Supporting information for

Schiff-base [4]helicene Zn(II) complexes as chiral emitters

Mariia Savchuk,[†,a] Steven Vertueux,[†,a] Thomas Cauchy,[a] Matthieu Loumaigne,[a] Francesco Zinna,[b] Lorenzo Di Bari,[b] Nicolas Zigon*[a] and Narcis Avarvari *[a]

[a] Univ Angers, CNRS, MOLTECH-Anjou, SFR MATRIX, F-49000 Angers, France. E-mail: nicolas.zigon@univ-angers.fr, narcis.avarvari@univ-angers.fr

[b] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via G. Moruzzi, 13, 56124, Pisa, Italy.

† These authors contributed equally to this work.

SUMMARY

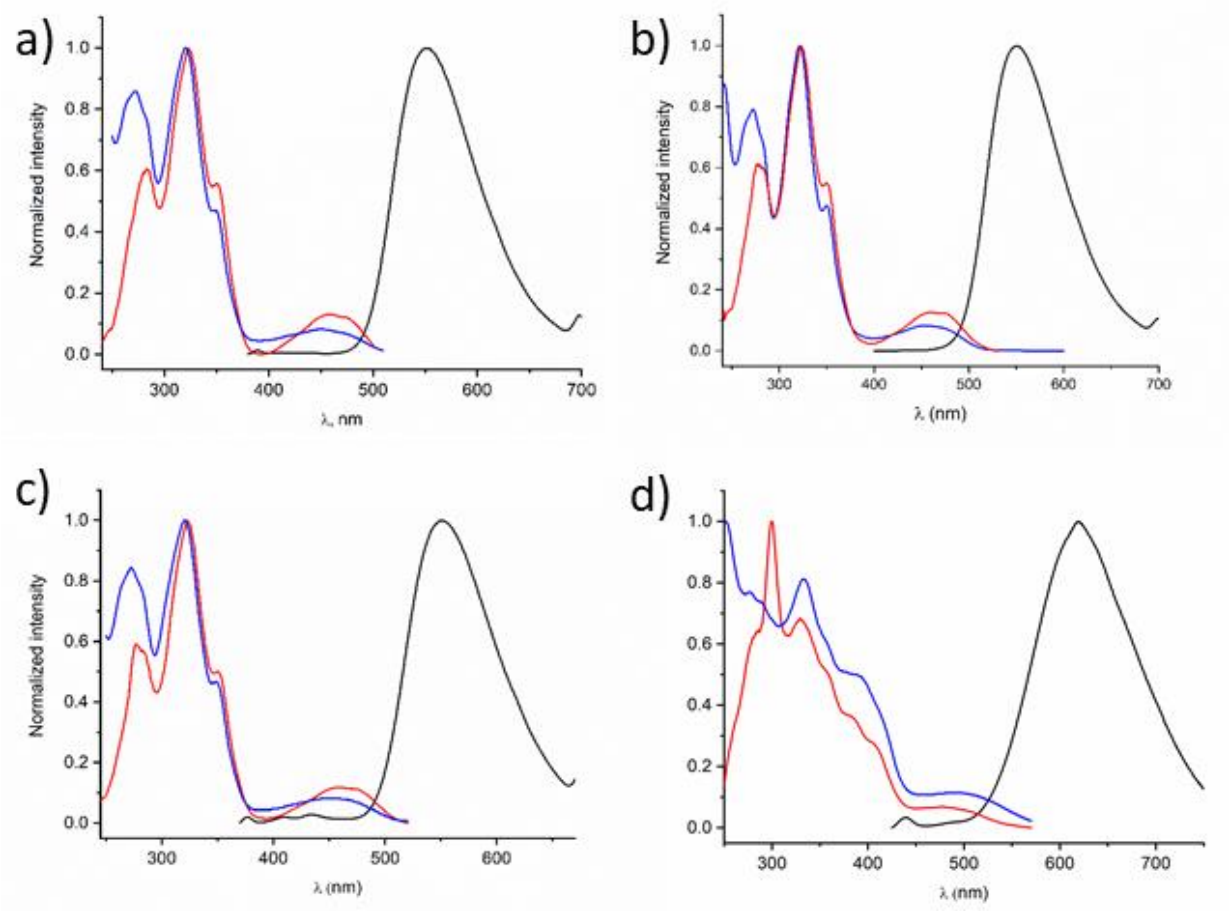


Figure S1. Normalized emission and excitation spectra (λ_{em} = 350 nm ; λ_{exc} = 530 nm) of the complexes a) **1**, b) **2**, c) **3** and d) **4** (THF, 10^{-5}M range, blue: absorption ; red: excitation ; black : emission).

	1	**2**	**3**	**4**
%QY	12	10	16	2.5
$\tau_{1/2}$ (ns)	1.2 ; 5.4	1.6 ; 6.1	1.3 ; 5.4	1.09 ; 3.15

Table S1: Quantum yields (QS 0.1N H_2SO_4) and fluorescence lifetime for compounds **1-4**.

X-Ray structure determinations Details about data collection and solution refinement are given in Table S2. Data collections were performed on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K_α radiation (λ = 1.54184 Å). The structures were solved by intrinsic phasing and refined on F^2 by full matrix least-squares techniques with SHELX programs (SHELXT 2018/2 and SHELXL 2018/3)[1,2] using the ShelXle and the Olex2 graphical user interfaces.[3,4] All non-H atoms were refined anisotropically and absorption was corrected by Gaussian

technique for **4** or multiscan empirical absorption using spherical harmonics with CrysAlisPro program for **1**, **8** and **9**. The H atoms were placed at calculated positions and refined using a riding model. Compound **1**, despite numerous crystallization trials and several X-Ray experiments with extended exposure time, could only be obtained as small needles with a weak diffracting power. The best data set was used and a cut-off at 1 Å was applied. Crystallographic data for the four structures have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 2080969 for **1**, 2080966 for **4**, 2080967 for **8**, 2080968 for **9**. These data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

	1	**4**	**8**	**9**
Formula sum	$C_{88}H_{68}N_4O_6Zn_2$	$C_{48}H_{36}N_2O_4Zn$	$C_{20}H_{15}NO_2$	$C_{19}H_{12}O_2$
Formula weight	1408.20	770.16	301.33	272.29
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	19.960(3)	8.1499(14)	10.7403(2)	16.1657(14)
b/Å	8.349(2)	30.4057(15)	10.84250(16)	4.0638(4)
c/Å	20.342(4)	17.238(3)	13.7128(3)	20.4368(16)
α/°	90	90	90	90
β/°	90.642(13)	121.19(2)	109.066(2)	109.294(9)
γ/°	90	90	90	90
V/Å^3	3389.7(13)	3654.2(13)	1509.27(5)	1267.2(2)
Z	2	4	4	4
D_c/g cm^{-3}	1.380	1.400	1.326	1.427
T/K	150.00(10)	293(2)	150.00(10)	150.00(10)
μ/mm^{-1}	1.360	1.334	0.686	0.734
Reflections collected	13252	13412	10197	5945
Independent reflection	7046[R_{int} = 0.1775]	6896[R_{int} = 0.1067]	3167[R_{int} = 0.0201]	2583[R_{int} = 0.0257]
final $R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0853/ 0.1557	0.0933/ 0.2204	0.0370/0.0986	0.0454/0.1218
$R_1{}^a$,$wR_2{}^b$ (all data)	0.2592/ 0.2361	0.1700/0.2875	0.0397/0.1021	0.510/0.1290
goodness-of-fit on F^2	0.940	1.026	1.055	1.036
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	-0.23/0.37	-0. 89/0.86	-0.21/0.18	-0.25/0.18
Completeness (%)	99.2 (1 Å resolution)	98.8	100.0	99.7
CCDC number	2080969	2080966	2080967	2080968

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2)+(aP)^2+bP]$ where $P= [max(F_0^2, 0) + 2F_c^2]/3$.

Table S2 : Crystallographic data, details of data collection and structure refinement parameters for compounds **1**, **4**, **8** and **9**.

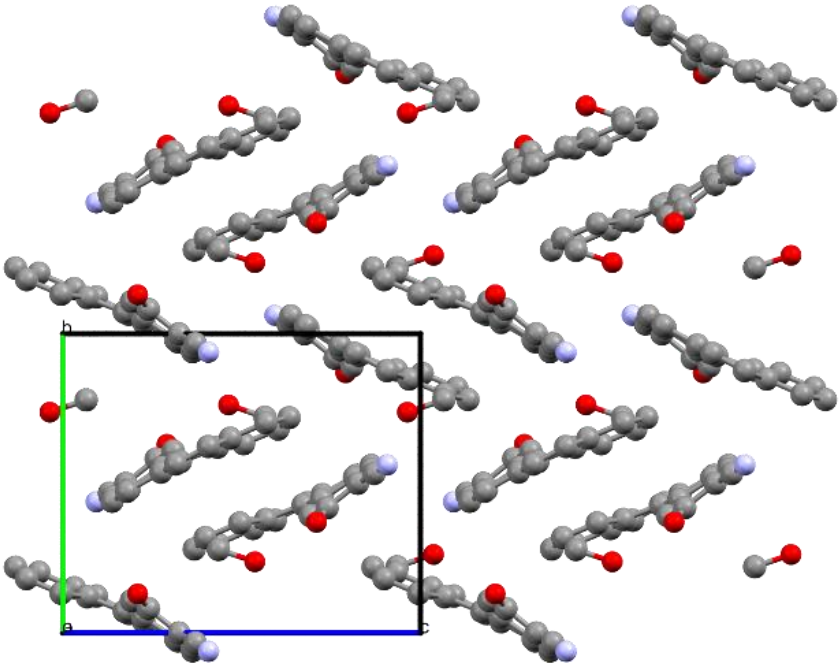


Figure S2. Packing diagram along *a* for compound **8** (hydrogen atoms omitted for the sake of clarity).

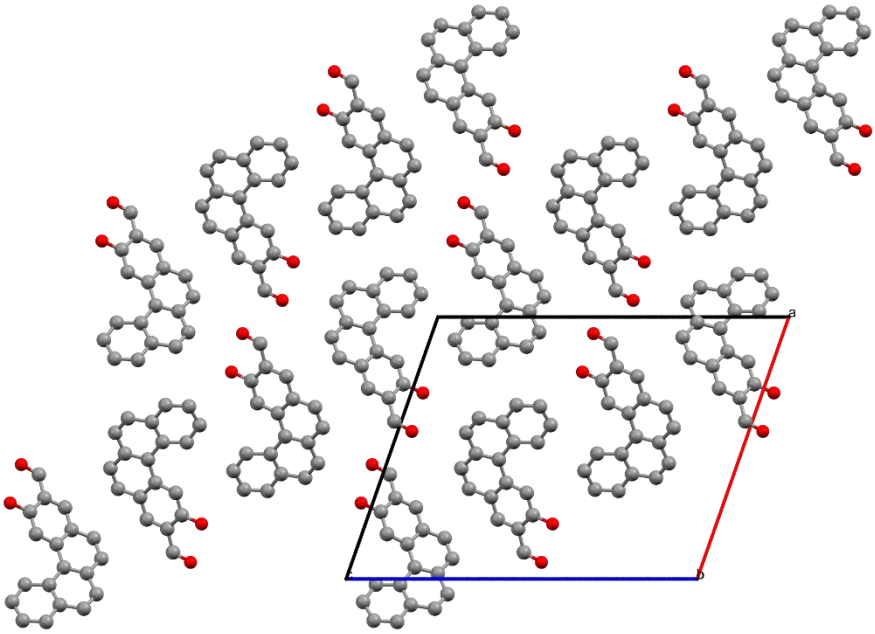


Figure S3. Packing diagram along b for compound **9** (hydrogen atoms omitted for the sake of clarity).

8			**9**		
C1	C2	1.376(2)	C1	C2	1.379(3)
C2	C3	1.403(2)	C2	C3	1.399(2)
C3	C4	1.365(2)	C3	C4	1.370(3)
C4	C5	1.411(2)	C4	C5	1.409(2)
C5	C6	1.431(2)	C5	C6	1.429(2)
C6	C1	1.419(1)	C5	C7	1.426(2)
C5	C7	1.426(1)	C7	C8	1.349(2)
C7	C8	1.347(2)	C8	C9	1.432(2)
C8	C9	1.430(2)	C9	C10	1.411(2)
C9	C10	1.413(1)	C10	C6	1.456(2)
C10	C6	1.454(2)	C9	C11	1.429(2)
C9	C11	1.429(2)	C11	C12	1.350(2)
C11	C12	1.348(2)	C12	C13	1.425(2)
C12	C13	1.430(1)	C13	C14	1.430(2)
C13	C14	1.430(1)	C14	C10	1.457(2)
C14	C10	1.458(2)	C13	C15	1.404(2)
C13	C15	1.404(2)	C15	C16	1.383(2)
C15	C16	1.381(1)	C16	C17	1.415(2)
C16	C17	1.415(2)	C17	C18	1.380(2)
C17	C18	1.380(2)	C18	C14	1.416(2)
C18	C14	1.414(1)	C16	C19	1.456(2)
C16	C19	1.435(2)	C19	O1	1.228(2)
C19	N1	1.143(2)	C17	O2	1.360(2)
C17	O1	1.349(1)	O2	O1	2.674(2)
O1	O2	2.658(1)			
O2	C20	1.396(2)			
Dihedral angle between the planes C1-C2-C3-C4-C5-C6 and C13-C14-C15-C16-C17-C18		22.51	Dihedral angle between the planes C1-C2-C3-C4-C5-C6 and C13-C14-C15-C16-C17-C18		27.12

Table S3. Selected bond distances (Å) and dihedral angle between two aromatic helicene planes for compounds **8** and **9**.

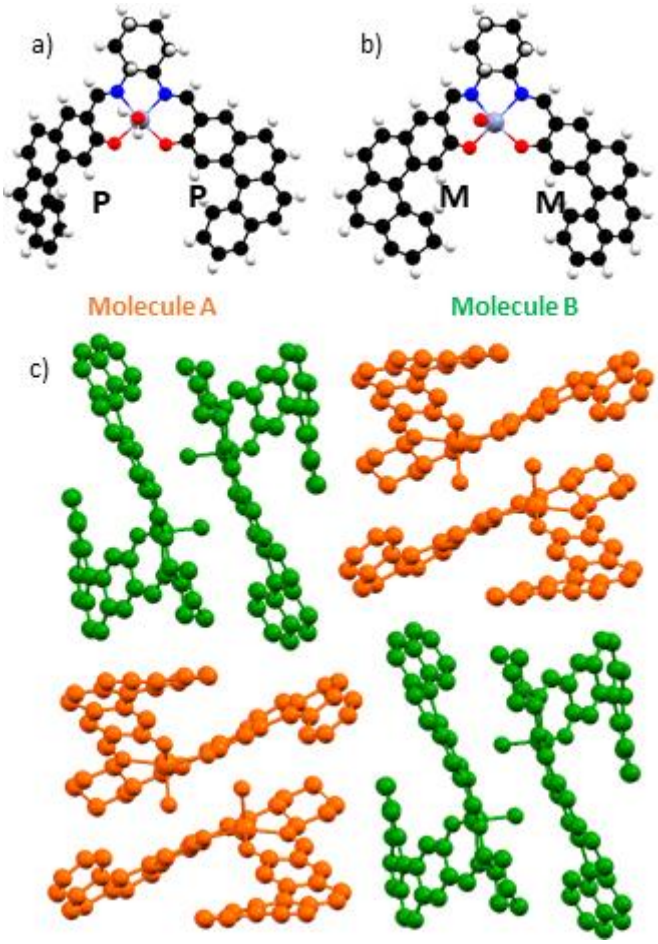


Figure S4. X-ray structure of complex **1** (Carbon: black ; Nitrogen : blue ; Oxygen : red ; Zinc : grey ; Hydrogen : white) and packing diagram along *b* for compound **1** (hydrogen atoms omitted for the sake of clarity).

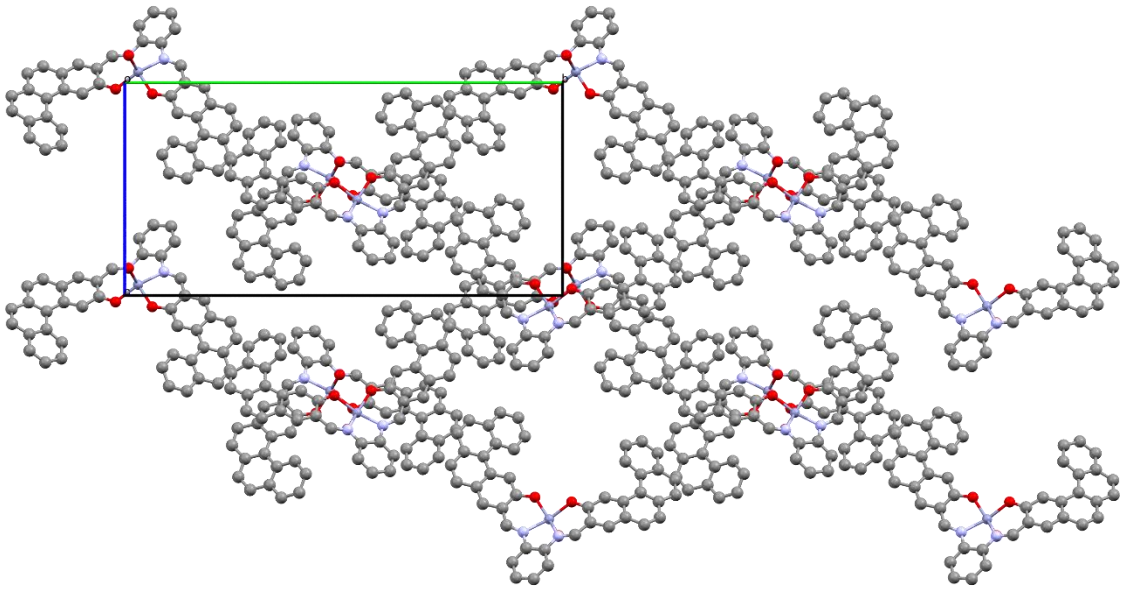


Figure S5. Packing diagram along *a* for compound **4** (hydrogen atoms and solvent molecule omitted for the sake of clarity).

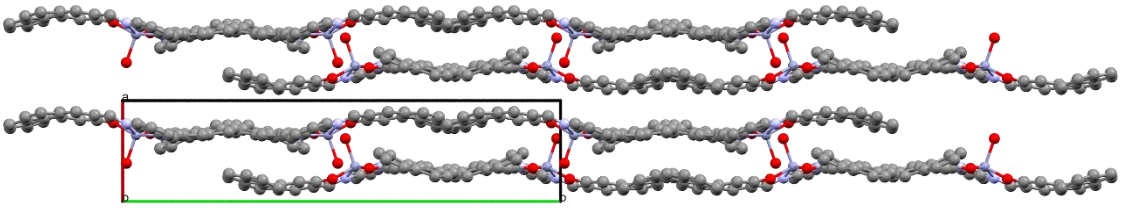


Figure S6. Packing diagram along *c* for compound **4** (hydrogen atoms and solvent molecule omitted for the sake of clarity).

1A (*R,R/P,P*)				**1B (*R,R/M,M*)**				**4**			
O1	Zn1	N1	91(1)	O4	Zn2	N3	90(1)	N1	Zn1	O2	90.5(3)
N1	Zn1	N2	80(1)	N3	Zn2	N4	79(1)	N1	Zn1	N2	79.6(3)
N2	Zn1	O2	90(1)	N4	Zn2	O5	90(1)	N2	Zn1	O3	89.2(2)
O2	Zn1	O1	93(1)	O5	Zn2	O4	96(1)	O3	Zn1	O2	89.1(2)
O1	Zn1	O3	101.0(9)	O4	Zn2	O6	96.0(9)	O2	Zn1	O4	106.3(2)
N1	Zn1	O3	102(1)	N3	Zn2	O6	94(1)	O3	Zn1	O4	100.7(2)
N2	Zn1	O3	102(1)	N4	Zn2	O6	114(1)	N2	Zn1	O4	100.5(3)
O2	Zn1	O3	93.3(9)	O5	Zn2	O6	98.0(9)	N1	Zn1	O4	104.2(3)
Dihedral angle between the planes C1-C2-C3-C4-C5-C6 and C13-C14-C15-C16-C17-C18			23.74	Dihedral angle between the planes C45-C46-C47-C48-C49-C50 and C57-C58-C59-C60-C61-C62			33.51	Dihedral angle between the planes C5-C6-C7-C8-C9-C10 and C17-C18-C19-C20-C21-C22			25.64
Dihedral angle between the planes C27-C28-C29-C30-C31-C32 and C39-C40-C41-C42-C43-C44			29.88	Dihedral angle between the planes C71-C72-C73-C74-C75-C76 and C83-C84-C85-C86-C87-C88			19.42	Dihedral angle between the planes C31-C32-C33-C34-C35-C36 and C43-C44-C45-C46-C47-C48			28.16

Table S4. Selected bond angles (˚) around the Zn atom and dihedral angle between two aromatic helicene planes for compounds **1** and **4**.

DFT and TD-DFT calculations

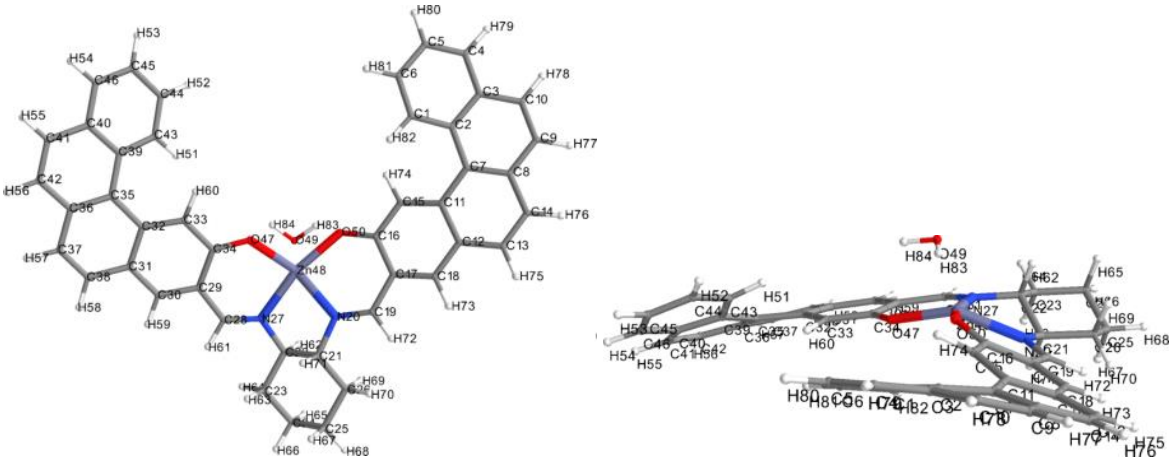


Figure S7. Chemical structure diagram of **1A (*R,R/P,P*)** with atomic numbering from two points of view.

1A (*R,R/P,P*)		
Total molecular energy	-3807.62956 Hartrees	
HOMO number	183	
LUMO+1 energies	-1.81 eV	
LUMO energies	-1.98 eV	
HOMO energies	-5.30 eV	
HOMO-1 energies	-5.40 eV	
Mean Mulliken atomic charge and standard deviation	0.0000 e-	0.1504 e-
Atoms with negatives charges under the standard deviation	**N°**	**Mulliken charge**
	O 50	-0.502
	O 47	-0.476
	N 20	-0.337
	N 27	-0.335
	O 49	-0.276
	C 33	-0.163
	C 15	-0.161
Atoms with positives charges over the standard deviation	**N°**	**Mulliken charge**
	H 84	+0.188
	H 83	+0.194
	C 34	+0.263
	C 16	+0.289
	Zn 48	+0.842
Geometry optimization specific results		
Converged nuclear repulsion energy	6594.70450 Hartrees	
Frequency and Thermochemistry specific results		
Sum of electronic and zero-point energy	-3806.95391 Hartrees	
Sum of electronic and thermal energies at 298.15 K	-3806.91444 Hartrees	
Enthalpy at 298.15 K	-3806.91350 Hartrees	
Gibbs free energy at 298.15 K	-3807.02704 Hartrees	
Entropy at 298.15 K	0.00038 Hartrees	

Table S5. Calculation report for **1A (*R,R/P,P*)**.

Frequencies	Intensity	Symmetry
3854	174	A
3654	394	A

1750	519	A
1727	1411	A
1715	103	A
1712	620	A
1693	105	A
1690	320	A
1683	327	A
1676	176	A
1675	291	A
1624	65	A
1575	88	A
1565	109	A
1551	171	A
1539	60	A
1504	168	A
1488	83	A
1397	122	A
1236	72	A
1229	78	A
1199	122	A
1197	52	A
786	74	A

Table S6. Most intense (> 20 km/mol) molecular vibrations in wavenumbersfor **1A (*R,R*/*P,P*)**.

E.S.	Symmetry	nm	cm^{-1}	Oscillator str.	Rotational str.	Tozer	dCT	qCT
1	Singlet-A	460	21714	0.005	-115.291	0.52	618.92	0.62
2	Singlet-A	450	22188	0.089	104.404	0.62	353.53	0.59
3	Singlet-A	422	23644	0.009	-10.359	0.54	438.09	0.6
4	Singlet-A	397	25161	0.006	0.666	0.44	731.92	0.76
5	Singlet-A	364	27460	0.267	-202.261	0.53	361.94	0.46
6	Singlet-A	355	28102	0.165	108.45	0.64	122.6	0.39
7	Singlet-A	338	29502	0.007	7.071	0.54	440.81	0.5
8	Singlet-A	330	30294	0.005	-13.906	0.45	449.43	0.5
9	Singlet-A	329	30375	0.151	64.346	0.55	317.46	0.39
10	Singlet-A	326	30626	0.012	-9.694	0.43	915.3	0.46
11	Singlet-A	324	30807	0.03	-0.163	0.53	344.57	0.42
12	Singlet-A	319	31309	0.426	-221.872	0.46	691.45	0.35
13	Singlet-A	317	31451	0.003	-3.263	0.39	561.66	0.49
14	Singlet-A	312	31987	0.637	284.714	0.53	308.06	0.32
15	Singlet-A	310	32249	0.027	16.884	0.45	836.72	0.66

Table S7. Results concerning the calculated mono-electronic excitations for **1A (*R,R*/*P,P*)**.

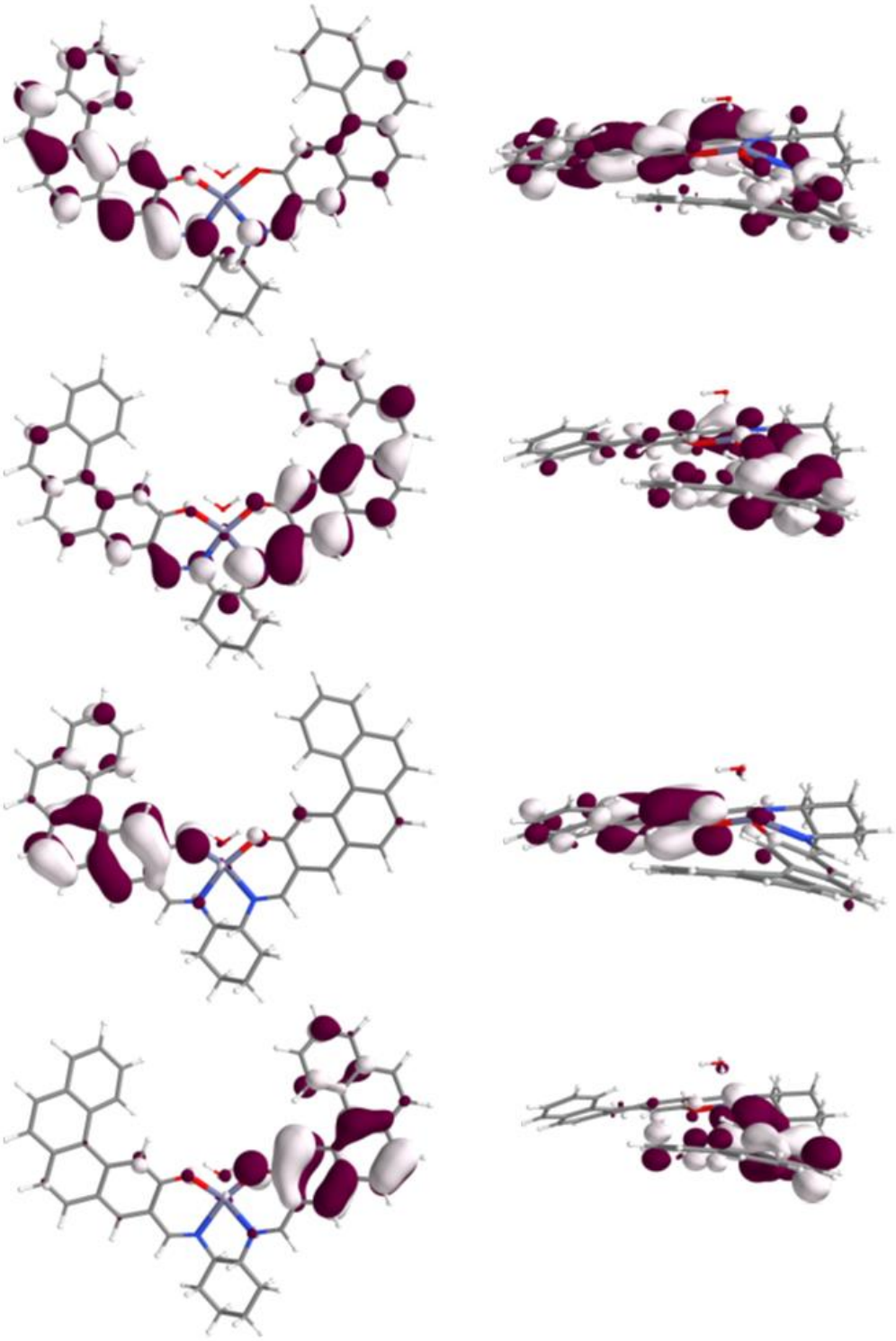


Figure S8. HOMO-1, HOMO, LUMO, and LUMO+1 (from bottom to top, two views each) for **1A (*R,R*/*P,P*)**.

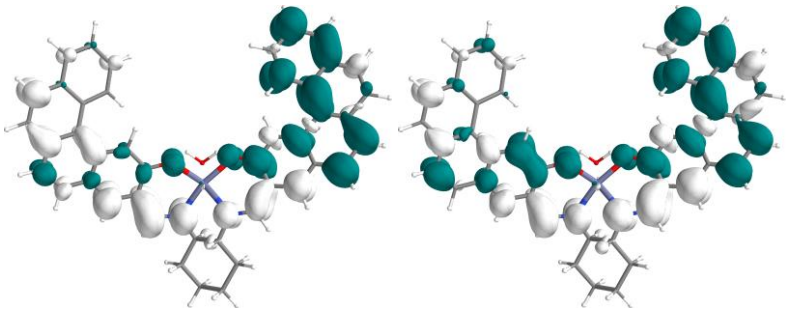


Figure S9. Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) for **1A (*R,R/P,P*)**. The excited electron and the hole regions are indicated by blue and white surfaces, respectively.

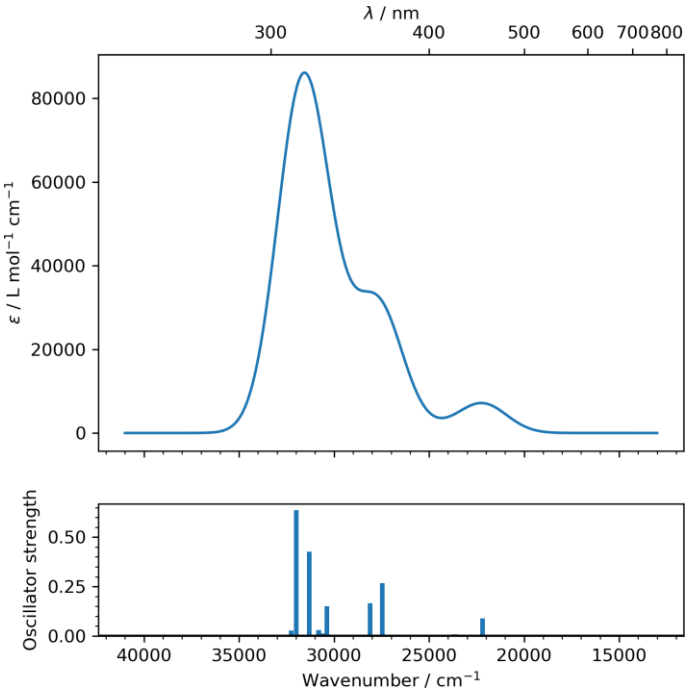


Figure S10. Calculated UV absorption spectrum for **1A (*R,R/P,P*)** with a gaussian broadening (FWHM = 3000 cm^{-1}).

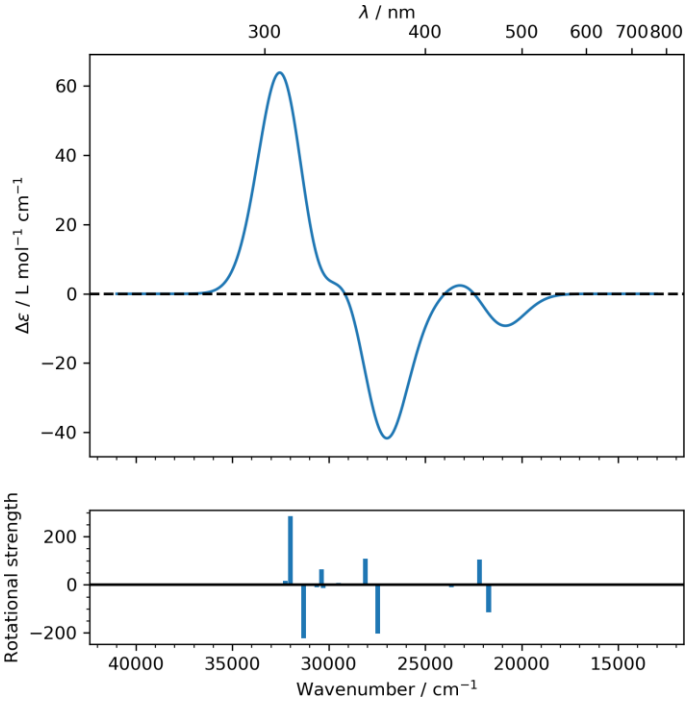


Figure S11. Calculated Circular Dichroism spectrum for **1A (*R,R/P,P*)** with a gaussian broadening (FWHM = 3000 cm^{-1}).

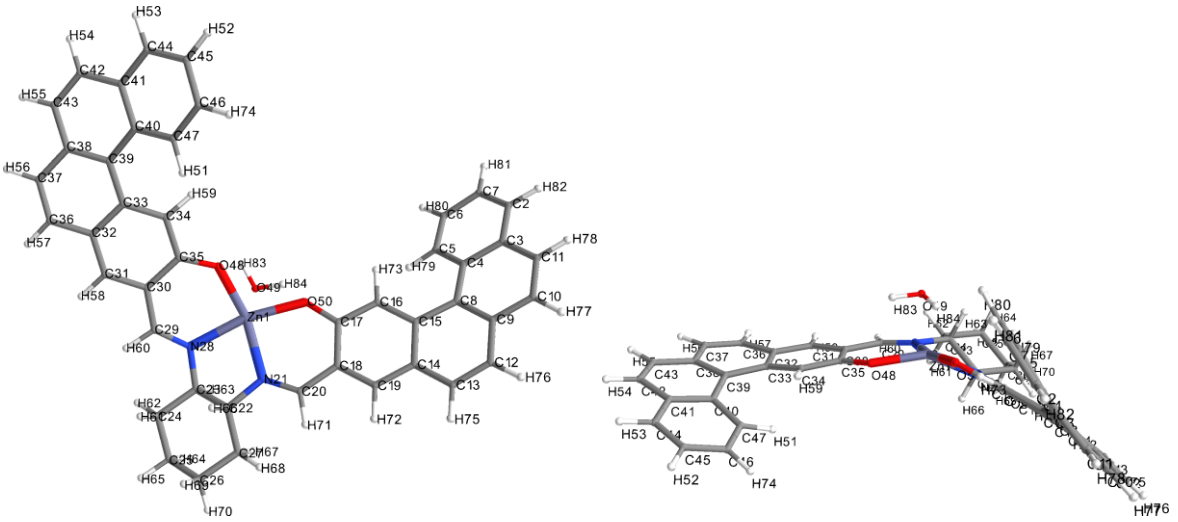


Figure S12. Chemical structure diagram of **1B (*R,R/M,M*)** with atomic numbering from two points of view.

1B (*R,R/M,M*)		
Total molecular energy	-3807.62944 Hartrees	
HOMO number	183	
LUMO+1 energies	-1.81 eV	
LUMO energies	-1.99 eV	
HOMO energies	-5.29 eV	
HOMO-1 energies	-5.40 eV	
Mean Mulliken atomic charge and standard deviation	0.0000 e-	0.1505 e-
Atoms with negatives charges under the standard deviation	**N°**	**Mulliken charge**
	O 50	-0.500
	O 48	-0.477
	N 21	-0.337
	N 28	-0.336
	O 49	-0.276
	C 16	-0.164
	C 34	-0.162
Atoms with positives charges over the standard deviation	**N°**	**Mulliken charge**
	H 83	+0.189
	H 84	+0.193
	C 35	+0.267
	C 17	+0.289
	Zn 1	+0.841
Geometry optimization specific results		
Converged nuclear repulsion energy	6583.11256 Hartrees	
Frequency and Thermochemistry specific results		
Sum of electronic and zero-point energy	-3806.95373 Hartrees	
Sum of electronic and thermal energies at 298.15 K	-3806.91426 Hartrees	
Enthalpy at 298.15 K	-3806.91332 Hartrees	
Gibbs free energy at 298.15 K	-3807.02723 Hartrees	
Entropy at 298.15 K	0.00038 Hartrees	

Table S8. Calculation report for **1B (*R,R/M,M*)**.

Frequencies	Intensity	Symmetry
3839	197	A
3654	373	A
1750	537	A
1727	1420	A
1715	102	A
1712	644	A
1693	94	A
1690	342	A
1683	335	A
1676	171	A
1675	309	A
1624	70	A
1575	92	A
1565	104	A
1551	178	A
1539	53	A
1504	171	A
1489	81	A
1398	125	A
1328	50	A
1299	53	A
1236	72	A

Table S9. Most intense (> 20 km/mol) molecular vibrations in wavenumbers for **1B (*R,R*/*M,M*)**.

E.S.	Symmetry	nm	cm^{-1}	Oscillator str.	Rotational str.	Tozer	dCT	qCT
1	Singlet-A	461	21659	0.014	-261.431	0.5	660.55	0.63
2	Singlet-A	451	22162	0.084	203.027	0.62	346.83	0.59
3	Singlet-A	425	23516	0.009	-8.579	0.53	499.98	0.61
4	Singlet-A	396	25221	0.006	6.688	0.41	756.34	0.78
5	Singlet-A	364	27420	0.272	-292.413	0.53	296.38	0.48
6	Singlet-A	356	28030	0.175	142.882	0.63	209.68	0.42
7	Singlet-A	341	29271	0.002	-3.679	0.52	515.96	0.55
8	Singlet-A	330	30226	0.001	-6.392	0.48	331.39	0.54
9	Singlet-A	328	30400	0.185	-544.048	0.54	289.91	0.42
10	Singlet-A	325	30696	0.031	73.714	0.51	738.16	0.44
11	Singlet-A	324	30791	0.037	31.674	0.44	701.48	0.43
12	Singlet-A	320	31223	0.232	-339.116	0.38	846.68	0.39
13	Singlet-A	317	31490	0.218	-389.484	0.3	895.78	0.49
14	Singlet-A	312	31983	0.576	722.044	0.51	315.56	0.34
15	Singlet-A	310	32172	0.05	67.78	0.34	855.81	0.70

Table S10. Results concerning the calculated mono-electronic excitations for **1B (*R,R*/*M,M*)**.

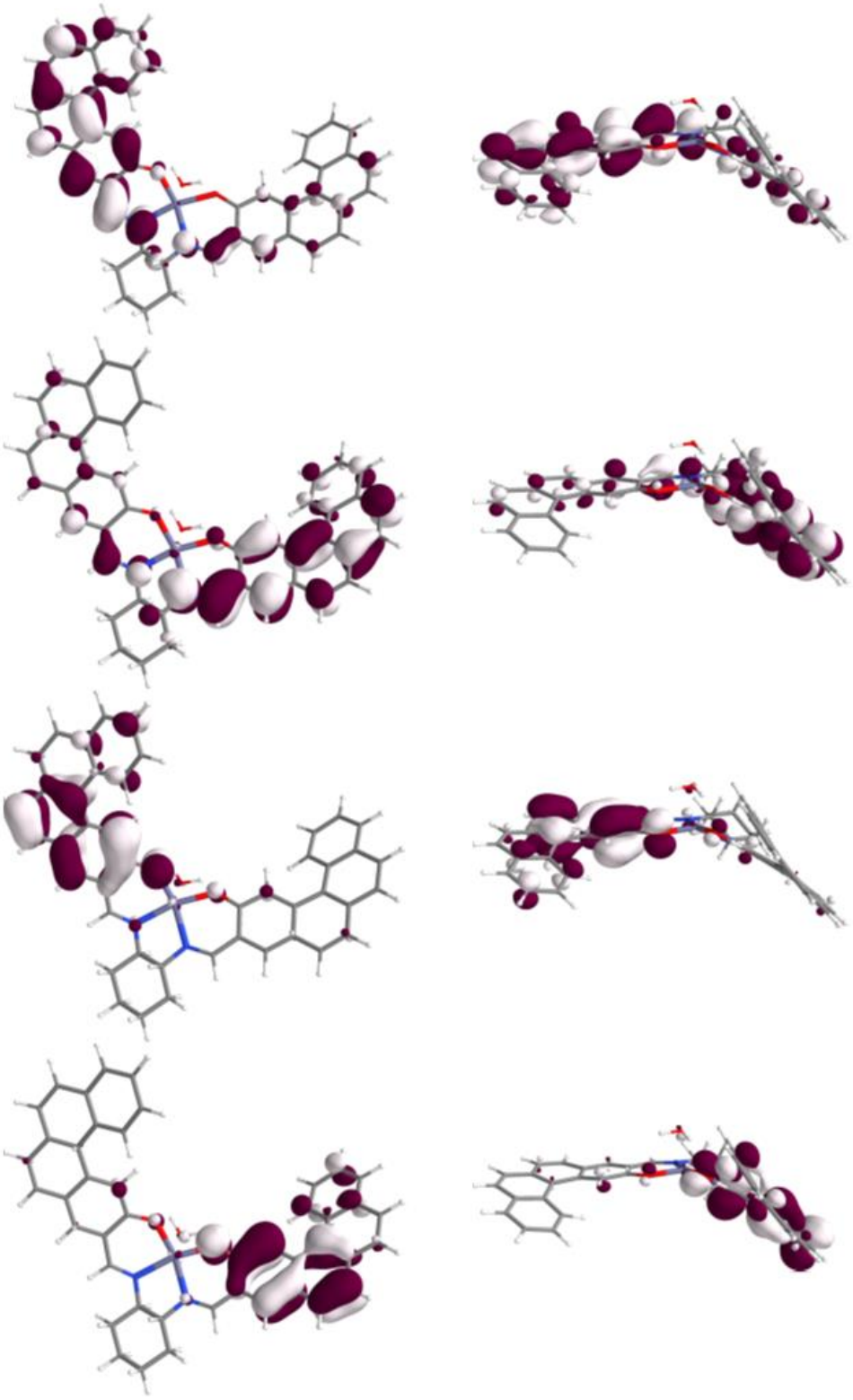


Figure S13. HOMO-1, HOMO, LUMO, and LUMO+1 (from bottom to top, two views each) for **1B (*R,R*/*M,M*)**.

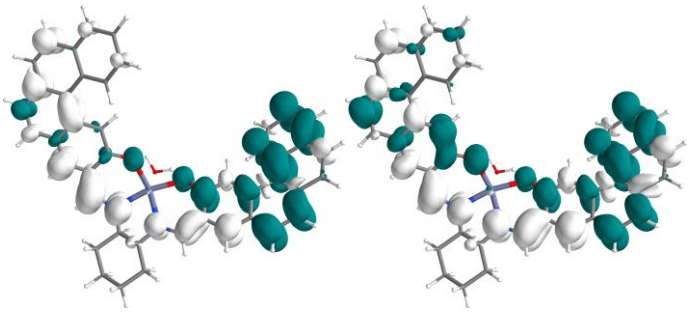


Figure S14. Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) for **1B (*R,R*/*M,M*)**. The excited electron and the hole regions are indicated by blue and white surfaces, respectively.

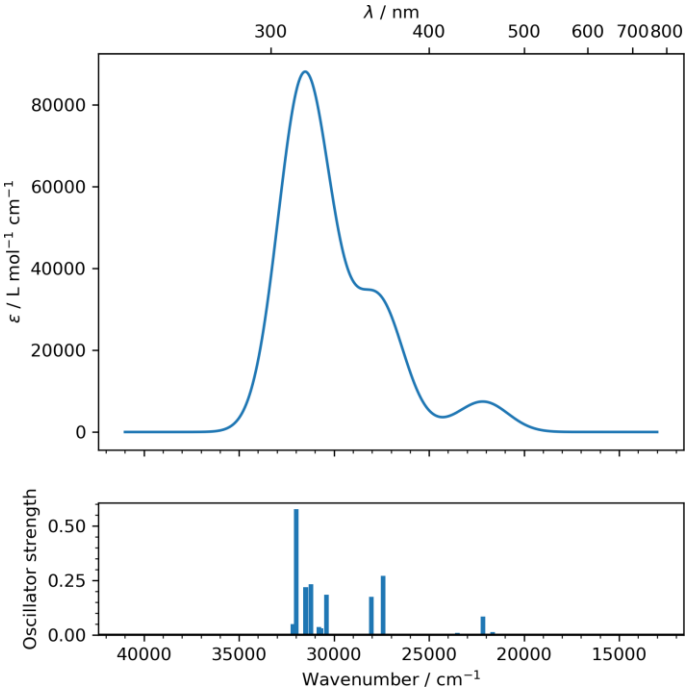


Figure S15. Calculated UV absorption spectrum for **1B (*R,R*/*M,M*)** with a gaussian broadening (FWHM = 3000 cm^{-1}).

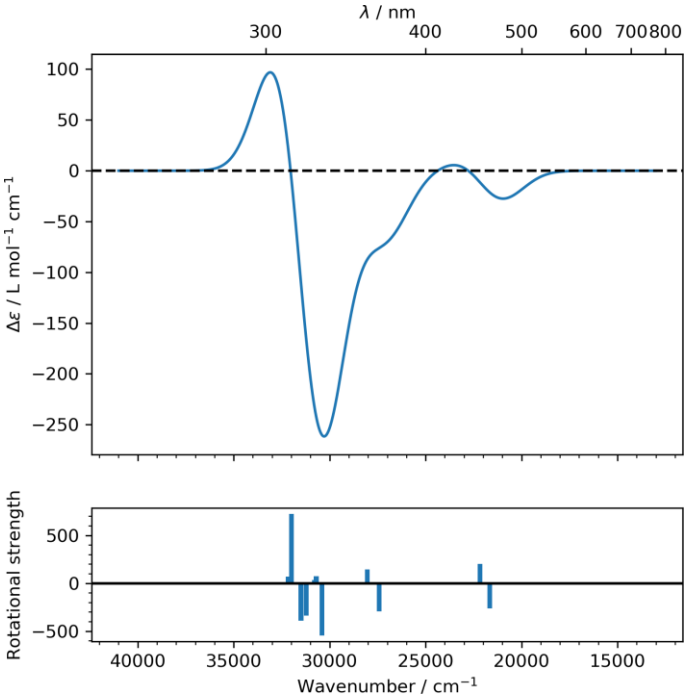
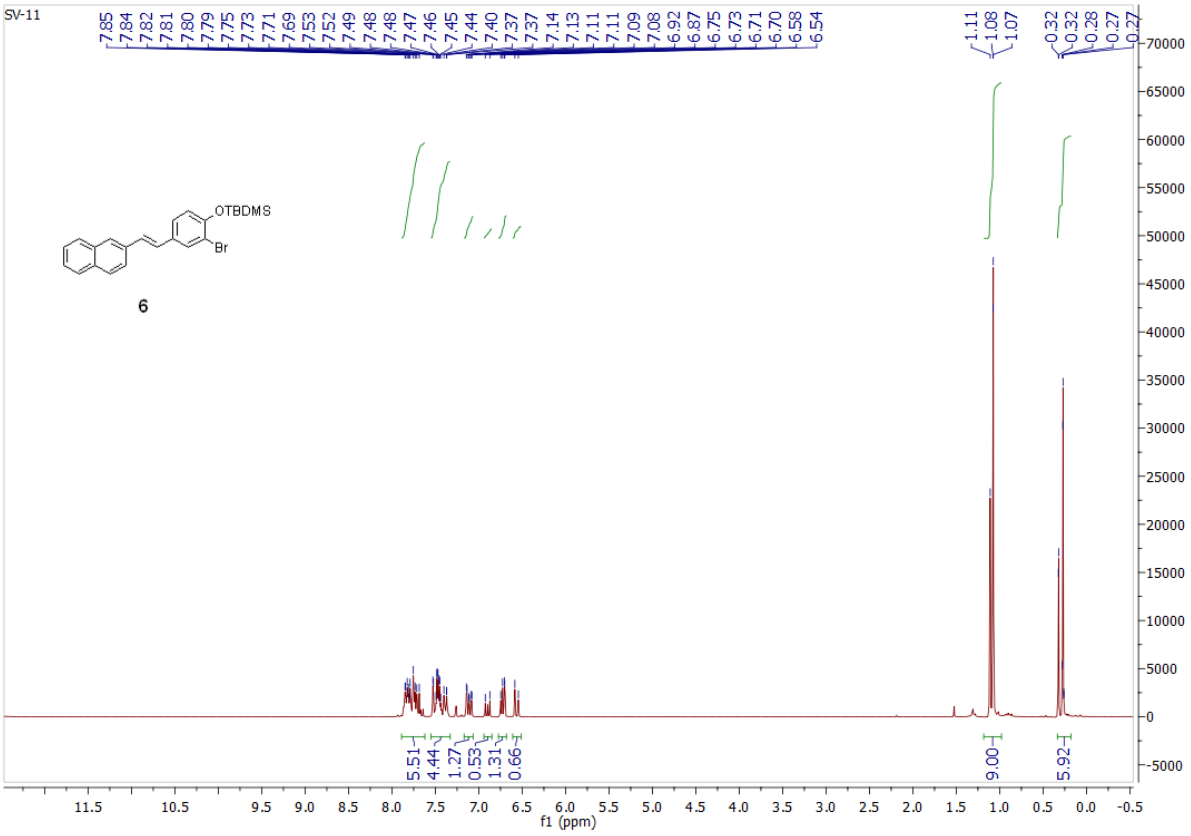
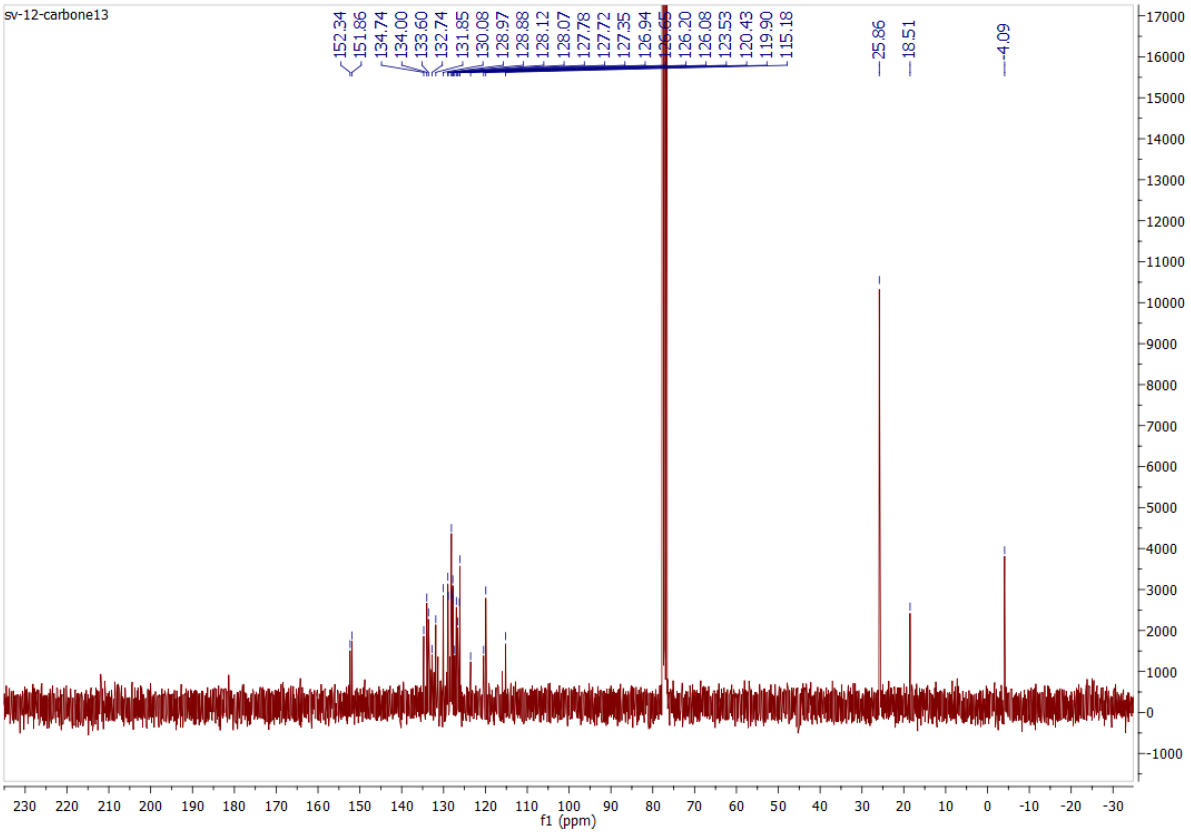


Figure S16. Calculated Circular Dichroism spectrum for **1B (*R,R*/*M,M*)** with a gaussian broadening (FWHM = 3000 cm^{-1}).

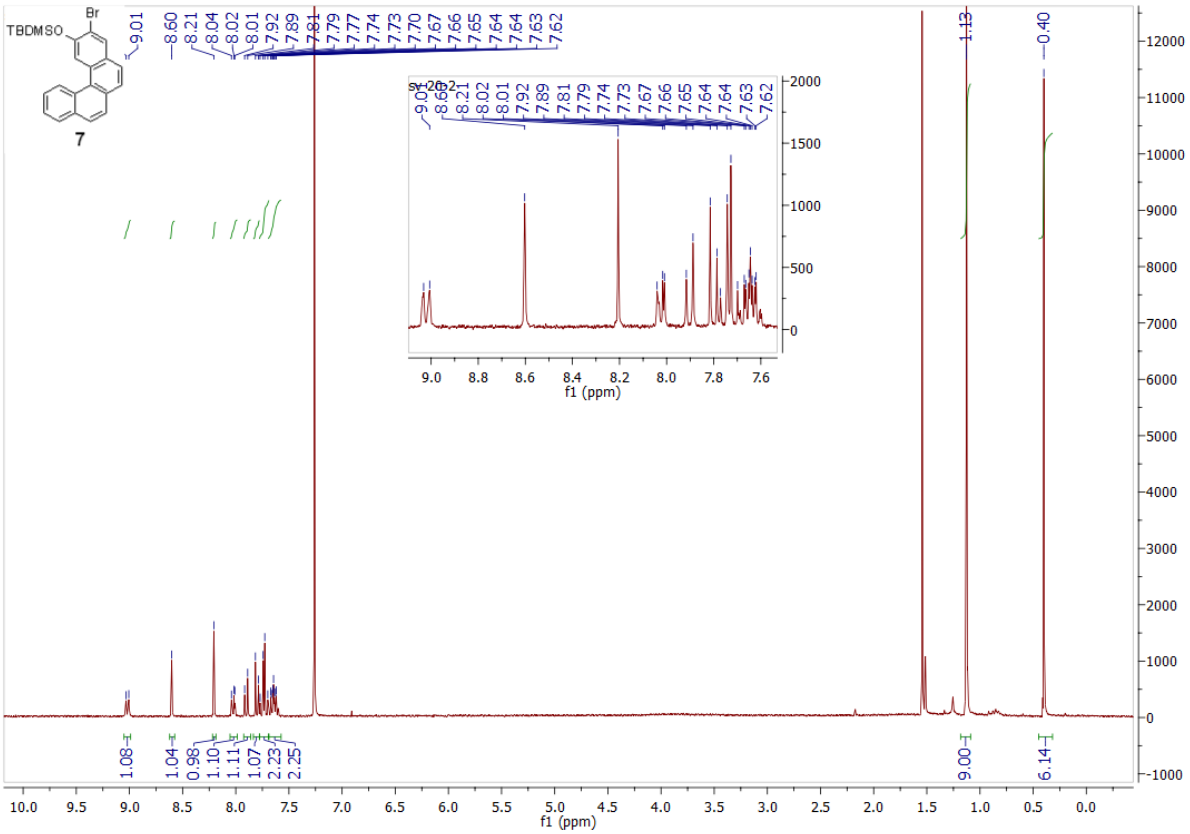
^{1}H NMR spectrum for compound **6.**



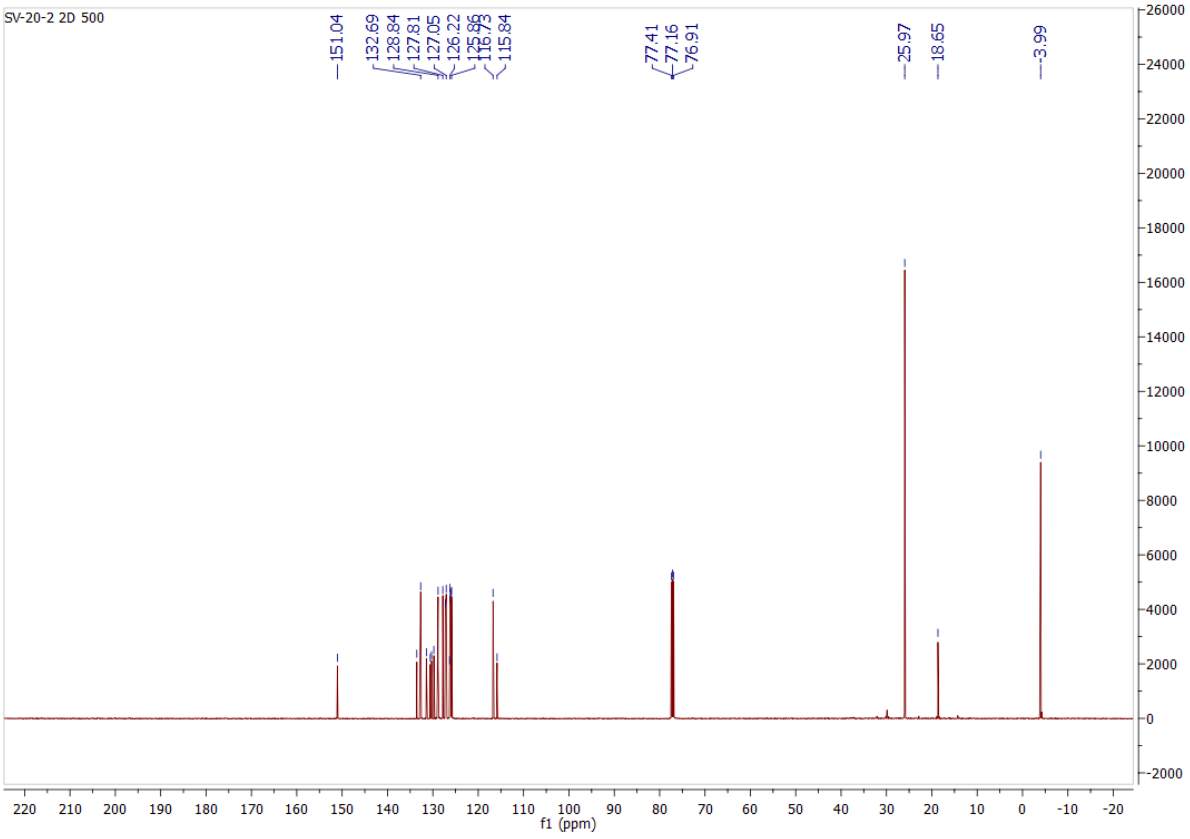
^{13}C NMR spectrum for compound **6.**



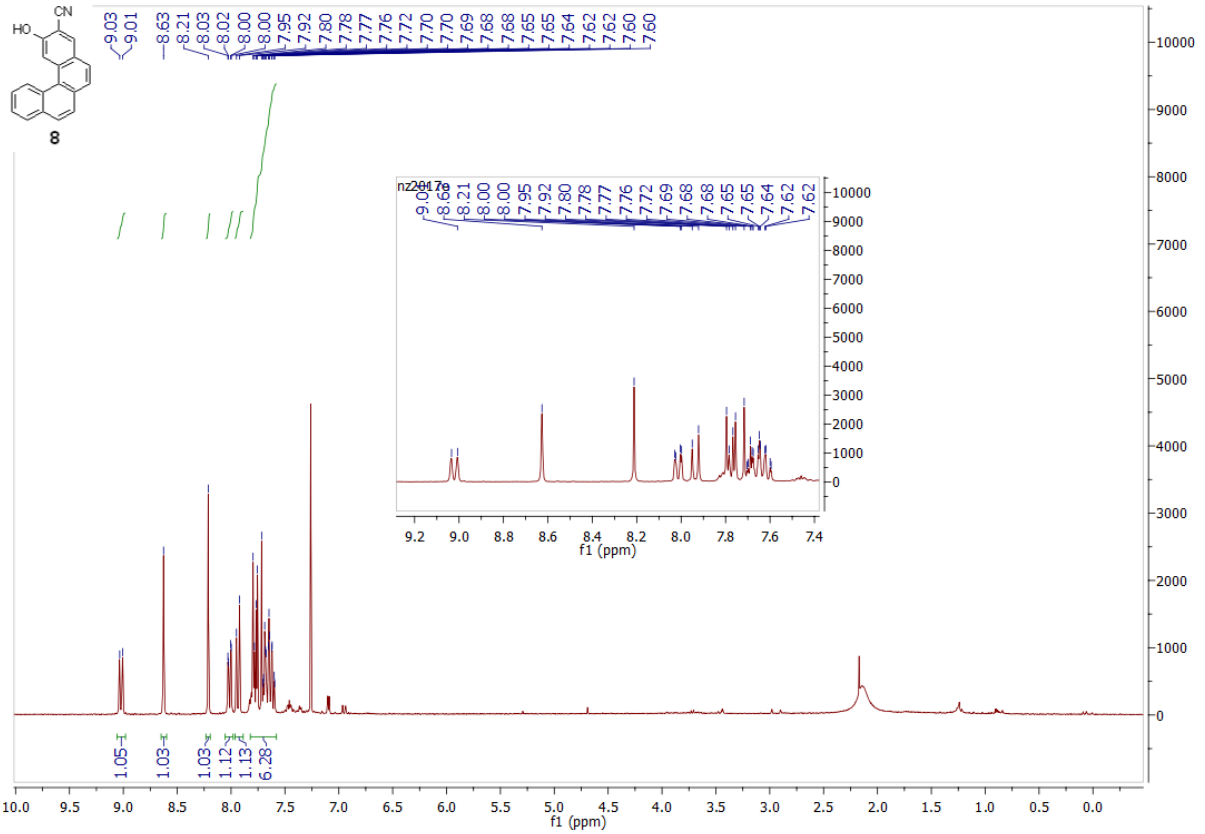
^{1}H NMR spectrum for compound **7.**



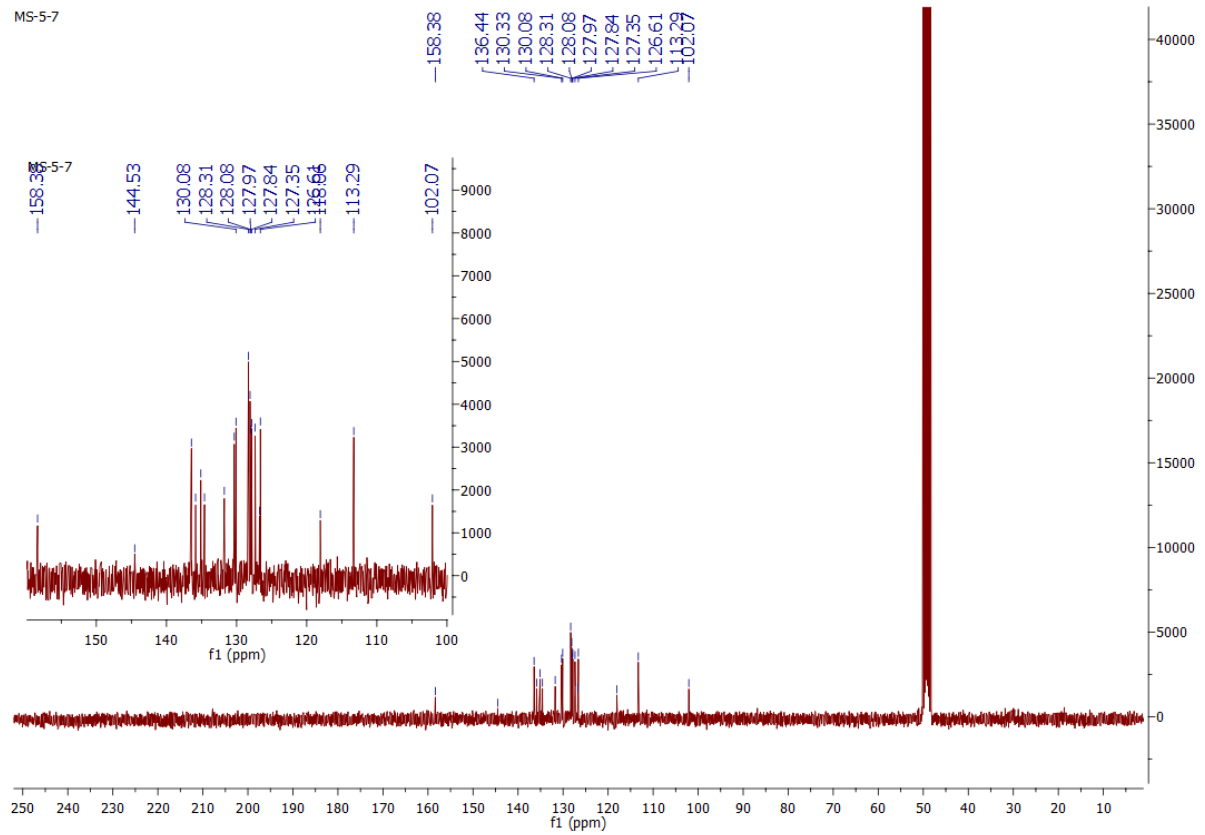
^{13}C NMR spectrum for compound **7.**



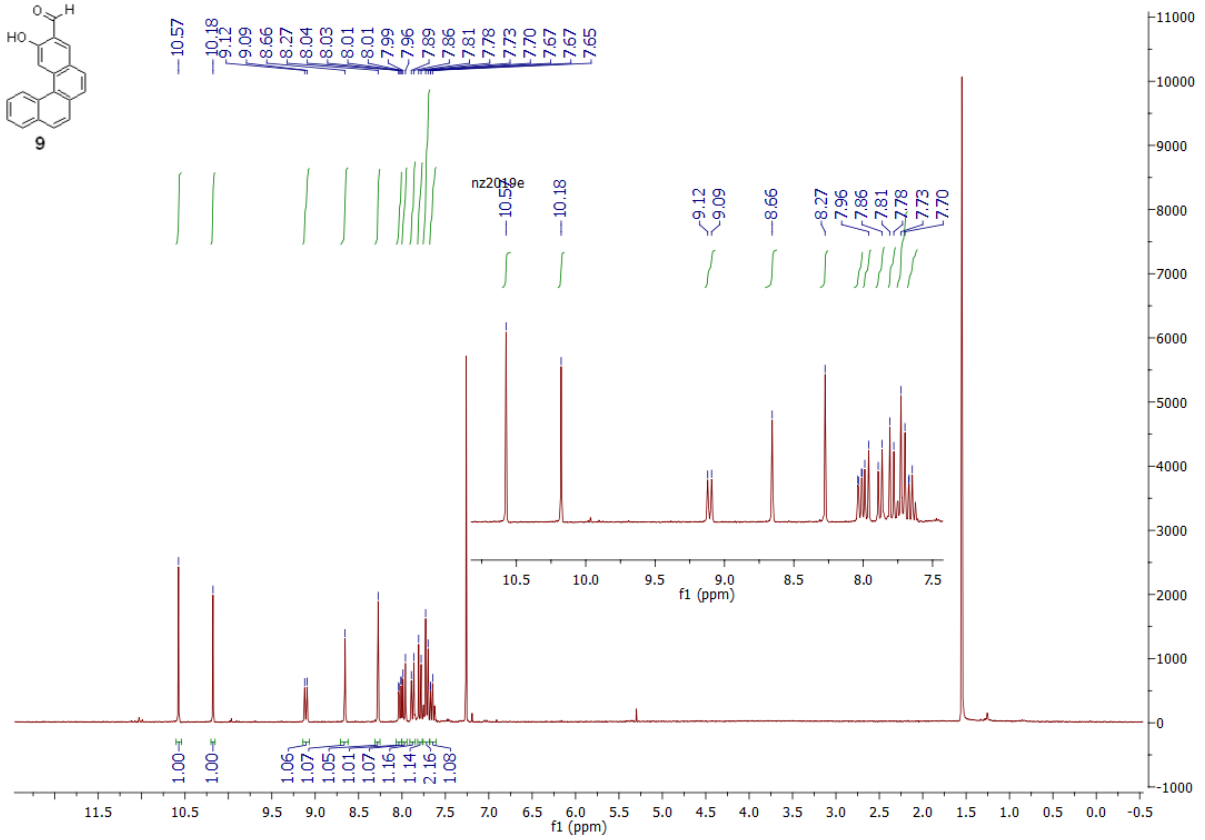
^{1}H NMR spectrum for compound **8.**



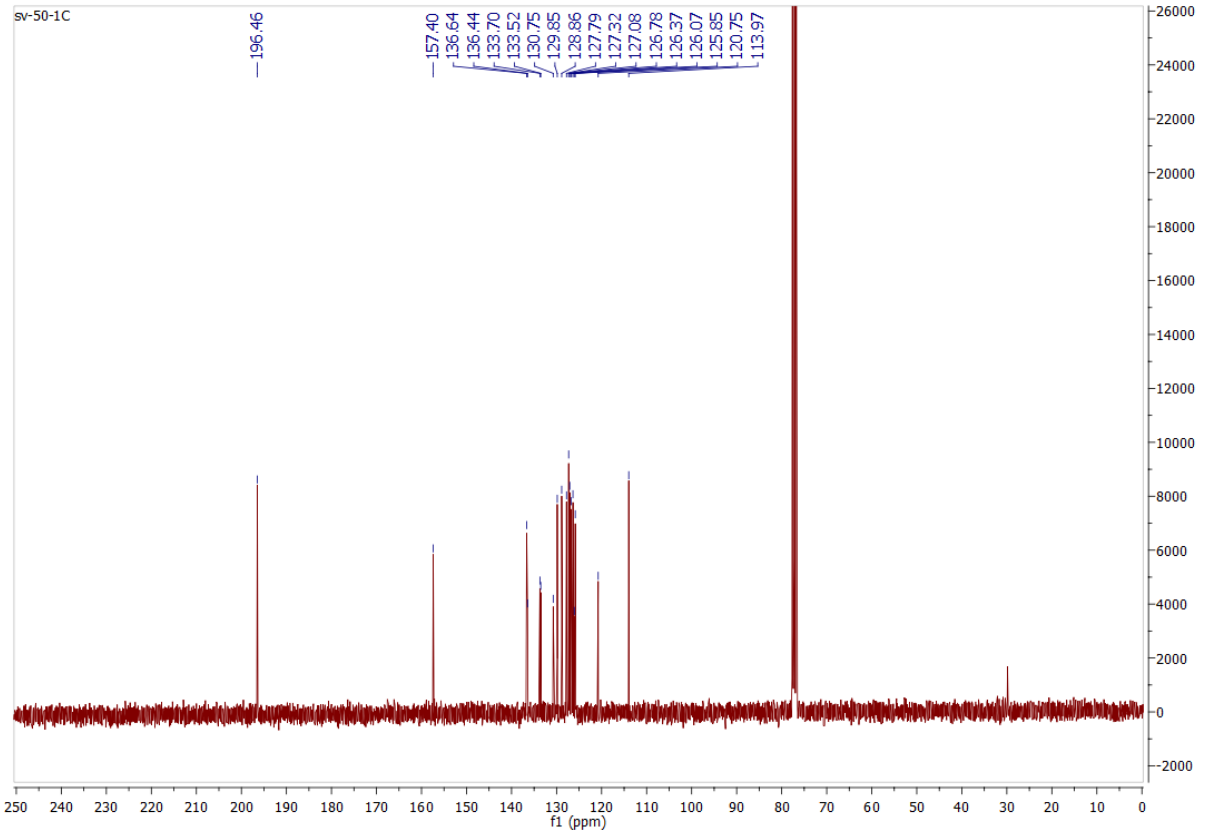
^{13}C NMR spectrum for compound **8.**



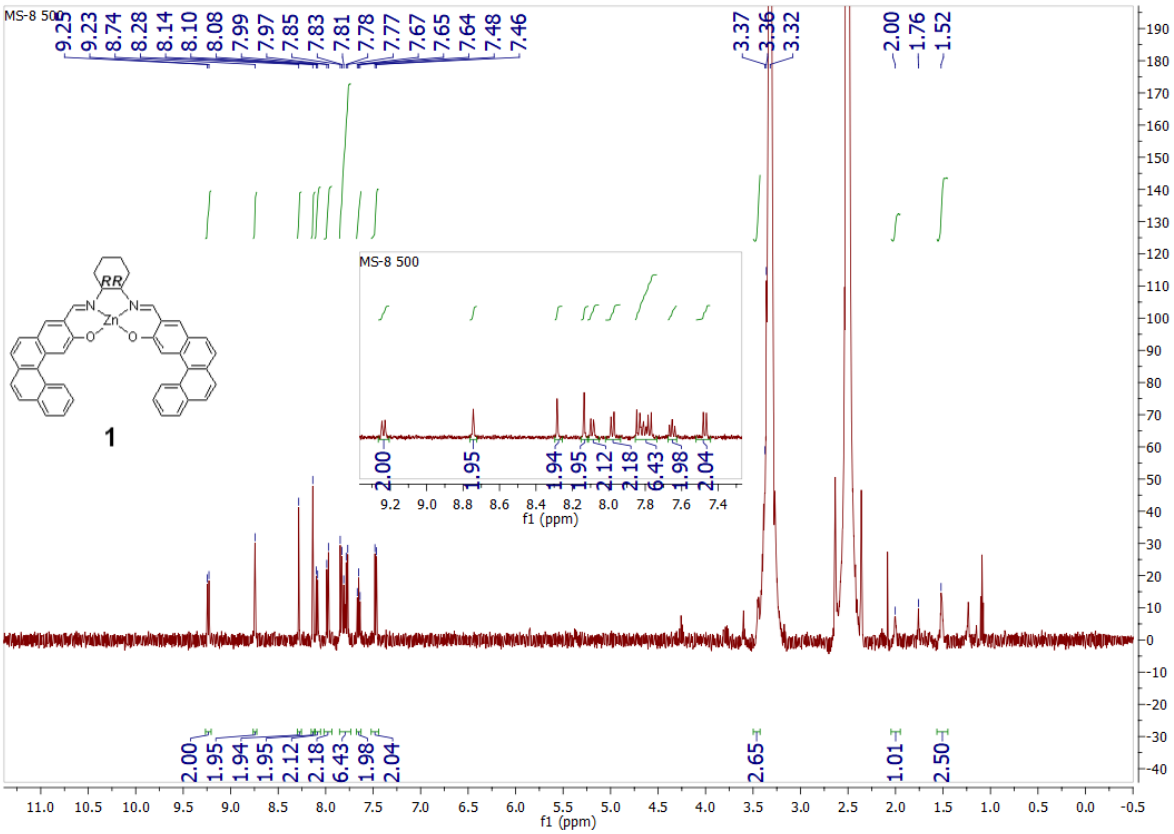
^{1}H NMR spectrum for compound **9.**



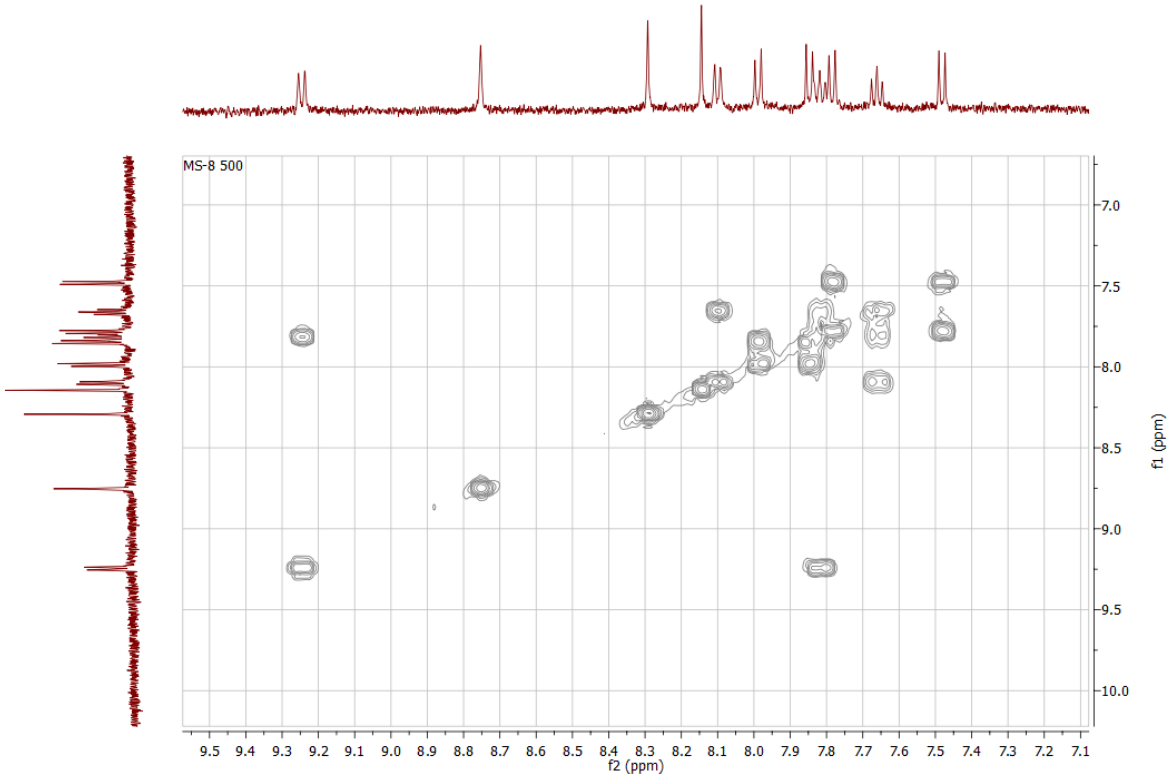
^{13}C NMR spectrum for compound **9.**



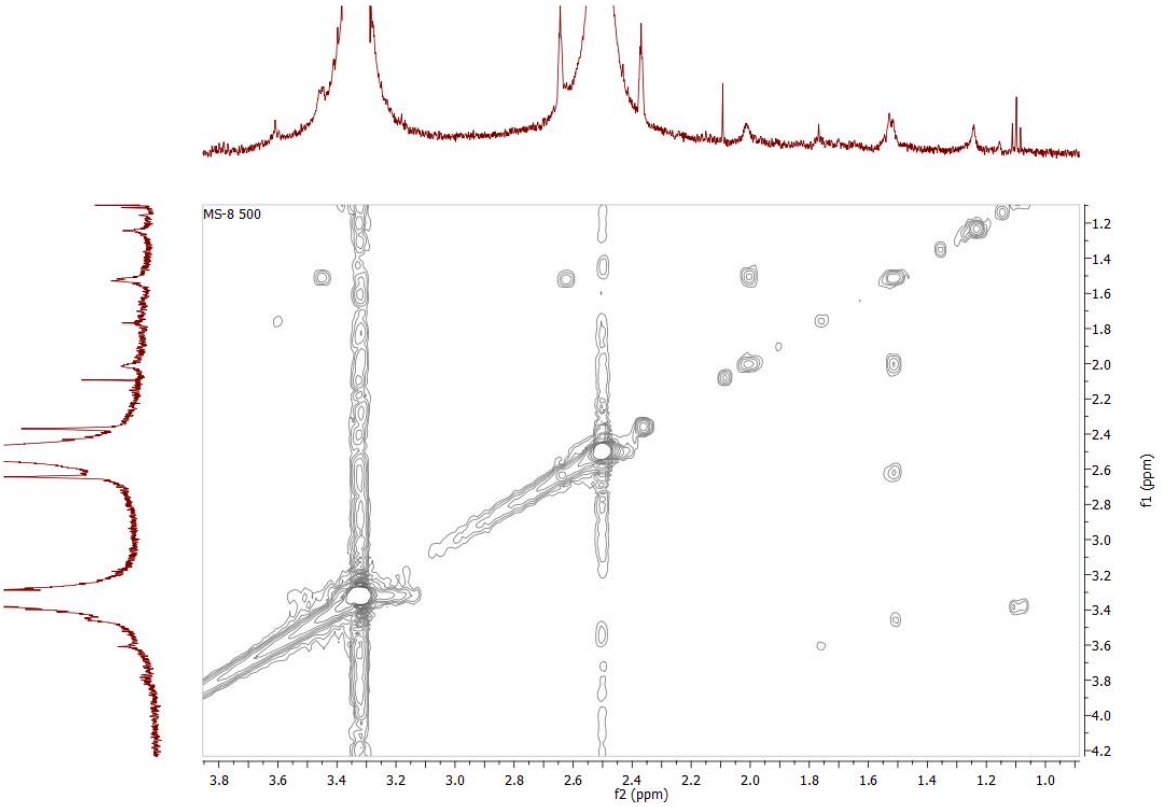
^{1}H NMR spectrum for compound **1.**



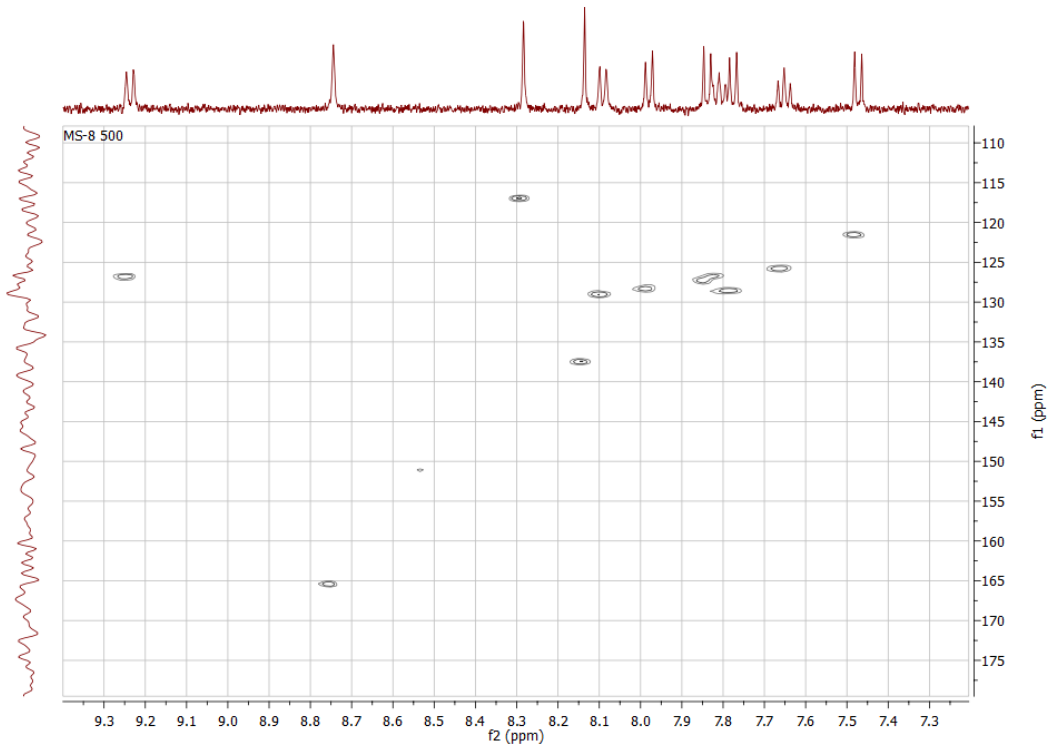
COSY ^{1}H-^{1}H 2-D NMR spectrum for compound **1** (aromatic region)**.**



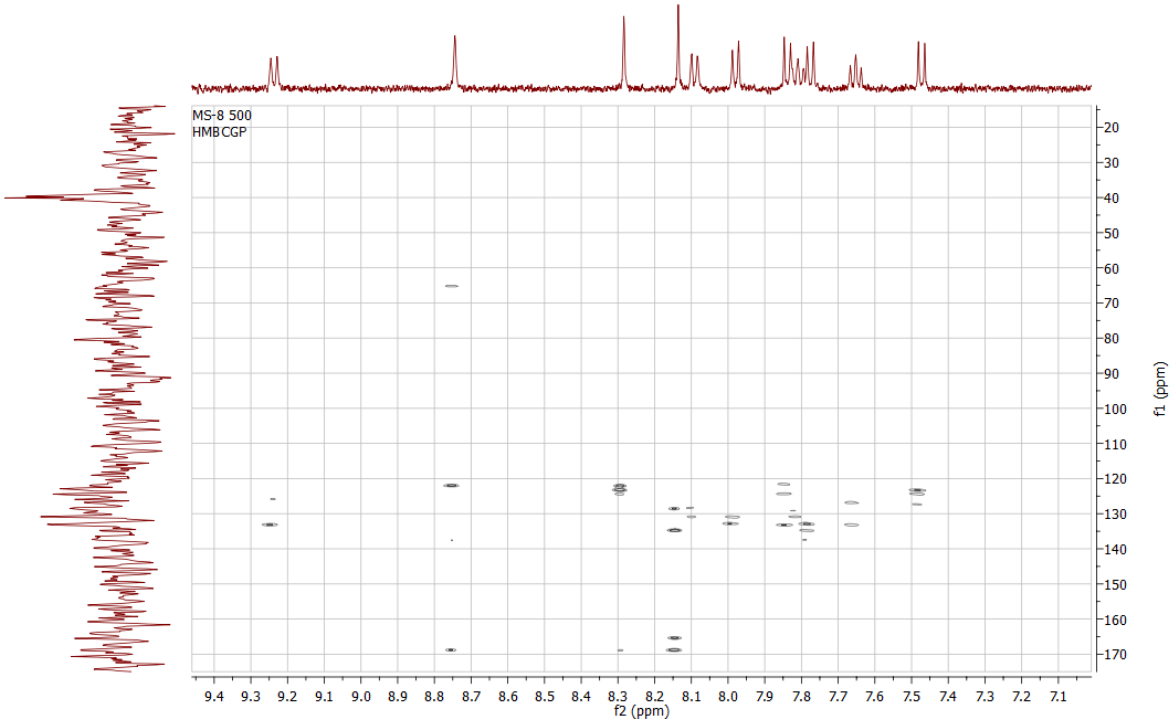
COSY ^{1}H-^{1}H 2-D NMR spectrum for compound **1** (aliphatic region)**.**



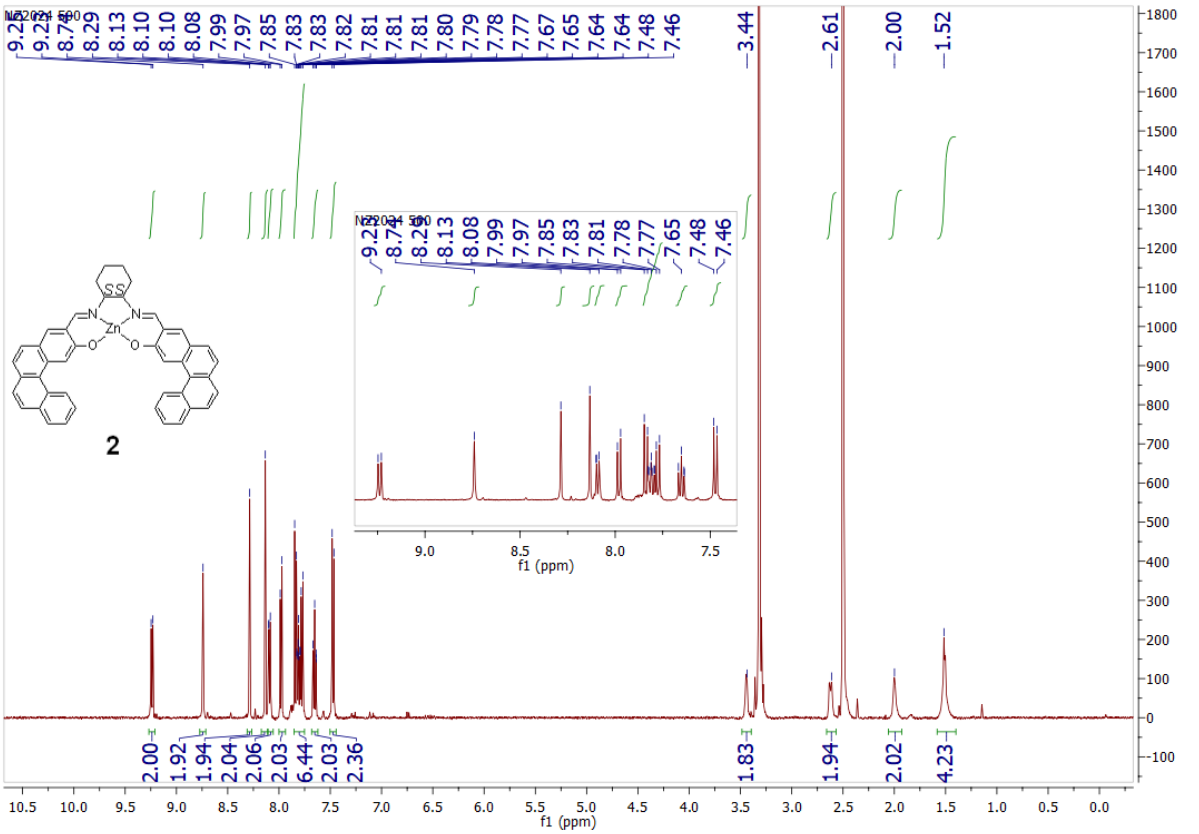
HSQC ^{1}H-^{13}C 2-D NMR spectrum for compound **1.**



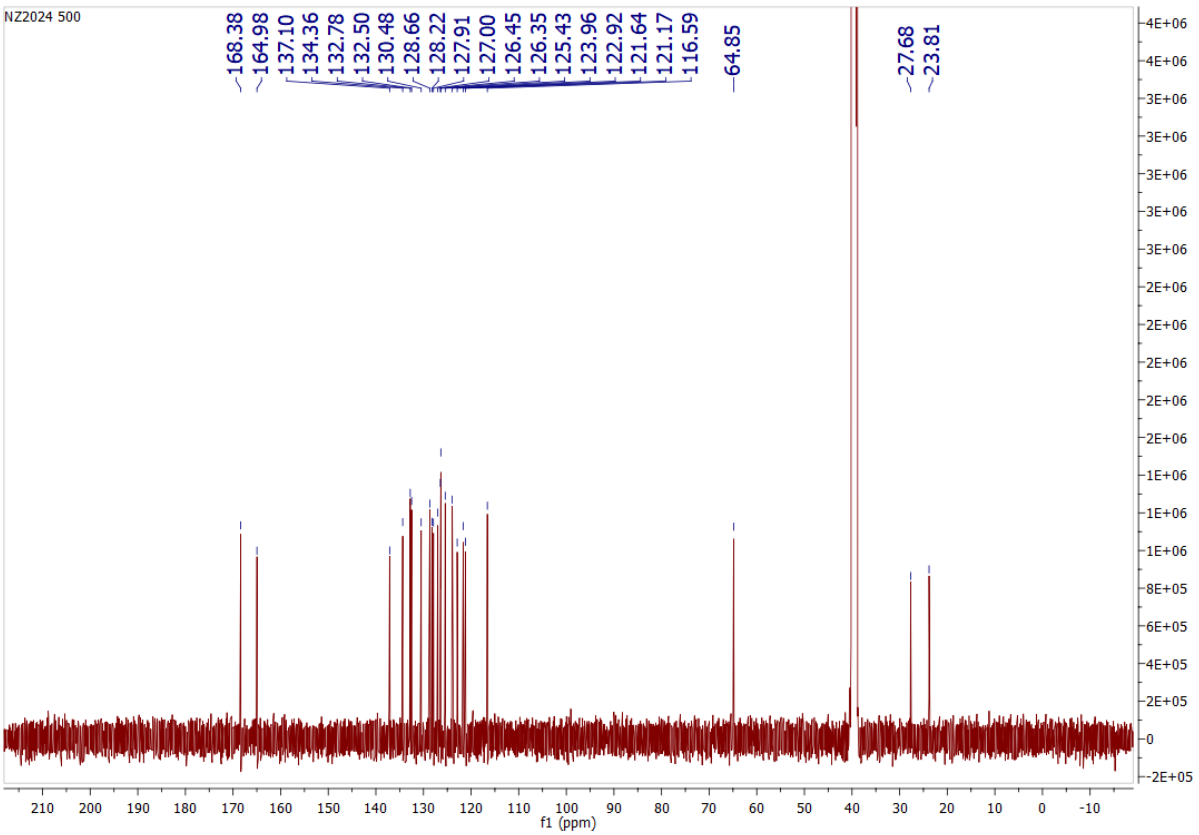
HMBC ^{1}H-^{13}C 2-D NMR spectrum for compound **1.**



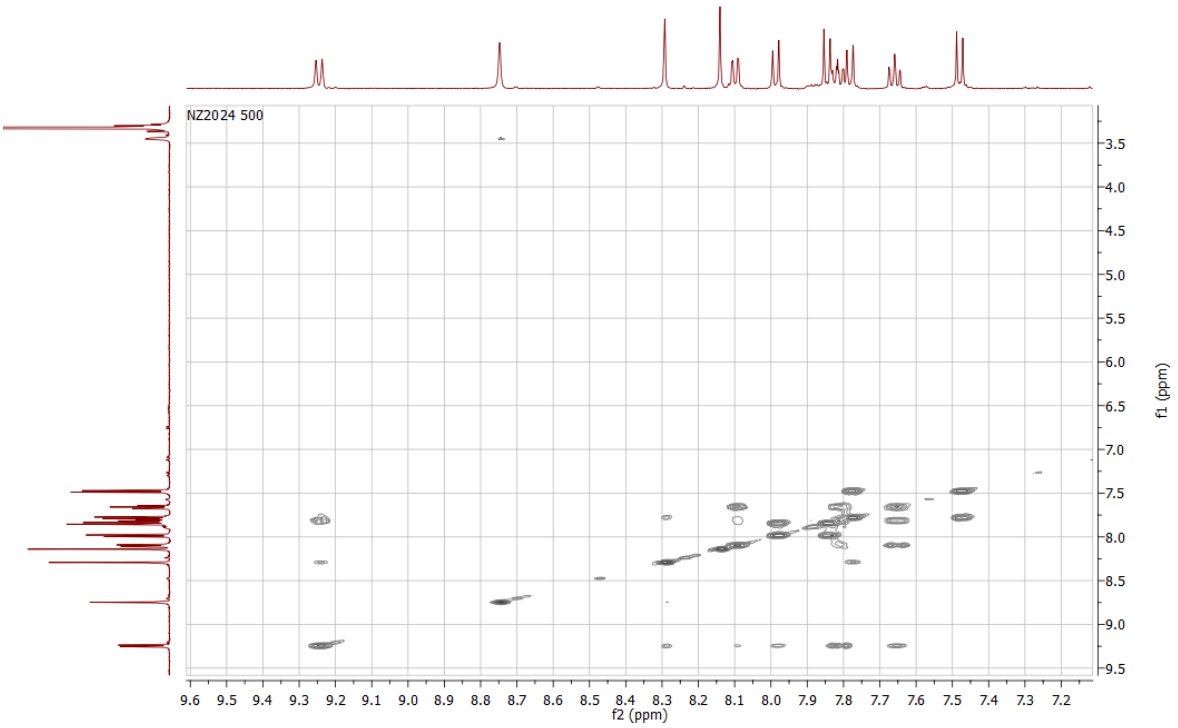
^{1}H NMR spectrum for compound **2.**



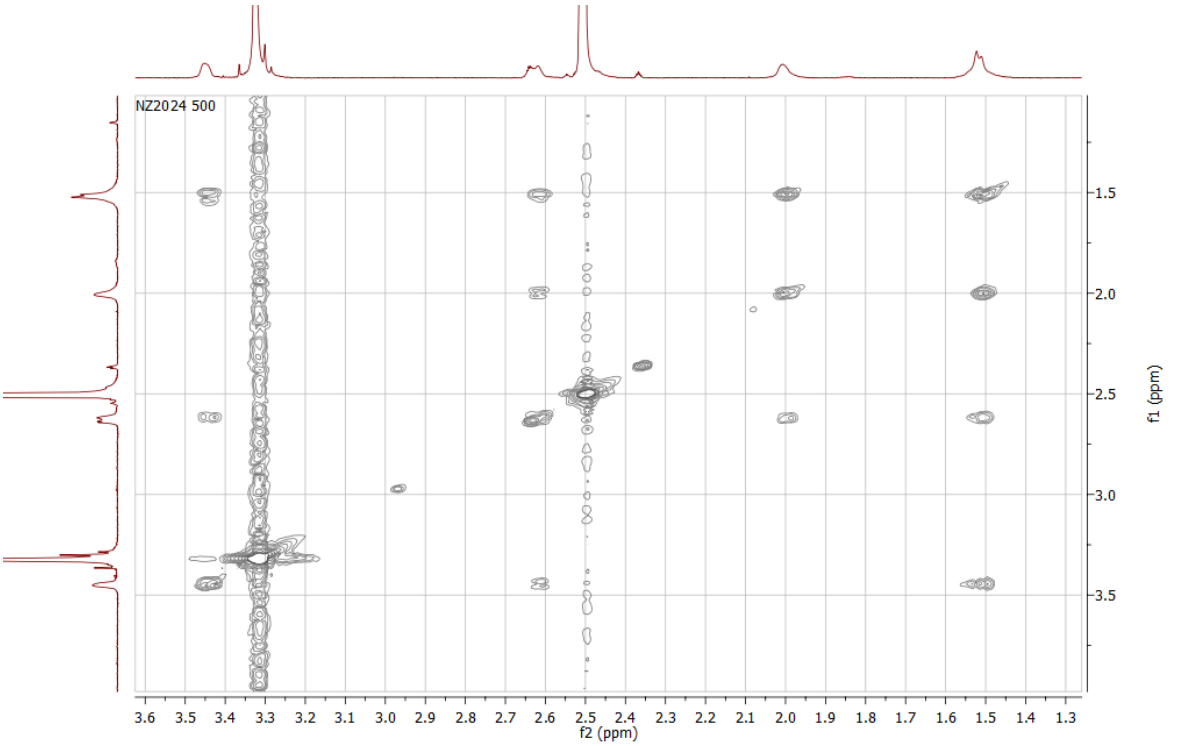
^{13}C NMR spectrum for compound **2.**



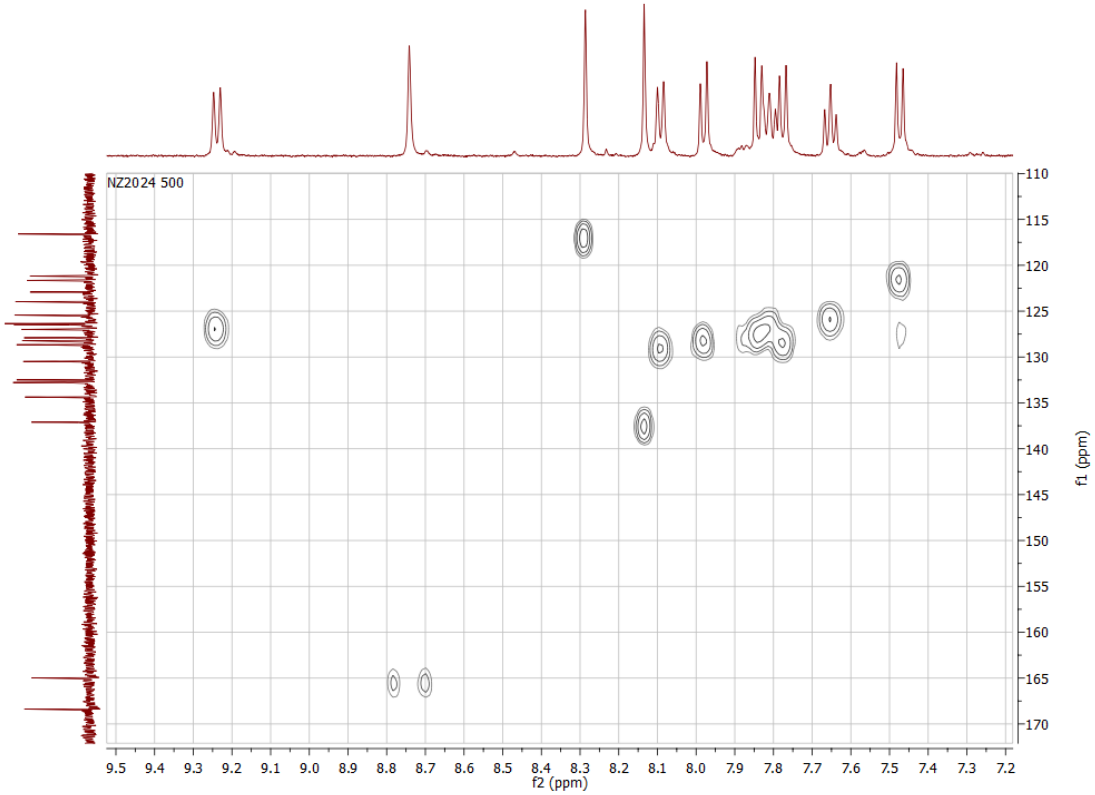
NOESY ^{1}H-^{1}H 2-D NMR spectrum for compound **2** (aromatic region)**.**



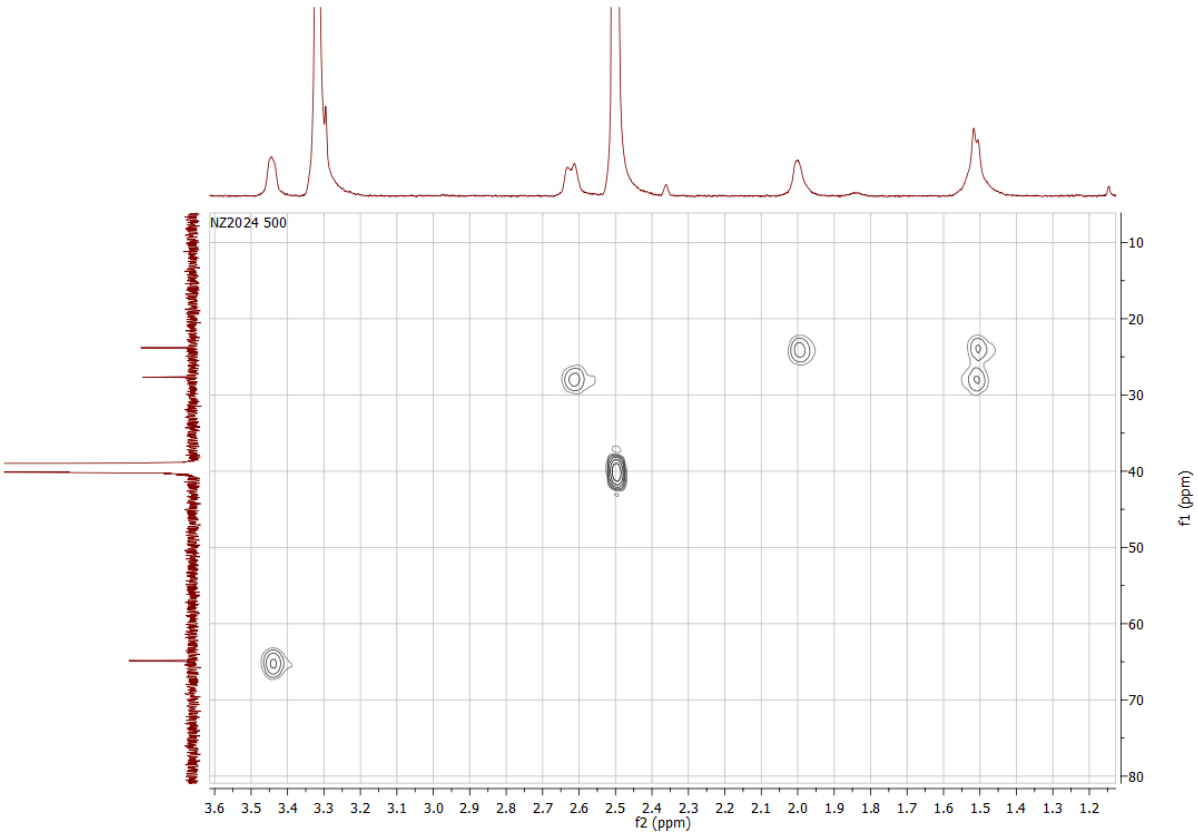
NOESY ^{1}H-^{1}H 2-D NMR spectrum for compound **2** (aliphatic region)**.**



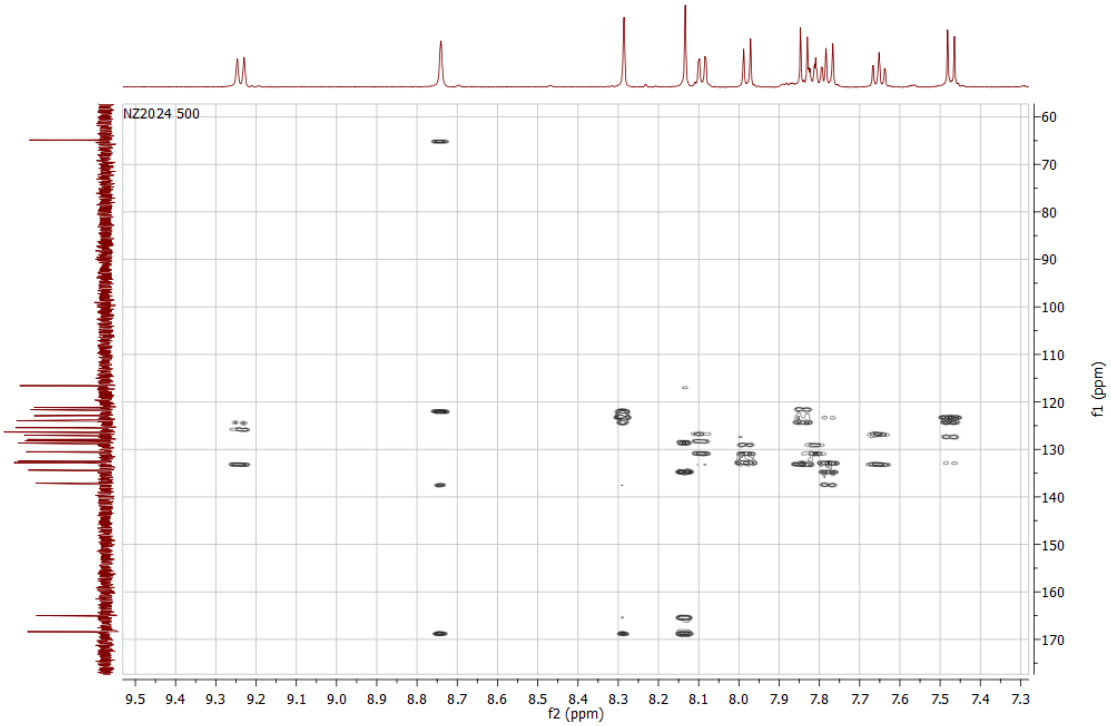
HSQC ^{1}H-^{13}C 2-D NMR spectrum for compound **2** (aromatic region)**.**



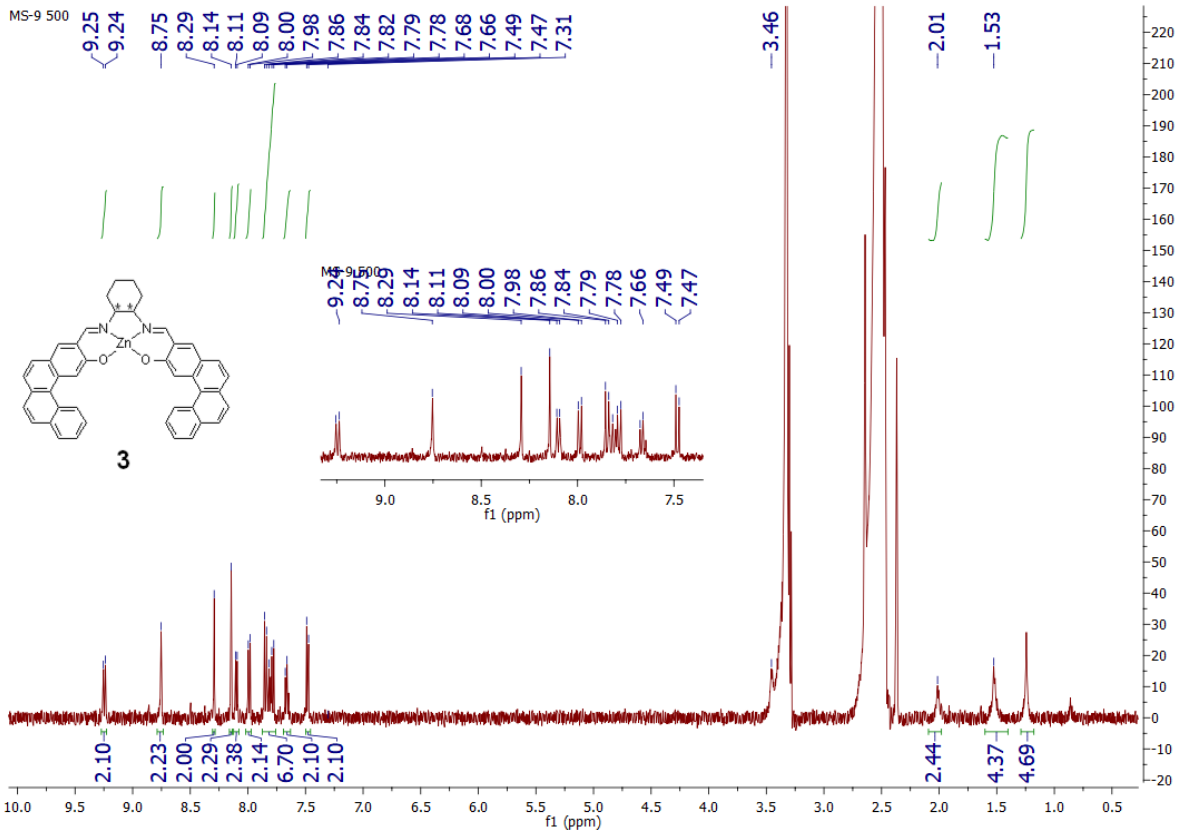
HSQC ^{1}H-^{13}C 2-D NMR spectrum for compound **2** (aliphatic region)**.**



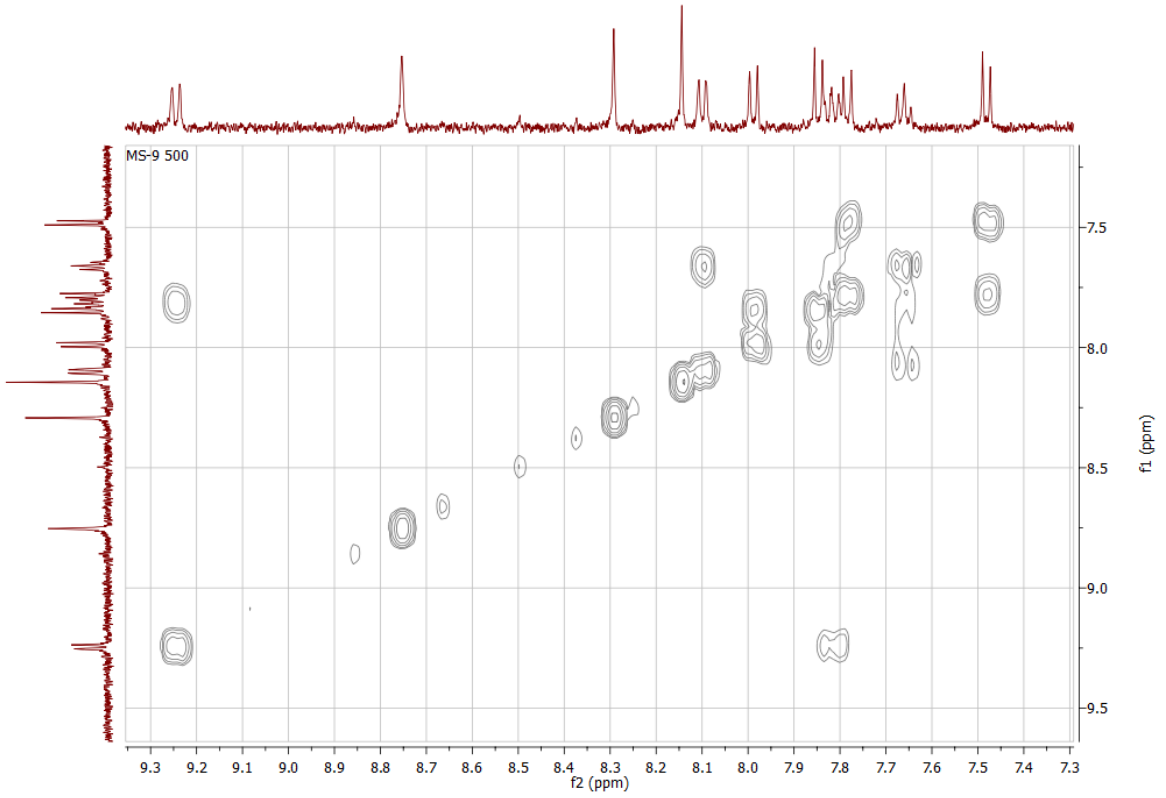
HMBC ^{1}H-^{13}C 2-D NMR spectrum for compound **2.**



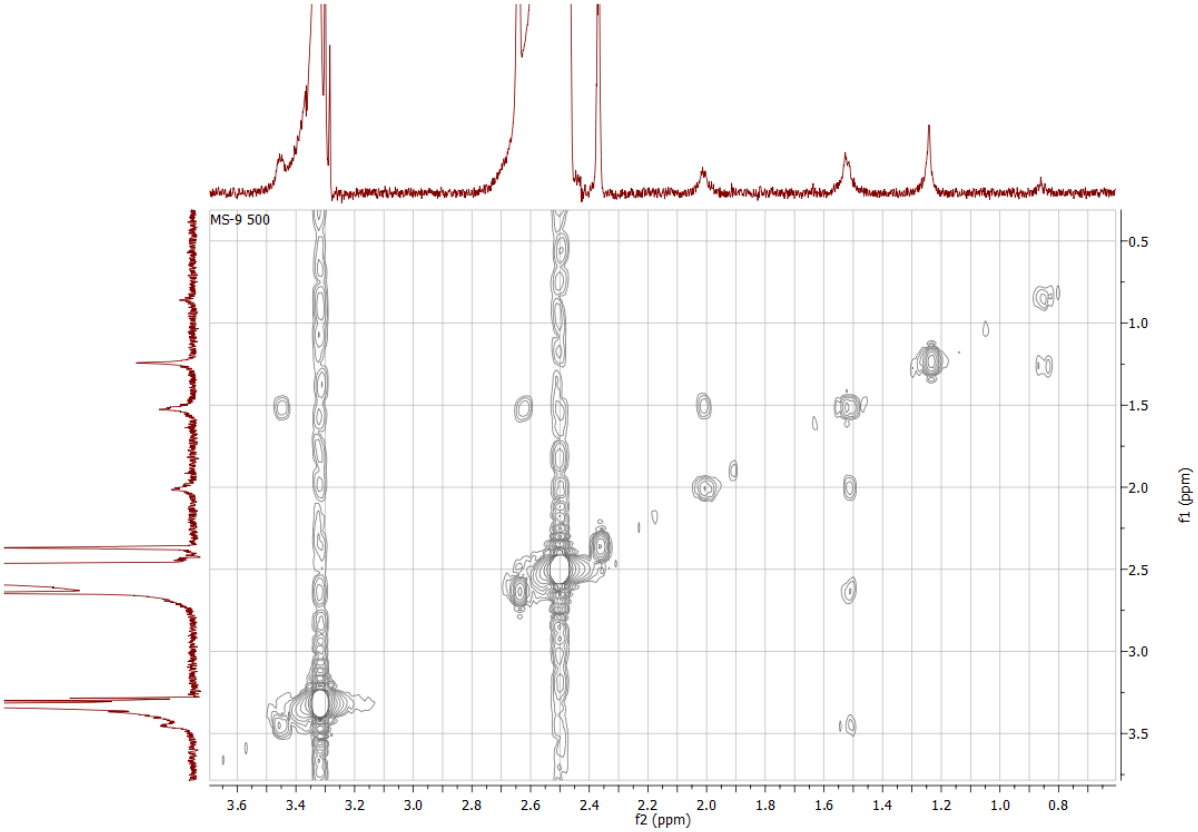
^{1}H NMR spectrum for compound **3.**



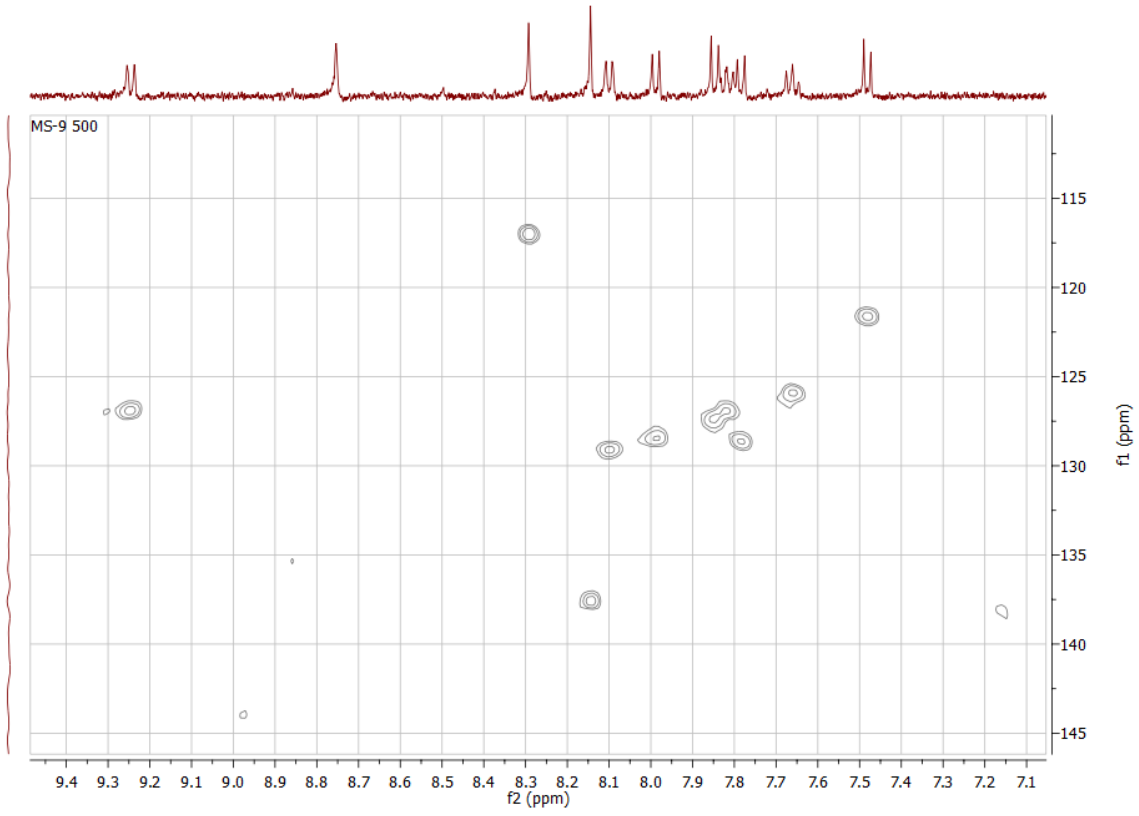
COSY ^{1}H-^{1}H 2-D NMR spectrum for compound **3** (aromatic region)**.**



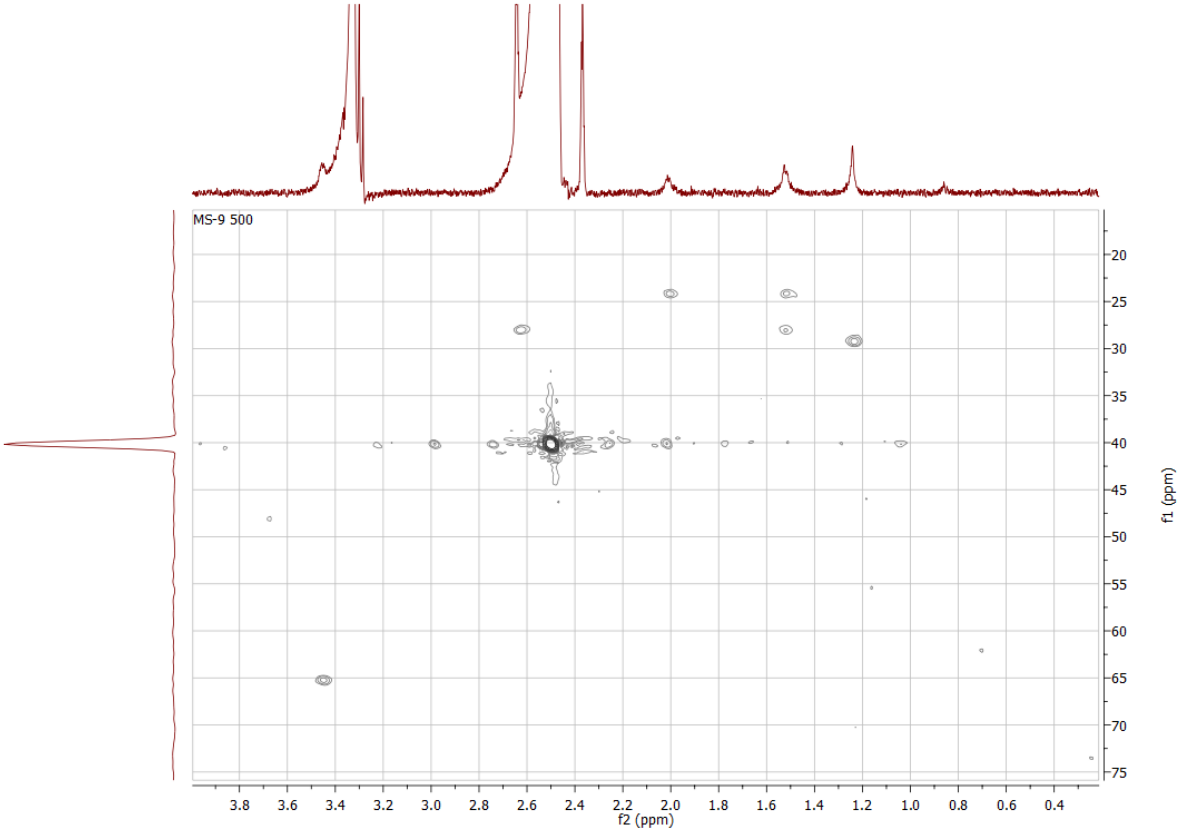
COSY ^{1}H-^{1}H 2-D NMR spectrum for compound **3** (aliphatic region)**.**



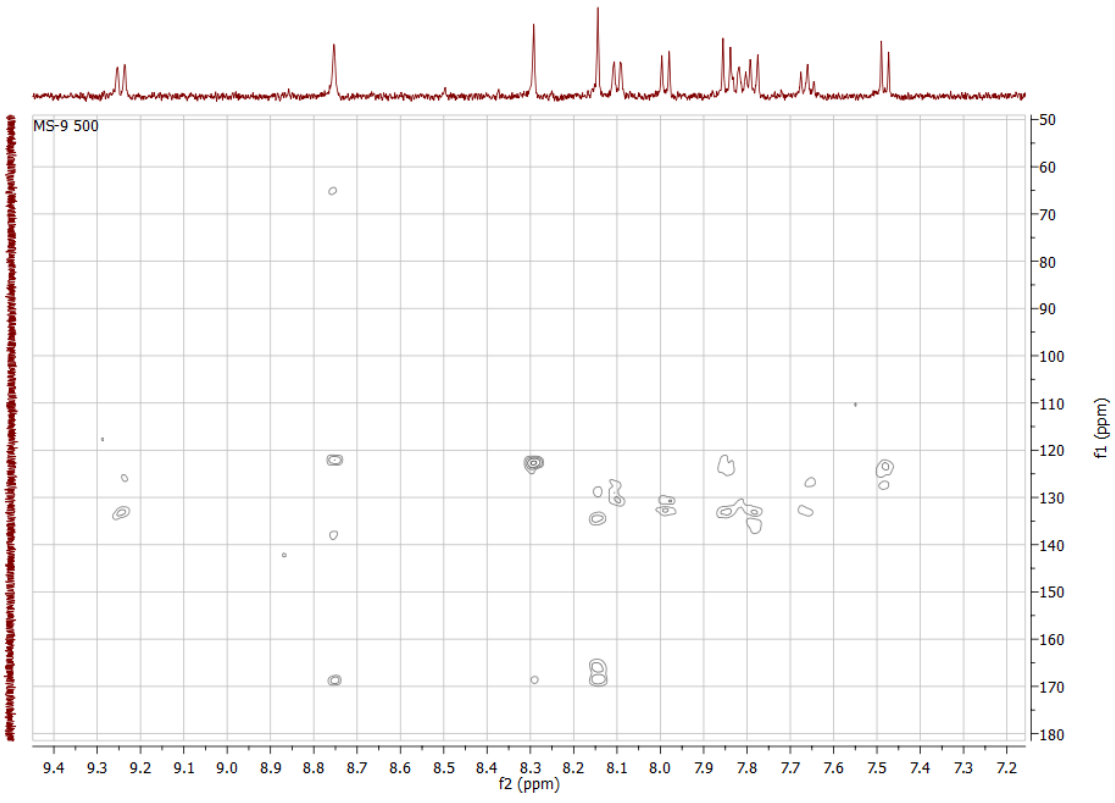
HSQC ^{1}H-^{13}C 2-D NMR spectrum for compound **3** (aromatic region)**.**



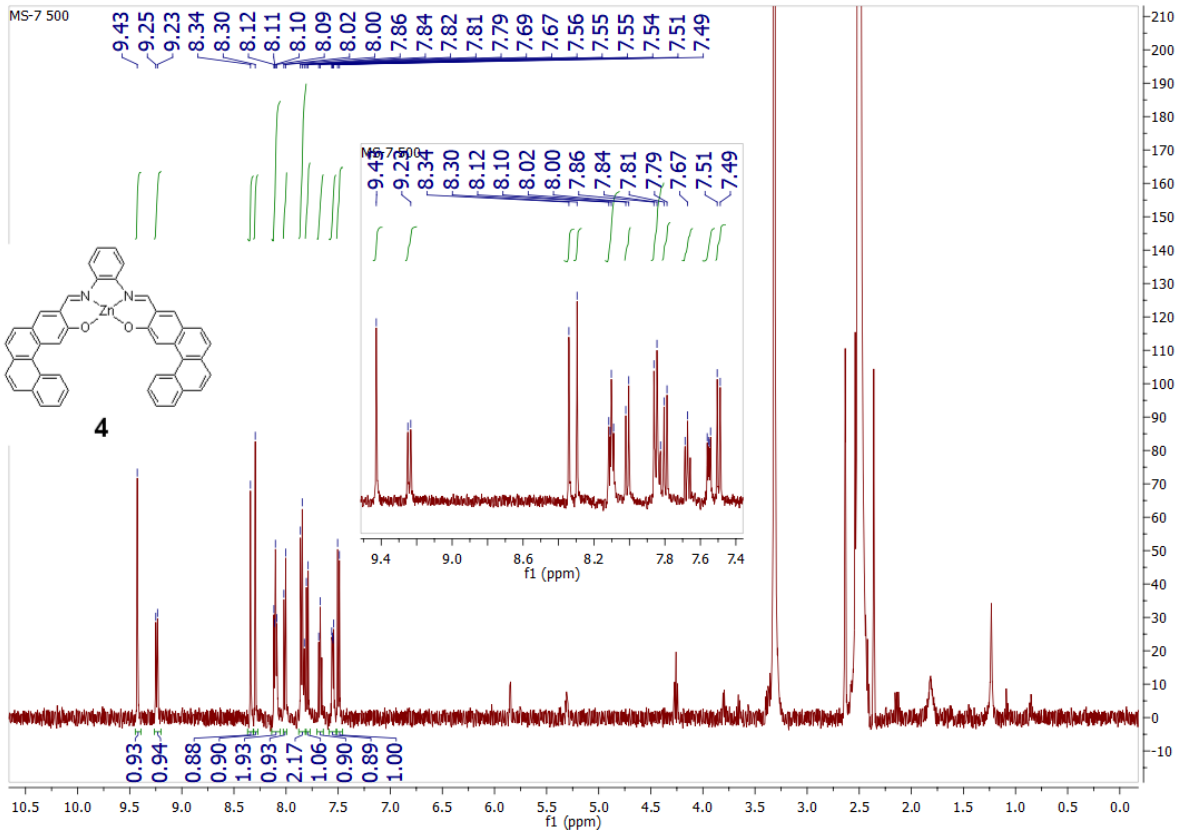
HSQC ^{1}H-^{13}C 2-D NMR spectrum for compound **3** (aliphatic region)**.**



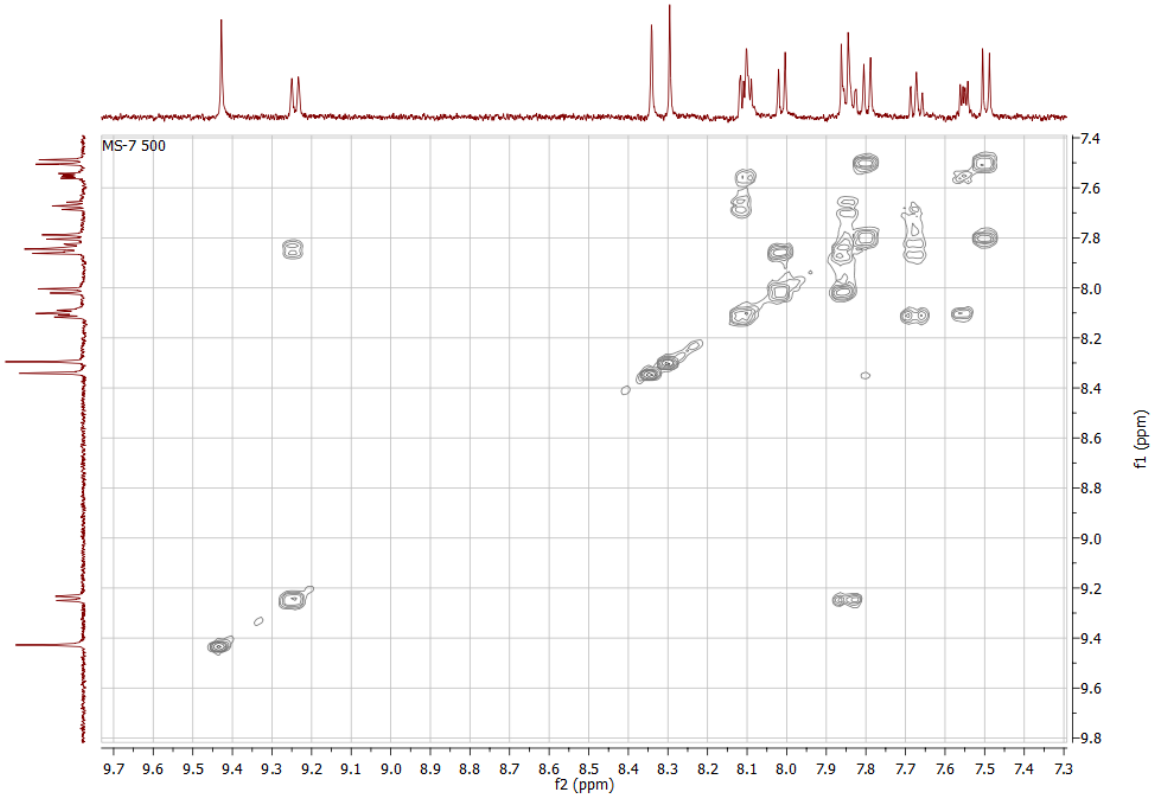
HMBC ^{1}H-^{13}C 2-D NMR spectrum for compound **3** (aromatic region)**.**



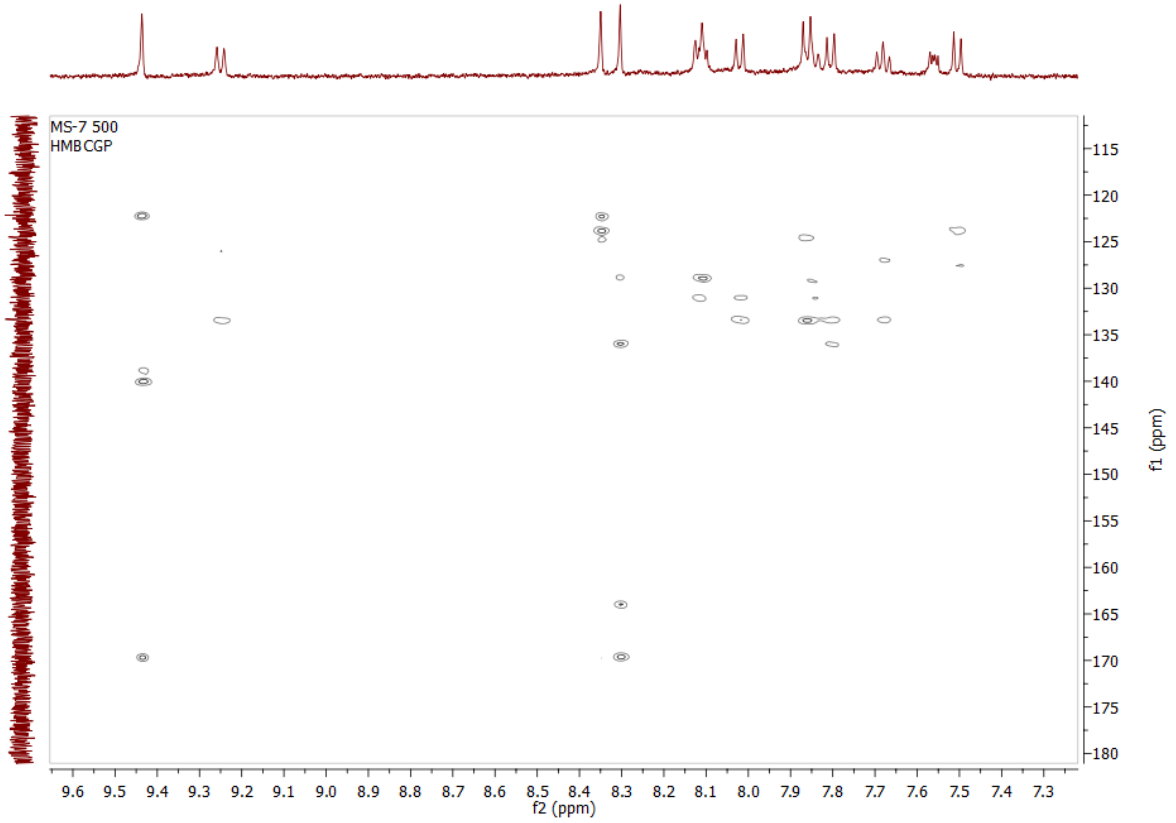
^{1}H NMR spectrum for compound **4.**



COSY ^{1}H-^{1}H 2-D NMR spectrum for compound **4.**



HMBC ^{1}H-^{13}C 2-D NMR spectrum for compound **4.**



References:

1 G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, 64, 112–122.
2 G. M. Sheldrick, *Acta Crystallogr. Sect. Found. Adv.*, 2015, 71, 3–8.
3 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, 44, 1281–1284.
4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. a. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, 42, 339–341.