Supporting Information

Structure-property relationships in unsymmetric bis(antiaromatics): Who wins the battle between pentalene and benzocyclobutadiene?

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S1 X-ray crystallography

Crystal growth:

Compound **9** was dissolved in acetone, and the solvent was slowly evaporated. After a week red, chip crystals appeared. The thicker and opaque crystals were polycrystals. Smaller crystals were measured (0.2 x 0.2 x 0.1 mm).

Intensity data were collected on a Rigaku RAXIS-RAPID II diffractometer (using graphite monochromator; Mo-Kα radiation, λ = 0.71075Å) at 123K in case of crystal **9**, at 123K. Crystals of compound **9** were measured with fiber loop with shine optic. Crystal Clear[1] (developed by Rigaku Company) software were used for data collection and refinement. Numerical absorption corrections[2] were applied to the data. The structures were solved by direct methods. Anisotropic full-matrix least-squares refinements were performed on F^2 for all non-hydrogen atoms. Hydrogen atoms bonded to C atoms were placed in calculated positions and refined in a riding-model approximation. The computer programs used for the structure solution, refinement and analysis of the structures were Shelx[3,4], Sir2014[5], Wingx[6] and Platon[7]. Details of crystallographic data, data collection and refinement for crystal of **9** is collected in Table S1-3.

Full Crystal data: $C_{37}H_{24}O$, *Fwt.*: 484.56, deep red, chip, size: 0.20 x 0.20 x 0.10 mm, monoclinic, space group *P* $2_1/n$, a = 10.2162(16)Å, b = 14.533(3)Å, c = 16.867(3)Å, α = 90°, β = 97.256(7)°, γ = 90°, V = 2484.2(7)Å^3, T = 123(2)K, Z= 4, F(000) = 1016, D_x = 1.296 Mg/m^3, μ = 0.076 mm^{-1}.

A crystal of compound **9** was mounted on a fiber. Cell parameters were determined by least-squares using 18487 (3.06° ≤ θ ≤ 25.33°) reflections.

Intensity data were collected on a Rigaku R-AXIS-RAPID diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 123(3) K in the range 3.056° ≤ θ ≤ 18.845°. A total of 18838 reflections were collected of which 1950 were unique [R(int) = 0.1630, R(σ) = 0.0755]; intensities of 1367 reflections were greater than 2σ(I). Completeness to θ = 0.995.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.997982 and 0.999168).

The structure was solved by direct methods (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement on F^2 for all non-hydrogen atoms yielded R_1 = 0.0688 and wR^2 = 0.1140 for 1332 [I>2σ(I)] and R_1 = 0.1110 and wR^2 = 0.1272 for all (1950) intensity data, (number of parameters = 344, goodness-of-fit = 1.137, the maximum and mean shift/esd is 0.001 and 0.000).

The maximum and minimum residual electron density in the final difference map was 0.15 and -0.20e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.03562.2003P)^2+2.2003P]$ where $P = (F_o^2+2F_c^2)/3$.

Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations, but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the *U*(eq) value of the atom they were bonded to.

Details of crystallographic data, data collection and refinement for crystal **9** is collected in Table S1-S3.

Table S1. Summary of crystallographic data, data collections, structure determination and refinement for compound **9**.

Empirical formula	$C_{37}H_{24}O$
Formula weight	484.56
Temperature (K)	123(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å
Crystal system	monoclinic
Space group	$P\,2_1/n$
Unit cell dimensions	a =10.2162(16)Å b =14.533(3)Å c =16.867(3)Å α =90° β =97.256(7)° γ =90°
Volume (Å^3)	2484.2(7)
Z, Z'	4, 1
Density (calculated) (Mg/m^3)	1.296
Absorption coefficient, μ (mm^{-1})	0.076
F(000)	1016
Crystal colour, description	deep red, chip
Crystal size (mm)	0.20 x 0.20 x 0.10
Absorption correction	numerical
Max. and min. transmission	0.997982 and 0.999168
θ–range for data collection	3.056 ≤ θ ≤ 18.845°
Index ranges	-9 ≤ h ≤9; -13≤ k ≤13; -15 ≤ l ≤15
Reflections collected	18838
Completeness to 2θ	0.995
Independent reflections	1950 [R(int) =0.1630]
Reflections I>2σ(I)	1367
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	1950 /0 /344
Goodness-of-fit on F^2	1.137
Final R indices [I>2σ(I)]	R_1 =0.0688, wR^2 =0.1140
R indices (all data)	R_1 =0.1110, wR^2 =0.1272
Max. and mean shift/esd	0.001;0.000
Largest diff. peak and hole (e.Å^{-3})	0.15 and -0.20

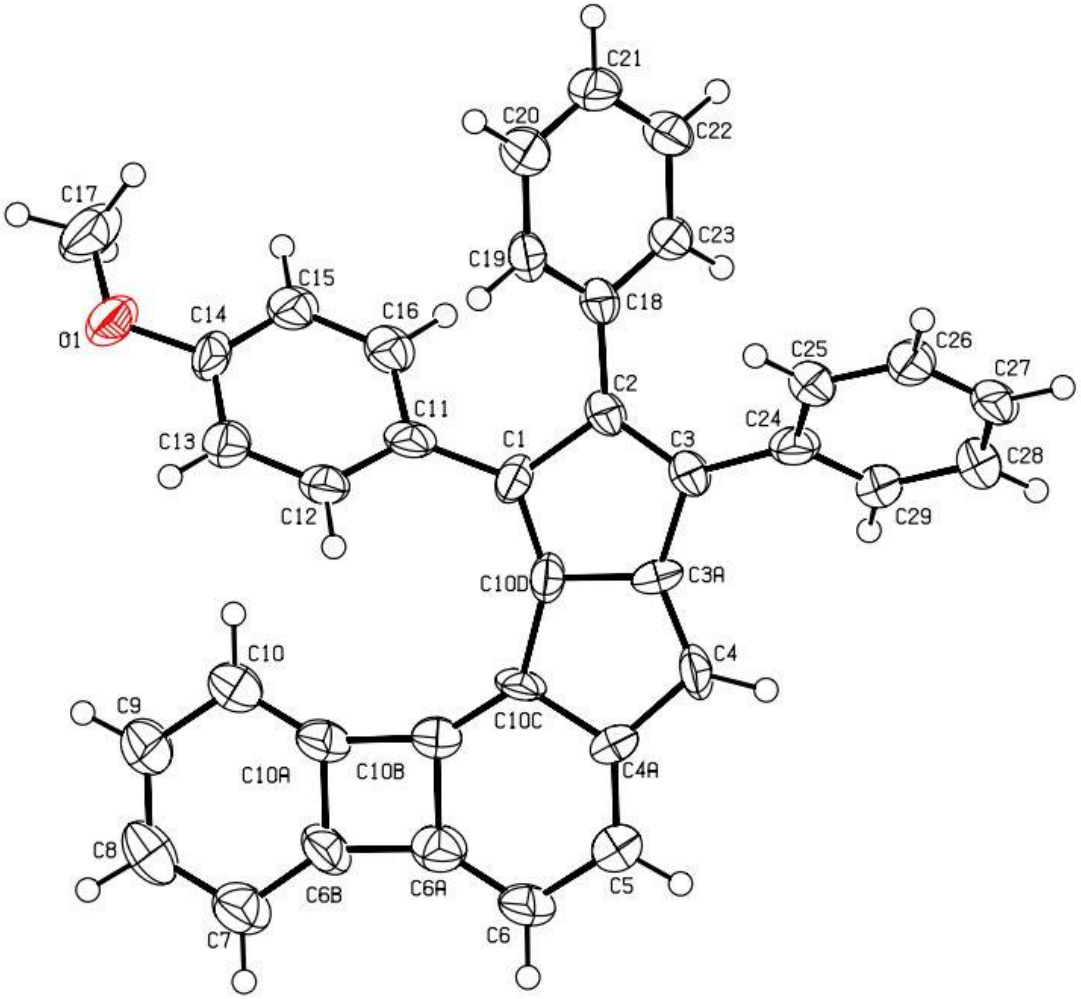


Figure S1. ORTEP style diagram of molecule **9** with atomic numbering. ORTEP representation of **9** is drawn at 50% probability level. Arbitrary numbering.

Table S2. Comparison of the packing motifs in the different crystals of compound **9**.

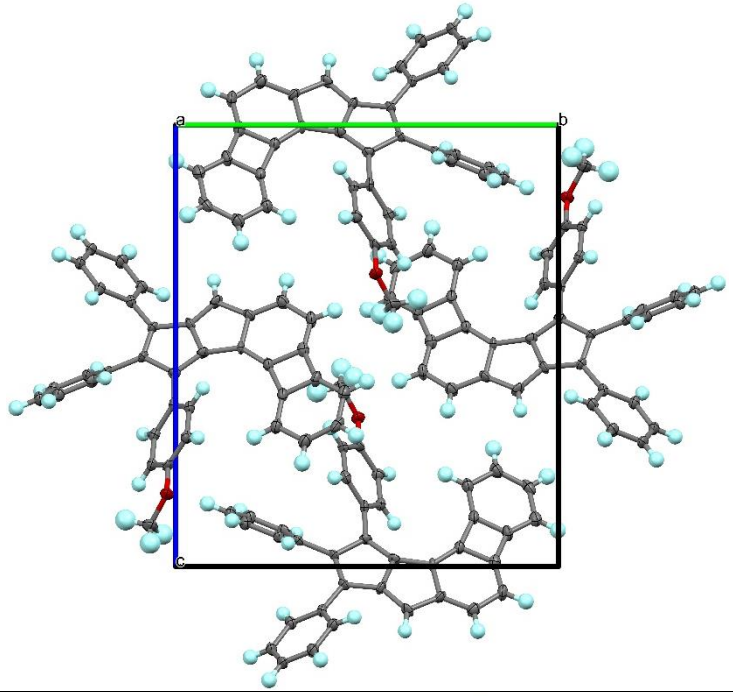
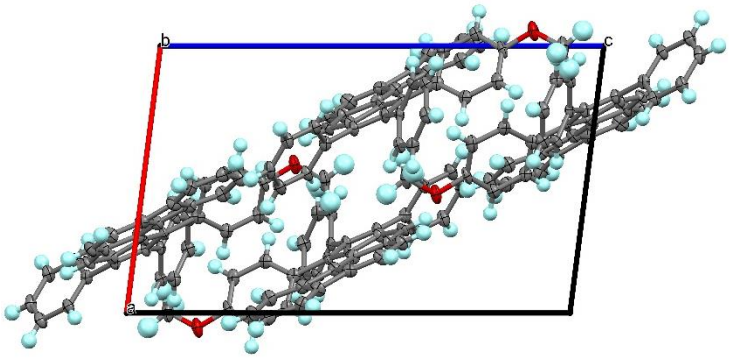
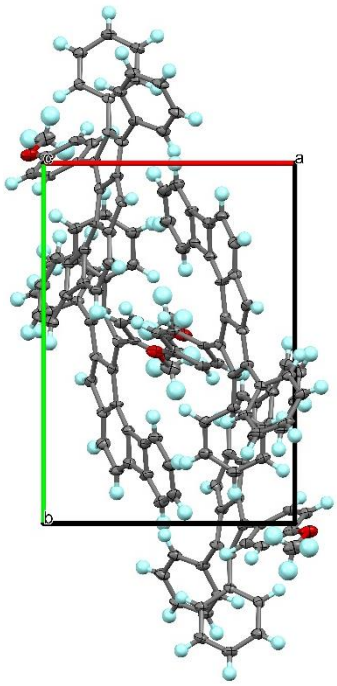
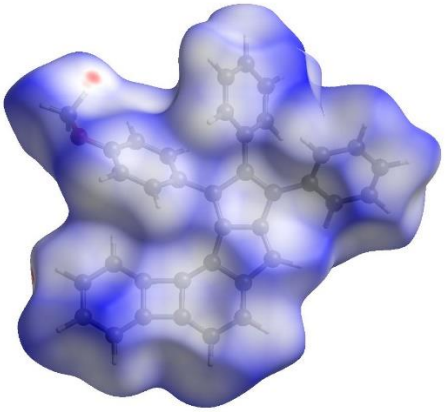
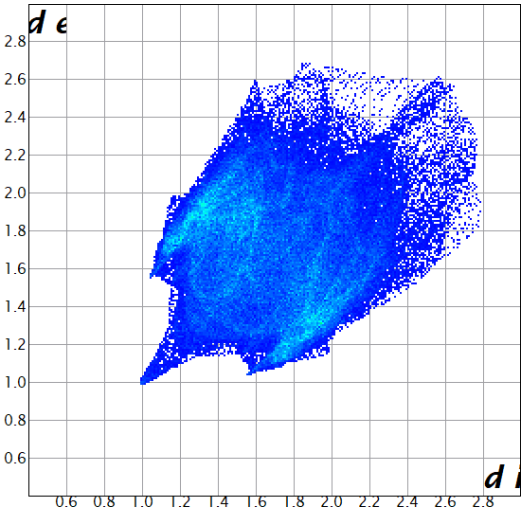
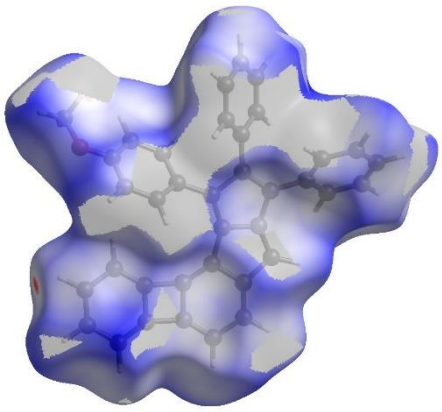
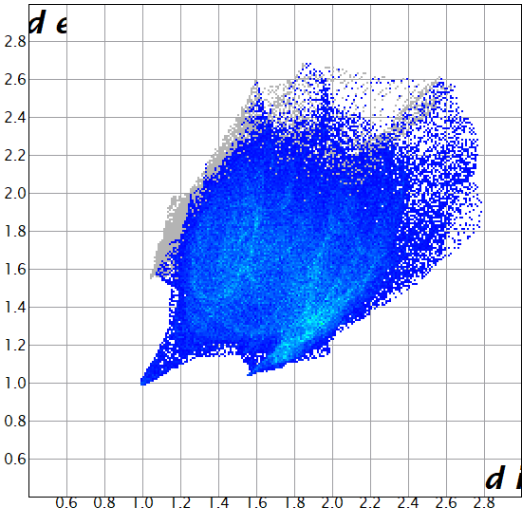
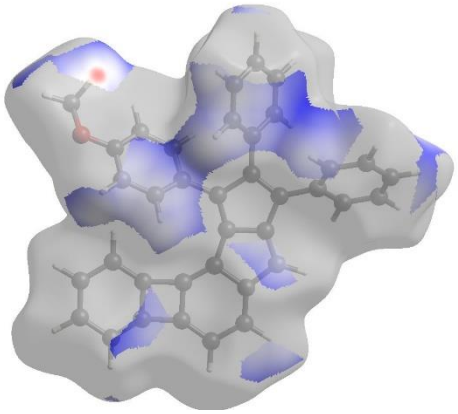
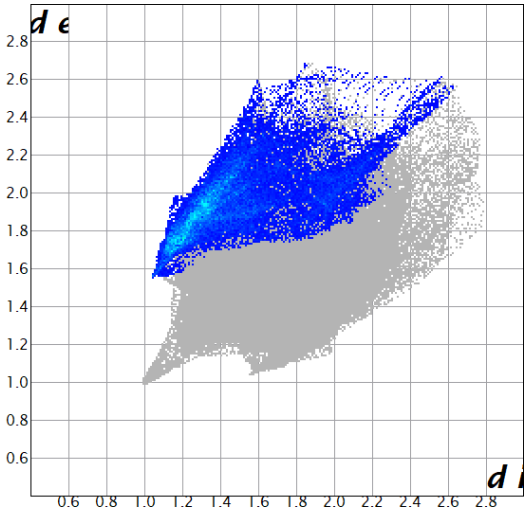
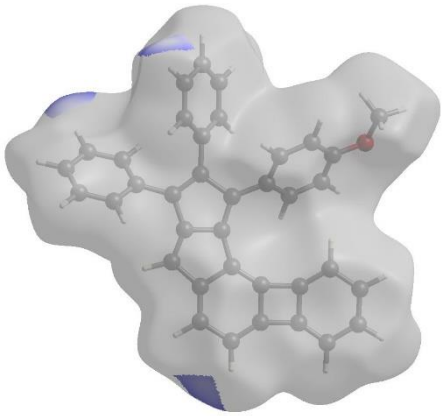
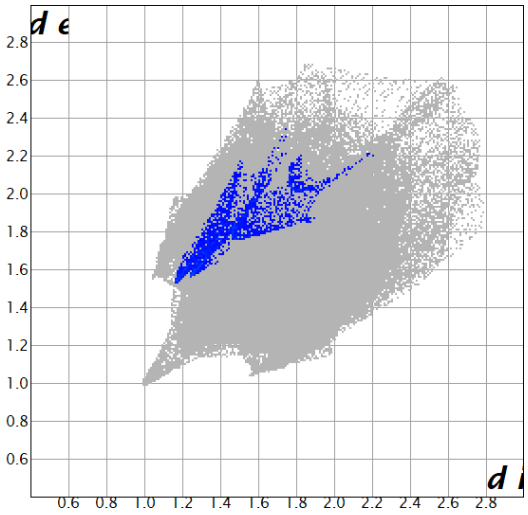
Direction	
a axis	
b axis	
c axis	

Table S3. Comparison of the Hirshfeld surface in the different crystals of compound **9**. More than ¾ (exactly 76.7%) of the contacts are H…H, O, C interactions. 23% of the H interactions are C…H and 2.2% are O…H interactions. It means around 1/3 are attractive and 2/3 are repulsive interactions of the hydrogen atom contacts.

	Hirshfeld surface	***fingerprint***
all the molecule contact		 100 % of the contacts
H contacts to the neighbouring molecule		 76.7 % of the full contacts

C contacts to the neighbouring molecule		 21.5 % of the full contacts
O contacts to the neighbouring molecule		 1.8 % of the full contacts

S2 UV-Vis spectra of compound 9 and 14 in different solvents

A Jasco V-750 UV-Vis spectrophotometer was used for the measurements. $CHCl_3$ was spectroscopic grade from VWR, and was treated with basic alumina before the measurment. CH_2Cl_2 and THF was freshly distilled from CaH_2 and Na, respectively, before measurments.

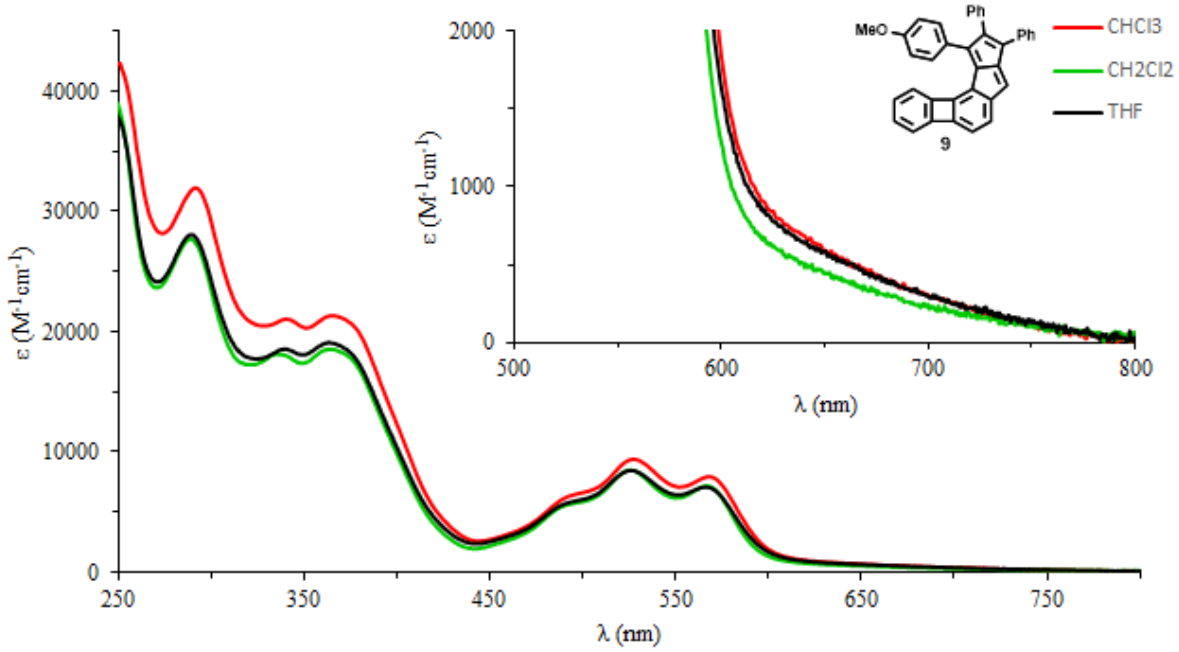


Figure S2. UV-Vis spectra of compound **9** in $CHCl_3$, CH_2Cl_2 and THF.

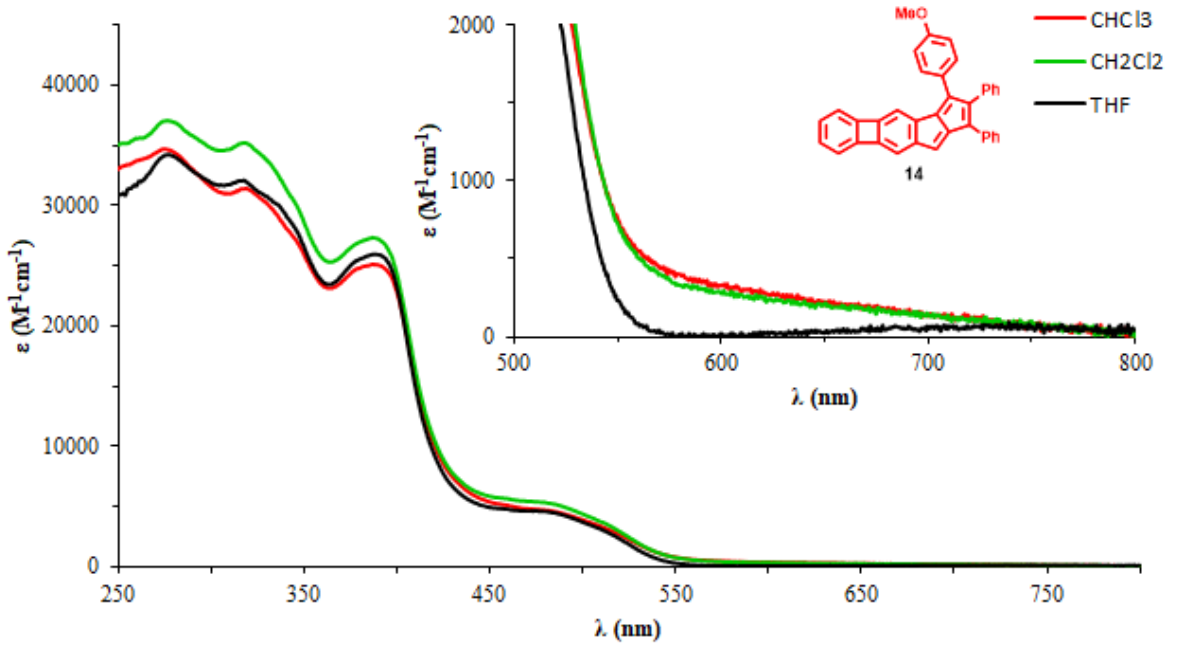


Figure S3. UV-Vis spectra of compound **14** in $CHCl_3$, CH_2Cl_2 and THF.

S3 Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed with a Metrohm Autolab PGSTAT10 type potentiostat/galvanostat in a standard three-electrode setup. Platinum wires were used as the working and counter electrodes and a Ag/AgCl wire as the pseudo-reference electrode. The recorded currents were normalized to the geometric surface area of the platinum working electrode. All measurements were carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, Sigma Aldrich, for electrochemical analysis, ≥99.0%) in dichloromethane (DCM, Sigma Aldrich, anhydrous, ≥99.8%, contains 40–150 ppm amylene as stabilizer) where 0.001 M of the compound was dissolved. The DCM was dried over 3Å molecular sieves and the Bu_4NPF_6 was dried in a vacuum oven at 180 °C to ensure water free environment. The electrochemical cell was sealed, and the electrolyte purged with an Ar stream for 5 minutes prior to measurements, to remove O_2 from the electrolyte.

The potential of the home-made Ag/AgCl pseudo-reference electrode was calibrated during the CV experiments, by measuring the formal potential of the ferrocene/ferrocenium redox couple (0.001 M ferrocene (98%, Aldrich) and 0.1 M Bu_4NPF_6 in DCM). The formal potential was determined by CV at multiple scan rates (+0.40 ± 0.01 V vs. Ag/AgCl).

Electrochemical results

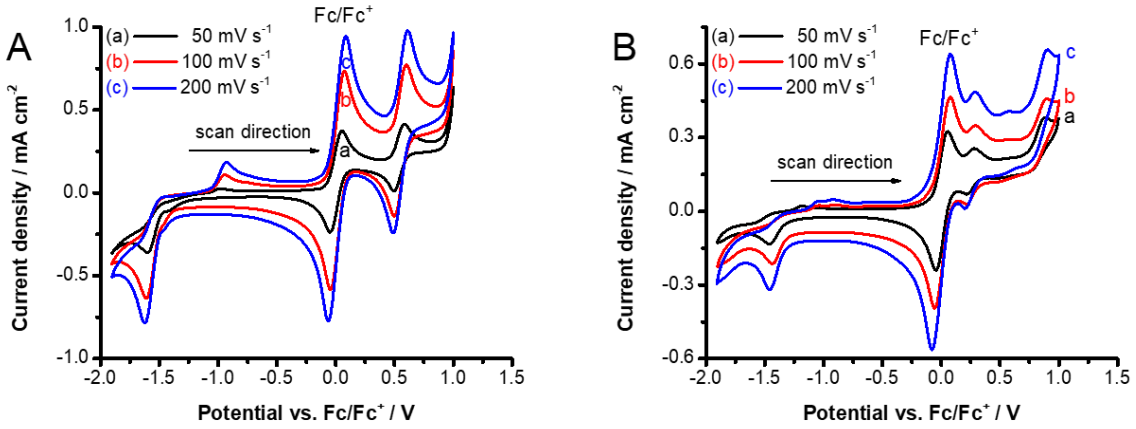


Figure S4. Cyclic voltammograms at different sweep rates recorded in 0.1 M Bu_4NPF_6 in DCM on a Pt working electrode with ferrocene as an internal standard for 0.001 M of dissolved **A**: compound **9**, and **B**: compound **14**.

The CV scans of compound **9** (Fig. S2 A) showed one irreversible reduction wave (-1.47 ± 0.02 V vs. Ag/AgCl) and one reversible redox wave (0.55 ± 0.01 V vs. Ag/AgCl) which can be correlated with the LUMO and HOMO position of the compound, respectively. In the case of compound **14** (Fig. S2 B) the shift of these redox waves was found (-1.32 ± 0.03 V vs. Ag/AgCl for the LUMO and 0.25 ± 0.01 V vs. Ag/AgCl for the HOMO) and a further irreversible oxidation wave (0.75 ± 0.01 V vs. Ag/AgCl) emerged.

S4 Computational studies

S4.1 General methods

All geometry optimizations were made with the Gaussian 16[8] package using the B3LYP[9] hybrid functional and the 6-311+G(d,p)[10] basis set. Analytical hessians were computed to confirm that the structure are minima. For triplet state optimizations, the unrestricted formalism was used.

Aromaticity has been assessed by means of magnetic, electronic and geometric indices computed also at (U)B3LYP/6-311+G(d,p) level. As magnetic indicators, the anisotropy of the induced current density (ACID)[11,12] plots and NICS-*XY* scans[13,14] were used. ACID plots give a qualitative picture of the ring-current nature so that clockwise and anticlockwise ring-currents indicate aromaticity and antiaromaticity character, respectively. NICS-*XY* scans, which take into account only π-contributions by employing the σ-model, provide quantitative information about diatropicity (negative values) and paratropicity (positive values) of the different circuits.

The multicenter index (MCI) and the aromatic fluctuation index (FLU) were employed as electronic indices. MCI is obtained from I_{ring} values as follows:

$$MCI(\mathcal{A}) = \frac{1}{2N}\sum_{P(\mathcal{A})} I_{ring}(\mathcal{A})$$

where $P(\mathcal{A})$ stands for a permutation operator which interchanges the atomic labels A_1, A_2 ... A_N to generate up to the *N*! permutations of the elements in the string $\mathcal{A}$, and the I_{ring} index is defined as:

$$I_{ring}(\mathcal{A}) = \sum_{i_1,i_2,\dots i_N} n_{i_1} \dots n_{i_N} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_N i_1}(A_N)$$

where $S_{ij}(A)$ is the overlap of natural orbitals *i* and *j* in the atom *A* defined within the QTAIM scheme,[15] and n_i are their occupancies. The higher the MCI, the more aromatic are the rings. FLU[16] was computed using delocalization indices, δ(A,B), with the expression:

$$FLU(\mathcal{A}) = \frac{1}{N}\sum_{i=1}^{N}\left[\left(\frac{V(A_i)}{V(A_{i-1})}\right)^{\alpha}\left(\frac{\delta(A_i,A_{i-1}) - \delta_{ref}(A_i,A_{i-1})}{\delta_{ref}(A_i,A_{i-1})}\right)\right]^2 \qquad (1)$$

where $A_0 \equiv A_N$ and the string $\mathcal{A} = \{A_1, A_2, \dots, A_N\}$ contains the ordered elements according to the connectivity of the N atoms in a ring or in a chosen circuit. V(A) is defined as:

$$V(A_i) = \sum_{A_j \neq A_i} \delta(A_i, A_j), \quad (2)$$

and α is a simple function to make sure that the first term is always greater or equal to 1. The delocalization indices of Eq. 1 were calculated using the overlaps between occupied molecular orbitals in the atomic basins generated by AIMAll program.[17] The $\delta_{ref}(C, C)$ reference value of 1.389 e used for C–C bond in FLU calculations corresponds to the $\delta(C, C)$ of benzene computed at the B3LYP/6-311+G(d,p) level of theory. FLU is close to 0 in aromatic species, and differs from it in non-aromatic ones. To analyze the Baird vs. Hückel-aromatic character of our systems in their triplet states, FLU values are split into α and β contributions. In Hückel-aromatic rings or circuits, identical or very similar values of FLU_α and FLU_β are expected, while significant differences ($\Delta FLU_{\alpha\beta} = FLU_\alpha - FLU_\beta \neq 0$) are predicted in Baird-aromatic systems. As an indicator of Hückel (low values) or Baird (high values) aromatic character, we defined the $\Delta FLU_{\alpha\beta}/FLU$ ratio (γ). As defined, γ allows consistent comparisons between species with different absolute aromaticity FLU values.[18] To compute FLU_α and FLU_β, the same Eq. 1 was used but now considering only the α or β MSOs and taking the $\delta_{ref}(C, C)$ reference value in Eq. 1 as half the reference value used for nonspin split FLU calculations. FLU and MCI were obtained with the ESI program.[19]

The aromatic character was also evaluated using HOMA[20,21] as a geometric index. It is defined as:

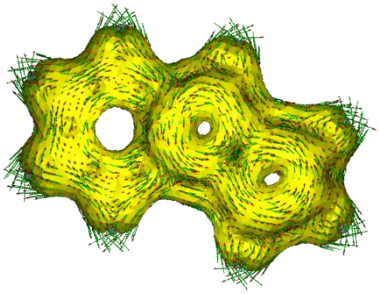
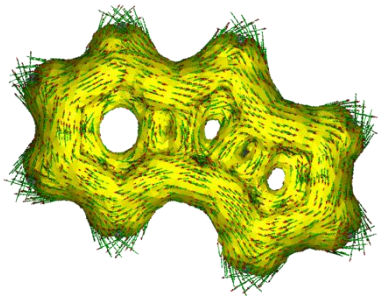
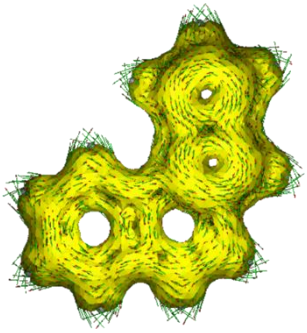
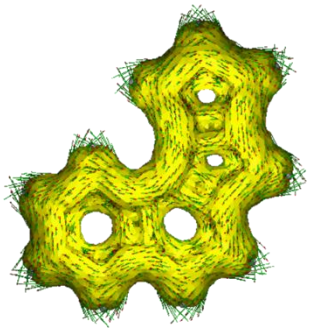
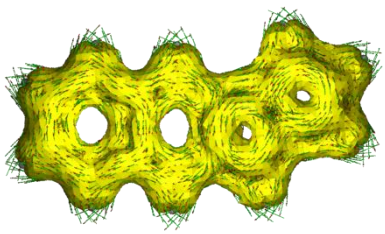
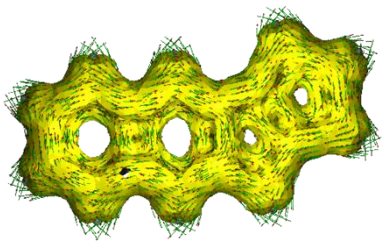
$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} \left(R_{opt} - R_i\right)^2$$

where *n* is the number of bonds considered, α is an empirical constant (for C–C, α = 257.7), R_{opt} is an optimal bond value (1.388 Å for C–C and R_i stands for a running bond length. This expression is optimized to give HOMA = 1 for fully aromatic systems, HOMA = 0 for a nonaromatic system, and negative HOMA values typically indicate antiaromaticity.

S4.2 Aromaticity analyses of the molecules and their conjugated cores

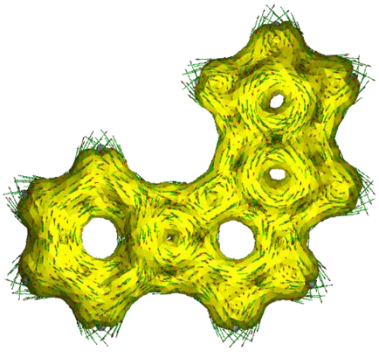
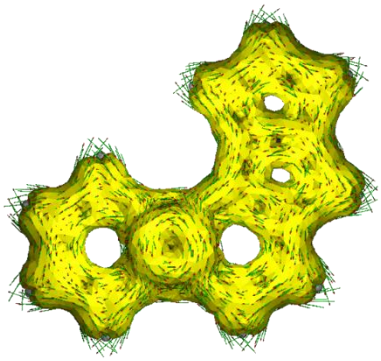
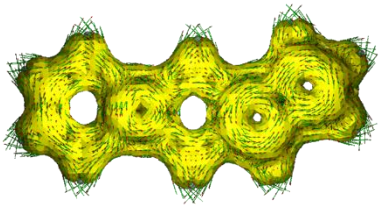
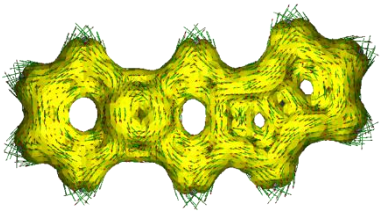
S4.2.1 ACID plots

Table S4. ACID plots of conjugated cores **17'**, **15'** and **16'** in their S_0 and the T_1 states. In the plots, the direction of the induced ring currents are shown by small arrows, where the red dots indicate the heads, while the green lines indicate the shafts of the arrows.

Entry	Molecule	S_0	T_1
1	**17'**	 Antiaromatic (AA) counter-clockwise ring-current through the pentalene ring; Weak aromatic (WA) clockwise ring-current in the benzene ring.	 Aromatic (A) clockwise ring-current in the perimeter.
2	**15'**	 AA ring-current in the pentalene ring; WA ring-current in the naphthalene ring.	 A ring-current in the perimeter.
3	**16'**	 Weak antiaromatic (WAA) ring-current in the pentalene part; A ring-current in the first benzene ring; the second benzene ring is non-aromatic (NA).	 A ring-current in the naphthalene ring; WA ring-current in the pentalene ring.

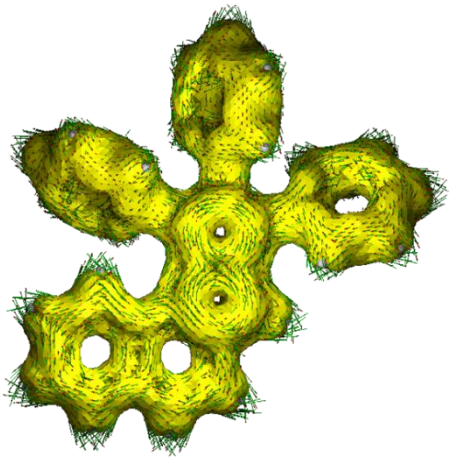
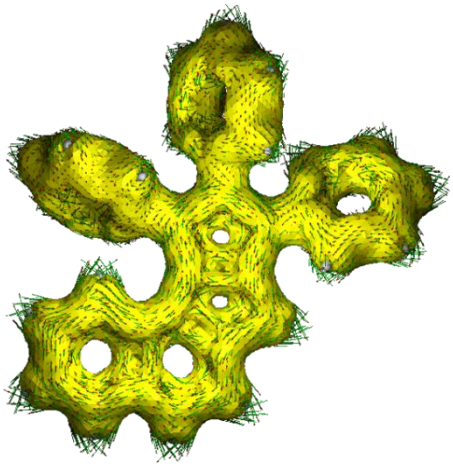
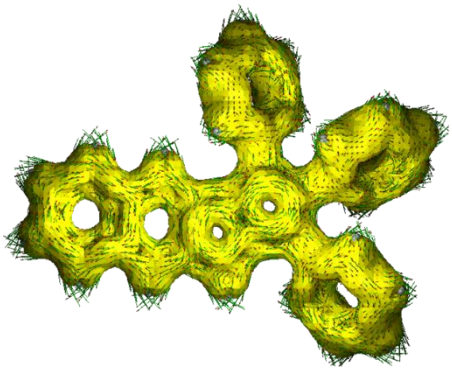
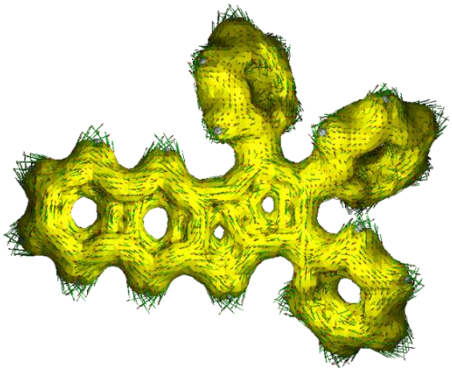
We can observe (Table S4) a larger change in aromaticity as the effect of the excitation from the ground state (S_0) to the first triplet state (T_1) in case of bent naphtho-pentalene (**15'**) compared to the linear derivative (**16'**). In the ground state (S_0) the antiaromaticity of the pentalene subunit is higher in the case of **15'** compared to **16'**.

Table S5. ACID plots of the conjugated cores **9'** and **14'** in the S_0 and the T_1 states.

Entry	Molecule	S_0	T_1
1	**9'**	 WAA ring-current in the pentalene ring; WAA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring; the middle benzene ring is NA.	 The pentalene and the middle benzene rings are NA; AA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring.
2	**14'**	 AA ring-current in the pentalene unit; WAA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring; the middle benzene ring is NA.	 A ring-current in the pentalene unit; WAA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring; the middle benzene ring is NA.

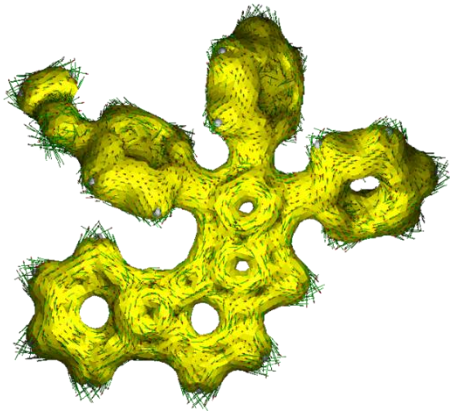
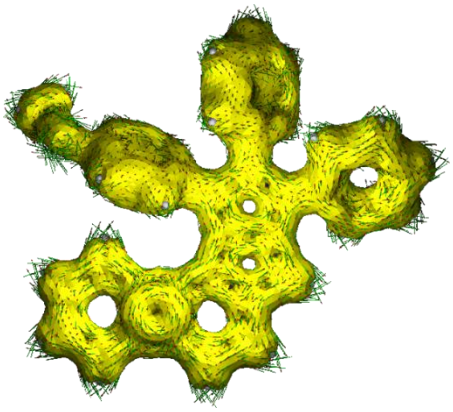
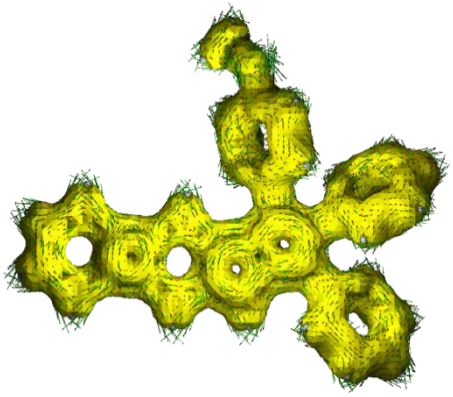
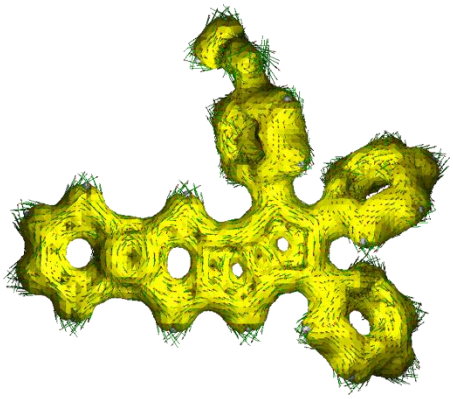
In case of the biphenyleno-pentalenes (Table S5) we can observe an opposite relationship of aromatic behavior compared to the naphtho-pentalenes (Table S4). In the case of the biphenyleno-pentalenes the linear derivative (**14'**) has a more antiaromatic pentalene moiety and shows a larger change in aromaticity as the effect of the excitation from the ground state (S_0) to the first triplet state (T_1).

Table S6. ACID plots of naphtho-pentalene derivatives **15** and **16** in their S_0 and the T_1 states.

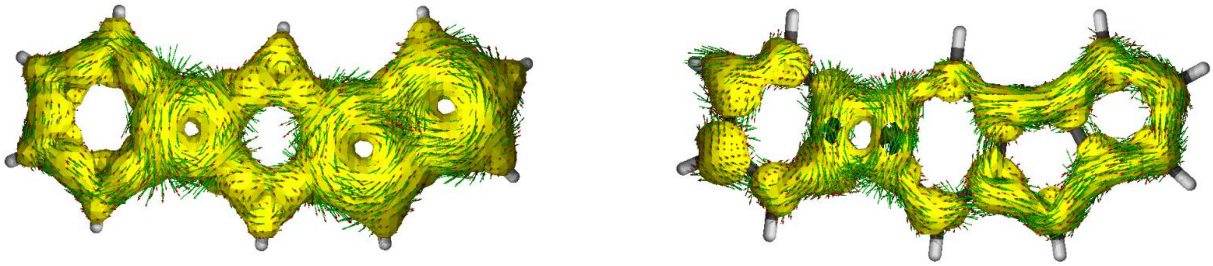
Entry	Molecule	S_0	T_1
1	**15**	 AA ring current in the pentalene unit; A ring current in the naphthalene unit.	 A ring current in the perimeter of the molecule.
2	**16**	 WAA ring current in the pentalene unit; A ring current in the first benzene ring; the second benzene ring is NA.	 The pentalene unit is NA; A ring current in the naphthalene unit.

According to the ACID plots the aromaticity relationship between molecules **15** and **16** is similar to that of **15'** and **16'**.

Table S7. ACID plots of biphenyleno-pentalene derivatives **9**, and **14** in their S_0 and the T_1 states.

Entry	Molecule	S_0	T_1
1	**9**	 WAA ring-current in the pentalene unit; WAA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring; the middle benzene ring is NA.	 The pentalene unit and the middle benzene ring are NA; AA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring.
2	**14**	 AA ring-current in the pentalene ring; WAA ring-current in the cyclobutadiene part; WA ring-current in the terminal benzene ring; the middle benzene ring is NA.	 A ring-current in the pentalene unit; WAA ring-current in the cyclobutadiene ring; WA ring-current in the terminal benzene ring; the middle benzene ring is NA.

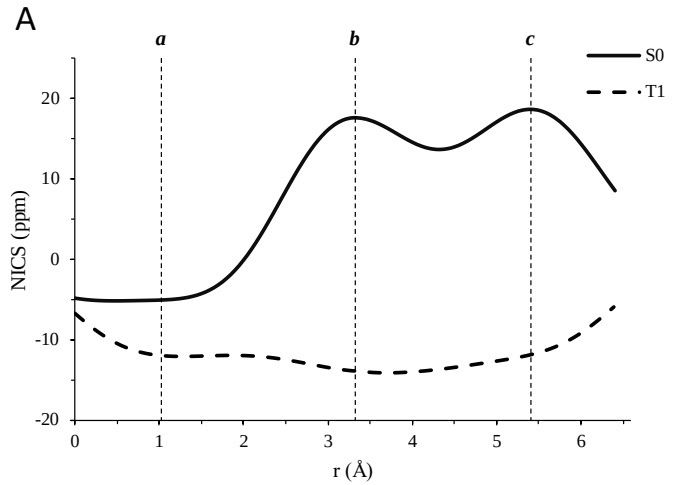
According to the ACID plots (Table S7) the aromaticity relationship between molecules **9** and **14** is similar to that of **9'** and **14'**. Based on the similarity of the ACID plots for further calculations we only used the conjugated cores of the molecules.

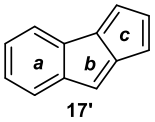


14' S_0 **14'** T_1

Figure S5. π-Only ACID plots of **14'** in its S_0 and the T_1 states.

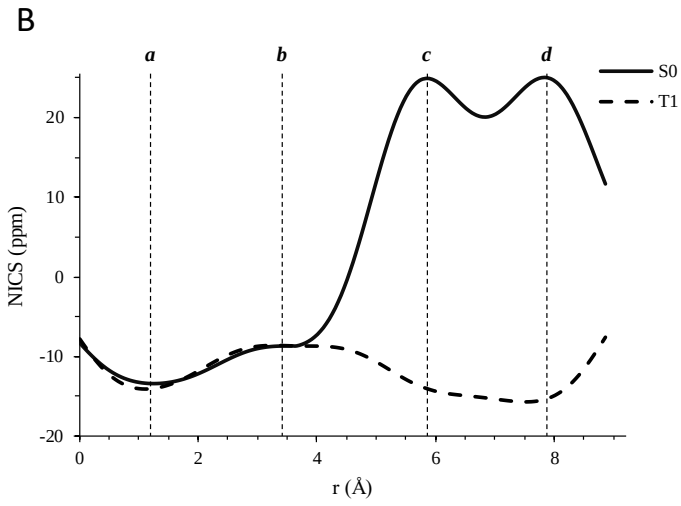
S4.2.2 NICS-*XY* scans and tables of HOMA values

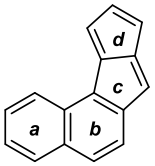




17'

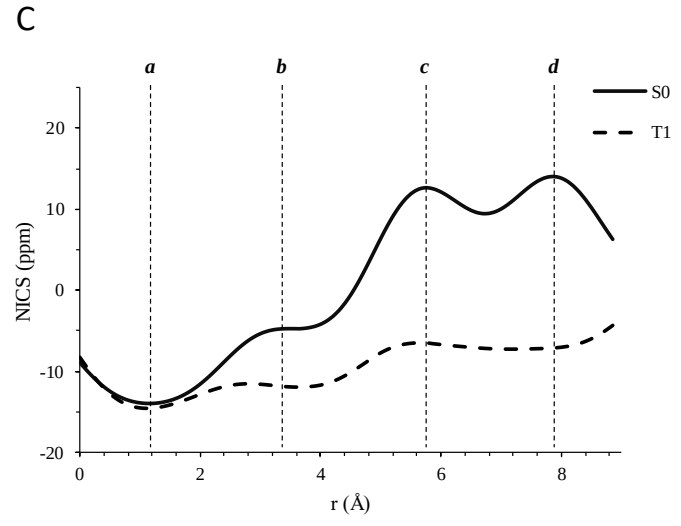
HOMA values (17')		
Rings	**S_0**	**T_1**
a	0.896	0.793
b	-0.241	0.200
c	-0.205	0.337
a+b	0.328	0.653
b+c	-0.122	0.540
a+b+c	0.266	0.766

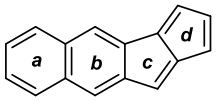




15'

HOMA values (15')		
Rings	**S_0**	**T_1**
a	0.699	0.849
b	0.802	0.561
c	-0.248	0.203
d	-0.241	0.387
a+b	0.855	0.748
b+c	0.194	0.484
c+d	-0.150	0.673
a+b+c	0.422	0.652
b+c+d	0.149	0.727
a+b+c+d	0.346	0.803



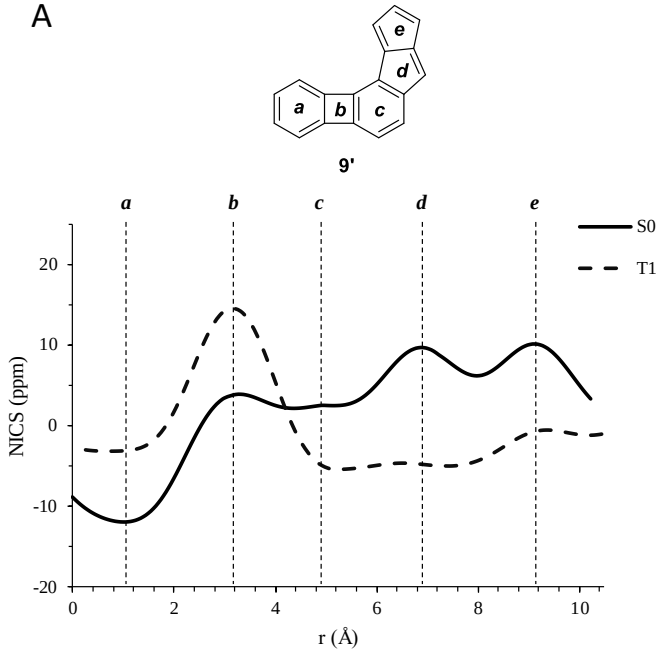


16'

HOMA values (16')		
Rings	**S_0**	**T_1**
a	0.851	0.763
b	0.511	0.497
c	-0.262	0.181
d	-0.096	0.312
a+b	0.714	0.700
b+c	0.213	0.593
c+d	-0.036	0.379
a+b+c	0.461	0.720
b+c+d	0.245	0.622
a+b+c+d	0.438	0.718

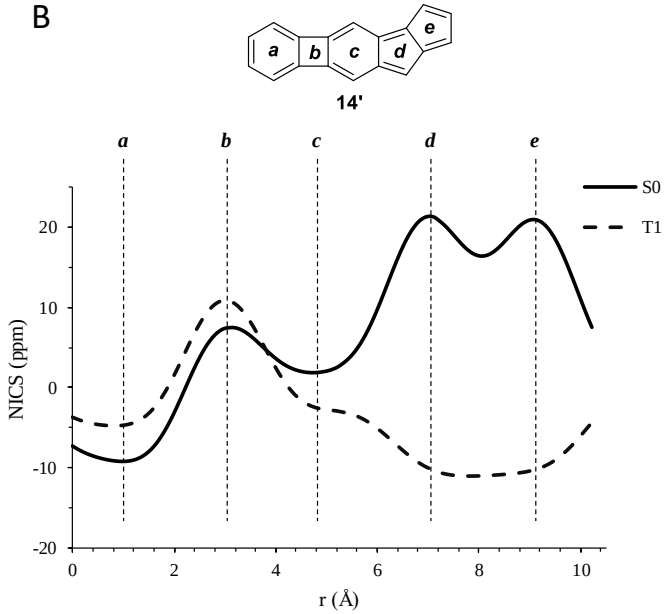
Figure S6. NICS-*XY* scans and HOMA values of **17'** (A), **15'** (B) and **16'** (C).

A



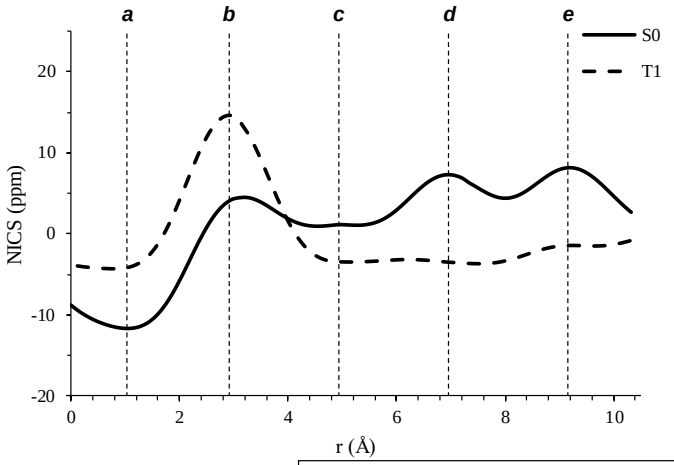
HOMA values (9')		
Rings	**S_0**	**T_1**
a	0.874	0.842
b	-0.829	-0.779
c	0.463	0.495
d	-0.222	0.097
e	-0.041	0.296
a+b	0.073	0.085
b+c	-0.094	-0.154
c+d	0.274	0.666
d+e	0.004	0.339
a+b+c	0.263	0.213
b+c+d	-0.097	0.163
c+d+e	0.301	0.685
a+b+c+d	0.189	0.372
b+c+d+e	0.006	0.287
a+b+c+d+e	0.221	0.434

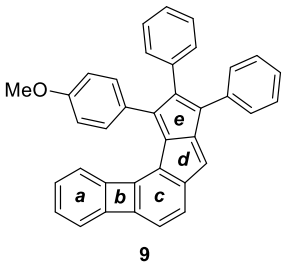
B



HOMA values (14')		
Rings	**S_0**	**T_1**
a	0.820	0.882
b	-0.989	-0.670
c	0.882	0.356
d	-0.184	0.080
e	-0.194	0.448
a+b	-0.050	0.169
b+c	0.029	-0.019
c+d	0.339	0.483
d+e	-0.123	0.606
a+b+c	0.277	0.323
b+c+d	-0.225	0.187
c+d+e	0.249	0.732
a+b+c+d	0.073	0.406
b+c+d+e	-0.181	0.464
a+b+c+d+e	0.057	0.585

Figure S7. NICS-*XY* scans and HOMA values of **9'** (A) and **14'** (B).





9

HOMA values (9)			
Rings	**S_0**	**T_1**	**Experimental (X-ray)**
a	0.875	0.852	0.859
b	-0.864	-0.804	-0.729
c	0.470	0.486	0.507
d	-0.149	0.151	-0.027
e	-0.194	0.129	-0.032
a+b	0.054	0.075	0.066
b+c	-0.104	-0.146	-0.034
c+d	0.350	0.679	0.313
d+e	-0.148	0.175	-0.079
a+b+c	0.255	0.221	0.265
b+c+d	-0.045	0.184	-0.045
c+d+e	0.226	0.563	0.193
a+b+c+d	0.226	0.389	0.197
b+c+d+e	-0.067	0.191	-0.071
a+b+c+d+e	0.164	0.361	0.136

Figure S8. NICS-*XY* scans and HOMA values of **9**.

The results for the substituted molecule (**9,** Figure S5) are in agreement with those of the corresponding conjugated core (**9',** Figure S4). Based on the similarity, the substituents have negligible effect on the aromaticity of the conjugated cores. The calculated HOMA values based on the optimized structure are in agreement with HOMA values calculated from the experimentally determined bond lengths.

S4.2.3 Electronic indices FLU and MCI

Table S8. FLU and MCI values of **9'** and **14'** in their S_0 and T_1 states.

Rings	9'					14'				
	Singlet		Triplet			Singlet		Triplet		
	MCI	FLU	MCI	FLU	ΔFLU/ FLU	MCI	FLU	MCI	FLU	ΔFLU/ FLU
a	0.053	0.004	0.052	0.006	0.34	0.054	0.006	0.050	0.004	0.30
b	0.023	0.048	0.025	0.046	0.06	0.022	0.045	0.026	0.047	0.11
c	0.031	0.017	0.025	0.014	0.24	0.045	0.005	0.018	0.020	0.40
a+b+c	-	0.017	-	0.018	0.00	-	0.015	-	0.017	0.07
c+d+e	-	0.024	-	0.011	0.96	-	0.025	-	0.010	0.48
a+b	0.000	0.023	0.000	0.021	0.00	-0.002	0.022	0.002	0.022	0.06
d+e	0.001	0.034	0.005	0.020	0.70	-0.001	0.036	-	0.011	0.78
Perimeter	-	0.022	-	0.014	0.40	-	0.025	-	0.011	0.16

Table S9. FLU and MCI values of **9'** and **14'** in their S_1 state.

Rings	9'		14'	
	S_1			
	MCI	FLU	MCI	FLU
a	0.054	0.006	0.050	0.005
b	0.022	0.047	0.024	0.050
c	0.023	0.013	0.019	0.016
a+b+c	-	0.019	-	0.017
c+d+e	-	0.007	-	0.011
a+b	-0.002	0.023	0.002	0.023
d+e	0.002	0.015	0.003	0.014
Perimeter	-	0.013	-	0.013

Table S10. FLU and MCI values of **15'** and **16'** in their S_0 and T_1 states.

Rings	15'					16'				
	Singlet		Triplet			Singlet		Triplet		
	MCI	FLU	MCI	FLU	ΔFLU/ FLU	MCI	FLU	MCI	FLU	ΔFLU/ FLU
a	0.034	0.012	0.042	0.006	0.13	0.043	0.006	0.036	0.009	0.08
b	0.032	0.008	0.016	0.017	0.25	0.023	0.017	0.019	0.015	0.20
a+b	0.008	0.008	0.004	0.011	0.20	0.006	0.011	0.005	0.010	0.01
c+d	-0.001	0.037	0.013	0.011	0.92	0.001	0.035	0.004	0.019	0.69
Perimeter	-	0.023	-	0.008	0.47	-	0.020	-	0.001	0.73

Table S11. FLU and MCI values of **15'** and **16'** in their S_1 state.

Rings	15'		16'	
	S_1			
	MCI	FLU	MCI	FLU
a	0.041	0.008	0.032	0.011
b	0.016	0.017	0.016	0.016
a+b	-	0.011	-	0.011
c+d	0.004	0.012	0.002	**0.015**
Perimeter	-	0.010	-	0.008

S4.3 Aromaticity analyses (NICS-*XY* scan, HOMA, FLU and MCI) of subunits benzocyclobutadiene (BCB, S1) and pentalene (S2)

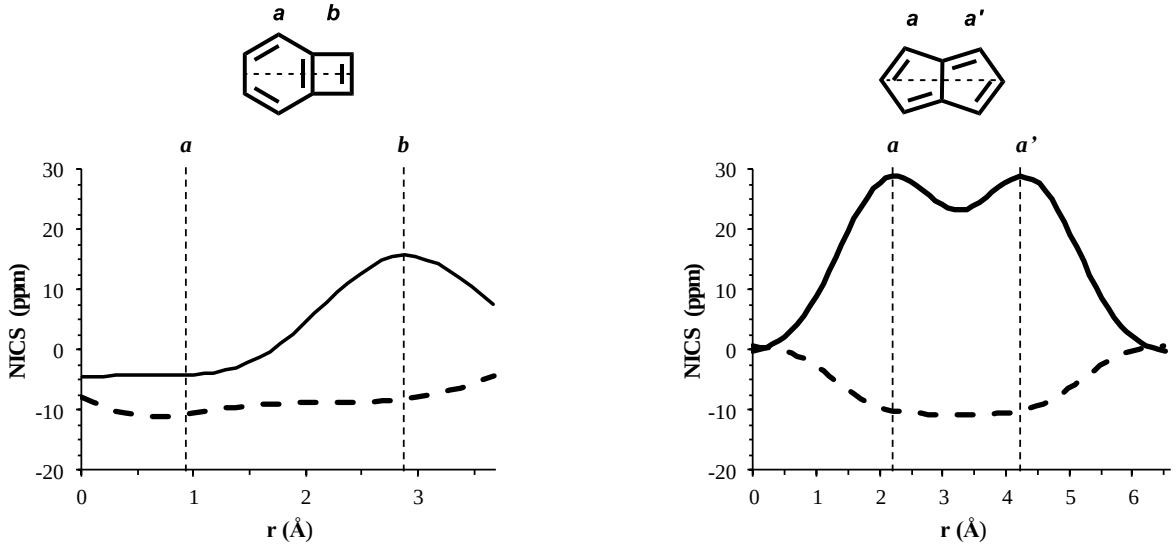


Figure S9. NICS-*XY* scans of **S1** and **S2** in their S_0 (solid line) and T_1 (dashed line) states.

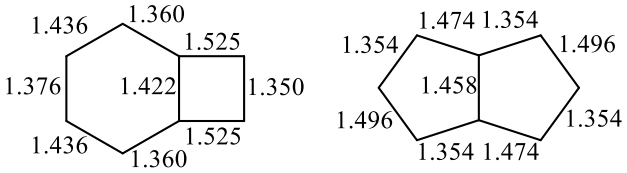
Table S12. HOMA values of **S1** and **S2** in their S_0 and T_1 states.

Rings	HOMA values			
	BCB		Pentalene	
	S_0	T_1	S_0	T_1
a	0.681	0.654	-	-
b	-1.593	-0.162	-	-
a+b	-0.460	0.568	-	-
a+a'	-	-	-0.388	0.820

Table S13. FLU and MCI (in bracket) values of **S1** and **S2** in their S_0 and T_1 states.

Rings	FLU (MCI) values			
	BCB		Pentalene	
	S_0	T_1	S_0	T_1
a	0.013 (0.050)	0.012 (0.020)	-	-
b	0.065 (0.021)	0.028 (0.066)	-	-
a+b	0.036 (-0.010)	0.009 (0.017)	-	-
a+a'	-	-	0.045 (-0.005)	0.004 (0.025)

Table S14. Comparison of HOMA values BCB and pentalene in compound **9'** and **14'**.



	9'	**14'**	Separate molecules	ΔHOMA(**9'** - sep. molecule)	ΔHOMA(**14'** - sep. molecule)
$HOMA_{BCB}$	0.073	-0.050	-0.460	0.533	0.410
$HOMA_{Pentalene}$	0.004	-0.123	-0.380	0.384	0.257

S4.4 Aromaticity analysis of subunits S1, S2, S3, S4, S5 and 17’

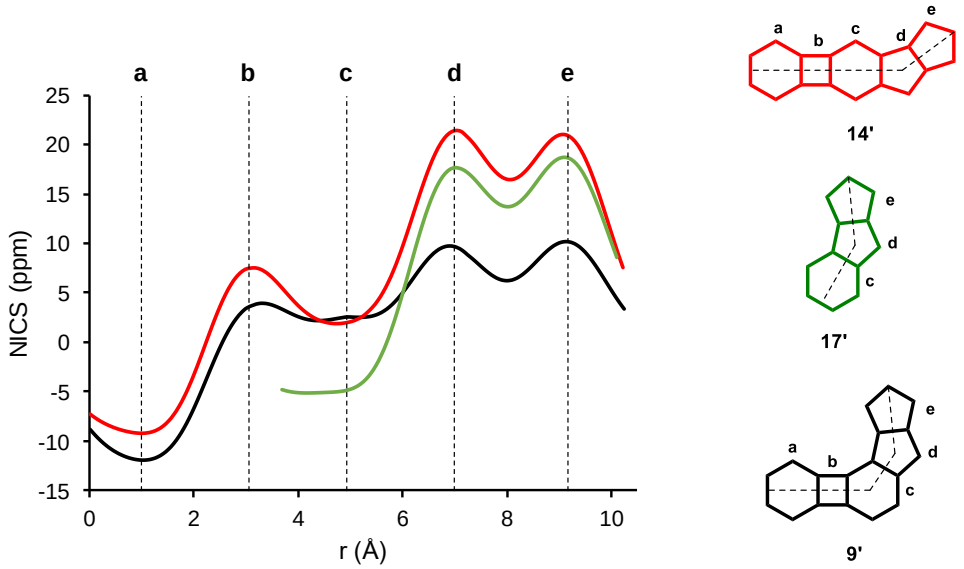


Figure S10. Comparison of NICS-*XY* scans of compounds **9’**, **14’** and **17’** in their S_0 states.

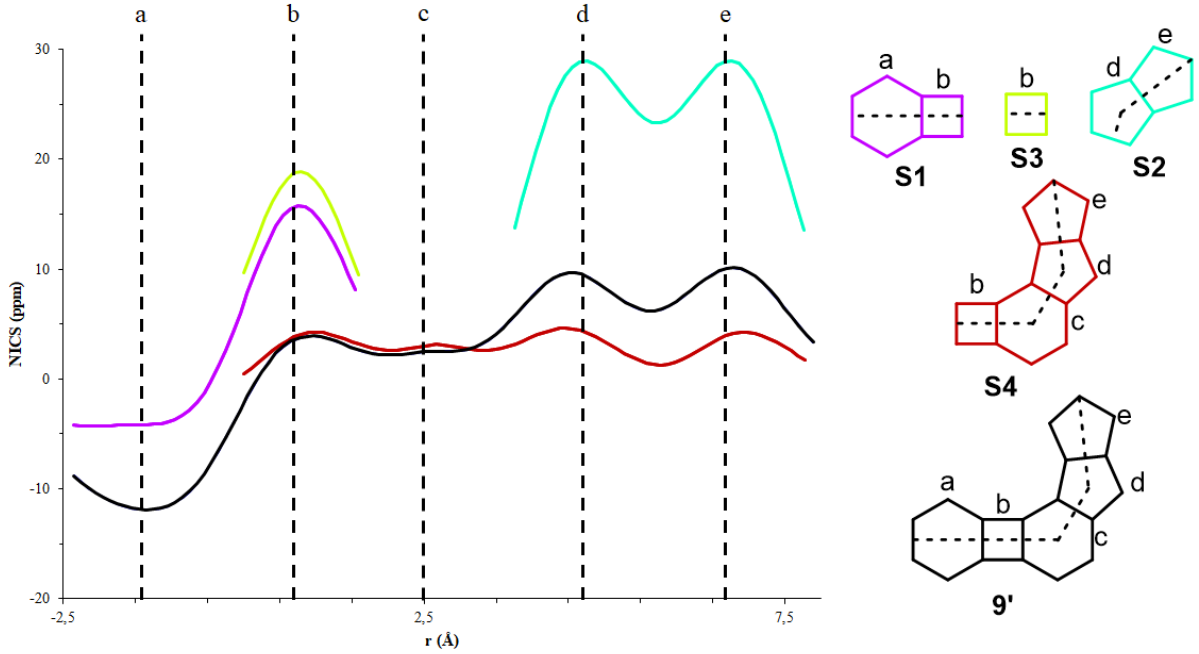


Figure S11. Comparison of NICS-*XY* scans of compounds **S1**, **S2**, **S3**, **S4** and **9’** in their S_0 states.

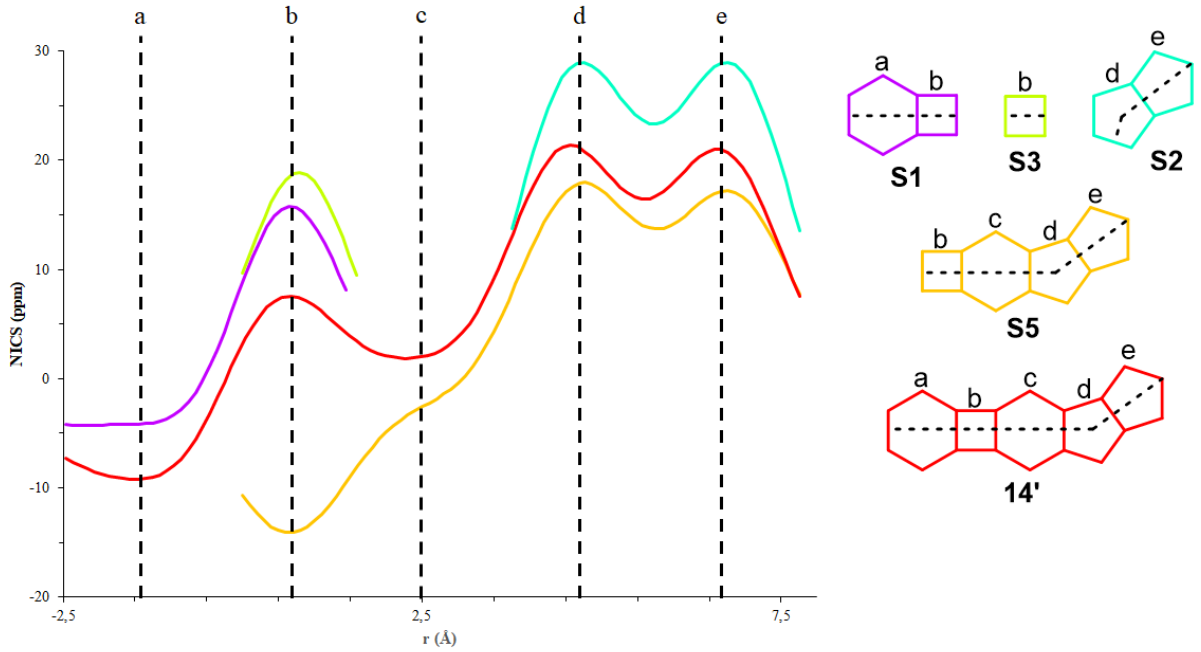
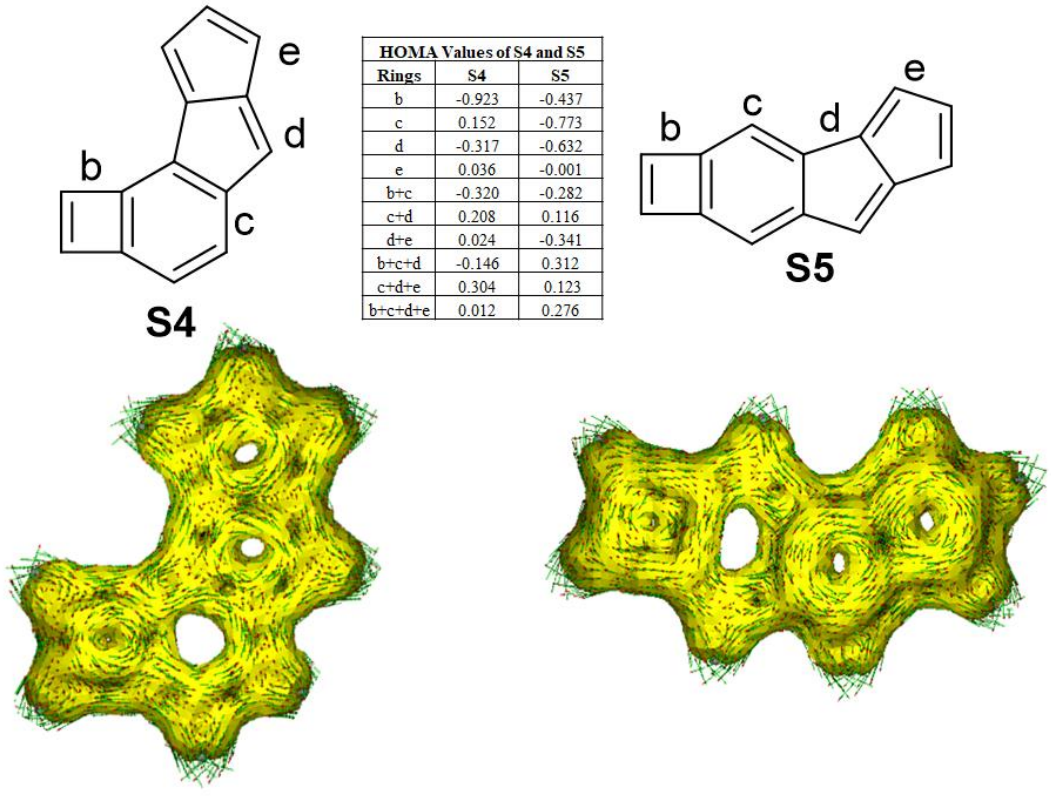


Figure S12. Comparison of NICS-*XY* scans of compounds **S1**, **S2**, **S3**, **S5** and **14'** in their S_0 states.

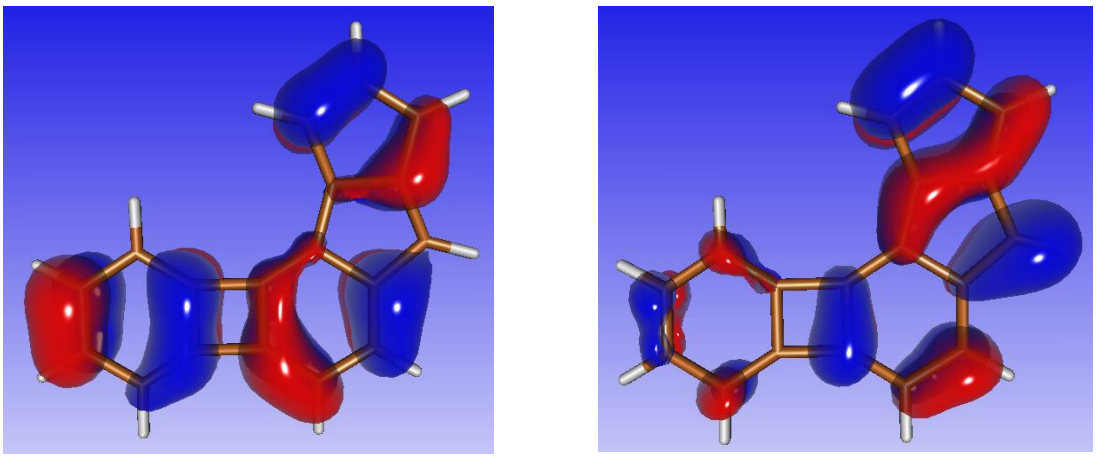


HOMA Values of S4 and S5		
Rings	S4	S5
b	-0.923	-0.437
c	0.152	-0.773
d	-0.317	-0.632
e	0.036	-0.001
b+c	-0.320	-0.282
c+d	0.208	0.116
d+e	0.024	-0.341
b+c+d	-0.146	0.312
c+d+e	0.304	0.123
b+c+d+e	0.012	0.276

Figure S13. HOMA values and ACID plots of compound **S4** and **S5**.

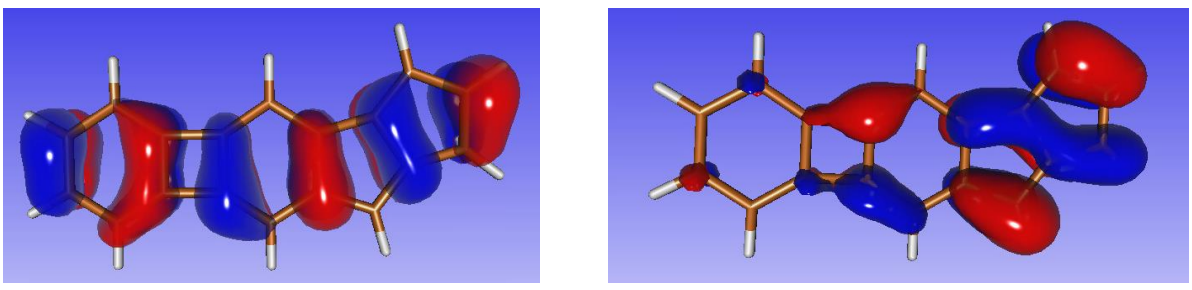
The results show, that in the angular case (**S4**), due to the bond localization in the central benzene ring, the antiaromaticity of both the cyclobutadiene and the pentalene units are strongly reduced (Figure S11). Regarding the linear case (**S5**), cyclobutadiene "wins the battle" and alleviate its antiaromaticity at the expense of maintained pentalene antiaromaticity (Figure S12). The overall outcome is similar to compounds **9'** and **14'**. However, in the linear case of **S5**, the cyclobutadiene unit gains a considerable aromatic character compared to the situation in **14'**, where it remains slightly antiaromatic along with some aromaticity gain in the terminal benzene ring. Thus, the aromaticity/antiaromaticity relationships between the subunits in **S5** versus **14'** show a clear difference between the two systems that suggest that in **14'** the 8π BCB subunit is more influential than the 4π cyclobutadiene ring itself.

S4.5 Calculated SOMOs of the radical anion and cation of 9' and 14'



SOMO (cation) SOMO (anion)

Figure S14. Calculated SOMOs of radical anion and cation of **9'**.

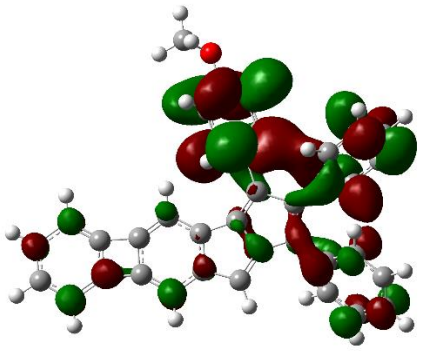
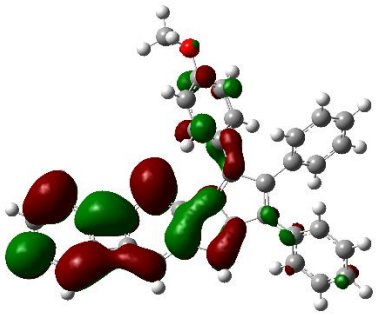
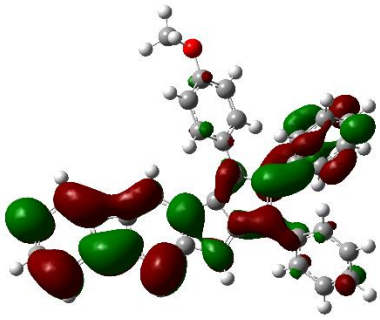
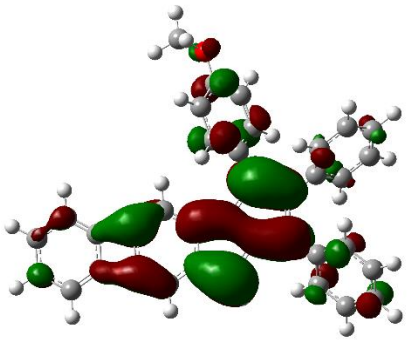


SOMO (cation) SOMO (anion)

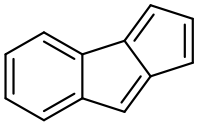
Figure S15. Calculated SOMOs of radical anion and cation of **14'**.

S4.6 Calculated LUMOs of 14

Table S15. Calculated LUMOs of **14**.

	
LUMO	LUMO+1
	
LUMO+2	LUMO+3

S4.7 Cartesian coordinates and absolute electronic energies



Cyclopenta[*a*]indene **17'**

S_0

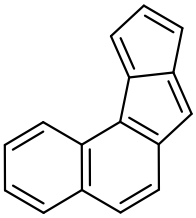
E_{el} = -462.150994853

	X	Y	Z
C	2.82591400	-1.07029900	0.00000100
C	3.16249200	0.27659100	-0.00000100
C	2.15834100	1.26327700	-0.00000400
C	0.83353400	0.86685600	-0.00000200
C	0.48679100	-0.51733600	0.00000200
C	1.47788200	-1.47978700	0.00000300
C	-0.41269100	1.66678600	0.00000500
C	-1.46745300	0.81563600	0.00000800
C	-0.98129700	-0.56898000	0.00000400
C	-2.92981700	0.76981700	-0.00001000
C	-3.27616800	-0.54406200	0.00001000
C	-2.05727700	-1.39308000	-0.00001300
H	3.60955700	-1.81948000	0.00000200
H	4.20522600	0.57232200	-0.00000400
H	2.42531800	2.31478700	-0.00000400
H	1.23090600	-2.53566200	0.00000600
H	-0.43792300	2.74974100	-0.00000100
H	-3.60074100	1.61617600	-0.00001300
H	-4.28469800	-0.93549100	0.00001700
H	-2.06917000	-2.47490300	-0.00002300

T_1

E_{el} = -462.121460345

	X	Y	Z
C	2.76888500	-1.12990700	0.00000200
C	3.13864200	0.22883900	-0.00000100
C	2.18357000	1.24399500	-0.00000400
C	0.82825600	0.90371900	-0.00000400
C	0.44717300	-0.49748200	0.00000000
C	1.42900200	-1.49783900	0.00000400
C	-0.35753400	1.72520600	-0.00000900
C	-1.46220200	0.85791200	0.00000800
C	-0.97375400	-0.53065400	0.00000000
C	-2.85560800	0.80753800	0.00002900
C	-3.23115300	-0.59747800	-0.00003500
C	-2.10009800	-1.40366900	0.00001100
H	3.53957000	-1.89177800	0.00000400
H	4.19154600	0.48872100	-0.00000300
H	2.49175800	2.28387200	-0.00000800
H	1.14606100	-2.54477400	0.00000800
H	-0.36729400	2.80593000	-0.00000900
H	-3.54976900	1.63580600	0.00003700
H	-4.25265100	-0.95515200	-0.00005600
H	-2.09029500	-2.48370600	0.00002200



Pentaleno[*1,2-a*]naphthalene **15'**

S_0

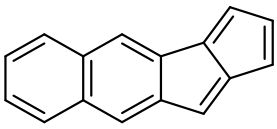
E_{el} = -615.825312168

	X	Y	Z
C	2.09217400	0.68591000	0.00000000
C	1.76557900	2.06214400	-0.00000100
C	0.44782100	2.48678100	0.00000000
C	-0.57576100	1.53147700	0.00000000
C	-0.29038700	0.15423200	0.00000000
C	1.04158100	-0.30290500	0.00000000
C	-2.04727700	1.72131500	0.00000000
C	-2.63125800	0.50010500	0.00000100
C	-1.59185500	-0.53568300	0.00000100
C	-3.93180700	-0.17392200	0.00000000
C	-3.67901600	-1.50715800	-0.00000100
C	-2.21021500	-1.74314600	-0.00000100
C	1.40095900	-1.68073700	0.00000100
C	2.71705100	-2.06612900	0.00000000
C	3.75144400	-1.09478800	0.00000000
C	3.44388100	0.24189600	0.00000000
H	2.57119800	2.78839000	-0.00000100
H	0.21315700	3.54584900	0.00000000
H	-2.53356900	2.68923800	0.00000000
H	-4.90135600	0.30223100	0.00000100
H	-4.41754100	-2.29740100	-0.00000200
H	-1.76105400	-2.72722900	-0.00000200
H	0.61690200	-2.42786700	0.00000100
H	2.97381900	-3.11958300	0.00000100
H	4.78700600	-1.41572900	0.00000000
H	4.23395700	0.98574900	-0.00000100

T_1

E_{el} = -615.803467813

	X	Y	Z
C	2.06722500	0.67862400	0.00000000
C	1.72483100	2.07016600	0.00000000
C	0.41943800	2.50537700	0.00000000
C	-0.62575100	1.56171400	0.00000000
C	-0.32611700	0.14312100	0.00000000
C	1.03081500	-0.31028000	0.00000000
C	-2.04774900	1.76205600	0.00000000
C	-2.63940300	0.49524600	0.00000000
C	-1.56913600	-0.52807500	0.00000000
C	-3.86826300	-0.17426700	0.00000000
C	-3.57767000	-1.57856400	-0.00000100
C	-2.19179600	-1.80018700	0.00000000
C	1.39898100	-1.67333000	0.00000000
C	2.72868800	-2.05103900	0.00000000
C	3.74636900	-1.08018200	0.00000000
C	3.41545600	0.26129200	0.00000000
H	2.53446100	2.79272300	-0.00000100
H	0.19553700	3.56654200	0.00000000
H	-2.54077400	2.72386100	0.00000000
H	-4.85717100	0.26074500	0.00000000
H	-4.32757600	-2.35922000	-0.00000200
H	-1.71714100	-2.76985400	0.00000000
H	0.62543000	-2.43101100	0.00000100
H	2.98941500	-3.10351700	0.00000000
H	4.78633000	-1.38550500	0.00000000
H	4.19599200	1.01521900	0.00000000



Pentaleno[*1,2-b*]naphthalene **16'**

S_0

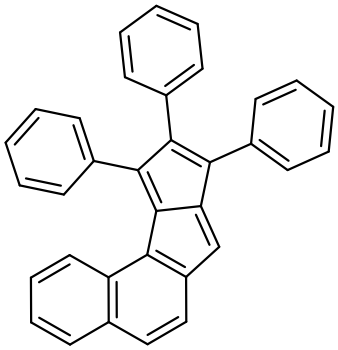
E_{el} = -615.834264240

	X	Y	Z
C	-1.71308700	-0.70296800	0.00000000
C	-1.90918300	0.71495700	0.00000000
C	-0.76690400	1.57988600	0.00000000
C	0.48915600	1.04548900	0.00000000
C	0.69119500	-0.39310100	0.00000000
C	-0.38091600	-1.23533600	0.00000000
C	1.80777000	1.69899500	0.00000000
C	2.76731900	0.73850000	0.00000100
C	2.14042200	-0.59154800	0.00000100
C	4.21117400	0.54517400	0.00000000
C	4.41981500	-0.80157900	-0.00000100
C	3.12893000	-1.52264900	0.00000000
C	-2.84735400	-1.54367500	0.00000000
C	-4.12512200	-1.01805500	0.00000000
C	-4.31716500	0.37562600	0.00000000
C	-3.22650900	1.22316700	0.00000000
H	-0.92061500	2.65457200	0.00000000
H	-0.25053000	-2.31263500	0.00000100
H	1.95090200	2.77267000	0.00000000
H	4.96529600	1.31811700	0.00000000
H	5.38456100	-1.29175900	-0.00000100
H	3.03169900	-2.59991300	-0.00000100
H	-2.70139700	-2.61897200	0.00000000
H	-4.98334000	-1.68048700	0.00000000
H	-5.32188800	0.78248000	0.00000000
H	-3.37193700	2.29863500	0.00000000

T_1

E_{el} = -615.800117704

	X	Y	Z
C	-1.68378400	-0.70481700	0.00000000
C	-1.89656600	0.72035300	0.00000000
C	-0.78282200	1.60673700	0.00000000
C	0.50151500	1.11066100	0.00000000
C	0.71612400	-0.34345700	0.00000000
C	-0.36135200	-1.21273500	0.00000000
C	1.78357900	1.76912300	0.00000000
C	2.76920600	0.76335800	0.00000000
C	2.12111900	-0.54326100	0.00000000
C	4.14885700	0.54051000	0.00000000
C	4.35484800	-0.90619300	-0.00000100
C	3.14223500	-1.55989800	0.00000000
C	-2.81158100	-1.56653400	0.00000000
C	-4.09193300	-1.06319600	0.00000000
C	-4.30085700	0.33501200	0.00000000
C	-3.22927100	1.20098200	0.00000000
H	-0.96558000	2.67668900	0.00000000
H	-0.20720000	-2.28706700	0.00000000
H	1.93488800	2.83914400	0.00000000
H	4.93835200	1.27900600	0.00000000
H	5.32599400	-1.38291100	-0.00000100
H	2.99349600	-2.62977500	0.00000000
H	-2.64557200	-2.63900100	0.00000000
H	-4.94246100	-1.73505200	0.00000000
H	-5.31220300	0.72586000	0.00000000
H	-3.39563000	2.27323200	0.00000000



8,9,10-Triphenylpentaleno[*1*,*2*-*a*]naphthalene **15**

S_0

E_{el} = -1309.15885217

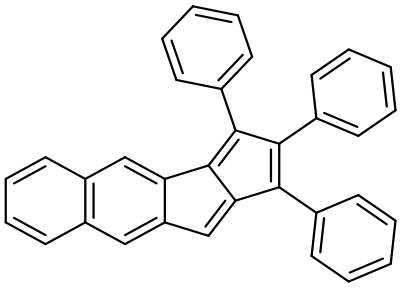
	X	Y	Z
C	-4.54343700	-1.70919000	0.00451800
C	-4.26085700	-3.07641000	0.23276500
C	-2.95875100	-3.53000000	0.30942000
C	-1.90822800	-2.61017300	0.19393600
C	-2.14102200	-1.22974100	0.02315300
C	-3.46646800	-0.75485500	-0.12501100
C	-0.45627400	-2.86620500	0.20035100
C	0.17818200	-1.68229800	0.02829300
C	-0.80079000	-0.59924300	-0.02031300
C	1.52759600	-1.10822700	0.00466100
C	1.36576700	0.25401300	-0.02508900
C	-0.11017200	0.58034600	0.00096400
C	-3.80246500	0.59423600	-0.43169900
C	-5.10954000	0.98961000	-0.56657800
C	-6.16612200	0.06007100	-0.40137300
C	-5.88456900	-1.25367600	-0.12672100
H	-5.08888200	-3.77059500	0.32751500
H	-2.74944400	-4.58419800	0.45642600
H	-0.00998400	-3.84349000	0.33324500
H	-3.00967700	1.31455800	-0.57033200
H	-5.33681000	2.02244000	-0.80598700
H	-7.19424600	0.38886700	-0.50349300
H	-6.68766500	-1.97508600	-0.01581500
C	-0.62063400	1.96347100	0.09003200
C	-1.37816600	2.36687600	1.19951100
C	-0.33763100	2.90551600	-0.90957800
C	-1.84564500	3.67469000	1.30311400
H	-1.59700100	1.64828000	1.98108200
C	-0.82006500	4.20788000	-0.81252200
H	0.25333100	2.61139300	-1.76887700
C	-1.57183900	4.59814300	0.29539200
H	-2.42684500	3.97023400	2.16946700
H	-0.60311600	4.92039500	-1.60046700
C	2.43425800	1.27259800	-0.10268700
C	2.52467800	2.31493100	0.83316400
C	3.39105400	1.21654100	-1.12862300
C	3.54515700	3.25912400	0.75334100
H	1.79730900	2.37902100	1.63373300
C	4.40765500	2.16373500	-1.21112800
H	3.33046000	0.42394800	-1.86529500
C	4.49057600	3.18825700	-0.26884500
H	3.60102500	4.05167500	1.49142900
H	5.13440100	2.10291200	-2.01378000
H	5.28242900	3.92619700	-0.33215500
C	2.76143600	-1.90789100	0.05527300
C	3.85089100	-1.53696900	0.86105000
C	2.86206300	-3.09639000	-0.68831700
C	4.99824900	-2.32154000	0.91397100
H	3.78862400	-0.63514300	1.45720000
C	4.01375700	-3.87733800	-0.63851700
H	2.03818400	-3.39497900	-1.32631200
C	5.08742800	-3.49394100	0.16316400
H	5.82413200	-2.01949900	1.54860400
H	4.07322300	-4.78480600	-1.22944000
H	5.98327600	-4.10310400	0.20537500
H	-1.93916400	5.61525800	0.37345900

T_1

E_{el} = -1309.13771479

	X	Y	Z
C	-4.48115100	-1.75404100	0.00503500
C	-4.17887700	-3.14348800	0.15871400
C	-2.88596300	-3.60515500	0.18576000
C	-1.82114100	-2.68788200	0.09612800
C	-2.06897700	-1.26432500	-0.00014200
C	-3.42109900	-0.79056700	-0.09921600
C	-0.41229600	-2.94928200	0.09666100
C	0.22877000	-1.71471100	0.01372600
C	-0.78300300	-0.64308100	0.00624700
C	1.51004300	-1.13823100	-0.00000900
C	1.30245600	0.30528500	-0.00425700
C	-0.08928200	0.59821500	0.02908900
C	-3.77656400	0.55682300	-0.33327800
C	-5.09957100	0.94763200	-0.41743900
C	-6.13549000	0.00767900	-0.27759800
C	-5.82320200	-1.32151400	-0.07587500
H	-5.00691100	-3.84075700	0.23451100
H	-2.68047400	-4.66607300	0.27807900
H	0.03805700	-3.92886700	0.16230100
H	-2.99907600	1.29498100	-0.45870100
H	-5.33711100	1.98998300	-0.59842200
H	-7.17054000	0.32346900	-0.34034000
H	-6.61302000	-2.06039200	0.01396000
C	-0.65507400	1.96689300	0.07993900
C	-1.35044000	2.40516300	1.21678300

C	-0.49028400	2.86054100	-0.98741800
C	-1.86517500	3.69767700	1.28413900
H	-1.48536600	1.72496200	2.05052600
C	-1.00972500	4.15156500	-0.92244800
H	0.04498300	2.53708500	-1.87262200
C	-1.69705600	4.57580900	0.21397600
H	-2.39752600	4.01845900	2.17280300
H	-0.87625000	4.82674700	-1.76047400
C	2.37661000	1.31027900	-0.08852800
C	2.43194000	2.40382300	0.79176400
C	3.37481900	1.19649900	-1.07202400
C	3.45193000	3.34567200	0.69443100
H	1.67752500	2.50717200	1.56158900
C	4.38369300	2.14824500	-1.17797600
H	3.34863600	0.36191000	-1.76228800
C	4.42927300	3.22504500	-0.29277100
H	3.48175500	4.17681000	1.39020700
H	5.13720800	2.04751700	-1.95120100
H	5.21962200	3.96311100	-0.37124000
C	2.77493800	-1.87203800	0.06533100
C	3.85912400	-1.42774000	0.84603800
C	2.92018100	-3.08867800	-0.62951500
C	5.03183900	-2.17068100	0.92883500
H	3.77199500	-0.50563500	1.40623300
C	4.09667300	-3.82605200	-0.54941000
H	2.10774700	-3.43906300	-1.25519900
C	5.15958500	-3.37199000	0.23138200
H	5.84851400	-1.81226800	1.54584700
H	4.18684600	-4.75431000	-1.10304200
H	6.07635100	-3.94704500	0.29570000
H	-2.09797700	5.58189900	0.26532500



1,2,3-Triphenylpentaleno[*1*,*2*-*b*]naphthalene **16**

S_0

E_{el} = -1309.17138848

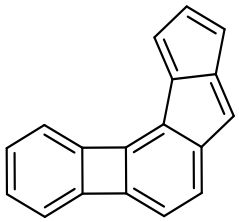
	X	Y	Z
C	-4.55202300	-0.03859600	0.02346000
C	-4.72548500	-1.45953200	0.00102000
C	-3.56974600	-2.30243300	-0.02912800
C	-2.32168600	-1.74582900	-0.03963200
C	-2.14073300	-0.30435400	-0.02566500
C	-3.23145700	0.51808500	0.00576000
C	-0.99861700	-2.38053200	-0.04513600
C	-0.05492600	-1.40195500	-0.02830900
C	-0.69342100	-0.08832900	-0.04119100
C	1.39305500	-1.21172700	-0.00956400
C	1.60353900	0.15065100	0.00236500
C	0.28255700	0.86696600	-0.01831400
C	-5.70067800	0.78326800	0.06008600
C	-6.96904800	0.23664100	0.07260900
C	-7.13851700	-1.16059500	0.04847100
C	-6.03492800	-1.98975200	0.01358800
H	-3.70290800	-3.37986800	-0.03873400
H	-3.12232600	1.59636900	0.02220000
H	-0.83769100	-3.45091100	-0.05179800
H	-5.57191100	1.86061000	0.07919100
H	-7.83793600	0.88450500	0.10111700
H	-8.13648500	-1.58384300	0.05798900
H	-6.16290700	-3.06735000	-0.00428100
C	0.09716100	2.32776600	0.02373400
C	0.76697300	3.12268100	0.96782500
C	-0.77908200	2.95674400	-0.87518700
C	0.55287800	4.49691100	1.02014900
H	1.44797200	2.65823600	1.67044600
C	-0.98334200	4.33316400	-0.82908700
H	-1.28524600	2.35944500	-1.62499900
C	-0.32045200	5.10856600	0.12154300
H	1.07104500	5.09184000	1.76400700
H	-1.65667800	4.80102900	-1.53898300
C	2.91219700	0.83643100	0.02828400
C	3.87213100	0.51285300	0.99989500
C	3.22810900	1.82560300	-0.91639900
C	5.10836500	1.15223300	1.02210400
H	3.64046500	-0.24221800	1.74176600
C	4.46798800	2.45880300	-0.89846100
H	2.50070300	2.09133700	-1.67448600
C	5.41259700	2.12611500	0.07143000
H	5.83447900	0.89069200	1.78391600
H	4.69555400	3.21427100	-1.64238200
H	6.37598300	2.62330500	0.08824300
C	2.37191500	-2.31108700	-0.06478000
C	2.19603500	-3.45407600	0.73352100
C	3.47808500	-2.27229300	-0.92935300
C	3.09801500	-4.51351800	0.67732800
H	1.35778900	-3.49908000	1.41957200
C	4.37685300	-3.33271800	-0.98656900
H	3.62364200	-1.40925900	-1.56719600
C	4.19303100	-4.45815100	-0.18317500
H	2.94746000	-5.38121000	1.31037400
H	5.22072500	-3.28282800	-1.66590200

H	4.89473500	-5.28330900	-0.22908600
H	-0.48051000	6.18020500	0.15967700

T_1

E_{el} = -1309.14076183

	X	Y	Z
C	-4.48958500	-0.07824600	0.03342200
C	-4.68015100	-1.50473900	0.02486600
C	-3.54976300	-2.36925000	0.00920700
C	-2.27589100	-1.84747400	-0.00004200
C	-2.08283600	-0.39394200	-0.00412000
C	-3.17432900	0.45431700	0.01639200
C	-0.98390400	-2.48789200	0.00339600
C	-0.01492400	-1.47173200	0.01579100
C	-0.66996800	-0.18183200	-0.01780600
C	1.38046100	-1.25251400	-0.00011300
C	1.57307500	0.22115700	-0.01123200
C	0.32856600	0.85393500	-0.03444300
C	-5.63008400	0.76477800	0.05815300
C	-6.90301300	0.24080000	0.07119400
C	-7.09008500	-1.15974300	0.06035700
C	-6.00434800	-2.00804500	0.03802700
H	-3.71041300	-3.44285600	0.00983300
H	-3.04182200	1.53002800	0.02760300
H	-0.82368500	-3.55592800	-0.00372400
H	-5.48106200	1.83969800	0.06708900
H	-7.76371900	0.89941900	0.09010000
H	-8.09496300	-1.56690800	0.07058800
H	-6.15296900	-3.08296700	0.03104900
C	0.04901900	2.30460400	-0.00833000
C	0.59209400	3.13741000	0.98152900
C	-0.79065100	2.88033400	-0.97484700
C	0.30656000	4.49982400	1.00199600
H	1.23434600	2.70987200	1.74212400
C	-1.07070500	4.24456600	-0.95763200
H	-1.21077000	2.25399400	-1.75407200
C	-0.52394100	5.06023300	0.03214200
H	0.73138900	5.12462200	1.77990300
H	-1.71333300	4.67087300	-1.72027600
C	2.87875700	0.90334300	0.04672300
C	3.82825000	0.55396900	1.02224200
C	3.20278600	1.92528200	-0.86087800
C	5.05292400	1.21104900	1.09288300
H	3.59711200	-0.23006400	1.73352300
C	4.43253000	2.57360800	-0.79558800
H	2.48709800	2.20261500	-1.62542000
C	5.36178600	2.22180700	0.18306800
H	5.76776000	0.93242500	1.85920800
H	4.66578000	3.35463900	-1.51075700
H	6.31821600	2.72975700	0.23538200
C	2.40344800	-2.28569500	-0.07857200
C	2.20403400	-3.52430400	0.56820300
C	3.58958500	-2.11730900	-0.82312400
C	3.14758700	-4.53998800	0.48081900
H	1.31241600	-3.66958500	1.1658130
C	4.52466600	-3.14143100	-0.91781300
H	3.76398900	-1.18814700	-1.34903000
C	4.31340100	-4.35582800	-0.26449800
H	2.97686500	-5.47729900	0.99888100
H	5.42169500	-2.99212200	-1.50846800
H	5.04768900	-5.15015200	-0.33584300
H	-0.74371800	6.12178000	0.04827100



Pentaleno[*1,2-a*]biphenylene **9'**

S_0

E_{el} = -691.988779582

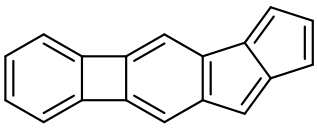
	X	Y	Z
C	3.74013300	-1.92224500	0.00000000
C	4.50484100	-0.75828400	0.00000300
C	3.91322300	0.52575400	-0.00000400
C	2.53773600	0.55238800	-0.00000300
C	1.75618300	-0.63772200	0.00000100
C	2.32667300	-1.88953500	0.00000200
C	1.29308400	1.38457000	-0.00000100
C	0.49966400	0.17457700	0.00000000
C	0.75070700	2.63562700	0.00000000
C	-0.68117100	2.70540800	0.00000100
C	-1.44541000	1.55986000	0.00000000
C	-0.85917900	0.22088800	0.00000000
C	-2.90497200	1.40936500	0.00000300
C	-3.21140800	0.08338600	0.00000000
C	-1.97760200	-0.71308600	0.00000000
C	-4.33262500	-0.84441500	-0.00000300
C	-3.79876500	-2.09986300	0.00000200
C	-2.32404800	-2.02825000	-0.00000200
H	4.24534300	-2.88158400	-0.00000600
H	5.58589300	-0.84094300	0.00000900
H	4.52546100	1.41983700	-0.00000100
H	1.74910800	-2.80621800	-0.00000300
H	1.34410200	3.54178800	-0.00000200
H	-1.16405800	3.67689200	0.00000300
H	-3.59734700	2.24253400	0.00000300

H	-5.38172400	-0.58781300	-0.00000500
H	-4.35919000	-3.02539500	0.00000500
H	-1.66997200	-2.88962900	-0.00000300

T_1

E_{el} = -691.955175113

	X	Y	Z
C	3.72088700	-1.91280700	0.00000300
C	4.48327100	-0.75036300	0.00004000
C	3.89260700	0.53911000	-0.00011300
C	2.52011400	0.56761700	-0.00007800
C	1.73875400	-0.62526500	0.00007000
C	2.30398300	-1.87650500	0.00009200
C	1.26685000	1.39329600	0.00000100
C	0.48727400	0.19451700	0.00001400
C	0.70861100	2.65145000	0.00002900
C	-0.70729600	2.73418200	0.00004800
C	-1.49880100	1.58742200	-0.00002800
C	-0.89009300	0.23636500	-0.00001700
C	-2.92280000	1.44045400	-0.00002500
C	-3.21240300	0.05885900	0.00000500
C	-1.96038300	-0.69421400	-0.00002200
C	-4.25242000	-0.86883500	0.00004600
C	-3.64493600	-2.20060900	-0.00003100
C	-2.27075600	-2.09785800	-0.00003800
H	4.22426700	-2.87294700	-0.00016300
H	5.56454000	-0.83247400	0.00018800
H	4.50777900	1.43107300	-0.00004700
H	1.72434700	-2.79200200	-0.00000300
H	1.30659600	3.55528400	-0.00002200
H	-1.18041100	3.71018300	0.00008700
H	-3.63172600	2.25641600	-0.00001400
H	-5.31560200	-0.67313500	0.00008600
H	-4.20641500	-3.12545000	-0.00003300
H	-1.56815700	-2.91784800	-0.00005100



Pentaleno[*1,2-b*]biphenylene **14'**

S_0

E_{el} = -691.981926944

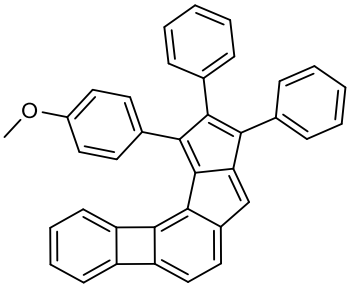
	X	Y	Z
C	4.87332600	-0.97965000	0.00000000
C	5.01947500	0.39858700	0.00000300
C	3.89841400	1.27319200	-0.00000400
C	2.66938800	0.66840000	-0.00000300
C	2.51940100	-0.74683300	0.00000200
C	3.59296300	-1.59761900	0.00000400
C	1.16914300	0.82446100	-0.00000100
C	1.02047500	-0.58473600	0.00000000
C	0.09031900	1.68774400	-0.00000100
C	-1.16921000	1.06369400	0.00000000
C	-1.31820600	-0.35295300	0.00000000
C	-0.21153100	-1.21474700	0.00000000
C	-2.51557600	1.67746400	0.00000100
C	-3.44380300	0.68849600	0.00000100
C	-2.76516600	-0.60773800	-0.00000100
C	-4.88537700	0.43314100	0.00000400
C	-5.04266000	-0.91620300	-0.00000100
C	-3.71131400	-1.57915700	-0.00000200
H	5.75940600	-1.60442300	-0.00000700
H	6.01728100	0.82284800	0.00001000
H	4.03440000	2.34831300	0.00000000
H	3.49848300	-2.67719800	-0.00000100
H	0.18881800	2.76751300	-0.00000100
H	-0.32879400	-2.29211100	-0.00000100
H	-2.68960600	2.74680200	0.00000200
H	-5.66977600	1.17578500	0.00000600
H	-5.98380200	-1.44903600	-0.00000200
H	-3.56676200	-2.65175700	-0.00000300

T_1

E_{el} = -691.963392464

	X	Y	Z
C	4.83215200	-0.98791000	0.00000000
C	4.98065300	0.40026900	0.00000200
C	3.86906900	1.26909700	0.00000000
C	2.63231000	0.66026100	-0.00000100
C	2.48008700	-0.75738300	0.00000000
C	3.56452700	-1.60853600	0.00000000
C	1.15586400	0.83287900	-0.00000100
C	0.99818300	-0.61469600	-0.00000100
C	0.10504500	1.71055300	-0.00000200
C	-1.17904500	1.10947600	0.00000000
C	-1.34049900	-0.35559700	0.00000000
C	-0.21941600	-1.23057300	-0.00000200
C	-2.46861400	1.72639300	0.00000100
C	-3.42593400	0.70610500	0.00000000
C	-2.72898300	-0.59762400	0.00000000
C	-4.80689100	0.45075100	-0.00000100
C	-4.96391400	-0.96389600	0.00000300
C	-3.70598300	-1.60982600	0.00000100
H	5.72160100	-1.60819900	-0.00000200
H	5.98007100	0.82037200	0.00000600
H	4.00215700	2.34440900	0.00000200
H	3.47385500	-2.68813000	-0.00000200
H	0.22171000	2.78826900	-0.00000200

H	-0.34992500	-2.30650200	-0.00000300
H	-2.64298600	2.79336500	0.00000100
H	-5.61052100	1.17272600	-0.00000200
H	-5.91777000	-1.47590000	0.00000400
H	-3.54985500	-2.67886100	0.00000000



1-(4-Methoxyphenyl)-2,3-diphenylpentaleno[*1,2-a*]biphenylene

9

S_0

E_{el} = -1460.57281945

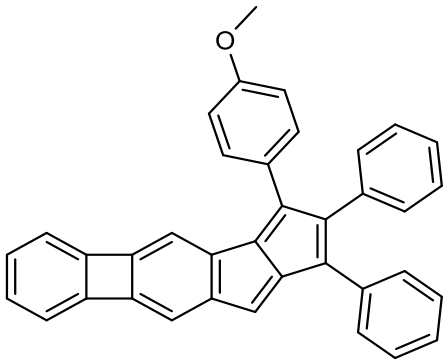
	X	Y	Z
C	5.80238600	0.03313300	-0.46915500
C	6.55917100	-1.13123300	-0.36899000
C	5.95845700	-2.39523300	-0.16969700
C	4.58657200	-2.39783200	-0.07173600
C	3.81286800	-1.20643600	-0.15833300
C	4.39162300	0.02379700	-0.36938700
C	3.34299100	-3.21100900	0.08166100
C	2.55025700	-2.00238100	0.01020900
C	2.81165900	-4.46145500	0.20421800
C	1.38531000	-4.53507300	0.24890600
C	0.61630900	-3.39309000	0.18254300
C	1.18797800	-2.04745300	0.08467800
C	-0.83862800	-3.26937000	0.15555000
C	-1.15983500	-1.95078500	0.04264500
C	0.04761700	-1.13339500	0.04625000
C	-2.31997200	-1.06768800	-0.01365400
C	-1.82501800	0.21928000	-0.02901400
C	-0.32547600	0.18439500	0.02917600
H	6.31089700	0.97719200	-0.63062800
H	7.63835000	-1.06625900	-0.45257500
H	6.56039500	-3.29413800	-0.10588000
H	3.82205900	0.93943300	-0.45381200
H	3.41335700	-5.36092000	0.25169300
H	0.90299600	-5.50395800	0.32476800
H	-1.52026800	-4.10838500	0.21302800
C	0.53369500	1.37605300	0.10011700
C	1.50681300	1.49408300	1.10913800
C	0.39695300	2.44185200	-0.79809200
C	2.29503200	2.62894500	1.22162900
H	1.62660600	0.68942800	1.82551100
C	1.19858300	3.57824600	-0.71144500
H	-0.34160500	2.38388700	-1.58831700
C	2.14919100	3.68034200	0.30886700
H	3.03282600	2.72197700	2.00958300
H	1.06730200	4.37188500	-1.43446500
C	-2.62348100	1.46256300	-0.08651700
C	-3.55549100	1.66672900	-1.11582300
C	-2.47603900	2.46510200	0.88496300
C	-4.31981000	2.82931600	-1.16764600
H	-3.67645100	0.90600800	-1.87829700
C	-3.24589300	3.62438700	0.83681400
H	-1.76140800	2.32858000	1.68811900
C	-4.17054200	3.81211300	-0.18975100
H	-5.03256100	2.96755400	-1.97328800
H	-3.12311600	4.38204200	1.60303900
H	-4.76788600	4.71621500	-0.22829600
C	-3.71607100	-1.53506500	0.01242600
C	-4.68565100	-0.92437400	0.82498400
C	-4.10452400	-2.64230600	-0.76120400
C	-5.99268800	-1.39993100	0.85723900
H	-4.40609800	-0.08035700	1.44311600
C	-5.41392300	-3.11522100	-0.73034000
H	-3.37682300	-3.11925100	-1.40783900
C	-6.36484000	-2.49621700	0.07915200
H	-6.72237800	-0.91631000	1.49743600
H	-5.69230700	-3.96563900	-1.34326800
H	-7.38407400	-2.86487700	0.10557400
O	2.97211800	4.75217500	0.49685700
C	2.85767600	5.86238100	-0.38408600
H	1.85813000	6.30777700	-0.33769900
H	3.59266800	6.58925200	-0.04237400
H	3.08290300	5.57843200	-1.41775100

T_1

E_{el} = -1460.53577054

	X	Y	Z
C	5.68469300	-0.06181600	-0.33725200
C	6.42589200	-1.23715200	-0.28973400
C	5.81128400	-2.50686500	-0.15638000
C	4.44047700	-2.50075300	-0.06824200
C	3.68146000	-1.29521500	-0.10434700
C	4.27065000	-0.06264500	-0.24826400
C	3.18079200	-3.30034900	0.03796100
C	2.41265700	-2.08870600	0.01483100
C	2.61978000	-4.55357400	0.09136100
C	1.20435400	-4.62254300	0.11352900
C	0.42690800	-3.46815500	0.08557900
C	1.03493300	-2.11820600	0.05782900
C	-0.99677800	-3.32628100	0.05647200
C	-1.28881000	-1.95179700	0.00424200

C	-0.05458300	-1.19144300	0.04906500
C	-2.36529500	-1.04530900	-0.01222100
C	-1.76318700	0.31592900	0.01448200
C	-0.37159000	0.20999900	0.07532800
H	6.20383500	0.88384700	-0.44582400
H	7.50652300	-1.18045100	-0.36154300
H	6.40563500	-3.41263200	-0.13274200
H	3.70969000	0.86107500	-0.28943100
H	3.21361900	-5.46001800	0.10215900
H	0.71800700	-5.59174500	0.14052900
H	-1.69897400	-4.14714700	0.07273700
C	0.59188300	1.33156800	0.13421400
C	1.40606200	1.51403700	1.26497000
C	0.69406600	2.26759000	-0.89820900
C	2.26520300	2.59790700	1.36716500
H	1.34914300	0.80343200	2.08218600
C	1.56401000	3.35590800	-0.81689500
H	0.08142200	2.15039000	-1.78452300
C	2.34959300	3.52969100	0.32542600
H	2.88407900	2.74132300	2.24485000
H	1.61328600	4.05438400	-1.64147600
C	-2.52187300	1.57578400	-0.07756000
C	-3.49170400	1.75315400	-1.07966700
C	-2.28965200	2.63496100	0.81596800
C	-4.19323600	2.94973900	-1.19086800
H	-3.68557600	0.95003900	-1.78069500
C	-3.00201000	3.82587100	0.71139800
H	-1.55356100	2.51614000	1.60147000
C	-3.95423800	3.99075000	-0.29425900
H	-4.92937400	3.06839900	-1.97827700
H	-2.81345100	4.62662300	1.41797000
H	-4.50625400	4.92027000	-0.37690900
C	-3.77774500	-1.39736200	0.03483400
C	-4.71862400	-0.63900400	0.76199700
C	-4.23687000	-2.55894700	-0.62216400
C	-6.05042200	-1.03128100	0.83281100
H	-4.39593900	0.24649500	1.29319500
C	-5.57129400	-2.93989200	-0.55847800
H	-3.53832500	-3.14400500	-1.20790600
C	-6.48647500	-2.17959500	0.17153400
H	-6.75143300	-0.43895300	1.41043500
H	-5.90123800	-3.82963500	-1.08349300
H	-7.52704300	-2.47909400	0.22423800
O	3.22432600	4.56056700	0.51675500
C	3.34457100	5.54736000	-0.49914600
H	2.39233600	6.06001500	-0.67321600
H	4.07794600	6.26368600	-0.13240800
H	3.70174200	5.11287200	-1.43922600



3-(4-Methoxyphenyl)-1,2-diphenylpentaleno[*1,2-b*]biphenylene **14**

S_0

E_{el} = -1460.56798383

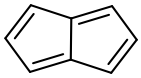
	X	Y	Z
C	7.83086000	-0.16510500	0.14468800
C	7.97799800	-1.54171100	0.07507100
C	6.85775500	-2.41427100	0.00265000
C	5.62808200	-1.80998100	0.00556000
C	5.47690300	-0.39623700	0.07637100
C	6.55026200	0.45240200	0.14706800
C	4.12925300	-1.96546400	-0.03612600
C	3.97884900	-0.55693500	0.03225000
C	3.05114200	-2.82438200	-0.09302600
C	1.78972200	-2.19967100	-0.08574900
C	1.63619400	-0.78047700	-0.03088100
C	2.75030000	0.07576200	0.03473900
C	0.45390500	-2.81598100	-0.10433200
C	-0.47556500	-1.82436600	-0.05726000
C	0.18877500	-0.53411200	-0.03802400
C	-1.92619900	-1.60108100	-0.02490800
C	-2.11128300	-0.23994100	0.02482100
C	-0.76439900	0.44549800	0.01133500
H	8.71621200	0.45848900	0.19926600
H	8.97580900	-1.96619900	0.07642300
H	6.99465800	-3.48803700	-0.05043700
H	6.45524800	1.53059700	0.20293200
H	3.14696700	-3.90370000	-0.13514900
H	2.63878900	1.15099000	0.09140500
H	0.28022600	-3.88393600	-0.13922100
C	-0.55338300	1.89736600	0.06160100
C	-1.23700300	2.71397500	0.98386600
C	0.35786200	2.51640400	-0.80291600
C	-0.99888900	4.07540100	1.05015800
H	-1.94919900	2.26924000	1.66749700
C	0.59336500	3.88968100	-0.76018200
H	0.87599800	1.91722100	-1.54264000
C	-0.08392900	4.67696200	0.17571700
H	-1.51393000	4.69886000	1.77097300
H	1.29368900	4.32799300	-1.45843800

C	-3.40299500	0.47575300	0.07429200
C	-4.35485900	0.17024200	1.05997200
C	-3.71298600	1.47581000	-0.86129400
C	-5.57697300	0.83538900	1.10350300
H	-4.12756700	-0.59229600	1.79569400
C	-4.93751600	2.13737900	-0.82007000
H	-2.99260700	1.72752300	-1.63089900
C	-5.87445600	1.82084700	0.16262800
H	-6.29680400	0.58580000	1.87527600
H	-5.15982400	2.90155900	-1.55674000
H	-6.82609200	2.33928300	0.19693400
C	-2.92663700	-2.67834700	-0.09923400
C	-2.75149000	-3.85602900	0.64744700
C	-4.05525700	-2.58299900	-0.92999300
C	-3.67736700	-4.89349400	0.57638400
H	-1.89481400	-3.94509900	1.30552700
C	-4.97625500	-3.62285900	-1.00422700
H	-4.20056000	-1.69263600	-1.52882200
C	-4.79415600	-4.78222200	-0.25010200
H	-3.52767900	-5.78852200	1.17031300
H	-5.83667600	-3.53001100	-1.65774900
H	-5.51383000	-5.59097500	-0.30839000
O	0.07005400	6.02345600	0.31093100
C	0.98392100	6.69666000	-0.54583200
H	0.94225100	7.74568900	-0.25805500
H	2.00509300	6.32411500	-0.41196800
H	0.69288900	6.59719100	-1.59698000

T_1

E_{el} = -1460.54934663

	X	Y	Z
C	7.75255200	-0.25894300	0.14183600
C	7.88625700	-1.64615800	0.07989800
C	6.76448800	-2.50108800	0.01407200
C	5.53529600	-1.87908100	0.01421800
C	5.39789500	-0.46107900	0.07652400
C	6.49069100	0.37560300	0.14194000
C	4.05497000	-2.03226900	-0.02420100
C	3.91302300	-0.58863700	0.03627100
C	2.99301200	-2.89425000	-0.07391100
C	1.71600500	-2.27659600	-0.06577300
C	1.56881000	-0.81464000	-0.01818900
C	2.70333000	0.04357200	0.03871300
C	0.42196100	-2.88342000	-0.08639800
C	-0.52341400	-1.85499400	-0.04244900
C	0.17656300	-0.56473600	-0.03015900
C	-1.91218700	-1.61141200	-0.02491800
C	-2.07097500	-0.17032900	0.01109700
C	-0.78796600	0.46684400	-0.00133400
H	8.64820200	0.35035900	0.19195900
H	8.88079000	-2.07773300	0.08332000
H	6.88585300	-3.57689800	-0.03246300
H	6.41104000	1.45504000	0.19179900
H	3.09505000	-3.97293200	-0.11137600
H	2.58932000	1.11888800	0.08967200
H	0.24014300	-3.94782700	-0.12148100
C	-0.51206600	1.91345100	0.05882400
C	-1.08828000	2.74094900	1.04091600
C	0.35697700	2.51267700	-0.86010300
C	-0.80497100	4.09528500	1.09930200
H	-1.75858500	2.30967300	1.77461000
C	0.64666800	3.87736800	-0.81879000
H	0.80406400	1.90639800	-1.64006400
C	0.06374400	4.67692300	0.16723400
H	-1.24414800	4.72583700	1.86316400
H	1.31513600	4.29795400	-1.55824000
C	-3.36048300	0.53876800	0.08094900
C	-4.32994600	0.17199200	1.03023000
C	-3.65236500	1.59985600	-0.79274300
C	-5.54368500	0.84765700	1.10704300
H	-4.12175400	-0.64096000	1.71537000
C	-4.87307600	2.26444900	-0.72394900
H	-2.92012800	1.89394900	-1.53480800
C	-5.82239600	1.89417400	0.22820600
H	-6.27406500	0.55537400	1.85333800
H	-5.08260100	3.07444700	-1.41378000
H	-6.77068600	2.41673700	0.28518100
C	-2.95516700	-2.63856700	-0.10929400
C	-2.80508100	-3.85403500	0.58527500
C	-4.10310300	-2.47564100	-0.90690500
C	-3.76229800	-4.85914300	0.49051700
H	-1.93952200	-3.99472800	1.22209900
C	-5.05634400	-3.48394800	-1.00336600
H	-4.23705600	-1.56008200	-1.46884500
C	-4.89408900	-4.68025000	-0.30451100
H	-3.62766800	-5.78216200	1.04401900
H	-5.92733100	-3.33712500	-1.63267800
H	-5.63978800	-5.46361300	-0.37952100
O	0.27459300	6.01870400	0.30419700
C	1.14538600	6.66654700	-0.61264100
H	1.16264000	7.71433200	-0.31711800
H	2.16037000	6.25785700	-0.55758700
H	0.77557800	6.58619000	-1.64073000



Pentalene

S_0

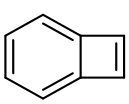
E_{el} = -308.451673

	X	Y	Z
C	-2.169985	0.061221	-0.000029
C	-1.222941	1.219852	0.000015
C	-1.465903	-1.095147	0.000088
C	-0.038037	-0.727960	-0.000005
C	0.038127	0.727883	-0.000009
C	1.222999	-1.219856	-0.000076
C	2.169946	-0.061138	0.000069
C	1.465788	1.095123	-0.000060
H	-1.870638	-2.096847	0.000123
H	1.532637	-2.257390	-0.000060
H	3.246732	-0.157946	0.000141
H	1.870626	2.096797	-0.000080
H	-3.246722	0.158199	-0.000078
H	-1.532600	2.257328	-0.000005

T_1

E_{el} = -308.437801

	X	Y	Z
C	-2.143798	0.000838	-0.000016
C	-1.337147	1.170908	-0.000021
C	-1.337537	-1.171049	0.000017
C	-0.000314	-0.743478	0.000014
C	0.000389	0.742847	-0.000009
C	1.337051	-1.170959	0.000025
C	2.143775	0.000064	-0.000002
C	1.337690	1.170744	-0.000008
H	-1.707244	-2.185915	0.000035
H	1.706053	-2.186186	0.000045
H	3.226396	-0.000463	-0.000003
H	1.705812	2.186226	-0.000019
H	-3.226420	0.000399	-0.000023
H	-1.705254	2.186458	-0.000036



Benzocyclobutadiene

S_0

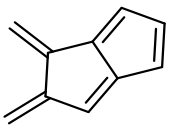
E_{el} = -308.441997

	X	Y	Z
C	-1.844033	-0.688296	-0.000148
C	-1.844060	0.688246	0.000145
C	-0.623397	1.443311	0.000276
C	0.521988	0.711262	0.000068
C	0.521989	-0.711152	-0.000066
C	-0.623352	-1.443297	-0.000274
C	2.046794	0.675032	-0.000432
C	2.046669	-0.675083	0.000432
H	-2.788747	-1.220096	-0.000202
H	-2.788779	1.220026	0.000198
H	-0.644456	2.526942	0.000269
H	-0.644313	-2.526927	-0.000268
H	2.825432	1.425070	-0.000829
H	2.825279	-1.425148	0.000823

T_1

E_{el} = -308.398812

	X	Y	Z
C	-1.804065	-0.713723	-0.000012
C	-1.804056	0.713713	0.000010
C	-0.630749	1.463649	0.000016
C	0.559494	0.733823	0.000006
C	0.559461	-0.733774	-0.000003
C	-0.630763	-1.463648	-0.000016
C	1.986382	0.740528	-0.000021
C	1.986344	-0.740568	0.000020
H	-2.760517	-1.224145	-0.000017
H	-2.760488	1.224165	0.000014
H	-0.658618	2.547179	0.000016
H	-0.658530	-2.547176	-0.000016
H	2.752947	1.501083	-0.000050
H	2.752923	-1.501103	0.000046



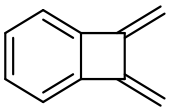
1,2-dimethylene-1,2-dihydropentalene

S_0

E_{el} = -385.891560573

	X	Y	Z
C	-1.70425700	1.21839100	0.00000000
C	-2.73876100	0.17783900	-0.00000200
C	-2.17529200	-1.07067400	0.00000200
C	-0.74555300	-0.86495300	0.00000000
C	-0.49730600	0.58833800	0.00000000
C	0.43903700	-1.52757800	0.00000000
C	1.54809100	-0.56817100	0.00000000

C	0.94378100	0.81350000	0.00000000
H	-1.90421000	2.28094100	0.00000000
H	-3.80151100	0.38529400	-0.00000300
H	-2.69391800	-2.01757000	0.00000400
H	0.58989600	-2.60057100	0.00000100
C	1.61621500	1.97292500	0.00000100
H	1.09679300	2.92371800	0.00000100
H	2.69913600	2.00658700	0.00000100
C	2.85000700	-0.89175700	-0.00000100
H	3.62832300	-0.13822900	-0.00000100
H	3.16972400	-1.92733700	-0.00000100

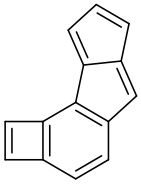


7,8-dimethylenebicyclo[4.2.0]octa-1,3,5-triene

S_0

E_{el} = -385.898896432

	X	Y	Z
C	-2.46312300	0.70153400	0.00002300
C	-1.27372600	1.44267600	-0.00049800
C	-0.10031000	-0.70454200	-0.00008200
C	-1.27367800	-1.44269500	0.00040700
C	-2.46310600	-0.70159700	0.00026900
H	-3.41398000	1.22295700	0.00001200
H	-1.29231400	2.52636900	-0.00088300
H	-1.29220800	-2.52638600	0.00085300
H	-3.41394900	-1.22304700	0.00064400
C	-0.10030600	0.70460100	-0.00045100
C	1.38693100	0.75784900	-0.00027700
C	1.38686600	-0.75789400	-0.00005000
C	2.32632000	-1.70227000	-0.00035200
H	2.07045300	-2.75545800	-0.00022500
H	3.37969200	-1.44671000	-0.00064800
C	2.32620300	1.70234000	0.00067000
H	3.37959700	1.44677800	0.00129500
H	2.07028700	2.75549100	0.00100000

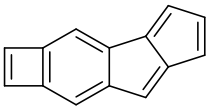


cyclobuta[*g*]cyclopenta[*a*]indene

S_0

E_{el} = -538.288419454

	X	Y	Z
C	2.58466400	-0.00037000	-0.00000800
C	2.61952500	1.35246100	0.00000000
C	1.33565300	2.02233400	-0.00000200
C	0.16931900	1.30541600	-0.00000500
C	0.14277100	-0.17620000	-0.00000800
C	1.35358600	-0.77330400	-0.00001000
C	-1.21254000	1.77083900	0.00000200
C	-2.04761400	0.69226500	0.00000700
C	-1.26140800	-0.55159400	-0.00000100
C	-3.44936800	0.32482700	0.00001000
C	-3.49228600	-1.04233800	-0.00000100
C	-2.13093200	-1.59987800	-0.00000900
C	2.19087200	-2.01760500	0.00001000
C	3.34349300	-1.29321000	0.00000800
H	3.53649700	1.92946600	0.00000600
H	1.30698000	3.10678800	0.00000100
H	-1.49655700	2.81642600	0.00000200
H	-4.29362300	0.99843000	0.00001900
H	-4.39182400	-1.64416500	-0.00000200
H	-1.90170500	-2.65675800	-0.00001900
H	1.97346200	-3.07669900	0.00002000
H	4.39235200	-1.55534100	0.00001500



cyclobuta[*f*]cyclopenta[*a*]indene

S_0

E_{el} = -538.276029086

	X	Y	Z
C	2.16610600	-0.86817200	-0.00000400
C	2.47045000	0.59761300	-0.00000400
C	1.52814600	1.56158400	-0.00000500
C	0.16620700	1.09019700	-0.00001500
C	-0.14022300	-0.41193800	-0.00002200
C	0.91841800	-1.38547900	-0.00001100
C	-1.01547500	1.77237900	-0.00000900
C	-2.09598500	0.79314900	-0.00001300
C	-1.50212600	-0.53706900	-0.00003000
C	-3.45187000	0.65582200	0.00003000
C	-3.75488900	-0.79205300	0.00002400
C	-2.59343500	-1.50643400	-0.00000500
C	3.60511800	-1.11825700	0.00001700
C	3.88473100	0.23678200	0.00002300
H	1.74679200	2.62408800	0.00000300
H	0.70094500	-2.44767400	-0.00001100
H	-1.12541400	2.84833700	-0.00000500
H	-4.19902000	1.43861500	0.00006300
H	-4.75477200	-1.20445300	0.00004400
H	-2.50298200	-2.58318400	-0.00001800

H	4.21739900	-2.00891700	0.00002800
H	4.80602100	0.80444400	0.00003800

S5 HRMS spectra

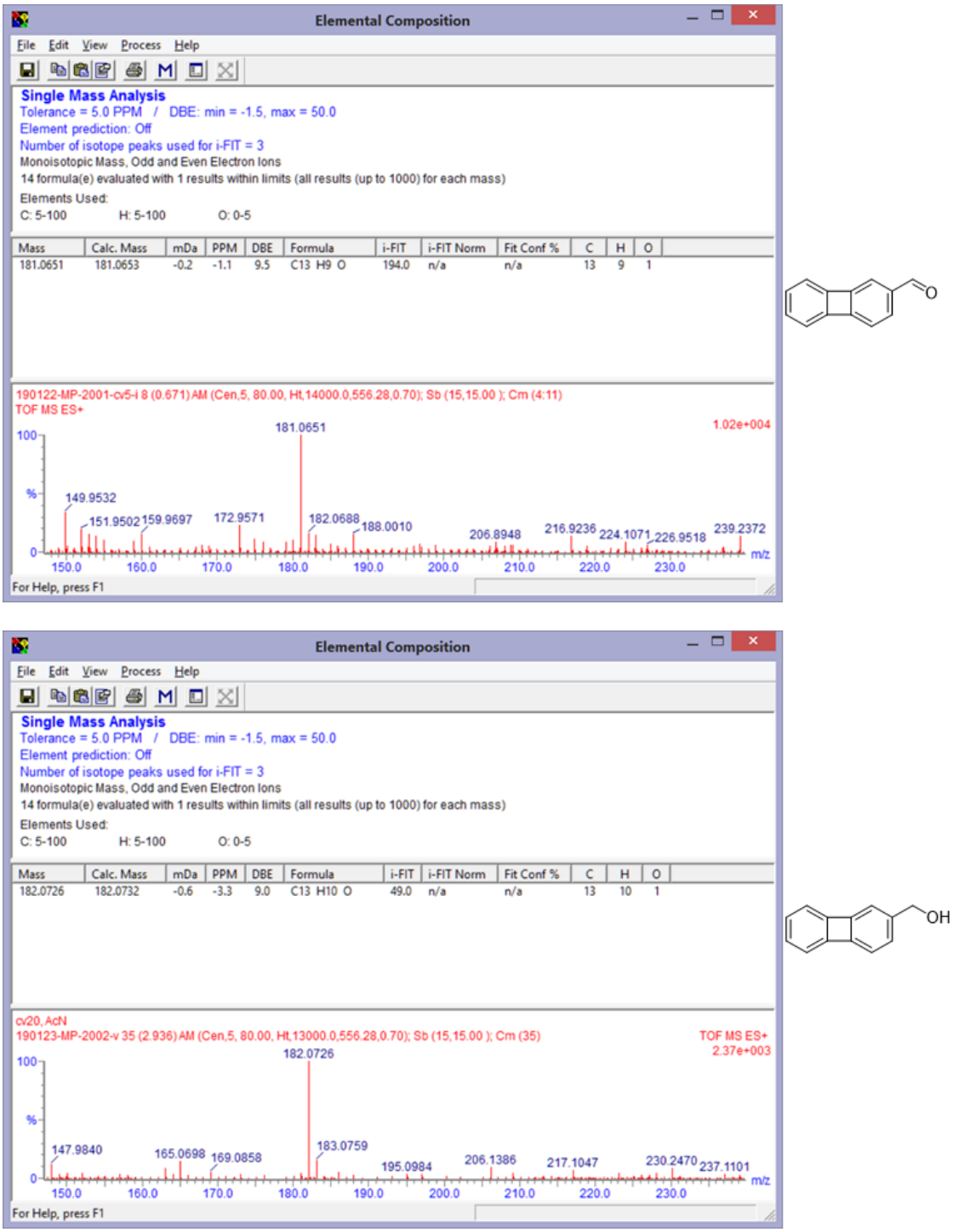


Figure S16: HRMS spectra of compound **3** (top) and **4** (bottom)

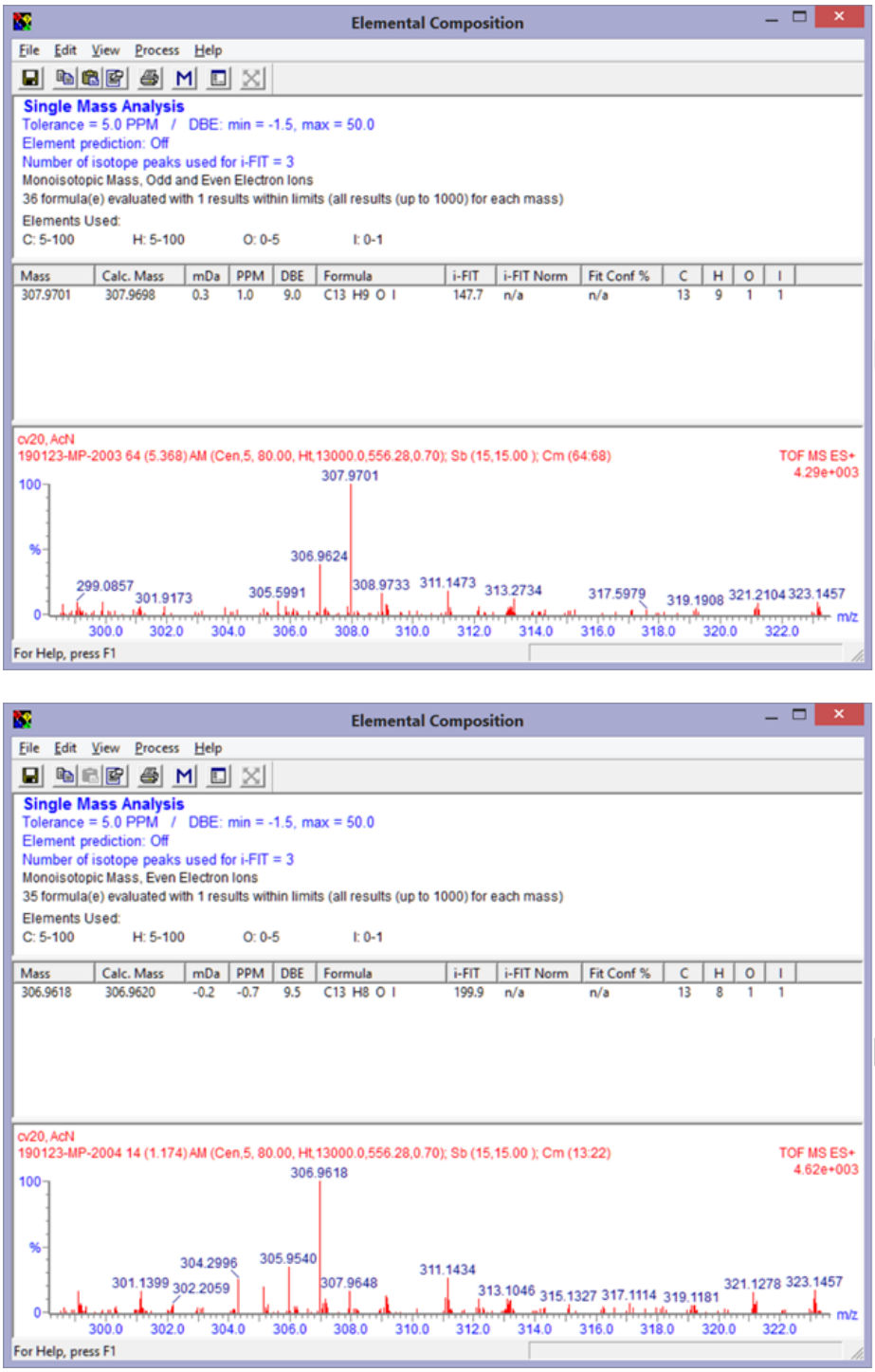


Figure S17: HRMS spectra of compound **5** (top) and **6** (bottom)

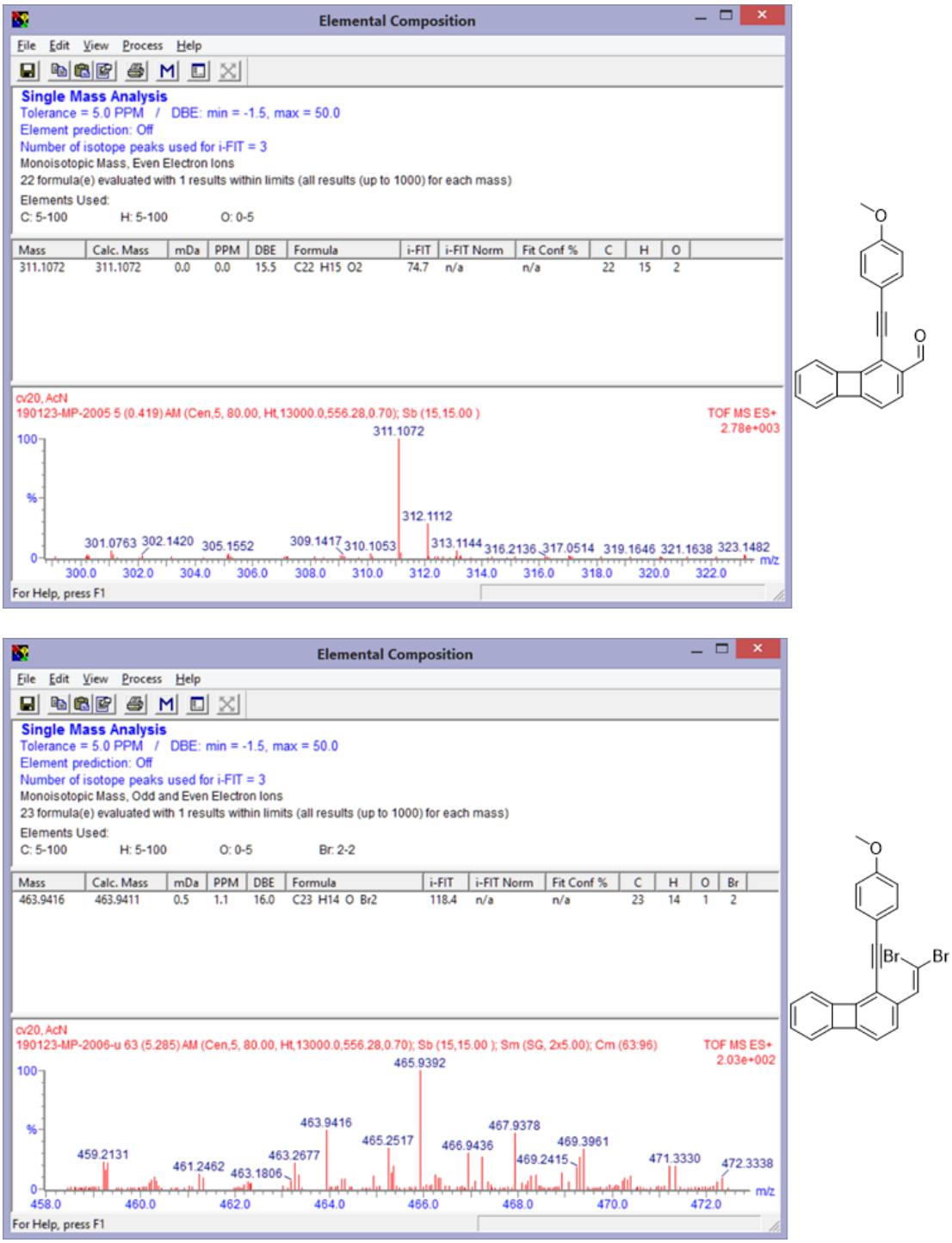


Figure S18: HRMS spectra of compound **7** (top) and **8** (bottom)

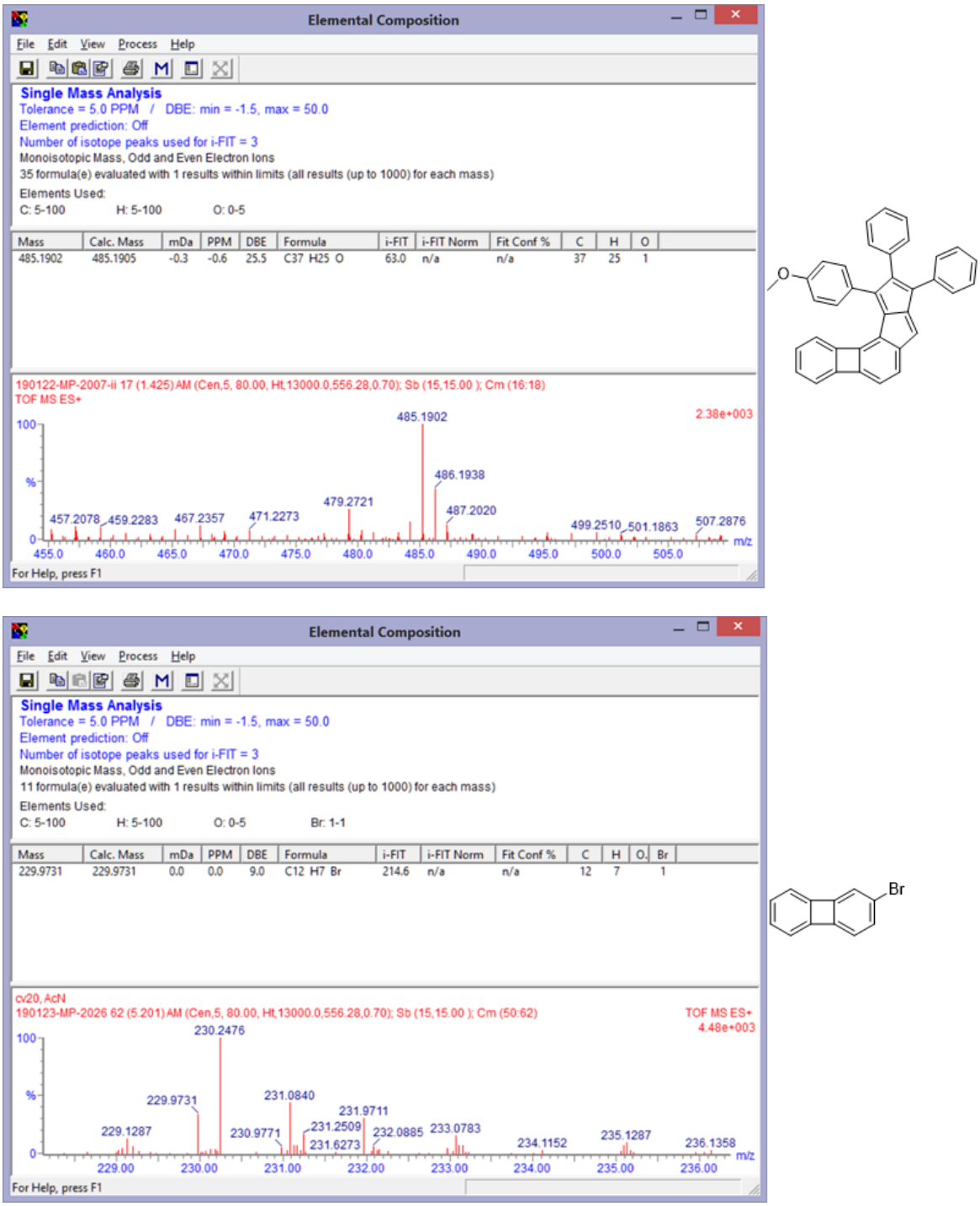


Figure S19: HRMS spectra of compound **9** (top) and **10** (bottom)

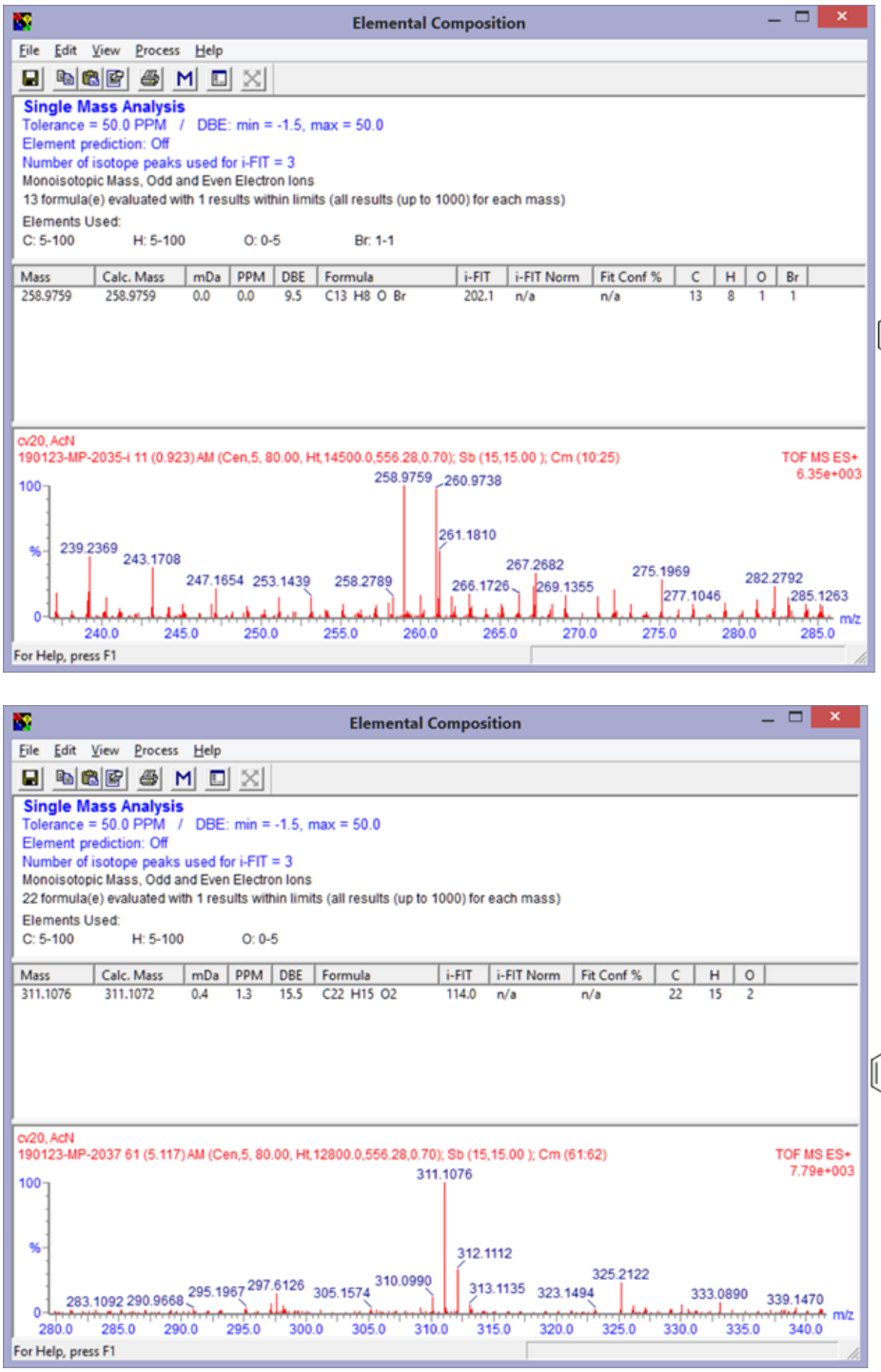


Figure S20: HRMS spectra of compound **11** (top) and **12** (bottom)

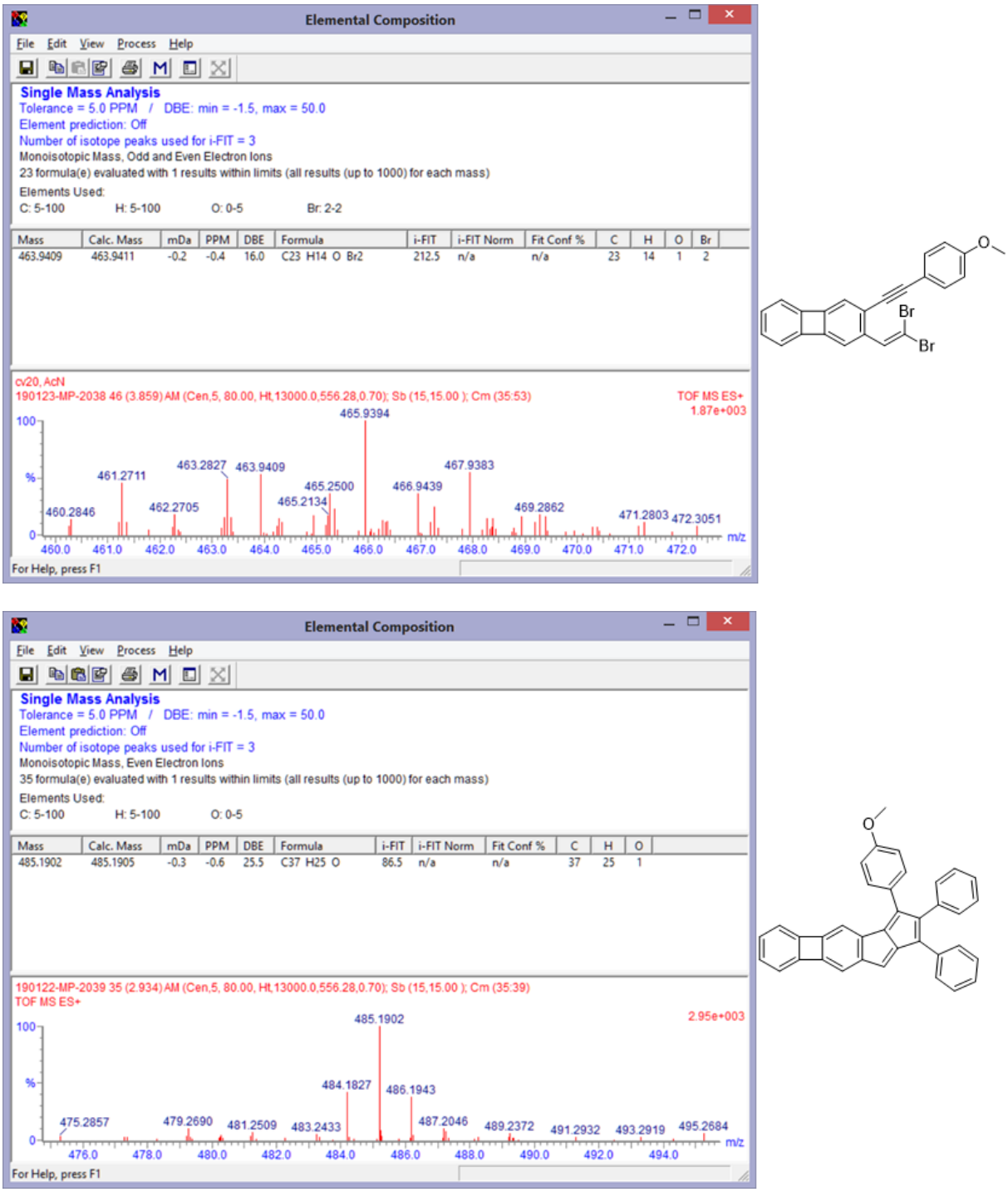


Figure S21: HRMS spectra of compound 1**3** (top) and 1**4** (bottom)

S6 NMR spectra

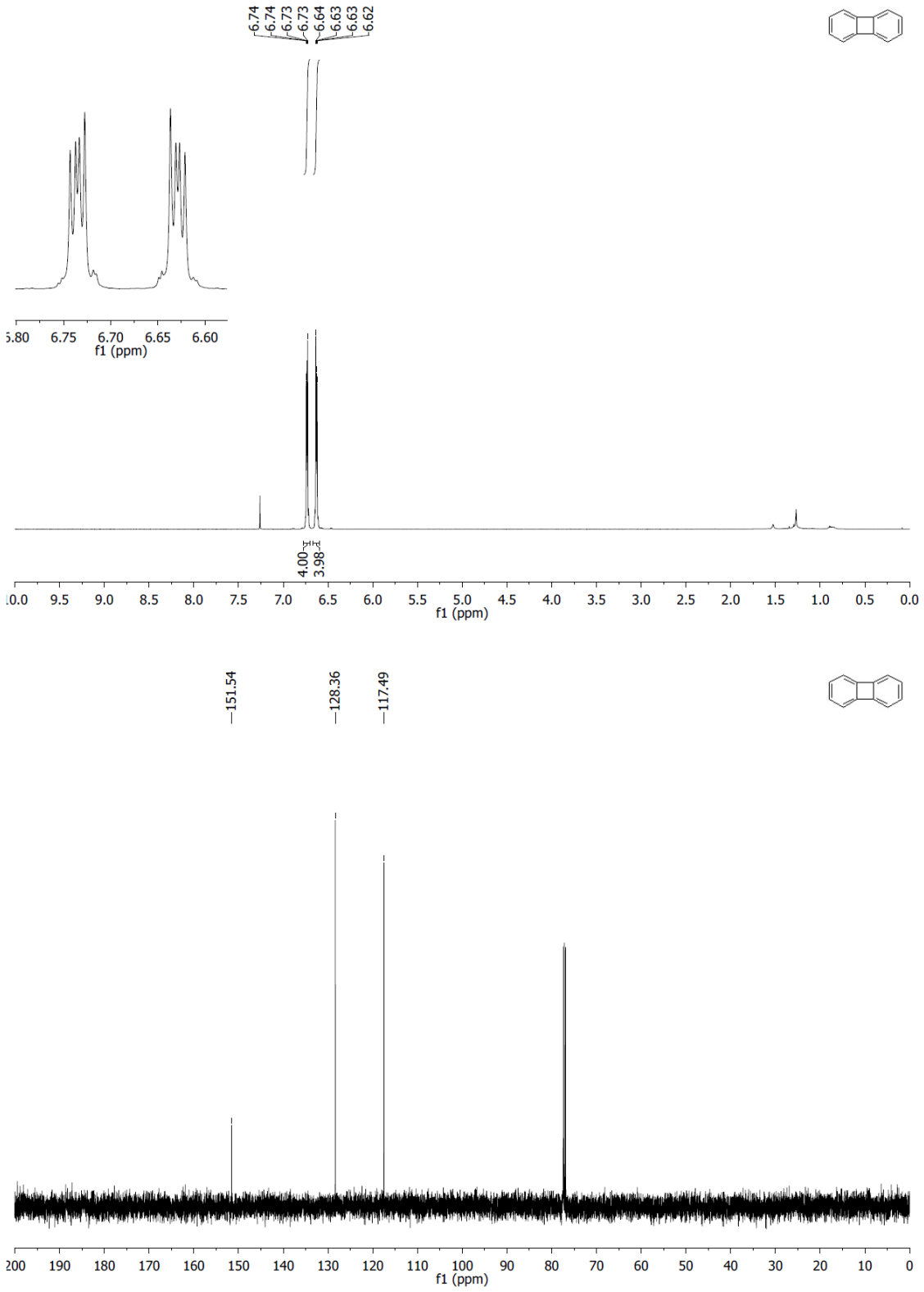


Figure S22: ^{1}H-NMR (500 MHz, top) and $^{13}C\{^{1}H\}$-NMR (126 MHz, bottom) spectra of **2** in $CDCl_3$.

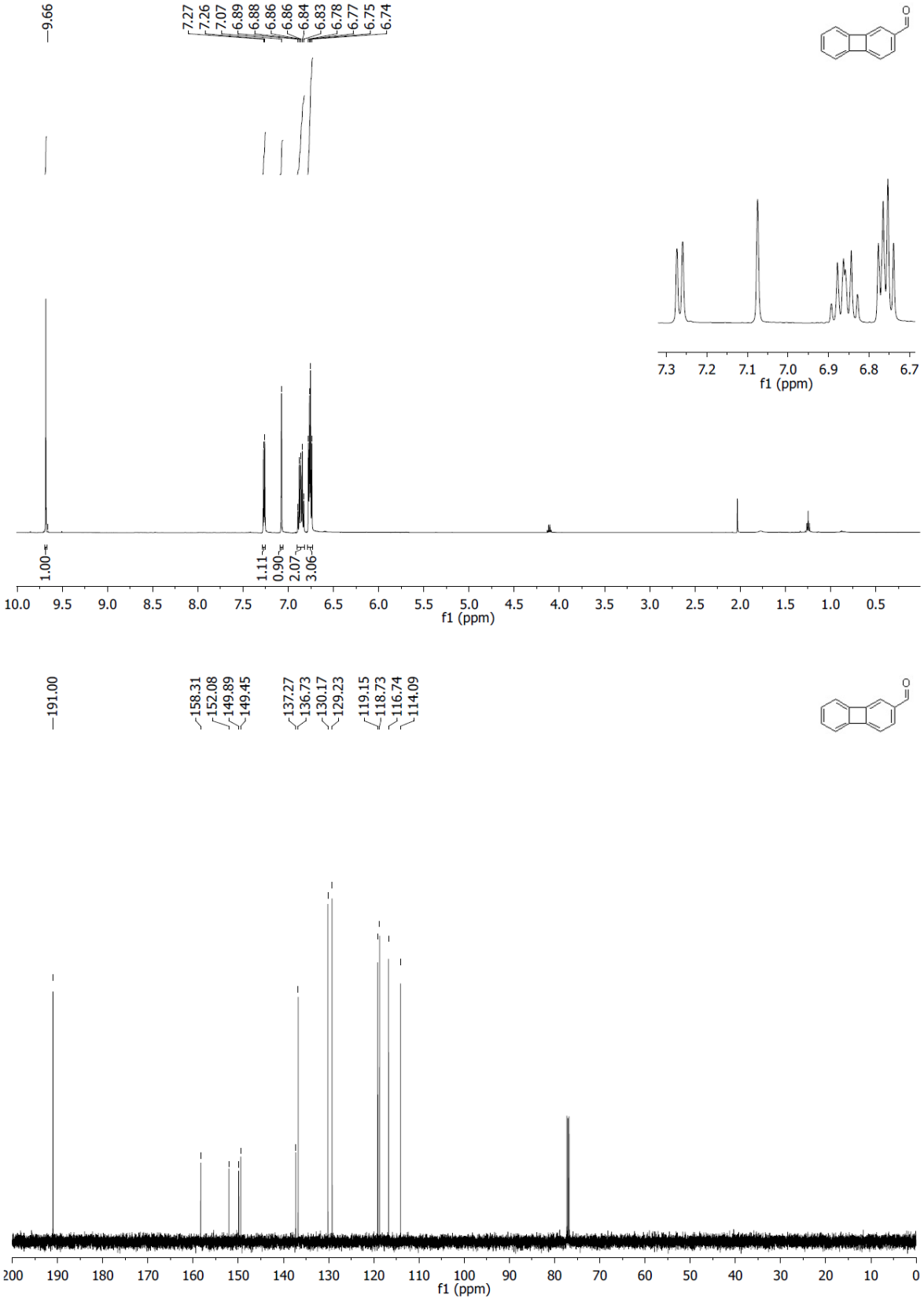


Figure S23: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) spectra of **3** in $CDCl_3$.

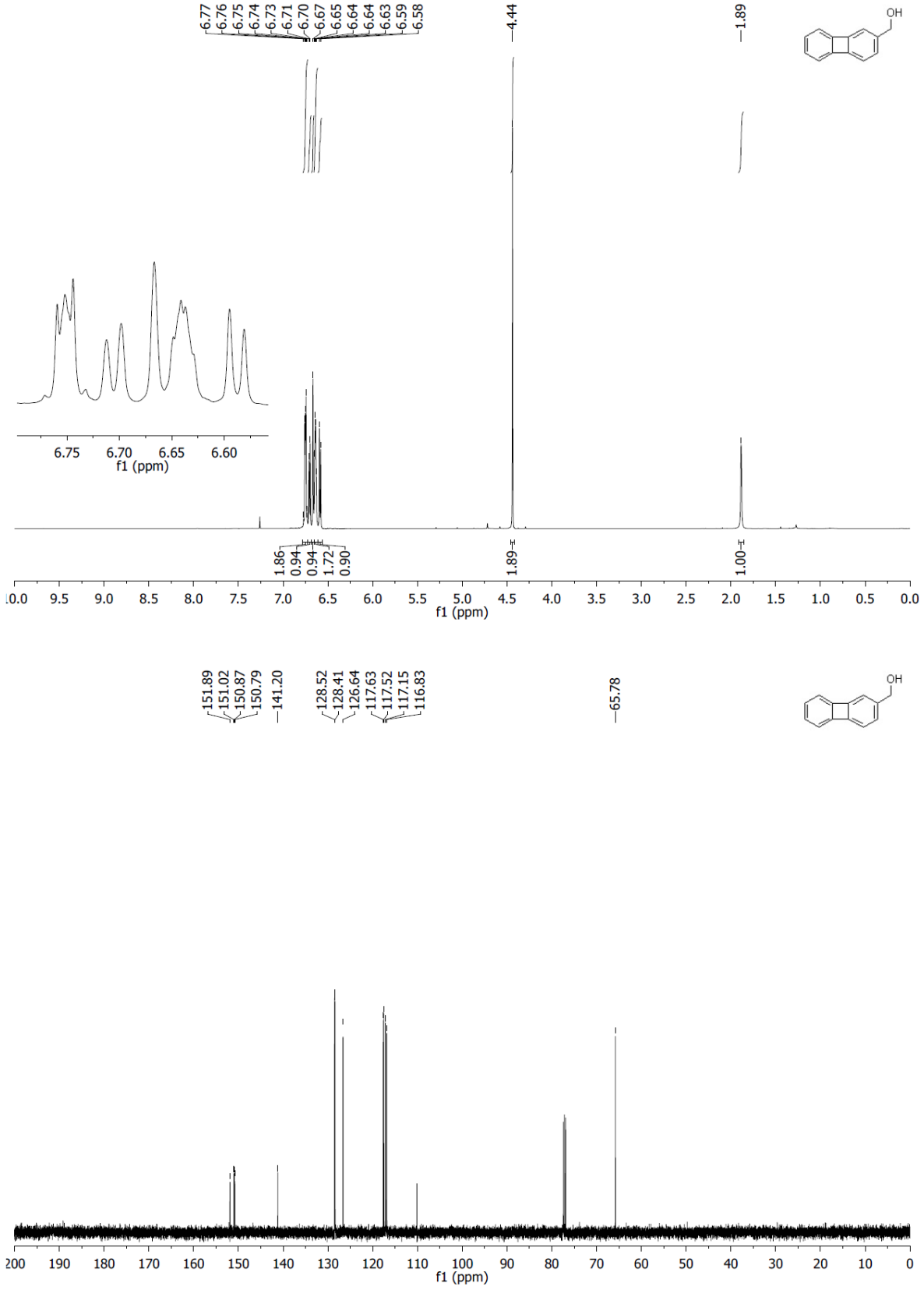


Figure S24: ^{1}H-NMR (500 MHz, top) and $^{13}C\{^{1}H\}$-NMR (126 MHz, bottom) spectra of **4** in $CDCl_3$.

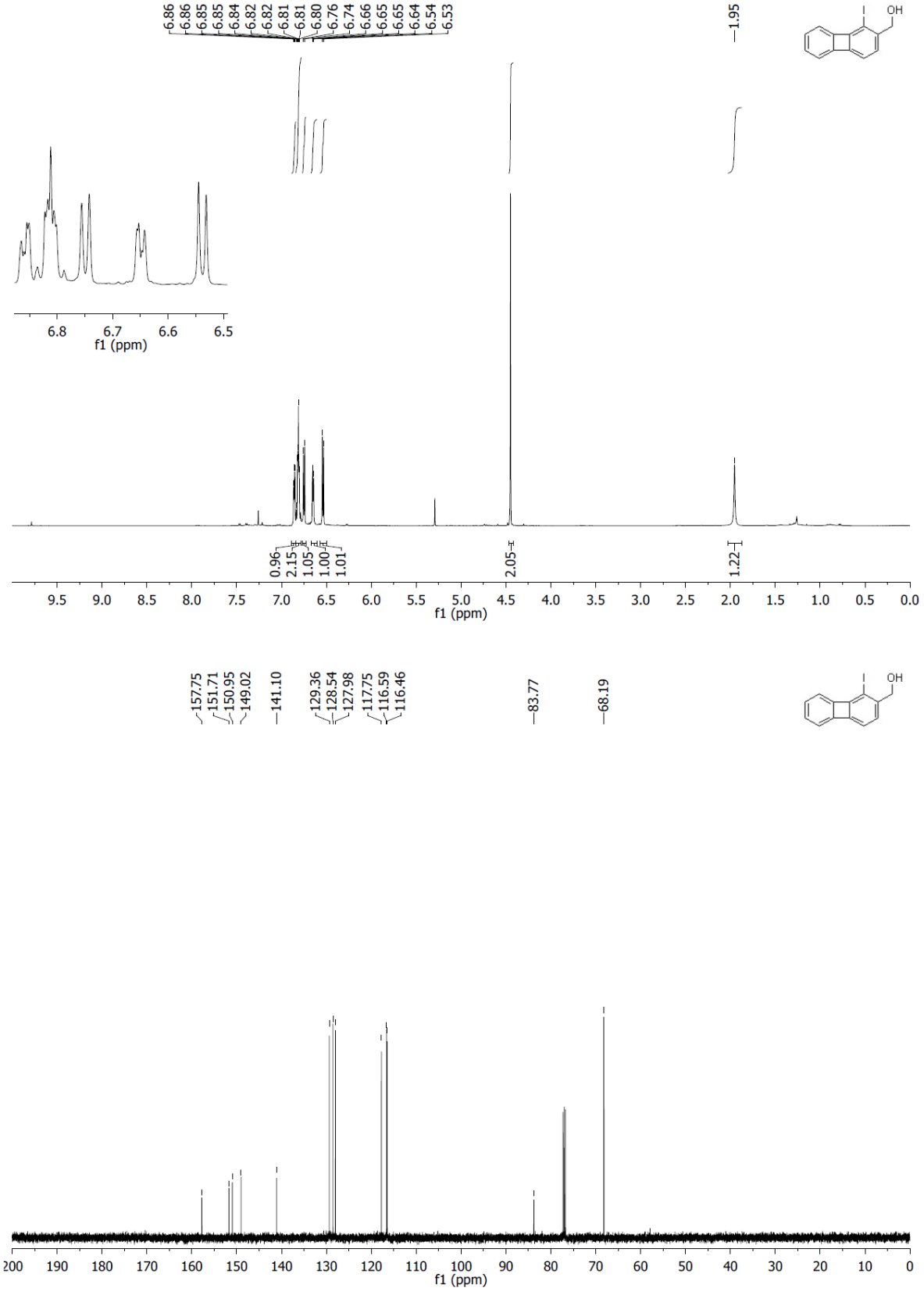


Figure S25: ^{1}H-NMR (500 MHz, top) and $^{13}C\{^{1}H\}$-NMR (126 MHz, bottom) spectra of **5** in $CDCl_3$.

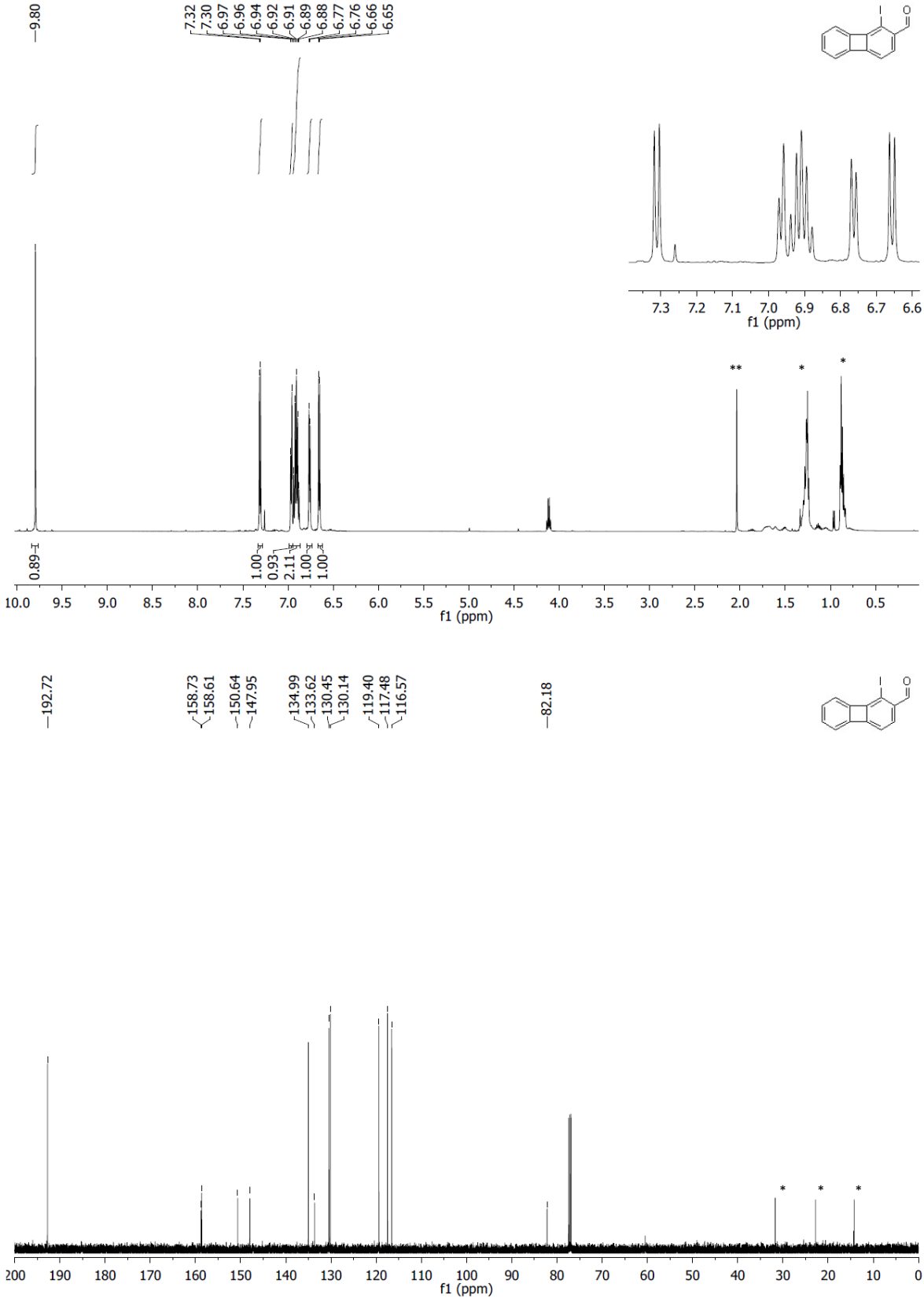


Figure S26: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) of **6** in $CDCl_3$. Impurities: * *n*-hexane ** acetone.

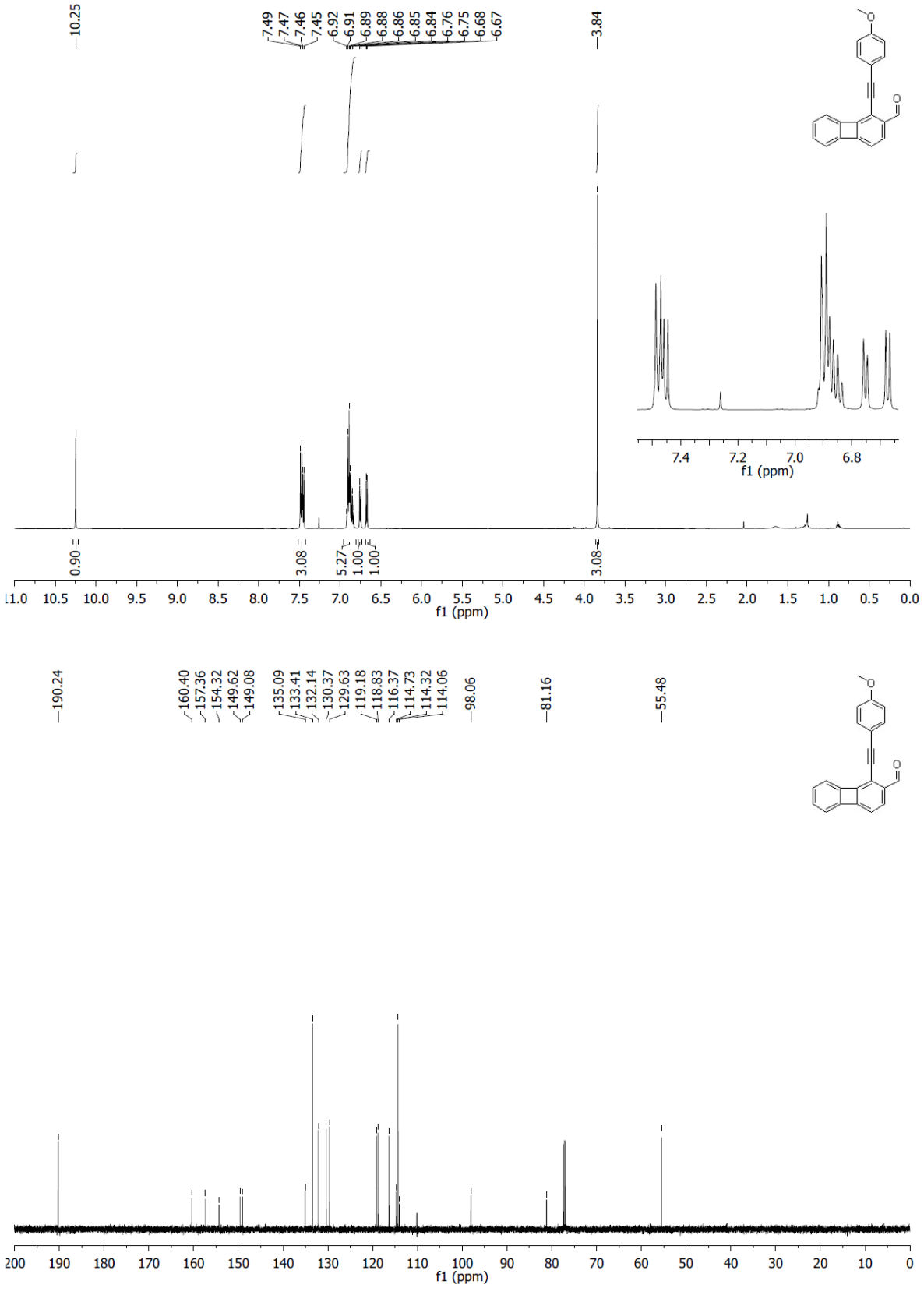


Figure S27: ^{1}H-NMR (500 MHz, top) and $^{13}C\{^{1}H\}$-NMR (126 MHz, bottom) spectra of **7** in $CDCl_3$.

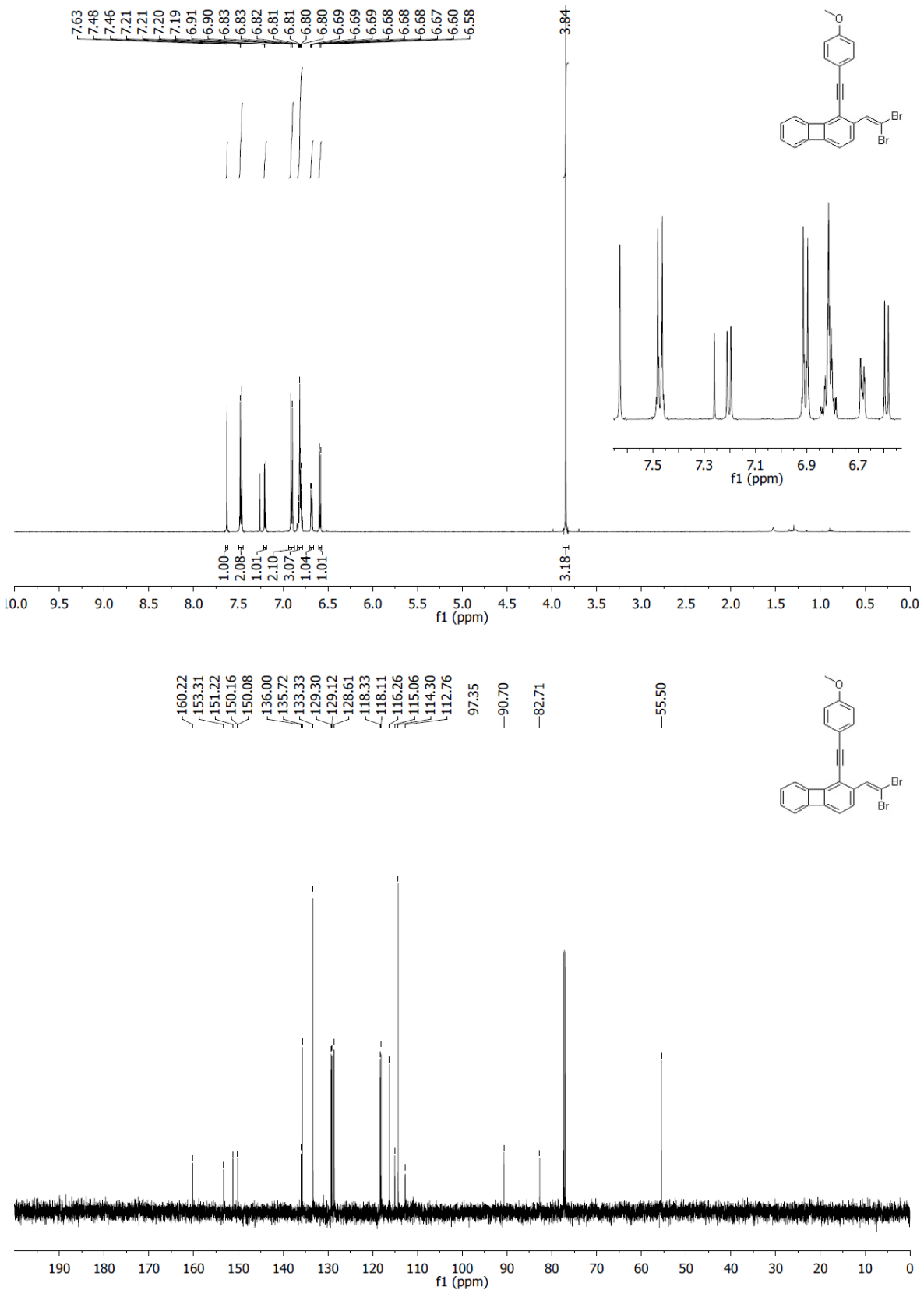


Figure S28: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) spectra of **8** in $CDCl_3$.

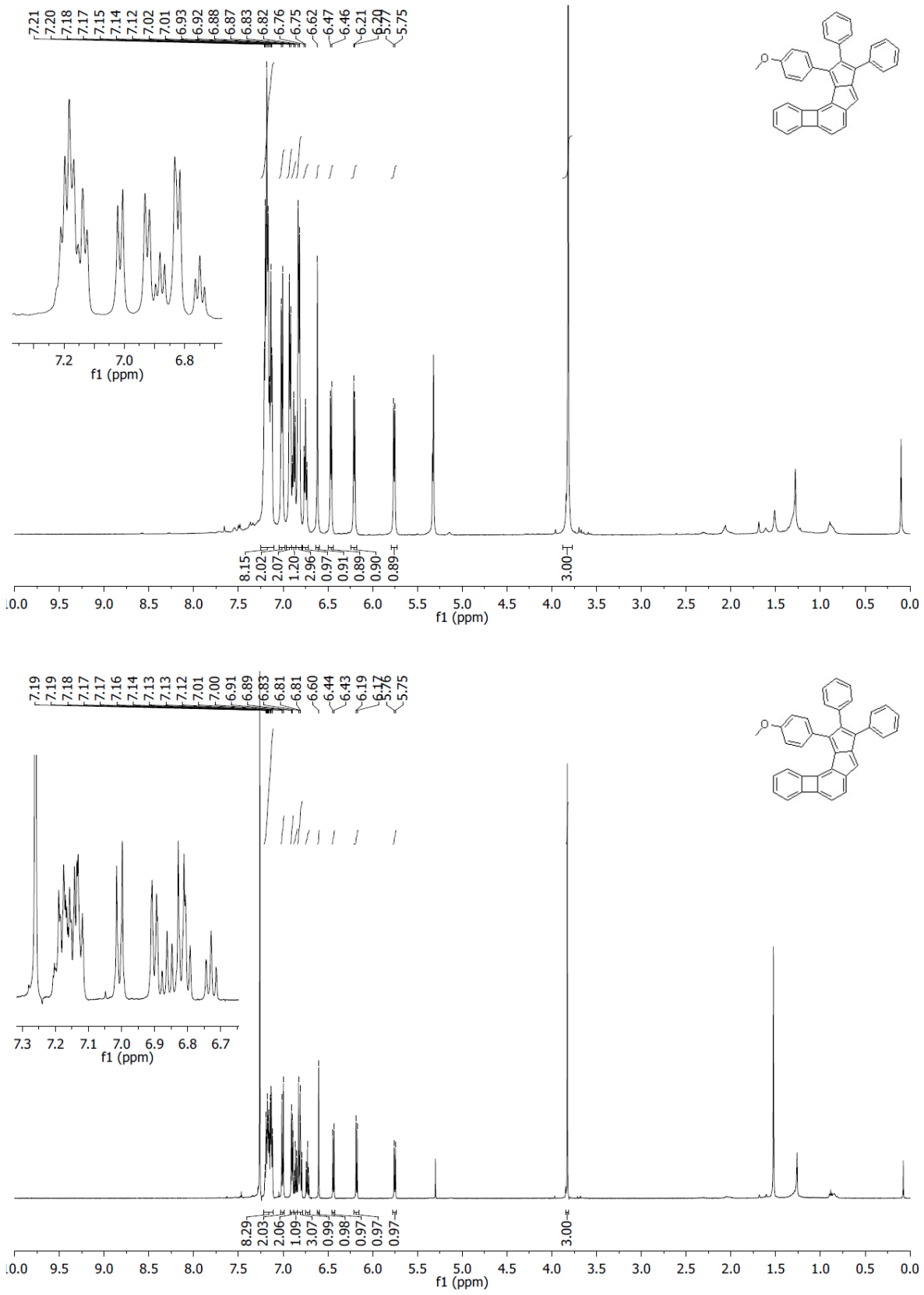


Figure S29: ^{1}H-NMR (500 MHz) in CD_2Cl_2 (top) and ^{1}H-NMR (500 MHz) in $CDCl_3$ (bottom) spectra of **9**.

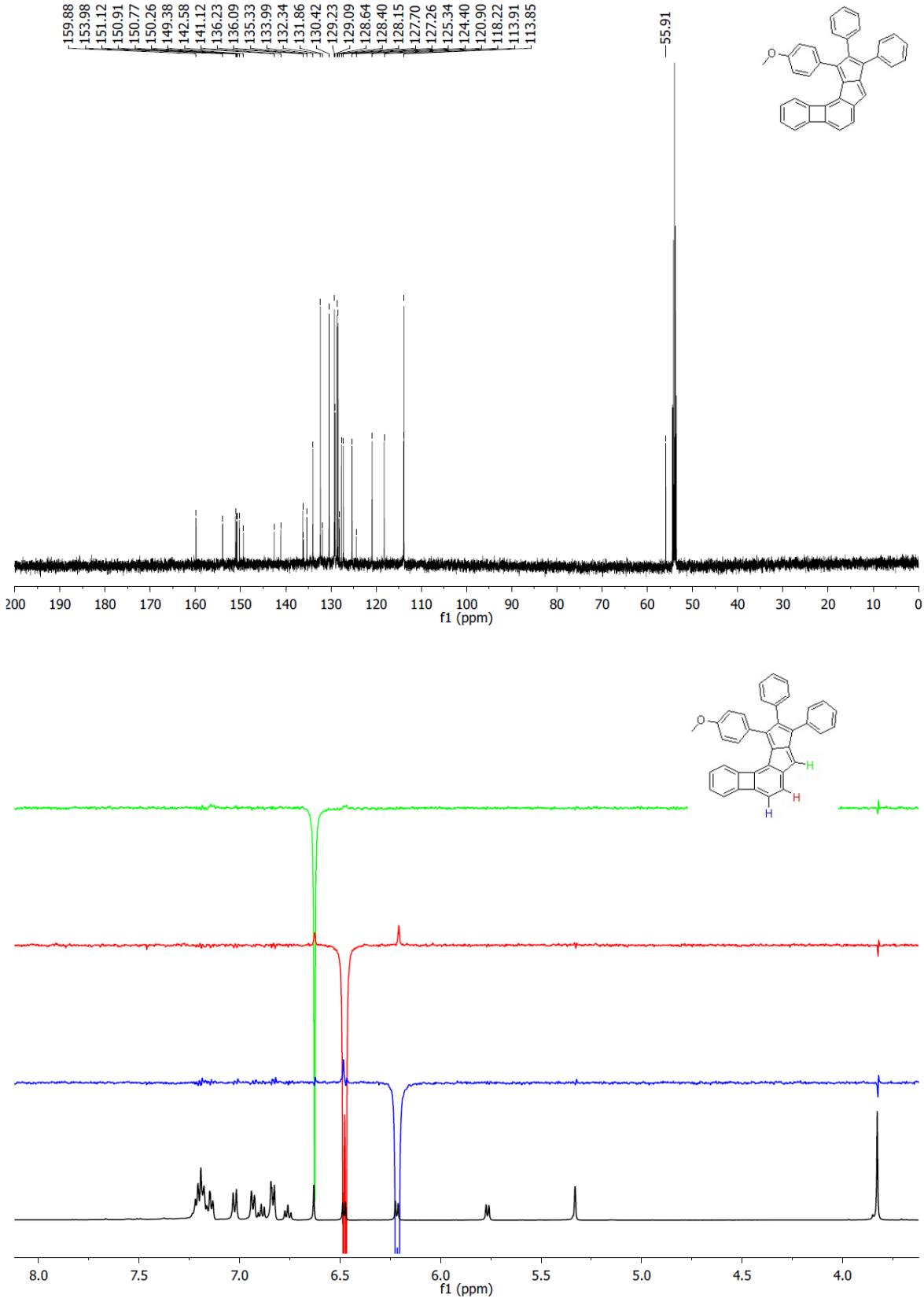


Figure S30: ^{13}C-NMR (126 MHz, top) and 1D-NOESY (at 6.64 ppm, 6.48 ppm and 6.22 ppm, bottom) spectra of **9** in $CDCl_3$.

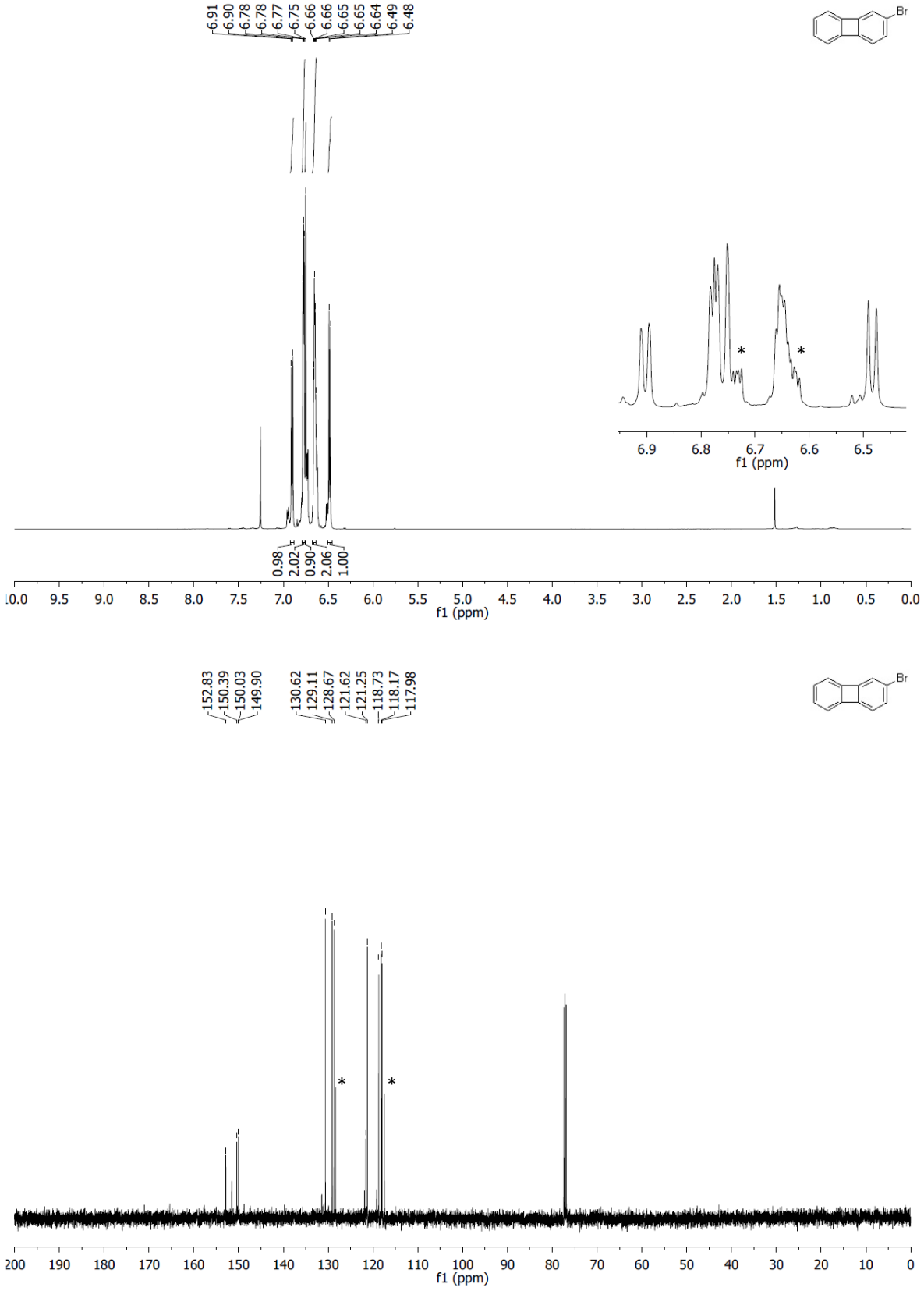


Figure S31: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) spectra of **10** in $CDCl_3$. Impurity: * **2**.

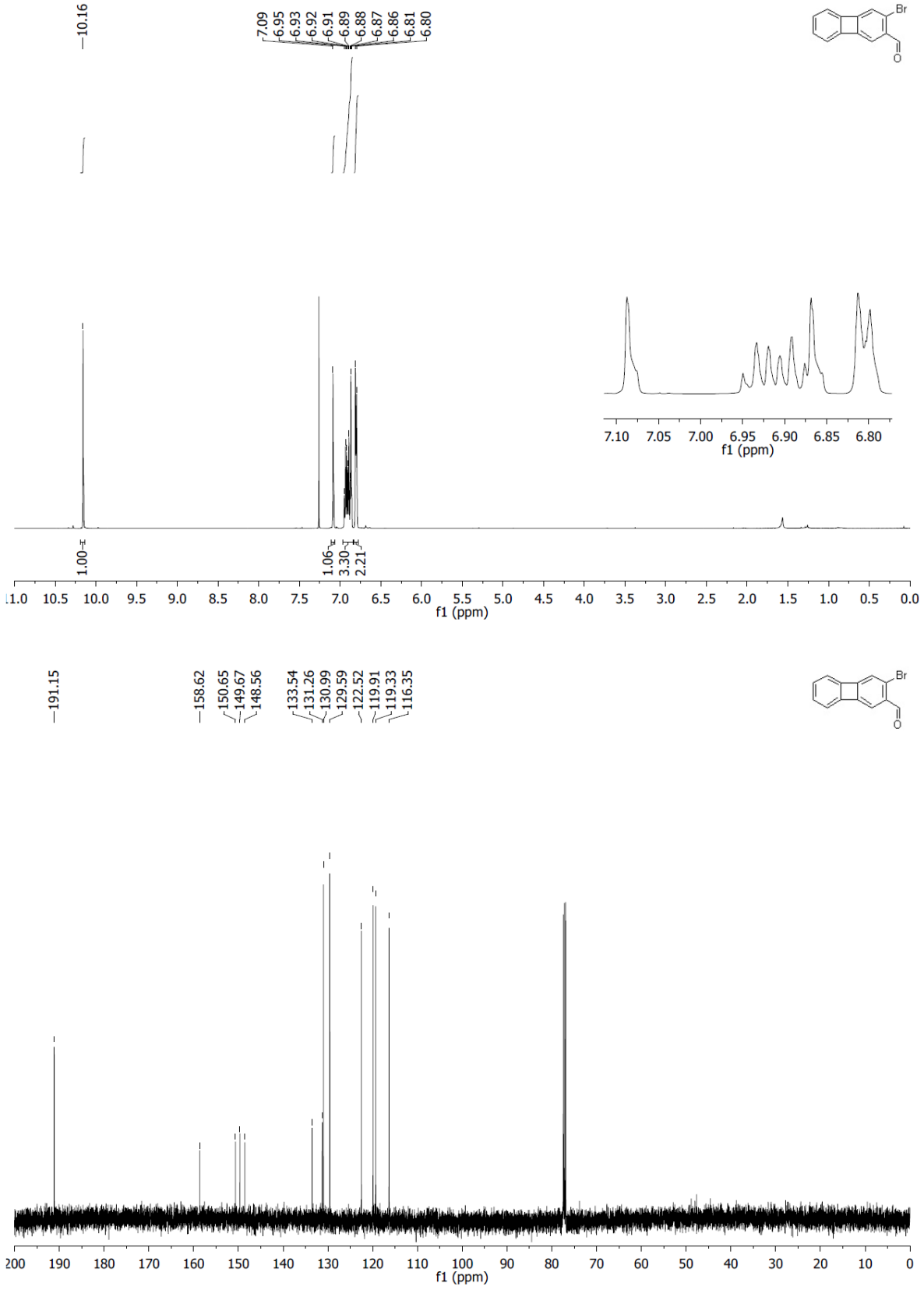


Figure S32: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) spectra of **11** in $CDCl_3$.

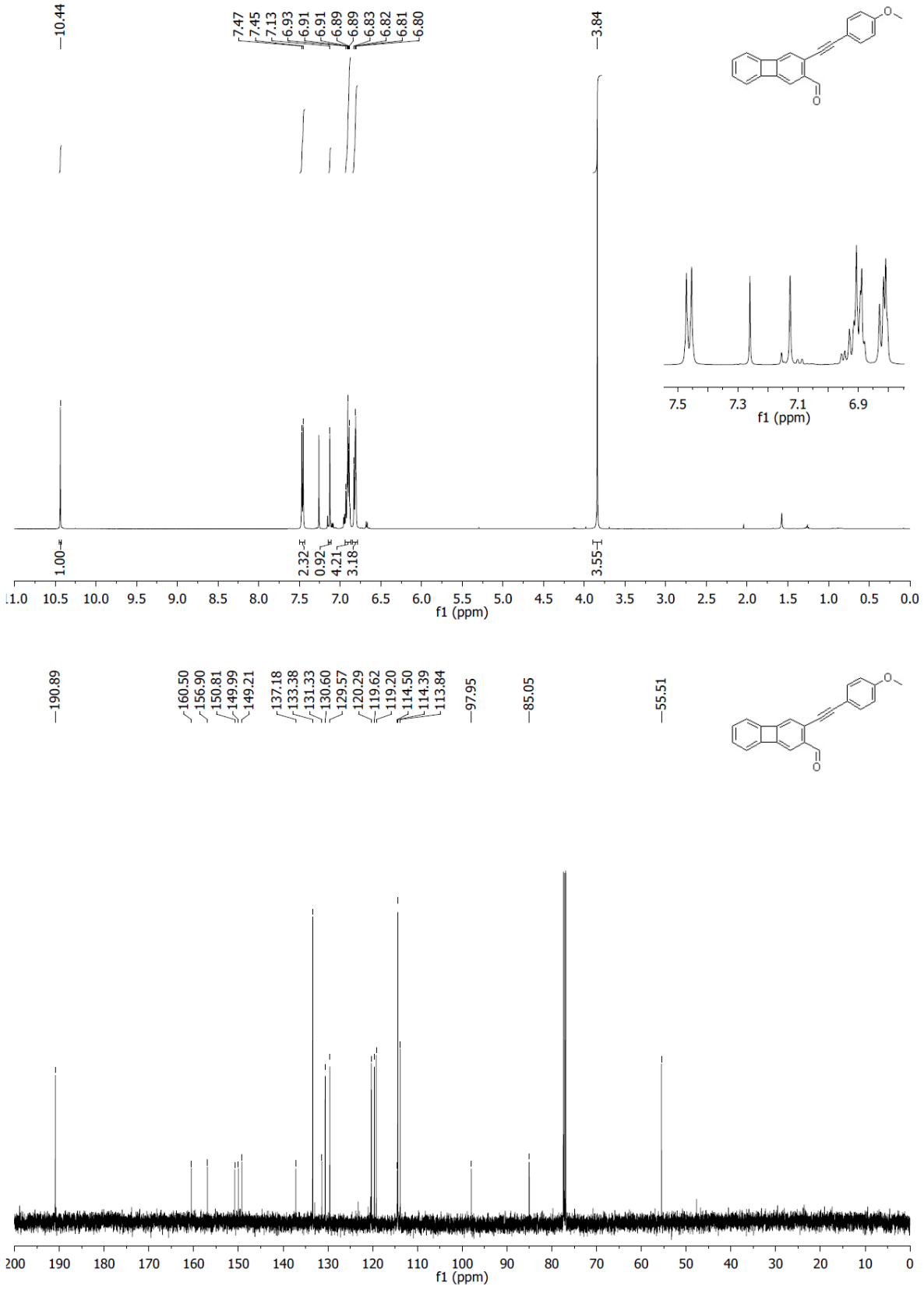


Figure S33: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) spectra of **12** in $CDCl_3$.

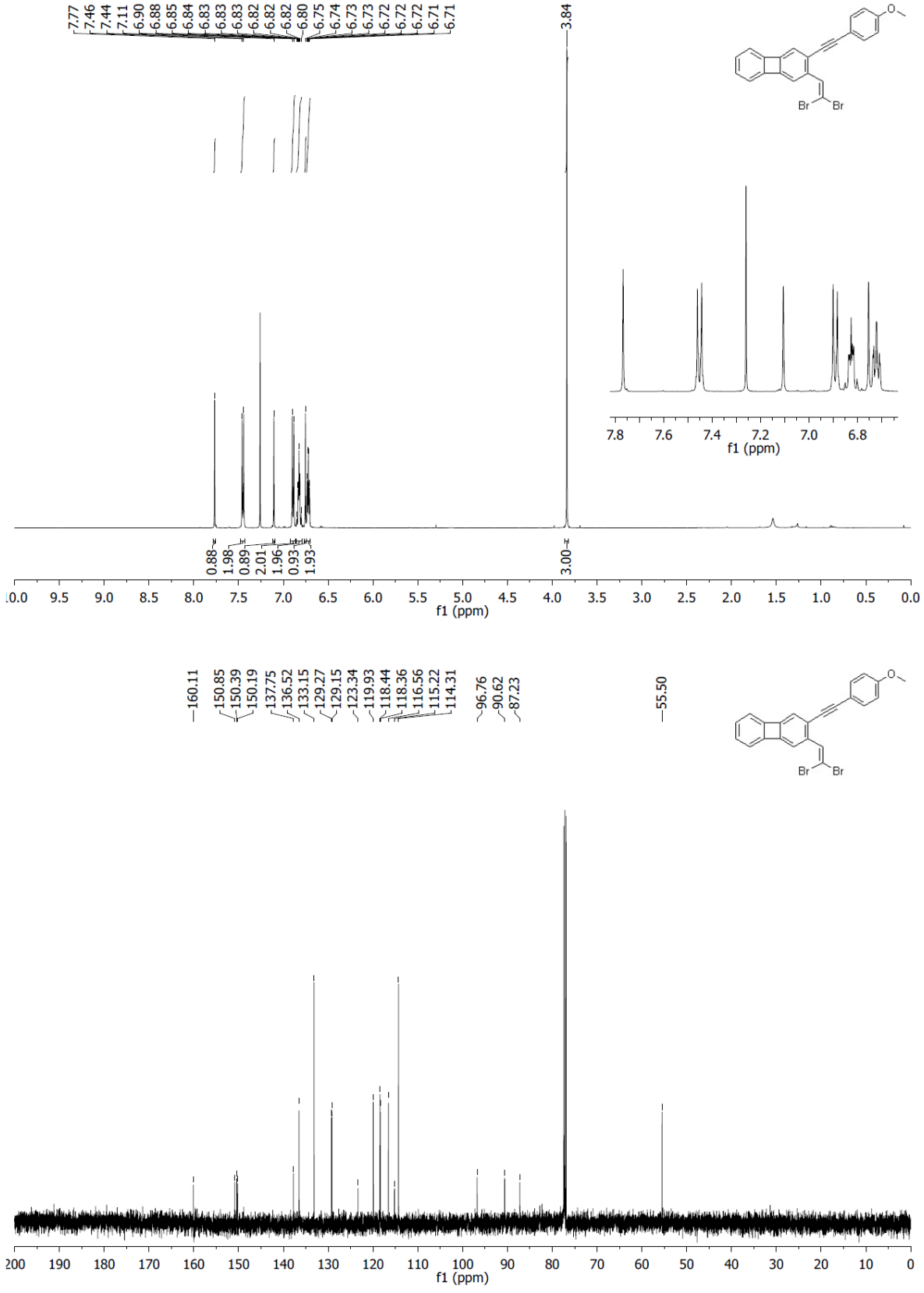


Figure S34: ^{1}H-NMR (500 MHz, top) and ^{13}C{^{1}H}-NMR (126 MHz, bottom) spectra of **13** in $CDCl_3$.

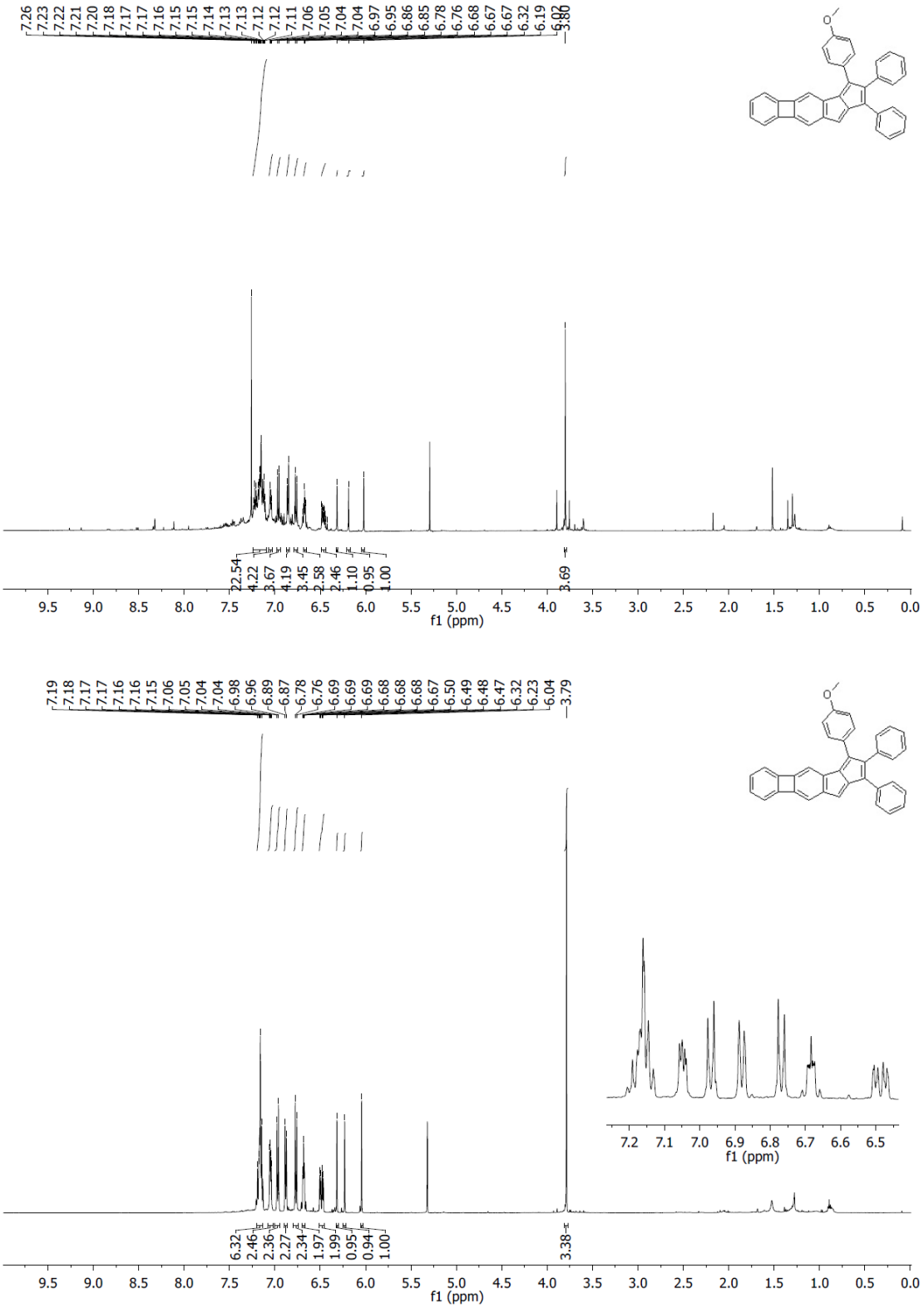


Figure S35: ^{1}H-NMR (500 MHz) in $CDCl_3$ (top) and ^{1}H-NMR (500 MHz) in CD_2Cl_2 (bottom) spectra of **14**. (Note that the spectrum in $CDCl_3$ shows the degradation of the product under slightly acidic conditions.)

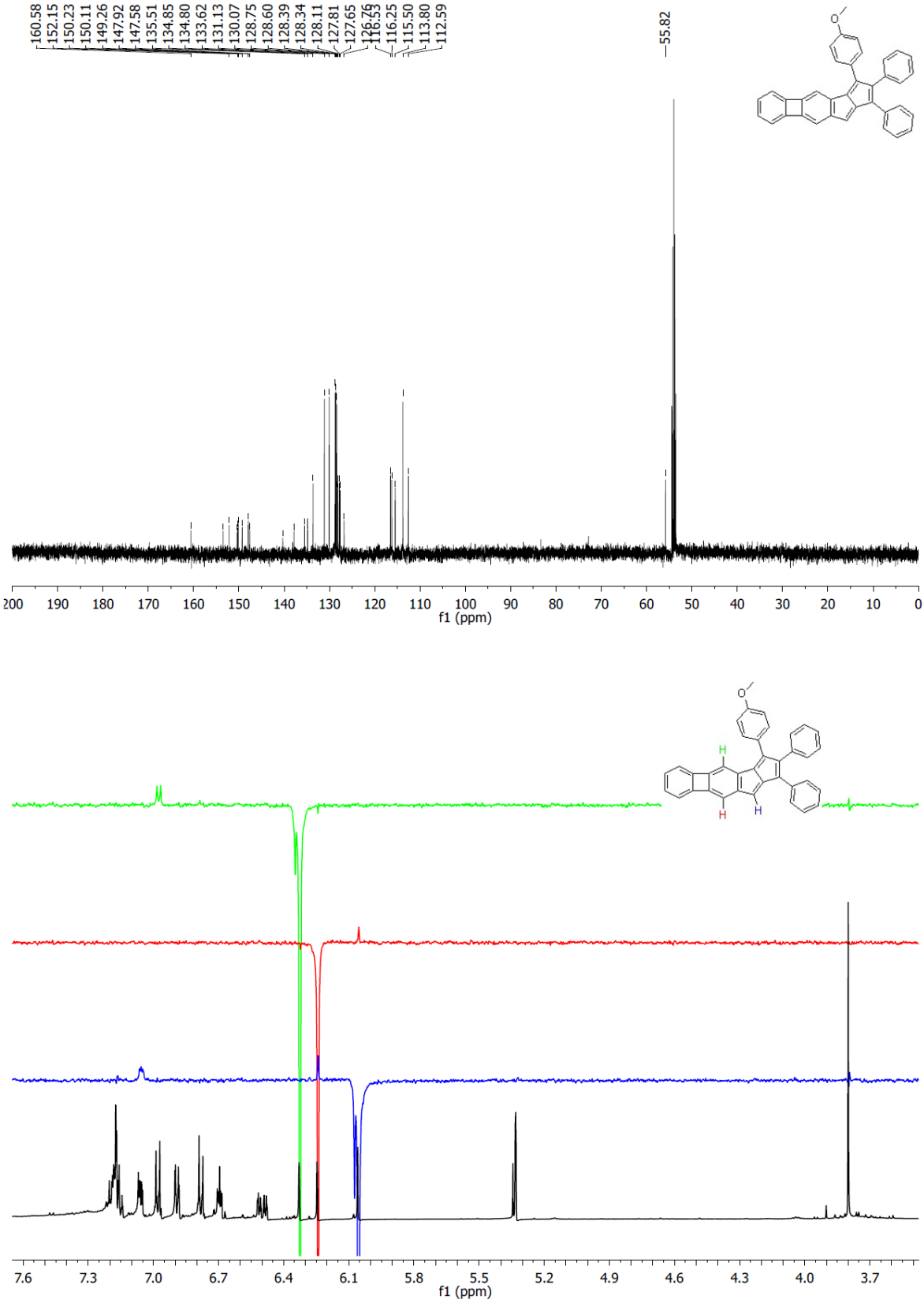


Figure S36: ^{13}C-NMR (126 MHz, top) and 1D-NOESY (at 6.33 ppm, 6.25 ppm and 6.06 ppm, bottom) spectra of **14** in $CDCl_3$.

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