.2, 14.32, 14.27, 14.26, 14.25, 14.23, 11.5, 11.4, 11.33, 11.29, 11.28. HRMS calcd for C₁₂₀H₁₄₈O₇ (M⁺), 1702.1298, found, 1702.1223.

Synthesis of P2-25

1,4-diethynyl-2,5-bis(ethylhexyloxy)benzene (S8)



Prepared following the established literature procedure.⁵¹

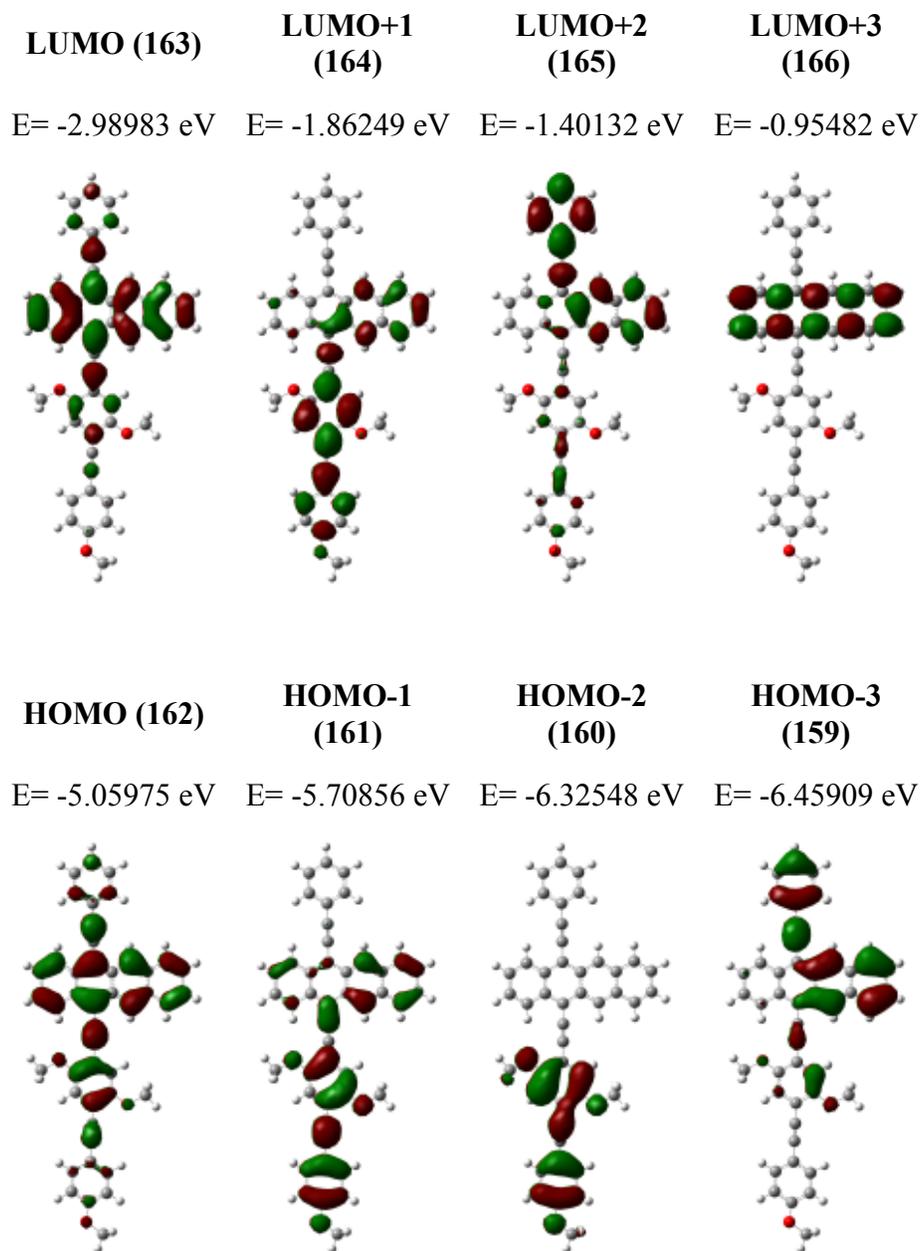
P2-25. A Schlenk tube was charged with <1 mg Pd(PPh₃)₄, and <1 mg CuI, and evacuated and refilled with argon three times. **9** (15 mg, 0.014 mmol, 1.0 eq), **10** (34 mg, 0.058 mmol, 4.0 eq), and **S8** (16.5 mg, 0.043 mmol, 3.0 eq) was dissolved in 3 mL 4:1 (v:v) toluene:diisopropylamine and sparged with argon for 30 minutes. The solution was added to the reaction vessel and the mixture stirred for 72 hours at room temperature. The reaction mixture was precipitated into 200 mL methanol and collected by centrifugation and decanting. The polymer was then dissolved in 2 mL of toluene and passed through a syringe filter to remove

insoluble catalyst residues, reprecipitated into 100 mL of methanol and isolated by centrifugation and decanting. M_n [g/mol]: 68k, M_w [g/mol]: 176k. ^1H NMR (500 MHz, CDCl_3): δ 9.37-9.35 (m, 0.5H), 8.75 (m, 0.5H), 8.17 (m, 0.5), 7.98-7.96 (m, 0.5H), 7.80-7.70 (m, 4H), 7.63 (m, 1H), 7.11-7.02 (m, 8H), 4.02-3.91 (m, 18H), 1.8 (m, 9H), 1.65-1.28 (m, 72H), 1.00-0.91 (m, 54H).

3.5 DFT Calculations

Dr. Zachary C. Smith from our laboratory carried out DFT calculations for the small molecules **A1**, **A2**, **A3**, and **25** by using theoretical methods to better understand their photophysical properties. Molecular geometries of each molecule studied were determined using sequential geometry optimizations. Within the B3LYP function, the three levels of theory used were 6-31G(d,p), 6-311G(d,p), and 6-311+G(d,p). All geometry optimizations were run in the chloroform PCM with the SCRF method. All molecular orbital and energy calculations were also carried out at the same three levels of theory. All time dependent calculations were carried out with the Tamm-Dancoff approximation, B3LYP functional and 6-31G(d,p) basis set. The calculations resulted in the first 40 electronic transitions of each molecule, starting at long wavelengths. The tables includes only transitions with an oscillator strength (f) greater than 0.2. Also, the orbital transitions were only included if they contributed to at least 20 % of the electronic transition. All DFT calculations were carried out in Gaussian 09.⁵⁴ The HOMO-3 to LUMO+3 molecular orbitals and tables containing all relevant time-dependent results can be seen in below.

A1

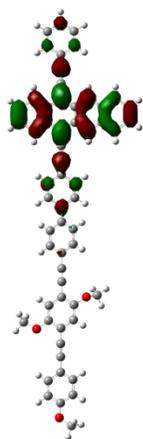


Excited State	Transition	<i>f</i>	λ (nm)	E (eV)
1	162→163 (94 %)	1.5942	624.53	1.9852
3	162→164 (79 %)	0.4557	423.61	2.9269
4	159→163 (54 %), 160→163 (25 %)	0.271	409.33	3.0289
5	160→163 (72 %), 159→163 (23 %)	0.2062	407.37	3.0435
7	162→165 (66 %)	0.3056	365.13	3.3956
9	161→164 (58 %), 156→163 (20 %)	0.3148	342.94	3.6153
19	162→166 (35 %), 157→163 (20 %)	0.8129	295.94	4.1895
25	161→166 (59 %)	0.4014	276.14	4.4899
34	157→164 (31 %)	0.848	255.57	4.8512

A2

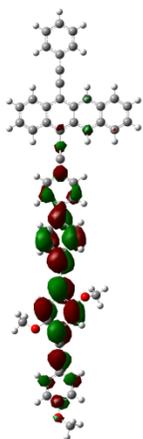
LUMO (209)

E= -3.02202
eV



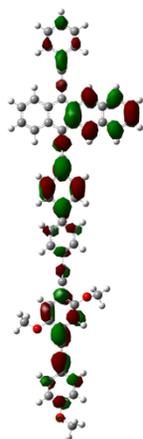
LUMO+1 (210)

E= -2.23998 eV



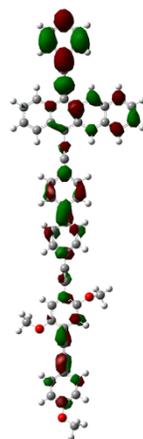
LUMO+2 (211)

E= -1.6287 eV



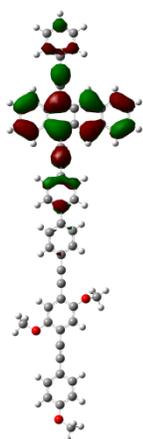
LUMO+3 (212)

E= -1.37803 eV



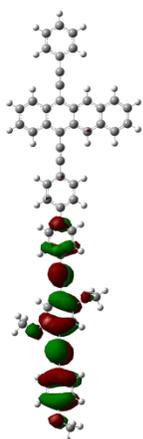
HOMO (208)

E= -5.16429
eV



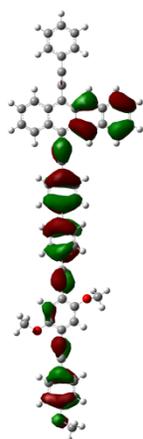
HOMO-1 (207)

E= -5.58023 eV



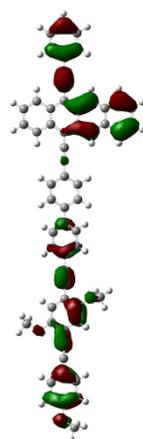
HOMO-2 (206)

E= -6.26396 eV



HOMO-3 (205)

E= -6.49949 eV

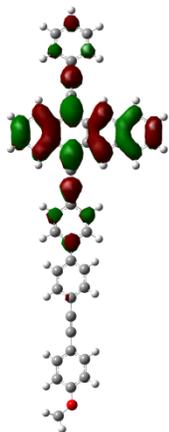


Excited State	Transition	<i>f</i>	λ (nm)	E (eV)
1	208→209 (94 %)	1.602	597.68	2.0744
3	208→210 (91 %)	0.2803	454.81	2.7261
4	206→209 (68 %)	0.7195	431.53	2.8731
5	207→210 (62 %)	1.3442	401.64	3.087
6	205→209 (34 %), 207→210 (27 %)	0.3251	392.68	3.1574
13	207→211 (48 %), 206→210 (42 %)	0.3195	331.95	3.735
26	208→217 (33 %), 200→209 (26 %)	0.2772	292.24	4.2426
28	200→209 (30 %), 196→209 (21 %)	0.5375	289.67	4.2802
30	196→209 (43 %)	0.3499	286.38	4.3293
32	203→210 (44 %), 206→211 (30 %)	0.2118	281.13	4.4102

A3

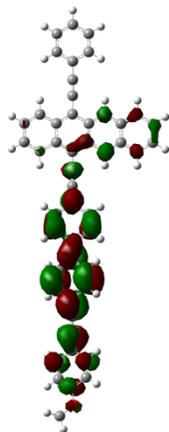
LUMO (167)

E= -3.00934
eV



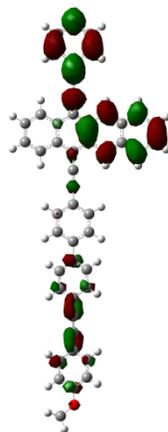
LUMO+1 (168)

E= -1.95686 eV



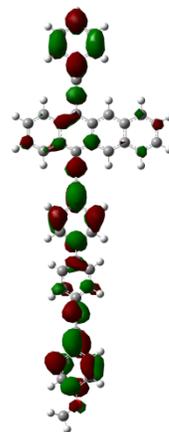
LUMO+2 (169)

E= -1.47637 eV



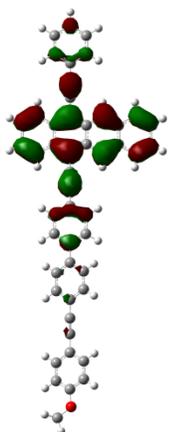
LUMO+3 (170)

E= -1.08301 eV



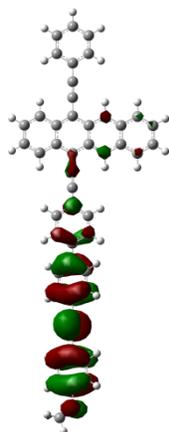
HOMO (166)

E= -5.15403
eV



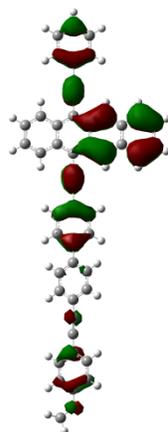
HOMO-1 (165)

E= -5.79109 eV



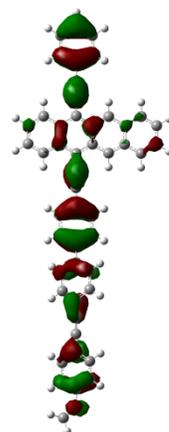
HOMO-2 (164)

E= -6.39411 eV



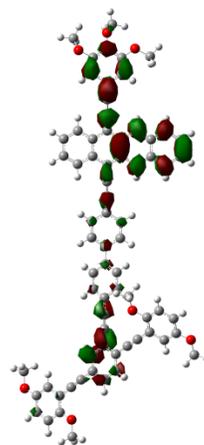
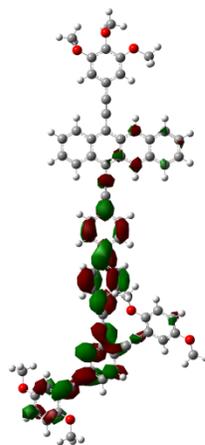
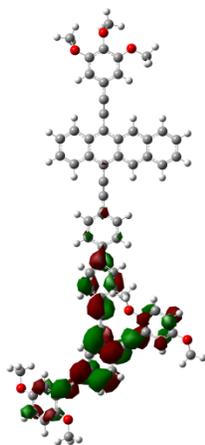
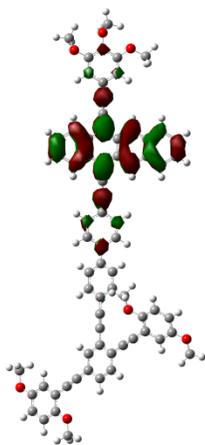
HOMO-3 (163)

E= -6.71247 eV

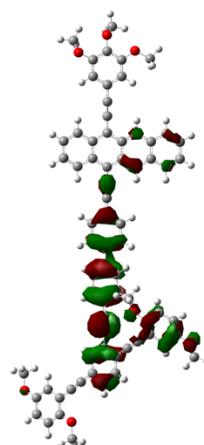
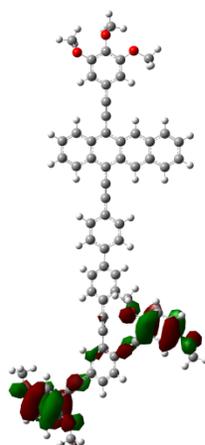
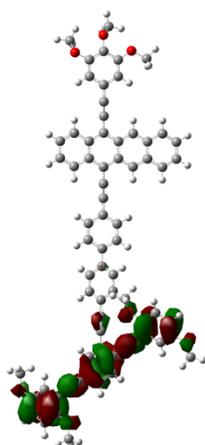
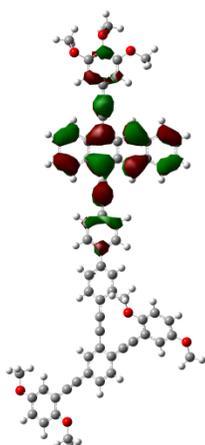


Excited State	Transition	<i>f</i>	λ (nm)	E (eV)
1	166→167 (95 %)	1.4116	594.73	2.0847
4	164→167 (50 %), 166→168 (41 %)	0.7166	413.59	2.9978
5	163→167 (58 %), 166→169 (21 %)	0.2786	374.78	3.3082
7	166→169 (58 %), 163→167 (30 %)	0.2782	358.56	3.4579
9	165→168 (86 %)	0.7378	342.65	3.6184
20	164→168 (47 %), 165→169 (21 %)	0.2141	293.23	4.2282
23	166→171 (40 %), 162→167 (27 %)	1.3052	287.33	4.3151
33	164→169 (72 %)	0.3093	265.91	4.6627
38	162→168 (42 %)	0.4421	257.38	4.8171

LUMO (267)	LUMO+1 (268)	LUMO+2 (269)	LUMO+3 (270)
E= -3.00398 eV	E= -2.31827 eV	E= -1.90336 eV	E= -1.46339 eV



HOMO (266)	HOMO-1 (265)	HOMO-2 (264)	HOMO-3 (263)
E= -5.13444 eV	E= -5.56864 eV	E= -5.88633 eV	E= -6.07917 eV



Excited State	Transition	<i>f</i>	λ (nm)	E (eV)
1	266→267 (95 %)	1.5128	600.53	2.0646
5	263→267 (51 %), 262→267 (27 %)	0.2657	445.55	2.7827
7	265→268 (91 %)	0.7244	419.04	2.9588
8	266→269 (80 %)	0.6743	409.29	3.0292
13	265→269 (50 %)	0.3836	370.23	3.3488
15	266→270 (47 %), 259→267 (22 %)	0.6439	362.48	3.4204
16	263→268 (61 %)	0.2381	355.22	3.4904
20	261→268 (60 %)	0.3415	328.27	3.7769
23	266→272 (24 %), 263→269 (21 %)	0.2414	318.73	3.8899
24	266→272 (28 %), 265→270 (21 %)	0.3424	317.17	3.909
38	261→269 (30 %), 264→270 (20 %)	0.3382	291.61	4.2518
39	264→270 (64 %)	0.2248	290.1	4.2738

3.6 References:

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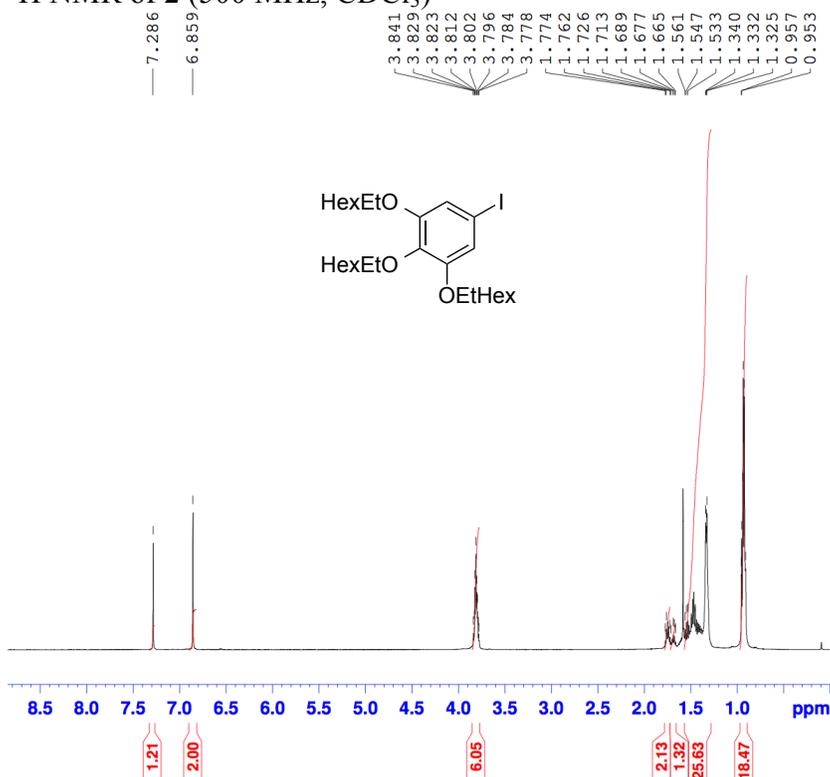
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Chapter 3 Appendix

^1H and ^{13}C NMR

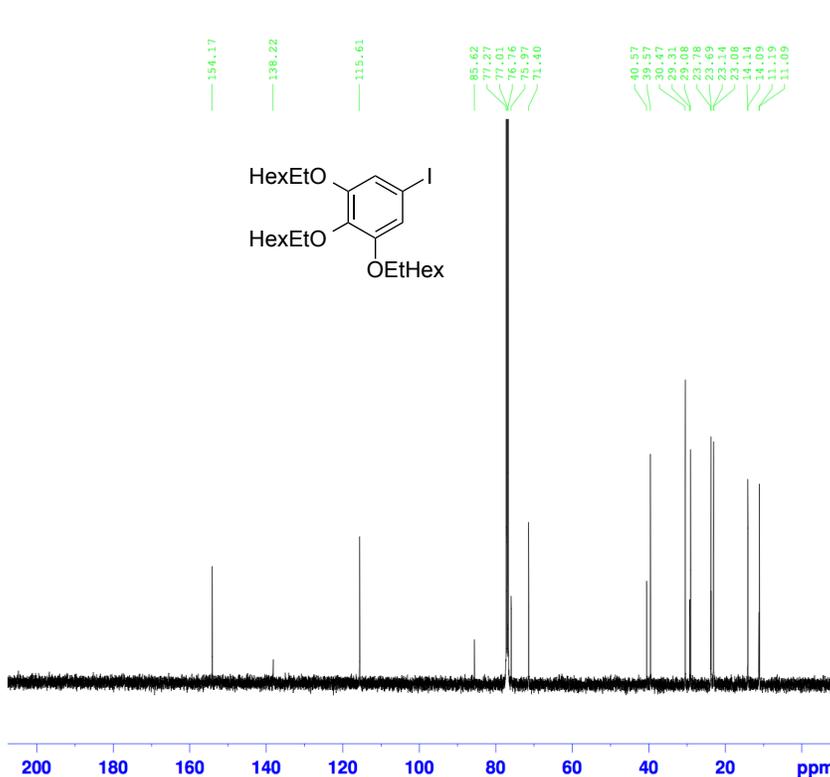
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SOLVENT   CDCl3
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DS         2
SWH        10000.000 Hz
FIDRES    0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         290.6 K
D1         0.50000000 sec
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D12        1
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D16        1
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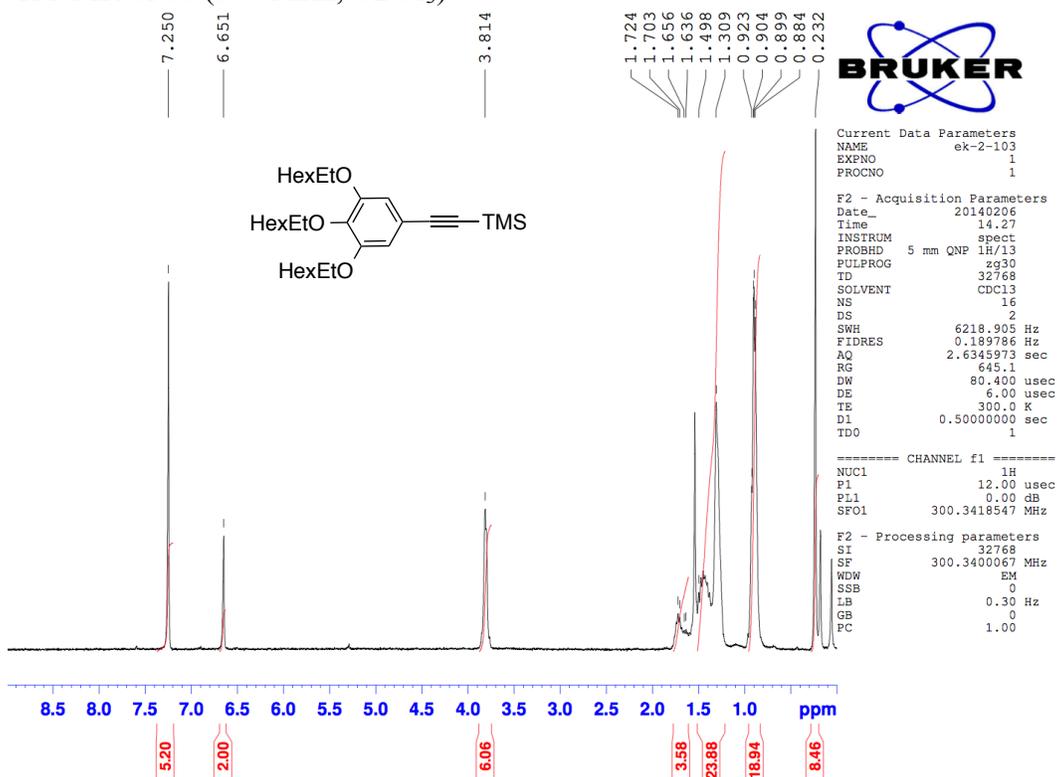
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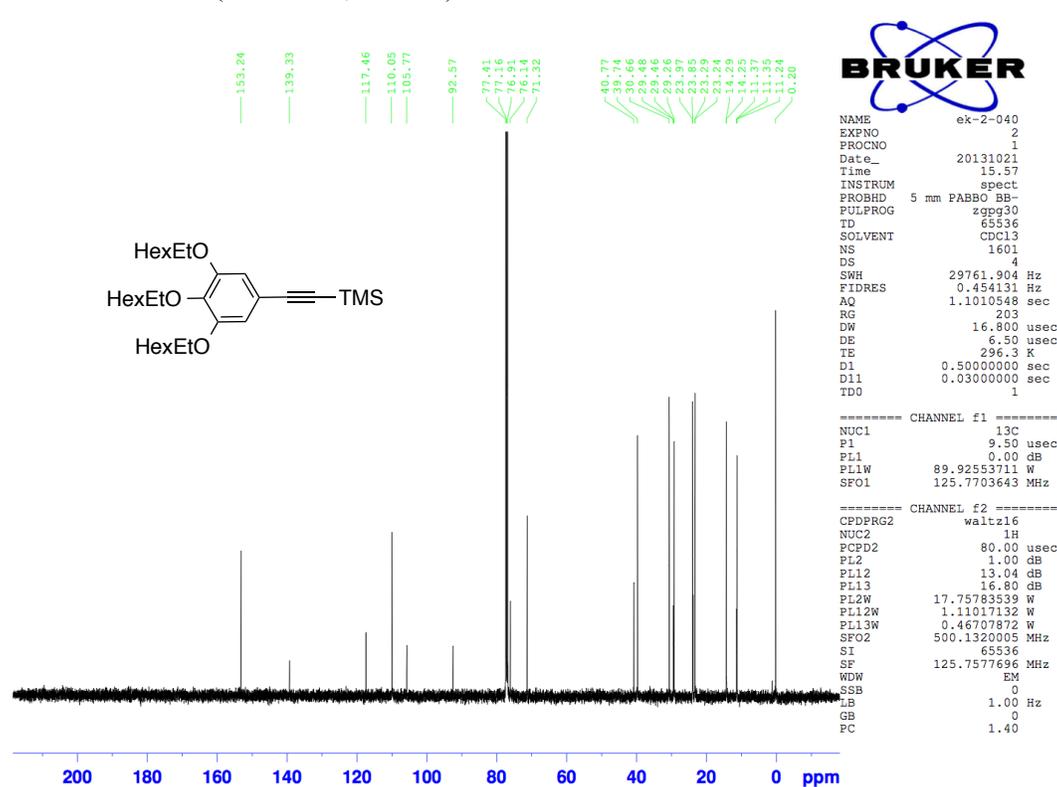
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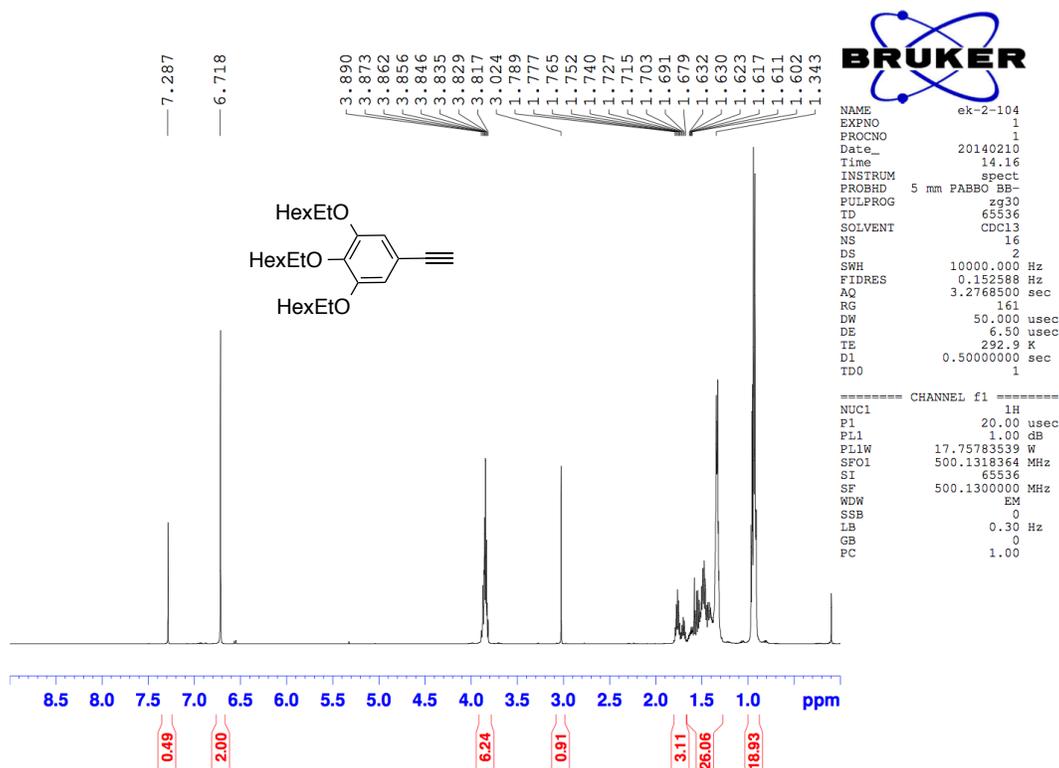
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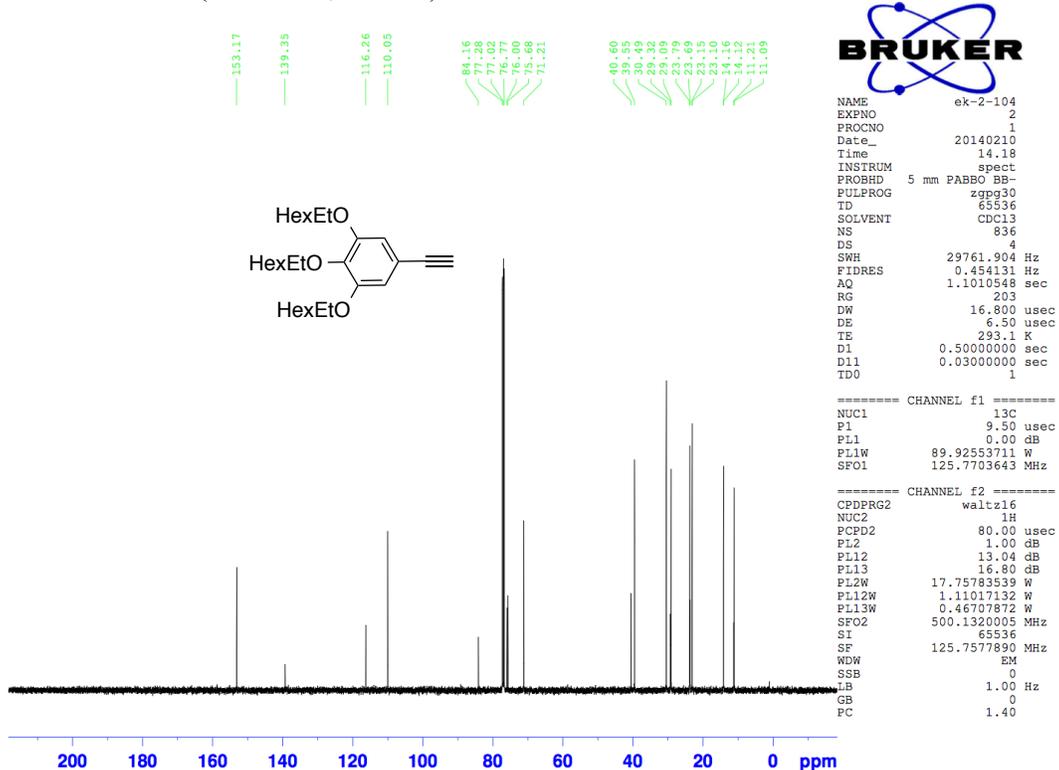
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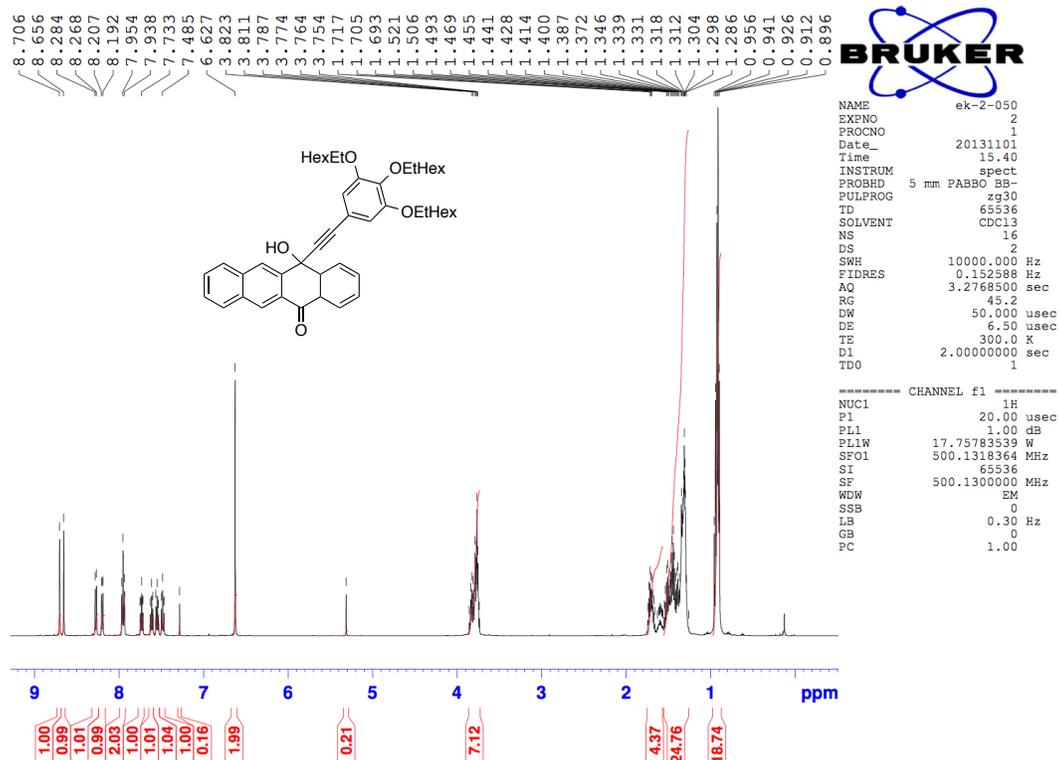
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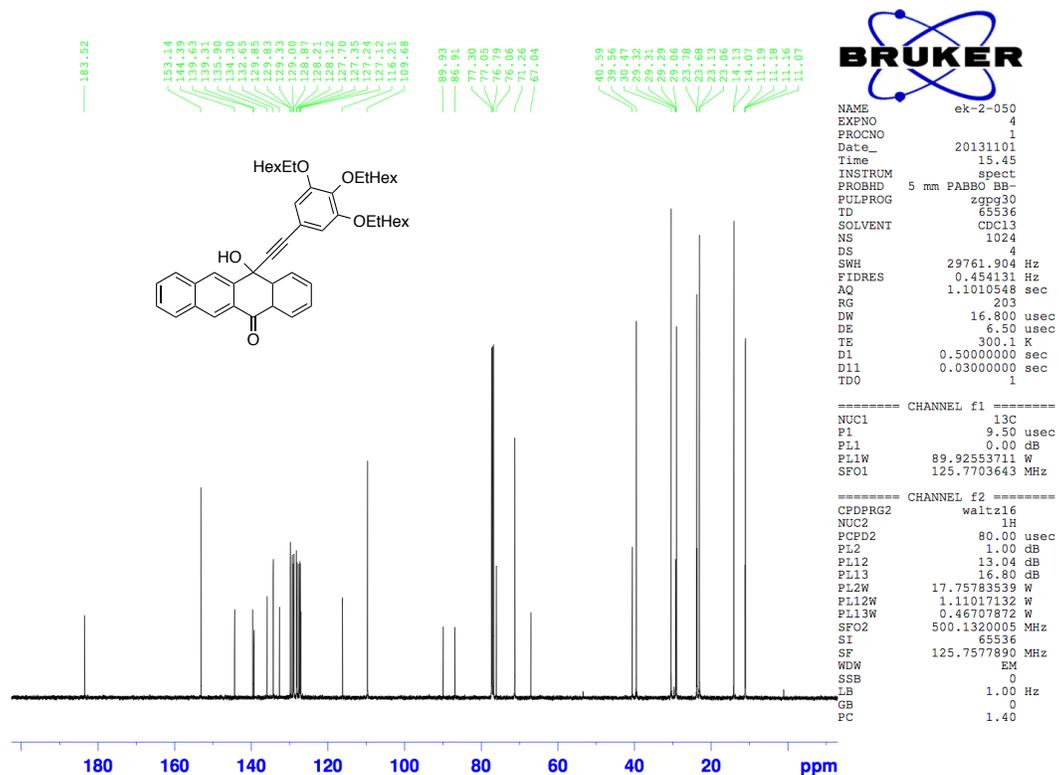
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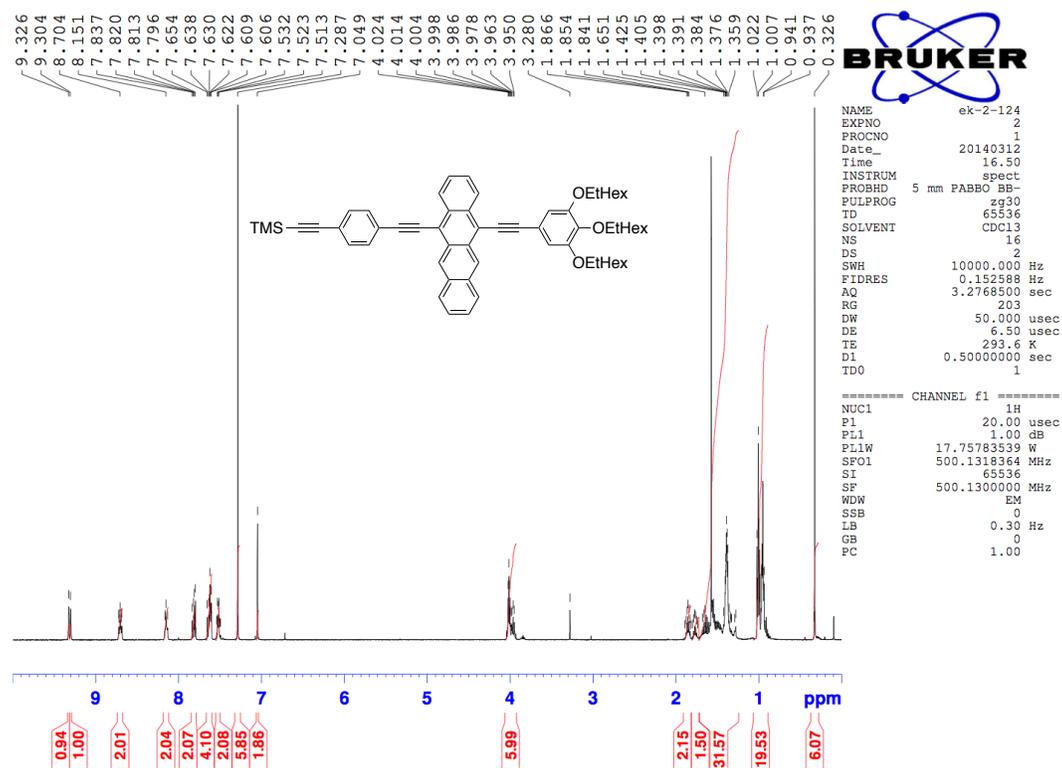
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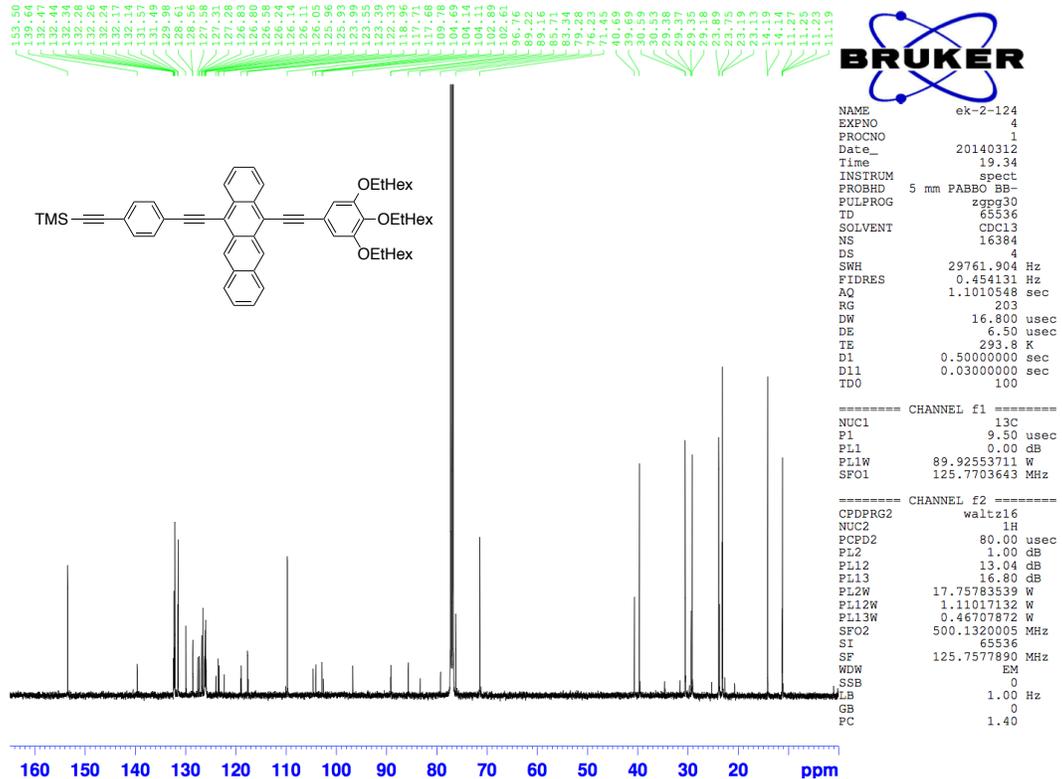
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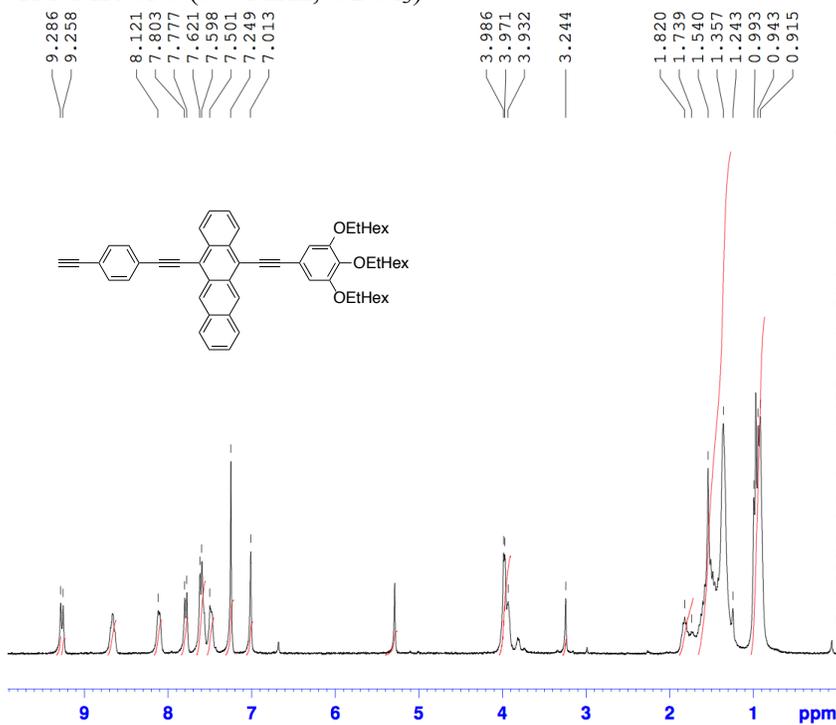
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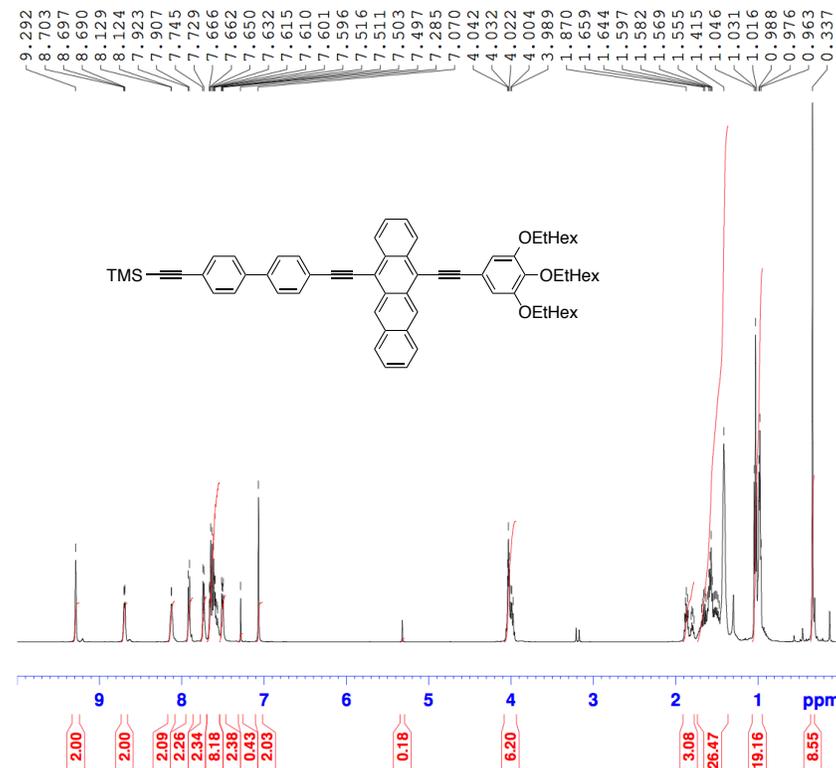


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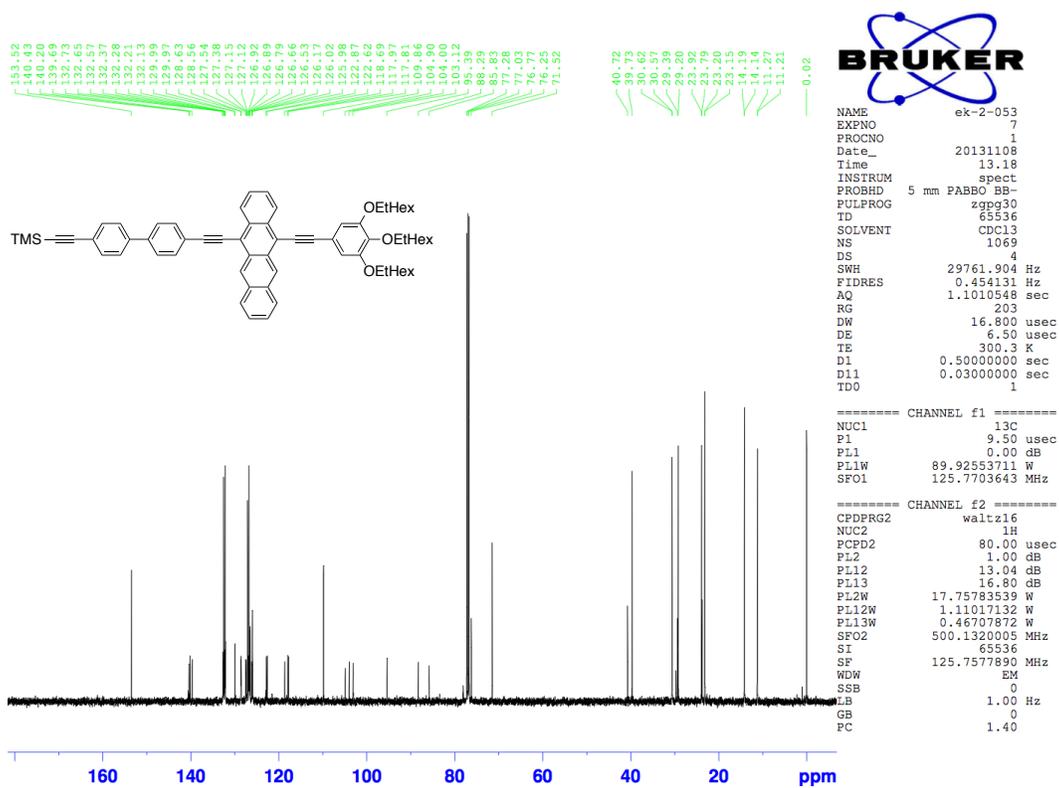
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¹H NMR of **6a** (500MHz, CDCl₃)

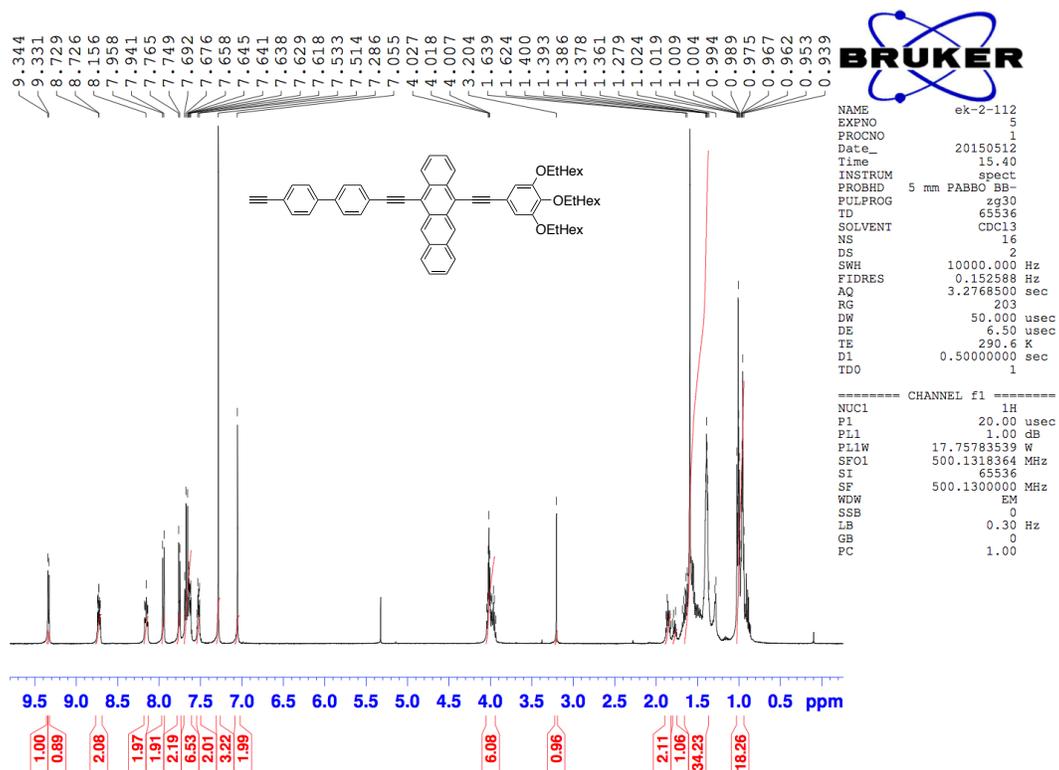


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 D1 5.00000000 sec
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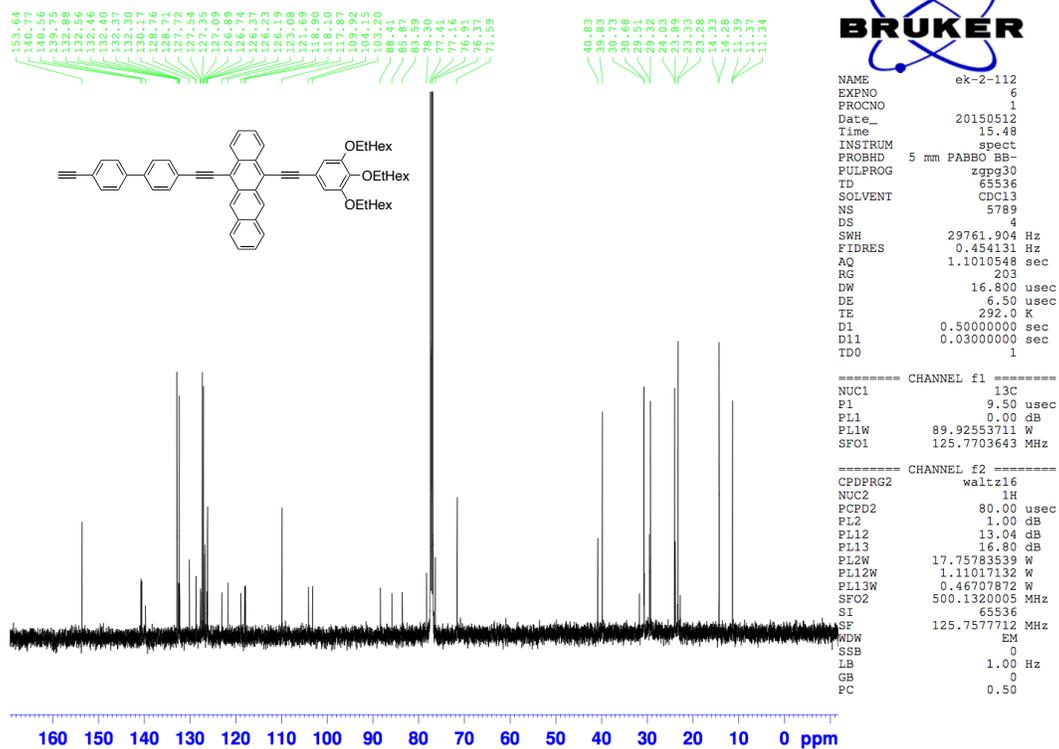
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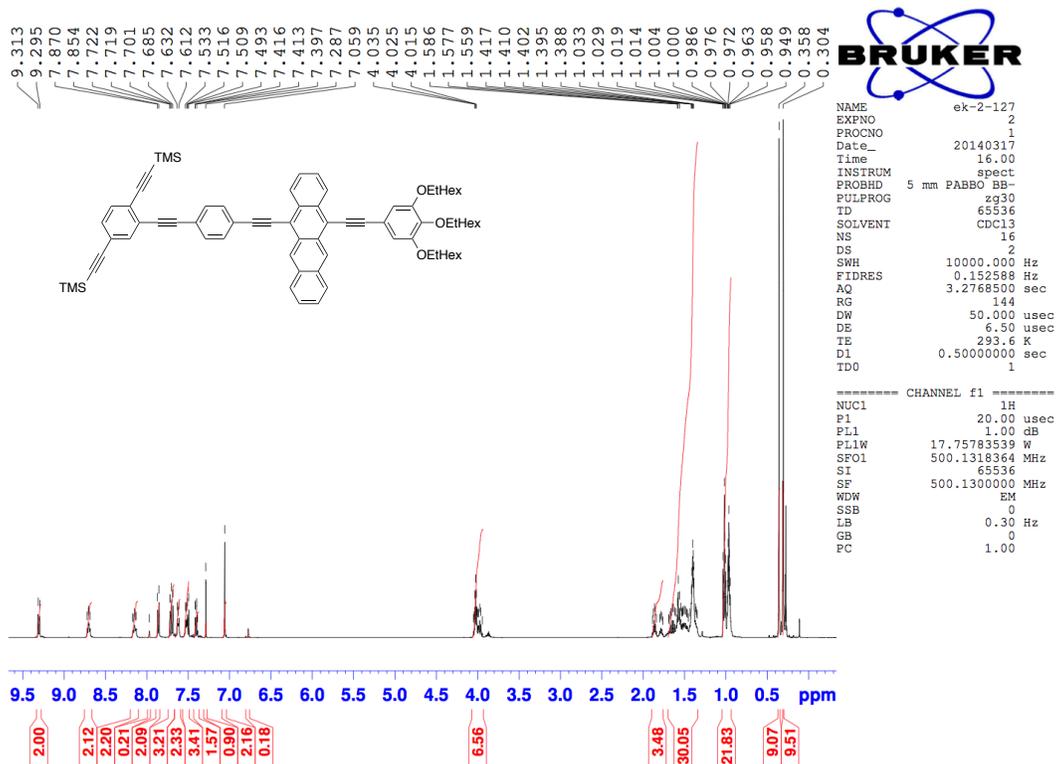
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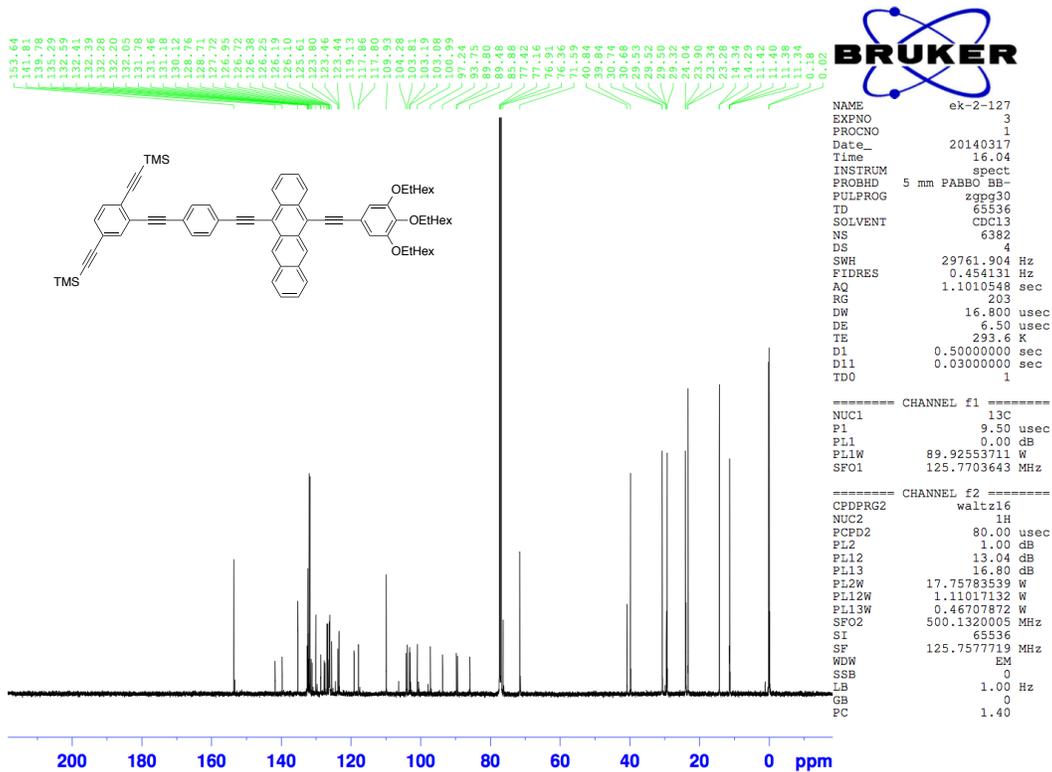
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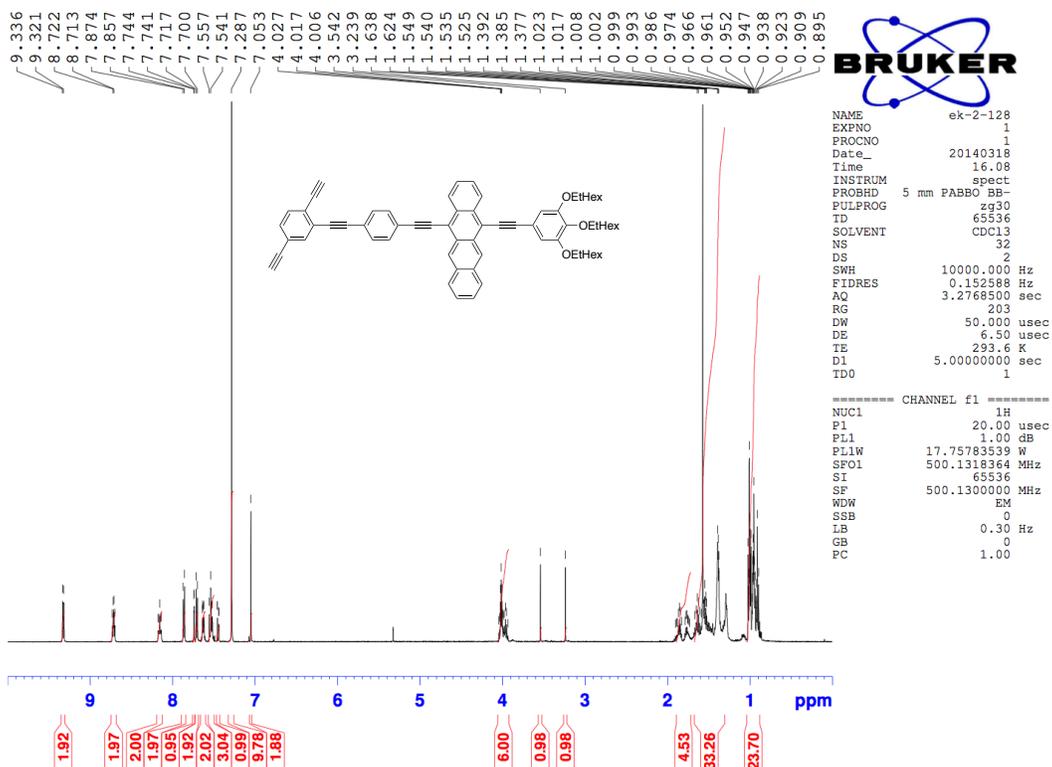
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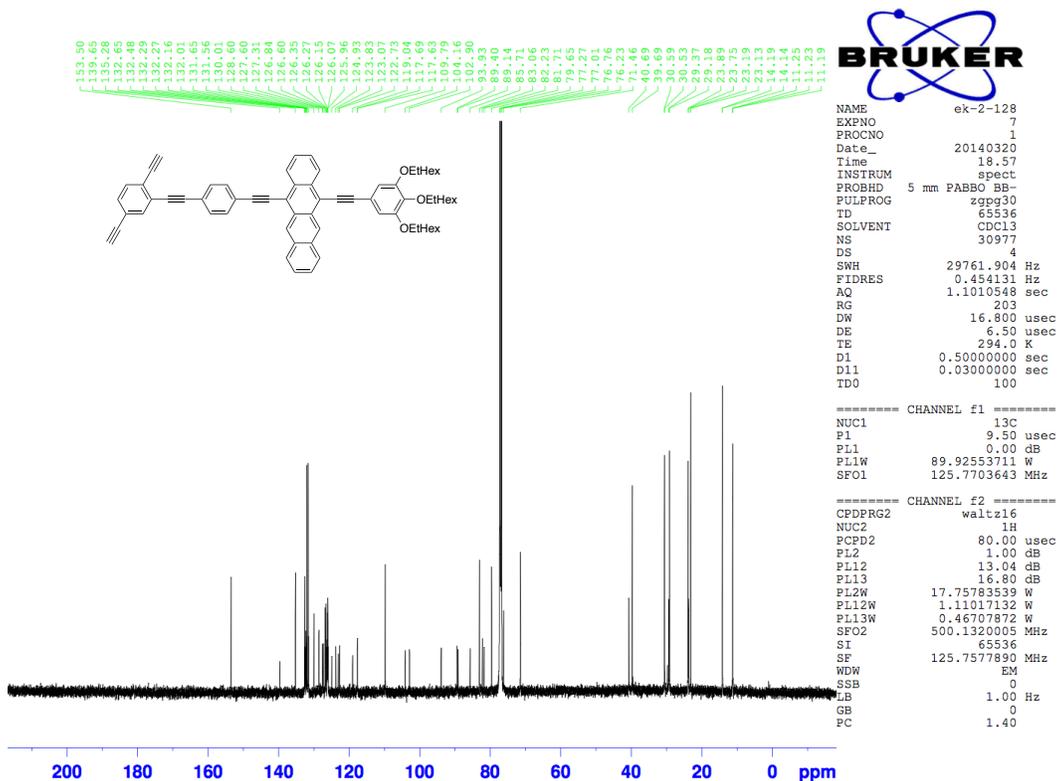
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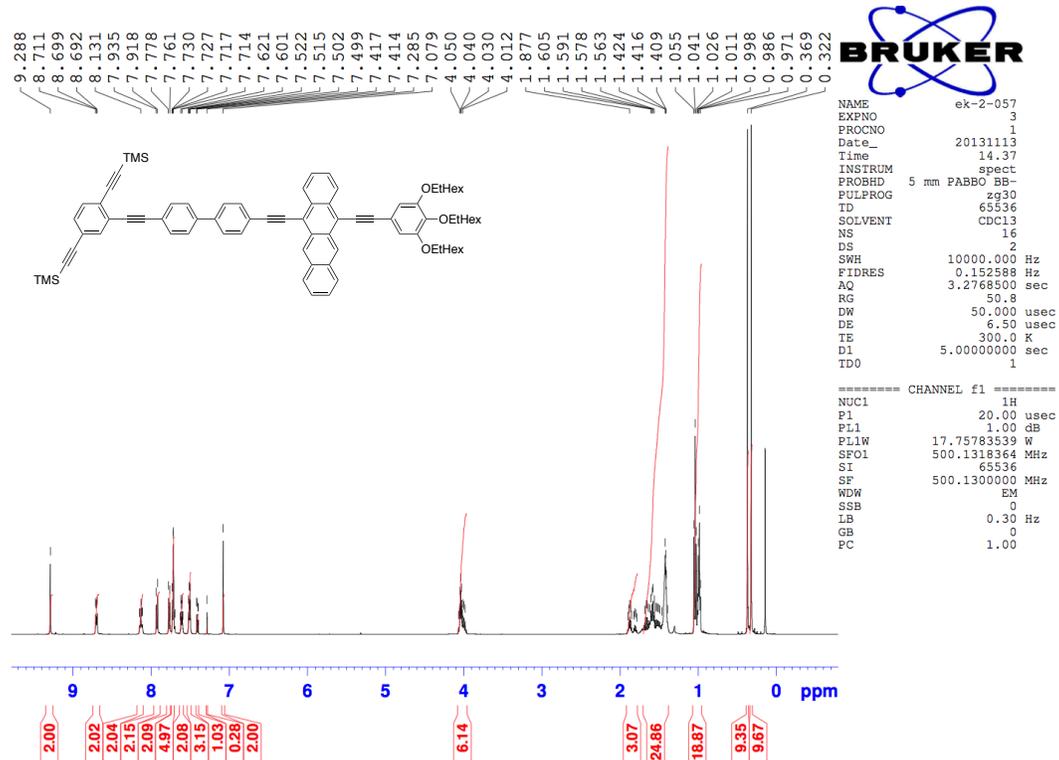
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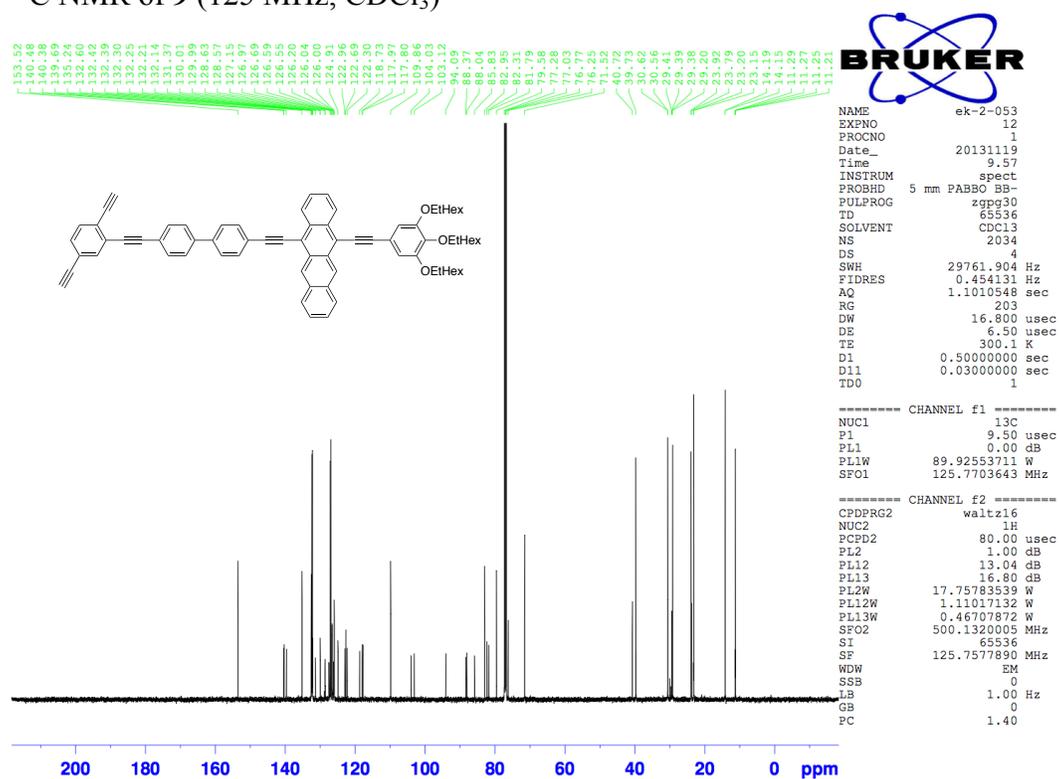
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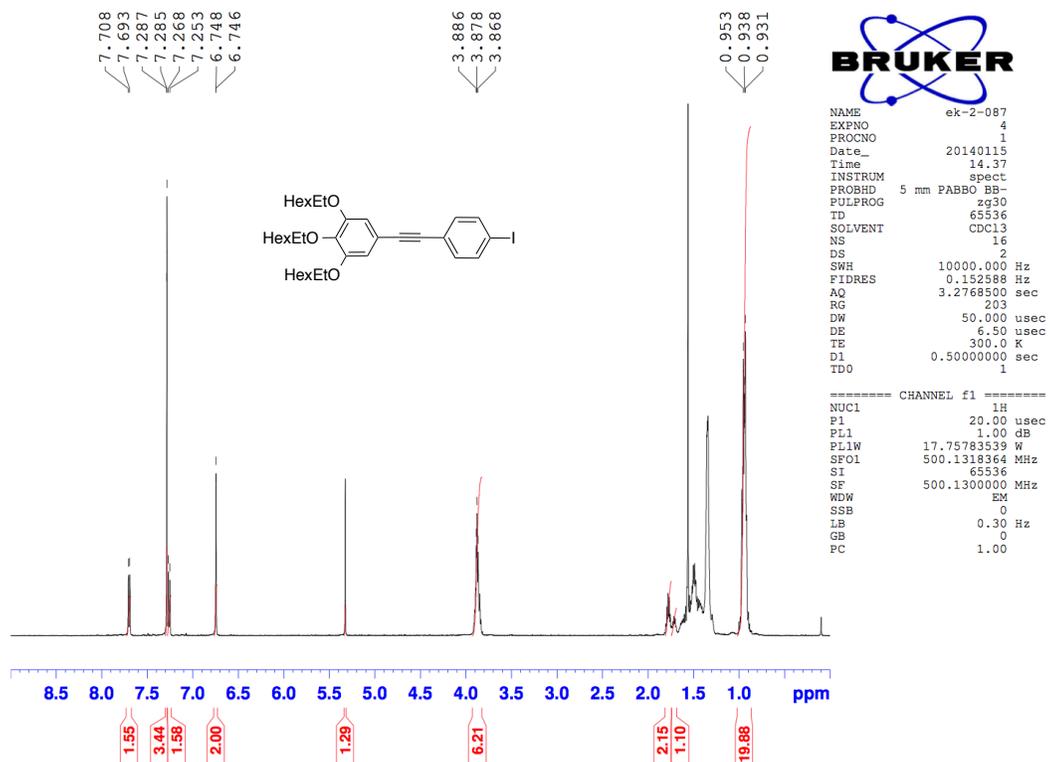
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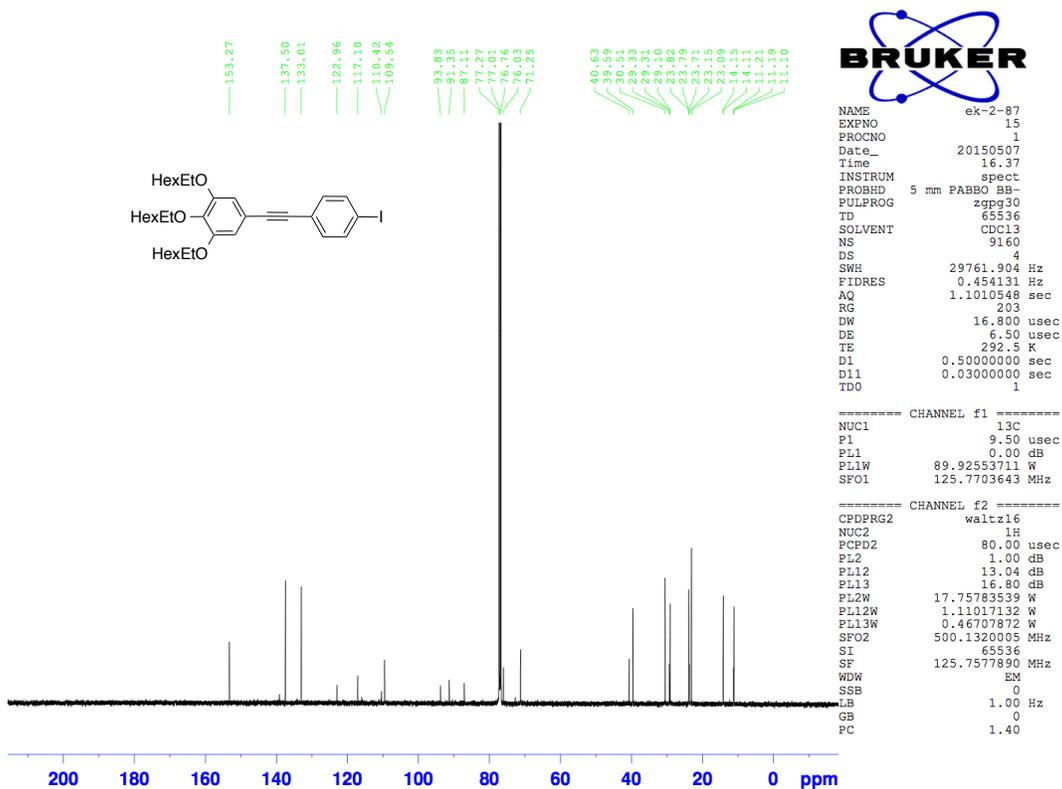
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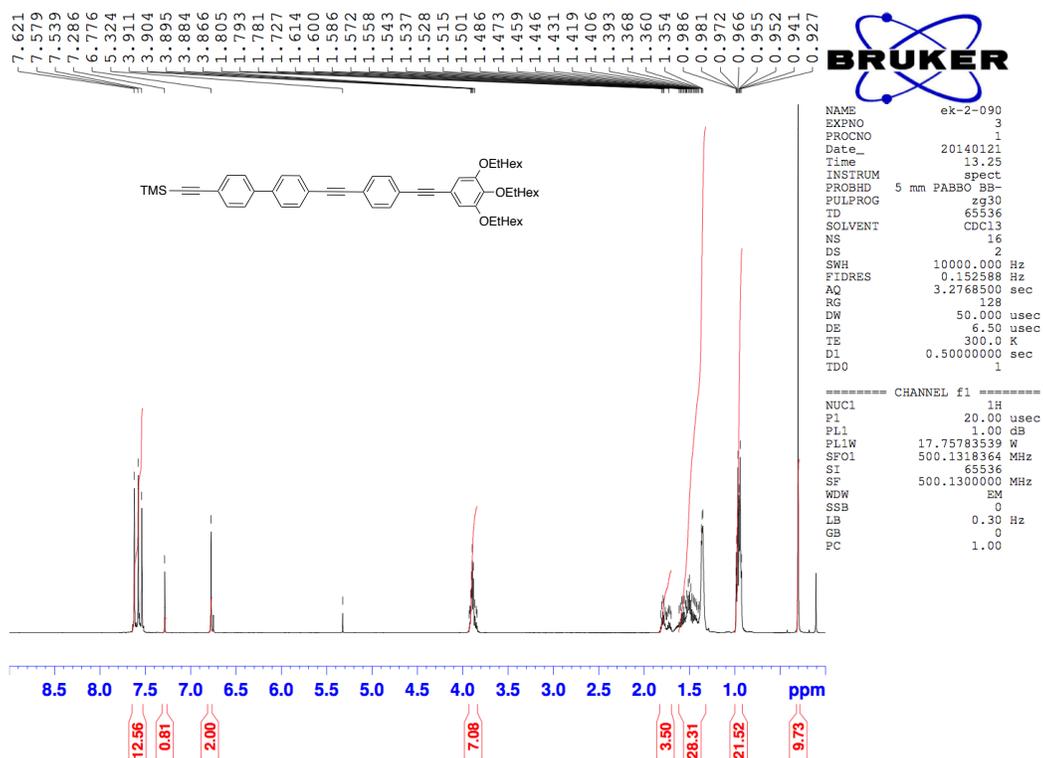
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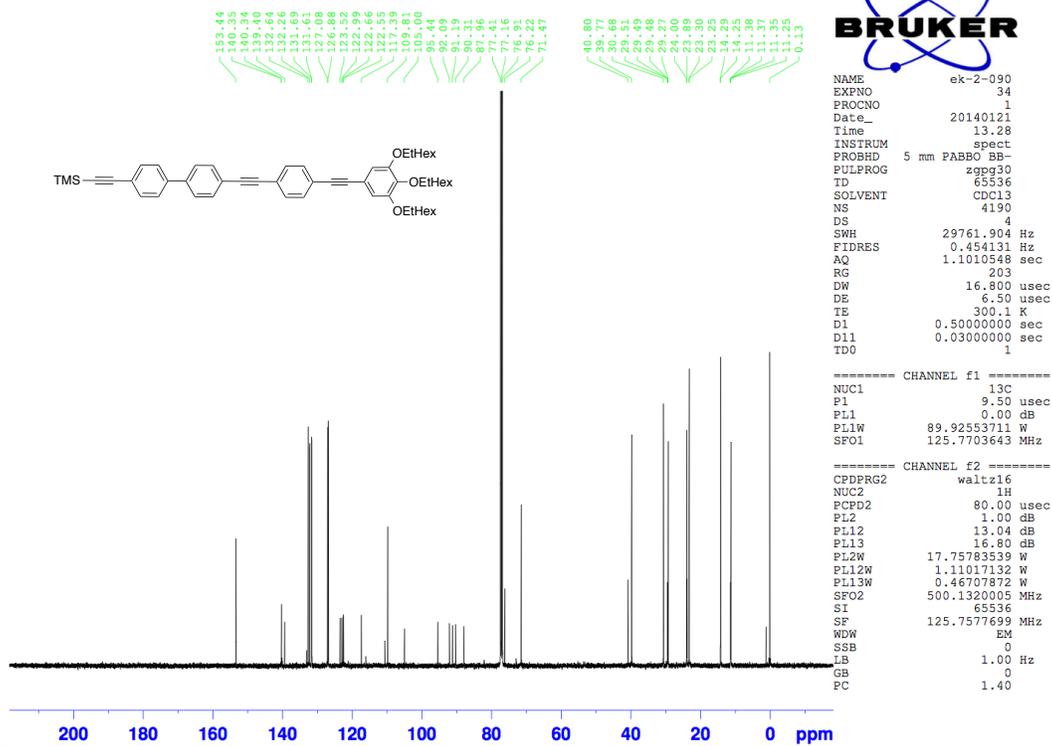
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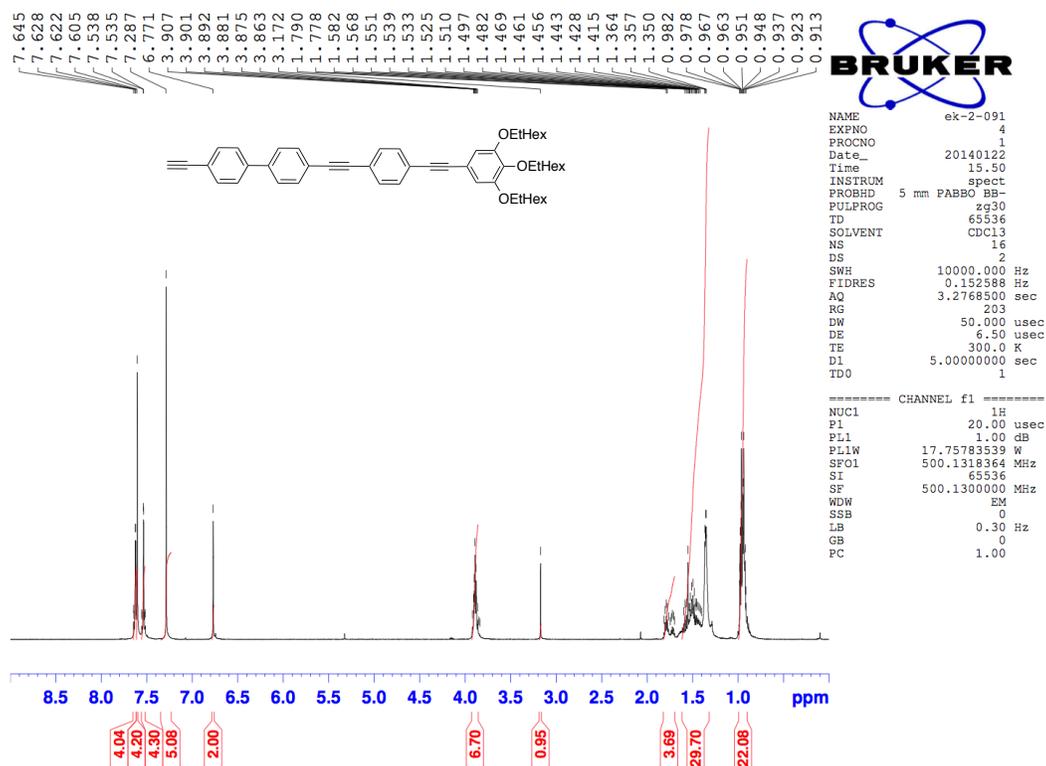
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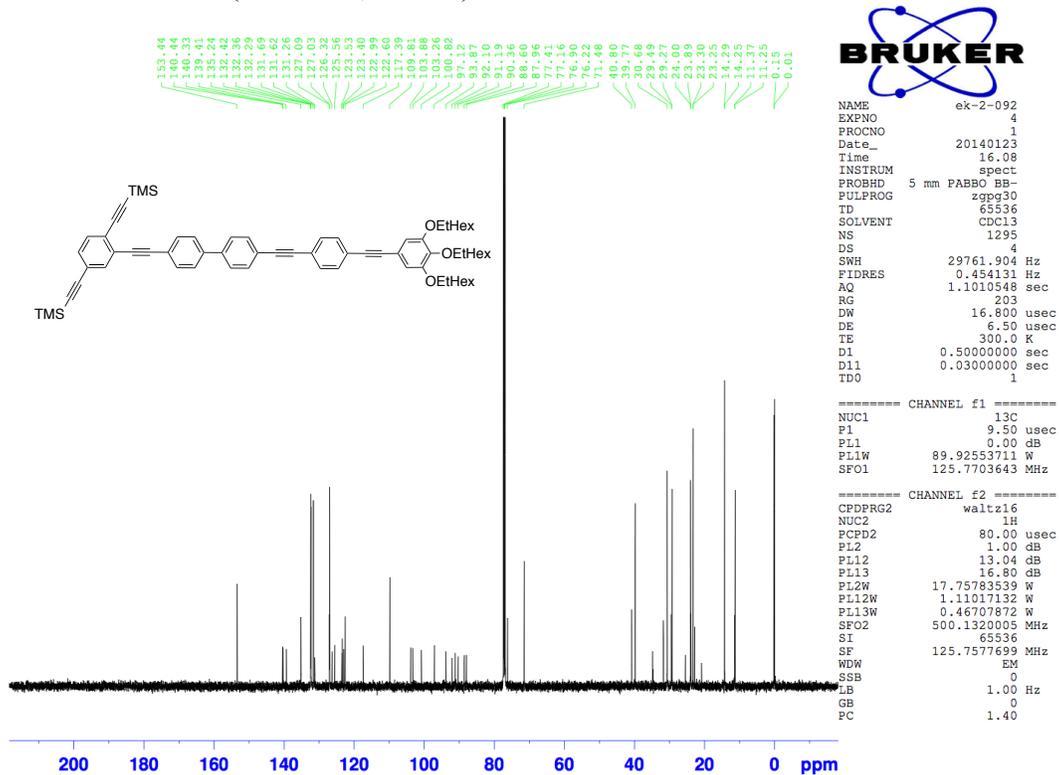
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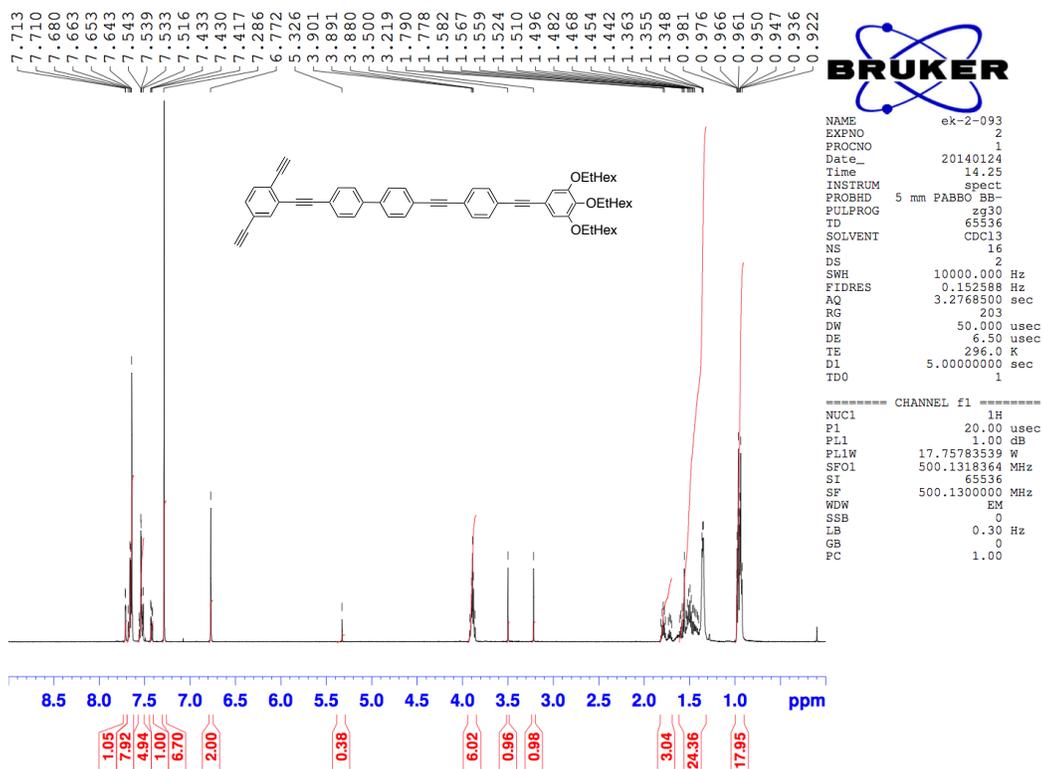
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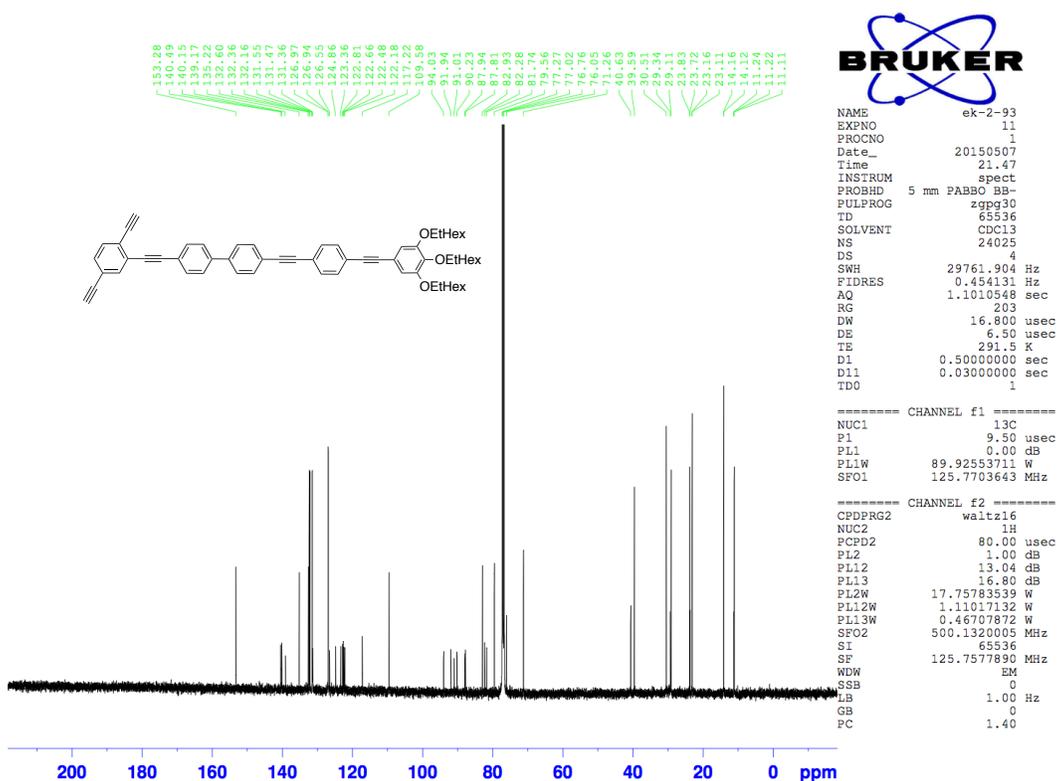
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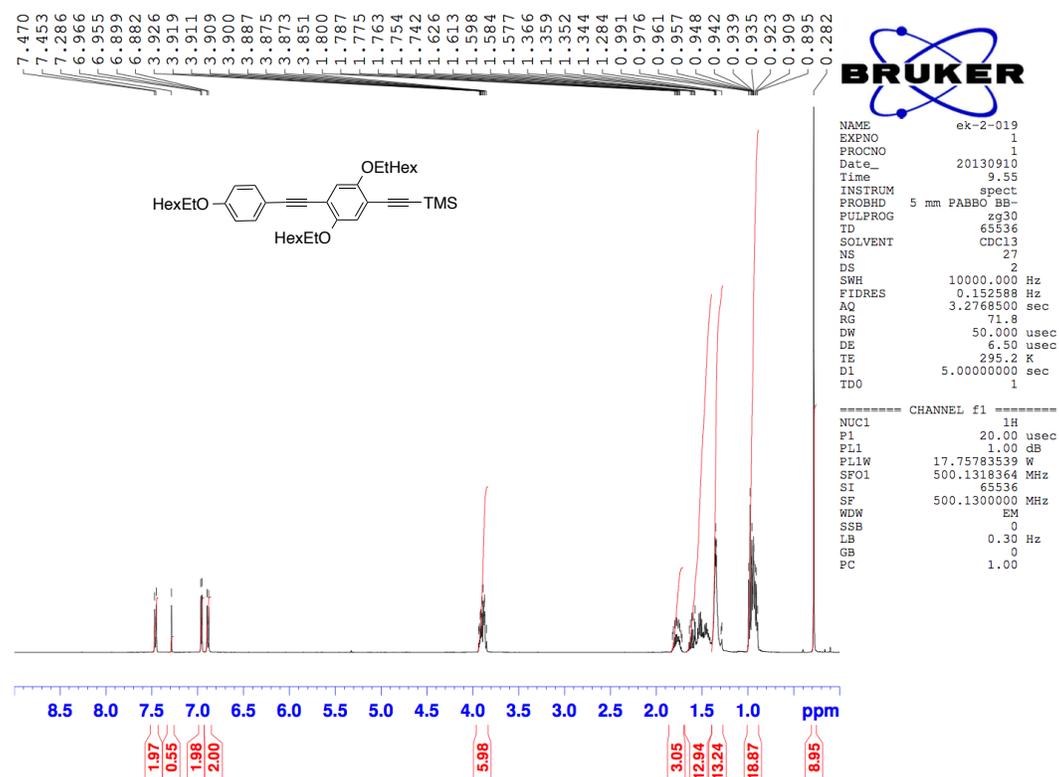
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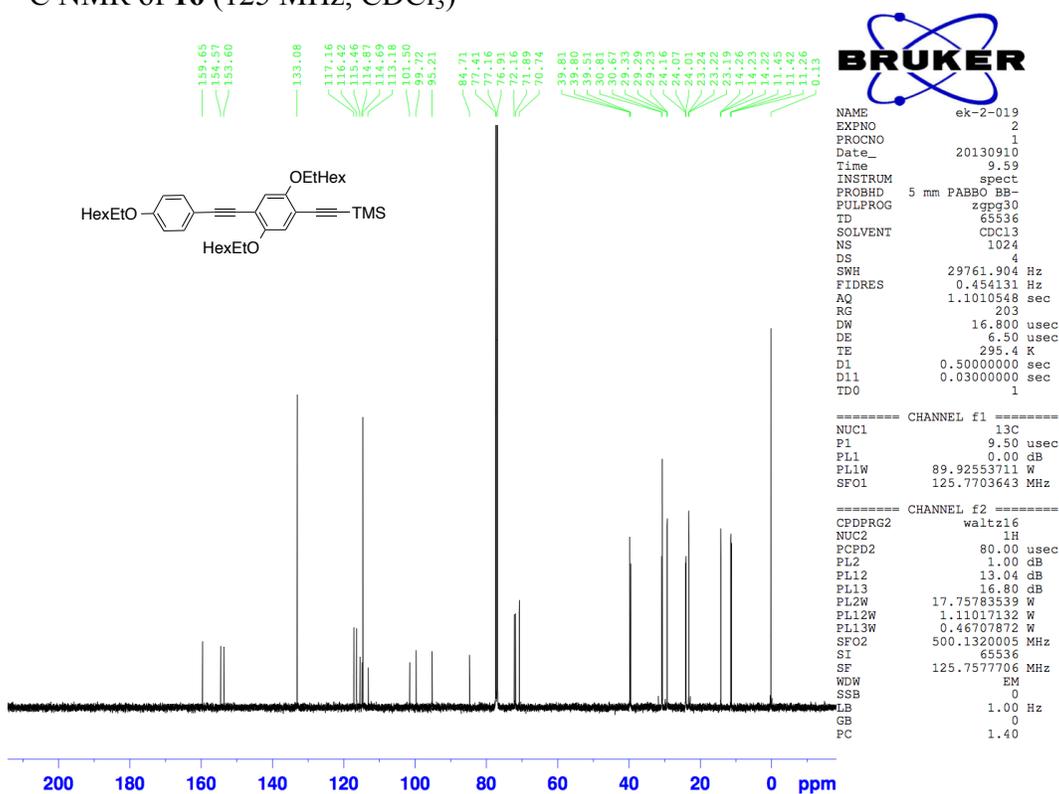
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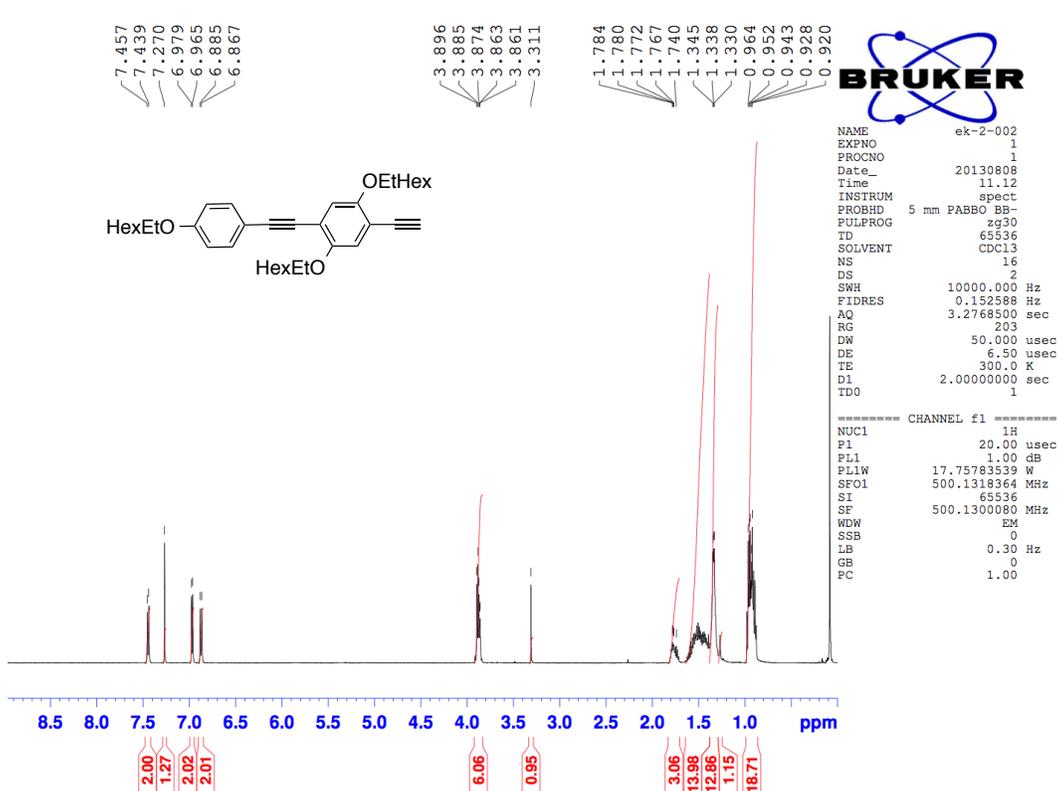
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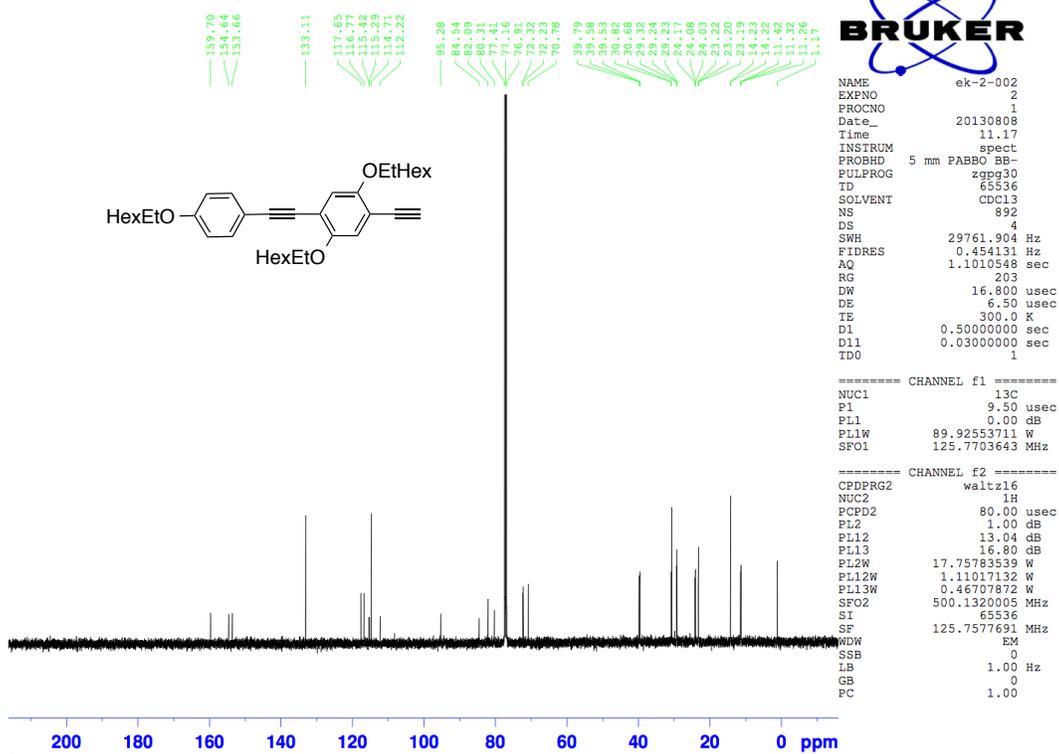
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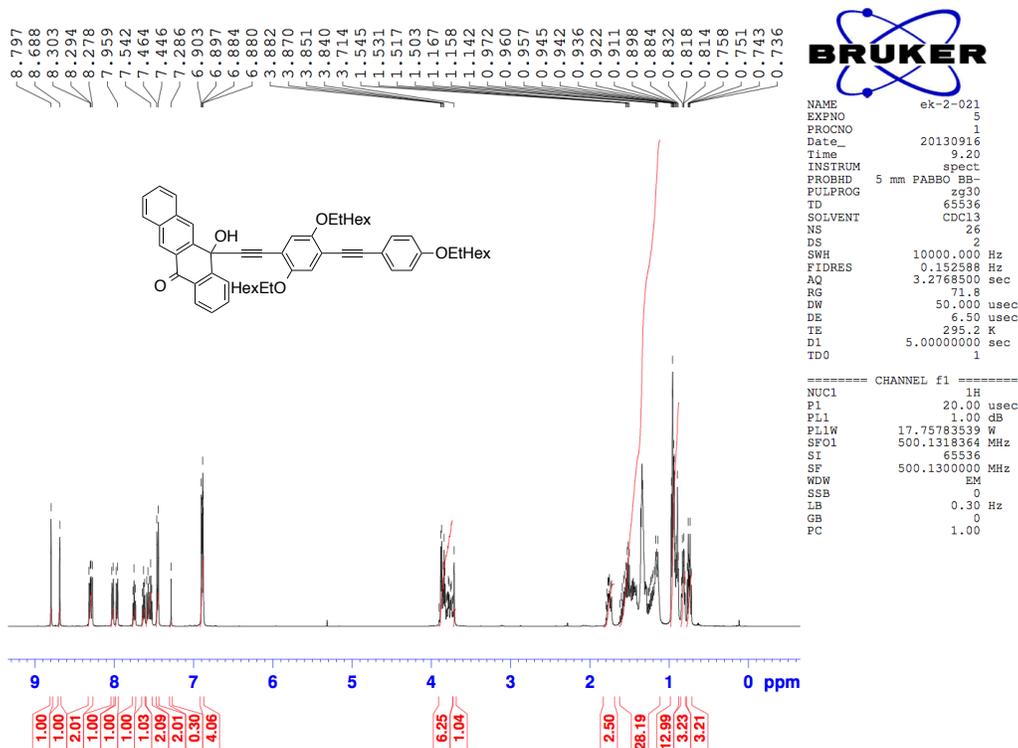
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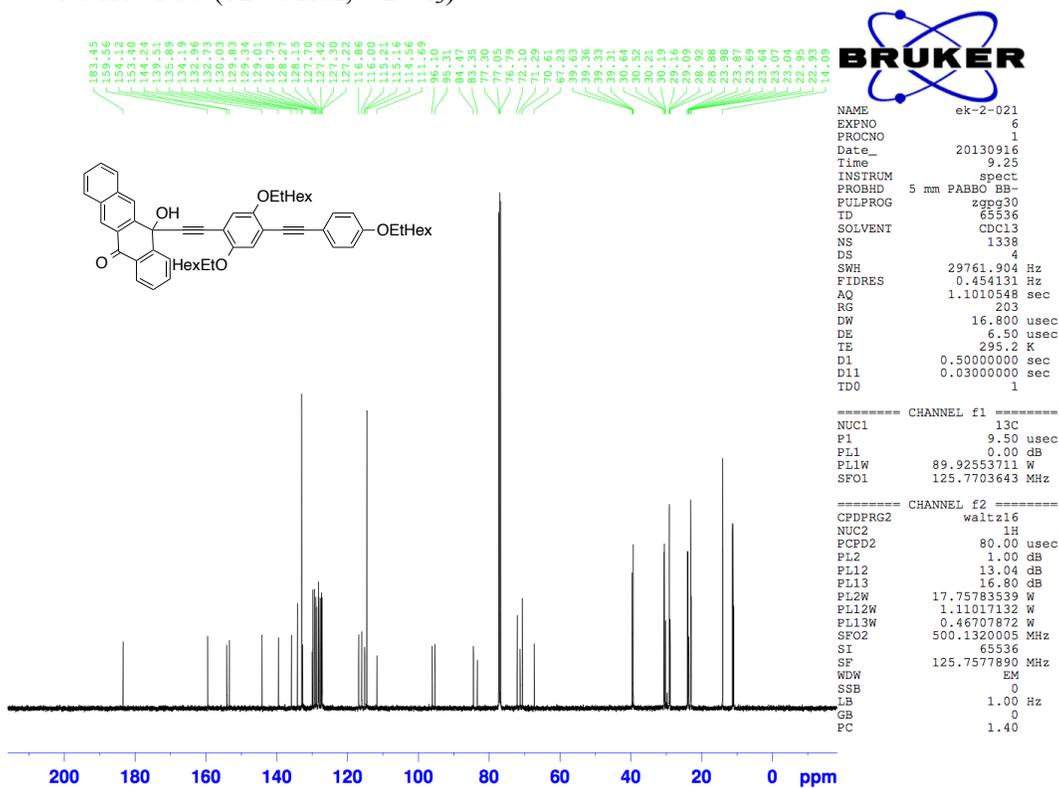
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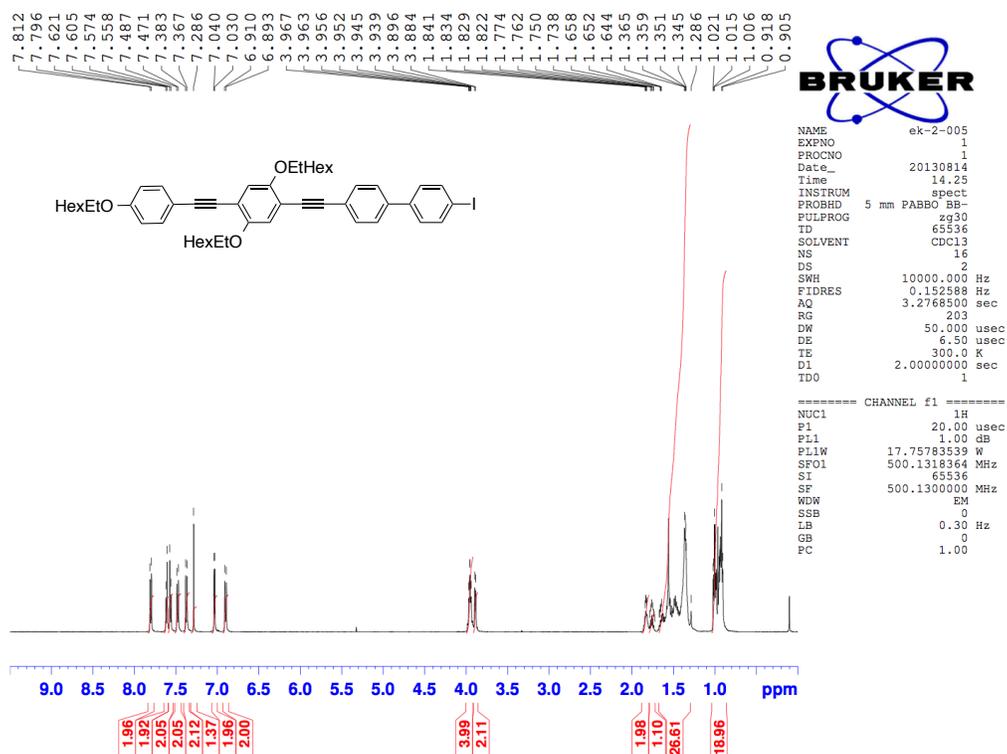
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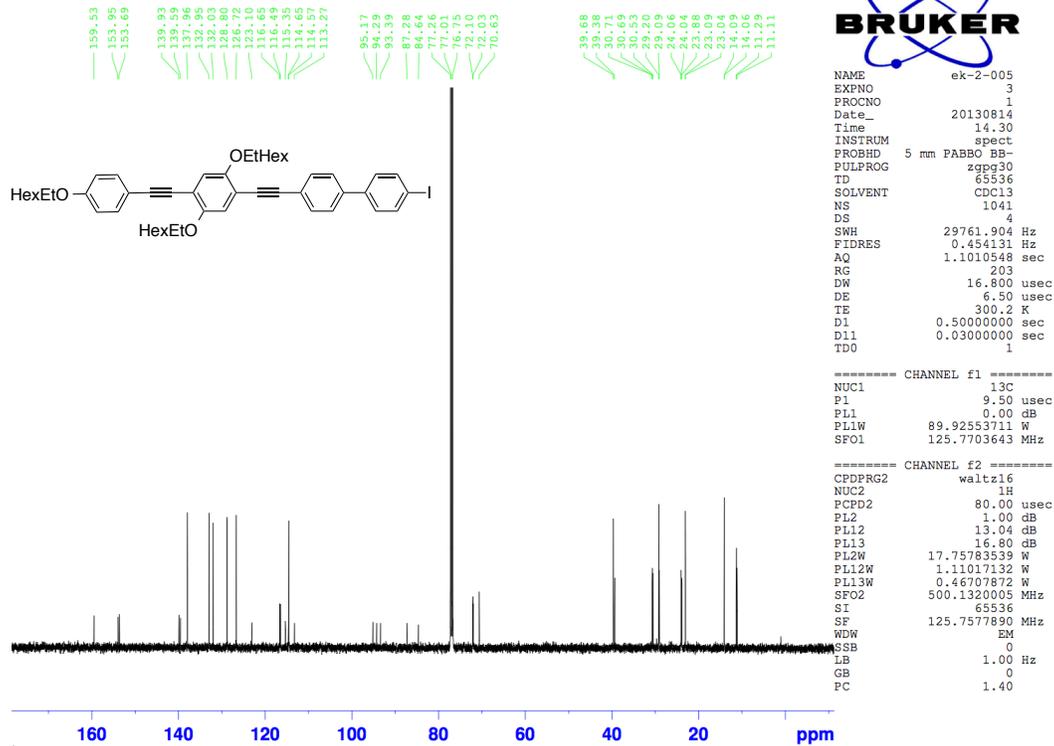
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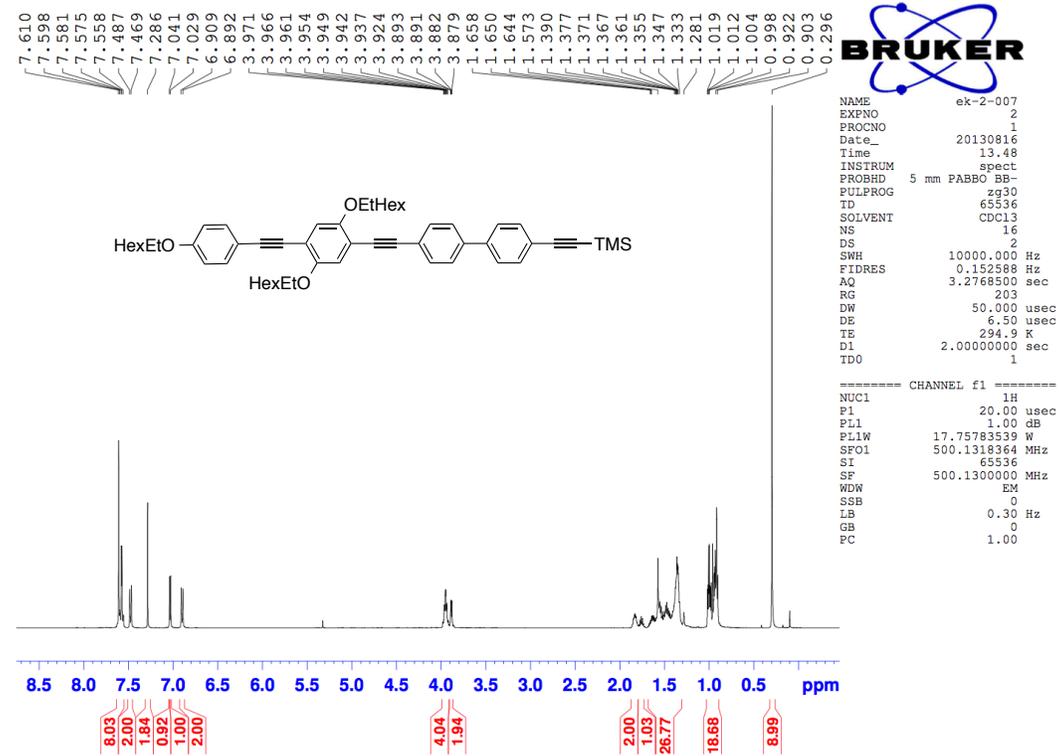
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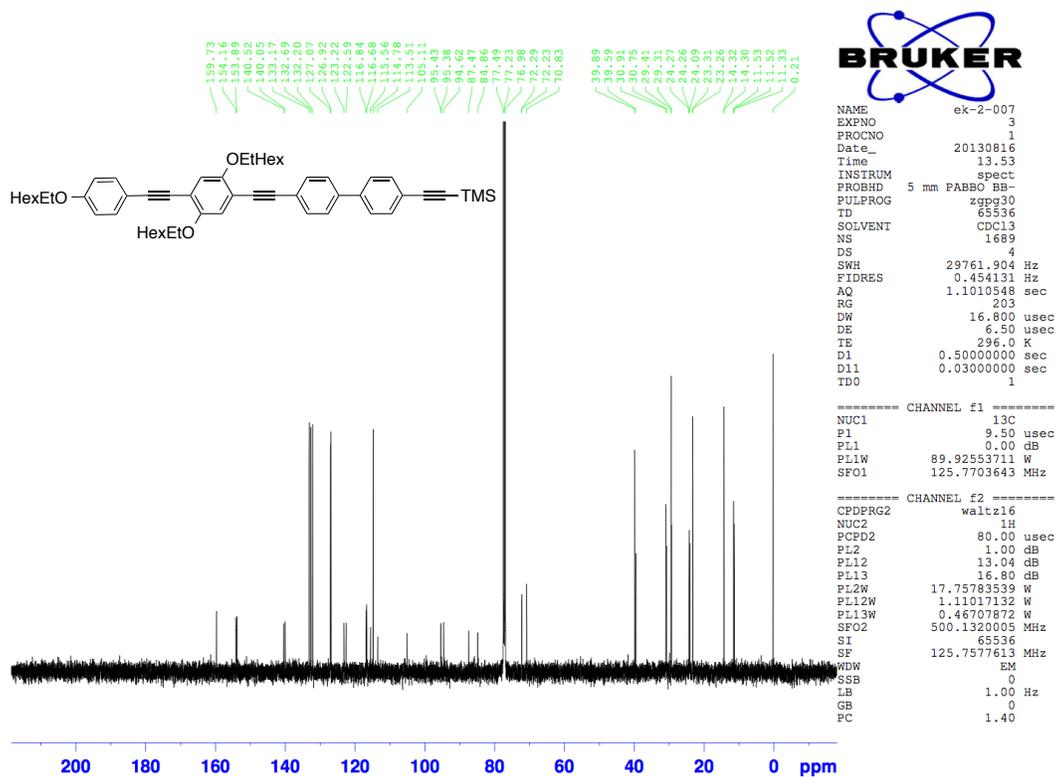
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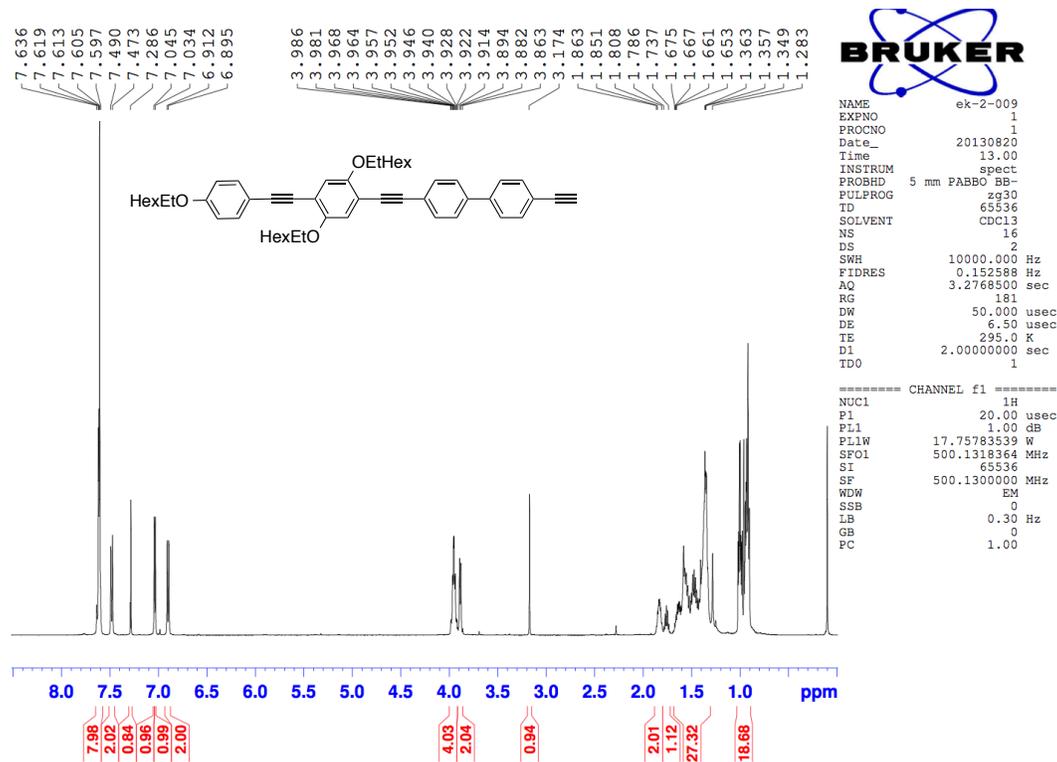
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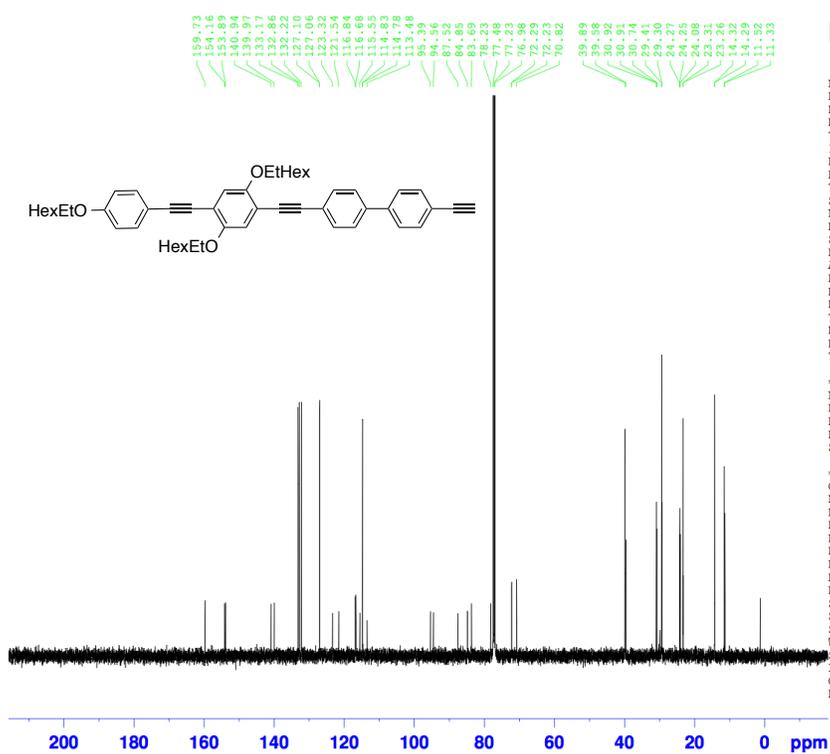
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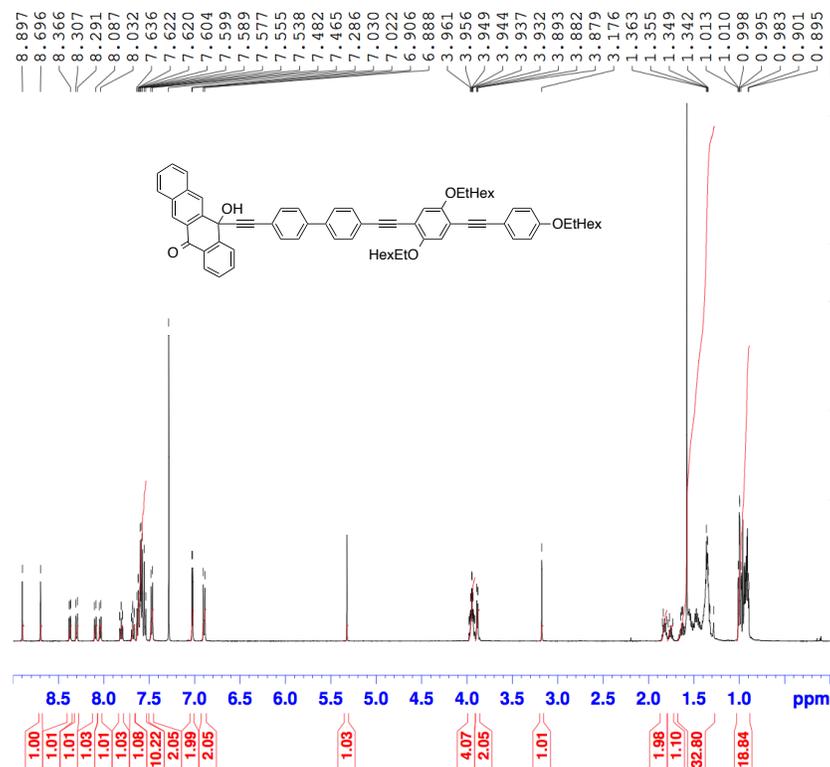
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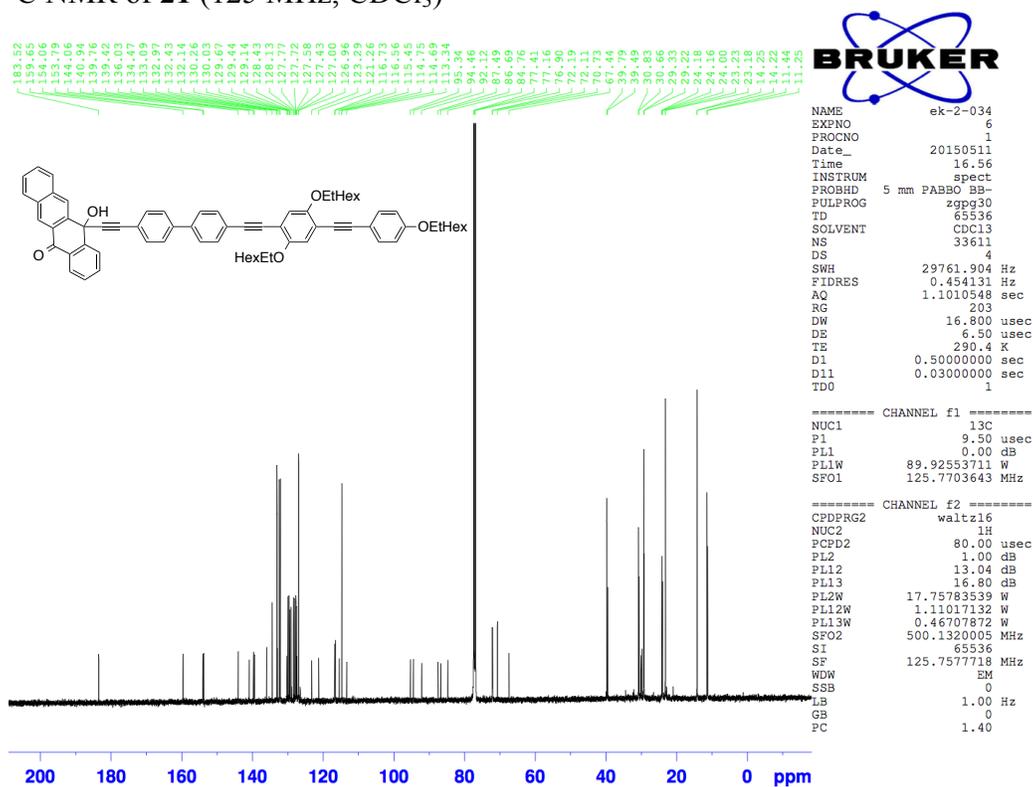


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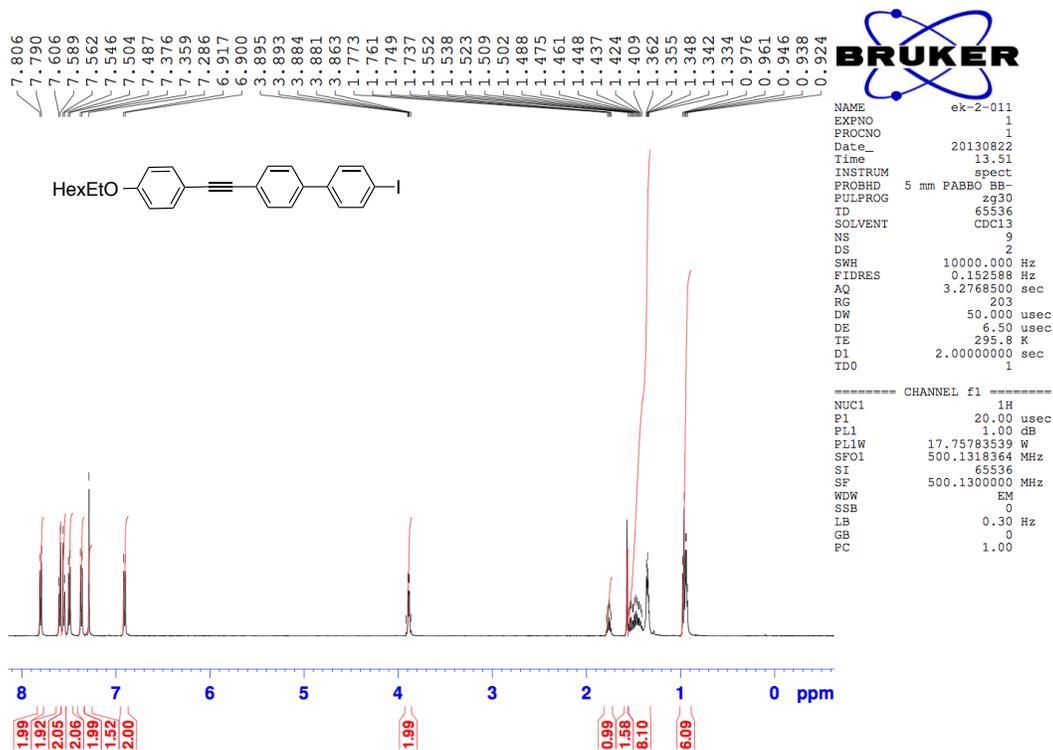
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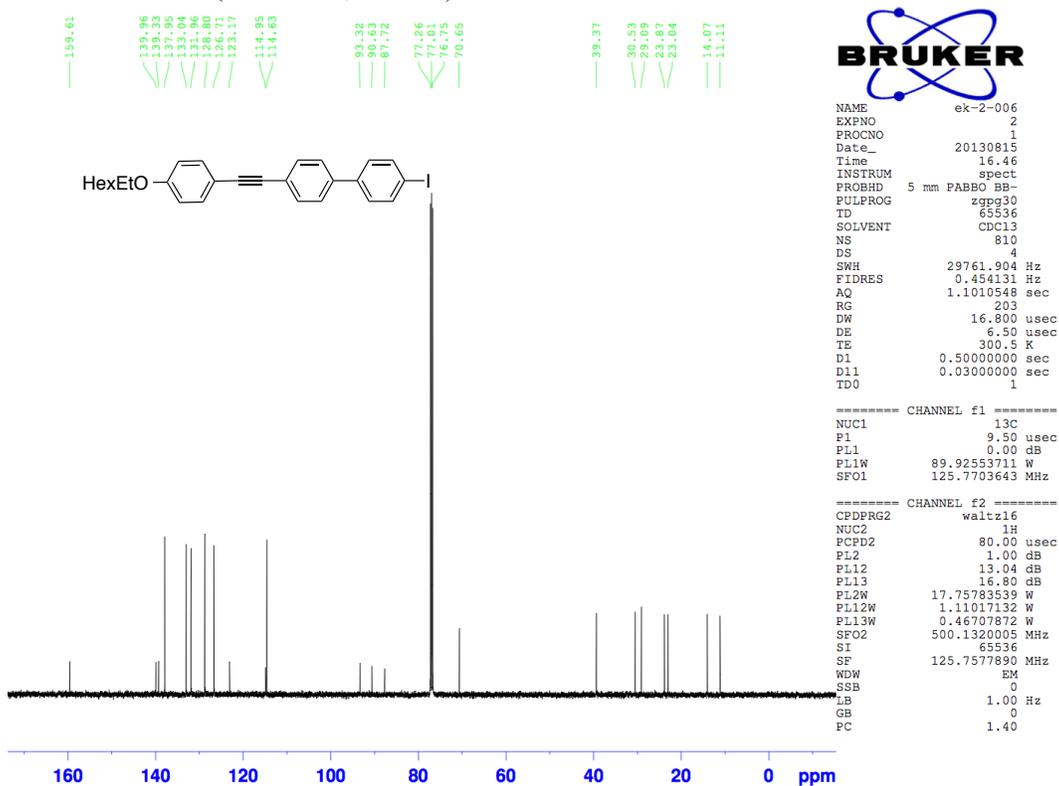
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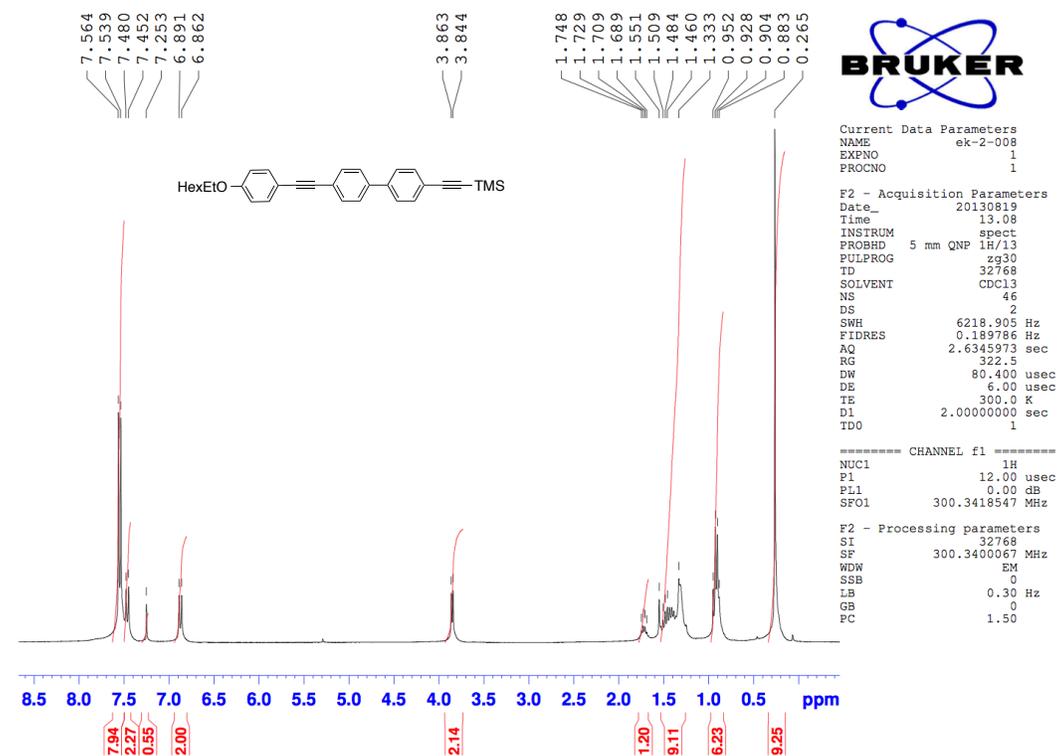
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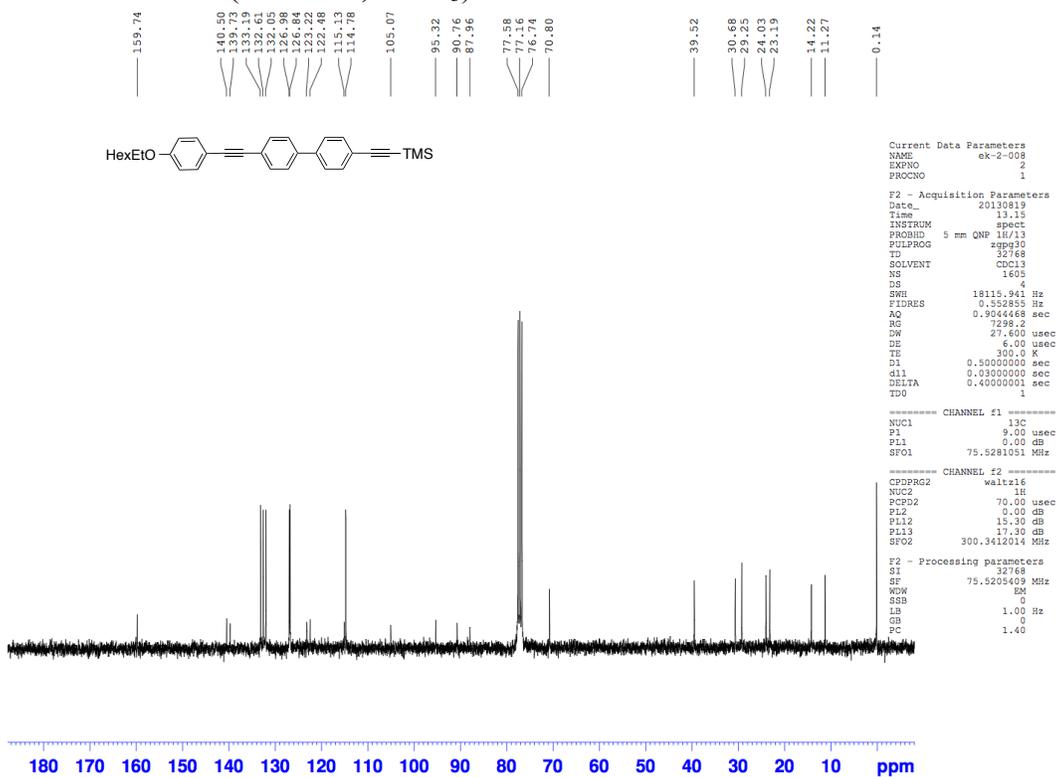
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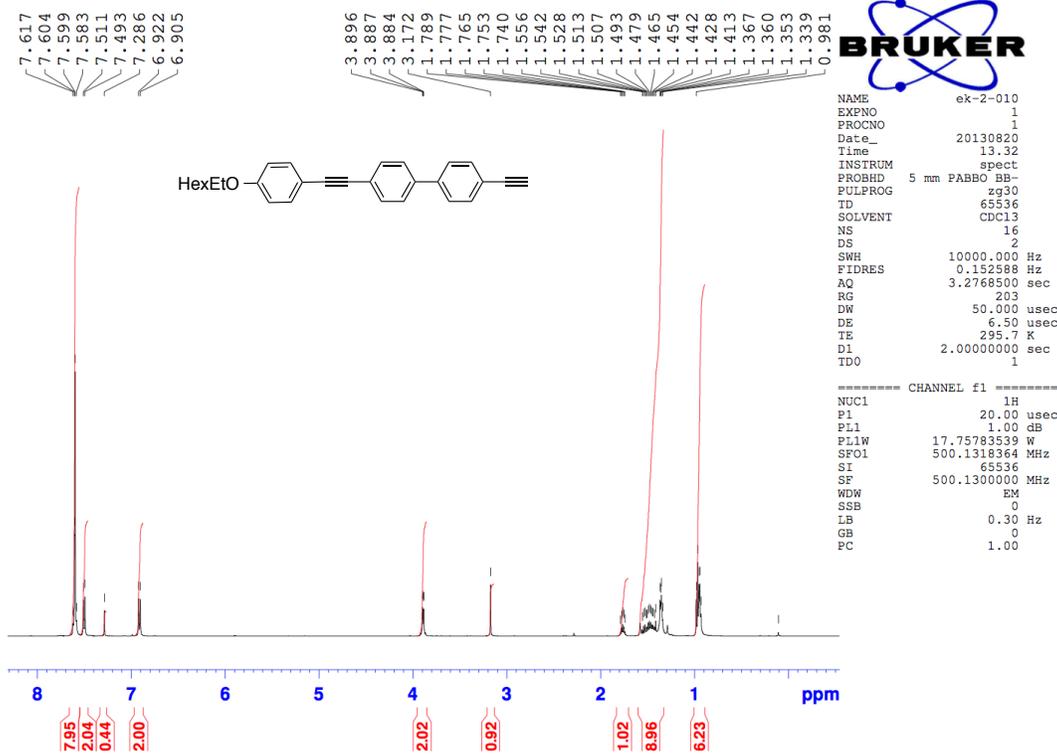
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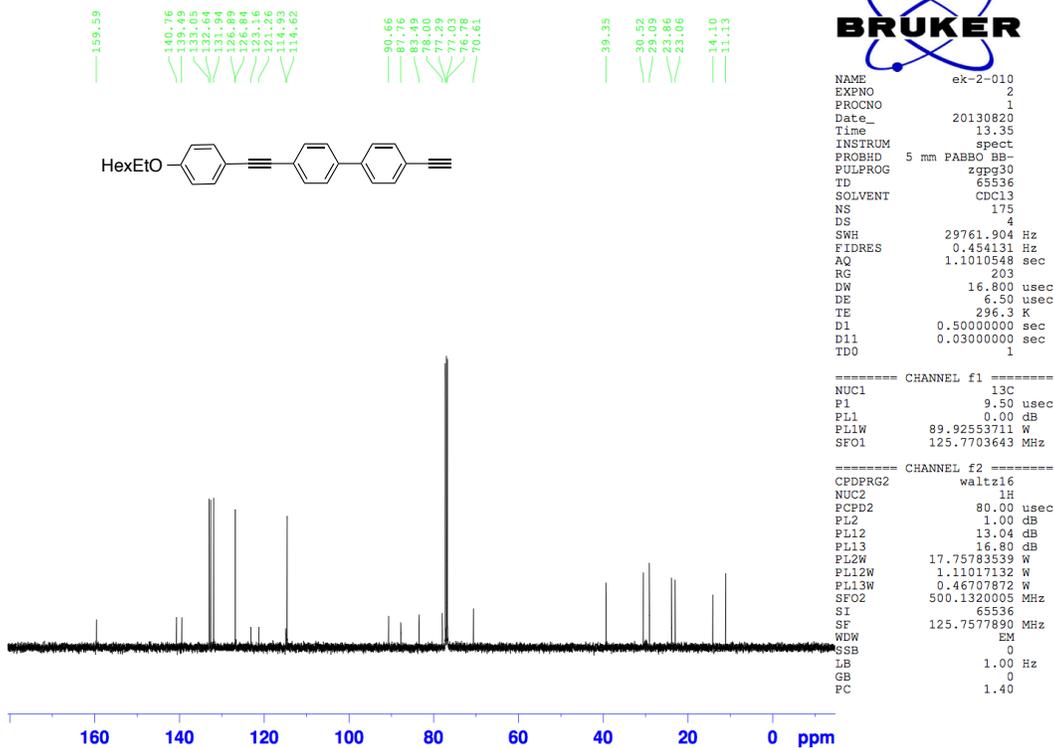
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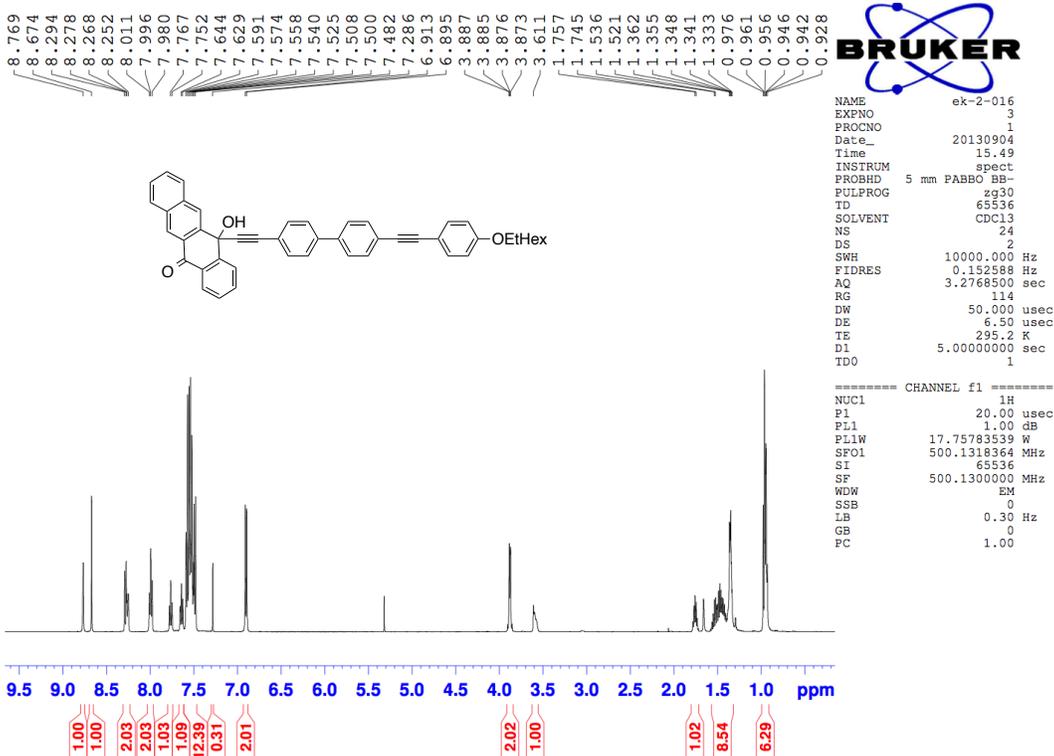
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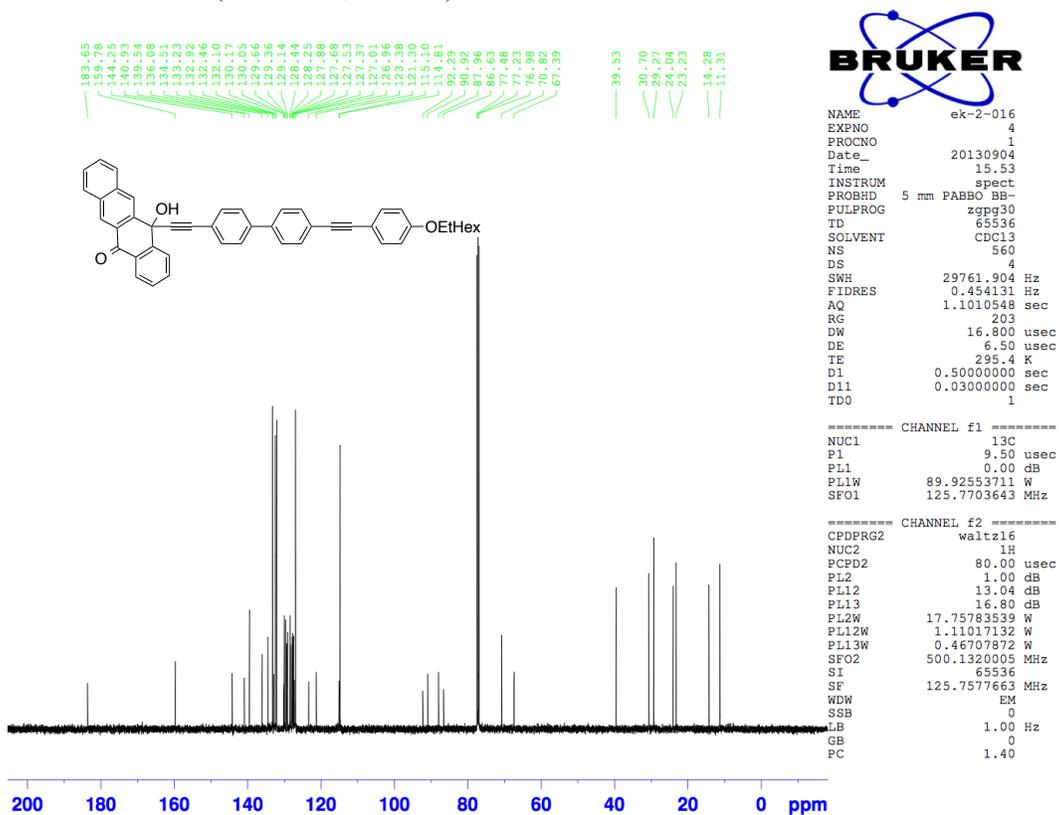
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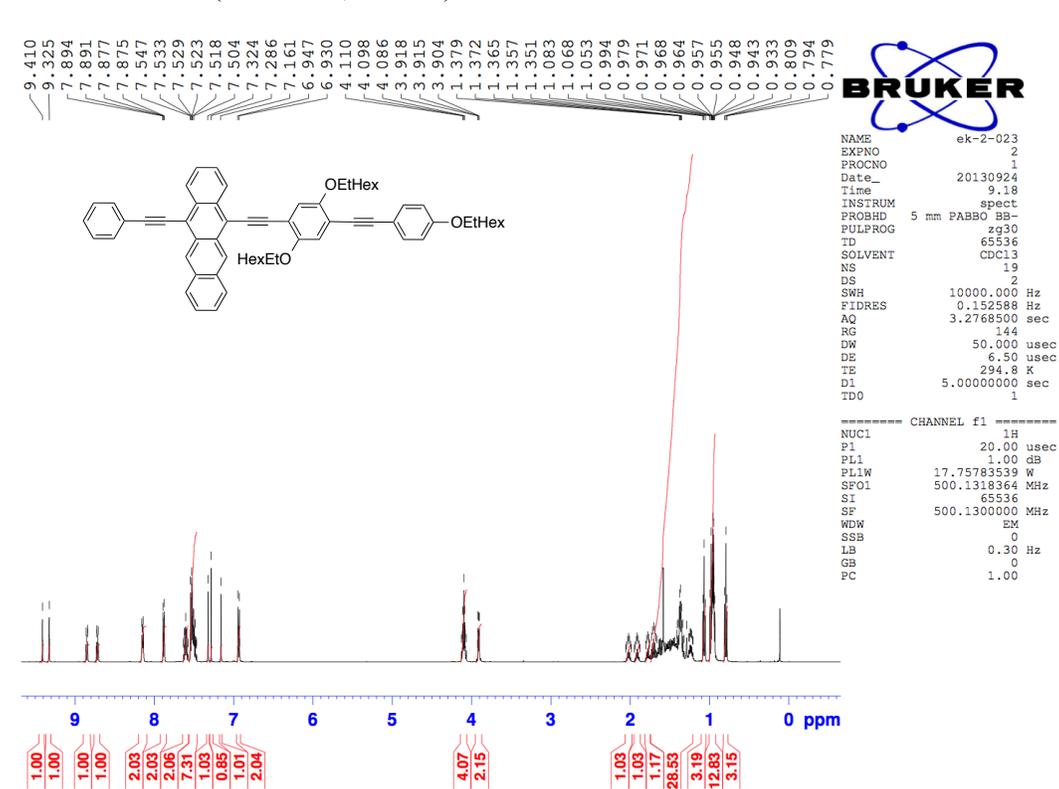
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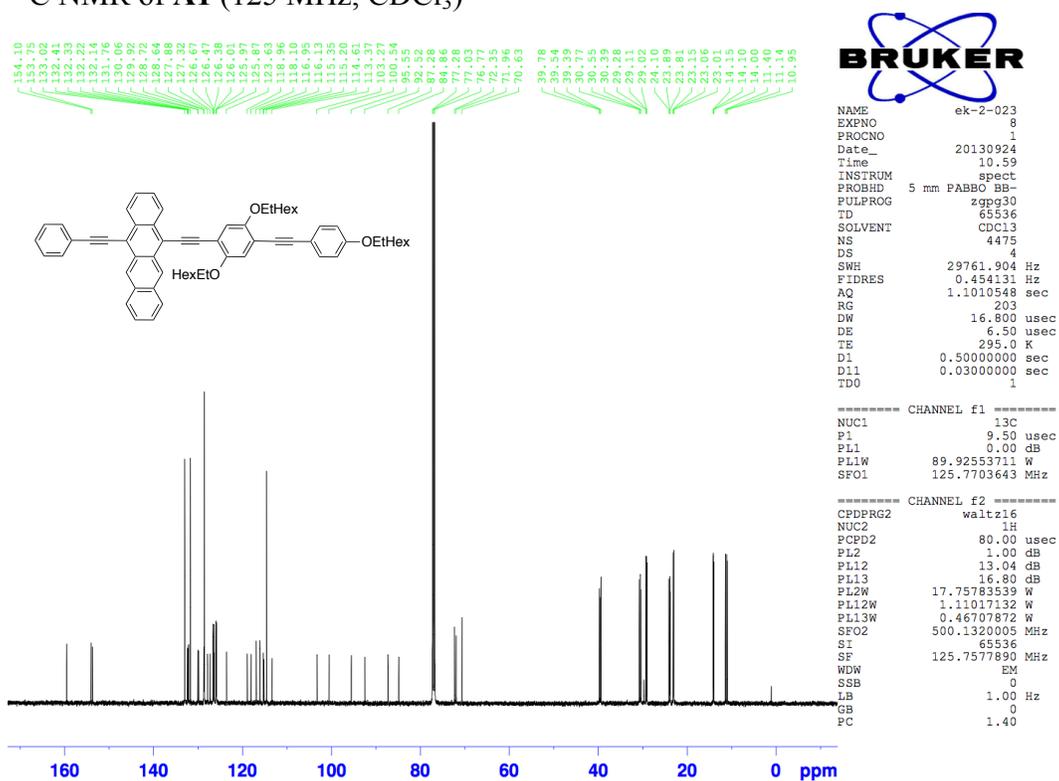
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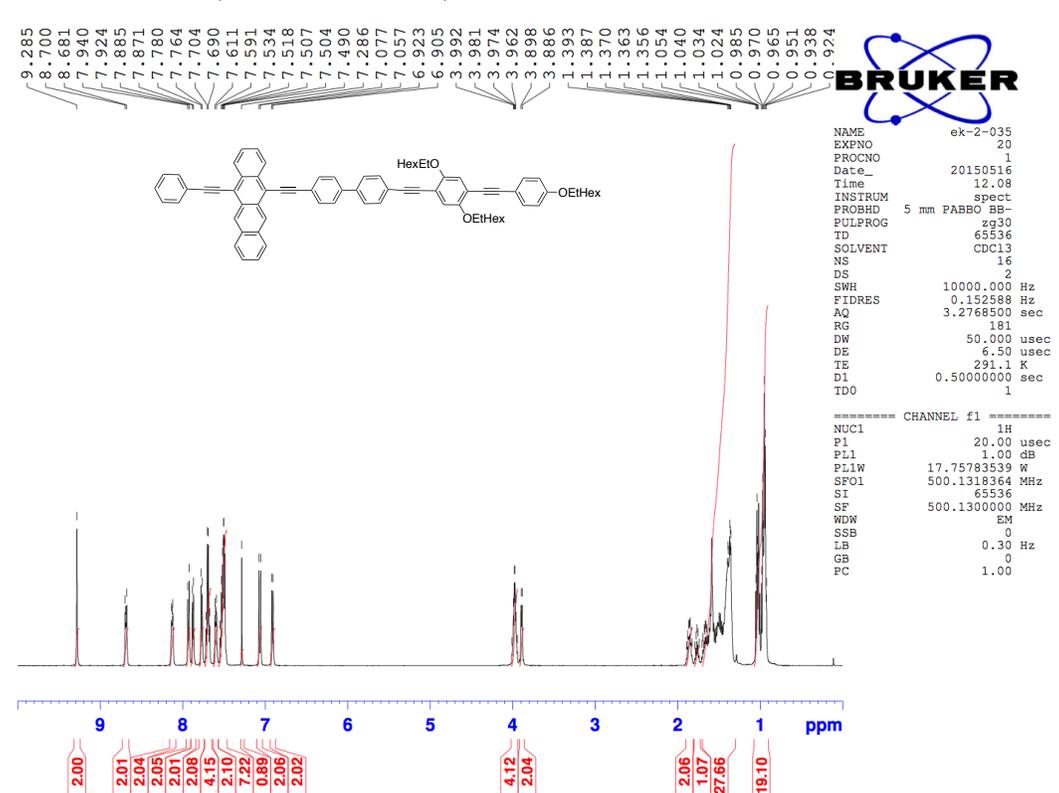
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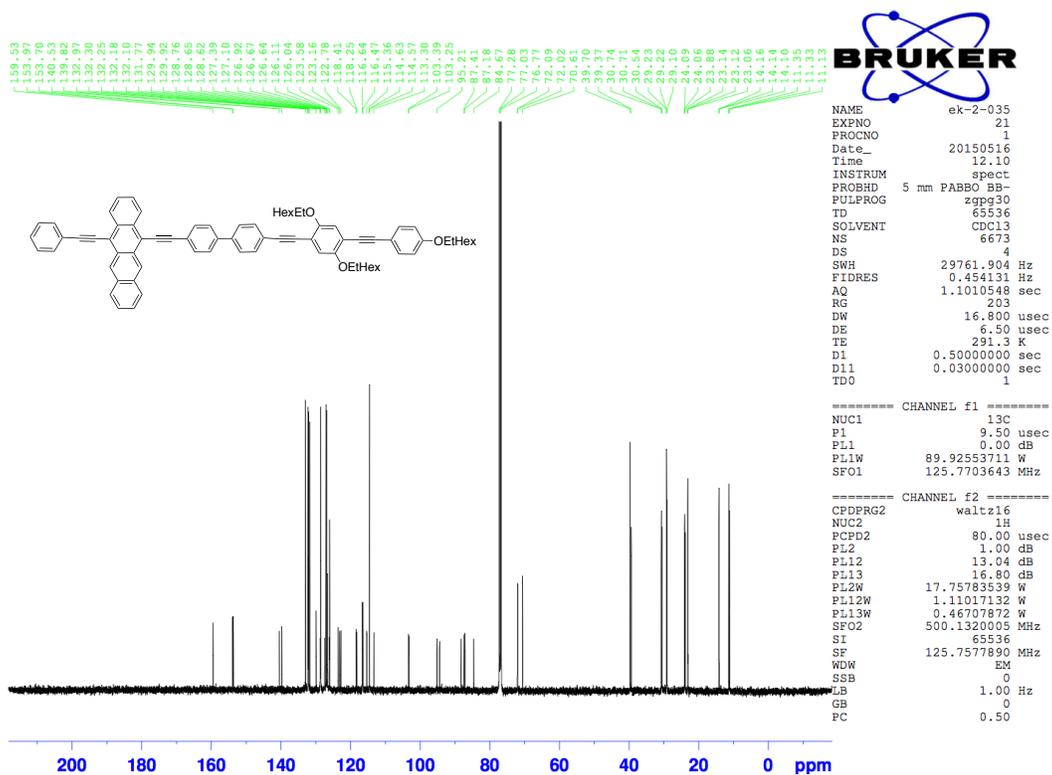
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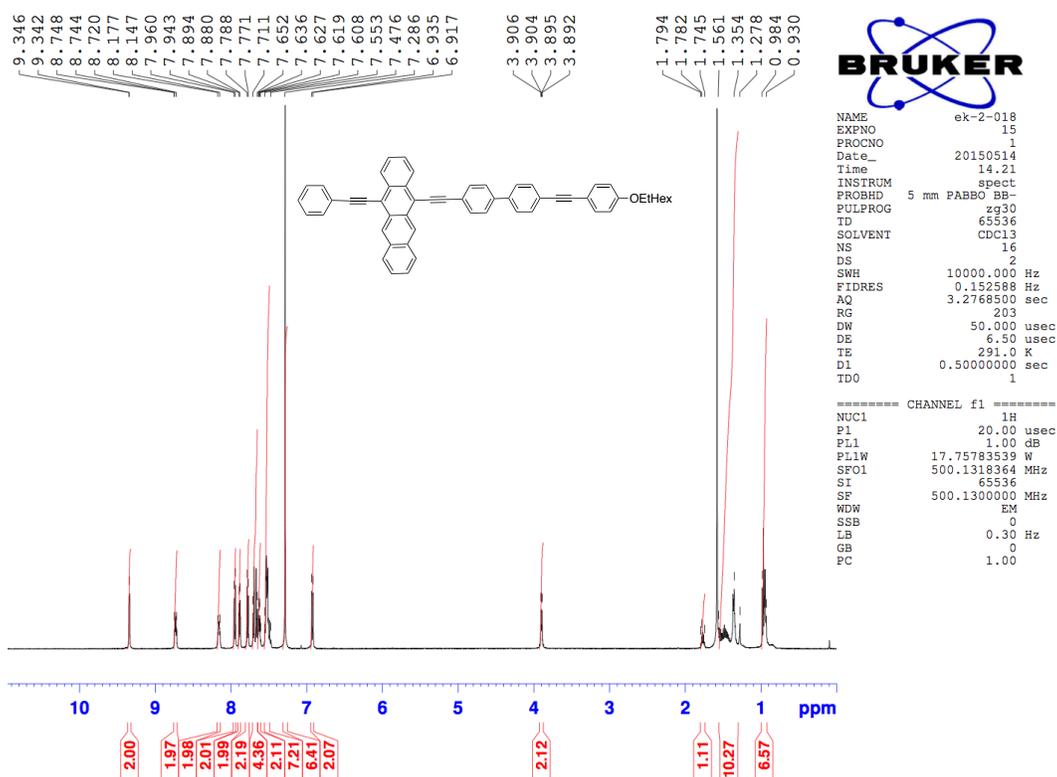
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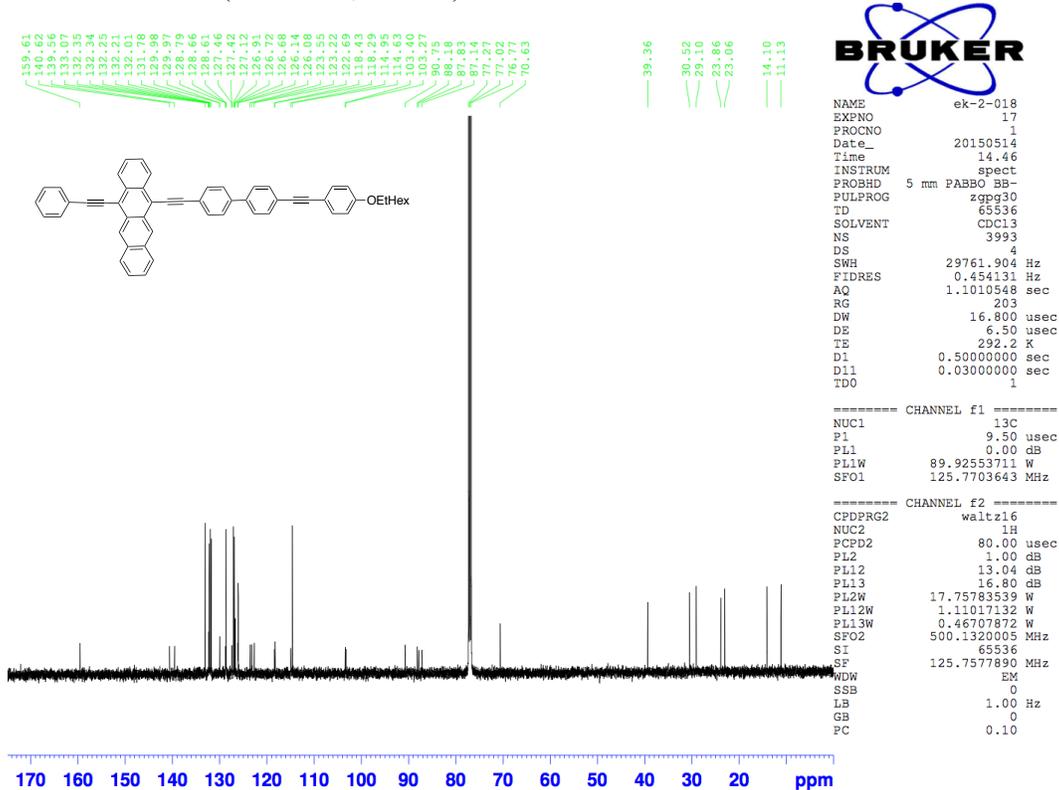
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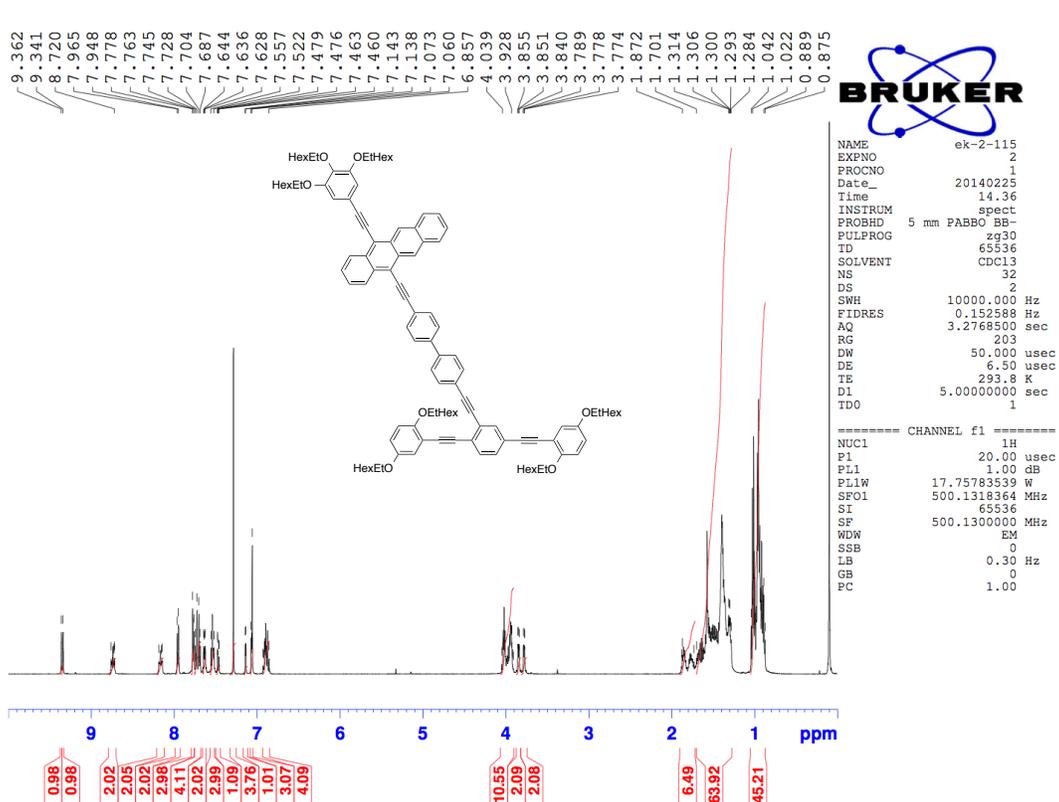
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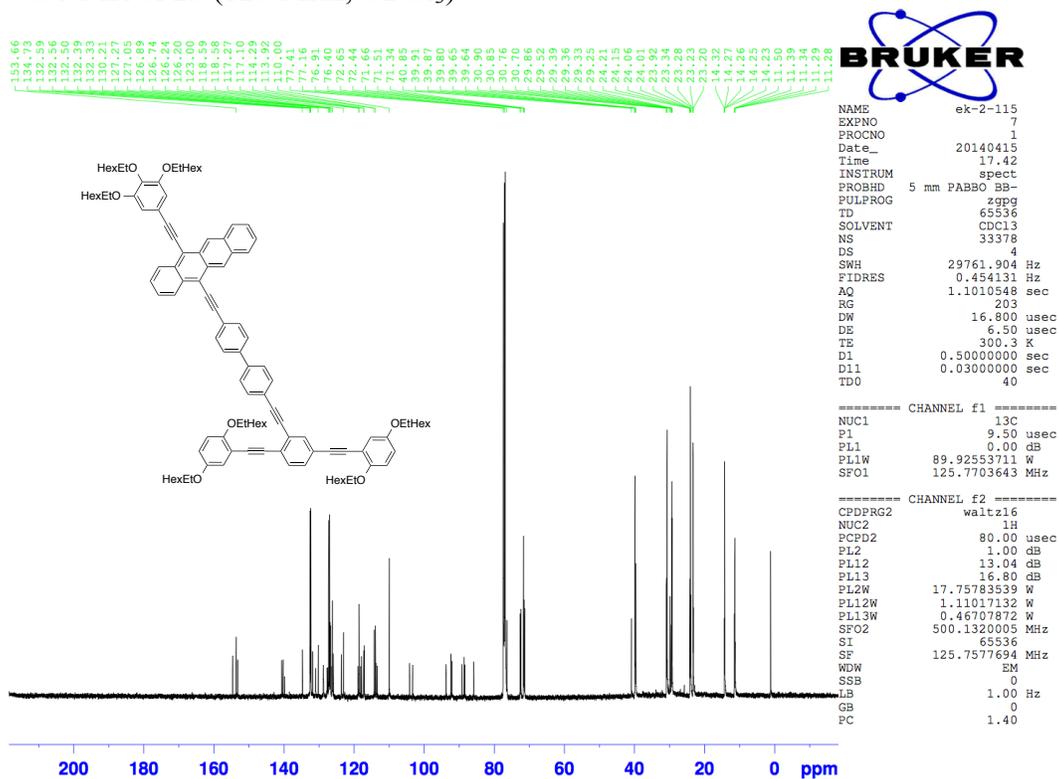
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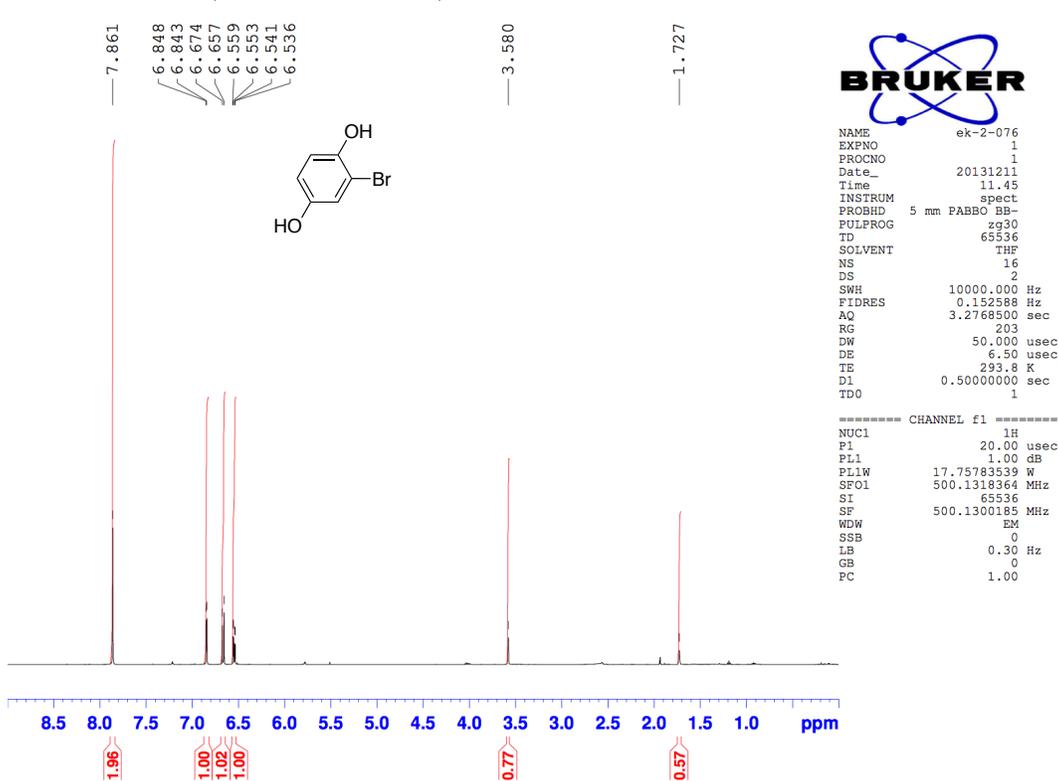
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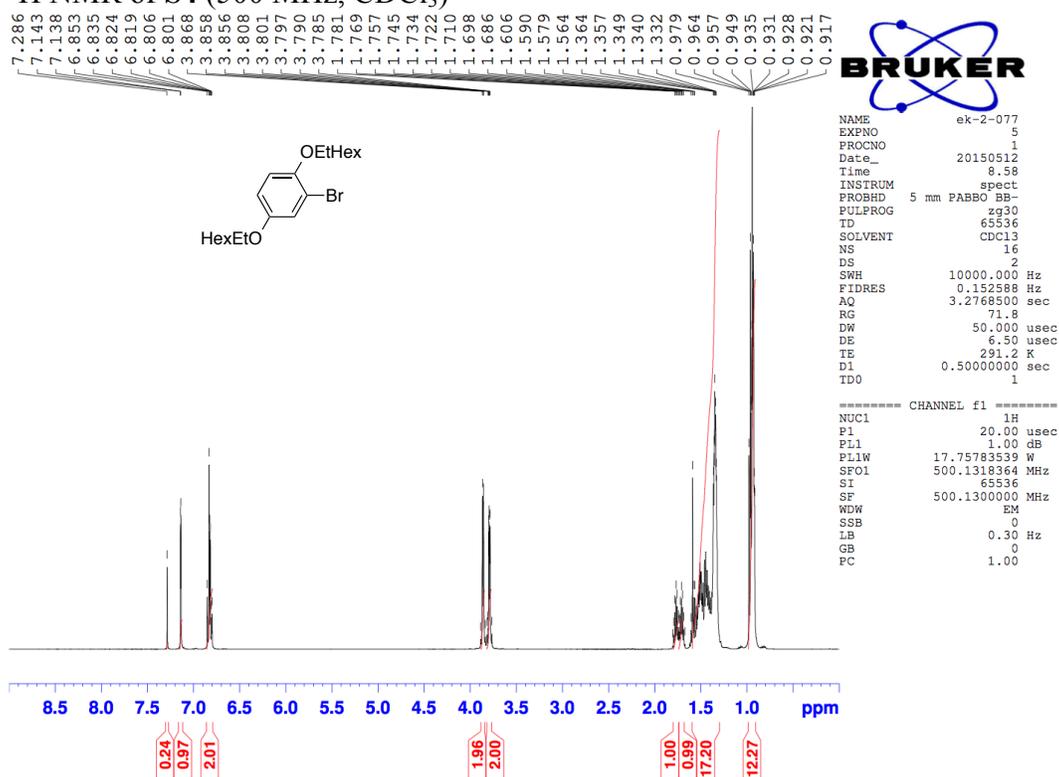
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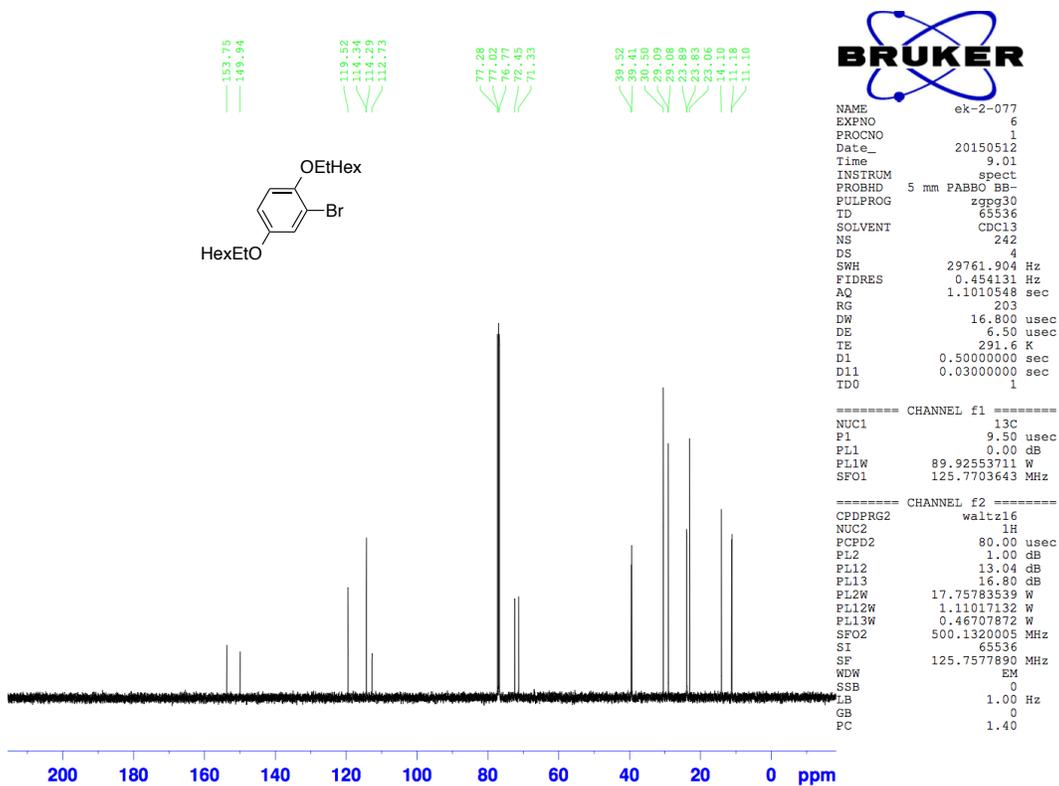
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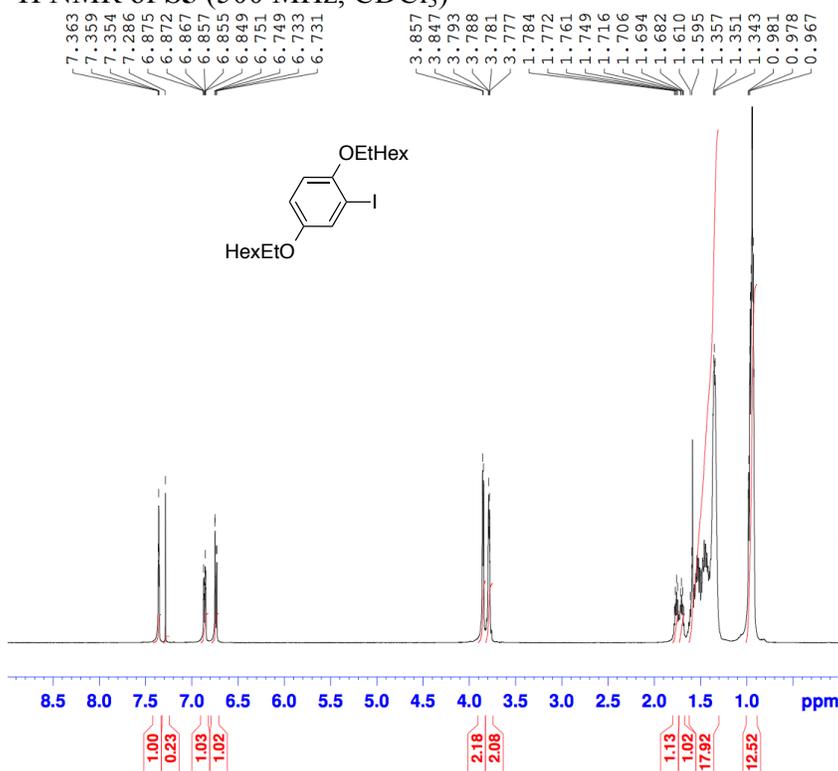
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¹³C NMR of S4 (125 MHz, CDCl₃)



¹H NMR of S5 (500 MHz, CDCl₃)

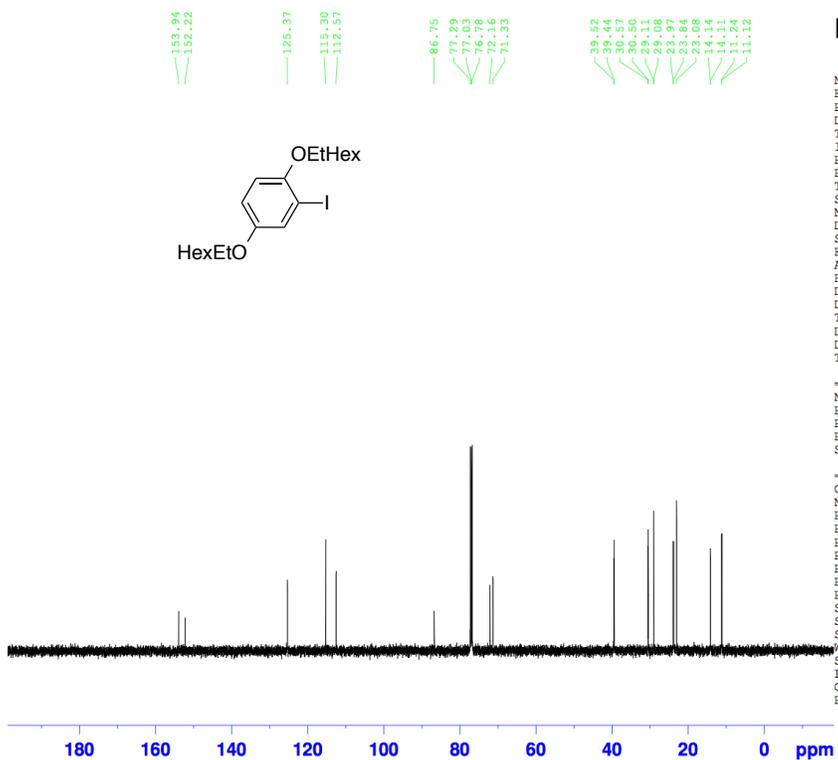


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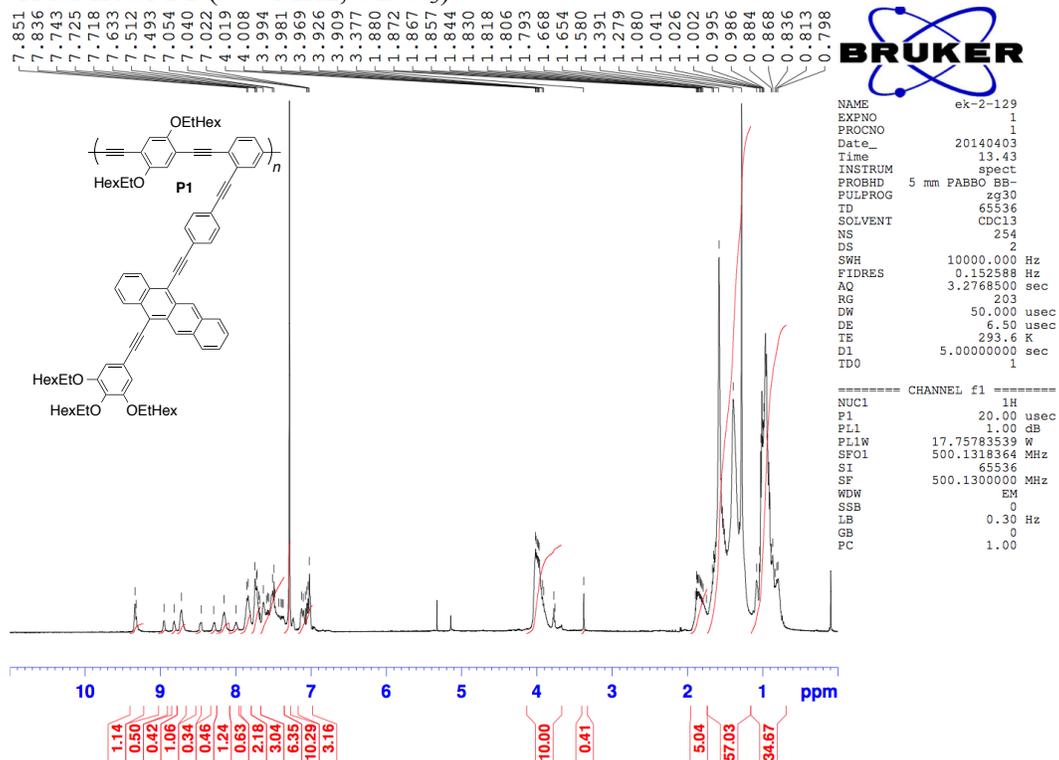
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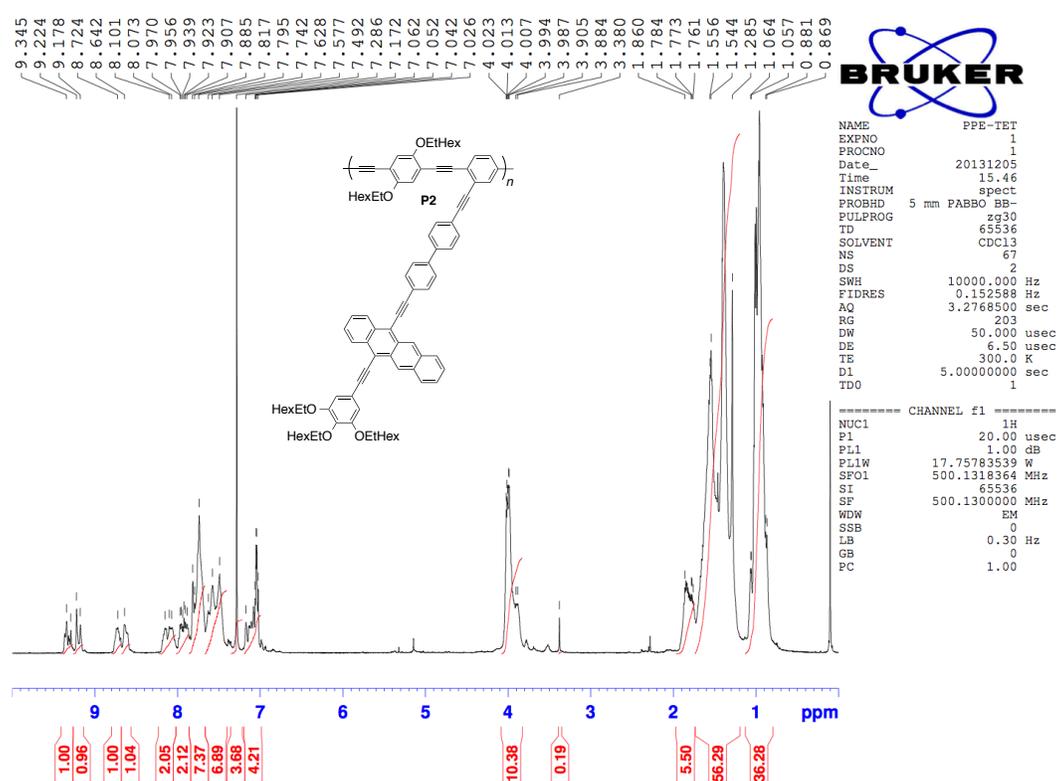
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PL2     -1.00 dB
PL12    13.04 dB
PL13    16.80 dB
PL2W    17.75783539 W
PL12W   1.11017132 W
PL13W   0.46707872 W
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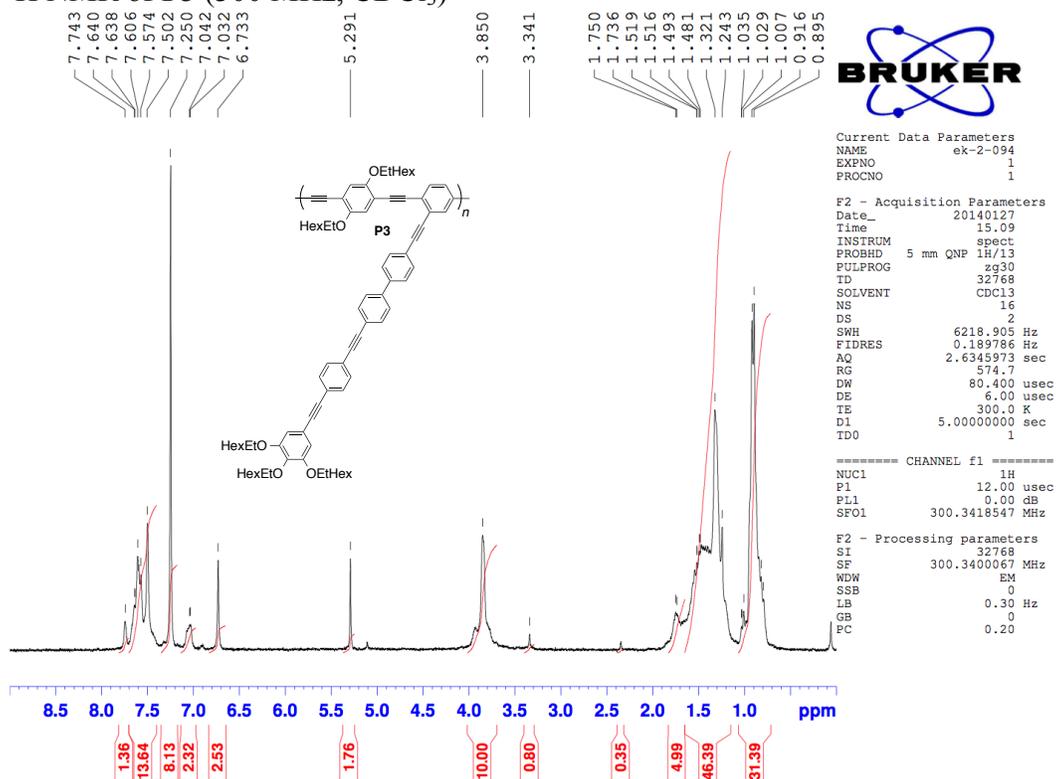
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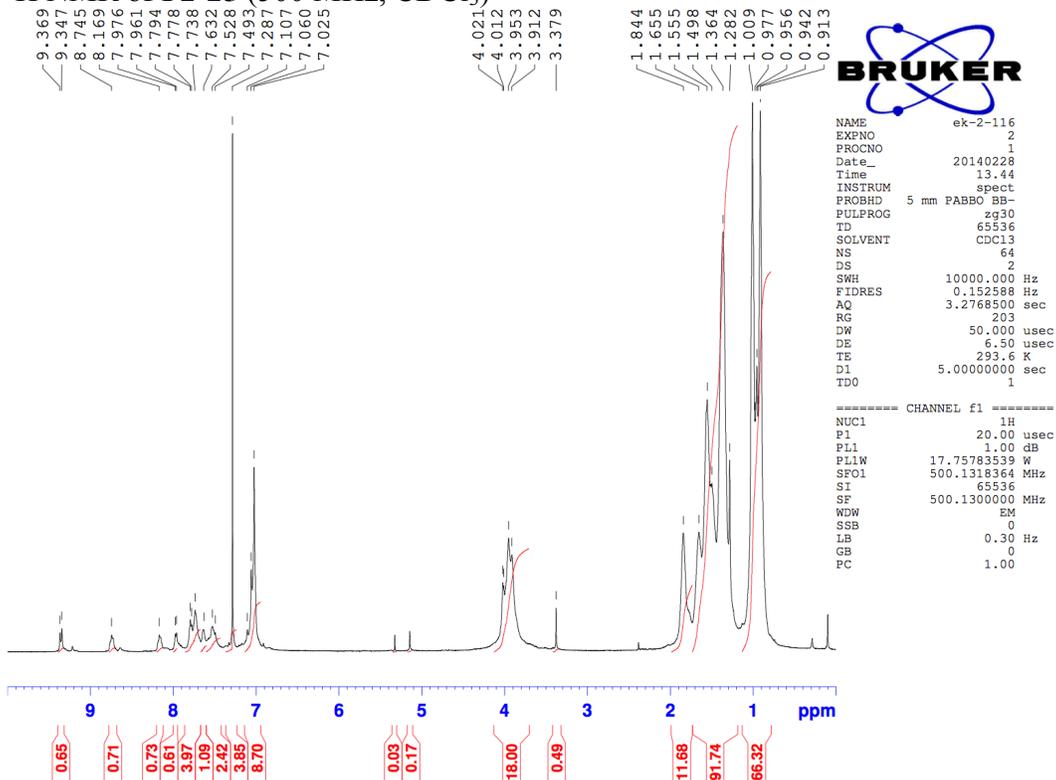
¹H NMR of P2 (500 MHz, CDCl₃)



¹H NMR of **P3** (300 MHz, CDCl₃)



¹H NMR of **P2-25** (500 MHz, CDCl₃)



Chapter 4:

Acene-Containing non-Conjugated Polymers That Show Ratiometric Fluorescent Response To Singlet Oxygen

4.1 Introduction

The structural properties of conjugated polymers (CPs) offer a number of advantages for their use in the detection of chemical and biomolecular targets.¹ According to the idea that was introduced by Swager and coworkers, properties of CPs, such as charge transport, emission yield, and exciton migration, can be easily altered by external agents in the form of changes in measurable signals.^{2,3} This strategy is useful in bioanalytical applications, such as the detection of various targets including DNA and proteins.⁴⁻⁶ Water solubility is necessary for biosensing in solution, which is commonly accomplished by using conjugated polyelectrolytes because they display the unique amplification properties of traditional CPs and also can be dissolved in highly polar solvents such as water. Conjugated polyelectrolytes (CPEs) are described as polymers that have π -delocalized electronic structures and are substituted with ionic functionalities to give water solubility.⁷ However, the hydrophobic conjugated polymer backbone may cause extensive aggregation in aqueous media.^{8,9}

The uses of CPEs for biosensing applications are typically based on interactions between biomolecule and CPs; therefore, may reduce the specificity toward analyte of interest.^{1,10} This strategy most often suffers from false positive signals because the charged nature of CPEs results in non-specific interactions between CPEs and biomolecules.^{11,12} Therefore, there is a need for developing systems, which rely on indirect analyte-CP interaction.

Singlet oxygen is one of the key reactive oxygen species used in photodynamic therapy because it is believed to be cytotoxic.¹³⁻¹⁵ It is also a

significant intermediate in the luminescent oxygen channeling immunoassays (LOCI). LOCI offers many advantages over other immunoassays, such as ELISA, due to its higher sensitivity and wider working range.^{16,17} Additionally, $^1\text{O}_2$ oxidizes polyaromatic acenes to endoperoxides through [4+2] cycloaddition.¹⁸⁻²¹ Our group has previously reported furan and acene linked conjugated polymers that respond singlet oxygen by altering the fluorescence intensity.^{22,23} These conjugated polymers respond $^1\text{O}_2$ in organic solvent by interruption of an electron or energy transfer induced by [4+2] cycloaddition. In this project, our aim was to design a similar system that will work in aqueous solutions due to possible future bioanalytical applications mentioned above. Herein, instead of using CPEs, we have decided to design such a system that will mimic the behavior of CPs, but will be prepared with an acrylic polymer formulation that is easier to make water soluble. Figure 4.1 shows the basic design and structure of this system. Later on in this project, we are planning to use these water-soluble polymers as dosimeters for sensitizer-labeled proteins without direct analyte-polymer interaction.

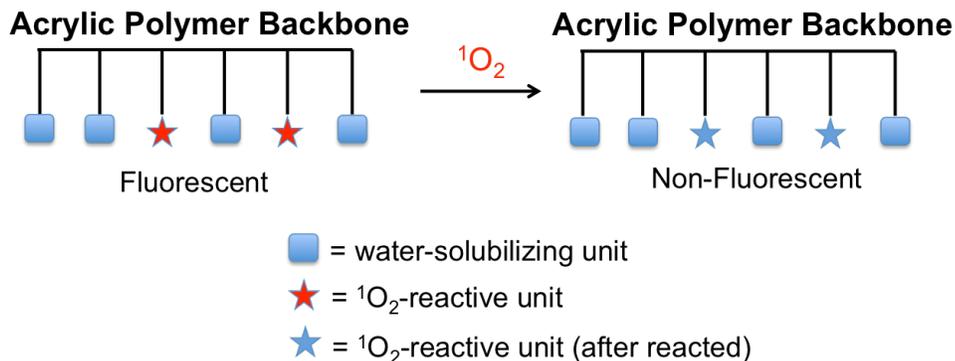


Figure 4.1. The initial design of an acrylic polymer that contains water-solubilizing and singlet oxygen reactive units.

4.2 Results and Discussion

Chart 4.1 shows the acrylic polymers with acene-containing side chains that we initially prepared and studied in this work. We chose acrylic polymer backbones for our polymers because of their facile synthesis via AIBN-initiated free radical polymerization at $65\text{ }^{\circ}\text{C}$ ²⁴ and modular solubility depending on the substituents. They are easier to make water soluble due to their more hydrophilic backbone, compared to CPs. Acenes were chosen as $^1\text{O}_2$ responsive unit due to our previous experience with the synthesis of differently substituted acenes.²⁵ We have decided to use diaryl-substituted acene derivatives because initial attempts for the AIBN initiated free radical polymerization using diethylnyl-substituted tetracene yielded a gel formation under classical radical polymerization conditions.

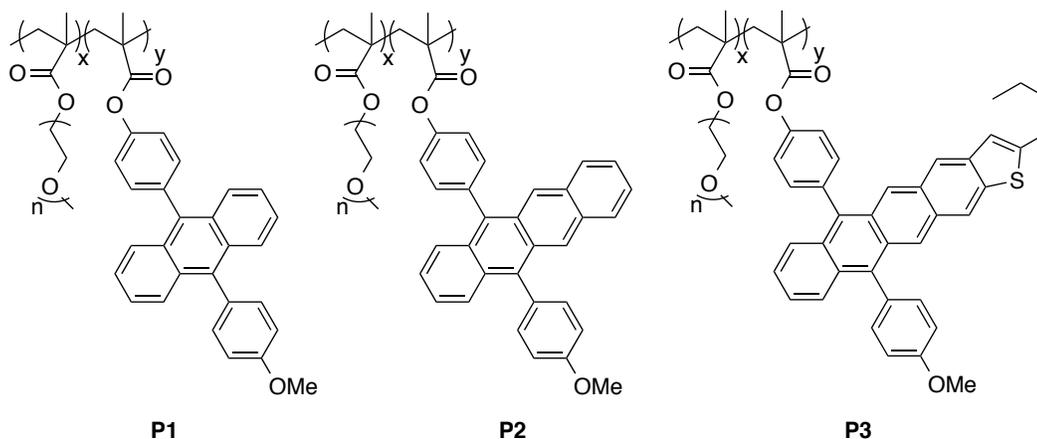
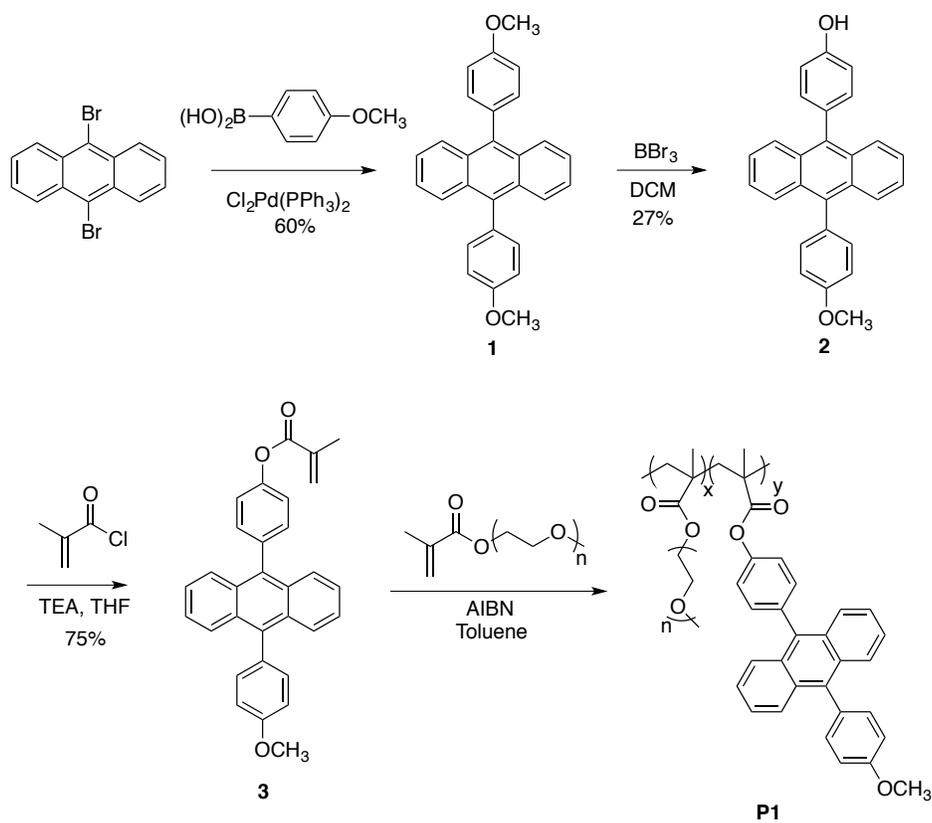


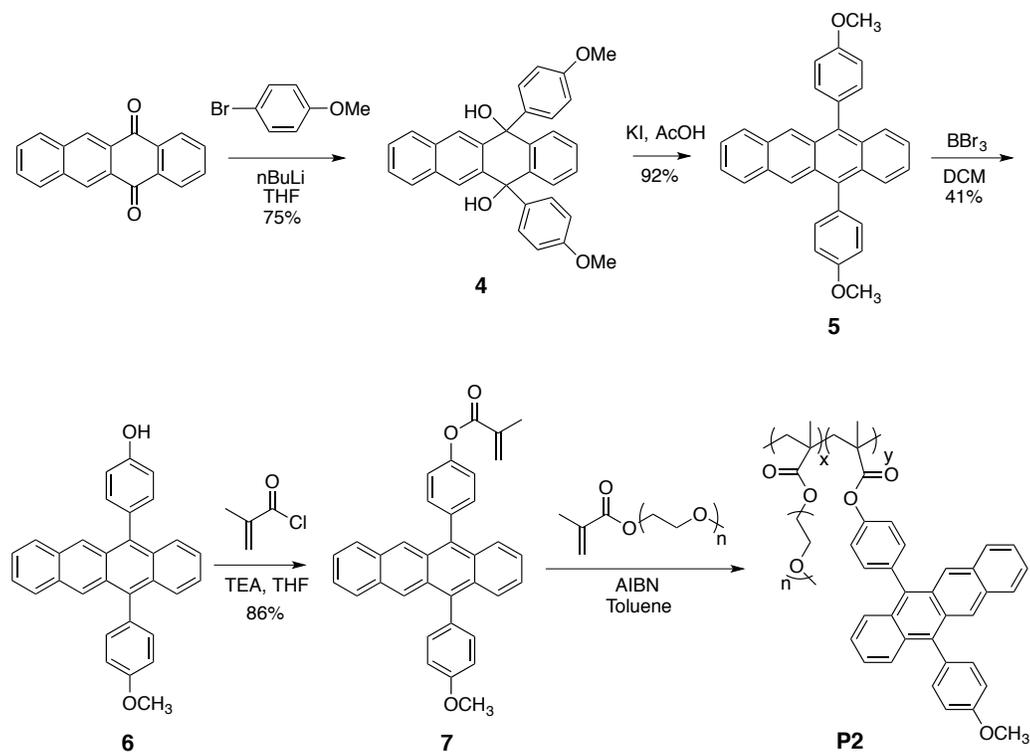
Chart 4.1. The structures of acene containing acrylic polymers. P1 contains anthracene, while P2 and P3 contain tetracene and tetracenomonothiophene, respectively.

4.2.1 Synthesis of Polymers that Contain Different Acenes as Side Chain

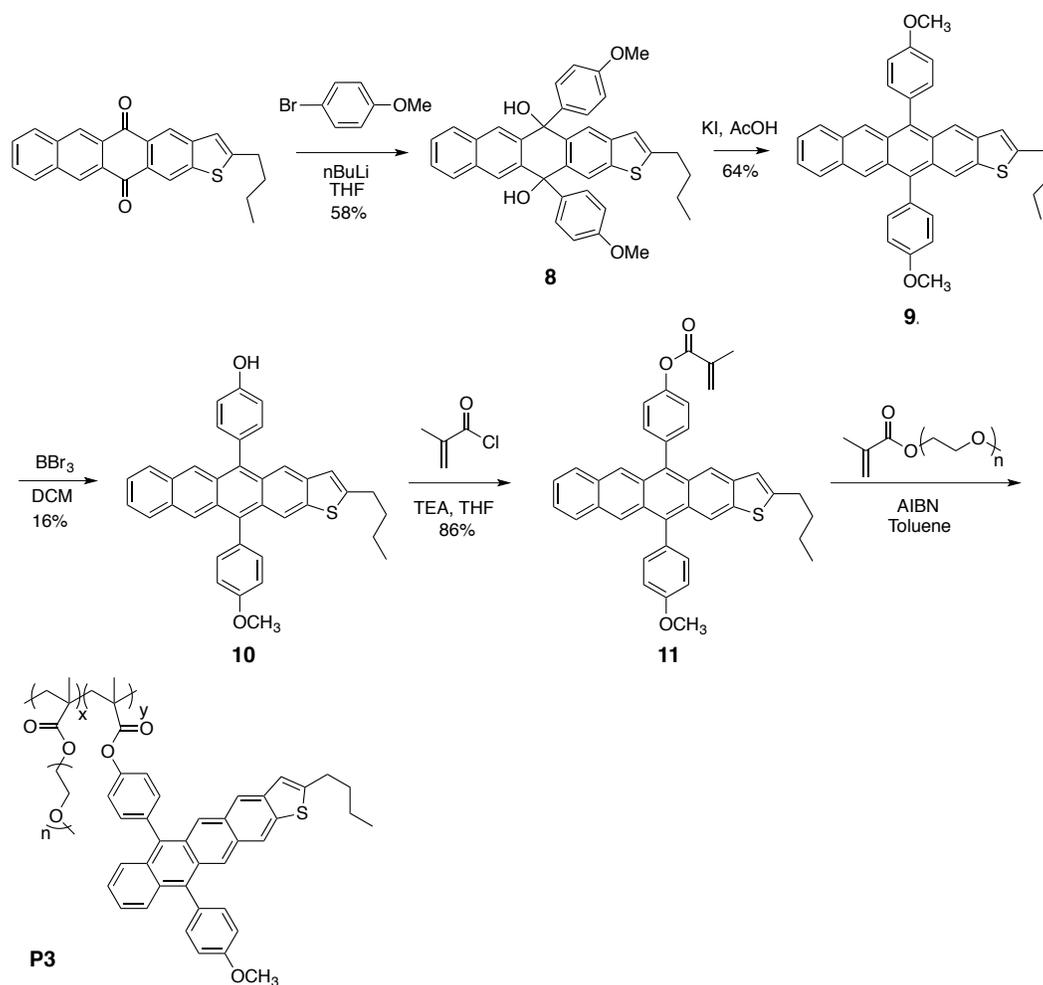
We prepared polymers **P1-P3** using free radical polymerization between the same poly(ethylene glycol) methyl ether methacrylate comonomer ($M_n=300$) and diaryl-substituted different acene monomers that can be used in acrylic polymer formulation. We prepared anthracene-linked polymer **P1** (Scheme 4.1) by addition of a slight excess of 4-methoxyphenylboronic acid, prepared using a previously reported strategy,²⁶ to 9,10-dibromoanthracene to yield **1**. Mono-deprotection of the methyl ether with BBr_3 followed by esterification with methacryloyl chloride yielded the desired anthracene-substituted monomer **3** that is amenable to free radical polymerization. We prepared tetracene and teracenomonothiophene (TMT)-linked polymers, **P2** and **P3**, (Scheme 4.2 and 4.3) by the addition of a slight excess of the lithium salt of 4-methoxybenzene, prepared using a previously reported strategy,²³ to either 5,12-tetracenequinone or 2-butyltetraceno[2,3-b]thiophene-5,12-dione (TMT quinone) followed by tin(II)-mediated reduction of the resulting diols to yield corresponding diaryl-substituted acenes **5** and **9**. Mono-deprotection of the methyl ether with BBr_3 followed by esterification with methacryloyl chloride yielded the corresponding monomers, **7** and **11**, which is useful in free radical polymerization. For the synthesis of TMT quinone, we followed a similar strategy that is published previously: 5-butylthiophene-2,3-dicarbaldehyde and anthracene-1,4-diol were reacted under basic conditions.²⁷ Finally, AIBN-initiated free radical polymerizations of monomers **3**, **7**, and **11** with poly(ethylene glycol) methyl ether methacrylate comonomer gave polymers **P1**, **P2**, and **P3**, respectively.



Scheme 4.1. Synthesis of anthracene-containing PEGMA, **P1**.



Scheme 4.2. Synthesis of tetracene-containing PEGMA, **P2**.



Scheme 4.3. Synthesis of tetracenomonothiophene (TMT)-containing PEGMA, **P3**.

4.2.2 Spectral Properties of P1-P3

We characterized each acene-containing polyethylene glycol methacrylate (PEGMA) by electronic absorbance spectrophotometry and fluorescence spectroscopy in H_2O . Figure 4.2 shows the normalized absorption spectra of polymers **P1-P3**. The shapes and spectral positions of these molecules are consistent with those reported in the literature and show characteristic bands of acenes: an intense absorbance band in the UV region of the spectrum and a lower

energy band that results from the vibronic transitions of linear acenes. The TMT-based long wavelength absorbance band between 475 and 575 nm is further red shifted due to the increased conjugation with respect to both tetracene and anthracene based long wavelength absorbance band, with the anthracene-based polymer displaying the most blue shifted absorbance.

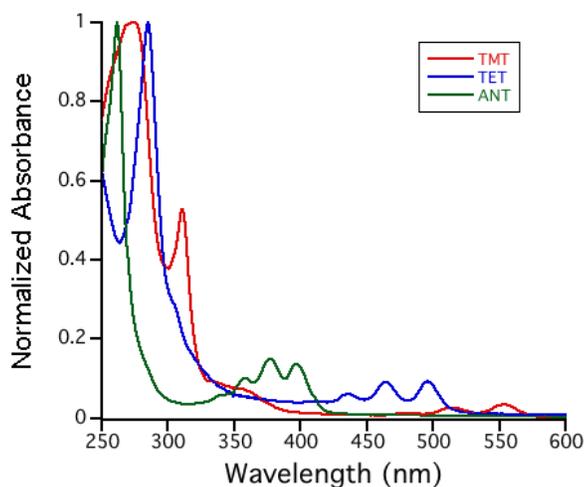


Figure 4.2. Normalized absorption spectra of acene containing **P1-P3**

Figure 4.3 shows normalized emission spectra of acene containing **P1-P3**. The emission spectra of all molecules follows a similar pattern to that found in absorbance: The emission of **P3** is red-shifted by 62 nm from **P2**, and **P2** is red-shifted by 85 nm from **P1** as a result of extended conjugation due to additional aromatic rings. All acenes described here are fluorescent with quantum yields of fluorescence of approximately 0.5. Absorption and emission maxima and quantum yields of all molecules are summarized in Table 4.1.

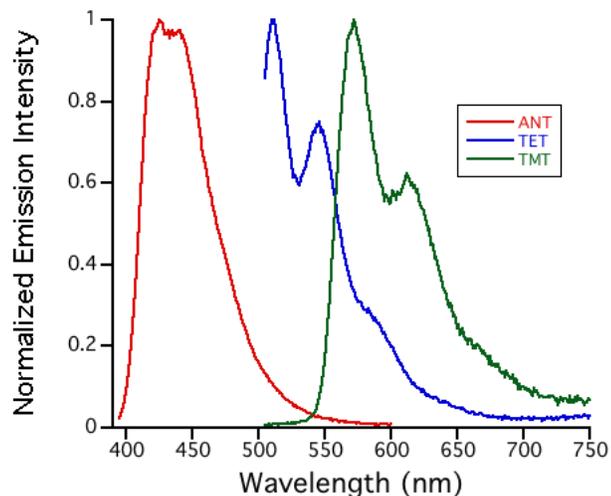


Figure 4.3. Normalized emission spectra of acene containing **P1-P3**

Table 4.1. Properties of **P1-P3**

Polymer	Mn(PDI)	$\lambda_{\text{max,abs}}(\text{nm})$	$\lambda_{\text{max,em}}(\text{nm})$	$\epsilon (\text{M}^{-1}\text{cm}^{-1})$	Φ_f
P1	36k (1.5)	377	425	-	-
P2	43k (1.5)	496	510	48k	0.52
P3	41k (1.4)	554	572	29k	0.44

4.2.3 $^1\text{O}_2$ Reactivity of P1-P3

To test our principal hypothesis that $^1\text{O}_2$ -induced oxidation of acene pendants on polymers would yield fluorescence quenching, we monitored the fluorescence spectra of **P1-P3** during photochemical generation of $^1\text{O}_2$ by selective irradiation of the photosensitizer MB in DI H_2O . The observations of fluorescence response of the acene linked non-conjugated polymers (NCPs) to $^1\text{O}_2$ are consistent with the oxidation of acene sides according to absorbance spectrum. All experiments were performed with identical concentrations of MB (at 653 nm) using a combination of high-pass filter (635 nm) and a Hg/Xe lamp to prevent

direct excitation of any chromophores other than MB. We followed the disappearance of the acenes as a function of irradiation time in each experiment by absorbance spectrophotometry followed by acquiring a fluorescence spectrum to monitor change in emission intensity. All polymers followed similar patterns in terms of decrease in emission intensity upon reaction with $^1\text{O}_2$, each with different reactivity. The absorbance and fluorescence spectra of all polymers can be found in experimental section. Upon cycloaddition reaction, the resulting absorbance data fit semilogarithmic linear regressions versus time with correlation coefficients of $R \geq 0.99$ and yielded relative pseudo-first order rate constants. Figure 4.4 shows the fits of the decrease in absorbance of the acene moieties to a pseudo-first order kinetic model. According to results, **P3** reacts two times faster than **P2**, and 12 times faster than **P1**.

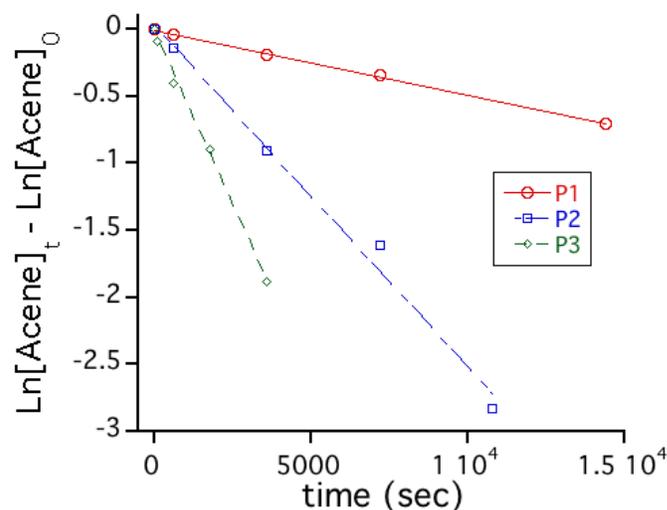


Figure 4.4. Pseudo-first-order kinetics of disappearance of the tetracene moiety of **P1**, **P2**, and **P3**.

The reactions of acenes in the NCPs are much more slower than we anticipated in H₂O. The polymer with the most reactive acene, **P3**, showed response to ¹O₂ with a 23% reduction in fluorescence intensity after 10 minutes of exposure to ¹O₂. The reaction was almost completed after 2 hours of exposure to ¹O₂ as shown in Figure 4.5. We attribute these results to two main reasons. First, lifetime of singlet oxygen in water is shorter than that of in chlorinated organic solvents.²⁸ Additionally, the amount of dissolved oxygen in water is less than that of in chlorinated organic solvents. In contrast to the slow response of **P3** in H₂O, exposure of **P3** to ¹O₂ under identical conditions but in D₂O led to significant change in the rate of reaction with a more than 50% reduction in the fluorescence intensity only after 2 minutes of exposure to ¹O₂ as shown in Figure 4.5. This change in the rate of reactivity can be explained with the longer lifetime of singlet oxygen in D₂O due to decreased coupling to bond vibrations in deuterated solvents.²⁸ **P1** and **P2** showed a similar response in D₂O with an increase in the rate of reaction as shown in experimental section Figure E1 and Figure E2, respectively.

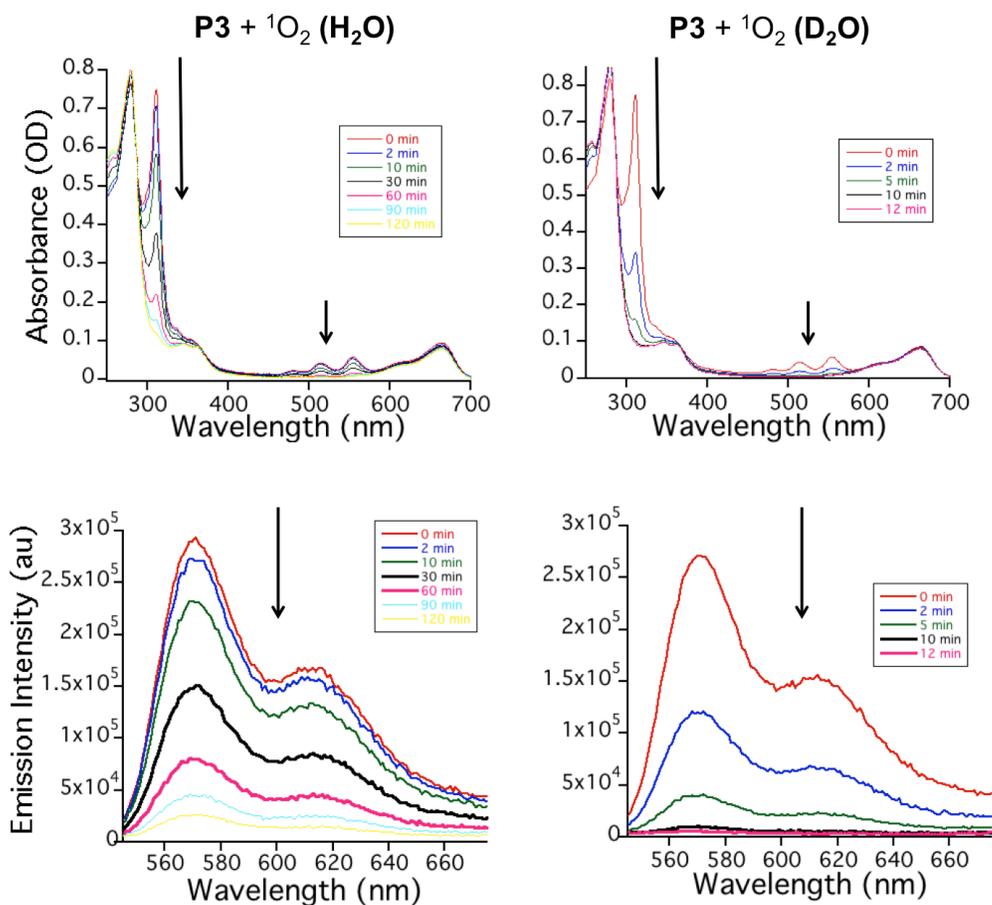


Figure 4.5. Singlet oxygen response of **P3** in H₂O (*left*) and D₂O (*right*).

4.2.4 Addition of Energy Donor

In light of this information collected from the reactions of **P1-P3** with ¹O₂, the next step was to introduce an energy donor to the system. That would improve the initial design in a way that instead of just fluorescence quenching, energy transfer from donor to the acceptor (acene) would yield a ratiometric response as represented in Chart 4.2. In this regard, coumarin was introduced as an energy donor because of facile synthesis of monomer that can be used in acrylic polymer formulation and good spectral overlap especially with **P2**.

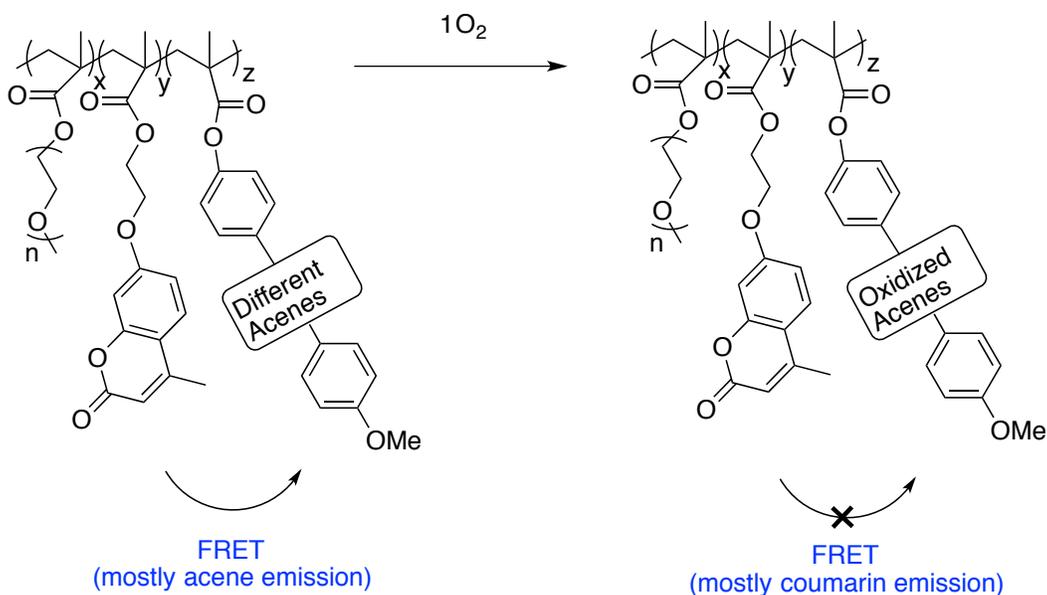


Chart 4.2. An illustration for design principle of Donor-Acceptor Polymers

4.2.5 Synthesis of Donor-Acceptor Polymers

Scheme 4.4 illustrates the synthetic scheme of coumarin-linked polymers with two different acenes: diaryltetracene (TET) and diaryltetracenomonothiophene (TMT). Alkylation of 7-hydroxy-4-methylcoumarin with 2-bromoethanol followed by the esterification with methacryloyl chloride yielded the desired coumarin-substituted monomer **13** that is amenable to free radical polymerization. We prepared the donor-acceptor polymers using AIBN-initiated free radical polymerization with the poly(ethylene glycol) methyl ether methacrylate comonomer ($M_n=300$), diaryl-substituted different acene monomers (**7** or **11**), and coumarin-substituted monomer **13**. We started with the preparation of the some polymers that contain 1% TET (the energy acceptor or A), but different amounts of coumarin (the energy donor or D). We chose TET as the comonomer to optimize the conditions because it requires

fewer steps to synthesize. The purpose is to keep the TET concentration as low as possible because of two main reasons: solubility in water and sensitivity. The 1% A and 5% D-containing polymer did not show complete energy transfer. Ideally, excitation of the donor chromophore results in emission from the acceptor chromophore in this scenario. However, although it shows a ratiometric response, an initial emission from the donor chromophore (coumarin) was observed before exposure to $^1\text{O}_2$ as shown in Figure 4.6. An increase in the local concentration of TET (acceptor) and coumarin (donor) moieties would increase the probability of creating donor-acceptor pair in the solution; therefore, would increase the efficiency of energy transfer. For this reason, we prepared a polymer that contains **5% A-10% D**. We also observed a ratiometric change in the fluorescence spectra this polymer upon reaction with $^1\text{O}_2$: while the emission at 515 nm decreased, emission at 396 nm increased. Also, almost none of the initial emission from the donor was observed, as shown in Figure 4.6, indicating an efficient energy transfer.

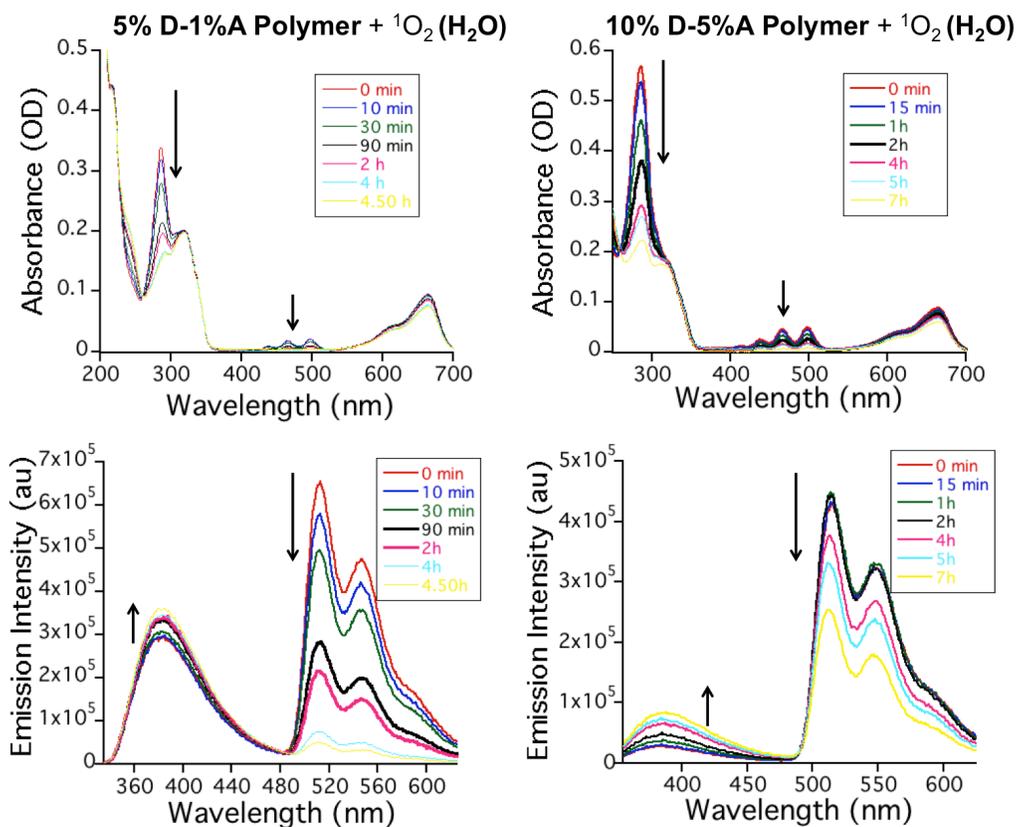
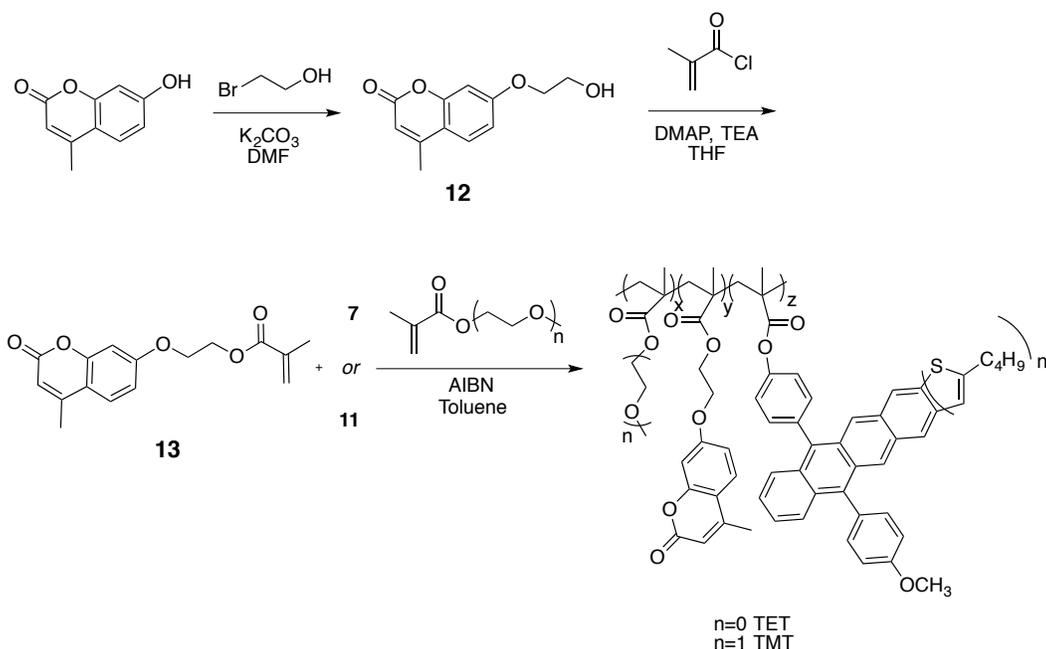


Figure 4.6. Singlet oxygen response of **5%D-1%TET** and **10%D-5%TET** polymers in H_2O .



Scheme 4.4. Synthesis of donor-acceptor polymers

4.2.6 $^1\text{O}_2$ Response of Donor-Acceptor Polymers

The 5% A-10% D polymer shows nearly completed energy transfer, but slower response to $^1\text{O}_2$ in terms of change in the fluorescence intensity although most of the acenes reacted by absorbance spectroscopy. Because TET side chains are very hydrophobic, they might tend to come together and the resulting high local concentration may be resulting in dynamic quenching like we have observed in conjugated polymers in previous chapter. Therefore, **3% A-15% D** and **2% A-15% D** polymers that contain less number of TET acceptor but more coumarin donors were prepared to optimize the conditions in terms of acceptor concentrations. According to the results of photophysical experiments performed with these polymers as shown in Figure E3 (experimental section), we decided to

move on with 2% acceptor containing conditions because of its faster response (Figure 4.7).

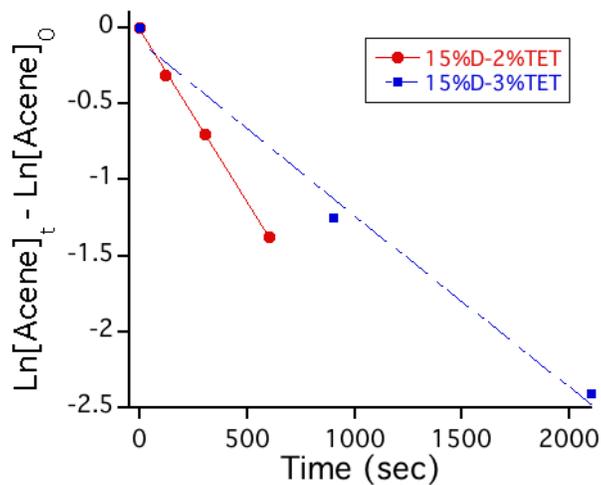


Figure 4.7. Pseudo-first-order kinetics of disappearance of the tetracene moiety of **15%D-2%TET** (red dots) and **15%D-3%TMT** (blue squares) polymers.

After we optimized the conditions by using diaryltetracene as an acceptor, we prepared a polymer with tetracenomonothiophene (TMT) with the best conditions that contains 15% of coumarin donor and 2% of TMT comonomer. As shown in Figure 4.8, it also showed a ratiometric change in the fluorescence spectra this polymer upon reaction with $^1\text{O}_2$. Figure 4.9 shows the comparison of ratiometric response of **15% D-2% TMT** compared to that of **15% D-2% TET**.

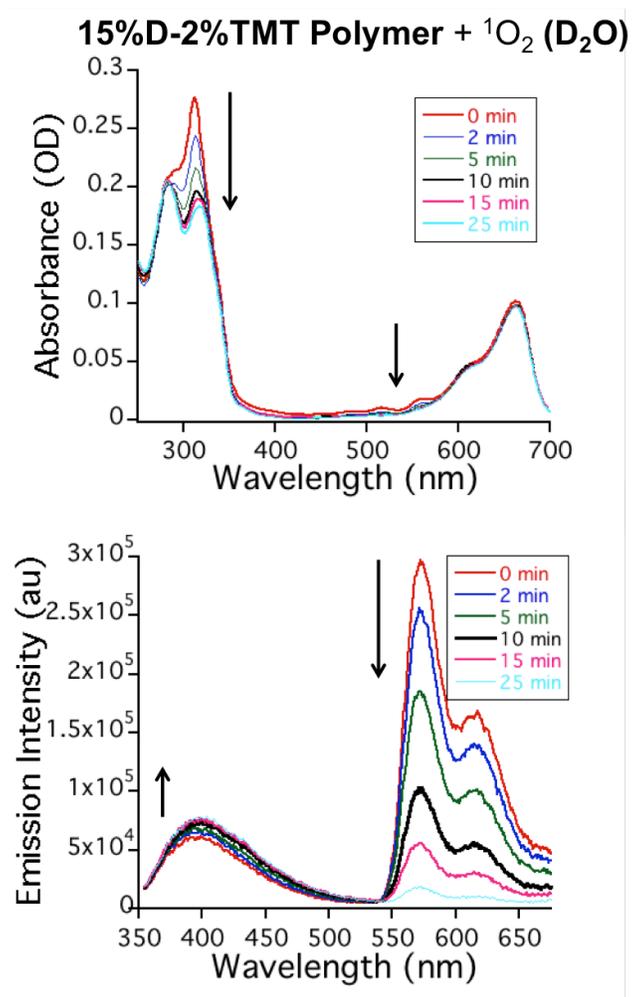


Figure 4.8. Singlet Oxygen Response of 15%D-2%TMT in D_2O .

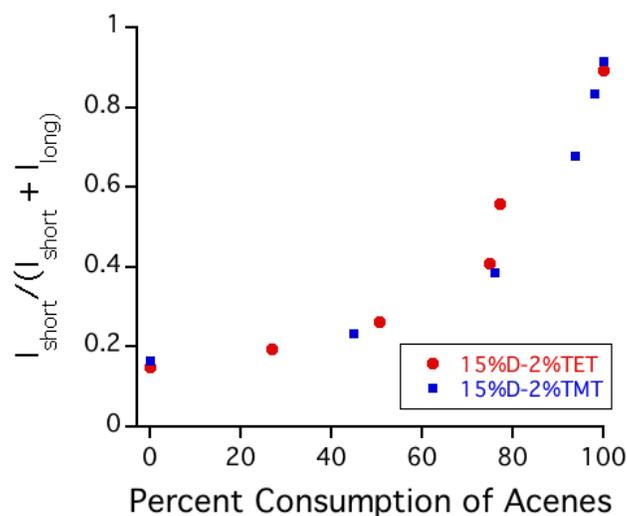


Figure 4.9. Comparison of ratiometric response of **15%D-2%TMT** (*blue dots*) compared to that of **15%D-2%TET** (*red dots*).

4.2.7 Comparison to Singlet Oxygen Sensor Green (SOSG)

We also compared singlet-oxygen response of **15% D-2% TET** polymer with that of commercially available fluorescent sensor named Singlet Oxygen Sensor Green (SOSG). SOSG is a detection reagent that is highly selective for singlet oxygen. In the light of previous studies, it is almost certain that SOSG is composed of fluorescein and anthracene moieties.^{29,30} It responds to singlet oxygen by turning on the emission of the fluorescein moiety as shown in Figure 4.10. According to the experiments performed under identical conditions, our polymer has a very compatible response in terms of rate as shown in Figure E4 in the experimental section. Additionally, the ratiometric response of our polymer is an important addition in terms of design perspective because it can improve the quantitative analysis through internal referencing.

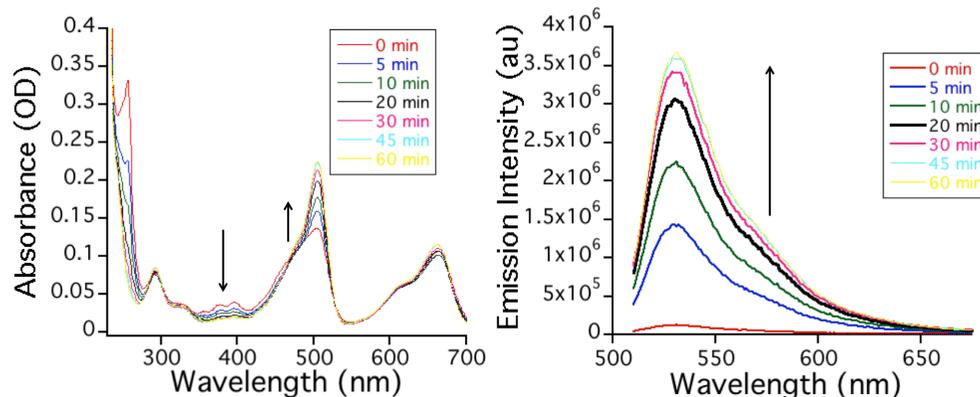


Figure 4.10. Singlet Oxygen Response of **SOSG**, a commercially available singlet-oxygen responsive reagent, in D_2O in the presence of MB.

4.2.8 Sensing the presence of labeled proteins

Figure 4.11 shows our approach using NCPs, which mimics the behavior of CPs for sensing the presence of labeled proteins. In this design, the NCP-based fluorescent dosimeter responds to 1O_2 that is generated by the sensitizer labeled to the protein. Therefore, it does not rely on direct interaction between the sensor and protein. To prove our hypothesis, Neutravidin protein was labeled with methylene blue, a commercially available dye with a reactive NHS-ester and 1O_2 sensitizer. The binding of protein (1 mM) to 10 mm polystyrene biotinylated microspheres in phosphate buffered saline (pH 7.4) yielded microspheres bound to methylene blue-labeled Neutravidin. The labeling and protein binding experiments are explained in detail in the experimental section.

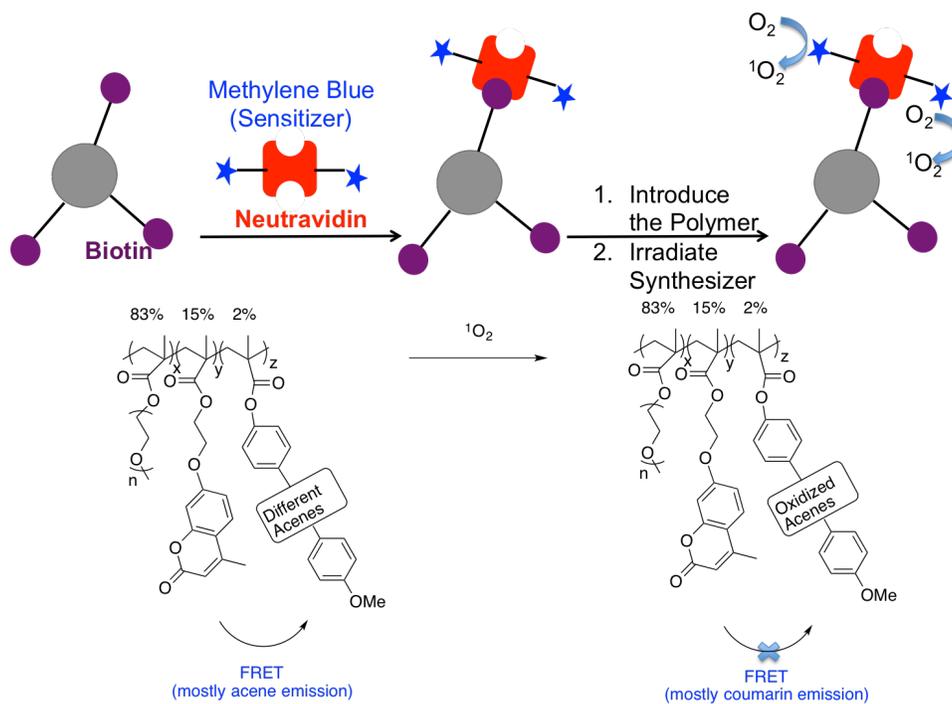


Figure 4.11. Experimental approach for determining presence of a sensitizer-labeled protein bound to the surface of the beads. Selective irradiation of a suspension of microsphere-bound MB labeled proteins generates 1O_2 , which reacts with the tetracene in polymer solution.

The centrifuged suspension of microspheres was diluted with D_2O , in which polymer was dissolved. We then monitored the fluorescence of the solution as a function of exposure to 1O_2 . 1O_2 was generated by irradiation of the solution with 635 nm high pass filter as in previous experiments. Figure 4.12 shows the fluorescent response of a **15% D-2% TET** solution to MB-labeled Neutravidin after 5 hours of exposure to singlet oxygen: no response to singlet oxygen generated by MB-labeled Neutravidin under these conditions.

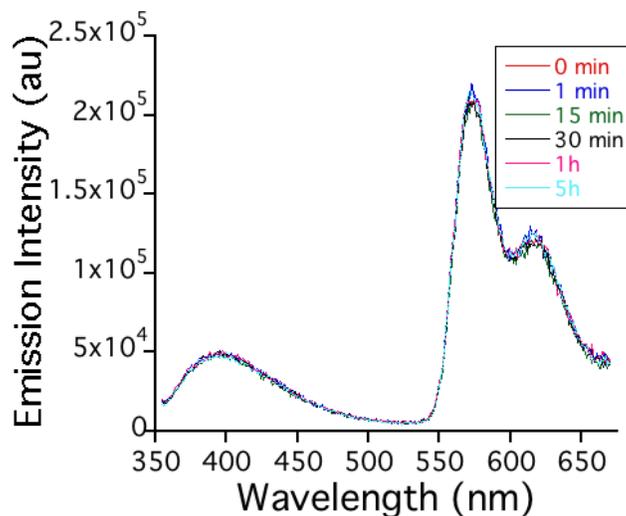


Figure 4.12. The fluorescent response of a **15%D-2%TET** solution to MB-labeled Neutravidin after exposure to singlet oxygen during 5 hours.

That made us take a step back and look at the singlet oxygen response in the presence of protein labeled with methylene blue. It showed a very slow response to $^1\text{O}_2$ in the presence of protein although concentration of methylene blue was kept about same with the previous experiments as can be seen Figure E5. We attribute this results to two main factors: a) NH-functionalized Methylene Blue can quench the $^1\text{O}_2$, and b) there may be good amount of free amine groups in the local environment due to the protein, which would quench the $^1\text{O}_2$. By taking into account of results previous published work in our lab,⁶ we have decided to label the protein with eosin instead of methylene blue.

Neutravidin protein was labeled with eosin, a commercially available dye with an amine-reactive isothiocyanate and $^1\text{O}_2$ sensitizer. The **15% D-2% TET** polymer showed ratiometric response to $^1\text{O}_2$ that was generated by irradiation of eosin-labeled protein as shown in Figure 4.13. However, when the polymer is dissolved in a solution of free eosin, there was a change in the absorption spectra of eosin itself as indication of aggregation. This is most probably as a result of hydrophobic-hydrophobic interactions with tetracene. These results suggest that eosin which is attached to the protein does not interact with the polymer noticeably most probably due to the fact that it is bound to protein which is bulky and water-soluble. Corresponding experiment by using SOSG in the presence of eosin-labeled neutravidin is very consistent with that of without protein. Our polymer has a very compatible response in terms of rate as shown in Figure E6 in the experimental section.

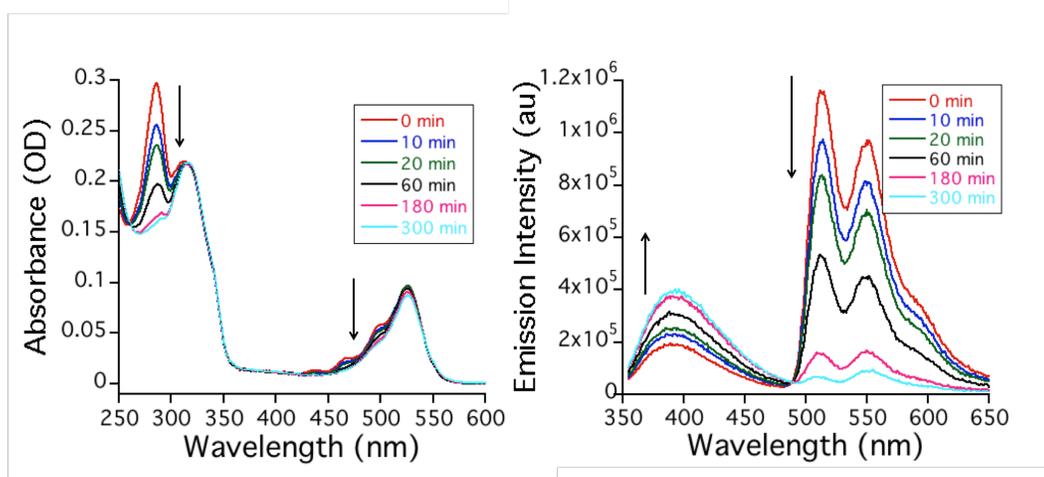


Figure 4.13. The response of **15%D-2%TET** in the presence of protein labeled with eosin.

4.3 Conclusion

This chapter demonstrates the synthesis and properties of a new series of diarylacene and coumarin linked non-conjugated polymers that show a ratiometric fluorescence response to $^1\text{O}_2$ by disrupting energy transfer. Our overall synthetic approach can be generalized for the preparation of water soluble counterparts of highly hydrophobic fluorescent molecules. Water solubility, the ratiometric response and the comparable rate of reaction between $^1\text{O}_2$ and diarylacenes in D_2O offer significant advantages over the commercially available dye, SOSG. The mimicking of the light harvesting properties of conjugated polymer electrolytes by using non-conjugated polymers makes the polymers developed in this study important candidates for bioanalytical applications, such as protein sensing, due to the indirect protein-NCP interaction. These results will help the development of new methods for the rational design of water soluble $^1\text{O}_2$ reactive materials as well as using them in bioanalytical applications.

4.4 Future Directions

Future experimentation will include the improvement of light harvesting properties by preparing block copolymers. This will help to keep the acene and coumarin moieties in a closer local environment, where the excitons generated can hop from one molecule to another. Another future experiment will be the improvement of the ratiometric response of diaryl-tetracenomonothiophene (DA-TMT) upon reaction with $^1\text{O}_2$, which offers more advantages in terms of reactivity. TMT reacts faster than TET; however, poorer spectral overlap between

coumarin and TMT limits its use in our experiments. Therefore, another donor, which has a better spectral overlap, should be introduced instead of coumarin. According to the previous work done in our lab,²⁵ lower reactivity towards to singlet oxygen granted with the good spectral overlap makes the diaryl-anthracenomonothiphenes (DA-AMT) a good candidate in this regard. Further effort will be focused on the development of these materials as well as optimizing the conditions for the protein sensing.

4.5 Experimental Considerations

4.5.1 General Considerations

All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (230-400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Chemical shifts are reported relative to residual protonated solvent for CHCl_3 . Molecular weight distribution measurements of the polymers were conducted with a Shimadzu Gel Permeation Chromatography (GPC) system equipped with a Tosoh TSKgel GMHhr-M mixed-bed column and guard column using either UV or refractive index detectors. The column was calibrated with low polydispersity poly(styrene) standards (Tosoh, PSt Quick Kit) with THF as the mobile phase eluting at 0.75 mL/min. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

4.5.2 Optical Experiments

All solution optical spectra were acquired of samples in quartz cuvettes (NSG Precision Cells). Electronic absorbance spectra were acquired with a Varian Cary-100 instrument in double-beam mode using a solvent-containing cuvette for background subtraction spectra. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Fluorescence spectra were acquired using sample absorbances less than 0.1 OD. Fluorescence quantum yields were determined relative to either quinine sulfate in 0.1 N H₂SO₄ or Coumarin 6 in ethanol. Irradiation of the methylene blue photosensitizer to generate ¹O₂ was performed with 200W Hg/Xe lamp (Newport-Oriel) equipped with a Hg/Xe lamp (Newport-Oriel) equipped with a condensing lens, recirculating water, shutter, and 635 nm high-pass filters.

4.5.2a Fluorescence Response to singlet Oxygen

A cuvette containing the test sample solution was irradiated for numerous timed intervals. Both the absorbance and fluorescence spectra were taken after each interval of irradiation. The absorbance for both methylene blue and samples was approximately 0.1 OD.

4.5.3 Supplementary Figures:

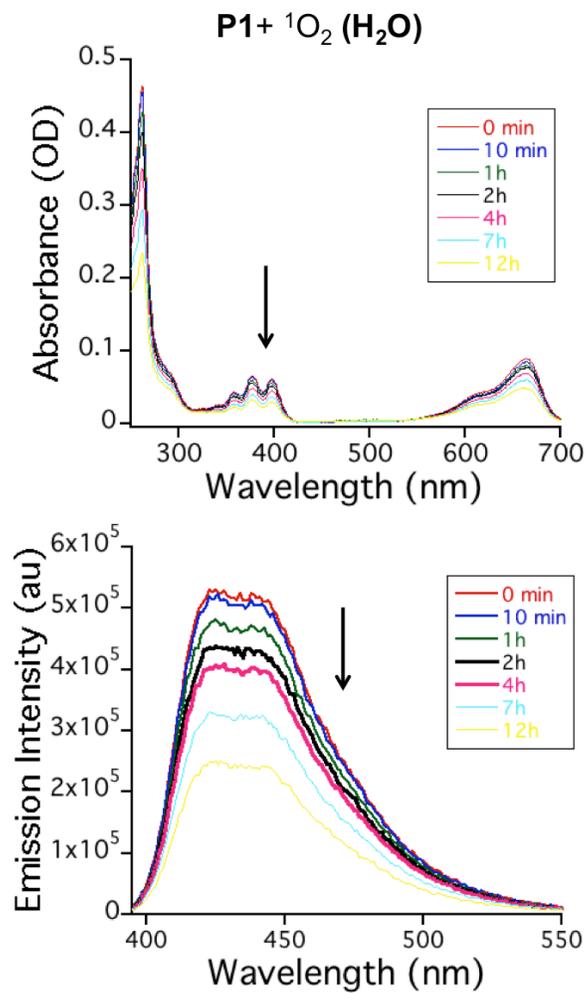


Figure E1. Singlet Oxygen Response of **P1** in H_2O

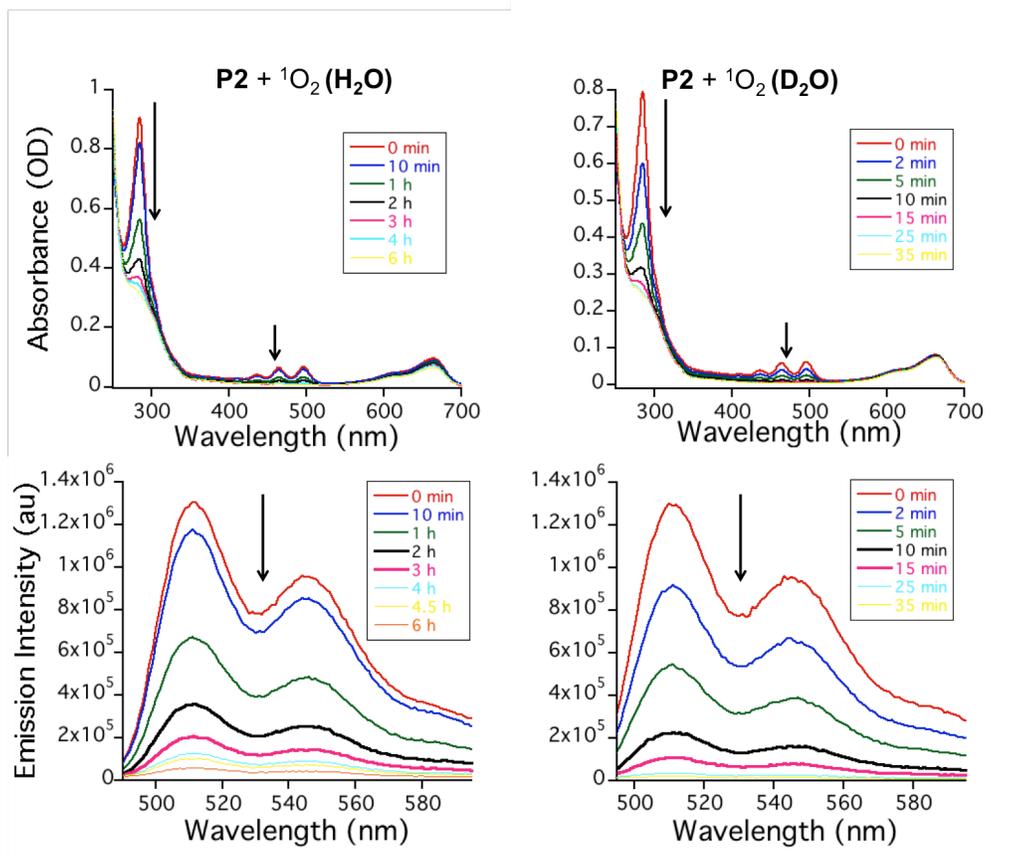


Figure E2. Singlet Oxygen Response of **P2** in H₂O and D₂O.

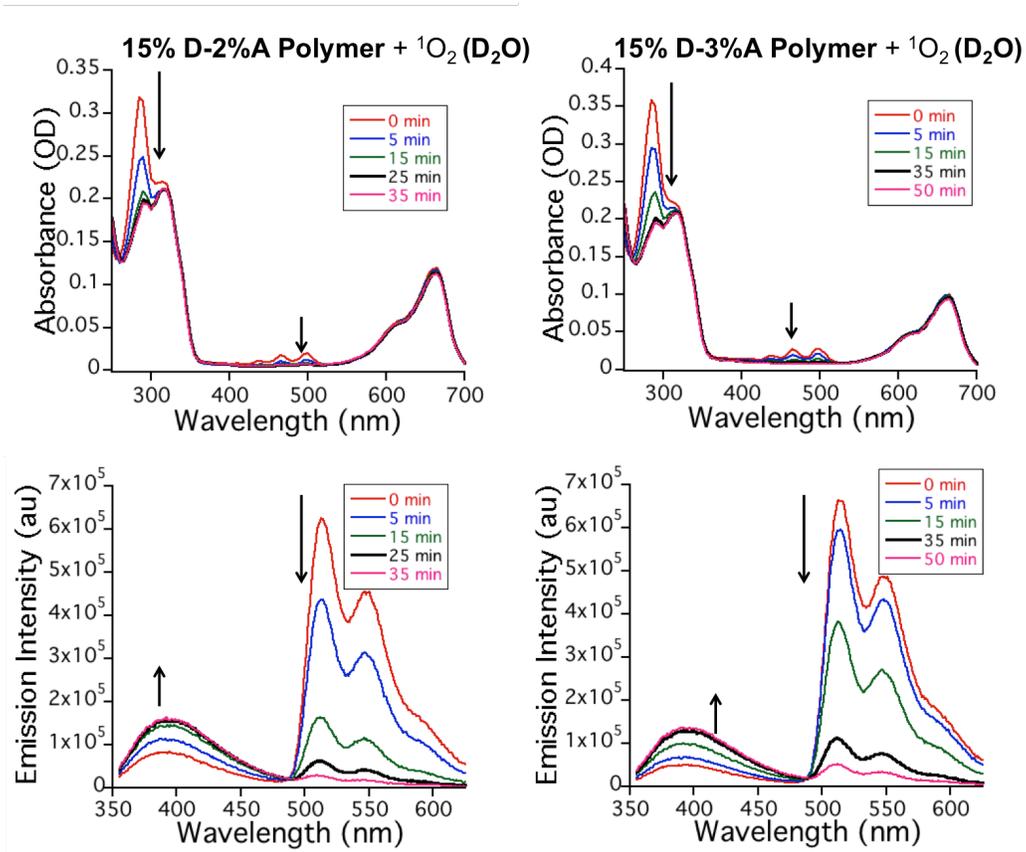


Figure E3. Singlet Oxygen Response of 15%D-2%TET and 15%D-3%TET polymers in H_2O .

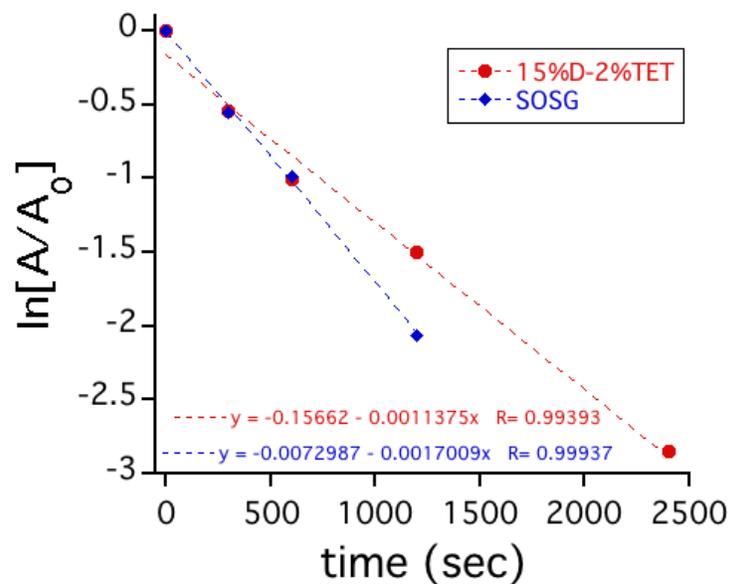


Figure E4. Pseudo-first-order kinetics of disappearance of the tetracene moiety of **15%D-2%TET** and **SOSG** in the presence of MB. (A is absorbance after reaction with singlet oxygen, while A_0 is absorbance before reaction.)

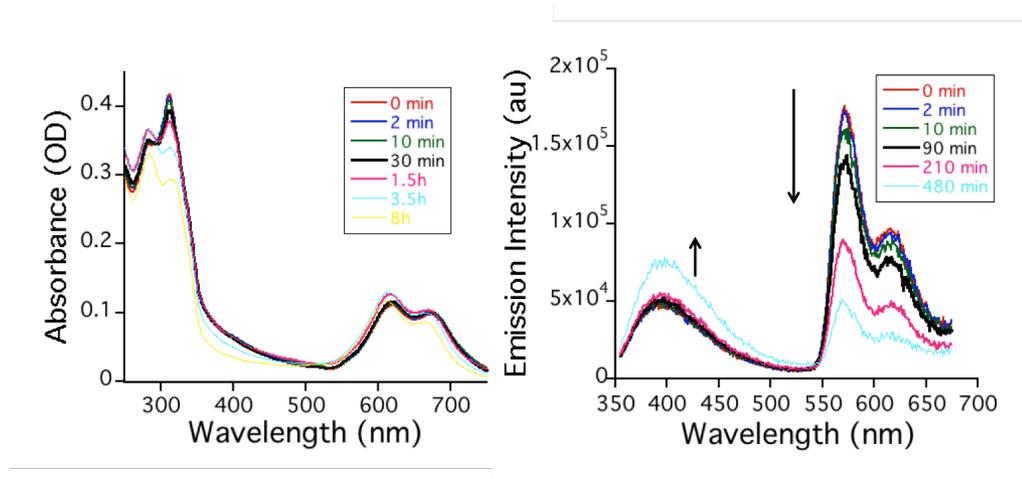


Figure E5. The response of **15%D-2%TET** in the presence of protein labeled with MB.

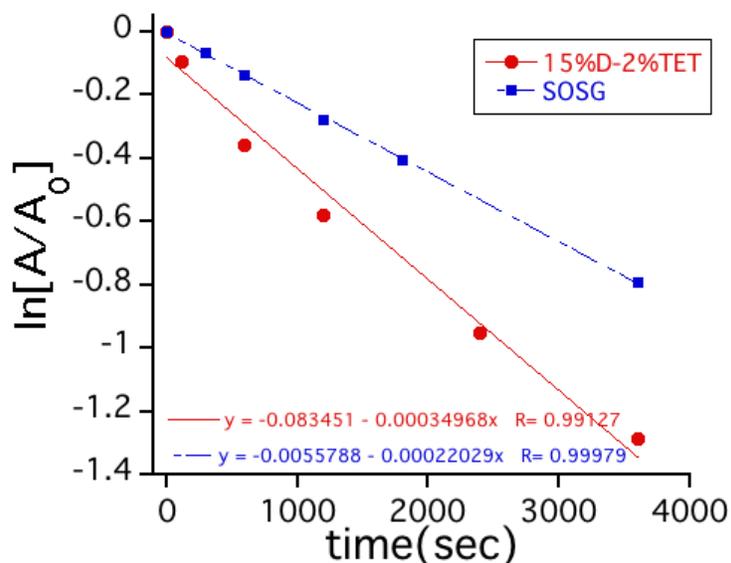


Figure E6. Pseudo-first-order kinetics of disappearance of the tetracene moiety of **15%D-2%TET** and **SOSG** in the presence of eosin-labeled protein. (A is absorbance after reaction with singlet oxygen, while A_0 is absorbance before reaction.)

4.5.4 Protein Labeling and Binding to Microspheres

4.5.4a Protein Labeling with Methylene Blue NHS ester

Neutravidin Biotin Binding Protein (7.5 mg, Thermo Scientific) was dissolved in 0.75 mL of 0.10 M bicarbonate buffer at pH 9.0 in an eppendorf tube. In another eppendorf tube, Methylene Blue NHS ester (2.6 mg) was dissolved in 0.26 mL of DMF and immediately added to the protein solution, with continuous stirring for an hour at room temperature. Sephadex column was prepared to separate the Neutravidin-Methylene Blue conjugate from any excess unlabeled Methylene Blue NHS ester. Approximately 5 g of Sephadex G-50 was allowed to swell overnight in excess distilled water. The Sephadex gel filtration column was then prepared using 0.10 M pH 9 carbonate buffer as the eluent. An absorbance

spectrum of the fraction containing the conjugate was acquired. The concentration of the labeled protein was determined as 0.8 μM at 280 nm by taking into account for additional absorbance at 280 nm from the methylene blue.

Biotinylated polystyrene microspheres (Bangs Labs), 1% solids in 1 mL with a diameter of 10 μm , were then washed three times with 10 mL of 0.10 M phosphate-buffered saline (PBS) buffer, pH 7.4. The washed microspheres was obtained by centrifugation at 4000 rpm for 5 min and decanting the solution. 10 mL of the solution of Neutravidin-Methylene Blue conjugate (0.8 μM) was added to the suspension of biotinylated microspheres and incubated for 30 min at room temperature with gentle stirring. Washing and centrifuging was done three times using 10 mL 0.10 M PBS (pH 7.4). The Neutravidin-Methylene Blue-bound microspheres were stored at 4 $^{\circ}\text{C}$ in 10 mL PBS. For the singlet oxygen response experiment, after centrifuging and decanting of the PBS, the polymer dissolved in D_2O was added the Neutravidin-Methylene Blue-bound microspheres.

4.5.4b Protein Labeling with Eosin

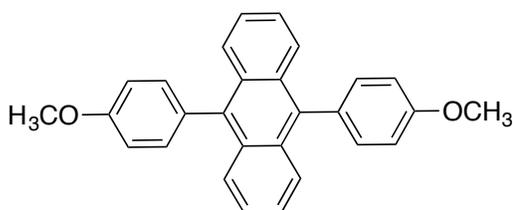
Neutravidin Biotin Binding Protein (10 mg, Thermo Scientific) was dissolved in 1.0 mL of 0.10 M bicarbonate buffer at pH 9.4 in an eppendorf tube. In another eppendorf tube, eosin-5-isothiocyanate (5 mg) was dissolved in 0.5 mL of DMF and 100 μL of it immediately added to the protein solution, with continuous stirring for an hour at room temperature. Sephadex column was prepared to separate the Neutravidin-Eosin conjugate from any excess Eosin. Approximately 5 g of Sephadex G-50 was allowed to swell overnight in excess

distilled water. The Sephadex gel filtration column was then prepared using 0.10 M pH 9.4 carbonate buffer as the eluent. An absorbance spectrum of the fraction containing the conjugate was acquired. The concentration of the labeled protein was determined as 0.6 μM at 280 nm by taking into account for additional absorbance at 280 nm from the methylene blue.

4.5.5 Detailed Synthetic Procedures

Synthesis of Anthracene containing Monomer

9,10-Bis-(4-methoxyphenyl)-anthracene (1)

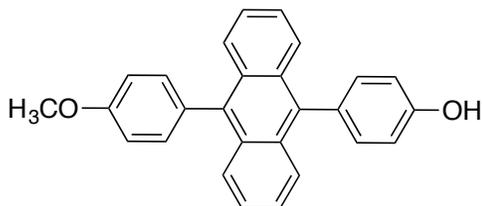


4-methoxyphenylboronic acid (525 mg, 3.45 mmol, 2.2 eq) and 9,10-dibromoanthracene (525 mg, 1.56

mmol, 1 eq) was placed in a 100 mL of two neck flask and evacuated and refilled with argon three times. Na_2CO_3 (415 mg, 3.92 mmol, 2.5 eq) was dissolved in 5 ml of DI H₂O and then added to reaction mixture followed by the addition of 30 ml of THF/Toluene (1:1) mixture. The suspension was then deoxygenated by sparging with argon for 30 minutes followed by the addition of $\text{Pd}(\text{PPh}_3)_4$ (52.5 mg, 0.045 mmol, 0.03 eq) under an argon atmosphere. The mixture was heated to 85 °C and stirred overnight. The mixture was then cooled to room temperature and stopped by adding water. Organics were extracted twice with Et_2O , and combined organic phases were washed with brine and dried over MgSO_4 , filtered and concentrated using rotary evaporation. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (3:1, v/v) to yield **1**.

Yield: 235 mg (60%). ^1H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.³¹

4-(10-(4-methoxyphenyl)anthracen-9-yl)phenol (**2**)



Compound **1** (215 mg, 0.55 mmol, 1.0 eq)

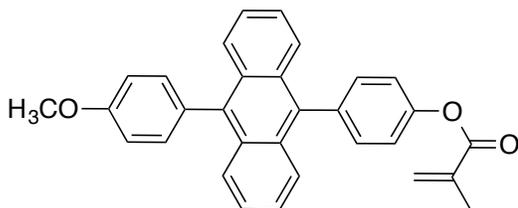
was suspended in 35 mL of dry CH_2Cl_2 ,

followed by the addition of BBr_3 (0.55

mL, 1.0 M in CH_2Cl_2 , 0.55 mmol, 1 eq) at

$-78\text{ }^\circ\text{C}$ under argon and stirred overnight at room temperature. The reaction was stopped by adding 10% $\text{HCl}_{(\text{aq})}$. Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with water and brine, dried over MgSO_4 , and filtered. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **2**. Yield: 55 mg (27%). ^1H NMR (500 MHz, CDCl_3): δ 7.77-7.76 (m, 4H), 7.43-7.41 (m, 2H), 7.38-7.35 (m, 6H), 7.18-7.16 (m, 2H), 7.11-7.09 (m, 2H), 4.89 (s, 1H), 3.99 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 159, 154.9, 132.6, 132.4, 131.4, 131.1, 130.3, 127.1, 126.9, 124.9, 124.8, 115.4, 113.9, 55.4.

4-(10-(4-methoxyphenyl)anthracen-9-yl)phenyl methacrylate (**3**)



Compound **2** (55 mg, 0.15 mmol, 1.0

eq) and DMAP (catalytic amount) was

placed in a 25 mL of two neck flask

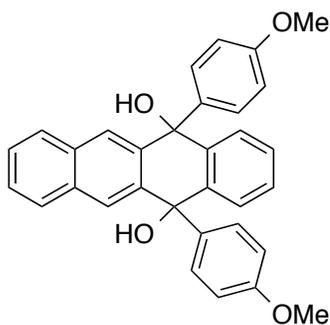
and evacuated and refilled with argon

three times. Then, 0.1 mL of dry Et_3N and 3.6 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (14.3 μL ,

0.15 mmol, 1 eq) at 0 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 5% aqueous NaHCO₃. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with water and brine, dried over MgSO₄, and filtered. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (1:1, v/v) to yield **3**. Yield: 50 mg (75%). ¹H NMR (500 MHz, CDCl₃): δ 7.79-7.74 (m, 4H), 7.53 (d, J=8.5 Hz, 2H), 7.43-7.40 (m, 4H), 7.38-7.36 (m, 4H), 7.18 (d, J=8.5 Hz, 2H), 6.49 (s, 1H), 5.86 (s, 1H), 3.99 (s, 3H), 2.18 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 165.9, 159.1, 150.4, 137.2, 136.6, 136, 135.9, 132.37, 132.36, 131.1, 130.2, 130, 127.4, 127.1, 126.9, 125.1, 124.9, 121.7, 113.9, 55.4, 18.4.

Synthesis of tetracene containing polymer

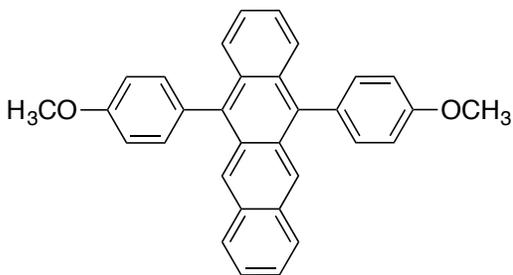
5,12-bis(4-methoxyphenyl)-5,12-dihydro-tetracene-5,12-diol (4)



30 mL dry THF was added to 1-bromo-4-methoxybenzene (6.8 mL, 54 mmol, 7 eq), followed by dropwise addition of *n*-butyllithium (29 mL, 46.5 mmol, 6 eq, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred *via* cannula to 5,12-naphthacenequinone (2 g, 7.75 mmol, 1 eq), which was dissolved in 100 mL dry THF and cooled to -78 °C. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. It was then washed with 10% aqueous HCl and extracted with CH₂Cl₂. The organic layer was washed with brine and dried over

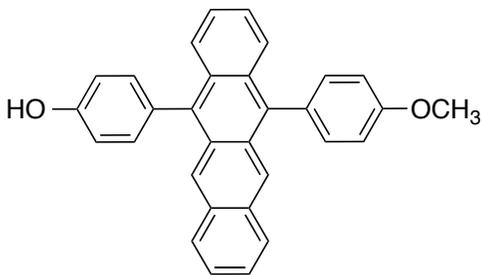
MgSO₄. The crude product was purified *via* flash chromatography using hexanes and EtOAc (1.5:1, v/v) to yield **4**. Yield: 2.77 g (75%). ¹H and ¹³C NMR of this compound is in good agreement with the same compound reported in the literature.³²

5,12-bis(4-methoxyphenyl)tetracene (**5**)



Compound **4** (2.77 g, 5.8 mmol, 1 eq) and potassium iodide (4.62 g, 28 mmol, 4.8 eq) was dissolved in 115 mL of Acetic acid at room temperature. The reaction mixture was then heated to 115 °C for 2 hour. After cooling to room temperature, 300 mL deionized H₂O was added to the reaction mixture, and the resulting orange solid was collected *via* vacuum filtration and washed with deionized H₂O. The crude product was used without further purification. Yield 2.3 g (92%). ¹H and ¹³C NMR of this compound is in good agreement with the same compound reported in the literature.³²

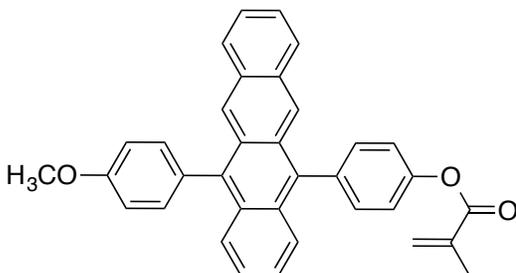
4-(12-(4-methoxyphenyl)tetracen-5-yl)phenol (**6**)



Compound **5** (500 mg, 1.13 mmol, 1.0 eq) was dissolved in 56 mL of dry CH₂Cl₂, followed by the addition of BBr₃ (1.13 mL, 1.0 M in CH₂Cl₂, 1.13 mmol, 1 eq) at -78 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 10% HCl_(aq). Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed

with water and brine, dried over MgSO_4 , and filtered. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **6**. Yield: 200 mg (41%). ^1H NMR (500 MHz, CDCl_3): δ 8.38 (s, 1H), 8.37 (s, 1H), 7.84-7.82 (m, 2H), 7.77-7.74 (m, 2H), 7.51-7.49 (m, 2H), 7.46-7.44 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.22 (m, 2H), 7.17-7.15 (m, 2H), 4.95 (s, 1H), 4.04 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 159.1, 155, 136.7, 136.5, 132.8, 132.6, 131.7, 131.4, 130.94, 130.93, 129.7, 129.51, 129.49, 128.44, 128.41, 127.1, 127, 125.8, 125.7, 125.14, 125.11, 124.7, 124.6, 115.5, 114, 55.4.

4-(12-(4-methoxyphenyl)tetracen-5-yl)phenyl methacrylate (**7**)

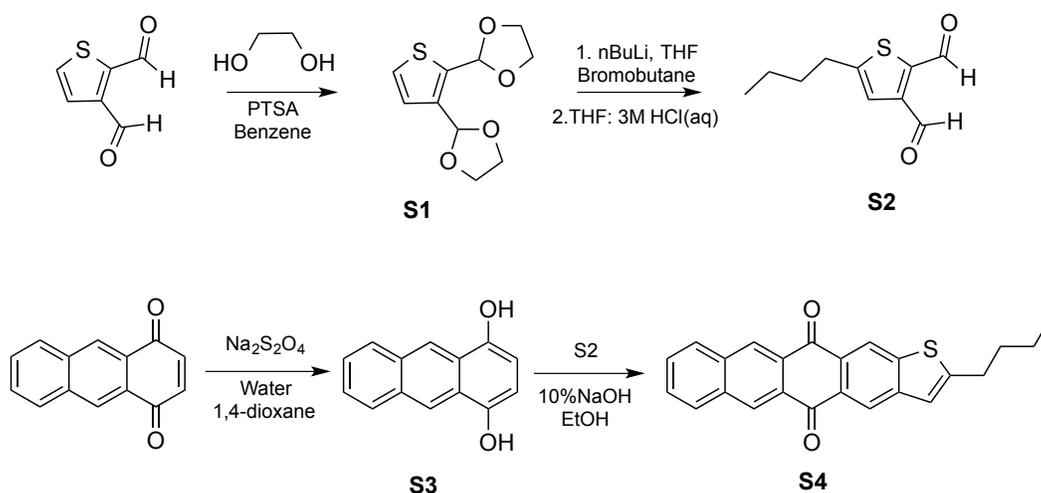


Compound **6** (160 mg, 0.38 mmol, 1.0 eq) and DMAP (4.8 mg, 0.04 mmol, 0.1 eq) was placed in a 25 mL two neck flask and evacuated and refilled

with argon three times. Then, 0.25 mL of dry Et_3N and 6 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (38 μL , 0.38 mmol, 1 eq) at 0 $^\circ\text{C}$ under argon and stirred overnight at room temperature. The reaction was stopped by adding 5% aqueous NaHCO_3 . Organics were extracted twice with CH_2Cl_2 , and combined organic phases were washed with water and brine, dried over MgSO_4 , and filtered. The crude product was purified *via* flash chromatography using hexanes and ethyl acetate (4:1, v/v) to yield **7**. Yield: 162 mg (86%). ^1H NMR (500 MHz, CDCl_3): δ 8.39 (s, 1H), 8.36 (s, 1H), 7.86-7.83 (m, 2H), 7.77-7.75 (m, 1H), 7.73-7.71 (m, 1H), 7.61-7.59 (m, 2H), 7.51-7.46 (m, 4H), 7.35-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.23 (m,

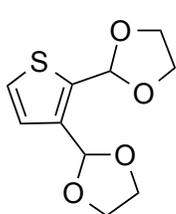
2H), 6.51 (s, 1H), 5.89 (t, 1H), 4.04 (s, 3H), 2.2 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 166, 159.2, 150.5, 137.1, 136.8, 136, 135.8, 132.6, 131.3, 131.1, 130.9, 129.6, 129.5, 129.4, 129.2, 128.43, 128.4, 127.5, 127.1, 126.9, 125.9, 125.5, 125.3, 125.2, 125.1, 124.9, 124.7, 121.8, 114, 55.4, 18.5.

Synthesis of TMT containing polymer



Scheme 4.5. Synthesis of TMT quinone.

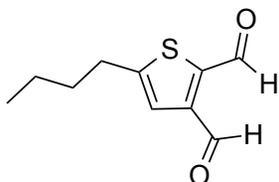
2,3-Bis(1,3-dioxolan-2-yl)thiophene (S1)



2,3-Thiophenedicarboxaldehyde (2 g, 14 mmol, 1.0 eq), *p*-toluenesulfonic acid monohydrate (6 mg, 0.03 mmol, 0.002 eq), and ethylene glycol (3.9 ml, 70 mmol, 5 eq) were dissolved in 25 mL of benzene. The mixture was refluxed and water was collected in a Dean-Stark trap. After cooling, the reaction mixture was washed with 10% NaOH, then H_2O and dried over MgSO_4 . The crude product was used directly in the next step without further purification. ^1H and ^{13}C NMR of this

compound is in good agreement with the same compound reported in the literature.³³

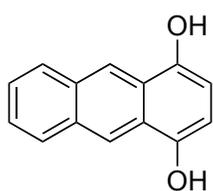
5-butyl-2,3-thiophenedicarboxaldehyde (S2)



Compound S1 (3 g, 13 mmol, 1 eq) was dissolved in 27 mL of dry THF under Argon and cooled to -78°C. *n*-BuLi (10.8mL, 17 mmol, 1.3 eq, 1.6 M in hexane) was then added dropwisely. After 75 minutes of stirring, 1-bromobutane (2.1 mL, 18 mmol, 1.4 eq) was added. The solution was left to warm to room temperature and stirred overnight. Organics were extracted twice with diethylether, and combined organic phases were washed with water and brine, dried over MgSO₄, and filtered. The crude product was purified *via* flash chromatography using hexanes and ethyl acetate (2:1, v/v) to yield 2,3-Bis(1,3-dioxolan-2-yl)-5-butylthiophene. Yield: 2 g (54%). The crude product was used directly in the next step without further purification.

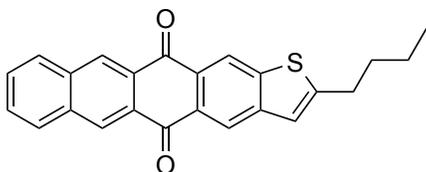
A solution of 1.4 g of 2,3-Bis(1,3-dioxolan-2-yl)-5-butylthiophene in 50 mL of THF:3M HCl (1:1) was stirred at room temperature for 4 hours. The mixture was extracted with diethylether. The combined organic phases was washed with water and brine, and dried over MgSO₄. The crude product was used directly in the next step without further purification. ¹H NMR (500 MHz, CDCl₃): δ 10.4 (s, 1H), 10.3 (s, 1H), 7.35 (s, 1H), 2.91 (t, 2H), 1.76-1.7 (m, 2H), 1.47-1.39 (m, 2H), 0.99 (t, 3H) ¹³C NMR (125 MHz, CDCl₃): δ 184.8, 182.2, 156.3, 145, 143.9, 126.9, 33.2, 30.2, 22.1, 13.7.

1,4-Dihydroxyanthracene (S3).



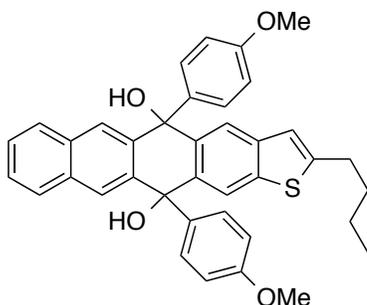
1,4-anthraquinone (850 mg, 4.1 mmol, 1 eq) and $\text{Na}_2\text{S}_2\text{O}_4$ (2.3 g, 15.5 mmol, 3.8 eq) was placed in a 100 ml round bottom flask and evacuated and refilled with argon three times. A solution of 40 ml of 1,4-dioxane: H_2O (1:1) was then added to the flask and stirred overnight at room temperature. The precipitate was collected by filtration and filtrate was diluted with EtOAc. Organic phase were washed twice with water and brine, dried over MgSO_4 , and filtered. The crude product was used directly in the next step without further purification. ^1H and ^{13}C NMR of this compound is in good agreement with the same compound reported in the literature.³⁴

2-butyltetraceno[2,3-b]thiophene-5,12-dione (TMT quinone) (S4)



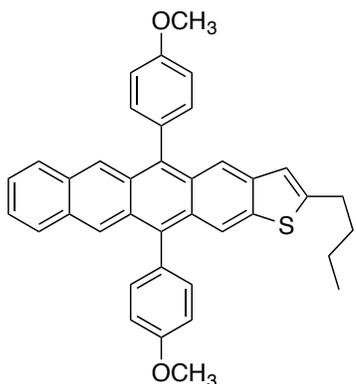
Compound **S2** (142 mg, 0.72 mmol, 1 eq) and **S3** (152 mg, 0.72 mmol, 1 eq) were dissolved in 6 mL of ethanol, and the mixture was vigorously stirred for 1 h at room temperature followed by the addition of 1 mL of 10% aqueous NaOH. After stirring at room temperature for 1 hour, the precipitate was collected via vacuum filtration. The crude product was used directly in the next step without further purification. Yield: 225 mg (85%). ^1H NMR (500 MHz, CDCl_3): δ 8.91 (s, 2H), 8.83 (s, 1H), 8.69 (s, 1H), 8.14-8.12 (m, 2H), 7.72-7.7 (m, 2H), 7.27 (s, 1H), 3.01 (t, 2H), 1.85-1.79 (m, 2H), 1.53-1.47 (m, 2H), 1.01 (t, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 183.3, 182.9, 154.1, 144.7, 144.3, 135.24, 135.19, 130.8, 130.3, 130.1, 129.5, 129.3, 122.4, 122.3, 121.7, 32.9, 30.9, 22.3, 13.8.

2-butyl-5,12-bis(4-methoxyphenyl)-5,12-dihydrotraceno[2,3-*b*]thiophene-5,12-diol(8)



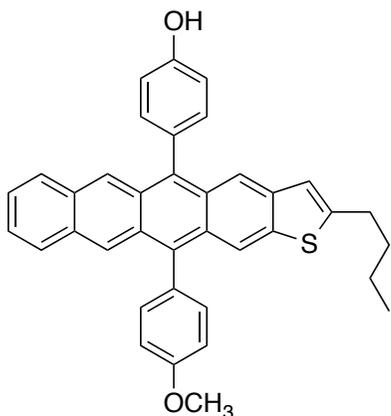
16 mL dry THF was added to 1-bromo-4-methoxybenzene (0.73 mL, 5.8 mmol, 4.6 eq), followed by dropwise addition of *n*-butyllithium (3.5 mL, 46.5 mmol, 5.7 eq, 1.6 M in hexanes) at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred *via* cannula to **S2** (470 mg, 1.26 mmol, 1 eq), which was dissolved in 16 mL dry THF and cooled to -78 °C. Upon completion of transfer, the reaction mixture was allowed to warm to room temperature and stirred overnight under argon. After removal of solvent, organics were dissolved in CH₂Cl₂ and then washed with 10% aqueous HCl. The combined organic layer was washed with brine and dried over MgSO₄. The crude product was purified *via* flash chromatography using hexanes and EtOAc (2:1, v/v) to yield **8**. Yield: 430 mg (58%). ¹H NMR (500 MHz, CDCl₃): δ 8.91 (s, 2H), 8.34 (s, 3H), 8.23 (s, 1H), 7.91-7.89 (m, 2H), 7.57-7.54 (m, 2H), 7.06 (s, 1H), 6.51 (m, 4H), 6.17-6.15 (m, 4H), 3.57 (s, 6H), 2.98 (t, 3H), 1.84-1.78 (m, 2H), 1.53-1.45 (m, 2H), 1.01 (t, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 158, 148, 140, 139.9, 139.7, 138.9, 138.1, 137.4, 135, 134.9, 132.6, 129, 128.9, 128.1, 126.2, 124.78, 124.77, 120.6, 119.9, 119.3, 112.6, 75.99, 75.97, 54.9, 33.2, 30.7, 22.3, 13.9.

2-butyl-5,12-bis(4-methoxyphenyl)tetraceno[2,3-*b*]thiophene (9)



Compound **8** (430 mg, 0.7 mmol) was dissolved in 15 mL of THF. Then, 20 mL of 10% HCl aqueous solution saturated with tin(II) chloride dehydrate was added to the reaction mixture. The solution stirred for 3 hours at room temperature. Organics were diluted with CH₂Cl₂ were washed with water and brine, dried over MgSO₄, and filtered. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (2:1, v/v) to yield X. Recrystallization from hexanes and dichloromethane yielded 260 mg (64%) of pure product. ¹H NMR (500 MHz, CDCl₃): δ 8.37 (s, 2H), 8.13 (s, 1H), 8.02 (s, 1H), 7.82-7.80 (m, 2H), 7.54-7.52 (m, 4H), 7.30-7.27 (m, 6H), 6.89 (s, 1H), 4.06 (s, 3H), 4.05 (s, 3H), 2.87 (t, 2H), 1.76-1.72 (m, 2H), 1.47-1.42 (m, 2H), 0.98 (t, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 159.2, 159.1, 149.5, 139.8, 138.2, 136.4, 135.2, 132.8, 132.7, 131.9, 131.7, 130.72, 130.7, 128.9, 128.8, 128.5, 128.1, 125.6, 125.5, 124.91, 124.9, 119.8, 119.2, 118.8, 114.1, 114, 55.5, 32.3, 31.1, 22.2, 13.8.

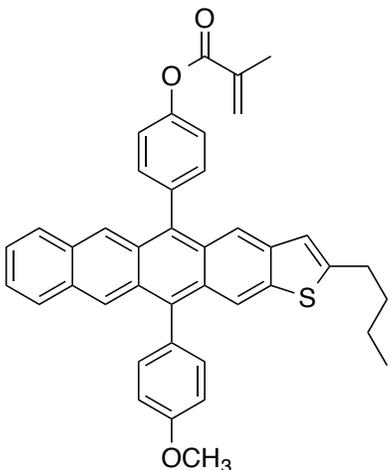
4-(2-butyl-12-(4-methoxyphenyl)tetraceno[2,3-*b*]thiophen-5-yl)phenol (**10**)



Compound **9** (227 mg, 0.41 mmol, 1.0 eq) was dissolved in 21 mL of dry CH₂Cl₂, followed by the addition of BBr₃ (0.41 mL, 1.0 M in CH₂Cl₂, 0.41 mmol, 1 eq) at -78 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 10% HCl_(aq). Organics were extracted twice with CH₂Cl₂, and

combined organic phases were washed with water and brine, dried over MgSO₄, and filtered. The crude product was purified *via* flash chromatography using pure dichloromethane to yield **10**. Yield: 35 mg (16%). ¹H NMR (500 MHz, CDCl₃): δ 8.36 (s, 2H), 8.12 (s, 1H), 8.00 (s, 1H), 7.81-7.80 (m, 2H), 7.53-7.52 (m, 2H), 7.49-7.47 (m, 2H), 7.30-7.25 (m, 4H), 7.20-7.18 (m, 2H), 6.89 (s, 1H), 5.09 (s, 1H), 4.06 (m, 3H), 2.86 (t, 2H), 1.77-1.71 (m, 2H), 1.48-1.40 (m, 2H), 0.97 (t, 3H).

4-(2-butyl-12-(4-methoxyphenyl)tetraceno[2,3-*b*]thiophen-5-yl)phenyl methacrylate (**11**)



Compound **10** (33 mg, 0.06 mmol, 1.0 eq) and DMAP (catalytic amount) was placed in a 25 mL two neck flask and evacuated and refilled with argon three times. Then, 45 uL of dry Et₃N and 1.5 mL of dry THF was added to the flask, followed by the addition of freshly distilled

methacryloyl chloride (6 μ L, 0.06 mmol, 1 eq) at 0 °C under argon and stirred overnight at room temperature. The reaction was stopped by adding 5% aqueous NaHCO₃. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with water and brine, dried over MgSO₄, and filtered. The crude product was purified *via* flash chromatography using hexanes and dichloromethane (1:1, v/v) to yield **11**. Yield: 162 mg (86%). ¹H NMR (500 MHz, CDCl₃): δ 8.33 (s, 1H), 8.29 (s, 1H), 8.09-8.05 (m, 1H), 7.97-7.93 (m, 1H), 7.79-7.77 (m, 2H), 7.62-7.59 (m, 2H), 7.52-7.45 (m, 4H), 7.28-7.21 (m, 3H), 6.87-6.85 (m, 1H), 6.5 (s, 1H), 5.86 (s, 1H), 4.03 (s, 3H), 2.83 (t, 2H), 2.18 (s, 3H), 1.73-1.67 (m, 2H), 1.44-1.37 (m, 2H), 0.93 (t, 3H).

General Polymerization Procedure

A or B or C (0.8 mol %), poly(ethylene glycol) methyl ether methacrylate comonomer, and 1% (w/w) azobisisobutyronitrile (AIBN) were dissolved in toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into diethyl ether. The collected polymer was dissolved in THF and precipitated into diethyl ether twice.

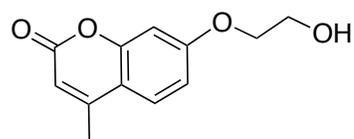
P1: ¹H NMR (500 MHz, CDCl₃): δ 4.11 (2H, broad), 3.69-3.67 (16H, broad), 3.57 (2H, broad), 3.41 (3H, broad), 1.8 (2H, broad), 1.05-0.89 (3H, broad). M_n [g/mol]: 36k, M_w [g/mol]: 55k (GPC).

P2: ^1H NMR (500 MHz, CDCl_3): δ 4.1 (2H, broad), 3.67 (16H, broad), 3.57 (2H, broad), 3.40 (3H, broad), 1.81 (2H, 3H, broad), 1.03-0.89 (broad). M_n [g/mol]: 47k, M_w [g/mol]: 92k (GPC).

P3: ^1H NMR (300 MHz, Tetrahydrofuran- d_8): δ 4.06 (2H, broad), 3.58 (16H, broad), 3.45 (2H, broad), 3.28 (3H, broad), 1.77 (2H, broad), 1.05-0.91(3H, broad). M_n [g/mol]: 41k, M_w [g/mol]: 58k(GPC).

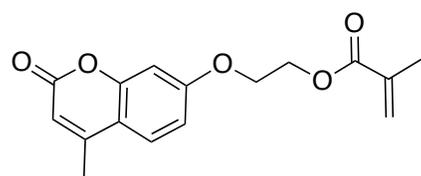
Synthesis of donor-acceptor polymers

7-(2-Hydroxyethoxy)-4-methylcoumarin (12)



A mixture of 7-hydroxy-4-methylcoumarin (1 g, 5.7 mmol, 1 eq), 2-bromoethanol (0.44 mL, 6.3 mmol, 1.1 eq) and potassium carbonate (2 g, 14.3 mmol, 2.5 eq) in 15 mL of ethanol was heated under reflux for overnight. Organics were diluted with diethylether and washed with water and brine, dried over MgSO_4 , and filtered. The crude product was pure enough to use in the next step without further purification. Yield: 1.1 g (88%)

7-(2-Methacryloyloxyethoxy)-4-methylcoumarin (13)



Compound **12** (500 mg, 2.27 mmol, 1.0 eq) and DMAP (28 mg, 0.2 mmol, 0.1 eq) was placed in a 100 mL two neck flask and evacuated and refilled with argon three times. Then, 2.5 mL of dry Et_3N and 37 mL of dry THF was added to the flask, followed by the addition of freshly distilled methacryloyl chloride (220 μL , 2.27 mmol, 1 eq) at 0 $^\circ\text{C}$ under argon and stirred overnight at room temperature. The reaction was stopped by adding 5%

aqueous NaHCO₃. Organics were extracted twice with CH₂Cl₂, and combined organic phases were washed with water and brine, dried over MgSO₄, and filtered. The crude product was purified by recrystallization from ethanol. Yield: 520 g (79%). ¹H NMR of this compound is in good agreement with the same compound reported in the literature.³⁵

5%D-1%A Polymer

Monomer **13** (14.6 mg, 0.05 mmol, 5 eq), monomer **7** (5 mg, 0.01 mmol, 1 eq), poly(ethylene glycol) methyl ether methacrylate comonomer (285.1 mg, 0.95 mmol, 95 eq), and azobisisobutyronitrile (AIBN) (3 mg, 1% (w/w)) were dissolved in 2 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into hexanes twice. ¹H NMR (500 MHz, CDCl₃): δ 4.1 (broad), 3.68 (broad), 3.57 (broad), 3.4 (broad), 1.75 (broad), 1.04-0.99 (broad). M_n [g/mol]: 30k, M_w [g/mol]: 54k (GPC).

10%D-5%A Polymer

Monomer **13** (23.3 mg, 0.08 mmol, 10 eq), monomer **7** (20 mg, 0.04 mmol, 5 eq), poly(ethylene glycol) methyl ether methacrylate comonomer (206.3 mg, 0.69 mmol, 85 eq), and azobisisobutyronitrile (AIBN) (2.5 mg, 1% (w/w)) were dissolved in 2 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was

precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into diethyl ether twice. M_n [g/mol]: 30k, M_w [g/mol]: 54k(GPC).

15%D-2%A Polymer

Monomer **13** (43.7 mg, 0.15 mmol, 15 eq), monomer **7** (10 mg, 0.02 mmol, 2 eq), poly(ethylene glycol) methyl ether methacrylate comonomer (251.7 mg, 0.84 mmol, 83 eq), and azobisisobutyronitrile (AIBN) (3 mg, 1% (w/w)) were dissolved in 2 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into diethyl ether twice. ^1H NMR (500 MHz, CDCl_3): δ 7.5 (broad), 6.98 (broad), 6.15 (broad), 4.35-4.22 (broad), 4.1 (2H, broad), 3.67 (16H, broad), 3.57 (2H, broad), 3.4 (3H, broad), 2.4 (broad), 1.8 (2H, broad), 1.04-0.9 (3H, broad). M_n [g/mol]: 34k, M_w [g/mol]: 50k(GPC).

15%D-3%A Polymer

Monomer **13** (29 mg, 0.1 mmol, 15 eq), monomer **7** (10 mg, 0.02 mmol, 3 eq), poly(ethylene glycol) methyl ether methacrylate comonomer (166 mg, 0.55 mmol, 82 eq), and azobisisobutyronitrile (AIBN) (2 mg, 1% (w/w)) were dissolved in 1.5 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into diethyl ether twice. ^1H NMR (500 MHz, CDCl_3): δ 7.5 (broad), 6.9 (broad), 6.15

(broad), 4.35-4.27 (broad), 4.1 (2H, broad), 3.66 (16H, broad), 3.57 (2H, broad), 3.4 (3H, broad), 2.43 (broad), 1.9-1.82 (2H, broad), 1.04-0.91 (3H, broad). M_n [g/mol]: 37k, M_w [g/mol]: 60k (GPC).

15%D-2%TMT Polymer

Monomer **13** (32 mg, 0.11 mmol, 15 eq), monomer **11** (9 mg, 0.015 mmol, 2 eq), poly(ethylene glycol) methyl ether methacrylate comonomer (185 mg, 0.62 mmol, 83 eq), and azobisisobutyronitrile (AIBN) (2.3 mg, 1% (w/w)) were dissolved in 1.5 mL of toluene and sparged with argon for 30 minutes. The reaction was then heated to 65 °C and stirred overnight. The reaction mixture was precipitated into hexanes. The collected polymer was dissolved in THF and precipitated into diethyl ether twice. ^1H NMR (500 MHz, CDCl_3): δ 7.5 (broad), 6.9 (broad), 6.15 (broad), 4.35-4.27 (broad), 4.11 (2H, broad), 3.67 (16H, broad), 3.57 (2H, broad), 3.4 (3H, broad), 2.43 (broad), 1.91-1.82 (2H, broad), 1.05-0.90 (3H, broad). M_n [g/mol]: 37k, M_w [g/mol]: 55k (GPC).

4.6 References:

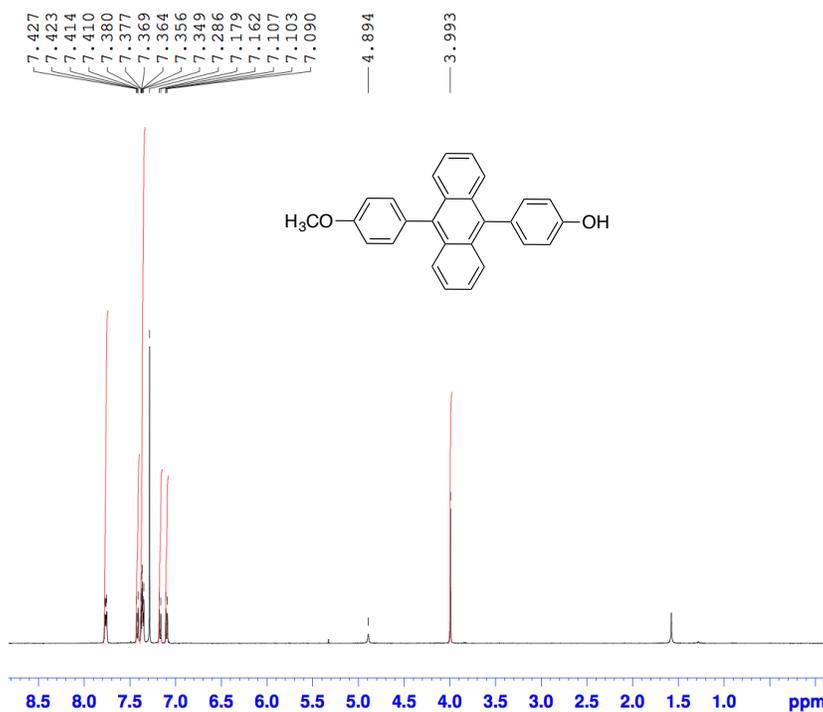
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Chapter 4 Appendix

^1H and ^{13}C NMR

¹H NMR of **2** (500 MHz, CDCl₃)

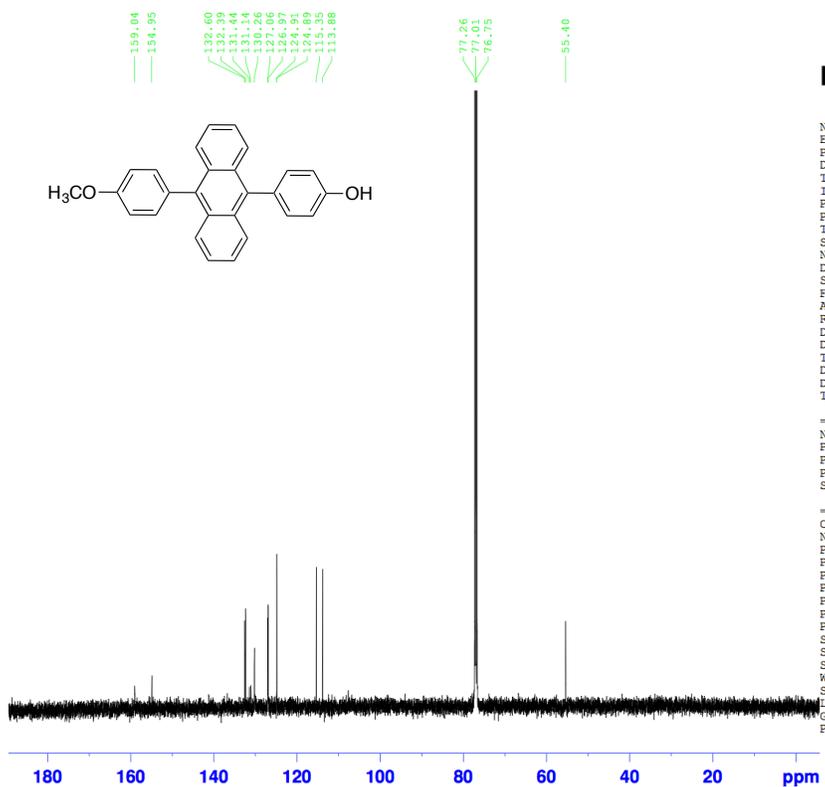


```

NAME      ek-3-017
EXPNO     1
PROCNO    1
Date_     20150504
Time      13.39
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        10000.000 Hz
FIDRES     0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         292.5 K
D1         0.50000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       1H
P1         20.00 usec
PL1        1.00 dB
PL1W       17.75783539 W
SFO1       500.1318364 MHz
SI         65536
SF         500.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR of **2** (125 MHz, CDCl₃)



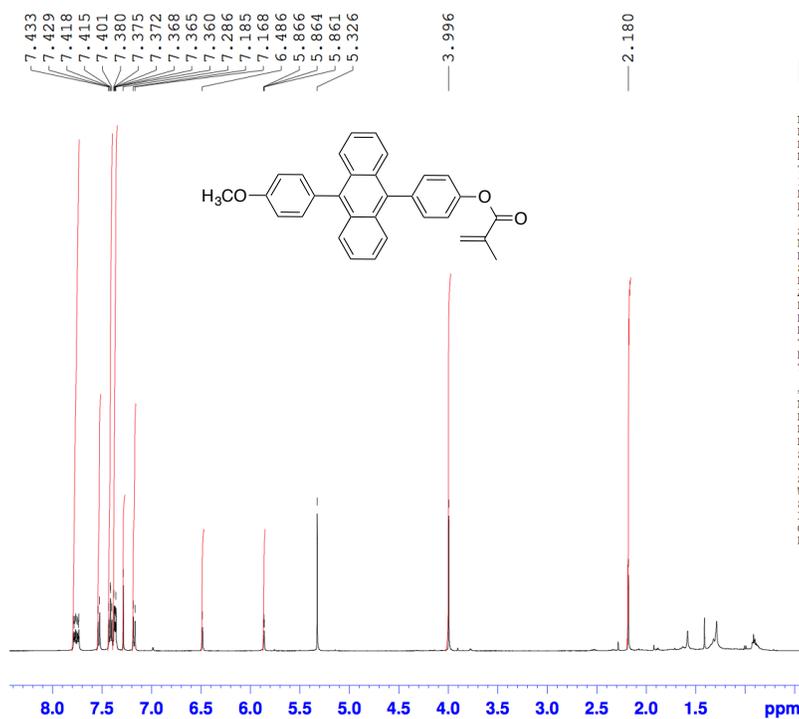
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EXPNO     2
PROCNO    1
Date_     20150504
Time      13.42
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         3801
DS         4
SWH        29761.904 Hz
FIDRES     0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         292.8 K
D1         0.50000000 sec
D11        0.03000000 sec
TDO        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.50 usec
PL1        0.00 dB
PL1W       89.92553711 W
SFO1       125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        1.00 dB
PL12       13.04 dB
PL13       16.80 dB
PL2W       17.75783539 W
PL12W     1.11017132 W
PL13W     0.46707872 W
SFO2       500.1320005 MHz
SI         65536
SF         125.7577890 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

¹H NMR of 3 (500 MHz, CDCl₃)



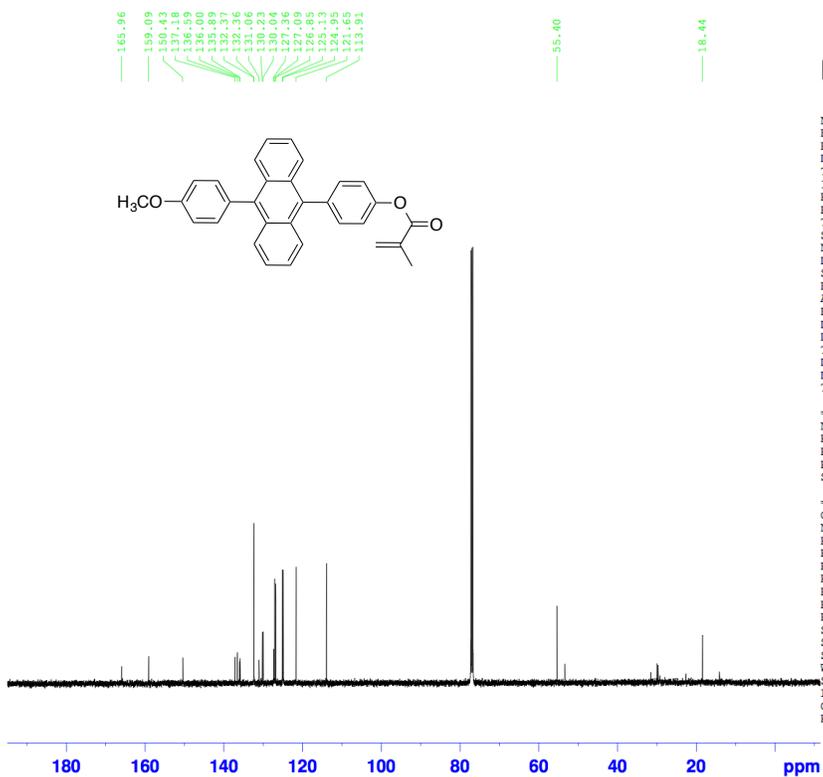
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EXPNO         1
PROCNO        1
Date_         20150505
Time          14.13
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
ID            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            203
DW            50.000 usec
DE            6.50 usec
TE            295.1 K
D1            0.50000000 sec
TDO           1
    
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            20.00 usec
PL1           1.00 dB
PL1W          17.75783539 W
SFO1          500.1318364 MHz
SI            65536
SF            500.1300000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

¹³C NMR of 3 (125 MHz, CDCl₃)



```

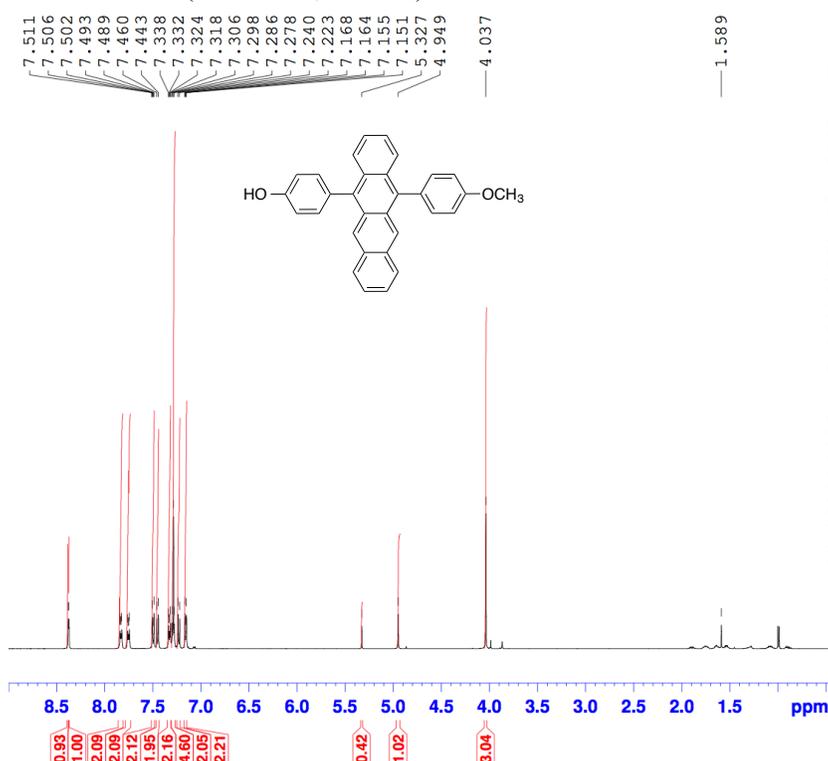
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EXPNO         2
PROCNO        1
Date_         20150505
Time          14.16
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
ID            65536
SOLVENT       CDCl3
NS            1518
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            295.3 K
D1            0.50000000 sec
D11           0.03000000 sec
TDO           1
    
```

```

===== CHANNEL f1 =====
NUC1          13C
P1            9.50 usec
PL1           0.00 dB
PL1W          89.92553711 W
SFO1          125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           1.00 dB
PL12          13.04 dB
PL13          16.80 dB
PL2W          17.75783539 W
PL12W         1.11017132 W
PL13W         0.46707872 W
SFO2          500.1320005 MHz
SI            65536
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

¹H NMR of 6 (500 MHz, CDCl₃)



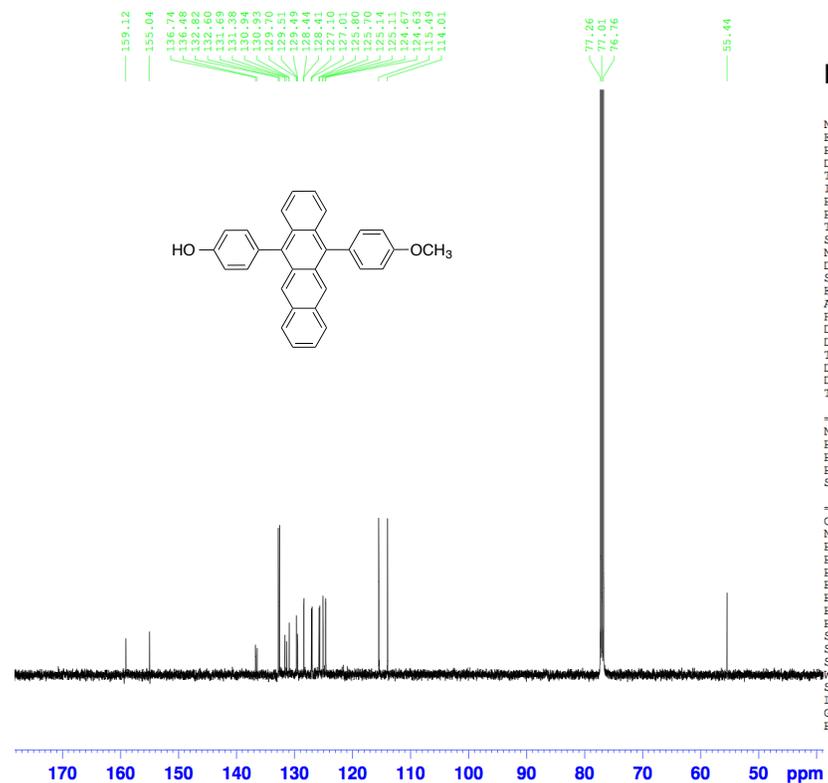
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PROCNO    1
Date_     20150318
Time      10.12
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH       10000.000 Hz
FIDRES    0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         291.6 K
D1         0.50000000 sec
TD0        1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        20.00 usec
PL1       1.00 dB
PL1W      17.75783539 W
SFO1      500.1318364 MHz
SI        65536
SF        500.1300000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```

¹³C NMR of 6 (125 MHz, CDCl₃)



```

NAME      ek-2-303
EXPNO     13
PROCNO    1
Date_     20150318
Time      10.38
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         3500
DS         4
SWH       29761.904 Hz
FIDRES    0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         293.2 K
D1         0.50000000 sec
D11        0.03000000 sec
TD0        1
    
```

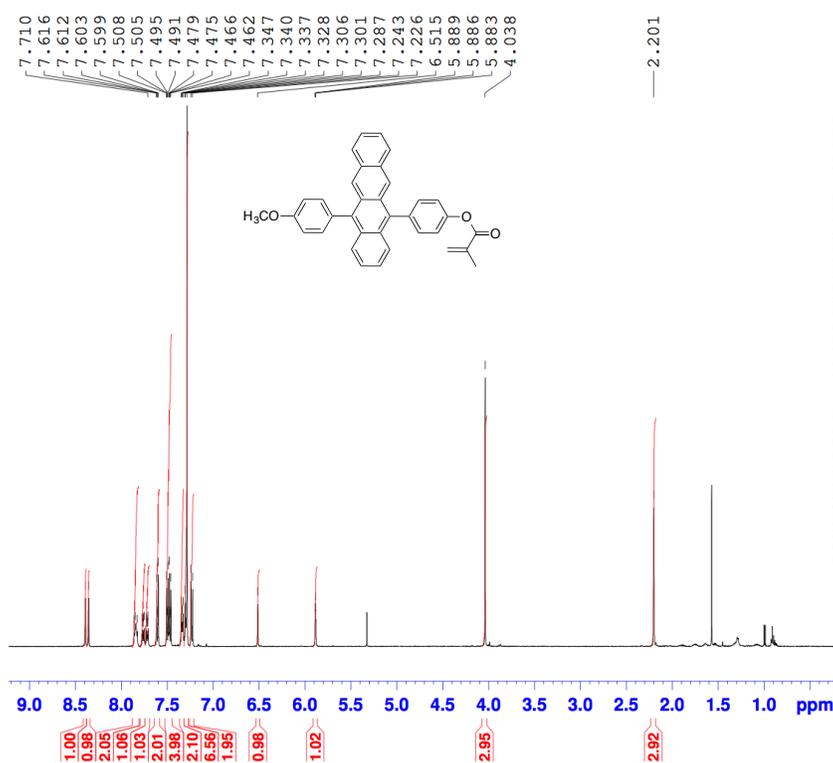
```

===== CHANNEL f1 =====
NUC1      13C
P1        9.50 usec
PL1       0.00 dB
PL1W      89.92553711 W
SFO1      125.7703643 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       1.00 dB
PL12      13.04 dB
PL13      16.80 dB
PL2W      17.75783539 W
PL12W     1.11017132 W
PL13W     0.46707872 W
SFO2      500.1320005 MHz
SI        65536
SF        125.7577890 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        0.20
    
```

¹H NMR of 7 (500 MHz, CDCl₃)

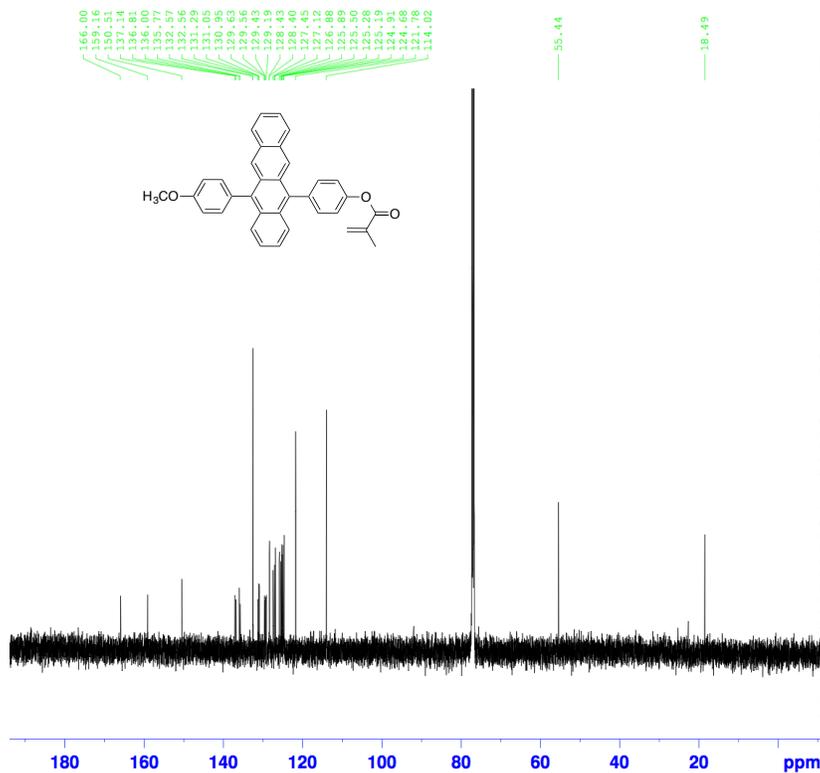


```

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EXPNO         2
PROCNO        1
Date_         20141010
Time          14.23
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
ID            65536
SOLVENT       CDCl3
NS            16
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            203
DW            50.000 usec
DE            6.50 usec
TE            293.6 K
D1            0.50000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            20.00 usec
PL1           1.00 dB
PL1W          17.75783539 W
SF01          500.1318364 MHz
SI            65536
SF            500.1300000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

¹³C NMR of 7 (125 MHz, CDCl₃)



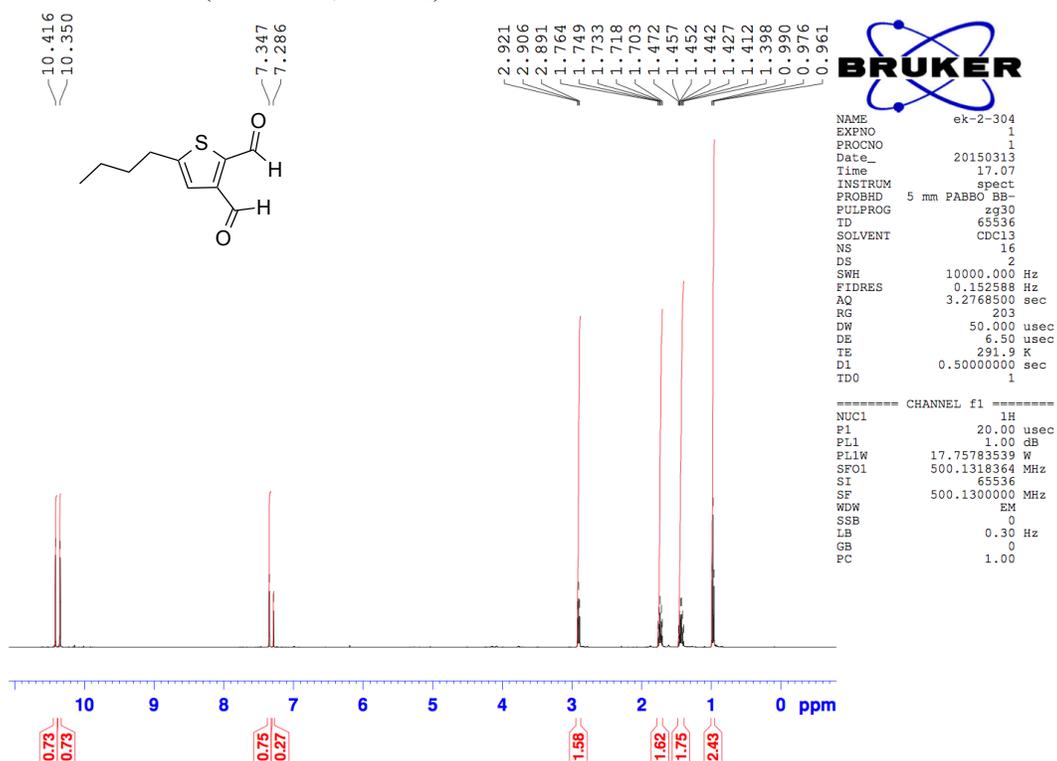
```

NAME          ek-2-248
EXPNO         3
PROCNO        1
Date_         20141010
Time          14.27
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
ID            65536
SOLVENT       CDCl3
NS            4
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            294.1 K
D1            0.50000000 sec
D11           0.03000000 sec
TD0           1

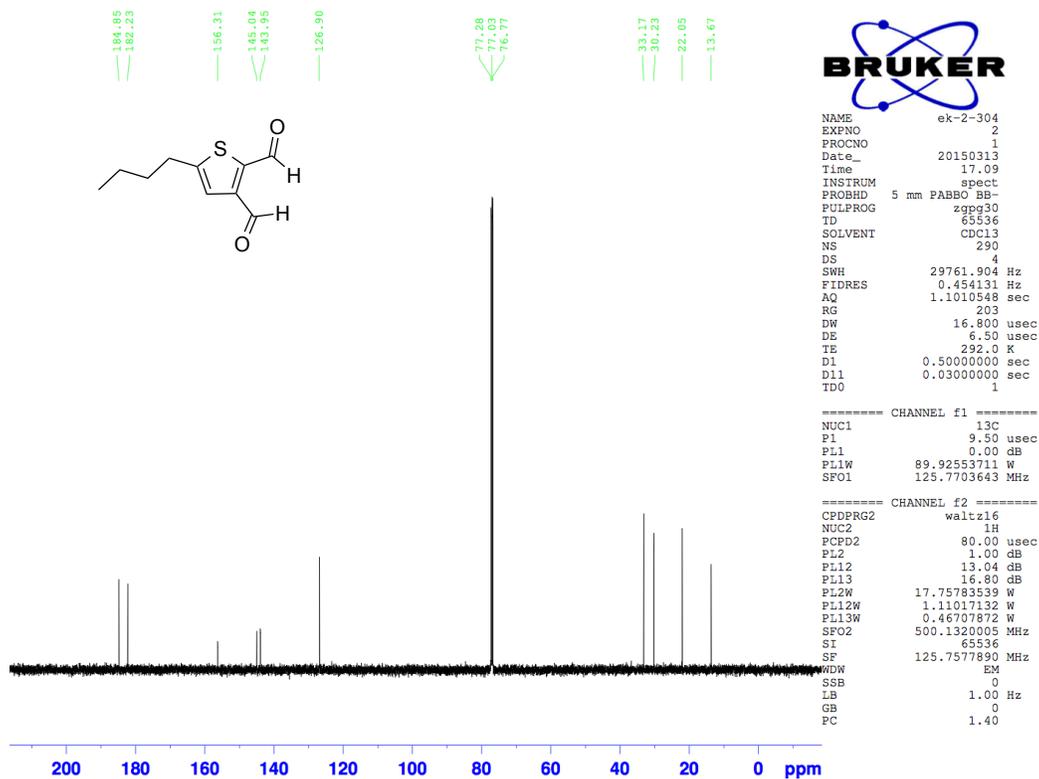
===== CHANNEL f1 =====
NUC1          13C
P1            9.50 usec
PL1           0.00 dB
PL1W          89.92553711 W
SF01          125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           1.00 dB
PL12          13.04 dB
PL13          16.80 dB
PL2W          17.75783539 W
PL12W         1.11017132 W
PL13W         0.46707872 W
SF02          500.1320005 MHz
SI            65536
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            0.70
    
```

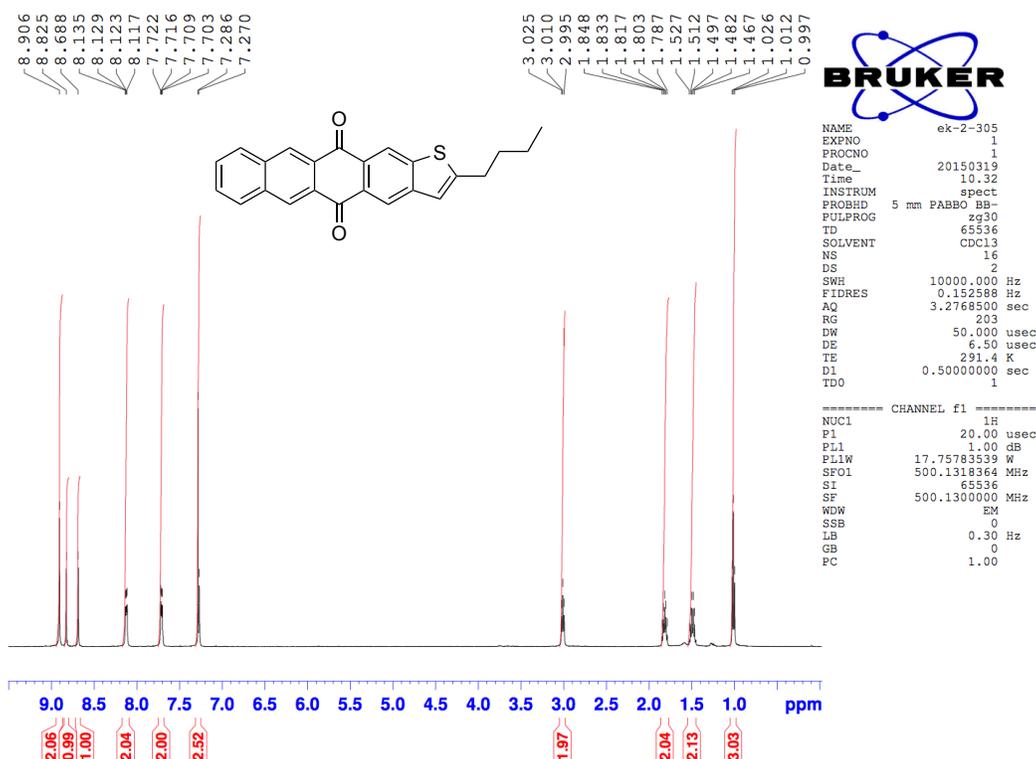
¹H NMR of S2 (500 MHz, CDCl₃)



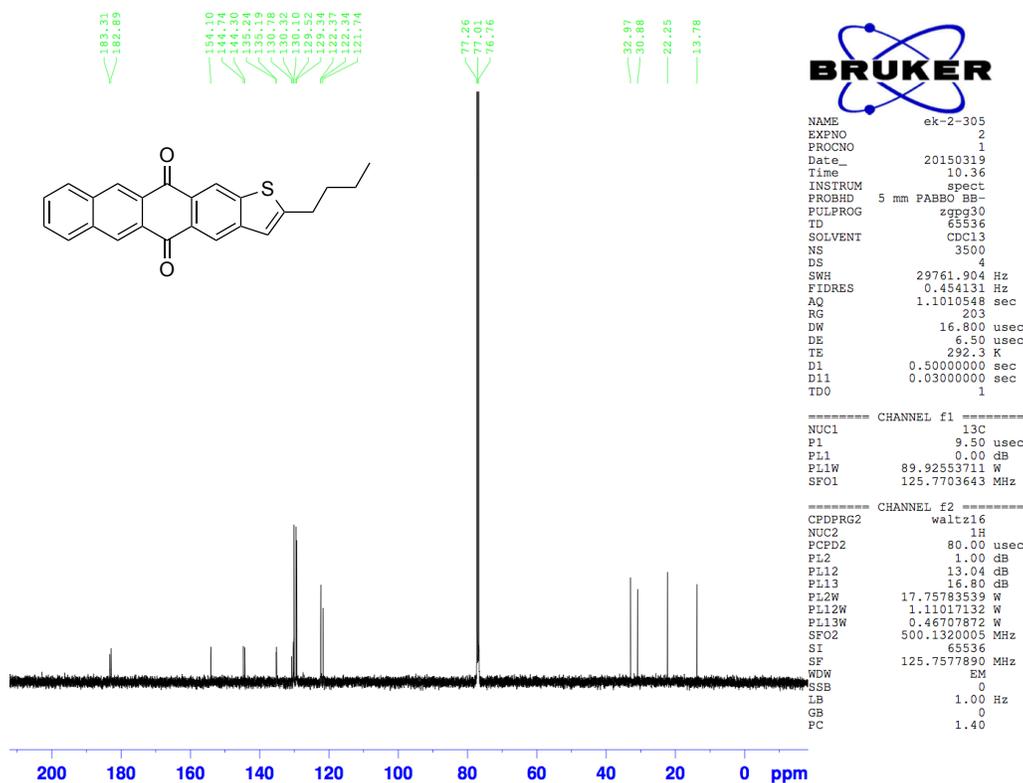
¹³C NMR of S2 (125 MHz, CDCl₃)



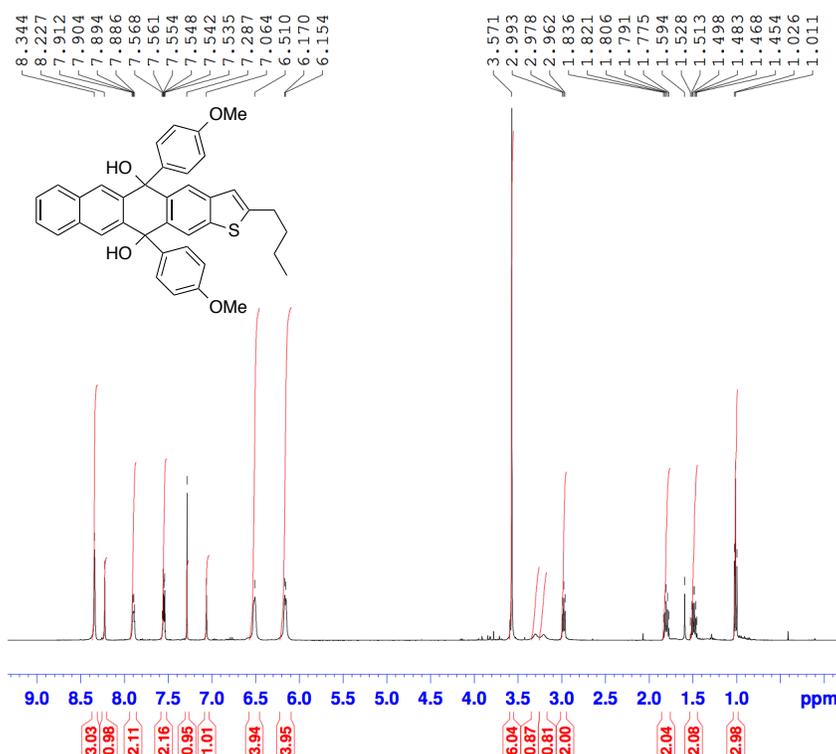
¹H NMR of S4 (500 MHz, CDCl₃)



¹³C NMR of S4 (125 MHz, CDCl₃)



¹H NMR of **8** (500 MHz, CDCl₃)



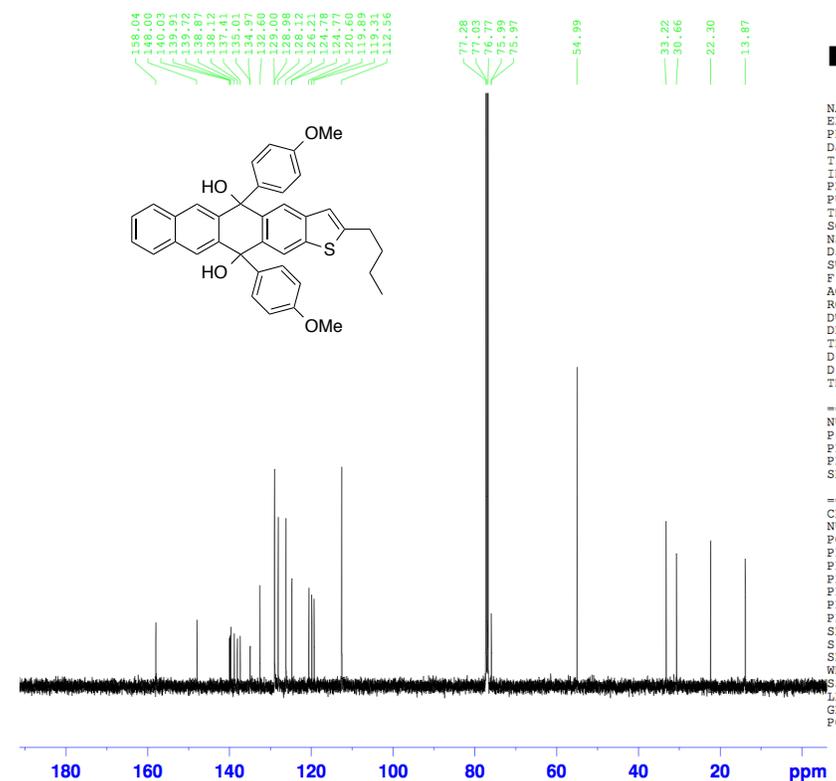
```

NAME      ek-2-309
EXPNO     5
PROCNO    1
Date_     20150701
Time      15.49
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        10000.000 Hz
FIDRES     0.152588 Hz
AQ         3.2768500 sec
RG         203
DW         50.000 usec
DE         6.50 usec
TE         291.4 K
D1         0.50000000 sec
D11        1
TDO        1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1         20.00 usec
PL1        1.00 dB
PL1W       17.75783539 W
SFO1      500.1318364 MHz
SI         65536
SE         EM
WDW        0
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

¹³C NMR of **8** (125 MHz, CDCl₃)



```

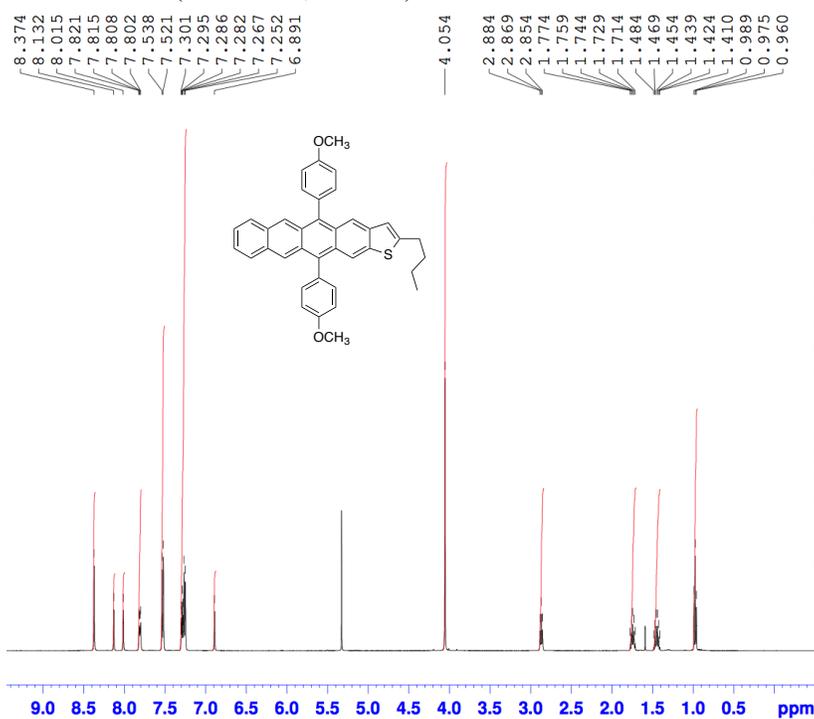
NAME      ek-2-309
EXPNO     56
PROCNO    1
Date_     20150701
Time      15.53
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         999
DS         4
SWH        29761.904 Hz
FIDRES     0.454131 Hz
AQ         1.1010548 sec
RG         203
DW         16.800 usec
DE         6.50 usec
TE         292.4 K
D1         0.50000000 sec
D11        0.03000000 sec
TDO        1
    
```

```

===== CHANNEL f1 =====
NUC1      13C
P1         9.50 usec
PL1        0.00 dB
PL1W       89.92553711 W
SFO1      125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     80.00 usec
PL2        1.00 dB
PL12       13.04 dB
PL13       16.80 dB
PL12W     17.75783539 W
PL12W     1.11017132 W
PL13W     0.46707872 W
SFO2      500.1320005 MHz
SI         65536
SE         EM
WDW        0
SSB        0
LB         1.00 Hz
GB         0
PC         0.70
    
```

¹H NMR of **9** (500 MHz, CDCl₃)

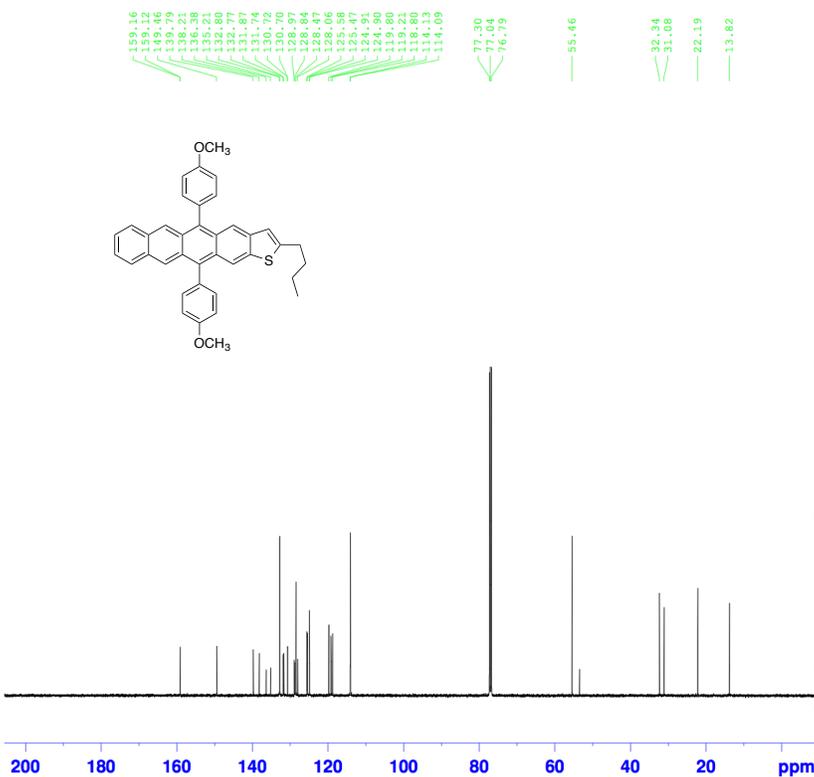


```

NAME          ek-3-001
EXPNO         1
PROCNO        1
Date_         20150416
Time          10.30
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            32
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2768500 sec
RG            161
DW            50.000 usec
DE            6.50 usec
TE            291.4 K
D1            0.5000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            20.00 usec
PL1           1.00 dB
PL1W          17.75783539 W
SFO1          500.1318364 MHz
SI            65536
SF            500.1300000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
```

¹³C NMR of **9** (125 MHz, CDCl₃)



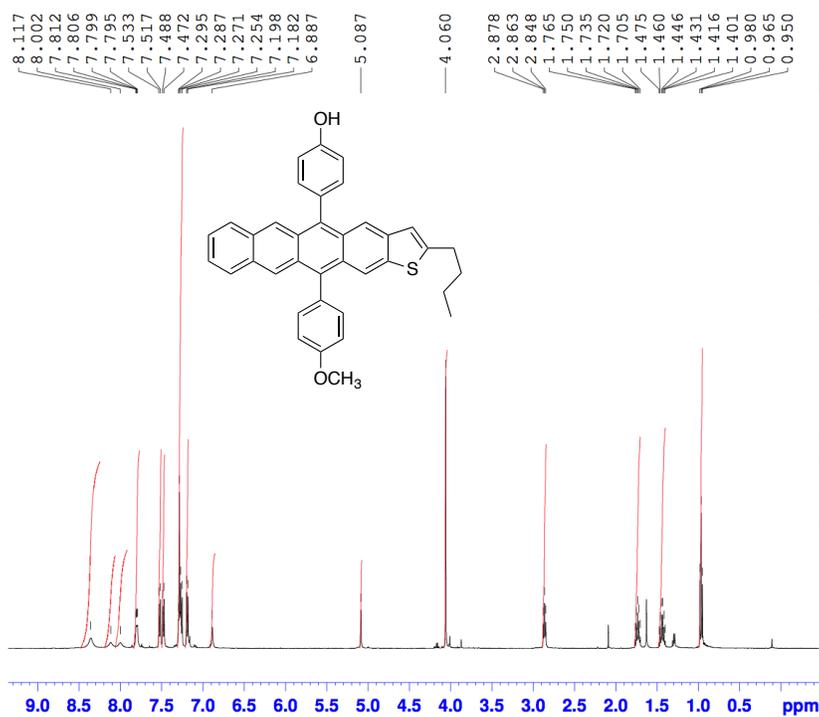
```

NAME          ek-3-001
EXPNO         4
PROCNO        1
Date_         20150416
Time          10.33
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            1743
DS            4
SWH           29761.904 Hz
FIDRES        0.454131 Hz
AQ            1.1010548 sec
RG            203
DW            16.800 usec
DE            6.50 usec
TE            291.5 K
D1            0.5000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            9.50 usec
PL1           0.00 dB
PL1W          89.92553711 W
SFO1          125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2        80.00 usec
PL2           1.00 dB
PL12         13.04 dB
PL13         16.80 dB
PL2W          17.75783539 W
PL12W        1.11017132 W
PL13W        0.46707872 W
SFO2          500.1320005 MHz
SI            65536
SF            125.7577890 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

¹H NMR of **10** (500 MHz, CDCl₃)

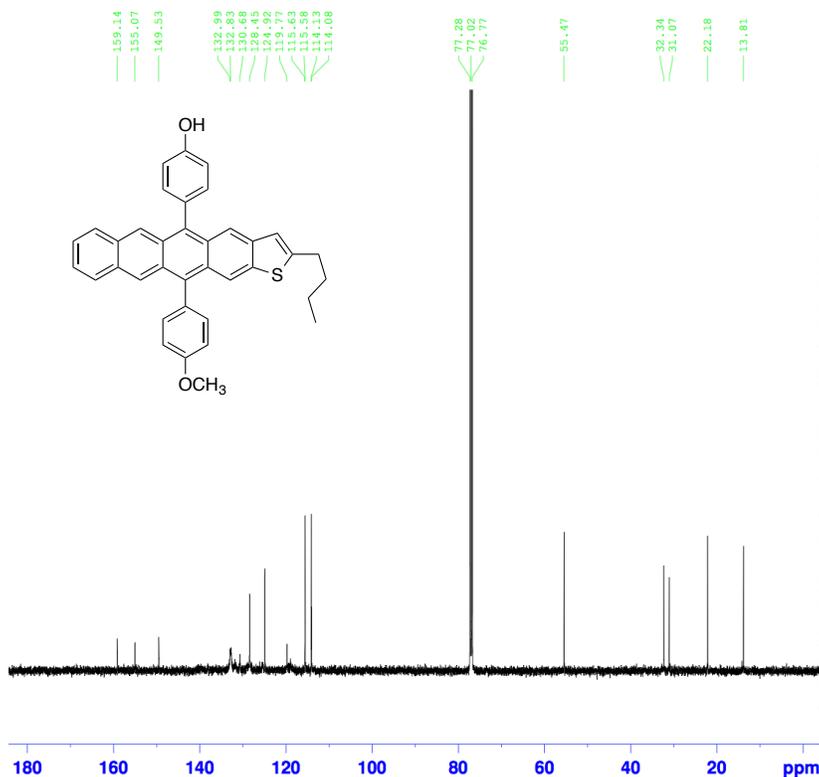


```

NAME      ek-3-005
EXPNO    10
PROCNO   1
Date_    20150706
Time     14.05
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ       3.2768500 sec
RG       203
DW       50.000 usec
DE       6.50 usec
TE       291.3 K
D1       0.50000000 sec
TDO      1

===== CHANNEL f1 =====
NUC1     1H
P1       20.00 usec
PL1      1.00 dB
PL1W     17.75783539 W
SFO1     500.1318364 MHz
SI       65536
SF       500.1300000 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
    
```

¹³C NMR of **10** (125 MHz, CDCl₃)



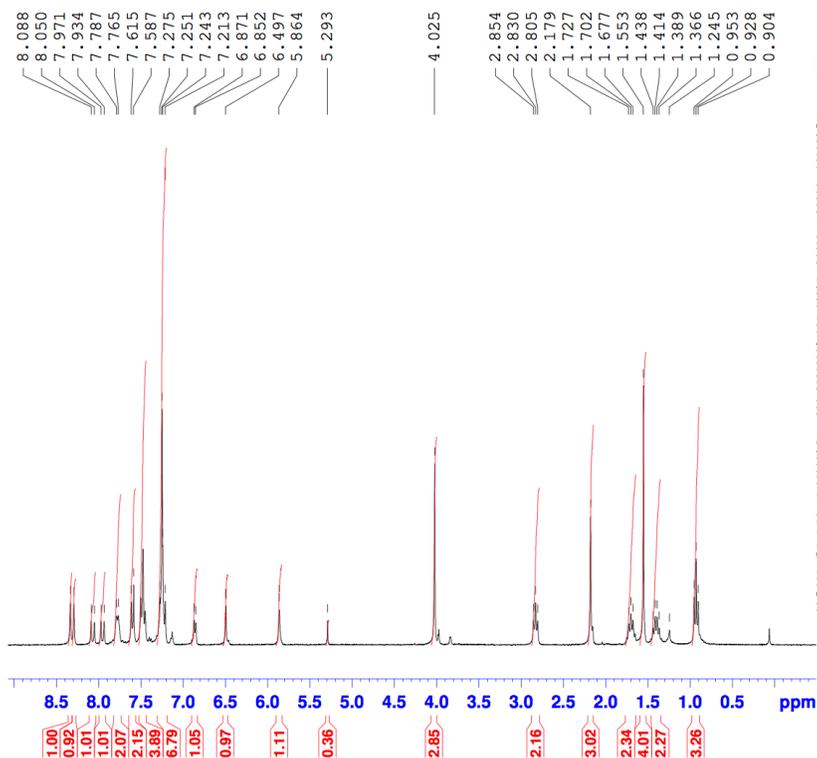
```

NAME      ek-3-005
EXPNO    12
PROCNO   1
Date_    20150706
Time     14.11
INSTRUM  spect
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       2939
DS       4
SWH      29761.904 Hz
FIDRES   0.454131 Hz
AQ       1.1010548 sec
RG       203
DW       16.800 usec
DE       6.50 usec
TE       292.4 K
D1       0.50000000 sec
D11      0.03000000 sec
TDO      1

===== CHANNEL f1 =====
NUC1     13C
P1       9.50 usec
PL1      0.00 dB
PL1W     89.92553711 W
SFO1     125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      1.00 dB
PL12     13.04 dB
PL13     16.80 dB
PL2W     17.75783539 W
PL12W    1.11017132 W
PL13W    0.46707872 W
SFO2     500.1320005 MHz
SI       65536
SF       125.7577890 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       0.90
    
```

¹H NMR of **11** (300 MHz, CDCl₃)



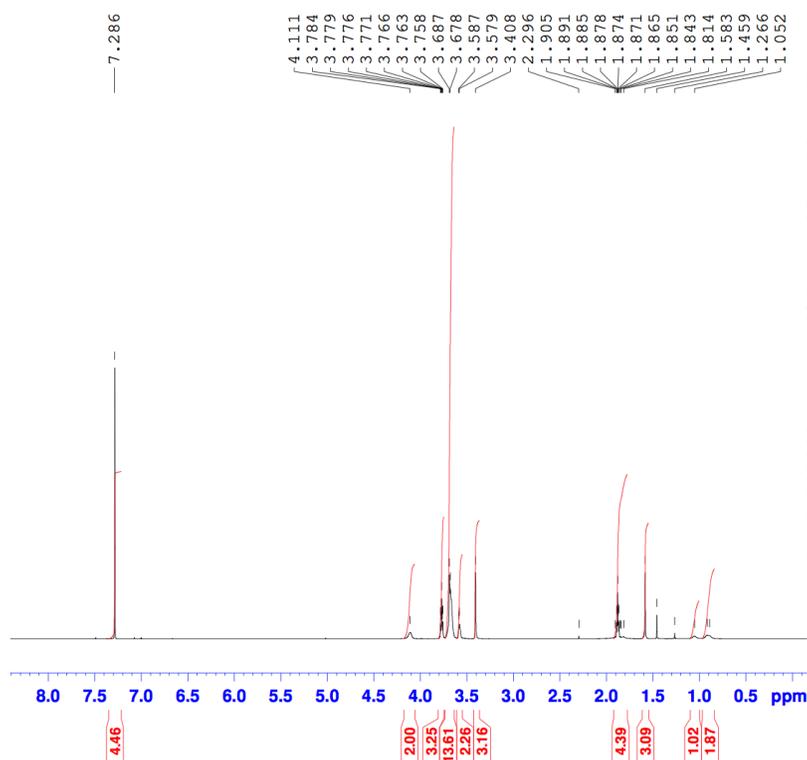
Current Data Parameters
NAME ek-3-006
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150422
Time 15.19
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 645.1
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.50000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 300.3418547 MHz

F2 - Processing parameters
SI 32768
SF 300.3400067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

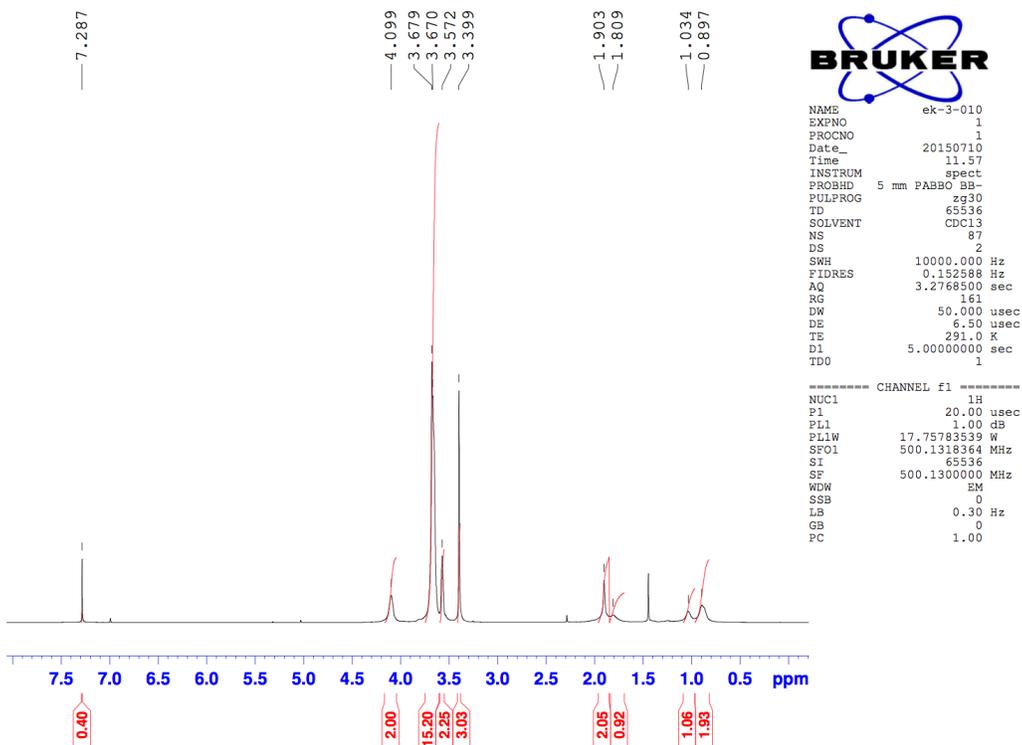
¹H NMR of **P1** (500 MHz, CDCl₃)



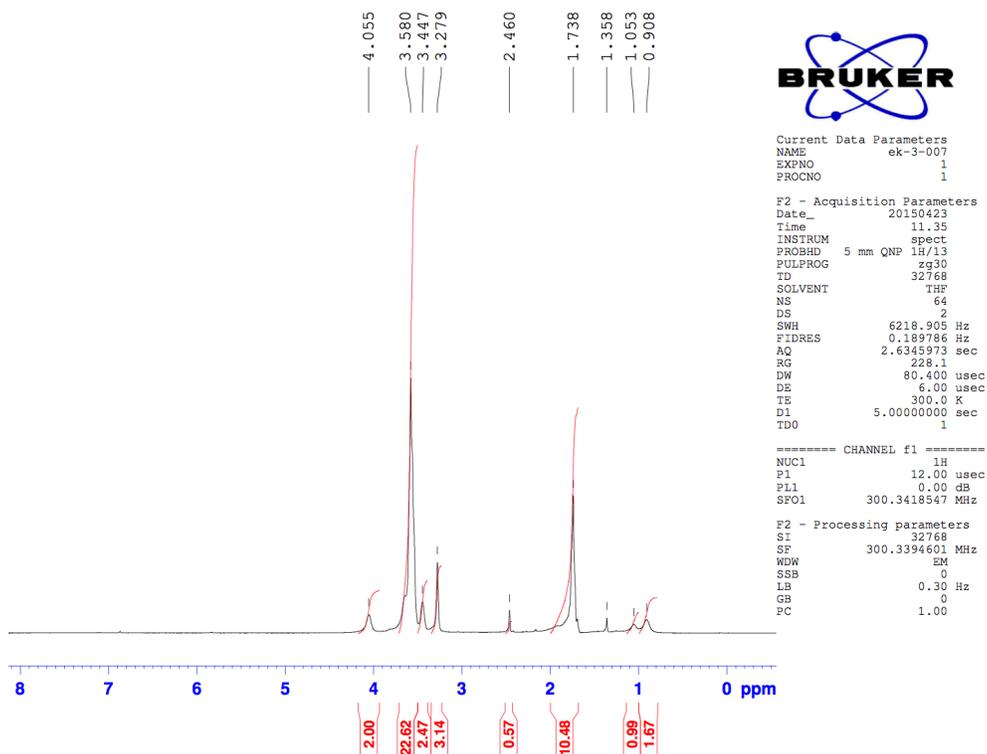
NAME ek-3-020
EXPNO 1
PROCNO 1
Date_ 20150506
Time 13.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 37
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 203
DW 50.000 usec
DE 6.50 usec
TE 300.1 K
D1 5.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 20.00 usec
PL1 1.00 dB
PL1W 17.75783539 W
SFO1 500.1318364 MHz
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

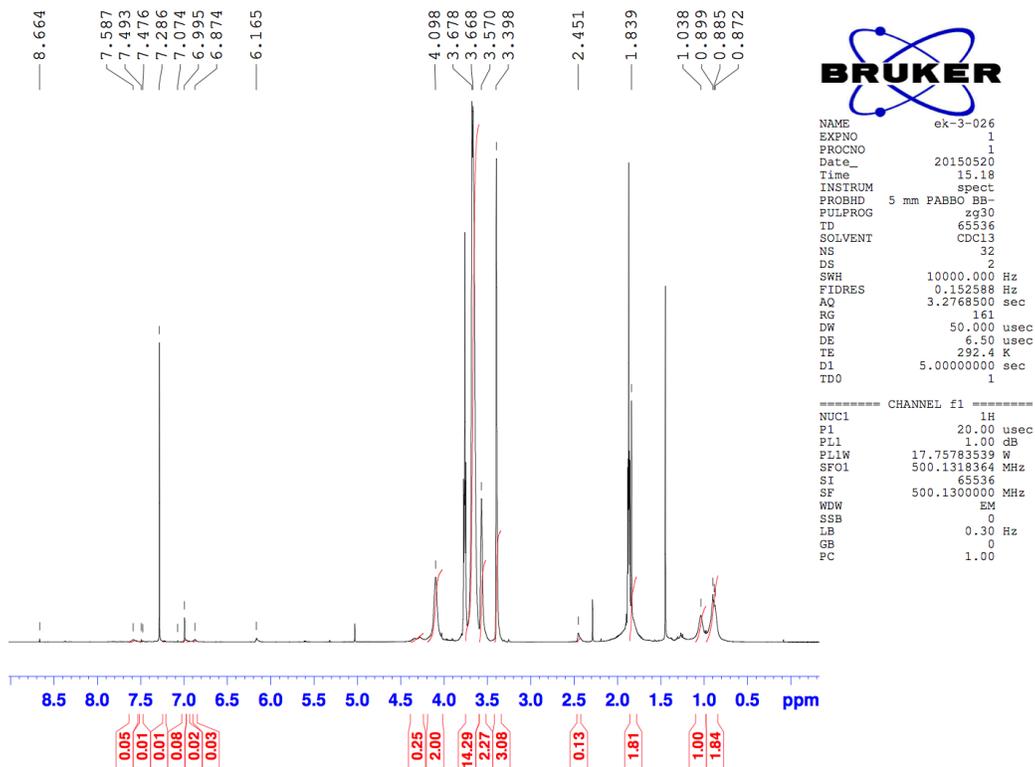
¹H NMR of **P2** (500 MHz, CDCl₃)



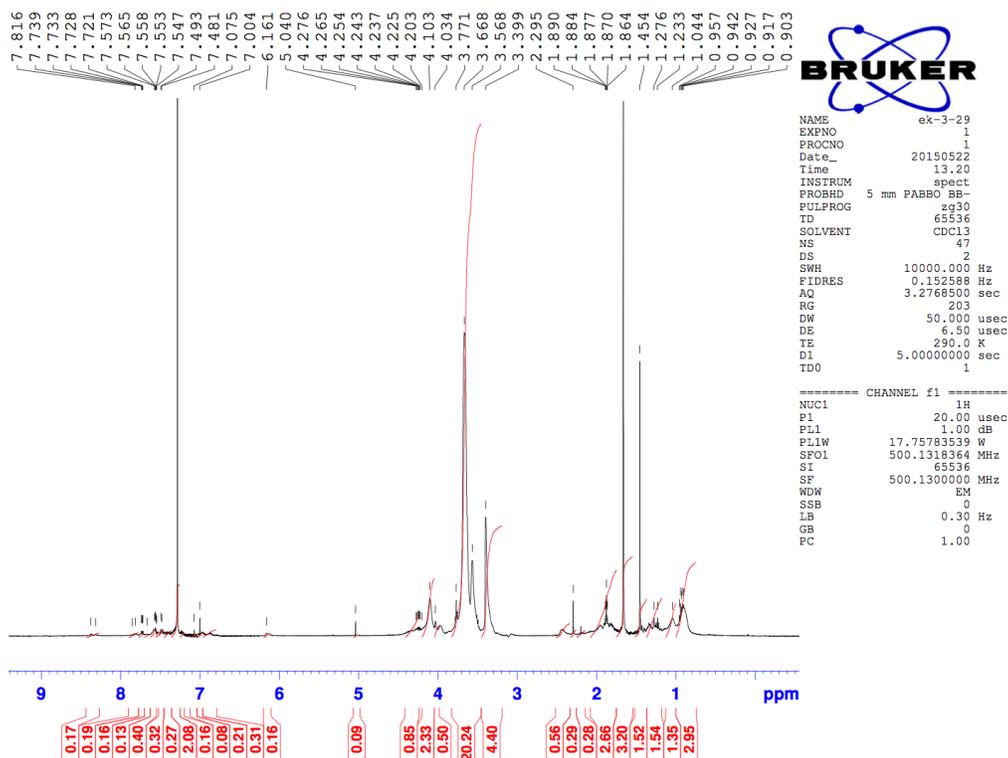
¹H NMR of **P3** (500 MHz, CDCl₃)



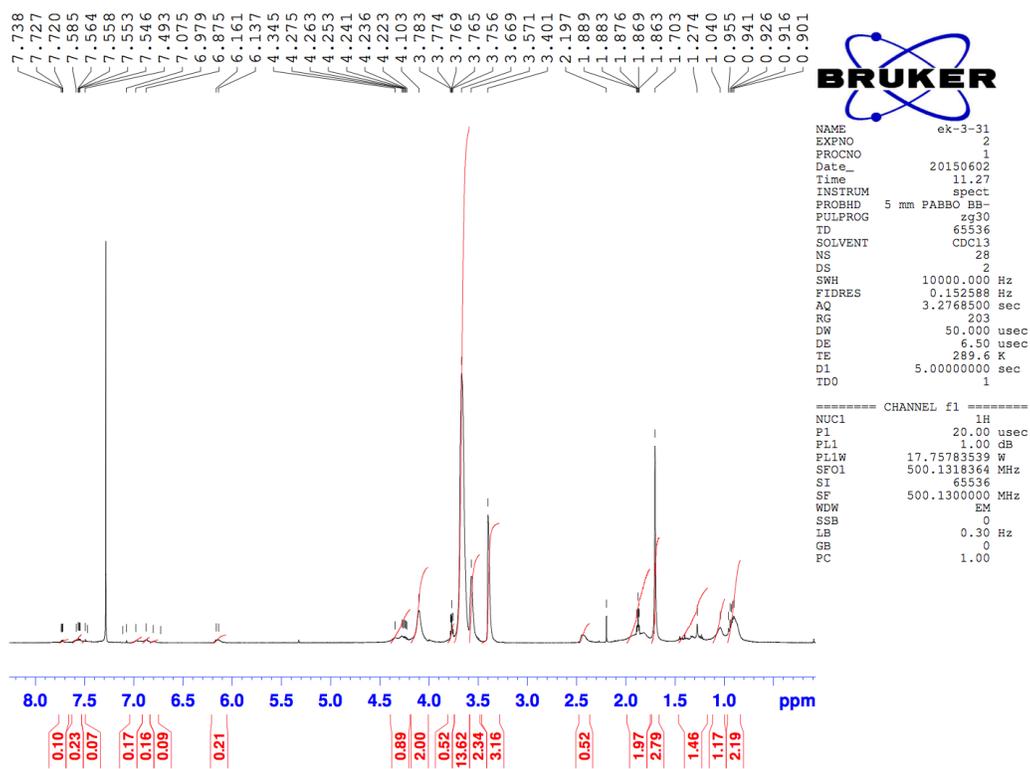
¹H NMR of 5%D-1%A(TET) (500 MHz, CDCl₃)



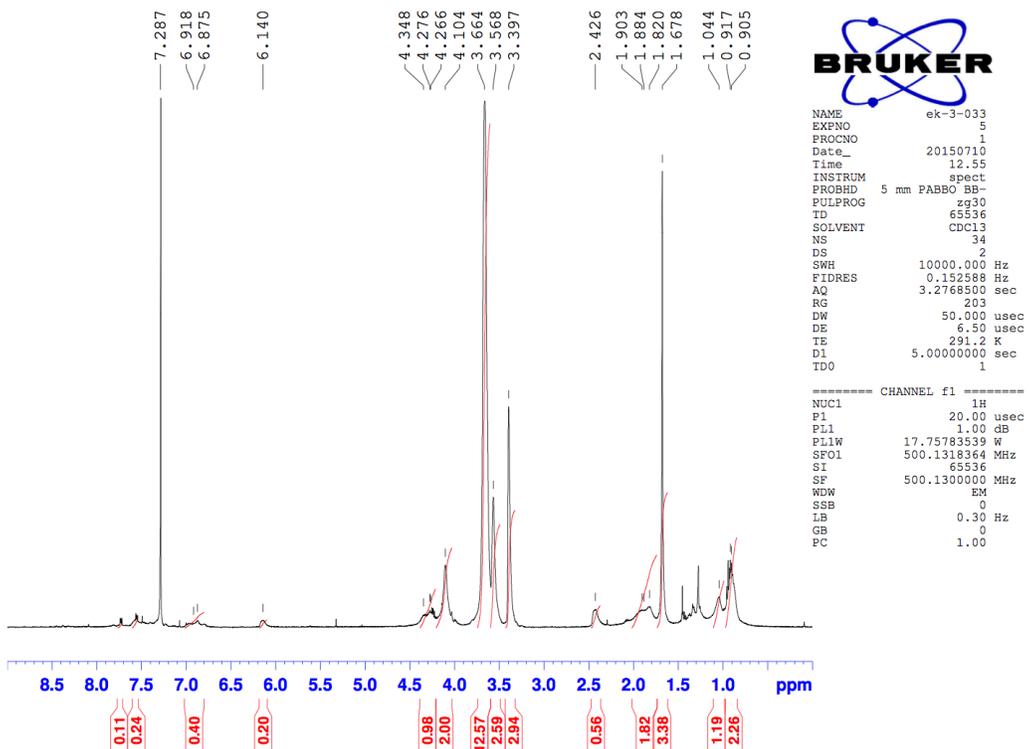
¹H NMR of 10%D-5%A(TET) (500 MHz, CDCl₃)



¹H NMR of 15%D-2%A(TET) (500 MHz, CDCl₃)



¹H NMR of 15%D-3%A(TET) (500 MHz, CDCl₃)



¹H NMR of 15%D-2%(TMT) (500 MHz, CDCl₃)

