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Supporting Information

Synthesis and Properties of Twisted and Helical Azulene Oligomers and Azulene-Based Polycyclic Hydrocarbons

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S1. Materials and methods

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE-III-400 (400 MHz for ^1H, 100 MHz for ^{13}C) or Bruker AVANCE-III-600 (600 MHz for ^1H, 150 MHz for ^{13}C). Spectra are reported (in δ) referenced to internal Me_4Si. Mass spectra were recorded on Thermo Scientific, Exactive Plus Orbitrap Mass Spectrometer for electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), or ITQ 700 GC/MS for electronic impact ionization (EI). IR spectra were recorded on JASCO FT/IR-610 Spectrometer. Melting points were determined with Yanaco melting point apparatus. Absorption spectra were recorded on Shimadzu UV-3600 spectrometer. Elemental analyses were performed on Perkin Elmer PE 2400-II CHNS/O analyzer and Yanaco MT-6 analyzer. Cyclic voltammetry (CV) measurements were performed on BAS Electrochemical Analyzer (Model 630E). Column chromatography was carried out using Kanto chemical silica gel 60N, 60-210 μm meshes. Preparative gel permeation chromatography was carried out using HPLC LC-918 system (Japan Analytical Industry, Co. Ltd) equipped with polystyrene gel column JAIGEL-1H.

Single-Crystal X-ray Diffraction

Data of **1** and **3** were collected using a Bruker APEX II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). Data of **4**•C_{60} were collected using a Rigaku HyPix-600 diffractometer with Cu Kα radiation (λ = 1.54187 Å). Single crystals were mounted on MiTeGen Dual-Thickness MicroMounts using a trace of mineral oil. Frames were collected, reflections were indexed and processed, and the files were scaled and corrected for absorption using Bruker *APEX3* program for **1** and **3** and Rigaku CrysAlis^{Pro} program for **4**•C_{60}. The space groups were assigned, and the structures were solved by direct methods using *XPREP* within the *SHELXTL* suite of programs and refined by full-matrix least-squares against F^2 with all reflections using *SHELXL-2014* (**1** and **2**) or *SHELXL-2018* (**4**•C_{60}) with the graphical interface *SHELXLE*. CCDC 1993531 for **1**, CCDC 1993535 for **3**, and CCDC 1993536 for **4**•C_{60} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

S2. Synthetic procedures and characterization data

Synthesis of 1,2':1',2''-terazulene (1)

To a dichloromethane (10 mL) solution of 1,2'-biazulene (100 mg, 0.39 mmol) was slowly dropped a dichloromethane (30 mL) solution of *N*-bromosuccinimide (70 mg, 0.39 mmol) at –78 °C under argon. After completion of the dropwise addition, the mixture was stirred for 3 hours. Thereafter, a saturated aqueous solution of sodium hydrogen carbonate (20 mL) was added, and the dichloromethane layer was washed with brine. After the dichloromethane solution was dried over sodium sulfate, 80 mL of hexane was added, and the mixture was filtered through aluminium oxide. The solvent of the filtrate was replaced with a mixed solvent of 1,2-dimethoxyethane/water (10:1, 44 mL) using a rotary evaporator. To this solution were added 2-(azulen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (100 mg, 0.39 mmol), palladium(II) acetate (2 mg, 0.01 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 8 mg, 0.02 mmol) and tripotassium phosphate (170 mg, 0.79 mmol). The mixture was refluxed for 5 hours under argon. Then, the reaction mixture was filtered through celite, extracted with hexane, and washed with brine. The hexane layer was dried over sodium sulfate, and the solution was concentrated using a rotary evaporator. The obtained crude product was purified by silica gel column chromatography using a mixed solvent of hexane/dichloromethane (4:1) as an eluent to obtain a green solid of **1**. (91 mg, 0.24 mmol 61%)

1: green solid
m.p. 104–108 °C
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.74 (d, *J* = 10.2 Hz, 1H), 8.72 (d, *J* = 9.6 Hz, 1H), 8.28 (d, *J* = 9.6 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.69 (s, 1H), 7.60 (d, *J* = 3.6 Hz, 1H), 7.53 (t, *J* = 10.2 Hz, 1H), 7.49 (t, *J* = 10.2 Hz, 1H), 7.42 (t, *J* = 9.0 Hz, 1H), 7.30 (s, 2H), 7.26 (d, *J* = 4.2 Hz, 1H), 7.18 (t, *J* = 9.0Hz, 1H), 7.16 (t, *J* = 9.0 Hz, 1H), 7.13 (t, *J* = 9.6 Hz, 1H), 7.10 (t, *J* = 9.6 Hz, 1H), 7.08 (t, *J* = 9.6 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$): δ 147.0, 146.3, 142.7, 141.8, 140.6, 140.2, 138.8, 138.2, 137.0, 136.9, 136.9, 136.4, 135.4, 135.4, 134.9, 134.8, 127.2, 125.7, 124.98, 124.54, 124.1, 123.9, 123.2, 119.6, 119.4, 118.3.
IR (KBr): ν_{max} 1567, 1509, 1380, 897, 781, 732 cm^{-1}
MS (ESI) *m*/*z*: 381.16 [M + H]$^+$.
UV-vis (THF) λ_{max} (ε): 234 (41500), 262 (51500), 289 (56000), 316 (49700), 432 (29600), 580 (1170) nm.
Anal. Calcd for $C_{30}H_{20}$: C, 94.70; H, 5.30. Found: C, 94.80; H,5.49.

Synthesis of 1,2':1',2'':1'',2'''-quaterazulene (2) and azuleno[1,2-*e*]dicyclohepta[*a*,*h*]-*as*-indacene (3)
To a dichloromethane (15 mL) solution of **1** (175 mg, 0.46 mmol) was slowly dropped a dichloromethane (45 mL) solution of *N*-bromosuccinimide (80 mg, 0.46 mmol) at –78 °C under argon. After completion of the dropwise addition, the mixture was stirred for 3 hours. Thereafter, a saturated aqueous solution of sodium hydrogen carbonate (30 mL) was added, and the dichloromethane layer was washed with brine. After the dichloromethane solution was dried over sodium sulfate, 80 mL of hexane was added, and the mixture was filtered through aluminium oxide. The solvent of the filtrate was replaced with a mixed solvent of 1,2-dimethoxyethane/water (10:1, 11 mL) using a rotary evaporator. To this solution were added 2-(azulen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) (115 mg, 0.45 mmol), palladium(II) acetate (3 mg, 0.01 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 9 mg, 0.023 mmol) and tripotassium phosphate (190 mg, 0.9 mmol). The mixture was refluxed for 15 hours under argon. Then, the reaction mixture was filtered through celite, extracted with hexane, and washed with brine. The hexane layer was dried over sodium sulfate, and the solution was concentrated using a rotary evaporator. The obtained crude product was purified by preparative gel permeation chromatography with chloroform to obtain a green solid of **2** (18 mg, 0.036 mmol 8%) and a black solid of **3** (63 mg, 0.16 mmol, 36%).

2: brown solid
m.p. 178–181 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 9.7 Hz, 1H), 8.46 (d, *J* = 9.8 Hz, 1H), 8.36-8.29 (m, 2H), 8.03 (d, *J* = 9.4 Hz, 1H), 7.84 (d, *J* = 9.8 Hz, 1H), 7.75 (s, 1H), 7.57 (d, *J* = 9.2 Hz, 2H), 7.50-7.48 (m, 3H), 7.24–7.15 (m, 4H), 7.10–7.03 (m, 3H), 7.02–6.89 (m, 2H), 6.75 (t, *J* = 9.8 Hz, 2H), 6.39 (s, 2H), 6.29 (t, *J* = 9.8 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 147.0, 146.6, 142.1, 141.7, 141.6, 139.8, 138.8, 138.4, 137.8, 137.4, 136.8, 136.1, 135.7, 135.6, 135.2, 135.1, 134.7, 134.4, 134.3, 133.8, 127.8, 126.9, 126.0, 124.33, 124.29, 124.0, 123.9, 123.1, 122.7, 122.3, 120.2, 118.5, 118.2, 117.5.
IR (KBr): ν_{max} 1722, 1568, 1512, 1511, 1460, 1384, 1261, 1096, 1028, 799, 726 cm^{-1}
MS (EI) *m*/*z*: 507.26 $[M + H]^+$.
UV-vis (THF) λ_{max} (ε): 258 (53600), 290 (57300), 430 (30300), 580 (1230) nm
Anal. Calcd for $C_{40}H_{26}$: C, 94.83; H, 5.17. Found: C, 94.71; H, 5.09.

3: black solid
m.p. 245–250 °C
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.37 (d, *J* = 9.5 Hz, 3H), 8.55 (d, *J* = 9.5 Hz, 3H), 8.49 (s, 3H), 7.67 (t, 3H, *J* = 9.5 Hz), 7.61 (t, *J* = 9.5 Hz, 3H), 7.41 (t, *J* = 9.5 Hz, 3H).
^{13}C NMR (150 MHz, $CDCl_3$): δ 143.9, 142.3, 139.1, 134.6, 134.0, 131.3, 125.8, 125.1, 120.0, 114.7

IR (KBr): ν_{max} 1574, 1531, 1414, 804, 757, 710, 687 cm^{-1}.

MS (ESI) *m*/*z*: 379.16 [M + H]$^+$.

UV-vis (THF) λ_{max} (ε): 257 (24400), 304 (26000), 397 (46500), 456 (61700), 743 (250, sh) nm

Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.12; H, 4.70.

Synthesis of azuleno[1,2-*e*]dicyclohepta[*a*,*h*]-*as*-indacene (3) and diazuleno[1,2-*a*:1',2'-*c*]-cyclopenta[*ef*]heptalene (4)

To a dichloromethane (15 mL) solution of **1** (175 mg, 0.46 mmol) was slowly dropped a dichloromethane (45 mL) solution of *N*-bromosuccinimide (80 mg, 0.46 mmol) at –78 °C under argon. After completion of the dropwise addition, the mixture was stirred for 3 hours. Thereafter, a saturated aqueous solution of sodium hydrogen carbonate (30 mL) was added, and the dichloromethane layer was washed with brine. After the dichloromethane solution was dried over sodium sulfate, 80 mL of hexane was added, and the mixture was filtered through aluminium oxide. The solvent of the filtrate was replaced with toluene (60 mL) using a rotary evaporator. To this solution were added tris(dibenzylideneacetone)dipalladium(0) (18 mg, 0.02 mmol), ligand (0.024 mmol) and caesium carbonate (290 mg, 0.9 mmol). The mixture was refluxed for 20 hours under argon. Then, the reaction mixture was filtered through celite and washed with brine. The hexane layer was dried over sodium sulfate, and the solution was concentrated using a rotary evaporator. The obtained crude product was purified by preparative gel permeation chromatography with chloroform to obtain black solids of **3** (16–69%) and **4** (12–18%).

4: black solid

m.p. 134–138 °C

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.84 (d, *J* = 9.6 Hz, 1H), 8.74 (d, *J* = 9.6 Hz, 1H), 8.22 (d, *J* = 4.2 Hz, 1H), 8.01 (d, *J* = 9.6 Hz, 1H), 7.89 (d, *J* = 9.6 Hz, 1H), 7.87 (d, *J* = 9.6 Hz, 1H), 7.74 (s, 1H), 7.61 (d, *J* = 10.8 Hz, 1H), 7.36 (t, *J* = 9.6 Hz, 1H), 7.31 (s, 1H), 7.24-7.16 (m, 3H), 7.10 (t, *J* = 9.6 Hz, 1H), 7.04 (t, *J* = 9.6 Hz, 1H), 6.98-6.94 (m. 2H), 6.66 (t, *J* = 9.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 150.0, 149.9, 147.8, 145.4, 143.8, 143.0, 141.64, 141.60, 141.2, 138.1, 137.0, 136.6, 135.4, 134.5, 134.2, 133.0, 132.9, 131.5, 127.8, 127.6, 126.9, 126.2, 126.1, 125.9, 125.8, 123.0, 120.8, 119.1, 117.9, 117.5, 114.7.

IR (KBr): ν_{max} 1562, 1508, 1407, 1026, 800, 713 cm^{-1}.

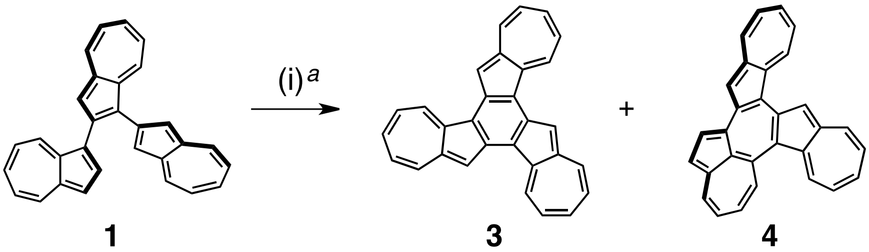
MS (ESI) *m*/*z*: 379.16 [M + H]$^{+\cdot}$

UV-vis (THF) λ_{max} (ε): 240 (24900), 350 (16000), 461 (30200), 870 (80, sh) nm

Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.25; H, 4.66.

S3. Additional spectra and data

Table S1. Conditions and Products for the Pd-Catalyzed Ring-Closing Reaction of 1



ligand	Yields / %	
	3	**4**
DPPF[b]	28	18
PPh_3	36	12
SPhos[c]	69	–
XPhos[d]	22	–
^{t}Bu-XPhos[e]	16	–

[a] Reagents and conditions: 1) NBS, CH_2Cl_2, –78 ºC, 3 h, 2) $[Pd(dba)_2]$, ligand, Cs_2CO_3, toluene, reflux, 24 h. [b] 1,10-Bis(diphenylphosphino)ferrocene. [c] 2-Dicyclohexylphosphino-2',6'-dimethoxybiphenyl. [d] 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl. [e] Di-*tert*-butyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine.

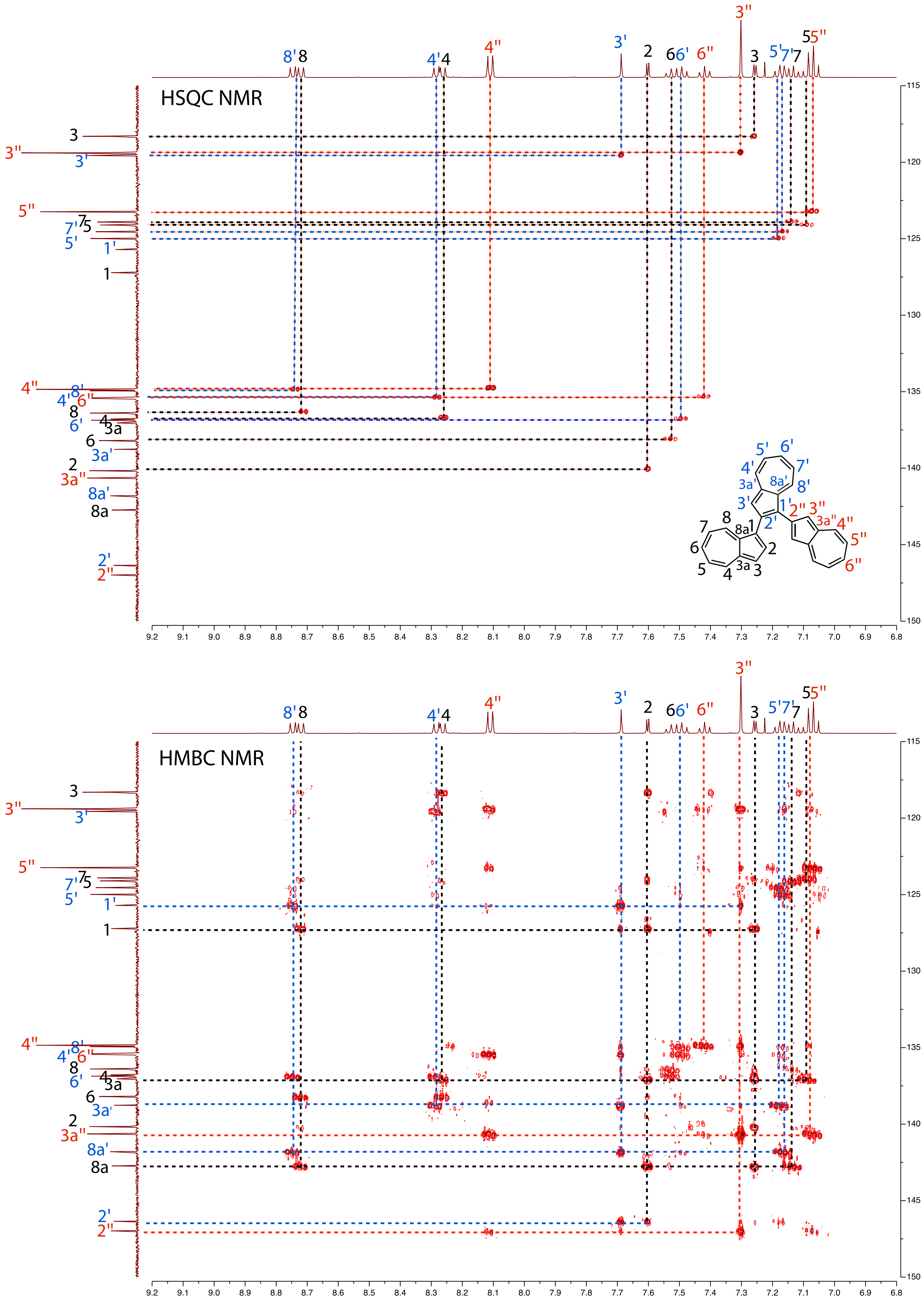
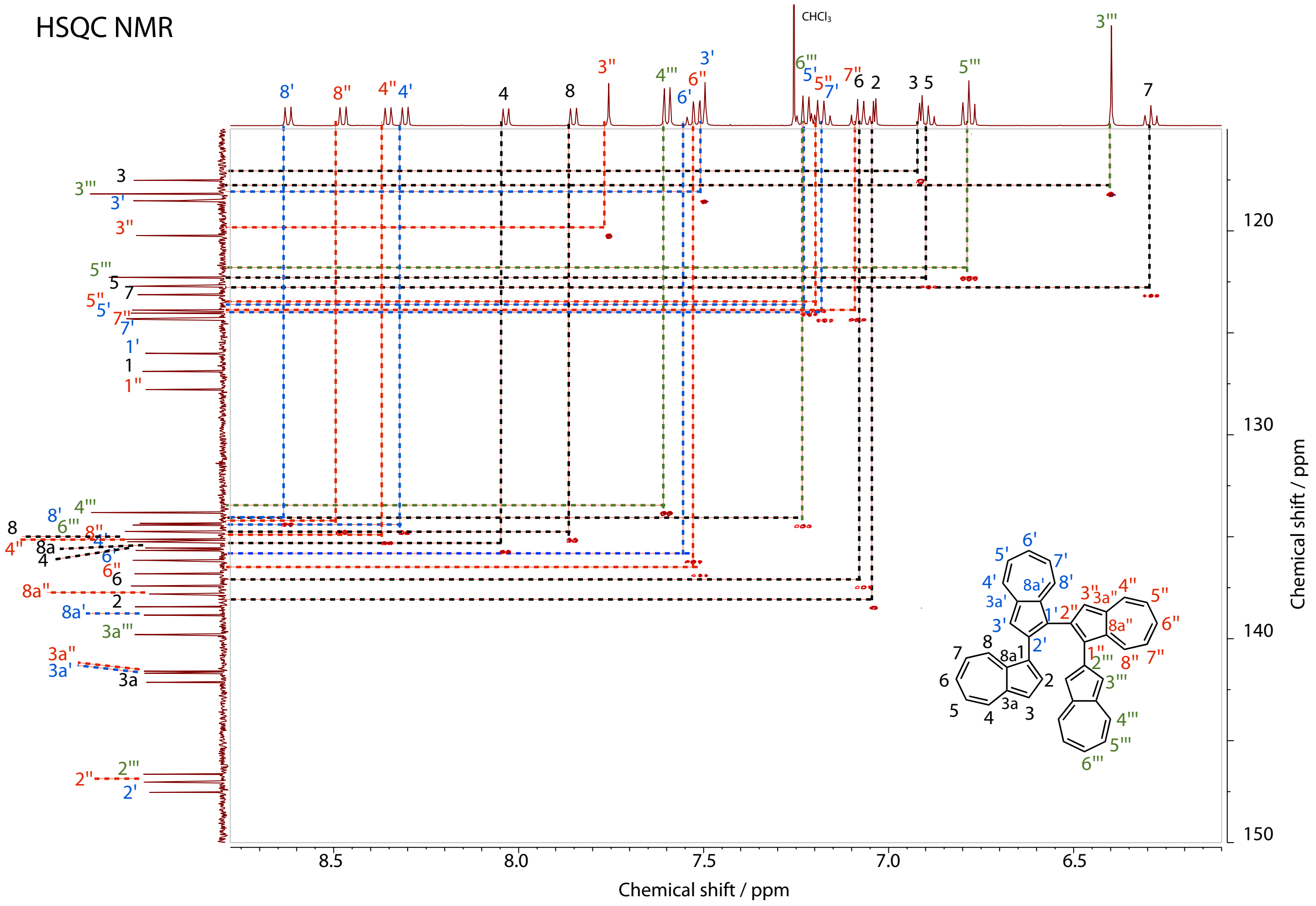


Figure S1. HSQC and HMBC NMR spectra of **1**.



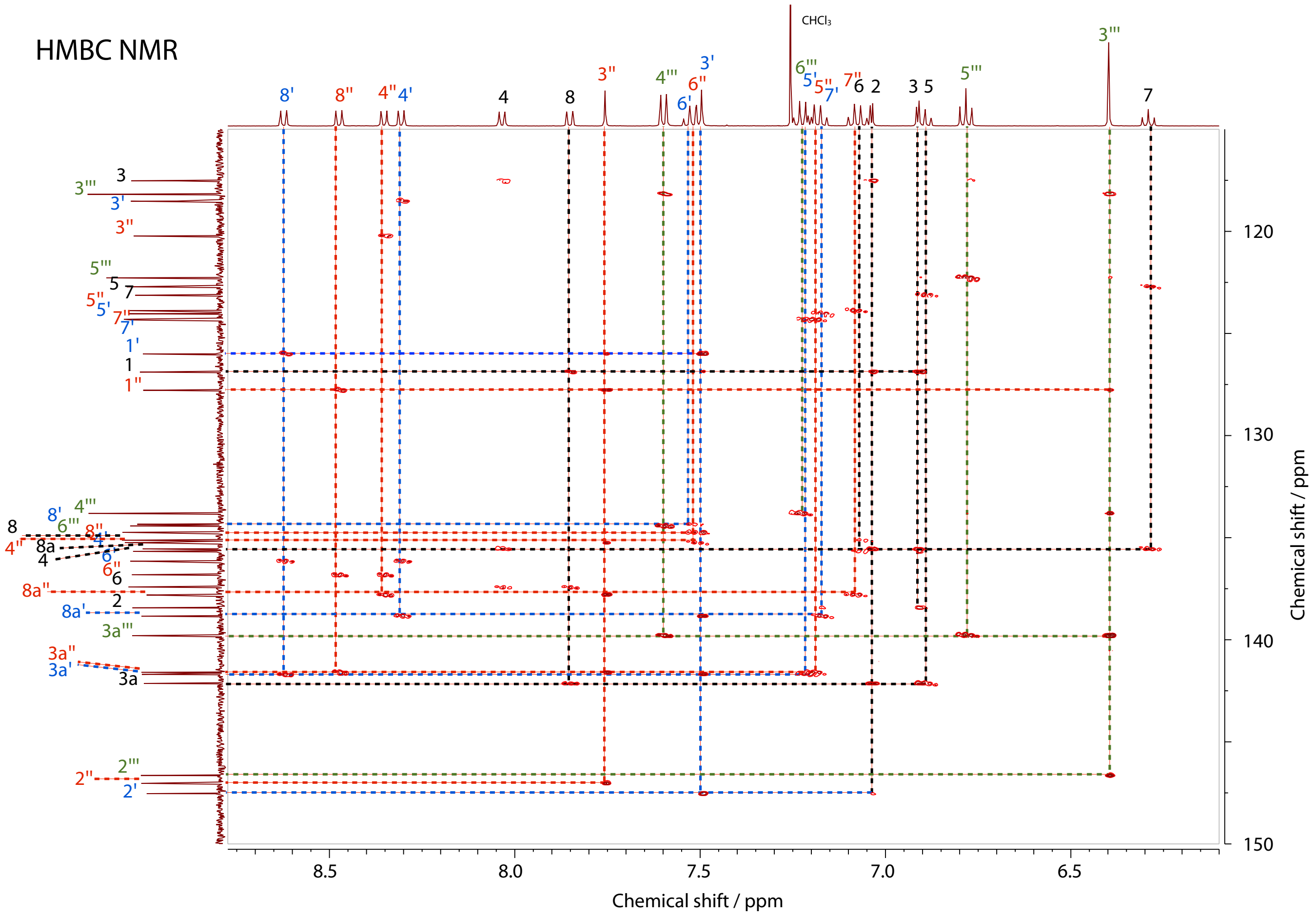
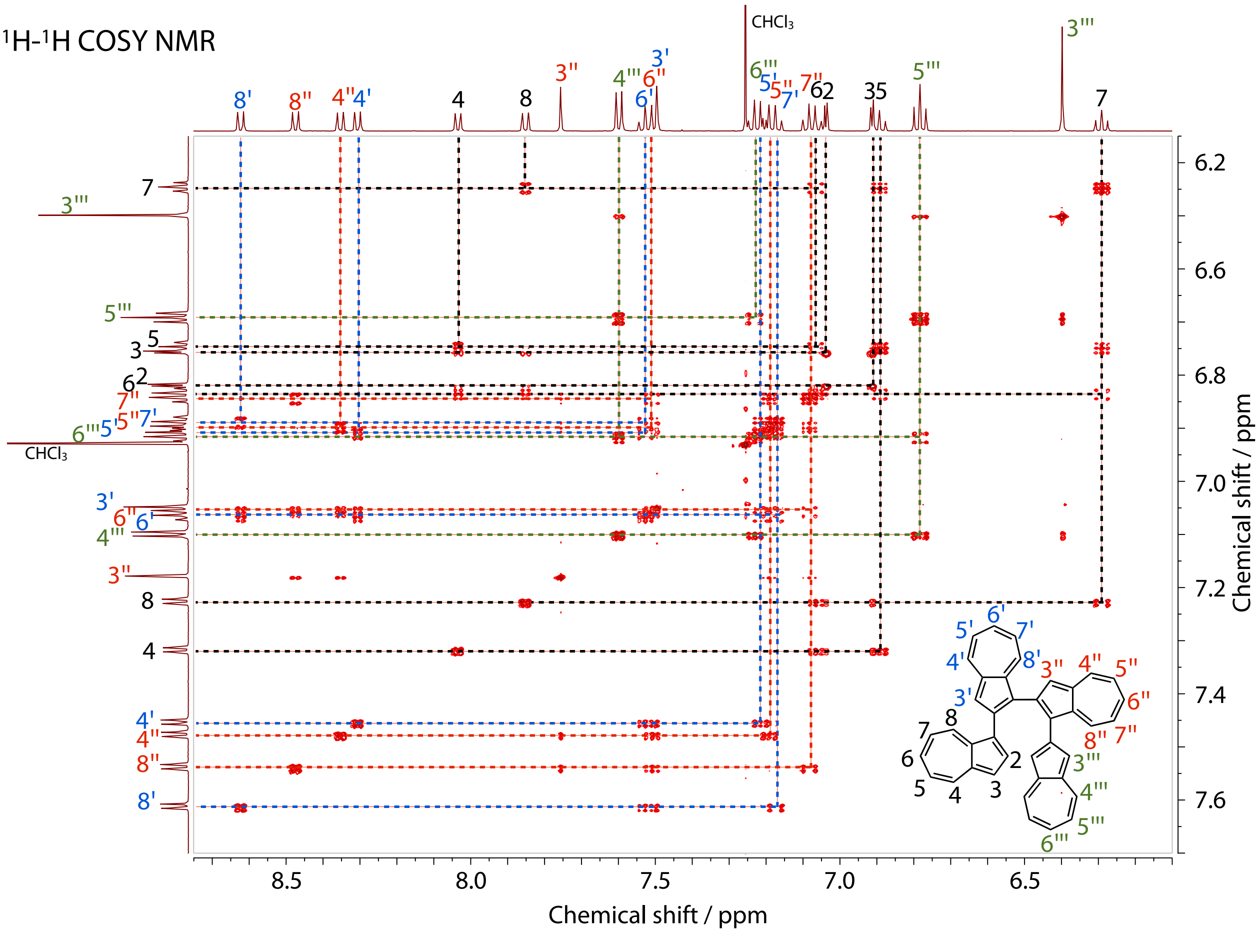
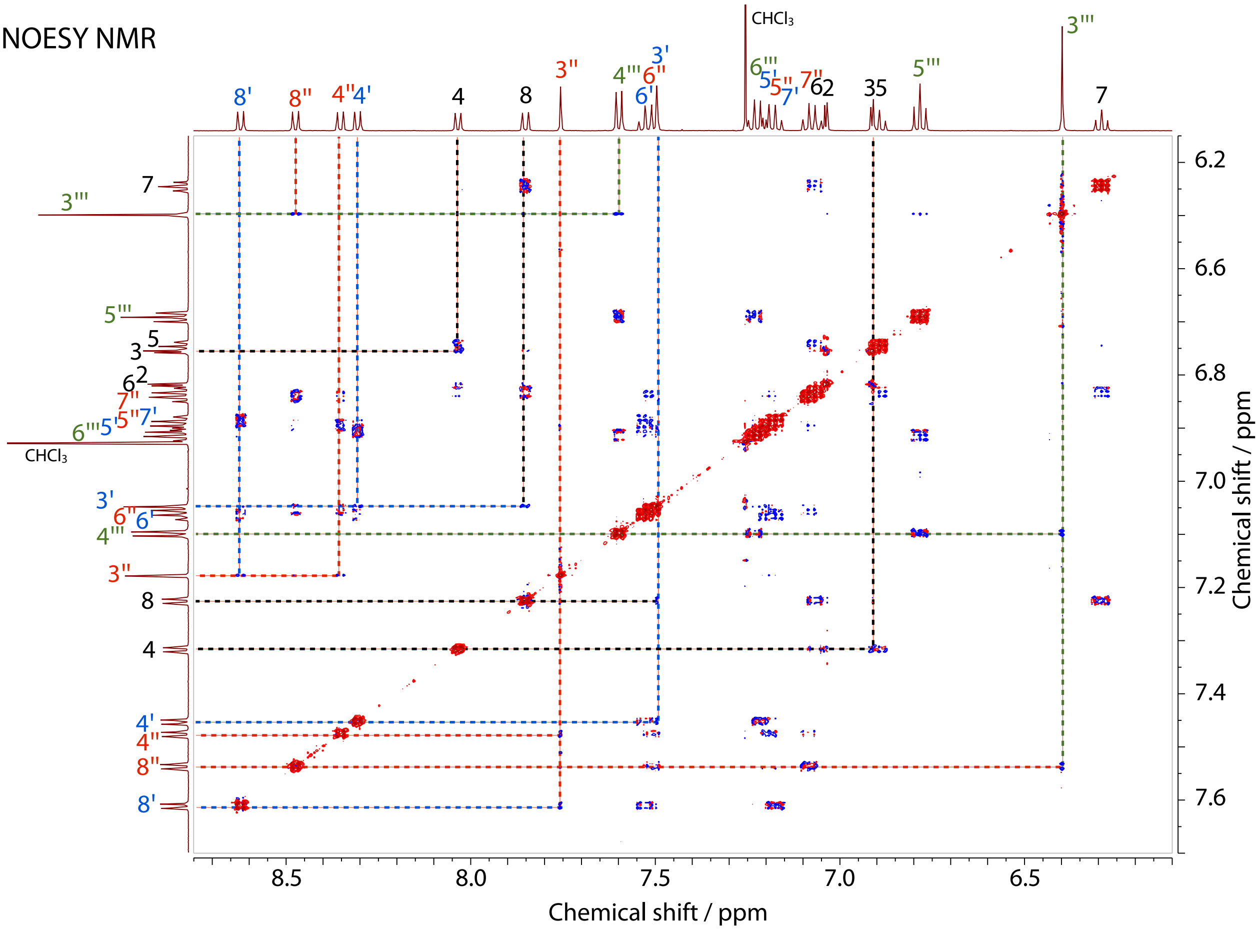


Figure S2. HSQC and HMBC NMR spectra of **2** in $CDCl_3$.



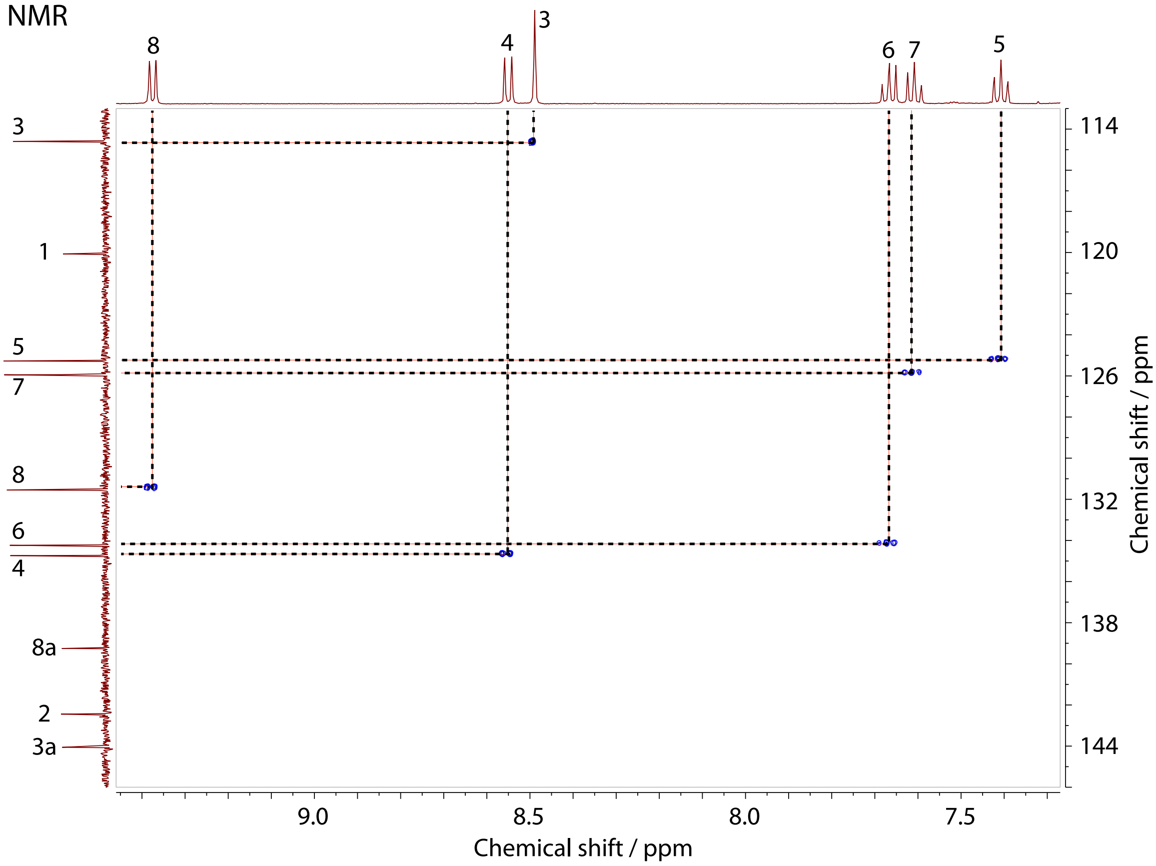
^1H-^1H COSY NMR



NOESY NMR

Figure S3. ^1H-^1H COSY and NOESY NMR spectra of **2** in $CDCl_3$.

HSQC NMR



HMBC NMR

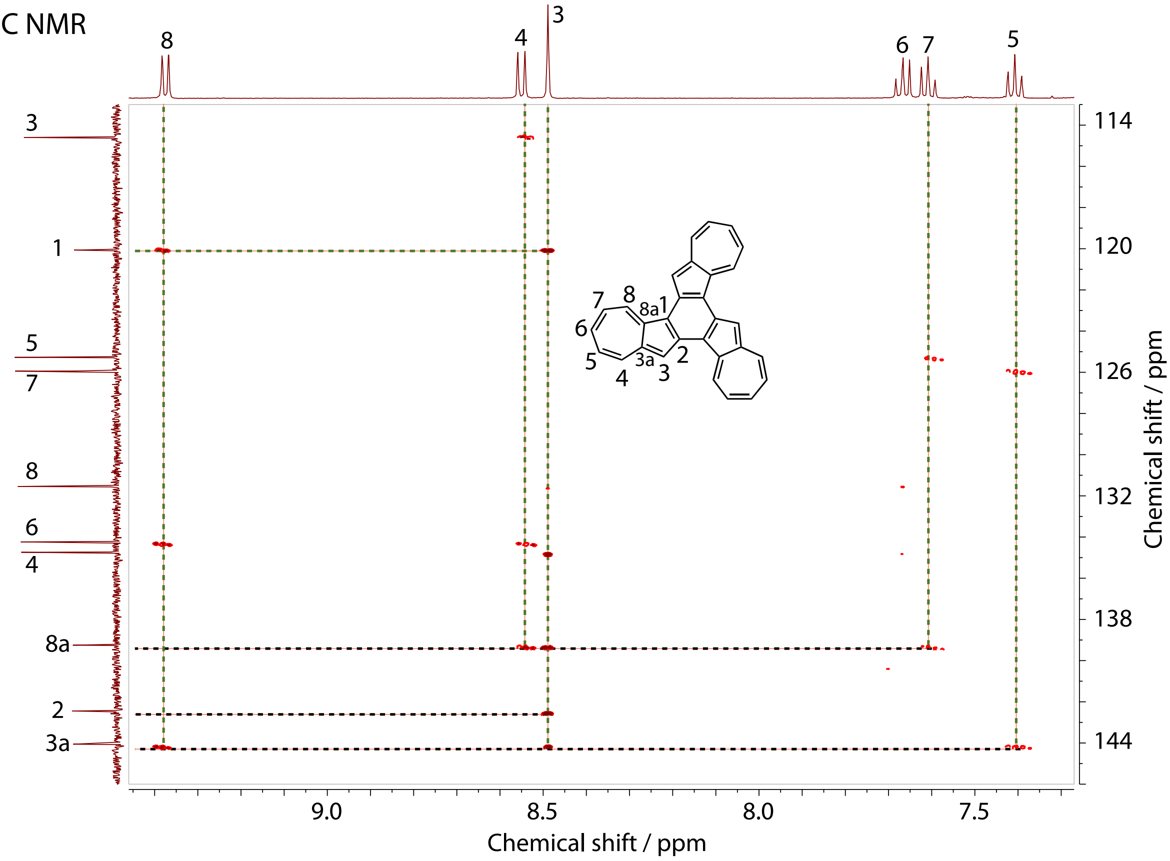
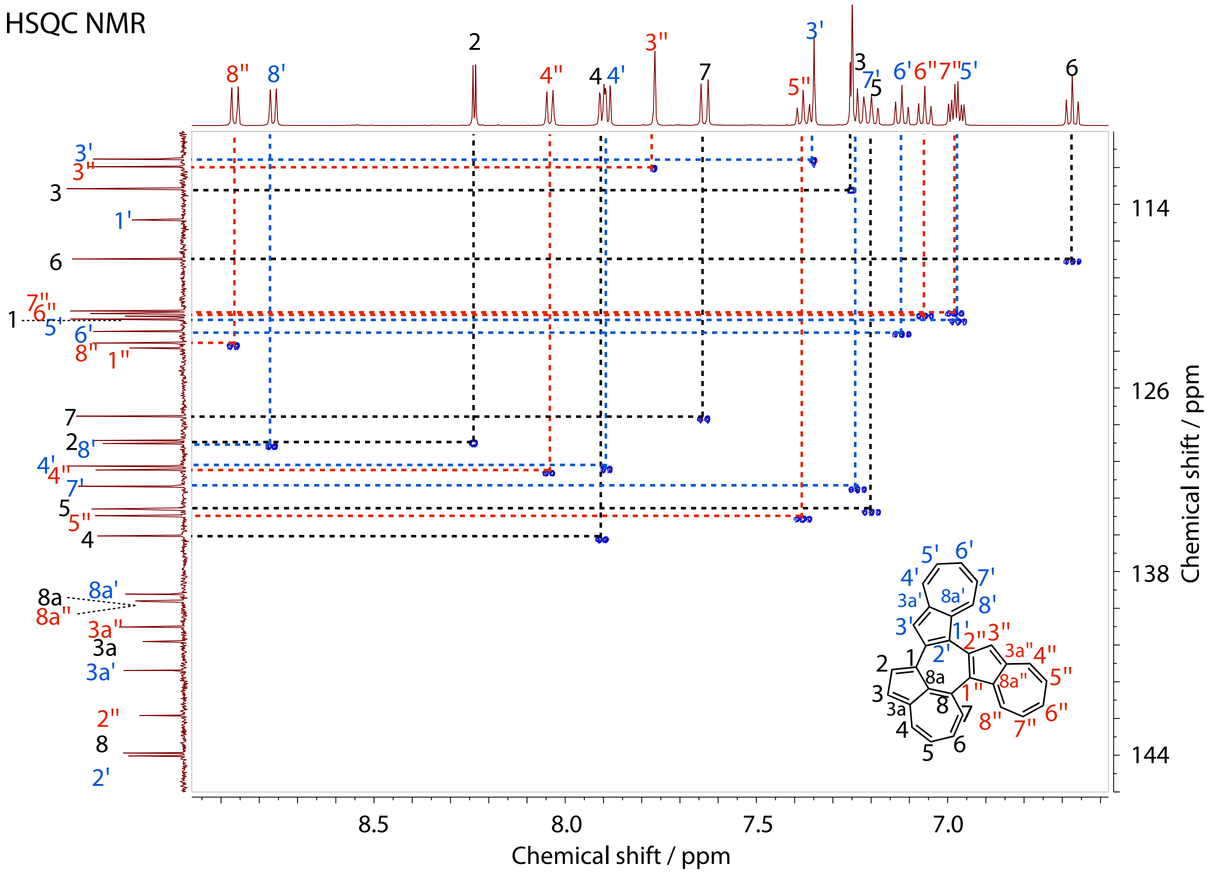


Figure S4. HSQC and HMBC NMR spectra of **3** in $CDCl_3$.



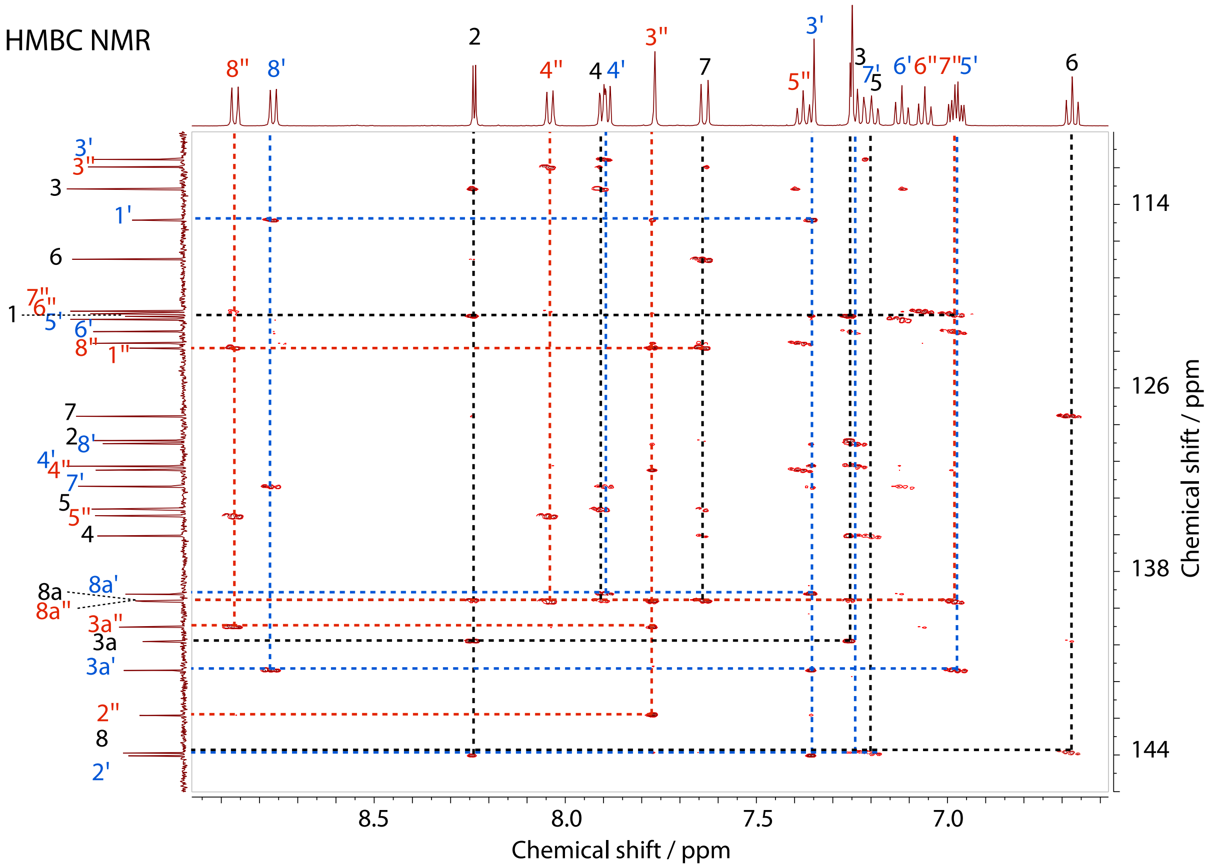
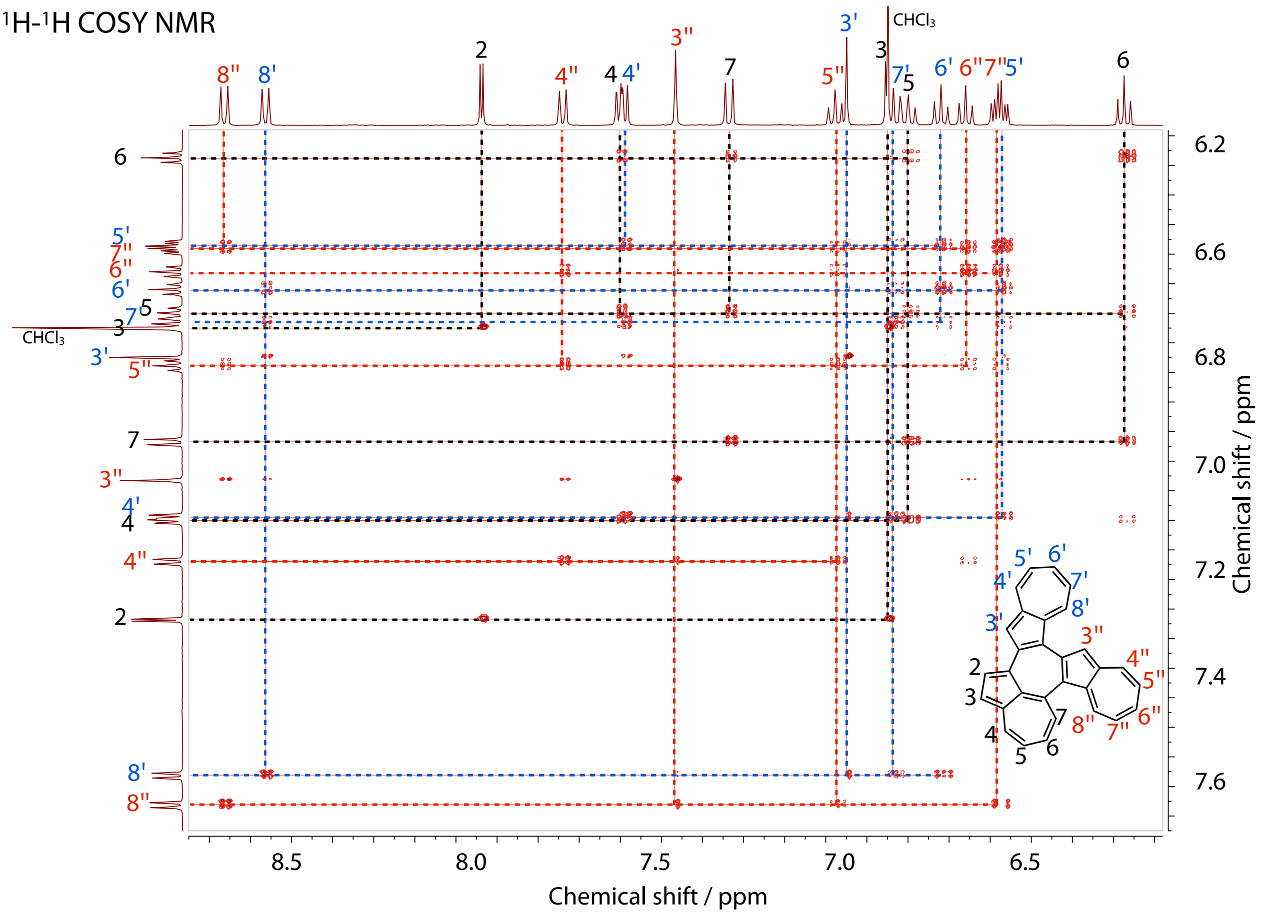


Figure S5 HSQC and HMBC NMR spectra of **4** in $CDCl_3$.


^{1}H-^{1}H COSY NMR

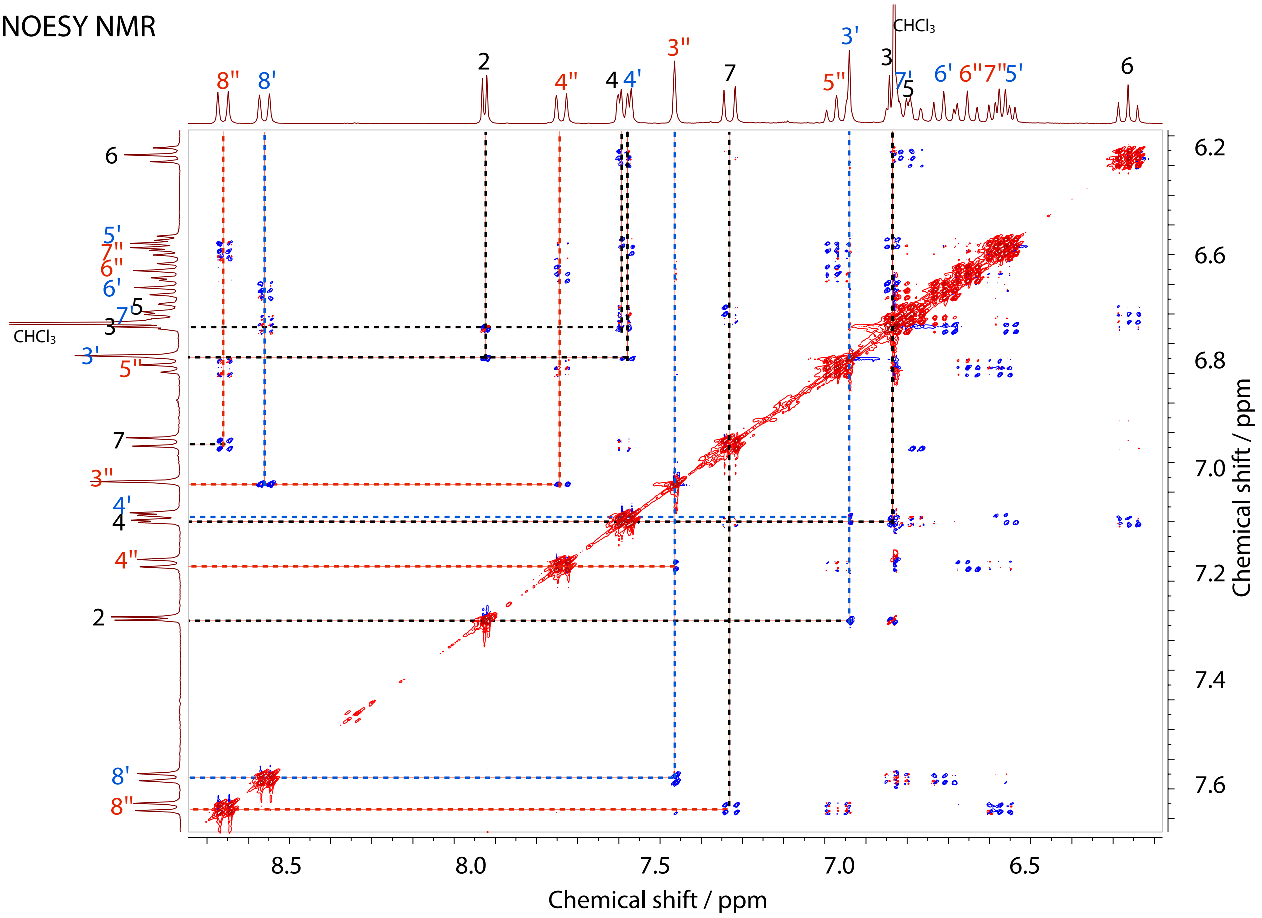

NOESY NMR

Figure S6. ^{1}H-^{1}H COSY and NOESY NMR spectra of **4** in $CDCl_3$.

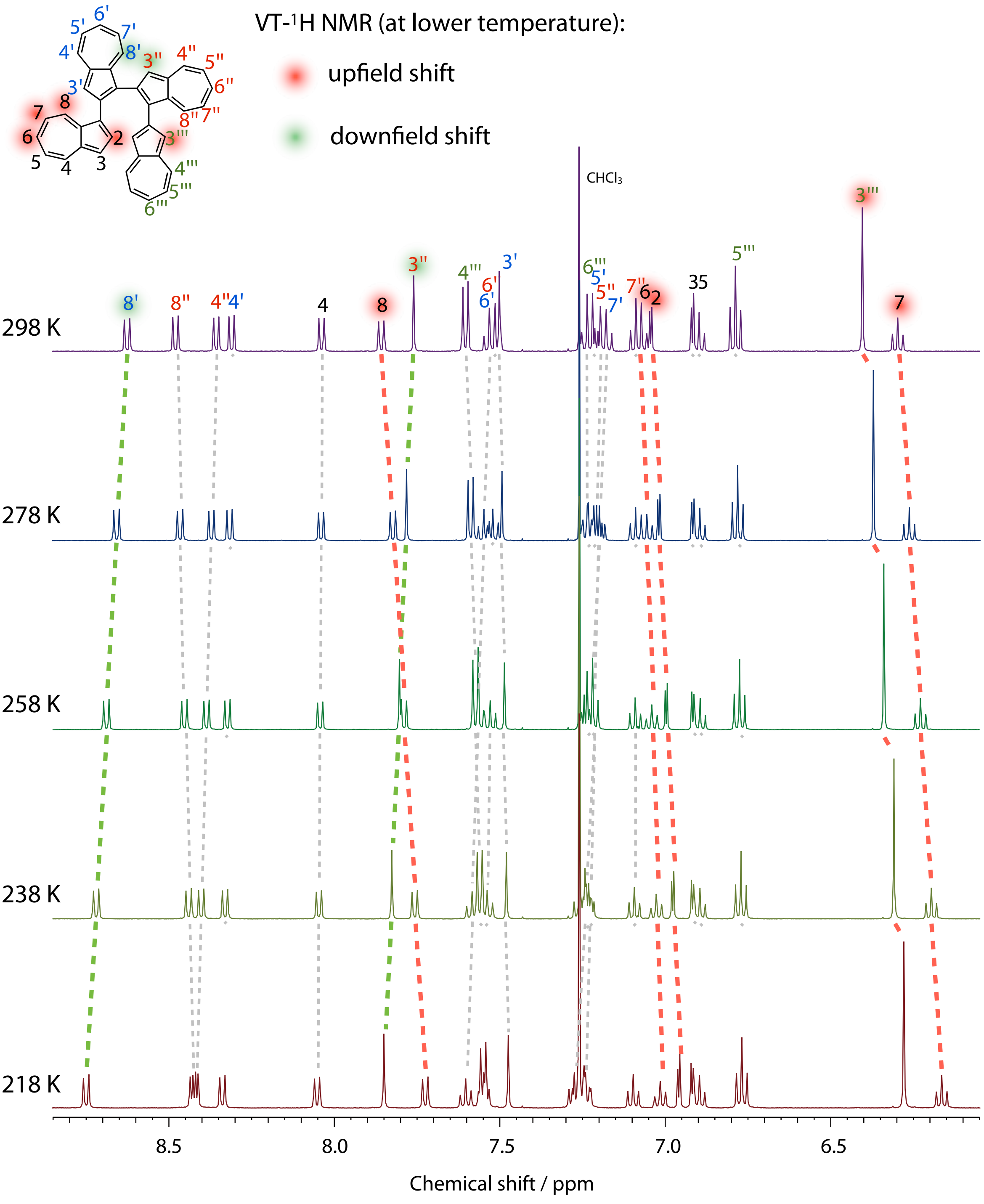


Figure S7. Valuable-Temperature ¹H NMR spectra of **2** in $CDCl_3$.

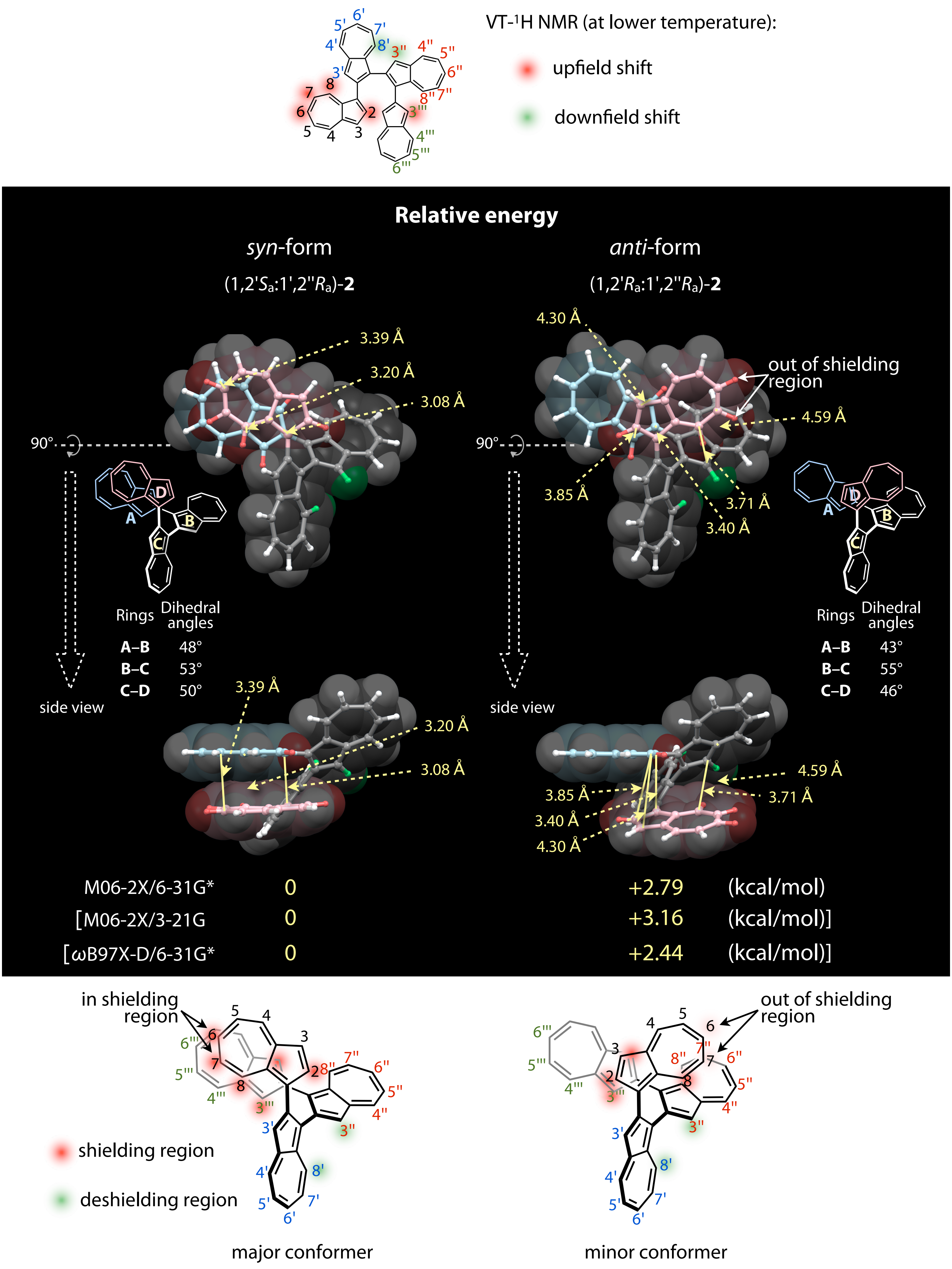


Figure S8. Relative energies for the *syn*- and *anti*-forms of **2**.

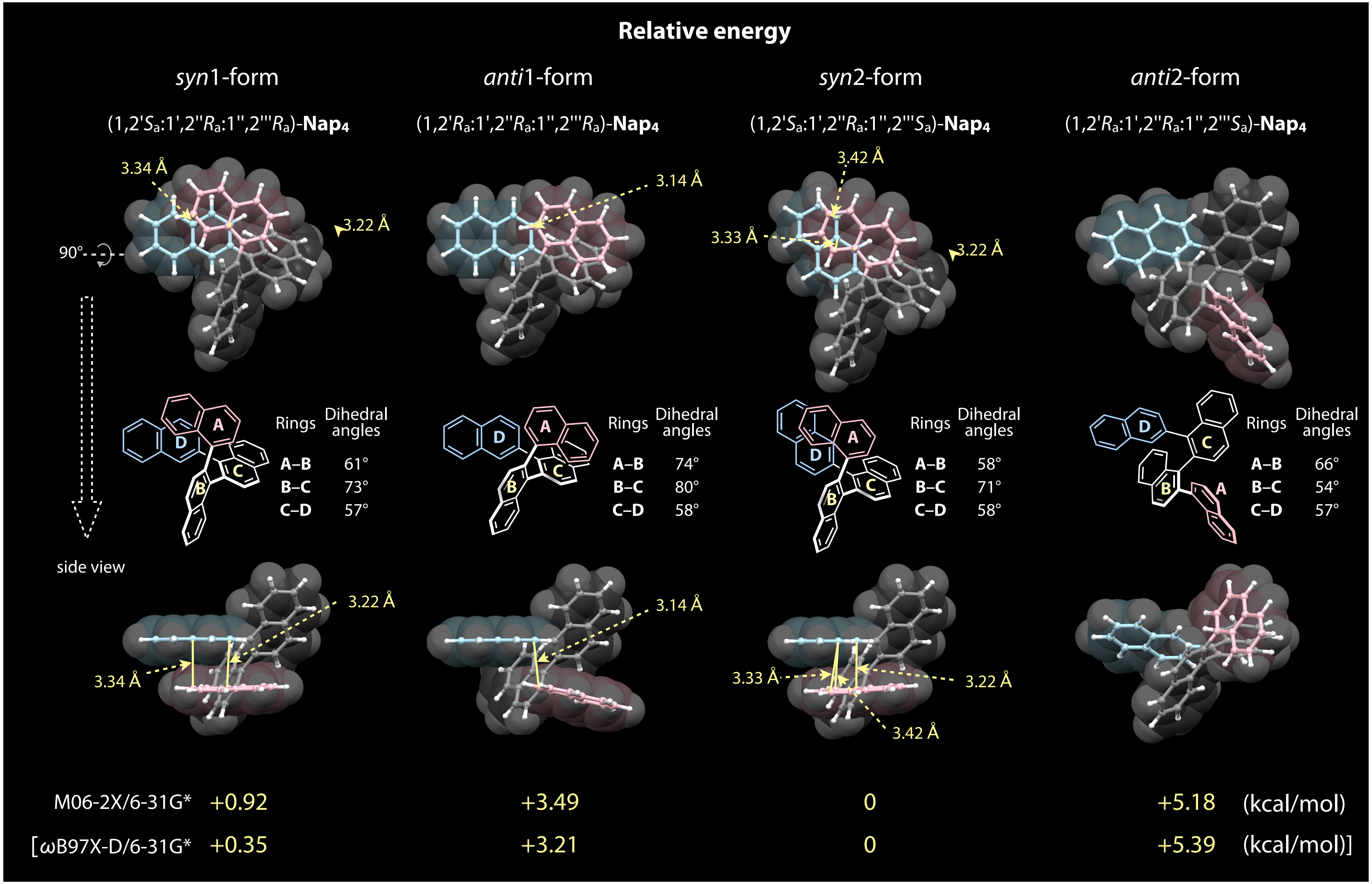


Figure S9. Relative energies for the *syn*- and *anti*-forms of 1,2':1',2'':1'',2'''-quaternaphthalene (**6**, **Nap₄**).

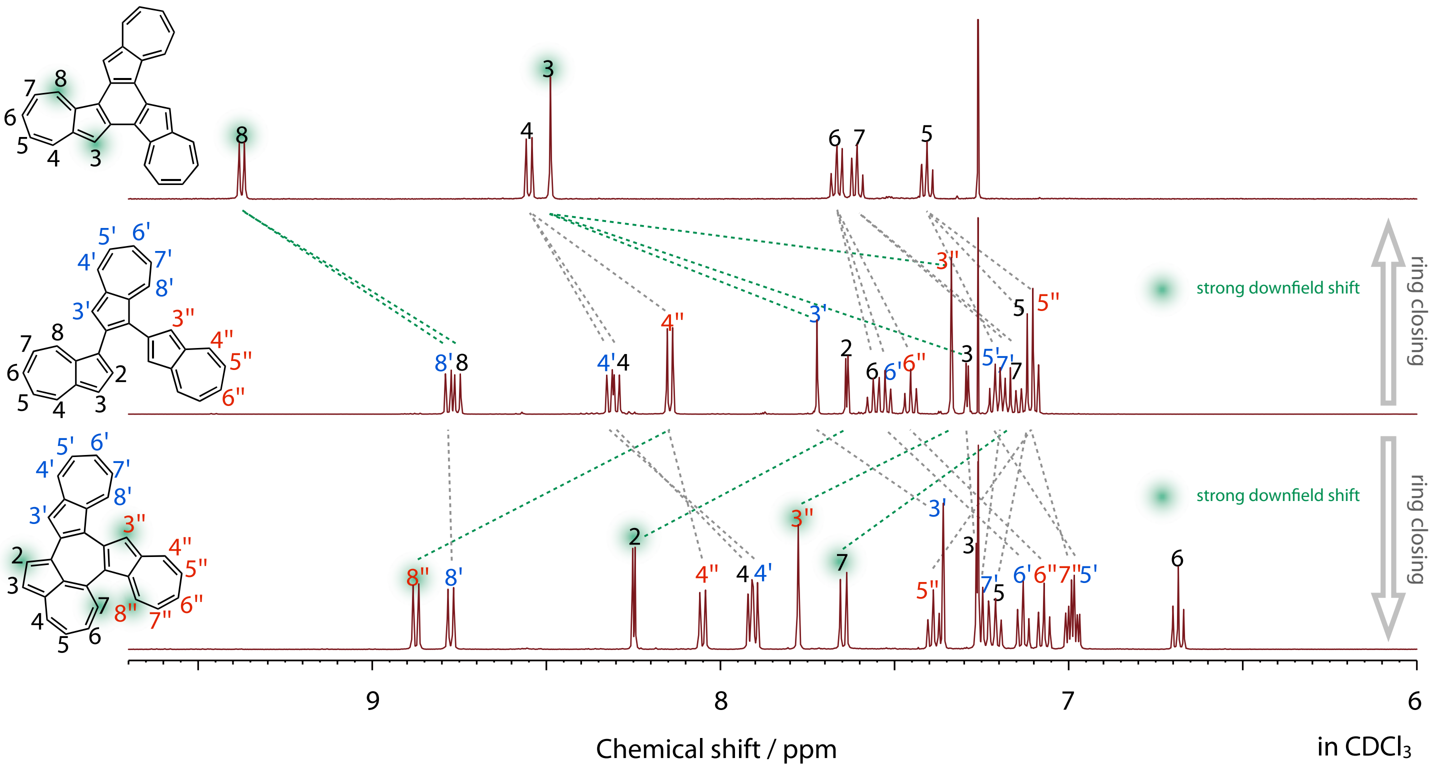


Figure S10. Comparison of ^{1}H NMR spectra of **1**,**3**, and **4**.

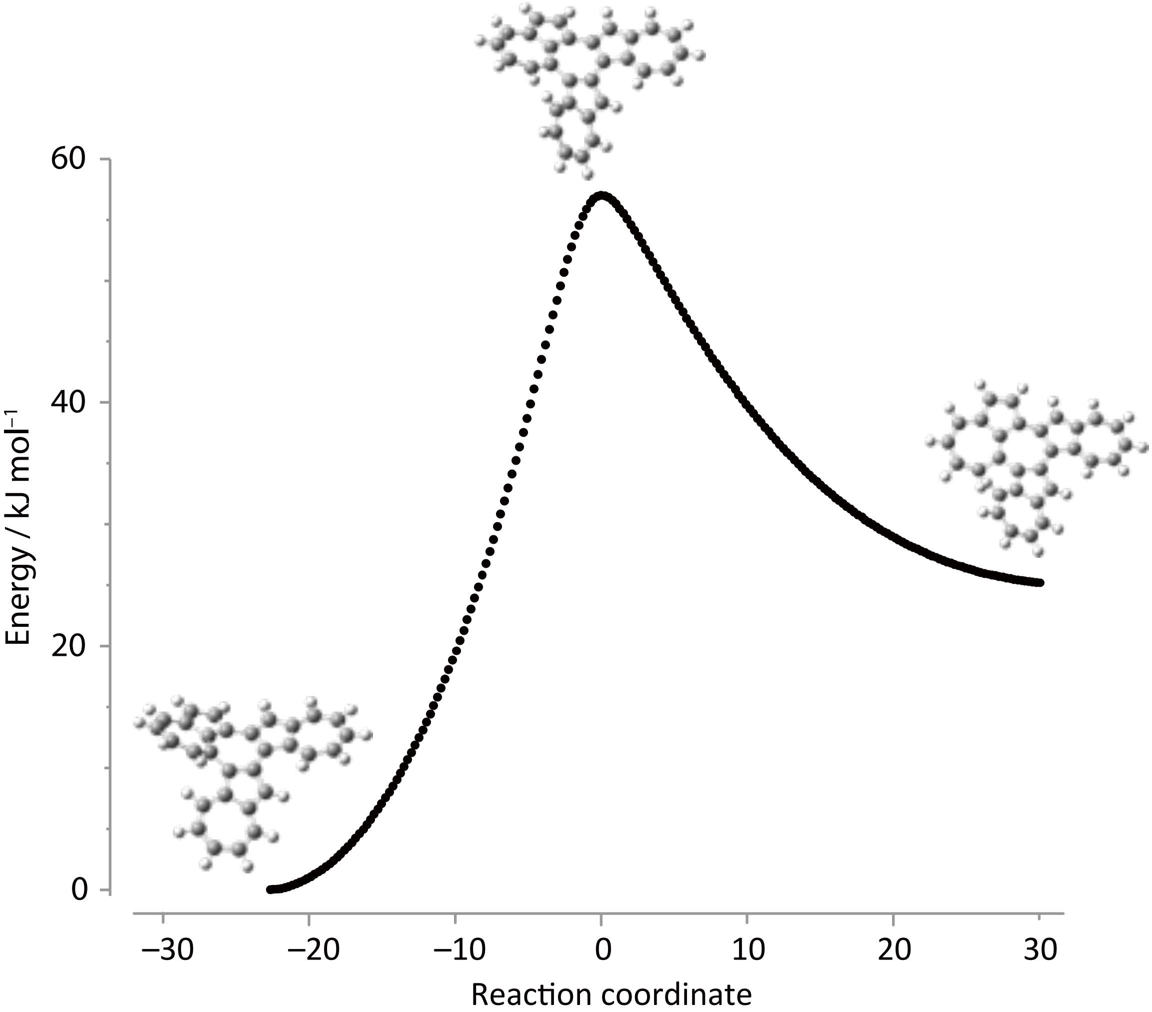


Figure S11. Energy profile for the inversion of **4** computed at the IRC-B3LYP/3-21G//B3LYP/3-21G level.

Table S2. Crystallographic parameters of **1**, **3**, and **4**•C_{60}.

Compd	**1**: $C_{30}H_{20}$	**3**: $C_{30}H_{18}$	**4**•C_{60}: $C_{30}H_{18}$•C_{60}•C_6H_5Cl
Crystal system (Space group)	triclinic ($P\bar{1}$)	monoclinic ($P2_1/c$)	triclinic ($P\bar{1}$)
a (Å)	8.971(4)	12.8311(19)	10.2317(3)
b (Å)	10.708(5)	13.989(2)	13.1426(5)
c (Å)	10.738(5)	11.0453(16)	20.7881(5)
α (°)	80.838(5)	90	81.645(3)
β (°)	84.122(6)	111.612(2)	81.442(2)
γ (°)	88.022(6)	90	69.189(3)
T (K)	90	120	120
V (Å$^{3)}$	1012.9(8)	1843.2(5)	2570.97(14)
Z	2	4	2
D_{calc} (g/cm^3)	1.247	1.364	1.565
Crystal size (mm)	0.324 × 0.323 × 0.189	0.259 × 0.220 × 0.041	0.144 × 0.113 × 0.091
Unique data	4147	4526	10070
Parameters	272	560	727
R_1 ($\sigma > 2.0$)	0.0557	0.0480	0.1431
wR_2 ($\sigma > 2.0$)	0.1728	0.1364	0.3816
Goodness-of-fit	1.176	0.865	1.061

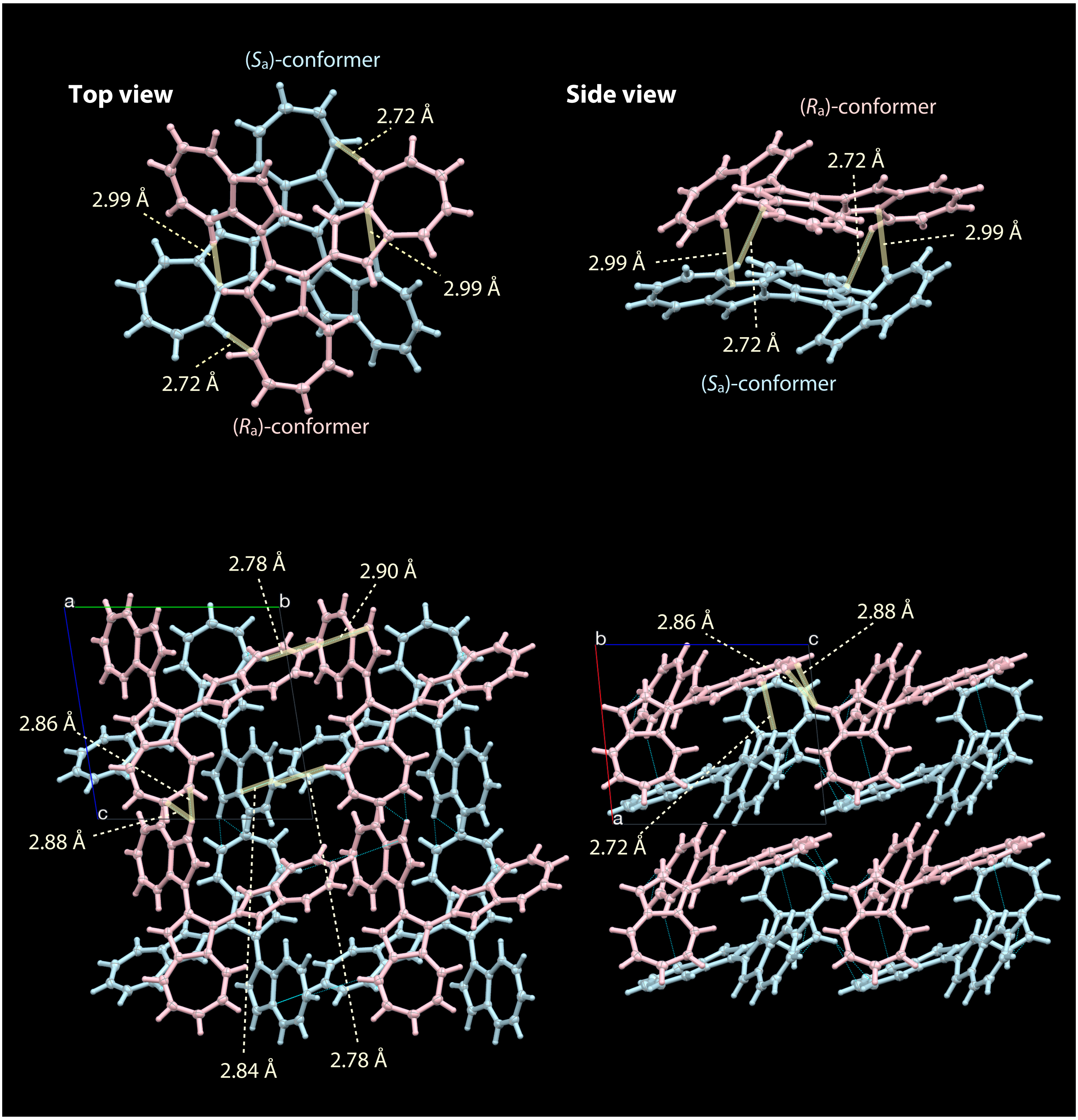


Figure S12. Crystal packing of **1**.

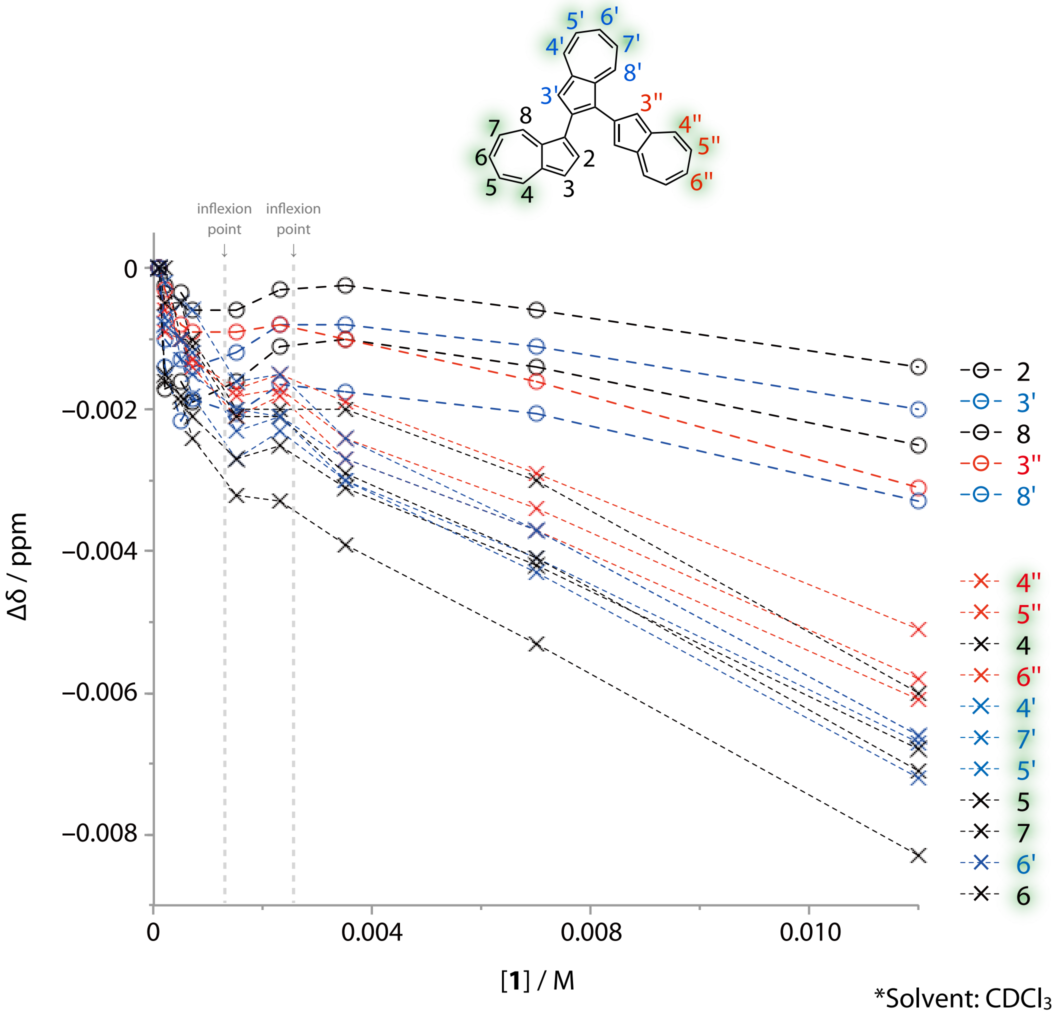
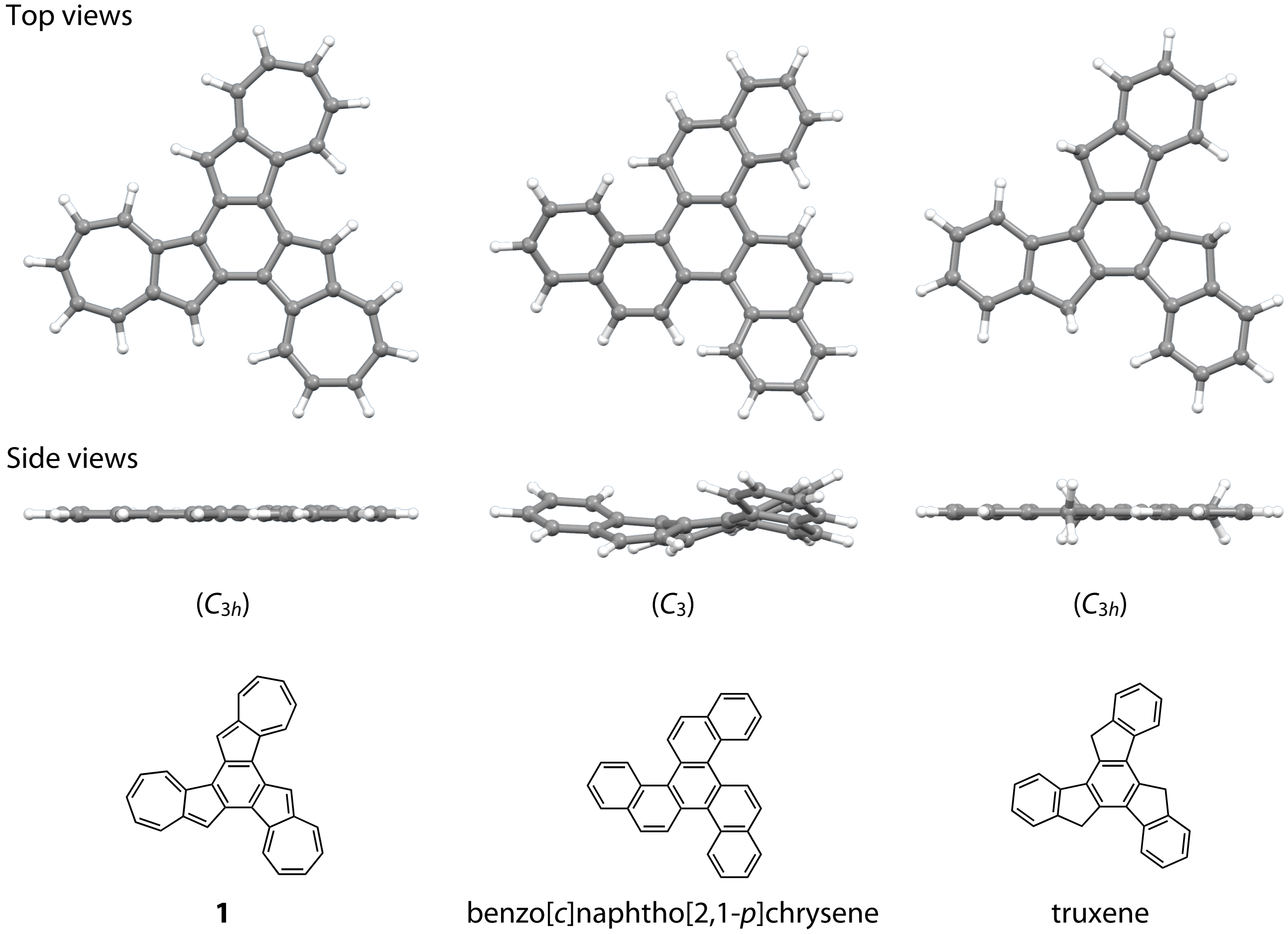


Figure S13. Concentration dependence of chemical shift of ^{1}H NMR signal of **1**.

Optimized structures



HOMO-LUMO levels

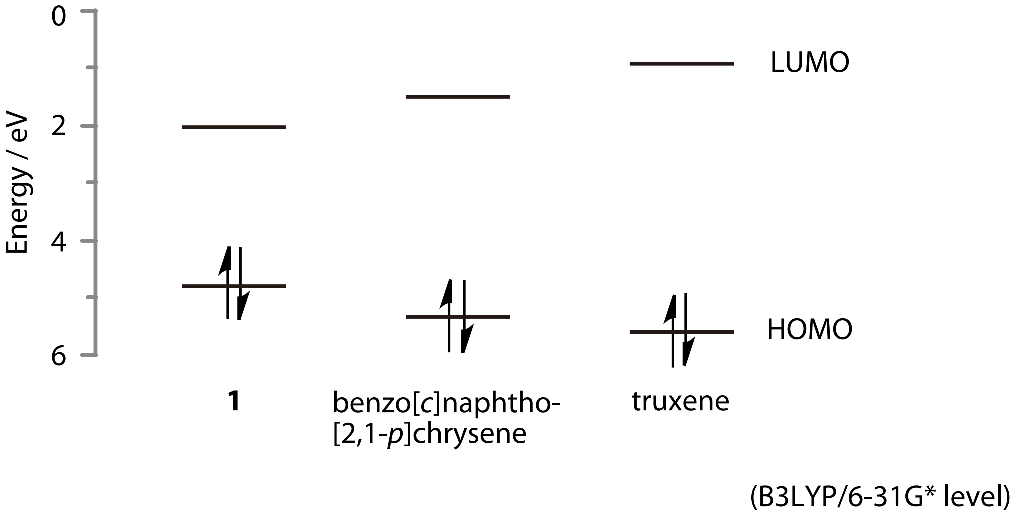
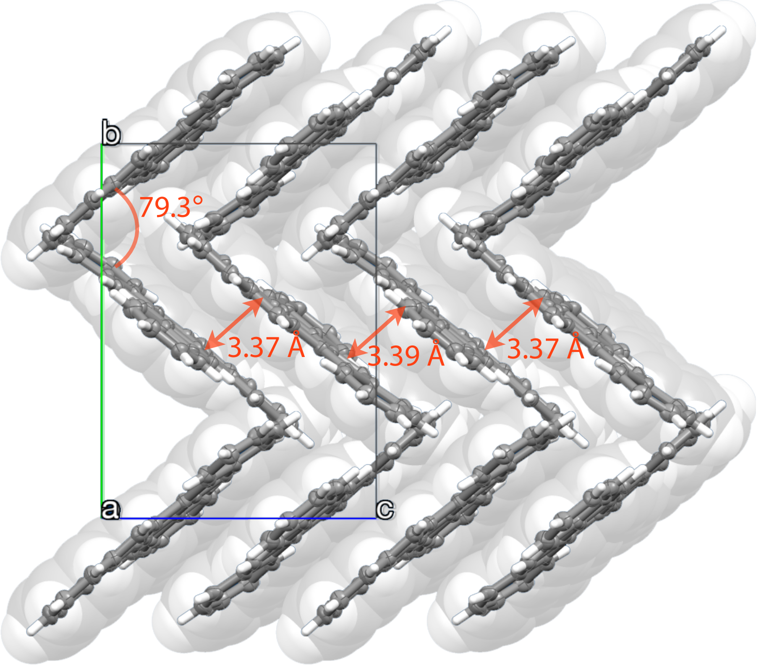


Figure S14. Optimized structures and HOMO-LUMO levels of **1**, benzo[*c*]naphtho[2,1-*p*]-chrysene, and truxene.



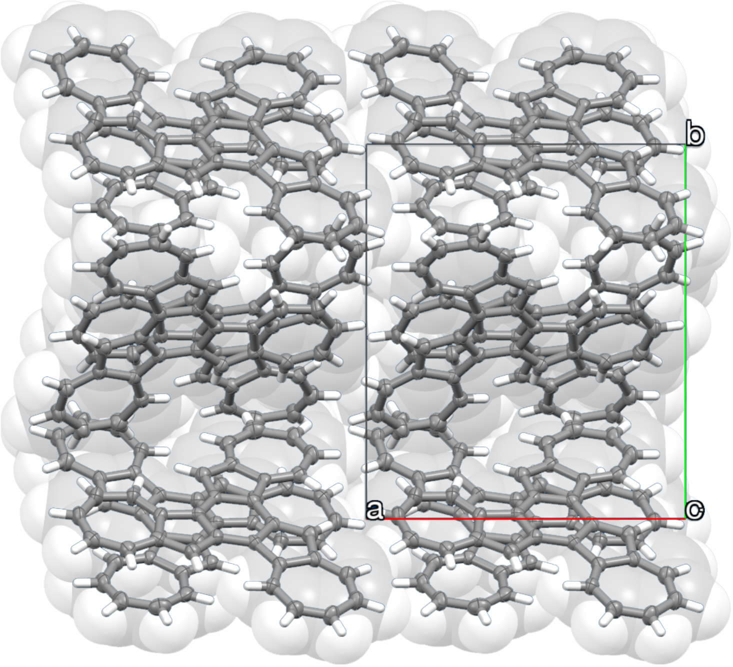


Figure S15. Crystal packing of **3**.

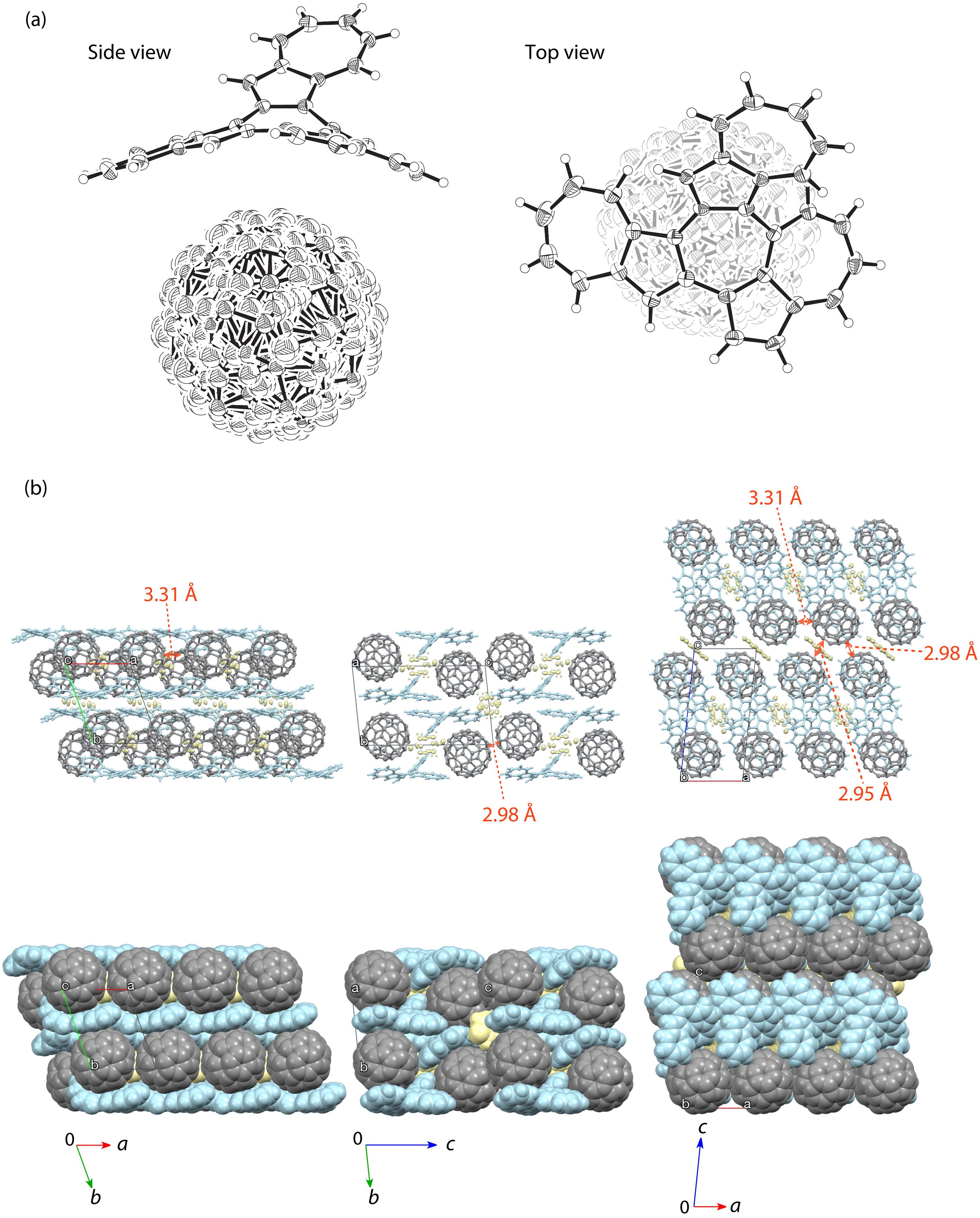
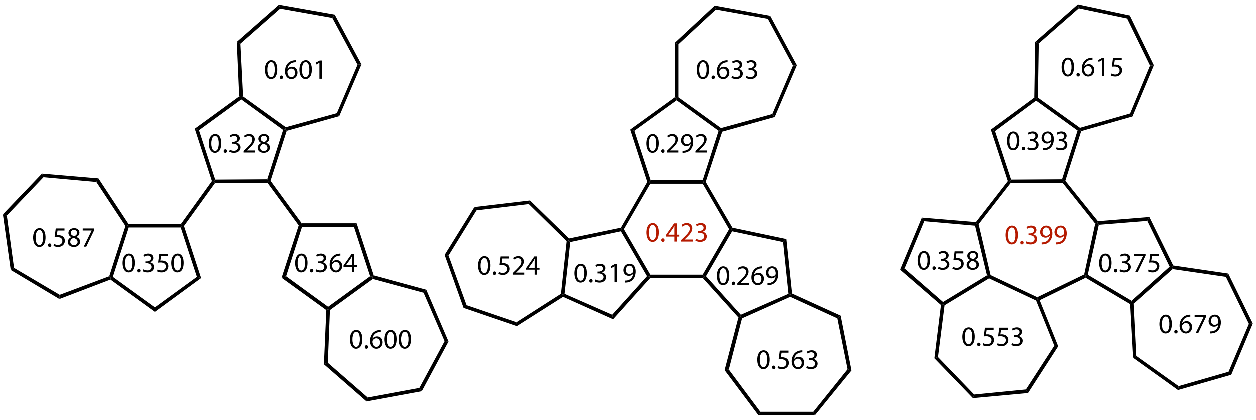


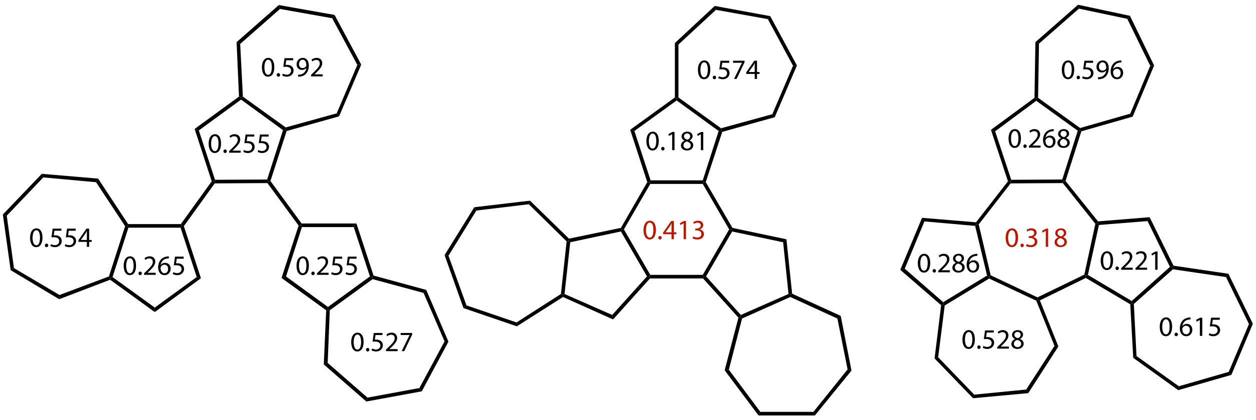
Figure S16. (a) ORTEP drawings of **4**•C$_{60}$. Chlorobenzene molecule is omitted for clarity. (b) Crystal packing of **4**•C$_{60}$•PhCl.

Experimental (X-ray analysis)



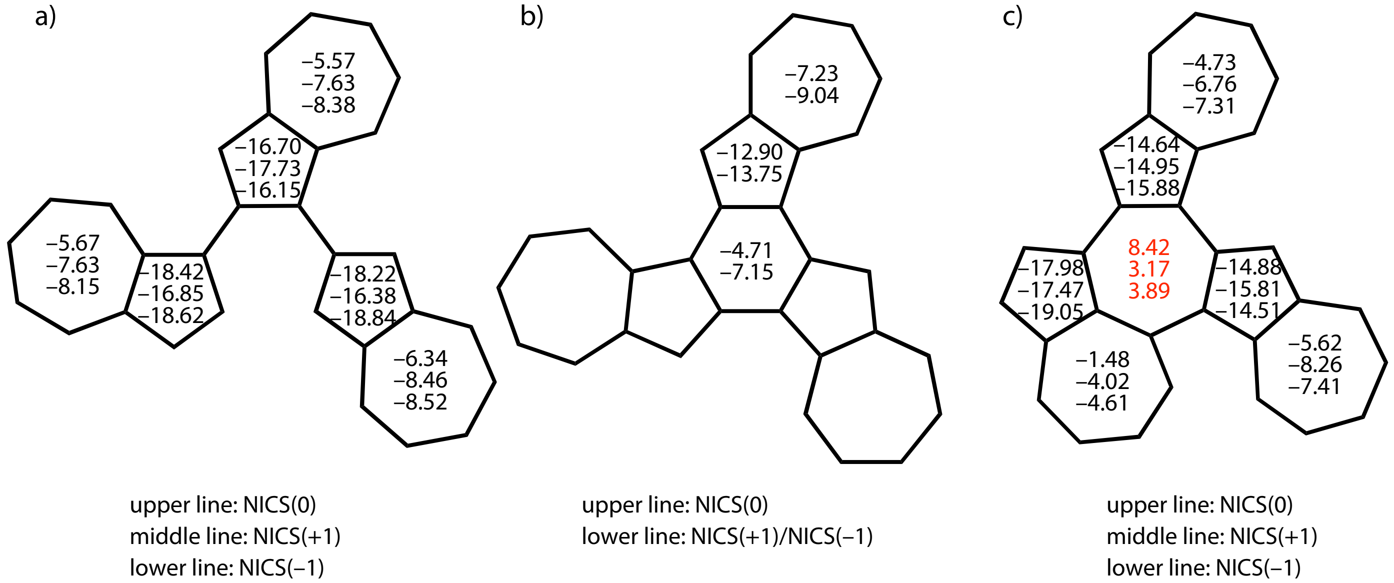
1 **3** **4**

Calculation (B3LYP/6-31G* level)



1 **3** **4**

Figure S17. Harmonic oscillator model of aromaticity (HOMA) values of **1**, **3**, and **4** reduced from the structures obtained by (a) single-crystal X-ray analysis and by (b) theoretical calculation.



* GIAO-HF/6-311+G(2d,p)//B3LYP/6-31G(d) level.

Figure S18. Nucleus-independent chemical shift [NICS(0) (upper), NICS(+1) (middle), and NICS(–1) (lower)] values of a) **1**, b) **3**, and c) **4**.

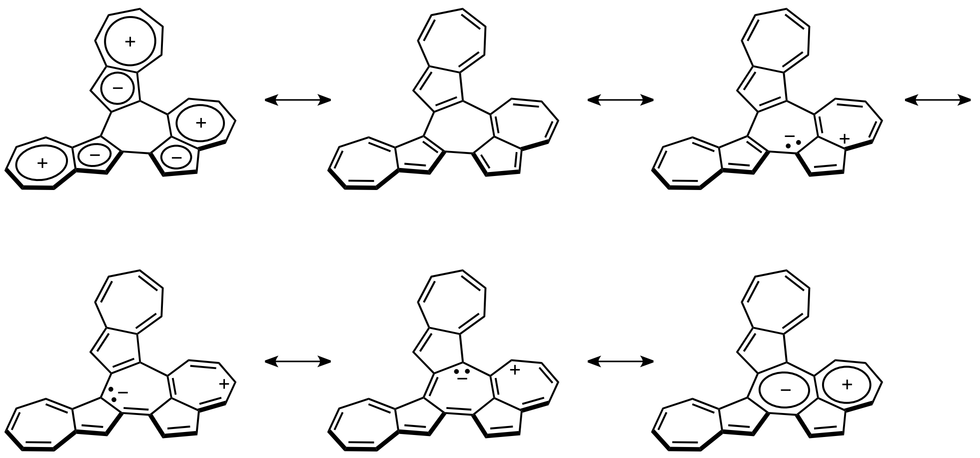


Figure S19. The speculated resonance structures of **4**.

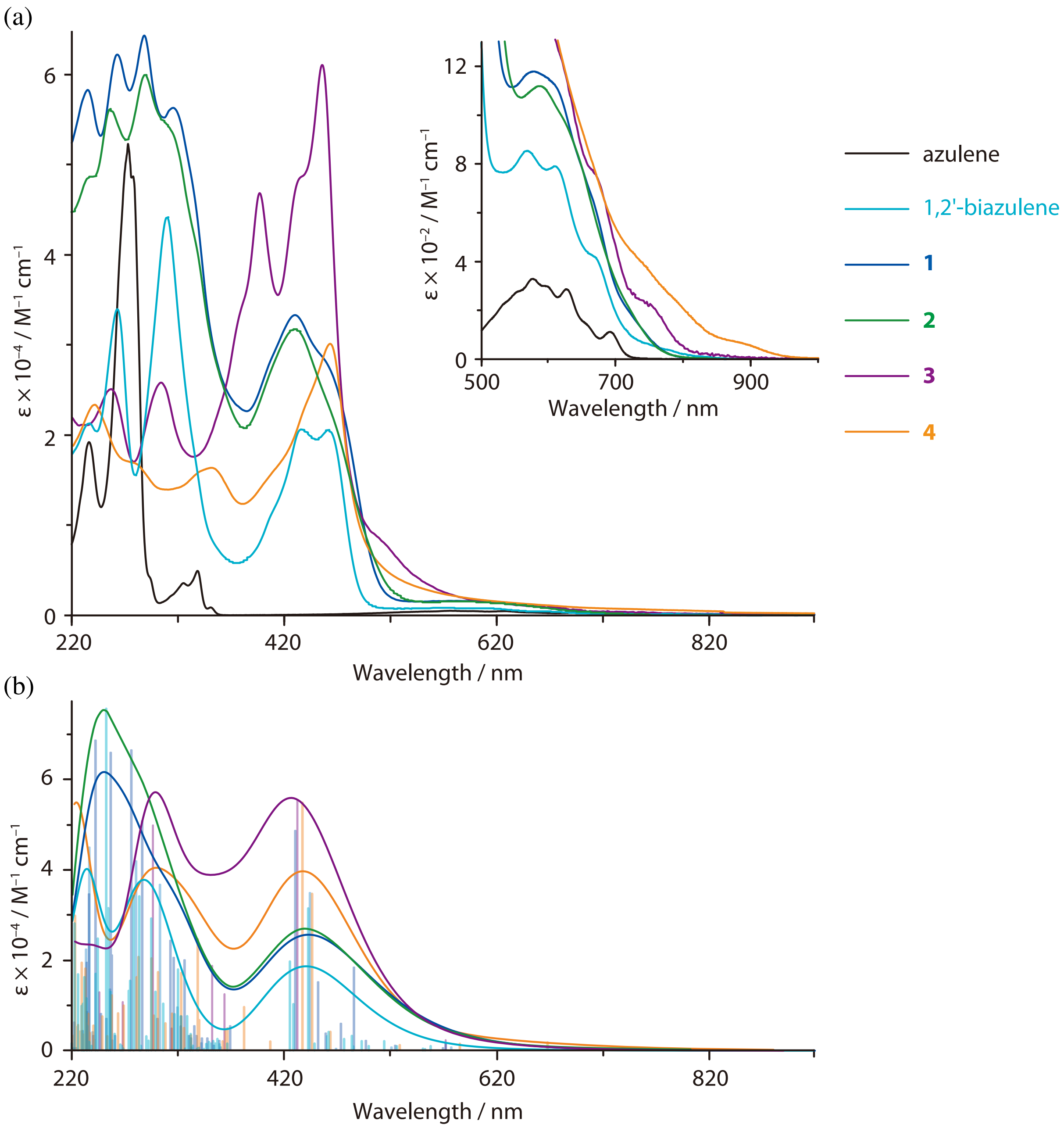


Figure S20. (a) UV-vis absorption spectra of azulene, 1,2'-biazulene, and **1**–**4** in THF. (b) TD-DFT calculation of 1,2'-biazulene, and **1**–**4** at TD-B3LYP/6-31G*//M06-2X/6-31G* level for **2** (*syn*-form) and TD-B3LYP/6-31G*//B3LYP/6-31G* level for others.

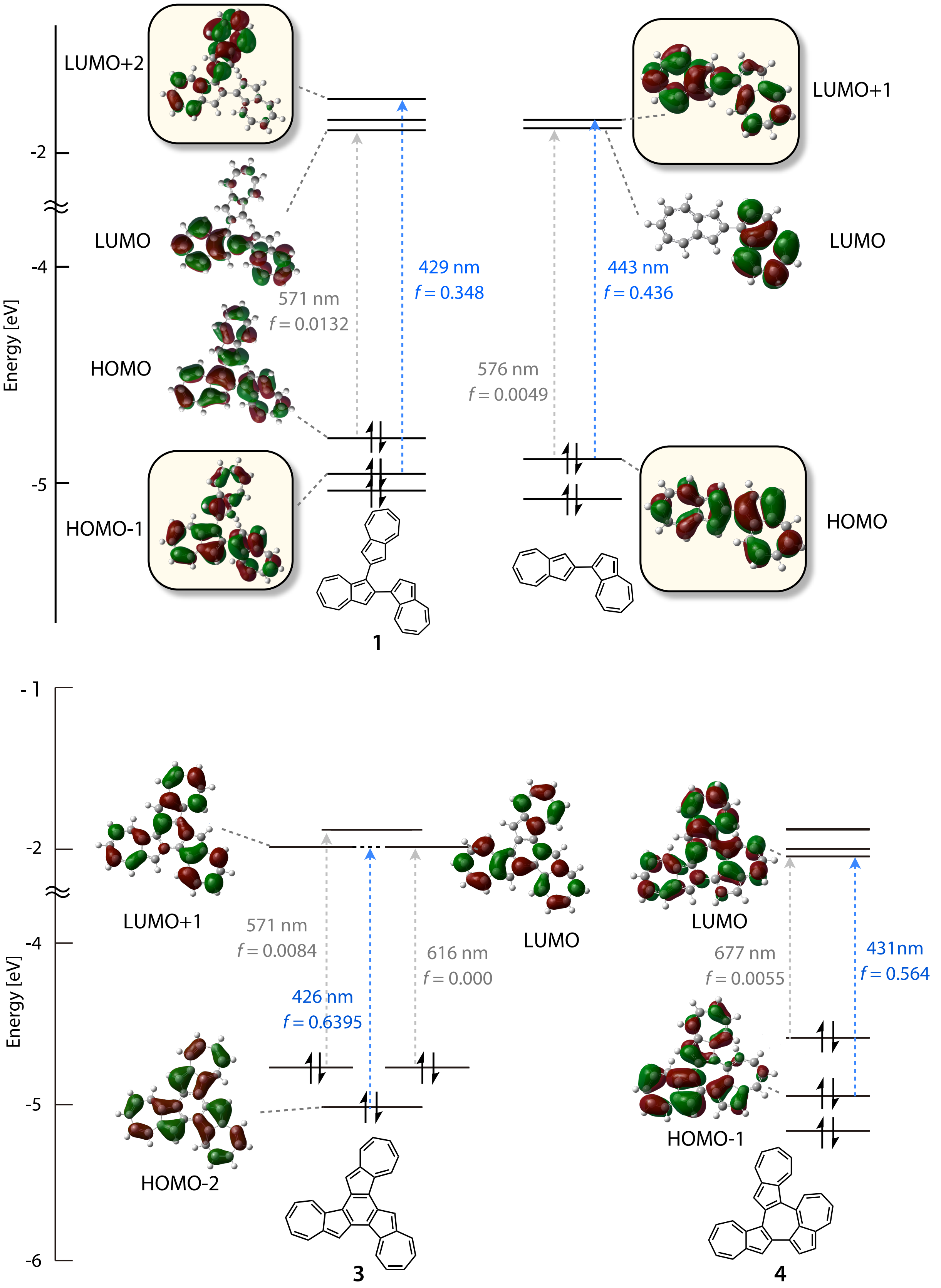


Figure S21. (a) MO diagrams of 1,2'-biazulene, **1**, **3**, and **4** calculated at TD-B3LYP/6-31G*//B3LYP/6-31G* level.

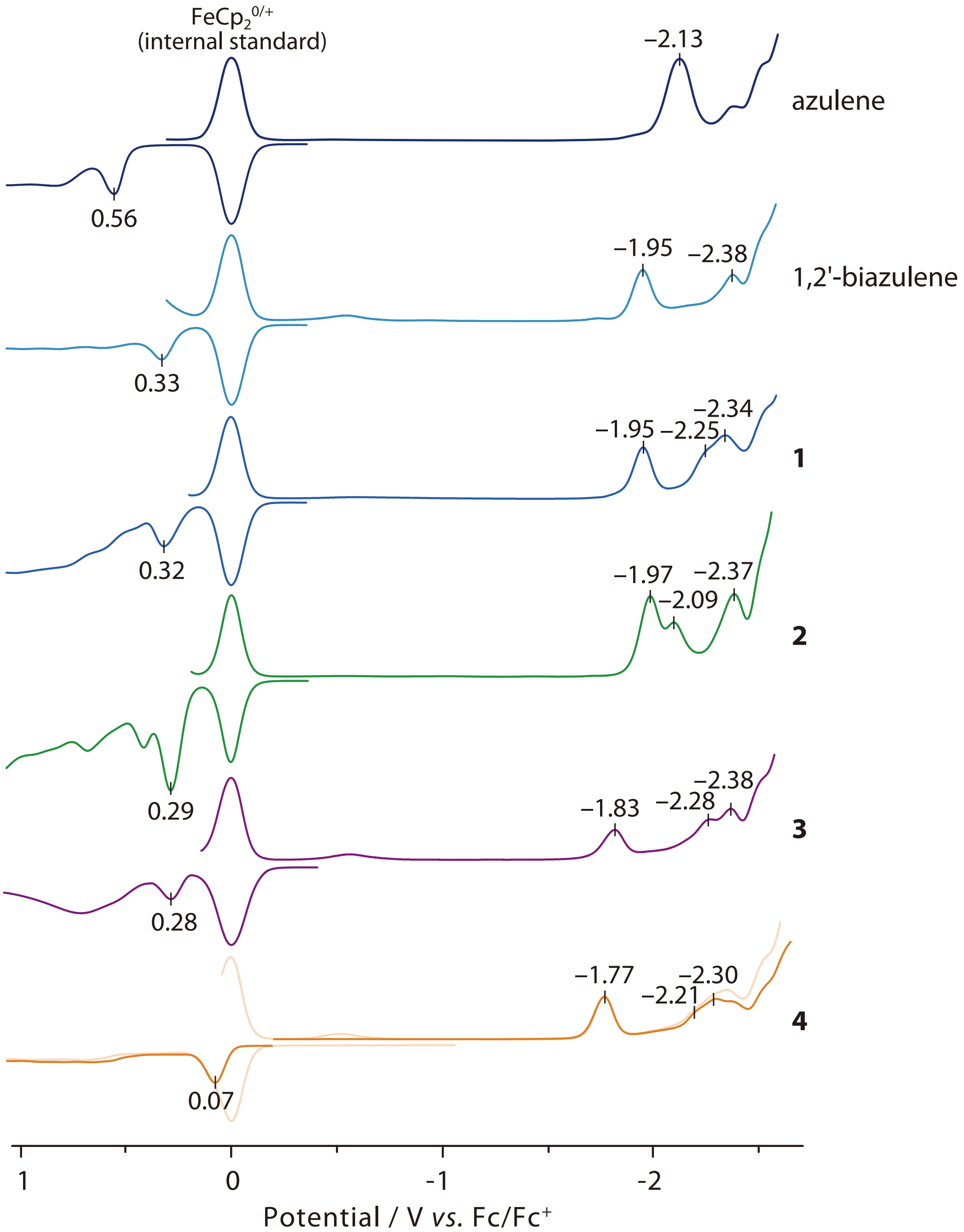
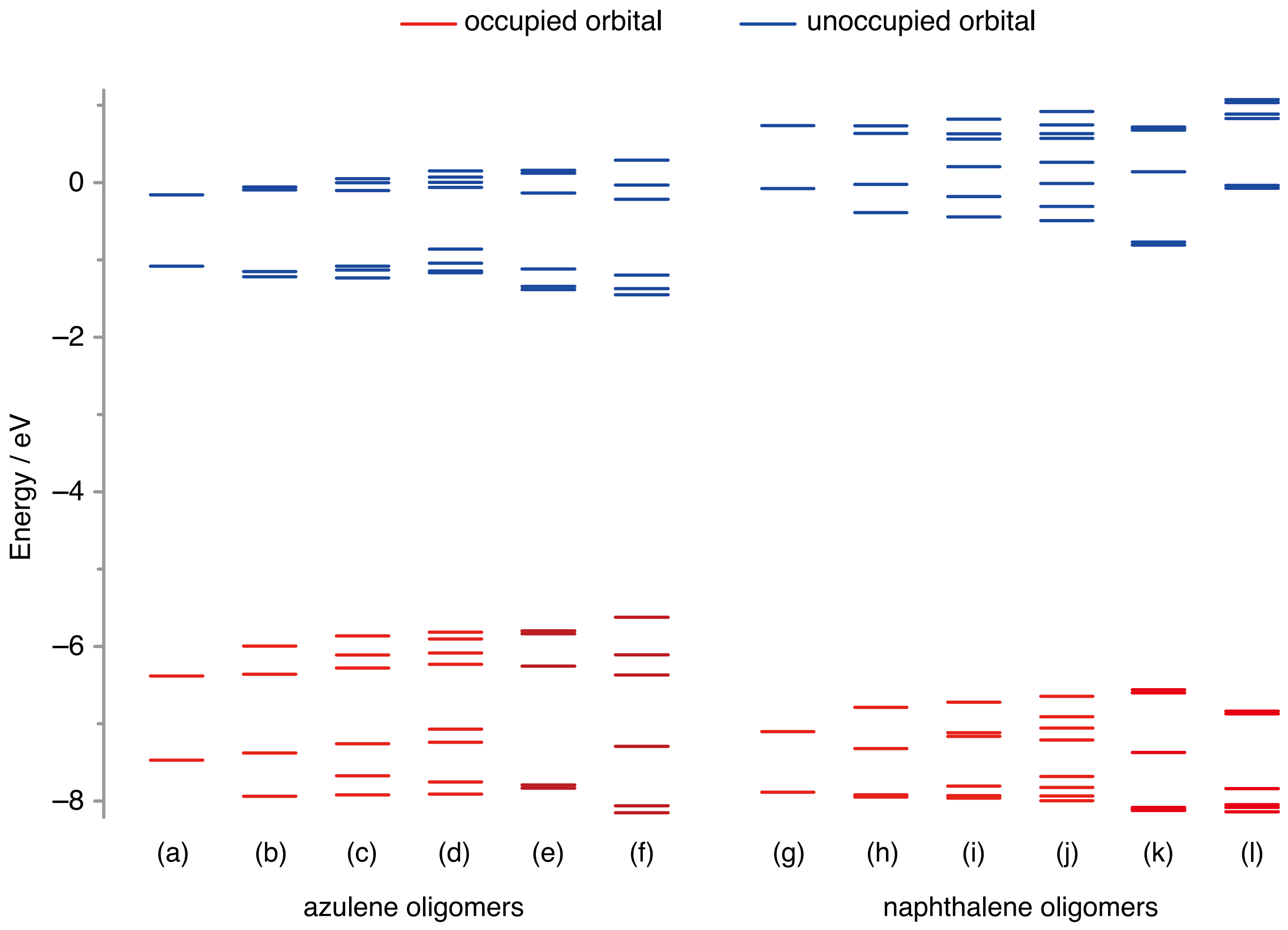
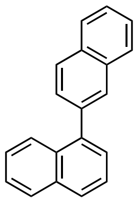
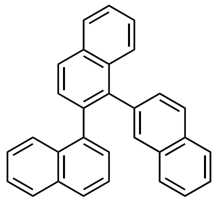


Figure S22. Square wave voltammograms of azulene, 1,2'-biazulene, and **1**–**4** (1.0 mM) on a Pt electrode in 1.0 M $^{n}Bu_4NPF_6$, PhCN. All solutions contain a ferrocene internal standard (1.0 mM).

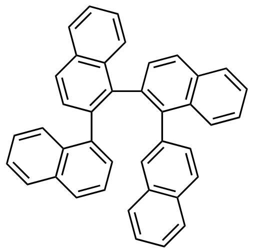




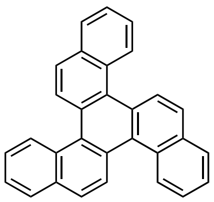
1,2'-binaphthalene



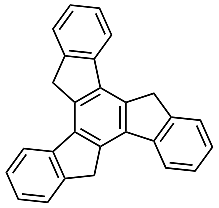
1,2':1',2''-ternaphthalene



1,2':1',2'':1'',2'''-quaternaphthalene (**6**)



benzo[*c*]naphtho[2,1-*p*]chrysene



truxene

Figure S23. MO diagrams of (a) azulene, (b) 1,2'-biazulene, (c) **1**, (d) **2**, (e) **3**, (f) **4**, (g) naphthalene, (h) 1,2'-binaphthalene, (i) 1,2':1',2''-ternaphthalene, (j) 1,2':1',2'':1'',2'''-quaternaphthalene (**6**), (k) benzo[*c*]naphtho[2,1-*p*]chrysene, and (l) truxene calculated at B3LYP/6-31G* level.