

Supplementary Information

Nanomolecular singlet oxygen photosensitizers based on hemiquinonoid-resorcinarenes, the fuchsonarenes

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1. Experimental

1.1 General. Reagents and dehydrated solvents (in septum-sealed bottles) used for syntheses and spectroscopic measurements were obtained from Tokyo Kasei Chemical Co., Wako Chemical Co. or Aldrich Chemical Co. and were used without further purification. Electronic absorption spectra were measured using JASCO V-570 UV/Vis/NIR spectrophotometer, Princeton Applied Research (PAR) diode array rapid scanning spectrometer or a Shimadzu UV/Visible spectrophotometer. Fluorescence spectra were measured using a JASCO FP-670 spectrofluorimeter. FTIR spectra were obtained from solid samples using a Thermo-Nicolet 760X FTIR spectrophotometer. ^1H NMR spectra were recorded on a JEOL AL300BX NMR spectrometer at 300 MHz, proton decoupled ^{13}C NMR were recorded at 76 MHz on a JEOL AL300BX NMR spectrometer at the stated temperatures. Data was processed using Delta version 5.0.5.1 and Always JNM-AL version 6.2. ^1H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) for CDCl_3 (δ 0.00) or the residual solvent peak for spectra recorded in d_6 -DMSO (δ 2.50). ^{13}C NMR chemical shifts (δ) are reported in ppm relative to the solvent employed. Coupling constants (J) are expressed in Hertz (Hz), shift multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), multiplet (m) and broad singlet (bs). High resolution ESI-MS measurements were performed using a Waters Ltd. Xevo-G2-XS-ToF spectrometer with direct infusion of samples using an Alliance e2695 HPLC system. Samples were dissolved in methanol. Electrospray conditions: cone voltage: 40V; capillary voltage: 3kV; desolvation temperature: 350 °C; desolvation gas flow (dry nitrogen, 500 L/hr); source temperature (120 °C). Leucine enkephalin was used as internal reference for HR-MS (for positive ion: M.W. = 556.2771 Da; for negative ion: M.W. = 554.2615 Da). Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF MS) were measured using a Shimadzu-Kratos model Axima CFR+ mass spectrometer with either *trans*-Ferulic acid or α -cyano-4-hydroxycinnamic acid (CHCA) as matrix. ESR spectra were measured using a JEOL JES-FA200 spectrometer with data recorded and processed using A-System version 1.6.5 PCI J/X-Band and FA-Manager version 1.2.9 V2 series using manganese as an internal standard. Samples were recorded in a glass capillary sealed at both ends filled to 50% capacity. Samples were irradiated using a 24W blue LED irradiation chamber (400-500 nm) equipped with a cooling fan. The synthesis and characterization of compounds rctt-1, rctt-1[Ox₁] and rccc-1[Ox₂] was carried out according to the

literature procedure.⁵¹ DFT calculations at the B3LYP/6-311G(d,p) level were carried out using Gaussian 2016⁵² at the Holland Computing Center of the University of Nebraska. Molecular orbital projections were generated using GaussView.⁵³

1.2 Electrochemistry. Differential pulsed voltammetry (DPV) were recorded on an EG&G Model 263A potentiostat using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas. Spectroelectrochemical study was performed by using a cell assembly (SEC-C) supplied by ALS Co., Ltd. (Tokyo, Japan). This assembly comprised of a Pt counter electrode, a 6 mm Pt Gauze working electrode, and an Ag/AgCl reference electrode in a 1.0 mm path length quartz cell. The optical transmission was limited to 6 mm covering the Pt gauze working electrode.

1.3 Singlet Oxygen Phosphorescence. The steady-state fluorescence and singlet oxygen photoluminescence spectra were measured by using a Horiba Jobin Yvon Nanolog UV-visible-NIR spectrofluorimeter equipped with a PMT (for UV-visible) and N₂-cooled InGaAs (for NIR) detectors. A right angle detection method was used for emission measurements. Solutions of compounds **1**, **2**, **3** and **4** were normalized to the absorption maxima of the meso-tetraphenylporphyrin reference used. Singlet oxygen quantum yields (Φ_{so}) were determined by comparison of the singlet oxygen photoluminescence maxima values of the reference⁵⁴ (I_{ref}) and compound being studied (I_{sample}) at approximately 1270 nm using the formula:

$$\Phi_{so} = \frac{I_{sample}}{I_{ref}} \times 0.55$$

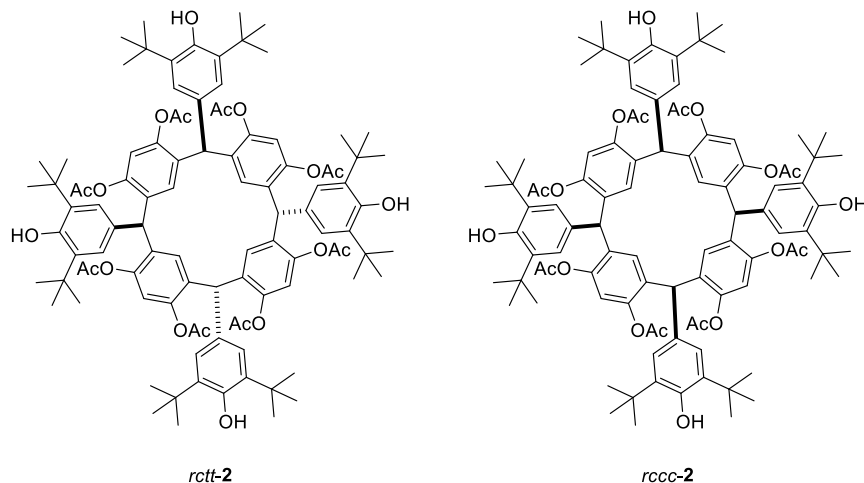
1.4 X-Ray Crystallography. Crystals were grown by diffusion of hexane into solutions of chloroform for rctt-**2**[Ox₁], rccc-**2**[Ox₂], rcct*-**3** and rctt-**3**[Ox₁], hexane into a solution of toluene for rctt-**4**, hexane into a solution of methanol for rccc-**2**, and hexane into a solution of dichloromethane for rctt-**2**. Data collections were performed using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) on a RIGAKU VariMax Saturn diffractometer equipped with a charge-coupled device (CCD) detector or a Bruker APEX CCD diffractometer. Prior to the diffraction experiment the crystals were flash-cooled to the given temperatures in a stream of cold nitrogen gas. Cell refinements and data reductions were carried

out using the d*trek program package in the CrystalClear software suite.⁵⁵ The structures were solved using a dual-space algorithm method (SHELXT)⁵⁶ and refined by full-matrix least squares on F2 using SHELXL-2014⁵⁷ in the WinGX program package.⁵⁸ Non-hydrogen atoms were anisotropically refined and hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times Ueq of the parent atoms and 1.5 times Ueq for methyl groups. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference numbers 1934744 (rctt-2), 1934745 (rctt-2[Ox₁]), 1934746 (rccc-2), 1934747 (rccc-2[Ox₂]), 1934748 (rcct*-3), 1934749 (rctt-3[Ox₁]) and 1934750 (rctt-4). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK <http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi>, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Crystals of these resorcinarene and pyrogallarene compounds usually contain large and variable quantities of poorly ordered solvents leading to poor crystallinity, large values for residuals and models containing non-stoichiometric values of solvent. Despite these features, the structures of the molecules could be modelled appropriately and the oxidation states of the molecules could also be observed from the corresponding C-O bond lengths at anti-oxidant substituents.

1.5 Femtosecond Transient Absorption Spectroscopy. Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with 290-2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is $\pm 10\%$.

2,4,6,8-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl octaacetate – rctt-2 & rccc-2



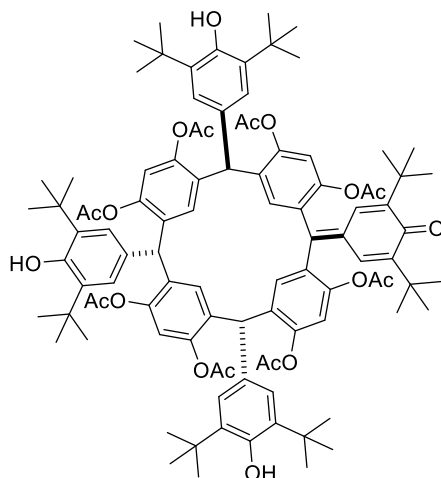
Crude **A** (5.7 g, 4.3 mmol) obtained by the above procedure (page S5) was dissolved in a mixture of pyridine (10 mL) and acetic anhydride (35 mL) and heated at 90 °C for 18 hours under a nitrogen atmosphere. The resulting suspension was filtered while hot to afford a yellow solid, *rctt-2* (Yield: 4.0 g, 57%). The filtrate was poured into water and the yellow precipitate was collected by filtration, dried and purified by column chromatography (SiO₂, 0-100% ethyl acetate in toluene) to give *rccc-2* as a yellow solid (Yield: 1.7 g, 24%).

rctt-2: ¹H NMR (300 MHz, CDCl₃) δ 6.92 (s, 2H), 6.90 (s, 2H), 6.73 (s, 2H), 6.24 (s, 2H), 5.49 (s, 4H), 4.93 (s, 4H), 2.09 (s, 12H), 1.79 (s, 12H), 1.20 (s, 72H); ¹³C NMR (76 MHz, CDCl₃) δ 168.7, 167.9, 151.9, 147.3, 146.3, 135.3, 133.5, 132.6, 130.5, 129.7, 128.2, 125.9, 117.4, 116.7, 44.7, 34.1, 30.4, 20.7, 20.3; IR (neat) ν (cm⁻¹) 1753 (C=O), 3629 (OH); TOF MS ES+ m/z: 1663.8 [M+Na]⁺, 1664.8 [M+H+Na]⁺, 1665.8 [M+2H+Na]⁺, 1666.8 [M+3H+Na]⁺; HR-MS calc. [C₁₀₀H₁₂₀O₂₀Na]⁺ 1663.8265, obs. 1663.8292.

rccc-2: ¹H NMR (300 MHz, CDCl₃) δ 7.33 (s, 2H), 6.81 (s, 2H), 6.75 (s, 4H), 6.50 (s, 2H), 6.35 (s, 4H), 6.03 (s, 2H), 5.42 (s, 4H), 4.94 (s, 4H), 2.06 (s, 12H), 1.60 (s, 12H), 1.26 (s, 36H), 1.14 (s, 36H); ¹³C NMR (76 MHz, CDCl₃) δ 168.3, 168.0, 151.9, 147.3, 146.9, 135.7, 134.7, 132.7, 131.2, 130.9, 130.8, 129.4, 128.7, 126.4, 124.7, 117.6, 115.5, 45.3, 34.3, 34.2, 34.0, 30.4, 30.4, 20.9, 20.9, 19.9, 19.9; IR (neat) ν (cm⁻¹) 1758 (C=O), 3635 (OH); TOF MS ES+ m/z: 1663.8 [M+Na]⁺, 1664.8 [M+H+Na]⁺, 1665.8 [M+2H+Na]⁺, 1666.8 [M+3H+Na]⁺; HR-MS calc. [C₁₀₀H₁₂₀O₂₀Na]⁺ 1663.8265, obs. 1663.8242.

Note: Resonances due to exchangeable protons were not visible in ¹H NMR spectra of these compounds.

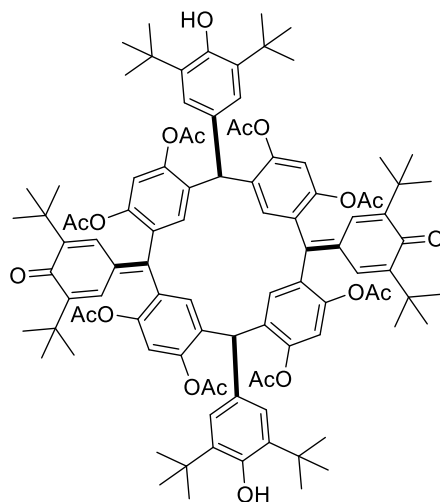
2,4,6-Tris(3,5-di-*tert*-butyl-4-hydroxyphenyl)-8-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl octaacetate –rctt-2[Ox₁]



2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (56 mg, 0.25 mmol, 4.0 equiv.) was added to a stirred solution of rctt-2 (100 mg, 0.061 mmol, 1.0 equiv.) in dichloromethane (7 mL) under a nitrogen atmosphere and stirred for 4 days. The reaction mixture was filtered through celite and the residue was washed with dichloromethane. The filtrate solvent was removed under reduced pressure and the residue was purified by preparative thin layer chromatography (SiO₂, 15% ethyl acetate in toluene) to give the title compound as a yellow solid (Yield: 70 mg, 70%).

¹H NMR (300 MHz, CDCl₃) δ 7.23 (s, 1H), 7.09 (s, 1H), 6.83-6.91 (m, 4H), 6.69-6.71 (m, 5H), 6.39 (s, 1H), 6.35 (s, 1H), 6.22 (s, 1H), 6.12 (s, 1H), 6.08 (s, 1H), 5.71 (s, 1H), 5.61 (s, 1H), 5.28 (s, 1H), 5.05 (s, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 2.30 (s, 3H), 2.11 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H), 1.88 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H), 1.12-1.27 (m, 63H), 0.93 (s, 9H); ¹³C NMR (76 MHz, CDCl₃) δ 186.5, 169.7, 168.9, 168.7, 168.6, 168.1, 168.0, 167.9, 167.7, 167.5, 166.9, 166.6, 152.6, 152.5, 152.0, 151.9, 151.8, 149.5, 149.2, 148.2, 147.8, 147.4, 147.3, 147.0, 146.9, 146.7, 146.6, 146.4, 146.3, 145.8, 144.0, 135.9, 135.6, 135.2, 134.8, 134.7, 133.5, 133.4, 133.3, 133.0, 133.0, 132.6, 132.2, 131.8, 131.6, 131.4, 131.2, 130.9, 130.5, 130.4, 130.2, 129.6, 129.4, 129.1, 128.7, 128.2, 126.9, 126.2, 126.0, 125.5, 124.8, 118.2, 117.8, 117.6, 117.4, 116.6, 45.4, 44.7, 44.5, 35.3, 35.3, 35.2, 35.1, 35.0, 34.4, 34.3, 34.2, 34.1, 34.0, 34.0, 30.3, 30.1, 29.7, 29.5, 29.4, 29.2, 21.3, 21.2, 20.9, 20.7, 20.4, 20.3, 20.1, 20.0, 19.8; TOF MS ES+ m/z: 1661.8 [M+Na]⁺, 1662.8 [M+H+Na]⁺, 1663.8 [M+2H+Na]⁺; IR (neat) ν (cm⁻¹) 1604 (C=O), 1766 (C=O), 3626 (OH); HR-MS calc. [C₁₀₀H₁₁₈O₂₀Na]⁺ 1661.8109, obs. 1661.8142.

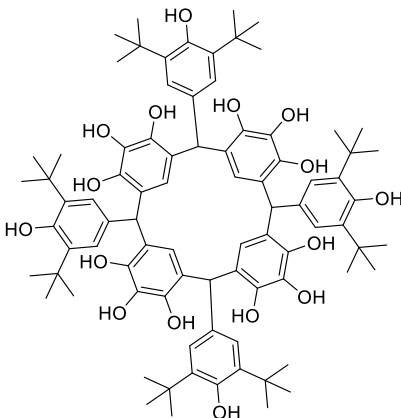
2,6-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,8-bis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl octaacetate – rccc-2[Ox₂]



2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (5.5 mg, 24.4 μmol , 4.0 equiv.) was added to a stirred solution of rccc-2 (10.0 mg, 6.1 μmol , 1.0 equiv.) in dichloromethane (1 mL) under a nitrogen atmosphere and stirred for 4 days. The reaction mixture was directly purified by preparative thin layer chromatography (SiO_2 , 40% ethyl acetate in toluene) to give the title compound as an orange solid (Yield: 8 mg, 80%).

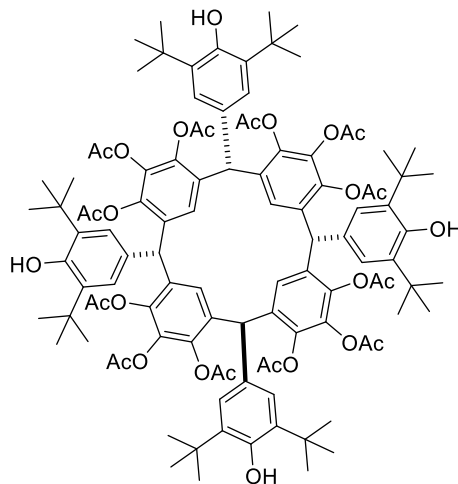
¹H NMR (300 MHz, *d*₆-DMSO, 373 K) δ 7.30 (s, 2H), 7.21 (s, 2H), 7.12 (s, 2H), 6.94 (s, 4H), 6.67 (s, 2H), 6.62 (s, 2H), 6.44 (s, 2H), 6.36 (s, 2H), 5.66 (s, 2H), 2.29 (s, 6H), 2.16 (s, 6H), 1.83 (s, 6H), 1.80 (s, 6H), 1.23 (s, 36H), 1.05 (s, 18H), 0.82 (s, 18H); ¹³C NMR (76 MHz, CDCl_3) δ 185.9, 168.2, 167.9, 167.7, 167.4, 152.6, 149.5, 148.5, 148.5, 148.4, 147.6, 6.3, 144.1, 135.5, 133.9, 132.5, 130.6, 130.1, 129.5, 129.3, 129.0, 128.9, 128.7, 126.5, 118.5, 117.5, 43.9, 35.2, 35.1, 34.4, 30.4, 29.5, 29.1, 21.0, 20.9, 20.9, 20.3; TOF MS ES+ *m/z*: 1659.8 [M+Na]⁺, 1660.8 [M+H+Na]⁺, 1661.8 [M+2H+Na]⁺; IR (neat) ν (cm^{-1}) 1609 (C=O), 1771 (C=O), 3642 (OH); HR-MS calc. [$\text{C}_{100}\text{H}_{116}\text{O}_{20}\text{Na}$]⁺ 1659.7952, obs. 1659.7952.

2,4,6,8-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphene-1⁴,1⁵,1⁶,3⁴,3⁵,3⁶,5⁴,5⁵,5⁶,7⁴,7⁵,7⁶-dodecaol (Precursor 'B')



Concentrated hydrochloric acid (0.5 mL) and pyrogallol (3.89 g, 30.8 mmol, 1.0 equiv.) were added to 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (7.23 g, 30.8 mmol, 1.0 equiv.) in ethanol (250 mL) at 90 °C and stirred for 8 hours under an atmosphere of nitrogen. The solid precipitate was filtered whilst hot and washed with hot ethanol to give the title compound as a white solid as a mixture of isomers (Yield: 7.3 g, 69%), which was used in subsequent steps without further purification. The ¹H NMR spectrum of this mixture is shown on page S45.

(2,4,6,8)-2,4,6,8-Tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁵,1⁶,3⁴,3⁵,3⁶,5⁴,5⁵,5⁶,7⁴,7⁵,7⁶-dodecyl dodecaacetate – rcct*-3

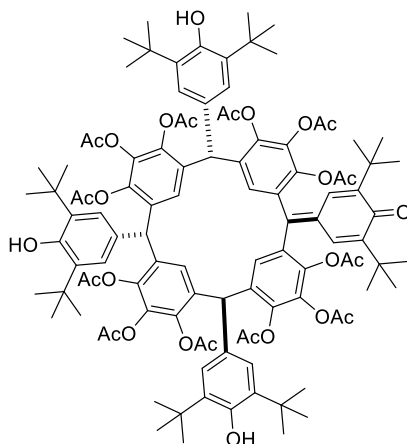


Crude **B** (2.0 g, 1.46 mmol) obtained in the previous step (page S9) was dissolved in a mixture of pyridine (20 mL) and acetic anhydride (10 mL) and heated at 90 °C for 18 hours under a nitrogen atmosphere. The reaction mixture was cooled, poured into water and the pale yellow precipitate was collected by filtration, dried and purified by column chromatography (SiO₂, 0-50% ethyl acetate in toluene) to give rcct*-**3** as a cream solid (Yield: 550 mg, 20%). A second isomer could also be isolated as a cream solid (Yield: 580 mg, 21%) but crystals suitable for X-ray crystallography could not be obtained.

¹H NMR (300 MHz, *d*₆-DMSO, 373K) δ 6.59-6.71 (m, 8H), 6.27-6.42 (m, 5H), 6.08-6.15 (m, 3H), 5.46 (s, 1H), 5.38 (s, 1H), 5.23 (bs, 2H), 2.11 (s, 12H), 1.97 (s, 12H), 1.80 (s, 12H), 1.22-1.25 (m, 72H); ¹³C NMR (76 MHz, *d*₆-DMSO, 373K) δ 166.2, 165.4, 151.5, 139.9, 139.5, 138.1, 137.1, 135.7, 135.4, 133.3, 133.0, 132.5, 130.4, 128.8, 125.0, 124.7, 33.7, 29.8, 19.1, 18.7; MALDI-TOF MS+ (CHCA) *m/z*: 1887.7 [M-3H+H₂O]⁺, 1889.4 [M-H+H₂O]⁺, 1891.4 [M+H+H₂O]⁺; IR (neat) *v* (cm⁻¹) 1777 (C=O), 3637 (OH).

Note: poor solubility of rcct*-**3** in *d*₆-DMSO at 373K lead to a poor signal-to-noise ratio in its ¹³C NMR spectrum.

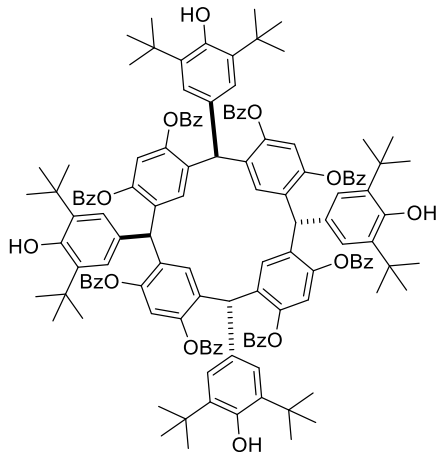
(2,6)-2,4,6-Tris(3,5-di-tert-butyl-4-hydroxyphenyl)-8-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁵,1⁶,3⁴,3⁵,3⁶,5⁴,5⁵,5⁶,7⁴,7⁵,7⁶-dodecacyl dodecaacetate – rctt-3[Ox₁]



2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (73 mg, 0.32 mmol, 4.0 equiv.) was added to a stirred solution of rctt*-**3** (150 mg, 0.08 mmol, 1.0 equiv.) in dichloromethane (5 mL) under a nitrogen atmosphere and stirred for 18 hours. The reaction mixture was filtered through celite with dichloromethane, the filtrate solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO₂, 0-50% ethyl acetate in toluene) to give the title compound as a yellow solid (Yield: 110 mg, 73%).

¹H NMR (300 MHz, CDCl₃) δ 6.75-6.92 (m, 7H), 6.42 (s, 1H), 6.26-6.35 (m, 3H), 6.07 (s, 1H), 5.68 (s, 1H), 5.58 (s, 1H), 5.40 (s, 1H), 5.03 (s, 1H), 4.94 (s, 1H), 4.91 (s, 1H), 2.17 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H), 2.12 (xs, 6H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.87 (s, 3H), 1.63 (s, 3H), 1.59 (s, 3H), 1.21-1.35 (m, 72H); ¹³C NMR (76 MHz, CDCl₃) δ 187.0, 168.0, 167.0, 166.8, 166.7, 166.4, 166.3, 166.2, 166.1, 166.1, 166.1, 166.0, 165.9, 153.0, 152.6, 152.3, 148.3, 147.9, 142.9, 142.8, 142.6, 141.6, 141.0, 140.9, 140.7, 140.6, 140.1, 138.0, 137.0, 136.4, 136.3, 136.3, 136.2, 135.3, 134.6, 134.5, 134.5, 134.5, 133.6, 133.5, 133.3, 132.5, 132.1, 131.3, 131.0, 130.8, 130.5, 129.5, 129.2, 129.2, 128.4, 128.0, 126.8, 126.5, 125.9, 125.5, 124.3, 77.6, 77.4, 77.2, 76.7, 46.0, 45.6, 45.5, 45.5, 35.5, 35.2, 34.6, 34.4, 34.3, 30.7, 30.7, 30.4, 29.8, 29.4, 21.5, 20.4, 20.3, 20.2, 20.2, 20.0, 19.6, 19.4; MALDI-TOF MS+ (*trans*-Ferulic acid) m/z: 1865.7 [M-5H]⁺, 1868.7 [M-2H]⁺; IR (neat) ν (cm⁻¹) 1611 (C=O), 1780 (C=O), 3634 (OH).

2,4,6,8-Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octayl octabenzoate – rctt-4



Isomer rctt-**A**^{S1} (1.0 g, 0.75 mmol) was dissolved in a mixture of pyridine (5 mL) and benzoic anhydride (3.40 g, 15 mmol, 20 equiv.) and heated at 90 °C for 18 hours under a nitrogen atmosphere. The reaction mixture was cooled, poured into methanol and the resulting precipitate was filtered to afford rctt-**4** (1.47 g, 92%) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, J = 7.0 Hz, 8H), 7.40-7.59 (m, 26H), 7.28 (s, 2H), 7.21 (t, J = 7.7 Hz, 8H), 7.02 (s, 2H), 6.74 (s, 2H), 6.56 (s, 4H), 6.47 (s, 4H), 5.88 (s, 4H), 4.69 (s, 4H), 0.93 (s, 36H), 0.83 (s, 36H); ¹³C-NMR (76 MHz, CDCl₃) δ 164.6, 163.1, 152.0, 147.6, 146.9, 135.5, 134.9, 133.9, 133.2, 132.9, 130.9, 130.7, 129.8, 129.3, 129.2, 129.1, 128.8, 128.4, 126.5, 125.9, 117.9, 117.2, 45.4, 34.1, 33.9, 30.3; MALDI-TOF MS⁺ (CHCA) m/z: 2154.7[M+H₂O]⁺; IR (neat) ν (cm⁻¹) 1601 (C=C), 1730 (C=O), 3622 (OH).

3. Additional X-Ray Crystal Structure Figures

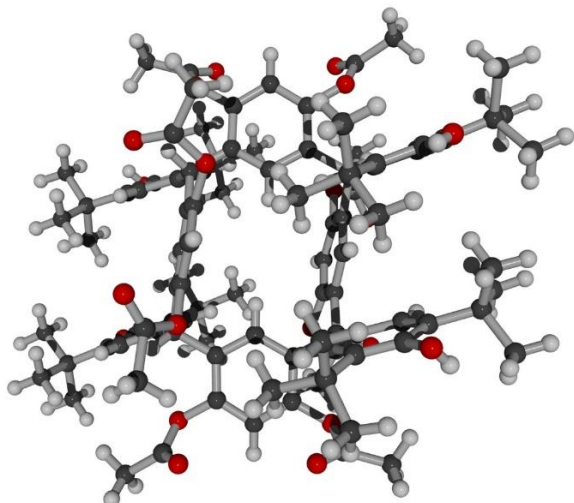


Figure S1. X-Ray crystal structure of compound *rctt-2*. Solvent of crystallization removed for clarity.

Empirical formula	C _{203.82} H _{244.63} Cl _{17.63} O ₄₀
Formula weight	3604.93
Temperature	160 K
Wavelength	0.71073
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 11.5721(4) Å, b = 16.6408(5) Å, c = 26.1539(8) α = 84.7250(10)°, β = 81.7580(10)°, γ = 89.9360(10)°
Volume	4692.9(3) Å ³
Z	1
Density (calculated)	1.206
Absorption coefficient	0.181
F(000)	1917
Crystal size	0.176 × 0.171 × 0.115 mm ³
Theta range for data collection	0.790 – 30.953°
Index ranges	-15 ≤ h ≤ 16, -15 ≤ k ≤ 24, -32 ≤ l ≤ 35
Reflections collected	26976
Independent reflections	19900 [R(int) = 0.0301]
Completeness to theta = 30.953°	85.6 %
Absorption correction	Multiscan
Max. and min. transmission	0.669 and 0.746
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	26976 / 0 / 1176
Goodness-of-fit on F ²	1.037
Final R indices [I > 2σ(I)]	R1 = 0.0698, wR2 = 0.1901
R indices (all data)	R1 = 0.0916, wR2 = 0.2105
Largest diff. peak and hole	1.478 and -0.858 e.Å ⁻³

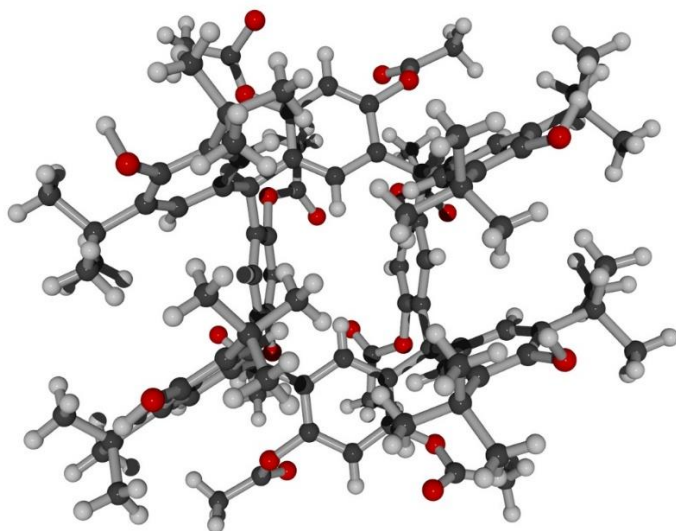


Figure S2. X-Ray crystal structure of compound *rccc-2*. Solvent of crystallization removed for clarity.

Empirical formula	C _{226.28} H _{248.42} O _{43.38}
Formula weight	3686.11
Temperature	113 K
Wavelength	0.71073
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a = 21.154(5) Å, b = 19.669(5) Å, c = 25.429(7) Å β = 90.270(8)°
Volume	10580(5) Å ³
Z	2
Density (calculated)	1.157
Absorption coefficient	0.079
F(000)	3930
Crystal size	0.151 × 0.074 × 0.017 mm ³
Theta range for data collection	0.963 – 24.897°.
Index ranges	-23 ≤ h ≤ 23, -21 ≤ k ≤ 22, -28 ≤ l ≤ 26
Reflections collected	15528
Independent reflections	9934 [R(int) = 0.0866]
Completeness to theta = 24.897°	84.3 %
Absorption correction	Multiscan
Max. and min. transmission	0.843 and 0.843
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	15528 / 0 / 1208
Goodness-of-fit on F ²	2.192
Final R indices [I > 2σ(I)]	R1 = 0.2114, wR2 = 0.5426
R indices (all data)	R1 = 0.2826, wR2 = 0.5671
Largest diff. peak and hole	1.048 and -0.803 e.Å ⁻³

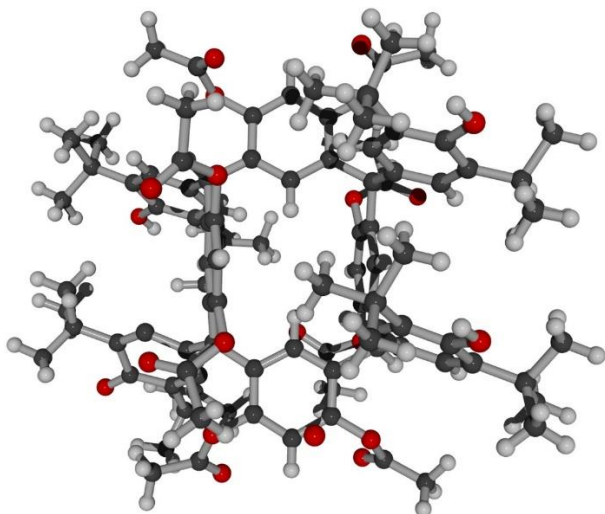


Figure S3. X-Ray crystal structure of compound *rctt-2*[Ox₁]. Solvent of crystallization removed for clarity.

Empirical formula	C ₁₀₆ H ₁₂₄ Cl ₁₆ O ₂₀
Formula weight	1930.74
Temperature	163 K
Wavelength	0.71073
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a = 19.6983(14) Å, b = 20.2034(14) Å, c = 26.3162(18) Å β = 97.770(1)°
Volume	10377.0(13) Å ³
Z	4
Density (calculated)	1.236
Absorption coefficient	0.232
F(000)	4088
Crystal size	0.207 × 0.182 × 0.094 mm ³
Theta range for data collection	1.216 – 25.242°
Index ranges	-24 ≤ h ≤ 26, -27 ≤ k ≤ 27, -35 ≤ l ≤ 35
Reflections collected	26208
Independent reflections	17150 [R(int) = 0.0470]
Completeness to theta = 25.242°	99.1 %
Absorption correction	Multiscan
Max. and min. transmission	0.668 and 0.746
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	26208 / 58 / 1249
Goodness-of-fit on F ²	1.517
Final R indices [I > 2σ(I)]	R1 = 0.1192, wR2 = 0.3589
R indices (all data)	R1 = 0.1573, wR2 = 0.3975
Largest diff. peak and hole	2.125 and -1.279 e.Å ⁻³

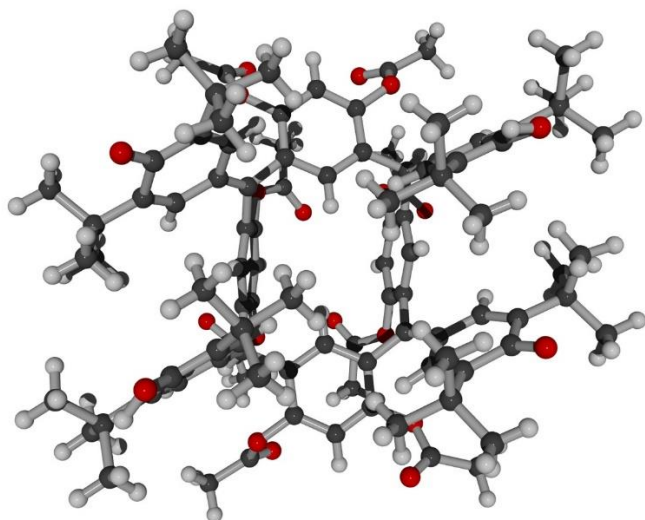


Figure S4. X-Ray crystal structure of compound *rccc-2*[Ox₂]. Solvent of crystallization removed for clarity.

Empirical formula	C _{107.91} H _{119.53} Cl _{12.27} O ₂₀
Formula weight	1816.99
Temperature	113 K
Wavelength	0.71073
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a = 21.532(3) Å, b = 19.643(3) Å, c = 25.299(4) Å β = 90.699(4)°
Volume	10700(3) Å ³
Z	4
Density (calculated)	1.128
Absorption coefficient	0.131
F(000)	3885
Crystal size	0.464 × 0.249 × 0.067 mm ³
Theta range for data collection	1.312 – 24.811°
Index ranges	-24 ≤ h ≤ 25, -23 ≤ k ≤ 22, -27 ≤ l ≤ 29
Reflections collected	17844
Independent reflections	14732 [R(int) = 0.0501]
Completeness to theta = 24.811°	96.7 %
Absorption correction	Multiscan
Max. and min. transmission	0.607 and 0.733
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17844 / 0 / 1273
Goodness-of-fit on F ²	2.412
Final R indices [I > 2σ(I)]	R1 = 0.1729, wR2 = 0.5187
R indices (all data)	R1 = 0.1893, wR2 = 0.5270
Largest diff. peak and hole	1.360 and -0.758 e.Å ⁻³

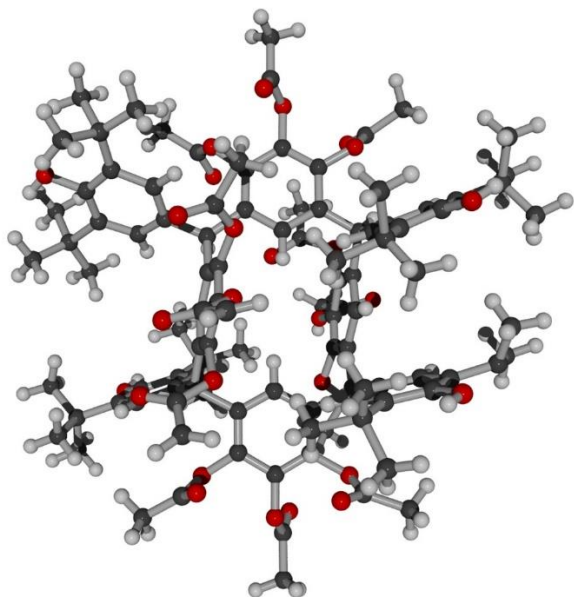


Figure S5. X-Ray crystal structure of compound *rcct**-**3**. Solvent of crystallization removed for clarity.

Empirical formula	C _{112.91} H ₁₂₆ Cl _{15.54} O ₂₈
Formula weight	2482.11
Temperature	113 K
Wavelength	0.71073
Crystal system	triclinic
Space group	P 1
Unit cell dimensions	a = 14.334(2) Å, b = 15.534(2) Å, c = 16.891(2) Å α = 69.752(4)°, β = 70.947(4)°, γ = 76.995(8)°
Volume	3308.6(8) Å ³
Z	1
Density (calculated)	1.246
Absorption coefficient	0.388
F(000)	1292
Crystal size	0.171 × 0.171 × 0.096 mm ³
Theta range for data collection	1.934 – 20.112°
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 12, -16 ≤ l ≤ 15
Reflections collected	8228
Independent reflections	7053 [R(int) = 0.0197]
Completeness to theta = 20.112°	1.31/0.66
Absorption correction	Multiscan
Max. and min. transmission	0.923 and 0.977
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8228 / 3 / 1248
Goodness-of-fit on F ²	1.629
Final R indices [I > 2σ(I)]	R1 = 0.1285, wR2 = 0.3326
R indices (all data)	R1 = 0.1411, wR2 = 0.3522
Largest diff. peak and hole	1.628 and -0.519 e.Å ⁻³

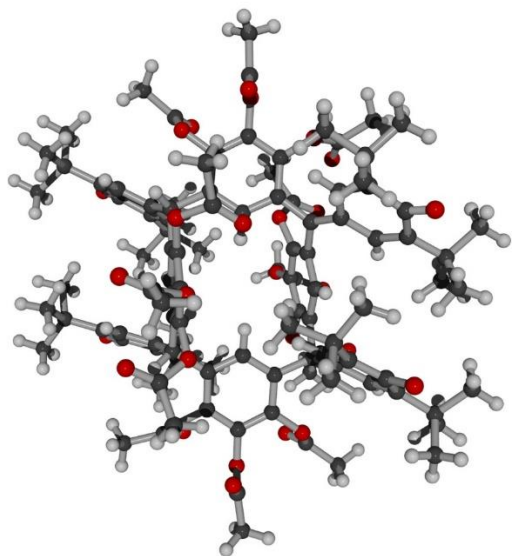


Figure S6. X-Ray crystal structure of compound *rctt-3*[Ox₁]. Solvent of crystallization removed for clarity.

Empirical formula	C _{115.06} H _{124.72} Cl _{9.97} O _{30.52}
Formula weight	2349.45
Temperature	113 K
Wavelength	0.71073
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 14.4911(11) Å, b = 17.0462(12) Å, c = 27.359(2) Å α = 72.867(2)°, β = 86.978(2)°, γ = 77.872(2)°
Volume	V = 6313.8(8) Å ³
Z	2
Density (calculated)	1.236
Absorption coefficient	0.290
F(000)	2458
Crystal size	0.185 × 0.169 × 0.143 mm ³
Theta range for data collection	0.779 – 31.572°
Index ranges	-20 ≤ h ≤ 21, -19 ≤ k ≤ 24, -40 ≤ l ≤ 37
Reflections collected	34518
Independent reflections	23919 [R(int) = 0.0260]
Completeness to theta = 31.572°	81.5 %
Absorption correction	Multiscan
Max. and min. transmission	0.923 and 0.977
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	34518 / 0 / 1433
Goodness-of-fit on F ²	1.727
Final R indices [I > 2σ(I)]	R1 = 0.1355, wR2 = 0.4054
R indices (all data)	R1 = 0.1697, wR2 = 0.4384
Largest diff. peak and hole	2.88 and -1.897 e.Å ⁻³

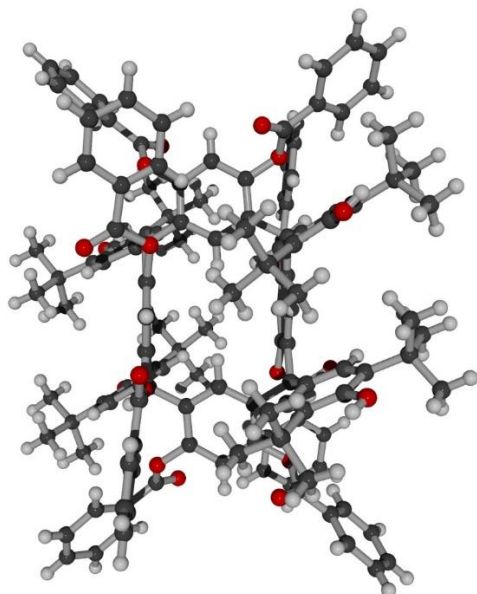


Figure S7. X-Ray crystal structure of compound *rctt-4*. Solvent of crystallization removed for clarity.

Empirical formula	C ₇₆ H ₇₄ Cl _{8.45} O ₂₈
Formula weight	1163.35
Temperature	113 K
Wavelength	0.71073
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 13.0381(3) Å, b = 16.6752(4) Å, c = 17.4483(4) Å α = 61.7110(10)°, β = 79.0370(10)°, γ = 74.2950(10)°
Volume	V = 3207.14(13) Å ³
Z	2
Density (calculated)	1.203
Absorption coefficient	0.080
F(000)	1236
Crystal size	0.268 × 0.209 × 0.117 mm ³
Theta range for data collection	2.175 – 36.906°
Index ranges	-22 ≤ h ≤ 19, -28 ≤ k ≤ 27, -29 ≤ l ≤ 25
Reflections collected	29697
Independent reflections	20630 [R(int) = 0.0400]
Completeness to theta = 25.242°	91.6 %
Absorption correction	Multiscan
Max. and min. transmission	0.399 and 0.439
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	29697 / 0 / 825
Goodness-of-fit on F ²	1.304
Final R indices [I > 2σ(I)]	R1 = 0.0666, wR2 = 0.1778
R indices (all data)	R1 = 0.0986, wR2 = 0.2040
Largest diff. peak and hole	3.520 and -0.459 e.Å ⁻³

4. Additional Figures

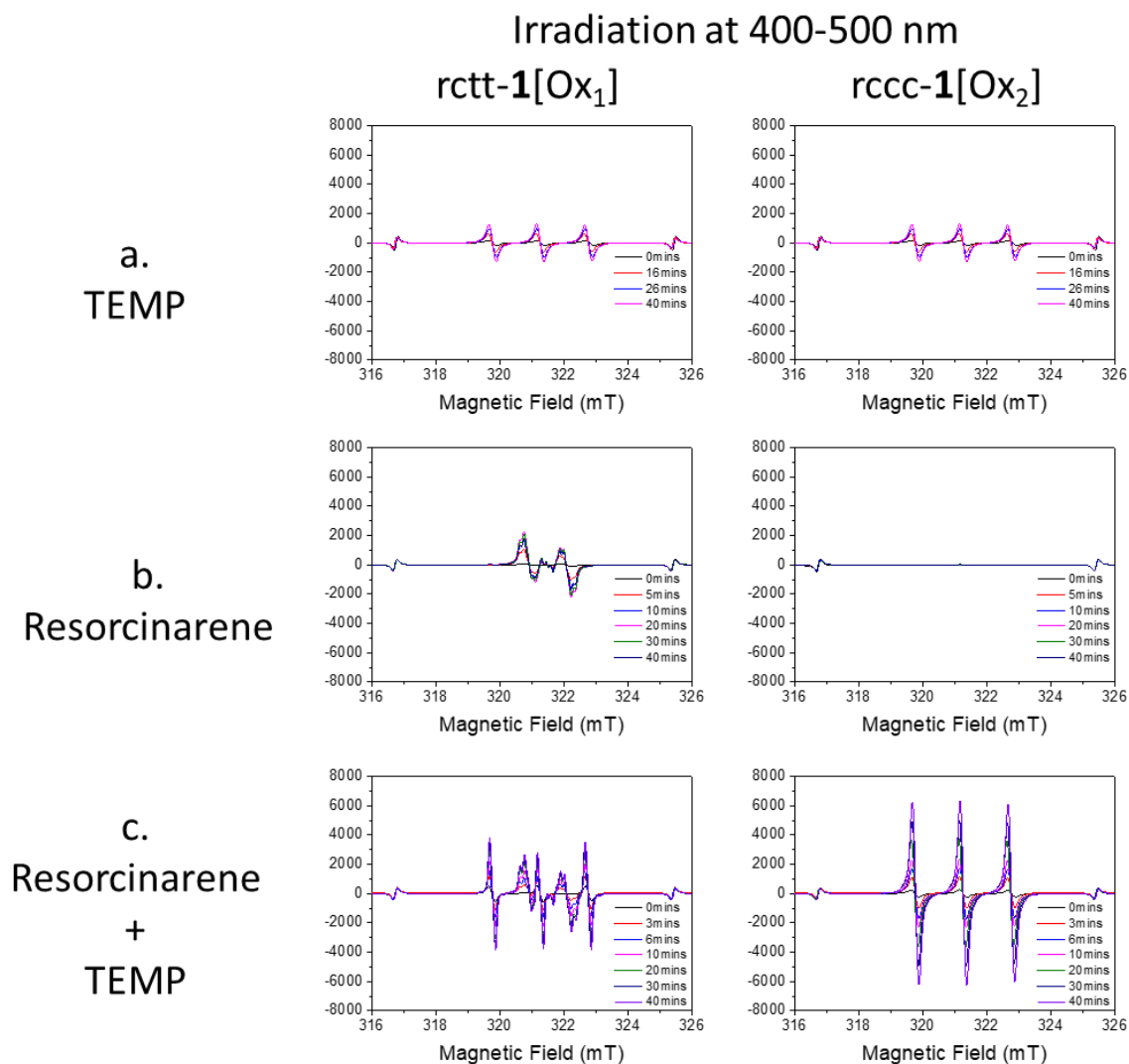


Figure S8. ESR spectrum in the presence and absence of spin trap for singlet oxygen (2,2,6,6-tetramethylpiperidone, TEMP) in chloroform. a. ESR spectra of TEMP (0.26 M, 50 μ L) during irradiation at 400-500 nm. b. ESR spectra of rctt-1[Ox₁] (1.26×10^{-3} M, 50 μ L) and rccc-1[Ox₂] (1.26×10^{-3} M, 50 μ L) during irradiation at 400-500 nm. c. ESR spectra of rctt-1[Ox₁] (1.26×10^{-3} M, total volume = 50 μ L) with TEMP (0.26M) and rccc-1[Ox₂] (1.26×10^{-3} M, total volume = 50 μ L) with TEMP (0.26 M) during irradiation at 400-500 nm.

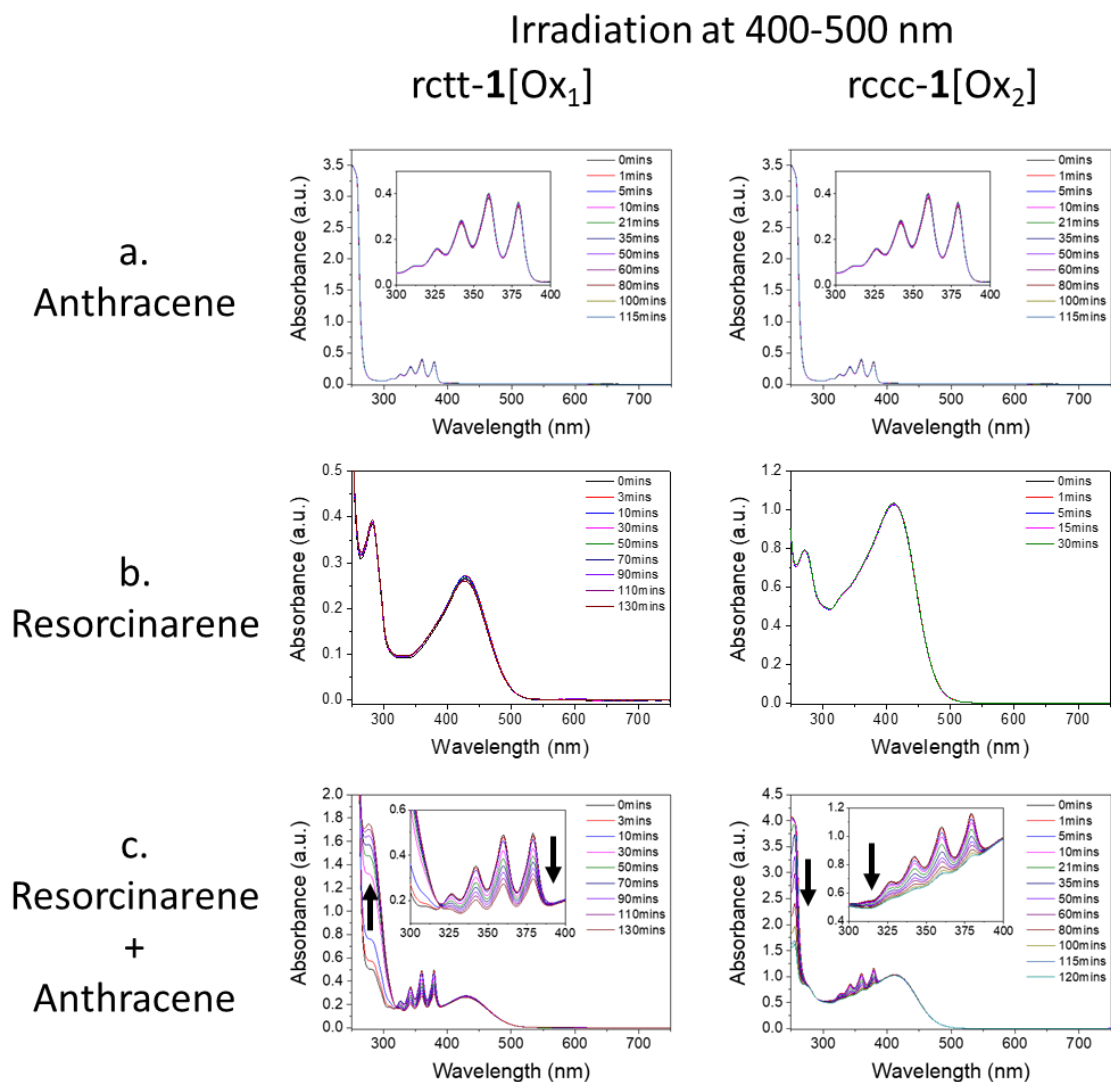


Figure S9. UV-Vis spectra with a singlet oxygen ¹O₂ endoperoxide trap (anthracene) in chloroform. a. UV-Vis spectra of anthracene (4.76×10^{-5} M, 3.0 mL) during irradiation at 400-500 nm in a 1 cm path-length quartz cuvette. b. UV-Vis spectra of rctt-1[Ox₁] (1.26×10^{-5} M, 50 μ L) and rccc-1[Ox₂] (1.36×10^{-5} M, 50 μ L) during irradiation at 400-500 nm in a 1 cm path-length quartz cuvette. c. UV-Vis spectra of rctt-1[Ox₁] (1.26×10^{-5} M, total volume = 3.0 mL) with anthracene (4.76×10^{-5} M) and rccc-1[Ox₂] (1.36×10^{-5} M, total volume = 3.0 mL) with anthracene (4.76×10^{-5} M) during irradiation at 400-500 nm in a 1 cm path-length quartz cuvette.

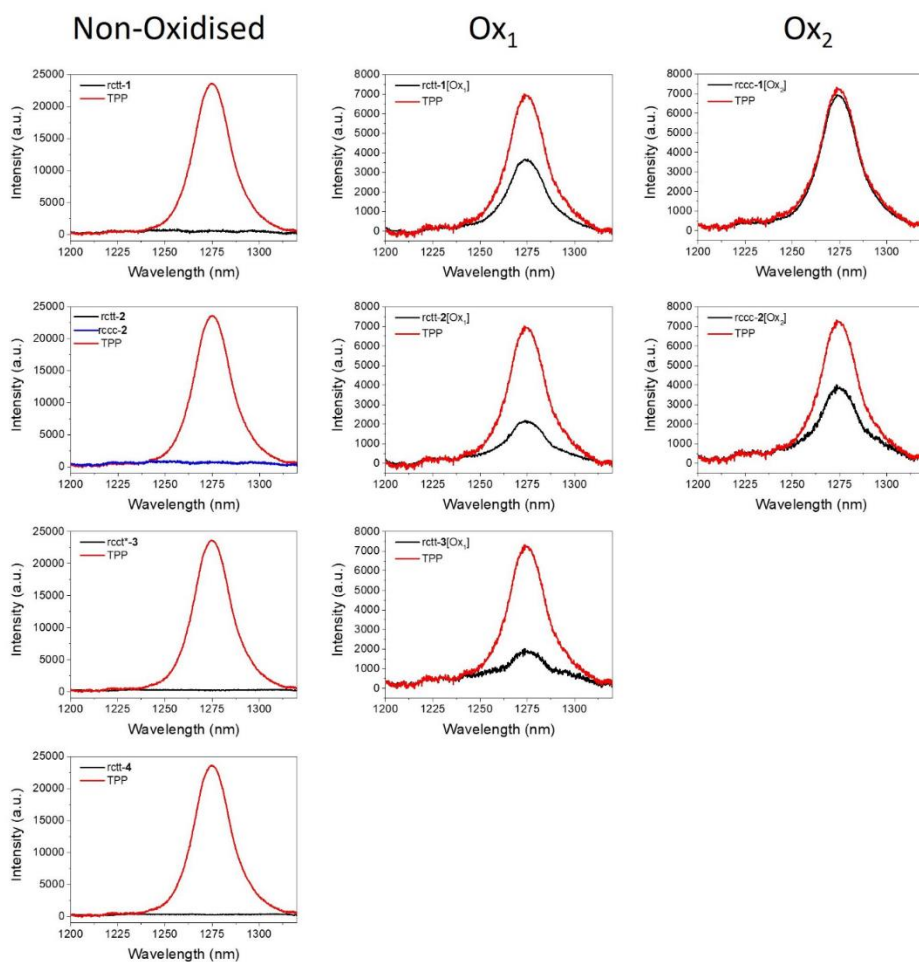


Figure S10. Singlet oxygen phosphorescence spectra for compound families **1**, **2**, **3** and **4** relative to meso-tetraphenylporphyrin reference (TPP, red lines) organized by oxidation state (horizontal) demonstrating increasing amounts of singlet oxygen generated as oxidation number increases (left to right).

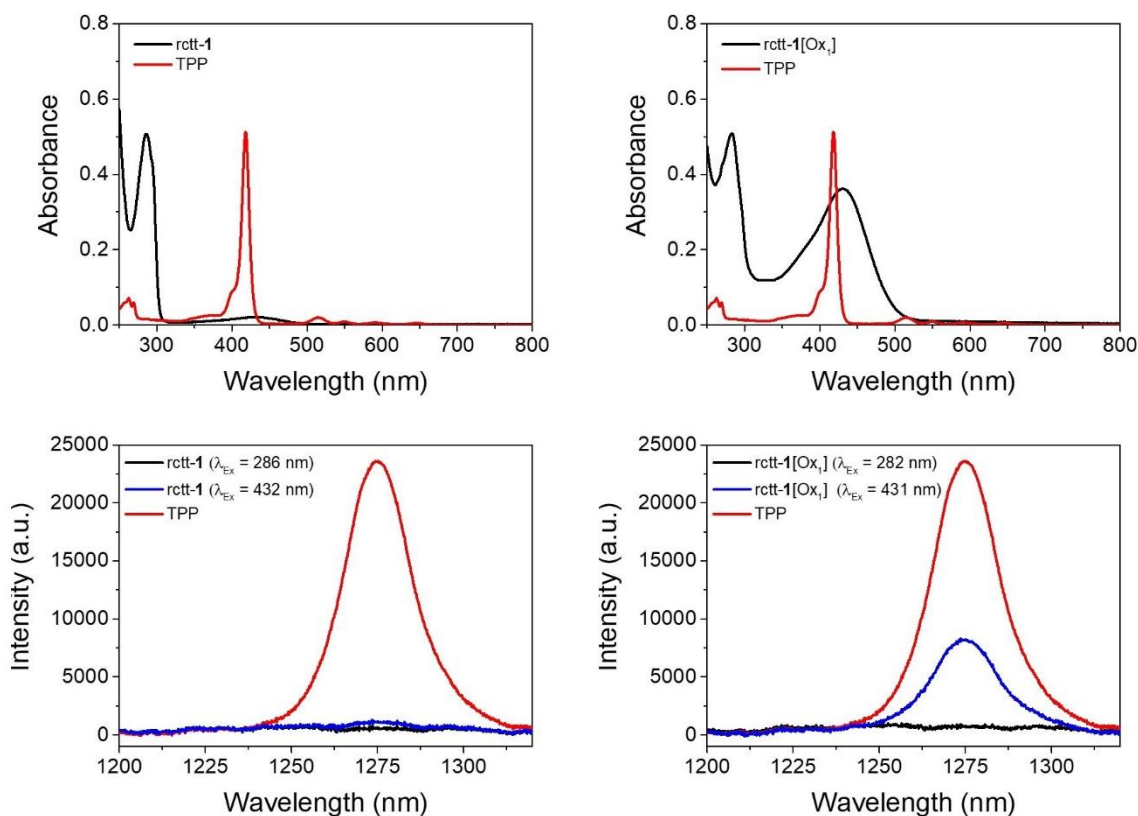


Figure S11. UV-Vis (top) and singlet oxygen phosphorescence (bottom) spectra for rctt-1 and rctt-1[Ox₁] relative to meso-tetraphenylporphyrin reference (TPP, red lines). Singlet oxygen phosphorescence spectra (bottom) have been recorded at two excitation wavelengths (282 nm and 431 nm), demonstrating that singlet oxygen is only generated during irradiation at the longer wavelength for oxidized compound and that no singlet oxygen is generated at either wavelength for non-oxidised compounds.

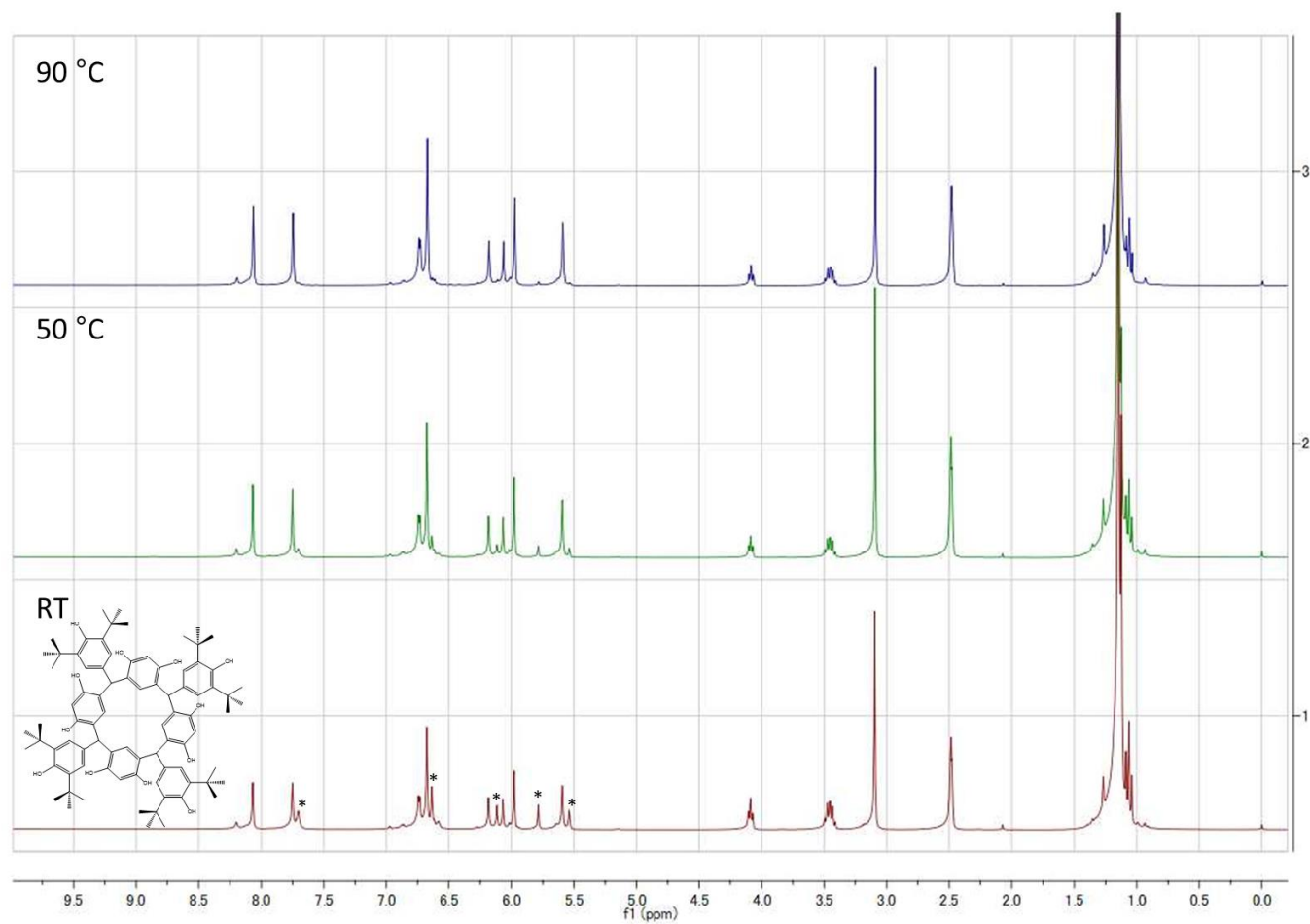


Figure S12. ¹H NMR spectra recorded at 70 °C in *d*₆-DMSO of Precursor 'A' synthesized at various reaction temperatures. The *rccc* isomer aromatic CH signals are marked with asterisks (*).

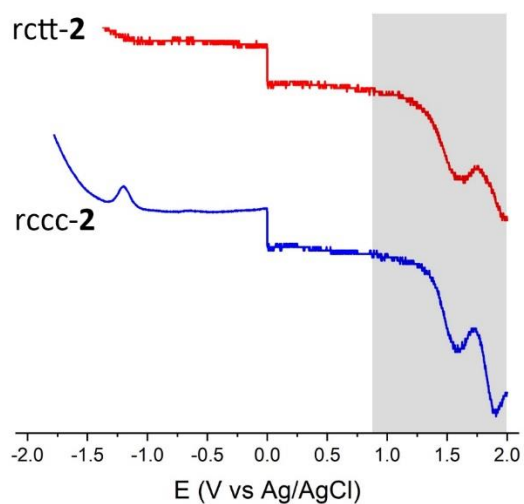


Figure S13. Differential pulsed voltammetry (DPV) of **rctt-2** and **rccc-2**. The peak at +1.6 V in both traces is associated with the first oxidation to $[Ox_1]$ -type. Compound **rccc-2** has an additional peak at +1.8 V associated with oxidation to the $[Ox_2]$ state. These data show that **rccc-2** and its $[Ox_1]$ form are more easily oxidized to the higher oxidation state enabling isolation of **rccc-2** $[Ox_2]$ while oxidation of **rctt-2** is not preferred.

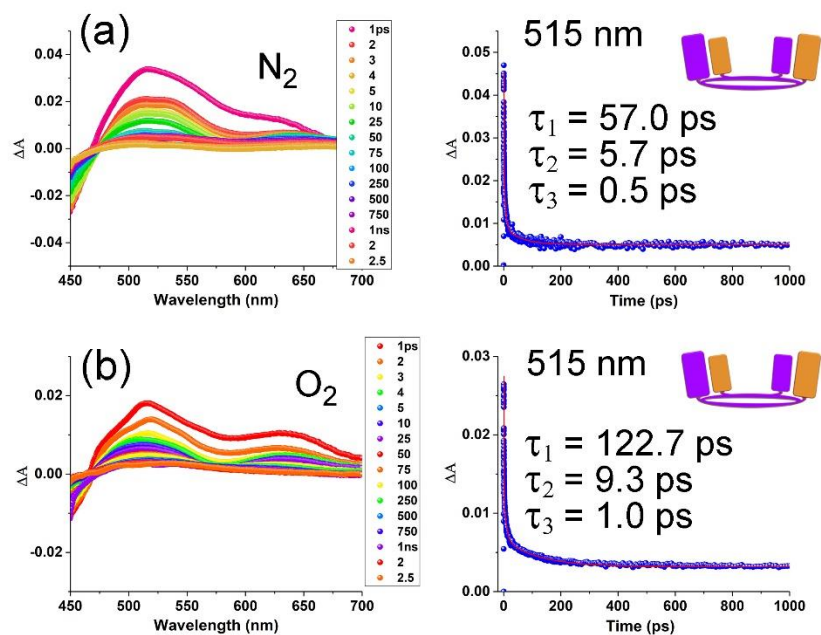


Fig. S14. Femtosecond transient absorption spectroscopy of rccc-1[Ox₂] in chloroform purged with (a) N₂ or (b) O₂. Traces at right show absorbance decay profiles at 520/510 nm for rccc-1[Ox₁] under N₂ and O₂.

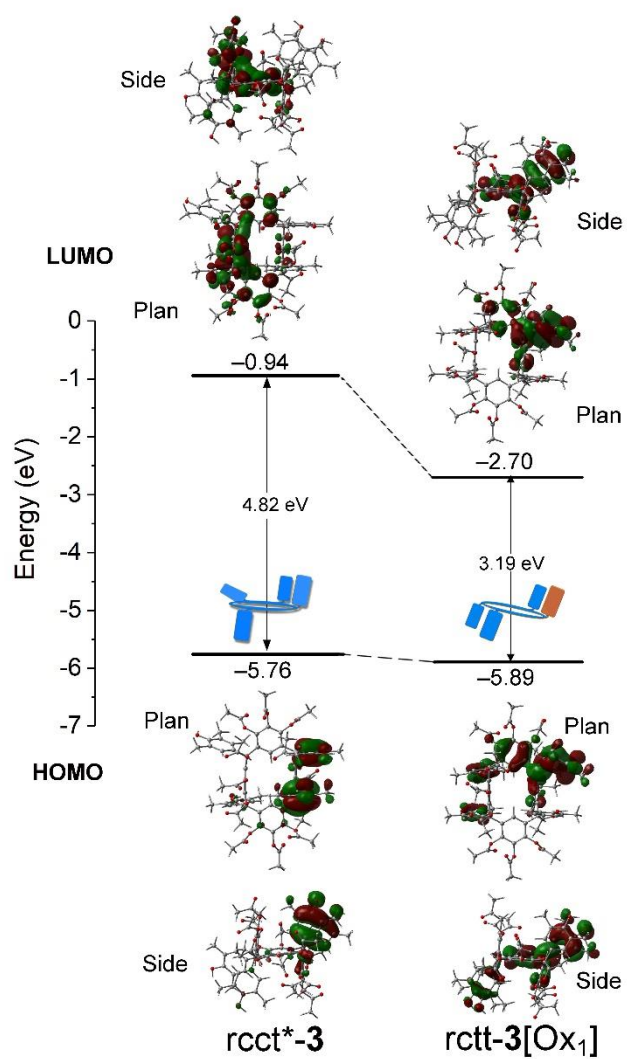


Figure S15. Structure and energy levels of frontier molecular orbitals of (from left) rcct*-3, rctt-3[Ox₁]. Plan and side elevations of each orbital are shown.

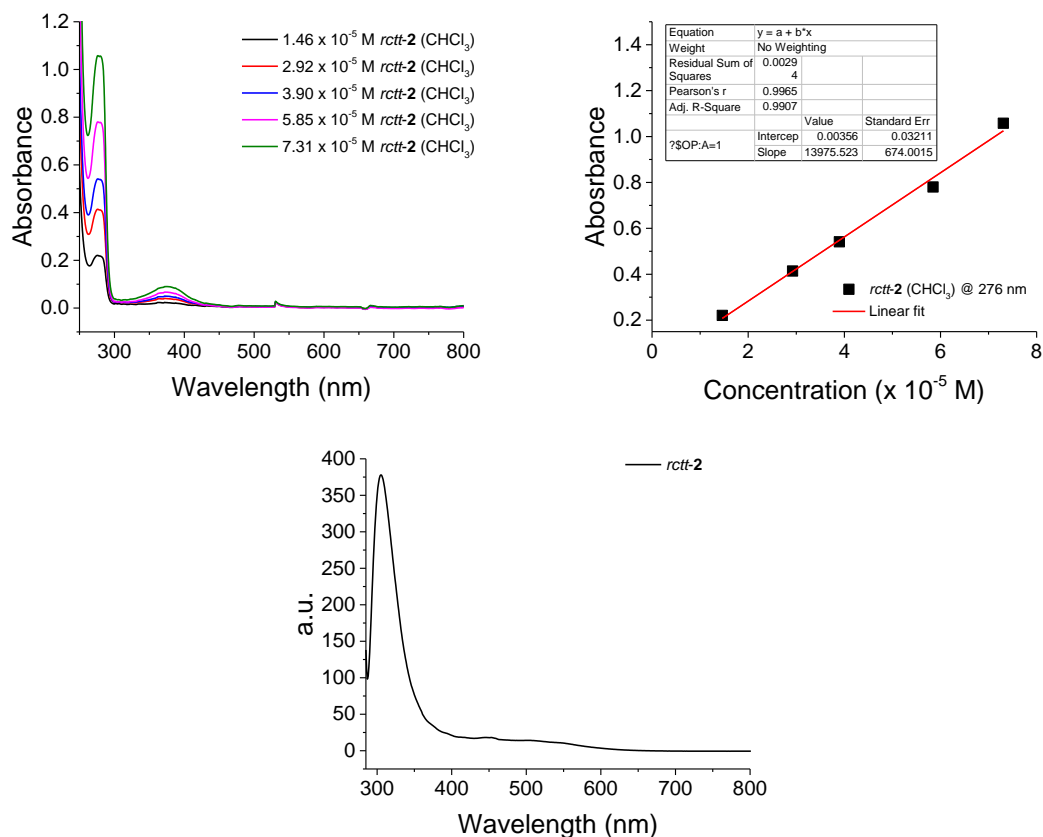
5. Absorption/Emission Spectroscopies

General Information

Concentration studies were carried out by making a series of serial dilutions in volumetric glassware and spectra were recorded using a 1 cm path length quartz cell with 4 polished faces at room temperature. Fluorescence spectra were recorded using a 1 cm path length quartz cell with 4 polished faces at room temperature.

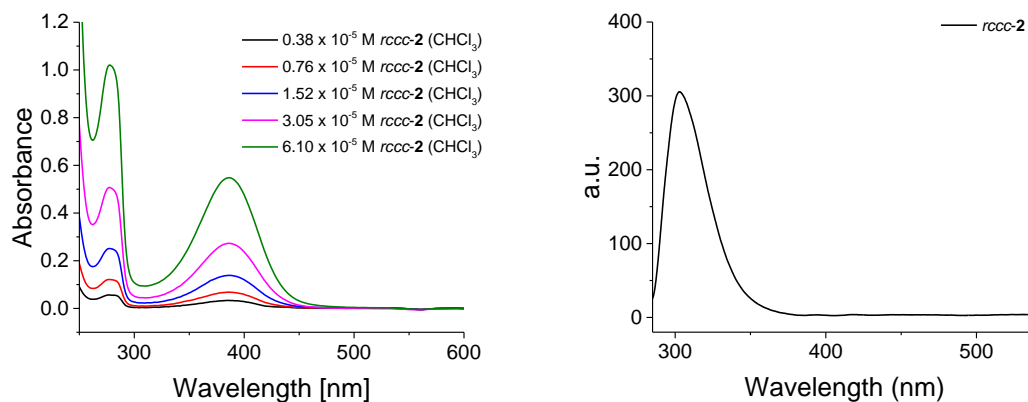
Absorption/Emission Spectroscopies of compounds *rctt-1*, *rctt-1*[Ox₁] and *rccc-1*[Ox₂] has been reported.^{S1}

rctt-2



(Top left) Electronic absorption spectra for *rctt-2* at various concentrations in CHCl₃. (Top right) Beer-Lambert plot of *rctt-2* with linear fit to determine the extinction co-efficient at 276 nm. (Bottom) Emission spectra with excitation at 275 nm for *rctt-2* at 9.15 x 10⁻⁵ mol dm⁻³ in CHCl₃.

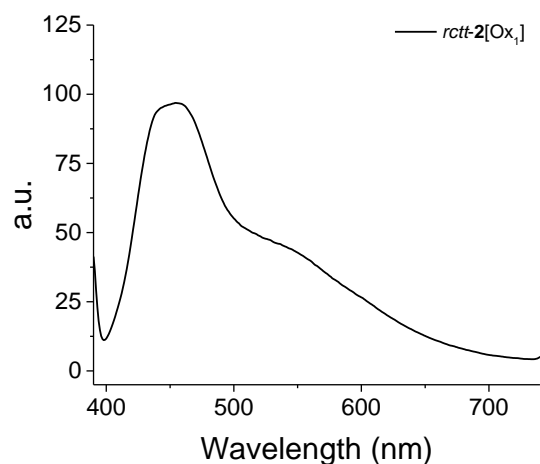
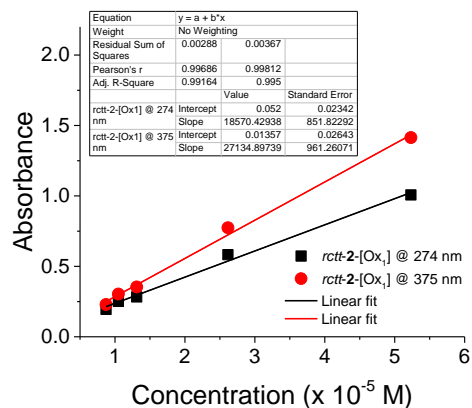
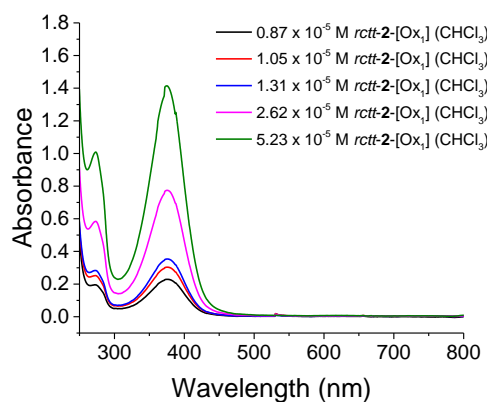
rccc-2



(Left) Electronic absorption spectra for *rccc-2* at various concentrations in CHCl_3 . (Right) Emission spectra with excitation at 275 nm for *rccc-2* at $6.10 \times 10^{-5} \text{ mol dm}^{-3}$ in CHCl_3 .

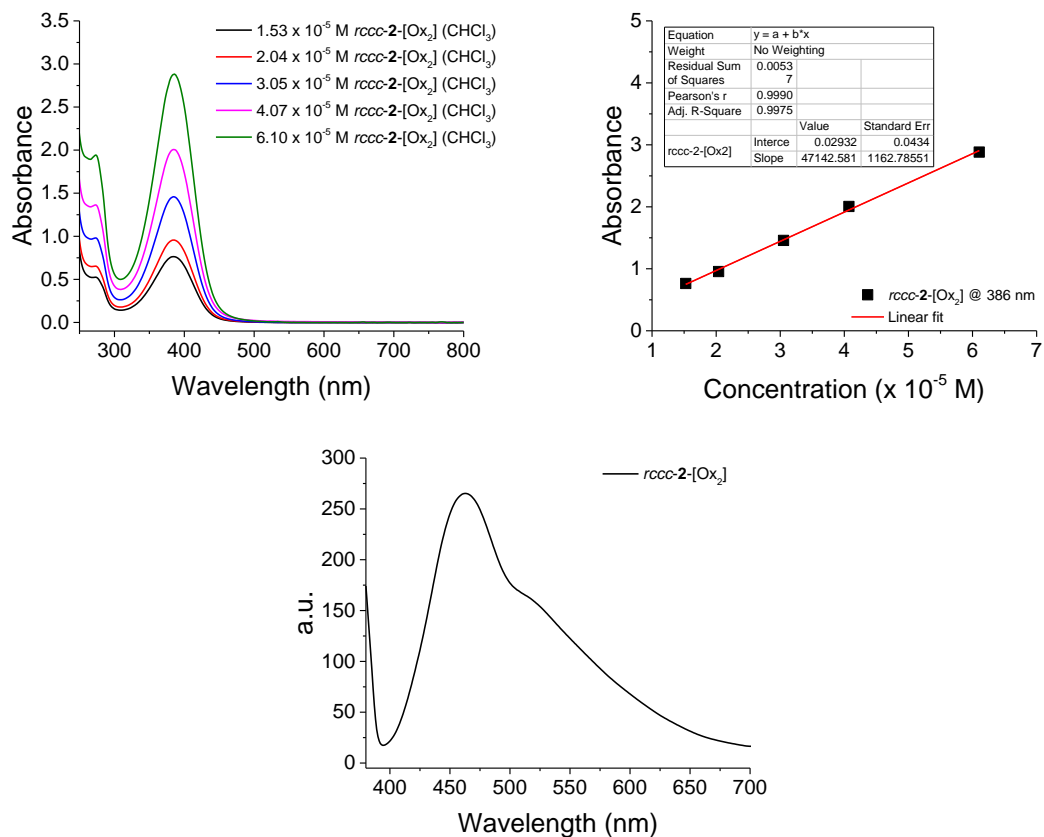
Note: Due to the presence of an oxidized impurity with an absorbance between 350-450 nm (suspected to be *rccc-2*[Ox₁]) the extinction co-efficient could not be calculated.

rctt-2[Ox₁]



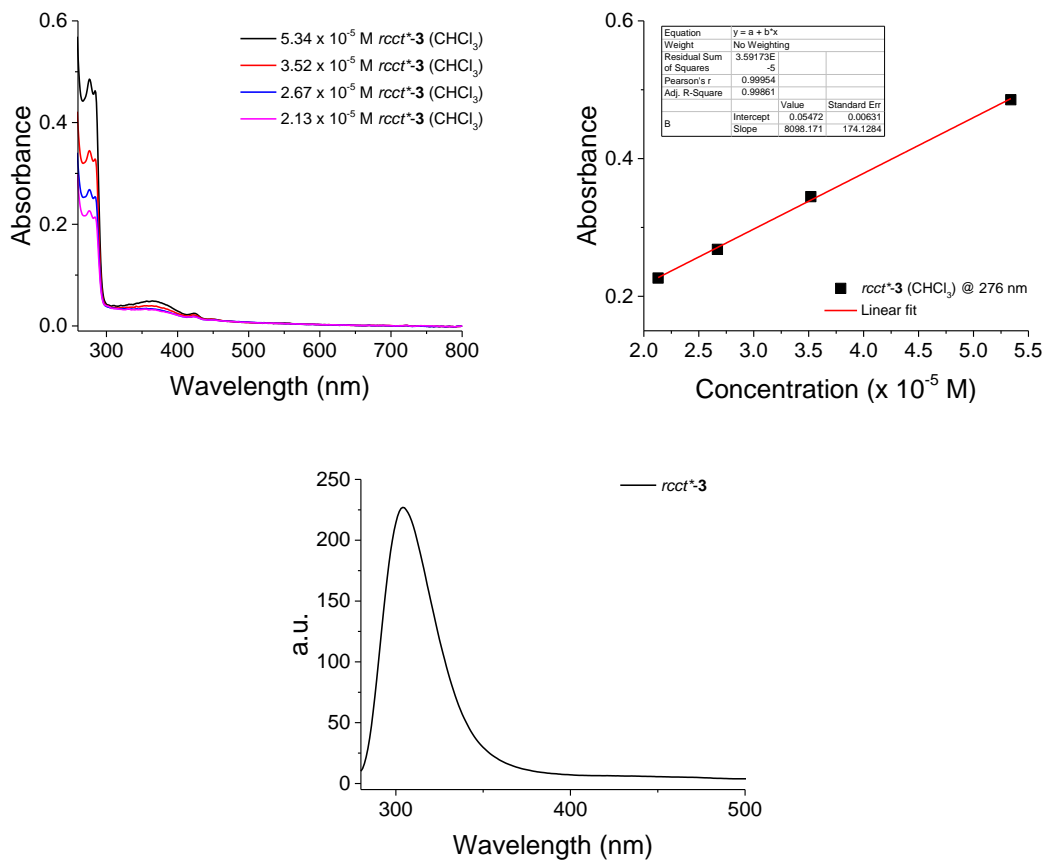
(Top left) Electronic absorption spectra for *rctt-2*[Ox₁] at various concentrations in CHCl₃. (Top right) Beer-Lambert plot of *rctt-2*[Ox₁] with linear fit to determine the extinction co-efficient at 274 nm and 375 nm. (Bottom) Emission spectra with excitation at 380 nm for *rctt-2*[Ox₁] at 5.23×10^{-5} mol dm⁻³ in CHCl₃.

rccc-2[Ox₂]



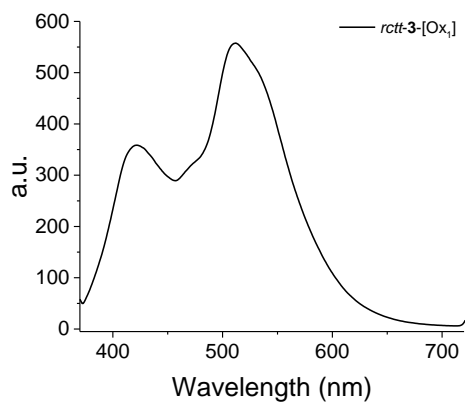
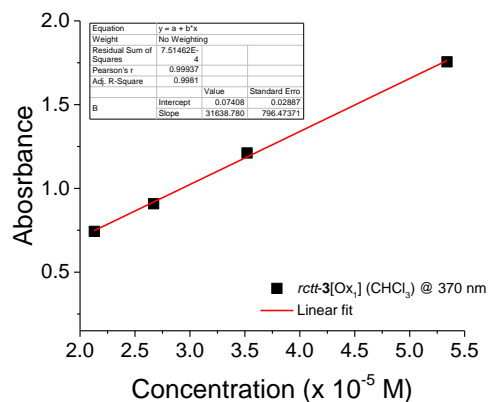
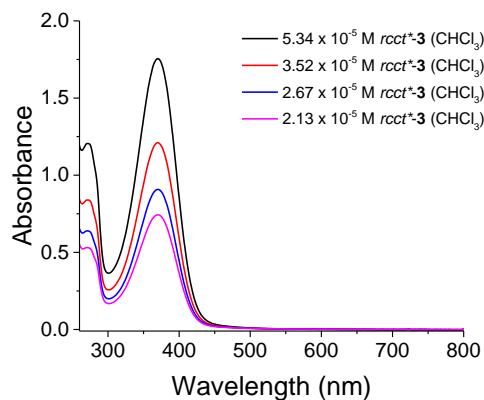
(Top left) Electronic absorption spectra for *rccc-2*[Ox₂] at various concentrations in CHCl₃. (Top right) Beer-Lambert plot of *rccc-2*[Ox₂] with linear fit to determine the extinction co-efficient at 386 nm. (Bottom) Emission spectra with excitation at 370 nm for *rccc-2*[Ox₂] at 6.10 x 10⁻⁵ mol dm⁻³ in CHCl₃.

*rcct**-3



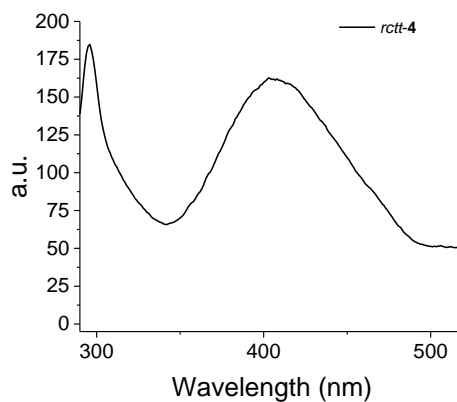
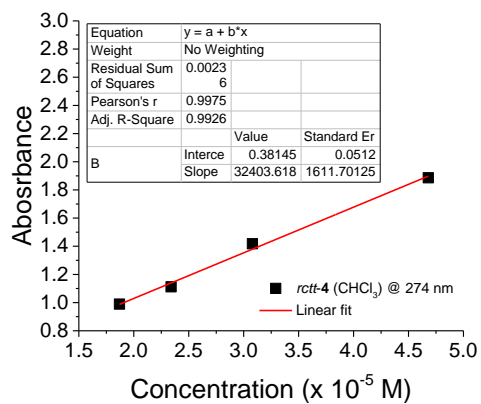
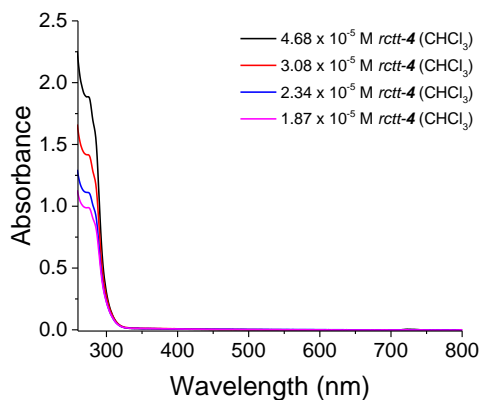
(Top left) Electronic absorption spectra for *rcct**-3 at various concentrations in CHCl₃. (Top right) Beer-Lambert plot of *rcct**-3 with linear fit to determine the extinction co-efficient at 276 nm. (Bottom) Emission spectra with excitation at 265 nm for *rcct**-3 at 5.34 × 10⁻⁵ mol dm⁻³ in CHCl₃.

rctt-3[Ox₁]



(Top left) Electronic absorption spectra for *rctt-3*[Ox₁] at various concentrations in CHCl₃. (Top right) Beer-Lambert plot of *rctt-3*[Ox₁] with linear fit to determine the extinction co-efficient at 370 nm. (Bottom) Emission spectra with excitation at 365 nm for *rctt-3*[Ox₁] at 5.34×10^{-5} mol dm⁻³ in CHCl₃.

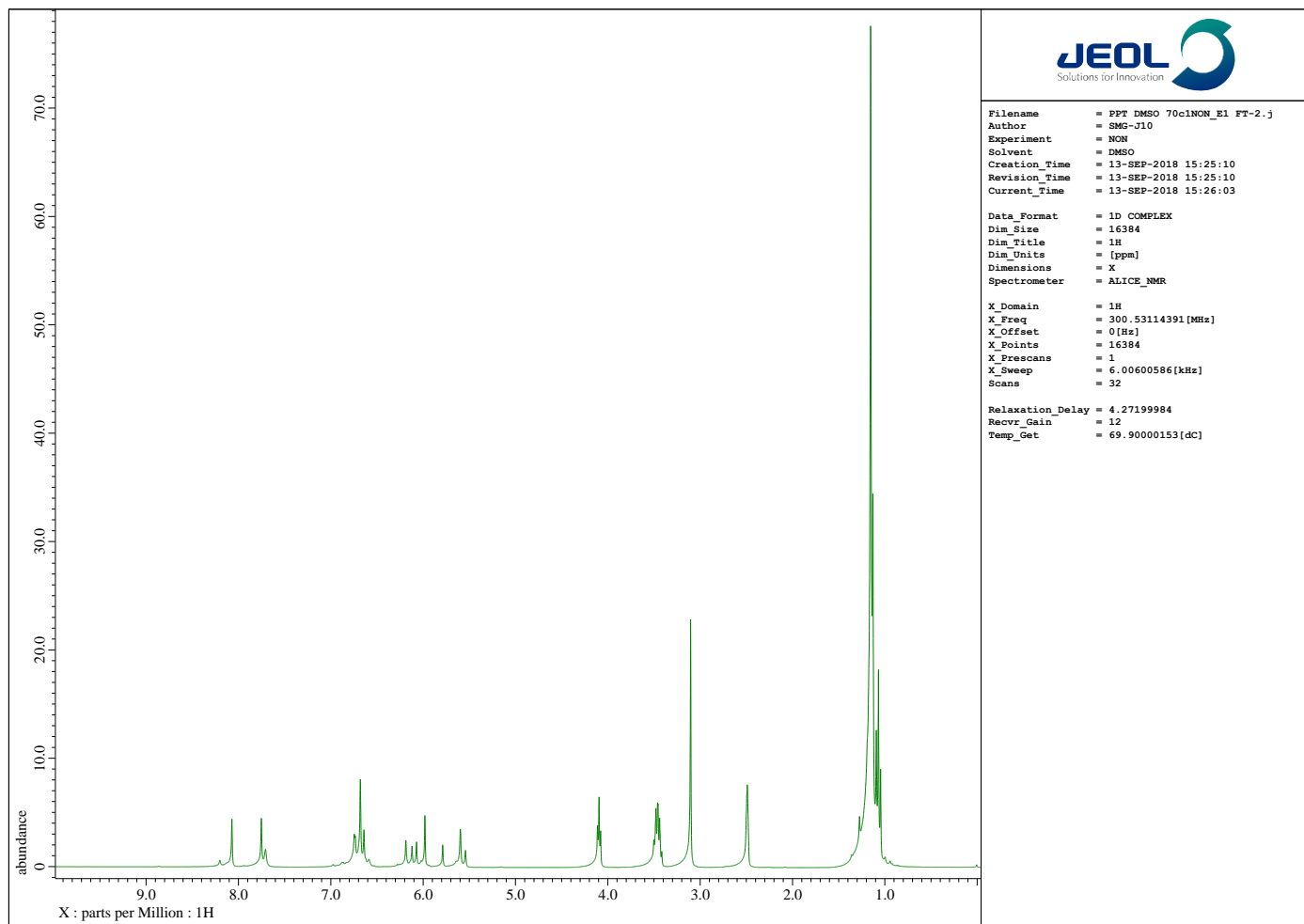
rctt-4



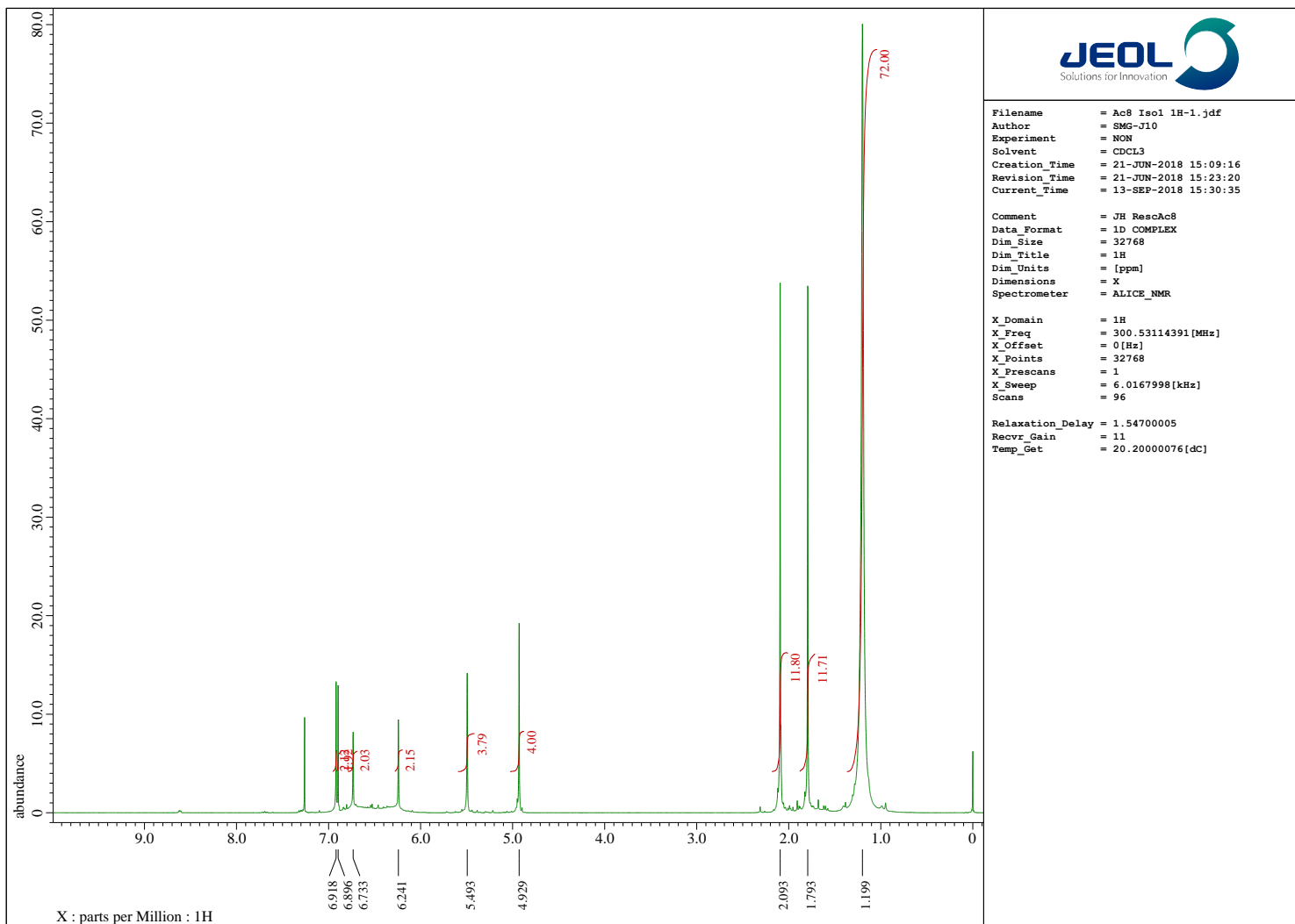
(Top left) Electronic absorption spectra for *rctt-4* at various concentrations in CHCl_3 . (Top right) Beer-Lambert plot of *rctt-4* with linear fit to determine the extinction co-efficient at 274 nm. (Bottom) Emission spectra with excitation at 270 nm for *rctt-4* at 4.68×10^{-5} mol dm^{-3} in CHCl_3 .

6. NMR and Mass spectra

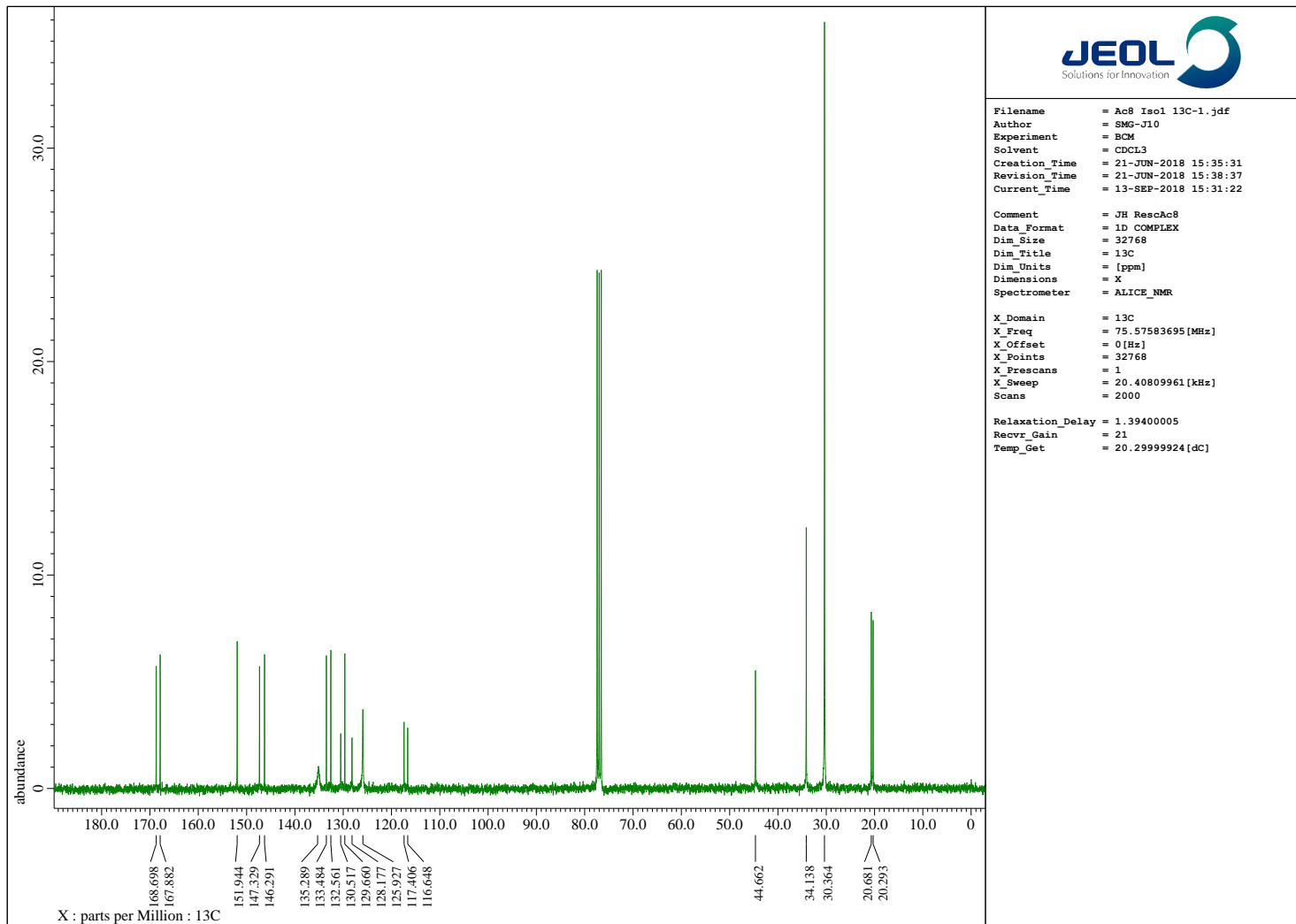
5 ¹H NMR Spectrum



rctt-2 ¹H NMR Spectrum



rctt-2 ¹³C NMR Spectrum



```

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Author       = SMG-J10
Experiment   = ECM
Solvent      = CDCL3
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Revision_Time = 21-JUN-2018 15:38:37
Current_Time  = 13-SEP-2018 15:31:22

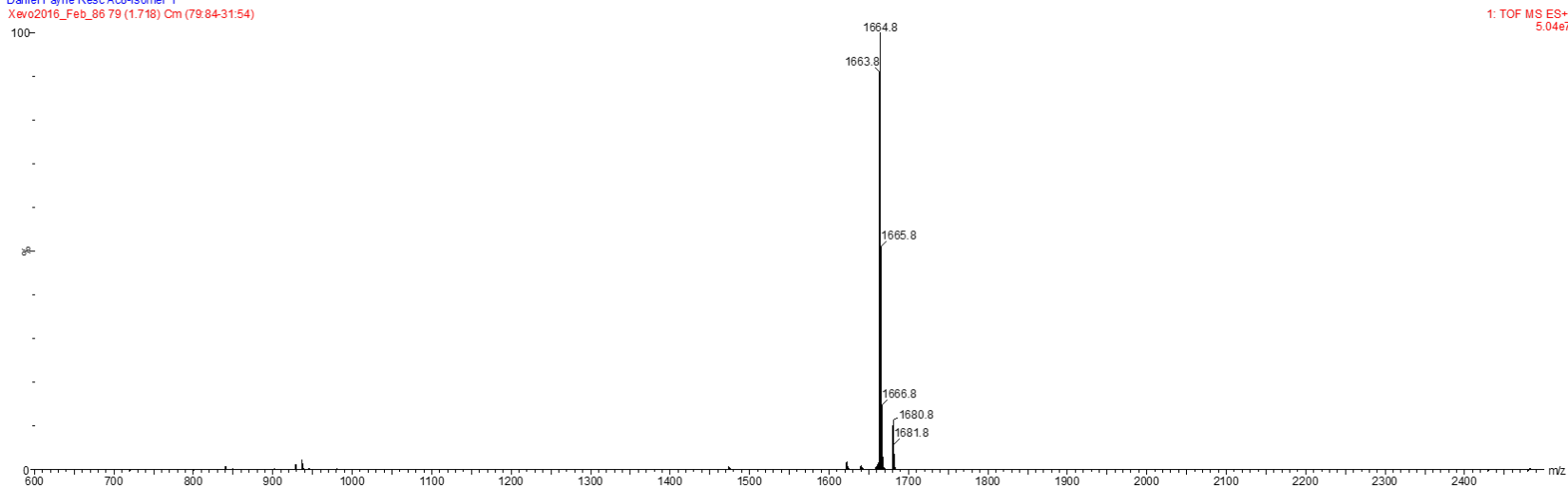
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Spectrometer = ALICE_NMR

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X_Points     = 32768
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Scans        = 2000

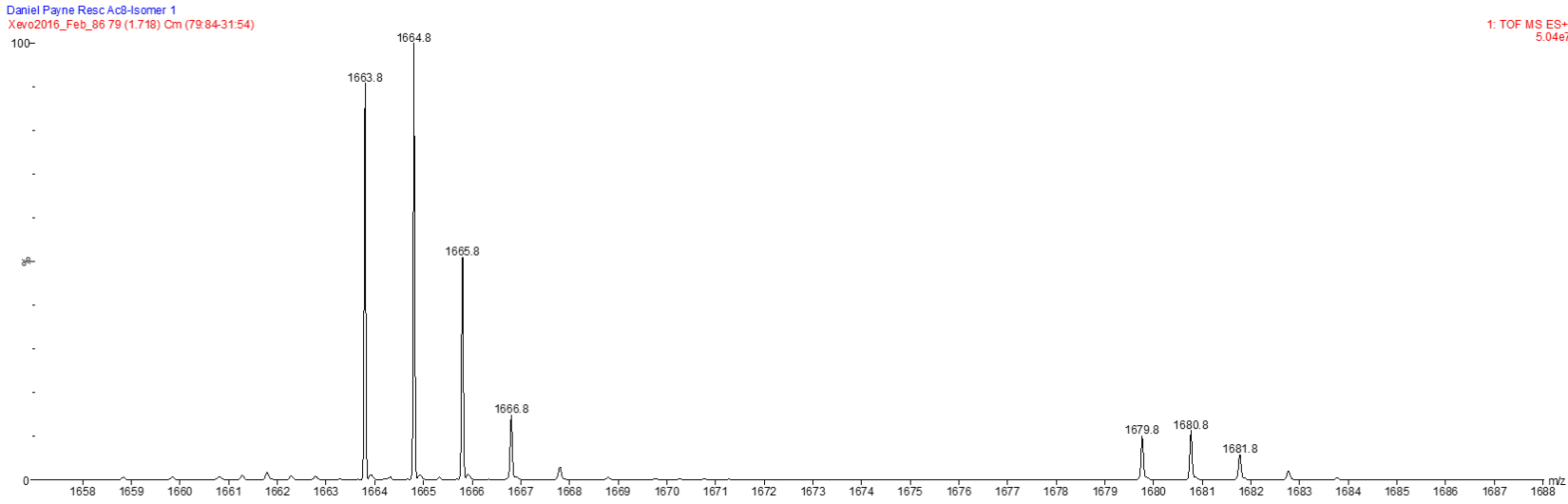
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rctt-2 mass Spectrum

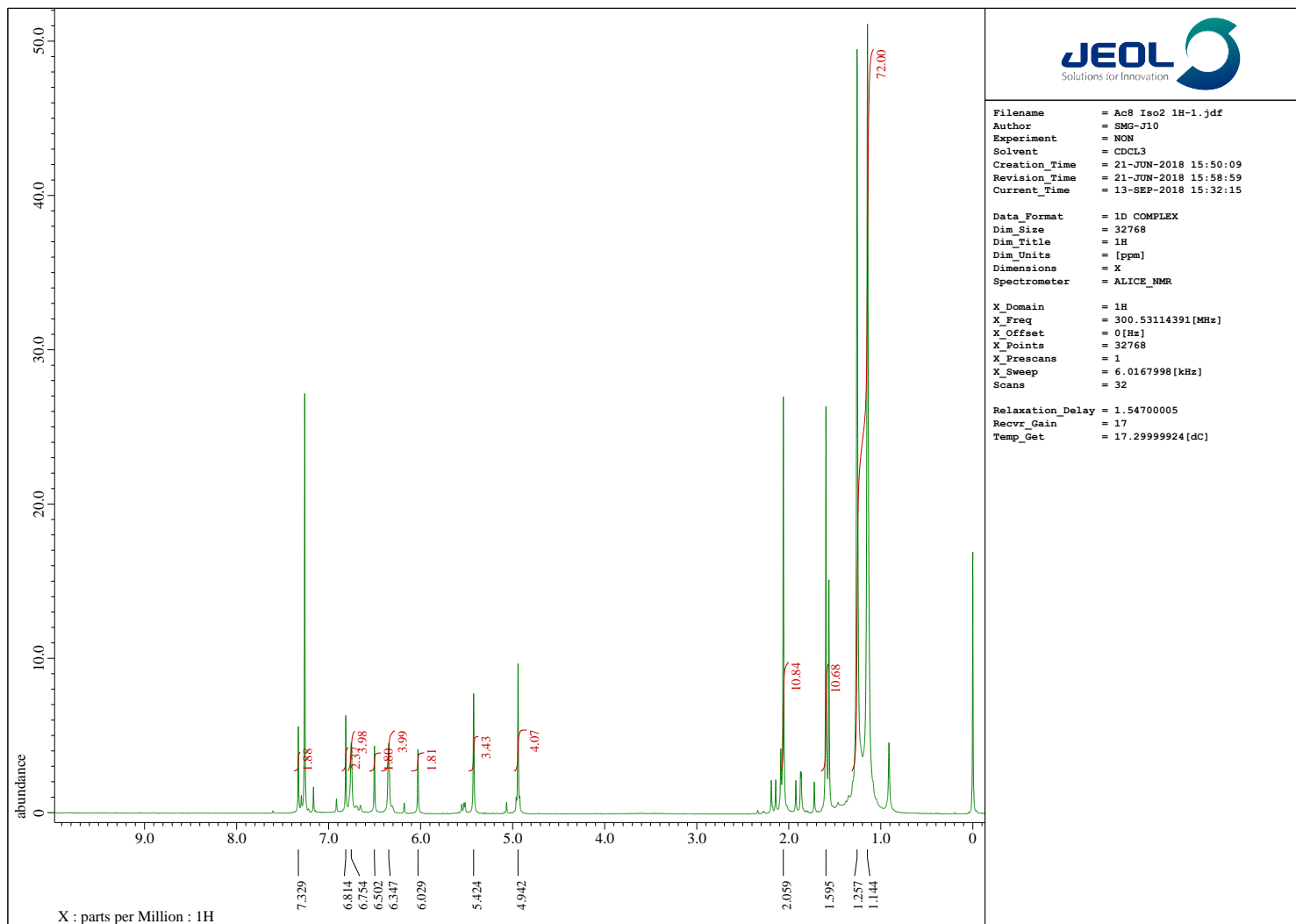
Daniel Payne Resc Ac8-Isomer 1
Xevo2016_Feb_86 79 (1.718) Cm (79.84-31:54)



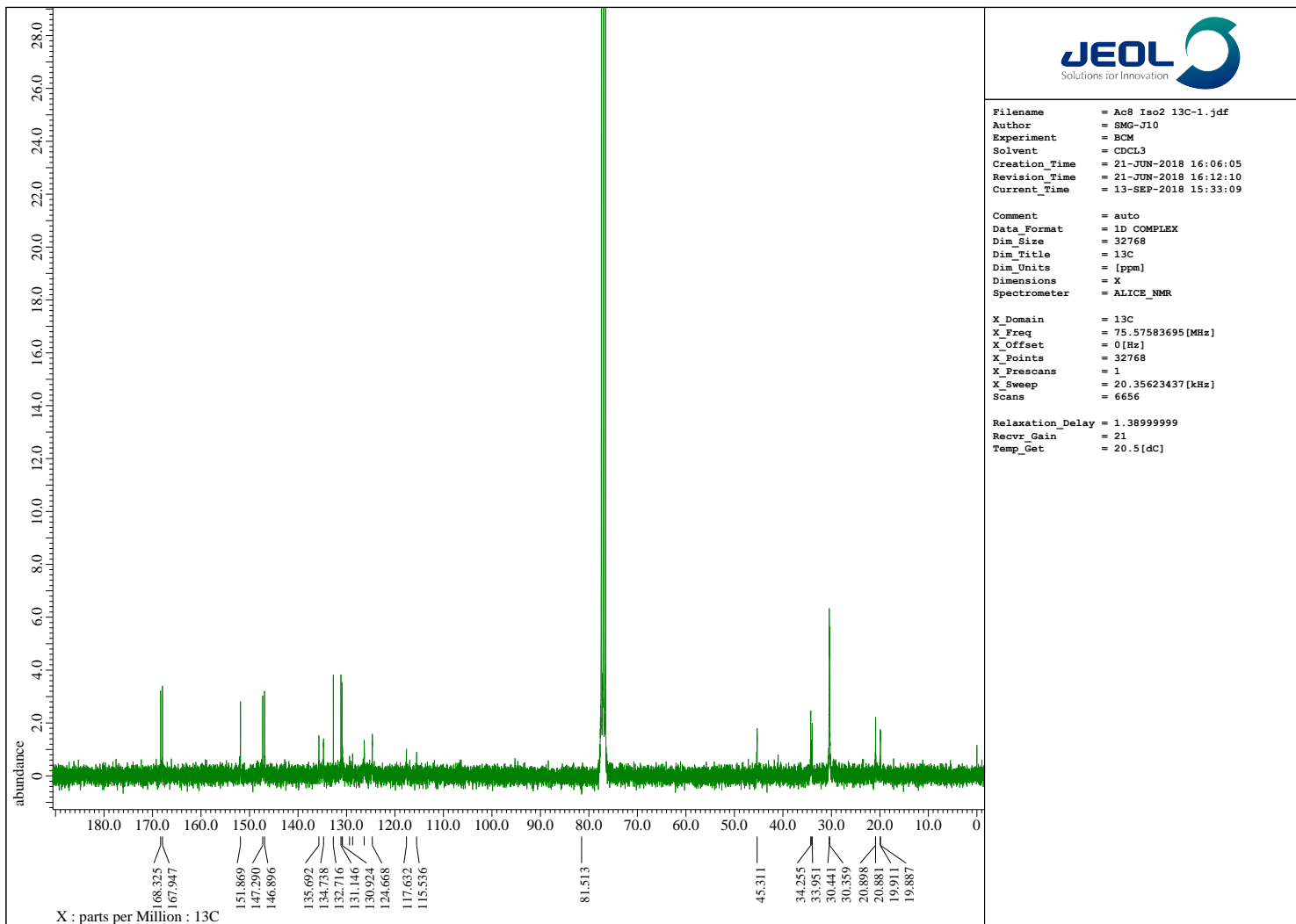
Daniel Payne Resc Ac8-Isomer 1
Xevo2016_Feb_86 79 (1.718) Cm (79.84-31:54)



rccc-2 ¹H NMR Spectrum

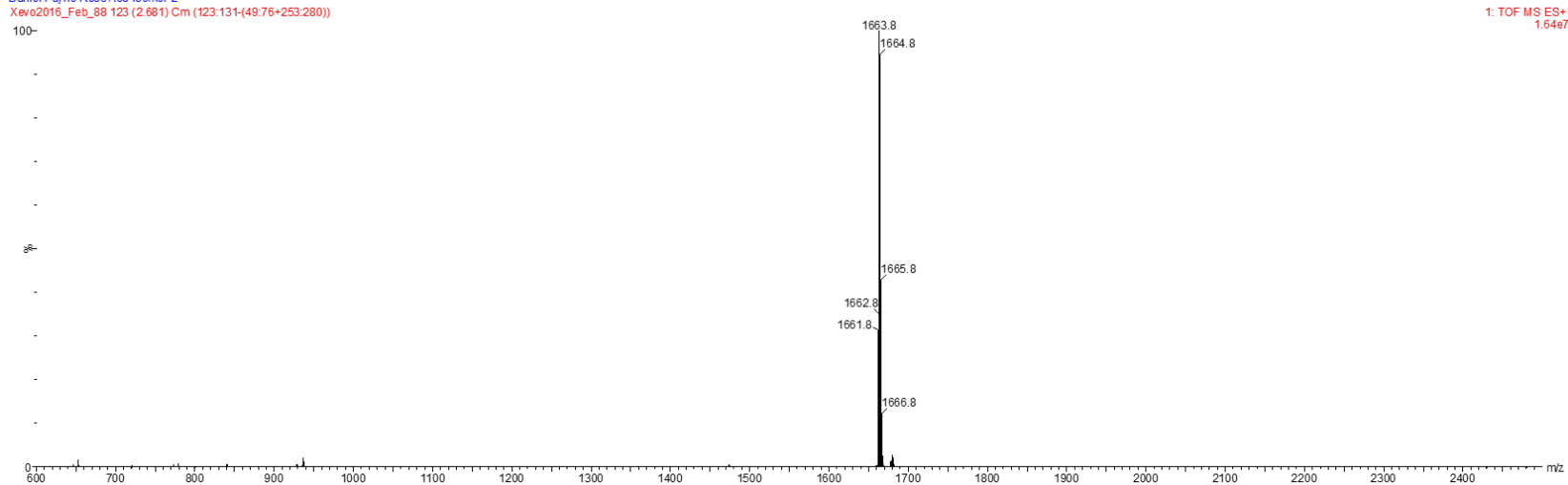


rccc-2 ¹³C NMR Spectrum

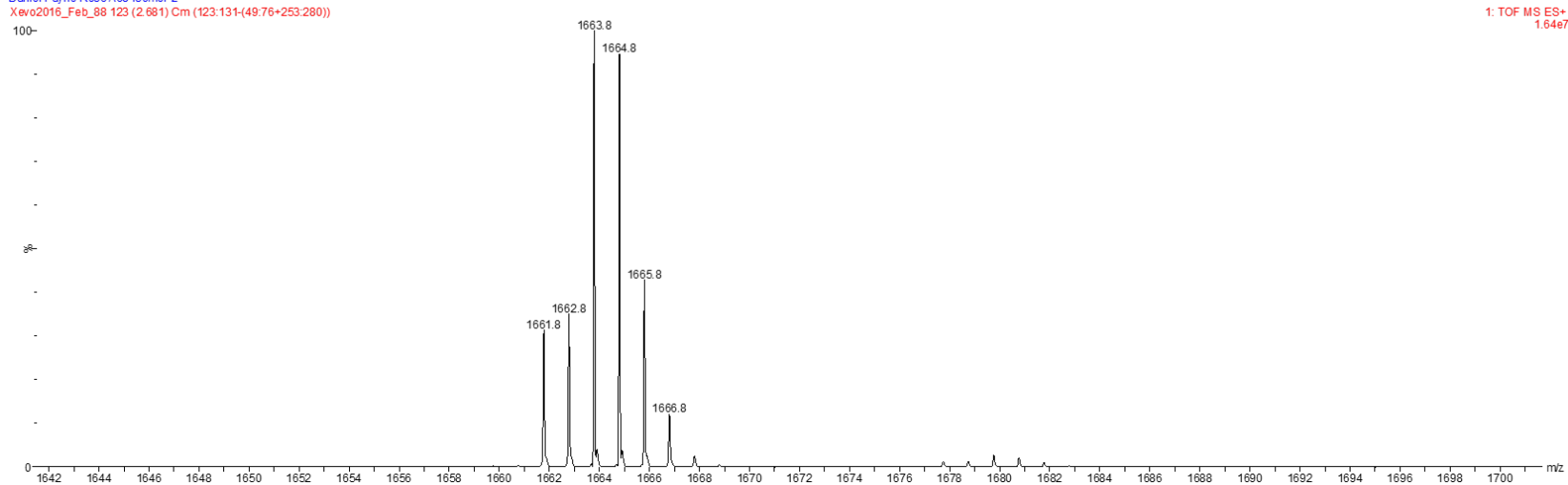


rccc-2 mass Spectrum

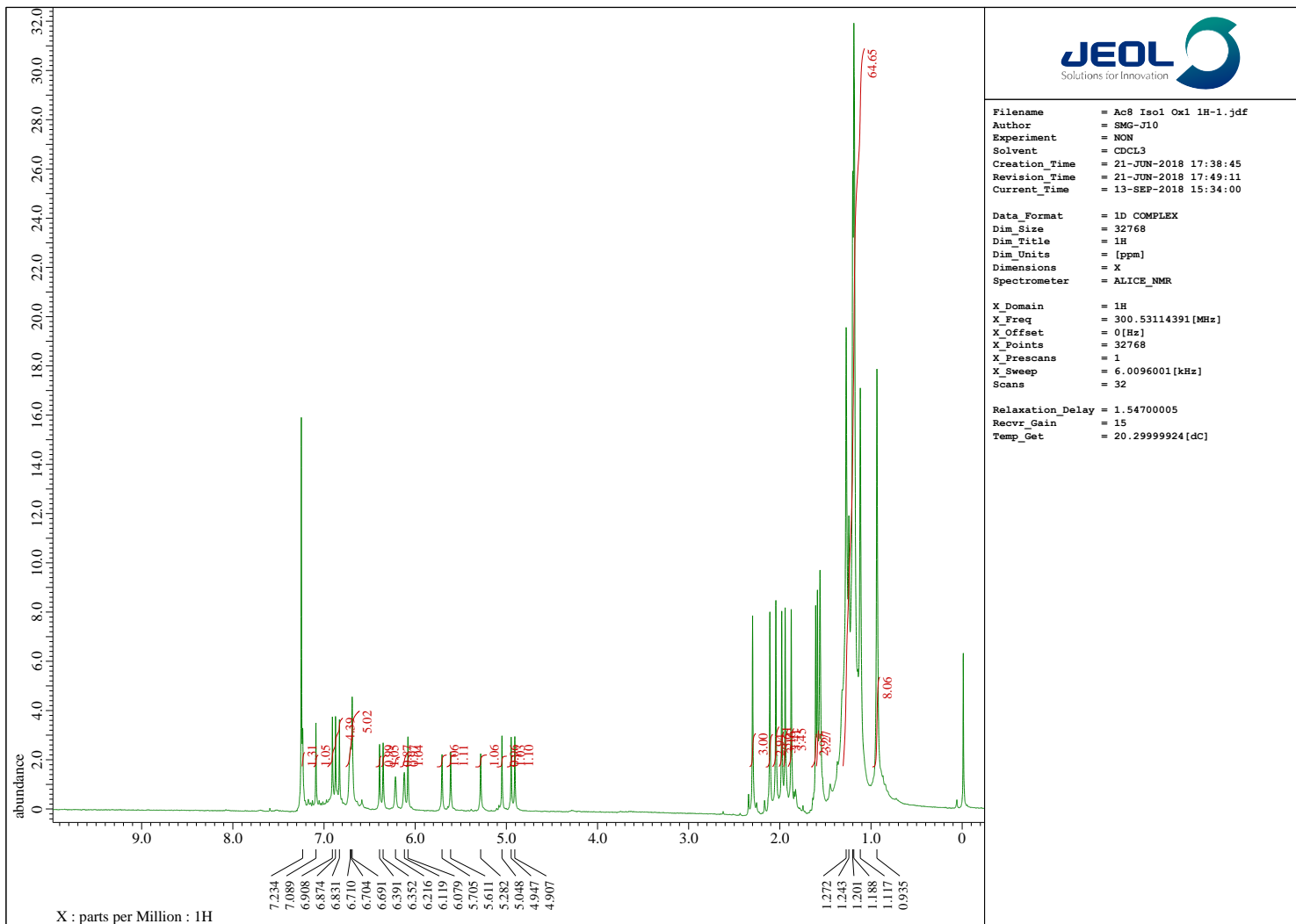
Daniel Payne Resc Ac8-Isomer 2
Xevo2016_Feb_88 123 (2.681) Cm (123:131-(49:76+253:280))



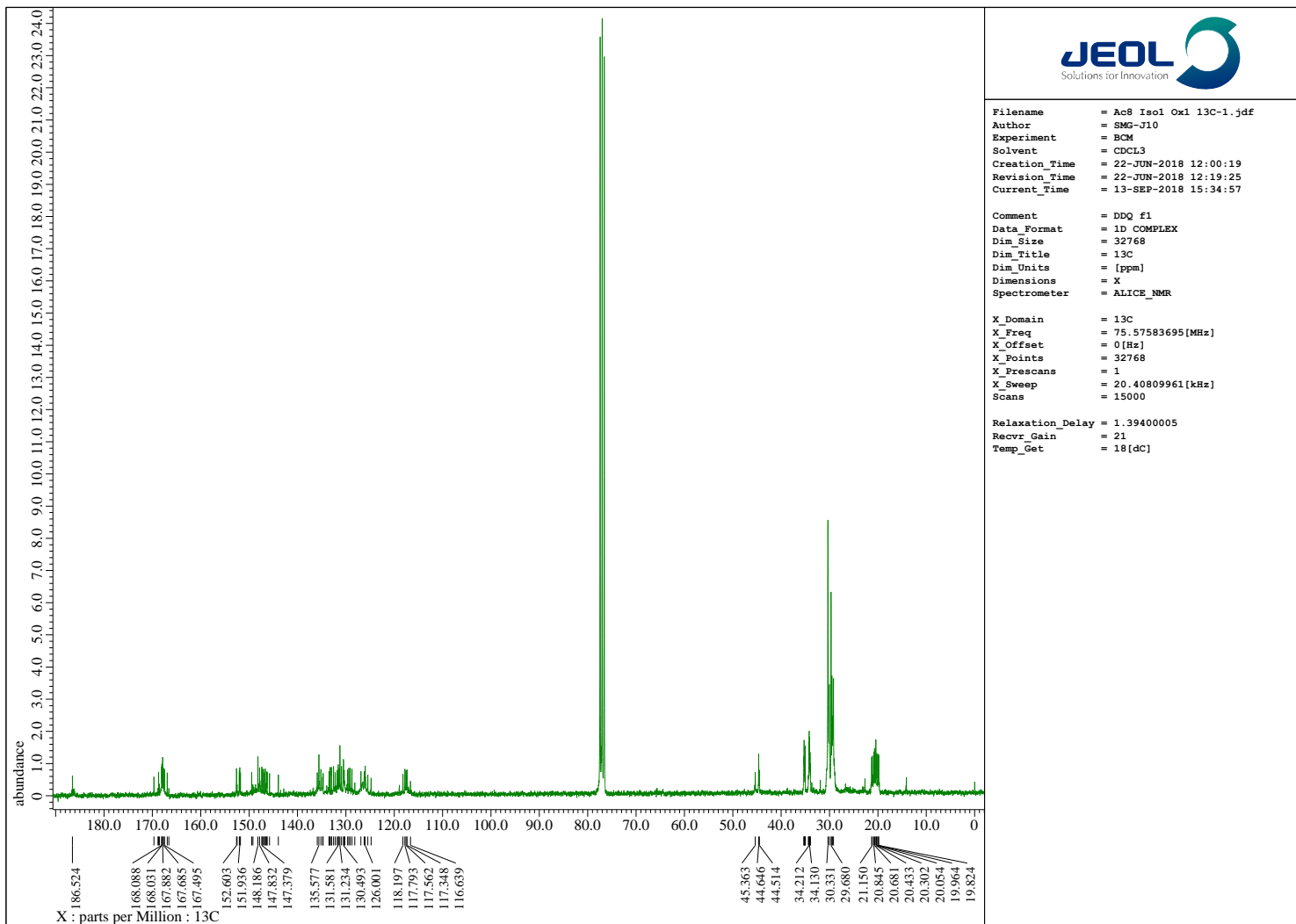
Daniel Payne Resc Ac8-Isomer 2
Xevo2016_Feb_88 123 (2.681) Cm (123:131-(49:76+253:280))



rctt-2[Ox₁] ¹H NMR Spectrum



rctt-2[Ox₁] ¹³C NMR Spectrum



Filename = Ac8 Iso1 Ox1 13C-1.jdf
 Author = SMG-J10
 Experiment = BCM
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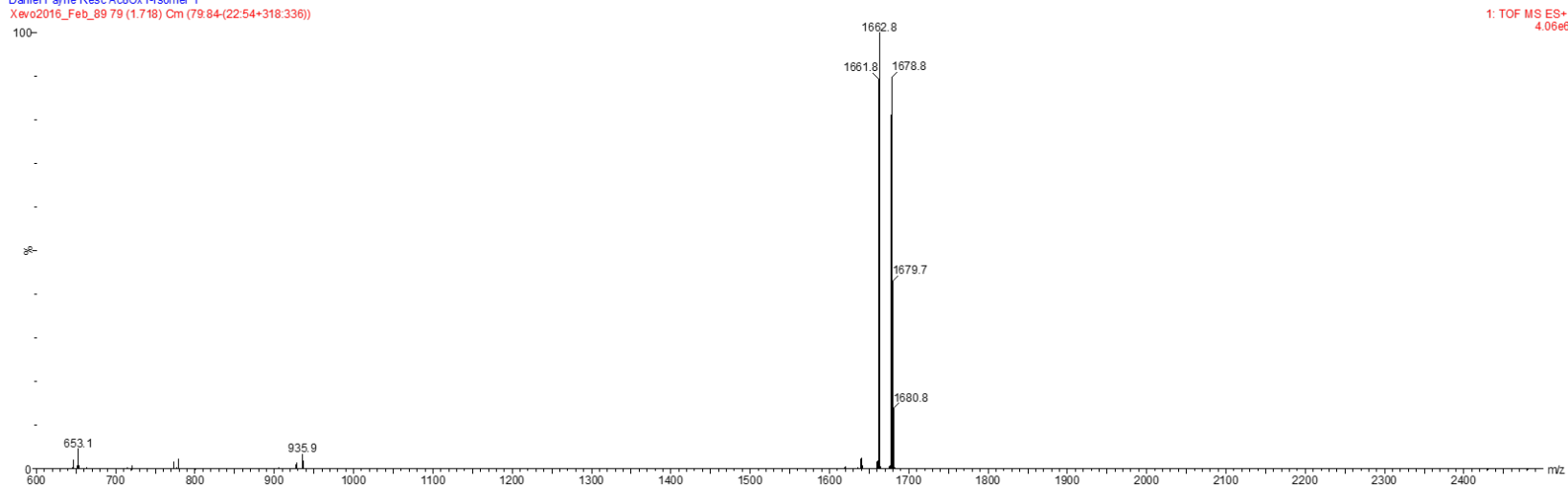
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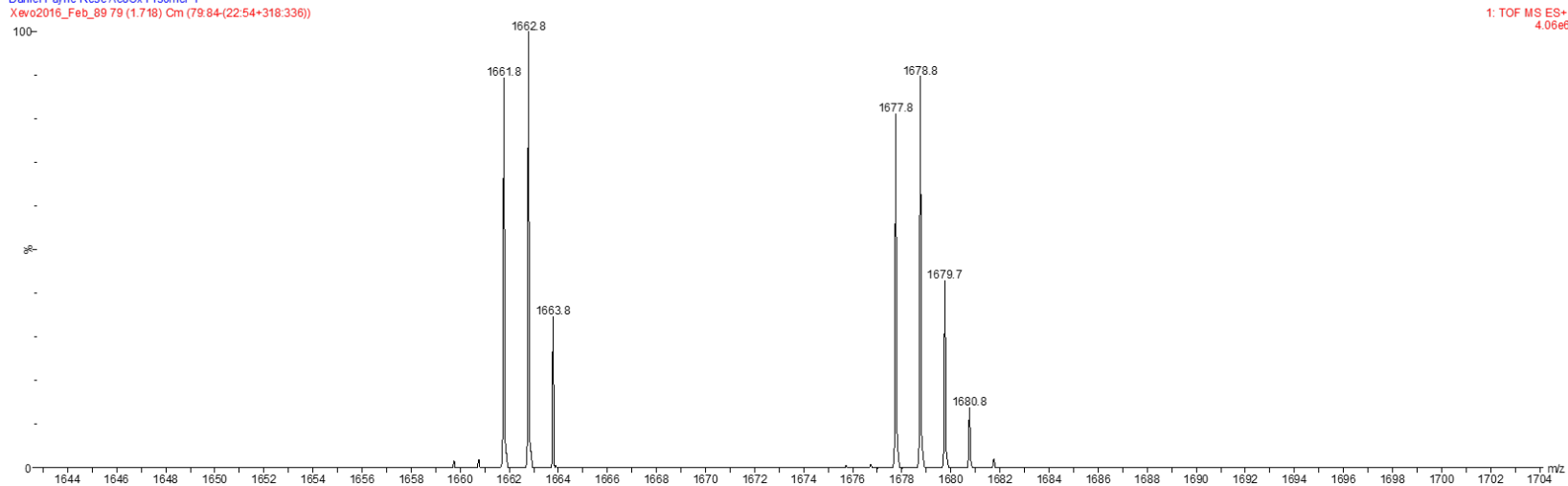
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 Temp_Get = 18[$^{\circ}$ C]

rctt-2[Ox₁] mass Spectrum

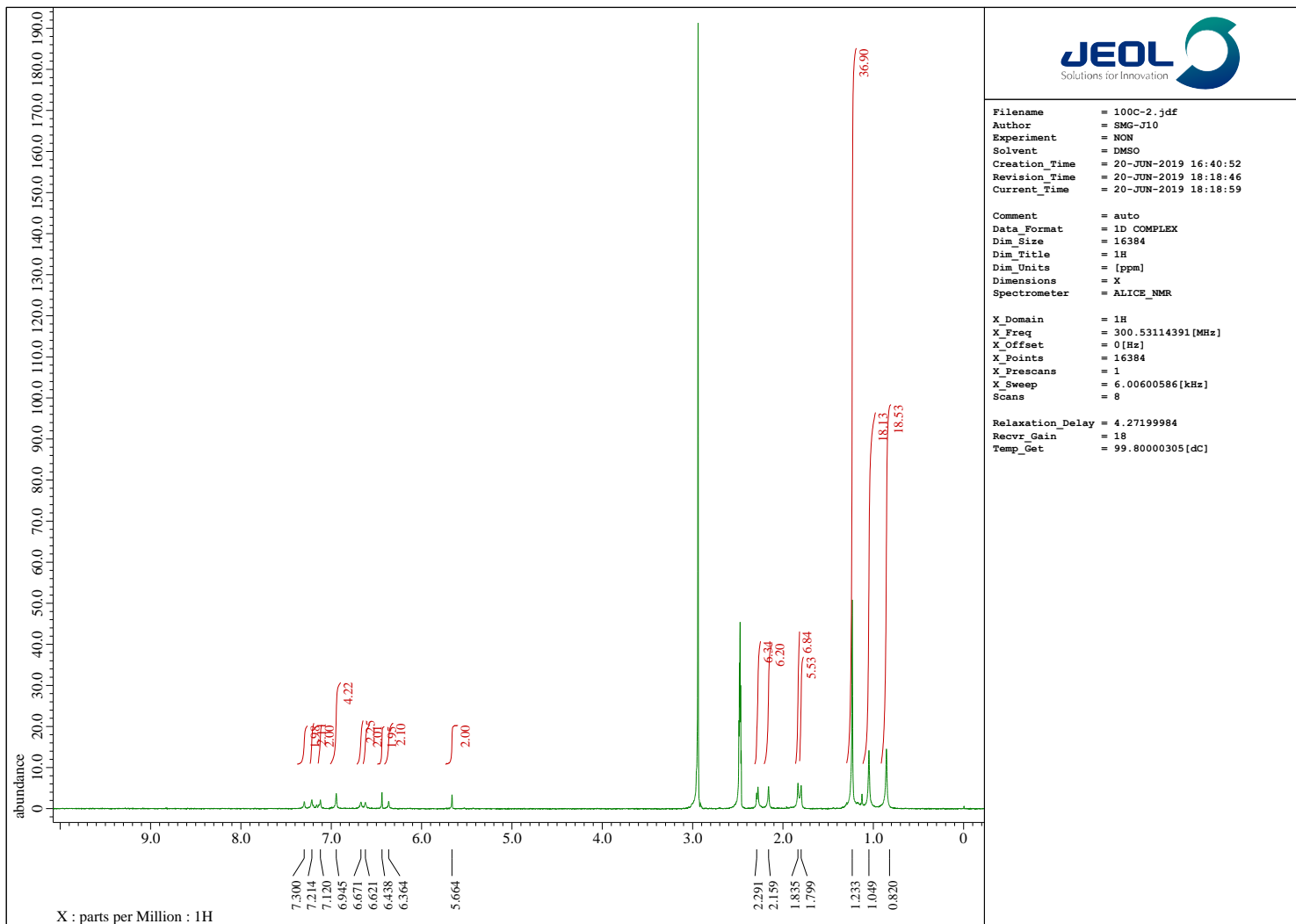
Daniel Payne Resc Ac8Ox1-Isomer 1
Xevo2016_Feb_89 79 (1.718) Cm (79.84-(22.54+318.336))



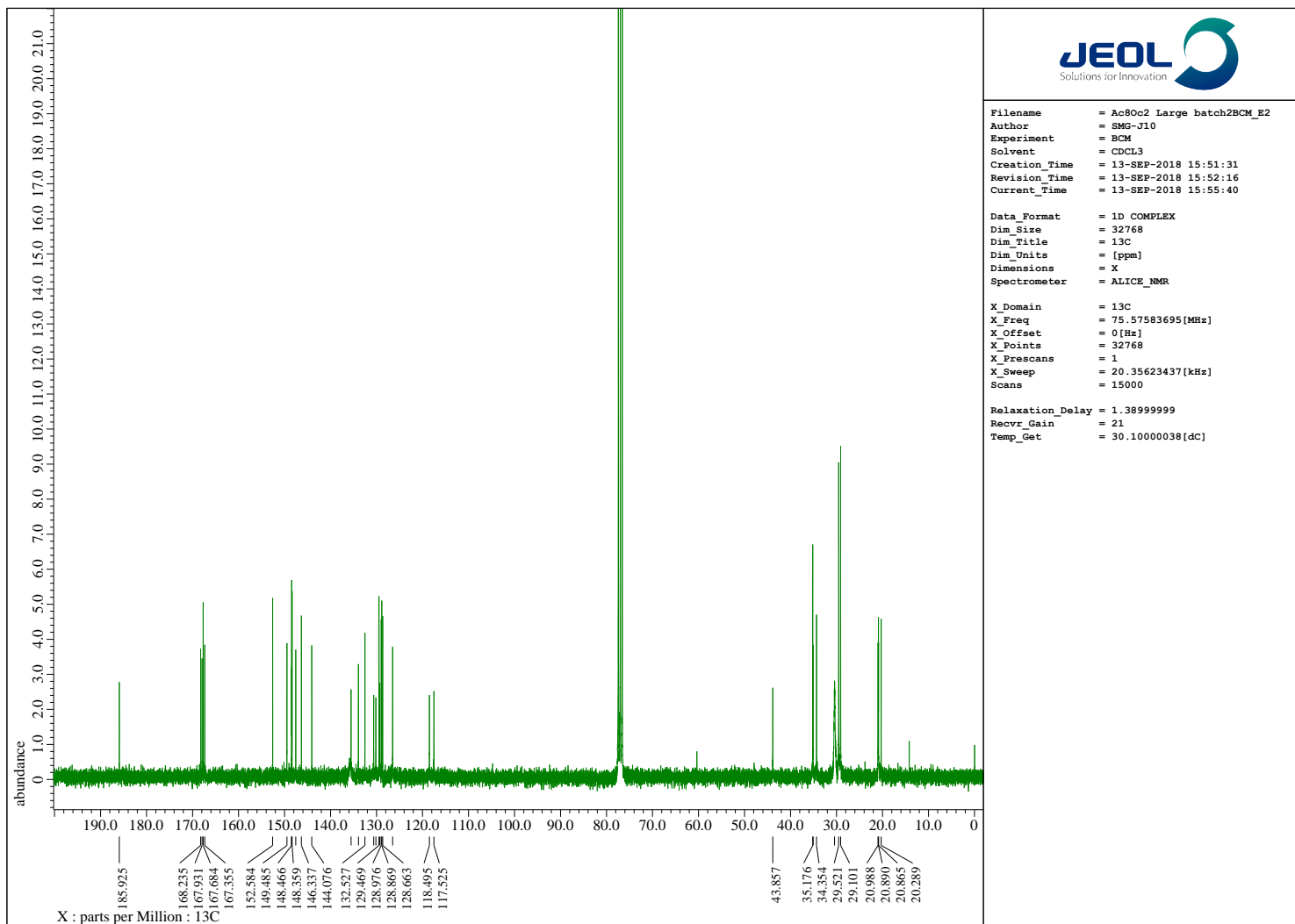
Daniel Payne Resc Ac8Ox1-Isomer 1
Xevo2016_Feb_89 79 (1.718) Cm (79.84-(22.54+318.336))



rccc-2[Ox₂] ¹H NMR Spectrum



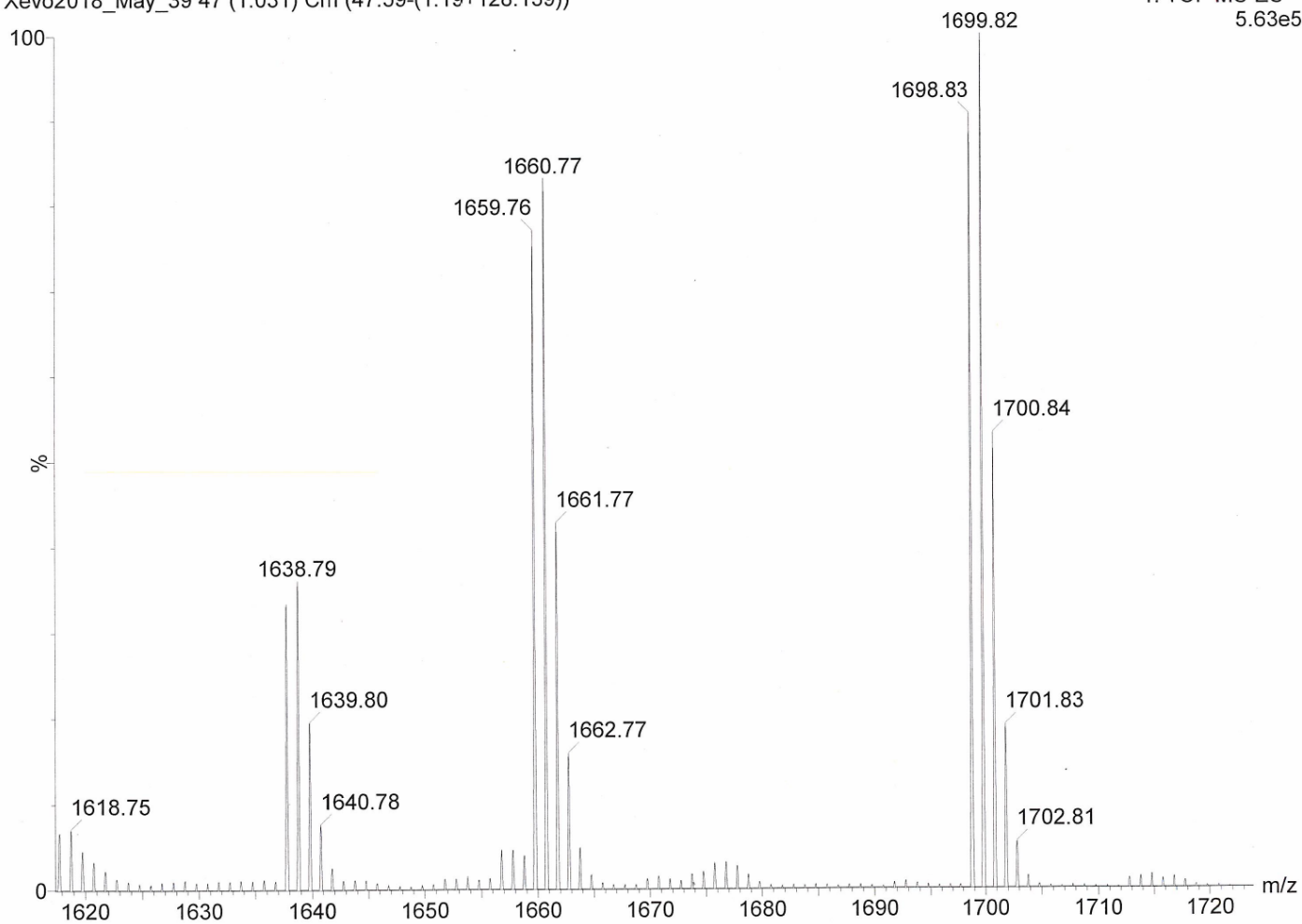
rccc-2[Ox₂] ¹³C NMR Spectrum



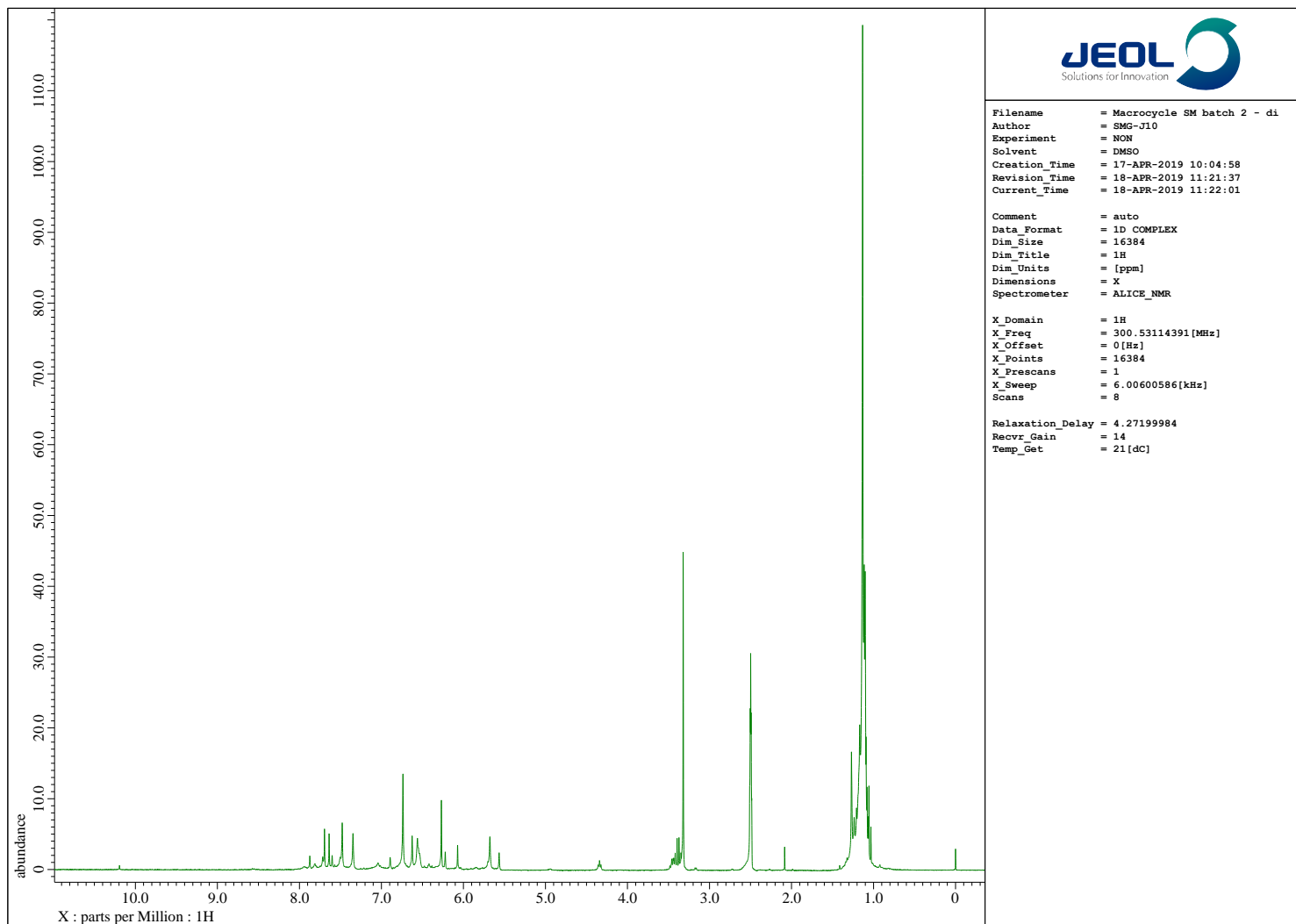
rccc-2[Ox₂] Mass Spectrum

Ac8 Iso2 (Ox)
Xevo2018_May_39 47 (1.031) Cm (47:59-(1:19+128:139))

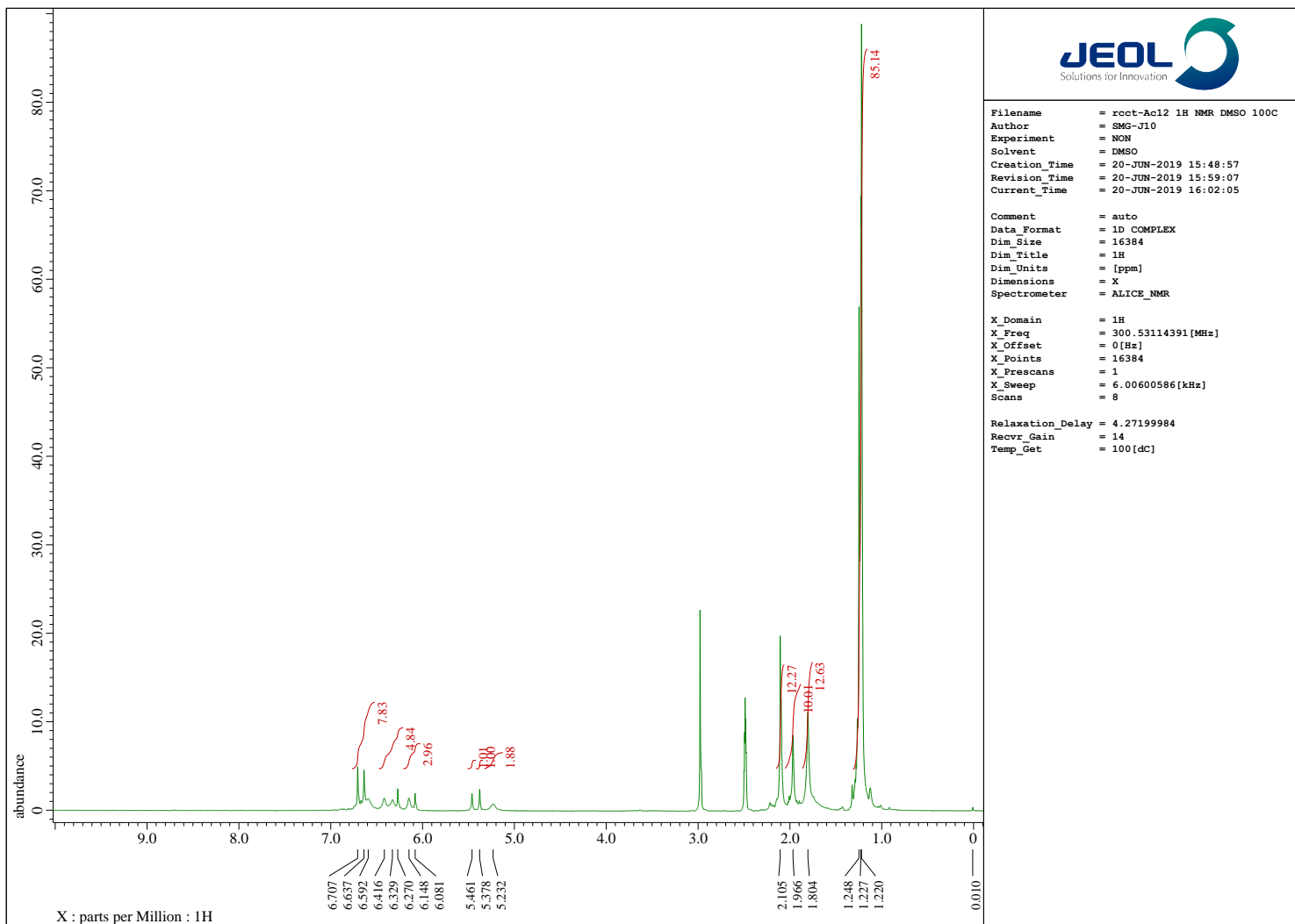
1: TOF MS ES+
5.63e5



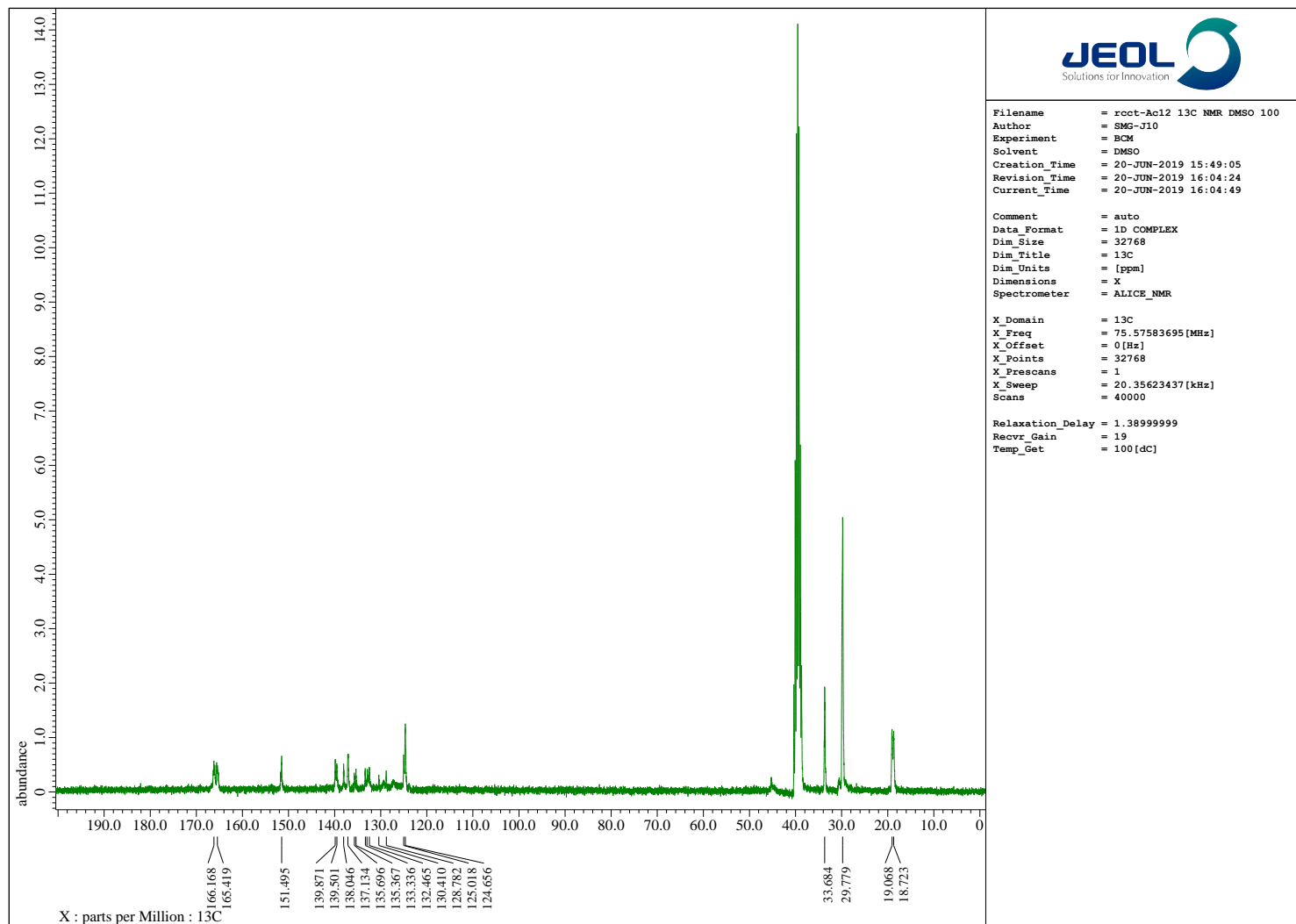
¹H NMR Spectrum of the pyrogallarene dodecaol Precursor 'B'.



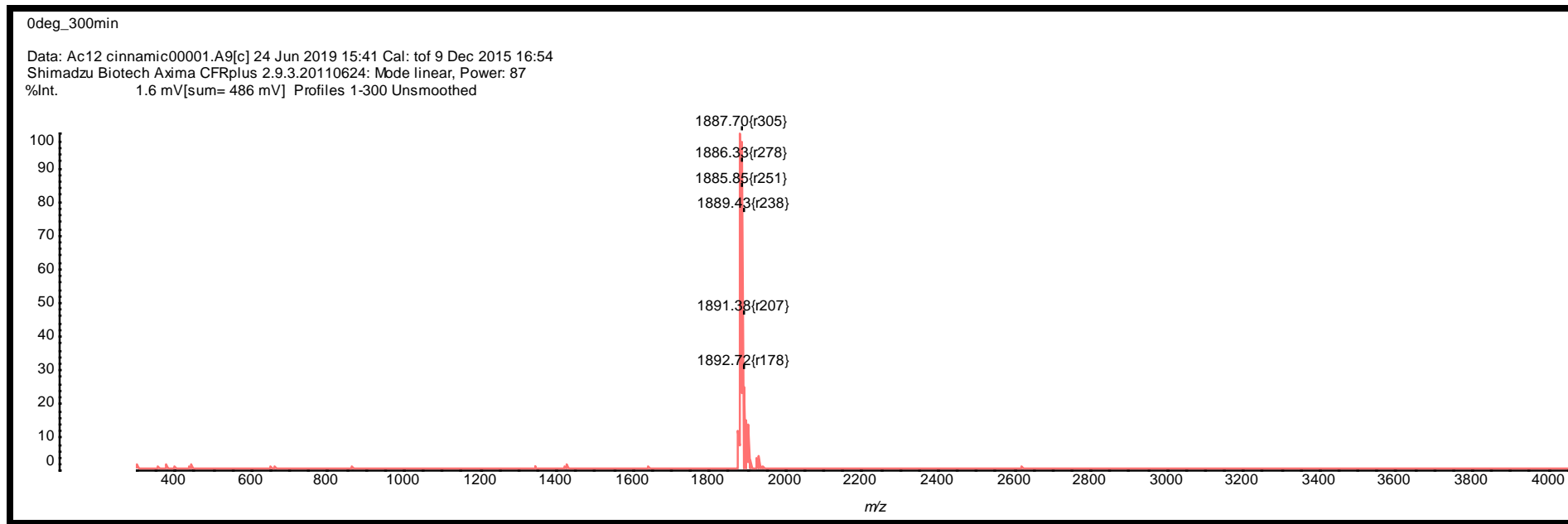
rcct*-3 ¹H NMR Spectrum



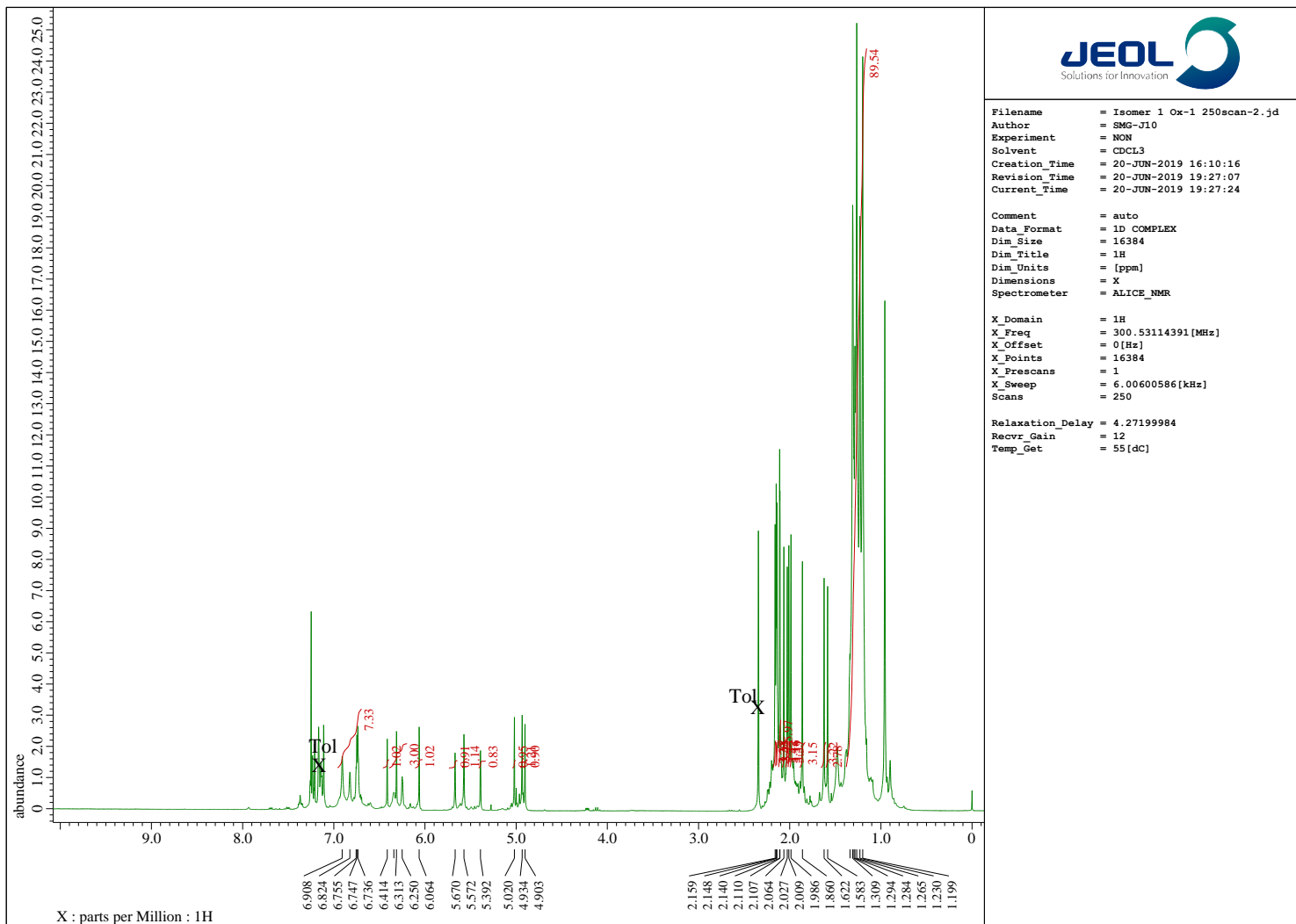
rcct*-3 ¹³C NMR Spectrum



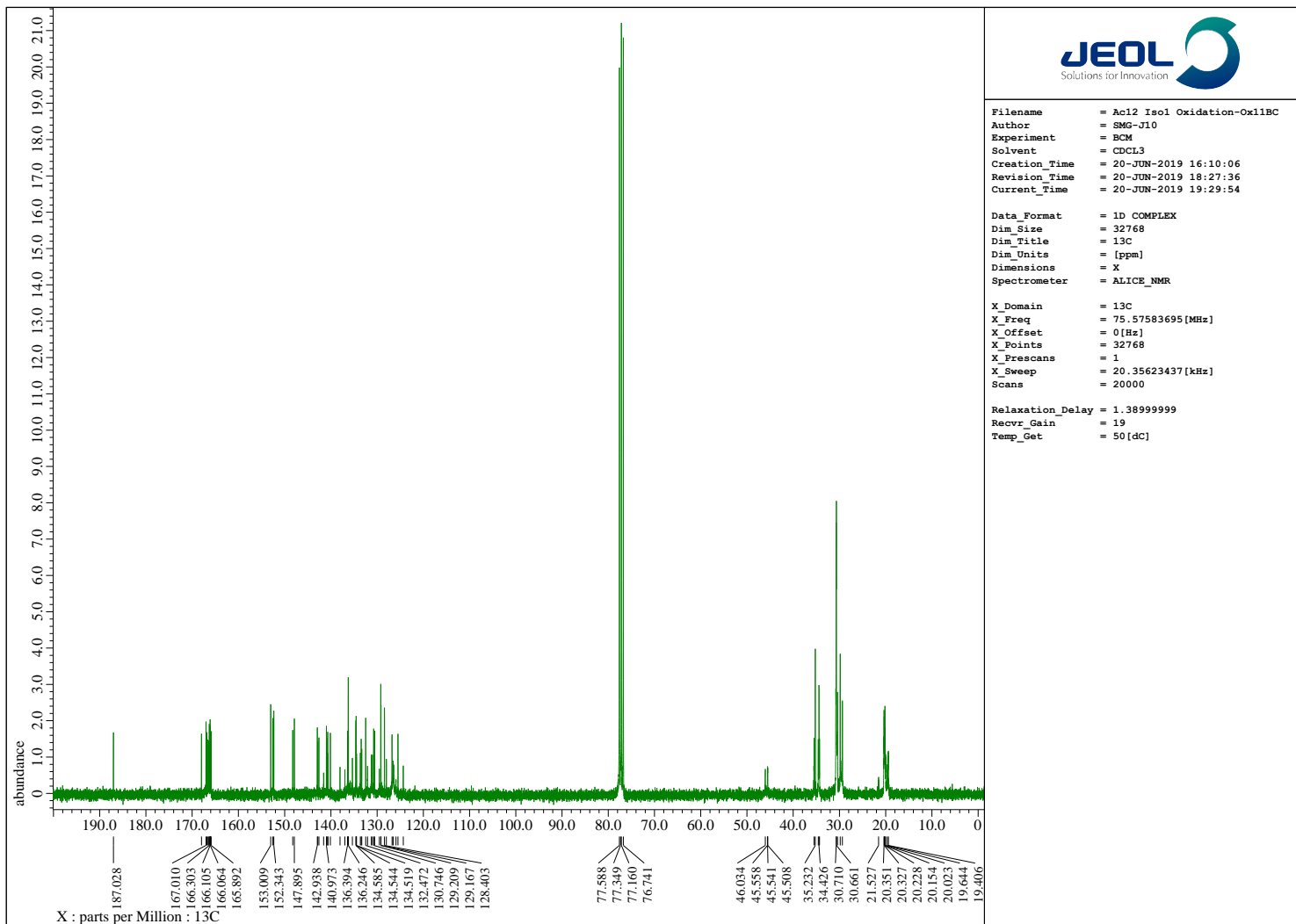
rcct*-3 Mass Spectrum



rctt-3[Ox₁] ¹H NMR Spectrum



rctt-3[Ox₁] ¹³C NMR Spectrum



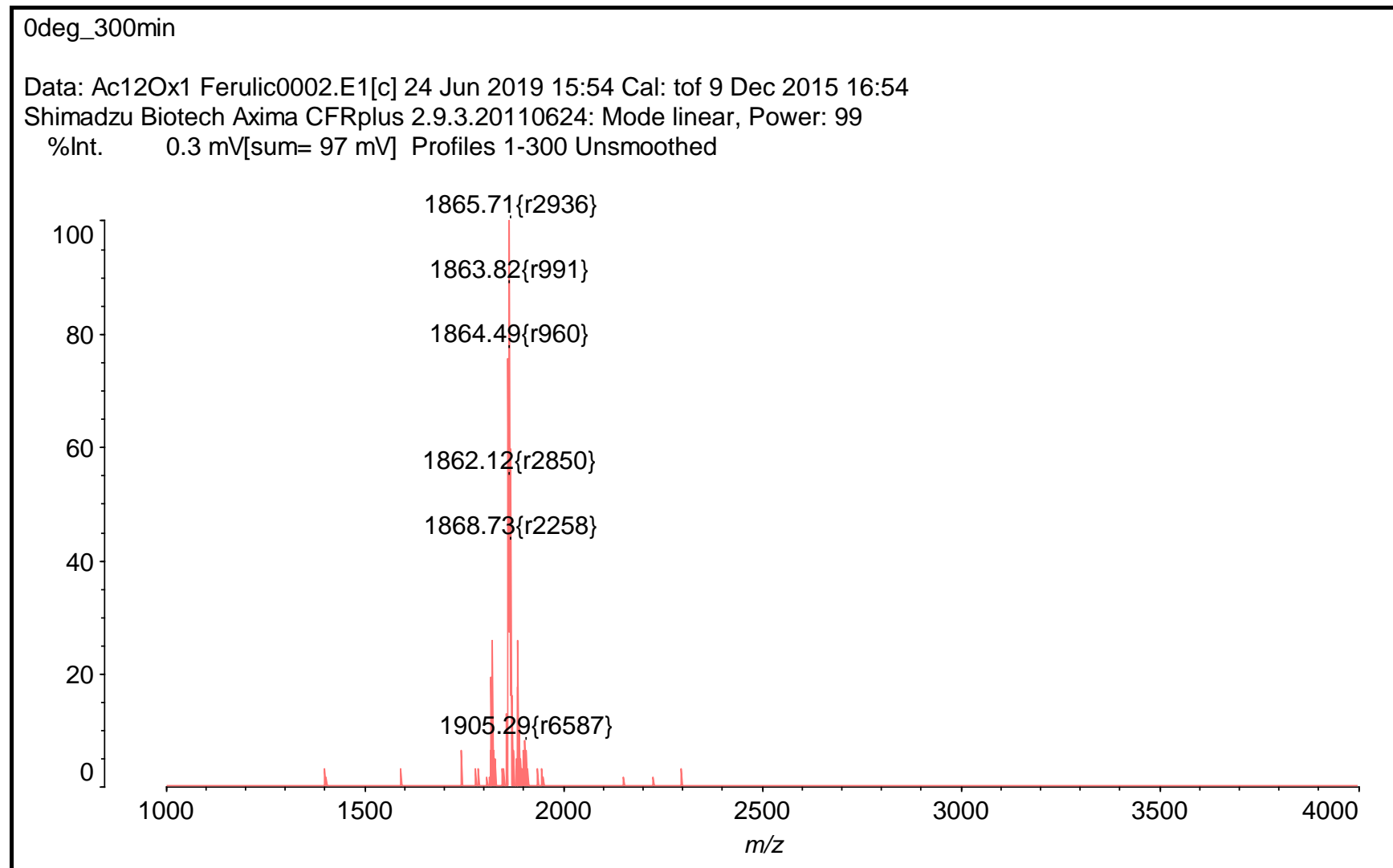
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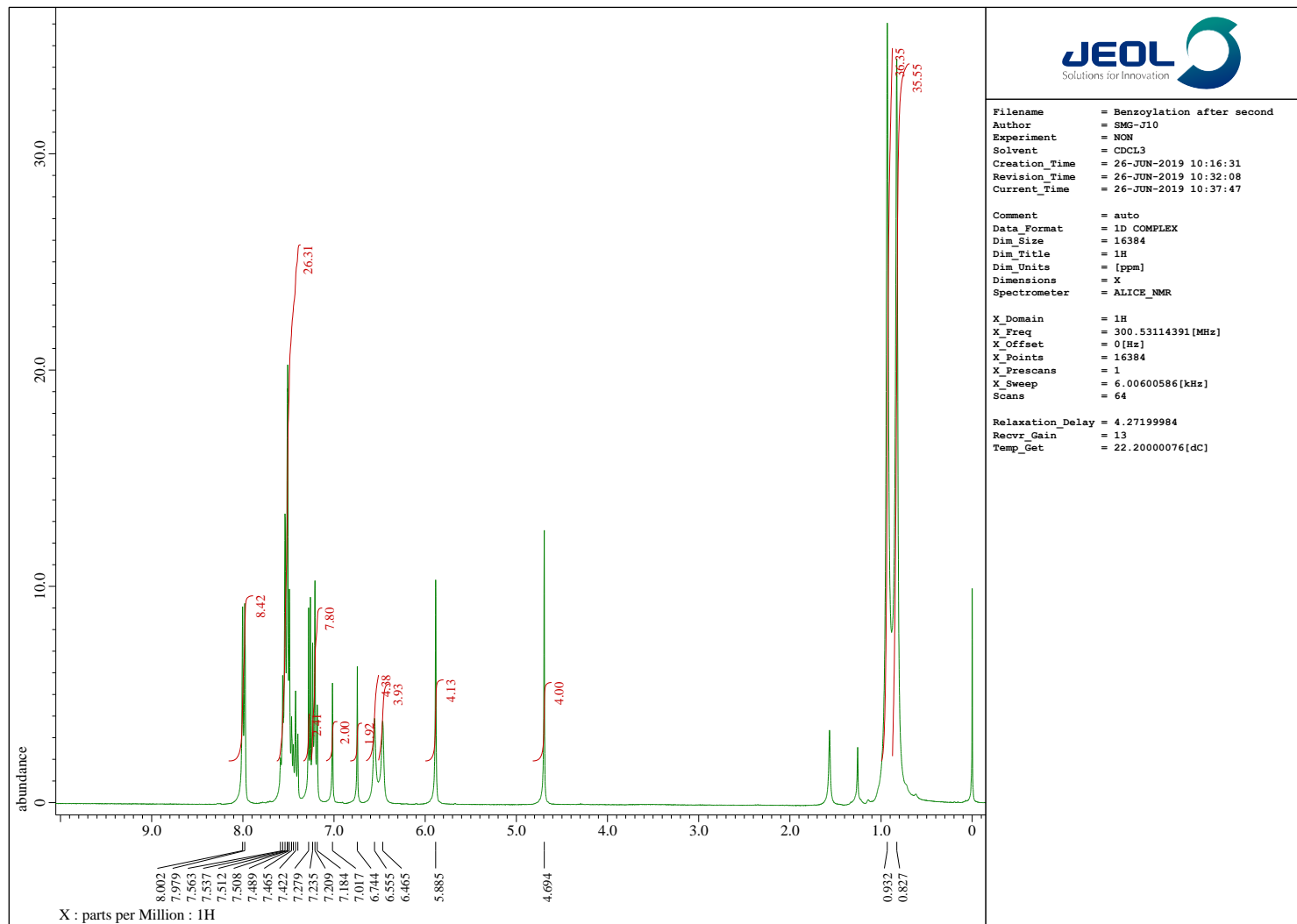
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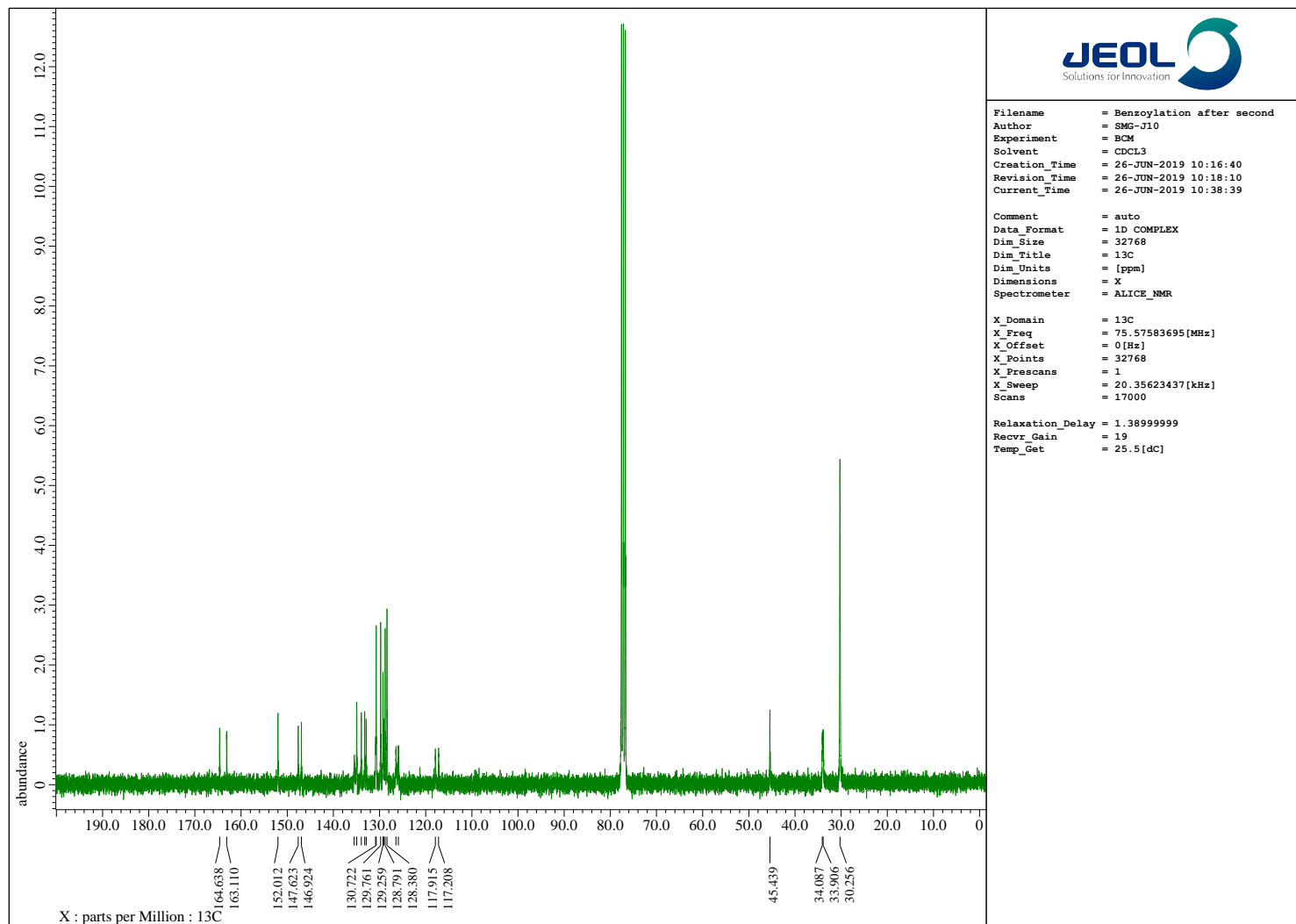
rctt-3[Ox₁] Mass Spectrum



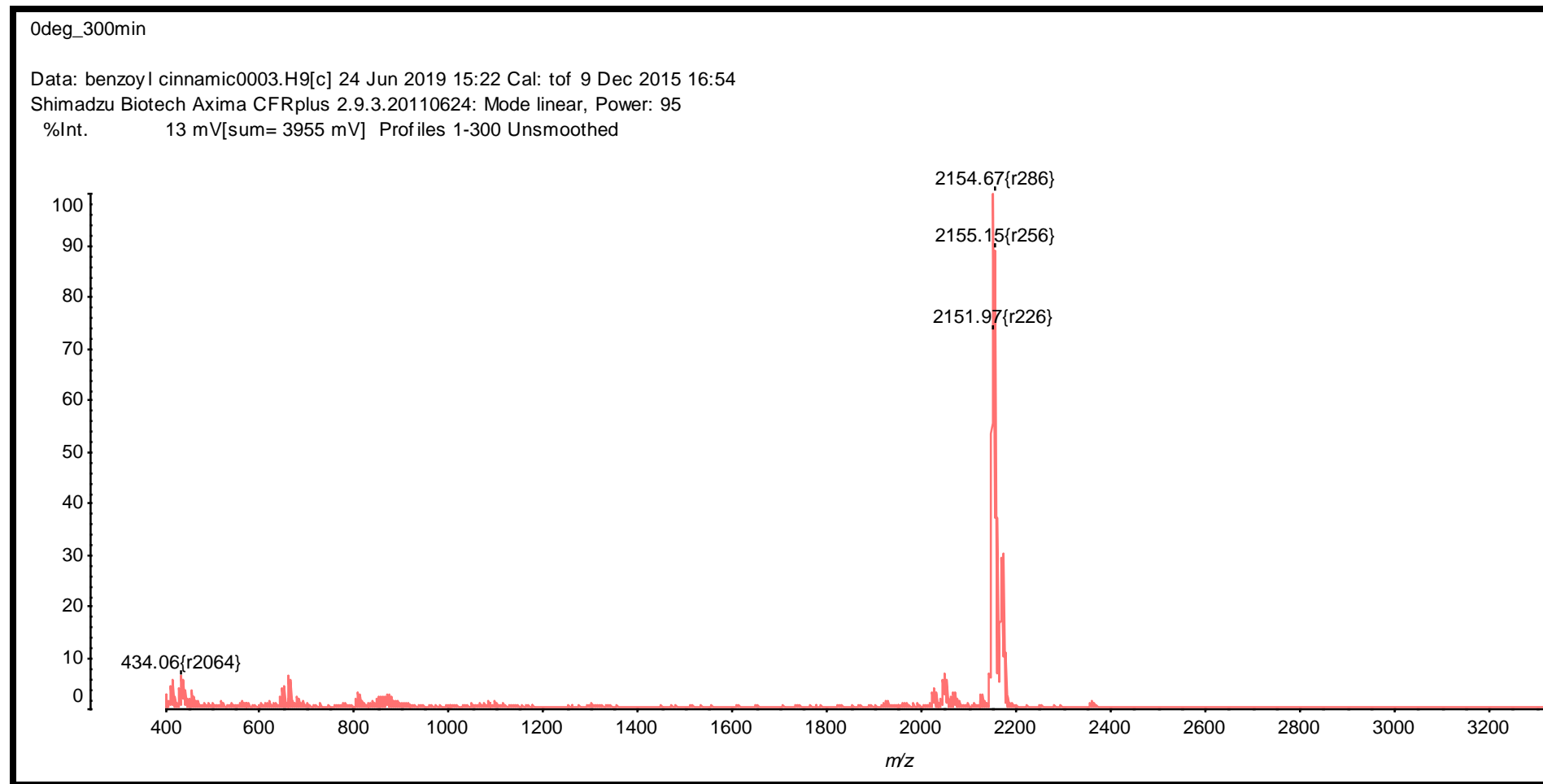
rctt-4 ¹H NMR Spectrum



rctt-4 ¹³C NMR Spectrum



rctt-4 Mass Spectrum



7. References

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