BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Electrosynthetic access to unsymmetrical oxaza[8]helicenes with high chiral stability and strong circularly polarized luminescence (CPL)

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Experimental procedures, synthetic details, NMR spectra, chiral HPLC chromatograms, DFT and TD-DFT calculations

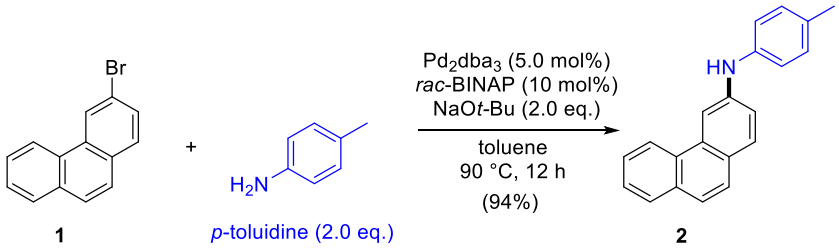
Contents

1. Materials and methods (synthetic procedures and spectra)

1.1. General experimental details

^{1}H-, and ^{13}C NMR spectra were recorded with JEOL JMN ECS 400 FT NMR or Bruker AVANCE II (^{1}H NMR 400 MHz, 600 MHz, and 700 MHz ^{13}C NMR 101 MHz, 151 MHz, or 176 MHz). ^{1}H NMR spectra are reported as follows: the chemical shift in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peak ($CDCl_3$) at 7.26 ppm, multiplicities (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were reported in ppm relative to the central line of triplet for $CDCl_3$ at 77.16 ppm. APCI−MS spectra were obtained with JMS−T100LC (JEOL). FT-IR spectra were recorded on a JASCO FT−IR system (FT/IR4100). UV–Vis absorption spectra were obtained on a JASCO V−670 spectrophotometers. CD spectra were recorded on a JASCO J−1500 spectropolarimeter. Emission spectra and CPL spectra were obtained at room temperature using a JASCO CPL − 300 spectrofluoropolarimeter (Tokyo, Japan). The absolute PL quantum yields were measured using an Absolute PL Quantum Yield Measurement System (C9920–02, Hamamatsu Photonics [Hamamatsu, Japan]) in the air at room temperature. All simple chemicals and solvents were purchased from commercial suppliers and used without further purification.

*1.2. General procedure for the synthesis of N-(p-tolyl)phenanthren-3-amine **2***



A toluene solution (30 mL) of **1**, *p*-toluidine (2.0 equiv), $Pd_2(dba)_3$ (5.0 mol %), BINAP (10 mol %), and NaO*t*-Bu (2.0 equiv) was stirred at 90 °C under N_2 atmosphere. After stirring for 12 h, the reaction mixture was filtered and the filtrate was directly purified on silica-gel to give **2** as a yellowish white solid (94% yield).

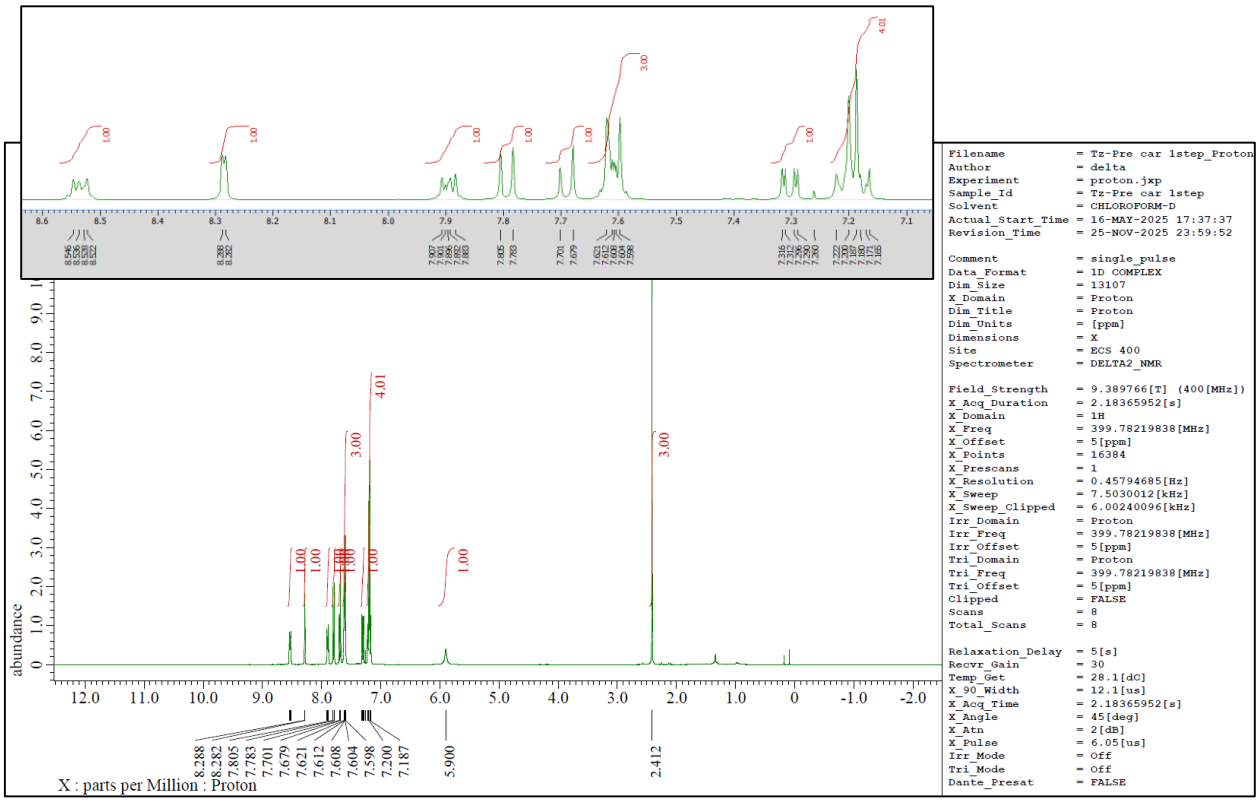
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.52-8.55 (m, 1H), 8.28 (d, *J* = 2.3 Hz, 1H), 7.88-7.91 (m, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 1H), 7.60-7.62 (m, 3H), 7.30 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.16-7.22 (m, 4H), 5.90 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 142.78, 140.30, 132.71, 131.78, 131.50, 130.16, 129.83, 129.72, 128.62, 126.77, 126.71, 126.64, 126.10, 124.17, 122.85, 119.30, 118.50, 107.96, 20.89.

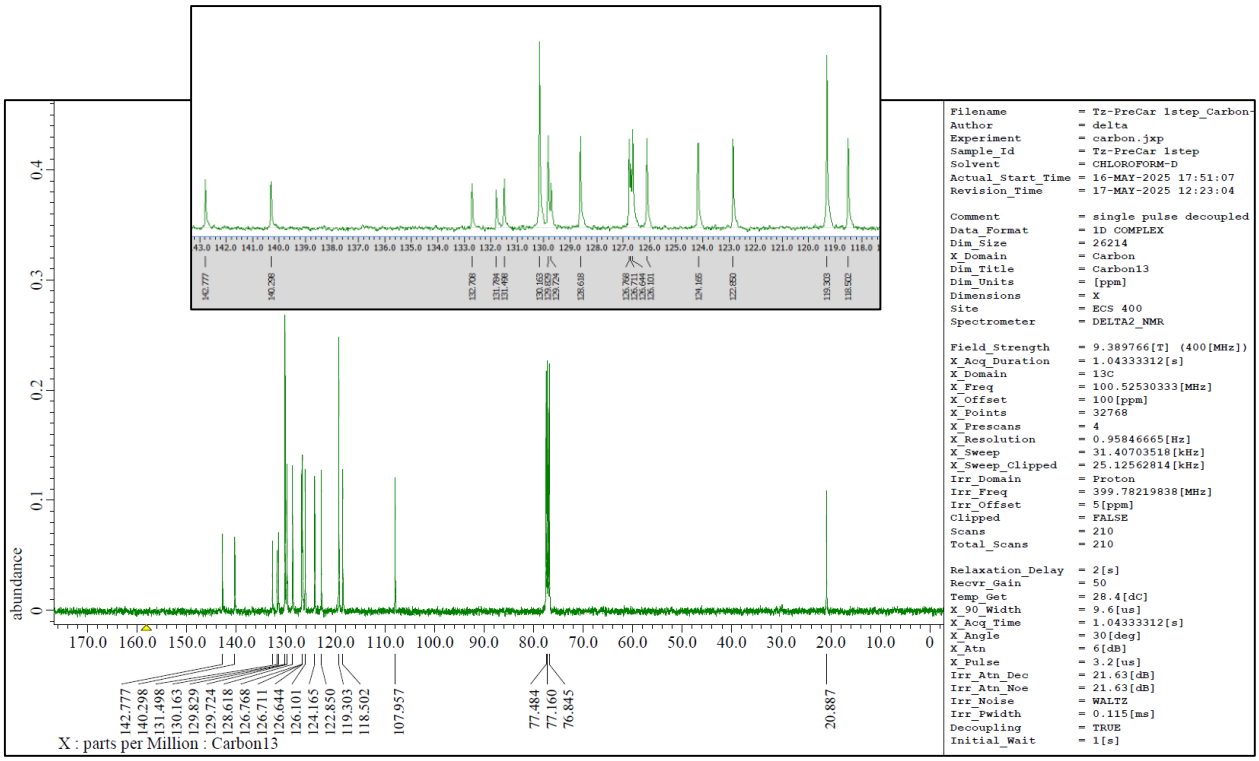
HRMS (APCI): calcd for $C_{21}H_{18}N^{+}$: m/z 284.1434 [M + H]+, found 284.1430.

IR (KBr): 3399, 3033, 2913, 1614, 1518, 1324, 809, 751 cm^{-1}.

m.p.: 121 – 122 °C.

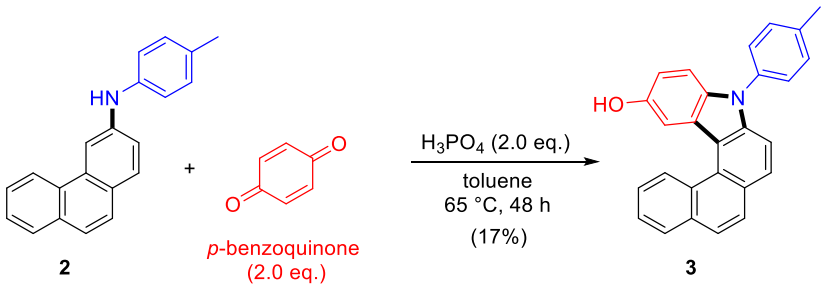


2 (^{1}H NMR, 400 MHz, $CDCl_3$).



2 (^{13}C NMR, 101 MHz, $CDCl_3$).

1.3. General procedure for the synthesis of 9-(p-tolyl)-9H-naphtho[2,1-c]carbazol-12-ol ***3***



To a solution of **2** and *p*−benzoquinone (2.0 equiv) in dry toluene (25 mL), *ortho*-phosphoric acid (2.0 equiv) dissolved in (25 mL) toluene was added dropwise. The reaction mixture was stirred at 65 °C for 48 h under N_2 atmosphere until its completion. Next, the reaction was quenched via water, extracted with EtOAc and the combined organic extracts dried over Na_2SO_4, and evaporated in vacuo. The crude mixture was purified on silica column chromatography (eluent: *n*−hexane/DCM/ethyl acetate) to give double **3** as a white solid in 17% yield.

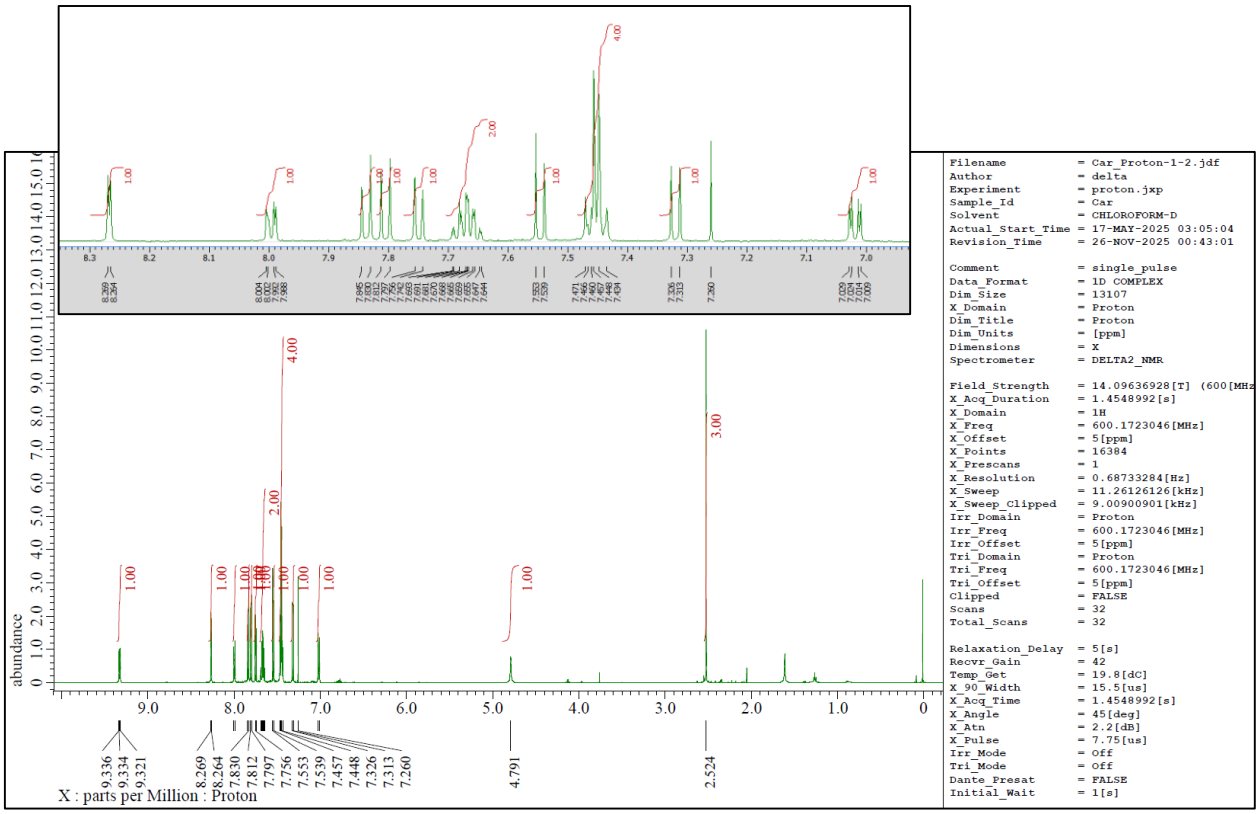
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.32-9.34 (m, 1H), 8.27 (d, *J* = 2.7 Hz, 1H), 8.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.64-7.69 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.43-7.47 (m, 4H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.7 Hz, 1H), 4.79 (s, 1H), 2.52 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.72, 141.90, 138.14, 136.59, 134.93, 133.30, 130.72, 129.56, 128.04, 127.95, 127.91, 127.63, 127.60, 127.40, 126.67, 124.68, 124.39, 124.21, 116.62, 114.52, 111.46, 111.13, 108.95, 21.43 (One carbon overlapped).

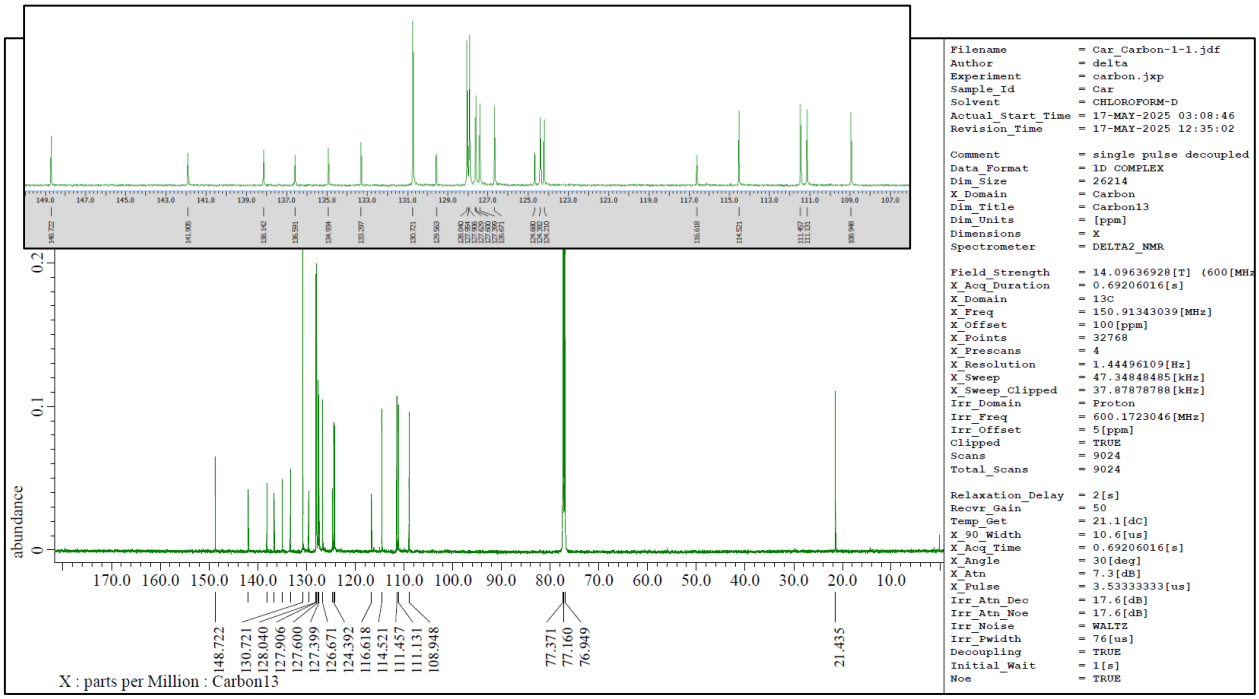
HRMS (APCI): calcd for $C_{27}H_{20}NO^+$: m/z 374.1539 [M + H]+, found 374.1538.

IR (KBr): 3331, 3040, 2922, 1512, 1449, 1342, 1196, 830 cm^{-1}.

mp: 210 – 211 °C.

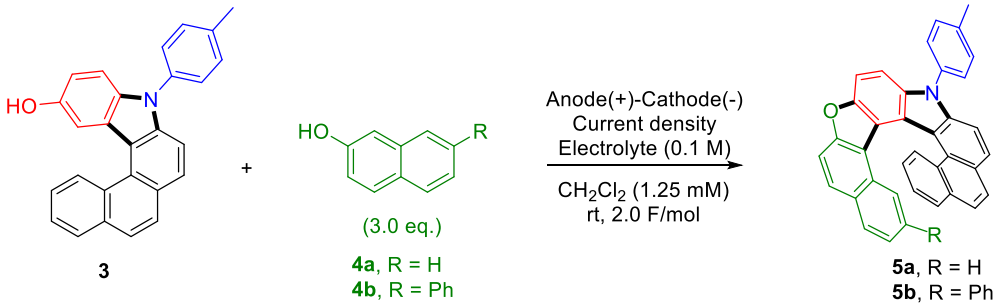


3 (^{1}H NMR, 600 MHz, $CDCl_3$).



3 (^{13}C NMR, 151 MHz, $CDCl_3$).

1.4. General procedure for the synthesis of 9-(p-tolyl)-9H-naphtho[2,1-c]carbazol-12-ol ***3***



				Yield %	
Anode(+)	**Cathode(-)**	**Bu_4NPF_6 (0.1 M)**	**Current density**	**5a**	**5b**
Pt	Pt	Bu_4NPF_6 (0.1 M)	J = 0.75 mA/cm^2	33%	17%
Pt	C	Bu_4NPF_6 (0.1 M)	J = 0.75 mA/cm^2	47%	35%
Pt	C	$LiClO_4$ (0.01 M)	J = 0.75 mA/cm^2	61%	<5%
Pt	C	Bu_4NPF_6 (0.01 M)	J = 0.5 mA/cm^2	55%	<5%
Pt	C	Bu_4NPF_6 (0.1 M)	J = 0.25 mA/cm^2	66%	41%
Pt	C	Bu_4NPF_6 (0.1 M)	J = 0.5 mA/cm^2	62%	45%
Pt	C	Bu_4NPF_6 (0.1 M)	J = 1.0 mA/cm^2	58%	21%

A 20 mL DCM solution of **3** (0.025 mmol), β-naphthol (0.075 mmol), and *n*-tetrabutylammonium hexafluorophosphate(V) (2.0 mmol) was transferred into an undivided electrolysis cell. This cell is equipped with one Pt anode and one carbon cathode connected to a DC power supply. At room temperature, a constant current of 2.0 mA was applied. After the completion of reaction, the electrolysis was stopped and crude mixture was purified by column chromatography (SiO_2, EtOAc/*n*-hexane) to afford oxaza[8]helicenes **5** as a yellow solid.

10-(p-Tolyl)-10H-naphtho[2,1-c]naphtho[1',2':4,5]furo[3,2-g]carbazole ***5a***

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 9.2 Hz, 1H), 7.79-7.80 (m, 2H), 7.73 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.57-7.60 (m, 4H), 7.49-7.53 (m, 4H), 6.95-6.99 (m, 1H), 6.86-6.90 (m, 1H), 6.36-6.41 (m, 2H), 2.57 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 153.69, 151.96, 140.90, 138.56, 138.50, 134.81, 132.13, 131.95, 130.86, 130.37, 129.39, 128.35, 128.21, 127.41, 127.36, 127.06, 127.02, 126.82, 126.79, 126.66, 125.84, 124.65, 124.08, 124.02, 123.31, 121.17, 119.02, 117.03, 116.66, 111.93, 110.77, 109.82, 108.94, 21.53 (One carbon overlapped).

HRMS (APCI): calcd for $C_{37}H_{24}NO^+$: m/z 498.1852 [M + H]+, found 498.1856.

IR (KBr): 3021, 2935, 1758, 1630, 1367, 1207, 899, 601 cm^{-1}.

mp: 241 – 242 °C.

2-Phenyl-10-(p-tolyl)-10H-naphtho[2,1-c]naphtho[1',2':4,5]furo[3,2-g]carbazole ***5b***

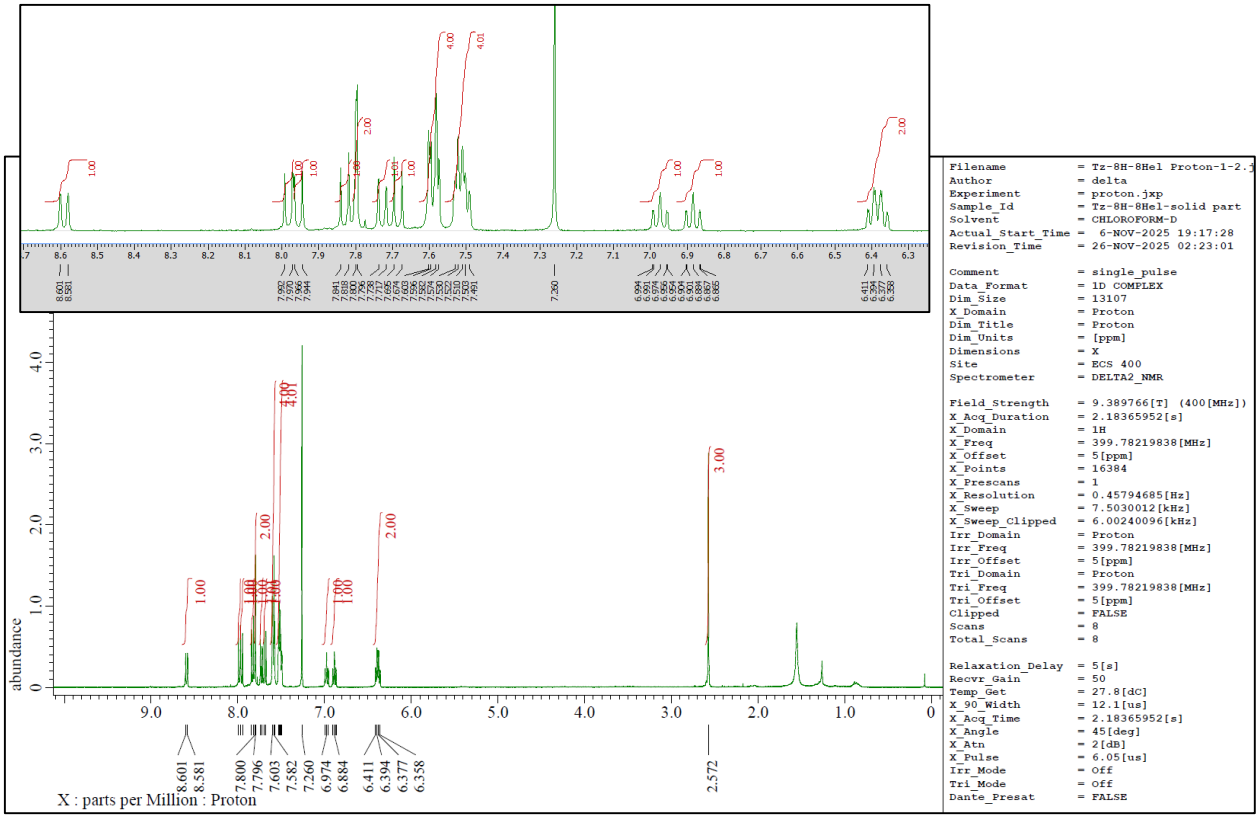
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 1.7 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 1H), 7.52-7.67 (m, 7H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.24-7.26 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.88 (t, *J* = 6.9 Hz, 1H), 6.82-6.83 (m, 2H), 6.40-6.43 (m, 1H), 2.57 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.04, 152.04, 140.83, 140.49, 138.65, 138.59, 136.61, 134.87, 131.74, 131.54, 130.92, 130.86, 128.61, 128.46, 128.26, 128.05, 127.86, 127.80, 127.47, 127.42, 127.18, 127.13, 126.81, 126.61, 125.71, 125.57, 125.55, 124.76, 123.73, 122.55, 121.79, 119.14, 117.21, 116.81, 111.98, 110.80, 109.79, 109.07, 21.52.

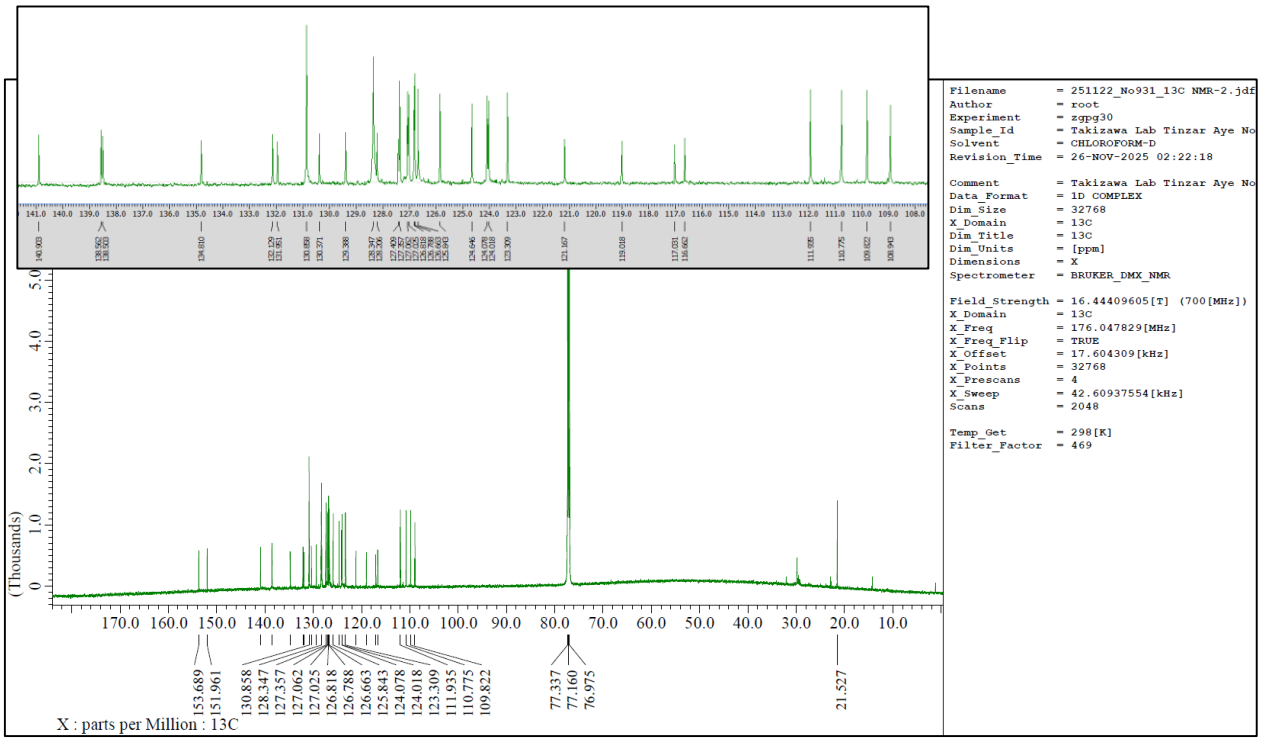
HRMS (APCI): calcd for $C_{43}H_{28}NO^{+}$: m/z 574.2165 [M + H]+, found 574.2163.

IR (KBr): 2953, 2927, 1658, 1581, 1514, 1084, 795, 753 cm^{-1}.

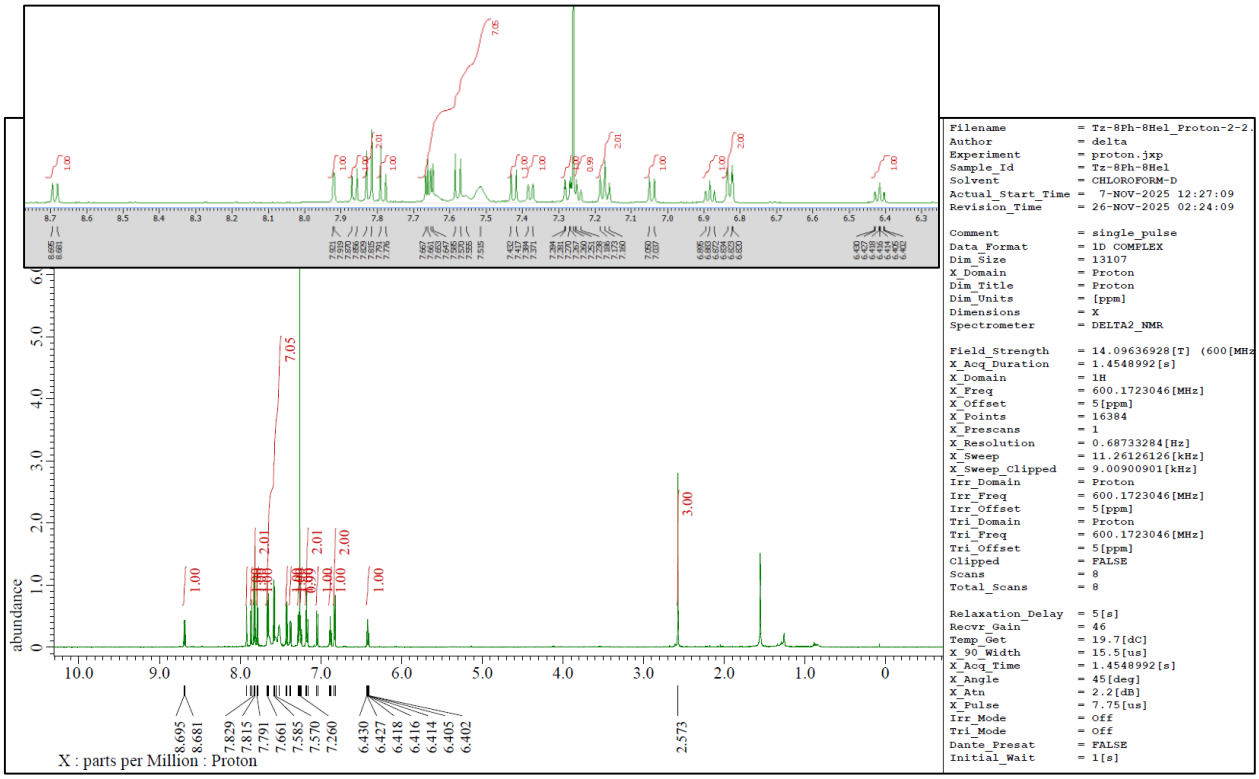
mp: >300 °C.



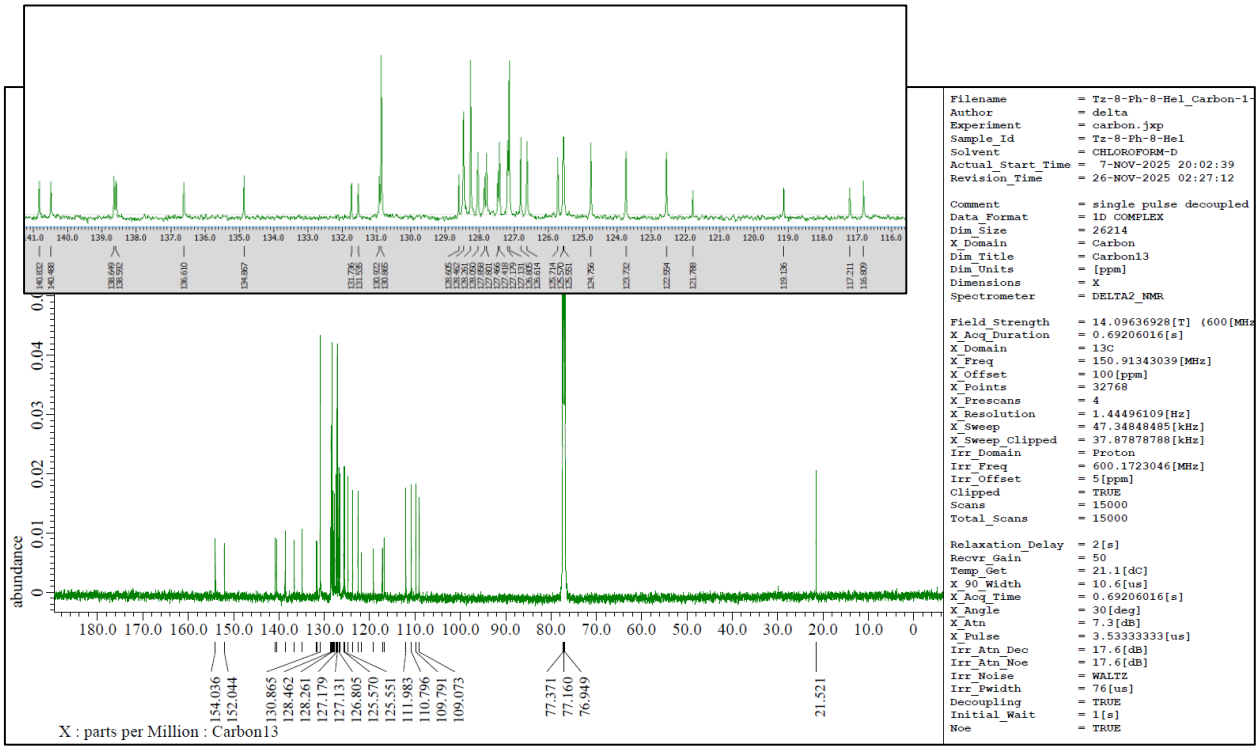
5a (^{1}H NMR, 400 MHz, $CDCl_3$).



5a (^{13}C NMR, 176 MHz, $CDCl_3$).

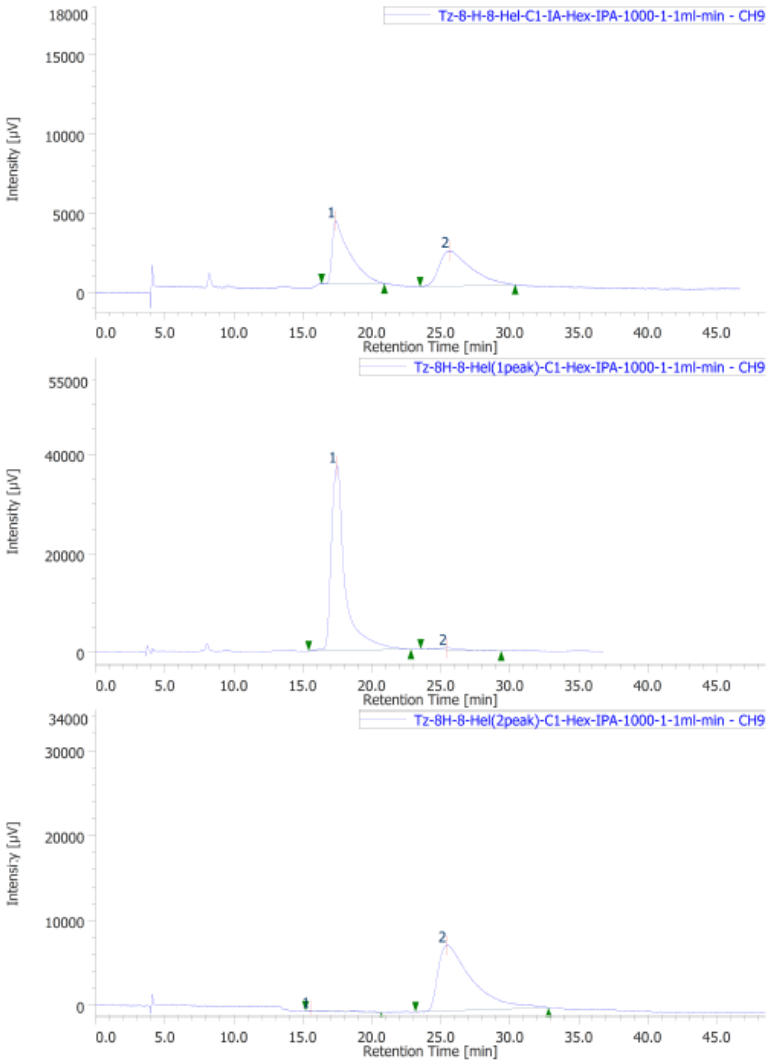


5b (^{1}H NMR, 600 MHz, $CDCl_3$).



5b (^{13}C NMR, 151 MHz, $CDCl_3$).

*2. HPLC Chiral resolution of compounds **5a,b** & **6a,b***



Channel & Peak Information Table

Chromatogram Name: Tz-8-H-8-Hel-C1-IA-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 295.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	17.380	348154	3985	49.707	63.990	N/A	1100	2.686	3.369	
2	Unknown	9	25.647	352259	2243	50.293	36.010	N/A	634	N/A	1.723	

Chromatogram Name: Tz-8H-8-Hel(1peak)-C1-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 295.0nm

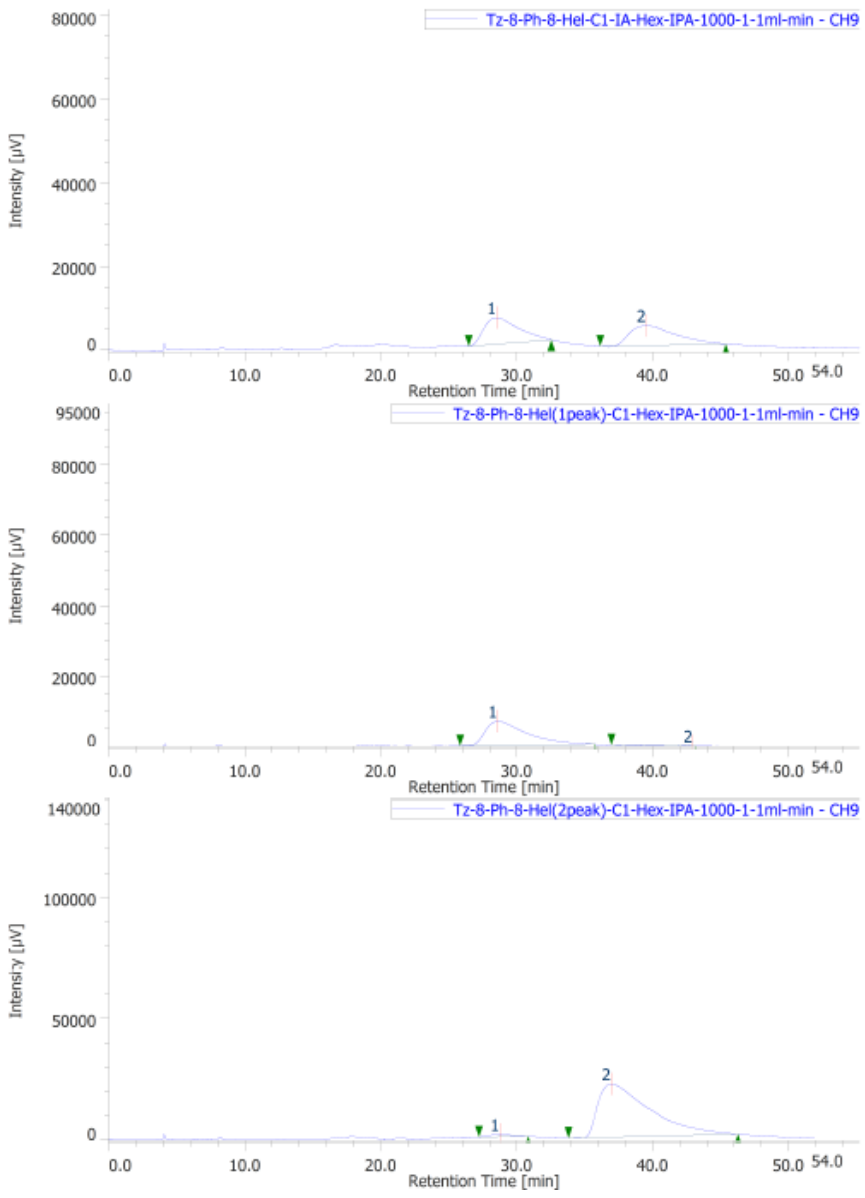
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	17.487	2589978	37306	98.511	99.052	N/A	2237	3.535	2.117	
2	Unknown	9	25.467	39148	357	1.489	0.948	N/A	1117	N/A	1.682	

Chromatogram Name: Tz-8H-8-Hel(2peak)-C1-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 295.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	15.547	3549	17	0.270	0.220	N/A	48	1.515	11.192	
2	Unknown	9	25.427	1310048	7710	99.730	99.780	N/A	611	N/A	3.006	

HPLC (Chiral analytical IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 1.0 mL/min, λ = 295 nm, t_1 (*P*)-**5a** = 17.3 min, t_2 (*M*)-**5a** = 25.6 min.

HPLC (Chiral semi-preparative IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 5.0 mL/min, λ = 295 nm, t_1 (*P*)-**5a** = 69.2 min, t_2 (*M*)-**5a** = 98.3 min.



Channel & Peak Information Table

Chromatogram Name: Tz-8-Ph-8-Hel-C1-IA-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 270.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	28.513	1107975	6302	50.155	57.175	N/A	575	2.007	1.587	
2	Unknown	9	39.527	1101115	4720	49.845	42.825	N/A	640	N/A	1.721	

Chromatogram Name: Tz-8-Ph-8-Hel(1peak)-C1-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 270.0nm

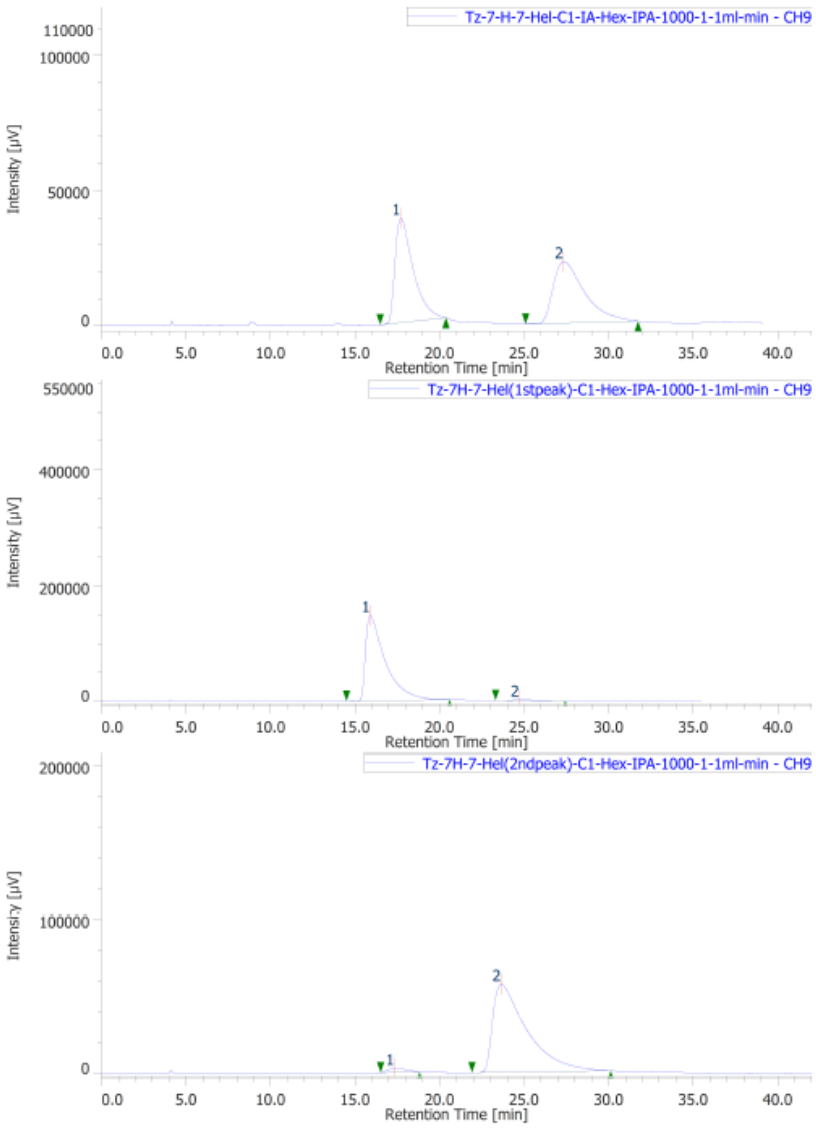
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	28.593	1465719	6915	98.841	99.817	N/A	462	1.851	2.205	
2	Unknown	9	42.967	17194	13	1.159	0.183	N/A	281	N/A	0.516	

Chromatogram Name: Tz-8-Ph-8-Hel(2peak)-C1-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 270.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	28.743	107931	863	1.833	3.800	N/A	988	1.570	1.181	
2	Unknown	9	36.953	5779217	21838	98.167	96.200	N/A	469	N/A	2.805	

HPLC (Chiral analytical IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 1.0 mL/min, λ = 270 nm, t_1 (*P*)-**5b** = 28.5 min, t_2 (*M*)-**5b** = 39.5 min.

HPLC (Chiral semi-preparative IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 5.0 mL/min, λ = 270 nm, t_1 (*P*)-**5b** = 98.2 min, t_2 (*M*)-**5b** = 124.2 min.



Channel & Peak Information Table

Chromatogram Name: Tz-7-H-7-Hel-C1-IA-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 270.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	17.703	2874740	38579	49.534	62.985	N/A	1412	3.743	2.027	
2	Unknown	9	27.340	2928772	22672	50.466	37.015	N/A	1113	N/A	1.923	

Chromatogram Name: Tz-7H-7-Hel(1stpeak)-C1-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 270.0nm

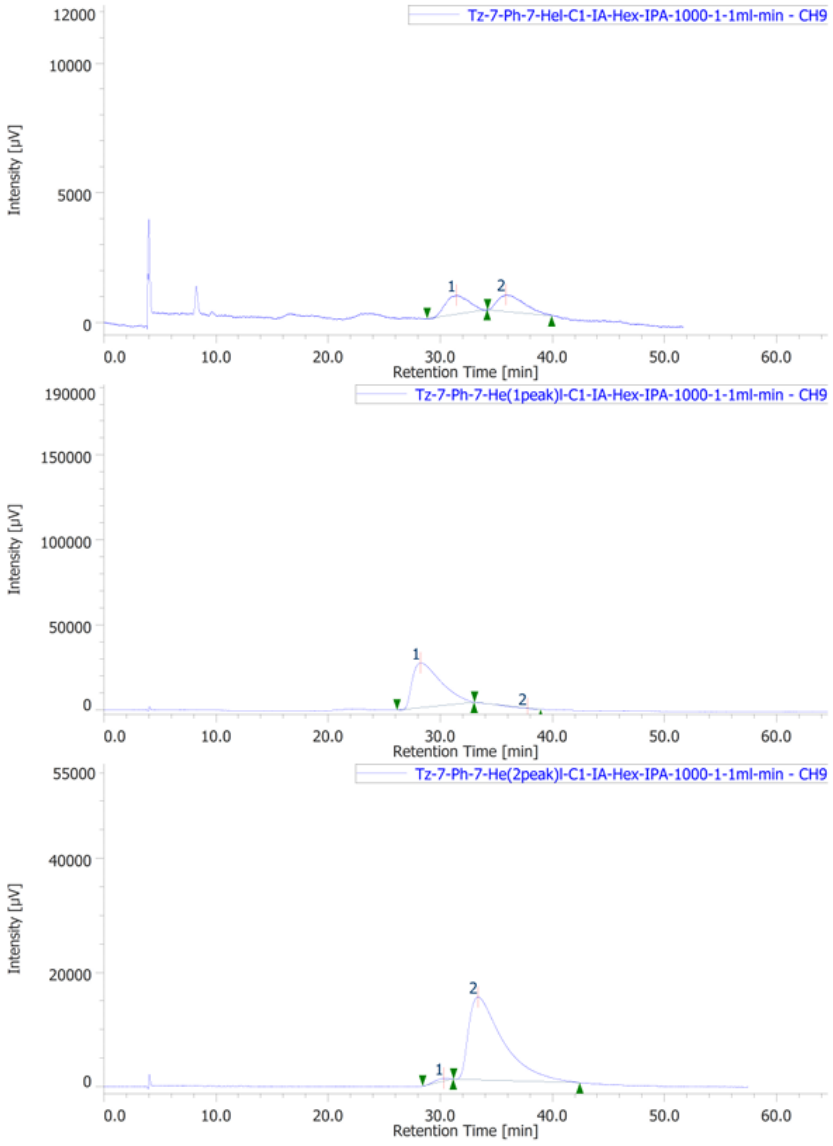
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	15.900	12045906	148389	98.981	99.263	N/A	1086	3.577	3.060	
2	Unknown	9	24.720	124011	1101	1.019	0.737	N/A	1076	N/A	1.613	

Chromatogram Name: Tz-7H-7-Hel(2ndpeak)-C1-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 270.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	17.340	195402	2579	2.376	4.317	N/A	1018	2.257	1.378	
2	Unknown	9	23.643	8029908	57144	97.624	95.683	N/A	762	N/A	2.886	

HPLC (Chiral analytical IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 1.0 mL/min, λ = 270 nm, t_1 (*P*)-**6a** = 17.7 min, t_2 (*M*)-**6a** = 27.3 min.

HPLC (Chiral semi-preparative IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 5.0 mL/min, λ = 270 nm, t_1 (*P*)-**6a** = 59.3 min, t_2 (*M*)-**6a** = 95.1 min.



Channel & Peak Information Table

Chromatogram Name: Tz-7-Ph-7-Hel-C1-IA-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 290.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	31.430	103595	732	49.126	52.802	N/A	935	1.039	1.114	
2	Unknown	9	35.863	107281	654	50.874	47.198	N/A	1042	N/A	1.867	

Chromatogram Name: Tz-7-Ph-7-He(1peak)l-C1-IA-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 290.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	28.270	4621428	26352	98.534	98.731	N/A	572	1.947	2.098	
2	Unknown	9	37.760	68780	339	1.466	1.269	N/A	895	N/A	0.622	

Chromatogram Name: Tz-7-Ph-7-He(2peak)l-C1-IA-Hex-IPA-1000-1-1ml-min-CH9
Sample Name
Channel Name: 290.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	30.333	43238	506	1.380	3.374	N/A	2413	0.793	0.779	
2	Unknown	9	33.377	3090288	14497	98.620	96.626	N/A	652	N/A	2.640	

HPLC (Chiral analytical IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 1.0 mL/min, λ = 290 nm, t_1 (*P*)-**6b** = 31.4 min, t_2 (*M*)-**6b** = 35.8 min.

HPLC (Chiral semi-preparative IA column), *n*-Hexane / iPrOH = 1000/1, Flow rate: 5.0 mL/min, λ = 290 nm, t_1 (*P*)-**6b** = 112.2 min, t_2 (*M*)-**6b** = 131.3 min.

3. *DFT and TD-DFT calculations to study the optoelectronic features*

All DFT calculations were performed using the Gaussian 16 and Gaussian 9 packages of programs. The geometries of the structures of oxaza[7]helicenes **6** and oxaza[8]helicenes **5** were optimized at both the ground S_0 and excited S_1 states, calculated with the MN15/6-311G (2d,p)/SMD=chloroform level of theory. All stationary points were identified as stable minima by frequency calculations, and the geometry optimization was achieved using the standard criteria in Gaussian software. The nucleus-independent chemical shift (NICS) indices were calculated at the center of each ring (NICS($_0$)), 1 Å and 2 Å above/below the center (NICS($_{1,2}$)) within the gauge-independent atomic orbital (GIAO) approximation at MN15/6-311G (2d,p)/SMD=chloroform level of theory and visualized using py.Aroma: an intuitive graphical user interface for diverse aromaticity analyses. For the anisotropy of the induced current density (AICD) simulations, the AICD-3.0.4 software was used. TD-DFT calculations were performed on optimized structures at the lowest energy singlet excited state (S_1).

*3.1. Molecular orbitals of **5** and **6***

Table S1. Selected molecular orbitals of **5a** optimized in the ground state S_0 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

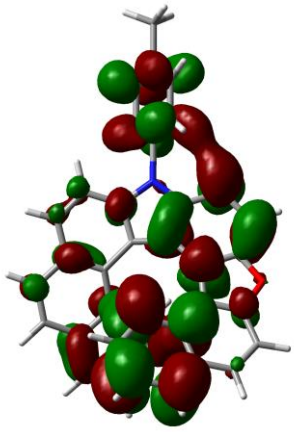
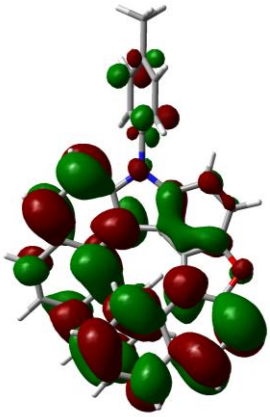
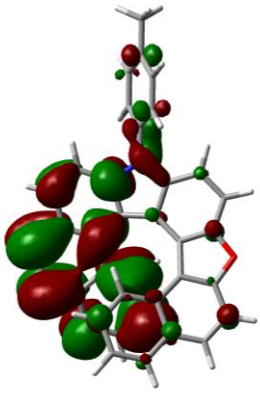
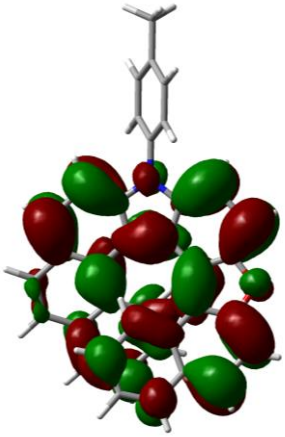
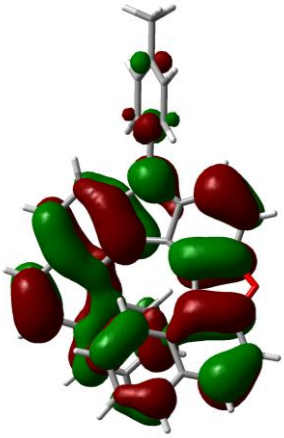
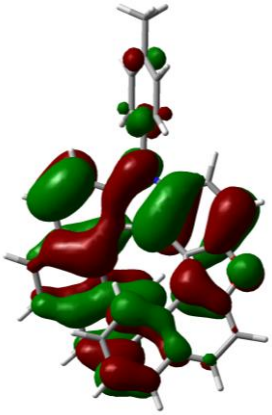
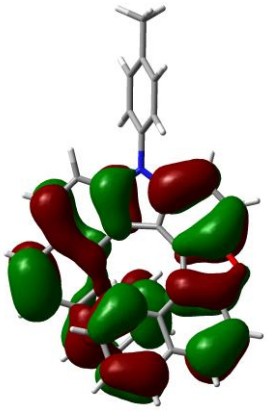
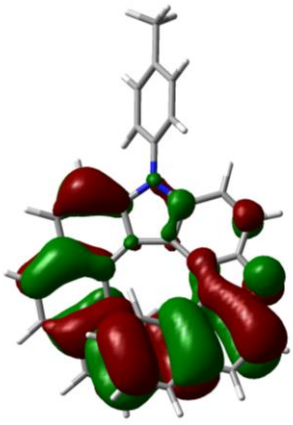
 LUMO+3 (−0.122 eV)	 LUMO+2 (−0.2667 eV)	 LUMO+1 (−0.426 eV)
 LUMO (−1.157 eV)	 HOMO (−5.886 eV)	 HOMO−1 (−6.249 eV)
 HOMO−2 (−6.693 eV)	 HOMO−3 (−7.168 eV)	

Table S2. Selected molecular orbitals of **5a** optimized in the excited state S_1 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

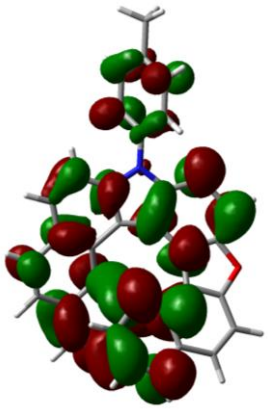
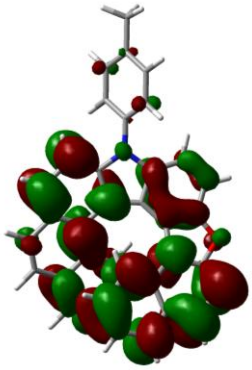
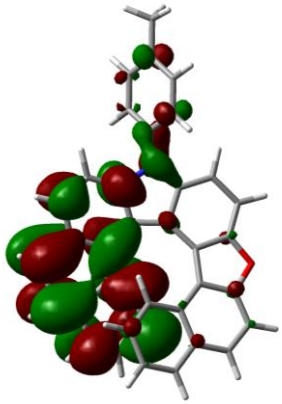
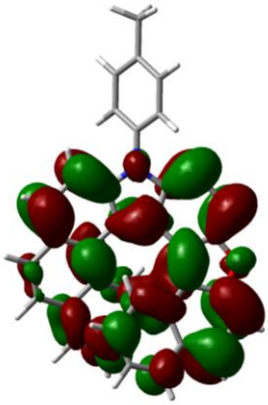
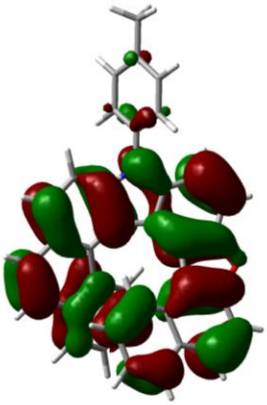
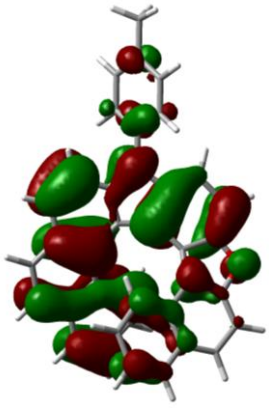
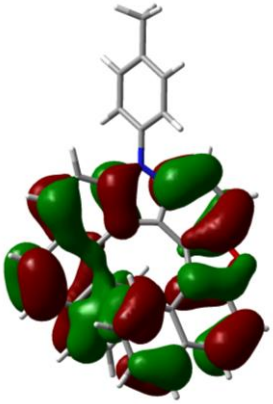
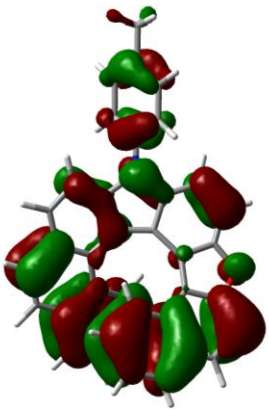
 LUMO+3 (0.069 eV)	 LUMO+2 (−0.336 eV)	 LUMO+1 (−0.477 eV)
 LUMO (−1.437 eV)	 HOMO (−5.662 eV)	 HOMO−1 (−6.238 eV)
 HOMO−2 (−6.676 eV)	 HOMO−3 (−7.131 eV)	

Table S3. Selected molecular orbitals of **5b** optimized in the ground state S_0 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

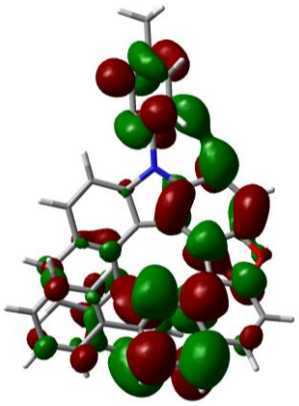
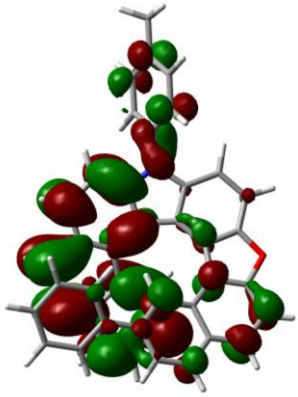
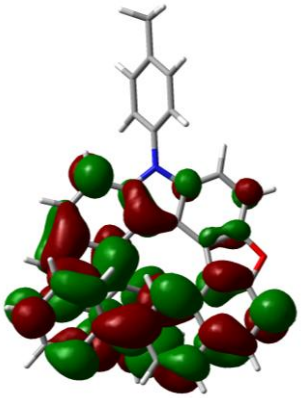
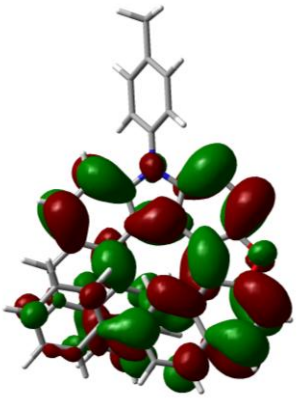
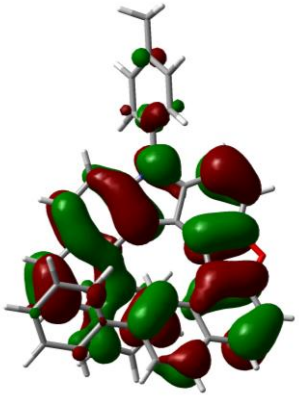
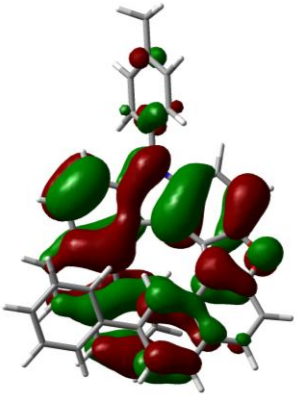
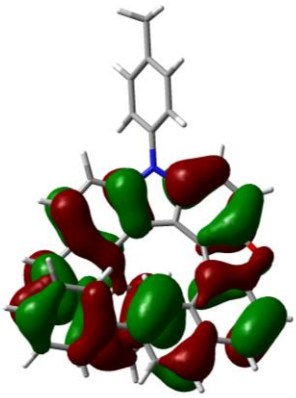
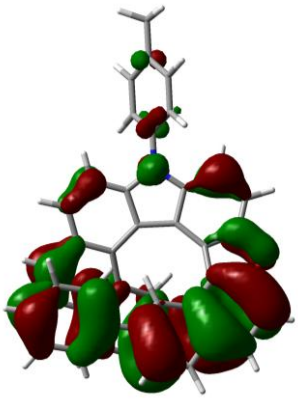
 LUMO+3 (0.071 eV)	 LUMO+2 (−0.366 eV)	 LUMO+1 (−0.526 eV)
 LUMO (−1.204 eV)	 HOMO (−5.858 eV)	 HOMO−1 (−6.243 eV)
 HOMO−2 (−6.606 eV)	 HOMO−3 (−6.961 eV)	

Table S4. Selected molecular orbitals of **5b** optimized in the excited state S_1 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

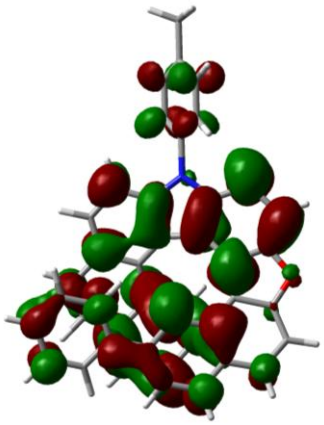
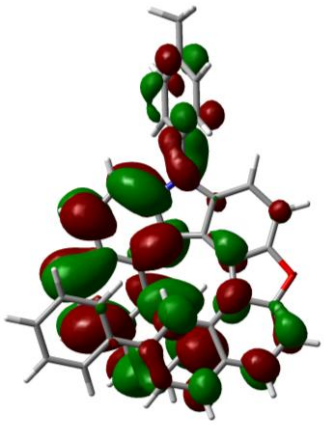
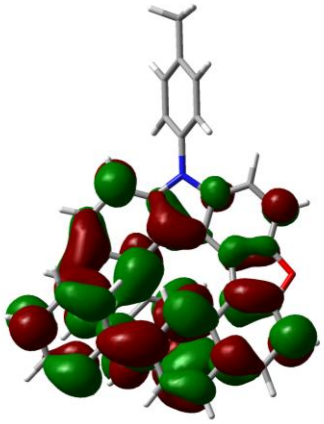
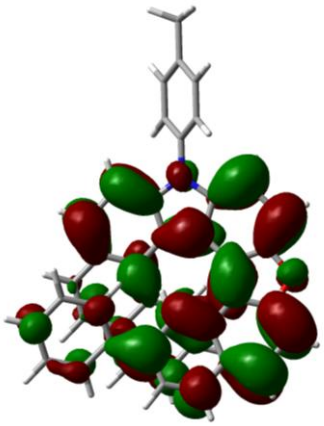
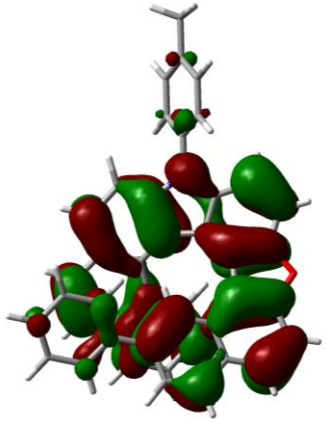
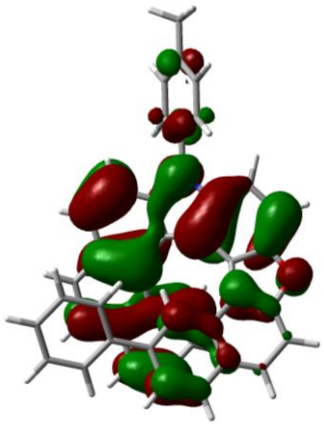
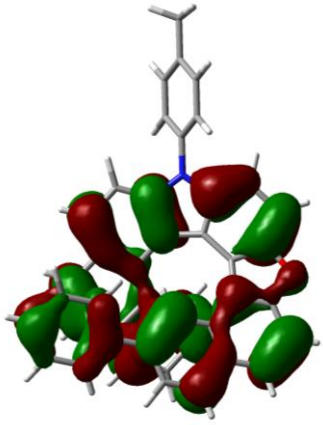
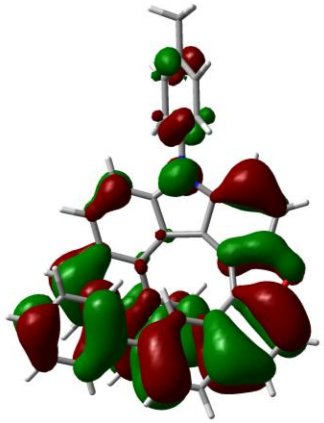
 LUMO+3 (−0.002 eV)	 LUMO+2 (−0.437 eV)	 LUMO+1 (−0.581 eV)
 LUMO (−1.509 eV)	 HOMO (−5.597 eV)	 HOMO−1 (−6.228 eV)
 HOMO−2 (−6.588 eV)	 HOMO−3 (−6.887 eV)	

Table S5. Selected molecular orbitals of **6a** optimized in the ground state S_0 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

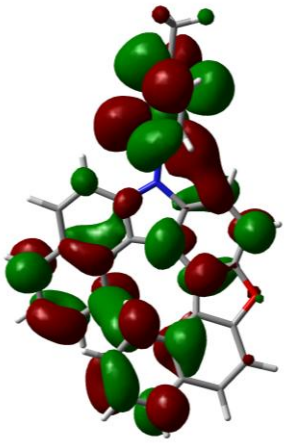
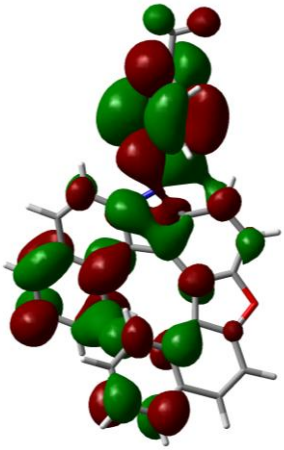
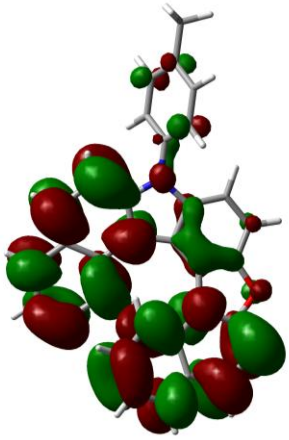
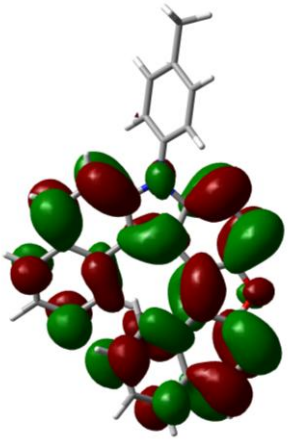
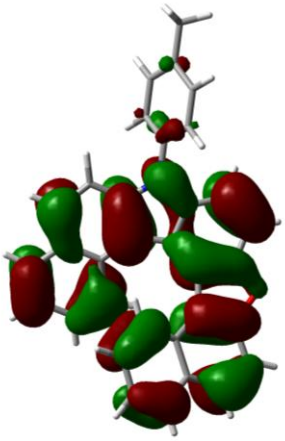
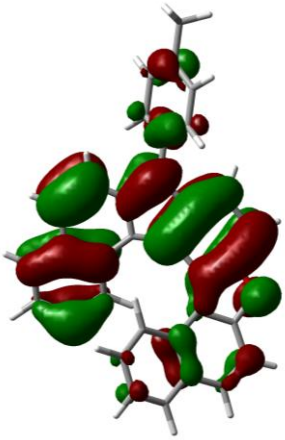
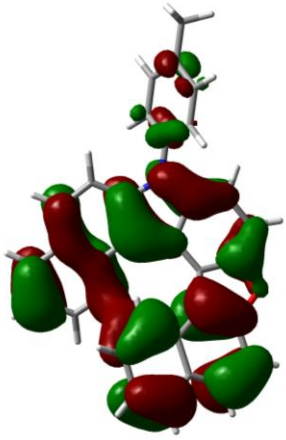
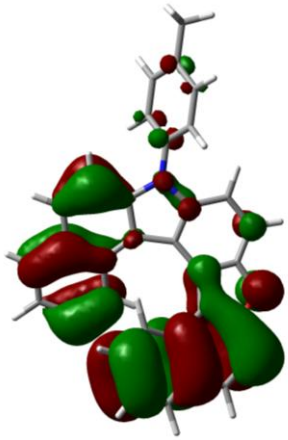
 LUMO+3 (0.122 eV)	 LUMO+2 (0.104 eV)	 LUMO+1 (−0.276 eV)
 LUMO (−1.076 eV)	 HOMO (−5.911 eV)	 HOMO−1 (−6.343 eV)
 HOMO−2 (−6.867 eV)	 HOMO−3 (−7.277 eV)	

Table S6. Selected molecular orbitals of **6a** optimized in the excited state S_1 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

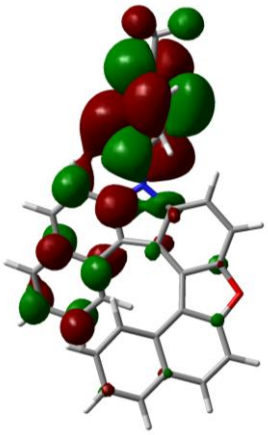
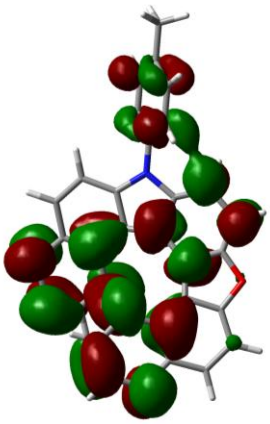
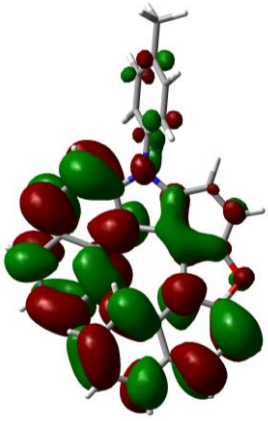
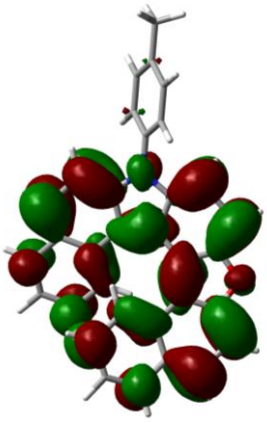
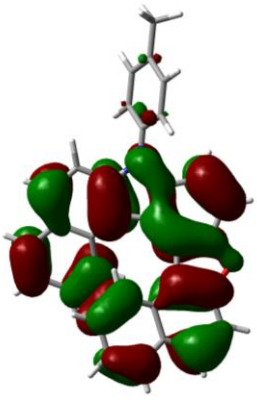
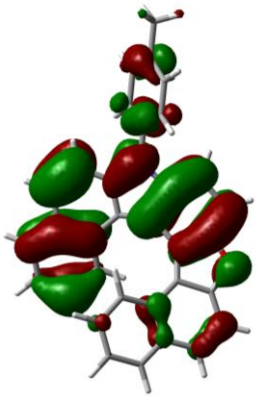
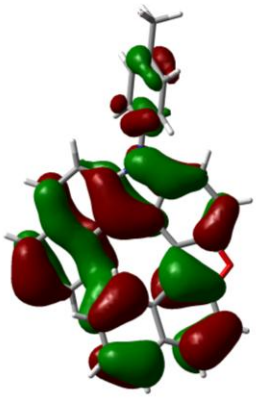
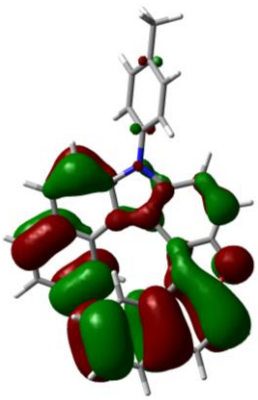
 LUMO+3 (0.111 eV)	 LUMO+2 (0.064 eV)	 LUMO+1 (−0.374 eV)
 LUMO (−1.390 eV)	 HOMO (−5.638 eV)	 HOMO−1 (−6.404 eV)
 HOMO−2 (−6.836 eV)	 HOMO−3 (−7.289 eV)	

Table S7. Selected molecular orbitals of **6b** optimized in the ground state S_0 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

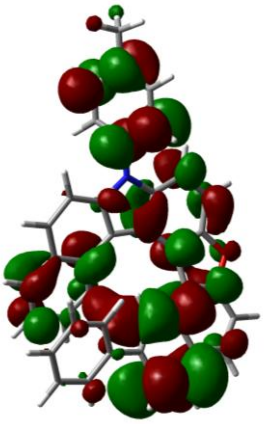
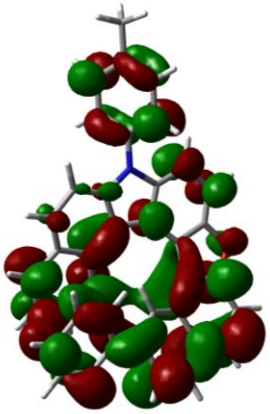
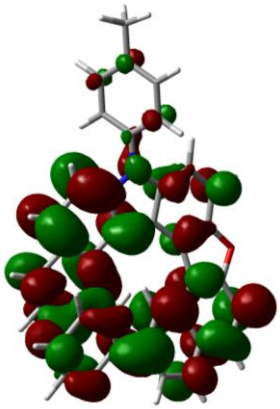
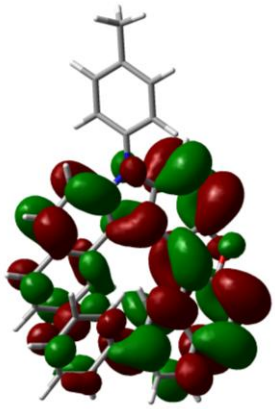
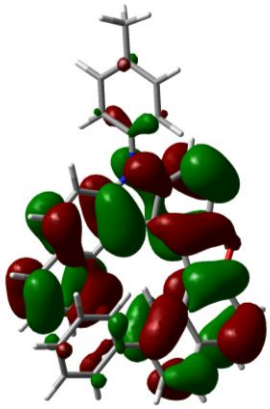
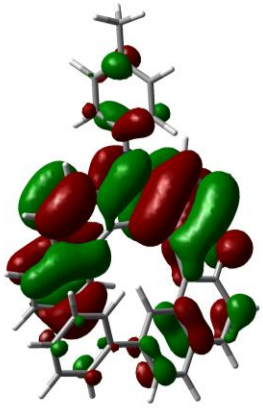
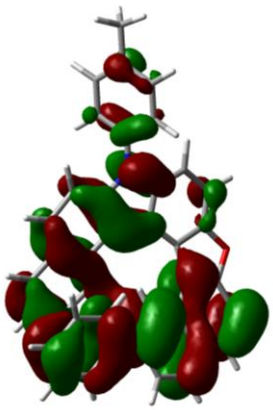
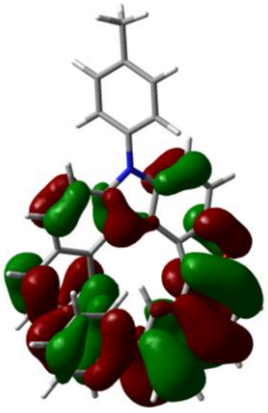
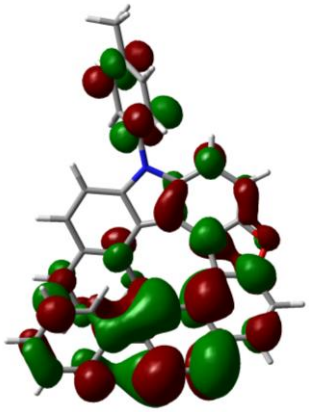
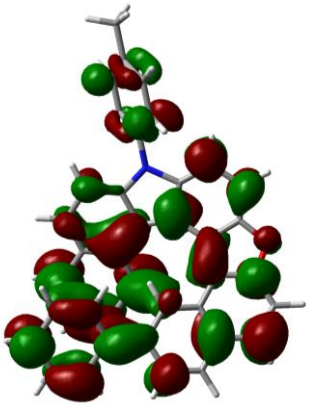
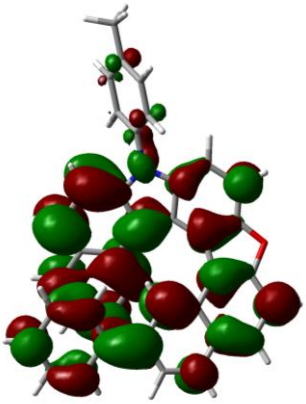
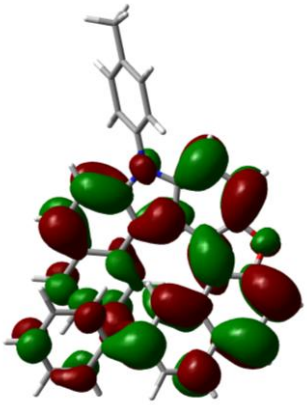
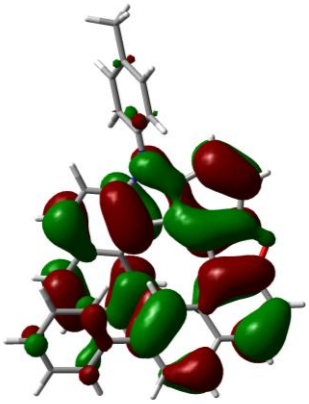
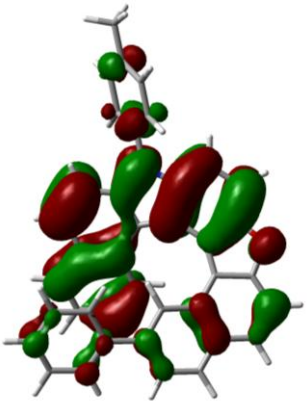
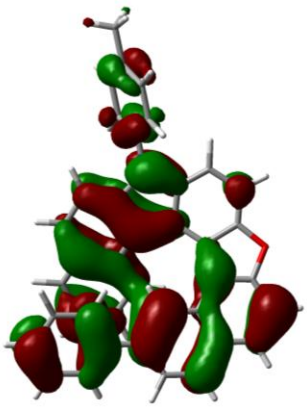
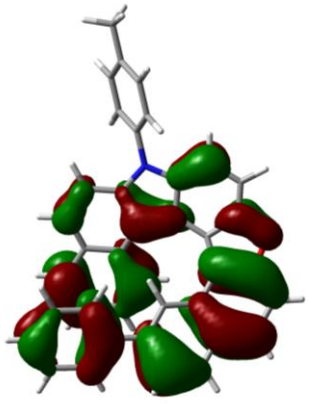
 LUMO+3 (0.060 eV)	 LUMO+2 (0.008 eV)	 LUMO+1 (−0.411 eV)
 LUMO (−1.153 eV)	 HOMO (−5.863 eV)	 HOMO−1 (−6.310 eV)
 HOMO−2 (−6.753 eV)	 HOMO−3 (−7.036 eV)	

Table S8. Selected molecular orbitals of **6b** optimized in the excited state S_1 calculated at MN15/6-311G (2d,p)/SMD=chloroform level of theory (isosurface value = 0.02 a.u.).

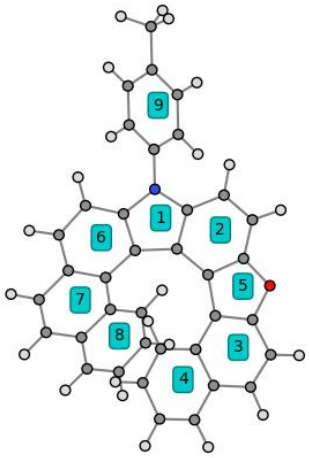
 LUMO+3 (0.033 eV)	 LUMO+2 (−0.086 eV)	 LUMO+1 (−0.528 eV)
 LUMO (−1.497 eV)	 HOMO (−5.594 eV)	 HOMO−1 (−6.362 eV)
 HOMO−2 (−6.710 eV)	 HOMO−3 (−7.035 eV)	

*3.2. Aromaticity of oxaza[8]helicenes **5a** and **5b** and oxaza[7]helicenes **6a** and **6b***

Aromaticity of oxaza[8]helicene **5a**

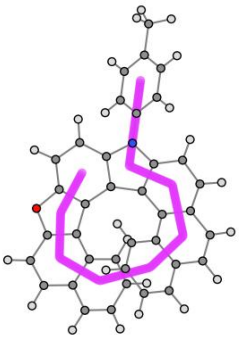
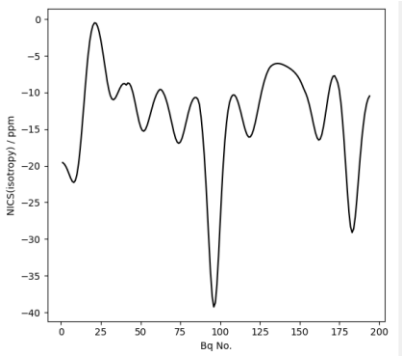
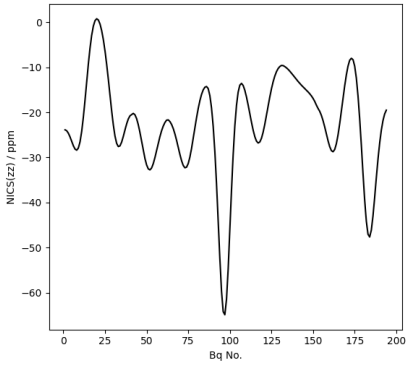
calculated at MN15/6-311G(2d,p)/SMD=chloroform level of theory

NICS(r)iso and NICS(r)zz of oxaza[8]helicene **5a**

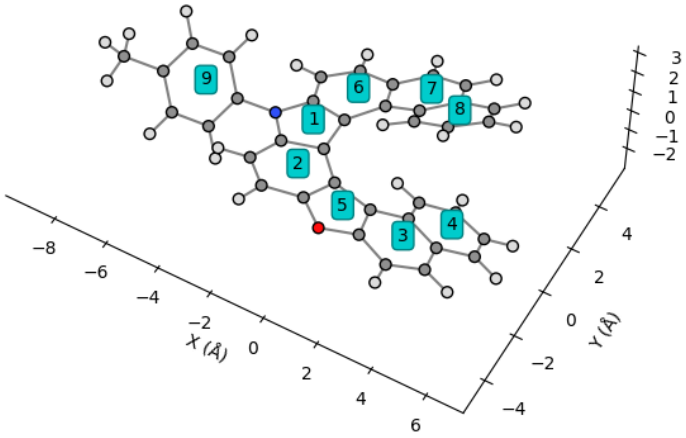


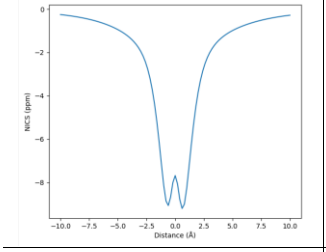
Ring	NICS(0)iso	NICS(0)zz	NICS(1)iso	NICS(1)zz	NICS(−1)iso	NICS(−1)zz	NICS(2)iso	NICS(2)zz	NICS(−2)iso	NICS(−2)zz
1	−7.6807	−3.2454	−8.2843	−21.3718	−8.1334	−20.6912	−3.8317	−13.9206	−3.7174	−13.4315
2	−8.6859	−9.2086	−10.2550	−23.2268	−9.5810	−24.5487	−4.9516	−14.2120	−4.3824	−15.9015
3	−7.7115	−6.2145	−10.8719	−19.3004	−9.0484	−17.5548	−5.8426	−12.7225	−4.2442	−9.2955
4	−8.7492	−13.7272	−12.4878	−26.9720	−11.9342	−21.8963	−6.5154	−17.2658	−8.5893	−15.4612
5	−6.3502	−6.5185	−8.0473	−14.7666	−6.1080	−13.4278	−4.2697	−10.0887	−2.4383	−9.4424
6	−6.9549	−6.9685	−9.3902	−23.4066	−9.9421	−21.4734	−4.5981	−15.5899	−5.0755	−13.3815
7	−4.2867	−0.3153	−6.8485	−12.4373	−9.2251	−15.5489	−3.0189	−6.7323	−5.4520	−11.3380
8	−8.7096	−13.5232	−11.8980	−21.1693	−12.6577	−26.1373	−10.4494	−20.4188	−6.5215	−16.2742
9	−6.6370	−4.3897	−9.1430	−10.4015	−9.0805	−10.1881	−3.9091	−4.3879	−3.8920	−4.1956

NICS-XY-Scan of oxaza[8]helicene **5a**

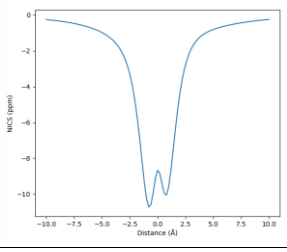
Path of NICS-XY-Scan	NICS(iso)-XY-Scan	NICS(zz)-XY-Scan
		

Integral NICS of oxaza[8]helicene **5a**

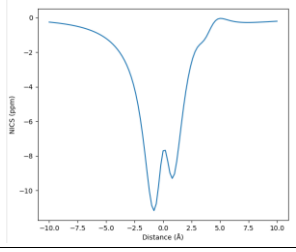




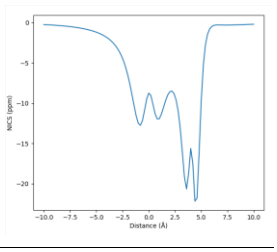
NICS(iso) plot of **ring 1**



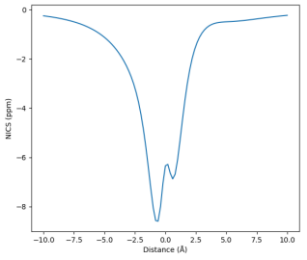
NICS(iso) plot of **ring 2**



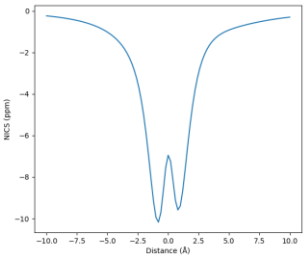
NICS(iso) plot of **ring 3**



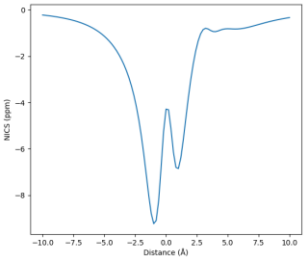
NICS(iso) plot of **ring 4**



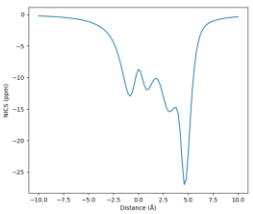
NICS(iso) plot of **ring 5**



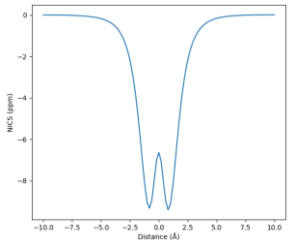
NICS(iso) plot of **ring 6**



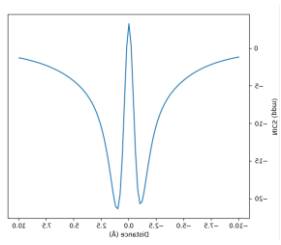
NICS(iso) plot of **ring 7**



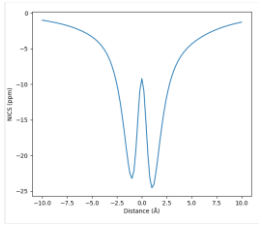
NICS(iso) plot of **ring 8**



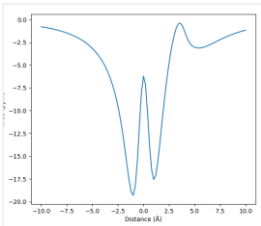
NICS(iso) plot of **ring 9**



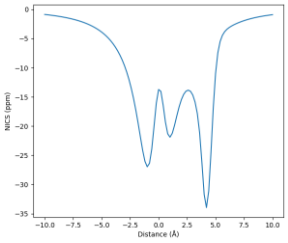
NICS(zz) plot of **ring 1**



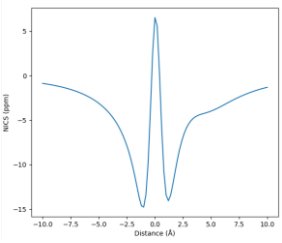
NICS(zz) plot of **ring 2**



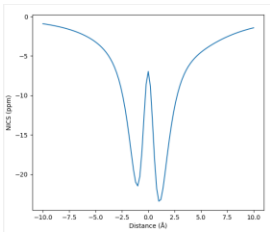
NICS(zz) plot of **ring 3**



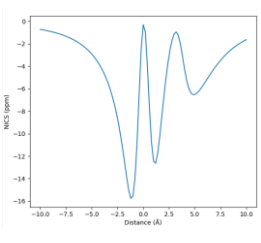
NICS(zz) plot of **ring 4**



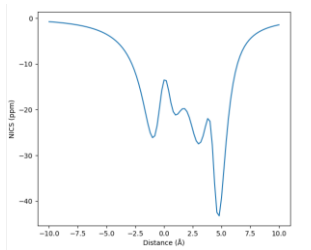
NICS(zz) plot of **ring 5**



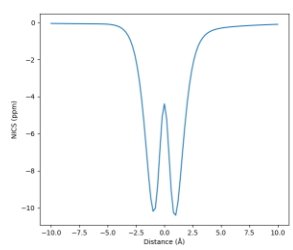
NICS(zz) plot of **ring 6**



NICS(zz) plot of **ring 7**

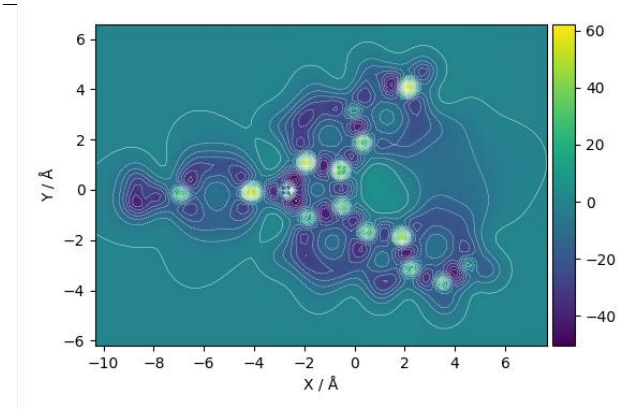


NICS(zz) plot of **ring 8**

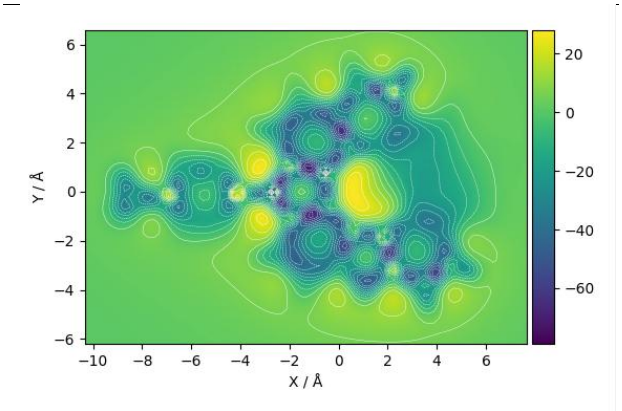


NICS(zz) plot of **ring 9**

2D NICS/ICSS of oxaza[8]helicene **5a**

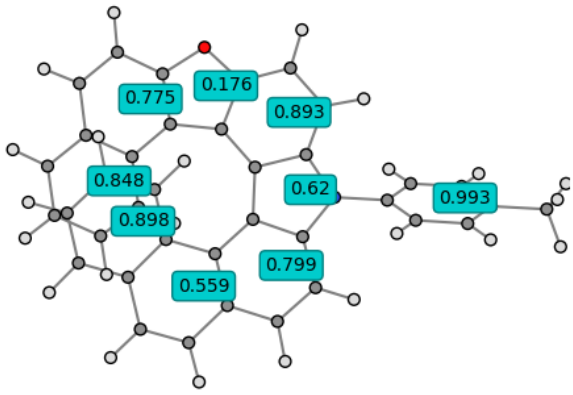


2D heatmap on the XY plane
Component of shielding tensors: isotropy

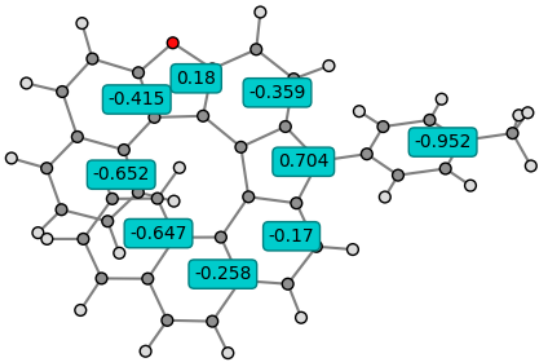


2D heatmap on the XY plane
Component of shielding tensors: zz

HOMA & HOMER of oxaza[8]helicene **5a**



HOMA

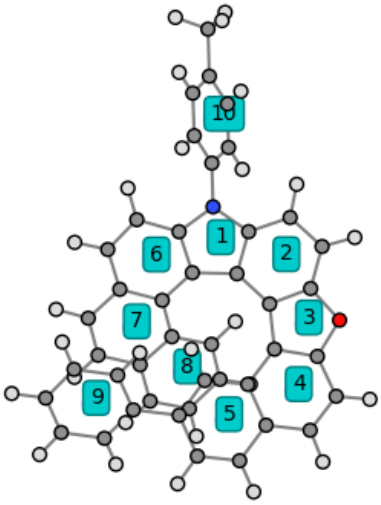


HOMER

Aromaticity of oxaza[8]helicene **5b**

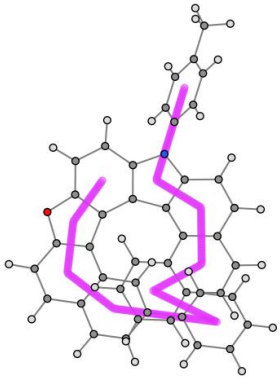
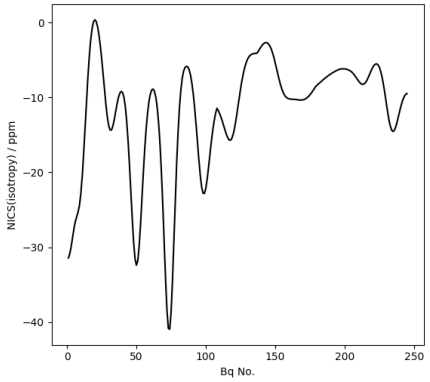
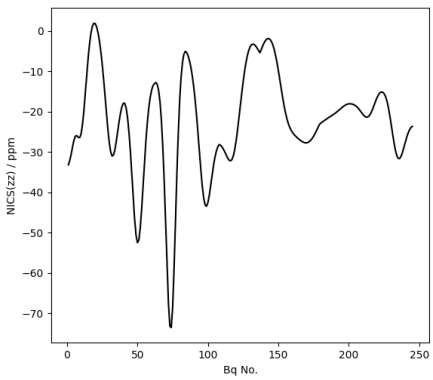
calculated at MN15/6-311G(2d,p)/SMD=chloroform level of theory

NICS(r)iso and NICS(r)zz of oxaza[8]helicene **5b**

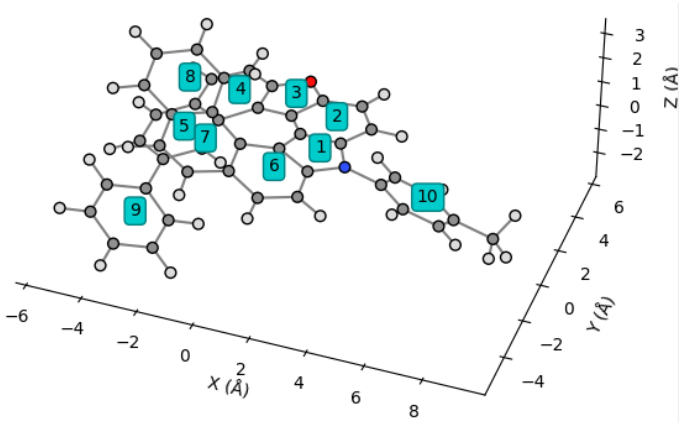


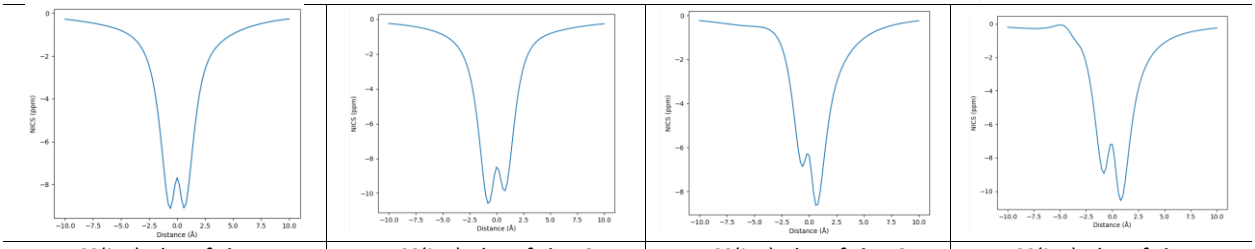
Ring	NICS(0)iso	NICS(0)zz	NICS(1)iso	NICS(1)zz	NICS(−1)iso	NICS(−1)zz	NICS(2)iso	NICS(2)zz	NICS(−2)iso	NICS(−2)zz
1	−7.6849	−2.6687	−8.1883	−20.4763	−8.1703	−20.9474	−3.7528	−12.9341	−3.6372	−13.2464
2	−8.4967	−9.2370	−9.3971	−23.9009	−10.1197	−25.5406	−4.3183	−14.9135	−4.8243	−16.2146
3	−6.3578	−8.3685	−6.0779	−14.7351	−8.0368	−18.0392	−2.3812	−9.6493	−4.1541	−13.2754
4	−7.1953	−6.6968	−8.7059	−21.2757	−10.3183	−23.8900	−5.5283	−12.6401	−3.9904	−16.6285
5	−8.1380	−13.1461	−11.4082	−28.8561	−11.5002	−29.5298	−5.9686	−22.2860	−8.3319	−19.0744
6	−7.0955	−7.1580	−10.0985	−22.9620	−9.4179	−22.1909	−5.1908	−14.8444	−4.4009	−12.9079
7	−5.0023	−3.5368	−9.5587	−20.3947	−8.2448	−17.8808	−5.6700	−15.6083	−6.8661	−14.7353
8	−8.7017	−17.4693	−12.5827	−31.7387	−11.8066	−29.5572	−6.5472	−20.2190	−10.6712	−29.7028
9	−7.3122	−11.6059	−10.9898	−25.3527	−10.3033	−23.4533	−8.6432	−20.0927	−5.0459	−14.1120
10	−6.6325	−1.5874	−9.0984	−1.8854	−9.1052	−2.0720	−3.8938	−1.4671	−3.8865	−1.1021

NICS-XY-Scan of oxaza[8]helicene **5b**

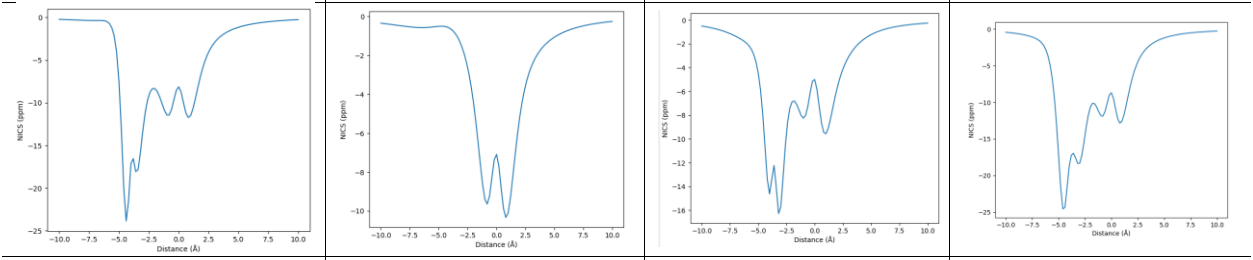
Path of NICS-XY-Scan	NICS(iso)-XY-Scan	NICS(zz)-XY-Scan
		

Integral NICS of oxaza[8]helicene **5b**

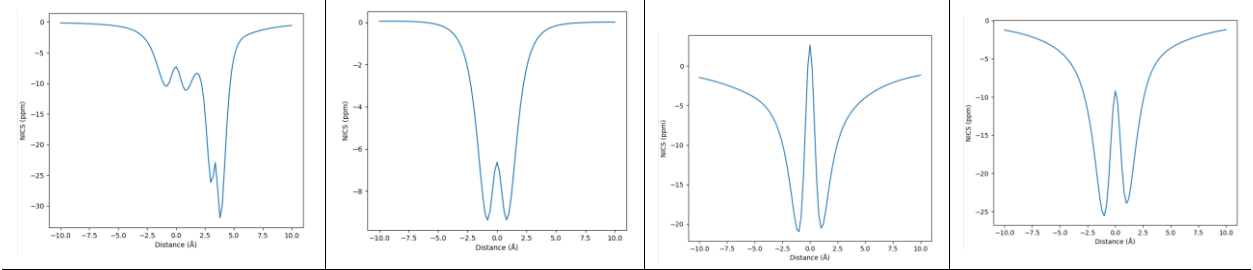




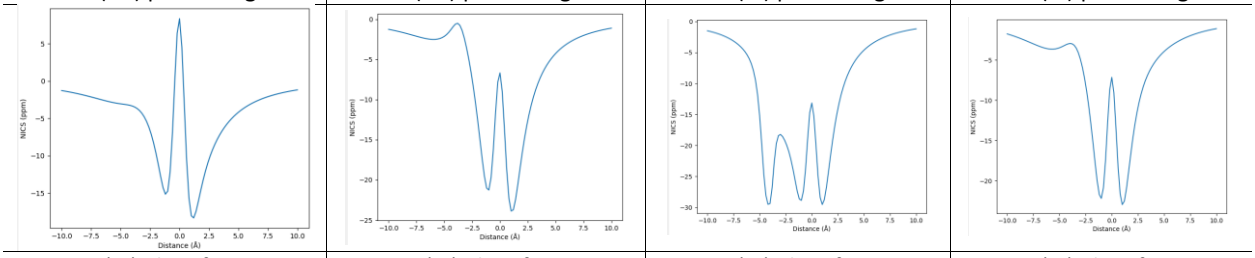
NICS(iso) plot of **ring 1** | NICS(iso) plot of **ring 2** | NICS(iso) plot of **ring 3** | NICS(iso) plot of **ring 4**



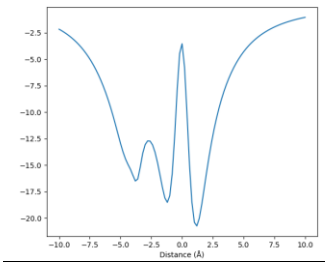
NICS(iso) plot of **ring 5** | NICS(iso) plot of **ring 6** | NICS(iso) plot of **ring 7** | NICS(iso) plot of **ring 8**



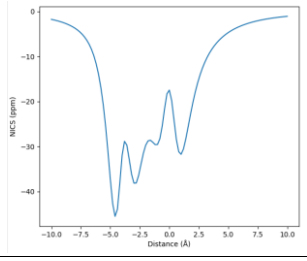
NICS(iso) plot of **ring 9** | NICS(iso) plot of **ring 10** | NICS(zz) plot of **ring 1** | NICS(zz) plot of **ring 2**



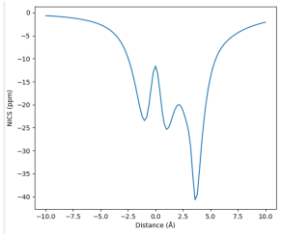
NICS(zz) plot of **ring 3** | NICS(zz) plot of **ring 4** | NICS(zz) plot of **ring 5** | NICS(zz) plot of **ring 6**



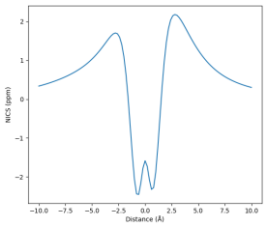
NICS(zz) plot of **ring 7**



NICS(zz) plot of **ring 8**

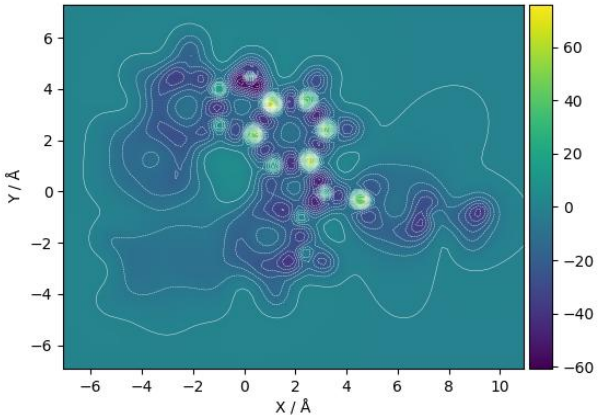


NICS(zz) plot of **ring 9**

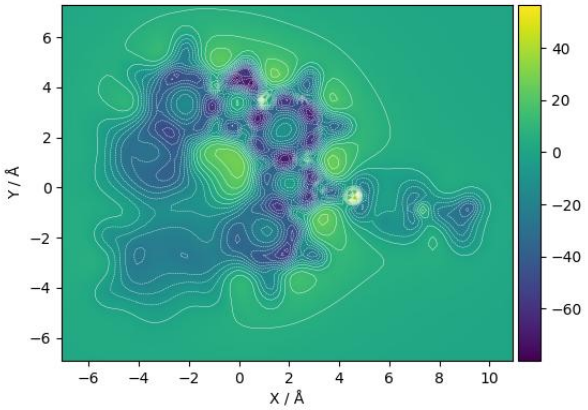


NICS(zz) plot of **ring 10**

2D NICS/ICSS of oxaza[8]helicene **5b**

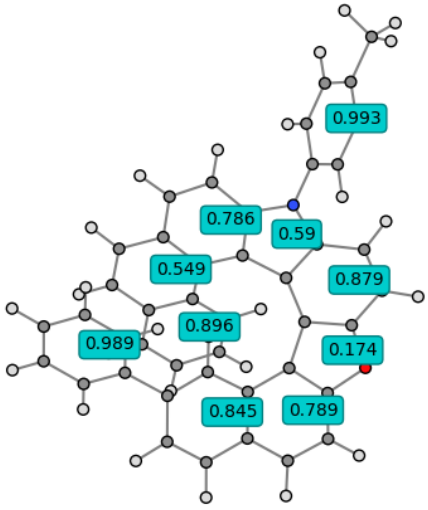


2D heatmap on the XY plane
Component of shielding tensors: isotropy

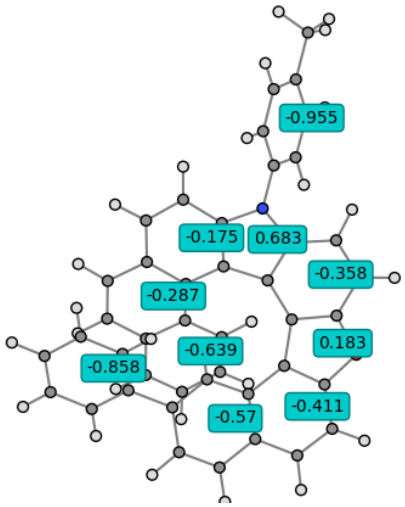


2D heatmap on the XY plane
Component of shielding tensors: zz

HOMA & HOMER of oxaza[8]helicene **5b**



HOMA

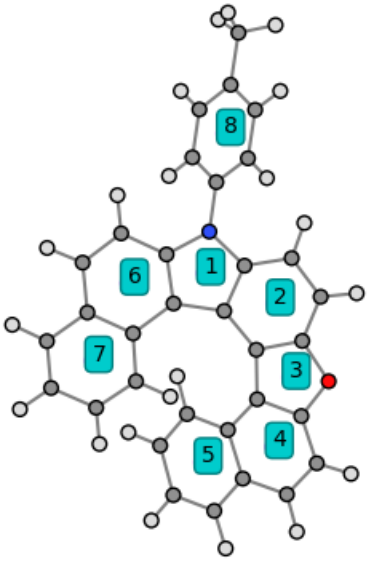


HOMER

Aromaticity of oxaza[7]helicene **6a**

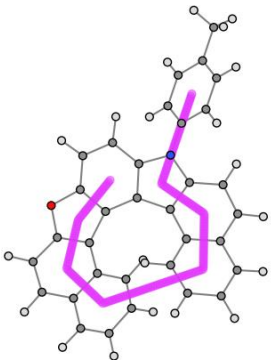
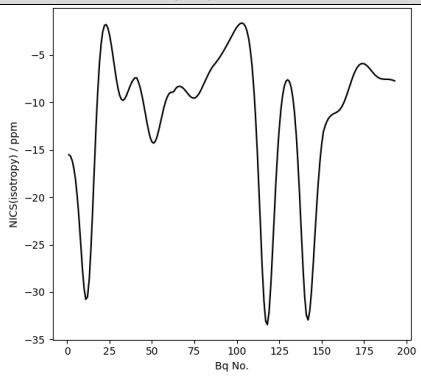
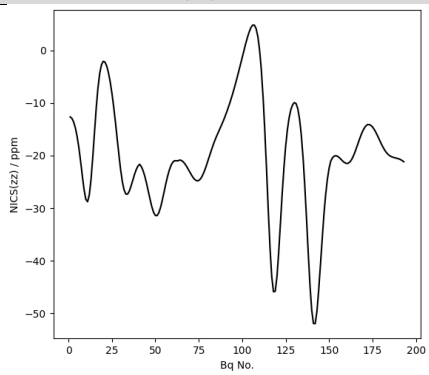
calculated at MN15/6-311G(2d,p)/SMD=chloroform level of theory

NICS(r)iso and NICS(r)zz of oxaza[7]helicene **6a**

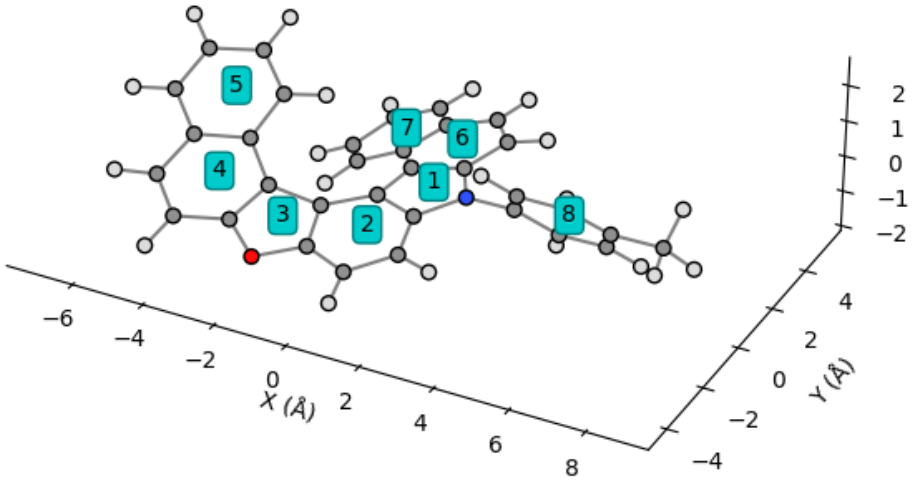


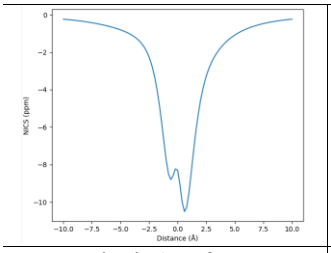
Ring	NICS(0)iso	NICS(0)zz	NICS(1)iso	NICS(1)zz	NICS(−1)iso	NICS(−1)zz	NICS(2)iso	NICS(2)zz	NICS(−2)iso	NICS(−2)zz
1	−8.3087	2.0407	−9.4589	−22.7069	−7.7606	−21.0183	−4.5867	−14.3857	−3.3544	−13.7096
2	−8.9425	−10.1419	−10.2814	−25.8592	−10.2716	−23.8268	−5.0295	−17.0420	−4.8411	−14.5659
3	−6.1553	6.6647	−6.1255	−14.5502	−7.9692	−14.6701	−2.7800	−11.5234	−4.1831	−9.9745
4	−7.4746	−6.2563	−8.6524	−18.0353	−10.8315	−19.1517	−4.1485	−11.7755	−5.6878	−12.1590
5	−7.7471	−10.7680	−9.9080	−16.0091	−11.8944	−24.6869	−4.3460	−6.1104	−6.1336	−15.7961
6	−6.4027	−4.1169	−10.1162	−21.0927	−8.1715	−19.8983	−5.3856	−14.2827	−4.1137	−14.2628
7	−7.6833	−11.2043	−11.8176	−27.8283	−9.7313	−20.3508	−6.0569	−17.5196	−4.1945	−9.5103
8	−6.7369	−4.1074	−9.1696	−9.0288	−9.2195	−8.9832	−3.9623	−3.7307	−3.9704	−3.2093

NICS-XY-Scan of oxaza[7]helicene **6a**

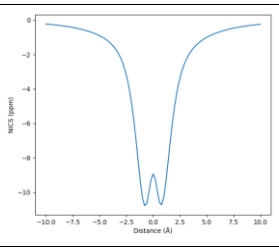
Path of NICS-XY-Scan	NICS(iso)-XY-Scan	NICS(zz)-XY-Scan
		

Integral NICS of oxaza[7]helicene **6a**

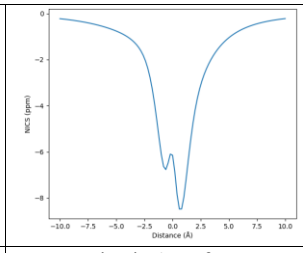




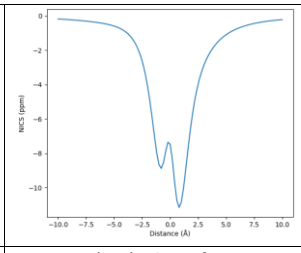
NICS(iso) plot of **ring 1**



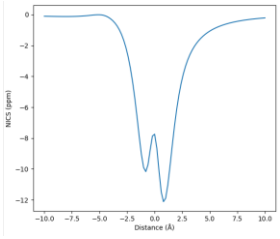
NICS(iso) plot of **ring 2**



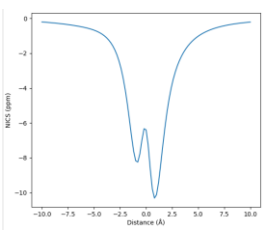
NICS(iso) plot of **ring 3**



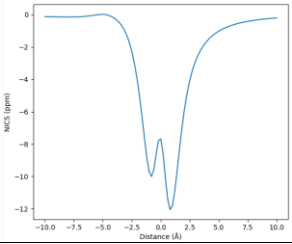
NICS(iso) plot of **ring 4**



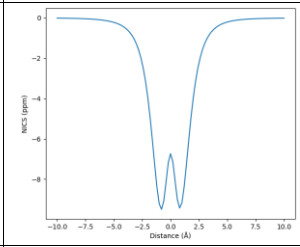
NICS(iso) plot of **ring 5**



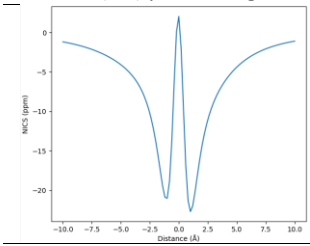
NICS(iso) plot of **ring 6**



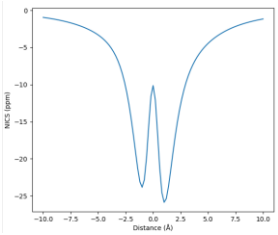
NICS(iso) plot of **ring 7**



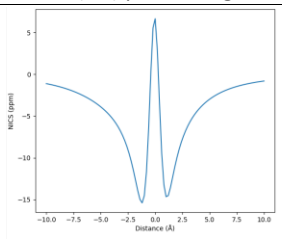
NICS(iso) plot of **ring 8**



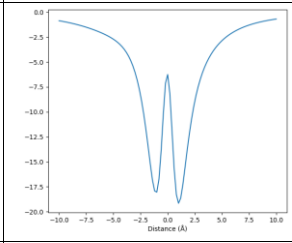
NICS(zz) plot of **ring 1**



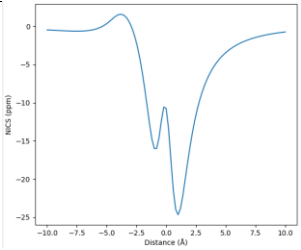
NICS(zz) plot of **ring 2**



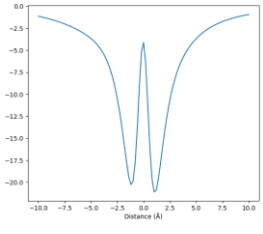
NICS(zz) plot of **ring 3**



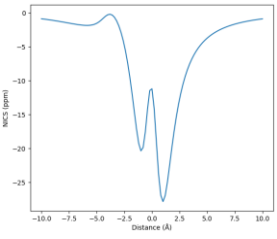
NICS(zz) plot of **ring 4**



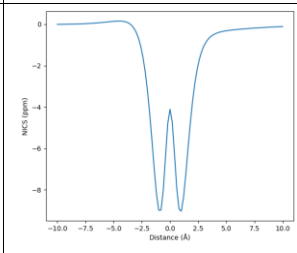
NICS(zz) plot of **ring 5**



NICS(zz) plot of **ring 6**

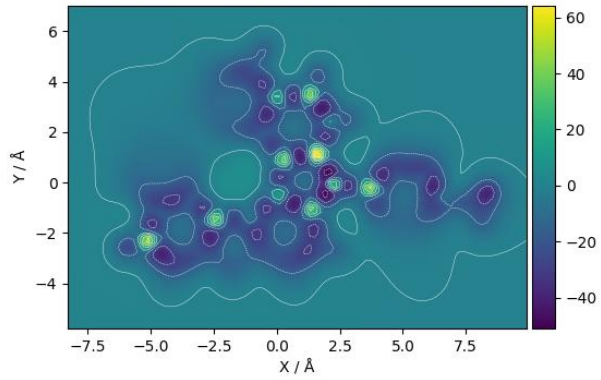


NICS(zz) plot of **ring 7**

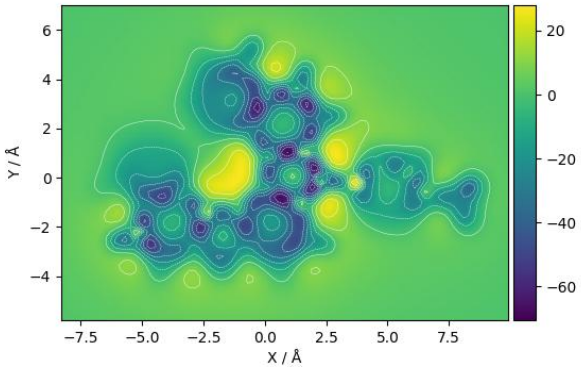


NICS(zz) plot of **ring 8**

2D NICS/ICSS of oxaza[7]helicene **6a**

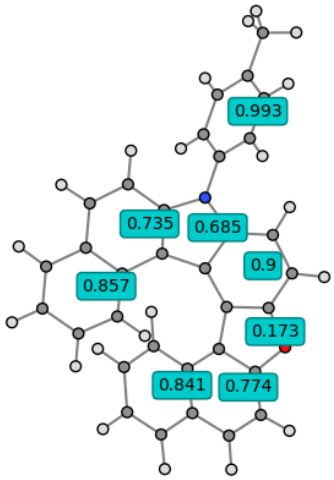


2D heatmap on the XY plane
Component of shielding tensors: isotropy

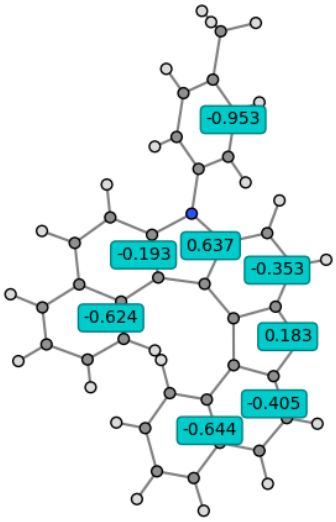


2D heatmap on the XY plane
Component of shielding tensors: zz

HOMA & HOMER of oxaza[7]helicene **6a**



HOMA

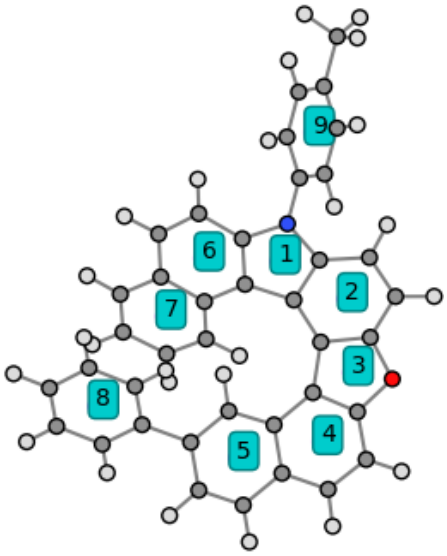


HOMER

Aromaticity of oxaza[7]helicene **6b**

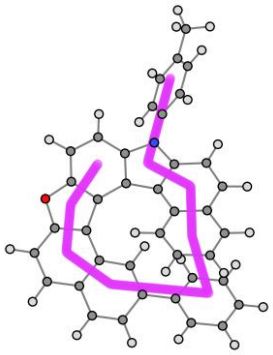
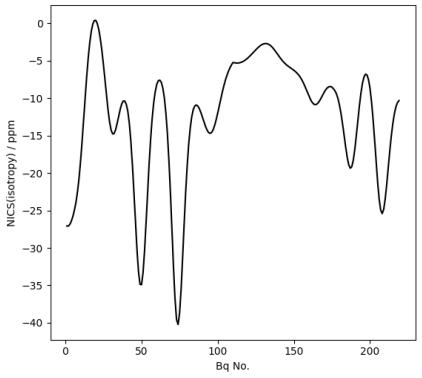
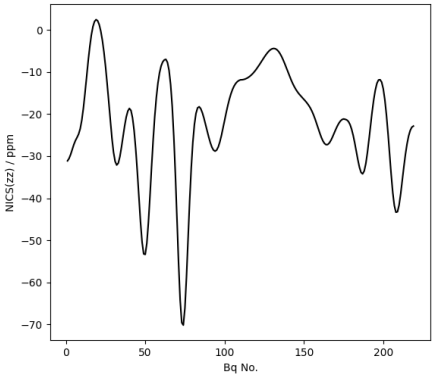
calculated at MN15/6-311G(2d,p)/SMD=chloroform level of theory

NICS(r)iso and NICS(r)zz of oxaza[7]helicene **6b**

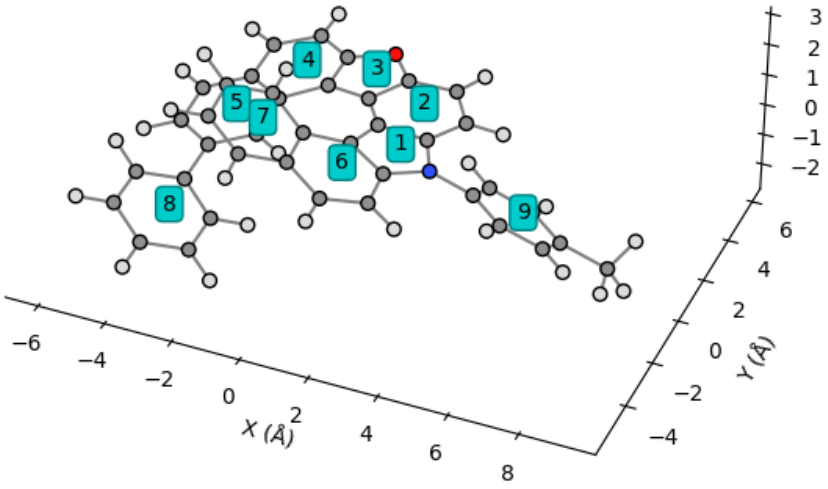


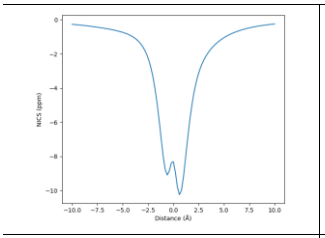
Ring	NICS(0)iso	NICS(0)zz	NICS(1)iso	NICS(1)zz	NICS(−1)iso	NICS(−1)zz	NICS(2)iso	NICS(2)zz	NICS(−2)iso	NICS(−2)zz
1	−8.3150	1.3510	−9.2025	−21.9716	−7.9986	−20.5720	−4.3940	−13.6072	−3.3946	−12.8897
2	−8.7488	−9.7255	−9.9118	−24.8346	−10.2832	−25.8586	−4.8303	−16.1068	−4.8095	−16.2758
3	−6.2651	8.9204	−6.1919	−15.6185	−7.9788	−17.5687	−2.7461	−11.7064	−4.0900	−12.8079
4	−7.0664	6.1361	−8.6268	−21.2623	−10.2274	−23.2406	−4.1546	−14.1826	−5.3532	−15.7598
5	−7.1652	−9.1458	−9.6218	−22.2722	−10.7812	−26.9891	−4.1581	−11.4255	−5.5543	−17.6373
6	−6.3721	−3.9477	−9.9594	−20.2640	−8.2919	−17.5414	−5.3412	−14.0229	−3.9510	−10.5795
7	−8.1833	−13.1759	−11.9969	−28.1300	−10.9515	−22.5163	−6.1801	−18.0539	−8.6863	−17.3792
8	−7.2525	−10.6049	−11.3873	−24.4980	−10.2039	−22.7086	−8.5246	−18.3957	−4.9885	−13.6138
9	−6.7255	−2.0520	−9.2035	−2.7227	−9.1665	−3.0339	−3.9671	0.9623	−3.9426	0.2914

NICS-XY-Scan of oxaza[7]helicene **6b**

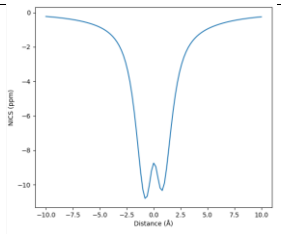
Path of NICS-XY-Scan	NICS(iso)-XY-Scan	NICS(zz)-XY-Scan
		

Integral NICS of oxaza[7]helicene **6b**

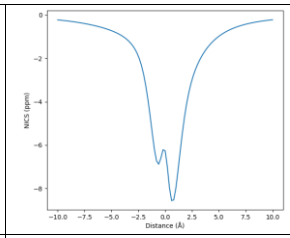




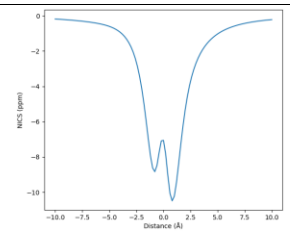
NICS(iso) plot of **ring 1**



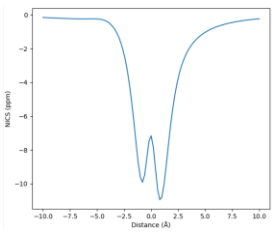
NICS(iso) plot of **ring 2**



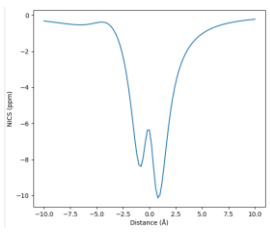
NICS(iso) plot of **ring 3**



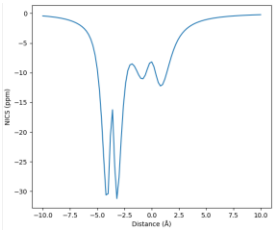
NICS(iso) plot of **ring 4**



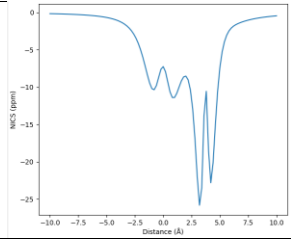
NICS(iso) plot of **ring 5**



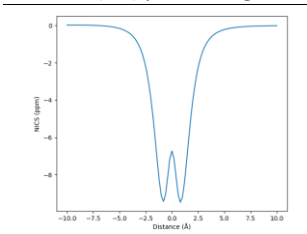
NICS(iso) plot of **ring 6**



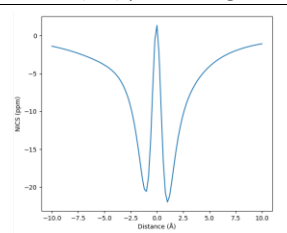
NICS(iso) plot of **ring 7**



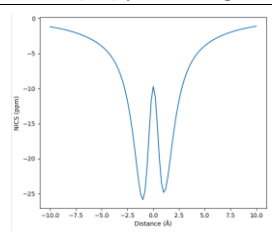
NICS(iso) plot of **ring 8**



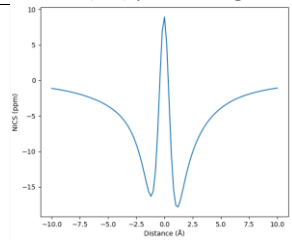
NICS(iso) plot of **ring 9**



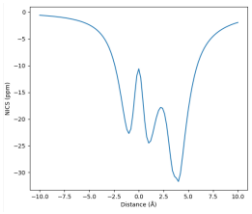
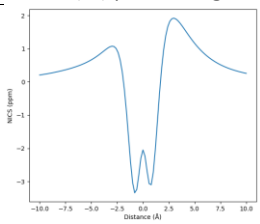
NICS(zz) plot of **ring 1**



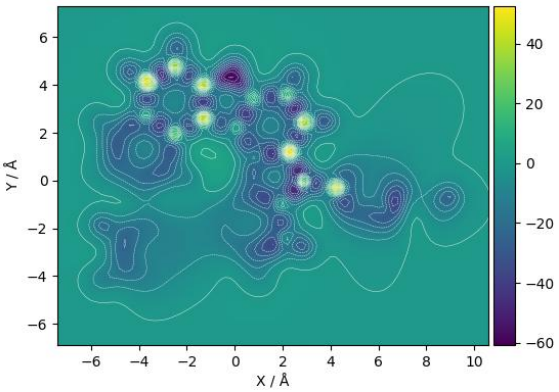
NICS(zz) plot of **ring 2**



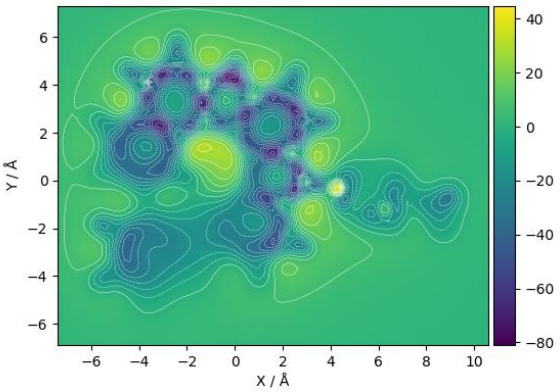
NICS(zz) plot of **ring 3**

NICS(zz) plot of **ring 4**	NICS(zz) plot of **ring 5**	NICS(zz) plot of **ring 6**	NICS(zz) plot of **ring 7**
			
NICS(zz) plot of **ring 8**	NICS(zz) plot of **ring 9**		

2D NICS/ICSS of oxaza[7]helicene **6b**

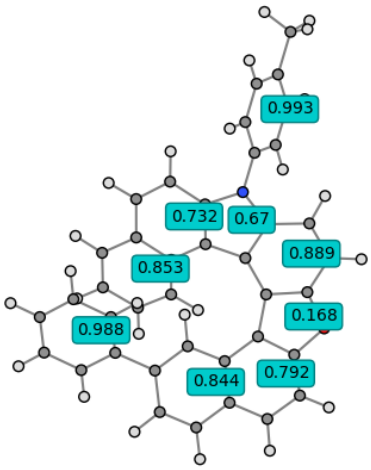


2D heatmap on the XY plane
Component of shielding tensors: isotropy

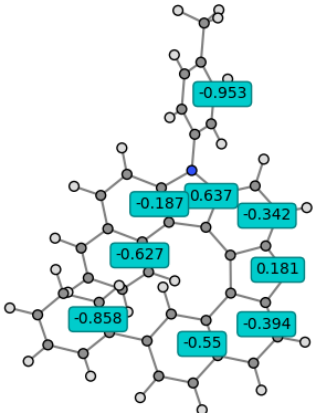


2D heatmap on the XY plane
Component of shielding tensors: zz

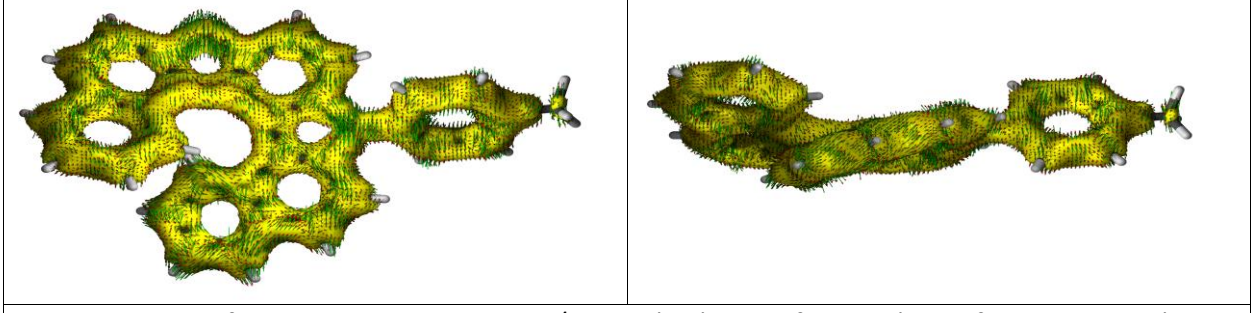
HOMA & HOMER of oxaza[7]helicene **6b**



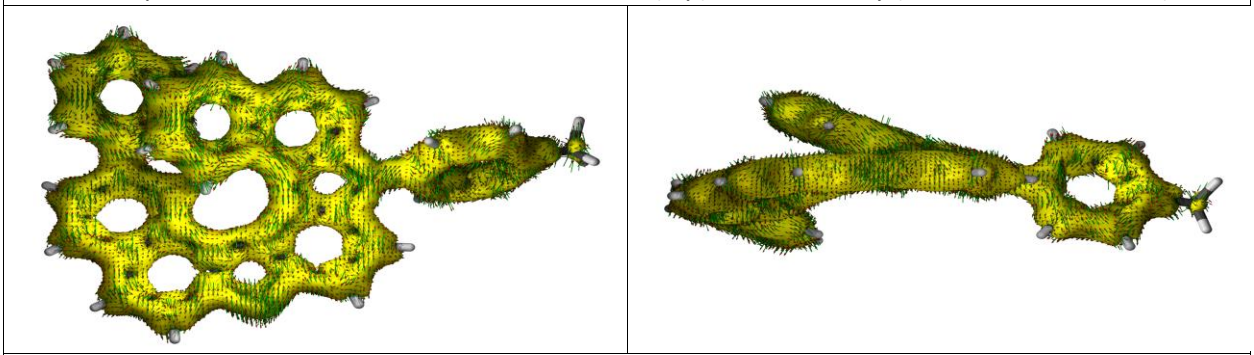
HOMA



HOMER



ACID plots of **6a** calculated at the B3LYP/6-311G(d,p) level of theory (isosurface value: 0.05).



ACID plots of **6b** calculated at the B3LYP/6-311G(d,p) level of theory (isosurface value: 0.05).

3.3. Time-dependent density-functional theory (TD-DFT) calculations

Table S9. Summary of the TD-DFT calculation results of **5a** (S_0 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	3.2184	385.24	0.2849	HOMO	LUMO	93
S_2	3.5497	349.28	0.1384	HOMO−1	LUMO	89
				HOMO	LUMO+1	3
S_3	3.9157	316.64	0.0772	HOMO−2	LUMO	37
				HOMO	LUMO+2	26
				HOMO−1	LUMO+1	19
				HOMO	LUMO+1	5

S_1~S_3

Table S10. Summary of the TD-DFT calculation results of **5b** (S_0 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	3.1482	393.83	0.2208	HOMO	LUMO	93
S_2	3.5229	351.94	0.1093	HOMO−1	LUMO	86
				HOMO	LUMO+1	5
S_3	3.8247	324.17	0.2923	HOMO−2	LUMO	32
				HOMO−1	LUMO+1	6
				HOMO−1	LUMO+2	7
				HOMO	LUMO+1	28
				HOMO	LUMO+2	12

S_1~S_3

Table S11. Summary of the TD-DFT calculation results of **6a** (S_0 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	3.3483	370.29	0.4725	HOMO	LUMO	95
S_2	3.7374	331.74	0.246	HOMO−1	LUMO	86
				HOMO	LUMO+4	4
S_3	4.0938	302.86	0.1291	HOMO−2	LUMO	29
				HOMO−1	LUMO+2	2
				HOMO	LUMO+1	57

S_1~S_3

Table S12. Summary of the TD-DFT calculation results of **6b** (S_0 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	3.2279	384.1	0.3322	HOMO	LUMO	95
S_2	3.6851	336.45	0.259	HOMO−1	LUMO	84
				HOMO−1	LUMO+1	3
				HOMO	LUMO+2	3
S_3	3.9633	312.83	0.2679	HOMO−3	LUMO	2
				HOMO−2	LUMO	19
				HOMO	LUMO+1	65

S_1~S_3

Table S13. Summary of the TD-DFT calculation results of **5a** (S_1 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	2.7622	448.86	0.3146	HOMO	LUMO	96
S_2	3.2909	376.75	0.0947	HOMO−1	LUMO	88
				HOMO	LUMO+1	4
S_3	3.7281	332.57	0.1648	HOMO−2	LUMO	51
				HOMO−1	LUMO+1	13
				HOMO	LUMO+1	3
				HOMO	LUMO+2	23
S_4	3.7751	328.42	0.5069	HOMO−1	LUMO	5
				HOMO	LUMO+1	83
S_5	3.9293	315.54	0.0037	HOMO−2	LUMO	33
				HOMO	LUMO+2	58
S_6	4.04	306.89	0.0603	HOMO−4	LUMO	7
				HOMO−3	LUMO	34
				HOMO−1	LUMO+1	2
				HOMO−1	LUMO+2	4
				HOMO	LUMO+2	3
				HOMO	LUMO+3	25
				HOMO	LUMO+5	3
				HOMO	LUMO+6	5
S_7	4.1192	300.99	0.0726	HOMO−5	LUMO	5
				HOMO−4	LUMO	31
				HOMO−2	LUMO	6

				HOMO−1	LUMO+1	10
				HOMO−1	LUMO+2	12
				HOMO	LUMO+3	18
				HOMO	LUMO+6	5
S_8	4.2737	290.11	0.1386	HOMO−4	LUMO	17
				HOMO−3	LUMO	15
				HOMO−1	LUMO+1	46
				HOMO	LUMO+2	8
S_9	4.3452	285.34	0.1749	HOMO−4	LUMO	10
				HOMO−3	LUMO	24
				HOMO−1	LUMO+1	11
				HOMO−1	LUMO+2	4
				HOMO	LUMO+3	43
S_{10}	4.4801	276.75	0.1022	HOMO−4	LUMO	4
				HOMO−3	LUMO	6
				HOMO−1	LUMO+2	50
				HOMO	LUMO+4	24

S_1~S_{10}

Table S14. Summary of the TD-DFT calculation results of **5b** (S_1 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	2.6301	471.4	0.2234	HOMO	LUMO	96
S_2	3.2443	382.16	0.063	HOMO−1	LUMO	86
				HOMO	LUMO+1	6
S_3	3.5866	345.69	0.4981	HOMO−2	LUMO	17
				HOMO−1	LUMO	5
				HOMO−1	LUMO+2	4
				HOMO	LUMO+1	60
				HOMO	LUMO+2	3
S_4	3.6648	338.31	0.0561	HOMO−2	LUMO	44
				HOMO−1	LUMO	2
				HOMO−1	LUMO+2	3
				HOMO	LUMO+1	25
				HOMO	LUMO+2	20
S_5	3.7666	329.17	0.1763	HOMO−2	LUMO	25

				HOMO−1	LUMO+1	2
				HOMO	LUMO+2	60
S_6	3.8409	322.8	0.1682	HOMO−3	LUMO	53
				HOMO−1	LUMO+1	6
				HOMO	LUMO+2	5
				HOMO	LUMO+3	9
				HOMO	LUMO+4	9
				HOMO	LUMO+5	3
S_7	4.0319	307.51	0.0522	HOMO−6	LUMO	3
				HOMO−4	LUMO	14
				HOMO−2	LUMO	5
				HOMO−1	LUMO+1	2
				HOMO−1	LUMO+2	19
				HOMO	LUMO+3	39
				HOMO	LUMO+4	4
S_8	4.1714	297.22	0.0595	HOMO−6	LUMO	3
				HOMO−4	LUMO	19
				HOMO−3	LUMO	29
				HOMO−1	LUMO+1	5
				HOMO−1	LUMO+2	5
				HOMO	LUMO+2	3
				HOMO	LUMO+3	11
				HOMO	LUMO+4	16
S_9	4.2505	291.7	0.1008	HOMO−4	LUMO	6
				HOMO−1	LUMO+1	64
				HOMO−1	LUMO+2	5
				HOMO	LUMO+2	2
				HOMO	LUMO+3	9
				HOMO	LUMO+4	4
S_{10}	4.2992	288.39	0.2822	HOMO−4	LUMO	11
				HOMO−3	LUMO	6
				HOMO−1	LUMO+1	7
				HOMO−1	LUMO+2	44
				HOMO	LUMO+3	20

S_1~S_{10}

Table S15. Summary of the TD-DFT calculation results of **6a** (S_1 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	2.8262	438.7	0.4852	HOMO	LUMO	97
S_2	3.5281	351.42	0.2441	HOMO−1	LUMO	86
				HOMO	LUMO+5	5
S_3	3.8194	324.62	0.1513	HOMO−2	LUMO	16
				HOMO	LUMO+1	77
S_4	4.028	307.8	0.0569	HOMO−2	LUMO	67
				HOMO−1	LUMO+1	3
				HOMO	LUMO+1	19
S_5	4.0848	303.53	0.0021	HOMO−3	LUMO	17
				HOMO−2	LUMO	3
				HOMO−2	LUMO+5	3
				HOMO−1	LUMO+1	3
				HOMO	LUMO+2	55
				HOMO	LUMO+4	3
				HOMO	LUMO+5	3
				HOMO	LUMO+6	4
S_6	4.1924	295.74	0.0484	HOMO−4	LUMO	8
				HOMO−3	LUMO	21
				HOMO−3	LUMO+1	3
				HOMO−1	LUMO+1	7
				HOMO	LUMO+2	32
				HOMO	LUMO+3	5
				HOMO	LUMO+4	2
				HOMO	LUMO+5	7
				HOMO	LUMO+6	7
S_7	4.3646	284.07	0.24	HOMO−5	LUMO	3
				HOMO−3	LUMO	3
				HOMO−2	LUMO	5
				HOMO−2	LUMO+3	3
				HOMO−1	LUMO+2	2
				HOMO	LUMO+3	40
				HOMO	LUMO+4	5
				HOMO	LUMO+5	21
				HOMO	LUMO+6	2
S_8	4.5351	273.39	0.0473	HOMO−4	LUMO	3

				HOMO−1	LUMO	4
				HOMO−1	LUMO+1	25
				HOMO−1	LUMO+3	3
				HOMO	LUMO+3	31
				HOMO	LUMO+5	20
				HOMO	LUMO+6	3
S_9	4.6529	266.47	0.1252	HOMO−4	LUMO	47
				HOMO−3	LUMO	30
				HOMO	LUMO+2	2
				HOMO	LUMO+5	5
				HOMO	LUMO+6	3
S_{10}	4.702	263.68	0.2386	HOMO−4	LUMO	3
				HOMO−3	LUMO	4
				HOMO−1	LUMO+1	21
				HOMO−1	LUMO+3	2
				HOMO	LUMO+3	4
				HOMO	LUMO+4	27
				HOMO	LUMO+5	2
				HOMO	LUMO+6	21

S_1~S_{10}

Table S16. Summary of the TD-DFT calculation results of **6b** (S_1 state geometry) at MN15/6-311G(2d,p)/SMD=chloroform level of theory.

Excited states	Energy (eV)	Wavelength (nm)	Oscillator strength	Major contributions (%)		
S_1	2.6652	465.19	0.307	HOMO	LUMO	97
S_2	3.449	359.48	0.2588	HOMO−1	LUMO	84
S_3	3.6602	338.74	0.3576	HOMO−2	LUMO	8
				HOMO−1	LUMO	3
				HOMO	LUMO+1	81
S_4	3.7972	326.51	0.0586	HOMO−3	LUMO	2
				HOMO−2	LUMO	68
				HOMO−1	LUMO+1	5
				HOMO	LUMO+1	9
				HOMO	LUMO+3	6
S_5	3.9401	314.68	0.0474	HOMO−3	LUMO	38
				HOMO−2	LUMO	8
				HOMO	LUMO+1	3

				HOMO	LUMO+2	3
				HOMO	LUMO+3	32
				HOMO	LUMO+4	3
S_6	4.0269	307.89	0.0761	HOMO−5	LUMO	4
				HOMO−3	LUMO	7
				HOMO	LUMO+2	71
				HOMO	LUMO+3	3
S_7	4.2514	291.63	0.4405	HOMO−5	LUMO	9
				HOMO−3	LUMO	24
				HOMO−2	LUMO	7
				HOMO−1	LUMO+1	5
				HOMO	LUMO+3	20
				HOMO	LUMO+4	11
				HOMO	LUMO+6	7
S_8	4.2914	288.91	0.2334	HOMO−5	LUMO	2
				HOMO−3	LUMO	14
				HOMO−1	LUMO	3
				HOMO−1	LUMO+1	16
				HOMO	LUMO+2	10
				HOMO	LUMO+3	24
				HOMO	LUMO+4	14
				HOMO	LUMO+6	4
S_9	4.4174	280.67	0.1182	HOMO−4	LUMO	9
				HOMO−3	LUMO	4
				HOMO−1	LUMO+1	37
				HOMO	LUMO+4	35
S_{10}	4.5464	272.71	0.0367	HOMO−5	LUMO	44
				HOMO−4	LUMO	2
				HOMO	LUMO+2	6
				HOMO	LUMO+5	2
				HOMO	LUMO+6	28
				HOMO	LUMO+7	3

S_1~S_{10}

Table S17. Screening TD-DFT calculations of *oxaza[n]helicenes* using different basis sets

	Level of theory	$S_0 \rightarrow S_1$ transitions				
		|μ| (10^{-20} esu cm)[a]	|m| (10^{-20} erg G^{-1})[b]	$\cos(\theta_{\mu,m})$[c]	(R) (10^{-40} (erg esu cm G^{-1})[d]	g_{cal}[e] (10^{-3})
5b	MN15/6-311+g(2d,p) (smd, solvent=chloroform)	471.9	2.7	−0.174	−219.6	−0.0039
	MN15/6-31+g(2d,p) (smd, solvent=chloroform)	472.7	2.7	−0.173	−218.1	−0.0039
	MN15/6-31+g(d,p) (smd, solvent=chloroform)	474.9	2.6	−0.167	−207.1	−0.0037
	MN15/6-311g(d,p) (smd, solvent=chloroform)	477.1	2.6	−0.184	−229.6	−0.0040
	MN15/cc-pvdz (smd, solvent=chloroform)	481.0	2.6	−0.191	−239.0	−0.0041
	MN15/lanl2dz (smd, solvent=chloroform)	477.5	2.3	−0.173	−189.4	−0.0033
	MN15/lanl2mb (smd, solvent=chloroform)	512.3	1.8	−0.147	−136.8	−0.0021
	MN15/dgdzvp2 (smd, solvent=chloroform)	476.8	2.6	−0.177	−221.9	−0.0039
	MN15/6-311g(2d,p) (iefpcm, solvent=chloroform)	463.4	2.6	−0.186	−228.9	−0.0043
	MN15/lanl2mb gas phase	450.4	1.8	−0.193	−156.6	−0.0031
	MN15/lanl2dz gas phase	399.4	2.3	−0.214	−196.3	−0.0049
	MN15/lanl2mb (cpcm, solvent=chloroform)	509.9	1.8	−0.147	−136.1	−0.0021
	MN15/lanl2dz (cpcm, solvent=chloroform)	478.3	2.3	−0.176	−191.6	−0.0034
	MN15/lanl2mb (iefpcm, solvent=chloroform)	502.4	1.8	−0.151	−137.3	−0.0022
	MN15/lanl2dz (iefpcm, solvent=chloroform)	467.1	2.3	−0.176	−187.8	−0.0034
	MN15/lanl2mb (ipcm, solvent=chloroform)	450.4	1.8	−0.193	−156.7	−0.0031
	MN15/lanl2dz/qzv (smd, solvent=chloroform)	477.5	2.3	−0.173	−189.4	−0.0033
	MN15/lanl2dz/dga2 (smd, solvent=chloroform)	477.5	2.3	−0.173	−189.4	−0.0033
	MN15/lanl2dz/def2sv (smd, solvent=chloroform)	477.5	2.3	−0.173	−189.4	−0.0033
	MN15/lanl2mb/def2sv (smd, solvent=chloroform)	512.3	1.8	−0.147	−136.8	−0.0021
	MN15/lanl2mb/qzv (smd, solvent=chloroform)	512.3	1.8	−0.147	−136.8	−0.0021
	MN15/lanl2mb/dga2 (smd, solvent=chloroform)	512.3	1.8	−0.147	−136.8	−0.0021
6b	MN15/lanl2mb scrf=(ipcm, solvent=chloroform)	514.9	1.9	−0.143	−137.2	−0.0021
	MN15/lanl2mb scrf=(iefpcm, solvent=chloroform)	569.0	1.9	−0.114	−121.0	−0.0015
5a	MN15/lanl2mb scrf=(iefpcm, solvent=chloroform)	553.8	1.2	−0.103	−68.7	−0.0009
	MN15/lanl2mb scrf=(ipcm, solvent=chloroform)	494.2	1.2	−0.142	−84.0	−0.0014
6a	MN15/lanl2mb scrf=(iefpcm, solvent=chloroform)	665.4	1.1	−0.078	−54.8	−0.0005

[a] Electric transition dipole moments (ETDM) for the $S_0 \rightarrow S_1$ transitions. [b] Magnetic transition dipole moments (MTDM) for the $S_0 \rightarrow S_1$ transitions. [c] The angle between ETDM and MTDM vectors. [d] Rotational strength. [e] Dimensionless values.

Theoretically calculated radiative rate constants $k_{f,calcd}$

$$\boldsymbol{k_{f,calcd}} = \frac{16\pi^3}{3h\varepsilon_0}\nu^3(\mathrm{D}+\mathrm{G}) \quad Equation\ (S1)$$

Table S18. Calculation of the radiative rate constants $k_{f,calcd}$ of oxaza[*n*]helicenes

	λ_{ex}[a] /nm	ν[b] /cm^{-1}	ν^3 (× 10^{13})	(D) (×10^{-40} (esu^2 cm^2)[c]	(G) (×10^{-40} (erg^2 G^{-2})[d]	(D + G) (×10^{-40})[e]	$k_{f,calcd}$ /ns^{-1}	Φ_f
5a	381	26246.7	1.8	306733.0	1.439	306734.5	0.17370	25.1%
5b	368	27173.9	2.0	252356.9	3.280	252360.2	0.15859	22.6%
6a	385	25974.0	1.8	442754.5	1.128	442755.6	0.24299	40.1%
6b	374	26738.0	1.9	323757.6	3.485	323761.1	0.19383	38.9%

[a] For the $S_1 \rightarrow S_0$ transitions. [b] Deexcitation energy (in cm^{-1}) was converted as follows: ν (cm^{-1}) = 10^7 / λ_{ex} (nm). [c] Electric dipole strength = $|\mu|^2$. [d] Magnetic dipole strength = $|m|^2$. [e] Calculated at MN15/lanl2mb (iefpcm, solvent=chloroform) level of theory.

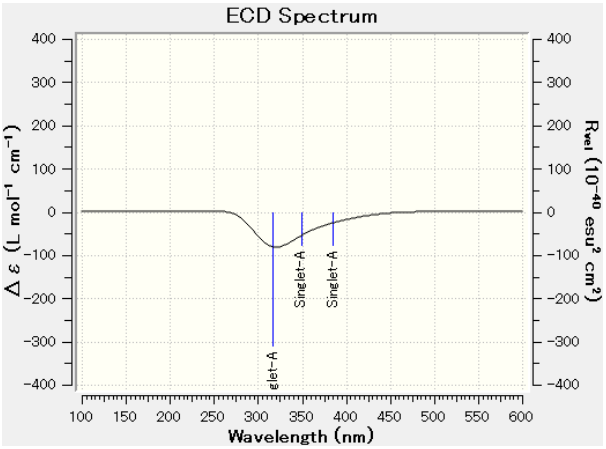
ETDM and MTDM of oxaza[8]helicenes and oxaza[7]helicenes

Table S19. Calculation of ETDM and MTDM of oxaza[8]helicenes **5a** & **5b** and oxaza[7]helicenes **6a** & **6b**

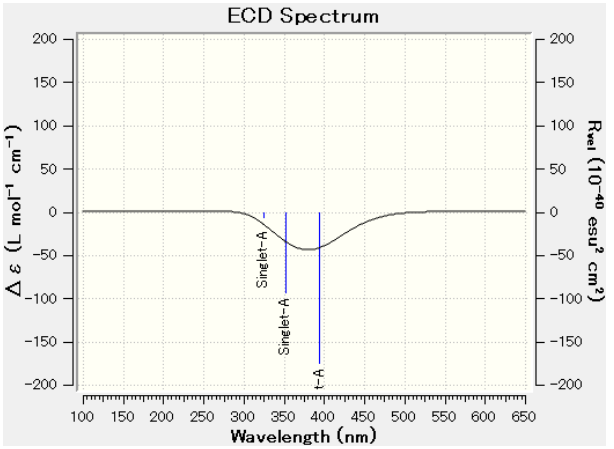
	$S_1 \rightarrow S_0$ transition											
	$\lvert\mu_x\rvert$	$\lvert\mu_y\rvert$	$\lvert\mu_z\rvert$	$\lvert\mu'\rvert$	$\lvert m_x\rvert$	$\lvert m_y\rvert$	$\lvert m_z\rvert$	$\lvert m'\rvert$	$\theta_{\mu,m}$ (deg)[c]	cos($\theta_{\mu,m}$)	(R) (×10^{-40} (erg esu cm G^{-1})[d]	g_{cal}[e] (×10^3)
	(×10^{-20} esu cm)[a]				(×10^{-20} erg G^{-1})[b]							
5a	−437.7	−327.2	89.6	553.8	−0.2	0.2	−1.2	1.20	95.9	−0.103	−68.7	0.90
5b	−434.6	178.6	−177.7	502.4	−0.3	0.2	1.8	1.81	98.7	−0.151	−137.3	2.18
6a	−560.1	−354.6	57.1	665.4	−0.2	0.3	−1.0	1.06	94.5	−0.078	−54.8	0.50
6b	−497.5	236.8	−141.9	569.0	−0.3	−0.1	1.8	1.87	96.5	−0.114	−121.0	1.50

[a] Electric transition dipole moments (ETDM) for the $S_1 \rightarrow S_0$ transitions. [b] Magnetic transition dipole moments (MTDM) for the $S_1 \rightarrow S_0$ transitions. [c] The angle between ETDM and MTDM vectors. [d] Rotational strength. [e] Dimensionless values. Calculated at MN15/lanl2mb (iefpcm, solvent=chloroform) level of theory.

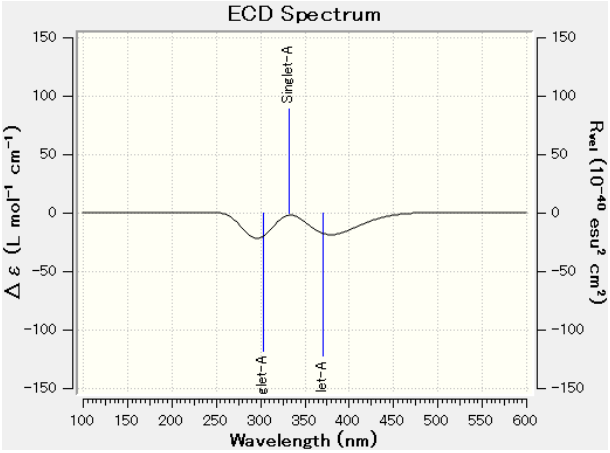
Simulated ECD spectrum of (*M*)-oxaza[7] & oxaza[8]helicenes



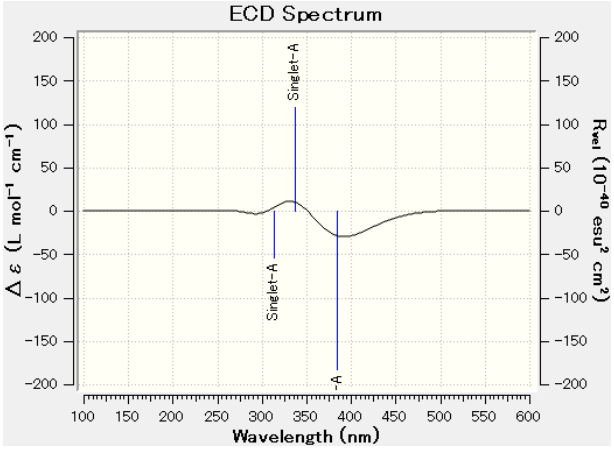
Simulated ECD spectrum of (*M*)−**5a** at MN15/6−311G(2d,p) (SMD, solvent=chloroform); (Wavelength (nm) = 316.64, R_{vel} (10^{-40} esu^2 cm^2) = −308.3914.



Simulated ECD spectrum of (*M*)−**5b** at MN15/6−311G(2d,p) (SMD, solvent=chloroform); (Wavelength (nm) = 393.83, R_{vel} (10^{-40} esu^2 cm^2) = −174.9947.

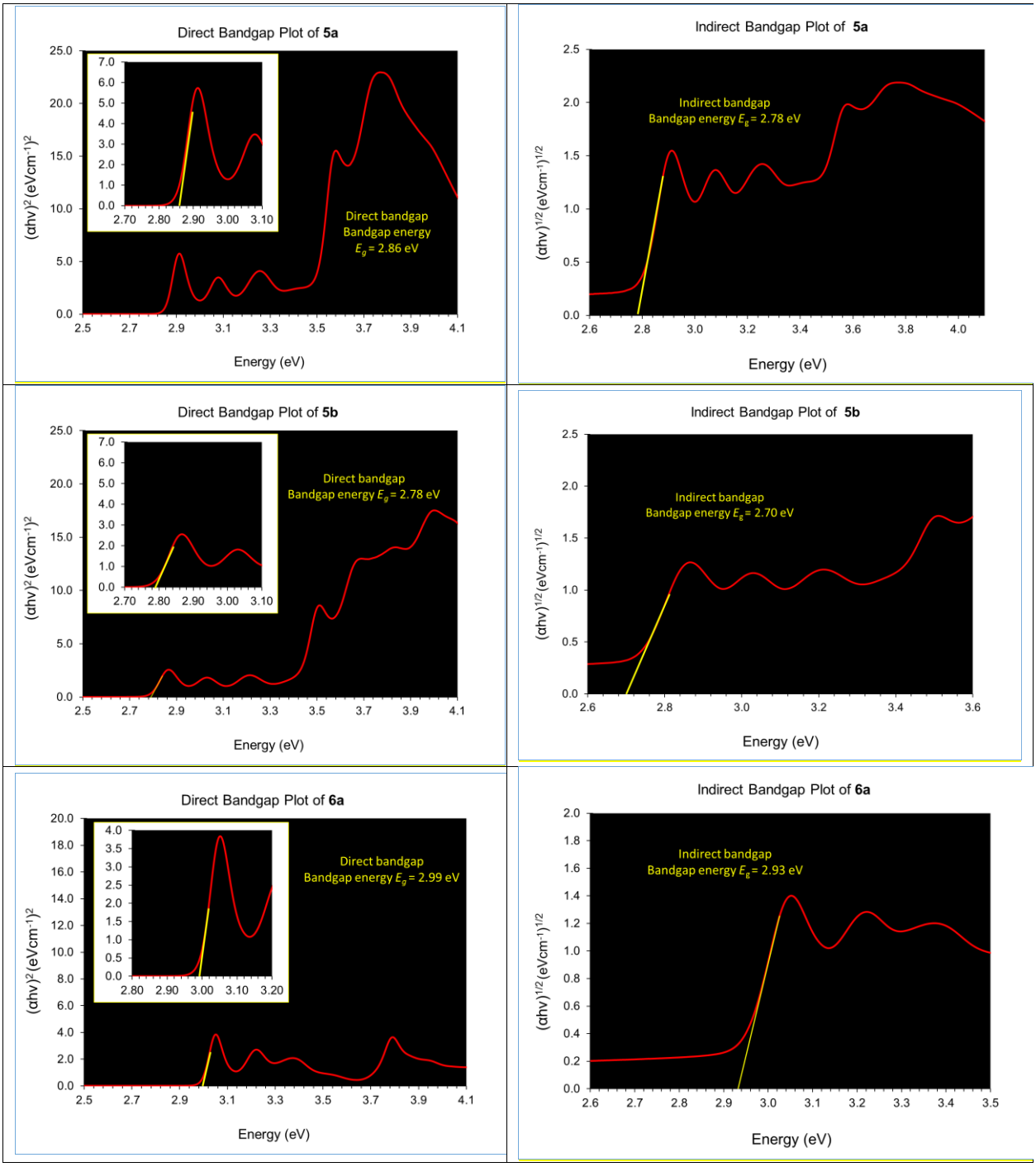


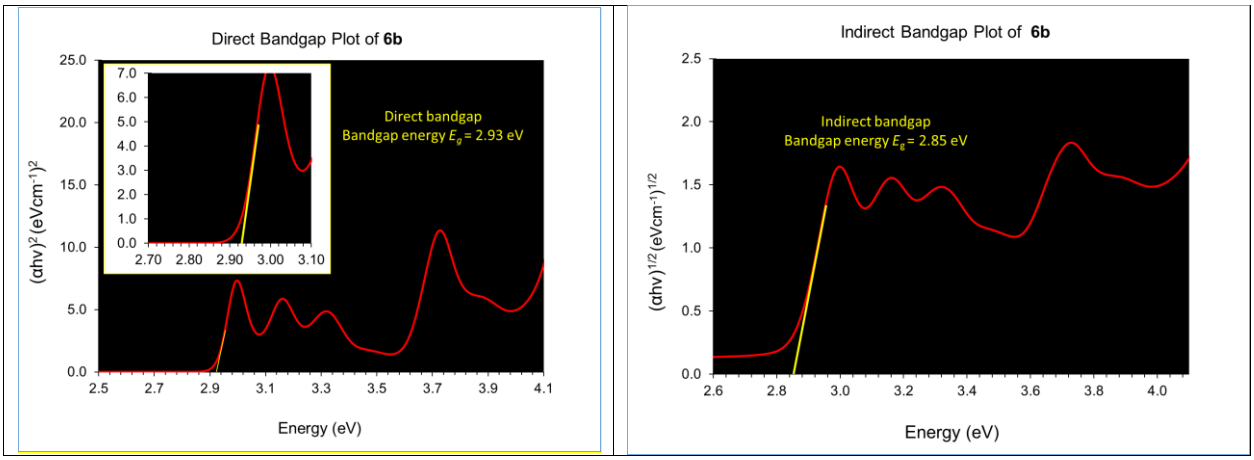
Simulated ECD spectrum of (*M*)−**6a** at MN15/6−311G(2d,p) (SMD, solvent=chloroform); (Wavelength (nm) = 302.86, R_{vel} (10^{-40} esu^2 cm^2) = −117.5699.



Simulated ECD spectrum of (*M*)−**6b** at MN15/6−311G(2d,p) (SMD, solvent=chloroform); (Wavelength (nm) = 384.10, R_{vel} (10^{-40} esu^2 cm^2) = −182.8564.

4. *Calculation of band gap energy from UV–Vis absorption (Tauc Plots)*




Direct Bandgap Plot of 6b
Direct bandgap
Bandgap energy E_g = 2.93 eV
$(\alpha h\nu)^2$ (eVcm^{-1})^2
Energy (eV)
Indirect Bandgap Plot of 6b
Indirect bandgap
Bandgap energy E_g = 2.85 eV
$(\alpha h\nu)^{1/2}$ (eVcm^{-1})$^{1/2}$
Energy (eV)