Electronic Supplementary Material (ESI) for ChemComm.

Sumanene Derivatives Functionalized at the Internal Carbon

Contents

1. Characterization of bromosumanenone (3)

Since the single crystal of **3** suitable for X-ray analysis was not obtained, the structure of **3** was determined by the combination of the mass spectrometry, IR, NMR, and calculation. The observed signal at 197.8 ppm in ^{13}C-NMR spectrum and the band at 1656 cm^{-1} in IR spectrum clearly indicated the existence of a carbonyl group in the structure of **3**. The signal at 57.7 ppm in ^{13}C-NMR spectrum was assigned to be the carbon of CBr. Two aromatic doublet pairs of the signals in ^{1}H-NMR spectrum support the existence of two benzene rings, which excludes the possibility of the addition of Br at the two benzene rings. Accordingly, there are 5 possible regioisomers or stereoisomers **3a-e** for bromodienone structure **3** (Figure S1). Among them, the structures **3d** and **3e** were excluded because of the absence of the corresponding α-methine proton in the ^{1}H-NMR spectrum. The signal at 5.47 ppm in the ^{1}H-NMR spectrum which associated with the ^{13}C signal at 113.5 ppm in HMQC (Figure S14) also indicated the existence of an olefinic proton of dienone. In addition, the olefinic carbon was observed in DEPT-135 (Figure S13), which was assigned to be -CH-. The signal at 57.7 ppm in ^{13}C-NMR spectrum was assigned to be the quaternary sp^3-carbon of CBr that was inactive in DEPT-135.

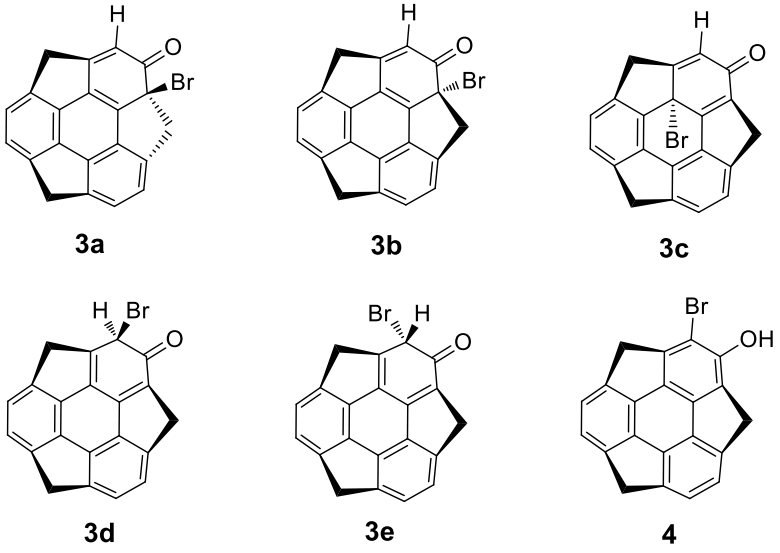

Figure S1 Structure of *o*-bromohydroxysumanene **2** and five possible structures of **3**

To clarify the position of bromide among **3a**, **3b**, and **3c**, we employed the comparison of the experimental ^{13}C-NMR chemical shifts and the calculated ones. The ^{13}C-NMR chemical shifts of **3a-c** were calculated by GIAO method at ωB97XD/6-311++G(d,p) level (Figure S2, Table S1). The calculated ^{13}C-NMR signals of **3b** were well-matched with the observed signals, while those of **3a** and **3c** gave significant differences. Experimental HMQC, HMBC, and NOESY correlations of **4** were also consistent to the structure of **3b** (Figure S3, Table S2). Thus, we concluded the structure of bromosumaneneone **3** to be **3b**.

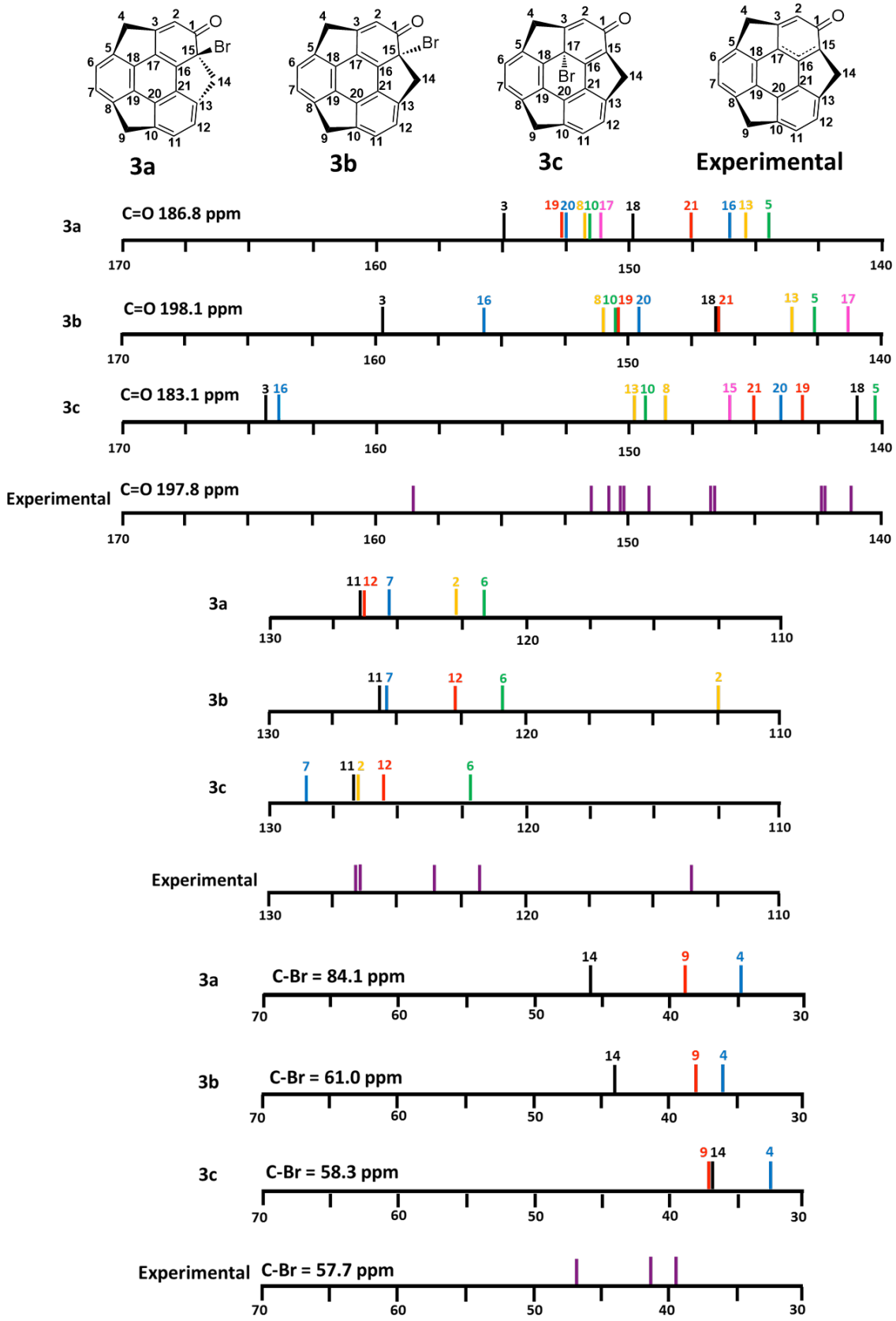

Figure S2 Comparison between calculated ^{13}C-NMR (B3LYP/6-311+G(2d,p) with tetramethylsilane as a standard at 0 ppm) and observed NMR of **3**.

Table S1 Calculated ^{13}C NMR chemical shifts of **3b** and experimental values of **3**

Calculated[a]		Experimental[b]		Calculated[a]		Experimental[b]	
C=O	198.1	C=O	197.8	C(17)	141.3	C	141.2
C(3)	159.7	C	158.5	CH(11)	125.7	CH	126.6
C(16)	155.8	C	151.5	CH(7)	125.3	CH	126.4
C(8)	151.0	C	150.8	CH(12)	122.7	CH(12)	123.5
C(10)	150.5	C	150.2	CH(6)	120.9	CH(6)	121.9
C(19)	150.4	C	150.1	CH(2)	112.5	CH(2)	113.5
C(20)	149.6	C	149.2	CBr(15)	61.0	CBr(15)	57.7
C(18)	146.6	C	146.8	CH_2(14)	44.1	CH_2(13)	46.8
C(21)	146.5	C	146.6	CH_2(9)	38.0	CH_2(9)	41.4
C(13)	143.5	C	142.4	CH_2(4)	36.0	CH_2(4)	39.6
C(5)	143.7	C	142.3				

[a]The ^{13}C-NMR were calculated at GIAO/B3LYP/6-311+G(2d,p) on the optimized structure **3b** by ωB97XD/6-311++G(d,p). Tetramethylsilane as a reference at 0 ppm. [b]Measured in CD_2Cl_2 solution.

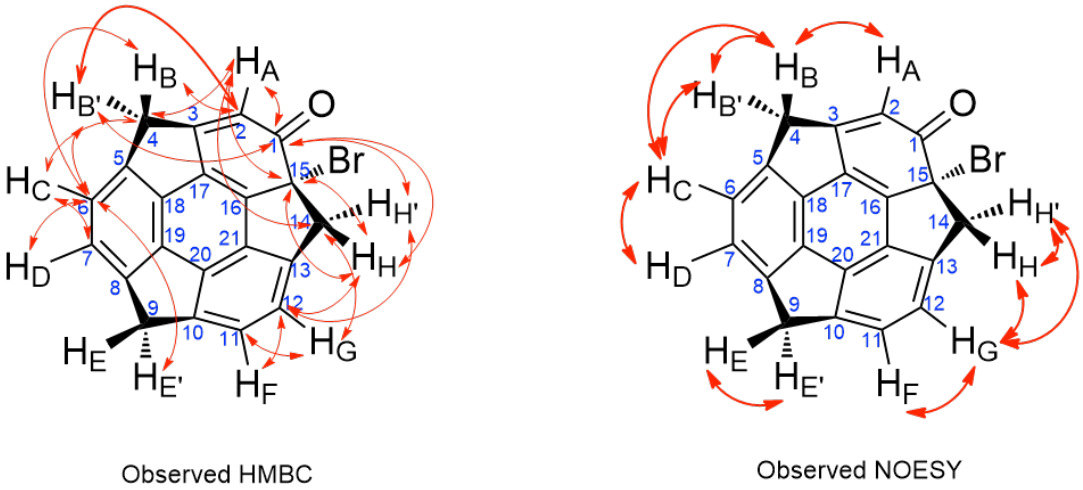

Figure S3 Observed HMBC and NOESY of **3**

Table S2 ^{1}H, ^{13}C lists and HMBC correlation of **3**

C (DEPT)	HMQC; ^{1}H (ppm)[a]	^{13}C (ppm)	HMBC[b] (^{2}J, ^{3}J and ^{4}J)
C=O (1)	-	197.8	H_A, $H_{B'}$, H_H, $H_{H'}$
CH (2)	5.47 (*d*, 1.6)	113.5	H_B, $H_{B'}$
CH_2 (4)	3.41 (*d*, 19.2), 4.55 (*d*, 18.4)	39.7	H_A, H_c
CH (6)	6.99 (*d*, 7.2)	121.9	H_B, $H_{B'}$, H_D, $H_{E'}$
CH (7)	7.32 (*d*, 8.8)	126.6	H_C (w)
CH_2 (9)	3.58 (*d*, 19.2), 4.72 (*d*, 19.6)	41.4	H_D overlaps with H_F
CH (11)	7.30 (*d*, 8.4)	126.4	H_G (w)
CH (12)	6.94 (*d*, 7.2)	123.5	H_F, H_H, $H_{H'}$
CH_2 (14)	3.49 (*d*, 18.8), 4.17 (*d*, 18.8)	46.8	H_A, H_G
C-Br (15)	-	57.7	H_I, $H_{I'}$, H_A

[a] Alphabet and value in parenthesis are multiplicity and *J* coupling constant in Hz.
[b] Relaxation delay = 4 s.

2. Experimental

General Information

All chemicals were reagent grade and used as received unless otherwise mentioned. Commercially available *N*-bromosuccinimide was purified by recrystalization from water. ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL JNM-ECZS at 23 °C at 400 and 100 MHz, respectively. A residual solvent peak was used as an internal standard (^{1}H-NMR: $CDCl_3$ 7.24 ppm, CD_2Cl_2 5.32 ppm; ^{13}C-NMR: $CDCl_3$ 77.0 ppm, CD_2Cl_2 53.8 ppm). High resolution mass spectra (HRMS) were measured on a JEOL JMS-700 using fast atom bombardment (FAB) mode. Gel permeable chromatography (GPC) was conducted on JAIGEL 1H and 2H using a JAI Recycling Preparative HPLC LC-908W with $CHCl_3$ as eluent. Infrared (IR) spectra were recorded on a JASCO FT IR-4100 spectrometer. UV–visible absorption spectra were recorded on a JASCO V-670 spectrometer. Fluorescence spectra were recorded on a JASCO FP6500 spectrometer. Melting points were determined on Standford Research Systems MPA 100 and were uncorrected. Merck pre-coated TLC plate (silica gel 60 F254 0.25 mm) was used for thin-layer chromatography (TLC) analysis. Preparative thin-layer chromatography (PTLC) was prepared using Wako Wakogel B-5F.

Bromosumanenone (3)

Light was avoided through the experiment by covering the glasswares containing the compound **3** with aluminum foil, because the conversion from **3** to **4** was promoted by light. To a solution of **2**[2] (6.0 mg, 0.021 mmol) in dry CH_2Cl_2 (5 mL) under N_2 atmosphere was added *N*-bromosuccinimide (4.4 mg, 0.026 mmol) at 0 °C. After addition of NBS, the solution color gradually changed from colorless to orange within 3 min and TLC checking indicated that **2** was consumed within 5 min. Solvent was removed by evaporation in vacuum at 0 °C. The residue was dissolved in cold 40 mL hexane by sonication and the solution was washed with cold water (15 mL x 3) to remove succinimide and remaining NBS. The organic layer was dried over Na_2SO_4, filtered through cotton, and evaporated in vacuum at 0 °C to afford **3** as an orange solid (7.1 mg, 92% yield).

Mp: 46 °C (decomp.); ^{1}H NMR (CD_2Cl_2): δ 7.32 (*d*, *J* = 7.6 Hz, 1H), 7.30 (*d*, *J* = 7.2 Hz, 1H), 6.99 (*d*, *J* = 7.2 Hz, 1H), 6.94 (*d*, *J* = 7.2 Hz, 1H), 5.47 (*d*, *J* = 1.6 Hz, 1H), 4.72 (*d*, *J* = 19.6 Hz, 1H), 4.54 (*d*, *J* = 18.0 Hz, 1H), 4.17 (*d*, *J* = 19.2 Hz, 1H), 3.57 (*d*, *J* = 19.6 Hz, 1H), 3.48 (*d*, *J* = 18.8 Hz, 1H), 3.41 (*d*, *J* = 18.4 Hz, 1H); ^{13}C NMR (CD_2Cl_2): 197.8, 158.5, 151.5, 150.8, 150.2, 150.15, 149.2, 146.8, 146.6, 142.4, 142.36, 141.2, 126.6, 126.4, 123.5, 121.9, 113.5, 57.7, 46.8, 41.4, 39.6 ppm; IR (KBr): υ 3038, 2924, 1655, 1548, 1408, 929, 799 cm^{-1}. HRMS (FAB) m/z: Calcd. for $C_{21}H_{13}OBr$ $[M]^+$ 357.9993, found 358.0004.

o-Bromohydroxysumanene (4) from hydroxysumanene (2)

0.5 mL of 49 mM Bromine in dry CH_2Cl_2 (0.025 mmol) was added dropwise to a solution of **2**[2] (6.0 mg, 0.021 mmol) in 5 mL dry CH_2Cl_2 at 0 °C over 30 min under N_2 atmosphere. After completion of reaction, excess bromine was quenched by saturated aqueous $Na_2S_2O_3$ solution. The reaction mixture was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were washed with water (5mL x 3) and brine, dried over Na_2SO_4 filtered through cotton, and evaporated in vacuum. The crude product was purified by PTLC (50% CH_2Cl_2/hexane) to give **4** as a pale orange solid (6.8 mg, 88% yield).

o-Bromohydroxysumanene (4) from bromosumanenone (3)

0.5 mL of 1.78 mM trifluoroacetic acid (0.891 μmol) in dry CH_2Cl_2 was added dropwise to a solution of **3** (3.2 mg, 8.91 μmol) in 5 mL dry CH_2Cl_2 at 0 °C. The reaction was quenched by H_2O (5 mL) after completion of reaction. The reaction mixture was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layers were washed with water (5 mL x 3) and brine, dried

over Na_2SO_4, filtered through cotton, and evaporated in vacuum. The crude product was purified by PTLC (50% CH_2Cl_2/hexane) to give **4** as a pale orange solid (2.9 mg, 91% yield).

Mp: 105 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ 7.13-7.03 (*m*, 4H), 5.80 (*brs*, 1H), 4.66 (*d*, *J* = 21.6 Hz, 1H), 4.63 (*d*, *J* = 20.0 Hz, 1H), 4.60 (*d*, *J* = 21.2 Hz, 1H), 3.56 (*d*, *J* = 20.0 Hz, 1H), 3.40 (*d*, *J* = 19.6 Hz, 1H), 3.38 (*d*, *J* = 19.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): 151.2, 149.5, 149.3, 149.0, 148.9, 148.8, 148.4, 147.9, 147.69, 147.68, 147.0, 141.6, 131.7, 123.9, 123.5, 123.4, 122.8, 106.9, 43.3, 41.6, 39.9 ppm; IR (KBr): υ 3461 (br), 2920, 1715, 1684, 1635, 1400, 1259, 784 cm^{-1}; HRMS (FAB) m/z: Calcd. for $C_{21}H_{13}OBr$ $[M]^+$ 357.9993, found 358.0006.

Hydroxysumanenone (5) from hydroxysumanene (2)

To a solution of **2**[2] (6.0 mg, 0.021 mmol) in 5 mL dry CH_2Cl_2 was added *N*-bromosuccinimide (4.4 mg, 0.026 mmol) at 0 °C under N_2 atmosphere. After completion of reaction, solvent was removed by evaporation in vacuum at 0 °C. 50% THF/H_2O (10 mL) was added to the residue and the solution was stirred at 0 °C until it became homogeneous. Silver acetate (5.4 mg, 0.032 mmol) was added to the solution and the mixture was stirred for 15 min at 0 °C. The mixture was diluted with water (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The organic layer was dried over Na_2SO_4, filtered through cotton, and evaporated in vacuum. The crude residue was purified by PTLC (10% EtOAc/CH_2Cl_2) to give **5** (2.5 mg, 40% yield) as a yellow solid.

Mp: 61 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ 7.31 (*d*, *J* = 8.0 Hz, 1H), 7.17 (*d*, *J* = 8.0 Hz, 1H), 7.07 (*d*, *J* = 8.4 Hz, 1H), 6.85 (*d*, *J* = 8.0 Hz, 1H), 5.74 (*d*, *J* = 2.4 Hz, 1H), 4.44 (*d*, *J* = 16.8 Hz, 1H), 4.41 (*d*, *J* = 19.6 Hz, 1H), 4.14 (*d*, *J* = 22.0 Hz, 1H), 3.245 (*d*, *J* = 17.2 Hz, 1H), 3.240 (*d*, *J* = 21.2 Hz, 1H), 3.08 (*d*, *J* = 22.0 Hz, 1H), 2.85 (*brs*, 1H); ^{13}C NMR ($CDCl_3$): 186.4, 162.1, 161.6, 148.5, 148.3, 147.8, 145.0, 144.9, 144.1, 143.9, 141.0, 139.7, 129.8, 128.0, 125.5, 125.47, 125.4, 70.4, 40.7, 40.6, 36.8 ppm; IR (KBr): υ 3375 (br), 2928, 1651, 1624, 1037, 786 cm^{-1}; HRMS (FAB) m/z: Calcd. for $C_{21}H_{12}O_2$ $[M]^+$ 296.0837, found 296.0847.

Methoxysumanenone (6)

To a solution of **2** (6.0 mg, 0.021 mmol) in dry CH_2Cl_2 (5 mL) was added *N*-bromosuccinimide (4.4 mg, 0.026 mmol) at 0 °C under N_2 atmosphere. After completion of reaction, solvent was removed by evaporation in vacuum at 0 °C. Methanol (10 mL) was added to the residue and the solution was stirred at 0 °C for 30 min. Solvent was removed by evaporation in vacuum. The residue was purified by PTLC (CH_2Cl_2) to give **6** (2.7 mg, 40% yield) as a yellow solid.

Mp: 112 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ 7.30 (*d*, *J* = 7.6 Hz, 1H), 7.16 (*d*, *J* = 8.0 Hz, 1H), 7.06 (*d*, *J* = 7.6 Hz, 1H), 6.85 (*d*, *J* = 8.0 Hz, 1H), 5.84 (*d*, *J* = 2.4 Hz, 1H), 4.41 (*d*, *J* = 20.0 Hz, 1H), 4.35 (*d*, *J* = 17.6 Hz, 1H), 4.17 (*d*, *J* = 22.0 Hz, 1H), 3.63 (*s*, 3H), 3.23 (*d*, *J* = 20.4 Hz, 1H), 3.21 (*d*, *J* = 17.6 Hz, 1H), 3.08 (*d*, *J* = 22.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): 186.5, 159.8, 159.5, 148.3, 148.1, 147.4, 147.2, 145.7, 144.5, 144.3, 141.4, 138.9, 129.6, 127.9, 127.1, 125.3, 123.3, 75.6, 52.8, 40.7, 40.68, 37.2 ppm; IR (KBr): υ 2920, 1651, 1396, 1050, 792 cm^{-1}. ; HRMS (FAB) m/z: Calcd. for $C_{22}H_{14}O_2$ $[M+H]^+$ 311.1072, found 311.1061.

Separation of enantiomers of 5 and 6 by chiral SFC

The enantiomers of **5** (4.6 mg) or **6** (5.2 mg) were separated by using a JASCO supercritical fluid chromatography (SFC) system equipped with CD and UV detectors (254 nm) and a DAICEL chiral column CHIRALPAX IA to afford (+)-**5** (2.1 mg) and (-)-**5** (2.3 mg) (Figure S4) or (+)-**7** (2.5 mg) and (-)-**6** (2.4 mg) (Figure S5). Each enantiomer was obtained with >99% ee as indicated by the chiral SFC analysis of the obtained samples (Figure S6-9)
(+)-**5** (t_R=13.26 min): $[\alpha]^{20}_D$= +210.7 (*c*=0.015, CH_2Cl_2). (-)-**5** (t_R=14.96 min): $[\alpha]^{20}_D$= -202.0 (*c*=0.005, CH_2Cl_2). (+)-**6** (t_R=7.03 min): $[\alpha]^{20}_D$= +249.5 (*c*=0.02, CH_2Cl_2). (-)-**6** (t_R=8.54 min): $[\alpha]^{20}_D$= -246.7 (*c*=0.015, CH_2Cl_2).

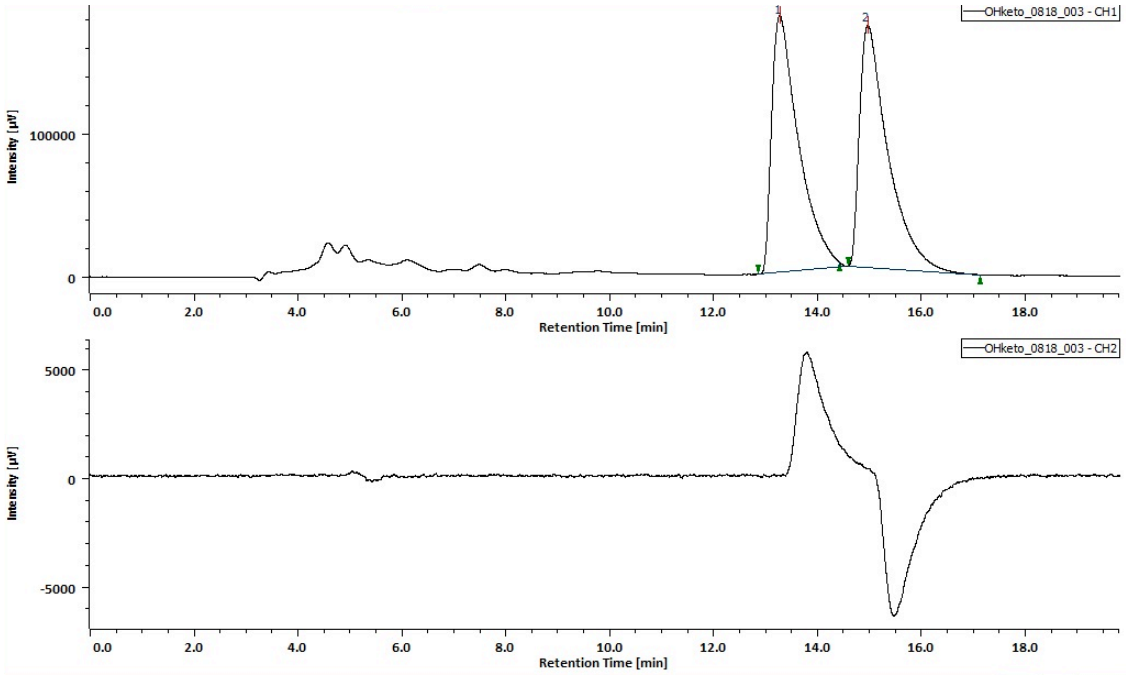

Figure S4 SFC chart of hydroxysumanenone **5**. Column CHIRALPAK IA (eluent= CH_2Cl_2 0.8 mL/min, CO_2 0.8 mL/min), UV and CD detector absorbed at 254 nm.
For UV detector : peak 1, t_R=13.26 min, area% 50.097
peak 2, t_R=14.96 min, area% 49.903

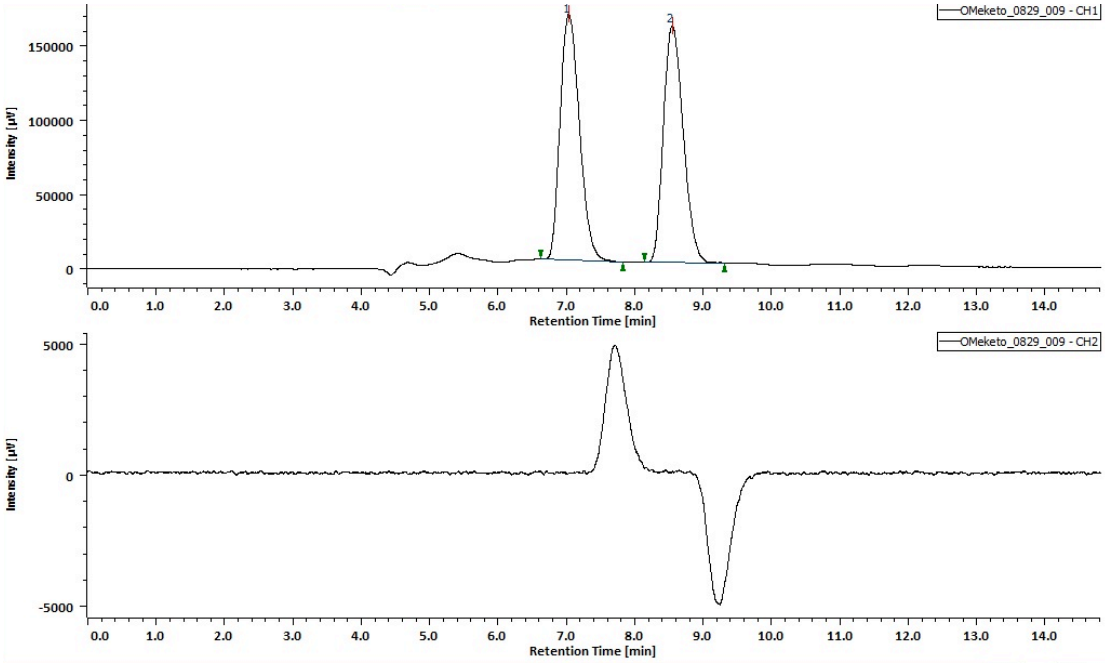

Figure S5 SFC chart of methoxysumanenone **6**. Column CHIRALPAK IA (eluent=CH_2Cl_2 0.5 mL/min, CO_2 0.8 mL/min), UV and CD detector absorbed at 254 nm.
For UV detector : peak 1, t_R=7.03 min, area% 50.967
peak 2, t_R=8.54 min, area% 49.033

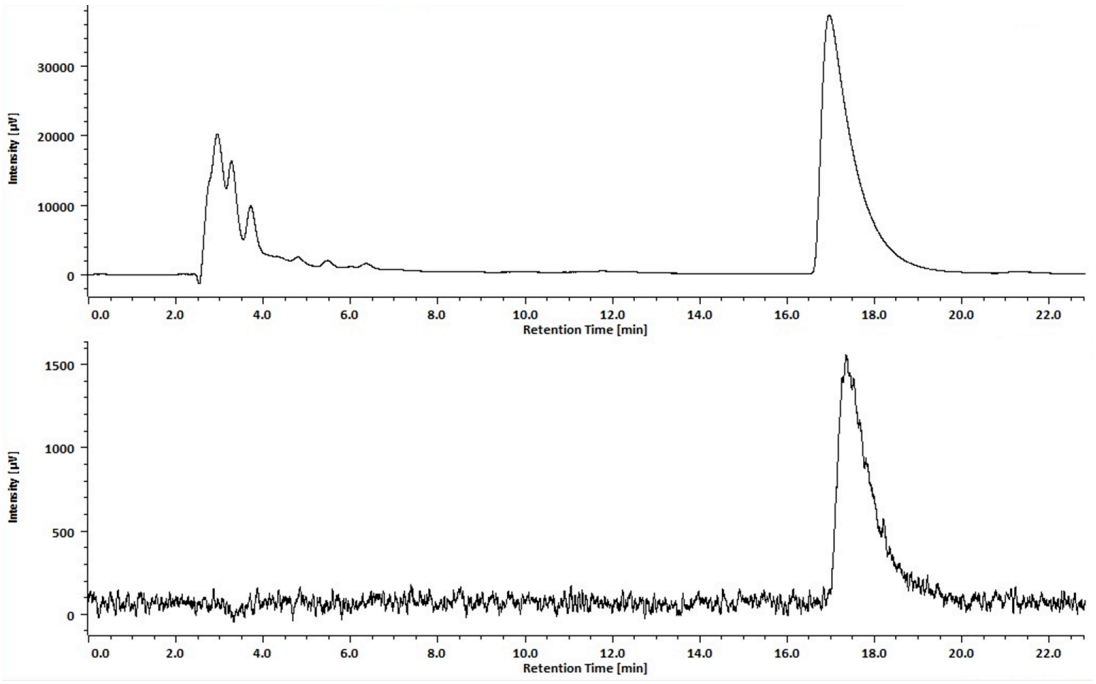

Figure S6 SFC chart of the separated (+)-**5**. Column CHIRALPAK IA (eluent=CH_2Cl_2 0.8 mL/min, CO_2 0.8 mL/min), UV and CD detector absorbed at 254 nm.
For UV detector : t_R=16.93 min

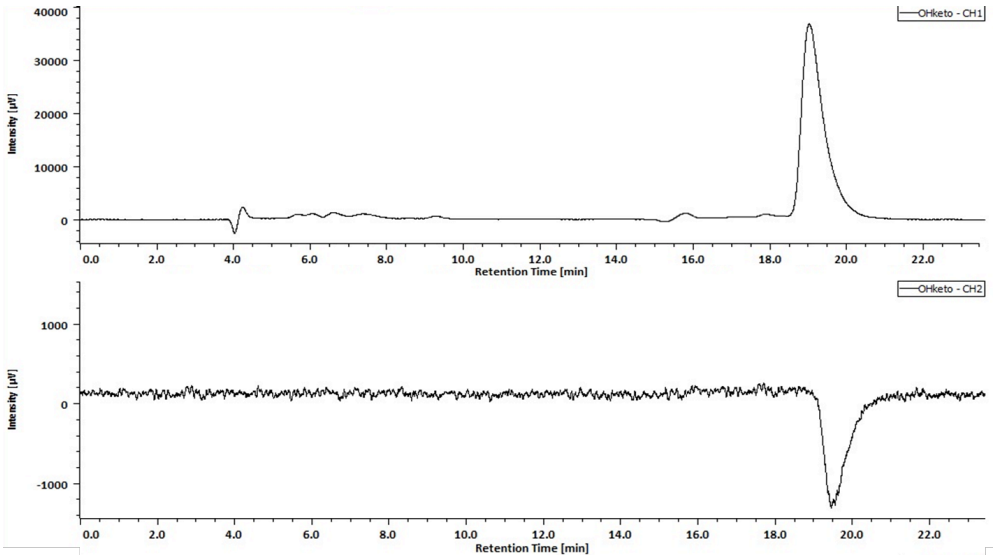

Figure S7 SFC chart of the separated (-)-**5**. Column CHIRALPAK IA (eluent= CH_2Cl_2 0.8 mL/min, CO_2 0.8 mL/min), UV and CD detector absorbed at 254 nm.
For UV detector : t_R=18.97 min

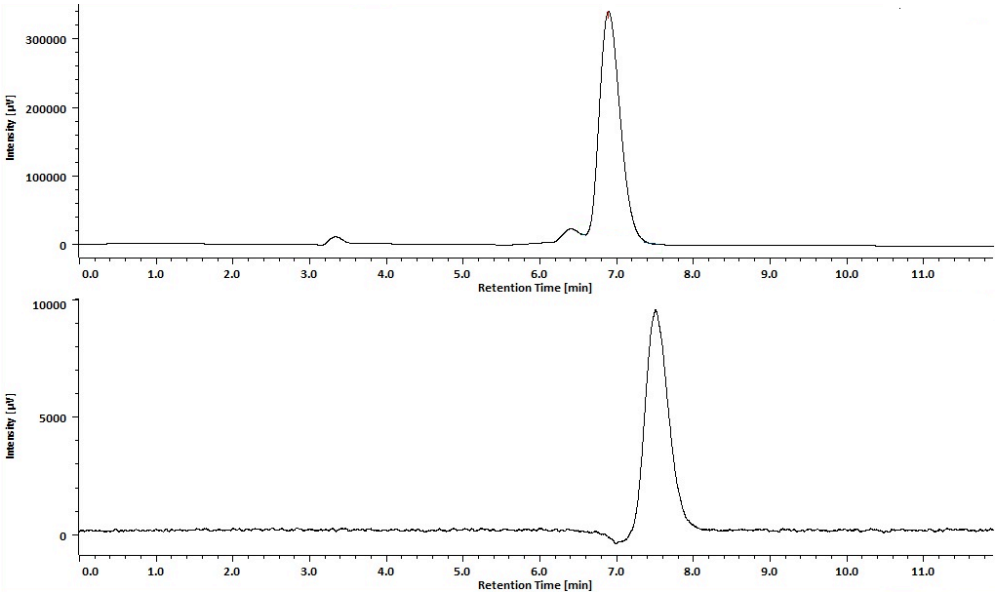

Figure S8 SFC chart of the separated (+)-**6**. Column CHIRALPAK IA (eluent= CH_2Cl_2 0.5 mL/min, CO_2 0.8 mL/min), UV and CD detector absorbed at 254 nm.
For UV detector : t_R=6.89 min

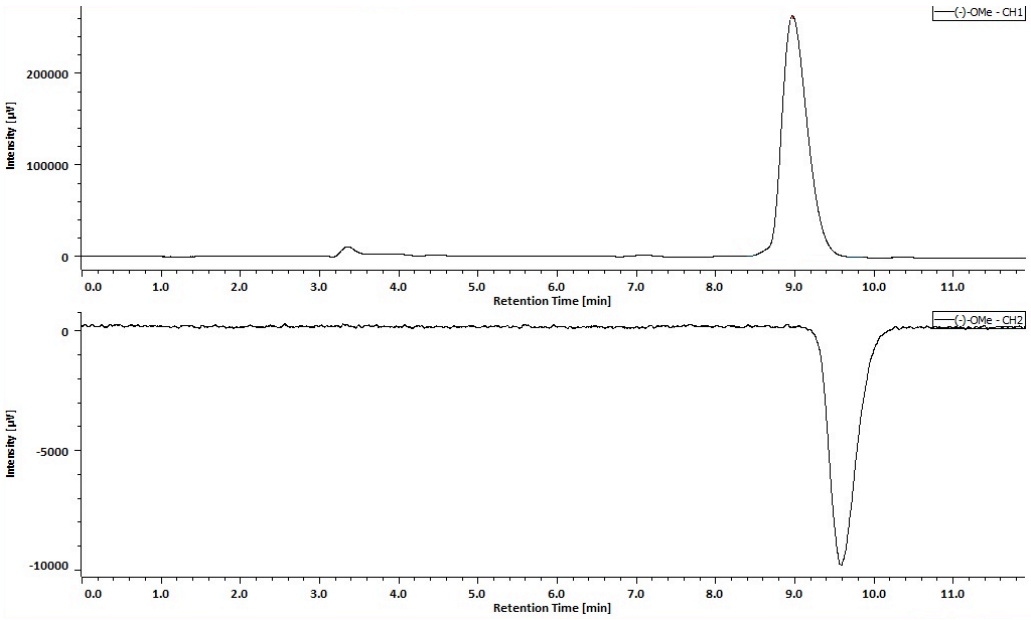

Figure S9 SFC chart of the separated (-)-**6**. Column CHIRALPAK IA (eluent= CH_2Cl_2 0.5 mL/min, CO_2 0.8 mL/min), UV and CD detector absorbed at 254 nm.
For UV detector : t_R=8.96 min

3. X-Ray analysis data

The single crystals of (+)-**5** and (−)-**5** were obatined by the crystalization of separated pure enantiomers from 20%MeOH/CH_2Cl_2. The diffraction data for (+)-**5** and (−)-**5** were recorded on a RIGAKU/MSC XtaLAB P200 X-ray diffractometer with a Cu-target (λ = 1.54187 Å) equipped with a two-dimensional X-ray detector (PILATUS 200K/R) at 150 K in house. The diffraction images were processed by using CrysAlisPro.[3] The structures were solved by direct methods (SHELXS)[4] and refined by full-matrix least squares calculations on F^2 (SHELXL)[5] using the Olex2 program package.[6] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-1512434 for (−)-**5** and CCDC-1512435 for (+)-**5**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html

(+)-**5**: $C_{21}H_{12}O_2$, *M*r = 296.31, crystal dimensions 0.08 × 0.05 × 0.02 mm^3, trigonal, $P3_1$, a = 9.982914(7) Å, b = 9.98291(7) Å, c = 11.95223(9) Å, V = 1031.56(2) Å^3, T = −123 °C, Z = 3, ρ_{calcd}= 1.431 g cm^{-3}, μ = 7.28 cm^{-1}, 2859 unique reflections out of 2886 with $I>2\sigma(I)$, 217 parameters, 5.116°<θ<76.313°, R_1= 0.0332, wR_2= 0.1092, GOF = 1.063, Flack parameter = 0.08(6).

(−)-**5**: $C_{21}H_{12}O_2$, *M*r = 296.31, crystal dimensions 0.10 × 0.05 × 0.02 mm^3, Trigonal, $P3_2$, a = 9.98192(9) Å, b = 9.98192(9) Å, c = 11.95006(8) Å, V = 1031.17(2) Å^3, T = −123 °C, Z = 3, ρ_{calcd}= 1.431 g cm^{-3}, μ = 7.28 cm^{-1}, 2804 unique reflections out of 2913 with $I>2\sigma(I)$, 217 parameters, 5.116°<θ<77.063°, R_1= 0.0420, wR_2= 0.1253, GOF = 1.114, Flack parameter = 0.14(8).

4. Comparison of the absorption-emission spectra between 1, 5 and 6

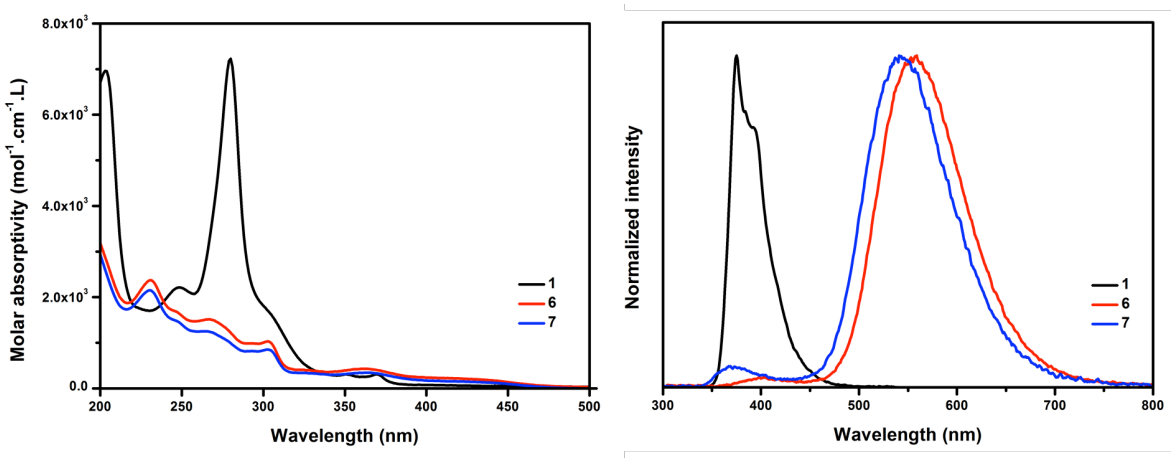

Figure 4 Absorption (left) and emission (right) spectra of **1**, **5** and **6** in CH_3CN. The emission spectra were excited at the absorption maxima.

5. NMR spectra

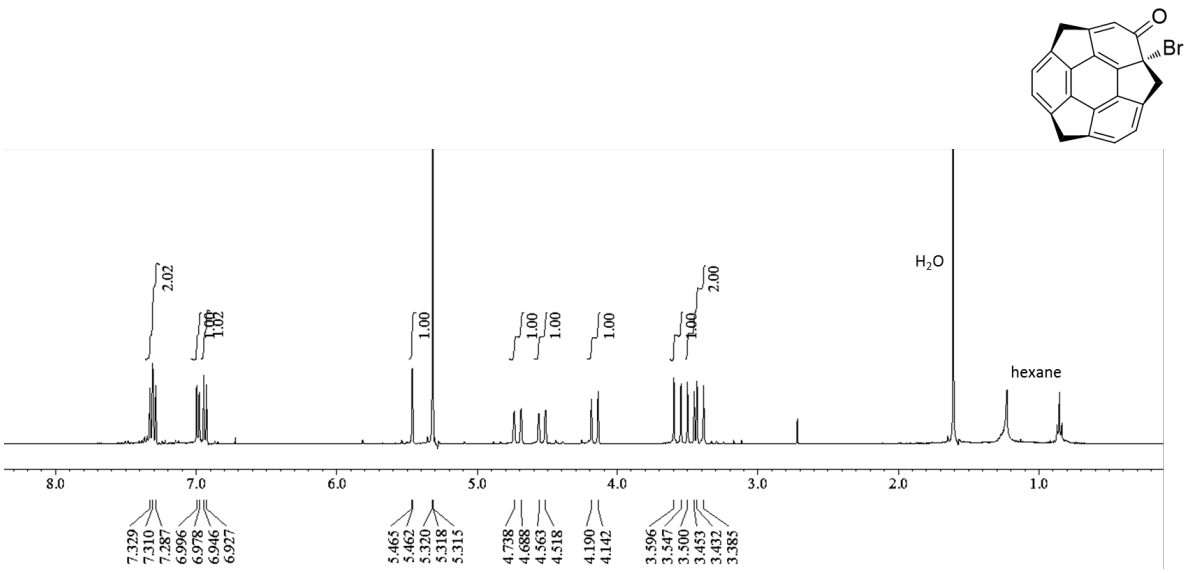

Figure S11. ^{1}H-NMR spectrum of bromosumanenone **3** (CD_2Cl_2)

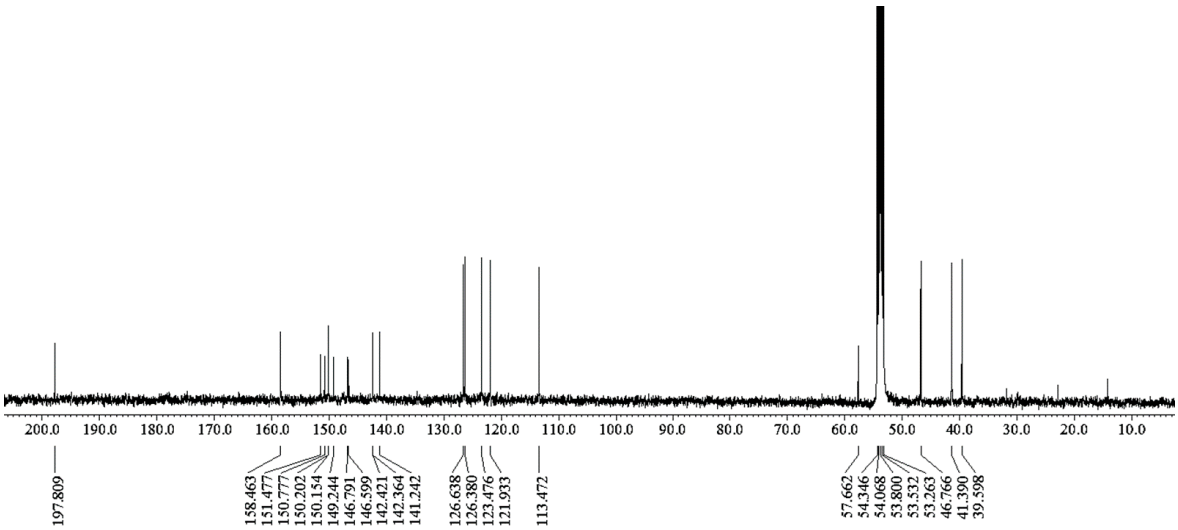

Figure S12. ^{13}C-NMR spectrum of bromosumanenone **3** (CD_2Cl_2)

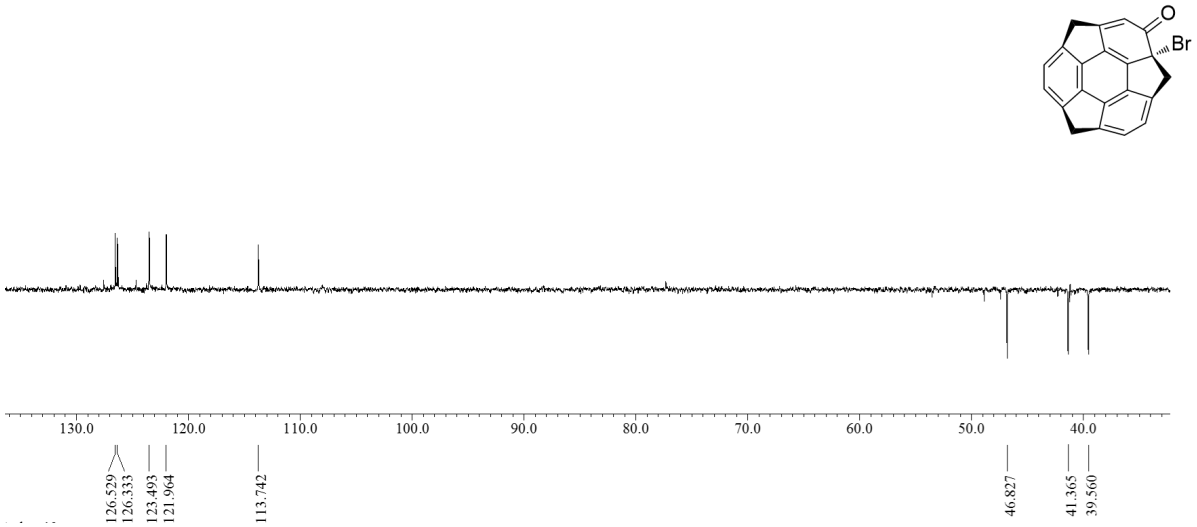

Figure S13. DEPT-135 spectrum of bromosumanenone **3** (CD_2Cl_2)

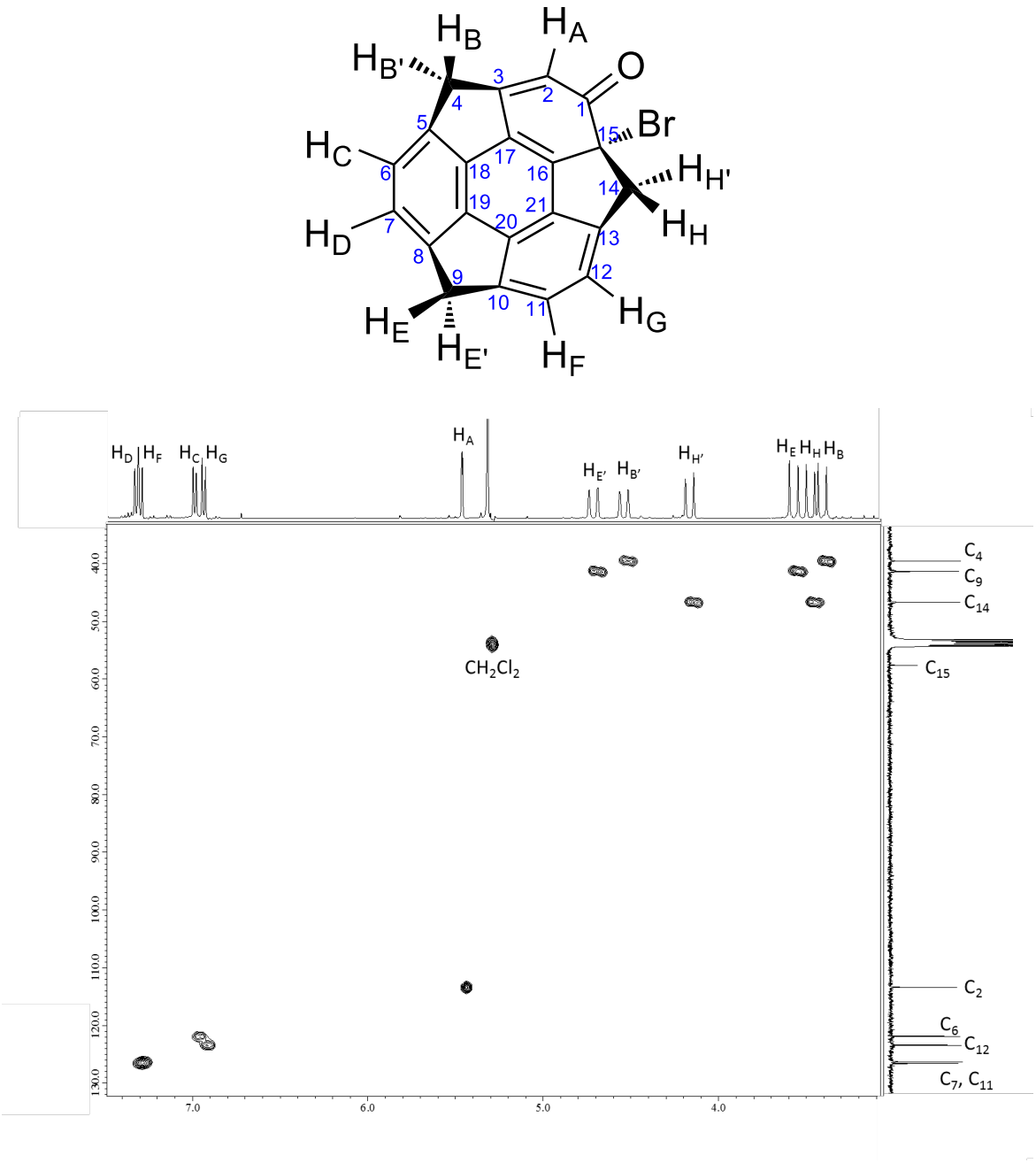

Figure S14. HMQC spectrum of bromosumanenone **3** (CD_2Cl_2)

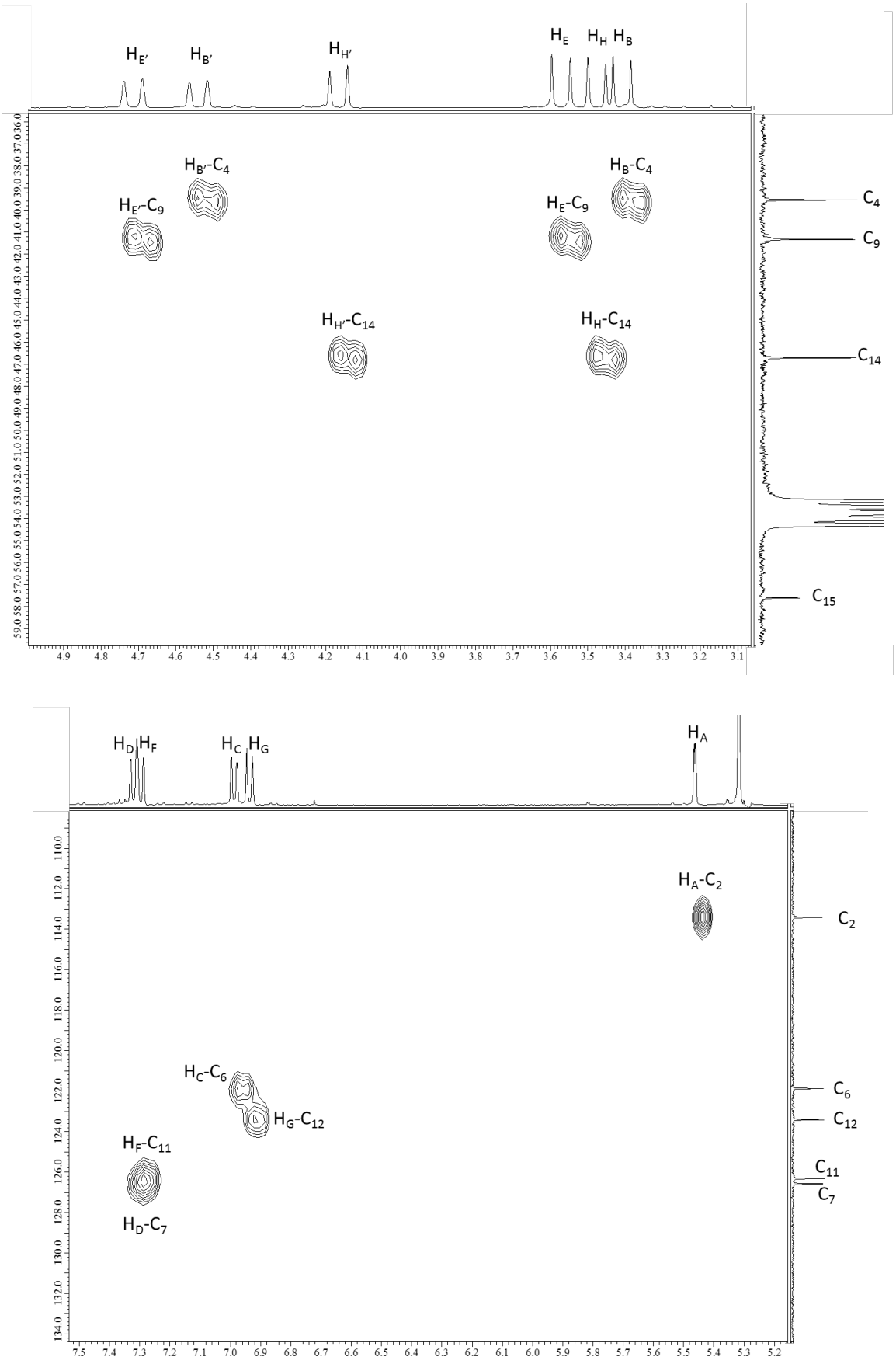

Figure S15. Enlarged HMQC spectrum of bromosumanenone **3** (CD_2Cl_2)

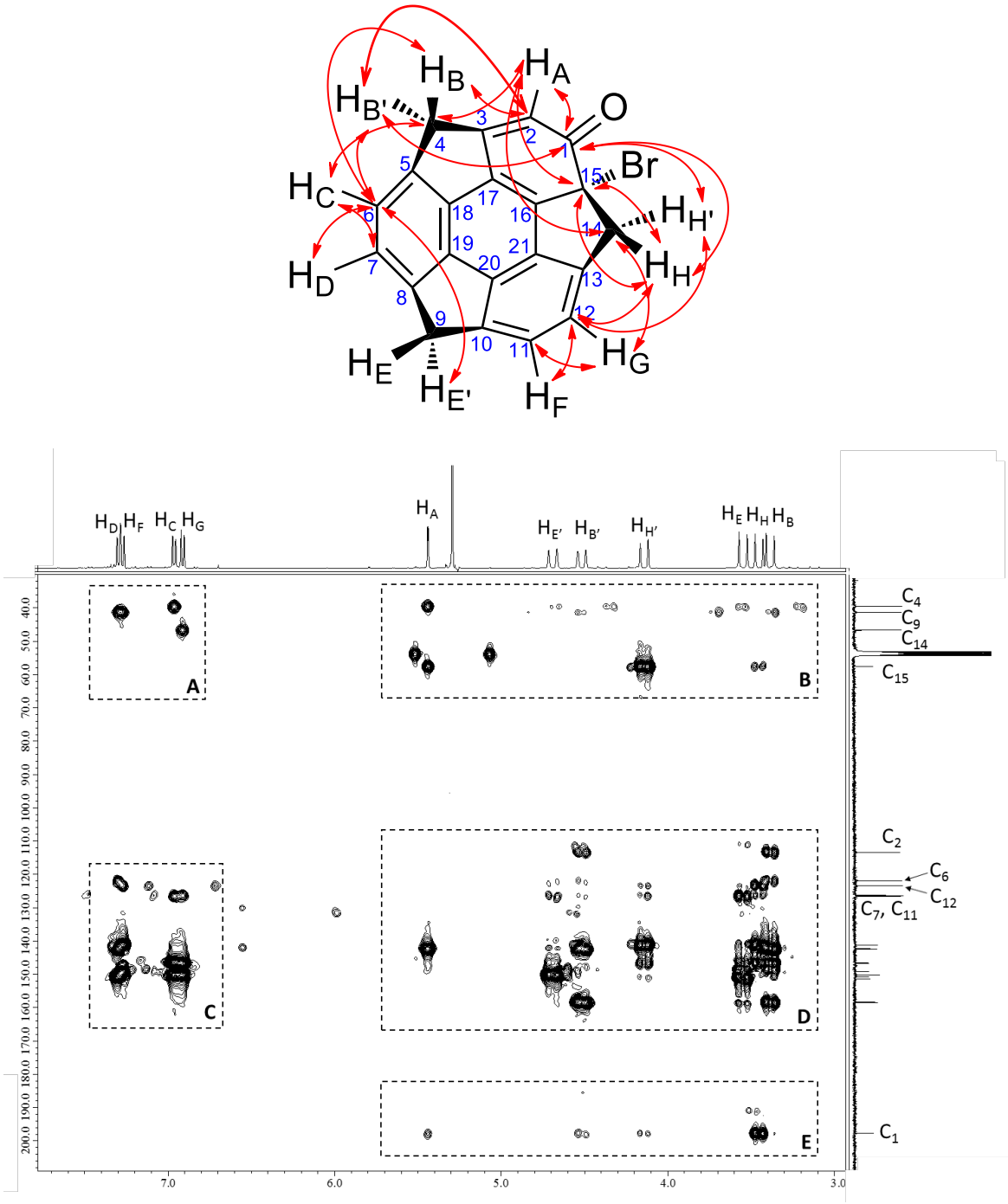

Figure S16. HMBC spectrum of bromosumanenone **3** (CD_2Cl_2), relaxation delay 4 s

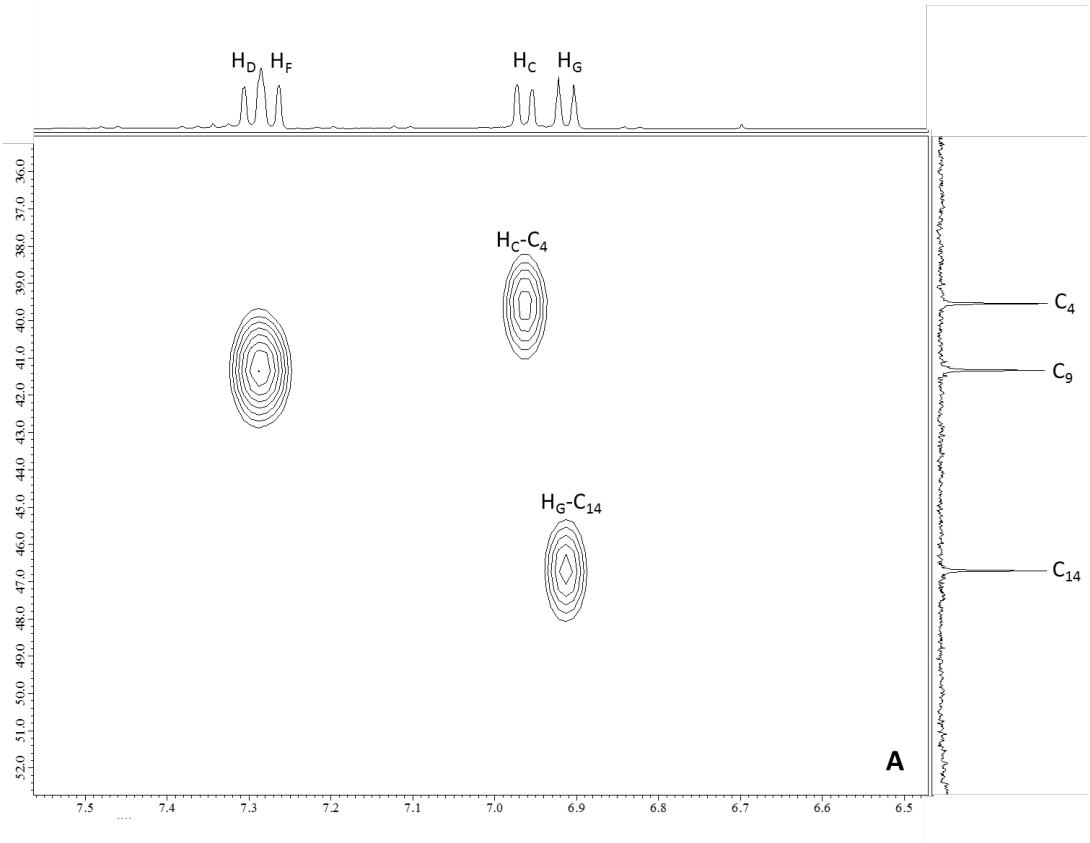

Figure S17. Enlarged area A of HMBC spectrum of bromosumanenone **3** (CD_2Cl_2)

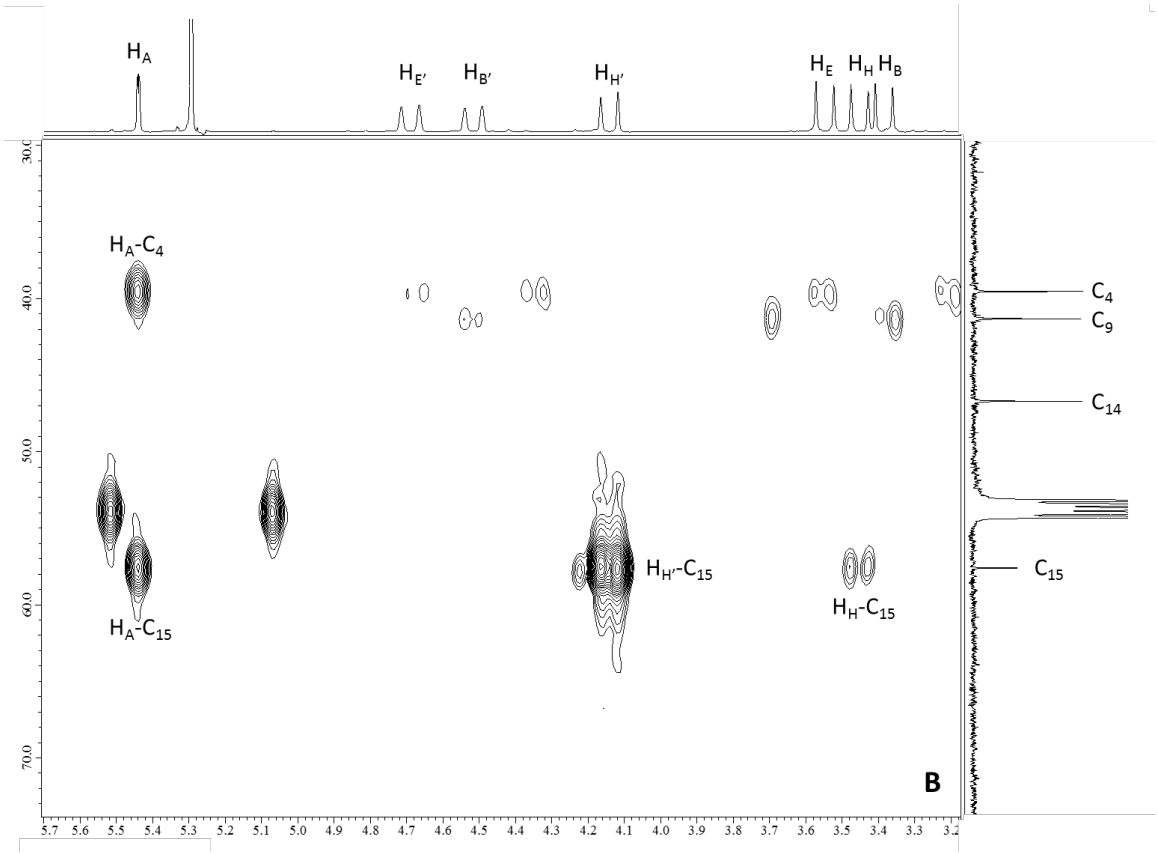

Figure S18. Enlarged area B of HMBC spectrum of bromosumanenone **3** (CD_2Cl_2)

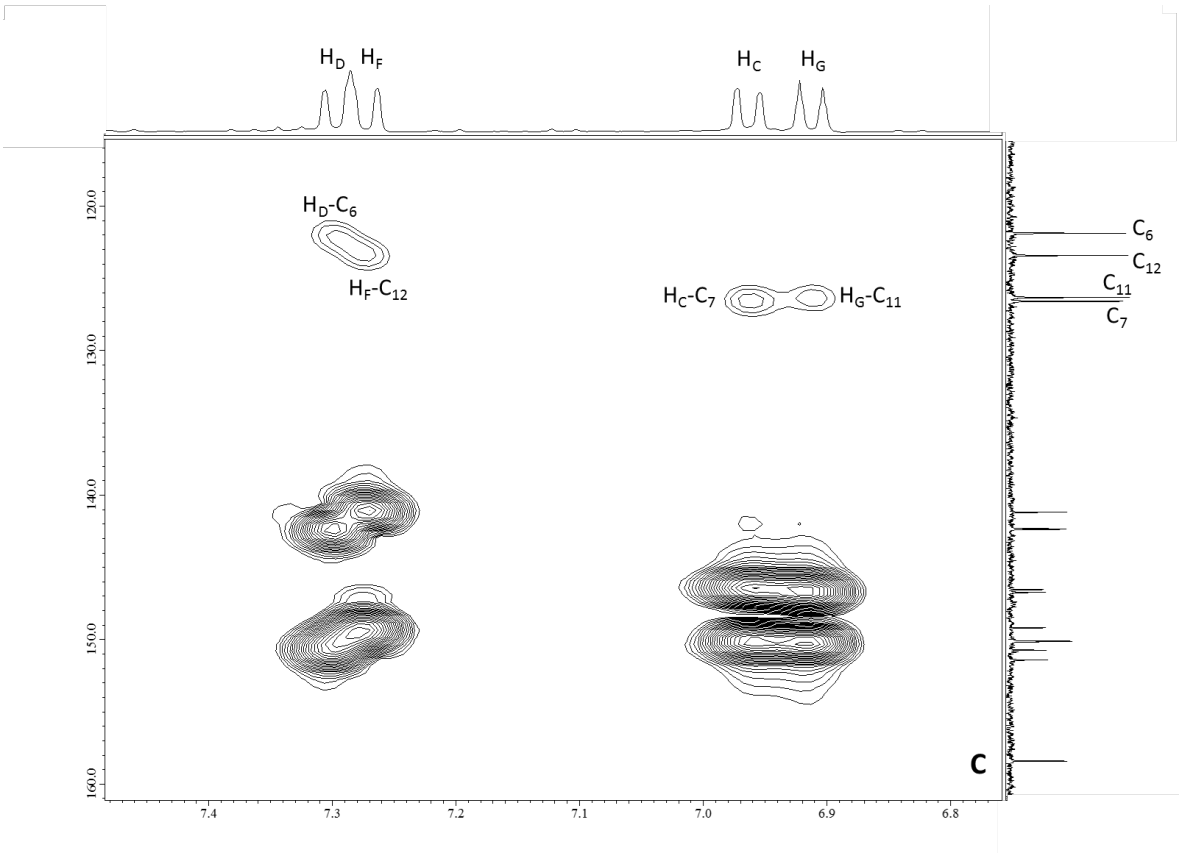

Figure S19. Enlarged area C of HMBC spectrum of bromosumanenone **3** (CD_2Cl_2)

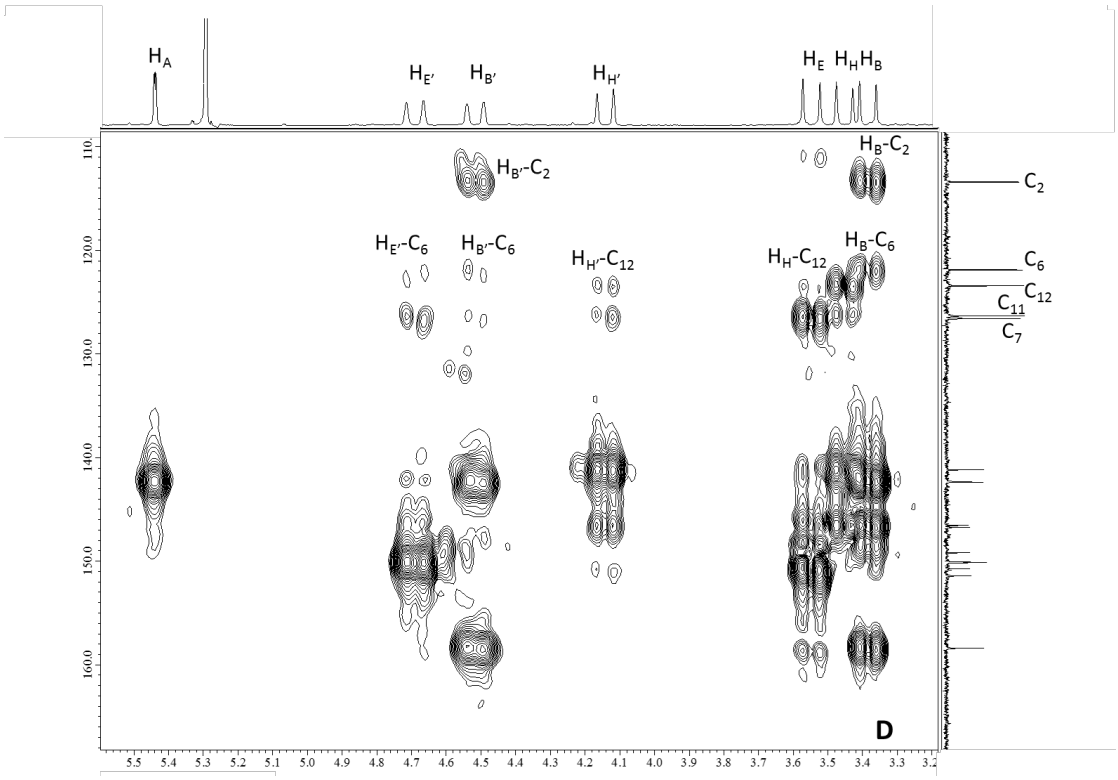

Figure S20. Enlarged area D of HMBC spectrum of bromosumanenone **3** (CD_2Cl_2)

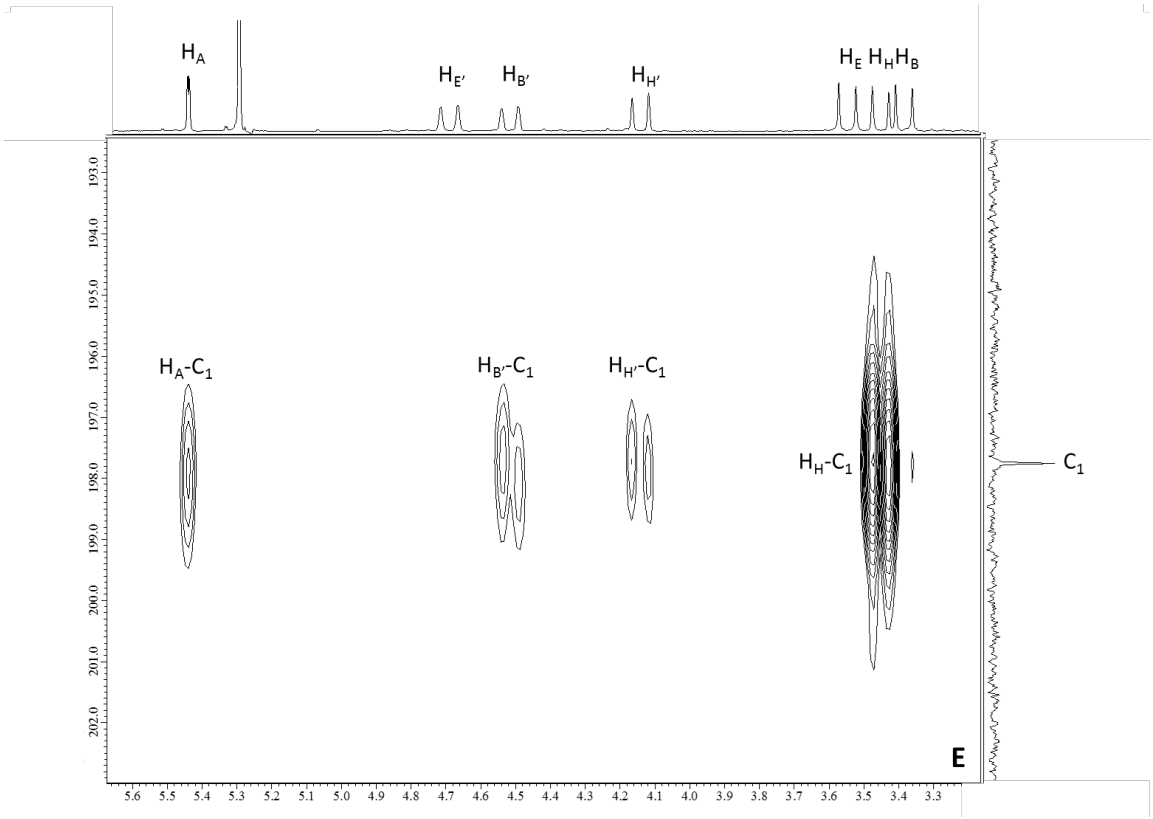

Figure S21. Enlarged area E of HMBC spectrum of bromosumanenone **3** (CD_2Cl_2)

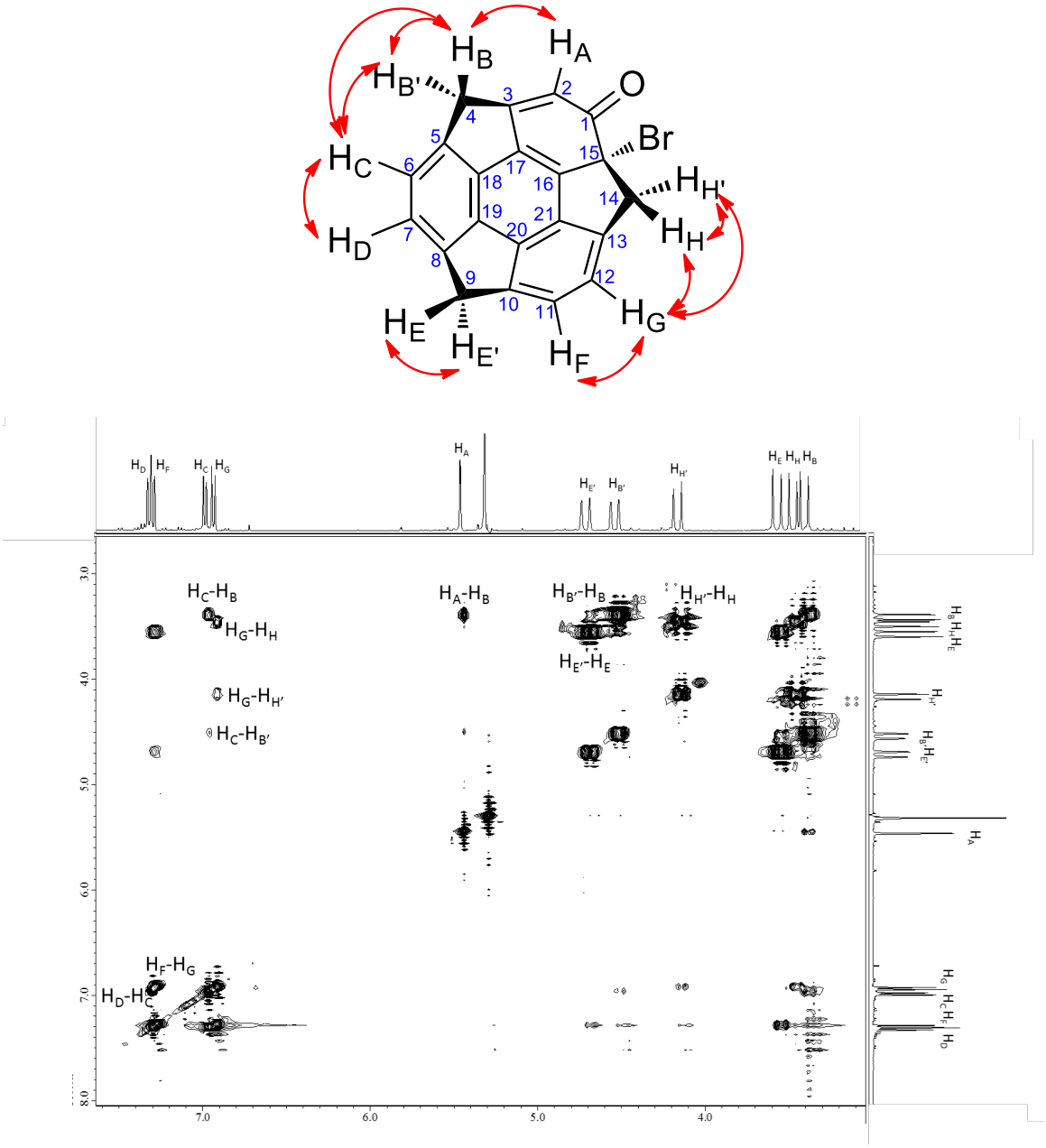

Figure S22. NOESY spectrum of bromosumanenone **3** (CD_2Cl_2)

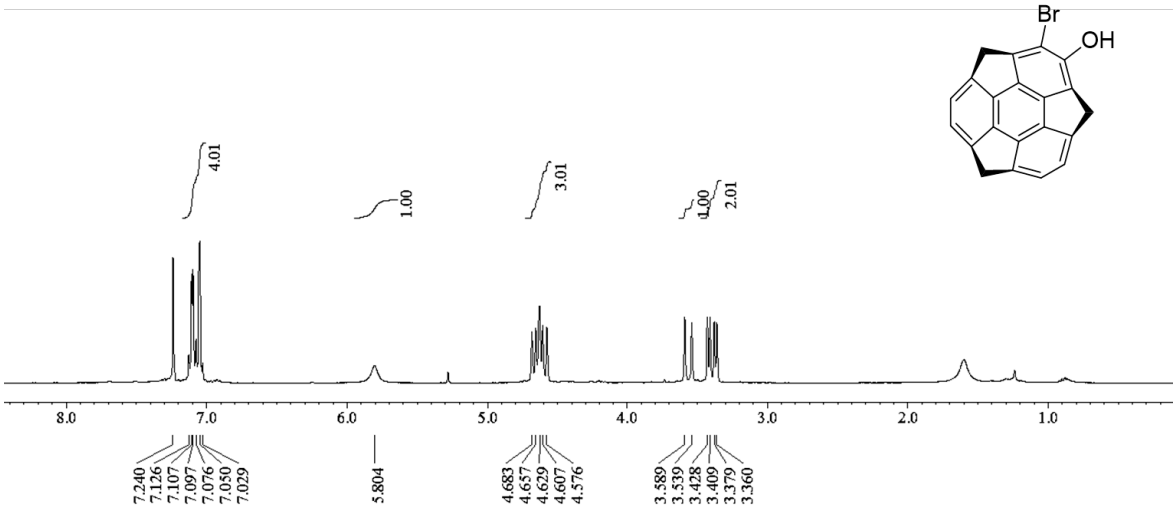

Figure S23. ^{1}H-NMR spectrum of *o*-bromohydroxysumanene **4** ($CDCl_3$)

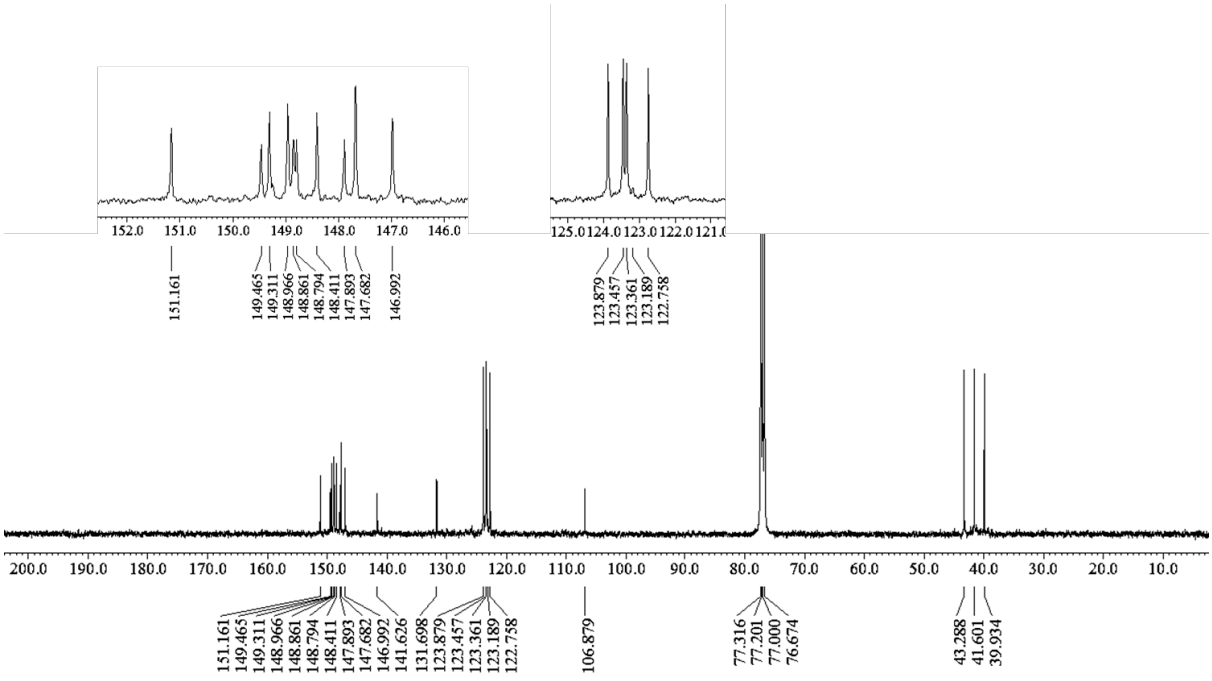

Figure S24. ^{13}C-NMR spectrum of *o*-bromohydroxysumanene **4** ($CDCl_3$)

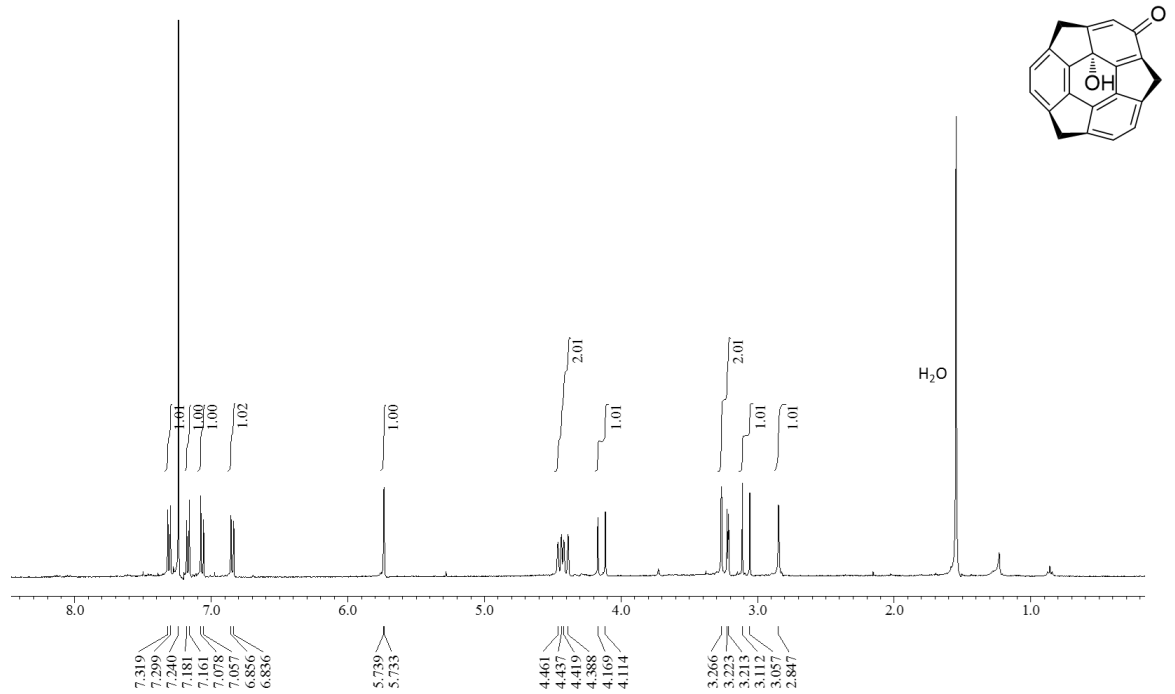

Figure S25. ^{1}H-NMR spectrum of hydroxysumanenone **5** ($CDCl_3$)

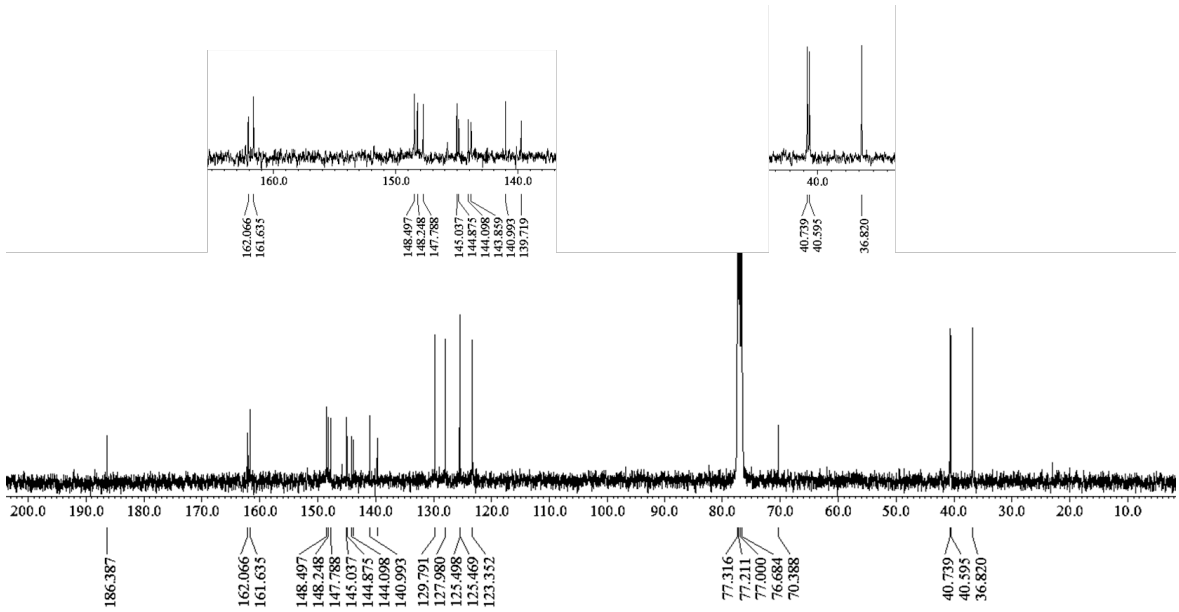

Figure S26. ^{13}C-NMR spectrum of hydroxysumanenone **5** ($CDCl_3$)

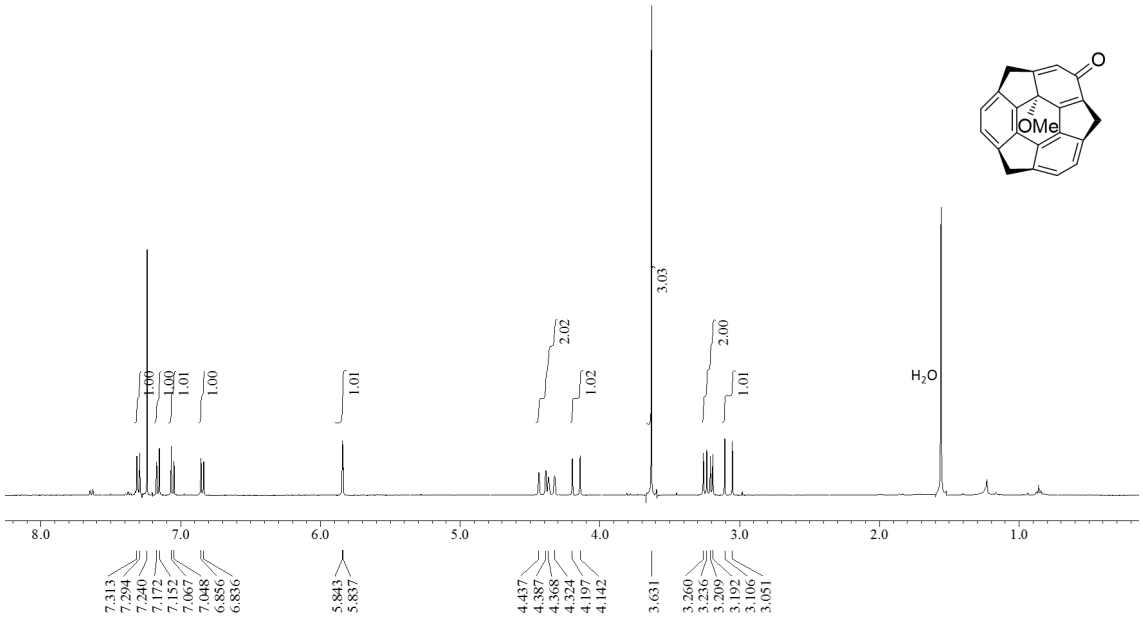

Figure S27. ^{1}H-NMR spectrum of methoxysumanenone **6** ($CDCl_3$)

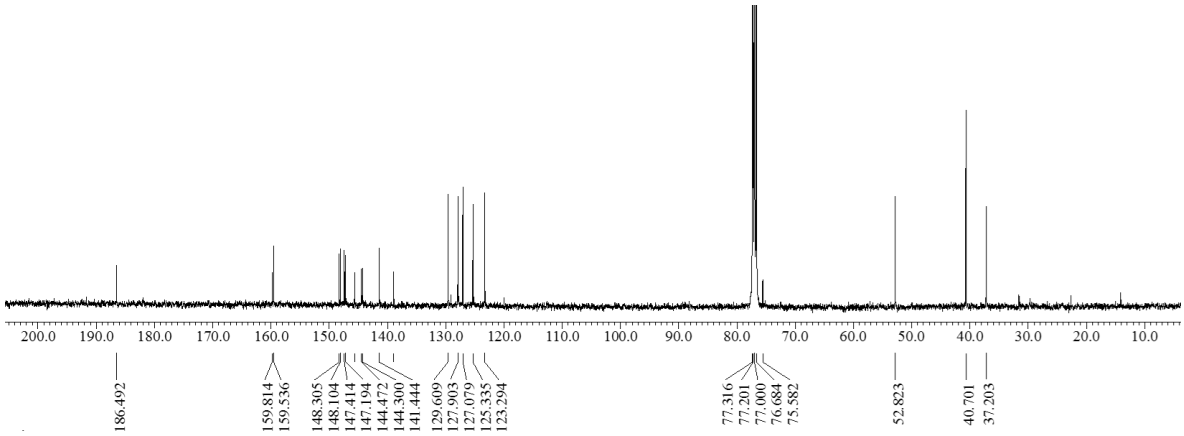

Figure S28. ^{13}C-NMR spectrum of methoxysumanenone **6** ($CDCl_3$)

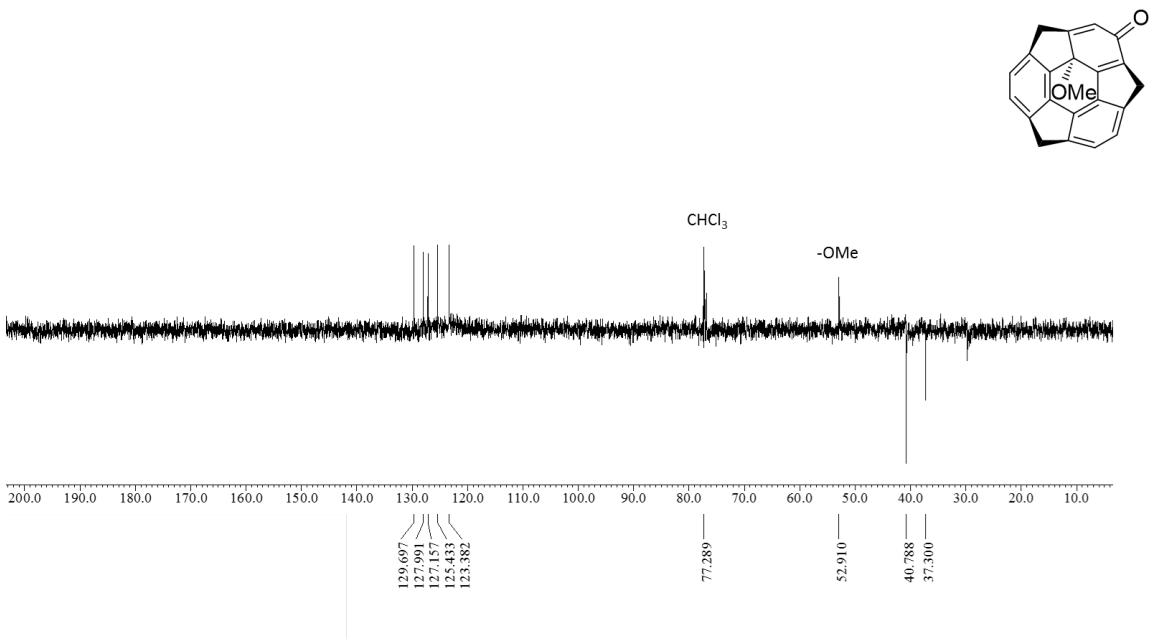

Figure S29. DEPT-135 spectrum of methoxysumanenone **6** ($CDCl_3$)

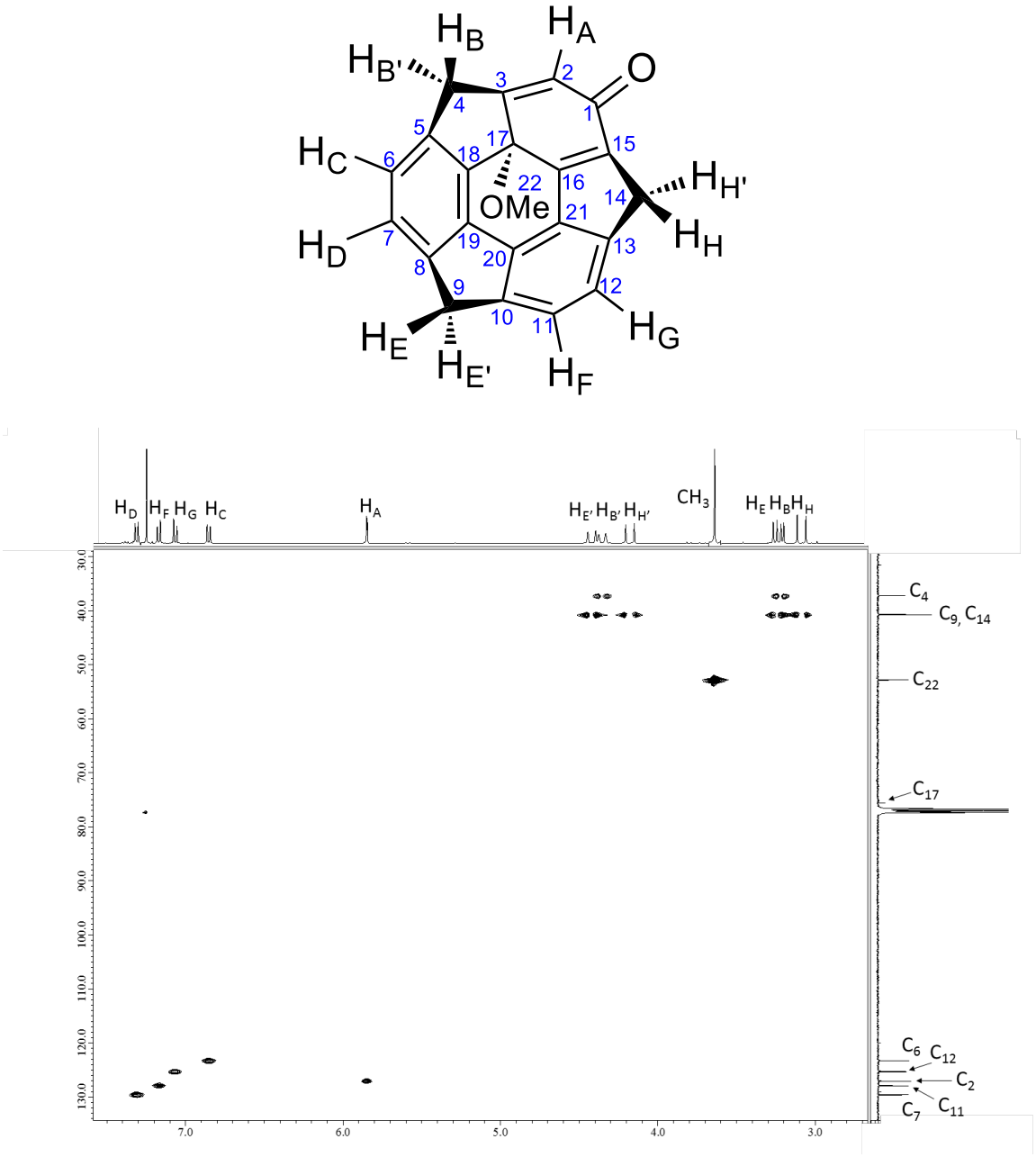

Figure S30. HMQC spectrum of methoxysumanenone **6** ($CDCl_3$)

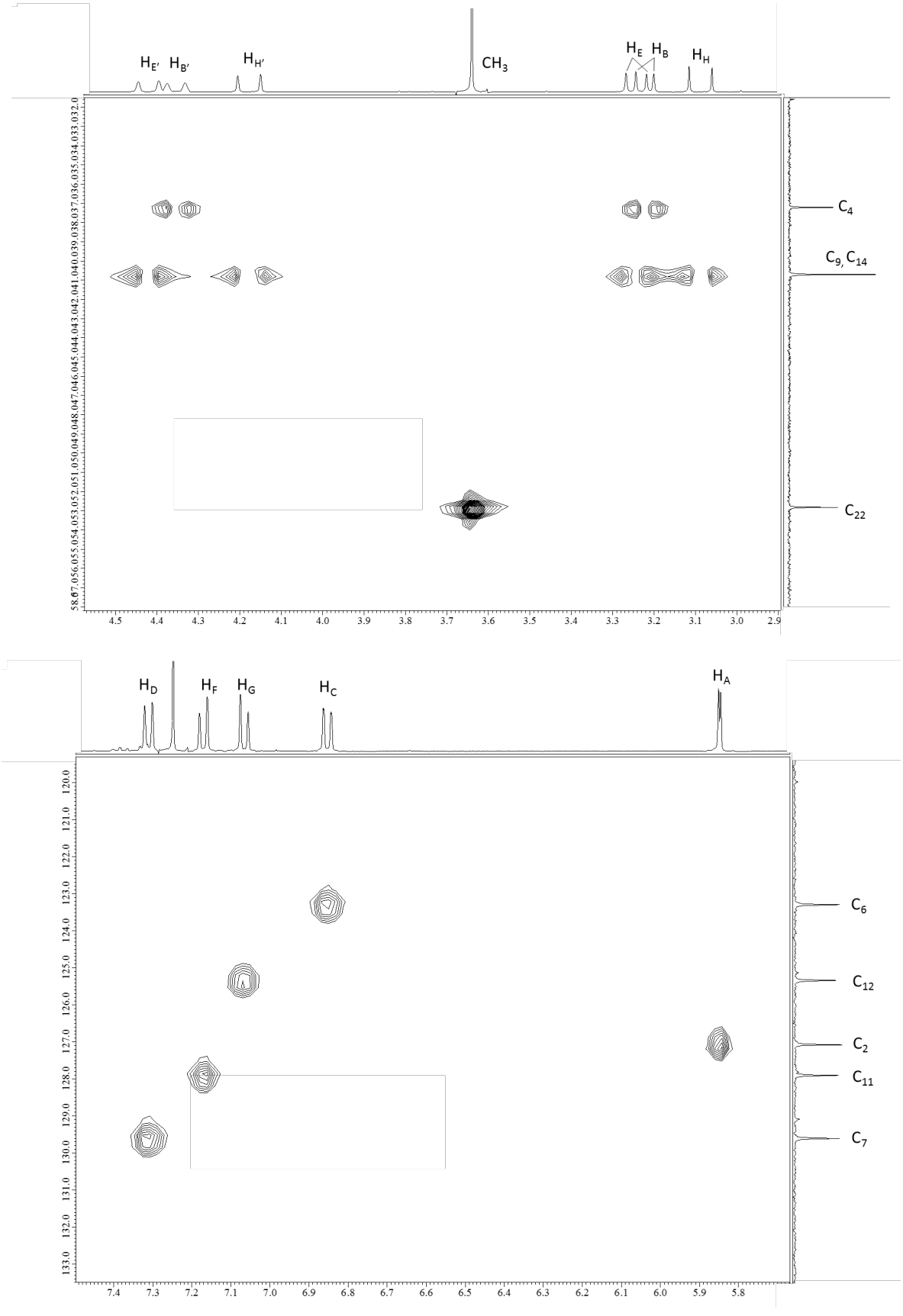

Figure S31. Enlarged HMQC spectrum of methoxysumanenone **6** ($CDCl_3$)

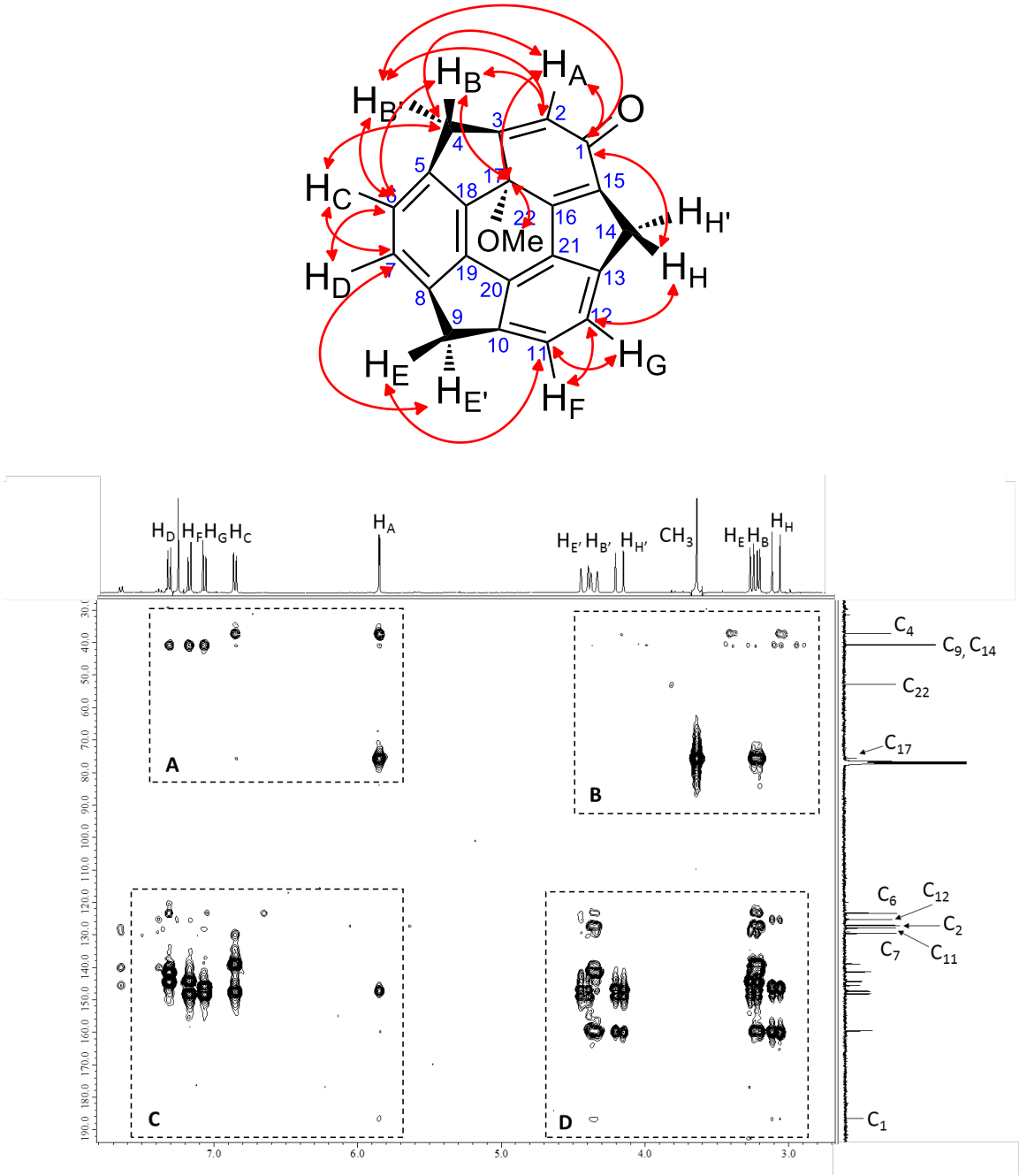

Figure S32. HMBC spectrum of methoxysumanenone **6** ($CDCl_3$), relaxation delay 4 s

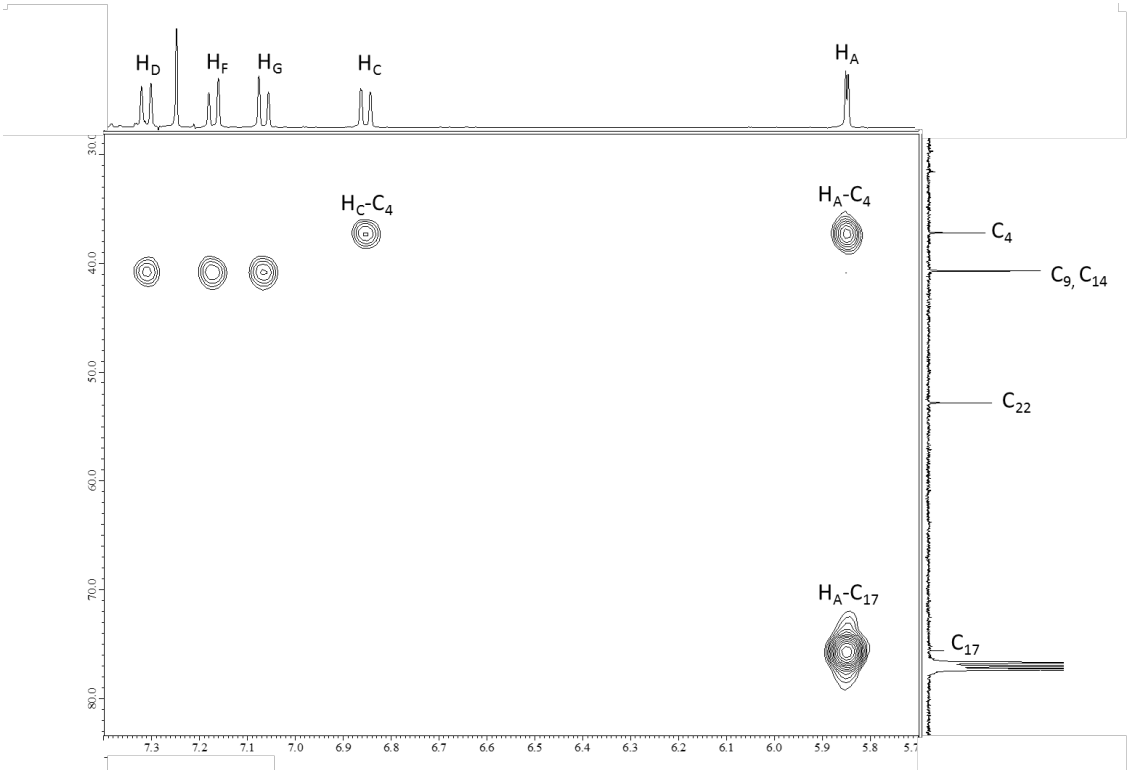

Figure S33. Enlarged area A of HMBC spectrum of methoxysumanenone **6** ($CDCl_3$)

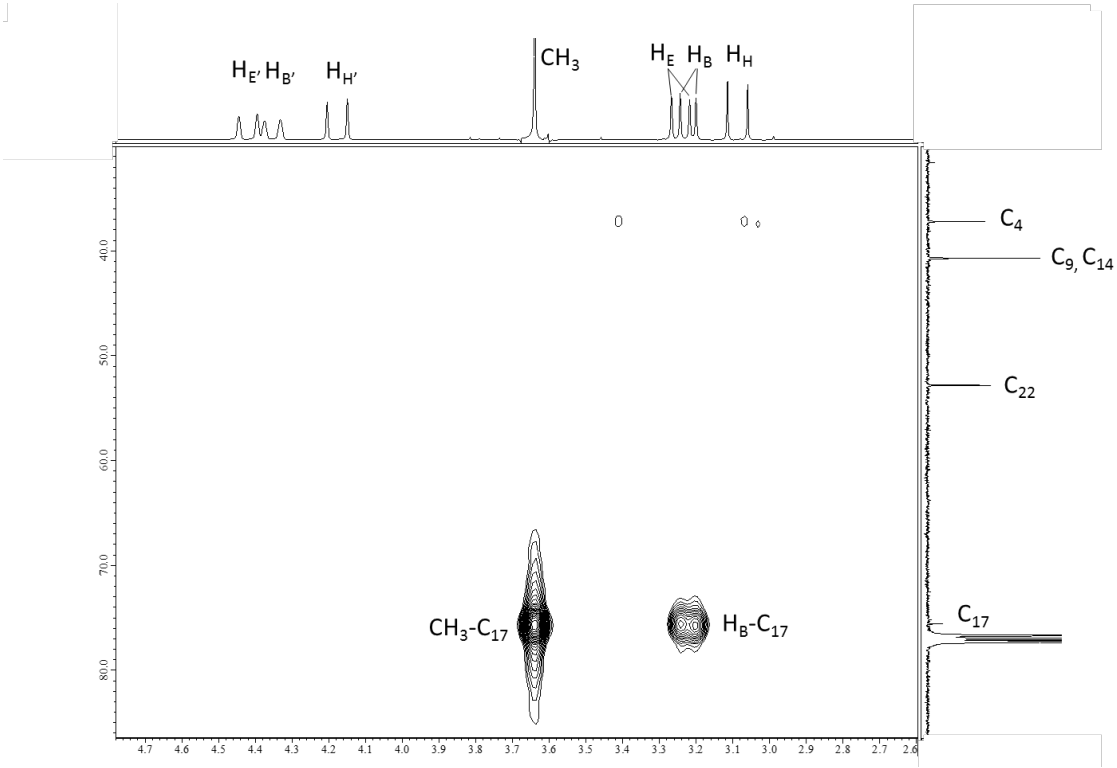

Figure S34. Enlarged area B of HMBC spectrum of methoxysumanenone **6** ($CDCl_3$)

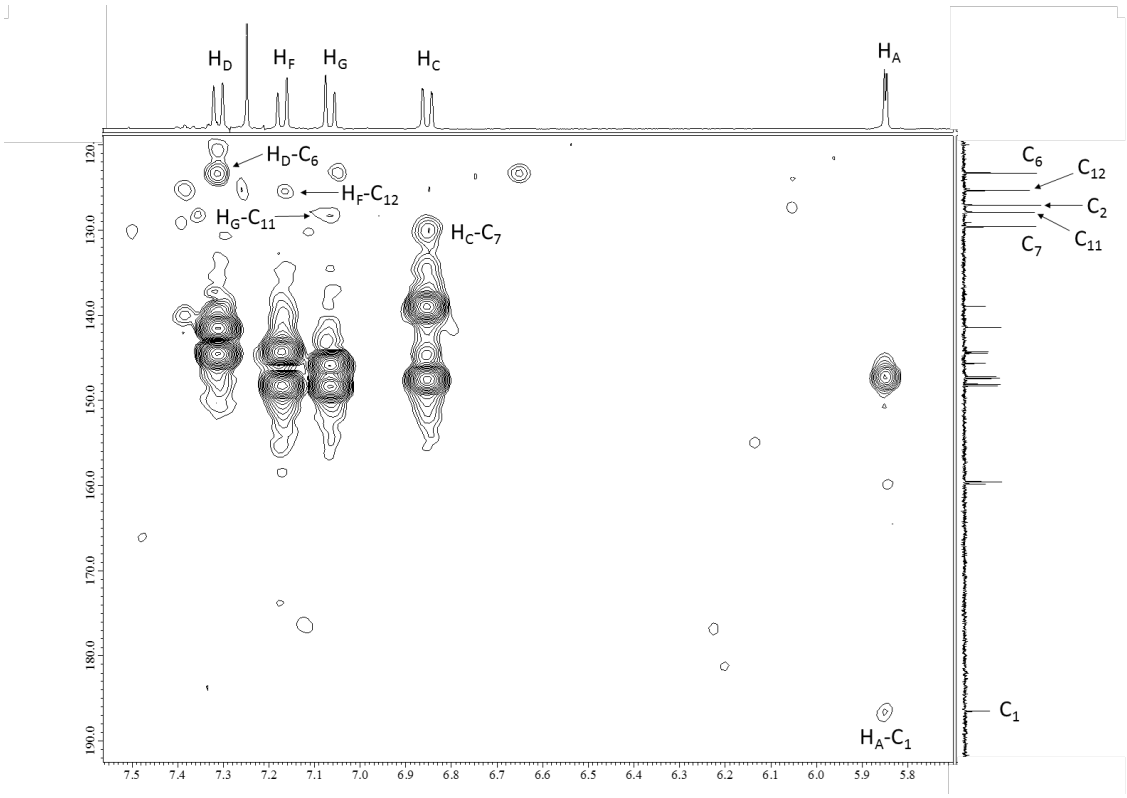

Figure S35. Enlarged area C of HMBC spectrum of methoxysumanenone **6** ($CDCl_3$)

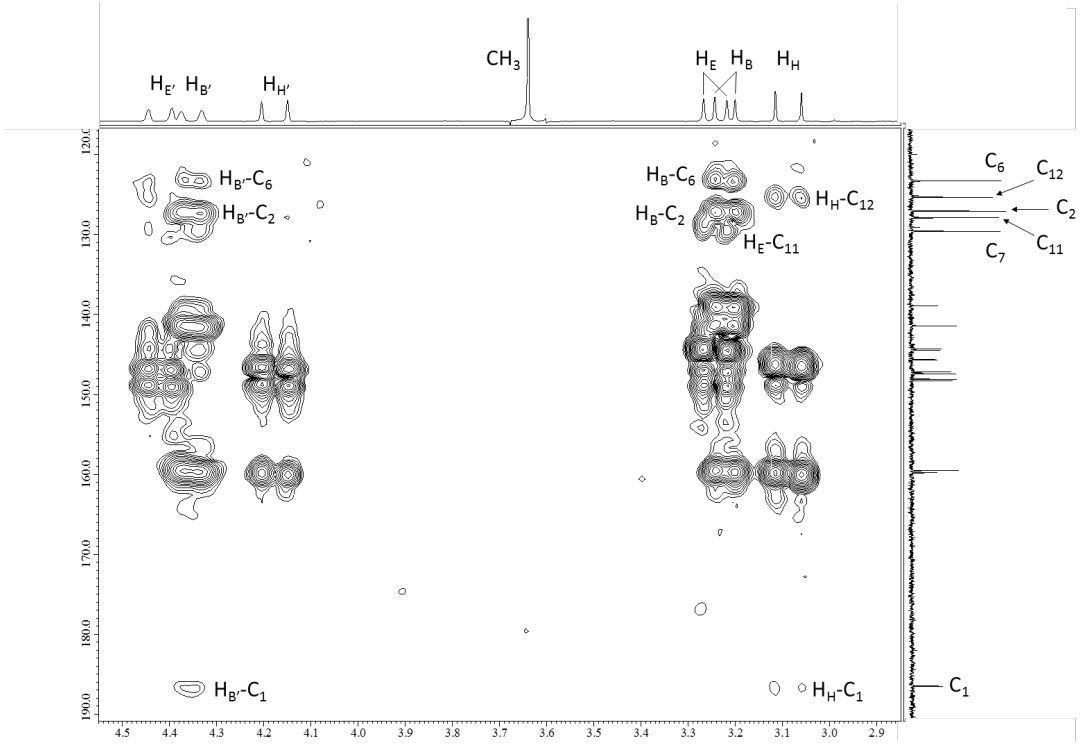

Figure S36. Enlarged area D of HMBC spectrum of methoxysumanenone **6** ($CDCl_3$)

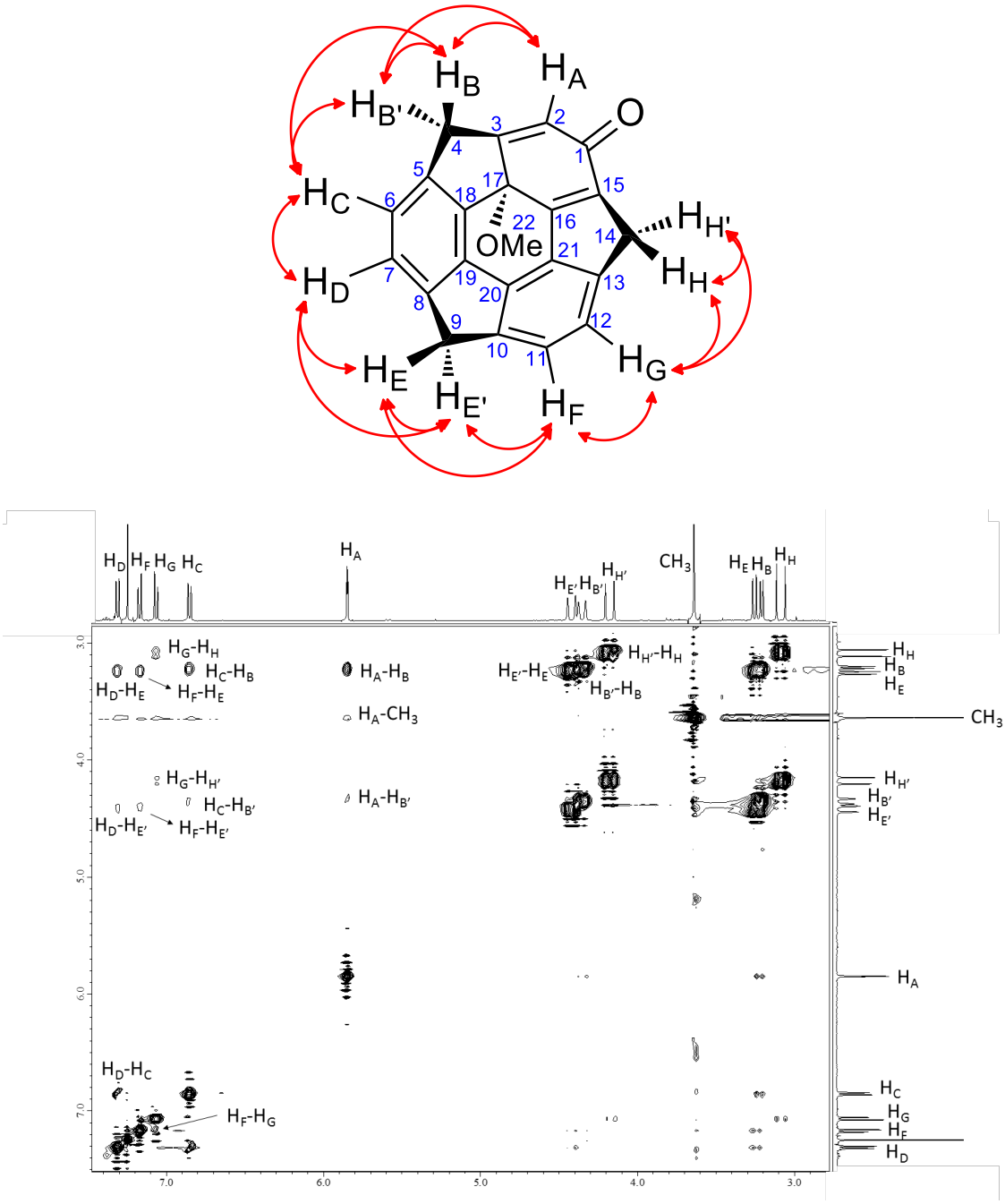

Figure S37. NOESY spectrum of methoxysumanenone **6** ($CDCl_3$)

6. Computational data

All the computational results were obtained by Gaussian09.[2]

3a [wb97xd/6-311++g(d,p)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-1.23751	1.39961	-0.88031
C	-2.08624	0.31152	-0.78182
C	-1.5844	-1.00794	-0.94677
C	-0.23572	-1.2039	-1.15947
C	0.61871	-0.08242	-1.12962
C	-2.35774	-1.93256	-0.24512
C	0.44122	-2.35698	-0.75706
C	0.92055	2.26868	-0.52671
C	-1.44533	2.57247	-0.14887
C	-3.20728	0.3096	0.04814
C	-0.10468	3.3461	-0.10934
H	-0.10345	4.18551	-0.81228
H	0.11347	3.74282	0.88347
C	-1.73156	-3.12766	0.0847
H	-2.2512	-3.88134	0.66736
C	-2.61157	2.62713	0.60039
H	-2.81964	3.48085	1.237
C	-3.4905	1.50423	0.69554
H	-4.31434	1.5723	1.39857
C	-3.59765	-1.1702	0.27746
H	-4.50732	-1.44069	-0.26897
H	-3.77491	-1.37618	1.33504
C	-0.34152	-3.34394	-0.17735
H	0.10635	-4.25178	0.21237
C	0.14952	1.17746	-1.07568
C	1.9531	-2.00502	-0.77878
H	2.37229	-2.16092	-1.77882
H	2.55457	-2.55228	-0.05717
C	1.88401	-0.4729	-0.49114
C	2.881	0.69814	-0.61422
O	4.05126	0.57104	-0.85191
Br	1.57095	-0.40237	1.5586
C	2.23651	2.05544	-0.32402
H	2.91339	2.79523	0.08779

E(RwB97XD) -3456.10027815 a.u.

Imaginary frequency 0

3b [wb97xd/6-311++g(d,p)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.90322	1.38103	0.9031
C	2.20558	1.02266	0.64913
C	2.55704	-0.36911	0.54483
C	1.60077	-1.34726	0.70899
C	0.22819	-1.00471	0.98707
C	3.64784	-0.53366	-0.29215
C	1.66683	-2.56364	0.04443
C	-1.32443	0.86601	0.77062
C	0.34861	2.54612	0.40221
C	3.05023	1.79623	-0.12946
C	0.2486	-3.15209	0.03693
C	-1.17568	2.34772	0.40351
H	0.15378	-4.05547	0.64852
H	-0.06397	-3.42159	-0.97543
H	-1.7052	3.00234	1.10476
H	-1.6022	2.53633	-0.5857
C	-1.99884	-1.65474	0.31826
C	3.81107	-1.80347	-0.85727
H	4.63137	-2.00468	-1.53909
C	1.21947	3.41649	-0.26365
H	0.85227	4.33844	-0.70278
C	2.5596	3.04547	-0.52677
H	3.15523	3.70261	-1.15206
C	4.18306	0.87481	-0.63295
H	5.13661	1.08364	-0.13631
H	4.34288	0.99166	-1.70734
C	2.83204	-2.81138	-0.68915
H	2.95019	-3.73452	-1.24681
O	-2.82813	-2.42132	-0.10479
C	-0.12027	0.38044	1.10862

C	-2.43034	-0.13431	0.62786
H	-3.41582	0.26259	0.75514
C	-0.59965	-1.99239	0.5785
Br	-1.63941	-2.61431	2.05506

E(RwB97XD) -3456.12419399 a.u.

Imaginary frequency 0

3c [wb97xd/6-311++g(d,p)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.40507	-1.40795	0.54436
C	-1.53295	-0.62319	0.55968
C	-1.44813	0.81198	0.70383
C	-0.20504	1.40539	0.73065
C	0.98981	0.59399	0.67025
C	-2.54021	1.41978	0.10725
C	0.02273	2.63933	0.13694
C	1.96536	1.2638	0.0425
C	1.80703	-1.62499	-0.10834
C	-0.35137	-2.56563	-0.20847
C	-2.6865	-0.95959	-0.13524
C	1.50993	2.70055	-0.22185
C	1.12054	-2.96445	-0.38245
H	2.07853	3.42116	0.37547
H	1.65535	2.97295	-1.27047
H	1.41838	-3.71867	0.35336
H	1.34796	-3.34826	-1.3781
C	3.06644	0.4878	-0.5823
C	-2.37152	2.73926	-0.32846
H	-3.18441	3.26908	-0.81477
C	-1.53125	-2.99027	-0.82803
H	-1.54202	-3.88886	-1.43591
C	-2.69608	-2.19639	-0.78256
H	-3.55882	-2.51494	-1.35904
C	-3.54133	0.31364	-0.27273
H	-4.41077	0.29492	0.39351
H	-3.91321	0.44349	-1.29169
C	-1.09727	3.34493	-0.31619
H	-0.98488	4.3116	-0.79609
O	4.04135	1.0007	-1.0913
C	0.95067	-0.88097	0.89882
C	2.81311	-0.99839	-0.7242
H	3.44833	-1.48832	-1.45576
Br	1.37619	-1.36408	2.69705

E(RwB97XD) -3456.12126011 a.u.

Imaginary frequency 0

3b [wb97xd/6-311g(d,p) nosymm freq scrf(pcm,solvent=Dichloromethane)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.65369	0.83332	-0.59262
C	4.17261	1.3056	0.57309
C	4.99146	1.17889	1.76826
C	4.69124	2.28104	2.6186
C	5.66494	2.80557	3.44309
C	5.69622	4.15775	3.79809
C	6.03345	0.26364	-0.69913
C	9.19586	3.07076	3.19735
C	6.97836	2.26821	3.39398
C	7.25563	1.20918	2.54619
C	6.22146	0.62107	1.77095
C	6.79514	-0.10123	0.61098
C	8.3322	0.21409	0.67562
C	9.47788	2.00407	2.29512
C	8.49778	1.09967	1.91612
C	3.07138	2.331	0.89058
C	3.66764	3.07862	2.09836
C	3.60955	4.39016	2.53795
C	4.62251	4.93044	3.3881
C	7.14169	4.47618	4.23237
C	7.91921	3.25148	3.70589
H	9.96859	3.81542	3.35831
H	8.62398	0.74861	-0.23179
H	8.9197	-0.70291	0.7139
H	10.44776	1.99748	1.80892
H	2.1363	1.82397	1.15317
H	2.87035	2.98767	0.0431

H	2.86584	5.07421	2.14268
H	4.59718	5.99698	3.5865
H	7.22973	4.57752	5.3194
H	7.50141	5.40495	3.78509
O	6.57765	0.14584	-1.76879
H	4.18122	1.03143	-1.54784
Br	6.45067	-2.05126	0.81126

E(RwB97XD) -3456.12289851 a.u.

Imaginary frequency 0

HBr [wb97xd/6-311g(d,p) scrf(pcm,solvent=Dichloromethane)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

Br	2.88991	-1.92039	1.68036
H	4.27098	-1.99096	1.32091

E(RwB97XD) -2574.78104753 a.u.

Imaginary frequency 0

INT1a [wb97xd/6-311g(d,p) scrf(pcm,solvent=Dichloromethane)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.66036	0.89052	-0.62428
C	4.18625	1.35995	0.55225
C	4.98858	1.2029	1.74972
C	4.68594	2.28789	2.62165
C	5.65896	2.79141	3.46126
C	5.69369	4.13653	3.84386
C	6.00395	0.28666	-0.72539
C	9.19089	3.0613	3.22431
C	6.97266	2.25415	3.40159
C	7.25321	1.21407	2.53001
C	6.21961	0.6466	1.7416
C	6.79143	-0.05251	0.56806
C	8.32562	0.28305	0.62247
C	9.47438	2.01837	2.29435
C	8.49399	1.12335	1.89392
C	3.09189	2.3867	0.87159
C	3.67181	3.10033	2.10694
C	3.61559	4.40333	2.57293
C	4.62415	4.92121	3.44271
C	7.13758	4.44402	4.28872
C	7.91323	3.23064	3.7365
H	9.96204	3.80333	3.40197
H	8.59703	0.86626	-0.2606
H	8.93061	-0.6228	0.60979
H	10.44208	2.02816	1.80465
H	2.14895	1.87849	1.10037
H	2.91231	3.0626	0.0353
H	2.88051	5.09909	2.18295
H	4.60292	5.98374	3.66065
H	7.22427	4.52205	5.37737
H	7.49975	5.38146	3.86328
O	6.54156	0.07898	-1.80244
H	4.17337	1.10815	-1.56757
H	5.7353	0.2942	-3.32258
Br	5.06912	0.47676	-4.61268
Br	6.47684	-2.01266	0.76503

E(RwB97XD) -6030.91434166 a.u.

Imaginary frequency 0

TS1a [wb97xd/6-311g(d,p) scrf(pcm,solvent=Dichloromethane)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.51498	0.56643	-0.45563
C	4.11801	1.16294	0.68656
C	5.02179	1.1368	1.80411
C	4.72851	2.18832	2.6835
C	5.7443	2.72171	3.4651
C	5.77258	4.07025	3.81148
C	5.89894	0.00081	-0.57957
C	9.27364	2.98693	3.18238
C	7.05992	2.18177	3.41721
C	7.3336	1.12999	2.56571
C	6.27799	0.57289	1.77205
C	6.8057	0.07646	0.58941
C	8.32552	0.17498	0.64617

C	9.54912	1.91527	2.2863
C	8.55748	1.0138	1.91659
C	3.02617	2.19311	1.02448
C	3.66978	2.96602	2.18937
C	3.62237	4.27933	2.62244
C	4.66995	4.82437	3.42883
C	7.22334	4.40777	4.21041
C	7.99787	3.17565	3.70104
H	10.04643	3.7337	3.32661
H	8.6999	0.66931	-0.2532
H	8.78309	-0.8177	0.6805
H	10.51319	1.90731	1.79029
H	2.10171	1.69525	1.3312
H	2.79599	2.83383	0.17353
H	2.86265	4.95986	2.25611
H	4.64176	5.89117	3.62361
H	7.32974	4.54146	5.29138
H	7.56893	5.32483	3.73073
O	6.48367	0.04617	-1.73934
H	5.83428	0.03648	-2.51777
Br	4.50967	0.01057	-4.09832
H	3.94964	0.60069	-1.38042
Br	5.79346	-2.16019	0.10691

E(RwB97XD) -6030.88804111 a.u.

Imaginary frequency 1

INT2a [wb97xd/6-311g(d,p) scrf(pcm,solvent=Dichloromethane)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.95437	0.34474	-0.74052
C	4.3957	1.03578	0.46147
C	5.18317	1.12167	1.5463
C	4.83109	2.28256	2.33753
C	5.78299	2.93716	3.0874
C	5.73415	4.30211	3.32382
C	6.24362	-0.54138	-0.48608
C	9.33986	3.35217	2.89785
C	7.15009	2.48283	3.08713
C	7.51391	1.39052	2.33895
C	6.54113	0.66563	1.5663
C	7.13615	0.00153	0.56683
C	8.65136	0.20452	0.65757
C	9.71669	2.2179	2.13878
C	8.77621	1.24262	1.78943
C	3.29466	2.1034	0.5689
C	3.77349	2.96067	1.75182
C	3.61613	4.30515	2.09884
C	4.58943	4.9708	2.88075
C	7.16029	4.75719	3.70919
C	8.01986	3.53166	3.32802
H	10.07828	4.13551	3.03506
H	9.0398	0.59701	-0.28637
H	9.1867	-0.72806	0.86466
H	10.72299	2.18904	1.73409
H	2.31085	1.65152	0.73887
H	3.22748	2.69686	-0.3457
H	2.81919	4.89952	1.66428
H	4.48624	6.04282	3.01344
H	7.24126	5.00022	4.77407
H	7.45969	5.64508	3.1474
H	4.23954	-0.23993	-1.31539
O	6.9473	-0.85308	-1.60674
Br	5.48735	1.80146	-2.027
H	6.35357	-1.13994	-2.30533
Br	5.38915	-2.29863	0.22721

E(RwB97XD) -6030.89461633 a.u.

Imaginary frequency 0

TS2a [wb97xd/6-311g(d,p) scrf=(solvent=dichloromethane,pcm)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.64151	-0.02996	-0.23722
C	0.4794	-0.94866	-0.06671
C	-0.67544	-0.45053	0.43068
C	-1.7869	-1.33621	0.1207
C	-3.05129	-0.8246	-0.07152

C	-3.9462	-1.39283	-0.97871
C	1.33145	1.47826	-0.04342
C	-4.34796	2.32828	-1.21624
C	-3.26901	0.60088	0.01203
C	-2.22646	1.45931	0.30497
C	-0.90753	0.94523	0.48045
C	0.03533	1.91122	0.19782
C	-0.69526	3.24273	-0.09755
C	-3.27914	3.21704	-0.90952
C	-2.16772	2.76645	-0.19843
C	0.21918	-2.37228	-0.60375
C	-1.33084	-2.44446	-0.58786
C	-2.25776	-3.11915	-1.38751
C	-3.56398	-2.59532	-1.58004
C	-4.9947	-0.30498	-1.35484
C	-4.3214	0.98959	-0.81204
H	-5.12569	2.68282	-1.88273
H	-0.35209	3.68052	-1.03782
H	-0.55362	3.96642	0.71177
H	-3.29153	4.20572	-1.35142
H	0.68497	-3.12178	0.04749
H	0.61234	-2.48839	-1.61642
H	-1.95497	-3.97285	-1.982
H	-4.20413	-3.07422	-2.31141
H	-5.96222	-0.48911	-0.8757
H	-5.13408	-0.25109	-2.43702
H	2.43852	-0.26934	0.47657
O	2.26168	2.37843	-0.33224
Br	2.42826	-0.24242	-2.05398
H	3.14757	1.997	-0.55215
Br	2.42377	0.85297	2.72001

E(RwB97XD) -6030.89218042 a.u.

Imaginary frequency 1

INT3a [wb97xd/6-311g(d,p) scrf=(solvent=dichloromethane,pcm)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.66805	-0.06366	-0.47692
C	0.62827	-0.97492	0.02953
C	-0.39964	-0.39749	0.69875
C	-1.4775	-1.33875	0.8644
C	-2.77679	-0.89238	0.9383
C	-3.84507	-1.63633	0.45512
C	1.2438	1.38139	-0.72376
C	-4.52844	1.95768	-0.32385
C	-3.05014	0.50845	0.81576
C	-2.02553	1.42492	0.65444
C	-0.68695	0.96987	0.55108
C	0.08381	1.87848	-0.16816
C	-0.79003	3.10823	-0.4671
C	-3.47889	2.89992	-0.49503
C	-2.18681	2.61014	-0.06539
C	0.32739	-2.46085	-0.14446
C	-1.14371	-2.55782	0.2981
C	-2.20932	-3.38754	-0.06082
C	-3.54936	-2.93128	0.02102
C	-5.00937	-0.65746	0.19662
C	-4.31157	0.71672	0.27863
H	-5.48091	2.18036	-0.79301
H	-0.74875	3.3841	-1.52228
H	-0.47445	3.9792	0.11442
H	-3.6834	3.78814	-1.08161
H	1.01132	-3.07156	0.45564
H	0.46002	-2.76468	-1.18592
H	-2.02885	-4.34541	-0.53618
H	-4.32432	-3.56664	-0.39353
H	-5.80784	-0.75809	0.93829
H	-5.45488	-0.82006	-0.78655
H	2.43698	0.05018	0.37794
O	2.02253	2.16441	-1.43138
Br	2.71786	-0.77499	-1.94995
H	2.70533	1.65421	-1.89336
Br	3.8626	0.26159	1.96423

E(RwB97XD) -6030.90286566 a.u.

Imaginary frequency 0

TS3a [wb97xd/6-311g(d,p) scrf=(solvent=dichloromethane,pcm)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.03343	-0.38151	1.06595
C	-1.12149	-1.32186	0.98204
C	-2.40521	-0.87325	0.77285
C	-2.64475	0.52929	0.60646
C	-1.60954	1.44483	0.68278
C	-0.28101	0.98773	0.87174
C	-3.75731	0.74523	-0.19264
C	-1.60858	2.63693	-0.04366
C	0.62904	1.90114	0.34793
C	1.11626	-0.9551	0.63347
C	-0.67172	-2.53646	0.49143
C	-3.3414	-1.61038	0.05993
C	-0.1575	3.13553	-0.12415
C	0.86064	-2.4387	0.38374
C	1.88269	1.40656	0.05602
C	-3.83628	1.99221	-0.81628
C	-1.63263	-3.36043	-0.1006
C	-2.95786	-2.90196	-0.31078
C	-4.42032	-0.62657	-0.43878
C	-2.77461	2.93358	-0.74392
O	2.79793	2.19426	-0.45593
C	2.24205	-0.04162	0.37637
Br	3.58967	-0.74184	-0.83669
H	0.02276	4.00044	0.52068
H	0.11455	3.42095	-1.14178
H	1.39601	-3.0564	1.11364
H	1.21881	-2.73331	-0.606
H	-4.66242	2.2213	-1.48114
H	-1.35236	-4.31431	-0.53372
H	-3.62293	-3.53171	-0.89146
H	-5.36224	-0.73219	0.10839
H	-4.63901	-0.77909	-1.49733
H	-2.84513	3.82758	-1.3527
H	2.85667	0.24313	1.49976
H	3.56542	1.68679	-0.76141
Br	3.18232	1.96198	2.39512

E(RwB97XD) -6030.90186843 a.u.

Imaginary frequency 1

***o*-Bromohydroxysumanene (4)**

[wb97xd/6-311g(d,p), scrf(pcm,solvent=Dichloromethane)]

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	4.76152	0.01599	-0.3372
C	4.23947	0.83009	0.66418
C	5.03738	0.96125	1.80433
C	4.71274	2.17126	2.50113
C	5.67832	2.81483	3.25946
C	5.69047	4.2024	3.43305
C	6.0945	-0.53274	-0.29088
C	9.2571	3.02087	3.16276
C	7.0068	2.28055	3.32677
C	7.32687	1.11942	2.6394
C	6.32641	0.45156	1.85941
C	6.91546	-0.25613	0.81182
C	8.45163	-0.19405	1.00882
C	9.58643	1.82445	2.45053
C	8.60332	0.88484	2.11805
C	3.15918	1.93969	0.72078
C	3.68513	2.86482	1.85487
C	3.59911	4.23501	2.1266
C	4.59411	4.8995	2.91189
C	7.13549	4.5911	3.85693
C	7.94108	3.29598	3.55294
H	10.04013	3.76732	3.27736
H	8.95733	0.09885	0.08211
H	8.8747	-1.16435	1.30325
H	10.59958	1.73191	2.06571
H	2.16125	1.53232	0.93386
H	3.0867	2.46339	-0.23888
H	2.84589	4.8533	1.64324
H	4.53771	5.98362	2.98019
H	7.19345	4.87542	4.91712

H	7.50975	5.44476	3.28097
O	6.62441	-1.21343	-1.34016
H	5.97543	-1.22063	-2.06833
Br	3.78081	-0.21514	-1.98036

E(RwB97XD) -3456.13461435 a.u.

Imaginary frequency 0

TD-DFT Calculations

TD-DFT Calculation of **1**

b3lyp/6-311+g(d,p)

(68,69: degenerated HOMO, 70,71: degenerated LUMO)

Excited State 1: energy = 3.8272 eV=323.95 nm, oscillator strength=0.0004

68 -> 71 -0.49528

69 -> 72 0.49574

Excited State 2: energy = 3.9927 eV=310.53 nm, oscillator strength=0.0000

68 -> 72 0.49670

69 -> 71 0.49915

Excited State 3: energy = 4.0203 eV=308.39 nm, oscillator strength=0.0011

67 -> 71 0.17558

69 -> 70 0.67713

Excited State 4: energy = 4.0217 eV=308.29 nm, oscillator strength=0.0012

67 -> 72 0.17562

68 -> 70 0.67712

Excited State 5: energy = 4.4537 eV=278.38 nm, oscillator strength=0.3308

68 -> 71 0.47732

69 -> 72 0.47643

Excited State 6: energy = 4.4538 eV=278.38 nm, oscillator strength=0.3309

68 -> 72 0.47828

69 -> 71 -0.47589

Excited State 7: energy = 4.7771 eV=259.54 nm, oscillator strength=0.0000

67 -> 70 0.69985

Excited State 8: energy = 4.8117 eV=257.67 nm, oscillator strength=0.0722

67 -> 71 0.65427

69 -> 70 -0.17991

Excited State 9: energy = 4.8126 eV=257.63 nm, oscillator strength=0.0721

67 -> 72 0.65408

68 -> 70 -0.18220

Excited State 10: energy = 5.1101 eV=242.63 nm, oscillator strength=0.0319

67 -> 71 -0.13422

68 -> 73 0.45578

68 -> 74 0.11574

69 -> 73 -0.11704

69 -> 74 0.46056

Excited State 11: energy = 5.1103 eV=242.62 nm, oscillator strength=0.0319

67 -> 72 -0.13439

68 -> 73 0.11534

68 -> 74 -0.45395

69 -> 73 0.46223

69 -> 74 0.11740

Excited State 12: energy = 5.1994 eV=238.46 nm, oscillator strength=0.0000

65 -> 71 -0.10345

66 -> 72 -0.10506

68 -> 73 -0.13412

68 -> 74 0.46838

69 -> 73 0.46018

69 -> 74 0.13197

Excited State 13: energy = 5.2409 eV=236.57 nm, oscillator strength=0.0103

65 -> 72 -0.18982

66 -> 71 0.18907

68 -> 73 0.43314

68 -> 74 0.12422

69 -> 74 -0.42821

Excited State 14: energy = 5.2884 eV=234.44 nm, oscillator strength=0.0000

69 -> 75 0.69584

Excited State 15: energy = 5.2900 eV=234.37 nm, oscillator strength=0.0000
68 -> 75 0.69578

Excited State 16: energy = 5.5243 eV=224.43 nm, oscillator strength=0.0041
68 -> 77 -0.40624
69 -> 76 0.56506

Excited State 17: energy = 5.5309 eV=224.17 nm, oscillator strength=0.0006
68 -> 76 -0.43985
69 -> 77 0.53548

Excited State 18: energy = 5.5312 eV=224.15 nm, oscillator strength=0.0007
68 -> 77 0.56308
69 -> 76 0.40413

Excited State 19: energy = 5.5352 eV=223.99 nm, oscillator strength=0.0000
67 -> 75 0.17679
68 -> 76 0.52642
69 -> 77 0.42955

Excited State 20: energy = 5.7400 eV=216.00 nm, oscillator strength=0.0330
65 -> 71 0.11468
66 -> 70 0.49174
66 -> 72 -0.10283
67 -> 73 -0.21950
67 -> 74 0.34230

TD-DFT Calculation of **3b**
b3lyp/6-311+g(d,p)
(90: HOMO, 91: LUMO)
Excited State 1: energy = 2.5417 eV=487.79 nm, oscillator strength=0.0390
88 -> 91 -0.10468
90 -> 91 0.69133

Excited State 2: energy = 3.0044 eV=412.67 nm, oscillator strength=0.0271
89 -> 91 0.69196
90 -> 92 0.12686

Excited State 3: energy = 3.2444 eV=382.15 nm, oscillator strength=0.0067
88 -> 91 0.67278
90 -> 91 0.11202

Excited State 4: energy = 3.7947 eV=326.73 nm, oscillator strength=0.0251
87 -> 91 -0.20222
90 -> 92 0.63003

Excited State 5: energy = 3.9266 eV=315.75 nm, oscillator strength=0.0432
86 -> 91 0.25737
87 -> 91 0.53142
90 -> 93 -0.20656

Excited State 6: energy = 4.0582 eV=305.51 nm, oscillator strength=0.0054
86 -> 91 0.58069
90 -> 94 0.23053

Excited State 7: energy = 4.1314 eV=300.10 nm, oscillator strength=0.0144
85 -> 91 0.53495
90 -> 93 -0.36525

Excited State 8: energy = 4.1844 eV=296.30 nm, oscillator strength=0.0103
85 -> 91 0.33664
90 -> 93 0.42587

Excited State 9: energy = 4.3330 eV=286.14 nm, oscillator strength=0.1625
87 -> 91 0.30591
90 -> 94 0.51860

Excited State 10: energy = 4.4575 eV=278.15 nm, oscillator strength=0.1188
89 -> 92 0.51089

Excited State 11: energy = 4.5290 eV=273.76 nm, oscillator strength=0.0271
84 -> 91 0.57147
89 -> 93 -0.22894

Excited State 12: energy = 4.6252 eV=268.06 nm, oscillator strength=0.0614
89 -> 92 0.20835
89 -> 93 0.22947
89 -> 94 0.37003

Excited State 13: energy = 4.7825 eV=259.24 nm, oscillator strength=0.1690
89 -> 93 0.45451
89 -> 94 -0.38901
90 -> 92 0.17022

Excited State 14: energy = 4.8476 eV=255.76 nm, oscillator strength=0.1583
83 -> 91 0.45781
89 -> 92 0.19845
89 -> 93 0.18795

Excited State 15: energy = 5.0093 eV=247.51 nm, oscillator strength=0.0954
90 -> 95 0.56012

Excited State 16: energy = 5.0906 eV=243.55 nm, oscillator strength=0.0047
88 -> 92 0.64604
90 -> 96 0.23370

Excited State 17: energy = 5.1442 eV=241.02 nm, oscillator strength=0.0002
88 -> 92 -0.23049
90 -> 96 0.58715

Excited State 18: energy = 5.1786 eV=239.42 nm, oscillator strength=0.0113
88 -> 93 0.56102
90 -> 96 0.20295

Excited State 19: energy = 5.2235 eV=237.36 nm, oscillator strength=0.0017
90 -> 97 0.68587

Excited State 20: energy = 5.3134 eV=233.34 nm, oscillator strength=0.0453
87 -> 92 0.53257
89 -> 95 -0.34811

TD-DFT Calculation of **5**
b3lyp/6-311+g(d,p)
(77: HOMO, 78: LUMO)

Excited State 1: energy = 2.7744 eV=446.89 nm, oscillator strength=0.0266
74 -> 78 -0.12359
77 -> 78 0.69125

Excited State 2: energy = 3.1201 eV=397.37 nm, oscillator strength=0.0055
74 -> 78 0.49242
75 -> 78 -0.37338
76 -> 78 0.29462
77 -> 78 0.10446

Excited State 3: energy = 3.4026 eV=364.39 nm, oscillator strength=0.0658
74 -> 78 -0.17693
75 -> 78 0.23855
76 -> 78 0.61296
77 -> 79 0.13176

Excited State 4: energy = 3.7616 eV=329.61 nm, oscillator strength=0.0456
74 -> 78 0.43003
75 -> 78 0.52837
77 -> 79 0.10092

Excited State 5: energy = 4.1617 eV=297.92 nm, oscillator strength=0.0662
73 -> 78 0.19732
76 -> 80 -0.12774
77 -> 79 0.60645
77 -> 80 -0.16305

Excited State 6: energy = 4.3222 eV=286.85 nm, oscillator strength=0.0283
71 -> 78 -0.29033
73 -> 78 0.59277
77 -> 79 -0.18733

Excited State 7: energy = 4.5222 eV=274.17 nm, oscillator strength=0.0516
71 -> 78 -0.34977
73 -> 78 -0.11966
75 -> 79 0.11209
77 -> 79 0.14351
77 -> 80 0.53641

Excited State 8: Singlet-A 4.5369 eV 273.28 nm f=0.0116
70 -> 78 -0.11419
71 -> 78 0.45119
72 -> 78 0.32368
73 -> 78 0.17255

75 -> 79 0.11198
77 -> 80 0.29883

Excited State 9: energy = 4.6303 eV=267.77 nm, oscillator strength=0.0538
71 -> 78 0.12799
76 -> 79 0.55850
77 -> 79 0.12251
77 -> 80 0.15747
77 -> 81 0.28757

Excited State 10: energy = 4.6946 eV=264.10 nm, oscillator satrength=0.0530
71 -> 78 -0.16654
72 -> 78 0.56621
73 -> 78 -0.14039
77 -> 81 0.28219

Excited State 11: energy = 4.9115 eV=252.44 nm, oscillator strength=0.1021
72 -> 78 -0.11708
74 -> 79 -0.12562
75 -> 79 -0.16879
76 -> 79 -0.34117
76 -> 80 0.33139
77 -> 80 0.17346
77 -> 81 0.37360

Excited State 12: energy = 4.9634 eV=249.80 nm, oscillator sctrength=0.0198
75 -> 79 0.34544
76 -> 79 0.11987
76 -> 80 0.52841
77 -> 79 0.11276
77 -> 80 -0.10882
77 -> 81 -0.11736

Excited State 13: energy = 5.1450 eV=240.98 nm, oscillator=0.0014
74 -> 79 0.52408
74 -> 80 -0.25269
75 -> 79 -0.19889
75 -> 80 0.22552
76 -> 80 0.12634
76 -> 81 -0.16487

Excited State 14: energy = 5.2480 eV=236.25 nm, oscillator strength=0.0111
74 -> 79 0.27354
74 -> 80 0.41635
75 -> 79 -0.29135
75 -> 80 -0.35829

Excited State 15: energy = 5.2591 eV=235.75 nm, oscillator sctrength=0.0300
70 -> 78 0.40086
74 -> 80 -0.17621
76 -> 81 0.40231
77 -> 82 -0.25793
77 -> 83 0.14097

Excited State 16: energy 5.2750 eV=235.04 nm, oscillator strength=0.1804
70 -> 78 0.32629
74 -> 79 0.16225
74 -> 80 0.16349
75 -> 79 0.32860
76 -> 80 -0.17061
76 -> 81 -0.15835
77 -> 81 0.27434
77 -> 83 -0.21503

Excited State 17: energy = 5.3525 eV=231.64 nm, oscillator strength=0.0818
69 -> 78 0.10949
70 -> 78 0.28099
74 -> 79 -0.22627
74 -> 80 0.21280
75 -> 79 -0.20124
75 -> 80 0.31217
76 -> 79 0.10774
76 -> 81 -0.21671
77 -> 81 -0.14293
77 -> 86 -0.15534

Excited State 18: energy = 5.3768 eV=230.59 nm, oscillator strength=0.0191
70 -> 78 0.13395
75 -> 79 0.11481
77 -> 82 0.36766
77 -> 83 0.53885

Excited State 19: energy = 5.4085 eV=229.24 nm, oscillator strength=0.0219

69 -> 78 -0.11963
74 -> 80 0.10096
75 -> 80 0.21217
76 -> 81 0.41006
77 -> 82 0.37663
77 -> 83 -0.25632

Excited State 20: energy = 5.4563 eV=227.23 nm, oscillator strength=0.0055

69 -> 78 0.64184
75 -> 80 -0.13866
77 -> 82 0.16765

TD-DFT Calculation of **6**

b3lyp/6-311+g(d,p)

(81: HOMO, 82: LUMO)

Excited State 1: energy = 2.7707 eV=447.48 nm, oscillator strength=0.0247

78 -> 82 -0.13270
81 -> 82 0.68888

Excited State 2: energy = 3.1115 eV=398.47 nm, oscillator strength=0.0062

78 -> 82 0.47274
79 -> 82 0.36049
80 -> 82 -0.32419
81 -> 82 0.11904

Excited State 3: energy = 3.4169 eV=362.85 nm, oscillator strength=0.0669

78 -> 82 0.19845
79 -> 82 0.25505
80 -> 82 0.59761
81 -> 83 -0.13731

Excited State 4: energy = 3.7456 eV=331.01 nm, oscillator strength=0.0469

78 -> 82 -0.44255
79 -> 82 0.51571

Excited State 5: energy = 3.9484 eV=314.01 nm, oscillator strength=0.0026

76 -> 82 -0.16147
77 -> 82 0.66636
79 -> 82 0.12154

Excited State 6: energy = 4.1595 eV=298.07 nm, oscillator strength=0.0723

76 -> 82 0.12515
80 -> 82 0.10842
80 -> 83 0.10078
80 -> 84 -0.13363
81 -> 83 0.62341
81 -> 84 0.16134

Excited State 7: energy = 4.4266 eV=280.09 nm, oscillator strength=0.0271

75 -> 82 -0.13692
76 -> 82 0.62861
77 -> 82 0.13909
81 -> 83 -0.15127
81 -> 84 0.10749

Excited State 8: energy = 4.5300 eV=273.69 nm, oscillator strength=0.0557

75 -> 82 0.20814
79 -> 83 0.15282
81 -> 83 -0.10169
81 -> 84 0.60742
81 -> 85 0.13127

Excited State 9: energy = 4.6219 eV=268.26 nm, oscillator strength=0.0528

75 -> 82 -0.16356
80 -> 83 0.56696
81 -> 83 -0.12611
81 -> 84 0.14262
81 -> 85 -0.26613

Excited State 10: energy = 4.6981 eV=263.90 nm, oscillator strength=0.0454

75 -> 82 0.58235
76 -> 82 0.10043
81 -> 85 -0.30360

Excited State 11: energy = 4.9119 eV=252.42 nm, oscillator strength=0.0982

75 -> 82 0.12311
78 -> 83 -0.18640
79 -> 83 0.18061
80 -> 83 0.34714
80 -> 84 0.28473
81 -> 84 -0.19140

81 -> 85 0.36690

Excited State 12: energy = 4.9555 eV=250.20 nm, oscillator strength=0.0189
78 -> 84 -0.10043
79 -> 83 -0.33858
80 -> 84 0.54340
81 -> 83 0.11783

Excited State 13: energy = 5.1120 eV=242.53 nm, oscillator strength=0.0027
78 -> 83 0.55798
78 -> 84 0.19332
79 -> 83 0.22387
79 -> 84 0.15259
80 -> 84 0.16109
80 -> 85 0.14408

Excited State 14: energy = 5.1757 eV=239.55 nm, oscillator strength=0.0002
81 -> 86 0.69476

Excited State 15: energy = 5.2076 eV=238.08 nm, oscillator strength=0.0056
73 -> 82 0.46996
74 -> 82 0.10948
78 -> 83 -0.20821
78 -> 84 0.36224
79 -> 83 -0.12510
79 -> 84 0.20522

Excited State 16: energy = 5.2242 eV=237.33 nm, oscillator strength=0.0242
73 -> 82 0.37062
74 -> 82 0.28997
78 -> 84 -0.32117
79 -> 83 0.19509
79 -> 84 -0.27411
80 -> 85 -0.13437

Excited State 17: energy = 5.2636 eV=235.55 nm, oscillator strength=0.0109
73 -> 82 -0.31552
74 -> 82 0.35771
78 -> 84 0.19122
80 -> 85 -0.31323
81 -> 87 0.27765

Excited State 18: energy = 5.2791 eV=234.86 nm, oscillator strength=0.2006
74 -> 82 -0.28295
78 -> 83 -0.11243
78 -> 84 0.13514
79 -> 83 0.37698
80 -> 84 0.16957
80 -> 85 -0.20082
81 -> 85 -0.31525

Excited State 19: energy = 5.3483 eV=231.82 nm, oscillator strength=0.0816
73 -> 82 -0.14082
74 -> 82 0.26792
78 -> 83 -0.18762
78 -> 84 -0.18922
79 -> 83 0.17614
79 -> 84 0.39685
80 -> 85 0.18022
81 -> 85 -0.12774
81 -> 92 0.15320

Excited State 20: energy = 5.3982 eV=229.68 nm, oscillator strength=0.0237
79 -> 84 -0.13494
80 -> 84 -0.10013
80 -> 85 0.44315
81 -> 87 0.46805

7. References

1. Y. L. Chow, D. C. Zhao and C. I. Johansson, *Can. J. Chem.*, 1988, **66**, 2556-2564.
2. DOI: 10.1021/acs.joc.6b02046
3. CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
4. G.M. Sheldrick, University of Gottingen, Germany, 1996.
5. G.M. Sheldrick, *Acta Cryst.,* 2015, **C71**, 3-8.
6. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst*., 2009, **42**, 339-341.