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Electronic Supplementary Information

Selective oxidative conversion of triaryldihydro[$C_{59}N$]fullerenes: a model case for carbon allotrope oxygenation

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1 General Methods

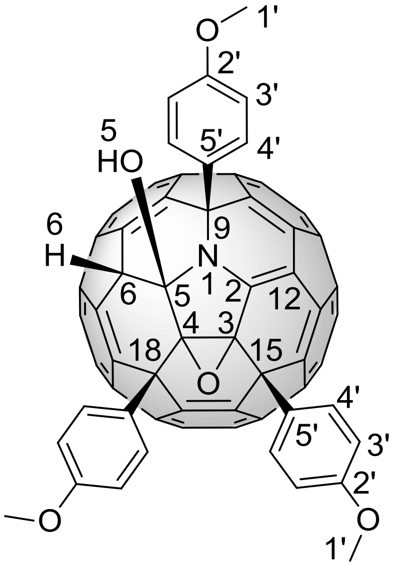
Ketolactam and dihydrotris(4'-methoxyphenyl)azafullerene derivatives were prepared as reported previously.[1, 2] All reagents and solvents were purchased from commercial sources (Aldrich, Acros, $CDCl_3$ and ODCB-d_4 from Deutero). C_{60} (99%) was provided by *io li tec* nanomaterials. Reactions were monitored by thin layer chromatograpy (TLC) on silica $60F_{254}$ TLC aluminium foils (Merck). Products were isolated by column chromatograpy using silica gel (deactivated, 0.04-0.063 mm/230-400 mesh ASTM, Macherey-Nagel).The NMR chemical shifts (δ)are reported in parts per million (ppm) with reference to residual proton and carbon signals of $CDCl_3$ (δ = 7.24 ppm in ^{1}H, 77.00 ppm in ^{13}C), and 1,2-dichlorobenzene-d_4 (ODCB-d_4) (δ = 132.60 ppm in ^{13}C).^{1}H NMR coupling constants (J) are reported in hertz (Hz), and multiplicity is indicated as follows: br (broadened), s (singlet), d (doublet).

All ^{13}C NMR spectra were measured with pulse delay times of 8s. IR spectra were recorded with a Bruker Tensor 27 or a Varian 660 FT-IR-spectrometer on a ZnSe window. The signals are labeled with the following abbreviations: vs (very strong), s (strong), m (medium), w (weak), vw (very weak**).** UV/Vis spectra were recorded with a Cary 5000 UV-Vis-NIR spectrophotometer. MALDI-TOF mass spectra were recorded with a Shimadzu AXIMA Confidence spectrometer. High resolution mass spectra were measured on an UHR-TOF Bruker maXis 4G spectrometer using atmospheric pressure photo ionization (APPI) or electrospray ionization (ESI).

2 Synthesis and Characterization

Oxygenation product **5**:

The mixture of the four isomers of dihydrotris(4'-methoxyphenyl)azafullerene adducts (14 mg, 13.4 µmol) was dissolved in 2 mL air saturated $CDCl_3$. The solution was filled into a NMR tube and irradiated with a 500 W lamp using an aqueous dichromate solution filter and water cooling. The color of the solution already changed after 2 min of irradiation from orange to green. The reaction was monitored by TLC and ^{1}H NMR spectroscopy. Photooxidation was stopped after 15 min when the TLC showed the formation of green main product **5** (R_f = 0.48 in toluene/ethyl acetate (9:1)). The reaction mixture was purified by subsequent column chromatography on silica gel (50 g, toluene) and compound **5** (5.2 mg; 4.2 µmol; 36%) was obtained as green solid after precipitation form CS_2/pentane and drying in vacuum.



^{1}H NMR [400 MHz, $CDCl_3$, RT]: δ (ppm) = 7.83 (d, ^3J = 8.8 Hz, 2 H, **4'**), 7.79 (d, ^3J = 8.8 Hz, 2 H, **4''**), 7.78 (d, ^3J = 8.8 Hz, 2 H, **4''**), 7.03 (d, ^3J = 8.8 Hz, 2 H, **3'**), 6.96 (d, ^3J = 8.8 Hz, 4 H, **3''**), 5.61 (d, ^4J = 1.3 Hz, 1 H, **6**), 4.12 (d, ^4J = 1.3 Hz, 1 H, **7**), 3.86 (s, 3 H, **1'**), 3.82 (s, 3 H, **1''**), 3.81 (s, 3 H, **1''**).

^{13}C NMR [100 MHz, $CDCl_3$, RT]: δ (ppm) = 160.19 (1 C, **2**), 160.01 (1 C, **2'**), 159.42 (1 C, **2''**), 159.39 (1 C, **2''**), 150.93 (1 C), 150.89 (1 C), 150.87 (1 C), 150.70 (1 C), 149.94 (1 C), 149.75 (1 C), 149.57 (1 C), 149.53 (1 C), 149.47 (1 C), 148.62 (1 C), 148.59 (1 C), 148.57 (1 C), 148.24 (1 C), 148.18 (1 C), 147.98 (1 C), 147.95 (1 C), 147.72 (1 C), 147.61 (1 C), 147.55 (1 C), 147.53 (1 C), 147.17 (1 C), 146.99 (1 C), 146.95 (1 C), 146.92 (1 C), 146.88 (1 C), 146.65 (1 C), 146.48 (1 C), 146.46 (2 C), 145.13 (1 C), 144.99 (1 C), 144.91 (1 C), 144.79 (1 C), 144.39 (2 C), 144.12 (1 C), 144.02 (1 C), 143.68 (1 C), 143.28 (1 C), 142.98 (1 C), 142.58 (1 C), 142.40 (1 C), 142.31 (1 C), 142.04 (1 C), 141.89 (1 C), 141.75 (1 C), 141.22 (1 C), 140.79 (1 C), 140.35 (1 C), 131.82 (1 C, **5'**), 131.69 (1 C, **5''**), 130.66 (1 C, **5''**), 129.11 (2 C, **4'**), 129.03 (2 C, **4'**), 128.98 (2 C, **4'**), 114.57 (2 C, **3'**), 114.43 (2 C, **3'**), 114.37 (2 C, **3'**), 109.34 (1 C, **12**), 91.95 (1 C, **5**), 77.51 (1 C, *epoxy*-C), 75.22(1 C, *epoxy*-C), 74.07 (1 C, **9**), 58.11 (1 C, *sp*^{3}-C), 55.83 (1 C, *sp*^{3}-C), 55.43 (1 C, **1'**), 55.38 (1 C, **1'**), 55.36 (1 C, **1'**), 51.50 (1 C, **6**).

A ^{13}C NMR spectrum in ODCB-d_4 was additionally measured to clarify the existence of the signal at 77.51 ppm (in $CDCl_3$).

^{13}C NMR [100 MHz, ODCB-d_4, RT]: δ (ppm) = 160.58 (1 C, **2**), 160.35 (1 C, **2’**), 159.76 (1 C, **2’**), 159.69 (1 C, **2’**), 151.37 (1 C), 151.35 (1 C), 151.14 (1 C), 151.11 (1 C), 150.10 (1 C), 150.07 (1 C), 149.93 (1 C), 149.76 (1 C), 149.62 (1 C), 149.00 (1 C), 148.77 (1 C), 148.75 (1 C), 148.40 (2 C), 148.14 (1 C), 148.10 (1 C), 147.90 (1 C), 147.77 (2 C), 147.72 (1 C), 147.69 (1 C), 147.36 (1 C), 147.18 (1 C), 147.11 (2 C), 147.07 (1 C), 146.81 (1 C), 146.64 (2 C), 146.61 (1 C), 145.46 (1 C), 145.20 (1 C), 145.18 (1 C), 145.03 (1 C), 144.74 (1 C), 144.66 (1 C), 144.27 (1 C), 144.24 (1 C), 143.84 (1 C), 143.55 (1 C), 143.21 (1 C), 142.73 (1 C), 142.65 (1 C), 142.63 (1 C), 142.18 (1 C), 142.13 (1 C), 142.07 (1 C), 141.43 (1 C), 141-03 (1 C), 140.83 (1 C), 114.77 (2 C, **3’**), 114.70 (2 C, **3’**), 114.67 (2 C, **3’**), 109.75 (1 C, **12**), 92.31 (1 C, **5**), 77.86 (1 C, *epoxy*-C), 75.66(1 C, *epoxy*-C), 74.52 (1 C, **9**), 58.64 (1 C, sp^3-C), 56.20 (1 C, sp^3-C), 55.20 (1 C, **1’**), 55.09 (1 C, **1’**), 55.04 (1 C, **1’**), 51.86 (1 C, **6**). Signals between 126 and 134 ppm overlapped with those of the solvent.

FT-IR (ZnSe) ν (cm^{-1}): 3495 (w), 2997 (vw), 2950 (w), 2927 (w), 2902 (vw), 2832 (w), 1606 (m), 1552 (w), 1510 (vs), 1460 (m), 1439 (w), 1417 (w), 1383 (m), 1359 (w), 1300 (m), 1253 (s), 1179 (s), 1133 (vw), 1116 (vw), 1060 (m), 1034 (s), 1019 (m), 963 (w), 948 (w), 920 (w), 909 (w), 879 (m), 798 (m), 767 (w), 737 (vw), 701 (w), 649 (m), 622 (w), 598 (vw), 589 (vw), 571 (w), 557 (w), 546 (w), 535 (w).

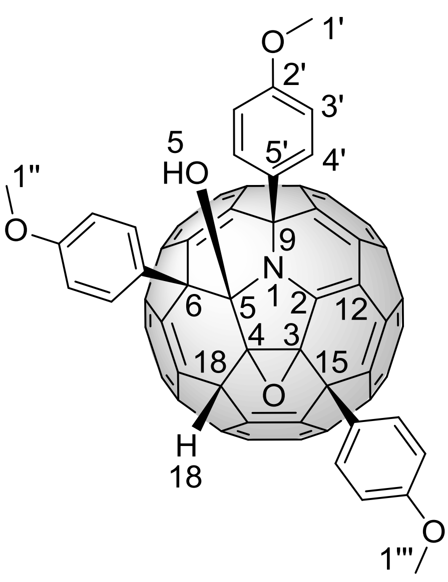
UV/Vis (CH_2Cl_2) λ_{max} (nm): 254, 374, 395, 440, 580, 627.

MALDI-TOF MS (matrix: dctb, CH_2Cl_2): *m/z* (% Int.)= 1077 (100) $[M]^{+\cdot}$, 996 (15) $[C_{59}NH_3OHO-(C_6H_4OCH_3)+Na]^+$, 954 (15) $[M-(C_6H_4OCH_3)-O]^+$.

HRMS (APPI; toluene/ACN): *m/z* calcd for $C_{80}H_{23}NO_5^{+\cdot}$ $[M]^{+\cdot}$: 1077.157074, found: 1077.156145.

Oxygenation product **8**:

Pure isomer **1** (6.1 mg, 5.8 µmol) was dissolved in 2 mL oxygen saturated $CS_2/CDCl_3$. The solution was filled into a NMR tube and irradiated with a 500 W lamp using an aqueous dichromate solution filter and water cooling. The reaction was monitored by TLC and ^{1}H NMR spectroscopy. After 10 min of irradiation the starting material was completely converted to an orange compound (R_f = 0.22 in toluene/ethyl acetate (9:1)) and partly to a green compound **8** (R_f = 0.43 in toluene/ethyl acetate (9:1)). The orange solution was stored in the dark. The color of the reaction mixture slowly turned green overnight and compound **9** was detected with 100% conversion. The solvent was evaporated and compound **9** (4.4 mg; 4.1 µmol; 70%) was isolated as a green solid.



^{1}H NMR [400 MHz, $CDCl_3/CS_2$, RT]: δ (ppm) = 7.85 (d, ^3J = 8.8 Hz, 2 H, **4’’’**), 7.76 (d, ^3J = 8.8 Hz, 2 H, **4’**), 7.47 (d, ^3J = 8.8 Hz, 2 H, **4’’**), 7.03 (d, ^3J = 8.8 Hz, 2 H, **3’’’**), 6.96 (d, ^3J = 8.8 Hz, 2 H, **3’’**), 6.83 (d, ^3J = 8.8 Hz, 2 H, **3’**), 5.33 (s, 1 H, **18**), 4.20 (s, 1 H, **5**), 3.87 (s, 3 H, **1’’’**), 3.83 (s, 3 H, **1’**), 3.76 (s, 3 H, **1’’**).

^{13}C NMR [100 MHz, $CDCl_3/CS_2$ RT]: δ (ppm) = 159.75 (1 C, **2’**), 159.43 (1 C, **2’’’**), 159.11 (1 C, **2**), 158.72 (1 C, **2’’**), 151.04 (1 C), 150.86 (1 C), 150.53 (1 C), 150.37 (1 C), 150.06 (1 C), 149.91 (1 C), 149.79 (1 C), 149.450(1 C), 149.44 (1 C), 148.58 (1 C), 148.42 (1 C), 148.14 (1 C), 147.93 (1 C), 147.90 (1 C), 147.87 (2 C), 147.60 (1 C), 147.59 (1 C), 147.45 (2 C), 147.17 (1 C), 146.87 (2 C), 146.81 (1 C), 146.58 (2 C), 146.48 (1 C), 146.35 (1 C), 146.24 (1 C), 146.08 (1 C), 146.04 (1 C), 145.69 (1 C), 145.08 (1 C), 144.80 (1 C), 144.65 (1 C), 144.62 (1 C), 144.49 (1 C), 143.86 (1 C), 143.64 (1 C), 143.59 (1 C), 143.35 (1 C), 142.65 (1 C), 142.46 (1 C), 142.17 (1 C), 141.72 (1 C), 141.49 (1 C), 141.09 (1 C), 140.75 (1 C), 140.45 (1 C), 139.36 (1 C), 133.72 (1 C, **5’’**), 132.03 (1 C, **5’**), 130.66 (2 C, **4’’**), 130.28 (1 C, **5’’’**), 129.41 (2 C, **4’’’**), 127.84 (2 C, **4’**), 114.47 (2 C, **3’**), 114.31 (2 C, **3’’’**), 114.41 (2 C, **3’’**), 109.43 (1 C, **12**), 92.81 (1 C, **5**), 73.89 (1 C, **3**), 73.43 (1 C, **9**), 73.31 (1 C, **4**), 61.79 (1 C, **6**), 57.86 (1 C, **15**), 55.19 (1 C, **1’’’**), 55.13 (1 C, **1’**), 55.00 (1 C, **1’’**), 41.43 (1 C, **18**).

FT-IR (ZnSe) ν (cm^{-1}): 3492 (w), 2953 (m), 2924 (s), 2852 (m), 1606 (m), 1509 (vs), 1461 (m), 1439 (vw), 1417 (vw), 1380 (w), 1299 (m), 1252 (s), 1179 (s), 1115 (w), 1091 (w), 1033 (m), 908 (w), 880 (m), 794 (vw), 648 (w), 619 (w), 568 (vw), 546 (vw).

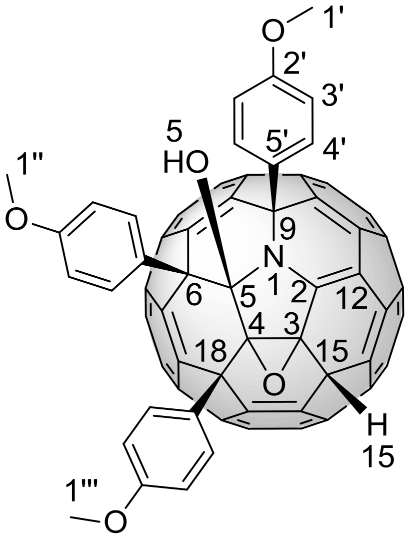
UV/Vis (CH_2Cl_2) λ_{max} (nm): 255, 357, 396, 440, 580, 631.

MALDI-TOF MS (matrix: dctb, CH_2Cl_2): *m/z* (% Int.)= 1077 (100) $[M]^{+\cdot}$, 954 (50) $[M-(C_6H_4OCH_3)-O]^+$.
HRMS (APPI; toluene/ACN): *m/z* calcd for $C_{80}H_{23}NO_5^{+\cdot}$ $[M]^{+\cdot}$: 1077.157074, found: 1077.156032.

Oxygenation product **9**:

Pure isomer **4** (8.2 mg, 7.8 µmol) was dissolved in 5 mL oxygen saturated $CS_2/CDCl_3$. The solution was filled into a NMR tube and irradiated with a 500 W lamp using an aqueous dichromate solution filter and water cooling. The reaction was monitored by TLC and ^{1}H NMR spectroscopy. After 3 min of irradiation the starting material was completely converted to an orange compound (R_f = 0.36 in toluene/ethyl acetate (9:1)) and partly to a green compound **9** (R_f = 0.56 in toluene/ethyl acetate

(9:1)). Photooxidation was stopped after a total irraditation time of 5 min and the orange solution was stored in the dark. The color of the reaction mixture slowly turned green and after 1h compound **9** was detected with 100% conversion. The solvent was evaporated and compound **9** (7.8 mg; 7.2 µmol; 92%) was isolated as a green solid.



^{1}H NMR [400 MHz, CDCl$_3$, RT]: δ (ppm) = 7.83 (d, ^{3}J = 8.9 Hz, 2 H, **4’**), 7.81 (d, ^{3}J = 8.9 Hz, 2 H, **4’’’**), 7.41 (d, ^{3}J = 8.9 Hz, 2 H, **4’’**), 7.05 (d, ^{3}J = 8.9 Hz, 2 H, **3’**), 6.96 (d, ^{3}J = 8.9 Hz, 2 H, **3’’’**), 6.79 (d, ^{3}J = 8.9 Hz, 2 H, **3’’**), 5.14 (s, 1 H, **15**), 4.55 (s, 1H, **5**), 3.87 (s, 3 H, **1’**), 3.84 (s, 3 H, **1’’’**), 3.77 (s, 3 H, **1’’**).

^{13}C NMR [100 MHz, CDCl$_3$, RT]: δ (ppm) = 159.93 (1 C, **2’**), 159.45 (1 C, **2’’’**), 158.97 (1 C, **2’’**), 158.07 (1 C, **2**), 152.12 (1 C), 151.08 (1 C), 150.66 (1 C), 149.94 (1 C), 149.79 (1 C), 149.37 (1 C), 149.17 (1 C), 148.63 (1 C), 148.54 (1 C), 148.22 (1 C), 148.10 (1 C), 148.07 (1 C), 148.02 (1 C), 147.98 (1 C), 147.70 (1 C), 147.62 (1 C), 147.60 (1 C), 147.59 (1 C), 147.47 (1 C), 147.44 (1 C), 147.16 (1 C), 146.93 (1 C), 146.85 (2 C), 146.75 (1 C), 146.72 (1 C), 146.61 (1 C), 146.48 (1 C), 146.36 (1 C), 145.79 (1 C), 145.59 (1 C), 145.56 (1 C), 145.53 (1 C), 145.32 (1 C), 144.93 (1 C), 144.47 (1 C), 144.32 (1 C), 144.02 (1 C), 143.53 (1 C), 143.52 (1 C), 143.37 (1 C), 143.29 (1 C), 142.88 (1 C), 142.67 (1 C), 142.58 (1 C), 142.53(1 C), 142.17 (1 C), 140.94 (1 C), 140.69 (1 C), 140.22 (1 C), 133.42 (1 C, **5’’**), 132.47 (1 C, **5’**), 131.62 (2 C, br. signal, **4’’**), 130.96 (1 C, **5’’’**), 129.61 (2 C, **4’’’**), 127.71 (2 C, **4’**), 114.71 (2 C, **3’**), 114.43 (2 C, **3’’’**), 113.25 (2 C, **3’’**), 110.16 (1 C, **12**), 93.54 (1 C, **5**), 76.48 (1 C, **3**), 73.62 (1 C, **9**), 72.66 (1 C, **4**), 61.82 (1 C, **6**), 55.56 (1 C, **18**), 55.48 (1 C, **1’/1’’/1’’’**), 55.43 (1 C, **1’/1’’/1’’’**), 55.26 (1 C, **1’/1’’/1’’’**), 46.30 (1 C, **15**).

FT-IR (ZnSe) ν (cm^{-1}): 3448 (w), 2999 (vw), 2952 (w), 2927 (w), 2905 (vw), 2834 (w), 1606 (m), 1560 (vw), 1510 (vs), 1461 (m), 1439 (w), 1418 (w), 1386 (w), 1299 (m), 1254 (s), 1181 (s), 1114 (w), 1098 (w), 1034 (s), 908 (m), 880 (w), 835 (w), 732 (m), 649 (w), 613 (vw), 569 (vw).

UV/Vis (CH$_2$Cl$_2$) λ_{max} (nm): 255, 357, 400, 438, 580, 630.

MALDI-TOF MS (without matrix, CH$_2$Cl$_2$): *m/z* (% Int.)= 1077 (100) $[M]^{+\cdot}$.

HRMS (ESI; toluene/ACN, neg.): *m/z* calcd for $C_{80}H_{22}NO_5^-$ $[M-H]^-$: 1076.15035, found: 1076.14687.

3 NMR and FTIR spectra

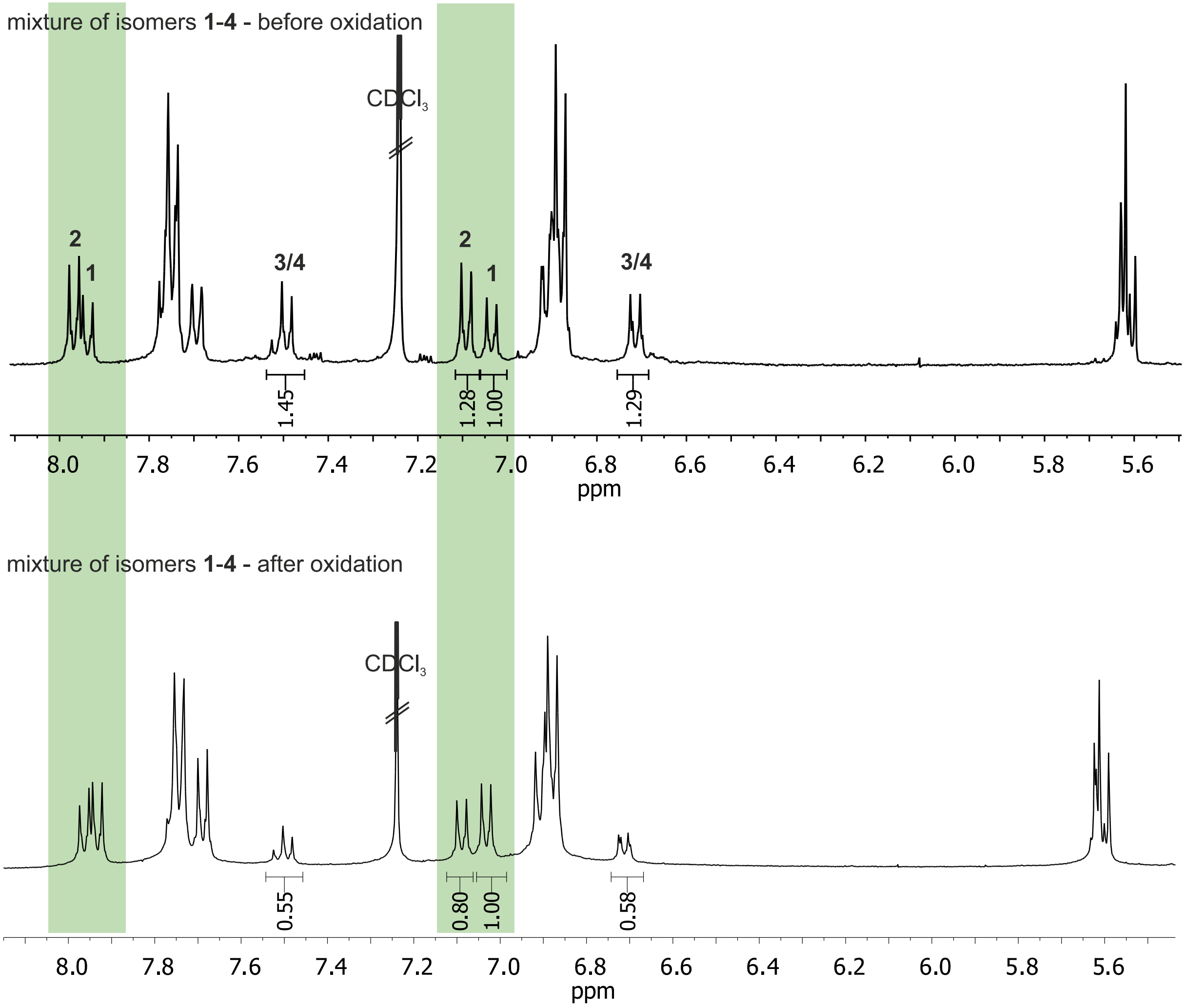


Figure S1. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of the mixture of the mixture of isomers **1-4** before and after photooxidation (short-time treatment with air and light).

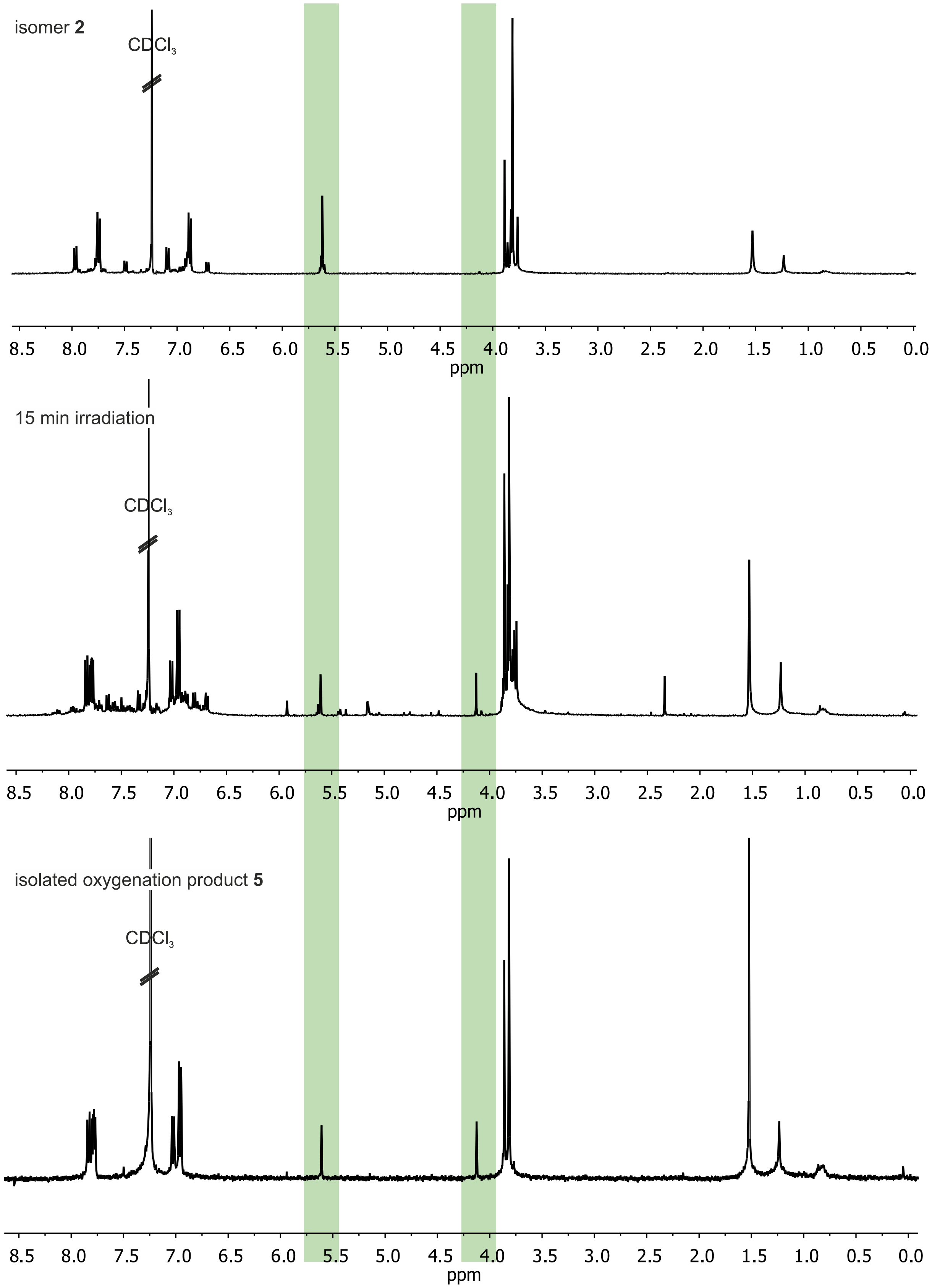


Figure S 2. ^{1}H NMR tracking experiment spectra: photooxidation of isomer **2** (impurity: small amount of isomer **3**) to oxygenation product **5** (400 MHz, $CDCl_3$).

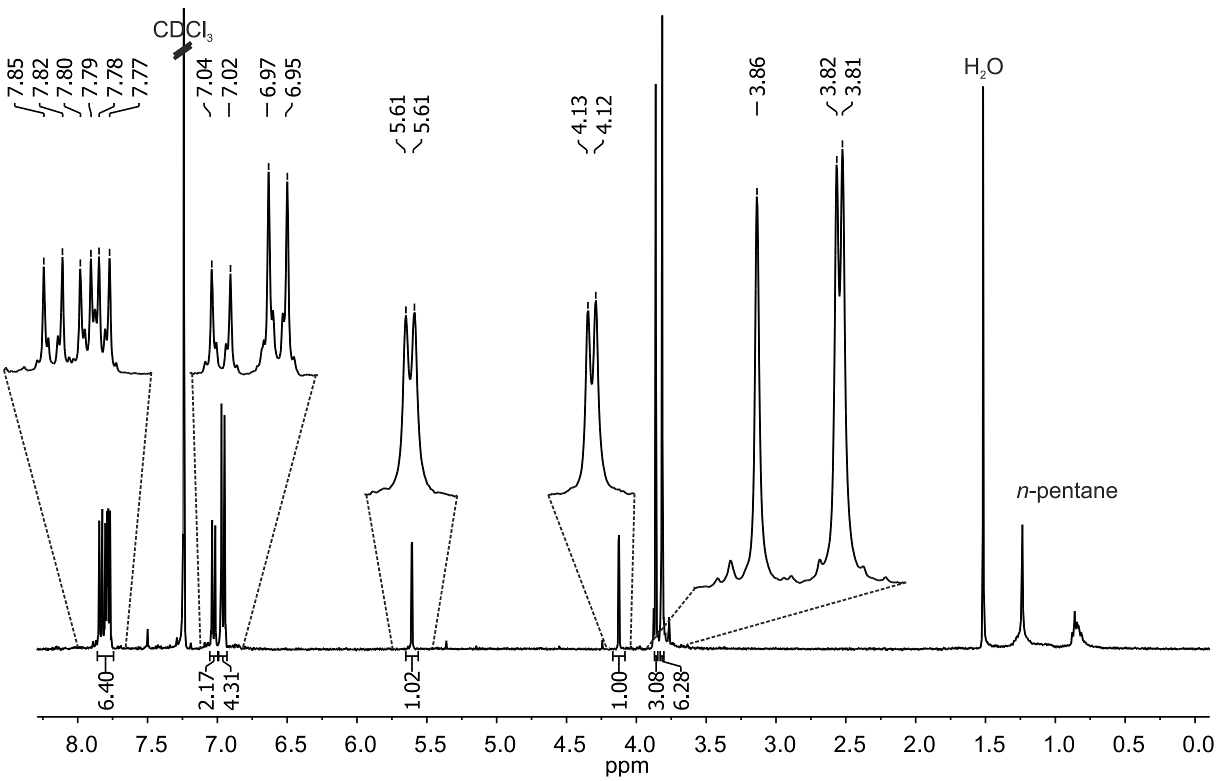


Figure S3. ^{1}H NMR spectrum of oxygenation product **5** (400 MHz, $CDCl_3$).

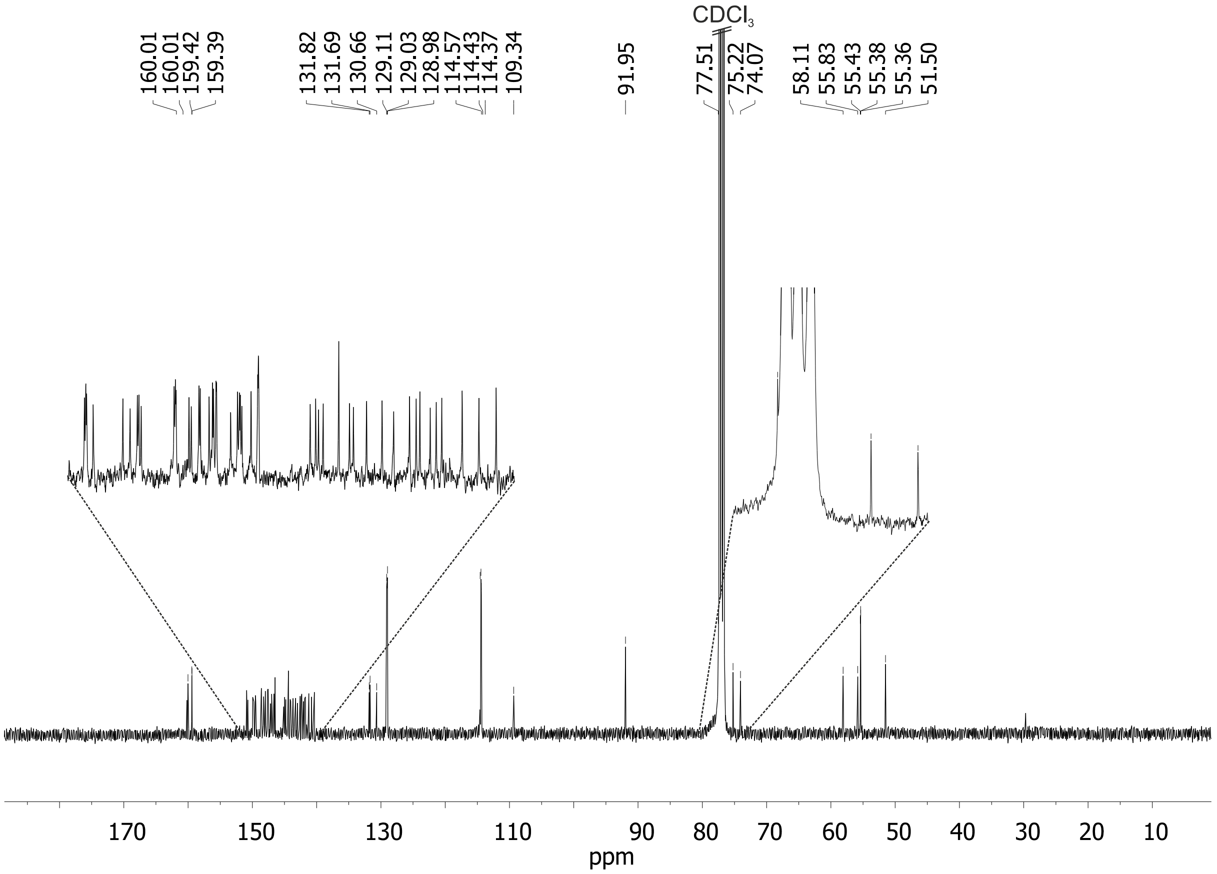


Figure S4. ^{13}C NMR spectrum of oxygenation product **5** (100 MHz, $CDCl_3$).

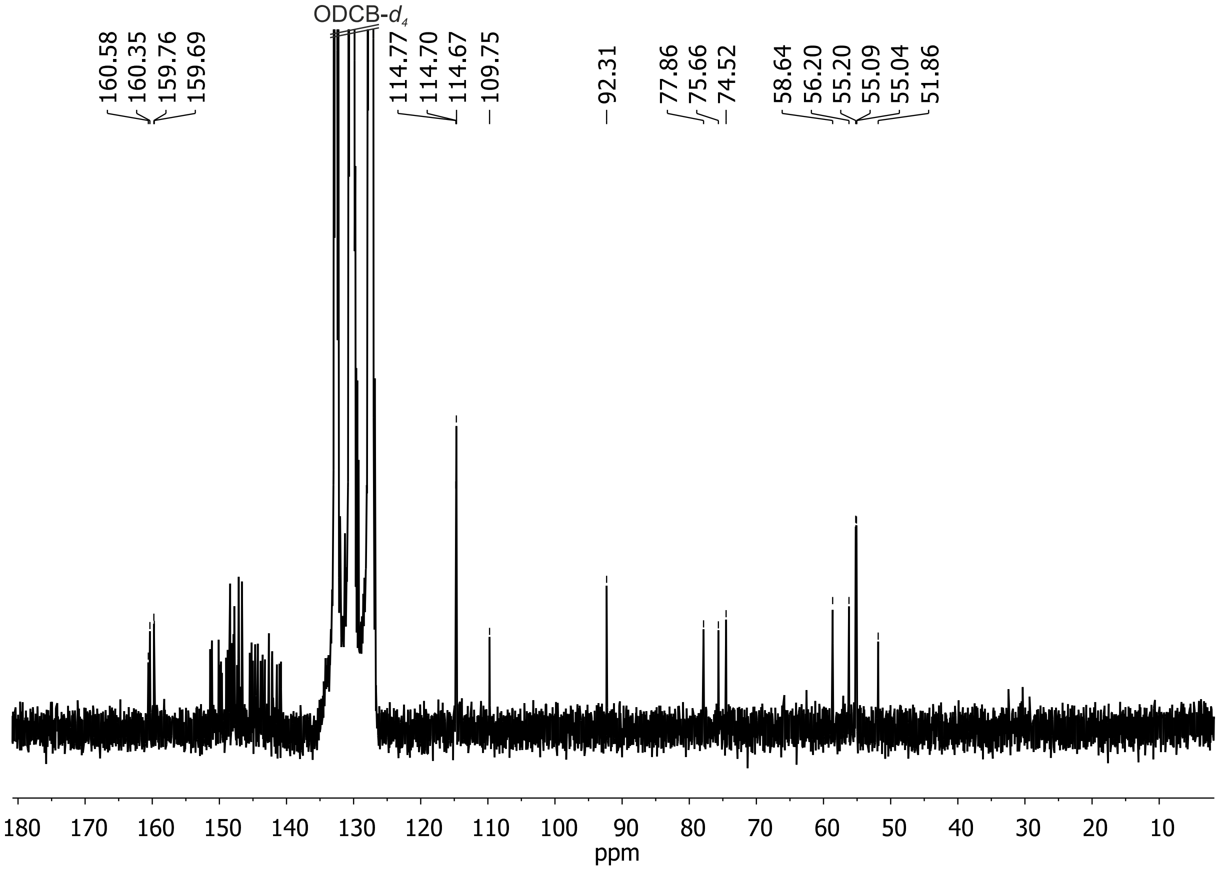


Figure S5. ^{13}C NMR spectrum of oxygenation product **5** (100 MHz, CDCB-d_4).

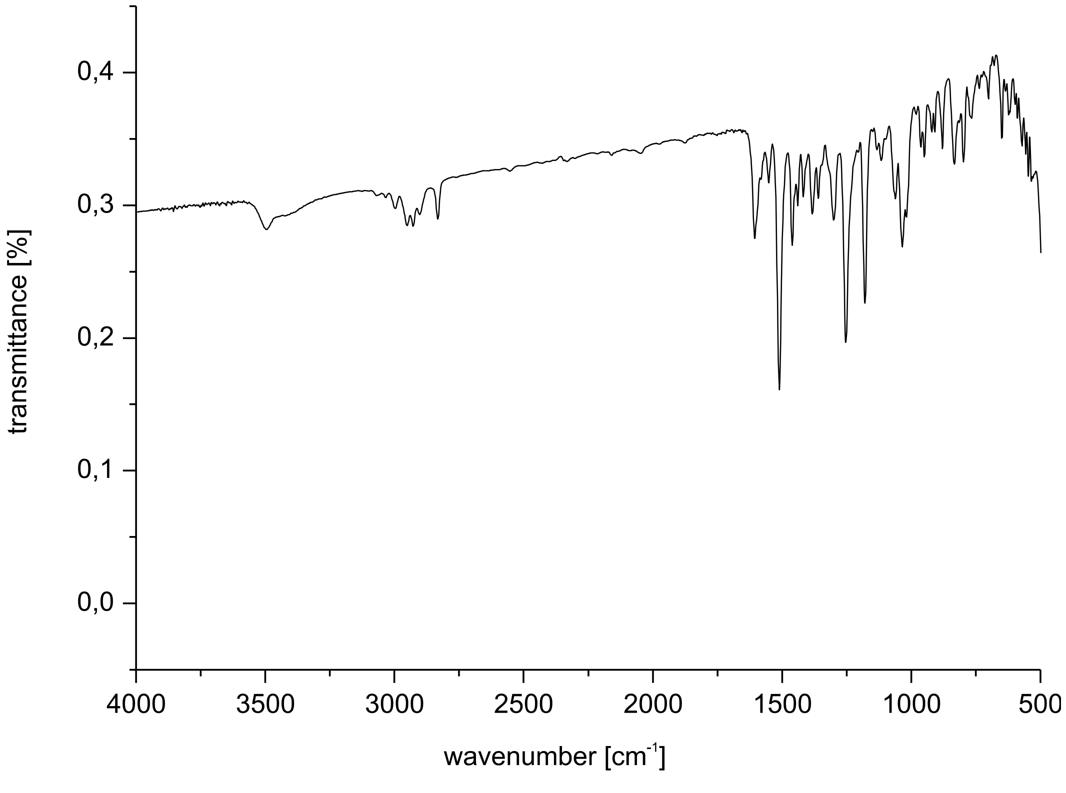


Figure S6. FTIR spectrum of oxygenation product **5** on a ZnSe window.

Table S1. Selected data from the calculated ^{13}C NMR spectrum of compound **5** at the B3LYP/6-31G(d) level. The geometry optimization and vibrational frequency calculation were also conducted at B3LYP/6-31G(d) level using Gaussian 09.[3]

atom number	functional group	calculated chemical shift (calibrated with C_{60})	experimental chemical shift (100 MHz, $CDCl_3$)
6	-C-H	57.26	51.50
1′	$-OCH_3$	56.51	55.36
1′	$-OCH_3$	56.61	55.38
1′	$-OCH_3$	56.67	55.43
18	sp^3-C	64.06	55.83
15	sp^3-C	65.20	58.11
9	sp^3-C	80.12	74.07
4	epoxy-C	81.17	75.22
3	epoxy-C	82.17	77.51
5	-C-OH	96.73	91.95
12	enamine	111.07	109.34
2	enamine	150.33	160.19

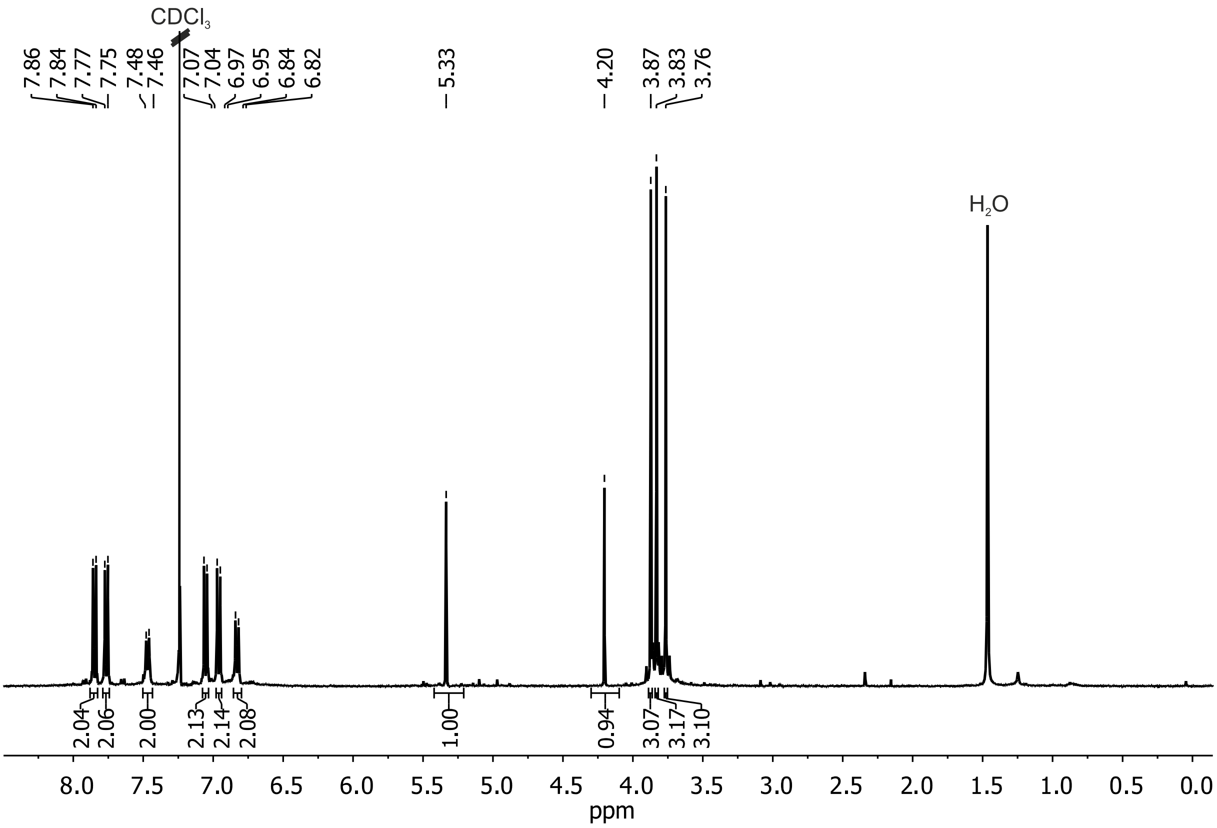


Figure S7. ^{1}H NMR spectrum of oxygenation product **8** (400 MHz, $CDCl_3/CS_2$).

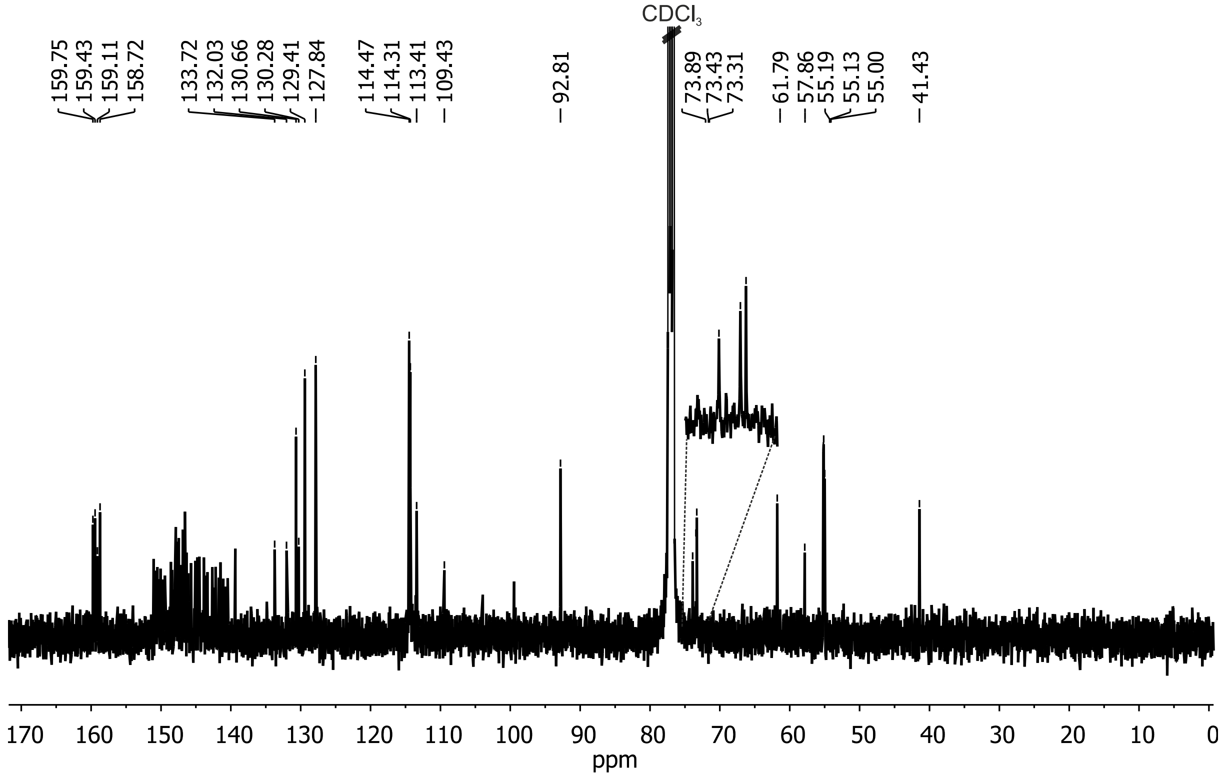


Figure S8. ^{13}C NMR spectrum of oxygenation product **8** (100 MHz, $CDCl_3/CS_2$).

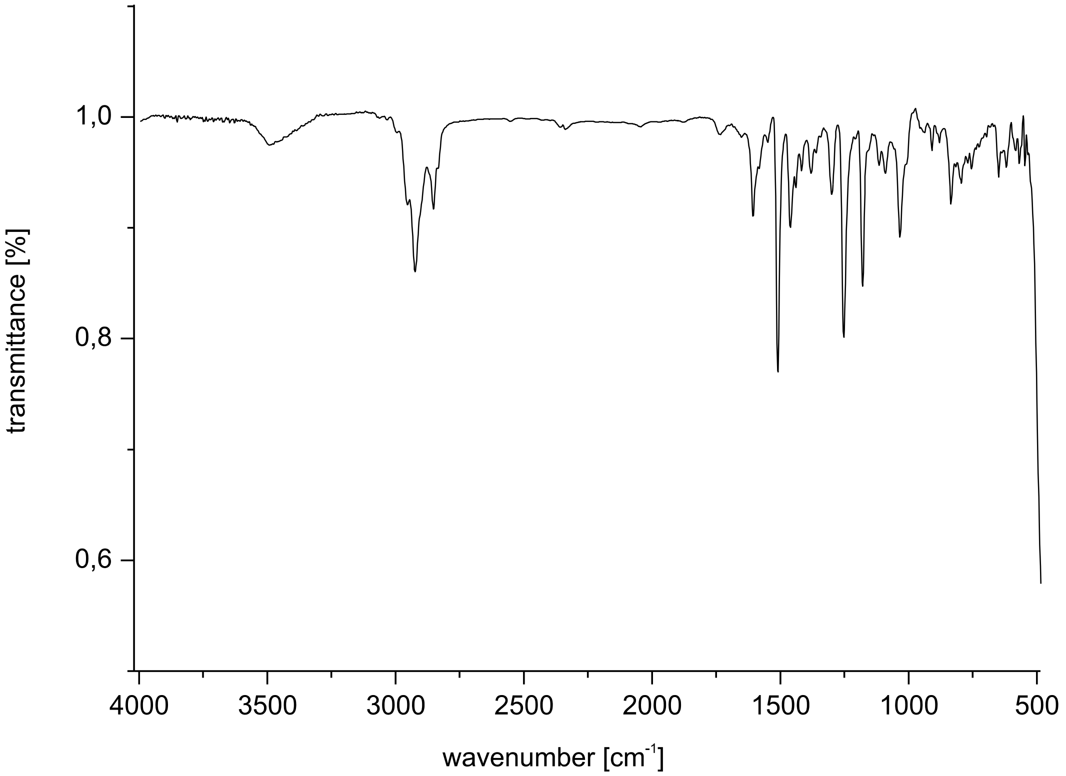


Figure S9. FTIR spectrum of oxygenation product **8** on a ZnSe window.

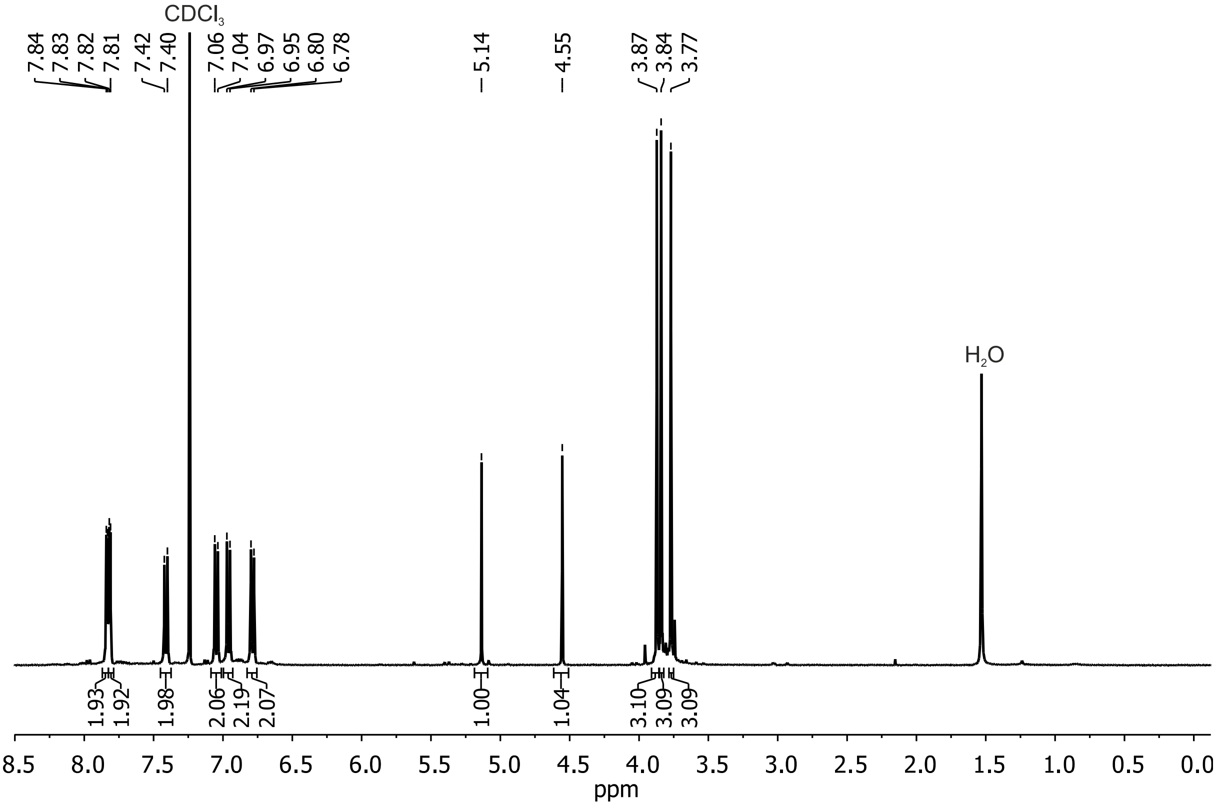


Figure S10. ^{1}H NMR spectrum of oxygenation product **9** (400 MHz, $CDCl_3$).

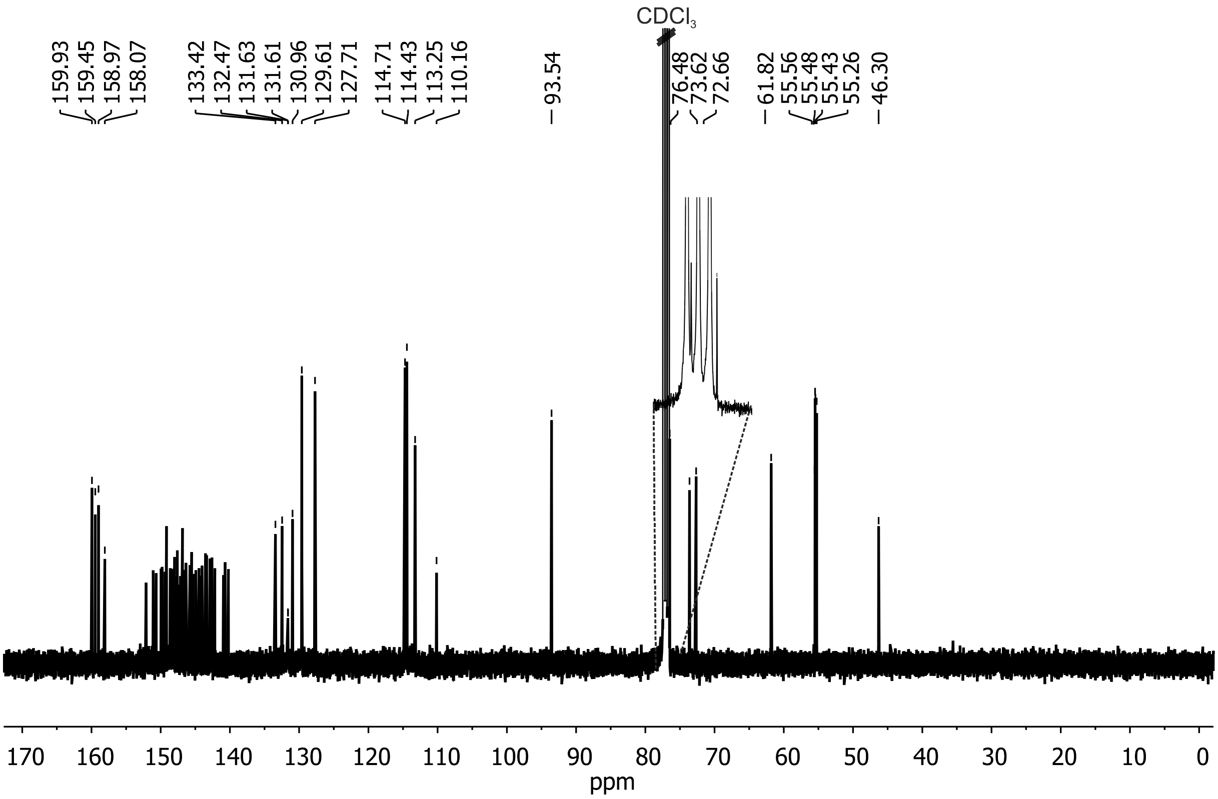


Figure S11. ^{13}C NMR spectrum of oxygenation product **9** (100 MHz, $CDCl_3$).

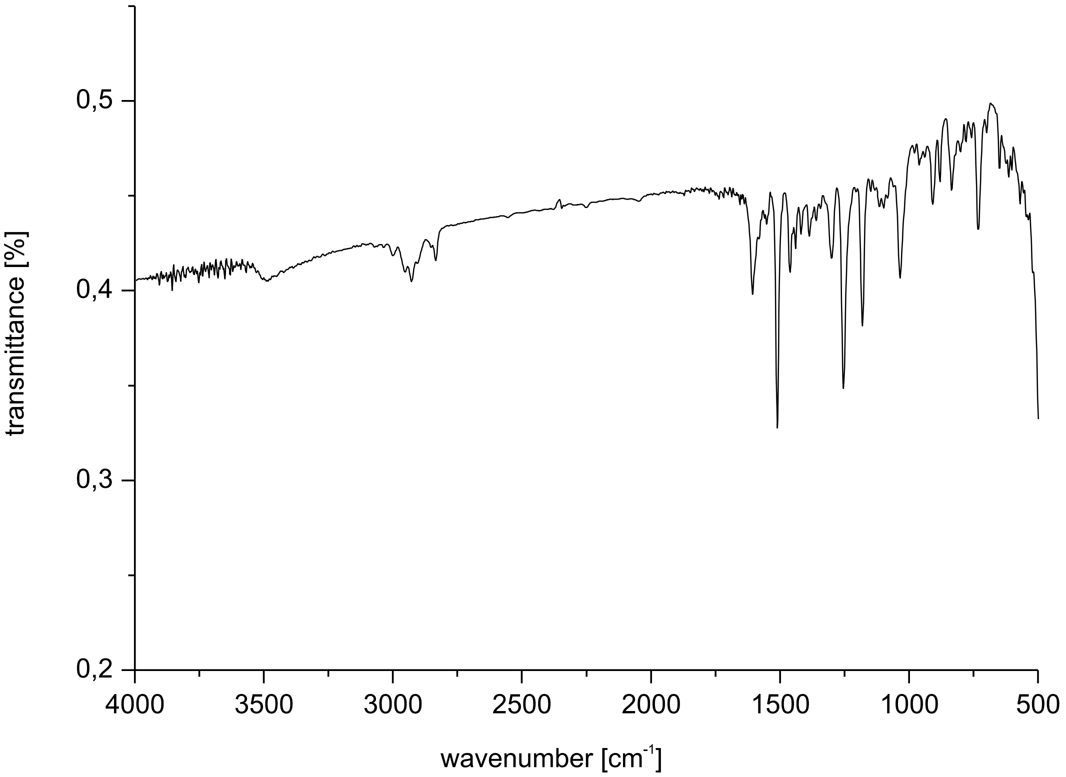


Figure S12. FTIR spectrum of oxygenation product **9** on a ZnSe window.

4 X-Ray Crystallographic Analysis of Compound 2

Intensity data was measured on a single crystal of compound **2** with a Bruker Kappa APEX 2 *IµS* Duo diffractometer using CuK_{α} radiation (QUAZAR focussing Montel optics, λ = 1.54178 Å). Data were corrected for Lorentz and polarization effects; a semi-empirical absorption correction on the basis of multiple scans was applied (SADABS 2008/1). [4a] The structure was solved by direct methods and refinement was carried out by full-matrix least-squares procedures on F^2 with SHELXTL NT 6.12. [4b] All non-hydrogen atoms were refined anisotropically. The compound crystallized with one $CDCl_3$ per formula unit. This solvent molecule was disordered. Two preferred orientations were refined resulting in site occupancies of 90.9(2) and 9.1(2) % for the atoms, Cl1, Cl2, Cl3 and Cl1A, Cl2A, and Cl3A, respectively. SAME, SIMU, and SADI restraints were applied. Treatment of hydrogen atoms: The positions of the hydrogen atoms H5 and H11 attached to the $C_{59}N$ moiety were derived from a difference fourier synthesis and allowed to ride on their carrier atoms. All other hydrogen atoms were placed in positions of optimized geometry. The isotropic displacement parameters of all H atoms were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5. CCDC-967868 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement for compound **2**.

Identification code	rn1301	
Empirical formula	$C_{81}H_{23}Cl_3DNO_3$	
Formula weight M_r	1166.36	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system, space group	monoclinic, $P2_1/n$ (Nr. 14)	
Unit cell dimensions	a = 19.878(2) Å	α = 90°
(e.s.d.'s in parentheses)	b = 10.050(1) Å	β = 107.877(6)°
	c = 24.271(3) Å	γ = 90°
Volume	4614.3(8) A^3	
Z	4	
Calculated density	1.677 Mg/m^3	
Absorption coefficient μ	2.349 mm^{-1}	
F(000)	2368	

Crystal size	0.15 x 0.12 x 0.04 mm
Crystal shape and color	plate, red
θ range for data collection	3.8 to 68.3°
Limiting indices	-23<=h<=23, -12<=k<=11, -28<=l<=14
Reflections collected / unique	25540 / 8129 [R(int) = 0.052]
Completeness to θ = 68.28	96.2%
Absorption correction	SADABS (semiempirical from multiple measurements of equivalent reflections)
Max. and min. transmission	0.685 and 0.753
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8129 / 51 / 826
Goodness-of-fit on F^2 (S)	1.373
Final R indices [I>2σ(I)]	R_1 = 0.0742, wR_2 = 0.2194
Largest diff. peak and hole	0.520 and -0.929 eÅ^{-3}

References:

1. M. von Delius, F. Hauke and A. Hirsch, *Eur. J. Org. Chem.*, 2008, 4109-4119.
2. R. Neubauer, F. W. Heinemann, F. Hampel, Y. Rubin and A. Hirsch, *Angew. Chem.*, 2012, **124**, 11892-11896; *Angew. Chem. Int. Ed.*, 2012, **51**, 11722-11726.
3. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
4. a) *SADABS*, Bruker AXS, Inc., **2009**, Madison WI., U.S.A., b) G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122.