Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of sterically congested double helicene by alkyne cycloisomerization

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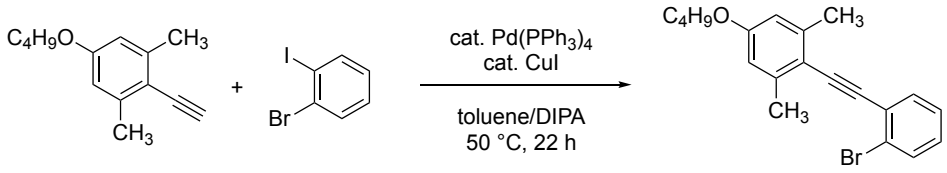
1. Instrumentation and materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. ^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on a JEOL JNM-ECA600II spectrometer. Chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V 670 spectrometer. High-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive ionization mode. X-ray data were obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics. Cyclic voltammograms were obtained under the following conditions; solvent: CH_2Cl_2, electrolyte: 0.1 M Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt, reference electrode: $Ag/AgNO_3$, scan rate: 0.05 V/s. Gel permeation chromatography (GPC) was conducted using a JAIGEL-2HR Plus equipped with a JAI LabACE LC-7080 plus preparative HPLC instrument. All calculations were carried out using the *Gaussian 16* software package.[1] Initial geometry for the calculations of **1** was obtained from the X-ray crystal structure. All calculations were performed with the density functional theory (DFT) method with the restricted B3LYP[2] level, employing the 6-31G(d) basis sets.

Dry toluene was purchased from KANTO CHEMICAL CO., INC. as a dehydrated grade. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Experimental procedures and compound data

1-Bromo-2-(2,6-dimethyl-4-butoxyphenylethynyl)benzene S1

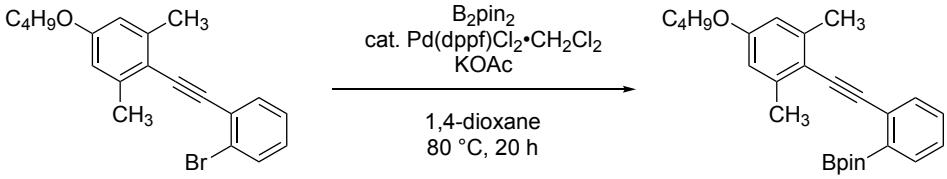


S1

To a mixture of 1-bromo-2-iodobenzene (12.3 g, 43.5 mmol), copper(I) iodide (CuI) (0.16 g, 0.83 mmol), and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (0.49 g, 0.42 mmol) in a degassed toluene/diisopropylamine (DIPA) mixture (*v*/*v* =4/1; 330 mL) was added 5-butoxy-2-ethynyl-1,3-dimethylbenezene[3] (8.40 g, 41.5 mmol). After stirring at 50 °C for 22 h, the mixture was cooled to room temperature and diluted with hexane. The solution was washed with aqueous 1 N HCl, saturated aqueous $NaHCO_3$, and water, and then dried over Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane/chloroform (*v*/*v* =9/1) as the eluent to give the desired product **S1** as a pale yellow solid (11.3 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.61 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.55 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.27 (dt, *J* = 1.2, 11.4 Hz, 1H), 7.14 (dt, *J* = 1.7, 11.5 Hz, 1H), 6.63 (s, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 2.53 (s, 6H), 1.76 (quin, *J* = 7.1 Hz, 2H), 1.49 (sext, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 159.2, 142.6, 133.2, 132.6, 128.8, 127.1, 126.5, 125.0, 114.9, 113.2, 94.9, 92.4, 67.7, 31.4, 21.7, 19.4, 14.0 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{20}H_{22}BrO$ 357.0849; Found 357.0842.

Boronic acid S2



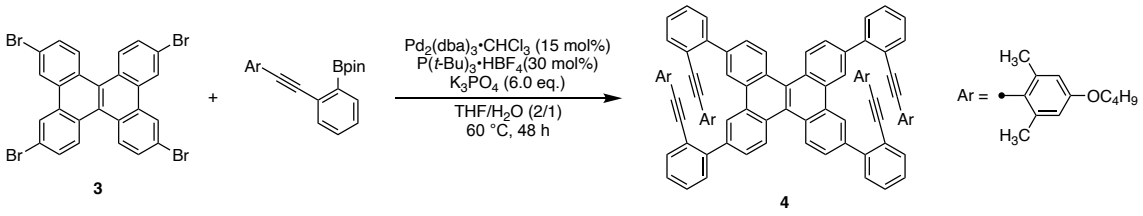
S1 **S2**

To a mixture of **S1** (1.19 g, 3.32 mmol), bis(pinacolato)diboron ($(Bpin)_2$) (1.01 g, 3.99 mmol), and potassium acetate (1.31 g, 13.4 mmol) in anhydrous 1,4-dioxane (17 mL) was added [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct ($Pd(dppf)Cl_2 \cdot CH_2Cl_2$) (0.11 g, 0.13 mmol). After stirring at 80 °C for 20 h, the mixture was cooled

to room temperature and diluted with chloroform. The solution was washed with water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was passed through a short pad of silica gel using hexane/ethyl acetate (*v*/*v* = 9/1) as the eluent. After removing the solvent by evaporation, a pale yellow solid (1.11 g) containing the target compound **S2** obtained, which was used for the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.82 (dd, J = 0.95, 7.5 Hz, 1H), 7.57 (dd, J = 0.58, 7.8 Hz, 1H), 7.38 (dt, J = 1.5, 11.4 Hz, 1H), 7.27 (dt, J = 1.2, 11.2 Hz, 1H), 6.62 (s, 2H), 3.96 (t, J = 6.5 Hz, 2H), 2.56 (s, 6H), 1.76 (quin, J = 7.0 Hz, 2H), 1.49 (sext, J = 7.5 Hz, 2H), 0.98 (t, J = 7.4 Hz, 1H) ppm. δ = 1.27, 1.26 is peaks of impurities by B_2pin_2.; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 158.7, 142.5, 135.9, 133.2, 130.6, 129.3, 126.9, 116.0, 113.0, 97.3, 90.0, 84.0, 67.7, 31.5, 25.2, 25.0, 24.7, 21.7, 19.4, 14.0 ppm; HRMS (APCI): $[M]^+$ Calcd for $C_{26}H_{33}BO_3$ 403.2554; Found 403.2543.

Precursor 4

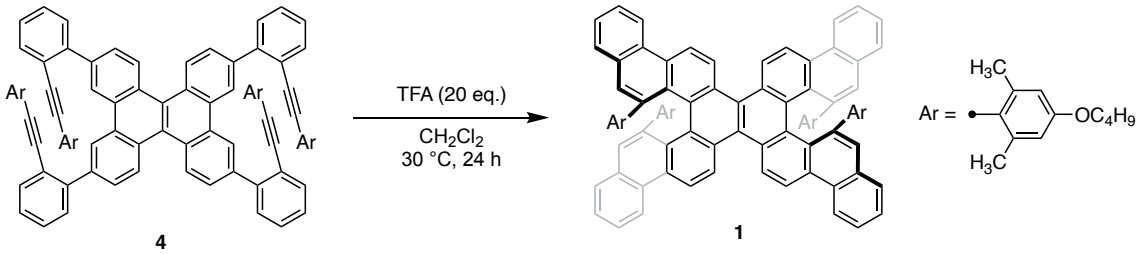


A Schlenk flask containing 2,7,10,15-tetrabromodibenzo[*g*,*p*]chrysene **(3)** (26 mg, 40 μmol), *ortho*-alkynylphenylboronic acid (97 mg, 240 μmol), $Pd_2(dba)_3$·$CHCl_3$ (8.3 mg, 8 μmol), P(t-Bu)$_3$·HBF_4 (4.6 mg, 16 μmol), and K_3PO_4 (51 mg, 240 μmol) was purged with N_2. To the mixture, degassed dry toluene (0.6 mL) and water (0.3 mL) were added. The mixture was stirred at 60 °C for 48 h. The reaction mixture was cooled to room temperature. The reaction mixture was extracted with CH_2Cl_2. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent *in vacuo*, the mixture was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 1/1). The roughly purified mixture was further purified by GPC with $CHCl_3$ as eluent. After removal of the solvent *in vacuo*, compound **4** (20 mg, 13 μmol, 35%) was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.69 (d, J = 1.7 Hz, 4H), 8.79 (d, J = 8.5 Hz, 4H), 7.99 (dd, J = 1.6, 8.5 Hz, 4H), 7.73–7.71 (m, 4H), 7.46–7.44 (m, 4H), 7.40–7.38 (m, 8H), 6.43 (s, 8H), 3.79 (t, J = 6.5 Hz, 8H), 2.21 (s, 24H), 1.65 (quin, J = 7.0 Hz, 8H), 1.39 (sext, J = 7.5 Hz, 8H), 0.90 (t, J = 7.4 Hz, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$, 298 K): δ = 158.7, 143.0, 142.2,

139.4, 133.2, 130.9, 129.9, 129.0, 128.7, 128.6, 128.3, 128.2, 127.7, 127.4, 124.6, 123.2, 96.0, 91.2, 67.6, 31.2, 29.8, 21.4, 19.3, 14.0 ppm; HRMS (APCI): $[M+H]^+$ Calcd for $C_{106}H_{97}O_4$ 1433.7381; Found 1433.7340.

Sterically congested double helicene 1



4 1

A Schlenk flask containing compound **4** (19 mg, 13 μmol) was purged with N_2. To the flask, degassed CH_2Cl_2 (1.0 mL) and 2,2,2-trifluoroacetic acid (0.02 mL) were added. The mixture was stirred at 30 °C for 24 h. The reaction mixture was quenched with $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic phase was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent *in vacuo*, the mixture was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 1/1). After removal of the solvent *in vacuo*, compound **1** (5.8 mg, 4.0 μmol, 31%) was obtained as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.75 (d, J = 4.2 Hz, 4H), 8.63 (s, 8H), 7.79–7.76 (m, 8H), 7.64 (t, J = 7.0 Hz, 4H), 7.17 (s, 4H), 6.04 (d, J = 2.4 Hz, 4H), 5.94 (d, J = 2.4 Hz, 4H), 4.08–4.01 (m, 8H), 1.99 (quin, J = 7.2 Hz, 8H), 1.74 (sext, J = 7.5 Hz, 8H), 1.53 (s, 12H), 1.25 (s, 12H), 1.23 (t, J = 7.6 Hz, 12H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$, 298 K): δ = 156.7, 138.0, 137.5, 134.1, 132.2, 130.8, 129.7, 129.5, 127.9, 126.7, 126.6, 126.5, 124.4, 123.3, 122.4, 114.4, 113.1, 67.7, 29.9, 20.8, 19.7, 19.2 ppm.; HRMS (APCI): $[M+H]^+$ Calcd for $C_{106}H_{97}O_4$ 1433.7381; Found 1433.7344.; Preparative resolution was conducted by HPLC using a chiral column (Daicel Chiralpak IA: 20×250 mm, 254 nm UV detector, rt, eluent: 40% CH_2Cl_2 in hexane, flow rate: 6 mL/min, retention time: 8.99 min for 1st fraction and 10.63 min for 2nd fraction); Purities of the obtained enantiomers were determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3: 4.6×250 mm, 254 nm UV detector, 293 K, eluent: 10% propan-2-ol in hexane, flow rate: 1 mL/min, retention time: 3.78 min for 1st fraction and 4.35 min for 2nd fraction).

3. NMR spectra

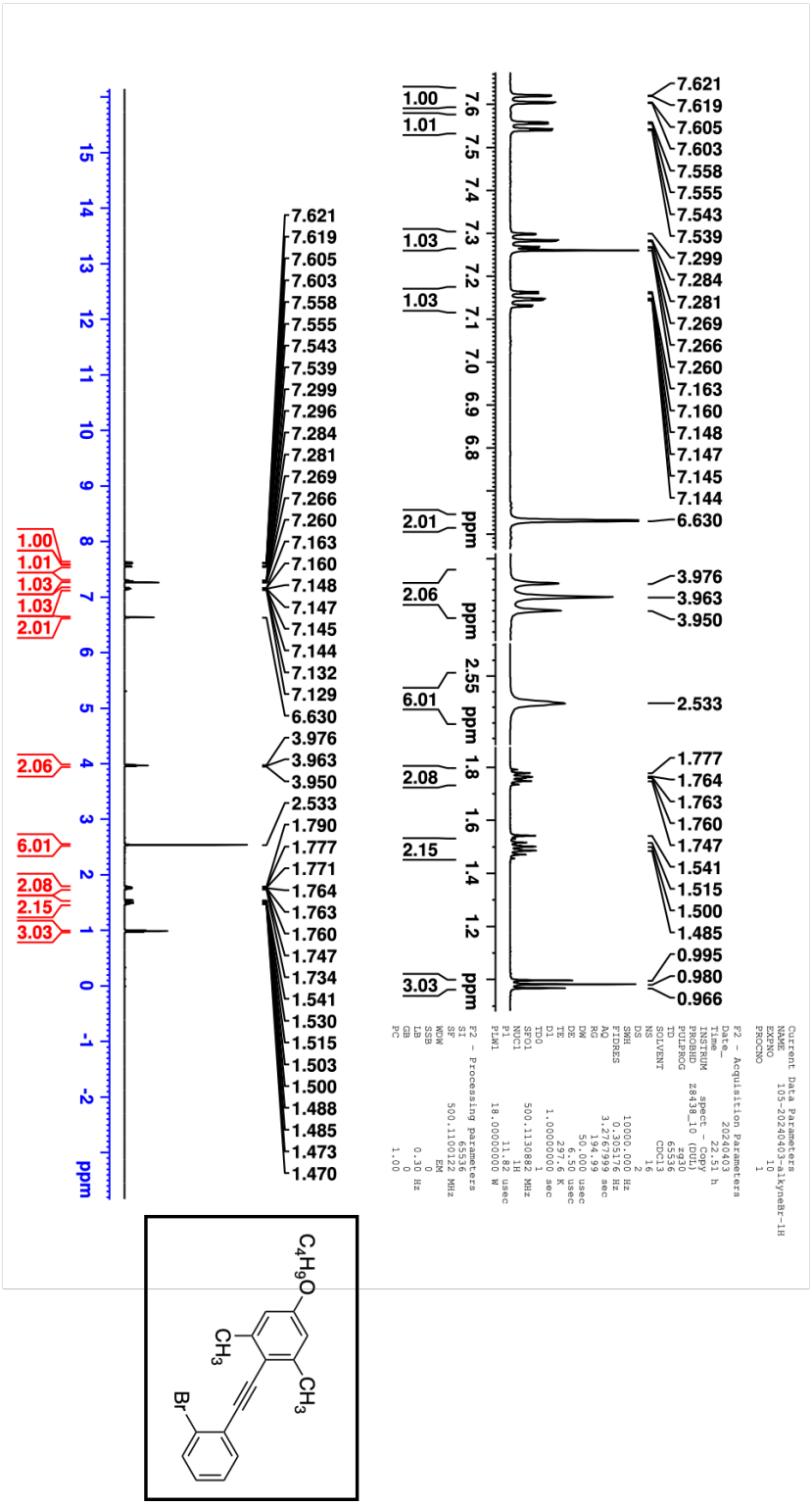


Figure S1. ^{1}H NMR spectrum of **S1** in $CDCl_3$ at 25 °C.

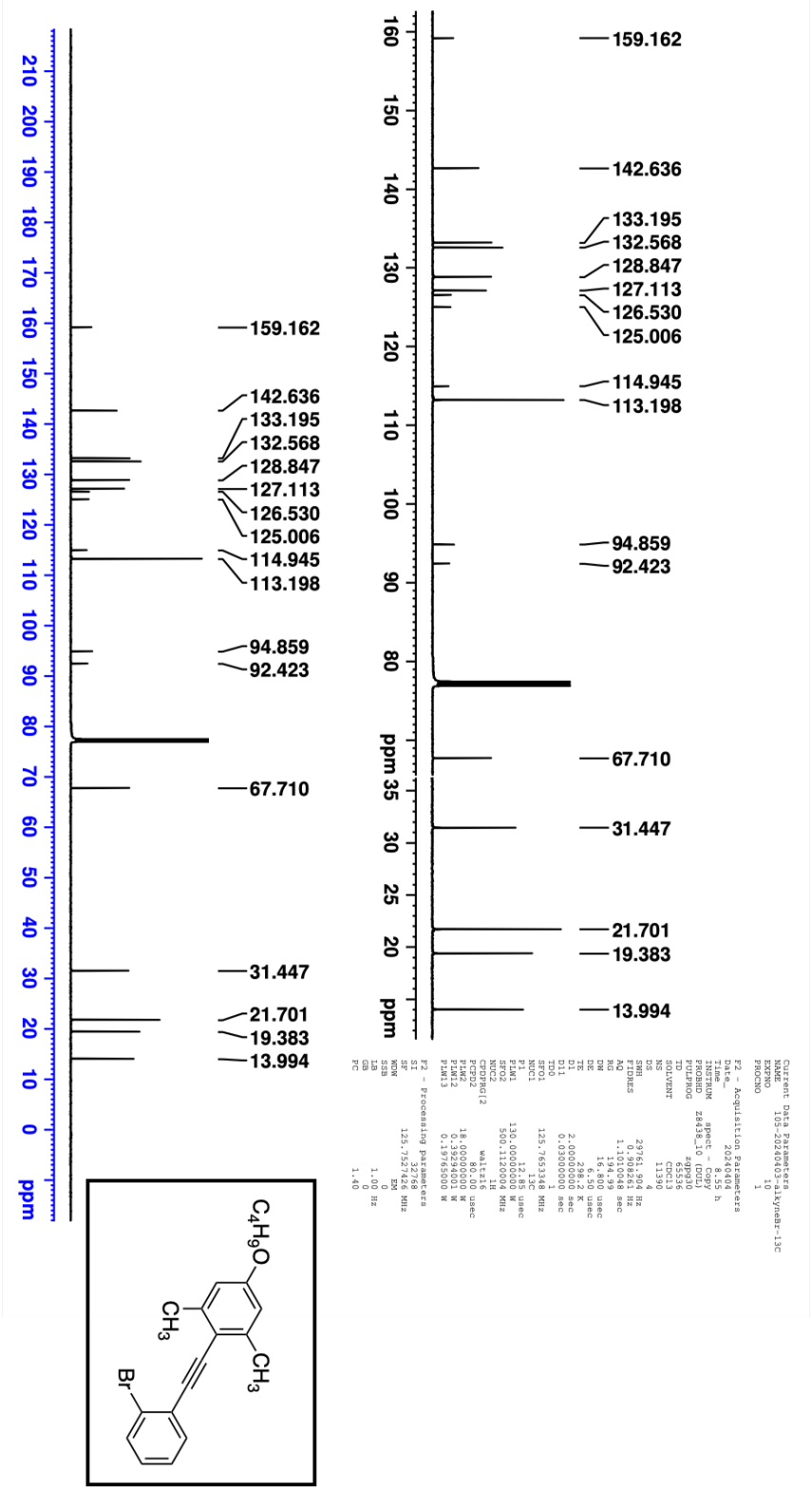


Figure S2. ^{13}C NMR spectrum of **S1** in $CDCl_3$ at 25 °C.

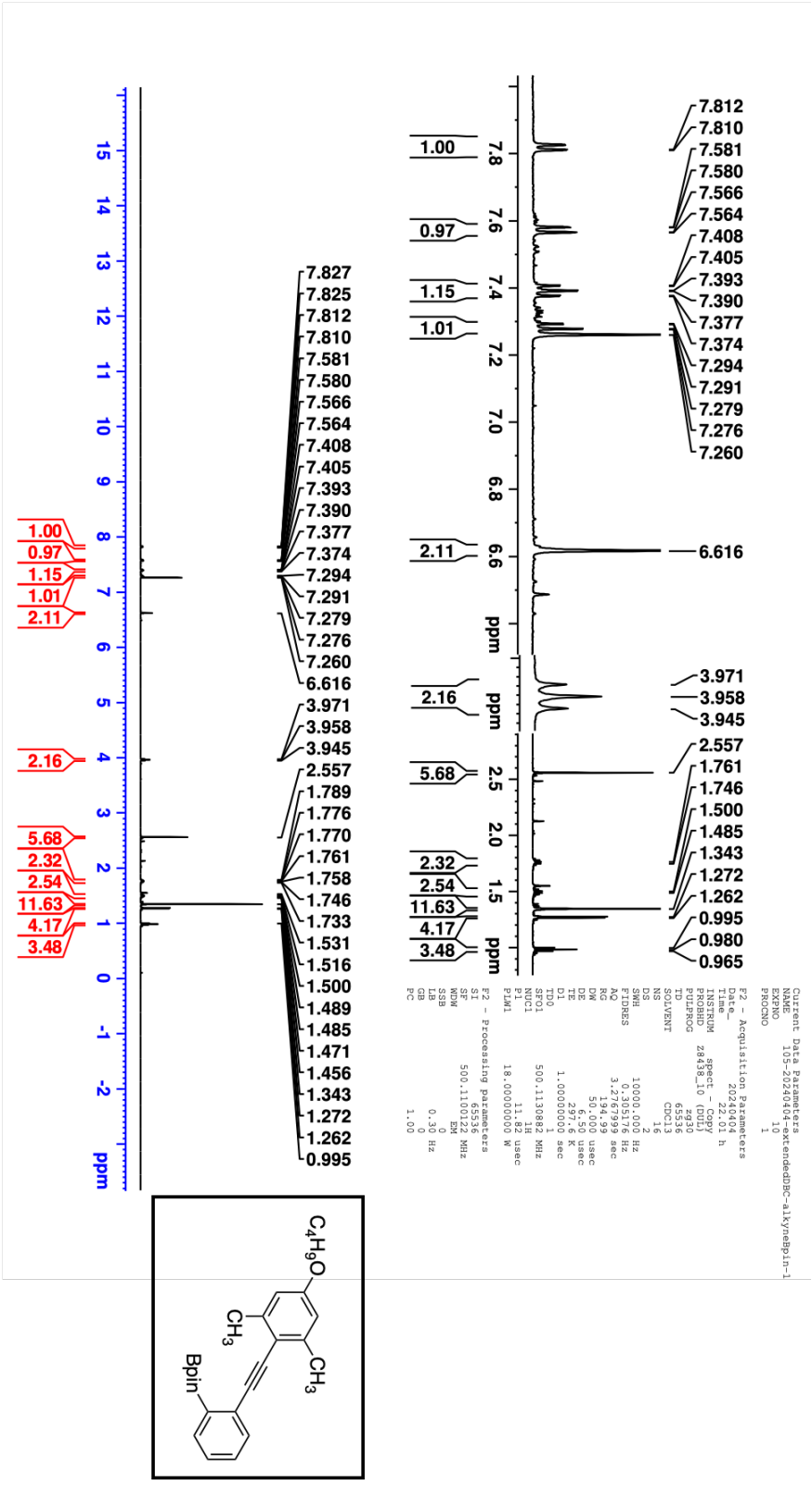


Figure S3. ^{1}H NMR spectrum of **S2** without further purification in $CDCl_3$ at 25 °C.

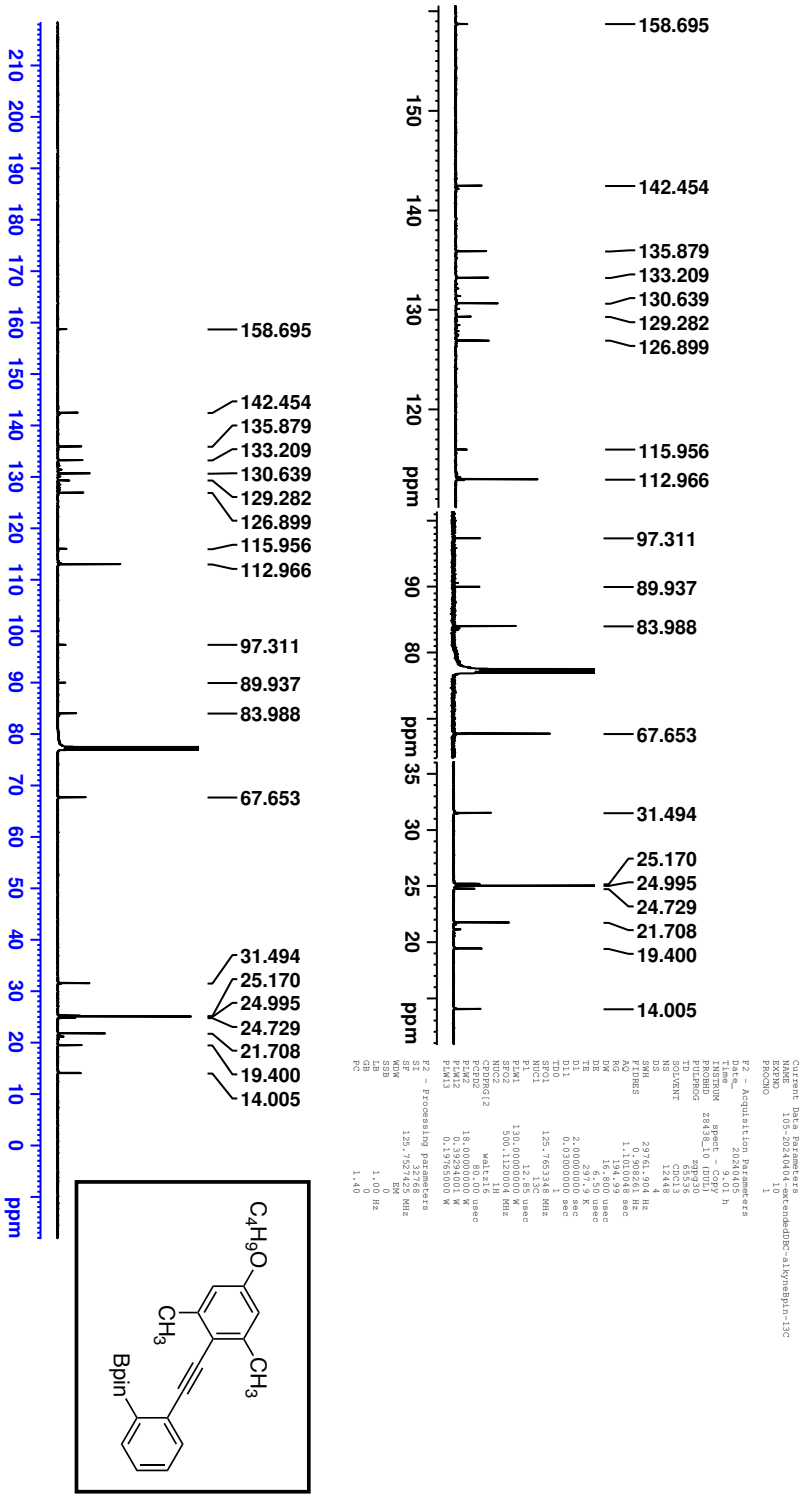


Figure S4. ^{13}C NMR spectrum of **S2** without further purification in $CDCl_3$ at 25 °C.

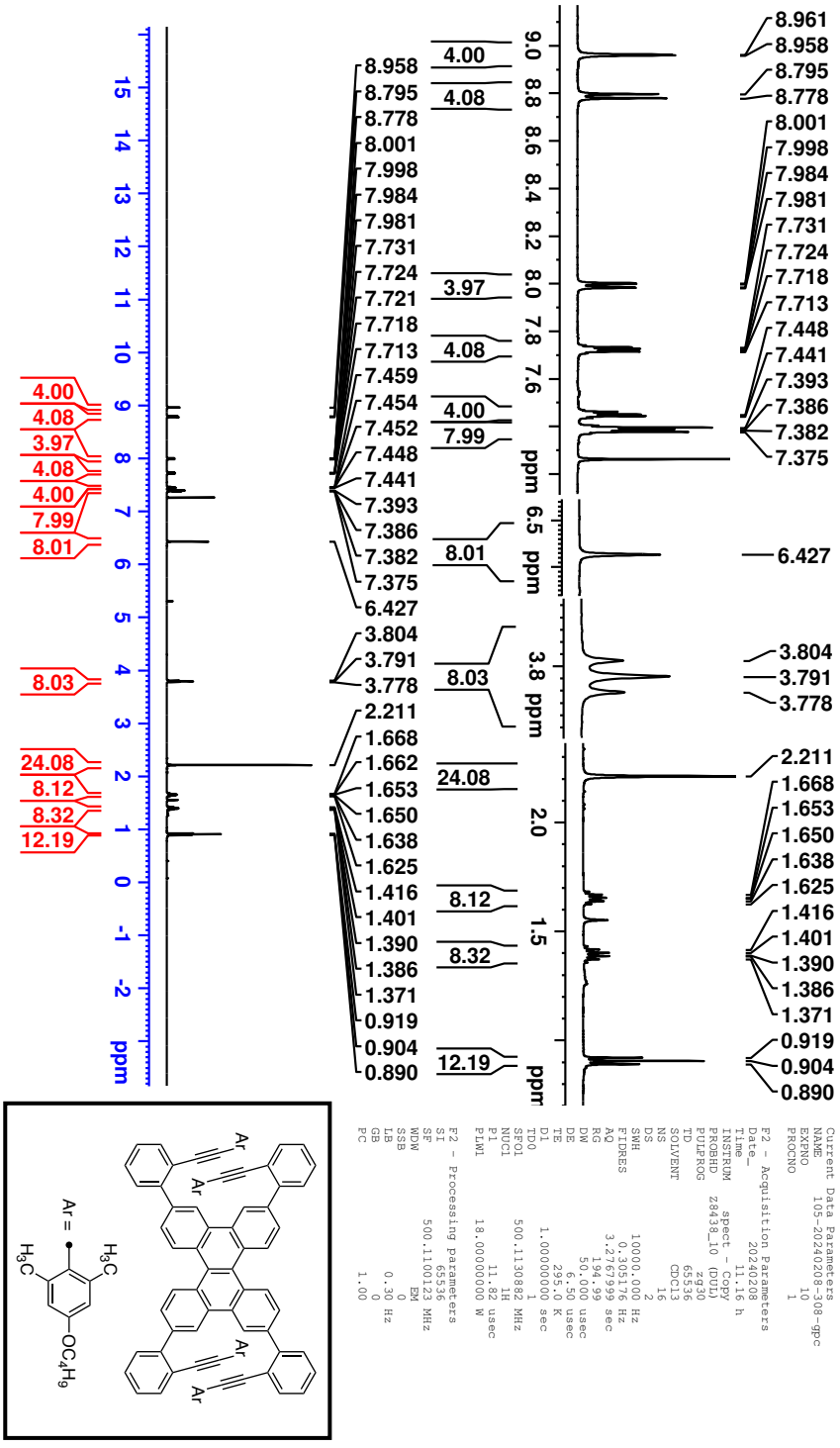


Figure S5. ^{1}H NMR spectrum of **4** in $CDCl_3$ at 25 °C.

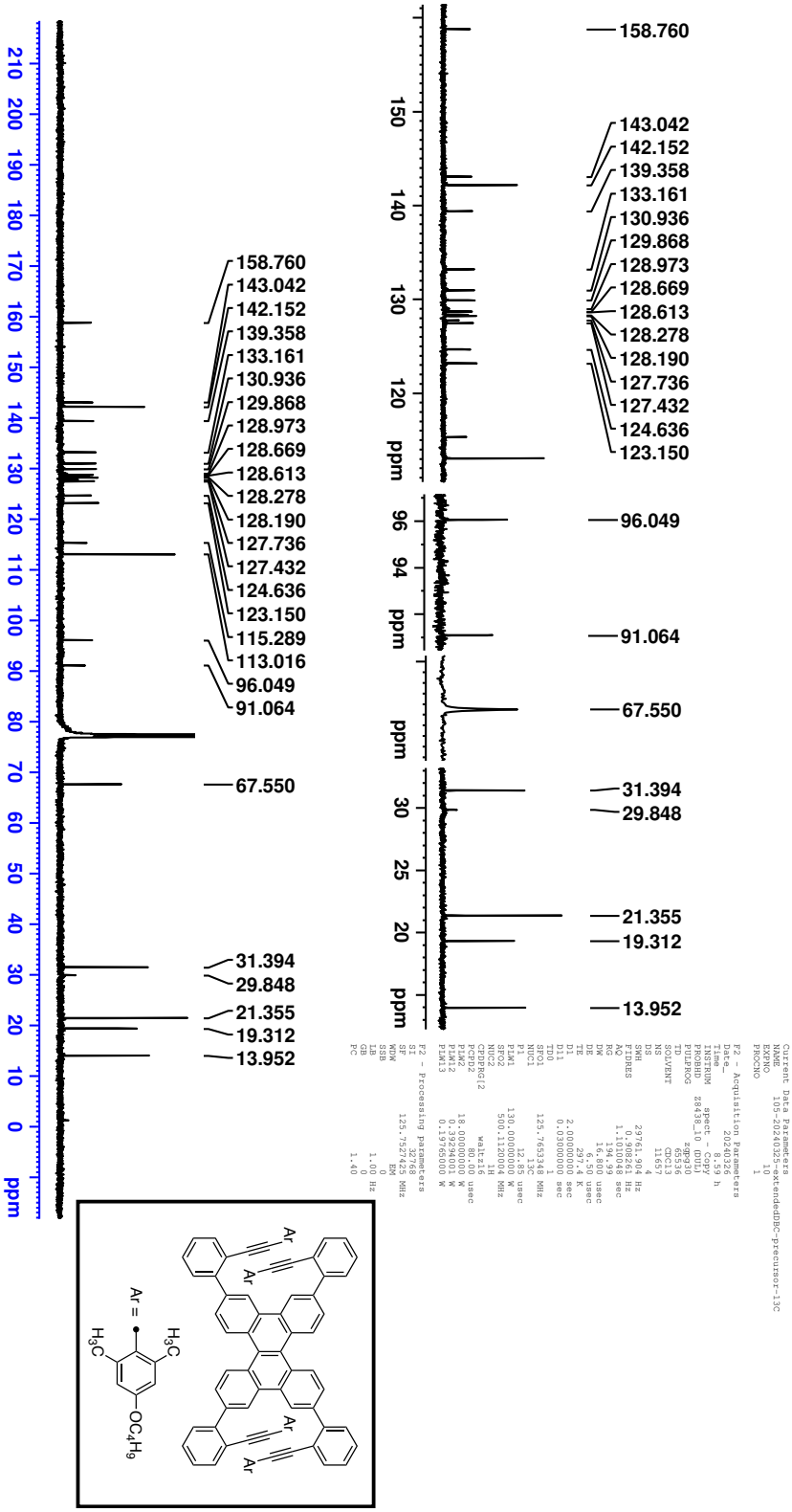


Figure S6. ^{13}C NMR spectrum of **4** in $CDCl_3$ at 25 °C.

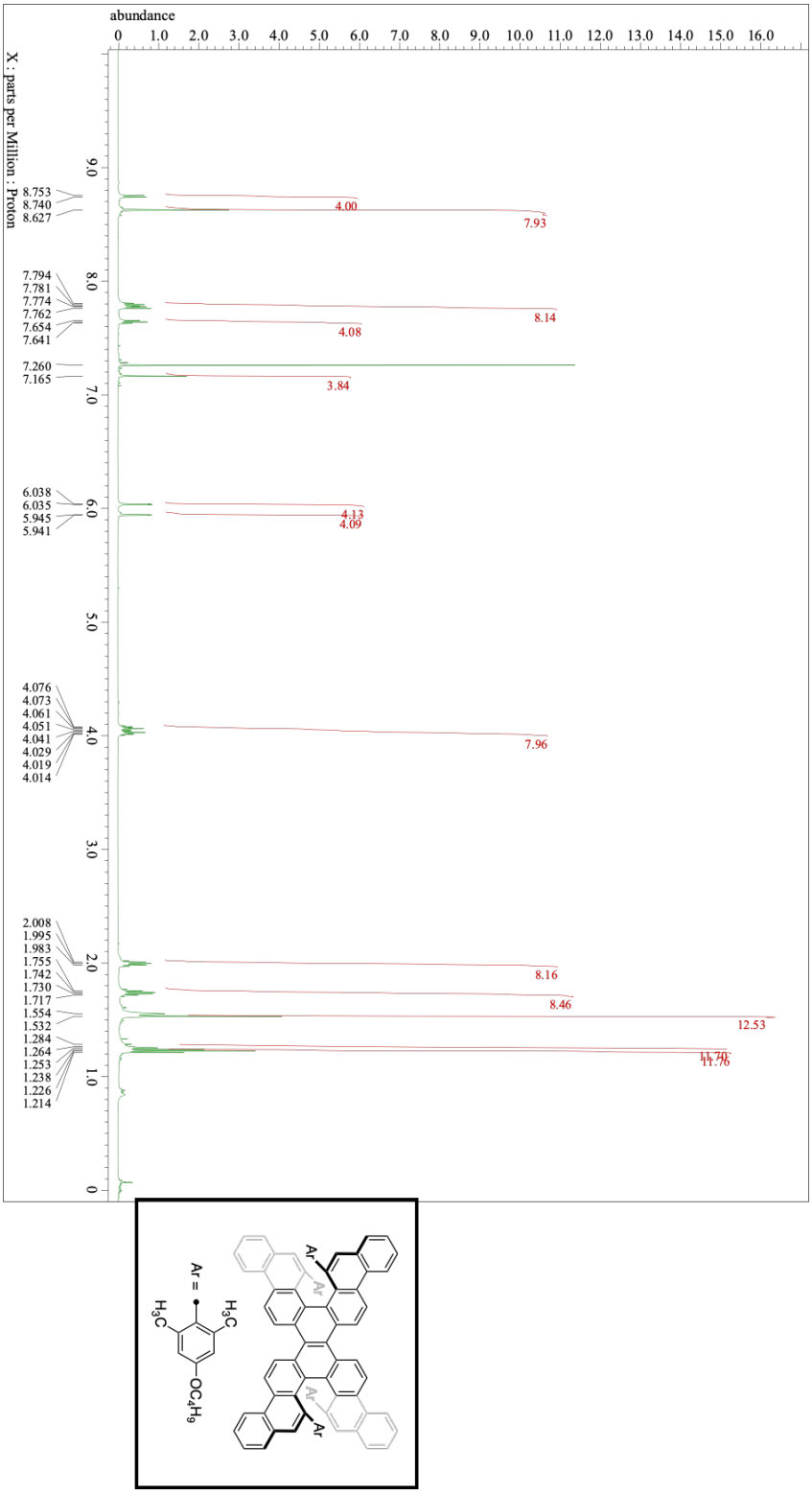


Figure S7. ^{1}H NMR spectrum of **1** in $CDCl_3$ at 25 °C.

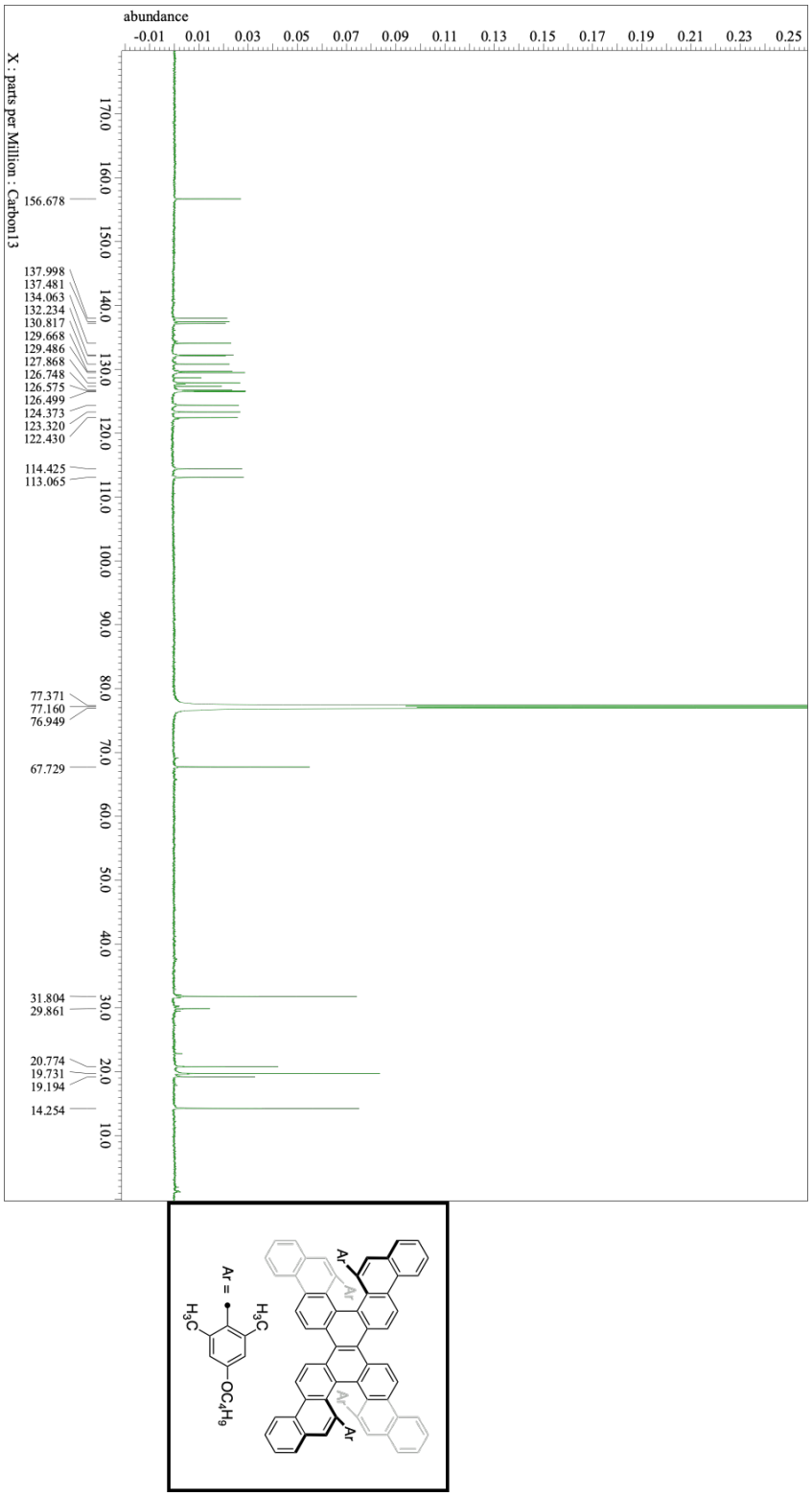


Figure S8. ^{13}C NMR spectrum of **1** in $CDCl_3$ at 25 °C.

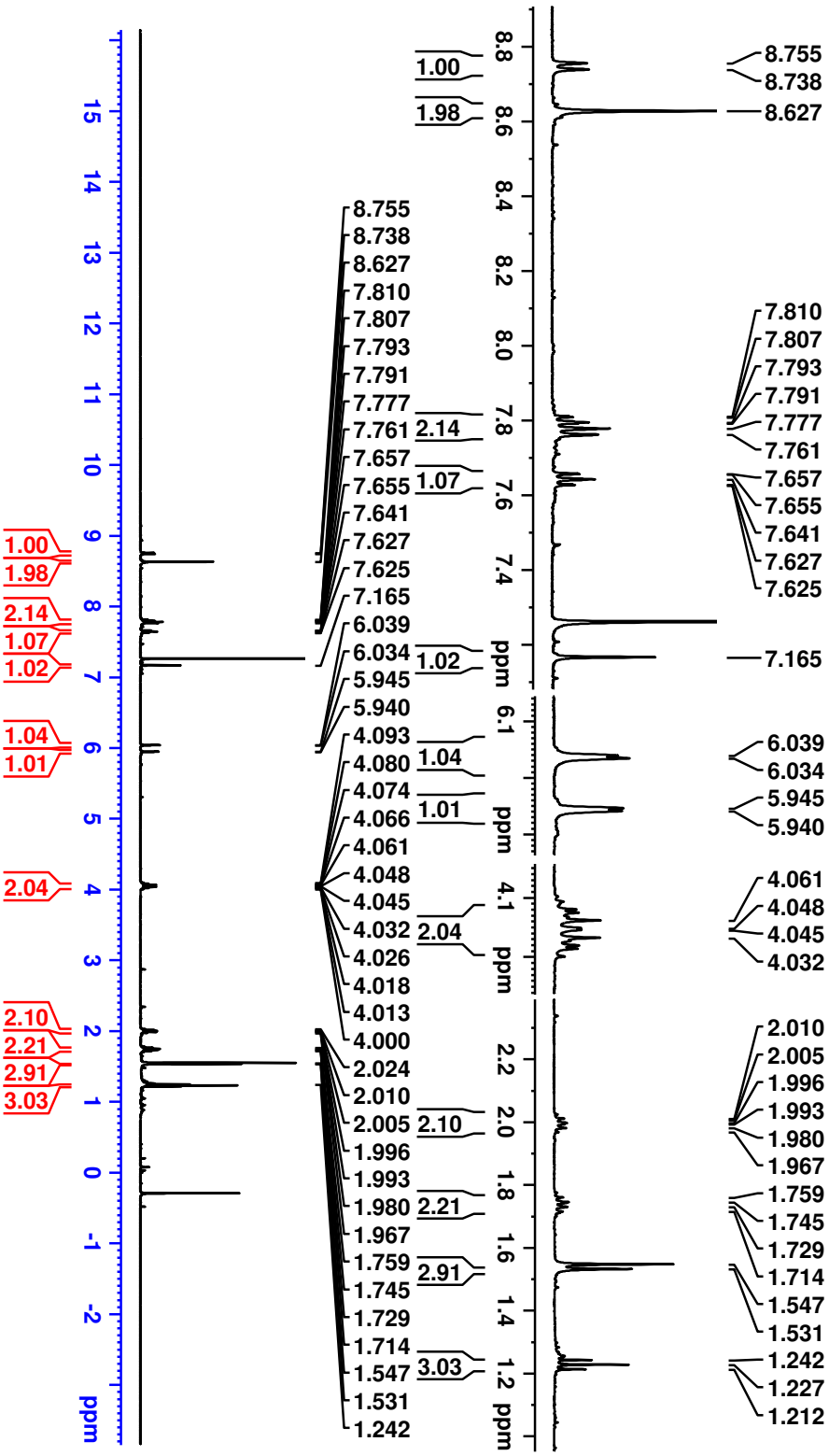


Figure S9. ^{1}H NMR spectrum of the crude mixture given by the cycloisomerization of **4** in $CDCl_3$ at 25 °C.

4. Mass spectra

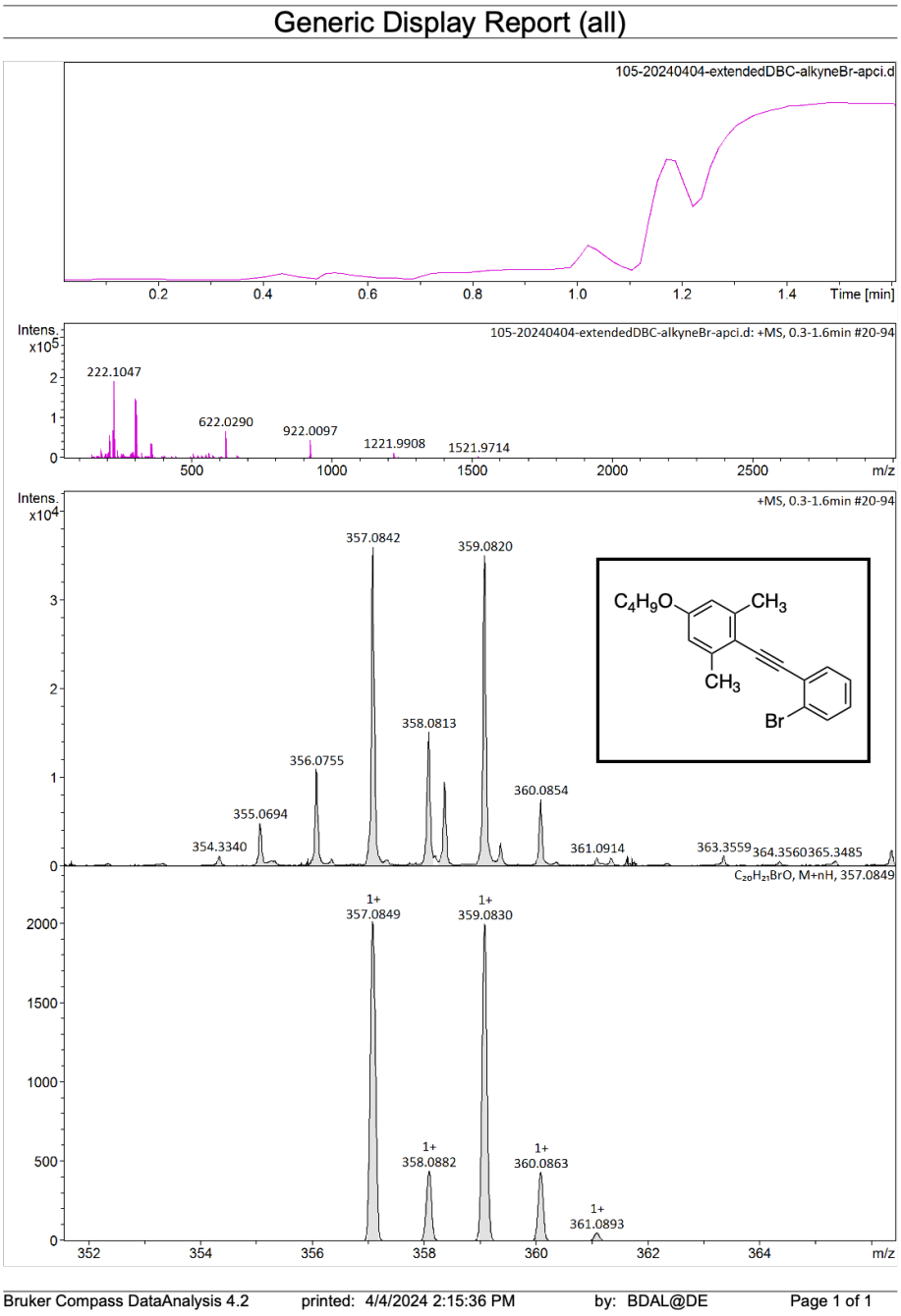


Figure S10. APCI-TOF mass spectrum of **S1**.

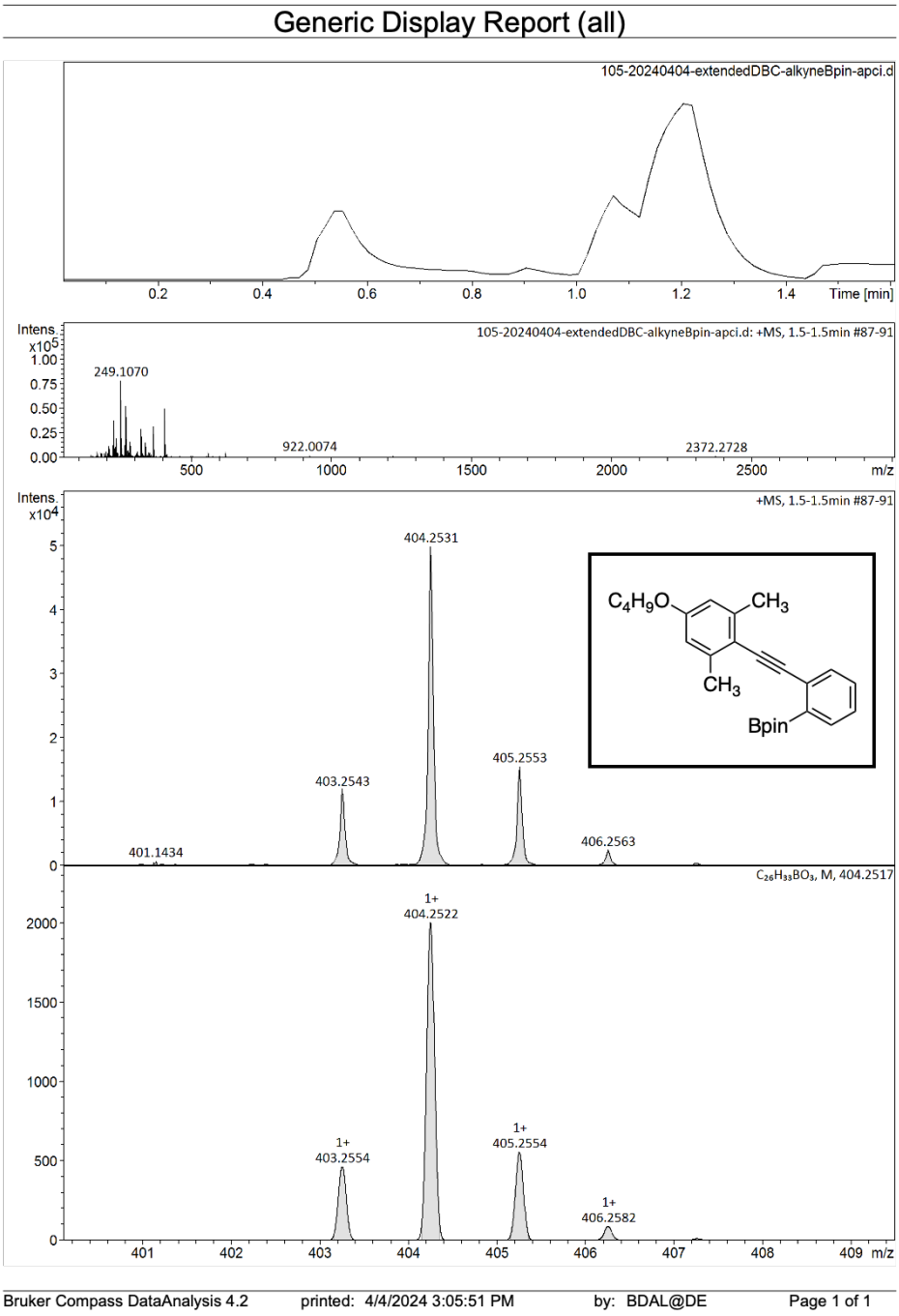


Figure S11. APCI-TOF mass spectrum of **S2**.

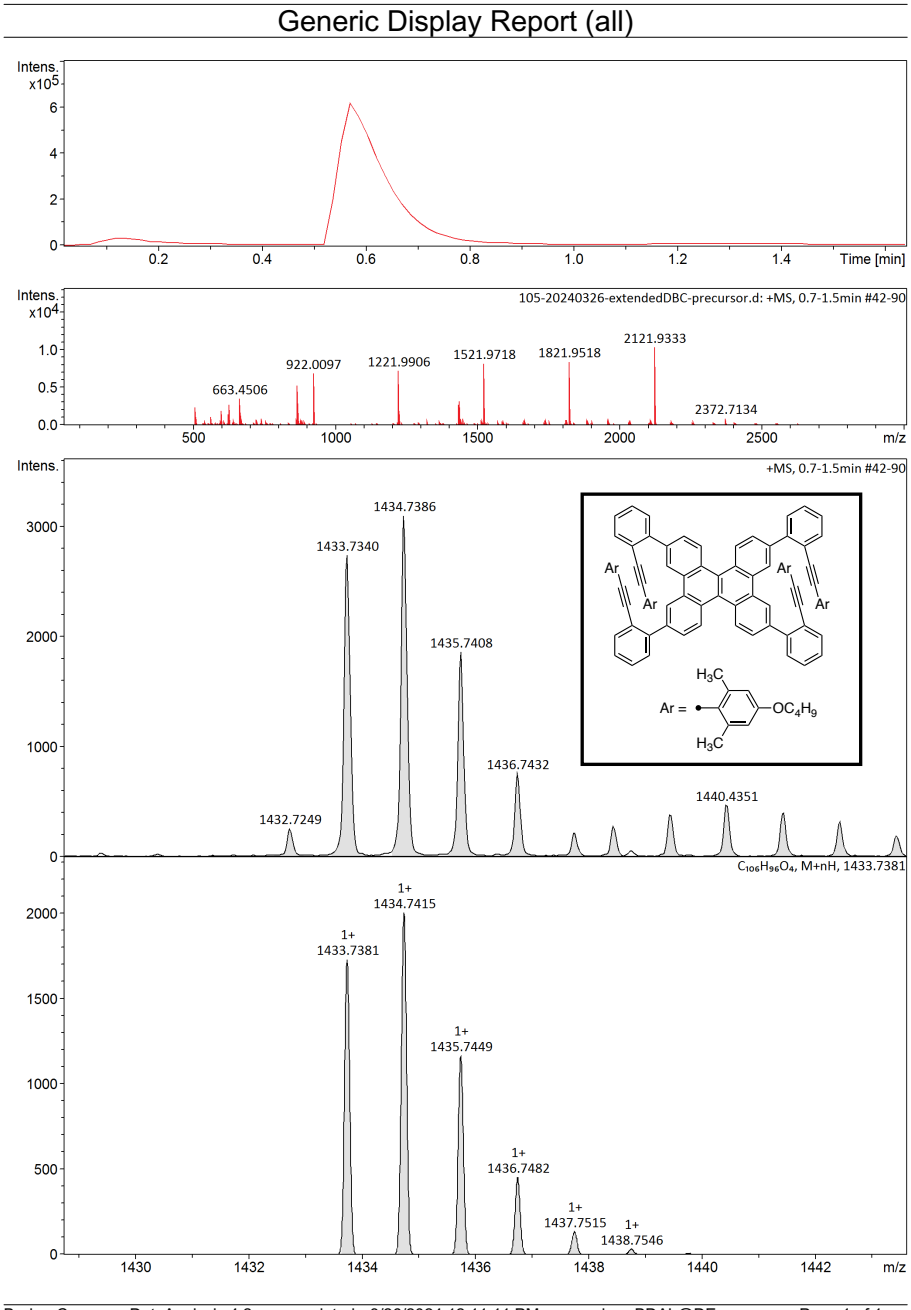


Figure S12. APCI-TOF mass spectrum of **4**.

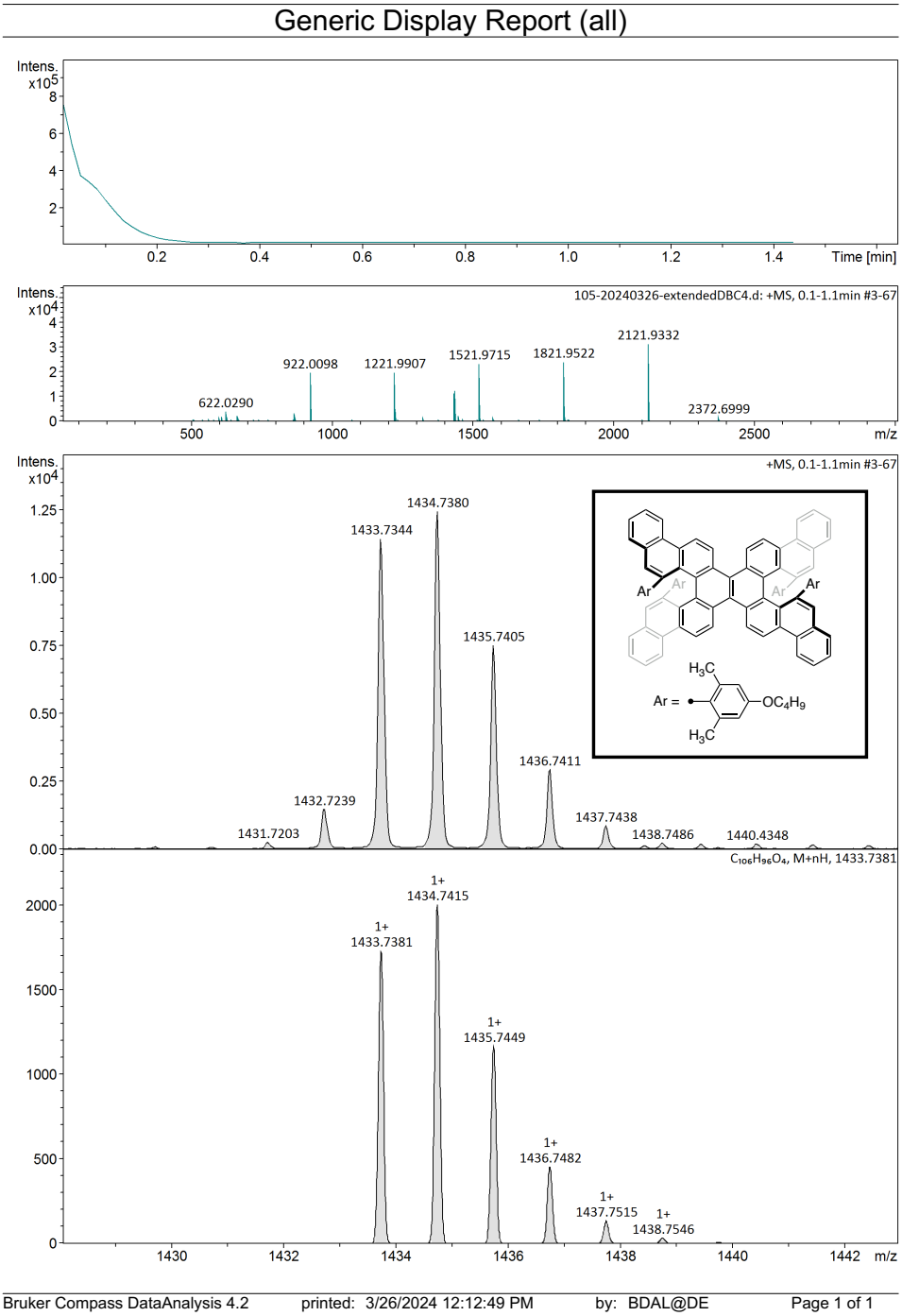


Figure S13. APCI-TOF mass spectrum of **1**.

5. Crystal data

Table S1. Crystallographic data of **1**

compound	**1**
Formula	$C_{106}H_{96}O_4$, $CHCl_3$
Formula weight	1553.19
Crystal system	triclinic
Space group	*P*-1 (No. 2)
Crystal color	yellow
Crystal description	block
a [Å]	10.8817(3)
b [Å]	15.6692(4)
c [Å]	25.2074(6)
α [°]	92.731(2)
β [°]	92.591(2)
γ [°]	108.886(2)
V [Å^3]	4061.44(19)
Z	2
d_{calcd} [g cm^{-3}]	1.270
R_1 ($I > 2\sigma(I)$)	0.0739
wR_2 (all data)	0.2077
Goodness-of-fit	1.005
Temperature [K]	93
Solvent	$CHCl_3$/MeOH
CCDC No.	2345868

6. Resolution and inversion dynamics

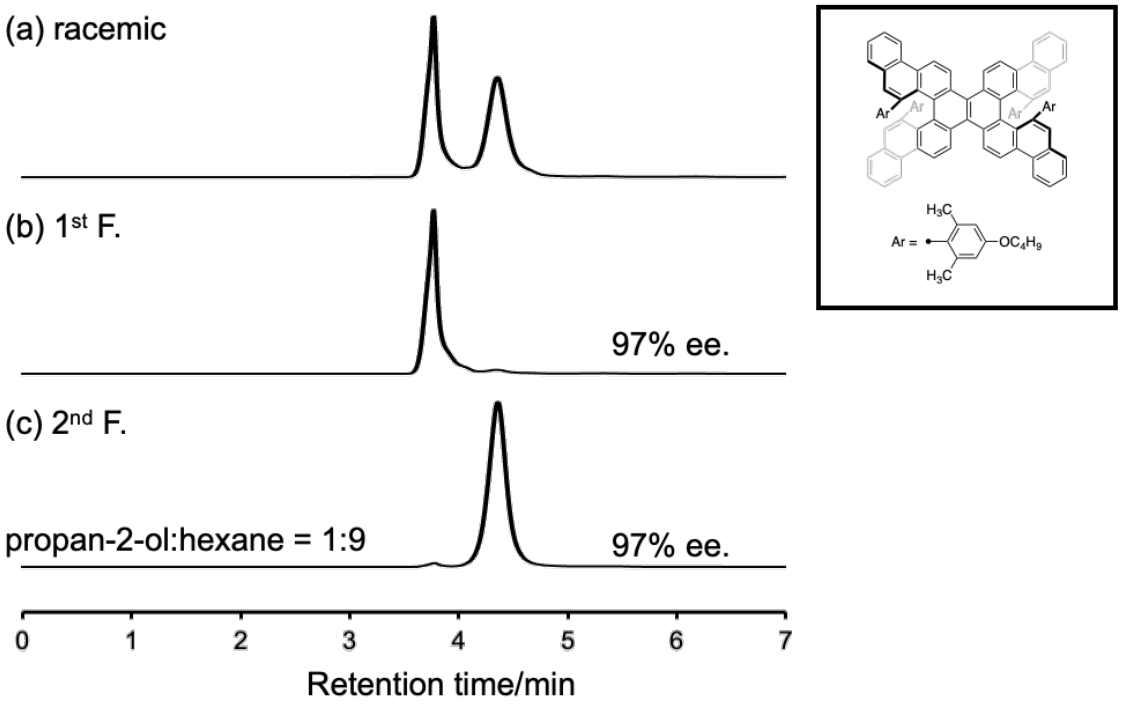


Figure S14. HPLC charts of (a) racemic **1**, (b) 1st fraction, and (c) 2nd fraction.

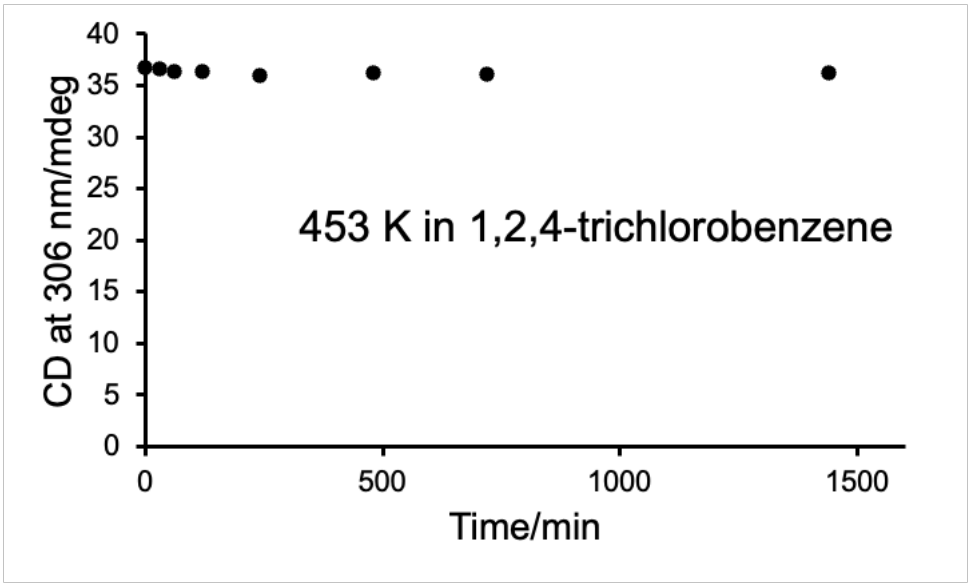


Figure S15. Plots of CD intensities of (*M*,*M*)-**1** at 306 nm versus time.

7. Cyclic voltammograms

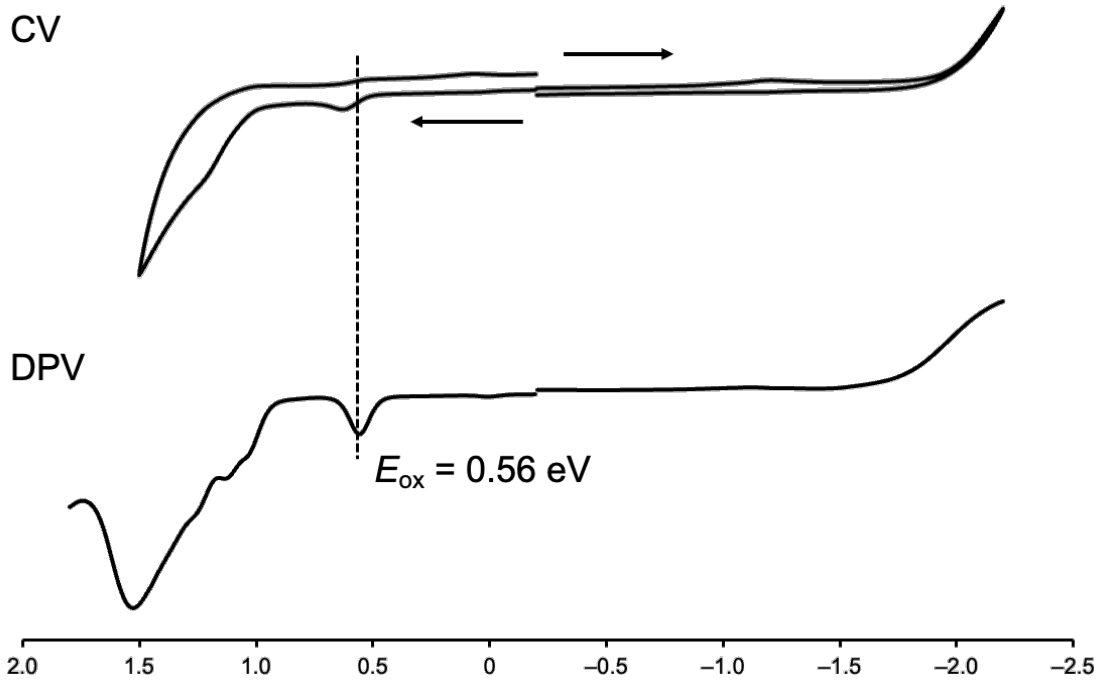


Figure S16. Cyclic and differential pulse voltammograms of **1**.

8. DFT Calculations

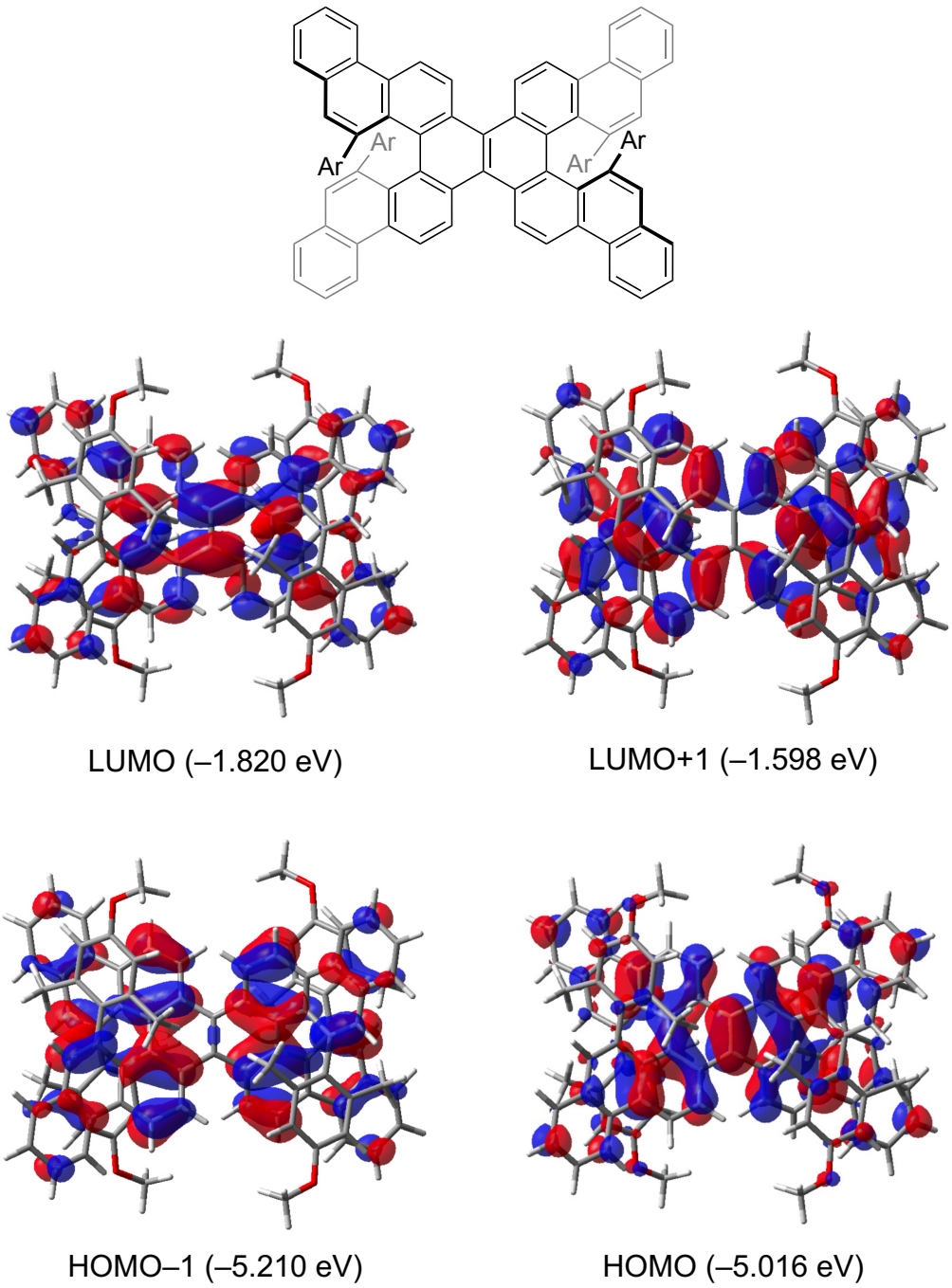
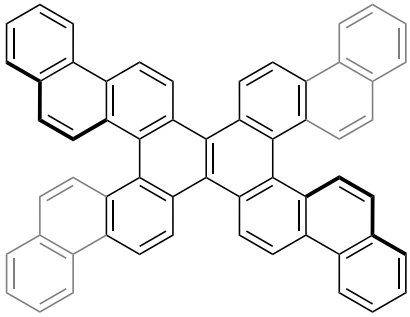
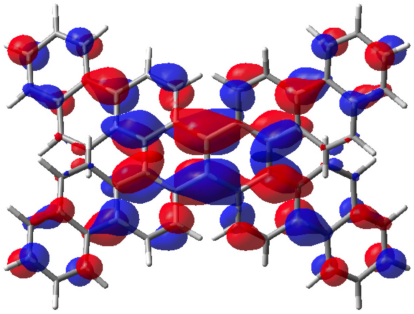
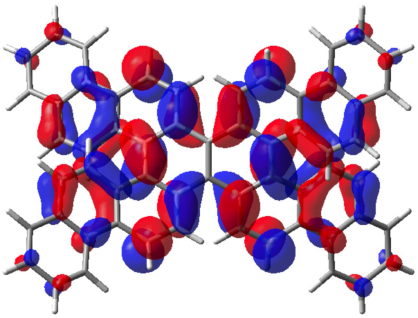


Figure S17. Calculated molecular orbitals of **1** (isovalue = 0.02).

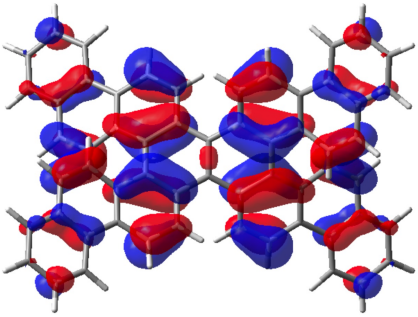




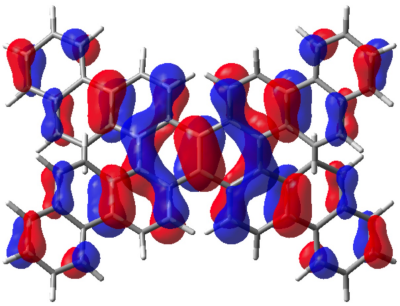
LUMO (–1.804 eV)



LUMO+1 (–1.513 eV)



HOMO–1 (–5.428 eV)



HOMO (–5.179 eV)

Figure S18. Calculated molecular orbitals of **1′** (isovalue = 0.02).

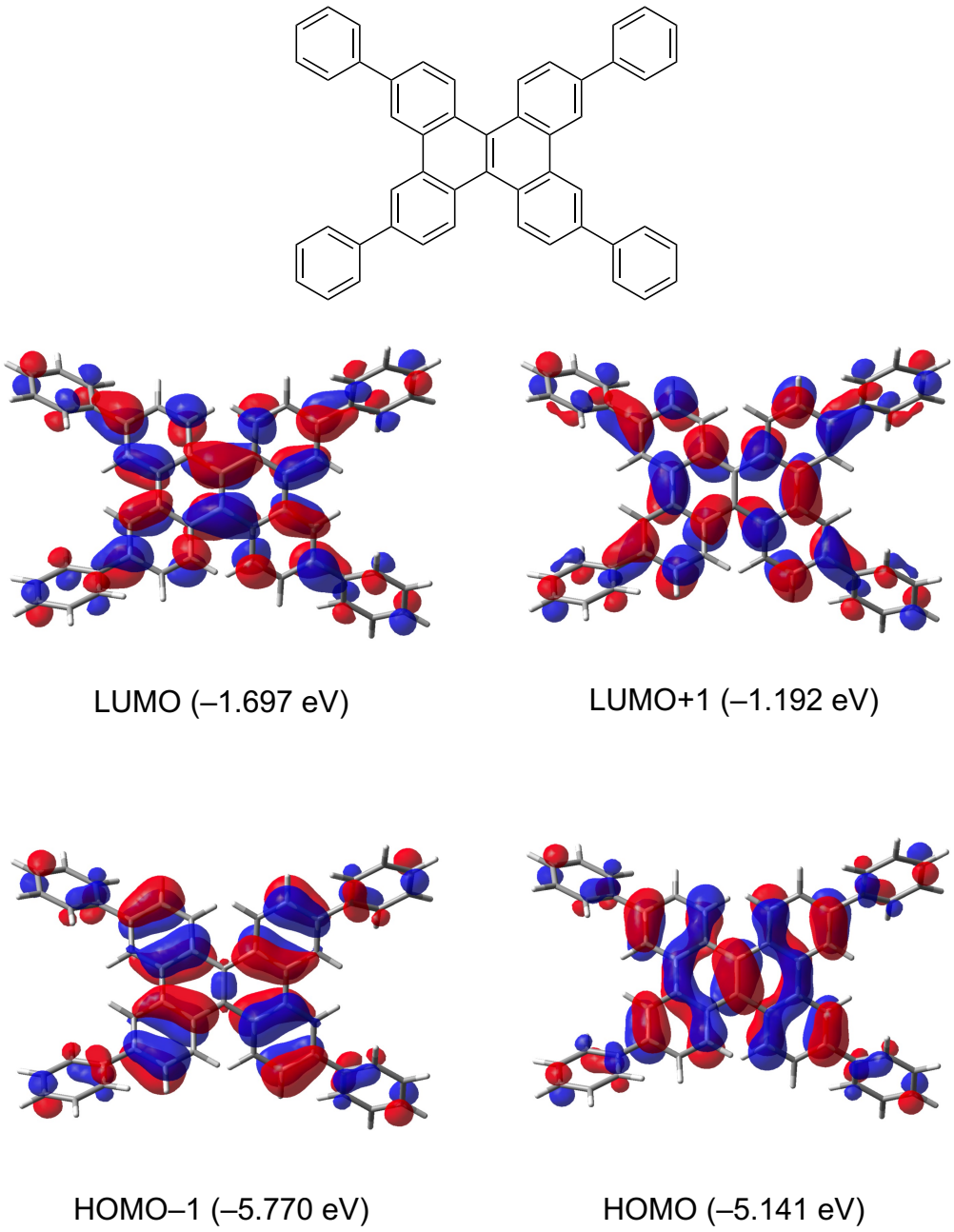


Figure S19. Calculated molecular orbitals of **4′** (isovalue = 0.02).

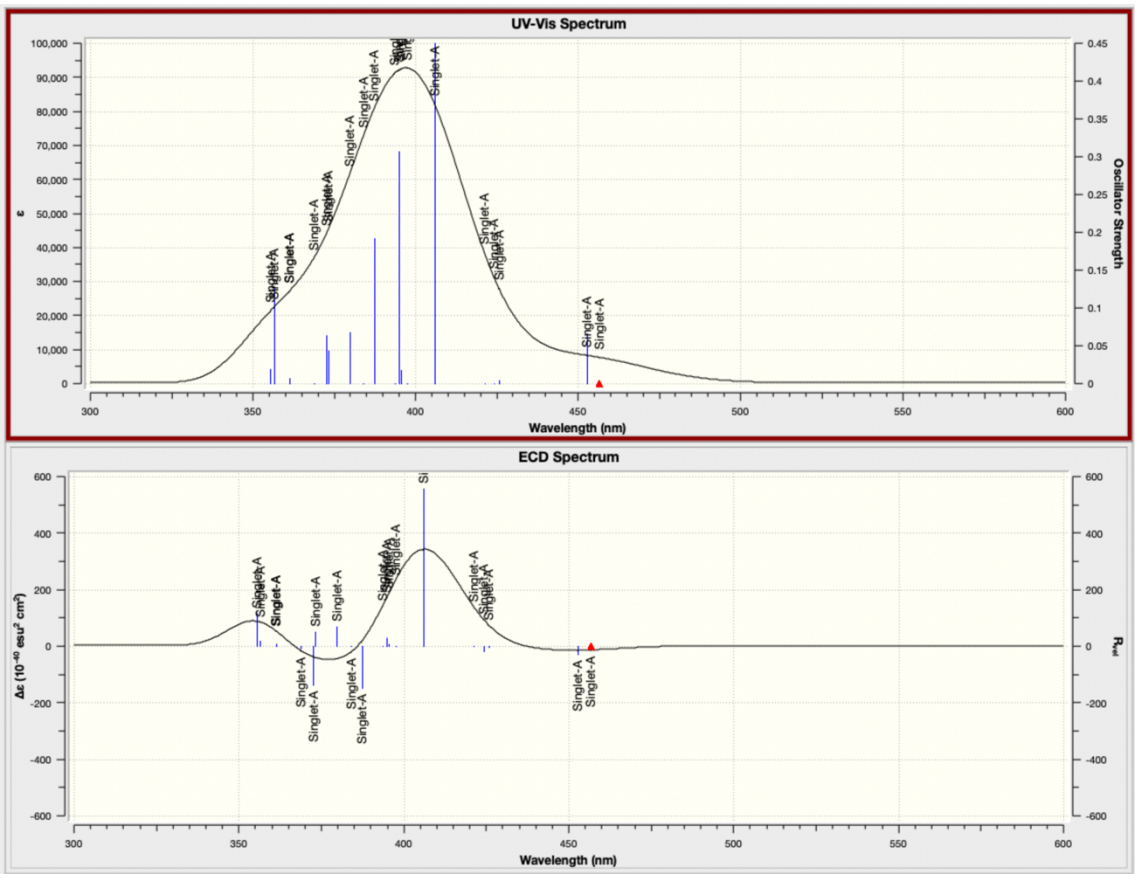


Figure S20. Simulated absorption (top) and CD (bottom) spectra of **4**.

Table S2. Cartesian coordinate and geometry of (*M*,*M*)-**1**.

O	3.799334	-5.482375	2.609181
O	-3.79979	-5.482181	-2.609279
O	-3.799943	5.482257	2.609072
C	2.442716	-0.614929	-0.387149
C	1.262871	-2.677962	-0.920848
C	1.237748	-1.366236	-0.376552
C	3.584029	-2.411572	-1.61308
C	-1.237808	1.366298	-0.376354
C	-2.442785	-0.61492	0.387111
C	4.754274	-2.947059	-2.284242
C	2.423332	-3.206479	-1.426762
C	-1.23784	-1.366255	0.376422
C	-0.00003	-0.704065	-0.000024
C	1.237791	1.366212	0.376603
C	-2.442765	0.614971	-0.387094
C	-3.539401	-1.04092	1.22112
C	-0.000019	0.704076	0.000085
C	3.539379	1.040787	1.221212
C	3.539355	-1.040893	-1.22117
C	-4.485888	-0.11789	1.848074
C	2.135902	-0.890465	3.345036
C	-2.42345	-3.206555	1.426508
C	-1.262948	2.678088	-0.920475
C	5.745791	-2.039363	-2.748859
C	2.44273	0.61486	0.387193
C	-4.754327	-2.947114	2.284162
C	4.964888	-4.331025	-2.493996
C	5.220178	-2.307181	1.535301
C	-4.258976	1.365345	1.982788
C	-1.262987	-2.678028	0.920586
C	3.584127	2.411472	1.613081
C	-3.539351	1.040981	-1.22113
C	4.258801	-1.365509	1.982898
C	4.485852	0.117702	1.848123
C	-3.584102	-2.411628	1.612958
C	-3.584046	2.411706	-1.612898
C	5.745922	2.039186	2.748777
C	3.893379	-4.126106	2.453757
C	4.754444	2.946914	2.284148
C	-5.525322	-0.639679	2.577759
C	5.52534	0.639448	2.577761
C	4.485885	-0.117845	-1.848026
C	-5.745814	-2.039423	2.748845
C	5.017545	-3.666759	1.764512
C	3.148114	-1.829197	2.724145
C	5.525331	-0.63963	-2.577709
C	-4.258834	-1.365276	-1.982989
C	-6.88843	-2.531741	3.422838
C	-4.485763	0.117958	-1.848214
C	-3.148278	1.829164	2.723961
C	6.494649	-1.89675	0.83058
C	6.098158	-4.792398	-3.138841
C	-2.423405	3.206633	-1.426395
C	-3.148151	-1.829086	-2.724174
C	-2.135803	-0.890448	-3.344979
C	2.135951	0.890718	-3.344727
C	-5.220462	2.306899	1.535224
C	6.888396	-2.531691	-3.422863
C	7.066934	-3.887066	-3.615698
C	2.971128	-3.202932	2.943861
C	-4.964963	-4.331081	2.493898
C	-4.754261	2.947213	-2.284099
C	1.262967	2.677939	0.920898
C	-5.220351	-2.306838	-1.535463
C	-5.745668	2.039523	-2.748951
C	-7.066998	-3.887116	3.61563
C	3.148338	1.829292	-2.723885
C	-2.971311	-3.202833	-2.943895
C	2.423458	3.206419	1.426787
C	-5.525129	0.639775	-2.577975
C	5.220513	2.306887	-1.535079
C	-2.135876	0.89057	3.344758
C	6.494989	1.896274	-0.830458
C	-5.017847	-3.666438	-1.764656
C	-6.098232	-4.792447	3.138746
C	4.259013	1.365396	-1.982708
C	-2.971443	3.202904	2.943658
C	-3.893696	-4.125905	-2.453843
C	6.888614	2.531495	3.422645
C	-5.017986	3.66651	1.764441
C	4.965168	4.330884	2.493757
C	-6.494816	-1.896232	-0.830844
C	-6.494931	1.896344	0.830565
C	-3.893849	4.125981	2.453625
O	3.800068	5.482364	-2.60872
C	-4.964964	4.331197	-2.493646
C	-6.888254	2.531866	-3.422975
C	-7.066886	3.887259	-3.615597
C	7.067266	3.886876	3.615337
C	6.09852	4.792237	3.138473
C	5.018065	3.666535	-1.764195
C	-6.098218	4.792586	-3.138509
C	2.971555	3.203039	-2.943517
C	3.893968	4.126063	-2.45338
H	0.347445	-3.253774	-0.980198
H	2.408902	-4.221213	-1.808691
H	1.599373	-1.391862	4.156928
H	1.38761	-0.553062	2.618811
H	2.610792	0.005783	3.755703
H	-2.409024	-4.22134	1.808301
H	-0.347543	3.253945	-0.979717
H	4.248248	-5.051297	-2.113729
H	-0.347585	-3.253886	0.979849
H	-6.190423	0.04238	3.100997
H	6.190402	-0.042628	3.101027
H	5.7388	-4.39693	1.409531

H	6.190467	0.042439	-3.100886
H	-7.62912	-1.821061	3.78211
H	6.92018	-2.743422	0.284183
H	6.329316	-1.086176	0.119368
H	7.255417	-1.552472	1.542953
H	6.243796	-5.860899	-3.272906
H	-2.408983	4.221426	-1.808169
H	-1.599204	-1.391903	-4.156791
H	-2.610569	0.00583	-3.755715
H	-1.387573	-0.553105	-2.61866
H	1.599638	1.392121	-4.156762
H	2.610616	-0.00574	-3.755168
H	1.387477	0.553692	-2.618503
H	7.629118	-1.821028	-3.782106
H	7.95205	-4.256374	-4.126452
H	2.111283	-3.527823	3.519512
H	-4.248342	-5.051373	2.113635
H	0.34756	3.25378	0.980268
H	-7.952125	-4.256435	4.126355
H	-2.111483	-3.527833	-3.519511
H	2.409084	4.221156	1.808716
H	-6.190129	-0.042263	-3.101369
H	-1.387187	0.553883	2.618593
H	-1.599821	1.391845	4.157047
H	-2.610466	-0.006073	3.754867
H	7.255754	1.552197	-1.542947
H	6.920515	2.742814	-0.283859
H	6.329679	1.085507	-0.119466
H	-5.739205	-4.396533	-1.409729
H	-6.243876	-5.860949	3.272801
H	-2.111574	3.527928	3.519203
H	7.629312	1.820811	3.781896

H	-5.739366	4.396577	1.409496
H	4.248548	5.05116	2.113458
H	-7.255217	-1.551085	-1.543177
H	-6.920916	-2.743039	-0.285108
H	-6.329244	-1.086198	-0.119064
H	-6.920066	2.742729	0.283411
H	-6.329753	1.085139	0.120047
H	-7.25595	1.55292	1.543089
H	-4.248415	5.051469	-2.113205
H	-7.628881	1.821196	-3.782399
H	-7.951994	4.25659	-4.126346
H	7.952455	4.256171	4.125973
H	6.244251	5.860738	3.272431
H	5.739427	4.396562	-1.409143
H	-6.243929	5.861098	-3.272405
H	2.111745	3.52811	-3.519119
C	2.689764	5.997461	-3.322134
H	2.670058	5.636711	-4.359393
H	1.739177	5.737645	-2.836481
H	2.809154	7.082891	-3.321753
C	-2.689544	5.997321	3.322351
H	-2.669686	5.636514	4.35959
H	-1.739022	5.737534	2.836553
H	-2.808936	7.082751	3.32205
C	2.688835	-5.997327	3.322392
H	2.669032	-5.636639	4.359675
H	1.738368	-5.737307	2.836615
H	2.808034	-7.082777	3.321966
C	-2.689379	-5.997229	-3.322554
H	-2.669572	-5.636483	-4.359816
H	-1.738861	-5.737354	-2.836797
H	-2.80871	-7.082665	-3.32218

Negative frequency = zero

Sum of electronic and thermal free energies = –3925.061731 Hartree

Table S3. Cartesian coordinate and geometry of (*P*,*M*)-**1**.

O	-3.903544	4.948751	3.521167
C	-2.427785	0.646406	-0.317348
C	-1.291378	2.781954	-0.497406
C	-1.20349	1.362467	-0.380326
C	-3.639921	2.645827	-1.100859
C	-4.8157	3.293422	-1.645854
C	-2.48956	3.400875	-0.730274
C	-1.203472	-1.362522	0.380393
C	-3.577295	-1.227393	0.996819
C	-3.577293	1.227321	-0.99678
C	-2.186781	0.324575	3.445513
C	-5.806872	2.485234	-2.271361
C	-2.427776	-0.646478	0.317399
C	-5.031481	4.693209	-1.597371
C	-5.294104	1.99673	1.906539
C	-3.63991	-2.6459	1.100906
C	-4.31732	1.001289	2.172213
C	-4.53172	-0.434099	1.765106
C	-5.80685	-2.485343	2.271431
C	-3.983196	3.640127	3.128332
C	-4.815688	-3.293509	1.645884
C	-5.582562	-1.082425	2.37117
C	-4.531684	0.434016	-1.765095
C	-5.106506	3.295803	2.373657
C	-3.211592	1.33999	2.985329
C	-5.582559	1.082319	-2.371118
C	-6.573576	1.706475	1.152614
C	-6.170394	5.260929	-2.136174
C	-2.186656	-0.324337	-3.445509
C	-6.955986	3.091234	-2.835592
C	-7.141052	4.456421	-2.768226
C	-3.050179	2.655563	3.444917
C	-1.29135	-2.78201	0.497496
C	-3.211383	-1.33987	-2.985396
C	-2.489529	-3.400942	0.730365
C	-5.293855	-1.996884	-1.906695
C	-6.573366	-1.706777	-1.15278
C	-4.317165	-1.001331	-2.172283
C	-6.955949	-3.091366	2.835673
C	-5.031476	-4.693293	1.597331
O	-3.902963	-4.948671	-3.521462
C	-7.141014	-4.45655	2.768257
C	-6.170379	-5.261032	2.136136
C	-5.106122	-3.295909	-2.373887
C	-3.049831	-2.655402	-3.445058
C	-3.982757	-3.640077	-3.128554
H	-0.40428	3.378692	-0.31803
H	-2.527043	4.483861	-0.735099
H	-1.748827	0.636591	4.399463
H	-1.363762	0.217879	2.730013
H	-2.625317	-0.667309	3.584796
H	-4.311287	5.336915	-1.104208
H	-6.25271	-0.509547	3.006435
H	-5.839868	4.067392	2.158761
H	-6.252704	0.50944	-3.006386
H	-7.003548	2.631649	0.758318
H	-6.414419	1.026031	0.315552
H	-7.328741	1.248549	1.804389
H	-6.318819	6.335393	-2.069944
H	-1.74874	-0.636212	-4.399522
H	-2.625246	0.667542	-3.584644
H	-1.363603	-0.217695	-2.730038
H	-7.695248	2.456897	-3.31918
H	-8.030238	4.911657	-3.195752
H	-2.192078	2.882517	4.06824
H	-0.404253	-3.378762	0.318167
H	-2.526986	-4.483928	0.735231
H	-7.328495	-1.248702	-1.80449
H	-7.00337	-2.632027	-0.758696
H	-6.414237	-1.02651	-0.315566
H	-7.695199	-2.457045	3.3193
H	-4.311307	-5.336972	1.104094
H	-8.030182	-4.911808	3.195795
H	-6.318822	-6.33549	2.069838
H	-5.839422	-4.067576	-2.15906
H	-2.191692	-2.882236	-4.068373
C	-2.800891	-5.338803	-4.321611
H	-2.781034	-4.79794	-5.277398
H	-1.845646	-5.179919	-3.802748
H	-2.932355	-6.405406	-4.515459
C	-2.801544	5.339034	4.321341
H	-2.781674	4.798224	5.277158
H	-1.846261	5.180216	3.802527
H	-2.93312	6.405634	4.515127
C	0.054575	0.658477	-0.251132
C	1.305979	1.147017	-0.835776
C	0.054584	-0.658513	0.251194
C	2.50501	0.43347	-0.582279
C	1.34827	2.165655	-1.82634
C	1.305985	-1.147002	0.835865
C	2.505014	-0.433472	0.582342
C	3.602562	0.509456	-1.514616
C	2.511404	2.46039	-2.4917
H	0.44742	2.698438	-2.098002
C	1.348258	-2.165595	1.826472
C	3.602565	-0.50944	1.514686
C	4.539408	-0.588402	-1.756349
C	3.661774	1.639817	-2.381177
H	2.501193	3.266041	-3.217334
C	2.511388	-2.460323	2.491848
H	0.447399	-2.698341	2.098176
C	3.661768	-1.639769	2.381291
C	4.539419	0.588422	1.756398
C	4.306464	-2.01481	-1.331411
C	5.580104	-0.382619	-2.628103
C	4.832181	1.877947	-3.205675

H	2.50116	-3.265948	3.217513
C	4.832156	-1.877879	3.205819
C	4.306495	2.014821	1.331414
C	5.580104	0.382657	2.62817
C	3.193464	-2.717331	-1.846236
C	5.267733	-2.725696	-0.56862
C	5.812136	0.852347	-3.305133
H	6.237845	-1.215707	-2.862014
C	5.053413	3.084557	-3.911764
C	5.81212	-0.852286	3.305251
C	5.053355	-3.084458	3.911968
C	3.193474	2.717356	1.846176
C	5.267801	2.725689	0.568653
H	6.237852	1.215745	2.862059
C	2.179358	-2.070095	-2.764739
C	3.015428	-4.075049	-1.543453
C	5.064316	-4.073784	-0.28012
C	6.541762	-2.083836	-0.064428
C	6.955268	1.04905	-4.115442
C	6.186954	3.263369	-4.683945
H	4.344628	3.901098	-3.823686
C	6.955237	-1.048967	4.115584
C	6.186882	-3.26325	4.684174
H	4.344555	-3.900991	3.823921
C	2.17932	2.070153	2.764649
C	3.01545	4.075068	1.543352
C	5.064394	4.073765	0.280107
C	6.541852	2.083812	0.064543
H	1.440242	-1.479893	-2.210983
H	1.632617	-2.834204	-3.327
H	2.654035	-1.395578	-3.483919
C	3.938801	-4.753718	-0.749807

H	2.153826	-4.588566	-1.956199
H	5.785393	-4.622152	0.3188
H	6.964921	-2.666841	0.758658
H	6.37618	-1.066441	0.293314
H	7.304232	-2.029838	-0.852094
C	7.144791	2.235871	-4.79497
H	7.687432	0.248206	-4.188754
H	6.340962	4.205049	-5.203911
C	7.144734	-2.235763	4.795165
H	7.687416	-0.248134	4.188871
H	6.340862	-4.204907	5.204191
H	1.632641	2.83428	3.326949
H	2.653942	1.395565	3.483796
H	1.440157	1.480039	2.21086
C	3.938854	4.753711	0.749724
H	2.153832	4.588595	1.956053
H	5.785496	4.622117	-0.318798
H	7.304272	2.02985	0.852261
H	6.965057	2.66679	-0.758538
H	6.376297	1.066403	-0.29317
O	3.844435	-6.071778	-0.394172
H	8.03012	2.381381	-5.40794
H	8.030054	-2.381255	5.408152
O	3.844504	6.071759	0.394043
C	2.729218	-6.810992	-0.858888
C	2.729272	6.81099	0.858694
H	2.702909	-6.860662	-1.955984
H	1.782088	-6.386736	-0.498312
H	2.847732	-7.819332	-0.456898
H	2.702917	6.860689	1.955787
H	1.782156	6.386728	0.498089
H	2.847807	7.819319	0.456682

Negative frequency = zero

Sum of electronic and thermal free energies = –3925.049495 Hartree

Table S4. Cartesian coordinate and geometry of **1′**.

C	2.460155	0.642728	0.348321
C	1.227303	2.665085	0.941498
C	1.23972	1.366331	0.363485
C	3.564851	2.490075	1.58902
C	-1.23972	-1.366323	0.363501
C	-2.460176	0.642664	-0.348403
C	4.732432	3.033931	2.267165
C	2.357712	3.224113	1.480653
C	-1.239762	1.366295	-0.363585
C	-0.000008	0.699319	-0.000053
C	1.23976	-1.366294	-0.363576
C	-2.460157	-0.642727	0.348328
C	-3.587436	1.158039	-1.086227
C	0.000008	-0.699315	-0.00005
C	3.587438	-1.15805	-1.086216
C	3.587385	1.15812	1.086177
C	-2.357809	3.224057	-1.480728
C	-1.227287	-2.665062	0.941544
C	5.836712	2.17644	2.545247
C	2.460174	-0.642668	-0.348398
C	-4.73256	3.033859	-2.267122
C	4.82865	4.387781	2.670265
C	-1.227374	2.665049	-0.941605
C	3.564933	-2.490007	-1.58905
C	-3.587383	-1.158111	1.08619
C	-3.56494	2.490004	-1.589043
C	-3.564837	-2.49006	1.589057
C	5.836814	-2.176361	-2.545225
C	4.732543	-3.033864	-2.267142
C	-5.762621	0.803622	-2.149004
C	5.762649	-0.80365	-2.148944
C	-5.836806	2.176346	-2.545252
C	5.762578	0.803733	2.148936
C	-6.970719	2.686491	-3.219075
C	5.951361	4.867661	3.319632
C	-2.357692	-3.224085	1.480715
C	6.97061	2.686582	3.219099
C	7.032463	4.011154	3.603296
C	-4.828827	4.387736	-2.670117
C	-4.732423	-3.033923	2.26719
C	1.227369	-2.665051	-0.941592
C	-5.836725	-2.176446	2.54523
C	-7.032616	4.011085	-3.603191
C	2.357796	-3.224057	-1.480726
C	-5.762598	-0.803742	2.148913

C	-5.951552	4.867618	-3.319459
C	6.970732	-2.686506	-3.219043
C	4.828795	-4.387726	-2.670193
C	-4.828621	-4.387763	2.670324
C	-6.970636	-2.686599	3.219052
C	-7.032474	-4.011165	3.603275
C	7.032618	-4.011087	-3.603199
C	5.951524	-4.867607	-3.319524
C	-5.951341	-4.867651	3.319669
H	0.291062	3.204417	1.015149
H	2.286068	4.214493	1.915884
H	-2.286193	4.214425	-1.915995
H	-0.291041	-3.20438	1.015218
H	4.020488	5.077518	2.451962
H	-0.291142	3.204389	-1.015292
H	-6.577628	0.13907	-2.425622
H	6.577675	-0.139108	-2.425528
H	6.577614	0.139202	2.42552
H	-7.799221	2.013211	-3.426657
H	5.999022	5.91395	3.609175
H	-2.286032	-4.214448	1.915983
H	7.799132	2.013313	3.426641
H	7.910335	4.393377	4.116931
H	-4.020705	5.077491	-2.451718
H	0.291137	-3.204395	-1.015257
H	-7.910497	4.393303	-4.116814
H	2.28617	-4.214421	-1.915997
H	-6.577645	-0.139216	2.425477
H	-5.999251	5.913925	-3.608931
H	7.799246	-2.013229	-3.42659
H	4.02065	-5.077474	-2.451862
H	-4.020441	-5.07749	2.45206
H	-7.799179	-2.013344	3.426552
H	-7.910358	-4.393396	4.116883
H	7.910504	-4.393308	-4.116809
H	5.999209	-5.913904	-3.609033
H	-5.998978	-5.913931	3.609252
C	-4.702291	0.322523	-1.443991
C	4.702258	0.322622	1.443916
C	4.702311	-0.322544	-1.443945
C	-4.702269	-0.322623	1.443912
H	-4.676863	0.725351	1.174639
H	-4.676851	-0.725461	-1.174758
H	4.676854	-0.725351	1.17464
H	4.676886	0.725435	-1.174695

Negative frequency = zero

Sum of electronic and thermal free energies = –2228.931791 Hartree

Table S5. Cartesian coordinate and geometry of **1″**.

C	-2.455702	-0.628409	0.36966
C	-1.240482	-2.675946	0.91004
C	-1.237901	-1.362189	0.372314
C	-3.60914	-2.522103	1.447927
C	1.237908	1.362185	0.37234
C	2.455713	-0.628428	-0.369643
C	-4.824139	-3.146626	1.941294
C	-2.401327	-3.256968	1.348557
C	1.237906	-1.362197	-0.372308
C	0.000005	-0.700266	0.000006
C	-1.237883	1.362191	-0.372328
C	2.45571	0.628406	0.369703
C	3.590944	-1.137716	-1.102732
C	0.00001	0.70026	0.000007
C	-3.590903	1.137714	-1.10281
C	-3.590936	-1.137701	1.102744
C	4.683798	-0.303869	-1.591243
C	2.401311	-3.256963	-1.348606
C	1.240477	2.675935	0.910079
C	-5.948749	-2.322776	2.221741
C	-2.45569	0.62842	-0.369694
C	4.824108	-3.146611	-1.941408
C	-4.959114	-4.542501	2.133708
C	-5.665925	-2.014935	-1.484673
C	4.585254	1.173123	-1.790764
C	1.240475	-2.675944	-0.910057
C	-3.609088	2.522112	-1.448009
C	3.590929	1.137691	1.102813
C	-4.585237	-1.173099	-1.79094
C	-4.683766	0.303884	-1.591336
C	3.609129	-2.522104	-1.447971
C	3.609122	2.522087	1.448021
C	-5.948688	2.322797	-2.221855
C	-4.509042	-3.920302	-2.422921
C	-4.824072	3.146639	-1.941406
C	5.807003	-0.908974	-2.098387
C	-5.806987	0.909015	-2.098417
C	-4.683797	-0.303868	1.591271
C	5.948709	-2.322752	-2.22187
C	-5.628336	-3.374372	-1.794023
C	-3.465827	-1.735611	-2.427512
C	-5.807029	-0.908993	2.098331
C	4.585257	-1.173138	1.790893
C	7.149471	-2.904757	-2.692821
C	4.683789	0.303851	1.591326
C	3.46567	1.735684	-2.426985
C	-6.145723	-5.093387	2.582555
C	2.401311	3.256952	1.348634
C	3.46586	-1.735662	2.427475
C	5.666049	2.014921	-1.484773
C	-7.149532	-2.904796	2.692618
C	-7.252112	-4.269921	2.869753
C	-3.428492	-3.093567	-2.738633
C	4.95907	-4.542478	-2.133891
C	4.82411	3.146602	1.941424
C	-1.240441	2.675943	-0.910066
C	5.665931	-2.014971	1.484569
C	5.948721	2.32275	2.22187
C	7.252038	-4.269875	-2.87002
C	-3.465798	1.735596	2.427431
C	3.428525	-3.093627	2.738557
C	-2.401271	3.256969	-1.348619
C	5.807013	0.90897	2.098416
C	-5.665958	2.014957	1.484748
C	5.628341	-3.374418	1.793879
C	6.145658	-5.093349	-2.582811
C	-4.58525	1.173109	1.790912
C	3.428272	3.093654	-2.738036
C	4.509061	-3.92036	2.422791
C	-7.149459	2.904823	-2.692756
C	5.6284	3.374371	-1.79406
C	-4.95903	4.542512	-2.133843
C	4.508934	3.920352	-2.422607
C	4.959079	4.542474	2.133867
C	7.149494	2.904765	2.692779
C	7.252065	4.269887	2.869946
C	-7.252021	4.269947	-2.869914
C	-6.145627	5.093405	-2.582714
C	-5.628346	3.374383	1.794144
C	6.145679	5.093355	2.582745
C	-3.428438	3.093541	2.738595
C	-4.509008	3.920289	2.422985
H	-0.308363	-3.219318	1.001775
H	-2.364554	-4.275998	1.71664
H	2.364524	-4.27598	-1.716722
H	0.308356	3.219307	1.001799
H	-4.133831	-5.205634	1.89836
H	0.308352	-3.219307	-1.001801
H	6.599182	-0.285467	-2.504332
H	-6.599177	0.285528	-2.504371
H	-6.472537	-4.007328	-1.53387
H	-6.599216	-0.285503	2.504286
H	7.992949	-2.254586	-2.913362
H	-6.22467	-6.169691	2.710006
H	2.364529	4.275977	1.716728
H	-7.993017	-2.254632	2.913152
H	-8.179848	-4.708947	3.22648
H	-2.555463	-3.504502	-3.239453
H	4.133794	-5.205618	-1.898538
H	-0.308316	3.219307	-1.001785
H	8.179757	-4.708889	-3.226806
H	2.555507	-3.504572	3.239389
H	-2.364483	4.275995	-1.716711
H	6.599201	0.285475	2.50436
H	6.47253	-4.007372	1.533682
H	6.224595	-6.169647	-2.710313

H	2.555104	3.50463	-3.23858
H	-7.992948	2.254665	-2.91329
H	6.472691	4.007298	-1.534129
H	-4.133743	5.20564	-1.898492
H	4.133799	5.205609	1.898515
H	7.992978	2.2546	2.913311
H	8.179794	4.708908	3.226698
H	-8.179748	4.708977	-3.226661
H	-6.22456	6.169707	-2.710182
H	-6.472563	4.00735	1.534071
H	6.22462	6.169656	2.710218
H	-2.555374	3.504457	3.23937

H	-4.4782	4.979174	2.665971
H	-6.532323	1.601944	0.976802
H	-2.627983	1.098752	2.694813
H	-2.628029	-1.09878	-2.694973
H	-4.478253	-4.979196	-2.665873
H	-6.532253	-1.601904	-0.976679
H	2.627776	1.098881	-2.694218
H	4.478096	4.979256	-2.665505
H	6.532518	1.601848	-0.977055
H	6.532248	-1.601931	0.976564
H	4.478271	-4.979261	2.66571
H	2.628073	-1.098834	2.69498

Negative frequency = zero

Sum of electronic and thermal free energies = –3152.800807 Hartree

Table S6. Cartesian coordinate and geometry of **4′**.

C	-2.486832	-0.691929	0.231359
C	-1.268883	-2.702543	0.83869
C	-1.248974	-1.391375	0.303649
C	-3.68371	-2.653295	1.104422
C	1.248979	1.391331	0.303926
C	2.48685	-0.69185	-0.231547
C	-4.95139	-3.308705	1.511563
C	-2.444945	-3.318031	1.221552
C	1.249007	-1.391292	-0.304036
C	0.000007	-0.699564	-0.000132
C	-1.249006	1.391372	-0.303742
C	2.486835	0.6919	0.231482
C	3.670188	-1.344712	-0.626679
C	-0.000003	0.699582	0.000015
C	-3.67019	1.34482	-0.626436
C	-3.670149	-1.344857	0.626425
C	2.444997	-3.31777	-1.222276
C	1.268896	2.702394	0.839228
C	-6.138753	-3.092584	0.790967
C	-2.48685	0.691911	-0.231406
C	4.951464	-3.308397	-1.512111
C	-5.000215	-4.162936	2.62677
C	1.268922	-2.70235	-0.839353
C	-3.683782	2.653254	-1.104442
C	3.670161	1.344757	0.62665
C	3.683751	-2.653052	-1.10493
C	3.683728	2.653101	1.104898
C	-6.138819	3.092519	-0.790897
C	-4.951486	3.308645	-1.511542
C	6.138719	-3.092576	-0.791255
C	7.331476	-3.704492	-1.173342
C	-6.192412	-4.7761	3.008596
C	2.444961	3.31781	1.222188
C	-7.331481	-3.704577	1.173011
C	-7.36401	-4.549613	2.283835
C	5.000399	-4.162224	-2.627621
C	4.951414	3.308439	1.512137
C	-1.268947	2.702534	-0.838798
C	6.138768	3.092448	0.791486
C	7.364119	-4.549134	-2.284461
C	-2.44503	3.318004	-1.221624

C	6.192621	-4.775312	-3.009484
C	-7.331569	3.704492	-1.172904
C	-5.000365	4.162858	-2.62676
C	5.000257	4.162466	2.6275
C	7.331502	3.70437	1.173625
C	7.364047	4.549202	2.284603
C	-7.364151	4.54951	-2.283739
C	-6.192584	4.776002	-3.008549
C	6.192459	4.775559	3.009421
H	-0.334752	-3.226361	0.998616
H	-2.411879	-4.329215	1.616684
H	2.411973	-4.328868	-1.617633
H	0.334766	3.226175	0.999278
H	-4.10157	-4.325777	3.215218
H	0.334784	-3.22611	-0.999428
H	8.23501	-3.528772	-0.595289
H	-6.207474	-5.425753	3.87986
H	2.411901	4.328915	1.617522
H	-8.235083	-3.528608	0.59514
H	-8.293202	-5.028098	2.581181
H	4.101819	-4.324799	-3.216242
H	-0.334828	3.226359	-0.998765
H	8.293333	-5.027556	-2.581843
H	-2.411993	4.329184	-1.616769
H	6.207801	-5.424656	-3.880976
H	-8.235147	3.528519	-0.594996
H	-4.101744	4.325701	-3.215245
H	4.101622	4.325199	3.215992
H	8.235095	3.528504	0.59571
H	8.293244	5.027632	2.582024
H	-8.293361	5.02798	-2.581057
H	-6.207688	5.425641	-3.879823
H	6.207534	5.425052	3.880805
H	6.117995	2.460112	-0.091819
H	4.604127	0.794328	0.618007
H	-6.118015	2.460033	0.0923
H	-4.604148	0.794373	-0.617882
H	-4.604113	-0.794419	0.617909
H	-6.117992	-2.460086	-0.092222
H	4.604177	-0.79432	-0.617974
H	6.117838	-2.460363	0.092135

Negative frequency = zero

Sum of electronic and thermal free energies = –1924.092714 Hartree

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