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UNIVERSITY OF CALIFORNIA,
IRVINE

The Aza-Diels—Alder Reaction:
Novel Chemistry for the
Synthesis of Quinoline-based Materials

DISSERTATION

submitted in partial satisfaction of the requirements
for the full degree of

DOCTOR OF PHILOSOPHY

in Materials Science and Engineering

By

Mehran Jawed Umerani

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2019

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ABSTRACT OF THE DISSERTATION

The Aza-Diels—Alder Reaction:
Novel Chemistry for the
Synthesis of Quinoline-based Materials

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Polyquinolines have been studied since the early 1970s for their favorable chemical, optical, electrical, and mechanical properties. These properties have allowed polyquinolines to demonstrate their value in optoelectronics and biomedical applications. To date, polyquinolines are prepared primarily through a limited number of synthetic strategies, including Suzuki couplings, the Sonogashira reaction, and the Friedlander synthesis. This work demonstrates the application of the aza-Diels–Alder (Povarov) reaction for the synthesis of AB-type, AABB-type, sequence-specific, and bioconjugate quinoline model compounds and polymers. Our approach furnishes molecules with a unique architecture and connectivity, and therefore, may represent a welcome addition to the polymer chemist's toolkit, by providing facile access to a diverse library of quinoline-type materials.

CHAPTER 1 Introduction

1.1 Overview of the Dissertation

This dissertation aims to outline the development of the aza-Diels–Alder reaction for the synthesis of polyquinolines. Polyquinolines have been studied since the early 1970s for their exceptional optoelectronic properties, high chemical inertness, excellent thermal stability, and exquisite mechanical robustness.^{1–36} These favorable properties have enabled polyquinolines to evince their promise in not only optoelectronics,^{7–19} but also in biological applications.^{20–36} To date, polyquinolines have been produced through a limited number of synthetic strategies, namely, Suzuki couplings,^{37,38} the Sonogashira reaction,³⁹ and the Friedlander synthesis (Figure 1.1 and Figure 1.2).^{1,14,40–44} Specifically, the Friedlander reaction has served as the workhorse of polyquinoline synthesis; Figure 1.3A illustrates a retrosynthetic analysis of typical AB-type and AABB-type Friedlander polymerizations. In these reaction schemes, monomers are classified as AB-type monomers, containing both the amino ketone group and the ketomethylene moiety in a single molecule, or AA-type and BB-type monomers containing bis(aminoketone) or bis(ketomethylene) groups, respectively. While effective, all of these rooted methodologies suffer from disadvantages; they frequently require difficult multistep monomer syntheses, yield products with poor solubility, or provide access to only a limited number of structural motifs. For example, the Friedlander synthesis often demands the resulting quinoline macromolecules to possess complex side chain substituents for enhanced solubility,^{45–51} and cannot provide access to certain backbone architectures. Therefore, we sought to develop a new methodology for the synthesis of polyquinolines, which bypasses the aforementioned deficiencies.

Chemical Strategy	M _w (kg mol ⁻¹)	M _n (kg mol ⁻¹)	PDI	Yield (%)	Reference
Friedlander	38.0	21.0	1.81	92	Chiang, C.-L. <i>et al. Chem. Mater.</i> 2002, 14, 682.
Friedlander	60.1	27.3	2.20	89	Kim, J. L. <i>et al. Macromolecules</i> 2000, 33, 5880.
Friedlander	27.1	12.6	2.15	93	Krüger, H. <i>et al. Macromol. Chem. Phys.</i> 2003, 204, 1607.
Friedlander	64.9	23.5	2.76	93	Tonzola, C. J. <i>et al. Adv. Mater.</i> 2002, 14, 1086.
Friedlander	23.1	6.60	3.50	90	Zhu, Y. <i>et al. Macromolecules</i> 2003, 36, 8958.
Sonogashira	155	50.2	3.10	88	Bangcuyo, C.G. <i>et al. Macromolecules</i> 2002, 35, 1563.
Sonogashira	15.1	6.60	2.30	77	Nagata, Y. <i>et al. Macromolecules</i> 2008, 41, 2809.
Sonogashira	24.5	11.2	2.20	83	Tokoro, Y. <i>et al. Macromolecules</i> 2009, 42, 2988.
Suzuki	35.0	20.1	1.74	66	Siemssen, B. <i>et al. Mol. Cryst. Liq. Cryst.</i> 2007, 462, 159.
Suzuki	62.0	20.6	3.01	60	Tomar, M. <i>et al. Polym Int</i> 2012, 61, 1318.
Suzuki	66.1	26.4	2.50	98	Zhan, X. <i>et al. Macromolecules</i> 2002, 35, 2529.

Table 1.1. The Suzuki, Sonogashira, and Friedlander reactions are traditionally the most frequented polymerization strategies for polyquinoline synthesis.

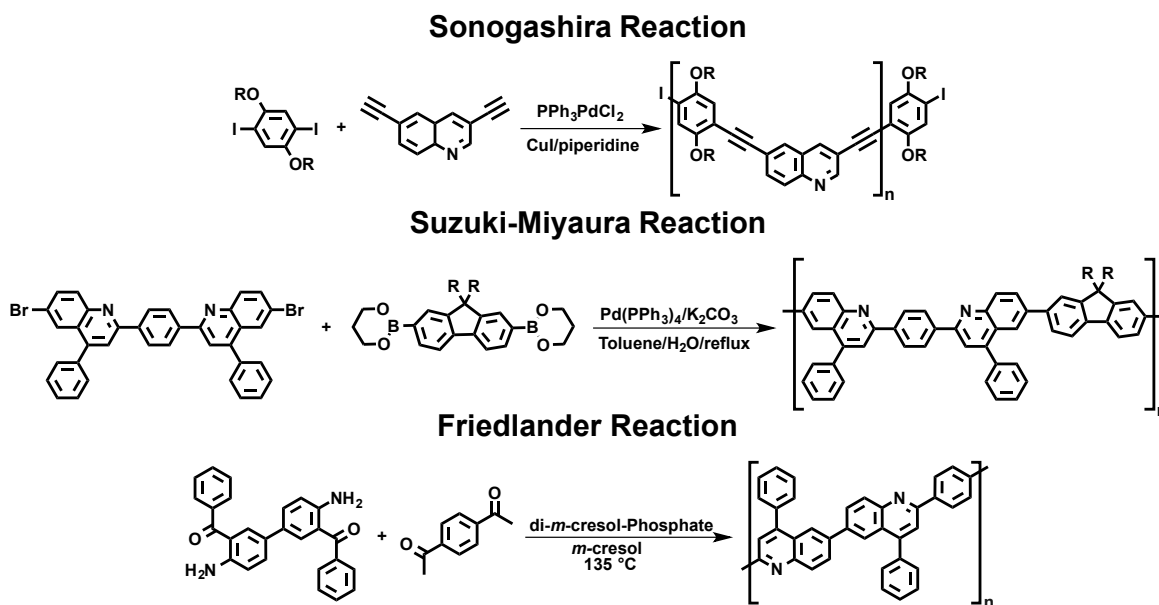


Figure 1.1. The Suzuki, Sonogashira, and Friedlander routes to polyquinoline synthesis.

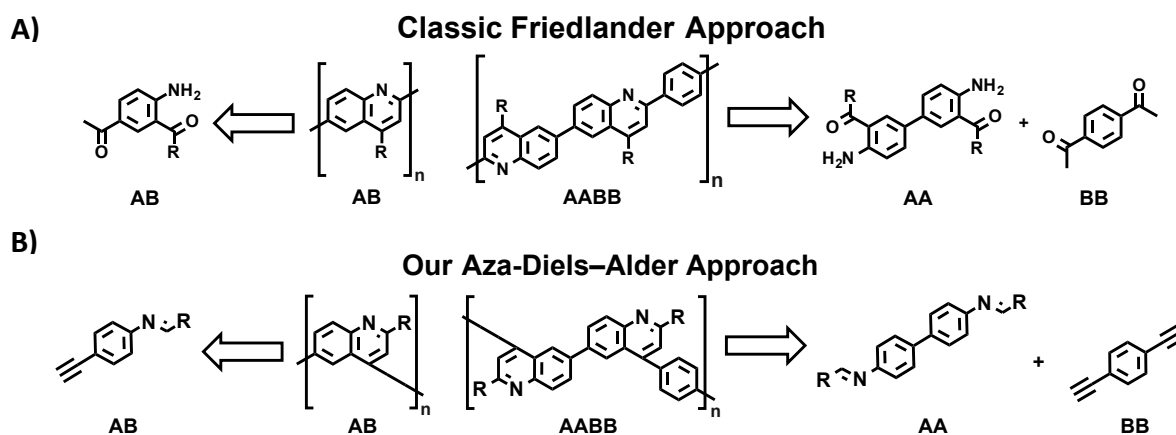
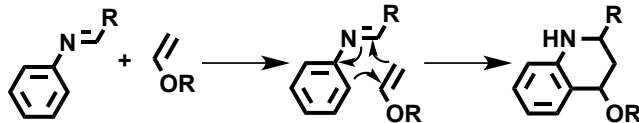


Figure 1.2. (A) A comparison of the AB and AABB routes to polyquinolines *via* the Friedlander reaction and (B) our AB and AABB routes to polyquinolines *via* the aza-Diels–Alder reaction.

Inspired by the Friedlander approach (Figure 1.3A), we intuited a simple strategy to access polyquinolines with an unprecedented 4,6-connectivity (Figure 1.3B); to access this architecture, we proposed the Povarov reaction (Figure 1.4).^{52,53} The Povarov reaction is variant of the aza-Diels–Alder reaction; an example of this is the reaction between an electron-deficient Schiff-base and an electron rich enol-ether. This reaction is modular, switching the enol ether with an electron-rich alkyne, and

adding a Lewis or Bronsted acid catalyst and sacrificial oxidant, results in a fully-oxidized quinoline as the product. Furthermore, the Povarov reaction is highly regioselective, almost exclusively introducing functional groups at the 4 position of the quinoline ring (Figure 1.4).

The classic Povarov reaction provides access to quinolines



A modern variant of the Povarov reaction with an alkyne

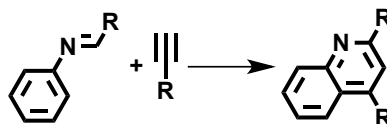


Figure 1.3. The Povarov reaction provides access to hydroquinoline (top). A modern variant of the Povarov reaction proceeds with the addition of an alkyne, affording quinoline (bottom).

In Chapter 1, we investigate the aza-Diels–Alder approach for the preparation of polyquinolines using AB-type and AABB-type polymerization methodologies (Figure 1.3B).⁵²⁻⁵⁶ We first validated our retrosynthetic abstraction by preparing and characterizing a small quinoline model compound *via* the aza-Diels–Alder reaction.^{52,53} Following, we synthesized an AB-type bifunctional monomer in a single step from inexpensive, commercially available reagents. Next, we adapted the conditions used for the preparation of the model compound, and synthesize polyquinolines *via* an AB-type aza-Diels–Alder polymerization reaction.⁵⁴⁻⁵⁶

In Chapter 2, we expand the upon the quinoline core, here, we utilized the optimized aza-Diels–Alder reaction conditions for the synthesis of a benzoquinoline model compound.^{52,53} We next demonstrated the scope of this chemistry by preparing a small library of benzoquinolines featuring electron withdrawing, electron donating, sterically congested, or branched alkyl functionalities at their 2 positions. Subsequently, in Chapter 3, we prepared an AB-type bifunctional monomer using the conditions validated for the model compounds to synthesize an AB-type benzoquinoline macromolecules *via* an aza-Diels–Alder polymerization reaction.⁵⁴⁻⁵⁶ In this effort, we demonstrated the scope and modularity of our methodology by preparing macromolecules of various sizes that feature different peripheral substituents.

In Chapter 4, we sought to further improve and expand our methodology by employing an AABB-type aza-Diels–Alder polymerization reaction. To validate our approach, we first synthesized

and characterized a series of biquinoline model compounds.^{52,53} We in turn used these conditions and combined an AA-type diimine monomer with a commercially available BB-type diethynyl benzene monomer in an AABB-type polymerization reaction, producing AABB-type polyquinolines.⁵⁴⁻⁵⁶

In Chapter 5, we expand upon the AABB-type polyquinoline architecture, we utilized the optimized aza-Diels–Alder reaction conditions for the synthesis of a diquinolineanthracene model compound.^{52,53} In addition, we demonstrated the preparation of a small library of diquinolineanthracenes symmetrically substituted with quinolines that feature electron-withdrawing, electron-donating, and/or sterically congested functionalities at their pendant rings' 2 positions. Finally, we used these conditions and combine commercially-available AA-type diimine and BB-type diethynylantracene monomers in an AA/BB-type polymerization reaction, producing AABB-type polydiquinolineanthracenes.⁵⁴⁻⁵⁶

In Chapter 6, we explored a sequence-controlled strategy for the preparation of polyquinolines. Taking inspiration from a solid-phase approach, we began by first preparing a quinoline monomer which was amenable for coupling on to a solid-support. Here, we used the aza-Diels–Alder reaction to synthesize an fmoc-protected quinoline amino acid which was subsequently iteratively coupled to produce quinoline α -peptide dimers, pentamers, decamers, and eicosamers. Our new strategy provided foundation for the synthesis of larger protein-polymer hybrid materials.

In Chapter 7, we expanded upon the solid-phase approach for the preparation of a quinoline-containing reflectin bioconjugate. We began by first designing and performing structural characterization on a truncated reflectin variant that could recapitulate the properties of a full-length reflectin protein. Following we modified the truncated reflectin variant at the N-terminus and observed a transition from a partially structured protein to one that largely exhibited helical character. Our bioconjugate approach offered a unique strategy for controlling the conformation of an unstructured protein and may be utilized to further control its self-assembly.

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CHAPTER 2 An Aza-Diels–Alder Route to AB-type Polyquinolines

2.1 Abstract

Polyquinolines have been studied since the early 1970s due to their favorable chemical, optical, electrical, and mechanical properties. However, surprisingly few synthetic strategies have been developed for the preparation of these polymers. Herein, we demonstrate the application of the aza-Diels–Alder (Povarov) reaction for the synthesis of soluble polyquinolines from a bifunctional monomer. Our approach furnishes polyquinolines with a unique architecture and connectivity in only two synthetic steps from inexpensive, commercially available reagents. The reported strategy may therefore represent a welcome addition to the polymer chemist’s toolkit by providing ready access to a diverse library of polyquinoline-type materials.

2.2 Introduction

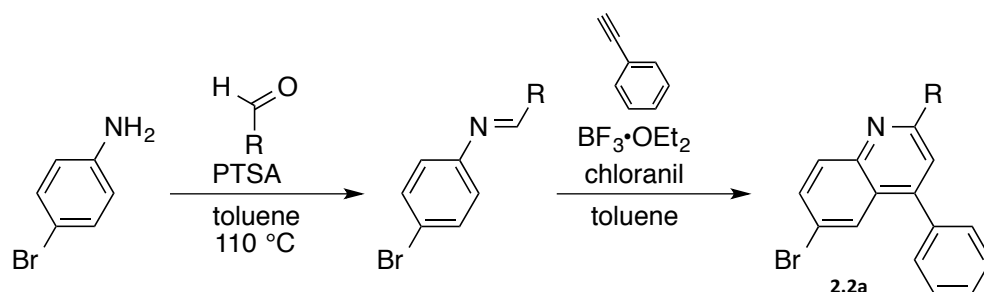
Polyquinolines have been studied in both academia and industry since the early 1970s due to their impressive chemical stability as well as their excellent optical, electrical, and mechanical properties.¹⁻¹⁸ Such favorable properties have enabled polyquinolines to demonstrate their promise for not only optoelectronic⁷⁻¹³ but also biomedical¹⁴⁻¹⁸ applications. To date, polyquinolines have been prepared via a limited number of synthetic strategies, including Suzuki couplings,^{19,20} the Sonogashira reaction,²¹ oxidative polymerizations,²² and the Friedländer synthesis.^{1,23-29} The latter approach has proven particularly effective, as demonstrated in seminal studies by Jenekhe and co-workers.^{12,13,29-33} However, the known routes to polyquinolines suffer from some disadvantages; they frequently necessitate difficult multistep monomer syntheses, yield products with poor solubility, or provide access to only a limited number of structural motifs. For example, the Friedländer synthesis often requires the resulting polyquinolines to possess complex side chain substituents for enhanced solubility³⁴⁻³⁹ and cannot provide access to certain backbone architectures, such as those containing

4,6-linked quinoline subunits. Thus, given the aforementioned limitations, there remains a need for the development of alternative routes to polyquinoline-type materials.

Herein, we report an aza-Diels–Alder strategy for the preparation of soluble 4,6-linked polyquinolines in only two steps.^{40,41} We first validate our approach by preparing and characterizing a small molecular model compound. Subsequently, we synthesize an AB-type bifunctional monomer in a single step from inexpensive, commercially available reagents. Next, we adapt the conditions used for the preparation of the model compound and synthesize 4,6-linked, soluble polyquinolines via a Diels–Alder AB-type polymerization reaction.^{42–44} We definitively confirm the identity of our polymers with size exclusion chromatography (SEC), ¹H nuclear magnetic resonance (¹H NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and ultraviolet visible (UV–vis) spectroscopy. Overall, our findings constitute a facile approach to a new family of polyquinolines.

2.3 Results and Discussion

We began our studies by synthesizing model quinoline compounds via the aza-Diels–Alder (Povarov) reaction,^{40,41} as illustrated in Scheme 2.1. We first formed Schiff bases **2.1a** and **2.1b** in a single step from commercially available reagents by using known literature protocols.⁴⁵ We next reacted the Schiff bases with phenylacetylene in the presence of a Lewis acid mediator and the sacrificial oxidant chloranil,^{46–50} which helped avoid endogenous consumption of the imine.⁵¹ Here, we screened a number of Lewis acids known to mediate the Povarov reaction,⁴¹ finding that BF₃·OEt₂ provided both the best yield and the desired regioselectivity. Overall, our mild and straightforward reaction conditions exclusively produced **2.2a** and **2.2b** as the products in good yields (Scheme 2.1).



Scheme 2.1. Synthesis of Model Quinolines **2.2a** and **2.2b**

We proceeded to characterize model compound **2.2a** with ^1H NMR spectroscopy (Figure 2.1A). The ^1H NMR spectrum featured three apparent doublets at 8.19, 8.11, and 7.80 ppm; a broad apparent singlet at 8.04 ppm; and a singlet at 7.84 ppm. We tentatively assigned the doublet at 8.19 ppm to the ortho position of one of the quinoline's pendant phenyl groups (**H_a**) and the narrow singlet at 8.04 ppm to position 3 on the quinoline ring (**H_b**). We assigned the remaining doublets at 8.11 and 7.80 ppm to positions 7 and 8 of the quinoline ring, respectively (**H_d** and **H_e**), and the broad apparent singlet at 8.04 ppm to position 5 of the quinoline ring (**H_c**). Our postulated assignments for all of the proton resonance peaks were further validated via 2D correlation spectroscopy (COSY) experiments (Supporting Figure S2.1).⁵²

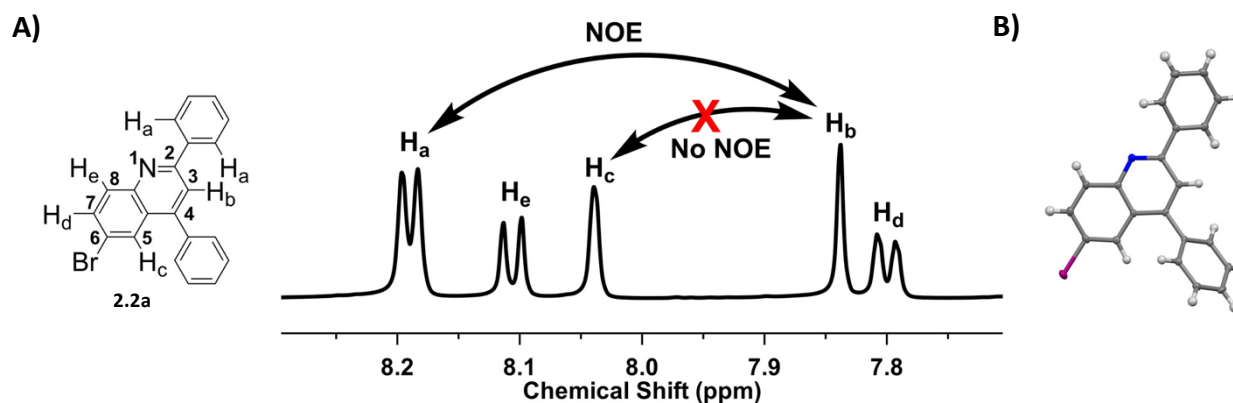


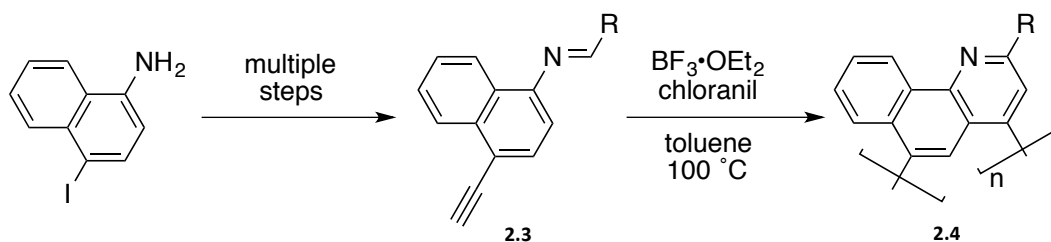
Figure 2.1: (A) Chemical structure (left) and ^1H NMR spectrum (right) of compound **2.2a**. The assignment of each proton resonance for **2.2a** was facilitated by COSY experiments, and the regiochemistry of **2.2a** was determined *via* NOE experiments. (B) Corresponding X-ray crystal structure of **2.2a**, which validates the ^1H NMR NOE analysis. The hydrogen, carbon, nitrogen, and bromine atoms are colored white, gray, blue, and purple, respectively.

It is important to note that the NMR spectra obtained for our crude Povarov reaction mixtures indicated the presence of a single regioisomer (Supporting Figure S2.2). To confirm this observation,

we evaluated the regioisomers' identities via 1D nuclear Overhauser effect (NOE) experiments, as illustrated for model compound **2.2a** (Supporting Figures S2.3–S2.5).⁵² For **2.2a**, we observed an enhancement in the NOE signal between protons **H_a** and **H_b** on the quinoline ring, indicating their proximity. However, we did not observe an enhancement in the NOE signal between **H_b** and **H_c**. These findings confirmed that only a single regioisomer was produced during the course of our reaction.

We sought to further characterize the absolute configuration of our product. We therefore grew crystals of **2.2a** and determined its structure with standard X-ray crystallography techniques (Figure 2.1B). An analysis of the structure indicated that the pendant phenyl substituents were twisted out of planarity relative to the quinoline ring system, with the phenyl ring at position 2 of the quinoline possessing a smaller dihedral angle (24°) than the phenyl ring at position 4 (45°). This difference was likely due to the absence of a hydrogen on the pyridinic nitrogen and the consequent reduced allylic strain at position 2. Altogether, the X-ray crystallography analysis unequivocally confirmed the identity of **2.2a**.

Having validated the regioselectivity of our reaction conditions, we next prepared the bifunctional AB-type monomer necessary for the polymerization reaction illustrated in Scheme 2.2. The design of this monomer incorporated the requisite alkyne and aldimine functional groups within a single substrate as well as an alkyl chain for enhanced solubility. By adapting the reaction conditions used to synthesize **2.1a** and **2.1b**, we produced Schiff base **2.3** in 43% isolated yield. Notably, the preparation of the monomer required inexpensive, commercially available reagents and only a single synthetic step.



Scheme 2.2. Synthesis of Bifunctional Monomer **2.3** and Polyquinoline **2.4**.

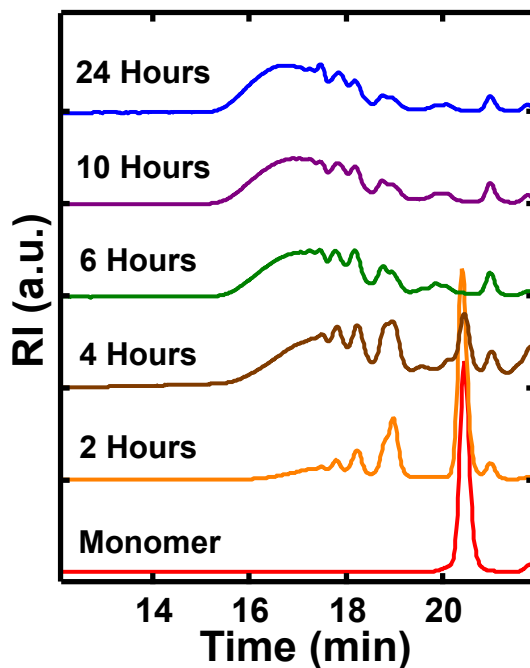


Figure 2.2: SEC-RI analysis of the polymerization reaction. The reaction was monitored at intervals of 2 h (orange trace), 4 h (brown trace), 6 h (green trace), 10 h (purple trace), and 24 h (blue trace). A chromatogram corresponding to monomer **2.3** is shown for comparison (red trace). The peak corresponding to the monomer disappears by 6 h and is replaced by oligomeric and polymeric products. After 10 h, there is little increase in the size of the polymer.

We subsequently used the reaction conditions optimized for the synthesis of compounds **2.2a** and **2.2b** to polymerize monomer **2.3**. The reaction progress was monitored by size exclusion chromatography with a refractive index detector (SEC-RI), as illustrated in Figure 2.2. Initially, a chromatogram of a sample of the pure monomer showed a single sharp peak, as expected (Figure 2.2, red trace). Subsequently, 2h after the start of the reaction, monomer consumption was accompanied by the appearance of small oligomers (Figure 2.2, orange trace). After 4 h, the

chromatogram indicated the presence of higher molecular weight species (Figure 2.2, brown trace), and after 6 h, the monomer was completely consumed, leading to the appearance of additional higher molecular weight species (Figure 2.2, green trace). Moreover, after 10 h, the chromatogram showed only a slight enhancement in the size of the polymeric product (Figure 2.2, purple trace), with essentially no further increase observed after 24 h (Figure 2.2, blue trace). The gradual molecular weight buildup during the reaction and the high apparent polydispersity of the crude product were consistent with a step-growth mechanism and closely resembled literature reports for Diels–Alder AB-type polymerizations.^{42–44, 53}

We proceeded to purify polymer **2.4** for further analysis. We first quenched our reaction mixture by addition of aqueous sodium bicarbonate after a period of 24 h. Per literature precedent, we then treated the crude mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ),⁵⁴ definitively ensuring the rearomatization of the reaction products and the elimination of any potential remaining defects.^{43,55} We in turn used a two-step size exclusion chromatography/ethanol precipitation procedure to remove low molecular weight contaminants and isolate purified polymer **2.4** in moderate yield (see Supporting Information for Experimental Details). After purification, the polyquinoline was analyzed with size exclusion chromatography via a multiangle light scattering detector (SEC-MALS) to obtain its unambiguous molecular weight; a representative chromatogram is shown in Figure 2.3. The purified material possessed a number-average molecular weight (M_n) of 10.1 kg mol⁻¹ and a polydispersity index (PDI) of 1.04, corresponding to a degree of polymerization of ~32. This material was used for all subsequent characterization steps.

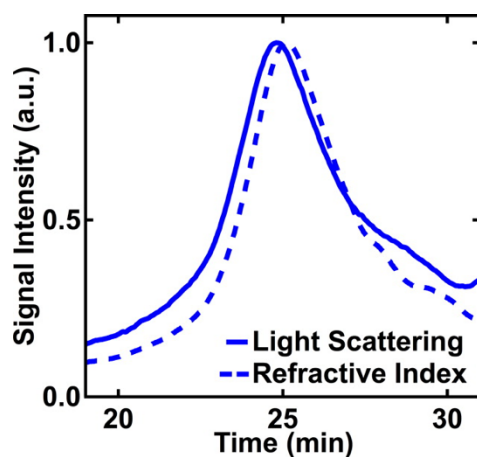


Figure 2.3: SEC-MALS analysis of polyquinoline **2.4** after DDQ treatment and purification. Chromatograms from both the light scattering detector (solid blue trace) and the refractive index detector (dashed blue trace) are shown. The main peaks correspond to the purified polymer.

We proceeded to analyze purified polymer **2.4** with ^1H NMR spectroscopy by comparing its spectrum to the spectra of model quinoline **2.2b** and monomer **2.3** (Figure 2.4). First, we noted that the NMR spectrum of **2.4** featured signal broadening, as expected for a polymeric material (Figure 2.4C). The resonances of the aromatic peaks between 7.0 and 8.5 ppm (Figure 2.4C) were also shifted downfield relative to the aromatic region of the monomer (Figure 2.4B) but were in a similar location to those found for the aromatic region of the model quinoline (Figure 2.4A). In addition, the NMR spectra of **2.2b** (Figure 2.4A) and **2.4** (Figure 2.4C) lacked the characteristic peaks at 3.15 and 8.41 ppm associated with the alkyne and aldimine proton resonances of **2.3**, respectively. These peaks were prominent in the spectrum of monomer **2.3** (H_f and H_g in Figure 2.4B). Finally, the integration ratio between the aromatic and aliphatic regions of **2.4** was $\sim 1:2$, as would be expected based on the postulated structure and repeat unit of our polymer. In their totality, our observations indicated the formation of an extended aromatic system consisting of 4,6-linked quinoline subunits.

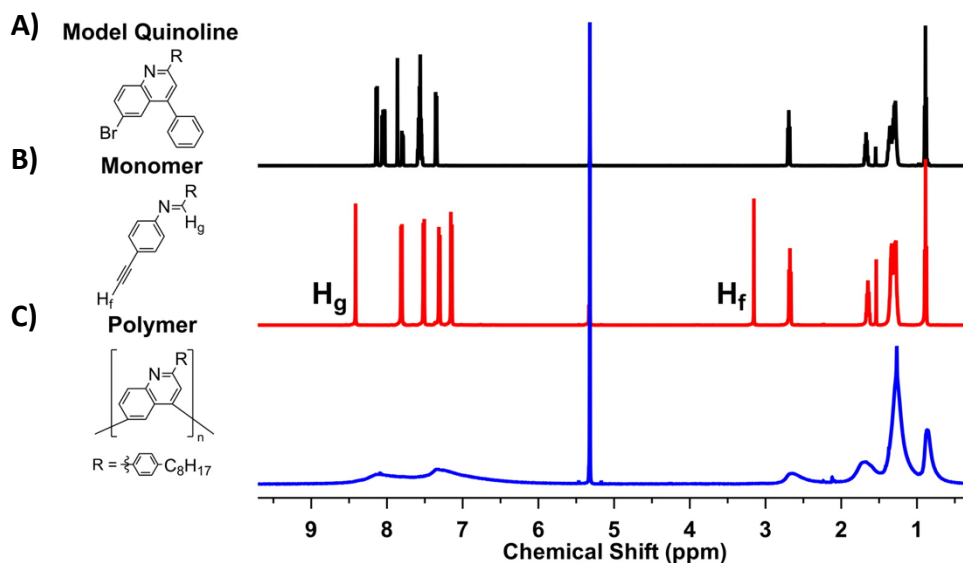


Figure 2.4: (A) Structure (left) and ^1H NMR spectra (right) of model quinoline **2.2b**. (B) Structure (left) and ^1H NMR spectra (right) of monomer **2.3**. Note the presence of alkyne and aldimine proton resonances (labeled H_f and H_g) for **2.3**. (C) Structure (left) and ^1H NMR spectra (right) of polyquinoline **2.4**. The spectrum of the polyquinoline exhibits the expected signal broadening.

We in turn analyzed polyquinoline **2.4** with FTIR spectroscopy, comparing its spectrum to those obtained for model quinoline **2.2b** and monomer **2.3** (Figure 2.5). The spectrum of **2.4** revealed a cluster of peaks at $1500\text{--}1600\text{ cm}^{-1}$, which could be attributed in part to its aromatic quinoline core.⁵⁶⁻
⁵⁸ This spectrum also featured broad peaks at 1616 , 2216 , and 3298 cm^{-1} that we tentatively assigned based on literature precedent to the polymer's imine, alkyne CC, and alkyne CH terminal functionalities, respectively (Figure 2.5, blue trace).^{59,60} These proposed assignments were corroborated by the spectrum of **2.3**, which featured peaks at 1626 , 2146 , and 3319 cm^{-1} , presumably corresponding to its imine, alkyne CC, and alkyne CH functionalities, respectively (Figure 2.5, red trace).^{59,60} The assignments were further supported by the spectrum of **2.2b**, which lacked the imine and alkyne peaks but did feature a cluster of peaks at $1500\text{--}1600\text{ cm}^{-1}$, likely in part due to its quinoline core (Figure 2.5, black trace).⁵⁶⁻⁵⁸ Together, our observations provided additional confirmation of the

identity of **2.4** and indicated that some of the polymer's imine and alkyne terminal groups (which were not readily detected with ^1H NMR) probably remained intact after the reaction and work-up.

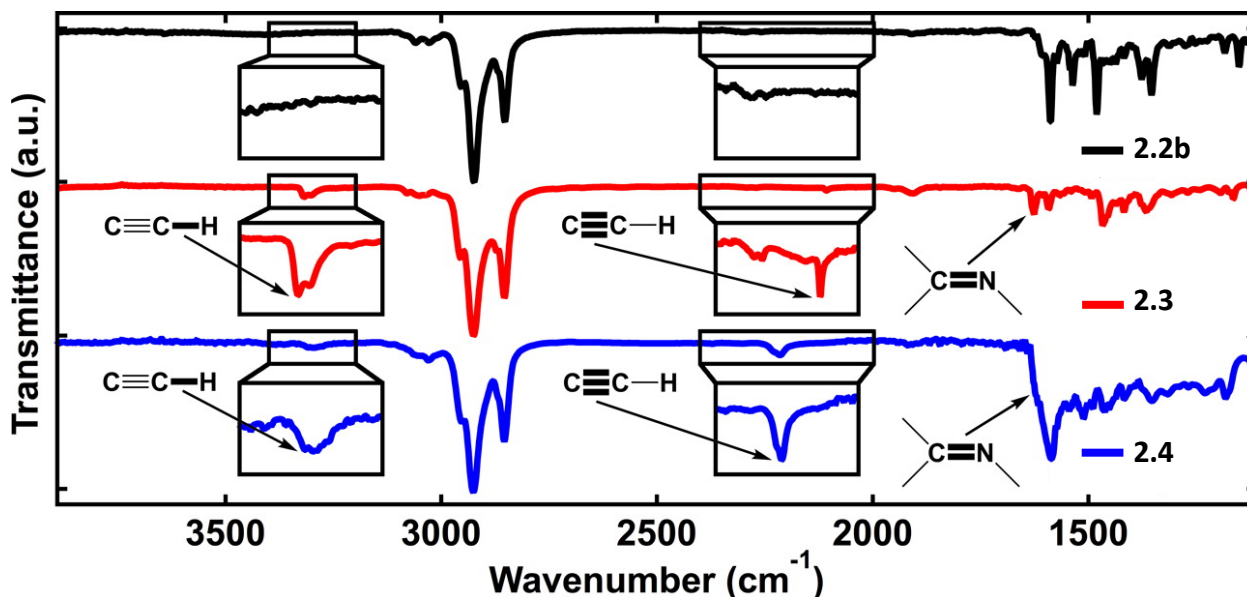


Figure 2.5. FTIR spectra obtained for model quinoline **2.2b** (black trace), monomer **2.3** (red trace), and polyquinoline **2.4** (blue trace). The insets show a close-up of the approximate alkyne CC and alkyne CH regions for each material, with peaks in these regions present for the monomer and the polyquinoline but not for the model compound. The spectra of the monomer and the polyquinoline also feature peaks indicative of an aldimine functionality.

Finally, we investigated the optical properties of polymer **2.4** with UV-vis spectroscopy (Figure 2.6). The spectrum obtained for **2.4** featured broad peaks at 275 and 338 nm, with an absorption onset at 460 nm (Figure 2.6, blue trace). By comparison, the spectrum of model quinoline **2.2b** featured sharper peaks at 275, 335, and 348 nm, with an absorption onset at 365 nm (Figure 2.6, black trace), and the spectrum of monomer **2.3** featured peaks at 277 and 327 nm, with an absorption onset at 386 nm (Figure 2.6, red trace). The broadening and red-shift in the absorption onset observed for the polyquinoline's spectrum, relative to the spectra of both the monomer and the model quinoline, were consistent with the formation of a macromolecule with an extended π -conjugated system.

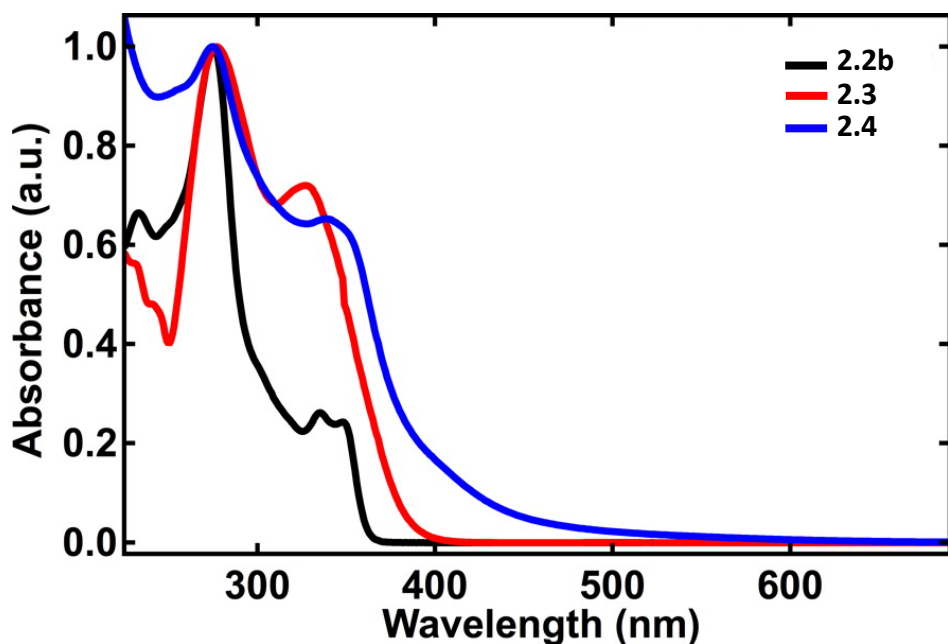


Figure 2.6. Normalized UV-vis absorbance spectra obtained for model quinoline **2.2b** (black trace), monomer **2.3** (red trace), and polyquinoline **2.4** (blue trace). Note that the spectrum of the polyquinoline is broadened and red-shifted with respect to the spectrum of the model quinoline, indicating the formation of an extended π -conjugated system.

2.4 Conclusions

In summary, we have demonstrated a previously unknown synthetic route to polyquinolines, which features a number of advantages. First, our approach proceeds in two simple synthetic steps and requires only commercially available starting materials, making it amenable to scale-up. Given the simple procedures described herein and the large number of commercially available benzaldehyde derivatives, our strategy can provide facile access to a diverse library of new polyquinoline-type materials. Second, our scheme furnishes polyquinolines linked at the 4,6-positions of the quinoline ring, which have never been previously reported and cannot be accessed via the Friedländer reaction (the current workhorse of polyquinoline synthesis). Because of this new architecture, our products exhibit excellent solubility, without requiring heavily branched alkyl side chain substituents or backbone spacers. Finally, to the best of our knowledge, these findings constitute the first report of the application of the Povarov reaction to an AB-type Diels–Alder polymerization. Overall, our

synthetic strategy may represent a welcome addition to the polymer chemist's toolkit for the preparation of polyquinoline-derived materials for a variety of organic electronics applications.

2.5 Supporting Information

2.5.1. General Information and Procedures

A. Materials. All chemicals were purchased from Acros Organics or Sigma-Aldrich, and all solvents were obtained from Fisher Scientific and used as received unless otherwise noted. The toluene used to prepare the model systems and polymer was dried with 3 Å molecular sieves and stored under argon.^{S1} All glassware was oven dried at 150 °C overnight. The reactions were performed under dry argon unless otherwise noted.

B Compound Purification Procedures. Flash chromatography was performed using a CombiFlash Rf 200 purification system manufactured by Teledyne Isco. Deactivated silica gel was prepared by flushing the silica gel cartridge with 1/9 triethylamine/hexanes, followed by hexanes to remove excess triethylamine. Preparatory size exclusion chromatography for the polyquinolines was performed with chloroform as the mobile phase using a gravity fed column (70 mm x 254 mm) containing BioBeads SX-1 resin (200-400 mesh, Bio-Rad Laboratories). Additional purification-relevant information and protocols are noted below as required.

C. Reaction Product Characterization Procedures. All intermediates and products were characterized with a combination of nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, Fourier transform infrared (FTIR) spectroscopy, and/or ultraviolet-visible (UV- vis) spectroscopy. The ¹H NMR spectra were obtained on a Bruker AVANCE400, a Bruker DRX500, or an AVANCE600 instrument. The ¹³C NMR spectra were obtained on a Bruker DRX500 outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes). Chemical shifts were reported in ppm for ¹H and ¹³C NMR. The chemical shifts for the NMR data were referenced as follows: for samples in CDCl₃, the ¹H NMR were referenced to CDCl₃ at 7.26, and the ¹³C NMR were referenced to CDCl₃

at 77.16; for samples in CD₂Cl₂, the ¹H NMR were referenced to the solvent peak at 5.32, and the ¹³C NMR were referenced to the solvent peak at 54.00. The data are labeled as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet), the coupling constants in Hertz, and the integration value. The high-resolution electrospray mass spectrometry (HRMS ESI) data was obtained at the University of California, Irvine Mass Spectrometry Facility on a Waters LCT Premier electrospray time-of-flight instrument. FTIR spectra were obtained on a Nicolet Nexus 670 FTIR spectrophotometer. The UV-vis spectra were collected on an Agilent Cary 100 Series spectrophotometer in tetrahydrofuran (THF) at room temperature.

D. Polymer Characterization and Analysis Procedures. The polyquinolines were analyzed with size exclusion chromatography (SEC). For the crude polymer, the SEC analysis was performed in THF using an Agilent Technologies 1260 Infinity Series separations module equipped with two ResiPore GPC columns connected in series (7.5 mm x 300 mm, multiple pore size, 3 μm) from Agilent Technologies. The separations module was connected to an Agilent 1260 infinity dual angle light scattering, refractive index, and viscometer detectors in series. The flow rate was 1.0 mL/min with an injection volume of 50 – 100 μL and an approximate sample concentration of 1.0 mg/mL.

The purified polymer was characterized by size exclusion chromatography via multi- angle light scattering (SEC-MALS). The SEC analysis was performed using an Agilent Technologies 1260 Infinity Series separations module equipped with two GPC columns (7.8 mm x 300 mm, 10⁴ Å pore size, 5 μm and 7.8 mm x 300 mm, 100 Å pore size, 5 μm) from MZ Analysentechnik. The separations module was connected to a DAWN HELEOS II MALS detector equipped with a 785 nm laser and bandpass interference filters with 20 nm bandwidth in front of the photodiodes to minimize fluorescence effects (Wyatt Technology Corp.). The concentration was measured by an Optilab TrEX differential refractive index detector at 785 nm (Wyatt Technology Corp.). The flow rate was 0.7

mL/min with an injection volume of 100 μ L and an approximate sample concentration of 3.0 mg/mL. The above system was used to determine the molecular weight (M_w and M_n) and PDI values reported for the purified polymer. The molecular weight data were analyzed with the Astra 6.1.2 software suite by using a dn/dc of 0.27 mL/g. For purified polyquinoline **2.4**, corresponding to Figure 2.3, the analysis yielded values of $M_n = 10.1 \text{ kg mol}^{-1}$, $M_w = 10.4 \text{ kg mol}^{-1}$, and $M_w/M_n = 1.04$.

2.5.2. Detailed Experimental Procedures

A. N-Benzylidene-4-bromoaniline (2.1a). 4-Bromoaniline (0.51 g, 3.0 mmol), benzaldehyde (2.0 mmol, 0.21 g), 3 Å molecular sieves (2.0 g), and 20 mL of toluene were added to a 75 mL pressure vessel equipped with a stir bar. The pressure vessel was sealed and brought to 130 °C in an oil bath. After 16 hours, the mixture was cooled to room temperature. The reaction mixture was then filtered through celite, and the solvent was removed *in vacuo*. The mixture was purified by flash chromatography using deactivated silica gel, with pure hexanes as the mobile phase. After chromatography, the material was precipitated from pentane at –78 °C to yield the product as a white solid (0.48 g, 93%). ^1H NMR (600 MHz, CDCl_3) δ = 8.43 (s, 1H), 7.96 – 7.87 (m, 2H), 7.54 – 7.45 (m, 5H), 7.15 – 7.05 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ = 160.8, 151.1, 136.1, 132.3, 131.8, 129.0, 128.9, 122.7, 119.4; (^1H NMR and ^{13}C NMR spectroscopic data match those previously reported);^{S2} HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{11}\text{BrN}$ ($M + \text{H}$)⁺ 260.0075, found 260.0070; IR (KBr Pellet) 3077, 3057, 3022, 3001, 2896, 1626, 1522 cm^{-1} .

B. N-*p*-Octylbenzylidene-4-bromoaniline (2.1b). 4-Bromoaniline (0.41 g, 2.4 mmol), 4-octylbenzaldehyde (2.0 mmol, 0.44 g), 3 Å molecular sieves (3.0 g), and 20 mL of toluene were added to a 75 mL pressure vessel equipped with a stir bar. The pressure vessel was sealed and brought to 130 °C in an oil bath. After 16 hours, the mixture was cooled to room temperature. The reaction mixture was filtered through celite, and the solvent was removed *in vacuo*. The mixture was purified

by flash chromatography using deactivated silica gel, with pure hexanes as the mobile phase. After chromatography, the material was precipitated from pentane at $-78\text{ }^{\circ}\text{C}$ to yield the product as a white solid (0.54 g, 73%). ^1H NMR (600 MHz, CDCl_3) δ 8.39 (s, 1H), 7.80 (d, $J = 7.6\text{ Hz}$, 2H), 7.50 (d, $J = 7.8\text{ Hz}$, 2H), 7.29 (d, $J = 7.7\text{ Hz}$, 2H), 7.08 (d, $J = 7.8\text{ Hz}$, 2H), 2.67 (t, $J = 7.7\text{ Hz}$, 2H), 1.71–1.60 (m, 2H), 1.41 – 1.18 (m, 10H), 0.89 (t, $J = 6.8\text{ Hz}$, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 160.9, 151.4, 147.4, 133.7, 132.3, 129.08, 129.05, 122.7, 119.2, 36.2, 32.0, 31.4, 29.6, 29.42, 29.39, 22.8, 14.3; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{27}\text{BrN}$ ($\text{M} + \text{H}$) $^+$ 372.1327, found 372.1331; IR (KBr Pellet) 2965, 2947, 2927, 2917, 2880, 2856, 1631, 1607 cm^{-1} .

C. 6-Bromo-2,4-diphenylquinoline (2.2a). N-Benzylidene-4-bromoaniline (**2.1a**, 0.26 g, 1.0 mmol), phenylacetylene (0.16 mL, 0.15 g, 1.5 mmol), chloranil (0.27 g, 1.1 mmol), and toluene (14 mL) were added to a 75 mL pressure vessel equipped with a stir bar under argon. $\text{BF}_3 \cdot \text{OEt}_2$ (0.14 mL, 0.16 g, 1.1 mmol) was added to the mixture and the pressure vessel was sealed and brought to $110\text{ }^{\circ}\text{C}$ in an oil bath. After 24 hours, the mixture was cooled and diluted with CH_2Cl_2 (50 mL). The reagents were in turn quenched with saturated NaHCO_3 (aq., 50 mL), and the organics were then washed with saturated NaHCO_3 (aq., 3 x 50 mL). The organics were poured through a cotton plug, and the solvent was removed *in vacuo*. The solids were triturated with hexanes and purified by flash chromatography (0/10 CH_2Cl_2 /hexanes to 7/3 CH_2Cl_2 /hexanes) to afford the product as a white solid (0.27 g, 75% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.19 (d, $J = 7.9\text{ Hz}$, 2H), 8.11 (br d, $J = 8.9\text{ Hz}$, 1H), 8.04 (br s, 1H), 7.84 (s, 1H), 7.80 (d, $J = 8.9\text{ Hz}$, 1H), 7.61 – 7.46 (m, 8H); (^1H NMR spectroscopic data match those previously reported);^{S3} ^{13}C NMR (151 MHz, CDCl_3) δ 157.3, 148.5, 147.6, 139.3, 137.9, 133.1, 132.0, 129.8, 129.6, 129.04, 128.97, 128.86, 127.9, 127.7, 127.1, 120.6, 120.2; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{27}\text{BrN}$ ($\text{M} + \text{H}$) $^+$ 360.0388, found 360.0377; IR (KBr) 3057, 3030, 2920, 2850, 1589 cm^{-1} .

D. 6-Bromo-2-*p*-octylphenyl-4-phenylquinoline (2.2b). N-*p*-Octylbenzylidene-4-bromoaniline (**2.1b**, 0.25 g, 0.67 mmol), phenylacetylene (0.11 mL, 0.10 g, 1.01 mmol), chloranil (0.18 g, 0.74 mmol), and toluene (15 mL) were added to a 75 mL pressure vessel equipped with a stir bar under argon. BF₃·OEt₂ (0.10 mL, 0.12 g, 0.8 mmol) was added to the mixture, and the pressure vessel was sealed before being brought to 150 °C in an oil bath. After 24 hours, the mixture was cooled and diluted with CH₂Cl₂ (50 mL), and the reagents were then quenched with saturated NaHCO₃ (aq., 50 mL). The organics were subsequently washed with saturated NaHCO₃ (aq., 4 x 50 mL). The organics were in turn poured through a cotton plug, and the solvent was removed *in vacuo*. The solids were purified by flash chromatography (0/10 ethyl acetate/hexanes to 3/7 ethyl acetate/hexanes) to afford the product as a white solid (0.28 g, 89% yield). ¹H NMR (600 MHz, CDCl₃) δ = 8.15 – 8.06 (m, 3H), 8.03 (s, 1H), 7.82 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.50 (m, 5H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.61 (m, 2H), 1.40 – 1.23 (m, 10H), 0.89 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (151 MHz, CD₂Cl₂) δ = 157.5, 148.8, 148.0, 145.6, 138.4, 137.0, 133.4, 132.3, 130.1, 129.5, 129.3, 129.2, 128.4, 127.9, 127.5, 120.6, 120.3, 36.3, 32.5, 32.0, 30.1, 29.92, 29.86, 23.3, 14.5; HRMS (ESI) *m/z* calculated for C₂₉H₃₁BrN (M + H)⁺ 472.1640, found 472.1625; IR (KBr) 3060, 3028, 2953, 2924, 2853, 1588 cm⁻¹; UV (THF) λ_{max} nm (ε): 348 (9440), 335 (10200), 275 (39000), 233 (26000).

E. N-*p*-Octylbenzylidene-4-ethynylaniline (2.3). 4-Ethynylaniline (0.75 g, 6.4 mmol), 4-octylbenzaldehyde (1.7 g, 7.6 mmol), 3 Å molecular sieves (3.0 g), and 60 mL of toluene were added to a 100 mL pressure vessel equipped with a stir bar under argon. The pressure vessel was sealed and brought to 130 °C in an oil bath. After 16 hours, the mixture was cooled to room temperature. The reaction mixture was then filtered through celite, and the solvent was removed *in vacuo*. The mixture was purified by flash chromatography using deactivated silica gel with pure hexanes as the mobile phase. After chromatography, the material was precipitated from pentane at –78 °C to yield the product as a pale yellow solid (0.86 g, 43%). ¹H NMR (600 MHz, CDCl₃) δ = 8.40 (s, 1H), 7.81 (d, *J*

= 8.0 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.10 (s, 1H), 2.67 (t, J = 7.6 Hz, 2H), 1.81 – 1.51 (m, 2H), 1.40 – 1.20 (m, 10H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ = 161.0, 152.8, 147.5, 133.8, 133.2, 129.10, 129.08, 121.1, 119.4, 83.8, 36.2, 32.0, 31.4, 29.6, 29.43, 29.40, 22.8, 14.3; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{28}\text{N}$ ($\text{M} + \text{H}$) $^+$ 318.2222, found 318.2230; IR (KBr) 3299, 2955, 2925, 2854, 2107, 1738, 1627, 1593 cm^{-1} ; UV (THF) λ_{max} nm (ϵ): 327 (19400), 277 (13900).

F. Poly[(2-*p*-octylphenyl)quinoline-4,6-diyl] (2.4). N-*p*-Octylbenzylidene-4-ethynylaniline (2.3, 0.50 g, 1.6 mmol), chloranil (0.43 g, 1.7 mmol), and toluene (22 mL) were added to a 75 mL pressure vessel equipped with a stir bar under argon. $\text{BF}_3 \cdot \text{OEt}_2$ (0.38 mL, 0.25 g, 1.7 mmol) was added to the mixture and the pressure vessel was sealed and brought to 100 °C in an oil bath. After 24 hours, the mixture was cooled and diluted with CH_2Cl_2 (100 mL). The reagents were in turn quenched with saturated NaHCO_3 (aq., 100 mL), and the organics were then washed with saturated NaHCO_3 (aq., 3 x 100 mL). The organics were subsequently poured through a cotton plug, and the solvent was removed *in vacuo*. The solids were dissolved in 50 mL of toluene and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.72 g, 2.14 mmol) was added to the mixture. After 24 hours of stirring at room temperature, the mixture was diluted with CH_2Cl_2 (100 mL), and the reagents were then quenched with saturated NaHCO_3 (aq., 100 mL). The organics were then washed with saturated NaHCO_3 (aq., 3 x 100 mL). The organics were in turn poured through a cotton plug, and the solvent was removed *in vacuo*. The mixture was taken up in a minimum amount of CHCl_3 and purified by size exclusion chromatography (Bio-Bead SX-1 resin, with CHCl_3 as the mobile phase) and precipitation from ethanol to yield the product as an ochre colored powder (0.17 g, 34% yield). ^1H NMR (600 MHz, CD_2Cl_2) δ = 9.17–5.76 (m, broad, 8H), 3.11–0.22 (m, broad, 18H); IR (KBr) 3319, 2926, 2854, 2216, 1616, 1585 cm^{-1} ; UV (THF) λ_{max} nm (ϵ): 333 (26400, sh), 275 (38900).

2.5.3. Spectroscopic Characterization Data

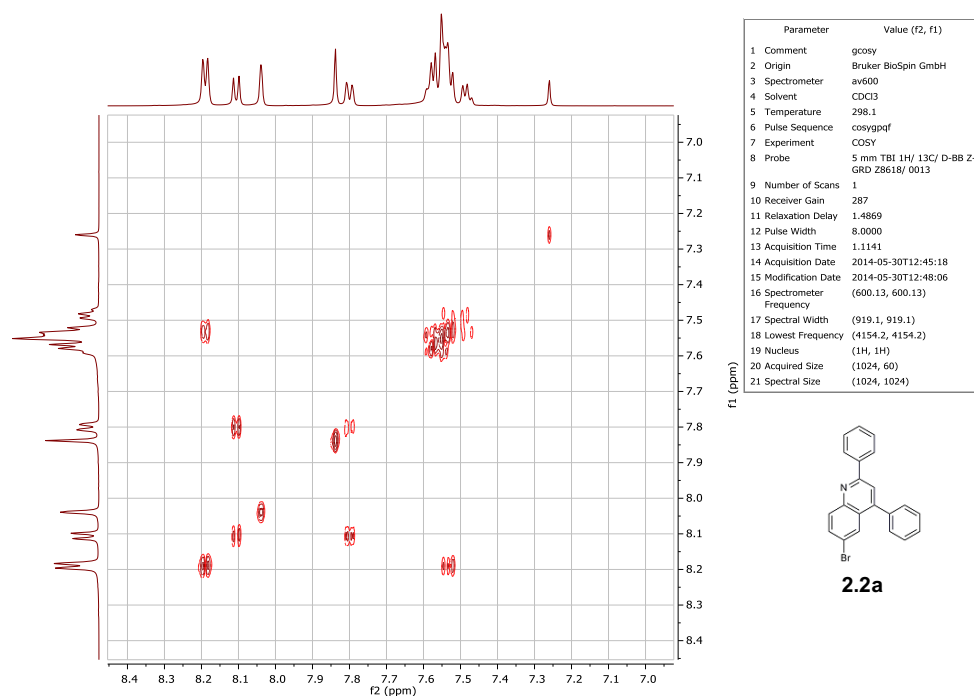


Figure S2.1. The COSY spectrum obtained of compound **2.2a**. This spectrum was used to assign aromatic protons.

Crude Reaction Mixture

Parameter	Value
1 Comment	¹ H spectrum
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	av600
4 Solvent	CDCl ₃
5 Temperature	298.0
6 Pulse Sequence	zg30
7 Experiment	1D
8 Probe	5 mm TBI 1H/ 13C/ D-BB Z-GRD Z9618/ 0013
9 Number of Scans	8
10 Receiver Gain	128
11 Relaxation Delay	0.1000
12 Pulse Width	8.0000
13 Acquisition Time	5.0998
14 Acquisition Date	2014-05-29T15:19:40
15 Modification Date	2014-05-29T15:20:15
16 Spectrometer	600.13
Frequency	
17 Spectral Width	9615.4
18 Lowest Frequency	640.8
19 Nucleus	¹ H
20 Acquired Size	49037
21 Spectral Size	131072

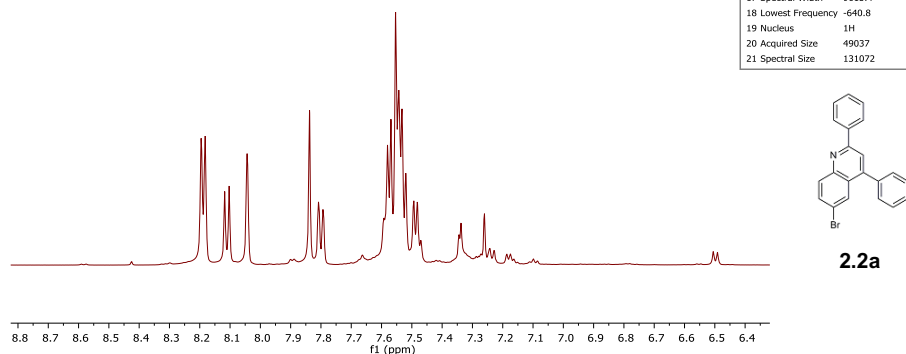


Figure S2.2. The ¹H NMR spectrum obtained for the crude compound **2.2a**.

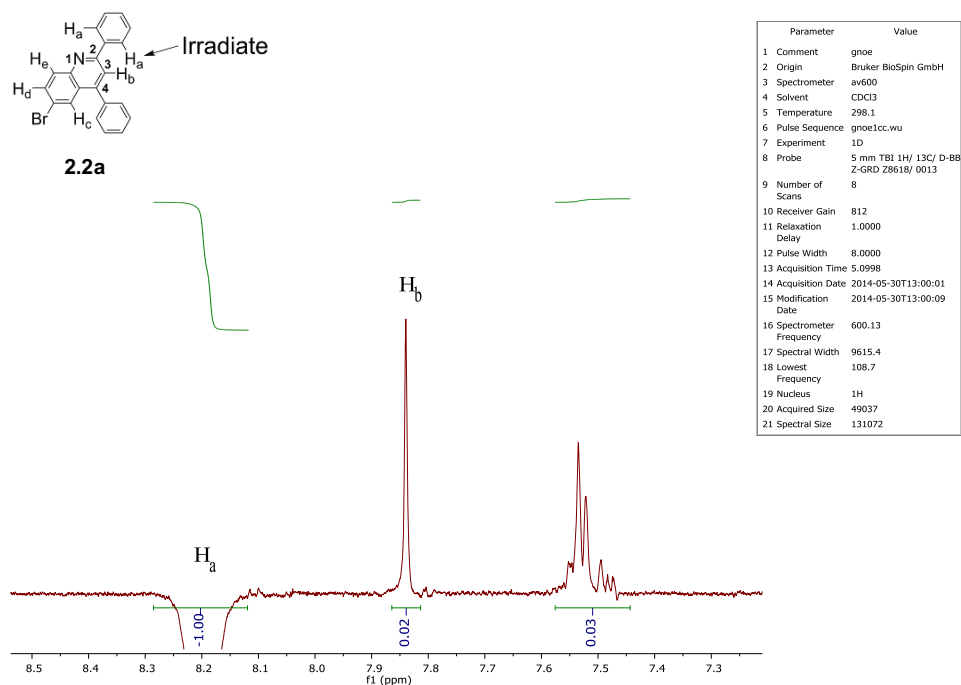
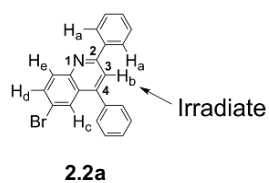


Figure S2.3. The NOE spectrum obtained for compound **2.2a**, where H_a was irradiated. Irradiation of H_a leads to an enhancement of the NOE signal between H_a and H_b .



Parameter	Value
1 Comment	gnoe
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	av600
4 Solvent	CDCl ₃
5 Temperature	298.1
6 Pulse Sequence	gnoe1cc.wu
7 Experiment	1D
8 Probe	5 mm TBI 1H/ 13C/ D-BB Z-GRD Z8618/ 0013
9 Number of Scans	8
10 Receiver Gain	1030
11 Relaxation Delay	1.0000
12 Pulse Width	8.0000
13 Acquisition Time	5.0998
14 Acquisition Date	2014-05-30T12:51:17
15 Modification Date	2014-05-30T12:52:07
16 Spectrometer	600.13
Frequency	
17 Spectral Width	9615.4
18 Lowest	-103.3
Frequency	
19 Nucleus	1H
20 Acquired Size	49037
21 Spectral Size	131072

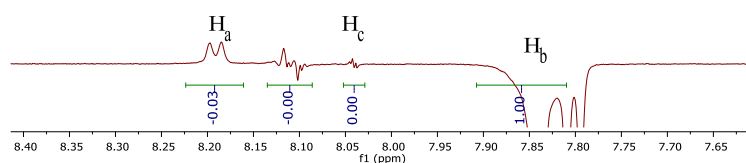


Figure S2.4: The NOE spectrum obtained for compound **2.2a**, where **H_b** was irradiated. Irradiation of **H_b** leads to an enhancement of the NOE signal between **H_a** and **H_b**. There is no enhancement in the NOE signal between **H_b** and **H_c**.

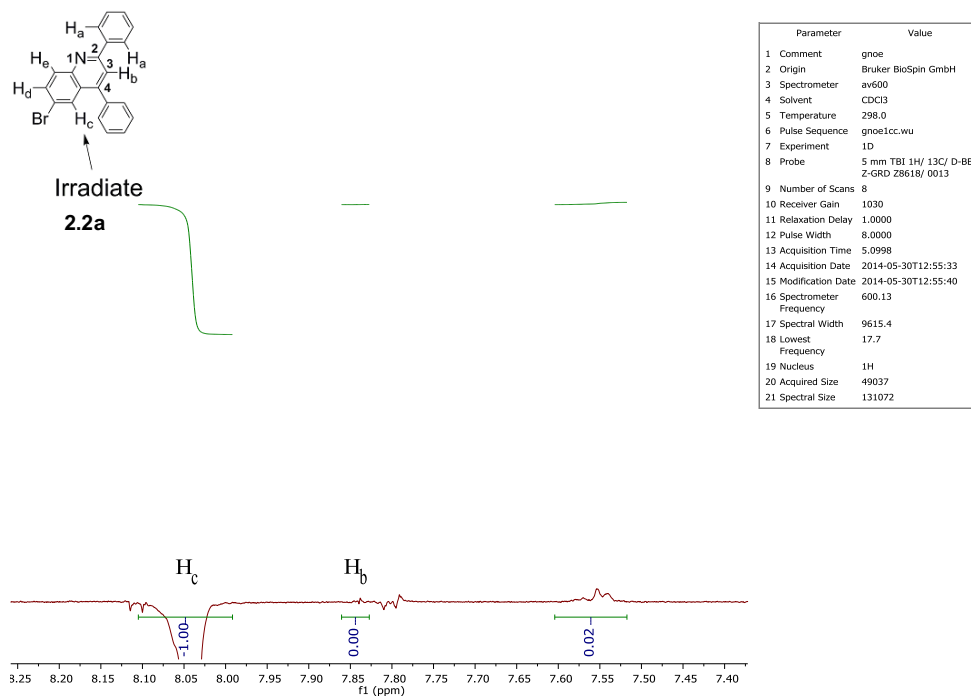


Figure S2.5. An NOE spectrum obtained of compound **2.2a**, where H_c was irradiated. There is no enhancement in the NOE signal between H_b and H_c .

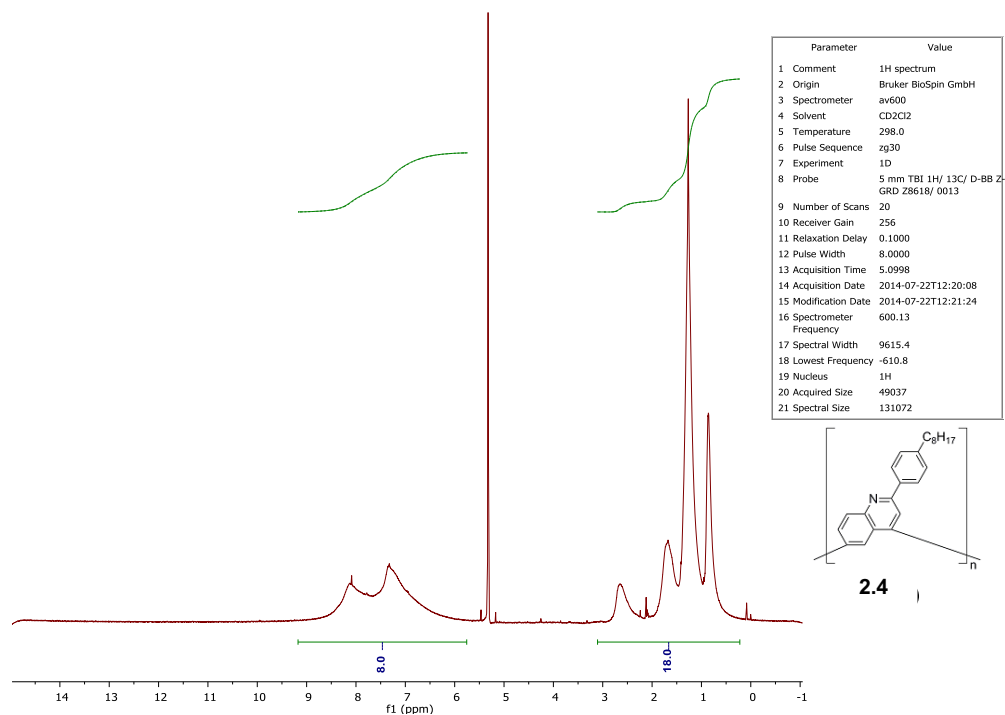


Figure S2.6. The ¹H NMR spectrum obtained for purified material **2.4**.

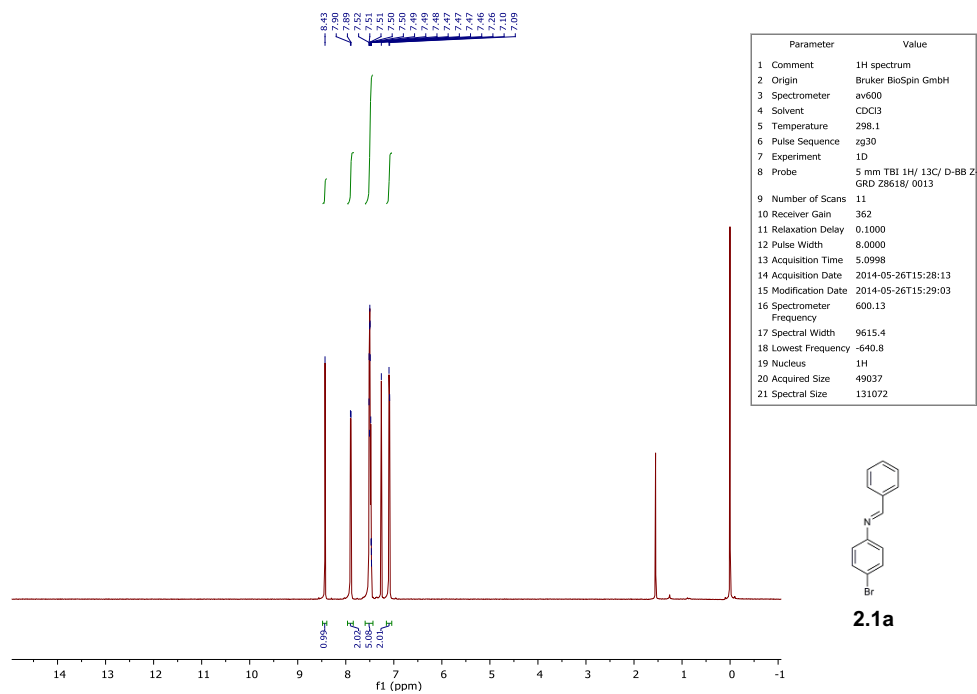


Figure S2.7. The ^1H NMR spectrum obtained for compound **2.1a**.

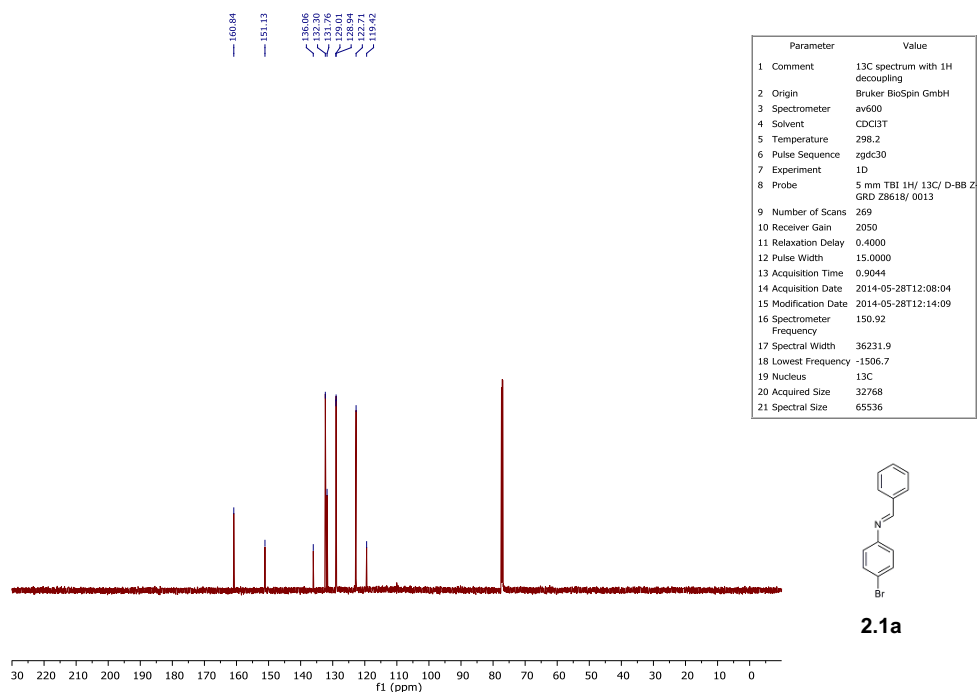


Figure S2.8. The ¹³C NMR spectrum obtained for compound **2.1a**.

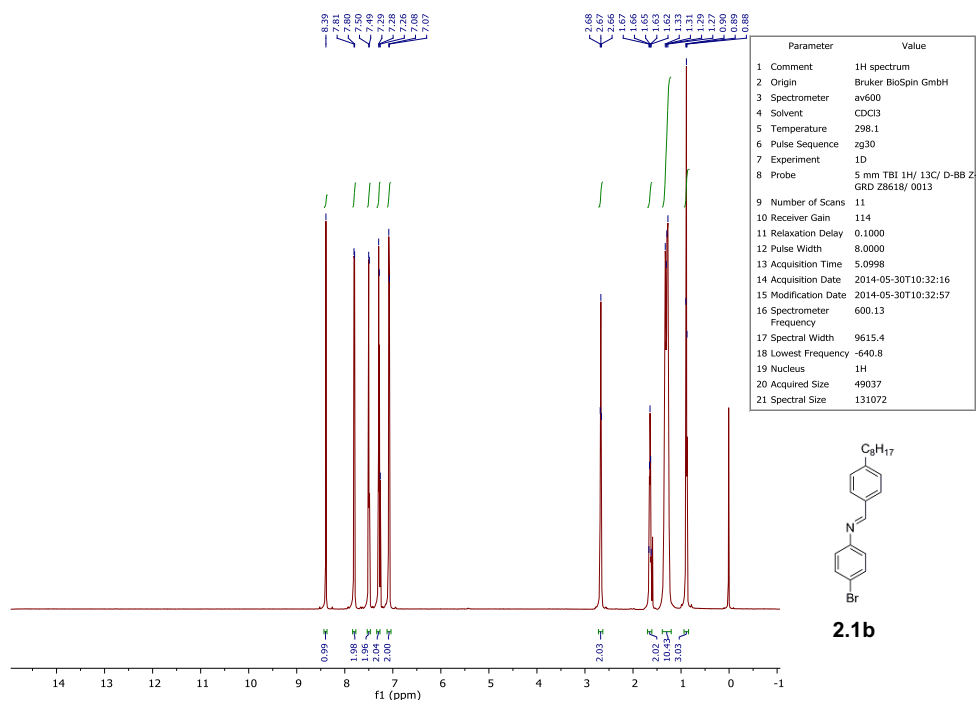


Figure S2.9. The ¹H NMR spectrum obtained for compound **2.1b**.

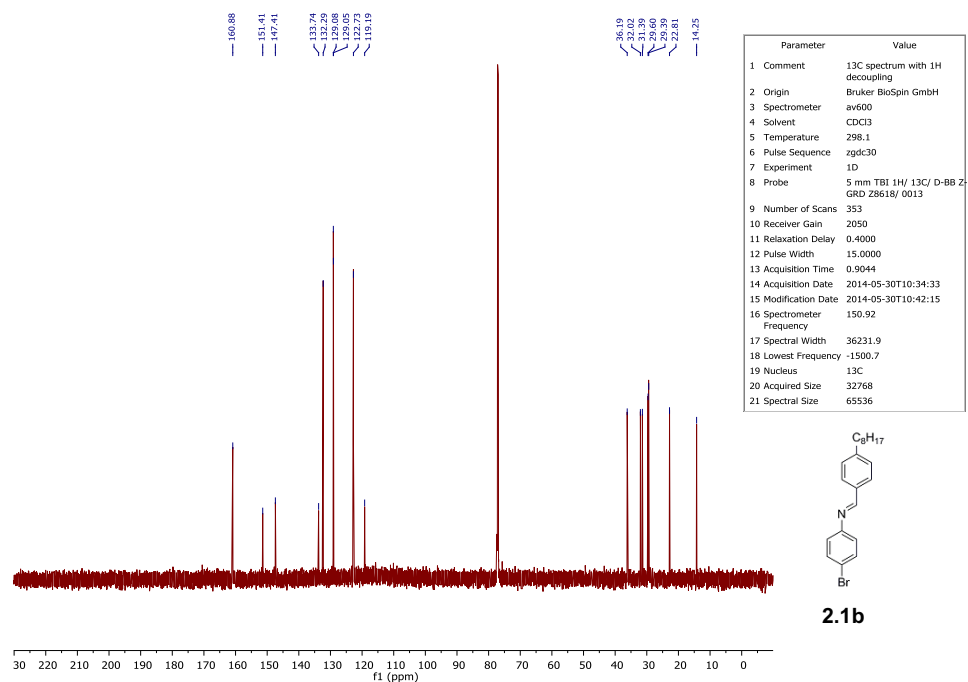


Figure S2.10. The ¹³C NMR spectrum obtained for compound **2.1b**.

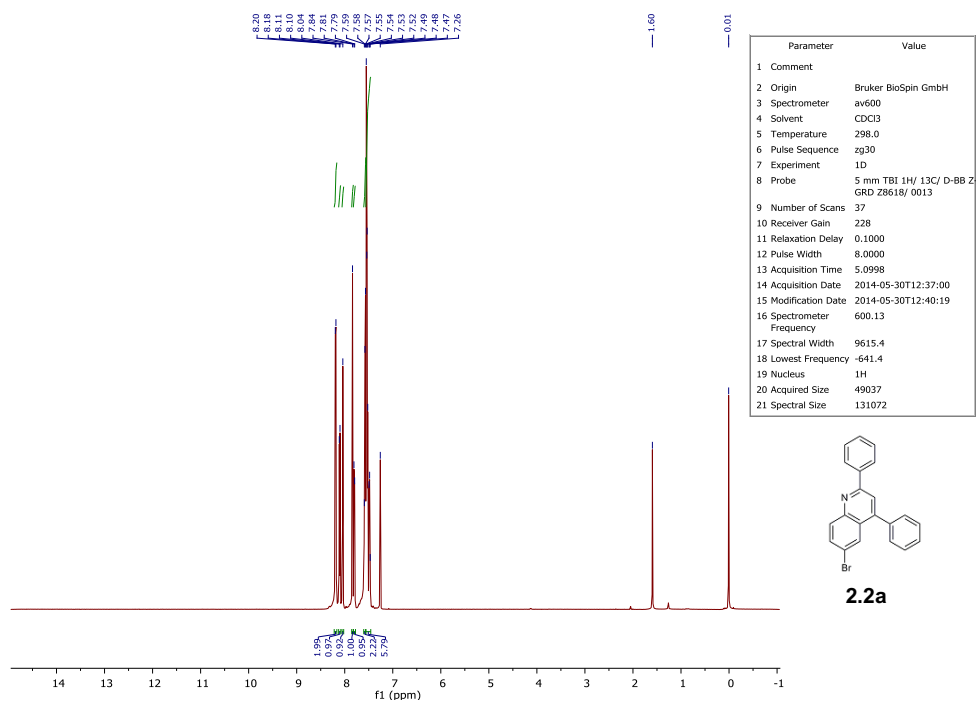


Figure S2.11. The ^1H NMR spectrum obtained for compound **2.2a**.

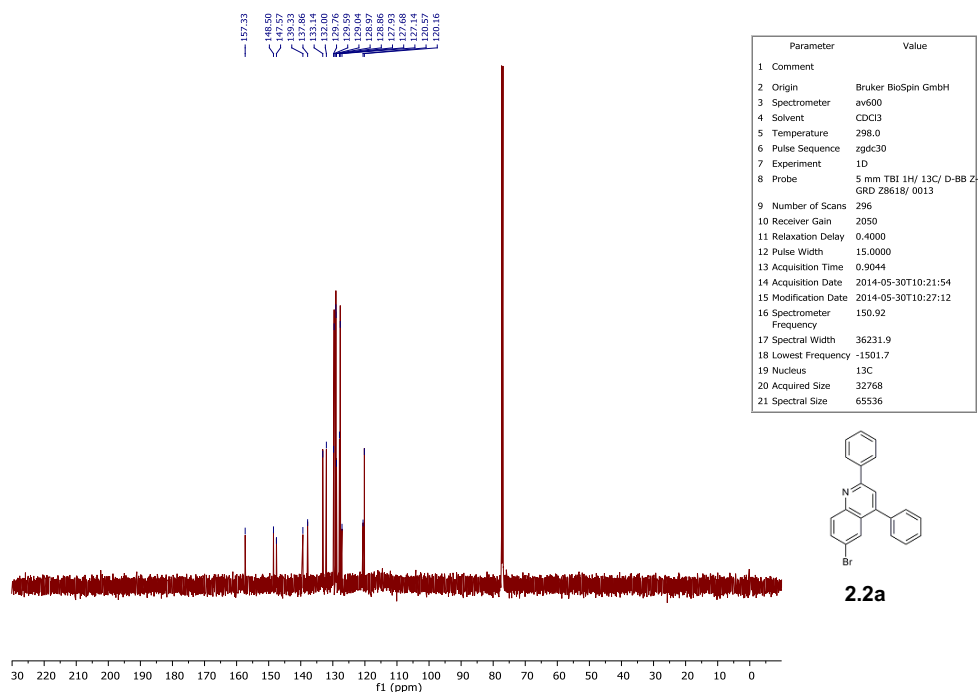


Figure S2.12. The ^{13}C NMR spectrum obtained for compound **2.2a**.

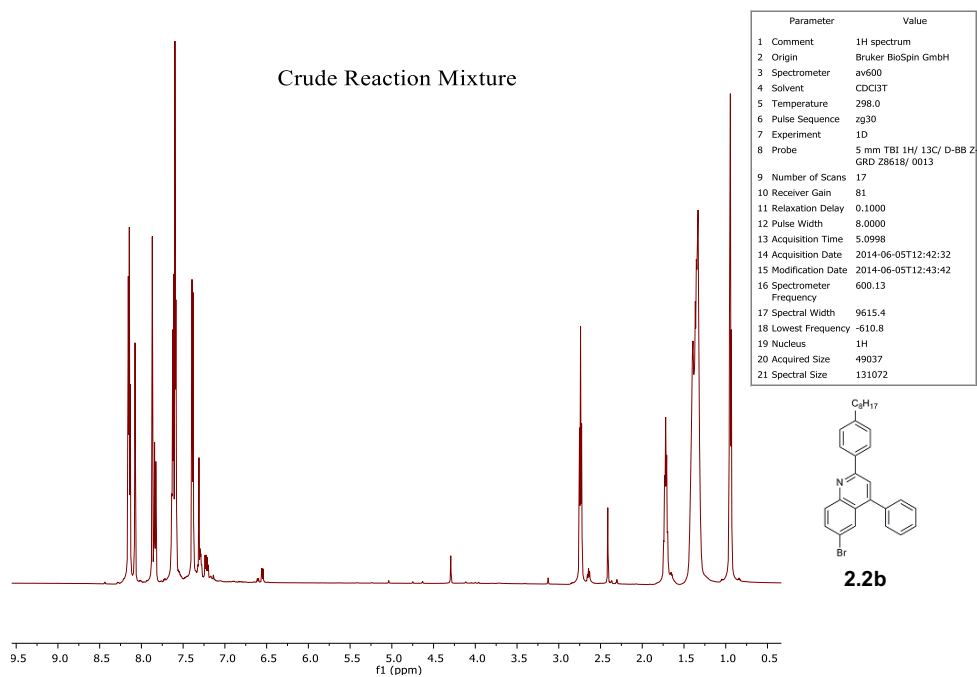


Figure S2.13. The ¹H NMR spectrum obtained for the crude reaction mixture to produce compound **2.2b**.

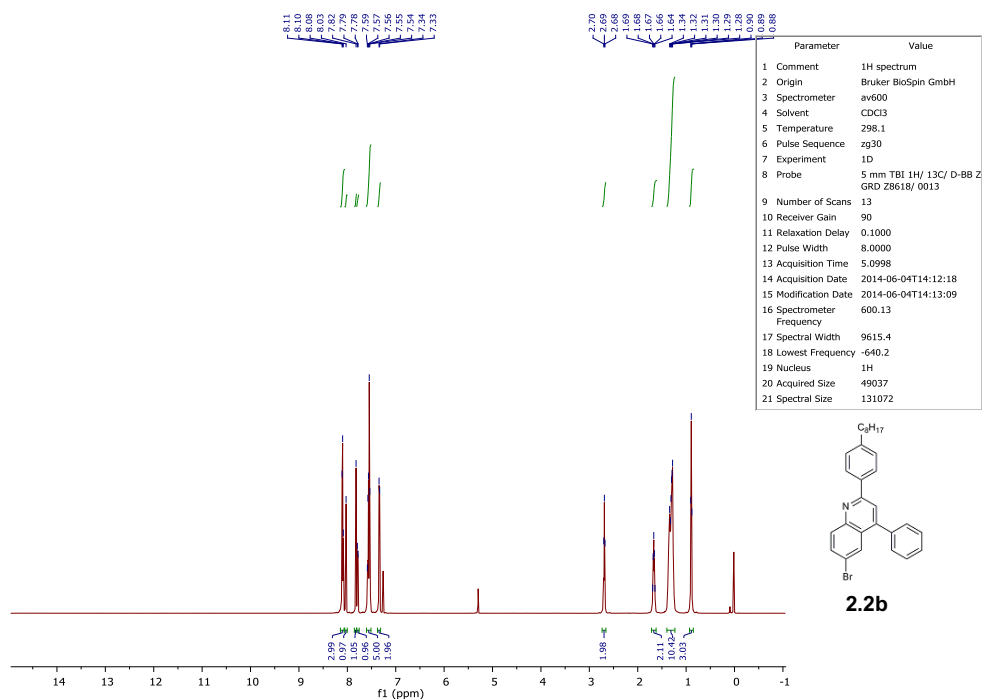


Figure S2.14. The ^1H NMR spectrum obtained for compound **2.2b**.

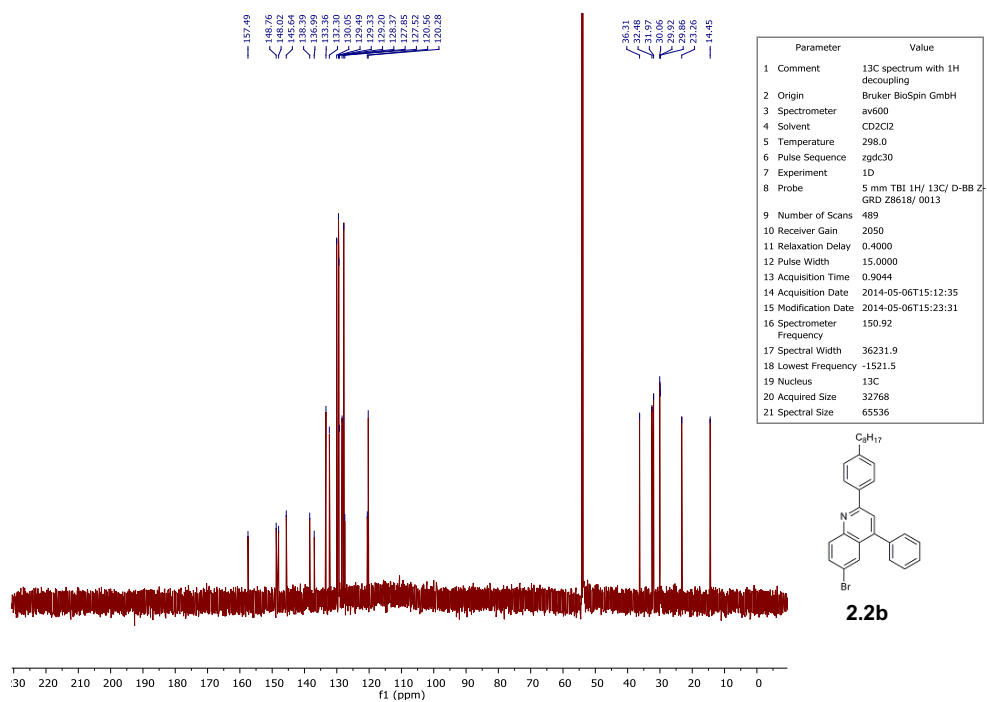


Figure S2.15. The ¹³C NMR spectrum obtained for compound **2.2b**.

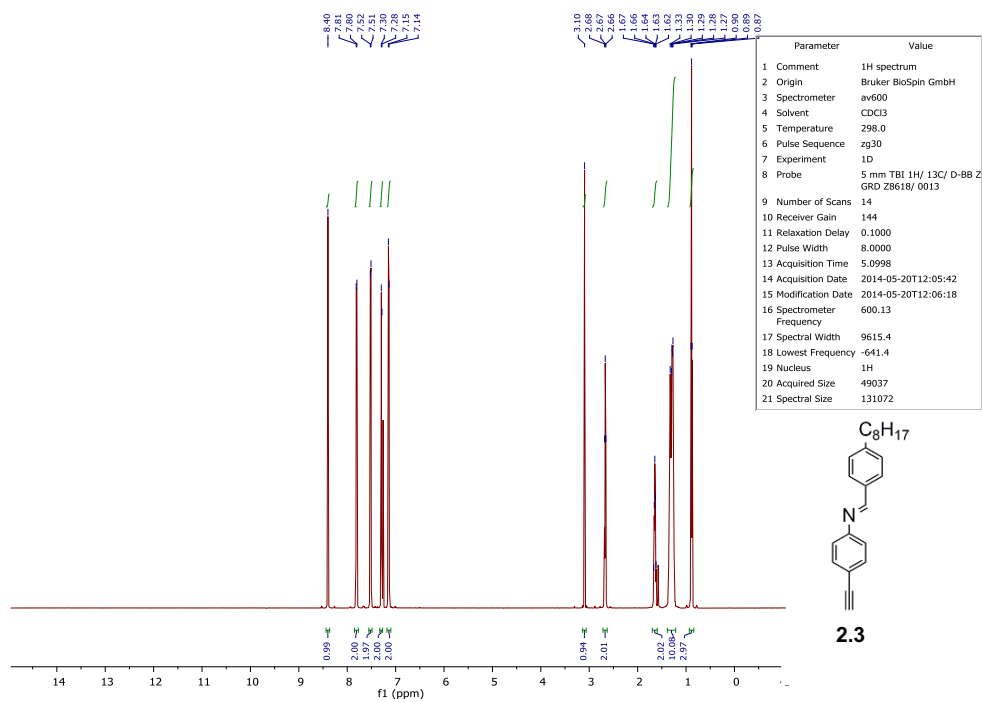


Figure S2.16. The ^1H NMR spectrum obtained for compound **2.3**.

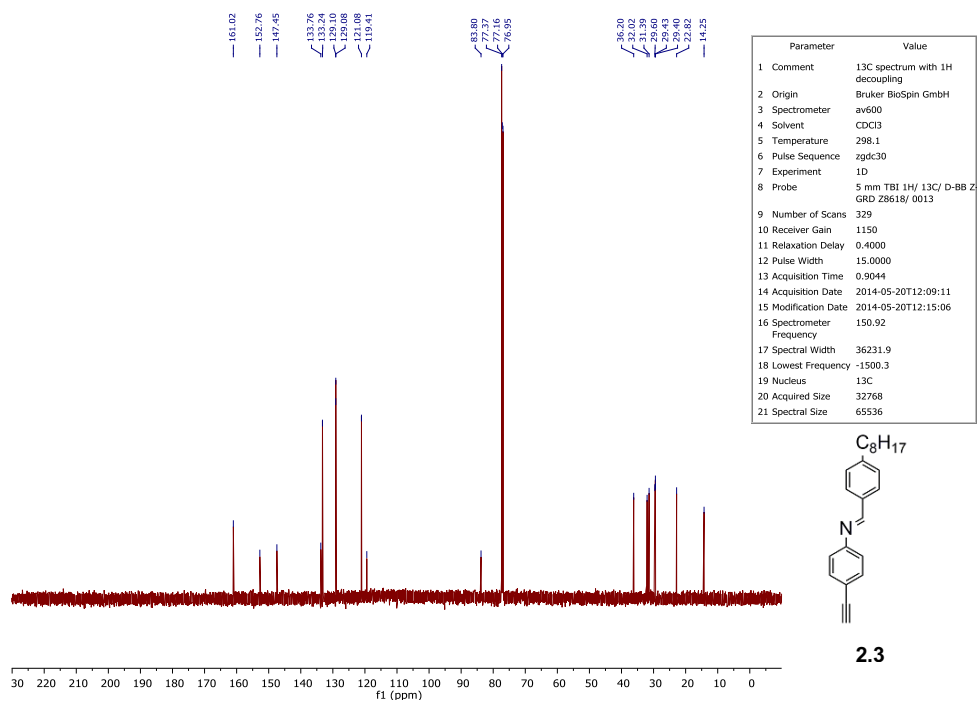


Figure S2.17. The ¹³C NMR spectrum obtained for compound **2.3**.

2.5.4. X-ray Data Collection, Structure Solution, and Refinement

A. General Experimental Procedures. A crystal of **2.2a** was prepared by slow evaporation of solvent from a tetrahydrofuran solution of the compound. A colorless crystal with dimensions of approximately 0.172 x 0.222 x 0.384 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2^{S4} program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT^{S5} and SADABS^{S6} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL^{S7} program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups *Pbcm* and *Pca21*. It was later determined that the noncentrosymmetric space group *Pca21* was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors^{S8} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.0463$ and $Goof = 1.038$ for 250 variables refined against 3947 data ($0.73 \text{ \AA}$), $R1 = 0.0177$ for those 3857 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.^{S9}

B. Definitions for the Crystallographic Analysis.

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Identification code	2.2a
Empirical formula	C ₂₁ H ₁₄ Br N
Formula weight	360.24
Temperature	88(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pca</i> 2 ₁
Unit cell dimensions	a = 7.6677(10) Å α = 90°. b = 10.2755(13) Å β = 90°. c = 19.816(3) Å γ = 90°.
Volume	1561.3(3) Å ³
Z	4
Density (calculated)	1.533 Mg/m ³
Absorption coefficient	2.631 mm ⁻¹
F(000)	728
Crystal color	colorless
Crystal size	0.384 x 0.222 x 0.172 mm ³

Theta range for data collection	1.982 to 29.030°
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-26 \leq l \leq 26$
Reflections collected	17905
Independent reflections	3947 [R(int) = 0.0194]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.7087 and 0.4786
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3947 / 1 / 250
Goodness-of-fit on F ²	1.038
Final R indices [I>2sigma(I) = 3857 data]	R1 = 0.0177, wR2 = 0.0460
R indices (all data, 0.73Å)	R1 = 0.0183, wR2 = 0.0463
Absolute structure parameter	0.0847(19)
Largest diff. peak and hole	0.293 and -0.199 e.Å ⁻³

Table S2.1. Crystal data and structure refinement for **2.2a**.

	x	y	z	U(eq)
Br(1)	7791(1)	698(1)	-4(1)	22(1)
N(1)	10523(2)	5033(2)	1758(1)	14(1)
C(1)	10052(3)	4095(2)	1304(1)	13(1)
C(2)	10206(3)	2778(2)	1513(1)	16(1)
C(3)	9597(3)	1783(2)	1117(1)	17(1)
C(4)	8791(3)	2086(2)	497(1)	15(1)
C(5)	8691(2)	3330(2)	254(1)	14(1)
C(6)	9362(3)	4371(2)	649(1)	12(1)
C(7)	9324(3)	5709(2)	446(1)	12(1)
C(8)	9785(2)	6628(2)	914(1)	13(1)
C(9)	10326(2)	6264(2)	1575(1)	12(1)
C(10)	10713(3)	7274(2)	2089(1)	13(1)
C(11)	11838(3)	7004(2)	2627(1)	16(1)
C(12)	12152(3)	7926(2)	3124(1)	18(1)
C(13)	11360(3)	9148(2)	3085(1)	19(1)
C(14)	10256(3)	9435(2)	2550(1)	18(1)
C(15)	9928(3)	8503(2)	2056(1)	16(1)
C(16)	8831(2)	6126(2)	-248(1)	12(1)
C(17)	7712(2)	7194(2)	-324(1)	14(1)
C(18)	7218(3)	7621(2)	-961(1)	17(1)
C(19)	7853(3)	6998(2)	-1534(1)	19(1)
C(20)	9001(3)	5957(2)	-1467(1)	17(1)
C(21)	9485(3)	5518(2)	-828(1)	14(1)

Table S2.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2.2a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Br(1)-C(4)	1.899(2)
N(1)-C(9)	1.325(3)
N(1)-C(1)	1.367(3)
C(1)-C(2)	1.421(3)
C(1)-C(6)	1.429(3)
C(2)-C(3)	1.371(3)
C(3)-C(4)	1.409(3)
C(4)-C(5)	1.368(3)
C(5)-C(6)	1.421(3)
C(6)-C(7)	1.434(3)
C(7)-C(8)	1.371(3)
C(7)-C(16)	1.488(3)
C(8)-C(9)	1.422(3)
C(9)-C(10)	1.485(3)
C(10)-C(11)	1.399(3)
C(10)-C(15)	1.401(3)
C(11)-C(12)	1.388(3)
C(12)-C(13)	1.396(3)
C(13)-C(14)	1.388(3)
C(14)-C(15)	1.393(3)
C(16)-C(21)	1.400(3)
C(16)-C(17)	1.401(3)
C(17)-C(18)	1.390(3)
C(18)-C(19)	1.392(3)

C(19)-C(20)	1.392(3)
C(20)-C(21)	1.394(3)
C(9)-N(1)-C(1)	117.52(17)
N(1)-C(1)-C(2)	117.23(18)
N(1)-C(1)-C(6)	123.75(17)
C(2)-C(1)-C(6)	118.97(18)
C(3)-C(2)-C(1)	120.99(19)
C(2)-C(3)-C(4)	118.92(19)
C(5)-C(4)-C(3)	122.51(19)
C(5)-C(4)-Br(1)	119.70(16)
C(3)-C(4)-Br(1)	117.79(15)
C(4)-C(5)-C(6)	119.31(19)
C(5)-C(6)-C(1)	118.96(17)
C(5)-C(6)-C(7)	124.03(18)
C(1)-C(6)-C(7)	116.94(17)
C(8)-C(7)-C(6)	117.68(19)
C(8)-C(7)-C(16)	119.57(17)
C(6)-C(7)-C(16)	122.74(18)
C(7)-C(8)-C(9)	121.17(18)
N(1)-C(9)-C(8)	122.46(18)
N(1)-C(9)-C(10)	117.14(17)
C(8)-C(9)-C(10)	120.40(18)
C(11)-C(10)-C(15)	118.62(19)
C(11)-C(10)-C(9)	120.55(18)

C(15)-C(10)-C(9)	120.82(18)
C(12)-C(11)-C(10)	120.8(2)
C(11)-C(12)-C(13)	119.9(2)
C(14)-C(13)-C(12)	120.0(2)
C(13)-C(14)-C(15)	120.0(2)
C(14)-C(15)-C(10)	120.6(2)
C(21)-C(16)-C(17)	118.69(19)
C(21)-C(16)-C(7)	122.59(18)
C(17)-C(16)-C(7)	118.69(17)
C(18)-C(17)-C(16)	120.8(2)
C(17)-C(18)-C(19)	120.0(2)
C(20)-C(19)-C(18)	119.8(2)
C(19)-C(20)-C(21)	120.3(2)
C(20)-C(21)-C(16)	120.39(19)

Table S2.3. Bond lengths [Å] and angles [°] for **2.2a**.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Br(1)	33(1)	13(1)	21(1)	-2(1)	0(1)	-6(1)
N(1)	16(1)	13(1)	13(1)	1(1)	1(1)	0(1)
C(1)	13(1)	13(1)	13(1)	0(1)	2(1)	0(1)
C(2)	21(1)	13(1)	13(1)	3(1)	2(1)	2(1)
C(3)	22(1)	12(1)	18(1)	2(1)	4(1)	1(1)
C(4)	16(1)	12(1)	16(1)	-3(1)	4(1)	-2(1)
C(5)	12(1)	14(1)	14(1)	-1(1)	3(1)	0(1)
C(6)	11(1)	11(1)	12(1)	0(1)	3(1)	1(1)
C(7)	11(1)	12(1)	12(1)	2(1)	1(1)	2(1)
C(8)	14(1)	11(1)	13(1)	2(1)	2(1)	0(1)
C(9)	12(1)	13(1)	12(1)	0(1)	2(1)	0(1)
C(10)	15(1)	14(1)	10(1)	1(1)	3(1)	-3(1)
C(11)	17(1)	16(1)	14(1)	1(1)	1(1)	-1(1)
C(12)	19(1)	22(1)	14(1)	1(1)	0(1)	-4(1)
C(13)	22(1)	18(1)	16(1)	-3(1)	4(1)	-6(1)
C(14)	21(1)	13(1)	19(1)	-2(1)	4(1)	-1(1)
C(15)	17(1)	16(1)	15(1)	1(1)	2(1)	-1(1)
C(16)	12(1)	11(1)	12(1)	1(1)	0(1)	-3(1)
C(17)	14(1)	12(1)	15(1)	-1(1)	0(1)	-2(1)
C(18)	16(1)	14(1)	22(1)	4(1)	-3(1)	-1(1)
C(19)	21(1)	22(1)	14(1)	5(1)	-5(1)	-6(1)
C(20)	21(1)	18(1)	13(1)	-1(1)	1(1)	-5(1)
C(21)	15(1)	12(1)	16(1)	-1(1)	1(1)	0(1)

Table S2.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2.2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	x	y	z	U(eq)
H(2A)	10780(40)	2620(30)	1940(14)	19
H(3A)	9660(40)	950(30)	1269(15)	21
H(5A)	8130(30)	3500(30)	-179(14)	16
H(8A)	9790(30)	7460(30)	793(13)	15
H(11A)	12360(40)	6190(30)	2636(15)	19
H(12A)	12920(30)	7710(30)	3484(16)	22
H(13A)	11540(40)	9710(30)	3436(15)	22
H(14A)	9730(40)	10290(30)	2527(18)	21
H(15A)	9130(40)	8730(30)	1704(13)	19
H(17A)	7230(30)	7610(20)	69(19)	16
H(18A)	6420(40)	8280(30)	-983(14)	21
H(19A)	7500(40)	7290(30)	-1977(16)	23
H(20A)	9420(40)	5530(30)	-1853(15)	21
H(21A)	10200(40)	4810(30)	-786(14)	17

Table S2.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for **2.2a**.

C(9)-N(1)-C(1)-C(2)	-177.73(18)
C(9)-N(1)-C(1)-C(6)	-0.2(3)
N(1)-C(1)-C(2)-C(3)	173.24(19)
C(6)-C(1)-C(2)-C(3)	-4.4(3)
C(1)-C(2)-C(3)-C(4)	-0.7(3)
C(2)-C(3)-C(4)-C(5)	4.3(3)
C(2)-C(3)-C(4)-Br(1)	-174.92(16)
C(3)-C(4)-C(5)-C(6)	-2.5(3)
Br(1)-C(4)-C(5)-C(6)	176.71(14)
C(4)-C(5)-C(6)-C(1)	-2.8(3)
C(4)-C(5)-C(6)-C(7)	-179.91(19)
N(1)-C(1)-C(6)-C(5)	-171.37(18)
C(2)-C(1)-C(6)-C(5)	6.1(3)
N(1)-C(1)-C(6)-C(7)	6.0(3)
C(2)-C(1)-C(6)-C(7)	-176.51(19)
C(5)-C(6)-C(7)-C(8)	170.83(18)
C(1)-C(6)-C(7)-C(8)	-6.4(3)
C(5)-C(6)-C(7)-C(16)	-9.9(3)
C(1)-C(6)-C(7)-C(16)	172.91(17)
C(6)-C(7)-C(8)-C(9)	1.6(3)
C(16)-C(7)-C(8)-C(9)	-177.68(17)
C(1)-N(1)-C(9)-C(8)	-5.1(3)
C(1)-N(1)-C(9)-C(10)	175.49(17)
C(7)-C(8)-C(9)-N(1)	4.5(3)

C(7)-C(8)-C(9)-C(10)	-176.14(18)
N(1)-C(9)-C(10)-C(11)	24.0(3)
C(8)-C(9)-C(10)-C(11)	-155.42(19)
N(1)-C(9)-C(10)-C(15)	-154.40(18)
C(8)-C(9)-C(10)-C(15)	26.2(3)
C(15)-C(10)-C(11)-C(12)	0.9(3)
C(9)-C(10)-C(11)-C(12)	-177.45(18)
C(10)-C(11)-C(12)-C(13)	-0.9(3)
C(11)-C(12)-C(13)-C(14)	0.2(3)
C(12)-C(13)-C(14)-C(15)	0.6(3)
C(13)-C(14)-C(15)-C(10)	-0.5(3)
C(11)-C(10)-C(15)-C(14)	-0.2(3)
C(9)-C(10)-C(15)-C(14)	178.17(19)
C(8)-C(7)-C(16)-C(21)	133.5(2)
C(6)-C(7)-C(16)-C(21)	-45.7(3)
C(8)-C(7)-C(16)-C(17)	-44.3(3)
C(6)-C(7)-C(16)-C(17)	136.41(19)
C(21)-C(16)-C(17)-C(18)	1.9(3)
C(7)-C(16)-C(17)-C(18)	179.83(18)
C(16)-C(17)-C(18)-C(19)	-0.9(3)
C(17)-C(18)-C(19)-C(20)	-0.8(3)
C(18)-C(19)-C(20)-C(21)	1.4(3)
C(19)-C(20)-C(21)-C(16)	-0.4(3)
C(17)-C(16)-C(21)-C(20)	-1.2(3)

C(7)-C(16)-C(21)-C(20)	-179.10(19)
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Table S2.6. Torsion angles [°] for **2.2a**.

2.5.5. Supporting References

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3.1 Abstract

Graphene nanoribbons (GNRs) represent promising materials for the next generation of nanoscale electronics. However, despite substantial progress towards the bottom-up synthesis of chemically and structurally well-defined all-carbon GNRs, strategies for the preparation of their nitrogen-doped analogs remain at a nascent stage. This scarce literature precedent is surprising given the established use of substitutional doping for tuning the properties of electronic materials. Herein, we report the synthesis of a previously unknown class of polybenzoquinoline-based materials, which have potential as GNR precursors. Our scalable and facile approach employs few synthetic steps, inexpensive commercial starting materials, and straightforward reaction conditions. Moreover, due to the importance of quinoline derivatives for a variety of applications, the reported findings may hold implications across a diverse range of chemical and physical disciplines.

3.2 Introduction

Graphene nanoribbons (GNRs), which are narrow strips of graphene featuring a quantum confinement-induced bandgap, constitute a promising class of materials for the next generation of semiconductor devices.^{1–10} The electronic properties of GNRs are exquisitely sensitive to their width, heteroatom content, and edge character.^{3–5} Thus, much research effort has been devoted to the preparation of GNRs that are structurally and chemically defined at the atomic level.^{6–10} Although traditional top-down lithographic approaches have exhibited only limited success in this regard,^{6–10} more recent studies have demonstrated the bottom-up preparation of pristine GNRs via the surface-assisted^{11–22} or solution-phase^{23–32} synthesis of nanoribbon precursor polymers, followed by their cyclodehydrogenation. To date, these bottom-up strategies have primarily focused on all-carbon systems, with only a limited number of studies describing the preparation of nitrogen-containing GNR

frameworks.^{20–22,31,32} Given the immense potential of substitutional nitrogen doping for tailoring the properties of GNRs, the sparse literature precedent is surprising and likely arises from the challenges associated with the incorporation of heteroatoms at arbitrary locations in graphitic materials.^{33,34}

Herein, we describe the modular synthesis of polybenzoquinolines, which constitute a generic class of GNR precursor polymers, and, to the best of our knowledge, have never been previously reported. We first develop general aza-Diels–Alder reaction conditions for the synthesis of a series of benzoquinoline model compounds. Subsequently, we prepare an AB-type bifunctional monomer and use the conditions validated for the model compounds to synthesize a congested polybenzoquinoline via a Diels–Alder-type polymerization reaction.^{35–37} We in turn demonstrate the scope and modularity of our methodology by preparing polybenzoquinolines of various sizes that feature different peripheral substituents. Overall, our findings enable facile and rapid access to a previously unknown family of benzoquinoline-based materials, which may prove valuable for a wide range of applications.

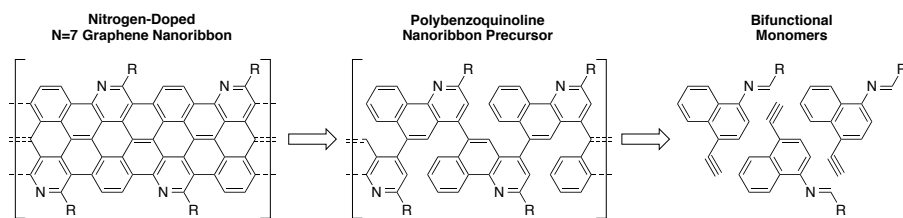


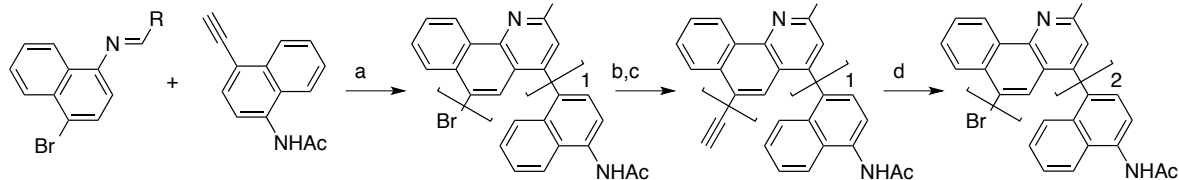
Figure 3.1. Illustration of a synthetic strategy for the preparation of a nitrogen-doped $N=7$ armchair graphene nanoribbon. The desired steps consist of the Diels–Alder-type polymerization of bifunctional monomers to furnish a polybenzoquinoline nanoribbon precursor, which can in turn be cyclodehydrogenated into the target nitrogen-doped graphene nanoribbon.

3.3 Results and Discussion

As our synthetic target, we selected a nitrogen-doped $N=7$ armchair GNR (Figure 3.1, left). We envisioned the preparation of this target by surface-assisted cyclodehydrogenation of a polymeric precursor, as demonstrated by Müllen, Fasel, and co-workers for the conversion of polyanthracenes into analogous unsubstituted, all-carbon, GNRs.^{11–13} Here, to enable the formation of a well-defined

nitrogen-doped GNR, we designed an alternative unreported precursor consisting of benzoquinoline subunits linked at their 4 and 6 positions (Figure 3.1, middle). We in turn drew inspiration from the synthesis of quinoline heterocycles via the aza-Diels–Alder (Povarov) reaction^{38–44} and pictured the construction of the benzoquinoline subunits from alkyne- and aldimine-modified monomers (Figure 3.1, right). Consequently, we postulated that polymerization of the bifunctional monomers would furnish the desired polybenzoquinoline precursor (Figure 3.1, middle), which could ultimately be cyclodehydrogenated into a nitrogen-doped $N=7$ armchair GNR (Figure 3.1, left). We began our studies by synthesizing benzoquinoline model compounds **3.3a**, **b** and **3.5a**, **b** via the Povarov reaction,^{38–44} as illustrated in Scheme 3.1A. To prepare model compounds **3.3a** and **3.3b**, we first formed aldimines **3.1a** and **3.1b** by using a known literature protocol.⁴⁵ We then reacted naphthyl alkyne **3.2** with **3.1a** or **3.1b** in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as the Lewis acid mediator and chloranil as the sacrificial oxidant,^{46–50} producing benzoquinolines **3.3a** or **3.3b**, respectively. Next, to prepare model compounds **3.5a** and **3.5b**, we converted the pendant bromides of compounds **3.3a** and **3.3b** to alkynes, forming **3.4a** and **3.4b**, respectively. We then reacted alkyne **3.4** with aldimine **3.1a**, producing benzoquinolines **3.5a**, and alkyne **3.4b** with aldimine **3.1b**, producing benzoquinoline **3.5b**. This linear synthetic strategy furnished the desired regioisomerically pure products in moderate yields.

A)



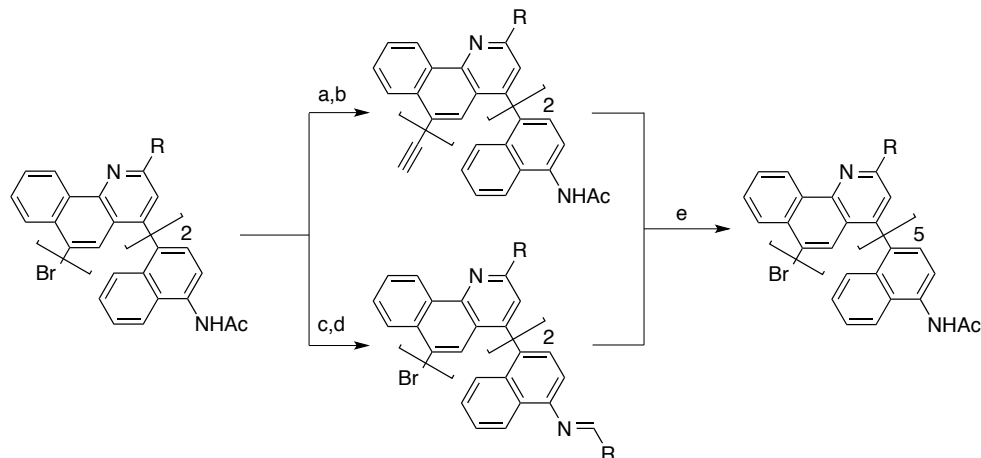
Reagents: (a) $\text{BF}_3 \cdot \text{OEt}_2$

(b) (TIPS)acetylene, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, XPhos, 100 °C

(c) TBAF

(d) 5, $\text{BF}_3 \cdot \text{OEt}_2$, chloranil, 150 °C

B)



Reagents: (a) (TIPS)acetylene, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, XPhos, 100 °C, 96%

(b) TBAF, 86% yield

(c) HCl 12N, 100 °C, 82% yield

(d) 4-octylbenzaldehyde, PTSA, molecular sieves, 110 °C, 79% yield

(e) $\text{BF}_3 \cdot \text{OEt}_2$, chloranil, 150 °C, 63%

Scheme 3.1. (A) Synthesis of benzoquinoline model compounds **3.3a**, **3.3b**, **3.5a**, and **3.5b** (TIPS=triisopropylsilyl, XPhos=2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl, TBAF=tetrabutylammonium fluoride). (B) Synthesis of benzoquinoline model compound **3.8** (PTSA=*p*-toluenesulfonic acid).

We in turn sought to prepare pentameric compound **3.8** as a longer model benzoquinoline (Scheme 3.1B). To construct **3.8**, we used **3.5b** as the sole starting material and generated complementary building blocks **3.6** and **3.7**. Thus, to synthesize **3.6**, we converted the pendant bromide of **3.5b** to an alkyne, and to synthesize **3.7**, we converted the acetyl-protected amine of **3.5b** to an aldimine. We subsequently combined alkyne **3.6** and aldimine **3.7** under our standard Povarov conditions, furnishing compound **3.8**. Here, by independently modifying the bromide and

amine termini of our precursors, we avoided an arduous linear synthesis to produce a benzoquinoline macromolecule.

We characterized our benzoquinoline model compounds (**3.3a**, **3.3b**, **3.5a**, **3.5b**, and **3.8**) with ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and/or X-ray crystallography (see the Supporting Information for details). In particular, we grew crystals of **3.3a** and **3.5a** and determined their solid-state structures through standard X-ray crystallography techniques (Figure 3.2).⁵¹ Although the resolution of **3.5a** was poor, both crystal structures confirmed that our reaction conditions produced only the desired regioisomers and

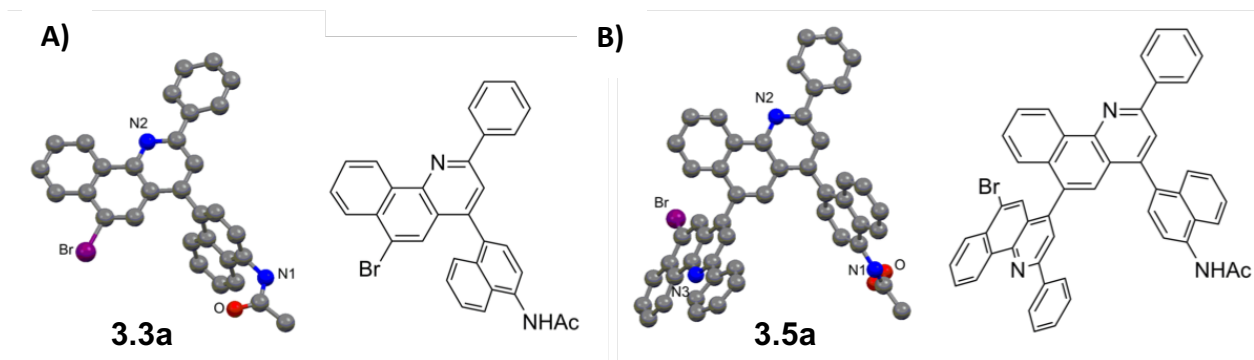
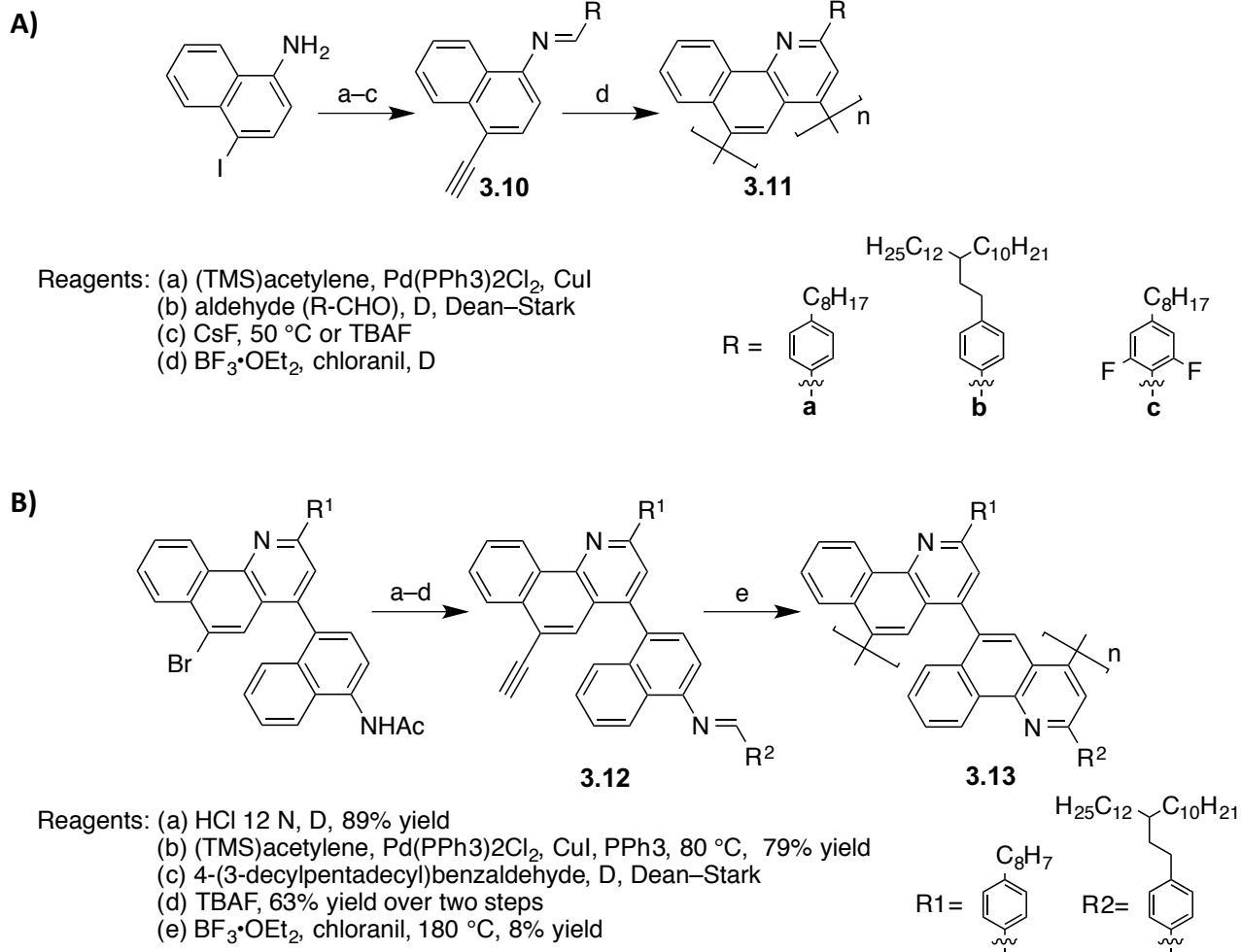


Figure 3.2. (A) The X-ray crystal structure and the corresponding chemical structure for benzoquinoline **3.3a**. (B) The X-ray crystal structure and the corresponding chemical structure for benzoquinoline **3.5a**. For both crystal structures, the carbon, nitrogen, oxygen, and bromine atoms are indicated in gray, blue, red, and purple, respectively. Note that the hydrogen atoms and solvent molecules have been omitted for clarity.

connectivity, as further supported by a detailed NMR analysis for **3.3b** (Supporting Figures S3.1–S3.9). The crystal structures also revealed that the naphthyl moieties of both **3.3a** and **3.5b** were almost completely orthogonal with respect to their neighboring benzoquinoline subunits (Figure 3.2A, B) and that the two constituent benzoquinoline subunits of **3.5a** were twisted out of planarity with respect to one another (Figure 3.2B). Altogether, these experiments definitively confirmed the identity of our compounds.

With our model compounds in hand, we proceeded to prepare an elongated benzoquinoline macromolecule. Thus, we produced polybenzoquinoline **3.11a** through polymerization of an AB-type bifunctional monomer via the Povarov reaction. To this end, we first synthesized monomer **3.10a** from 4-iodonaphthylamine **3.9** in only three steps (Scheme 3.2A). The design of **3.10a** incorporated the requisite alkyne and aldimine functional groups within a single substrate, as well as an alkyl chain for enhanced solubility. We next used the reaction conditions optimized for the synthesis of **3.3b**, **3.5b**, and **3.8** (Scheme 3.1) to polymerize **3.10a**, furnishing polybenzoquinoline **3.11a** (Scheme 3.2A). We analyzed the resulting reaction mixture via size-exclusion chromatography with a refractive index detector (SEC-RI), and through calibration with standards, we obtained a number average molecular weight (M_n) of 2730 g mol⁻¹, a weight average molecular weight (M_w) of 5420 g mol⁻¹, and a polydispersity index (PDI) of 1.98 for crude **3.11a** (Supporting Figure S3.10.). The PDI of the crude product was consistent with a step-growth polymerization mechanism, as expected for a Diels–Alder-type reaction.³⁵⁻³⁷



Scheme 3.2. (A) Synthesis of monomers **3.10a–10c** and polybenzoquinolines **3.11a–11c** (TMS=trimethylsilyl). (B) Synthesis of monomer **3.12** and polybenzoquinoline **3.13**.

We subsequently processed and again characterized polybenzoquinoline **3.11a**. We first terminated the reaction by addition of phenylacetylene and purified the resulting material through sequential precipitation/chromatography (see the Supporting Information for details). We then

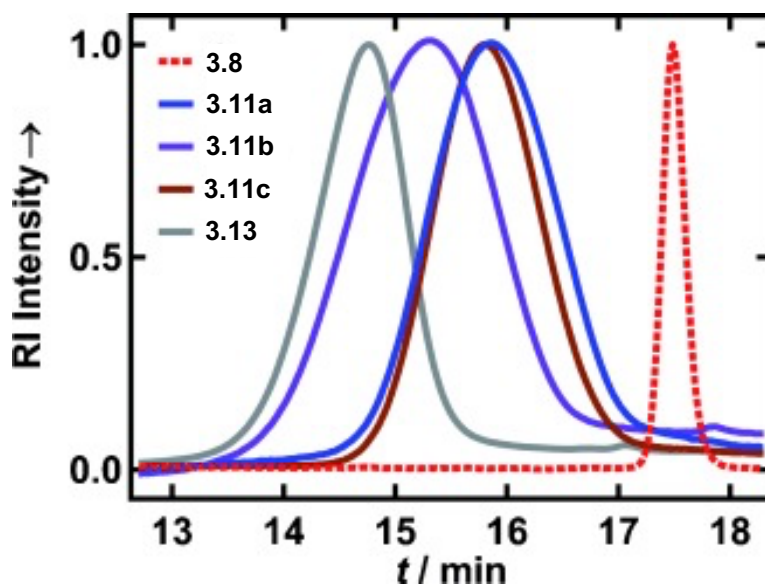


Figure 3.3: The SEC-RI chromatograms obtained for polybenzoquinolines **3.11a** (solid blue line), **3.11b** (solid purple line), **3.11c** (solid brown line), and **3.13** (solid gray line), as well as for benzoquinoline model compound **3.8** (dashed red line). The chromatograms have been normalized for clarity.

Compound	M_n [g mol ⁻¹]	M_w [g mol ⁻¹]	PDI	$n^{[b]}$
3.8	2110 ^[a]	2120 ^[a]	1.01	5
3.11a	7840	10 500	1.34	21
3.11b	15 500	22 300	1.44	25
3.11c	8960	10 900	1.22	22
3.13	29 600	36 200	1.22	60

Table 3.1. The tabulated M_n , M_w , and PDI values for **3.8**, **3.11a**, **3.11b**, **3.11c**, and **3.13**, as calculated from the chromatograms in Figure 3.3. Note the excellent agreement between the calculated and actual molecular weights of **3.8**. analyzed **3.11a** by SEC-RI with respect to calibration standards. Our measurement yielded a M_n of 7840 g mol⁻¹, a M_w of 10 500 g mol⁻¹, and a PDI of 1.34, corresponding to about 21 main chain benzoquinoline subunits for purified **3.11a** (Figure 3.3 and Table 3.1). For comparison, the same measurement for monodisperse benzoquinoline model compound **3.8** yielded a M_n of 2110 g mol⁻¹, a M_w of 2120 g mol⁻¹, and a PDI of 1.01, confirming the accuracy of our analysis (Figure 3.3 and Table 3.1). Notably, despite its aromatic character and crowded architecture, **3.11a** was readily soluble in most common organic solvents, presumably due to a partially contorted geometry, as observed for our model compounds in the solid state. Our observations were consistent with the preparation of an extended polybenzoquinoline.

We further characterized **3.3b**, **3.5b**, **3.8**, and **3.11 a** with ultraviolet-visible (UV/Vis) spectroscopy (Figure 3.4). The spectra obtained for **3.3b**, **3.5b**, and **3.8** showed characteristic absorbance peaks with maxima at nearly identical positions of 297, 314, 352, and 370 nm. By comparison, the spectrum obtained for **3.11a** featured broadened absorption maxima at similar

positions and an onset of absorption that was red-shifted from 380 to 450 nm. Together, these measurements corroborated the formation of an extended polybenzoquinoline system for **3.11a**.

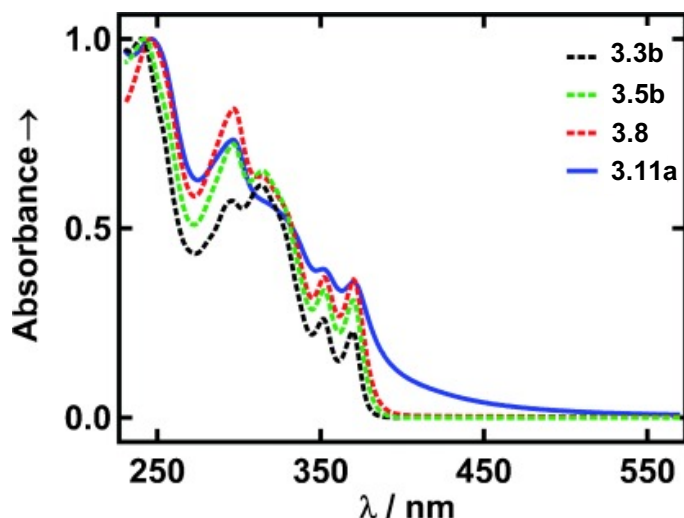


Figure 3.4. The UV/Vis absorbance spectra obtained for benzoquinoline model compounds **3.3b** (dashed black line), **3.5b** (dashed green line), and **3.8** (dashed red line), as well as polybenzoquinoline **3.11a** (solid blue line). Note that the spectrum of the polybenzoquinoline is broadened and red-shifted with respect to the spectra of the model compounds. The spectra have been normalized for clarity.

We next sought to demonstrate that our polymerization strategy was modular and capable of accommodating different peripheral substituents. Thus, we leveraged the reaction conditions already validated for the synthesis of **3.10a** to prepare monomers **3.10b** and **3.10c**, which incorporated branched alkyl chain and fluorine substituents, respectively (Scheme 3.2A). We then used conditions similar to those developed for the synthesis of **3.3b**, **3.5b**, **3.8**, and **3.11a** to furnish polybenzoquinoline **3.11b** from **3.10b** and polybenzoquinoline **3.11c** from **3.10c** (Scheme 3.2A). Our standard purification and analysis procedures yielded the data shown in Figure 3.3 and Table 3.1 for **3.11b** and **3.11c**, confirming the success of our polymerization reactions. The preparation of distinct polybenzoquinolines under similar conditions underscored the potential general scope of our approach.

Finally, we applied our polymerization strategy to the preparation of an even longer, sequence-variable polybenzoquinoline macromolecule. We slightly modified the procedure required for the preparation of **3.10a–10c** to convert **3.3b** into bifunctional monomer **3.12** in four steps (Scheme 3.2B). The design of **3.12** incorporated the requisite alkyne and aldimine functional groups, an expanded aromatic core containing an additional benzoquinoline subunit, and alternating linear and branched alkyl side chains. Polymerization of **3.12** under our standard reaction conditions furnished polybenzoquinoline **3.13**. Per our SEC-RI measurement, this polymer featured a M_n of 29,600 g mol⁻¹, a M_w of 36,200 g mol⁻¹, and a PDI of 1.22, corresponding to about 60 main chain benzoquinoline subunits (Figure 3.3 and Table 3.1). Moreover, despite its increased size relative to **3.11a–11c**, **3.13** exhibited good solubility in common organic solvents. Overall, these findings demonstrated the potential modularity of our approach, portending favorably for the synthesis of polybenzoquinoline-based graphene nanoribbon precursors with tunable sequence contexts.

3.4 Conclusion

In summary, we have developed a new methodology for the preparation of polybenzoquinolines, which is significant for several reasons. First, the aza-Diels–Alder (Povarov) reaction has been employed for the synthesis of benzoquinolines only in a limited number of previous instances.^{40–44} To the best of our knowledge, the current study represents the first reported synthesis of modular polybenzoquinolines using the Povarov (or any other) reaction. Second, our scalable approach employs few synthetic steps, inexpensive precursor materials, and straightforward reaction conditions. These advantageous features facilitate the preparation of crowded yet soluble polymers with variable peripheral substituents and sizes. Given the large number of commercially available benzaldehyde derivatives, our strategy may also provide access to a diverse family of benzoquinoline-based materials. Third, the reported polybenzoquinolines constitute a novel class of precursor polymers for $N=7$ armchair GNRs (Figure 3.1), which have been prepared exclusively from polyanthracenes to

date.^{11–19} Due to the propensity of some anthracene derivatives to oxidation and undesirable photochemistry,^{52,53} our precursors may prove advantageous for the preparation of diverse libraries of GNRs with designer electronic properties. Finally, we note that our polybenzoquinolines could find a number of alternative applications; indeed, quinoline derivatives are privileged scaffolds in medicinal chemistry,^{54,55} ubiquitous ligands in inorganic chemistry,^{56,57} and promising materials for organic electronic devices.^{58–61} Consequently, the presented synthetic methodology may prove generally valuable across a broad swath of chemical and physical disciplines.

3.5 Supporting Information

3.5.1. General Information and Procedures

A. Materials and General Experimental Procedures. All chemicals were purchased from Acros Organics, Sigma-Aldrich, or Combi-Blocks. All solvents were obtained from Fisher Scientific and used as received, unless otherwise noted. Toluene was dried with 3 Å molecular sieves and stored under argon. Degassed solvents were prepared by using three freeze-pump-thaw cycles. The glassware was oven dried at 150°C overnight. All reactions were performed under dry argon, unless otherwise noted.

B. Compound Purification Procedures. Flash chromatography was performed using a CombiFlash Rf 200 purification system (Teledyne Isco, Inc.) according to the manufacturer's recommended protocols. When required, the silica gel columns/cartridges were flushed with 1/9 triethylamine/hexanes to deactivate the silica gel, followed by hexanes to remove excess triethylamine. Preparatory size exclusion chromatography for oligobenzoquinoline **3.8** and the polybenzoquinolines was performed with chloroform as the mobile phase using a gravity fed column containing Sephadex LH-20 (GE Healthcare Life Sciences), BioBeads SX-1 resin (200– 400 mesh, Bio-Rad Laboratories, Hercules, CA), or Toyopearl HW-55S resin (Tosoh Bioscience, LLC.). Additional purification-relevant information and protocols are noted below as required.

C. Reaction Product Characterization Procedures. All intermediates and products were characterized with a combination of ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, ¹H-¹H correlation spectroscopy (COSY), ¹H nuclear Overhauser effect (NOE) spectroscopy, mass spectrometry, and ultraviolet-visible (UV-vis) spectroscopy. The ¹H NMR spectra were obtained on a Bruker AVANCE400, a Bruker DRX500, or an AVANCE600 instrument. The ¹³C NMR, ¹H-¹H

COSY, and ^1H NOE spectra were obtained on a Bruker DRX500 outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes). Chemical shifts were reported in ppm for both ^1H and ^{13}C NMR. The chemical shifts for the NMR data were referenced as follows: 1) for samples in CDCl_3 , the ^1H NMR was referenced to tetramethylsilane (TMS) at 0.00 or the solvent peak at 7.26 ppm, and the ^{13}C NMR was referenced to CDCl_3 at 77.16 ppm; for samples in CD_2Cl_2 , the ^1H NMR was referenced to the solvent peak at 5.32 ppm, and the ^{13}C NMR was referenced to the solvent peak at 54.00 ppm; and 2) for samples in $\text{DMSO}-d_6$, the ^1H NMR was referenced to the solvent peak at 3.33 ppm, and the ^{13}C NMR was referenced to the solvent peak at 39.52 ppm. The data were labeled as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet), coupling constants in Hertz, and integration values. Accurate mass measurements via electrospray ionization (ESI) high resolution mass spectrometry (HRMS) were obtained at the University of California, Irvine Mass Spectrometry Facility on a Waters LCT Premier time-of-flight instrument. Accurate mass measurements via chemical ionization (CI) and electron ionization (EI) HRMS were obtained at the University of California, Irvine Mass Spectrometry Facility on a Waters GCT Premier time-of-flight instrument. MALDI-TOF mass spectra were recorded on an AB Sciex TOF/TOF 5800 series mass spectrometer using a 349 nm Nd:YAG laser and dithranol as the matrix. The UV-vis spectra were collected on an Agilent Cary 100 Series spectrophotometer at room temperature in tetrahydrofuran (THF).

D. Polymer Characterization and Analysis Procedures. The oligobenzoquinolines and polybenzoquinolines were analyzed *via* size exclusion chromatography with a refractive index detector (SEC-RI). The SEC-RI measurement was performed in THF using an Agilent Technologies 1260 Infinity Series separations module equipped with two Agilent ResiPore columns connected in series (7.5 mm x 300 mm, 3 μm particle size). The separations module was connected to Agilent 1260

infinity dual angle light scattering, refractive index, and viscosity detectors in series. The flow rate was ~ 1.0 mL/min with an injection volume of $\sim 25 - 100$ μ L and sample concentration of $\sim 1.0 - 2.5$ mg/mL. Molecular weights (M_n and M_w) were estimated from a calibration curve using polystyrene standards (EasiVial PS-H, Agilent). The accuracy of this calibration curve was validated for benzoquinoline model compound **3.8** (actual molecular weight of 2093 g mol^{-1}); the SEC-RI measurements indicated an M_n of 2110 g mol^{-1} and M_w of 2120 g mol^{-1} for **3.8**.

3.5.2. Detailed Experimental Procedures

1. (E)-N-Benzylidene-4-bromo-1-naphthylamine (3.1a). 4-Bromonaphthylamine (2.0 g, 9.0 mmol), benzaldehyde (1.05 g, 1.01 mL, 9.9 mmol), and p-toluenesulfonic acid (0.08 g, 0.45 mmol) were dissolved in toluene (180 mL). Molecular sieves ($3 \text{ \AA}$, 1.0 g) were added to the reaction mixture, which was then brought to reflux. After 24 hours, the mixture was cooled and poured into a 200 mL saturated aqueous sodium bicarbonate solution. The mixture was extracted with ethyl acetate (150 mL x 2), and the organic layer was rinsed with brine (100 mL). The organics were dried with sodium sulfate, and the solvent was removed in vacuo. The resulting product was purified by flash chromatography using silica gel deactivated with 10% triethylamine in hexanes (1/19 ethyl acetate/hexanes). The product crystallized from cold pentane as a pale yellow solid (2.09 g, 75%): ^1H NMR (500 MHz, CDCl_3) δ = 8.53 (s, 1H), 8.39 (d, $J = 8.2$ Hz, 1H), 8.25 (d, $J = 8.2$ Hz, 1H), 8.02 (dd, $J = 7.6, 6.8$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.65 (dt, $J = 7.1, 1.1$ Hz, 1H), 7.58 – 7.51 (m, 4H), 6.92 ppm (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ = 160.8, 149.3, 136.3, 132.2, 131.9, 130.09, 130.07, 129.2, 129.0, 127.9, 127.1, 126.6, 124.6, 119.9, 113.2 ppm; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{11}\text{BrN}$ $[\text{M} - \text{H}]^+$ 308.0075, found 308.0078.

2. (E)-4-Bromo-N-(4-octylbenzylidene)-1-naphthylamine (3.1b). 4-Bromonaphthylamine (1.11 g, 5.0 mmol), 4-octylbenzaldehyde (1.27 g, 1.35 mL, 5.8 mmol), and p-toluenesulfonic acid (0.05 g, 0.3 mmol) were dissolved in ethanol (20 mL). Molecular sieves (3 Å, 3.1 g) were added to the reaction mixture, which was then brought to reflux. After 24 hours, the mixture was cooled and poured into a 50 mL saturated aqueous sodium bicarbonate solution. The mixture was extracted with ethyl acetate (50 mL), and the organic layer was rinsed with brine (50 mL). The organics were dried with sodium sulfate, and the solvent was removed in vacuo. The resulting product was purified by flash chromatography using silica gel deactivated with 10% triethylamine in pentane (99/1 pentane/diethyl ether to 19/1 pentane/diethyl ether). The product crystallized upon standing and was washed with cold pentane to yield a pale yellow solid (1.65 g, 78%): ¹H NMR (400 MHz, CDCl₃) δ = 8.50 (s, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.60 (m, 1H), 7.59 – 7.52 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.59 (m, 2H), 1.45 – 1.21 (m, 10H), 0.90 ppm (t, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 160.8, 149.6, 147.5, 134.0, 132.3, 130.2, 130.1, 129.2, 129.1, 127.9, 127.1, 126.5, 124.7, 119.6, 113.2, 36.2, 32.0, 31.5, 29.6, 29.5, 29.4, 22.8, 14.3 ppm; HRMS (ESI) *m/z* calcd for C₂₅H₂₈BrN [M + H]⁺ 422.1483, found 422.1477.

3. N-(4-((Trimethylsilyl)ethynyl)naphthalen-1-yl)acetamide (SI-3.1). 4-Bromo-1-acetamidonaphthalene (2.5 g, 9.5 mmol), Pd(PPh₃)₂Cl₂ (1.3 g, 1.9 mmol), CuI (0.4 g, 1.9 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.9 g, 1.9 mmol) were dissolved in a degassed mixture of diisopropyl amine (20 mL) and toluene (50 mL) under argon. Trimethylsilylacetylene (4.7 g, 6.7 mL, 47 mmol) was added to the mixture, which was brought to 90°C. After 4 hours, the reaction mixture was cooled and poured into ethyl acetate (100 mL). The combined organics were washed sequentially with water (50 mL x 2) and brine (50 mL). The organics were dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (diethyl

ether) to yield a white solid (2.1 g, 79% yield): ^1H NMR (499 MHz, CDCl_3) δ =8.39 (ddd, J = 8.2, 1.3, 0.7 Hz, 1H), 8.00 – 7.75 (m, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.64 – 7.45 (m, 3H), 2.23 (br s, 3H), 0.34 ppm (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ =169.0, 134.1, 133.1, 131.0, 127.3, 127.0, 126.8, 126.5, 120.8, 119.9, 118.3, 103.0, 99.5, 24.6, 0.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{NNaOSi}$ $[\text{M} + \text{Na}]^+$ 304.1134, found 304.1122.

4. N-(4-Ethynynaphthalen-1-yl)acetamide (3.2). Tetrabutylammonium fluoride (1 M solution in THF, 15 mL, 15 mmol) was added to a solution of **SI-3.1** (2.1 g, 7.5 mmol) in THF (75 mL). After 1 hour, the mixture was poured into ethyl acetate (100 mL) and washed sequentially with a saturated sodium bicarbonate solution (50 mL), water (50 mL), and brine (50 mL). The organics were dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (1/1 ethyl acetate/hexanes) to yield a white solid (1.4 g, 87% yield): ^1H NMR (500 MHz, CD_2Cl_2) δ =8.36 (d, J = 8.4 Hz, 1H), 8.06 – 7.75 (m, 3H), 7.75 – 7.44 (m, 3H), 3.55 (s, 1H), 2.23 ppm (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ =169.5, 134.5, 134.3, 131.6, 127.6, 127.2, 121.7, 120.4, 117.5, 82.5, 81.9, 24.6 ppm; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{NNaO}$ $[\text{M} + \text{Na}]^+$ 232.0738, found 232.0731.

5. N-(4-(6-Bromo-2-phenylbenzo[h]quinolin-4-yl)naphthalen-1-yl)acetamide (3.3a). Naphthyl imine (**3.1a**, 0.53 g, 1.7 mmol), naphthyl alkyne (**3.2**, 0.30 g, 1.4 mmol) and chloranil (0.39 g, 1.6 mmol) were dissolved in toluene (20 mL) under argon. Molecular sieves (3 Å, 0.50 g) were added to the reaction mixture, which was then stirred at room temperature. Subsequently, $\text{BF}_3 \cdot \text{OEt}_2$ (0.31 g, 0.27 mL, 2.2 mmol) was added to the mixture, and the temperature was brought to 80°C. After 15 hours, the mixture was cooled to room temperature, and the solids were dissolved in chloroform (50 mL). The molecular sieves were filtered off, and the organics were washed with a saturated sodium bicarbonate solution (50 mL x 3). The aqueous solution was washed with chloroform (50 mL x 2).

The organics were combined and dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (1/4 ethyl acetate/chloroform) to yield a white solid (0.56 g, 76% yield): ^1H NMR (500 MHz, DMSO- d_6) δ = 10.16 (s, 1H), 9.59 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.4 Hz, 2H), 8.34 – 8.22 (m, 3H), 7.96 (m, 3H), 7.67 – 7.37 (m, 8H) 2.28 ppm (s, 3H); ^{13}C NMR (126 MHz, DMSO- d_6) δ = 169.2, 155.0, 147.0, 144.9, 138.2, 134.8, 132.3, 131.8, 131.5, 131.3, 130.0, 129.0, 128.6, 127.6, 127.4, 127.0, 126.23, 126.18, 125.8, 125.1, 124.7, 123.4, 121.6, 121.2, 120.9, 23.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{31}\text{H}_{21}\text{BrN}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$ 539.0735, found 539.0748.

6. N-(4-(6-Bromo-2-(4-octylphenyl)benzo[h]quinolin-4-yl)naphthalen-1-yl)acetamide (3.3b).

Naphthyl imine (**3.1b**, 0.55 g, 1.3 mmol) and naphthyl alkyne (**3.2**, 0.25 g, 1.2 mmol) were dissolved in toluene (25 mL) under argon. Molecular sieves (3 Å, 0.50 g) were added to the reaction mixture, which was then stirred at room temperature. After 30 minutes, a suspension of chloranil (0.32 g, 1.3 mmol) in toluene (10 mL) was transferred to the mixture *via* cannula. Subsequently, $\text{BF}_3 \cdot \text{OEt}_2$ (0.19 g, 0.17 mL, 1.3 mmol) was added to the reaction mixture, and the temperature was brought to 80°C. After 15 hours, the mixture was cooled to room temperature, and the solids were dissolved in chloroform (50 mL). The molecular sieves were filtered off, and the organics were washed with a saturated sodium bicarbonate solution (50 mL x 5). The aqueous solution was washed with chloroform (50 mL x 2). The organics were combined and dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (3/7 ethyl acetate/dichloromethane) to yield a white solid (0.54 g, 71% yield): ^1H NMR (500 MHz, CDCl_3) δ = 9.66 (d, J = 8.4 Hz, 1H), 8.35 – 8.22 (m, 3H), 8.10 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.99 (s, 1H), 7.88 – 7.77 (m, 2H), 7.73 – 7.63 (m, 2H), 7.63 – 7.51 (m, 2H), 7.51 – 7.44 (m, 1H), 7.44 – 7.33 (m, 3H), 2.70 (t, J = 7.7 Hz, 3H), 2.42 (s, 2.4H, NHCOCH_3), 2.08 (s, 0.4H, NHCOCH_3), 1.68 (p, J = 7.5 Hz, 2H), 1.49 – 1.17 (m, 10H), 0.88 ppm (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 169.1, 155.5, 146.7, 146.1,

145.0, 136.8, 133.6, 133.2, 133.1, 132.7, 132.3, 129.4, 129.2, 127.9, 127.7, 127.5, 127.0, 126.98, 126.90, 126.85, 125.6, 125.1, 122.5, 121.2, 120.8, 36.0, 32.1, 31.6, 29.7, 29.5, 29.4, 24.7, 22.8, 14.3 ppm; HRMS (ESI) m/z calcd for $C_{39}H_{37}BrN_2NaO$ $[M + Na]^+$ 651.1987, found 651.1984; UV-vis (THF): $\lambda_{max}(\epsilon)$ =370 (11800), 352 (13600), 314 (32000), 296 (29800), 240 nm (52500).

7. N-(4-(6-Ethynyl-2-phenylbenzo[h]quinolin-4-yl)naphthalen-1-yl)acetamide (3.4a). Compound **3.3a** (0.29 g, 0.57 mmol), $Pd(CH_3CN)_2Cl_2$ (0.06 g, 0.23 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.11 g, 0.23 mmol) were dissolved in a degassed mixture of diisopropyl amine (1.19 mL) and toluene (10 mL). Triisopropylsilylacetylene (0.52 g, 0.64 mL, 2.85 mmol) was added to the mixture, which was brought to 100°C. After 12 hours, the reaction mixture was cooled, poured into methylene chloride (30 mL), and sequentially extracted with water (30 mL) and brine (30 mL). The organics were dried with sodium sulfate, and the solvent was removed in vacuo. The resulting intermediate was purified by flash chromatography (1/4 ethyl acetate/dichloromethane). Immediately after flash chromatography, the intermediate was dissolved in THF (30 mL), and tetrabutylammonium fluoride (1 M solution in THF, 1.14 mL, 1.14 mmol) was added to this solution with stirring. After 5 minutes at room temperature, the reaction mixture was poured into dichloromethane (20 mL) and sequentially washed with saturated sodium bicarbonate (40 mL) and brine (40 mL). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (3/7 ethyl acetate/dichloromethane) to yield a white solid (0.13 g, 50% yield over two steps): 1H NMR (500 MHz, $CDCl_3$) δ =9.64 (d, J = 7.9 Hz, 1H) 8.44 – 8.32 (m, 3H), 8.13 – 7.96 (m, 3H), 7.90 – 7.75 (m, 2H), 7.70 (br s, 1H), 7.63 (s, 1H), 7.61 – 7.34 (m, 8H), 3.35 (s, 1H), 2.41 ppm (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ =173.9, 169.2, 155.9, 147.5, 146.7, 139.3, 133.7, 133.1, 133.0, 132.8, 131.8, 129.8, 129.2, 129.1, 127.70, 127.66, 127.0, 126.97, 126.86, 126.2, 125.4, 124.1, 121.21, 121.16, 120.9, 119.3, 82.5, 81.7, 24.6 ppm; HRMS (ESI) m/z calcd for $C_{33}H_{22}N_2NaO$ $[M + Na]^+$ 485.1630, found 485.1626.

8. N-(4-(6-Ethynyl-2-(4-octylphenyl)benzo[h]quinolin-4-yl)naphthalen-1-yl)acetamide (3.4b).

Compound **3.3b** (0.50 g, 0.79 mmol), Pd(CH₃CN)₂Cl₂ (0.04 g, 0.16 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.23 g, 0.48 mmol) were dissolved in a degassed mixture of diisopropyl amine (16.5 mL) and toluene (75 mL). Triisopropylsilylacetylene (0.58 g, 0.71 mL, 3.2 mmol) was added to the mixture, which was brought to 100°C. After 4 hours, the reaction was cooled, poured into ethyl acetate (50 mL), and sequentially extracted with water (50 mL) and brine (50 mL). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The resulting intermediate was purified by flash chromatography (3/7 ethyl acetate/dichloromethane). Immediately following flash chromatography, the intermediate was dissolved in THF (34 mL), and tetrabutylammonium fluoride (1 M solution in THF, 1.34 mL, 1.34 mmol) was added to this solution with stirring. After 5 minutes at room temperature, the reaction mixture was poured into ethyl acetate (50 mL) and sequentially washed with saturated sodium bicarbonate (50 mL) and brine (50 mL). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (2/5 ethyl acetate/hexanes) to yield a white solid (0.33 g, 73% yield over two steps): ¹H NMR (500 MHz, CDCl₃) δ=9.64 (ap. d, *J* = 7.9 Hz, 1H), 8.39 (d, *J* = 7.7 Hz, 1H), 8.33 – 8.24 (m, 2H), 8.07 (d, *J* = 7.4 Hz, 1H), 8.04 – 7.98 (m, 2H), 7.88 – 7.75 (m, 2H), 7.70 (s, 1H), 7.65 – 7.52 (m, 3H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.31 (m, 3H), 3.34 (s, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 2.3H, NHCOCH₃), 2.08 (s, 0.4H, NHCOCH₃), 1.68 (p, *J* = 7.6 Hz, 2H), 1.42 – 1.22 (m, 10H), 0.89 ppm (t, *J* = 6.7 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ=169.2, 156.0, 147.4, 146.7, 145.0, 136.8, 133.8, 133.1, 133.0, 132.8, 131.8, 129.23, 129.18, 129.0, 127.64, 127.57, 127.1, 126.9, 126.8, 126.2, 125.4, 123.9, 121.2, 121.0, 120.9, 119.0, 110.1, 82.4, 81.8, 36.0, 32.1, 31.6, 29.9, 29.7, 29.5, 29.4, 24.6, 22.8, 14.3 ppm; HRMS (ESI) *m/z* calcd for C₄₁H₃₈N₂NaO [M + Na]⁺ 597.2882, found 597.2906.

9. N-(4-(6-Bromo-2,2'-diphenyl-[4,6'-bibenzo[h]quinolin]-4'-yl)naphthalen-1-yl)acetamide

(3.5a). Compound **3.4a** (0.13 g, 0.28 mmol), naphthyl imine (**3.1a**, 0.11 g, 0.34 mmol), chloranil (0.08 g, 0.31 mmol), and molecular sieves (3 Å, 0.10 g) were suspended in toluene (7 mL) under argon. After stirring for 20 minutes, the mixture was transferred *via* cannula to a 75 mL pressure vessel, leaving the molecular sieves behind. $\text{BF}_3 \cdot \text{OEt}_2$ (0.06 g, 0.05 mL, 0.42 mmol) was then added to the reaction mixture. The pressure vessel was sealed, and the temperature was brought to 150°C. After 4 hours, the vessel was cooled to room temperature. The reaction mixture was poured into chloroform (100 mL) and sequentially washed with saturated sodium bicarbonate (100 mL) and brine (100 mL). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (3/10 ethyl acetate/chloroform) to yield a white solid (0.08 g, 37% yield): ^1H NMR (500 MHz, CDCl_3) δ = 9.83 (d, J = 8.1 Hz, 1H), 9.58 (m, 1H), 8.45 (d, J = 8.1 Hz, 2H), 8.28 – 8.20 (m, 3H), 8.13 (m, 1H), 8.05 – 7.30 (m, 21 H), 2.27 ppm (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ = 169.1, 156.0, 155.8, 155.33, 155.26, 146.8, 146.5, 145.9, 139.5, 139.2, 135.1, 134.9, 133.8, 132.92, 132.85, 132.6, 132.3, 132.23, 132.20, 129.8, 129.7, 129.4, 129.3, 129.1, 129.0, 128.9, 127.9, 127.74, 127.72, 127.7, 127.61, 127.56, 127.5, 127.4, 127.2, 127.0, 126.9, 126.8, 126.7, 126.5, 126.2, 125.8, 125.7, 125.5, 125.2, 125.09, 125.05, 124.9, 122.8, 121.3, 121.1, 121.0, 120.7, 29.9, 24.5, 24.4 ppm; HRMS (ESI) m/z calcd for $\text{C}_{50}\text{H}_{32}\text{BrN}_3\text{NaO}$ $[\text{M} + \text{Na}]^+$ 792.1627, found 792.1608.

10. N-(4-(6-Bromo-2,2'-bis(4-octylphenyl)-[4,6'-bibenzo[h]quinolin]-4'-yl)naphthalen-1-yl)acetamide (3.5b). Compound **3.4b** (0.19 g, 0.30 mmol), naphthyl imine (**3.1b**, 0.14 g, 0.34 mmol), chloranil (0.08 g, 0.33 mmol), and molecular sieves (3 Å, 0.6 g) were suspended in toluene (40 mL) under argon. After stirring for 20 minutes, the mixture was transferred *via* cannula to a 75 mL pressure vessel, leaving the molecular sieves behind. $\text{BF}_3 \cdot \text{OEt}_2$ (0.13 g, 0.12 mL, 0.9 mmol) was then added to the reaction mixture. The pressure vessel was sealed, and the temperature was brought to 150°C. After 4 hours, the vessel was cooled to room temperature. The reaction mixture was poured into chloroform (100 mL) and sequentially washed with saturated sodium bicarbonate (100 mL) and brine (100 mL).

The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (3/10 ethyl acetate/hexanes) to yield a white solid (0.24 g, 80% yield): ^1H NMR (600 MHz, CDCl_3) δ = 9.81 – 9.74 (m, 1H), 9.48 (br d, J = 7.5 Hz, 1H), 8.33 – 8.25 (m, 2H), 8.16 – 8.10 (m, 1H), 8.08 (d, J = 8.2 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.88 – 7.61 (m, 6H), 7.61 – 7.44 (m, 5H), 7.44 – 7.29 (m, 6H), 7.24 – 7.16 (m, 2H), 2.66 (br t, J = 7.2 Hz, 2H), 2.57 (br t, J = 7.5 Hz, 2H), 2.11 (br s, 2.8H, NHCOCH_3), 1.82 (br s, 0.4H, NHCOCH_3), 1.72 – 1.61 (m, 2H), 1.57 (p, J = 7.4 Hz, 2H), 1.27 (m, J = 25.9, 14.0, 7.5 Hz, 20H), 0.91 – 0.78 ppm (m, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ = 169.2, 169.1, 156.0, 155.8, 155.33, 155.27, 147.9, 147.6, 146.7, 146.5, 146.3, 145.9, 145.8, 144.9, 144.8, 144.7, 136.9, 136.6, 134.8, 134.6, 133.9, 133.1, 132.9, 132.8, 132.6, 132.33, 132.27, 132.1, 129.2, 129.00, 128.96, 128.9, 128.84, 128.80, 127.79, 127.75, 127.7, 127.58, 127.56, 127.5, 127.42, 127.37, 127.3, 127.2, 127.1, 126.9, 126.8, 126.59, 126.55, 126.5, 126.24, 126.16, 125.8, 125.7, 125.4, 125.2, 124.91, 124.87, 124.8, 123.9, 123.8, 122.5, 122.3, 121.7, 121.3, 121.19, 121.17, 121.1, 120.9, 36.0, 35.9, 32.04, 32.00, 31.54, 31.48, 31.47, 31.0, 29.7, 29.6, 29.5, 29.43, 29.39, 24.3, 24.2, 22.82, 22.79, 14.3, 14.2 ppm; HRMS (ESI) m/z calcd for $\text{C}_{66}\text{H}_{64}\text{BrN}_3\text{NaO}$ $[\text{M} + \text{Na}]^+$ 1018.4130, found 1018.3970; UV-vis (THF): $\lambda_{\text{max}}(\epsilon)$ = 370 (30200), 353 (32700), 314 (63400), 297 (70400), 242 nm (92600).

11. N-(4-(2,2'-Bis(4-octylphenyl)-6-((triisopropylsilyl)ethynyl)-[4,6'-bibenzo[h]quinolin]-4'-yl)naphthalen-1-yl)acetamide (SI-3.2). Compound **3.5b** (0.30 g, 0.3 mmol), $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (0.02 g, 0.08 mmol), and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.03 g, 0.06 mmol) were dissolved in a degassed mixture of diisopropyl amine (4.5 mL) and toluene (30 mL) under argon. Triisopropylsilylacetylene (0.22 g, 0.27 mL, 1.2 mmol) was added to the reaction mixture, which was brought to 100°C. After 12 hours, additional $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ was added to the mixture (0.03 g, 0.12 mmol). After 24 hours, the reaction was cooled to room temperature, washed with brine (50 mL), and dried with sodium sulfate. The solvent was then removed in vacuo. The product was purified by flash

chromatography (1/10 ethyl acetate/hexanes) to yield a white solid (0.32 g, 96% yield): ^1H NMR (500 MHz, CDCl_3) δ = 9.93 – 9.82 (m, 1H), 9.62 – 9.54 (m, 1H), 8.51 – 8.44 (m, 1H), 8.40 (d, J = 7.7 Hz, 2H), 8.20 (d, J = 8.0 Hz, 1H), 8.17 – 8.08 (m, 2H), 7.95 – 7.75 (m, 6H), 7.74 – 7.52 (m, 6H), 7.51 – 7.35 (m, 5H), 7.35 – 7.27 (m, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.71 – 2.60 (m, 2H), 2.19 (s, 2.3H, NHCOCH_3), 1.93 (s, 0.3H, NHCOCH_3), 1.81 – 1.70 (m, 2H), 1.70 – 1.59 (m, 2H), 1.50 – 1.25 (m, 20H), 1.25 – 1.08 (m, 18H), 0.99 – 0.87 ppm (m, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ = 169.2, 156.0, 155.8, 155.5, 147.8, 147.6, 147.0, 146.9, 146.7, 146.5, 146.4, 144.9, 144.8, 144.7, 136.9, 136.7, 136.6, 135.0, 134.9, 134.0, 133.9, 133.3, 133.1, 133.0, 132.7, 132.6, 132.4, 132.29, 132.25, 131.71, 131.67, 129.2, 129.0, 128.9, 128.8, 128.4, 128.1, 128.0, 127.64, 127.56, 127.5, 127.44, 127.39, 127.3, 126.9, 126.6, 126.5, 126.40, 126.35, 126.31, 126.26, 125.7, 125.6, 125.3, 124.9, 123.9, 123.73, 123.68, 121.8, 121.5, 121.2, 121.1, 120.94, 120.85, 120.7, 120.3, 120.2, 105.0, 104.8, 96.9, 96.8, 36.0, 35.9, 32.04, 32.00, 31.6, 31.5, 29.7, 29.6, 29.5, 29.44, 29.40, 24.2, 24.1, 22.82, 22.79, 18.9, 18.8, 14.27, 14.25, 11.5, 11.4 ppm; MALDI (dithranol) m/z calcd for $\text{C}_{77}\text{H}_{85}\text{N}_3\text{OSi}$ $[\text{M} + \text{H}]^+$ 1097, found 1097.

12. N-(4-(6-Ethynyl-2,2'-bis(4-octylphenyl)-[4,6'-bibenzo[h]quinolin]-4'-yl)naphthalen-1-yl)acetamide (3.6). Compound **SI-3.2** (0.32 g, 0.29 mmol) was dissolved in THF (10 mL), and tetrabutylammonium fluoride (1 M solution in THF, 0.56 mL, 0.56 mmol) was added to this solution with stirring. After 15 minutes, the reaction mixture was poured into ethyl acetate (50 mL) and sequentially washed with saturated sodium bicarbonate (50 mL) and brine (50 mL). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (1/10 to 3/10 ethyl acetate/hexanes) to yield a white solid (0.23 g, 84% yield): ^1H NMR (500 MHz, CDCl_3) δ = 9.85 (d, J = 8.2 Hz, 1H), 9.55 (d, J = 7.9 Hz, 1H), 8.35 (m, 3H), 8.23 – 8.05 (m, 3H), 8.02 – 7.69 (m, 6H), 7.69 – 7.27 (m, 12H), 3.37 (s, 0.5H), 3.31 (s, 0.5H), 2.75 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.2 Hz, 2H), 2.20 (brs, 2.2H), 1.91 (br s, 0.3H), 1.73 (m, 2H), 1.66 (m, 2H), 1.50 – 1.17 (m, 20H), 0.99 – 0.85 ppm (m, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ = 169.24, 169.18,

156.0, 155.83, 155.77, 147.9, 147.6, 147.1, 147.0, 146.7, 146.5, 146.4, 144.9, 144.8, 136.9, 136.59, 136.58, 135.0, 134.7, 133.9, 133.1, 132.9, 132.7, 132.6, 132.5, 132.3, 132.2, 131.6, 129.2, 129.1, 129.0, 128.95, 128.85, 128.8, 127.81, 127.76, 127.6, 127.5, 127.4, 127.2, 127.0, 126.9, 126.8, 126.7, 126.6, 126.5, 126.3, 126.2, 126.1, 126.0, 125.73, 125.68, 125.3, 125.0, 124.9, 123.9, 123.8, 123.68, 123.65, 121.7, 121.3, 121.2, 121.1, 120.9, 120.7, 119.0, 118.8, 82.4, 81.9, 81.7, 36.0, 35.9, 32.04, 32.01, 31.6, 31.5, 29.7, 29.6, 29.5, 29.44, 29.40, 24.3, 24.2, 22.83, 22.80, 14.28, 14.26 ppm; MALDI (dithranol) m/z calcd for $C_{68}H_{66}N_3O$ $[M + H]^+$ 940.5, found 940.5.

13. 4-(6-Bromo-2,2'-bis(4-octylphenyl)-[4,6'-bibenzo[h]quinolin]-4'-yl)-1-naphthylamine (SI-3.3). Compound **3.5b** (0.50 g, 0.50 mmol) was suspended in 280 mL of ethanol. Concentrated hydrochloric acid (55 mL, 660 mmol) was slowly added to the solution, and the mixture was then brought to reflux. After 24 hours, the mixture was cooled, and sodium carbonate (34.5 g, 326 mmol) dissolved in water (200 mL) was slowly added with vigorous stirring. The mixture was extracted with dichloromethane (200 mL x 3), the combined organics were filtered through a cotton plug, and the solvent was removed in vacuo. The product was purified by flash chromatography (1/20 to 1/10 ethyl acetate/hexanes) to yield a tan solid (0.39 g, 82% yield): 1H NMR (500 MHz, $CDCl_3$) δ = 9.88 (d, J = 8.4 Hz, 1H), 9.61 (t, J = 8.5 Hz, 1H), 8.40 (d, J = 7.9 Hz, 2H), 8.25 (d, J = 8.0 Hz, 1H), 8.19 – 8.06 (m, 3H), 7.92 – 7.70 (m, 5H), 7.70 – 7.53 (m, 3H), 7.53 – 7.32 (m, 7H), 7.27 (d, J = 8.3 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 7.7 Hz, 0.5H), 6.70 (d, J = 7.6 Hz, 0.5H), 4.16 (s, 1H), 2.75 (t, J = 7.7 Hz, 2H), 2.71 – 2.59 (m, 2H), 1.74 (p, J = 7.5 Hz, 2H), 1.70 – 1.59 (m, 2H), 1.50 – 1.24 (m, 20H), 1.01 – 0.88 ppm (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 156.0, 155.8, 155.4, 155.1, 148.8, 148.6, 146.8, 146.6, 146.53, 146.50, 145.83, 145.81, 144.70, 144.68, 144.6, 143.0, 137.18, 137.16, 136.6, 136.5, 134.4, 134.3, 134.0, 133.0, 132.9, 132.8, 132.7, 132.6, 132.39, 132.36, 132.2, 132.1, 129.2, 129.1, 128.92, 128.90, 128.71, 128.67, 128.6, 128.2, 127.73, 127.67, 127.59, 127.58, 127.38, 127.35, 127.32, 127.30, 126.9, 126.7, 126.61, 126.57, 126.5, 126.4, 126.1, 125.8, 125.7, 125.50, 125.46,

125.31, 125.27, 125.1, 125.0, 124.9, 124.37, 124.35, 123.6, 123.3, 122.3, 121.60, 121.58, 121.4, 121.2, 121.0, 120.7, 109.2, 109.0, 36.0, 35.89, 35.85, 32.05, 32.02, 31.6, 31.5, 31.4, 29.7, 29.6, 29.51, 29.45, 29.4, 22.84, 22.81, 14.29, 14.27 ppm; MALDI (dithranol) m/z calcd for $C_{64}H_{63}BrN_3$ $[M + H]^+$ 952, found 952.

14. (E)-4-(6-Bromo-2,2'-bis(4-octylphenyl)-[4,6'-bibenzo[h]quinolin]-4'-yl)-N-(4-octylbenzylidene)naphthalen-1-amine (3.7). Compound **SI-3.3** (0.23 g, 0.24 mmol), 4-octylbenzaldehyde (0.11g, 0.11 mL, 0.49 mmol), and p-toluenesulfonic acid (2.0 mg, 0.01 mmol) were dissolved in toluene (25 mL). Molecular sieves (3 Å, 1.2 g) were added to the reaction mixture, which was heated to 110°C. After 12 hours, the reaction mixture was cooled to room temperature, poured into ethyl acetate (50 mL), and sequentially washed with saturated sodium bicarbonate (50 mL) and brine (50 mL). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by recrystallization from pentane to yield a pale yellow solid (0.22 g, 79% yield): 1H NMR (600 MHz, $CDCl_3$) δ = 9.89 (d, J = 8.0 Hz, 1H), 9.62 (d, J = 7.7 Hz, 1H), 8.57 – 8.35 (m, 4H), 8.31 – 8.10 (m, 4H), 7.98 – 7.84 (m, 4H), 7.83 – 7.66 (m, 4H), 7.65 – 7.54 (m, 4H), 7.54 – 7.40 (m, 4H), 7.39 – 7.27 (m, 4H), 7.12 (d, J = 7.3 Hz, 1H), 2.77 (t, J = 7.1 Hz, 2H), 2.69 (t, J = 7.2 Hz, 4H), 1.80 – 1.73 (m, 2H), 1.73 – 1.63 (m, 4H), 1.51 – 1.25 (m, 30H), 1.01 – 0.88 ppm (m, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 160.8, 155.8, 155.5, 150.2, 148.1, 147.3, 146.8, 146.5, 145.8, 144.8, 144.7, 137.1, 136.7, 134.8, 134.1, 133.4, 133.0, 132.7, 132.5, 132.3, 132.2, 129.19, 129.15, 129.0, 128.8, 128.3, 127.8, 127.6, 127.5, 127.4, 127.0, 126.9, 126.2, 126.0, 125.9, 125.8, 125.5, 125.4, 124.9, 124.8, 124.1, 122.4, 121.3, 121.0, 112.5, 36.2, 36.0, 35.9, 32.1, 32.03, 32.02, 31.6, 31.5, 31.4, 29.7, 29.64, 29.59, 29.53, 29.46, 29.42, 29.39, 22.9, 22.8, 14.29, 14.26 ppm; MALDI (dithranol) m/z calcd for $C_{79}H_{83}BrN_3$ $[M + H]^+$ 1153, found 1153.

15. N-(4-(6-Bromo-2,2',2'',2''',2''''-pentakis(4-octylphenyl)-[4,6':4',6'':4'',6''':4''',6''''-quinquebenzo[h]quinolin]-4''''-yl)naphthalen-1-yl)acetamide (3.8). Compound **3.6** (0.82 g, 0.87 mmol), compound **3.7** (1.00 g, 0.87 mmol), and chloranil (0.24 g, 0.98 mmol) were dissolved in toluene in a 75 mL pressure vessel. $\text{BF}_3 \cdot \text{OEt}_2$ (0.37 g, 0.33 mL, 2.6 mmol) was added to the reaction mixture, and the pressure vessel was sealed, with the temperature brought to 150°C. After 24 hours, the vessel was cooled to room temperature. The reaction mixture was poured into dichloromethane (100 mL) and washed with saturated sodium bicarbonate (100 mL x 6). The organic layer was dried with sodium sulfate, and the solvent was removed in vacuo. The product was purified by flash chromatography (0/1 to 3/20 ethyl acetate/hexanes) to yield the pure product (0.84 g). The remaining crude material was purified by a size exclusion column (Sephadex LH-20) with chloroform as the mobile phase to yield additional purified product (0.30 g). The total combined product was isolated as a pale yellow solid (1.14 g, 63% yield): ^1H NMR (600 MHz, CDCl_3) δ = 10.02 – 9.05 (m, 5H), 8.51 – 6.98 (m, 52H), 2.92 – 2.55 (m, 10H), 2.37 – 1.13 (m, 63H), 0.98 – 0.78 ppm (m, 15H); MALDI (dithranol) m/z calcd for $\text{C}_{147}\text{H}_{146}\text{BrN}_6\text{O}$ $[\text{M} + \text{H}]^+$ 2090, found 2090; UV-vis (THF) $\lambda_{\text{max}}(\epsilon)$ = 370 (70800), 352 (72000), 314 (123000), 297 (153000), 246 nm (168000).

16. 4-((Trimethylsilyl)ethynyl)-1-naphthylamine (SI-3.4). 4-Iodo-1-naphthylamine was prepared according to reported protocols.^{S1} Compound **3.9** (5.43 g, 20.2 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.283 g, 0.403 mmol), and CuI (0.154 g, 0.809 mmol) were dissolved in a degassed mixture of diisopropyl amine (60 mL) and toluene (150 mL). Trimethylsilylacetylene (4.30 mL, 30.4 mmol) was added to the reaction mixture, which was stirred overnight at room temperature. Subsequently, the mixture was filtered through a pad of Celite and washed with hexanes (50 mL). The filtrate was then sequentially washed with water (50 mL x 2) and brine (50 mL). The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (0/100 to 1/2 ethyl acetate/hexanes) to give an oil after solvent evaporation (4.19 g, 87%): ^1H NMR

(500 MHz, CDCl₃) δ = 8.32 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 4.33 (s, 2H), 0.31 ppm (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ = 143.4, 134.6, 132.1, 127.2, 127.0, 125.4, 123.0, 121.0, 111.0, 109.0, 104.3, 96.9, 0.4 ppm; HRMS (CI) m/z calcd for C₁₅H₁₈NSi [M + H]⁺ 240.1208, found 240.1197.

17. N-p-Octylbenzylidene-4-((trimethylsilyl)ethynyl)-1-naphthylamine (SI-3.5). A solution of compound **SI-3.4** (1.70 g, 7.10 mmol) and 4-octylbenzaldehyde (1.55 g, 7.10 mmol) in benzene (50 mL) was heated to reflux, while water was removed with a Dean-Stark trap. During the course of the reaction, the solution was concentrated *via* removal of solvent through the Dean-Stark trap. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). After the solution was cooled to room temperature, the solvent was removed in vacuo, and the resulting viscous brown oil was taken into ethanol (50 mL). The resulting solution was stored overnight at -20°C to give a yellow precipitate, which was collected by filtration and washed with cold ethanol. The product was isolated as a yellow solid (2.48 g, 79%): ¹H NMR (500 MHz, CDCl₃) δ = 8.50 (s, 1H), 8.35 – 8.32 (m, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 7.5 Hz, 1H), 2.69 (t, J = 8.0 Hz, 2H), 1.69 – 1.63 (m, 2H), 1.37 – 1.27 (m, 10H), 0.89 (t, J = 7.0 Hz, 3H), 0.34 ppm (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ = 160.8, 150.3, 147.5, 134.0, 131.5, 129.3, 129.1, 128.7, 127.4, 126.3, 126.2, 124.5, 118.3, 112.4, 103.6, 99.3, 36.2, 32.0, 31.5, 29.6, 29.45, 29.41, 22.8, 14.3, 0.3 ppm; HRMS (ESI) m/z calcd for C₃₀H₃₈NSi [M + H]⁺ 440.2773, found 440.2765.

18. N-p-Octylbenzylidene-4-ethynyl-1-naphthylamine (3.10a). A solution of compound **SI-3.5** (2.08 g, 4.73 mmol) and CsF (2.15 g, 14.2 mmol) in methanol (100 mL) was stirred at 50°C for 2h. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The resulting yellow solution was cooled to room temperature, filtered through a PTFE syringe filter

(0.45 μm), and stored at -20°C overnight to give a yellow precipitate. The precipitate was collected by filtration and washed with cold methanol. The product was isolated as a yellow solid (1.33 g, 76%): ^1H NMR (500 MHz, CDCl_3) δ = 8.50 (s, 1H), 8.36 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 7.5 Hz, 1H), 3.49 (s, 1H), 2.70 (t, J = 8.0 Hz, 2H), 1.70 – 1.64 (m, 2H), 1.39 – 1.28 (m, 10H), 0.89 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ = 161.0, 150.6, 147.6, 134.1, 134.0, 131.9, 129.3, 129.1, 128.6, 127.5, 126.4, 126.0, 124.6, 117.2, 112.4, 82.2, 81.9, 36.2, 32.0, 31.5, 29.6, 29.45, 29.41, 22.8, 14.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{30}\text{N}$ $[\text{M} + \text{H}]^+$ 368.2378, found 368.2383.

19. Poly[2-(4-octylphenyl)benzo[h]quinoline-4,6-diyl] (3.11a). Chloranil (0.401 g, 1.63 mmol), toluene (10 mL), and $\text{BF}_3 \cdot \text{OEt}_2$ (0.16 mL, 1.0 mmol) were combined in a pressure vessel, and the reaction mixture was heated to 100°C . A solution of compound **3.10a** (0.400 g, 1.09 mmol) in dry toluene (6.0 mL) was then added to the mixture *via* syringe pump at a rate of 1.5 mL/h. Subsequently, the pressure vessel was sealed, and the reaction mixture was stirred at a temperature of 120°C for 44 h. The reaction mixture was then cooled to room temperature, prior to addition of phenylacetylene (0.12 mL, 1 mmol) in 1,2-dichloroethane (16 mL). The reaction mixture was further stirred at 100°C for 24 h and was then again cooled to room temperature. After the resulting solids were dissolved in chloroform (50 mL), the solution was stirred for 1 h at room temperature. The solution was sequentially washed with saturated sodium bicarbonate (50 mL x 5), water (50 mL) and brine (50 mL). The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. This crude product was precipitated from methanol (50 mL) and further purified by size exclusion chromatography (Bio-Bead SX-1 resin), with chloroform as the mobile phase. After evaporation of the solvent and precipitation from methanol, the product was isolated by filtration as a brown solid (0.142 g, 36% isolated yield): ^1H NMR (500 MHz, CD_2Cl_2) δ = 9.68 (br s, 1H), 8.27 – 7.05 (br m, 9H), 2.69 (br m, 2H), 1.65 – 0.87 ppm (br m, 15H); SEC (vs polystyrene standards) M_n =

7840 g mol⁻¹, M_w = 10500 g mol⁻¹, and PDI = 1.34.

20. 2-Decyltetradecanal (SI-3.6). Dess-Martin periodinane (30.0 g, 70.7 mmol) was dissolved in dry dichloromethane (250 mL) under argon. 2-Decyltetradecanol (20.0 g, 56.5 mmol) was then added to the reaction mixture *via* syringe pump over a period of 20 minutes. After 5 hours, a saturated sodium bicarbonate solution (100 mL) and a saturated sodium thiosulfate solution (50 mL) were added to the reaction mixture with rapid stirring. After another 2 hours, the organic layer was filtered through a cotton plug, and the solvent was removed in vacuo. The product was purified by flash chromatography (0/1 to 1/5 ethyl acetate/hexanes) to yield a white solid (19.4 g, 97% yield): ¹H NMR (500 MHz, CDCl₃) δ = 9.54 (d, J = 2.8 Hz, 1H), 2.21 (qd, J = 8.4, 4.2 Hz, 1H), 1.68 – 1.12 (m, 40H), 0.87 ppm (t, J = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ = 206.0, 52.2, 45.6, 32.4, 32.07, 32.06, 29.86, 29.82, 29.79, 29.76, 29.75, 29.72, 29.62, 29.59, 29.51, 29.48, 29.1, 27.5, 27.2, 22.8, 14.3 ppm (Note that the ¹H NMR and ¹³C NMR data match previously reported spectra.^{S2}); HRMS (CI) m/z calcd for C₂₄H₅₂NO [M + NH₄]⁺ 370.4049, found 370.4037.

21. 11-(2,2-Dibromovinyl)tricosane (SI-3.7). Carbon tetrabromide (18.9 g, 57.0 mmol) was dissolved in dichloromethane (50 mL). This solution was cooled to 0 °C, and triphenylphosphine (29.8 g, 113 mmol) was added under a stream of argon, inducing the appearance of an orange color and precipitation. After 20 minutes of stirring, a solution of 2-decyltetradecanal (**SI-3.6**, 10.0 g, 28.4 mmol) in dichloromethane (50 mL) was added to the reaction mixture dropwise over 2 minutes. After 3 hours, the reaction mixture was poured into dichloromethane (200 mL) and washed with sodium bicarbonate (200 mL). The solvent was then removed in vacuo, and the resulting solids were dissolved in a minimum amount of dichloromethane and precipitated with hexanes. The solids were in turn filtered off and discarded, with the mother liquor removed in vacuo. The precipitation was then repeated a second time. The product was purified by flash chromatography (hexanes) to yield a white solid (12.3 g, 85% yield): ¹H NMR (500 MHz, CDCl₃) δ = 6.11 (d, J = 9.9 Hz, 1H), 2.36 (m, J = 6.9

Hz, 1H), 1.47 – 1.16 (m, 40H), 0.89 ppm (t, J = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ = 144.0, 87.7, 43.9, 34.7, 32.1, 29.93, 29.88, 29.86, 29.84, 29.82, 29.76, 29.73, 29.70, 29.57, 29.54, 27.3, 22.9, 14.3 ppm; HRMS could not be readily obtained due to the instability of the molecule.

22. 11-Ethynyltricosane (SI-3.8). 11-(2,2-Dibromovinyl)tricosane (**SI-3.7**, 12.2 g, 24.0 mmol) was dissolved in THF (120 mL). This solution was cooled to -78°C , and n-butyl-lithium (1.5 M in hexanes, 48 mL, 72 mmol) was added *via* a syringe pump over a period of 30 minutes. After 1 hour, the reaction mixture was warmed to 0°C . Subsequently, the mixture was poured into a saturated solution of ammonium chloride (200 mL) and extracted with dichloromethane (200 mL). The organic layer was filtered through a cotton plug, and the solvent was removed in vacuo. The product was purified by flash chromatography (hexanes) to yield a colorless transparent oil (7.74 g, 93% yield): ^1H NMR (400 MHz, CDCl_3) δ = 2.37 – 2.23 (m, 1H), 2.07 – 1.98 (m, 1H), 1.57 – 1.18 (m, 40H), 0.88 ppm (t, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ = 88.5, 69.0, 35.2, 32.1, 31.7, 29.86, 29.84, 29.82, 29.80, 29.75, 29.69, 29.53, 29.52, 27.4, 22.9, 14.3 ppm; HRMS (CI) m/z calcd for $\text{C}_{25}\text{H}_{52}\text{N}$ [$\text{M} + \text{NH}_4$] $^+$ 366.4100, found 366.4111.

23. 4-(3-Decylpentadec-1-yn-1-yl)benzaldehyde (SI-3.9). 4-Bromobenzaldehyde (3.08 g, 16.6 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.234 g, 0.333 mmol), and CuI (0.127 g, 0.667 mmol) were dissolved in a degassed mixture of diisopropyl amine (50 mL) and toluene (50 mL). Compound **SI-3.8** (6.97 g, 20.0 mmol) was added to the reaction mixture, which was stirred overnight at room temperature. Subsequently, the mixture was filtered through a pad of Celite and washed with hexanes (50 mL). The filtrate was then sequentially washed with water (50 mL x 2) and brine (50 mL). The organic layers were dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (0/100 to 1/9 ethyl acetate/hexanes). After solvent evaporation, the product was obtained as a pale yellow solid (5.62 g, 74%): ^1H NMR (500 MHz, CDCl_3) δ = 9.98 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 2.58 – 2.53 (m, 1H), 1.55 – 1.26 (m, 40H),

0.88 ppm (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 191.7, 135.0, 132.3, 130.9, 129.6, 99.2, 81.3, 35.1, 32.7, 32.1, 29.85, 29.82, 29.80, 29.78, 29.74, 29.66, 29.5, 27.6, 22.8, 14.3$ ppm; HRMS (CI) m/z calcd for $\text{C}_{32}\text{H}_{56}\text{NO}$ $[\text{M} + \text{NH}_4]^+$ 470.4362, found 470.4367.

24. 4-(3-Decylpentadecyl)benzaldehyde (SI-3.10). Palladium on activated carbon (10 wt %, 0.260 g, 0.244 mmol), compound **SI-3.9** (5.54 g, 12.2 mmol), and benzene (60 mL) were combined in a reaction vessel. The reaction vessel was charged with hydrogen under constant stirring. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The crude product was purified by flash chromatography (0/100 to 1/9 ethyl acetate/hexanes) to yield a colorless oil (4.56 g, 82%): ^1H NMR (500 MHz, CDCl_3) $\delta = 9.97$ (s, 1H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 2.67 – 2.64 (m, 2H), 1.58 – 1.55 (m, 2H), 1.36 – 1.26 (m, 41H), 0.88 ppm (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 192.2, 151.1, 134.5, 130.1, 129.2, 37.3, 35.4, 33.61, 33.58, 32.1, 30.2, 29.85, 29.82, 29.81, 29.5, 26.7, 22.8, 14.3$ ppm; HRMS (CI) m/z calcd for $\text{C}_{32}\text{H}_{60}\text{NO}$ $[\text{M} + \text{NH}_4]^+$ 474.4675, found 474.4672.

25. (4-(3-Decylpentadecyl)benzylidene)-4-((trimethylsilyl)ethynyl)-1-naphthylamine (SI-3.11). A solution of compound **SI-3.4** (1.50 g, 6.26 mmol) and **SI-3.10** (2.38 g, 5.21 mmol) in benzene (50 mL) was heated to reflux, while water was removed with a Dean-Stark trap. During the course of the reaction, the mixture was concentrated *via* removal of solvent through the Dean-Stark trap. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). After the solution was concentrated in vacuo, the resulting material was taken into ethanol (50 mL), cooled to -20°C , and decanted. This decanting process was repeated three times leaving behind a yellow oil, which was used in subsequent steps without further purification (3.53 g, quantitative): ^1H NMR (500 MHz, CDCl_3) $\delta = 8.49$ (s, 1H), 8.34 (t, $J = 7.5$ Hz, 2H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.97 (d, J

= 7.5 Hz, 1H), 2.67 (t, J = 8.0 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.38 – 1.27 (m, 41H), 0.89 – 0.86 (m, 6H), 0.34 ppm (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ = 160.8, 150.3, 147.9, 134.03, 134.00, 131.5, 129.3, 129.1, 128.7, 127.4, 126.3, 126.2, 124.5, 118.3, 112.4, 103.6, 99.3, 37.3, 35.6, 33.6, 33.4, 32.1, 30.3, 29.9, 29.8, 29.5, 26.8, 22.8, 14.3, 0.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{47}\text{H}_{71}\text{NNaSi}$ $[\text{M} + \text{Na}]^+$ 700.5253, found 700.5244.

26. (4-(3-Decylpentadecyl)benzylidene)-4-ethynyl-1-naphthylamine (3.10b).

Tetrabutylammonium fluoride (1 M in THF, 1.22 mL, 1.22 mmol) was added to a solution of **SI-3.11** (0.553 g, 0.815 mmol) in THF (10 mL) at 0°C, and the reaction mixture was stirred for 2 h. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The reaction was quenched with methanol (5 mL), and the resulting solution was concentrated in vacuo, prior to being taken into CH_2Cl_2 (50 mL). The organics were sequentially washed with saturated sodium bicarbonate (25 mL), water (3 x 20 mL), and brine (20 mL). The organic layer was then dried over anhydrous sodium sulfate. After the solution was concentrated in vacuo, the resulting material was taken into ethanol (50 mL), cooled to -20°C, and decanted. This decanting process was repeated three times leaving behind a yellow oil (0.45 g, 91%): ^1H NMR (500 MHz, CDCl_3) δ = 8.49 (s, 1H), 8.36 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 7.5 Hz, 1H), 3.48 (s, 1H), 2.67 (t, J = 8.0 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.38 – 1.27 (m, 41H), 0.89 – 0.86 ppm (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ = 161.0, 150.6, 148.0, 134.1, 134.0, 131.9, 129.3, 129.1, 128.7, 127.5, 126.3, 126.0, 124.6, 117.2, 112.4, 82.2, 81.9, 37.3, 35.6, 33.6, 33.4, 32.1, 30.3, 29.9, 29.8, 29.5, 26.8, 22.8, 14.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{63}\text{NNa}$ $[\text{M} + \text{Na}]^+$ 628.4858, found 628.4835.

27. Poly[2-(4-(3-decylpentadecyl)phenyl)benzo[h]quinoline-4,6-diyl] (3.11b). Chloranil (0.548 g, 2.23 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.14 mL, 1.13 mmol), and toluene (6 mL) were combined in a pressure vessel, and the reaction mixture was heated to 100°C. A solution of compound **3.10b** (0.450 g, 0.74 mmol)

in dry toluene (5.0 mL) was then added to the mixture via a syringe pump at a rate of 1.25 mL/h. Subsequently, the pressure vessel was sealed, and the temperature was elevated to 180°C at a rate of 20°C/h. The reaction mixture was stirred at a temperature of 180°C for 24 h. The mixture was then cooled to room temperature, prior to addition of phenylacetylene (0.48 mL, 4.37 mmol) in 1,2-dichloroethane (11 mL). The reaction mixture was further stirred at 100°C for 24 h and was then again cooled to room temperature. After the resulting solids were dissolved in chloroform (50 mL), the solution was stirred for 1 h at room temperature, washed with saturated sodium bicarbonate (50 mL x 5), and the organic layer was dried with anhydrous sodium sulfate. The solvent was removed in vacuo, and the crude product was precipitated from methanol. This crude product was further purified by size exclusion chromatography (Bio-Bead SX-1 resin) with chloroform as the mobile phase. After evaporation of the solvent and precipitation from methanol, the product was isolated by filtration as a brown solid (0.083 g, 18% isolated yield): ¹H NMR (500 MHz, CD₂Cl₂) δ = 9.69 (br s, 1H), 8.24 – 7.33 (br m, 9H), 2.67 (br m, 2H), 1.56 – 0.87 ppm (br m, 49H); SEC (vs polystyrene standards) *M_n* = 15500 g mol⁻¹, *M_w* = 22300 g mol⁻¹, and PDI = 1.44.

28. 2,6-Difluoro-4-(oct-1-yn-1-yl)benzaldehyde (SI-3.12). 4-Bromo-2,5-difluorobenzaldehyde (1.50 g, 6.79 mmol), Pd(PPh₃)₂Cl₂ (0.143 g, 0.204 mmol), and CuI (0.078 g, 0.41 mmol) were dissolved in a degassed mixture of diisopropyl amine (15 mL) and toluene (35 mL). 1-Octyne (1.50 mL, 10.2 mmol) was then added to the reaction mixture. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). Subsequently, the mixture was filtered through a pad of Celite and washed with hexanes (50 mL). The filtrate was then sequentially washed with water (50 mL x 2) and brine (50 mL). The organic layers were dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (0/100 ethyl to 1/9 acetate/hexanes). After solvent evaporation, the product was obtained as a yellow solid (1.57 g, 92%): ¹H NMR (500 MHz, CDCl₃) δ = 10.29 (s, 1H), 6.97 (d, *J* =

9.5 Hz, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 1.64 – 1.58 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.28 (m, 4H), 0.91 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ = 184.1 (t, $J = 4.2$ Hz), 163.0 (dd, $J = 261$, 7.0 Hz), 132.8 (t, $J = 13.2$ Hz), 115.5 (dd, $J = 21.2$, 4.8 Hz), 113.5 (t, $J = 11$ Hz), 98.3, 78.6 (t, $J = 3.5$ Hz), 31.4, 28.7, 28.3, 22.7, 19.7, 14.2 ppm; HRMS (CI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{F}_2\text{NO}$ $[\text{M} + \text{NH}_4]^+$ 268.1513, found 268.1510.

29. 2,6-Difluoro-4-octylbenzaldehyde (SI-3.13). Palladium on activated carbon (10 wt %, 0.134 g, 0.126 mmol), **SI-3.12** (1.57 g, 6.27 mmol), and benzene (50 mL) were combined in a reaction vessel. The reaction vessel was charged with hydrogen under constant stirring. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The crude product was purified by flash chromatography (0/100 to 1/9 ethyl acetate/hexanes) to yield a yellow oil (1.46 g, 91%): ^1H NMR (500 MHz, CDCl_3) δ = 10.30 (s, 1H), 6.81 (d, $J = 10.0$ Hz, 2H), 2.64 (t, $J = 8.0$ Hz, 2H), 1.65 – 1.59 (m, 2H), 1.31 – 1.26 (m, 10H), 0.88 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ = 184.6 (t, $J = 4.2$ Hz), 163.2 (dd, $J = 261$, 6.4 Hz), 154.0 (t, $J = 10$ Hz), 112.4 (dd, $J = 20$, 3.8 Hz), 112.1 (t, $J = 11$ Hz), 36.4, 32.0, 30.5, 29.4, 29.3, 29.2, 22.8, 14.2 ppm; HRMS (CI) m/z calcd for $\text{C}_{15}\text{H}_{24}\text{F}_2\text{NO}$ $[\text{M} + \text{NH}_4]^+$ 272.1826, found 272.1824.

30. (2,6-Difluoro-4-octylbenzylidene)-4-((trimethylsilyl)ethynyl)-1-naphthylamine (SI-3.14). A solution of compound **SI-3.4** (1.05 g, 4.39 mmol) and compound **SI-3.13** (1.02 g, 4.01 mmol) in benzene (50 mL) was heated to reflux, while water was removed with a Dean-Stark trap. During the course of the reaction, the mixture was concentrated via removal of solvent through the Dean-Stark trap. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The solution was concentrated in vacuo, and the resulting pale brown oil was precipitated from cold methanol. After filtration, the product was obtained as a yellow solid (1.20 g, 63%): ^1H NMR (500 MHz, CDCl_3) δ = 8.72 (s, 1H), 8.36 – 8.32 (m, 2H), 7.70 (d, $J = 7.5$ Hz, 1H),

7.62 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 9.5$ Hz, 2H), 2.65 (t, $J = 8.0$ Hz, 2H), 1.68 – 1.62 (m, 2H), 1.33 – 1.28 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.34 ppm (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ = 162.3 (dd, $J = 257, 7.0$ Hz), 151.7, 150.5, 149.9 (t, $J = 10$ Hz), 134.0, 131.4, 128.5, 127.5, 126.5, 126.1, 124.6, 119.0, 112.20 (dd, $J = 20.2, 3.8$ Hz), 112.16, 111.5 (t, $J = 12.5$ Hz), 103.4, 99.6, 36.1, 32.0, 30.7, 29.5, 29.3, 29.2, 22.8, 14.2, 0.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{35}\text{F}_2\text{NNaSi}$ $[\text{M} + \text{Na}]^+$ 498.2404, found 498.2413.

31. (2,6-Difluoro-4-octylbenzylidene)-4-ethynyl-1-naphthylamine (3.10c). A solution of compound **SI-3.14** (0.400 g, 0.841 mmol) and CsF (0.288 g, 1.90 mmol) in methanol (20 mL) was stirred at 50°C for 2 h. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The resulting yellow solution was cooled to room temperature, filtered through a PTFE syringe filter (0.45 μm), and stored at -20°C overnight to afford a yellow precipitate. The precipitate was collected by filtration and washed with cold methanol. The product was isolated as a yellow solid (0.277 g, 82%): ^1H NMR (500 MHz, CDCl_3) δ = 8.72 (s, 1H), 8.37 – 8.35 (m, 2H), 7.74 (d, $J = 7.5$ Hz, 1H), 7.62 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 9.5$ Hz, 2H), 3.49 (s, 1H), 2.65 (t, $J = 8.0$ Hz, 2H), 1.68 – 1.62 (m, 2H), 1.33 – 1.25 (m, 10H), 0.89 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ = 162.3 (dd, $J = 257, 7.0$ Hz), 151.9, 150.8, 150.0 (t, $J = 10$ Hz), 134.0, 131.8, 128.5, 127.6, 126.6, 126.0, 124.6, 117.9, 112.2 (dd, $J = 20.2, 3.8$ Hz), 112.1, 111.4 (t, $J = 12$ Hz), 82.1, 36.1, 32.0, 30.7, 29.5, 29.3, 29.2, 22.8, 14.2 ppm; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{F}_2\text{NNa}$ $[\text{M} + \text{Na}]^+$ 426.2009, found 426.2012.

32. Poly[2-(2,6-difluoro-4-octylphenyl)benzo[h]quinoline-4,6-diyl] (3.11c). Chloranil (2.21 g, 8.99 mmol), toluene (30 mL), and $\text{BF}_3 \cdot \text{OEt}_2$ (0.56 mL, 4.5 mmol) were combined in a pressure vessel, and the reaction mixture was heated to 100°C. A solution of compound 3.10c (1.212 g, 3.00 mmol) in dry toluene (15 mL) was then added to the mixture via syringe pump at a rate of 3.75 mL/h. Subsequently, the pressure vessel was sealed, and the reaction mixture was stirred at a temperature of 120°C for 44

h. The mixture was then cooled to room temperature, prior to addition of phenylacetylene (1.98 mL, 18.0 mmol) in 1,2-dichloroethane (20 mL). The reaction mixture was further stirred at 100°C for 24 h and was then again cooled to room temperature. After the resulting solids were dissolved in chloroform (50 mL), the solution was stirred for 1 h at room temperature. The solution was then sequentially washed with saturated sodium bicarbonate (50 mL x 5), water (50 mL), and brine (50 mL). The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was precipitated from methanol (50 mL) and further purified by size exclusion chromatography (Bio-Bead SX-1 resin), with chloroform as the mobile phase. After evaporation of the solvent and precipitation from methanol, the product was isolated as a brown solid (0.491 g, 41% isolated yield): ¹H NMR (500 MHz, CD₂Cl₂) δ = 9.43 – 9.25 (br m, 1H), 7.91 – 6.93 (br m, 7H), 2.68 (br m, 2H), 1.66 – 0.82 ppm (br m, 15H); SEC (vs polystyrene standards) *M_n* = 8960 g mol⁻¹, *M_w* = 10900 g mol⁻¹, and PDI = 1.22.

33. 4-(6-Bromo-2-(4-octylphenyl)benzo[h]quinolin-4-yl)-1-naphthylamine (SI-3.15). Compound **3.3b** (0.630 g, 1.00 mmol) was suspended in a mixture of ethanol (120 mL), chloroform (80 mL), and concentrated HCl (62 mL), and the mixture was brought to reflux. After 24 hours, the mixture was cooled, and sodium carbonate (34.5 g, 326 mmol) dissolved in water (200 mL) was slowly added with vigorous stirring. The mixture was extracted with dichloromethane (200 mL x 3), the combined organic layers were filtered through a cotton plug, and the solvent was removed in vacuo. The product was purified by flash chromatography (1/20 to 1/10 ethyl acetate/hexanes) to yield an off-white solid (0.522 g, 89%): ¹H NMR (500 MHz, CDCl₃) δ = 9.66 (d, *J* = 8.0 Hz, 1H), 8.29 – 8.26 (m, 3H), 8.00 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.75 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.33 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.37 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.67 (quint, *J* = 7.5 Hz, 2H), 1.38 – 1.27 (m, 10H), 0.88 ppm (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ = 155.5, 147.8, 146.1, 144.8, 143.1, 137.0, 133.2, 132.8, 132.3, 129.2, 129.1, 128.5, 127.8,

127.5, 127.4, 127.3, 126.8, 126.7, 126.3, 125.7, 125.6, 125.4, 123.6, 122.1, 121.6, 121.3, 109.2, 36.0, 32.0, 31.6, 29.6, 29.5, 29.4, 22.8, 14.3 ppm; HRMS (ESI) m/z calcd for $C_{37}H_{35}BrN_2Na$ $[M + Na]^+$ 609.1881, found 609.1861.

34. 4-(2-(4-Octylphenyl)-6-((trimethylsilyl)ethynyl)benzo[h]quinolin-4-yl)-1-naphthylamine (SI-3.16). **SI-3.15** (0.881 g, 1.50 mmol), $Pd(PPh_3)_2Cl_2$ (0.054 g, 0.077 mmol), CuI (0.015 g, 0.079 mmol), and PPh_3 (0.039 g, 0.149 mmol) were dissolved in a mixture of pyridine (6 mL) and triethylamine (9 mL). Trimethylsilylacetylene (1.26 mL, 8.92 mmol) was added to the reaction mixture, which was stirred overnight at 80°C. The consumption of the starting materials was monitored by TLC analysis (33/67 ethyl acetate/hexanes). Subsequently, the reaction mixture was cooled to room temperature, filtered through a pad of Celite, and washed with diethyl ether (50 mL). The filtrate was then concentrated in vacuo. After solvent evaporation, the crude product was purified by flash chromatography (0/100 to 35/65 ethyl acetate/hexanes) to yield a yellow solid (0.721 g, 79%): 1H NMR (500 MHz, $CDCl_3$) δ =9.63 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 2H), 7.98 (s, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.69 (s, 1H), 7.48 – 7.43 (m, 2H), 7.34 – 7.30 (m, 4H), 6.91 (d, J = 7.5 Hz, 1H), 4.32 (s, 2H), 2.67 (t, J = 7.5 Hz, 2H), 1.67 – 1.64 (m, 2H), 1.37 – 1.26 (m, 10H), 0.87 (t, J = 6.5 Hz, 3H), 0.26 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ =155.7, 148.4, 146.6, 144.8, 142.9, 137.0, 133.1, 132.9, 131.9, 129.1, 128.9, 128.8, 128.4, 127.5, 127.4, 126.8, 126.7, 126.6, 126.2, 125.4, 125.3, 124.5, 123.6, 121.5, 121.2, 119.6, 109.2, 103.3, 99.9, 36.0, 32.0, 31.6, 29.6, 29.5, 29.4, 22.8, 14.3, 0.2 ppm; HRMS (ESI) m/z calcd for $C_{42}H_{45}N_2Si$ $[M + H]^+$ 605.3352, found 605.3355.

35. 4-(3-Decylpentadecyl)benzylidene-4-(2-(4-octylphenyl)-6-((trimethylsilyl)ethynyl)benzo[h]quinolin-4-yl)-1-naphthylamine (SI-3.17). A solution of compound **SI-3.16** (0.302 g, 0.50 mmol) and compound **SI-3.10** (0.228 g, 0.50 mmol) in benzene (50 mL) was heated to reflux, while water was removed with a Dean-Stark trap. During the course of the reaction, the mixture

was concentrated via removal of solvent through the Dean- Stark trap. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The solution was cooled to room temperature, and the solvent was evaporated to give a viscous brown oil, which was used in the next step without further purification. For the analytical sample, the material was taken into ethanol (50 mL), cooled to -20°C, and decanted. This decanting process was repeated three times leaving behind a yellow oil: ¹H NMR (500 MHz, CDCl₃) δ = 9.63 (d, *J* = 7.5 Hz, 1H), 8.67 (s, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.38 (d, *J* = 7.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 2H), 8.03 – 8.00 (m, 3H), 7.83 – 7.77 (m, 2H), 7.64 (s, 1H), 7.57 – 7.51 (m, 2H), 7.46 – 7.35 (m, 6H), 7.22 (d, *J* = 7.5 Hz, 1H), 2.71 – 2.68 (m, 4H), 1.71 – 1.61 (m, 4H), 1.43 – 1.25 (m, 51H), 0.90 – 0.87 (m, 9H), 0.26 ppm (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ = 160.9, 155.7, 150.2, 147.9, 147.8, 146.6, 144.9, 137.0, 134.1, 133.6, 133.1, 132.6, 131.8, 129.3, 129.15, 129.12, 129.08, 128.9, 128.7, 128.1, 127.6, 127.5, 127.3, 126.3, 126.2, 126.0, 125.4, 124.6, 124.2, 121.1, 119.9, 112.4, 103.1, 100.1, 37.3, 36.0, 35.7, 33.6, 33.5, 32.1, 32.0, 31.6, 30.3, 29.9, 29.8, 29.7, 29.54, 29.48, 29.44, 26.8, 22.9, 22.8, 14.29, 14.27, 0.2 ppm; MS (ESI) *m/z* calcd for C₇₄H₉₉N₂Si [M + H]⁺ 1043.8; found, 1043.8.

36. (4-(3-Decylpentadecyl)benzylidene)-4-(6-ethynyl-2-(4-octylphenyl)benzo[h]quinolin-4-yl)-1-naphthylamine (3.12). Tetrabutylammonium fluoride (1 M in THF, 1.22 mL, 1.22 mmol) was added to a solution of **SI-3.17** (0.52 g, 0.50 mmol) in THF (10 mL) at room temperature, and the reaction mixture was stirred for 2 h. The consumption of the starting materials was monitored by TLC analysis (1/9 ethyl acetate/hexanes). The reaction mixture was diluted with diethyl ether (50 mL) and then sequentially washed with saturated sodium bicarbonate (25 mL), water (3 x 25mL), and brine (25 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The product was purified by flash chromatography using a neutral alumina as the media (0/100 to 2/8 diethyl ether/n-pentane). After solvent evaporation, the product was obtained as a yellow foam (0.306 g, 63% over two steps): ¹H NMR (500 MHz, CDCl₃) δ = 9.64 (d, *J* = 8.0 Hz, 1H), 8.66 (s, 1H), 8.51

(d, $J = 8.5$ Hz, 1H), 8.40 (d, $J = 8.0$ Hz, 1H), 8.31 (d, $J = 8.5$ Hz, 2H), 8.05 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 2H), 7.84 – 7.77 (m, 2H), 7.69 (s, 1H), 7.56 – 7.51 (m, 2H), 7.45 – 7.36 (m, 6H), 7.21 (d, $J = 7.5$ Hz, 1H), 3.34 (s, 1H), 2.72 – 2.68 (m, 4H), 1.71 – 1.61 (m, 4H), 1.40 – 1.29 (m, 51H), 0.90 – 0.87 ppm (m, 9H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 160.9, 156.0, 150.3, 147.93, 147.91, 146.7, 145.0, 136.9, 134.1, 133.4, 133.0, 132.6, 131.9, 129.5, 129.3, 129.16, 129.12, 129.07, 128.9, 128.0, 127.61, 127.56, 127.3, 126.17, 126.16, 125.9, 125.4, 124.6, 124.1, 121.1, 118.9, 112.4, 82.2, 81.9, 37.3, 36.0, 35.7, 33.6, 33.5, 32.1, 32.0, 31.6, 30.3, 29.9, 29.8, 29.7, 29.54, 29.48, 29.44, 26.8, 22.86, 22.83, 14.29, 14.27$ ppm; HRMS (ESI) m/z calcd for $\text{C}_{71}\text{H}_{90}\text{N}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 993.7002, found 993.6985.

37. Poly[2'-(4-(3-decylpentadecyl)phenyl)-2-(4-octylphenyl)-4,6'-bibenzo[h]quinolone-4',6-diyl] (3.13). Chloranil (0.184 g, 0.75 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.08 mL, 0.65 mmol), and toluene (1.75 mL) were combined in a pressure vessel, and the reaction mixture was heated to 100°C . A solution of compound **3.12** (0.243 g, 0.25 mmol) in dry toluene (2.0 mL) was then added to the mixture via a syringe pump at a rate of 2.0 mL/h. Subsequently, the pressure vessel was sealed, and the temperature was elevated to 180°C at a rate of $20^\circ\text{C}/\text{h}$. The reaction mixture was stirred at a temperature of 180°C for 24 h. The reaction mixture was then cooled to room temperature, prior to the addition of phenylacetylene (0.17 mL, 1.5 mmol) in 1,2-dichloroethane (3.75 mL). The reaction mixture was further stirred at 100°C for 24 h and was then again cooled to room temperature. After the resulting solids were dissolved in chloroform (50 mL), the solution was stirred for 1 h at room temperature. The solution was then sequentially washed with saturated sodium bicarbonate (50 mL x 5), water (50 mL) and brine (50 mL). The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was precipitated from methanol and further purified by size exclusion chromatography (Toyopearl HW-55S resin) with chloroform as the mobile phase. After evaporation of the solvent and precipitation from methanol, the product was isolated by filtration as a brown solid (0.020 g, 8% isolated yield): ^1H NMR (500 MHz, CD_2Cl_2) $\delta = 9.68 - 9.48$ (br m, 2H),

8.23 – 7.33 (br m, 18H), 2.67 (br m, 4H), 1.53 – 0.83 ppm (br m, 64H); SEC (vs polystyrene standards)

$M_n = 29600 \text{ g mol}^{-1}$, $M_w = 36200 \text{ g mol}^{-1}$, and PDI = 1.22.

3.5.3. NMR Characterization of Crude and Purified 3.3b

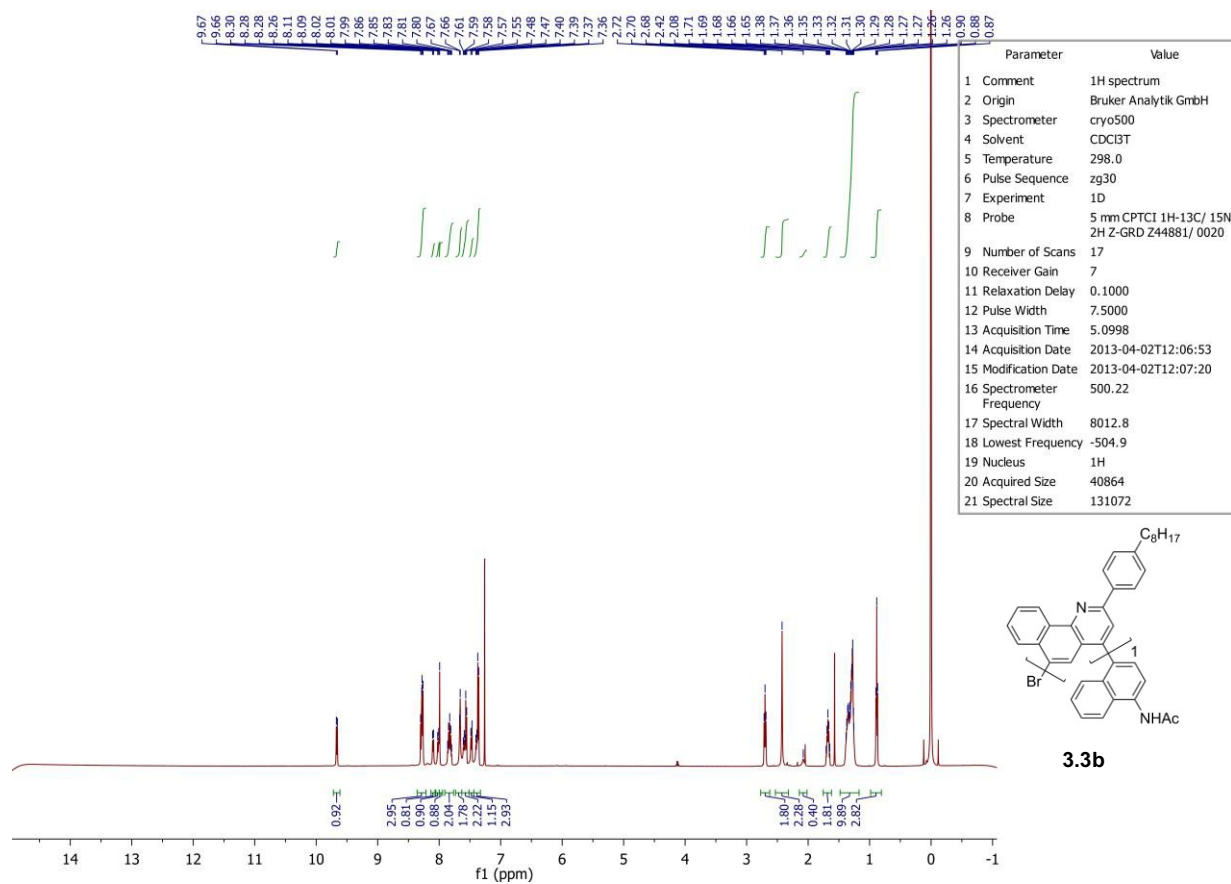


Figure S3.1. The ¹H NMR spectrum obtained for purified compound **3.3b**.

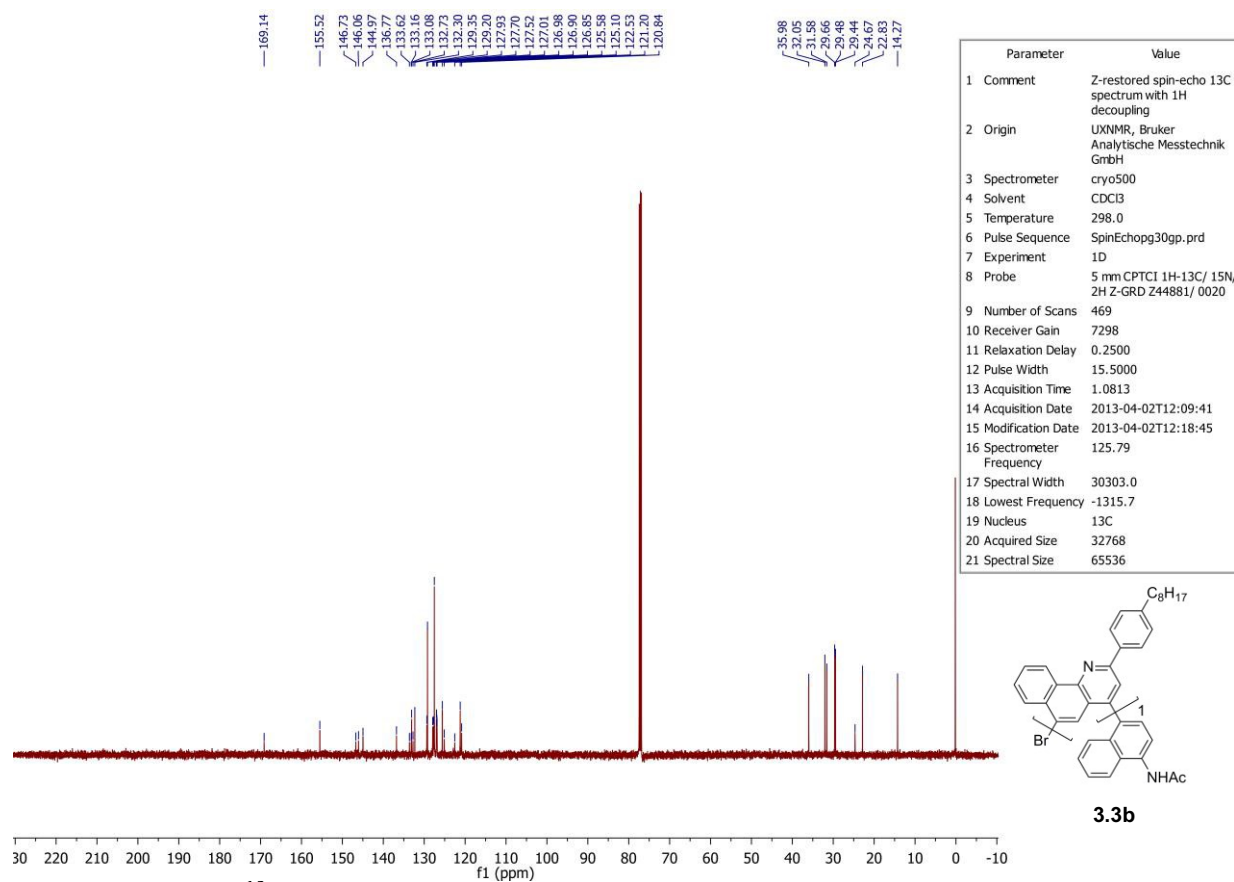


Figure S3.2. The ^{13}C NMR spectrum obtained for purified compound **3.3b**.

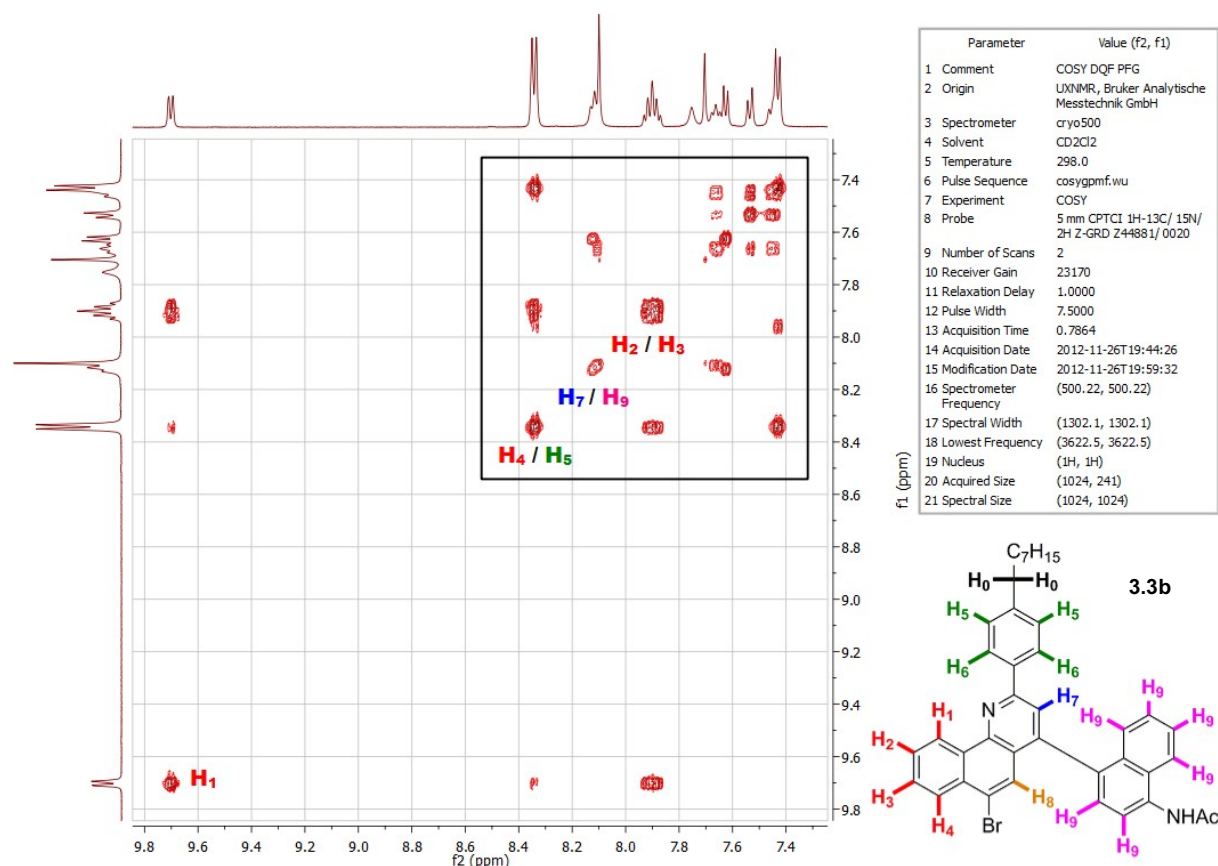


Figure S3.3. A COSY NMR spectrum obtained for compound **3.3b**. The downfield proton at 9.7 ppm (**H₁**) was assigned to the proton at the 10 position of the benzoquinoline ring system. The clear separation between the signal associated with **H₁**, and the other adjacent protons provided a convenient probe for the regioselectivity of the reaction. Note that only a single resonance was observed in this region; the presence of multiple isomers would have resulted in multiple peaks for **H₁**. The spectrum also enabled assignment of protons **H₂–H₄** in the same spin system, as well as the singlet proton resonance corresponding to **H₇**. The boxed region is shown in greater detail in Figure S3.4.

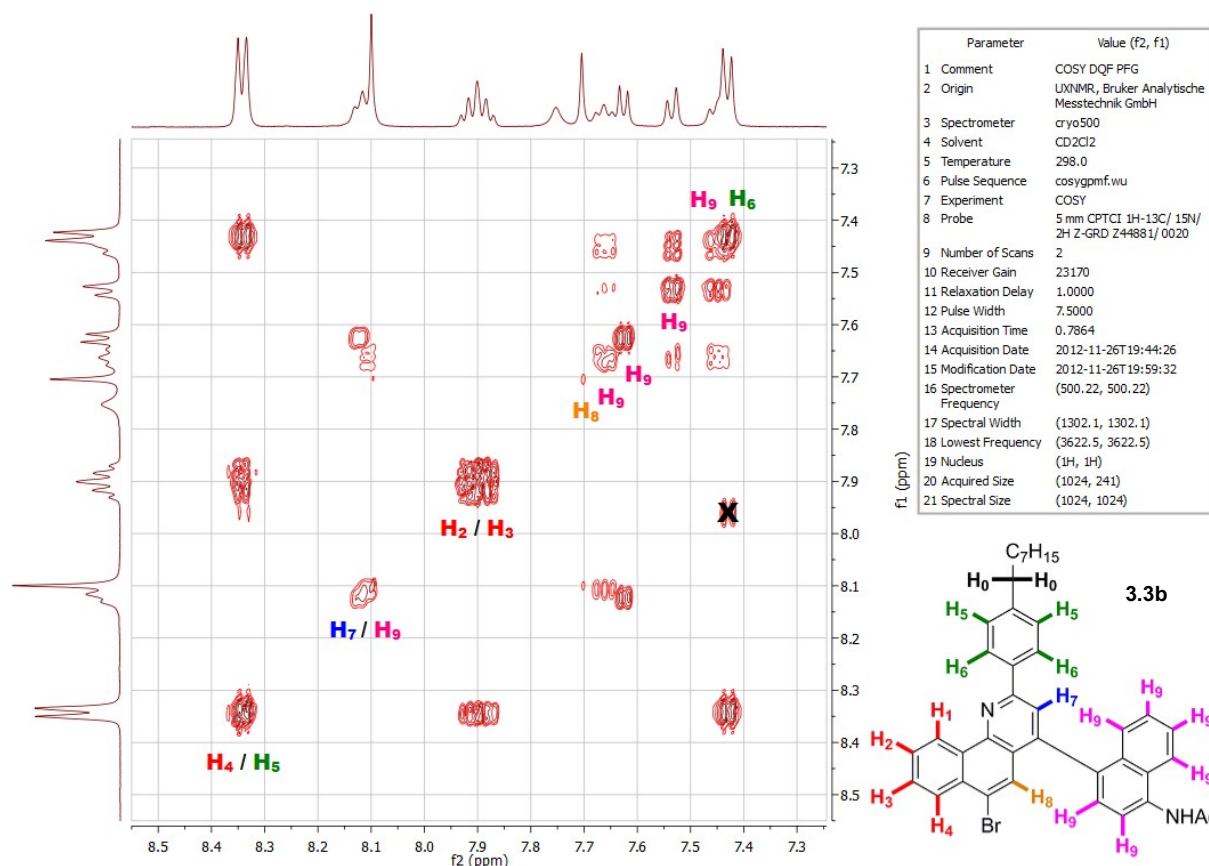


Figure S3.4. A close up of the region between 7.24 ppm and 8.55 ppm for the COSY spectrum obtained for compound **3.3b**. This region enabled assignment of the protons corresponding to the pendant phenyl ring (**H5** and **H6**), the remaining singlet adjacent to the bromine (**H8**), and the protons corresponding to the naphthyl ring (**H9**). The assignments provided additional confirmation of the identity of the molecule.

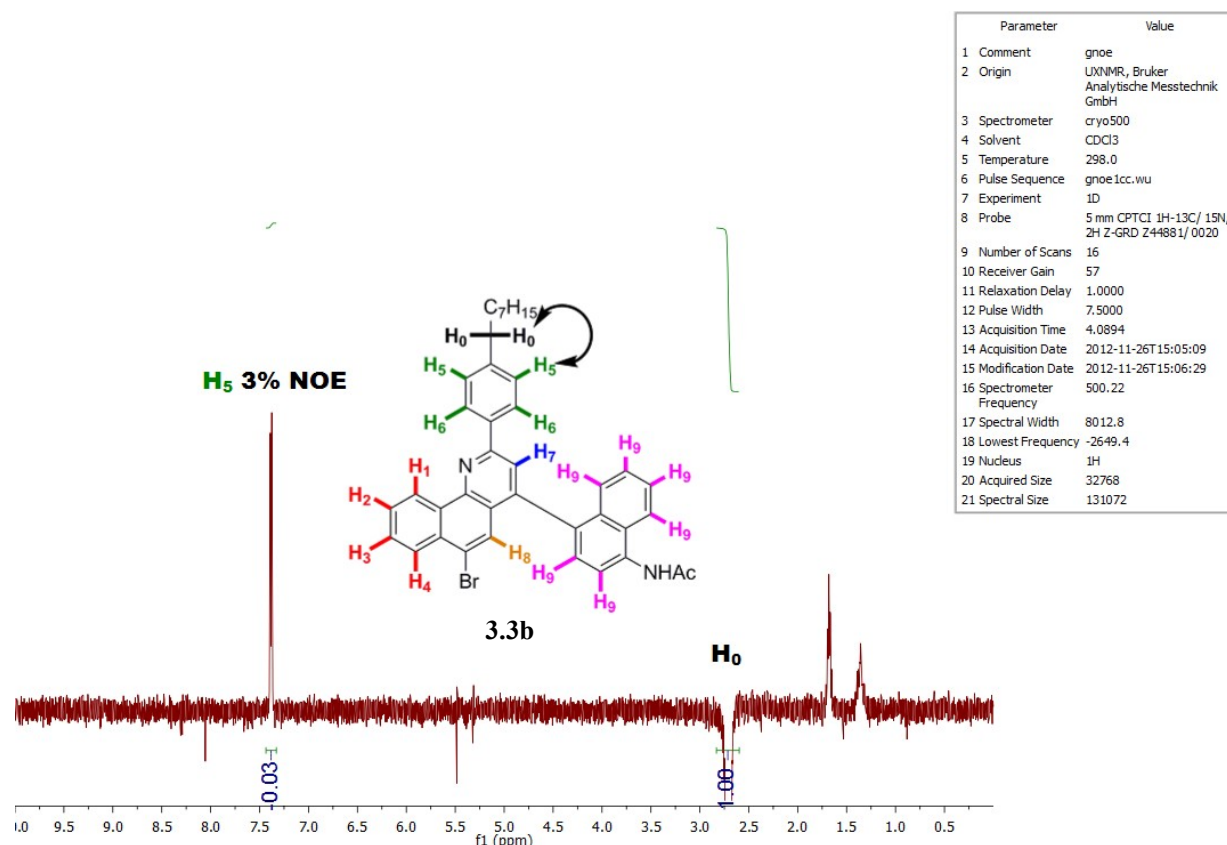


Figure S3.5. An NOE spectrum obtained for compound **3.3b**, where the proton at 2.7 ppm (**H₀**) was irradiated. The irradiation of **H₀** resulted in an enhancement of the NOE signal between **H₀** and the proton at 7.4 ppm (**H₅**). This experiment facilitated assignment of the protons on the pendant phenyl ring adjacent to the octyl chain.

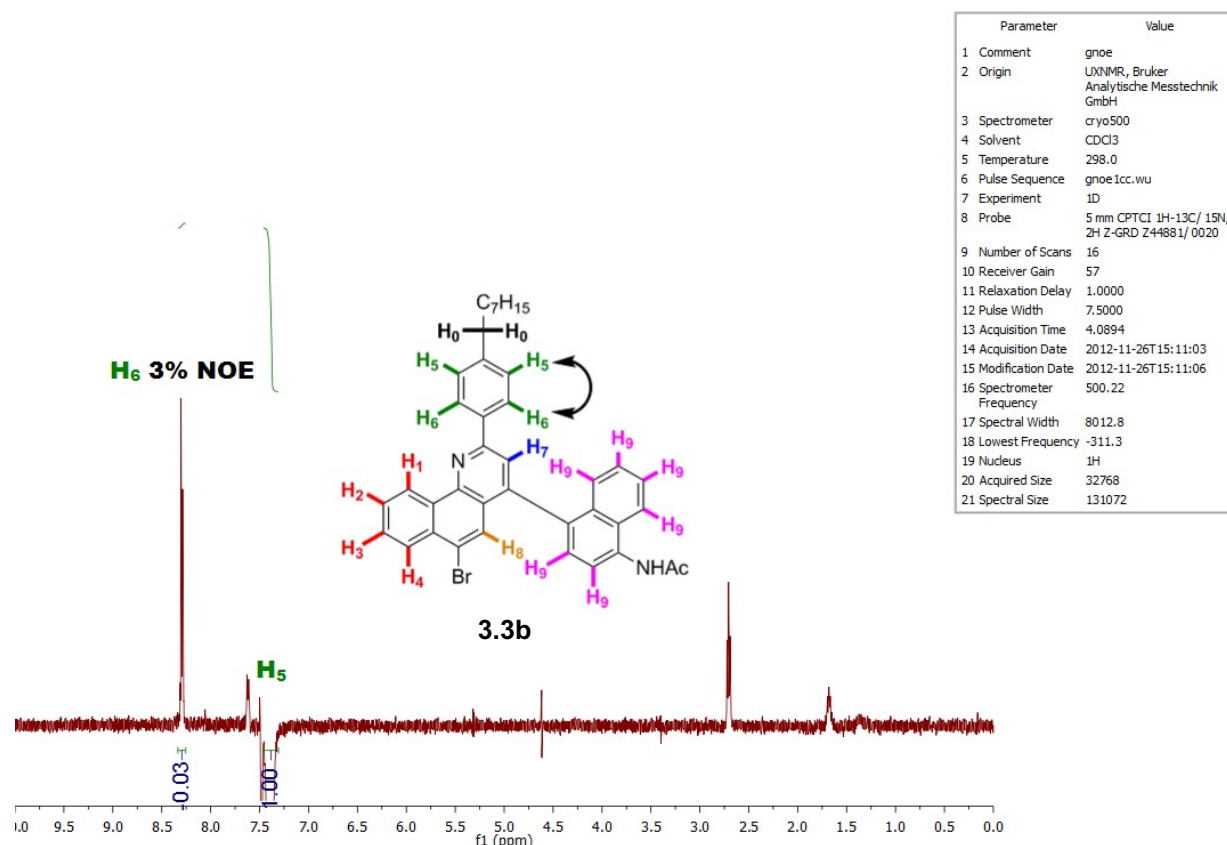


Figure S3.6. An NOE spectrum obtained for compound **3.3b**, where the proton at 7.4 ppm (**H₅**) was irradiated. The irradiation of **H₅** resulted in an enhancement of the NOE signal between **H₅** and the proton at 8.3 ppm (**H₆**). This experiment facilitated assignment of the other proton (**H₆**) on the pendant phenyl ring adjacent to the octyl chain. The assignment of **H₆** facilitated subsequent conformation of the identity of the regioisomer *via* the experiments in Figures S3.7 and S3.8.

3.5.4 X-ray Data Collection, Structure Solution, and Refinement

1. X-ray Data Collection, Structure Solution and Structure Refinement for 3.3a.

A crystal of **3.3a** was prepared by slow evaporation of solvent from an acetonitrile solution of the compound. A colorless crystal of approximate dimensions 0.130 x 0.228 x 0.483 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2^{S3} program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT^{S4} and SADABS^{S5} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL^{S6} program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2₁/c that was later determined to be correct. The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques.^{S7} The analytical scattering factors^{S8} for neutral atoms were used throughout the analysis. There was one acetonitrile solvent present per formula unit. The hydrogen atoms associated with the solvent were included using a riding model. All other hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0722 and Goof = 1.040 for 428 variables refined against 5506 data (0.79 Å), R1 = 0.0276 for those 4880 data with I > 2.0σ(I). The following definitions were used for the analysis:

$$\bullet wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$\bullet R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

$$\bullet Goof = S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the total number of parameters refined}$$

Identification code	3.5a	
Empirical formula	C ₅₀ H ₃₂ Br N ₃ O • 2(C ₃ H ₆ O)	
Formula weight	886.85	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 11.983(4) Å	α = 76.872(5)°.
	<i>b</i> = 14.025(5) Å	β = 79.833(4)°.
	<i>c</i> = 14.252(5) Å	γ = 68.817(5)°.
Volume	2163.4(14) Å ³	
<i>Z</i>	2	
Density (calculated)	1.361 Mg/m ³	
Absorption coefficient	1.001 mm ⁻¹	
<i>F</i> (000)	920	
Crystal color	colorless	
Crystal size	0.272 x 0.213 x 0.092 mm ³	
Theta range for data collection	1.832 to 24.862°	
Index ranges	-14 ≤ <i>h</i> ≤ 14, -16 ≤ <i>k</i> ≤ 16, -16 ≤ <i>l</i> ≤ 16	
Reflections collected	20059	
Independent reflections	7416 [<i>R</i> (int) = 0.0852]	
Completeness to theta = 25.500°	92.1 %	
Absorption correction	Numerical	

Max. and min. transmission	1.0000 and 0.6938
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7416 / 0 / 561
Goodness-of-fit on F ²	1.010
Final R indices [I>2sigma(I) = 4293 data]	R1 = 0.0814, wR2 = 0.1997
R indices (all data, 0.85Å)	R1 = 0.1453, wR2 = 0.2397
Extinction coefficient	0.0041(16)
Largest diff. peak and hole	1.076 and -1.234 e.Å ⁻³

Table S6. Crystal data and structure refinement for **3.5a**.

	x	y	z	U(eq)
Br(1)	-4231(1)	9063(1)	18922(1)	47(1)
N(1)	518(4)	8625(4)	20107(3)	35(1)
N(2)	-5756(4)	10270(5)	24021(3)	41(1)
N(3)	-2613(6)	14864(5)	21168(4)	58(2)
O(1)	-3596(10)	15607(8)	19847(8)	64(3)
O(1A)	-4006(15)	15828(12)	20174(13)	69(5)
C(1)	-431(5)	9068(5)	21635(4)	35(2)
C(2)	-1527(5)	9165(5)	21412(4)	33(2)
C(3)	-1620(5)	9001(5)	20485(4)	35(2)
C(4)	-2713(5)	9097(5)	20178(4)	35(2)
C(5)	-2743(5)	8932(5)	19287(4)	36(2)
C(6)	-1687(5)	8694(5)	18615(4)	38(2)
C(7)	-1730(6)	8596(6)	17659(4)	45(2)
C(8)	-701(5)	8419(6)	17032(4)	46(2)
C(9)	363(5)	8351(5)	17313(4)	44(2)
C(10)	430(5)	8419(5)	18244(4)	37(2)
C(11)	-607(5)	8609(5)	18896(4)	36(2)
C(12)	-552(5)	8746(5)	19874(4)	31(1)
C(13)	598(5)	8771(5)	20978(4)	36(2)
C(14)	1809(5)	8586(5)	21230(4)	38(2)
C(15)	2805(5)	8100(6)	20636(4)	48(2)
C(16)	3945(6)	7900(6)	20858(5)	57(2)

C(17)	4119(6)	8207(6)	21658(5)	57(2)
C(18)	3131(6)	8693(6)	22249(5)	52(2)
C(19)	1992(5)	8887(6)	22046(4)	43(2)
C(20)	-2618(5)	9442(5)	22115(4)	30(1)
C(21)	-3109(5)	10430(6)	22258(4)	36(2)
C(22)	-4187(5)	10760(6)	22920(4)	37(2)
C(23)	-4696(5)	10007(6)	23413(4)	40(2)
C(24)	-4166(5)	8957(6)	23297(4)	38(2)
C(25)	-4612(6)	8190(7)	23809(4)	47(2)
C(26)	-4097(7)	7203(7)	23704(5)	58(2)
C(27)	-3054(6)	6899(6)	23069(5)	55(2)
C(28)	-2582(6)	7629(6)	22555(5)	43(2)
C(29)	-3100(5)	8660(6)	22642(4)	39(2)
C(30)	-4728(5)	11792(6)	23063(4)	41(2)
C(31)	-5783(6)	12014(6)	23689(4)	46(2)
C(32)	-6267(5)	11243(6)	24132(4)	40(2)
C(33)	-7445(6)	11496(7)	24745(4)	48(2)
C(34)	-8103(6)	12495(7)	24906(5)	58(2)
C(35)	-9220(6)	12707(8)	25441(5)	65(2)
C(36)	-9673(7)	11923(8)	25813(5)	66(3)
C(37)	-9034(7)	10931(8)	25691(5)	67(3)
C(38)	-7911(6)	10700(7)	25155(5)	57(2)
C(39)	-4199(5)	12599(5)	22595(4)	42(2)

C(40)	-4365(6)	13077(6)	21639(5)	47(2)
C(41)	-3842(6)	13812(6)	21170(5)	53(2)
C(42)	-3164(6)	14126(6)	21631(5)	48(2)
C(43)	-2981(5)	13670(5)	22625(4)	40(2)
C(44)	-2310(6)	13952(6)	23154(5)	46(2)
C(45)	-2166(6)	13510(6)	24101(5)	48(2)
C(46)	-2661(6)	12754(6)	24551(5)	50(2)
C(47)	-3307(5)	12445(6)	24062(4)	43(2)
C(48)	-3512(5)	12906(6)	23088(4)	40(2)
C(49)	-2913(8)	15585(7)	20376(6)	67(2)
C(50)	-2184(10)	16293(8)	20089(7)	99(4)
C(51)	-3188(9)	14529(7)	16515(7)	77(3)
O(2)	-2019(8)	14089(7)	16366(7)	86(3)
C(52)	-3892(14)	15128(11)	15817(11)	92(4)
C(53)	-3701(13)	14136(11)	17498(10)	79(4)
O(2A)	-2720(20)	15205(17)	16097(17)	94(7)
C(52A)	-4260(20)	14600(20)	16090(20)	63(7)
C(53A)	-3700(30)	14720(30)	17620(20)	75(9)
C(54)	438(9)	5200(8)	21909(7)	79(3)
O(3)	-603(8)	5327(8)	21830(7)	70(3)
C(55)	1323(13)	4269(10)	22448(10)	88(4)
C(56)	873(18)	6016(15)	21354(15)	86(7)
O(3A)	-350(20)	4851(19)	21722(16)	76(7)

C(55A)	740(60)	4450(40)	22800(40)	99(18)
C(56A)	860(30)	6180(30)	21560(30)	50(9)

Table S3.7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.5a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Br(1)-C(5)	1.879(6)
N(1)-C(12)	1.323(7)
N(1)-C(13)	1.328(7)
N(2)-C(32)	1.312(9)
N(2)-C(23)	1.384(7)
N(3)-C(49)	1.337(9)
N(3)-C(42)	1.404(9)
O(1)-C(49)	1.196(12)
O(1A)-C(49)	1.296(17)
C(1)-C(2)	1.357(8)
C(1)-C(13)	1.403(8)
C(2)-C(3)	1.421(8)
C(2)-C(20)	1.487(8)
C(3)-C(12)	1.393(8)
C(3)-C(4)	1.405(8)
C(4)-C(5)	1.350(8)
C(5)-C(6)	1.428(8)
C(6)-C(11)	1.378(8)
C(6)-C(7)	1.412(8)
C(7)-C(8)	1.368(8)
C(8)-C(9)	1.368(9)
C(9)-C(10)	1.371(8)
C(10)-C(11)	1.394(8)

C(11)-C(12)	1.466(8)
C(13)-C(14)	1.473(8)
C(14)-C(15)	1.387(9)
C(14)-C(19)	1.400(8)
C(15)-C(16)	1.372(9)
C(16)-C(17)	1.379(10)
C(17)-C(18)	1.379(10)
C(18)-C(19)	1.362(8)
C(20)-C(21)	1.342(9)
C(20)-C(29)	1.425(8)
C(21)-C(22)	1.453(8)
C(22)-C(23)	1.400(9)
C(22)-C(30)	1.401(9)
C(23)-C(24)	1.413(9)
C(24)-C(25)	1.378(9)
C(24)-C(29)	1.432(8)
C(25)-C(26)	1.327(10)
C(26)-C(27)	1.398(10)
C(27)-C(28)	1.355(9)
C(28)-C(29)	1.377(9)
C(30)-C(31)	1.392(8)
C(30)-C(39)	1.467(9)
C(31)-C(32)	1.385(9)

C(32)-C(33)	1.492(8)
C(33)-C(34)	1.386(11)
C(33)-C(38)	1.393(10)
C(34)-C(35)	1.384(9)
C(35)-C(36)	1.361(12)
C(36)-C(37)	1.358(12)
C(37)-C(38)	1.390(9)
C(39)-C(40)	1.390(9)
C(39)-C(48)	1.398(9)
C(40)-C(41)	1.381(10)
C(41)-C(42)	1.365(9)
C(42)-C(43)	1.436(9)
C(43)-C(44)	1.396(9)
C(43)-C(48)	1.419(9)
C(44)-C(45)	1.364(9)
C(45)-C(46)	1.377(9)
C(46)-C(47)	1.359(9)
C(47)-C(48)	1.415(8)
C(49)-C(50)	1.495(11)
C(51)-O(2A)	1.26(2)
C(51)-O(2)	1.311(12)
C(51)-C(52)	1.346(15)
C(51)-C(52A)	1.48(3)

C(51)-C(53)	1.496(16)
C(51)-C(53A)	1.63(3)
C(54)-O(3)	1.218(12)
C(54)-O(3A)	1.30(2)
C(54)-C(56)	1.44(2)
C(54)-C(55A)	1.46(6)
C(54)-C(55)	1.499(16)
C(54)-C(56A)	1.58(4)
C(12)-N(1)-C(13)	118.7(5)
C(32)-N(2)-C(23)	118.3(6)
C(49)-N(3)-C(42)	127.9(6)
C(2)-C(1)-C(13)	120.7(5)
C(1)-C(2)-C(3)	118.7(5)
C(1)-C(2)-C(20)	121.3(5)
C(3)-C(2)-C(20)	120.0(5)
C(12)-C(3)-C(4)	120.7(5)
C(12)-C(3)-C(2)	116.1(5)
C(4)-C(3)-C(2)	123.2(5)
C(5)-C(4)-C(3)	120.4(5)
C(4)-C(5)-C(6)	121.7(5)
C(4)-C(5)-Br(1)	118.3(4)
C(6)-C(5)-Br(1)	119.9(4)
C(11)-C(6)-C(7)	119.2(5)

C(11)-C(6)-C(5)	118.8(5)
C(7)-C(6)-C(5)	121.9(5)
C(8)-C(7)-C(6)	119.4(6)
C(9)-C(8)-C(7)	121.0(6)
C(8)-C(9)-C(10)	120.4(6)
C(9)-C(10)-C(11)	119.7(6)
C(6)-C(11)-C(10)	120.2(5)
C(6)-C(11)-C(12)	120.0(5)
C(10)-C(11)-C(12)	119.8(5)
N(1)-C(12)-C(3)	124.8(5)
N(1)-C(12)-C(11)	117.0(5)
C(3)-C(12)-C(11)	118.2(5)
N(1)-C(13)-C(1)	120.9(5)
N(1)-C(13)-C(14)	117.3(5)
C(1)-C(13)-C(14)	121.7(5)
C(15)-C(14)-C(19)	118.7(5)
C(15)-C(14)-C(13)	118.9(6)
C(19)-C(14)-C(13)	122.4(6)
C(16)-C(15)-C(14)	120.5(6)
C(15)-C(16)-C(17)	120.5(6)
C(18)-C(17)-C(16)	119.1(6)
C(19)-C(18)-C(17)	121.1(6)
C(18)-C(19)-C(14)	120.0(6)

C(21)-C(20)-C(29)	121.4(6)
C(21)-C(20)-C(2)	118.6(5)
C(29)-C(20)-C(2)	120.0(6)
C(20)-C(21)-C(22)	121.6(6)
C(23)-C(22)-C(30)	120.0(6)
C(23)-C(22)-C(21)	117.5(6)
C(30)-C(22)-C(21)	122.5(6)
N(2)-C(23)-C(22)	121.0(7)
N(2)-C(23)-C(24)	117.4(6)
C(22)-C(23)-C(24)	121.5(6)
C(25)-C(24)-C(23)	122.9(6)
C(25)-C(24)-C(29)	117.8(7)
C(23)-C(24)-C(29)	119.3(6)
C(26)-C(25)-C(24)	122.4(6)
C(25)-C(26)-C(27)	120.6(7)
C(28)-C(27)-C(26)	118.9(8)
C(27)-C(28)-C(29)	121.9(7)
C(28)-C(29)-C(20)	123.1(6)
C(28)-C(29)-C(24)	118.4(6)
C(20)-C(29)-C(24)	118.5(6)
C(31)-C(30)-C(22)	116.8(6)
C(31)-C(30)-C(39)	121.2(7)
C(22)-C(30)-C(39)	122.0(5)

C(32)-C(31)-C(30)	120.6(7)
N(2)-C(32)-C(31)	123.2(6)
N(2)-C(32)-C(33)	116.1(6)
C(31)-C(32)-C(33)	120.6(7)
C(34)-C(33)-C(38)	118.8(6)
C(34)-C(33)-C(32)	122.6(7)
C(38)-C(33)-C(32)	118.6(7)
C(35)-C(34)-C(33)	120.8(8)
C(36)-C(35)-C(34)	119.4(9)
C(37)-C(36)-C(35)	121.1(7)
C(36)-C(37)-C(38)	120.5(8)
C(37)-C(38)-C(33)	119.3(8)
C(40)-C(39)-C(48)	118.0(6)
C(40)-C(39)-C(30)	120.4(6)
C(48)-C(39)-C(30)	121.6(6)
C(41)-C(40)-C(39)	121.6(6)
C(42)-C(41)-C(40)	121.7(7)
C(41)-C(42)-N(3)	122.8(6)
C(41)-C(42)-C(43)	119.0(7)
N(3)-C(42)-C(43)	118.2(6)
C(44)-C(43)-C(48)	118.9(6)
C(44)-C(43)-C(42)	122.8(6)
C(48)-C(43)-C(42)	118.3(6)

C(45)-C(44)-C(43)	121.1(7)
C(44)-C(45)-C(46)	120.4(6)
C(47)-C(46)-C(45)	120.6(6)
C(46)-C(47)-C(48)	121.0(7)
C(39)-C(48)-C(47)	120.7(6)
C(39)-C(48)-C(43)	121.3(6)
C(47)-C(48)-C(43)	118.0(6)
O(1)-C(49)-N(3)	124.4(9)
O(1A)-C(49)-N(3)	115.4(10)
O(1)-C(49)-C(50)	119.9(9)
O(1A)-C(49)-C(50)	124.5(10)
N(3)-C(49)-C(50)	115.0(7)
O(2)-C(51)-C(52)	124.2(11)
O(2A)-C(51)-C(52A)	114.0(17)
O(2)-C(51)-C(53)	112.8(10)
C(52)-C(51)-C(53)	122.0(12)
O(2A)-C(51)-C(53A)	108.7(17)
C(52A)-C(51)-C(53A)	104.1(17)
O(3)-C(54)-C(56)	114.8(12)
O(3A)-C(54)-C(55A)	95(3)
O(3)-C(54)-C(55)	127.5(11)
C(56)-C(54)-C(55)	117.5(12)
O(3A)-C(54)-C(56A)	139.1(19)

C(55A)-C(54)-C(56A) 125(3)

Table S8. Bond lengths [Å] and angles [°] for **3.5a**.

	U11	U22	U33	U23	U13	U12
Br(1)	26(1)	98(1)	23(1)	-19(1)	4(1)	-26(1)
N(1)	27(3)	66(4)	12(2)	-7(2)	2(2)	-18(3)
N(2)	24(3)	91(5)	12(3)	-13(3)	5(2)	-25(3)
N(3)	61(4)	74(5)	40(4)	6(3)	-16(3)	-29(4)
C(1)	31(3)	66(5)	13(3)	-8(3)	3(2)	-23(3)
C(2)	27(3)	63(4)	10(3)	-9(3)	7(2)	-20(3)
C(3)	25(3)	66(5)	17(3)	-8(3)	2(2)	-18(3)
C(4)	30(3)	61(4)	19(3)	-9(3)	1(3)	-19(3)
C(5)	28(3)	68(5)	15(3)	-8(3)	4(2)	-22(3)
C(6)	27(3)	74(5)	14(3)	-11(3)	5(2)	-20(3)
C(7)	28(3)	87(5)	20(3)	-21(3)	3(3)	-16(3)
C(8)	31(3)	85(5)	19(3)	-20(3)	6(3)	-14(3)
C(9)	30(3)	77(5)	22(3)	-16(3)	8(3)	-16(3)
C(10)	27(3)	69(5)	18(3)	-13(3)	5(2)	-18(3)
C(11)	31(3)	59(4)	18(3)	-10(3)	4(3)	-16(3)
C(12)	22(3)	60(4)	11(3)	-7(3)	5(2)	-17(3)
C(13)	30(3)	58(4)	19(3)	-4(3)	2(3)	-19(3)
C(14)	29(3)	68(5)	19(3)	0(3)	2(3)	-24(3)
C(15)	29(3)	96(6)	20(3)	-17(4)	3(3)	-22(4)
C(16)	29(4)	104(6)	39(4)	-24(4)	7(3)	-21(4)
C(17)	29(4)	110(7)	42(4)	-14(4)	-4(3)	-34(4)
C(18)	39(4)	95(6)	28(4)	-11(4)	-4(3)	-28(4)

C(19)	29(3)	82(5)	20(3)	-10(3)	1(3)	-24(3)
C(20)	26(3)	54(5)	12(3)	-7(3)	2(2)	-16(3)
C(21)	27(3)	79(6)	10(3)	-2(3)	2(2)	-30(3)
C(22)	25(3)	77(5)	14(3)	-10(3)	0(2)	-23(3)
C(23)	28(3)	90(6)	12(3)	-14(3)	6(2)	-34(4)
C(24)	29(3)	74(5)	15(3)	-8(3)	2(3)	-25(3)
C(25)	37(4)	89(6)	25(4)	-17(4)	13(3)	-37(4)
C(26)	57(5)	88(7)	37(4)	-7(4)	12(4)	-42(5)
C(27)	50(4)	72(5)	47(5)	-12(4)	4(4)	-28(4)
C(28)	45(4)	63(5)	26(4)	-9(3)	5(3)	-27(4)
C(29)	31(3)	80(6)	14(3)	-4(3)	1(3)	-31(4)
C(30)	30(3)	79(5)	13(3)	-12(3)	4(3)	-18(4)
C(31)	33(4)	83(5)	20(3)	-13(3)	1(3)	-16(4)
C(32)	26(3)	82(6)	12(3)	-13(3)	1(2)	-16(4)
C(33)	24(3)	107(6)	12(3)	-14(4)	2(3)	-21(4)
C(34)	31(4)	115(7)	27(4)	-21(4)	6(3)	-23(4)
C(35)	34(4)	124(8)	30(4)	-17(5)	5(3)	-21(5)
C(36)	30(4)	128(8)	17(4)	0(4)	3(3)	-10(5)
C(37)	34(4)	123(8)	31(4)	9(5)	7(3)	-30(5)
C(38)	33(4)	105(6)	21(4)	-5(4)	9(3)	-17(4)
C(39)	26(3)	61(5)	29(4)	-13(3)	6(3)	-3(3)
C(40)	43(4)	72(5)	26(4)	-7(3)	-10(3)	-18(4)
C(41)	54(5)	76(6)	29(4)	-4(4)	-5(3)	-24(4)

C(42)	38(4)	68(5)	33(4)	-6(4)	1(3)	-15(4)
C(43)	29(3)	65(5)	22(3)	-12(3)	6(3)	-12(3)
C(44)	37(4)	71(5)	31(4)	-15(3)	4(3)	-19(3)
C(45)	40(4)	82(6)	31(4)	-20(4)	5(3)	-29(4)
C(46)	38(4)	95(6)	23(3)	-18(4)	5(3)	-27(4)
C(47)	33(3)	77(5)	18(3)	-11(3)	10(3)	-20(3)
C(48)	20(3)	78(5)	19(3)	-23(3)	6(2)	-6(3)
C(49)	69(6)	77(6)	57(5)	5(5)	-25(4)	-28(5)
C(50)	139(10)	106(8)	68(7)	24(6)	-40(7)	-71(7)

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^*U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	x	y	z	U(eq)
H(3A)	-1994	14850	21432	69
H(1B)	-360	9203	22241	42
H(4A)	-3435	9279	20599	42
H(7A)	-2467	8653	17453	54
H(8A)	-726	8343	16391	55
H(9A)	1061	8255	16859	52
H(10A)	1179	8337	18445	45
H(15A)	2697	7905	20071	57
H(16A)	4621	7546	20457	68
H(17A)	4909	8085	21801	68
H(18A)	3246	8897	22806	63
H(19A)	1322	9227	22459	51
H(21A)	-2742	10924	21917	44
H(25A)	-5314	8373	24252	56
H(26A)	-4440	6699	24064	70
H(27A)	-2681	6192	22999	66
H(28A)	-1875	7424	22122	52
H(31A)	-6176	12701	23814	56
H(34A)	-7784	13041	24645	69
H(35A)	-9665	13394	25547	78
H(36A)	-10450	12071	26164	79
H(37A)	-9356	10392	25973	80

H(38A)	-7467	10005	25070	68
H(40A)	-4850	12894	21299	57
H(41A)	-3956	14106	20510	64
H(44A)	-1948	14461	22849	55
H(45A)	-1721	13723	24452	58
H(46A)	-2550	12447	25209	60
H(47A)	-3626	11911	24378	52
H(50A)	-2292	16652	19419	148
H(50B)	-1332	15886	20141	148
H(50C)	-2449	16807	20519	148
H(52A)	-3494	15591	15390	137
H(52B)	-4665	15545	16114	137
H(52C)	-4030	14686	15438	137
H(53A)	-3236	13402	17700	118
H(53B)	-4542	14209	17477	118
H(53C)	-3662	14540	17962	118
H(52D)	-4149	14816	15381	95
H(52E)	-4974	15119	16354	95
H(52F)	-4377	13925	16238	95
H(53D)	-3514	15308	17734	112
H(53E)	-3316	14095	18077	112
H(53F)	-4572	14874	17710	112
H(55A)	1026	3681	22586	132

H(55B)	1419	4428	23058	132
H(55C)	2101	4092	22052	132
H(56A)	437	6342	20780	128
H(56B)	1735	5721	21153	128
H(56C)	743	6538	21754	128
H(55D)	497	3851	22797	148
H(55E)	317	4774	23356	148
H(55F)	1610	4213	22830	148
H(56D)	218	6763	21256	75
H(56E)	1581	6013	21098	75
H(56F)	1052	6365	22124	75

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3.5a**.

3.5.5 Supporting References

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CHAPTER 4 An Aza-Diels–Alder Route to AABBB-type Polybiquinolines

4.1 Abstract

Polyquinolines have attracted attention as functional materials due to their excellent combination of optical, electrical, chemical, thermal, and mechanical properties. However, only a handful of synthetic routes for the preparation of these polymers have been established to date. Here, we demonstrate the preparation of polyquinolines *via* an AA/BB-type aza-Diels–Alder polymerization reaction. This approach requires only commercial starting materials and two straightforward synthetic steps to furnish the desired products in high yield. Overall, our modular and general route may afford new opportunities for the rational design and preparation of quinoline-based materials.

4.2 Introduction

Polyquinolines have been studied as functional materials since the 1970s due to their excellent optical, electrical, chemical, thermal, and mechanical properties.^{1–36} These favorable features have made polyquinolines attractive in device applications, such as highly stable packaging for microelectronics^{6,7} and active layers for organic light emitting diodes.^{2–5} However, despite their proven utility, polyquinolines are currently prepared *via* only a handful of synthetic routes, including Suzuki couplings,^{8,9} the Sonogashira reaction,^{10,11} oxidative polymerizations,^{12,13} and the Friedländer synthesis.^{1,14–35} Moreover, our group has recently demonstrated that polyquinolines can be readily obtained from an AB-type aza-Diels–Alder (Povarov)^{37,38} polymerization reaction, albeit in moderate yield.³⁶ While effective, all of these entrenched methodologies possess somewhat limited versatility because they typically require difficult-to-synthesize starting materials, proceed in low overall yields, and/or do not provide ready access to certain backbone architectures or main chain substituents.³⁶ Thus, there exists a need for the development of novel synthetic approaches to polyquinoline-based materials.

Herein, we describe a facile aza-Diels–Alder (Povarov) reaction-based approach to polyquinolines. To validate our reaction conditions, we first synthesize and characterize a series of diimine starting materials and biquinoline model compounds. We in turn use these conditions and combine an AA-type diimine monomer with a commercially available BB-type diethynyl benzene monomer in an AA/BB-type polymerization reaction,^{39–41} producing a zigzag polyquinoline in high yield. Subsequently, we verify the identity of this polymer with nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC). We also obtain insight into the properties of our polyquinolines and biquinolines through ultraviolet visible (UV-vis) spectroscopy, fluorescence spectroscopy, cyclic voltammetry, and density functional theory calculations. Overall, our approach establishes a general, modular, and high yield route to quinoline-based functional materials for applications in organic electronics.

4.3 Results and Discussion

For our strategy, we drew inspiration from the Friedländer approach, which to date has served as the workhorse of polyquinoline synthesis.^{1,16–37} As an example, Figure 4.1A illustrates a retrosynthetic analysis of a typical AA/BB-type Friedländer polymerization, which entails the reaction of a bis(aminoketone) monomer with a bis(ketomethylene) monomer to furnish a linear polyquinoline. Here, we merged concepts from both this method and our previous studies of the Povarov reaction^{36,42–44} to design the strategy shown in Figure 4.1B. We envisioned that reacting a diimine monomer with a diethynyl monomer would produce a zigzag polyquinoline in an AA/BB-type aza-Diels–Alder polymerization. Thus, we set out to evaluate this alternative methodology.

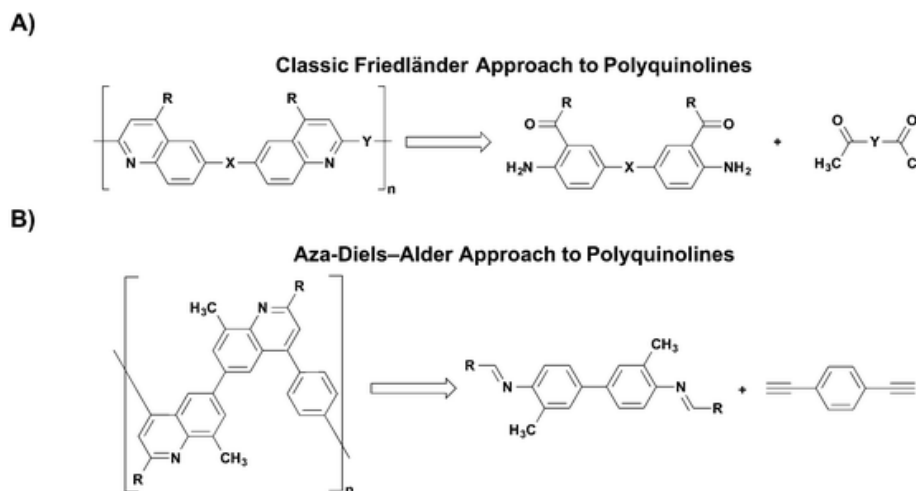
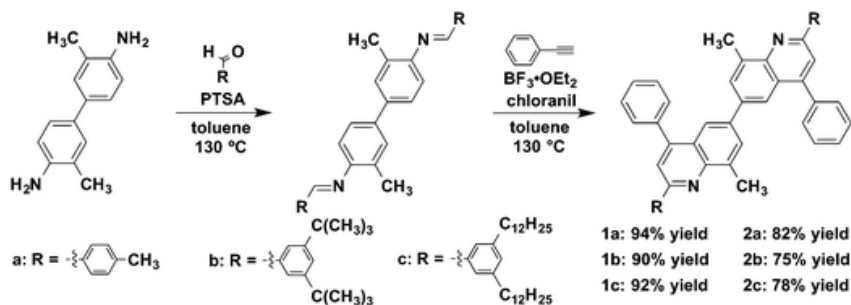


Figure 4.1. (A) An illustration of the synthesis of linear polyquinolines via the classic Friedländer approach. (B) An illustration of the synthesis of zigzag polyquinolines via an aza-Diels-Alder approach.

We began our studies by synthesizing model biquinoline compounds **4.2a–c** *via* the Povarov reaction, as illustrated in Scheme 1. First, we used established literature protocols to form bis(aldimines) **4.1a–c**.^{36,42–44} Next, we reacted **4.1a–c** with phenylacetylene in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as a Lewis acid mediator and chloranil⁴⁵ as an oxidant, furnishing biquinolines **4.2a–c**. Overall, our synthesis utilized mild conditions and commercial starting materials to produce regioisomerically pure products in excellent yield.



Scheme 4.1. Synthesis of imines **4.1a–c** and model biquinoline compounds **4.2a–4.2c**.

We characterized model compounds **4.2a–c** with standard techniques, including nuclear magnetic resonance (NMR) spectroscopy (Supporting Figures S4.1–S4.18). As an example, the aromatic region of the ^1H NMR spectrum for **4.2b** is illustrated in Figure 4.2A (Supporting Figure S4.9

for the full integrated spectrum). The aromatic region featured two apparent doublets at 8.15 and 7.99 ppm; a broad singlet at 7.94 ppm; a sharp singlet at 7.88 ppm; and a singlet, which presumably overlapped with a multiplet, at 7.60 ppm. We assigned the doublet at 8.15 ppm to the protons at the *ortho* positions of the quinolines' *tert*-butyl-substituted phenyl groups (**H_a**) and the doublet at 7.99 ppm to the proton at position 7 of the quinoline cores (**H_b**). We in turn assigned the broad singlet at 7.94 ppm to the proton at position 5 of the quinoline cores (**H_c**) and the sharp singlet at 7.88 ppm to position 2 of the quinoline cores (**H_d**). Finally, we attributed the complex signal at 7.60 ppm to the proton at the *para* positions of the quinolines' *tert*-butyl-substituted phenyls (**H_e**), as well as to an overlapping multiplet from the quinolines' unsubstituted pendant phenyl protons. Our proposed assignments for all of the proton resonances were validated by 2D correlation spectroscopy (COSY) experiments (Supporting Figure S4.1), which provided further confirmation of our compound's chemical structure.⁴⁶

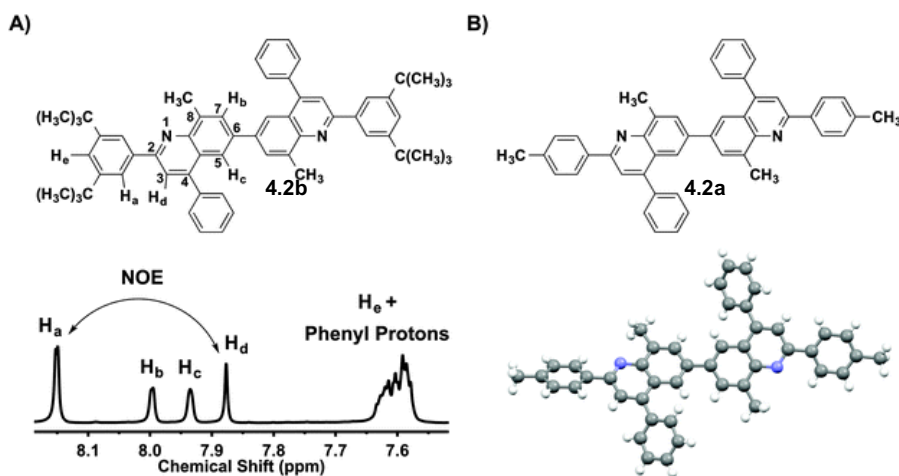


Figure 4.2. (A) The chemical structure (top) and partial ¹H NMR spectrum (bottom) of compound **4.2b**. The proton assignments for **4.2b** were verified by COSY experiments, and the regiochemistry of **4.2b** was determined from NOE experiments. (B) The chemical structure (top) and the corresponding X-ray crystal structure (bottom) of compound **4.2a**. The hydrogen, carbon, and nitrogen atoms are colored white, gray, and blue, respectively.

To gain insight into the regioisomeric identity of our products, we sought to observe the Nuclear Overhauser Effect (NOE) (Figure 4.2A and Supplementary Figure S4.2).⁴⁶ For these experiments, we again focused on compound **4.2b** because its spectrum was straightforward to interpret. We observed a

clear enhancement in the NOE signal between proton **H_a** of the quinoline systems and proton **H_a** of the pendant *tert*-butyl-substituted phenyl groups, confirming their proximity (Figure 4.2A). This observation suggested that our reaction conditions produced the desired regioisomer, in agreement with previous findings for analogous quinoline and benzoquinoline systems.^{36,42–44}

We confirmed the connectivity and absolute configurations of our compounds with X-ray crystallography (Figure 4.2B). For these experiments, we focused on compound **4.2a** because it readily produced crystals of sufficient quality for X-ray diffraction analysis. The crystal structure revealed that the quinolines featured pendant methyl-substituted phenyl rings at the 2 position and pendant unsubstituted phenyl rings at the 4 position (Figure 4.2B), validating the NOE analysis. Moreover, we found that the connected aromatic systems (quinolines and phenyls) were all twisted out of planarity relative to one another (Figure 4.2B), presumably due to steric interactions. Together with the COSY experiments, the crystal structure definitively confirmed the identity of **4.2a**, and thus, the regioselectivity of our reaction conditions.

Having evaluated the regiospecificity of our strategy, we proceeded to prepare polyquinolines, as illustrated in Scheme 4.2. Here, we reacted diimine **4.1c** with diethynyl benzene under the conditions developed for the synthesis of **4.2a–c**. The progress of this polymerization was monitored by size exclusion chromatography with a refractive index detector (SEC-RI), as illustrated by the representative chromatograms in Figure 4.3A. Initially, a chromatogram of the starting materials showed a single sharp peak, corresponding to monomer **4.1c** (Figure 4.3A, red trace). Subsequently, after 2 h, monomer consumption was accompanied by the appearance of low molecular weight oligomers (Figure 4.3A, orange trace). In turn, after 4h, the monomer was nearly completely consumed, leading to the appearance of additional higher molecular weight species (Figure 4.3A, green trace). Furthermore, after 8 h, the chromatogram showed only a slight enhancement in the size of the polymeric product (Figure

precipitation; the polyquinoline possessed a weight average molecular weight (M_w) of 33.1 kg mol⁻¹, a number average molecular weight (M_n) of 14.5 kg mol⁻¹, and a polydispersity index (PDI) of 2.28. The polydispersity of our polymer supported the notion of a step-growth mechanism and again matched literature precedent for Diels–Alder polymerizations.^{41–45}

We further analyzed polyquinoline **4.3c** via ¹H NMR spectroscopy, with model biquinoline **4.2c** serving as a useful reference (Figure 4.4 and Supplementary Figure S4.17, S4.19). We first noted that the ¹H NMR spectra of both **4.3c** and **4.2c** featured resonances between 7.0 and 8.5 ppm in the aromatic region, which could be associated with the quinoline and phenyl moieties, as well as resonances between 0.0 and 3.0 ppm in the alkyl region, which could be associated with the methyl and dodecyl functionalities (Figure 4.4). Although the observed signals were in similar positions for both the polymer and the model compound, the spectrum of **4.3c** featured significant broadening relative to the spectrum of **4.2c**, as expected for a polymeric material (Figure 4.4). Moreover, the integration ratio between the aromatic and alkyl regions of **4.3c** was ~1 : 6, matching predictions based on the structure of the model biquinoline and the repeat unit of the polyquinoline (Supplementary Figure S4.19). Overall, our analysis confirmed the formation of an extended macromolecule comprised of linked biquinoline and phenyl subunits.

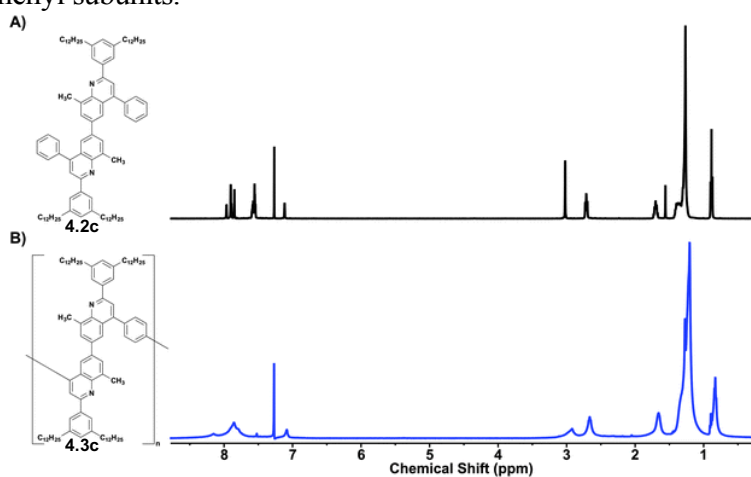


Figure 4.4. (A) The chemical structure (left) and ¹H NMR spectrum (right) of model compound **4.2c**. (B) The chemical structure (left) and ¹H NMR spectrum (right) of polymer **4.3c**. Note that the ¹H NMR spectrum of the polymer is generally broadened with respect to the spectrum of the model compound.

We in turn investigated the electronic properties of polyquinoline **4.3c** and model biquinoline **4.2c** with UV-vis spectroscopy (Figure 4.5). The spectrum obtained for **4.3c** featured peaks at 291 nm and 363 nm, as well as an absorption onset of 435 nm (Figure 4.5, solid blue trace). In comparison, the spectrum obtained for **4.2c** featured peaks at 288 nm and 363 nm with extinction coefficients of $\epsilon_{288} = 8.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and $\epsilon_{363} = 3.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively, as well as an absorption onset of 425 nm (Figure 4.5, solid black trace). In general, relative to the spectrum of the model biquinoline, the spectrum of the polyquinoline was broadened and tailed into the red. Overall, our observations were consistent with the formation of a π -conjugated macromolecule.

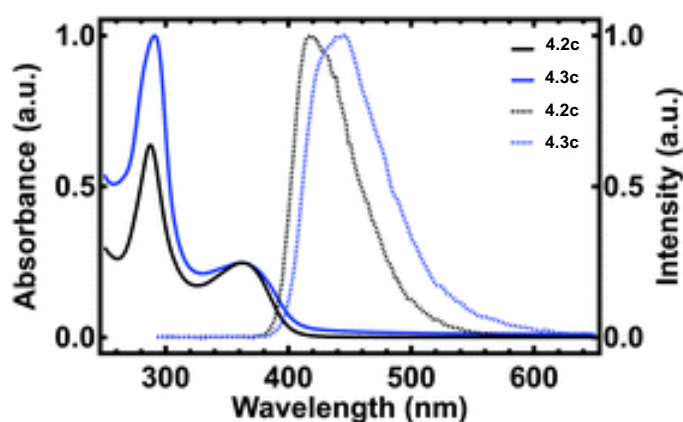


Figure 4.5. The normalized UV-vis absorbance spectra obtained for model compound **4.2c** (solid black trace) and polymer **4.3c** (solid blue trace), and the normalized fluorescence emission spectra obtained for model compound **4.2c** (dashed black trace) and polymer **4.3c** (dashed blue trace).

We next interrogated the photophysical properties of polyquinoline **4.3c** and model biquinoline **4.2c** with fluorescence spectroscopy (Figure 4.5). The emission spectrum obtained for **4.3c** featured a peak at 446 nm (Figure 4.5, dashed blue trace), while the emission spectrum obtained for **4.2c** featured a peak at 419 nm (Figure 4.5, dashed black trace). The polyquinoline therefore only possessed a moderate increase in its Stokes shift when compared to the biquinoline, as might be expected from the polymer's zigzag architecture. Furthermore, the emission maxima found for both **4.3c** and **4.2c** were within the range of values ($\sim 400 \text{ nm}$ to $\sim 600 \text{ nm}$) reported for various

quinoline-based materials.^{3,4,8–12,16,17,28–35} Together, these observations further confirmed the formation of a macromolecule containing quinoline subunits.

We subsequently studied the electrochemical properties of thin films from both polyquinoline **4.3c** and model biquinoline **4.2c** with cyclic voltammetry (Figure 4.6). At reductive potentials, the voltammogram obtained for **4.3c** featured a quasi-reversible redox couple with a midpoint potential of -1.83 V vs. Ag/AgCl (corresponding to an energy of ~ -2.6 eV) and an irreversible cathodic wave with a peak potential of -2.13 V vs. Ag/AgCl (Figure 4.6, blue trace). The voltammogram obtained for **4.2c** featured one quasi-reversible redox couple with a midpoint potential of -1.81 V vs. Ag/AgCl (corresponding to an energy of ~ -2.6 eV) and another quasi-reversible redox couple with a midpoint potential -2.04 V vs. Ag/AgCl (Figure 4.6, black trace). Moreover, within our accessible potential window, the voltammograms obtained for both the polyquinoline and biquinoline did not display any couples at oxidative potentials. Overall, the electrochemical measurements demonstrated that the redox properties of our polymers and model compounds were quite similar to those previously reported for other polyquinolines and quinoline derivatives.^{2,4,9–12,16,17,30–35}

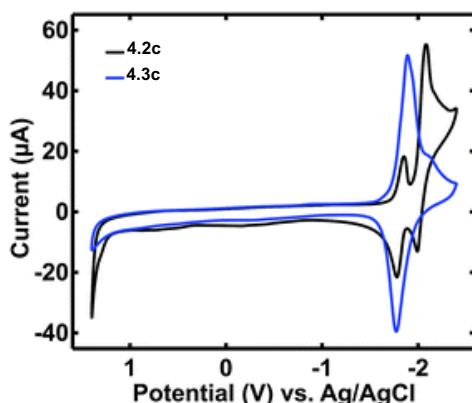


Figure 4.6. The cyclic voltammograms obtained for thin films of model compound **4.2c** (black trace) and polymer **4.3c** (blue trace).

To gain additional insight into the electronic properties of our materials and interpret the electrochemical findings, we performed density functional theory (DFT) calculations for model biquinoline **4.2c**. From the calculations, we obtained the equilibrium molecular geometry of **4.2c**, as well as the shapes and energies of its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (Figure 4.7). Here, we found a LUMO energy of -2.0 eV

(Figure 4.7B), allowing us to assign the LUMO to the redox couple observed at a potential of -1.81 V vs. Ag/AgCl (and an energy of -2.6 eV). These experimental and theoretical LUMO energies were both within the range of values (~ -2 eV to ~ -3 eV) reported for various quinoline-based materials.^{2,4,9–12,16,17,30–35} Moreover, we found a HOMO energy of -5.6 eV (Figure 4.7B). Although the HOMO could not be readily assigned to a redox couple within our potential window, the calculated energy was again within the range (~ -5 eV to ~ -6 eV) reported for various quinoline-based materials.^{2,4,9–12,16,17,30–35} Together with the validated functionality of various polyquinolines and quinoline derivatives, our analysis suggested that materials based on the biquinoline motif may hold promise as electron-transporting organic semiconductors, which remain relatively rare.^{2,5,49–52}

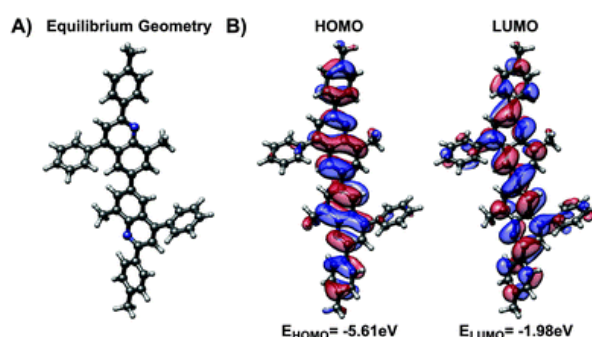


Figure 4.7. (A) The energy minimized equilibrium geometry for model compound **4.2a**, as obtained from DFT calculations. (B) The shapes and energies of the HOMO (left) and LUMO (right) for **4.2a**.

4.4 Conclusion

In summary, we have designed and validated a facile method for the preparation of zigzag polyquinolines *via* an AA/BB-type aza-Diels–Alder polymerization reaction. The resulting polymers were characterized *via* a combination of chromatographic, spectroscopic, electrochemical, and computational techniques (with biquinoline model compounds serving as comparative standards when appropriate). Our experiments confirmed the identities of the polymers and indicated that their properties were analogous to those of other quinoline-based materials.

Notably, the reported strategy appears to be advantageous from a synthetic perspective. First, the general methodology leverages straightforward and readily accessible chemistry, *i.e.* imine formation and the Povarov reaction. Second, the procedure requires inexpensive commercially-available starting materials, only two synthetic steps, and mild conditions. Third, the polymeric products appear to require

minimal purification, outside of a precautionary rearomatization and precipitation step. Finally, the entire process proceeds in an excellent overall yield of ~87%. Therefore, the reported approach may prove valuable for a broad range of chemists and materials scientists.

The described strategy is also favorable from a materials design perspective. Indeed, although our aza-Diels–Alder polymerization reaction may not readily furnish linear polyquinolines identical to ones obtained *via* the Friedlander approach, it can, in principle, provide access to a diverse set of zigzag polyquinolines containing 4,6-linked quinoline subunits. For example, a wide range of substituted bis(aldimine) monomers can be prepared from commercially-available benzaldehyde derivatives, enabling the installation of nearly arbitrary substituents on the periphery of our polymers. Moreover, any diethynyl-substituted molecule can serve as the monomer, making it possible to modify the backbone of our polymers. Given its intrinsic modularity, our approach may present new opportunities for the preparation of diverse quinoline-based organic electronic materials with rationally engineered and customizable properties.

4.5 Supporting Information

4.5.1. General Information and Procedures

A. Materials. All chemicals were purchased from Sigma Aldrich or Acros Organics. The solvents were purchased from Fisher Scientific and used as received, unless otherwise noted. The toluene was dried with 3 Å molecular sieves and stored under Argon. The glassware was oven dried at 150 °C. The reactions were performed under dry argon unless otherwise noted.

B. Compound Purification Procedures. Flash chromatography was performed using a CombiFlash Rf200 purification system (Teledyne Isco, Inc.) according to the manufacturer's recommended protocols. When required, the silica gel columns/cartridges were flushed with 1/9 triethylamine/hexanes to deactivate the silica gel, followed by hexanes to remove excess triethylamine. Additional purification-relevant information and protocols are noted below as appropriate.

C. Reaction Product Characterization Procedures. The intermediates and products were characterized with a combination of ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, ^1H - ^1H correlation spectroscopy (COSY), ^1H nuclear Overhauser effect (NOE) spectroscopy, mass spectrometry, elemental analysis, ultraviolet-visible (UV-vis) spectroscopy, and/or fluorescence spectroscopy. The ^1H NMR, ^{13}C NMR, ^1H - ^1H COSY, and ^1H NOE spectra were obtained on either a Bruker AVANCE400 instrument, a Bruker DRX500 instrument, a Bruker DRX500 instrument outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes), or an AVANCE600 instrument. The chemical shifts were reported in ppm for both ^1H and ^{13}C NMR. The chemical shifts for the NMR data were referenced as follows: for samples in CDCl_3 , the ^1H NMR was referenced to tetramethylsilane (TMS) at 0.00 or the residual CHCl_3 peak at 7.26 ppm, and the ^{13}C NMR was referenced to the residual CHCl_3 peak at 77.16 ppm. For samples in C_6D_6 , the ^1H NMR

was referenced to the residual C₆D₅H peak at 7.16 ppm, and the ¹³C NMR was referenced to the residual C₆D₅H at 128.06 ppm. The data were labeled with the chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet), coupling constants in Hertz, and integration values. Accurate mass measurements were obtained *via* electrospray ionization (ESI) high resolution mass spectrometry (HRMS) at the University of California, Irvine Mass Spectrometry Facility on a Waters LCT Premier time-of-flight instrument. Accurate mass measurements were also obtained *via* chemical ionization (CI) and electron ionization (EI) HRMS at the University of California, Irvine Mass Spectrometry Facility on a Waters GCT Premier time-of-flight instrument. MALDI-TOF mass spectra were recorded on an AB Sciex TOF/TOF 5800 series mass spectrometer using a 349 nm Nd:YAG laser and dithranol as the matrix. The UV-Vis spectroscopy measurements were performed on an Agilent Cary 100 Series Spectrophotometer, and the fluorescence spectroscopy measurements were performed on a Cary Eclipse Spectrophotometer.

D. Polymer Characterization and Analysis Procedures. The crude and purified polymers were analyzed *via* size exclusion chromatography with a refractive index detector (SEC-RI). The SEC-RI measurement was performed in benzene using an Agilent Technologies 1260 Infinity Series separations module equipped with two Agilent ResiPore columns connected in series (7.5 mm x 300 mm, 3 μm particle size). The separations module was connected to Agilent 1260 infinity dual angle light scattering, refractive index, and viscosity detectors in series. The flow rate was ~ 1.0 mL/min with an injection volume of ~ 25 – 100 μL and a sample concentration of ~ 1.0 – 2.5 mg/mL. Molecular weights (M_n and M_w) were estimated from a calibration curve by using polystyrene standards (EasiVial PS-H, Agilent).

E. Electrochemical Measurements. Cyclic voltammetry experiments were performed with a CHI832C electrochemical analyzer in an oxygen free dimethylformamide solution supplemented with 0.1 M tetrabutylammonium tetrafluoroborate (TbABF₄). A glassy carbon electrode (BASi) served as the working electrode, a Pt wire (CH Instruments, Inc.) served as the counter electrode, and an Ag/AgCl electrode (Warner Instruments) served as the reference. For the experiments, thin films of the model compound or polymer were dropcast onto a glassy carbon electrode and allowed to dry in ambient prior to measurements.

4.5.2. Detailed Synthetic Protocols.

A. (*N⁴E,N^{4'}E*)-3,3'-dimethyl-*N⁴,N^{4'}*-bis(4-methylbenzylidene)-[1,1'-biphenyl]-4,4'-diamine (4.1a). Orthotolidine (2.12 g, 9.98 mmol), 4-methylbenzaldehyde (3.59 g, 29.9 mmol), 3 Å molecular sieves (2.0 g), and 48 mL of toluene were added to a 75 mL pressure vessel. The pressure vessel was sealed and brought to 130 °C in an oil bath. After 24 hours, the mixture was cooled to room temperature and filtered through Celite. The reaction mixture was then washed with a saturated aqueous sodium bicarbonate solution (15 mL × 3). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. Subsequently, the crude material was boiled in hexanes and filtered to yield a dark yellow solid (3.90 g, 94%): ¹H NMR (600 MHz, C₆D₆) δ = 8.25 (s, 2H), 7.85 (d, *J* = 7.9 Hz, 4H), 7.58 (s, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 7.7 Hz, 4H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.56 (s, 6H), 2.08 (s, 6H); ¹³C NMR (151 MHz, C₆D₆) δ = 158.9, 150.9, 141.5, 138.9, 134.9, 133.0, 129.7, 129.3, 125.7, 118.5, 110.4, 21.5, 18.4. HRMS (ESI) *m/z* calcd. for C₃₀H₂₈N₂Na [M+Na]⁺ 439.2150, found 439.2137.

B. (*N⁴E,N^{4'}E*)-*N⁴,N^{4'}*-bis(3,5-di-*tert*-butylbenzylidene)-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (4.1b). Orthotolidine (0.38 g, 1.78 mmol), 3,5-di-*tert*-butylbenzaldehyde (1.0 g, 4.58 mmol), 3 Å molecular sieves (2.0 g), and 18 mL of toluene were added to a 75 mL pressure vessel. The vessel was sealed and brought to 130 °C in an oil bath. After 24 hours, the mixture was cooled to room temperature and filtered through Celite. The reaction mixture was then washed with a saturated aqueous sodium bicarbonate solution (15 mL × 3). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography using deactivated silica gel (9/1 hexanes/ethyl acetate). Subsequently, the crude

material was washed with ethanol to yield a yellow solid (1.04 g, 90%): ^1H NMR (500 MHz, CDCl_3) δ = 8.43 (s, 2H), 7.81 (d, J = 7.8 Hz, 4H), 7.59 (s, 2H), 7.50 (s, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 2.45 (s, 6H), 1.40 (s, 36H); ^{13}C NMR (126 MHz, CDCl_3) δ = 160.5, 151.5, 150.6, 138.2, 136.1, 132.4, 128.8, 125.9, 125.2, 123.3, 118.3, 35.1, 31.6, 18.2. HRMS (ESI) m/z calcd. for $\text{C}_{44}\text{H}_{56}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 635.4341, found 635.4339.

C. 3,5-di(dodec-1-yn-1-yl)benzaldehyde (SI-4.1). 3,5-Dibromobenzaldehyde (10.0 g, 37.9 mmol), copper iodide (0.71 g, 3.73 mmol) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2.65 g, 3.78 mmol) were dissolved in a degassed 1:1 mixture of diisopropyl amine and toluene (200 mL). 1-Dodecyne (18.9 g, 114 mmol) was added to the solution, and the mixture was then heated to 100 °C. After 16 hours, the reaction was cooled, poured into methylene chloride (100 mL), and sequentially washed with water (50 mL) and brine (50 mL). The organics were dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The resulting crude solid was purified by flash chromatography (hexane) to yield a colorless oil (12.1 g, 73%): ^1H NMR (600 MHz, CDCl_3) δ 9.92 (s, 1H), 7.75 (s, 2H), 7.62 (s, 1H), 2.40 (t, J = 7.1 Hz, 4H), 1.60 (quint, J = 7.2 Hz, 4H), 1.44 (quint, J = 7.0 Hz, 4H), 1.27 (m, 24H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ 191.3, 139.9, 136.51, 131.49, 125.6, 92.8, 78.9, 32.0, 29.74, 29.67, 29.5, 29.3, 29.0, 28.7, 22.8, 19.5, 14.3. HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{50}\text{ON}$ $[\text{M}+\text{NH}_4]^+$ 452.3893, found 452.3887.

D. 3,5-didodecylbenzaldehyde (SI-4.2). Palladium on activated carbon (10 wt. %, 0.22 g, 0.21 mmol), compound **SI-4.1** (6.0 g, 13.8 mmol), and ethyl acetate (138 mL) were combined in a reaction vessel, which was then charged with hydrogen under constant stirring. After the starting material was consumed (as monitored by ^1H NMR), the reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo*. The crude product was purified by flash chromatography (hexanes) to yield a white solid (5.55 g, 91%): ^1H NMR (600 MHz, CDCl_3) δ

=9.97 (s, 1H), 7.51 (s, 2H), 7.26 (s, 1H), 2.69 – 2.61 (m, 4H), 1.63 (quint, $J = 7.5$ Hz, 4H), 1.38 – 1.26 (m, 36H), 0.88 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (151 MHz, CDCl_3) δ = 193.0, 143.9, 136.8, 135.2, 127.3, 35.8, 32.1, 31.5, 29.83, 29.80, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3. HRMS (ESI) m/z calcd. for $\text{C}_{31}\text{H}_{58}\text{ON}$ $[\text{M}+\text{NH}_4]^+$ 460.4518, found 460.4510.

E. ($N^4E,N^4'E$)- N^4,N^4' -bis(3,5-didodecylbenzylidene)-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (4.1c). Orthotolidine (1.52 g, 7.16 mmol) and 3,5-didodecylbenzaldehyde (**SI-4.2**, 7.00 g, 15.8 mmol) were dissolved in 72 mL of ethanol in a round bottom flask equipped with a reflux condenser. The flask was purged with argon and then brought to 130 °C in an oil bath. After 24 hours, the mixture was cooled to room temperature, with the pure product precipitating from the solution (as an oil). Subsequently, the solution was decanted from the precipitated pure product, and the solvent was removed *in vacuo*. The second crude oil aliquot remaining from this evaporation process was precipitated with ethanol. The products from the first and second precipitations were combined to yield an orange oil (6.99 g, 92%): ^1H NMR (500 MHz, CDCl_3) δ = 8.38 (s, 2H), 7.58 (s, 4H), 7.50 (s, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.14 (s, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 2.66 (t, $J = 7.7$ Hz, 8H), 2.45 (s, 6H), 1.67 (quint, $J = 7.4$ Hz, 8H), 1.42 – 1.17 (m, 72H), 0.89 (t, $J = 6.9$ Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ = 160.1, 150.6, 143.6, 136.6, 132.4, 129.9, 128.9, 126.4, 125.2, 118.3, 35.9, 32.1, 31.7, 29.9, 29.84, 29.82, 29.8, 29.7, 29.6, 29.5, 22.9, 18.2, 14.3. MALDI m/z calcd. for $\text{C}_{76}\text{H}_{121}\text{N}_2$ $[\text{M}+\text{H}]^+$ 1062.0, found 1061.8.

F. 8,8'-dimethyl-4,4'-diphenyl-2,2'-di-*p*-tolyl-6,6'-biquinoline (4.2a). Diimine **4.1a** (2.07 g, 4.97 mmol), phenylacetylene (1.52 g, 1.63 mL, 14.9 mmol), chloranil (1.34 g, 5.45 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (0.78 g, 0.70 mL, 5.50 mmol), and 57 mL of toluene were added to a 75 mL pressure vessel. The pressure vessel was sealed and brought to 130 °C in an oil bath. After 24 hours, the mixture was cooled to room temperature and filtered through a cotton plug. The reaction mixture

was then washed with saturated aqueous sodium bicarbonate (20 mL $\times$ 3). Subsequently, the organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The resulting material was boiled in hexanes and filtered to yield a dark yellow solid (2.52 g, 82%): ^1H NMR (500 MHz, CDCl_3) δ = 8.21 (d, J = 7.7 Hz, 4H), 7.96 (s, 2H), 7.86 (d, J = 16.9 Hz, 4H), 7.57 – 7.54 (m, 10H), 7.34 (d, J = 7.6 Hz, 4H), 3.00 (s, 6H), 2.45 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.1, 149.4, 147.3, 139.5, 139.0, 138.5, 138.0, 137.1, 129.8, 129.7, 129.2, 128.7, 128.4, 127.5, 125.9, 121.9, 119.0, 21.5, 18.8. HRMS (ESI) m/z calcd. for $\text{C}_{46}\text{H}_{36}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 639.2776, found 639.2799.

G. 2,2'-bis(3,5-di-*tert*-butylphenyl)-8,8'-dimethyl-4,4'-diphenyl-6,6'-biquinoline (4.2b).

Diimine **4.1b** (1.03 g, 1.68 mmol), phenylacetylene (0.94 g, 1.01 mL, 9.20 mmol), chloranil (0.49 g, 2.00 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (0.78 g, 0.70 mL, 5.50 mmol), and 37 mL of toluene were added to a 75 mL pressure vessel. The pressure vessel was sealed and brought to 130 $^\circ\text{C}$ in an oil bath. After 24 hours, the mixture was cooled to room temperature and filtered through a cotton plug. The reaction mixture was then washed with saturated aqueous sodium bicarbonate (15 mL $\times$ 3). Subsequently, the organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (9/1 hexanes/ethyl acetate). The resulting material was washed with ethanol to yield a pale yellow solid (1.03 g, 75%): ^1H NMR (500 MHz, CDCl_3) δ = 8.15 (s, 4H), 8.00 (s, 2H), 7.94 (s, 2H), 7.88 (s, 2H), 7.64 – 7.59 (m, 12H), 3.05 (s, 6H), 1.47 (s, 36H); ^{13}C NMR (126 MHz, CDCl_3) δ 156.4, 151.3, 149.3, 147.3, 139.4, 139.1, 138.5, 138.1, 129.8, 129.3, 128.7, 128.4, 125.9, 123.8, 122.2, 121.9, 119.6, 35.2, 31.7, 18.7. HRMS (ESI) m/z calcd. for $\text{C}_{60}\text{H}_{64}\text{N}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 835.4341, found 835.4339.

H. 2,2'-bis(3,5-didodecylphenyl)-8,8'-dimethyl-4,4'-diphenyl-6,6'-biquinoline (4.2c). Diimine **4.1c** (1.0 g, 0.94 mmol), phenylacetylene (0.69 g, 0.74 mL, 6.78 mmol), chloranil (0.61 g, 2.48

mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.35 g, 0.31 mL, 2.47 mmol), and 25 mL of toluene were added to a 75 mL pressure vessel. The pressure vessel was sealed and brought to 130 °C in an oil bath. After 24 hours, the mixture was cooled to room temperature and filtered through a cotton plug. The reaction mixture was then washed with saturated aqueous sodium bicarbonate (15 mL $\times$ 3). Subsequently, the organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (9/1 hexanes/ethyl acetate). Subsequently, the crude material was washed with ethanol to yield a yellow solid (0.93 g, 78%): ^1H NMR (500 MHz, CDCl_3) δ = 7.96 (d, J = 1.5 Hz, 2H), 7.90 (s, 4H), 7.89 (s, 2H), 7.84 (s, 2H), 7.56 (s, 10H), 7.11 (s, 2H), 3.01 (s, 6H), 2.71 (t, 8H), 1.69 (quint, J = 7.5 Hz, 8H), 1.26 (s, 72H), 0.88 (t, J = 7.0 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.8, 149.3, 147.3, 143.5, 139.4, 139.1, 138.5, 138.1, 129.9, 129.8, 129.2, 128.7, 128.3, 125.9, 125.2, 121.9, 119.6, 36.3, 32.1, 31.8, 29.9, 29.8, 29.7, 29.6, 29.5, 22.9, 18.8, 14.3. MALDI m/z calcd. for $\text{C}_{92}\text{H}_{129}\text{N}_2$ $[\text{M}+\text{H}]^+$ 1262.0, found 1262.1.

I. Poly[2,2'-bis(3,5-didodecylphenyl)-8,8'-dimethyl-6,6'-biquinoline-4-4'-(4-phenyl)-diyl] (4.3). Diimine **4.1c** (0.4002 g, 3.77 mmol), 1,4-diethynylbenzene (0.0477g, 0.377 mmol), chloranil (0.22 g, 0.89 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.12 g, 0.11 mL, 0.85 mmol), and 20 mL of toluene were added to a 75 mL pressure vessel. The pressure vessel was sealed and brought to 150 °C in an oil bath. After 72 hours, the mixture was cooled to room temperature and filtered through a cotton plug. The reaction mixture was then washed with saturated aqueous sodium bicarbonate (10 mL $\times$ 3). Subsequently, the organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The solids were dissolved in 10 mL toluene and 2,3-dichloro-5,6-cyano-1,4-benzoquinone (0.11 g, 0.48 mmol) was added to the mixture. After 24 hours of stirring at room temperature, the mixture was diluted with CH_2Cl_2 , and the reaction was then quenched with saturated aqueous sodium bicarbonate (10 mL). The organics were washed with saturated aqueous sodium

bicarbonate (4 mL $\times$ 3), and poured through a cotton plug. The solvent was subsequently removed *in vacuo*. The crude material was precipitated from ethanol to yield a brown solid (0.423 g, 95%): ^1H NMR (500 MHz, CDCl_3) δ = 8.32 – 8.03 (3H), 8.00 – 7.62 (7H), 7.58 – 7.47 (1H), 7.17 – 6.99 (1H), 3.22 – 2.80 (5H), 2.78 – 2.48 (5H), 1.94 – 1.52 (8H), 1.50 – 1.19 (46H), 0.96 – 0.82 (9H); ^{13}C NMR (126 MHz, CDCl_3) δ 143.4, 125.1, 36.3, 32.0, 31.8, 29.84, 29.81, 29.7, 29.6, 29.51, 29.50, 22.8, 14.3.

4.5.3. Compiled Spectroscopic Data

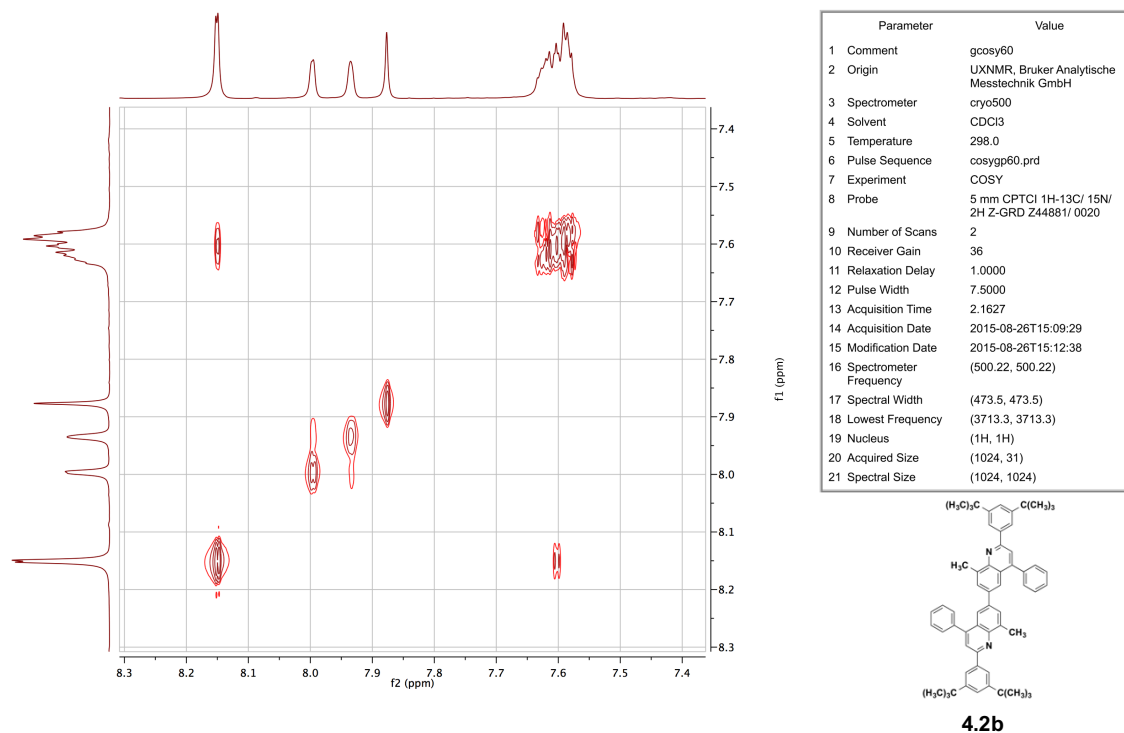


Figure S4.1. The COSY spectrum obtained for compound **4.2b**. This spectrum was used to assign the aromatic protons.

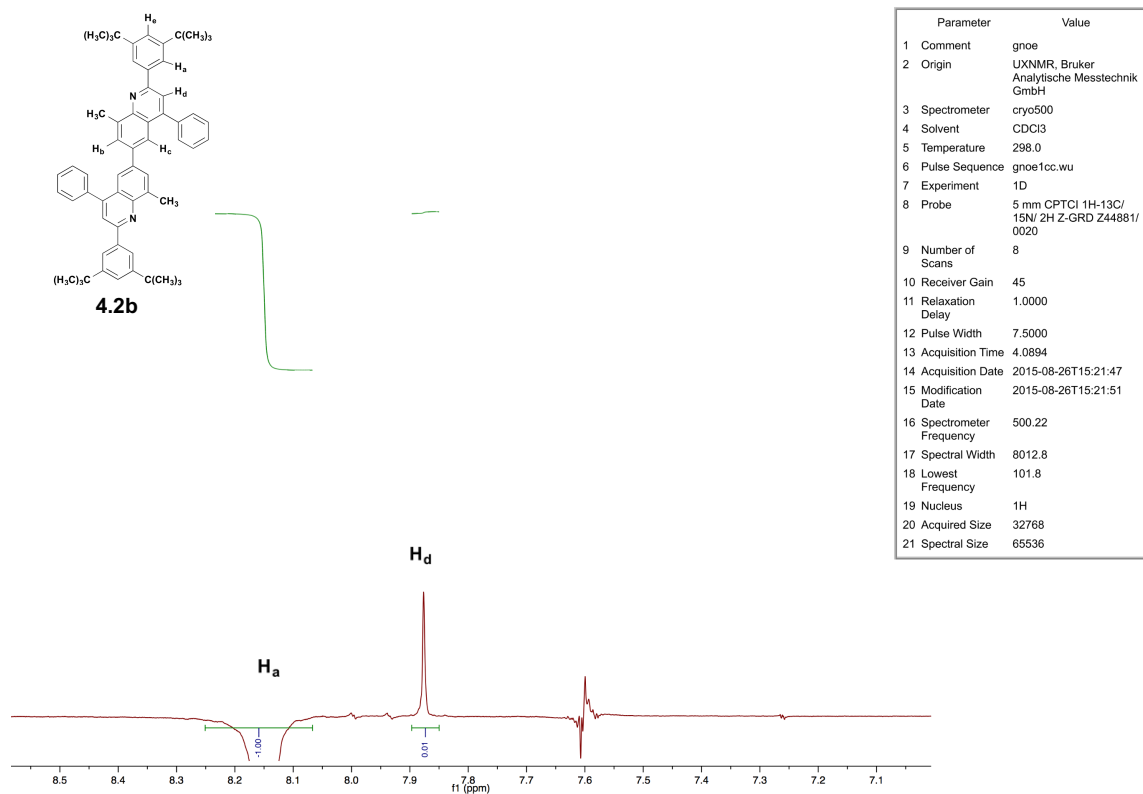


Figure S4.2. The NOE spectrum obtained for compound **4.2b**, where **H_a** was irradiated.

Irradiation of **H_a** leads to an enhancement of the NOE signal between **H_a** and **H_d**.

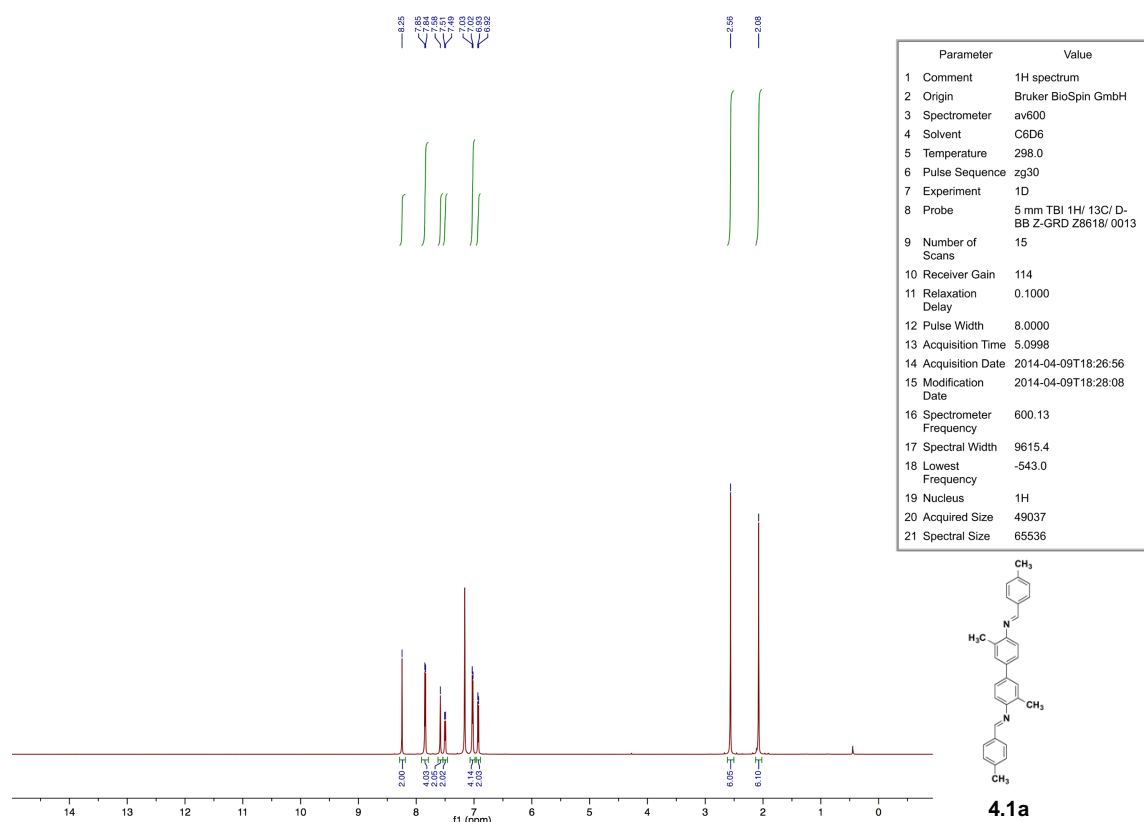


Figure S4.3. The ¹H NMR spectrum obtained for **4.1a**.

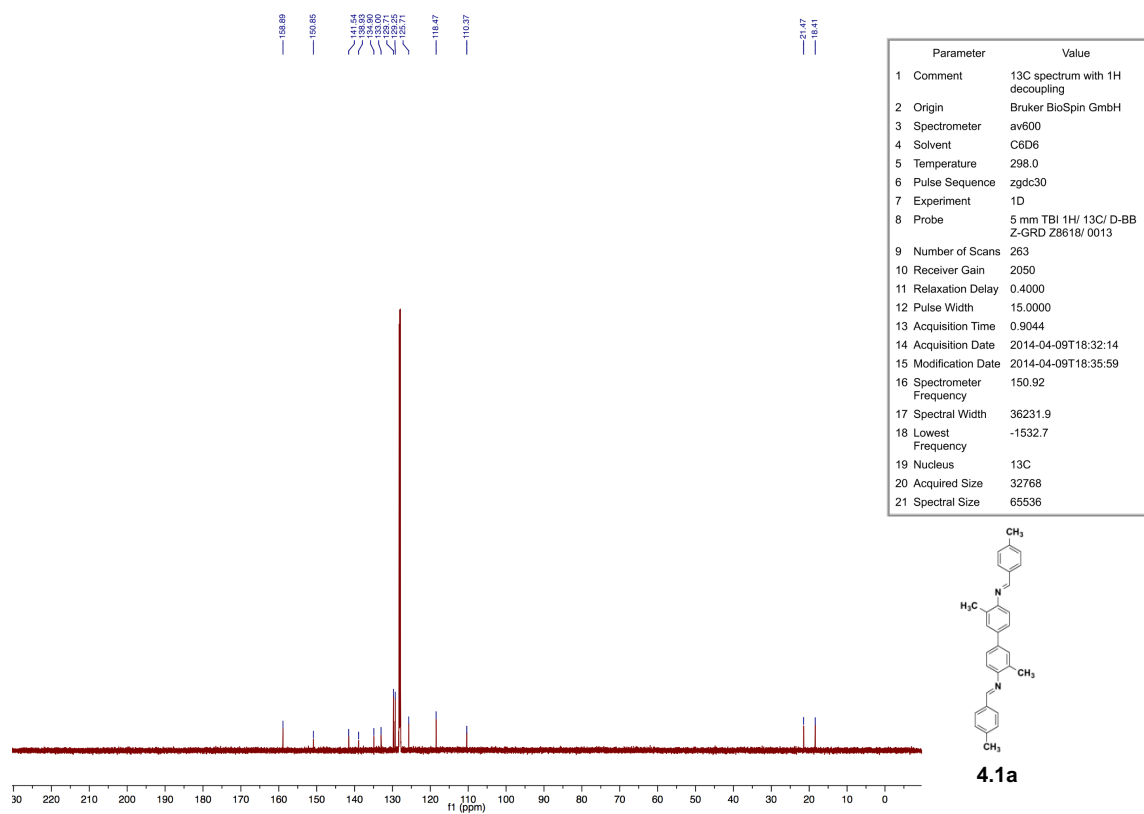


Figure S4.4. The ¹³C NMR spectrum obtained for **4.1a**.

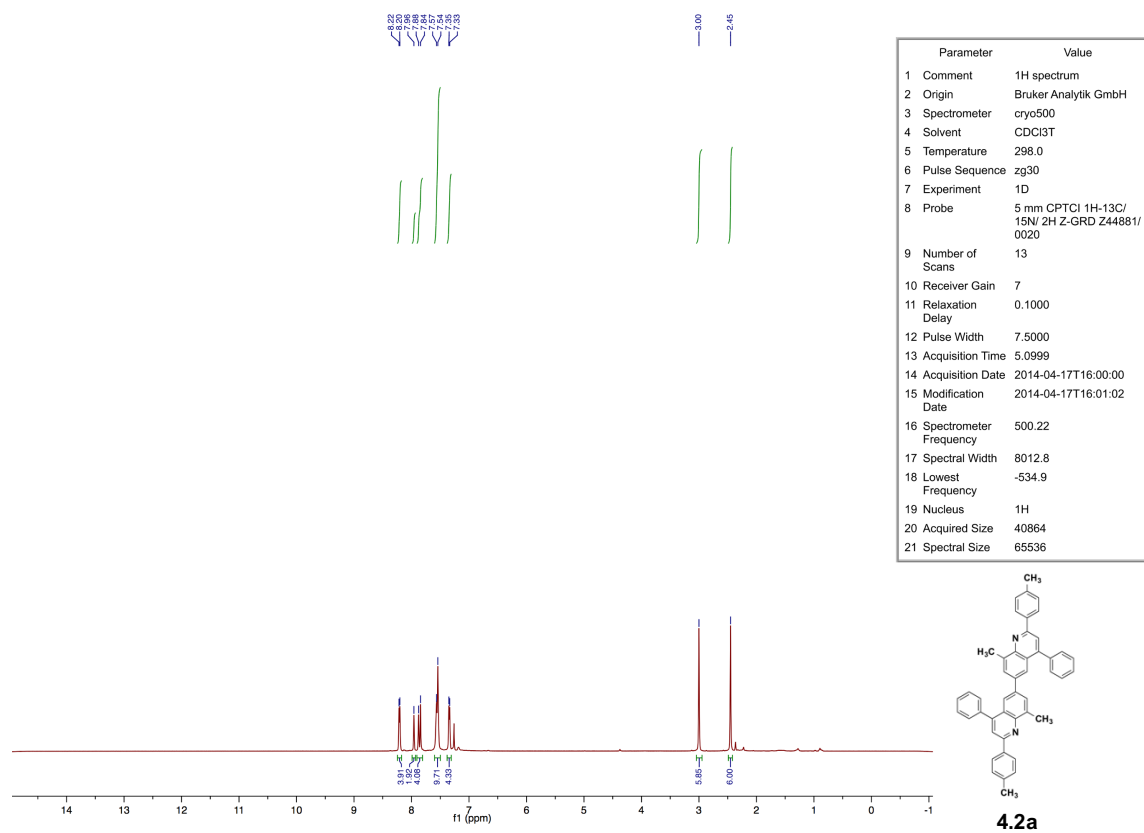


Figure S4.5. The ^1H NMR spectrum obtained for **4.2a**.

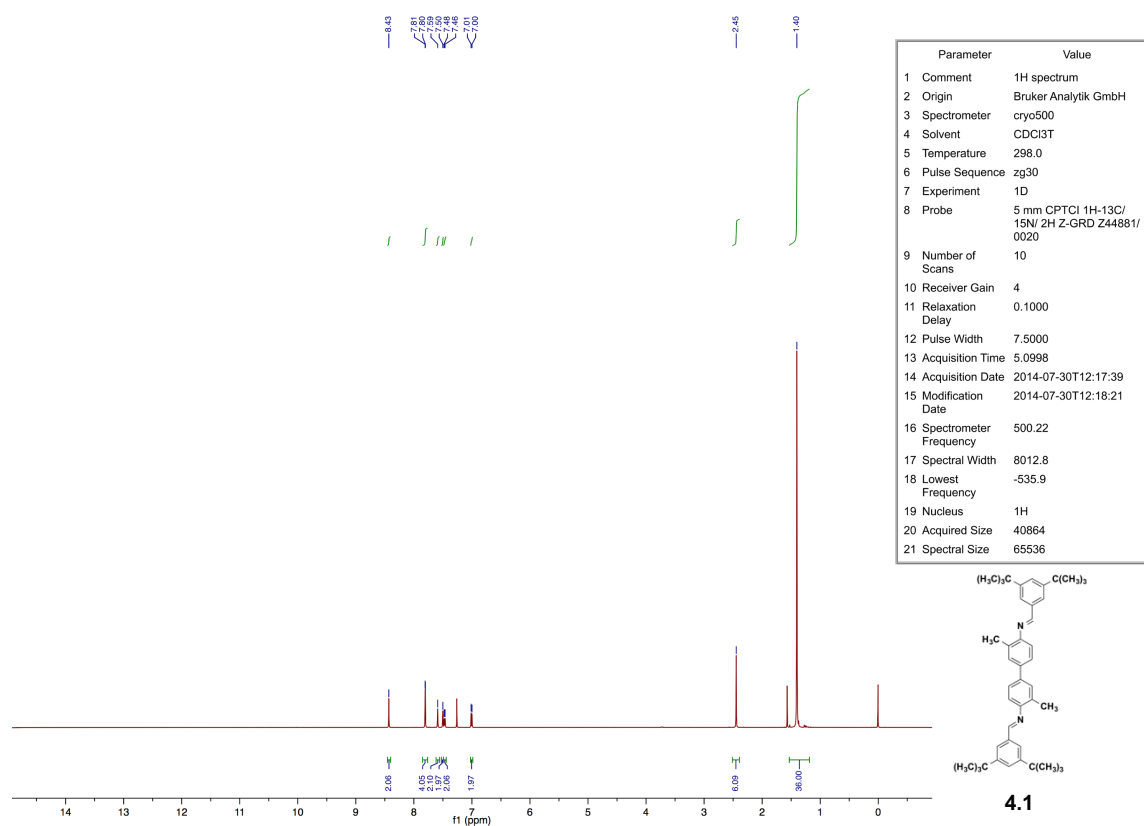


Figure S4.7. The ^1H NMR spectrum obtained for **4.1b**.

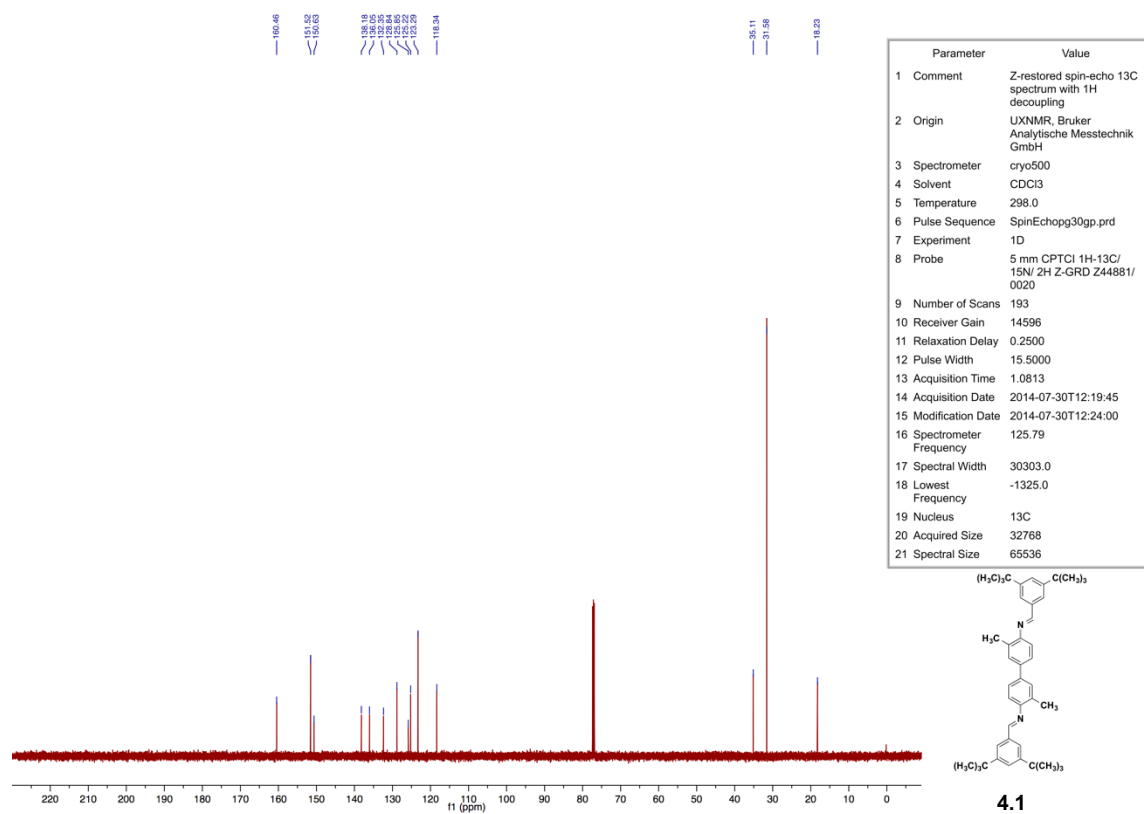


Figure S4.8. The ^{13}C NMR spectrum obtained for **4.1b**.



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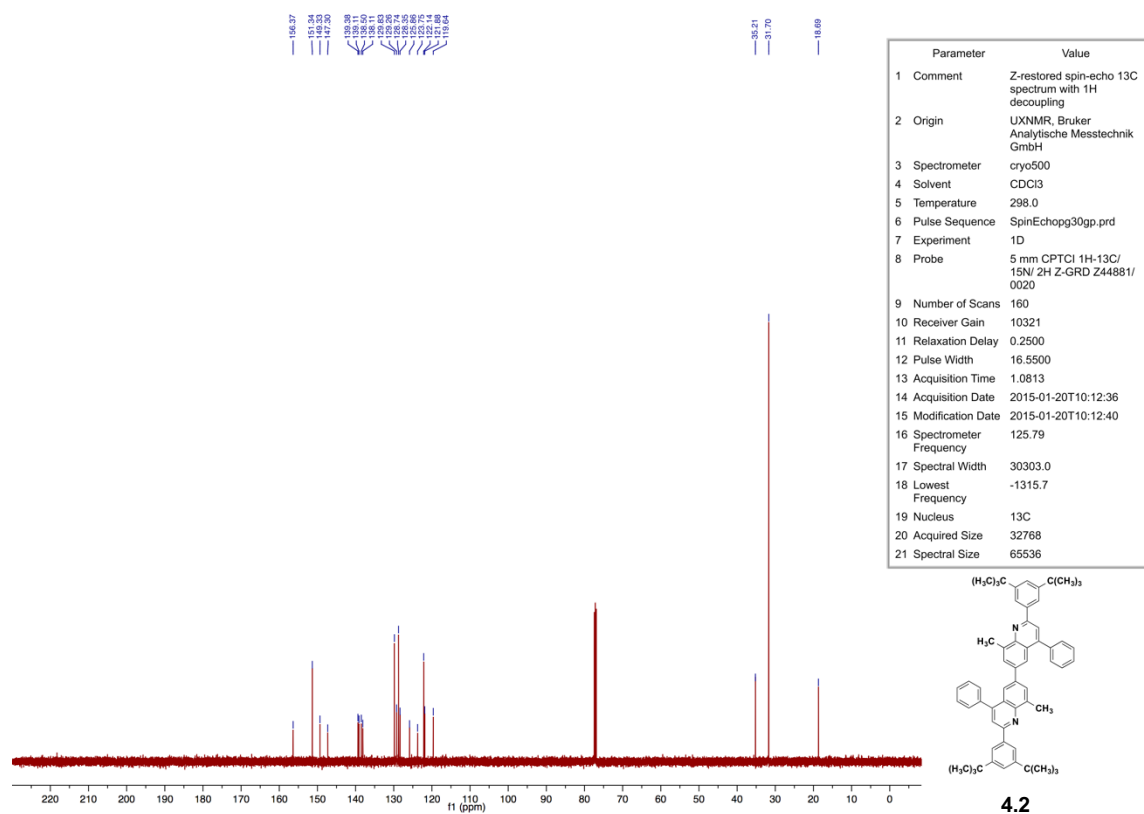


Figure S4.10. The ^{13}C NMR spectrum obtained for **4.2b**.

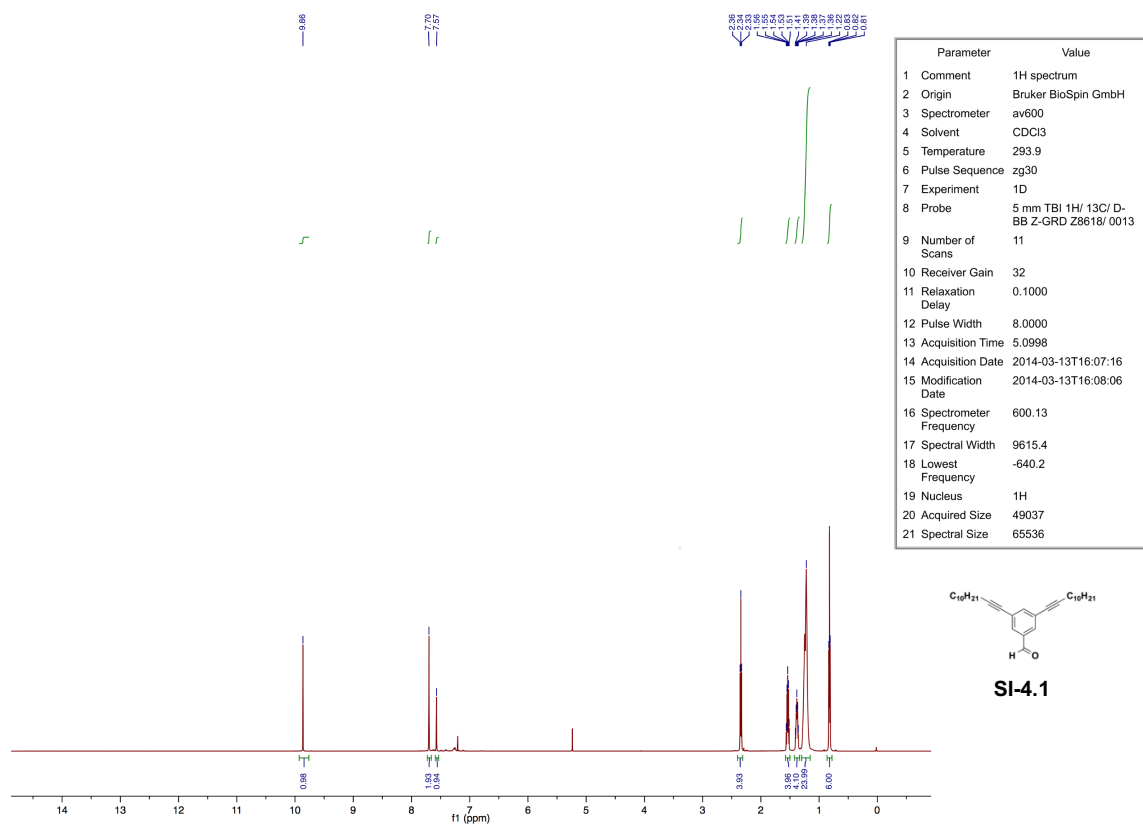


Figure S4.11. The ^1H NMR spectrum obtained for **SI-4.1**.

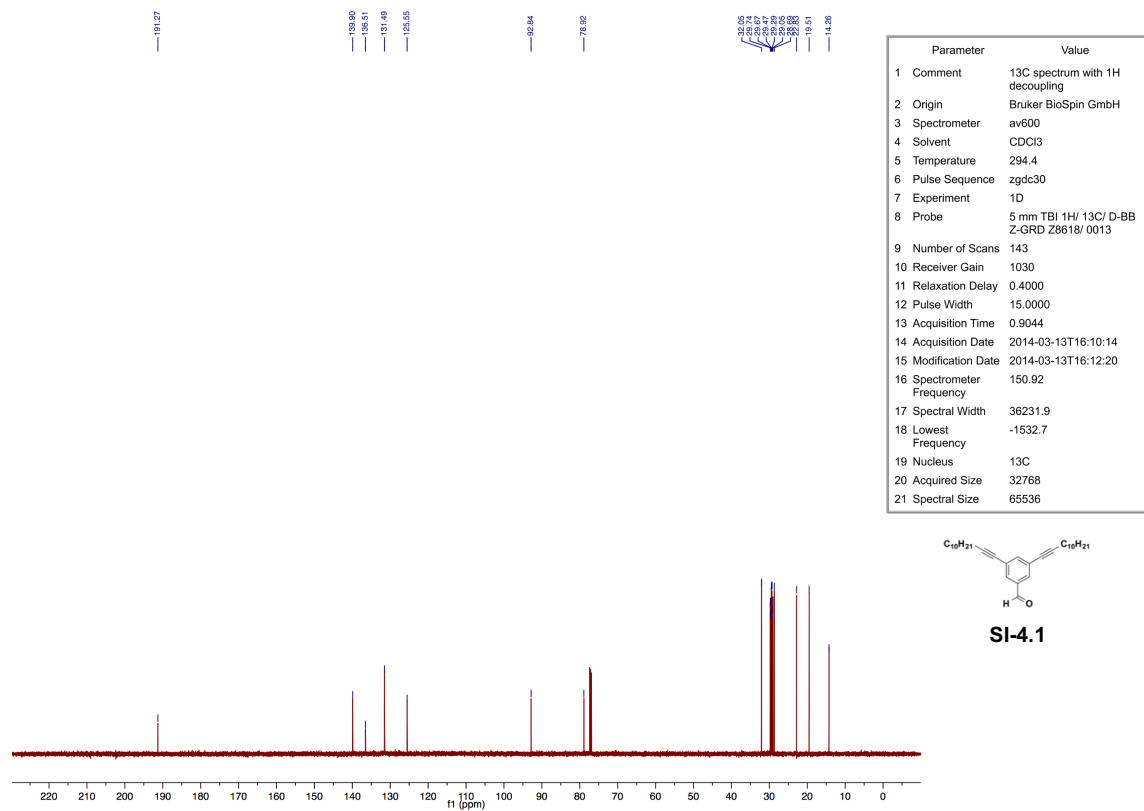


Figure S4.12. The ¹³C NMR spectrum obtained for **SI-4.1**.

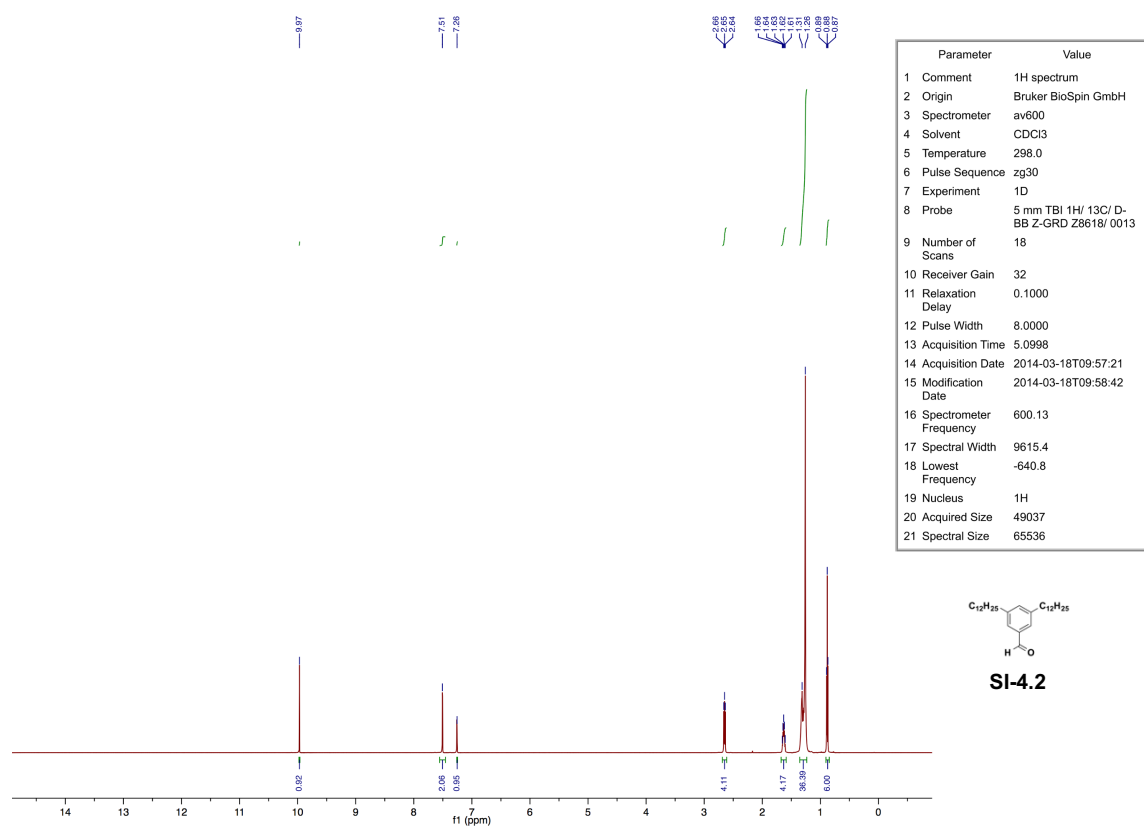


Figure S4.13. The ^1H NMR spectrum obtained for **SI-4.2**.

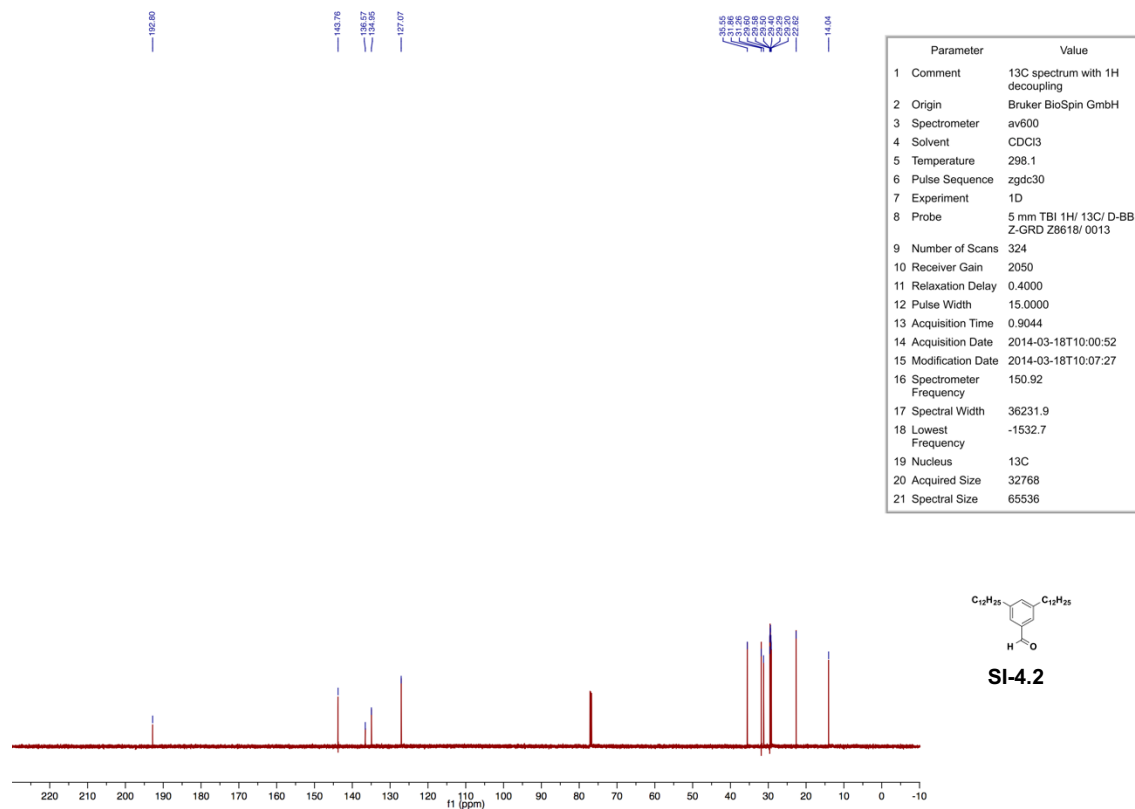


Figure S4.14. The ¹³C NMR spectrum obtained for **SI-4.2**.

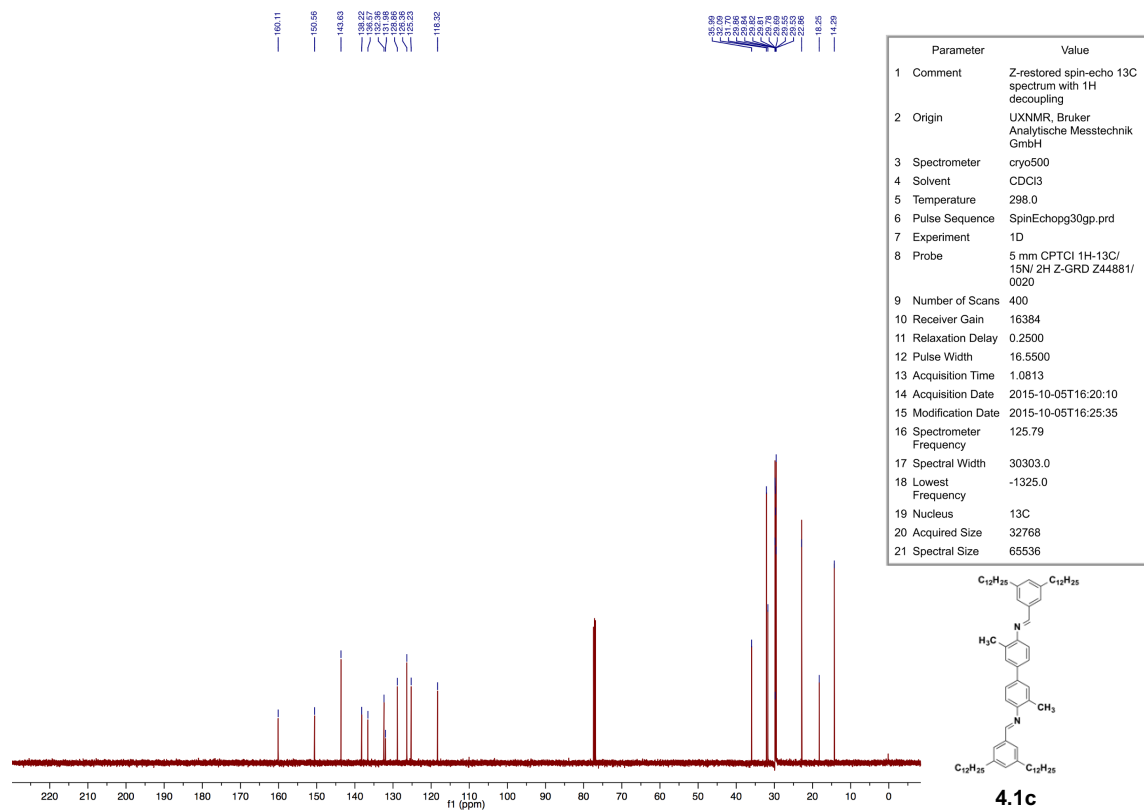
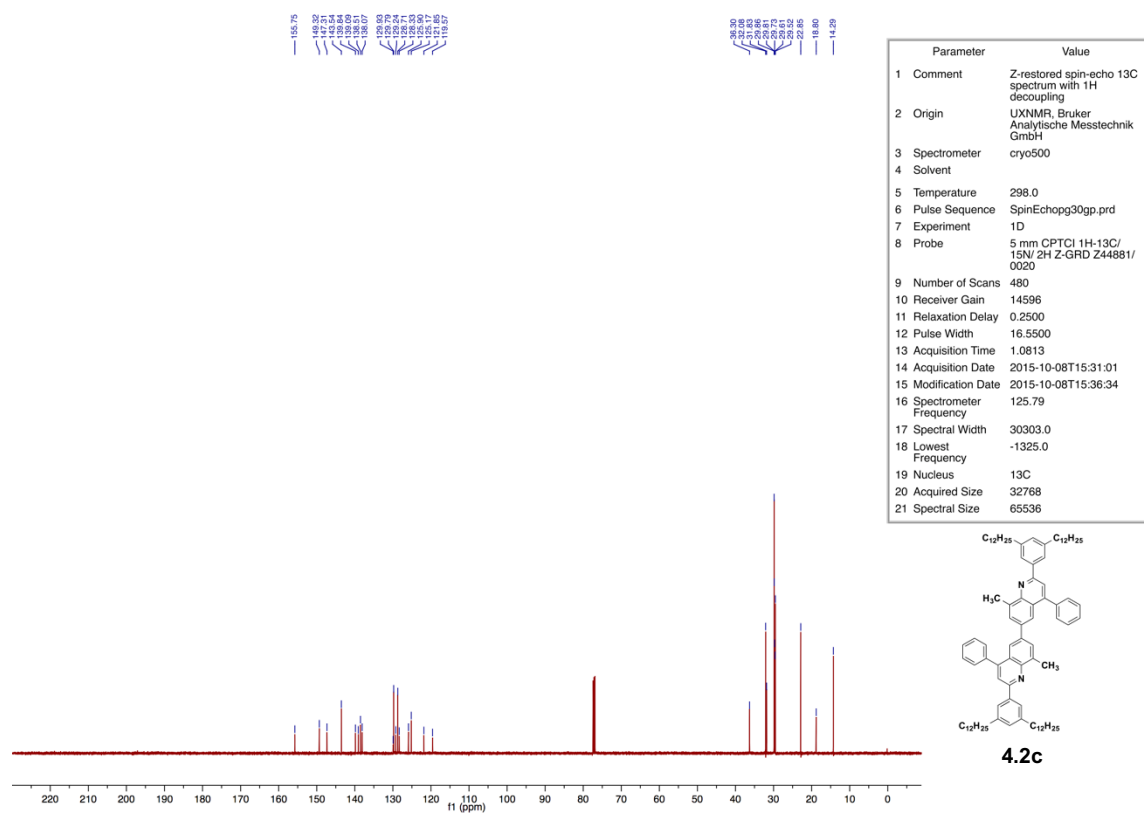


Figure S4.16. The ^{13}C NMR spectrum obtained for **4.1c**.



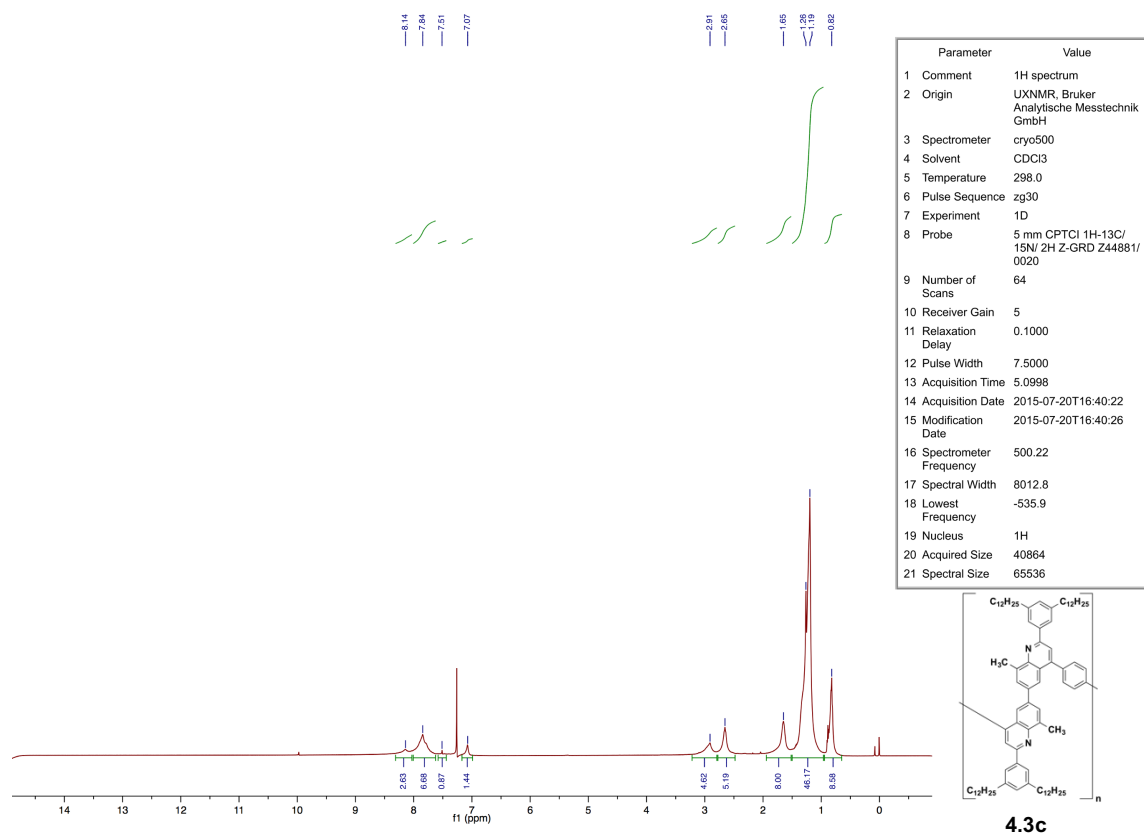


Figure S4.19. The ^1H NMR spectrum obtained for **4.3c**.

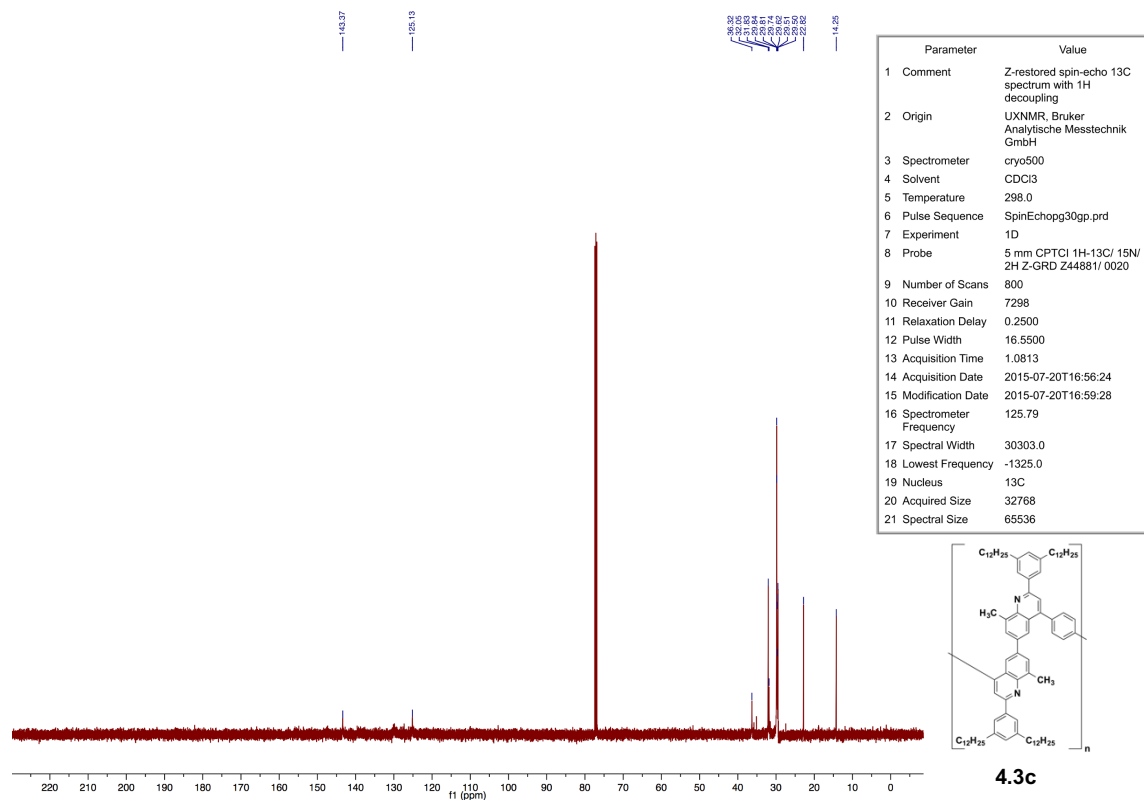
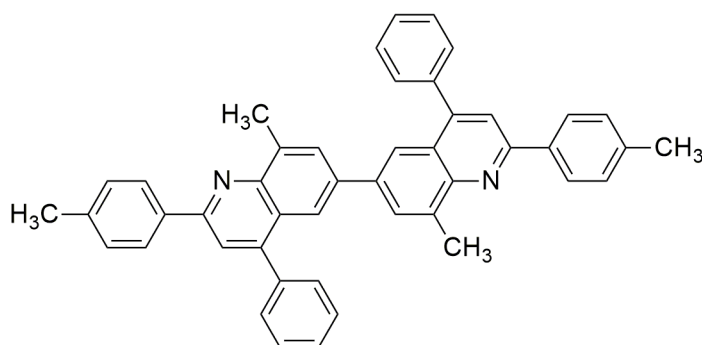


Figure S4.20. The ^{13}C NMR spectrum obtained for **4.3c**.

4.5.4. Equilibrium Structure Obtained from Density Functional Theory Calculations

A. Computational Details of the Simulations. Ground state density functional theory calculations were performed in Gaussian 09.^{S1} The structural optimization was performed using the DFT–B3LYP hybrid functional and a 6-311g(d,p) basis set. The initial conformation for the structural optimization was set based on the X-ray crystallographic data obtained for biquinoline **4.2a**. The frequency calculation indicated that the structure had attained its equilibrium geometry.



Compound **4.2a**

Imaginary Frequencies = 0

Energy = −1884.60534888 hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	−5.72438	0.11503	−0.09752
C	−3.51773	0.73737	−0.40506
C	−3.02464	−0.56117	−0.06321
C	−3.99491	−1.55154	0.29336
C	−5.32611	−1.20142	0.25675
C	−2.58862	1.76822	−0.75884
C	−1.63351	−0.81329	−0.12408
H	−6.07222	−1.9445	0.50522
C	−0.73836	0.1805	−0.47182
C	−1.24612	1.47357	−0.77727
H	−1.27026	−1.80136	0.12412
H	−0.54659	2.24982	−1.06733
C	0.72027	−0.08553	−0.52646

C	1.63745	0.87428	-0.14224
C	1.20477	-1.3487	-0.96609
C	3.02838	0.61481	-0.17306
H	1.29366	1.83038	0.22925
C	2.5432	-1.66055	-1.0009
H	0.48801	-2.09064	-1.30065
C	3.49365	-0.67376	-0.58371
C	4.0202	1.56902	0.21979
C	5.33917	1.17362	0.22384
C	5.70723	-0.13871	-0.17696
H	6.1036	1.89331	0.4854
C	-7.15962	0.50057	-0.1346
C	-8.14361	-0.20885	0.56524
C	-7.56421	1.6178	-0.88068
C	-9.47949	0.17829	0.51266
H	-7.872	-1.05573	1.18397
C	-8.89803	1.99496	-0.93434
H	-6.80958	2.1815	-1.41335
C	-9.88477	1.28131	-0.24189
H	-10.2177	-0.38451	1.07505
H	-9.1823	2.86076	-1.52466
C	7.13002	-0.5691	-0.18433
C	8.10875	0.07494	0.58254
C	7.52681	-1.66452	-0.96609
C	9.43268	-0.35416	0.56137
H	7.84087	0.90355	1.22725
C	8.84877	-2.08395	-0.98757
H	6.77541	-2.17733	-1.5521
C	9.83074	-1.43583	-0.22704
H	10.16678	0.15845	1.17476
H	9.12738	-2.93148	-1.60645
C	-3.61437	-2.93703	0.68718
C	-4.10968	-4.0349	-0.02806
C	-2.7951	-3.17538	1.7994
C	-3.78982	-5.33564	0.35338
H	-4.73701	-3.86374	-0.8957
C	-2.48165	-4.47606	2.18379
H	-2.41729	-2.33719	2.37351
C	-2.97541	-5.56029	1.4607
H	-4.17604	-6.17302	-0.21697
H	-1.8536	-4.64215	3.05186
H	-2.72762	-6.5726	1.75917
C	3.67283	2.96631	0.60132

C	4.03188	3.46604	1.85943
C	3.02356	3.82153	−0.29983
C	3.74329	4.7826	2.21077
H	4.52617	2.81191	2.56893
C	2.74295	5.13951	0.04911
H	2.75703	3.45451	−1.2844
C	3.09863	5.62332	1.30682
H	4.02059	5.14998	3.1925
H	2.2502	5.79071	−0.66421
H	2.8757	6.64864	1.5793
N	−4.83802	1.04442	−0.41566
N	4.80541	−1.0161	−0.58609
C	−3.09618	3.13876	−1.11859
H	−3.73433	3.1003	−2.00565
H	−3.7101	3.5522	−0.31506
H	−2.26586	3.81954	−1.31587
C	3.02273	−3.00884	−1.46717
H	3.67083	−2.91345	−2.34258
H	3.61885	−3.50016	−0.69453
H	2.17922	−3.65176	−1.72555
C	11.2701	−1.88577	−0.27411
H	11.74758	−1.57916	−1.21116
H	11.84908	−1.45734	0.54659
H	11.34939	−2.97462	−0.21244
C	−11.3362	1.68508	−0.3253
H	−11.7752	1.37851	−1.28109
H	−11.925	1.2242	0.47045
H	−11.4531	2.76946	−0.24903

4.5.5. X-ray Data Collection, Structure Solution, and Refinement

A. General Procedures. A crystal of **4.2a** was prepared by slow evaporation from a tetrahydrofuran solution of the compound. A colorless crystal with dimensions of approximately $0.087 \times 0.149 \times 0.385 \text{ mm}^3$ was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2^{S2} program package was used to determine the unit-cell parameters and for data collection (15 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT^{S3} and SADABS^{S4} to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL^{S5} program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space groups $P2_1/c$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors^{S6} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.1591$ and $\text{Goof} = 1.021$ for 437 variables refined against 6190 data ($0.82 \text{ \AA}$), with $R1 = 0.0515$ for those 4355 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.^{S7}

B. Definitions for the Crystallographic Analysis

$$wR2 = [\sum[w(F_o^2 - F_2^2)] / [\sum[w(o^2)^2]]]^{1/2}$$

$$R1 = \sum||F_o| - |F_c|| / \sum|F_o|$$

$$\text{Goof} = S = [\sum ow(F_o^2 - F_2^2)] / (n-p)]^{1/2}$$

where n is the number of reflections and p is the total number of parameters refined.

Identification code	4.2a	
Empirical formula	C ₄₆ H ₃₆ N ₂	
Formula weight	616.77	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 19.825(3) Å	<i>a</i> _a = 19
	<i>b</i> = 7.4082(10) Å	<i>b</i> _b = 95.552(2)°.
	<i>c</i> = 22.347(3) Å	<i>g</i> = 90°.
Volume	3266.7(8) Å ³	
<i>Z</i>	4	
Density (calculated)	1.254 Mg/m ³	
Absorption coefficient	0.072 mm ⁻¹	
<i>F</i> (000)	1304	
Crystal color	colorless	
Crystal size	0.385 x 0.149 x 0.087 mm ³	
Theta range for data collection	1.831 to 25.682°	
Index ranges	-24 ≤ <i>h</i> ≤ 24, -9 ≤ <i>k</i> ≤ 9, -27 ≤ <i>l</i> ≤ 27	
Reflections collected	32407	
Independent reflections	6190 [<i>R</i> (int) = 0.0555]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8620 and 0.8176	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	6190 / 0 / 437	
Goodness-of-fit on <i>F</i> ²	1.021	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>) = 4355 data]	<i>R</i> 1 = 0.0515, <i>wR</i> 2 = 0.1390	
<i>R</i> indices (all data, 0.82Å)	<i>R</i> 1 = 0.0816, <i>wR</i> 2 = 0.1591	
Largest diff. peak and hole	0.328 and -0.299 e.Å ⁻³	

Table S4.1. Crystal data and structure refinement for **4.2a**.

	x	y	z	U(eq)
N(1)	−1312(1)	3376(2)	3461(1)	22(1)
N(2)	3139(1)	2669(2)	1831(1)	20(1)
C(1)	577(1)	3111(3)	2764(1)	20(1)
C(2)	509(1)	3508(3)	3376(1)	22(1)
C(3)	−104(1)	3600(3)	3607(1)	23(1)
C(4)	−710(1)	3324(3)	3215(1)	20(1)
C(5)	−1877(1)	3160(3)	3103(1)	20(1)
C(6)	−1872(1)	2952(3)	2474(1)	21(1)
C(7)	−1279(1)	2884(3)	2209(1)	21(1)
C(8)	−656(1)	3014(3)	2591(1)	19(1)
C(9)	−7(1)	2853(3)	2386(1)	20(1)
C(10)	−148(1)	4011(4)	4260(1)	40(1)
C(11)	−2523(1)	3195(3)	3389(1)	20(1)
C(12)	−3129(1)	2542(3)	3100(1)	23(1)
C(13)	−3720(1)	2557(3)	3382(1)	24(1)
C(14)	−3730(1)	3212(3)	3965(1)	23(1)
C(15)	−3126(1)	3864(3)	4253(1)	25(1)
C(16)	−2536(1)	3862(3)	3972(1)	23(1)
C(17)	−4378(1)	3239(3)	4268(1)	31(1)
C(18)	−1297(1)	2762(3)	1543(1)	23(1)
C(19)	−899(1)	3886(3)	1217(1)	26(1)
C(20)	−948(1)	3805(3)	592(1)	32(1)
C(21)	−1383(1)	2598(3)	286(1)	34(1)
C(22)	−1785(1)	1487(3)	602(1)	32(1)
C(23)	−1748(1)	1575(3)	1226(1)	27(1)
C(24)	1257(1)	3004(3)	2537(1)	20(1)
C(25)	1337(1)	3367(3)	1925(1)	22(1)
C(26)	1949(1)	3275(3)	1695(1)	22(1)
C(27)	2538(1)	2772(3)	2082(1)	19(1)
C(28)	3680(1)	2152(3)	2177(1)	20(1)
C(29)	3663(1)	1772(3)	2797(1)	21(1)
C(30)	3079(1)	1962(3)	3074(1)	19(1)
C(31)	2473(1)	2431(3)	2703(1)	19(1)
C(32)	1825(1)	2587(3)	2917(1)	20(1)

C(33)	2017(1)	3722(3)	1047(1)	27(1)
C(34)	4338(1)	2102(3)	1908(1)	19(1)
C(35)	4873(1)	1011(3)	2143(1)	22(1)
C(36)	5491(1)	1060(3)	1905(1)	24(1)
C(37)	5604(1)	2186(3)	1427(1)	26(1)
C(38)	5067(1)	3249(3)	1188(1)	25(1)
C(39)	4446(1)	3213(3)	1421(1)	22(1)
C(40)	6285(1)	2270(3)	1182(1)	40(1)
C(41)	3124(1)	1788(3)	3741(1)	19(1)
C(42)	2661(1)	851(3)	4053(1)	23(1)
C(43)	2746(1)	726(3)	4677(1)	29(1)
C(44)	3295(1)	1519(3)	5001(1)	33(1)
C(45)	3772(1)	2408(3)	4701(1)	30(1)
C(46)	3686(1)	2550(3)	4079(1)	24(1)

Table S4.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times$

10^3) for **4.2a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

N(1)-C(5)	1.323(2)
N(1)-C(4)	1.362(2)
N(2)-C(28)	1.316(2)
N(2)-C(27)	1.368(2)
C(1)-C(9)	1.379(3)
C(1)-C(2)	1.420(3)
C(1)-C(24)	1.487(3)
C(2)-C(3)	1.368(3)
C(3)-C(4)	1.431(3)
C(3)-C(10)	1.502(3)
C(4)-C(8)	1.427(3)
C(5)-C(6)	1.415(3)
C(5)-C(11)	1.486(3)
C(6)-C(7)	1.368(3)
C(7)-C(8)	1.435(3)
C(7)-C(18)	1.489(3)
C(8)-C(9)	1.412(3)
C(11)-C(16)	1.395(3)
C(11)-C(12)	1.395(3)
C(12)-C(13)	1.383(3)
C(13)-C(14)	1.392(3)
C(14)-C(15)	1.389(3)
C(14)-C(17)	1.510(3)
C(15)-C(16)	1.381(3)
C(18)-C(23)	1.396(3)
C(18)-C(19)	1.399(3)
C(19)-C(20)	1.391(3)
C(20)-C(21)	1.378(3)
C(21)-C(22)	1.385(3)
C(22)-C(23)	1.390(3)
C(24)-C(32)	1.378(3)
C(24)-C(25)	1.419(3)
C(25)-C(26)	1.365(3)
C(26)-C(27)	1.433(3)
C(26)-C(33)	1.503(3)

C(27)-C(31)	1.429(3)
C(28)-C(29)	1.417(3)
C(28)-C(34)	1.489(3)
C(29)-C(30)	1.372(3)
C(30)-C(31)	1.436(3)
C(30)-C(41)	1.491(3)
C(31)-C(32)	1.418(3)
C(34)-C(35)	1.395(3)
C(34)-C(39)	1.396(3)
C(35)-C(36)	1.383(3)
C(36)-C(37)	1.390(3)
C(37)-C(38)	1.389(3)
C(37)-C(40)	1.507(3)
C(38)-C(39)	1.382(3)
C(41)-C(42)	1.391(3)
C(41)-C(46)	1.401(3)
C(42)-C(43)	1.392(3)
C(43)-C(44)	1.379(3)
C(44)-C(45)	1.378(3)
C(45)-C(46)	1.388(3)
C(5)-N(1)-C(4)	118.45(17)
C(28)-N(2)-C(27)	117.89(17)
C(9)-C(1)-C(2)	117.80(18)
C(9)-C(1)-C(24)	121.36(18)
C(2)-C(1)-C(24)	120.84(18)
C(3)-C(2)-C(1)	123.00(18)
C(2)-C(3)-C(4)	119.07(18)
C(2)-C(3)-C(10)	120.91(18)
C(4)-C(3)-C(10)	120.01(17)
N(1)-C(4)-C(8)	123.38(18)
N(1)-C(4)-C(3)	117.67(17)
C(8)-C(4)-C(3)	118.94(17)
N(1)-C(5)-C(6)	121.84(18)
N(1)-C(5)-C(11)	116.85(17)
C(6)-C(5)-C(11)	121.29(18)
C(7)-C(6)-C(5)	121.53(18)

C(6)-C(7)-C(8)	117.78(18)
C(6)-C(7)-C(18)	119.78(18)
C(8)-C(7)-C(18)	122.39(17)
C(9)-C(8)-C(4)	119.15(18)
C(9)-C(8)-C(7)	124.03(18)
C(4)-C(8)-C(7)	116.82(17)
C(1)-C(9)-C(8)	121.86(18)
C(16)-C(11)-C(12)	117.55(18)
C(16)-C(11)-C(5)	120.20(18)
C(12)-C(11)-C(5)	122.23(18)
C(13)-C(12)-C(11)	121.02(19)
C(12)-C(13)-C(14)	121.23(19)
C(15)-C(14)-C(13)	117.76(19)
C(15)-C(14)-C(17)	121.31(19)
C(13)-C(14)-C(17)	120.92(19)
C(16)-C(15)-C(14)	121.23(19)
C(15)-C(16)-C(11)	121.20(19)
C(23)-C(18)-C(19)	118.46(19)
C(23)-C(18)-C(7)	119.82(19)
C(19)-C(18)-C(7)	121.61(18)
C(20)-C(19)-C(18)	120.6(2)
C(21)-C(20)-C(19)	120.4(2)
C(20)-C(21)-C(22)	119.7(2)
C(21)-C(22)-C(23)	120.4(2)
C(22)-C(23)-C(18)	120.4(2)
C(32)-C(24)-C(25)	118.40(18)
C(32)-C(24)-C(1)	121.13(18)
C(25)-C(24)-C(1)	120.45(18)
C(26)-C(25)-C(24)	122.66(19)
C(25)-C(26)-C(27)	119.21(18)
C(25)-C(26)-C(33)	121.12(19)
C(27)-C(26)-C(33)	119.66(18)
N(2)-C(27)-C(31)	123.49(17)
N(2)-C(27)-C(26)	117.30(17)
C(31)-C(27)-C(26)	119.20(17)
N(2)-C(28)-C(29)	122.51(18)

N(2)-C(28)-C(34)	117.73(17)
C(29)-C(28)-C(34)	119.60(17)
C(30)-C(29)-C(28)	121.44(18)
C(29)-C(30)-C(31)	117.37(18)
C(29)-C(30)-C(41)	118.11(17)
C(31)-C(30)-C(41)	124.40(17)
C(32)-C(31)-C(27)	118.88(18)
C(32)-C(31)-C(30)	124.02(18)
C(27)-C(31)-C(30)	117.10(17)
C(24)-C(32)-C(31)	121.57(18)
C(35)-C(34)-C(39)	117.79(18)
C(35)-C(34)-C(28)	121.75(18)
C(39)-C(34)-C(28)	120.42(18)
C(36)-C(35)-C(34)	120.66(19)
C(35)-C(36)-C(37)	121.71(19)
C(38)-C(37)-C(36)	117.44(19)
C(38)-C(37)-C(40)	121.2(2)
C(36)-C(37)-C(40)	121.4(2)
C(39)-C(38)-C(37)	121.4(2)
C(38)-C(39)-C(34)	120.96(19)
C(42)-C(41)-C(46)	117.36(18)
C(42)-C(41)-C(30)	124.43(17)
C(46)-C(41)-C(30)	118.15(17)
C(41)-C(42)-C(43)	120.90(19)
C(44)-C(43)-C(42)	120.7(2)
C(45)-C(44)-C(43)	119.5(2)
C(44)-C(45)-C(46)	119.9(2)
C(45)-C(46)-C(41)	121.57(19)

Table S4.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4.2a**.

	U11	U22	U33	U23	U13	U12
N(1)	16(1)	24(1)	26(1)	0(1)	2(1)	0(1)
N(2)	18(1)	20(1)	20(1)	-3(1)	2(1)	-1(1)
C(1)	18(1)	16(1)	26(1)	1(1)	1(1)	3(1)
C(2)	19(1)	25(1)	21(1)	0(1)	-1(1)	-1(1)
C(3)	22(1)	26(1)	22(1)	-2(1)	2(1)	-2(1)
C(4)	17(1)	20(1)	24(1)	0(1)	3(1)	1(1)
C(5)	18(1)	17(1)	26(1)	2(1)	0(1)	2(1)
C(6)	18(1)	21(1)	25(1)	0(1)	-3(1)	1(1)
C(7)	18(1)	19(1)	24(1)	-1(1)	0(1)	2(1)
C(8)	19(1)	16(1)	23(1)	1(1)	1(1)	1(1)
C(9)	20(1)	20(1)	20(1)	-2(1)	1(1)	2(1)
C(10)	23(1)	73(2)	24(1)	-8(1)	2(1)	-7(1)
C(11)	19(1)	18(1)	24(1)	3(1)	0(1)	2(1)
C(12)	22(1)	22(1)	24(1)	0(1)	2(1)	0(1)
C(13)	19(1)	24(1)	30(1)	2(1)	-1(1)	-3(1)
C(14)	19(1)	21(1)	29(1)	6(1)	2(1)	3(1)
C(15)	22(1)	29(1)	25(1)	-1(1)	2(1)	2(1)
C(16)	17(1)	26(1)	26(1)	-1(1)	-1(1)	0(1)
C(17)	21(1)	40(1)	34(1)	0(1)	4(1)	0(1)
C(18)	17(1)	25(1)	24(1)	-1(1)	-4(1)	8(1)
C(19)	18(1)	34(1)	26(1)	0(1)	-1(1)	4(1)
C(20)	23(1)	44(1)	30(1)	6(1)	4(1)	5(1)
C(21)	30(1)	51(2)	22(1)	-2(1)	-1(1)	9(1)
C(22)	27(1)	36(1)	30(1)	-6(1)	-8(1)	7(1)
C(23)	20(1)	31(1)	28(1)	0(1)	-3(1)	5(1)
C(24)	20(1)	18(1)	23(1)	-2(1)	2(1)	-1(1)
C(25)	18(1)	24(1)	22(1)	-2(1)	-2(1)	1(1)
C(26)	24(1)	21(1)	21(1)	-3(1)	0(1)	-1(1)
C(27)	21(1)	15(1)	21(1)	-2(1)	3(1)	0(1)
C(28)	21(1)	16(1)	22(1)	-4(1)	1(1)	-1(1)
C(29)	19(1)	22(1)	21(1)	-1(1)	0(1)	0(1)
C(30)	19(1)	18(1)	20(1)	-2(1)	0(1)	-2(1)
C(31)	19(1)	15(1)	21(1)	-2(1)	1(1)	-2(1)

C(32)	21(1)	19(1)	20(1)	−2(1)	2(1)	0(1)
C(33)	22(1)	38(1)	21(1)	3(1)	1(1)	5(1)
C(34)	18(1)	20(1)	20(1)	−7(1)	1(1)	−3(1)
C(35)	23(1)	23(1)	21(1)	−2(1)	1(1)	0(1)
C(36)	19(1)	25(1)	29(1)	−6(1)	0(1)	2(1)
C(37)	22(1)	23(1)	36(1)	−10(1)	7(1)	−5(1)
C(38)	27(1)	25(1)	24(1)	−1(1)	8(1)	−6(1)
C(39)	21(1)	23(1)	21(1)	−3(1)	0(1)	1(1)
C(40)	28(1)	34(1)	60(2)	−5(1)	16(1)	−4(1)
C(41)	17(1)	22(1)	19(1)	0(1)	0(1)	5(1)
C(42)	19(1)	27(1)	22(1)	0(1)	0(1)	0(1)
C(43)	26(1)	40(1)	23(1)	3(1)	6(1)	−3(1)
C(44)	28(1)	48(2)	21(1)	1(1)	0(1)	−1(1)
C(45)	23(1)	41(1)	24(1)	−4(1)	−4(1)	−4(1)
C(46)	21(1)	28(1)	22(1)	0(1)	3(1)	−1(1)

Table S4.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4.2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{22} + \dots + 2 h k a^* b^* U^{12}]$

	x	y	z	U(eq)
H(2A)	908	3718	3638	26
H(6A)	-2291	2856	2230	26
H(9A)	28	2559	1977	24
H(10A)	297	4394	4445	60
H(10B)	-293	2928	4465	60
H(10C)	-478	4981	4298	60
H(12A)	-3136	2081	2703	27
H(13A)	-4127	2113	3174	29
H(15A)	-3120	4320	4651	30
H(16A)	-2131	4323	4179	28
H(17A)	-4273	3057	4702	47
H(17B)	-4678	2270	4104	47
H(17C)	-4604	4406	4196	47
H(19A)	-593	4713	1424	31
H(20A)	-679	4587	376	39
H(21A)	-1408	2527	-140	41
H(22A)	-2088	660	392	38
H(23A)	-2031	823	1438	32
H(25A)	948	3686	1664	26
H(29A)	4065	1377	3025	25
H(32A)	1782	2400	3332	24
H(33A)	1571	4039	846	40
H(33B)	2196	2673	848	40
H(33C)	2326	4745	1025	40
H(35A)	4812	226	2469	27
H(36A)	5848	305	2073	29
H(38A)	5127	4018	857	30
H(39A)	4088	3954	1248	26
H(40A)	6238	2868	789	60
H(40B)	6458	1043	1137	60
H(40C)	6602	2953	1459	60
H(42A)	2281	290	3837	27
H(43A)	2422	88	4882	35

H(44A)	3344	1452	5427	39
H(45A)	4159	2924	4920	36
H(46A)	4015	3178	3878	28

Table 4.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4.2a**.

C(9)-C(1)-C(2)-C(3)	1.6(3)
C(24)-C(1)-C(2)-C(3)	−179.20(19)
C(1)-C(2)-C(3)-C(4)	−1.3(3)
C(1)-C(2)-C(3)-C(10)	179.5(2)
C(5)-N(1)-C(4)-C(8)	−1.3(3)
C(5)-N(1)-C(4)-C(3)	178.64(18)
C(2)-C(3)-C(4)-N(1)	178.24(18)
C(10)-C(3)-C(4)-N(1)	−2.6(3)
C(2)-C(3)-C(4)-C(8)	−1.8(3)
C(10)-C(3)-C(4)-C(8)	177.3(2)
C(4)-N(1)-C(5)-C(6)	−2.5(3)
C(4)-N(1)-C(5)-C(11)	179.04(16)
N(1)-C(5)-C(6)-C(7)	2.9(3)
C(11)-C(5)-C(6)-C(7)	−178.74(18)
C(5)-C(6)-C(7)-C(8)	0.6(3)
C(5)-C(6)-C(7)-C(18)	−176.76(18)
N(1)-C(4)-C(8)-C(9)	−175.38(18)
C(3)-C(4)-C(8)-C(9)	4.7(3)
N(1)-C(4)-C(8)-C(7)	4.6(3)
C(3)-C(4)-C(8)-C(7)	−175.32(18)
C(6)-C(7)-C(8)-C(9)	175.92(18)
C(18)-C(7)-C(8)-C(9)	−6.8(3)
C(6)-C(7)-C(8)-C(4)	−4.1(3)
C(18)-C(7)-C(8)-C(4)	173.25(18)
C(2)-C(1)-C(9)-C(8)	1.5(3)
C(24)-C(1)-C(9)-C(8)	−177.76(18)
C(4)-C(8)-C(9)-C(1)	−4.6(3)
C(7)-C(8)-C(9)-C(1)	175.43(19)
N(1)-C(5)-C(11)-C(16)	15.3(3)
C(6)-C(5)-C(11)-C(16)	−163.18(19)
N(1)-C(5)-C(11)-C(12)	−163.41(18)
C(6)-C(5)-C(11)-C(12)	18.1(3)
C(16)-C(11)-C(12)-C(13)	−0.1(3)
C(5)-C(11)-C(12)-C(13)	178.65(18)
C(11)-C(12)-C(13)-C(14)	−0.4(3)

C(12)-C(13)-C(14)-C(15)	0.5(3)
C(12)-C(13)-C(14)-C(17)	179.46(19)
C(13)-C(14)-C(15)-C(16)	-0.1(3)
C(17)-C(14)-C(15)-C(16)	-179.06(19)
C(14)-C(15)-C(16)-C(11)	-0.4(3)
C(12)-C(11)-C(16)-C(15)	0.4(3)
C(5)-C(11)-C(16)-C(15)	-178.29(18)
C(6)-C(7)-C(18)-C(23)	-44.2(3)
C(8)-C(7)-C(18)-C(23)	138.5(2)
C(6)-C(7)-C(18)-C(19)	132.0(2)
C(8)-C(7)-C(18)-C(19)	-45.2(3)
C(23)-C(18)-C(19)-C(20)	-0.7(3)
C(7)-C(18)-C(19)-C(20)	-176.99(19)
C(18)-C(19)-C(20)-C(21)	-0.8(3)
C(19)-C(20)-C(21)-C(22)	1.4(3)
C(20)-C(21)-C(22)-C(23)	-0.4(3)
C(21)-C(22)-C(23)-C(18)	-1.1(3)
C(19)-C(18)-C(23)-C(22)	1.7(3)
C(7)-C(18)-C(23)-C(22)	178.02(18)
C(9)-C(1)-C(24)-C(32)	-155.45(19)
C(2)-C(1)-C(24)-C(32)	25.3(3)
C(9)-C(1)-C(24)-C(25)	25.9(3)
C(2)-C(1)-C(24)-C(25)	-153.35(19)
C(32)-C(24)-C(25)-C(26)	1.7(3)
C(1)-C(24)-C(25)-C(26)	-179.59(18)
C(24)-C(25)-C(26)-C(27)	0.8(3)
C(24)-C(25)-C(26)-C(33)	-178.18(19)
C(28)-N(2)-C(27)-C(31)	3.1(3)
C(28)-N(2)-C(27)-C(26)	-177.88(17)
C(25)-C(26)-C(27)-N(2)	179.00(17)
C(33)-C(26)-C(27)-N(2)	-2.0(3)
C(25)-C(26)-C(27)-C(31)	-1.9(3)
C(33)-C(26)-C(27)-C(31)	177.10(18)
C(27)-N(2)-C(28)-C(29)	-2.5(3)
C(27)-N(2)-C(28)-C(34)	-177.94(16)
N(2)-C(28)-C(29)-C(30)	-1.4(3)

C(34)-C(28)-C(29)-C(30)	174.00(18)
C(28)-C(29)-C(30)-C(31)	4.5(3)
C(28)-C(29)-C(30)-C(41)	-171.58(18)
N(2)-C(27)-C(31)-C(32)	179.60(17)
C(26)-C(27)-C(31)-C(32)	0.5(3)
N(2)-C(27)-C(31)-C(30)	0.1(3)
C(26)-C(27)-C(31)-C(30)	-178.93(17)
C(29)-C(30)-C(31)-C(32)	176.72(18)
C(41)-C(30)-C(31)-C(32)	-7.4(3)
C(29)-C(30)-C(31)-C(27)	-3.8(3)
C(41)-C(30)-C(31)-C(27)	172.02(18)
C(25)-C(24)-C(32)-C(31)	-3.1(3)
C(1)-C(24)-C(32)-C(31)	178.21(18)
C(27)-C(31)-C(32)-C(24)	2.0(3)
C(30)-C(31)-C(32)-C(24)	-178.57(18)
N(2)-C(28)-C(34)-C(35)	-156.60(18)
C(29)-C(28)-C(34)-C(35)	27.8(3)
N(2)-C(28)-C(34)-C(39)	25.8(3)
C(29)-C(28)-C(34)-C(39)	-149.78(19)
C(39)-C(34)-C(35)-C(36)	1.1(3)
C(28)-C(34)-C(35)-C(36)	-176.53(18)
C(34)-C(35)-C(36)-C(37)	-0.1(3)
C(35)-C(36)-C(37)-C(38)	-1.0(3)
C(35)-C(36)-C(37)-C(40)	178.3(2)
C(36)-C(37)-C(38)-C(39)	0.9(3)
C(40)-C(37)-C(38)-C(39)	-178.28(19)
C(37)-C(38)-C(39)-C(34)	0.1(3)
C(35)-C(34)-C(39)-C(38)	-1.1(3)
C(28)-C(34)-C(39)-C(38)	176.55(18)
C(29)-C(30)-C(41)-C(42)	-137.4(2)
C(31)-C(30)-C(41)-C(42)	46.8(3)
C(29)-C(30)-C(41)-C(46)	39.7(3)
C(31)-C(30)-C(41)-C(46)	-136.1(2)
C(46)-C(41)-C(42)-C(43)	1.7(3)
C(30)-C(41)-C(42)-C(43)	178.90(19)
C(41)-C(42)-C(43)-C(44)	-0.4(3)

C(42)-C(43)-C(44)-C(45)	−1.5(3)
C(43)-C(44)-C(45)-C(46)	2.0(4)
C(44)-C(45)-C(46)-C(41)	−0.7(3)
C(42)-C(41)-C(46)-C(45)	−1.1(3)
C(30)-C(41)-C(46)-C(45)	−178.50(19)

Table 4.6. Torsion angles [°] for **4.2a**.

4.5.6. References

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5.1 Abstract

This study describes the synthesis of modular diquinolineanthracene and polydiquinolineanthracene derivatives. The reported facile and scalable aza-Diels–Alder-based approach requires mild conditions, proceeds in two steps, uses commercially available starting materials, and accommodates varying functionalities. Given the known utility of the acene and quinoline motifs, the synthesized molecules and polymers hold promise for organic electronics applications.

5.2 Introduction

Organic semiconductors (OSCs) have been touted as promising materials for the next generation of optoelectronic devices, such as organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field effect transistors (OFETs).¹⁻¹⁰ Within this context, acenes (polycyclic aromatic hydrocarbons consisting of linearly fused benzene rings) have emerged as widely studied OSCs due to their synthetic modularity, reasonable processability, controllable solid-state self-assembly characteristics, and favorable charge transport behavior.¹¹⁻²⁵ Thus, much research effort has focused on the molecular engineering of acenes for improved materials properties (and device performance).¹¹⁻²⁵ As examples, symmetric functionalization of pentacenes' peripheries with silylethynyl substituents has been shown to enhance their solubility, stability, and crystallinity.¹¹⁻¹⁹ Moreover, doping of the pentacenes' aromatic cores with nitrogen atoms has been shown to elicit n-type or even ambipolar (both n-type and p-type) charge transport behavior in the solid state.¹⁹⁻²⁵ Consequently, given the technological potential of acene derivatives, there exists a strong impetus for the continued development of new synthetic routes to these materials.

Herein, we report the synthesis of diquinolineanthracene and polydiquinolineanthracene derivatives via the aza-Diels–Alder (Povarov) reaction.^{26,27} First, we demonstrate the preparation of a series of diquinolineanthracenes symmetrically substituted with quinolines that feature electron-withdrawing, electron-donating, and/or sterically congested functionalities at their 2-positions. Next, we use identical conditions to furnish polydiquinolineanthracenes from commercially available AA-type diimine and BB-type diethynylantracene monomers in an AA/BB-type polymerization reaction. Finally, we obtain insight into the properties of our materials via size exclusion chromatography (SEC), ultraviolet–visible (UV-vis) spectroscopy, density functional theory (DFT) calculations, and/or cyclic voltammetry (CV). Overall, our approach constitutes a facile and modular route to a new class of acene-based molecules and polymers for potential applications in organic electronic devices.

5.3 Results and Discussion

For the design of our materials, we sought inspiration from the classic quinoline and anthracene organic semiconductors. Although both of these molecules have been studied for decades, there have been few reports of the synthesis of anthracenes symmetrically substituted with quinolines or benzoquinolines (Figure 5.1A).^{28–31} This dearth of literature precedent is surprising because molecular frameworks combining anthracenes (known p-type OSCs)^{11,12} and quinolines (known n-type OSCs)^{32,33} might be expected to possess highly desirable ambipolar charge transport properties. Consequently, we envisioned the synthesis of anthracenes modified with quinolines at the 6- and 13-positions (in analogy to the well-known triisopropylsilylethynyl-substituted acenes),^{11–19} as well as the synthesis of corresponding polyanthracenes bridged with biquinolines (Figure 5.1B). We theorized that such hybrid materials could be readily obtained via

our group's previously reported Povarov reaction-based methodologies.^{30,34-37}

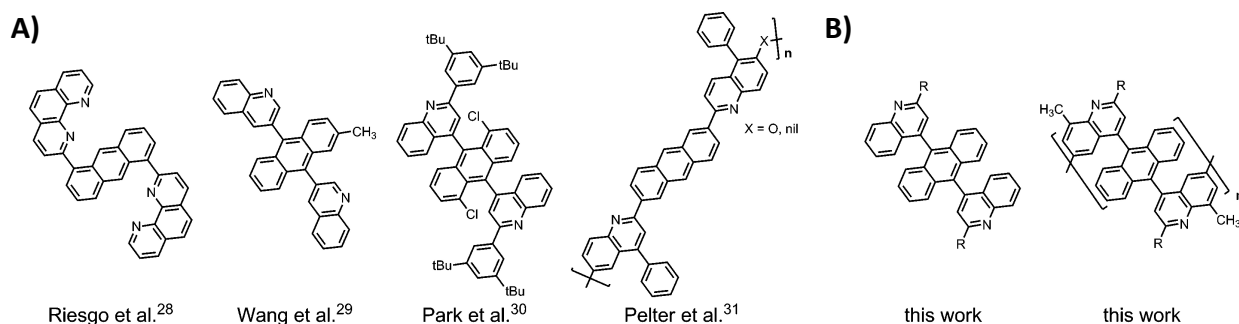
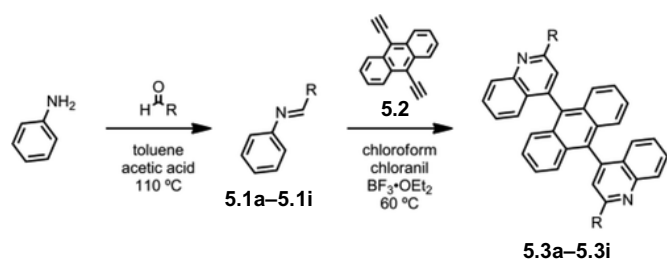


Figure 5.1: (A) Previously reported diquinolineanthracene and polydiquinolineanthracene variants. (B) Modular diquinolineanthracene and polydiquinolineanthracene derivatives presented here.

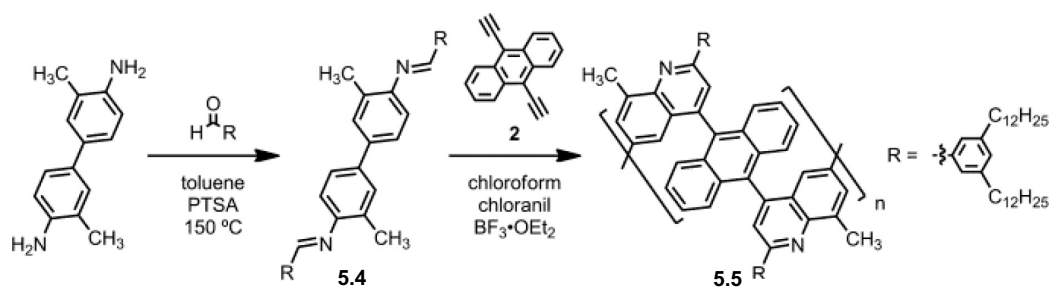
We began our studies by preparing a small library of diquinolineanthracenes via the Lewis acid-promoted aza-Diels–Alder reaction (Table 5.1). Thus, we first synthesized aldimine precursors **5.1a–5.1i** from aniline and various commercially available aldehydes via established literature protocols.^{30,34-37} Next, we reacted each of these aldimines with commercially available 9,10-diethynylantracene **5.2**, in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as the Lewis acid mediator and chloranil as the sacrificial oxidant,^{30,34-37} obtaining diquinolineanthracenes **5.3a–5.3i**, as confirmed by ^1H and ^{13}C NMR spectroscopy (Supporting Figures S5.1 to S5.42). Notably, our reaction conditions readily enabled the preparation of diquinolineanthracenes featuring electron-withdrawing groups (entries 1, 2, 3, and 6 in Table 5.1) and electron-donating groups (entry 9 in Table 5.1) on their peripheries. Moreover, the protocol accommodated sterically hindered aldimines with ortho substituents on their pendant phenyl rings (entries 6 and 7 in Table 5.1). Together, these experiments demonstrated that our approach could furnish a diverse set of diquinolineanthracenes from commercial reagents in few synthetic steps.

Having demonstrated the scope of our strategy, we proceeded to prepare a prototypical polydiquinolineanthracene via the same method (Scheme 5.1). Thus, we first synthesized diimine **5.4** from commercially available *o*-toluidine and *p*-didodecyl benzaldehyde in one step via optimized protocols. Next, we reacted diimine **5.4** with commercially available 9,10-diethynylantracene **5.2** in conditions similar to those developed for the synthesis of **5.3a–5.3i**, obtaining polydiquinolineanthracene **5.5**. After a 48h period, we quenched the reaction with aqueous sodium bicarbonate, treated the mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (to ensure rearomatization),^{34,35,37} and precipitated the products with ethanol. We analyzed crude polydiquinolineanthracene **5.5** via size-exclusion chromatography with a refractive index detector (SEC-RI) and obtained a number-average molecular weight (M_n) of 9.5 kg mol⁻¹, a weight-average molecular weight (M_w) of 20.2 kg mol⁻¹, and a polydispersity index (PDI) of 2.12 (Figure 5.2). Subsequently, we purified the crude products via chromatography (see the SI for details). We then analyzed purified polydiquinolineanthracene **5.5** via SEC-RI and obtained a M_n of 15.3 kg mol⁻¹, a M_w of 22.7 kg mol⁻¹, and a PDI of 1.48 (Figure 5.2). Overall, the experiments demonstrated that our synthetic strategy could be readily extended to the preparation of macromolecular materials under mild reaction conditions.



entry	compound	R	Povarov reaction yield (%)
1	5.3a		80
2	5.3b		75
3	5.3c		71
4	5.3d		65
5	5.3e		65
6	5.3f		62
7	5.3g		52
8	5.3h		44
9	5.3i		15

Table 5.1: Synthesis of 9,10-Diquinolineanthracenes **5.3a–5.3i**.



Scheme 5.1. Synthesis of Polydiquinolineanthracene **5.5**.

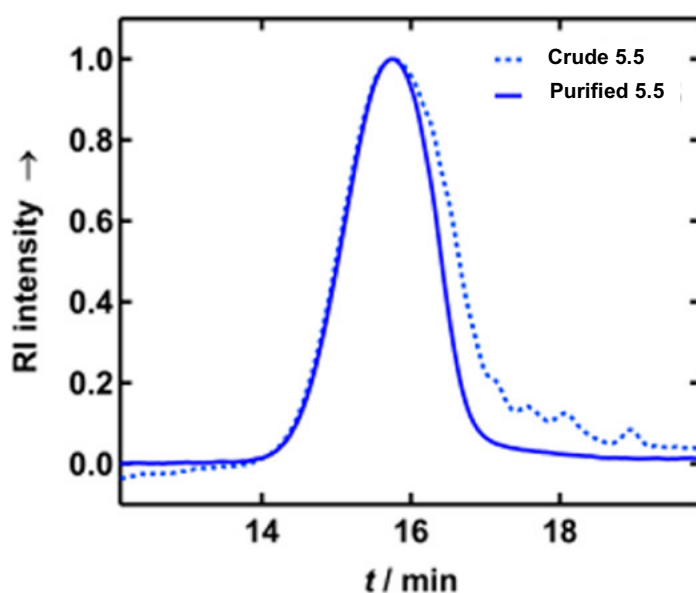


Figure 5.2. SEC-RI chromatograms obtained for crude polydiquinolineanthracene **5.5** (light blue dashed line) and purified polydiquinolineanthracene **5.5** (blue solid line).

We next investigated the electronic properties of diquinolineanthracenes **3a–3i** and polydiquinolineanthracene **5.5** with UV-vis spectroscopy. As a specific example, the spectrum obtained for diquinolineanthracene **5.3h** featured absorption peaks with maxima at 329, 340, 356, 375, and 395 nm (Figure 5.3, Supporting Figure S5.43, and Supporting Table S5.1). Interestingly, the observed peaks were red-shifted but qualitatively similar to the ones found for the molecule's anthracene and 2-phenylquinoline parent compounds (Supporting Figure S5.43), hinting that the transitions at <350 nm arose both from the anthracene and quinoline moieties and that the

transitions at >350 nm arose primarily from the anthracene moiety. More generally, the spectra obtained for **5.3a–5.3i** featured minor relative red/blue shifts and analogous characteristics, i.e., peak clusters and/or broad humps at wavelengths between 270 and 350 nm and three peaks and/or shoulders at wavelengths between 350 and 450 nm (Figure 5.3, Supporting Figure S5.43a, and Supporting Table S5.1). For polydiquinolineanthracene **5.5**, the spectrum featured absorption peaks/shoulders with maxima at 283, 343, 359, 378, and 398 nm (Figure 5.3). Here, the observed peaks were in similar positions but featured distinct intensity ratios relative to the ones found for the polymer's small molecular analogue **5.3h** (Figure 5.3). Moreover, the spectrum for polydiquinolineanthracene **5.5** was substantially broadened and possessed a red-shifted absorption onset, when compared to the spectrum of **5.3h** (Figure 5.3). Altogether, our observations matched expectations for materials from anthracene and quinoline subunits that were at least partially electronically decoupled from one another.

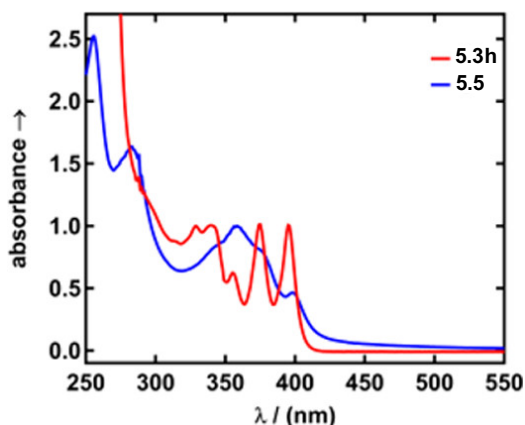


Figure 5.3. UV-vis absorbance spectra obtained for diquinolineanthracene **5.3h** (red trace) and polydiquinolineanthracene **5.5** (blue trace). Note that the spectra have been scaled relative to one another for clarity.

To gain additional insight into the electronic properties of our materials, we performed DFT calculations for diquinolineanthracenes **5.3a–5.3i**. As a specific example, the calculations for diquinolineanthracene **5.3e** yielded two nearly isoenergetic isomers (denoted here as *cis* and *trans*) with distinct equilibrium geometries and shapes for the HOMO, LUMO, and

LUMO + 1 (Figure 5.4). For both the *cis* and *trans* isomers, the calculations revealed that the peripheral quinoline moieties were out of planarity with the central anthracene (Figure 5.4). Moreover, we found that the HOMO and LUMO were primarily localized on the central anthracene, with corresponding energies of -5.6 and -2.1 eV, respectively, and that the LUMO + 1 was primarily localized on the peripheral quinolines, with an energy of -1.8 eV (Figure 5.4). More generally, the calculations indicated that the installation of electron-withdrawing groups on the quinolines lowered the HOMO, LUMO, and LUMO + 1 energies for compounds **5.3a**, **5.3b**, **5.3c**, and **5.3f** relative to those of unsubstituted **5.3d**, while the installation of alkyl substituents and/or electron-donating groups on the quinolines maintained or raised the HOMO, LUMO, and LUMO + 1 energies for compounds **5.3e**, **5.3g**, **5.3h**, and **5.3i** relative to those of unsubstituted **5.3d** (SI Figures S5.44–S5.61 and SI Table S5.2). The calculations confirmed that our materials' anthracene and quinoline subunits were electronically decoupled and implied that they might support the transport of both holes and electrons.

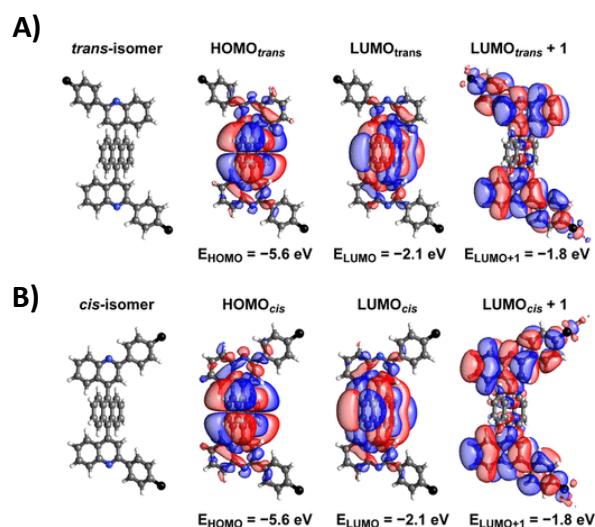


Figure 5.4. (A) Energy minimized equilibrium geometry (far left), HOMO isosurface (middle left), LUMO isosurface (middle right), and LUMO + 1 isosurface (far right) for the *trans* isomer of diquinolineanthracene **5.3e**, as obtained from DFT calculations. (B) Energy minimized equilibrium geometry (far left), HOMO isosurface (middle left), LUMO isosurface (middle right), and LUMO + 1 isosurface (far right) for the *cis* isomer of diquinolineanthracene **5.3e**, as obtained from DFT calculations. The energies of the molecular orbitals are also shown. Note that the octyl chains have been removed for clarity.

Finally, we studied the redox activity of diquinolineanthracene **5.3h** and polydiquinolineanthracene **5.5** with cyclic voltammetry. For diquinolineanthracenes **5.3h**, the voltammogram featured a quasi-reversible redox couple with a midpoint potential of +1.52 V vs Ag/AgCl (corresponding to an energy of ~ -6.1 eV), a quasi-reversible redox couple with a midpoint potential of -1.84 V vs Ag/AgCl (corresponding to an energy of ~ -2.7 eV), and a cathodic wave with a peak potential of -2.19 V vs Ag/AgCl (corresponding to an energy of ~ -2.3 eV) (Figure 5.5). Interestingly, these redox couples/waves were similar to the ones found for the molecule's anthracene and 2-phenylquinoline parent compounds (SI Figure S5.62). This similarity enabled assignment of the couple at oxidative potentials to the central anthracene moiety, as well as assignment of the couple and wave at reductive potentials to the central anthracene and peripheral quinoline moieties (Supporting Figure S5.62). The general assignments were further corroborated by the HOMO, LUMO, and LUMO + 1 energies of -5.6 , -2.1 , and -1.8 eV, respectively, calculated for **5.3e** (Figure 5.4). For polydiquinolineanthracene **5.5**, the voltammogram featured an anodic wave with a peak potential of +1.62 V vs Ag/AgCl, a quasi-reversible redox couple with a midpoint potential of -1.88 V vs Ag/AgCl, and a cathodic wave with a peak potential of -2.28 V vs Ag/AgCl (Figure 5.5). In agreement with expectations for a macromolecular system, the redox couples/waves possessed distinct idealities and potentials compared to the ones found for the polymer's small molecular analogue **5.3h** (Figure 5.5). Together with the above observations, the measurements and analysis supported the notion that our modular small molecules and polymers could serve as ambipolar charge transport materials.

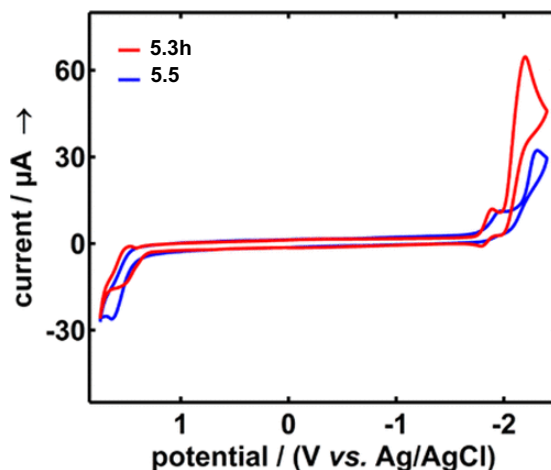


Figure 5.5. Cyclic voltammogram of diquinolineanthracene **5.3h** (red trace) and polydiquinolineanthracene **5.5** (blue trace).

5.4 Conclusion

In conclusion, we have designed and developed a general strategy for the synthesis of both diquinolineanthracenes and polydiquinolineanthracenes, and our findings hold significance for several reasons. First, our method uses mild conditions, two straightforward synthetic steps, and commercially available starting materials. Second, the described reactions are readily scalable and proceed on a multigram scale. Third, our modular approach accommodates various peripheral substituents, including electron-donating, electron-withdrawing, and sterically hindered groups. Finally, our study constitutes a rare example of the synthesis of either diquinolineanthracenes or polydiquinolineanthracenes via any method and the first report of the synthesis of these materials via the aza-Diels–Alder reaction. Overall, the reported strategy constitutes a novel and facile route to materials that integrate both the quinoline and acene motifs and therefore hold promise for applications in organic electronics.

5.5 Supporting Information

5.5.1. General Information and Procedures

1. Materials. All chemicals and solvents were purchased from Sigma Aldrich, Acros Organics, or Combi-Blocks. The toluene, chloroform, and tetrahydrofuran were dried with 3 Å molecular sieves and stored under Argon. The glassware was oven dried at 150 °C. The reactions were performed under dry argon unless otherwise noted. 3,5-didodecylbenzaldehyde and (N4E,N4'E)-N4,N4'-bis(3,5-didodecylbenzylidene)-3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diimine (**5.4**) were prepared as reported previously.^{S1}

2. Compound Purification Procedures. Flash chromatography was performed using a CombiFlash R_f200 purification system (Teledyne Isco, Inc.) according to the manufacturer's recommended protocols. When required, the silica gel columns/cartridges were flushed with 1/9 triethylamine/hexanes to deactivate the silica gel, followed by hexanes to remove excess triethylamine. Additional purification-relevant information and protocols are noted below as appropriate.

3. Reaction Product Characterization Procedures. The intermediates and products were characterized with a combination of ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and ultraviolet-visible (UV/Vis) spectroscopy. The ¹H NMR, ¹³C NMR were obtained on either a Bruker AVANCE400 instrument, a Bruker DRX500 instrument, a Bruker DRX500 instrument outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes), or an AVANCE600 instrument. The chemical shifts were reported in ppm for both ¹H and ¹³C NMR. The chemical shifts for the NMR data were referenced as follows: for samples in CDCl₃, the ¹H

NMR was referenced to tetramethylsilane (TMS) at 0.00 or the residual CHCl_3 peak at 7.26 ppm, and the ^{13}C NMR was referenced to the residual CHCl_3 peak at 77.16 ppm. The data were labeled with the chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet), coupling constants in Hertz, and integration values. Accurate mass measurements were obtained *via* electrospray ionization (ESI) high resolution mass spectrometry (HRMS) at the University of California, Irvine Mass Spectrometry Facility on a Waters LCT Premier time-of-flight instrument. MALDI-TOF mass spectra were recorded on an AB Sciex TOF/TOF 5800 series mass spectrometer using a 349 nm Nd:YAG laser and dithranol or 2-(4'-Hydroxybenzeneazo)benzoic acid (HABA) as the matrix. The UV/Vis spectroscopy measurements were performed on an Agilent Cary 100 Series Spectrophotometer. All UV/Vis spectra were obtained with tetrahydrofuran as the solvent.

4. Polymer Characterization and Analysis Procedures. The crude and purified polymers were analyzed *via* size exclusion chromatography with a refractive index detector (SEC-RI). The SEC-RI measurement was performed in benzene at 60 °C using an Agilent Technologies 1260 Infinity Series separations module equipped with two Agilent ResiPore columns connected in series (7.5 mm x 300 mm, 3 μm particle size). The separations module was connected to Agilent 1260 infinity dual angle light scattering, refractive index, and viscosity detectors in series. The flow rate was ~ 1.0 mL/minute with an injection volume of $\sim 25 - 100$ μL and a sample concentration of $\sim 1.0 - 2.5$ mg/mL. Molecular weights (M_n and M_w) were estimated from a calibration curve by using polystyrene standards (EasiVial PS-H, Agilent).

5. Electrochemical Measurements. Cyclic voltammetry experiments were performed with a CHI832C electrochemical analyzer in an oxygen free 1:2 acetonitrile:toluene solution supplemented with 0.1 M tetrabutylammonium tetrafluoroborate (TbABF₄). A glassy carbon electrode (BASi) served as the working electrode, a Pt wire (CH Instruments, Inc.) served as the counter electrode, and an Ag/AgCl electrode (Warner Instruments) served as the reference. The electrochemical potentials were converted to energies using ferrocene as a standard.

5.5.2. General Synthetic Protocols

A. Representative Procedure for the Formation of Aldimines *Via* a Dean–Stark Apparatus

A solution of aldehyde (94.1 mmol), aniline (94.1 mmol), and acetic acid (ca. ~0.1 ml) in toluene (250 mL) was heated to reflux, with removal of water *via* a Dean–Stark trap. After 16 hours, the mixture was cooled and the solvent was removed *in vacuo* to afford the product.

B. Representative Procedure for the Formation of Diquinolineanthracenes

A solution of aldimine (2.63 mmol), 9,10-bisethynylantracene (0.889 mmol), chloranil (1.75 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (2.75 mmol) in chloroform (30 mL) under dry argon was heated to 60 °C. After 48 hours, the reaction mixture was cooled and diluted with chloroform (100 mL). Subsequently, the reaction was washed with a saturated aqueous sodium bicarbonate solution (100 mL $\times$ 3) and water (100 mL $\times$ 3). The organics were poured through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified with a combination of sequential washes with organic solvent and/or flash chromatography typically yielding a mixture of atropisomers of the product.

5.5.3. Detailed Synthetic Protocols

1. N-(4-bromobenzylidene)aniline (5.1a). The product was prepared according to representative procedure A. Additional purification *via* recrystallization from methanol yielded the product as a white solid (17.5 g, 72%): ^1H NMR (500 MHz, CDCl_3) δ 8.41 (s, 1H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.28 – 7.18 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 159.1, 151.8, 135.3, 132.2, 130.3, 129.4, 126.4, 126.0, 121.0 ppm.. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{BrN}$ $[\text{M} + \text{H}]^+$ 260.0075, found 260.0070.

2. N-(4-cyanobenzylidene)aniline (5.1b). The product was prepared according to representative procedure A. Additional purification *via* recrystallization from methanol yielded the product as a white solid (7.12 g, 84%): ^1H NMR (500 MHz, CDCl_3) δ 8.50 (s, 1H), 8.02 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.0, 151.1, 140.1, 132.7, 129.4, 129.2, 127.1, 121.1, 118.6, 114.5 ppm; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2$ $[\text{M} + \text{H}]^+$ 207.0922, found 207.0925.

3. N-(4-nitrobenzylidene)aniline (5.1c). A mixture of aniline (7.38 g, 7.24 mL, 79.3 mmol), *p*-nitrobenzaldehyde (10.0g, 66.2 mmol), *p*-toluenesulfonic acid mono hydrate (0.02 g, 0.10 mmol), 3 Å molecular sieves (20 g) in toluene (135 mL) was sealed in a pressure vessel and stirred at 130 °C for 16 hours. The reaction mixture was then cooled to room temperature and filtered through celite. Subsequently, the solvent was removed *in vacuo* and the crude product was purified *via* recrystallization from methanol to yield a white solid (9.72 g, 65%): ^1H NMR (500 MHz, CDCl_3) δ 8.56 (s, 1H), 8.33 (d, $J = 8.7$ Hz, 2H), 8.08 (d, $J = 8.8$ Hz, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.33 –

7.25 (m, 3H)); ^{13}C NMR (126 MHz, CDCl_3) δ 157.5, 151.0, 149.4, 141.7, 129.52, 129.46, 127.2, 124.1, 121.1 ppm. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$ 227.0821, found 227.0852.

4. N-benzylideneaniline (5.1d). The product was prepared according to representative procedure A. The product was isolated as a white solid (16.3 g, 96%): ^1H NMR (500 MHz, CDCl_3) δ 8.45 (s, 1H), 7.96 – 7.85 (m, 2H), 7.52 – 7.43 (m, 3H), 7.39 (t, $J = 7.9$ Hz, 2H), 7.24 – 7.18 (m, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.6, 152.2, 136.3, 131.5, 129.3, 128.93, 128.90, 126.1, 121.0 ppm. HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{N}$ $[\text{M} + \text{H}]^+$ 182.0970, found 182.0979.

5. N-(4-octylbenzylidene)aniline (5.1e). The product was prepared according to representative procedure A. Additional purification *via* flash chromatography using deactivated silica gel and pentane as the mobile phase yielded the product as a white solid (4.85 g, 59%): ^1H NMR (500 MHz, CDCl_3) δ 8.42 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 2H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.23 – 7.18 (m, 3H), 2.66 (t, $J = 7.7$ Hz, 2H), 1.64 (t, $J = 7.5$ Hz, 2H), 1.40 – 1.20 (m, 10H), 0.88 (t, $J = 6.7$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.5, 152.5, 147.0, 134.0, 129.2, 129.00, 128.95, 125.8, 121.0, 36.2, 32.0, 31.4, 29.6, 29.42, 29.39, 22.8, 14.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{27}\text{N}$ $[\text{M} + \text{H}]^+$ 294.2222, found 294.2214.

6. N-(4-bromo-2,6-difluorobenzylidene)aniline (5.1f). The product was prepared according to representative procedure A. The product was isolated as a white solid (24.6 g, 93%): ^1H NMR (500 MHz, CDCl_3) δ 8.59 (s, 1H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.28 (d, $J = 7.3$ Hz, 1H), 7.26 – 7.19 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.0, 162.90, 160.87, 160.8, 152.3, 150.5, 129.4, 126.9,

125.0, 120.9, 116.5, 116.3, 113.3ppm; HRMS (ESI) m/z calcd for $C_{13}H_8NBrF_2$ $[M + Na]^+$ 317.9706, found 317.9714.

7. N-(2,4,6-trimethylbenzylidene)aniline (5.1g). The product was prepared according to representative procedure A. Additional purification *via* flash chromatography using deactivated silica gel and 1/9 ethyl; acetate/hexanes as the mobile phase yielded the product as a white solid (19.8 g, 94%): 1H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.17 (d, $J = 7.3$ Hz, 2H), 6.93 (s, 2H), 2.53 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 153.2, 140.0, 138.7, 130.7, 129.9, 129.2, 125.7, 120.9, 21.4, 21.2 ppm; HRMS (ESI) m/z calcd for $C_{16}H_{17}NO$ $[M + H]^+$ 224.1439, found 224.1440.

8. N-(3,5-didodecylbenzylidene)aniline (5.1h). A mixture of aniline (0.214 g, 0.21 mL, 2.29 mmol), 3,5-didodecylbenzaldehyde^{S1} (1.00g, 2.26 mmol), glacial acetic acid (ca. ~0.1 mL), molecular sieves (1.0 g), in toluene (30 mL) was sealed in a pressure vessel and stirred at 150 °C for 16 hours. The reaction mixture was then cooled to room temperature and filtered through celite. Subsequently, the solvent was removed *in vacuo* to yield the product as a brown oil (1.10 g, 94%): 1H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.54 (s, 2H), 7.44 – 7.36 (m, 2H), 7.25 – 7.17 (m, 3H), 7.13 (s, 1H), 2.66 – 2.62 (m, 4H), 1.65 (q, $J = 7.4$ Hz, 4H), 1.38 – 1.22 (m, 44H), 0.88 (t, $J = 6.9$ Hz, 7H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 143.7, 132.2, 129.3, 126.5, 125.9, 121.02, 36.0, 32.1, 31.7, 29.84, 29.83, 29.81, 29.76, 29.7, 29.5, 22.9, 14.3 ppm; MALDI (dithranol) m/z calcd for $C_{37}H_{59}N$ $[M + H]^+$ 518.5, found 518.4.

9. N-(4-methoxybenzylidene)aniline (5.1i). The product was prepared according to representative procedure A. Additional purification *via* recrystallization from methanol yielded the product as a white solid (17.1 g, 86%): ^1H NMR (500 MHz, CDCl_3) δ 8.39 (s, 1H), 7.86 (d, J = 8.7 Hz, 2H), 7.42 – 7.35 (m, , 2H), 7.25 – 7.18 (m, 3H), 6.99 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.4, 159.9, 152.5, 130.6, 129.4, 129.2, 125.7, 121.0, 114.3, 55.6 ppm. HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{NO}$ $[\text{M} + \text{Na}]^+$ 234.0895, found 234.0906.

10. 9,10-bis((triisopropylsilyl)ethynyl)anthracene (SI-5.1). Triisopropylsilylacetylene (13.4 g, 16.5 mL, 73.6 mmol) was dissolved in tetrahydrofuran (100 mL) in a 2-neck round bottom flask under argon and cooled to -78°C . *n*-Butyllithium (27.6 mL, 2.5 M hexanes, 69.0 mmol) was added to the solution over 10 minutes *via* syringe pump. After 1 hour, the vessel was warmed to 0°C for 5 minutes and then again cooled to -78°C . Subsequently, 9,10-Anthraquinone (6.02 g, 28.9 mmol) was dissolved in tetrahydrofuran (150 mL) in a 2-neck round bottom flask under argon and cooled to -78°C , and the contents of the vessel containing triisopropylsilylacetylene and *n*-butyllithium was transferred to this solution *via* cannula needle. After one hour of stirring at -78°C , the mixture was brought to 0°C . After 15 hours the solution was warmed to 20°C and stirred for 30 minutes. Next, the solution was diluted with diethyl ether (200 mL) and washed with water ($300\text{ mL} \times 3$). The organics were in turn dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo* to yield 13.2 g of an off-white solid. This solid was then dissolved in tetrahydrofuran (300 mL), and anhydrous SnCl_2 (21.9 g, 115 mmol) was added to the flask. The reaction flask was heated to 60°C for 16 hours. Subsequently, the solution cooled to room temperature, diluted with diethyl ether (300 mL), and washed with water ($300\text{ mL} \times 3$). The organics were dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The final crude product was

purified by the flash chromatography with hexanes as the mobile phase to yield a yellow solid (4.00 g, 26%). ^1H NMR (500 MHz, CDCl_3) δ 8.63 (dd, $J = 6.6, 3.3$ Hz, 4H), 7.60 (dd, $J = 6.7, 3.2$ Hz, 4H), 1.40 – 1.15 (m, 42); ^{13}C NMR (126 MHz, CDCl_3) δ 132.6, 127.4, 126.9, 118.8, 105.0, 103.5, 19.1, 11.7 ppm. MALDI (dithranol) m/z calcd for $\text{C}_{36}\text{H}_{50}\text{Si}_2$ $[\text{M}]^+$ 538.3, found 538.3.

11. 9,10-Diethynylanthracene (5.2). Compound **SI-5.1** (4.00 g, 7.42 mmol) was dissolved in tetrahydrofuran (80 mL) and argon was bubbled through the solution for 5 minutes. The reaction vessel was then cooled to -78°C , and tetrabutylammonium fluoride (16.5 mL, 1.0 M in tetrahydrofuran, 16.5 mmol) was added over 10 minutes *via* syringe pump. After 30 minutes, the solution was warmed to 0°C and held at this temperature for 5 minutes. Subsequently, a saturated aqueous sodium bicarbonate solution (30 mL) was slowly added to the reaction mixture. The reaction mixture was then diluted with chloroform (300 mL) and washed with water (200 mL $\times$ 3). The organics were removed *in vacuo* and the crude material was purified by rinsing with hexanes (50 mL) to yield the product as an orange solid (1.47 g, 88%). ^1H NMR (600 MHz, CDCl_3) δ 8.61 (dd, $J = 6.6, 3.3$ Hz, 4H), 7.62 (dd, $J = 6.7, 3.2$ Hz, 4H), 4.07 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 132.6, 127.19, 127.17, 118.0, 90.0, 80.3 ppm; MALDI (HABA) m/z calcd for $\text{C}_{18}\text{H}_{10}$ $[\text{M}]^+$ 226.1, found 226.1.

12. 9,10-bis(2-(4-bromophenyl)quinolin-4-yl)anthracene (5.3a). The product was prepared according to representative procedure B. The crude product was washed with acetone (40 mL), followed by a wash with pentane (40 mL) to yield a light ivory solid (0.543 g, 80%): ^1H NMR (500 MHz, CDCl_3) δ 8.41 (br s, 2H), 8.23 – 8.14 (m, 4H), 8.10 (s, 0.85H), 8.03 (s, 1.16H), 7.85 – 7.78 (m, 2H), 7.72 – 7.66 (m, 4H), 7.53 – 7.49 (m, 4H), 7.45 – 7.29 (m, 8H); ^{13}C NMR (126 MHz,

CDCl_3) δ 132.3, 129.9, 129.5, 127.9, 126.7, 126.5, 126.4, 121.6 ppm; HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{26}\text{N}_2\text{Br}_2$ $[\text{M} + \text{H}]^+$ 741.0541, found 741.0540.

13. 9,10-bis(2-(4-cyanophenyl)quinolin-4-yl)anthracene (5.3b). The product was prepared according to representative procedure B. The crude product was washed with acetone (40 mL), followed by a wash with pentane (40 mL) to yield a light ivory solid (0.416 g, 75%): ^1H NMR (500 MHz, CDCl_3) δ 8.47 – 8.39 (m, 6H), 8.14 (s, 0.33), 8.08 (s, 1.49H), 7.88 – 7.82 (m, 6H), 7.52 – 7.48 (m, 4H), 7.47 – 7.27 (m, 8.82H), 7.14 (d, $J = 7.9$ Hz, 0.64H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.8, 133.3, 132.9, 130.8, 130.5, 130.0, 128.7, 128.5, 128.3, 128.0, 127.0, 126.8, 126.6, 126.5, 125.4, 121.6, 118.9, 113.2 ppm; MALDI (dithranol) m/z calcd for $\text{C}_{46}\text{H}_{27}\text{N}_4$ $[\text{M} + \text{H}]^+$ 635.2, found 635.2.

14. 9,10-bis(2-(4-nitrophenyl)quinolin-4-yl)anthracene (5.3c). The product was prepared according to representative procedure B. The crude product was washed with acetone (40 mL), followed by a wash with pentane (40 mL) to yield a yellow solid (0.423 g, 71%): ^1H NMR (500 MHz, CDCl_3) δ 8.51 (d, $J = 8.8$ Hz, 1.15H), 8.48 (d, $J = 8.8$ Hz, 2.90H), 8.45 – 8.38 (m, 6H), 8.18 (s, 0.52H), 8.11 (s, 1.44H), 7.88 – 7.83 (m, 2H), 7.54 – 7.49 (m, 4H), 7.48 – 7.39 (m, 2H), 7.37 – 7.29 (m, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 154.5, 148.9, 148.7, 147.5, 145.3, 133.3, 130.9, 130.7, 130.0, 128.63, 128.61, 128.2, 128.0, 126.7, 126.6, 126.4, 124.3, 121.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{26}\text{N}_2\text{Br}_2$ $[\text{M} + \text{H}]^+$ 675.2032, found 675.2050.

15. 9,10-bis(2-phenylquinolin-4-yl)anthracene (5.3d). The product was prepared according to representative procedure B. The crude product was washed with acetone (40 mL), followed by a

wash with pentane (40 mL) to yield a light ivory solid (0.338 g, 65%): ^1H NMR (500 MHz, CDCl_3) δ 8.44 – 8.36 (m, 2H), 8.34 – 8.26 (m, 4H), 8.14 (s, 0.56H), 8.09 (s, 1.44H), 7.87 – 7.73 (m, 2H), 7.59 – 7.46 (m, 10H), 7.43 – 7.36 (m, 2H), 7.35 – 7.28 (m, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.1, 148.8, 146.6, 139.5, 133.5, 130.3, 130.1, 130.0, 129.6, 129.0, 127.7, 126.9, 126.7, 126.23, 126.17, 126.1, 121.9 ppm; HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{28}\text{N}_2$ $[\text{M} + \text{H}]^+$ 585.2331, found 585.2318.

16. 9,10-bis(2-(4-octylphenyl)quinolin-4-yl)anthracene (5.3e). The product was prepared according to representative procedure B. The crude product was washed with hexanes (100 mL) followed by flash chromatography with chloroform as the mobile phase to yield an ivory solid (0.466 g, 65%): ^1H NMR (500 MHz, CDCl_3) δ 8.40 – 8.34 (m, 2H), 8.24 – 8.17 (m, 4H), 8.12 (s, 0.64 H), 8.07 (s, 1.36 H), 7.84 – 7.72 (m, 2H), 7.57 – 7.51 (m, 4H), 7.39 – 7.27 (m, 12H), 2.73 – 2.65 (m, 4H), 1.73 – 1.62 (m, 4H), 1.47 – 1.20 (m, 20H), 0.88 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.2, 148.9, 146.6, 144.9, 137.0, 133.6, 130.0, 129.2, 127.7, 126.9, 126.3, 126.2, 125.4, 121.9, 39.5, 36.0, 32.0, 31.6, 29.7, 29.4, 22.8, 14.3 ppm; HRMS (ESI) m/z calcd for $\text{C}_{60}\text{H}_{60}\text{N}_2$ $[\text{M} + \text{H}]^+$ 809.4835, found 809.4807.

17. 9,10-bis(2-(4-bromo-2,6-difluorophenyl)quinolin-4-yl)anthracene (5.3f). The product was prepared according to representative procedure B. The crude product was washed with acetone (40 mL), followed by a wash with pentane (40 mL) to yield a light ivory solid (0.443 g, 62%): ^1H NMR (500 MHz, CDCl_3) δ = 8.43 – 8.37 (m, 2H), 7.86 – 7.77 (m, 3.40H), 7.72 (s, 0.56), 7.56 – 7.51 (m, 4H), 7.48 – 7.28 (m, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ = 161.7, 159.71, 159.65, 149.1, 149.0, 148.8, 146.41, 146.40, 132.93, 132.92, 130.53, 130.50, 130.47, 130.42, 130.36, 130.0,

129.5, 128.0, 127.9, 126.7, 126.44, 126.42, 126.41, 126.00, 125.99, 122.8, 117.9, 116.33, 116.28, 116.2, 116.11, 116.10 ppm; HRMS (ESI) m/z calcd for $C_{44}H_{22}N_2Br_2F_4 [M + H]^+$ 813.0164, found 813.0174.

18. 9,10-bis(2-(2,4,6-trimethylphenyl)quinolin-4-yl)anthracene (5.3g). The product was prepared according to representative procedure B. Additional purification *via* flash chromatography with chloroform as the mobile phase yielded the product as an ivory solid (0.320 g, 52%): 1H NMR (500 MHz, $CDCl_3$) δ = 8.37 (d J = 8.3 Hz, 2H), 7.83 – 7.73 (m, 2H), 7.59 (s, 2H), 7.57 – 7.50 (m, 4H), 7.39 – 7.30 (m, 6H), 7.27 – 7.21 (m, 2 H), 6.99 (s, 4H), 2.35 (s, 6H), 2.25 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 160.6, 148.8, 146.0, 137.89, 137.88, 137.8, 135.70, 135.69, 133.3, 130.24, 130.18, 130.00, 129.98, 129.96, 128.7, 127.4, 127.03, 126.99, 126.67, 126.65, 126.4, 126.3, 126.2, 126.1, 126.0, 22.5, 21.31, 21.29, 20.6, 14.2 ppm; HRMS (ESI) m/z calcd for $C_{50}H_{40}N_2 [M + H]^+$ 669.3270, found 669.3284.

19. 9,10-bis(2-(3,5-didodecylphenyl)quinolin-4-yl)anthracene (5.3h). The product was prepared according to representative procedure B. Additional purification *via* flash chromatography with dichloromethane as the mobile phase yielded the product as a light ivory solid (0.487 g, 44%): 1H NMR (500 MHz, $CDCl_3$) δ = 8.43 – 8.38 (m, 2H), 8.12 (s, 0.83H), 8.07 (s, 1.23H), 7.94 – 7.88 (m, 4H), 7.78 (q, J = 9.5, 8.6 Hz, 2H), 7.58 – 7.53 (m, 4H), 7.41 – 7.25 (m, 8H), 7.14 – 7.13 (m, 2H), 2.74 – 2.65 (m, 8H), 1.74 – 1.65 (m, 8H), 1.42 – 1.18 (m, 76H), 0.91 – 0.85 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 157.7, 148.9, 146.5, 143.8, 139.4, 133.7, 130.4, 130.2, 130.0, 127.8, 126.9, 126.2, 125.3, 122.3, 36.3, 32.1, 31.90, 31.85, 29.84, 29.80, 29.79,

29.71, 29.65, 29.5, 22.9, 14.3 ppm ; MALDI (dithranol) m/z calcd for $C_{92}H_{125}N_2$ $[M + H]^+$ 1258.0, found 1257.8.

20. 9,10-bis(2-(4-methoxyphenyl)quinolin-4-yl)anthracene (5.3i). The product was prepared according to representative procedure B. Additional purification *via* flash chromatography with chloroform as the mobile phase yielded the product as a light ivory solid (0.087 g, 15%): 1H NMR (500 MHz, $CDCl_3$) δ = 8.39 – 8.34 (m, 2H), 8.30 – 8.23 (m, 4H), 8.09 (s, 0.58H), 8.03 (s, 1.44H), 7.80 – 7.73 (m, 2H), 7.57 – 7.52 (m, 4H), 7.36 – 7.28 (m, 7.23H), 7.24 – 7.21 (m, 0.66H), 7.09 – 7.05 (m, 4H), 3.90 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 161.2, 156.7, 148.9, 130.1, 130.0, 129.2, 127.6, 126.9, 126.6, 126.3, 126.2, 121.5, 114.5, 55.6 ppm; HRMS (ESI) m/z calcd for $C_{46}H_{32}N_2O_2$ $[M + H]^+$ 645.2542, found 645.2534.

21. Poly[2,2'-bis(3,5-didodecylphenyl)-8,8'-dimethyl-6,6'-biquinoline-4-4'-(9-anthracenyl)-diyl] (5.5). A solution of aldimine **5.4**^{SI} (0.400 g, 0.377 mmol), 9,10-Diethynylantracene **2** (0.085 g, 0.377 mmol), chloranil (0.186 g, 0.756 mmol), $BF_3 \cdot OEt_2$ (0.11 g, 0.096 mL, 0.75 mmol), in toluene (20 mL) was sealed in a pressure vessel and stirred at 150 °C for 48 hours. The reaction mixture was then cooled to room temperature and then washed with saturated aqueous sodium bicarbonate (50 mL $\times$ 3). Subsequently, the organics were filtered through a cotton plug and the solvent was removed *in vacuo*. The crude mixture was dissolved in toluene (10 mL) and 2,3-dichloro-5,6-cyano-1,4-benzoquinone (0.11 g, 0.48 mmol) was added to the mixture. After 24 hours of stirring at room temperature, the mixture was diluted with CH_2Cl_2 (10 mL), and the reagents were then quenched with saturated aqueous sodium bicarbonate (10 mL). The organics were washed with saturated aqueous sodium bicarbonate (50 mL $\times$ 3) and the remaining solids

filtered. Next, the solvent was removed *in vacuo* and the crude polymer was dissolved in dichloromethane and precipitated from ethanol. The polymer was further purified by size exclusion chromatography (Bio-Bead SX-1 resin with benzene as the mobile phase) to yield the product as a dark brown solid (0.045 g, 9%): ^1H NMR (500 MHz, CDCl_3) δ = 8.50 – 7.28 (br m, 12H), 7.25 – 6.35 (br m, 5H), 3.29 – 0.52 (br m, 106H); ^{13}C NMR (126 MHz, CDCl_3) δ = 32.1, 29.8, 29.5, 22.8, 14.3.; SEC (vs polystyrene standards) M_n = 15.3 kg mol $^{-1}$, a M_w = 22.7 kg mol $^{-1}$, and PDI = 1.48

22. One pot procedure for: 9,10-bis(2-phenylquinolin-4-yl)anthracene (5.3d). A solution of Aniline (0.490 g, 0.48 mL, 5.26 mmol), benzaldehyde (0.563 g, 5.31 mmol), glacial acetic acid (ca. ~.05 mL), molecular sieves (2.0 g) in chloroform (60 mL) was heated to 70 °C. After 24 hours, the reaction mixture was cooled and 9,10-Diethynylanthracene (**5.2**) (0.400 g, 1.77 mmol), chloranil (0.868 g, 3.53 mmol), and $\text{BF}_3 \cdot \text{OEt}_2$ (0.78 g, 0.68 mL, 5.51 mmol) were added to the reaction and the flask was again heated to 70 °C. After an additional 48 hours, the mixture was cooled and diluted with chloroform (100 mL). Subsequently, the organics were washed with a saturated aqueous sodium bicarbonate solution (100 mL $\times$ 3) and water (100 mL $\times$ 3). The organic layer was diluted with chloroform (3000 mL) and filtered through celite and the solvent was removed *in vacuo*. The crude product was washed with acetone (80 mL) and then purified by flash chromatography using dichloromethane as the mobile phase to yield a light ivory solid (0.750 g, 72%). *The characterization data matched the data obtained for the two-pot procedure for the formation of 5.3d*

23. One pot procedure for: 9,10-bis(2-(4-octylphenyl)quinolin-4-yl)anthracene (5.3e). A solution of Aniline (0.245 g, 0.24 mL, 2.63 mmol), *p*-octylbenzaldehyde (0.578 g, 0.62 mL, 2.65

mmol), glacial acetic acid (ca. ~.05 mL), molecular sieves (1.0 g) in chloroform (30 mL) was heated to 70 °C. After 24 hours, the reaction mixture was cooled and 9,10-Diethynylanthracene (**5.2**) (0.200 g, 0.885 mmol), chloranil (0.434 g, 1.76 mmol) and BF₃•OEt₂ (0.391 g, 0.34 mL, 2.75 mmol) were added to the reaction and the flask was again heated to 70 °C. After an additional 72 hours, the mixture was cooled and diluted with chloroform (100 mL). Subsequently, the organics were washed with a saturated aqueous sodium bicarbonate solution (100 mL × 3) and water (100 mL × 3). The organic layer was diluted with chloroform (1500 mL) and filtered through celite and the solvent was removed *in vacuo*. The crude product was washed with hexanes (40 mL), followed by a wash with acetone (10 mL) to yield the product as an ivory solid (0.547 g, 76%). *The characterization data matched the data obtained for the two-pot procedure for the formation of 5.3e.*

5.5.4. Compiled Spectroscopic and Analytical Data

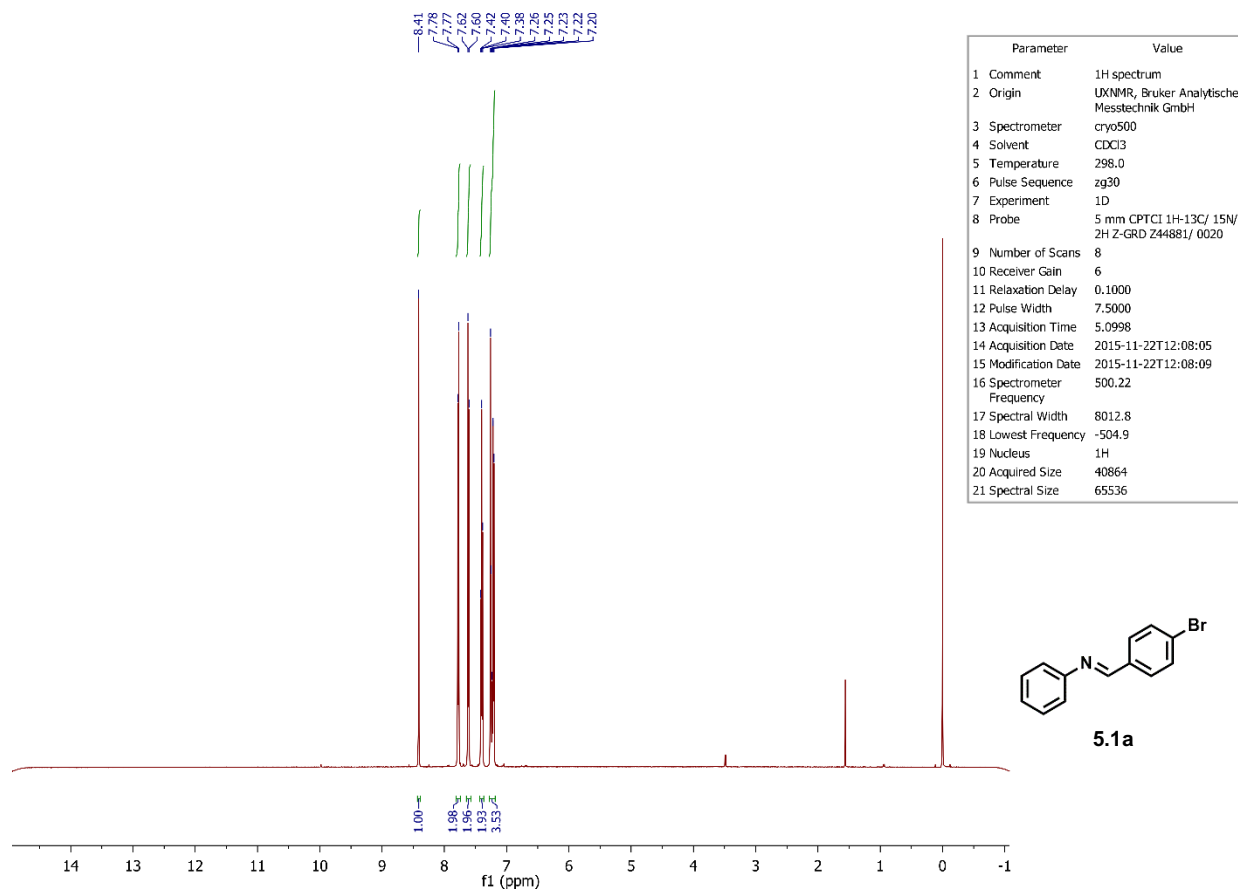


Figure S5.1. The ^1H NMR spectrum obtained for **5.1a**.

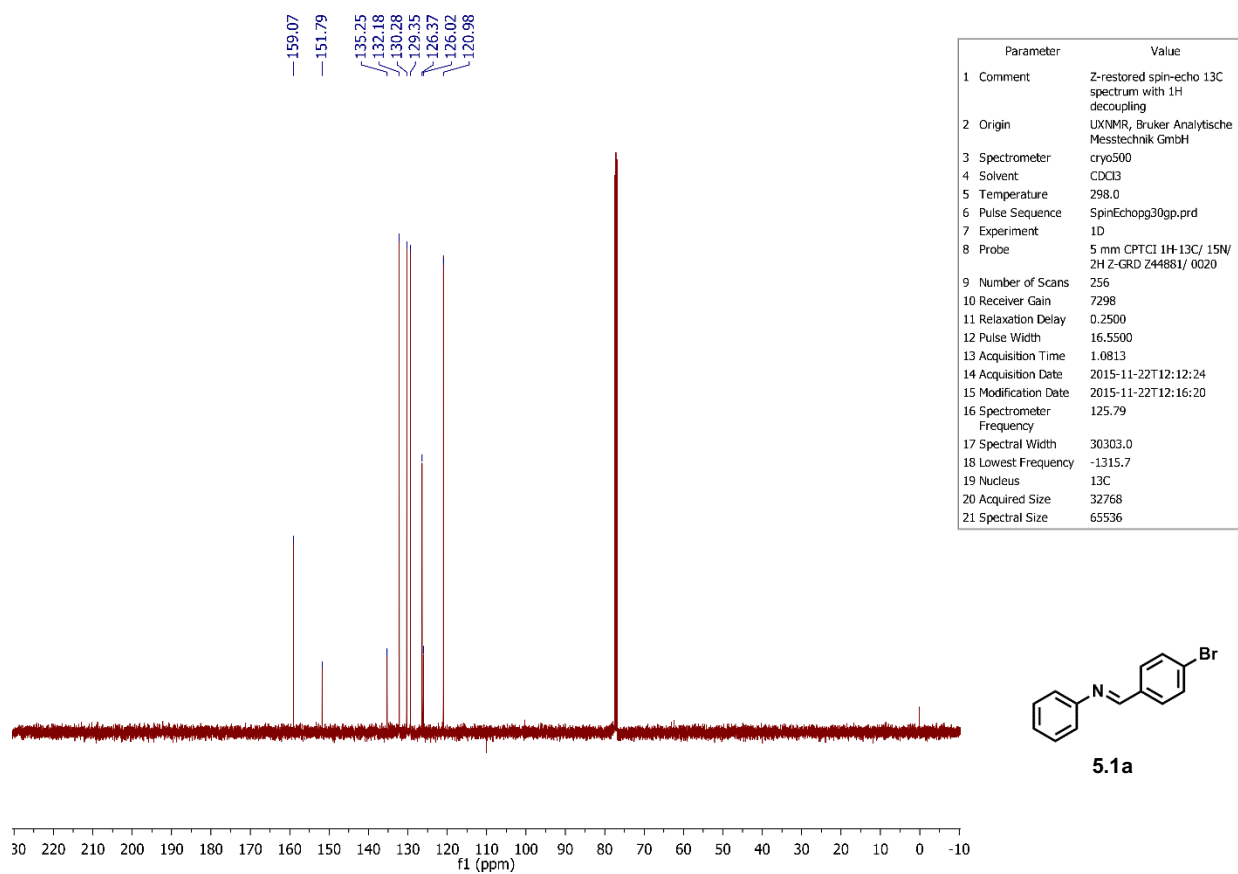


Figure S5.2. The ^{13}C NMR spectrum obtained for **5.1a**.

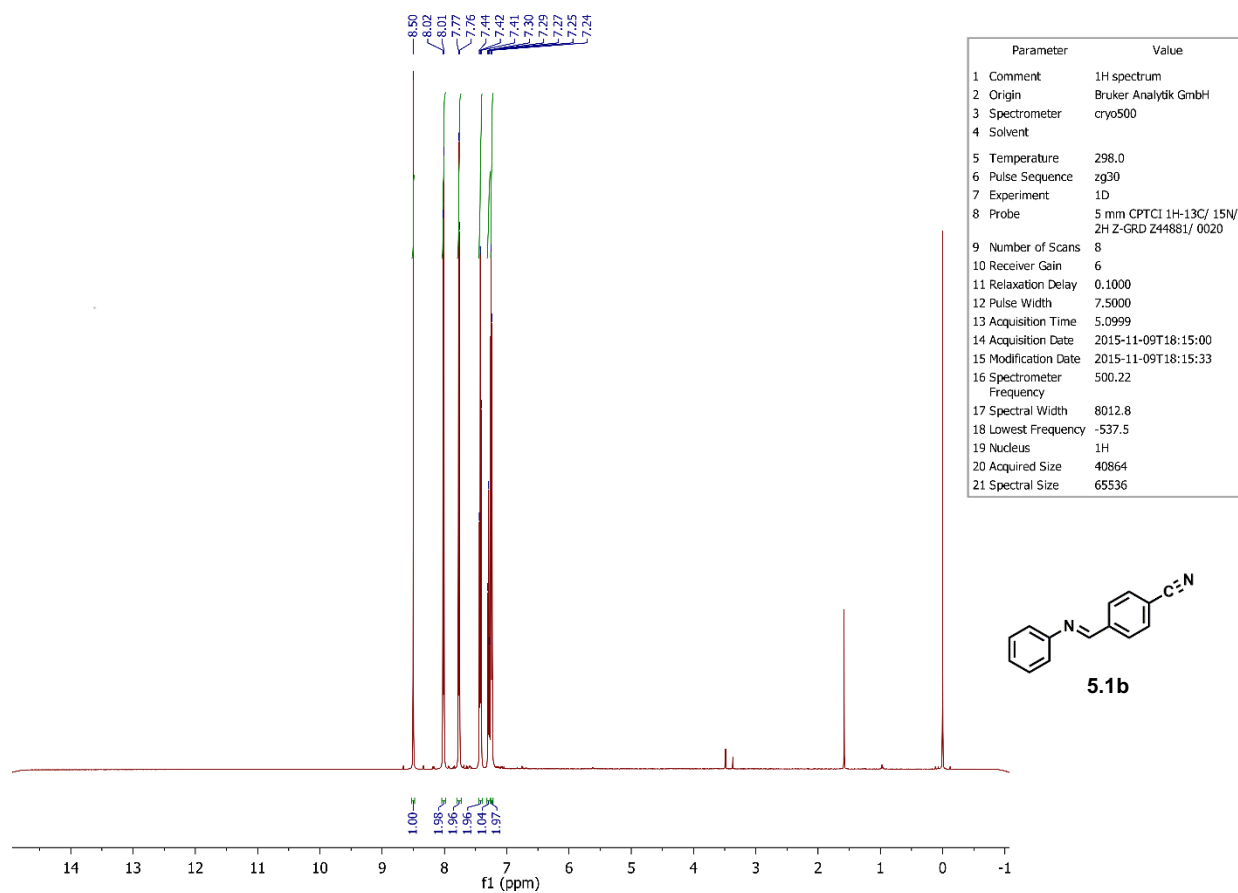


Figure S5.3. The ^1H NMR spectrum obtained for **5.1b**.

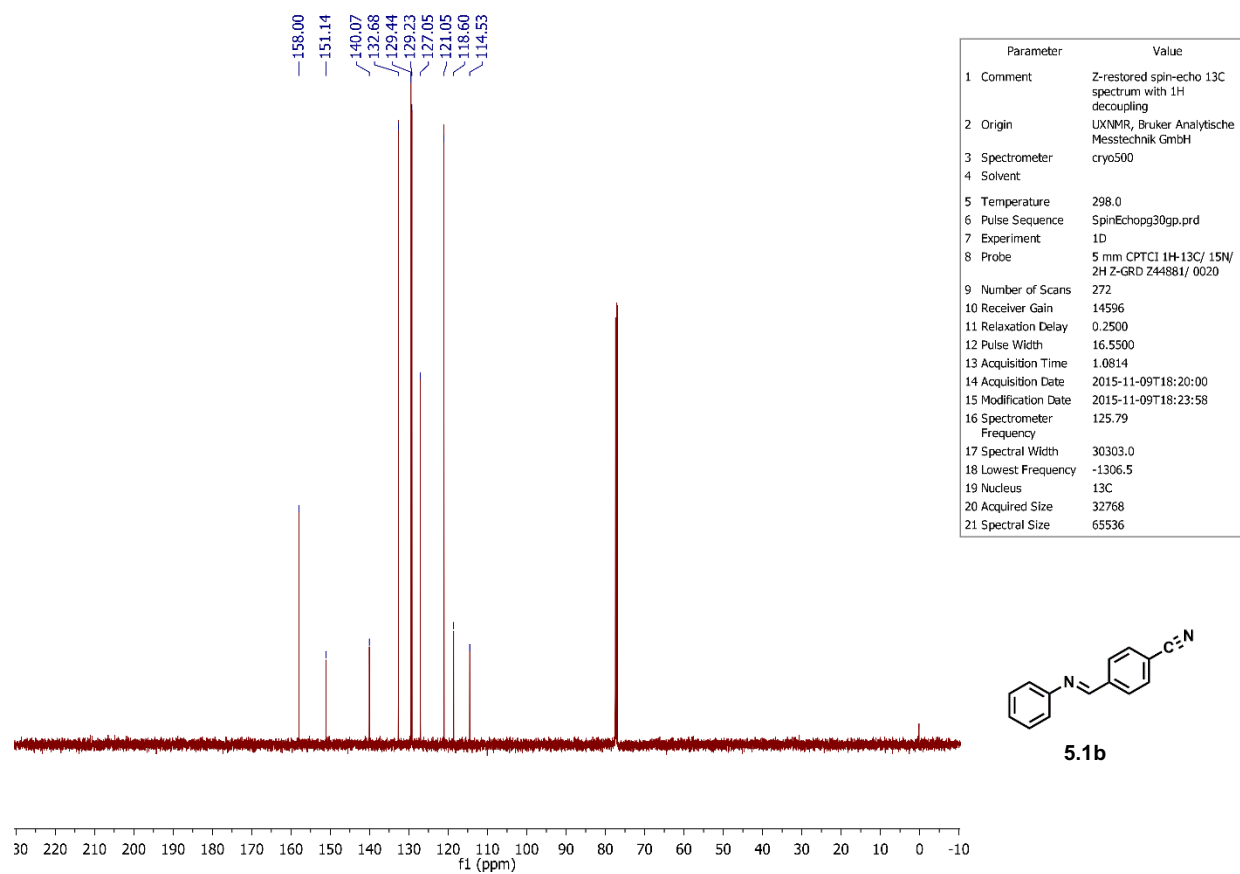


Figure S5.4. The ^{13}C NMR spectrum obtained for **5.1b**.

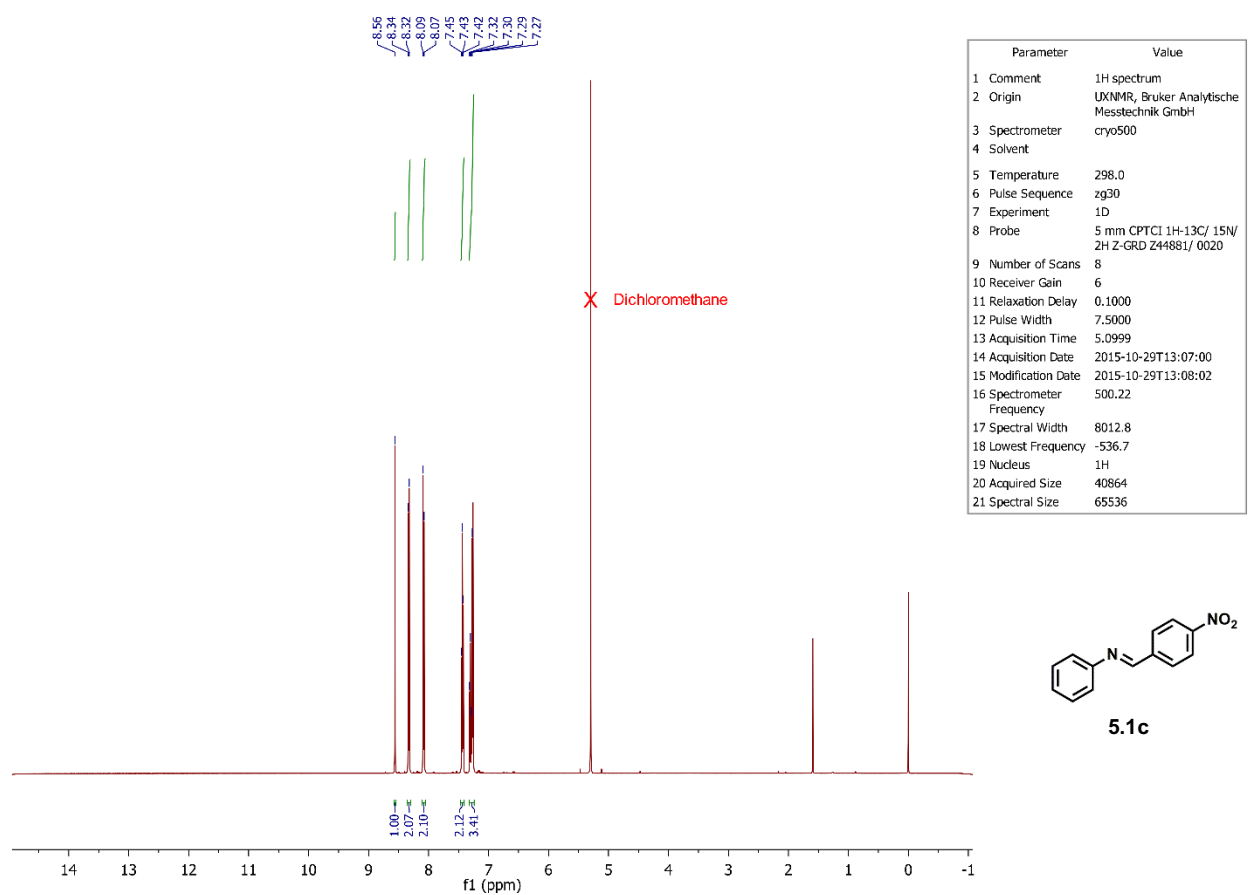


Figure S5.5. The ^1H NMR spectrum obtained for **5.1c**.

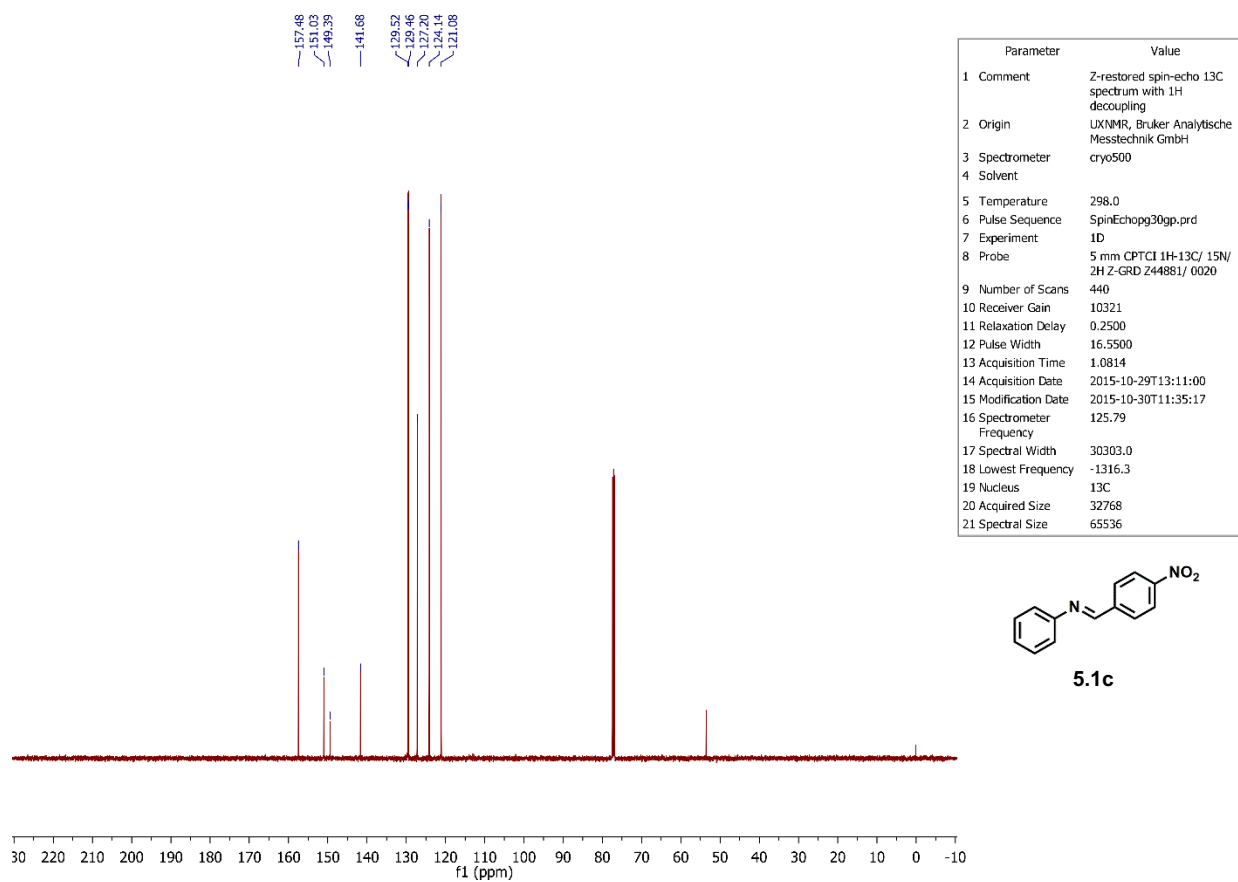


Figure S5.6. The ^{13}C NMR spectrum obtained for **5.1c**.

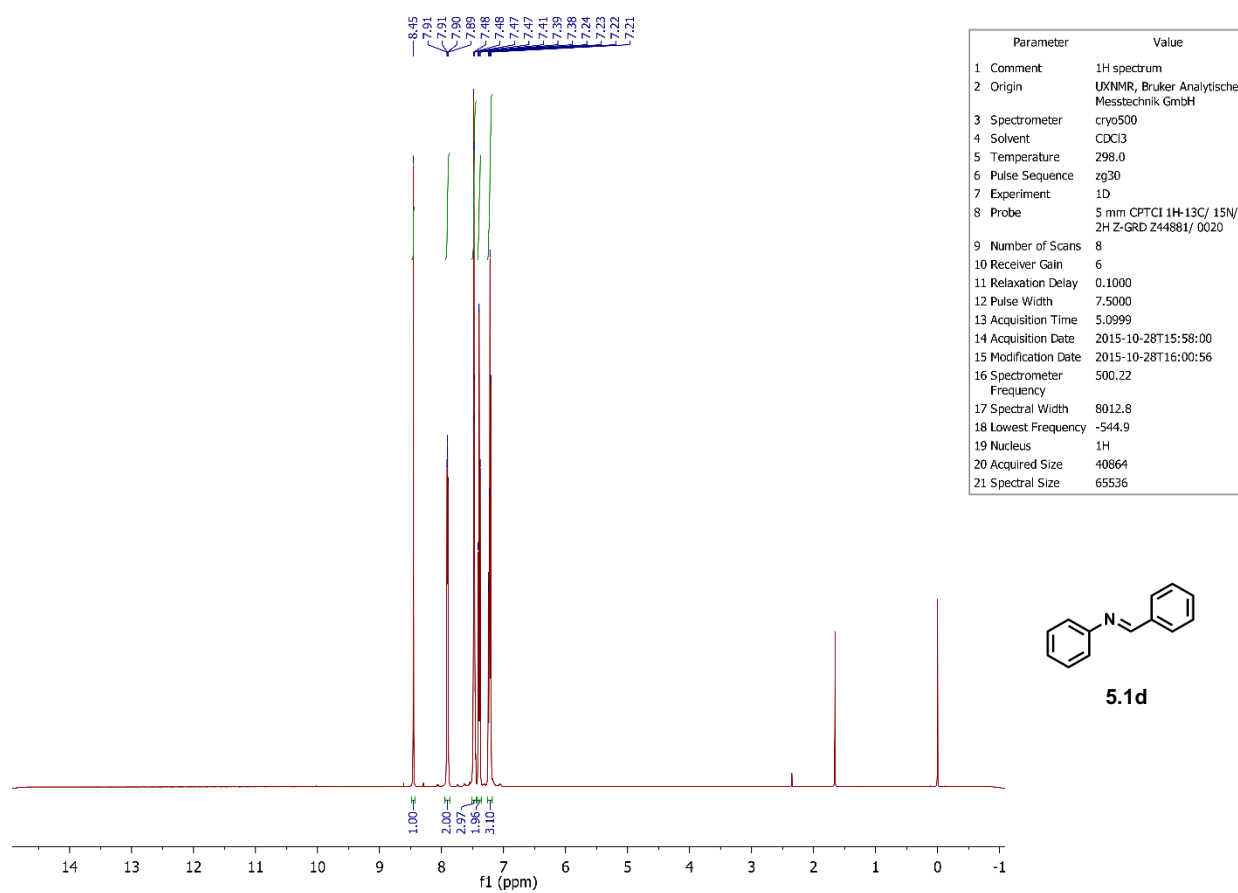


Figure S5.7. The ¹H NMR spectrum obtained for **5.1d**.

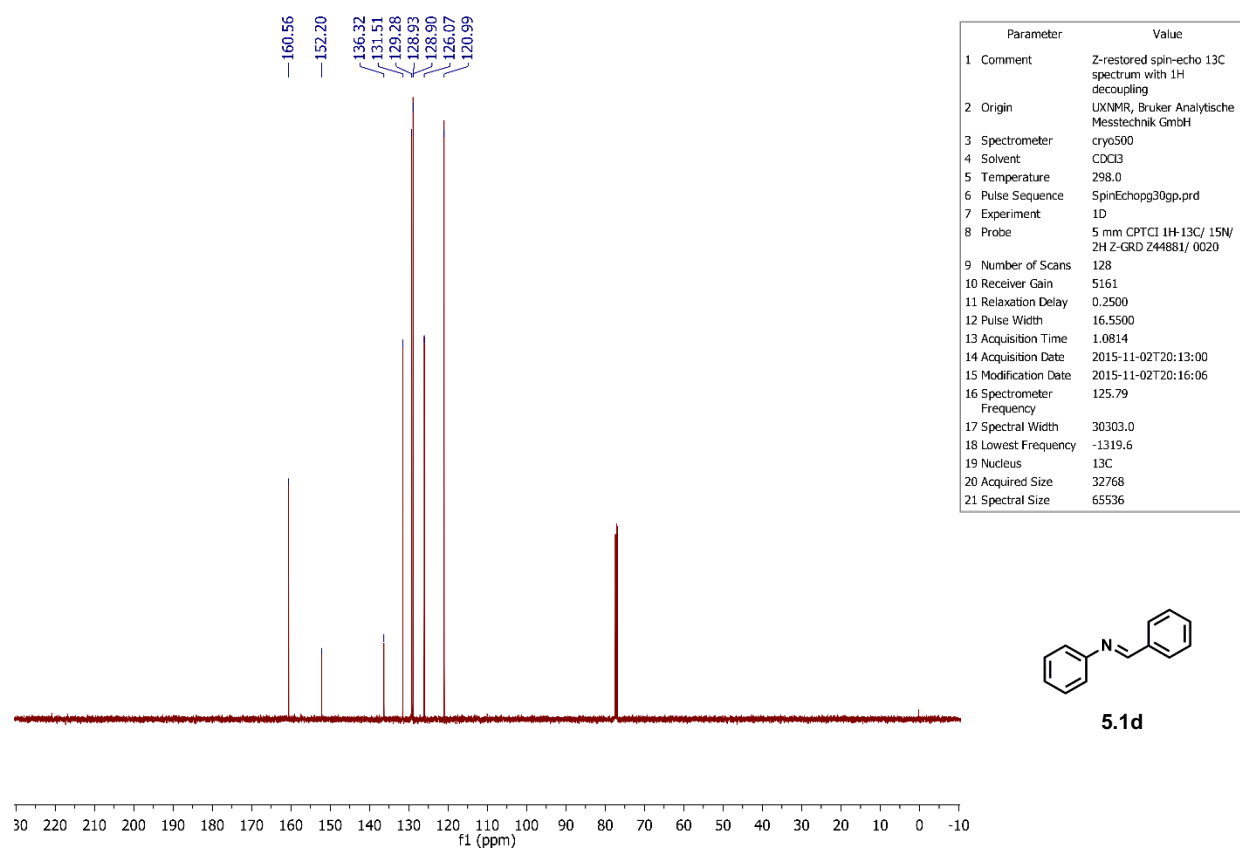


Figure S5.8. The ^{13}C NMR spectrum obtained for **5.1d**.

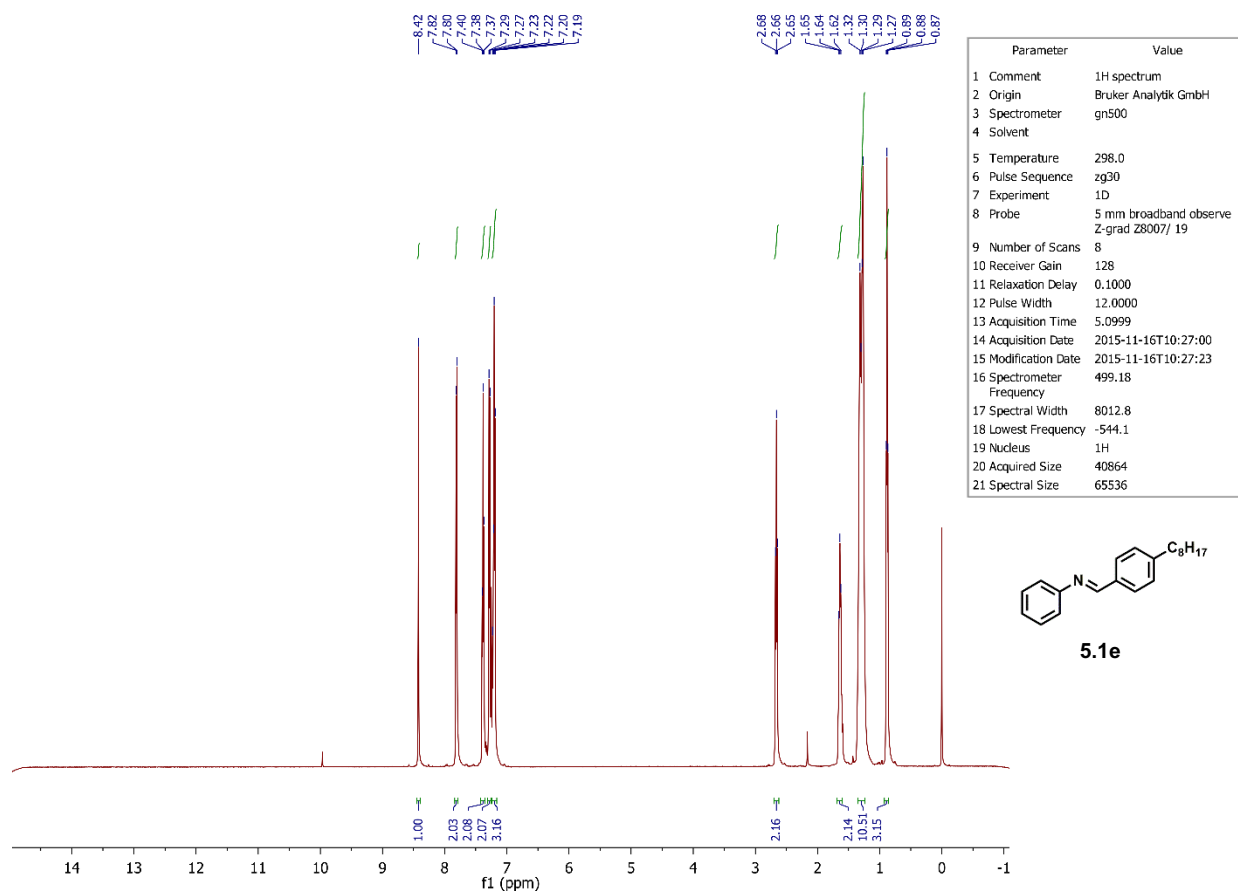


Figure S5.9. The ^1H NMR spectrum obtained for **5.1e**.

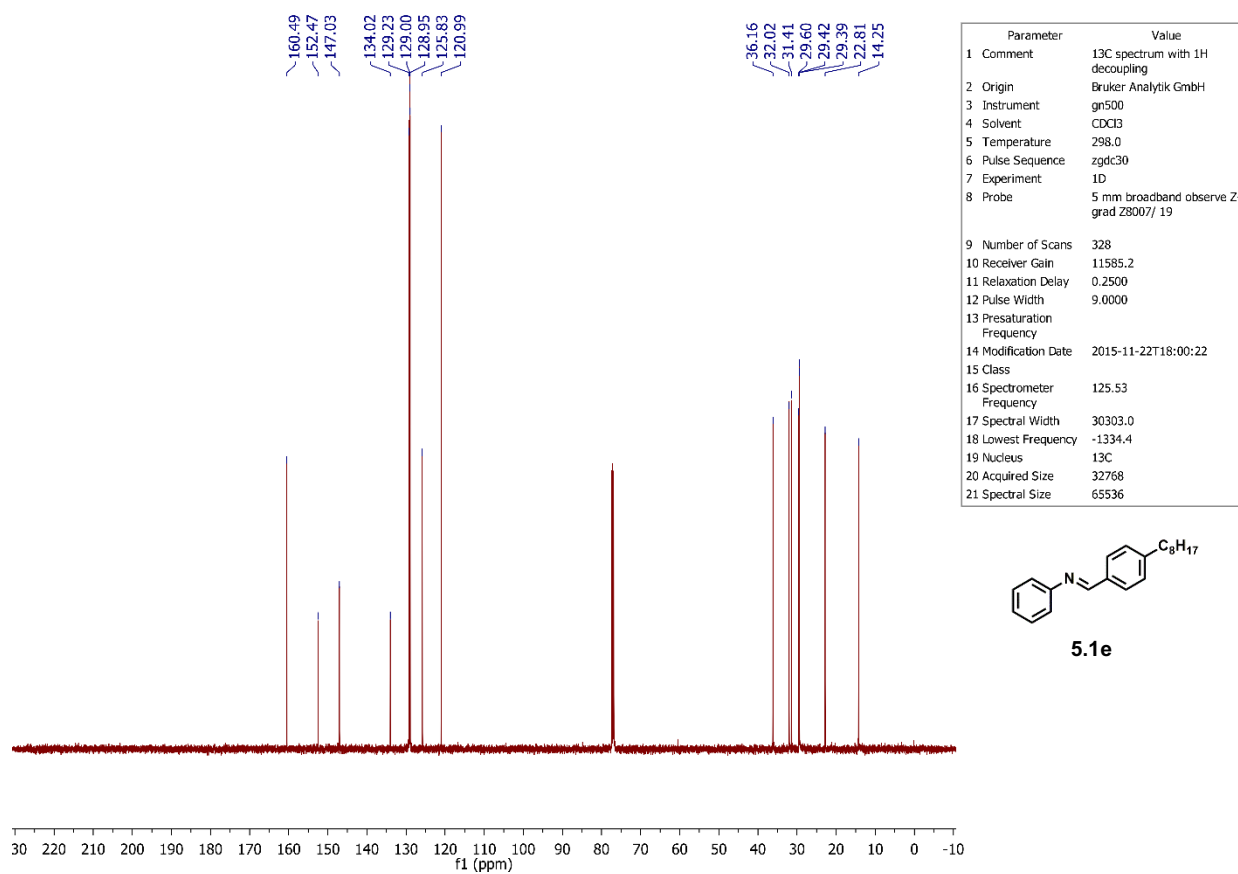


Figure S5.10. The ¹³C NMR spectrum obtained for **5.1e**.

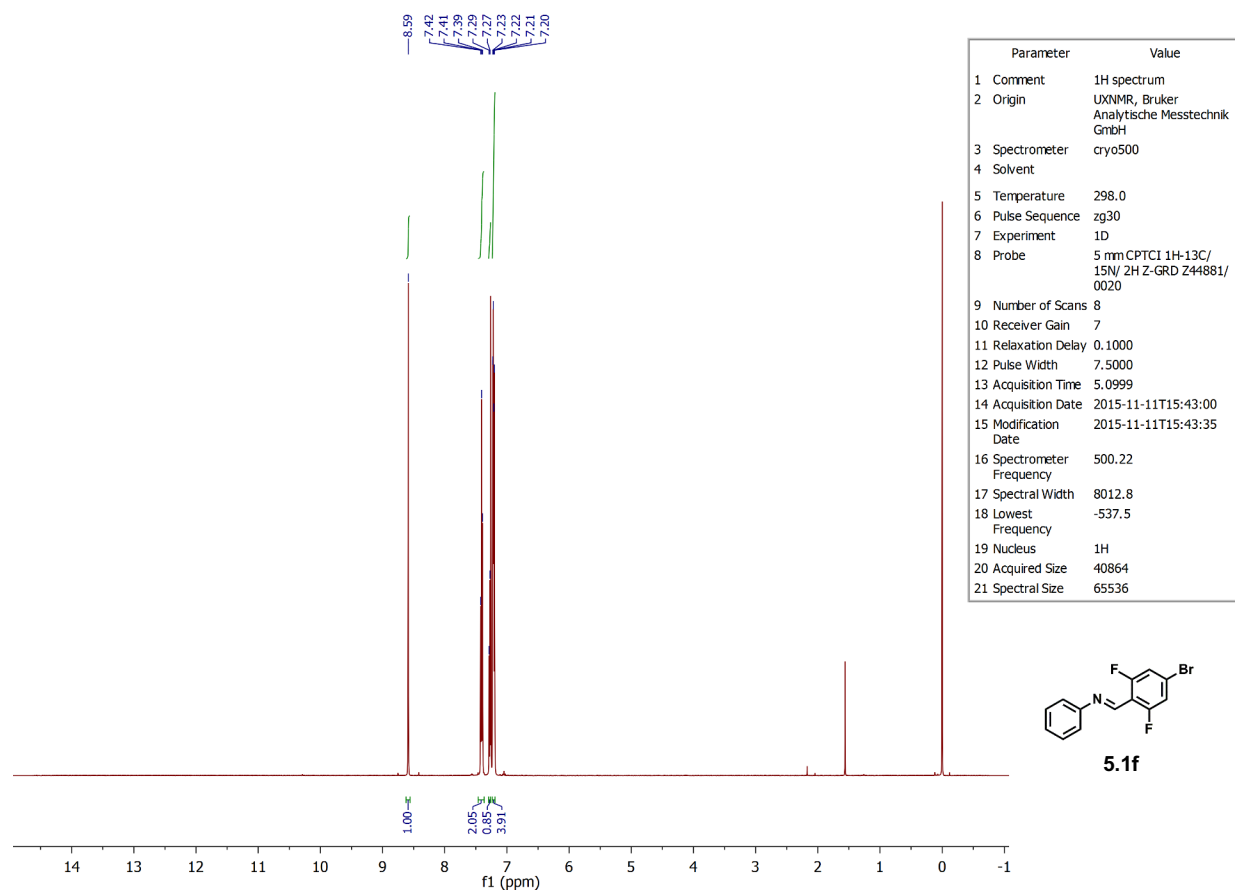


Figure S5.11. The ^1H NMR spectrum obtained for **5.1f**.

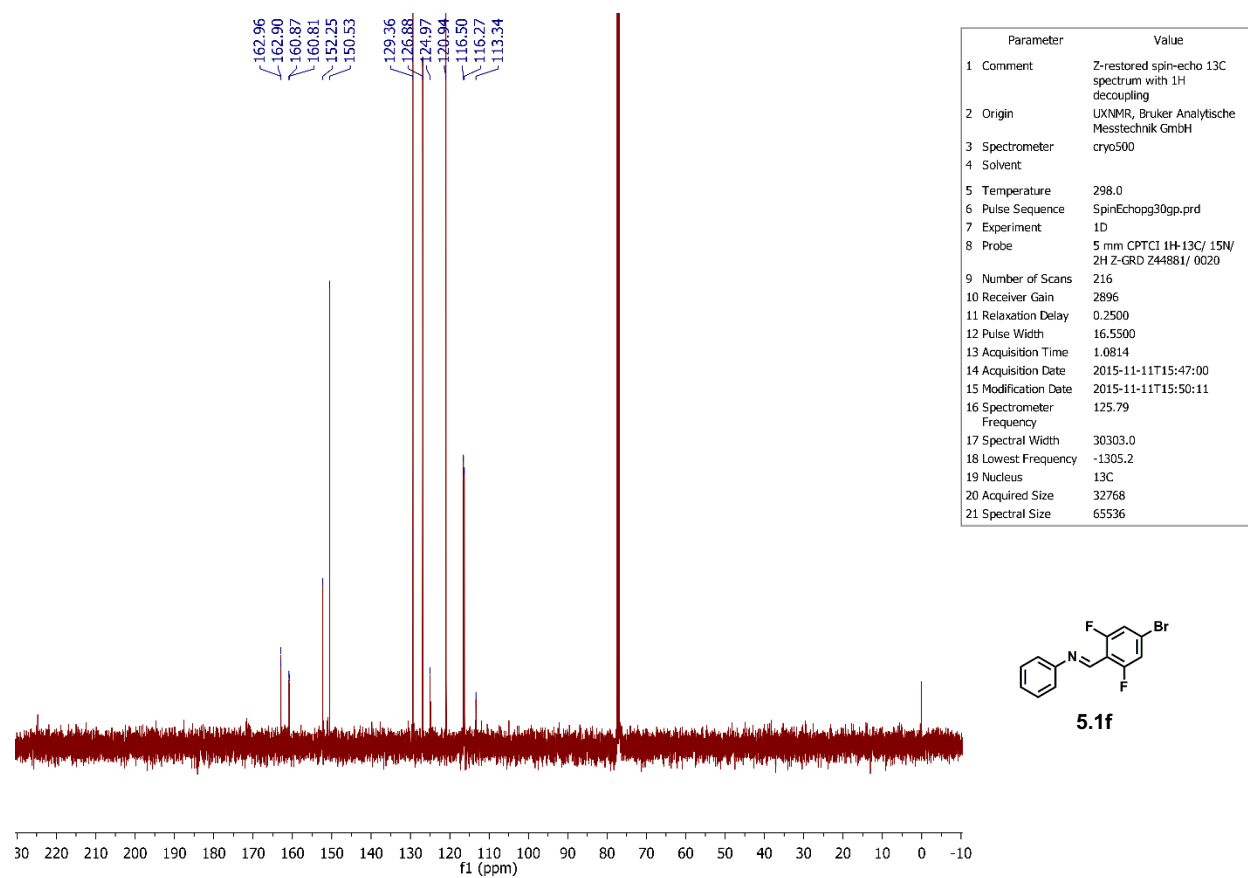


Figure S5.12. The ^{13}C NMR spectrum obtained for **5.1f**.

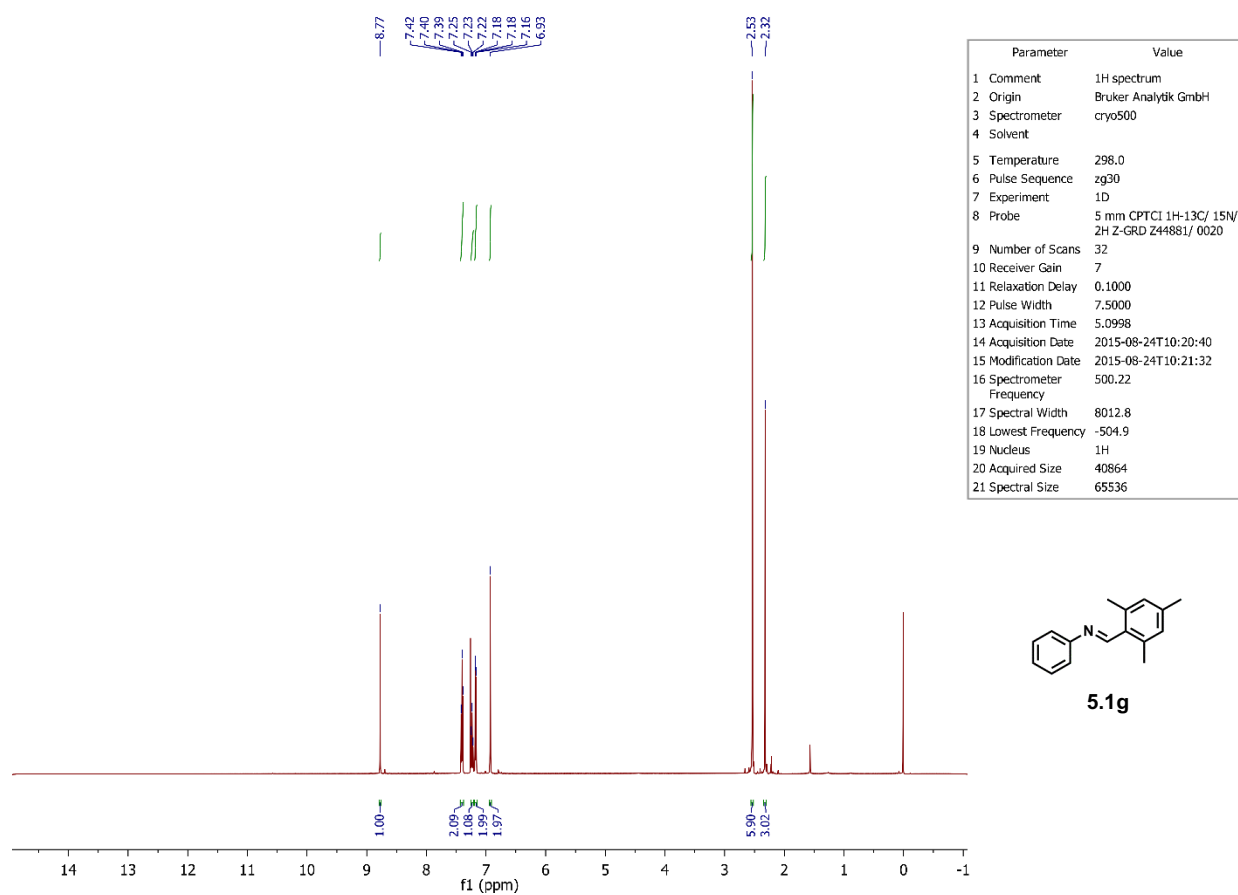


Figure S5.13. The ¹H NMR spectrum obtained for **5.1g**.

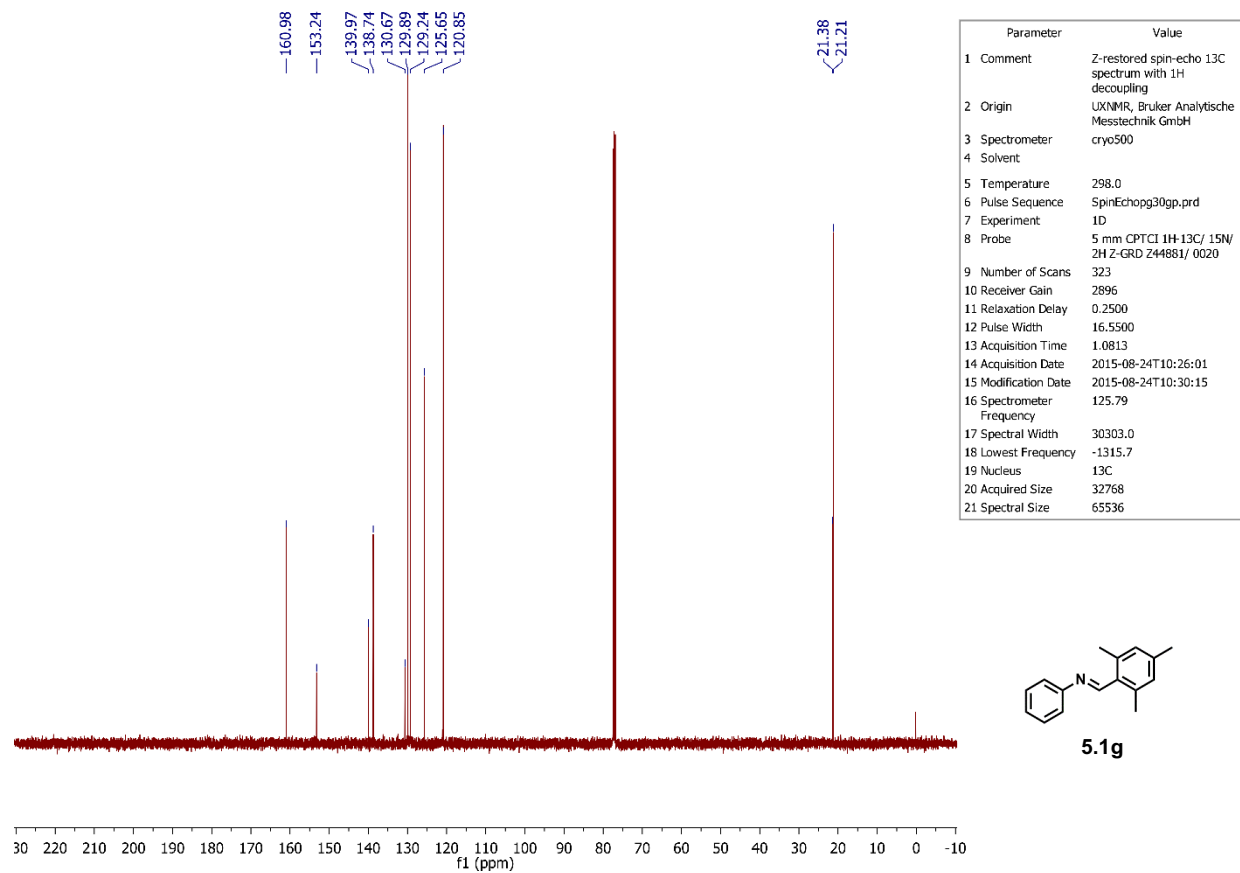


Figure S5.14. The ^{13}C NMR spectrum obtained for **5.1g**.

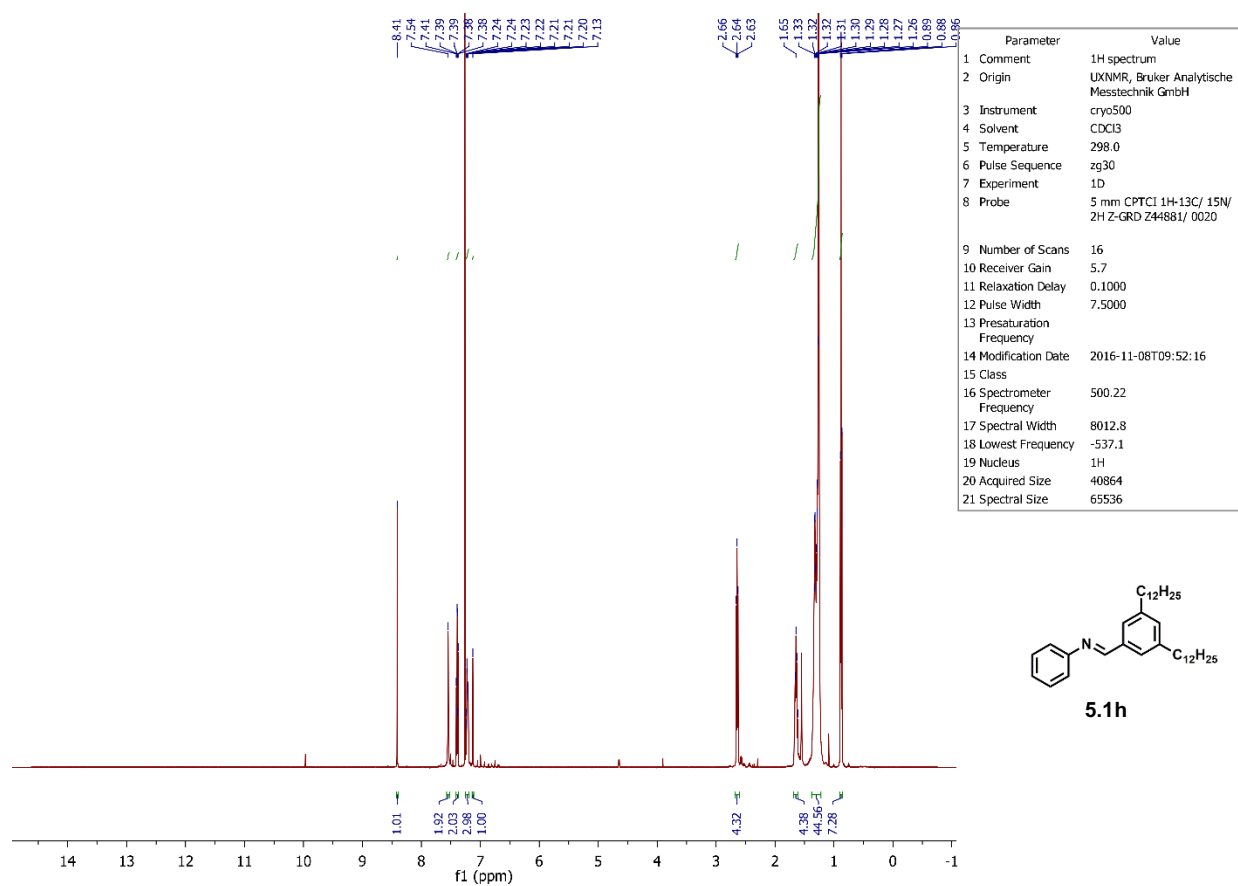


Figure S5.15. The ^1H NMR spectrum obtained for **5.1h**.

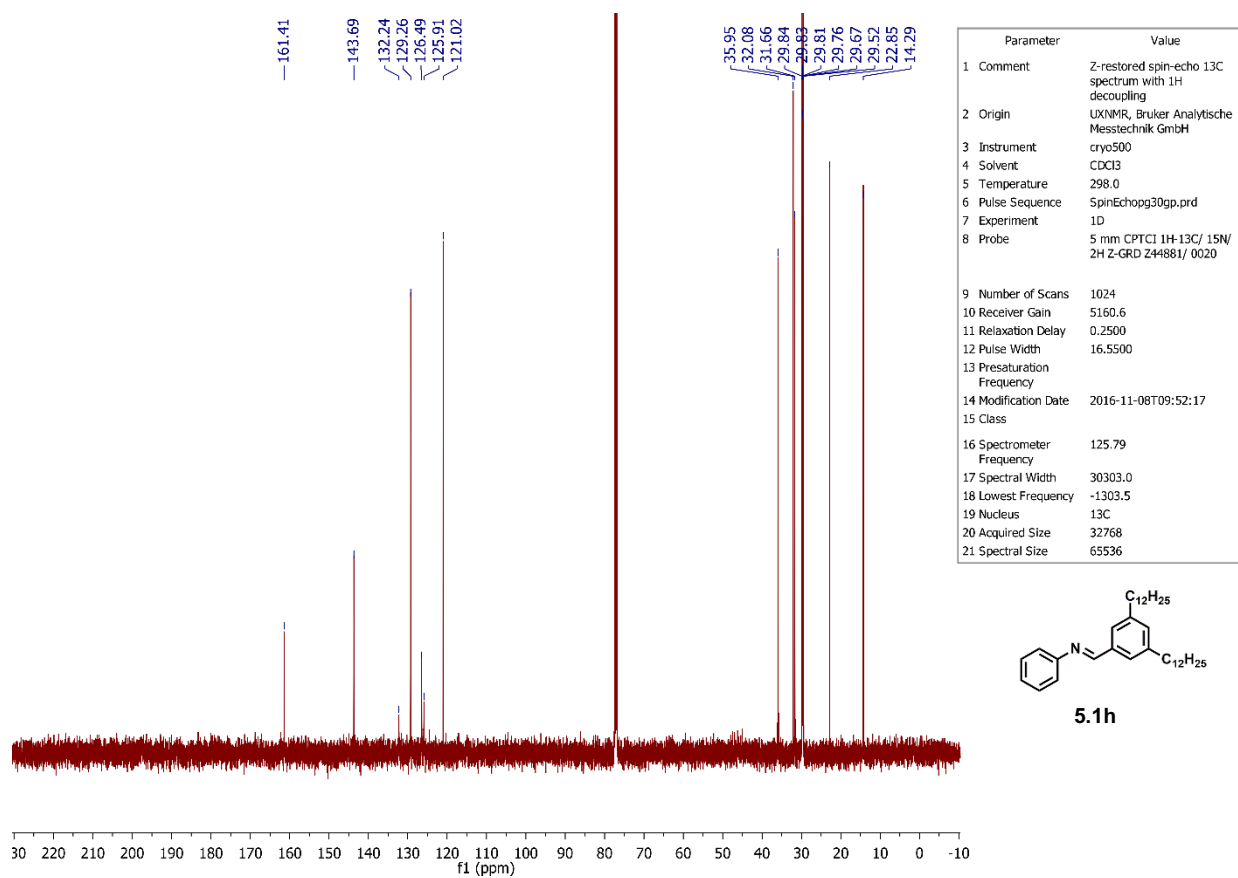


Figure S5.16. The ^{13}C NMR spectrum obtained for **5.1h**.

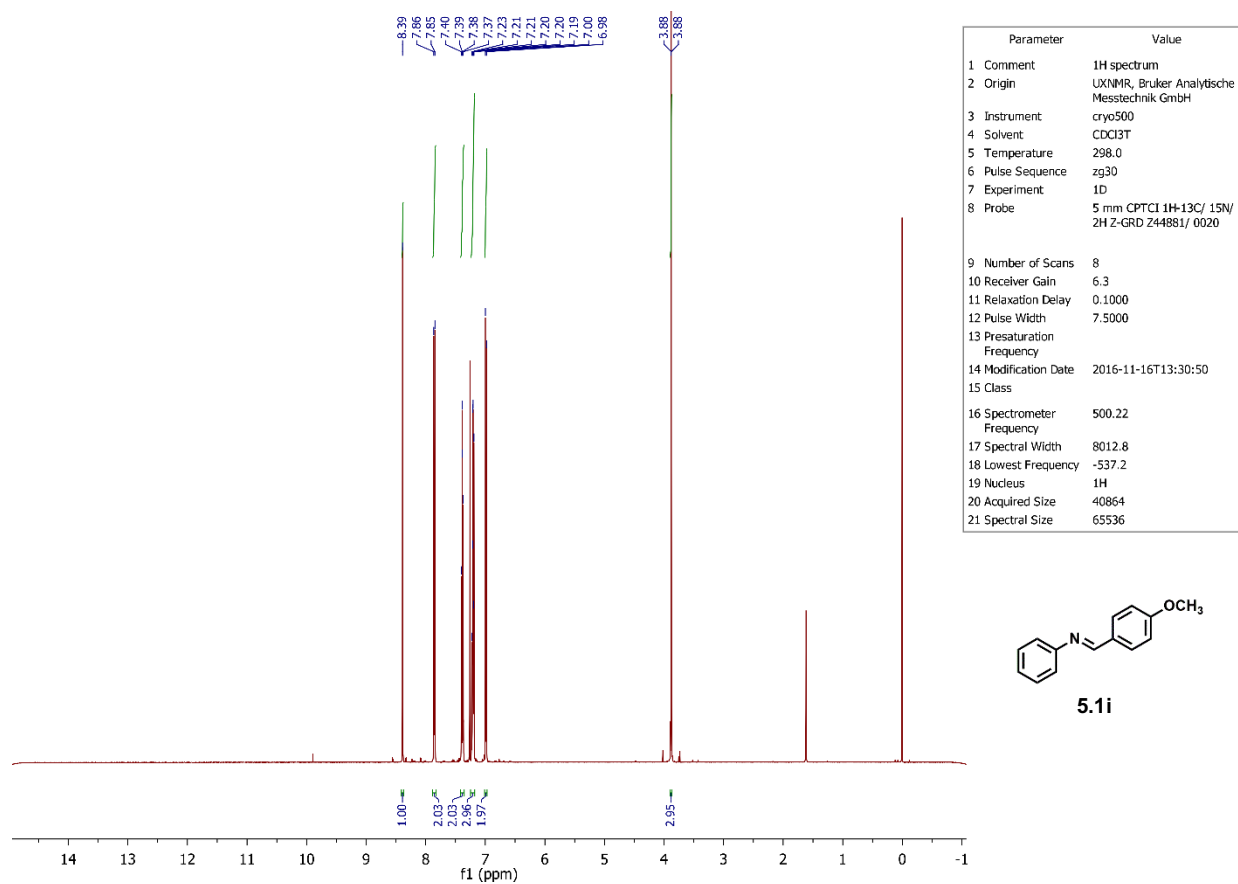


Figure S5.17. The ^1H NMR spectrum obtained for **5.1i**.

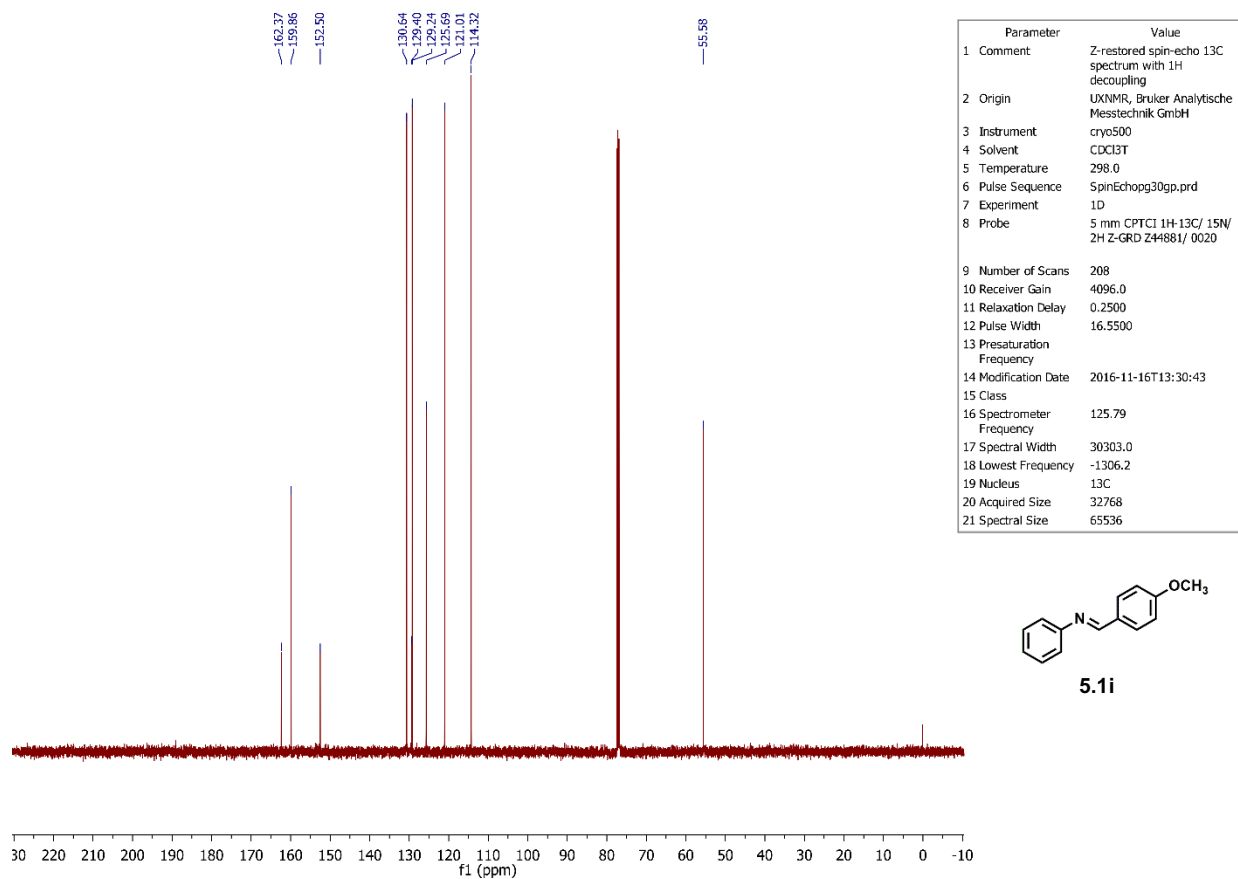


Figure S5.18. The ¹³C NMR spectrum obtained for **5.1i**.

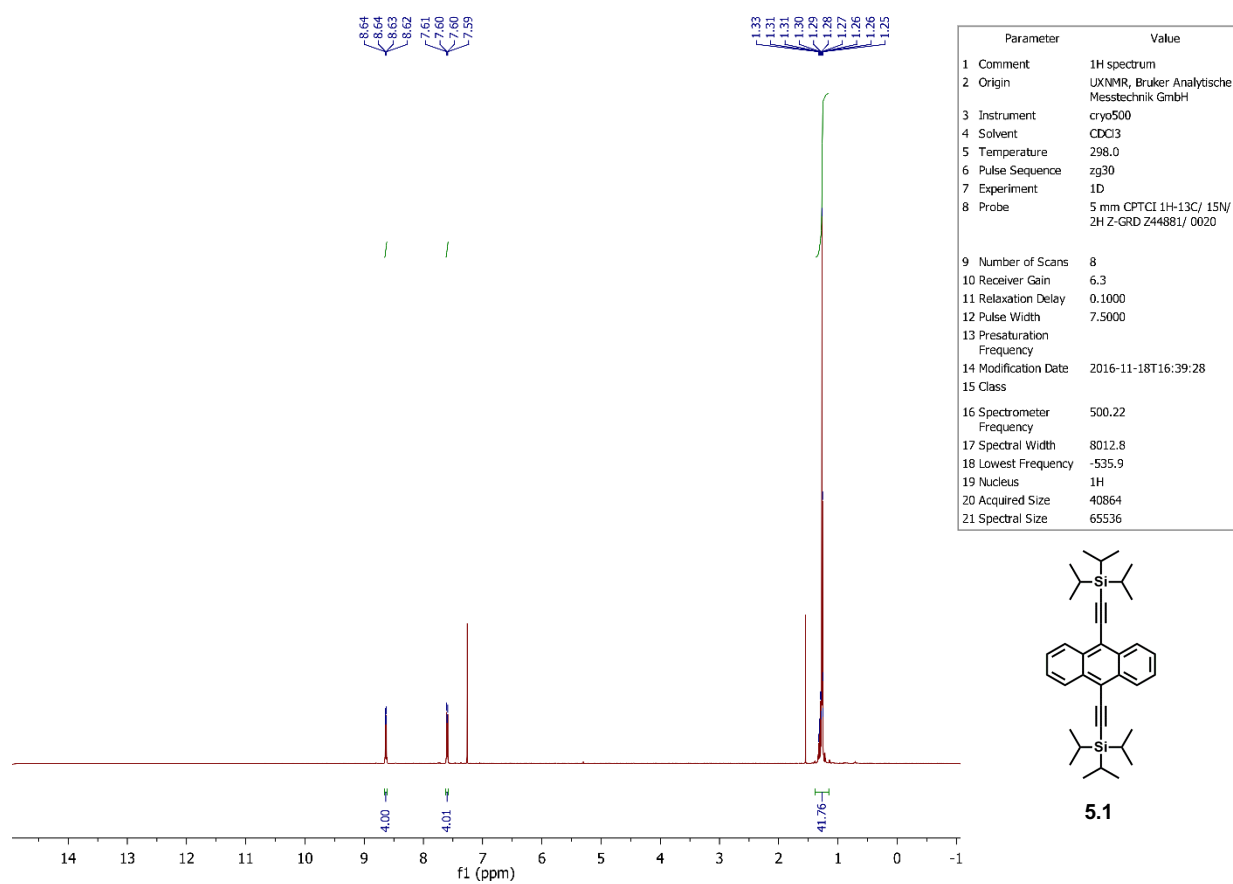


Figure S5.19. The ¹H NMR spectrum obtained for **SI-5.1**.

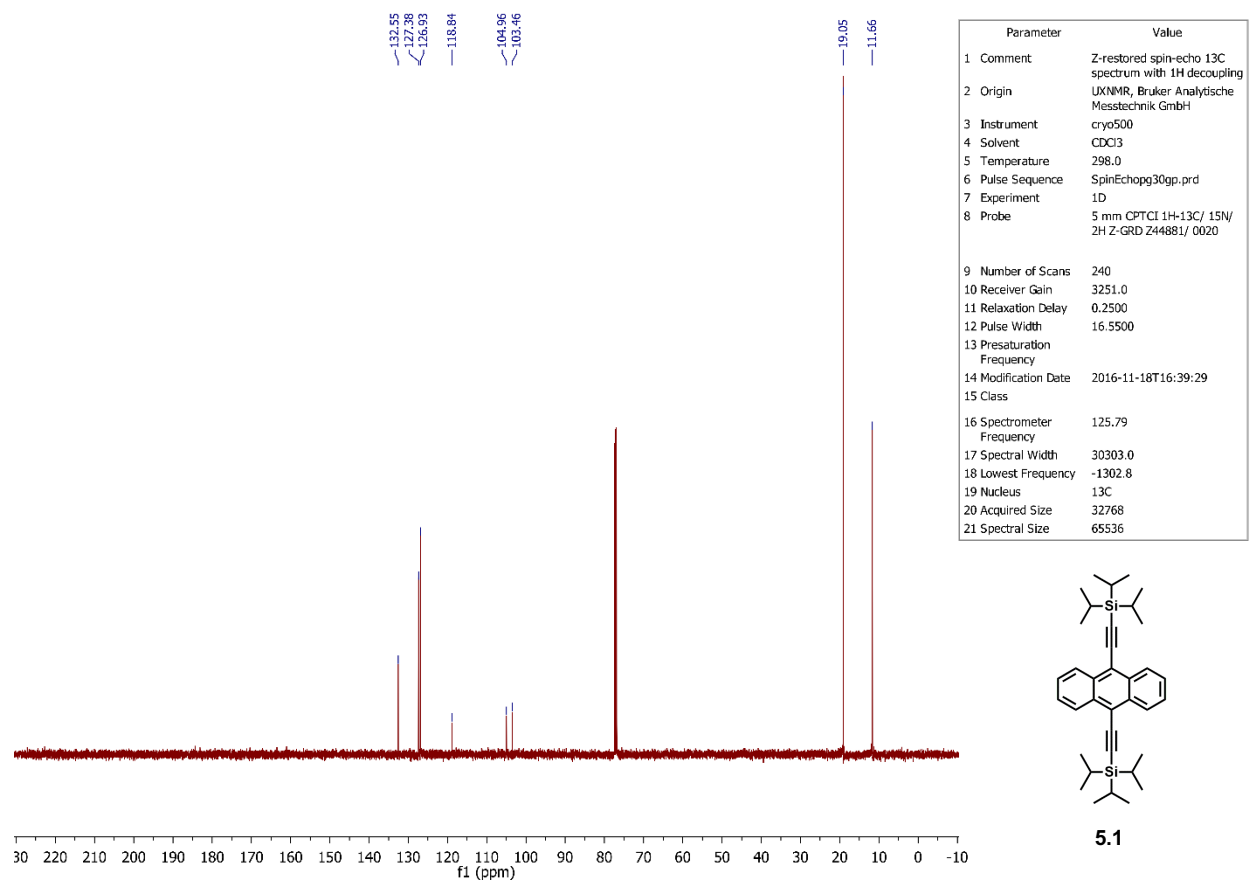


Figure S5.20. The ^{13}C NMR spectrum obtained for **SI-5.1**.

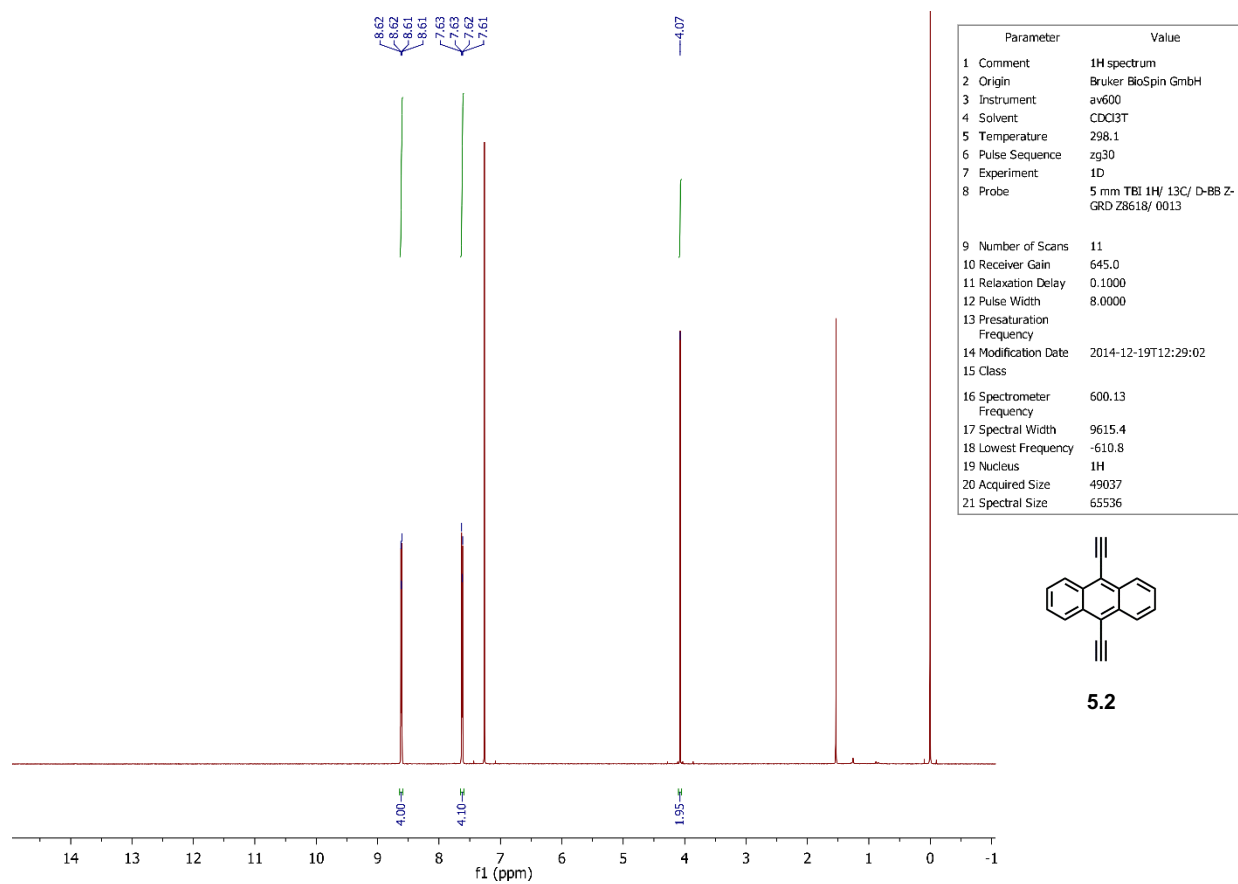


Figure S5.21. The ¹H NMR spectrum obtained for **5.2**.

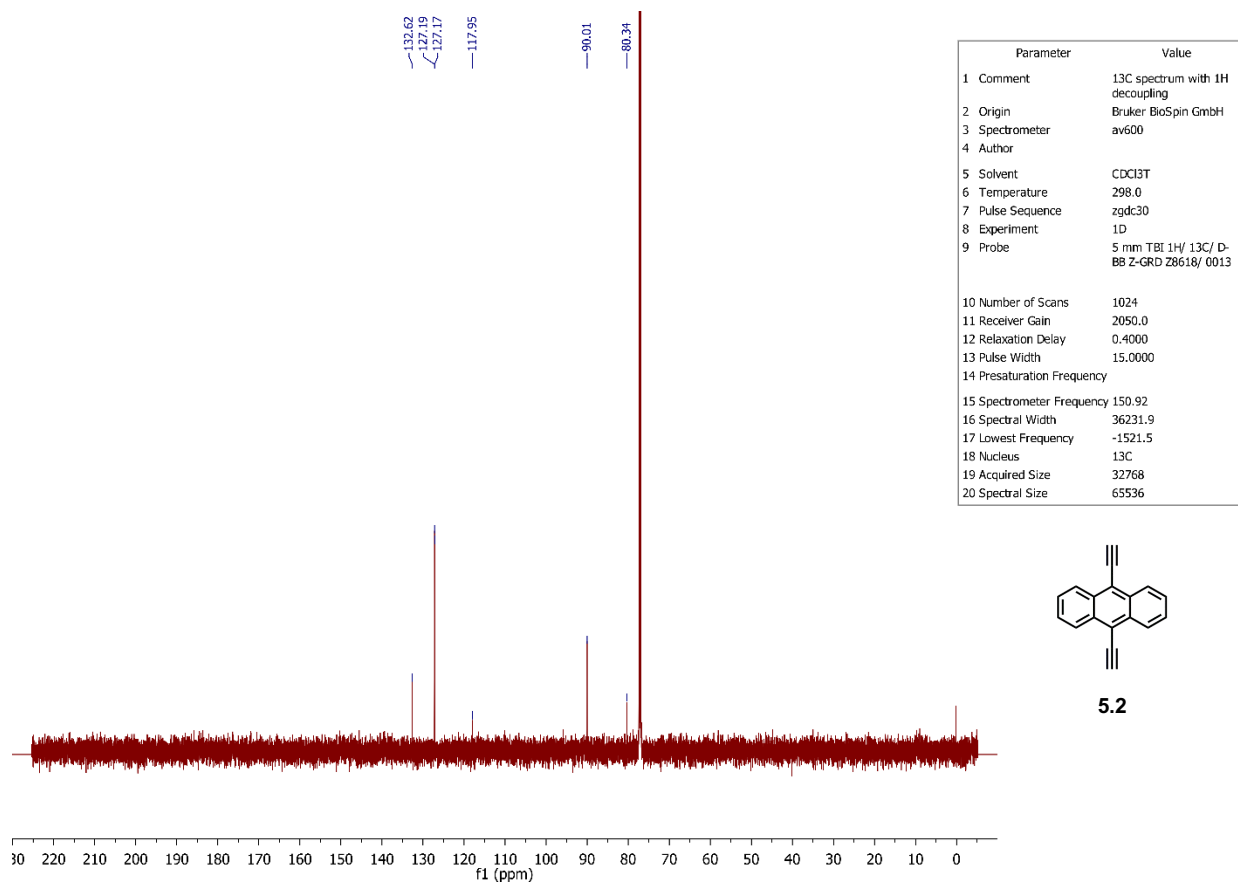


Figure S5.22. The ¹³C NMR spectrum obtained for **5.2**.

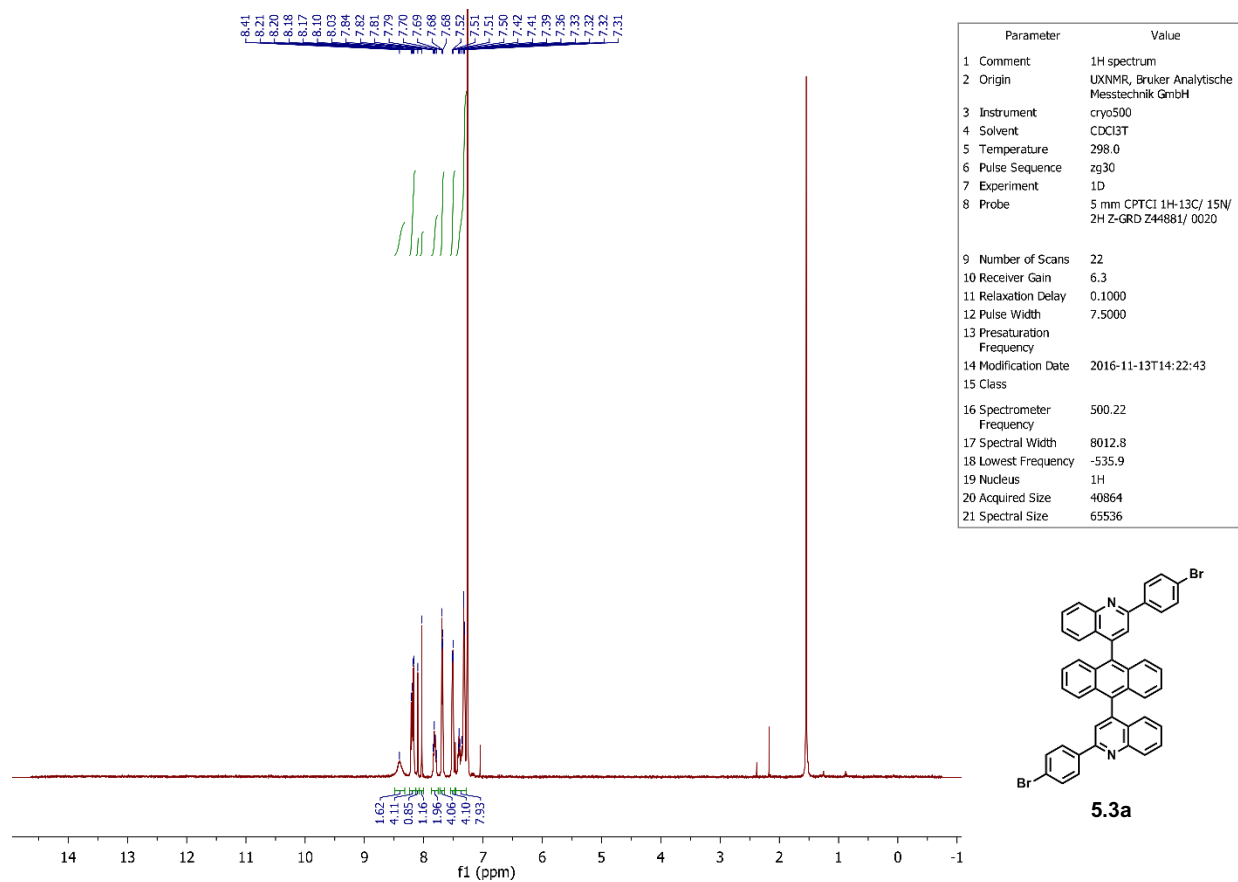


Figure S5.25. The ^1H NMR spectrum obtained for **5.3a**.

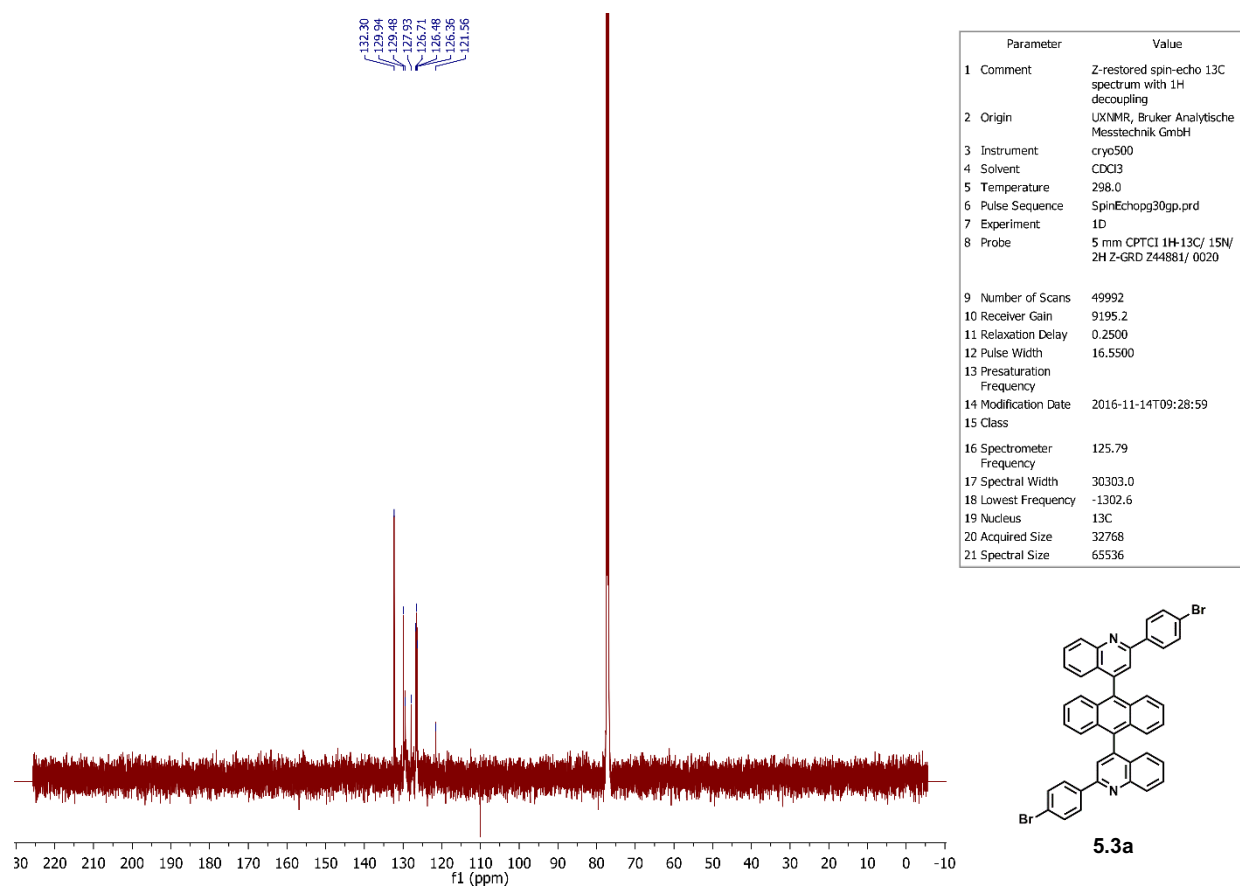


Figure S5.26. The ^{13}C NMR spectrum obtained for **5.3a**.

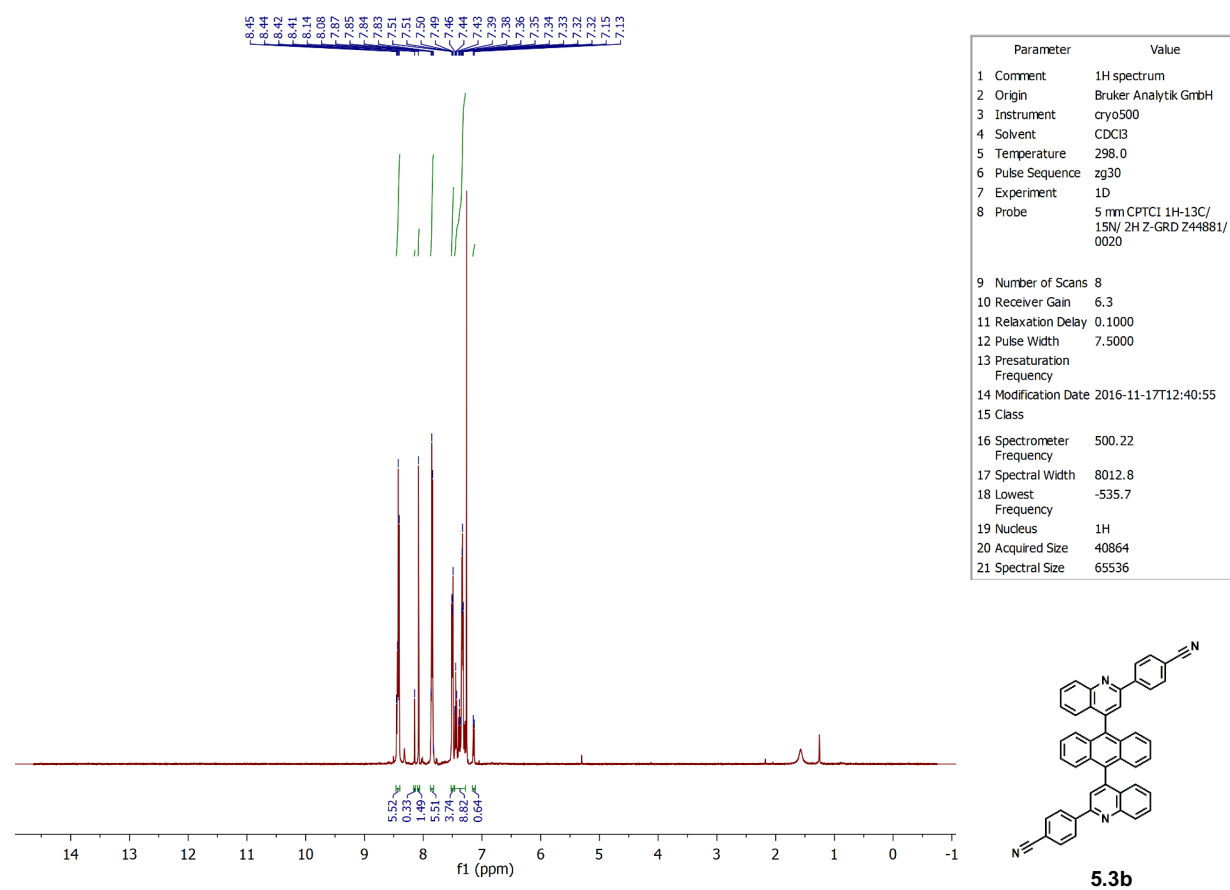


Figure S5.27. The ^1H NMR spectrum obtained for **5.3b**.

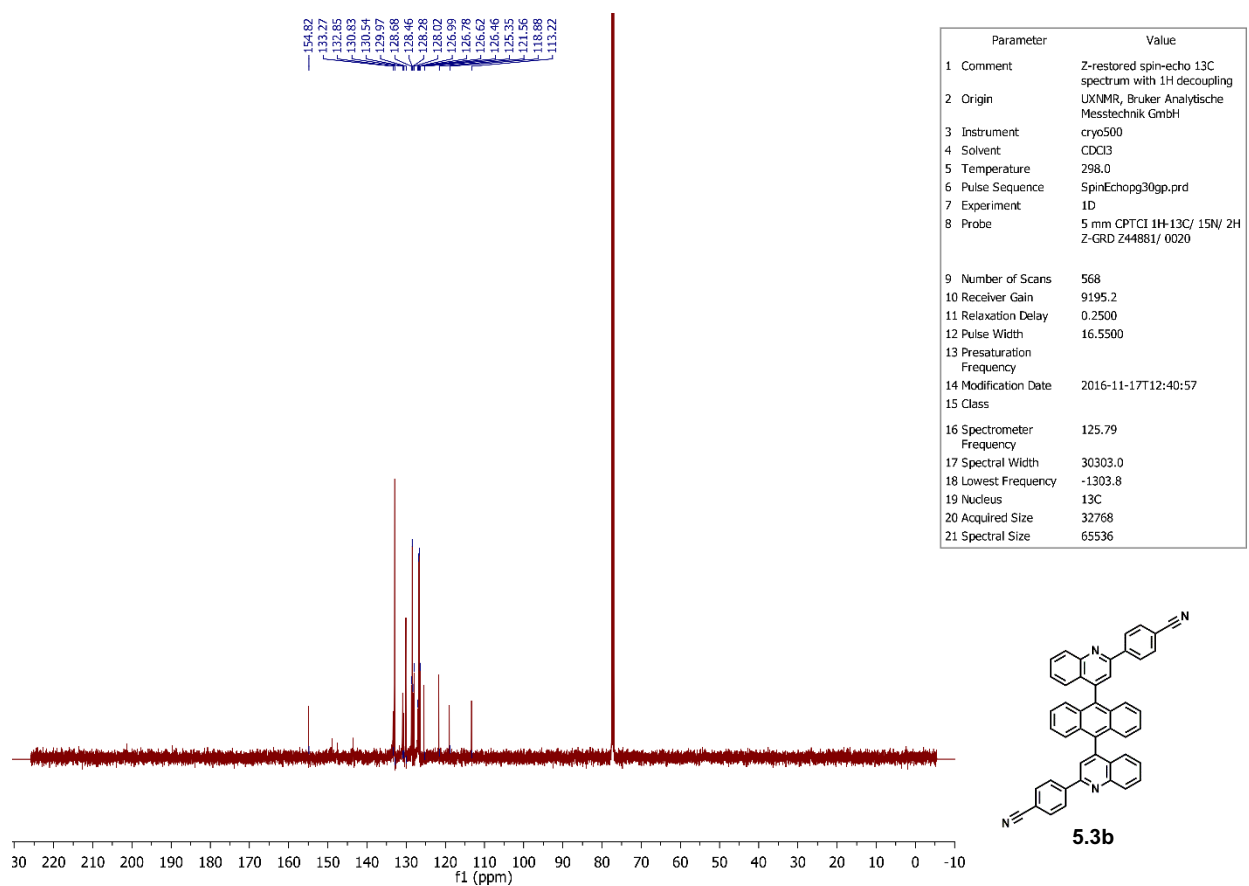


Figure S5.28. The ^{13}C NMR spectrum obtained for **5.3b**.

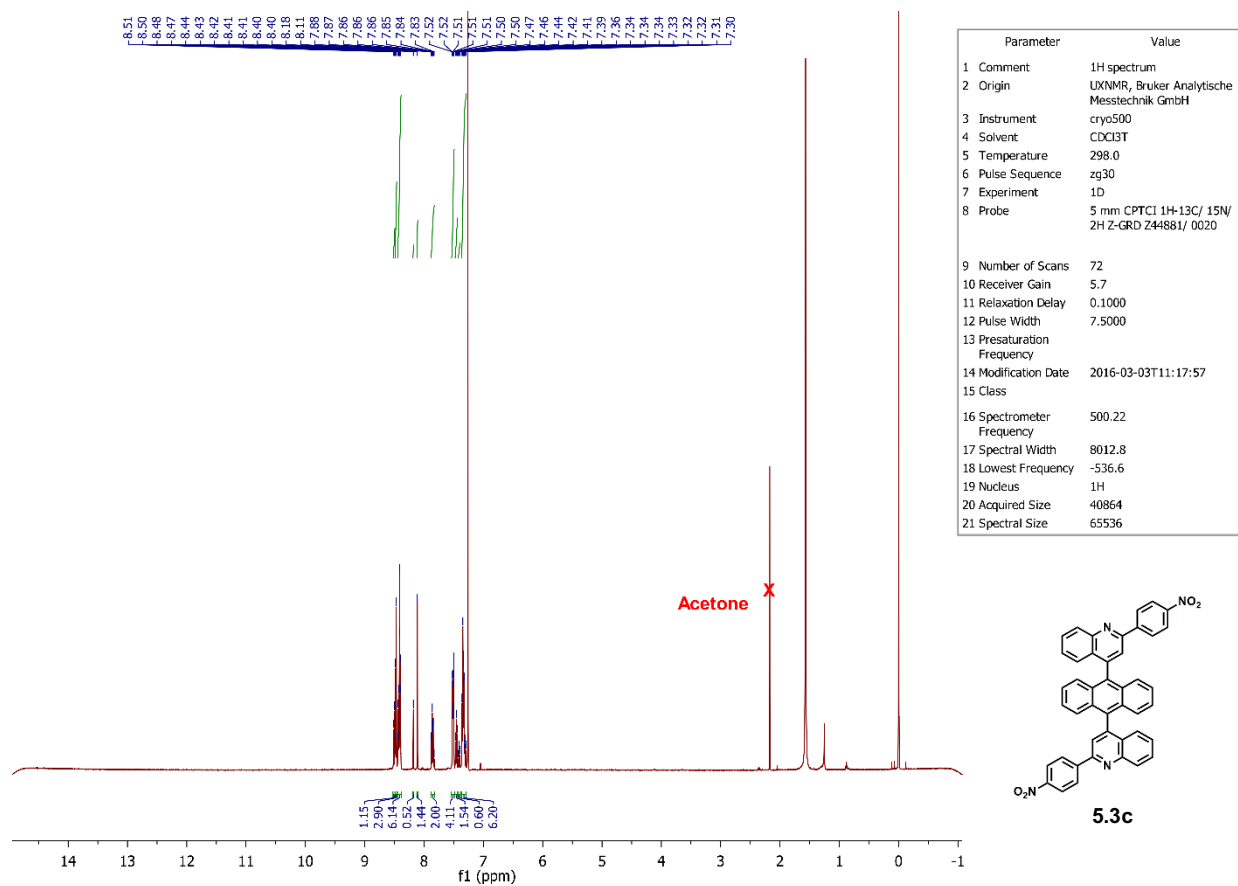


Figure S5.29. The ^1H NMR spectrum obtained for **5.3c**.

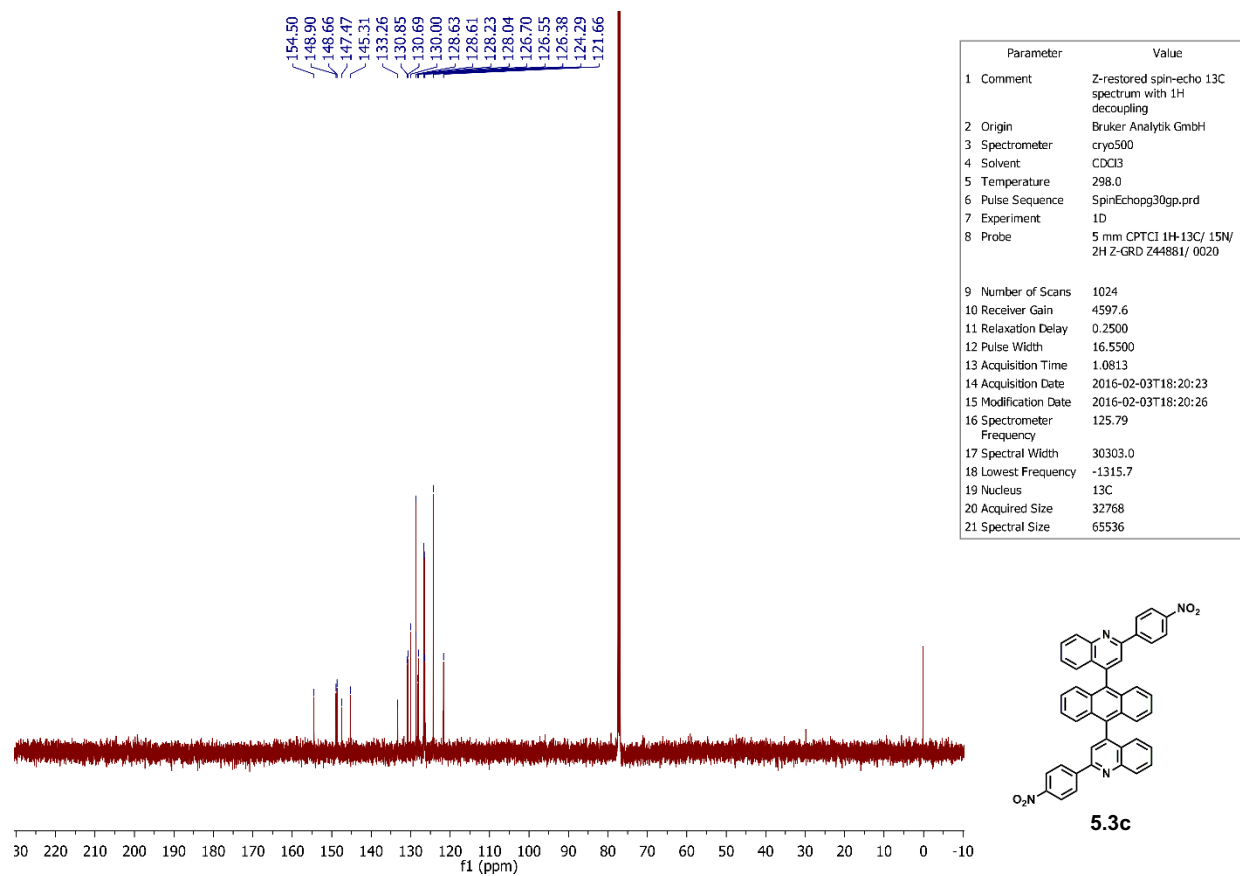


Figure S5.30. The ^{13}C NMR spectrum obtained for **5.3c**.

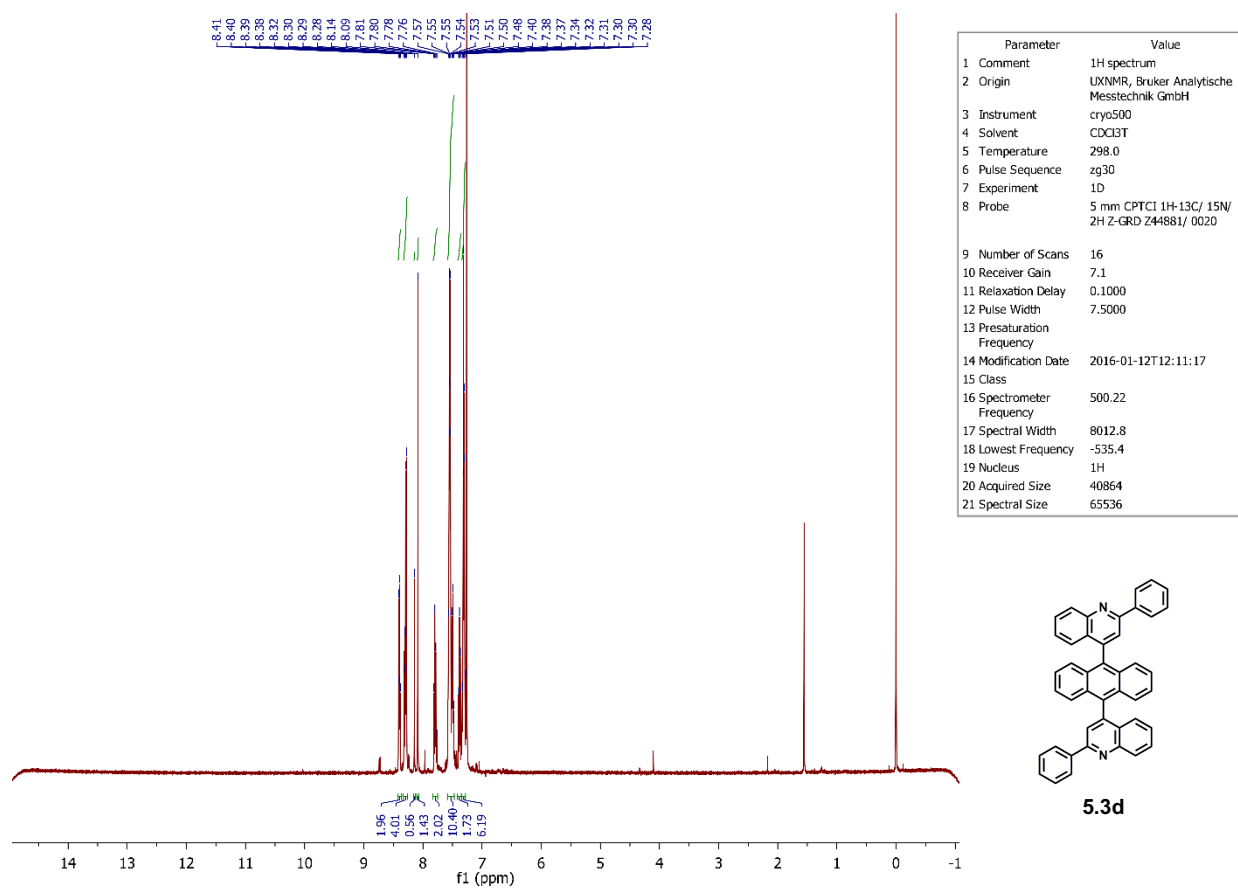


Figure S5.23. The ¹H NMR spectrum obtained for **5.3d**.

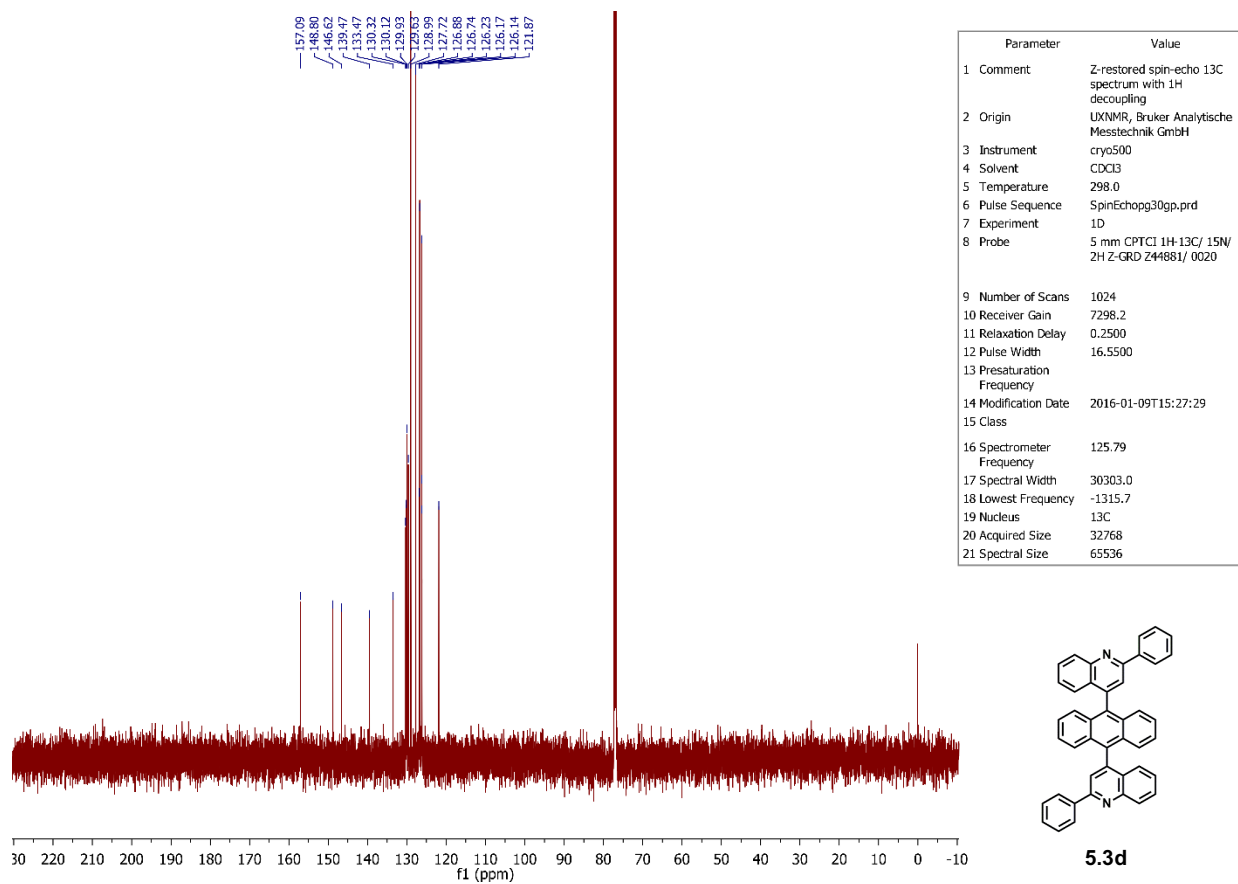


Figure S5.24. The ^{13}C NMR spectrum obtained for **5.3d**.

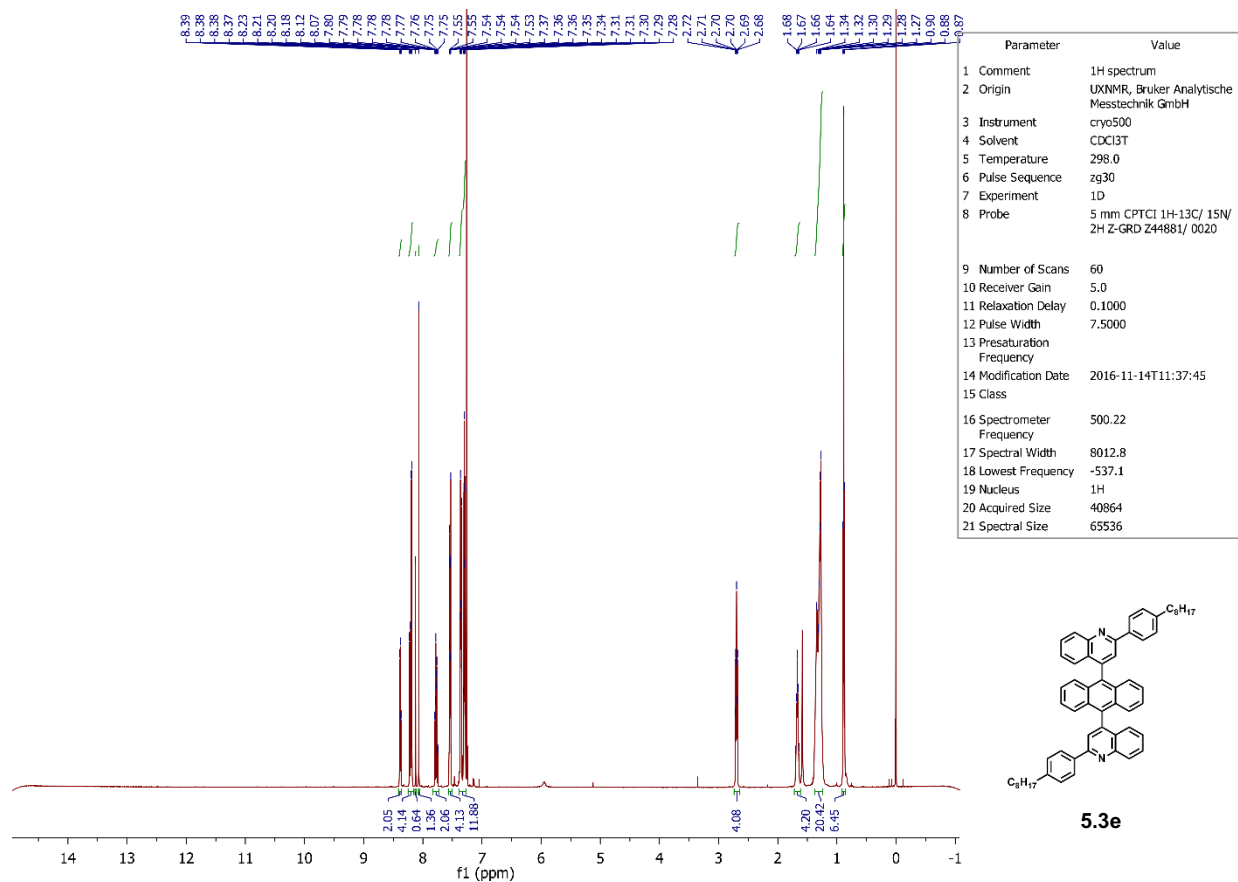


Figure S5.31. The ^1H NMR spectrum obtained for **5.3e**.

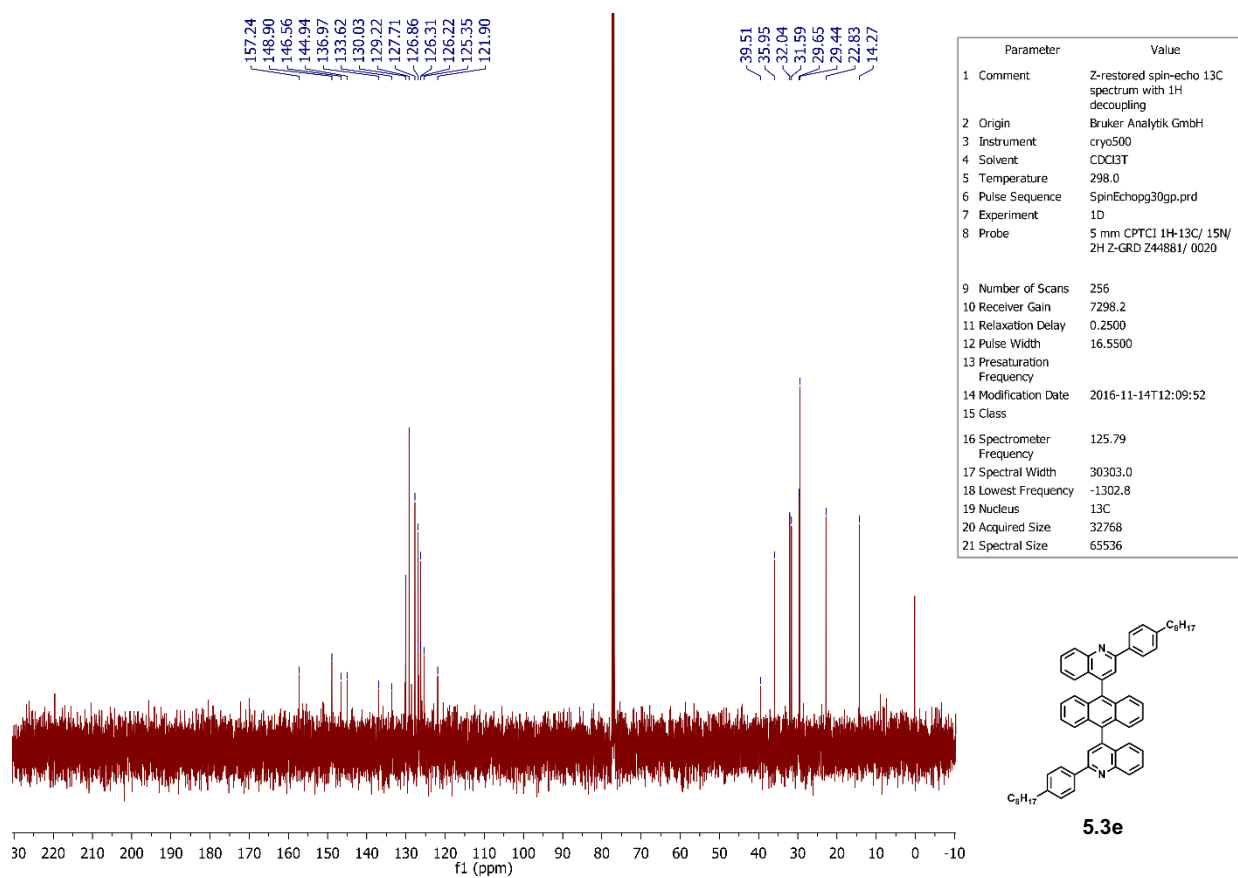


Figure S5.32. The ^{13}C NMR spectrum obtained for **5.3e**.

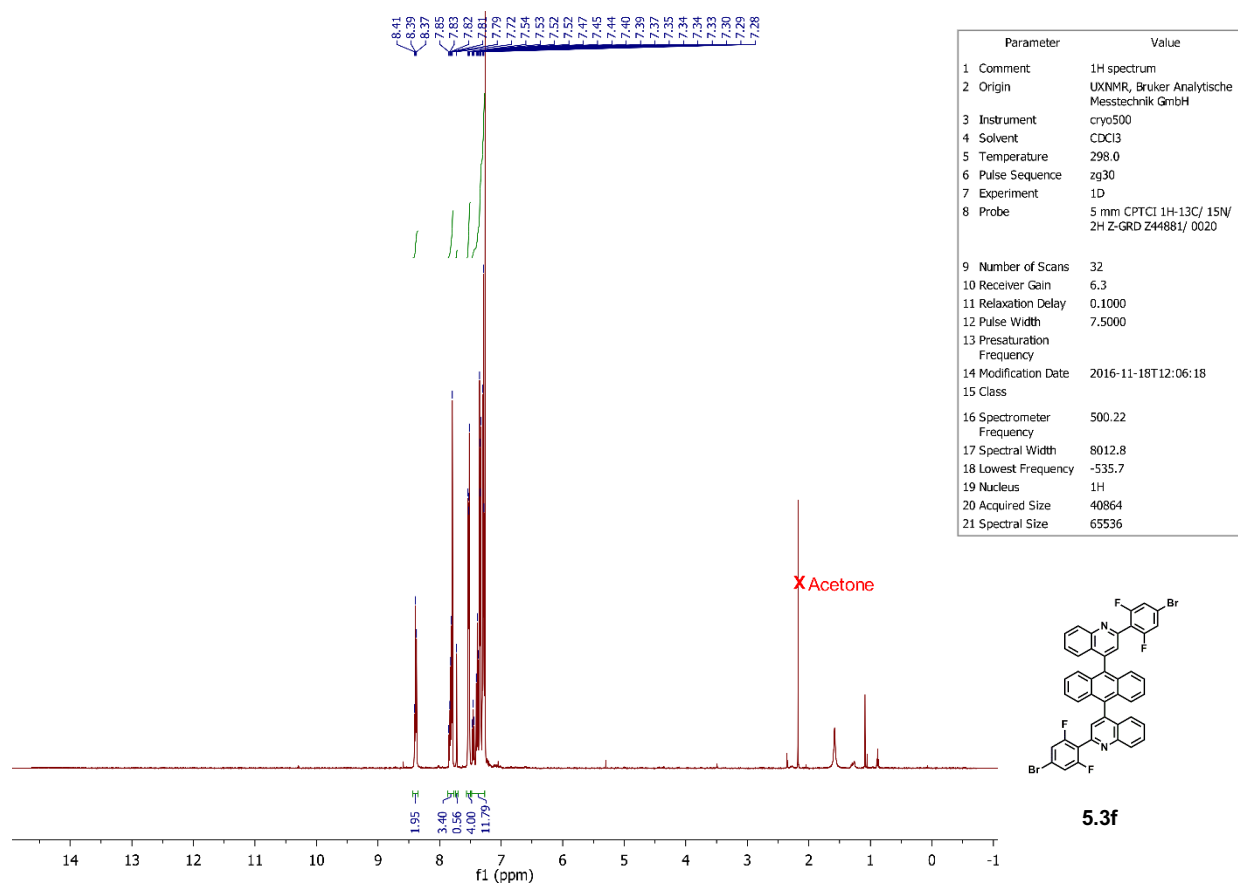


Figure S5.33. The ^1H NMR spectrum obtained for **5.3f**.

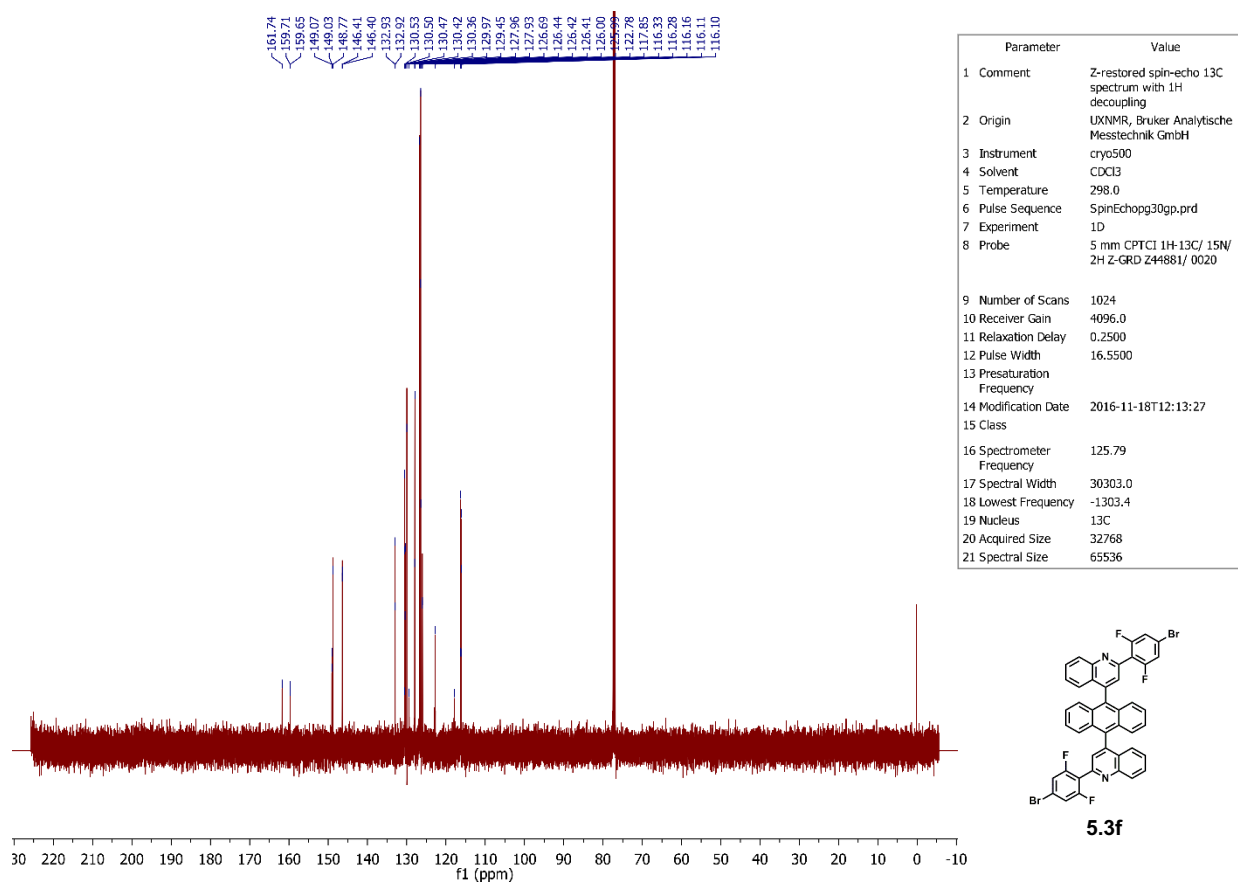


Figure S5.34. The ^{13}C NMR spectrum obtained for **5.3f**.

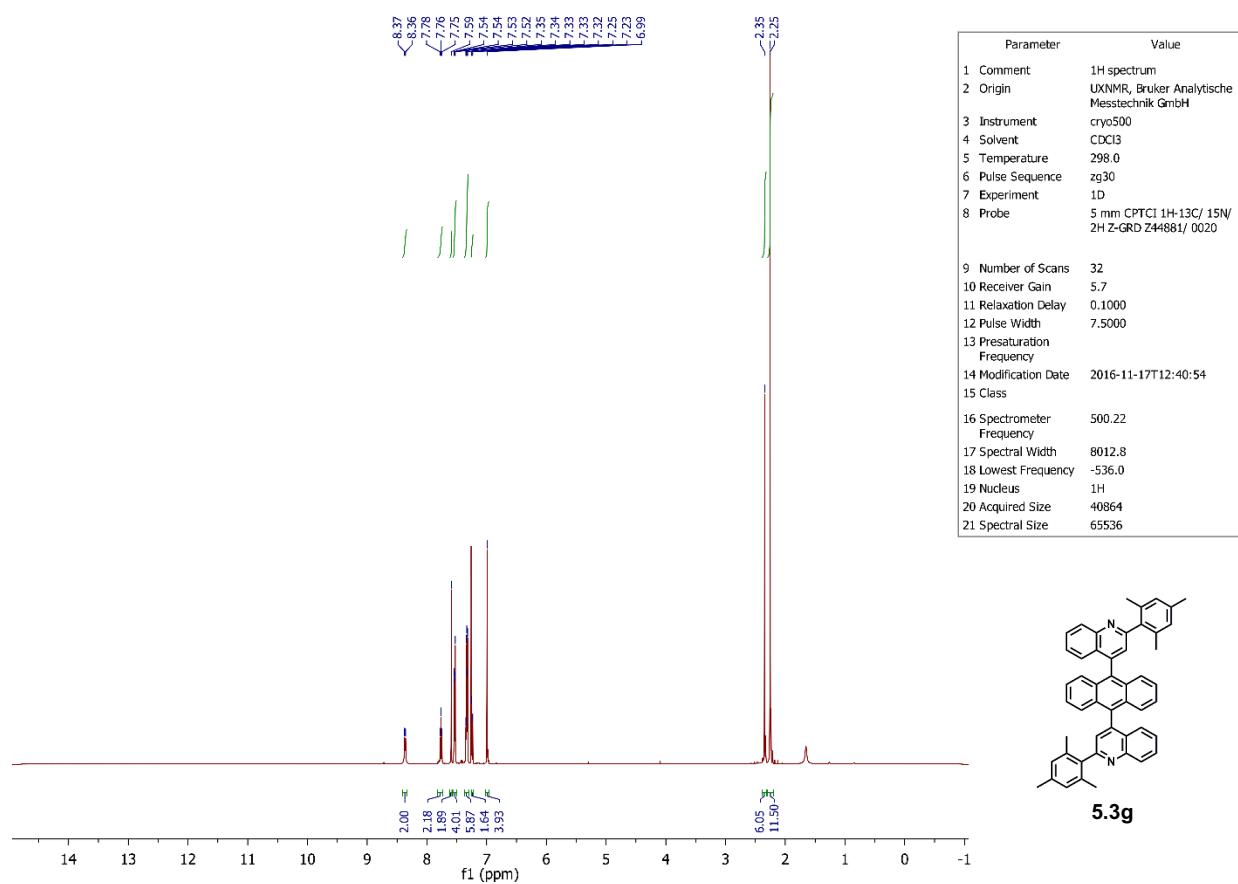


Figure S5.35. The ^1H NMR spectrum obtained for **5.3g**.

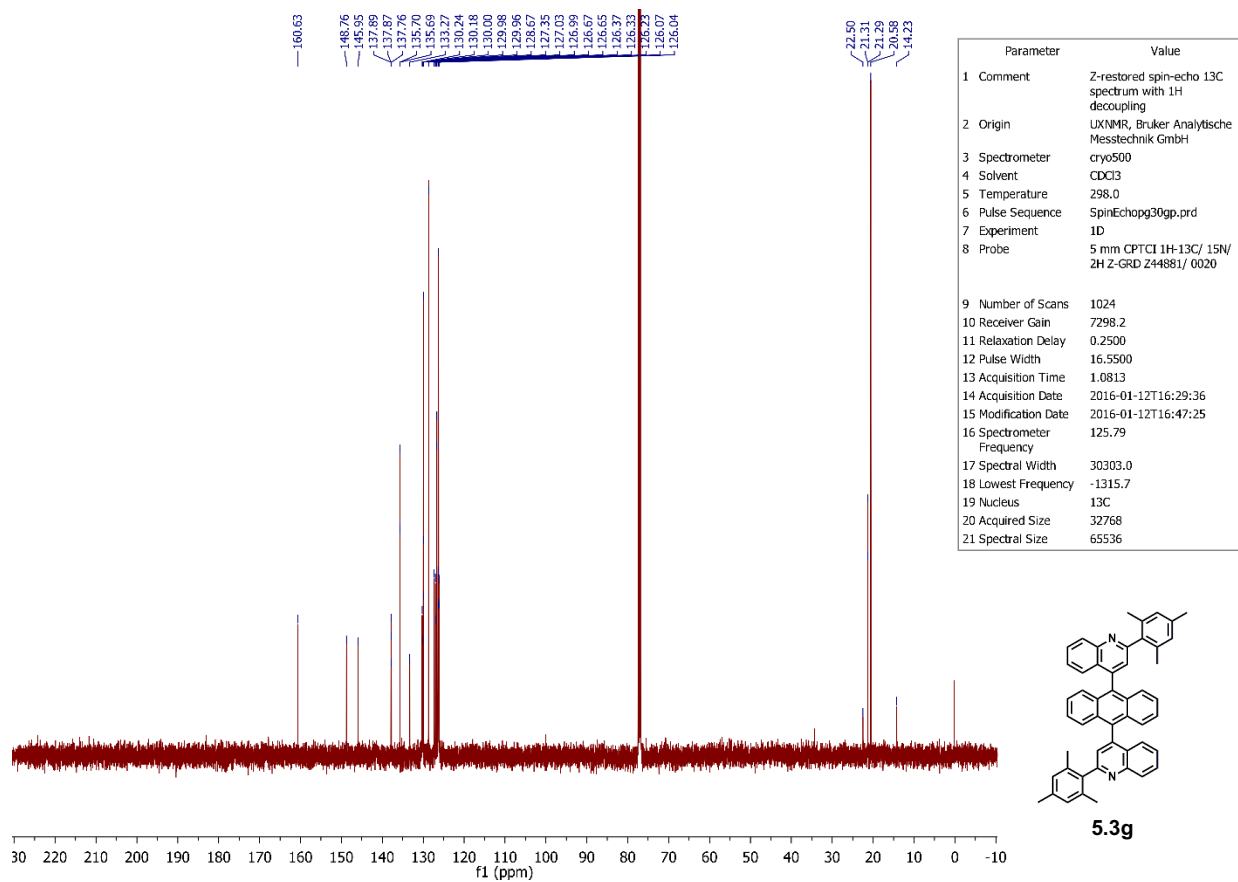


Figure S5.36. The ^{13}C NMR spectrum obtained for **5.3g**.

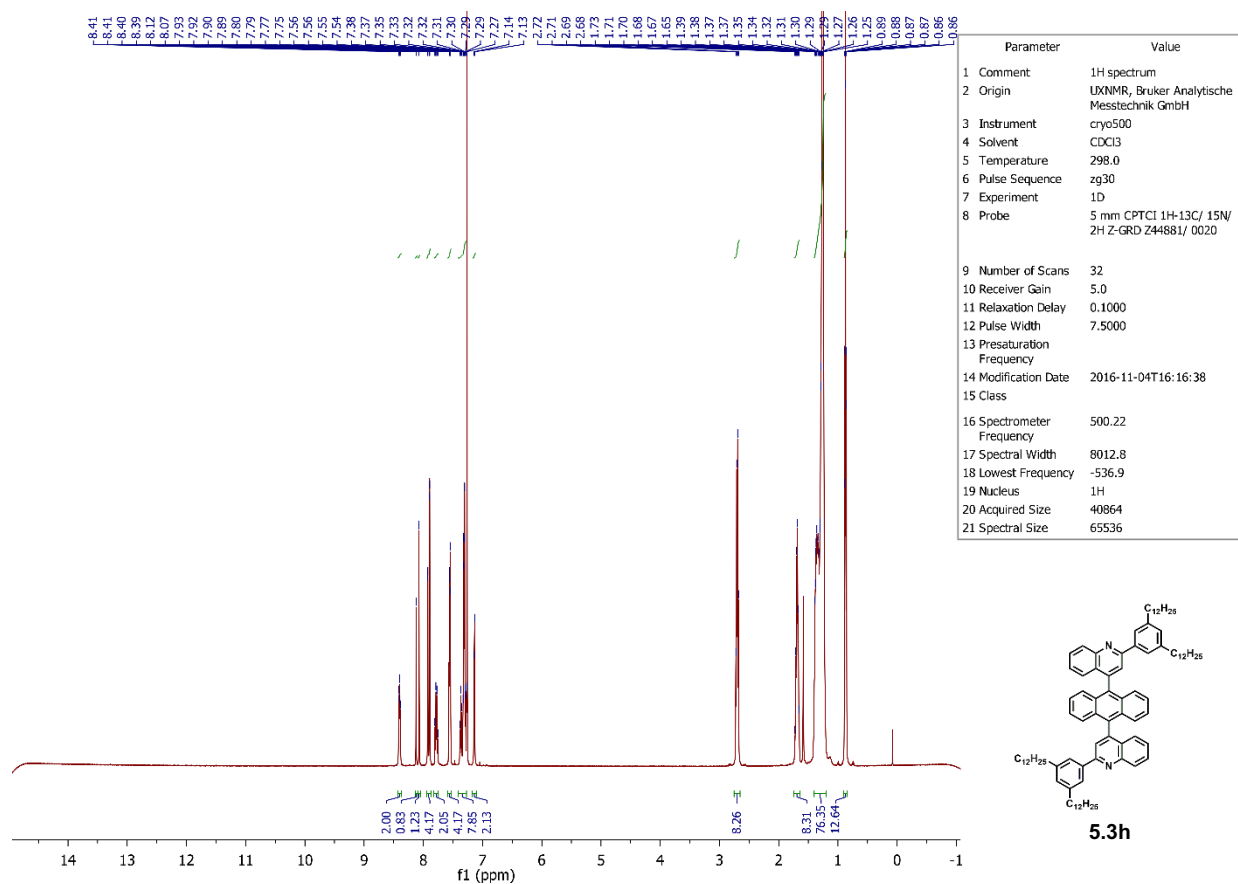


Figure S5.37. The ¹H NMR spectrum obtained for **5.3h**.

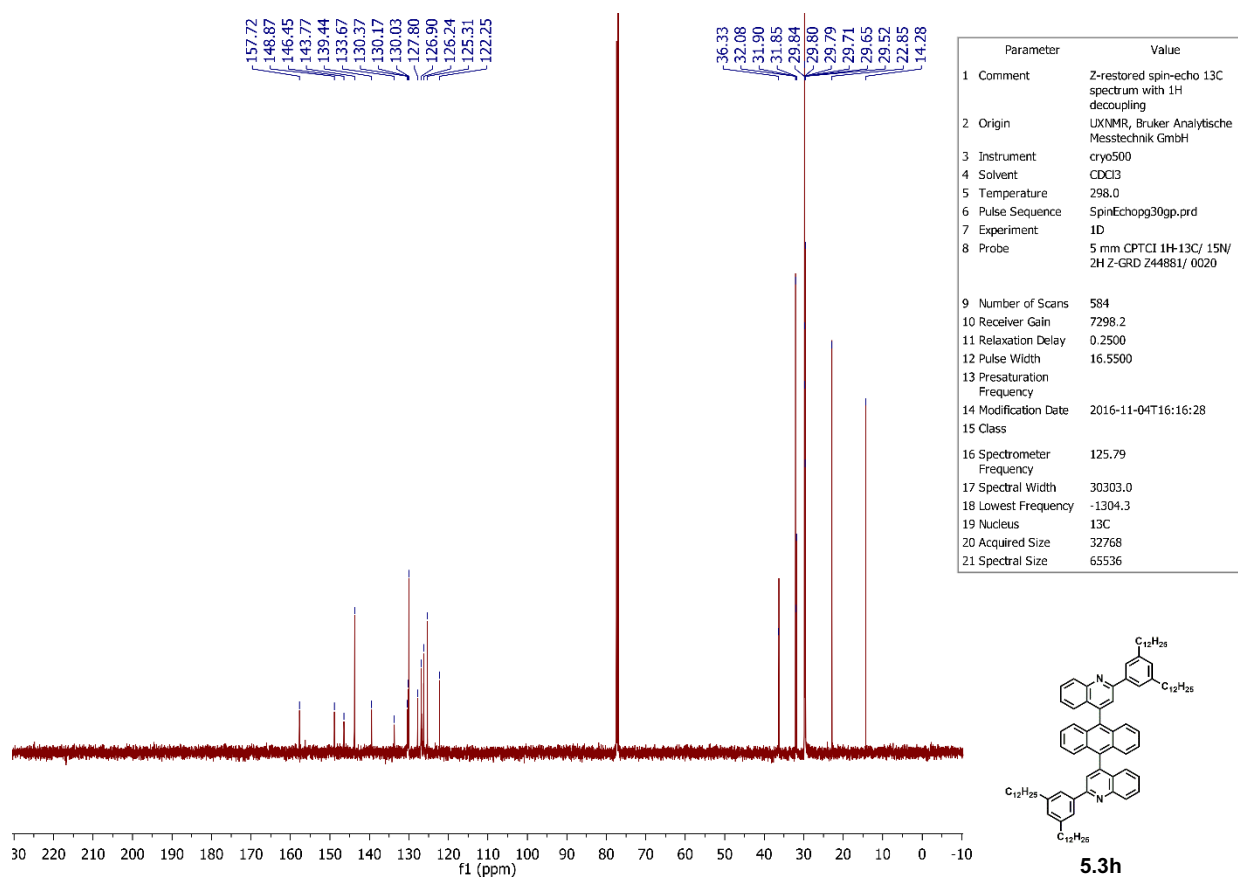


Figure S5.38. The ^{13}C NMR spectrum obtained for **5.3h**.

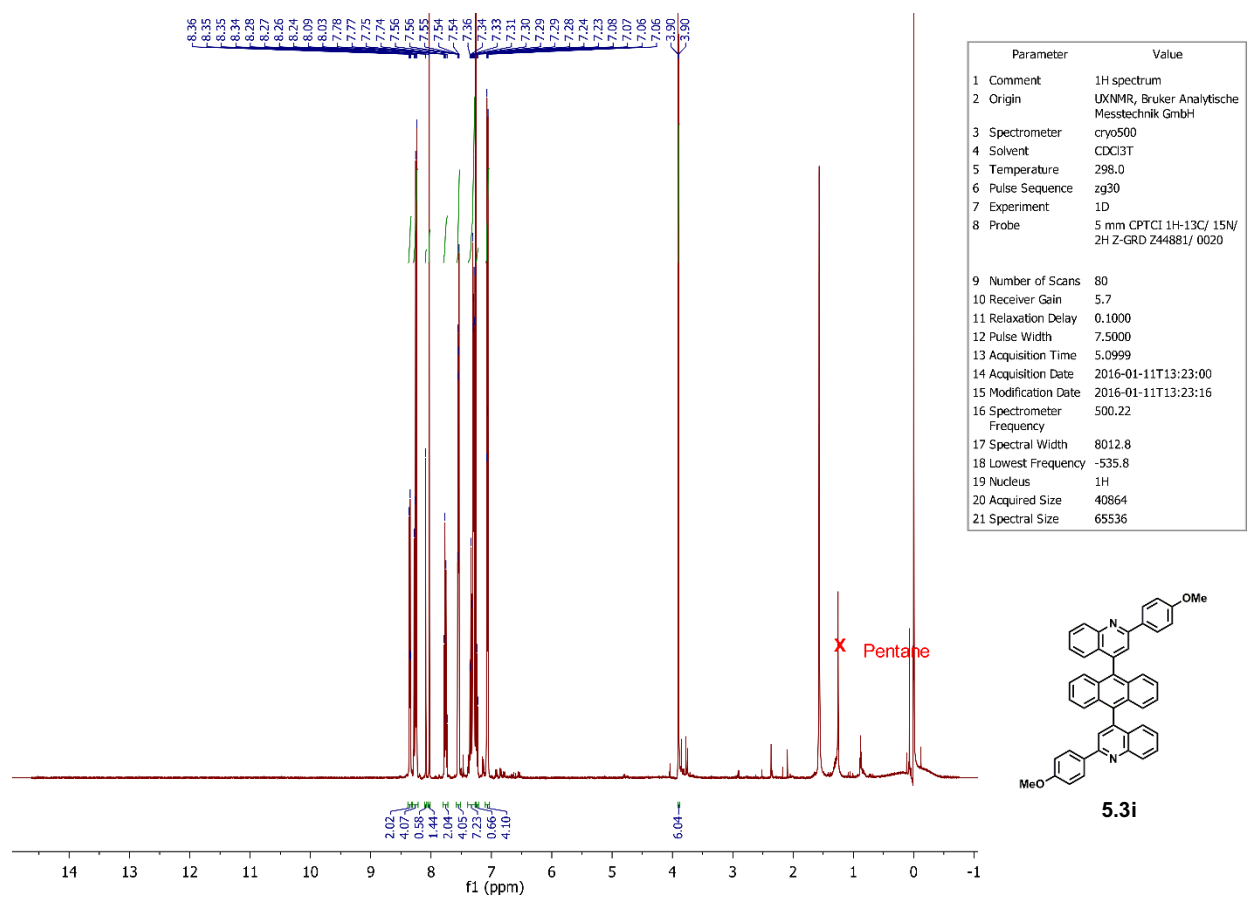


Figure S5.39. The ^1H NMR spectrum obtained for **5.3i**.

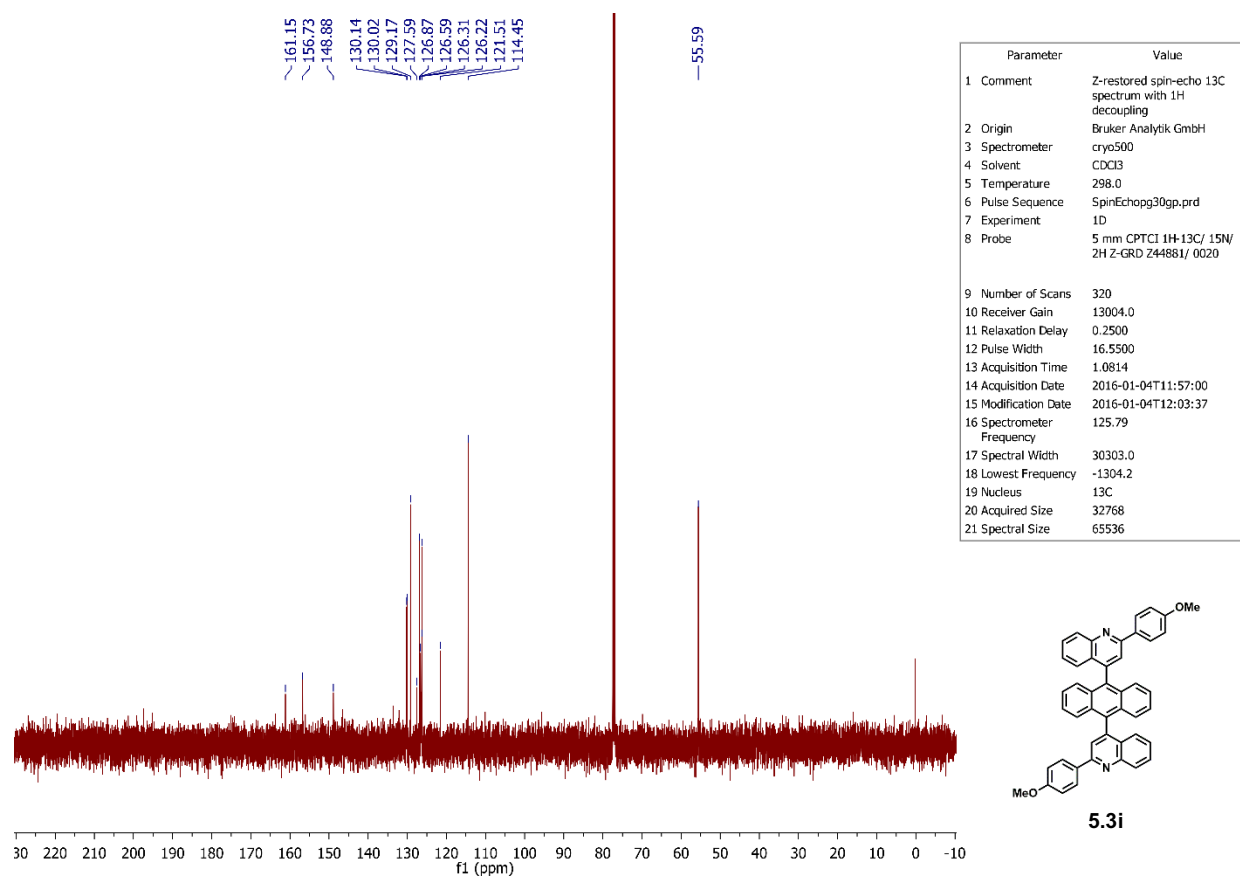


Figure S5.40. The ^{13}C NMR spectrum obtained for **5.3i**.

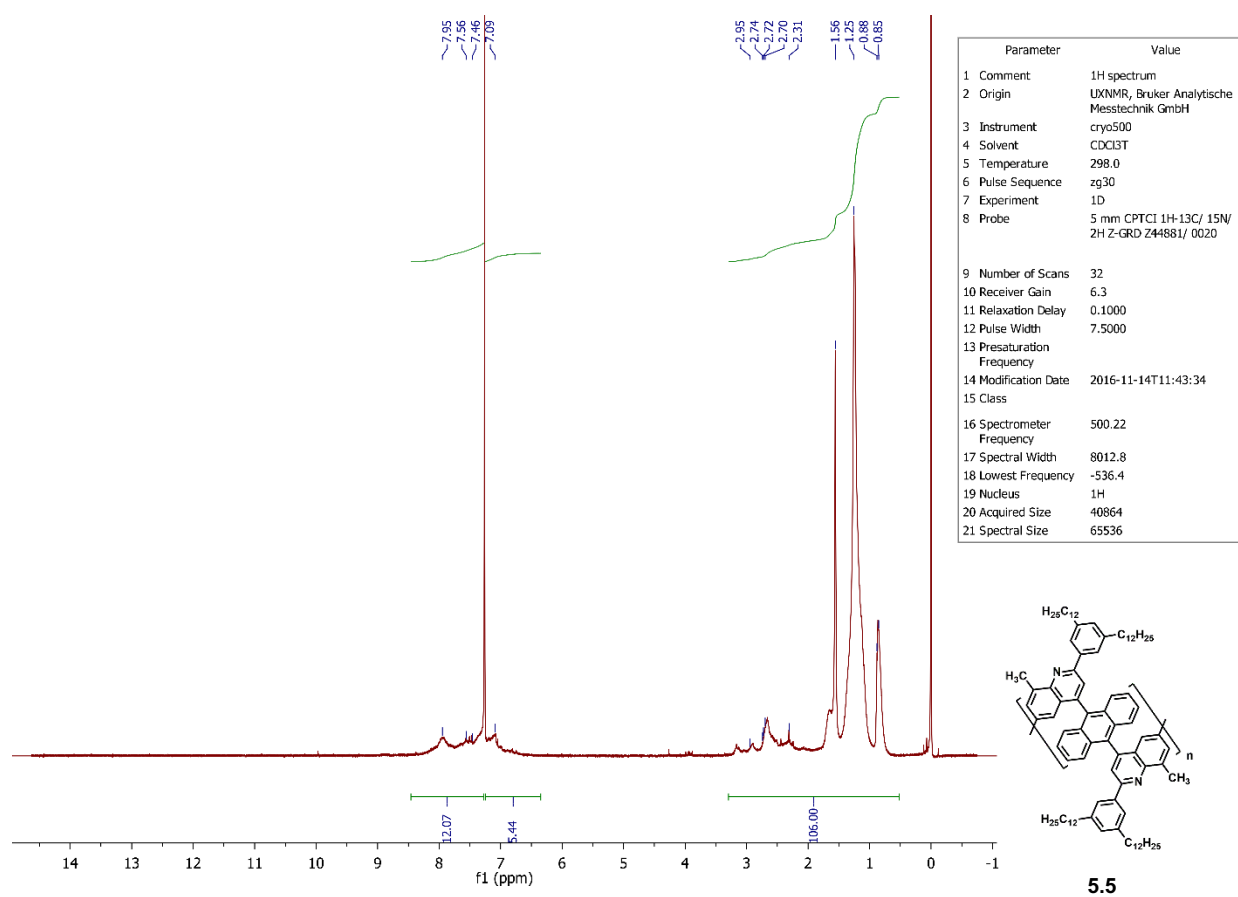


Figure S5.41. The ^1H NMR spectrum obtained for **5.5**.

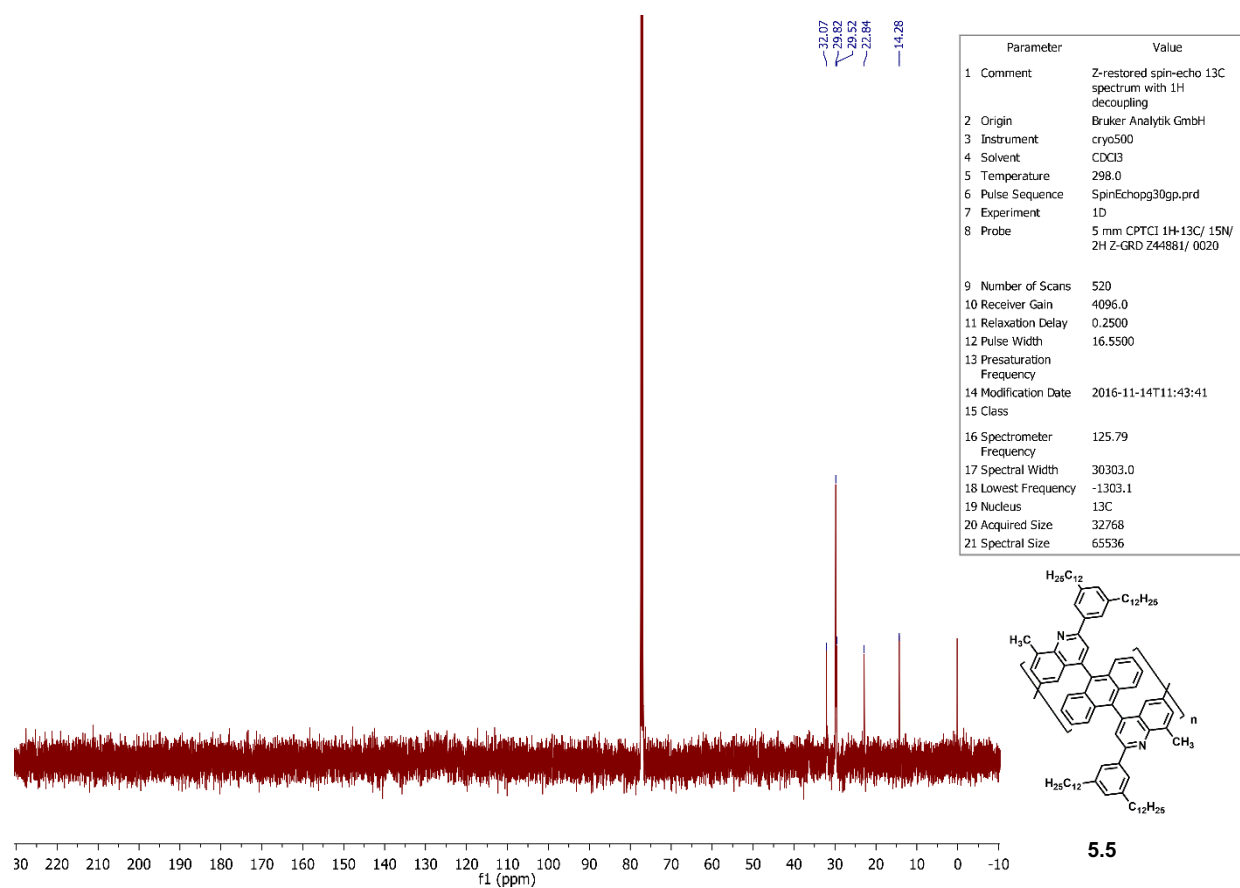


Figure S5.42. The ^{13}C NMR spectrum obtained for **5.5**.

5.5.5. Compiled UV/Vis Analytical Data

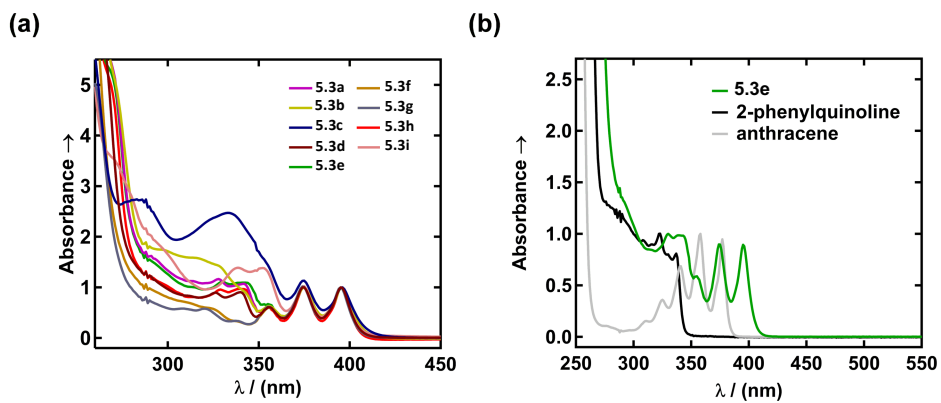


Figure S5.43. (a) The UV/vis absorbance spectra obtained for the diquinolineanthracene model compounds, (b) The UV/vis absorbance spectra obtained for the diquinolineanthracene model compound **5.3e** (green trace), 2-phenylquinoline (black trace), and anthracene (light grey trace).

entry	compound	R	λ_{max} (nm)
1	5.3a		328, 342, 356, 374, 395
2	5.3b		328 (sh.) ^[a] , 343 (sh.) ^[a] , 356, 375, 395
3	5.3c		283, 333, 354 (sh.) ^[a] , 375, 396
4	5.3d		326, 340, 355, 374, 395
5	5.3e		330, 339 (sh.) ^[a] , 343, 355, 375, 395
6	5.3f		324 (sh.) ^[a] , 339 (sh.) ^[a] , 356, 375, 395
7	5.3g		309, 320, 337, 355, 374, 395
8	5.3h		329, 340, 356, 375, 395
9	5.3i		338, 352, 374, 395

[a] (sh.) = shoulder

Table S5.1. The annotated UV/vis absorbance peak data obtained for the diquinolineanthracene model compounds.

5.5.6. Equilibrium Structure Obtained from Density Functional Theory Calculations

Ground state density functional theory calculations were performed with Gaussian 09.^{S2} The structural optimizations were performed using the DFT-B3LYP hybrid functional and a 6-311g(d,p) basis set. Frequency calculations confirmed that the optimized structures reached their equilibrium geometries.

Compound	Isomer	HOMO	LUMO	LUMO+1	E _g
5.3a	<i>trans</i>	−5.74	−2.26	−2.03	3.47
	<i>cis</i>	−5.79	−2.32	−2.09	3.48
5.3b	<i>trans</i>	−5.97	−2.50	−2.48	3.48
	<i>cis</i>	−5.97	−2.49	−2.48	3.48
5.3c	<i>trans</i>	−6.00	−2.86	−2.86	3.14
	<i>cis</i>	−6.00	−2.85	−2.85	3.15
5.3d	<i>trans</i>	−5.66	−2.19	−1.89	3.48
	<i>cis</i>	−5.66	−2.19	−1.90	3.48
5.3e	<i>trans</i>	−5.62	−2.14	−1.82	3.48
	<i>cis</i>	−5.62	−2.14	−1.82	3.48
5.3f	<i>trans</i>	−5.74	−2.26	−2.03	3.47
	<i>cis</i>	−5.74	−2.26	−2.04	3.47
5.3g	<i>trans</i>	−5.67	−2.20	−1.73	3.47
	<i>cis</i>	−5.67	−2.20	−1.74	3.47
5.3h^{*a}	<i>trans</i>	−5.62	−2.14	−1.83	3.48
	<i>cis</i>	−5.62	−2.15	−1.83	3.47

5.3i	<i>trans</i>	-5.60	-2.12	-1.75	3.48
	<i>cis</i>	-5.57	-2.09	-1.75	3.48

Table S5.2. The calculated HOMO – 1, HOMO, LUMO, LUMO + 1, and HOMO – LUMO gap energies for the cis and trans isomers of compounds **5.3a–5.3i**

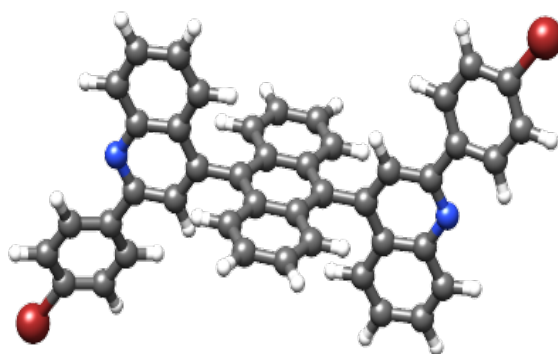


Figure S5.44. The energy minimized geometry for compound **5.3a** *trans* isomer.

Imaginary Frequencies = 0

Energy = -6950.61 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.41300	0.57800	-3.66900
C	-0.41300	-0.57800	-3.66900
C	-0.81100	-1.14200	-2.49000
C	-0.41600	-0.59100	-1.23000
C	0.41600	0.59100	-1.23000
C	0.81100	1.14200	-2.49000
C	-0.81700	-1.16500	-0.00700
C	-0.41500	-0.59100	1.21500
C	0.41500	0.59100	1.21500
C	0.81700	1.16500	-0.00700
C	-0.80900	-1.14300	2.47600
C	-0.41100	-0.57900	3.65400

C	0.41100	0.57900	3.65400
C	0.80900	1.14300	2.47600
C	1.66200	2.40200	−0.00800
C	−1.66200	−2.40200	−0.00800
C	−3.08800	−2.33100	0.00500
C	−3.80300	−3.57000	0.02600
N	−3.18400	−4.77900	0.02000
C	−1.86500	−4.82600	−0.00800
C	−1.07100	−3.64300	−0.01300
C	3.08800	2.33100	0.00500
C	3.80300	3.57000	0.02600
N	3.18400	4.77900	0.02000
C	1.86500	4.82600	−0.00800
C	1.07100	3.64300	−0.01300
C	3.81700	1.11500	0.00800
C	5.19100	1.12500	0.03100
C	5.89900	2.34900	0.05300
C	5.22200	3.54400	0.05000
C	−3.81700	−1.11500	0.00800
C	−5.19100	−1.12500	0.03100
C	−5.89900	−2.34900	0.05300
C	−5.22200	−3.54400	0.05000
C	−1.23700	−6.17500	−0.01600

C	1.23700	6.17500	−0.01600
C	1.99000	7.29000	0.37900
C	1.44000	8.56500	0.38800
C	0.11700	8.73600	−0.01100
C	−0.65300	7.65300	−0.42000
C	−0.08900	6.38100	−0.41800
C	0.08900	−6.38100	−0.41800
C	0.65300	−7.65300	−0.42000
C	−0.11700	−8.73600	−0.01100
C	−1.44000	−8.56500	0.38800
C	−1.99000	−7.29000	0.37900
Br	0.65300	−10.49200	−0.00400
Br	−0.65300	10.49200	−0.00400
H	0.72600	1.01300	−4.61100
H	−0.72600	−1.01300	−4.61100
H	−1.43900	−2.02300	−2.49900
H	1.43900	2.02300	−2.49900
H	−1.43400	−2.02700	2.48400
H	−0.72300	−1.01600	4.59600
H	0.72300	1.01600	4.59600
H	1.43400	2.02700	2.48400
H	0.00800	−3.71100	0.00300
H	−0.00800	3.71100	0.00300

H	3.27600	0.17700	−0.00700
H	5.73900	0.19000	0.03300
H	6.98300	2.34000	0.07000
H	5.73900	4.49600	0.06400
H	−3.27600	−0.17700	−0.00700
H	−5.73900	−0.19000	0.03300
H	−6.98300	−2.34000	0.07000
H	−5.73900	−4.49600	0.06400
H	3.01900	7.13800	0.67800
H	2.03000	9.41600	0.70200
H	−1.67600	7.79900	−0.74100
H	−0.69600	5.55200	−0.76000
H	0.69600	−5.55200	−0.76000
H	1.67600	−7.79900	−0.74100
H	−2.03000	−9.41600	0.70200
H	−3.01900	−7.13800	0.67800

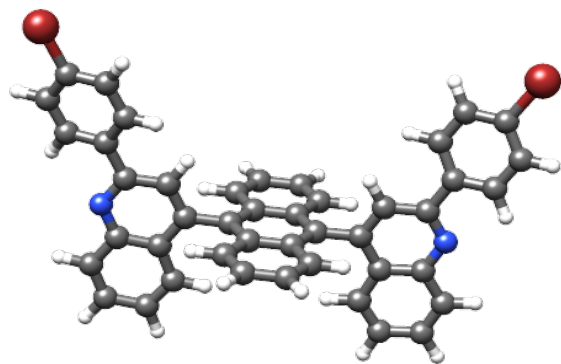


Figure S5.45. The energy minimized geometry for compound **5.3a** *cis* isomer.

Imaginary Frequencies = 0

Energy = -6950.61 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	3.58600	1.02700	-1.63800
C	3.71000	-0.38800	-1.63800
C	2.59600	-1.17900	-1.63100
C	1.28100	-0.61300	-1.62500
C	1.15500	0.82600	-1.62500
C	2.35100	1.61200	-1.63100
C	0.12400	-1.41800	-1.62000
C	-1.15500	-0.82600	-1.62500
C	-1.28100	0.61300	-1.62500
C	-0.12400	1.41800	-1.62000
C	-2.35100	-1.61200	-1.63100
C	-3.58600	-1.02700	-1.63800

C	−3.71000	0.38800	−1.63800
C	−2.59600	1.17900	−1.63100
C	−0.25500	2.90900	−1.59300
C	0.25500	−2.90900	−1.59300
C	0.31600	−3.67700	−2.79500
C	0.41900	−5.09700	−2.65900
N	0.47300	−5.72100	−1.45300
C	0.43200	−4.99400	−0.35100
C	0.31200	−3.57500	−0.39100
C	−0.31600	3.67700	−2.79500
C	−0.41900	5.09700	−2.65900
N	−0.47300	5.72100	−1.45300
C	−0.43200	4.99400	−0.35100
C	−0.31200	3.57500	−0.39100
C	−0.27000	3.11200	−4.09400
C	−0.32400	3.91500	−5.20800
C	−0.42500	5.32000	−5.07400
C	−0.47200	5.89800	−3.83000
C	0.27000	−3.11200	−4.09400
C	0.32400	−3.91500	−5.20800
C	0.42500	−5.32000	−5.07400
C	0.47200	−5.89800	−3.83000
C	0.49700	−5.72600	0.94300

C	-0.49700	5.72600	0.94300
C	-0.83900	5.09200	2.14500
C	-0.89700	5.79800	3.34200
C	-0.60700	7.15800	3.34200
C	-0.27000	7.81800	2.16300
C	-0.22200	7.10000	0.97500
C	0.83900	-5.09200	2.14500
C	0.89700	-5.79800	3.34200
C	0.60700	-7.15800	3.34200
C	0.27000	-7.81800	2.16300
C	0.22200	-7.10000	0.97500
Br	0.67600	-8.13900	4.98700
Br	-0.67600	8.13900	4.98700
H	4.47700	1.64400	-1.64300
H	4.69500	-0.84000	-1.64400
H	2.69900	-2.25600	-1.63200
H	2.26600	2.69100	-1.63000
H	-2.26600	-2.69100	-1.63000
H	-4.47700	-1.64400	-1.64300
H	-4.69500	0.84000	-1.64400
H	-2.69900	2.25600	-1.63200
H	0.24200	-3.00900	0.52800
H	-0.24200	3.00900	0.52800

H	−0.19200	2.03600	−4.19700
H	−0.28900	3.47300	−6.19700
H	−0.46700	5.94000	−5.96200
H	−0.55100	6.97000	−3.69900
H	0.19200	−2.03600	−4.19700
H	0.28900	−3.47300	−6.19700
H	0.46700	−5.94000	−5.96200
H	0.55100	−6.97000	−3.69900
H	−1.08900	4.03800	2.16000
H	−1.17000	5.29700	4.26200
H	−0.04800	8.87700	2.17400
H	0.03000	7.59700	0.04700
H	1.08900	−4.03800	2.16000
H	1.17000	−5.29700	4.26200
H	0.04800	−8.87700	2.17400
H	−0.03000	−7.59700	0.04700

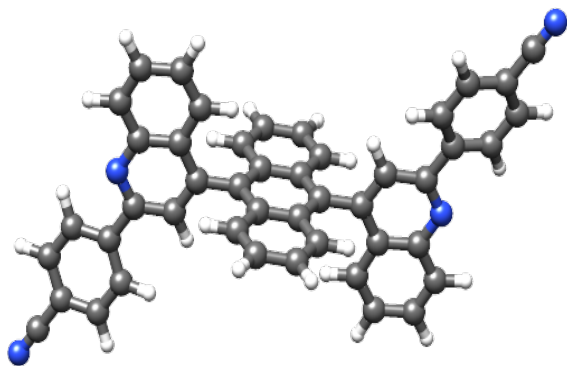


Figure S5.46. The energy minimized geometry for compound **5.3b** *trans* isomer.

Imaginary Frequencies = 0

Energy = -1988.05 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.65200	-0.28200	3.67300
C	-0.65200	0.28200	3.67300
C	-1.28700	0.55200	2.49400
C	-0.66500	0.28200	1.23300
C	0.66500	-0.28200	1.23300
C	1.28700	-0.55200	2.49400
C	-1.31100	0.55300	0.01000
C	-0.66500	0.28200	-1.21200
C	0.66500	-0.28200	-1.21200
C	1.31100	-0.55300	0.01000
C	-1.28800	0.55000	-2.47300
C	-0.65300	0.28000	-3.65100

C	0.65300	−0.28000	−3.65100
C	1.28800	−0.55000	−2.47300
C	2.69800	−1.11700	0.01100
C	−2.69800	1.11700	0.01100
C	−2.93200	2.52500	0.00000
C	−4.29400	2.96300	−0.02100
N	−5.34400	2.10200	−0.01900
C	−5.10800	0.80200	0.00800
C	−3.78600	0.27600	0.01400
C	2.93200	−2.52500	0.00000
C	4.29400	−2.96300	−0.02100
N	5.34400	−2.10200	−0.01900
C	5.10800	−0.80200	0.00800
C	3.78600	−0.27600	0.01400
C	1.89800	−3.49500	0.00000
C	2.19900	−4.83600	−0.02000
C	3.54600	−5.26900	−0.04100
C	4.57000	−4.35500	−0.04200
C	−1.89800	3.49500	0.00000
C	−2.19900	4.83600	−0.02000
C	−3.54600	5.26900	−0.04100
C	−4.57000	4.35500	−0.04200
C	−6.29700	−0.09500	0.01300

C	6.29700	0.09500	0.01300
C	6.21900	1.43400	0.42100
C	7.34200	2.24900	0.41900
C	8.57800	1.73800	0.00200
C	8.66900	0.39800	−0.40200
C	7.54300	−0.40900	−0.39100
C	−7.54300	0.40900	−0.39100
C	−8.66900	−0.39800	−0.40200
C	−8.57800	−1.73800	0.00200
C	−7.34200	−2.24900	0.41900
C	−6.21900	−1.43400	0.42100
C	9.73600	2.57600	−0.00700
N	10.67200	3.25400	−0.01500
C	−9.73600	−2.57600	−0.00700
N	−10.67200	−3.25400	−0.01500
H	1.14400	−0.49600	4.61500
H	−1.14400	0.49600	4.61500
H	−2.28100	0.98000	2.50300
H	2.28100	−0.98000	2.50300
H	−2.28300	0.97600	−2.48200
H	−1.14500	0.49300	−4.59300
H	1.14500	−0.49300	−4.59300
H	2.28300	−0.97600	−2.48200

H	−3.62500	−0.79400	−0.00300
H	3.62500	0.79400	−0.00300
H	0.86700	−3.16500	0.01500
H	1.40100	−5.56900	−0.01900
H	3.76600	−6.33000	−0.05600
H	5.60900	−4.65900	−0.05500
H	−0.86700	3.16500	0.01500
H	−1.40100	5.56900	−0.01900
H	−3.76600	6.33000	−0.05600
H	−5.60900	4.65900	−0.05500
H	5.28000	1.84800	0.76800
H	7.27000	3.28000	0.74400
H	9.62400	0.00000	−0.72300
H	7.60500	−1.44600	−0.69200
H	−7.60500	1.44600	−0.69200
H	−9.62400	0.00000	−0.72300
H	−7.27000	−3.28000	0.74400
H	−5.28000	−1.84800	0.76800

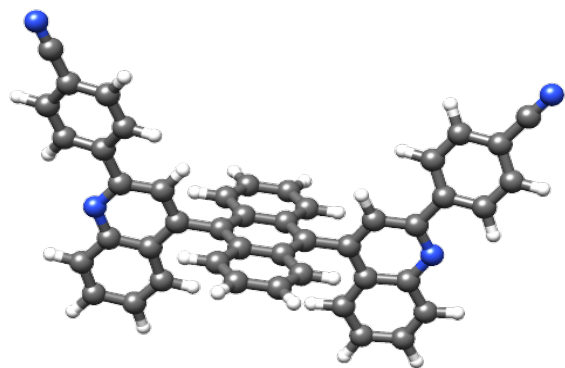


Figure S5.47. The energy minimized geometry for compound **5.3b** *cis* isomer.

Imaginary Frequencies = 0

Energy = -1988.05 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-3.66300	-0.70400	-0.97900
C	-3.66100	0.71600	-0.98100
C	-2.48100	1.40500	-0.97500
C	-1.22100	0.72400	-0.96800
C	-1.22400	-0.72000	-0.96800
C	-2.48600	-1.39600	-0.97200
C	0.00200	1.42300	-0.96300
C	1.22400	0.72000	-0.96800
C	1.22100	-0.72400	-0.96800
C	-0.00200	-1.42300	-0.96300
C	2.48600	1.39600	-0.97200
C	3.66300	0.70400	-0.97900

C	3.66100	−0.71600	−0.98100
C	2.48100	−1.40500	−0.97500
C	−0.00400	−2.92000	−0.93600
C	0.00400	2.92000	−0.93600
C	0.01900	3.69000	−2.13700
C	0.04300	5.11400	−2.00300
N	0.03900	5.74000	−0.79800
C	0.00800	5.01100	0.30300
C	0.00000	3.58900	0.26600
C	−0.01900	−3.69000	−2.13700
C	−0.04300	−5.11400	−2.00300
N	−0.03900	−5.74000	−0.79800
C	−0.00800	−5.01100	0.30300
C	0.00000	−3.58900	0.26600
C	−0.02000	−3.12200	−3.43700
C	−0.04300	−3.92800	−4.55000
C	−0.06800	−5.33600	−4.41700
C	−0.06700	−5.91700	−3.17400
C	0.02000	3.12200	−3.43700
C	0.04300	3.92800	−4.55000
C	0.06800	5.33600	−4.41700
C	0.06700	5.91700	−3.17400
C	0.00200	5.75000	1.59600

C	−0.00200	−5.75000	1.59600
C	−0.40900	−7.09200	1.62600
C	−0.41800	−7.81000	2.81100
C	−0.00700	−7.19900	4.00500
C	0.41300	−5.86200	3.98700
C	0.41300	−5.15200	2.79500
C	−0.41300	5.15200	2.79500
C	−0.41300	5.86200	3.98700
C	0.00700	7.19900	4.00500
C	0.41800	7.81000	2.81100
C	0.40900	7.09200	1.62600
C	−0.01400	−7.93400	5.23200
N	−0.02000	−8.52800	6.22300
C	0.01400	7.93400	5.23200
N	0.02000	8.52800	6.22300
H	−4.60600	−1.23900	−0.98400
H	−4.60200	1.25400	−0.98800
H	−2.48900	2.48700	−0.97700
H	−2.49700	−2.47900	−0.97000
H	2.49700	2.47900	−0.97000
H	4.60600	1.23900	−0.98400
H	4.60200	−1.25400	−0.98800
H	2.48900	−2.48700	−0.97700

H	0.01400	3.01800	1.18500
H	−0.01400	−3.01800	1.18500
H	−0.00200	−2.04400	−3.53900
H	−0.04300	−3.48400	−5.53900
H	−0.08600	−5.95600	−5.30600
H	−0.08300	−6.99200	−3.04300
H	0.00200	2.04400	−3.53900
H	0.04300	3.48400	−5.53900
H	0.08600	5.95600	−5.30600
H	0.08300	6.99200	−3.04300
H	−0.71500	−7.55700	0.69800
H	−0.74100	−8.84300	2.82300
H	0.74300	−5.39200	4.90400
H	0.76300	−4.12700	2.80400
H	−0.76300	4.12700	2.80400
H	−0.74300	5.39200	4.90400
H	0.74100	8.84300	2.82300
H	0.71500	7.55700	0.69800

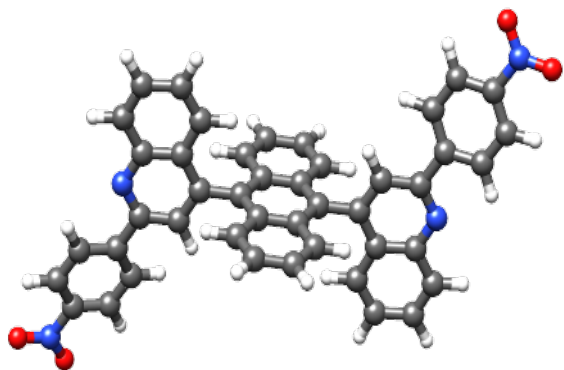


Figure S5.48. The energy minimized geometry for compound **5.3c** *trans* isomer.

Imaginary Frequencies = 0

Energy = -2212.63 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.31700	-0.63600	3.67200
C	-0.31700	0.63600	3.67200
C	-0.62200	1.25500	2.49300
C	-0.31800	0.64800	1.23200
C	0.31800	-0.64800	1.23200
C	0.62200	-1.25500	2.49300
C	-0.62400	1.27800	0.01000
C	-0.31800	0.64900	-1.21300
C	0.31800	-0.64900	-1.21300
C	0.62400	-1.27800	0.01000
C	-0.62000	1.25600	-2.47300
C	-0.31600	0.63600	-3.65200

C	0.31600	−0.63600	−3.65200
C	0.62000	−1.25600	−2.47300
C	1.26500	−2.63200	0.01000
C	−1.26500	2.63200	0.01000
C	−2.68300	2.78800	−0.00100
C	−3.19600	4.12300	−0.02200
N	−2.39500	5.21900	−0.02000
C	−1.08400	5.05600	0.00800
C	−0.48500	3.76500	0.01400
C	2.68300	−2.78800	−0.00100
C	3.19600	−4.12300	−0.02200
N	2.39500	−5.21900	−0.02000
C	1.08400	−5.05600	0.00800
C	0.48500	−3.76500	0.01400
C	3.59400	−1.70100	−0.00100
C	4.94900	−1.92800	−0.02200
C	5.45700	−3.24800	−0.04300
C	4.60200	−4.32200	−0.04300
C	−3.59400	1.70100	−0.00100
C	−4.94900	1.92800	−0.02200
C	−5.45700	3.24800	−0.04300
C	−4.60200	4.32200	−0.04300
C	−0.25500	6.29300	0.01400

C	0.25500	−6.29300	0.01400
C	−1.08400	−6.28800	0.43100
C	−1.83800	−7.45400	0.43000
C	−1.24300	−8.63500	0.00500
C	0.08500	−8.67800	−0.40900
C	0.82700	−7.50700	−0.39800
C	1.08400	6.28800	0.43100
C	1.83800	7.45400	0.43000
C	1.24300	8.63500	0.00500
C	−0.08500	8.67800	−0.40900
C	−0.82700	7.50700	−0.39800
N	2.04100	9.87800	−0.00400
O	3.20500	9.80800	0.36900
O	1.49000	10.90300	−0.38300
N	−2.04100	−9.87800	−0.00400
O	−3.20500	−9.80800	0.36900
O	−1.49000	−10.90300	−0.38300
H	0.55900	−1.11400	4.61400
H	−0.55900	1.11400	4.61400
H	−1.10500	2.22300	2.50300
H	1.10500	−2.22300	2.50300
H	−1.10000	2.22600	−2.48300
H	−0.55500	1.11600	−4.59400

H	0.55500	−1.11600	−4.59400
H	1.10000	−2.22600	−2.48300
H	0.59200	3.66300	−0.00200
H	−0.59200	−3.66300	−0.00200
H	3.20700	−0.69000	0.01400
H	5.63800	−1.09000	−0.02100
H	6.52900	−3.40900	−0.05800
H	4.96300	−5.34300	−0.05700
H	−3.20700	0.69000	0.01400
H	−5.63800	1.09000	−0.02100
H	−6.52900	3.40900	−0.05800
H	−4.96300	5.34300	−0.05700
H	−1.54600	−5.37400	0.78400
H	−2.86900	−7.46500	0.75600
H	0.51100	−9.61800	−0.73000
H	1.86400	−7.51000	−0.70500
H	1.54600	5.37400	0.78400
H	2.86900	7.46500	0.75600
H	−0.51100	9.61800	−0.73000
H	−1.86400	7.51000	−0.70500

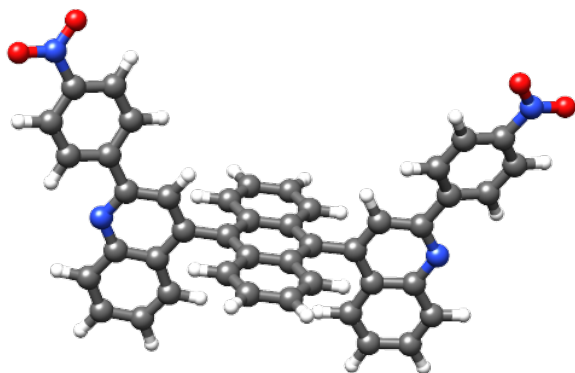


Figure S5.49. The energy minimized geometry for compound **5.3c** *cis* isomer.

Imaginary Frequencies = 0

Energy = -2212.63 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	3.66200	0.71000	-1.28500
C	3.66200	-0.71000	-1.28300
C	2.48300	-1.40000	-1.27600
C	1.22300	-0.72200	-1.27200
C	1.22300	0.72200	-1.27200
C	2.48300	1.40000	-1.27900
C	0.00000	-1.42200	-1.26700
C	-1.22300	-0.72200	-1.27200
C	-1.22300	0.72200	-1.27200
C	0.00000	1.42200	-1.26700
C	-2.48300	-1.40000	-1.27900
C	-3.66200	-0.71000	-1.28500

C	−3.66200	0.71000	−1.28300
C	−2.48300	1.40000	−1.27600
C	0.00100	2.92000	−1.24000
C	−0.00100	−2.92000	−1.24000
C	0.01100	−3.69000	−2.44200
C	0.03300	−5.11400	−2.30800
N	0.03000	−5.74000	−1.10300
C	0.00100	−5.01100	−0.00200
C	−0.00500	−3.58900	−0.03800
C	−0.01100	3.69000	−2.44200
C	−0.03300	5.11400	−2.30800
N	−0.03000	5.74000	−1.10300
C	−0.00100	5.01100	−0.00200
C	0.00500	3.58900	−0.03800
C	−0.01200	3.12200	−3.74100
C	−0.03300	3.92700	−4.85400
C	−0.05400	5.33500	−4.72200
C	−0.05400	5.91700	−3.47800
C	0.01200	−3.12200	−3.74100
C	0.03300	−3.92700	−4.85400
C	0.05400	−5.33500	−4.72200
C	0.05400	−5.91700	−3.47800
C	−0.00500	−5.75100	1.29100

C	0.00500	5.75100	1.29100
C	0.42500	5.15200	2.48800
C	0.42600	5.86200	3.68100
C	0.00000	7.18400	3.67300
C	-0.41600	7.81200	2.50300
C	-0.40700	7.09300	1.31800
C	-0.42500	-5.15200	2.48800
C	-0.42600	-5.86200	3.68100
C	0.00000	-7.18400	3.67300
C	0.41600	-7.81200	2.50300
C	0.40700	-7.09300	1.31800
N	0.00500	-7.94400	4.94000
O	-0.37100	-7.36500	5.95100
O	0.38600	-9.10700	4.90200
N	-0.00500	7.94400	4.94000
O	0.37100	7.36500	5.95100
O	-0.38600	9.10700	4.90200
H	4.60400	1.24700	-1.29200
H	4.60400	-1.24700	-1.28800
H	2.49300	-2.48300	-1.27500
H	2.49300	2.48300	-1.28000
H	-2.49300	-2.48300	-1.28000
H	-4.60400	-1.24700	-1.29200

H	−4.60400	1.24700	−1.28800
H	−2.49300	2.48300	−1.27500
H	0.01000	−3.01900	0.88100
H	−0.01000	3.01900	0.88100
H	0.00400	2.04400	−3.84300
H	−0.03200	3.48300	−5.84300
H	−0.07000	5.95600	−5.61100
H	−0.06800	6.99200	−3.34800
H	−0.00400	−2.04400	−3.84300
H	0.03200	−3.48300	−5.84300
H	0.07000	−5.95600	−5.61100
H	0.06800	−6.99200	−3.34800
H	0.77800	4.12800	2.49600
H	0.75400	5.41400	4.60900
H	−0.73800	8.84400	2.53900
H	−0.71600	7.55600	0.39100
H	−0.77800	−4.12800	2.49600
H	−0.75400	−5.41400	4.60900
H	0.73800	−8.84400	2.53900
H	0.71600	−7.55600	0.39100

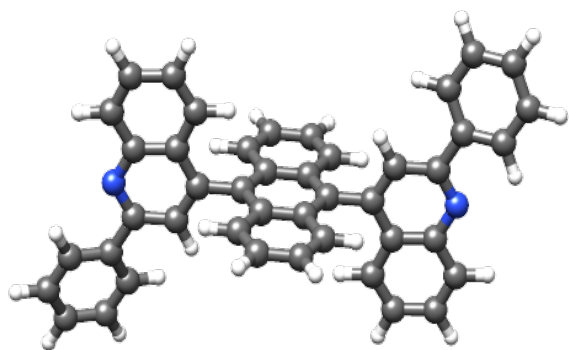


Figure S5.50. The energy minimized geometry for compound **5.3d** *trans* isomer.

Imaginary Frequencies = 0

Energy = -1803.52 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-0.41000	-0.58000	3.65200
C	0.41000	0.58000	3.65200
C	0.80600	1.14500	2.47300
C	0.41400	0.59200	1.21300
C	-0.41400	-0.59200	1.21300
C	-0.80600	-1.14500	2.47300
C	0.81500	1.16700	-0.00900
C	0.41400	0.59200	-1.23100
C	-0.41400	-0.59200	-1.23100
C	-0.81500	-1.16700	-0.00900
C	0.80800	1.14400	-2.49200
C	0.41100	0.57900	-3.67100

C	−0.41100	−0.57900	−3.67100
C	−0.80800	−1.14400	−2.49200
C	−1.65900	−2.40400	−0.01000
C	1.65900	2.40400	−0.01000
C	3.08500	2.33400	0.00300
C	3.79900	3.57300	0.02500
N	3.18100	4.78300	0.01900
C	1.86100	4.82900	−0.00900
C	1.06800	3.64500	−0.01400
C	−3.08500	−2.33400	0.00300
C	−3.79900	−3.57300	0.02500
N	−3.18100	−4.78300	0.01900
C	−1.86100	−4.82900	−0.00900
C	−1.06800	−3.64500	−0.01400
C	−3.81500	−1.11900	0.00500
C	−5.18900	−1.12900	0.02800
C	−5.89600	−2.35300	0.05100
C	−5.21800	−3.54800	0.04900
C	3.81500	1.11900	0.00500
C	5.18900	1.12900	0.02800
C	5.89600	2.35300	0.05100
C	5.21800	3.54800	0.04900
C	1.22900	6.17700	−0.01500

C	-1.22900	-6.17700	-0.01500
C	-1.96700	-7.28900	0.41600
C	-1.40100	-8.55800	0.42300
C	-0.08800	-8.74600	-0.00800
C	0.65200	-7.65200	-0.45000
C	0.08800	-6.37900	-0.45200
C	-0.08800	6.37900	-0.45200
C	-0.65200	7.65200	-0.45000
C	0.08800	8.74600	-0.00800
C	1.40100	8.55800	0.42300
C	1.96700	7.28900	0.41600
H	0.35300	-9.73600	-0.00300
H	-0.35300	9.73600	-0.00300
H	-0.72000	-1.01800	4.59400
H	0.72000	1.01800	4.59400
H	1.42900	2.03000	2.48200
H	-1.42900	-2.03000	2.48200
H	1.43400	2.02700	-2.50100
H	0.72300	1.01600	-4.61300
H	-0.72300	-1.01600	-4.61300
H	-1.43400	-2.02700	-2.50100
H	-0.01100	3.71500	0.00300
H	0.01100	-3.71500	0.00300

H	−3.27400	−0.18000	−0.01100
H	−5.73700	−0.19400	0.02900
H	−6.98000	−2.34500	0.06900
H	−5.73500	−4.50000	0.06400
H	3.27400	0.18000	−0.01100
H	5.73700	0.19400	0.02900
H	6.98000	2.34500	0.06900
H	5.73500	4.50000	0.06400
H	−2.98800	−7.13400	0.74000
H	−1.98500	−9.40500	0.76700
H	1.66900	−7.78800	−0.79900
H	0.67500	−5.54700	−0.82200
H	−0.67500	5.54700	−0.82200
H	−1.66900	7.78800	−0.79900
H	1.98500	9.40500	0.76700
H	2.98800	7.13400	0.74000

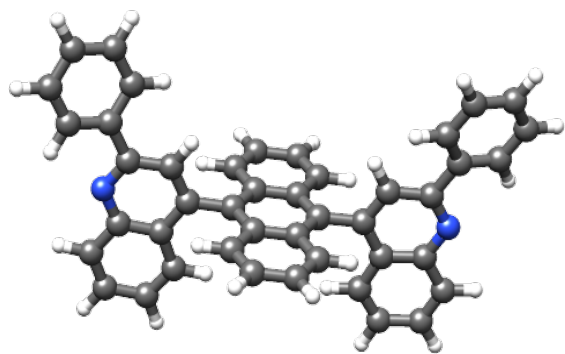


Figure S5.51. The energy minimized geometry for compound **5.3d** *cis* isomer.

Imaginary Frequencies = 0

Energy = −1803.52 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	3.66700	0.68000	−0.52400
C	3.65500	−0.74100	−0.52300
C	2.47100	−1.42100	−0.51600
C	1.21600	−0.73200	−0.51100
C	1.22800	0.71200	−0.51100
C	2.49400	1.38000	−0.51800
C	−0.01200	−1.42400	−0.50700
C	−1.22800	−0.71200	−0.51100
C	−1.21600	0.73200	−0.51100
C	0.01200	1.42400	−0.50700
C	−2.49400	−1.38000	−0.51800
C	−3.66700	−0.68000	−0.52400

C	−3.65500	0.74100	−0.52300
C	−2.47100	1.42100	−0.51600
C	0.02500	2.92100	−0.48100
C	−0.02500	−2.92100	−0.48100
C	−0.01900	−3.69000	−1.68400
C	−0.00800	−5.11400	−1.54900
N	−0.01800	−5.74100	−0.34400
C	−0.04000	−5.01500	0.75900
C	−0.03400	−3.59100	0.72000
C	0.01900	3.69000	−1.68400
C	0.00800	5.11400	−1.54900
N	0.01800	5.74100	−0.34400
C	0.04000	5.01500	0.75900
C	0.03400	3.59100	0.72000
C	0.01300	3.12100	−2.98200
C	−0.00200	3.92500	−4.09700
C	−0.01400	5.33300	−3.96400
C	−0.00800	5.91500	−2.72000
C	−0.01300	−3.12100	−2.98200
C	0.00200	−3.92500	−4.09700
C	0.01400	−5.33300	−3.96400
C	0.00800	−5.91500	−2.72000
C	−0.05200	−5.74800	2.05500

C	0.05200	5.74800	2.05500
C	−0.36800	7.08600	2.09700
C	−0.37000	7.79200	3.29300
C	0.05600	7.18100	4.47200
C	0.48600	5.85700	4.44300
C	0.48300	5.14600	3.24600
C	0.36800	−7.08600	2.09700
C	0.37000	−7.79200	3.29300
C	−0.05600	−7.18100	4.47200
C	−0.48600	−5.85700	4.44300
C	−0.48300	−5.14600	3.24600
H	0.05500	7.73400	5.40500
H	−0.05500	−7.73400	5.40500
H	4.61400	1.20900	−0.53100
H	4.59300	−1.28500	−0.52800
H	2.47100	−2.50300	−0.51400
H	2.51200	2.46200	−0.51800
H	−2.51200	−2.46200	−0.51800
H	−4.61400	−1.20900	−0.53100
H	−4.59300	1.28500	−0.52800
H	−2.47100	2.50300	−0.51400
H	−0.01200	−3.02300	1.64000
H	0.01200	3.02300	1.64000

H	0.02100	2.04300	−3.08400
H	−0.00500	3.48000	−5.08500
H	−0.02500	5.95400	−4.85300
H	−0.01400	6.99000	−2.59000
H	−0.02100	−2.04300	−3.08400
H	0.00500	−3.48000	−5.08500
H	0.02500	−5.95400	−4.85300
H	0.01400	−6.99000	−2.59000
H	−0.68800	7.55300	1.17500
H	−0.70500	8.82400	3.30700
H	0.83100	5.37700	5.35100
H	0.84400	4.12500	3.24300
H	0.68800	−7.55300	1.17500
H	0.70500	−8.82400	3.30700
H	−0.83100	−5.37700	5.35100
H	−0.84400	−4.12500	3.24300

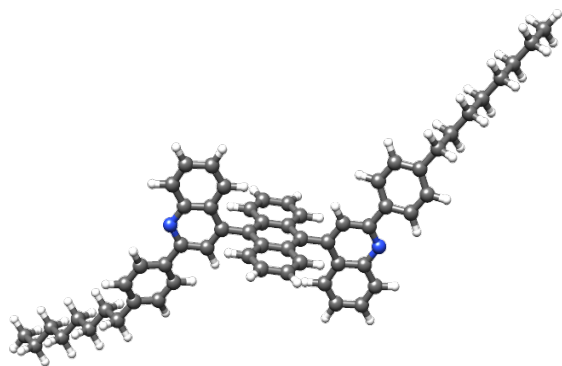


Figure S5.52. The energy minimized geometry for compound **5.3e** *trans* isomer.

Imaginary Frequencies = 0

Energy = -2432.72 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.41700	0.57500	4.44700
C	-0.41700	-0.57500	4.44700
C	-0.82100	-1.13500	3.26900
C	-0.42100	-0.58700	2.00800
C	0.42100	0.58700	2.00800
C	0.82100	1.13500	3.26900
C	-0.82800	-1.15800	0.78600
C	-0.42100	-0.58700	-0.43600
C	0.42100	0.58700	-0.43600
C	0.82800	1.15800	0.78600
C	-0.82000	-1.13600	-1.69700
C	-0.41700	-0.57500	-2.87500

C	0.41700	0.57500	−2.87500
C	0.82000	1.13600	−1.69700
C	1.68500	2.38600	0.78500
C	−1.68500	−2.38600	0.78500
C	−3.11100	−2.30200	0.78600
C	−3.83700	−3.53300	0.80700
N	−3.23100	−4.74900	0.81300
C	−1.91100	−4.81000	0.79900
C	−1.10700	−3.63300	0.79400
C	3.11100	2.30200	0.78600
C	3.83700	3.53300	0.80700
N	3.23100	4.74900	0.81300
C	1.91100	4.81000	0.79900
C	1.10700	3.63300	0.79400
C	3.82800	1.07800	0.77600
C	5.20200	1.07400	0.78600
C	5.92200	2.29100	0.80800
C	5.25600	3.49200	0.81800
C	−3.82800	−1.07800	0.77600
C	−5.20200	−1.07400	0.78600
C	−5.92200	−2.29100	0.80800
C	−5.25600	−3.49200	0.81800
C	−1.29400	−6.16300	0.80700

C	1.29400	6.16300	0.80700
C	−0.03600	6.38300	0.42500
C	−0.58400	7.66200	0.44600
C	0.17000	8.76700	0.85100
C	1.50000	8.54500	1.22800
C	2.05500	7.27300	1.20400
C	−2.05500	−7.27300	1.20400
C	−1.50000	−8.54500	1.22800
C	−0.17000	−8.76700	0.85100
C	0.58400	−7.66200	0.44600
C	0.03600	−6.38300	0.42500
C	−1.37900	17.35300	−4.50400
C	−1.58100	16.62100	−3.17400
C	−0.99200	15.20600	−3.16500
C	−1.19000	14.46500	−1.83800
C	−0.60000	13.05000	−1.83000
C	−0.80000	12.31000	−0.50200
C	−0.20800	10.89700	−0.49500
C	−0.41700	10.15900	0.84200
C	1.37900	−17.35300	−4.50400
C	1.58100	−16.62100	−3.17400
C	0.99200	−15.20600	−3.16500
C	1.19000	−14.46500	−1.83800

C	0.60000	−13.05000	−1.83000
C	0.80000	−12.31000	−0.50200
C	0.20800	−10.89700	−0.49500
C	0.41700	−10.15900	0.84200
H	0.73400	1.00800	5.38900
H	−0.73400	−1.00800	5.38900
H	−1.45500	−2.01200	3.27700
H	1.45500	2.01200	3.27700
H	−1.45400	−2.01300	−1.70500
H	−0.73300	−1.00900	−3.81700
H	0.73300	1.00900	−3.81700
H	1.45400	2.01300	−1.70500
H	−0.02900	−3.71300	0.82000
H	0.02900	3.71300	0.82000
H	3.27700	0.14600	0.76100
H	5.74100	0.13300	0.77800
H	7.00600	2.27200	0.81500
H	5.78200	4.43900	0.83200
H	−3.27700	−0.14600	0.76100
H	−5.74100	−0.13300	0.77800
H	−7.00600	−2.27200	0.81500
H	−5.78200	−4.43900	0.83200
H	−0.65300	5.55900	0.08700

H	−1.61700	7.80200	0.14300
H	2.10800	9.38400	1.55300
H	3.08500	7.11200	1.49400
H	−3.08500	−7.11200	1.49400
H	−2.10800	−9.38400	1.55300
H	1.61700	−7.80200	0.14300
H	0.65300	−5.55900	0.08700
H	−1.81000	18.35800	−4.47700
H	−1.85100	16.81100	−5.33000
H	−0.31600	17.45400	−4.74200
H	−1.12800	17.20500	−2.36400
H	−2.65300	16.56700	−2.94700
H	−1.44500	14.62200	−3.97700
H	0.08000	15.26000	−3.39300
H	−0.73800	15.05000	−1.02700
H	−2.26300	14.41100	−1.61100
H	−1.05200	12.46500	−2.64100
H	0.47200	13.10400	−2.05500
H	−0.35000	12.89500	0.31000
H	−1.87300	12.25500	−0.27700
H	−0.65600	10.30500	−1.30300
H	0.86500	10.94500	−0.71300
H	−1.49000	10.10500	1.05600

H	0.03300	10.74900	1.64800
H	1.81000	−18.35800	−4.47700
H	1.85100	−16.81100	−5.33000
H	0.31600	−17.45400	−4.74200
H	1.12800	−17.20500	−2.36400
H	2.65300	−16.56700	−2.94700
H	1.44500	−14.62200	−3.97700
H	−0.08000	−15.26000	−3.39300
H	0.73800	−15.05000	−1.02700
H	2.26300	−14.41100	−1.61100
H	1.05200	−12.46500	−2.64100
H	−0.47200	−13.10400	−2.05500
H	0.35000	−12.89500	0.31000
H	1.87300	−12.25500	−0.27700
H	0.65600	−10.30500	−1.30300
H	−0.86500	−10.94500	−0.71300
H	1.49000	−10.10500	1.05600
H	−0.03300	−10.74900	1.64800

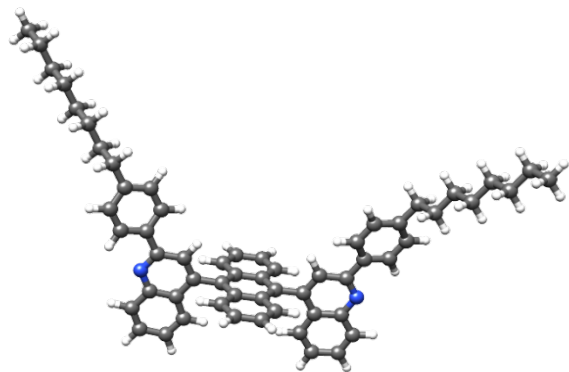


Figure S53. The energy minimized geometry for compound **5.3e** *cis* isomer.

Imaginary Frequencies = 0

Energy = -2432.72 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-3.61800	0.90400	-2.97700
C	-3.69400	-0.51500	-2.97800
C	-2.55300	-1.26700	-2.97200
C	-1.25900	-0.65600	-2.96500
C	-1.18200	0.78600	-2.96500
C	-2.40500	1.53000	-2.96900
C	-0.07500	-1.42200	-2.96000
C	1.18200	-0.78600	-2.96500
C	1.25900	0.65600	-2.96500
C	0.07500	1.42200	-2.96000
C	2.40500	-1.53000	-2.96900
C	3.61800	-0.90400	-2.97700

C	3.69400	0.51500	−2.97800
C	2.55300	1.26700	−2.97200
C	0.15500	2.91700	−2.93300
C	−0.15500	−2.91700	−2.93300
C	−0.18000	−3.68700	−4.13600
C	−0.23400	−5.10900	−3.99900
N	−0.27600	−5.73500	−2.79400
C	−0.26800	−5.00800	−1.69000
C	−0.19700	−3.58500	−1.73200
C	0.18000	3.68700	−4.13600
C	0.23400	5.10900	−3.99900
N	0.27600	5.73500	−2.79400
C	0.26800	5.00800	−1.69000
C	0.19700	3.58500	−1.73200
C	0.14500	3.12000	−5.43500
C	0.16300	3.92500	−6.54900
C	0.21500	5.33200	−6.41500
C	0.25000	5.91100	−5.17000
C	−0.14500	−3.12000	−5.43500
C	−0.16300	−3.92500	−6.54900
C	−0.21500	−5.33200	−6.41500
C	−0.25000	−5.91100	−5.17000
C	−0.31800	−5.73700	−0.39500

C	0.31800	5.73700	−0.39500
C	0.69700	5.11500	0.80100
C	0.73500	5.82600	1.99600
C	0.39300	7.18000	2.04500
C	0.01700	7.80000	0.84700
C	−0.01700	7.09800	−0.35000
C	−0.69700	−5.11500	0.80100
C	−0.73500	−5.82600	1.99600
C	−0.39300	−7.18000	2.04500
C	−0.01700	−7.80000	0.84700
C	0.01700	−7.09800	−0.35000
C	−6.15600	−13.00500	8.18000
C	−4.79400	−12.34100	7.95600
C	−4.71400	−11.54700	6.64700
C	−3.35400	−10.88000	6.41400
C	−3.27500	−10.08600	5.10500
C	−1.91400	−9.41900	4.87300
C	−1.83900	−8.62600	3.56400
C	−0.46700	−7.95900	3.33700
C	6.15600	13.00500	8.18000
C	4.79400	12.34100	7.95600
C	4.71400	11.54700	6.64700
C	3.35400	10.88000	6.41400

C	3.27500	10.08600	5.10500
C	1.91400	9.41900	4.87300
C	1.83900	8.62600	3.56400
C	0.46700	7.95900	3.33700
H	−4.53100	1.48900	−2.98100
H	−4.66300	−1.00100	−2.98500
H	−2.61900	−2.34700	−2.97200
H	−2.35600	2.61100	−2.96700
H	2.35600	−2.61100	−2.96700
H	4.53100	−1.48900	−2.98100
H	4.66300	1.00100	−2.98500
H	2.61900	2.34700	−2.97200
H	−0.15300	−3.01700	−0.81200
H	0.15300	3.01700	−0.81200
H	0.10400	2.04300	−5.53700
H	0.13700	3.48100	−7.53800
H	0.22800	5.95400	−7.30300
H	0.29200	6.98500	−5.03900
H	−0.10400	−2.04300	−5.53700
H	−0.13700	−3.48100	−7.53800
H	−0.22800	−5.95400	−7.30300
H	−0.29200	−6.98500	−5.03900
H	0.98800	4.07100	0.80800

H	1.03600	5.31800	2.90700
H	−0.26000	8.85000	0.85500
H	−0.30400	7.58800	−1.27100
H	−0.98800	−4.07100	0.80800
H	−1.03600	−5.31800	2.90700
H	0.26000	−8.85000	0.85500
H	0.30400	−7.58800	−1.27100
H	−6.18000	−13.56200	9.12000
H	−6.39200	−13.70500	7.37200
H	−6.95800	−12.26000	8.21500
H	−4.57100	−11.67400	8.79700
H	−4.01000	−13.10800	7.96100
H	−4.93800	−12.21500	5.80500
H	−5.49900	−10.78000	6.64200
H	−3.13000	−10.21200	7.25600
H	−2.56900	−11.64700	6.42000
H	−3.49900	−10.75300	4.26300
H	−4.05900	−9.31800	5.10000
H	−1.69000	−8.75100	5.71500
H	−1.12900	−10.18700	4.87800
H	−2.05800	−9.28900	2.71800
H	−2.61700	−7.85400	3.55500
H	0.31000	−8.73200	3.34300

H	−0.25100	−7.29300	4.17900
H	6.18000	13.56200	9.12000
H	6.39200	13.70500	7.37200
H	6.95800	12.26000	8.21500
H	4.57100	11.67400	8.79700
H	4.01000	13.10800	7.96100
H	4.93800	12.21500	5.80500
H	5.49900	10.78000	6.64200
H	3.13000	10.21200	7.25600
H	2.56900	11.64700	6.42000
H	3.49900	10.75300	4.26300
H	4.05900	9.31800	5.10000
H	1.69000	8.75100	5.71500
H	1.12900	10.18700	4.87800
H	2.05800	9.28900	2.71800
H	2.61700	7.85400	3.55500
H	−0.31000	8.73200	3.34300
H	0.25100	7.29300	4.17900

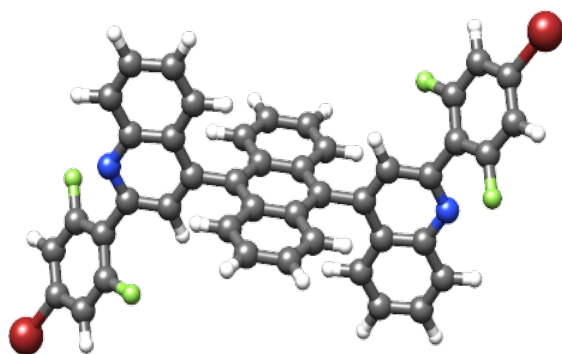


Figure S54. The energy minimized geometry for compound **5.3f** *trans* isomer.

Imaginary Frequencies = 0

Energy = -7347.64 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.69400	0.21700	-3.65800
C	-0.55400	0.89200	-3.57900
C	-1.18300	1.04200	-2.37600
C	-0.61100	0.52800	-1.16800
C	0.65900	-0.15500	-1.24800
C	1.27800	-0.28800	-2.53200
C	-1.25100	0.67300	0.07900
C	-0.65900	0.15500	1.24800
C	0.61100	-0.52800	1.16800
C	1.25100	-0.67300	-0.07900
C	-1.27800	0.28800	2.53200

C	−0.69400	−0.21700	3.65800
C	0.55400	−0.89200	3.57900
C	1.18300	−1.04100	2.37600
C	2.57300	−1.37200	−0.16100
C	−2.57300	1.37200	0.16100
C	−2.66100	2.78800	0.32000
C	−3.96800	3.36500	0.38000
N	−5.10700	2.62600	0.29900
C	−4.99500	1.32100	0.15800
C	−3.74300	0.65400	0.08200
C	2.66100	−2.78800	−0.32000
C	3.96800	−3.36500	−0.38000
N	5.10700	−2.62600	−0.29900
C	4.99500	−1.32100	−0.15800
C	3.74300	−0.65400	−0.08200
C	1.53100	−3.63900	−0.42000
C	1.69000	−4.99500	−0.57200
C	2.98300	−5.56600	−0.63000
C	4.09700	−4.76900	−0.53600
C	−1.53100	3.63900	0.42000
C	−1.69000	4.99500	0.57200
C	−2.98300	5.56600	0.63000
C	−4.09800	4.76900	0.53600

C	-6.26300	0.54400	0.06700
C	6.26300	-0.54400	-0.06700
C	6.50600	0.58400	-0.85400
C	7.68300	1.31500	-0.81900
C	8.67600	0.89800	0.06000
C	8.50200	-0.21000	0.87900
C	7.30300	-0.90500	0.79600
C	-6.50600	-0.58400	0.85400
C	-7.68300	-1.31500	0.81900
C	-8.67600	-0.89800	-0.06000
C	-8.50200	0.21000	-0.87900
C	-7.30300	0.90500	-0.79600
Br	-10.31700	-1.87500	-0.14500
F	-7.13900	1.95300	-1.61600
F	-5.54900	-0.98700	1.71700
Br	10.31700	1.87500	0.14500
F	5.54900	0.98700	-1.71700
F	7.13900	-1.95300	1.61600
H	1.18200	0.10500	-4.61900
H	-1.00700	1.29000	-4.48000
H	-2.13300	1.55600	-2.32400
H	2.23100	-0.79600	-2.60100
H	-2.23100	0.79600	2.60100

H	−1.18200	−0.10500	4.61900
H	1.00700	−1.29000	4.48000
H	2.13300	−1.55600	2.32400
H	−3.71400	−0.42100	−0.03700
H	3.71400	0.42100	0.03700
H	0.53900	−3.20500	−0.37600
H	0.81900	−5.63600	−0.64800
H	3.09000	−6.63800	−0.74900
H	5.10100	−5.17600	−0.57700
H	−0.53900	3.20500	0.37600
H	−0.81900	5.63600	0.64800
H	−3.09000	6.63800	0.74900
H	−5.10100	5.17600	0.57700
H	7.80500	2.17000	−1.46800
H	9.26100	−0.53900	1.57500
H	−7.80500	−2.17000	1.46800
H	−9.26100	0.53900	−1.57500

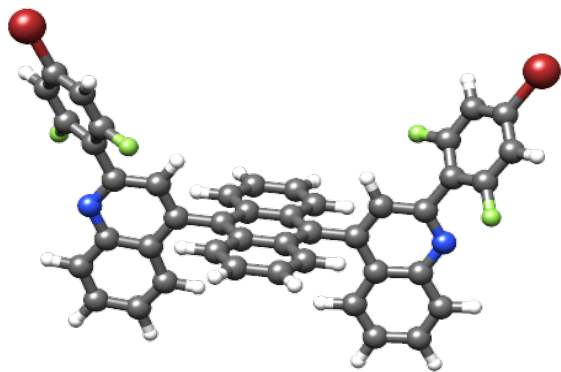


Figure S55. The energy minimized geometry for compound **5.3f** *cis* isomer.

Imaginary Frequencies = 0

Energy = -7347.64 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-3.38900	-1.55900	-1.69000
C	-3.72600	-0.17900	-1.69000
C	-2.74500	0.77200	-1.68700
C	-1.35900	0.41200	-1.68400
C	-1.01600	-0.99100	-1.68500
C	-2.08000	-1.95000	-1.68600
C	-0.33700	1.38200	-1.68400
C	1.01600	0.99100	-1.68500
C	1.35900	-0.41200	-1.68400
C	0.33700	-1.38200	-1.68400
C	2.08000	1.95000	-1.68600
C	3.38900	1.55900	-1.69000

C	3.72600	0.17900	−1.69000
C	2.74500	−0.77200	−1.68700
C	0.69300	−2.83600	−1.66700
C	−0.69300	2.83600	−1.66700
C	−0.81200	3.59200	−2.87200
C	−1.14800	4.97700	−2.75300
N	−1.35900	5.58600	−1.55500
C	−1.24700	4.86300	−0.46000
C	−0.91300	3.48200	−0.47300
C	0.81200	−3.59200	−2.87200
C	1.14800	−4.97700	−2.75300
N	1.35900	−5.58600	−1.55500
C	1.24700	−4.86300	−0.46000
C	0.91300	−3.48200	−0.47300
C	0.61800	−3.04400	−4.16600
C	0.74900	−3.83100	−5.28500
C	1.07900	−5.20100	−5.16600
C	1.27500	−5.76200	−3.92800
C	−0.61800	3.04400	−4.16600
C	−0.74900	3.83100	−5.28500
C	−1.07900	5.20100	−5.16600
C	−1.27500	5.76200	−3.92800
C	−1.48000	5.56300	0.83400

C	1.48000	−5.56300	0.83400
C	0.86300	−6.77800	1.15100
C	1.08300	−7.46000	2.33900
C	1.96500	−6.90700	3.25900
C	2.61100	−5.70100	3.01100
C	2.34700	−5.06500	1.80900
C	−0.86300	6.77800	1.15100
C	−1.08300	7.46000	2.33900
C	−1.96500	6.90700	3.25900
C	−2.61100	5.70100	3.01100
C	−2.34700	5.06500	1.80900
Br	2.29500	−7.82200	4.90400
F	−0.01600	−7.31000	0.28800
F	2.98500	−3.89900	1.56800
Br	−2.29500	7.82200	4.90400
F	−2.98500	3.89900	1.56800
F	0.01600	7.31000	0.28800
H	−4.17600	−2.30400	−1.69100
H	−4.76800	0.11900	−1.69100
H	−3.01100	1.82000	−1.68000
H	−1.83200	−3.00300	−1.68300
H	1.83200	3.00300	−1.68300
H	4.17600	2.30400	−1.69100

H	4.76800	−0.11900	−1.69100
H	3.01100	−1.82000	−1.68000
H	−0.83200	2.94000	0.46100
H	0.83200	−2.94000	0.46100
H	0.36400	−1.99500	−4.26000
H	0.59800	−3.40100	−6.26800
H	1.17800	−5.80700	−6.05900
H	1.52900	−6.80800	−3.80400
H	−0.36400	1.99500	−4.26000
H	−0.59800	3.40100	−6.26800
H	−1.17800	5.80700	−6.05900
H	−1.52900	6.80800	−3.80400
H	0.56500	−8.39000	2.52400
H	3.30500	−5.26000	3.71200
H	−0.56500	8.39000	2.52400
H	−3.30500	5.26000	3.71200

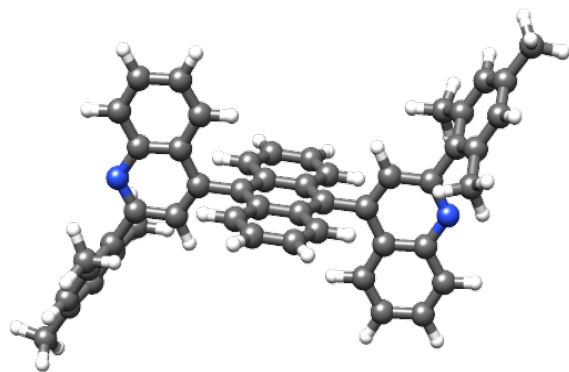


Figure S5.56. The energy minimized geometry for compound **5.3g** *trans* isomer.

Imaginary Frequencies = 0

Energy = -2039.47 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.01000	0.71000	3.66800
C	-0.01000	-0.71000	3.66800
C	-0.01700	-1.40000	2.48900
C	-0.00700	-0.72200	1.22900
C	0.00700	0.72200	1.22900
C	0.01700	1.40000	2.48900
C	-0.01100	-1.42400	0.00700
C	-0.00800	-0.72200	-1.21500
C	0.00800	0.72200	-1.21500
C	0.01100	1.42400	0.00700
C	-0.02300	-1.40000	-2.47600
C	-0.01400	-0.71000	-3.65500

C	0.01400	0.71000	−3.65500
C	0.02300	1.40000	−2.47600
C	0.00000	2.92100	0.00600
C	0.00000	−2.92100	0.00600
C	−1.21000	−3.68000	0.03100
C	−1.09300	−5.10500	0.04000
N	0.10700	−5.75200	0.02200
C	1.21000	−5.03100	−0.01200
C	1.19200	−3.60800	−0.01700
C	1.21000	3.68000	0.03100
C	1.09300	5.10500	0.04000
N	−0.10700	5.75200	0.02200
C	−1.21000	5.03100	−0.01200
C	−1.19200	3.60800	−0.01700
C	2.50300	3.09600	0.05000
C	3.62600	3.88800	0.07700
C	3.51000	5.29700	0.08600
C	2.27300	5.89200	0.06900
C	−2.50300	−3.09600	0.05000
C	−3.62600	−3.88800	0.07700
C	−3.51000	−5.29700	0.08600
C	−2.27300	−5.89200	0.06900
C	2.52200	−5.75700	−0.02800

C	−2.52200	5.75700	−0.02800
C	−2.98400	6.39300	1.13900
C	−4.21500	7.04900	1.10800
C	−4.99600	7.10200	−0.04800
C	−4.51200	6.47200	−1.19400
C	−3.28800	5.79900	−1.20600
C	3.28800	−5.79900	−1.20600
C	4.51200	−6.47200	−1.19400
C	4.99600	−7.10200	−0.04800
C	4.21500	−7.04900	1.10800
C	2.98400	−6.39300	1.13900
C	−6.30800	7.84800	−0.06300
C	−2.17500	6.37300	2.41500
C	−2.80200	5.16100	−2.48800
C	6.30800	−7.84800	−0.06300
C	2.17500	−6.37300	2.41500
C	2.80200	−5.16100	−2.48800
H	0.02000	1.24700	4.61000
H	−0.02000	−1.24700	4.61000
H	−0.03300	−2.48200	2.49700
H	0.03300	2.48200	2.49700
H	−0.04400	−2.48200	−2.48400
H	−0.02700	−1.24700	−4.59700

H	0.02700	1.24700	−4.59700
H	0.04400	2.48200	−2.48400
H	2.13100	−3.06800	−0.02900
H	−2.13100	3.06800	−0.02900
H	2.59300	2.01700	0.04300
H	4.60900	3.43100	0.09100
H	4.40600	5.90800	0.10700
H	2.15300	6.96900	0.07300
H	−2.59300	−2.01700	0.04300
H	−4.60900	−3.43100	0.09100
H	−4.40600	−5.90800	0.10700
H	−2.15300	−6.96900	0.07300
H	−4.57300	7.53100	2.01300
H	−5.09900	6.50900	−2.10700
H	5.09900	−6.50900	−2.10700
H	4.57300	−7.53100	2.01300
H	−6.82900	7.75900	0.89400
H	−6.97100	7.47300	−0.84600
H	−6.15100	8.91600	−0.25000
H	−1.21400	6.87400	2.27600
H	−1.95900	5.35000	2.73800
H	−2.71300	6.87500	3.22200
H	−3.46300	5.41400	−3.31900

H	−2.76300	4.07000	−2.41600
H	−1.79400	5.50200	−2.74300
H	6.97100	−7.47300	−0.84600
H	6.15100	−8.91600	−0.25000
H	6.82900	−7.75900	0.89400
H	2.71300	−6.87500	3.22200
H	1.21400	−6.87400	2.27600
H	1.95900	−5.35000	2.73800
H	2.76300	−4.07000	−2.41600
H	1.79400	−5.50200	−2.74300
H	3.46300	−5.41400	−3.31900

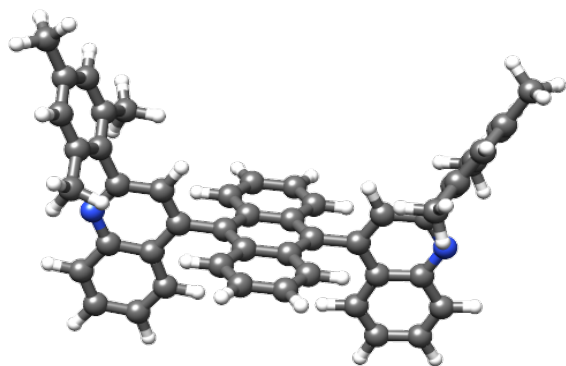


Figure S5.57. The energy minimized geometry for compound **5.3g** *cis* isomer.

Imaginary Frequencies = 0

Energy = -2039.47 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-3.66500	0.69200	-1.00900
C	-3.65800	-0.72900	-1.01200
C	-2.47500	-1.41300	-1.00400
C	-1.21800	-0.72800	-0.99500
C	-1.22500	0.71600	-0.99400
C	-2.49000	1.38800	-1.00000
C	0.00700	-1.42400	-0.98700
C	1.22500	-0.71600	-0.99400
C	1.21800	0.72800	-0.99500
C	-0.00700	1.42400	-0.98700
C	2.49000	-1.38800	-1.00000
C	3.66500	-0.69200	-1.00900

C	3.65800	0.72900	−1.01200
C	2.47500	1.41300	−1.00400
C	−0.01400	2.92100	−0.95100
C	0.01400	−2.92100	−0.95100
C	0.03900	−3.70100	−2.14700
C	0.05700	−5.12400	−2.00400
N	0.04700	−5.74900	−0.79300
C	0.01300	−5.00900	0.29700
C	−0.00100	−3.58700	0.25300
C	−0.03900	3.70100	−2.14700
C	−0.05700	5.12400	−2.00400
N	−0.04700	5.74900	−0.79300
C	−0.01300	5.00900	0.29700
C	0.00100	3.58700	0.25300
C	−0.05000	3.14200	−3.45100
C	−0.07700	3.95300	−4.55900
C	−0.09400	5.36000	−4.41800
C	−0.08500	5.93200	−3.17000
C	0.05000	−3.14200	−3.45100
C	0.07700	−3.95300	−4.55900
C	0.09400	−5.36000	−4.41800
C	0.08500	−5.93200	−3.17000
C	0.00500	−5.71000	1.62200

C	−0.00500	5.71000	1.62200
C	−1.17400	6.34100	2.08700
C	−1.15000	6.97800	3.32800
C	−0.00100	7.01400	4.11800
C	1.15000	6.39600	3.62900
C	1.16900	5.74200	2.39500
C	−1.16900	−5.74200	2.39500
C	−1.15000	−6.39600	3.62900
C	0.00100	−7.01400	4.11800
C	1.15000	−6.97800	3.32800
C	1.17400	−6.34100	2.08700
C	−0.01000	7.68500	5.47100
C	−2.44300	6.34300	1.26700
C	2.45600	5.11800	1.90200
C	2.44300	−6.34300	1.26700
C	0.01000	−7.68500	5.47100
C	−2.45600	−5.11800	1.90200
H	−4.61000	1.22300	−1.01600
H	−4.59700	−1.27000	−1.02200
H	−2.47800	−2.49500	−1.00900
H	−2.50300	2.47000	−1.00000
H	2.50300	−2.47000	−1.00000
H	4.61000	−1.22300	−1.01600

H	4.59700	1.27000	−1.02200
H	2.47800	2.49500	−1.00900
H	−0.01200	−3.03000	1.18200
H	0.01200	3.03000	1.18200
H	−0.03700	2.06400	−3.56000
H	−0.08500	3.51400	−5.55100
H	−0.11500	5.98600	−5.30300
H	−0.09600	7.00600	−3.03000
H	0.03700	−2.06400	−3.56000
H	0.08500	−3.51400	−5.55100
H	0.11500	−5.98600	−5.30300
H	0.09600	−7.00600	−3.03000
H	−2.05500	7.46200	3.68500
H	2.06200	6.43000	4.21800
H	−2.06200	−6.43000	4.21800
H	2.05500	−7.46200	3.68500
H	−0.67100	8.55500	5.48000
H	0.99100	8.01600	5.75800
H	−0.36300	6.99800	6.24800
H	−2.76800	5.32500	1.02700
H	−2.29500	6.86300	0.31700
H	−3.25400	6.83400	1.80800
H	3.28300	5.36300	2.57100

H	2.71200	5.47800	0.90200
H	2.38900	4.02800	1.84500
H	3.25400	−6.83400	1.80800
H	2.76800	−5.32500	1.02700
H	2.29500	−6.86300	0.31700
H	−0.99100	−8.01600	5.75800
H	0.36300	−6.99800	6.24800
H	0.67100	−8.55500	5.48000
H	−2.71200	−5.47800	0.90200
H	−2.38900	−4.02800	1.84500
H	−3.28300	−5.36300	2.57100

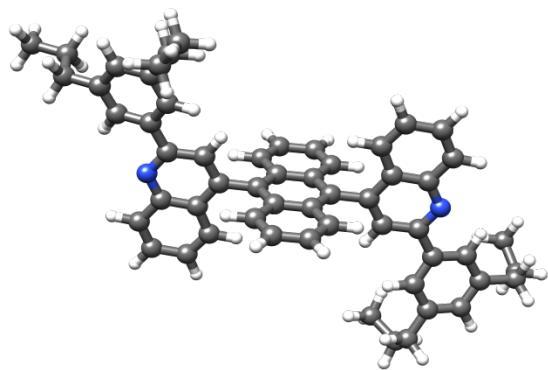


Figure S5.58. The energy minimized geometry for compound **5.3h*** *trans* isomer.

Imaginary Frequencies = 0

Energy = -2275.42 Hartrees

* The *n*-dodecyl chains present in compound **5.3h** were abbreviated to propyl chains to reduce computational complexity during the structure optimization step.

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-0.44547	-0.88395	-3.42989
C	0.82320	-0.24735	-3.49324
C	1.40113	0.25412	-2.36186
C	0.75408	0.15627	-1.08857
C	-0.53911	-0.48444	-1.02537
C	-1.10228	-0.99708	-2.23762
C	1.34282	0.66650	0.08546
C	0.67346	0.55823	1.32059
C	-0.61955	-0.08276	1.38383
C	-1.20873	-0.59218	0.20956

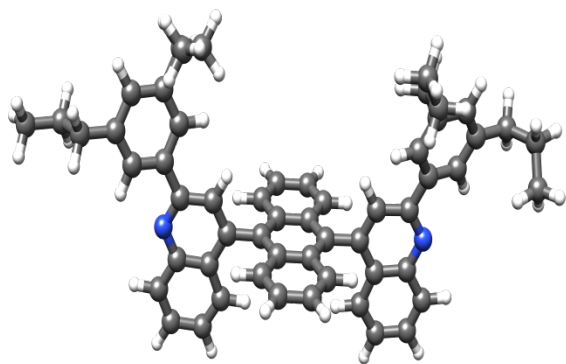
C	1.23591	1.07201	2.53285
C	0.57965	0.95805	3.72538
C	−0.68795	0.31935	3.78909
C	−1.2657	−0.18216	2.6576
C	−2.55942	−1.23632	0.27533
C	2.69168	1.31474	0.02263
C	2.83623	2.71432	−0.21974
C	4.16792	3.2309	−0.28387
N	5.27006	2.45579	−0.11129
C	5.11945	1.16469	0.12695
C	3.82955	0.56184	0.18889
C	−2.70826	−2.63857	0.49893
C	−4.04076	−3.15623	0.53125
N	−5.14103	−2.37527	0.37206
C	−4.98679	−1.07700	0.17988
C	−3.69509	−0.47853	0.11653
C	−1.61890	−3.52761	0.68028
C	−1.83854	−4.86895	0.88539
C	−3.15600	−5.38198	0.91786
C	−4.2319	−4.54652	0.74468
C	1.74403	3.59855	−0.40731
C	1.96017	4.93443	−0.64855
C	3.27688	5.44632	−0.71322

C	4.35546	4.61545	−0.53485
C	6.35672	0.35662	0.30952
C	−6.22084	−0.2611	0.01235
C	−6.2246	1.12473	0.21677
C	−7.38988	1.87816	0.06195
C	−8.56382	1.22011	−0.31274
C	−8.59570	−0.16283	−0.5197
C	−7.41905	−0.89022	−0.34804
C	7.58413	0.86553	−0.13431
C	8.76735	0.14552	0.02304
C	8.71003	−1.10519	0.64771
C	7.50536	−1.64065	1.11026
C	6.33624	−0.8979	0.9329
H	−0.89227	−1.28073	−4.33444
H	1.33293	−0.16087	−4.4461
H	2.36825	0.73639	−2.41789
H	−2.06909	−1.48162	−2.19735
H	2.20171	1.55855	2.4924
H	1.02605	1.35585	4.6297
H	−1.19694	0.23115	4.74221
H	−2.23178	−0.66647	2.71408
H	3.73638	−0.50426	0.34687
H	−3.59829	0.58118	−0.0785

H	−0.60972	−3.13488	0.655
H	−0.99850	−5.54001	1.02382
H	−3.31324	−6.44229	1.08141
H	−5.25117	−4.91246	0.76691
H	0.73550	3.20633	−0.35908
H	1.11799	5.60200	−0.79075
H	3.4314	6.50244	−0.90417
H	5.37395	4.98185	−0.57648
H	−5.31812	1.63283	0.52622
H	−7.41155	−1.96423	−0.48752
H	7.59509	1.84535	−0.59468
H	5.40768	−1.29942	1.32157
H	−9.47605	1.79685	−0.44179
H	9.62923	−1.66694	0.79359
C	−7.39162	3.36468	0.34293
C	−7.75423	3.70727	1.80107
H	−8.10201	3.86276	−0.32648
H	−6.40496	3.78242	0.11384
C	−7.75643	5.21316	2.0761
H	−7.04561	3.20778	2.4708
H	−8.73849	3.2851	2.03135
H	−8.48199	5.73142	1.44124
H	−6.77344	5.65314	1.88071

C	−9.86963	−0.84933	−0.96065
C	−10.01434	−0.93683	−2.49212
H	−10.73422	−0.31489	−0.55099
H	−9.90132	−1.86107	−0.54184
C	−11.30806	−1.62861	−2.92915
H	−9.15014	−1.47197	−2.90042
H	−9.97283	0.07414	−2.9126
H	−12.18851	−1.09389	−2.55891
H	−11.35873	−2.65269	−2.54606
C	10.08956	0.69269	−0.47257
C	10.57523	0.0696	−1.79943
H	10.85481	0.52236	0.29255
H	10.00874	1.77778	−0.59593
C	9.6873	0.39371	−3.00338
H	10.64738	−1.01718	−1.67805
H	11.59359	0.42524	−1.99238
H	9.63067	1.47397	−3.17155
H	8.66777	0.02762	−2.85927
C	7.47754	−2.99491	1.78818
H	8.28346	−3.04015	2.52864
C	7.63091	−4.19004	0.82322
H	6.54004	−3.10358	2.34424
C	6.47285	−4.3472	−0.1655

H	7.72612	−5.10353	1.42087
H	8.57182	−4.08493	0.27168
H	5.52297	−4.49175	0.35963
H	6.36922	−3.46608	−0.80374
H	−8.01438	5.42624	3.11691
H	−11.38363	−1.67784	−4.01875
H	10.08115	−0.06383	−3.91507
H	6.62673	−5.2133	−0.81477



S5.59. The energy minimized geometry for compound **5.3h*** *cis* isomer.

Imaginary Frequencies = 0

Energy = -2275.42 Hartrees

* The *n*-dodecyl chains present in compound 3h were abbreviated to propyl chains to reduce computational complexity during the structure optimization step.

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	0.6468	-2.10109	-3.59315
C	-0.77372	-2.10054	-3.56751
C	-1.4425	-1.94851	-2.38634
C	-0.74155	-1.78836	-1.14832
C	0.70267	-1.79116	-1.17412
C	1.35807	-1.95091	-2.43681
C	-1.42101	-1.63262	0.07627
C	-0.69782	-1.49002	1.27689
C	0.74659	-1.49382	1.2512
C	1.42600	-1.63916	0.02558

C	-1.35334	-1.34065	2.54078
C	-0.64206	-1.20671	3.69912
C	0.77857	-1.21187	3.67408
C	1.44749	-1.34993	2.49124
C	2.92328	-1.6176	-0.00573
C	-2.91837	-1.60534	0.09726
C	-3.68503	-2.79786	0.2672
C	-5.10798	-2.66057	0.28704
N	-5.73708	-1.46576	0.13923
C	-5.01412	-0.37261	-0.03029
C	-3.58968	-0.41432	-0.04429
C	3.69076	-2.81745	0.09671
C	5.11293	-2.69194	0.01667
N	5.74242	-1.49702	-0.13334
C	5.01803	-0.39438	-0.20458
C	3.59432	-0.42712	-0.15313
C	3.12132	-4.10562	0.25915
C	3.92309	-5.21927	0.33934
C	5.32955	-5.09622	0.25871
C	5.91133	-3.86248	0.10095
C	-3.1149	-4.08662	0.42183
C	-3.9172	-5.19003	0.59024
C	-5.32472	-5.05517	0.61137

C	-5.90708	-3.82055	0.46298
C	-5.75019	0.9123	-0.19056
C	5.74784	0.89197	-0.36951
C	5.18093	2.11447	0.00761
C	5.87212	3.3172	-0.16079
C	7.14786	3.27802	-0.72586
C	7.74796	2.07123	-1.10587
C	7.03808	0.88756	-0.91683
C	-5.14335	2.05218	-0.73063
C	-5.84721	3.25077	-0.87988
C	-7.18425	3.28994	-0.48094
C	-7.82374	2.1664	0.0567
C	-7.0957	0.98742	0.1955
H	1.16636	-2.22207	-4.53691
H	-1.32708	-2.22206	-4.49179
H	-2.52457	-1.94884	-2.37469
H	2.43982	-1.95161	-2.46471
H	-2.4352	-1.33598	2.56777
H	-1.16155	-1.0964	4.64424
H	1.33179	-1.10625	4.60042
H	2.52964	-1.35336	2.47975
H	-3.02135	0.50008	-0.14903
H	3.02910	0.48937	-0.26017

H	2.04387	−4.20042	0.31889
H	3.47718	−6.19935	0.46505
H	5.94879	−5.98394	0.32344
H	6.98567	−3.73879	0.0392
H	−2.03673	−4.19019	0.40535
H	−3.471	−6.17105	0.70724
H	−5.9444	−5.93493	0.7445
H	−6.98225	−3.68916	0.47223
H	4.19354	2.14122	0.45555
H	7.47192	−0.06311	−1.20026
H	−4.11419	2.0133	−1.06947
H	−7.56101	0.09913	0.60428
H	7.68492	4.21008	−0.882
H	−7.74288	4.21519	−0.59202
C	−9.28618	2.22104	0.43989
C	−10.23029	1.86087	−0.72365
H	−9.53398	3.2254	0.80175
H	−9.47066	1.53464	1.27334
H	−10.04293	2.54384	−1.55968
C	−11.70837	1.91605	−0.32932
H	−9.97872	0.85876	−1.08722
H	−11.99099	2.91708	0.01176
H	−11.92798	1.21628	0.48309

C	−5.15763	4.47431	−1.44703
H	−4.57195	4.1795	−2.32451
C	−4.22178	5.19166	−0.45043
H	−5.91223	5.18439	−1.8023
C	−4.94342	5.81342	0.74772
H	−3.67664	5.97251	−0.99259
H	−3.46738	4.48062	−0.09525
H	−5.67873	6.55682	0.42268
H	−5.47206	5.05701	1.33317
C	5.26517	4.62608	0.29436
H	4.17469	4.57858	0.1982
H	5.59984	5.43373	−0.36632
C	5.62375	4.98818	1.74868
C	5.00426	6.31208	2.20344
H	6.71400	5.03526	1.84513
H	5.29543	4.17783	2.40877
H	5.34091	7.14357	1.57626
H	3.91161	6.27853	2.14863
C	9.14008	2.06479	−1.70238
C	10.26887	2.29775	−0.67527
H	9.20266	2.84294	−2.47107
H	9.31122	1.1102	−2.21079
H	10.0957	3.25152	−0.16397

H	11.21195	2.40989	−1.22201
C	10.41077	1.17892	0.35987
H	10.6224	0.21976	−0.12345
H	9.49766	1.05786	0.94784
H	−12.35426	1.65818	−1.17294
H	−4.23629	6.31642	1.41285
H	5.27738	6.54381	3.23638
H	11.22987	1.38906	1.05308

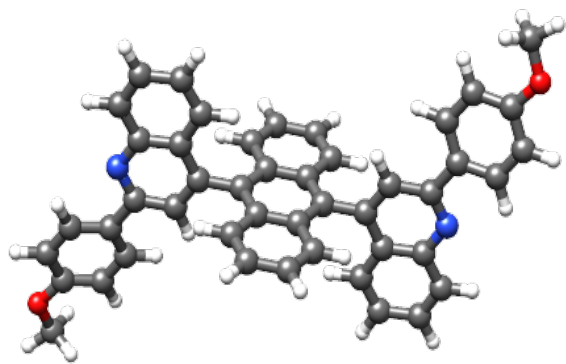


Figure S5.60. The energy minimized geometry for compound **5.3i** *trans* isomer.

Imaginary Frequencies = 0

Energy = -2032.63 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-0.31500	0.63700	-3.67400
C	0.31500	-0.63700	-3.67400
C	0.61900	-1.25700	-2.49600
C	0.31700	-0.64900	-1.23500
C	-0.31700	0.64900	-1.23500
C	-0.61900	1.25700	-2.49600
C	0.62400	-1.28000	-0.01300
C	0.31800	-0.64900	1.20900
C	-0.31800	0.64900	1.20900
C	-0.62400	1.28000	-0.01300
C	0.62100	-1.25500	2.47000
C	0.31600	-0.63600	3.64800

C	−0.31600	0.63600	3.64800
C	−0.62100	1.25500	2.47000
C	−1.26600	2.63300	−0.01200
C	1.26600	−2.63300	−0.01200
C	2.68600	−2.78500	−0.02800
C	3.19700	−4.12000	−0.04800
N	2.39800	−5.21900	−0.03900
C	1.08600	−5.06200	−0.01000
C	0.48900	−3.76700	−0.00700
C	−2.68600	2.78500	−0.02800
C	−3.19700	4.12000	−0.04800
N	−2.39800	5.21900	−0.03900
C	−1.08600	5.06200	−0.01000
C	−0.48900	3.76700	−0.00700
C	−3.59500	1.69800	−0.03300
C	−4.95200	1.92100	−0.05700
C	−5.45900	3.24100	−0.07900
C	−4.60300	4.31500	−0.07400
C	3.59500	−1.69800	−0.03300
C	4.95200	−1.92100	−0.05700
C	5.45900	−3.24100	−0.07900
C	4.60300	−4.31500	−0.07400
C	0.25500	−6.29300	0.00000

C	−0.25500	6.29300	0.00000
C	1.09600	6.28700	0.35800
C	1.85700	7.45500	0.36600
C	1.26600	8.66800	0.00700
C	−0.09000	8.69300	−0.34900
C	−0.83300	7.52800	−0.34700
C	−1.09600	−6.28700	0.35800
C	−1.85700	−7.45500	0.36600
C	−1.26600	−8.66800	0.00700
C	0.09000	−8.69300	−0.34900
C	0.83300	−7.52800	−0.34700
O	1.91000	9.86700	−0.02600
C	3.28700	9.90900	0.32300
O	−1.91000	−9.86700	−0.02600
C	−3.28700	−9.90900	0.32300
H	−0.55400	1.11700	−4.61600
H	0.55400	−1.11700	−4.61600
H	1.09700	−2.22700	−2.50400
H	−1.09700	2.22700	−2.50400
H	1.10200	−2.22500	2.47800
H	0.55700	−1.11500	4.59000
H	−0.55700	1.11500	4.59000
H	−1.10200	2.22500	2.47800

H	−0.58800	−3.66400	−0.02200
H	0.58800	3.66400	−0.02200
H	−3.20600	0.68700	−0.01700
H	−5.63900	1.08300	−0.06000
H	−6.53100	3.40200	−0.09800
H	−4.96500	5.33600	−0.08800
H	3.20600	−0.68700	−0.01700
H	5.63900	−1.08300	−0.06000
H	6.53100	−3.40200	−0.09800
H	4.96500	−5.33600	−0.08800
H	1.57900	5.36700	0.66200
H	2.89700	7.40500	0.65800
H	−0.53300	9.64200	−0.62400
H	−1.88100	7.54600	−0.61400
H	−1.57900	−5.36700	0.66200
H	−2.89700	−7.40500	0.65800
H	0.53300	−9.64200	−0.62400
H	1.88100	−7.54600	−0.61400
H	3.89000	9.29200	−0.35100
H	3.44900	9.58400	1.35700
H	3.58700	10.95000	0.22300
H	−3.89000	−9.29200	−0.35100
H	−3.44900	−9.58400	1.35700

H	-3.58700	-10.95000	0.22300
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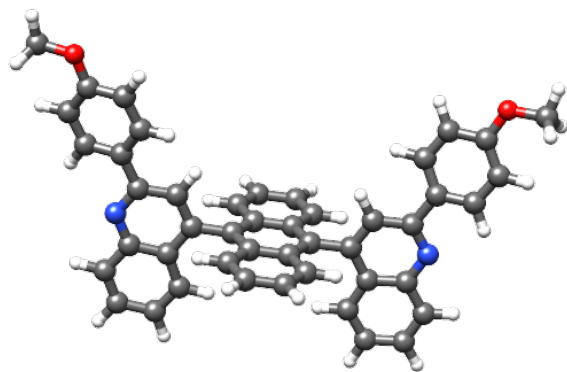


Figure S5.61. The energy minimized geometry for compound **5.3i** *cis* isomer.

Imaginary Frequencies = 0

Energy = -2032.63 Hartrees

Cartesian Coordinates (angstroms)

Atom	X	Y	Z
C	-3.66200	-0.70500	-1.06800
C	-3.66000	0.71500	-1.06900
C	-2.48100	1.40400	-1.06300
C	-1.22100	0.72400	-1.05600
C	-1.22300	-0.72100	-1.05600
C	-2.48500	-1.39700	-1.06100
C	0.00200	1.42400	-1.05200
C	1.22300	0.72100	-1.05600
C	1.22100	-0.72400	-1.05600
C	-0.00200	-1.42400	-1.05200
C	2.48500	1.39700	-1.06100
C	3.66200	0.70500	-1.06800

C	3.66000	−0.71500	−1.06900
C	2.48100	−1.40400	−1.06300
C	−0.00300	−2.92200	−1.02600
C	0.00300	2.92200	−1.02600
C	0.01800	3.68900	−2.23100
C	0.04000	5.11300	−2.09500
N	0.03300	5.74100	−0.89100
C	0.00600	5.01700	0.21500
C	0.00000	3.59100	0.17300
C	−0.01800	−3.68900	−2.23100
C	−0.04000	−5.11300	−2.09500
N	−0.03300	−5.74100	−0.89100
C	−0.00600	−5.01700	0.21500
C	0.00000	−3.59100	0.17300
C	−0.02000	−3.12000	−3.52900
C	−0.04400	−3.92300	−4.64400
C	−0.06700	−5.33000	−4.51200
C	−0.06600	−5.91200	−3.26800
C	0.02000	3.12000	−3.52900
C	0.04400	3.92300	−4.64400
C	0.06700	5.33000	−4.51200
C	0.06600	5.91200	−3.26800
C	0.00100	5.74800	1.50700

C	−0.00100	−5.74800	1.50700
C	0.35600	−5.13700	2.72200
C	0.35500	−5.84600	3.91100
C	−0.00700	−7.19800	3.92800
C	−0.36000	−7.82700	2.72900
C	−0.34900	−7.10300	1.54100
C	−0.35600	5.13700	2.72200
C	−0.35500	5.84600	3.91100
C	0.00700	7.19800	3.92800
C	0.36000	7.82700	2.72900
C	0.34900	7.10300	1.54100
O	0.01800	−7.80500	5.14500
C	−0.33100	−9.18100	5.22600
O	−0.01800	7.80500	5.14500
C	0.33100	9.18100	5.22600
H	−4.60500	−1.24100	−1.07300
H	−4.60200	1.25300	−1.07600
H	−2.48700	2.48600	−1.06300
H	−2.49400	−2.47900	−1.05800
H	2.49400	2.47900	−1.05800
H	4.60500	1.24100	−1.07300
H	4.60200	−1.25300	−1.07600
H	2.48700	−2.48600	−1.06300

H	0.01400	3.02100	1.09200
H	−0.01400	−3.02100	1.09200
H	−0.00300	−2.04100	−3.63000
H	−0.04500	−3.47700	−5.63300
H	−0.08600	−5.95100	−5.40100
H	−0.08100	−6.98700	−3.13900
H	0.00300	2.04100	−3.63000
H	0.04500	3.47700	−5.63300
H	0.08600	5.95100	−5.40100
H	0.08100	6.98700	−3.13900
H	0.66100	−4.09900	2.74500
H	0.63800	−5.37600	4.84500
H	−0.64300	−8.87000	2.70900
H	−0.61400	−7.58700	0.61000
H	−0.66100	4.09900	2.74500
H	−0.63800	5.37600	4.84500
H	0.64300	8.87000	2.70900
H	0.61400	7.58700	0.61000
H	−0.23800	−9.44800	6.27800
H	0.34900	−9.80300	4.63300
H	−1.36100	−9.35400	4.89800
H	0.23800	9.44800	6.27800
H	−0.34900	9.80300	4.63300

H	1.36100	9.35400	4.89800
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5.5.7. Compiled Electrochemical Data

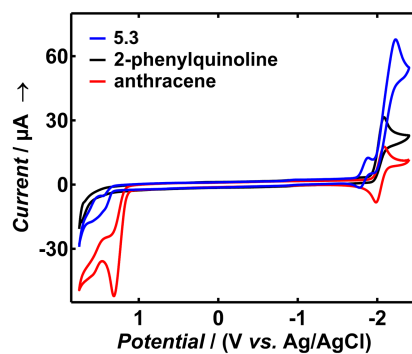


Figure S5.62. The cyclic voltammogram of diquinolineanthracene **5.3e** (blue trace), 2-phenylquinoline (black trace), and anthracene (red trace).

5.5.8. Supporting References

S1. Umerani, M. J.; Dibble, D. J.; Wardrip, A. G.; Mazaheripour, A.; Vargas, E.; Ziller, J. W.; Gorodetsky, A. A., *J. Mater. Chem. C* **2016**, *4*, 4060–4066.

S2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., *Gaussian 09*, Revision C.01; Gaussian, Inc., Wallingford, CT, **2010**.

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6.1 Abstract

Quinoline oligoamides have been shown to form predictable and stable helical architectures and have sparked interest due to their ability access to chemical arrangements that are not found in nature, but may interact with naturally occurring proteins in unprecedented or biologically relevant ways. The current approach to producing sequence-specific quinoline oligoamides, utilizes automated solid-phase peptide synthesis (SPPS) of quinoline δ -amino acids. However, given the backbone architecture of these quinoline δ -polypeptides, there are limitations in geometric flexibility, reducing the potential 3-Dimensional conformations. In addition, the quinoline monomers often lack chemical modularity; there are a limited number of electron withdrawing, electron donating, and sterically hindering groups that have been furnished onto the quinoline core. In this study, we utilize the aza-Diels–Alder reaction to prepare quinoline α -amino acids, which we subsequently iteratively couple using SPPS to produce quinoline α -polypeptides. Overall, this work will allow for elucidating and studying various quinoline-based peptidic architectures which may be realized through self-assembly strategies, molecular wire ensembles, or as biomolecular scaffolds.

6.2 Introduction

Polyquinolines have been studied since the early 1970s for their exceptional optoelectronic properties, high chemical inertness, excellent thermal stability, and exquisite mechanical robustness.^{1–36} These features have enabled polyquinolines to evince their promise in optoelectronics,^{7–19} as OLEDs, and in biology, as biomimetic proteins.^{20–36} To date, polyquinolines are prepared *via* only a handful of synthetic routes, including Suzuki couplings,^{37,38} the

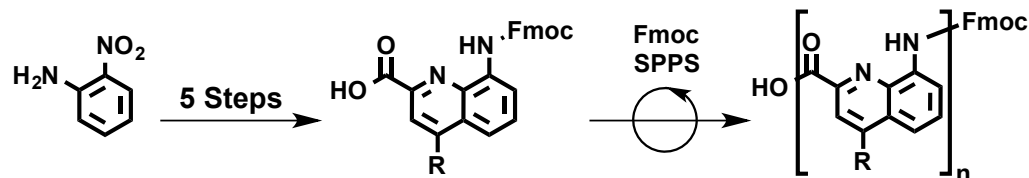
Sonogashira reaction, oxidative polymerizations,³⁹ Friedländer synthesis,^{1,14,40-44} and solid-phase peptide synthesis.²⁰⁻³⁶ Given the wide utility of these polymers, there has been tremendous effort in designing atomically precise quinoline macromolecules as designer materials; in this regard, the solid-support strategy has been highly developed, and is particularly effective in producing length, and sequence-specific quinoline δ -polypeptides in the form of helical macromolecules.²⁰⁻³⁶ In particular, this bio-inspired synthetic approach is favorable due to sequence, and length specificity, in addition to being amenable for integration with biological systems. However, given the backbone architecture of classic quinoline polypeptides, there are limitations in geometric flexibility, reducing the number of potential conformations, and thus restricting their functionality. Therefore, finding alternative strategies in customizing quinoline biomacromolecules in a sequence-specific fashion remains to be an intriguing research task.

Herein, we report an aza-Diels–Alder approach for the synthesis of a novel quinoline α -polypeptides from commercially available starting materials.⁴⁵⁻⁴⁹ Our strategy utilizes solid-phase peptide synthesis to iteratively couple quinoline α -amino acids to produce quinoline α -peptide dimers, pentamers, decamers, and eicosamers in high purity and good yield. We definitively confirm the identity of our polypeptides with size exclusion chromatography (SEC), ¹H nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, ultraviolet visible (UV–Vis) spectroscopy, fluorescence spectroscopy, and circular dichroism (CD). Overall, our approach establishes a novel route to producing modular quinoline polypeptides derived from quinoline α -amino acids, and provides foundation for the synthesis of larger protein-polymer hybrid materials.

6.3 Results and Discussion

For our strategy, we drew inspiration from quinoline delta-polypeptides as previously demonstrated in the literature. As an example, Figure 6.1A illustrates the synthesis of quinoline

A) Classic Approach to Sequence Controlled Quinoline Polypeptides



Novel Approach to Sequence Controlled Quinoline Polypeptides

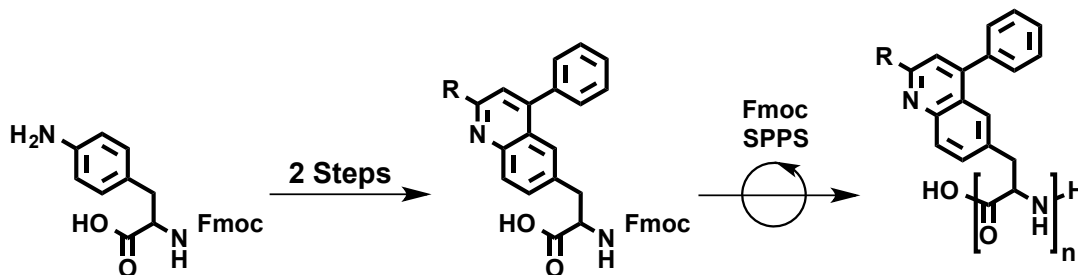
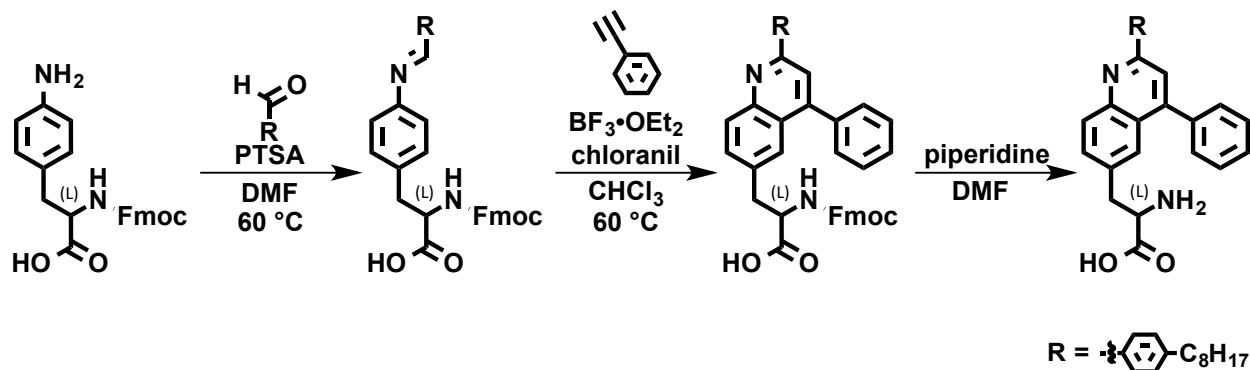


Figure 6.1. The classic approach for the preparation of quinoline polypeptides through iterative coupling of δ -amino acids (top). Our aza-Diels–Alder approach for the preparation of quinoline polypeptides through iterative coupling of α -amino acids (bottom).

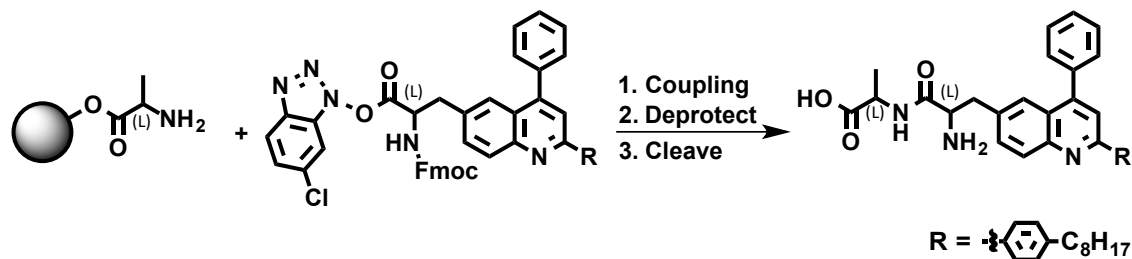
quinoline delta-polypeptides up to 8 repeat units. Here, we merged concepts from both this method, and our previous studies of the Povarov reaction to design the strategy shown in Figure 6.1B. We envisioned that in two steps, beginning with fmoc-protected 4-amino-(L)-phenylalanine, we could synthesize an unnatural quinoline alpha-amino acid using the Povarov reaction. Thus, we set out to evaluate this alternative methodology.

We began our studies by synthesizing a model quinoline alpha-amino acid *via* the Povarov reaction.^{45–49} First, we used established literature protocols to form imine **6.1**.⁵⁰ Next, we reacted imine **6.1** with phenylacetylene in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ as a lewis acid mediator, and chloranil as a sacrificial oxidant, providing quinoline amino acid **6.2** (Scheme 6.1).^{51–56} Our synthesis



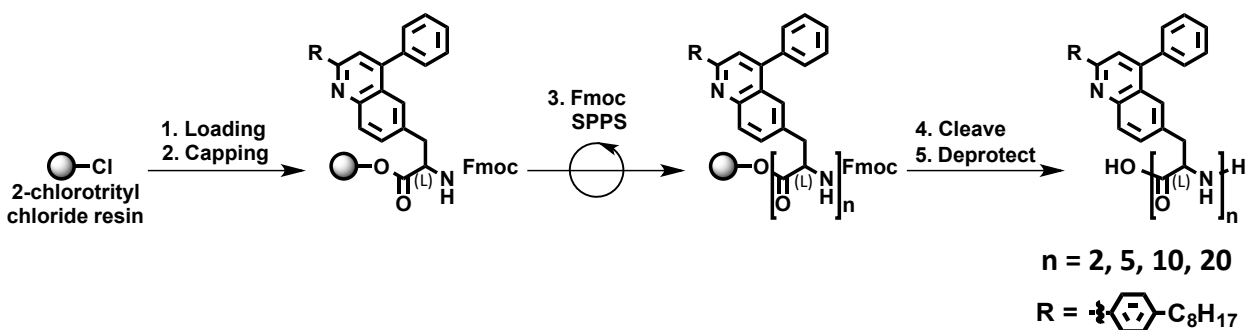
utilized mild conditions, and commercial starting materials to produce regioisomerically pure products, as confirmed by ^1H - ^1H 2D NMR spectroscopy (Supporting Figure S6.1), MALDI, UV-Vis, and HPLC (Supporting Figure S6.2), in good yield. Overall, our Povarov approach constitutes a facile route to a novel regiospecific quinoline amino acid.

Having demonstrated the preparation of regiospecific quinoline amino acids, we sought to further confirm its enantiomeric identity. Here, we used established solid-phase peptide synthesis protocols to couple quinoline amino acid **6.2** to L-alanine (Scheme 6.2). Following, we confirmed the enantiomeric identity of the quinoline-alanine dimer by using ^1H - ^1H 2D NMR spectroscopy,^{59,60} along with UV-Vis, MALDI, and HPLC (Supporting Figure S6.3). From the HPLC trace, we observed the product elute as a single sharp peak around 11.8min, suggesting that only the (L)-quinoline-(L)-alanine dimer was formed. In total, our quinoline amino acid building blocks were enantiomerically pure.



Scheme 6.2. Synthesis of quinoline-alanine dimer **6.3**.

Having prepared the quinoline amino acids, we proceeded to synthesize the quinoline oligopeptides. Here, we leveraged a solid-phase peptide synthesis strategy to iteratively couple quinoline amino acid **6.2** (Scheme 6.3).^{61,62} First, we loaded **6.2** onto a 2-chlorotrityl chloride resin, followed by capping. Next, we manually coupled amino acids to produce oligopeptides of $n = 2, 5, 10$ using standard fmoc solid-phase peptide synthesis protocols. After each synthesis cycle, the products were cleaved from solid support, deprotected, and subsequently purified using flash chromatography. We analyzed each of the oligopeptides using size-exclusion chromatography with a multi-angle light scattering detector (SEC-MALS) (Figure 6.1). From the SEC-MALS, we observed the 2mer (**6.4**), 5mer (**6.5**), and 10mer (**6.6**), eluting at retention times of 10.5 mins, 9.8 mins, and 9.2mins, respectively. For **6.4**, we obtained M_n of 0.9, an M_w of 1.8 kg/mol, with a PDI of 1.9. For **6.5**, we obtained M_n of 3.8, an M_w of 4.7 kg/mol, with a PDI of 1.2. For **6.6**, we obtained M_n of 7.9, an M_w of 9.1 kg/mol, with a PDI of 1.2. All the oligopeptides were within the expected molecular weight distributions, and possessed low PDI values. Overall, our strategy afforded novel quinoline oligopeptides with unique connectivity.



Scheme 6.3. Synthesis of quinoline oligo- and polypeptides **6.4** – **6.7**.

We next investigated the electronic properties of the quinoline oligopeptides. Here we prepared samples in THF, and interrogated them using UV-Vis, and fluorescence spectroscopy (Figure 6.1). From the UV-Vis plots of **6.4**, **6.5**, and **6.6**, we observed an absorbance maximum around 240nm, and two smaller peaks around 333nm, and 346nm, with an absorption onset around 360nm. From the fluorescence spectra, we noted that **6.4**, **6.5**, and **6.6** possessed emission maxima at 376nm, 378nm, 381nm, respectively. The UV-Vis traces agreed with one another; they possessed similar shapes with little observable red-shift, as expected for a non-conjugated polymer. The fluorescence traces possessed maxima that were similar to other quinoline-containing materials, and exhibited a stokes shift as the length of the oligopeptides increased. Altogether, our observations matched expectations for materials derived from quinoline based materials.

Next, we wanted to gain insight onto the conformation of our quinoline oligopeptides. Here, we prepared samples of **6.4**, **6.5**, and **6.6** in THF, and interrogated them with circular dichroism spectroscopy (Figure 6.2). For **6.4**, we noted positive peaks at 224nm, and 254nm, and one negative peak at 276 nm. In the case of **6.5**, we noted positive peaks at 226nm, and 250nm,

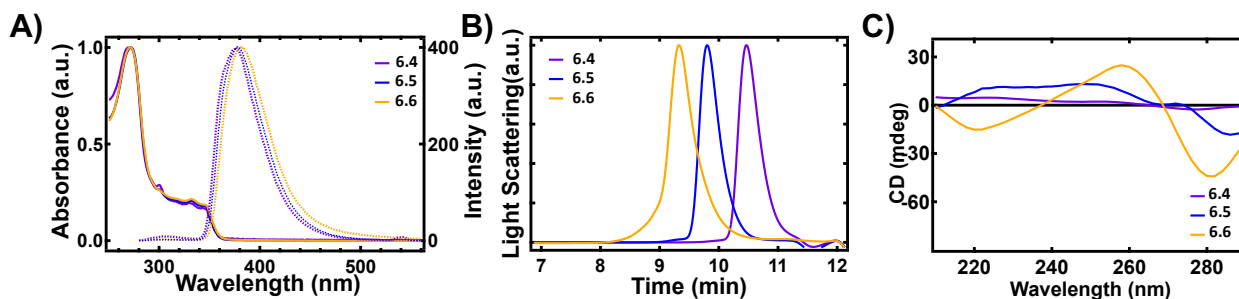


Figure 6.2. Absorbance (solid) and fluorescence (dotted) spectra (left), the MALS chromatogram (middle), and the circular dichroism spectra obtained for quinoline oligopeptides **6.4** – **6.6** (right).

and one negative peak at 286 nm. For **6.6**, we observed two negative peaks at 220nm and 280nm, and one positive peak at 258nm. From our results, we noted that as the oligopeptides increased in length, they adopted helical character as indicated by the increased negative ellipticity around 220nm. These findings suggested that the quinoline oligopeptides adopt an elongated conformation.

Having established a general methodology for synthesizing quinoline alpha-oligopeptides, we sought to prepare longer variants. Here, we leveraged our established solid-phase strategy to prepare a quinoline polypeptide 20mer (**6.7**). We analyzed **6.7** using SEC-MALS (Figure 6.2); from the chromatogram we observed the polymer elute at a retention times of 8.9 mins, with an M_n of 10.6, an M_w of 11.5 kg/mol, with a PDI of 1.1. Our analysis indicated that our obtained molecular weight distributions were within 15% of the expected size, and possessed a low PDI value (~1.1). Overall, iterative coupling of quinoline monomers on solid support is amenable to producing quinoline alpha-polypeptides.

We next investigated the electronic properties of the quinoline polypeptide. Here we prepared a sample of **6.7** in THF, and interrogated it using UV-Vis, and fluorescence spectroscopy

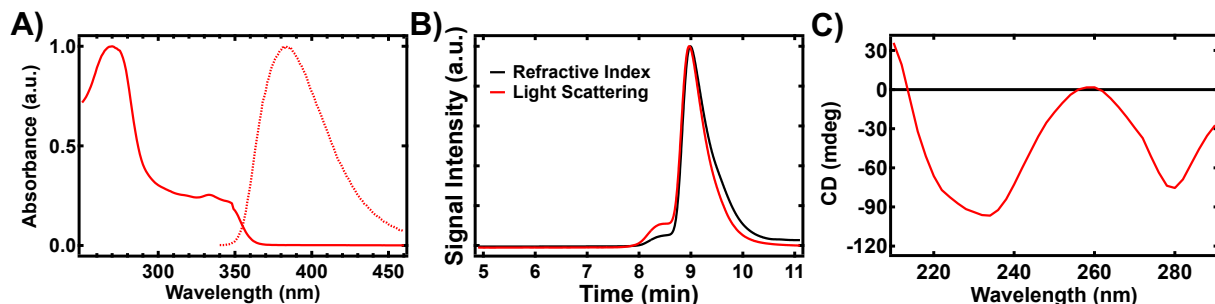


Figure 6.3. Absorbance (solid) and fluorescence (dotted) spectra (left), MALS chromatogram (middle), and the circular dichroism spectra obtained for **6.7** (right).

(Figure 6.2). From the UV-Vis spectrum, we observed a maximum at 270nm, and two small peaks around 330nm, and 350nm, with an absorption onset around 360nm. In the fluorescence spectra, we noted an emission maximum at 383nm. The UV-Vis trace of the 20mer is broadened relative to the oligopeptides, as expected, given the formation of a larger macromolecule. Overall, the results matched expectations for materials derived from quinoline subunits.

Following, we wanted to gain insight onto the conformation of our quinoline polypeptide. First, we prepared a sample of **6.7** in THF, and interrogated it with circular dichroism spectroscopy (Figure 6.2). Here, we noted negative peaks at 234nm, and 280nm, and one positive peak at 259 nm. Compared to the largest quinoline oligopeptide, we noted increased negative ellipticity around 230nm, and 280nm, suggesting helical character. Our preliminary assessment suggested that the quinoline polypeptide adopts an elongated conformation.

6.4 Conclusion

In conclusion, a new type of quinoline polypeptide was synthesized by iterative coupling novel quinoline alpha-amino acids, prepared *via* the Povarov reaction. Our reactions proceed under mild conditions, and the products of which, are easily purified and afforded in good yield. The

quinoline amino acid building block produced is regioselective, in addition to being enantiomerically pure. Iterative coupling of these building blocks produces elongated, helical structures, which share similar optoelectronic properties to other quinoline-containing materials. Further study and modification of these quinoline based molecules may offer new potential candidates for biologically derived photonic materials.

6.5 Supporting Information

6.5.1. General Information and Procedures

A. Materials. All chemicals were purchased from Acros Organics, ChemPep Inc., or Sigma-Aldrich, and all solvents were obtained from Fisher Scientific and used as received unless otherwise noted. The dimethylformamide used to prepare the model system and polymer was dried

with 3 Å molecular sieves and stored under argon. All glassware was oven dried at 150 °C overnight. The reactions were performed under dry argon unless otherwise noted.

B. Compound Purification Procedures. Flash chromatography was performed using a CombiFlash Rf 200 purification system manufactured by Teledyne Isco. When necessary, the silica gel columns/cartridges were flushed with 1/9 triethylamine/chloroform to deactivate the silica gel and then with chloroform to remove excess triethylamine. High performance liquid chromatography (HPLC) on an Agilent 1260 Infinity system using a reverse phase C18 column. For purification, the gradient was evolved from 95% Buffer A:5% Buffer B to 5% Buffer A:95% Buffer B at a flow rate of 4 mL/min over 35 min (Buffer A: 99.9% water, 0.1% trifluoroacetic acid; Buffer B: 95% acetonitrile, 4.9% water, 0.1% trifluoroacetic acid). Additional purification-relevant information and protocols are noted below as appropriate.

C. Reaction Product Characterization Procedures. All intermediates and products were characterized with a combination of nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, multi-angle light scattering size-exclusion chromatography (MALS-SEC), high-performance liquid chromatography (HPLC), and/or ultraviolet-visible (UV-vis) spectroscopy. The ^1H NMR and ^{13}C NMR spectra were obtained on an AVANCE600 instrument. Chemical shifts were reported in ppm for ^{13}H and ^{13}C NMR. The chemical shifts for the NMR data were referenced as follows: for samples in CDCl_3 , the ^1H NMR were referenced to CDCl_3 at 7.26, and the ^{13}C NMR were referenced to CDCl_3 at 77.16; for samples in DMF, the ^1H NMR were referenced to the solvent peak at 8.03, and the ^{13}C NMR were referenced to the solvent peak at 163.15; for samples in DMSO, the ^1H NMR were referenced to the solvent peak at 2.50, and the ^{13}C NMR were referenced to the solvent peak at 39.51. The data are labeled as follows: chemical shift, multiplicity

(s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), the coupling constants in Hertz, and the integration value. MALDI-TOF mass spectra were recorded on an AB Sciex TOF/TOF 5800 series mass spectrometer using a 349 nm Nd:YAG laser and dithranol or 2, 5-Dihydroxybenzoic acid (DHB) as the matrix. The UV-vis spectra were collected on an Agilent Cary 100 Series spectrophotometer in tetrahydrofuran (THF) at room temperature.

D. Polymer Characterization and Analysis Procedures. The polymers were analyzed *via* size exclusion chromatography with a multi-angle light scattering detector (SEC-MALS) by using a Malvern Omnisec Reveal separations module equipped with two Malvern single-pore columns connected in series (7.8 mm x 300 mm, 3 μ m particle size). The separations module was connected to a refractive index, UV-vis, viscometry, and multi-angle light scattering detectors in series. The flow rate was $\sim$.8 mL/min with an injection volume of $\sim$ 25 – 100 μ L and sample concentration of $\sim$ 1.0 – 2.5 mg/mL. Molecular weights (M_n and M_w) were estimated from a calibration curve using polystyrene standards (Malvern). The accuracy of this calibration curve was validated for polypeptide **6** (actual molecular weight of 4644 g mol⁻¹); the SEC-RI measurements indicated an M_n of 4416 g mol⁻¹ and M_w of 5004 g mol⁻¹ for polypeptide **6.6**.

6.5.2. Detailed Experimental Procedures

1. (E)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(4-((4-octylbenzylidene)amino)phenyl)propanoic acid (6.1). Fmoc-4-amino-(L)-phenylalanine (2.0 g, 4.97 mmol), 4-octylbenzaldehyde (1.302 g, 1.40 mL, 5.96 mmol), and *p*-toluene sulfonic acid were dissolved in DMF (40 mL). Molecular sieves (3 Å, 4.0 g) were added to the reaction mixture, and brought to 60° C. After 24 hours, the mixture was cooled and poured into 200mL CH₂Cl₂. The mixture was

washed gently with sodium bicarbonate (40 mL x 3), then with water (50 mL x 6), and lastly with brine (50 mL x 3). The organics were dried with sodium sulfate, and concentrated *in vacuo*. The product was purified with flash chromatography (95:5 chloroform: methanol) to yield a yellow solid, which was subsequently suspended in hexanes and filtered over a Whatman paper (2.4 g, 79%): ^1H NMR (600 MHz, $\text{DMF-}d_7$) δ = 8.58 (s, 1H), 7.93 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.6 Hz, 1H), 7.72 (dd, J = 7.1, 3.8 Hz, 2H), 7.43 (m, 4H), 7.39 (d, J = 7.8 Hz, 2H), 7.34 (m, 2H), 7.25 (d, J = 7.9 Hz, 2H), 4.48 (m, 1H), 4.24 (m, 3H), 3.29 (dd, J = 13.8 Hz, 4.2 Hz, 1H), 3.08 (dd, J = 13.5 Hz, 10.4 Hz, 1H), 2.69 (t, J = 7.7 Hz, 2H), 2.12 (s, 1H), 1.65 (m, 2H), 1.39 – 1.19 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, DMF) δ = 174.5, 160.9, 157.4, 151.6, 147.8, 145.29, 145.28, 142.22, 142.20, 137.0, 135.5, 131.2, 129.9, 129.8, 128.8, 128.2, 126.6, 126.5, 122.0, 121.2, 67.4, 57.1, 48.1, 37.9, 36.6, 32.8, 32.3, 31.13, 30.4, 30.21, 30.15, 23.5, 14.7. MALDI m/z calcd for $\text{C}_{39}\text{H}_{43}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 603.314, found 603.249.

2. 2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(2-(4-octylphenyl)-4-phenylquinolin-6-yl)propanoic acid (SI-6.1). **6.1** (4.6 g, 7.7 mmol), phenylacetylene (2.3 g, 2.5 mL, 23.0 mmol), and chloranil (2.07 g, 8.4 mmol) were dissolved in CHCl_3 (120 mL) under argon. Molecular sieves were added to the reaction mixture, which was then stirred at room temperature. Subsequently, $\text{BF}_3 \cdot \text{OEt}_2$ (1.6 g, 1.5 mL, 11.5 mmol) was added to the reaction mixture, and the temperature was brought up to 60°C. After 16 hours, the molecular sieves were filtered and the reaction was poured into CH_2Cl_2 . The mixture was washed with sodium bicarbonate (100 mL x 3), then water (100 mL x 3), and lastly with brine (100 mL x 3). The organics were dried with sodium sulfate, and concentrated *in vacuo*. The product was purified with flash chromatography (95:5 chloroform: methanol) and subsequently precipitated in ethanol to yield a white solid (2.47 g, 46%): ^1H NMR

(600 MHz, DMF-*d*₇) δ = 8.53 (d, J = 7.9 Hz, 2H), 8.17 (d, J = 8.7 Hz, 1H), 8.05 (s, 1H), 7.98 (s, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.86 (m, 2H), 7.73 (d, J = 7.2 Hz, 2H), 7.66 (t, J = 7.6 Hz, 2H), 7.58 (m, 3H), 7.43 (d, J = 8.1 Hz, 1H), 7.40 (q, J = 7.5 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 4.57 (m, 1ppH), 4.21 (m, 3H), 3.44 (dd, J = 13.9, 4.5 Hz, 1H), 3.26 (dd, J = 13.8, 10.1 Hz, 1H), 2.71 (t, J = 7.7 Hz, 2H), 1.68 (p, J = 7.5 Hz, 2H), 1.20 – 1.42 (m, 10H), 0.87 (t, J = 6.9 Hz, 3H). ¹³C NMR (151 MHz, DMF) δ = 174.3, 157.4, 156.9, 149.7, 149.0, 145.6, 145.3, 145.2, 142.20, 142.18, 139.3, 137.9, 137.7, 132.5, 130.9, 129.9, 129.8, 129.6, 128.8, 128.7, 128.5, 128.2, 128.1, 126.7, 126.50, 126.46, 126.3, 121.1, 120.1, 67.4, 56.9, 48.1, 38.4, 36.5, 32.8, 32.4, 23.6, 14.8. MALDI m/z calcd for C₄₇H₄₇N₂O₄ [M+H]⁺ 703z.346 found 703.206.

3. 2-amino-3-(2-(4-octylphenyl)-4-phenylquinolin-6-yl)propanoic acid (6.2). **SI-6.1** (1.0 g, 1.4 mmol) was dissolved in DMF (10 mL). Piperidine (.12 g, .14 mL, 1.42 mmol) was added to the mixture and stirred for 30 minutes. The reaction was poured into CH₂Cl₂ (100 mL) and washed with water (30 mL x 6), then with brine (30 mL x 6). The organics were dried with sodium sulfate, and concentrated *in vacuo*. The product was purified with flash chromatography (90:10 chloroform: methanol) to yield a white solid (0.57 g, 83%): ¹H NMR (600 MHz, Chloroform-*d*) δ = 8.15 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 7.8 Hz, 2H), 7.77 (s, 1H), 7.69 (s, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 3.99 (s, 1H), 3.27 (d, J = 13.5 Hz, 1H), 3.06 (dd, J = 14.4, 8.8 Hz, 1H), 2.64 (t, J = 7.2 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.33 – 1.23 (m, 10H), 0.86 (t, J = 6.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ = 173.7, 156.7, 150.3, 146.9, 145.2, 137.8, 135.8, 134.2, 131.8, 129.7, 129.3, 129.1, 128.8, 128.7, 127.9, 126.6, 125.7, 120.2, 56.1, 36.6, 35.9, 31.9, 31.4, 29.6, 29.4, 29.4, 22.7, 14.2. MALDI m/z calcd for C₃₂H₃₇N₂O₂ [M+H]⁺ 481.278 found 481.161.

4. Alanine-Quinoline Dimer (6.3). *Resin loading.* 2-Chlorotriyl chloride resin (300 mg, 1.2 mmol/g) was added to 10-mL Bio-Rad Poly-Prep chromatography column. The resin was loaded with a solution of fmoc-(L)-alanine (56 mg, 0.18 mmol) and 2,4,6-collidine (300 μ L) in dry CH_2Cl_2 (7 mL). The suspension was agitated for 12 h. The solution was washed with dry CH_2Cl_2 (3x). A mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{DIPEA}$ (17:2:1, 8 mL) was added to the resin and agitated for 1 h to cap unloaded resin sites. The solution was drained, and the resin was washed with dry CH_2Cl_2 (3x) and with MeOH (3x). The resin was dried by purging nitrogen gas through the poly-prep chromatography column. The resin loading was determined to be 0.08 mmol [0.27 mmol/g] through UV analysis of the Fmoc cleaved product. The loaded resin was suspended in dry DMF and transferred to a 25-mL hand coupling solid-phase peptide synthesis reaction vessel. The linear peptide was synthesized through the following cycles: *i.* Fmoc deprotection with 20% (v/v) piperidine in DMF (3 mL) for 30 min, *ii.* resin washing with dry DMF (3x), *iii.* coupling of fmoc-(L)-alanine (0.54 mmol, 168 mg) with HCTU (0.54 mmol, 105 mg) in 20% (v/v) 2,4,6-collidine in dry DMF (3 mL) for 1 h, and *iv.* resin washing with dry DMF (3x). Coupling of fmoc-(L)-alanine onto free N-terminus was assessed by MALDI-TOF and Isco. After completing the linear peptide synthesis, the resin was transferred to the 10-mL Bio-Rad Poly-Prep chromatography column. The resin was then washed with dry DMF (3x) and dry CH_2Cl_2 (3x). To cleave the peptide, the resin was treated with 20% hexafluoroisopropanol in dry CH_2Cl_2 (6 mL) followed by agitation for 1 h. The filtrate was collected in a round-bottom flask. The resin was washed with a second aliquot of 20% hexafluoroisopropanol then washed with dry CH_2Cl_2 (3x). The filtrates were combined and concentrated under reduced pressure to afford a white residue. The residue was placed under vacuum (< 10 mTorr) to remove any residual solvents. The product was purified with

flash chromatography (chloroform) to yield a white solid (31 mg, 54%): ^1H NMR (600 MHz, DMSO- d_6) δ = 8.9 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 8.4 Hz, 2H), 8.15 (m, 3H), 8.02 (s, 1H), 7.85 (s, 1H), 7.82 (m, 1H), 7.73 – 7.69 (m, 2H), 7.65 – 7.60 (m, 2H), 7.62 – 7.55 (m, 1H), 7.38 (d, J = 8.0 Hz, 2H), 4.30 (p, J = 7.2 Hz, 1H), 4.14 – 4.05 (m, 1H), 3.32 (dd, J = 14.2, 5.0 Hz, 1H), 3.06 (dd, J = 14.2, 8.6 Hz, 1H), 2.67 (t, J = 7.6 Hz, 2H), 1.62 (m, 2H), 1.35 – 1.21 (m, 14H), 0.86 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ = 173.7, 167.7, 158.2, 157.9, 155.4, 148.7, 144.4, 137.5, 135.6, 133.4, 131.7, 129.8, 128.8, 127.4, 126.2, 124.9, 119.0, 116.7, 114.8, 53.3, 47.7, 40.0, 39.9, 39.8, 39.7, 39.5, 39.4, 39.2, 39.1, 34.9, 31.3, 30.8, 28.8, 28.7, 22.1, 17.3, 13.9. MALDI m/z calcd for $\text{C}_{35}\text{H}_{42}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$ 552.315 found 552.231.

5. Synthesis of Polymers. *Resin loading.* 2-Chlorotrityl chloride resin (300 mg, 1.2 mmol/g) was added to 10-mL Bio-Rad Poly-Prep chromatography column. The resin was loaded with a solution of compound **1** (126 mg, 0.18 mmol) and 2,4,6-collidine (300 μL) in dry CH_2Cl_2 (7 mL). The suspension was agitated for 12 h. The solution was washed with dry CH_2Cl_2 (3x). A mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{DIPEA}$ (17:2:1, 8 mL) was added to the resin and agitated for 1 h to cap unloaded resin sites. The solution was drained, and the resin was washed with dry CH_2Cl_2 (3x) and with MeOH (3x). The resin was dried by purging nitrogen gas through the poly-prep chromatography column. The resin loading was determined to be 0.08 mmol [0.27 mmol/g] through UV analysis of the Fmoc cleaved product. The loaded resin was suspended in dry DMF and transferred to a 25-mL hand coupling solid-phase peptide synthesis reaction vessel. The linear peptide was synthesized through the following cycles: *i.* Fmoc deprotection with 20% (v/v) piperidine in DMF (3 mL) for 30 min, *ii.* resin washing with dry DMF (3x), *iii.* coupling of compound **6.1** (126 mg, 0.18 mmol) with HCTU (0.54 mmol, 105 mg) in 20% (v/v) 2,4,6-collidine in dry DMF (3 mL) for

1 h, and *iv.* resin washing with dry DMF (3x). Coupling of compound **6.1** onto free N-terminus was assessed by MALDI-TOF and Isco. After completing the linear peptide synthesis, the resin was transferred to the 10-mL Bio-Rad Poly-Prep chromatography column. The resin was then washed with dry DMF (3x) and dry CH₂Cl₂ (3x). To cleave the peptide, the resin was treated with 20% hexafluoroisopropanol in dry CH₂Cl₂ (6 mL) followed by agitation for 1 h. The filtrate was collected in a round-bottom flask. The resin was washed with a second aliquot of 20% hexafluoroisopropanol then washed with dry CH₂Cl₂ (3x). The filtrates were combined and concentrated under reduced pressure, and subsequently placed under vacuum (< 10 mTorr) to remove any residual solvents. This strategy was used to afford the fmoc-protected quinoline polypeptides, (Q₂-fmoc (**SI-6.2**), Q₅-fmoc (**SI-6.3**), Q₁₀-fmoc (**SI-6.4**), Q₂₀-fmoc (**SI-6.5**)), and the deprotected quinoline amino acids (Q₂-NH₂ (**6.4**), Q₅-NH₂ (**6.5**), Q₁₀-NH₂ (**6.6**), Q₂₀-NH₂ (**6.7**)).

6.5.3. Spectroscopic Characterization Data

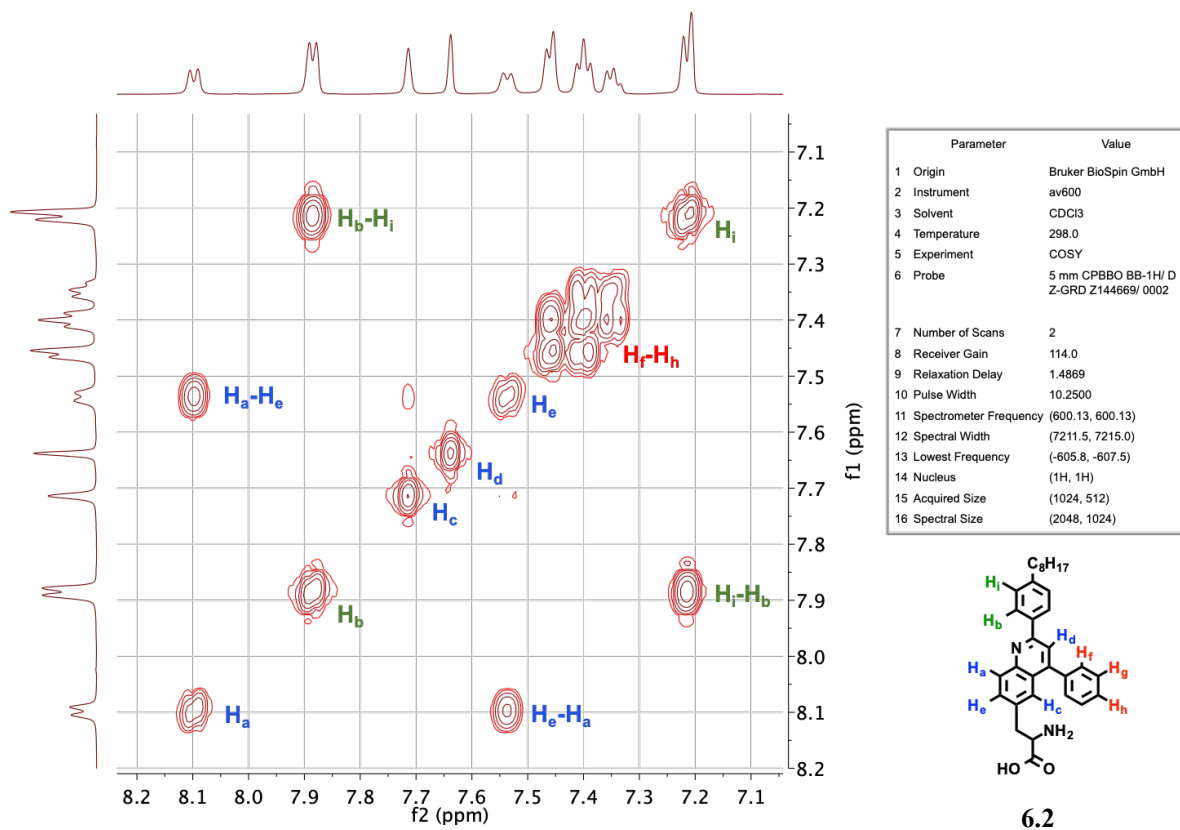


Figure S6.1. The COSY spectrum obtained for compound **6.2**. This spectrum was used to assign aromatic protons.

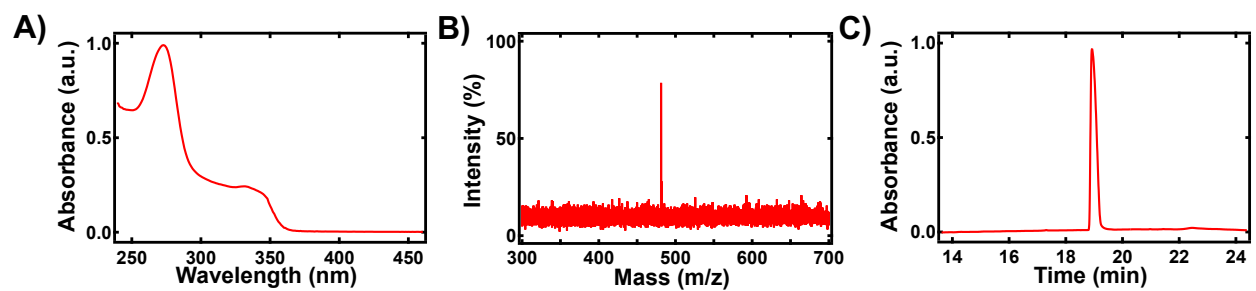


Figure S6.2. (A) UV-Vis, (B) MALDI, and (C) HPLC spectra obtained for quinoline amino acid

6.2.

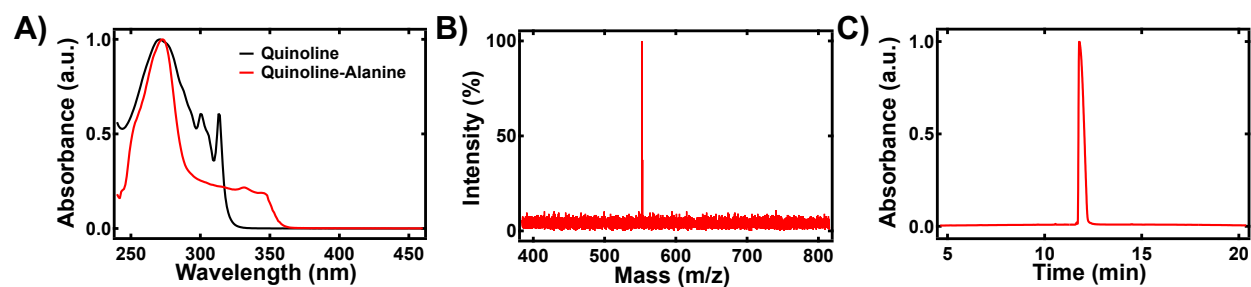


Figure S6.3. (A) UV-Vis, (B) MALDI, and (C) HPLC spectra obtained for quinoline-alanine dimer **6.3**.

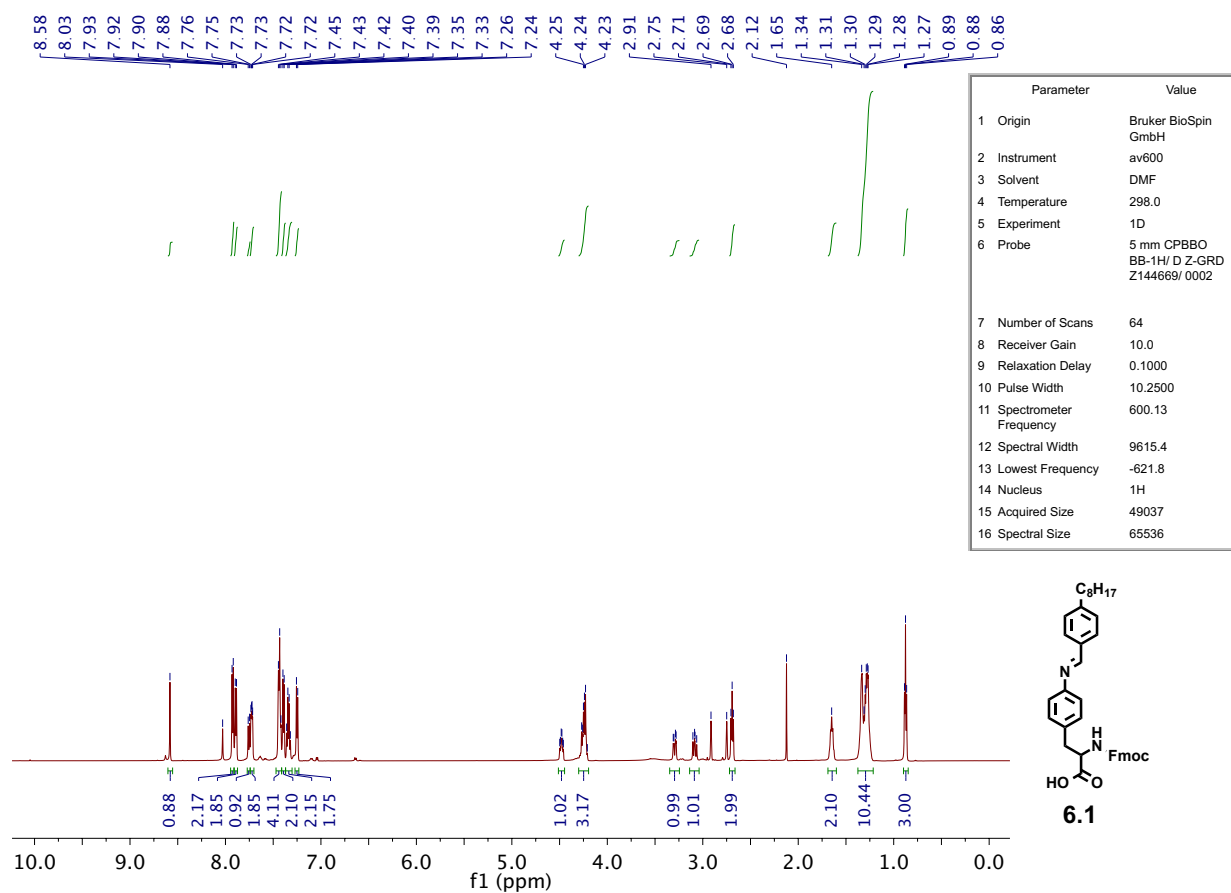


Figure S6.4. The ¹H NMR spectrum obtained for imine **6.1**.

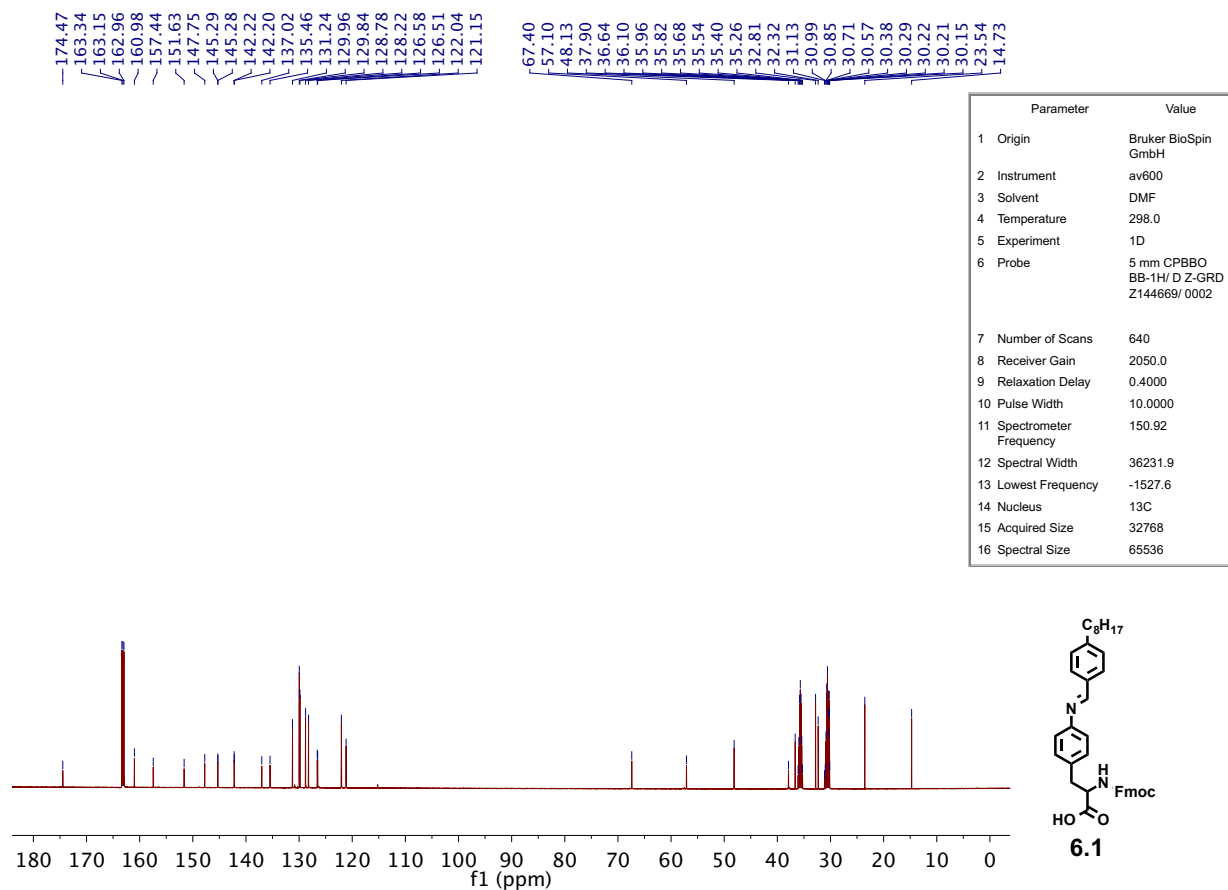


Figure S6.5. The ¹³C NMR spectrum obtained for imine **6.1**.

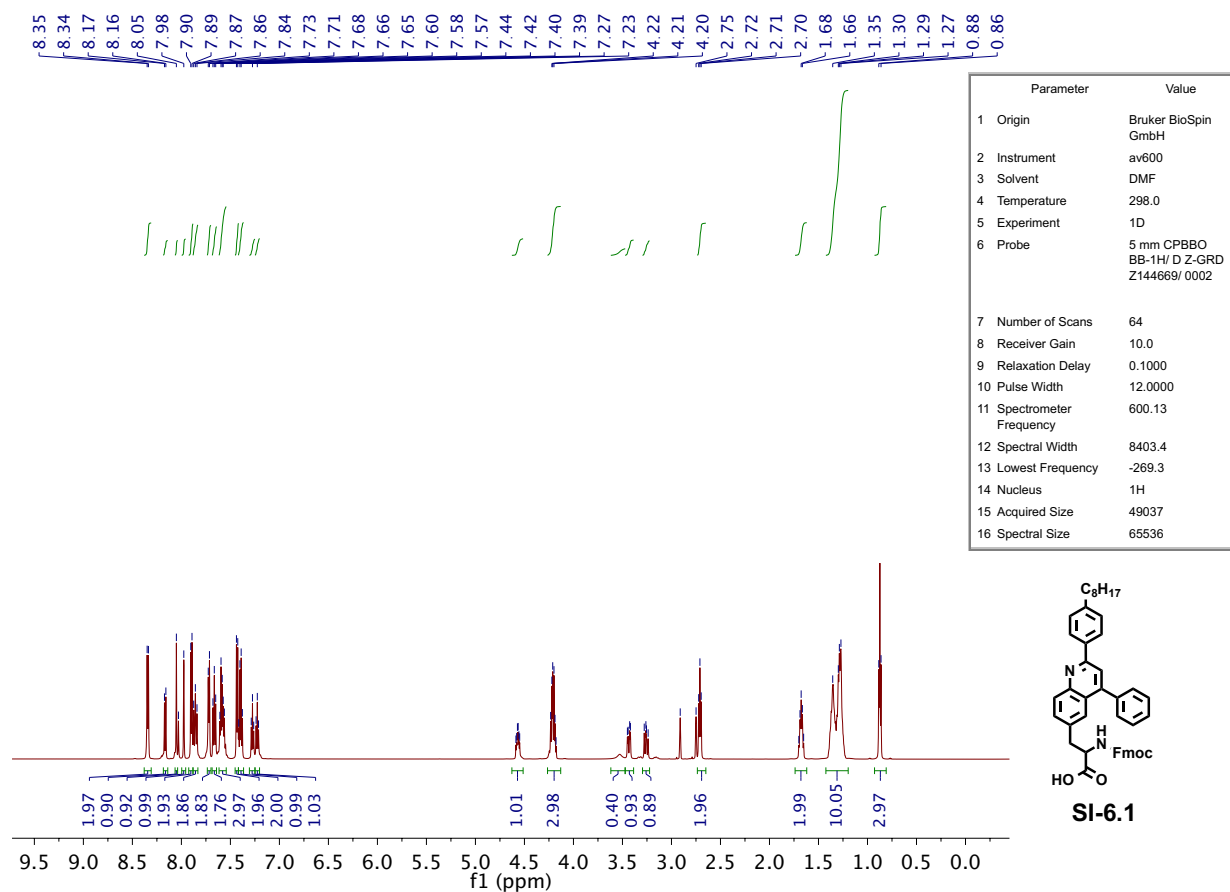


Figure S6.6. The ¹H NMR spectrum obtained for fmoc-protected quinoline amino acid **SI-6.1**.

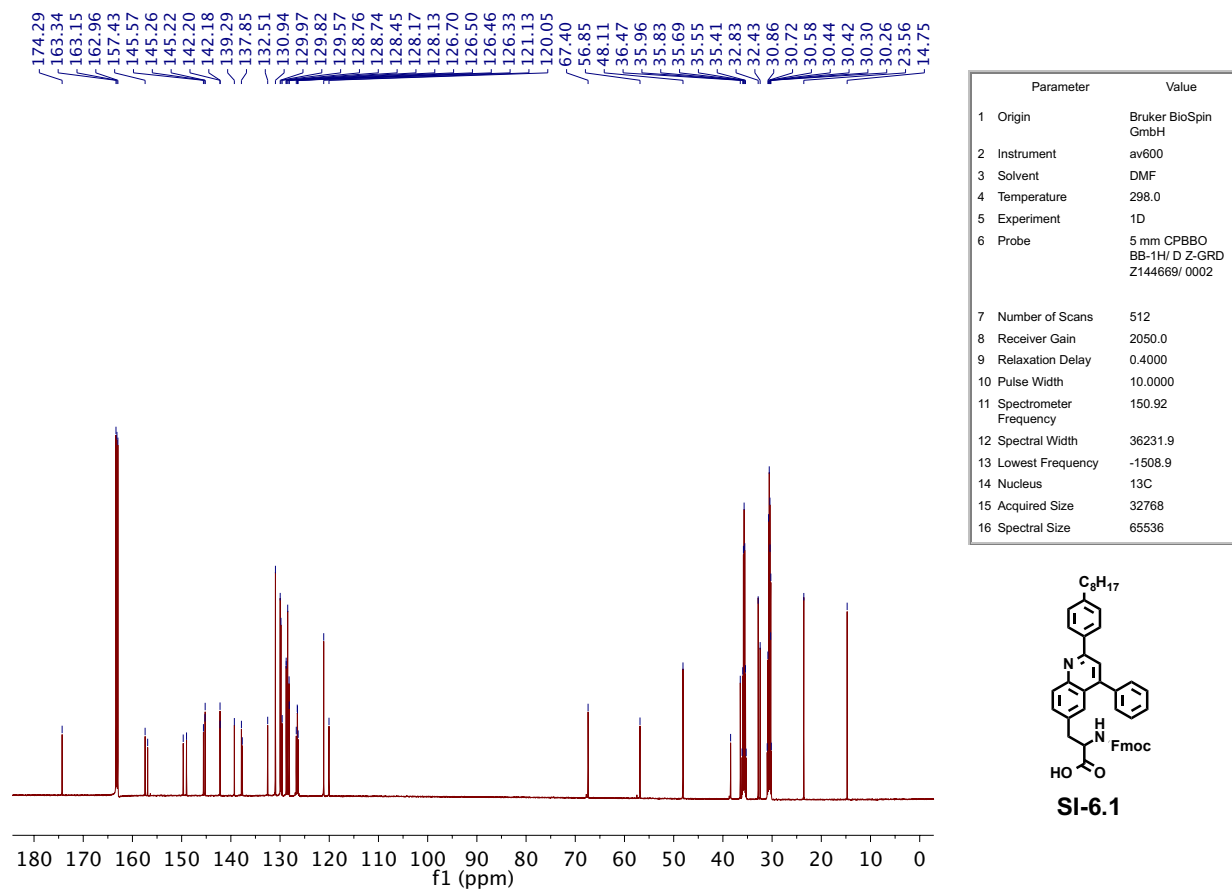


Figure S6.7. The ^{13}C NMR spectrum obtained for fmoc-protected quinoline amino acid **SI-6.1**.

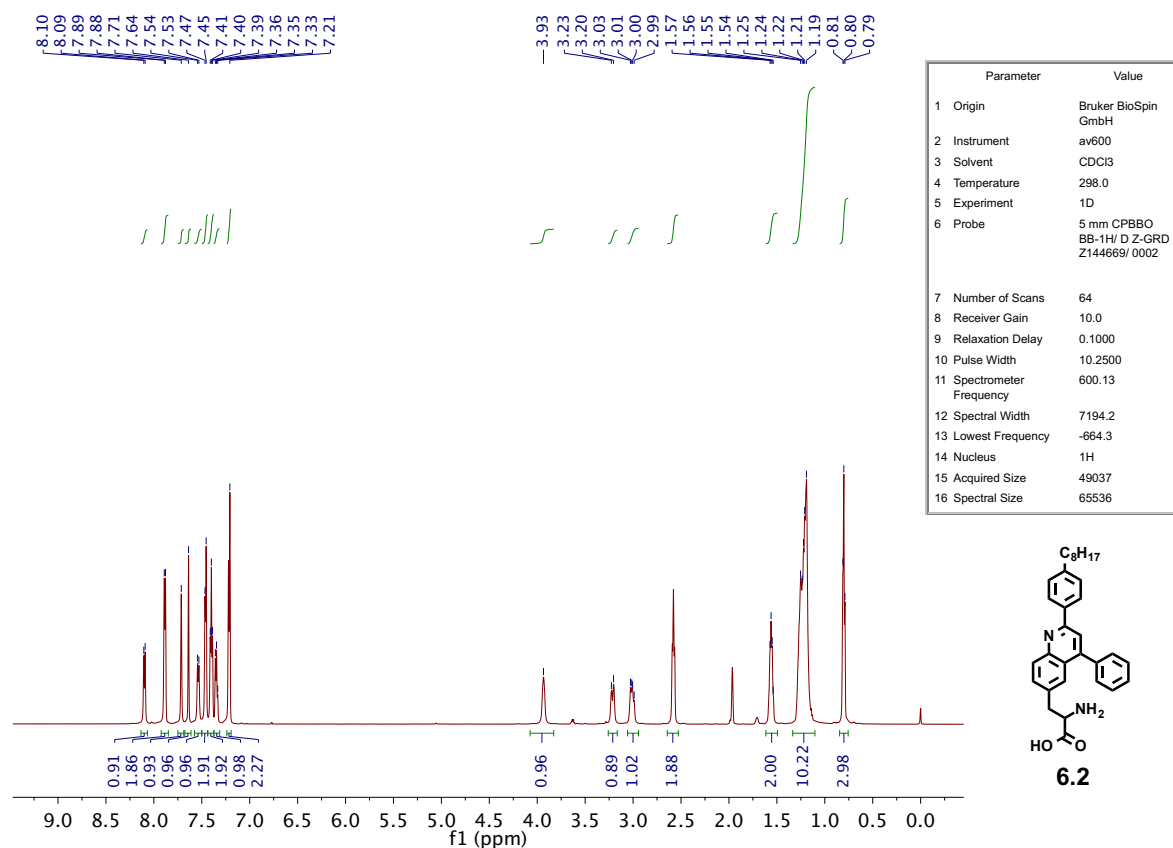


Figure S6.8. The ¹H NMR spectrum obtained for quinoline amino acid **6.2**.

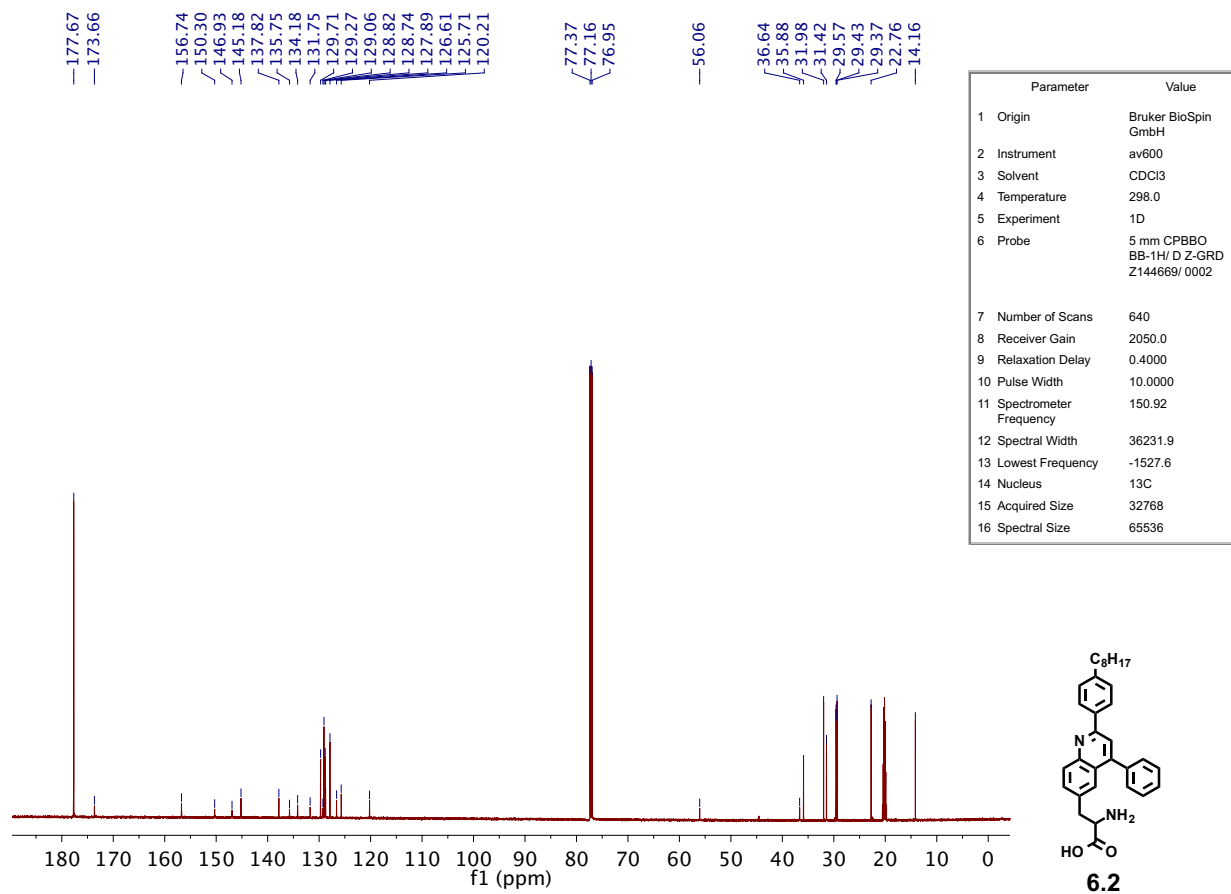


Figure S6.9. The ¹³C NMR spectrum obtained for quinoline amino acid **6.2**.

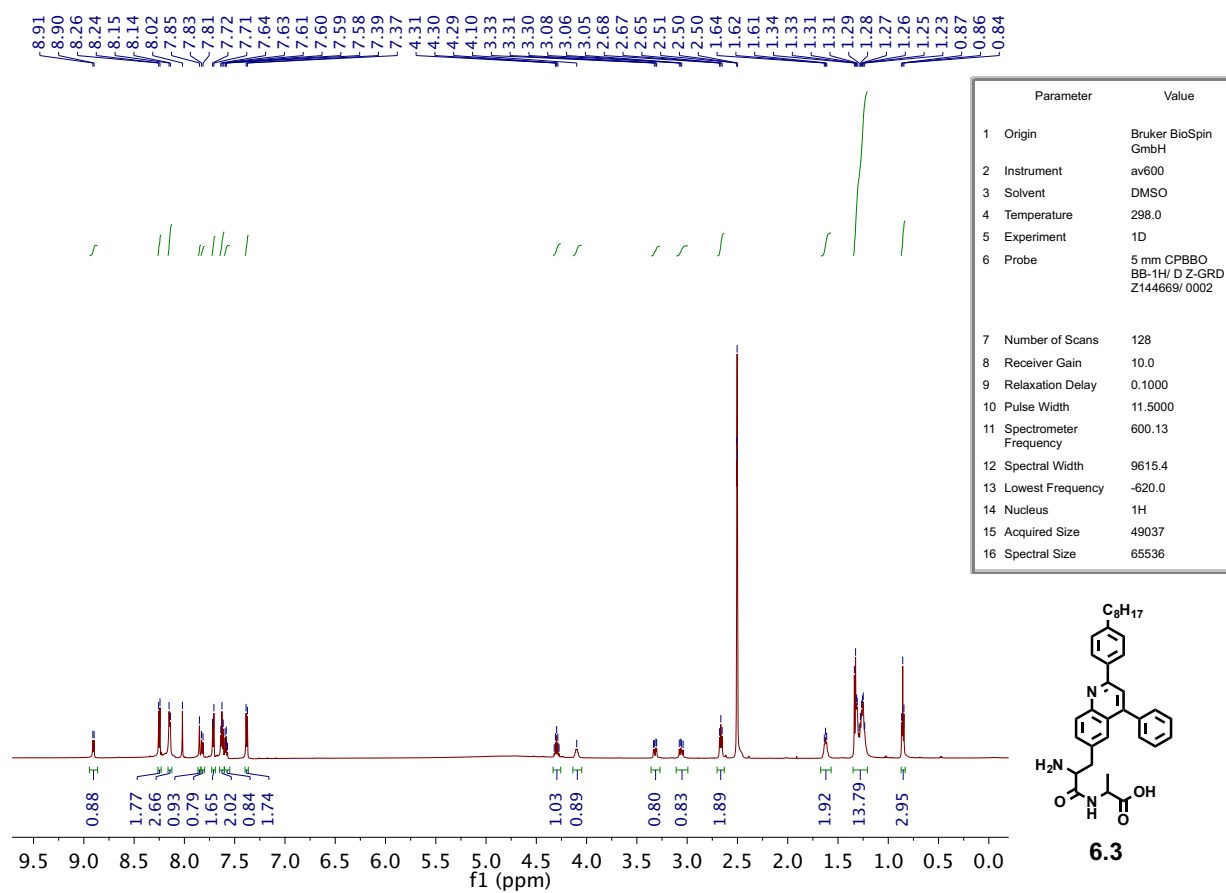


Figure S6.10. The ¹H NMR spectrum obtained for quinoline-alanine dimer **6.3**.

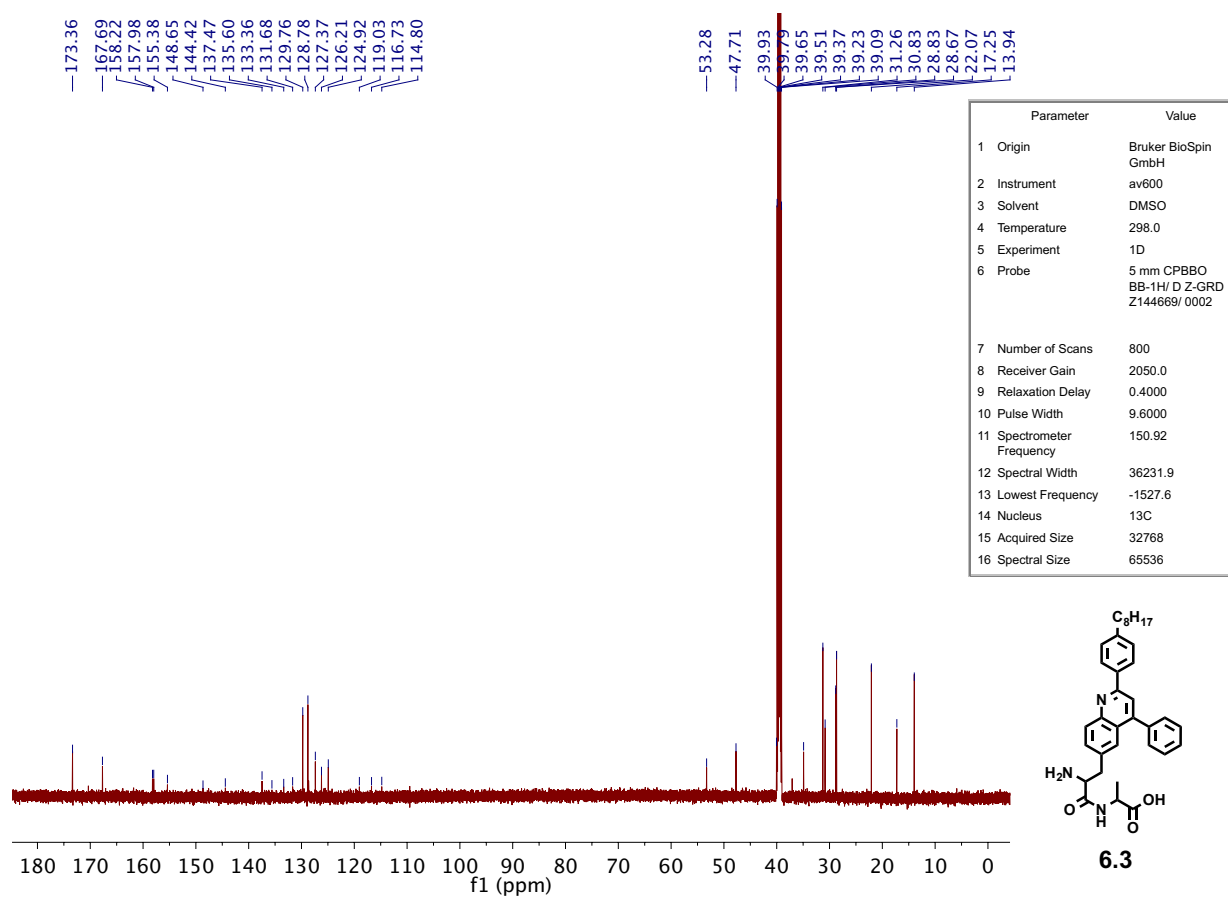


Figure S6.11. The ¹³C NMR spectrum obtained for quinoline-alanine dimer **6.3**.

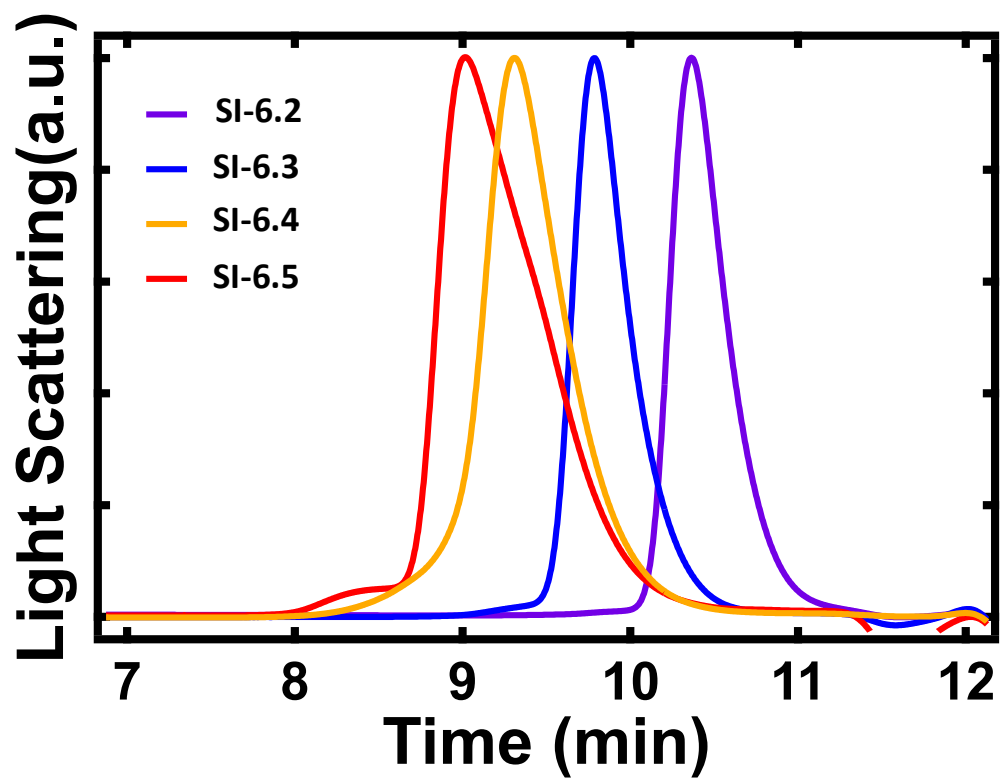


Figure S6.11. The MALS chromatogram obtained for fmoc-protected quinoline polypeptide 2mer (SI-6.2), 5mer (SI-6.3), 10mer (SI-6.4), 20mer (SI-6.5).

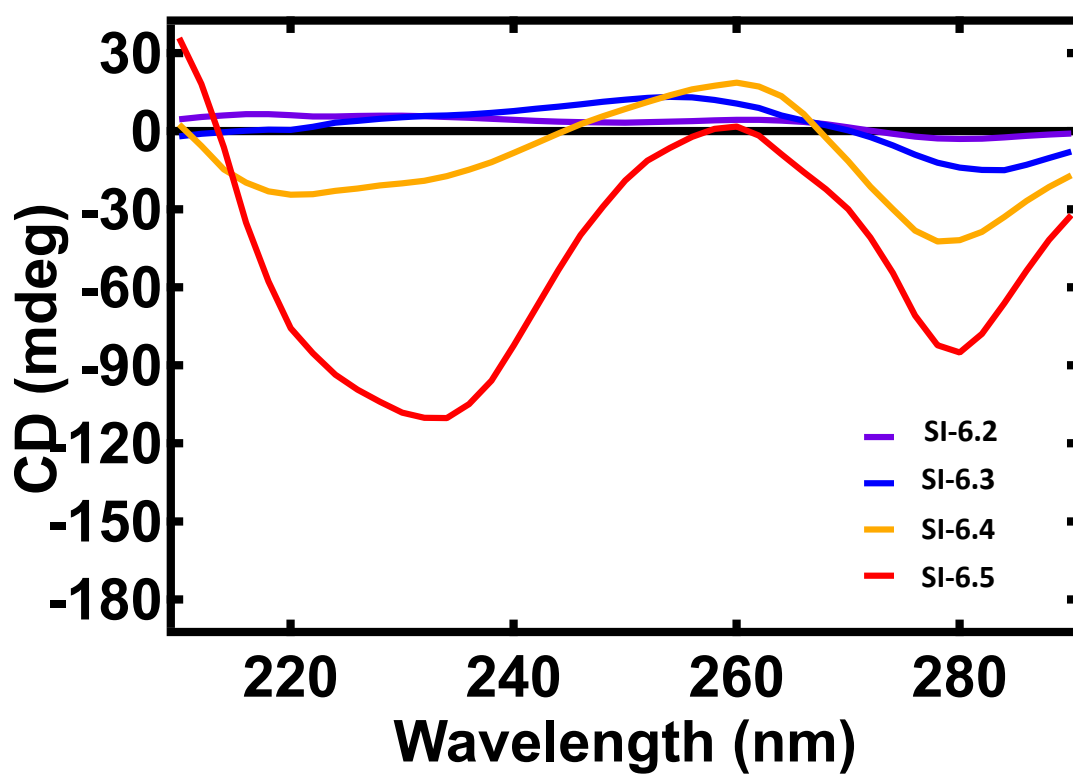


Figure S6.12. The circular dichroism spectra obtained for fmoc-protected quinoline polypeptide 2mer (SI-6.2), 5mer (SI-6.3), 10mer (SI-6.4), and 20mer (SI-6.5).

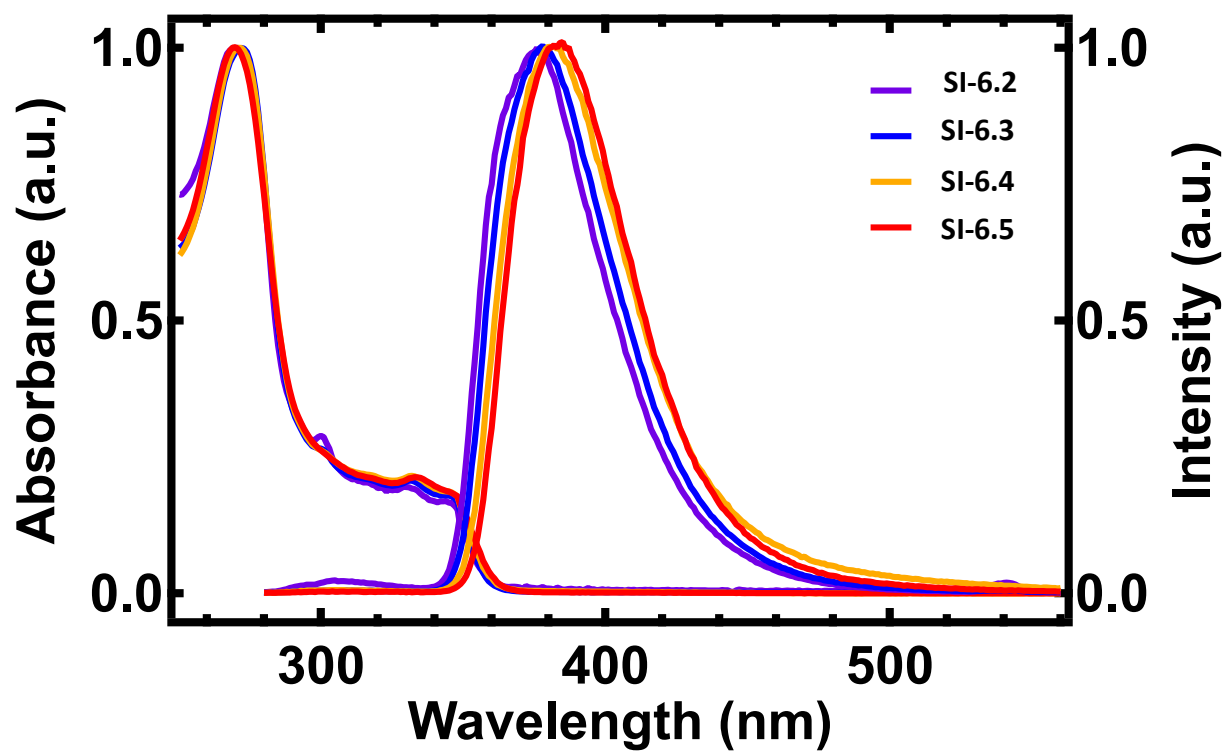


Figure S6.13. The UV-vis spectra obtained for fmoc-protected quinoline polypeptide 2mer (SI-6.2), 5mer (SI-6.3), 10mer (SI-6.4), and 20mer (SI-6.5).

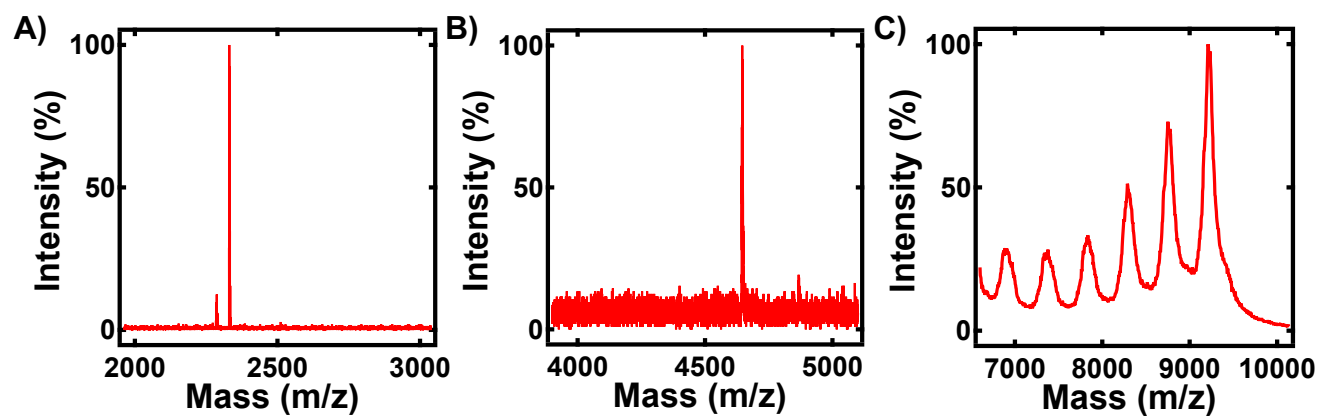


Figure S6.12. (A) The MALDI spectrum obtained for **6.5**. A peak was observed with an m/z of 2332. (B) The MALDI spectrum obtained for **6.6**. A peak was observed with an m/z of 4645. (C) The MALDI spectrum obtained for **6.7**. A peak was observed with an m/z of 9213.

6.5.4. Supporting References

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6.6 References

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Chapter 7 Structure and Induced Self-Assembly of a Truncated Reflectin Variant

7.1 Abstract

Cephalopods possess unrivaled camouflage and signaling abilities that are enabled by their sophisticated skin architecture, which is comprised of both reflective cells (iridophores) and pigment-containing organs (chromatophores). The optical functionality of these cells (and thus cephalopod skin) critically relies upon subcellular structures partially composed of a unique class of structural proteins known as reflectins, which possess an unusual sequence composed of repeating domains and variable linkers, which in turn are rich in aromatic and charged amino acid residues. Although a tremendous effort has been made to elucidate and control the secondary and tertiary structures of reflectins, most studies to date have only been able to demonstrate control over the aggregation of the protein, with no reliable means to control the structure of a reflectin protein. Herein we perform an in-depth bioinformatics analysis to design a truncated reflectin variant which exhibits the same functional characteristics as > 60% of all reflectins, characterize the protein at multiple length-scales (atomistic to μm) to define the precise secondary structure of a reflectin variant and ensuing, we demonstrate an unprecedented method for controlling the self-assembly of RfA1TM through modification with a quinoline amino acid. Our findings provide insight into the structure and assembly of reflectins, and holds broad implications for the design of cephalopod-inspired materials.

7.2 Introduction

Cephalopods (e.g. squids, octopuses, and cuttlefish) have fascinated scientists and the general populace alike for millennia due to their unique ability to instantaneously alter their appearance.¹⁻⁶ Squids, like the one shown in Figure 7.1A are able to do this via their unique skin architecture which contains a combination of reflective cells (e.g. iridophores, shown in Figure

7.1B) that enable structural coloration and pigment-containing cells (as part of larger organs, called chromatophores, shown in Figure 7.1C) that enable pigmentary coloration.^{2,5} More specifically, iridophore cells contribute to structural coloration via their cellular geometry, wherein an infolding of the membrane forms periodic, alternating arrangements (i.e. lamellar structures) containing proteinaceous platelets, where each lamella is separated by extracellular space (Figure 1D).⁷⁻¹⁵ The geometry of the lamellae (spacing and thickness) and the internal platelets (aggregation state of the proteinaceous platelets), which are actively controlled in some squids but passively controlled in most other cephalopods enable the iridophore to effectively transmit and reflect specific wavelengths of light, and act like biological Bragg stacks with narrowband reflectances (Figure 7.1B).⁷⁻¹⁵ In contrast, chromatophore organs have a central chromatophore pigment cell, which enables pigmentary coloration that is surrounded by radial muscle cells and sheath cells (Figure 7.1E).^{8,9,16-18} The central pigment cell contains an internalized sacculus containing networks of pigment- and protein-based granules and is actively stretched from a punctate to an expanded state by radial muscle cells, thus effectively acting as a pigment-based spectral filter (Figure 7.1C).^{8,9,16-18} In addition, sheath cells within the chromatophore organ, contain protein-based granules, which are presumed to supplement the pigment-based coloration with additional structural coloration. As scientists unearthed more about the skin components of cephalopods that enabled color change, they began to delve into the subcellular components that enabled this amazing display of color.

In cephalopods, it was found that the subcellular structures (like the proteinaceous platelets of iridophores and the sheath cells of chromatophore organs) that enabled structural color were composed primarily of a unique class of proteins, called reflectins. Reflectins were first isolated from the light organ of the *Euprymna scolopes* squid and were immediately benchmarked as

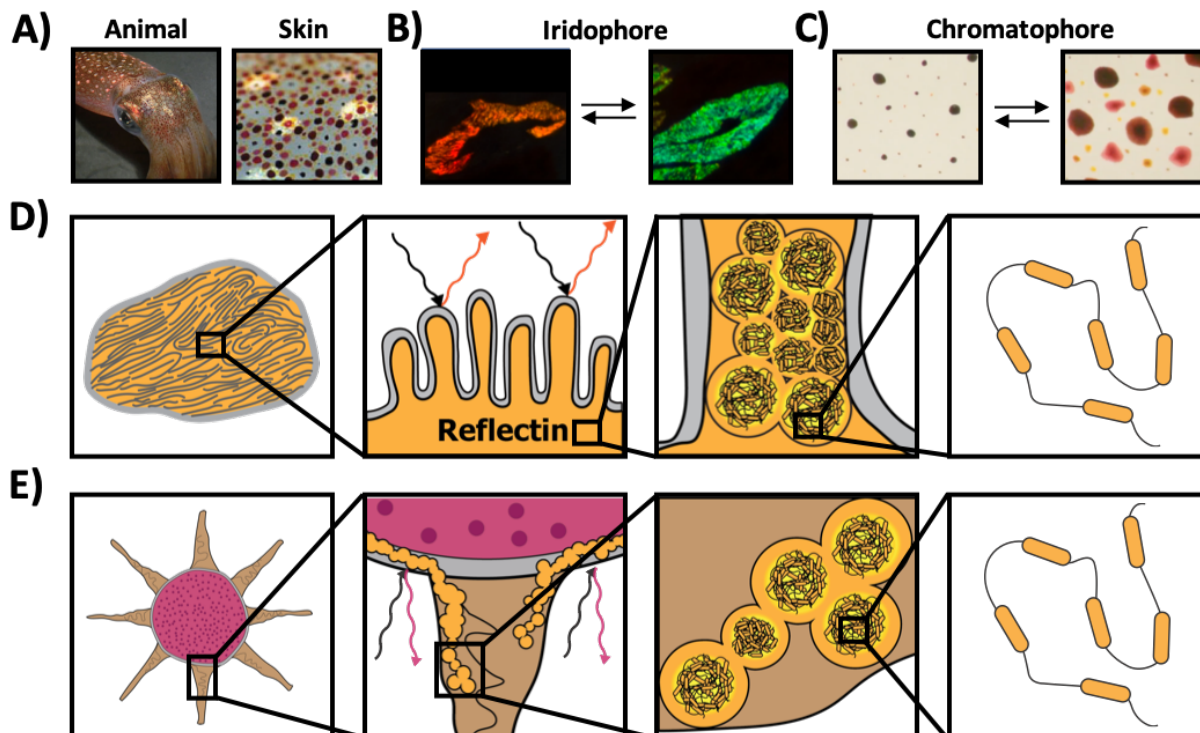


Figure 7.1. (A) An image of the cephalopod *D. Pealeii* (left), and a close-up image of its skin (right), which is comprised of leucophores, iridophores, and chromatophores. (B) An image of an iridophore, an optically active cell in the cephalopod skin responsible for cephalopod iridescence. Shown, is the iridophore switching between red (left) and green (right) reflective states. (C) An image of a chromatophore organ, a pigment-containing cell surrounded by radial muscle cells and sheath cells, responsible for pigmented cephalopod skin coloration. (D) A cartoon representation of the iridophore demonstrating infoldings of the membrane (left). Examination of the iridophore surface reveals a lamellar structure, which acts as a Bragg reflector (middle left). Within the lamellae are proteinaceous platelets comprised of reflection isoforms that can self-assemble to alter the spacing between lamellae (middle right). One of the reflectin isoforms contained within the platelets is Reflectin A1 (right). (E) A cartoon representation of the chromatophore organ demonstrating a central pigment-filled cell (pink) surrounded by radial muscle cells and sheath cells (brown) (left). Reflectin nanoparticles are located within the sheath cells (middle left). The reflectin nanoparticles are composed of multiple reflectin isoforms (middle right), one of which is reflectin A1 (right). [The images in (A) are reproduced from R. T. Hanlon, the images in (B) are reproduced from D. E. Morse, and the images in (C) are reproduced from a video by R. T. Hanlon.]

unusual because of their amino acid sequence.¹⁹ First, reflectins were found to have generally conserved motifs of the form $(M/F-D-X_5)(M-D-X_5)_n(M-D-X_{3/4})$ separated by variable linker regions containing a large fraction of aromatic and charged residues.¹⁹ In addition to these residues, their amino acid sequence was also enriched in methionine, glycine, and arginine.^{14,19} Surprisingly, the amino acid sequence of reflectins broadly lacked the hydrophobic amino acids (valine, alanine, leucine, and isoleucine), which typically make up a large fraction of most proteins.^{19–21} The

identification of this class of proteins soon led to their study both *in vivo* to elucidate their role within cephalopods and *in vitro* to understand their fundamental material properties. Studies focusing on reflectins *in vivo* demonstrated active control over the specific wavelengths reflected by iridophores *via* charge neutralization or chemical activation of phosphorylation sites within the reflectin protein, which in turn altered the geometry and spacing of the lamellae in iridophores.^{11,13,22} In addition, a recent study has surmised that reflectins enable structural coloration in sheath cells via thin-film like interference effects, caused by the deformation of the cells during the expansion and contraction of the chromatophore organs.¹⁶ Simultaneously, *in vitro* studies of reflectins have demonstrated the flexibility of the protein, both in regards to the numerous structures it can self-assemble into (e.g. nanoparticles,^{13,23–26} microfibers,²⁵ and hexagonal plates)²⁶ as well as the multitude of structures that the protein can be processed to form (e.g. thin films,^{25–28} fibers,²⁵ and diffraction gratings)²⁵ In addition, these structures can be further tuned via a variety of chemical and electrical stimuli to alter the assembly and aggregation state of the protein.^{13,18,24–29} Altogether, reflectin proteins' unique amino acid sequence, and structural versatility have motivated studies to better understand and characterize the secondary structure of this family of proteins.

Several groups have attempted to address this lack of a defined structure for reflectins by studying multiple isoforms across a variety of cephalopod species (Supporting Table 1). First, Kramer *et al.* prepared buffered solutions of *E. scolopes* reflectin 1a, precipitated the protein, and extruded fibers, to enhance secondary structural alignment.²⁵ They then performed wide angle X-ray diffraction on the fiber bundles and single fibers with various solvent conditions to induce beta-sheet and alpha-helical character, and found two amorphous peaks, which were reminiscent of wide-angle X-ray scattering (WAXS) spectra demonstrating beta-sheet character in proteins,

and suggested the possibility that reflectins could be induced to form specific secondary structures.²⁵ Next, Qin and co-workers expressed a reflectin variant (composed of a concatenation of a repeated motif) from the *E. scolopes* reflectin 1a, and prepared lyophilized powders and dried films for further structural analyses.³⁰ By performing Fourier transform infrared spectroscopy (FTIR) and circular dichroism (CD) on the reflectin powders and films, they found that the protein was primarily disordered (> 50% random coil) with some fraction of beta turns (> 25 %) and beta strands (> 10%) and a very small fraction of alpha helices (< 5%).³⁰ Guan *et al.* prepared buffered solutions of the first repeated domain in *S. officinalis* reflectin 2 and performed CD spectroscopy. They also found that the protein had some beta character (> 25% beta sheets and ~ 10% beta turns) and some alpha-helical features (> 10%).²⁶ Levenson and co-workers prepared buffered solutions of reflectins A1, A2, B, and C from *Doryteuthis opalescens* and investigated the effects of pH titration on the charged state and thus the structure of the protein. By modeling the hydrophobic moments of the reflectins, they found that the repeated motifs had a propensity to form amphipathic beta sheets or helices, which they further supported with helical modeling.²³ However, their WAXS experiments showed no sign of helices, although beta structure was apparent.²³ Thus, by combining their modeling and experimental work, they predicted that helices may form a transition state that are ultimately replaced by beta structures.²³ Tao *et al.* also looked at the self-assembly of reflectin A1 from *D. opalescens* and prepared them in either guanidine hydrochloride (GdHCl) to maintain the protein as monomers or NaCl to cause them to aggregate.¹³ WAXS analyses on these preparations of reflectin found that without NaCl (in GdHCl only), reflectin showed no apparent secondary structure, appearing primarily disordered.¹³ However, after exposure to >10 mM NaCl, WAXS spectra of clusters of reflectin nanoparticles showed significant beta-sheet structure, and appeared consistent with the peptide backbone interactions predicted to occur between two

adjacent nanoparticles.¹³ Naughton *et al.* prepared films of reflectin A1 from *Doryteuthis pealeii* and performed grazing incidence wide angle X-ray scattering (GIWAXS) to evaluate the presence of secondary structure.²⁴ Their GIWAXS profile matched the characteristic WAXS separation distances known for beta-sheets, and together with their deuterium exchange mass spectrometry (DXMS) measurements and hydrophobic moment calculations suggested that these secondary structures would be located primarily within the repeated motifs.²⁴ Williams and co-workers studied reflectin A2 from *D. pealeii* using replica exchange molecular dynamics simulations in conjunction with homology modeling and found that reflectin monomers were highly dominated by alpha-helical motifs within their conserved domains and unstructured within their variable linker regions.¹⁶ Altogether, the studies found that reflectins are able to form a variety of secondary structures, all of which are primarily confined to their repeated motifs, nevertheless, the atomic-resolution structure of the reflectin family of proteins and control over their self-assembly still remain elusive to date.

Herein, we report a multi-faceted approach to unambiguously characterize the secondary structure of a truncated reflectin variant with atomic-resolution and demonstrate control over the chemically induced self-assembly of the protein. First, we used bioinformatics to re-define the conserved domains within all currently known reflectins and to rationally design a representative reflectin variant, composed of a conserved domain and a variable linker region from a full-length reflectin protein. Next, we performed computational analyses and molecular dynamics simulations on our truncated reflectin variant to evaluate regions of possible secondary structure, and to evaluate the propensity of the variant to form ordered secondary structures. Subsequently, we heterologously expressed our designer reflectin protein (both unlabeled and uniformly labeled with ¹⁵N, ¹³C) with high yields, and characterized the respective biophysical attributes (purity, labeling

efficiency, solvent exposure of side chains, and overall secondary structure) of the proteins. Then, we used the unlabeled protein to perform SAXS measurements to resolve the size, shape, and order of the truncated reflectin variant. In addition, we used the ^{15}N -, ^{13}C - labeled protein to perform nuclear magnetic resonance (NMR) spectroscopy to obtain an atomic resolution structure of the truncated reflectin variant. Finally, we demonstrated that an aqueous solution of the truncated reflectin variant could be chemically modified to controllably alter its self-assembly and secondary structure. Taken together, we demonstrate the atomic resolution structure of a truncated reflectin variant and tunable control of its secondary structure with chemical modification.

7.3. Results and Discussion

We began our experiments by comparing and evaluating the sequences of all available reflectin isoforms *via* a bioinformatics approach. Here, we began by taking into consideration the previous work done by Levenson *et al.* whereby they evaluated 4 reflectin sequences from a single cephalopod species to identify two conserved motifs.²³ We sought to expand upon this work by performing a broader analysis on all known reflectins across a variety of cephalopod species. For this purpose, we located 51 reflectins from 6 different cephalopod species by using a basic local alignment search tool (BLAST), quantified the homology of proteins' amino acid sequences as well as identified any conserved motifs with Clustal Omega, and then predicted the secondary structures expected for reflectins with SSpro (Figure 7.2A).³¹⁻³⁶ Based on this analysis, we surmised that reflectins' sequences consisted of repeating conserved motifs interspersed among variable linker regions, in agreement with previous reports. Furthermore, we were able to expand, generalize, and subclassify the 200 discovered motifs into three distinct types, i.e. N-terminal, internal, or C-terminal, with additional precision (Figure 7.2B-7.2D). The 28 residue-long N-terminal motifs, denoted as RMN, accounted for 16 % of all motifs and were present in 73 % of

reflectins. These common variants featured relatively little sequence diversity, as they always

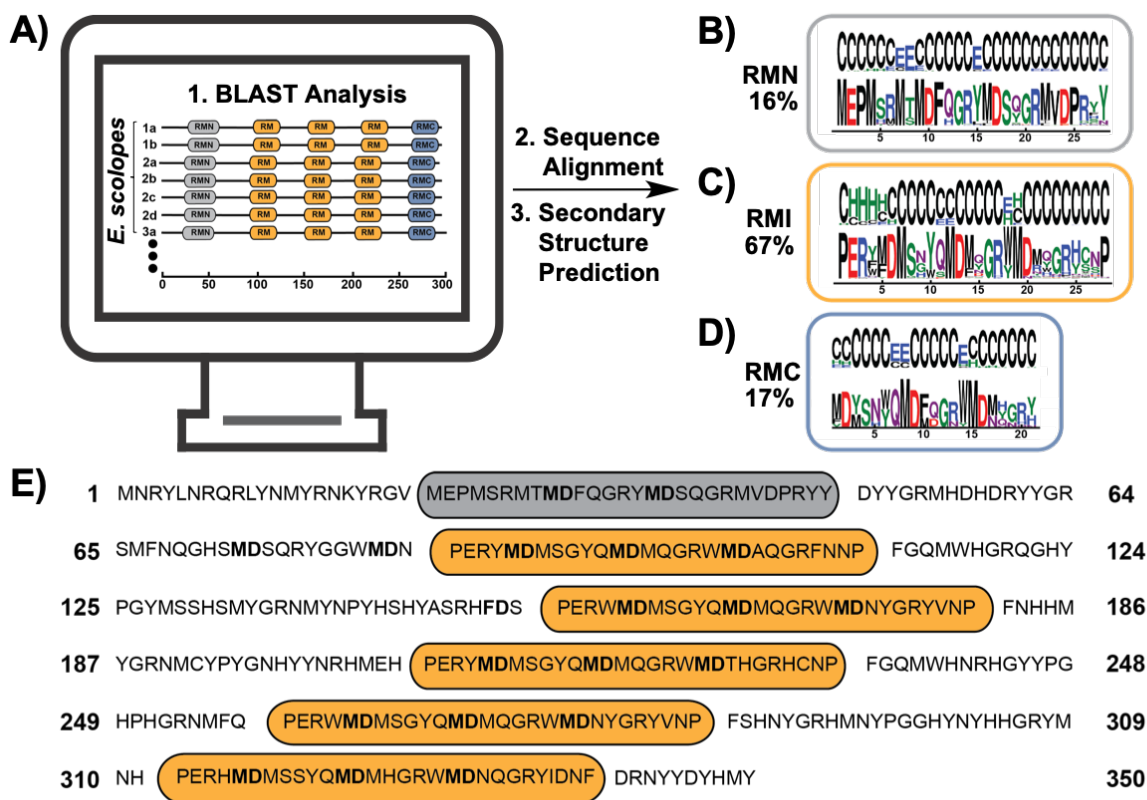


Figure 7.2. (A) A schematic of our bioinformatics approach starting with (1) BLAST analysis, (2) sequence alignment, and (3) secondary structure prediction. (B) A logo of the RMN domain which is 28 amino acids long, and is comprised mostly of random coil with a small fraction of beta-sheets. The RMN constitutes the 16% of the repeat domains found across the 51 reflectin sequences. (C) A logo of the RMI domain which is 28 amino acids long, and is comprised mostly of random coil with a small fraction of helices, and beta sheets. The RMI motif constitutes the 67% of the repeat domains found across the 51 reflectin sequences. (D) A logo of the RMC domain, which is 21 amino acids long, and is comprised mostly of random coil with a small fraction of beta-sheets. The RMC motif constitutes 17% of the repeat domains found across the 51 reflectin sequences. (E) The full-length RfA1 sequence from *D. pealeii*, which contains a single RMN domain (highlighted in grey) and five RMI domains (highlighted in orange). All MD dyads are bolded.

started with an MEPM segment, contained multiple MD dyads, and were composed almost entirely of basic, acidic, hydroxylic, and sulfur-containing amino acids (Figure 7.2B). Their predicted secondary structures consisted mostly of random coils, with some beta strand character in proximity to the MD dyads (Figure 7.2B). The 28 residue-long internal motifs, denoted as RMI, accounted for 67 % of all motifs and were present in 94 % of reflectins. These common variants

featured somewhat higher sequence diversity, as they generally started with a PER segment and typically contained MD dyads, and were enriched in various polar and charged amino acids (Figure 7.2C). Their predicted secondary structures consisted mostly of random coils, with alpha helical character near the PER segment and beta strand character near the MD dyads (Figure 7.2C). The 21 residue-long C-terminal motifs, denoted as RMC, accounted for 17 % of all motifs and were present in 76 % of reflectins. These less common variants did feature some sequence diversity, as they contained multiple MD dyads and were enriched in basic, acidic, hydroxylic, and amidic amino acids (Figure 7.2D). Their predicted secondary structures consisted mostly of random coils, with alpha helical or beta strand character in proximity to the MD dyads (Figure 7.2D). Overall, our findings categorized reflectins' unique sequences, identified their constituent conserved motifs in additional detail, and afforded insight into the proteins' potential structural characteristics.

Given full length reflectins' notorious propensity for uncontrolled aggregation, we leveraged our bioinformatics analysis for the design of a “minimal” truncated reflectin variant that would capture the essential characteristics of these proteins and might prove more amenable to atomic-resolution structural characterization. As the parent isoform for our truncated variant, we selected reflectin A1 (RfA1) from *D. pealeii* because this protein contains representative RMN and RMI motifs between variable linker regions, features a > 60 % homology with most of the other reflectins, and possesses extensively-studied physical properties (Figure 7.2E). From this isoform, we selected the first RMI motif (and its preceding linker region) as our model truncated reflectin, denoted as RfA1TM, for several reasons. First, analogues of RfA1TM's sequence are found in reflectin isoforms from all of our analyzed cephalopod species. Additionally, a similar truncated variant from an *E. scolopes* reflectin isoform has been shown to recapitulate the self-assembly and optical properties of its parent protein. Furthermore, RfA1's motifs have a generally

enhanced capacity for the formation of beta sheets or alpha helices, based on hydrophobic moment calculations. We expected that the systematic study of RfA1TM's secondary and tertiary structure (or lack thereof) would provide a better understanding of full-length RfA1, and by extension, of the entire reflectin family of proteins.

We sought to obtain preliminary models for RfA1TM's likely three-dimensional structure with molecular dynamics (MD) simulations. For this purpose, we obtained structural predictions for RfA1TM (Figure 7.3A) with the webserver Phyre2 and RaptorX, refined these predictions with short simulations in implicit solvent, and used the refined structures as seeds for longer simulations in explicit solvent (Figure 7.3B).^{37,38} This procedure yielded the evolution of RfA1TM's likely conformation, which was amenable to further analysis. As one example, Figure 7.3C shows the last snapshot of RfA1TM's likely conformation produced during a representative Phyre2-initiated ~ 500 ns simulation. This snapshot indicated a disk-shaped geometry with a radius of gyration (R_g) of ~12.9 Å for RfA1TM. The protein featured a partially disordered secondary structure, which consisted of random coils (~ 41 %), beta sheets (~ 6%), helices (~ 5%), beta turns (~ 17%), and bends (~ 31%). As another example, Figure 7.3D shows the last snapshot of RfA1TM's likely conformation produced during a representative RaptorX-initiated ~ 500 ns simulation. This snapshot indicated a disk-shaped geometry with an R_g of ~ 13.9 Å for RfA1TM. The protein again featured a partially disordered secondary structure, which consisted of random coils (~ 42 %), beta sheets (~ 3%), helices (~ 6%), beta turns (~ 19%), and bends (~ 30%). Notably, the two representative snapshots' z-scores of -1.35 and -2.25 were well within the range of values reported for the experimentally-determined three-dimensional structures of similarly-sized proteins (Figure 7.3E). Furthermore, the presence of beta turns/bridges and helices within RfA1TM's conserved motif was in general agreement with our bioinformatics predictions. These

molecular dynamics simulations suggested that RfA1TM likely featured a specific geometry and possessed some distinct structural elements, i.e. was partially folded.

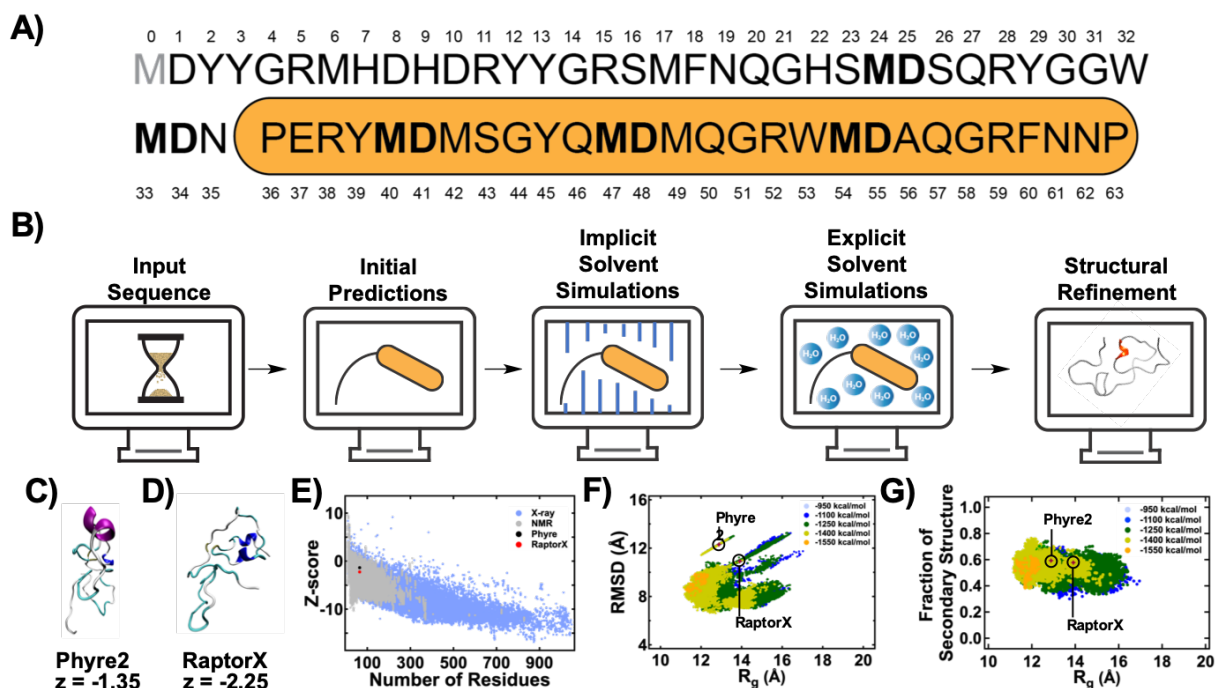


Figure 7.3. (A) The RfA1TM sequence, with all native amino acids colored black, the MD dyads bolded, and the RMI domain highlighted in orange. Each amino acid is numbered for reference. (B) A schematic of the molecular dynamics approach to predict structures for RfA1TM. First the RfA1TM sequence is input into the appropriate web servers (left) to attain initial predictions (middle left), which are subsequently evaluated in implicit solvent conditions (middle) and further refined under explicit solvent conditions (middle right) to obtain a final structure (right). (C) A representative snapshot from Phyre 2 with random coils in white and helices in red. (D) A representative snapshot from RaptorX with random coils in white and helices in red. (E) A z-Score plot of all protein structures solved by X-ray (blue) and NMR (grey), with our representative snapshots from Phyre2 (black), and RaptorX (red) overlaid. (F) A plot of RMSD as a function of R_g from the last 400ns of 8 total molecular dynamics simulations. (G) A plot of the fraction of secondary structure vs. R_g from the last 400ns of the ensemble of molecular dynamics simulations, with the representative snapshots shown.

Given the diverse range of structural characteristics reported for reflectins, we next sought to better understand the conformational landscape that was accessible to RfA1TM. Thus, we performed eight independent ~ 500 ns molecular dynamics simulations (in addition to the two above), with four of them initiated from Phyre2 structural predictions and four of them initiated from RaptorX structural predictions.^{31,32} We then extracted and analyzed RfA1TM's likely conformations from the last ~ 400 ns of these ten simulations (at time intervals of 0.1 ns). Figure

3F shows the free energy surface for our Phyre2- and RaptorX-initiated snapshots as a function of the root-mean-square deviation of their atomic positions (RMSD) and their R_g . This plot suggested that RfA1TM was highly flexible and could adopt a variety of different conformations, with its RMSD ranging from ~ 7 Å to ~ 13 Å and R_g ranging from ~ 11 Å to ~ 17 Å. Here, the protein's lowest energy conformations were generally some of the most compact and were clustered together near an RMSD of ~ 9 Å and an R_g of ~ 12 Å. Figure 7.3G shows the free energy surface for our Phyre2- and RaptorX-initiated snapshots as a function of their fraction of secondary structure and R_g . This plot suggested that RfA1TM featured a partial but variable degree of order, with its fraction of secondary structure ranging from ~ 0.3 to ~ 0.75 and R_g ranging from ~ 11 Å to ~ 17 Å. Interestingly, the protein's lowest energy compact conformations near an R_g of ~ 12 Å featured an intermediate degree of order but were almost entirely composed of beta sheets/turns/bends (Supporting Figure 7.1). Overall, the molecular dynamics simulations revealed that RfA1TM sampled a large conformational space but was likely always partially folded, portending favorably for the investigation of its three-dimensional structure with experimental techniques.

Having gained computational insight into the likely structure of our designer truncation mutant, we proceeded to produce both native and $^{13}\text{C},^{15}\text{N}$ - isotopically-labeled variants of this protein by adapting protocols previously reported for full length RfA1. To produce the unlabeled variant, we first transformed *Escherichia coli* with a plasmid encoding for RfA1TM and selected for cells containing our gene of interest with carbenicillin (Figure 7.4A).^{39–42} We then grew colonies from the resulting bacteria in lysogeny broth and induced protein expression, leading to the formation of RfA1TM-containing inclusion bodies.²⁷ We in turn harvested the cells via centrifugation, lysed them with detergent, and collected the inclusion bodies via filtration.²⁷ We next trituated the

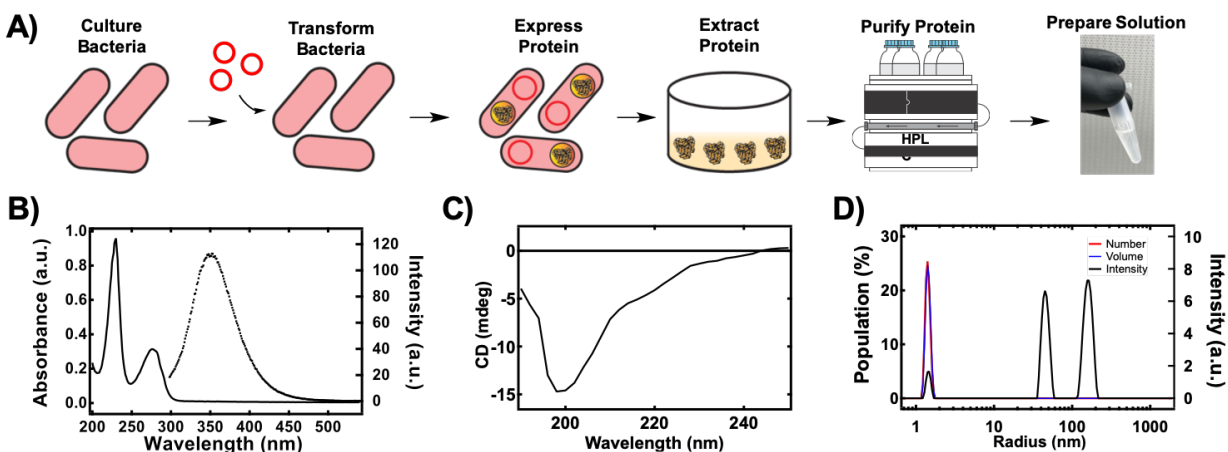


Figure 7.4. (A) A schematic of the expression, and purification of RfA1 truncation mutant. The procedure entails culturing competent *E. coli* cells transformed with the designed plasmid for expression of the truncated variant, followed by protein expression, and subsequent protein extraction by cell lysis. The inclusion bodies were prepared, filtered, and purified via high performance liquid chromatography (HPLC). (B) A representative plot of the UV-Vis absorption spectra (solid line) and the fluorescence spectra (dotted line) for a buffered solution of RfA1TM. (C) A representative circular dichroism spectra for a buffered solution of RfA1TM. (D) A representative dynamic light scattering spectra showing the number fraction (red), volume fraction (blue), and intensity (black) for a buffered solution of RfA1TM.

inclusion bodies and collected the crude unlabeled protein, which was purified via high-performance liquid chromatography (HPLC) (Supporting Figure 7.2A). We confirmed the identity of the unlabeled protein with matrix-assisted laser desorption mass spectrometry (MALDI), which indicated a mass of $\sim 7,860$ Da (Supporting Figure 2B), and tryptic digestion in tandem with mass spectrometry, which indicated a sequence coverage of $\sim 100\%$ (Supporting Figure 7.2C). To produce the ^{13}C -, ^{15}N -labeled variant, we followed a very similar procedure as for the unlabeled variant, with one exception. After selecting for cells containing our gene of interest, we first grew the colonies in minimal media, rather than lysogeny broth, prior to inducing protein expression and forming RfA1TM-containing inclusion bodies.^{43,44} As with the unlabeled protein, we then triturated the inclusion bodies and collected the crude labeled protein, which was purified via HPLC (Supporting Figure 3A). We likewise confirmed the identity of the labeled protein with MALDI, which indicated a mass of $\sim 8,280$ Da and a labeling efficiency of $> 98\%$ (Supporting Figure 3B), and tryptic digestion in tandem with mass spectrometry, which indicated a sequence

coverage of > 96 % Supporting Figure 3C). In general, our highly-optimized protocols typically yielded both native and isotopically-labeled RfA1TM with relatively high yields of tens of milligrams per liter and excellent purities of > 96 %.

After isolating our designer truncation mutant, we initially assessed the aggregation state of unlabeled RfA1TM in solution via a suite of common biophysical methods, i.e. ultraviolet-visible absorption spectroscopy (UV/Vis), fluorescence spectroscopy, CD spectroscopy, and dynamic light scattering (DLS) measurements. For this purpose, we dialyzed the solubilized protein into a low-pH, low-ionic strength buffer, e.g. pH 3.2, 20 mM ammonium formate, with the goal of mitigating its likely propensity for aggregation (a notorious problem for all reported reflectin isoforms).²⁴ For such solutions, the UV/Vis absorption spectra revealed a main peak at ~ 280 nm, which corresponded to absorption by RfA1TM's aromatic amino acids, as well as little tailing, which indicated the absence of significant aggregation (Figure 7.4B). Additionally, the fluorescence emission spectra exhibited a main peak at ~ 350 nm due to emission from RfA1TM's tryptophan residues, some of which were likely solvent exposed (Figure 7.4B). Moreover, the CD spectra featured a single negative band at ~ 200 nm and few other sharp features, suggesting that the protein was primarily disordered or interconverted between multiple distinct conformations (Figure 7.4C). Last, the DLS volume and intensity distributions showed that the protein was primarily monomeric with a hydrodynamic radius (R_h) of ~ 14 Å, with a small proportion of larger aggregates (correlating to < 5 % of the total population) (Figure 7.4D). Notably, we found that our solutions were stable, with little change in their biophysical characteristics over periods of weeks. Taken together, the above biophysical characterization experiments indicated that RfA1TM would be amenable to further detailed characterization via techniques that required the protein to be monomeric and well-dispersed in solution.

We proceeded to evaluate the geometry of RfA1TM in solution with small-angle x-ray scattering (SAXS). Towards this end, we prepared RfA1TM solutions, irradiated them with collimated monochromatic X-rays, recorded 2-D scattering patterns, and then evaluated the resulting data (Figure 7.5A). First, we circularly integrated the 2-D scattering patterns obtained for RfA1TM solutions and plotted the scattering intensity $I(q)$ as a function of the scattering vector q over our accessible range (Figure 7.5B).^{46–51} Next, using the unified fit model, which accounts for the scattering intensity's low- q ($< 0.07 \text{ \AA}^{-1}$) Guinier region and high- q ($> 0.07 \text{ \AA}^{-1}$) Porod region, we obtained an R_g of $\sim 16 \text{ \AA}$ and a Porod exponent value of ~ 2 , indicating that RfA1TM's overall shape resembled a disk.^{52–55} Notably, there was reasonable agreement between the

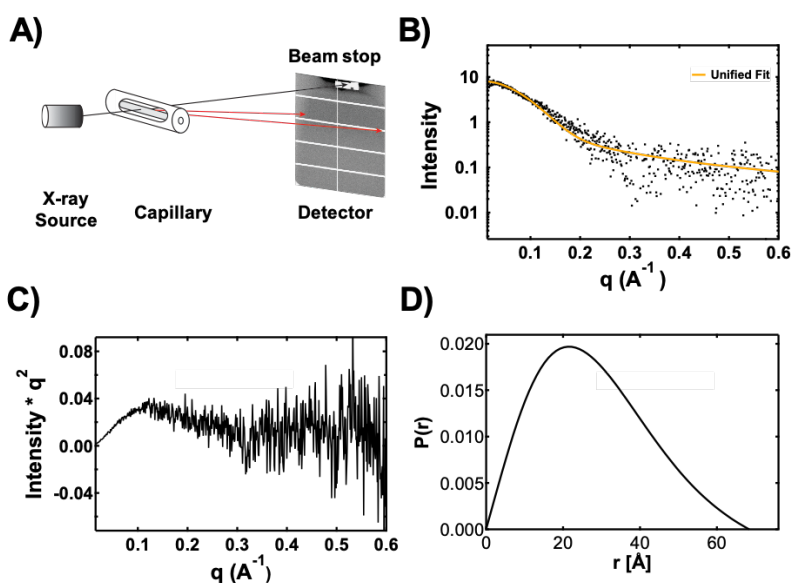


Figure 7.5. (A) A schematic of the small-angle X-ray scattering experiment for RfA1TM, whereby incident X-rays are scattered by in-solution proteins resulting in a 2D pattern. (B) A 1D plot of the scattering intensity $I(q)$ versus the scattering vector q from the experimental SAXS data (black dots), and overlaid with the simulated Phyre (blue trace) and the RaptorX (red trace) scattering profiles, along with the unified fit. (C) A Kratky plot of the integrated scattering intensity times the square of the scattering vector $I(q) \times q^2$ versus the scattering vector q . (D) A representative plot of the distance distribution $P(r)$ versus the distance r .

experimental scattering intensity and the one simulated by using a unified fit model that assumed ellipsoidal, monodisperse, and non-interacting proteins (Figure 7.5B).^{52–55} Subsequently, we generated a plot of $I(q) \cdot q^2$ as a function of q , i.e. a Kratky plot (Figure 7.5C). The curve featured

a distinct peak at $q \approx 0.12 \text{ \AA}^{-1}$ followed by a decay and plateau at higher q values, revealing that RfA1TM was partially folded (Figure 7.5C).^{52–55} Last, we extracted the pair-wise distance distribution function $P(r)$ as a function of the distance r from our scattering intensity profile (Figure 7.5D). The curve revealed a single main peak at $r \approx 21 \text{ \AA}$ and a tail that reached a maximum dimension of $D_{max} \approx 68 \text{ \AA}$, suggesting that RfA1TM was partially folded and disk-shaped (Figure 7.5D), as confirmed by the unified fit.^{47,52–55} Taken together, our analysis provided detailed insight into the size, shape, and intermolecular interactions of solution-borne RfA1TM.

We next sought to obtain additional confirmation for our understanding of RfA1TM's overall geometry. Thus, we compared the scattering intensity profiles measured for solution-borne RfA1TM with the scattering intensity profiles calculated from the Phyre2- and RaptorX-initiated molecular dynamics simulations (Supporting Figure 7.4). Here, the experimental data closely matched the profile calculated for our representative snapshot from the Phyre2-initiated simulation (Supporting Figure 7.4), with the high quality of the fit indicated by a χ^2 value of ~ 0.75 (Supporting Figure 7.4). Moreover, the experimental data likewise closely matched the profile calculated for our representative snapshot from the RaptorX-initiated simulation (Supporting Figure 7.4), with the high quality of the fit indicated by a χ^2 value of ~ 0.69 (Supporting Figure 7.4). In general, we found that the experimental data most closely resembled the profiles simulated from snapshots wherein the protein adopted a disk-shaped geometry. The excellent agreement between experiment and theory provided further validation for our analyses and established a foundation for the exploration of RfA1TM's three-dimensional structure with atomic-resolution nuclear magnetic resonance spectroscopy (NMR).

We initially evaluated the possibility of obtaining high-resolution structural information for RfA1TM with nuclear magnetic resonance (NMR) spectroscopy. For this purpose, we prepared

buffered solutions containing monomeric, ^{13}C - and ^{15}N -labeled RfA1TM, and recorded one-dimensional and two-dimensional NMR (Figure 7.6A).^{56,57} First, we acquired one-dimensional proton NMR (^1H -1D) spectrum for isotopically labeled RfA1TM, which featured signals in multiple different regions (Figure 7.6B). Specifically, the spectrum revealed 1) three closely-spaced clusters of peaks between $\delta \sim 6.6$ to ~ 7.6 ppm, which presumably corresponded to the aromatic and amino protons of the side chains; 2) a broad cluster of overlapping peaks between $\delta \sim 7.6$ to ~ 8.8 ppm, which likely corresponded to the amide protons on the protein's polypeptide backbone; and 3) two distinct singlets between $\delta \sim 9.8$ to ~ 10 ppm, which corresponded to the N-H protons associated with the indole side chains of the protein's two tryptophans (Figure 6B). Next, we obtained two-dimensional heteronuclear single quantum coherence (^{15}N -HSQC) spectra for isotopically labeled RfA1TM, which featured 61 different cross-peaks (Figure 7.6C). In particular, the ^{15}N -HSQC revealed 1) separate cross-peaks between $\delta \sim 108$ to ~ 111 ppm in the ^{15}N dimension and $\delta \sim 7.8$ to ~ 8.4 ppm in the ^1H dimension that corresponded to the 8 glycine residues, i.e. G4, G14, G21, G30, G31, G44, G51, and G58 (Figure 7.6C); 2) independent cross-peaks between $\delta \sim 115$ to ~ 117 ppm in the ^{15}N dimension and $\delta \sim 8.2$ to ~ 8.4 ppm in the ^1H dimension that corresponded to the 4 serine residues, i.e. S16, S23, S26, and S43; and 3) distinct cross-peaks between $\delta \sim 117$ to ~ 119 ppm in the ^{15}N dimension and $\delta \sim 8.2$ to ~ 8.5 ppm in the ^1H dimension that corresponded to the 3 histidine residues, i.e. H7, H9, and H22 (Figure 7.6C). Furthermore, the remaining 46 cross-peaks between $\delta \sim 117$ ppm to ~ 125 ppm in the ^{15}N dimension and $\delta \sim 7.8$ to ~ 8.7 ppm in the ^1H dimension, many of which were clustered together and/or exhibited overlap, could be readily correlated with the other residues (Figure 7.6C and Supporting Figure 7.5). Overall, our observation of distinct signals for RfA1TM's amino acid side chains and polypeptide backbone indicated the protein likely possessed some structural order, i.e.

was partially folded, and thus would be amenable to further investigation with multidimensional NMR techniques.

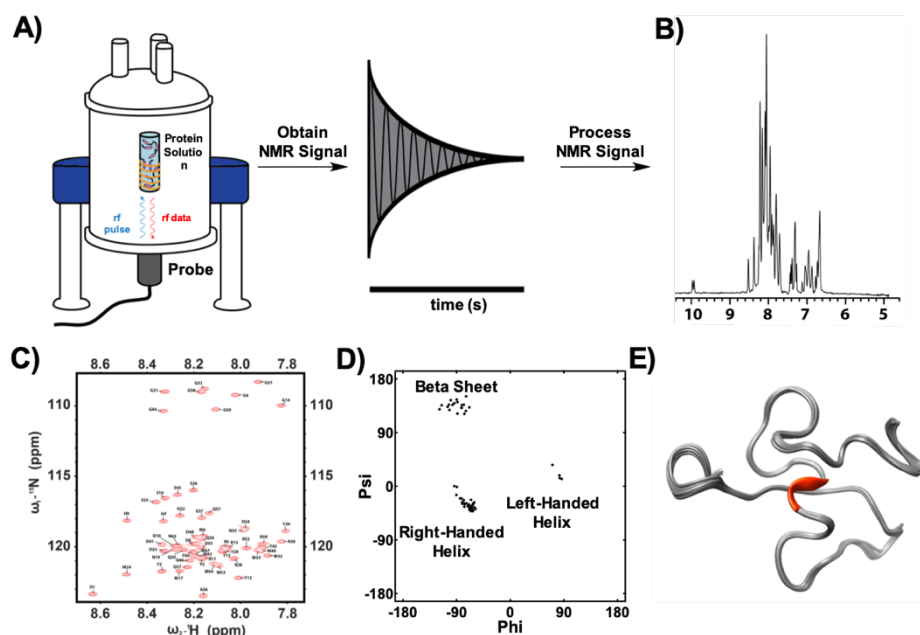


Figure 7.6. (A) A schematic of a standard NMR experiment, whereby a protein solution is placed into a uniform magnetic field, and subsequently probed with radio frequency pulses to provide an NMR spectrum. (B) A ^1H -1D NMR spectra of the RfA1 truncation mutant. (C) A ^1H - ^{15}N HSQC spectra of the RfA1 truncation mutant; cross peaks are labeled using one letter amino acid abbreviations. (D) A Ramachandran plot of the torsion angles obtained from the chemical shifts obtained by NMR. (E) The solution NMR structure of the RfA1 truncation mutant.

We next investigated the conformation of RfA1TM's polypeptide backbone with more advanced NMR techniques. For this purpose, we probed solutions of ^{13}C - and ^{15}N -labeled RfA1TM with HNCA, HN(CO)CA, HNCACB and CBCA(CO)NH experiments, which yielded the chemical shifts associated with the protein's amide nitrogens, amide protons, alpha carbons, alpha protons, beta carbons, beta protons, and carbonyl carbons, allowing us to complete an unambiguous sequential backbone assignment.^{56,57} Based on these chemical shifts, we used TALOS+ software to predict the phi and psi backbone torsional angles for RfA1TM and formulated a corresponding Ramachandran plot, wherein the residues populated regions associated

with various secondary structural elements (Figure 7.6D).^{58,59} First, within the beta sheet region of the Ramachandran plot for RfA1TM, we found that 19 residues were distributed between psi angles of $\sim 115^\circ$ and $\sim -155^\circ$ and phi angles of $\sim -60^\circ$ and $\sim -125^\circ$ (Figure 7.6D). In addition, within the right-handed helix region of the Ramachandran plot for RfA1TM, we found that 39 residues were clustered between psi angles of $\sim -50^\circ$ and $\sim 5^\circ$ and phi angles of $\sim -100^\circ$ and $\sim -50^\circ$ (Figure 7.6D). Furthermore, within the left-handed helix region of the Ramachandran plot for RfA1TM, we found that 4 residues were located between psi angles of $\sim 5^\circ$ and $\sim 40^\circ$ and phi angles of $\sim 65^\circ$ and $\sim 90^\circ$, (Figure 7.6D). Interestingly, the experimental torsion angles were in reasonable agreement with those derived from the representative Phyre2- and RaptorX-initiated molecular dynamics snapshots (Supporting Figure 7.6); here, the differences between the experimental and simulated torsion angles was expected and likely arose from the conformational flexibility of our protein. Overall, our findings showed that RfA1TM's residues featured torsion angles consistent with either beta or helical character and thus suggested that the protein possessed some secondary structural elements.

We next sought to obtain the relative spatial arrangement of RfA1TM's different amino acids, and thus obtain the protein's three-dimensional structure. Towards this end, we probed solutions of ^{13}C - and ^{15}N -labeled RfA1TM with 1) ^{15}N -edited NOESY-HSQC to verify our backbone assignment; 2) HAHB(CO)NH, CC(CO)NH, HCCH-TOCSY, (H)CCH-TOCSY, and ^{13}C -edited NOESY-HSQC experiments to obtain chemical shifts from the aliphatic protons and carbons; 3) ^{13}C -edited NOESY-HSQC experiments to obtain chemical shifts from the aromatic protons and carbons, and 4) ^{15}N -/ ^{13}C -edited NOESY-HSQC experiments to obtain NOE distance restraints between the protons, and carbons of neighboring residues in the amino acid sequence.^{56,57} Based on the experimentally obtained chemical shifts and NOE restraints, we used the CYANA

software to calculate a representative structural ensemble for RfA1TM, which consisted of 20 plausible lowest energy models, and used the YASARA software to refine the models in a simulated aqueous solvent environment.^{60–62} We then used the Chimera software to visualize and analyze the structural ensembles such as the one shown in Figure 7.6E.⁶³ First, with standard constraints, which considered a minimum helix and beta strand length of three residues, and a minimum hydrogen bond energy of -0.5 kcal/mol, we found that the protein was primarily disordered and featured a single helix located at PER.⁶⁴ Within a van der Waals overlap of 0.4 angstrom of the helix, we observed the acidic residues D10, D34, and D55; the basic residues R11, R15, and R52; aromatic residues Y12, Y13, Y39, W32, and W53; aliphatic residue A56; the amidic residues N35 and Q50; the sulfur containing residues, M17, and M33; and the hydroxylic residue, S16. Notably, the PER motif was stabilized by hydrogen bonds from the side chains of the surrounding residues S16, D34, and Q50. Here, we observed hydrogen bonding between the hydroxyl residue from the sidechain of S16 and the backbone carbonyl of the arginine residue. Furthermore, we noted hydrogen bonding from the carboxyl functional group from the side chain of N35, and the amide, and amine functional groups on the sidechain of the arginine residue. Lastly, we discovered a hydrogen bond between the amine functional group of Q50 and the backbone carbonyl of the glutamic acid residue. Notably, our observation of an alpha helix at the PER site of the conserved motif was in remarkable agreement with the bioinformatics predictions of helical character in this region of the RfA1TM sequence. Furthermore, the NMR secondary chemical shifts of carbonyl and alpha carbon nuclei also confirm the presence of alpha helix at PER motif (Supporting Figure 7.7), interestingly, positive deviations of experimentally obtained chemical shifts from the predicted ones for random coil protein can also be observed for the residues 3-10, which, based on this information, should also have propensity towards alpha helical

fold.⁶⁵ Interestingly, under looser constraints, which considered a minimum helix length of three residues, a minimum beta strand length of two residues, and a minimum hydrogen bond energy of -0.05 kcal/mol, we observed the formation of three additional helices and one beta strand, which resulted in an increase in fraction of secondary structure from ~5% to ~30%. Here, we found that the percentage of secondary structure in the NMR model closely matched the percentage found in both the Phyre2- and RaptorX-initiated molecular dynamics simulations (Supporting Figure 7.5). Overall, our analyses suggested that RfA1TM is highly flexible, with variable secondary structure features.

Next, we wanted to obtain additional confirmation for the three-dimensional geometry of RfA1TM. Thus, we compared the simulated NMR scattering profile with the experimental SAXS scattering profile. Here, the scattering profile from our NMR model closely matched the profile from the SAXS experiment, with a high-quality fit indicated by a χ^2 value of ~ 1.0 (Supporting Figure 7.4). In general, we found the NMR model closely resembled the SAXS model, wherein the protein shared a similar disk-shaped geometry with a R_g of 12.33 Å. We further found excellent agreement between the simulated scattering profile from the NMR model and the Phyre2- and RaptorX-initiated molecular dynamics simulations. Overall, the exceptional agreement between the experimental and simulated models further validates our understanding of RfA1TM's three-dimensional structure.

Next, we designed a mild strategy to coax RfA1TM to form ordered secondary structures. We proposed modifying the N-terminus of RfA1TM with a quinoline-containing α -amino acid as precedent has shown that the addition of aromatic small molecules has the potential to induce the formation of secondary structures. Here, we used solid-phase peptide synthesis to iteratively couple amino acids affording the desired quinoline-modified RfA1TM (RfA1TM*) (Figure

7.7A).⁶⁶ Following, we purified quinoline-modified RfA1TM using HPLC, and ensured its identity using mass spectrometry (Supporting Figures S7.8 and S7.9). Next, we sought to determine any observable biophysical changes to RfA1TM* as a result of the quinoline bioconjugation. To this end, we characterized RfA1TM* using UV-vis, CD and DLS. From the UV-vis spectrum, we observed the evolution of a new peak around 350nm due to the presence of the quinoline. In the CD spectrum, we noted the evolution of a new band around 220nm, indicative of the formation of helical structures. From the DLS spectra, we observed a shift in the particle size from ~ 1.8 nm to ~ 24 nm suggesting that these helical structures were interacting to form larger aggregates. Overall, our experiments suggested that bioconjugation was sufficient to induce self-assembly of RfA1TM in aqueous solution.

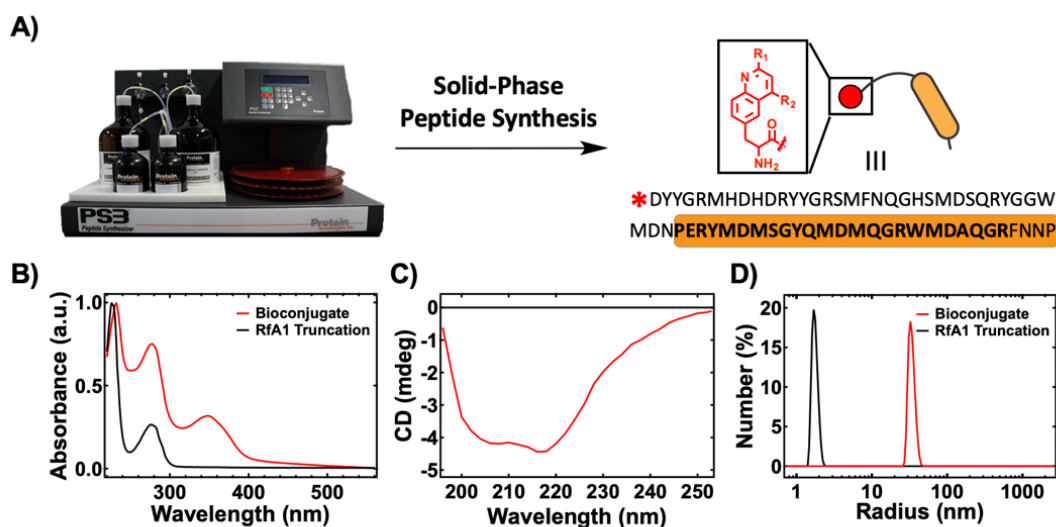


Figure 7.7. (A) A SPPS strategy affords RfA1TM* (B) A representative plot of the UV-Vis absorption spectra for a solution of RfA1TM*(red trace) and RfA1TM (black trace). (C) A representative circular dichroism spectrum for a buffered solution of RfA1TM*. (D) A representative dynamic light scattering spectra showing the number fraction for a solution of RfA1TM* (red trace) and RfA1TM (black trace).

7.4. Conclusion

Using a combination of bioinformatics, molecular dynamics, biophysical characterization, SAXS, and NMR, we have elucidated the structure of a representative reflectin variant (RfA1TM) with atomistic resolution. First, using SAXS and biophysical characterization, we demonstrated that the protein (when stabilized in low pH aqueous conditions) could be maintained as monomeric (non-interacting) protein nanoparticles which were disk-shaped. Second, we used a combination of NMR, molecular dynamics, and biophysical characterization techniques to demonstrate that the reflectin variant in fact could have a variety of beta-turn/strand/sheet character as well as alpha-helical character, and the expanse of its structural landscape resides in the protein's ability to sample numerous low energy conformations that had > 30% secondary structure, which supported our preliminary bioinformatics analyses and molecular dynamics simulations. In addition, we used NMR spectroscopy to definitively demonstrate that the PER motif within the conserved domain had an alpha-helical structure, which supported our bioinformatics predictions. Interestingly, using the NMR model we were able to deduce that the stability of the protein with the alpha helical structure was enabled via hydrogen bonding by the surrounding polar and charged amino acids. Thus, our findings have conclusively demonstrated that reflectins, previously assumed to be intrinsically disordered proteins, in fact are partially folded and have a strong propensity to sample a range of secondary structural motifs, particularly within their conserved domain.

Utilizing our improved understanding of RfA1TM's secondary structure, we demonstrated a strategy to control the structure and assembly of the protein in solution. Previous studies have extruded fibers from reflectin precipitates in buffered solutions or exposed the purified reflectin protein to various chemical stimuli (salt, pH, organic solvents) in order to induce the formation of specific secondary structures.^{23–29} However, these techniques typically use harsh solvent

conditions that can denature the protein and have limited applicability within the context of further processing or characterization of the protein for subsequent applications. In our current study, we deliberately tune RfA1TM using a quinoline bioconjugation approach resulting in helical character when prepared in aqueous solutions. From a materials science perspective, this result is particularly exciting as it demonstrates a direct correlation between the secondary structure of the protein and its assembly in solution, paving the way for the development of other RfA1TM-like proteins with reconfigurable assembly states that can be precisely engineered. In addition, from a processing perspective, the ability to fully manipulate the protein at an atomic level is particularly promising for the future development of bio-electronic or bio-optical devices based on RfA1TM-like proteins, as it enables us to directly probe the protein without the addition of harsh detergents, ionic liquids, or other extraneous solvents. Altogether, our control over RfA1TM's secondary structure and assembly in aqueous solution exhibits the possibility of processing reflectins with minimal interference from exogenous molecules with the addition of a mild stimulus, highlighting its potential for use as a structurally dynamic biomaterial.

The findings in this study also provide insight into the dynamic changes in the *in vivo* assembly of reflectin proteins within cephalopod skin cells, like iridophores. Classically, it was hypothesized that tensional forces acting on the periphery of iridophores could alter the spacing between the iridophore lamellae or platelets.^{10,15} More recently, it has been suggested that the electrostatic forces between reflectin platelets within the iridophore lamellae effectively control their dimensions, and that phosphorylation-based charge neutralization could effectively neutralize reflectins and cause a spectral-shift in the light transmitted by iridophores.^{10,13,64} Our current study demonstrates that modification with a quinoline amino acid is sufficient to alter the geometry of reflectin assembly from disordered particles in solution to ones with helical character. Given the

large class of primarily disordered proteins that are sensitive chemical modification our experiments suggest that reflectins may be able to tune the lamellar spacings or the platelet dimensions within iridophores via multiple stimuli, enabling the rapid changes in cephalopod skin iridescence. Taken together, our study highlights the importance of chemical modification in the structural landscape of reflectins and opens the possibility of multiple stimuli-dependent pathways that enable the seemingly instantaneous changes in the appearance of cephalopod skin.

In conclusion, we have unambiguously solved the atomic resolution structure of a reflectin variant and demonstrated chemical stimuli induced control over the proteins' secondary structure and self-assembly. We believe that our findings have fundamentally redefined our understanding of reflectins for several reasons. This is the first study that elucidates the secondary structure of a reflectin variant with atomic resolution. The findings in the study confirm previous hypotheses that suggested reflectin had a propensity to form secondary structures and confirmed that the repeated motif has helical character. In particular, the bioinformatics analyses have redefined the repeated motifs, which will help future studies apply their findings more broadly to the family of reflectin proteins. In addition, the strategy used in this study to characterize the secondary structure of RfA1TM sets the groundwork for solving the atomic resolution structure of full length reflectin proteins. Second, the control of both the secondary structure and assembly of a reflectin variant in aqueous solution *via* modification with an unnatural amino acid, is hitherto unprecedented. This finding opens up the possibility of developing strategies to tune the secondary structure of full length reflectins in aqueous solution (i.e. without the use of other chemical stimuli like salts, denaturants, and organic solvents) thus enhancing the potential of using reflectins as a biomaterial in a wide variety of applications such as bioelectronics. In addition, the bioconjugation-induced structural changes highlight the sensitivity of reflectins and provide additional parameters by which

to tune reflectins' structure and function *in vitro*. Finally, our findings that bioconjugation also results in the formation of helical structures have interesting implications for our understanding of the *in vivo* optical capabilities of cephalopod skin components. Overall, our findings provide insight into the structure and assembly of reflectins, hold significance for the improved design and processing of cephalopod-inspired materials, and redefine our fundamental understanding of cephalopod physiology.

7.5. Supporting Information

7.5.1. General Information and Procedures

A. Bioinformatics Analysis. Reflectin sequences were identified by iterated BLAST^{S1} searches against all NCBI databases^{S2} and the UniProtKB database^{S3}; here, the reflectin sequences described in Figure 7.1 of Levenson, *et al.*^{S4} were used to initiate the search. At each iteration, the various alignments returned by BLAST were analyzed manually to find any occurrence of the conserved sites named RMN and RM₁₋₈ in Levenson, *et al.*^{S4}. Each protein identified with any number of such sites was then added to the list of reflectin sequences for the next iteration. The process ended with 51 reflectin sequences representing 33 unique proteins. The remaining 18 sequences were either full-length isoforms of the unique proteins resulting from distinct assemblies of the corresponding genomes or partial fragments of the unique reflectin sequences resulting from incomplete, lower quality, genome assemblies. A full description of the 51 sequences is provided in Supplementary file Dataset.xlsx.

For each reflectin sequence obtained during the previous step, we manually identified the RMN and RM₁₋₈ sites using the same definition for each site than the one provided in Levenson *et al.* We identified 38 RMN sites total among the 51 reflectin sequences previously selected, and observed a single RMN site for 31 out of the 33 unique full-length protein sequences (93.9 %), none otherwise. 200 occurrences of the RM₁₋₈ sites were identified in total, with the number of such sites per protein sequence ranging from 0 to 8. The individual sequences of the RMN and RM₁₋₈ sites were then extracted including up to 10 additional amino acids on each end of the sites and the two groups of sequences were separately aligned using Clustal Omega^{S5}. From these initial alignments, we observed on one side a highly conserved 28 amino acid long RMN site which was consistent with the literature, and on the other side two distinct groups of RM₁₋₈ sites. The first one

was a 28 amino acid long group of highly conserved sites starting with the three amino-acids PER, finishing with the amino-acid P, and extending the RM₁₋₈ site definition from Levenson *et al.* by 8 additional amino acids (Figure 7.2). This group, named RMI afterwards, contains 80% of the 200 RM₁₋₈ sites previously identified. The second one was a group of conserved sites more closely matching the previously published pattern for the RM₁₋₈ sites: M/FD(X)₅MD(X)₅MDX_{3/4}. This group, named RMC afterwards, contains the remaining 20% of the 200 RM₁₋₈ sites previously identified. The sequences for the three groups of sites resulting from this initial analysis were then resized to match the corresponding site size, 28, 28, and 21 respectively, and re-aligned using Clustal Omega. The corresponding patterns and sequence logos are provided in Figure 7.1B–D.

Following, we used SSpro^{S7} to predict the 3-class secondary structure (Helices, Beta-sheets, and Coils) of the 51 reflectin sequences previously described. The full-length predictions obtained using this machine learning based predictor were used to extract the predicted secondary structure of each RMN, RMI, and RMC site previously identified by simply extracting the corresponding positions on the full-length prediction. The resulting secondary structure sequences for each group of sites were then aligned using in-house tools such that their alignment matches with the alignment of the corresponding protein sequences. A sequence logo result is provided for each group in Figure 7.2.

B. Molecular Dynamics Simulations. In this study, two software packages for protein structure modeling, Phyre2^{S8} and RaptorX^{S9}, were used to predict an initial structure of the RfA1 truncation mutant composed of 64 amino acids (Figure 7.3A). These two prediction tools have been widely used to precisely estimate various unverified protein structures.^{S10} From the two initial structures, additional short MD simulations in implicit solvent conditions were employed for further structural refinements of the two RfA1 truncation mutant models. Implicit solvent simulations can

significantly reduce the computational resources and time required for structural conversions of protein structures and, therefore, have been widely used for protein structural refinement under various conditions including the protein folding process.^{S11} For MD simulations in implicit solvent conditions, AMBER 2018 package^{S12} with FF14SB force field^{S13} was used. First, 10,000 steps of energy minimization were used; then the system was heated up to 300 K in 50 ps with 200 kcal/mol of harmonic constraint on RfA1 truncation mutant using the Berendsen thermostat.^{S14} After the heating, 10,000 steps of energy minimization were carried out followed by four additional short MD simulations with a gradual decrease in the energy for harmonic constraint in the order of 2.0, 1.0, 0.5, and 0.1 kcal/mol. After system was equilibrated, a 100-ns production run was performed in implicit solvent conditions. In this study, two different structures predicted by Phyre2 and RaptorX followed by MD simulations in implicit solvent condition were used as the initial structures for further simulations in explicit solvent conditions.

Two initial structures obtained by implicit solvent MD simulations were solvated into a TIP3P water box^{S15} separately and counter ions (9 Na⁺ ions) were added to neutralize the simulation systems. All-atom MD simulations in explicit solvent conditions were performed with AMBER 2018 package^{S12} with FF14SB force field^{S13}. More specifically, we employed 6 individual MD simulations for each case in order to obtain more enhanced conformational sampling (total 11 simulations – 5 for Phyre2 and 6 for RaptorX based structures). For the explicit solvent conditions, each MD simulation started with a minimization for 10,000 steps while holding RfA1 truncation mutant fixed followed by a 200 ps short NPT run. Then a second short MD run was employed for 200 ps with 25 kcal/mol restraint on the RfA1 truncation mutant. Another 1,000 steps of minimization were performed with 20 kcal/mol harmonic constraint energy followed by four additional minimization steps with a gradual decrease in the harmonic restraint energy on

RfA1 truncation mutant in the order of 15, 10, 5, and 0 (no constraint) kcal/mol. Then, the entire system was gradually heated up to 300 K using the Berendsen thermostat.^{S14} Production simulations were carried out for 500 ns per individual simulations under NPT condition with a 2 fs time step. Particle Mesh Ewald (PME) summation method^{S16} was used to calculate the long-range electrostatic potential under periodic boundary condition in all directions. Aforementioned multiple-step simulation protocol has been previously used for MD simulations of various biomolecules including nucleic acids or proteins.^{S17} A schematic of the MD simulation approach for this study is illustrated in Figure 7.3B.

Z-score analysis was performed for the RfA1 truncation mutant model using PROSA software^{S18,S19} (Figure 7.3E). Z-score measures the deviation of the total energy of the protein model with respect to the energy distribution from random conformations and indicates overall protein model quality.^{S18} The lowest Z-scores we obtained were -1.35 for the Phyre2 based structure and -2.25 for the RaptorX based structure of RfA1 truncation mutant. As these scores are located within the range of scores experimentally observed for native proteins of similar size using both NMR and X-ray, these RfA1 truncation mutant structures with the lowest Z-scores were selected as the representative structures (Figures 7.3C, D).

Based on 10 different MD simulations, we analyzed structural and energetical properties of RfA1 truncation mutant models including the fraction of ordered structure, radius of gyration (R_g), and the internal energy and plotted these three results into one plot to illustrate the energy-structure correlations of RfA1 truncation mutant (Figures 7.3F, G and Supporting Figure S7.1). Internal non-bonded energy was calculated via pair-wise interactions between all possible pairs of non-covalently bonded protein atoms, which includes electrostatic and van der Waals (vdW) contributions. Cut-off distance for non-bonded calculated interactions is 12.0 Å for both

electrostatic and vdW interactions. For the fraction of ordered structures, we first defined secondary structures of each amino acid through DSSP assignment^{S20} and then calculated the fraction of secondary structure by dividing the number of amino acids with a specific secondary structure by the total residue number of RfA1 truncation mutant. Analyses for the R_g , internal non-bonded energy, and secondary structure analyses of RfA1 truncation mutant were calculated using CPPTRAJ version 18 module in AMBER 2018 package^{S21} and their correlations are shown in Figures 7.3F,G and Supporting Figure S7.1.

C. Expression, Purification and Uniform ^{13}C , ^{15}N Labeling of Reflectin A1 Truncation Mutant. To express sufficient quantities of protein for subsequent structural analyses via small angle x-ray scattering (SAXS) and nuclear magnetic resonance (NMR), we revised our standard protocol^{S22,S23} for the expression of the new truncated variant. First, we used protocols validated for the full length reflectin A1 to heterologously express the truncated variant in *E. coli*, and confirmed the sequestration of the protein within inclusion bodies (as reported for full length reflectins A1 and A2). The cells were lysed to isolate the inclusion bodies, which were subsequently isolated via detergent-based extraction and centrifugation. The protein was isolated from the inclusion bodies by filtration followed by high performance liquid chromatography (HPLC), obtaining typical purities of > 95%. Finally, the identity of the protein was confirmed *via* in-gel tryptic digestion followed by mass spectrometry. Secondary characterization was also performed via in-solution tryptic digestion and tandem mass spectrometry, as well as MALDI.

Furthermore, to express isotopically labeled protein, the same protocol was followed as for the unlabeled RfA1TM, with minor changes in the expression protocol. Rather than heterologously expressing the new truncated variant in LB broth, typically used for protein expression in *E. coli*,

the truncated reflectin isoform was expressed in minimal media enriched with ^{13}C and ^{15}N . Subsequent lysis, purification, and characterization steps were identical to that of the unlabeled protein.

D. Sample Preparation for Biophysical Characterization. Samples for biophysical characterization were prepared by dissolving lyophilized, purified unlabeled RfA1TM in 20 mM ammonium formate buffer at pH 3.2, followed by dialysis in the buffer. The dialyzed protein was then diluted to 5 mg/mL and 1.25 mg/mL for characterization by dynamic light scattering (DLS) and small-angle x-ray scattering (SAXS), respectively. The 5 mg/mL solution was further diluted to 0.1 mg/mL for characterization by circular dichroism (CD), ultraviolet-visible (UV-VIS) absorption and Fluorescence spectroscopy.

E. Dynamic Light Scattering (DLS). DLS analysis was performed on a Malvern Zetasizer Nano-S instrument. Sample concentration was 5 mg/mL for the biophysical characterization of the protein in buffer. All measurements were performed with samples equilibrated at 25°C for 120 s. At least five runs, ten measurements each were taken per sample to ensure equilibration and stability.

F. Circular Dichroism (CD). All circular dichroism measurements were performed on a JASCO J-810 CD spectropolarimeter at the Laser Spectroscopy Labs, UC Irvine. Data shown is an average of ten scans. Sample concentration was 0.1 mg/mL for all measurements.

G. Ultraviolet-visible (UV-vis) Spectroscopy. All UV-VIS absorption measurements were performed on a Cary-60 absorption spectrometer at the Laser Spectroscopy Labs, UC Irvine. Sample concentration was 0.1 mg/mL for all measurements.

H. Fluorescence Spectroscopy. All fluorescence measurements were performed on a Cary Eclipse Fluorimeter at the Laser Spectroscopy Labs, UC Irvine. Excitation and emission slit widths

were 2.5 nm and 10 nm respectively for all measurements. Sample concentration was 0.1 mg/mL for all measurements.

I. Small Angle X-ray Scattering Experiments. Small-Angle X-ray Scattering (SAXS) experiments were performed at the SAXS beamline at Elettra Synchrotron Light Laboratory (Trieste, Italy) at room temperature,^{S24} with a radiation photon energy of 8 keV (wavelength $\lambda = 1.54 \text{ \AA}$) and sample-to-detector distance of 0.75 m. The range of the investigated momentum transfer q was $-0.011 - 0.902 \text{ \AA}^{-1}$, where $q = 4\pi\sin\theta/\lambda$ is the modulus of the vector q (the vector q is defined as the difference between the wave propagation vectors of the incident and scattered beam, both equal to $2\pi/\lambda$), and 2θ is the scattering angle. Unlabeled RfA1TM was prepared at 1.25 mg/mL in 20 mM ammonium formate buffer at pH 3.2 and transferred into a glass capillary with 1.5 mm diameter, perpendicular to the incident X-ray beam for SAXS measurements. For data collection, each sample was exposed to the X-ray beam for 20 s for 3 scans (1 min total) to avoid for radiation damage, and the 2D images were recorded using the Pilatus3 1M detector (Dectris, Switzerland). The radial averaging and the image calibration were conducted using the FIT2D software.^{S25,S26} The obtained curves were corrected for buffer scattering, transmissions and detector efficiency. The collected data was analyzed with BioXTAS RAW^{S27} and IRENA software packages.^{S28}

J. Nuclear Magnetic Resonance (NMR) Experiments. Samples for NMR experiments were prepared by first dialyzing lyophilized, purified isotopically labeled RfA1TM in 20 mM Ammonium formate buffer at pH 3.2. The dialyzed sample was then diluted to 0.6 mM and an appropriate volume of D₂O was added to the sample to obtain a 10% D₂O (v/v) concentration. For NMR experiments on isotopically labeled RfA1TM performed in ~100% D₂O, 0.7mL of the original sample was centrifuged in a pierce protein concentrator at 8000 rpm at 25 °C for a total

time period of 15 minutes. After centrifugation, the sample volume decreased from 0.7mL to 0.09 mL, and was resuspended in 100% D₂O to bring the total volume to 0.7mL; this process was repeated a total of two times and the sample concentration was measured *via* nanodrop.

All experiments used for structure calculation on ¹³C, ¹⁵N-labeled RfA1TM were performed on a Varian VNMRS 800 MHz NMR spectrometer using triple ¹H/¹³C/¹⁵N resonance cold probe-head with inverse detection at 298 K. All recorded spectra were processed using the NMRPipe software^{S29} and subsequently analyzed using CARA.^{S30} Backbone chemical shifts were obtained with the help of standard triple resonance HNCO, HNCA, HN(CO)CA, HNCACB and CBCA(CO)NH NMR experiments, and afterwards assigned to specific amino acid residues using MARS program.^{S31} The backbone assignment was further confirmed by analysis of sequential and medium-range NOEs in 3D ¹⁵N-edited NOESY-HSQC experiment. In addition, ¹H and ¹³C resonances in aliphatic side chains were assigned using HAHB(CO)NH, CC(CO)NH, HCCH-TOCSY, (H)CCH-TOCSY, and ¹³C-edited NOESY-HSQC experiments. Aromatic ¹H and ¹³C resonances were also assigned using a ¹³C-edited NOESY-HSQC 3D experiment. Finally, NOE distance restraints were derived from 3D ¹⁵N-edited and ¹³C-edited NOESY-HSQC experiments based on which, an ensemble of 20 lowest energy models was calculated with CYANA^{S32} in solvent implicit environment. Calculated models were further refined in water solvent explicit environment using YASARA program.^{S33} Experimentally obtained chemical shifts of carbonyl and alpha carbons were also compared to the chemical shifts of the same nuclei predicted by using POTENCI,^{S34} which conducts calculation of chemical shifts for complete random coil protein based on residue sequence, temperature, pH and ionic strength.

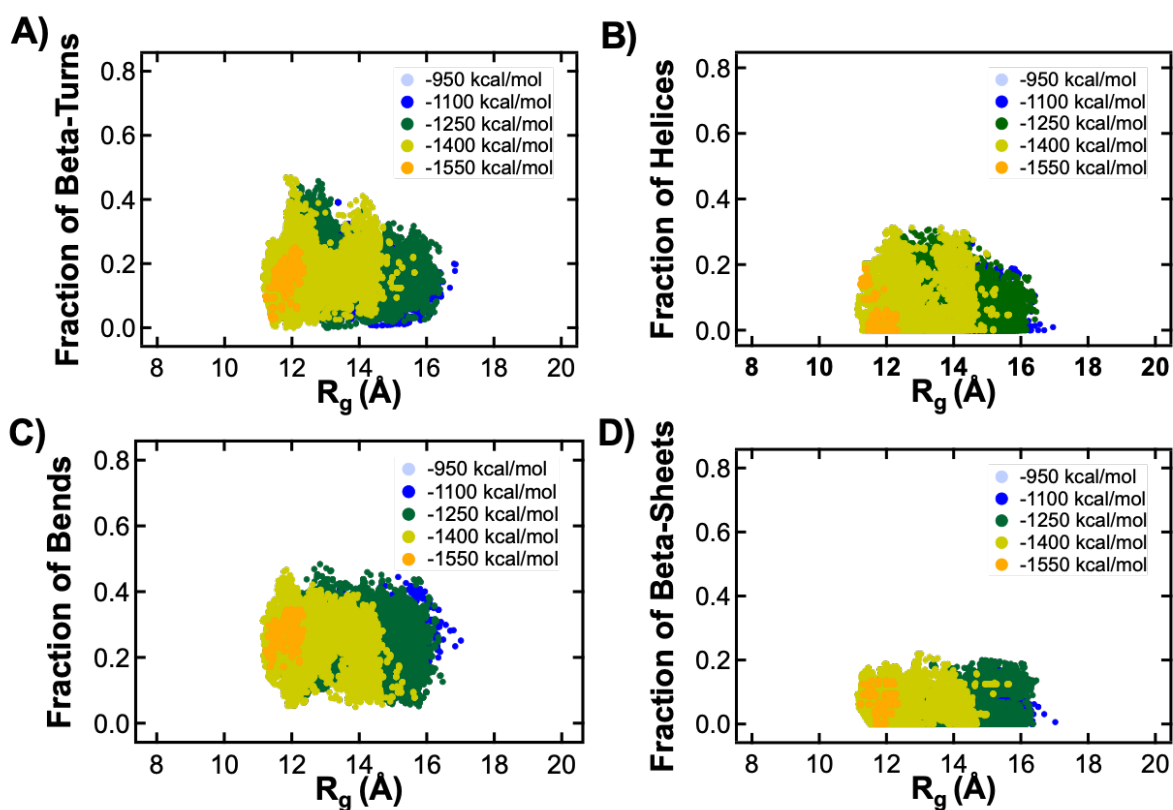
K. RfA1TM Bioconjugation

RfA1TM* was synthesized using solid-phase peptide synthesis by Ontores and was purified *via* HPLC before use.^{S36}

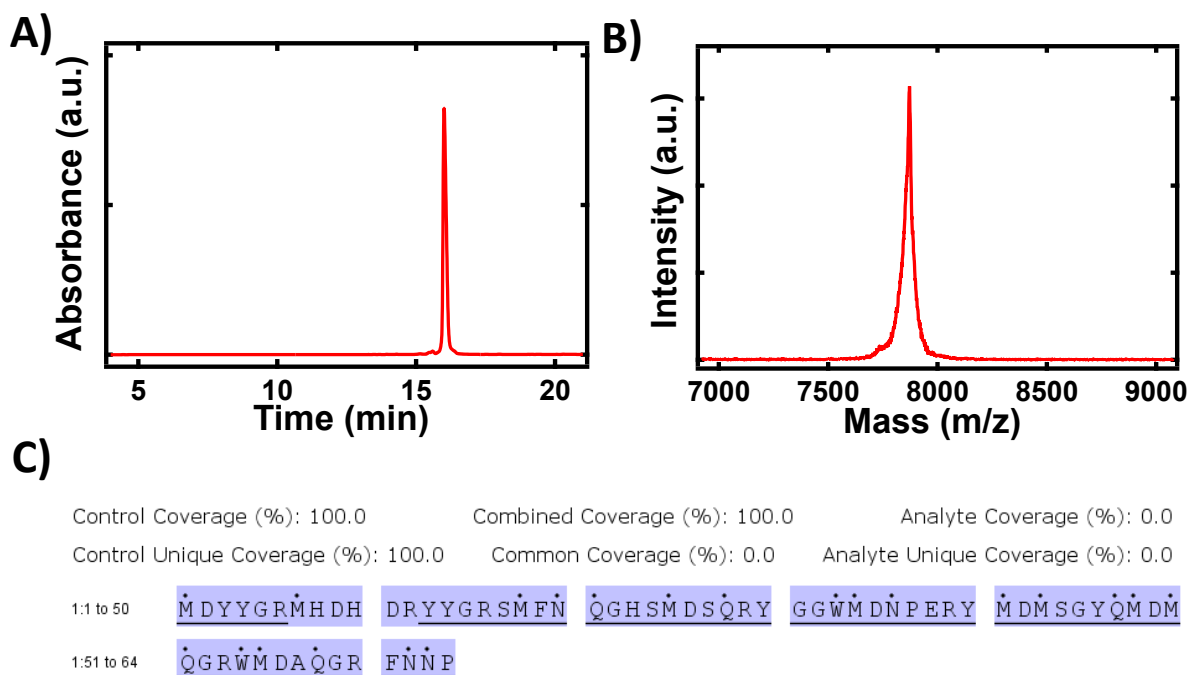
7.5.2. Tables and Figures

Species	Reflectin Isoform	Structural Characterization Techniques	Experimental Conditions	Type of stimuli investigated	Self-assembled structures reported	Secondary structures reported	References
E. scolopes	Reflectin 1a	SEM, TEM, WAXRD	7 M Guanidine Hydrochloride; 55 mM Tris pH 8.2, 264 mM NaCl, 11 mM KCl, 0.055% PEG, 7 M GdHCl; 55 mM Tris pH 8.2, 264 mM NaCl, 11 mM KCl, 0.055% PEG, 7 M GdHCl, 100 mM reduced glutathione, 10 mM oxidized glutathione; HFIP; BMIM	Chemical - ionic strength, redox environment	Nanospheres, Filaments, Ribbons, Fibers, Diffraction Gratings	Amorphous with potential beta-sheet character	Kramer, R. M. et. al. Nat. Mater. 2007, 6, 533-538.
E. scolopes	Reflectin 1a truncation "refCBA"	FTIR, CD, SEM, AFM, Diffraction	Milli-Q water; HFIP	Chemical -Relative humidity; Processing at different protein concentrations	Lamellar stacks, Nanospheres, Diffraction gratings,	Random coil, Turns, Strands, Helices	Qin, G. et. al. J. Polym. Sci. Part B 2013, 51, 254-264.
S. officinalis	Reflectin 2 "SoRef2" and mutants	Cryo-EM, SAXS, CD	20 mM Tris-HCl, 150 mM NaCl, 0.05% SDS, pH 8.0; 20 mM Tris, 0.05% SDS, pH 8.0; 20 mM Tris, 150 mM NaCl, pH 8.0	Chemical - Aromatic compounds; Ionic strength	Hexagonal nanostructures, Globular nanoparticles Elongated particles	Beta sheets	Guan, Z. et. al. Curr. Biol. 2017, 27, 2833-2842.
D. opalescens	ReflectinA1, ReflectinA2	DLS, TEM, CD, AFM	Acetate buffer, pH4.5; 5 mM MOPS, pH 6.5, 7.0, 7.5, 8.0	Chemical – pH	Nanospheres	Beta sheets, Helices	Levenson, R. et al. J. Biol. Chem. 2019, doi: 10.1074/jbc.RA119.010339
D. opalescens	ReflectinA1, ReflectinA2, Reflectin B, Reflectin C	DLS, CD, WAXS, TEM, Computational	Water; 5 mM MOPS, pH 7.5; 15 – 250 mM Acetate, pH 4.5	Chemical – pH	Nanospheres	Beta sheets, Helices	Levenson, R. et al. J. Biol. Chem. 2015, 219, 4058-4068.
D. opalescens	Reflectin A1	SAXS, WAXS, DLS, CD, SEM, TEM	Water; 0-400 mM NaCl	Chemical – ionic strength, protein concentration	Nanospheres, Bead-on-a-string assemblies, connected networks, close-packed assemblies	Disordered, Beta sheets	Tao, A. R. et. al. Biomaterials 2010, 31, 793-801.
D. pealeii	Reflectin A1	SEM, DLS, SAXS, GISAXS, GIWAXS, DXMS, Computational	Milli-Q water	Chemical -Relative Humidity	Nanospheres	Beta sheets	Naughton, K. L. et. al. Adv. Mater. 2016, 28, 8405–8412.
D. pealeii	Reflectin A2	Computational		NA	NA	Alpha helical motifs with unstructured linker regions	Williams, T. L. et. al. Nat. Comm. 2019, 10, 1004-1019.
D. pealeii	Reflectin A1 truncation mutant	MD, NMR, SAXS, CD, DLS, AFM	Ammonium formate pH 3.2	Mechanical agitation	Nanospheres, Fibrils, Bead-on-a-string assemblies	Random coil, Beta sheets, Alpha helical motifs	This work

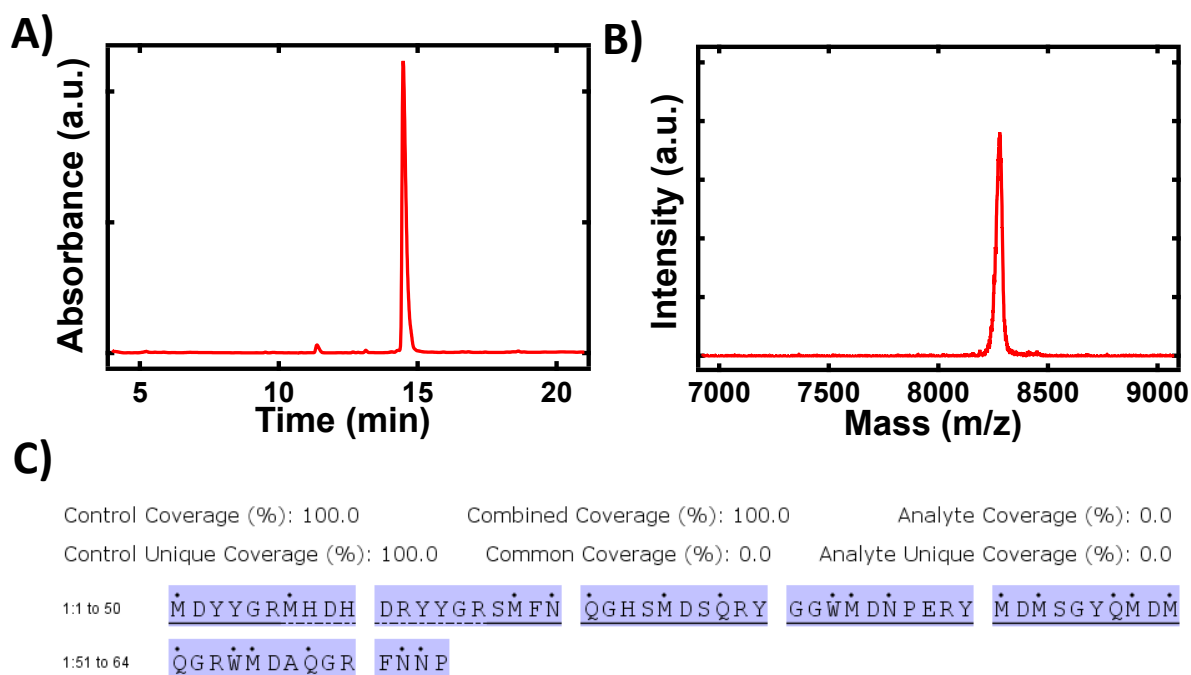
Table S7.1. A table of structural characterization performed for reflectin isoforms to date.



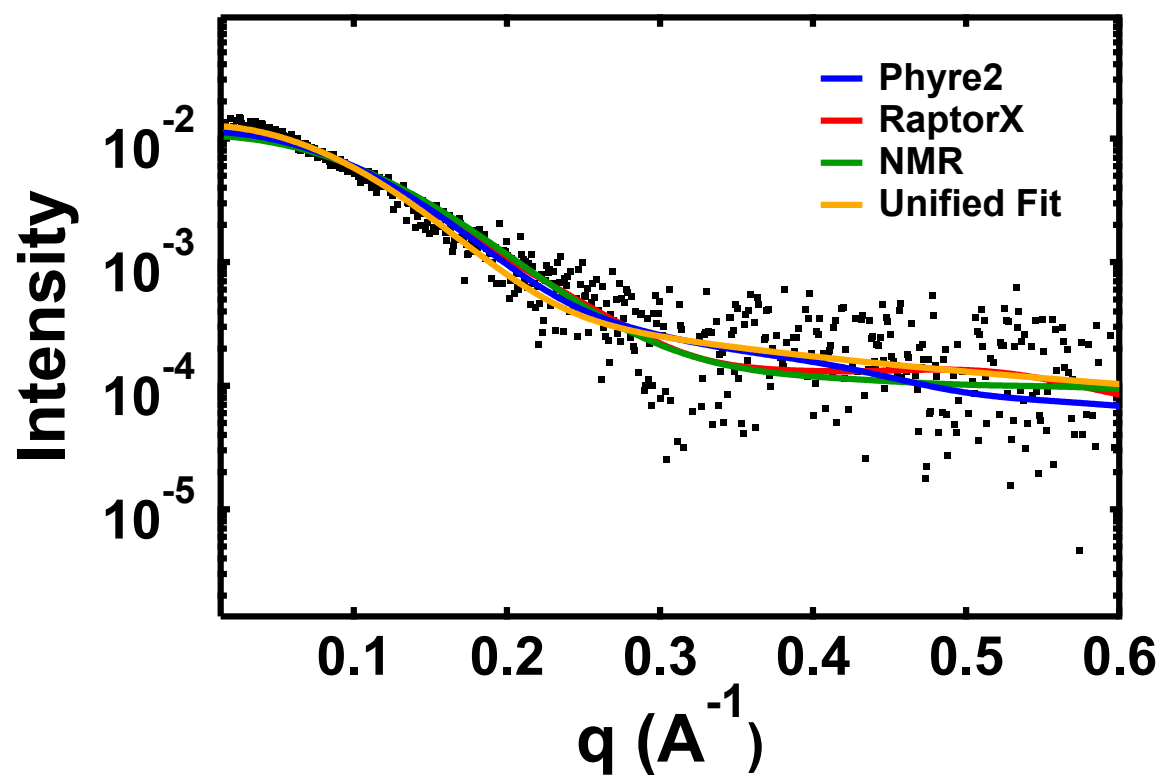
SI Figure 7.1. (A) Fraction of beta-turns as a function of radius of gyration (R_g) for RfA1TM (B) Fraction of helices as a function of radius of gyration (R_g) for RfA1TM (C) Fraction of bends as a function of radius of gyration (R_g) for RfA1TM (D) Fraction of beta-turns as a function of radius of gyration (R_g) for RfA1TM.



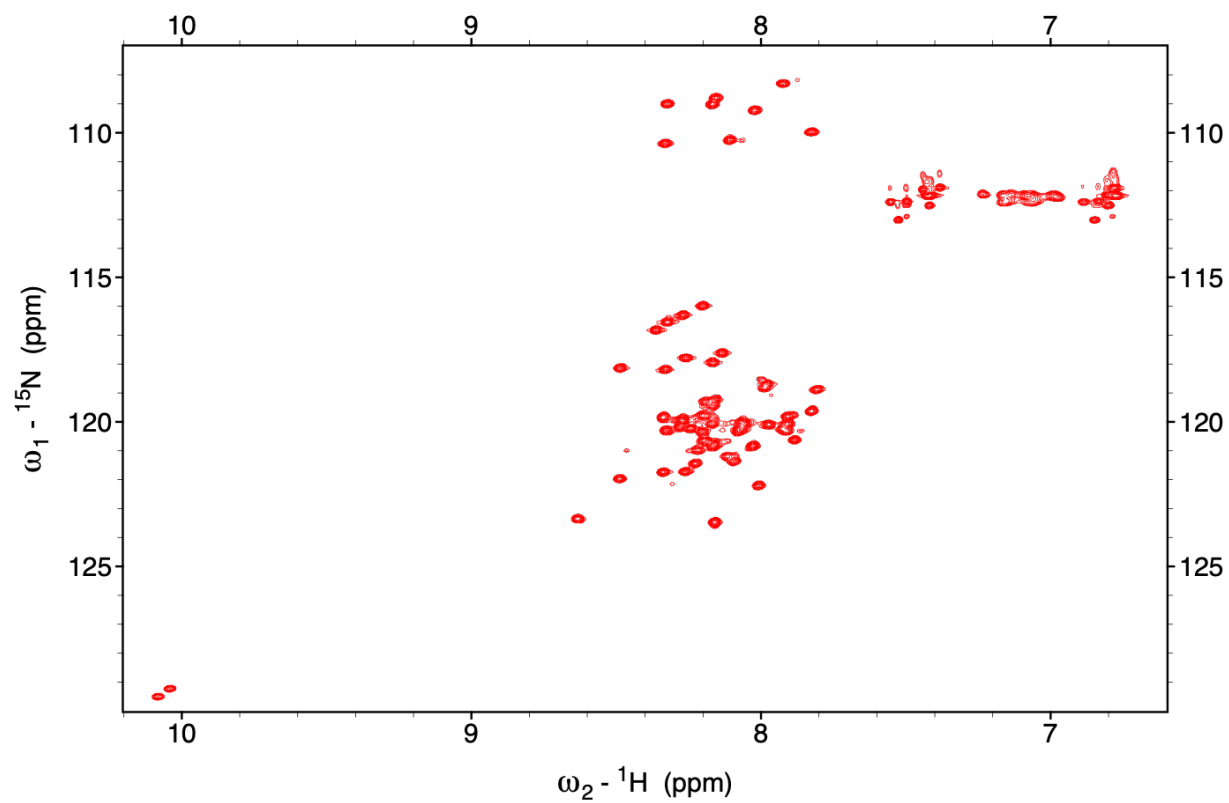
SI Figure 7.2. (A) A plot of the HPLC chromatogram of the unlabeled RfA1TM. A peak was observed at 16.4 minutes. (B) Mass spectrum of purified unlabeled RfA1TM. A peak was observed at 7862 Da. (C) A peptide sequence coverage map obtained from in-gel tryptic digest tandem mass spectrometry analysis of the of unlabeled RfA1TM.



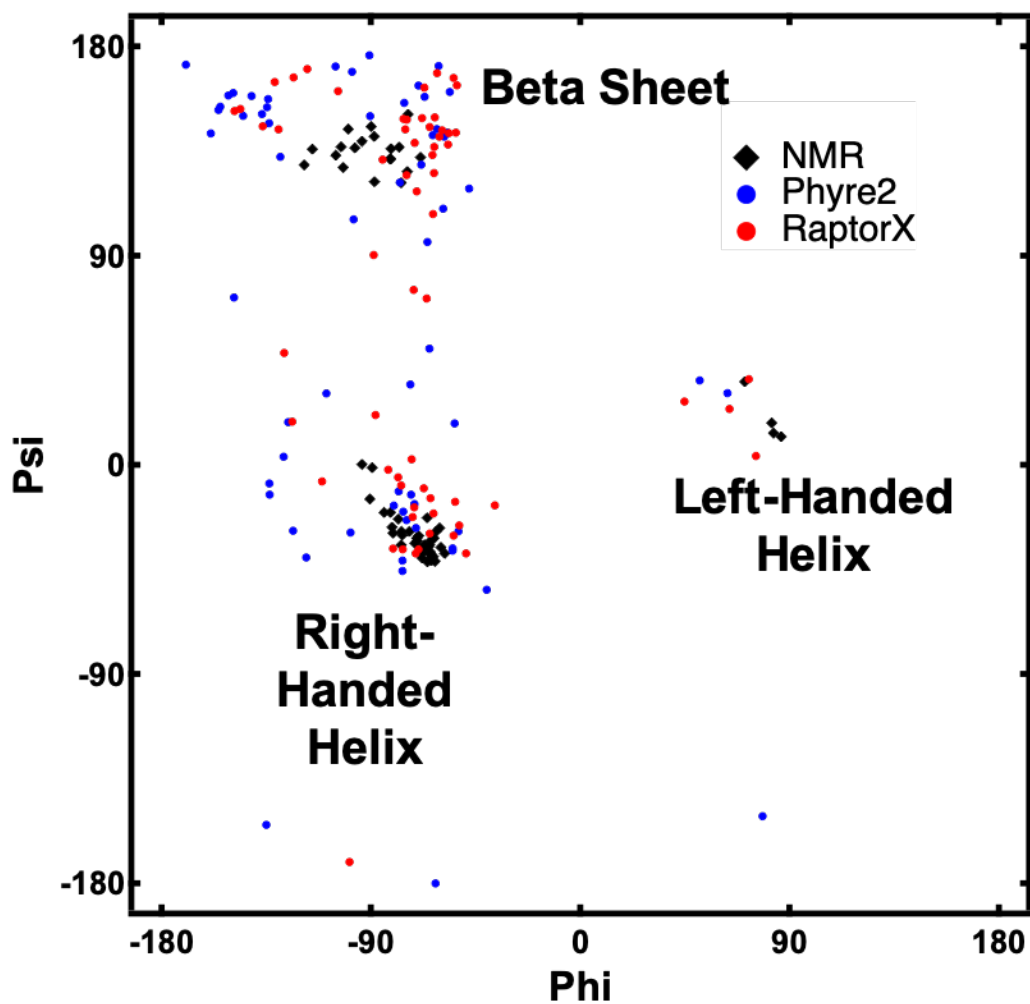
SI Figure 7.3. (A) A plot of the HPLC chromatogram of the labeled RfA1TM. A peak was observed at 14.5 minutes (B) Mass spectrum of purified labeled RfA1TM. A peak was observed at 8286 Da. (C) A peptide sequence coverage map obtained from the in-gel tryptic digest tandem mass spectrometry analysis of the of labeled RfA1TM.



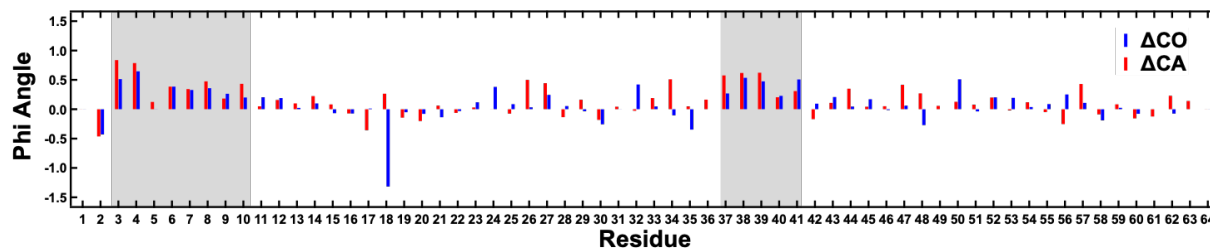
SI Figure 7.4. The SAXS scatter plots. The black dots represent the experimental data, the blue line represents the Phyre2-derived data, the red line represents the RaptorX-derived data, the green line represents the NMR-derived data, and the yellow line represents unified fit.



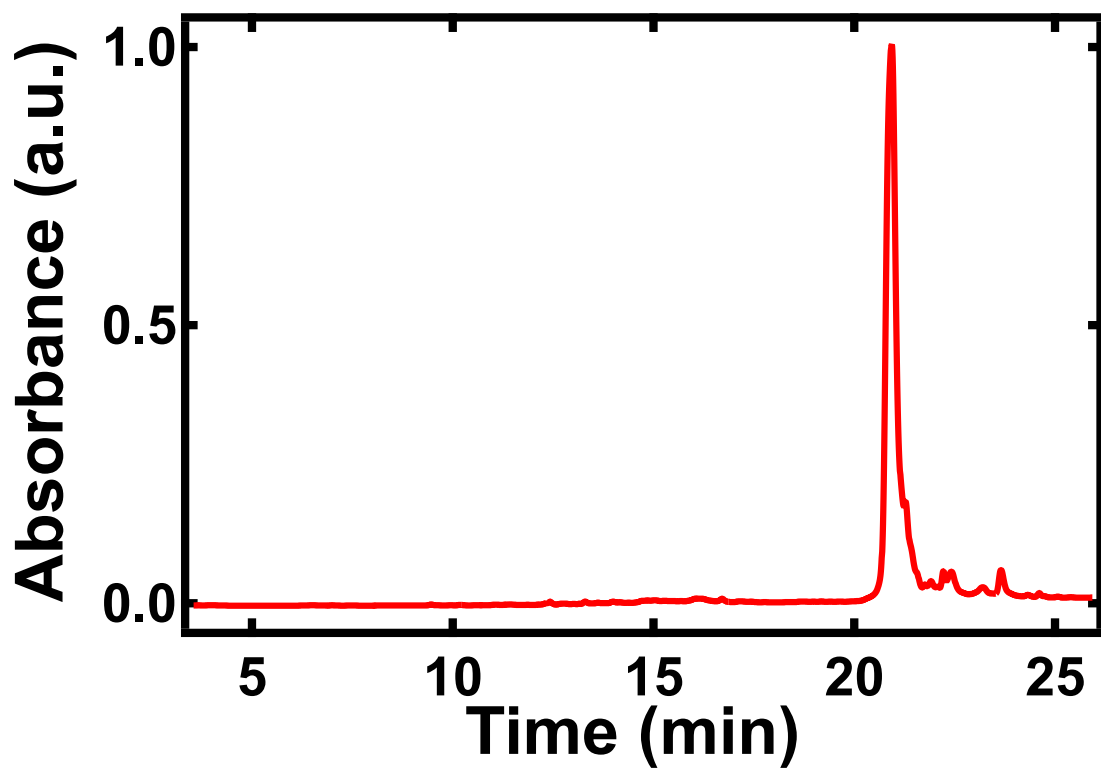
SI Figure 7.5. A ^1H - ^{15}N HSQC spectra of the RfA1 truncation mutant.



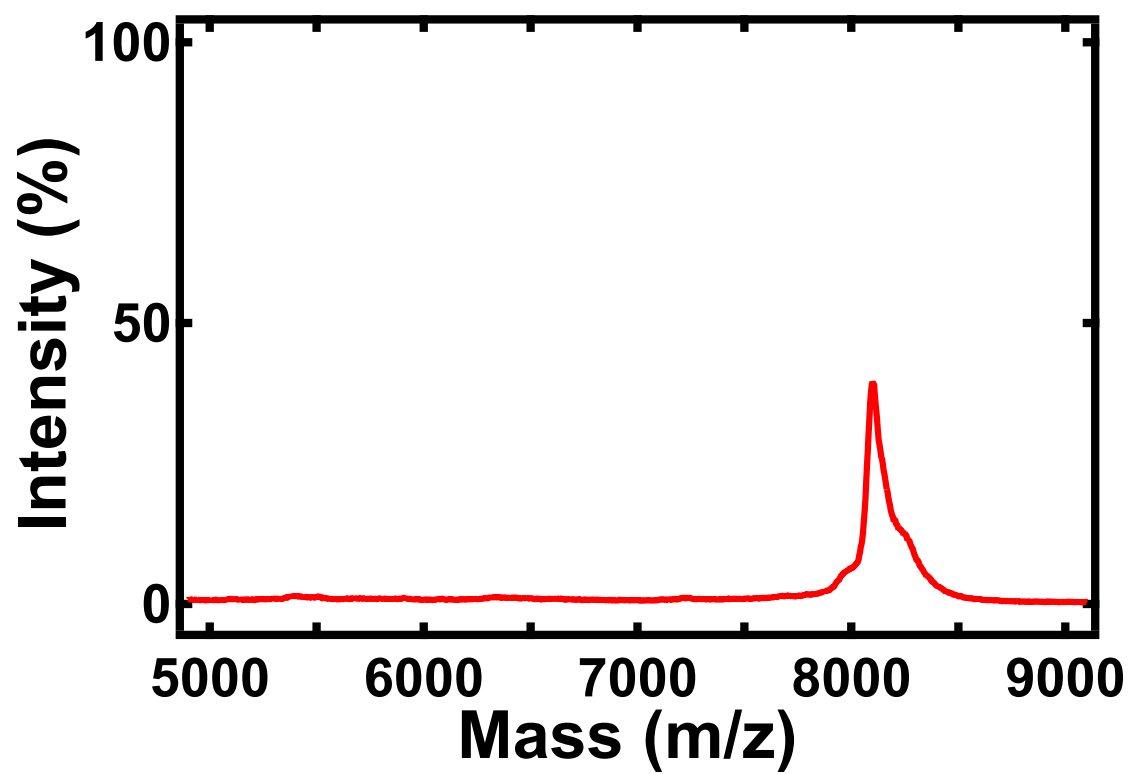
SI Figure 7.6. A Ramachandran plot of the torsion angles derived from the backbone of RfA1 TM. The black dots represent the NMR-derived torsion angles, blue dots represent the Phyre2-derived torsion angles, the red dots represent the RaptorX-derived torsion angles. Regions correlating to the presence of beta-sheets, right-handed helices, and left-handed helices are indicated on the plot.



SI Figure 7.7. Variation of secondary chemical shifts along AA sequence which represents differences between experimentally obtained carbonyl and alpha carbon chemical shifts and their values for complete random coil protein predicted by POTENCI program. Shaded in grey are the regions where positive deviations of chemical shifts obtained from NMR experiments correspond to a structural propensity towards alpha-helical fold.



SI Figure 7.8. A plot of the HPLC chromatogram of RfA1TM*. A peak was observed at 14.5 minutes.



SI Figure 7.9. Mass spectrum of purified unlabeled RfA1TM*. A peak was observed at 8098 Da.

7.5.3. Supporting References

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Chapter 8 Summary and Conclusions

In conclusion, we have developed the aza-Diels–Alder reaction for the synthesis of quinoline polymers, copolymers, and bioconjugates. Our findings are significant for a number of reasons. First, we have demonstrated a previously unknown synthetic route to AB polyquinolines using the aza-Diels–Alder reaction, which features a number of advantages. Our approach proceeds in two simple synthetic steps, requires only commercially available starting materials, and our scheme furnishes an unprecedented type of polyquinolines linked at the 4,6-positions of the quinoline ring. Second, we expand our strategy for the first reported synthesis of modular polybenzoquinolines using the aza-Diels–Alder reaction. Our approach employs few synthetic steps, inexpensive precursor materials, and straightforward reaction conditions, which allows for the preparation of crowded yet soluble polymers with variable peripheral substituents and sizes. Furthermore, our strategy may also provide access to a diverse family of benzoquinoline-based materials, including a class of precursor polymers for $N = 7$ armchair GNRs, which have been prepared exclusively from polyanthracenes to date. Third, we used the aza-Diels–Alder polymerization reaction to provide access to a diverse set of zigzag AABB polyquinolines containing 4,6-linked quinoline subunits. Our strategy offers intrinsic modularity and may present new opportunities for the preparation of diverse quinoline-based organic electronic materials with rationally engineered and customizable properties. Fourth, we built upon the AABB strategy to employ the aza-Diels–Alder strategy for the synthesis of both diquinolineanthracenes and polydiquinolineanthracenes using mild conditions and commercially available starting materials. Our approach accommodates various peripheral substituents, including electron-donating, electron-withdrawing, and sterically hindered groups. This facile route offers materials that

integrate both the quinoline and acene motifs and therefore hold promise for applications in organic electronics. Fifth, we developed a new type of quinoline polypeptide synthesized by iterative coupling novel quinoline α -amino acids, prepared *via* the Povarov reaction. Our reactions proceed under mild conditions, are easily purified, and afforded in good yield. We found that these quinoline α -polypeptides form helical structures, which share similar optoelectronic properties to other quinoline-containing materials and may offer new potential candidates for biologically derived photonic materials. Lastly, we use our quinoline α -amino acid to prepare a reflectin A1 truncation mutant (RfA1TM) bioconjugate. The bioconjugation-induced structural changes highlight the sensitivity of reflectins and provide additional parameters by which to tune reflectins' structure and function *in vitro*. Our findings that bioconjugation also results in the formation of helical structures have interesting implications for our understanding of the *in vivo* optical capabilities of cephalopod skin components. Overall, scope of work provides insight into the synthesis of quinoline-based materials using the aza-Diels–Alder reaction and, holds significance for the improved design and processing of functional materials.