

UC Irvine

UC Irvine Electronic Theses and Dissertations

Title

An aza-Diels-Alder approach to nitrogen-containing tetrabenzoacene derivatives

Permalink

<https://escholarship.org/uc/item/37h6b2cw>

Author

Peng, Ethan

Publication Date

2024

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA,
IRVINE

An aza-Diels-Alder approach to nitrogen-containing tetrabenzoacene derivatives

THESIS

submitted in partial satisfaction requirements

for the degree of

MASTER OF SCIENCE

in Materials Science and Engineering

by

Ethan Ryan Peng

Thesis Committee:

Professor Alon A. Gorodetsky, Chair

Professor Stacy Marla Copp

Professor David Kisailus

2024

TABLE OF CONTENTS

LIST OF FIGURES.....	iii
ACKNOWLEDGEMENTS.....	iv
ABSTRACT OF THE THESIS.....	v
INTRODUCTION.....	1
EXPERIMENTAL WORK.....	5
Part 1. Synthesis and Results of Tetrabenzoacene Derivatives.....	5
1.1. Synthesis of Dodecyl-Substituted Tetrabenzopentacene.....	5
1.2. Synthesis of Tetrabenzoheptacene.....	7
1.3. Synthesis of Amino-Functionalized and Bromo-Functionalized Tetrabenzopentacene...	8
1.4. Synthesis of Dimeric Tetrabenzopentacene.....	10
1.5. Electronic Properties of Synthesized Tetrabenzoacene Derivatives.....	13
Part 2. Supporting Information.....	16
2.1. General Methods.....	16
2.2. Detailed Synthetic Protocol.....	18
2.3. ¹ H NMR and ¹³ C NMR Spectroscopy Data.....	32
2.4. UV-Vis Spectroscopy Data.....	70
CONCLUSION.....	71
REFERENCES.....	72

LIST OF FIGURES

Figure 1. (A) Top row: The previously-reported all-carbon and oxidized tetrabenzo[<i>de,hi,op,st</i>]pentacenes. Bottom row: The previously-reported nitrogen- and boron-containing tetrabenzo[<i>de,hi,op,st</i>]pentacenes. (B) The tetrabenzoacene derivatives reported in this work.....	4
Scheme 1. The synthesis of dodecyl-substituted tetrabenzopentacene 4	6
Scheme 2. The synthesis of tetrabenzoheptacene 7	7
Scheme 3. The synthesis of amino-functionalized tetrabenzopentacene 11 and bromo-functionalized tetrabenzopentacene 12	9
Scheme 4. The synthesis of dimeric tetrabenzopentacene 19	12
Figure 2. The UV-Vis absorption spectra measured for 4 (black trace), 7 (red trace), 11 (blue trace), 12 (green trace), 19 (purple trace). Note that the absorption spectra were normalized by using their maximum absorbance peak within the 600 nm to 700 nm wavelength range to facilitate direct comparisons.....	15

ACKNOWLEDGEMENTS

Firstly, I would like to express my gratitude the chair of my thesis committee and advisor, Professor Alon A. Gorodetsky, for his mentorship and continuous support of my master's study. I would also like to appreciate other committee members, Professor Stacy Copp and Professor David Kisailus for their time and help on the thesis.

Besides my advisor, I would like to extend my gratitude to my fellow lab mates in the Gorodetsky lab who have mentored me throughout my graduate career.

Lastly, I would like to thank my family and friends for the never-ending love, support, and being a constant source of inspiration.

The text of this thesis is an adaptation of the material as it appears in “An aza-Diels-Alder approach to nitrogen-containing tetrabenzoacene derivatives” in RSC Advances, used with permission from the Royal Society of Chemistry ([CC BY 3.0](#)). Alon A. Gorodetsky directed and supervised research which forms the basis for the thesis. Author contributions: conceptualization, Alon A. Gorodetsky (A.A.G.); methodology, A.A.G., David J Dibble (D.J.D.); investigation, Ethan Ryan Peng (E.R.P.), Anthony M. Burke (A.M.B.) , D.J.D., Chandra B. KC (C.B.C.), Reina Kurakake (R.K.), Philip Dennison (P.D.) and Robert Lopez (R.L.) (synthesis, NMR characterization and MS characterization) and E.R.P. and Panyiming Liu (P.L.) (UV-Vis characterization); data curation, E.R.P. (synthesis, NMR, MS, and UV-Vis curation) and A.M.B. (NMR, and MS curation); writing—original draft preparation, A.A.G.; writing—review and editing, A.A.G., E.R.P. and A.M.B.; visualization, E.R.P.; supervision, A.A.G.; project administration, A.A.G.; funding acquisition, A.A.G.

ABSTRACT OF THE THESIS

An aza-Diels Alder approach to nitrogen-containing tetrabenzoacene derivatives

By

Ethan Ryan Peng

Master of Science in Materials Science and Engineering

University of California, Irvine, 2024

Professor Alon A. Gorodetsky, Irvine, Chair

Acenes and *N*-heteroacenes have been synthesized and studied for over a century because of their fundamentally interesting materials properties and promise for device applications. Within this context, our laboratory has previously synthesized nitrogen-containing tetrabenzo[*de,hi,op,st*]pentacenes via an aza-Diels–Alder reaction-based approach, and herein, we expand our methodology to obtain substituted, expanded, functionalized, and dimeric tetrabenzoacenes. Overall, our study adds to the limited number of tetrabenzoacene derivatives reported to date and may open further opportunities for these materials in organic optoelectronics applications.

INTRODUCTION

Acenes, which are compounds that consist of linearly fused benzene rings and possess a single aromatic sextet, have been extensively studied for >100 years. [1-19] The history of acenes began in the earth 20th century with the isolation and characterization of simpler acenes such as naphthalene and anthracene. It was not until the early 1930's until pentacene, a larger acene with five fused benzene rings, was synthesized and characterized which marked a significant milestone. These polycyclic aromatic hydrocarbons are widely investigated as organic functional materials because of their fundamentally interesting electronic structures and photophysical properties [1-3, 12, 15, 17] as well as because of their demonstrated potential for thin film transistor and organic optoelectronics applications. [1, 2, 9, 19] Several synthetic routes to acene variants such as pentacene have therefore been reported, including nucleophilic addition or direct reduction of acene quinones, oxidation/dehydrogenation of hydroacenes, and retrocycloaddition of bridged acene precursors. [1, 2, 4, 12, 14, 17]

Within this context, *N*-heteroacenes, which are a subset of acenes containing nitrogen atoms, have also attracted much attention from researchers. [1, 4-8, 10-13, 16, 18] The incorporation of nitrogen atoms into the acene backbone alters the electronic structure, thus resulting in several enhanced properties relative to the traditional acene. [1, 5, 7, 10-12, 16-18] These nitrogen-containing molecules often exhibit enhanced oxidative stability, as the electron-withdrawing nature of nitrogen atoms reduce the susceptibility of oxidative degradation. [5, 7, 10-12, 16-18] Additionally, nitrogen atoms provide additional electronic tunability by shifting the energy level of the molecule's molecular orbitals which enable control over bandgap levels. [1, 7, 10-12, 16, 18] *N*-heteroacenes also demonstrate ambipolar charge transport in transistors which allow for efficient transport of electrons and holes. [1, 10-12, 16, 18] Furthermore, these molecules

offer improved light absorption/emission in optoelectronic devices due to nitrogen atoms shifting the absorption spectrum and increasing light emission efficiency [5, 7, 11, 12, 18] [1, 5, 7, 10-12, 16-18] Several synthetic routes to *N*-heteroacene derivatives have accordingly been reported, including the direct oxidation of hydroazaacenes, condensation of diamines with orthoquinones or dihydroxy compounds, and Pd catalyzed coupling of aromatic diamines with activated aryl halides. [4-6, 8, 11-13, 18] Consequently, there exists significant motivation for the continued development of facile approaches to the synthesis of *N*-heteroacene derivatives.

Correspondingly, tetrabenzo[*de,hi,op,st*]pentacenes, which are acene variants with benzene rings fused to a linear pentacene core, have been investigated intermittently for >90 years (Fig. 1A, top row). [20–31] These molecules were viewed as interesting because of their surprising photochromic behavior when oxidized, impressive thermal stabilities, and unexpected electrical properties. [24, 25, 27, 30, 31] Such all-carbon tetrabenzopentacenes were typically obtained through base-mediated cyclodehydrohalogenation of chlorinated dinaphthylanthracene precursors and could be further converted into their endoperoxide forms by reversible oxidation. [21, 25, 26, 30] Most recently, monomeric and polymeric heterotetrabenzo[*de,hi,op,st*]pentacenes, which contain nitrogen or boron atoms, have been reported by different laboratories (Fig. 1A, bottom row). [32-34] These molecules and polymers exhibited favorable photophysical properties, altered electrochemical characteristics, and distinct electronic structures. [32-34] Such nitrogen- and boron-containing tetrabenzopentacene variants were obtained through base-mediated cyclodehydrohalogenation, nickel-mediated Yamamoto-type dehalogenation, or surface-assisted cyclodehydrogenation of various corresponding anthracene precursors. [32-34] To date, tetrabenzopentacenes of any kind are accessible through only a few synthetic routes, whose scope and modularity have not been adequately explored.

Herein, we report a general and modular aza-Diels–Alder reaction-based approach to substituted, expanded, functionalized, and dimeric nitrogen-containing tetrabenzoacenes (Fig. 1B). First, we synthesize a nitrogen-containing tetrabenzopentacene bearing pendant phenyl rings substituted with dodecyl chains, thus demonstrating incorporation of solubilizing functionalities (Fig. 1B, compound **I**). Second, we synthesize a nitrogen-containing tetrabenzoheptacene, thus describing expansion of the molecular aromatic core of our compound (Fig. 1B, compound **II**). Third, we synthesize a nitrogen-containing tetrabenzopentacene featuring amino and bromo functional groups, thus showing installation of reactive electron-withdrawing and electron-donating handles (Fig. 1B, compound **III**). Fourth, we synthesize a dimeric nitrogen-containing tetrabenzopentacene, thus furnishing a potentially valuable larger model compound (Fig. 1B, compound **IV**). Last, we comparatively investigate the electronic properties of our various tetrabenzoacene derivatives with ultraviolet-visible (UV-Vis) spectroscopy. Our synthetic strategy affords multiple new nitrogen-containing tetrabenzo[*de,hi,op,st*]pentacene variants and may enhance the utility of this class of molecules in organic optoelectronics applications.

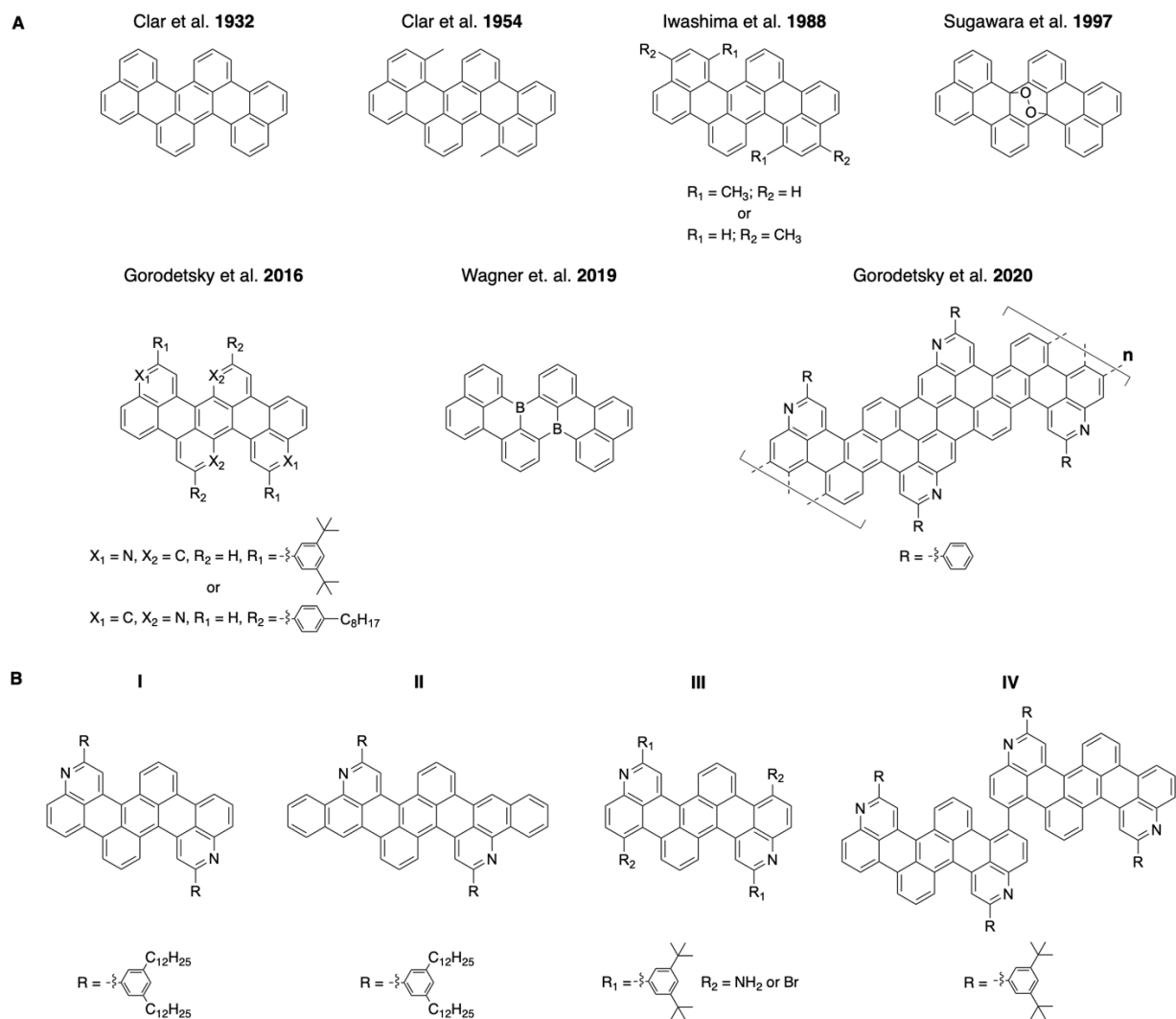


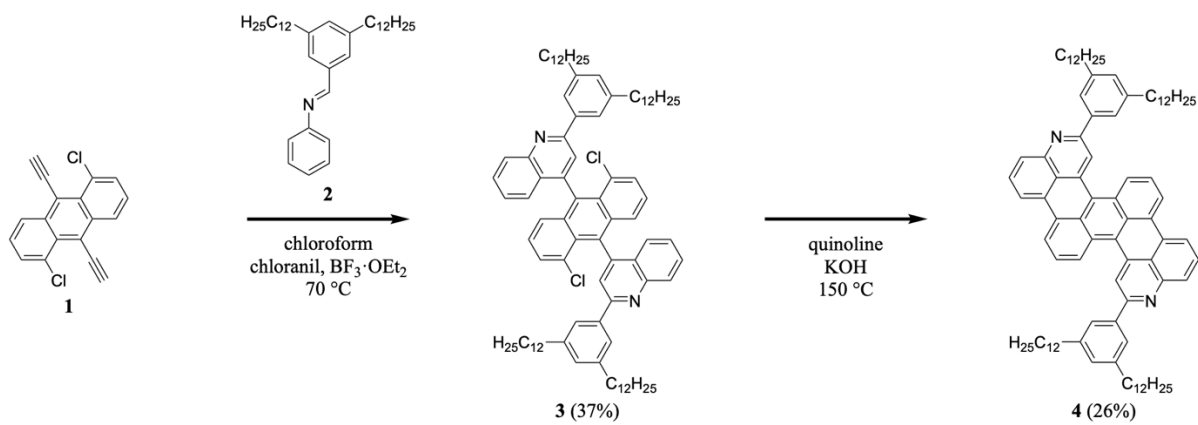
Figure 1. (A) Top row: The previously-reported all-carbon and oxidized tetrabenzo[*de,hi,op,st*]pentacenes. Bottom row: The previously reported nitrogen- and boron-containing tetrabenzo[*de,hi,op,st*]pentacenes. (B) The tetrabenzoacene derivatives reported in this work.

EXPERIMENTAL WORK

PART 1. SYNTHESIS AND RESULTS FOR TETRABENZOACENE DERIVATIVES

1.1. Synthesis of Dodecyl-Substituted Tetrabenzopentacene

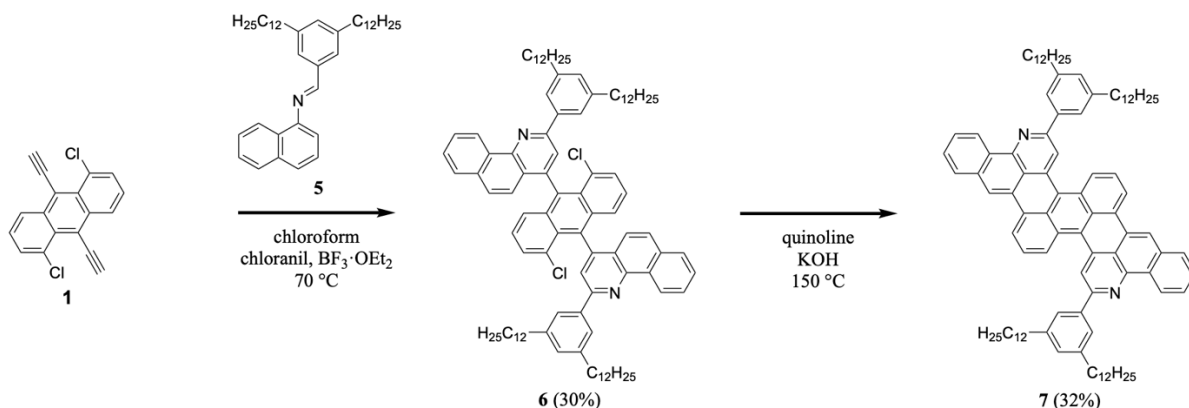
We began our efforts by synthesizing a nitrogen-containing tetrabenzopentacene derivative bearing pendant phenyl rings substituted with dodecyl chains (Scheme 1). First, we reacted 1,5-dichloro-9,10-diethynylanthracene **1** with 3,5-didodecylphenyl-substituted phenylaldimine **2** under our highly optimized general aza-Diels–Alder reaction conditions (i.e., chloroform as the solvent, $\text{BF}_3 \cdot \text{OEt}_2$ as the Lewis acid catalyst, and chloranil as the oxidant), forming two quinoline moieties and obtaining intermediate **3** in a reasonable yield of 37% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S1 - S4). [32, 34–41] Next, we cyclodehydrohalogenated diquinolineanthracene variant **3** under standard conditions (i.e., quinoline as the solvent and KOH as the base), forming two intramolecular carbon–carbon bonds and furnishing dodecyl-substituted tetrabenzopentacene product **4** in a more modest yield of 26% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S5, S6). [32, 42] These experiments demonstrated that our tetrabenzopentacene was readily modified with extended alkyl chains, which can mitigate aggregation and enhance solubility for acenes. [1, 2, 39]



Scheme 1. The synthesis of dodecyl-substituted tetrabenzopentacene **4**.

1.2. Synthesis of Tetrabenzoheptacene

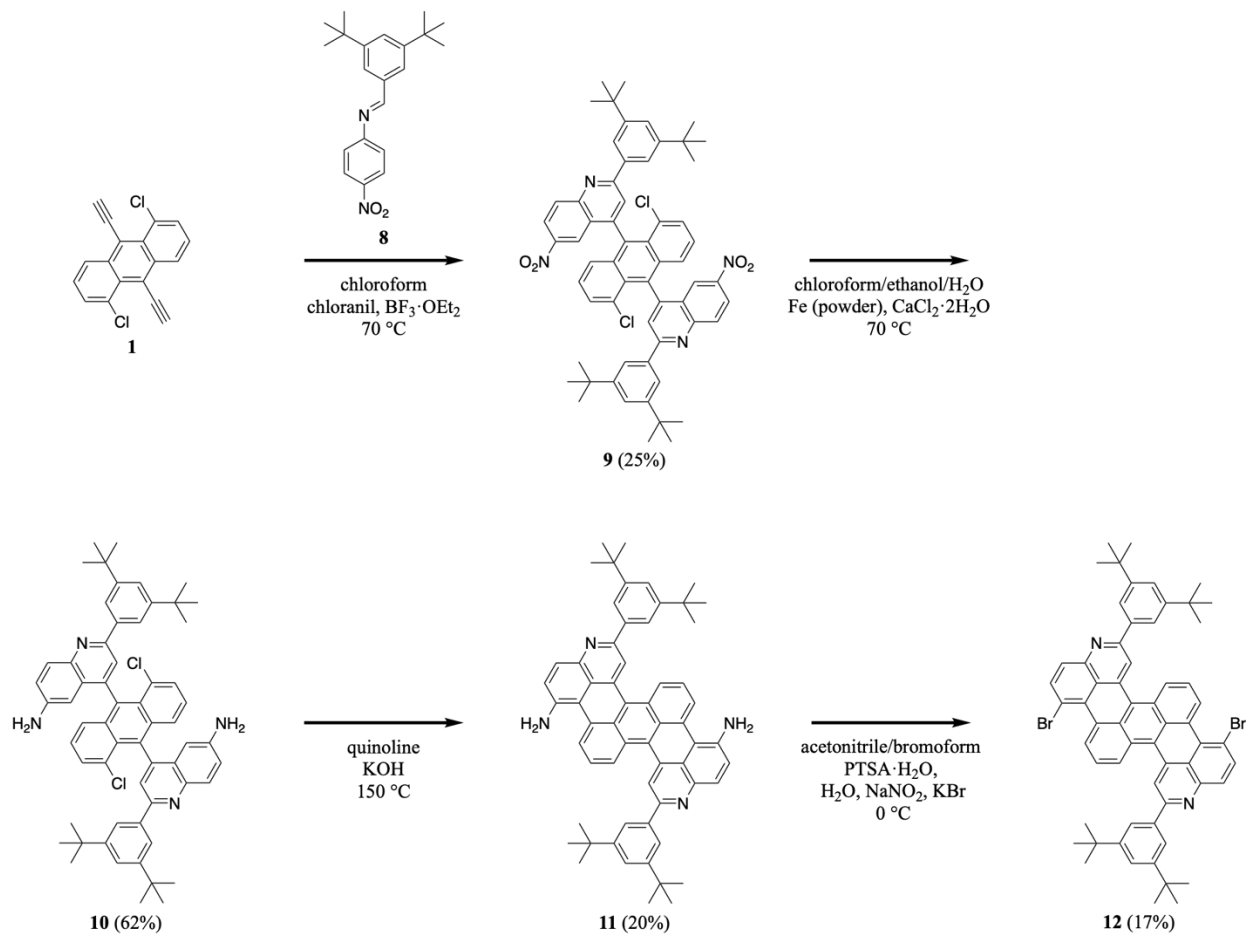
We continued our efforts by synthesizing a nitrogen-containing tetrabenzoheptacene derivative (Scheme 2). First, we reacted 1,5-dichloro-9,10-diethynylantracene **1** with 3,5-didodecylphenyl-substituted naphthylaldimine **5** under our established general aza-Diels–Alder reaction conditions, forming two benzoquinoline moieties and obtaining intermediate **6** in a reasonable yield of 30% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S7 - S12). [32, 34–41] Next, we cyclodehydrohalogenated diquinolineanthracene variant **6** under our validated standard conditions, forming two intramolecular carbon–carbon bonds and furnishing dodecyl-substituted tetrabenzoheptacene product **7** in a comparable yield of 32% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S13, S14). [32, 42] These experiments demonstrated that our tetrabenzopentacene's core aromatic motif was readily expanded to a heptacene, which can possess improved functional properties and serve as a model longer acene. [3, 17, 43]



Scheme 2. The synthesis of tetrabenzoheptacene **7**.

1.3. Synthesis of Amino-Functionalized and Bromo-Functionalized Tetrabenzopentacene

We extended our efforts by synthesizing nitrogen-containing tetrabenzopentacene derivatives featuring amino and bromo functional groups (Scheme 3). First, we reacted 1,5-dichloro-9,10-diethynylanthracene **1** with 3,5-di-tert-butylphenyl-substituted 4-nitrophenylaldimine **8** under our standard aza-Diels–Alder reaction conditions, forming two nitroquinoline moieties and obtaining intermediate **9** in a moderate yield of 25% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S15 - S20). [32, 34–41] Next, we reduced **9**'s nitro groups using routine catalytic transfer hydrogenation conditions (*i.e.*, chloroform/ethanol/water as the solvents and Fe/CaCl₂ as the reducing reagents), forming two 6-aminoquinoline moieties and generating intermediate **10** in a good yield of 62% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S21, S22). [44] Then, we cyclodehydrohalogenated diquinolineanthracene variant **10** under our validated standard conditions, forming two intramolecular carbon–carbon bonds and furnishing amino-functionalized tetrabenzopentacene product **11** in a moderate yield of 20% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S23, S24). [32, 42] Last, we converted tetrabenzopentacene **11**'s amino groups to bromo groups using established Sandmeyer-type reaction conditions (*i.e.*, acetonitrile/bromoform as the solvents and NaNO₂/KBr/PTSA as the acid system), affording bromo-functionalized tetrabenzopentacene product **12** in a moderate yield of 17% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S25, S26). [45] These experiments demonstrated that our tetrabenzopentacene was readily substituted with ubiquitous electron-donating and electron-withdrawing groups, which readily tune molecular electronic properties [10, 15, 16, 18] and can enable various metal-catalyzed cross-coupling or functionalization reactions. [46–49]

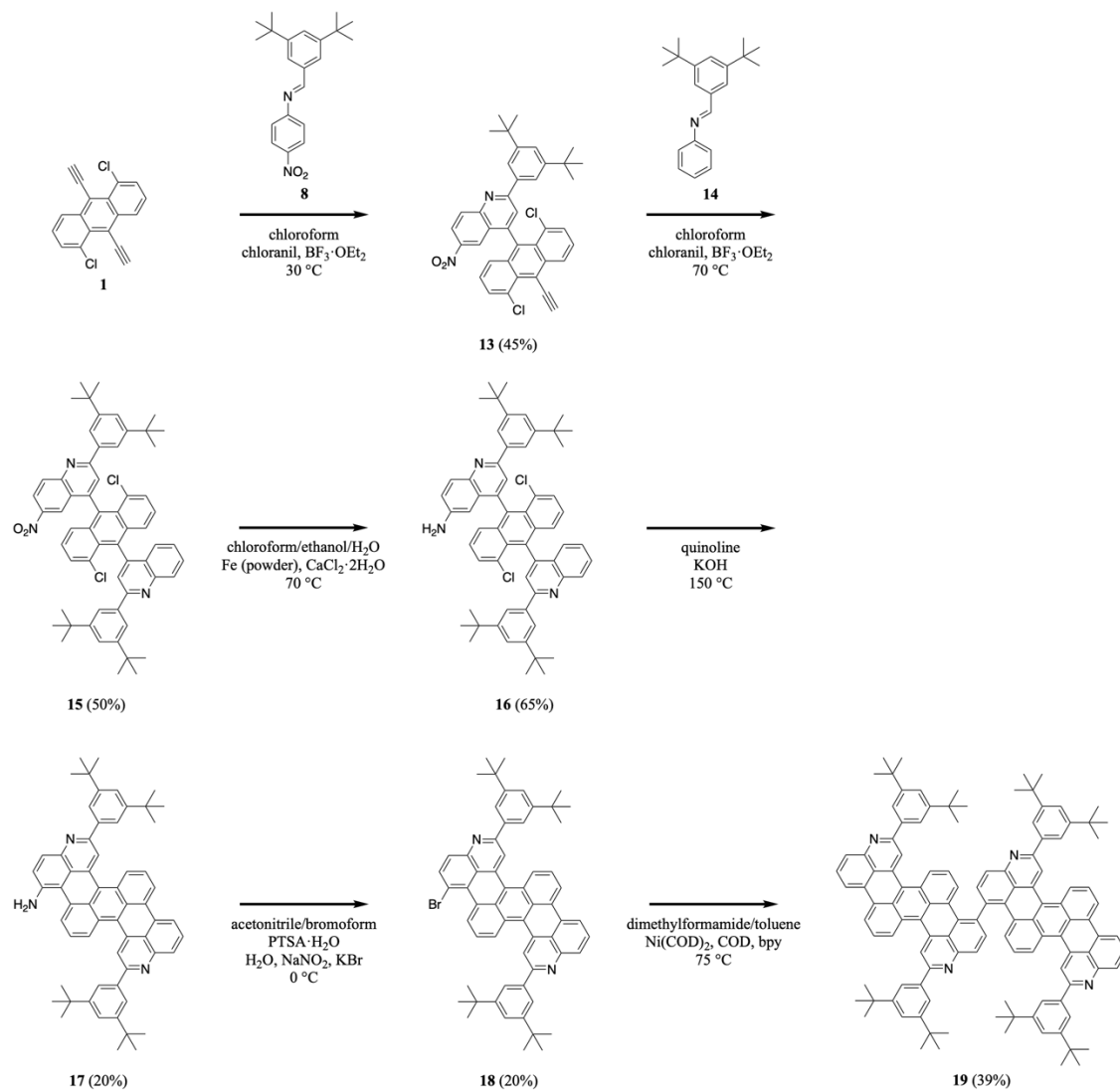


Scheme 3. The synthesis of amino-functionalized tetrabenzopentacene **11** and bromo-functionalized tetrabenzopentacene **12**.

1.4. Synthesis of Dimeric Tetrabenzopentacene

We further advanced our efforts by synthesizing a dimeric nitrogen-containing tetrabenzopentacene derivative (Scheme 4). First, we reacted 1,5-dichloro-9,10-diethynylanthracene **1** with 3,5-di-*tert*-butylphenyl-substituted 4-nitrophenylaldimine **8** under slightly modified milder aza-Diels–Alder reaction conditions (*i.e.*, at a lower temperature), forming a nitroquinoline moiety and generating intermediate **13** in a good yield of 45% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S27, S28). [32, 34–41] Next, we reacted quinolineanthracene variant **13** with 3,5-di-*tert*-butylphenyl-phenylaldimine **14** under our standard aza-Diels–Alder reaction conditions, forming a quinoline moiety and generating intermediate nitro-functionalized quinolineanthracene variant **15** in a good yield of 50% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S29, S30). [32, 34–41] Then, we reduced **15**'s nitro group using routine catalytic transfer hydrogenation conditions, forming amino-functionalized quinolineanthracene variant **16** in a good yield of 65% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S31, S32). [44] In turn, we cyclodehydrohalogenated diquinolineanthracene variant **16** under our validated standard conditions, forming two intramolecular carbon–carbon bonds and furnishing intermediate **17** in a moderate yield of 20% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S33, S34). [32, 42] Subsequently, we converted tetrabenzopentacene **17**'s amino group to a bromo group using established Sandmeyer-type reaction conditions, affording intermediate **18** in a moderate yield of 20% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S35, S36). [45] Last, we cross-coupled the bromo groups of two tetrabenzopentacene **18**'s with each other using well-known Ullmann reaction conditions (*i.e.*, dimethylformamide/toluene as the solvents and Ni(COD)₂/COD/bpy as the transition metal

catalyst system), affording dimeric tetrabenzopentacene product **19** in a reasonable yield of 39% (see Part 2. Supporting Information 2.1., Part 2.2., and Part 2.3. Supplementary Figs. S37, S38). [50] These experiments demonstrated that our tetrabenzopentacene could be site-specifically substituted with single halogen functional groups, which are amenable to many routine cross-coupling reactions, [46–49] and moreover could be readily assembled into larger molecular frameworks, which opens opportunities for the synthesis of corresponding nitrogen-containing graphene nanoribbons. [16, 34, 51]



Scheme 4. The synthesis of dimeric tetrabenzopentacene **19**.

1.5. Electronic Properties of Synthesized Tetrabenzoacene Derivatives

We last investigated the electronic properties of our tetrabenzoacene derivatives by means of UV-Vis spectroscopy (Fig. 2). First, the spectrum obtained for dodecyl-substituted tetrabenzopentacene **4** featured prominent absorption peaks with maxima at 641 nm and 592 nm as well as a shoulder at 541 nm, with the addition of extended side chains mitigating aggregation but not significantly shifting the absorption peaks relative to those of the analogous previously-reported *tert*-butyl-substituted tetrabenzopentacene (Fig. 2 and Fig. S39). [32] The decrease in absorption in the dodecyl-substituted tetrabenzopentacene spectrum near 300 nm is attributed to the quinoline component, while the local maxima peaks at 409 nm, 391 nm, 372 nm, 353 nm, and 330 nm further highlight the tetrabenzopentacene backbone's extended conjugation. Second, the spectrum obtained for dodecyl-substituted tetrabenzoseptacene **7** featured prominent absorption peaks with maxima at 648 nm and 598 nm as well as a shoulder at 547 nm, with the extension of the aromatic core only slightly red shifting the absorption peaks relative to those of the analogous *tert*-butyl- and dodecyl-substituted tetrabenzopentacenes (Fig. 2 and Fig. S39). The decrease in absorption in the dodecyl-substituted tetrabenzoseptacene spectrum near 300 nm is attributed to the quinoline component, while the shoulder at 417 and the local maxima peaks at 387 nm and 367 nm further highlight tetrabenzoseptacene's slight red shift. Third, the spectrum obtained for amino-functionalized tetrabenzopentacene **11** featured prominent absorption peaks at 668 nm and 622 nm as well as a small shoulder at 554 nm, with the introduction of the two electron-donating amino groups substantially red-shifting the absorption peaks relative to those of the analogous *tert*-butyl- and dodecyl-substituted tetrabenzopentacenes (Fig. 2 and Fig. S39). The decrease in absorption in the amino-functionalized tetrabenzopentacene's spectrum near 350 nm is attributed to the quinoline component, while the shoulders at 457 nm and 438 nm further highlight amino-

functionalized tetrabenzopentacene's substantial red shift. Fourth, the spectrum obtained for bromo-functionalized tetrabenzopentacene **12** featured prominent absorption peaks at 623 nm and 576 nm as well as a shoulder at 521 nm, with the introduction of the two electron-withdrawing bromo groups substantially blue-shifting the absorption peaks relative to those of the analogous *tert*-butyl- and dodecyl-substituted tetrabenzopentacenes (Fig. 2 and Fig. S39). The decrease in absorption in the bromo-functionalized tetrabenzopentacene's spectrum near 350 nm is attributed to the quinoline component, while the shoulders at 446 nm and 417 nm and local maxima peak at 398 nm further highlight bromo-functionalized tetrabenzopentacene's substantial blue shift. Last, the spectrum obtained for dimeric tetrabenzopentacene **19** featured prominent absorption peaks at 631 nm and 590 nm and no obvious shoulders other than the two shoulders at 413 nm and 392 nm attributed to the tetrabenzopentacene core, with the covalent linkage of the tetrabenzopentacene moieties causing aggregation and broadening/blue-shifting the absorption peaks relative to those of the monomeric tetrabenzopentacenes in agreement with precedent for some previously-reported acenes (Fig. 2 and Fig. S39). [52, 53] Overall, these measurements showed that the electronic properties of our nitrogen-containing tetrabenzoacene derivatives could be controlled to some extent via the described synthetic strategies.

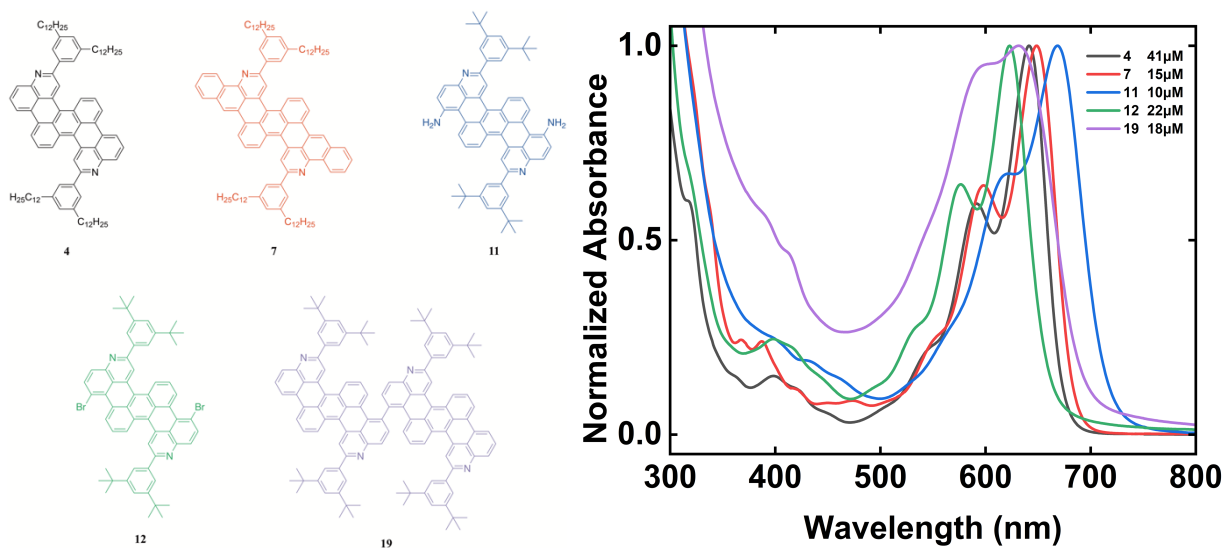


Figure 2. The UV-Vis absorption spectra measured for **4** (black trace), **7** (red trace), **11** (blue trace), **12** (green trace), **19** (purple trace). Note that the absorption spectra were normalized by using their maximum absorbance peak within the 600 nm to 700 nm wavelength range to facilitate direct comparisons.

PART 2. SUPPORTING INFORMATION

2.1. General Methods

A. Materials and conditions. All chemicals and solvents were purchased from Sigma Aldrich, Acros Organics, CombiBlocks, or Thermo Fisher Scientific. Toluene and chloroform were routinely dried with 3 Å molecular sieves and stored under argon. The glassware was oven dried at temperatures of 150 – 200 °C. The reactions were performed under dry argon unless otherwise noted. Additional protocols are noted below for specific compounds where appropriate.

B. Compound purification. Flash chromatography was performed using a CombiFlash Rf 200 purification system (Teledyne ISCO, Inc.) according to the manufacturer's recommended protocols. Chromatography solvents are reported as percentages followed by solvent combinations. Additional purification-relevant information is noted below for specific compounds where appropriate.

C. Nuclear magnetic resonance (NMR) spectroscopy characterization. The intermediates and products were characterized with ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy in the University of California, Irvine Nuclear Magnetic Resonance Facility. The NMR measurements were performed on either a Bruker DRX500 instrument outfitted with a CryoProbe (Bruker TCI 500 MHz, 5 mm diameter tubes) or an AVANCE600 instrument outfitted with a CryoProbe (Bruker CBBFO 600 MHz, 5 mm diameter tubes). The NMR experiments were typically performed at compound concentrations of $\sim 1 \text{ mg mL}^{-1}$ to $\sim 10 \text{ mg mL}^{-1}$. The chemical shifts were reported in ppm for both the ^1H and ^{13}C NMR spectra. The chemical shifts for the NMR data were referenced as follows: for compounds in CDCl_3 , the ^1H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm or the residual CHCl_3 peak at 7.26 ppm, and the ^{13}C NMR spectra were referenced to the residual CHCl_3 peak at 77.16 ppm; for compounds in CS_2 , the ^1H

NMR spectra were referenced to TMS at 0.00 ppm, and the ^{13}C NMR spectra were referenced to TMS at 0.00 ppm. Both the ^1H and ^{13}C NMR data were labeled with the chemical shifts, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br s = broad singlet), coupling constants in Hertz, and integration values. The NMR spectra were processed and analyzed by using the MestReNova software package.

D. Mass (MS) spectroscopy characterization. The intermediates and products were characterized with electrospray ionization (ESI) high resolution mass spectrometry (HRMS) or matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry at the University of California, Irvine Mass Spectrometry Facility. The HRMS measurements were performed on a Waters LCT Premier time-of-flight instrument, and the MALDI-TOF measurements were performed on an AB SCIEX TOF/TOFTM 5800 series mass spectrometer using a 349 nm Nd:YAG laser with either TCNQ or dithranol as the matrix. The mass spectra were processed and analyzed by using the standard MassLynx and TOF/TOF Series Explorer software packages.

E. Ultraviolet-visible (UV-Vis) spectroscopy characterization. The products were characterized with UV-Vis spectroscopy at the University of California, Irvine Laser Spectroscopy Laboratory. The measurements were performed on a Jasco-V670 Absorption Spectrometer. The measurements were conducted in ambient atmosphere at room temperature. The UV-Vis spectroscopy experiments were repeated for at least three independently prepared solutions in CHCl_3 for each compound at concentrations between $\sim 10\ \mu\text{M}$ and $\sim 41\ \mu\text{M}$ (Fig. 2) or at concentrations between $\sim 35\ \mu\text{M}$ and $\sim 84\ \mu\text{M}$ (Fig. S39). The spectra were processed and analyzed with the Jasco Spectra Manager Suite and Origin software packages.

2.2. Detailed Synthetic Protocols

A. 1,5-Dichloro-9,10-diethynylantracene (1). ((1,5-Dichloroanthracene-9,10-diyl)bis(ethyne-2,1-diyl))bis(triisopropylsilane) (0.9770 g, 1.607 mmol) was dissolved in tetrahydrofuran (77 mL) under argon and cooled to -78 °C. Tetrabutylammonium fluoride (1 M, 4.8 mmol) in tetrahydrofuran (4.8 mL) was added dropwise to the solution over 13 minutes, and the mixture was stirred at -78 °C for 1 hour. The mixture was warmed to 0 °C and placed into a dry ice/acetone bath when a color change was observed. The mixture was diluted with a saturated aqueous sodium bicarbonate solution (25 mL), subsequently warmed to room temperature, and further diluted with a saturated sodium bicarbonate solution (50 mL). The reaction mixture was poured into dichloromethane (700 mL), the aqueous and organic phases were separated, and the aqueous phase was extracted with dichloromethane (100 mL). The combined organics were washed with a saturated sodium bicarbonate solution (50 mL) and brine (100 mL). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by washing with cold hexanes to obtain the desired product (0.4440 g, 94%), and the characterization data matched those previously reported. [32]

B. (*E*)-1-(3,5-Didodecylphenyl)-*N*-phenylmethanimine (2). Aniline (0.21 mL, 2.32 mmol), 3,5-didodecylbenzaldehyde (1.00 g, 2.26 mmol), glacial acetic acid (0.10 mL, 1.75 mmol), and 3 Å molecular sieves (1.00 g) were combined in toluene (30 mL). The mixture was sealed in a pressure vessel and heated at 150 °C for 16 hours. The reaction mixture was cooled and filtered through Celite, and the solvent was removed *in vacuo*. The crude product was isolated without further purification in the yields previously reported (1.10 g, 94%), and the characterization data matched those previously reported. [39]

C. 4,4'-(1,5-Dichloroanthracene-9,10-diyl)bis(2-(3,5-didodecylphenyl)quinoline) (3).

Compound **2** (6.57 g, 12.7 mmol), 1,5-dichloro-9,10-diethynylantracene **1** (1.25 g, 4.23 mmol), chloranil (2.29 g, 9.31 mmol), and $\text{BF}_3 \cdot \text{OEt}_2$ (1.57 mL, 12.7 mmol) were dissolved in chloroform (200 mL) under argon. The reaction mixture was heated at 70 °C for 48 hours. The reaction mixture was cooled, poured into chloroform (300 mL), and washed with a saturated aqueous sodium bicarbonate solution (500 mL \times 4) and water (500 mL \times 3). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was triturated with ethanol and purified by flash chromatography (100/0 to 70/30 hexanes/ethyl acetate) to obtain the desired product as two atropisomers (2.05 g (*isomer 1* + *isomer 2*), 37%). (*isomer 1*): ^1H NMR (500 MHz, CDCl_3) δ 8.36 (d, J = 8.4 Hz, 2H), 8.02 (s, 2H), 7.90 (s, 4H), 7.75 (ddd, J = 8.5, 6.8, 1.4 Hz, 2H), 7.51 – 7.48 (m, 2H), 7.47 (s, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.13 (t, J = 8.1 Hz, 4H), 2.70 (t, J = 7.9 Hz, 8H), 1.69 (quint, J = 7.7 Hz, 8H), 1.42 – 1.20 (m, 55H), 0.87 (t, J = 6.9 Hz, 12H); (*isomer 2*): ^1H NMR (500 MHz, CDCl_3) δ 8.36 (d, J = 8.5 Hz, 2H), 7.94 (s, 2H), 7.86 (s, 4H), 7.77 (ddd, J = 8.3, 6.5, 1.6 Hz, 2H), 7.47 (t, J = 7.8 Hz, 4H), 7.43 – 7.35 (m, 4H), 7.16 – 7.10 (m, 4H), 2.69 (t, J = 7.8 Hz, 8H), 1.68 (quint, J = 7.8 Hz, 8H), 1.46 – 1.07 (m, 76H), 0.87 (t, J = 6.9 Hz, 13H); (*isomer 1*): ^{13}C NMR (151 MHz, CDCl_3) δ 157.1, 148.6, 148.1, 143.8, 139.5, 134.1, 133.4, 131.2, 130.4, 130.3, 130.1, 129.8, 129.1, 127.8, 127.4, 126.7, 126.3, 125.9, 125.3, 122.5, 36.3, 32.1, 31.9, 29.84, 29.80, 29.72, 29.69, 29.5, 22.8, 14.3; (*isomer 2*): ^{13}C NMR (126 MHz, CDCl_3) δ 157.2, 148.7, 148.2, 143.7, 139.5, 134.1, 133.5, 131.3, 130.4, 130.3, 130.1, 129.8, 129.2, 127.7, 127.5, 126.8, 126.5, 125.9, 125.3, 122.3, 36.3, 32.1, 31.9, 29.84, 29.80, 29.71, 29.67, 29.51, 22.8, 14.3; MALDI (dithranol) m/z calcd. for $\text{C}_{92}\text{H}_{123}\text{Cl}_2\text{N}_2$ $[\text{M}+\text{H}]^+$ 1325.9, found 1325.9.

D. 2,11-Bis(3,5-didodecylphenyl)dibenzo[hi:st]dipyrido[2,3,4-de:2,3,4-op]pentacene (4).

Anhydrous quinoline (38 mL) was added to compound **3** (0.500 g, 0.377 mmol) and powdered KOH (2.54 g, 45.3 mmol) under argon, and the solution was sparged with argon for 15 minutes. The mixture was heated at 150 °C for 2 hours. The reaction mixture was cooled, poured into chloroform (100 mL), and washed with water (100 mL), an aqueous 2.4 M HCl solution (100 mL × 4), water (100 mL × 2), and a saturated aqueous sodium bicarbonate solution (100 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 (100/0 to 90/10 hexanes/ethyl acetate) to obtain the desired product as a dark blue solid (0.124 g, 26%). ¹H NMR (600 MHz, CDCl₃) δ 8.58 (d, *J* = 8.6 Hz, 2H), 8.40 (s, 2H), 8.29 – 8.23 (m, 4H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.74 (m, 6H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.14 (s, 2H), 2.72 (t, *J* = 7.9 Hz, 8H), 1.71 (quint, *J* = 7.6 Hz, 8H), 1.52 – 1.00 (m, 72H), 0.86 (t, *J* = 7.0 Hz, 12H); ¹³C NMR (151 MHz, CDCl₃) δ 158.6, 149.6, 143.7, 139.8, 138.6, 130.8, 130.03, 130.00, 129.9, 129.5, 129.23, 129.20, 127.9, 127.7, 126.3, 125.1, 123.7, 121.4, 120.3, 119.4, 36.3, 32.1, 31.7, 29.9, 29.8, 29.7, 29.6, 29.5, 22.8, 14.3; HRMS (ESI) *m/z* calcd. for C₉₂H₁₂₁N₂ [M+H]⁺ 1253.9530, found 1253.9557.

E. N-(3,5-Didodecylbenzylidene)naphthalen-1-amine (5). 1- Naphthylamine (2.13 g, 14.9 mmol), 3,5-didodecylbenzaldehyde (6.00 g, 13.6 mmol), and glacial acetic acid (0.10 mL, 1.75 mmol) were dissolved in toluene (200 mL). The vessel containing the solution was equipped with a Dean–Stark trap, and the mixture was refluxed for 24 hours. 3 Å molecular sieves (10.0 g) were added to the solution, and the mixture was refluxed for another 24 hours. The reaction mixture was cooled and filtered through Celite, and the solvent was removed *in vacuo*. The crude product was purified by rinsing with methanol, dissolution in a minimum amount of chloroform, and

precipitation from methanol to obtain the desired product (6.13 g, 80%). ¹H NMR (500 MHz, CDCl₃) δ 8.52 (s, 1H), 8.41 – 8.36 (m, 1H), 7.90 – 7.85 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.68 (s, 2H), 7.57 – 7.51 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 2.71 (t, *J* = 7.9 Hz, 4H), 1.71 (quint, *J* = 7.5 Hz, 4H), 1.44 – 1.23 (m, 37H), 0.92 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 161.3, 149.8, 143.7, 136.5, 134.0, 132.2, 128.9, 127.7, 126.6, 126.5, 126.2, 125.8, 125.7, 124.2, 112.9, 36.0, 32.1, 31.7, 29.85, 29.81, 29.78, 29.69, 29.55, 29.52, 22.9, 14.3; HRMS (ESI) *m/z* calcd. for C₄₁H₆₁NNa [M + Na]⁺ 590.4702, found 590.4702.

F. 4,4'-(1,5-Dichloroanthracene-9,10-diyl)bis(2-(3,5-didodecylphenyl)benzo[*h*]quinoline) (6).

Compound **5** (2.71 g, 4.77 mmol), 1,5-dichloro-9,10-diethynylantracene **1** (0.47 g, 1.59 mmol), chloranil (0.78 g, 3.17 mmol), and BF₃·OEt₂ (0.59 mL, 4.78 mmol) were dissolved in chloroform (80 mL) under argon. The reaction mixture was heated at 70 °C for 48 hours. The reaction mixture was cooled, poured into chloroform (100 mL), and washed with a saturated aqueous sodium bicarbonate solution (100 mL × 3) and water (100 mL × 3). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was triturated with hot ethanol, purified by flash chromatography (100/0 to 80/20 hexanes/chloroform), redissolved in chloroform, and precipitated from ethanol to obtain the desired product as two atropisomers (0.69 g (*isomer 1* + *isomer 2*), 30%). (*isomer 1*): ¹H NMR (500 MHz, CDCl₃) δ 9.71 (d, *J* = 8.2 Hz, 2H), 8.16 (s, 2H), 8.07 (s, 4H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.86 (t, *J* = 8.3 Hz, 2H), 7.77 – 7.73 (m, 2H), 7.64 (d, *J* = 9.1 Hz, 2H), 7.51 – 7.46 (m, 4H), 7.20 (d, *J* = 8.9 Hz, 2H), 7.16 (s, 2H), 7.12 (dd, *J* = 9.0, 7.2 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 8H), 1.74 (quint, *J* = 7.6 Hz, 8H), 1.50 – 1.15 (m, 71H), 0.87 (t, *J* = 7.0 Hz, 12H); (*isomer 2*): ¹H NMR (500 MHz, CDCl₃) δ 9.71 (d, *J* = 8.2 Hz, 2H), 8.06 (s, 2H), 8.03 (s, 4H), 7.93 (d, *J* = 8.1 Hz, 2H), 7.90 – 7.84 (m, 2H), 7.79 – 7.74 (m, 2H), 7.69 (d, *J* =

8.9f Hz, 2H), 7.51 – 7.45 (m, 4H), 7.30 (d, $J = 9.0$ Hz, 2H), 7.15 – 7.08 (m, 4H), 2.73 (t, $J = 7.8$ Hz, 8H), 1.72 (quint, $J = 7.6$ Hz, 8H), 1.45 – 1.22 (m, 74H), 0.87 (t, $J = 7.0$ Hz, 12H); (*isomer 1*): ^{13}C NMR (126 MHz, CDCl_3) δ 155.3, 148.5, 146.1, 143.7, 139.6, 134.5, 134.0, 133.5, 132.3, 131.4, 130.4, 130.1, 128.5, 128.0, 127.8, 127.4, 127.3, 126.7, 125.9, 125.4, 125.3, 123.6, 122.4, 36.4, 32.1, 32.0, 29.9, 29.84, 29.82, 29.76, 29.70, 29.5, 22.8, 14.3; (*isomer 2*): ^{13}C NMR (126 MHz, CDCl_3) δ 155.4, 148.5, 146.1, 143.7, 139.6, 134.4, 134.0, 133.5, 132.3, 131.5, 130.4, 130.0, 128.5, 128.0, 127.9, 127.7, 127.5, 127.3, 126.7, 126.0, 125.4, 125.2, 123.8, 122.2, 36.4, 32.1, 31.9, 29.86, 29.82, 29.81, 29.74, 29.66, 29.5, 22.8, 14.3; MALDI (dithranol) m/z calcd. for $\text{C}_{100}\text{H}_{127}\text{Cl}_2\text{N}_2$ $[\text{M}+\text{H}]^+$ 1425.9, found 1425.6.

G. 2,13-Bis(3,5-didodecylphenyl)dibenzo[*jk:yz*]dipyrido[2,3,4-*fg*:2,3,4-*uv*]heptacene (7).

Anhydrous quinoline (35 mL) was added to compound **6** (0.500 g, 0.350 mmol) and powdered KOH (2.36 g, 42.1 mmol) under argon, and the solution was sparged with argon for 15 minutes. The mixture was heated at 150 °C for 2 hours. The reaction mixture was cooled, poured into chloroform (100 mL), and washed with water (100 mL), an aqueous 2.4 M HCl solution (100 mL \times 4), water (100 mL \times 2), and a saturated aqueous sodium bicarbonate solution (100 mL \times 3). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (100/0 to 80/20 hexanes/chloroform) to obtain the desired product as a dark blue solid (0.151 g, 32%). ^1H NMR (500 MHz, CDCl_3) δ 9.32 (d, $J = 7.5$ Hz, 2H), 8.47 (d, $J = 8.6$ Hz, 2H), 8.44 (s, 2H), 8.32 (s, 2H), 8.15 (d, $J = 7.6$ Hz, 2H), 7.94 – 7.86 (m, 6H), 7.71 – 7.61 (m, 4H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.15 (s, 2H), 2.76 (t, $J = 7.8$ Hz, 8H), 1.75 (quint, $J = 7.6$ Hz, 8H), 1.48 – 1.17 (m, 77H), 0.85 (t, $J = 7.0$ Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 156.0, 147.0, 143.5, 139.9, 138.3, 133.8, 131.4, 130.0, 129.8, 129.1, 129.0, 128.5, 128.3,

127.9, 127.5, 127.3, 127.1, 126.1, 125.1, 121.4, 121.0, 120.9, 118.8, 36.3, 32.1, 31.8, 29.89, 29.87, 29.83, 29.80, 29.7, 29.5, 22.8, 14.3; MALDI (TCNQ) m/z calcd. for $C_{100}H_{124}N_2 [M]^+$ 1353.0, found 1352.7; HRMS (ESI) m/z calcd. for $C_{100}H_{125}N_2 [M+H]^+$ 1353.9843, found 1353.9814.

H. (E)-1-(3,5-Di-*tert*-butylphenyl)-N-(4-nitrophenyl)methanimine (8). p-Nitro aniline (6.95 g, 50.3 mmol), 3,5-ditertbutylbenzaldehyde (10.0 g, 45.8 mmol), glacial acetic acid (0.10 mL, 1.75 mmol), and 3 Å molecular sieves (20.0 g) were combined in toluene (135 mL). The mixture was sealed in a pressure vessel and heated at 130 °C for 16 hours. The reaction mixture was cooled and filtered through Celite, and the solvent was removed *in vacuo*. The crude product was purified by recrystallization from methanol to obtain the desired product (8.52 g, 55%). 1H NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.27 (dt, $J = 9.5, 2.5, 2H$), 7.76 (d, $J = 1.9$ Hz, 2H), 7.63 (t, $J = 1.8$ Hz, 1H), 7.24 (dt, $J = 9.4, 2.5, 2H$), 1.39 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 158.6, 151.9, 145.5, 135.0, 127.1, 125.2, 123.9, 121.4, 35.1, 31.5. MALDI m/z calcd. for $C_{21}H_{27}N_2O_2 [M+H]^+$ 339.2, found 339.1

I. 4,4'-(1,5-dichloroanthracene-9,10-diyl)bis(2-(3,5-di-*tert*-butylphenyl)-6-nitroquinoline) (9): Compound **8** (6.86 g, 20.3 mmol), 1,5-dichloro-9,10-diethynylanthracene **1** (3.00 g, 10.2 mmol), and chloranil (7.46 g, 30.3 mmol) were dissolved in chloroform (500 mL) under argon. $BF_3 \cdot OEt_2$ (3.76 mL, 30.5 mmol) was added to the solution, and the mixture was heated at 70 °C for 16 hours. The reaction mixture was cooled and washed with a saturated aqueous sodium bicarbonate solution (100 mL \times 3) and water (100 mL \times 3). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (100/0 to 90/10 hexanes/ethyl acetate) to obtain the desired product (2.46 g

(*isomer 1* + *isomer 2*), 25%). (*isomer 1*): ^1H NMR (600 MHz, CDCl_3) δ 8.53 (dd, $J = 9.2, 2.3$ Hz, 2H), 8.50 (d, $J = 9.2$ Hz, 2H), 8.21 (s, 2H), 8.18 (d, $J = 2.2$ Hz, 2H), 8.17-8.15 (m, 4H), 7.65 (s, 2H), 7.55 (d, $J = 7.1$ Hz, 2H), 7.42 (d, $J = 9.2$ Hz, 2H), 7.22 (dd, $J = 9.1, 7.1$ Hz, 2H), 1.44 (s, 34H); (*isomer 2*): ^1H NMR (600 MHz, CDCl_3) δ 8.55 (dd, $J = 9.2, 2.5$ Hz, 2H), 8.50 (d, $J = 9.2$ Hz, 2H), 8.30 (d, $J = 2.4$ Hz, 2H), 8.12 (d, $J = 1.8$ Hz, 4H), 8.08 (s, 2H), 7.63 (t, $J = 1.8$ Hz, 2H), 7.55 (dd, $J = 7.1, 1.1$ Hz, 2H), 7.41 (dd, $J = 9.2, 1.1$ Hz, 2H), 7.22 (dd, $J = 9.1, 7.1$ Hz, 2H), 1.42 (s, 35H); (*isomer 1*): ^{13}C NMR (151 MHz, CDCl_3) δ 169.7, 161.1, 151.9, 150.6, 150.5, 145.6, 141.0, 137.8, 133.6, 132.8, 132.2, 131.1, 131.0, 128.1, 127.6, 127.5, 126.7, 125.4, 124.1, 123.4, 123.0, 122.5, 119.1, 35.3, 31.7; (*isomer 2*): ^{13}C NMR (151 MHz, CDCl_3) δ 160.7, 151.9, 150.6, 150.4, 145.8, 141.0, 137.8, 133.5, 132.9, 132.1, 131.2, 131.1, 128.1, 127.6, 127.3, 126.8, 125.3, 123.7, 123.6, 123.2, 122.4, 119.0, 35.3, 31.7, HRMS (ESI) m/z calcd. for $\text{C}_{60}\text{H}_{56}\text{Cl}_2\text{N}_4\text{O}_4\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 989.3576, found 989.3599.

J. 4,4'-(1,5-dichloroanthracene-9,10-diyl)bis(2-(3,5-di-*tert*-butylphenyl)quinolin-6-amine) (10): Compound **9** (1.00 g, 1.03 mmol), Fe powder (3.63 g, 65.0 mmol), and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (3.17 g, 21.6 mmol) were dissolved in ethanol (400 mL), chloroform (250 mL), and water (40 mL). The mixture was refluxed at 70 °C for 16 hours. The reaction mixture was cooled, filtered through Celite, and washed with water (100 mL \times 2). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (80/20 hexanes/ethyl acetate) to obtain the desired product (0.5793 g, 62%). ^1H NMR (500 MHz, CDCl_3) δ 8.18 (d, $J = 8.8$ Hz, 2H), 8.06 (s, 4H), 7.88 (s, 2H), 7.61-7.51 (m, 4H), 7.50 (d, $J = 7.1$ Hz, 2H), 7.19 (dd, $J = 9.0, 2.4$ Hz, 2H), 7.15 (dd, $J = 9.0, 7.2$ Hz, 2H), 6.33 (d, $J = 2.5$ Hz, 2H), 3.77 (br s, 4H), 1.43 (s, 39H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.2, 151.3, 144.8, 143.3, 139.2, 134.5, 133.4,

131.5, 131.4, 130.5, 130.4, 128.0, 127.3, 125.7, 123.4, 122.7, 122.5, 121.9, 121.7, 106.6, 35.2, 31.7. MALDI m/z calcd. for $C_{60}H_{61}Cl_2N_4$ $[M+H]^+$ 907.4, found 907.3.

K. 2,11-bis(3,5-di-*tert*-butylphenyl)perylene[1,2,3-*de*:7,8,9-*d'e'*]diquinoline-6,15-diamine (11): Anhydrous quinoline (70 mL) was added to compound **10** (1.00 g, 1.10 mmol) and powdered KOH (5.65 g, 101 mmol) under argon, and the solution was sparged with argon for 20 minutes. The mixture was heated at 150 °C for 2 hours. The reaction mixture was cooled, poured into chloroform (100 mL), and washed with water (50 mL \times 2), an aqueous 2.4 M HCl solution (50 mL \times 2), a saturated aqueous sodium bicarbonate solution (50 mL \times 2), and water (50 mL \times 2). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (70/30 hexanes/ethyl acetate) to obtain the desired product as a dark blue solid (0.1840 g, 20%). 1H NMR (600 MHz, $CDCl_3$) δ 8.33 (dd, J = 12.1, 8.0 Hz, 4H), 8.26 (s, 2H), 7.94 (d, J = 1.7 Hz, 4H), 7.88 (d, J = 8.9 Hz, 2H), 7.56 (t, J = 1.8 Hz, 2H), 7.39 (t, J = 8.0 Hz, 2H), 7.14 (d, J = 8.9 Hz, 2H), 4.55 (br s, 4H), 1.43 (s, 41H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 151.3, 144.4, 143.3, 139.7, 137.1, 130.4, 130.1, 129.8, 128.2, 127.0, 126.6, 126.2, 125.4, 123.5, 123.3, 121.7, 120.8, 118.5, 112.6, 35.2, 31.7. HRMS (ESI) m/z calcd. for $C_{60}H_{59}N_4$ $[M + H]^+$ 835.4740, found 835.4731.

L. 6,15-dibromo-2,11-bis(3,5-di-*tert*-butylphenyl)perylene[1,2,3-*de*:7,8,9-*d'e'*]diquinoline (12): Compound **11** (0.10 g, 0.12 mmol) and *p*-toluenesulfonic acid monohydrate (1.82 g, 9.57 mmol) were dissolved in CH_3CN (10 mL) and $CHBr_3$ (5 mL) at 0 °C, and the solution was stirred under argon for 10 minutes. $NaNO_2$ (0.49 g, 7.1 mmol) and KBr (1.14 g, 9.58 mmol) in water (5 mL) were added to the solution, and the mixture was stirred at 0 °C for 10 minutes. The reaction

mixture was diluted with chloroform (50 mL) and washed with a saturated aqueous sodium bicarbonate solution (50 mL × 2) and water (50 mL × 2). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (90/10 hexane/ethyl acetate) to obtain the desired product as a dark blue film (0.0193 g, 17%). ¹H NMR (500 MHz, CDCl₃) δ 9.18 (d, *J* = 7.2 Hz, 2H), 8.53 (d, *J* = 8.7 Hz, 2H), 8.26 (s, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 8.00 – 7.94 (m, 6H), 7.61 (t, *J* = 1.8 Hz, 2H), 7.47 (t, *J* = 8.1 Hz, 2H), 1.44 (s, 37H). ¹³C NMR (126 MHz, CDCl₃) δ 158.8, 151.6, 148.0, 139.0, 137.9, 137.3, 129.6, 129.5, 129.1, 128.7, 128.1, 126.9, 126.72, 126.66, 126.5, 125.7, 124.2, 122.1, 119.7, 117.8, 35.3, 31.7. MALDI *m/z* calcd. for C₆₀H₅₅Br₂N₂ [M+H]⁺ 961.3, found 961.2; HRMS (ESI) *m/z* calcd. for C₆₀H₅₅Br₂N₂ [M+H]⁺ 961.2732, found 961.2715.

M. 2-(3,5-di-tert-butylphenyl)-4-(1,5-dichloro-10-ethynylantracen-9-yl)-6-nitroquinoline (13): Compound **8** (3.43 g, 10.1 mmol), 1,5-dichloro-9,10-diethynylantracene **1** (3.00 g, 10.2 mmol), and chloranil (3.73 g, 15.2 mmol) was dissolved in chloroform (350 mL) under argon. BF₃·OEt₂ (1.88 mL, 15.2 mmol) was added to the solution, and the mixture was heated at 30 °C for 16 hours. The reaction mixture was cooled and washed with a saturated aqueous sodium bicarbonate solution (100 mL × 3) and water (100 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 (90/10 hexanes/ethyl acetate) to obtain the desired product (2.8877 g, 45%). ¹H NMR (500 MHz, CDCl₃) δ 9.13 – 9.07 (m, 1H), 8.52 – 8.42 (m, 3H), 8.09 – 8.05 (m, 2H), 7.94 (s, 1H), 7.66 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.61 (t, *J* = 1.8 Hz, 1H), 7.57 (s, 1H), 7.56 (d, *J* = 1.8 Hz, 1H), 7.20 – 7.17 (m, 1H), 7.15 – 7.11 (m, 1H), 4.38 (s, 1H), 1.44 – 1.30 (m, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 169.7, 160.7, 151.8, 141.0, 136.7, 133.2, 132.2, 132.0, 131.6, 131.2, 130.74, 130.65,

130.0, 128.1, 127.2, 126.8, 126.5, 125.3, 123.7, 123.4, 123.0, 122.4, 96.6, 35.3, 31.6; MALDI m/z calcd. for $C_{39}H_{33}Cl_2N_2O_2$ $[M+H]^+$ 631.19, found 631.16.

N. (*E*)-1-(3,5-Di-*tert*-butylphenyl)-*N*-phenylmethanimine (14). Aniline (5.01 mL, 55.4 mmol), 3,5-di-*tert*-butylbenzaldehyde (10.0 g, 45.8 mmol), and *p*-toluenesulfonic acid monohydrate (0.44 g, 2.31 mmol) were dissolved in toluene (250 mL). The vessel containing the solution was equipped with a Dean-Stark trap, and the mixture was refluxed for 16 hours. The reaction mixture was cooled and washed with a saturated aqueous sodium bicarbonate solution (250 mL). The organics were dried with anhydrous sodium sulfate, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography to obtain the pure product in the yields previously reported (12.0 g, 89%), and the characterization data matched those previously reported. [32]

O. 2-(3,5-Di-*tert*-butylphenyl)-4-(1,5-dichloro-10-(2-(3,5-di-*tert*-butylphenyl)quinolin-4-yl)anthracen-9-yl)-6-nitroquinoline (15): Compound **14** (1.40 g, 4.77 mmol), compound **13** (2.00 g, 3.17 mmol), and chloranil (1.16 g, 4.72 mmol) were dissolved in chloroform (150 mL) under argon. $BF_3 \cdot OEt_2$ (0.55 mL, 4.46 mmol) was added to the solution, and the mixture was heated at 70 °C for 16 hours. The reaction mixture was cooled and 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 by flash chromatography (80/20 hexanes/ethyl acetate) to obtain the desired product (1.4584 g, 50%). 1H NMR (500 MHz, $CDCl_3$) δ 8.59 – 8.48 (m, 2H), 8.41 (d, J = 8.5 Hz, 1H), 8.32 (d, J = 2.5 Hz, 1H), 8.14 (d, J = 1.9 Hz, 2H), 8.13 – 8.04 (m, 3H), 7.95 (s, 1H), 7.86 – 7.75 (m, 1H), 7.68 – 7.60

(m, 1H), 7.60 – 7.54 (m, 2H), 7.56 – 7.49 (m, 3H), 7.49 – 7.41 (m, 2H), 7.37 (d, $J = 9.0$ Hz, 1H), 7.22 – 7.13 (m, 2H), 1.46 (s, 18H), 1.44 (s, 18H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.8, 157.6, 151.83, 151.82, 151.4, 151.1, 150.4, 148.3, 148.1, 145.6, 138.9, 137.8, 135.2, 133.6, 133.5, 132.1, 131.80, 131.77, 130.9, 130.6, 130.3, 129.9, 129.0, 128.3, 128.1, 127.55, 127.51, 127.47, 127.1, 126.9, 126.6, 126.5, 126.2, 125.3, 124.1, 123.8, 123.4, 122.41, 122.38, 122.2, 122.1, 35.31, 35.29, 35.25, 31.71, 31.67; MALDI m/z calcd. for $\text{C}_{60}\text{H}_{58}\text{Cl}_2\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 922.39, found 922.33.

P. 2-(3,5-Di-*tert*-butylphenyl)-4-(1,5-dichloro-10-(2-(3,5-di-*tert*-butylphenyl)quinolin-4-yl)anthracen-9-yl)quinolin-6-amine (16). Compound **15** (2.00 g, 2.17 mmol), Fe powder (3.63 g, 65.0 mmol), and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (3.17 g, 21.6 mmol) were dissolved in ethanol (400 mL), chloroform (250 mL), and water (40 mL). The mixture was refluxed at 70 °C for 16 hours. The reaction mixture was cooled, filtered through Celite, and washed with water (100 mL \times 2). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (80/20 hexanes/ethyl acetate) to obtain the desired product (1.2538 g, 65%). ^1H NMR (500 MHz, CDCl_3) δ 8.39 (d, $J = 8.0$ Hz, 1H), 8.19 (d, $J = 8.7$ Hz, 1H), 8.09 (d, $J = 1.8$ Hz, 2H), 8.02 (d, $J = 1.8$ Hz, 2H), 7.99 (s, 1H), 7.86 (s, 1H), 7.77 (ddd, $J = 8.4, 6.7, 1.5$ Hz, 1H), 7.61 – 7.45 (m, 6H), 7.43 – 7.36 (m, 1H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.21 (d, $J = 8.9$ Hz, 1H), 7.18 – 7.09 (m, 2H), 6.36 (d, $J = 2.5$ Hz, 1H), 3.82 (br s, 2H), 1.42 (s, 18H), 1.41 (s, 18H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.8, 151.5, 151.3, 148.1, 144.8, 143.5, 138.9, 133.5, 133.4, 131.6, 131.1, 130.5, 130.40, 130.35, 129.7, 129.1, 128.0, 127.7, 127.5, 127.3, 126.6, 126.3, 125.9, 124.1, 123.4, 122.6, 122.4, 122.1, 121.9, 121.7, 119.2, 106.7, 35.3, 35.2, 31.7; MALDI m/z calcd. for $\text{C}_{60}\text{H}_{60}\text{Cl}_2\text{N}_3$ $[\text{M}+\text{H}]^+$ 892.42, found 892.33.

Q. 2,11-Bis(3,5-di-*tert*-butylphenyl)perylene[1,2,3-*de*:7,8,9-*d'e'*]diquinolin-6-amine (17):

Anhydrous quinoline (70 mL) was added to compound **16** (1.0 g, 1.1 mmol) and powdered KOH (5.650 g, 100.7 mmol) under argon, and the solution was sparged with argon for 20 minutes. The mixture was heated at 150 °C for 2 hours. The reaction mixture was cooled, poured into chloroform (100 mL), and washed with water (50 mL × 2), an aqueous 2.4 M HCl solution (50 mL × 2), a saturated aqueous sodium bicarbonate solution (50 mL × 2), and water (50 mL × 2). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (70/30 hexanes/ethyl acetate) to obtain the desired product (0.1821 g, 20%). ¹H NMR (500 MHz, CDCl₃) δ 8.58 (d, *J* = 8.7 Hz, 1H), 8.51 (d, *J* = 7.5 Hz, 1H), 8.49 – 8.43 (m, 2H), 8.31 (s, 1H), 8.19 – 8.11 (m, 2H), 8.07 – 8.02 (m, 2H), 8.00 (d, *J* = 2.0 Hz, 2H), 7.95 (d, *J* = 1.8 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.49 – 7.44 (m, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 4.81 (br s, 2H), 1.46 (s, 17H), 1.42 (s, 17H); ¹³C NMR (126 MHz, CDCl₃) δ 159.1, 155.6, 151.43, 151.36, 150.6, 149.5, 144.6, 143.9, 139.6, 139.5, 139.1, 130.8, 130.6, 130.0, 129.8, 129.6, 129.4, 129.0, 128.8, 128.6, 127.9, 127.6, 127.0, 126.7, 125.6, 125.3, 123.92, 123.87, 123.83, 123.4, 123.1, 122.1, 121.8, 121.6, 121.3, 121.2, 119.9, 119.5, 118.7, 112.5, 35.3, 35.2, 31.72, 31.70; MALDI *m/z* calcd. for C₆₀H₅₈N₃ [M+H]⁺ 820.46, found 820.50.

R. 6-Bromo-2,11-bis(3,5-di-*tert*-butylphenyl)perylene[1,2,3-*de*:7,8,9-*d'e'*]diquinoline (18):

Compound **17** (0.20 g, 0.24 mmol) and *p*-toluenesulfonic acid monohydrate (1.82 g, 9.57 mmol) were dissolved in CH₃CN (15 mL) and CHBr₃ (5 mL) at 0 °C, and the solution was stirred under argon for 10 minutes. NaNO₂ (0.49 g, 7.1 mmol) and KBr (1.14 g, 9.58 mmol) in water (5 mL) were added to the solution, and the mixture was stirred at 0 °C for 10 minutes. The reaction mixture was diluted with chloroform (50 mL) and washed with saturated aqueous sodium bicarbonate

solution (50 mL × 2) and water (50 mL × 2). The organics were filtered through a cotton plug, and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (90/10 hexanes/ethyl acetate) to obtain the desired product (0.0424 g, 20%). ¹H NMR (500 MHz, CDCl₃) δ 9.43 (d, *J* = 7.6 Hz, 1H), 8.76 (d, *J* = 8.7 Hz, 1H), 8.61 (d, *J* = 8.6 Hz, 1H), 8.49 (s, 1H), 8.44 (s, 1H), 8.33 (t, *J* = 7.7 Hz, 2H), 8.20 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.04 (d, *J* = 1.8 Hz, 2H), 8.01 – 7.95 (m, 3H), 7.85 (t, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 8.1 Hz, 2H), 7.65 – 7.55 (m, 3H), 1.44 (s, 19H), 1.43 (s, 19H); ¹³C NMR (126 MHz, CDCl₃) δ 159.3, 158.9, 151.6, 151.5, 149.6, 148.1, 139.4, 139.0, 138.7, 137.9, 137.5, 130.8, 130.1, 130.0, 129.6, 129.5, 129.39, 129.37, 129.2, 129.0, 128.7, 128.6, 127.9, 127.8, 127.0, 126.9, 126.8, 126.6, 126.2, 125.7, 124.2, 124.1, 123.8, 122.1, 122.0, 121.7, 120.4, 120.2, 119.2, 117.8, 35.28, 35.26, 31.72, 31.69; MALDI *m/z* calcd. for C₆₀H₅₆BrN₂ [M+H]⁺ 883.36, found 883.34.

S. 2,2',11,11'-tetrakis(3,5-di-tert-butylphenyl)-6,6'-biperyleno[1,2,3-de:7,8,9-d'e']diquinoline (19): 2,2'-Bipyridyl (0.0703 g, 0.450 mmol) and 1,5-cyclooctadiene (0.05 mL, 0.41 mmol) were dissolved in dimethylformamide (5 mL), and the solution was added to bis(cyclooctadiene)nickel (0.12 g, 0.44 mmol) under argon. The mixture was heated at 60 °C for 30 minutes. Compound **18** (0.20 g, 0.23 mmol) in toluene (10 mL) was added to the solution, and the mixture was heated at 75 °C for 48 hours. The reaction mixture was cooled and washed with an aqueous 1.2 M HCl solution (10 mL), a saturated aqueous sodium bicarbonate solution (10 mL × 2), and water (10 mL × 3). The solvent was removed *in vacuo*. The crude product was purified with flash chromatography (90/10 hexanes/ethyl acetate) and size exclusion chromatography using Bio-bead SX-1 resin (with toluene as the mobile phase) to obtain the desired product as a dark blue film (0.0708 g, 39%). ¹H NMR (600 MHz, CS₂) δ 8.78 (d, *J* = 8.5 Hz, 2H), 8.64 (d, *J* = 8.6 Hz,

2H), 8.56 (s, 2H), 8.45 (s, 2H), 8.39 (d, $J = 7.6$ Hz, 2H), 8.30 (d, $J = 7.7$ Hz, 2H), 8.24 (d, $J = 7.7$ Hz, 2H), 8.05 (d, $J = 8.3$ Hz, 2H), 8.00 (d, $J = 8.7$ Hz, 2H), 7.97 (d, $J = 1.6$ Hz, 4H), 7.90 (d, $J = 1.7$ Hz, 4H), 7.78 (t, $J = 8.0$ Hz, 2H), 7.72 (t, $J = 7.9$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.42 (t, $J = 1.6$ Hz, 2H), 7.34 (t, $J = 1.5$ Hz, 2H), 7.29 (t, $J = 8.1$ Hz, 2H), 1.30 (s, 36H), 1.22 (s, 37H); ^{13}C NMR (151 MHz, CS_2) δ 157.7, 157.5, 150.3, 150.2, 149.2, 148.5, 139.7, 138.4, 138.3, 137.84, 137.80, 133.4, 130.5, 130.3, 130.1, 129.8, 129.53, 129.50, 129.4, 129.3, 129.0, 128.9, 128.4, 127.6, 127.5, 127.3, 126.3, 126.2, 126.1, 125.3, 123.4, 123.2, 123.1, 121.71, 121.65, 121.2, 120.0, 118.8, 118.4, 34.5, 34.4, 31.34, 31.26; HRMS (ESI) m/z calcd. for $\text{C}_{120}\text{H}_{111}\text{N}_4$ $[\text{M} + \text{H}]^+$ 1607.8809, found 1607.8804.

2.3. ¹H NMR and ¹³C NMR Spectroscopy Data

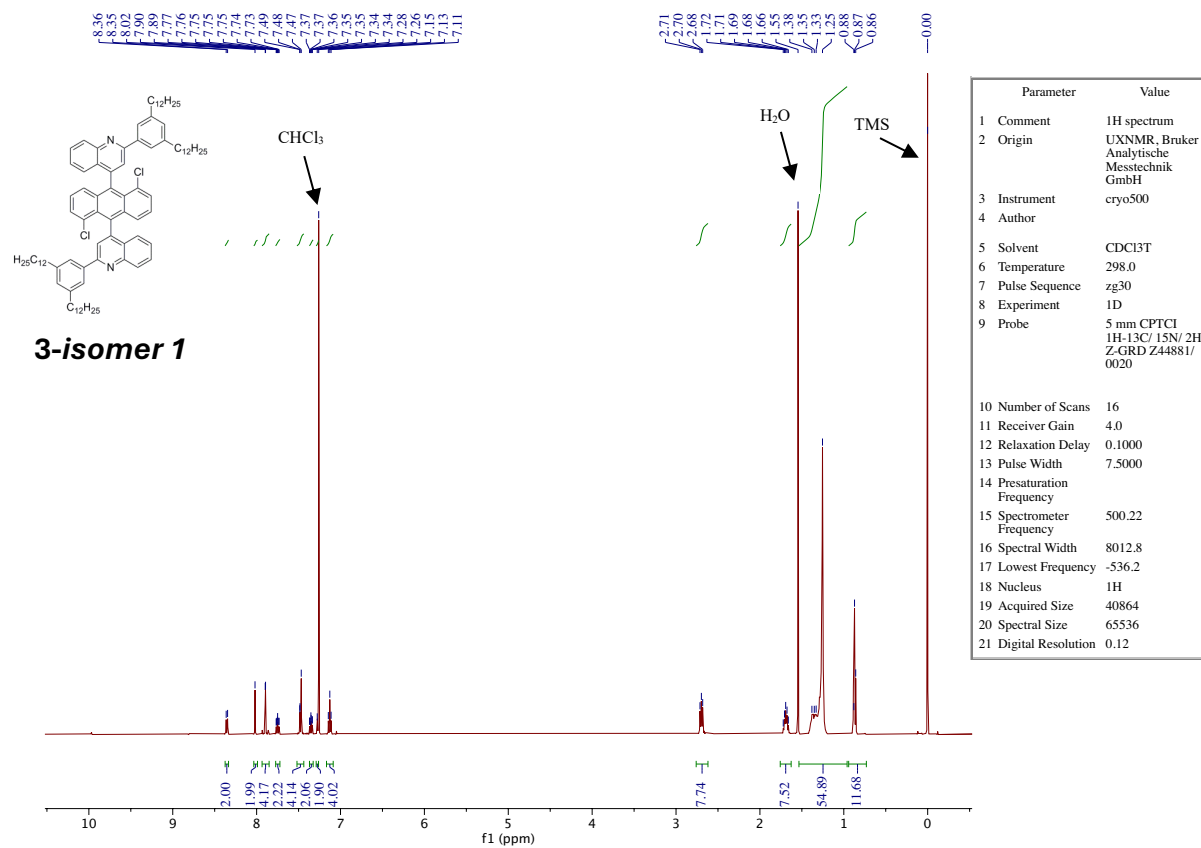


Figure S1. The ¹H NMR spectrum obtained for **3-isomer 1**.

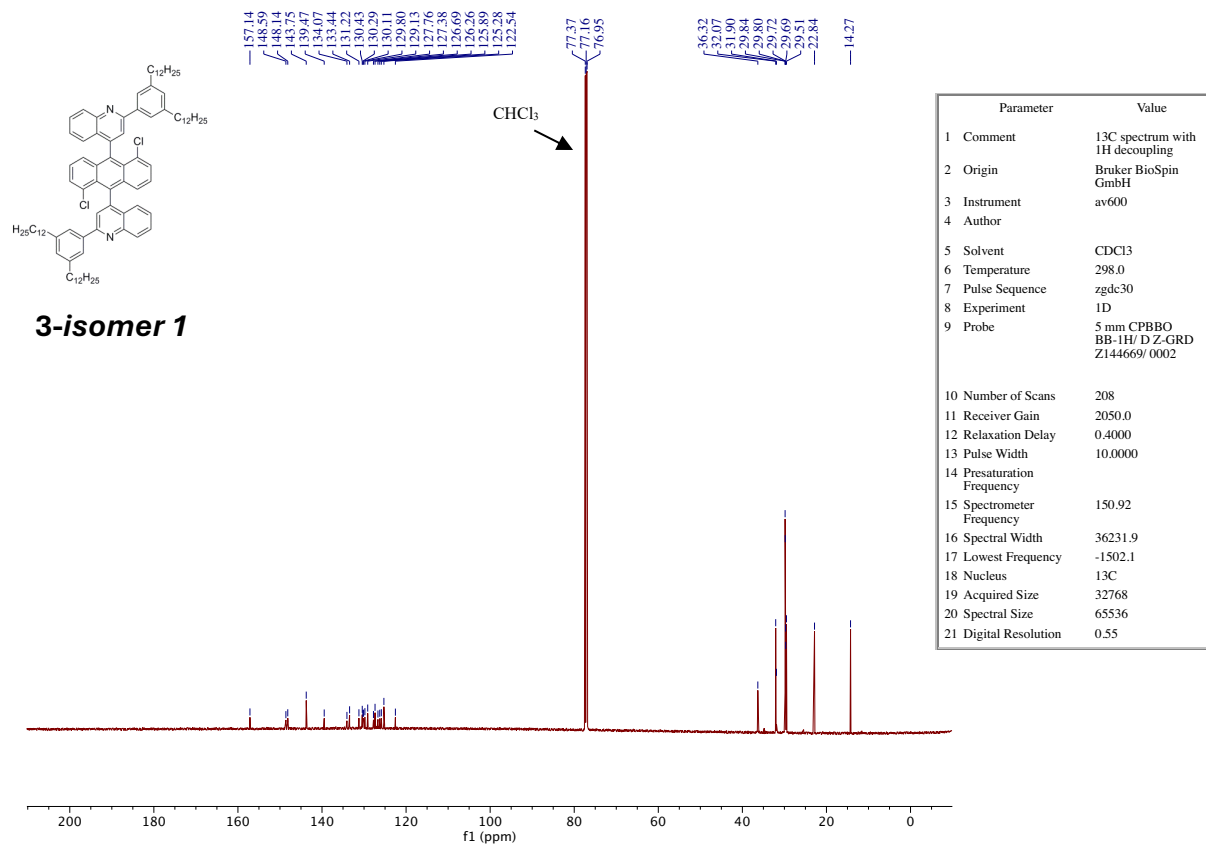


Figure S2. The ¹³C NMR spectrum obtained for **3-isomer 1**.

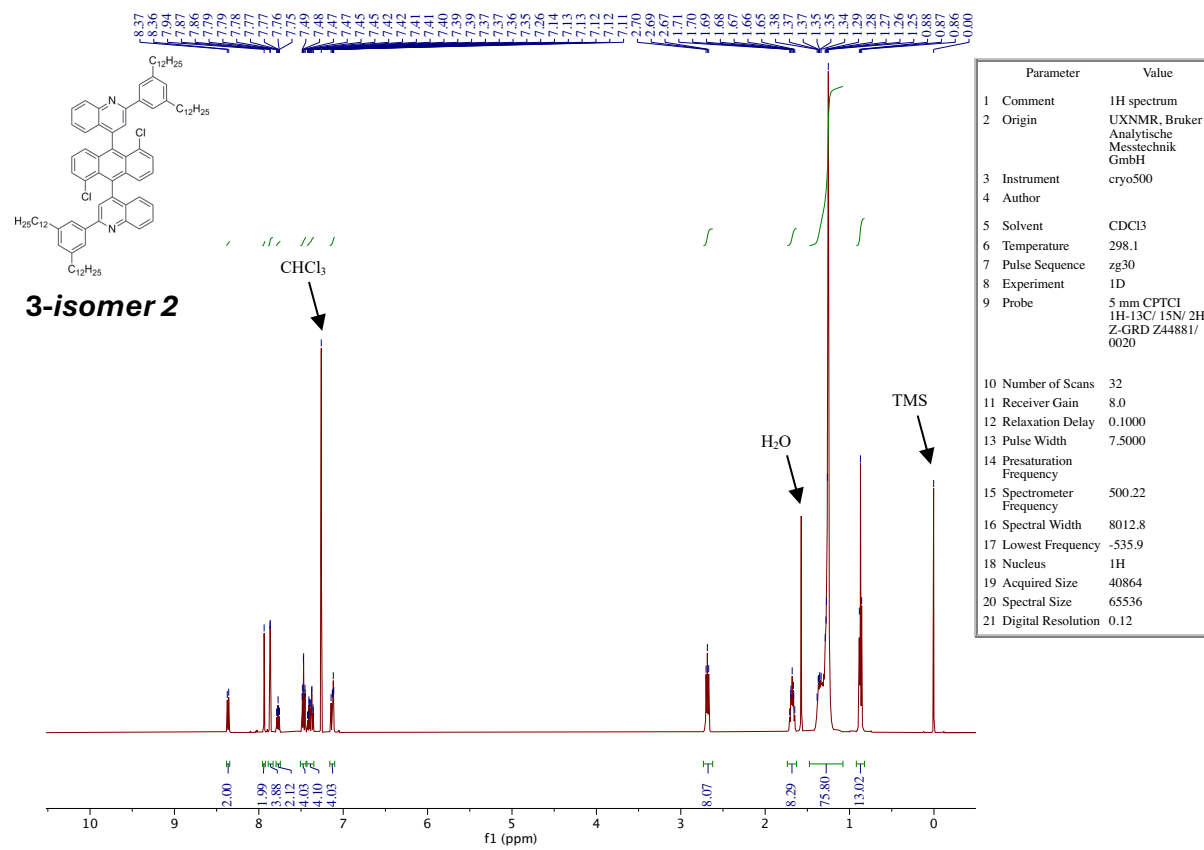


Figure S3. The ¹H NMR spectrum obtained for **3-isomer 2**.

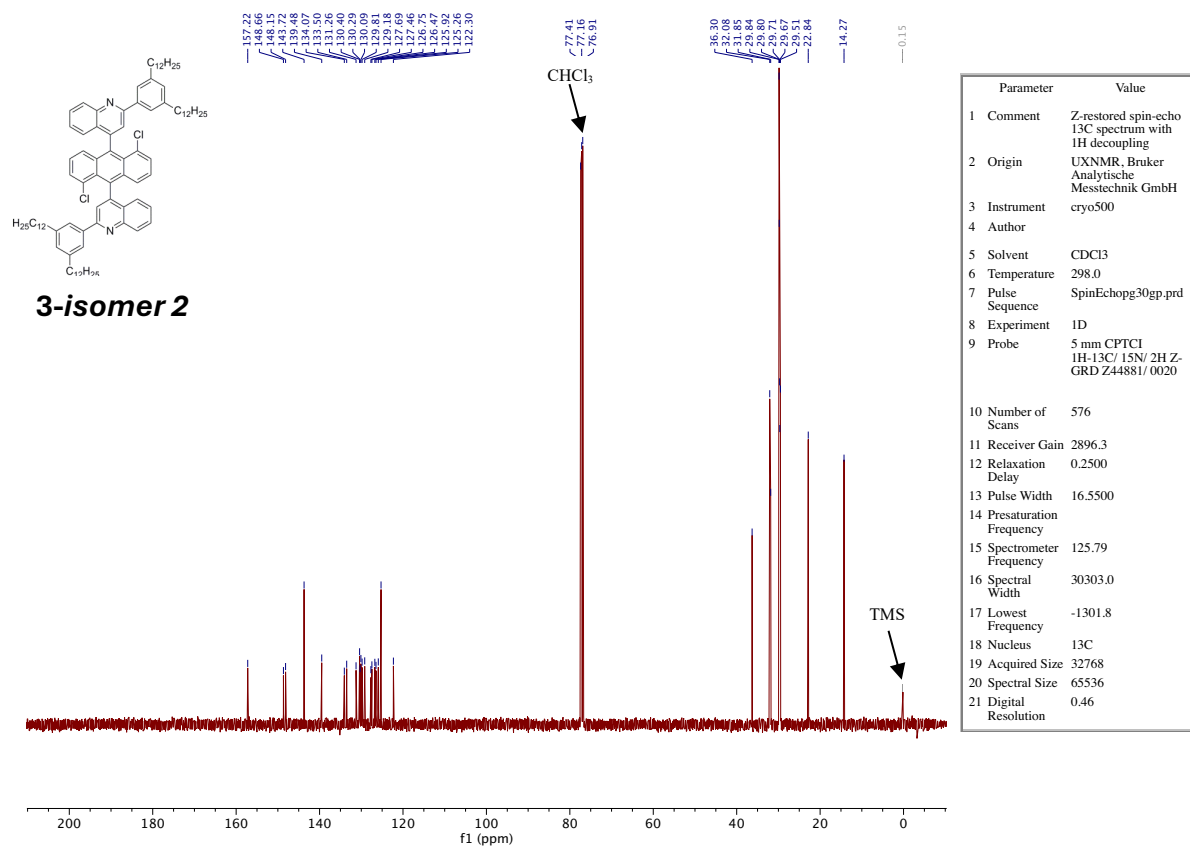


Figure S4. The ^{13}C NMR spectrum obtained for **3-isomer 2**.

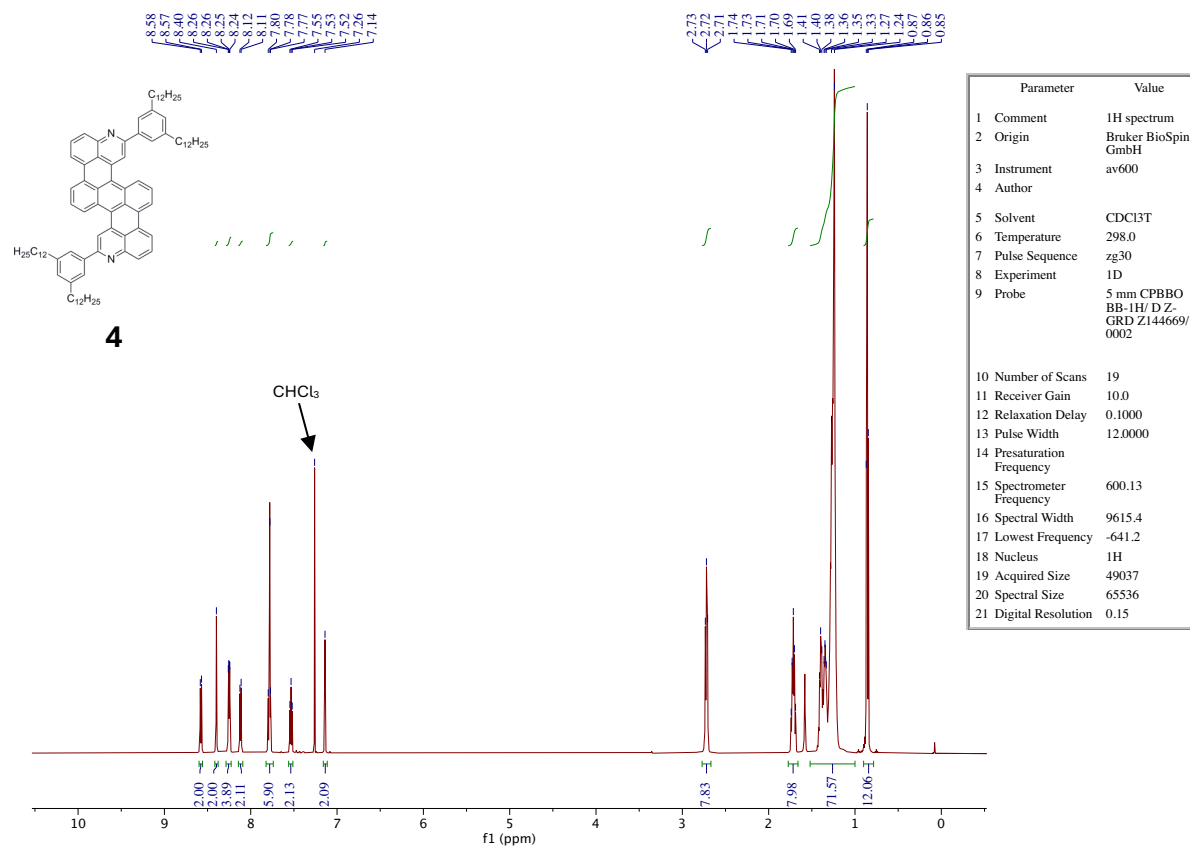


Figure S5. The 1H NMR spectrum obtained for **4**.

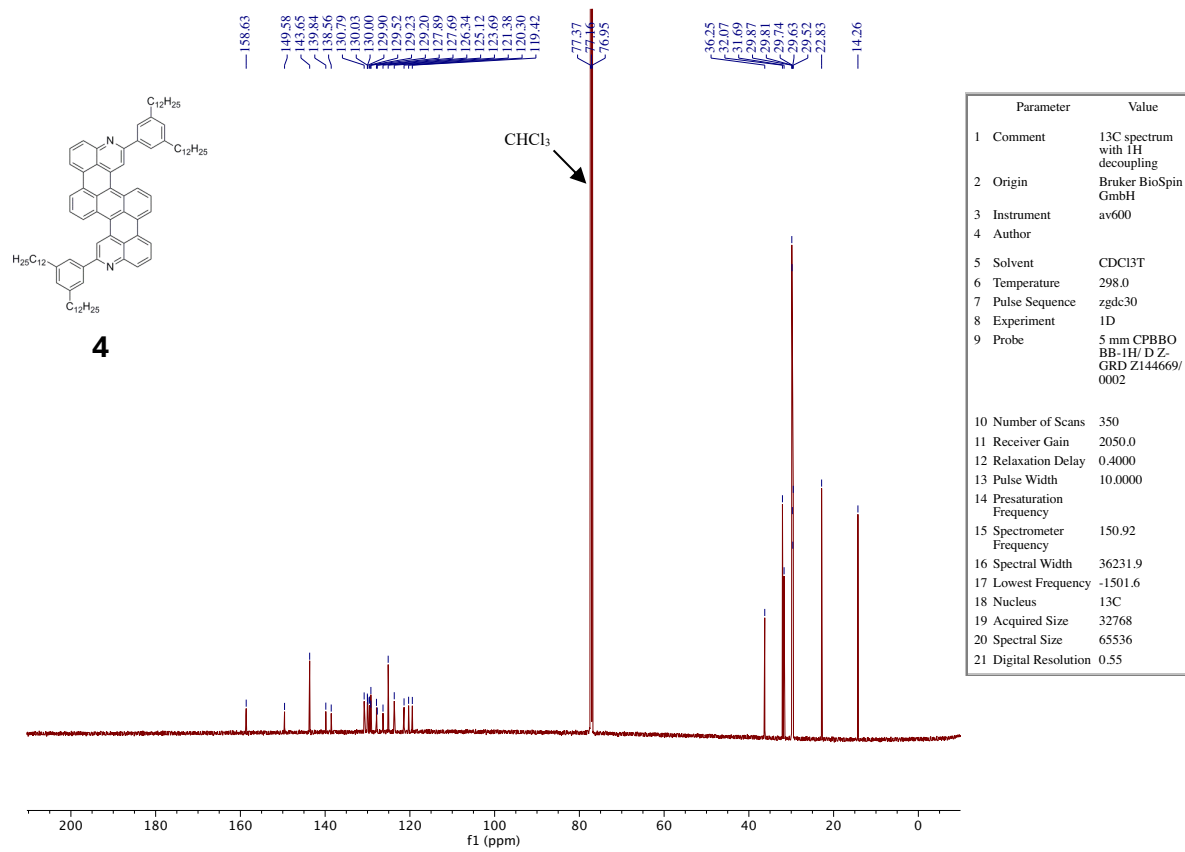


Figure S6. The ^{13}C NMR spectrum obtained for **4**.

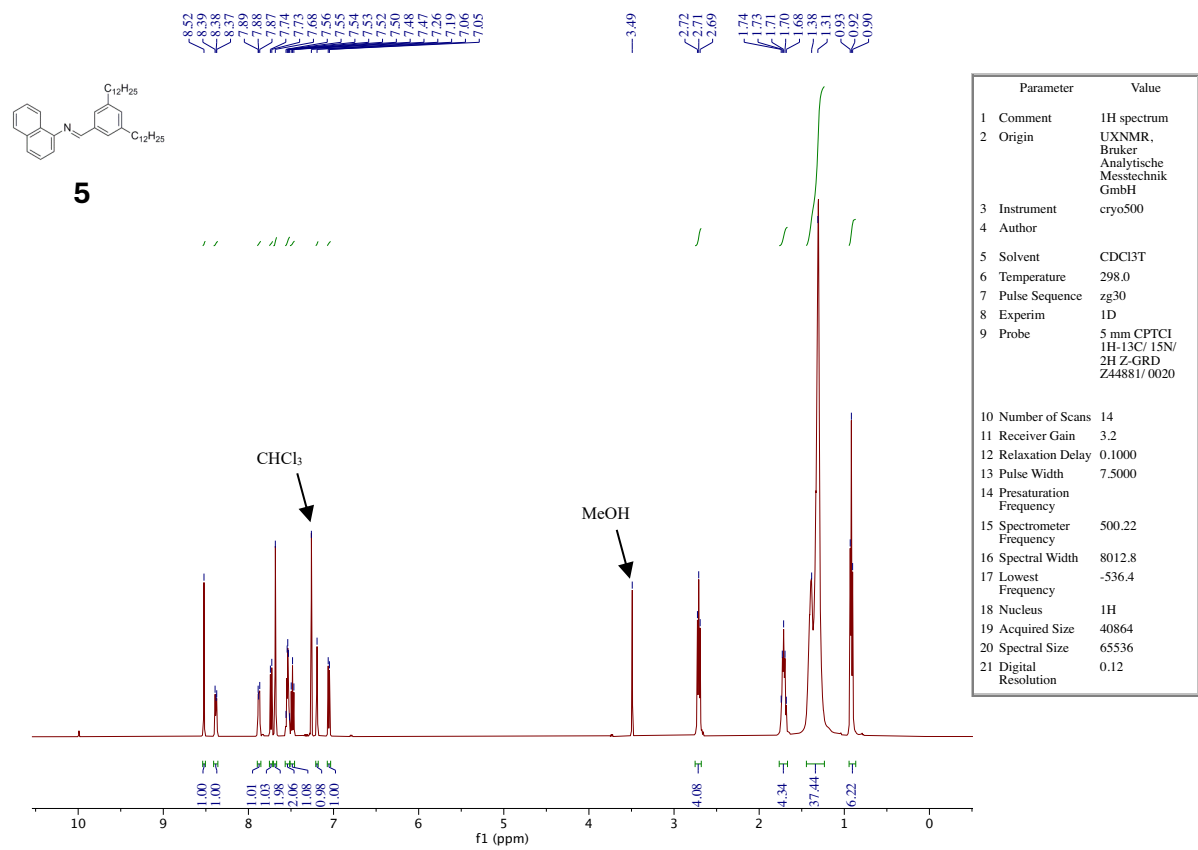


Figure S7. The ¹H NMR spectrum obtained for **5**.

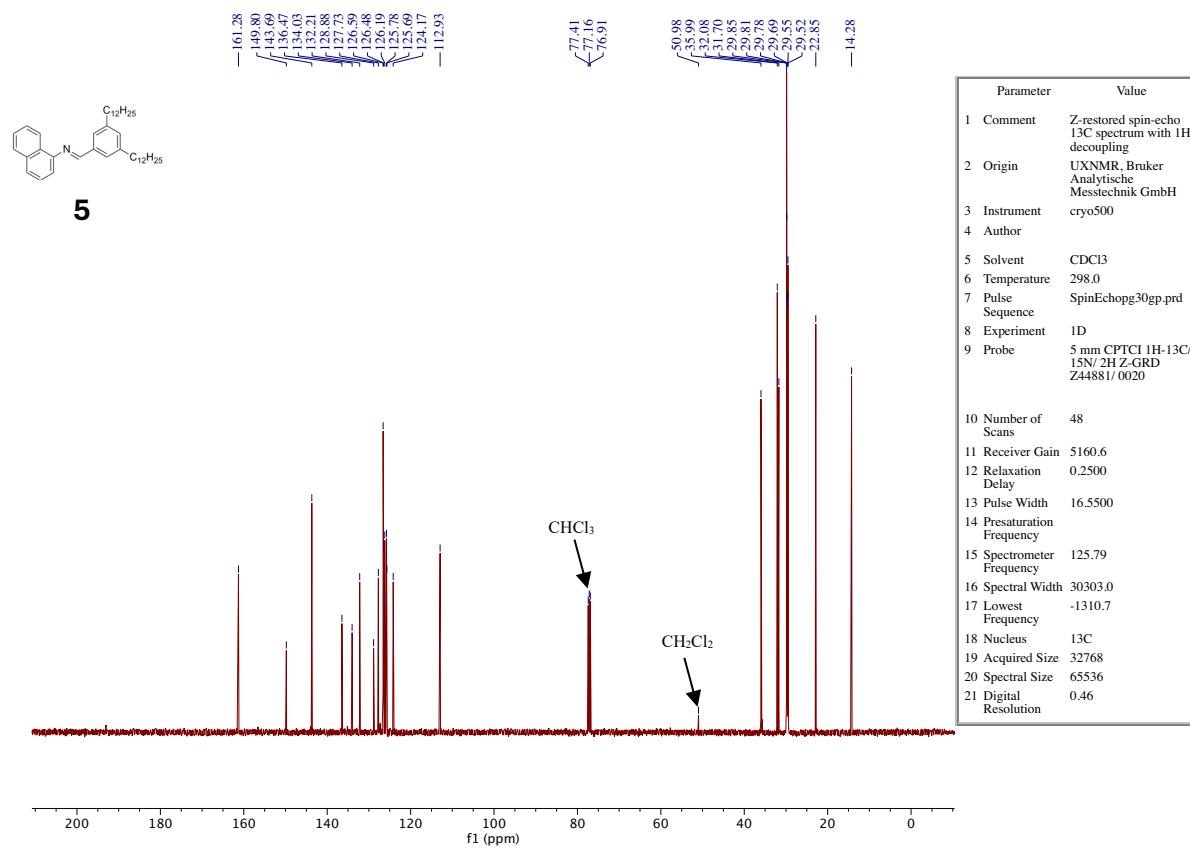


Figure S8. The ¹³C NMR spectrum obtained for **5**.

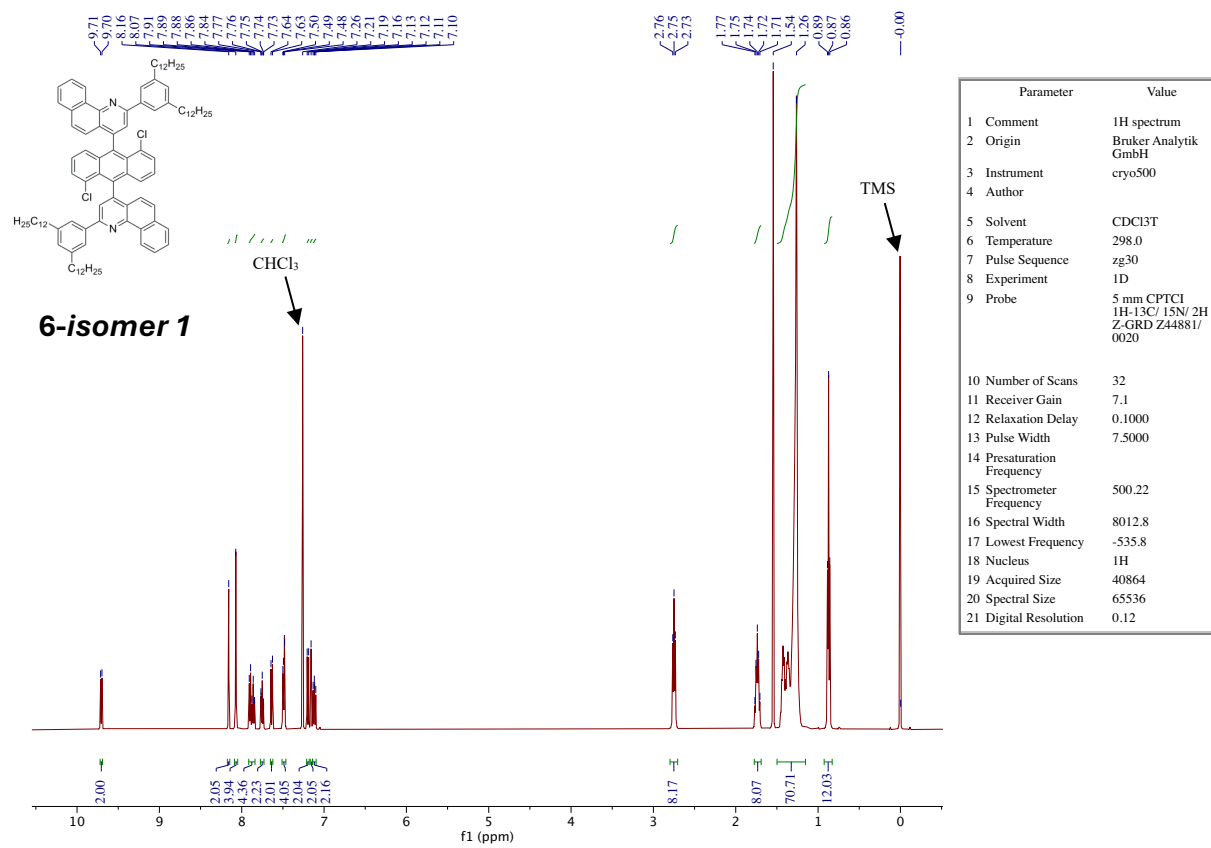


Figure S9. The ¹H NMR spectrum obtained for **6-isomer 1**.

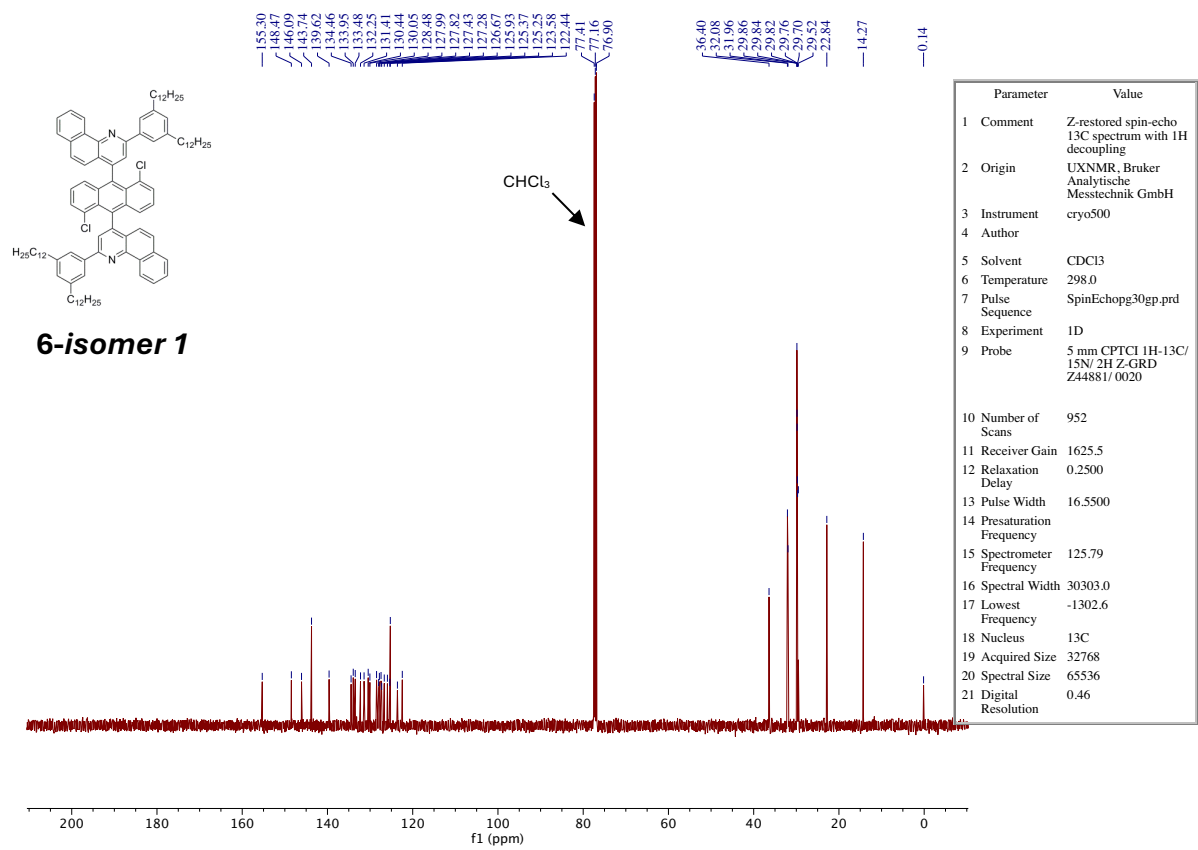


Figure S10. The ^{13}C NMR spectrum obtained for **6-isomer 1**.

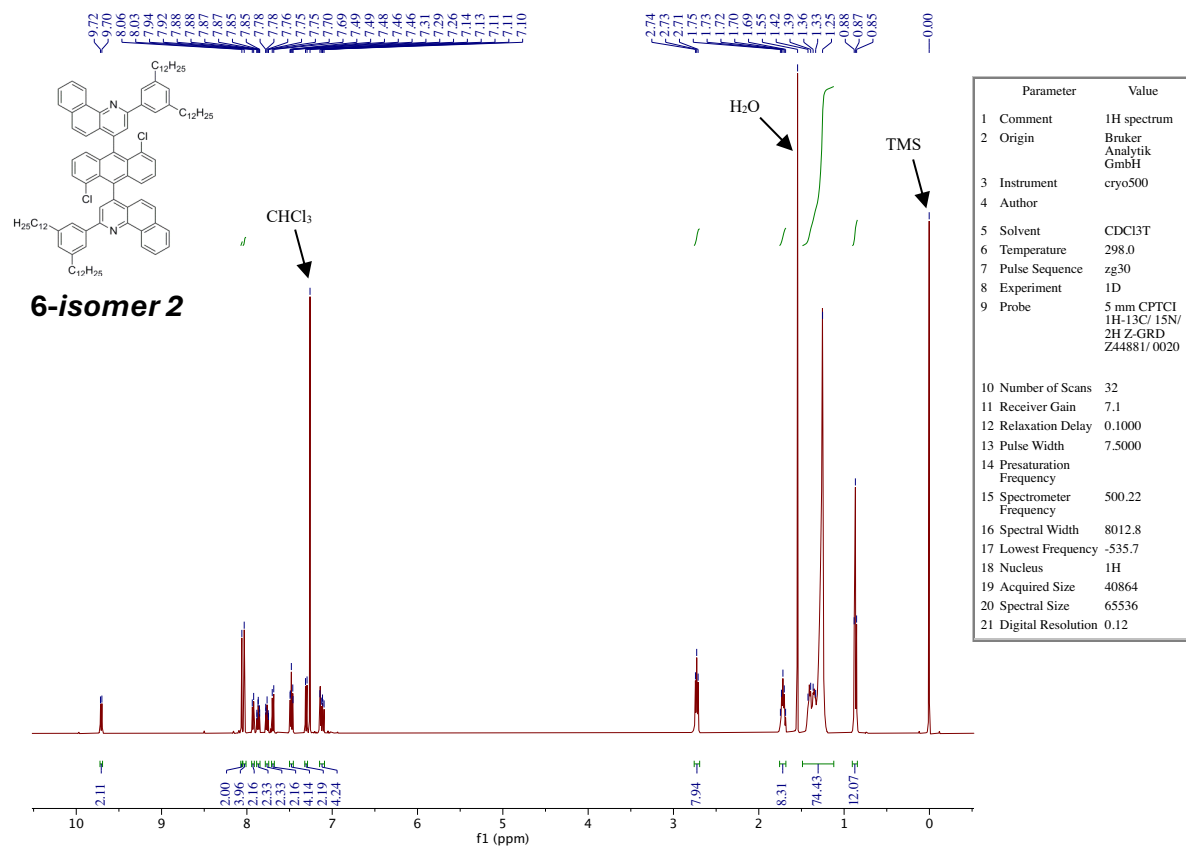


Figure S11. The ¹H NMR spectrum obtained for **6-isomer 2**.

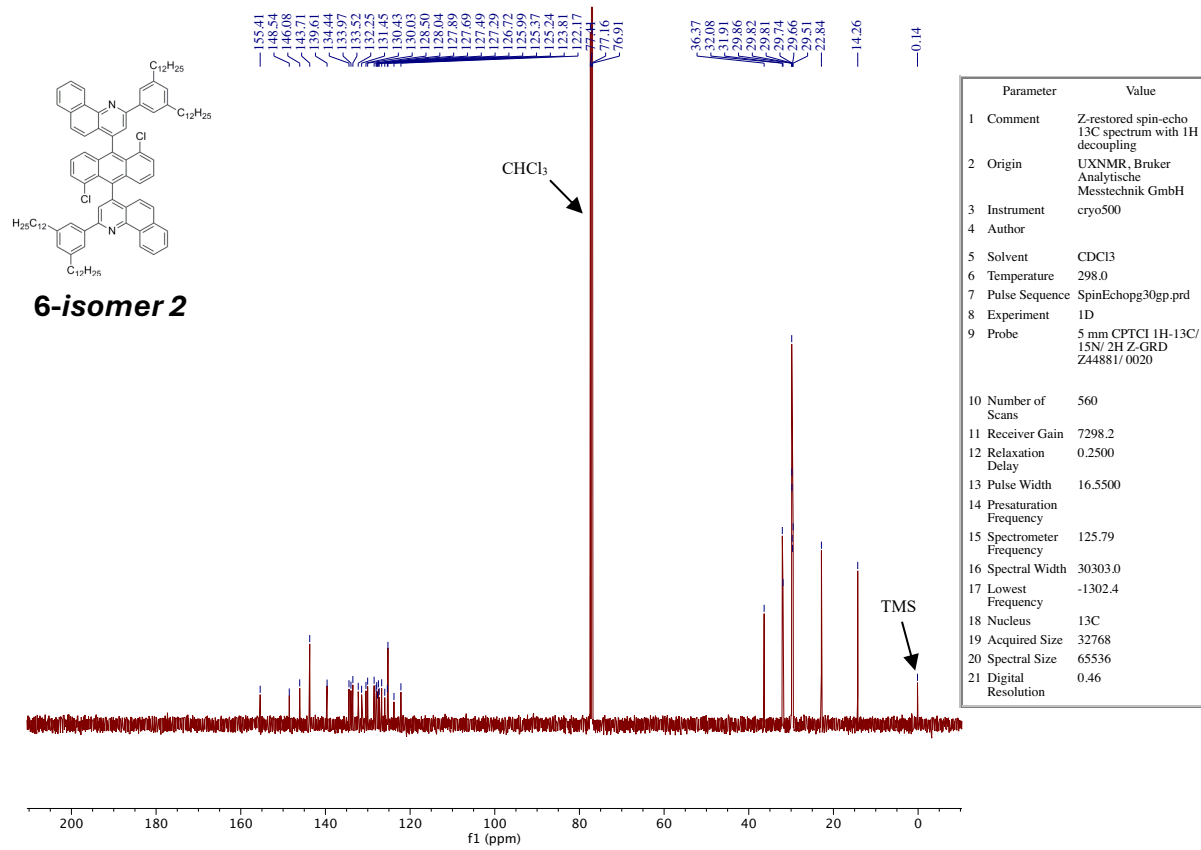


Figure S12. The ^{13}C NMR spectrum obtained for **6-isomer 2**.

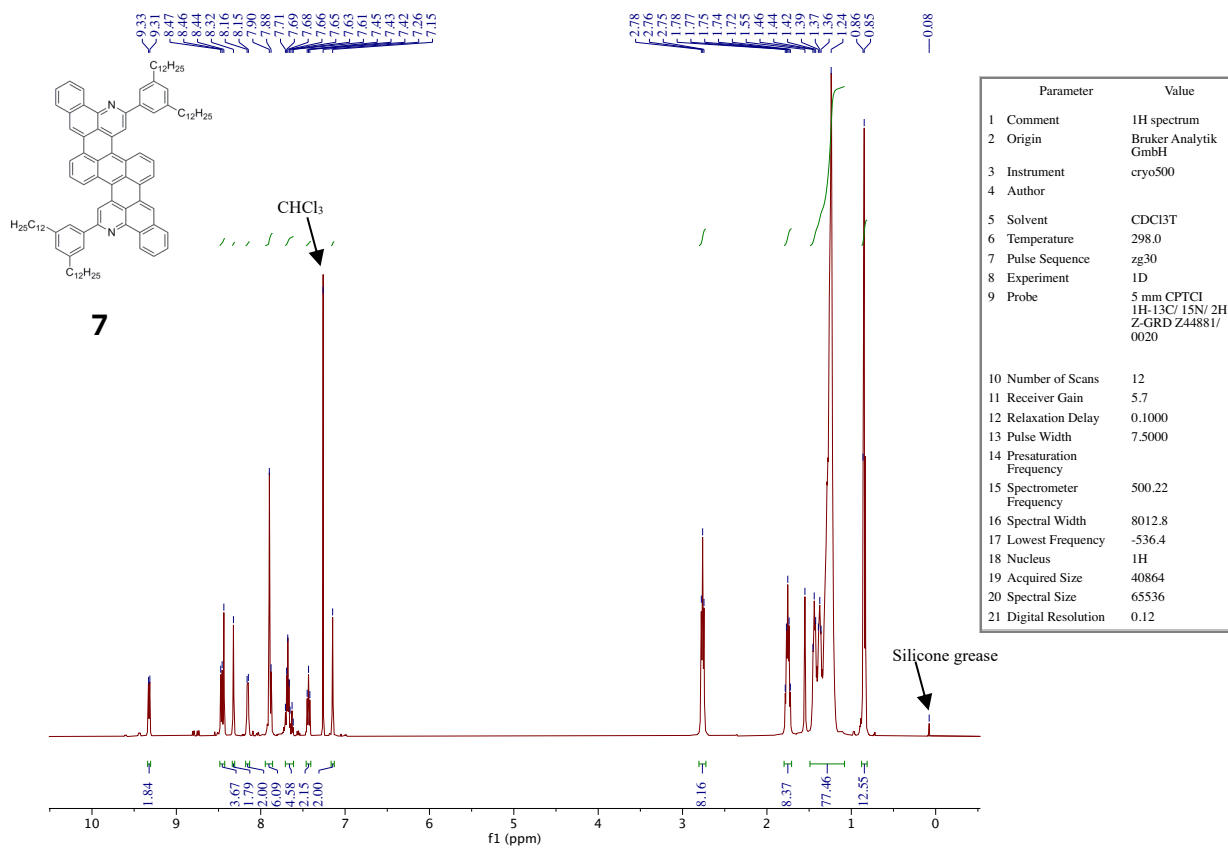


Figure S13. The ¹H NMR spectrum obtained for **7**.

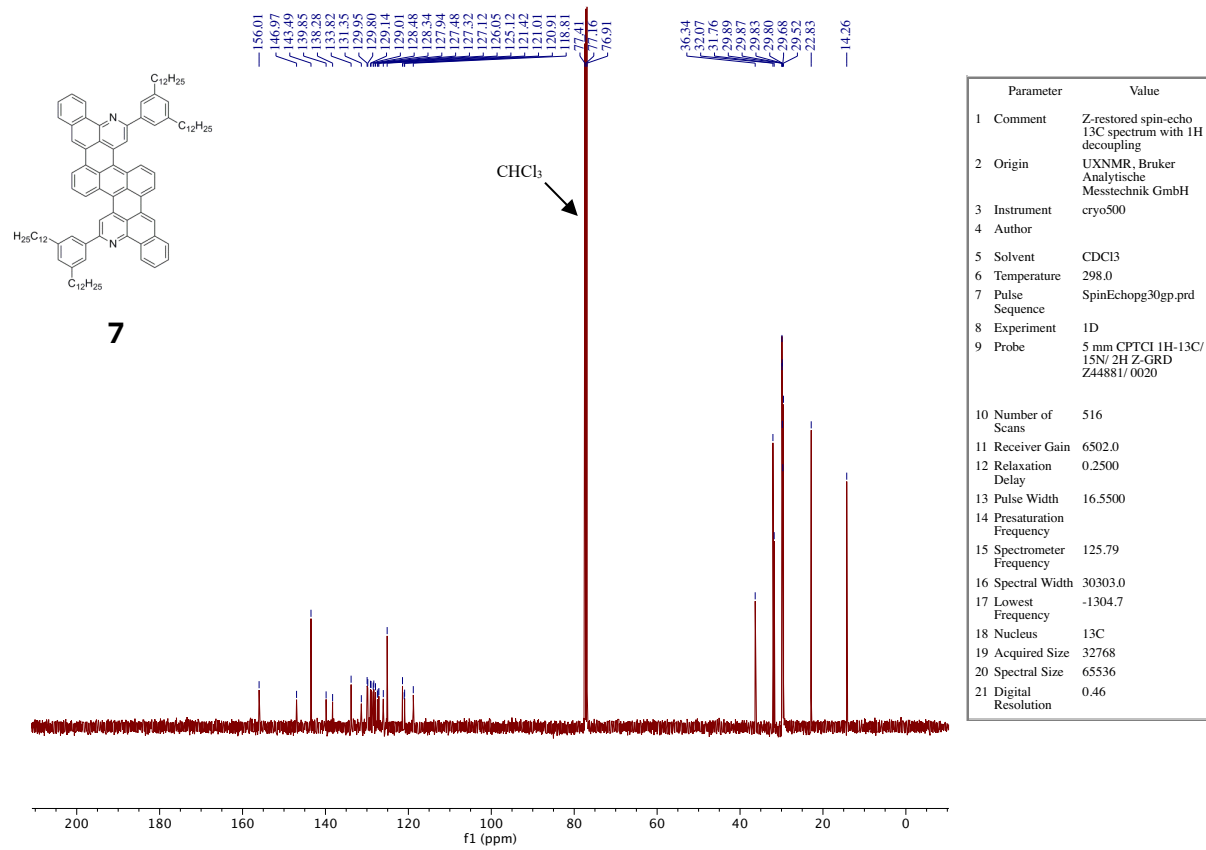


Figure S14. The ¹³C NMR spectrum obtained for **7**.

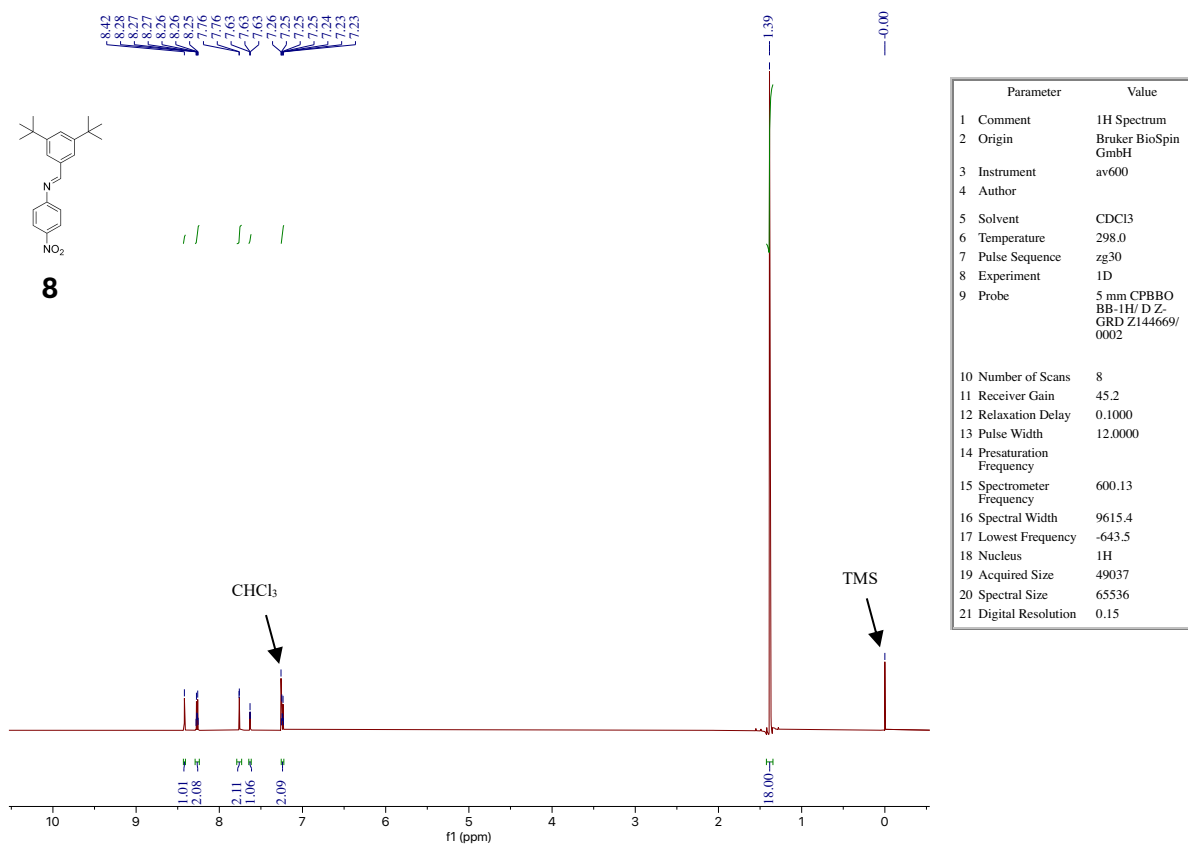


Figure S15. The ¹H NMR spectrum obtained for **8**.

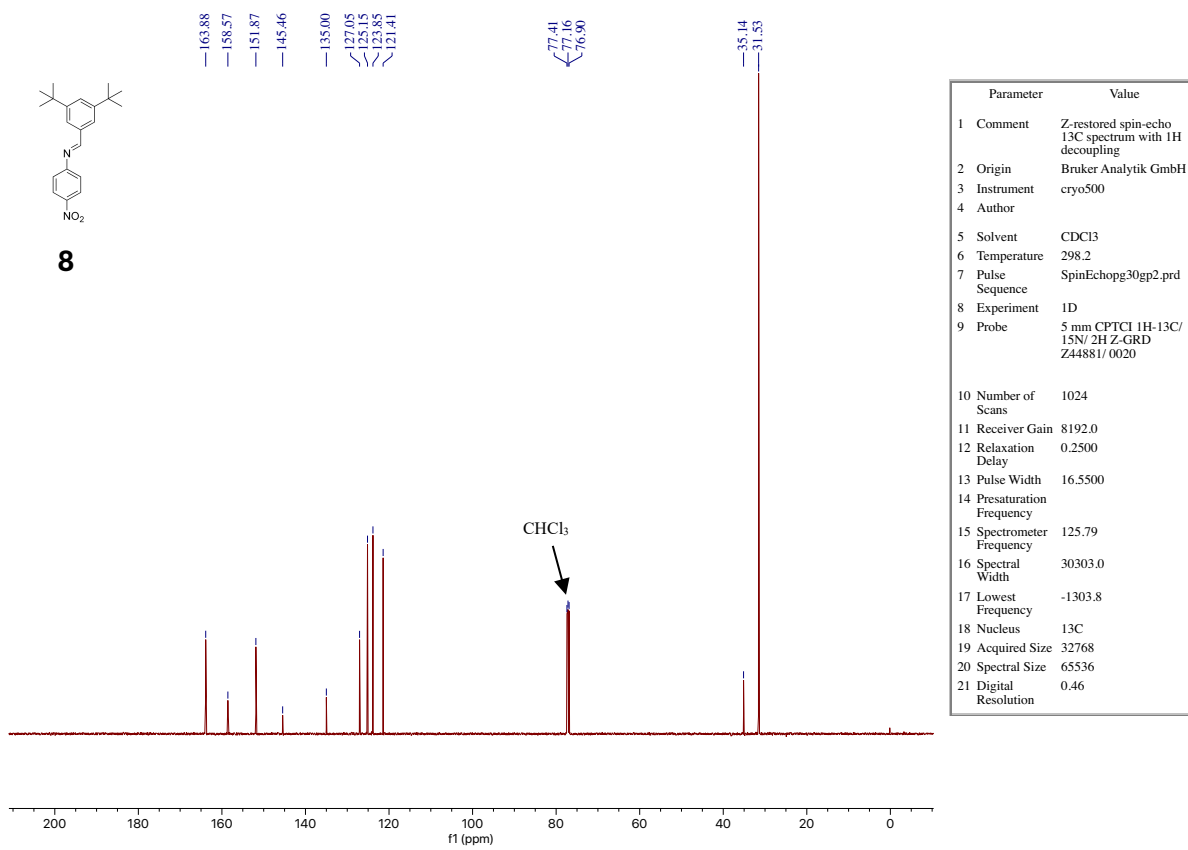


Figure S16. The ^{13}C NMR spectrum obtained for **8**.

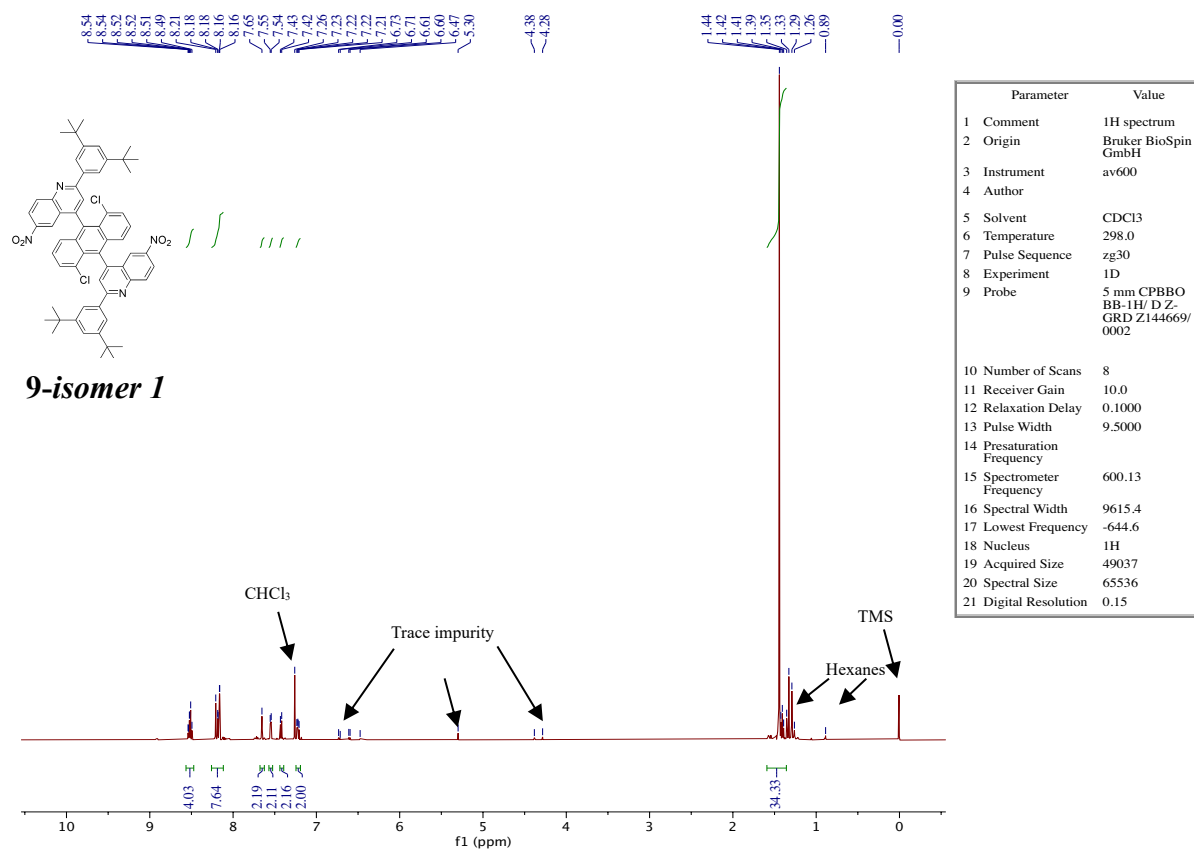


Figure S17. The ^1H NMR spectrum obtained for **9-isomer 1**.

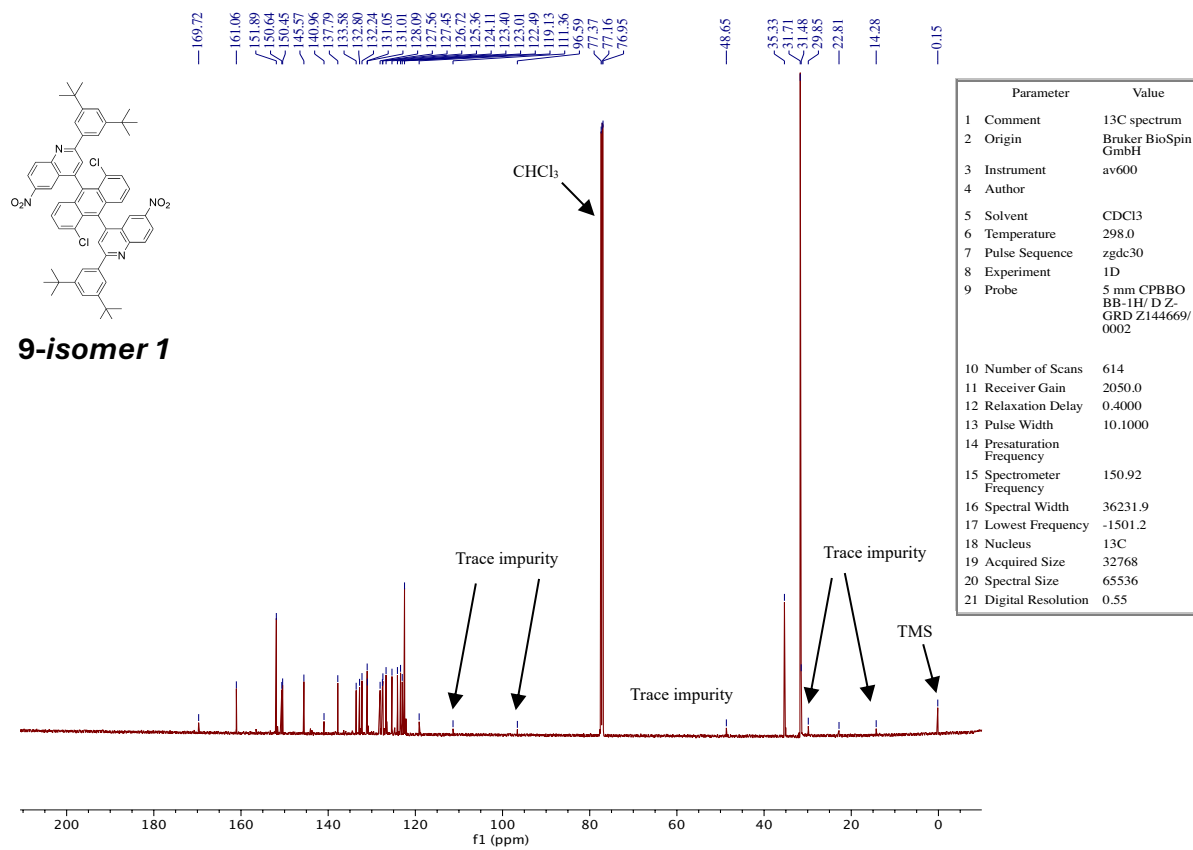


Figure S18. The ^{13}C NMR spectrum obtained for **9-isomer 1**.

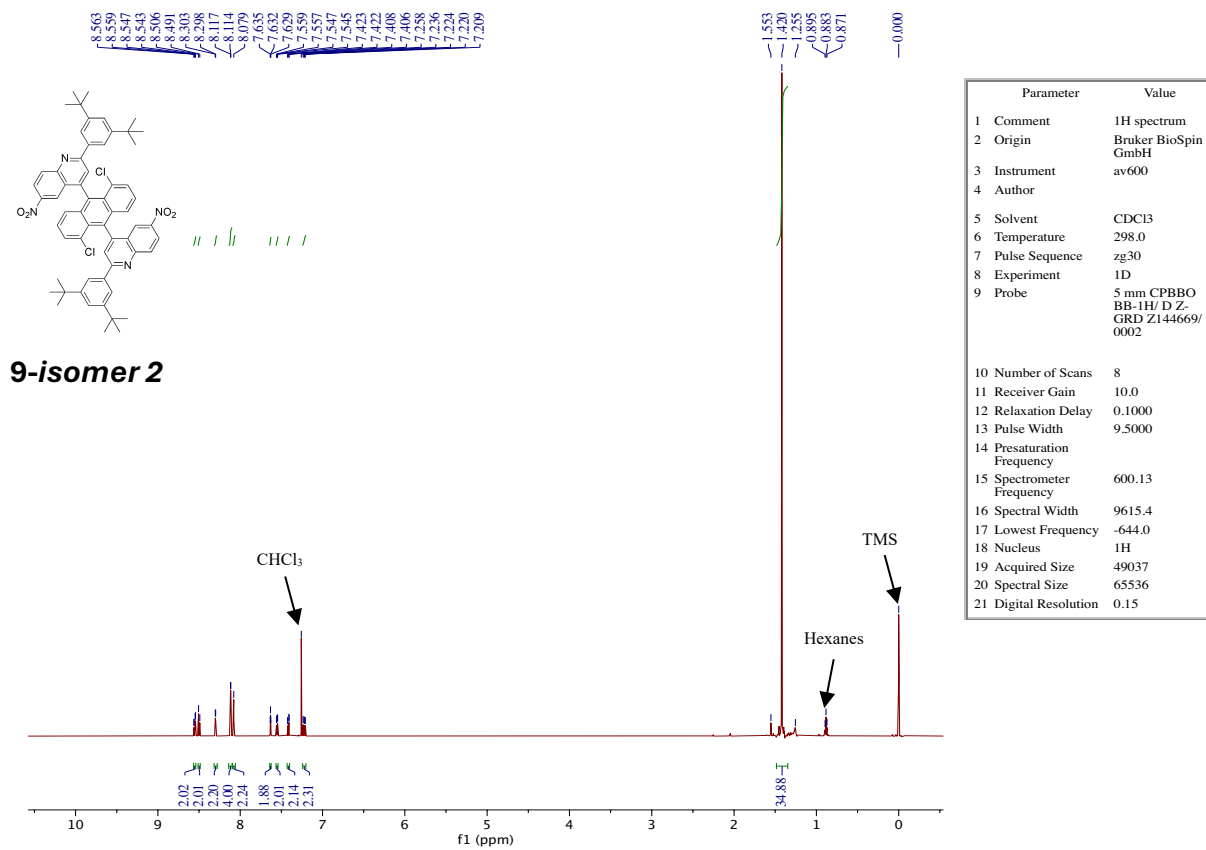


Figure S19. The ¹H NMR spectrum obtained for **9-isomer 2**.

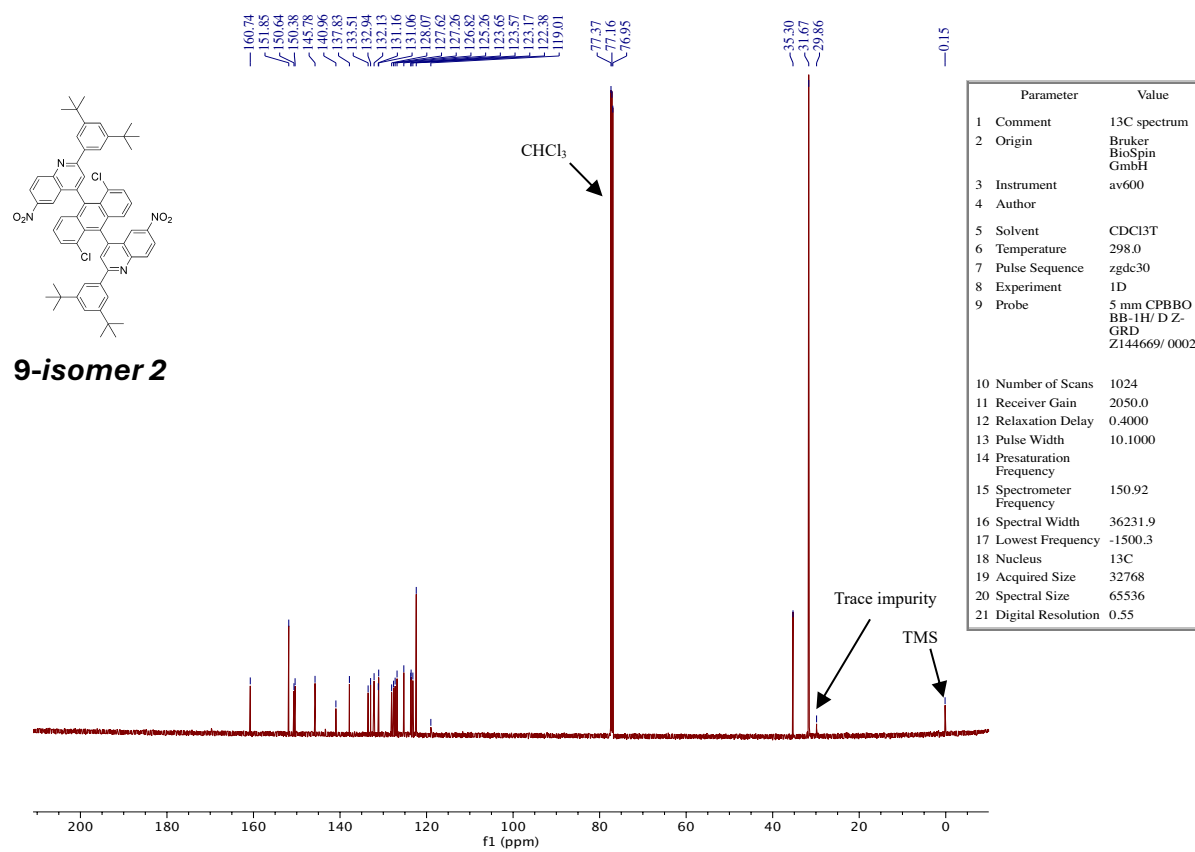


Figure S20. The ¹³C NMR spectrum obtained for **9-isomer 2**.

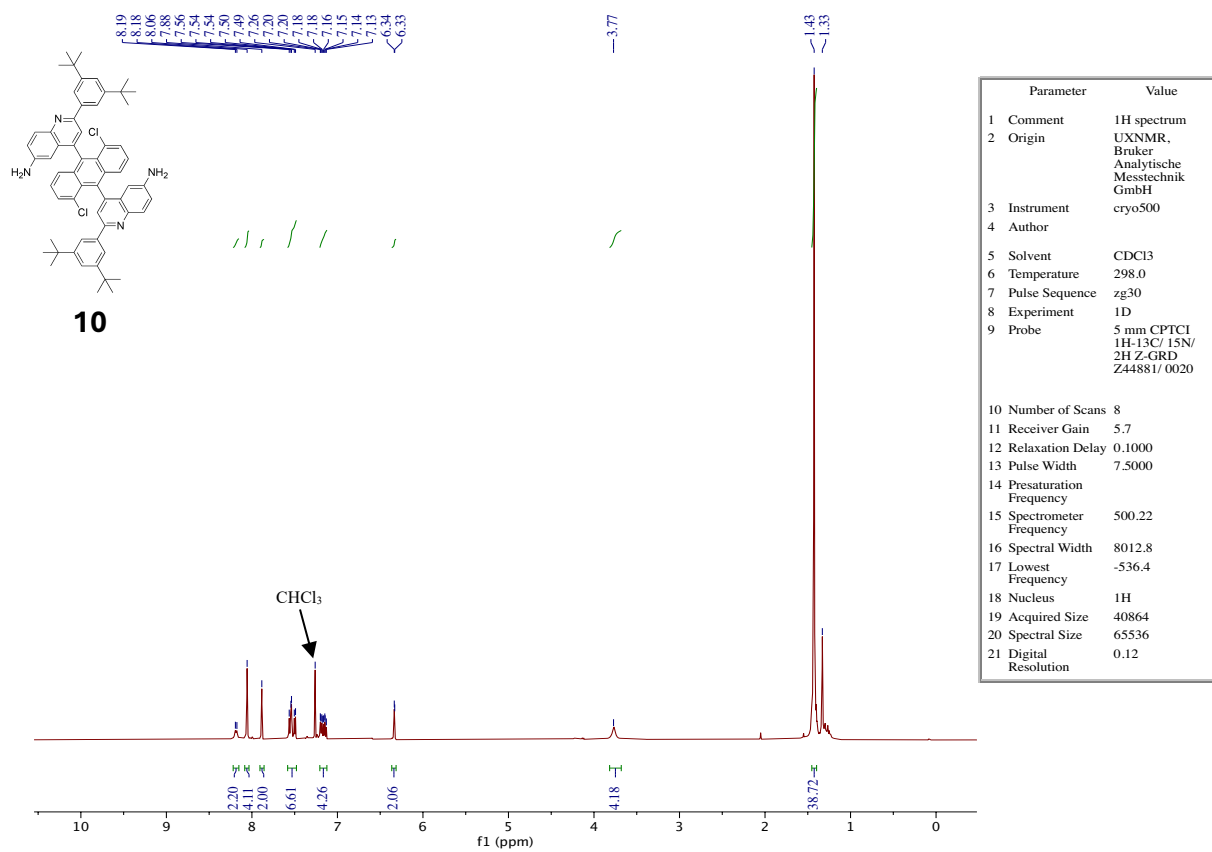


Figure S21. The ¹H NMR spectrum obtained for **10**.

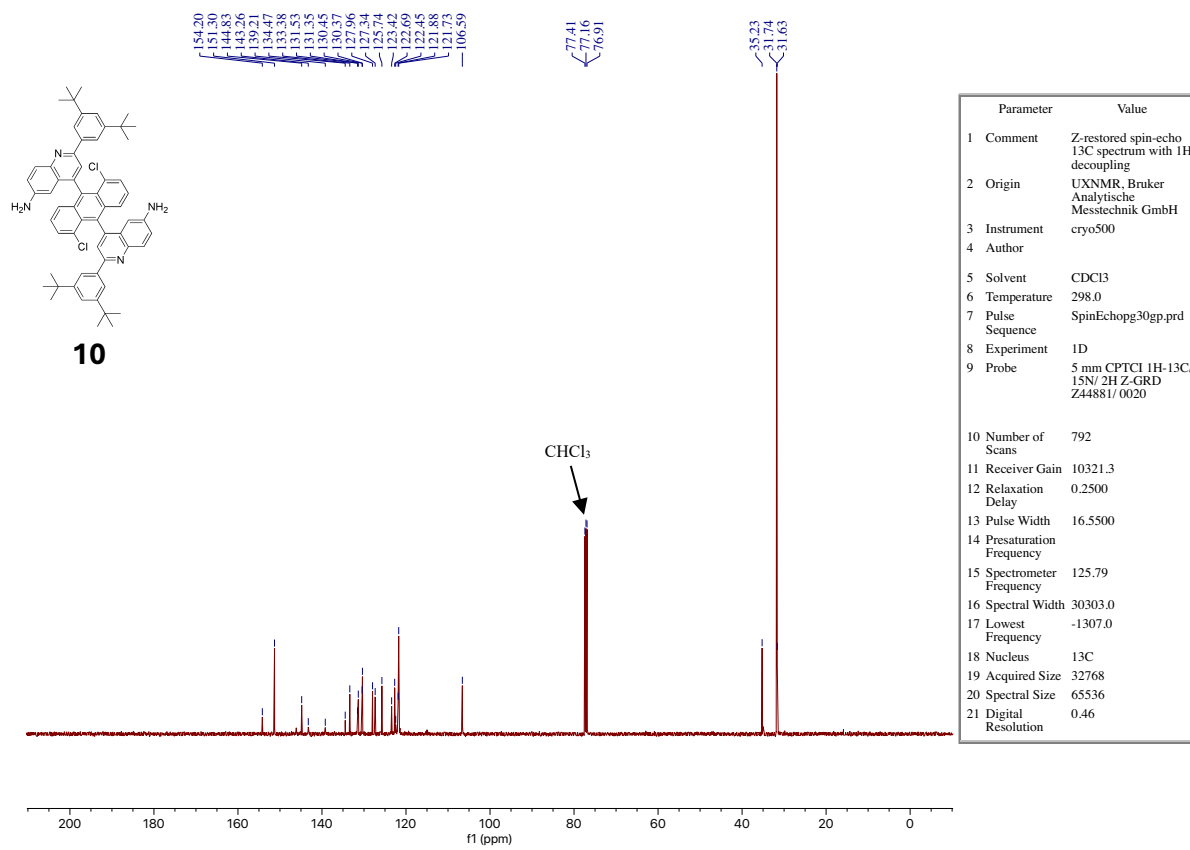


Figure S22. The ¹³C NMR spectrum obtained for **10**.

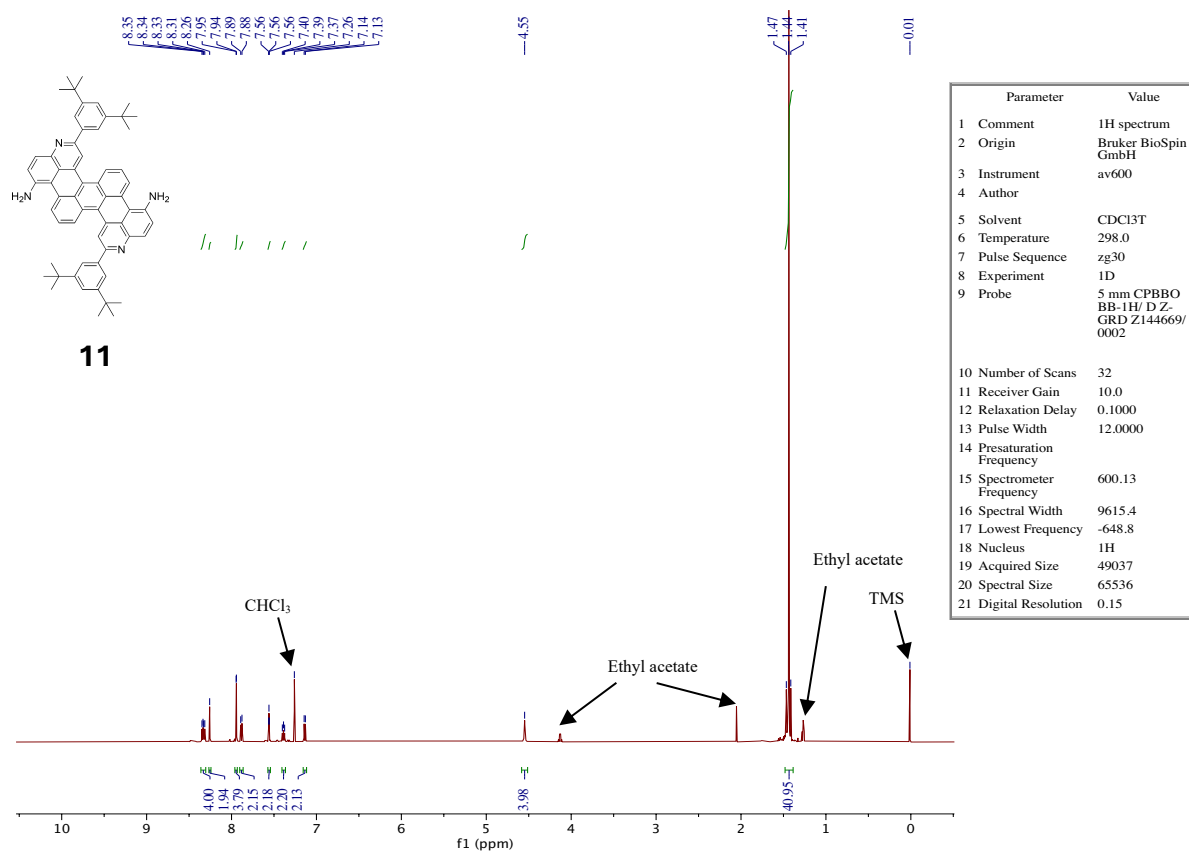


Figure S23. The ¹H NMR spectrum obtained for **11**.

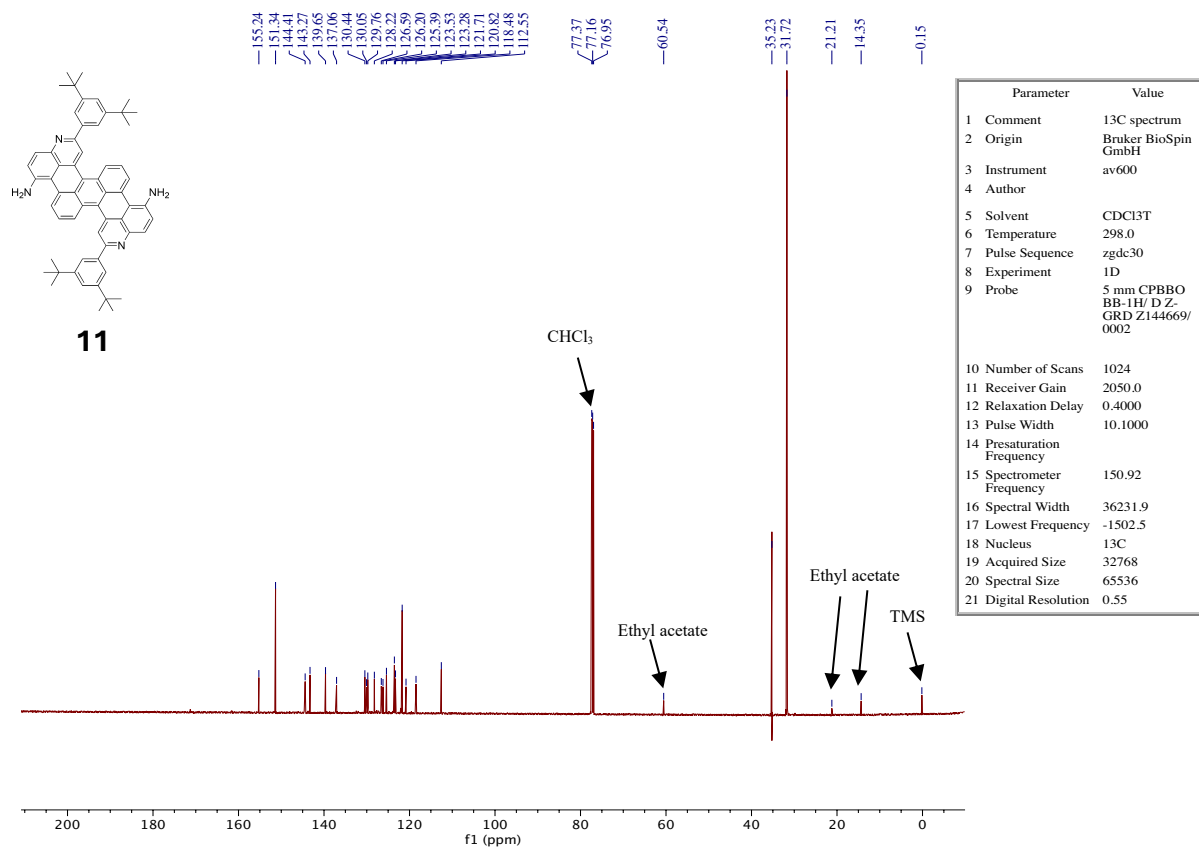


Figure S24. The ^{13}C NMR spectrum obtained for **11**.

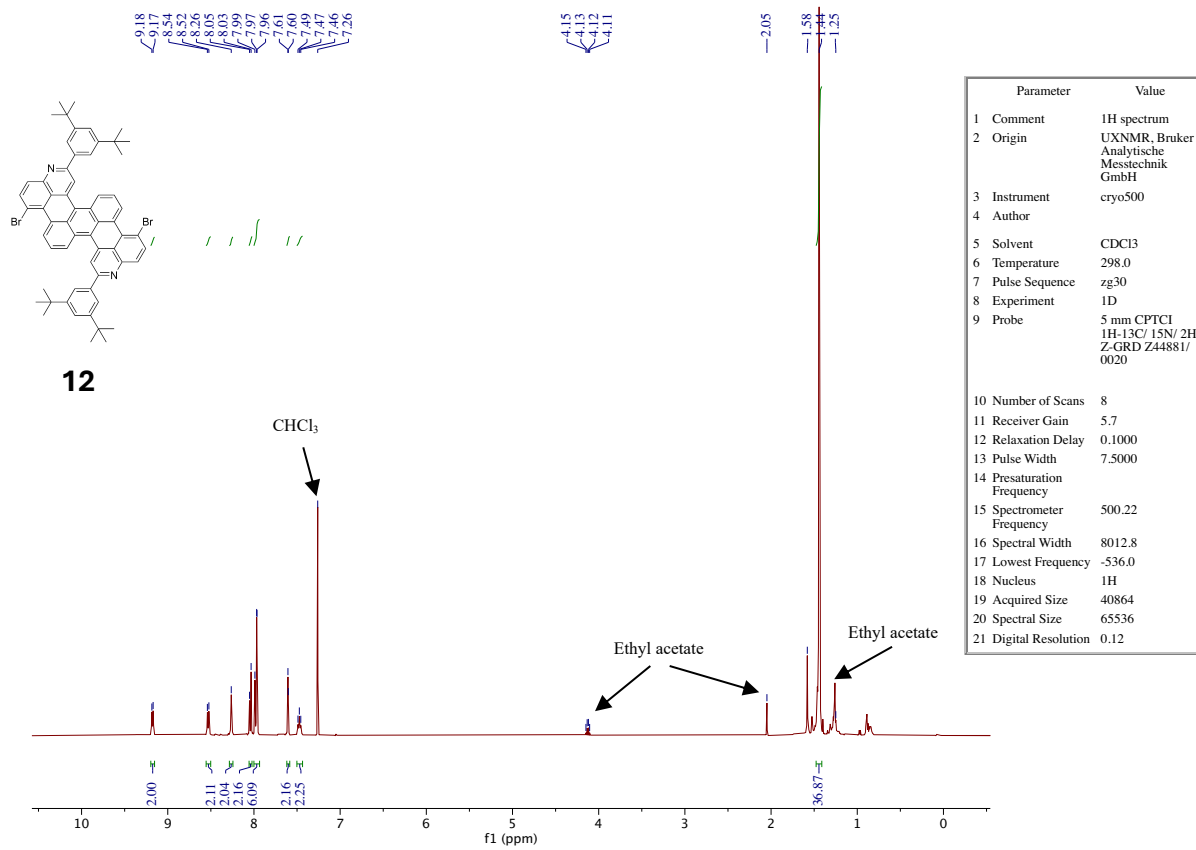


Figure S25. The ¹H NMR spectrum obtained for **12**.

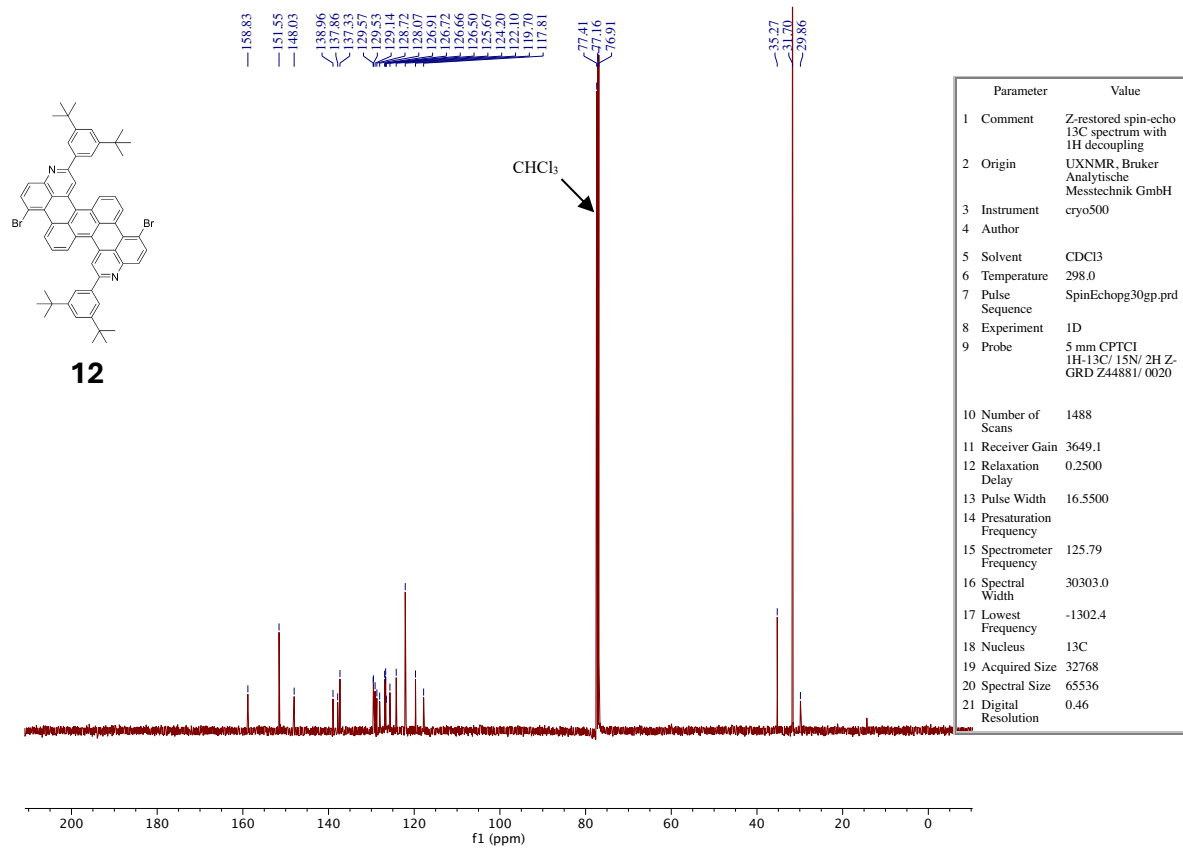


Figure S26. The ¹³C NMR spectrum obtained for **12**.

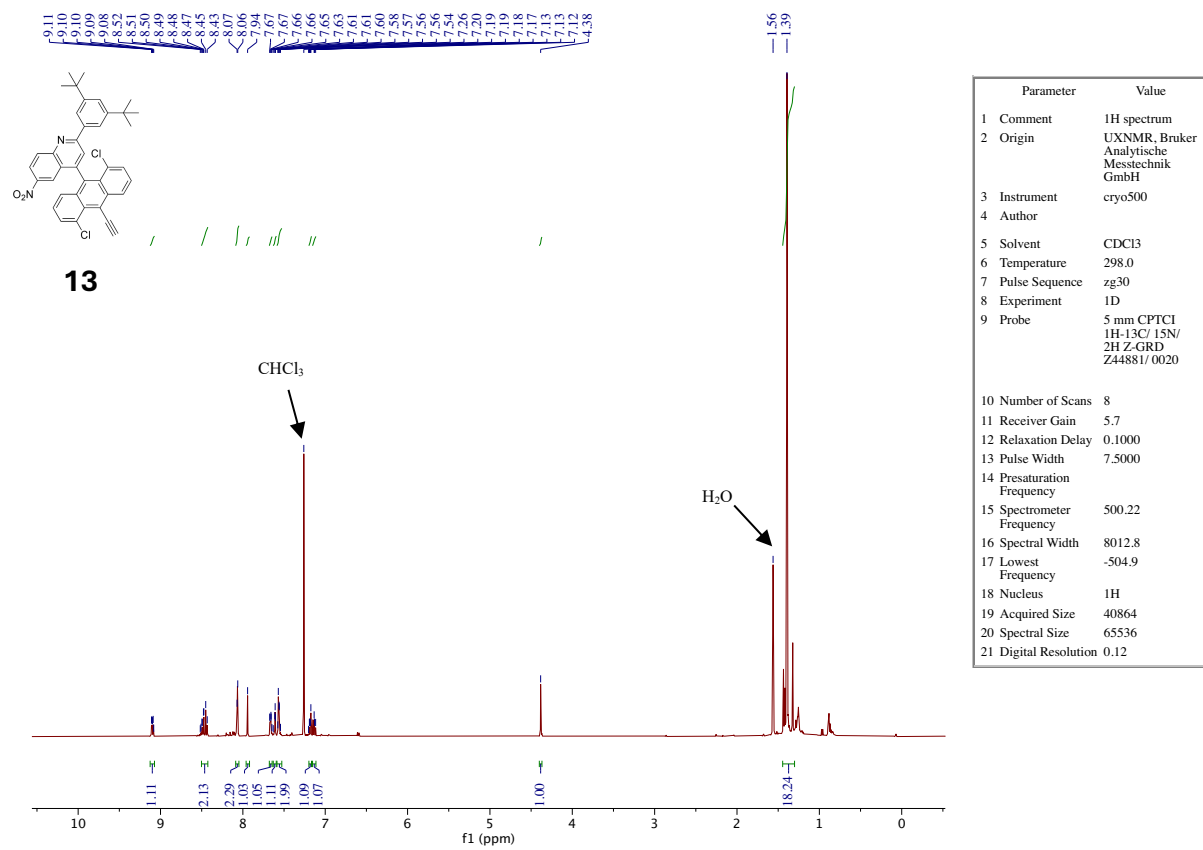


Figure S27. The ¹H NMR spectrum obtained for **13**.

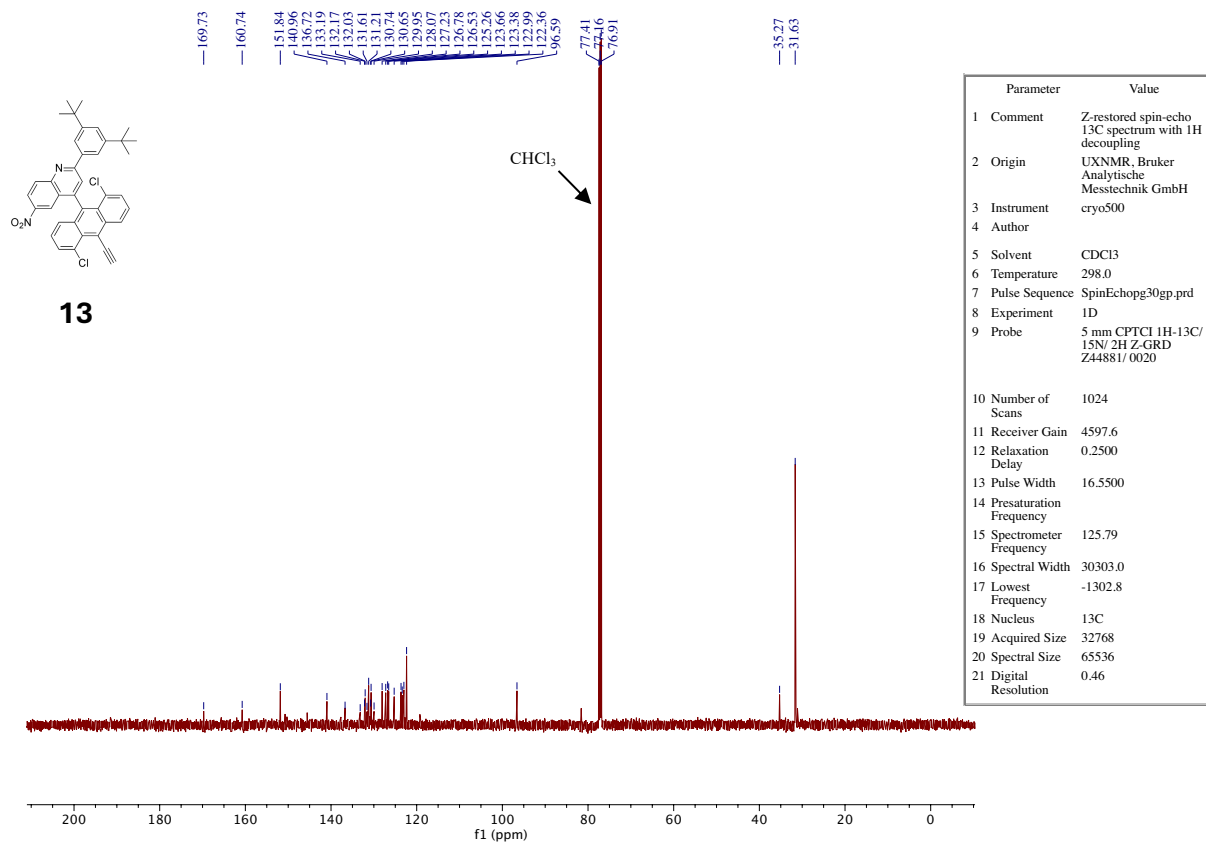


Figure S28. The ^{13}C NMR spectrum obtained for **13**.

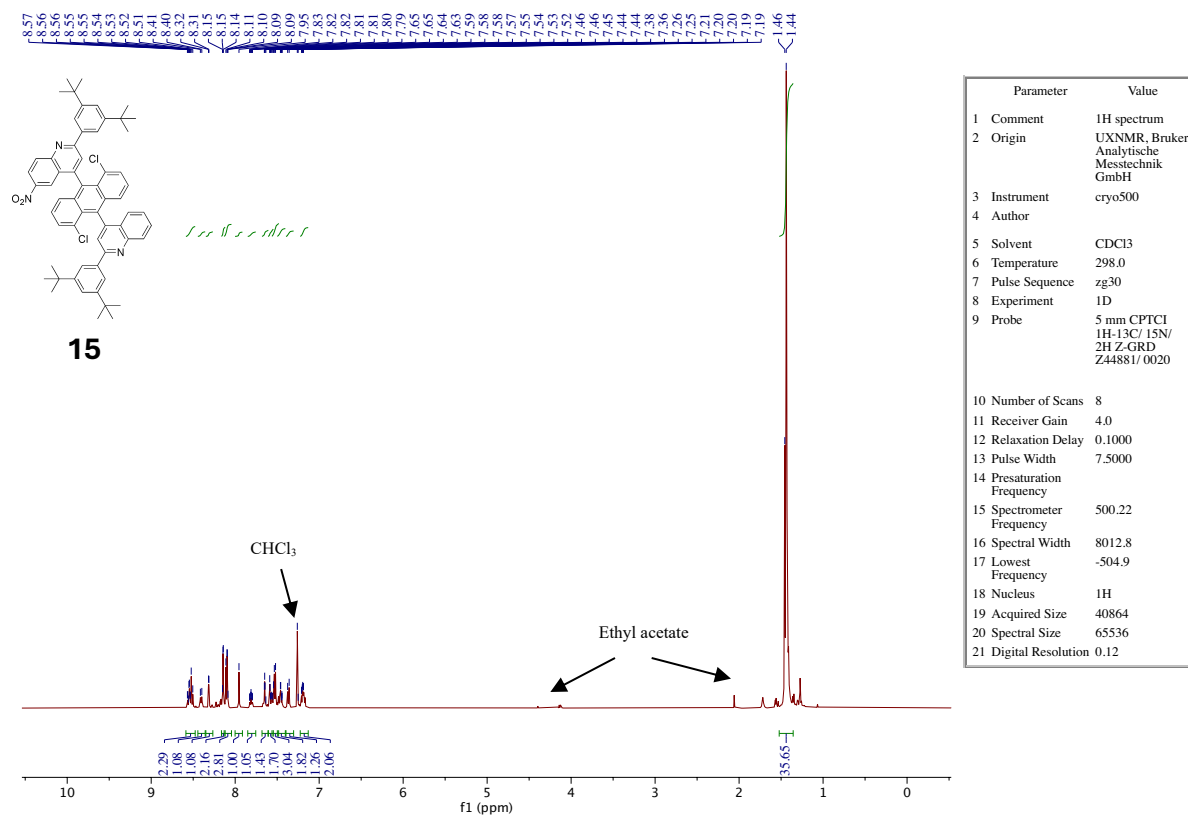


Figure S29. The ¹H NMR spectrum obtained for **15**.

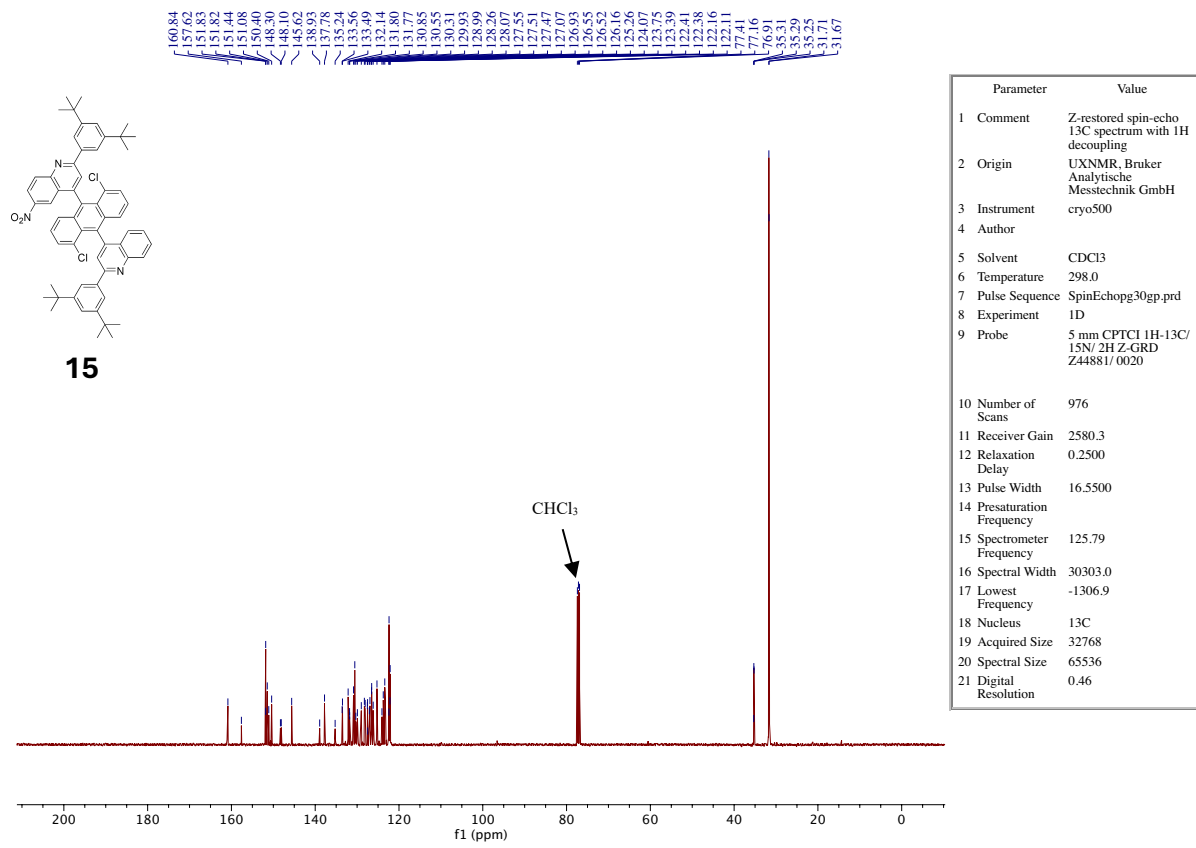


Figure S30. The ¹³C NMR spectrum obtained for **15**.

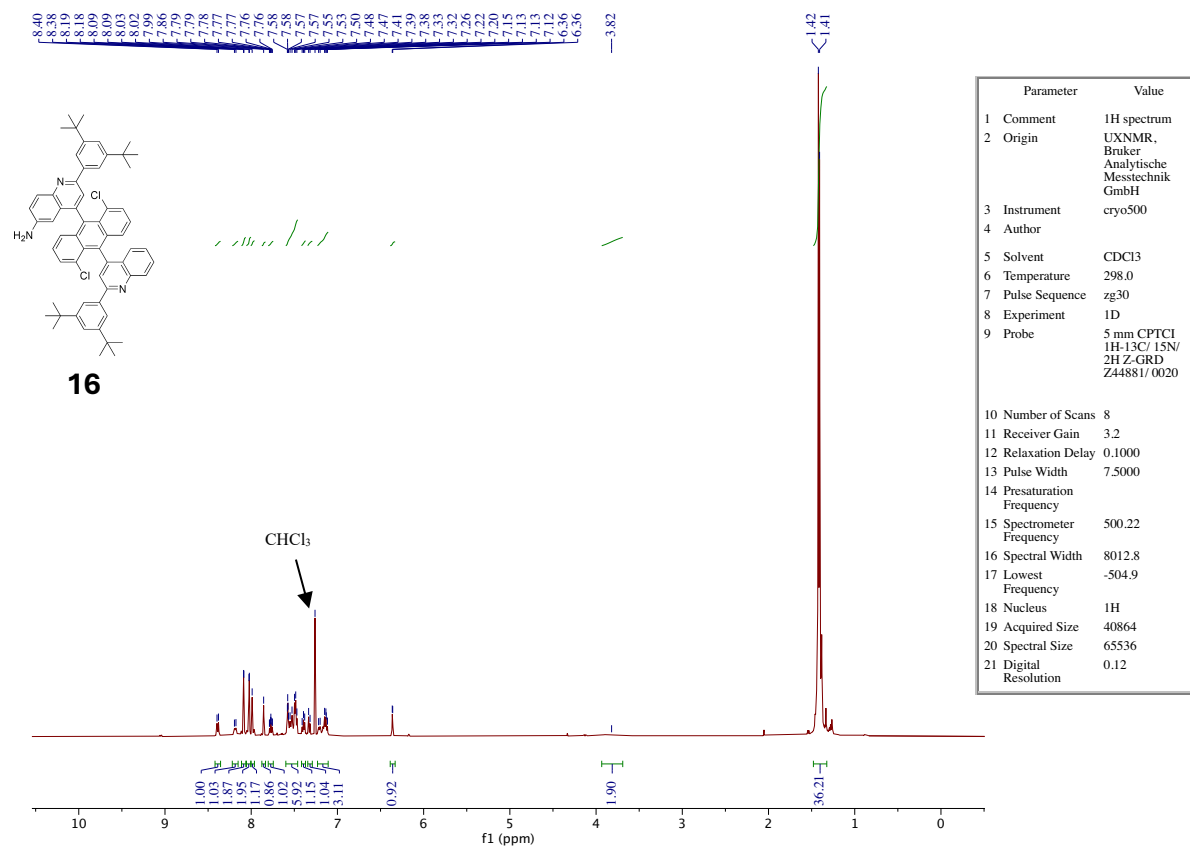


Figure S31. The ¹H NMR spectrum obtained for **16**.

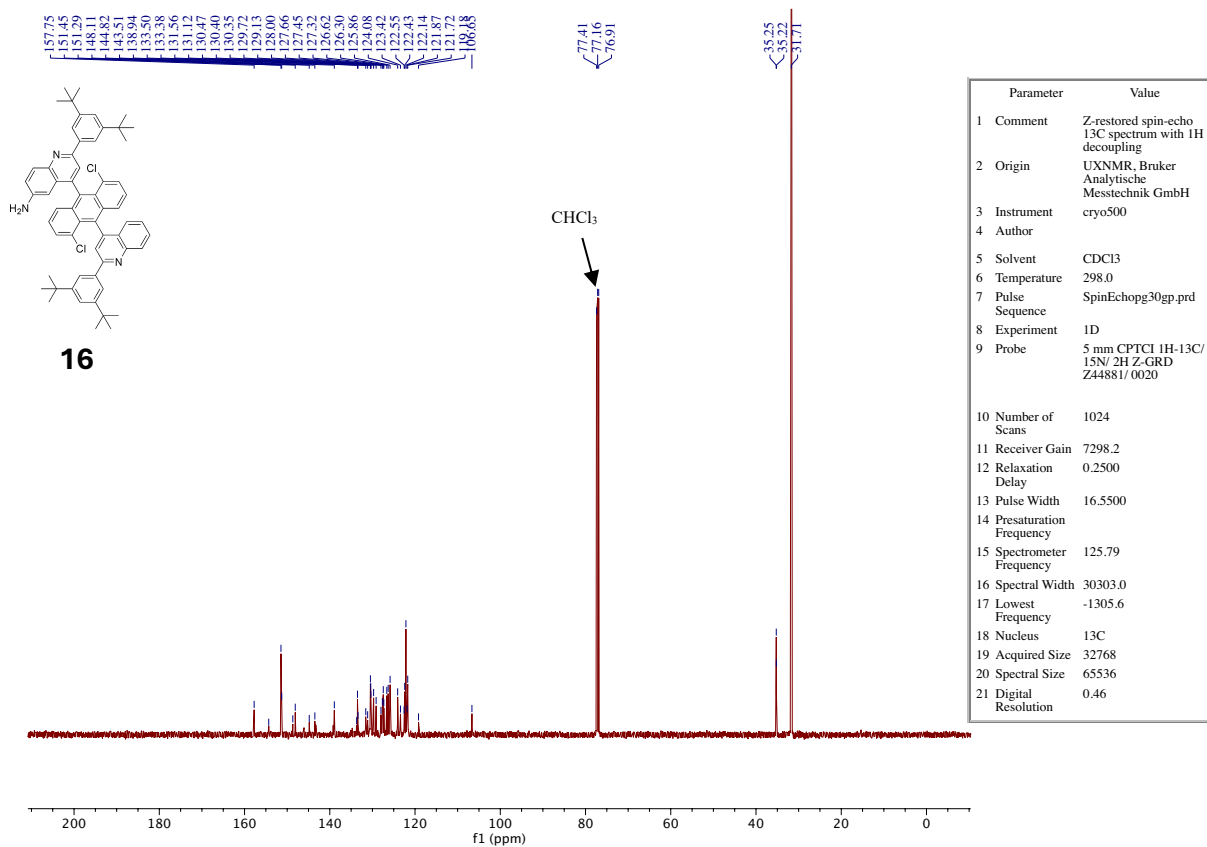


Figure S32. The ¹³C NMR spectrum obtained for **16**.

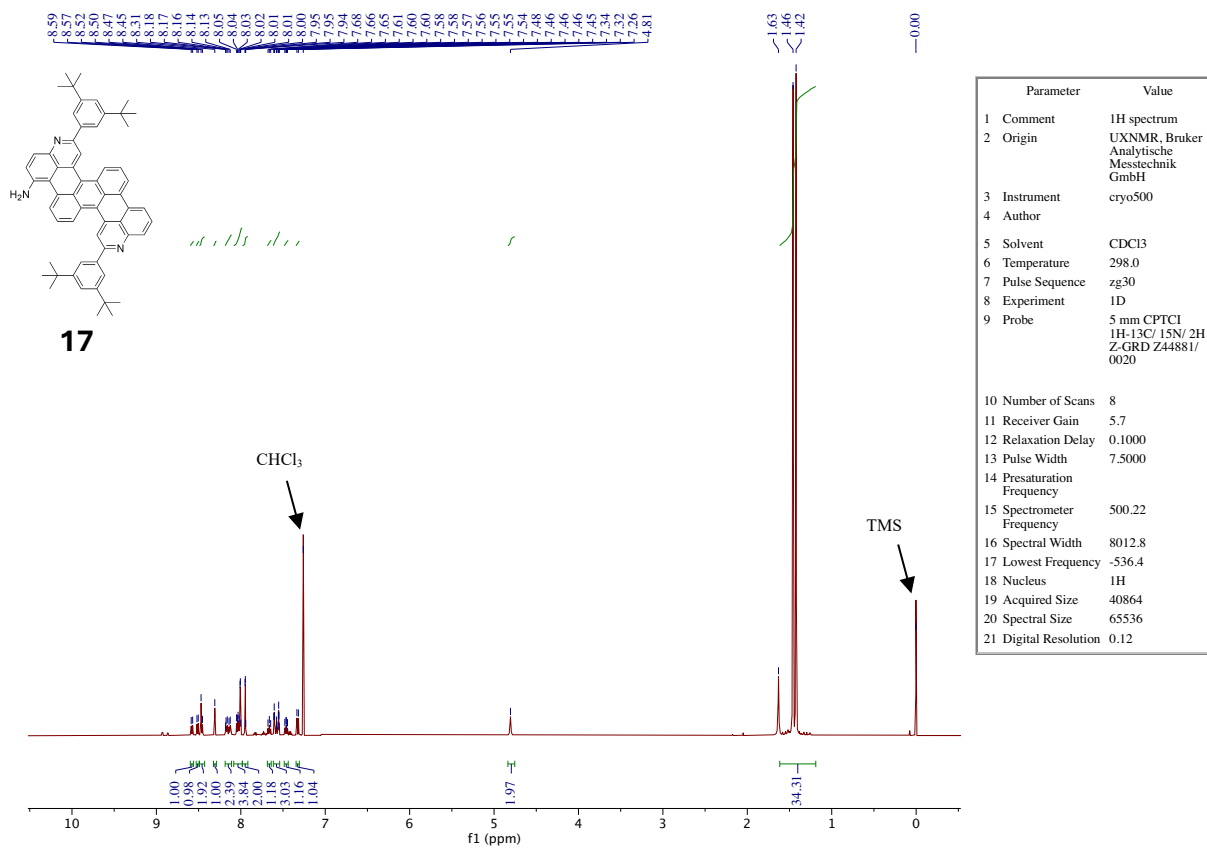


Figure S33. The ¹H NMR spectrum obtained for **17**.

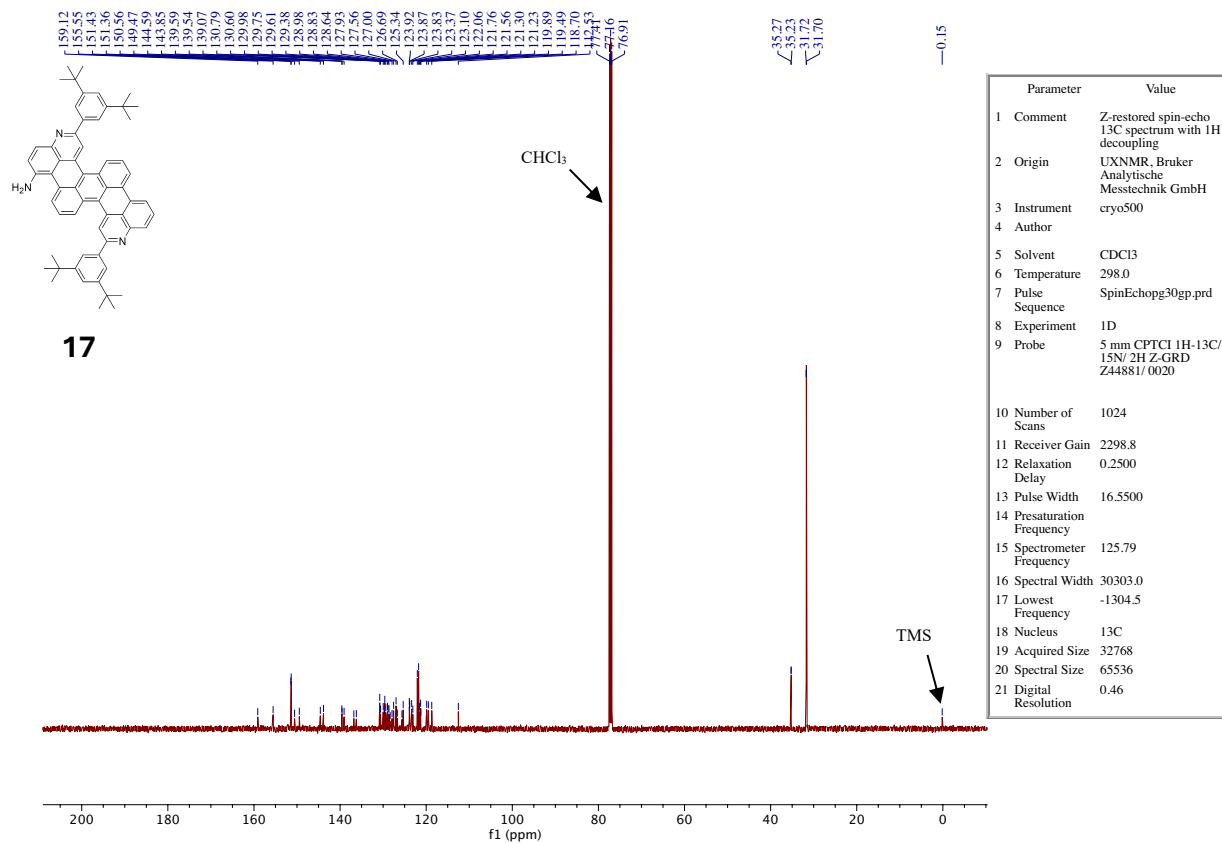


Figure S34. The ¹³C NMR spectrum obtained for **17**.

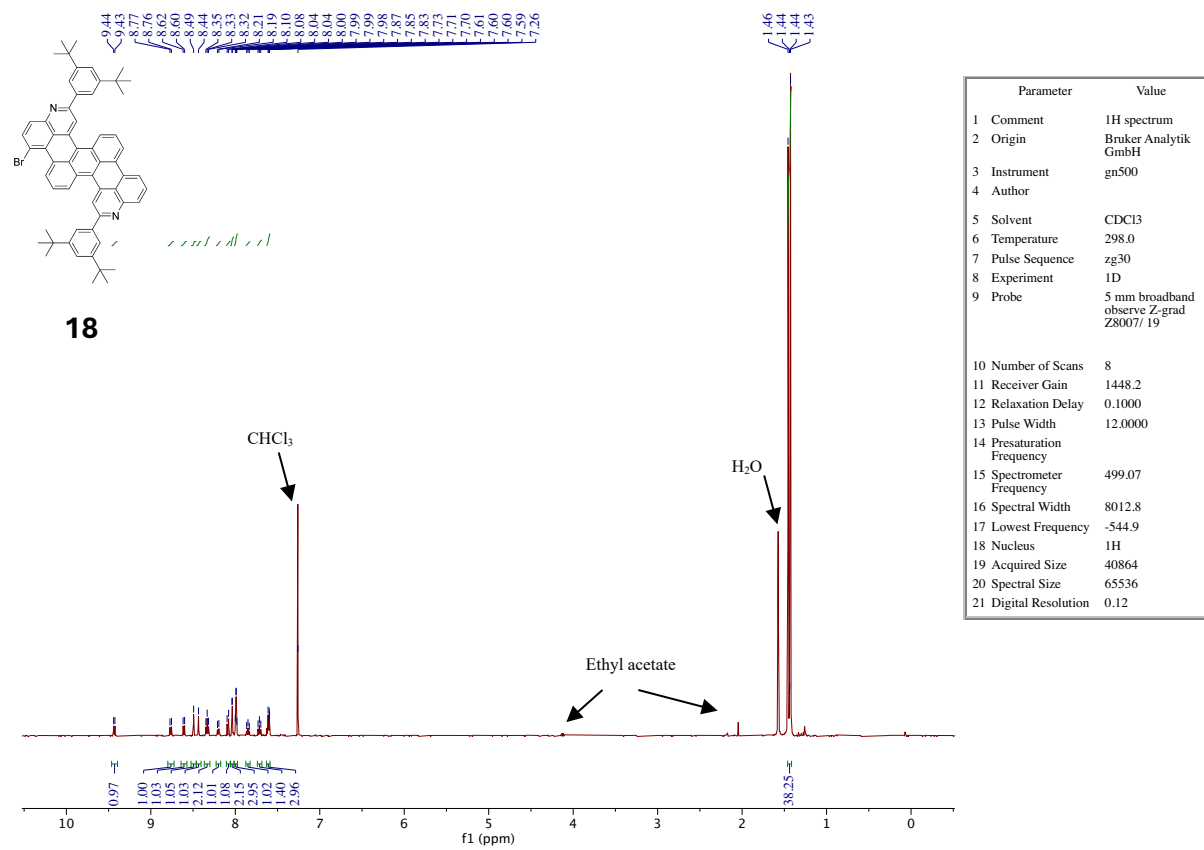


Figure S35. The ¹H NMR spectrum obtained for **18**.

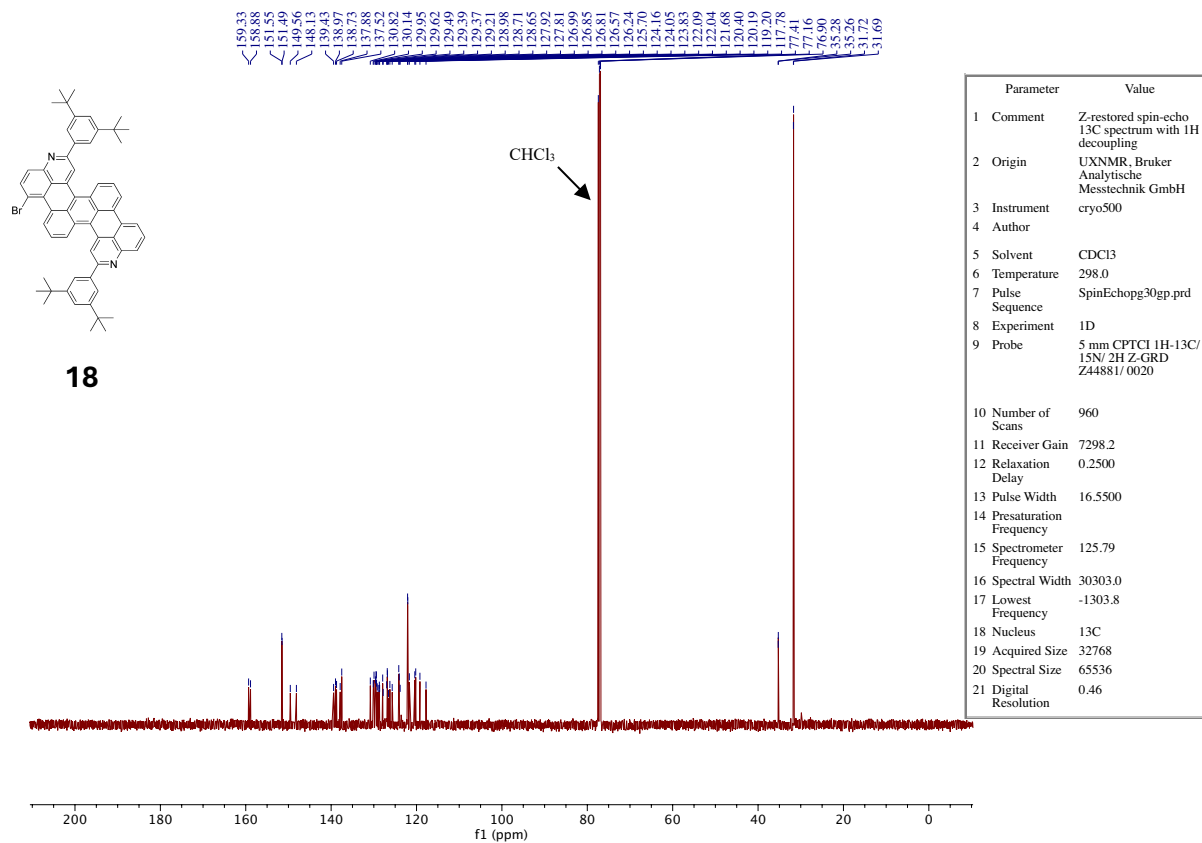


Figure S36. The ¹³C NMR spectrum obtained for **18**.

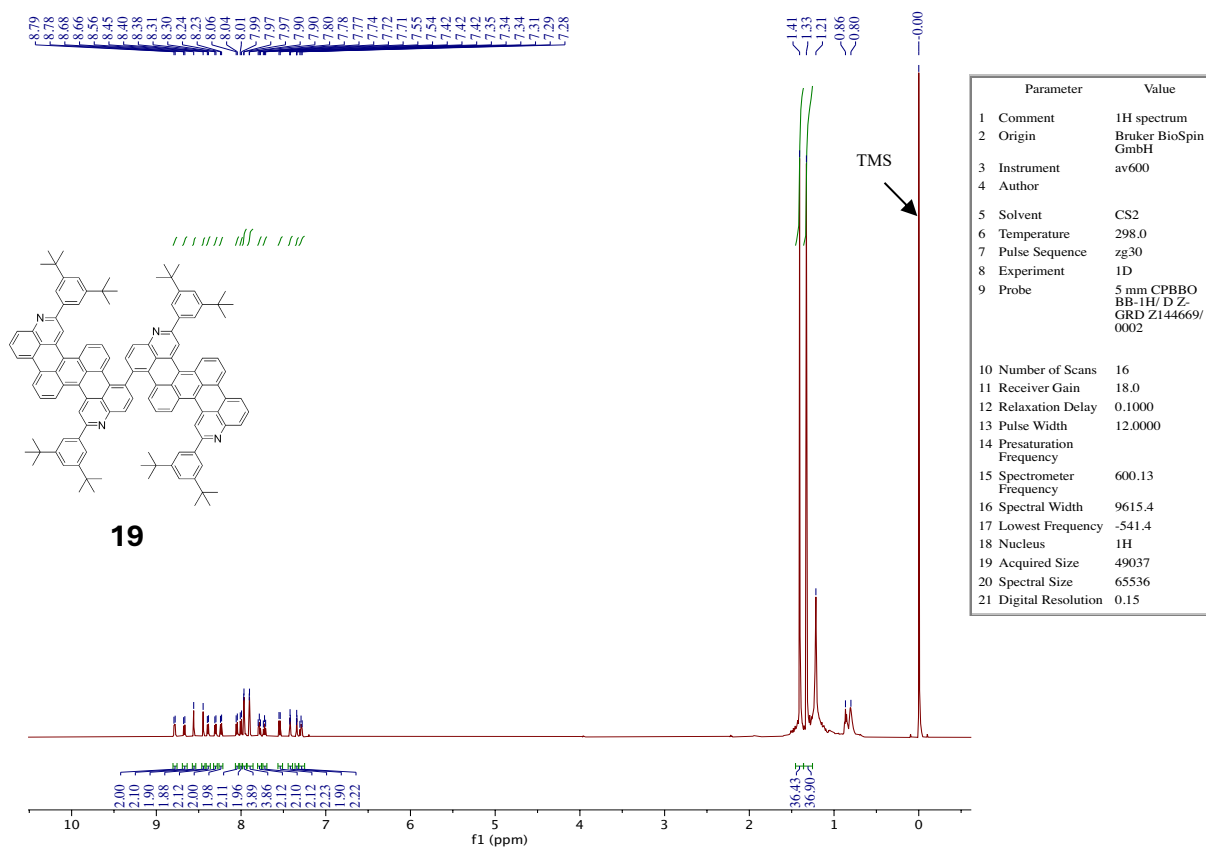


Figure S37. The ^1H NMR spectrum obtained for **19**.

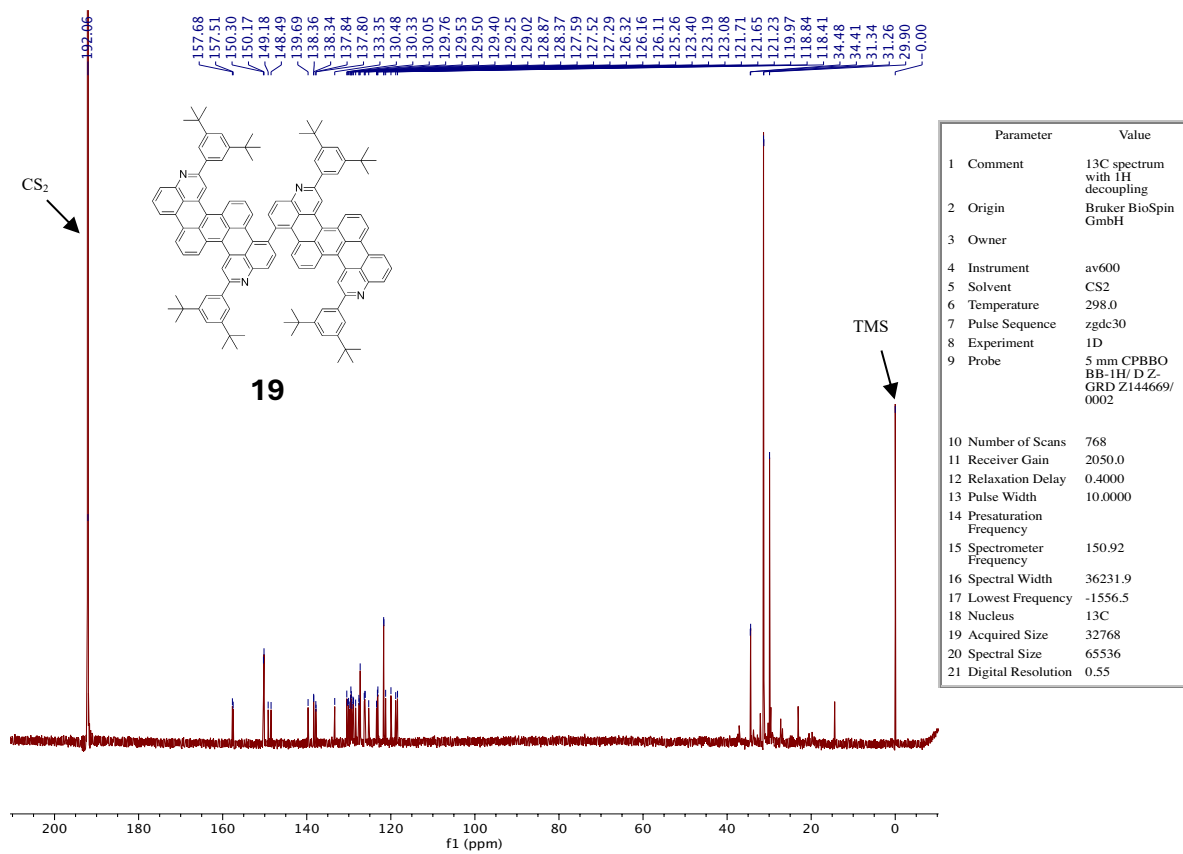


Figure S38. The ¹³C NMR spectrum obtained for **19**.

2.4. UV-Vis Spectroscopy Data

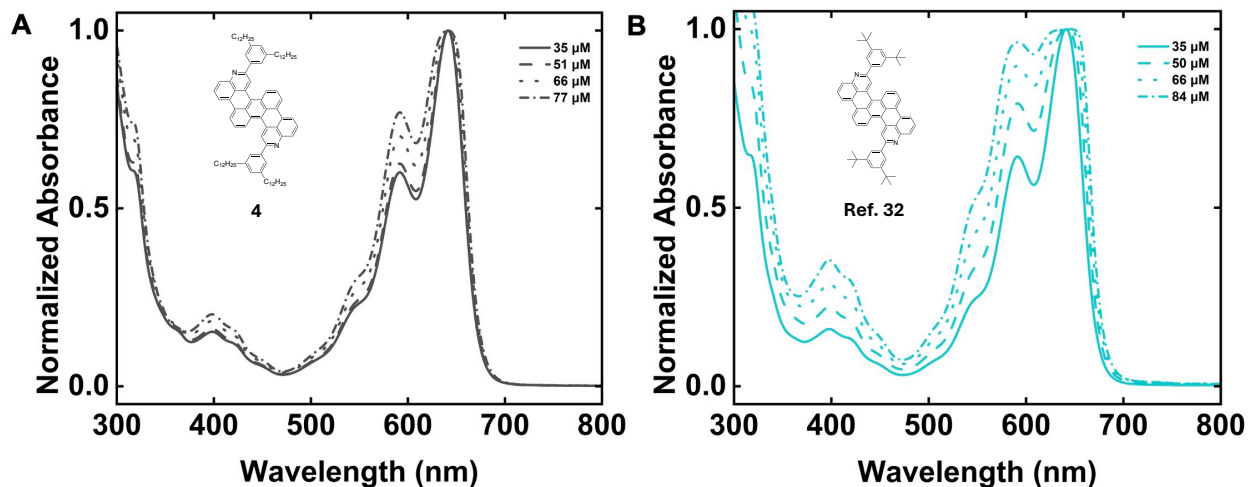


Figure S39. (A) The UV-Vis absorption spectra measured for dodecyl-substituted tetrabenzopentacene **4** at different concentrations. (B) The UV-Vis absorption spectra measured for a previously-reported tetrabenzopentacene analogue at different concentrations (see reference 32). Note that the absorption spectra were normalized by using their maximum absorbance peak within the 600 nm to 700 nm wavelength range to facilitate direct comparisons.

CONCLUSIONS

In summary, we have described the synthesis and characterization of substituted, expanded, functionalized, and dimeric nitrogen-containing tetrabenzocenes, and our findings hold significance for several reasons. First, the modification of our tetrabenzopentacenes with extended alkyl chains not only enhances solubility and mitigates aggregation but could also eventually simplify their processing from common organic solvents within the context of transistor applications. [1, 2, 7, 9, 10, 19] Second, the straightforward substitution of our tetrabenzopentacenes with electron-donating amino and electron-withdrawing bromo groups readily affords tuning of their optical and electrochemical properties in a manner advantageous for optoelectronics applications. [1, 2, 11, 16, 18, 19] Third, the site-specific substitution of our tetrabenzopentacenes with reactive amine and bromine functional handles immediately opens opportunities for their further modification via common chemical reactions, *e.g.*, Stille, Suzuki, Heck, and Ullmann couplings. [46–48] Last, the expansion and dimerization of our tetrabenzopentacenes suggests that they may prove useful as model compounds for nitrogen-containing acenes and could even serve as precursors for nitrogen-doped graphene nanoribbons. [3, 16, 17, 34, 43, 51] Overall, our synthetic methodology substantively adds to the small number of tetrabenzocene derivatives reported to date and may open further opportunities for these materials in organic optoelectronics applications.

REFERENCES

1. J. E. Anthony, Functionalized Acenes and Heteroacenes for Organic Electronics, *Chem. Rev.*, 2006, **106**, 5028–5048.
2. J. E. Anthony, The Larger Acenes: Versatile Organic Semiconductors, *Angew. Chem. Int. Ed.*, 2008, **47**, 452–483.
3. H. F. Bettinger, Electronic structure of higher acenes and polyacene: The perspective developed by theoretical analyses, *Pure Appl. Chem.*, 2010, **82**, 4, 905–915.
4. H. Qu and C. Chi, Synthetic Chemistry of Acenes and Heteroacenes, *Curr. Org. Chem.*, 2010, **14**, 2070–2108.
5. U. H. F. Bunz, N-Heteroacenes, *Chem. Eur. J.*, 2009, **15**, 6780–6789.
6. U. H. F. Bunz, The larger N-heteroacenes, *Pure Appl. Chem.*, 2010, **82**, 953–968.
7. Q. Miao, N-Heteropentacenes and N-Heteropentacenequinones: From Molecules to Semiconductors, *Synlett*, 2012, **23**, 326–336.
8. U. H. F. Bunz, J. U. Engelhart, B. D. Lindner and M. Schaffroth, Large N-Heteroacenes: New Tricks for Very Old Dogs?, *Angew. Chem. Int. Ed.*, 2013, **52**, 3810–3821.
9. M. Watanabe, K. Y. Chen, Y. J. Chang and T. J. Chow, Acenes Generated from Precursors and Their Semiconducting Properties, *Acc. Chem. Res.*, 2013, **46**, 1606–1615.
10. Q. Miao, Ten Years of N-Heteropentacenes as Semiconductors for Organic Thin-Film Transistors, *Adv. Mater.*, 2014, **26**, 5541–5549.
11. U. H. F. Bunz, The larger Linear N-Heteroacenes, *Acc. Chem. Res.*, 2015, **48**, 1676–1686.
12. Q. Miao, *Polycyclic Arenes and Heteroarenes: Synthesis, Properties, and Applications*, Wiley-VCH, Weinheim, 2015.
13. U. H. F. Bunz and J. U. Engelhart, The Palladium Way to N-Heteroacenes, *Chem. Eur. J.*, 2016, **22**, 4680–4689.
14. R. Dorel and A. M. Echavarren, Strategies for the Synthesis of Higher Acenes, *Eur. J. Org. Chem.*, 2016, **2017**, 14–24.
15. S. Dong, A. Ong and C. Chi, Photochemistry of various acene based molecules, *J. Photochem. Photobiol. C: Photoche. Rev.*, 2019, **38**, 27–46.
16. U. H. F. Bunz and J. Freudenberg, N-Heteroacenes and N-Heteroarenes as N-Nanocarbon Segments, *Acc. Chem. Res.*, 2019, **52**, 1575–1587.
17. M. Müller, L. Ahrens, V. Brosius, J. Freudenberg and U. H. F. Bunz, Unusual stabilization of larger acenes and heteroacenes, *J. Mater. Chem. C*, 2019, **7**, 14011–14034.
18. K. Kotwica, I. Wielgus and A. Proń, Azaacenes Based Electroactive Materials: Preparation, Structure, Electrochemistry, Spectroscopy and Applications—A Critical Review, *Materials*, 2021, **14**, 5155.
19. Y. Yunus, N. A. Mahadzir, M. N. M. Ansari, T. H. T. A. Aziz, A. M. Afdzaluddin, H. Anwar, M. Wang and A. G. Ismail, Review of the Common Deposition Methods of Thin-Film Pentacene, Its Derivatives, and Their Performance, *Polymers*, 2022, **14**, 1112.
20. E. Clar and A. Guzzi, Die Synthese des 1.9, 5.10-Di-[peri-naphthylen]-anthracens (Zur Kenntnis mehrkerniger aromatischer Kohlenwasserstoffe und ihrer Abkömmlinge, 18. Mitteil.), *Ber. Dtsch. Chem. Ges. B*, 1932, **65**, 1521-1525.
21. E. Clar, W. Kelly and J. W. Wright, Aromatic Hydrocarbons. Part LXVI. Diperinaphthyleneanthracenes, *J. Chem. Soc.*, 1954, 1108-1111.

22. N. Sato, H. Inokuchi, K. Seki, J. Aoki and S. Iwashima, Ultraviolet Photoemission Spectroscopic Studies of Six Nanocyclic Aromatic Hydrocarbons in the Gaseous and Solid States, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 1929-1936.
23. T. Ueda, M. Ohno, H. Harada, S. Iwashima, J. Aoki and T. Kan, Effect of Overcrowding in Mass Spectra for Six Violanthrenes, *Org. Mass Spectrom*, 1983, **18**, 105–109.
24. K. Imaeda, T. Enoki, H. Inokuchi, J. Aoki, M. Takekawa and S. Iwashima, Electric and magnetic-properties of tetrabenzo[de,hi,op,st]pentacene-alkali metal-complexes, *Chem. Lett.*, 1984, **13**, 331–334.
25. R. H. Schmidt, The Endoperoxide of Tetrabenzopentacene. A New Photochromic Endoperoxide, *Z. Naturforsch. A*, 1984, **39A**, 998–1002.
26. T. Ueda, Z. Abliz, S. Iwashima, J. Aoki, M. Takekawa and T. Kan, Effect of Overcrowding on Mass Spectra of Polycyclic Aromatic Hydrocarbons; Co-operative Double Cyclization of Two Methyl Substituents at Overcrowded Positions, *J. Chem. Soc. Perkin Trans. 2*, 1988, 1053-1056.
27. T. Asahi, M. Yudasaka, K. Nakanishi, S. Iwashima, J. Aoki, N. Sato and H. Inokuchi, Rectification Properties of In/Tetrabenzo [de, hi, op, st] Pentacene/Au Devices, *Phys. Status Solidi. A*, 1990, **122**, K97–K100.
28. S. A. Tucker, A. I. Zvaigzne, W. E. Acree, J. C. Fetzer and M. Zander, Polycyclic Aromatic Hydrocarbon Solute Probes. Part IX: Evaluation of Additional Pentaphene, Pentacene, and Pyranthrene Compounds as Possible Solvent Polarity Probes, *Appl. Spectrosc.*, 1991, **45**, 424–428.
29. A. Izuoka, K. Wakui, T. Fukuda, N. Sato and T. Sugawara, Refined Molecular Structure of Tetrabenzo[de,hi,op,st]pentacene, *Acta Cryst.*, 1992, **C48**, 900–902.
30. A. Izuoka, T. Murase, M. Tsukada, Y. Ito, T. Sugawara, A. Uchida, N. Sato and H. Inokuchi, Crystal Structure and Thermodynamical Behavior of Tetrabenzo[de,hi,op,st]pentacene Endoperoxide, *Tetrahedron Lett.*, 1997, **38**, 245–248.
31. B. X. Mi, Z. Q. Gao, M. W. Liu, K. Y. Chan, H. L. Kwong, N. B. Wong, C. S. Lee, L. S. Hung and S. T. Lee, New polycyclic aromatic hydrocarbon dopants for red organic electroluminescent devices, *J. Mater. Chem.*, 2002, **12**, 1307–1310.
32. Y. S. Park, D. J. Dibble, J. Kim, R. C. Lopez, E. Vargas and A. A. Gorodetsky, Synthesis of Nitrogen-Containing Rubicene and Tetrabenzopentacene Derivatives, *Angew. Chem. Int. Ed.*, 2016, **55**, 3352–3355.
33. J. Radtke, K. Schickedanz, M. Bamberg, L. Menduti, D. Schollmeyer, M. Bolte, H. W. Lerner and M. Wagner, Selective access to either a doubly boron-doped tetrabenzopentacene or an oxadiborepin from the same precursor, *Chem. Sci.*, 2019, **10**, 9017–9027.
34. Z. Feng, A. Mazaheripour, D. J. Dibble, P. Wagner, G. Czap, G. Kladnik, A. Cossaro, A. Verdini, L. Floreano, G. Bavdek, W. Ho, G. Comelli, D. Cvetko, A. Morgante and A. A. Gorodetsky, Bottom-up synthesis of nitrogen-containing graphene nanoribbons from the tetrabenzopentacene molecular motif, *Carbon*, 2020, **170**, 677–684.
35. D. J. Dibble, M. J. Umerani, A. Mazaheripour, Y. S. Park, J. W. Ziller and A. A. Gorodetsky, An Aza-Diels–Alder Route to Polyquinolines, *Macromolecules*, 2015, **48**, 557–561.
36. D. J. Dibble, Y. S. Park, A. Mazaheripour, M. J. Umerani, J. W. Ziller and A. A. Gorodetsky, Synthesis of Polybenzoquinolines as Precursors for Nitrogen-Doped Graphene Nanoribbons, *Angew. Chem. Inter. Ed.*, 2015, **54**, 5883–5887.