

Supporting Information

Chiral Picene Synthesis and Unexpected Transformations Catalyzed by Brønsted Acid

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and Wesley A. Chalifoux

Table of Contents

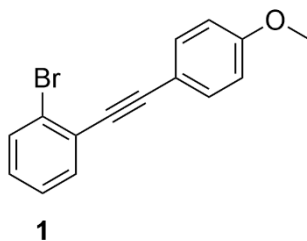
General Experimental.....	S3
Synthesis and Characterization.....	S4
Control Experiment.....	S9
Photophysical Characterization.....	S17
NMR Spectroscopy	S19
References.....	S27

General Experimental

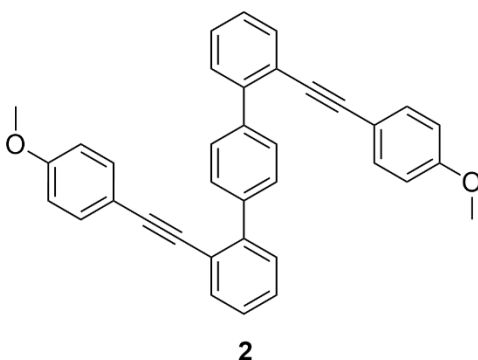
Reagents were purchased reagent grade from commercial suppliers and used without further purification unless otherwise noted. Anhydrous tetrahydrofuran (THF), dichloromethane (DCM), and toluene were dried using a PureSolv MD 7 solvent drying system. Anhydrous THF used is spectrophotometric grade 99.7+% unstabilized. Triethylamine was distilled under N₂ from calcium hydride. Where appropriate, reactions were performed in standard, dry glassware under an inert atmosphere of N₂. Purification of the crude products was carried out by column chromatography using silica gel technical grade 60 Å (40–63 µm). Thin-layer chromatography (TLC) was performed on glass sheets covered with silica gel 60 F₂₅₄ which were visualized under UV light. NMR spectra were recorded on a 400, 500, 600, 700, or 800 MHz NMR spectrometer in CDCl₃, C₆D₆, (CD₃)₂CO or CD₂Cl₂. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to residual protium in the NMR solvent (CDCl₃, δ 7.26; C₆D₆, δ 7.16; (CD₃)₂CO, δ 2.05; CD₂Cl₂, δ 5.32). Data for ¹H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad, appt = apparent), coupling constant (*J*) in hertz, and integration. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonance of the NMR solvent (CDCl₃, δ 77.16).

Infrared (IR) spectra were recorded on a Thermo Nicolet 8700 FTIR, and continuum FTIR microscope, neat or as films. Only major functional group peaks are reported as cm⁻¹. High-resolution mass spectra (HRMS) were obtained from a ThermoScientific Orbitrap Exactive instrument (DART), ThermoScientific Orbitrap Exploris 240 instrument (DART), or a Bruker 9.4T Apex-Qe FTICR instrument (MALDI). Commercially available chemicals were used without further purification. X-ray crystallographic analysis was performed using a Bruker SMART APEX single-crystal X-ray diffractometer at the Department of Chemistry, University of Nevada, Reno and a Bruker D8 Venture/PHOTON III diffractometer at the Department of Chemistry, University of Alberta. UV–Vis spectroscopy measurements were carried out on a Beckman Coulter DU® 800 UV/Visible spectrophotometer at rt with quartz cuvettes having one-centimeter path length. The wavelengths are recorded in nm. The system includes a visible lamp (tungsten) and a UV lamp (deuterium-halogen). The fluorescence spectra were recorded on a Horiba-PTI QM-8075-11 Fluorescence System instrument.

Synthesis and Characterization



Compound 1 was synthesized following a literature procedure and the characterization data matches previously reported data.^[46]

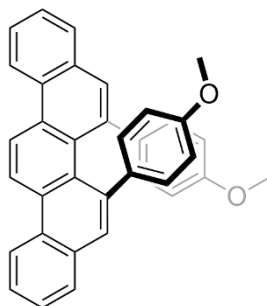


Compound 2: In a round bottom flask, a mixture of THF (30 mL) and H₂O (8 mL) was deoxygenated for 15 min via bubbling with N₂. 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (500 mg, 1.52 mmol), **1** (957 mg, 3.33 mmol), K₂CO₃ (838 mg, 6.07 mmol), and Pd(PPh₃)₄ (174 mg, 0.607 mmol) were added, and the resulting mixture was heated to reflux and stirred under a N₂ atmosphere for 24 h. The reaction mixture was cooled to rt, diluted with DCM (15 mL), and the resulting mixture was washed with H₂O (30 mL), followed by brine (30 mL). The organic phase was dried over MgSO₄ then filtered. The filtrate was concentrated to dryness under reduced pressure and the crude product was purified by column chromatography (silica gel, hexane/DCM 2:1) to afford **2** (686 mg, 92%) as a light yellow solid. *R*_f = 0.47 (hexane/DCM 1:1); IR (neat) 3061, 2958, 2215, 1606, 1590, 1509 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.78 (s, 4H), 7.66 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.50 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.41 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 2H), 7.34 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 2H), 7.27–7.24 (m, 4H; partially obscured by residual CHCl₃ signal), 6.74–6.71 (m, 4H), 3.75 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 143.4, 139.9, 133.0, 132.9, 129.7, 129.0, 128.3, 127.2, 122.2, 115.7, 114.1, 92.7, 88.3, 55.4; HRMS (DART(+)-MS) *m/z* for C₃₆H₂₇O₂ [M+H]⁺ calc'd 491.2006, found 491.2006.

Synthesis of Compounds 3 and 4 with TFA

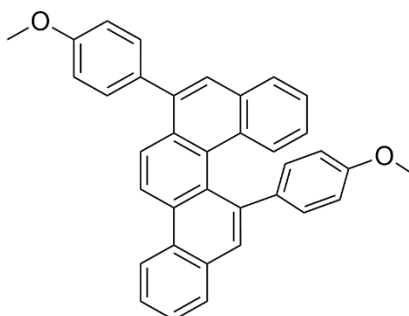
In a flame-dried flask under a N₂ atmosphere, **2** (100 mg, 0.204 mmol) was dissolved in anhydrous DCM (50 mL). The solution was cooled to 0 °C, then TFA (0.78 mL) was added to the solution dropwise over 1 min. After stirring under a N₂ atmosphere for 6 h, the reaction mixture was quenched with saturated NaHCO₃ (10 mL), washed with H₂O (2 x 40 mL), then brine (40 mL). The organic phase was dried over MgSO₄ then filtered. The filtrate was concentrated to dryness under reduced pressure to afford a crude ratio of compounds **3** and **4**, in a 1:1.3 ratio respectively.

The crude mixture was purified by column chromatography (silica gel, hexane/DCM 1:1) to afford compounds **3** and **4**.



3

Compound 3: Obtained as a pale yellow solid (44 mg, 44%). R_f = 0.26 (hexane/DCM 1:1); IR (neat) 3061, 2953, 2929, 2855, 1606, 1507, 1464 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.87 (s, 2H), 8.76 (d, J = 8.3 Hz, 2H), 7.89 (dd, J = 8.2, 1.4 Hz, 2H), 7.68 (ddd, J = 7.0, 7.0, 1.4 Hz, 2H), 7.62 (ddd, J = 7.0, 7.0, 1.0 Hz, 2H), 7.45 (s, 2H), 6.83–6.39 (br m, 8H), 3.81 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.4, 139.5, 136.4, 132.4, 131.0, 129.2 (br), 128.4, 128.3, 127.6 (br), 126.9, 126.4, 123.1, 121.9, 114.9 (br), 112.6 (br), 55.5; HRMS (DART(+)-MS) m/z for $\text{C}_{36}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc'd 491.2006, found 491.2002.

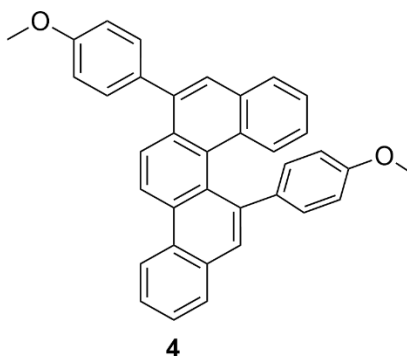


4

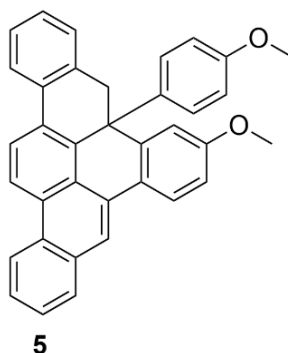
Compound 4: Obtained as a yellow solid (56 mg, 56%). R_f = 0.39 (hexane/DCM 1:1); IR (DCM, cast) 3061, 2956, 2835, 1608, 1509, 1465 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.76–8.73 (m, 2H), 8.12 (d, J = 8.8 Hz, 1H), 8.04 (dd, J = 7.5, 1.6 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.94 (s, 1H), 7.76 (s, 1H), 7.72–7.65 (m, 3H), 7.61–7.58 (m, 2H), 7.25 (ddd, J = 7.0, 6.9, 1.1 Hz, 1H; partially obscured by residual CHCl_3 signal), 7.13–7.10 (m, 2H), 6.99 (ddd, J = 7.0, 7.0, 1.3 Hz, 1H), 6.56 (br s, 2H), 3.95 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.3, 158.2, 139.1, 137.4, 136.7, 133.4, 132.3, 131.8, 131.4, 131.1, 130.63, 130.62, 129.9, 129.6, 129.5, 129.3, 128.8, 128.5, 128.0, 127.0, 126.7, 126.4, 125.8, 125.3, 124.3, 123.3, 121.2, 114.0, 113.6 (br), 55.6, 55.4 (one signal missing due to coincidental overlap); HRMS (DART(+)-MS) m/z for $\text{C}_{36}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$ calc'd 491.2006, found 491.1999.

Synthesis of Compounds 4, 5, and 6 with TFA+TfOH

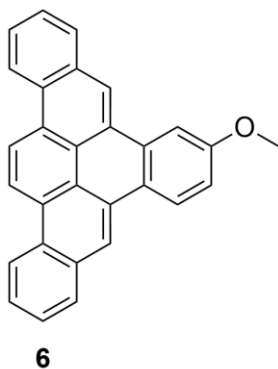
In a flame-dried flask under a N₂ atmosphere, **2** (202 mg, 0.412 mmol) was dissolved in anhydrous DCM (100 mL). The solution was cooled to 0 °C, then TFA (1.56 mL, 21 mmol) was added to the solution dropwise over 2 minutes. After stirring under N₂ atmosphere for 4 hours, a DCM solution (10 mL) of TfOH (140 mg, 0.93 mmol) was slowly added to the reaction mixture at 0 °C, and the reaction warmed to room temperature and stirred overnight. The reaction mixture was quenched with saturated NaHCO₃ (75 mL), washed with H₂O (75 mL) then brine (75 mL). The organic phase was dried over MgSO₄ then filtered. The filtrate was concentrated to dryness under reduced pressure, and the crude mixture was purified by column chromatography (silica gel, hexane/DCM 1:1) to give products **4**, **5**, and **6**.



Compound 4: Obtained as a yellow solid (81 mg, 40%). The spectroscopic characterization data of the product obtained by this method were consistent with those of the same compound synthesized using the TFA-mediated procedure described above.



Compound 5: Obtained as a white solid (14 mg, 7%). *R*_f = 0.27 (hexane/DCM 1:1); IR (DCM, cast) 3055, 2957, 2836, 2280, 1608, 1576, 1508, 1465 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.73 (d, *J* = 8.8 Hz, 1H), 8.69–8.67 (m, 1H), 8.26 (s, 1H), 8.13 (appt t, *J* = 8.6 Hz, 2H), 7.94 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.82–7.79 (m, 1H), 7.65–7.59 (m, 2H), 7.48–7.44 (m, 1H), 7.30–7.28 (m, 2H), 7.27 (2H; partially obscured by residual CHCl₃ signal), 6.90 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.82–6.79 (m, 2H), 6.41–6.37 (m, 2H), 4.24 (d, *J* = 15.6 Hz, 1H), 3.89 (s, 3H), 3.78 (d, *J* = 15.6 Hz, 1H), 3.52 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.0, 157.2, 144.1, 138.2, 135.4, 134.8, 134.3, 132.5, 132.1, 130.1, 129.9, 129.1, 128.9, 128.8, 128.3, 127.8, 127.3, 127.2, 126.5, 125.8, 123.9, 123.8, 123.7, 122.9, 122.2, 119.6, 113.3, 112.8, 112.6, 55.5, 55.0, 44.8, 40.7 (one signal missing due to coincidental overlap); HRMS (DART(+)-MS) *m/z* for C₃₆H₂₇O₂ [M+H]⁺ calc'd 491.2006, found 491.1996.



Compound 6: Obtained as a yellow-orange solid (71 mg, 35%). R_f = 0.76 (hexane/DCM 1:1); IR (DCM, cast) 3421, 2961, 2925, 2854, 2229, 1688, 1607, 1507, 1464 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.21 (appt s, 2H), 9.01 (d, 1H, J = 7.6 Hz), 9.00 (d, 1H, J = 6.9 Hz), 8.99 (s, 1H), 8.95 (s, 1H), 8.73 (d, J = 8.9 Hz, 1H), 8.27 (appt d, 1H), 8.24–8.22 (m, 2H), 7.85–7.75 (m, 4H), 7.32 (dd, J = 8.9, 2.6 Hz, 1H), 4.12 (s, 3H); ^{13}C NMR (201 MHz, CDCl_3) δ 159.9, 132.3, 131.8, 131.6, 129.4, 129.2, 129.0, 128.8, 128.6, 128.5, 128.3, 128.2, 126.9, 126.84, 126.80, 126.3, 125.8, 124.62, 124.61, 124.0, 123.12, 123.08, 122.4, 122.3, 121.0, 120.0, 116.3, 107.1, 55.8; HRMS (MALDI-FTICR, DCTB MATRIX) m/z for $\text{C}_{29}\text{H}_{18}\text{O}$ [M^+] calc'd 382.1352, found 382.1354.

TFA-Promoted Benzannulation of Compound 2 Monitored by NMR

In a vial, compound **2** (6 mg, 0.012 μmol) was dissolved in CD_2Cl_2 (3 mL). The solution was stirred until homogenous, then 0.70 mL of the solution was added to an NMR tube that was then capped. The tube was cooled to 0 $^\circ\text{C}$, then TFA (11.0 μL , 0.143 μmol) was added and the reaction was monitored by NMR.

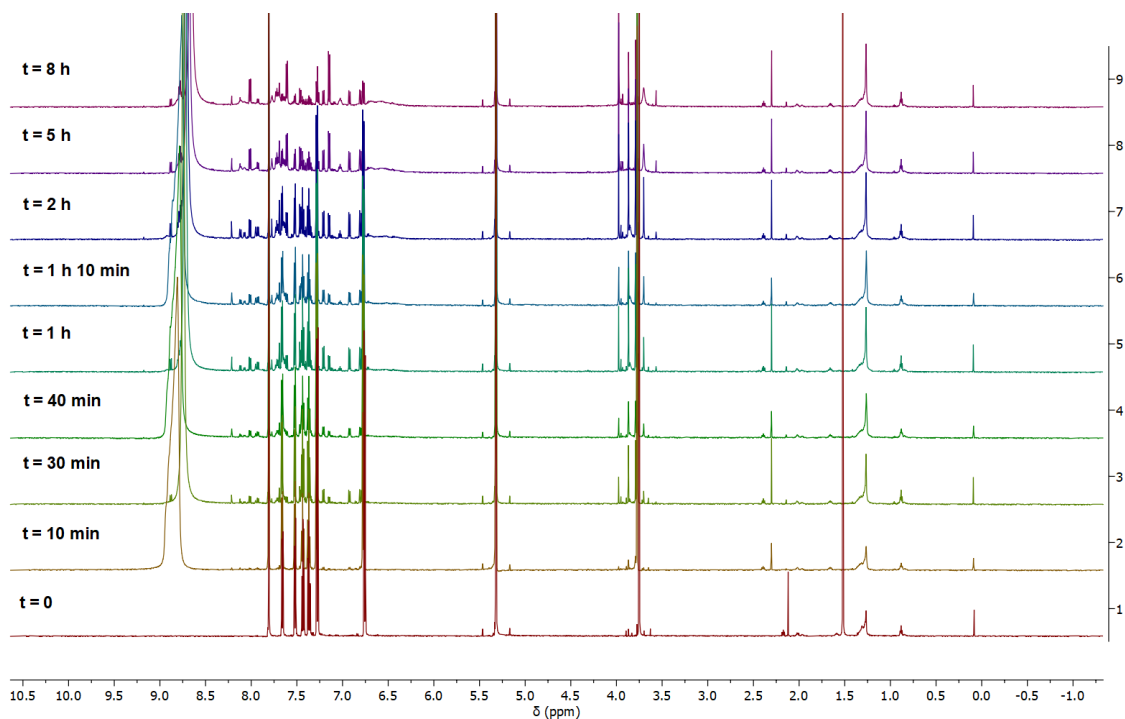


Figure S1. Stacked ^1H NMR spectra (600 MHz, CD_2Cl_2 , 0 $^\circ\text{C}$) monitoring the TFA-promoted benzannulation of compound **2** over time.

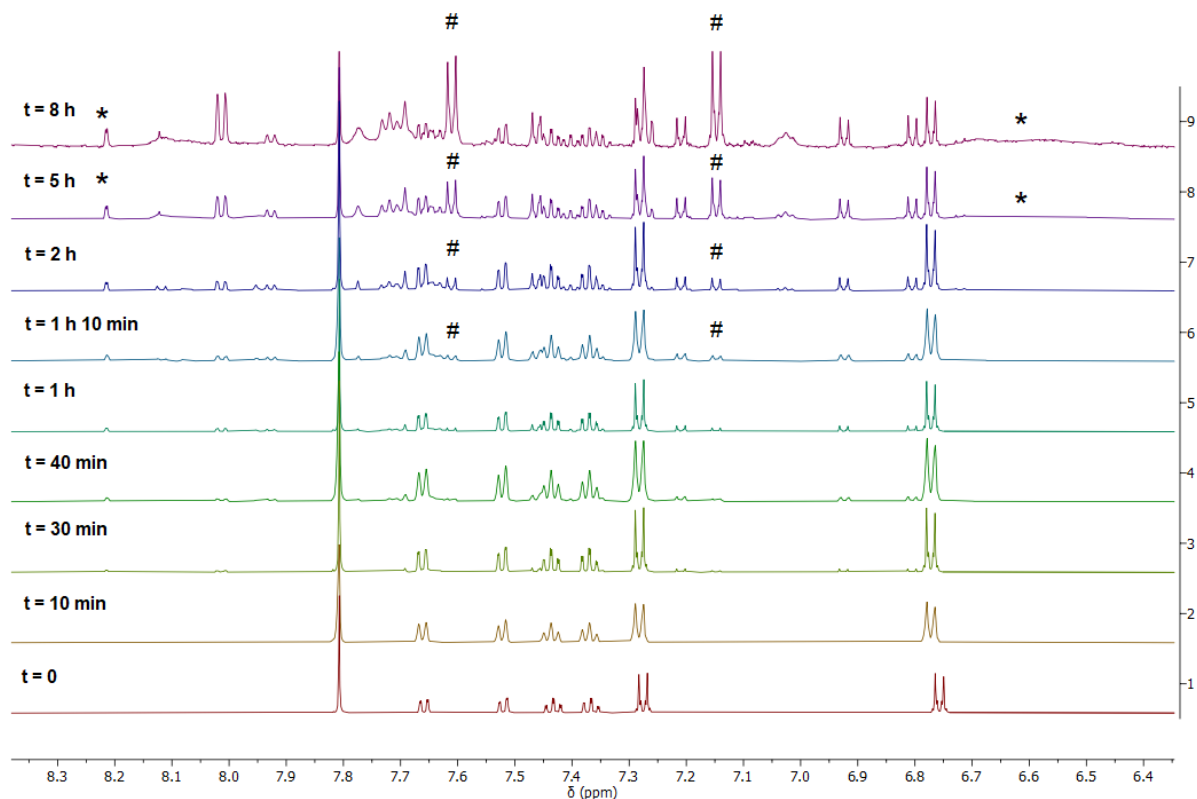


Figure S2. Inset of **Figure S1** showing formation of compounds **3** (*) and **4** (#) with selected peaks highlighted.

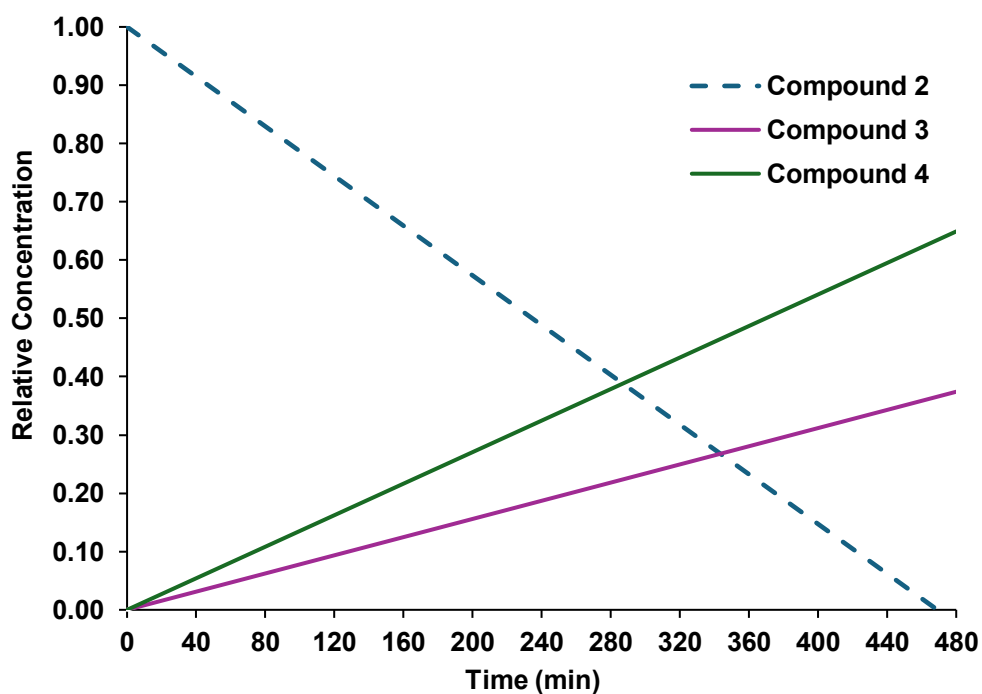
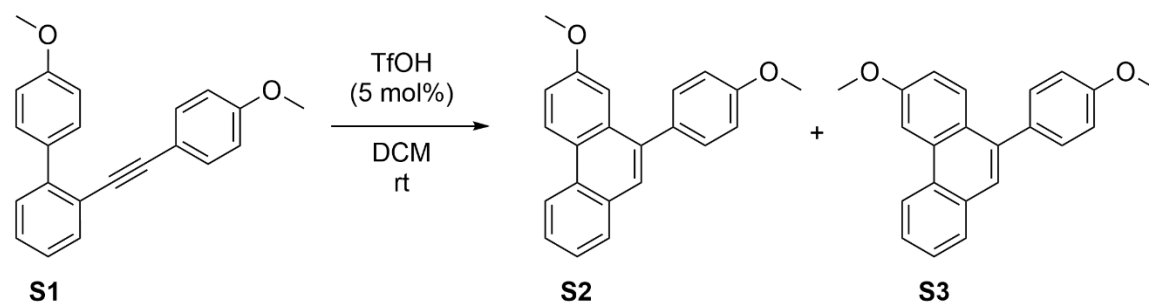


Figure S3. Linear plot of the TFA-promoted benzannulation of compound **2** forming compounds **3** and **4** over 480 minutes based on **Figure S1**.

Control Experiment



Scheme S1. Control experiment conditions for investigation of the Brønsted acid-mediated alkyne benzannulation mechanistic pathway of compounds **3** and **4**.

Characterization of compound **S2** matches previously reported data.^[31] Minor signals in the isolated product mixture (Figure S26) are attributed to compound **S3**. Notably, the previously reported spectroscopic data for **S2** also contain these signals, which were not previously identified.^[31] The structure of **S3** is supported by comparison to the ¹H NMR spectrum of 3-methoxyphenanthrene.^[47]

The formation of **S2** and **S3** from this experiment supports the proposed mechanistic pathways for compounds **3** and **4**. As shown in Figure S4, protonation of the alkyne in **S1** by Brønsted acid generates a cationic intermediate. Compound **S2** may form through the conventional alkyne benzannulation pathway, in which the π electrons of **S1** attack the vinyl carbocation through a 6-*endo*-dig cyclization (red carbon). Subsequent deprotonation of the 2-methoxyphenanthrene derivative restores aromaticity, affording **S2** and regenerating the acid catalyst. Alternatively, a 5-*endo*-dig cyclization (blue carbon) may generate a spirocyclic intermediate that undergoes bond migration (red arrow), followed by rearomatization to also yield **S2**.

The formation of **S3** provides further evidence for the spirocyclic pathway. Following the 5-*endo*-dig cyclization (blue carbon), an alternative bond migration (blue arrow), and subsequent rearomatization forms **S3**. Although previously unrecognized in the reported synthesis of **S2**,^[31] this minor product supports the involvement of a spirocyclic intermediate whereas the predominant formation of **S2** is consistent with both pathways.

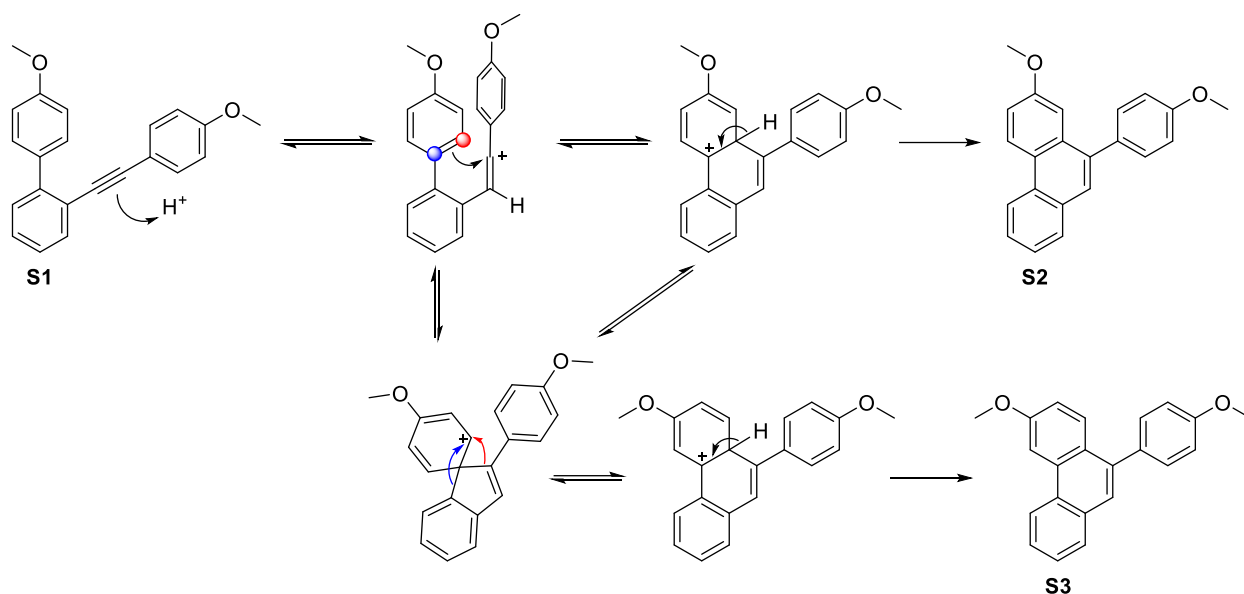


Figure S4. Proposed mechanistic pathways for the formation of compounds **S2** and **S3**.

X-Ray Crystallography^[48-51]

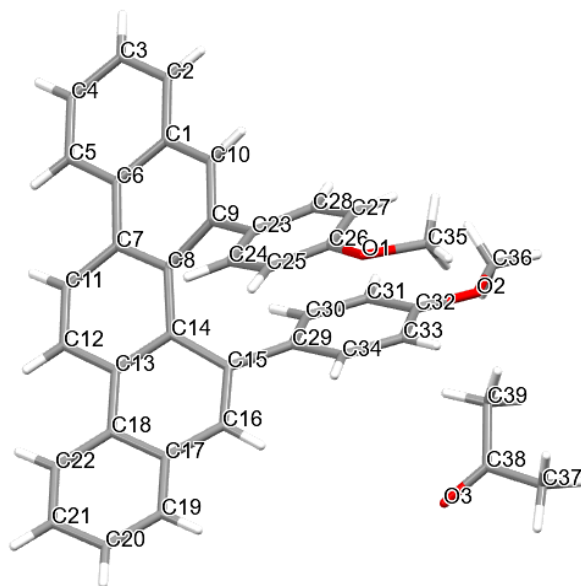


Figure S5. Crystal structure of **3**.

Table S1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{39}H_{32}O_3$
Formula weight	548.64
Temperature	100(2) K
Wavelength	0.71073 Å

Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 12.6371(3) \text{ \AA}$ $\alpha = 112.93^\circ$. $b = 15.2284(4) \text{ \AA}$ $\beta = 96.26^\circ$. $c = 17.5862(4) \text{ \AA}$ $\gamma = 108.02^\circ$.
Volume	$2860.12(12) \text{ \AA}^3$
Z	4
Density (calculated)	1.274 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	1160
Crystal size	$0.400 \times 0.160 \times 0.100 \text{ mm}^3$
Theta range for data collection	1.303 to 29.575° .
Index ranges	$-17 \leq h \leq 17$, $-21 \leq k \leq 21$, $-24 \leq l \leq 24$
Reflections collected	69441
Independent reflections	16046 [$R(\text{int}) = 0.0402$]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.7163
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16046 / 6 / 788
Goodness-of-fit on F^2	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0512$, $wR_2 = 0.1350$
R indices (all data)	$R_1 = 0.0756$, $wR_2 = 0.1456$
Extinction coefficient	n/a
Largest diff. peak and hole	0.671 and $-0.580 \text{ e.\AA}^{-3}$

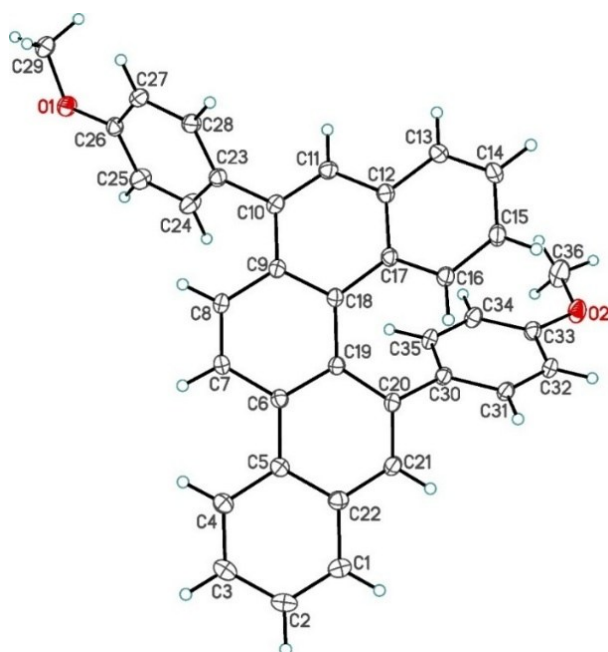


Figure S6. Crystal structure of **4**.

Table S2. Crystal data and structure refinement for **4**.

formula	C ₃₆ H ₂₆ O ₂
formula weight	490.57
crystal colour and habit	colourless plate
crystal dimensions (mm)	0.32 x 0.17 x 0.04
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (an alternate setting of <i>P</i> 2 ₁ / <i>c</i> [No. 14])
unit cell parameters	
<i>a</i> (Å)	12.5378(3)
<i>b</i> (Å)	9.4860(2)
<i>c</i> (Å)	21.9988(6)
β (deg)	105.0417(9)
<i>V</i> (Å ³)	2526.75(11)
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.290
μ (mm ⁻¹)	0.611
diffractometer	Bruker D8 Venture/PHOTON III
radiation (<i>I</i> [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	−100
scan type	<i>w</i> and <i>f</i> scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	144.27
total data collected	57523 (−15 ≤ <i>h</i> ≤ 15, −11 ≤ <i>k</i> ≤ 11, −27 ≤ <i>l</i> ≤ 27)
independent reflections	4978 (<i>R</i> _{int} = 0.0410)

number of observed reflections (<i>NO</i>)	4720 [$F_o^2 \geq 2s(F_o^2)$]
structure solution method	intrinsic phasing (<i>SHELXT-2018/2</i>)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-2019/1</i>)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	1.0000–0.7289
data/restraints/parameters	4978 / 0 / 346
extinction coefficient (<i>x</i>)	0.00148(19)
goodness-of-fit (<i>S</i>) ^{<i>g</i>} [all data]	1.018
final <i>R</i> indices ^{<i>h</i>}	
<i>R</i> ₁ [$F_o^2 \geq 2s(F_o^2)$]	0.0369
<i>wR</i> ₂ [all data]	0.0985
largest difference peak and hole	0.248 and –0.154 e Å ^{–3}

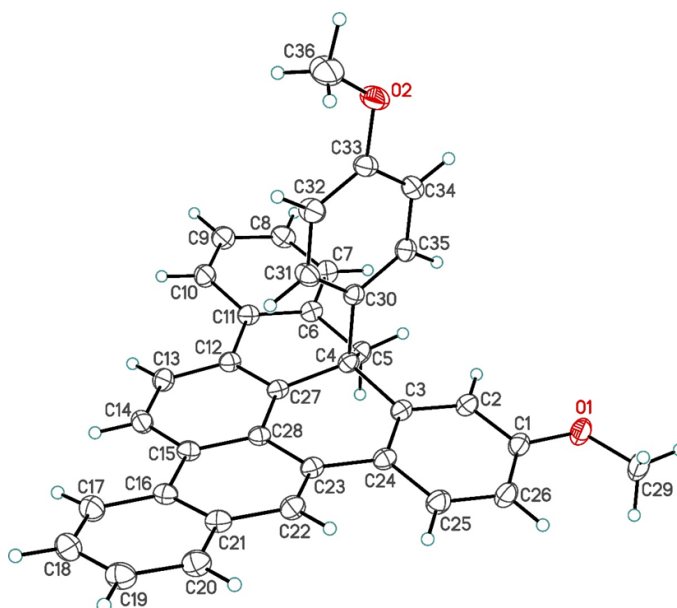


Figure S7. Crystal structure of **5**.

Table S3. Crystal data and structure refinement for **5**.

formula	C ₃₆ H ₂₆ O ₂
formula weight	490.57
crystal colour and habit	colourless block
crystal dimensions (mm)	0.28 x 0.11 x 0.05
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters	
<i>a</i> (Å)	9.1516(4)
<i>b</i> (Å)	9.3293(4)
<i>c</i> (Å)	16.1267(7)
<i>a</i> (deg)	85.0209(19)

<i>b</i> (deg)	76.3769(17)
<i>g</i> (deg)	65.4954(16)
<i>V</i> (Å ³)	1217.51(9)
<i>Z</i>	2
<i>r</i> _{calcd} (g cm ⁻³)	1.338
<i>μ</i> (mm ⁻¹)	0.081
diffractometer	Bruker D8 Venture/PHOTON III
radiation (<i>λ</i> [Å])	Mo Kα (0.71073) (microfocus source)
temperature (°C)	−100
scan type	<i>w</i> and <i>f</i> scans (0.5°) (2 s exposures)
data collection 2 <i>θ</i> limit (deg)	52.08
total data collected	49654 (−11 ≤ <i>h</i> ≤ 11, −11 ≤ <i>k</i> ≤ 11, −19 ≤ <i>l</i> ≤ 19)
independent reflections	4794 (<i>R</i> _{int} = 0.0738)
number of observed reflections (<i>NO</i>)	3839 [<i>F</i> _o ² ≥ 2 <i>s</i> (<i>F</i> _o ²)]
structure solution method	intrinsic phasing (<i>SHELXT</i> -2018/2)
refinement method	full-matrix least-squares on <i>F</i> ² (<i>SHELXL</i> -2019/1)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	1.0000–0.9270
data/restraints/parameters	4794 / 0 / 345
goodness-of-fit (<i>S</i>) [all data]	1.079
final <i>R</i> indices ^g	
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2 <i>s</i> (<i>F</i> _o ²)]	0.0448
<i>wR</i> ₂ [all data]	0.1280
largest difference peak and hole	0.205 and −0.195 e Å ⁻³

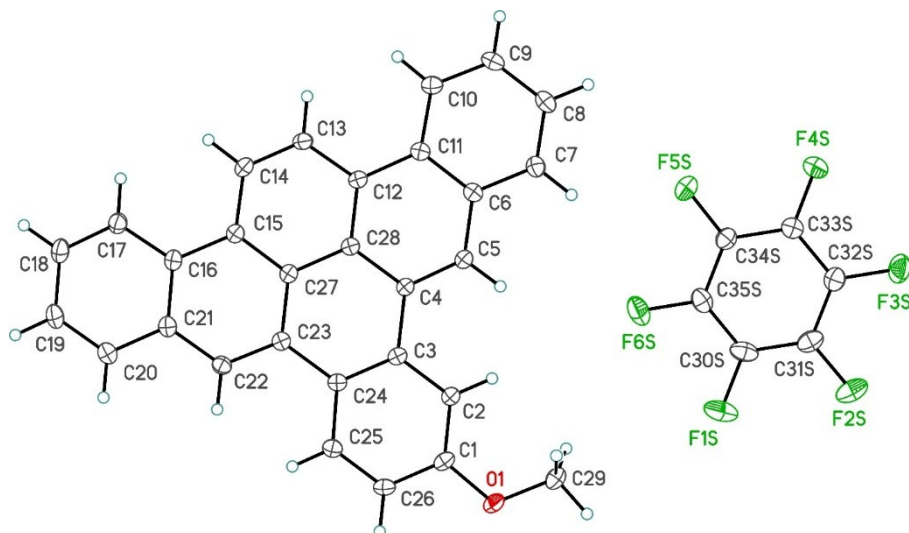


Figure S8. Crystal structure of **6**.

Table S4. Crystal data and structure refinement for **6**.

formula	$\text{C}_{29}\text{H}_{18}\text{O} \cdot \text{C}_6\text{F}_6$
formula weight	568.49
crystal colour and habit	pale-green prism
crystal dimensions (mm)	0.16 x 0.08 x 0.05
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters	
<i>a</i> (Å)	7.2247(3)
<i>b</i> (Å)	12.3147(5)
<i>c</i> (Å)	14.1825(6)
<i>a</i> (deg)	78.2220(17)
<i>b</i> (deg)	83.2971(18)
<i>g</i> (deg)	79.5471(17)
<i>V</i> (Å ³)	1210.58(9)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.560
μ (mm ⁻¹)	1.066
diffractometer	Bruker D8 Venture/PHOTON III
radiation (<i>I</i> [Å])	Cu Ka (1.54178) (microfocus source)
temperature (°C)	−100
scan type	<i>w</i> and <i>f</i> scans (1.5°) (q-dep. exp. from 5-35 s)
data collection 2 <i>q</i> limit (deg)	140.41
total data collected	31516 ($-8 \leq h \leq 8$, $-15 \leq k \leq 14$, $-17 \leq l \leq 17$)
independent reflections	4507 ($R_{\text{int}} = 0.0413$)
number of observed reflections (<i>NO</i>)	3885 [$F_o^2 \geq 2s(F_o^2)$]
structure solution method	intrinsic phasing (<i>SHELXT-2018/2</i>)

refinement method	full-matrix least-squares on F^2 (SHELXL-2019/3)
absorption correction method	numerical
range of transmission factors	1.0000–0.8468
data/restraints/parameters	4507 / 0 / 380
goodness-of-fit (S) [all data]	1.034
final R indices	
R_1 [$F_o^2 \geq 2s(F_o^2)$]	0.0378
wR_2 [all data]	0.1047
largest difference peak and hole	0.219 and -0.264 e $\text{\AA}^{-3}$

Photophysical Characterization

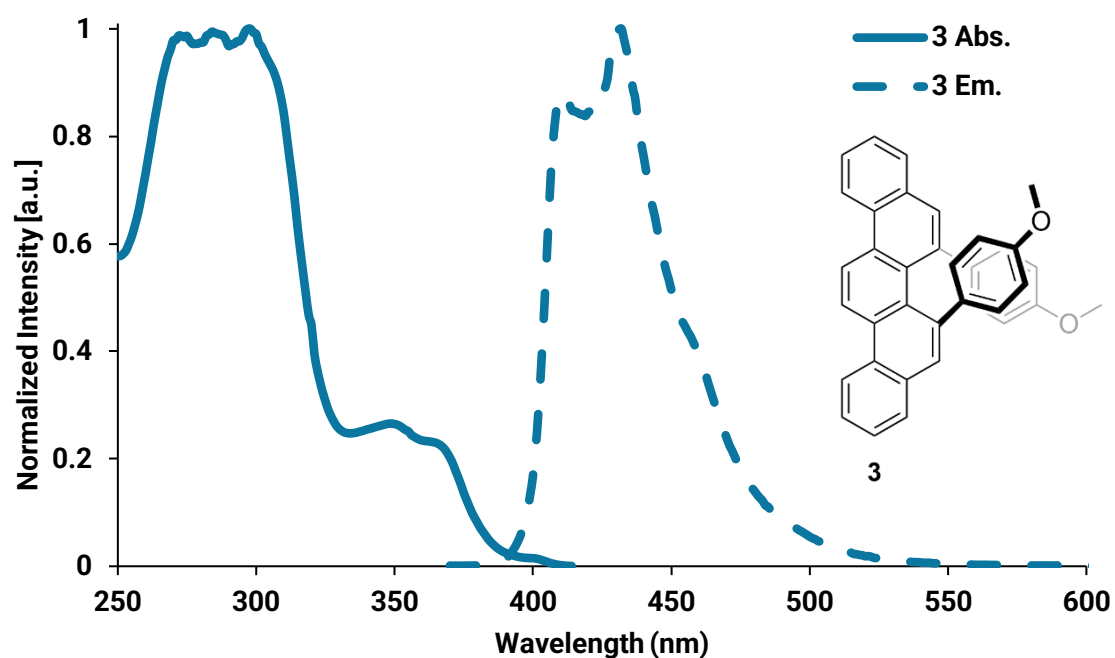


Figure S9. Normalized UV-Vis absorption and emission spectra of compound **3** in DCM (emission: $\lambda_{\text{ex}} = 365$ nm).

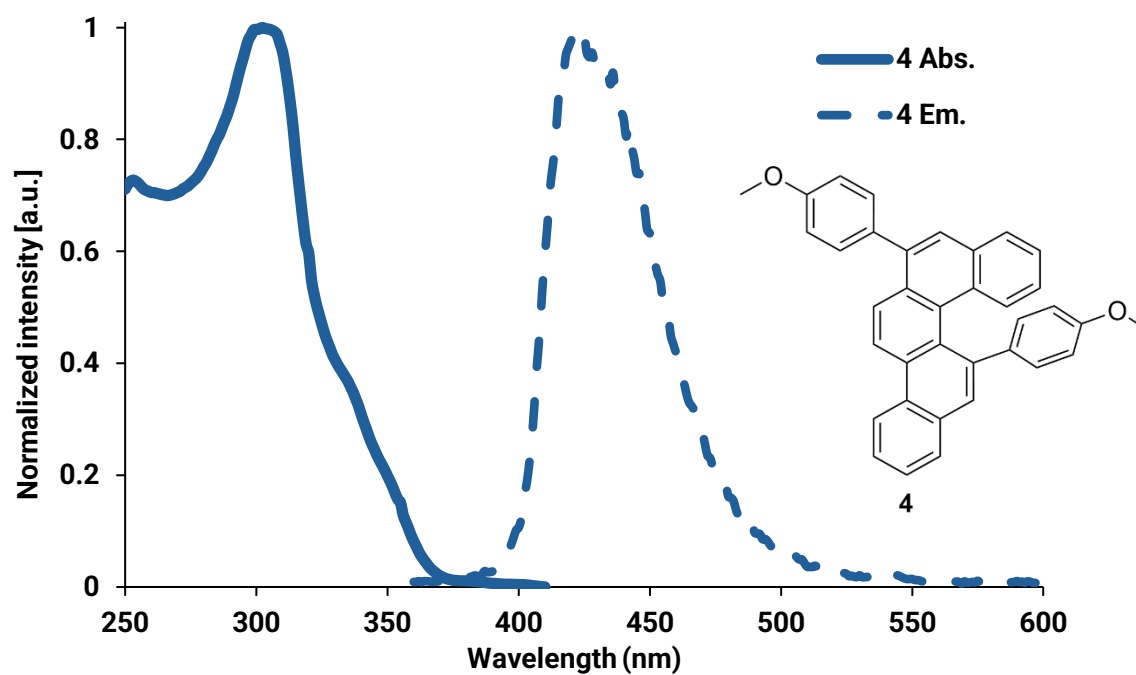


Figure S10. Normalized UV-Vis absorption and emission spectra of compound **4** in DCM (emission: $\lambda_{\text{ex}} = 302$ nm).

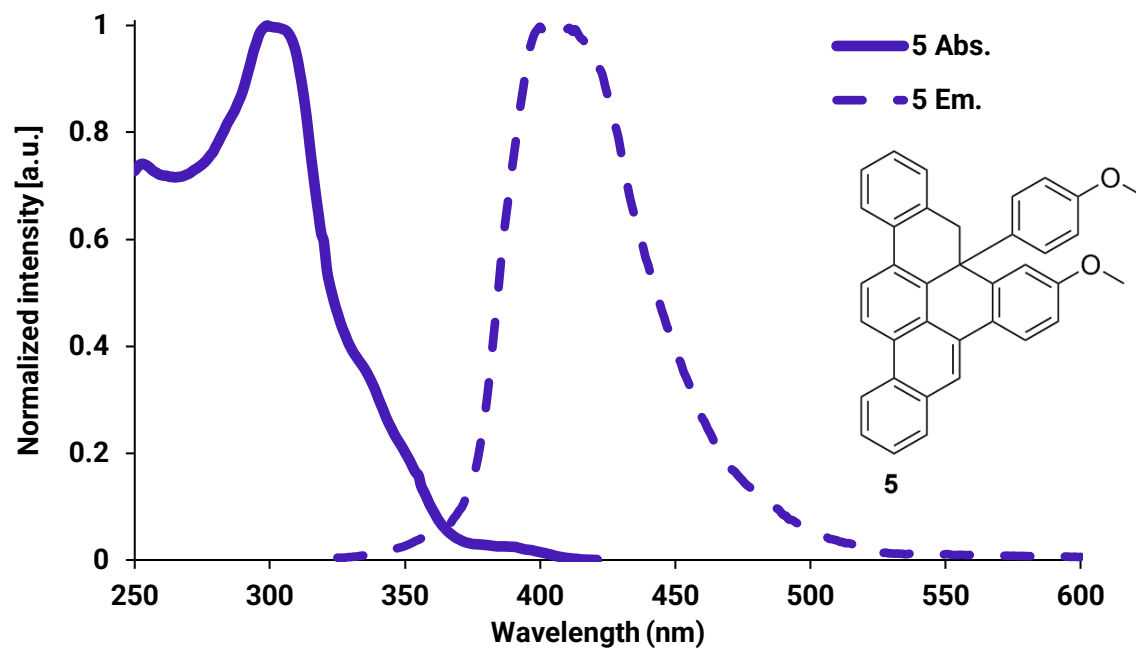


Figure S11. Normalized UV-Vis absorption and emission spectra of compound **5** in DCM (emission: $\lambda_{\text{ex}} = 340$ nm).

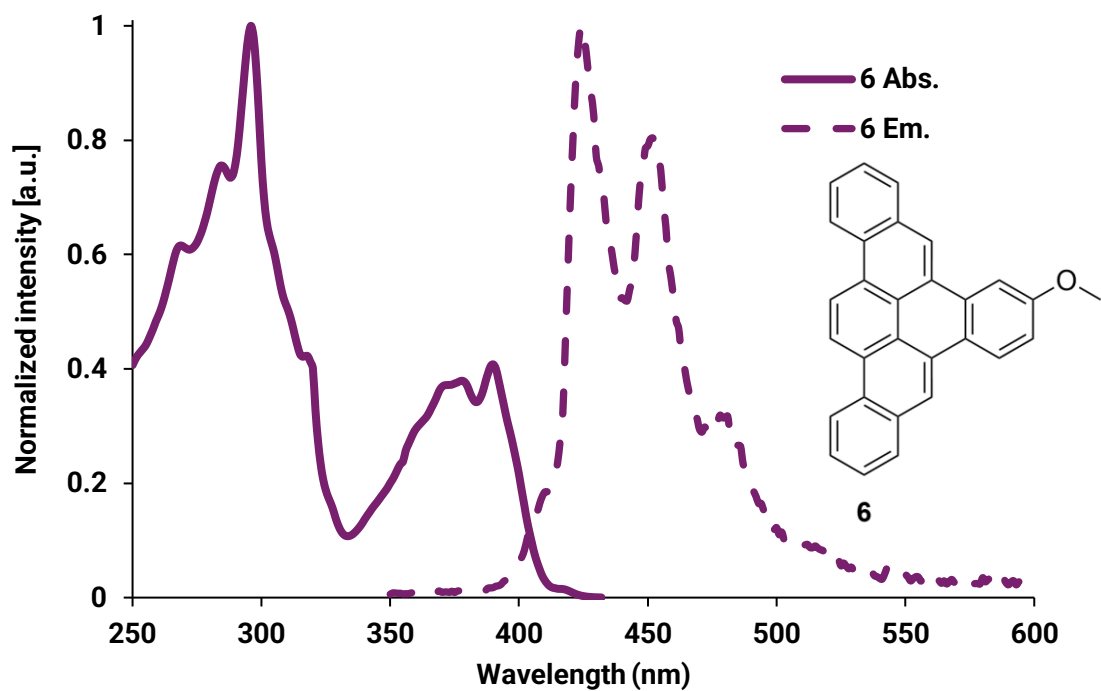


Figure S12. Normalized UV-Vis absorption and emission spectra of compound **6** in DCM (emission: $\lambda_{\text{ex}} = 300$ nm).

NMR Spectroscopy

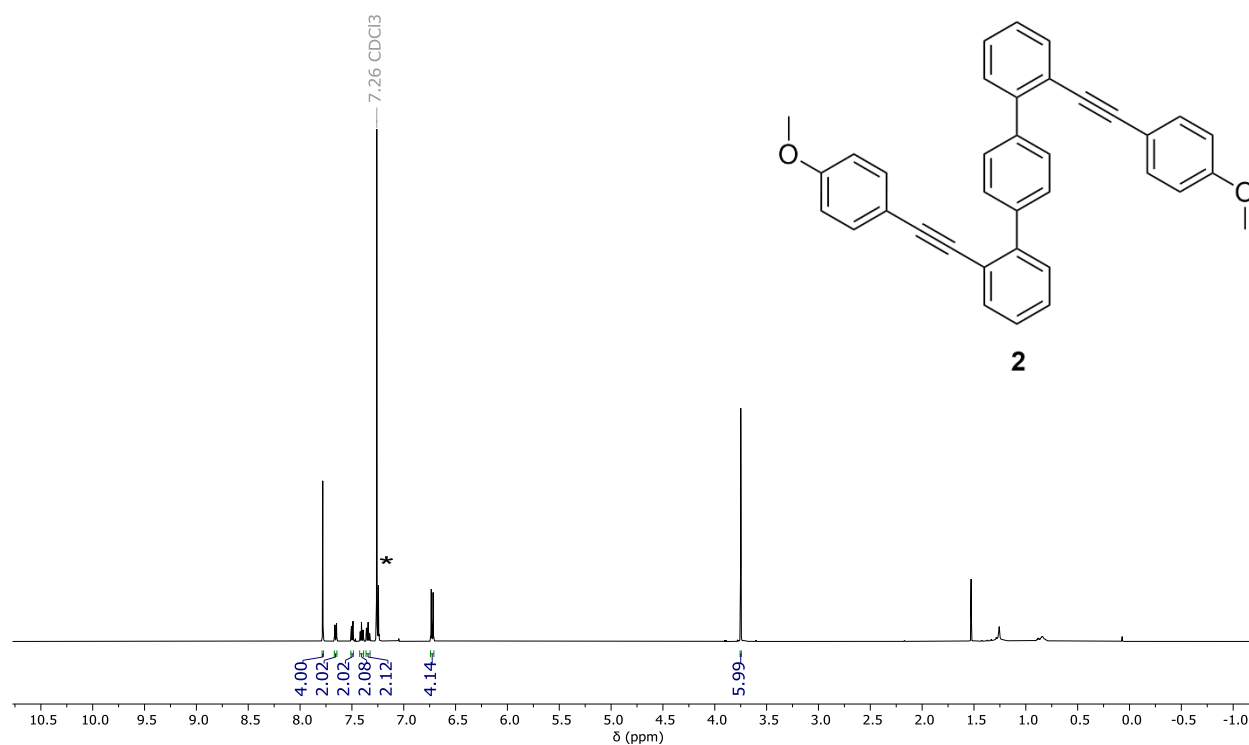


Figure S13. ¹H NMR (500 MHz, CDCl₃) spectrum of compound **2**. (*Note: signal from 7.27–7.24 (m, 4H) partially obscured by residual CHCl₃ signal.)

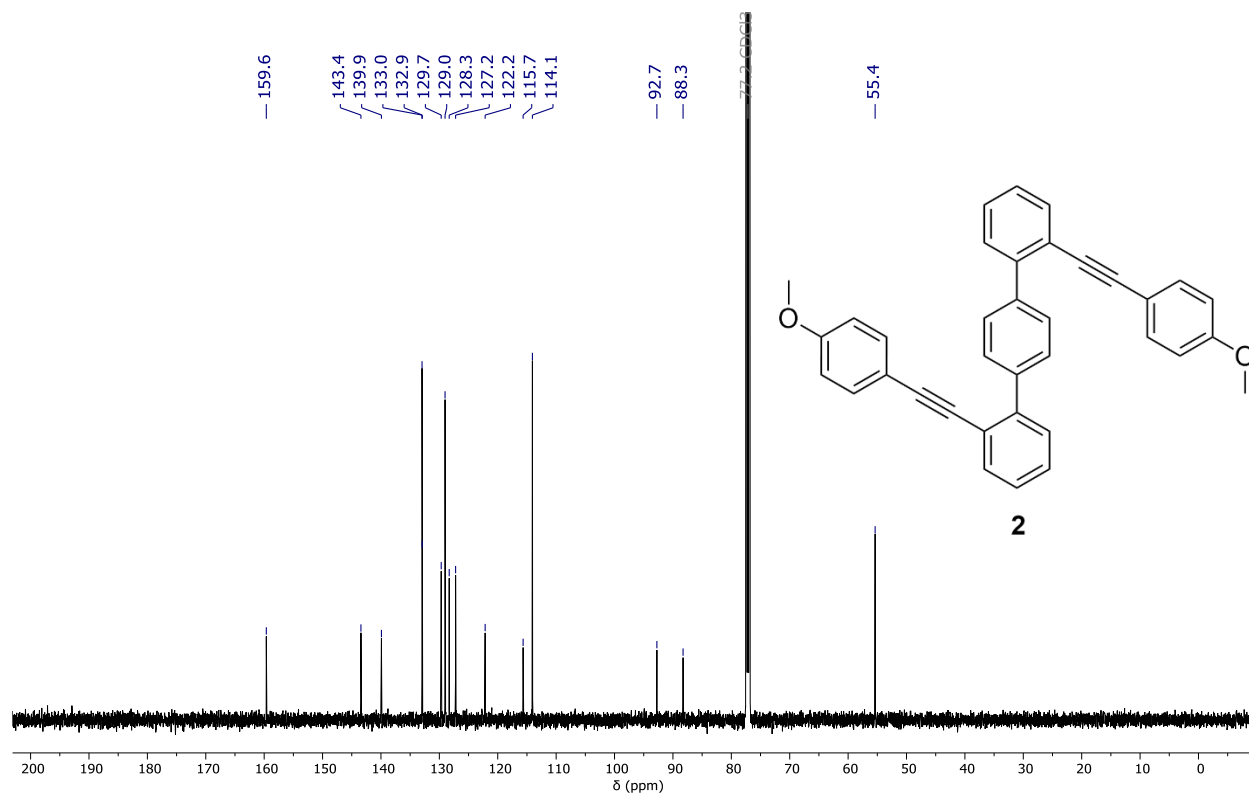


Figure S14. ¹³C NMR (125 MHz, CDCl₃) spectrum of compound **2**.

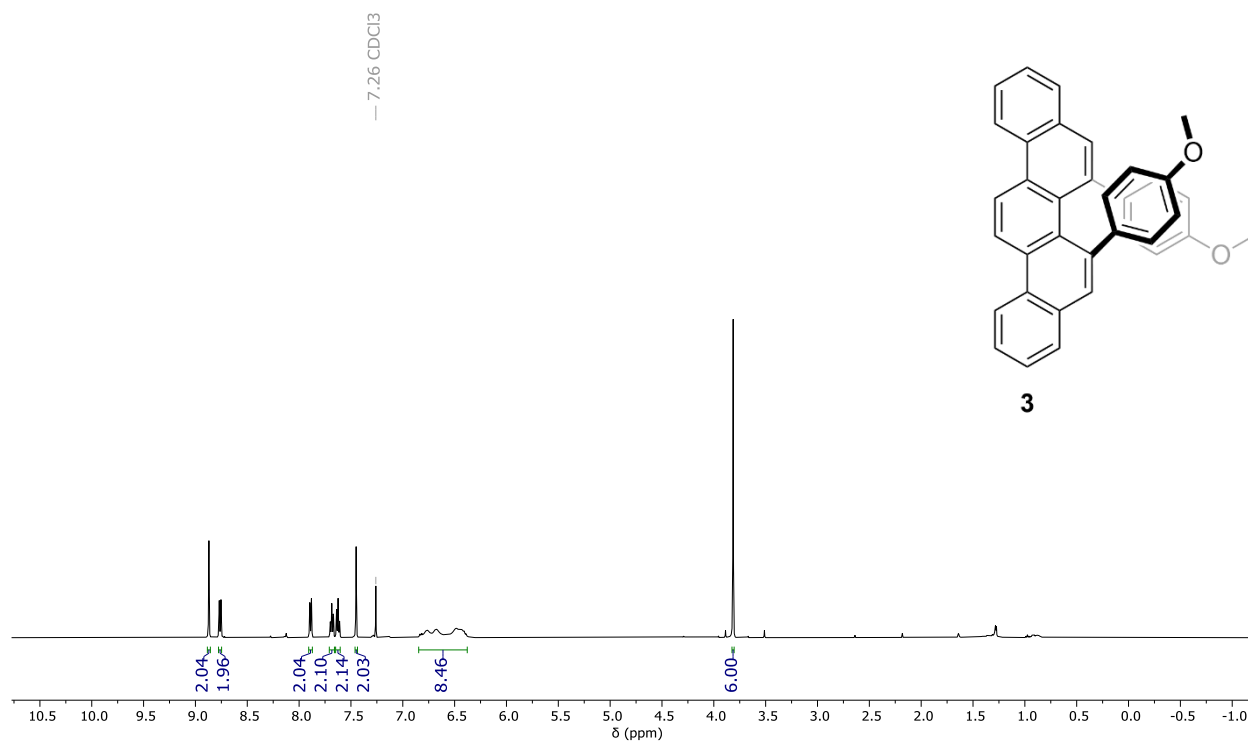


Figure S15. ¹H NMR (500 MHz, CDCl₃) spectrum of compound **3**.

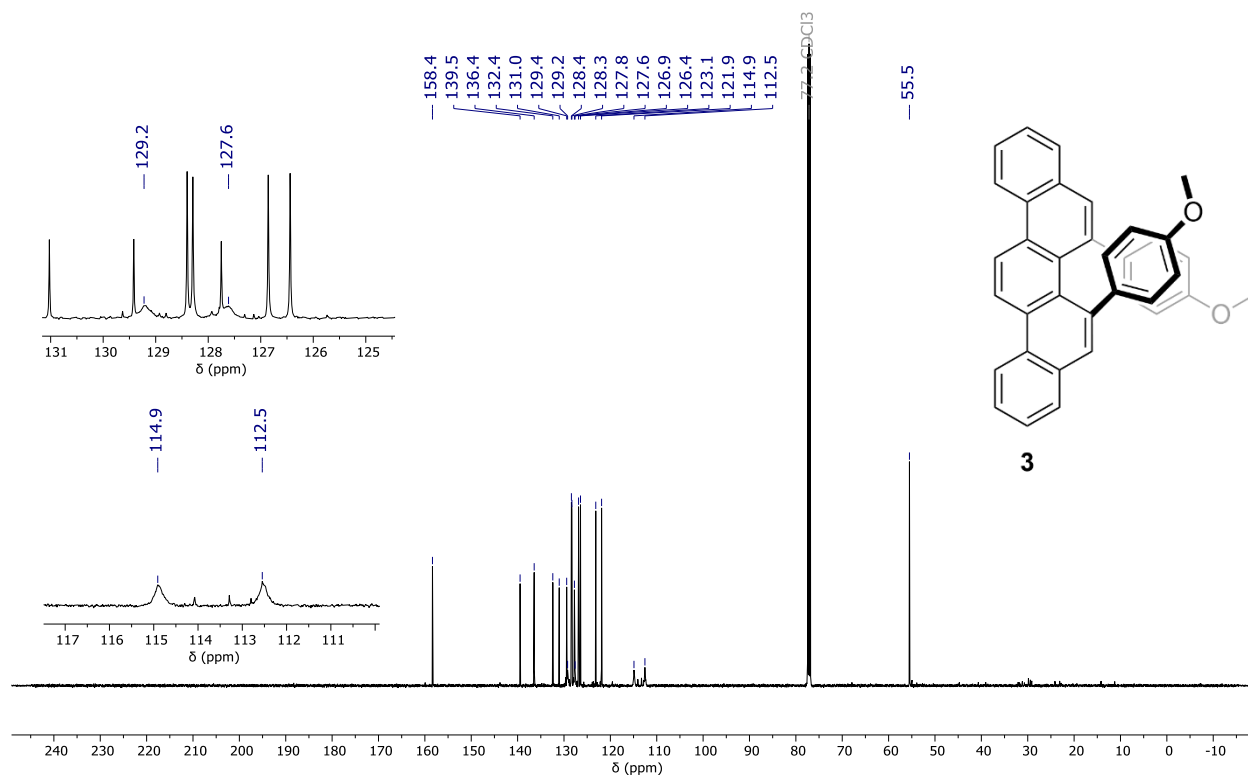


Figure S16. ¹³C NMR (125 MHz, CDCl₃) spectrum of compound **3**. Inset demonstrates signals that are broadened in the spectrum.

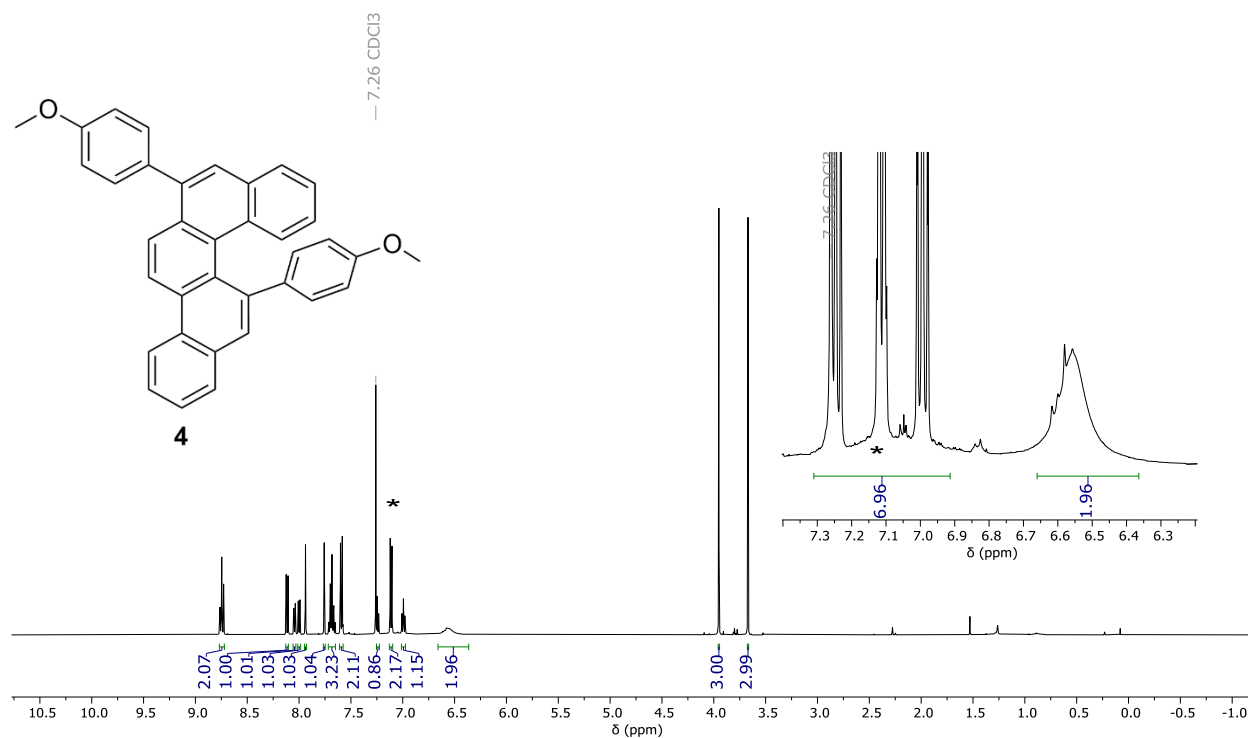


Figure S17. ¹H NMR (500 MHz, CDCl₃) spectrum of compound **4**. (*Note: Signal from 7.25–6.97 (br s, 2H) overlapped, see VT NMR Figure S18 for resolution.)

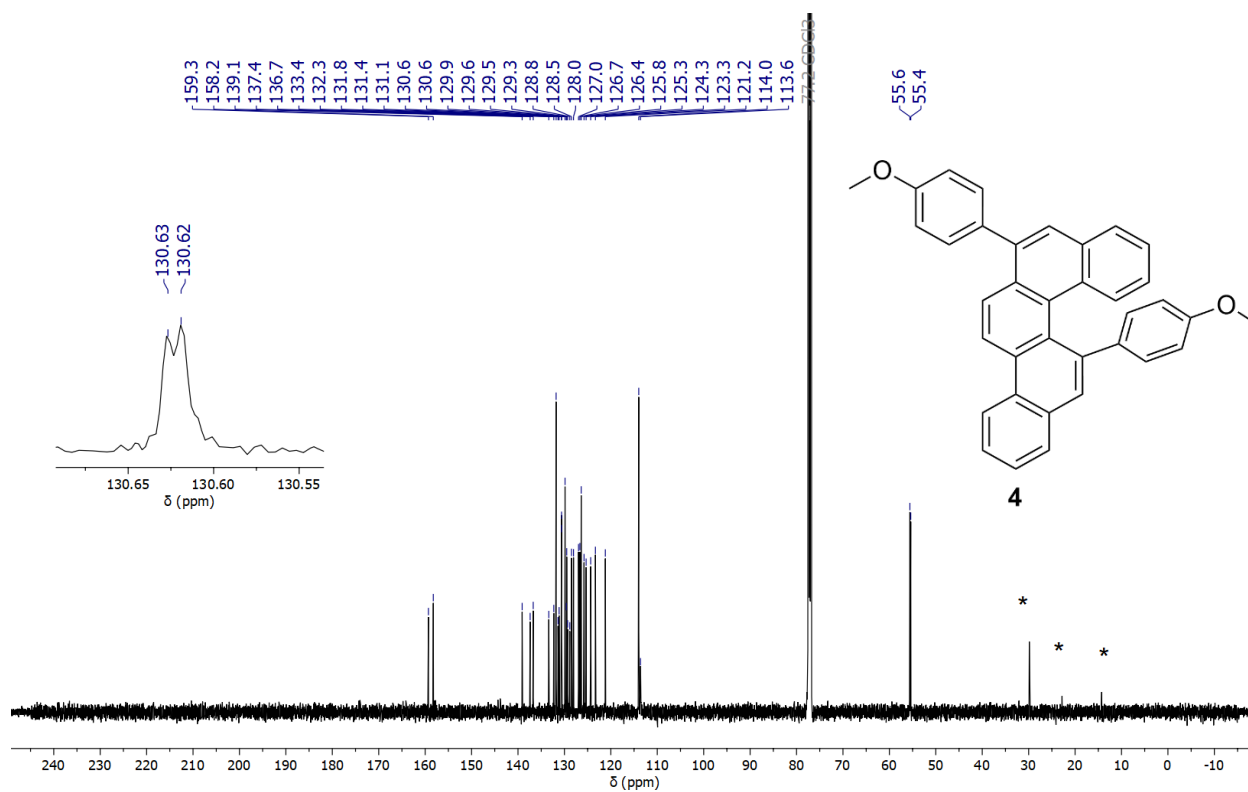


Figure S18. ¹³C NMR (126 MHz, CDCl₃) spectrum of compound **4** (*residual *n*-hexanes).

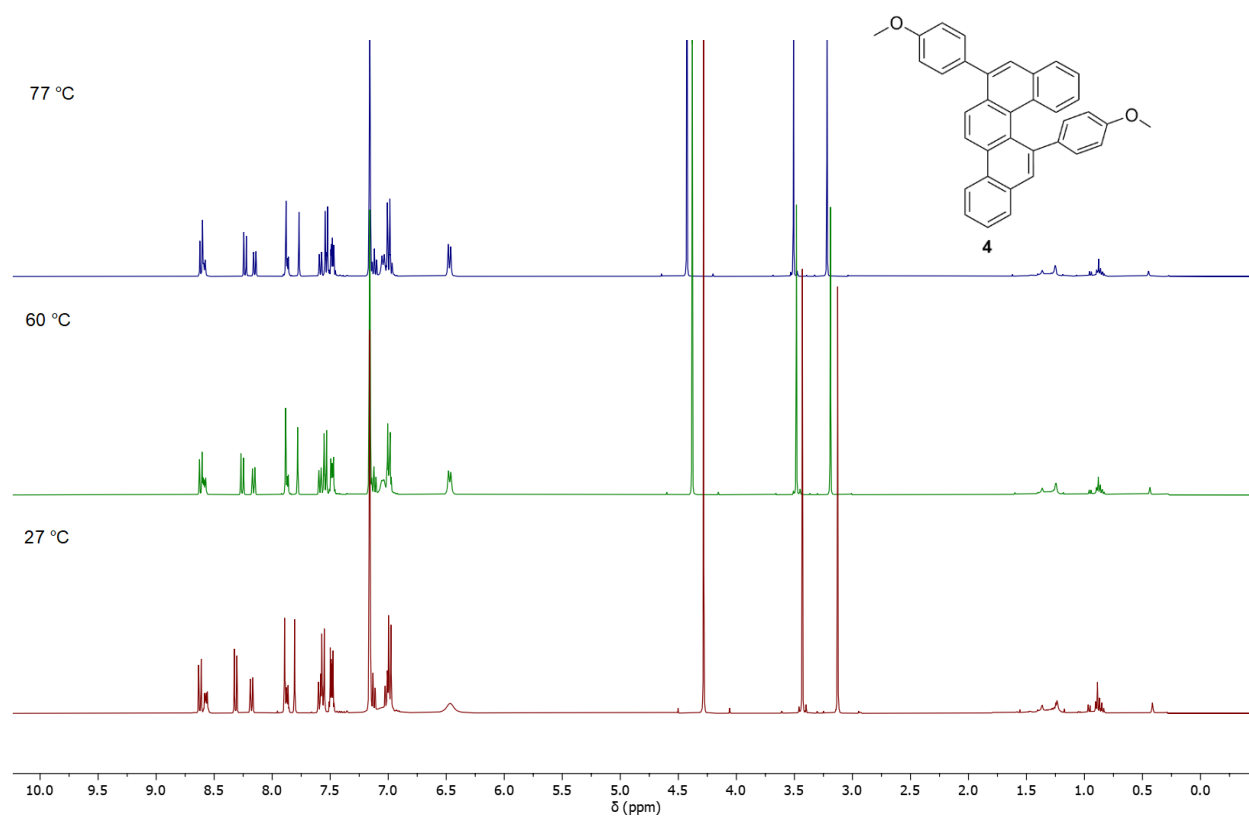


Figure S19. ^1H NMR (400 MHz, C_6D_6) of compound **4** at variable temperatures resolving signals broadened in the baseline due to restricted rotation of the aryl in the cove.

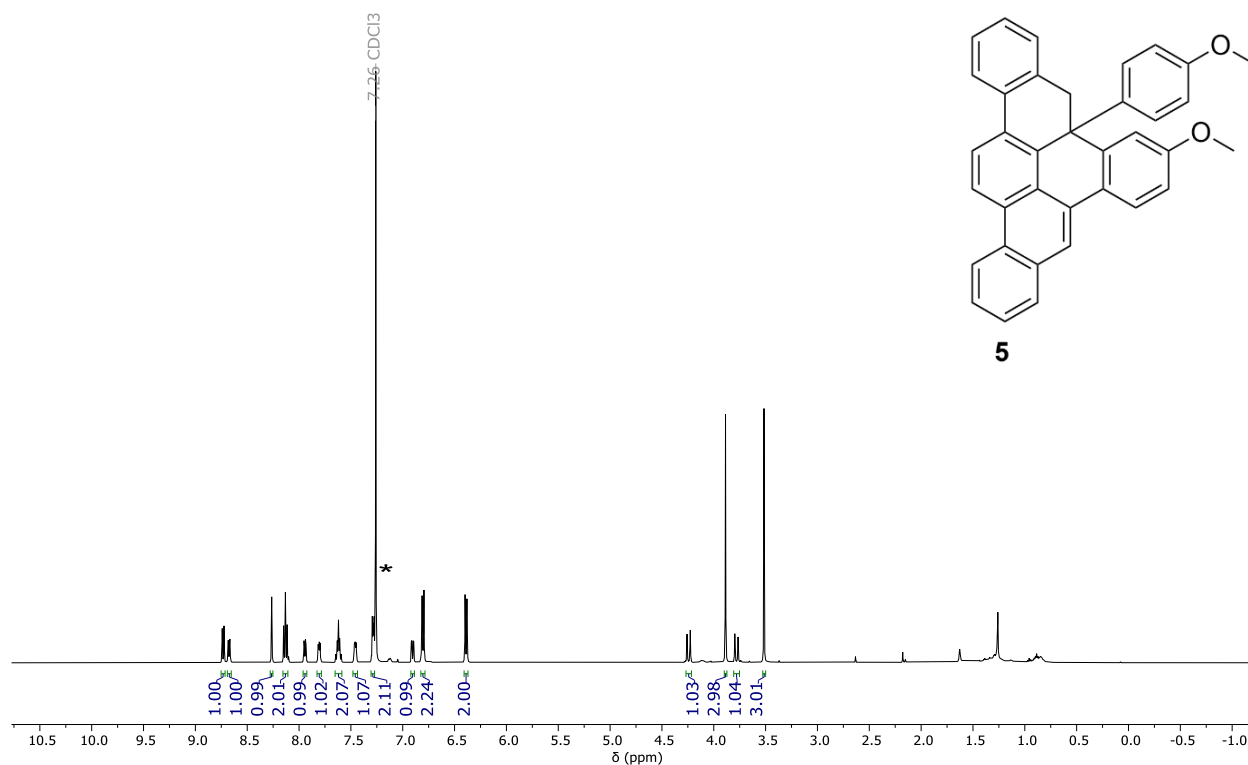


Figure S20. ¹H NMR (500 MHz, CDCl₃) spectrum of compound **5**. (*Note: signal from 7.27–7.26 (2H) partially obscured by residual CHCl₃ signal.)

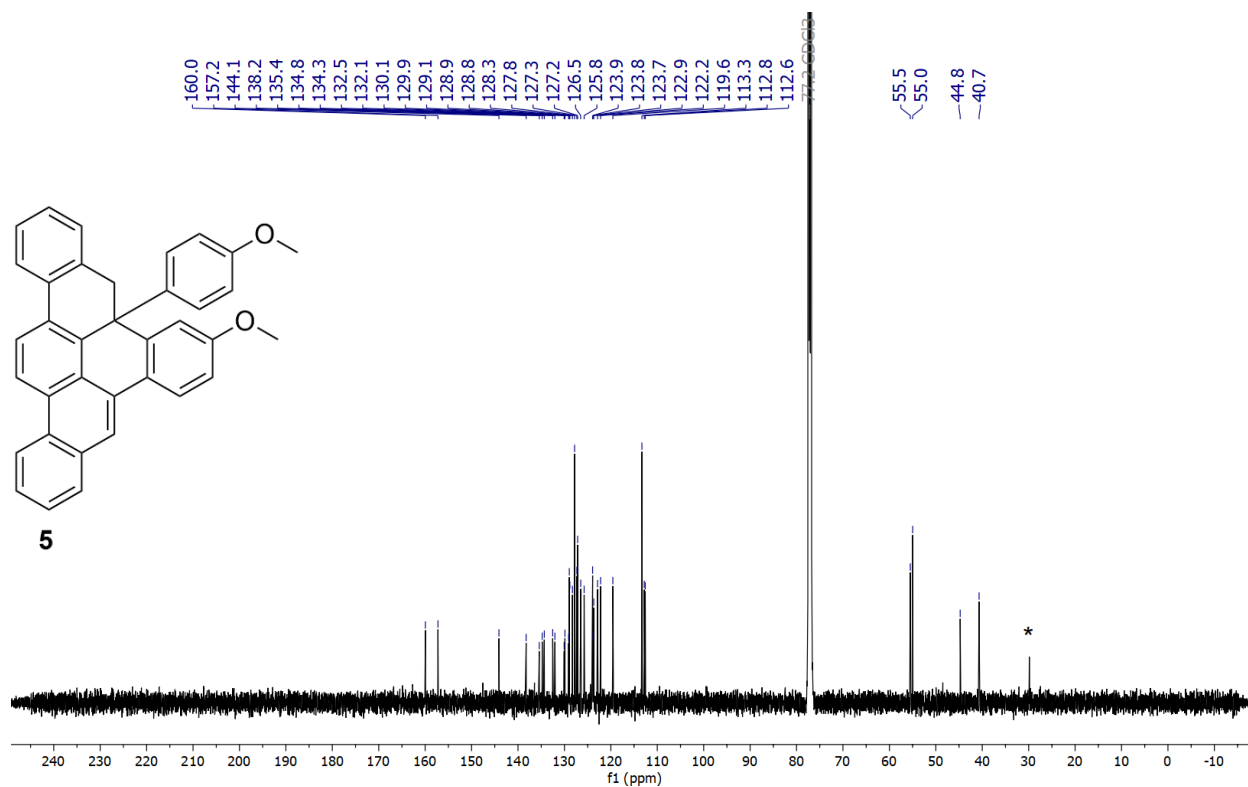


Figure S21. ¹³C NMR (126 MHz, CDCl₃) spectrum of compound **5** (*H grease).

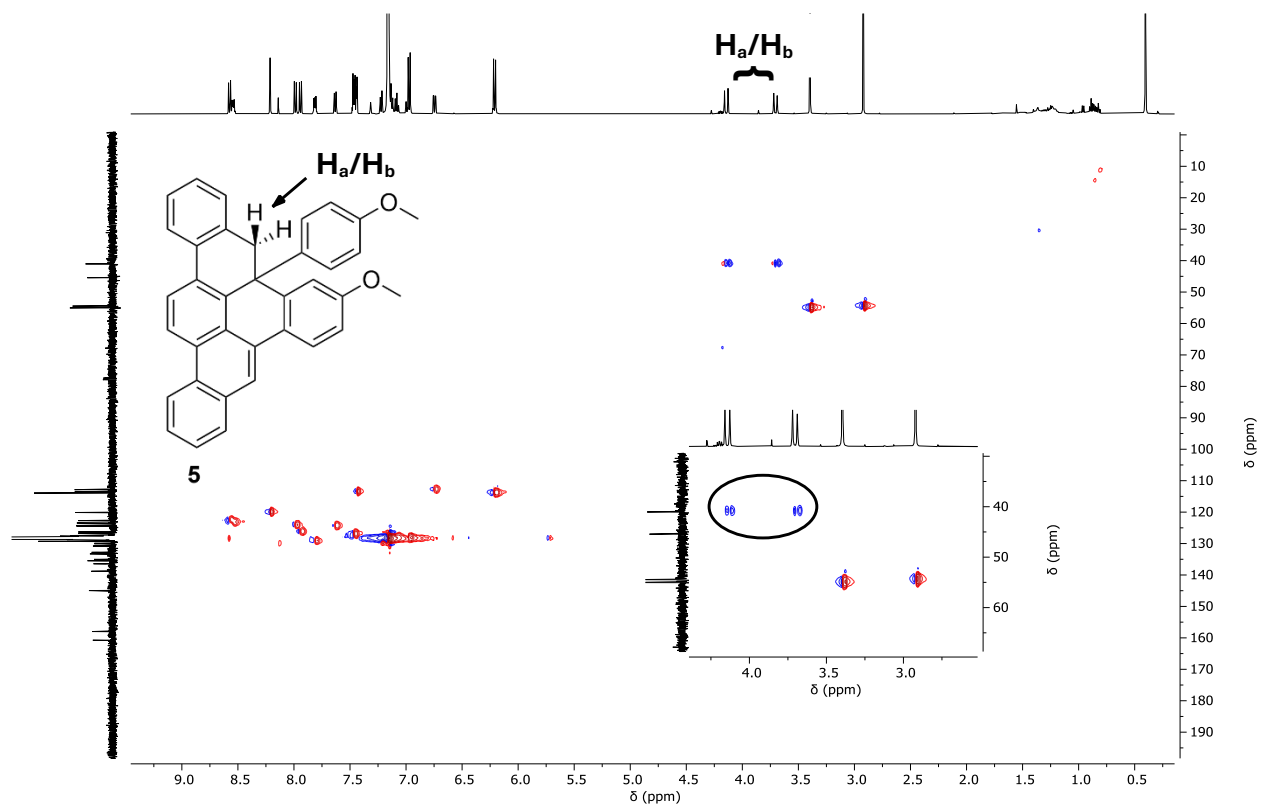


Figure S22. ^1H - ^{13}C HSQC (500 MHz, C_6D_6) spectrum of compound **5**. Inset shows correlation of diastereotopic H_a/H_b to the same carbon.

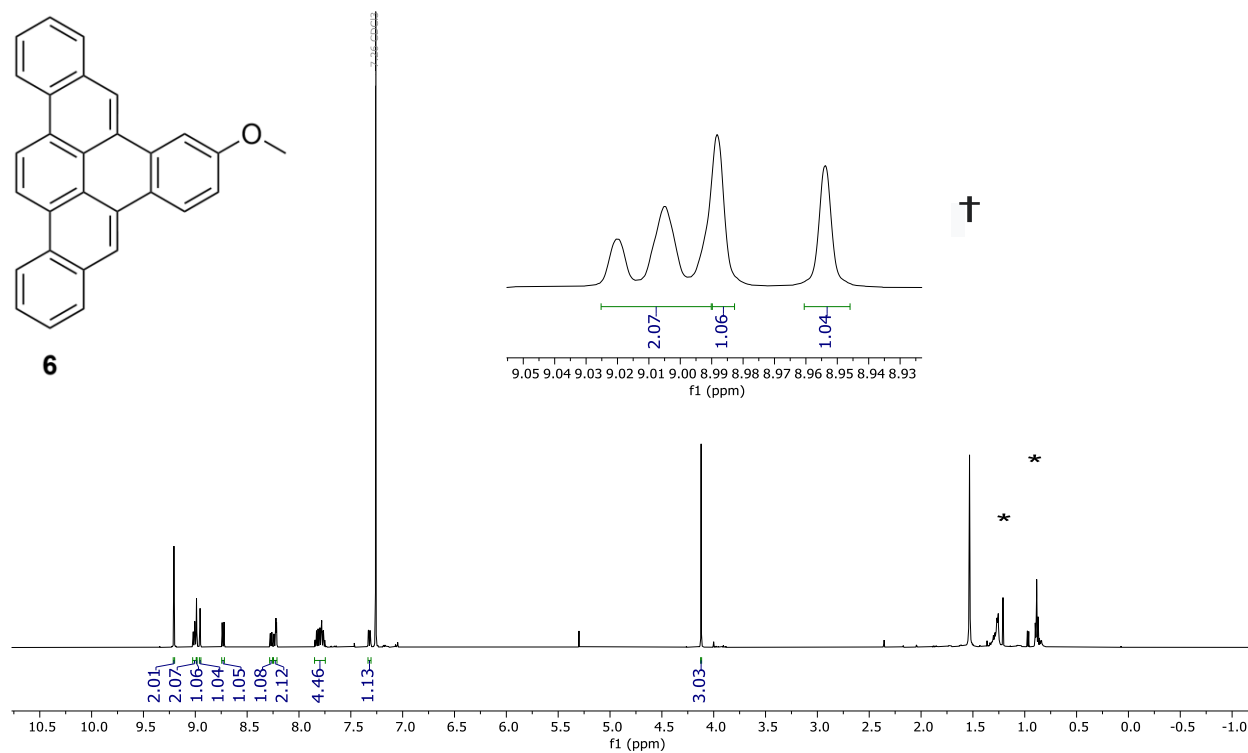


Figure S23. ^1H NMR (500 MHz, CDCl_3) spectrum of compound **6** (*H-grease, † water). Inset shows overlaps of doublets (9.00 and 9.01 ppm) with singlet at 8.99 ppm.

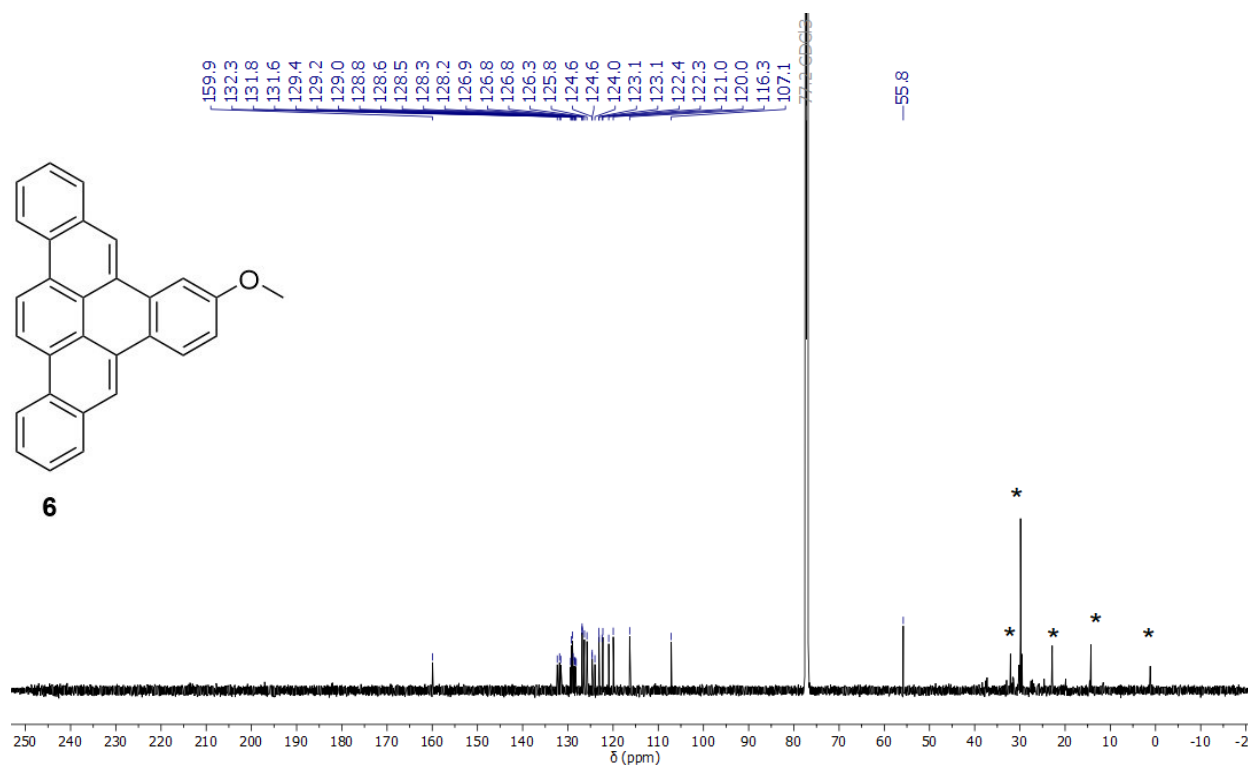


Figure S24. ^{13}C NMR (201 MHz, CDCl_3) spectrum of compound **6** (*H-grease, silicone grease, *n*-hexanes).

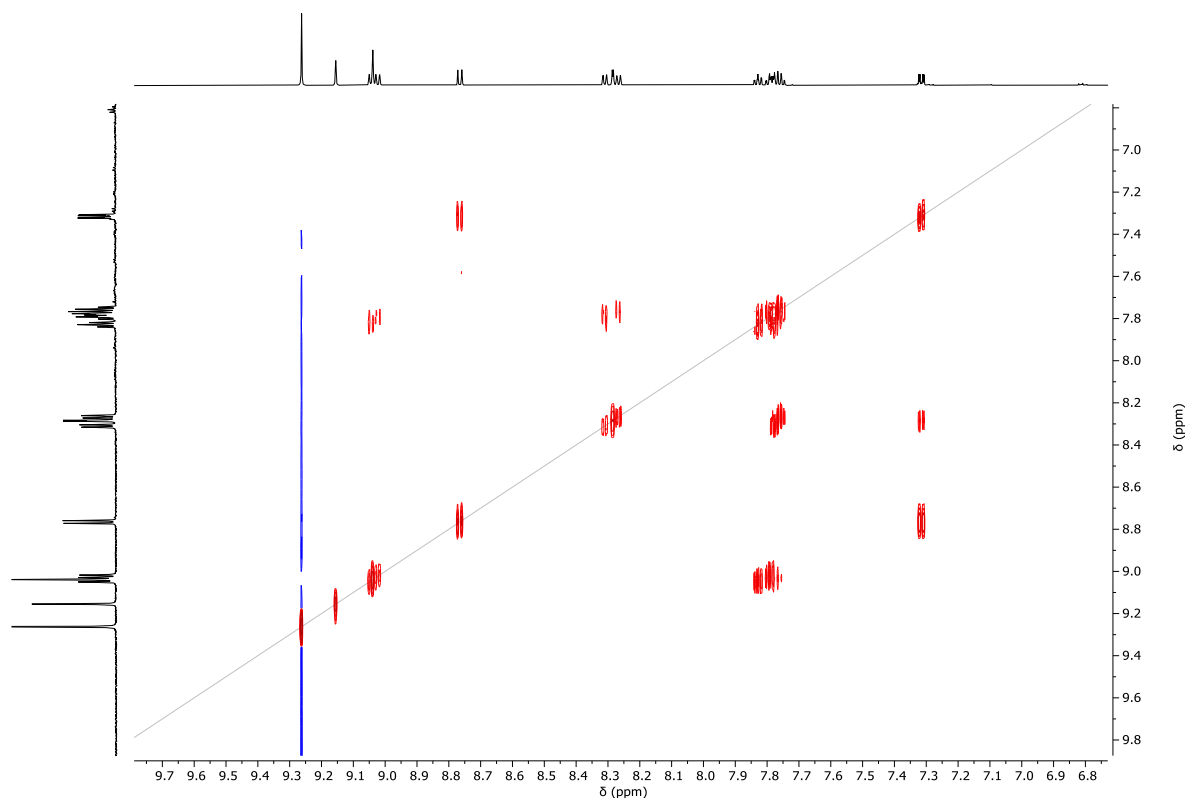


Figure S25. ^1H - ^1H COSY (700 MHz, $(\text{CD}_3)_2\text{CO}$) spectrum of aromatic region for compound **6**.

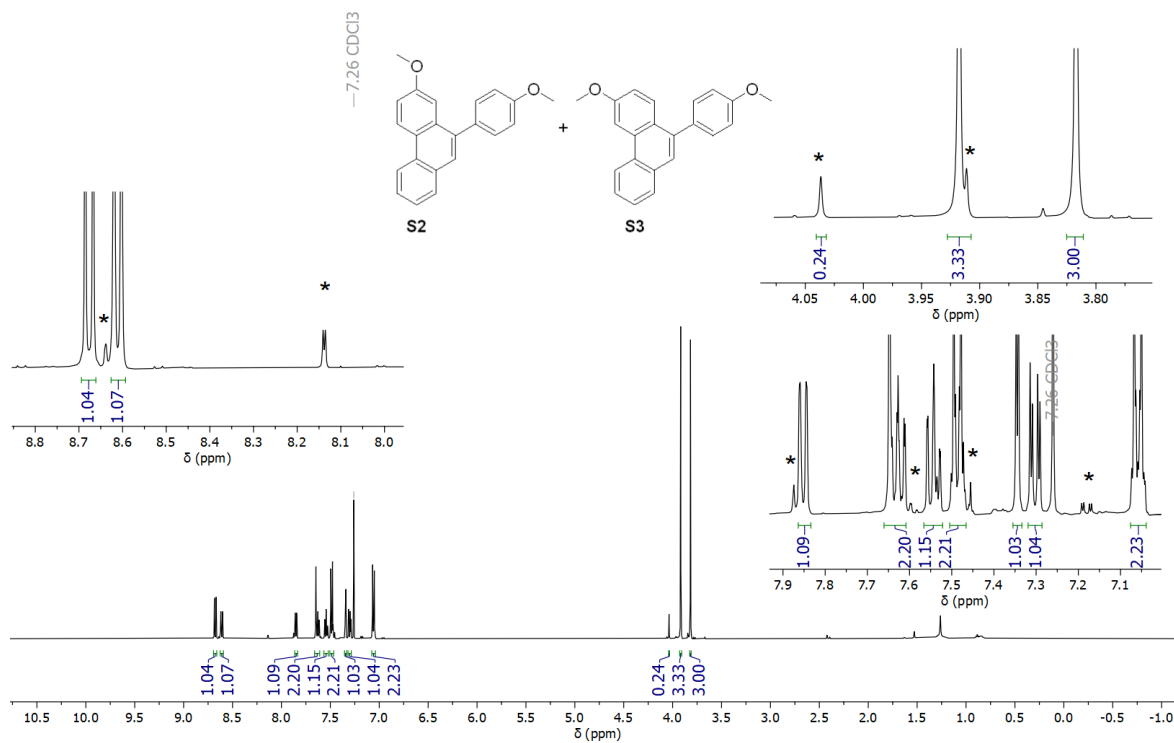


Figure S26. ^1H NMR (500 MHz, CDCl_3) spectrum of compounds **S2+S3**. Insets denote signals attributed to compound **S3** with an asterisk.

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