Chiral cyclic [n]spirobifluorenylenes: carbon nanorings consisting of helically arranged quaterphenyl rods illustrating partial units of woven patterns

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1. Figures (S1-S12)

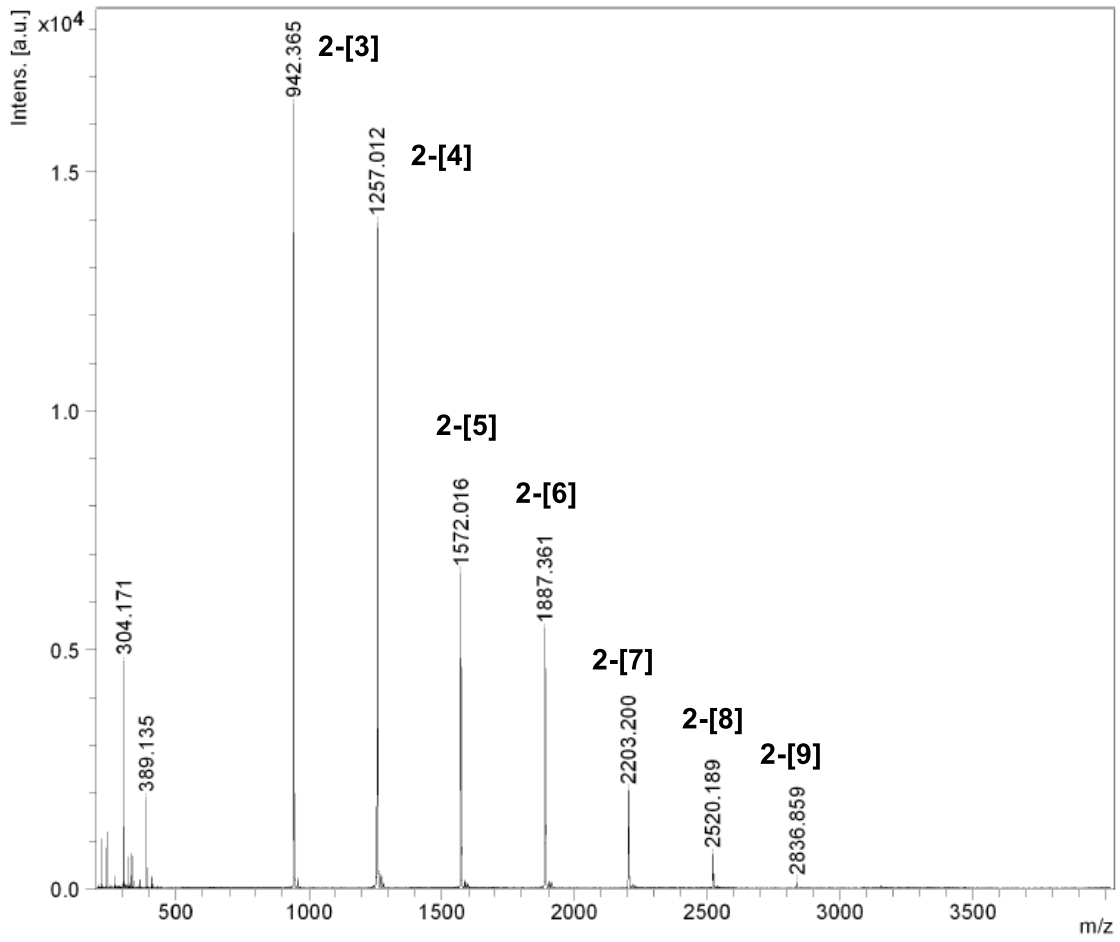
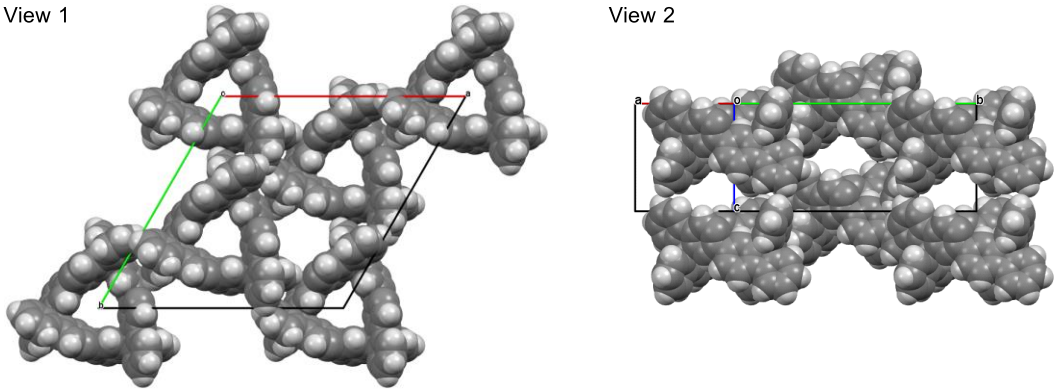


Fig. S1. MALDI-TOF-MS spectrum of the crude products after purified by short silica-gel column chromatography.

(a)



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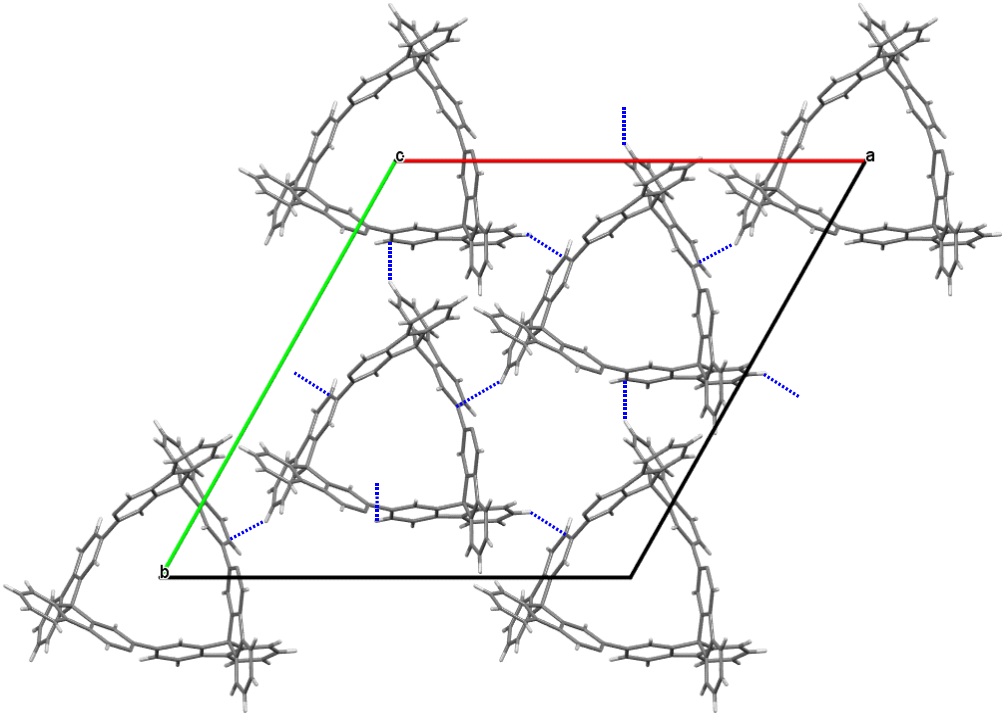
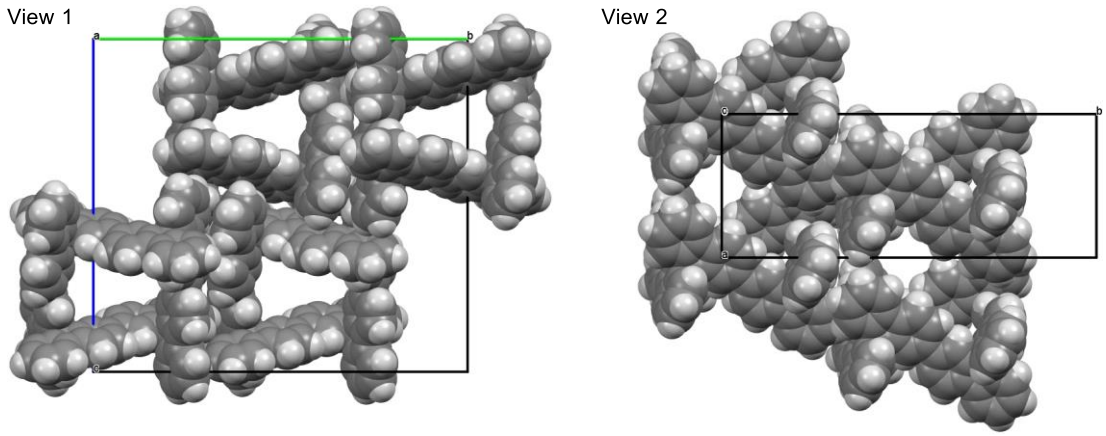


Fig. S2. (a) Unit cell of the crystal structure for (*S*,*S*,*S*)-**2-[3]** in the X-ray crystallography, (b) where the blue dotted lines show intermolecular CH-π interaction.

(a)



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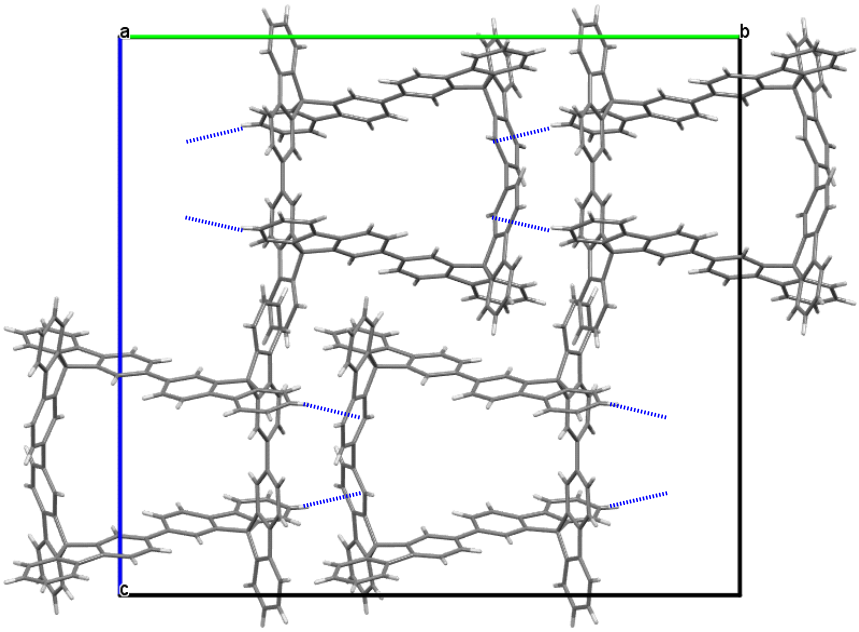


Fig. S3. (a) Unit cell of the crystal structure for (*S*,*S*,*S*,*S*)-**2-[4]** in the X-ray crystallography, (b) where the blue dotted lines show intermolecular CH-π interaction.

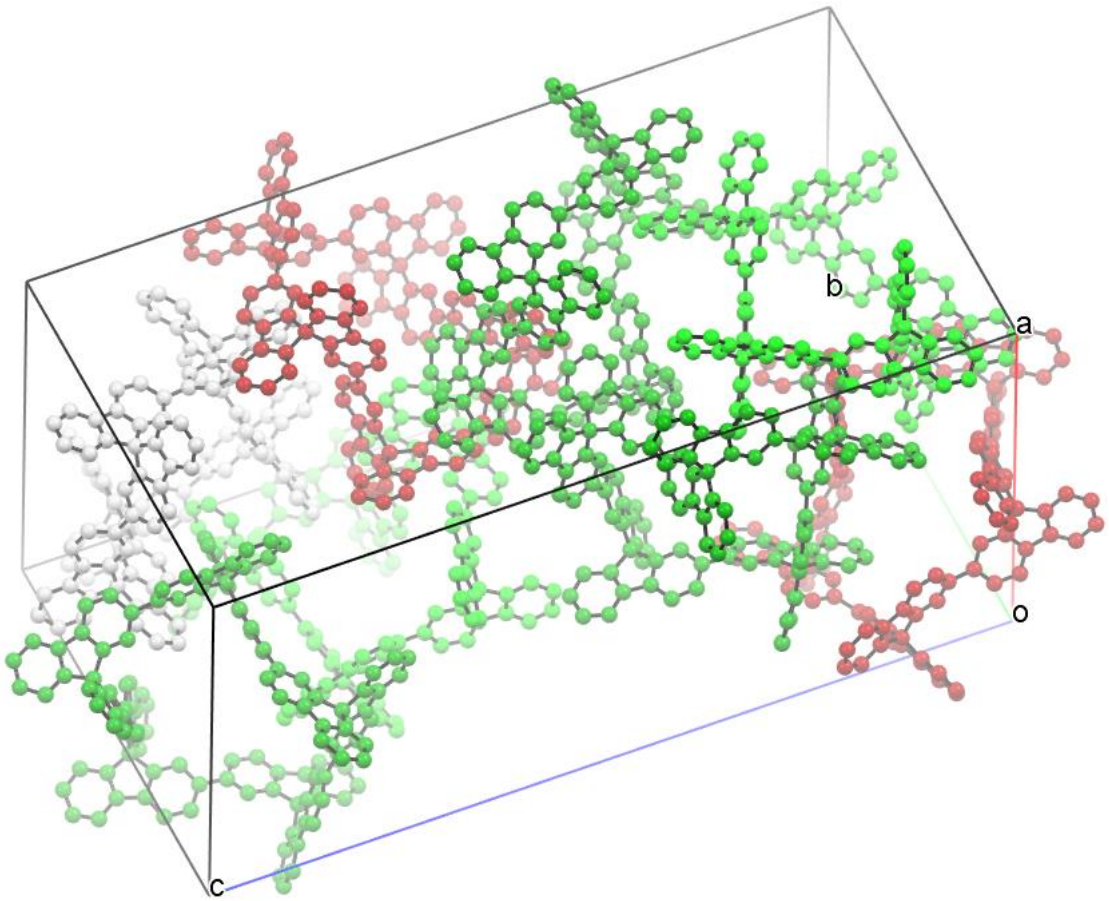


Fig. S4. Unit cell of the crystal structure for (*S*,*S*,*S*,*S*,*S*)-**2-[5]** in the X-ray crystallography. There are 8 molecules in a unit cell. The molecules are colored by symmetry operation in Mercury. Hydrogen atoms are omitted for the sake of clarity. Solvent molecules are removed in the refinement process except one toluene molecule, where this toluene is also omitted for the sake of clarity.

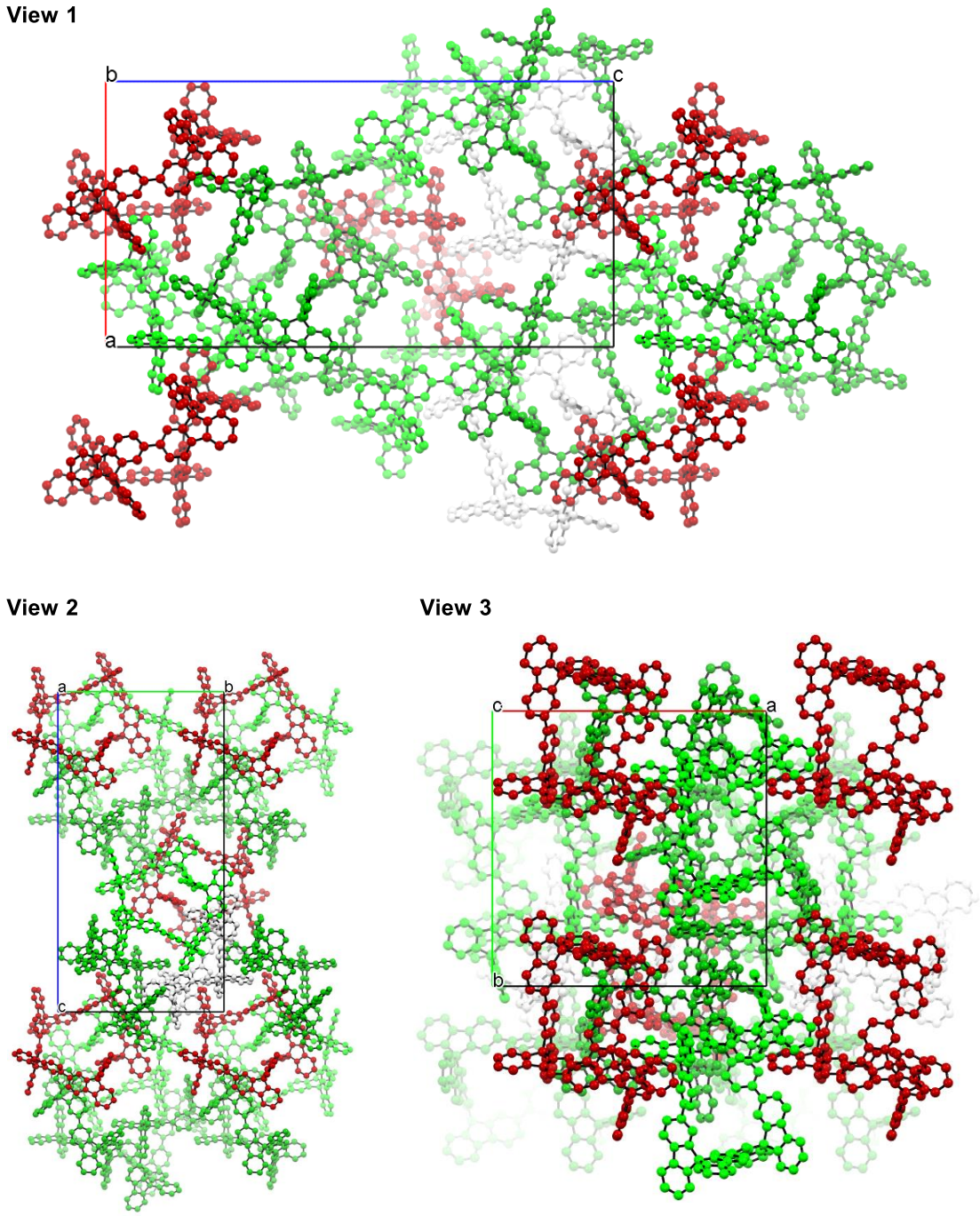


Fig. S5. Packing structure of the crystal structure for (*S*,*S*,*S*,*S*,*S*)-**2-[5]** in the X-ray crystallography. The molecules are colored by symmetry operation in Mercury. Hydrogen atoms are omitted for the sake of clarity. Solvent molecules are removed in the refinement process.

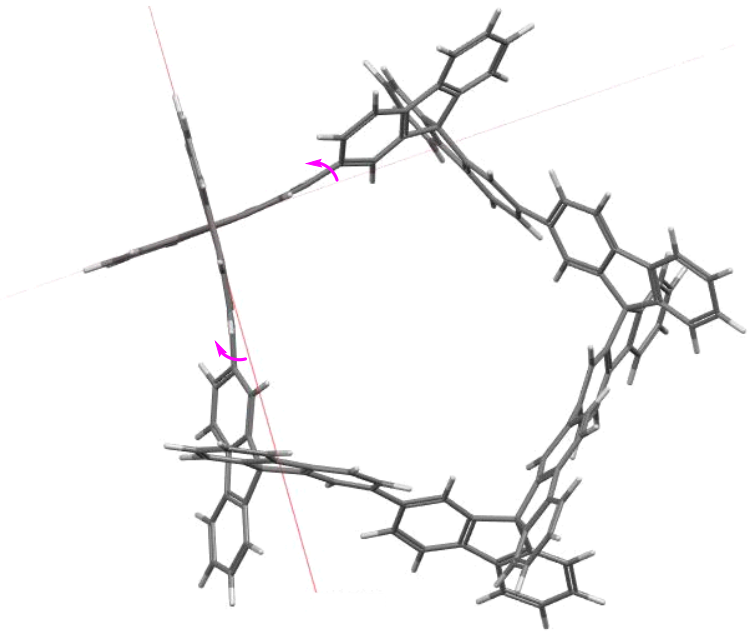


Fig. S6. Slightly tilted fluorene planes in the optimized structure of **2-[5]** [B3LYP-D3/6-31G(d,p)].

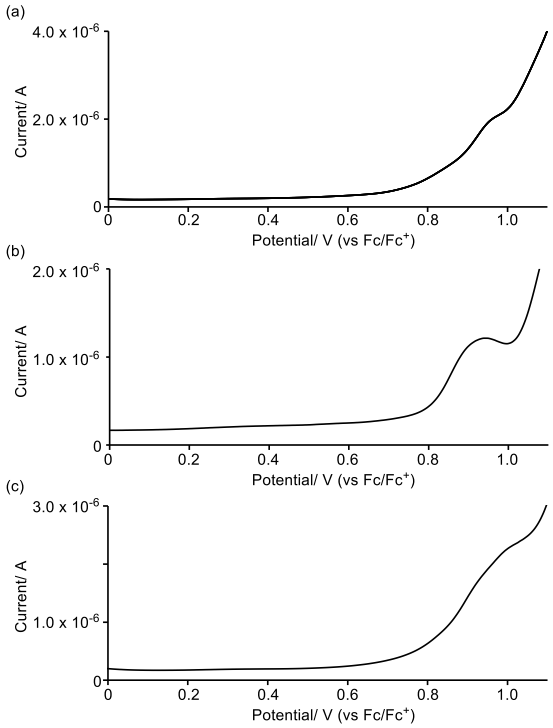


Fig. S7. Differential pulse voltammograms for (a) **2-[3]**, (b) **2-[4]**, and (c) **2-[5]** in CH_2Cl_2 under N_2 (working electrode: Pt, scan rate: 200 mV/s, supporting electrolyte: 0.1 M NBu_4BF_4, and concentration: 1.67 x 10^{-4} M for **2-[3]**, 8.2 x 10^{-5} M for **2-[4]**, and 6.5 x 10^{-5} M for **2-[5]**).

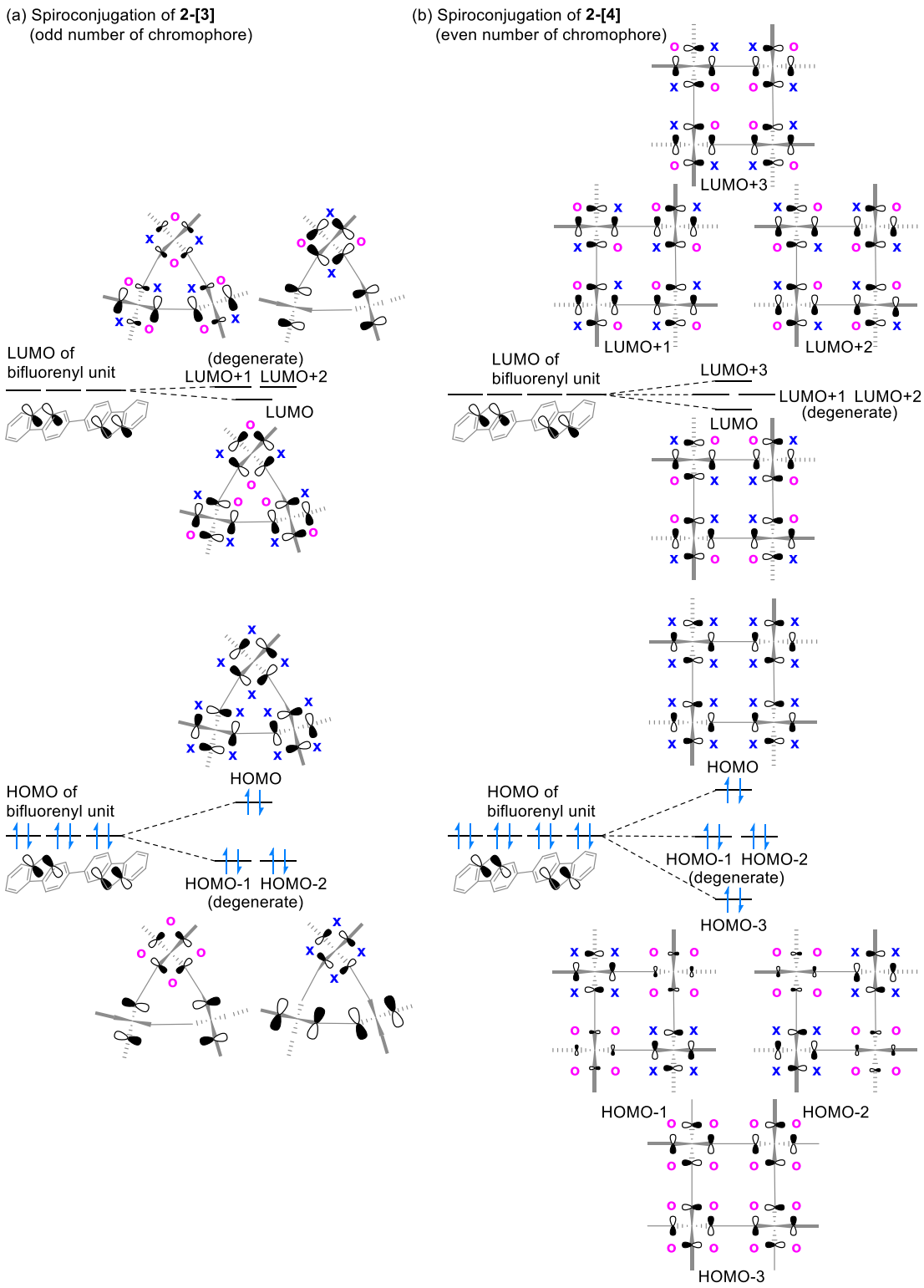


Fig. S8. Schematic drawing of molecular orbitals around spirocarbon for (a) **2-[3]** and (b) **2-[4]**.

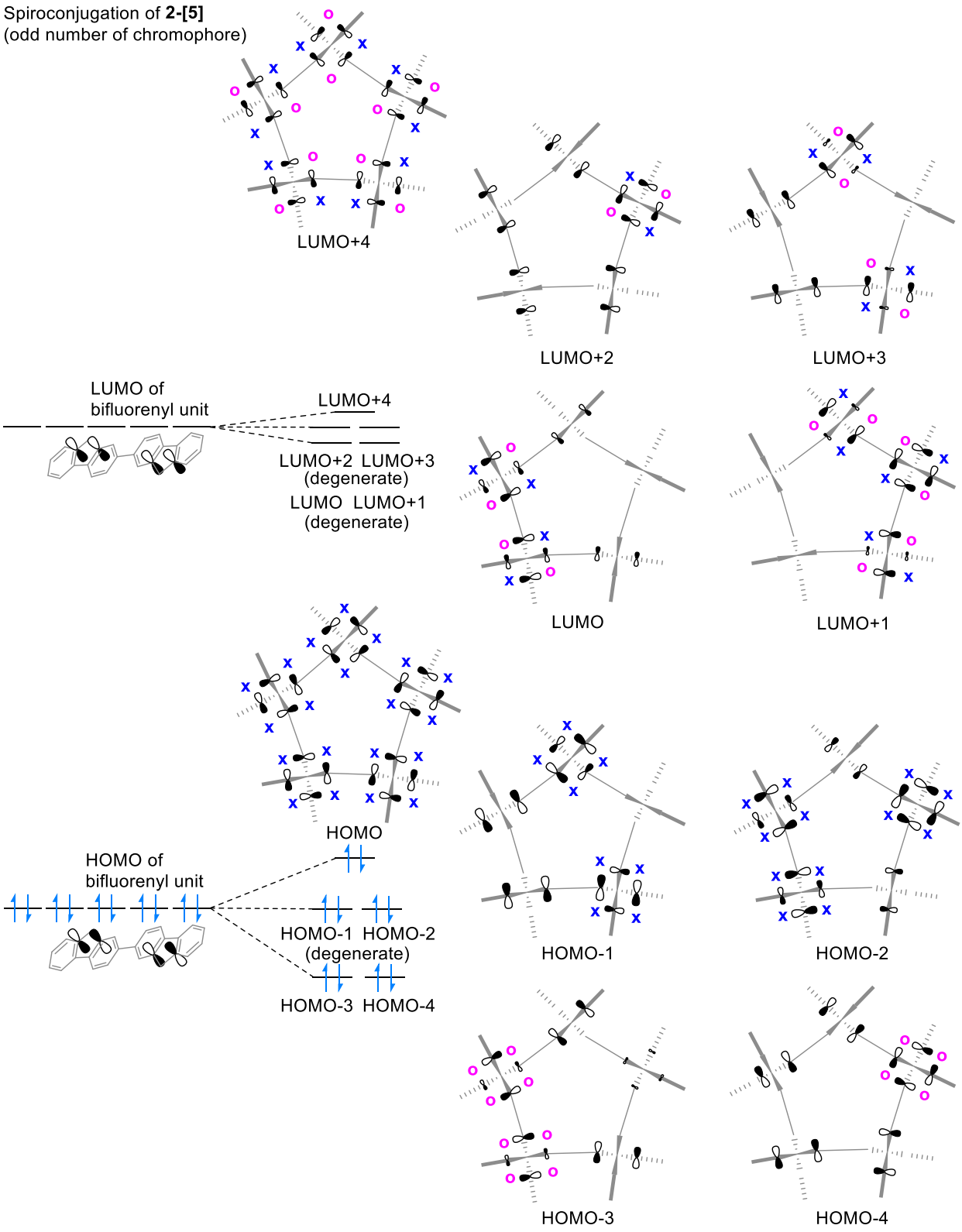


Fig. S9. Schematic drawing of molecular orbitals around spirocarbon for **2-[5]**.

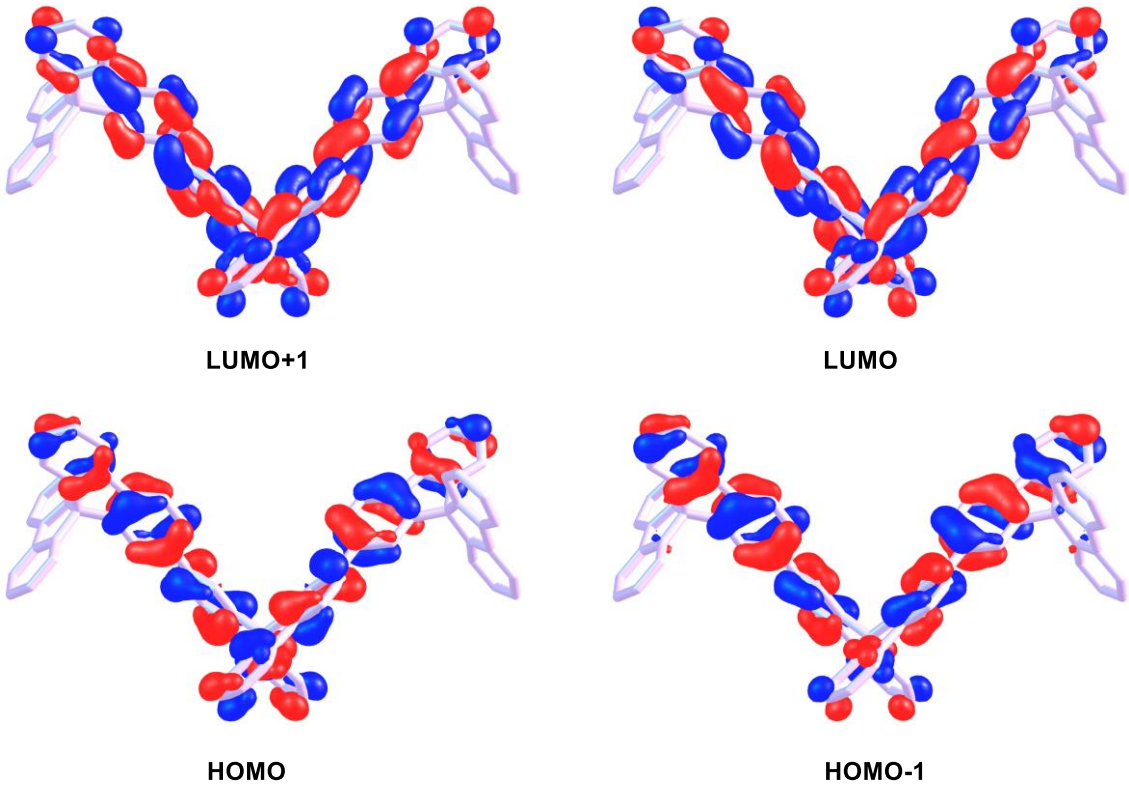
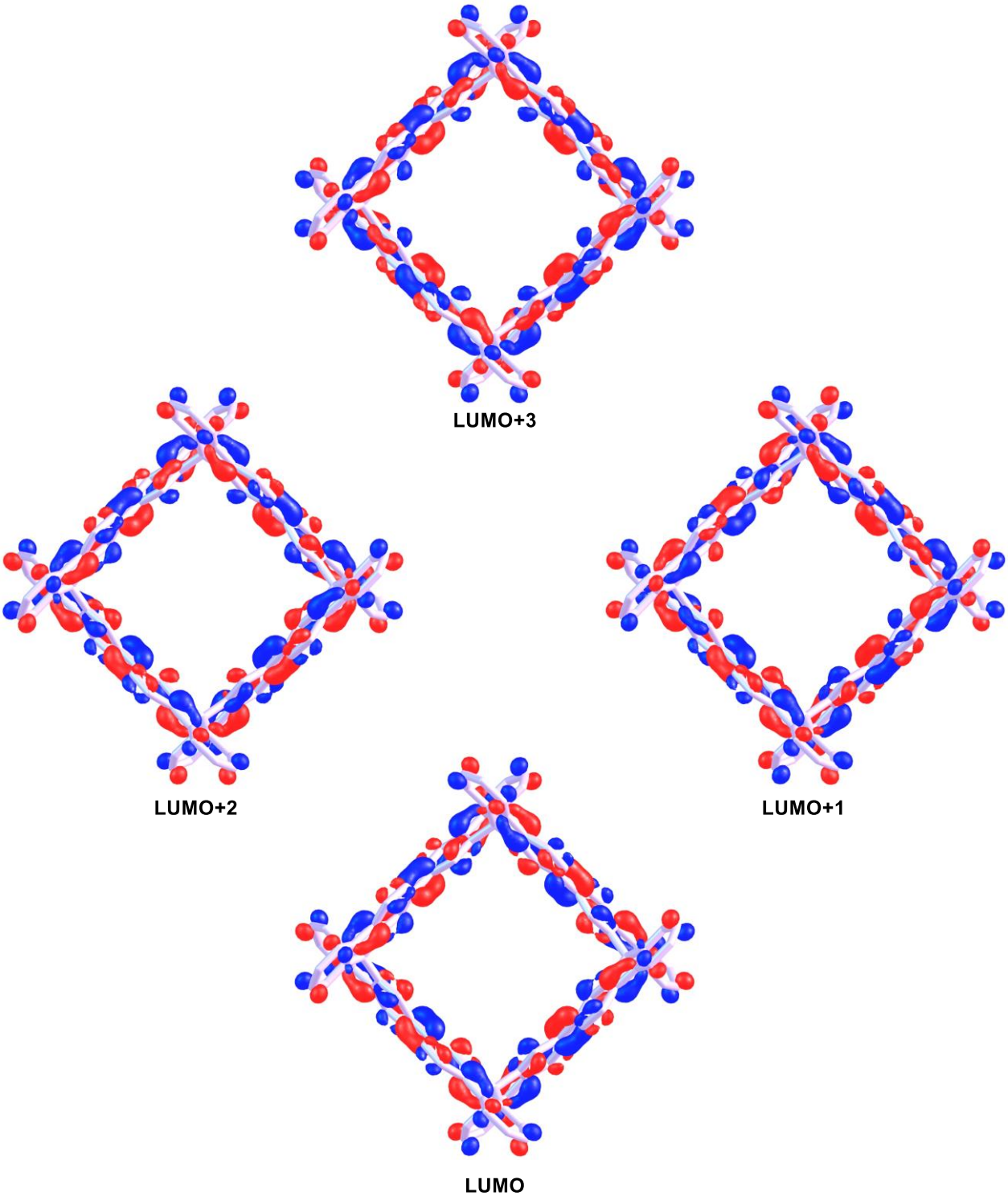


Fig. S10. Molecular orbitals from HOMO-1 to LUMO+1 for acyclic 3-mer **5** [B3LYP-D3/6-31G(d,p)] (contour value is 0.025).



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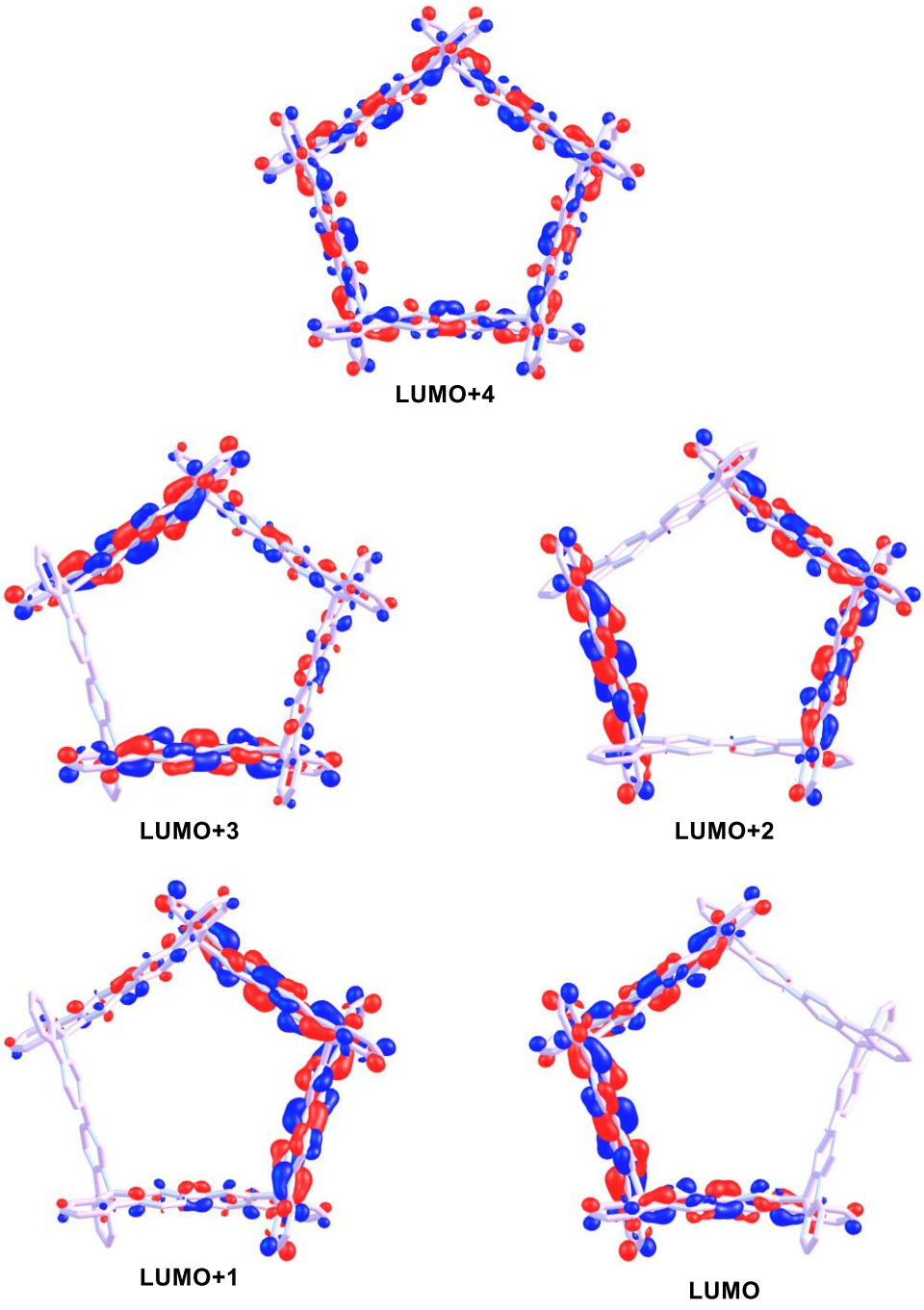
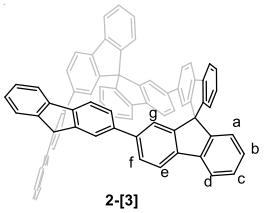


Fig. S12. Molecular orbitals from LUMO to LUMO+4 for **2-[5]** [B3LYP-D3/6-31G(d,p)] (contour value is 0.025).

2. Table (S1-S2)

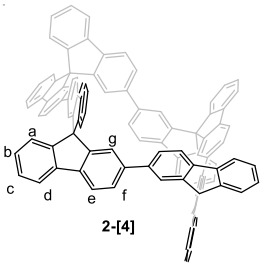
Table S1. Calculated ^{1}H NMR chemical shifts (ppm) for **2-[3]**, **2-[4]**, and **2-[5]** [GIAO-B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p)], and experimental ones for them (400 MHz).

		Chemical shift (ppm)						
	Compound	a	b	c	d	e	f	g
Calc[a]	**2-[3]**	6.93	7.14	7.40	7.77	7.62	7.03	6.55
Exp (CD_2Cl_2)	**2-[3]**	6.83	7.15	7.38	7.80	7.64	7.12	6.46
$\Delta\delta$ (calc **2-[3]** – exp **2-[3]**)		0.10	0.01	0.02	-0.03	-0.02	-0.09	0.09



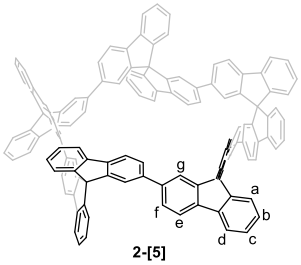
2-[3]

		Chemical shift (ppm)						
	Compound	a	b	c	d	e	f	g
Calc[a]	**2-[4]**	6.82	7.12	7.39	7.77	7.62	7.05	6.95
Exp ($CDCl_3$)	**2-[4]**	6.72	7.11	7.37	7.80	7.62	7.09	6.80
$\Delta\delta$(calc **2-[4]** – exp **2-[4]**)		0.10	0.01	0.02	-0.03	0.00	-0.04	0.15



2-[4]

		Chemical shift (ppm)						
	Compound	a	b	c	d	e	f	g
Calc[a]	**2-[5]**	6.76	7.11	7.39	7.75	7.63	7.10	7.16
Exp ($CDCl_3$)	**2-[5]**	6.67	7.07	7.35	7.79	7.65	7.14	6.76
$\Delta\delta$(calc **2-[5]** – exp **2-[5]**)		0.09	0.04	0.04	-0.04	-0.02	-0.03	0.4



2-[5]

Table S2. Orbital energy for **5** and **2-[3]** [B3LYP-D3/6-31G(d,p)].

E/ eV	
5	**2-[3]**
-1.246 (L+1)	-1.19 (L+1, L+2) [degenerate]
-1.253 (L)	-1.24 (L)
-5.32 (H)	-5.32 (H)
-5.40 (H-1)	-5.43 (H-1, H-2) [degenerate]

H: HOMO, L: LUMO

3. General and Materials

General

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were measured on a JEOL ECS400 spectrometer. CD_2Cl_2 and $CDCl_3$ were used as a solvent and the corresponding solvent peak (^{1}H, δ5.32 and 7.26 for residual $CDHCl_2$ and $CHCl_3$; ^{13}C, 53.8 and 77.0 ppm for CD_2Cl_2 and $CDCl_3$) was used as a reference. Recycling preparative HPLC was performed on Japan Analytical Industry LC-9225NEXT with tandemly arranged GPC columns (JAIGEL-1H + JAIGEL-2H) using chloroform as a solvent. Infrared spectra were recorded on a JASCO FT/IR-480plus. MALDI-TOF mass spectrum was recorded on a BRUKER AUTOFLEX III mass spectrometer. Fast atom bombardment (FAB) mass spectrum was measured on a JEOL JMS-DX-303 spectrometer using FAB mode. Optical resolution was performed on JASCO HPLC system. Absorption spectra were measured on a JASCO V-670 spectrometer. Emission spectra were measured on a JASCO FP-8500 spectrometer. Quantum yield was measured on HAMAMATSU C11347-01 or JASCO FP-8500 spectrometer. Circular dichroism (CD) spectra were measured on a JASCO J-820AC spectrometer. Circular polarized luminescence (CPL) spectra were measured on a JASCO CPL-300 spectrometer. Data collection for X-ray crystallographic structural analysis was performed on a Rigaku/XtaLAB Pro P200 Hybrid Photon Counting diffractometer (Cu-Kα, λ = 1.54184 Å) at 123 K. The structures were solved with direct methods, using SHELXT-2018/3, and refined with full-matrix least-squares, using SHELXL-2018/3. All calculations were conducted using a Gaussian 09 suite program (G09RevD.01).[S1] Optimization was performed at the B3LYP-D3[S2]/6-31G(d,p) level of theory except the calculation in Scheme 2 and Tables S1. Harmonic vibration frequency analysis was conducted with the optimized structures at the same level of theory to verify all stationary points as local minima (with no imaginary frequency).

Materials

$Ni(cod)_2$ was purchased from TCI Co., LTD. Dry and degassed THF was prepared using a Glass Contour Solvent Dispensing System. Column chromatography was performed with Wakogel® C-200. Other reagents were purchased from commercial sources and used without further purification. Chiral triflates (*R*)-**3** and (*S*)-**3** were prepared according to the reported procedure using the corresponding chiral diol.[S2] The chiral diol was prepared by optical resolution using HPLC [CHIRAL ART Amylose-SA phase (250 x 20 mm)] with $CHCl_3$/2-propanol (95:5 v/v) as eluent (a flow rate 6 mL/min, and a detection wavelength λ = 254 nm) at 25 ºC.[S3] Absolute configuration was confirmed by comparison of the optical rotation with the reported values.[S4] The racemic diol was prepared from 9,9'-spirobi[*9H*-fluorene], which was also prepared, [S5] according to the reported procedure. [S6]

References

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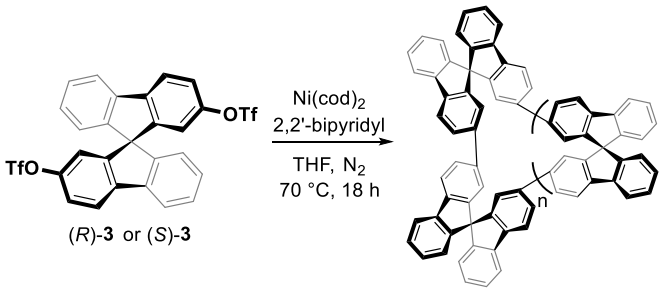
4. Experimental Procedure

Synthesis of (*R* or *S*)-2-[n]



Chiral ditriflate (*R*)-**3** (400 mg, 0.65 mmol, >99%ee) and 2,2'-bipyridyl (357 mg, 2.29 mmol) was added to a three-necked flask. The atmosphere in the flask was evacuated and transferred into N_2-filled glove-box. To the flask were added $Ni(cod)_2$ (630 mg, 2.29 mmol) and dry and degassed THF (30 mL). Then, the flask was taken out from the glove-box. The mixture was stirred at 70 °C for 18 hours under N_2. The mixture was cooled down to room temperature. The crude residue was filtered through a dry silica-gel column (eluted with $CHCl_3$) to give the crude products (146 mg). The ^1H NMR yields based on the spirobifluorene monomer was determined by the 1,3,5-trimethoxybenzene (40%, 3-mer: 4-mer: 5-mer = 1.0: 0.91: 0.38). The crude products (40 mg out of 146 mg) were suspended in chloroform (8 mL). The suspension was filtered through a membrane filter. The filtrate (including 37 mg) was purified by recycling preparative HPLC with tandemly arranged GPC columns (JAIGEL-1H + JAIGEL-2H) using chloroform as a solvent to give the desired product (*R*,*R*,*R*)-**2-[3]** (11.2 mg, 0.012 mmol), (*R*,*R*,*R*,*R*)-**2-[4]** (10.0 mg, 0.0079 mmol), and (*R*,*R*,*R*,*R*,*R*)-**2-[5]** (4.7 mg, 0.0030 mmol), respectively as white solids. Synthesis of (*S*,*S*,*S*)-**2-[3]**, (*S*,*S*,*S*,*S*)-**2-[4]**, and (*S*,*S*,*S*,*S*,*S*)-**2-[5]** was performed similarly to that of *R*-isomer. Crude products (129 mg), ^1H NMR yield (34%, 3-mer: 4-mer: 5-mer = 1.0: 0.80: 0.35), GPC purification (30 mg out of 129 mg was purified): (*S*,*S*,*S*)-**2-[3]** (7.9 mg, 0.0084 mmol), (*S*,*S*,*S*,*S*)-**2-[4]** (8.2 mg, 0.0065 mmol), and (*S*,*S*,*S*,*S*,*S*)-**2-[5]** (4.0 mg, 0.0025 mmol).

Single crystals of (*S*,*S*,*S*)-**2-[3]**, (*S*,*S*,*S*,*S*)-**2-[4]**, and (*S*,*S*,*S*,*S*,*S*)-**2-[5]** for the X-ray crystallographic analysis were obtained from toluene/MeOH = 10/1 and CH_2Cl_2/MeOH = 10/1, and toluene/hexane = 9/1, respectively, at room temperature.

(*S*,*S*,*S*)-**2-[3]**: IR (KBr) cm^{-1} 3060, 1458, 1446, 1425, 1400, 1250, 824; ^1H NMR (400 MHz, CD_2Cl_2) δ = 7.83 (d, *J* = 7.8 Hz, 6H, d), 7.68 (d, *J* = 7.8 Hz, 6H, e), 7.41 (dd, *J* = 7.5, 7.5 Hz, 6H, c), 7.17 (dd, *J* = 7.5, 7.5 Hz, 6H, b), 7.11 (d, *J* = 8.2 Hz, 6H, f), 6.80 (d, *J* = 7.3 Hz 6H, a), 6.43 (s, 6H, g) ppm, assigned with reference to the simulated value based on GIAO-DFT calculation (Table S1); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 149.9, 148.7, 142.2, 142.1, 140.9, 128.3, 128.2, 127.2, 124.5, 124.1, 120.6, 120.4, 66.2 ppm; HRMS (FAB) *m*/*z* calculated for $C_{75}H_{42}$ (M), 942.3301; found, 942.3287.

Crystal data for (*S*,*S*,*S*)-**2-[3]**: trigonal, space group *R*3 (#146), a = 25.07149(13) Å, b = 25.07149(13) Å, c = 11.09028(7) Å, α = 90°, β = 90°, γ = 120°, V = 6037.17(7) Å^3, Z = 9; $R1$ = 0.0593; $wR2$ = 0.1696. Solvent molecules are removed in the refinement process by using solvent mask routine function in Olex2. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-1991410. Absolute configuration has not been established by anomalous-dispersion effects in diffraction measurements on the crystal. The enantiomer has been assigned by reference to an unchanging chiral centre in the synthetic procedure

(*S*,*S*,*S*,*S*)-**2-[4]**: IR (KBr) cm^{-1} 3056, 1458, 1445, 1423, 1401, 1252, 821; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, J = 7.8 Hz, 8H, d), 7.62 (d, J = 7.8 Hz, 8H, e), 7.38 (dt, J = 0.9, 7.5, 7.5 Hz, 8H, c), 7.11 (ddd, J = 0.9, 7.8, 7.8 Hz, 8H, b), 7.09 (dd, J = 1.4, 5.0 Hz, 8H, f), 6.80 (brs, 8H, g), 6.72 (d, J = 7.3 Hz 8H, a) ppm, assigned with reference to the simulated value based on GIAO-DFT calculation; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.4, 149.2, 141.7, 140.6, 140.4, 127.9, 127.8, 127.1, 124.3, 121.5, 120.1, 120.0, 66.0 ppm; HRMS (FAB) *m*/*z* calculated for $C_{100}H_{56}$ (M), 1256.4387; found, 1256.4382.

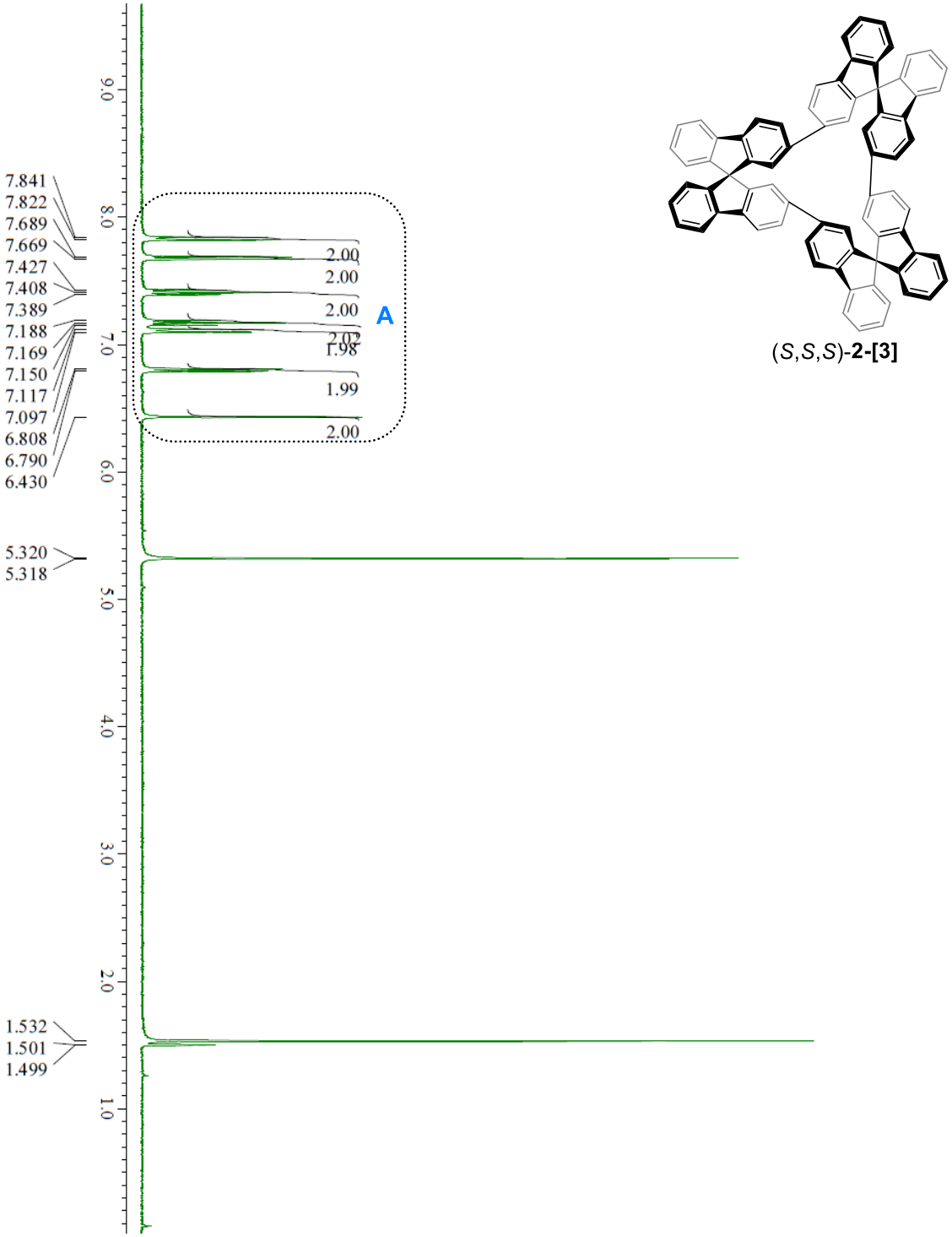
Crystal data for (*S*,*S*,*S*,*S*)-**2-[4]**: orthorhombic, space group *C*2 2 2$_1$ (#20), a = 11.6264(2) Å, b = 30.0390(4) Å, c = 26.9101(4) Å, α = 90°, β = 90°, γ = 90°, V = 9398.2(2) Å^3, Z = 8; $R1$ = 0.0619; w$R2$ = 0.1934. Solvent molecules are removed in the refinement process by using solvent mask routine function in Olex2. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC- 1991411. Absolute configuration has not been established by anomalous-dispersion effects in diffraction measurements on the crystal. The enantiomer has been assigned by reference to an unchanging chiral centre in the synthetic procedure.

(*S*,*S*,*S*,*S*,*S*)-**2-[5]**: IR (KBr) cm^{-1} 3060, 1458, 1446, 1419, 1399, 1254, 822; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, J = 7.8 Hz, 10H, d), 7.65 (d, J = 7.8 Hz, 10H, e), 7.35 (dd, J = 7.3, 7.3 Hz, 10H, c), 7.14 (dd, J = 1.4, 9.2 Hz, 10H, f), 7.07 (dd, J = 7.3 7.3 Hz, 10H, b), 6.76 (brs, 10H, g), 6.67 (d, J = 7.8 Hz 10H, a) ppm, assigned with reference to the simulated value based on GIAO-DFT calculation; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.3, 149.1, 141.8, 141.5, 140.8, 127.8(x3), 124.1, 123.0, 120.1, 120.0, 66.2 ppm; HRMS (FAB) *m*/*z* calculated for $C_{125}H_{70}$ (M), 1570.5464; found, 1570.5478.

Crystal data for (*S*,*S*,*S*,*S*,*S*)-**2-[5]**: tetragonal, space group *P* 4$_3$ 2$_1$ 2 (#96), a = 23.18260(10) Å, b = 23.18260(10) Å, c = 44.5679(5) Å, α = 90°, β = 90°, γ = 90°, V = 23952.3(3) Å^3, Z = 8; $R1$ = 0.0650; w$R2$ = 0.1795. Solvent molecules except one toulene are removed in the refinement process by using SQUEEZE routine function in PLATON because the refinement for the structure of solvent molecules was unsuccessful due to their significant disorder. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-1999349. Absolute configuration has not been established by anomalous-dispersion effects in diffraction measurements on the crystal. The enantiomer has been assigned by reference to an unchanging chiral centre in the synthetic procedure.

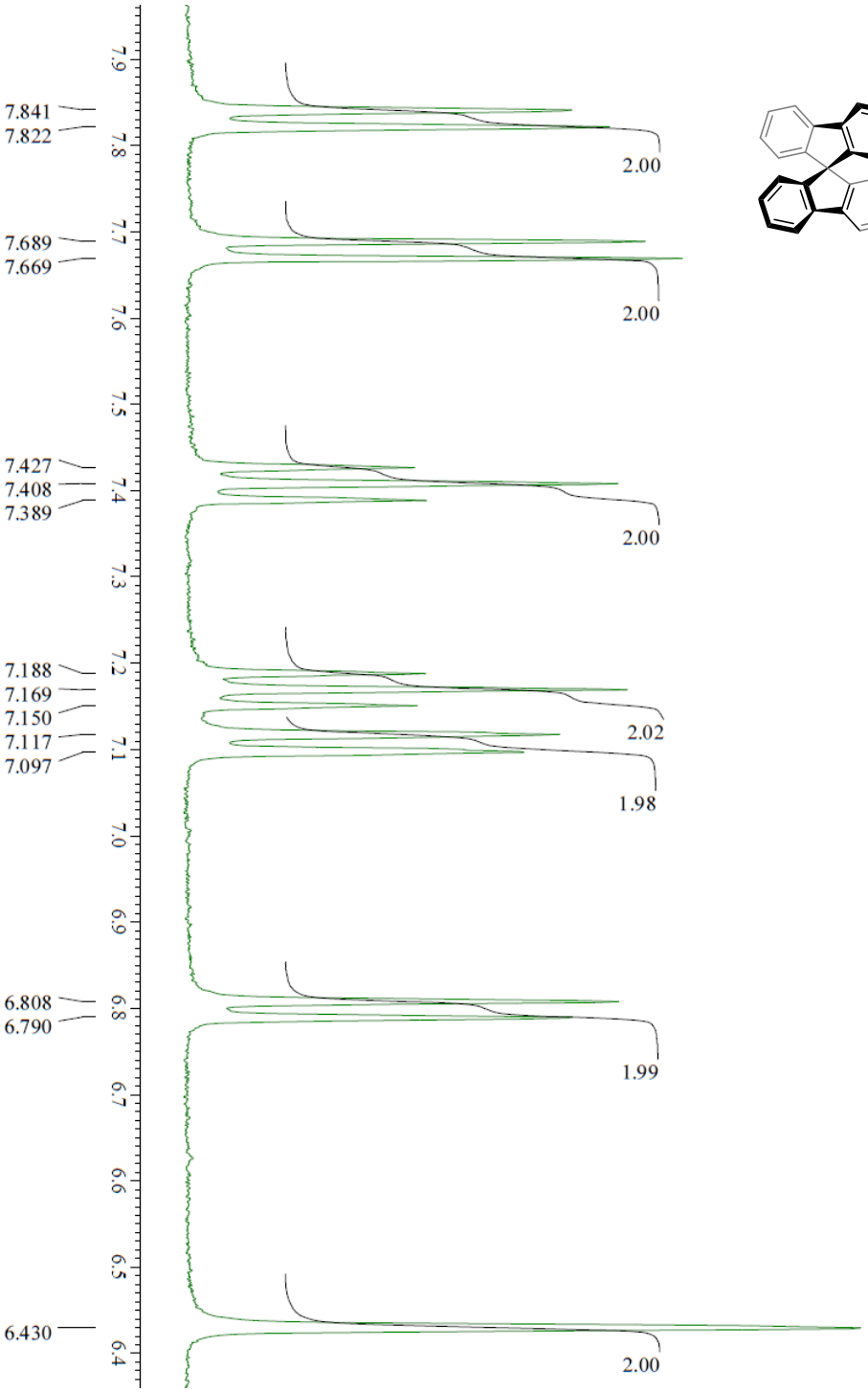
5. NMR Spectra

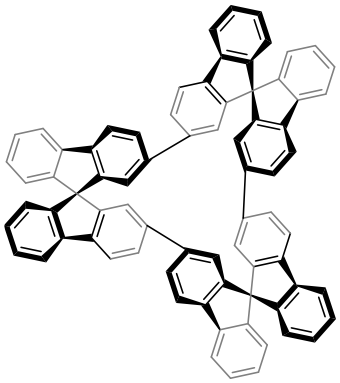
^{1}H NMR spectrum of (*S*,*S*,*S*)-**2-[3]** (400 MHz, CD_2Cl_2)



(*S*,*S*,*S*)-**2-[3]**

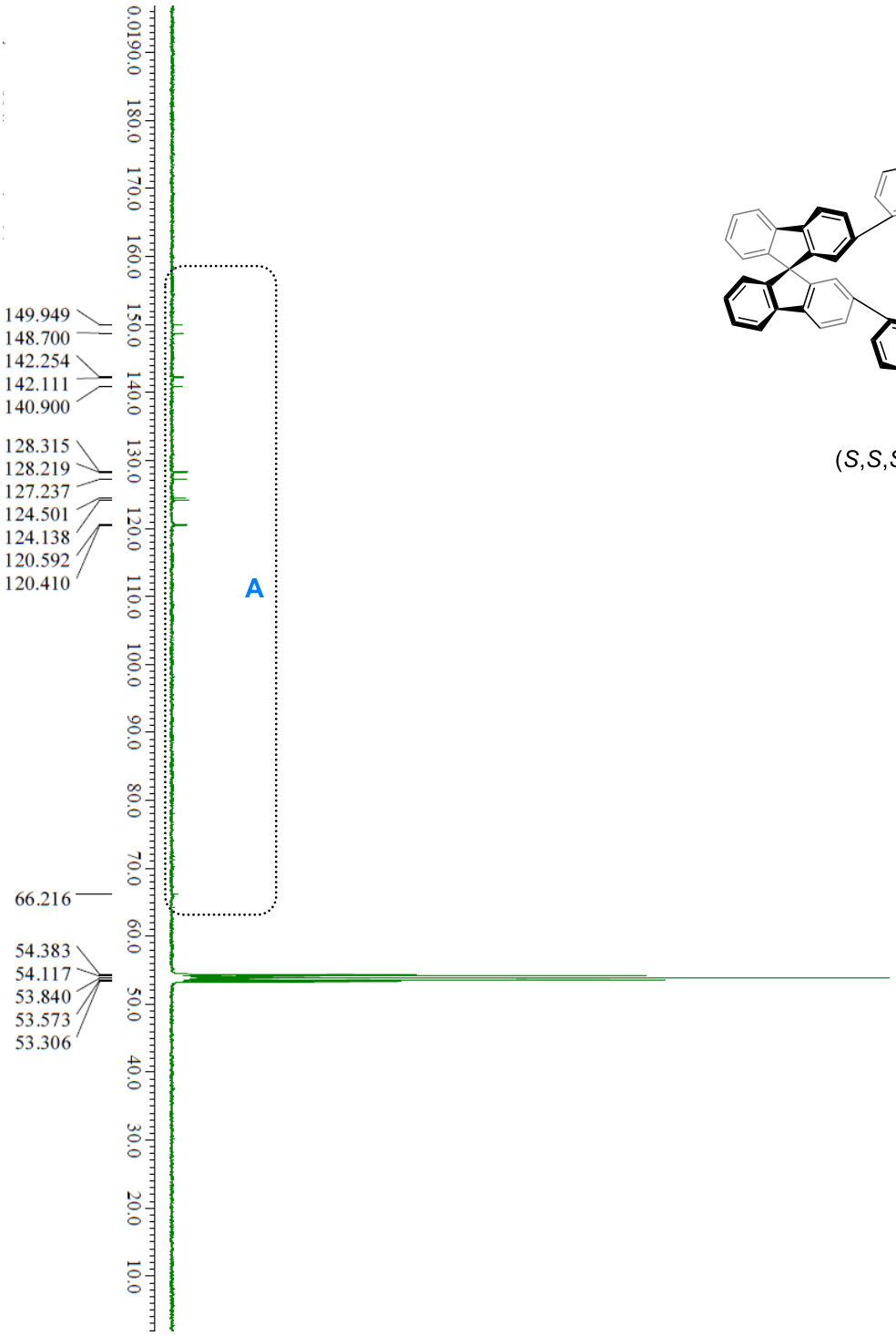
Enlarged view A





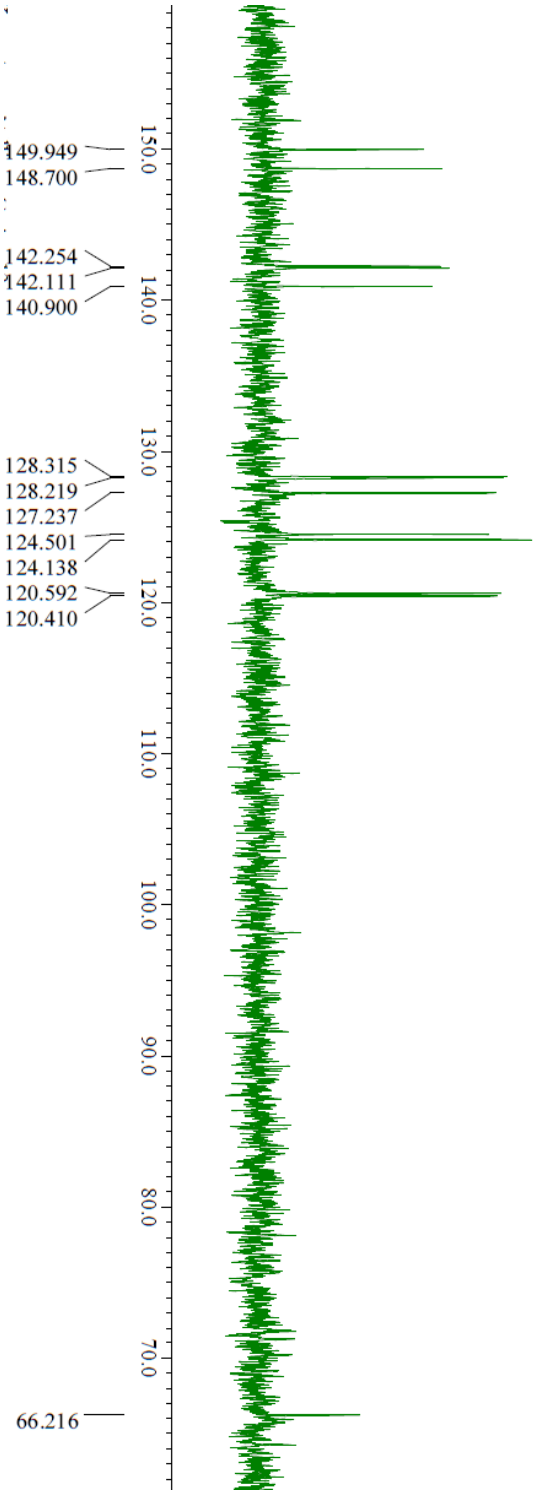
(*S*,*S*,*S*)-**2-[3]**

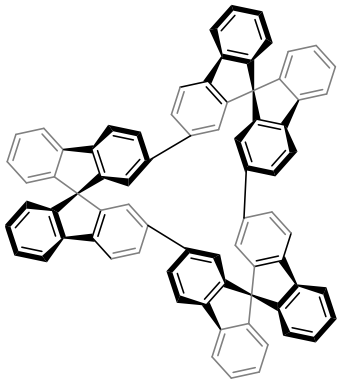
^{13}C NMR spectrum of (*S*,*S*,*S*)-**2-[3]** (100 MHz, CD_2Cl_2)



(*S*,*S*,*S*)-**2-[3]**

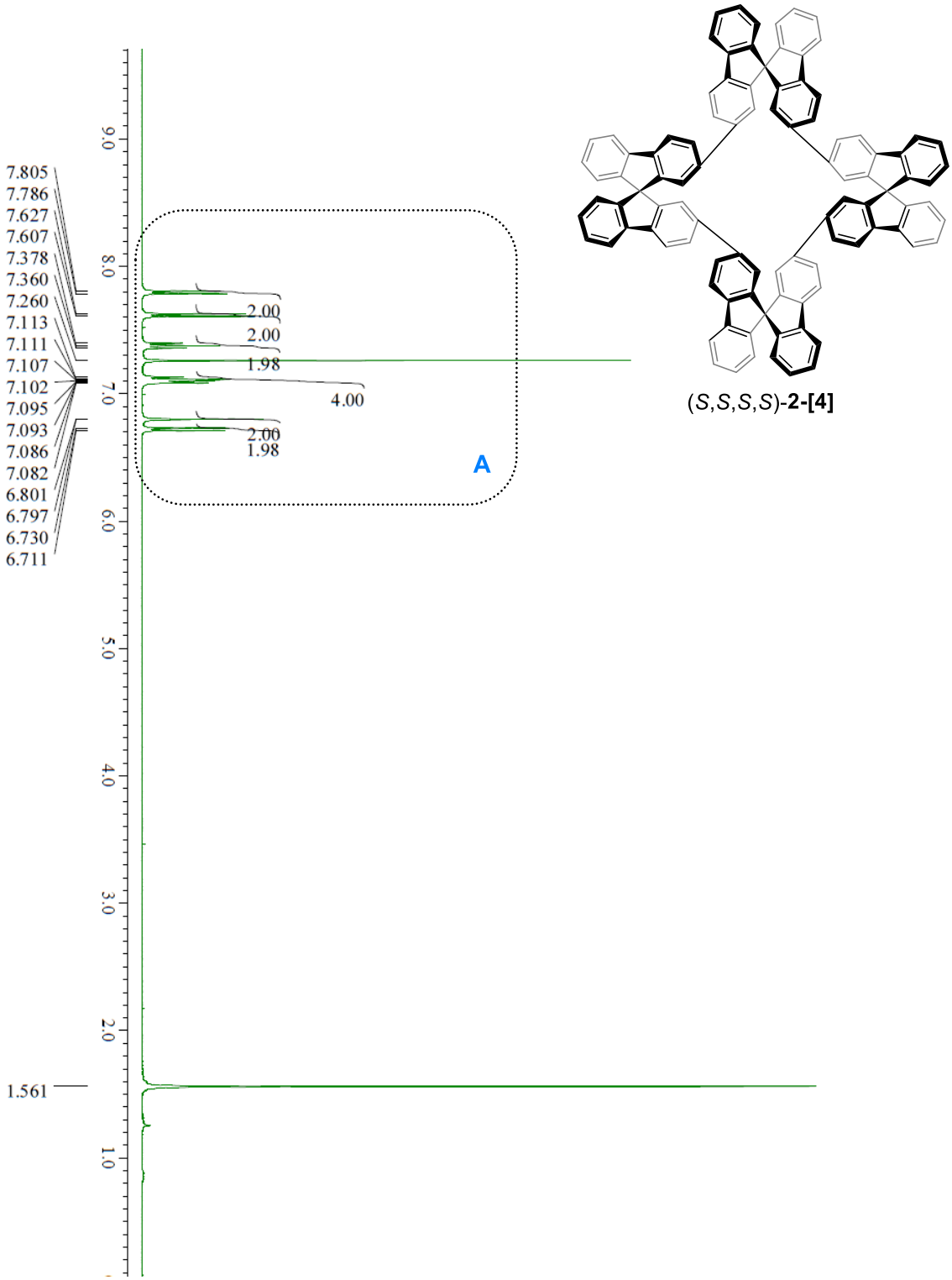
Enlarged view A





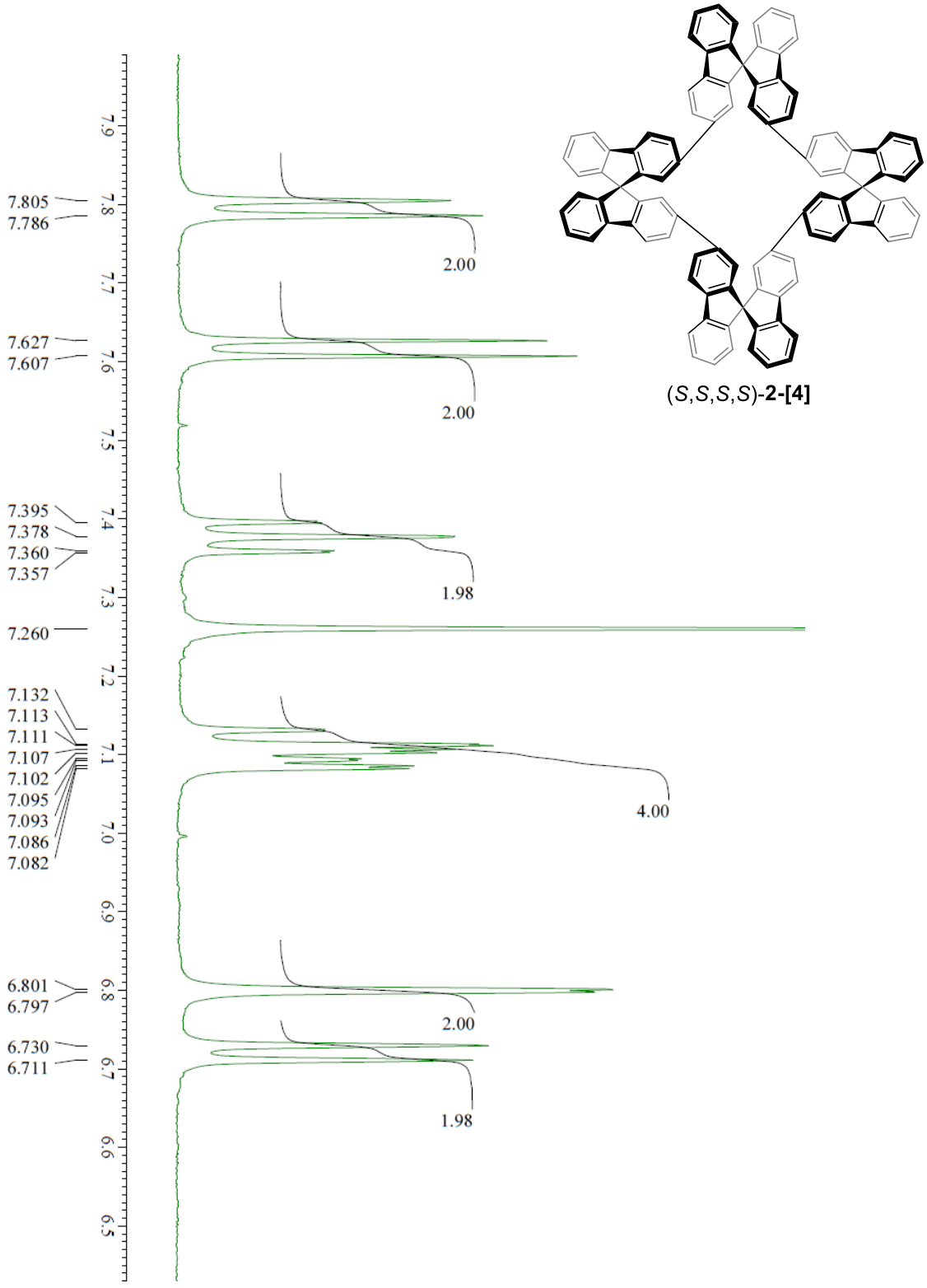
(*S*,*S*,*S*)-**2-[3]**

^{1}H NMR spectrum of (*S*,*S*,*S*,*S*)-**2-[4]** (400 MHz, $CDCl_3$)



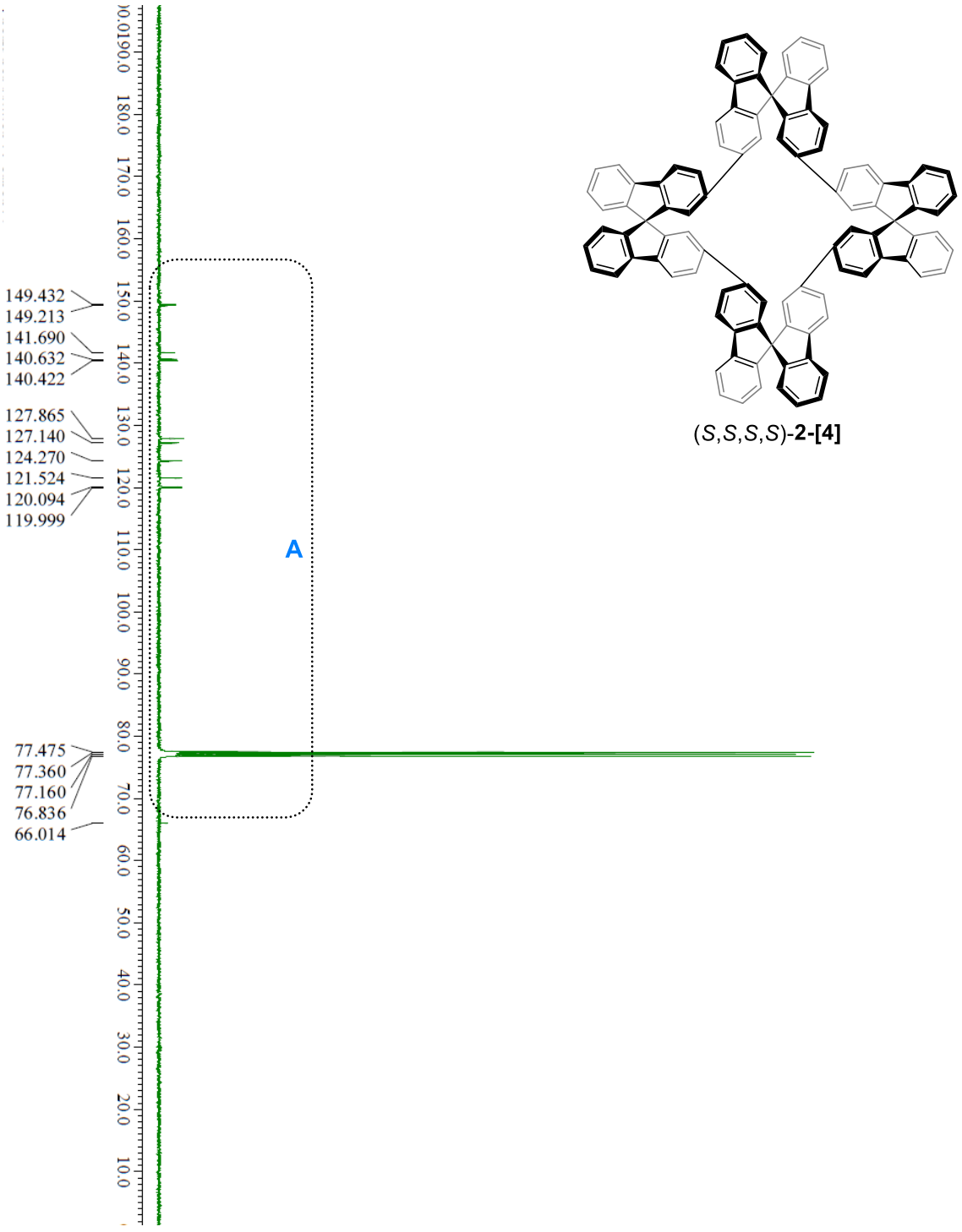
(*S*,*S*,*S*,*S*)-**2-[4]**

Enlarged view A

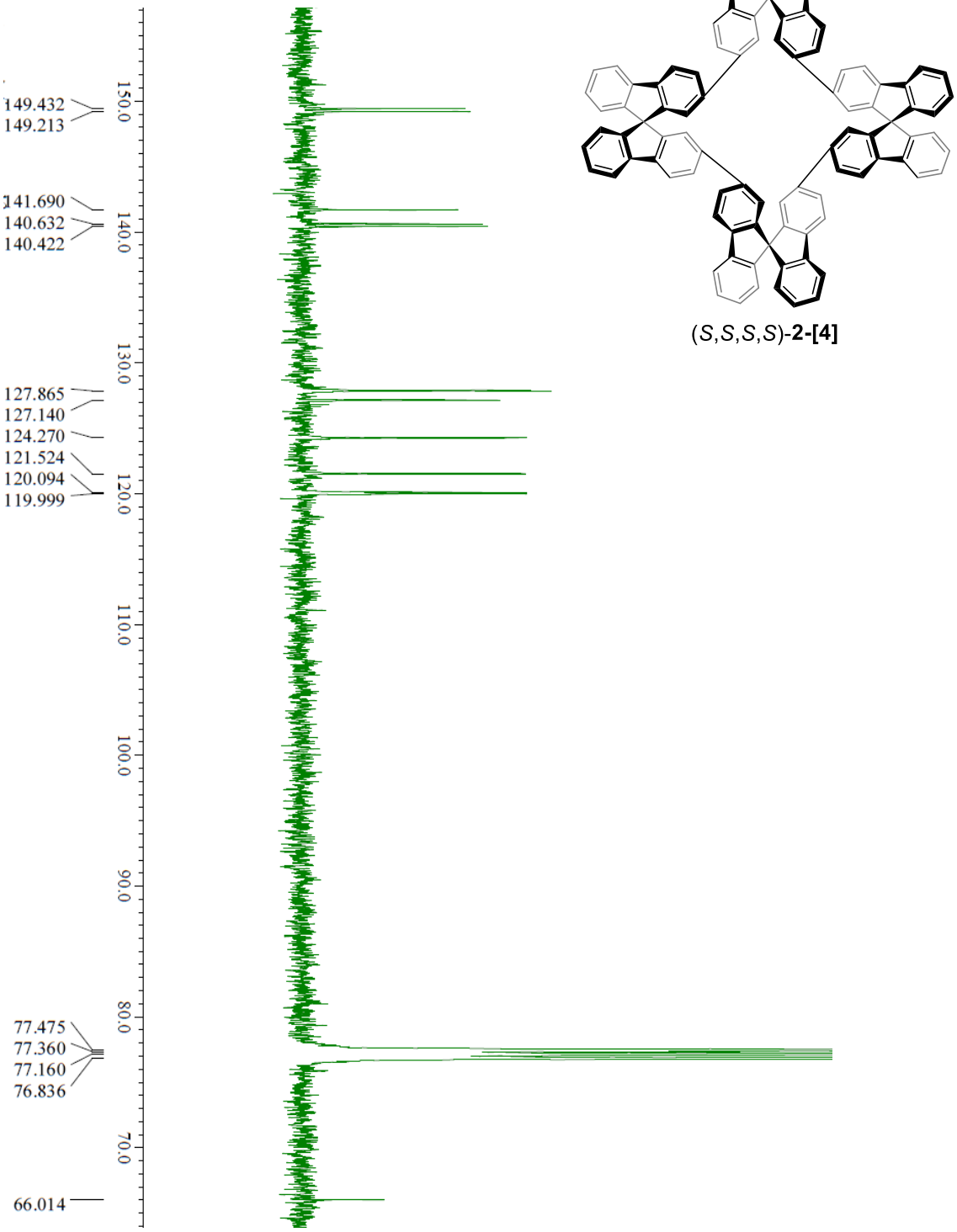


(*S*,*S*,*S*,*S*)-**2-[4]**

^{13}C NMR spectrum of (*S*,*S*,*S*,*S*)-**2-[4]** (100 MHz, $CDCl_3$)

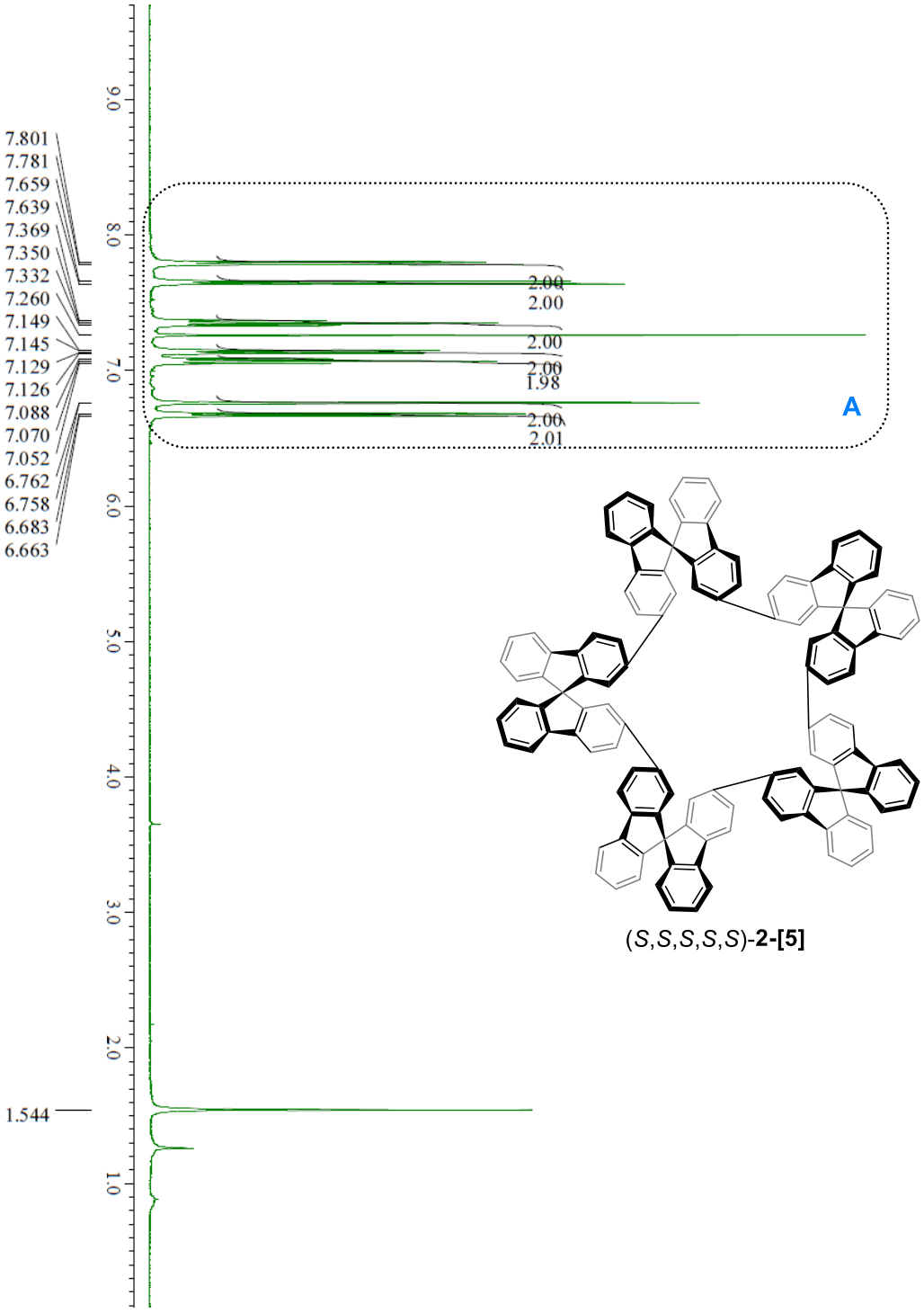


Enlarged view A



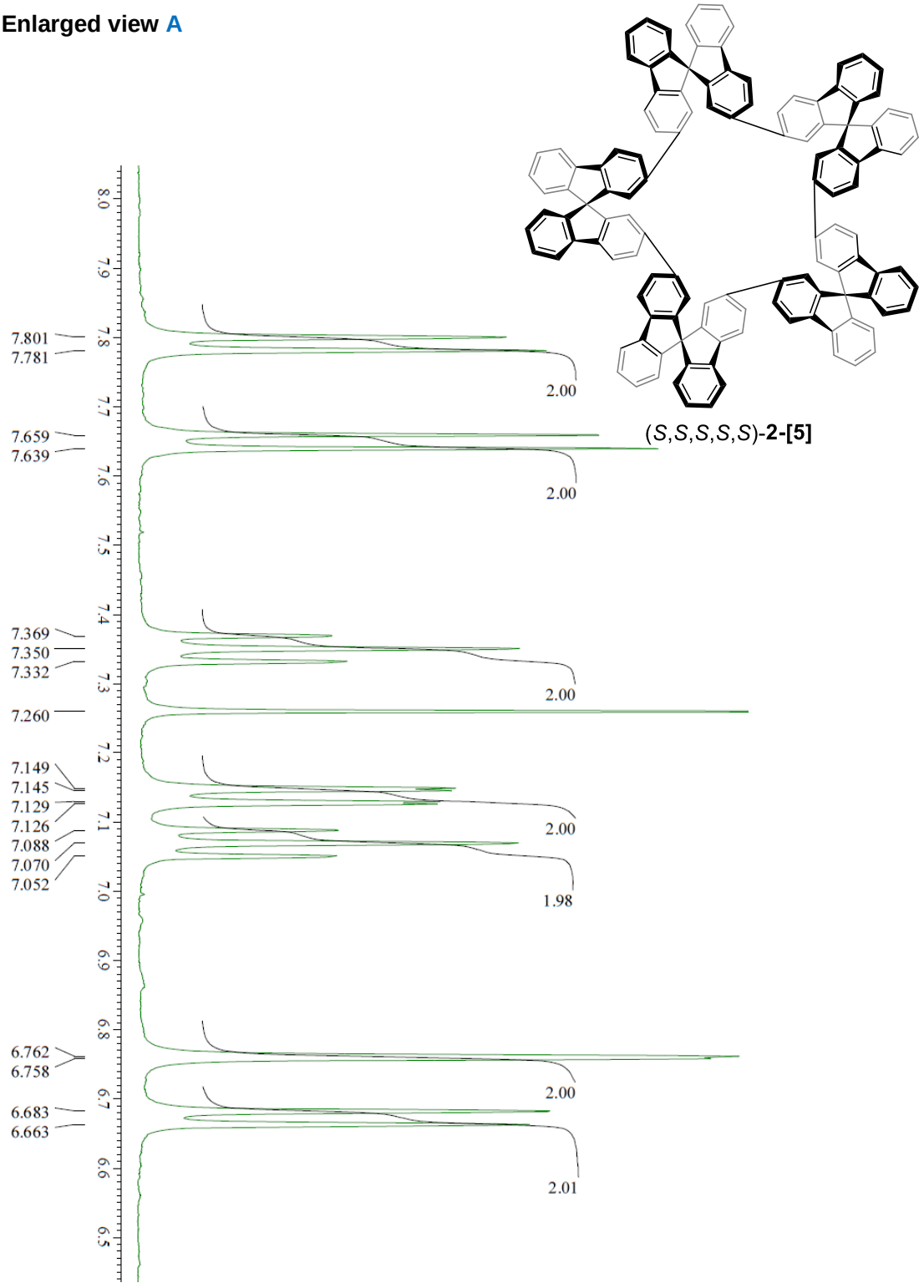
(*S*,*S*,*S*,*S*)-**2-[4]**

^{1}H NMR spectrum of (*S*,*S*,*S*,*S*,*S*)-**2-[5]** (400 MHz, $CDCl_3$)

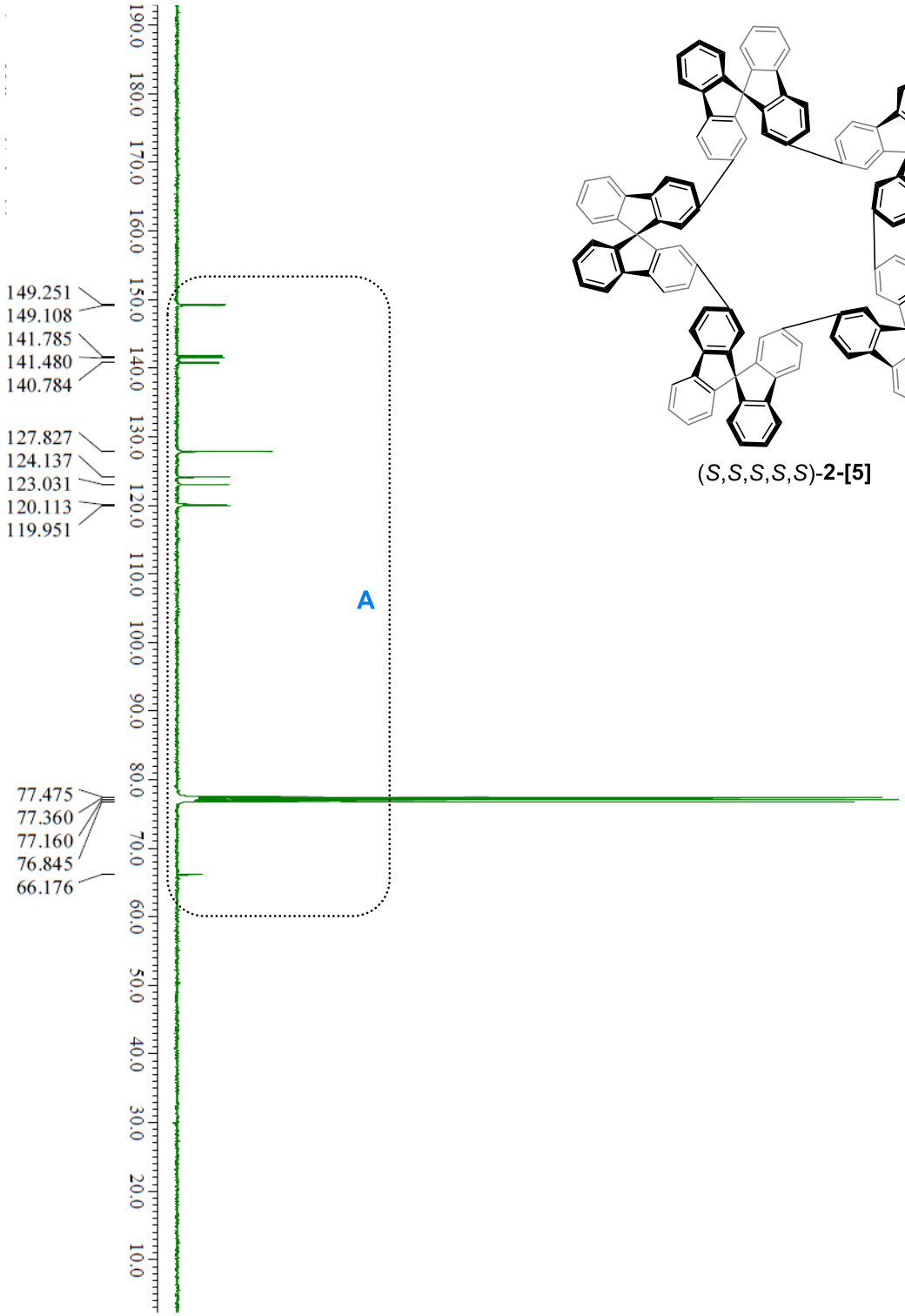


(*S*,*S*,*S*,*S*,*S*)-**2-[5]**

Enlarged view A

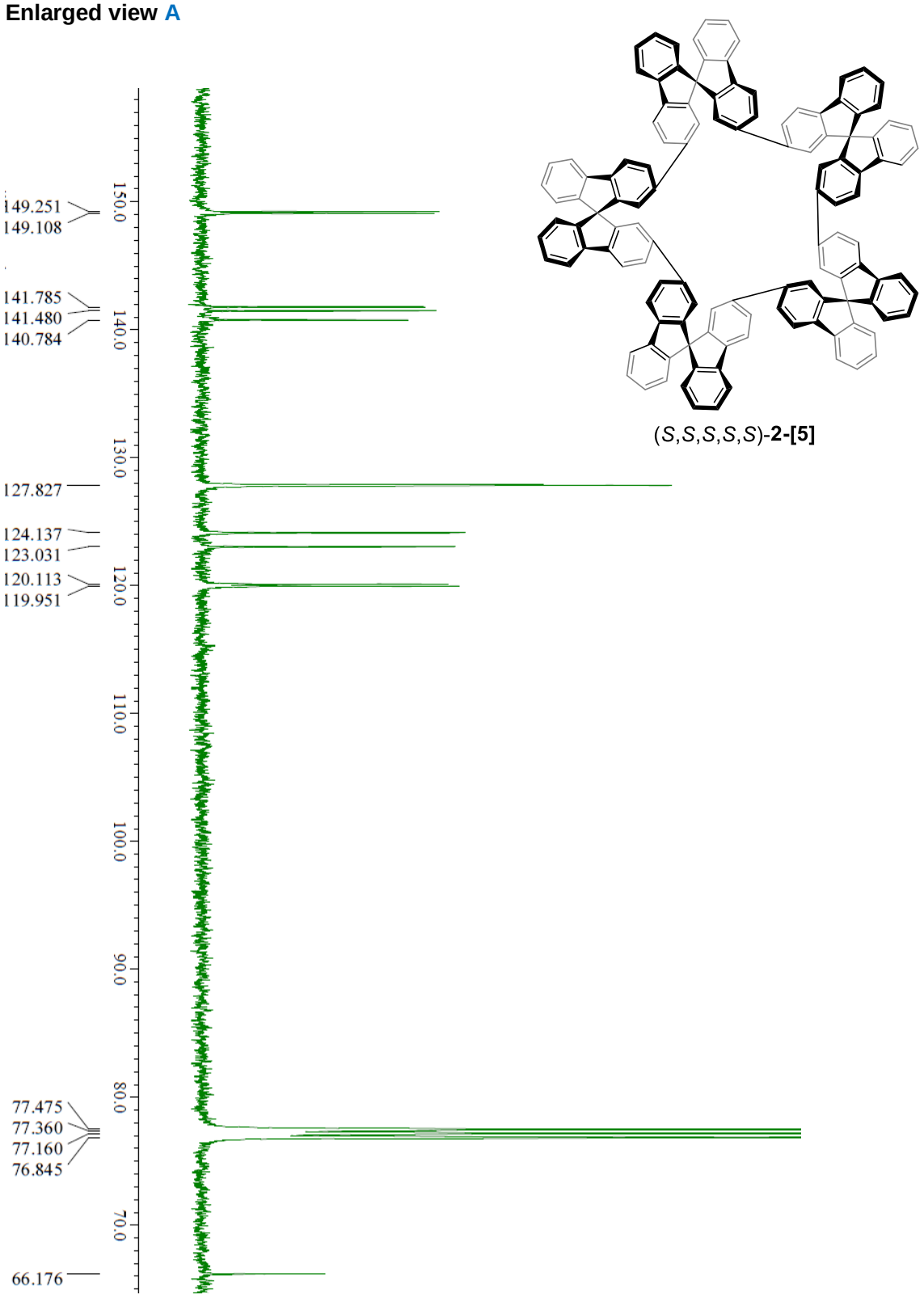


^{13}C NMR spectrum of (*S*,*S*,*S*,*S*,*S*)-**2-[5]** (100 MHz, $CDCl_3$)



(*S*,*S*,*S*,*S*,*S*)-**2-[5]**

Enlarged view A



(*S*,*S*,*S*,*S*,*S*)-**2-[5]**

6. Cartesian Coordinates of Optimized Structures

Cartesian coordinates for (*S*,*S*,*S*)-**2-[3]**, optimized at the B3LYP-D3/6-31G(d,p) level of theory

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.178113	4.133174	0.451631
C	-1.502161	4.398364	1.793933
C	-0.616379	5.458924	2.288654
C	0.268995	5.823152	1.255447
C	0	4.997163	0
C	-0.268995	5.823152	-1.255447
C	0.616379	5.458924	-2.288654
C	1.502161	4.398364	-1.793933
C	1.178113	4.133174	-0.451631
C	-1.833993	3.146939	-0.265165
C	-2.832085	2.380494	0.363933
C	-3.155781	2.654654	1.70719
C	-2.505288	3.658769	2.423368
C	-0.54137	6.086941	3.533039
C	0.422813	7.078661	3.72912
C	1.299842	7.437609	2.698823
C	1.22677	6.808292	1.450968
C	-1.22677	6.808292	-1.450968
C	-1.299842	7.437609	-2.698823
C	-0.422813	7.078661	-3.72912
C	0.54137	6.086941	-3.533039
C	2.505288	3.658769	-2.423368
C	3.155781	2.654654	-1.70719
C	2.832085	2.380494	-0.363933
C	1.833993	3.146939	0.265165
C	-4.16849	-1.046311	-0.451631
C	-4.560176	-0.898272	-1.793933
C	-5.035756	-2.195662	-2.288654
C	-4.908501	-3.144532	-1.255447
C	-4.32767	-2.498581	0
C	-5.177495	-2.67862	1.255447
C	-4.419377	-3.263262	2.288654
C	-3.058015	-3.500092	1.793933
C	-2.990377	-3.086863	0.451631
C	-3.642326	0.014815	0.265165
C	-3.477611	1.26241	-0.363933
C	-3.876889	1.40566	-1.70719
C	-4.42123	0.340258	-2.423368
C	-5.542131	-2.57463	-3.533039
C	-5.918893	-3.905497	-3.72912
C	-5.791238	-4.844501	-2.698823
C	-5.282769	-4.46656	-1.450968
C	-6.509539	-2.341732	1.450968
C	-7.091079	-2.593109	2.698823
C	-6.341707	-3.173163	3.72912
C	-5.00076	-3.512311	3.533039
C	-1.915943	-3.999027	2.423368
C	-0.721107	-4.060314	1.70719
C	-0.645526	-3.642905	0.363933
C	-1.808333	-3.161754	-0.265165
C	4.908501	-3.144532	1.255447
C	5.035756	-2.195662	2.288654
C	4.560176	-0.898272	1.793933
C	4.16849	-1.046311	0.451631
C	4.32767	-2.498581	0
C	2.990377	-3.086863	-0.451631
C	3.058015	-3.500092	-1.793933
C	4.419377	-3.263262	-2.288654
C	5.177495	-2.67862	-1.255447
C	5.282769	-4.46656	1.450968

C	5.791238	-4.844501	2.698823	C	-8.132423	-2.336483	2.869325
C	5.918893	-3.905497	3.72912	C	-6.808432	-3.362052	4.691506
C	5.542131	-2.57463	3.533039	C	-4.422159	-3.962528	4.334666
C	4.42123	0.340258	2.423368	C	-1.950449	-4.327103	3.458365
C	3.876889	1.40566	1.70719	C	0.173195	-4.446263	2.187282
C	3.477611	1.26241	0.363933	C	-1.765353	-2.800979	-1.288412
C	3.642326	0.014815	-0.265165	C	5.182046	-5.190365	0.647447
C	1.808333	-3.161754	0.265165	C	6.089665	-5.874643	2.869325
C	0.645526	-3.642905	-0.363933	C	6.315838	-4.215249	4.691506
C	0.721107	-4.060314	-1.70719	C	5.642729	-1.848438	4.334666
C	1.915943	-3.999027	-2.423368	C	4.722606	0.474413	3.458365
C	5.00076	-3.512311	-3.533039	C	3.763979	2.373123	2.187282
C	6.341707	-3.173163	-3.72912	C	3.308395	-0.128352	-1.288412
C	7.091079	-2.593109	-2.698823	C	1.765353	-2.800979	1.288412
C	6.509539	-2.341732	-1.450968	C	-0.173195	-4.446263	-2.187282
C	-3.937174	2.07314	2.187282	C	1.950449	-4.327103	-3.458365
C	-2.772157	3.85269	3.458365	C	4.422159	-3.962528	-4.334666
C	-1.22057	5.810965	4.334666	C	6.808432	-3.362052	-4.691506
C	0.492594	7.577301	4.691506	C	8.132423	-2.336483	-2.869325
C	2.042758	8.211126	2.869325	C	7.086011	-1.892601	-0.647447
C	1.903965	7.082966	0.647447	C	-6.089665	-5.874643	-2.869325
C	-1.903965	7.082966	-0.647447	C	-1.543042	2.92933	-1.288412
C	-2.042758	8.211126	-2.869325	H	-3.937174	2.07314	2.187282
C	-0.492594	7.577301	-4.691506	H	-2.772157	3.85269	3.458365
C	1.22057	5.810965	-4.334666	H	-1.22057	5.810965	4.334666
C	2.772157	3.85269	-3.458365	H	0.492594	7.577301	4.691506
C	3.937174	2.07314	-2.187282	H	2.042758	8.211126	2.869325
C	1.543042	2.92933	1.288412	H	1.903965	7.082966	0.647447
C	-3.308395	-0.128352	1.288412	H	-1.903965	7.082966	-0.647447
C	-3.763979	2.373123	-2.187282	H	-2.042758	8.211126	-2.869325
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C	-5.642729	-1.848438	-4.334666	H	1.22057	5.810965	-4.334666
C	-6.315838	-4.215249	-4.691506	H	2.772157	3.85269	-3.458365
C	-5.182046	-5.190365	-0.647447	H	3.937174	2.07314	-2.187282
C	-7.086011	-1.892601	0.647447	H	1.543042	2.92933	1.288412

H	-3.308395	-0.128352	1.288412
H	-3.763979	2.373123	-2.187282
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H	-5.642729	-1.848438	-4.334666
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H	-5.182046	-5.190365	-0.647447
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H	-6.808432	-3.362052	4.691506
H	-4.422159	-3.962528	4.334666
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H	0.173195	-4.446263	2.187282
H	-1.765353	-2.800979	-1.288412
H	5.182046	-5.190365	0.647447
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H	6.315838	-4.215249	4.691506
H	5.642729	-1.848438	4.334666
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H	3.308395	-0.128352	-1.288412
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H	6.808432	-3.362052	-4.691506
H	8.132423	-2.336483	-2.869325
H	7.086011	-1.892601	-0.647447
H	-6.089665	-5.874643	-2.869325
H	-1.543042	2.92933	-1.288412

Cartesian coordinates for (*R*,*R*,*R*,*R*)-**2-[4]**, optimized at the B3LYP-D3/6-31G(d,p) level of theory.

	Coordinates (Angstroms)		
Atomic	X	Y	Z
Type			
C	-0.327664	7.131319	1.244473
C	0.532966	6.79162	2.30565
C	1.477244	5.773407	1.833175
C	1.18803	5.478806	0.488577
C	0	6.307357	0
C	0.327664	7.131319	-1.244473
C	-0.532966	6.79162	-2.30565
C	-1.477244	5.773407	-1.833175
C	-1.18803	5.478806	-0.488577
C	-1.322558	8.084722	1.40976
C	-1.455917	8.70863	2.655239
C	-0.603222	8.373934	3.713908
C	0.397397	7.413369	3.54831
C	2.546063	5.137219	2.465673
C	3.325269	4.239635	1.738078
C	3.05533	3.951567	0.384384
C	1.954211	4.577953	-0.231009
C	1.322558	8.084722	-1.40976
C	1.455917	8.70863	-2.655239
C	0.603222	8.373934	-3.713908
C	-0.397397	7.413369	-3.54831
C	-2.546063	5.137219	-2.465673
C	-3.325269	4.239635	-1.738078
C	-3.05533	3.951567	-0.384384
C	-1.954211	4.577953	0.231009
C	-0.327664	-7.131319	-1.244473
C	0.532966	-6.79162	-2.30565
C	1.477244	-5.773407	-1.833175
C	1.18803	-5.478806	-0.488577
C	0	-6.307357	0
C	0.327664	-7.131319	1.244473
C	-0.532966	-6.79162	2.30565
C	-1.477244	-5.773407	1.833175
C	-1.18803	-5.478806	0.488577

C	-1.322558	-8.084722	-1.40976	C	-7.413369	0.397397	3.54831
C	-1.455917	-8.70863	-2.655239	C	-5.137219	2.546063	2.465673
C	-0.603222	-8.373934	-3.713908	C	-4.239635	3.325269	1.738078
C	0.397397	-7.413369	-3.54831	C	-3.951567	3.05533	0.384384
C	2.546063	-5.137219	-2.465673	C	-4.577953	1.954211	-0.231009
C	3.325269	-4.239635	-1.738078	C	-8.084722	1.322558	-1.40976
C	3.05533	-3.951567	-0.384384	C	-8.70863	1.455917	-2.655239
C	1.954211	-4.577953	0.231009	C	-8.373934	0.603222	-3.713908
C	1.322558	-8.084722	1.40976	C	-7.413369	-0.397397	-3.54831
C	1.455917	-8.70863	2.655239	C	-5.137219	-2.546063	-2.465673
C	0.603222	-8.373934	3.713908	C	-4.239635	-3.325269	-1.738078
C	-0.397397	-7.413369	3.54831	C	-3.951567	-3.05533	-0.384384
C	-2.546063	-5.137219	2.465673	C	-4.577953	-1.954211	0.231009
C	-3.325269	-4.239635	1.738078	C	6.79162	0.532966	-2.30565
C	-3.05533	-3.951567	0.384384	C	7.131319	-0.327664	-1.244473
C	-1.954211	-4.577953	-0.231009	C	4.577953	-1.954211	-0.231009
C	5.478806	-1.18803	0.488577	C	3.951567	-3.05533	0.384384
C	5.773407	-1.477244	1.833175	C	4.239635	-3.325269	1.738078
C	6.79162	-0.532966	2.30565	C	5.137219	-2.546063	2.465673
C	7.131319	0.327664	1.244473	C	7.413369	-0.397397	3.54831
C	6.307357	0	0	C	8.373934	0.603222	3.713908
C	5.478806	1.18803	-0.488577	C	8.70863	1.455917	2.655239
C	5.773407	1.477244	-1.833175	C	8.084722	1.322558	1.40976
C	-7.131319	-0.327664	1.244473	C	4.577953	1.954211	0.231009
C	-6.79162	0.532966	2.30565	C	3.951567	3.05533	-0.384384
C	-5.773407	1.477244	1.833175	C	4.239635	3.325269	-1.738078
C	-5.478806	1.18803	0.488577	C	5.137219	2.546063	-2.465673
C	-6.307357	0	0	C	7.413369	0.397397	-3.54831
C	-7.131319	0.327664	-1.244473	C	8.373934	-0.603222	-3.713908
C	-6.79162	-0.532966	-2.30565	C	8.70863	-1.455917	-2.655239
C	-5.773407	-1.477244	-1.833175	C	8.084722	-1.322558	-1.40976
C	-5.478806	-1.18803	-0.488577	H	-1.983267	8.337276	0.585572
C	-8.084722	-1.322558	1.40976	H	-2.227812	9.458252	2.802193
C	-8.70863	-1.455917	2.655239	H	-0.721208	8.866991	4.674466
C	-8.373934	-0.603222	3.713908	H	1.05762	7.15569	4.371572

H	2.789135	5.356337	3.501483
H	4.187907	3.782755	2.212615
H	1.703763	4.357386	-1.264096
H	1.983267	8.337276	-0.585572
H	2.227812	9.458252	-2.802193
H	0.721208	8.866991	-4.674466
H	-1.05762	7.15569	-4.371572
H	-2.789135	5.356337	-3.501483
H	-4.187907	3.782755	-2.212615
H	-1.703763	4.357386	1.264096
H	-1.983267	-8.337276	-0.585572
H	-2.227812	-9.458252	-2.802193
H	-0.721208	-8.866991	-4.674466
H	1.05762	-7.15569	-4.371572
H	2.789135	-5.356337	-3.501483
H	4.187907	-3.782755	-2.212615
H	1.703763	-4.357386	1.264096
H	1.983267	-8.337276	0.585572
H	2.227812	-9.458252	2.802193
H	0.721208	-8.866991	4.674466
H	-1.05762	-7.15569	4.371572
H	-2.789135	-5.356337	3.501483
H	-4.187907	-3.782755	2.212615
H	-1.703763	-4.357386	-1.264096
H	-8.337276	-1.983267	0.585572
H	-9.458252	-2.227812	2.802193
H	-8.866991	-0.721208	4.674466
H	-7.15569	1.05762	4.371572
H	-5.356337	2.789135	3.501483
H	-3.782755	4.187907	2.212615
H	-4.357386	1.703763	-1.264096
H	-8.337276	1.983267	-0.585572
H	-9.458252	2.227812	-2.802193
H	-8.866991	0.721208	-4.674466
H	-7.15569	-1.05762	-4.371572
H	-5.356337	-2.789135	-3.501483
H	-3.782755	-4.187907	-2.212615
H	-4.357386	-1.703763	1.264096
H	4.357386	-1.703763	-1.264096
H	3.782755	-4.187907	2.212615
H	5.356337	-2.789135	3.501483
H	7.15569	-1.05762	4.371572
H	8.866991	0.721208	4.674466
H	9.458252	2.227812	2.802193
H	8.337276	1.983267	0.585572
H	4.357386	1.703763	1.264096
H	3.782755	4.187907	-2.212615
H	5.356337	2.789135	-3.501483
H	7.15569	1.05762	-4.371572
H	8.866991	-0.721208	-4.674466
H	9.458252	-2.227812	-2.802193
H	8.337276	-1.983267	-0.585572

Cartesian coordinates for (*S*,*S*,*S*,*S*,*S*)-**2-[5]**, optimized at the B3LYP-D3/6-31G(d,p) level of theory.

	Coordinates (Angstroms)		
Atomic Type	X	Y	Z
C	-1.195198	6.819499	0.509977
C	-1.461237	7.129438	1.855993
C	-0.483314	8.120625	2.315332
C	0.360498	8.448398	1.237618
C	0	7.62592	0
C	-0.360498	8.448398	-1.237618
C	0.483314	8.120625	-2.315332
C	1.461237	7.129438	-1.855993
C	1.195198	6.819499	-0.509977
C	-2.025994	5.978395	-0.210769

C	-3.181566	5.446699	0.395719	C	-8.405613	2.402992	3.556511
C	-3.417478	5.737263	1.756144	C	-7.031449	-0.413037	2.490187
C	-2.565659	6.55967	2.490187	C	-6.512521	-1.477303	1.756144
C	-0.312096	8.736778	3.556511	C	-6.163277	-1.342727	0.395719
C	0.707465	9.680072	3.703648	C	-6.311858	-0.079409	-0.210769
C	1.543788	10.00315	2.628284	C	-3.041465	-6.219611	0.509977
C	1.37486	9.384329	1.384717	C	-3.008413	-6.62673	1.855993
C	-1.37486	9.384329	-1.384717	C	-4.382175	-6.853809	2.315332
C	-1.543788	10.00315	-2.628284	C	-5.257493	-6.623002	1.237618
C	-0.707465	9.680072	-3.703648	C	-4.482403	-6.169499	0
C	0.312096	8.736778	-3.556511	C	-4.674195	-7.046793	-1.237618
C	2.565659	6.55967	-2.490187	C	-5.164193	-6.285639	-2.315332
C	3.417478	5.737263	-1.756144	C	-5.372744	-4.908943	-1.855993
C	3.181566	5.446699	-0.395719	C	-4.975337	-4.814571	-0.509977
C	2.025994	5.978395	0.210769	C	-1.874949	-6.027473	-0.210769
C	-6.116392	3.244042	-0.509977	C	-0.627548	-6.27655	0.395719
C	-6.328952	3.592836	-1.855993	C	-0.607481	-6.650287	1.756144
C	-7.573822	2.96907	-2.315332	C	-1.780015	-6.814941	2.490187
C	-8.146304	2.267844	-1.237618	C	-4.882859	-7.251647	3.556511
C	-7.252681	2.356539	0	C	-6.262155	-7.415505	3.703648
C	-7.923504	2.953553	1.237618	C	-7.128654	-7.185302	2.628284
C	-7.872526	2.049752	2.315332	C	-6.628255	-6.783959	1.384717
C	-7.232046	0.813399	1.855993	C	-4.403685	-8.400204	-1.384717
C	-6.855066	0.97064	0.509977	C	-4.630753	-9.000133	-2.628284
C	-5.059725	3.77426	0.210769	C	-5.117452	-8.247181	-3.703648
C	-4.196961	4.708972	-0.395719	C	-5.38784	-6.884757	-3.556511
C	-4.400403	5.023127	-1.756144	C	-5.931339	-3.798828	-2.490187
C	-5.445784	4.467136	-2.490187	C	-6.137077	-2.6328	-1.756144
C	-8.212727	2.996634	-3.556511	C	-5.775431	-2.536395	-0.395719
C	-9.424915	2.318467	-3.703648	C	-5.153076	-3.645774	0.210769
C	-9.990617	1.622914	-2.628284	C	3.041465	-6.219611	-0.509977
C	-9.349882	1.592348	-1.384717	C	3.008413	-6.62673	-1.855993
C	-8.500172	4.207487	1.384717	C	4.382175	-6.853809	-2.315332
C	-9.036504	4.559372	2.628284	C	5.257493	-6.623002	-1.237618
C	-8.987677	3.664146	3.703648	C	4.482403	-6.169499	0

C	4.674195	-7.046793	1.237618	C	4.196961	4.708972	0.395719
C	5.164193	-6.285639	2.315332	C	5.059725	3.77426	-0.210769
C	5.372744	-4.908943	1.855993	C	6.311858	-0.079409	0.210769
C	4.975337	-4.814571	0.509977	C	6.163277	-1.342727	-0.395719
C	1.874949	-6.027473	0.210769	C	6.512521	-1.477303	-1.756144
C	0.627548	-6.27655	-0.395719	C	7.031449	-0.413037	-2.490187
C	0.607481	-6.650287	-1.756144	C	8.405613	2.402992	-3.556511
C	1.780015	-6.814941	-2.490187	C	8.987677	3.664146	-3.703648
C	4.882859	-7.251647	-3.556511	C	9.036504	4.559372	-2.628284
C	6.262155	-7.415505	-3.703648	C	8.500172	4.207487	-1.384717
C	7.128654	-7.185302	-2.628284	H	-1.798344	5.759425	-1.249174
C	6.628255	-6.783959	-1.384717	H	-4.318325	5.361491	2.229915
C	4.403685	-8.400204	1.384717	H	-2.79204	6.791466	3.527027
C	4.630753	-9.000133	2.628284	H	-0.959617	8.487886	4.392479
C	5.117452	-8.247181	3.703648	H	0.853573	10.16842	4.662754
C	5.38784	-6.884757	3.556511	H	2.330958	10.73943	2.760899
C	5.931339	-3.798828	2.490187	H	2.02383	9.626811	0.548259
C	6.137077	-2.6328	1.756144	H	-2.02383	9.626811	-0.548259
C	5.775431	-2.536395	0.395719	H	-2.330958	10.73943	-2.760899
C	5.153076	-3.645774	-0.210769	H	-0.853573	10.16842	-4.662754
C	8.146304	2.267844	1.237618	H	0.959617	8.487886	-4.392479
C	7.573822	2.96907	2.315332	H	2.79204	6.791466	-3.527027
C	6.328952	3.592836	1.855993	H	4.318325	5.361491	-2.229915
C	6.116392	3.244042	0.509977	H	1.798344	5.759425	1.249174
C	7.252681	2.356539	0	H	-4.92182	3.490087	1.249174
C	6.855066	0.97064	-0.509977	H	-3.764645	5.763763	-2.229915
C	7.232046	0.813399	-1.855993	H	-5.596281	4.754066	-3.527027
C	7.872526	2.049752	-2.315332	H	-7.775921	3.535551	-4.392479
C	7.923504	2.953553	-1.237618	H	-9.934506	2.330417	-4.662754
C	9.349882	1.592348	1.384717	H	-10.93411	1.101794	-2.760899
C	9.990617	1.622914	2.628284	H	-9.78104	1.050071	-0.548259
C	9.424915	2.318467	3.703648	H	-8.530244	4.899625	0.548259
C	8.212727	2.996634	3.556511	H	-9.493499	5.535539	2.760899
C	5.445784	4.467136	2.490187	H	-9.406969	3.954009	4.662754
C	4.400403	5.023127	1.756144	H	-8.368997	1.710251	4.392479

H	-7.321856	-0.556709	3.527027
H	-6.433517	-2.450179	2.229915
H	-6.033257	0.069433	-1.249174
H	-1.930414	-5.716513	-1.249174
H	0.342193	-6.875785	2.229915
H	-1.733116	-7.135531	3.527027
H	-4.212707	-7.430893	4.392479
H	-6.6674	-7.724703	4.662754
H	-8.198263	-7.318278	2.760899
H	-7.295811	-6.598676	0.548259
H	-4.021184	-8.977832	-0.548259
H	-4.426694	-10.05848	-2.760899
H	-5.286289	-8.728138	-4.662754
H	-5.765401	-6.302795	-4.392479
H	-6.250731	-3.853292	-3.527027
H	-6.645004	-1.79929	-2.229915
H	-4.840196	-3.602432	1.249174
H	1.930414	-5.716513	1.249174
H	-0.342193	-6.875785	-2.229915
H	1.733116	-7.135531	-3.527027
H	4.212707	-7.430893	-4.392479
H	6.6674	-7.724703	-4.662754
H	8.198263	-7.318278	-2.760899
H	7.295811	-6.598676	-0.548259
H	4.021184	-8.977832	0.548259
H	4.426694	-10.05848	2.760899
H	5.286289	-8.728138	4.662754
H	5.765401	-6.302795	4.392479
H	6.250731	-3.853292	3.527027
H	6.645004	-1.79929	2.229915
H	4.840196	-3.602432	-1.249174
H	9.78104	1.050071	0.548259
H	10.93411	1.101794	2.760899
H	9.934506	2.330417	4.662754
H	7.775921	3.535551	4.392479
H	5.596281	4.754066	3.527027
H	3.764645	5.763763	2.229915
H	4.92182	3.490087	-1.249174
H	6.033257	0.069433	1.249174
H	6.433517	-2.450179	-2.229915
H	7.321856	-0.556709	-3.527027
H	8.368997	1.710251	-4.392479
H	9.406969	3.954009	-4.662754
H	9.493499	5.535539	-2.760899
H	8.530244	4.899625	-0.548259