Supporting Information for:

Site-Selective [2+2+n] Cycloadditions for Rapid, Scalable Access to Alkynylated Polycyclic Aromatic Hydrocarbons

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General details

Unless otherwise stated, all manipulations of organometallic compounds were carried out in dry solvents under an atmosphere of nitrogen, using either standard Schlenk techniques or a glovebox. Pentane, toluene, tetrahydrofuran (THF), diethyl ether, and dichloromethane (CH_2Cl_2) were dried using a JC Meyers Phoenix SDS solvent purification system. Benzene was dried using a Vacuum Atmosphere solvent purification system. 1,2-Dichlorobenzene was distilled from CaH_2 at atmospheric pressure. Benzene-d_6 was freed from oxygen using three free-pump-thaw cycles and then dried for at least 48 h over 3 Å molecular sieves (5% by mass). All reaction solvents were stored over 3 Å molecular sieves. $[Ir(COD)Cl]_2$ was either purchased from Strem chemical or prepared according to the literature.[1] 2,4-Dibromo-1,5-diiodobenzene (**S1**),[2] 2,5-dibromo-1,4-diiodobenzene (**S2**),[3] 3,6-dibromo-2,7-diiodo-9,10-dimethoxyphenanthrene (**S4**),[4] 3,6-dibromo-2,7-bis(pent-1-ynyl)-9,10-dimethoxyphenanthrene (**S7**),[4] $EtC{\equiv}Mo(OC(CH_3)(CF_3)_2)_3(DME)$ (**Mo-2**),[5] $PdCl_2(IPr)(3\text{-chloropyridine})$,[6] $^{i}PrMgCl{\cdot}LiCl$,[7] Ir(COD)(dppe)Cl,[8] 1,4-bis(hexyloxy)but-2-yne,[9] 1,4-dimethoxy-2-butyne,[10] 2,2',4,4'-tetra(prop-1-yn-1-yl)-5,5'-dibromobiphenyl (**1b**),[11] and 1,5-dibromo-2,4-di(prop-1-yn-1-yl)benzene (**4b**)[11] were prepared by literature procedures or slight modifications thereof. Solutions of $ZnCl_2$ and $CuCN{\cdot}2LiCl$ in THF were prepared as follows. The precisely weighed masses of anhydrous salts were stirred in an approximate amount of THF until a homogeneous solution was obtained. For accurate determination of molarity, the solution was then quantitatively transferred to a graduated cylinder with the aid of additional THF. These solutions were stored over 3 Å molecular sieves (5% by mass) in a Teflon-stoppered flask. $^{n}BuLi$ and $^{i}PrMgCl{\cdot}LiCl$ were titrated by ^1H NMR spectroscopy immediately prior to use.[12] 1,4-Benzoquinone was purified by sublimation. All other reagents and solvents were purchased from commercial suppliers and used as received. “Room temperature”, “RT”, or “ambient temperature” refers to ~22 °C. Reaction temperatures represent the oil bath temperature (with a fully submersed, stirred solution) unless otherwise stated. Mass spectrometry was performed by the QB3/Chemistry Mass Spectrometry Facility at UC Berkeley (for EI and ESI spectra) and the Mass Spectrometry Facility at UC Riverside (for MALDI spectra). For MALDI, α-cyano-4-hydroxycinnamic acid was used as the matrix. Unless otherwise noted, NMR spectra were acquired at ambient temperature (~22 °C) using Bruker AV-600, AV-500, DRX-500, AV-400, and AV-300 spectrometers. Chemical shifts (δ) are given in ppm and referenced to residual solvent peaks for ^1H NMR spectra (δ = 7.26 ppm for chloroform-*d* and δ = 7.16 for benzene-d_6) and for $^{13}C\{^1H\}$ NMR spectra (δ = 77.16 ppm for chloroform-*d* and δ = 128.06 for benzene-d_6). For ^{19}F NMR spectra, chemical shifts are referenced to a 1,3,5-tris(trifluoromethyl)benzene internal standard (δ = –63.17 ppm[13] in benzene-d_6) and are reported relative to $CFCl_3$ at 0.00 ppm. ^1H NMR yields were determined using 1,3,5-trimethoxybenzene as internal standard. For greatest accuracy, yields were typically measured by acquisition of ^1H NMR spectra both before and after the reaction of interest, followed by a comparison of the amounts of starting material and desired product relative to the amount of added internal standard.

General notes on purification and product isolation

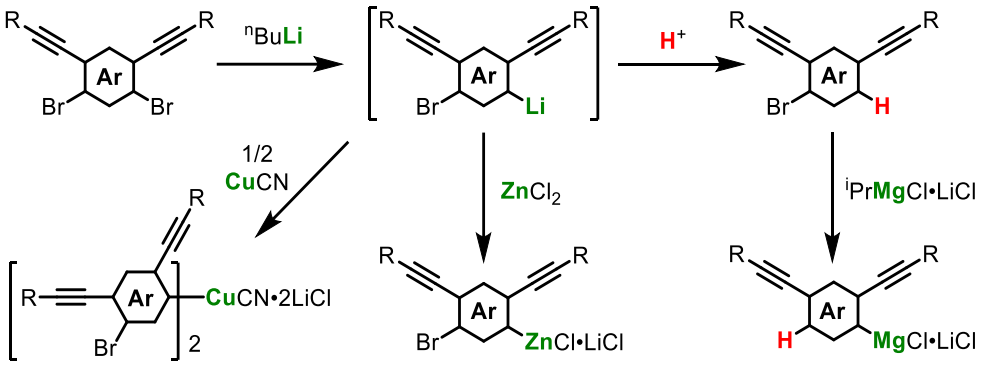
Chromatography
Column chromatography was carried out using Fischer Chemical 40–63 µm, 230–400 mesh silica gel. Preparatory thin layer chromatography (prep TLC) was carried out using Analtech Silica Gel GF UNIPLATES (1000 µm, 20 x 20 cm). For prep TLC, in a typical procedure, 35–50 mg of material was loaded onto one side of the plate and the solvent front was allowed to elute halfway up (i.e. 70–100 mg was separated per plate).

Isolation of solids *via* rotary evaporation
For most of the new oligoyne precursors (**1**), PAHs (**2**), and AEMs (**3**), the concentration of their solutions in "good" solvents (e.g. CH_2Cl_2) typically furnished a glassy, yellow/orange residue. For isolation of these compounds in powder form, co-evaporation with a poor solvent (usually hexanes) was necessary. Typically, the solution (e.g. the combined fractions from column chromatography) was concentrated *via* rotary evaporation in a round-bottomed flask, then the residue was transferred to a 20 mL vial with the minimal amount of CH_2Cl_2. The CH_2Cl_2 solution was then co-evaporated with hexanes *via* rotary evaporation, and residual solvents were removed under high vacuum to give the desired powder. This can be repeated with a larger hexanes/CH_2Cl_2 ratio of a powder is not obtained.

Isolation of fine powders via filtration
Several procedures below involve the precipitation of the desired product with an anti-solvent (e.g. MeOH). This often produced a very fine solid, which made filtration difficult. In these cases, filtration was greatly aided by celite, which was then extracted with CH_2Cl_2 for recovery of product. See above for important notes regarding rotary evaporation of CH_2Cl_2 solutions.

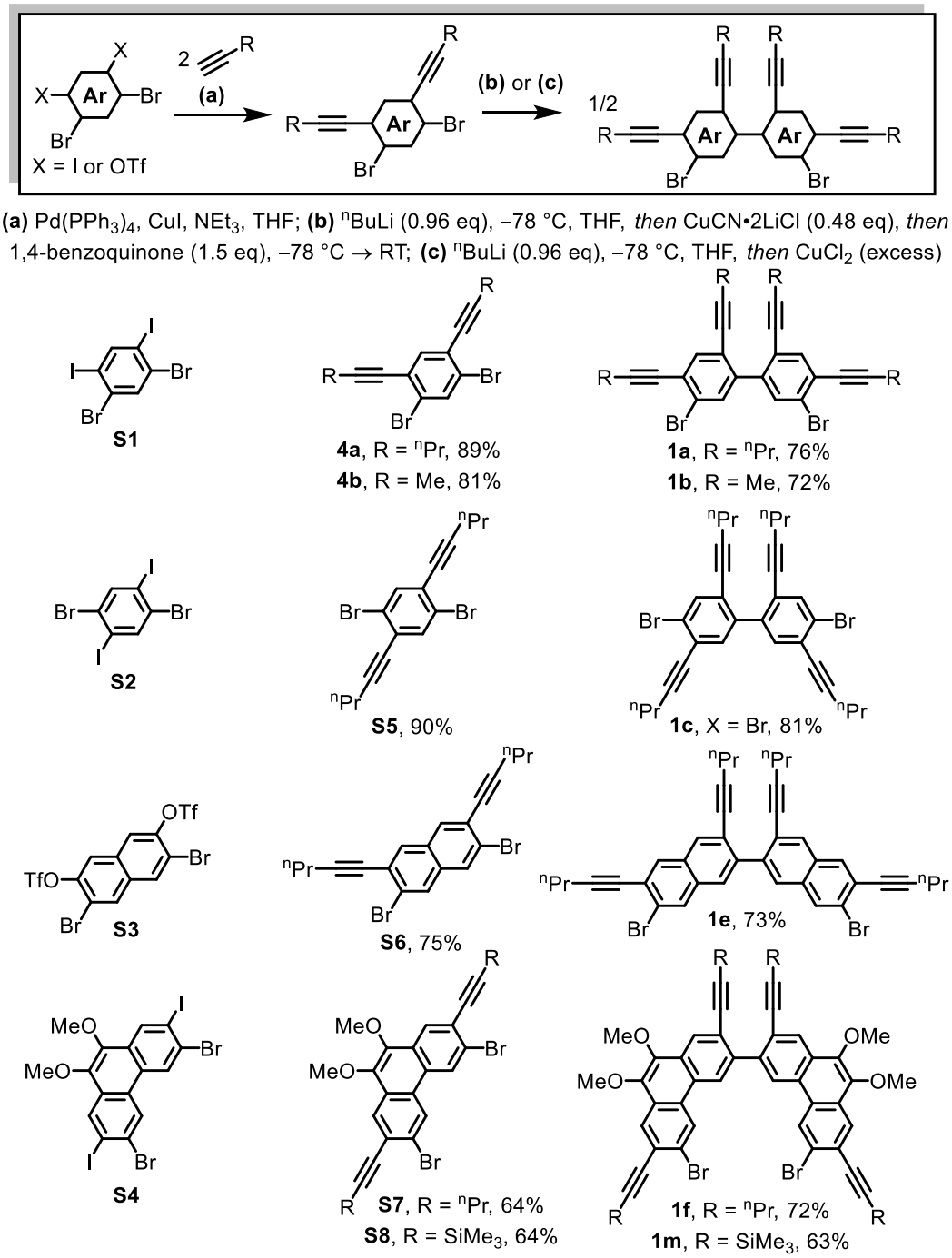
Modular synthesis of oligo(alkynyl)arylene precursors

The build-up of larger oligo(alkynyl)arylene substrates critically depends on the availability of unsymmetrical arylene building blocks for use as homo- and cross-coupling reaction partners. Lithium/bromine exchange, as depicted in Scheme S1, is highly effective for this purpose.[4,11,14] Generally, the dibrominated precursor is treated with 1 equiv of ^{n}BuLi to afford a mono-lithiated intermediate, which can then be either protodemetallated for isolation or transmetallated for direct use in a homo- or cross-coupling reaction (see below).



Scheme S1. General depiction of dibromoarene desymmetrization *via* lithium/bromine exchange.

The benzene, naphthalene, and phenanthrene building blocks **S1**–**S4** (Scheme S2) were synthesized in large quantities (30–100 grams per run) using previously-developed procedures (or slight modifications thereof).[2–4,15] These compounds were then subjected to a highly selective Sonogashira protocol that takes advantage of the superior reactivity of iodides[2] (or triflates[15]) over bromides, affording dibromides **4a**–**b** and **S5**–**S8** in good-to-excellent yields. The selective desymmetrization of these dibromides *via* lithium/halogen exchange enabled a subsequent Cu-mediated, oxidative homocoupling reaction. The use of higher order cuprates (i.e. *via* transmetallation to CuCN before oxidation with benzoquinone), as first developed by Lipshutz[16] and later improved by Iyoda,[17] consistently provided 70–80% yields for this this homocoupling reaction (i.e. **1a**, **1c**, **1e**, **1f**, and **1m**). The use of $CuCl_2$ as oxidative coupling reagent,[18] while operationally more convenient, generally provided lower yields. For example, the yield of compound **1a** was 53% with the use of $CuCl_2$ compared to 76% with CuCN/benzoquinone. In addition, **1f** was previously synthesized in 55% yield using $CuCl_2$,[4] but this yield dropped to 36% on a larger (~5x) scale (primarily due to difficulties with purification). The use of CuCN/benzoquinone solved this scalability problem and gave 6 grams **1f** in an improved (72%) yield.

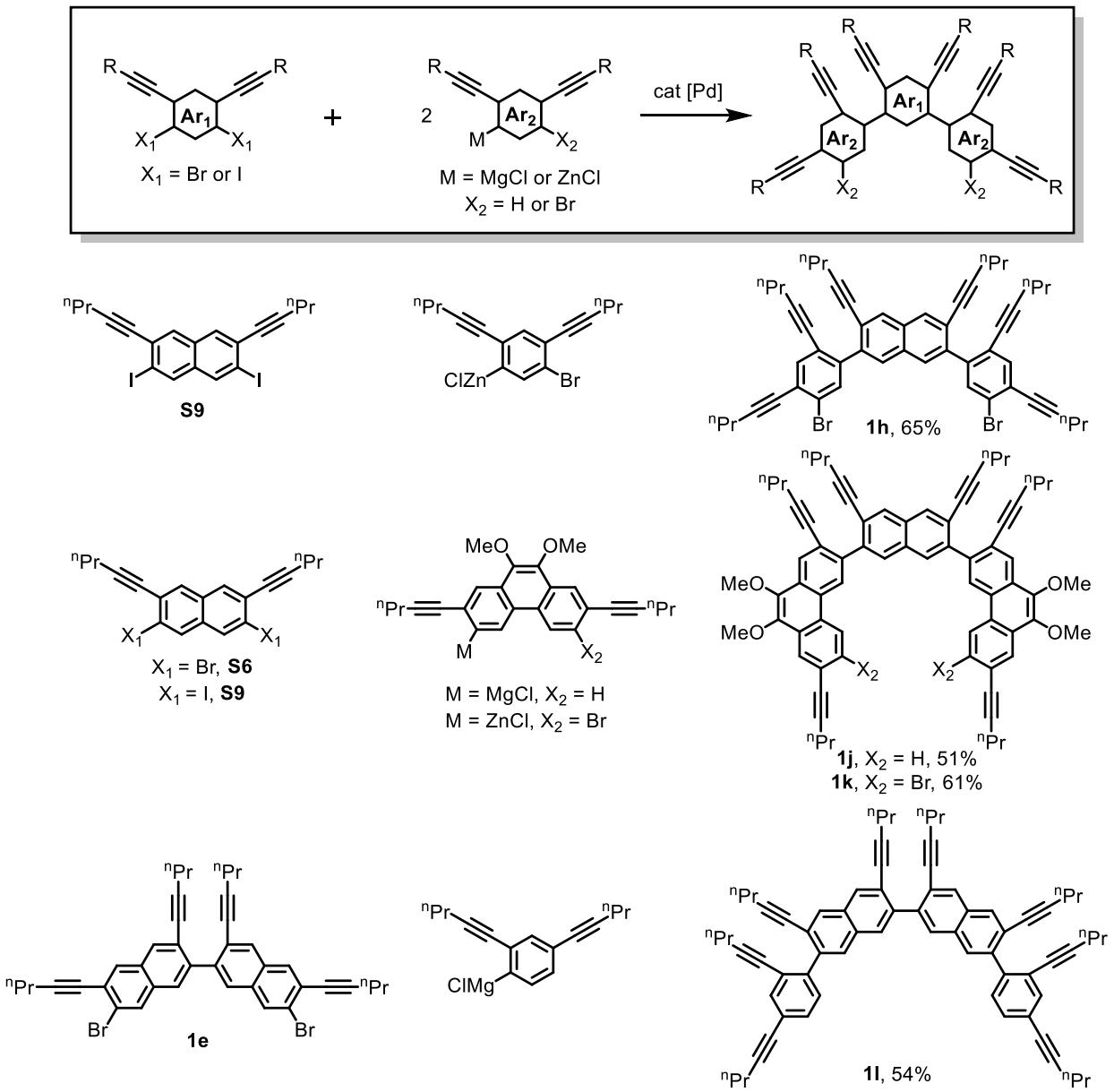


(a) $Pd(PPh_3)_4$, CuI, NEt_3, THF; **(b)** ^nBuLi (0.96 eq), –78 °C, THF, *then* CuCN•2LiCl (0.48 eq), *then* 1,4-benzoquinone (1.5 eq), –78 °C → RT; **(c)** ^nBuLi (0.96 eq), –78 °C, THF, *then* $CuCl_2$ (excess)

Scheme S2. Syntheses of substrates containing one diyne unit *via* Cu-mediated homocoupling.

The modularity of the precursor synthesis becomes evident when considering the synthesis of more complex substrates such as those shown in Scheme S3. Compounds **1h**–**1l** were isolated in moderate yields (51–65%) using standard Kumada or Negishi conditions. In addition to the modularity, there are a few other notable features of these cross-coupling reactions. First, they are directly analogous to those in our previous reports where both arene coupling partners possess an alkynyl group that is ortho to the coupling site.[4,11] Since only a few Pd catalysts have been screened, there is significant room for improvement in this transformation. Second, the

Negishi coupling can be performed in an “iodide-selective” fashion, with the preservation of the less-reactive bromides, as shown for **1h** and **1k**. Third, the synthesis of **1l** demonstrates how coupling reactions can be used in sequence to build up more complex precursors (since cross coupling partner **1e** was synthesized *via* homocoupling). *These features all point to the exciting possibility of iterative syntheses to build up arbitrarily complex substrates.*



Scheme S3. Syntheses of substrates containing two or three diyne units *via* Kumada or Negishi cross-coupling.

Comments about the $[Ir(COD)Cl]_2$ / dppe catalyst system

The reaction of 1.0 equiv of $[Ir(COD)Cl]_2$ with 2.0 equiv of dppe (in toluene or benzene*) gives the [2+2+2] pre-catalyst Ir(COD)(dppe)Cl. If dppe is present in excess, an orange/red precipitate (likely $Ir(dppe)_2Cl$[19,20]) is observed. The most reproducible way to achieve the desired catalyst loading is with isolated Ir(COD)(dppe)Cl (see procedures for compounds **2b**–**d** and **2j**–**l** below), which can be easily prepared in one step in nearly quantitative yield.[8] Isolated Ir(COD)(dppe)Cl is especially useful for smaller scale reactions where it is harder to get the correct 2:1 ratio of dppe to $[Ir(COD)Cl]_2$. Alternatively, Ir(COD)(dppe)Cl can be pre-formed *in situ* by addition of a solution of dppe in toluene to a solution of $[Ir(COD)Cl]_2$ in toluene (in the absence of the alkyne-containing reactants). This is demonstrated for compounds **2a**, **2e**, and **2h** below. Finally, the most user-friendly procedure, which has been tested in only one case (compound **2f**), is the addition of a solution of dppe in toluene to a solution of $[Ir(COD)Cl]_2$ *and* reactants in toluene.

*We did not notice any differences between toluene and benzene as solvents for the [2+2+2] reactions reported herein.

Sensitivity analysis for the site-selective [2+2+2] cycloaddition

This section provides more details on the sensitivity analysis for the synthesis of model triphenylene **2a**, which was briefly summarized in the main text. All yields provided below were measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (as described in the general details above). The baseline (and optimal) conditions reported in Scheme 2 of the main text are 1.5 equiv of 1,4-dimethoxy-2-butyne, 2% Ir(COD)(dppe)Cl, 80 °C, 1 h, 100 mM in benzene-d_6. Several critical parameters were systematically varied in three sets of experiments, which are summarized in Tables S1–3. In the first set of experiments (Table S1), monoyne equivalents were varied between 1.0 and 5.7. In the second set of experiments (Table S2), concentration was varied between 1 and 300 mM. In the third set of experiments (Table S3), Ir(COD)(dppe)Cl loading was varied between 0.4 and 10%. Time was varied in all three sets of experiments.

Yield of **2a**

Monoyne Equiv	0.25h	1h	10h
0.0	0%	0%	0%
1.0	79%	87%	87%
1.4	84%	93%	88%
1.7	90%	91%	83%
5.7	87%	87%	83%

Consumption of **1a**

Monoyne Equiv	0.25h	1h	10h
0.0	21%	24%	46%
1.0	86%	98%	100%
1.4	93%	100%	100%
1.7	99%	100%	100%
5.7	93%	100%	100%

Table S1. Yield of model triphenylene **2a** as a function of ***monoyne equivalents*** and time.

Yield of **2a**

Conc. (mM)	0.25h	1h	10h
300	88%	87%	84%
100	93%	91%	90%
10	71%	84%	94%
1	21%	28%	36%

Consumption of **1a**

Conc. (mM)	0.25h	1h	10h
300	96%	100%	100%
100	93%	100%	100%
10	69%	90%	100%
1	25%	34%	42%

Table S2. Yield of model triphenylene **2a** as a function of ***concentration*** and time.

Yield of **2a**

Ir Loading	0.25h	1h	10h
0.4%	22%	29%	37%
1%	66%	85%	91%
2%	85%	92%	87%
6%	92%	88%	82%
10%	92%	88%	82%

Consumption of **1a**

Ir Loading	0.25h	1h	10h
0.4%	23%	33%	41%
1%	70%	91%	100%
2%	90%	99%	100%
6%	99%	100%	100%
10%	99%	100%	100%

Table S3. Yield of model triphenylene **2a** as a function of ***catalyst loading*** and time.

Thermodynamic control in the generation of intermediate zirconacyclopentadiene annulated PAH 2m

To test the hypothesis that the site-selectivity of the Cp_2Zr-mediated [2+2+1] cycloaddition occurs under thermodynamic control, the following ^1H NMR experiment was performed (summarized in Figure S1). *Since the latter parts of this experiment were performed above the boiling point of benzene-d_6 in a sealed tube, a blast shield was used.* In a glovebox, tetrayne **1m** (31.0 mg, 0.0305 mmol, 1.0 equiv) and hexamethylbenzene (~7 mg; internal standard) were dissolved in benzene-d_6 (1.0 mL), transferred to a J-Young NMR tube, and analyzed by ^1H NMR spectroscopy (Figure S1b). The mixture was poured into a vial containing $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (14.4 mg, 0.0305 mmol, 1.0 equiv), and the homogeneous mixture was transferred back to the tube. ^1H NMR spectra were then periodically acquired after the time/temperature combinations that are specified in Figures S1c–e. The mixture remained homogeneous throughout these experiments. At the end of heating, **2m** was precipitated by addition of pentane (1.5 mL) to the tube. The solid was collected by filtration and analyzed by ^1H NMR (Figure S1f) for comparison. Quantitative analysis of these data revealed that after 10 min at 22 °C (Figure S1c) all $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ had been consumed to produce **2m** (~20%), starting **1m** (~30%), and a mixture of unidentified products (~50%). The unidentified products are likely to consist (at least partly) of oligomers resulting from intermolecular cycloadditions involving the peripheral alkynyl groups. After heating at 90 °C for 22 h (Figure S1d), the composition of the mixture changed, but the amount of **2m** remained at 20–25%. After heating at 105 °C for 18 h (Figure S1e), the composition of the mixture again changed, but this time the amount of **2m** increased to ~45% with a concomitant decrease in **1m** (to 15–20%) and unidentified products (to 35–40%). After heating at 115 °C for 5 h, no further changes were observed. Note that other likely side products, especially at high temperatures, are those resulting from oxidative addition of "Cp_2Zr" to the Ar-Br bond in **1m**, **2m**, or an oligomeric intermediate.

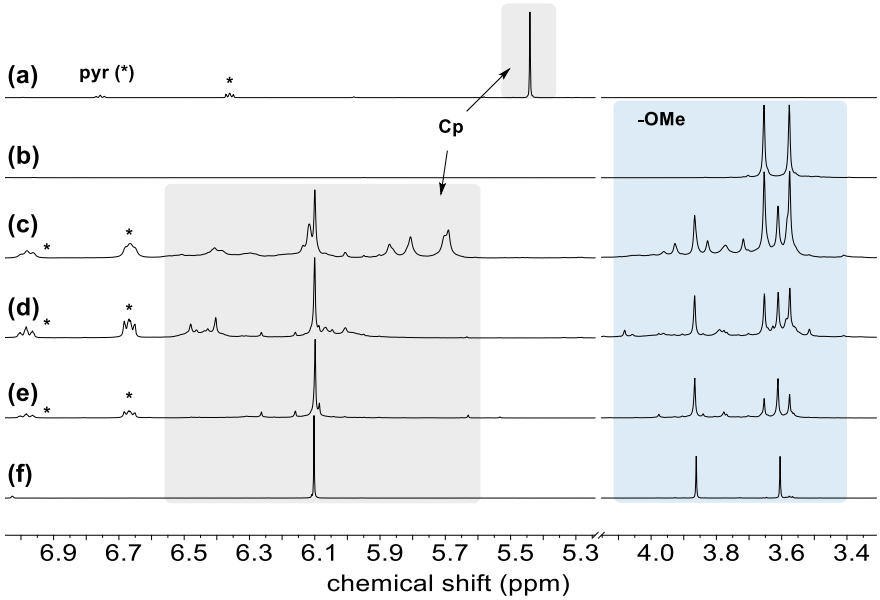


Figure S1. Partial ^1H NMR spectra (400 MHz, benzene-d_6) of the reaction between $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ and tetrayne **1m**: **(a)** $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$; **(b)** tetrayne **1m**; **(c)** 10 min at 22 °C; **(d)** 22 h at 90 °C; **(e)** 18 h at 105 °C; **(f)** isolated zirconacycle (**2m**).

Generation of hypothesized EtC≡Mo(OSiPh$_3$)$_3$ (Mo-1) from EtC≡Mo(OC(CH$_3$)(CF$_3$)$_2$)$_3$(DME) (Mo-2) and Ph$_3$SiOH

The current best catalyst for many alkyne metathesis applications are complexes of the general form R'C≡Mo(OSiAr$_3$)$_3$ (R' = aryl or alkyl), which have been heavily developed Fürstner and coworkers.[21–24] There are several different isolable catalyst precursors, most notably the base-stabilized derivatives R'C≡Mo(OSiAr$_3$)$_3$L (e.g., L = phen or Et$_2$O)[22] or bench stable N≡Mo(OSiAr$_3$)$_3$L (L = phen or pyr)[21]. An alternative way to access these catalysts is by ligand exchange, as shown by Moore and coworkers *via in situ* treatment of EtC≡Mo(N^{t}BuAr)$_3$ with excess Ph$_3$SiOH.[25,26] In the course of the current study, it was discovered that EtC≡Mo(OSiPh$_3$)$_3$ (**Mo-1**) can be analogously generated from the easily-prepared EtC≡Mo(OC(CH$_3$)(CF$_3$)$_2$)$_3$(DME) (**Mo-2**). Details of this ligand exchange are discussed in the following paragraph.

All alkyne metathesis reactions performed in this study use *in situ* generated **Mo-1**, which is typically formed by pre-mixing of **Mo-2** with 6 equiv of Ph$_3$SiOH. This ligand exchange reaction was initially investigated by ^{1}H and ^{19}F NMR spectroscopies, whereby a solution of **Mo-2** in benzene-d_6 was treated with 4, 6, and 9 equiv of Ph$_3$SiOH (Figures S2 and S3). With 6 and 9 equiv, the only observable species by ^{19}F NMR was free (CH$_3$)(CF$_3$)$_2$COH (with 4 equiv, 95% of the theoretical amount of (CH$_3$)(CF$_3$)$_2$COH was observed along with 5% of an unidentified species). Additionally, in all cases, the ^{1}H NMR spectra displayed identical, upfield-shifted propylidyne resonances (a methyl quartet at 1.5 ppm and a methylene triplet at –0.2 ppm). These data suggest that the ligand exchange goes to completion with > 4 equiv of Ph$_3$SiOH, producing metathesis active **Mo-1** that is likely in rapid equilibrium with various adducts of weakly bound[23] L-type ligands (e.g. Ph$_3$SiOH and DME).

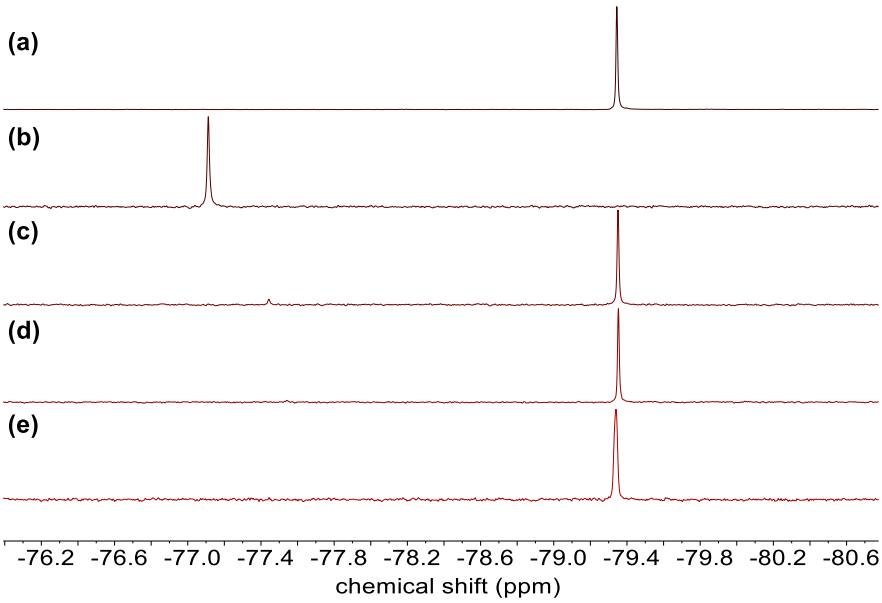


Figure S2. Partial ^{19}F NMR spectra (376 MHz, benzene-d_6) of **(a)** Authentic sample of (CH$_3$)(CF$_3$)$_2$COH; **(b)** EtC≡Mo(OC(CH$_3$)(CF$_3$)$_2$)$_3$(DME) (**Mo-2**); **(c) Mo-2** + 4 equiv of Ph$_3$SiOH; **(d) Mo-2** + 6 equiv of Ph$_3$SiOH; **(e) Mo-2** + 9 equiv of Ph$_3$SiOH. These spectra suggest that free (CH$_3$)(CF$_3$)$_2$COH is generated upon addition of > 4 equiv of Ph$_3$SiOH. Note that there is a small singlet (~5% by integration) at 77.4 ppm in spectrum (c), which may be due to incomplete ligand exchange.

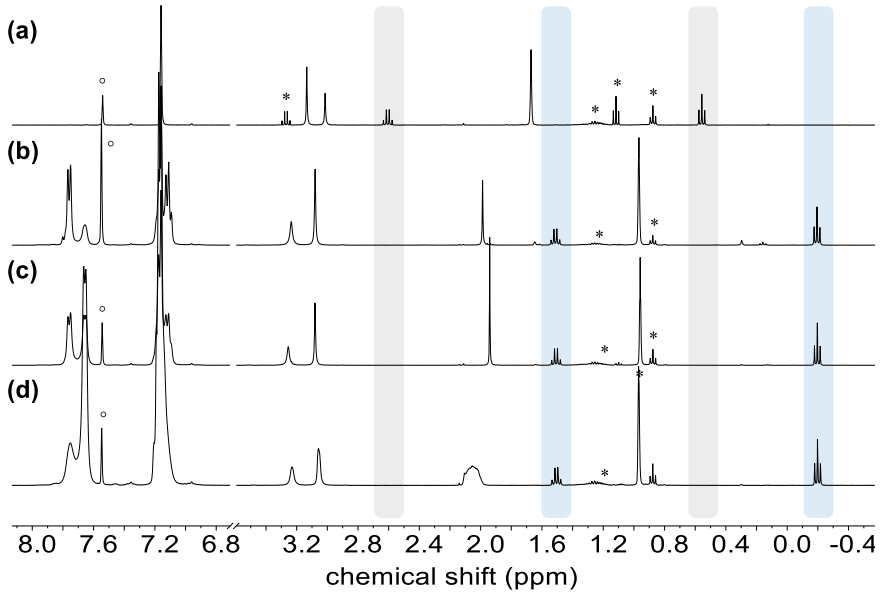


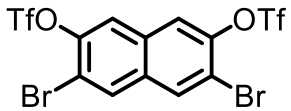
Figure S3. Partial ^{1}H NMR spectra (400 MHz, benzene-d_6) of **(a)** EtC≡Mo(OC(CH$_3$)(CF$_3$)$_2$)$_3$(DME) (**Mo-2**); **(b) Mo-2** + 4 equiv of Ph$_3$SiOH; **(c) Mo-2** + 6 equiv of Ph$_3$SiOH; **(d) Mo-2** + 9 equiv of Ph$_3$SiOH. These spectra suggest that the same new species is formed in all cases, which is hypothesized to be **Mo-1**. Note that **Mo-1** is likely in rapid equilibrium with various adducts of weakly bound[23] L-type ligands (e.g. Ph$_3$SiOH and DME). The highlighted (gray and blue) resonances are associated with the propylidyne group. Note that the hydroxyl resonances (between 1.8 and 2.3 ppm) are not comparable due to hydrogen bonding effects. *Glovebox solvents (pentane and diethyl ether);°1,3,5-tris(trifluoromethyl)benzene internal standard

Important note regarding the use of 5 Å molecular sieves (MS) to sequester 4-octyne

We observed that the source of the molecular sieves is of critical importance for the alkyne metathesis reactions performed herein. All successful reactions used pre-powdered 5 Å MS that were purchased from Sigma Aldrich and activated under high vacuum at ~300 °C* (until condensation of water ceased, then for another 24 h). The activated 5 Å MS were then stored in a solvent-free, nitrogen-filled glovebox until use. At the outset of our investigations, beaded 5 Å MS (3–5 mm, from Alfa Aesar) were activated as described above, then thoroughly ground with a mortar and pestle in a solvent-free, nitrogen-filled glovebox. *Use of these molecular sieves was not effective for the sequestration of 4-octyne*.

*Temperature of the sand bath.

Synthetic procedures and basic characterization data



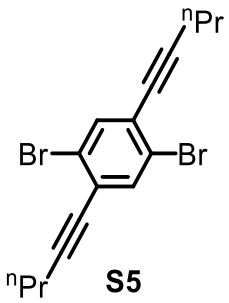
S3

3,6-dibromo-2,7-bis(trifluoromethanesulfonyloxy)naphthalene (S3)

Procedure: This compound was prepared by a modified* literature procedure.[15] A 500 mL Schlenk flask was charged with diol **S12** (20.0 g, 62.9 mmol, 1.0 equiv), dry pyridine (20.0 g, 252 mmol, 4.0 equiv), and CH_2Cl_2 (170 mL), and the solution was cooled to 0 °C with an ice/water bath. To the stirred solution was added Tf_2O (41.0 g, 145 mmol, 2.3 equiv) dropwise over ~10 min. The cold bath was removed, then the mixture was stirred for 2 h and quenched with aqueous HCl (0.5 M, 200 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (30 mL). The combined organic layers were dried with $MgSO_4$, diluted** with hexanes (200 mL), filtered through a plug of silica gel (20-25 g), then the plug was flushed with 1:1 hexanes:CH_2Cl_2 (100 mL). The filtrate was concentrated to ~150 mL *via* rotary evaporation, then the crystalline precipitate was collected on a fritted funnel and washed with hexanes (2 x 30 mL). After removal of residual solvents from the solid *in vacuo*, the yield of **S3**, a pale-yellow (nearly colorless) crystalline solid, was 29.5 g (81%).

Notes: *The major modifications were in the workup and purification steps; **In order to avoid precipitation of a solid, the mixture was filtered through the silica immediately after this dilution.

Characterization: ^{1}H NMR data matches that in the literature.[15]



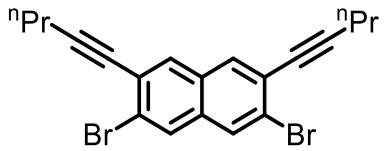
S5

1,4-dibromo-2,5-di(pent-1-yn-1-yl)benzene (S5)

Procedure: A 250 mL Schlenk flask with Teflon stopper was charged with diiodide **S2** (10.0 g, 20.5 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.36 g, 0.31 mmol, 0.015 equiv), and CuI (0.20 g, 1.03 mmol, 0.05 equiv), then the flask was evacuated and refilled with N_2. To this flask was added an N_2-sparged mixture of THF (28 mL) and triethylamine (14 mL), followed by 1-pentyne (3.07 g, 45.1 mmol, 2.2 equiv). The mixture was stirred at RT for 16 h, then diluted with hexanes (150 mL), and filtered. The filter cake was rinsed with hexanes (50 mL) and solvents were removed from the filtrate *via* rotary evaporation.* The residue was purified by column chromatography (100% hexanes) to afford **S5** (6.77 g, 90%) as a white solid.

Notes: *To ensure complete removal of THF and triethylamine, which can adversely affect the separation in the subsequent chromatographic purification, the residue obtained after the first concentration was dissolved in hexanes (30 mL) and solvents were removed again.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 7.59 (s, 2H), 2.44 (t, *J* = 7.0 Hz, 4H), 1.65 (q, *J* = 7.2 Hz, 4H), 1.07 (t, *J* = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (chloroform-*d,* 101 MHz): δ = 136.16, 126.59, 123.59, 98.12, 78.55, 22.04, 21.74, 13.69; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{16}H_{16}Br_2$, 365.9619; found, 365.9613.



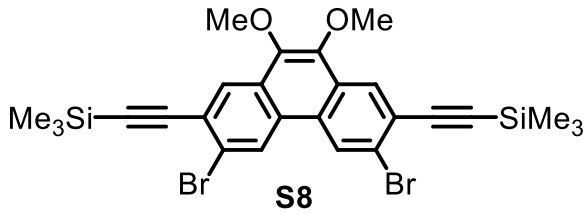
S6

2,7-dibromo-3,6-di(pent-1-yn-1-yl)naphthalene (S6)

Procedure: This procedure is a modified version of that reported by Takimiya and coworkers for a similar compound.[15] A 500 mL round-bottomed Schlenk flask was charged with ditriflate **S3** (21.0 g, 36.1 mmol, 1.0 equiv)**,** $Pd(PPh_3)_4$ (1.25 g, 1.08 mmol, 0.03 equiv), and CuI (0.41 g, 2.17 mmol, 0.06 equiv), and the flask subjected to three vacuum/N_2 cycles. To this flask was added DMF (56 mL) and NH^iPr_2 (28 mL) (both of which had been thoroughly sparged with N_2), followed 1-pentyne (4.92 g, 72.2 mmol, 2.0 equiv*). The flask was sealed with a ground-glass stopper and stirred for 20 h at RT**. The mixture was diluted with hexanes (150 mL) and washed with water (200 mL). The aqueous layer was extracted with hexanes (2 x 100 mL), then the combined organic layers were washed with aqueous HCl (3 M, 100 mL), dried with $MgSO_4$, and filtered through a plug of silica gel (20 g). The plug was flushed with hexanes (150 mL), solvents were removed *via* rotary evaporation, and the crude solid was recrystallized from EtOH (150 mL; boiling, then –25 °C) to afford **S6** (11.3 g, 75%) as small colorless needles.

Notes: *This reaction is very sensitive to stoichiometry. **Toward the beginning of the reaction there was a (delayed) exotherm. It is thus prudent to monitor for this exotherm and equalize the pressure of the flask to avoid over-pressurization.

Characterization: ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.92 (s, 2H), 7.80 (s, 2H), 2.48 (t, *J* = 6.9 Hz, 4H), 1.70 (h, *J* = 7.2 Hz, 4H), 1.11 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (151 MHz, Chloroform-*d*): δ = 132.84, 132.05, 130.34, 129.74, 124.52, 123.98, 96.27, 79.52, 22.17, 21.81, 13.78; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{20}H_{18}Br_2$, 415.9775; found, 415.9778.



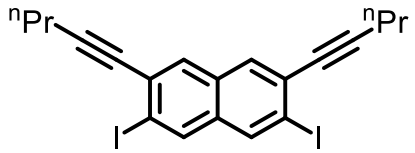
S8

3,6-dibromo-2,7-bis(trimethylsilylethynyl)-9,10-dimethoxyphenanthrene (S8)

Procedure: A 150 mL Schlenk flask with Teflon stopper was charged with diiodide **S4** (3.50 g, 5.41 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.16 g, 0.14 mmol, 0.025 equiv), and CuI (0.062 g, 0.33 mmol, 0.06 equiv), then the flask was evacuated and refilled with N_2 (3x). To this flask was added THF (24 mL) and triethylamine (12 mL) (both of which had been thoroughly deoxygenated), followed by deoxygenated trimethylsilylacetylene (1.09 g, 11.1 mmol, 2.1 equiv). The flask was sealed, and the stirred reaction mixture was heated at 70 °C for 24 h, then brought to RT, diluted with CH_2Cl_2 (100 mL), washed with aqueous HCl (3 M, 80 mL), dried with $MgSO_4$, and filtered. Solvents were removed from the filtrate *via* rotary evaporation, then the crude product was purified by column chromatography* (4:1 hexanes:CH_2Cl_2), followed by recrystallization from boiling EtOH to afford diyne **S8** (2.02 g, 64%) as a pale-yellow, crystalline solid.

Notes: *This might be better referred to as a "silica plug", as only one fraction was collected. It is important, however, that the plug be well equilibrated (as in a typical column) to avoid contamination of the product by Pd catalyst decomposition products.

Characterization: ^{1}H NMR (chloroform-*d*, 400 MHz): δ = 8.66 (s, 2H), 8.32 (s, 2H), 4.06 (s, 6H), 0.33 (s, 18H); ^{1}H NMR (benzene-d_6, 600 MHz): δ = 8.52 (s, 2H), 8.28 (s, 2H), 3.44 (s, 6H), 0.31 (s, 18H); ^{13}C{^{1}H} NMR** (chloroform-*d*, 151 MHz): δ = 143.64, 128.67, 127.83, 127.82, 126.70, 124.44, 123.27, 103.34, 100.81, 61.19, 0.01; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{26}H_{28}Br_2O_2Si_2$, 585.9995; found, 585.9989. **One aromatic resonance is missing (likely due to overlap)

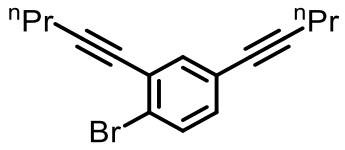


S9

2,7-diiodo-3,6-di(pent-1-yn-1-yl)naphthalene (S9)

Procedure: A solution of dibromide **S6** (2.09 g, 5.00 mmol, 1.0 equiv) in THF (25 mL) was cooled to –78 °C with a dry ice / acetone bath and to the stirred solution was added ^{t}BuLi (1.7 M in pentane, 11.8 mL, 20.0 mmol, 4.0 equiv) over 10–15 min. The resulting mixture was stirred for 1 h at –78 °C, then iodine (5.08 g, 20.0 mmol, 4.0 equiv) was added in one portion. After a further 10 min at –78 °C, the cold bath was removed, and the stirred mixture was allowed to warm to RT. After ~30 min at RT, the mixture was quenched with 3% aqueous sodium thiosulfate (120 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water (50 mL), dried with $MgSO_4$, filtered, and solvents were removed from the filtrate *via* rotary evaporation. The crude product was purified by elution through a plug of silica gel (15 g) with 9:1 hexanes:CH_2Cl_2 (150 mL), followed by recrystallization from hexanes (~20 mL total volume; boiling, then –25 °C), to afford diiodide **S9** (1.89 g, 77%) as beige needles.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 8.18 (s, 2H), 7.76 (s, 2H), 2.48 (t, *J* = 6.9 Hz, 4H), 1.71 (sext, *J* = 7.2 Hz, 4H), 1.12 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 136.54, 133.38, 131.38, 130.85, 128.30, 99.37, 95.65, 82.99, 22.13, 21.81, 13.91; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{20}H_{18}I_2$, 511.9498; found, 511.9495.



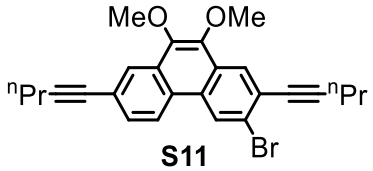
S10

1-bromo-2,4-di(pent-1-yn-1-yl)benzene (S10)

Procedure: A 250 mL Schlenk flask was charged with dibromide **4a** (2.51 g, 6.82 mmol, 1.00 equiv) and THF (34 mL), and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To the stirred solution was added *n*-butyllithium (1.64 M in hexanes, 4.28 mL, 7.02 mmol, 1.03 equiv) dropwise over 15-20 min, then the resulting mixture was stirred for a further 5 min at –78 °C. To this mixture was added N_2-sparged MeOH (0.83 mL, 21 mmol, 3.0 equiv) dropwise over 2-3 min, then the cold bath was removed. After 15 min (when most of the color had dissipated), the reaction mixture was quenched with saturated aqueous NH_4Cl (40 mL) and extracted with hexanes (40, then 20 mL). The organic layer was washed with saturated aqueous NaCl (50 mL), dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. To remove residual THF, the residue was dissolved in hexanes and solvents were removed under vacuum to afford monobromide **S10** (1.92 g, 97%) as a light-yellow oil, which was directly employed for the next step.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 7.45 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 8.3, 2.1 Hz, 1H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.66 (sext,

J = 7.3 Hz, 2H), 1.61 (sext, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (chloroform-*d,* 101 MHz): = δ 136.25, 132.26, 131.60, 126.23, 124.54, 123.32, 95.88, 91.86, 79.36, 79.10, 22.18, 22.14, 21.66, 21.51, 13.68, 13.67; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{16}H_{17}Br$, 288.0514; found, 288.0511.



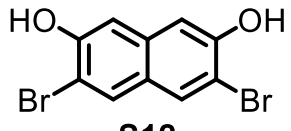
S11

3-bromo-9,10-dimethoxy-2,7-di(pent-1-yn-1-yl)phenanthrene (S11)

Procedure: A 250 mL Schlenk flask was charged with dibromide **S7** (6.00 g, 11.4 mmol, 1.0 equiv) and THF (115 mL), and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To this solution was added *n*-butyllithium (1.6 M in hexanes, 7.13 mL, 11.4 mmol, 1.0 equiv) dropwise over 15-20 min and the resulting mixture was stirred for a further 5 min at –78 °C. To this mixture was added N_2-sparged MeOH (4.5 mL, ~110 mmol, 10 equiv), then the cold bath was removed. As soon as the green color dissipated (~5 min), the reaction mixture was quenched with saturated aqueous NH_4Cl (40 mL) and extracted with ethyl acetate (90 mL, then 30 mL). The combined organic layers were washed with saturated aqueous NaCl (60 mL), dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was dissolved in a 3:1 mixture of hexanes:CH_2Cl_2 (60 mL) and the solution was filtered through a plug of silica gel (15 g), which was then flushed with the same solvent mixture (240 mL). Removal of solvents from the filtrate *via* rotary evaporation*, followed by high vacuum, afforded an off-white solid (5.0 g). This solid was a mixture of **S11** (89%**), starting **S7** (3%**), and doubly-debrominated **S7** (8%**), which was used*** without further purification. In a smaller-scale reaction, pure **S11** was isolated *via* column chromatography (1:4 CH_2Cl_2:hexanes) in 72% yield.

Notes: *To ensure complete removal of CH_2Cl_2, the initially obtained oil was re-dissolved in hexanes and solvents were removed again *via* rotary evaporation. **These values were determined by ^{1}H NMR spectroscopy. ***For simplification of the stoichiometry calculations in reactions involving this mixture, it was assumed to be pure **S11**.

Characterization: ^{1}H NMR (chloroform-*d*, 500 MHz): δ = 8.73 (s, 1H), 8.38 (d, *J* = 8.6 Hz, 1H), 8.26 (s, 1H), 8.23 (d, *J* = 1.7 Hz, 1H), 7.59 (dd, *J* = 8.6, 1.7 Hz, 1H), 4.06 (s, 3H), 4.06 (s, 3H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 1.73 (sext, *J* = 7.2 Hz, 2H), 1.69 (sext, *J* = 7.2 Hz, 2H), 1.13 (t, *J* = 7.4 Hz, 3H); 1.10 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (chloroform-*d*, 101 MHz): δ = 143.99, 143.49, 129.63, 129.30, 128.54, 128.07, 127.15, 126.49, 126.36, 125.43, 124.45, 123.38, 123.04, 122.89, 95.89, 91.87, 81.07, 80.03, 61.16, 61.08, 22.37, 22.25, 21.85, 21.70, 13.81; 13.80; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{26}H_{25}BrO_2$, 448.1038; found, 448.1045.

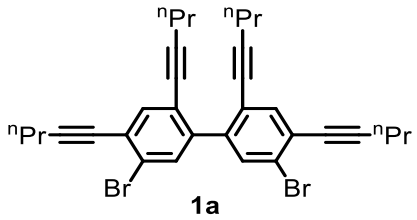


S12

3,6-dibromonaphthalene-2,7-diol (S12)

Procedure: This is a modified version of a literature procedure.[27] A 1000 mL round-bottom, 3-neck flask was equipped with a magnetic stirbar, dropping funnel, reflux condenser, and HBr trap (aqueous NaOH solution). The flask was charged with 2,7-dihydroxynaphthalene (12.7 g, 79.3 mmol, 1.0 equiv) and acetic acid (300 mL) and the dropping funnel with a solution of bromine

(50.7 g, 317 mmol, 4.0 equiv) in acetic acid (100 mL). The third neck was sealed with a rubber septum (to permit addition of tin later in the reaction), then the bromine solution was added dropwise to the stirred solution over 10-15 min. To this mixture was added water (40 mL), then the mixture was heated to 130 °C (reflux) after which the first 10% of the mossy tin (2.0 g, 17 mmol, 0.2 equiv) was added. The remaining 90% of the tin (17.8 g, 150 mmol, 1.9 equiv) was added in three equal portions over ~30 min. The mixture was heated for a further 2 h, then the hot mixture was poured into ice cold water (800 mL) and the precipitate was collected on a fritted funnel packed with celite. The solid was extracted with ethyl acetate (200, then 100 mL), then the extract was washed with water (200 mL) and saturated aqueous NaCl (100 mL), dried with $MgSO_4$, filtered, concentrated *via* rotary evaporation. Residual solvents were removed *in vacuo* to afford **S12** (20.1 g, 80%) as an off-white solid that was pure enough for the next step.
Characterization: ^{1}H NMR data matches that in the literature.[28]



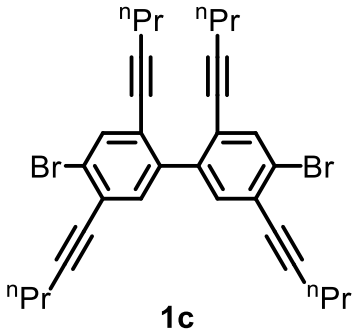
1a

Tetra(pentynyl)biphenyl Precursor (1a)
IUPAC name: 2,2',4,4'-tetra(pent-1-yn-1-yl)-5,5'-dibromobiphenyl
Procedure #1 ($CuCl_2$ as coupling reagent): This procedure is a slightly modified version of a literature procedure for a similar compound.[11] A 100 mL Schlenk flask was charged with diyne **4a** (3.50 g, 9.56 mmol, 1.0 equiv) and THF (48 mL), and the solution was cooled to –78 °C. To this solution was added *n*-butyllithium (1.6 M in hexanes, 5.7 mL, 9.1 mmol, 0.95 equiv) dropwise over 10–15 min and the resulting mixture was stirred for 10 min at –78 °C.* Copper(II) chloride (1.67 g, 12.4 mmol, 1.3 equiv) was then added in one portion, the cold bath was removed, and the reaction mixture was allowed to warm to 21 °C and stirred for 3 h at this temperature. The reaction mixture was quenched with 10% aqueous NH_4OH (50 mL) and extracted with ethyl acetate (50 mL). The organic layer was washed with saturated aqueous NaCl (50 mL) and dried with Na_2SO_4. Filtration and removal of solvents from the filtrate by rotary evaporation gave a brown oil. The oil was dissolved in hexanes (~20 mL) and the solution was eluted through a plug of silica gel. The plug was flushed with 10% CH_2Cl_2 in hexanes (until no further product was observed by TLC), then the filtrate was concentrated to ~2 mL and diluted with EtOH (12 mL), causing a large amount of crystalline solid to precipitate. The solid was collected by filtration, washed with EtOH (5 mL) and MeOH (5 mL), and dried under high vacuum. The yield of pure tetrayne **1a** was 1.45 g (53%) as an off-white solid.
Notes for Procedure #1: *Analysis of an aliquot (quenched with saturated aqueous NH_4Cl) by ^{1}H NMR spectroscopy revealed exclusive mono-metallation.
Procedure #2 (CuCN/benzoquinone as coupling reagent): The following procedure is an adaptation* of methodology developed by Iyoda and coworkers.[17] A 50 mL Schlenk flask was charged with diyne **4a** (407 mg, 1.11 mmol, 1.0 equiv) and THF (11 mL), and the solution was cooled to –78 °C. To the stirred solution was added *n*-butyllithium (1.6 M in hexanes, 0.69 mL, 1.11 mmol, 1.0 equiv) dropwise over 15–20 min, and the resulting mixture was stirred for 5 min at –78 °C. Next, CuCN·2LiCl (0.57 M in THF, 0.97 mL, 0.56 mmol, 0.50 equiv**) was added dropwise over ~5 min, the mixture was stirred for a further 30 min at –78 °C, then 1,4-benzoquinone (181 mg, 1.67 mmol, 1.5 equiv) was added in one portion against light N_2 flow, immediately producing a deep purple color. The cold bath was removed, and the reaction mixture was allowed to warm to RT and stirred for a further 2 h. The mixture was quenched with saturated

aqueous NH_4Cl (10 mL), diluted with hexanes (10 mL), filtered through celite, and the celite was rinsed with an additional portion of hexanes (10 mL). The filtrate was added to a separation funnel, the layers were separated, and the aqueous layer was extracted with hexanes (2 x 10 mL). The combined organic layers were washed with saturated aqueous NaCl (25 mL), dried with $MgSO_4$, filtered, and the filtrate was concentrated *via* rotary evaporation. The residue was purified by column chromatography (0–10% CH_2Cl_2 in hexanes) to afford tetrayne **1a** (243 mg, 76%) as a white solid.

Notes for Procedure #2: *The important changes include: 1) use of ^{n}BuLi instead of ^{t}BuLi; 2) use of THF-soluble CuCN·2LiCl rather than insoluble CuCN, which allows rapid formation of the cuprate at –78 °C. **The relative stoichiometry of the Ar-Li intermediate and CuCN appears to be important in achieving the optimal yield for this reaction.

Characterization: ^{1}H NMR (chloroform-*d,* 500 MHz): δ = 7.63 (s, 2H), 7.53 (s, 2H), 2.46 (t, *J* = 7.0 Hz, 4H), 2.21 (t, *J* = 6.9 Hz, 4H), 1.68 (h, *J* = 7.2 Hz, 4H), 1.46 (h, *J* = 7.3 Hz, 4H), 1.09 (t, *J* = 7.4 Hz, 6H), 0.87 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d,* 75 MHz): δ 141.10, 136.79, 133.84, 125.53, 123.59, 122.55, 96.23, 95.61, 79.03, 78.37, 22.17, 21.99, 21.75, 21.58, 13.72, 13.53; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{32}H_{31b}r_2$, 574.0871; found, 574.0868.



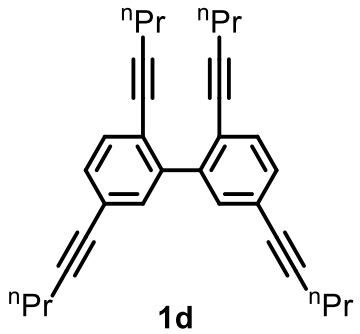
1c

Tetra(pentynyl)biphenyl Precursor (1c)

IUPAC name: 4,4'-dibromo-2,2',5,5'-tetra(pent-1-yn-1-yl)-1,1'-biphenyl

Procedure: This compound was prepared by procedure #2 for compound **1a**, with the following quantities and noted differences: diyne **S5** (3.45 g, 9.37 mmol, 1.0 equiv), *n*-butyllithium (1.64 M in hexanes, 5.49 mL, 9.00 mmol, 0.96 equiv), CuCN·2LiCl (0.47 M in THF, 9.57 mL, 4.50 mmol, 0.48 equiv), 1,4-benzoquinone (1.52 g, 14.1 mmol, 1.5 equiv), and THF (90 mL). The crude product was purified by column chromatography (0–7% CH_2Cl_2 in hexanes) to give tetrayne **1c** (2.19 g, 81%) as a waxy, white solid.

Characterization: ^{1}H NMR (chloroform-*d,* 500 MHz): δ = 7.66 (s, 2H), 7.42 (s, 2H), 2.44 (t, *J* = 7.0 Hz, 4H), 2.22 (t, *J* = 6.9 Hz, 4H), 1.65 (sext, *J* = 7.2 Hz, 4H), 1.45 (h, *J* = 7.2 Hz, 4H), 1.07 (t, *J* = 7.4 Hz, 6H), 0.85 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d,* 400 MHz): δ = 140.19, 135.52, 134.50, 124.77, 124.12, 124.01, 96.71, 96.65, 79.43, 78.57, 22.16, 21.92, 21.75, 21.60, 13.68, 13.44; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{32}H_{31b}r_2$, 574.0871; found, 574.0865.



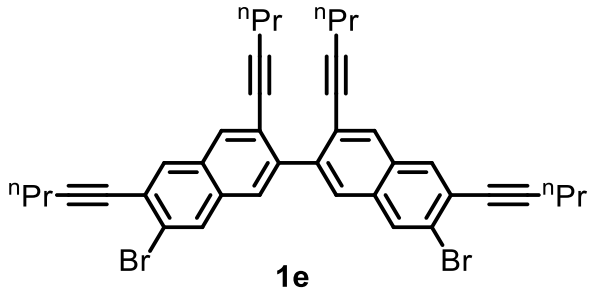
1d

Tetra(pentynyl)biphenyl Precursor (1d)

IUPAC name: 2,2',5,5'-tetra(pent-1-yn-1-yl)-1,1'-biphenyl

Procedure: A 100 mL Schlenk flask was charged with dibromide **1c** (1.00 g, 1.73 mmol, 1.0 equiv) and THF (35 mL), and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To this stirred solution was added *n*-butyllithium (1.64 M in hexanes, 3.2 mL, 5.19 mmol, 3.0 equiv) dropwise over ~5 min, and the resulting mixture was stirred for a further 20 min at –78 °C. Anhydrous HCl (2.0 M in ether, 3.45 mL, 6.9 mmol, 4.0 equiv) was then added dropwise over 2-3 min, the cold bath was removed, and saturated aqueous $NaHCO_3$ (50 mL) was added. The mixture was extracted with hexanes (50 mL, then 30 mL), then the combined organic layers were washed with saturated aqueous NaCl (50 mL), dried with $MgSO_4$, filtered, and concentrated *via* rotary evaporation. The residue was purified by elution through a plug of silica gel (10 g) with 10:1 hexanes/CH_2Cl_2 to afford **1d** (0.710 g, 98%) as a viscous, colorless oil.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 7.42 (d, *J* = 1.7 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 8.0, 1.7 Hz, 2H), 2.38 (t, *J* = 7.0 Hz, 4H), 2.20 (t, *J* = 6.9 Hz, 4H), 1.61 (sext, *J* = 7.2 Hz, 4H), 1.42 (sext, *J* = 7.1 Hz, 4H), 1.03 (t, *J* = 7.4 Hz, 6H), 0.83 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 142.47, 133.33, 131.96, 130.23, 122.78, 122.67, 95.02, 91.55, 80.69, 79.92, 22.33, 22.03, 21.66, 21.58, 13.67, 13.47; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{32}H_{34}$, 418.2661; found, 418.2666.



1e

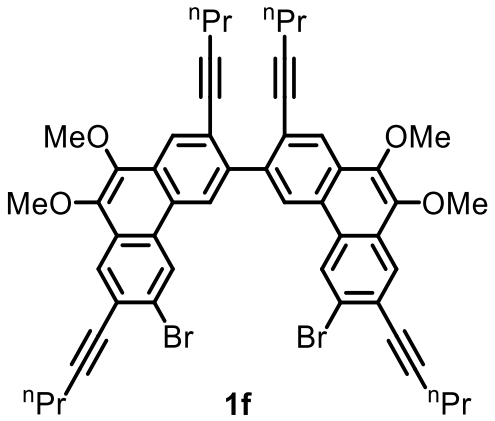
Tetra(pentynyl)binaphthalene Precursor (1e)

IUPAC name: 7,7'-dibromo-3,3',6,6'-tetra(pent-1-yn-1-yl)-2,2'-binaphthalene

Procedure: This compound was prepared by procedure #2 for compound **1a**, with the following quantities and noted differences: diyne **S6** (4.60 g, 11.0 mmol, 1.0 equiv), *n*-butyllithium (1.64 M in hexanes, 6.6 mL, 10.8 mmol, 0.98 equiv), CuCN·2LiCl (0.47 M in THF, 11.5 mL, 5.39 mmol, 0.49 equiv), 1,4-benzoquinone (1.78 g, 16.5 mmol, 1.5 equiv), and THF (110 mL). The crude product was purified by column chromatography (0–10% CH_2Cl_2 in hexanes) to give tetrayne **1e** (2.73 g, 73%) as a white solid.

Characterization: ^{1}H NMR (chloroform-*d*, 600 MHz): δ = 8.02 (s, 2H), 7.91 (s, 2H), 7.89 (s, 2H), 7.71 (s, 2H), 2.51 (t, *J* = 7.0 Hz, 4H), 2.13 (t, *J* = 6.8 Hz, 4H), 1.72 (sext, *J* = 7.2 Hz, 4H), 1.27 (sext, *J* = 7.2 Hz, 4H), 1.13 (t, *J* = 7.4 Hz, 6H), 0.67 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-

d, 151 MHz): δ = 141.12, 132.04, 131.94, 130.96, 130.86, 130.80, 127.81, 124.05, 123.23, 123.03, 95.74, 94.94, 79.94, 79.80, 22.24, 21.92, 21.82, 21.55, 13.80, 13.30; HRMS-ESI (m/z): $[M]^+$ calcd. for $C_{40}H_{36}Br_2$, 674.1184; found, 674.1178.



1f

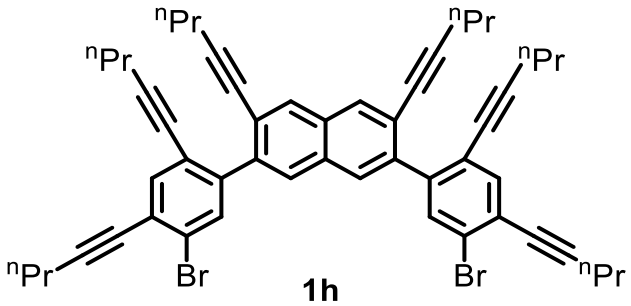
Tetra(pentynyl)biphenanthrene Precursor (1f)

IUPAC name: 6,6'-dibromo-9,9',10,10'-tetramethoxy-2,2',7,7'-tetra(pent-1-ynyl)-3,3'-biphenanthrene

Procedure: We previously synthesized **1f** *via* lithium/bromine exchange followed by oxidative coupling with $CuCl_2$.[4] This procedure gave diminished yield on a larger scale, so an alternative oxidative coupling method was sought. The following procedure is an adaptation* of methodology developed by Iyoda and coworkers.[17] A 500 mL Schlenk flask was charged with diyne **S7** (10.0 g, 18.9 mmol, 1.0 equiv) and THF (190 mL), and the solution was cooled to –78 °C. To the stirred solution was added *n*-butyllithium (1.64 M in hexanes, 11.0 mL, 18.1 mmol, 0.96 equiv) dropwise over 1 h, and the resulting mixture was stirred for 10 min at –78 °C. Next, CuCN·2LiCl (0.47 M in THF, 19.3 mL, 9.07 mmol, 0.48 equiv**) was added dropwise over ~30 min, the mixture was stirred for a further 30 min at –78 °C, then 1,4-benzoquinone (3.07 g, 28.4 mmol, 1.5 equiv) was added in one portion against light N_2 flow, immediately producing a deep purple color. The cold bath was removed, then the reaction mixture was allowed to warm to RT and stirred for a further 2 h. The mixture was quenched with saturated aqueous NH_4Cl (200 mL), diluted with hexanes (200 mL), and filtered through celite. The aqueous layer was extracted with hexanes (100 mL), then the combined organic layers were washed with saturated aqueous NaCl (100 mL), dried with $MgSO_4$, filtered, and the filtrate was concentrated *via* rotary evaporation. The residue was eluted through a short plug of silica gel with CH_2Cl_2 and solvents were removed *via* rotary evaporation. The crude was purified by column chromatography (33–40% CH_2Cl_2 in hexanes) to afford tetrayne **1f** (6.10 g, 72%) as an off-white solid.

Notes: *The important changes include: 1) use of ^{n}BuLi instead of ^{t}BuLi; 2) use of THF-soluble CuCN·2LiCl rather than insoluble CuCN, which allows rapid formation of the cuprate at –78 °C. **The relative stoichiometry of the Ar-Li intermediate and CuCN appears to be important in achieving the optimal yield for this reaction.

Characterization: ^{1}H NMR data matches the literature.[4]



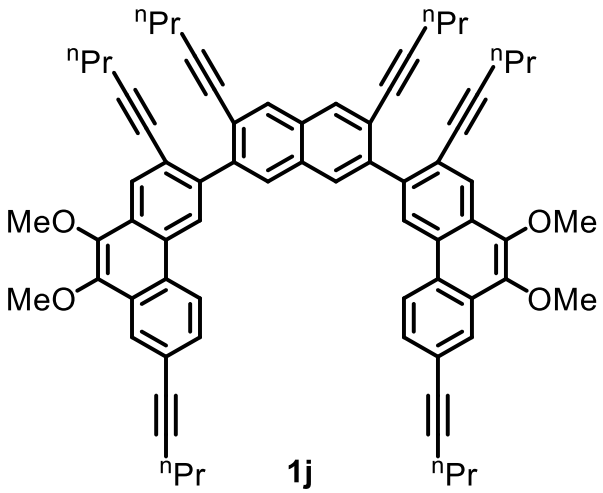
1h

Hexa(pentynyl)oligoarylene Precursor (1h)

IUPAC name: 2,7-bis(5-bromo-2,4-di(pent-1-yn-1-yl)phenyl)-3,6-di(pent-1-yn-1-yl)naphthalene

Procedure: A 250 mL Schlenk flask was charged with dibromide **4a** (3.24 g, 8.79 mmol, 3.0 equiv) and THF (38 mL), and the solution was cooled to –78 °C with a dry ice / acetone bath. To this solution was added *n*-butyllithium (1.62 M in hexanes, 5.06 mL, 8.20 mmol, 2.8 equiv) dropwise over ~10 min, and the resulting mixture was stirred for 5 min at –78 °C. Next, $ZnCl_2$ (0.84 M in THF, 11.9 mL, 9.96 mmol, 3.4 equiv) was added dropwise over ~2 min, the cold bath was removed, and the reaction mixture was allowed to warm to RT and stirred for 2 h (time after cold bath removal). To this solution was added diiodide **S9** (1.50 g, 2.93 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (0.34 g, 0.29 mmol, 0.10 equiv), then the flask was sealed with a ground glass stopper and the mixture was stirred at 35 °C for 12 h. The mixture was brought to RT, quenched with saturated aqueous NH_4Cl (50 mL), and extracted with EtOAc (2 x 50 mL). The combined extracts were washed with saturated aqueous NaCl (50 mL), dried with $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (mass of silica: 160 g; eluant: 0–10% CH_2Cl_2 in hexanes) to afford hexayne **1h** (1.59 g, 65%) as a sticky yellow/orange solid.

Characterization: ^{1}H NMR (chloroform-*d,* 600 MHz): δ = 7.92 (s, 2H), 7.75 (s, 2H), 7.67 (s, 2H), 7.57 (s, 2H), 2.47 (t, *J* = 6.9 Hz, 4H), 2.28 (t, *J* = 6.9 Hz, 4H), 2.10 (t, *J* = 6.9 Hz, 4H), 1.69 (sext, *J* = 7.2 Hz, 4H), 1.49 (sext, *J* = 7.2 Hz, 4H), 1.29 (sext, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H), 0.69 (t, *J* = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (chloroform-*d*, 151 MHz): δ = 143.10, 139.01, 136.61, 133.97, 131.68, 131.01, 130.68, 128.96, 125.12, 123.57, 123.18, 122.37, 95.88, 94.99, 94.80, 79.89, 79.14, 78.85, 22.20, 22.12, 21.90, 21.76, 21.66, 21.50, 13.71, 13.52, 13.32; HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{52}H_{51}Br_2$, 833.2352; found, 833.2356.



1j

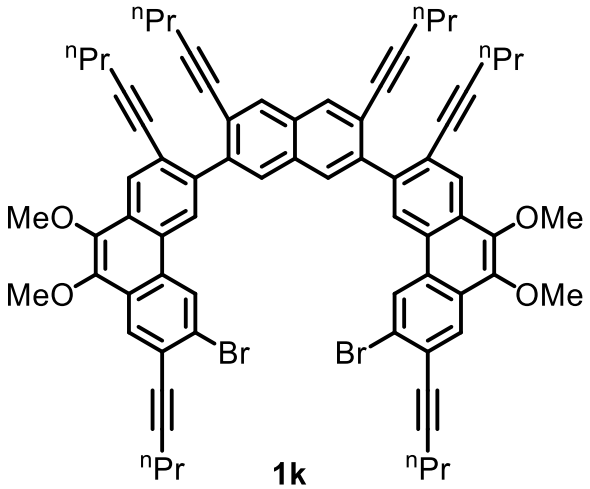
Hexa(pentynyl)oligoarylene Precursor (1j)

IUPAC name: 3,3'-(3,6-di(pent-1-yn-1-yl)naphthalene-2,7-diyl)bis(9,10-dimethoxy-2,7-di(pent-1-yn-1-yl)phenanthrene)

Procedure: A 25 mL flask equipped with Teflon stopper was charged with monobromide **S11** (1.06 g*, 2.36 mmol*, 4.0 equiv*) and ^{i}PrMgCl·LiCl (0.89 M in THF, 2.45 mL, 2.18 mmol, 3.7 equiv), then the mixture was diluted with THF (0.7 mL). The flask was sealed, and the stirred mixture was heated at 60 °C for 3 h. This mixture was transferred *via* syringe to another flask containing $PdCl_2$(IPr)(3-chloropyridine) (0.012 g, 0.018 mmol, 0.03 equiv) and dibromide **S6** (0.247 g, 0.590 mmol, 1.0 equiv), then THF (0.6 mL) was used for quantitative transfer. The resulting mixture was stirred at RT for 24 h, then quenched with saturated aqueous NH_4Cl (10 mL), extracted with CH_2Cl_2 (20 mL), dried with $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography** (30–40% CH_2Cl_2 in hexanes) to afford hexayne **1j** (0.285 g, 51%) as a foamy, pale-orange solid.

Notes: *See procedure for **S11** for details regarding purity of this compound and the implications for stoichiometry calculations. **These reaction conditions produce some homocoupled **S11**, which is difficult to remove by column chromatography. Thus, a careful gradient is required.

Characterization: ^{1}H NMR (chloroform-*d,* 600 MHz): δ = 8.67 (s, 2H), 8.49 (d, *J* = 8.6 Hz, 2H), 8.37 (s, 2H), 8.28 (d, *J* = 1.7 Hz, 2H), 8.06 (s, 2H), 7.95 (s, 2H), 7.57 (dd, *J* = 8.6, 1.8 Hz, 2H), 4.12 (s, 6H), 4.12 (s, 6H), 2.47 (t, *J* = 7.0 Hz, 4H), 2.23 (t, *J* = 6.9 Hz, 4H), 2.16 (t, *J* = 6.9 Hz, 4H), 1.70 (sext, *J* = 7.3 Hz, 4H), 1.39 (sext, *J* = 7.2 Hz, 4H), 1.29 (sext, *J* = 7.1 Hz, 4H), 1.11 (t, *J* = 7.4 Hz, 6H), 0.78 (t, *J* = 7.3 Hz, 6H), 0.67 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 143.93, 143.91, 140.98, 140.40, 131.57, 131.10, 131.03, 129.40, 129.25, 129.02, 128.36, 127.70, 127.07, 125.94, 125.47, 124.70, 123.20, 122.99, 122.88, 122.72, 94.35, 94.35, 91.40, 81.30, 80.68, 80.55, 61.19, 61.17, 22.41, 22.11, 22.02, 21.72, 21.71, 21.61, 13.78, 13.47, 13.32; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{72}H_{68}O_4$, 996.51; found, 996.47.



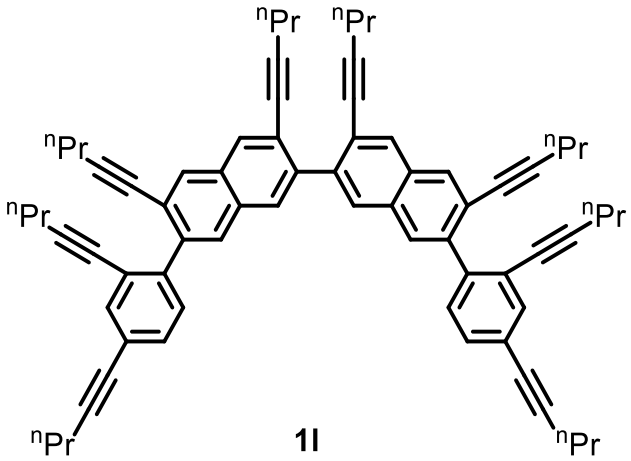
1k

Hexa(pentynyl)oligoarylene Precursor (1k)

IUPAC name: 6,6'-(3,6-di(pent-1-yn-1-yl)naphthalene-2,7-diyl)bis(3-bromo-9,10-dimethoxy-2,7-di(pent-1-yn-1-yl)phenanthrene)

Procedure: A 250 mL Schlenk flask was charged with dibromide **S7** (1.85 g, 3.51 mmol, 3.0 equiv) and THF (35 mL), and the solution was cooled to –78 °C with a dry ice / acetone bath. To this solution was added *n*-butyllithium (1.64 M in hexanes, 2.00 mL, 3.28 mmol, 2.8 equiv) dropwise over ~15 min, and the resulting mixture was stirred for 5 min at –78 °C. Next, $ZnCl_2$ (0.84 M in THF, 4.7 mL, 3.98 mmol, 3.4 equiv) was added dropwise over 3-4 min, the cold bath was removed, and the reaction mixture was allowed to warm to RT and stirred for 2 h (time after cold

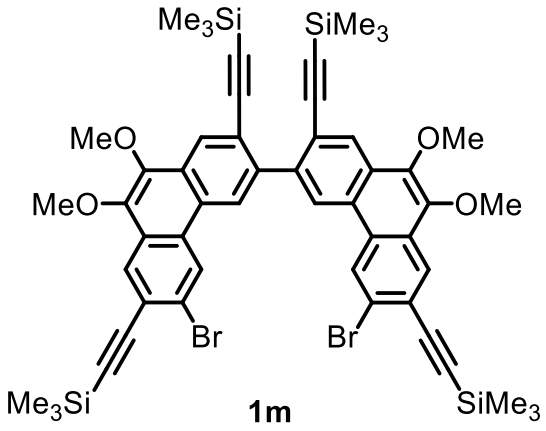
bath removal). To this solution was added (against light N_2 flow) diiodide **S9** (0.600 g, 1.17 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (0.135 g, 0.117 mmol, 0.10 equiv), then the flask was sealed with a ground glass stopper and the mixture was stirred at RT °C for 24 h. The mixture was poured into saturated aqueous NH_4Cl (50 mL) and extracted with CH_2Cl_2 (100 mL, then 50 mL). The combined extracts were dried with $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (mass of silica: 100 g; eluant: 25–40% CH_2Cl_2 in hexanes) to afford hexayne **1k** (0.825 g, 61%) as a foamy, orange/yellow solid.
Characterization: ^{1}H NMR (chloroform-*d,* 600 MHz): δ = 8.76 (s, 2H), 8.60 (s, 2H), 8.36 (s, 2H), 8.29 (s, 2H), 8.07 (s, 2H), 7.97 (s, 2H), 4.11 (s, 6H), 4.10 (s, 6H), 2.53 (t, *J* = 7.0 Hz, 4H), 2.24 (t, *J* = 6.9 Hz, 4H), 2.18 (t, *J* = 6.9 Hz, 4H), 1.73 (sext, *J* = 7.2 Hz, 4H), 1.40 (sext, *J* = 7.2 Hz, 4H), 1.33 (sext, *J* = 7.2 Hz, 4H), 1.14 (t, *J* = 7.4 Hz, 6H), 0.79 (t, *J* = 7.3 Hz, 6H), 0.70 (t, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d,* 151 MHz): δ = 143.98, 143.50, 140.66, 140.65, 131.64, 131.15, 131.04, 129.27, 128.78, 128.75, 128.29, 127.21, 126.60, 126.01, 125.94, 124.69, 124.46, 123.85, 123.08, 122.82, 95.90, 94.85, 94.52, 80.52, 80.47, 80.08, 61.23, 61.13, 22.26, 22.08, 22.07, 21.86, 21.70, 21.63, 13.80, 13.51, 13.39; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{72}H_{66}Br_2O_4$, 1152.33; found, 1152.26.



1l

Octa(pentynyl)oligoarylene Precursor (1l)
IUPAC name: 7,7'-bis(2,4-di(pent-1-yn-1-yl)phenyl)-3,3',6,6'-tetra(pent-1-yn-1-yl)-2,2'-binaphthalene
Procedure: A 25 mL flask equipped with Teflon stopper was charged with monobromide **S10** (0.807 g, 2.79 mmol, 4.0 equiv) and ^{i}PrMgCl·LiCl (0.89 M in THF, 2.9 mL, 2.58 mmol, 3.7 equiv), then the mixture was diluted with THF (1.0 mL). The flask was sealed, and the stirred mixture was heated at 60 °C for 3 h. This mixture was transferred *via* syringe to another flask containing $PdCl_2$(IPr)(3-chloropyridine) (0.014 g, 0.021 mmol, 0.03 equiv) and dibromide **1e** (0.472 g, 0.697 mmol, 1.0 equiv), then THF (2 mL) was used for quantitative transfer. The resulting mixture was stirred at RT for 15 h, then quenched with saturated aqueous NH_4Cl (20 mL) and extracted with hexanes (20 mL). The organic layer was washed with saturated aqueous NaCl (20 mL), dried with $MgSO_4$, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (10–20% CH_2Cl_2 in hexanes) to afford octayne **1l** (0.375 g, 54%) as a foamy, pale yellow/orange solid.
Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 7.96 (s, 2H), 7.95 (s, 2H), 7.78 (s, 2H), 7.78 (s, 2H), 7.56 (d, *J* = 1.6 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.34 (dd, *J* = 8.0, 1.6 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 4H), 2.25 (t, *J* = 6.9 Hz, 4H), 2.16 (t, *J* = 7.0 Hz, 4H), 2.13 (t, *J* = 7.3 Hz, 4H), 1.65 (sext, *J* = 7.2 Hz, 4H), 1.46 (sext, *J* = 7.2 Hz, 4H), 1.32 (sext, *J* = 7.2, 4H), 1.31 (sext, *J* = 7.2, 4H), 1.07 (t, *J* = 7.4 Hz, 6H), 0.88 (t, *J* = 7.4 Hz, 6H), 0.71 (t, *J* = 7.4 Hz, 6H), 0.71 (t, *J* = 7.4 Hz,

6H); $^{13}C\{^1H\}$ NMR (chloroform-*d*, 101 MHz): δ = 142.23, 141.04, 140.38, 135.23, 131.48, 130.99, 130.93, 130.61, 130.26, 129.89, 128.87, 128.72, 124.07, 123.21, 122.98, 122.36, 94.18, 94.11, 93.79, 90.82, 80.43, 80.32, 80.27, 79.69, 22.35, 22.08, 22.02, 22.00, 21.67, 21.60, 21.58, 21.49, 13.69, 13.51, 13.36, 13.34; $[M+H]^+$ calcd. for $C_{72}H_{71}$, 935.5550; found, 935.5541.



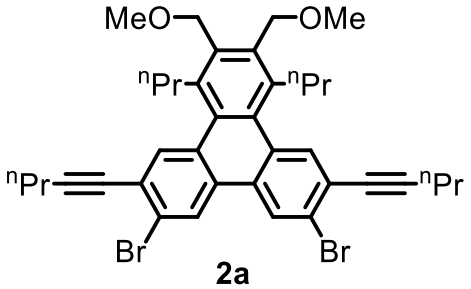
1m

Tetra(TMS-ethynyl)biphenanthrene (1m)

IUPAC name: 6,6'-dibromo-9,9',10,10'-tetramethoxy-2,2',7,7'-tetra(2-trimethylsilylethynyl)-3,3'-biphenanthrene

Procedure: This compound was prepared by the procedure for compound **1f**, with the following quantities and noted differences: dibromide **S8** (1.50 g, 2.54 mmol, 1.0 equiv), *n*-butyllithium (1.64 M in hexanes, 1.50 mL, 2.45 mmol, 0.96 equiv), CuCN·2LiCl (0.47 M in THF, 2.60 mL, 1.22 mmol, 0.48 equiv), 1,4-benzoquinone (0.413 g, 3.82 mmol, 1.5 equiv), and THF (25 mL). The crude product was purified by column chromatography (33% CH_2Cl_2 in hexanes) to afford **1m** (0.817 g, 63%) as an off-white solid.

Characterization: ^1H NMR (chloroform-*d*, 400 MHz): δ = 8.77 (s, 2H), 8.75 (s, 2H), 8.48 (s, 2H), 8.37 (s, 2H), 4.13 (s, 6H), 4.13 (s, 6H), 0.37 (s, 18H), -0.01 (s, 18H); $^{13}C\{^1H\}$ NMR (chloroform-*d*, 151 MHz): δ = 143.9, 143.7, 139.7, 129.2, 129.0, 128.5, 128.0, 127.2, 126.9, 126.3, 125.6, 123.9, 123.1, 122.6, 104.6, 103.6, 100.3, 99.4, 61.3, 61.2, 0.0, -0.2; HRMS-ESI (m/z): $[M]^+$ calcd. for $C_{52}H_{56}Br_2O_4Si_4$, 1014.1622; found, 1014.1625.



2a

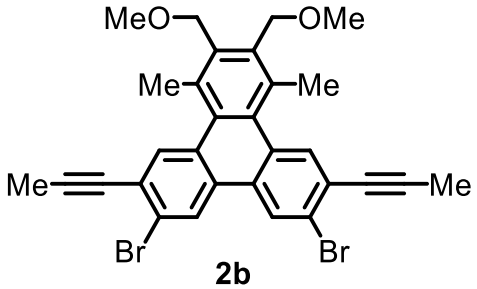
Pentynylated Triphenylene (2a)

IUPAC name: 7,10-dibromo-2,3-bis(methoxymethyl)-6,11-di(pent-1-yn-1-yl)-1,4-dipropyltriphenylene

Procedure: To a solution of $[Ir(COD)Cl]_2$ (3.5 mg, 0.0052 mmol, 0.01 equiv) in benzene (0.5 mL) was added (dropwise over ~1 min) a solution of dppe (4.2 mg, 0.010 mmol, 0.02 equiv) in benzene (0.5 mL). This mixture was immediately added to a flask containing a solution of tetrayne **1a** (300 mg, 0.521 mmol, 1.0 equiv) and 1,4-dimethoxy-2-butyne (89 mg, 0.782 mmol, 1.5 equiv) in

benzene (4 mL). The flask was sealed with a Teflon stopper and the stirred reaction mixture was heated at 80 °C for 2 h. The mixture was allowed to cool to RT and directly subjected to column chromatography (1:1 CH_2Cl_2:hexanes, then 100% CH_2Cl_2) to afford triphenylene **2a** (322 mg, 89%) as a colorless solid.

Characterization: ^{1}H NMR (benzene-d_6, 500 MHz): δ = 8.31 (s, 2H), 8.27 (s, 2H), 4.71 (s, 4H), 3.26 (s, 6H), 3.22 – 3.15 (m, 4H), 2.25 (t, *J* = 6.9 Hz, 4H), 1.72 (sext, *J* = 7.5 Hz, 4H), 1.49 (sext, *J* = 7.2 Hz, 4H), 0.99 (t, *J* = 7.4 Hz, 6H), 0.86 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 136.36, 136.23, 133.84, 132.36, 130.32, 129.86, 126.95, 124.20, 123.49, 95.91, 79.89, 68.90, 58.94, 34.54, 25.73, 22.22, 21.80, 14.27, 13.72; HRMS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{38}H_{42}O_{1b}r_2Na$, 711.1444; found, 711.1444.



2b

Propynylated Triphenylene (2b)

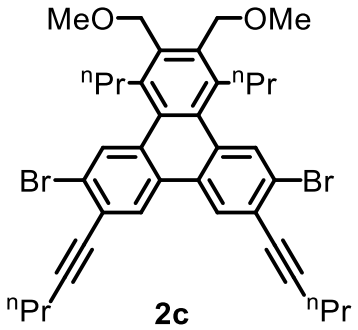
IUPAC name: 7,10-dibromo-2,3-bis(methoxymethyl)-1,4-dimethyl-6,11-di(prop-1-yn-1-yl)triphenylene

Procedure: A J-Young NMR tube was charged with a suspension of tetrayne **1b** (70.0 mg, 0.151 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (25.8 mg, 0.226 mmol, 1.5 equiv), and 1,3,5-trimethoxybenzene (9.8 mg; internal standard) in benzene-d_6 (1.0 mL). To this mixture was then added a solution of Ir(COD)(dppe)Cl (2.2 mg, 0.0030 mmol, 0.02 equiv) in benzene-d_6 (0.5 mL). The tube was sealed, and the mixture was heated at 80 °C for 1 h. The mixture initially became homogeneous, but a colorless crystalline solid quickly precipitated. In air, this solid was collected on a fritted funnel, washed with benzene-d_6 (1 mL) and hexanes (2 mL), and dried under a stream of air to afford triphenylene **2b** (53 mg, 61%) as a white solid. The filtrate was analyzed by ^{1}H NMR spectroscopy, which showed side product **5** in 8% yield. The filtrate was concentrated under reduced pressure and the residue was subjected to prep TLC (30% hexanes in CH_2Cl_2) to afford **5** as a colorless solid.

Variations: This reaction was also performed by independently varying two parameters (equivalents of 1,4-dimethoxy-2-butyne and concentration), under otherwise identical conditions. With 10 equivalents of 1,4-dimethoxy-2-butyne, the isolated yield of triphenylene **2b** improved to 73 mg (84%). Side product **5** was not observed. At 10x dilution (i.e. 10 mM concentration of starting **1b**), the yields of triphenylene **2b** and side product **5** were ~60% and 18%, respectively. In the latter case, the reaction mixture remained homogeneous for the entire 1 h.

*Characterization of **2b***: ^{1}H NMR (chloroform-*d*, 600 MHz): δ = 8.49 (s, 2H), 8.21 (s, 2H), 4.72 (s, 4H), 3.52 (s, 6H), 2.89 (s, 6H), 2.17 (s, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 135.7, 133.8, 132.6, 131.8, 130.2, 130.1, 127.1, 124.1, 123.7, 91.5, 79.0, 69.2, 58.9, 20.8, 4.89; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{30}H_{26}Br_2O_2$, 576.0291; found, 576.0292.

*Characterization of **5***: See below.



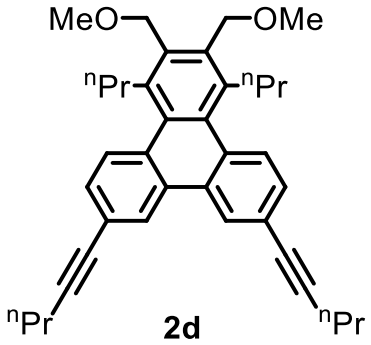
2c

Pentynylated Triphenylene (2c)

IUPAC name: 6,11-dibromo-2,3-bis(methoxymethyl)-7,10-di(pent-1-yn-1-yl)-1,4-dipropyltriphenylene

Procedure: A 25 mL Teflon-stoppered flask was charged with tetrayne **1c** (300 mg, 0.521 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (119 mg, 1.04 mmol, 2.0 equiv), and toluene (4.2 mL). To this flask was added a solution of Ir(COD)(dppe)Cl (7.6 mg, 0.0104 mmol, 0.02 equiv) in toluene (1.0 mL). The flask was sealed, and the stirred mixture was heated at 80 °C for 2 h. In air, volatile materials were removed *via* rotary evaporation, then the residue was subjected to column chromatography (40–50% CH_2Cl_2 in hexanes), affording triphenylene **2c** (254 mg, 71%) as a colorless solid. Monitoring of a smaller-scale (0.2x) reaction under identical conditions (in benzene-d_6) by ^{1}H NMR spectroscopy revealed that **2c** formed in 88% yield.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 8.41 (s, 2H), 8.27 (s, 2H), 4.69 (s, 4H), 3.53 (s, 6H), 3.25 – 3.14 (m, 4H), 2.52 (t, *J* = 7.0 Hz, 4H), 1.80 – 1.68 (m, 8H), 1.14 (t, *J* = 7.4 Hz, 6H), 0.96 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d,* 101 MHz): δ = 136.51, 136.46, 132.52, 132.15, 131.55, 128.54, 128.03, 124.18, 123.23, 96.09, 79.73, 68.83, 58.96, 34.54, 25.66, 22.25, 21.83, 14.34, 13.81; HRMS-ESI (m/z): $[M+Na]^+$ calcd. for $C_{38}H_{42}O_{1b}r_2Na$, 711.1444; found, 711.1441.



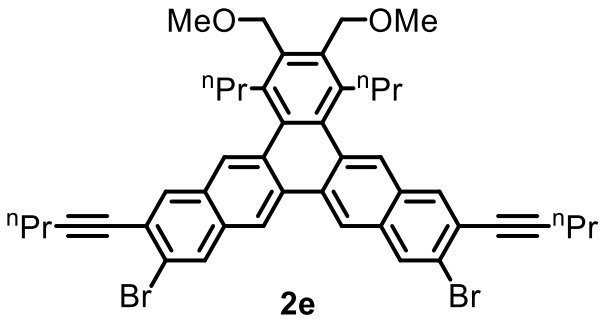
2d

Pentynylated Triphenylene (2d)

IUPAC name: 2,3-bis(methoxymethyl)-7,10-di(pent-1-yn-1-yl)-1,4-dipropyltriphenylene

Procedure: A 25 mL Teflon-stoppered flask was charged with tetrayne **1d** (300 mg, 0.717 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (163 mg, 1.43 mmol, 2.0 equiv), and toluene (5.2 mL). To this flask was added a solution of Ir(COD)(dppe)Cl (10.5 mg, 0.0143 mmol, 0.02 equiv) in toluene (2.0 mL). The flask was sealed, and the stirred mixture was heated at 80 °C for 2 h. In air, volatile materials were removed *via* rotary evaporation, then the residue was subjected to column chromatography (40–50% CH_2Cl_2 in hexanes), affording triphenylene **2d** (230 mg, 60%) as a sticky, colorless solid. Monitoring of a smaller-scale (0.2x) reaction under identical conditions (in benzene-d_6) by ^{1}H NMR spectroscopy revealed that **2d** formed in 84% yield.

Characterization: ^{1}H NMR (400 MHz, chloroform-*d*): δ = 8.45 (d, *J* = 1.7 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 8.5, 1.7 Hz, 2H), 4.70 (s, 4H), 3.53 (s, 6H), 3.31 – 3.20 (m, 4H), 2.46 (t, *J* = 7.0 Hz, 4H), 1.73 – 1.60 (m, 4H), 1.70 (sext, *J* = 7.2 Hz, 4H), 1.10 (t, *J* = 7.3 Hz, 6H), 0.87 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*): δ = 136.24, 135.45, 133.30, 130.53, 130.22, 129.09, 128.75, 126.66, 122.21, 91.18, 81.05, 69.02, 58.89, 34.72, 25.78, 22.42, 21.68, 14.50, 13.80; HRMS-ESI (m/z): [M+Na]$^{+}$ calcd. for $C_{38}H_{44}O_2Na$, 555.3234; found, 555.3239.



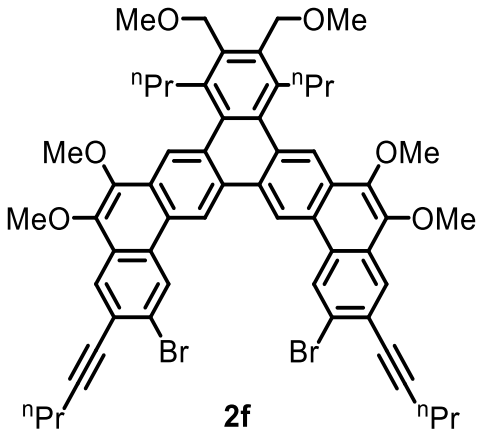
2e

Pentynylated Benzo[h]pentaphene (2e)

IUPAC name: 2,13-dibromo-7,8-bis(methoxymethyl)-3,12-di(pent-1-yn-1-yl)-6,9-dipropylbenzo[h]pentaphene

Procedure: To a stirred solution of $[Ir(COD)Cl]_2$ (21.6 mg, 0.032 mmol, 0.01 equiv) in benzene (2 mL) was added (dropwise over ~1 min) a solution of dppe (25.6 mg, 0.064 mmol, 0.02 equiv) in benzene (2 mL). This mixture was immediately added to a flask containing a solution of tetrayne **1e** (2.17 g, 3.21 mmol, 1.0 equiv) and 1,4-dimethoxy-2-butyne (0.73 g, 6.42 mmol, 2.0 equiv) in benzene (28 mL). The flask was sealed with a Teflon stopper and the reaction mixture was heated at 80 °C for 2 h. The mixture was allowed to cool to RT, hexanes (65 mL) was added, then the solid was collected by filtration and washed with hexanes (2 x 10 mL). The light orange solid was then dissolved in boiling benzene (~25 mL) and hexanes (50 mL) was added to the hot, stirred solution to produce an immediate precipitate. The mixture was allowed to cool to RT, then the precipitate was collected *via* filtration, washed with hexanes (10 mL), and dried under high vacuum to afford pure **2e** (1.80 g) as a pale-yellow solid. The filtrate was concentrated *via* rotary evaporation and the residue was subjected to column chromatography (0–50% CH_2Cl_2 in hexanes) to provide a further 0.23 g of compound **2e**. Total yield: 2.03 g (80%).

Characterization: ^{1}H NMR (chloroform-*d,* 500 MHz): δ = 8.72 (s, 2H), 8.28 (s, 2H), 8.28 (s, 2H), 8.00 (s, 2H), 4.72 (s, 4H), 3.57 (s, 6H), 3.39 – 3.31 (m, 4H), 2.53 (t, *J* = 7.0 Hz, 4H), 1.77 (sext, *J* = 7.2 Hz, 4H), 1.74 (sext, *J* = 7.2 Hz, 4H), 1.14 (t, *J* = 7.4 Hz, 6H), 0.94 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 136.50, 136.48, 134.38, 132.90, 131.68, 131.26, 131.13, 130.70, 130.68, 127.68, 123.63, 122.80, 121.58, 95.80, 79.99, 69.02, 58.99, 34.62, 25.92, 22.27, 21.88, 14.68, 13.83; HRMS-ESI (m/z): [M]$^{+}$ calcd. for $C_{46}H_{46}Br_2O_2$, 788.1865; found, 788.1859.



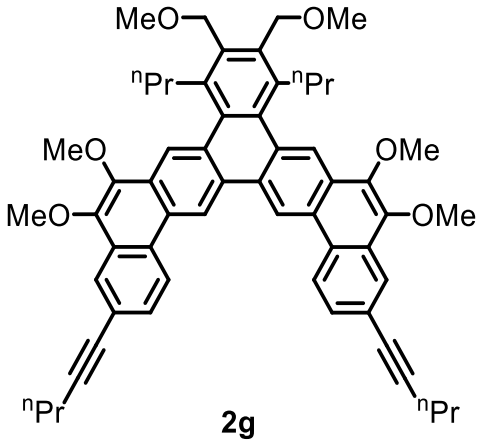
2f

Pentynylated Tribenzo[a,h,o]pentaphene (2f)

IUPAC name: 2,17-dibromo-5,6,13,14-tetramethoxy-9,10-bis(methoxymethyl)-3,16-di(pent-1-yn-1-yl)-8,11-dipropyltribenzo[a,h,o]pentaphene

Procedure: A 150 mL Teflon-stoppered flask was charged with $[Ir(COD)Cl]_2$ (0.026 g, 0.039 mmol, 0.010 equiv), tetrayne **1f** (3.50 g, 3.90 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (0.67 g, 5.9 mmol, 1.5 equiv), and toluene (37 mL). To the stirred, homogeneous solution was added (dropwise over ~1 min) a solution of dppe (0.031 g, 0.078 mmol, 0.020 equiv) in toluene (2 mL). The flask was sealed, and the stirred mixture was heated at 80 °C for 2 h. The mixture was allowed to cool to RT and diluted with hexanes (40 mL) under N_2. After 2-3 h, in air, the solid was collected on a fritted funnel and washed with hexanes (2 x 30 mL) to afford tribenzopentaphene **2f** (3.35 g, 85%) as a pale-yellow solid.

Characterization: ^{1}H NMR (chloroform-*d*, 600 MHz): δ = 9.64 (s, 2H), 9.17 (s, 2H), 8.93 (s, 2H), 8.34 (s, 2H), 4.80 (s, 4H), 4.13 (s, 6H), 4.13 (s, 6H), 3.59 (s, 6H), 3.46 – 3.38 (m, 4H), 2.57 (t, *J* = 7.0 Hz, 4H), 1.95 (sext, *J* = 7.3 Hz, 4H), 1.77 (sext, *J* = 7.2 Hz, 4H), 1.17 (t, *J* = 7.4 Hz, 6H), 1.01 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 144.67, 143.05, 136.58, 136.36, 134.43, 131.58, 130.00, 128.91, 128.52, 128.34, 127.28, 126.71, 126.04, 124.69, 123.17, 122.81, 117.90, 95.99, 80.21, 69.13, 61.18, 61.06, 58.96, 34.97, 25.85, 22.28, 21.90, 14.63, 13.83; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{58}H_{58}Br_2O_6$, 1008.26; found, 1008.21.

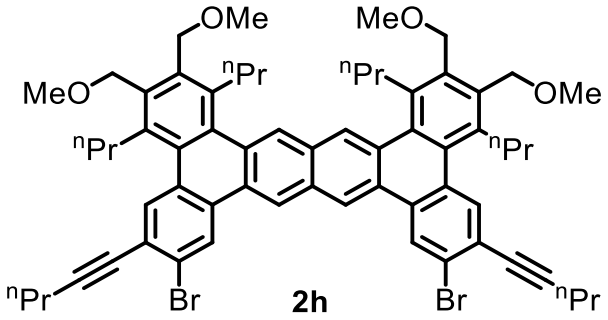


2g

Pentynylated Tribenzo[a,h,o]pentaphene (2g)

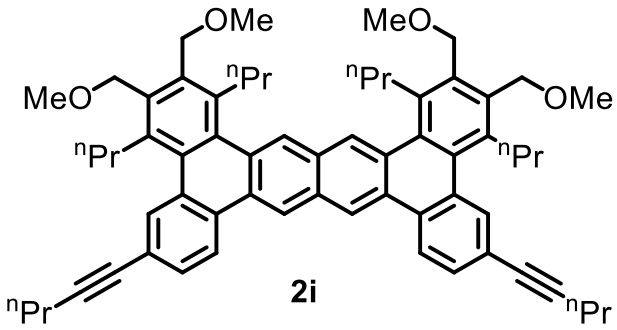
IUPAC name: 5,6,13,14-tetramethoxy-9,10-bis(methoxymethyl)-3,16-di(pent-1-yn-1-yl)-8,11-dipropyltribenzo[a,h,o]pentaphene

Procedure: A 10 mL Schlenk tube was charged with dibromide **2f** (0.100 g, 0.0989 mmol, 1.0 equiv) and THF (2.0 mL), and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To this stirred solution was added *n*-butyllithium (1.6 M in hexanes, 0.14 mL, 0.22 mmol, 2.2 equiv) dropwise over ~5 min, and the resulting mixture was stirred for a further 20 min at –78 °C. Anhydrous HCl (2.0 M in ether, 0.15 mL, 0.30 mmol, 3.0 equiv) was then added dropwise over 2-3 min, the cold bath was removed, and saturated aqueous NH_4Cl (10 mL) was added. The mixture was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated by rotary evaporation to afford **2g** (0.083 g, 98%) as a yellow solid.
Characterization: ^{1}H NMR (chloroform-*d*, 500 MHz): δ = 9.77 (s, 2H), 8.95 (s, 2H), 8.94 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 1.7 Hz, 2H), 7.77 (dd, *J* = 8.4, 1.7 Hz, 2H), 4.81 (s, 4H), 4.14 (s, 6H), 4.13 (s, 6H), 3.59 (s, 6H), 3.48 – 3.42 (m, 4H), 2.52 (t, *J* = 7.1 Hz, 4H), 1.95 (sext, *J* = 7.2 Hz, 4H), 1.74 (sext, *J* = 7.3 Hz, 4H), 1.14 (t, *J* = 7.4 Hz, 6H), 1.01 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 144.59, 143.43, 136.49, 136.10, 134.44, 131.07, 129.93, 129.56, 129.04, 127.90, 127.77, 127.06, 125.58, 123.01, 122.85, 122.66, 117.68, 91.42, 81.40, 69.11, 61.09, 61.04, 58.87, 34.98, 25.82, 22.41, 21.73, 14.61, 13.79; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{58}H_{60}O_6$, 852.44; found, 852.45.



2h

Pentynylated Tetrabenzo[a,c,j,l]tetracene (2h)
IUPAC name: 7,12-dibromo-2,3,16,17-tetrakis(methoxymethyl)-6,13-di(pent-1-yn-1-yl)-1,4,15,18-tetrapropyltetrabenzo[a,c,j,l]tetracene
Procedure: To a stirred solution of $[Ir(COD)Cl]_2$ (0.031 g, 0.046 mmol, 0.03 equiv) in toluene (2 mL) was added (dropwise over ~1 min) a solution of dppe (0.037 g, 0.092 mmol, 0.06 equiv) in toluene (2 mL). This mixture was immediately added to a 150 mL flask containing a solution of hexayne **1h** (1.28 g, 1.53 mmol, 1.0 equiv) and 1,4-dimethoxy-2-butyne (0.70 g, 6.1 mmol, 4.0 equiv) in toluene (26 mL). The flask was sealed with a Teflon stopper and the stirred reaction mixture was heated at 80 °C for 2 h. The mixture was allowed to cool to RT, then concentrated *via* rotary evaporation, and the residue was eluted through a plug of silica gel (40 g) with excess CH_2Cl_2 (until no more product was seen my TLC). The eluent was concentrated to ~10 mL, then MeOH (100 mL) was added. The resulting precipitate was collected on a fritted funnel, washed with MeOH (2 x 20 mL), and dried under high vacuum to afford PAH **2h** (1.30 g, 80%) as a bright-yellow solid.
Characterization: ^{1}H NMR (chloroform-*d*, 500 MHz): δ = 8.96 (s, 2H), 8.76 (s, 2H), 8.56 (s, 2H), 8.08 (s, 2H), 4.74 (s, 4H), 4.72 (s, 4H), 3.57 (s, 6H), 3.56 (s, 6H), 3.42 – 3.34 (m, 4H), 3.29 – 3.20 (m, 4H), 2.51 (t, *J* = 6.9 Hz, 4H), 1.88 (sext, *J* = 7.4 Hz, 4H), 1.77 – 1.67 (m, 8H), 1.13 (t, *J* = 7.4 Hz, 6H), 1.00 (t, *J* = 7.3 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 136.46, 136.34, 136.30, 136.17, 134.36, 134.16, 133.00, 131.96, 130.83, 130.70, 130.53, 130.11, 129.23, 128.29, 127.60, 124.24, 123.67, 122.15, 95.67, 80.01, 69.03, 68.95, 58.97, 58.91, 34.80, 34.49, 25.91, 25.81, 22.26, 21.82, 14.80, 14.33, 13.72; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{64}H_{70}Br_2O_4$, 1060.36; found, 1060.33.



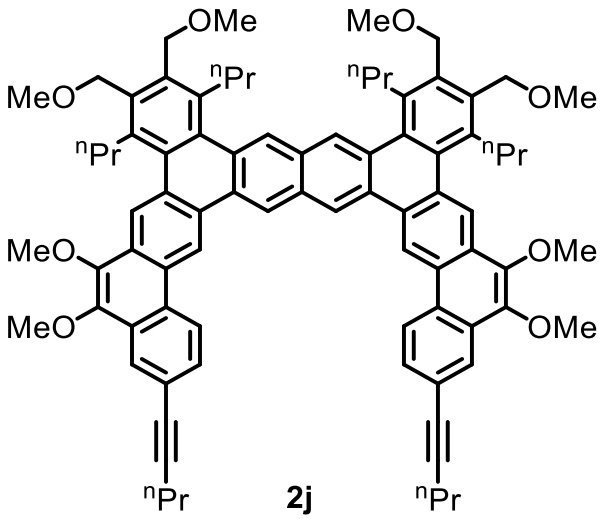
2i

Pentynylated Tetrabenzo[a,c,j,l]tetracene (2i)

IUPAC name: 2,3,16,17-tetrakis(methoxymethyl)-6,13-di(pent-1-yn-1-yl)-1,4,15,18-tetrapropyltetrabenzo[a,c,j,l]tetracene

Procedure: A 25 mL Schlenk tube was charged with dibromide **2h** (0.250 g, 0.235 mmol, 1.0 equiv) and THF (5 mL), and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To the stirred solution was added *n*-butyllithium (1.6 M in hexanes, 0.32 mL, 0.52 mmol, 2.2 equiv) dropwise over 7–10 min, and the resulting mixture was stirred for a further 5 min at –78 °C. Anhydrous HCl (2.0 M in ether, 0.35 mL, 0.71 mmol, 3.0 equiv) was then added dropwise over 2-3 min, the cold bath was removed, and saturated aqueous NH_4Cl (10 mL) was immediately added. The mixture was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated by rotary evaporation to afford **2i** (0.21 g, 99%) as a yellow solid, which was used without further purification.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz, [c] = 48 mM): δ = 8.99 (s, 2H), 8.59 (s, 2H), 8.51 (d, *J* = 8.3 Hz, 2H), 8.08 (d, *J* = 1.6 Hz, 2H), 7.59 (dd, *J* = 8.3, 1.5 Hz, 2H), 4.77 (s, 4H), 4.75 (s, 4H), 3.58 (s, 6H), 3.57 (s, 6H), 3.46 – 3.36 (m, 4H), 3.36 – 3.27 (m, 4H), 2.46 (t, *J* = 7.0 Hz, 4H), 1.92 (sext, *J* = 7.6, 4H), 1.81 – 1.64 (m, 8H), 1.10 (t, *J* = 7.4 Hz, 9H), 1.03 (t, *J* = 7.3 Hz, 9H), 0.94 (t, *J* = 7.3 Hz, 9H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 136.39, 136.23, 135.97, 135.85, 134.51, 133.73, 132.75, 131.91, 130.60, 130.36, 130.35, 130.30, 130.27, 129.76, 128.19, 124.03, 122.47, 121.73, 91.01, 81.26, 69.08, 69.06, 58.92, 58.84, 34.86, 34.56, 25.93, 25.92, 22.41, 21.68, 14.83, 14.34, 13.70; HRMS-ESI (m/z): $[M]^+$ calcd. for $C_{64}H_{72}O_4$, 904.5431; found, 904.5422.



2j

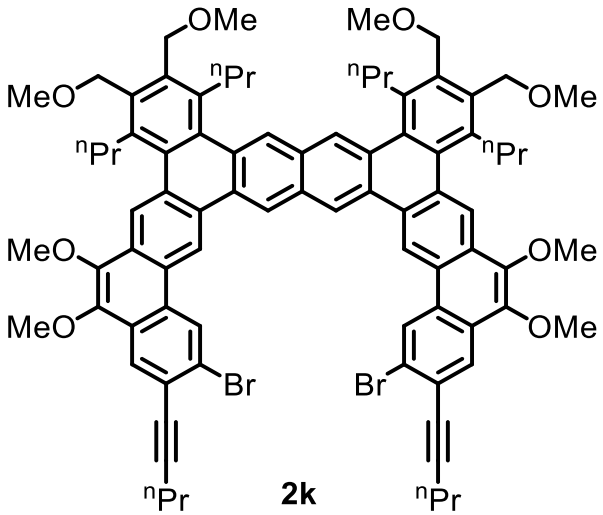
Pentynylated Tribenzo[a,h,o]phenanthro[2,3-q]hexaphene (2j)

IUPAC name: 5,6,19,20-tetramethoxy-9,10,15,16-tetrakis(methoxymethyl)-3,22-di(pent-1-yn-1-yl)-8,11,14,17-tetrapropyltribenzo[a,h,o]phenanthro[2,3-q]hexaphene

*Procedure #1 (from hexayne **1j**):* A 25 mL Teflon-stoppered flask charged with hexayne **1j** (233 mg, 0.234 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (107 mg, 0.936 mmol, 4.0 equiv), Ir(COD)(dppe)Cl (6.9 mg, 0.0094 mmol, 0.04 equiv), and toluene (4.7 mL). The flask was sealed, and the stirred mixture was heated at 80 °C for 2 h. In air, volatile materials were removed *via* rotary evaporation, then the residue was triturated with hexanes (10 mL) and solvents were removed again (to ensure complete removal of toluene). The resulting solid was dissolved in CH_2Cl_2 (~1 mL), then EtOH (30 mL) was added and the volume was reduced by to approximately 15 mL *via* rotary evaporation. The solid was collected on a fritted funnel, washed with MeOH (2 x 5 mL), and subjected to column chromatography (0–2% EtOAc in CH_2Cl_2), affording PAH **2j** (201 mg, 70%) as a pale-yellow solid. Monitoring of a smaller-scale (0.1x) reaction under identical conditions by ^{1}H NMR spectroscopy revealed that **2j** formed in 78% yield.

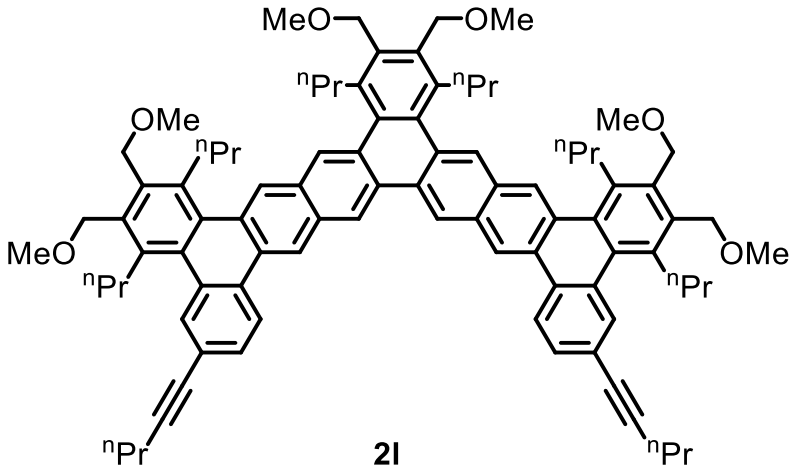
*Procedure #2 (from dibromide **2k**):* A 50 mL Schlenk tube was charged with dibromide **2k** (0.440 g, 0.318 mmol, 1.0 equiv) and THF (7 mL), and the solution was cooled to –78 °C with a CO_2(s)/acetone bath. To the stirred solution was added *n*-butyllithium (1.64 M in hexanes, 0.43 mL, 0.70 mmol, 2.2 equiv) dropwise over ~5 min, and the resulting mixture was stirred for a further 20 min at –78 °C. Anhydrous HCl (2.0 M in ether, 0.48 mL, 0.95 mmol, 3.0 equiv) was then added dropwise over 2-3 min, the cold bath was removed, and saturated aqueous NH_4Cl (20 mL) was immediately added. The mixture was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated by rotary evaporation to afford PAH **2j** (0.39 g, >99%) as a yellow solid, which was used without further purification.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz): δ = 9.82 (s, 2H), 9.38 (s, 2H), 9.01 (d, *J* = 8.5 Hz, 2H), 8.90 (s, 2H), 8.59 (s, 2H), 8.34 (d, *J* = 1.8 Hz, 2H), 7.80 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.81 (s, 4H), 4.79 (s, 4H), 4.15 (s, 6H), 4.14 (s, 6H), 3.61 (s, 6H), 3.60 (s, 6H), 3.53 – 3.39 (m, 8H), 2.53 (t, *J* = 7.0 Hz, 4H), 1.99 (sext, *J* = 7.6 Hz, 4H), 1.86 (sext, *J* = 7.7 Hz, 4H), 1.76 (sext, *J* = 7.2 Hz, 4H), 1.15 (t, *J* = 7.3 Hz, 6H), 1.05 (t, *J* = 7.2 Hz, 6H), 0.99 (t, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d,* 151 MHz): δ = 144.54, 143.40, 136.50, 136.37, 135.98, 135.88, 134.97, 134.49, 131.19, 130.98, 130.73, 130.62, 130.57, 129.97, 129.44, 129.03, 128.41, 128.09, 127.76, 127.15, 125.41, 123.02, 122.78, 122.49, 121.98, 118.09, 91.41, 81.25, 69.03, 68.96, 61.02, 60.94, 58.71, 58.71, 34.80, 34.73, 25.89, 25.70, 22.28, 21.58, 14.58, 14.47, 13.63; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{84}H_{88}O_8$, 1224.65; found, 1224.63.



2k

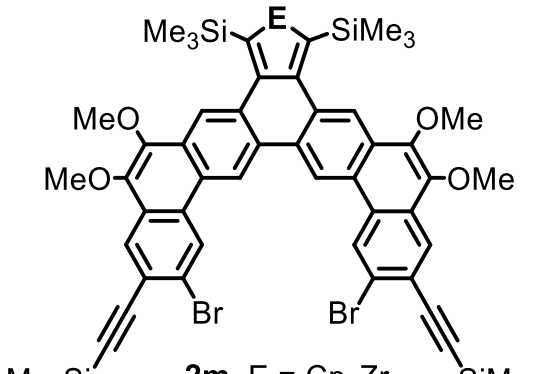
Pentynylated Tribenzo[a,h,o]phenanthro[2,3-q]hexaphene (2k)
IUPAC name: 2,23-dibromo-5,6,19,20-tetramethoxy-9,10,15,16-tetrakis(methoxymethyl)-3,22-di(pent-1-yn-1-yl)-8,11,14,17-tetrapropyltribenzo[a,h,o]phenanthro[2,3-q]hexaphene
Procedure: A 100 mL Teflon-stoppered flask charged with hexayne **1k** (550 mg, 0.476 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (217 mg, 1.90 mmol, 4.0 equiv), Ir(COD)(dppe)Cl (17.5 mg, 0.0238 mmol, 0.05 equiv), and benzene (9.5 mL). The flask was sealed, and the stirred mixture was heated at 80 °C for 5 h. The mixture was allowed to cool to RT, then hexanes (10 mL) was added. After 3 h, the precipitate was collected by filtration and washed with a 1:1 mixture of benzene/hexanes (2 x 4 mL) and hexanes (10 mL) to afford pure **2k** (480 mg, 73%) as a yellow solid. Monitoring of a smaller-scale (0.1x) reaction under identical conditions by ^{1}H NMR spectroscopy revealed that **2k** formed in 89% yield. It is also notable that the yield was essentially unchanged after 2 and 10 h of heating.
Characterization: ^{1}H NMR (chloroform-*d*, 600 MHz): δ = 9.74 (s, 2H), 9.48 (s, 2H), 9.27 (s, 2H), 8.88 (s, 2H), 8.59 (s, 2H), 8.34 (s, 2H), 4.81 (s, 4H), 4.79 (s, 4H), 4.13 (s, 6H), 4.13 (s, 6H), 3.61 (s, 6H), 3.60 (s, 6H), 3.51 – 3.46 (m, 4H), 3.46 – 3.40 (m, 4H), 2.58 (t, *J* = 7.0 Hz, 4H), 1.99 (sext, *J* = 7.2 Hz, 4H), 1.87 (sext, *J* = 6.8 Hz, 4H), 1.78 (sext, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.3 Hz, 6H), 1.05 (t, *J* = 7.2 Hz, 6H), 1.00 (t, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz): δ = 144.75, 143.06, 136.64, 136.48, 136.38, 136.16, 135.19, 134.46, 131.83, 130.94, 130.90, 130.76, 130.70, 130.36, 129.00, 128.55, 128.52, 128.51, 127.22, 126.71, 126.17, 124.60, 123.23, 122.73, 122.34, 118.30, 95.93, 80.21, 69.16, 69.09, 61.16, 61.03, 58.93, 58.90, 34.98, 34.88, 26.02, 25.83, 22.28, 21.88, 14.79, 14.68, 13.83; MS-MALDI-TOF (m/z): $[M]^{+}$ calcd. for $C_{84}H_{86}Br_2O_8$, 1380.47; found, 1380.44.



2l

Pentynylated Pentabenzo[a,c,j,q,s]heptaphene (2l)
IUPAC name: 2,3,8,9,14,15-hexakis(methoxymethyl)-18,27-di(pent-1-yn-1-yl)-1,4,7,10,13,16-hexapropylpentabenzo[a,c,j,q,s]heptaphene
Procedure: A 50 mL Teflon-stoppered flask was charged with octayne **1l** (313 mg, 0.335 mmol, 1.0 equiv), 1,4-dimethoxy-2-butyne (229 mg, 2.01 mmol, 6.0 equiv), and toluene (8 mL). To this flask was added a solution of Ir(COD)(dppe)Cl (14.8 mg, 0.0201 mmol, 0.06 equiv) in toluene (2.0 mL). The flask was sealed, and the stirred mixture was heated at 80 °C for 2 h. In air, volatile materials were removed *via* rotary evaporation, then the residue was subjected to column chromatography (0–2% EtOAc in CH_2Cl_2), affording PAH **2l** (305 mg, 74%) as a bright-yellow solid.
Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz, [c] = 8.0 mM): δ = 9.20 (s, 2H), 9.05 (s, 2H), 8.58 (s, 2H), 8.55 (d, *J* = 8.4 Hz, 2H), 8.49 (s, 2H), 8.09 (d, *J* = 1.6 Hz, 2H), 7.62 (dd, *J* = 8.2, 1.5

Hz, 2H), 4.77 (s, 4H), 4.77 (s, 4H), 4.75 (s, 4H), 3.60 (s, 6H), 3.58 (s, 6H), 3.57 (s, 6H), 3.48 – 3.37 (m, 8H), 3.36 – 3.28 (m, 4H), 2.47 (t, *J* = 7.0 Hz, 4H), 1.97 – 1.82 (m, 8H), 1.81 – 1.64 (m, 8H), 1.11 (t, *J* = 7.3 Hz, 6H), 1.03 (t, *J* = 6.4 Hz, 6H), 1.00 (t, *J* = 6.4 Hz, 6H), 0.94 (t, *J* = 7.3 Hz, 6H); $^{13}C\{^1H\}$ NMR (chloroform-*d*, 101 MHz): δ = 136.44, 136.36, 136.22, 136.15, 135.93, 135.81, 135.22, 134.48, 133.70, 132.73, 131.87, 131.12, 130.97, 130.85, 130.59, 130.53, 130.35, 130.30, 129.77, 128.50, 128.16, 123.98, 122.44, 122.42, 121.77, 90.99, 81.26, 69.09, 69.06, 69.03, 58.92, 58.90, 58.83, 34.85, 34.83, 34.54, 25.97, 25.91, 25.89, 22.39, 21.66, 14.83, 14.81, 14.32, 13.69; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{90}H_{100}O_6$, 1276.75; found, 1276.72.



2m, E = Cp_2Zr

2n, E = Se

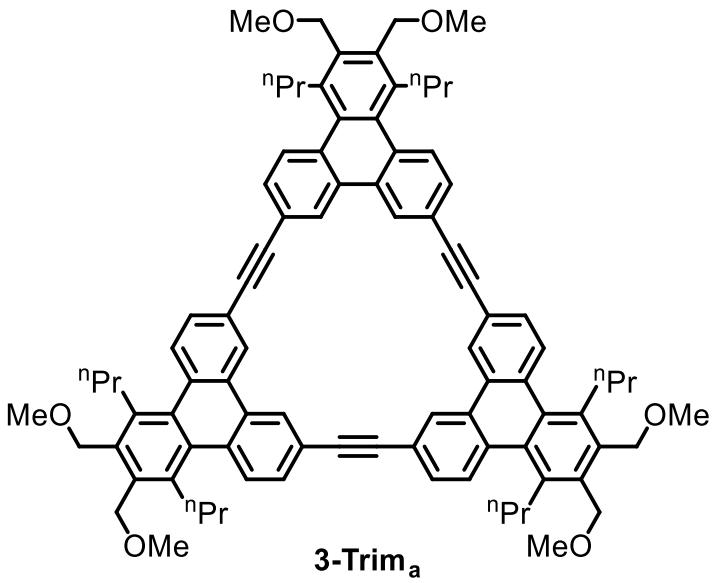
Selenophene-annulated PAH (2n)

Procedure: A 50 mL round-bottomed flask equipped with Teflon stopper was loaded with $Cp_2Zr(pyr)(Me_3SiC{\equiv}CSiMe_3)$ (0.133 g, 0.282 mmol) and hexanes (3 mL) and to this solution was quickly added a solution of tetrayne **1m** (0.287 g, 0.282 mmol) in hexanes (9 mL). The flask was sealed, and the stirred reaction mixture was heated at 95 °C (*caution: since this is well above the boiling point of hexanes, a blast shield should be used)* for 15 h. The supernatant was decanted, then the orange solid was washed with hexanes (2 x 5 mL) and dried under vacuum to give crude zirconacyclopentadiene **2m** (0.275 g), which was employed without purification as follows. Crude **2m** and $SeCl_2$(bipy) (68 mg, 0.22 mmol*) were added to a 50 mL round bottomed Schlenk flask, followed by CH_2Cl_2 (8 mL), and the resulting suspension was stirred vigorously for 5 min. In air, the mixture was filtered, then the filtrate was diluted to 30 mL with CH_2Cl_2, washed with 1M aqueous HCl (2 x 30 mL) and saturated aqueous $NaHCO_3$ (30 mL), dried with $MgSO_4$, and filtered again. Solvent was removed from the filtrate by rotary evaporation and the residue was purified by elution through a plug of silica gel (4 g) with 1:1 toluene/hexanes (~50 mL, or until no further **2n** was observed by TLC analysis), removal of solvents from the eluant, and trituration with hexanes (5 mL) to afford **2n** (0.126 g, 41%) as a light-yellow powder.

Notes: *Assuming **2m** is pure, this would be 1.0 equiv.

*Characterization of intermediate zirconacyclopentadiene annulated PAH (**2m**):* ^1H NMR (benzene-d_6, 600 MHz): δ = 8.83 (s, 2H), 8.74 (s, 2H), 8.53 (s, 2H), 8.44 (s, 2H), 6.10 (s, 10H), 3.86 (s, 6H), 3.60 (s, 6H), 0.39 (s, 18H), 0.35 (s, 18H).

*Characterization of selenophene annulated PAH (**2n**):* ^1H NMR (chloroform-*d*, 500 MHz): δ = 9.68 (s, 2H), 9.14 (s, 2H), 9.09 (s, 2H), 8.39 (s, 2H), 4.21 (s, 6H), 4.11 (s, 6H), 0.71 (s, 18H), 0.37 (s, 18H); $^{13}C\{^1H\}$ NMR (chloroform-*d*, 75 MHz): δ = 148.9, 146.2, 144.9, 142.7, 131.9, 129.5, 129.2, 128.9, 128.5, 127.8, 126.7, 125.9, 123.7, 123.0, 122.2, 117.8, 103.8, 100.2, 61.2, 60.8, 1.6, 0.1; Anal. Calcd for $C_{52}H_{56}Br_2O_4SeSi_4$: C, 56.98; H, 5.15. Found: C, 56.75; H, 4.91.



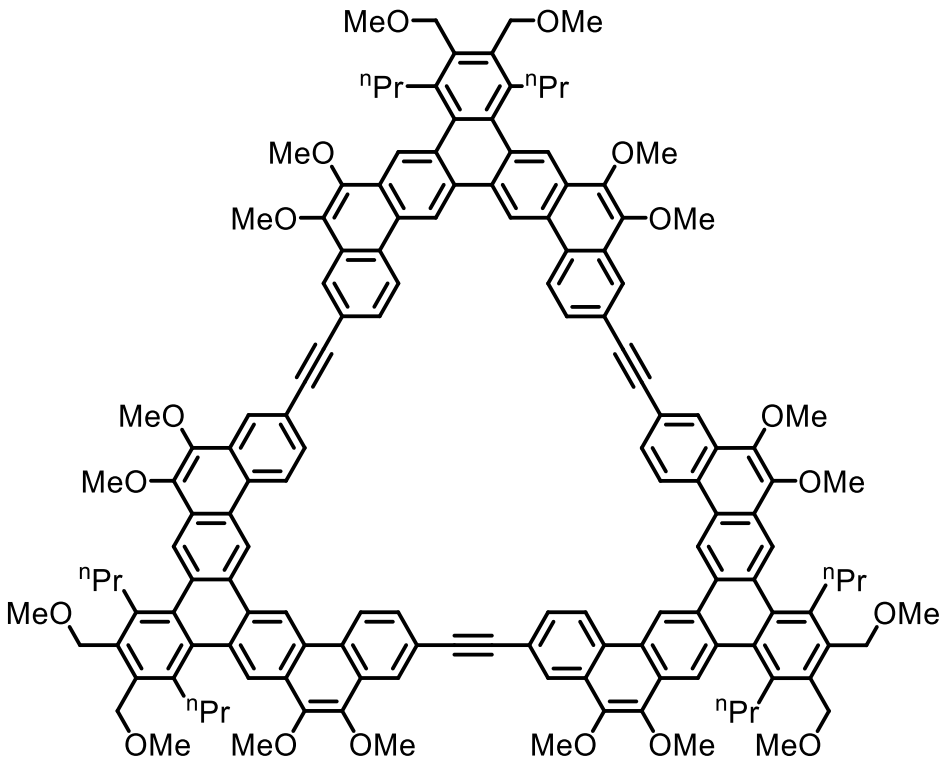
3-Trim$_a$

Small Trimeric Macrocycle (3-Trim$_a$)

Procedure: A 25 mL Teflon-stoppered flask equipped with magnetic stirbar was charged with PAH **2d** (117 mg, 0.220 mmol, 1.0 equiv), powdered 5 Å molecular sieves* (440 mg), and toluene (2 mL). To this flask was added a mixture of **Mo-2** (8.5 mg, 0.0110 mmol, 0.05 equiv), Ph_3SiOH (18.2 mg, 0.066 mmol, 0.30 equiv), and toluene (2.4 mL), which was prepared by addition of the latter to a mixture of the two solids. The flask was sealed, and the stirred mixture was heated at 80 °C for 16 h. The suspension, in addition to silica gel (1 g), was transferred to a round-bottomed flask, and volatile materials were removed *via* rotary evaporation. The powder was loaded onto a plug of silica gel (10 g), which was eluted with 10:1 CH_2Cl_2:EtOAc (100 mL, or until no further product was seen by TLC). The eluant was concentrated *via* rotary evaporation, the residue was dissolved in CH_2Cl_2 (1 mL), and MeOH (5 mL) was added.** The precipitate was collected by filtration and washed with MeOH (2 x 5 mL) to afford*** **3-Trim$_a$** (82 mg, 88%) as a beige solid.

Notes: *See general section (above) for important details on the source of these molecular sieves. **The purpose of this step is to remove Ph_3SiOH. ***See general section for details on optimal recovery of this solid.

Characterization: ^{1}H NMR (chloroform-*d,* 600 MHz): δ = 8.99 (d, *J* = 1.8 Hz, 6H), 8.13 (d, *J* = 8.4 Hz, 6H), 7.70 (dd, *J* = 8.4, 1.8 Hz, 6H), 4.75 (s, 12H), 3.56 (s, 18H), 3.38 – 3.26 (m, 12H), 1.74 (sext, *J* = 7.5 Hz, 12H), 0.95 (t, *J* = 7.3 Hz, 18H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 136.58, 135.87, 133.47, 131.20, 130.32, 129.03, 128.79, 127.48, 121.51, 90.90, 69.05, 58.93, 34.86, 25.90, 14.60; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{90}H_{90}O_6$, 1266.67; found, 1266.63.



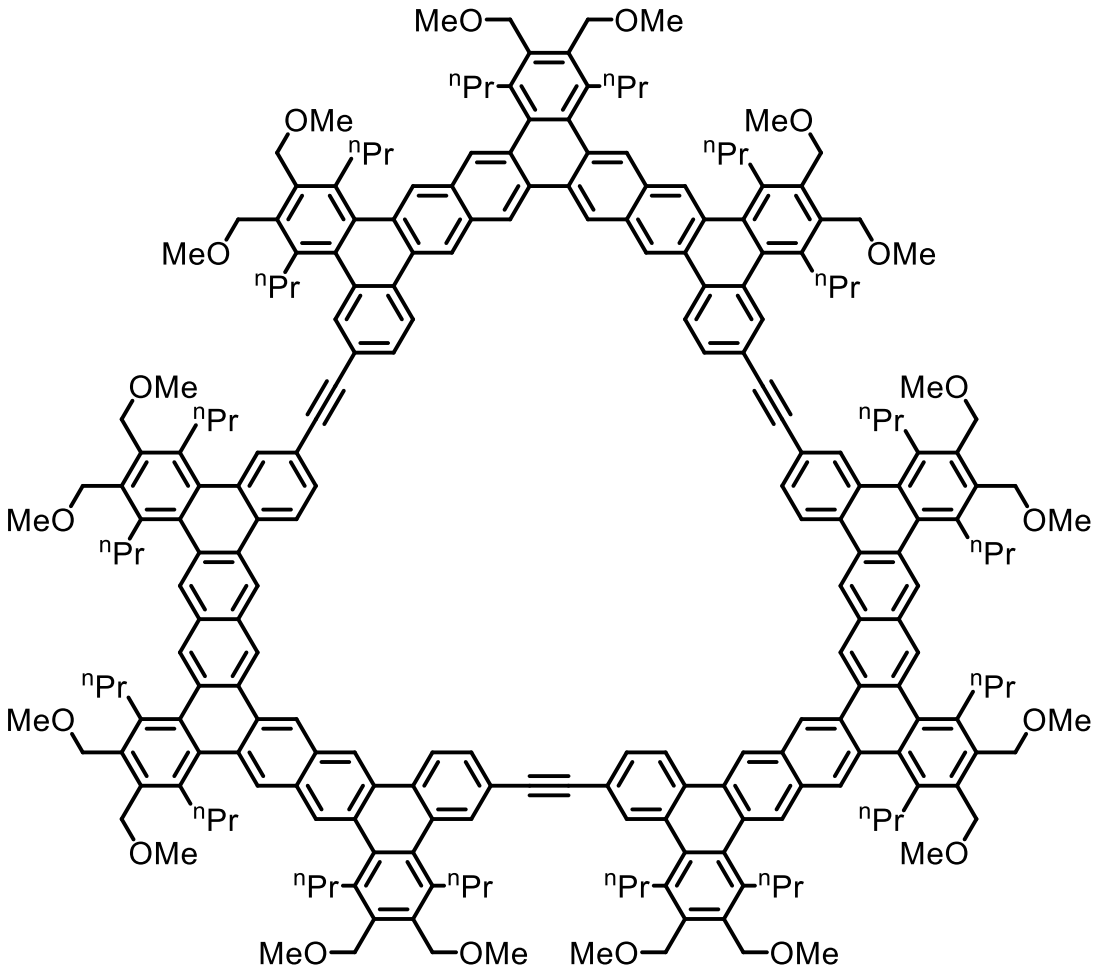
3-Trim$_b$

Medium Trimeric Macrocycle (3-Trim$_b$)

Procedure: A 50 mL Teflon-stoppered flask equipped with magnetic stirbar was charged with PAH **2g** (100 mg, 0.117 mmol, 1.0 equiv), powdered 5 Å molecular sieves* (234 mg), and 1,2-dichlorobenzene (2.0 mL). To this flask was added a mixture of **Mo-2** (9.0 mg, 0.0117 mmol, 0.10 equiv), Ph_3SiOH (19.4 mg, 0.0702 mmol, 0.60 equiv), and 1,2-dichlorobenzene (2.7 mL), which was prepared by addition of the latter to a mixture of the two solids. The flask was sealed, and the stirred mixture was heated at 80 °C for 16 h. After heating, the reaction mixture was cooled to RT, diluted with CH_2Cl_2 (40 mL), and directly loaded onto a silica gel column (20 g). The column was eluted with CH_2Cl_2 (~150 mL,** to ensure complete removal of 1,2-dichlorobenzene) and 10–20% EtOAc in CH_2Cl_2. The yield of **3-Trim$_b$**, a pale-yellow powder, was 75 mg (86%).

Notes: *See general section (above) for important details on the source of these molecular sieves. **Note that all eluate was during the initial CH_2Cl_2 elution was colorless and was thus discarded. If the yellow band begins to elute, it likely contains desired product and thus should be collected.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz, [c] = 1.9 mM): δ = 9.78 (s, 6H), 9.06 (d, *J* = 8.4 Hz, 6H), 8.91 (s, 6H), 8.36 (s, 6H), 8.11 (dd, *J* = 8.3, 1.3 Hz, 6H), 4.83 (s, 12H), 4.14 (s, 18H), 4.12 (s, 18H), 3.64 (s, 18H), 3.51 – 3.30 (m, 12H), 2.10 – 1.96 (m, 12H), 1.09 (t, *J* = 7.2 Hz, 18H); ^{13}C{^{1}H} NMR (chloroform-*d,* 176 MHz): δ = 144.07, 143.10, 136.63, 136.11, 134.41, 130.71, 129.47, 129.40, 129.36, 128.01, 127.47, 126.76, 124.91, 122.94, 122.24, 121.88, 117.38, 91.40, 69.20, 60.83, 60.76, 58.87, 35.19, 25.85, 14.87; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{150}H_{138}O_{18}$, 2226.99; found, 2226.98.



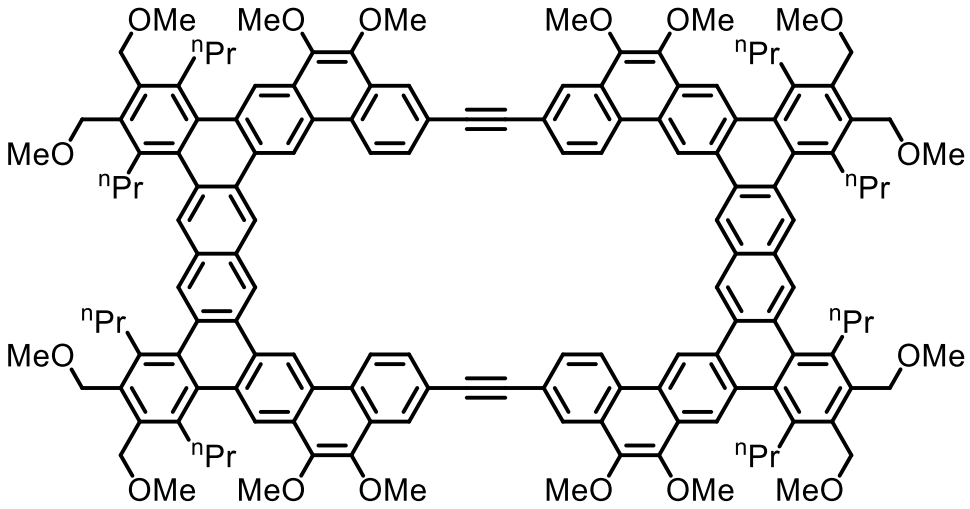
3-Trim$_c$

Large Trimeric Macrocycle (3-Trim$_c$)

Procedure: This compound was prepared by the same procedure as **3-Trim$_b$**, with the following quantities and noted differences: PAH **2l** (101 mg, 0.0790 mmol, 1.0 equiv), **Mo-2** (6.1 mg, 0.0079, 0.10 equiv), Ph_3SiOH (13.1 mg, 0.0474 mmol, 0.60 equiv), powdered 5 Å molecular sieves (158 mg), and 1,2-dichlorobenzene (9.0 mL). After heating, the reaction mixture was cooled to RT and directly loaded onto a silica gel column (20 g), which was eluted with CH_2Cl_2 (~200 mL,* to ensure complete removal of 1,2-dichlorobenzene) and 10–30% EtOAc in CH_2Cl_2. The yield of **3-Trim$_c$**, a bright-yellow powder, was 68 mg (74%).

Notes: *Note that all eluate during the initial CH_2Cl_2 elution was colorless and was thus discarded. If the yellow band begins to elute, it likely contains desired product and thus should be collected.

Characterization: ^{1}H NMR (chloroform-*d,* 400 MHz, [c] = 4.0 mM): δ = 9.32 (s, 6H), 9.18 (s, 6H), 8.74 (d, *J* = 8.6 Hz, 6H), 8.64 (s, 6H), 8.55 (s, 6H), 8.29 (s, 6H), 7.94 (dd, *J* = 8.1, 1.0 Hz, 6H), 4.82 (s, 12H), 4.82 (s, 12H), 4.80 (s, 12H), 3.62 (s, 18H), 3.62 (s, 18H), 3.61 (s, 18H), 3.53 – 3.37 (m, 36H), 2.04 – 1.75 (m, 36H), 1.07 (t, *J* = 7.2 Hz, 18H), 1.04 (t, *J* = 7.2 Hz, 18H), 1.03 (t, *J* = 7.2 Hz, 18H); ^{13}C{^{1}H} NMR (chloroform-*d*, 101 MHz): δ = 136.63, 136.61, 136.44, 136.23, 136.12, 135.95, 135.14, 134.57, 133.55, 131.95, 131.69, 131.25, 130.99, 130.95, 130.88, 130.81, 130.53, 130.38, 130.13, 128.34, 128.08, 124.21, 122.48, 122.11, 121.74, 91.10, 69.17, 69.13, 69.11, 58.94, 58.91, 58.86, 34.95, 34.88, 34.74, 26.00, 25.95, 25.92, 14.84, 14.82, 14.50; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{246}H_{258}O_{18}$, 3499.93; found, 3499.95.



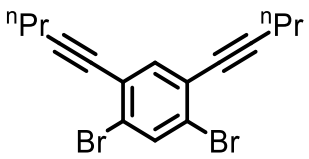
3-Dim

Dimeric Macrocycle (3-Dim)

Procedure: This compound was prepared by the same procedure as **3-Trim$_b$**, with the following quantities and noted differences: PAH **2j** (100 mg, 0.0816 mmol, 1.0 equiv), **Mo-2** (6.3 mg, 0.0082 mmol, 0.10 equiv), Ph_3SiOH (13.5 mg, 0.049 mmol, 0.60 equiv), powdered 5 Å molecular sieves (160 mg), and 1,2-dichlorobenzene (3.3 mL). After heating, MeOH (20 mL) was added, the suspension was filtered, and the solids were washed with MeOH (2 x 5 mL). The solid was suspended in CH_2Cl_2 (50 mL), the mixture was stirred vigorously for 30 min and filtered through a plug of silica gel (5 g). The plug was flushed with 1:1 CH_2Cl_2:EtOAc (50 mL) and the filtrate was concentrated *via* rotary evaporation. The residue was suspended in benzene (3–4 mL), then the suspension was stirred vigorously for 1 h and filtered. The solid was washed with benzene (1 mL) and hexanes (3 mL) to afford* **3-Dim** (76 mg, 84%) as a yellow solid.

Notes: *For optimal mass recovery, the solid was transferred to a 20 mL vial with the aid of CH_2Cl_2, which was then removed *via* rotary evaporation.

Characterization: ^{1}H NMR (chloroform-*d,* 500 MHz, [c] = 1.5 mM): δ = 9.94 (br s, 4H), 9.51 (br s, 4H), 9.23 (br s, 4H), 8.92 (br s, 4H), 8.61 (s, 4H), 8.53 (br s, 4H), 8.24 (br s, 4H), 4.84 (s, 8H), 4.81 (s, 8H), 4.17 (br s, 12H), 4.16 (br s, 12H), 3.64 (s, 12H), 3.63 (s, 12H), 3.57 – 3.36 (m, 16H), 2.09 – 1.97 (m, 8H), 1.97 – 1.85 (m, 8H), 1.09 (t, *J* = 7 Hz, 12H), 1.05 (t, *J* = 7 Hz, 12H); ^{13}C{^{1}H} NMR (chloroform-*d*, 151 MHz*,* 60 °C): δ = 144.83, 143.79, 136.97, 136.78, 136.54, 136.40, 135.24, 134.70, 131.60, 131.01, 130.93, 130.90, 130.82, 130.17, 130.08, 130.05, 128.61, 128.53, 128.41, 127.37, 125.13, 123.60, 122.68, 122.31, 122.13, 118.24, 91.86, 69.44, 69.38, 61.10, 61.05, 58.76, 58.76, 35.14, 35.07, 26.13, 25.88, 14.80, 14.72; MS-MALDI-TOF (m/z): $[M]^+$ calcd. for $C_{152}H_{148}O_{16}$, 2229.08; found, 2229.06.

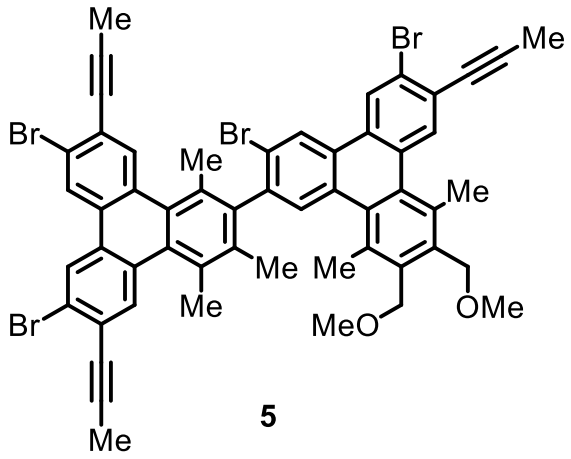


4a

1,5-dibromo-2,4-di(pent-1-ynyl)benzene (4a)

Procedure: This compound was prepared by a modified literature procedure.[14] A 250 mL Schlenk flask with Teflon stopper was charged with diiodide **S1** (10.0 g, 20.5 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (0.36 g, 0.31 mmol, 0.015 equiv), and CuI (0.20 g, 1.03 mmol, 0.05 equiv), then the flask was evacuated and refilled with N_2. To this flask was added an N_2-sparged mixture of THF (28 mL) and triethylamine (14 mL), followed by 1-pentyne (3.07 g, 45.1 mmol, 2.2 equiv). The mixture was stirred at RT for 24 h, then diluted with hexanes (150 mL), washed with aqueous HCl (3 M, 100 mL), dried with $MgSO_4$, and filtered. Solvents were removed from the filtrate *via* rotary evaporation, then the crude product purified by column chromatography (100% hexanes) to afford diyne **4a** (6.70 g, 89%) as yellow oil.

Characterization: ^{1}H NMR data matches that in the literature.[14]



5

Dimeric Side Product (5).

IUPAC name: 3',6',7,10-tetrabromo-10',11'-bis(methoxymethyl)-1,3,4,9',12'-pentamethyl-6,7',11-tri(prop-1-yn-1-yl)-2,2'-bitriphenylene

Procedure: The isolation of **5** is described in the procedure for **2b** (above).

Characterization: ^{1}H NMR (chloroform-*d*, 600 MHz): δ = 8.69 (s, 1H), 8.62 (s, 1H), 8.54 (s, 1H), 8.53 (s, 1H), 8.36 (s, 1H), 8.28 (s, 1H), 8.27 (s, 1H), 7.99 (s, 1H), 4.74 (s, 2H), 4.68 (s, 2H), 3.54 (s, 3H), 3.48 (s, 3H), 2.94 (s, 3H), 2.84 (s, 3H), 2.83 (s, 3H), 2.46 (s, 3H), 2.19 (s, 3H), 2.19 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (chloroform-*d*, 151 MHz): δ = 141.85, 140.81, 135.65, 135.65, 135.55, 133.97, 133.84, 133.28, 133.02, 132.72, 132.09, 131.87, 131.81, 131.12, 131.03, 130.56, 130.42, 130.38, 130.32, 130.29, 130.15, 130.14, 129.91, 129.85, 129.49, 127.72, 127.16, 127.10, 127.09, 124.21, 124.14, 124.06, 123.78, 123.47, 123.30, 123.03, 91.52, 91.48, 91.43, 79.06, 79.02, 78.99, 69.19, 69.17, 59.07, 58.97, 22.68, 21.86, 20.82, 20.74, 18.08, 4.92, 4.90, 4.89; HRMS-EI (m/z): $[M]^+$ calcd. for $C_{54}H_{42}Br_4O_2$, 1037.9913; found, 1037.9910.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra

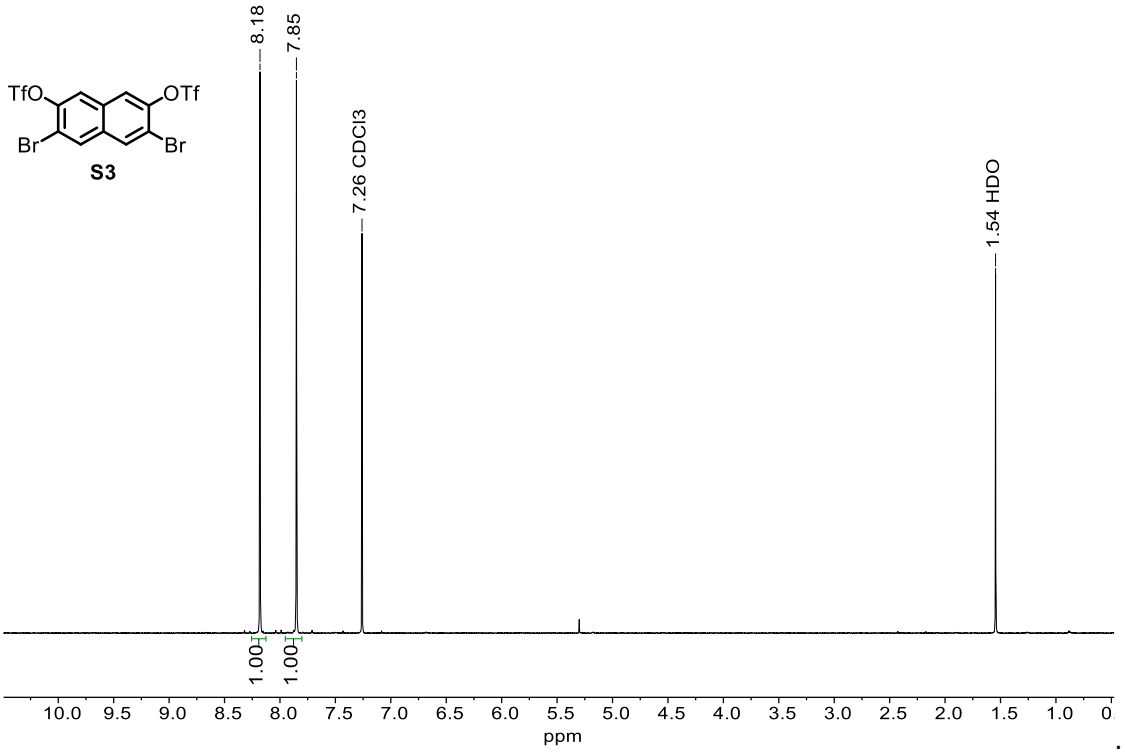


Figure S4. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **S3**.

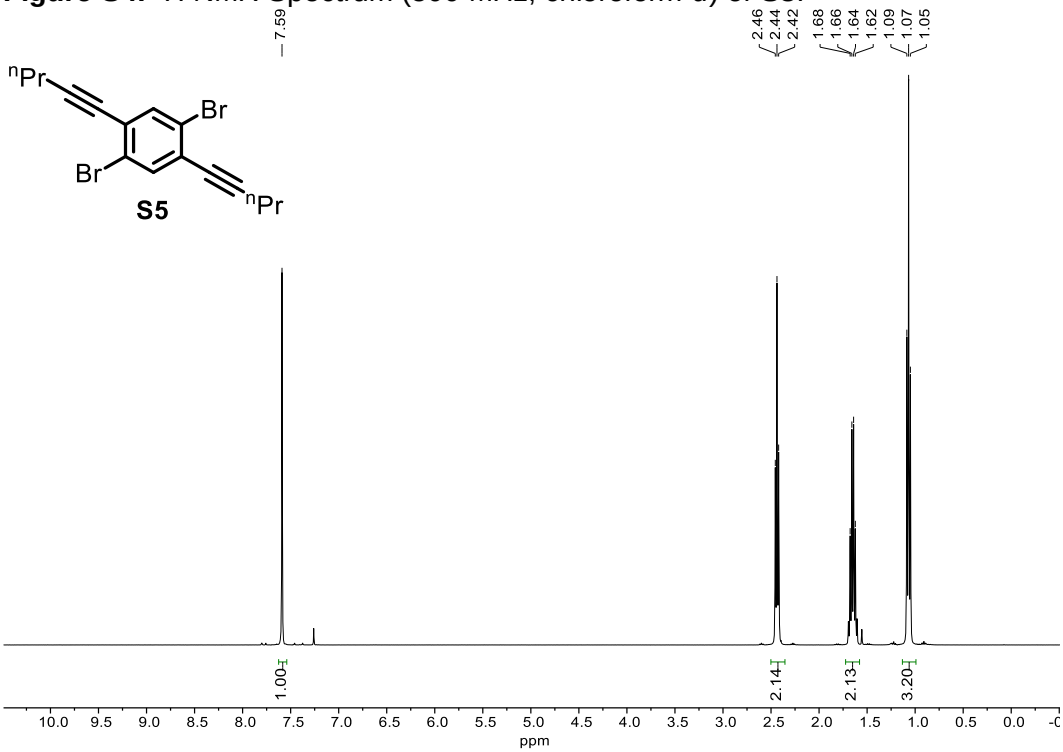


Figure S5. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **S5**.

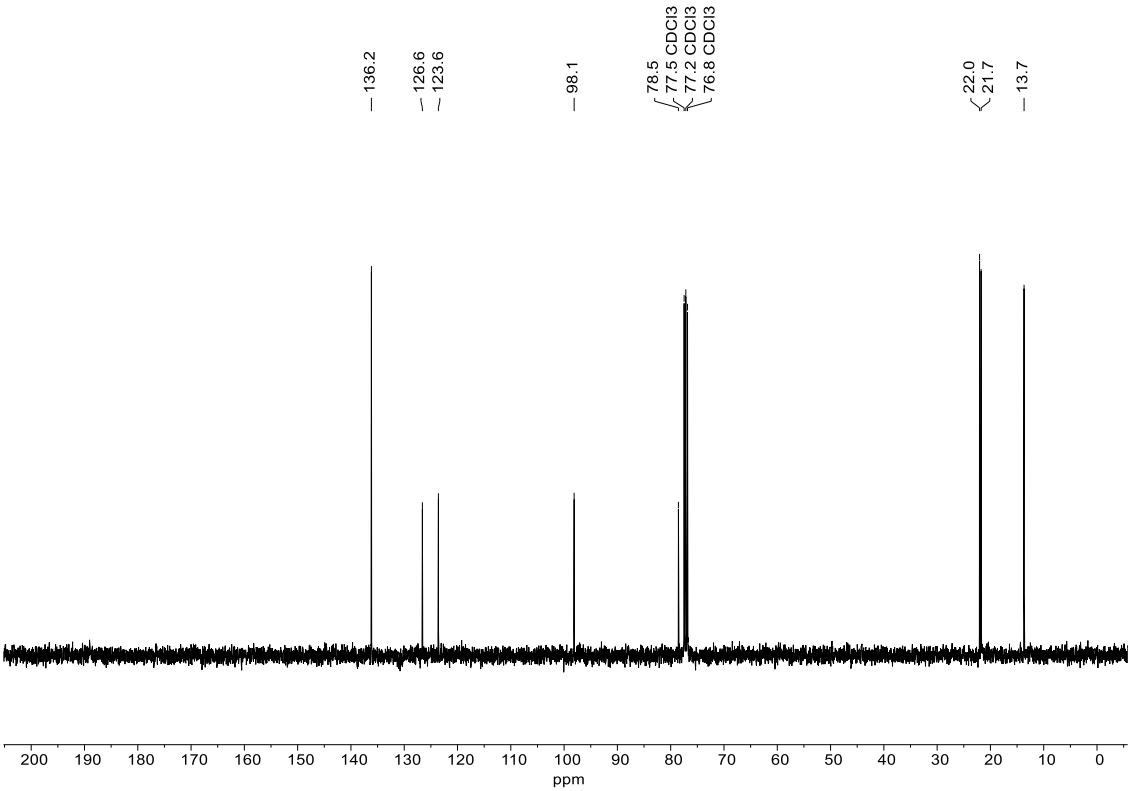


Figure S6. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **S5**.

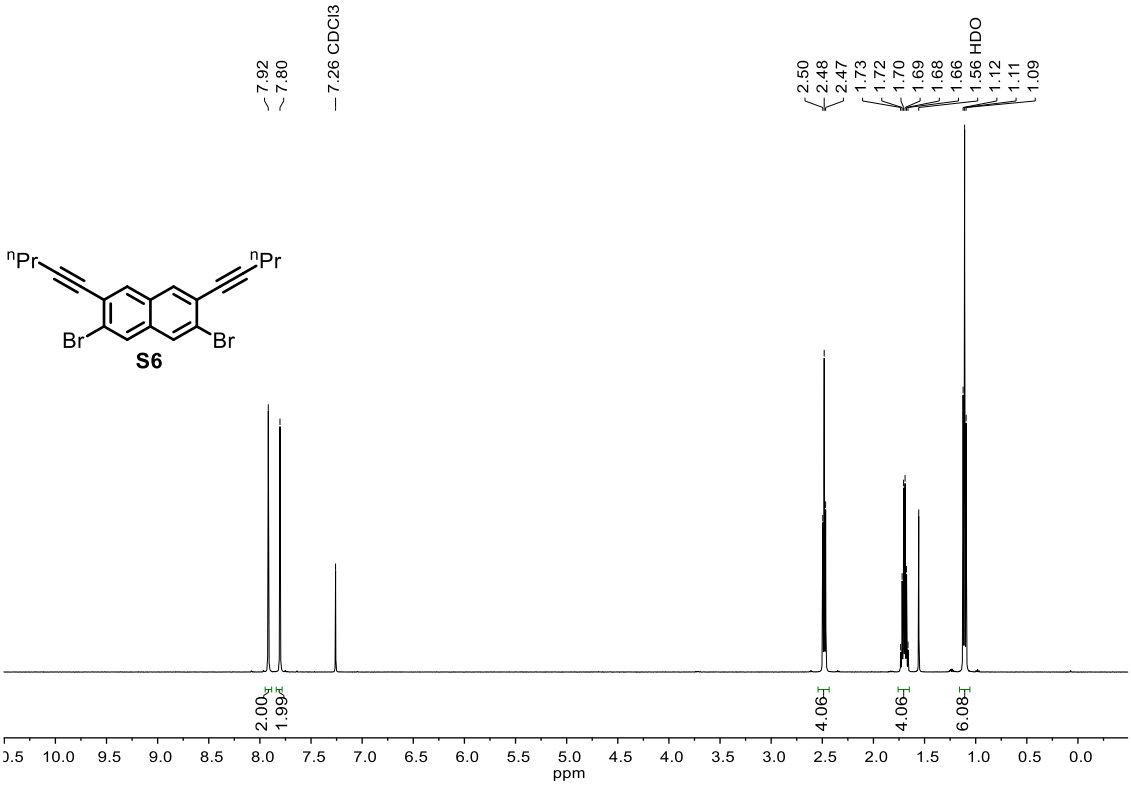


Figure S7. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **S6**.

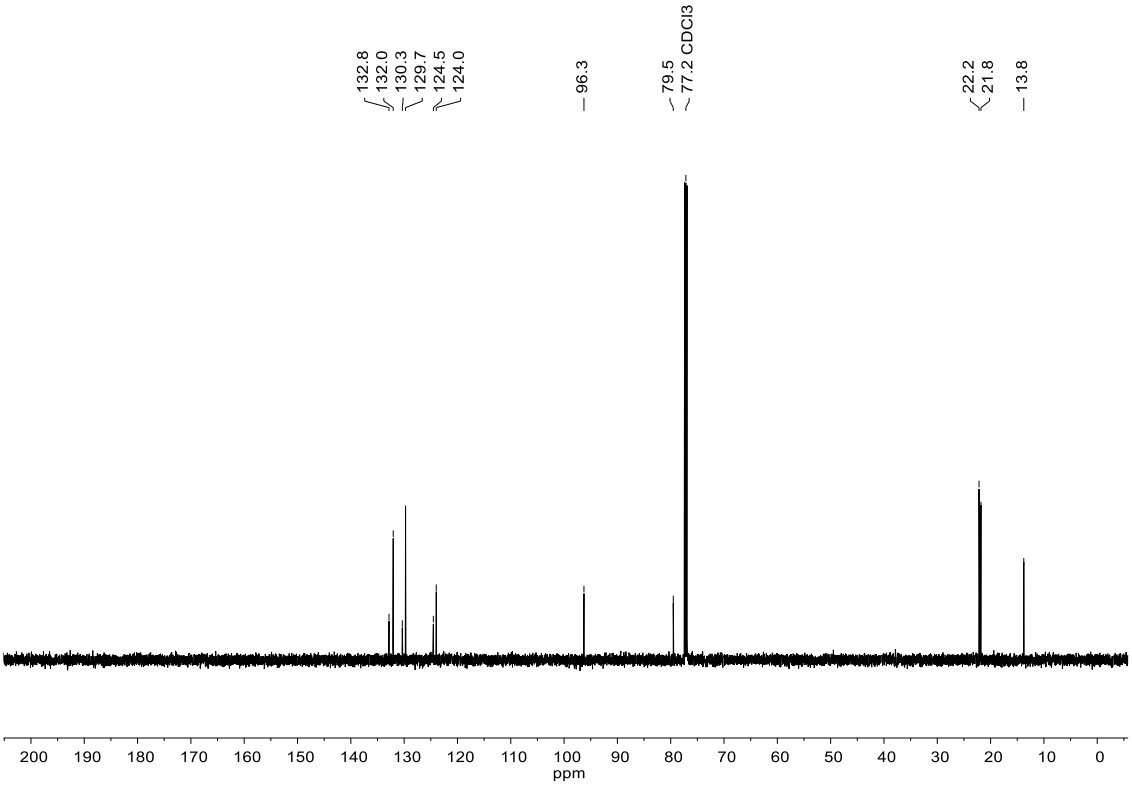


Figure S8. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **S6**.

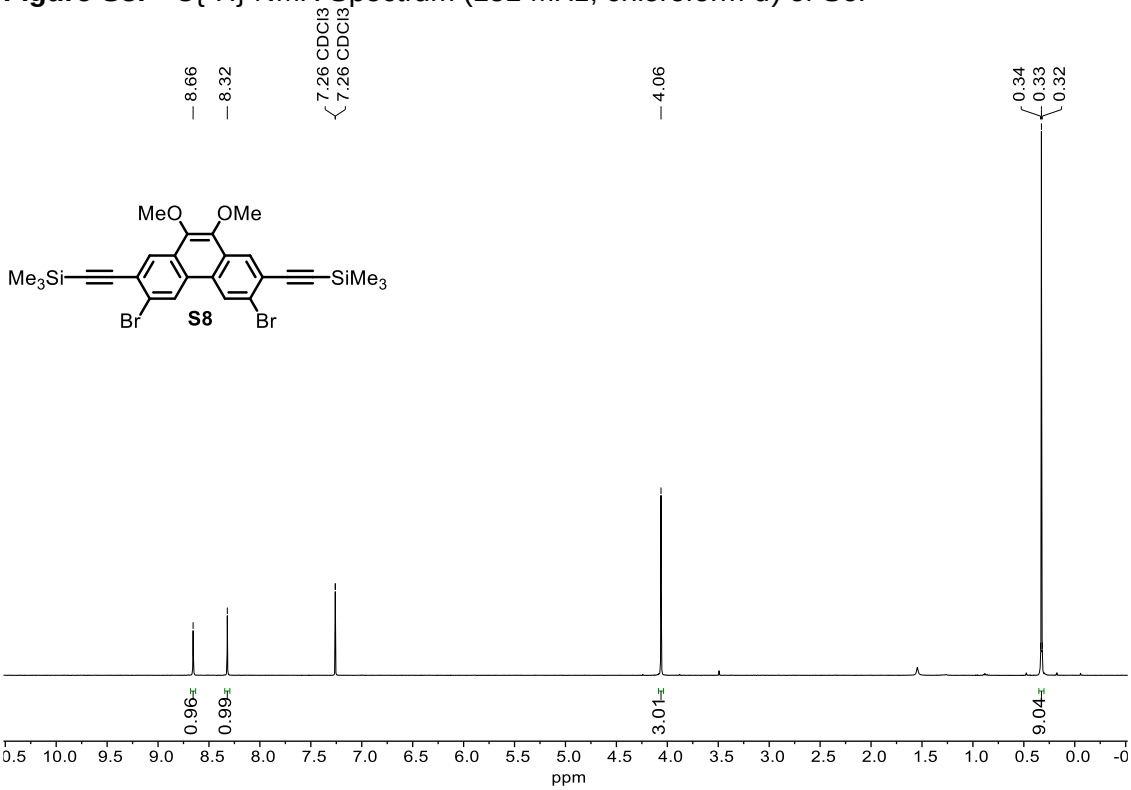


Figure S9. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **S8**.

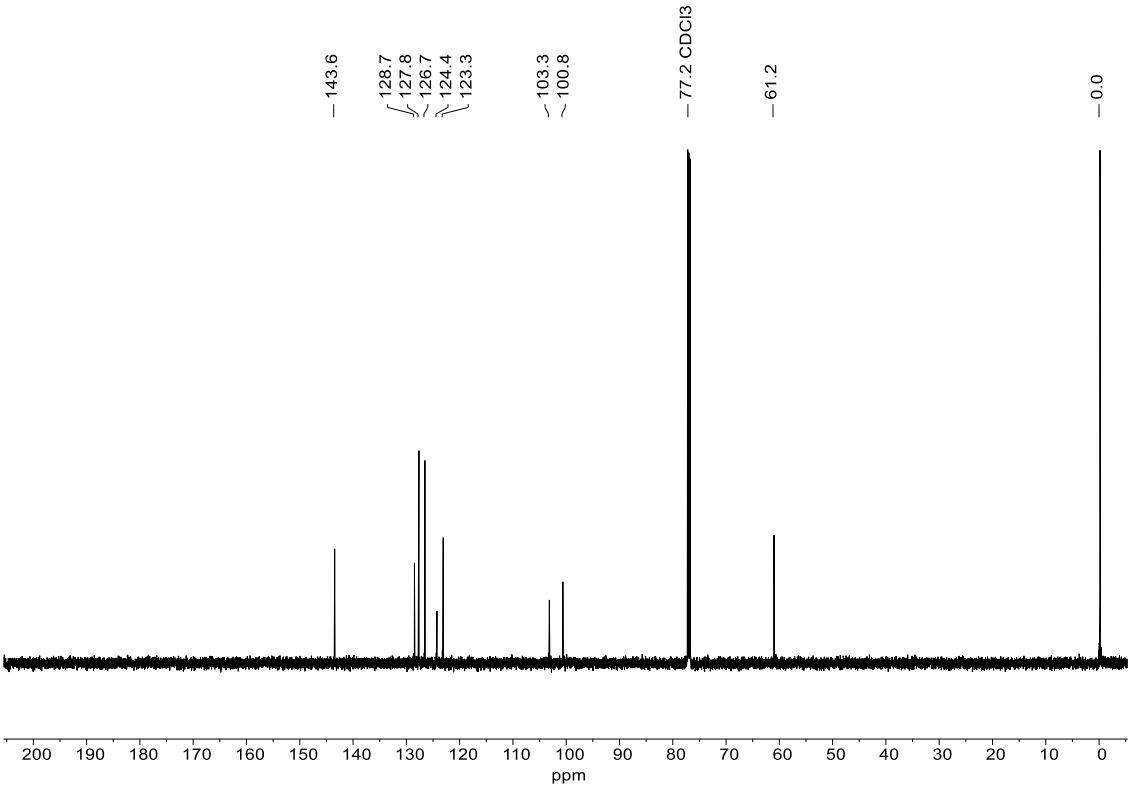


Figure S10. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **S8**.

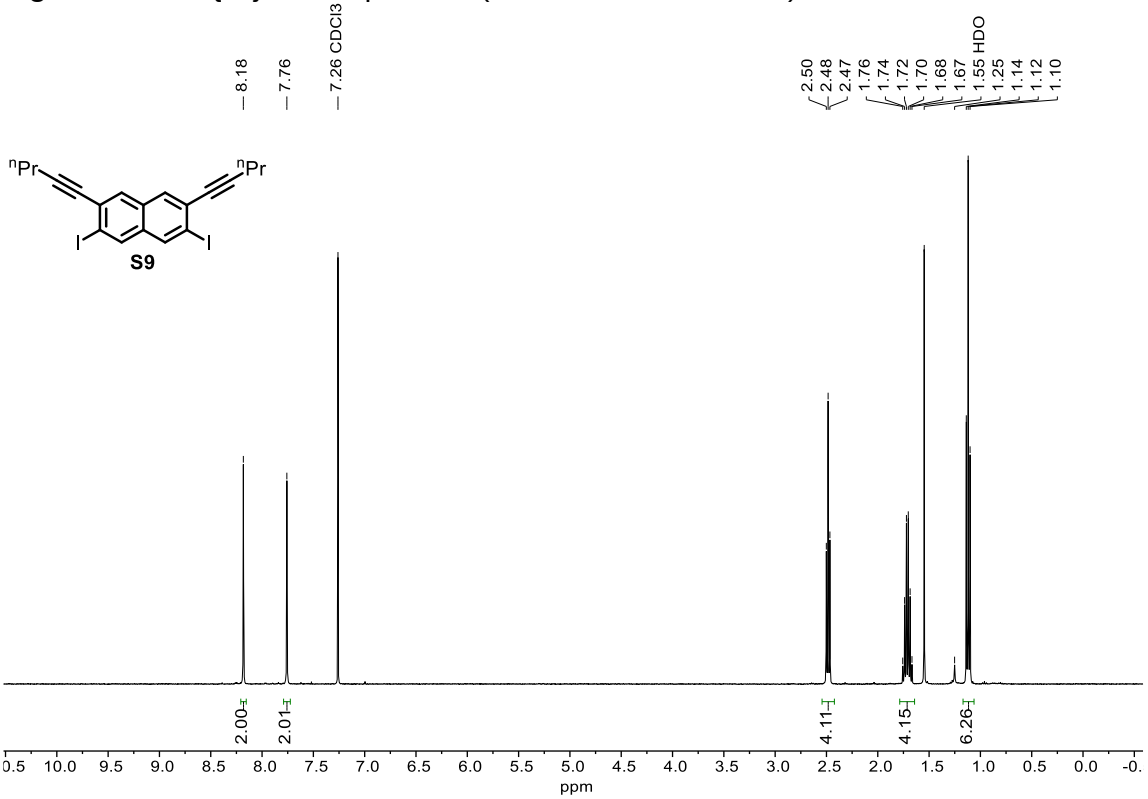


Figure S11. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **S9**.

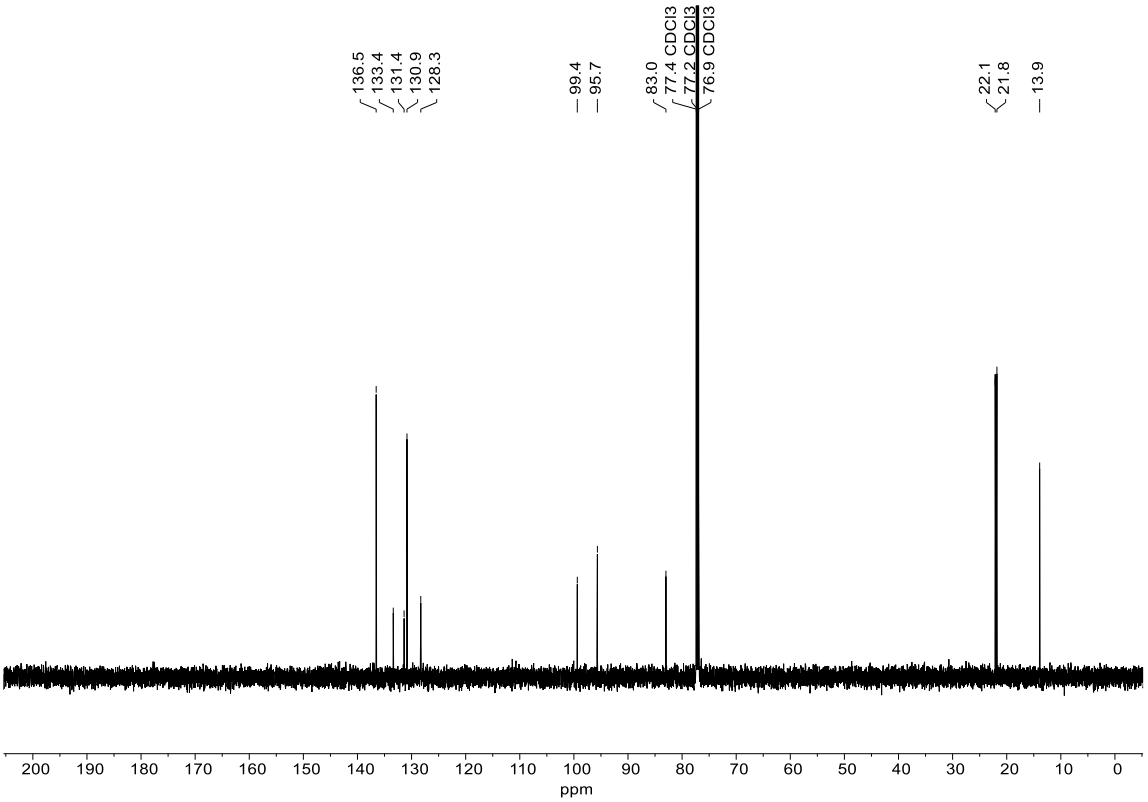


Figure S12. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **S9**.

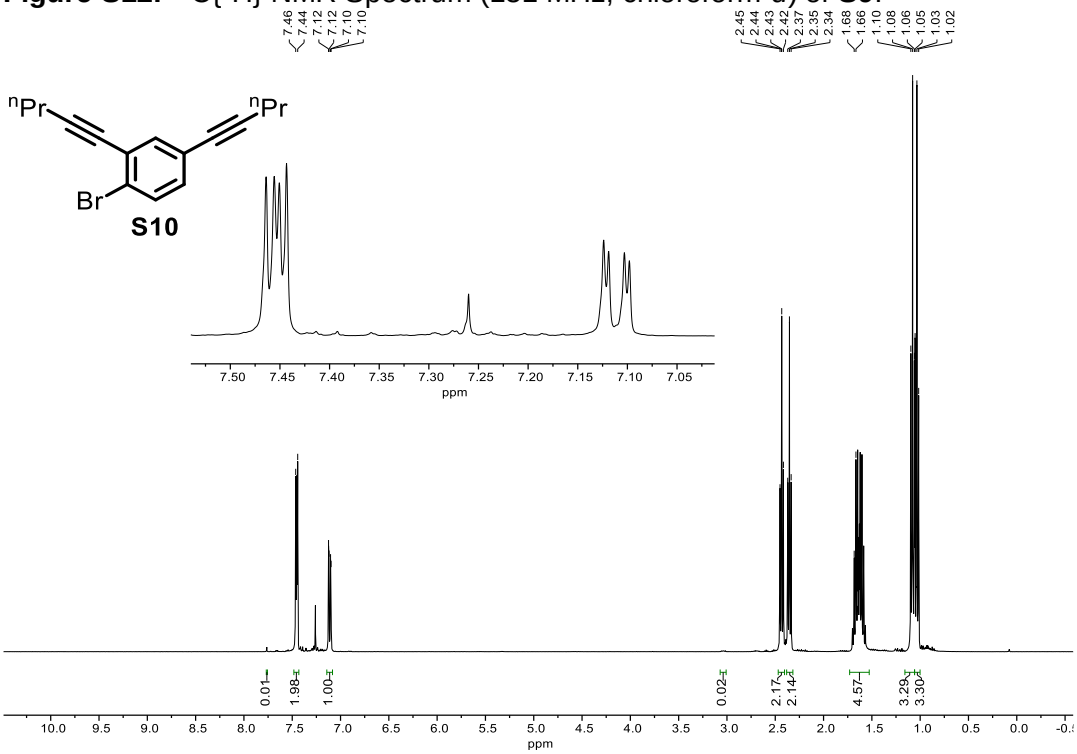


Figure S13. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **S10**.

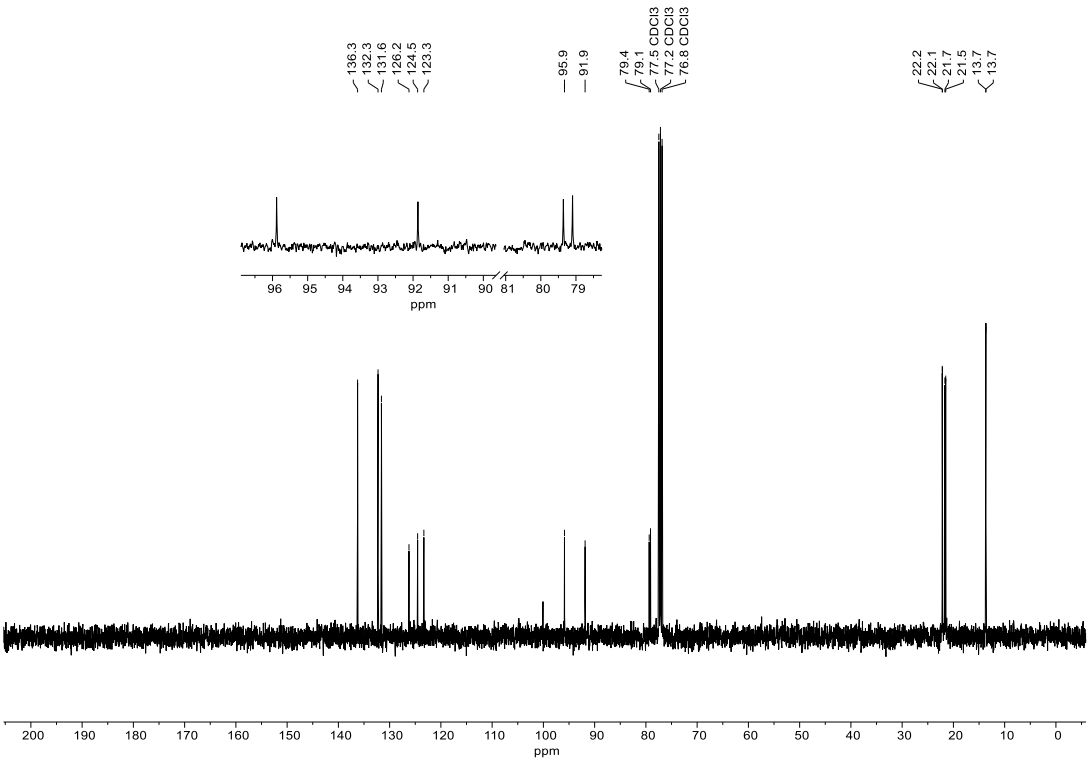


Figure S14. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **S10**.

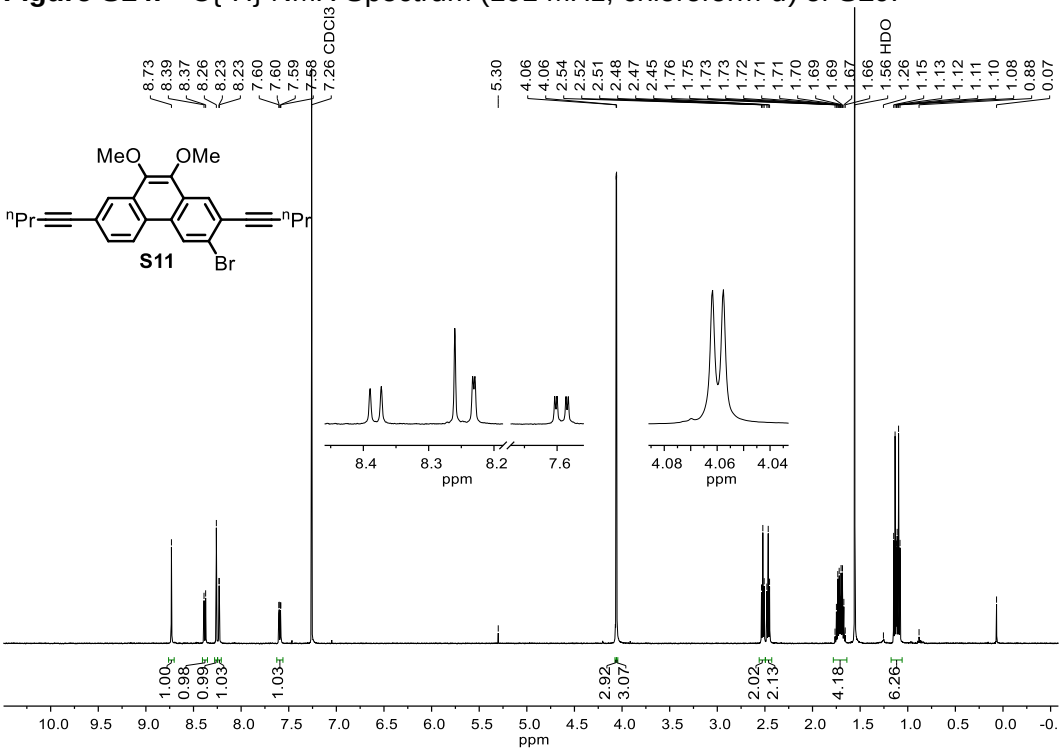


Figure S15. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of purified **S11**.

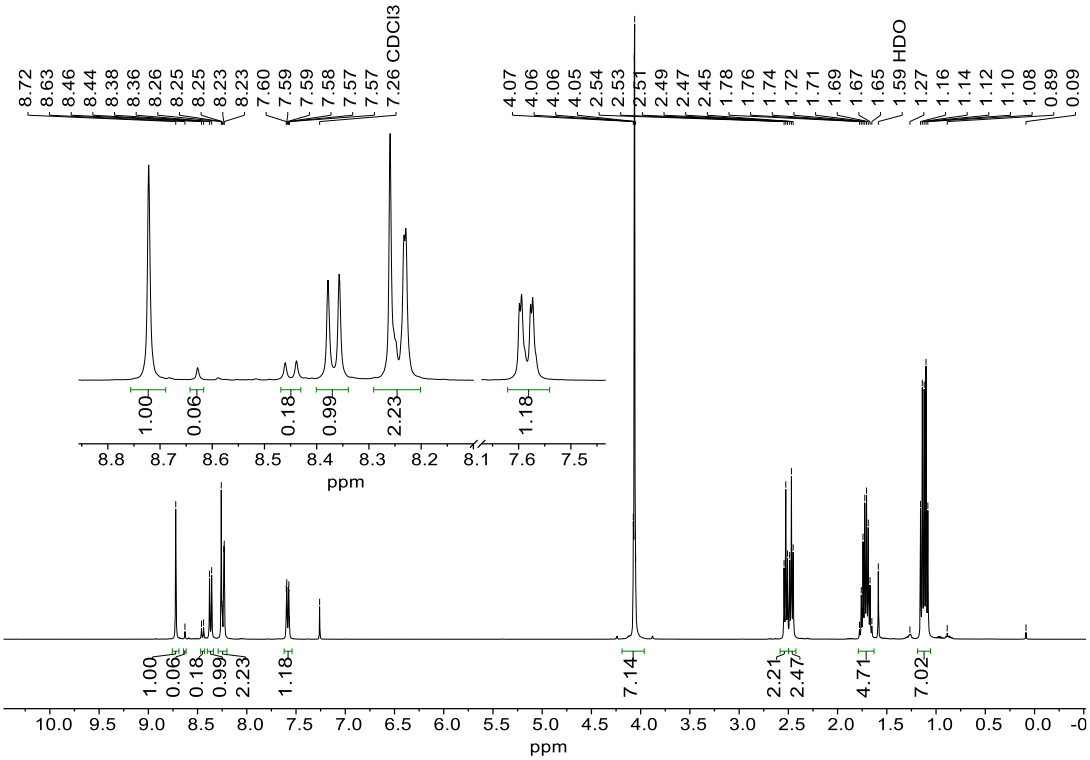


Figure S16. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of the mixture of starting **S7**, **S11**, and doubly protodebrominated **S7** (molar ratio: 0.03 : 1.0 : 0.09). This mixture was used without purification in the subsequent cross-coupling reaction.

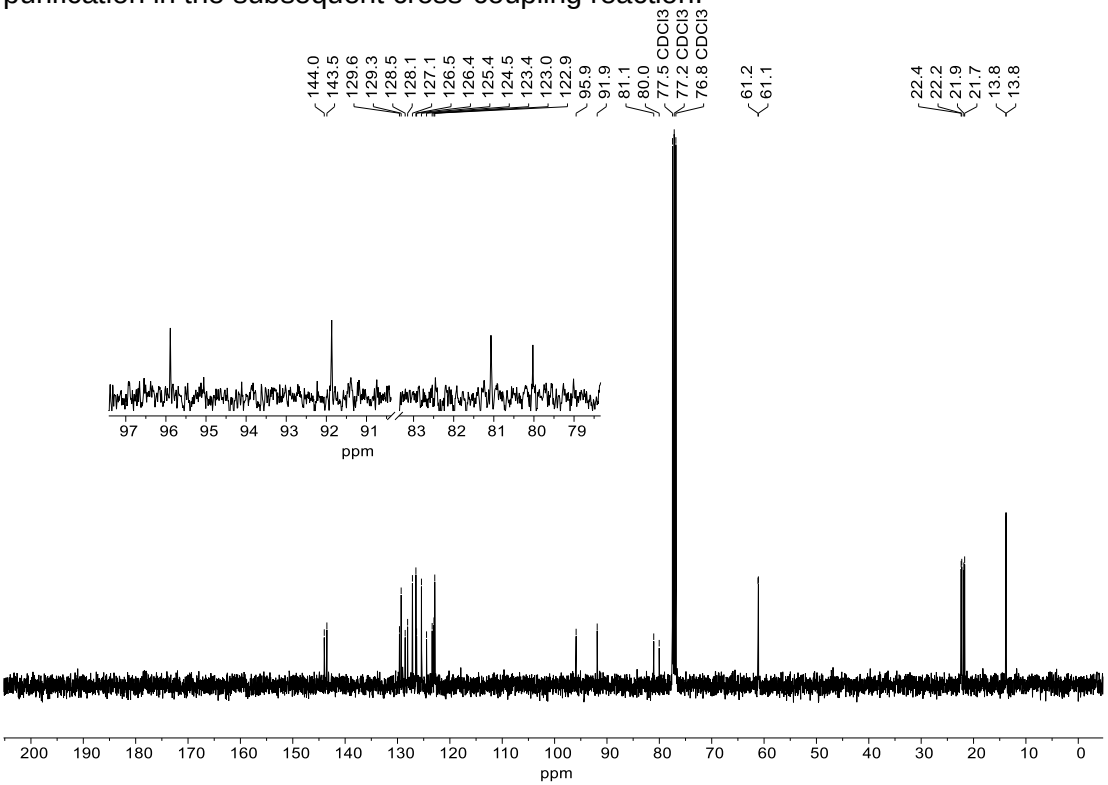


Figure S17. ^{13}C{^{1}H} NMR Spectrum (101 MHz, chloroform-*d*) of **S11**.

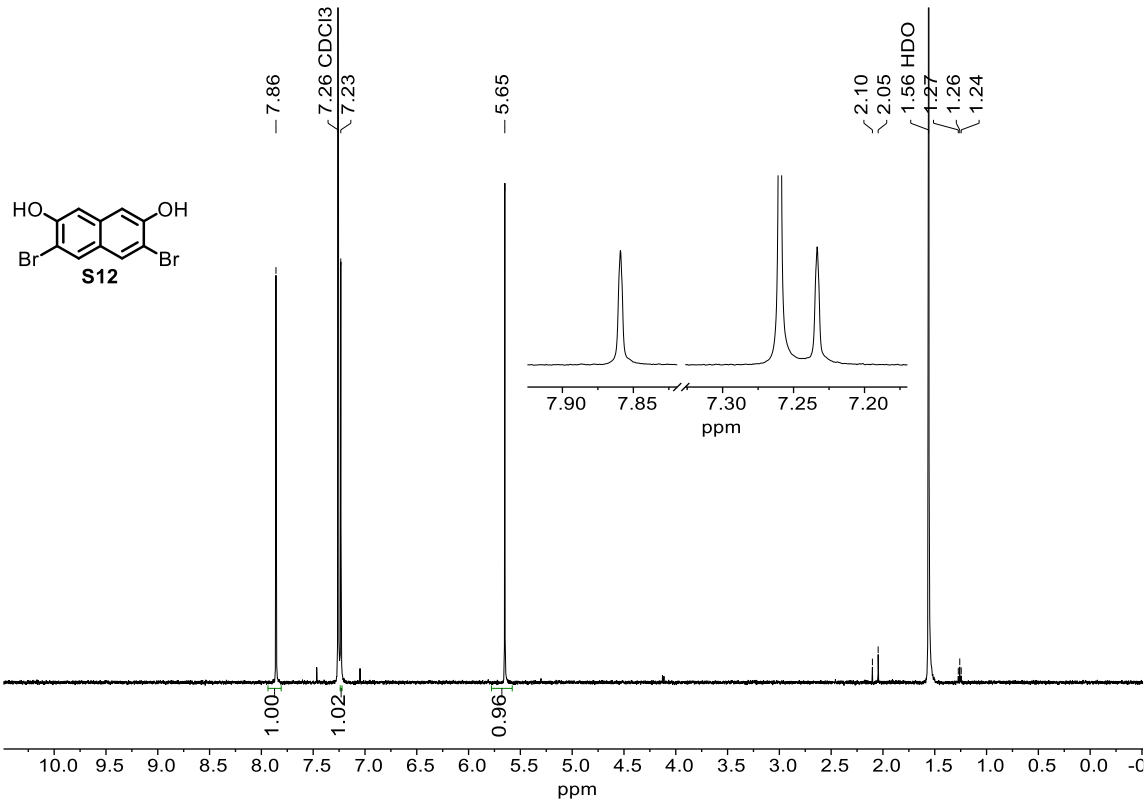


Figure S18. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **S12**.

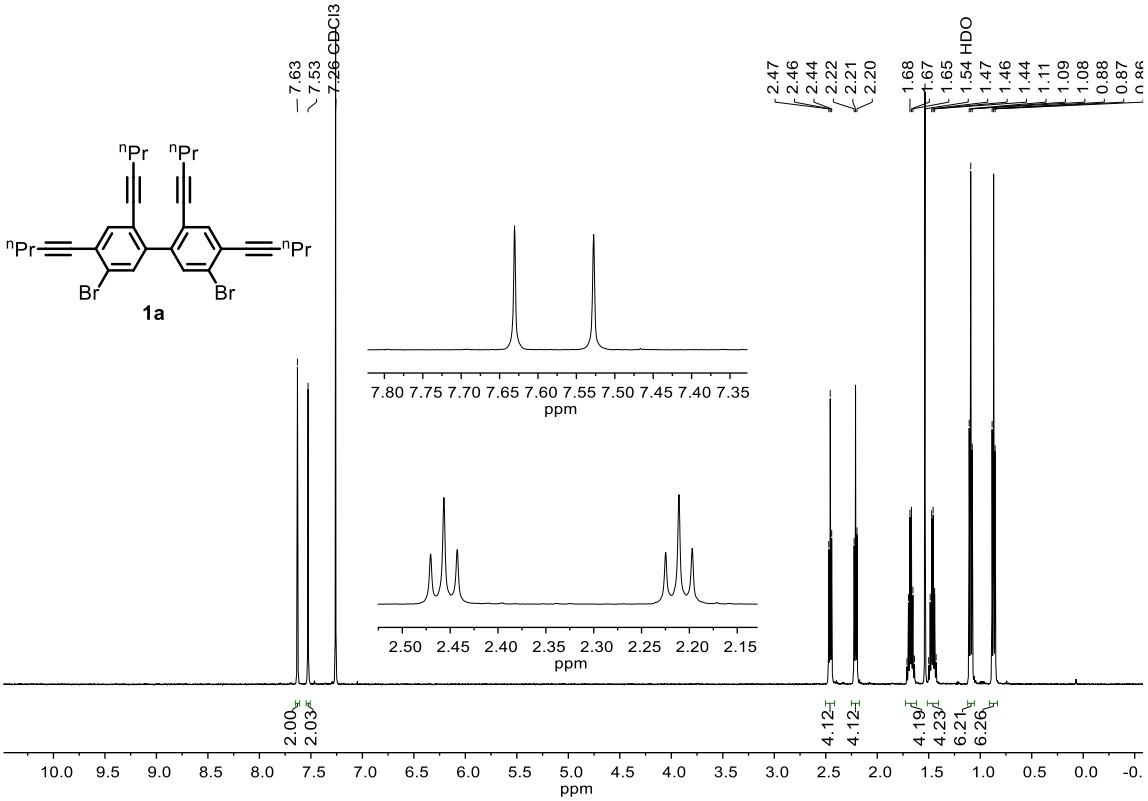


Figure S19. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **1a**.

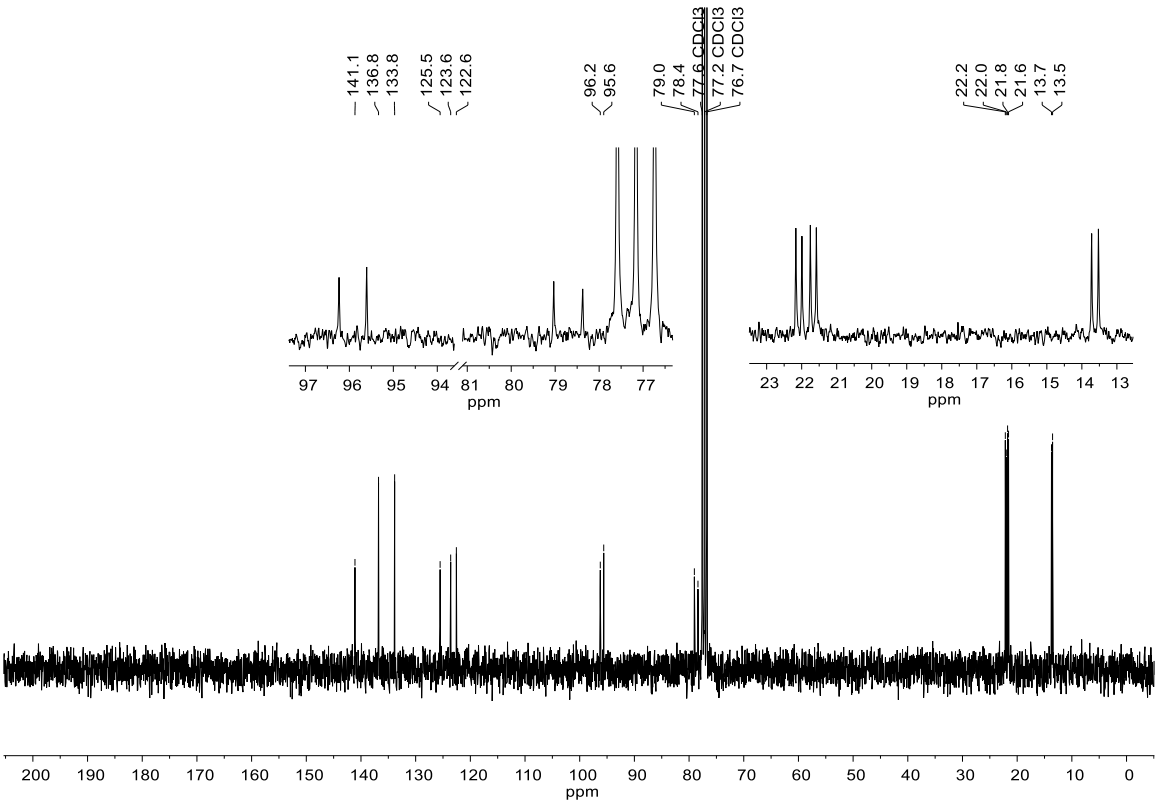


Figure S20. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, chloroform-*d*) of **1a**.

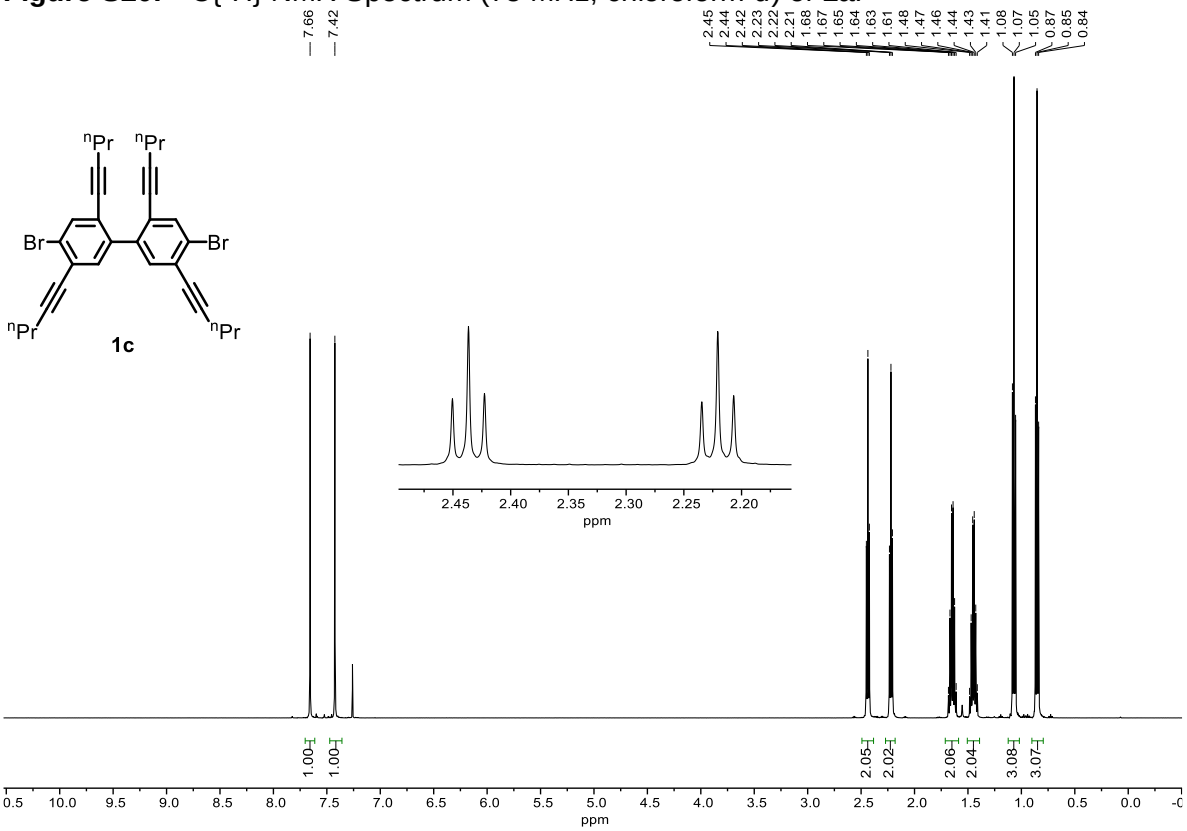


Figure S21. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **1c**.

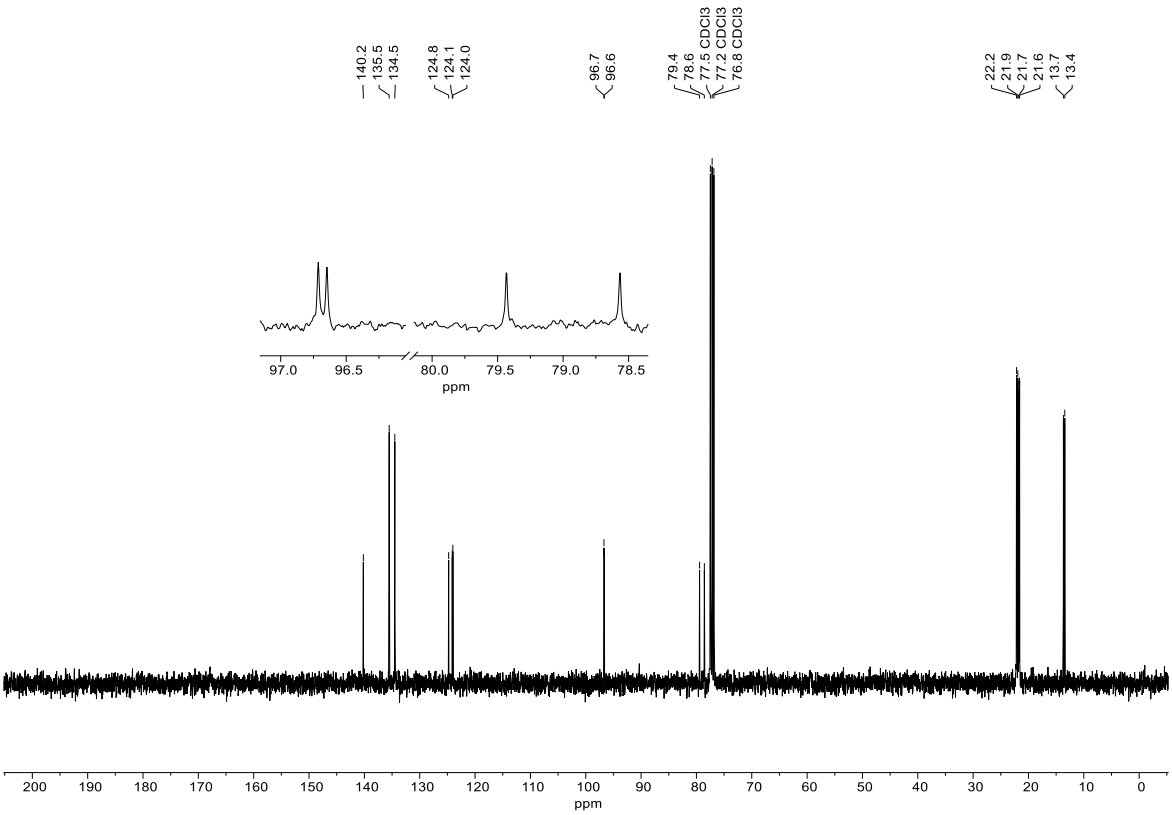


Figure S22. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **1c**.

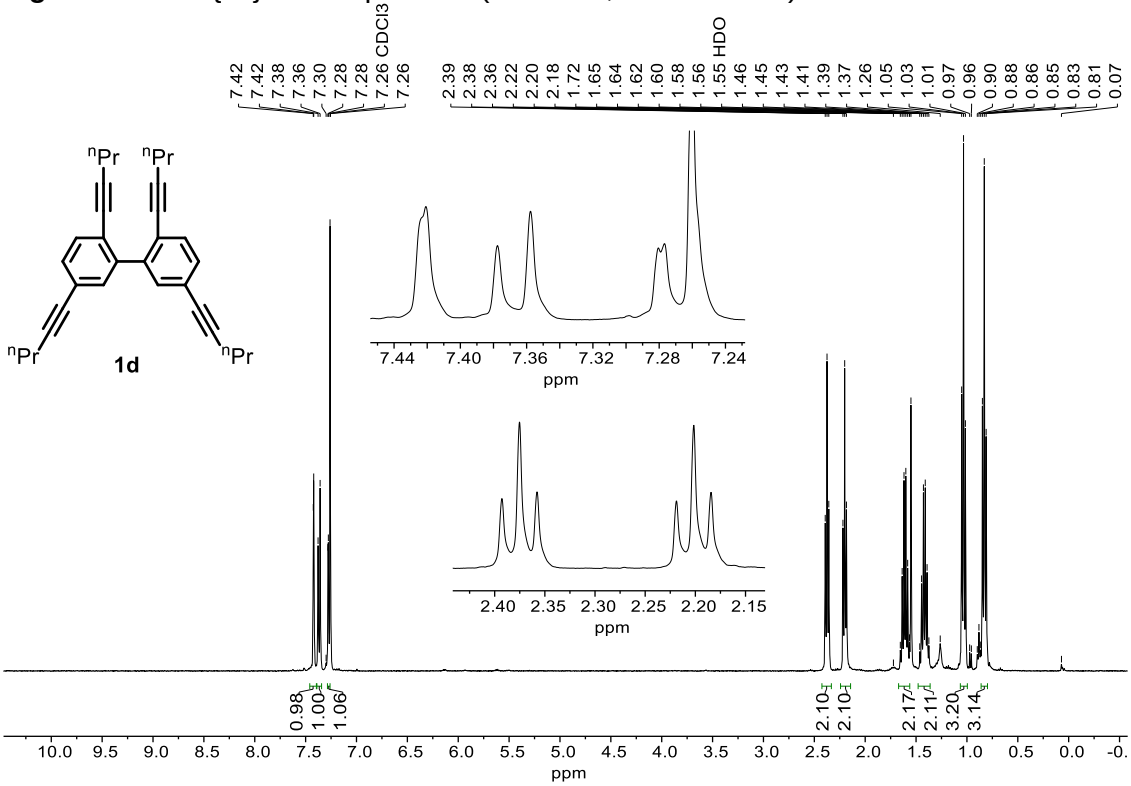


Figure S23. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **1d**.

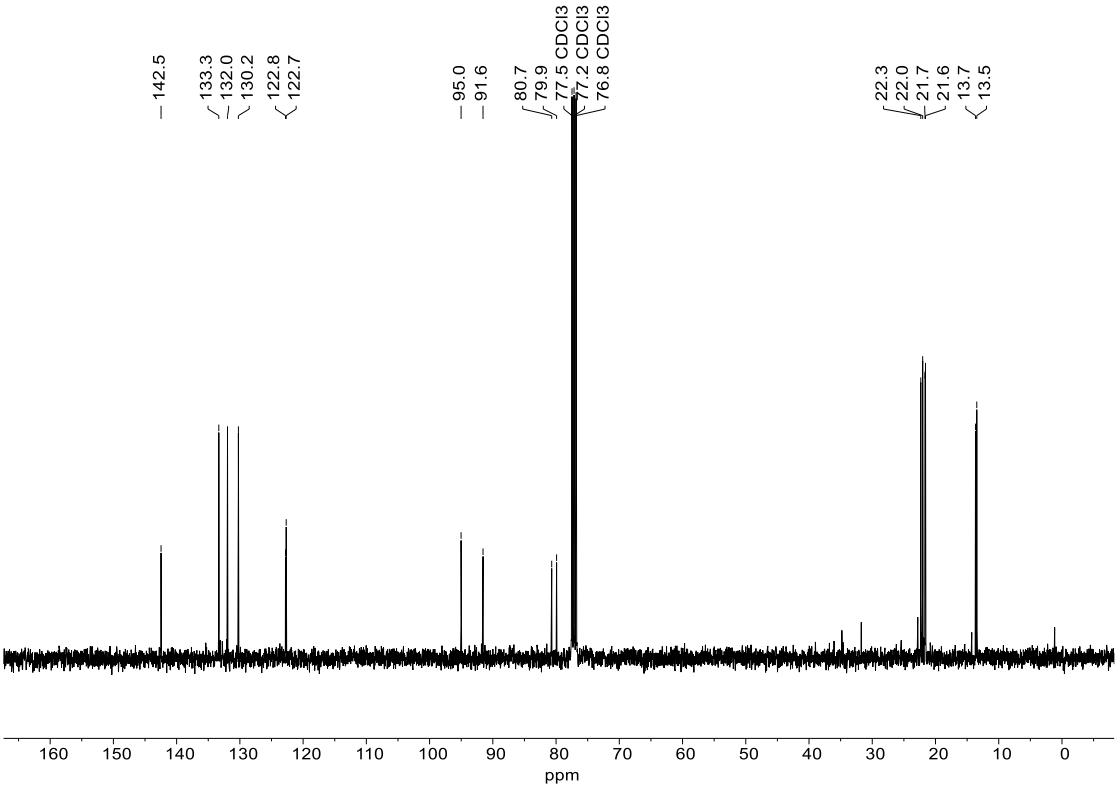


Figure S24. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **1d**.

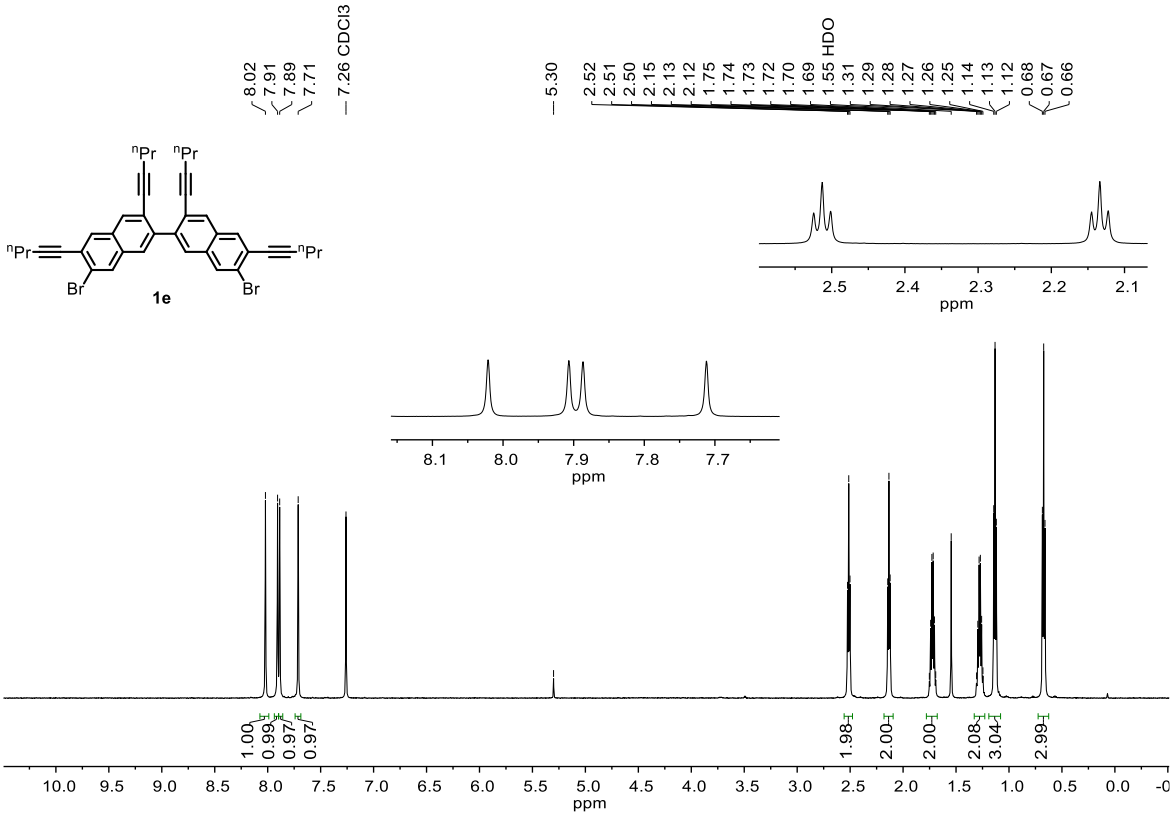


Figure S25. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **1e**.

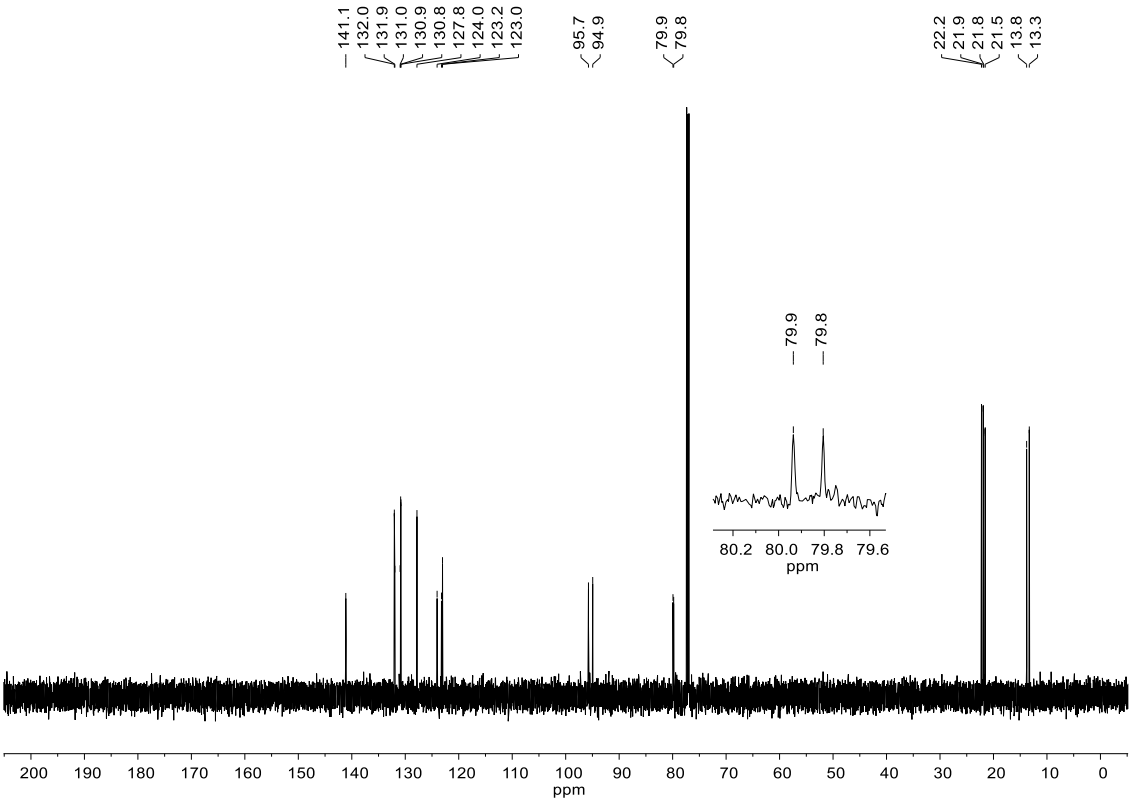


Figure S26. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **1e**.

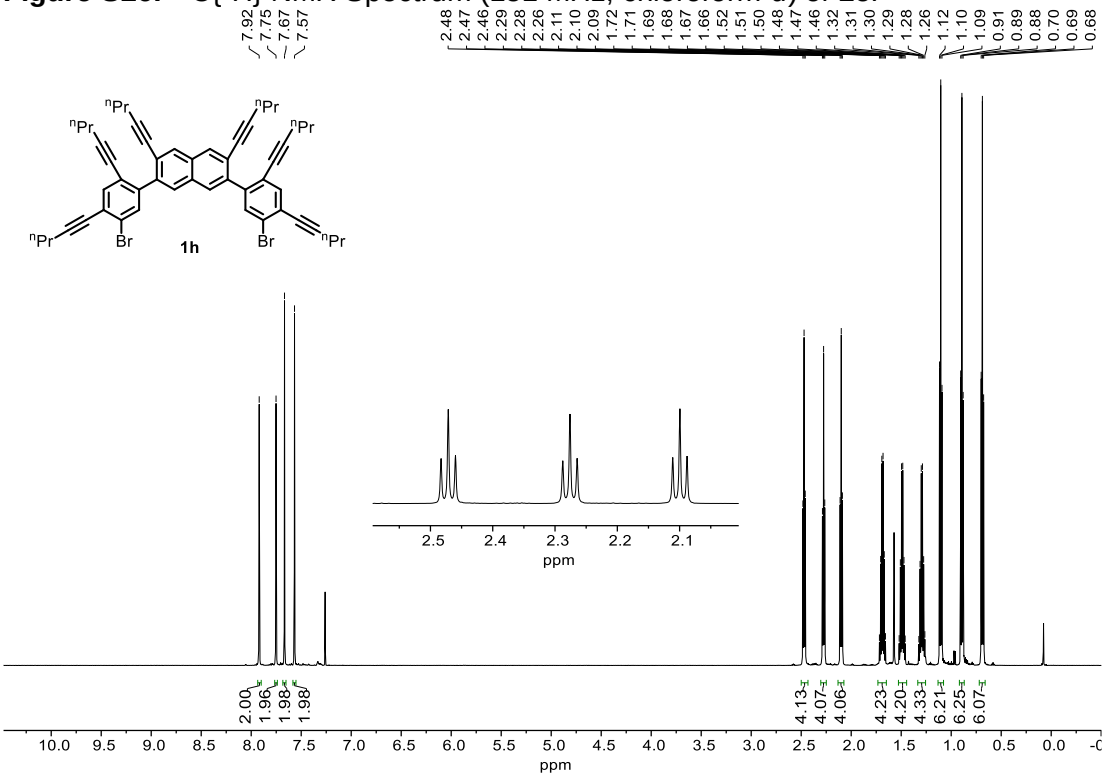


Figure S27. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **1h**.

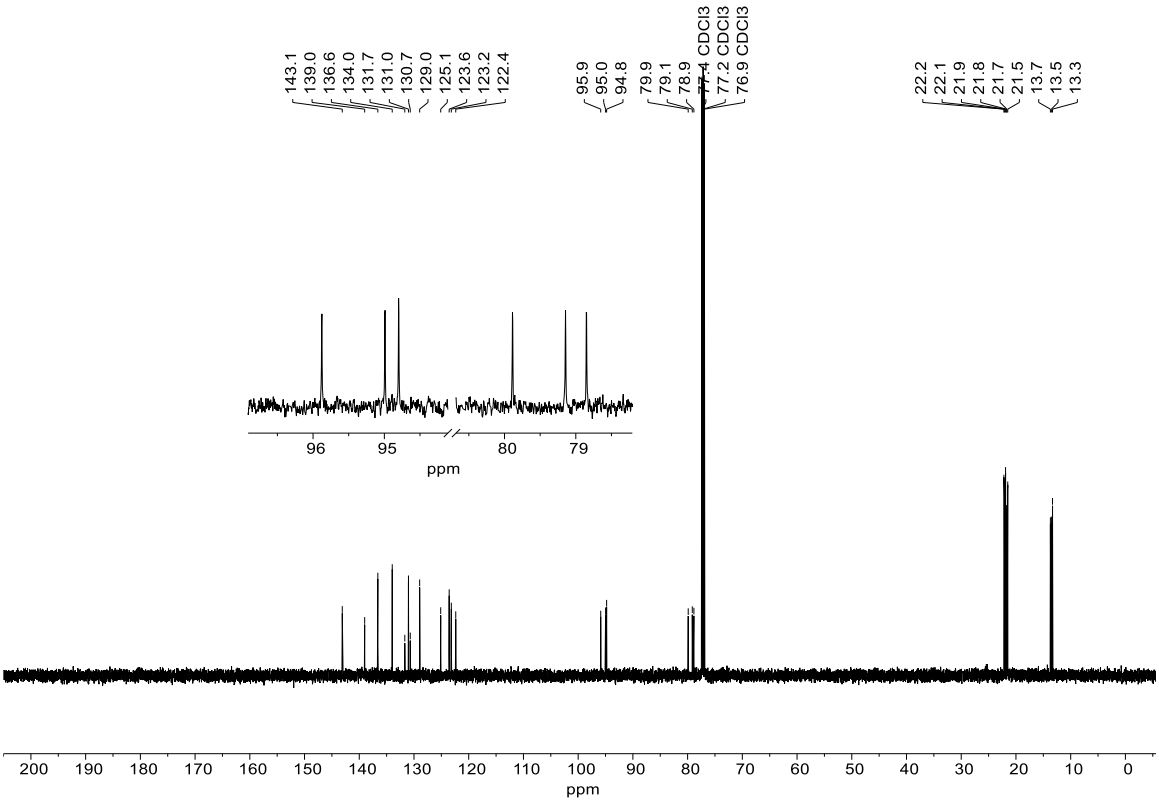


Figure S28. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **1h**.

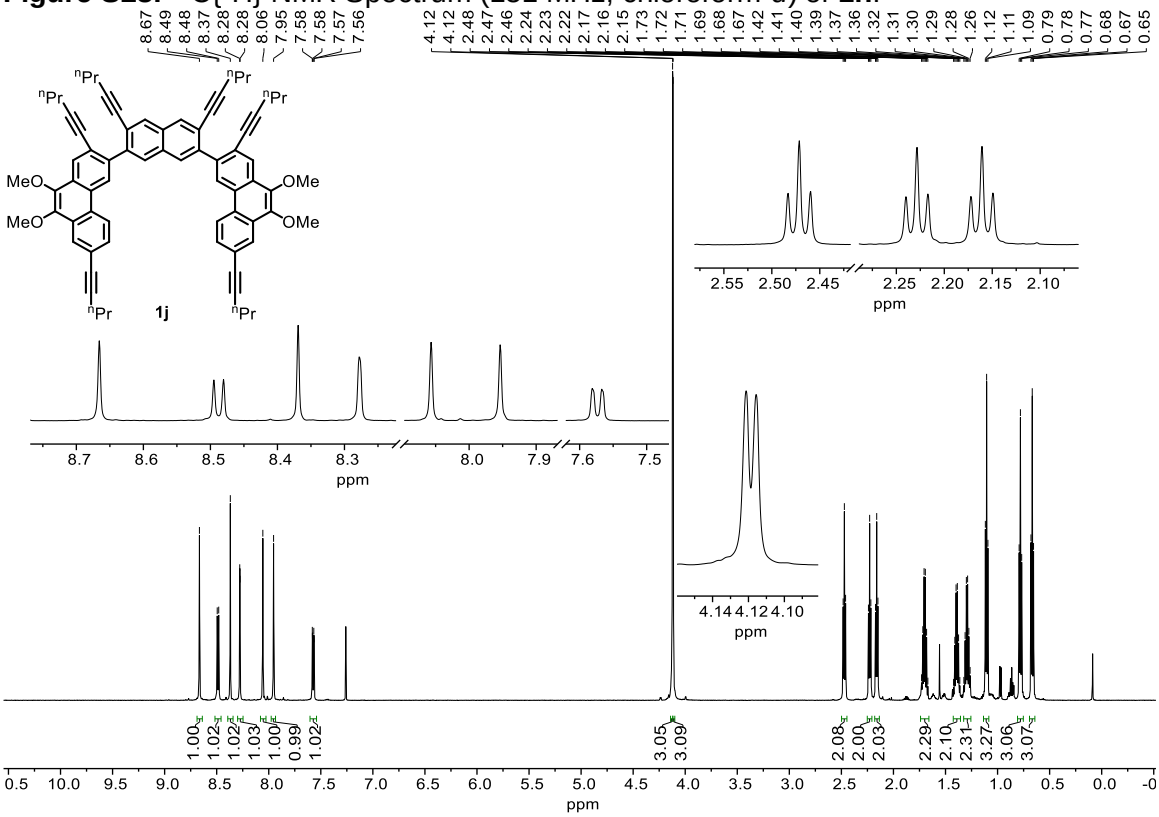


Figure S29. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **1j**.

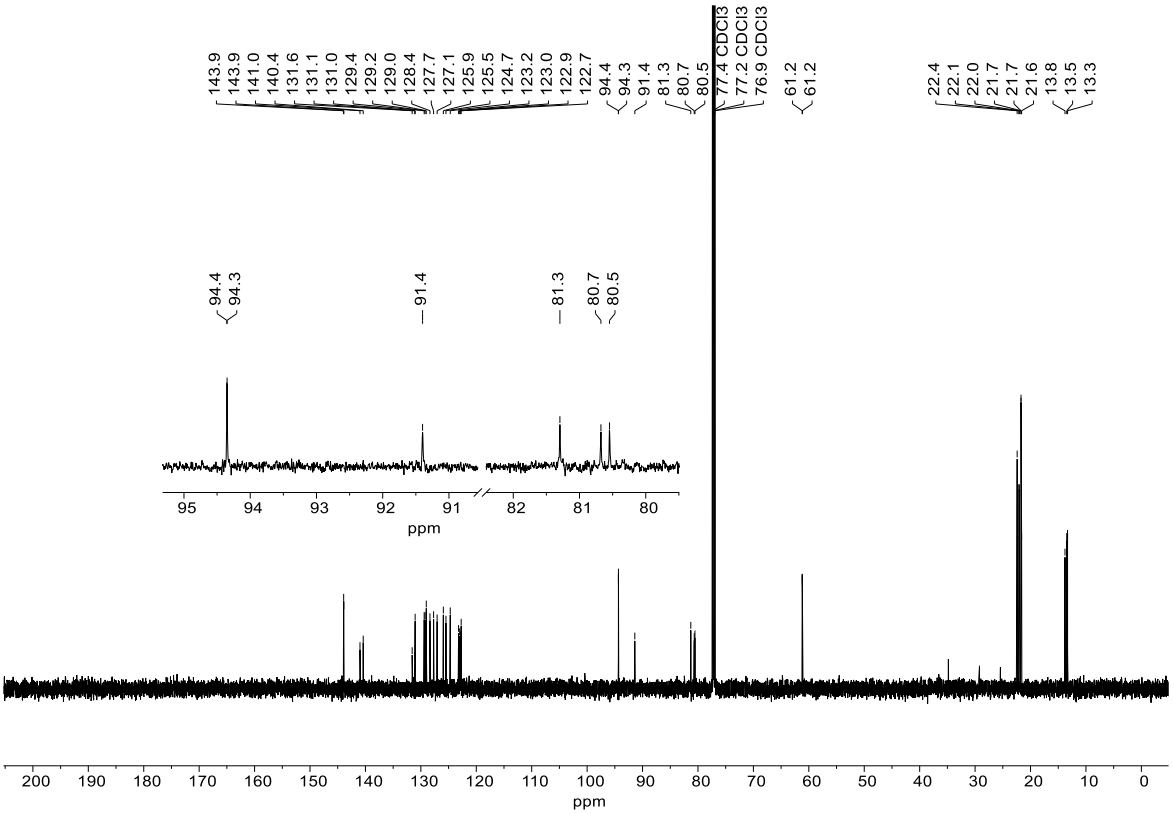


Figure S30. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **1j**.

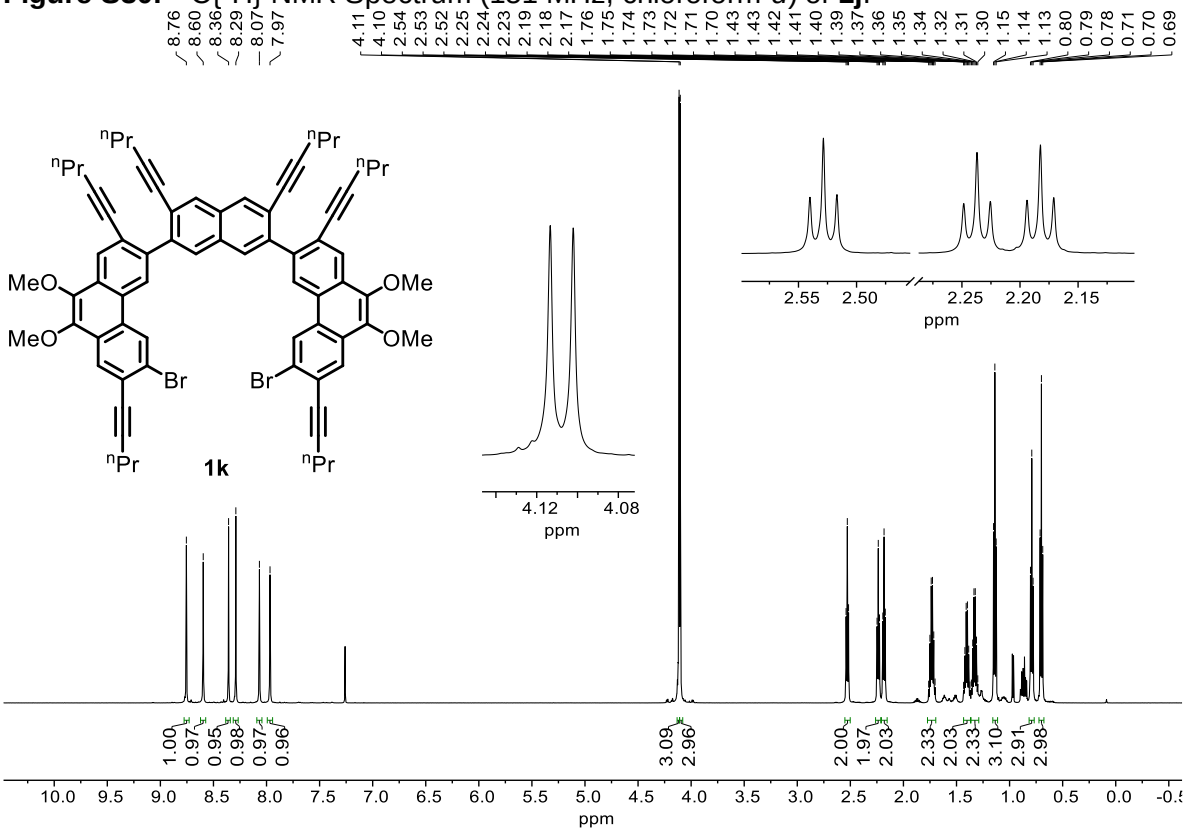


Figure S31. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **1k**.

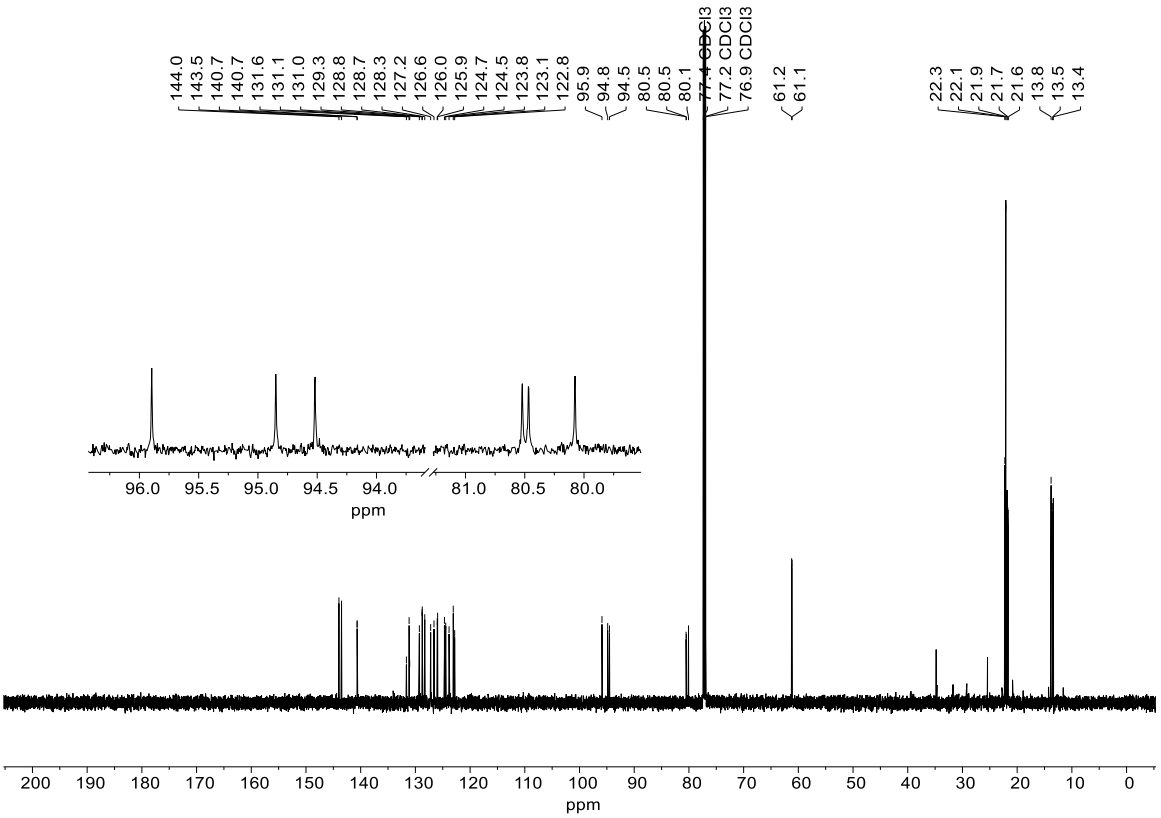


Figure S32. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **1k**.

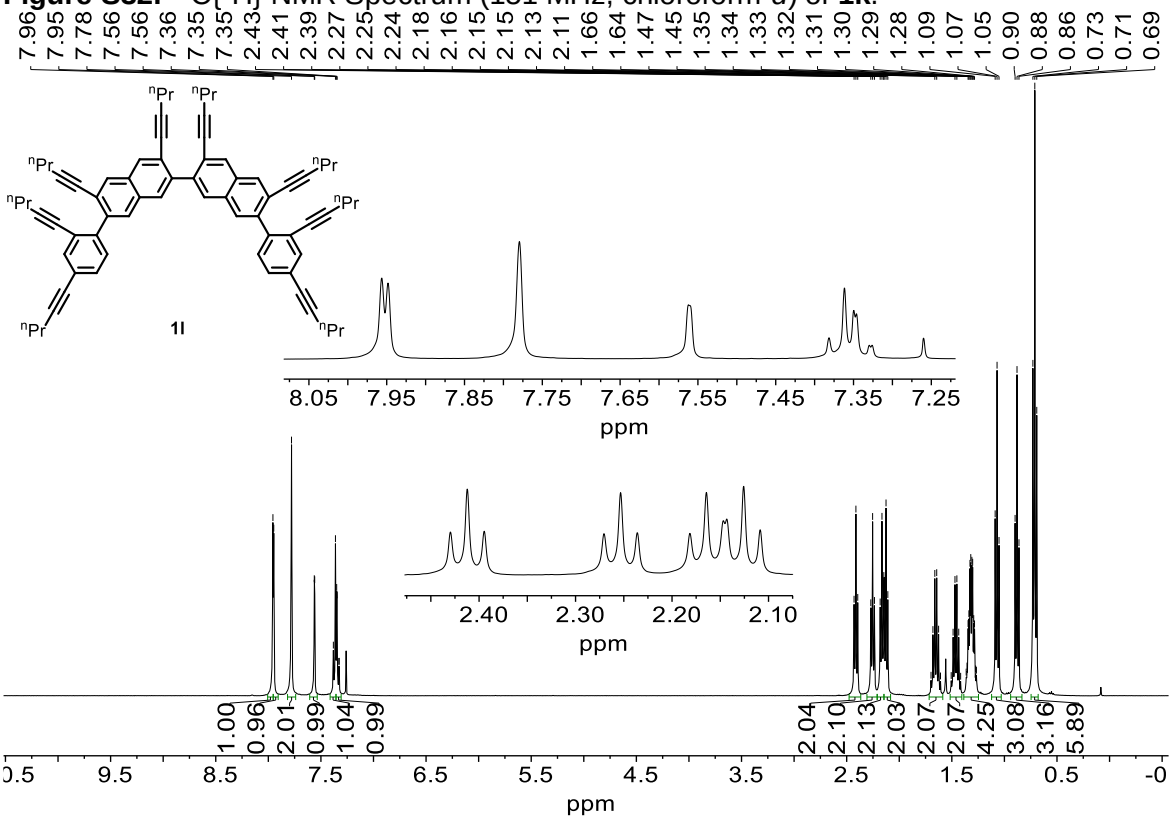


Figure S33. ^{1}H NMR Spectrum (101 MHz, chloroform-*d*) of **1l**.

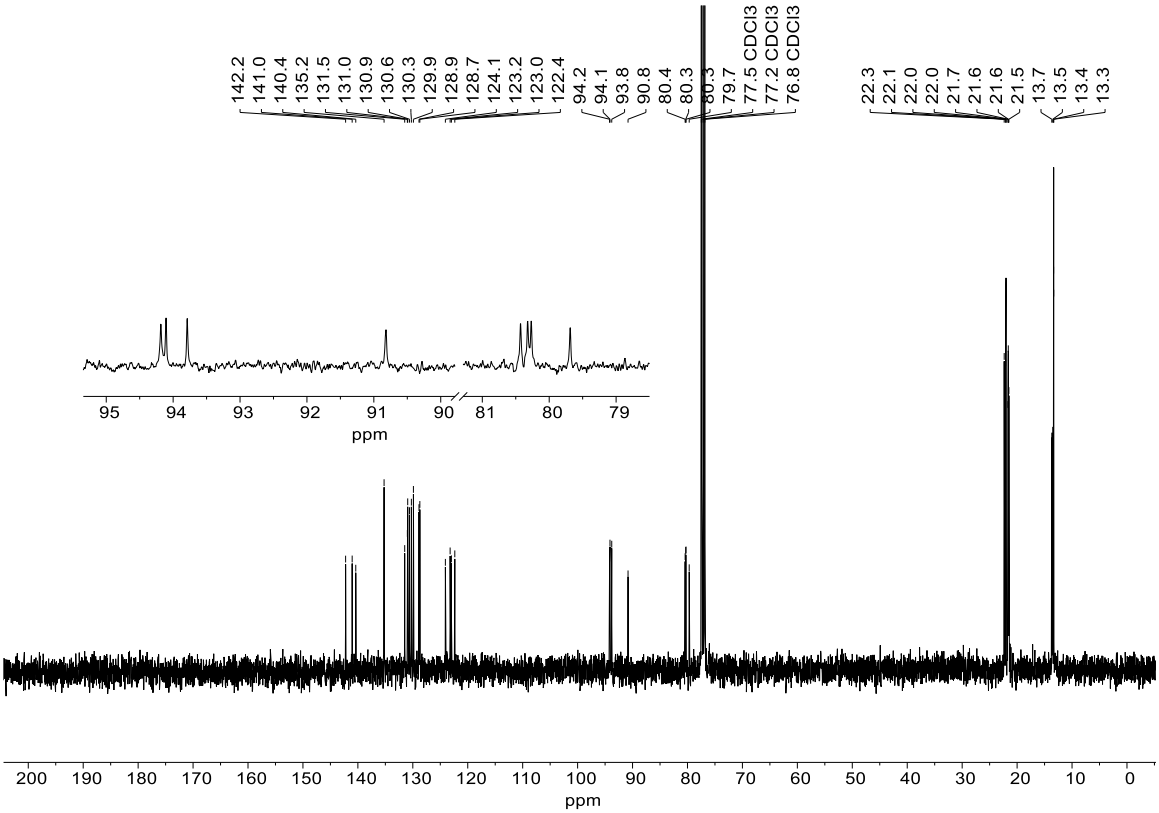


Figure S34. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **1l**.

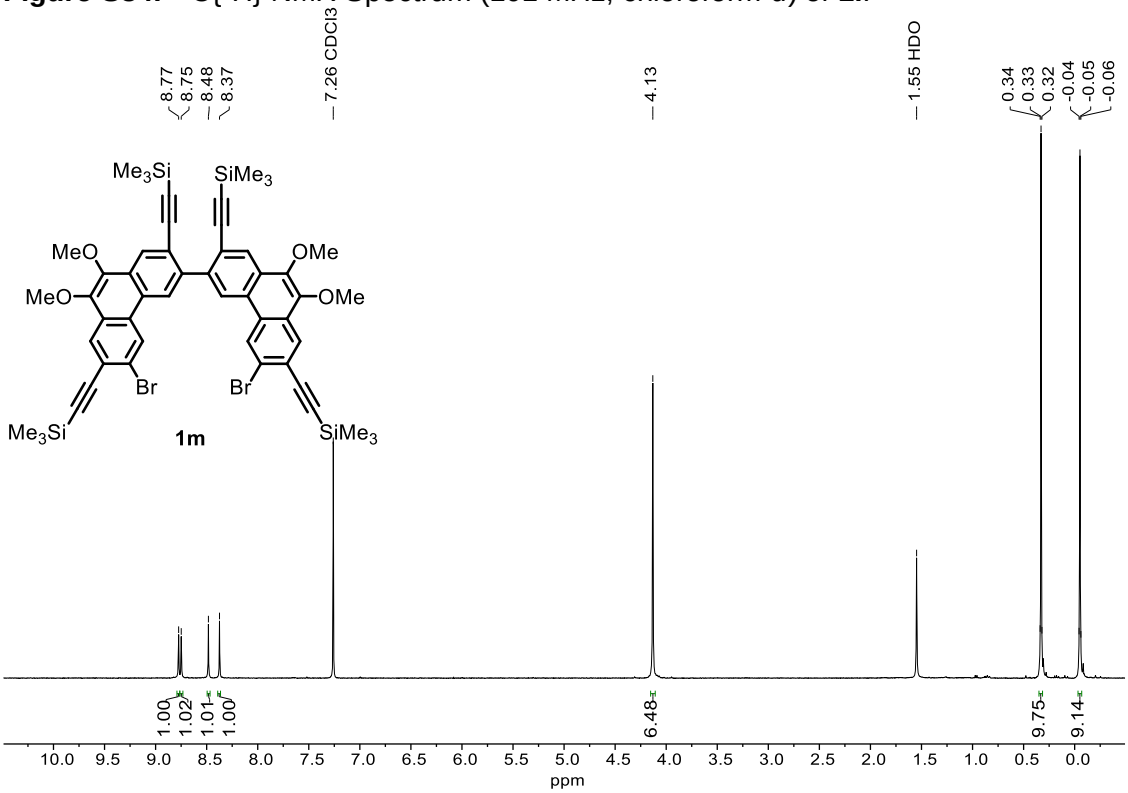


Figure S35. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **1m**.

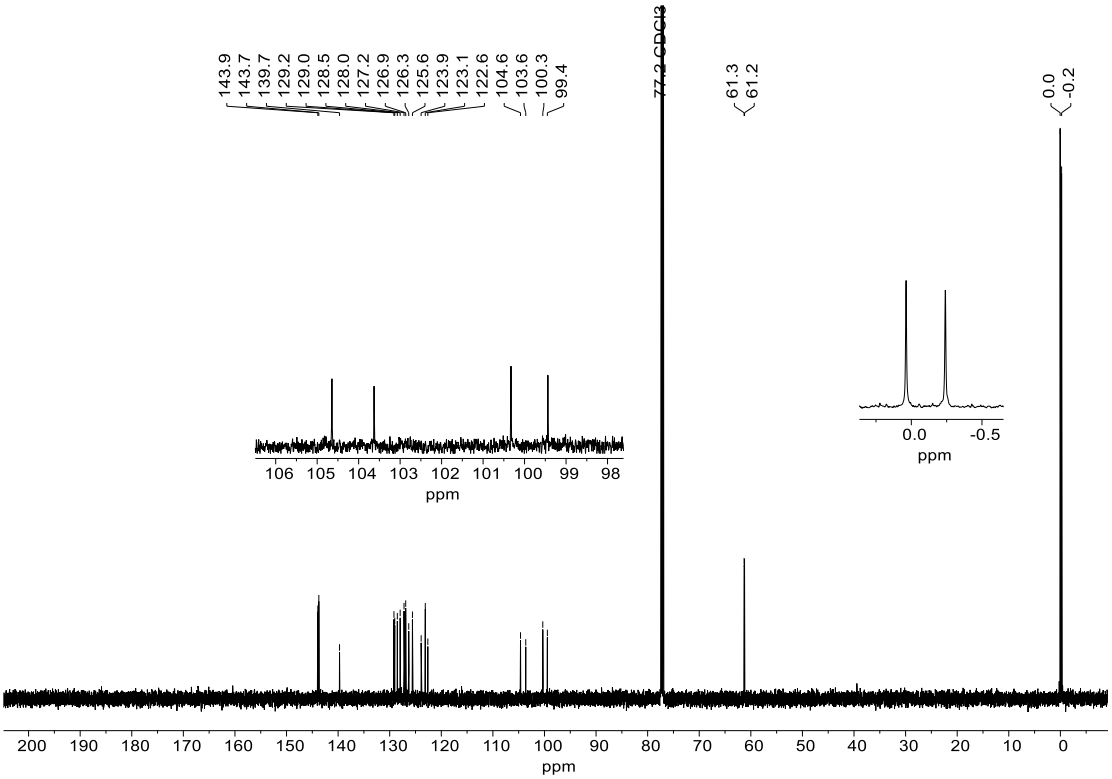


Figure S36. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **1m**.

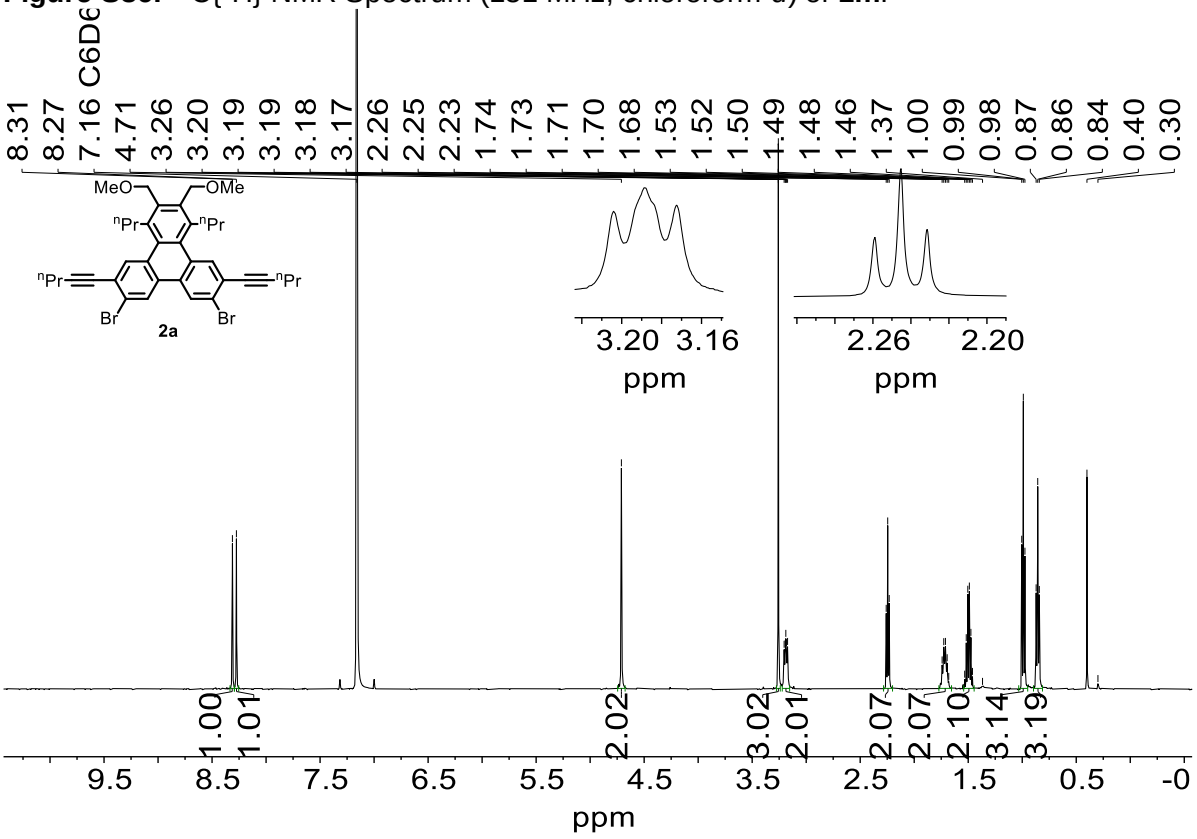


Figure S37. ^{1}H NMR Spectrum (500 MHz, benzene-d_6) of **2a**.

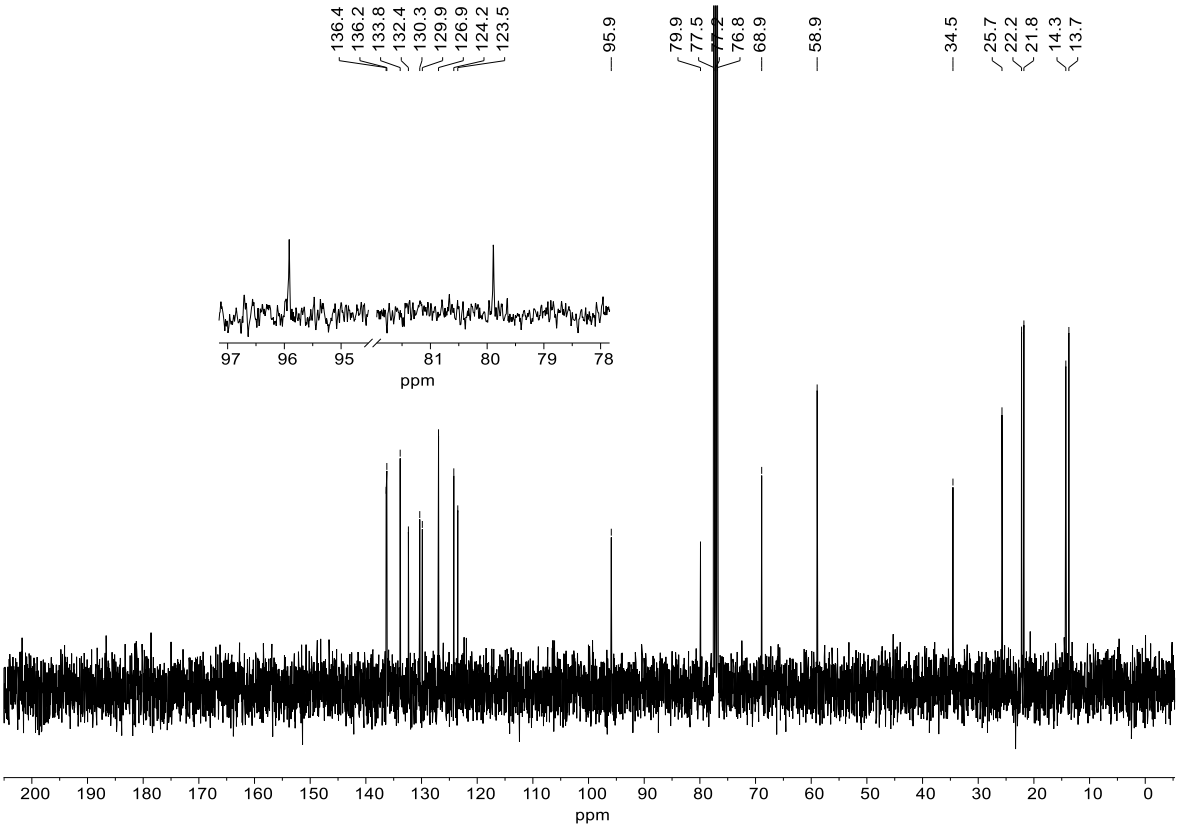


Figure S38. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **2a**.

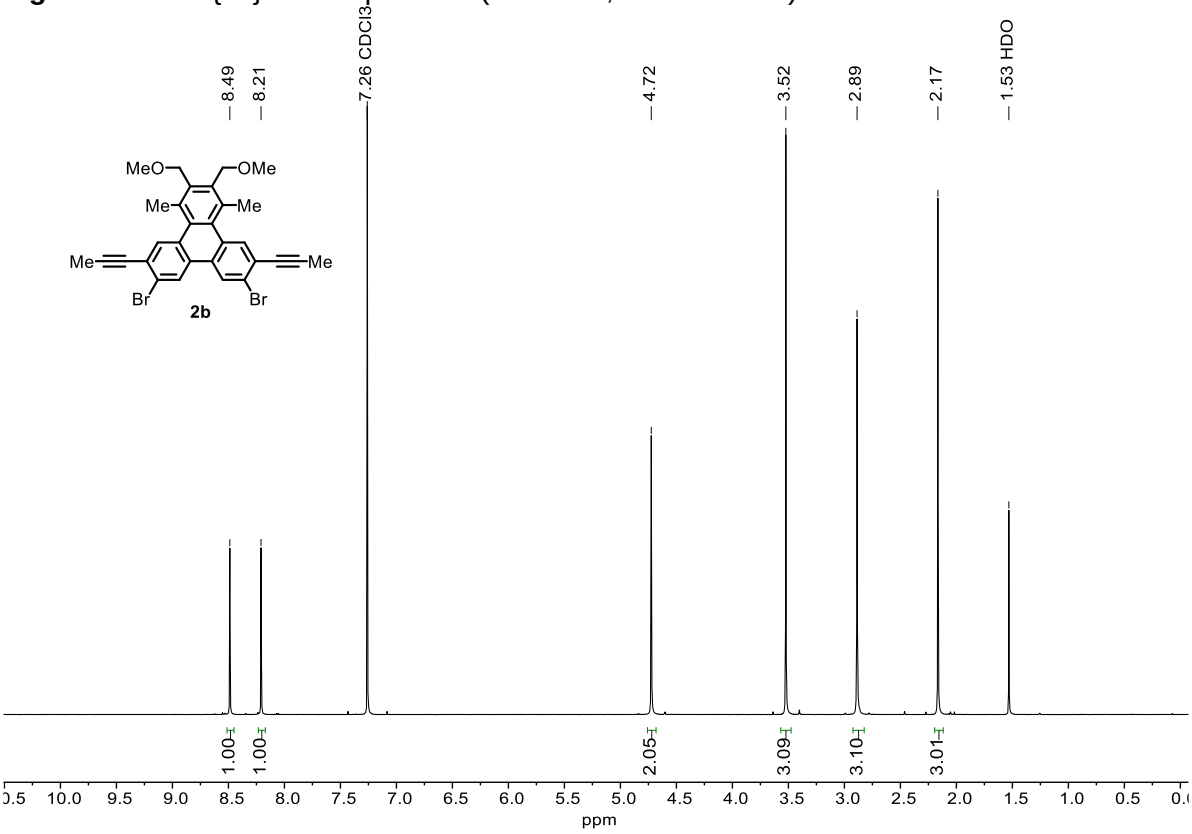


Figure S39. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **2b**.

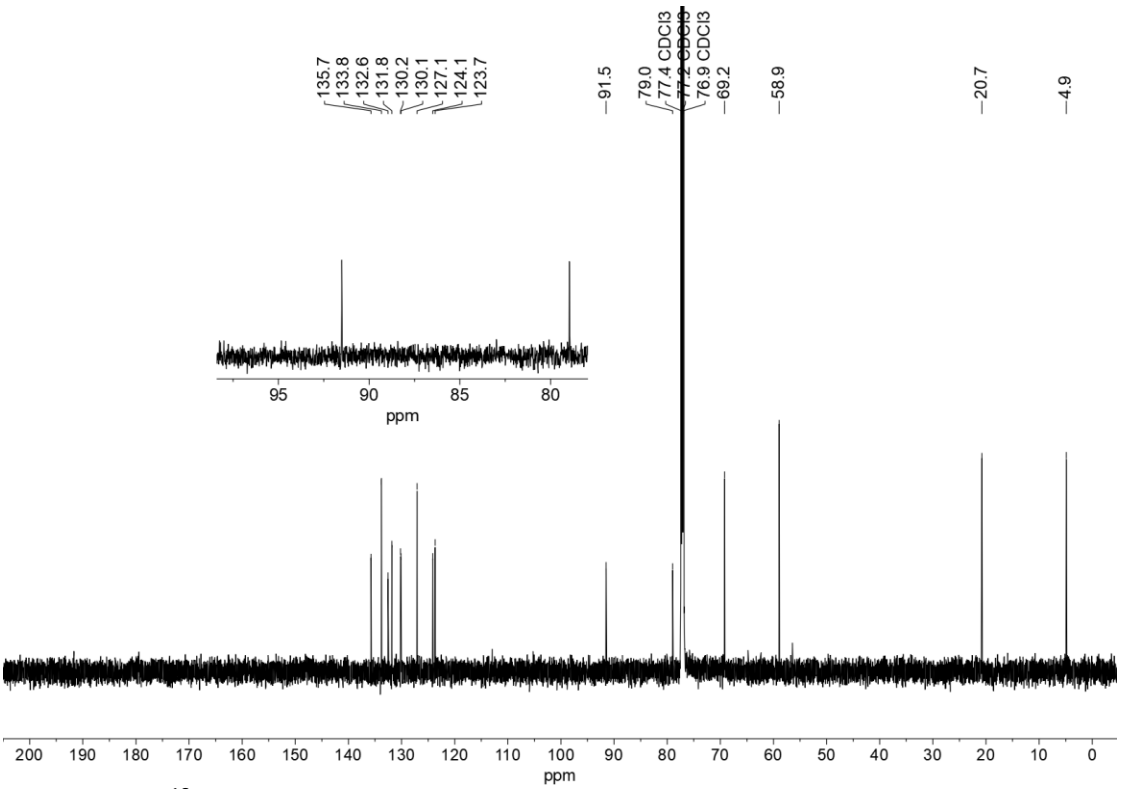


Figure S40. ^{13}C NMR Spectrum (151 MHz, chloroform-*d*) of **2b**.

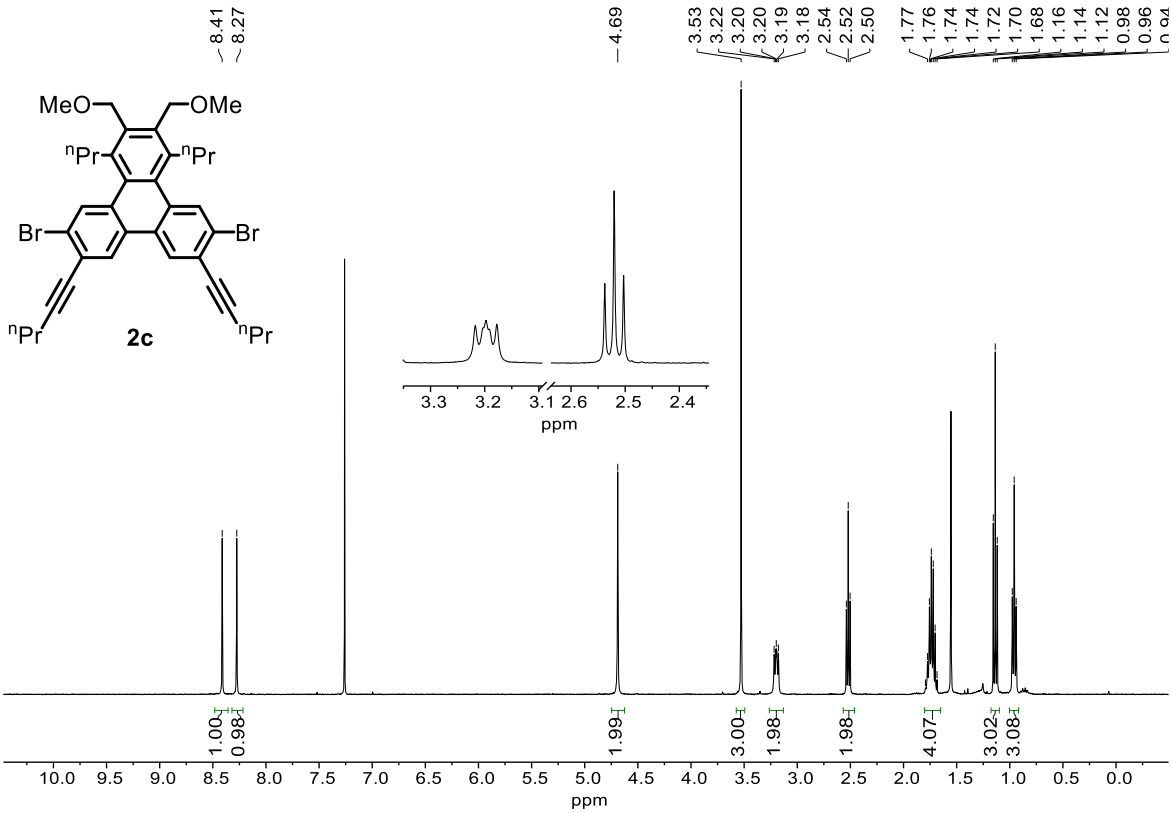


Figure S41. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **2c**.

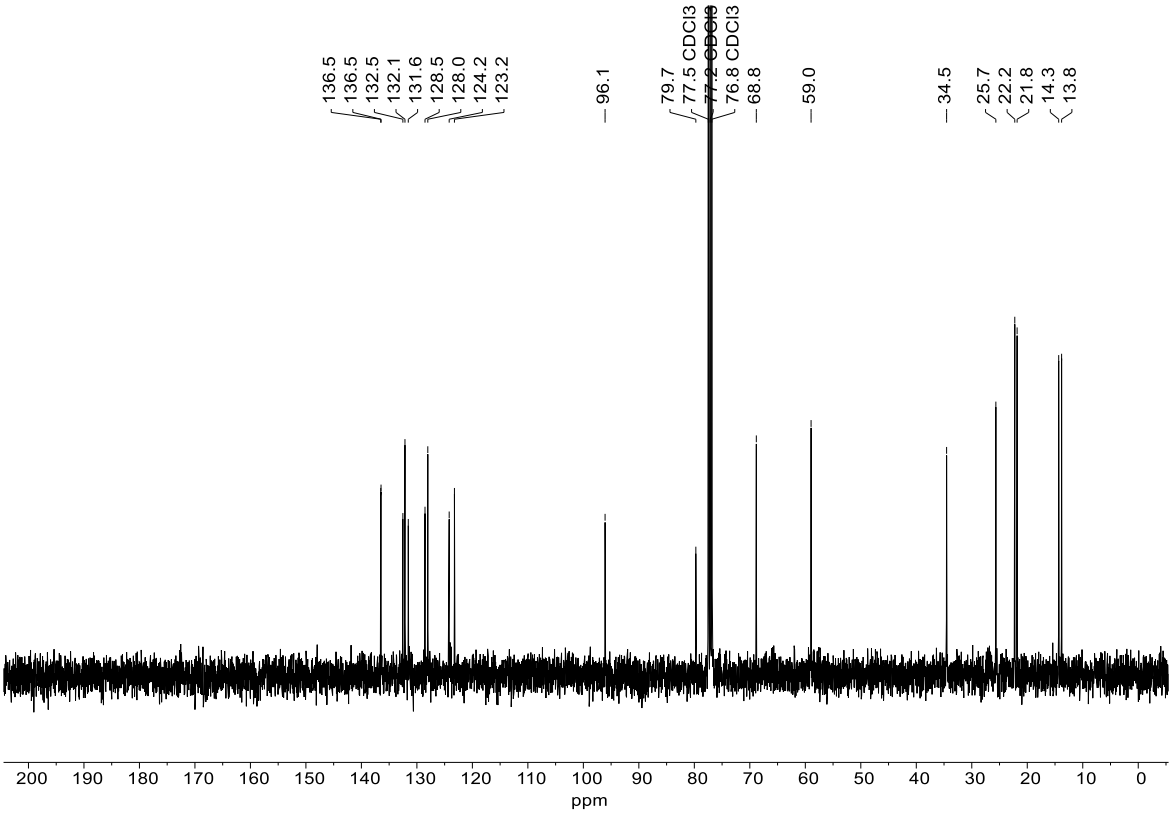


Figure S42. $^{13}C\{^{1}H\}$ NMR Spectrum (400 MHz, chloroform-*d*) of **2c**.

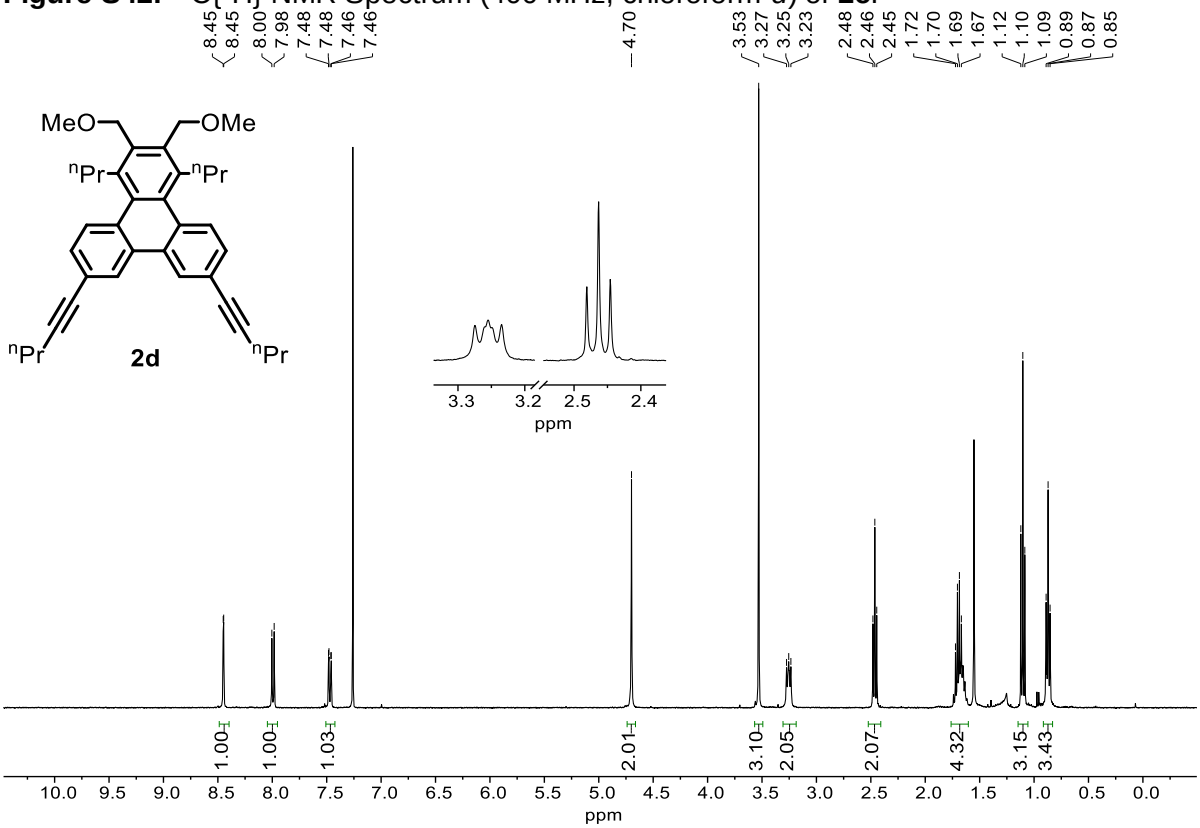


Figure S43. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **2d**.

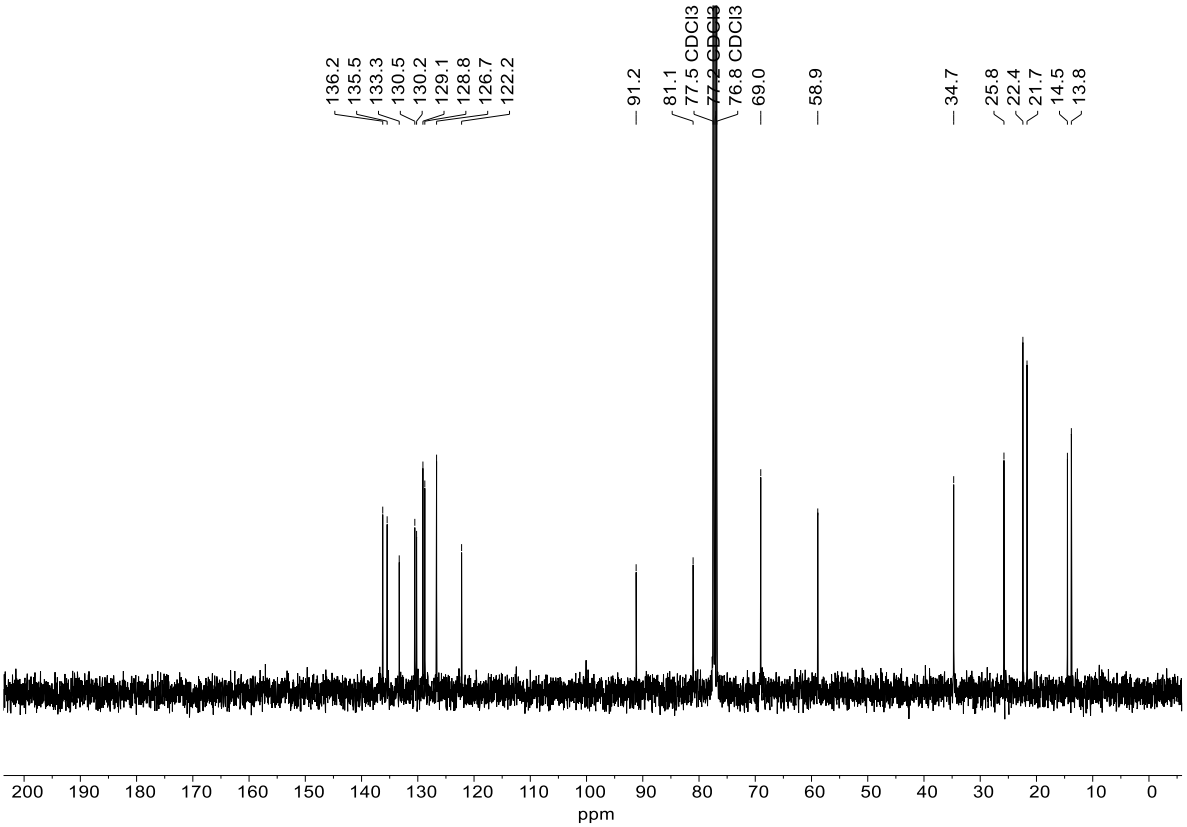


Figure S44. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **2d**.

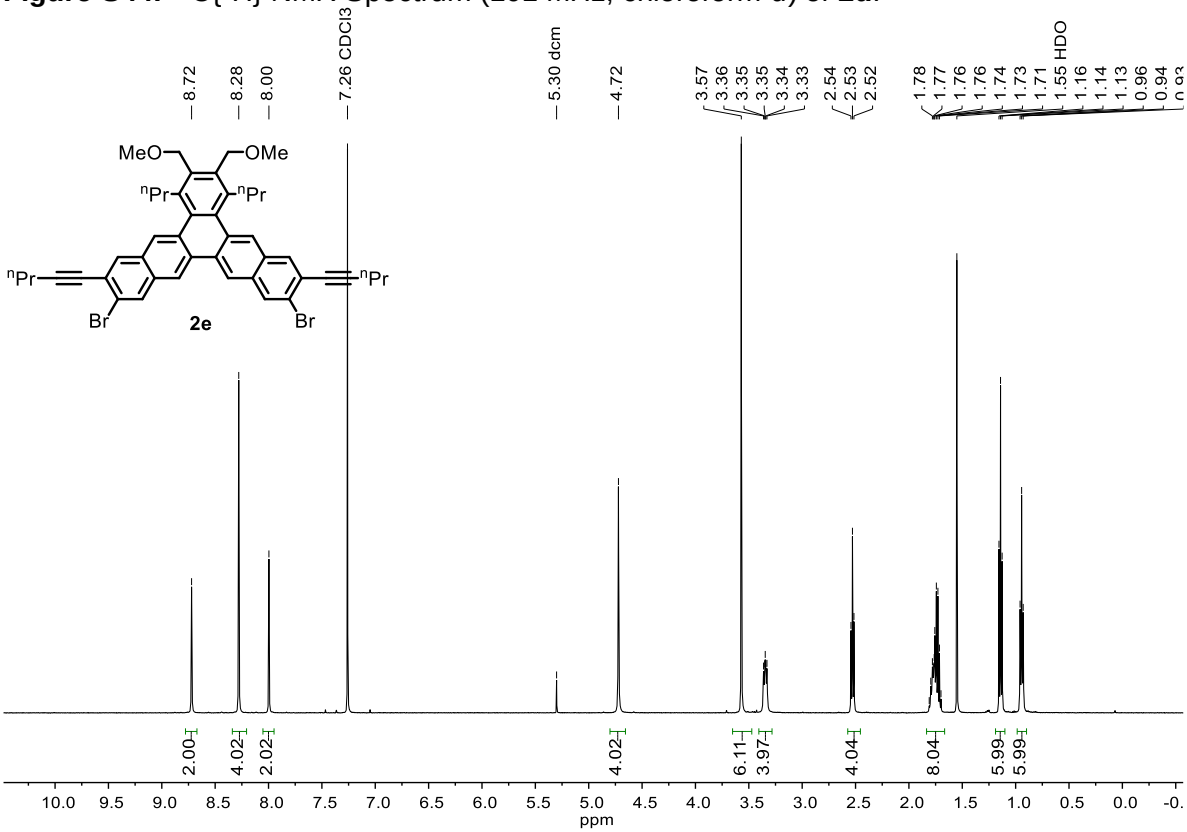


Figure S45. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **2e**.

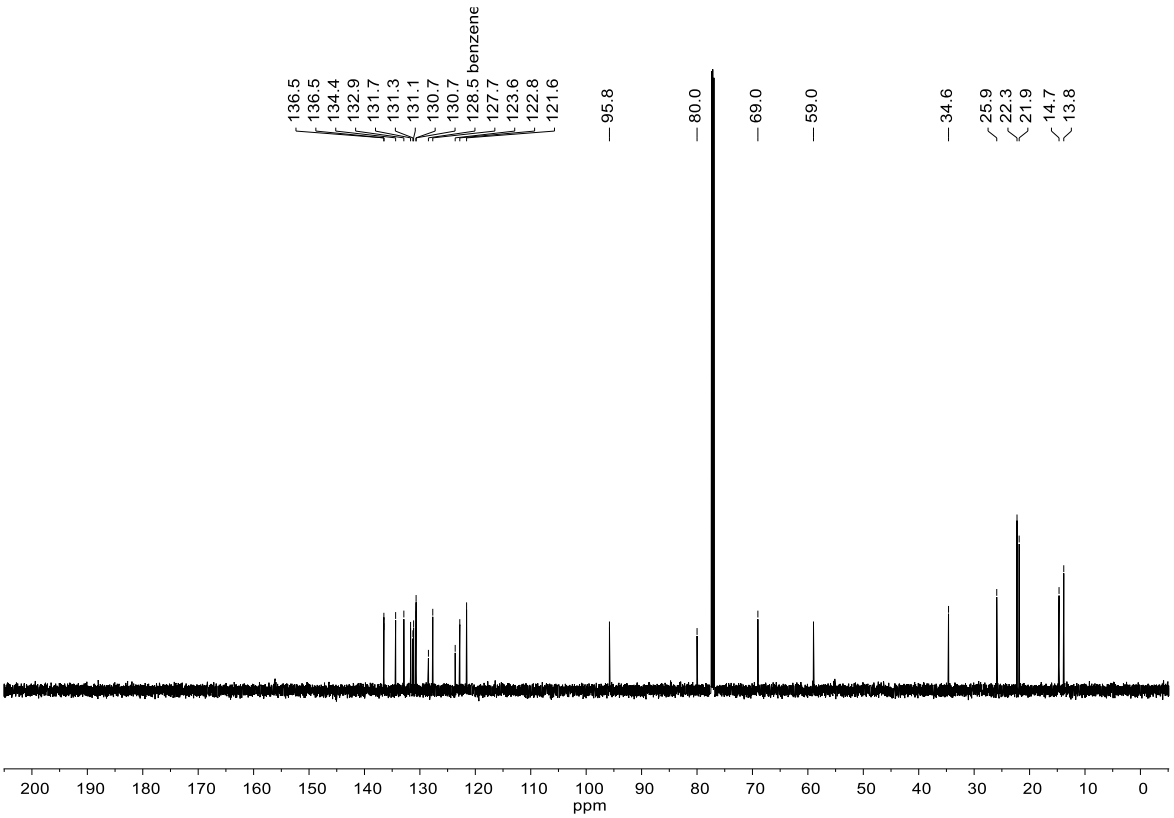


Figure S46. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **2e**.

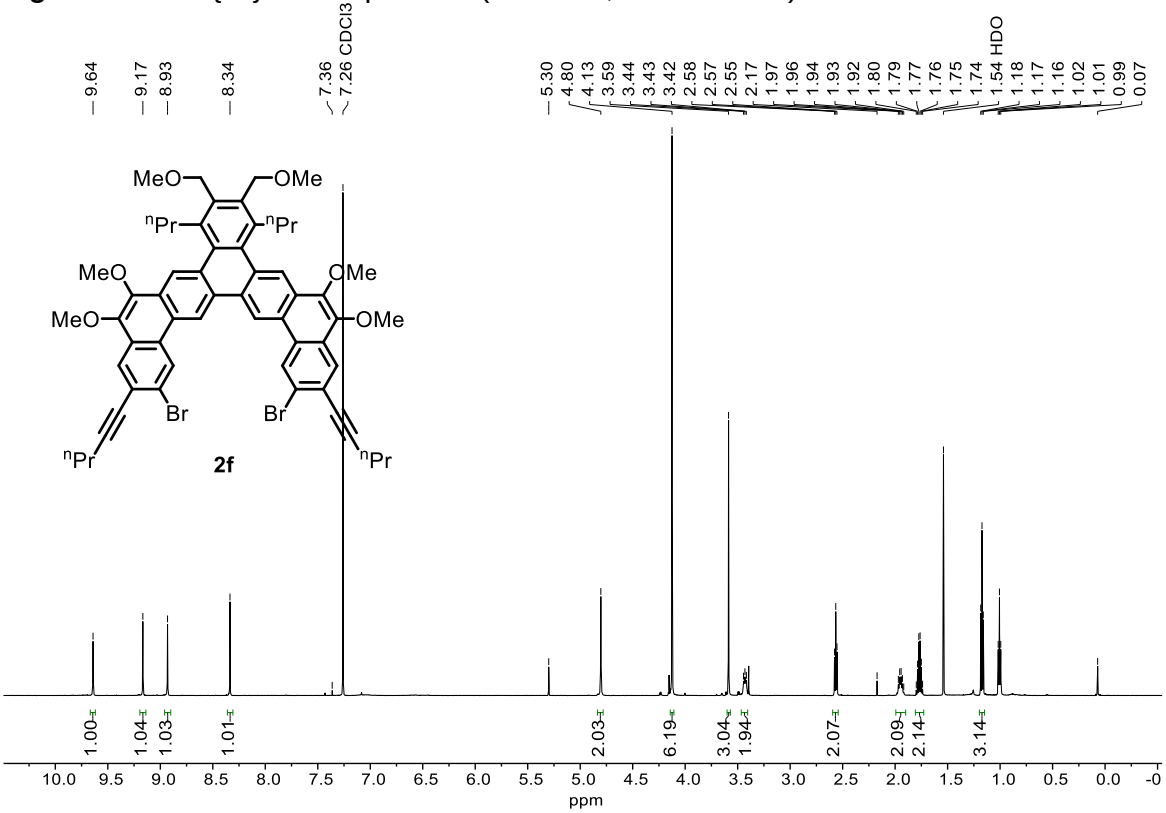


Figure S47. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **2f**.

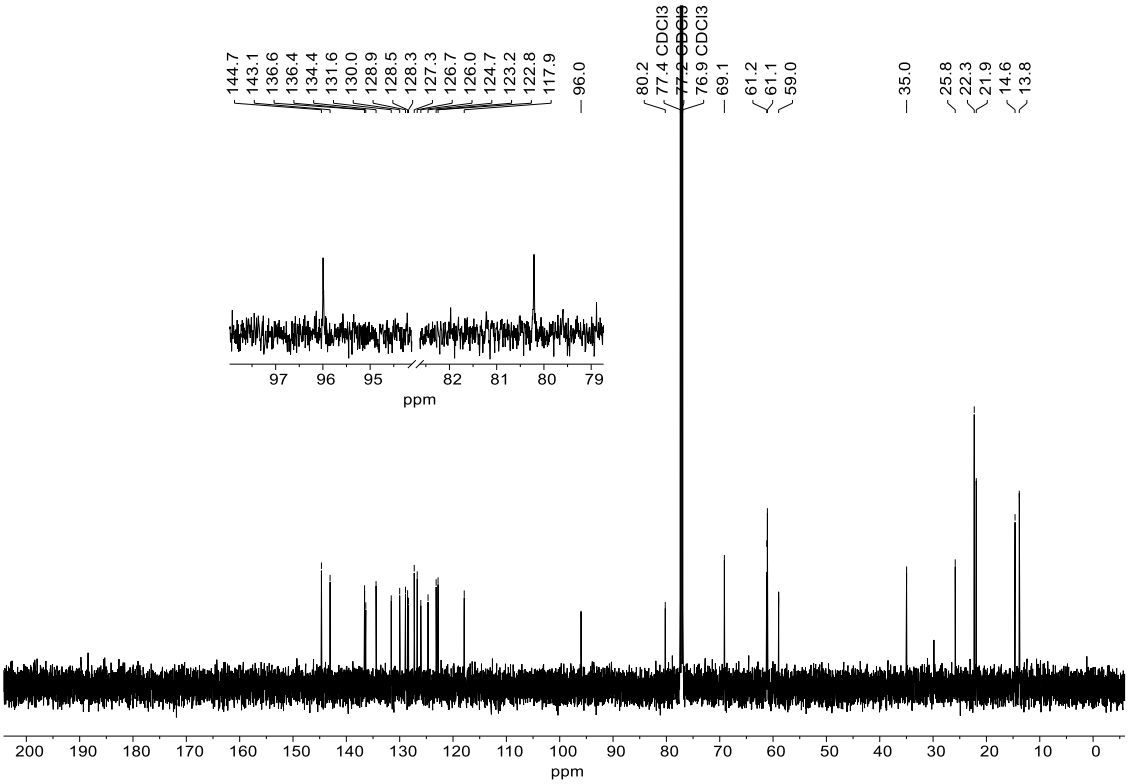


Figure S48. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **2f**.

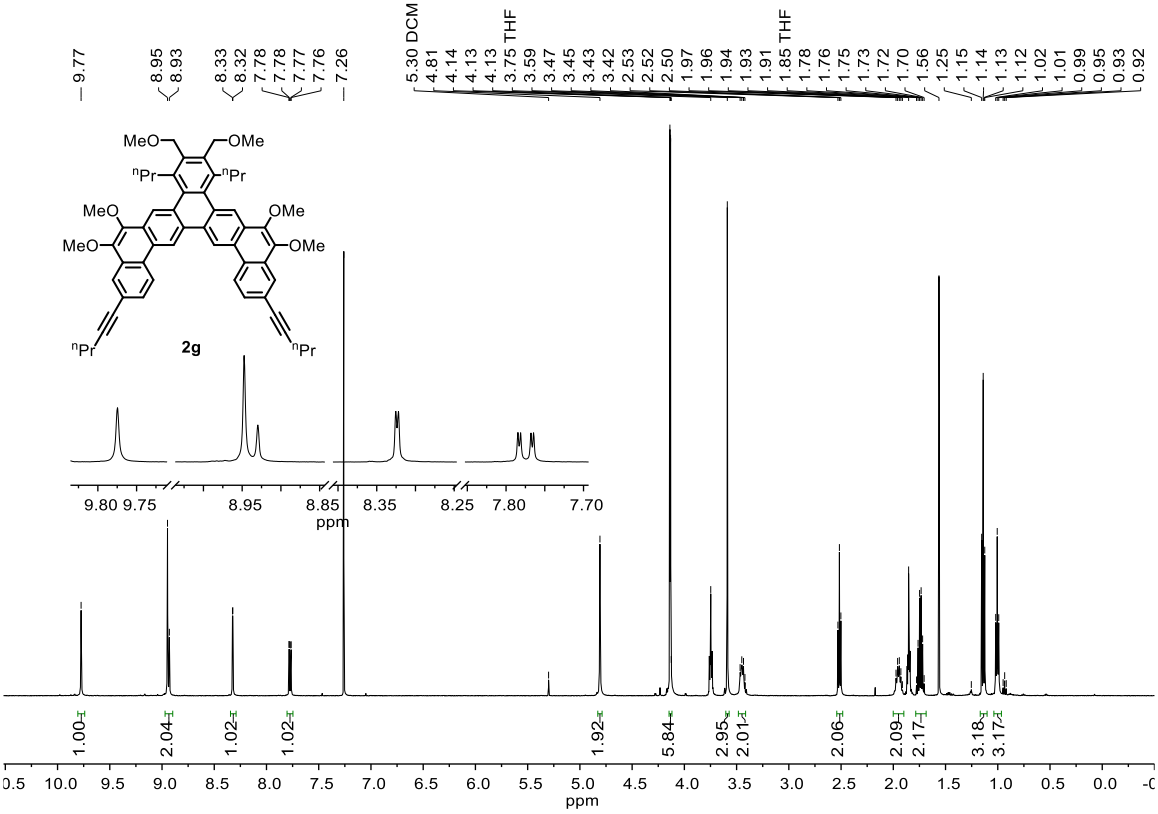


Figure S49. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **2g**.

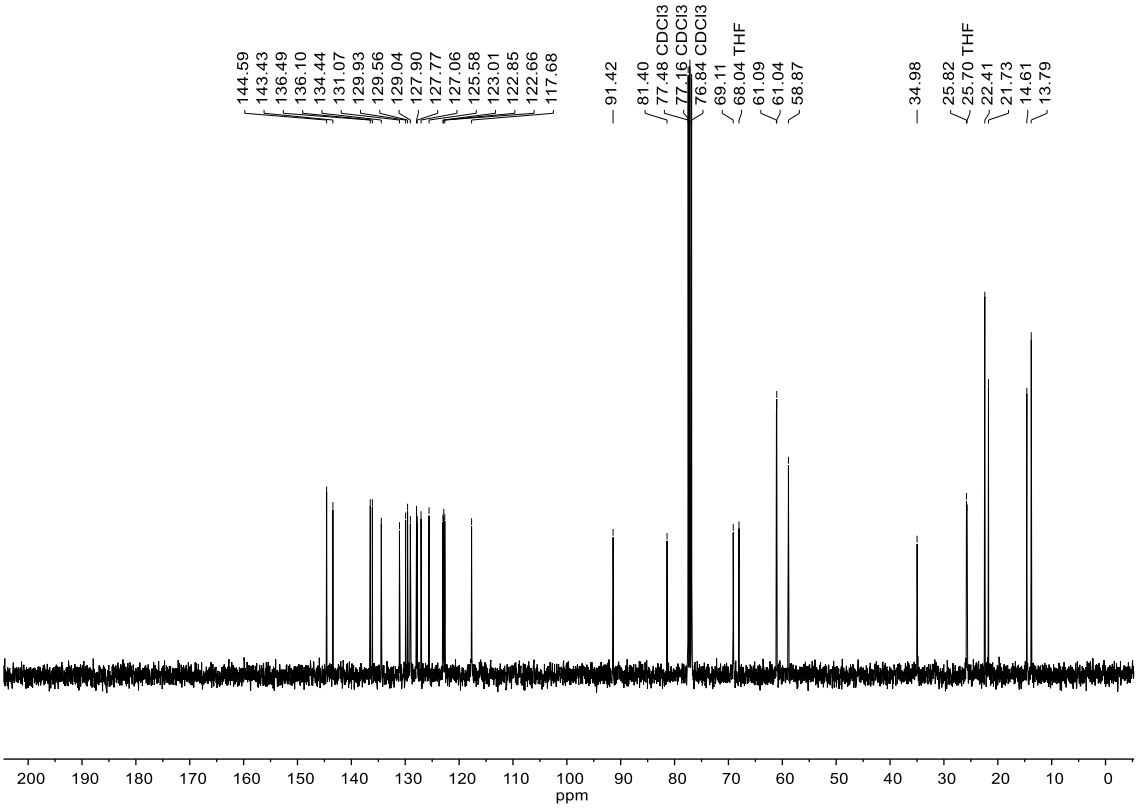


Figure S50. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **2g**.

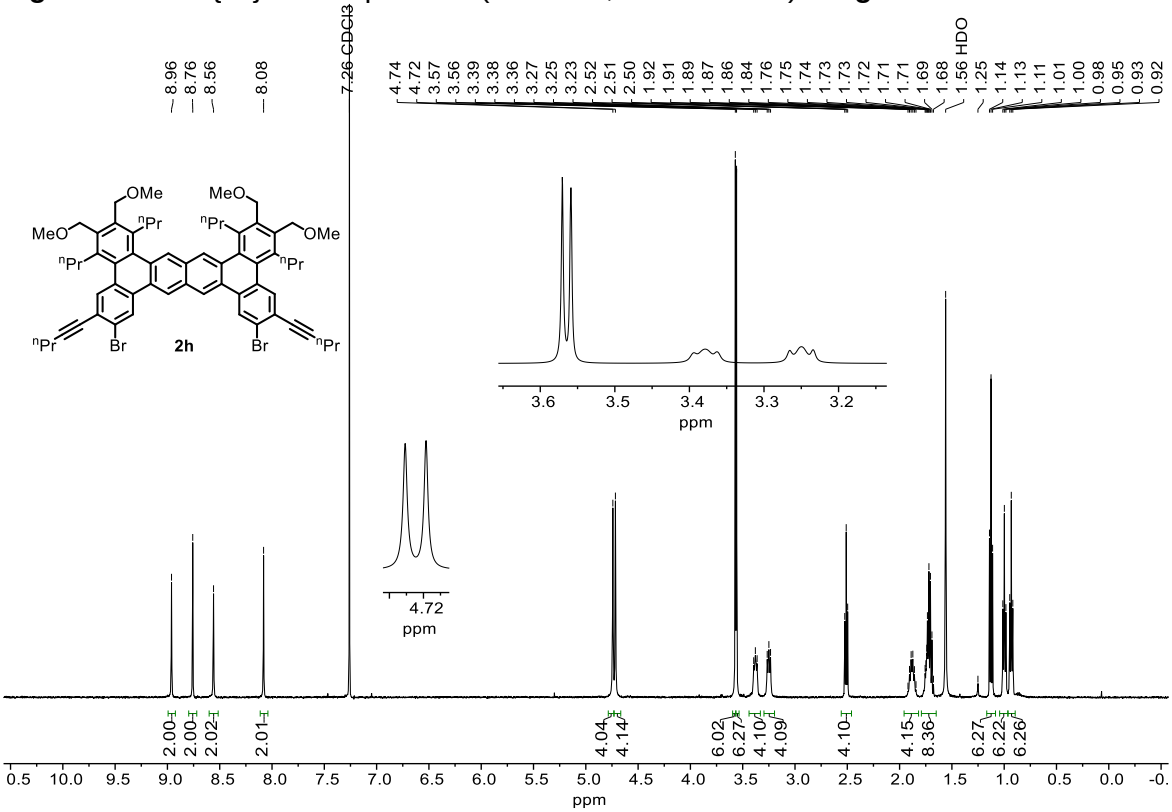


Figure S51. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **2h**.

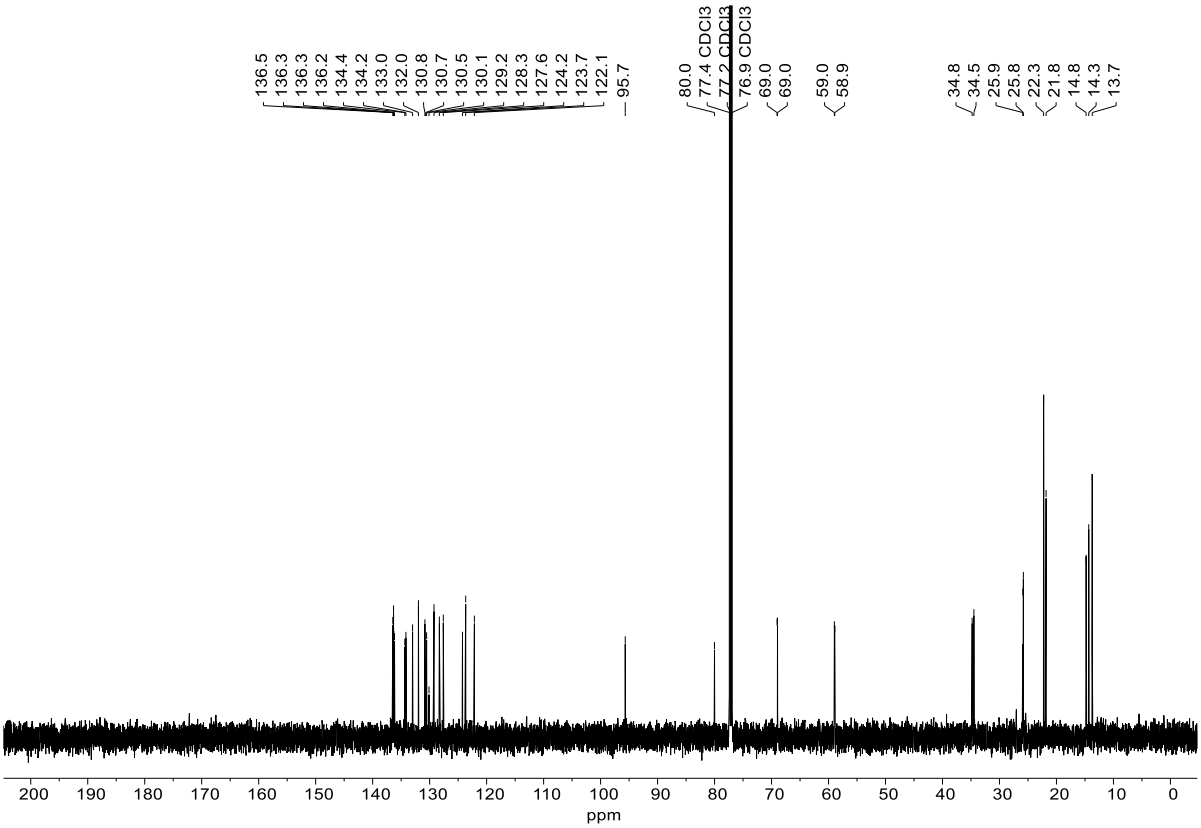


Figure S52. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **2h**.

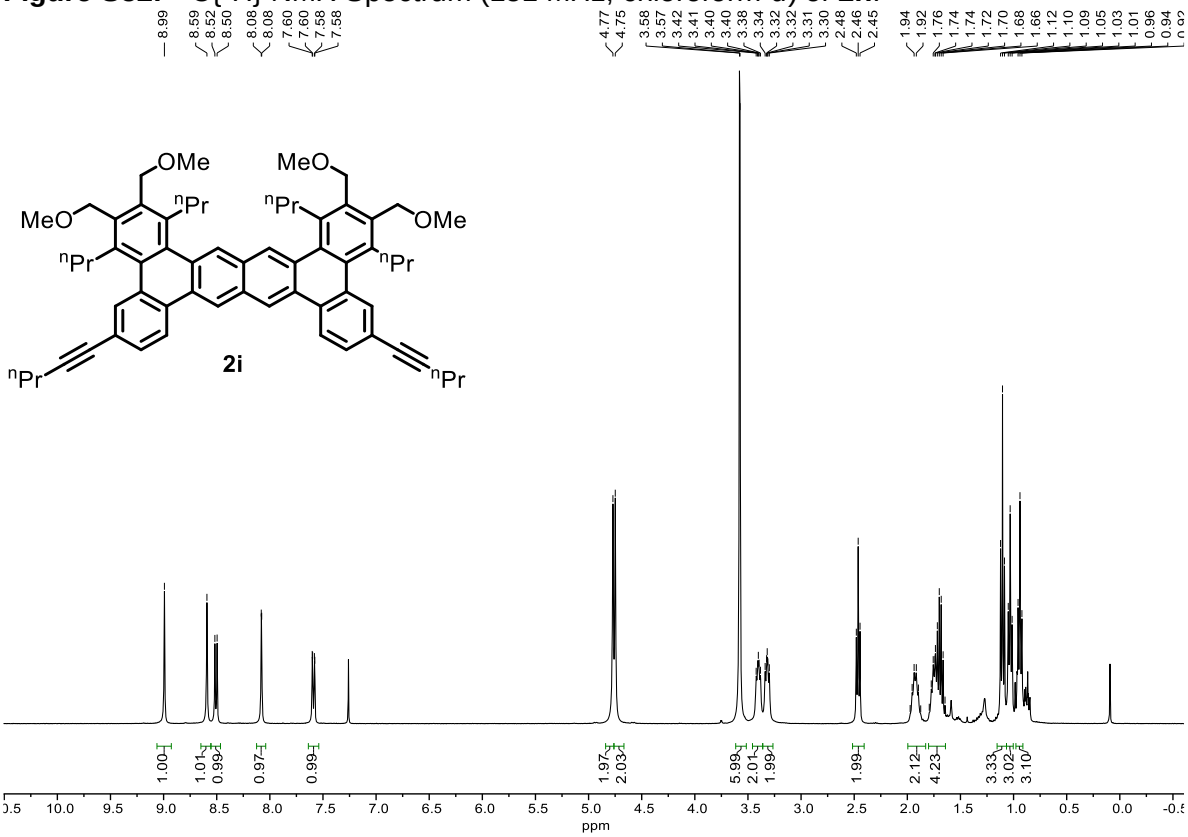


Figure S53. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **2i**.

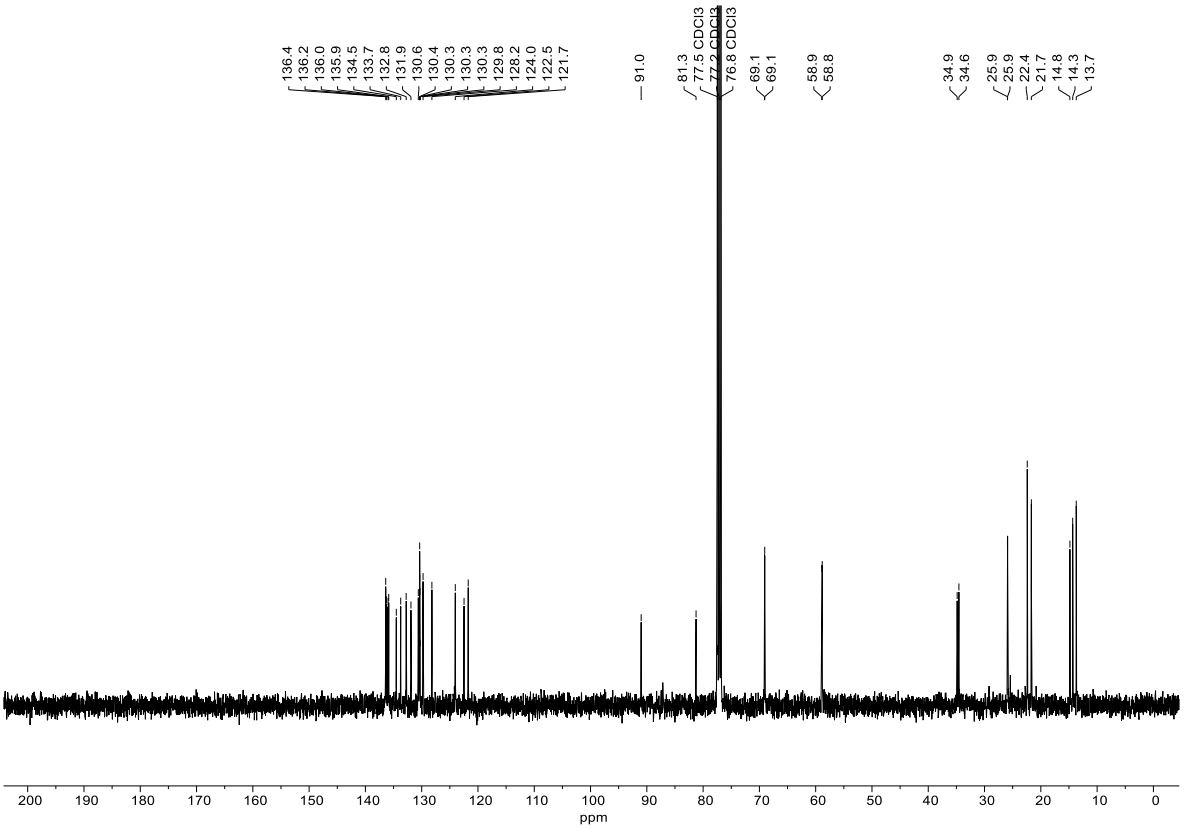


Figure S54. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **2i**.

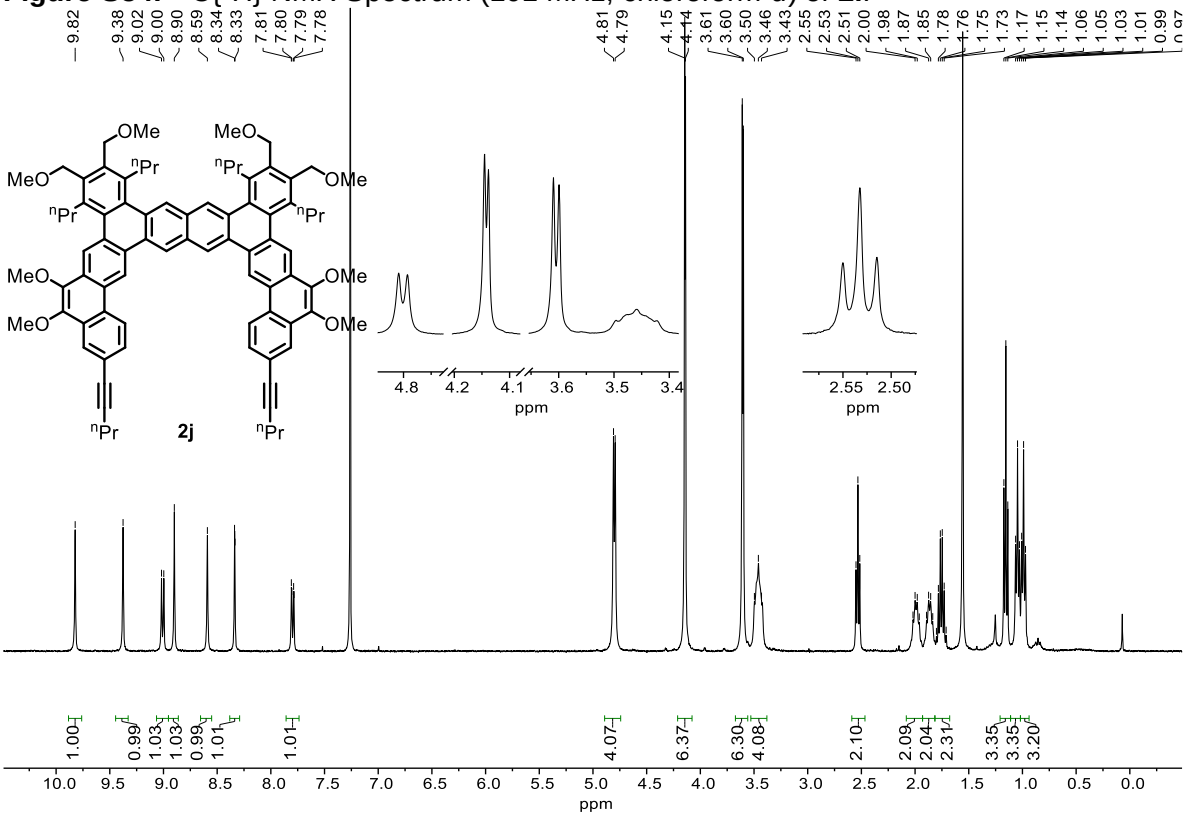


Figure S55. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **2j**.

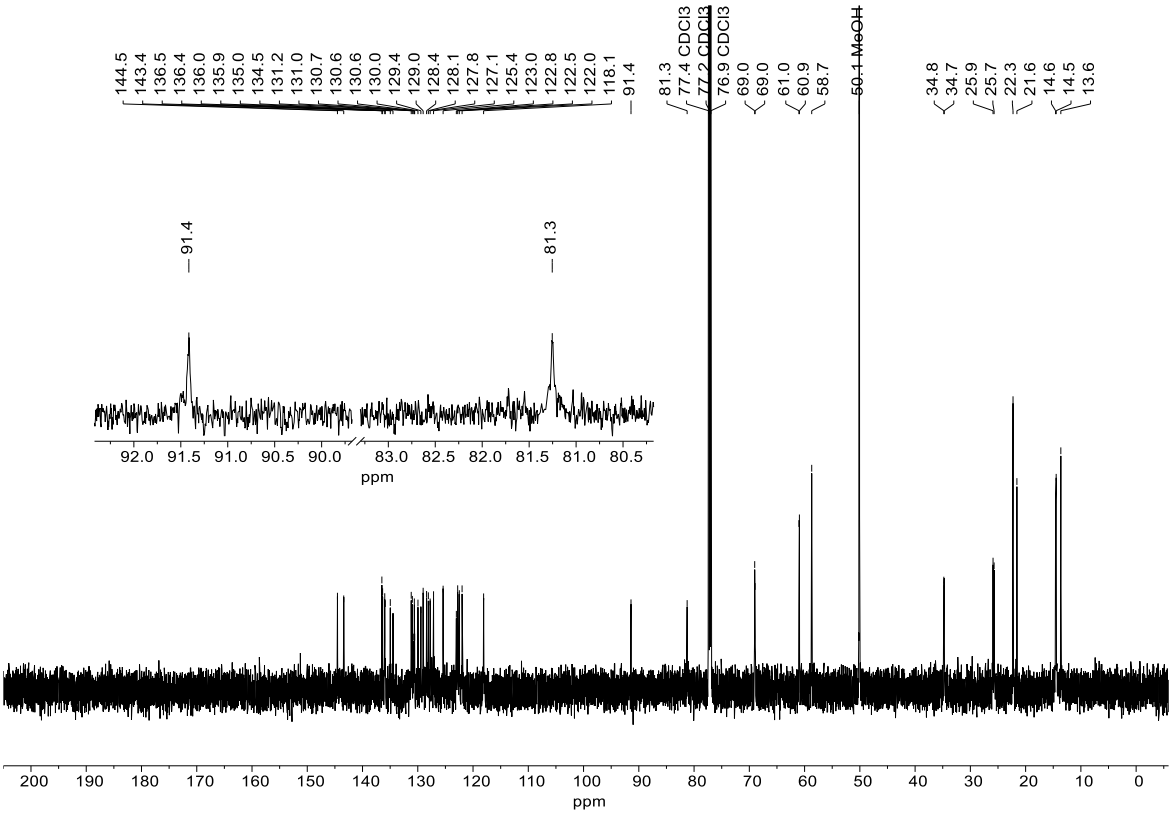


Figure S56. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **2j**.

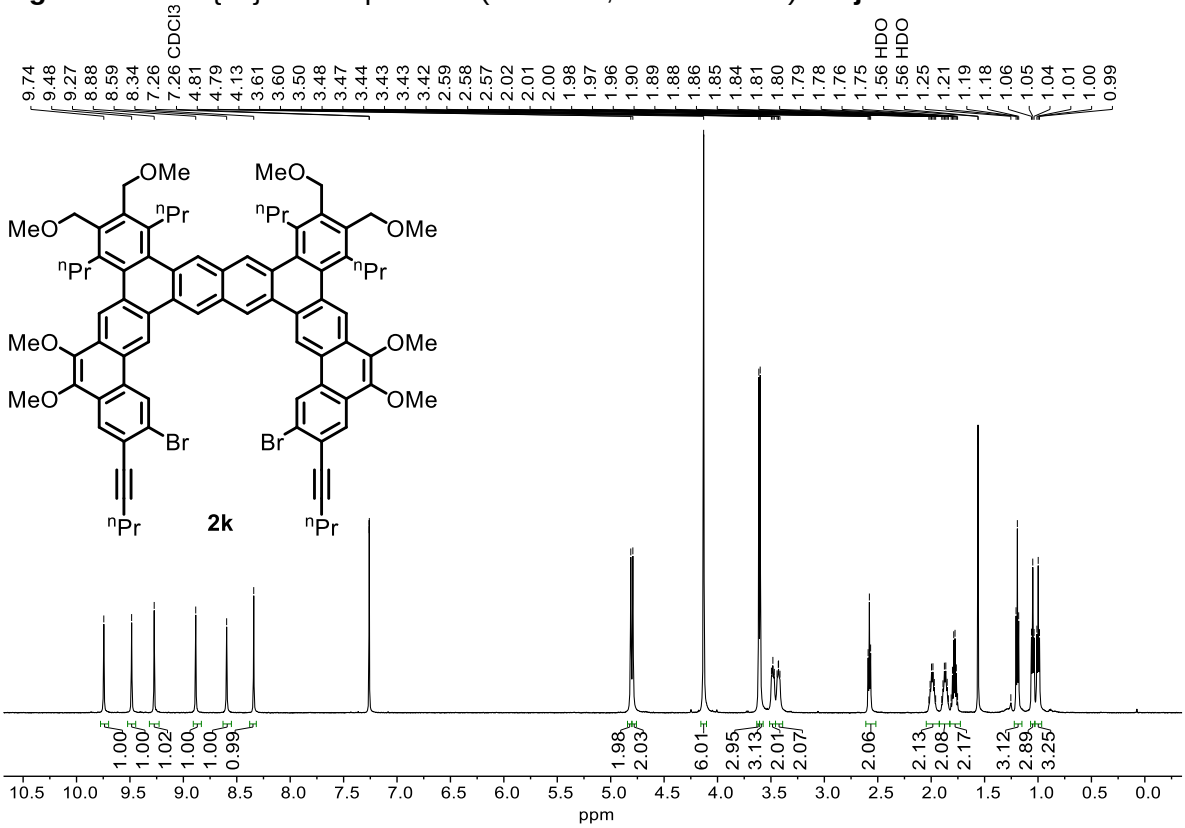


Figure S57. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **2k**.

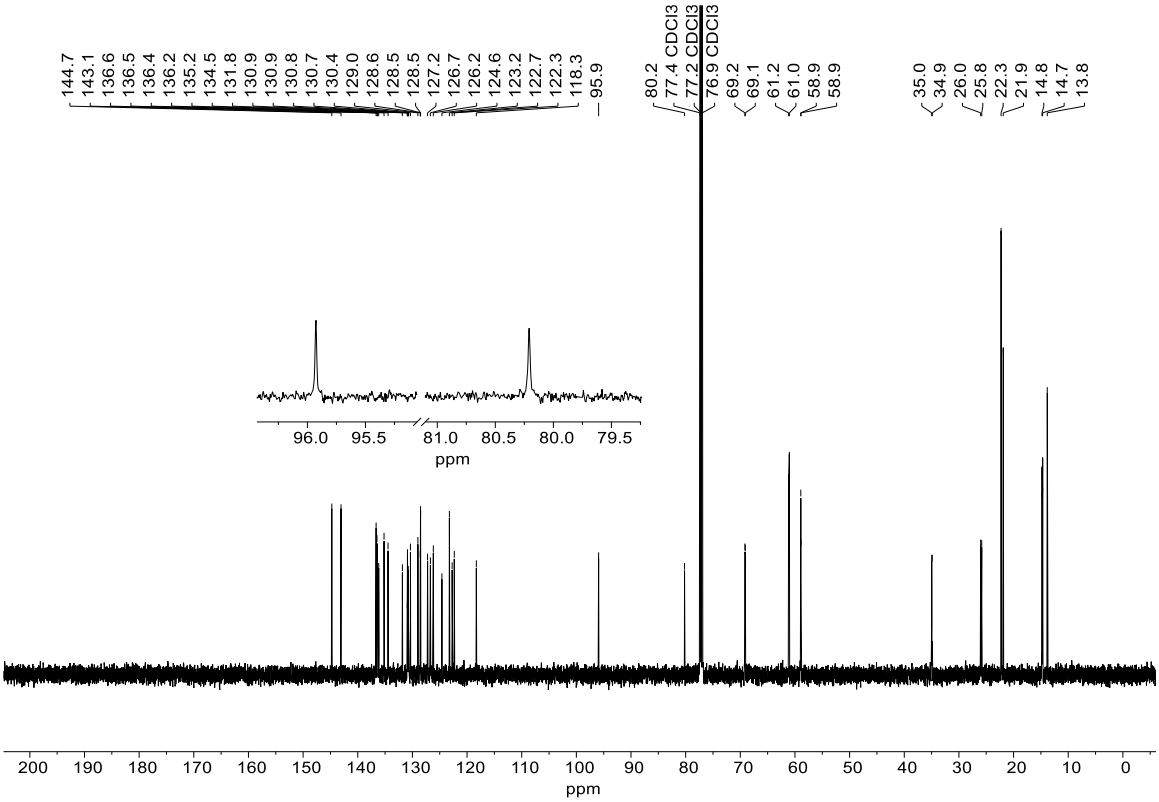


Figure S58. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*) of **2k**.

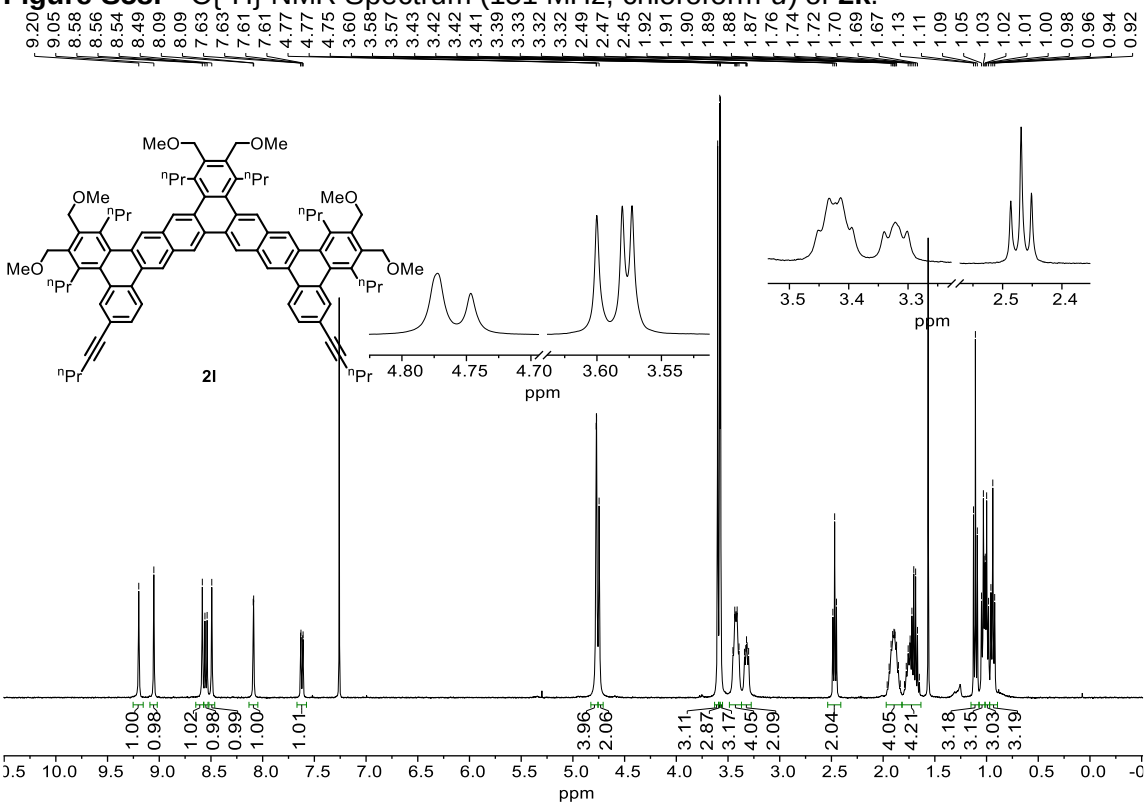


Figure S59. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **2l**.

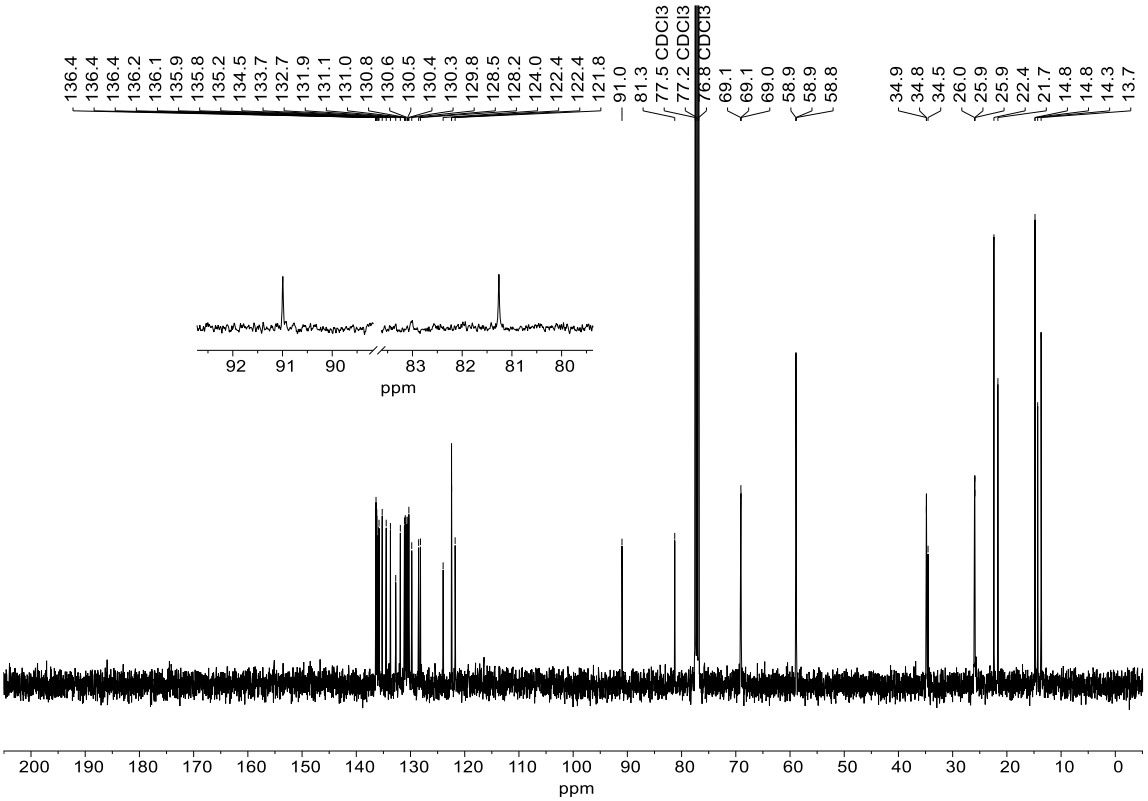


Figure S60. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **2l**.

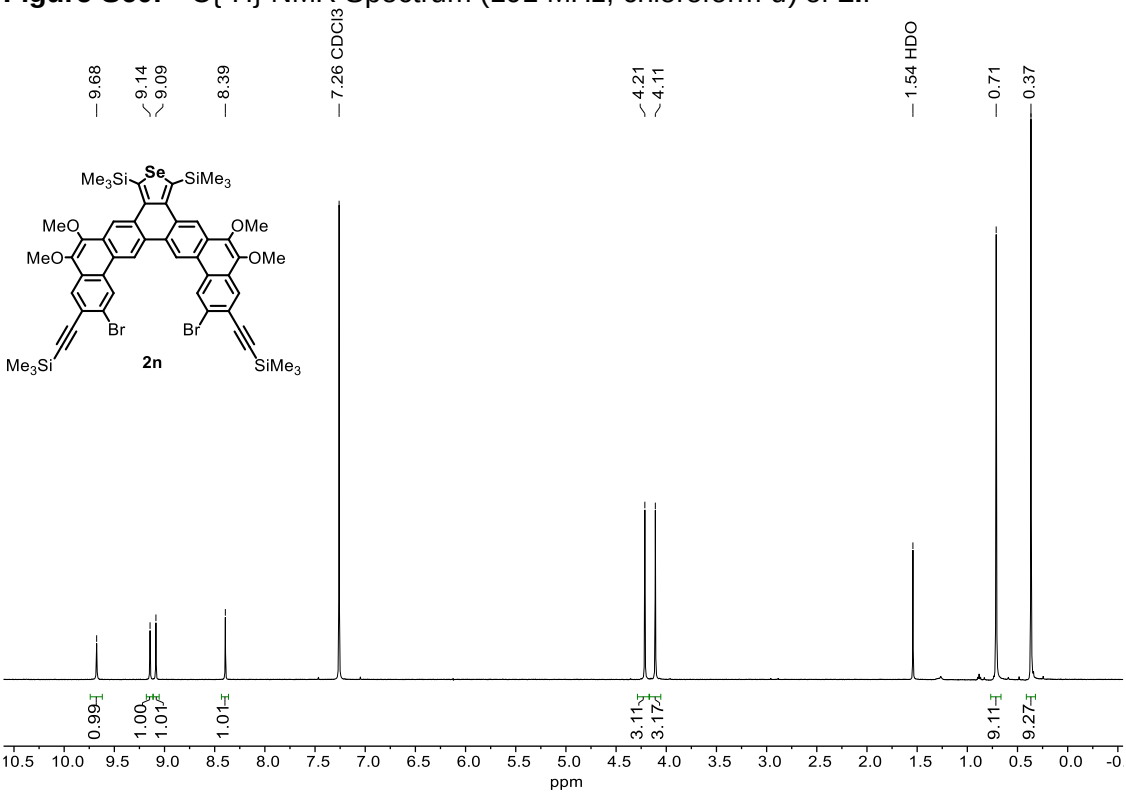


Figure S61. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **2n**.

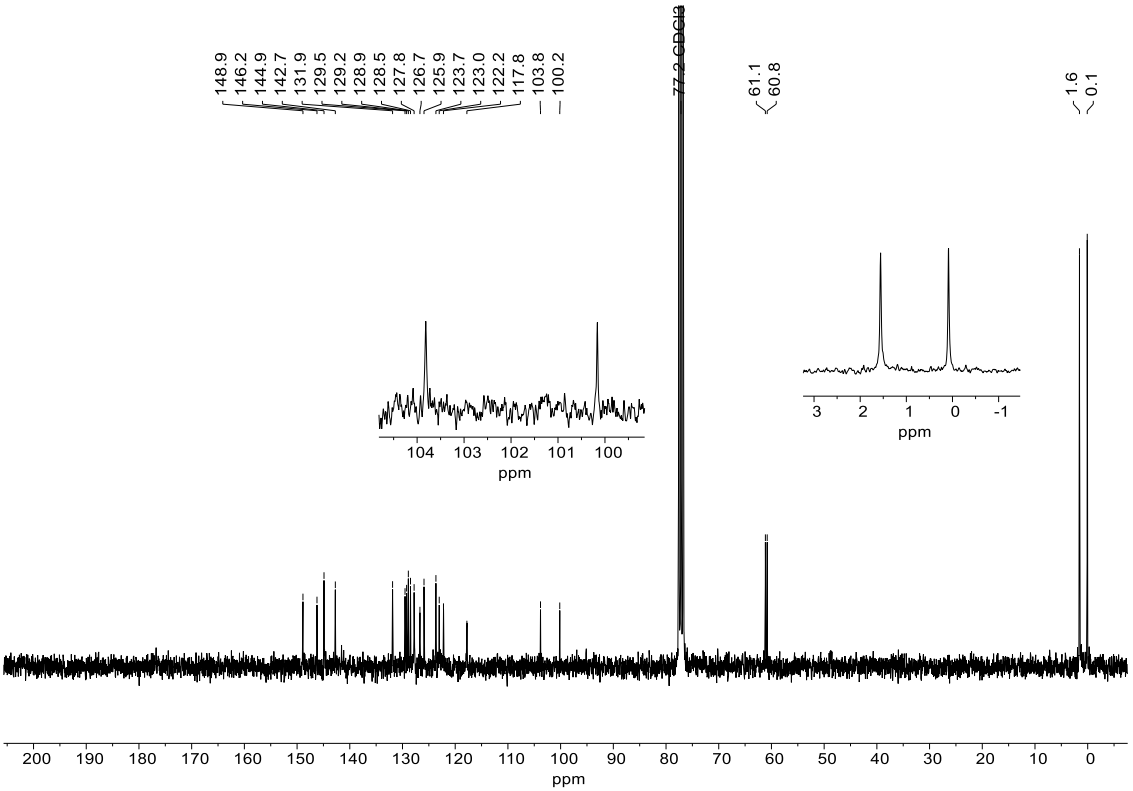


Figure S62. $^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, chloroform-*d*) of **2n**.

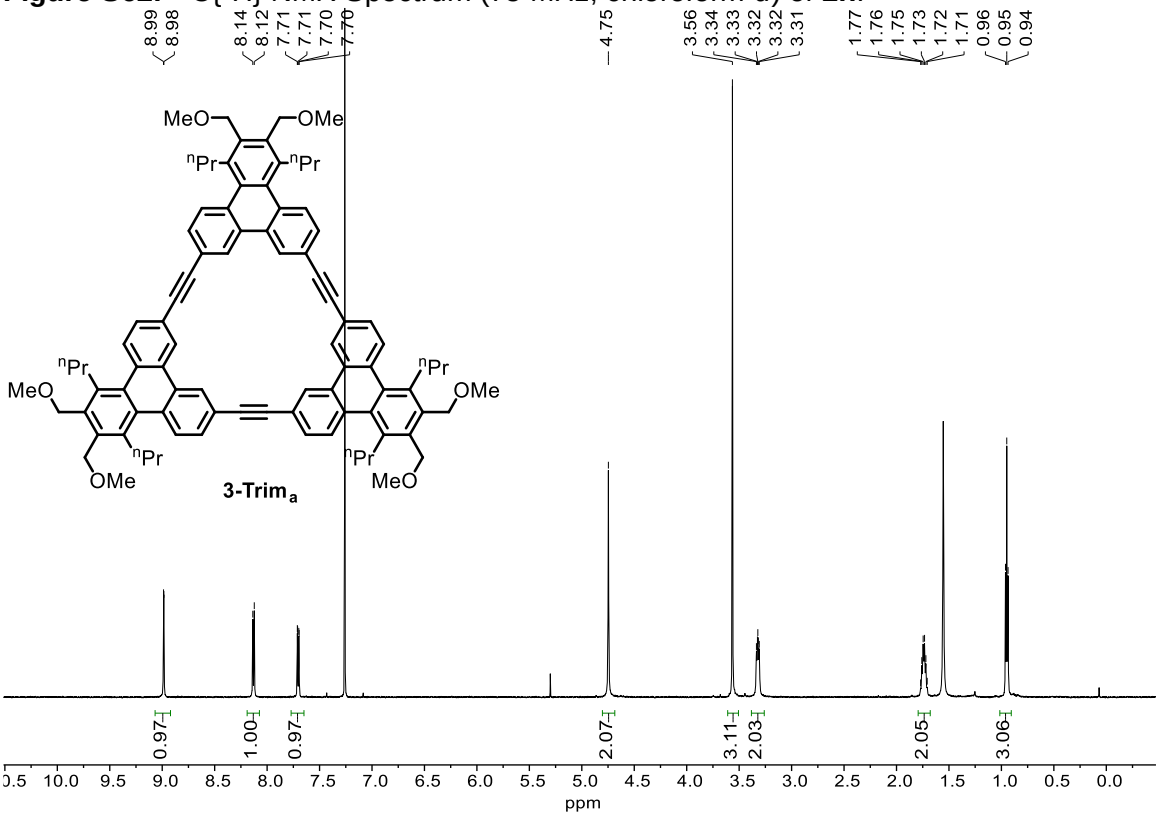


Figure S63. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **3-Trim$_a$**.

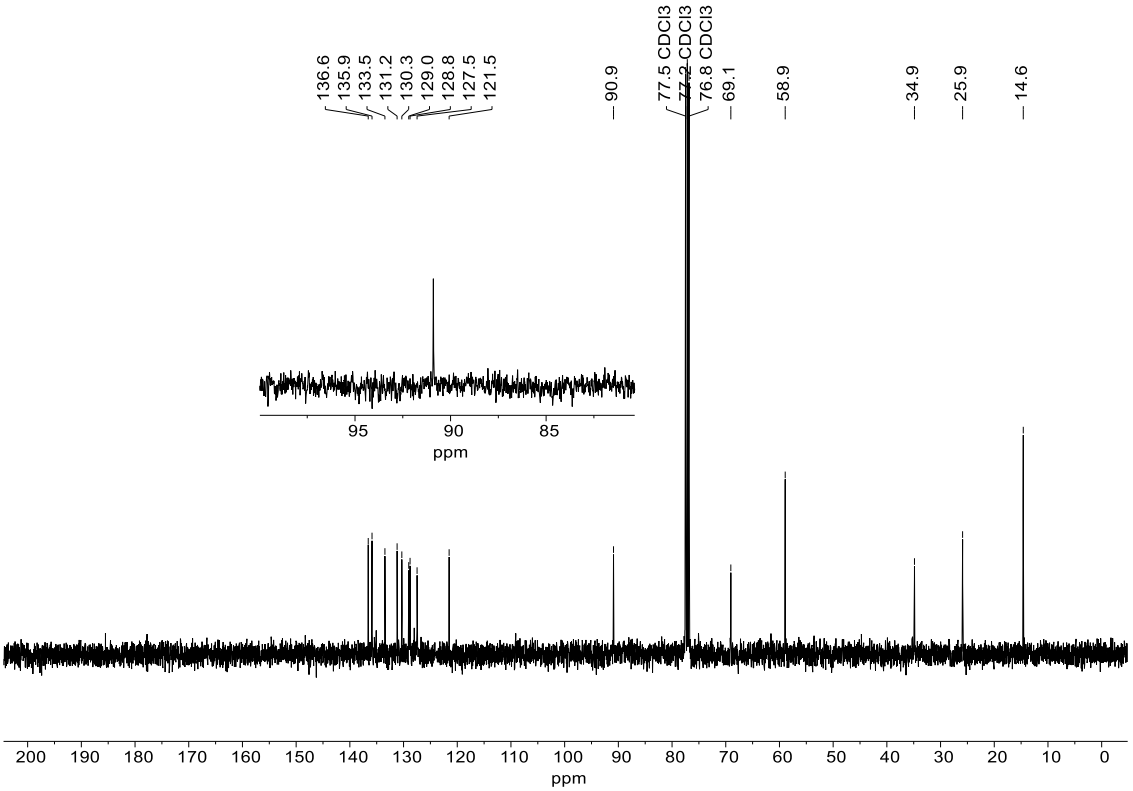


Figure S64. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **3-Trim$_a$**.

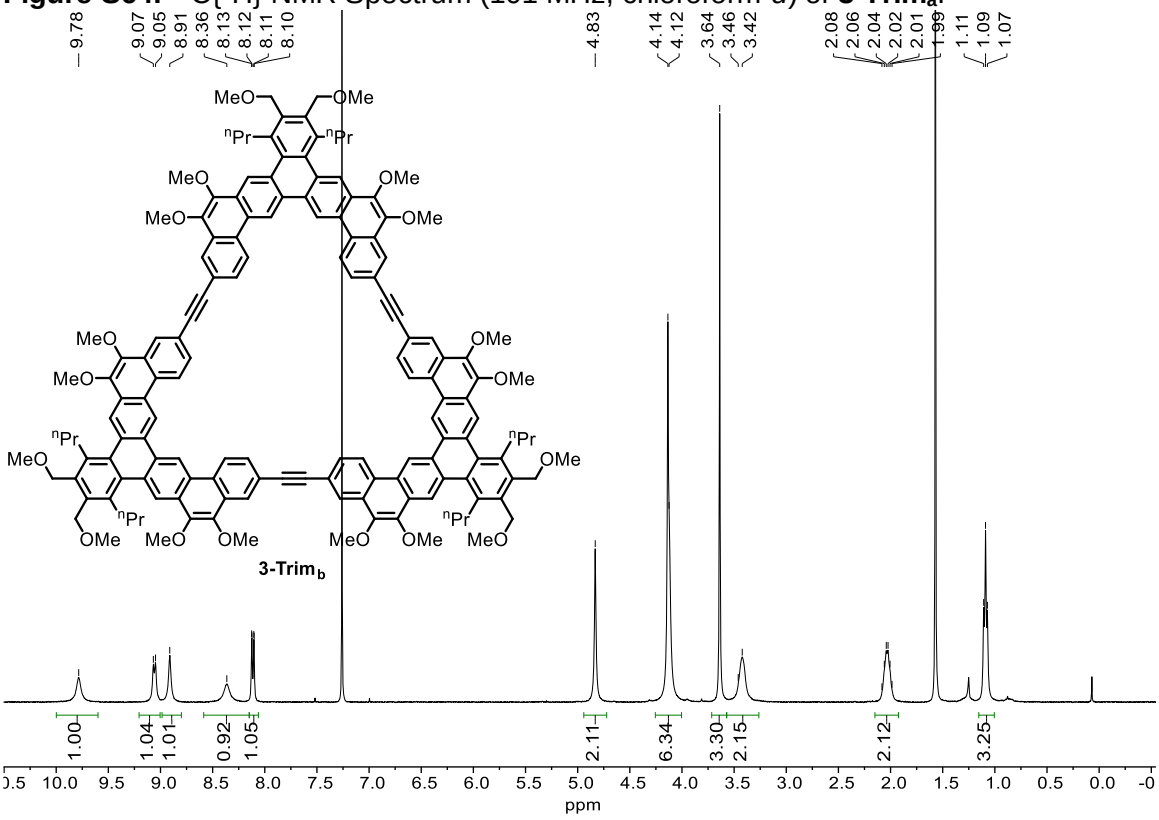


Figure S65. ^{1}H NMR Spectrum (400 MHz, chloroform-*d,* [c] = 1.9 mM) of **3-Trim$_b$**.

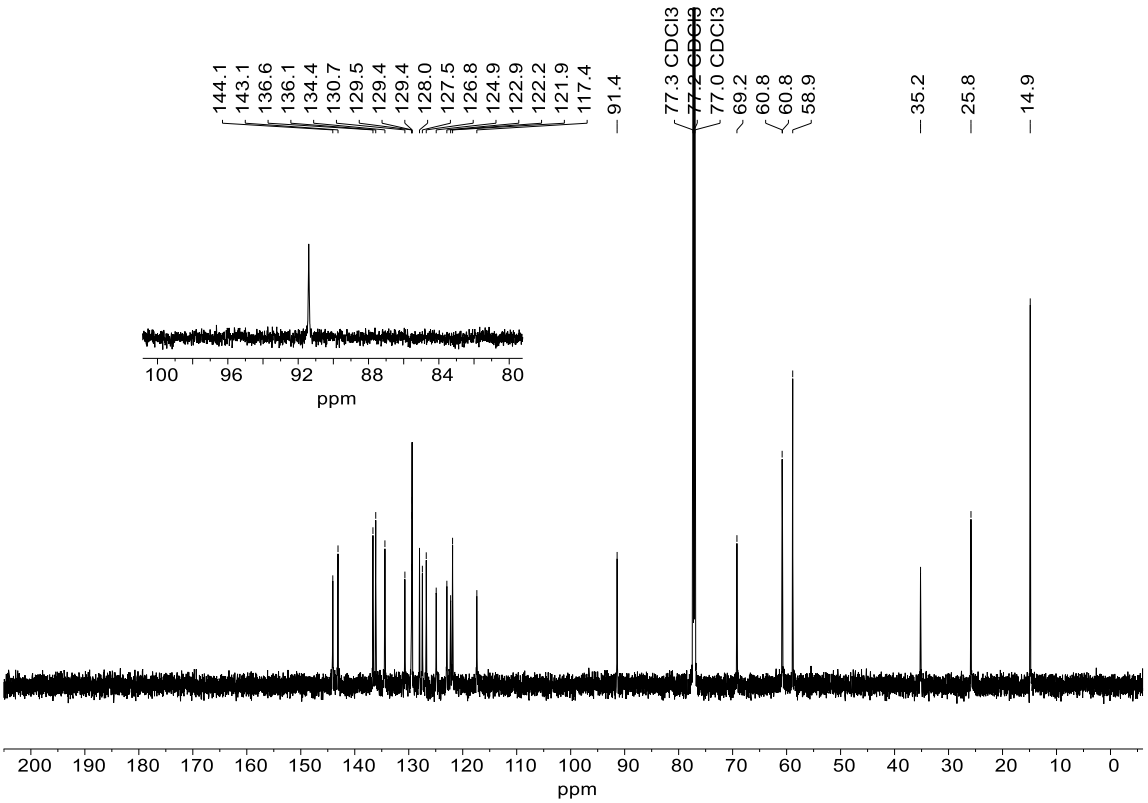


Figure S66. $^{13}C\{^{1}H\}$ NMR Spectrum (176 MHz, chloroform-*d*) of **3-Trim$_b$**.

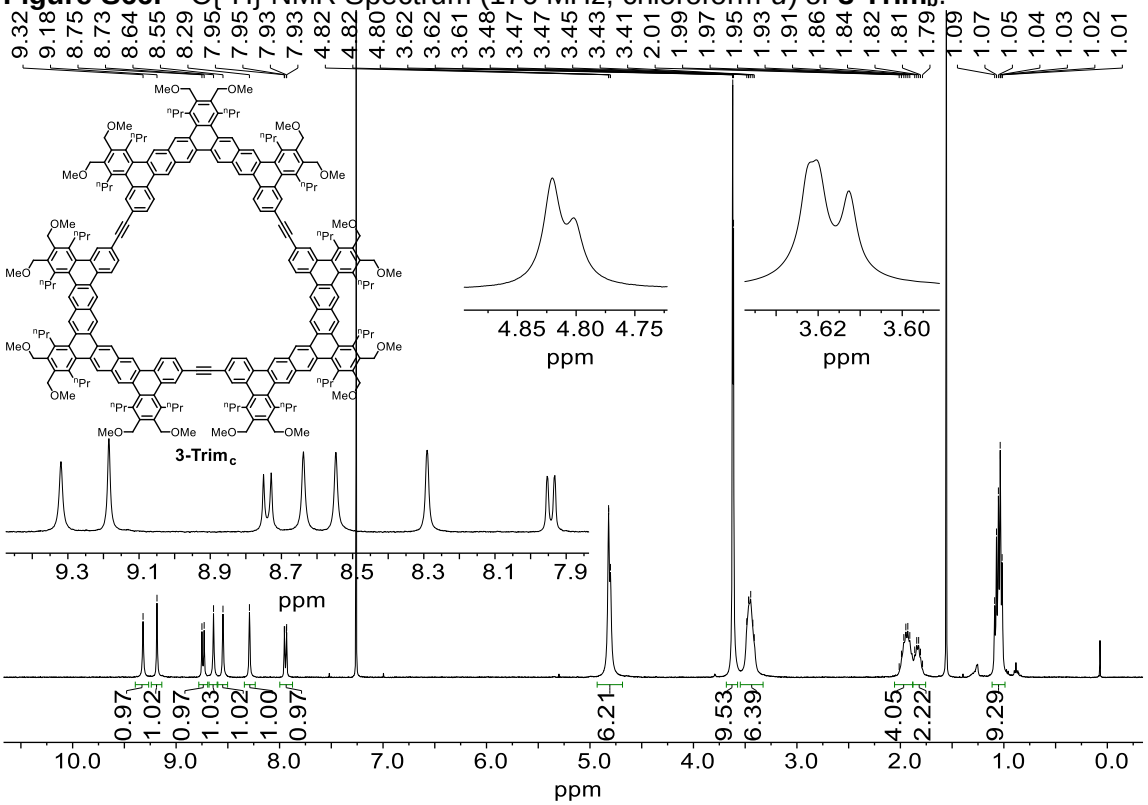


Figure S67. ^{1}H NMR Spectrum (400 MHz, chloroform-*d*) of **3-Trim$_c$**.

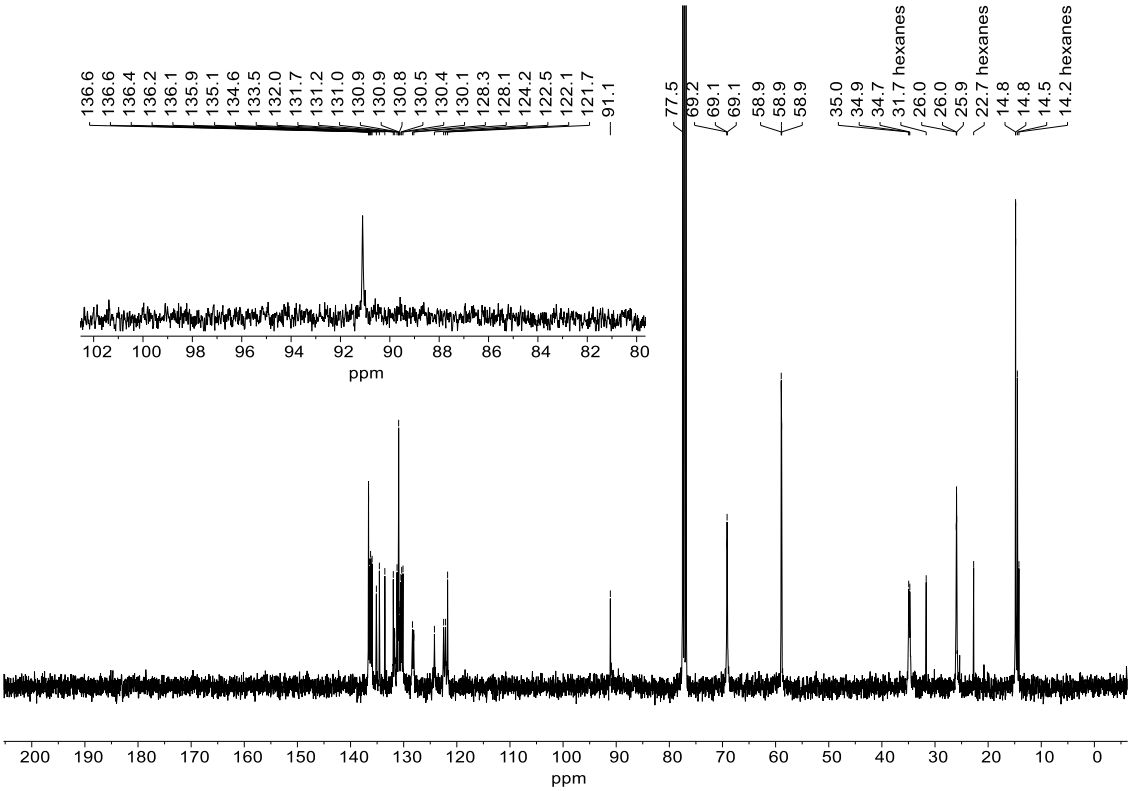


Figure S68. $^{13}C\{^{1}H\}$ NMR Spectrum (101 MHz, chloroform-*d*) of **3-Trim$_c$**.

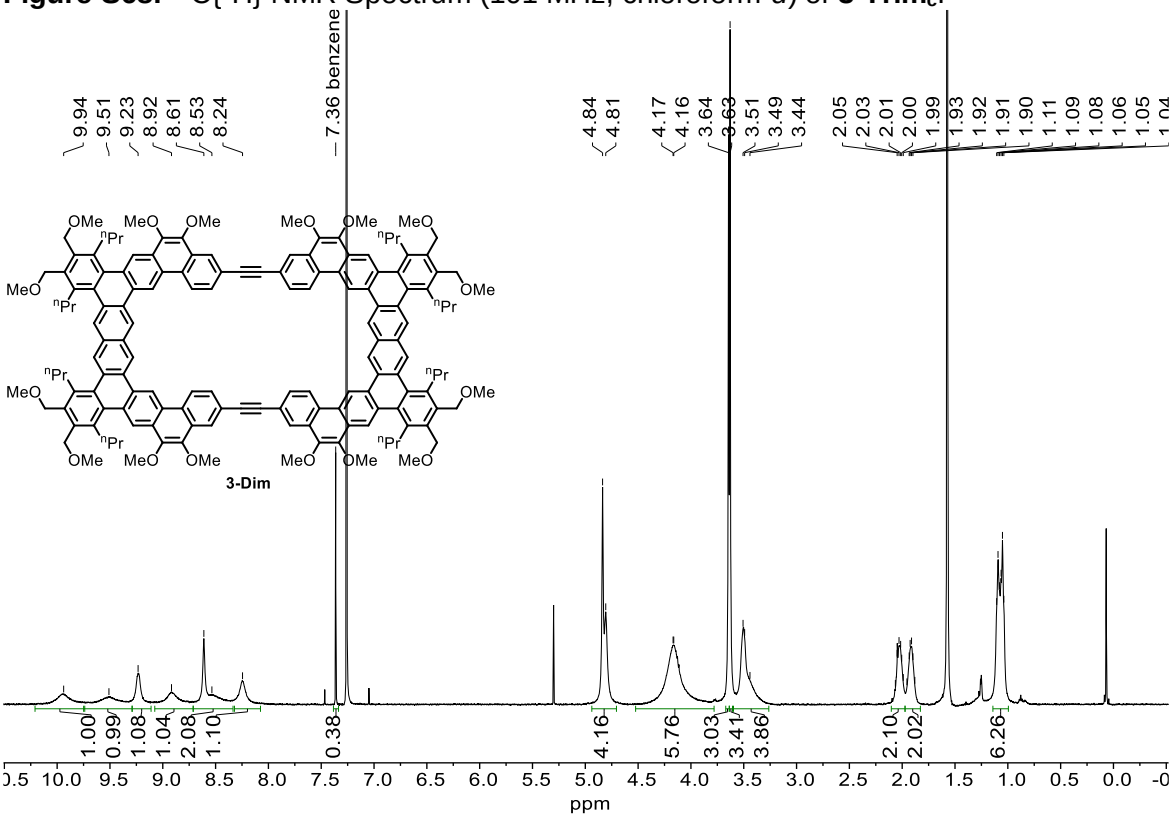


Figure S69. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*, [c] = 1.5 mM) of **3-Dim**.

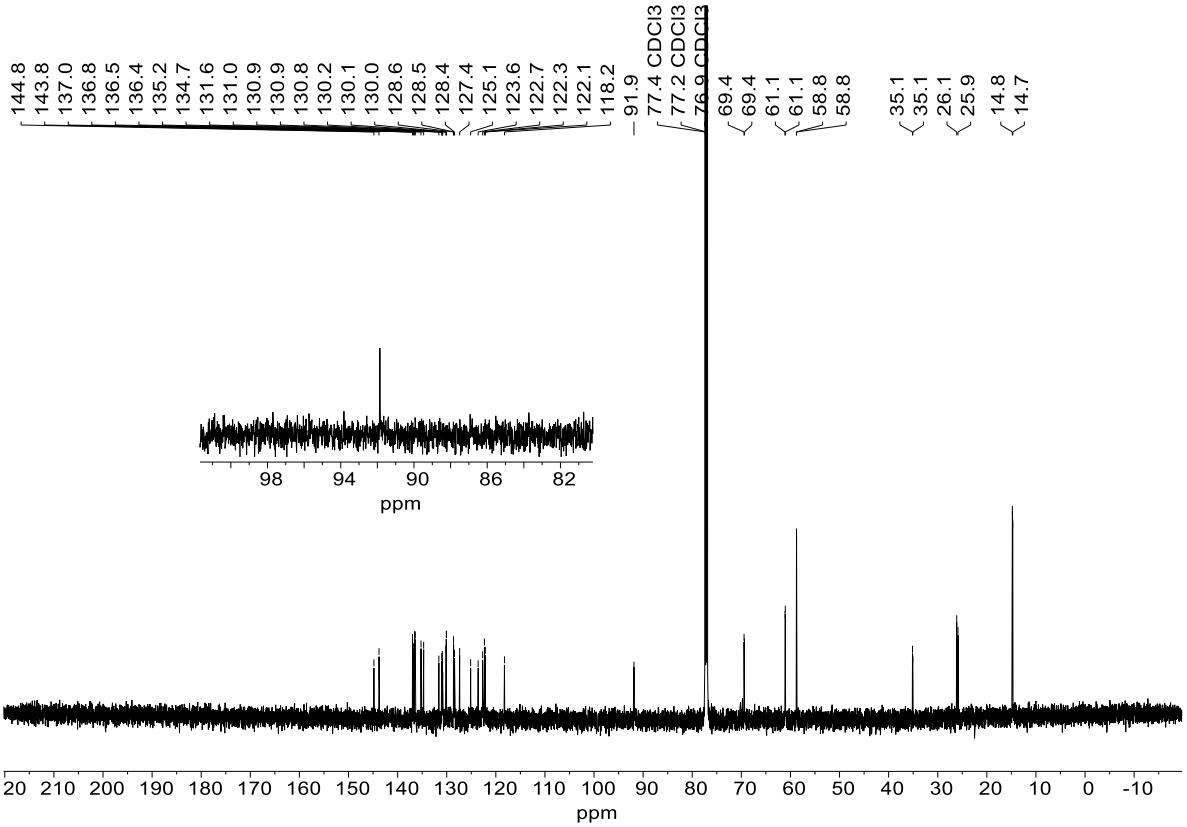


Figure S70. $^{13}C\{^{1}H\}$ NMR Spectrum (151 MHz, chloroform-*d*, 60 °C) of **3-Dim**.

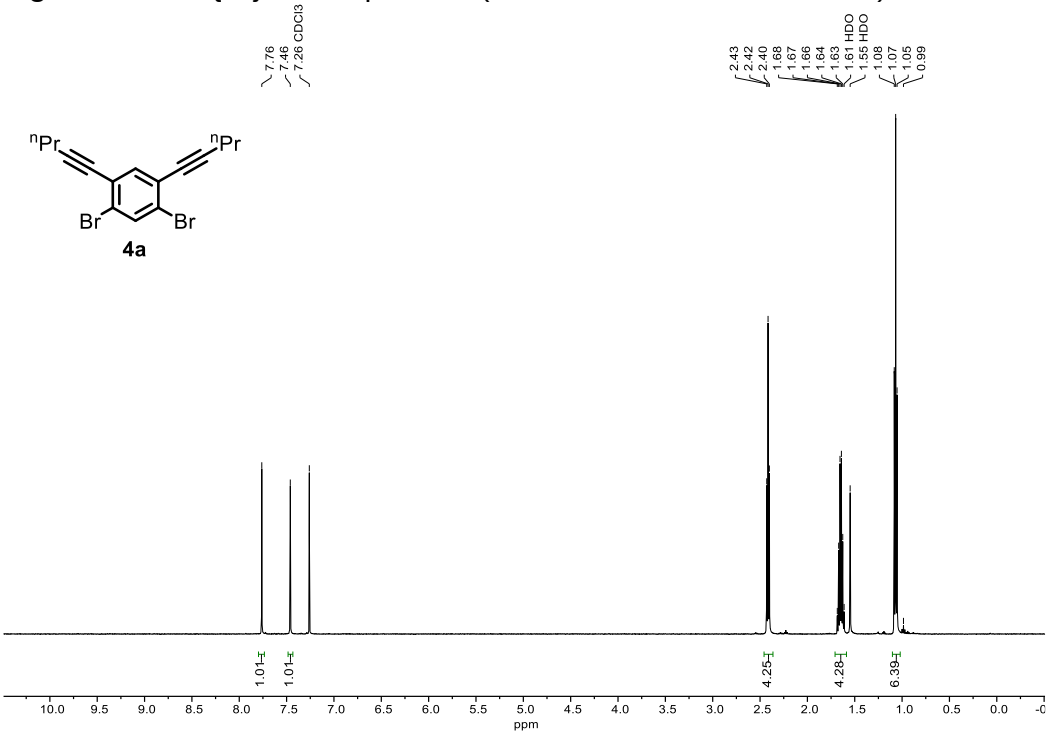


Figure S71. ^{1}H NMR Spectrum (500 MHz, chloroform-*d*) of **4a**.

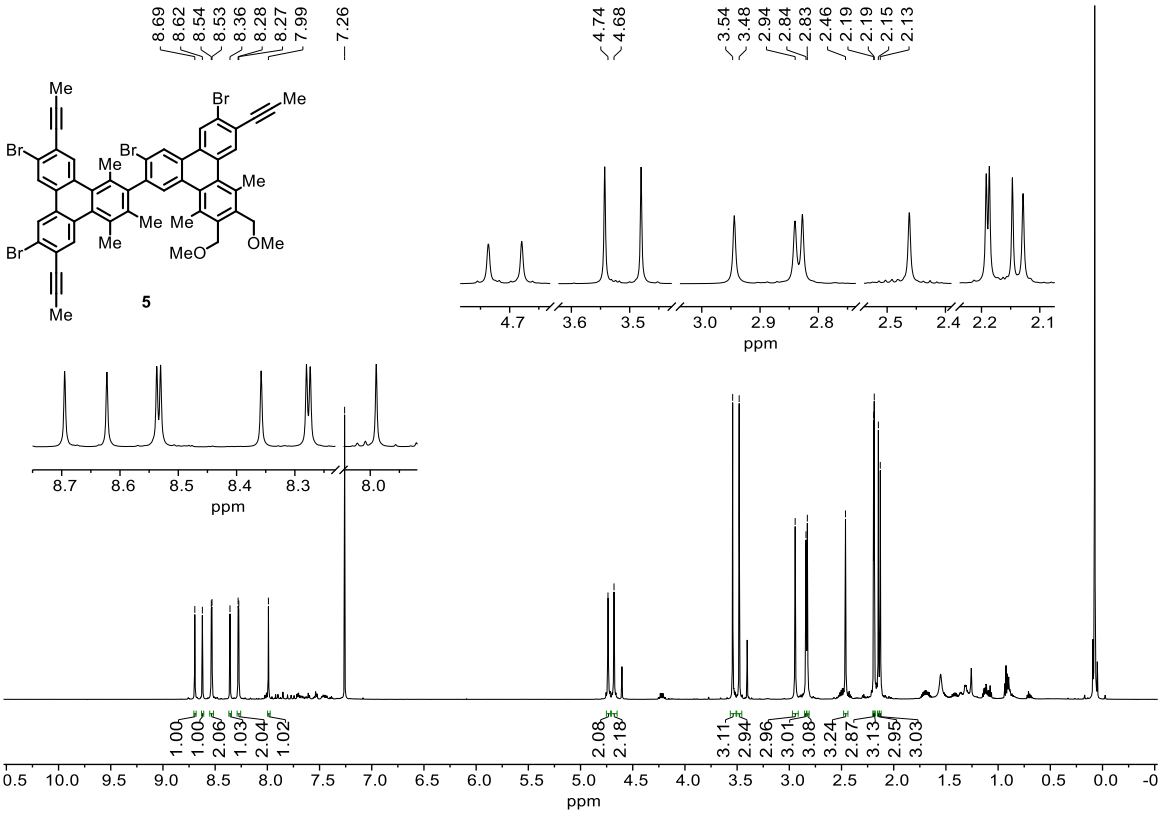


Figure S72. ^{1}H NMR Spectrum (600 MHz, chloroform-*d*) of **5**.

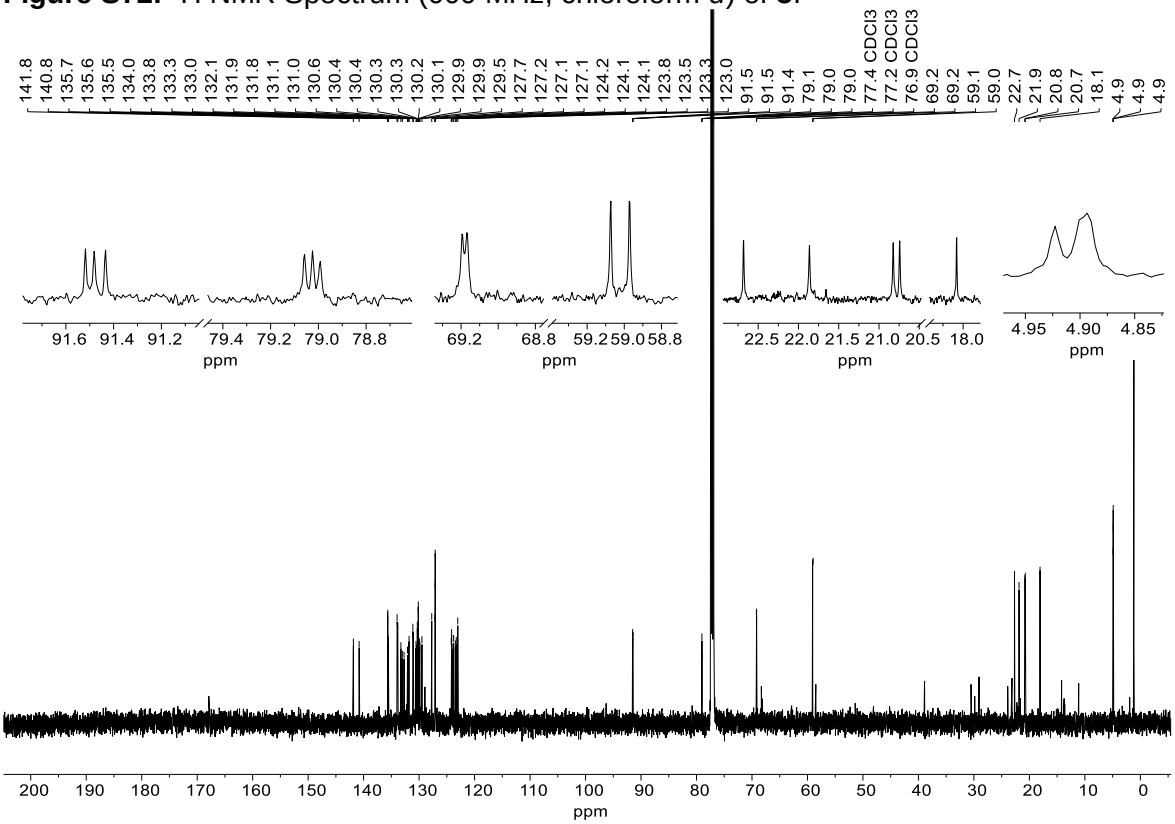


Figure S73. ^{13}C NMR Spectrum (151 MHz, chloroform-*d*) of **5**.

Variable concentration ^{1}H NMR spectra

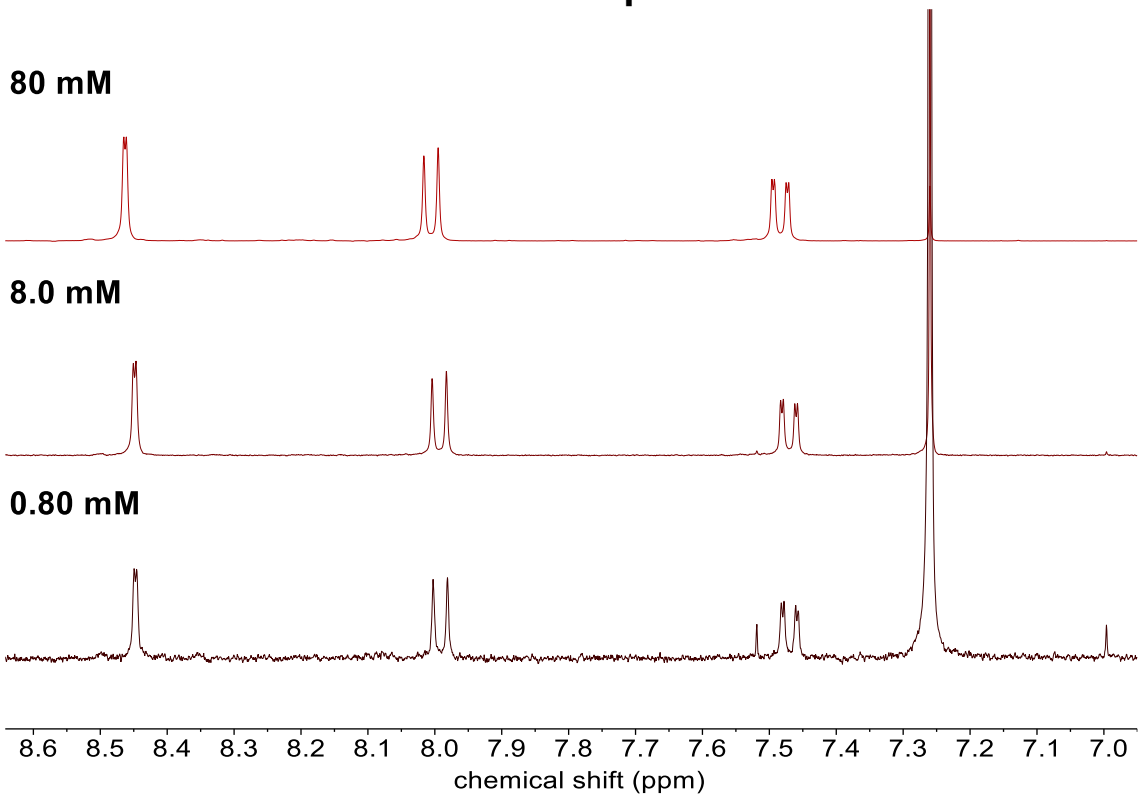


Figure S74. Variable concentration partial ^{1}H NMR spectra (400 MHz, chloroform-*d*) of **2d**.

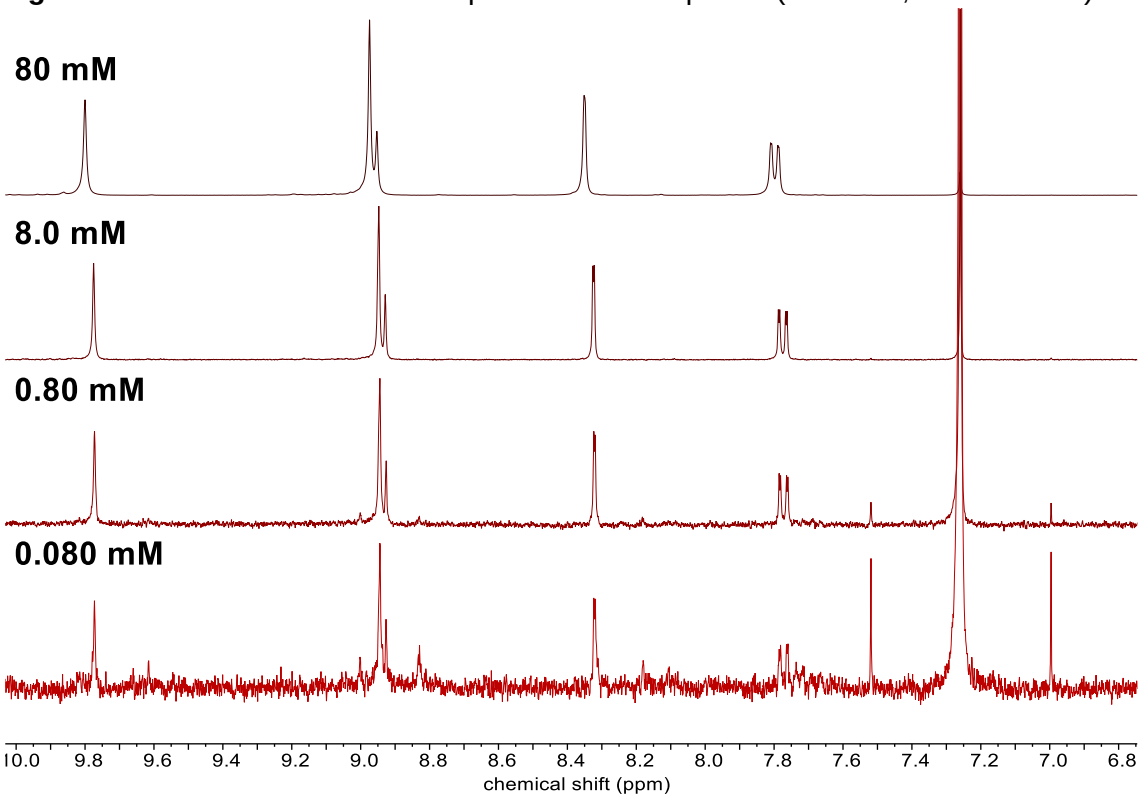


Figure S75. Variable concentration partial ^{1}H NMR spectra (400 MHz, chloroform-*d*) of **2g**.

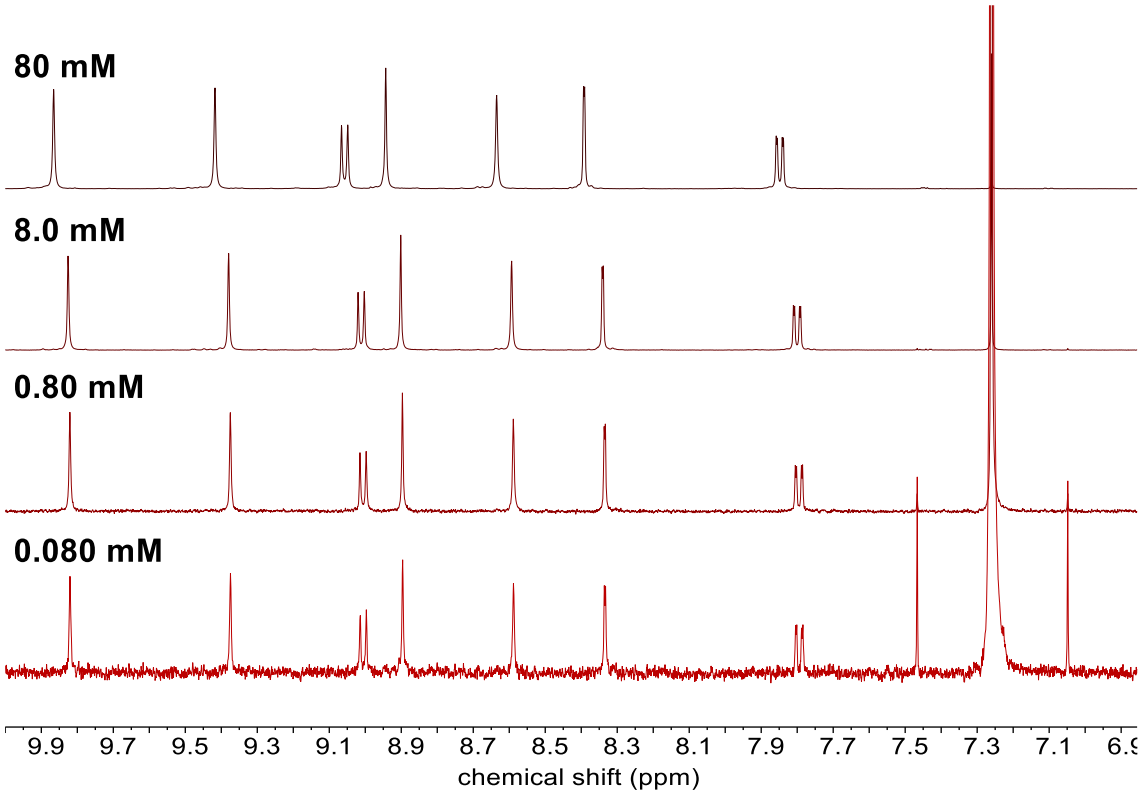


Figure S76. Variable concentration partial ^{1}H NMR spectra (500 MHz, chloroform-*d*) of **2j**.

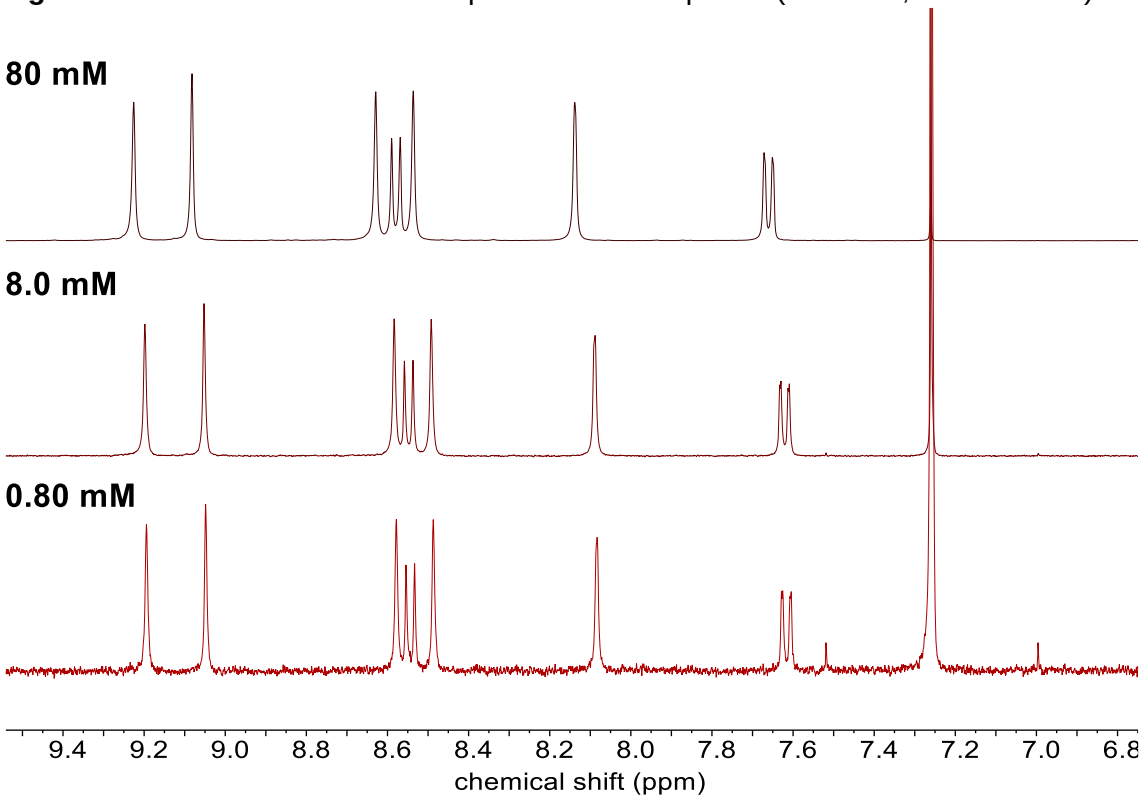


Figure S77. Variable concentration partial ^{1}H NMR spectra (400 MHz, chloroform-*d*) of **2l**.

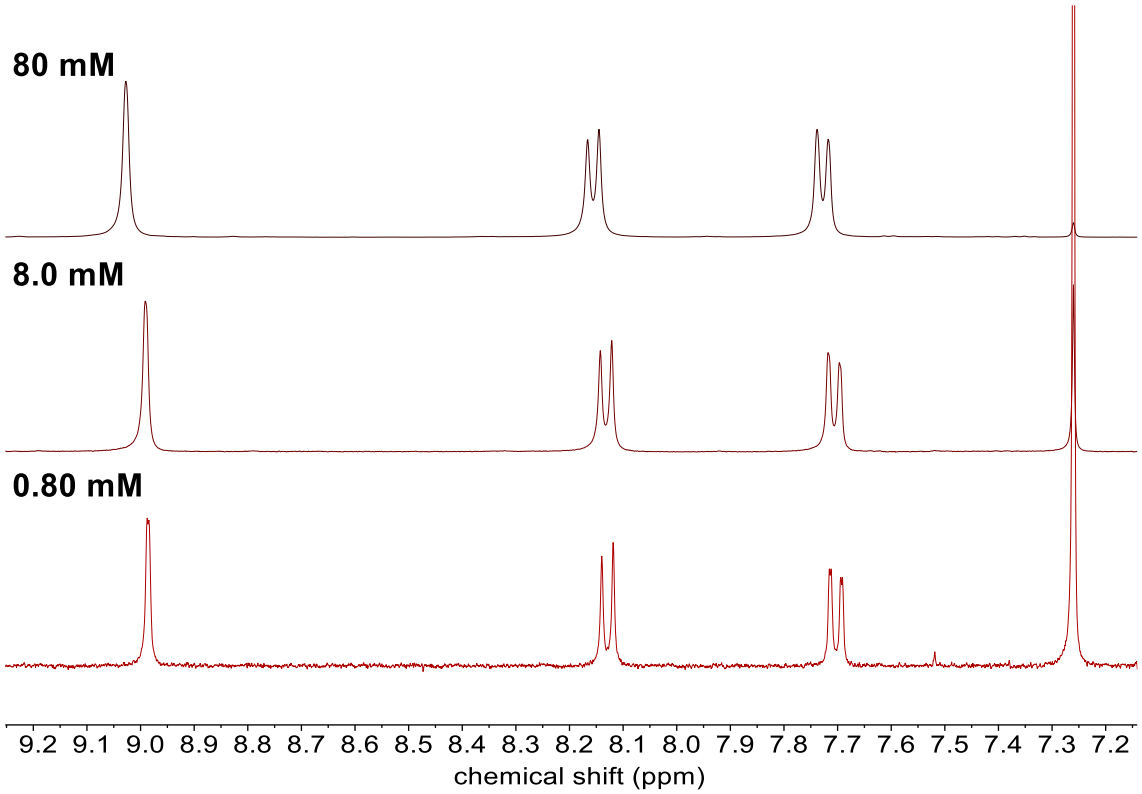


Figure S78. Variable concentration partial ^{1}H NMR spectra (400 MHz, chloroform-*d*) of **3-Trim$_{a}$**.

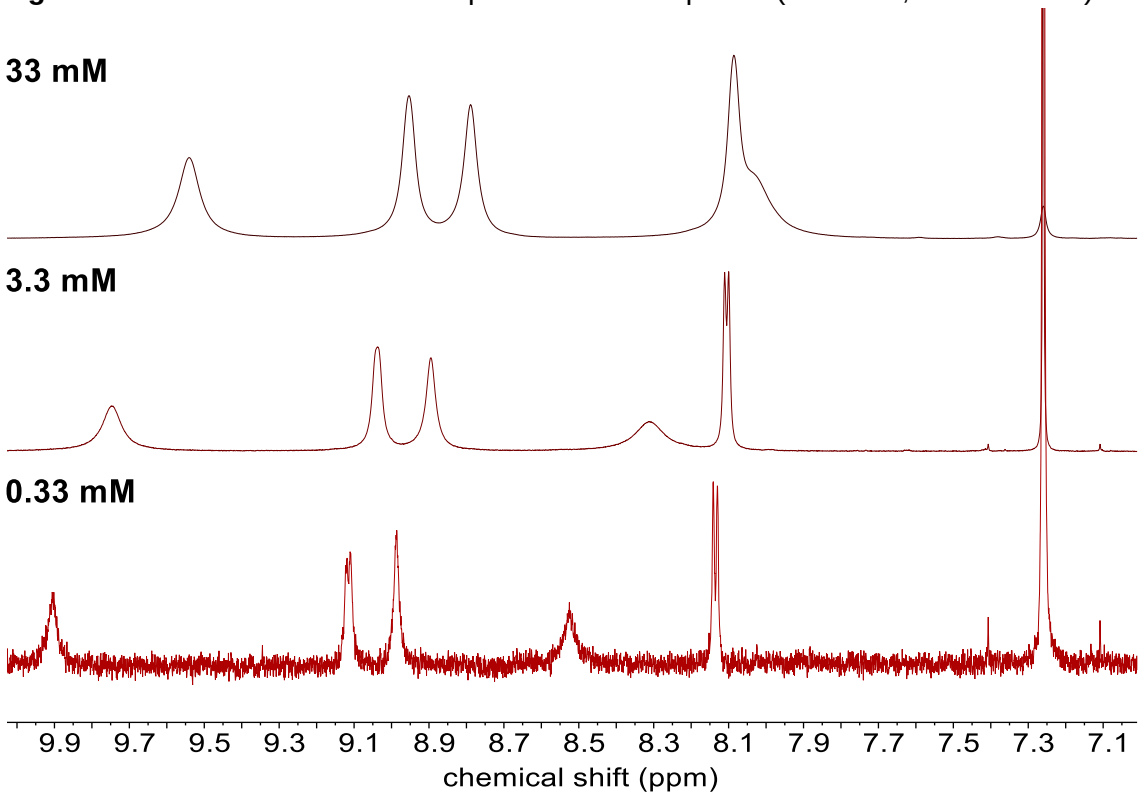


Figure S79. Variable concentration partial ^{1}H NMR spectra (700 MHz, chloroform-*d*) of **3-Trim$_{b}$**.

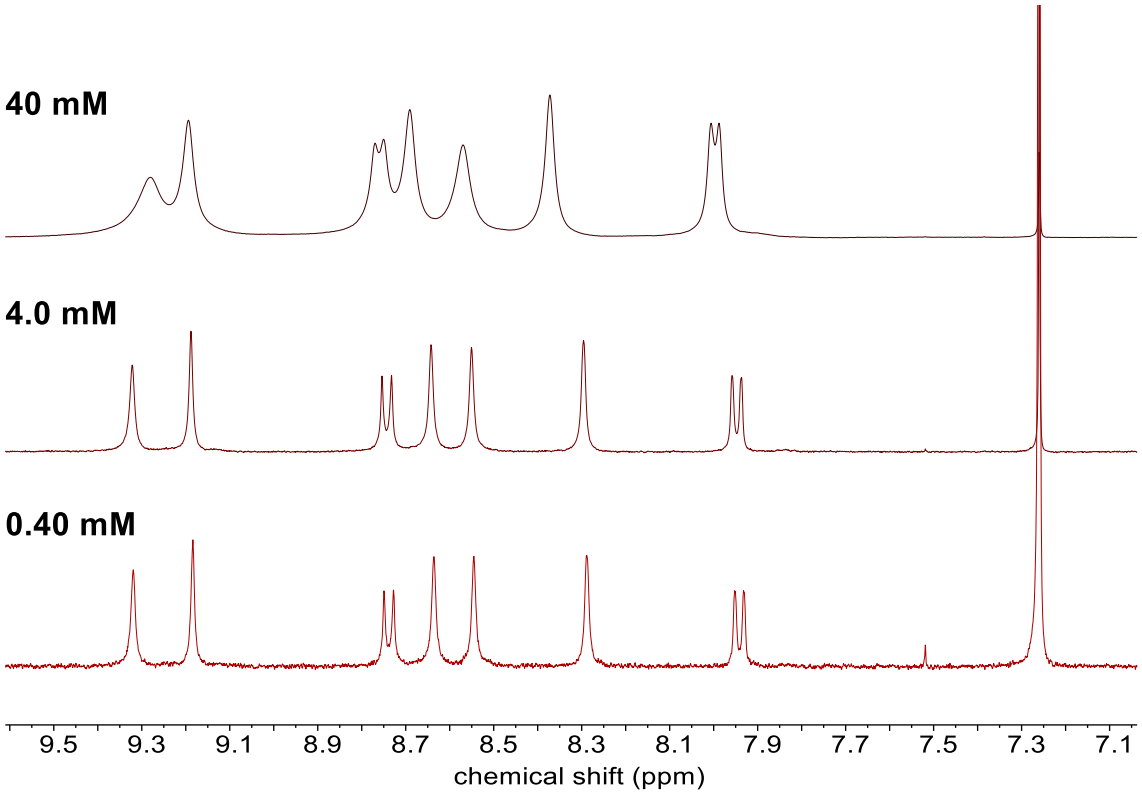


Figure S80. Variable concentration partial ^{1}H NMR spectra (400 MHz, chloroform-*d*) of **3-Trim$_c$**.

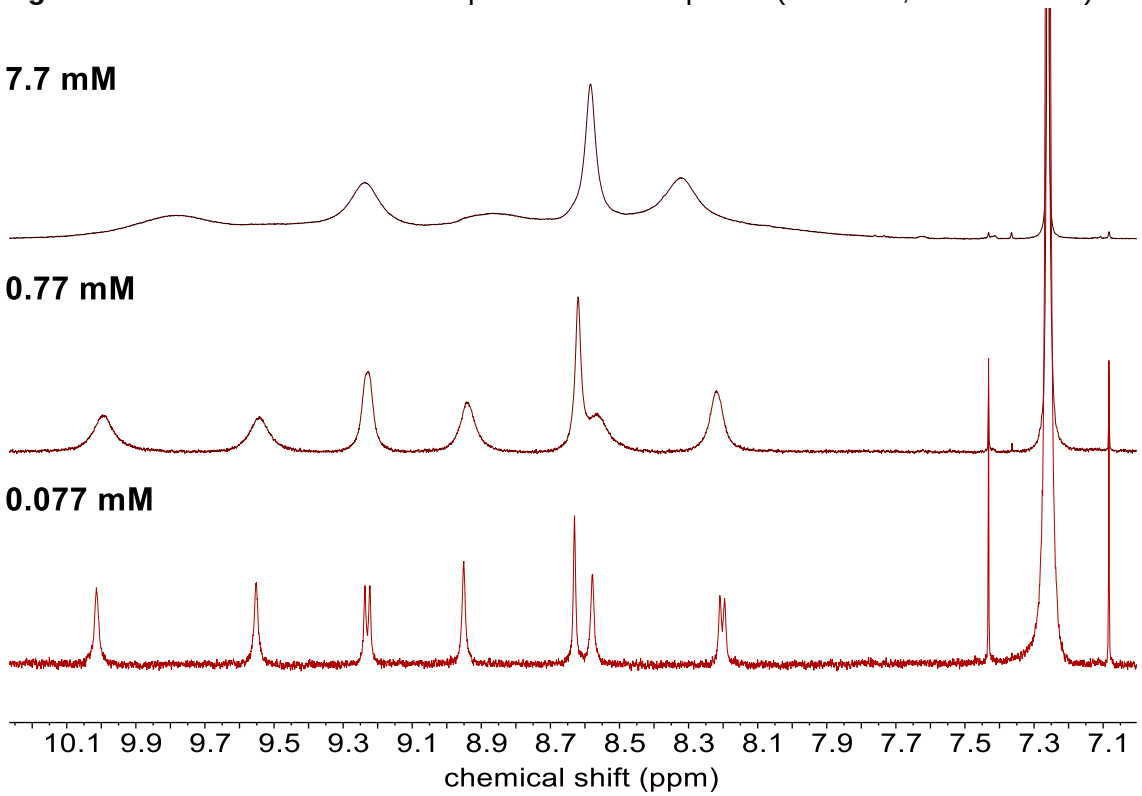


Figure S81. Variable concentration partial ^{1}H NMR spectra (600 MHz, chloroform-*d*) of **3-Dim**.

Photophysical characterization

UV/Vis spectra were recorded on a Varian Cary 300 Bio UV-Visible spectrophotometer. Emission spectra were recorded on a Varian Cary Eclipse Spectrometer. All compounds were subjected to preparatory thin layer chromatography (CH_2Cl_2/hexanes or CH_2Cl_2/EtOAc solvent system) prior to analysis to ensure high purity. The UV/Vis spectra that are shown represent the average of two measurements on separate samples to ensure accuracy of extinction coefficients. For sample preparation, each analyte was weighed on an analytical balance and dissolved in the appropriate amount of CH_2Cl_2 using a volumetric flask. A single dilution experiment (10x) was performed for each compound. For all compounds, the UV/vis spectra (plotted by molar absorptivity) are unchanged by this dilution. Emission spectra for all compounds are independent of excitation wavelength.

Compound	Absorption Onset, λ_{onset} (nm)[a,b]	Absorption Maximum, λ_{max} (nm)[a]	Emission Maximum, λ_{max} (nm)[a]	Photophysical E_g (eV)[a,c]
2d	375	297	414	3.31
3-Trim$_a$	393	351	426	3.16
2g	410	329	432	3.02
3-Trim$_b$	420	367	442	2.95
2l	438	339	465	2.83
3-Trim$_c$	442	384	468	2.81
2j	429	315, 344	452	2.89
3-Dim	431	365	453	2.88

Table S4. Summary of relevant photophysical properties. (a) Solvent = CH_2Cl_2; (b) Defined as the point at which the absorption and emission spectra intersect;[29] (c) Estimated from the absorption onset (λ_{onset}): $E_g = 1240/\lambda_{onset}$.

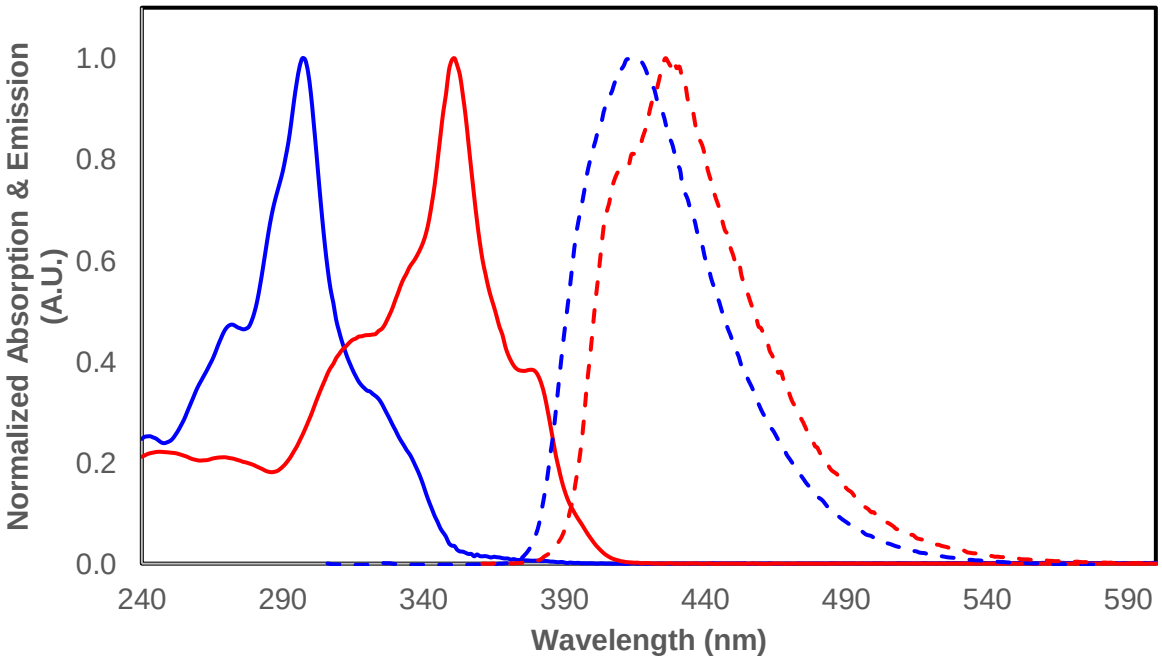


Figure S82. Normalized absorption (solid) and emission (dotted) spectra for AEM **3-Trim$_a$** (red) and its precursor PAH **2d** (blue) in CH_2Cl_2 solvent.

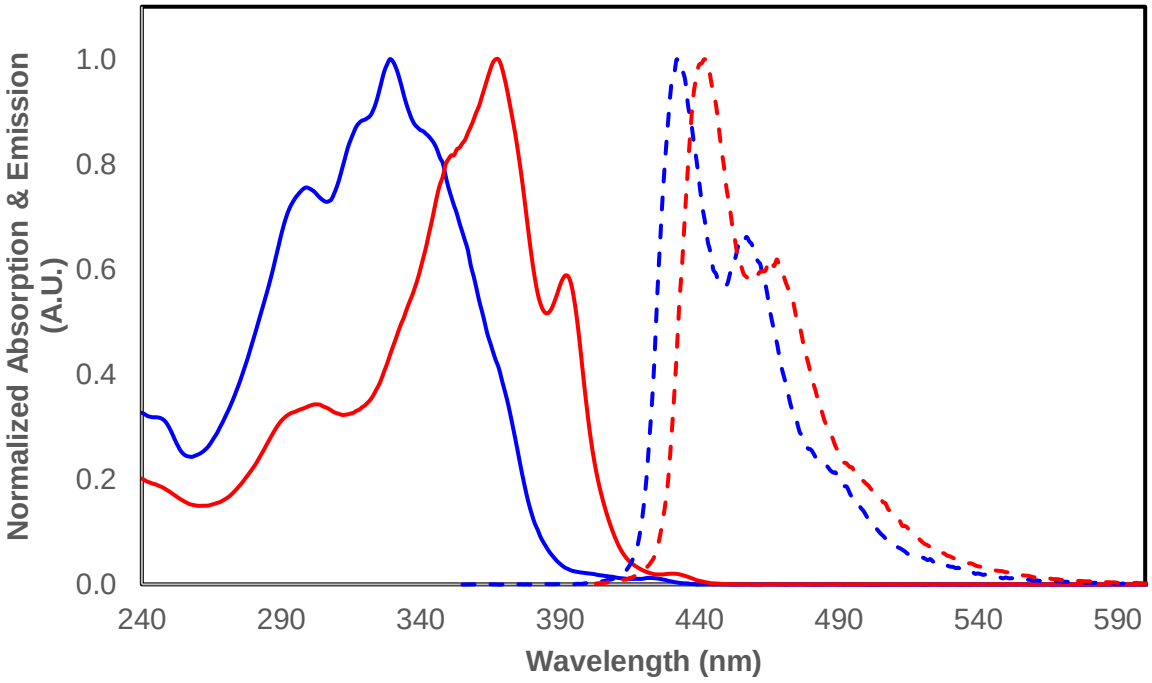


Figure S83. Normalized absorption (solid) and emission (dotted) spectra for AEM **3-Trim$_b$** (red) and its precursor PAH **2g** (blue) in CH_2Cl_2 solvent.

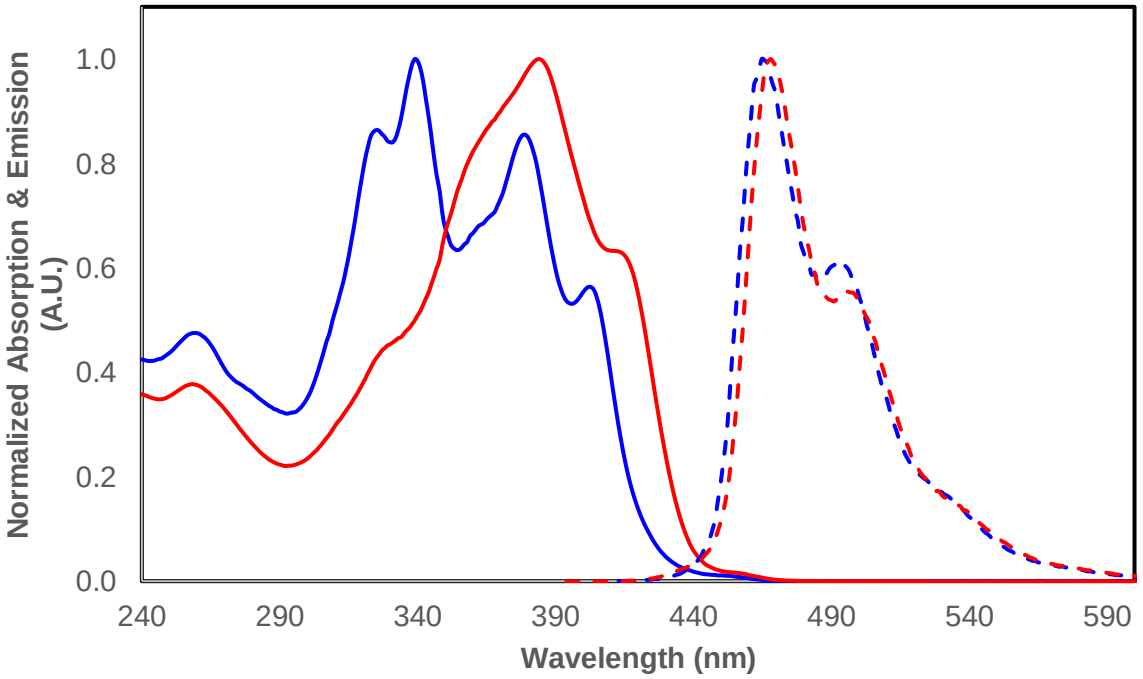


Figure S84. Normalized absorption (solid) and emission (dotted) spectra for AEM **3-Trim$_c$** (red) and its precursor PAH **2l** (blue) in CH_2Cl_2 solvent.

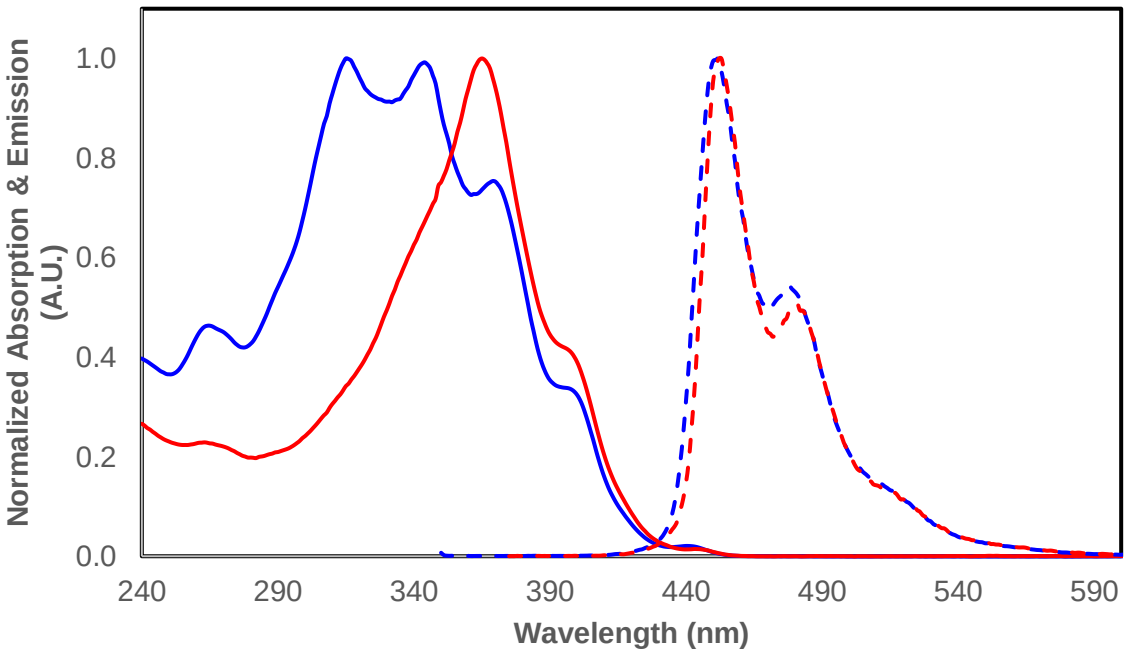


Figure S85. Normalized absorption (solid) and emission (dotted) spectra for AEM **3-Dim** (red) and its precursor PAH **2j** (blue) in CH_2Cl_2 solvent.

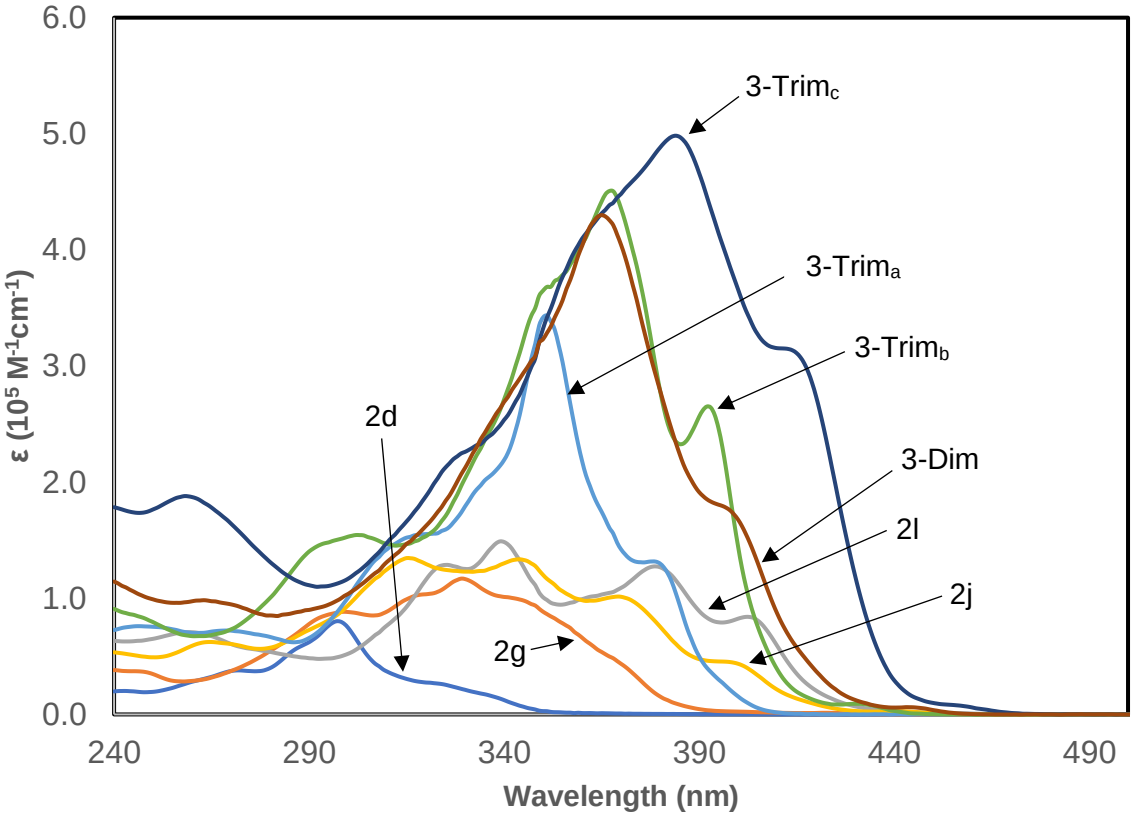


Figure S86. UV/Vis absorption spectra for PAHs **2d**, **2g**, **2l**, and **2j** and AEMs **3-Trim$_a$**, **3-Trim$_b$**, **3-Trim$_c$**, and **3-Dim** (ε = molar absorptivity).

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