Supporting Information

Visible-light Mediated Oxidative Ring Expansion of Anellated Cyclopropanes to Fused Endoperoxides with Antimalarial Activity

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Table of Contents

General Information

Solvents and Chemicals

All commercially available compounds were used as received. Anhydrous solvents were prepared by established laboratory procedures. Ethyl acetate, hexanes (40/60) and DCM were distilled prior to use in chromatography. [MesAcr]ClO_4 and [Ir(dtbbpy)ppy_2]PF_6 were prepared according to the literature.[1, 2]

2-Aryl-2-diazoacetates were prepared according to the literature from aryl acetates and tosylazide[3].

Light source in photoreactions

For irradiation, CREE XLamp XP-E D5-15 LED (λ = 450-465 nm, maximum at 455 nm) light emitting diodes were employed.

NMR spectroscopy

^{1}H, ^{13}C, ^{19}F and 2D spectra were recorded on BRUKER Avance 300 or BRUKER Avance III 400 "Nanobay" spectrometers. The spectra were recorded in $CDCl_3$ unless otherwise specified. The ^{1}H-NMR chemical shifts are reported as δ in parts per million (ppm) relative to the signal of $CHCl_3$ at 7.26 ppm. Coupling constants *J* are given in Hertz (Hz), with following indications for the multiplicity of the signals: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet; to indicate broad signals, the letter b is used in front of the multiplicity indication (e.g. bs = broad singlet).

The chemical shifts for ^{13}C-NMR are reported as δ in parts per million (ppm) relative to the center line of $CDCl_3$ at 77.0 ppm.

Chromatography

For column chromatography silica gel 60 (Merck, 0.040-0.063 mm particle size) was used. Thin layer chromatography (TLC) was performed on silica gel 60 F254 coated aluminum sheets (Merck) and visualized with UV and vanillin (2.5 g vanillin, 425 mL EtOH, 50 mL conc. AcOH, 25 mL conc. H_2SO_4) or $KMnO_4$ (1 g $KMnO_4$, 2 g Na_2CO_3, 100 mL H_2O) stain.

Further analytics

Melting points were determined on an OptiMelt MPA 100

FT-IR spectroscopy was carried out on an Agilent Technologies Cary 680 FTIR machine with diamond single reflection accessory.

Mass spectroscopy was carried out by the Central Analytical Laboratory of the University of Regensburg on Jeol AccuTOF GCX, Agilent Q-TOF 6540 UHD or ThermoQuest Finnigan TSQ 7000 systems.

X-ray crystallography was performed on Agilent Technologies SuperNova, Single source at offset/far, Atlas diffractometer or a GV1000, TitanS2 diffractometer at T = 123 K during data collection The structures were solved with the **ShelXT** (Sheldrick, 2015) structure solution using **Olex2** (Dolomanov *et al.*, 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimization.

Cyclic voltammetry was measured on an Autolab PGSTAT 302N setup at 20°C in MeCN containing $^{n}Bu_4NBF_4$ as supporting electrolyte. The electrochemical cell consisted of a glassy carbon working electrode, a platinum wire as counterelectrode and a silver wire as reference electrode. The solvent was degassed by N_2 sparging prior to the measurements, and the redox potentials were referenced against ferrocene as internal standard. The values were then calculated and reported in reference to SCE electrode.

Optical Rotation was measured using an Anton Paar MCP500 Polarimeter at 589 nm in the specified solvent.

Calorimetry was measured on a Perkin Elmer TGA 7 under synthetic air atmosphere.

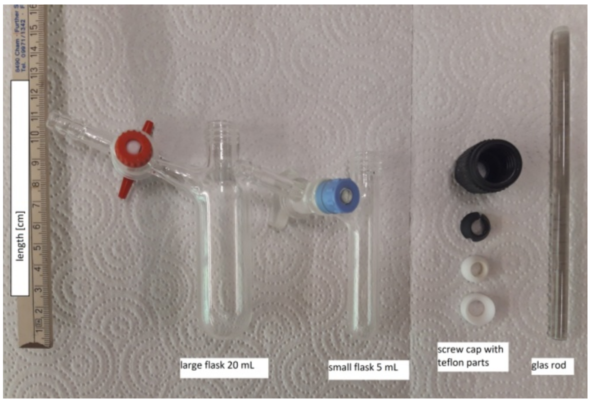
Chiral HPLC was carried out on a Varian 920-LC with Chiralpak AS-H, Phenomenex Lux Cellulose-1 or 2 as chiral stationary phase (as specified), using mixtures of ^{n}heptane and ^{i}PrOH as eluent.

Fluorescence intensity was measured with a Horiba Scientific FluoroMax4 Spectrofluorometer.

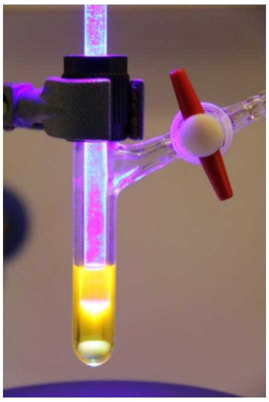
Fluorescence lifetime was measured with a Horiba DeltaPro Fluorescence Lifetime System equipped with a 370 nm Deltadiode DD-370.

Setup

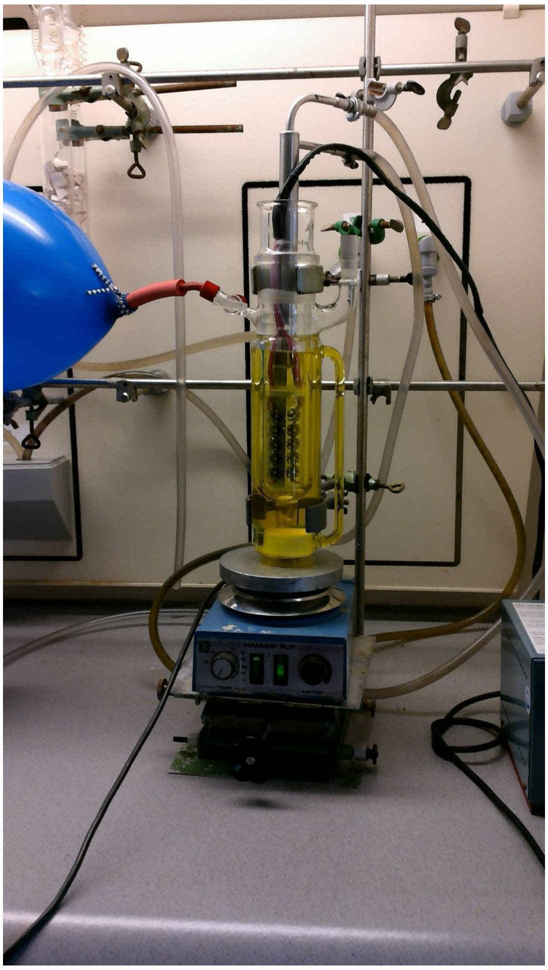
Pre-assembly:

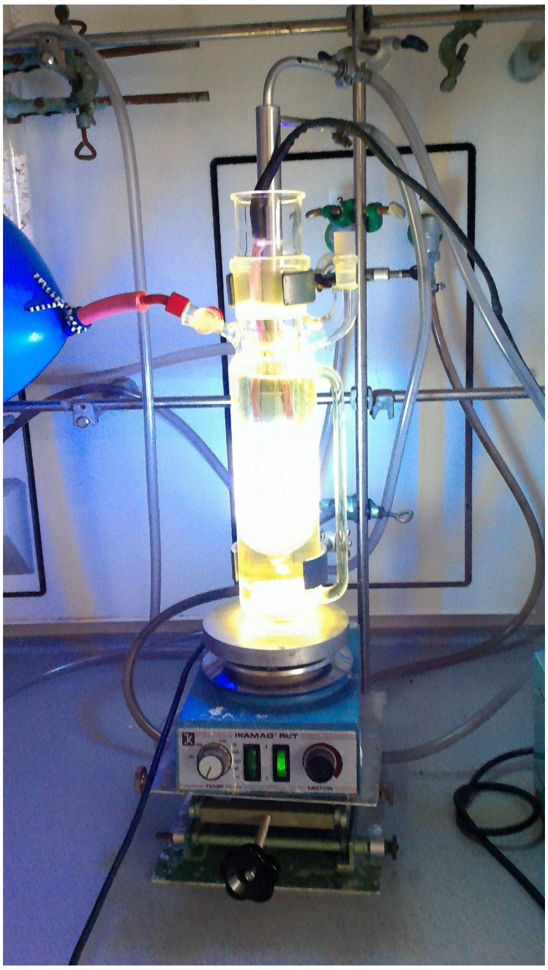


in operation:



Large scale setup:





Biological Testing

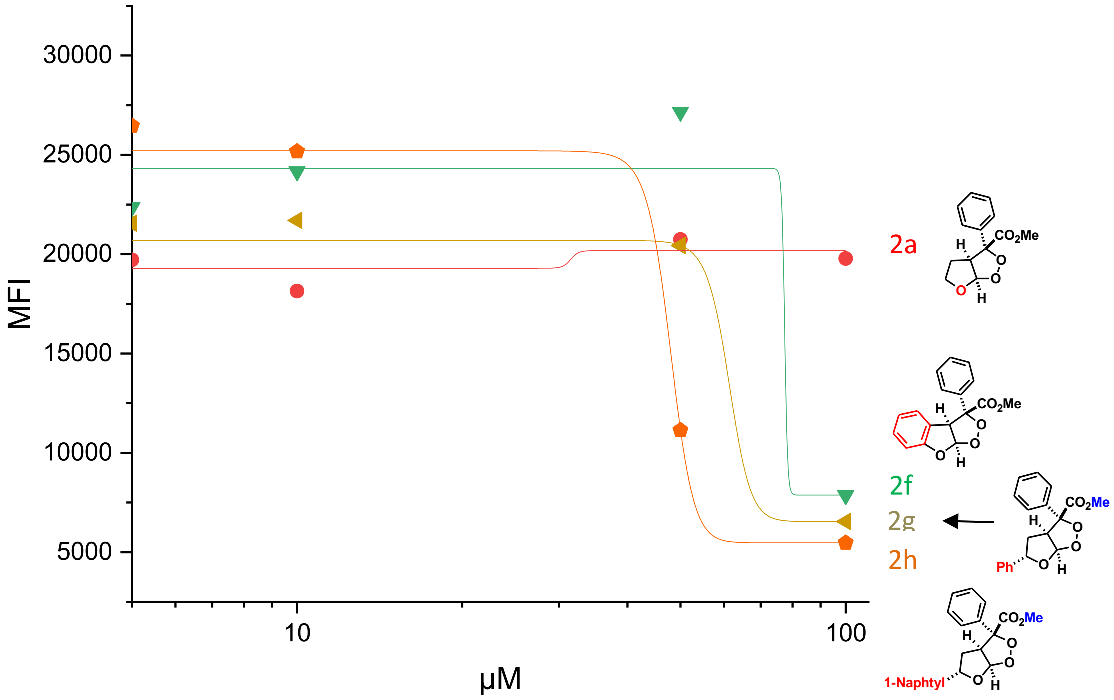
The anti-malarial activity was evaluated at the Max Planck Institute of Colloids and Interfaces, Berlin, following the protocol from Dery *et al*.[4]

Synchronized *Plasmodium falciparum* parasites were cultivated at 1% hematocrit as described by Radfar *et al*.[5] Parasitemia was determined by blood smears. Therefore, a small sample of medium was spread on a glass slide, fixed with methanol for 30 s and then stained with Giemsa staining solution (6%) for 15 min. Prior to the experiment, infected erythrocytes were diluted to 1% parasitemia and resuspended to 4% hematocrit.

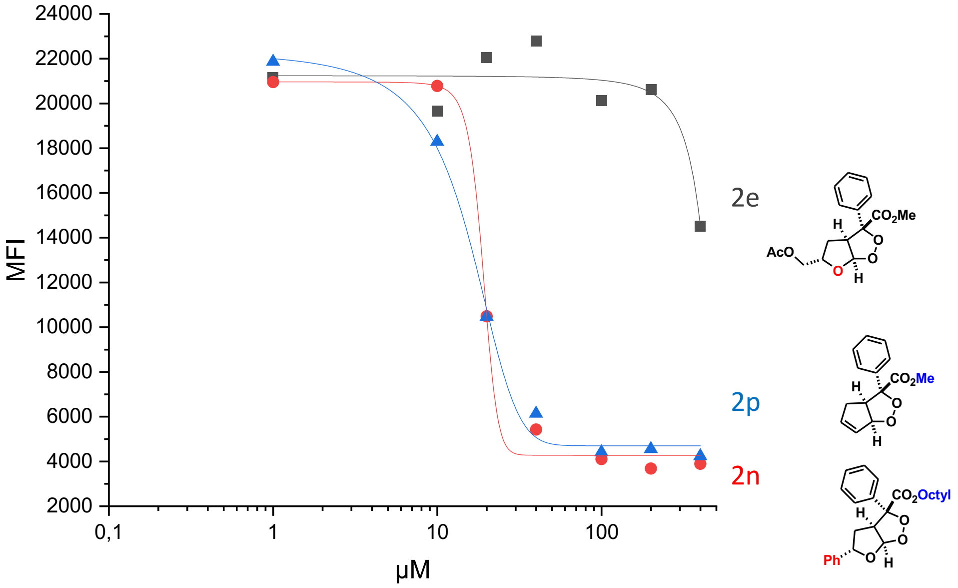
The samples were then weighed in (1-3 mg), dissolved in DMSO and a dilution series covering an appropriate range of concentrations was created. In a 96 well plate, 50 µL of drug solution were mixed with 50 µL of *Plasmodium* culture in triplicates for each concentration. In addition, three wells with 0.5% DMSO (negative control) and three wells with 8 µM artemisinin (positive control) were included.

The cultures were kept at 37 °C for 96 h, corresponding to two lifecycles of the parasites, and subsequently frozen. After adding 100 µL of lysis buffer (20 mM Tris (pH 7.5), 5 mM EDTA, 0.008% (W/V) saponin, and 0.08% (V/V) Triton X-100, 1x SYBR Green-1) to each well, the plate was incubated in the dark for 3 h. SYBR Green-1 intercalates with the nucleic acids from *Plasmodium* and its fluorescence intensity is thus proportional to the amount of parasites in culture. After the incubation time, the SYBR Green-1 fluorescence was measured at 528 nm and plotted vs. log(c). The plot was fitted with the dose-response function using Origin (originlab, Version 2018.b) and the IC50 determined using the software's Derived Parameters feature.

Dose-response function: $y = A_1 + \frac{A_2 - A_1}{1 + 10^{(log_{x}0 - x)p}}$

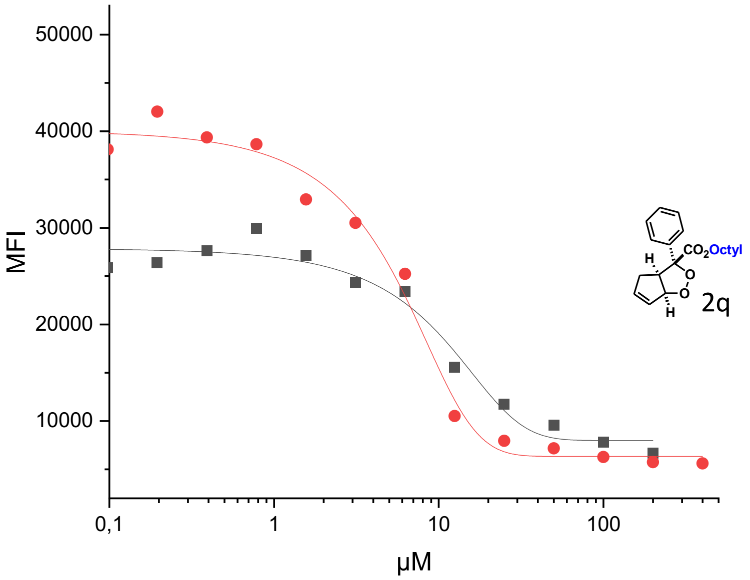


The first series of tests was performed with more data points under 1 µM concentration, as it was estimated that the compounds were in the range of the literature compounds reported by Xu et al.[6]. However, the first series of compounds turned out to have IC50 values between 10 and 100 µM, leading to the data points being too far apart to make accurate calculations for IC50 values (*vide supra*). The test could have been repeated for precise determination of these values, which was omitted as the IC50 values found for the first series were not in an interesting range (around 1 µM) to save valuable resources. Nevertheless, a trend was visible, as the least polar compound **2d** was the most active, while the most polar compound **2a** was virtually inactive. Therefore, two more series of less polar compounds were prepared and tested (*vide infra*) with data points chosen in a more appropriate range. The trend continued, as the introduction of non-polar groups (octyl-instead of methyl ester) lead to lower IC50 values.



	A1		A2		Log$_x$0		p		span		Statistics	
		σ_x-		σ_x-	IC50	σ_x-	V	σ_x-		σ_x-	χ^2	r^2
2b	-1646967	*)	21345	4157	931	746253	-0.004	0.06702	1668313	*)	2200410	0.698
2i	4274	391	20963	800	18,95	1,4257	-0.217	0.26268	16688	892	614177	0.990
2s	4697	393	23828	1968	15,19	1,85673	-0.068	0.01686	19130	2073	556136	0.989

*) 1.26786E10;

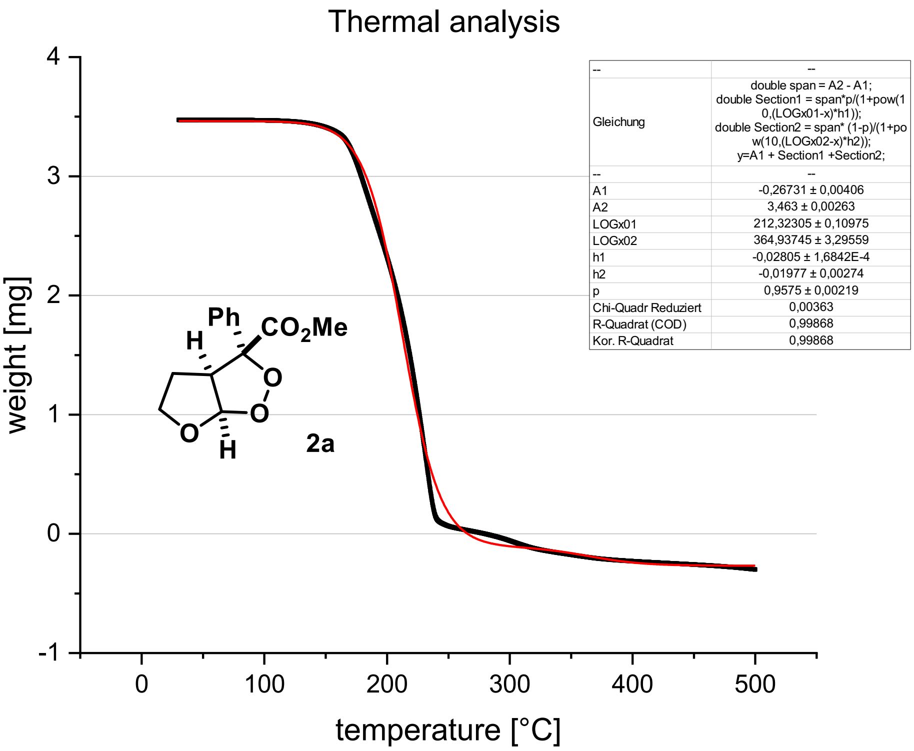


	A1		A2		Log$_x$0		p		span		Statistics	
		σ_x-		σ_x-	IC50	σ_x-	V	σ_x-		σ_x-	χ^2	r^2
2t$_1$	7974	1020	43082	26831	2.55	14.97	-0.0452	0.0242	35107	27172	2200410	0.698
2t$_2$	6322	831	61512	22828	2.17	4.22	-0.0898	0.0288	55189	23040	614177	0.990

Thermal Analysis

In order to determine the stability of the endoperoxides, thermogravimetric analysis (TGA) was performed on compound **2a**.

The compounds were weighed in under an atmosphere of synthetic air and heated from 30 °C to 500 °C at a rate of 10 °C/min while continuously measuring the sample weight. The weight was plotted against the temperature as shown below (**black**). The sigmoid curve (**red**) was fitted with the software program *Origin 2019b* from OriginLab. The minimum of the first derivative of said fit corresponds to the decomposition of the compound.



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Gleichung	double span = A2 - A1;
	double Section1 = span*p/(1+pow(10,(LOGx01-x)*h1));
	double Section2 = span* (1-p)/(1+pow(10,(LOGx02-x)*h2));
	y=A1 + Section1 +Section2;

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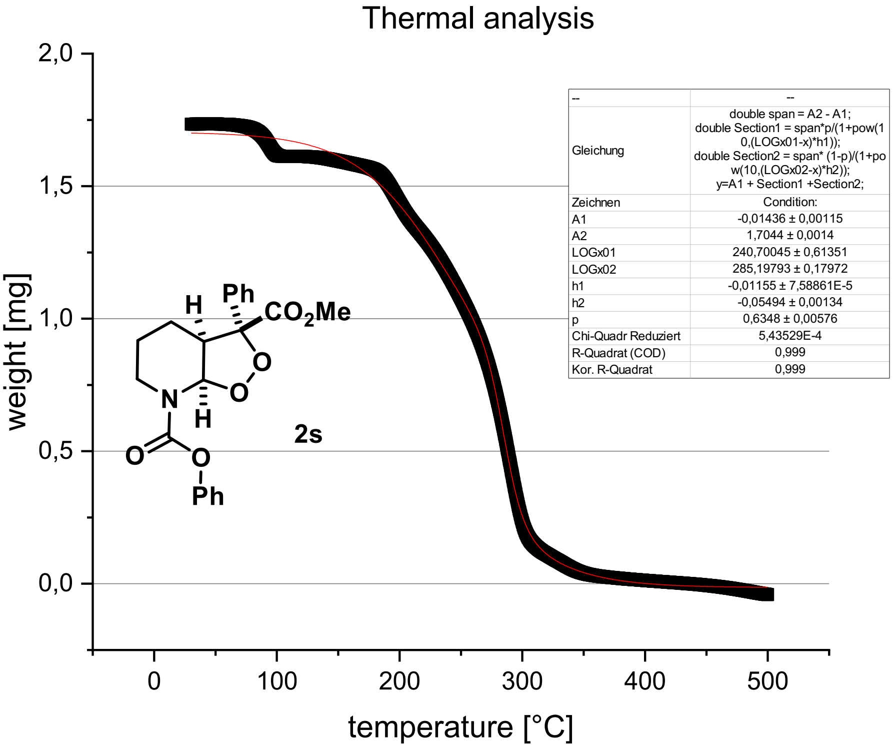
A1	-0,26731 ± 0,00406
A2	3,463 ± 0,00263
LOGx01	212,32305 ± 0,10975
LOGx02	364,93745 ± 3,29559
h1	-0,02805 ± 1,6842E-4
h2	-0,01977 ± 0,00274
p	0,9575 ± 0,00219
Chi-Quadr Reduziert	0,00363
R-Quadrat (COD)	0,99868
Kor. R-Quadrat	0,99868

Decomposition temperature: 212 °C.



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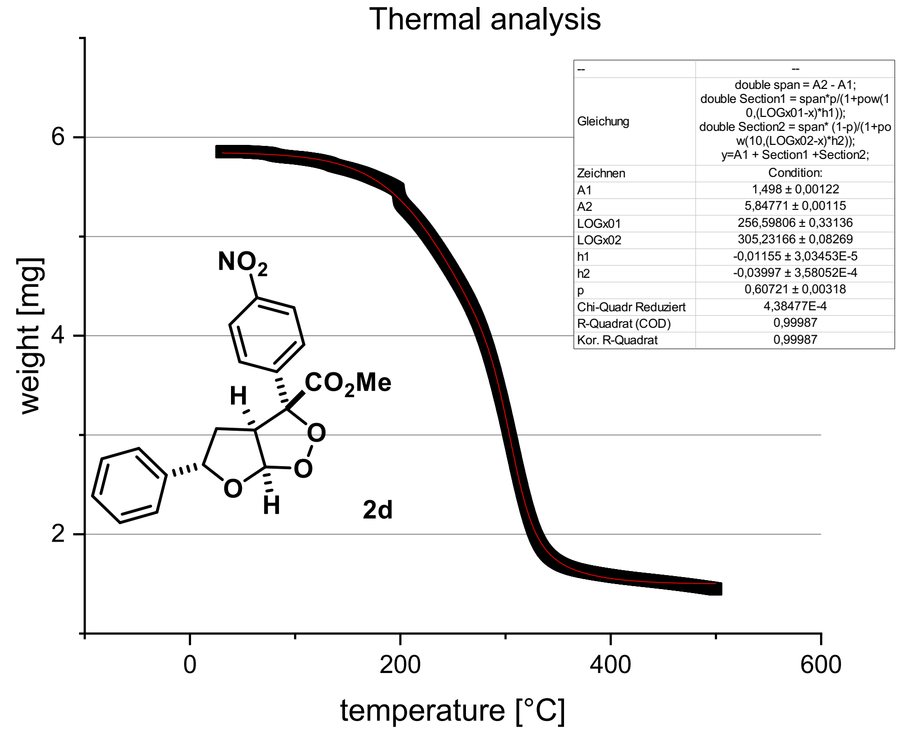
Gleichung	double span = A2 - A1;
	double Section1 = span*p/(1+pow(10,(LOGx01-x)*h1));
	double Section2 = span* (1-p)/(1+pow(10,(LOGx02-x)*h2));
	y=A1 + Section1 +Section2;

Zeichnen	Condition:
A1	-0,01436 ± 0,00115
A2	1,7044 ± 0,0014
LOGx01	240,70045 ± 0,61351
LOGx02	285,19793 ± 0,17972
h1	-0,01155 ± 7,58861E-5
h2	-0,05494 ± 0,00134
p	0,6348 ± 0,00576
Chi-Quadr Reduziert	5,43529E-4
R-Quadrat (COD)	0,999
Kor. R-Quadrat	0,999

Decomposition at 290 °C; presumably loss of residual water at 93°C.



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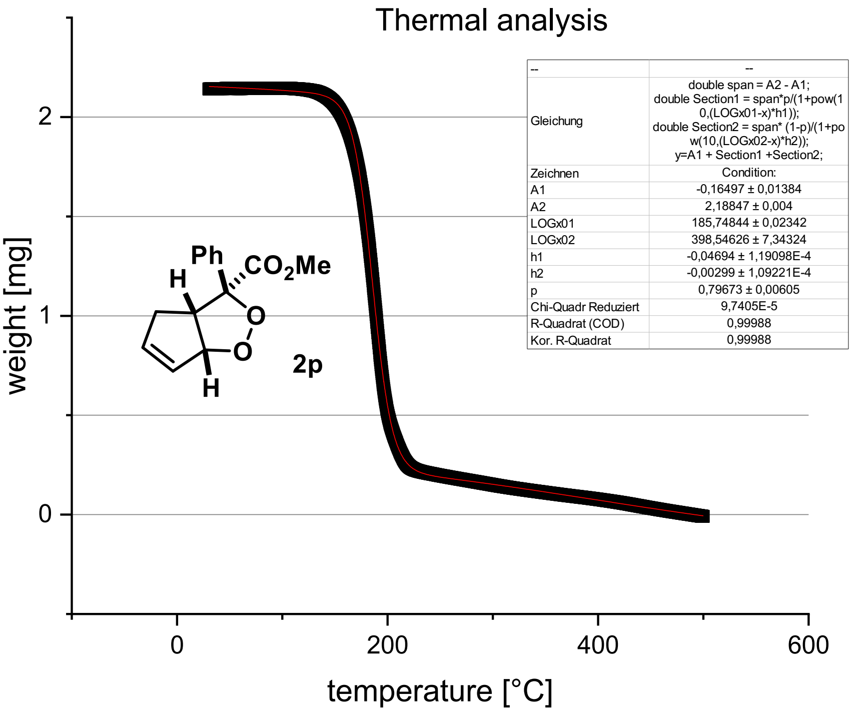
Gleichung	double span = A2 - A1;
	double Section1 = span*p/(1+pow(10,(LOGx01-x)*h1));
	double Section2 = span* (1-p)/(1+pow(10,(LOGx02-x)*h2));
	y=A1 + Section1 +Section2;

Zeichnen	Condition:
A1	1,498 ± 0,00122
A2	5,84771 ± 0,00115
LOGx01	256,59806 ± 0,33136
LOGx02	305,23166 ± 0,08269
h1	-0,01155 ± 3,03453E-5
h2	-0,03997 ± 3,58052E-4
p	0,60721 ± 0,00318
Chi-Quadr Reduziert	4,38477E-4
R-Quadrat (COD)	0,99987
Kor. R-Quadrat	0,99987

Decomposition at 303°C.



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Gleichung	double span = A2 - A1;
	double Section1 = span*p/(1+pow(10,(LOGx01-x)*h1));
	double Section2 = span* (1-p)/(1+pow(10,(LOGx02-x)*h2));
	y=A1 + Section1 +Section2;

Zeichnen	Condition:
A1	-0,16497 ± 0,01384
A2	2,18847 ± 0,004
LOGx01	185,74844 ± 0,02342
LOGx02	398,54626 ± 7,34324
h1	-0,04694 ± 1,19098E-4
h2	-0,00299 ± 1,09221E-4
p	0,79673 ± 0,00605
Chi-Quadr Reduziert	9,7405E-5
R-Quadrat (COD)	0,99988
Kor. R-Quadrat	0,99988

Decomposition at 189°C.

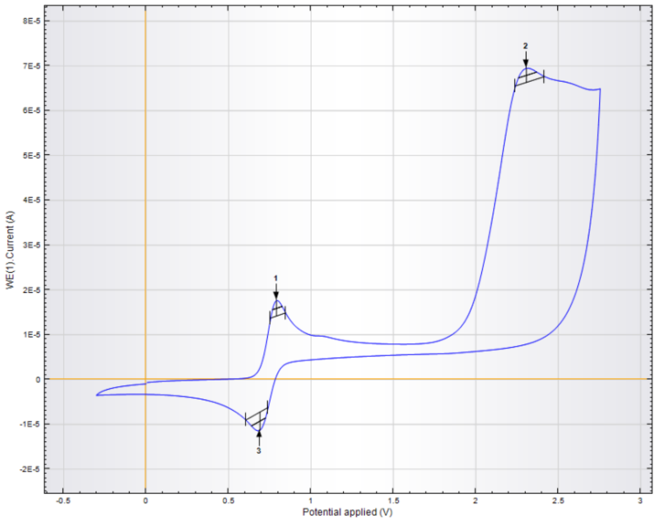
Cyclovoltammetry

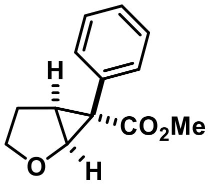
Cyclic voltammetry was used to determine the oxidation potential of some substrates and compared with the literature value[7] for $[MesAcr]^+$ of +2.07 V in the oxidative cycle. Ferrocene was used as internal standard (peaks are marked in *italics*), the potential vs. SCE is then calculated as follows:[8]

$$E_{1/2}[V] = E_S[V] - E_F[V] + C$$

($E_{1/2}[V]$: Redox potential vs. SCE; $E_S[V]$: Measured redox potential of the analyte; $E_F[V]$: Measured redox potential of ferrocene; Correction factor $C \coloneqq +0.38$ V)

Rac-methyl-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate **1a**

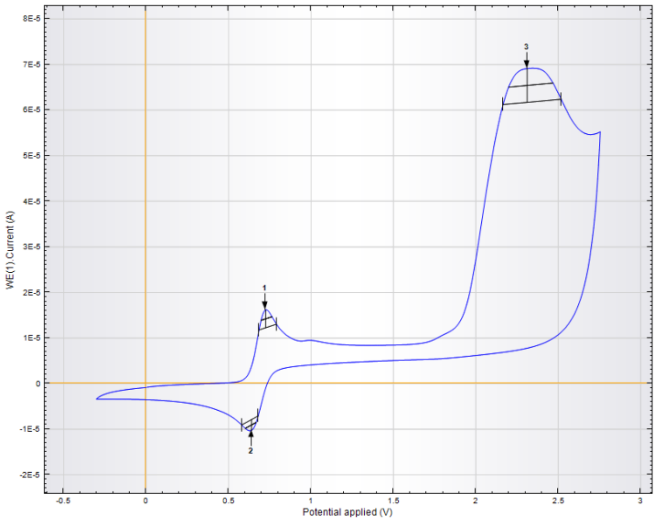


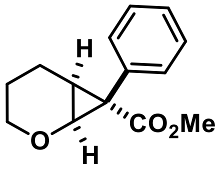


Index	Peak position
1	*0.79056*
2	2.3062
3	*0.68985*

$E_{(M/M+\cdot)}$: 1.95 V vs. SCE

Methyl 7-phenyl-2-oxabicyclo[4.1.0]heptane-7-carboxylate **1v**

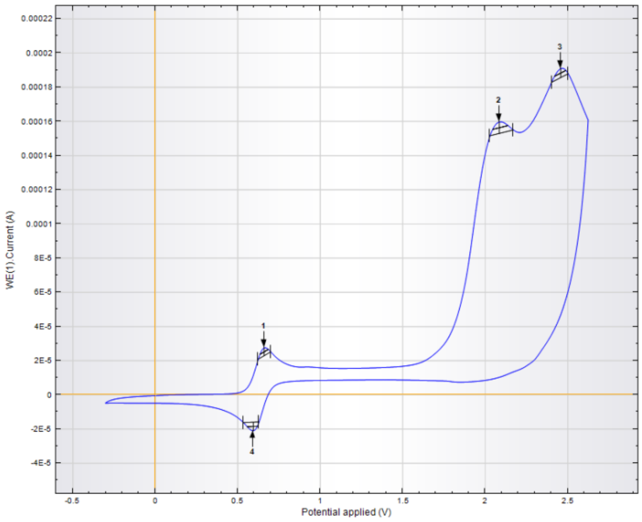


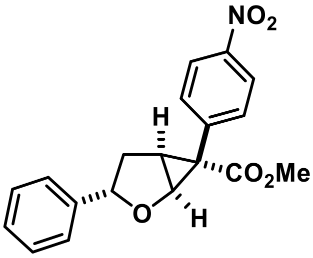


Index	Peak position
1	*0.7251*
2	*0.6395*
3	2.3112

$E_{(M/M+\cdot)}$: 2.00 V vs. SCE

Methyl 6-(4-nitrophenyl)-3-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate 1d





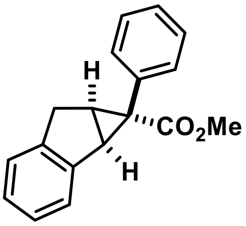
Index	Peak position
1	*0.65964*
2	2.0847
3	2.4573
4	*0.59418*

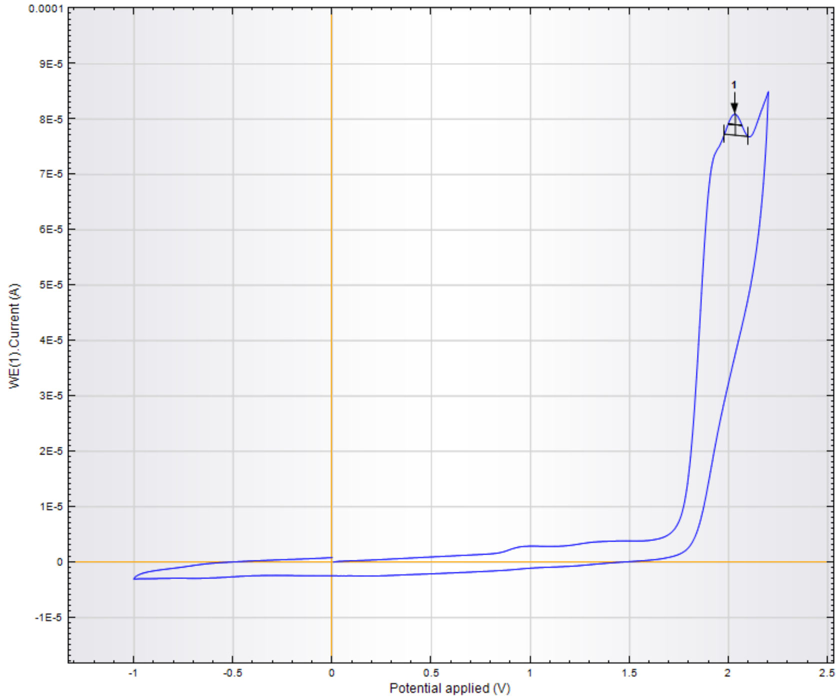
$E_{(M/M+\cdot)}$: 1.84 V vs. SCE for peak 2;

$E_{(M/M+\cdot)}$: 2.21 V vs. SCE for peak 3

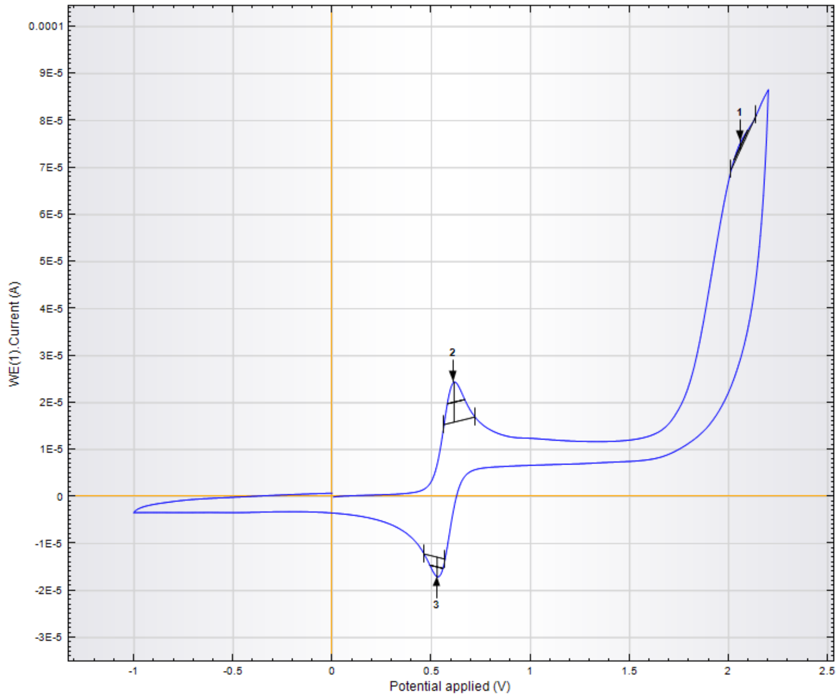
methyl 1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[a]indene-1-carboxylate

1o





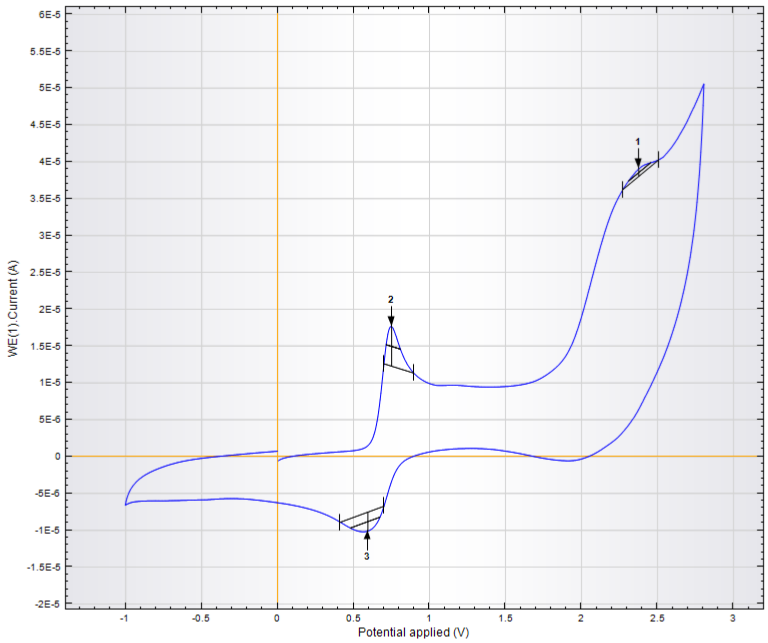
Index	Peak position
1	2.0343

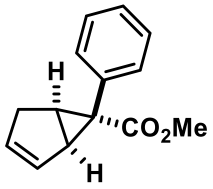


Index	Peak position
1	2.0595
2	0.61432
3	0.52872

$E_{(M/M+\cdot)}$: 1.87 V vs. SCE

methyl 6-phenylbicyclo[3.1.0]hex-2-ene-6-carboxylate 1p

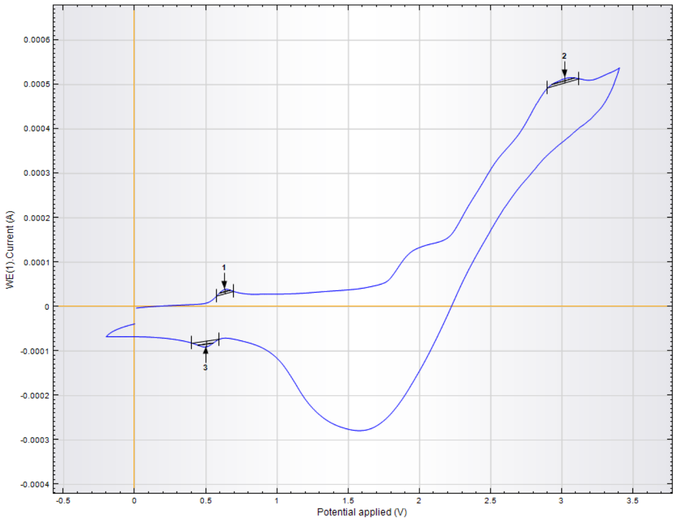


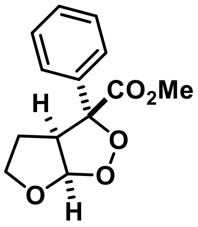


Index	Peak position
1	2.3767
2	0.75027
3	0.59418

$E_{(M/M+\cdot)}$: 2.08 V vs. SCE

Methyl 3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate 2a





Index	Peak position
1	*0.63446*
2	3.0212
3	*0.50354*

$E_{(M/M+\cdot)}$: 2.83 V vs. SCE

Fluorescence quenching

Fluorescence intensity and lifetime quenching can give indications about the interaction of catalyst and substrate. Therefore the intensity and lifetime of the fluorescence of the catalyst [MesAcr]ClO_4 are measured in the respective solvent. Then substrate **1a** is added successively, and the development of intensity and lifetime is analyzed.

Table 1: Measurements under air

probe	pure	25 µL	50 µL	100 µL	200 µL	500 µL	substpure
Intensity [au]	1878380	1828803	1792953	1787610	1773803	1779917	1744917
Lifetime [ns]	6,473319	6,062533	6,020994	5,968409	5,931989	5,947243	5,865632
Chi^2	1,153671	1,135958	1,18721	1,171837	1,147781	1,11271	1,1853
added vol. [L]	0	0,000025	0,00005	0,0001	0,0002	0,0005	n.A
total vol. [L]	0,002	0,002025	0,00205	0,0021	0,0022	0,0025	n.A
$n_{(cat)}$ [mmol]	0,00016	0,000162	0,000164	0,000168	0,000176	0,0002	n.A
$n_{(qu)}$ [mmol]	0	8E-05	0,00016	0,00032	0,00064	0,001601	n.A
$n_{(qu)}/n_{(cat)}$	0	0,49381	0,975576	1,904696	3,636237	7,999721	40
$I_{(qu)}/I_{(pure)}$	1	0,973607	0,954521	0,951676	0,944326	0,947581	0,928948
$t_{(add)}/t_{(pure)}$	1	0,936542	0,930125	0,922001	0,916375	0,918732	0,906124
$[I_{(pure)}/i_{(add)}]-1$	0	0,027109	0,047646	0,050777	0,058956	0,055319	0,076487

Excitation at 440 nm, emission measured between 450 and 600 nm, intensity at maximum is reported.

Table 2: Measurements under nitrogen

probe	pure	25 µL	50 µL	100 µL	200 µL	500 µL	substpure
Intensity [au]	1322897	1297073	1276573	1270797	1277430	1281240	1299920
Lifetime [ns]	7,789377	7,702887	7,710023	7,635077	7,634908	7,584592	7,605927
Chi^2	1,057809	1,063876	1,0761	1,076137	1,12047	1,100293	1,144738
added vol. [L]	0	0,000025	0,00005	0,0001	0,0002	0,0005	n.A
total vol. [L]	0,002	0,002025	0,00205	0,0021	0,0022	0,0025	n.A
$n_{(cat)}$ [mmol]	0,00016	0,000162	0,000164	0,000168	0,000176	0,0002	n.A
$n_{(qu)}$ [mmol]	0	8E-05	0,00016	0,00032	0,00064	0,001601	n.A
$n_{(qu)}/n_{(cat)}$	0	0,49381	0,975576	1,904696	3,636237	7,999721	40
$I_{(add)}/I_{(pure)}$	1	0,98048	0,964983	0,960617	0,965631	0,968511	0,982632
$t_{(qu)}/t_{(pure)}$	1	0,988896	0,989813	0,980191	0,980169	0,97371	0,976449
$[I_{(pure)}/i_{(add)}]-1$	0	0,019909	0,036287	0,040998	0,035592	0,032513	0,017675

Excitation at 440 nm, emission measured between 450 and 600 nm, intensity at maximum is reported.

The starting intensity of pure catalyst solution is lowered by approx. 20% under air compared to under nitrogen atmosphere.

Figure 1: Fluorescence intensity quenching

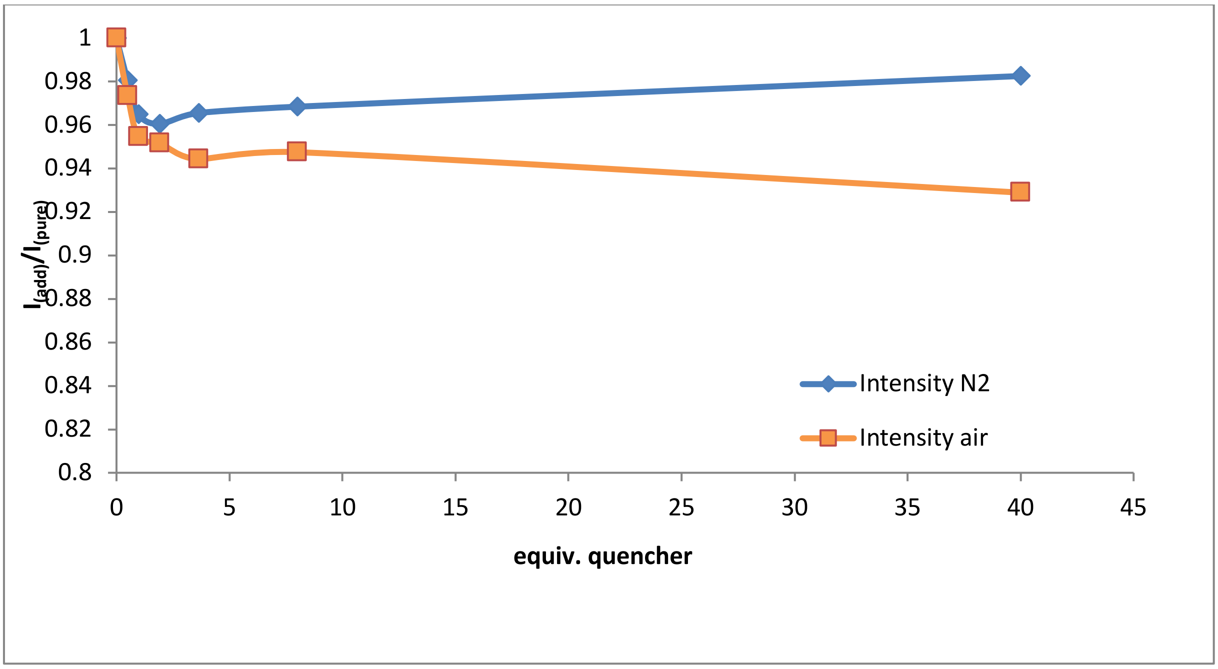
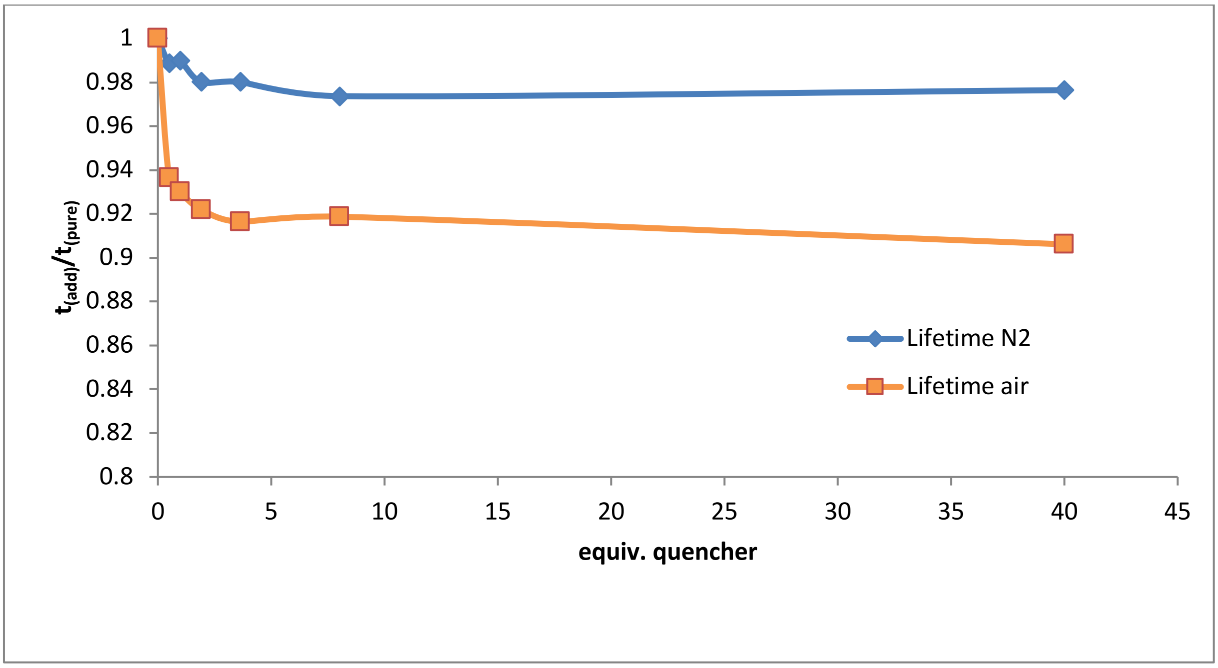


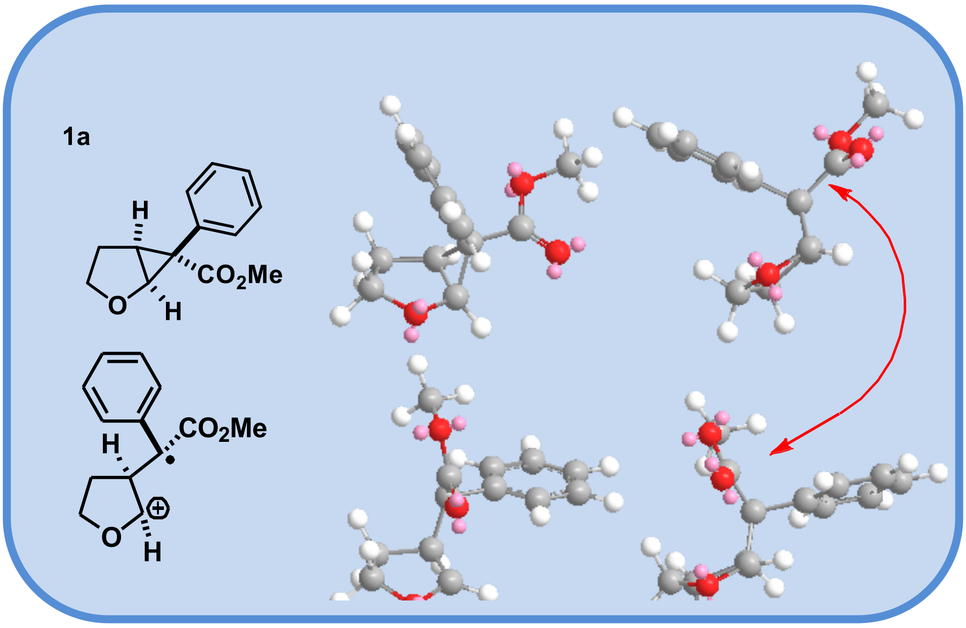
Figure 2: Fluorescence lifetime quenching



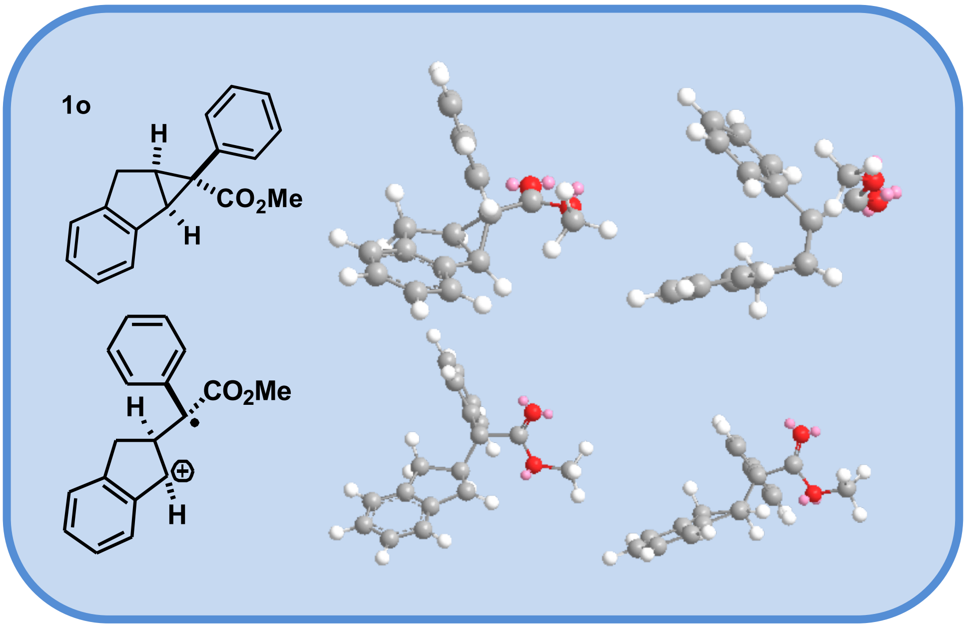
A stronger quenching is observed under air than under nitrogen atmosphere, but both show similar behavior. Overall quenching is low but significant, indicating that there is interaction between the catalyst and the substrate.

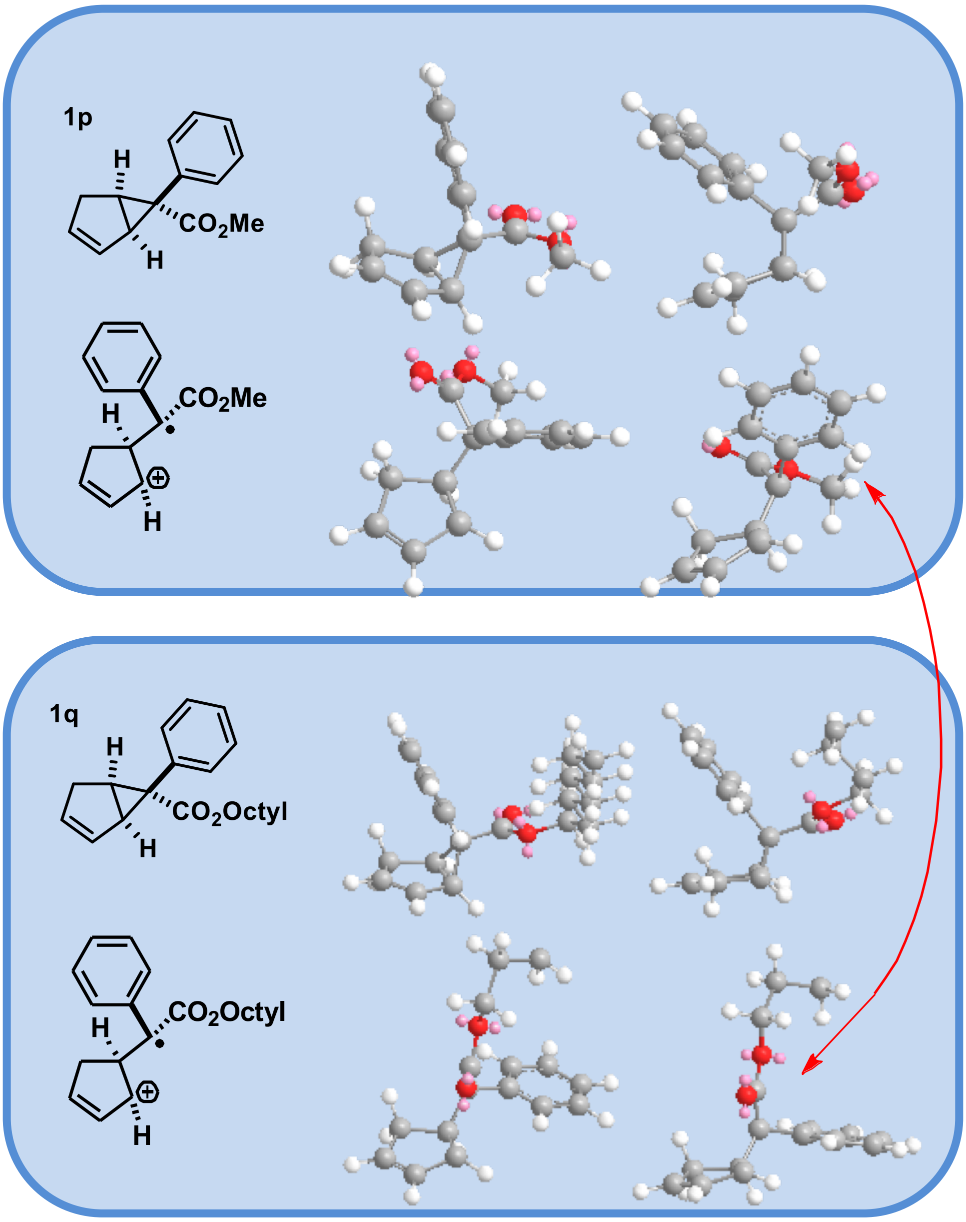
MM2 Minimization: Structural analysis

MM2 Structure Minimization was done using Chem3D Version 17.1.0.105 on the structures shown on the right. The minimized structures are shown from two different angles, and important features are marked with a red arrow and commented below the corresponding figure.

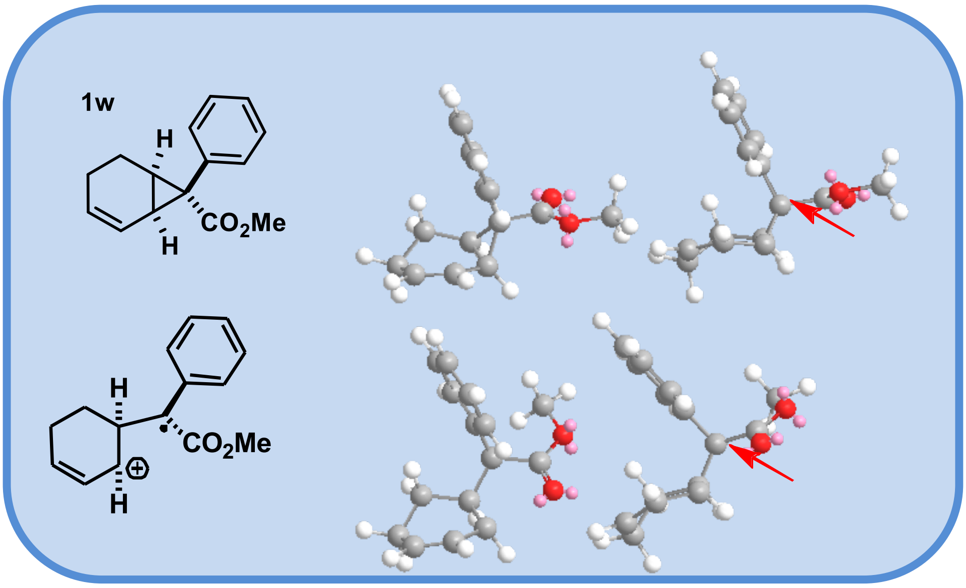


Orientation changes as observed in the actual diastereomeric distribution.

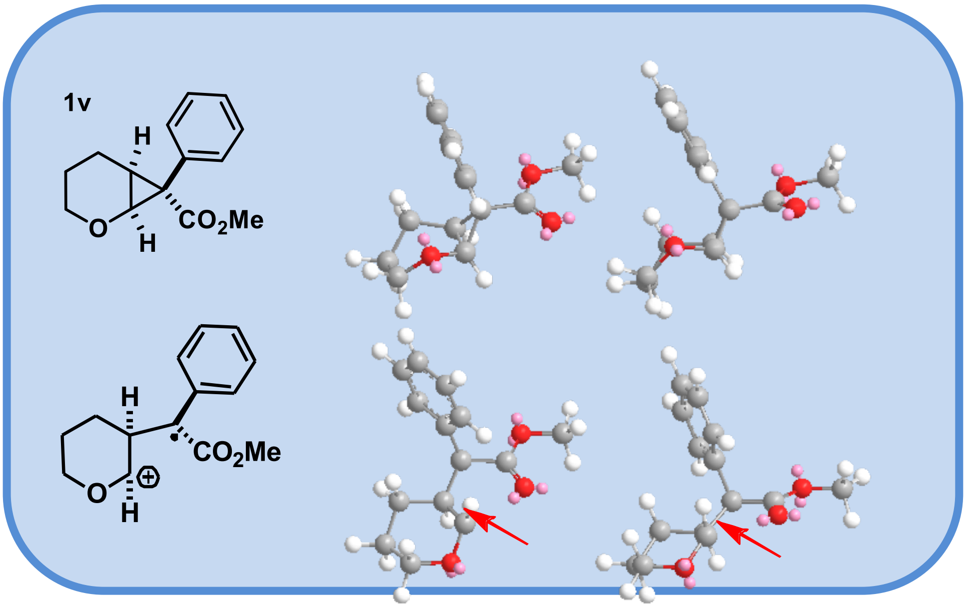




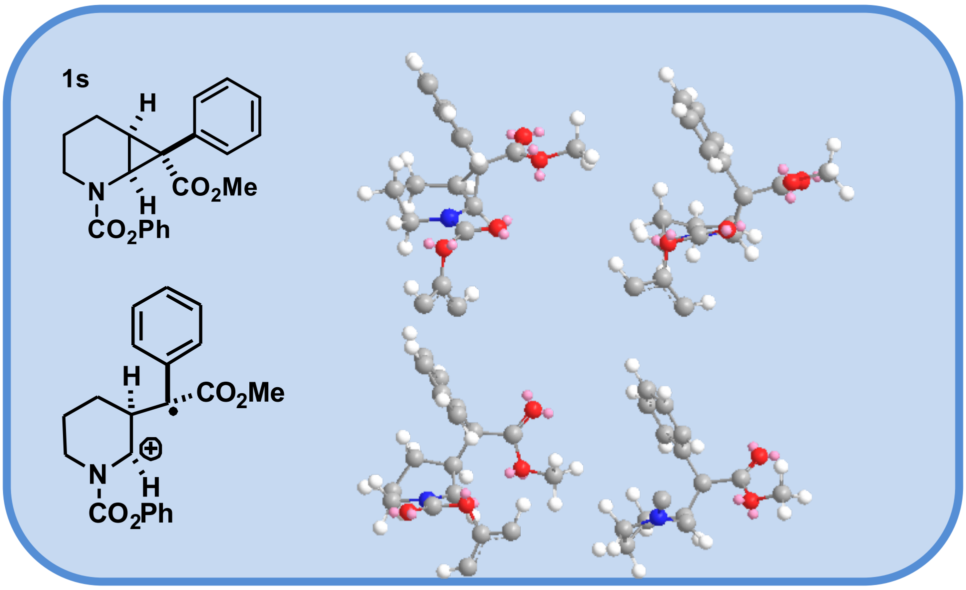
Parts of the octyl group are omitted for clarity; the octyl ester has a great impact on the orientation in the oxidized form, which is also observed in the actual diastereomeric outcome of the reactions.



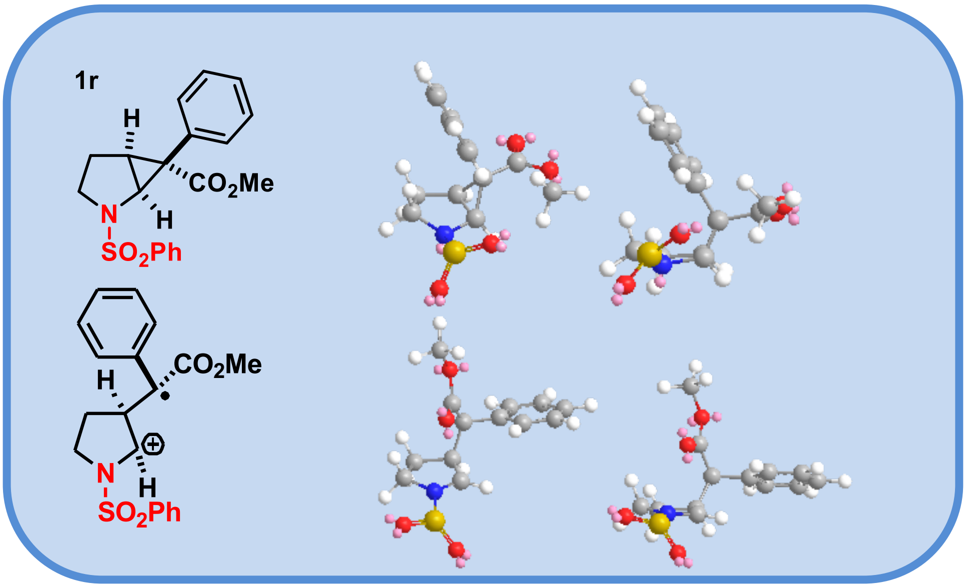
As there are other reactions (e.g. Schenck-ene) possible, this substrate seems to readily react under the conditions but not in the desired way, leading to the observed decomposition.



The proton marked has an unusual orientation compared to all other structures, especially to the piperidin-derived shown below, which might explain that this substrate did not undergo a reaction.



Parts of the protecting group are omitted for clarity; In contrast to the pyran derivative (above), the oxidized structures appears to be less bent.



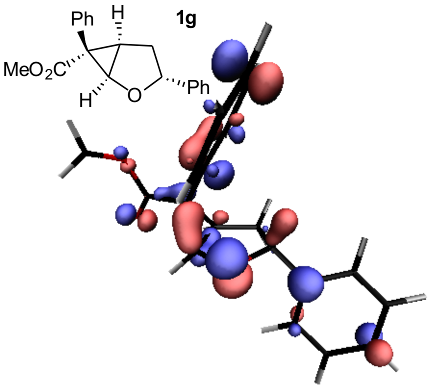
Parts of the protection group are omitted for clarity. The orientation of the ester changes analogously as for the furan derivative.

Gamess Optimization and Orbital Simulation

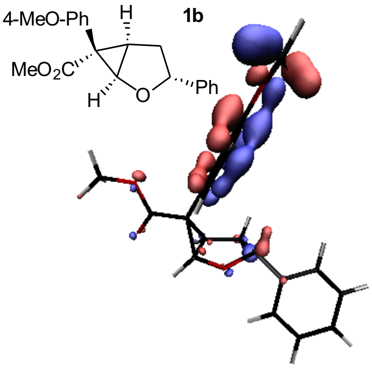
Gamess[9, 10] (General Atomic and Molecular Electronic Structure System, Version 2019.R1.P1.mkl) was used to assess the Highest Occupied Molecular Orbital (HOMO) of selected compounds in search of possible explanations for observed differences in reactivity (*vide infra*). More information on the program ´Gamess´c is available at https://www.msg.chem.iastate.edu/GAMESS/ . The input file for Gamess was partially prepared using 'Avogadro' (Version 1.2.0, www.avogadro.cc/) and further modified with the input given below. Avogadro and VMD[11] (Visual Molecular Dynamics, Version 1.9.3 https://www.ks.uiuc.edu/Research/vmd/) were used to visualize the results, the latter one to produce the pictures shown below.

Gamess input command:

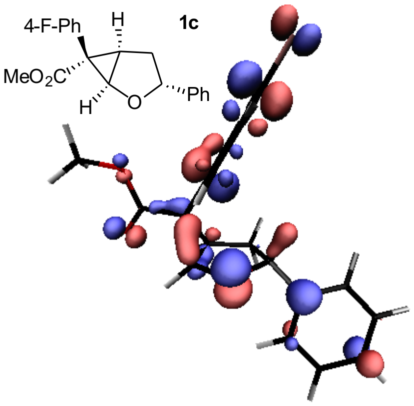
```
 $BASIS GBASIS=N31 NGAUSS=6 $END
 $CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE DFTTYP=B3LYP $END
 $STATPT OPTTOL=0.0001 NSTEP=250 $END
 $SYSTEM MWORDS=300 $END
```



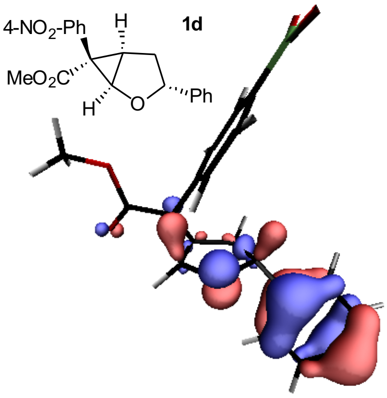
1g



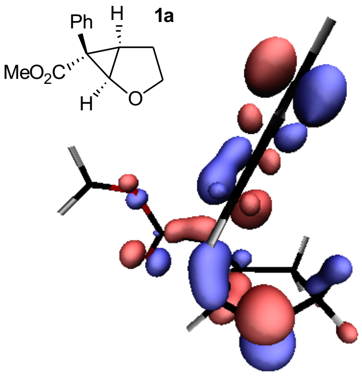
1b

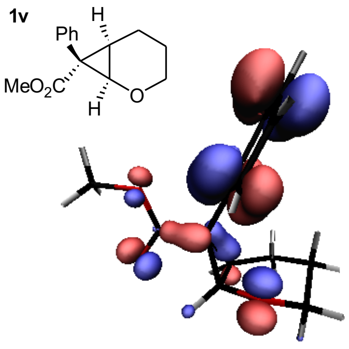


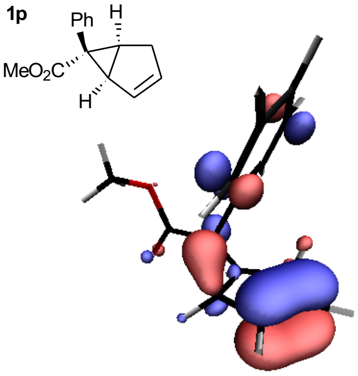
1c

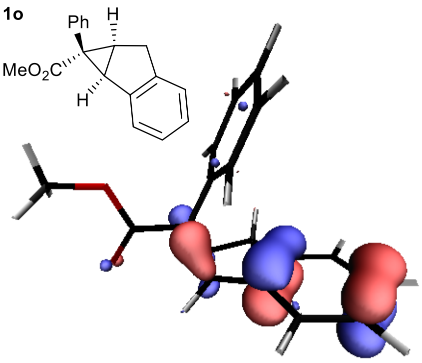


1d


1a

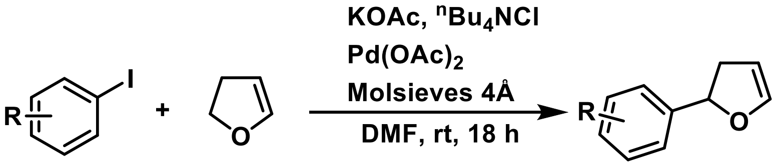

1v


1p


1o

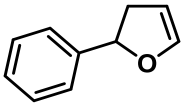
Synthesis of starting materials

General Procedure 1 (GP1) for the synthesis of 2-aryl-2,3-dihydrofurans



Following the literature procedure[12], a 100 mL round bottom flask was equipped with a magnetic stirbar and charged with KOAc (2.2 equiv.), ^{n}Bu$_4$NCl (2.5 equiv.) and crushed 4Å Molsieves (approx. a teaspoon per 5 mL DMF) which all was thoroughly stirred in DMF (1 mL per mmol of Ar-I). Then iodobenzene (1 equiv.), 2,3-dihydrofuran (5-10 equiv.) and Pd(OAc)$_2$ (5 mol%) were added successively in this order. The reaction mixture turned dark black within 10 min, and was further stirred for 18 h (over night) at room temperature. For work-up, Et$_2$O (approx. 10 mL per mmol Ar-I) was added and the resulting mixture filtered over a plug of celite. The filtrate was then washed twice with water and once with brine, dried over MgSO$_4$, filtrated and evaporated under reduced pressure. Purification of the crude by column chromatography yielded the pure product, which was then used in the next step.

2-phenyl-2,3-dihydrofuran ***(S1a)***



Following **GP1**, KOAc (1.08 g, 11 mmol, 2.2 equiv.), ^{n}Bu$_4$NCl (3.50 g, 12.5 mmol, 2.5 equiv.) and a spoonful of crushed Molsieves 4 Å were suspended in 5 mL DMF. Then iodobenzene (1.02 g, 1.86 mL and 2,3-dihydrofuran (3.5 mL, 45 mmol, 9 equiv.) was added. At last, Pd(OAc)$_2$ (56 mg, 0.25 mmol, 5 mol%) were added, and the reaction was stirred over night. After workup, the crude product was further purified by column chromatography (hexanes:EtOAc 19:1), yielding a colorless clear oil. (663 mg, 4.54 mmol, 91%);

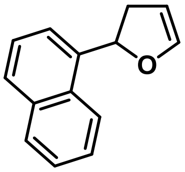
R$_f$ (hexanes:EtOAc 9:1) = 0.62; purple with vanillin.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.41 – 7.28 (m, 5H), 6.46 (q, *J* = 2.4 Hz, 1H), 5.52 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.97 (q, *J* = 2.6 Hz, 1H), 3.09 (ddt, *J* = 15.4, 10.7, 2.4 Hz, 1H), 2.62 (ddt, *J* = 15.2, 8.4, 2.4 Hz, 1H).

LR-MS (EI-MS): m/z calc. for C$_{10}$H$_{10}$O [M$^{+\cdot}$] 146.0731, found 146.0719.

Analytical data is in accordance with the literature[12].

2-(naphthalene-1-yl)-2,3-dihydrofuran ***(S1b)***



Following **GP1**, KOAc (1.1 g, 11 mmol, 2.2 equiv.), $^nBu_4NCl$ (3.47 g, 12.5 mmol, 2.5 equiv.) and a spoonful of crushed Molsieves 4 Å were suspended in 5 mL DMF. Then 1-iodonaphthalene (1.27 g 5 mmol, 1 equiv.), and 2,3-dihydrofuran (3.5 mL, 45 mmol, 9 equiv.) were added. At last, $Pd(OAc)_2$ (56 mg, 0.25 mmol, 5 mol%) was added, and the reaction was stirred over night. After workup the crude product was further purified by column chromatography (hexanes:EtOAc 19:1), yielding a colorless clear oil. (848 mg, 4.33 mmol, 86%);

R

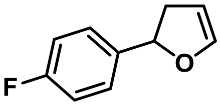
R_f (hexanes:EtOAc 9:1) = 0.55; brown with vanillin.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 – 7.88 (m, 2H), 7.81 (bd, *J* = 8.2 Hz, 1H), 7.61 (bdt, *J* = 7.1 Hz, 1H), 7.55 – 7.47 (m, 3H), 6.59 (q, *J* = 2.4 Hz, 1H), 6.19 (dd, *J* = 11.0, 8.4 Hz, 1H), 5.04 (q, *J* = 2.6 Hz, 1H), 3.30 (ddt, *J* = 15.1, 11.0, 2.4 Hz, 1H), 2.67 (ddt, *J* = 15.1, 8.4, 2.4 Hz, 1H).

LR-MS (EI-MS): m/z calc. for $C_{10}H_{10}O$ [$M^{+\cdot}$] 196.0888, found 196.0886.

Analytical data is in accordance with the literature[12].

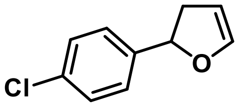
2-(4-fluorophenyl)-2,3-dihydrofuran ***(S1c)***



Following **GP1**, KOAc (1.04 g, 11 mmol, 2.2 equiv.), $^nBu_4NCl$ (3.3 g, 12 mmol, 2.5 equiv.) and a spoonful of crushed Molsieves 4 Å were suspended in 7 mL DMF. Then 1-fluoroiodobenzene (1.06 g 4.8 mmol, 1 equiv.), and 2,3-dihydrofuran (3.5 mL, 45 mmol, 10 equiv.) were added. At last, $Pd(OAc)_2$ (50 mg, 0.22 mmol, 5 mol%) was added, and the reaction was stirred over night. The crude product isolated after workup as yellowish oil (607 mg, 3.7 mmol, 77%), was used in the next step without further purification.

Analytical data is in accordance with the literature[13].

2-(4-chlorophenyl)-2,3-dihydrofuran ***(S1d)***



Following **GP1**, KOAc (1.1 g, 11 mmol, 2.2 equiv.), $^nBu_4NCl$ (3.5 g, 12.5 mmol, 2.5 equiv.) and a spoonful of crushed Molsieves 4 Å were suspended in 5 mL DMF. Then 4-chloroiodobenzene (1.20 g

5 mmol, 1 equiv.), and 2,3-dihydrofuran (3.5 mL, 45 mmol, 9 equiv.) were added. At last, $Pd(OAc)_2$ (56 mg, 0.25 mmol, 5 mol%) was added, and the reaction was stirred over night. After workup the crude product was further purified by column chromatography (hexanes:EtOAc 19:1), yielding a colorless clear oil. (741 mg, 4.12 mmol, 86%);

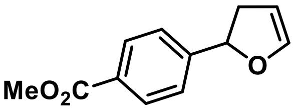
R$_f$ (hexanes:EtOAc 9:1) = 0.72; bright purple with vanillin.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 4H), 6.44 (q, *J* = 2.4 Hz, 1H), 5.49 (dd, *J* = 10.8, 8.2 Hz, 1H), 4.96 (q, *J* = 2.6 Hz, 1H), 3.08 (ddt, *J* = 15.3, 10.8, 2.4 Hz, 1H), 2.55 (ddt, *J* = 15.3, 8.2, 2.4 Hz, 1H).

LR-MS (EI-MS): m/z calc. for $C_{10}H_{10}O$ [$M^{+\cdot}$] 180.0342, found 180.0337.

Analytical data is in accordance with the literature[14].

Methyl-4-(2,3-dihydrofuran-2-yl)benzoate ***(S1e)***



Following **GP1**, KOAc (860 mg, 8.8 mmol, 2.2 equiv.), $^nBu_4NCl$ (2.78 g, 10 mmol, 2.5 equiv.) and a spoonful of crushed Molsieves 4 Å were suspended in 5 mL DMF. Then methyl 4-iodobenzoate (1.05 g 4 mmol, 1 equiv.), and 2,3-dihydrofuran (2.7 mL, 34 mmol, 8.5 equiv.) were added. At last, $Pd(OAc)_2$ (45 mg, 0.2 mmol, 5 mol%) was added, and the reaction was stirred over night. After workup the crude product was further purified by column chromatography (hexanes:EtOAc 99:1 to 19:1), yielding a colorless clear oil. (709 mg, 3.48 mmol, 87%);

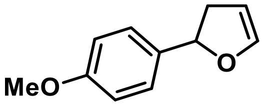
R$_f$ (hexanes:EtOAc 9:1) = 0.6; brownish with vanillin.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 6.47 (q, *J* = 2.4 Hz, 1H), 5.56 (dd, *J* = 10.8, 8.2 Hz, 1H), 4.96 (q, *J* = 2.5 Hz, 1H), 3.91 (s, 3H), 3.12 (ddt, *J* = 15.5, 10.9, 2.4 Hz, 1H), 2.56 (ddt, *J* = 15.2, 8.2, 2.4 Hz, 1H).

LR-MS (EI-MS): m/z calc. for $C_{12}H_{12}O_3$ [$M^{+\cdot}$] 204.0786, found 204.0790.

Analytical data is in accordance with the literature[15].

2-(4-methoxyphenyl)-2,3-dihydrofuran ***(S1f)***



Following **GP1**, KOAc (1.1 g, 11 mmol, 2.2 equiv.), $^nBu_4NCl$ (3.5 g, 12.5 mmol, 2.5 equiv.) and a spoonful of crushed Molsieves 4 Å were suspended in 5 mL DMF. Then 4-iodoanisole (1.17 g 5 mmol, 1 equiv.), and 2,3 dihydrofuran (3.5 mL, 45 mmol, 9 equiv.) were added. At last, $Pd(OAc)_2$ (56 mg, 0.25 mmol, 5 mol%) was added, and the reaction was stirred over night. After workup the crude product was further purified by column chromatography (hexanes:EtOAc 19:1), yielding a colorless clear oil. (751 mg, 4.27 mmol, 86%);

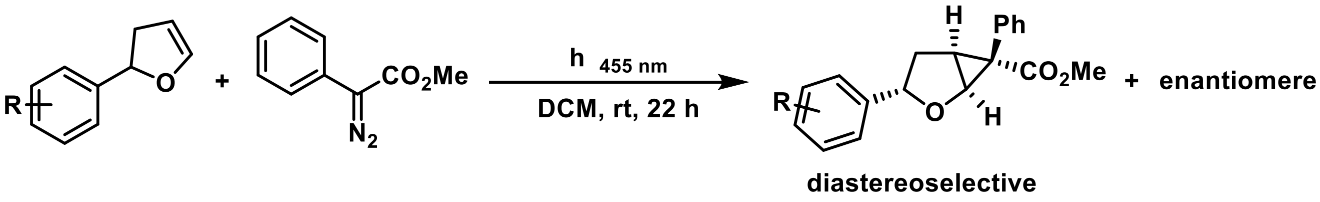
R_f (hexanes:EtOAc 9:1) = 0.57; dark brown with vanillin.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.26 (m, 3H), 6.97 – 6.79 (m, 2H), 6.43 (q, *J* = 2.4 Hz, 1H), 5.47 (dd, *J* = 10.6, 8.5 Hz, 1H), 4.96 (q, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.04 (ddt, *J* = 15.3, 10.6, 2.4 Hz, 1H), 2.61 (ddt, *J* = 15.2, 8.5, 2.4 Hz, 1H).

LR-MS (EI-MS): m/z calc. for $C_{10}H_{10}O$ $[M^{+\cdot}]$ 176.0837, found 176.0836.

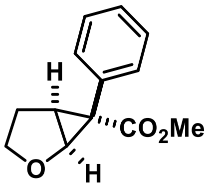
Analytical data is in accordance with the literature[12].

General Procedure 2 (GP2) for the photochemical cyclopropanation



Modifying the literature procedure[16] aryl 2,3-dihydrofuran (1 equiv.) and methyl 2-phenyl-2-diazoacetate (1.5 equiv.) were dissolved in dry DCM (approx. 6 mL per mmol dihydrofuran) in a schlenck tube equipped with a glass rod (see General Information for setup details). The mixture was degassed either by bubbling N_2 for 3 min or 3 freeze-pump-thaw cycles. After 24 h of blue light irradiation, the solvent was evaporated under reduced pressure and the crude mixture purified by column chromatography.

Methyl (1S*,5S*,6R*)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *(±)-1a*



Following GP2 2,3-dihydrofuran (1.0 mL, 14 mmol, 3 equiv.) was reacted with methyl 2-phenyl-2-diazoacetate (790 mg, 4.5 mmol, 1 equiv.) for 22 h in 20 mL DCM The crude product was purified by column chromatography (Hexanes:EtOAc 9:1) to yield 821 mg (3.77 mmol, 83%) of a viscous colorless oil (at room temperature) which solidified in the fridge to an amorphous substance.

R$_f$ (hexanes:EtOAc 4:1) = 0.35; greenish with vanillin.

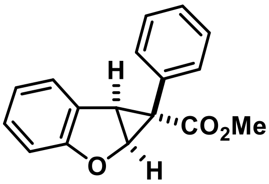
IR (neat): 3050, 2952, 2902, 1701, 1434, 1312, 1243, 1117, 1068, 1027, 943, 901, 859 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.43 – 7.28 (m, 5H), 4.50 (d, J = 5.7 Hz, 1H), 3.77 (ddd, J = 10.1, 8.4, 3.6 Hz, 1H), 3.56 (s, 3H), 2.65 (t, J = 5.7 Hz, 1H), 2.43 – 2.31 (m, 1H), 2.30 – 2.16 (m, 1H), 1.90 – 1.79 (m, 1H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 172.0, 132.2, 131.5, 128.5, 127.6, 70.2, 70.1, 52.4, 38.1, 32.5, 26.3.

HR-MS (EI-MS): m/z calc. for $C_{13}H_{14}O_3$ [M$^{+\cdot}$] 218.09375, found 218.09385.

Methyl 1-phenyl-1a,6b-dihydro-1H-cyclopropa[b]benzofuran-1-carboxylate ***1f***



Following GP2, benzo[b]furan (1.2 g, 10 mmol, 3 equiv.) and methyl 2-phenyl-2-diazoacetate (602 mg, 3.4 mmol, 1 equiv.) were reacted. Column chromatography (hexanes:EtOAc 19:1) yielded colorless crystalline solid (683 mg, 2.56 mmol, 76%).

R$_f$ (hexanes:EtOAc 9:1) = 0.4; bright red with vanillin.

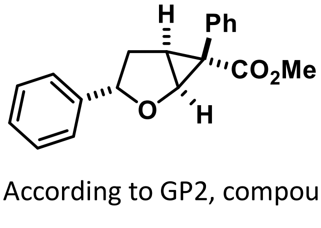
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.35 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.08 (s, 5H), 6.94 – 6.87 (td, J = 7.4, 1.3 Hz, 1H), 6.80 (td, *J* = 7.4, 1.1 Hz, 1H), 6.46 (dq, *J* = 8.1, 0.7 Hz, 1H), 5.36 (d, *J* = 5.5 Hz, 1H), 3.79 (dd, *J* = 5.5, 0.5 Hz, 1H), 3.67 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 173.3, 159.4, 132.5, 129.5, 128.0, 127.5, 127.1, 126.4, 125.0, 121.1, 109.6, 70.4, 52.7, 37.4, 30.9.

LR-MS (EI-MS): m/z calc. for $C_{17}H_{14}O_3$ [M$^{+\cdot}$] 266.0943, found 266.0937.

Analytical data is in accordance with the literature.[3]

Methyl (1R,3R,5R,6S)-3,6-diphenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate ***1g***



According to GP2, compound **S1a** (506 mg, 3.47 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (790 mg, 4.5 mmol, 1.3 equiv.) were reacted for 22 h in 20 mL DCM. Column chromatography (hexanes:EtOAc 9:1) yielded a colorless crystalline solid (737 mg, 2.50 mmol, 72%).

R$_f$ (hexanes:EtOAc 9:1) = 0.25; light brown with vanillin.

m.p.: 94 °C.

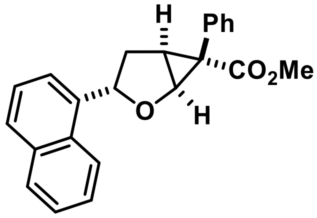
IR (neat): 3052, 2938, 2907, 2880, 1700, 1600, 1435, 1248, 1114, 1068, 1002, 946, 863 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 5H), 7.22 (m, 3H), 7.08 (m, 2H), 4.75 (d, *J* = 5.8 Hz, 1H), 3.60 (s+t overlap, 4H), 3.54 (s, 1H), 2.73 (t, *J* = 6.0 Hz, 1H), 2.35 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.16 (ddd, *J* = 13.4, 8.3, 6.0 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.2, 142.2, 132.4, 131.7, 128.7, 128.6, 128.4, 128.0, 127.7, 127.6, 125.5, 83.0, 70.2, 52.5, 37.6, 35.7, 32.3.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{18}O_3$ $[M^{+\cdot}]^+$ 294.12505, found 294.12494.

Methyl 3-(naphthalene-1-yl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate ***1h***



According to GP2, compound **S1b** (503 mg, 2.56 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (590 mg, 3.3 mmol, 1.3 equiv.) were reacted for 22 h in 15 mL DCM. Column chromatography (hexanes:EtOAc 9:1) yielded a colorless oil which solidified in the fridge (598 mg, 1.73 mmol, 68%).

R$_f$ (hexanes:EtOAc 9:1) = 0.4; light brown with vanillin.

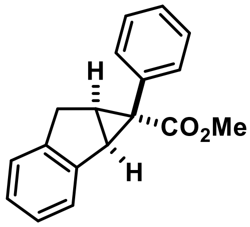
IR (neat): 3059, 2952, 1726, 1693, 1429, 1366, 1329, 1249, 1222, 1156, 1124, 1100, 1012, 989, 969, 880, 855, 773 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.50 (m, 5H), 7.45 – 7.36 (m, 5H), 7.32 (m, 1H), 4.89 (d, *J* = 5.8 Hz, 1H), 4.25 (t, *J* = 8.3 Hz, 1H), 3.64 (s, 3H), 2.81 (t, *J* = 5.8 Hz, 1H), 2.55 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.24 (ddd, *J* = 13.4, 8.3, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3): δ 172.2, 137.6, 133.9, 132.5, 131.8, 129.7, 128.8, 128.8, 128.6, 128.1, 128.0, 127.9, 126.0, 125.5, 125.5, 123.1, 122.3, 81.0, 70.1, 52.5, 37.7, 34.8, 32.4.

HR-MS (EI-MS): m/z calc. for $C_{23}H_{20}O_3$ $[M^{+\cdot}]$ 344.14070, found 344.13983.

Methyl (1S*,1aR*,6aR*)-1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[a]indene-1-carboxylate ***1o***



According to GP2, compound Indene (2.1 g, 18 mmol, 10 equiv.) and methyl 2-phenyl-2-diazoacetate (330 mg, 1.9 mmol, 1 equiv.) were reacted for 18 h in 6 mL DCM. Column chromatography (hexanes:EtOAc 19:1 to 9:1) yielded a colorless crystalline solid (460 mg, 1.74 mmol, 91%).

R$_f$ (hexanes:EtOAc 9:1) = 0.4; light brown with vanillin.

m.p.: 125 °C.

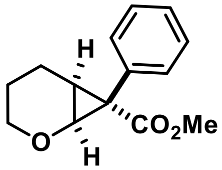
IR (neat): 3046, 2951, 2915, 2839, 1708, 1494, 1432, 1314, 1245, 1218, 1158, 1052, 942, 867 cm^{-1}.

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.13 – 7.00 (m, 4H), 6.99 – 6.84 (m, 3H), 6.72 (d, *J* = 7.5 Hz, 1H), 3.63 (s, 3H), 3.47 (d, *J* = 6.8 Hz, 1H), 3.23 (dd, *J* = 17.9, 6.7 Hz, 1H), 2.87 (t, *J* = 7.0 Hz, 1H), 2.75 (d, *J* = 17.9 Hz, 1H).

^{13}C NMR (75 MHz, CDCl$_3$): δ 174.0, 143.0, 141.4, 132.2, 132.1, 127.3, 126.5, 126.3, 126.1, 125.0, 124.1, 52.5, 40.7, 38.2, 33.2, 32.1.

HR-MS (EI-MS): m/z calc. for $C_{18}H_{16}O_3$ [M$^{+\cdot}$] 264.1144, found 264.1148.

Methyl 7-phenyl-2-oxabicyclo[4.1.0]heptane-7-carboxylate ***1v***



Following GP2, 3,4-dihydro-*2H*-pyran (2 g, 10 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (2.6 g, 15 mmol, 1.5 equiv.) were reacted. Column chromatography (hexanes:EtOAc 9:1) yielded a colorless crystalline solid (360 mg, 1.55 mmol, 88%).

R$_f$ (hexanes:EtOAc 4:1) = 0.33; light brown with vanillin.

m.p.: 110-113 °C.

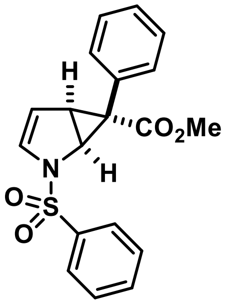
IR (neat): 3063, 2989, 2949, 2856, 1701, 1433, 1390, 1342, 1248, 1202, 1081, 1061, 972, 904 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38 – 7.28 (m, 5H), 4.21 (d, *J* = 7.5 Hz, 1H), 3.55 (s, 3H), 3.44 – 3.38 (m, 1H), 3.30 (ddd, *J* = 12.6, 10.7, 2.1 Hz, 1H), 2.16 (td, *J* = 7.3, 1.1 Hz, 1H), 2.01 (ddt, *J* = 14.2, 11.4, 7.0 Hz, 1H), 1.91 – 1.84 (m, 1H), 1.07 – 0.98 (m, 1H), 0.37 – 0.23 (m, 1H).

^{13}C NMR (101 MHz, CDCl3): δ 173.7, 133.2, 132.5, 128.0, 127.0, 64.5, 62.1, 52.3, 34.8, 25.3, 21.1, 17.4.

HR-MS (EI-MS): m/z calc. for $C_{14}H_{16}O_3$ [$M^{+\cdot}$] 232.10940, found 232.10881.

Methyl 6-phenyl-2-(phenylsulfonyl)-2-azabicyclo[3.1.0]hex-3-ene-6-carboxylate ***S1g***



1-(phenylsulfonyl)-1H-pyrrole (1.6 g, 7.7 mmol, 2 equiv.) and $Rh_2(OAc)_4$ were dissolved in 10 mL DCM and a solution of methyl 2-phenyl-2-diazoacetate (0.76 g, 3.8 mmol, 1 equiv.) in 5 mL DCM was added via a syringe pump over the course of 2 h. After completion of the reaction the solvent was removed and column chromatography (hexanes:EtOAc 9:1) yielded a colorless crystalline solid (562 mg, 1.58 mmol, 41%), which was used in the next step without additional purification.

R_f (hexanes:EtOAc 7:1) = 0.3; light brown with vanillin.

m.p.: 118-120 °C.

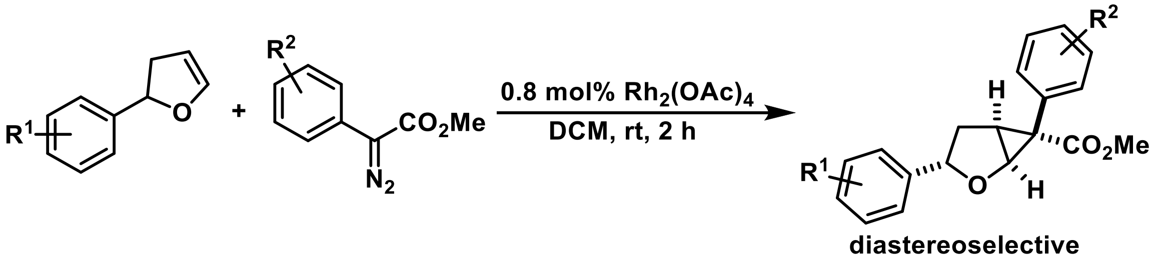
IR (neat): 3123, 2874, 2933, 2810, 2758, 1700, 1413, 1364, 1297, 1152, 1014, 831, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.25 (q, J = 4.9 Hz, 5H), 5.97 (d, J = 3.4 Hz, 1H), 5.31 (t, J = 3.1 Hz, 1H), 4.60 (dd, J = 6.6, 1.4 Hz, 1H), 3.57 (s, 3H), 3.17 (dd, J = 6.6, 2.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.3, 137.7, 133.3, 132.3, 130.6, 130.2, 129.3, 127.7, 127.3, 127.0, 111.4, 77.4, 77.1, 76.8, 52.6, 51.9, 38.5, 28.0.

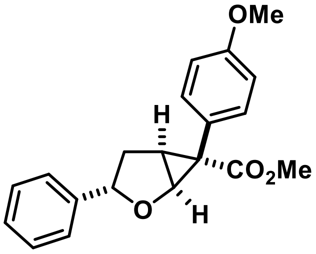
HR-MS (ESI-TOF): m/z calc. for $C_{19}H_{18}NO_4S$ [$M+H^{+\cdot}$] 356.0951, found 356.0954.

General Procedure 3 (GP3) for the $Rh_2(OAc)_4$ catalyzed cyclopropanation of phenyl-2,3-dihydrofurans



In an modification of commonly employed Rh-catalyzed cyclopropanations$^{e.g.3}$, a solution of 2-phenyl-2,3-dihydrofuran (1 equiv.) and $Rh_2(OAc)_4$ (0.08 mol%) in dry DCM (approx. 5 mL per mmol furan) in an 100 mL round bottom flask was degassed by bubbling N_2 for 3 min. The flask was then equipped with a rubber septum and a nitrogen balloon. In a separate flask, the methyl 2-aryl-2-diazoacetate (approx. 1.3 equiv.) was dissolved in dry DCM and the solution also degassed via N_2-bubbling for 3 min. This solution was then drawn up into a syringe and added to the solution of substrate and catalyst via a syringe pump over the course of 2-4 h. The resulting solution was stirred for further 2 h, then the solvent was removed under reduced pressure and the resulting crude purified by column chromatography.

Methyl (1S*,3S*,5S*,6R*)-6-(4-methoxy)-3-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1b*



Following GP3, compound **S1a** (562 mg, 3.86 mmol, 1.2 equiv.) and methyl 2-(4-methoxyphenyl)-2-diazoacetate (711 mg, 3.22 mmol, 1 equiv.) were reacted. Column chromatography (hexanes:EtOAc 9:1 ->7:1) yielded a colorless crystalline solid (554 mg, 1.70 mmol, 53%).

R_f (hexanes:EtOAc 9:1) = 0.18; yellow with vanillin.

m.p.: 98-100 °C.

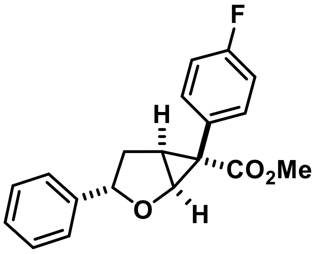
IR (neat): 3000, 2956, 2943, 2908, 2841, 1695, 1613, 1513, 1248, 1174, 1109, 1074, 1036, 862 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 2H), 7.29 – 7.16 (m, 3H), 7.11 (d, *J* = 7.0 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.74 (d, *J* = 5.8 Hz, 1H), 3.85 (s, 3H), 3.68 (t, *J* = 8.3 Hz, 1H), 3.60 (s, 3H), 2.71 (t, *J* = 5.9 Hz, 1H), 2.34 (dd, *J* = 13.3, 8.4 Hz, 1H), 2.16 (ddd, *J* = 13.5, 8.2, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 159.1, 142.4, 132.8, 128.4, 127.5, 125.5, 124.4, 114.2, 83.1, 70.2, 55.3, 52.4, 36.9, 35.7, 32.3.

HR-MS (EI-MS): m/z calc. for $C_{20}H_{21}O_4$ $[M+H^+]^+$ 325.1439, found 325.1434.

Methyl (1S*,3S*,5S*,6R*)-6-(4-fluorophenyl)-3-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1c*



Following GP3, compound **S1a** (226 mg, 1.55 mmol, 1.3 equiv.) and methyl 2-(4-fluorophenyl)-2-diazoacetate (230 mg, 1.18 mmol, 1 equiv.) were reacted. Column chromatography (hexanes:EtOAc 19:1 ->9:1) yielded a yellowish crystalline solid (132 mg, 0.42 mmol, 36%).

R_f (hexanes:EtOAc 9:1) = 0.22; brown with vanillin.

m.p.: 112-114 °C.

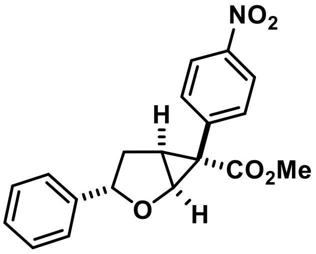
IR (neat): 3063, 2999, 2954, 2907, 2839, 1697, 1513, 1436, 1246, 1175, 1110, 1072, 1036, 862 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 2H), 7.30 – 7.19 (m, 3H), 7.16 – 7.08 (m, 4H), 4.76 (d, *J* = 5.8 Hz, 1H), 3.66 (t, *J* = 8.3 Hz, 1H), 3.61 (s, 3H), 2.75 (t, *J* = 5.8 Hz, 1H), 2.33 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.19 (ddd, *J* = 13.5, 8.4, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 162.4 (d), 142.1, 133.4 (d), 128.4, 128.3 (d), 127.6, 125.5, 115.8 (d), 83.2, 70.1, 52.4, 37.0, 35.6, 32.3.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{17}O_3F$ $[M^{+\cdot}]$ 312.11562, found 312.11497.

Methyl (1S*,3S*,5S*,6R*)-6-(4-nitrophenyl)-3-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1d*



Following GP3, compound **S1a** (340 mg, 0.84 mmol, 1.2 equiv.) and methyl 2-(4-nitrophenyl)-2-diazoacetate (156 mg, 0.71 mmol, 1 equiv.) were reacted. Column chromatography (hexanes:EtOAc 9:1 ->7:1) yielded a colorless crystalline solid (76 mg, 0.22 mmol, 32%).

The reaction was performed twice to obtain enough material for the follow-up reaction.

R_f (hexanes:EtOAc 9:1) = 0.18; yellow with vanillin.

m.p.: 181 °C

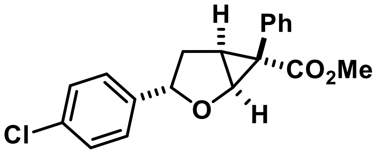
IR (neat): 3063, 2963, 2363, 1709, 1598, 1512, 1446, 1349, 1248, 1176, 1111, 1065, 943, 869 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.25 (m, 3H), 7.11 – 7.07 (m, 2H), 4.82 (d, *J* = 5.7 Hz, 1H), 3.65 (t, *J* = 8.2 Hz, 1H), 3.61 (s, 3H), 2.84 (t, *J* = 5.7 Hz, 1H), 2.36 – 2.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.7, 147.5, 141.6, 140.2, 132.8, 128.5, 127.8, 125.3, 123.8, 83.3, 70.0, 52.6, 37.5, 35.4, 32.7.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{17}NO_5$ [$M^{+\cdot}$] 339.11012, found 339.10954.

Methyl (1S*,3S*,5S*,6R*)-3-(4-chlorophenyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1i*



Following GP3, compound **S1c** (732 mg, 4.1 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (1.07 g, 6.1 mmol, 1.5 equiv.) were reacted. Column chromatography (hexanes:EtOAc 19:1 ->7:1) yielded a colorless oil which solidified in the fridge (598 mg, 3.13 mmol, 77%).

R_f (hexanes:EtOAc 9:1) = 0.42; light brown with vanillin.

m.p.: 162-164 °C

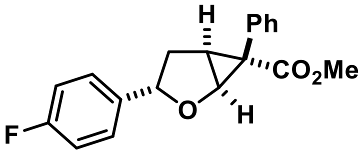
IR (neat): 3060, 2935, 1700, 1492, 1435, 1329, 1246, 1178, 1112, 1072, 1003, 944, 863, 831 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.37 (m, 5H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 4.75 (d, *J* = 5.8 Hz, 1H), 3.60 (s, 3H), 3.56 (t, *J* = 8.3 Hz, 1H), 2.73 (t, *J* = 5.8 Hz, 1H), 2.35 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.10 (ddd, *J* = 13.4, 8.3, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 140.8, 133.2, 132.3, 131.7, 128.7, 128.5, 127.8, 126.9, 82.3, 70.1, 52.5, 37.6, 35.8, 32.1.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{17}O_3Cl$ [$M^{+\cdot}$] 328.0860, found 328.0864.

Methyl (1S*,3S*,5S*,6R*)-3-(4-fluorophenyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1j*



Following GP3, compound **S1d** (607 mg, 3.7 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (930 mg, 5.3 mmol, 1.3 equiv.) were reacted to form a orange solution. Column chromatography (hexanes:EtOAc 9:1) yielded a colorless crystalline solid (595 mg, 1.91 mmol, 52%).

R_f (hexanes:EtOAc 9:1) = 0.37; light brown with vanillin.

m.p.: 151-153 °C

IR (neat): 3060, 2923, 1700, 1600, 1509, 1450, 1330, 1248, 1182, 1114, 1071, 1002, 944, 836 cm^{-1}.

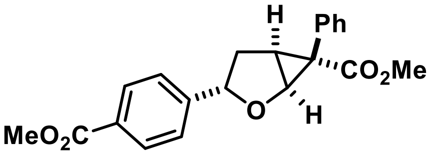
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 5H), 7.05 (m, 2H), 6.93 (m, 2H), 4.75 (d, *J* = 5.8 Hz, 1H), 3.60 (s, 3H), 3.57 (t, *J* = 8.3 Hz, 1H), 2.74 (t, *J* = 5.8 Hz, 1H), 2.34 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.16 – 2.09 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 163.4, 161.0, 137.9 (d), 132.4, 131.7, 128.7, 127.8, 127.3 (d), 115.2 (d), 82.4, 70.0, 52.5, 37.6, 35.8, 32.1. Doublets observed due to coupling with fluorine

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.56 (tt, *J* = 8.6, 5.4 Hz).

HR-MS (EI-MS): m/z calc. for $C_{19}H_{17}O_3F$ [$M^{+\cdot}$] 312.11562, found 312.11559.

Methyl (1S*,3S*,5S*,6R*)-3-(4-(methoxycarbonyl)phenyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1k*



Following GP3, compound **S1e** (633 mg, 3.1 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (810 mg, 4.6 mmol, 1.5 equiv.) were reacted. Column chromatography (hexanes:EtOAc 19:1 ->9:1) yielded a colorless crystalline solid (847 mg, 2.4 mmol, 77%).

R$_f$ (hexanes:EtOAc 9:1) = 0.25; brown with vanillin.

m.p.: 130 °C

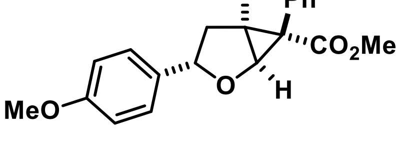
IR (neat): 3035, 2951, 2909, 1711, 1612, 1496, 1433, 1275, 1239, 1106, 1068, 947, 857 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.36 (m, 5H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.78 (d, *J* = 5.8 Hz, 1H), 3.87 (s, 3H), 3.65 (t, *J* = 8.3 Hz, 1H), 3.59 (s, 3H), 2.73 (t, *J* = 5.8 Hz, 1H), 2.39 (dd, *J* = 13.3, 8.3 Hz, 1H), 2.12 (ddd, *J* = 13.3, 8.3, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 166.8, 147.4, 132.2, 131.6, 129.8, 129.3, 128.7, 127.8, 125.2, 82.4, 70.2, 52.5, 52.1, 37.7, 35.7, 32.0.

HR-MS (APCI-MS): m/z calc. for $C_{21}H_{21}O_5$ [M+H]$^+$ 353.1384, found 353.1386.

Methyl (1S*,3S*,5S*,6R*)-3-(4-Methoxyphenyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1l*



Following GP3, compound **S1f** (573 mg, 3.26 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (695 mg, 3.95 mmol, 1.2 equiv.) were reacted. Column chromatography (hexanes:EtOAc 9:1) yielded a colorless solid (855 mg, 2.64 mmol, 81%).

R$_f$ (hexanes:EtOAc 9:1) = 0.25; brown with vanillin.

m.p.: 101-103 °C

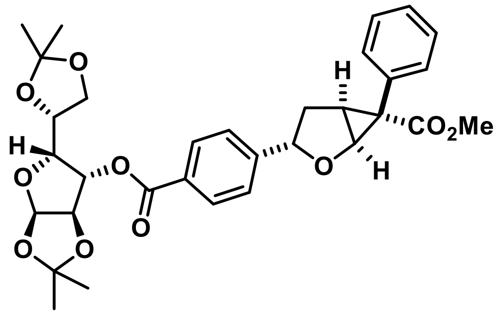
IR (neat): 3061, 2999, 2934, 1695, 1612, 1512, 1436, 1246, 1174, 1110, 1074, 1036, 1007, 862, 706cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 5H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.73 (d, *J* = 5.8 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.55 (t, *J* = 8.2 Hz, 1H), 2.74 (t, *J* = 5.8 Hz, 1H), 2.31 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.16 (ddd, *J* = 13.7, 8.3, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 159.1, 134.2, 132.5, 131.7, 128.7, 127.7, 127.0, 113.8, 82.8, 70.0, 55.3, 52.4, 37.6, 35.6, 32.3.

HR-MS (EI-MS): m/z calc. for $C_{20}H_{20}O_4$ [$M^{+\cdot}$] 324.13695, found 324.13606.

methyl (1R,3R,5R,6S)-3-(4-((((3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)carbonyl)phenyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate ***1m***



Following GP3, the corresponding dihydrofuran derivative (410 mg, 0.95 mmol, 1 equiv.) and methyl 2-phenyl-2-diazoacetate (190 mg, 1.05 mmol, 1.1 equiv.) were reacted. Column chromatography (hexanes:EtOAc 4:1 ->3:1) yielded a colorless oil (220 mg, 0.38 mmol, 40%).

R_f (hexanes:EtOAc 4:1) = 0.2; brown with vanillin.

IR (neat): 2956, 2906, 2840, 1740, 1713, 1612, 1516, 1368, 1219, 1177, 1030, 910, 835, 800 cm^{-1}.

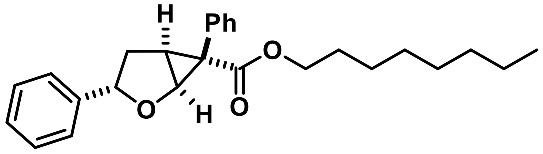
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 5H), 7.16 (d, *J* = 8.3 Hz, 2H), 5.92 (d, *J* = 3.7 Hz, 1H), 5.48 – 5.45 (m, 1H), 4.77 (d, *J* = 5.7 Hz, 1H), 4.60 (d, *J* = 3.7 Hz, 1H), 4.33 – 4.28 (m, 2H), 4.11 – 4.03 (m, 2H), 3.65 (t, *J* = 8.3 Hz, 1H), 3.59 (s, 3H), 2.73 (t, *J* = 5.8 Hz, 1H), 2.40 (dd, *J* = 13.3, 8.5 Hz, 1H), 2.10 (ddd, *J* = 13.8, 8.1, 6.2 Hz, 1H), 1.54 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 164.9, 148.1, 132.2, 131.6, 129.9, 128.8, 128.6, 127.8, 125.4, 125.3, 112.4, 109.4, 105.2, 83.4, 82.3, 82.3, 80.0, 72.6, 70.2, 67.3, 52.5, 37.7, 35.7, 31.9, 26.9, 26.8, 26.3, 25.2.

HR-MS (ESI-MS): m/z calc. for $C_{32}H_{36}O_{10}Na$ [$M+Na^+$]$^+$ 603.2199, found 603.2201.

Optical rotation (DCM): $[\alpha]_D^{20}$= 81.1°

Octyl (1S*,3S*,5S*,6R*)-3,6-diphenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate ***1n***



Following GP3, compound **S1a** (830 mg, 3.03 mmol, 1 equiv.) and octyl 2-phenyl-2-diazoacetate (891 mg, 6.1 mmol, 2 equiv.) were reacted. After reaction completion the crude was purified via column chromatography (hexanes:EtOAc 99:1), yielding a colorless oil (841 mg, 2.14 mmol, 70%).

R_f (hexanes:EtOAc 9:1) = 0.6; light brown with vanillin.

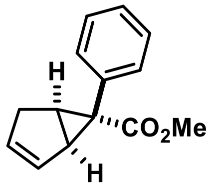
IR (neat): 3060, 2925, 2855, 1705, 1449, 1330, 1242, 1177, 1156, 1110, 1065, 972, 751, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.33 (m, 5H), 7.22 (m, 3H), 7.09 (d, *J* = 7.1 Hz, 2H), 4.75 (d, *J* = 5.8 Hz, 1H), 3.99 (td, *J* = 6.5, 1.4 Hz, 2H), 3.64 (t, *J* = 8.3 Hz, 1H), 2.72 (t, *J* = 5.9 Hz, 1H), 2.36 (dd, *J* = 13.3, 8.3 Hz, 1H), 2.16 (ddd, *J* = 13.7, 8.2, 6.1 Hz, 1H), 1.49 (p, *J* = 6.4 Hz, 2H), 1.25 (m, 11H), 0.89 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 142.3, 132.7, 131.6, 128.6, 128.4, 127.5, 127.5, 125.5, 82.9, 69.9, 65.2, 37.9, 35.8, 31.9, 31.8, 29.2, 29.1, 28.5, 25.8, 22.7, 14.2.

HR-MS (EI-MS): m/z calc. for $C_{26}H_{33}O_3$ $[M+H^+]^+$ 393.2424, found 393.2427.

Methyl (1S*,5R*,6S*)-6-phenylbicyclo[3.1.0]hex-2-ene-6-carboxylate ***1p***



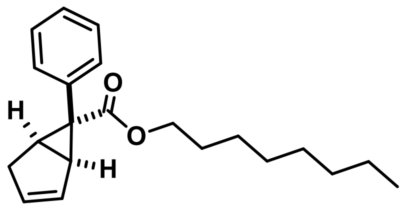
Following GP3, freshly distilled cyclopentadiene (1.8 mL, 21.3 mmol, 7 equiv.) and methyl 2-phenyl-2-diazoacetate (5.3 mL, 3.0 mmol, 1 equiv.) were reacted. Column chromatography (hexanes:EtOAc 99:1 ->9:1) yielded a colorless crystalline solid (318 mg, 1.49 mmol, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.20 (m, 3H), 7.15 – 7.05 (m, 2H), 5.78 – 5.71 (m, 1H), 5.24 – 5.16 (m, 1H), 3.58 (s, 3H), 3.00 – 2.87 (m, 1H), 2.72 – 2.56 (m, 2H), 2.14 – 1.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.5, 133.1, 133.0, 132.9, 129.7, 127.6, 126.8, 77.4, 77.1, 76.8, 52.5, 40.9, 37.9, 34.2, 32.4.

Analysis was in accordance with the literature[18].

Octyl (1S*,5R*,6S*)-6-phenylbicyclo[3.1.0]hex-2-ene-6-carboxylate ***1q***



Following GP3, freshly distilled cyclopentadiene (0.225 mL, 2.7 mmol, 5 equiv.) and octyl 2-Phenyl-2-diazoacetate (145 mg, 0.53 mmol, 1 equiv.) were reacted in presence of $Rh_2(OAc)_4$ (1.4 mg, 0.0032 mmol, 0.006 equiv.). Column chromatography (hexanes:EtOAc 99:1 ->9:1) yielded a colorless oil (85.9 mg, 0.275 mmol, 52%).

R$_f$ (hexanes:EtOAc 9:1) = 0.7.

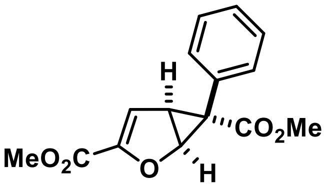
IR (neat): 3061, 2925, 2855, 1708, 1456, 1226, 1222, 1156, 1072, 972, 950, 866, 746 cm^{-1}.

^{1}H NMR (400 MHz CDCl$_3$): δ 7.35 – 7.26 (m, 2H), 7.25 – 7.18 (m, 2H), 7.12 – 7.06 (m, 2H), 5.76 (dt, *J* = 5.4, 2.0 Hz, 1H), 5.23 – 5.18 (m, 1H), 4.03 – 3.92 (m, 2H), 2.94 – 2.88 (m, 1H), 2.69 – 2.59 (m, 2H), 2.14 – 2.05 (m, 1H), 1.46 (p, *J* = 6.7 Hz, 2H), 1.23 (dd, *J* = 28.5, 8.5 Hz, 15H), 0.88 (t, *J* = 7.0 Hz, 4H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 174.0, 132.9, 132.7, 129.8, 127.5, 126.6, 65.1, 41.6, 40.5, 38.2, 34.2, 32.1, 31.8, 29.2, 29.1, 28.6, 25.8, 22.7, 14.2.

HR-MS (ESI-MS): m/z calc. for $C_{21}H_{29}O_2$ $[M+H^+]^+$ 313.2167, found 313.2162.

Dimethyl (3R*,5S*,6R*)-6-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate ***S1h***



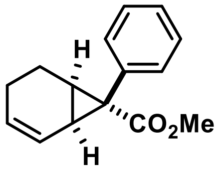
Following GP3, methyl 2-furoate (530 µL, 5 mmol, 2 equiv.) and methyl 2-phenyl-2-diazoacetate (440 mg, 2.5 mmol, 2 equiv.) were reacted. Column chromatography (hexanes:EtOAc 5:1) yielded a colorless crystalline solid (563 mg, 2.07 mmol, 88%).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 – 7.20 (m, 6H), 4.77 (dd, *J* = 10.5, 6.9 Hz, 1H), 4.61 (d, *J* = 6.1 Hz, 1H), 3.55 (s, 3H), 3.27 (s, 3H), 2.72 (ddd, *J* = 7.2, 6.1, 1.1 Hz, 1H), 2.59 (ddd, *J* = 13.9, 10.5, 7.2 Hz, 1H), 2.26 (ddd, *J* = 13.9, 6.9, 1.1 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 173.1, 158.8, 148.8, 132.2, 129.5, 128.0, 127.7, 114.12, 71.1, 52.8, 52.0, 39.5, 28.5.

Analytical data is in accordance with the literature[3].

Methyl (1S*,6R*,7S*)-7-phenylbicyclo[4.1.0]hept-2-ene-7-carboxylate ***1w***



Following the literature procedure[19], $AgSbF_6$ (179 mg, 0.52 mmol, 0.1 equiv.) was weighed into a flame dried Schlenck flask under N_2 atmosphere. The flask was wrapped in aluminum foil to exclude light and 10 mL dry DCM as well as Cyclohexadiene (2.4 mL, 25.2 mmol, 5 equiv.) were added. In a separate flask, methyl 2-phenyl-2-diazoacetate (970 mg, 5.5 mmol, 1 equiv.) was dissolved in 6 mL dry DCM and degassed by N_2 sparging, after which it was added to the cyclohexadiene-solution via a syringe pump over the course of 3 h. The solution was stirred for additional 1 h, then the solvent was removed under reduced pressure and the crude purified via column chromatography (hexanes:EtOAc 19:1 -> 9:1). The product was then recrystallized from Et_2O to remove remaining cyclohexadiene to yield white crystals (415 mg 1.8 mmol, 33%).

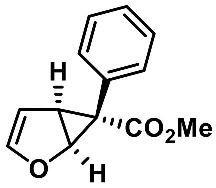
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 16.6 Hz, 5H), 6.03 (d, *J* = 9.4 Hz, 1H), 5.50 – 5.37 (m, 1H), 3.59 (s, 3H), 2.42 – 2.29 (m, 2H), 2.04 – 1.94 (m, 1H), 1.83 (s, 1H), 1.59 (dd, *J* = 15.7, 8.4 Hz, 1H), 0.47 (dt, *J* = 18.5, 9.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 134.7, 131.7, 128.4, 127.7, 126.9, 122.7, 52.4, 40.3, 27.7, 25.6, 21.0, 16.8.

Analytical data is in accordance with the literature[19].

Other substrates

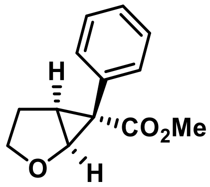
Methyl (1S,5S,6R)-6-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carboxylate ***(-)-S1i***



In an modification of GP2 and following the literature procedure[3], furan (150 µL, 2 mmol, 2 equiv.) and methyl 2-phenyl-2-diazoacetate (176 mg, 1 mmol, 1 equiv.) were reacted in presence of Rh_2(*S*-TCPTTL)$_4$ (1.8 mg, 1 µmol, 0.1 mol%) in dry hexanes (2 mL). After reaction completion, the solution was washed with 1M HCl, water and brine to remove the rhodium catalyst. Column chromatography (Hexanes:EtOAc 4:1) and repeated recrystallization from methanol afforded the product as white solid (145 mg, 0.67 mmol, 67%; 97% ee as determined by chiral HPLC).

Analytical data is in accordance with the literature[3].

Methyl (1S,5S,6R)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate ***(-)-1a***



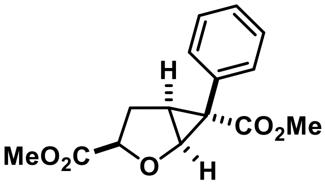
In an uncovered vial, **(-)-S1i** (120 mg, 0.55 mmol, 1 equiv.) was dissolved in EtOAc (10 mL), and Rh/C (8.1 mg, 0.0039 mmol, 0.7 mol%) was added. The vial was then placed in an autoclave and after purging with H_2 three times, the reaction was stirred under 30 bar H_2 for 2 h. The crude product was purified by column chromatography (Hexanes:EtOAc 9:1) to yield a viscous clear oil which solidified in the fridge (116 mg, 0.53 mmol, 97%).

Analytical data is identical to **(±)-1a**.

Optical rotation: $[\alpha]_D^{20}$=-66.6° in DCM.

Chiral HPLC chromatogram available; column: Phenomenex Lux Cellulose-1; eluent Heptane: iPrOH 99:1; Flow: 1 mL/min Retention time: 28.5, <u>29.6</u>. Enantiomeric excess 98% ee.

Dimethyl (1S*,3R*,5S*,6R*)-6-phenyl-2-oxabicyclo[3.1.0]hexane-3,6-dicarboxylate ***1t***



S1h (531 mg, 1.94 mmol, 1 equiv.) was dissolved in 5 mL EtOAc. Pd/C (5%w/w Pd, 40 mg, 0.019 mmol Pd, 0.1 equiv.) was added, and the solution was stirred in an autoclave at 25 bar H_2 for 2h. Then the solution was filtrated, the solvent evaporated under reduced pressure and the crude purified by column chromatography (hexanes:EtOAc 9:1 to 5:1), yielding a colorless crystalline solid (523 mg, 1.89 mmol, 97%)

R$_f$ (hexanes:EtOAc 4:1) = 0.36; reddish brown with vanillin.

m.p.: 140-142 °C.

IR (neat): 3028, 2957, 2849, 1752, 1735, 1700, 1497, 1435, 1232, 1155, 1084, 1025, 956, 862 cm^{-1}.

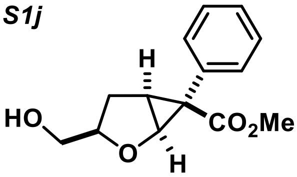
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38 – 7.22 (m, 5H), 4.77 (dd, *J* = 10.4, 6.9 Hz, 1H), 4.61 (d, *J* = 6.0 Hz, 1H), 3.55 (s, 3H), 3.26 (s, 3H), 2.72 (ddd, *J* = 7.1, 6.1, 1.0 Hz, 1H), 2.59 (ddd, *J* = 13.8, 10.4, 7.2 Hz, 1H), 2.26 (ddd, *J* = 13.9, 6.9, 1.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 171.7, 170.1, 133.3, 129.9, 128.2, 127.9, 83.6, 71.3, 52.5, 52.0, 41.2, 32.6, 29.0.

HR-MS (APCI-MS): m/z calc. for $C_{15}H_{17}O_5$ $[M+H^+]^+$ 277.1071, found 277.1074.

Methyl (1S*,3R*,5S*,6R*)-3-(hydroxymethyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate

S1j



1t (1.01 g, 3.6 mmol, 1 equiv.) was dissolved in a mixture of 15 mL THF and 25 mL MeOH, and $NaBH_4$ (281 mg, 7.7 mmol, 2.1 equiv.) was slowly added in portions (gas evolution!). The reaction was stirred over night, then the solvents were evaporated and the crude subjected to column chromatography (hexanes:EtOAc 2:1), yielding a colorless solid (554 mg, 2.23 mmol, 62%).

R$_f$ (hexanes:EtOAc 2:1) = 0.23; yellow with vanillin.

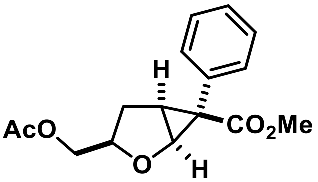
m.p.: 118 °C

IR (neat): 3469, 3043, 2954, 1707, 1446, 1332, 1252, 1103, 1252, 1103, 1047, 1026, 960, 863 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.32 (m, 3H), 7.28 – 7.22 (m, 2H), 4.56 – 4.45 (m, 2H), 3.57 (s, 3H), 3.03 (dd, *J* = 12.0, 3.1 Hz, 1H), 2.72 (ddd, *J* = 7.8, 6.2, 1.8 Hz, 1H), 2.43 (dd, *J* = 12.0, 6.1 Hz, 1H), 2.20 (dt, *J* = 13.5, 7.9 Hz, 1H), 1.60 (ddd, *J* = 13.6, 9.6, 1.9 Hz, 1H), 0.93 (bs, 1H).

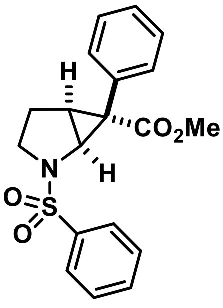
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7, 133.3, 131.4, 128.5, 127.9, 90.3, 69.5, 63.0, 52.3, 43.1, 33.2, 26.9.
HR-MS (ESI-MS): m/z calc. for $C_{14}H_{17}O_4$ $[M+H^+]^+$ 249.1121, found 249.1125.

Methyl (1S*,3R*,5S*,6R*)-3-(acetoxymethyl)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate *1e*



S1j (520 mg, 2.1 mmol, 1 equiv.) was dissolved in 10 mL DCM, and Triethylamine (400 µL, 2.9 mmol, 1.4 equiv) was added. Ac_2O was added (275 µL, 2.7 mmol, 1.3 equiv.) and the resulting cloudy solution stirred for 3 h. Then the solution was washed with 0.5 M HCl, $NaHCO_{3(aq,\ sat)}$, and brine. The organic phase was then dried over $MgSO_4$ and the crude was purified by crystallization from DCM/Et_2O, yielding colorless crystals (504 mg, 1.74 mmol, 83%).
R_f (hexanes:EtOAc 4:1) = 0.38; bright yellow with vanillin.
m.p.: 114-116 °C.
IR (neat): 3043, 2966, 2910, 1745, 1700, 1437, 1372, 1249, 1229, 1072, 1043, 962, 858 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 7.27 (m, 3H), 7.22 (dd, *J* = 8.0, 1.5 Hz, 2H), 4.65 – 4.46 (m, 2H), 3.54 (s, 3H), 3.31 (dd, *J* = 11.6, 3.5 Hz, 1H), 2.69 (ddd, *J* = 7.6, 6.1, 1.6 Hz, 1H), 2.58 (dd, *J* = 11.6, 8.4 Hz, 1H), 2.33 (ddd, *J* = 13.6, 8.4, 7.7 Hz, 1H), 1.92 (s, 3H), 1.44 (ddd, *J* = 13.6, 9.3, 1.6 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 171.6, 170.4, 133.3, 128.4, 127.9, 86.4, 70.6, 65.0, 52.3, 42.7, 32.6, 28.5, 20.7.
HR-MS (ESI-MS): m/z calc. for $C_{16}H_{19}O_5$ $[M+H^+]^+$ 291.1227, found 291.1231.

Methyl (1S*,5S*,6R*)-6-phenyl-2-(phenylsulfonyl)-2-azabicyclo[3.1.0]hexane-6-carboxylate *1r*



Compound **S1g** (422 mg, 1.18 mmol, 1 equiv.) was dissolved in 10 mL EtOAc and hydrogenated in the presence of Rh/C (5 w/w% Rh, 30 mg, 0.006 mmol, 0.5 mol%) under 30 bar H_2 in an autoclave. After 3 h, the dispersion was filtrated and the crude mixture subjected to column chromatography (hexanes: EtOAc 9:1 to 4:1), yielding the product (387 mg, 1.08 mmol, 92%) as colorless crystalline solid.

R$_f$ (hexanes:EtOAc 4:1) = 0.33; brown with vanillin.

m.p.: 128-130 °C.

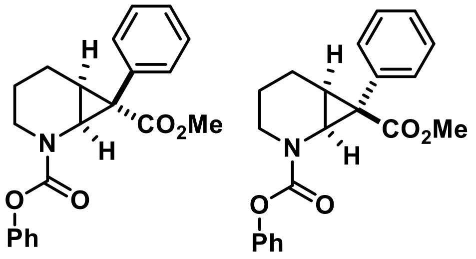
IR (neat): 3027, 2960, 2926, 1771, 1737, 1707, 1599, 1498, 1435, 1357, 1297, 1252, 1096, 954, 887, 820, 749, 671 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 – 7.81 (m, 2H), 7.66 – 7.50 (m, 3H), 7.32 (s, 5H), 4.27 (d, *J* = 6.8 Hz, 1H), 3.58 (s, 3H), 3.26 – 3.14 (m, 1H), 2.48 (dd, *J* = 6.6, 5.7 Hz, 1H), 1.97 – 1.76 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.83, 139.51, 132.88, 131.54, 131.26, 129.39, 128.74, 127.95, 127.00, 52.83, 51.84, 48.08, 37.27, 30.68, 25.09.

HR-MS (ESI-TOF): m/z calc. for $C_{19}H_{20}NO_4S$ $[M+H^+]^+$ 358.1108, found 358.1110.

7-methyl 2-phenyl 7-phenyl-2-azabicyclo[4.1.0]heptane-2,7-dicarboxylate ***1s***



7-methyl 2-phenyl 7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (500 mg, 1.43 mmol, 1 equiv.) was dissolved in 5 mL EtOAc, Rh/C (5% w/w Rh, 16 mg, 7.8 µmol, 0.5 mol%) was added and the vial placed in an autoclave. The solution was stirred under 25 bar H_2 for 1.5 h, then filtrated and the solvent was removed under reduced pressure. Column chromatography (hexanes:EtOAc 5:1) yields a white amorphous compound (403 mg, 1.15 mmol, 80%)

R$_f$ (hexanes:EtOAc 4:1) = 0.32; faint grey with vanillin.

m.p.: 76-78 °C

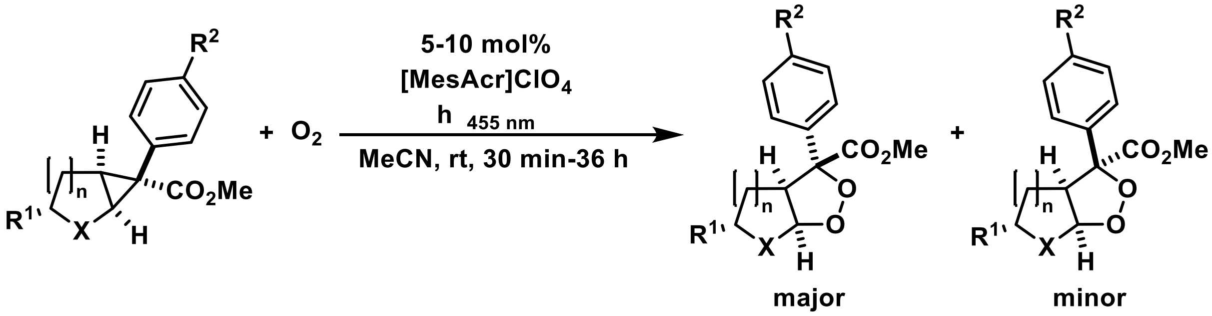
IR (neat): 3042, 2944, 2880, 1704, 1594, 1417, 1385, 1242, 1192, 1157, 1063, 965, 930, 801 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.30 (m, 7H), 7.30 – 7.12 (m, 3H), 3.94 (dd, *J* = 69.8, 9.3 Hz, 1H), 3.58 (d, *J* = 11.0 Hz, 3H), 3.35 (dd, *J* = 28.5, 14.5 Hz, 1H), 2.93 (dt, *J* = 53.6, 11.7 Hz, 1H), 2.44 (dt, *J* = 16.3, 7.9 Hz, 1H), 2.10 – 1.84 (m, 2H), 1.38 – 1.23 (m, 1H), 0.63 – 0.43 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 173.5, 155.6, 155.3, 151.4, 151.3, 133.2, 133.0, 131.8, 131.5, 129.5, 129.4, 128.7, 128.5, 127.6, 127.6, 125.6, 125.5, 121.8, 121.7, 52.7, 52.6, 42.5, 42.4, 42.0, 41.4, 35.0, 34.8, 24.9, 24.7, 21.1, 20.7, 18.6, 18.5.

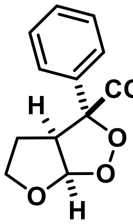
HR-MS (ESI-MS): m/z calc. for $C_{21}H_{22}NO_4$ $[M+H^+]^+$ 352.1543, found 352.1551.

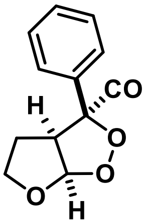
General procedure 4 (GP4) for the visible light mediated synthesis of endoperoxides from cyclopropanated heterocycles.



In an appropriate Schlenk-tube equipped with a magnetic stirbar, cyclopropanated heterocyclic starting material (1 equiv.) and catalyst [MesAcr]ClO_4 (0.05 – 0.1 equiv) were dissolved in dry MeCN (approx. 10 mL per mmol cyclopropane). An O_2 filled rubber ballon was attached and the vigorously stirred solution was irradiated at room temperature with blue light (455 nm) via a glas rod sticking into the solution until complete conversion of starting material was observed as judged by TLC (30 min- 36 h). Then the solvent was evaporated under reduced pressure and the diastereomeric ratio was determined from the crude reaction mixture via NMR. Column chromatography (hexanes/EtOAc) was used for purification. See General Information for pictures of the reaction setup When the diastereomers were inseparable, the IR spectrum of the mixture is given and overlapping NMR-signals are marked.

Methyl (3S*,3aS*,6aR*)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **methyl (3R*,3aS*,6aR*)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate** ***2a***


major


minor

Following GP4, compound **(±)-1a** (330 mg, 1.5 mmol, 1 equiv.) was dissolved in 15 mL MeCN and irradiated in the presence of [MesAcr]ClO_4 (30 mg, 0.075 mmol, 5 mol%) for 16 h. Column chromatography (hexanes:EtOAc 8% to 20%) allowed separation of the diastereomers, each yielding a colorless crystalline solid; major: 140.9 mg, minor: 35.2 mg; total: 176.1 mg (0.71 mmol, 47%).

<u>15 mmol scale</u>

In a 200 mL water cooled circulating immersion-well photoreactor, 3.27 g (15.0 mmol) (±)-1a and 309 mg (0.75 mmol, 5 mol%) [MesAcr]ClO4 where dissolved in 200 mL MeCN and saturated with O_2 by bubbling oxygen through the solution for 10 min. An O_2 filled balloon was attached and the solution was irradiated for 15 h with 30 Oslon SSL 80 LED (maximum 455 nm). After evaporation of the solvent under reduced pressure the oily residue was purified by flash chromatography (hexanes:EtOAc 10% to 20%). The diastereomers were separable by column chromatography, giving a combined yield of 1.46 g (5.83 mmol, 39%; Major diastereomer 1.19 g, Minor diastereomer 0.27 g)

Major

R_f (hexanes:EtOAc 4:1) = 0.13

; dark brown with vanillin.

m.p.: 110-112 °C

IR (neat): 2956, 2896, 1732, 1493, 1449, 1368, 1251, 1193, 1083, 1020, 989, 925, 860, 727, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.60 (m, 2H), 7.45 – 7.30 (m, 3H), 5.75 (d, *J* = 5.1 Hz, 1H), 4.20 (ddd, *J* = 10.5, 8.4, 6.1 Hz, 1H), 4.07 – 4.00 (m, 2H), 3.74 (s, 3H), 2.27 (dddd, *J* = 13.6, 10.4, 9.5, 8.1 Hz, 1H), 2.15 – 2.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 138.0, 128.7, 128.5, 126.3, 108.3, 92.7, 69.3, 60.8, 53.0, 29.7.

Minor

R_f (hexanes:EtOAc 4:1) = 0.25; dark brown with vanillin.

m.p.: 123-125 °C

IR (neat): 2990, 2958, 2899, 1739, 1494, 1449, 1370, 1311, 1271, 1240, 1205, 1064, 957, 931, 840, 810, 734, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.31 (m, 5H), 5.99 (d, *J* = 5.1 Hz, 1H), 4.49 (ddd, *J* = 9.8, 5.1, 2.0 Hz, 1H), 3.95 – 3.84 (m, 2H), 3.75 (s, 3H), 1.90 (dddd, *J* = 13.4, 10.8, 9.9, 8.4 Hz, 1H), 1.54 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 133.8, 129.0, 128.8, 125.5, 110.1, 108.9, 92.4, 69.5, 57.8, 53.5, 27.6.

HR-MS (EI-MS): m/z calc. for $C_{13}H_{15}O_5$ $[M+H^+]^+$ 251.0914, found 251.0913.

Crystals suitable for X-ray analysis (minor: CCDC 1980425, major: CCDC 1980424) were obtained by recrystallization from DCM/Et_2O.

(-)-2a

Analytical data is identical for (S)-isomers.

Optical rotation (S)-Major: $[a]_D^{20}$=-264.9° in DCM

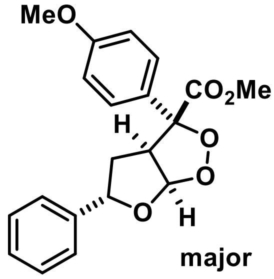
Optical rotation (S)-Minor: $[a]_D^{20}$=-259.9° in DCM

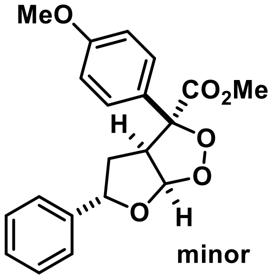
Chiral HPLC chromatogram available;

(S)-Major: column: Chiralpak AS-H; eluent Heptane:^{i}PrOH 95:5; Flow: 0.5 mL/min; Retention time [min]: 39.7, <u>55.3</u>; enantiomeric excess >98% ee.

(S)-minor: column: Phenomenex-Lux Cellulose 1; eluent Heptane:^{i}PrOH 99:1; Flow: 1 mL/min; Retention time [min]: <u>15.8</u>, 50.8; enantiomeric excess >99% ee.

Methyl (3R*,3aS*,5S*,6aR*)-3-(4-methoxyphenyl)-5-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **Methyl (3S*,3aS*,5S*,6aR*)-3-(4-methoxyphenyl)-5-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate** ***2b***





Following GP4, **1b** (64.7 mg, 0.2 mmol, 1 equiv.) was dissolved in 2.5 mL MeCN and irradiated with blue light for 16 h in the presence of [MesAcr]ClO$_4$ (6.3 mg, 0.015 mmol, 8 mol%). Column chromatography (hexanes:EtOAc 19:1 to 9:1) yielded the major diastereomer as colorless crystalline solid, (8.5 mg, 0.022 mmol, 11.3%); The minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio of 3:1 determined from the crude NMR as 15%

R$_f$ (hexanes:EtOAc 9:1) = 0.32; light brown with vanillin.

m.p.: 148 °C.

IR (neat): 3064, 2956, 2919, 2879, 2849, 1738, 1607, 1510, 1451, 1298, 1253, 1212, 1180, 1058, 1026, 992, 957, 932, 807, 771, 702 cm^{-1}.

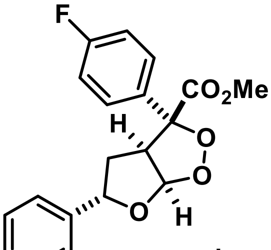
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60 (d, *J* = 8.9 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.94 (d, *J* = 8.9 Hz, 2H), 5.96 (d, *J* = 5.1 Hz, 1H), 5.46 (dd, *J* = 10.6, 5.5 Hz, 1H), 4.15 (ddd, *J* = 9.6, 5.1, 1.7 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.47 – 2.40 (m, 1H), 2.18 (dt, *J* = 13.9, 10.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 168.5, 159.9, 140.0, 129.9, 128.6, 128.2, 127.6, 126.0, 113.9, 108.1, 92.5, 81.8, 61.3, 55.4, 53.0, 38.2.

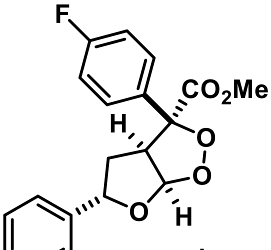
HR-MS (EI-MS): m/z calc. for $C_{20}H_{20}NaO_6$ [M+Na$^+$]$^+$ 379.1152, found 379.1147.

Methyl (3R*,3aS*,5S*,6aR*)-3-(4-fluorophenyl)-5-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and

Methyl (3S*,3aS*,5S*,6aR*)-3-(4-fluorophenyl)-5-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate ***2c***



major



minor

Following GP4, **1c** (99.5 mg, 0.3 mmol, 1 equiv.) was dissolved in 3 mL MeCN and irradiated with blue light for 70 h in the presence of $[\mathrm{MesAcr}]\mathrm{ClO_4}$ (9.6 mg, 0.023 mmol, 8 mol%). Column chromatography (hexanes:EtOAc 19:1 to 9:1) yielded the major diastereomer as colorless crystalline solid, (36.4 mg, 0.11 mmol, 35%); The minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio of 3:1 determined from the crude NMR as 47%

m.p.: 124-126 °C.

R$_f$ (hexanes:EtOAc 9:1) = 0.4; light brown with vanillin.

IR (neat): 3062, 2925, 2855, 1719, 1599 1495, 1450, 1379, 1359, 1228, 1129, 1068, 1021, 861 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 7.1, 1.5 Hz, 2H), 7.44 – 7.30 (m, 8H), 5.95 (d, *J* = 5.1 Hz, 1H), 5.47 (dd, *J* = 10.6, 5.5 Hz, 1H), 4.22 – 4.16 (m, 1H), 3.78 (s, 3H), 2.46 (ddd, *J* = 13.9, 5.6, 1.3 Hz, 1H), 2.20 (ddd, *J* = 13.9, 10.6, 9.6 Hz, 1H).

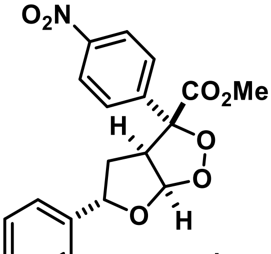
^{13}C NMR (101 MHz, $CDCl_3$): δ 178.5, 152.5, 140.0, 138.0, 128.8, 128.6, 128.6, 128.2, 126.3, 126.0, 108.1, 81.8, 61.4, 53.1, 38.2.

^{19}F NMR (377 MHz, $CDCl_3$): δ -115.58 (tt, J = 8.7, 5.4 Hz).

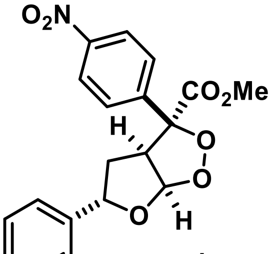
HR-MS (EI-MS): m/z calc. for $C_{19}H_{18}FO_5$ $[M+H^+]^+$ 345.1133, found 345.1134.

Methyl (3R*,3aS*,5S*,6aR*)-3-(4-nitrophenyl)-5-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and

Methyl (3S*,3aS*,5S*,6aR*)-3-(4-nitrophenyl)-5-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate ***2d***



major



minor

Following GP4, **1d** (115 mg, 0.34 mmol, 1 equiv.) was dissolved in 4 mL MeCN and irradiated with blue light for 70 h in the presence of [MesAcr]ClO$_4$ (13.5 mg, 0.03 mmol, 9 mol%). No significant further conversion was observed, so that the reaction was stopped albeit not all starting material was consumed. Column chromatography (hexanes:EtOAc 19:1 to 7:1) allowed for recovery of 42.2 mg **1d** as starting material, which is 36% of the total starting material. Therefore the conversion was 64%. The major diastereomer was isolated as colorless crystalline solid, (15.1 mg, 0.04 mmol, 18.7% brsm, 12.2% total); as the minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio of 3:1 determined from the crude NMR as 25% brsm.

R_f (hexanes:EtOAc 9:1) = 0.18; dark brown with vanillin.

m.p.: 164-167 °C.

IR (neat): 3492, 3073, 3030, 2958, 2918, 2851, 1739, 1597, 1516, 1347, 1258, 1174, 1134, 1071, 983, 921, 852, 737, 697 cm^{-1}.

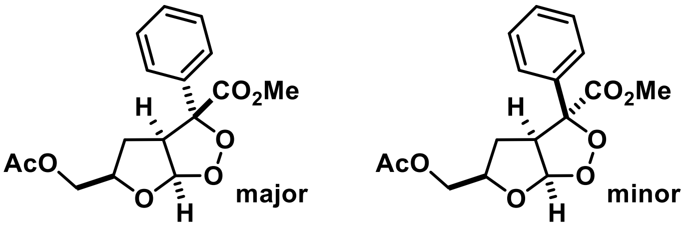
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.29 – 8.24 (m, 2H), 7.93 – 7.87 (m, 2H), 7.40 – 7.30 (m, 5H), 5.95 (d, *J* = 5.0 Hz, 1H), 5.47 (dd, *J* = 10.8, 5.4 Hz, 1H), 4.15 (ddd, *J* = 9.4, 5.0, 1.5 Hz, 1H), 3.82 (s, 3H), 2.50 – 2.43 (m, 1H), 2.22 (ddd, *J* = 14.0, 10.8, 9.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 167.2, 148.2, 144.9, 139.5, 128.7, 128.4, 127.8, 126.0, 123.7, 107.8, 92.3, 82.0, 62.2, 53.5, 38.2.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{18}NO_7$ $[M+H^+]^+$ 372.1078, found 372.1079.

Crystals suitable for X-ray analysis (major: CCDC 1980428) were obtained by recrystallization from DCM/Et$_2$O.

Methyl (3R*,3aS*,5R*,6aR*)-5-(acetoxymethyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **methyl (3S*,3aS*,5R*,6aR*)-5-(acetoxymethyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate** *2e*



Following GP4, **1b** (252 mg, 0.87 mmol, 1 equiv.) was dissolved in 10 mL MeCN and irradiated with blue light for 16 h in the presence of [MesAcr]ClO$_4$ (28.5 mg, 0.07 mmol, 8 mol%). Column chromatography (hexanes:EtOAc 9:1 to 4:1) yielded the major diastereomer as colorless oil (100.9 mg, 0.313 mmol, 36%); The minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio of 4:1 determined from the crude-NMR as 45%

R_f (hexanes:EtOAc 4:1) = 0.35.

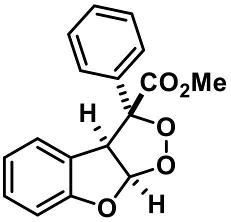
IR (neat): 3048, 2955, 2074, 1735, 1491, 1448, 1249, 1216, 1078, 1008, 917, 875, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.62 (m, 2H), 7.47 – 7.30 (m, 3H), 5.69 (d, *J* = 5.5 Hz, 1H), 4.42 – 4.30 (m, 2H), 4.26 (dd, *J* = 10.6, 6.3 Hz, 1H), 4.15 (ddd, *J* = 9.8, 7.3, 5.5 Hz, 1H), 3.73 (s, 3H), 2.50 (ddd, *J* = 13.4, 9.8, 6.7 Hz, 1H), 2.12 (s, 3H), 1.84 (dt, *J* = 13.4, 7.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 137.0, 128.9, 128.7, 126.1, 108.9, 92.6, 78.9, 66.0, 61.0, 53.1, 31.2, 21.0.

HR-MS (APCI-MS): m/z calc. for $C_{16}H_{19}O_7$ $[M+H^+]^+$ 323.1125, found 323.1131.

Methyl (3S*,3aS*,8aS*)-3-phenyl-3a,8a-dihydro-3H-[1,2]dioxolo[3,4-b]benzofuran-3-carboxylate *2f*



Following GP4, compound **1f** (133 mg, 0.5 mmol, 1 equiv.) was dissolved in 5 mL MeCN and irradiated in the presence of [MesAcr]ClO_4 (20.2 mg, 0.49 mmol, 10 mol%) for 2 h. Crude NMR showed only one diastereomer. Column chromatography (hexanes:EtOAc 9:1) yielded colorless oil (89 mg, 0.3 mmol, 60%).

R$_f$ (hexanes: EtOAc 9:1) = 0.58; bright red with vanillin.

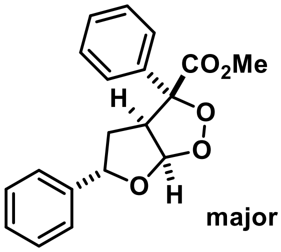
IR (neat): 3029, 2952, 2843, 1734, 1637, 1606, 1484, 1452, 1230, 1170, 1112, 1034, 973, 936, 798, 729, 753, 694 cm^{-1}.

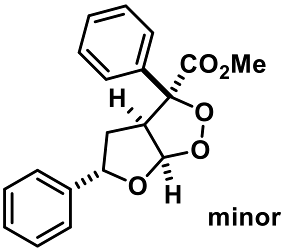
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 6.9 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.17 (td, *J* = 7.7, 1.6 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.89 (td, *J* = 7.4, 1.1 Hz, 1H), 6.64 (d, *J* = 9.8 Hz, 1H), 6.29 (d, *J* = 9.8 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 152.0, 140.1, 130.0, 128.6, 128.6, 126.9, 126.1, 125.2, 124.1, 121.9, 120.6, 116.7, 81.6, 53.1.

HR-MS (ESI-MS): m/z calc. for $C_{17}H_{15}O_3$ $[(M-O_2)+H^+]^+$ 267.1021, found 267.1019. *Note*: For this peroxide, no applied method would allow for detection of the actual peroxide, instead it seems to rapidly loose O_2 upon ionization. However, the substance was kept for 3 months at 4-6 °C and showed no signs of decomposition.

Methyl (3R*,3aS*,5S*,6aR*)-3,5-diphenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **Methyl (3S*,3aS*,5S*,6aR*)-3,5-diphenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate *2g***





Following GP4, **1g** (301 mg, 1.02 mmol, 1 equiv.) was dissolved in 10 mL MeCN and irradiated with blue light for 15 h in the presence of [MesAcr]ClO$_4$ (40 mg, 0.097 mmol, 10 mol%). Crude NMR revealed a diastereomeric ratio of 2.6:1. Column chromatography (hexanes:EtOAc 9:1) yielded the major diastereomer as white crystalline solid (132.7 mg, 0.405 mmol, 40%); The minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio determined as 55%;

R$_f$ (hexanes:EtOAc 9:1) = 0.2.

m.p.: 100-102 °C

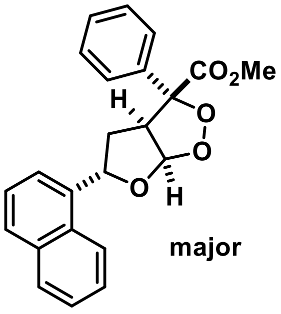
IR (neat): 3033, 2958, 1701, 1603, 1461, 1326, 1260, 1239, 1153, 1114, 1085, 1032, 962, 937, 902, 879, 811 cm^{-1}.

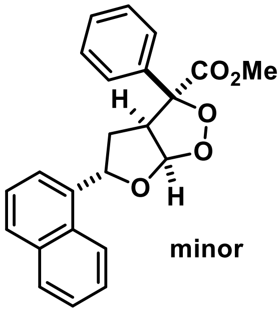
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 – 7.66 (m, 2H), 7.45 – 7.31 (m, 8H), 5.95 (d, *J* = 5.1 Hz, 1H), 5.47 (dd, *J* = 10.6, 5.5 Hz, 1H), 4.19 (ddd, *J* = 9.5, 5.1, 1.7 Hz, 1H), 3.78 (s, 3H), 2.47 (ddd, *J* = 13.9, 5.5, 1.3 Hz, 1H), 2.20 (ddd, *J* = 13.9, 10.6, 9.5 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 168.2, 140.0, 138.0, 128.7, 128.6, 128.6, 128.2, 126.3, 126.0, 108.1, 92.7, 81.8, 61.4, 53.1, 38.2.

HR-MS (ESI-MS): m/z calc. for $C_{19}H_{19}O_5$ [M+H$^+$]$^+$ 327.1227, found 327.1229.

Methyl (3R*,3aS*,5S*,6aR*)-5-(naphthalen-1-yl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **Methyl (3S*,3aS*,5S*,6aR*)-5-(naphthalen-1-yl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate** ***2h***





Following GP4, **1d** (282 mg, 0.81 mmol, 1 equiv.) was dissolved in 8 mL MeCN and irradiated with blue light for 13 h in the presence of [MesAcr]ClO$_4$ (33 mg, 0.08 mmol, 10 mol%). Crude NMR revealed a diastereomeric ratio of 3:1. Column chromatography (hexanes:EtOAc 3% to 10%) yielded a inseparable mixture of diastereomers as white crystalline solid (195 mg, 0.519 mmol, 64%);

R$_f$ (hexanes:EtOAc 9:1) = 0.55.

m.p.: 80-82 °C

IR (neat): 3064, 3030, 2951, 2844, 1738, 1594, 1441, 1321, 1239, 1196, 1142, 993, 955, 799 cm^{-1}.

Major as assigned from 2D-NMR

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.38 (m, 5H), 5.97 (d, *J* = 5.0 Hz, 1H), 5.52 (dd, *J* = 10.7, 5.6 Hz, 1H), 4.20 (ddd, *J* = 9.7, 5.1, 1.6 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 2.54 – 2.47 (m, 1H), 2.15 (dt, *J* = 13.9, 10.7, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 168.1, 166.9, 145.2, 137.8, 130.0, 129.9, 128.8, 128.6, 126.3, 125.8, 108.1, 92.7, 81.3, 61.3, 53.2, 52.2, 38.2.

Minor: as assigned from 2D-NMR

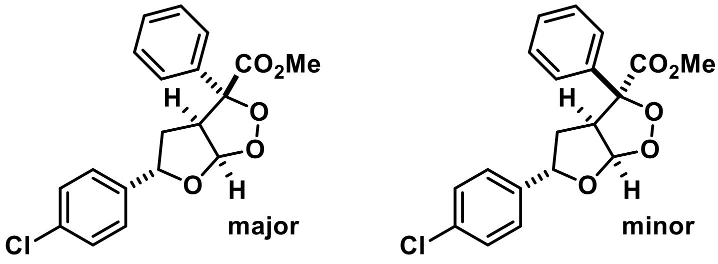
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.20 (d, *J* = 5.1 Hz, 1H), 5.23 (dd, *J* = 10.8, 5.6 Hz, 1H), 4.66 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 1.95 (dd, *J* = 13.5, 5.6 Hz, 1H), 1.81 (dt, *J* = 13.6, 10.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 172.2, 166.9, 145.3, 133.6, 129.8, 129.7, 129.2, 129.0, 125.6, 125.5, 108.7, 92.4, 81.3, 58.4, 53.6, 52.2, 36.1.

HR-MS (APCI-MS): m/z calc. for $C_{23}H_{24}NO_5$ [M+NH$_4^+$]$^+$ 394.1654, found 394.1645.

Methyl (3R*,3aS*,5S*,6aR*)-5-(4-chlorophenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and

Methyl (3S*,3aS*,5S*,6aR*)-5-(4-chlorophenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate ***2i***



Following GP4, **1e** (337 mg, 1.0 mmol, 1 equiv.) was dissolved in 10 mL MeCN and irradiated with blue light for 16 h in the presence of [MesAcr]ClO$_4$ (39 mg, 0.09 mmol, 9 mol%). Crude NMR revealed a diastereomeric ratio of 1.7:1. Column chromatography (hexanes:EtOAc 3% to 10%) yielded a inseparable mixture of diastereomers as white crystalline solid (159 mg, 0.44 mmol, 43%).

R$_f$ (hexanes:EtOAc 9:1) = 0.25. Light brown with vanillin.

m.p.: 62 °C

Ir (neat): 3069, 2952, 2899, 1727, 1600, 1493, 1448, 1252, 1120, 1061, 986, 969, 917, 756, 725 cm^{-1}.

Major

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.27 (m, 7H), 5.94 (d, *J* = 5.0 Hz, 1H), 5.43 (dd, *J* = 10.6, 5.4 Hz, 1H), 4.19 (dd, *J* = 8.6, 4.9 Hz, 1H), 3.78 (s, 3H), 2.46 (dd, *J* = 13.8, 5.0 Hz, 1H), 2.13 (dt, *J* = 13.8, 10.2 Hz, 1H),

Minor

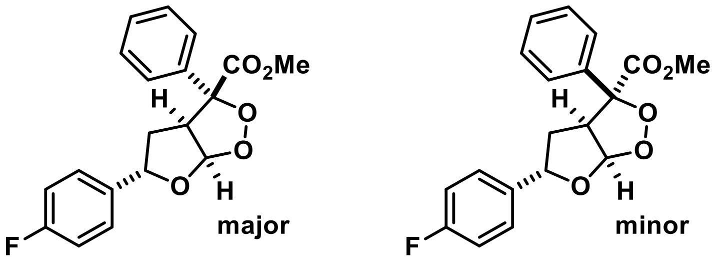
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.27 (m, 7H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.17 (d, *J* = 5.0 Hz, 1H), 5.15 (dd, *J* = 10.7, 5.6 Hz, 1H), 4.65 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.78 (s, 3H), 1.91 (dd, *J* = 13.4, 5.4 Hz, 1H), 1.79 (dt, *J* = 13.4, 10.2 Hz, 1H).

Mixture

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.3, 168.1, 138.7, 138.5, 137.8, 133.9, 133.6, 129.1, 129.0, 128.8, 128.6, 128.6, 127.4, 127.2, 126.3, 125.5, 108.6, 108.0, 92.6, 92.4, 81.2, 81.1, 61.3, 58.4, 53.6, 53.1, 38.3, 36.1.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{18}ClO_5$ [M+H$^+$]$^+$ 361.0837, found 361.0837.

Methyl (3R*,3aS*,5S*,6aR*)-5-(4-fluorophenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and
Methyl (3S*,3aS*,5S*,6aR*)-5-(4-fluorophenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate ***2j***



Following GP4, **1f** (310 mg, 1.0 mmol, 1 equiv.) was dissolved in 15 mL MeCN and irradiated with blue light for 16 h in the presence of [MesAcr]ClO$_4$ (40 mg, 0.1 mmol, 10 mol%). Crude NMR revealed a diastereomeric ratio of 3:1. Column chromatography (hexanes:EtOAc 3% to 10%) yielded a inseparable mixture of diastereomers as colorless crystalline solid (178 mg, 0.51 mmol, 51%).

R$_f$ (hexanes:EtOAc 9:1) = 0.25. Light brown with vanillin.

m.p.: 120-122 °C

Ir (neat): 3073, 2953, 2910, 1732, 1603, 1511, 1446, 1274, 1221, 1071, 1003, 918, 836, 724 cm^{-1}.

Major

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.72 – 7.66 (m, 2H), 7.46 – 7.29 (m, 5H), 7.09 – 6.93 (m, 2H), 5.94 (d, *J* = 5.0 Hz, 1H), 5.44 (dd, *J* = 10.7, 5.4 Hz, 1H), 4.20 (ddd, *J* = 9.5, 5.0, 1.6 Hz, 1H), 3.77 (d, *J* = 1.7 Hz, 3H), 2.45 (dddd, *J* = 14.0, 5.5, 1.6, 0.7 Hz, 1H), 2.16 (ddd, *J* = 14.0, 10.8, 9.5 Hz, 1H).

Minor

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.46 – 7.29 (m, 5H), 7.22 – 7.16 (m, 2H), 7.09 – 6.93 (m, 2H), 6.17 (d, *J* = 5.1 Hz, 1H), 5.16 (dd, *J* = 10.5, 5.8 Hz, 1H), 4.69 – 4.61 (m, 1H), 3.77 (d, *J* = 1.7 Hz, 3H), 1.95 – 1.75 (m, 2H).

<u>13C mixture:</u>

^{13}C NMR (75 MHz, CDCl$_3$) δ 169.1, 164.2, 160.9, 137.8, 135.7, 135.7, 135.6, 133.6, 129, 1, 128.9, 128.7, 128.5, 127.8, 127.7, 127.5, 126.2, 125.4, 115.6, 115.5, 115.3115.2, 108.5, 107.9, 92.6, 81.2, 61.3, 58.4, 53.6, 53.1, 38.3, 36.1

<u>^{19}F mixture:</u>

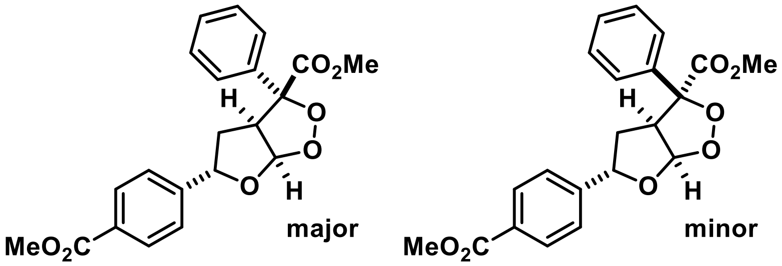
19F NMR (282 MHz, CDCl$_3$): δ -114.56 (tt, *J* = 8.6, 5.3 Hz), -114.81 (tt, *J* = 8.7, 5.3 Hz).

HR-MS (EI-MS): m/z calc. for $C_{19}H_{18}FO_5$ $[M+H^+]^+$ 345.1133, found 345.1131.

Crystals suitable for X-ray analysis (minor: CCDC 1980427) were obtained by recrystallization from DCM/Et$_2$O.

Methyl (3R*,3aS*,5S*,6aR*)-5-(4-(methoxycarbonyl)phenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and

Methyl (3S*,3aS*,5S*,6aR*)-5-(4-(methoxycarbonyl)phenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate ***2k***



Following GP4, **1g** (98 mg, 0.27 mmol, 1 equiv.) was dissolved in 3 mL MeCN and irradiated with blue light for 16 h in the presence of [MesAcr]ClO$_4$ (10 mg, 0.024 mmol, 9 mol%). Crude NMR revealed a diastereomeric ratio of 3:1. Column chromatography (hexanes:EtOAc 10% to 25%) allowed for separation of the diastereomers as white crystalline solids. Major: 42 mg, 0.11 mmol, 40.5%; Minor: 14 mg, 0.036 mmol, 13.5%); combined: 54%

<u>Major</u>

R$_f$ (hexanes:EtOAc 9:1) = 0.2. Light brown with vanillin.

m.p.: 172 °C.

IR (neat): 2999, 2955, 2904, 1720, 1433, 1255, 1192, 1068, 1007, 919, 882, 851, 800, 768, 722 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.38 (m, 5H), 5.97 (d, *J* = 5.0 Hz, 1H), 5.52 (dd, *J* = 10.7, 5.6 Hz, 1H), 4.20 (ddd, *J* = 9.7, 5.1, 1.6 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 2.54 – 2.47 (m, 1H), 2.15 (ddd, *J* = 13.9, 10.7, 9.5 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 168.1, 166.9, 145.2, 137.8, 130.0, 129.9, 128.8, 128.6, 126.3, 125.8, 108.1, 92.7, 81.3, 61.3, 53.2, 52.2, 38.2.

HR-MS (EI-MS): m/z calc. for $C_{21}H_{21}O_7$ $[M+H^+]^+$ 385.1282, found 385.1284.

Minor

R$_f$ (hexanes:EtOAc 9:1) = 0.18. Light brown with vanillin.

m.p.: 188 °C.

IR (neat): 2956, 2907, 2840, 1738, 1612, 1436, 1217, 1177, 1030, 976, 909, 882, 800, 763 cm^{-1}.

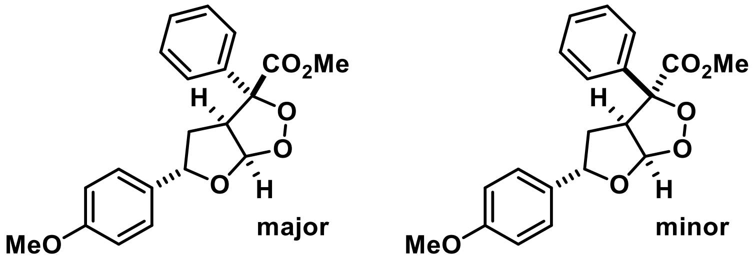
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.20 (d, *J* = 5.1 Hz, 1H), 5.23 (dd, *J* = 10.8, 5.6 Hz, 1H), 4.66 (dd, *J* = 9.6, 5.2 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 1.95 (dd, *J* = 13.5, 5.6 Hz, 1H), 1.81 (dt, *J* = 13.6, 10.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 172.2, 166.9, 145.3, 133.6, 129.8, 129.7, 129.2, 129.0, 125.6, 125.5, 108.7, 92.4, 81.3, 58.4, 53.6, 52.2, 36.1.

HR-MS (EI-MS): m/z calc. for $C_{21}H_{21}O_7$ $[M+H^+]^+$ 385.1282, found 385.1286.

Methyl (3R*,3aS*,5S*,6aR*)-5-(4-Methoxyphenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and

Methyl (3S*,3aS*,5S*,6aR*)-5-(4-Methoxyphenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate ***2l***



Following GP4, **1l** (98 mg, 0.47 mmol, 1 equiv.) was dissolved in 3 mL MeCN and irradiated with blue light for 16 h in the presence of [MesAcr]ClO$_4$ (10 mg, 0.024 mmol, 9 mol%). Crude NMR revealed a diastereomeric ratio of 3:1. Column chromatography (hexanes:EtOAc 5% to 10%) allowed for separation of the diastereomers, which were each isolated as clear crystalline material after removal of the solvent. Major: 85.4 mg, 0.24 mmol, 51%; Minor: 28.4 mg, 0.079 mmol, 17%); combined: 68%

Major

R$_f$ (hexanes:EtOAc 9:1) = 0.15. Light brown with vanillin.

m.p.: 145-147 °C

IR (neat): 2955, 2841, 1735, 1613, 1515, 1446, 1247, 1247, 1174, 1062, 1029, 985, 833, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.66 (m, 2H), 7.46 – 7.34 (m, 3H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.92 (d, *J* = 5.0 Hz, 1H), 5.42 (dd, *J* = 10.7, 5.4 Hz, 1H), 4.19 (ddd, *J* = 9.6, 5.1, 1.6 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.46 – 2.36 (m, 1H), 2.25 – 2.14 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 159.6, 138.0, 131.8, 128.7, 128.5, 127.5, 126.3, 114.0, 107.9, 92.7, 81.6, 61.4, 55.4, 53.1, 38.1.

HR-MS (EI-MS): m/z calc. for $C_{20}H_{21}O_6$ $[M+H^+]^+$ 357.1333, found 357.1331.

Minor

R$_f$ (hexanes:EtOAc 9:1) = 0.08. Light brown with vanillin.

m.p.: 158-161 °C

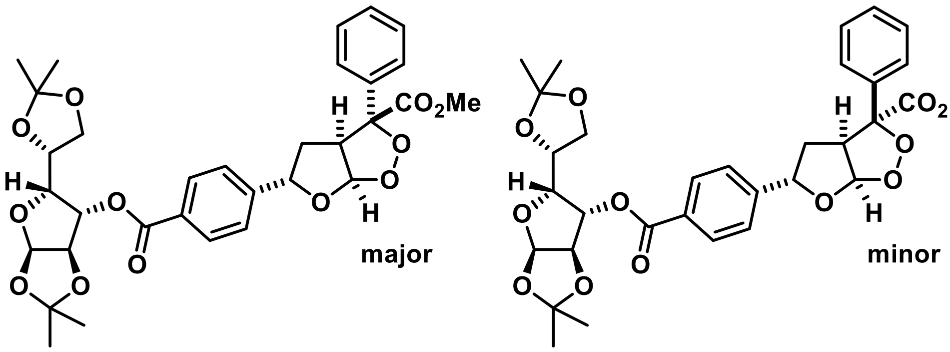
IR (neat): 3034, 2958, 1701, 1603, 1461, 1436, 1260, 1239, 1153, 1086, 1032, 962 879, 811, 750 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.3 Hz, 2H), 7.40 (dd, *J* = 14.8, 7.6 Hz, 5H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 5.5 Hz, 1H), 4.99 (dd, *J* = 10.3, 5.7 Hz, 1H), 4.25 (td, *J* = 9.1, 5.6 Hz, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 2.70 (ddd, *J* = 12.6, 8.7, 5.7 Hz, 1H), 2.01 (dt, *J* = 12.6, 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 159.6, 137.1, 132.3, 128.9, 128.7, 127.5, 126.1, 114.0, 108.2, 92.5, 82.7, 61.9, 55.4, 53.0, 38.1.

HR-MS (EI-MS): m/z calc. for $C_{20}H_{21}O_6$ $[M+H^+]^+$ 357.1333, found 357.1330.

Methyl (3R*,3aS*,5S*,6aR*)-5-(4-((((3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)carbonyl)phenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **Methyl (3S*,3aS*,5S*,6aR*)-5-(4-((((3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)carbonyl)phenyl)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate** ***2m***



Following GP4, **1m** (174 mg, 0.30 mmol, 1 equiv.) was dissolved in 5 mL MeCN and irradiated with blue light for 20 h in the presence of [MesAcr]ClO_4 (10.3 mg, 0.025 mmol, 8 mol%). Due to the introduction of a chiral residue (Diacetone-D-glucose) this reaction can lead to four different diastereomers. A pair of two diastereomers was purified by column chromatography (hexanes:EtOAc

10% to 50%), yielding a viscous clear oil (84 mg, 0.14 mmol, 46%). The material obtained showed a diastereomeric ratio for this pair of 3:1.

R_f (hexanes:EtOAc 2:1) = 0.2; dark brown with vanillin.

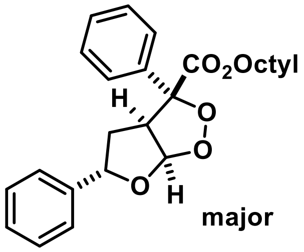
IR (neat): 3064, 3001, 2953, 2854, 1736, 1435, 1356, 1254, 1218, 1068, 1015, 949, 820 cm^{-1}.

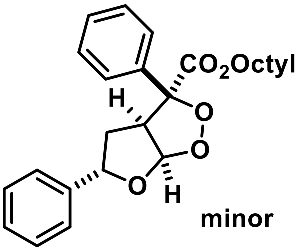
^{1}H NMR (300 MHz, Chloroform-*d*): δ 8.04 – 7.99 (m, 6H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.71 – 7.66 (m, 5H), 7.46 – 7.33 (m, 20H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.20 (d, *J* = 5.2 Hz, 1H), 6.01 – 5.91 (m, 7H), 5.56 – 5.45 (m, 7H), 5.23 (dd, *J* = 10.8, 5.6 Hz, 1H), 4.70 – 4.58 (m, 5H), 4.41 – 4.28 (m, 9H), 4.20 (dd, *J* = 9.0, 5.0 Hz, 3H), 4.14 – 4.04 (m, 8H), 3.80 – 3.76 (m, 11H), 2.50 (dd, *J* = 14.2, 5.6 Hz, 2H), 2.20 – 2.07 (m, 3H), 1.95 (dd, *J* = 13.6, 5.7 Hz, 1H), 1.78 (dt, *J* = 13.6, 9.8 Hz, 1H), 1.55 (d, *J* = 4.0 Hz, 12H), 1.40 (d, *J* = 5.6 Hz, 12H), 1.31 (d, *J* = 4.6 Hz, 12H), 1.25 (d, *J* = 7.3 Hz, 12H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 164.8, 145.7, 137.6, 130.0, 129.8, 129.1, 128.7, 128.5, 126.1, 125.8, 125.3, 112.4, 109.4, 108.0, 105.1, 92.5, 92.2, 83.3, 81.0, 79.9, 72.5, 67.2, 61.1, 53.5, 53.1, 26.8, 26.7, 26.2, 25.2.

HR-MS (ESI-MS): m/z calc. for $C_{32}H_{37}O_{12}$ [M+H$^+$]$^+$ 613.2280, found 613.2279.

Octyl (3R*,3aS*,5S*,6aR*)-3,5-diphenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate and **Octyl (3S*,3aS*,5S*,6aR*)-3,5-diphenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate** ***2n***





Following GP4, **1n** (475 mg, 1.21 mmol, 1 equiv.) was dissolved in 12 mL MeCN and irradiated with blue light for 15 h in the presence of [MesAcr]ClO_4 (49 mg, 0.12 mmol, 10 mol%). Crude NMR revealed a diastereomeric ratio of 3:1. Column chromatography (hexanes:EtOAc 99:1 to 9:1) yielded the major diastereomer as white solid (173 mg, 0.407 mmol, 34%) and a mixed fraction containing also the minor diastereomer (combined 232 mg, 0.547 mmol, 45%).

Major:

R_f (hexanes:EtOAc 9:1) = 0.7: Faint brown with vanillin.

m.p.: 153 °C

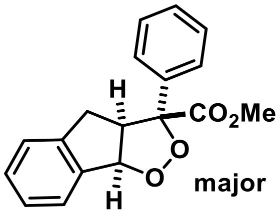
Ir (neat): 2923, 2854, 1737, 1495, 1451, 1376, 1341, 1249, 1212, 1066, 1006, 917, 875, 782 cm^{-1}.

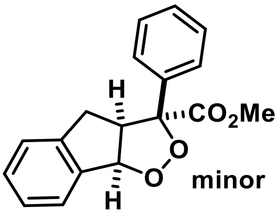
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.45 – 7.32 (m, 8H), 5.96 (d, *J* = 5.1 Hz, 1H), 5.48 (dd, *J* = 10.7, 5.5 Hz, 1H), 4.25 – 4.07 (m, 3H), 2.57 – 2.42 (m, 1H), 2.19 (ddd, *J* = 13.9, 10.6, 9.5 Hz, 1H), 1.67 – 1.57 (m, 2H), 1.22 (s, 10H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 140.0, 138.2, 128.7, 128.6, 128.5, 128.2, 126.3, 126.0, 108.0, 92.6, 81.9, 66.4, 61.3, 38.2, 31.8, 29.2, 29.1, 28.5, 25.8, 22.7, 14.2.

HR-MS (ESI-MS): m/z calc. for $C_{26}H_{32}O_5$ $[M+NH_4^+]^+$ 442.2593, found 442.2597.

Methyl (3R*,3aR*,8aR*)-3-phenyl-3,3a,8,8a-tetrahydroindeno[2,1-c][1,2]dioxole-3-carboxylate and **Methyl (3S*,3aR*,8aR*)-3-phenyl-3,3a,8,8a-tetrahydroindeno[2,1-c][1,2]dioxole-3-carboxylate** ***2o***





Following GP4, **1o** (132 mg, 0.5 mmol, 1 equiv.) was dissolved in 10 mL MeCN and irradiated with blue light for 10 h in the presence of [MesAcr]ClO_4 (16.5 mg, 0.04 mmol, 8 mol%). Crude NMR revealed a diastereomeric ratio of 2.8:1. Column chromatography (hexanes:EtOAc 19:1 to 7:1) yielded the major diastereomer as white crystalline solid, (63.7 mg, 0.21 mmol, 43.9%); The minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio determined from the crude NMR as 59%;

m.p.: 146-148 °C

IR (neat): 30423062, 2920, 2855, 2342, 1739, 1461, 1445, 1335, 1236, 1064, 932, 815, 784 cm^{-1}.

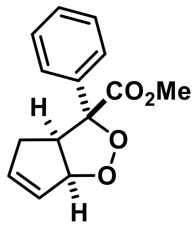
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.32 (m, 5H), 7.26 (t, *J* = 6.8 Hz, 2H), 5.58 (d, *J* = 6.9 Hz, 1H), 4.40 (ddd, *J* = 9.0, 6.8, 5.3 Hz, 1H), 3.72 (s, 3H), 3.43 (dd, *J* = 17.2, 9.1 Hz, 1H), 3.22 (dd, *J* = 17.2, 5.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.6, 143.2, 139.1, 138.4, 129.8, 128.5, 128.4, 127.4, 126.1, 125.9, 124.5, 92.9, 89.2, 60.3, 52.7, 35.7.

HR-MS (APCI-MS): m/z calc. for $C_{18}H_{17}O_4$ $[M+H^+]^+$ 297.1121, found 297.1123.

Crystals suitable for X-ray analysis (major: CDC 1980432) were obtained by recrystallization from DCM/Et_2O.

Methyl (3R*,3aR*,6aS*)-3-phenyl-3,3a,4,6a-tetrahydrocyclopenta[c][1,2]dioxole-3-carboxylate *2p*



Following GP4, compound **1p** (53 mg, 0.25 mmol, 1 equiv.) was dissolved in 3 mL MeCN and irradiated in the presence of [MesAcr]ClO_4 (10.4 mg, 0.025 mmol, 10 mol%) for 13 h. Column chromatography (hexanes:EtOAc 19:1) yielded an ochre crystalline solid (39.4 mg, 0.157 mmol, 63%).; only one diastereomer was observed in the crude NMR.

R$_f$ (hexanes:EtOAc 9:1) = 0.18; dark brown with vanillin.

IR (neat): 3064, 3001, 2953, 2854, 1736, 1435, 1356, 1254, 1218, 1068, 1015, 949, 820 cm^{-1}.

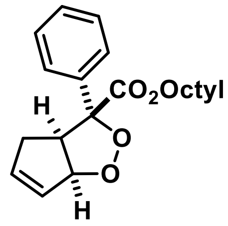
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.68 (m, 2H), 7.44 – 7.31 (m, 3H), 6.11 (dt, *J* = 6.0, 2.4 Hz, 1H), 5.80 (dq, *J* = 5.7, 2.2 Hz, 1H), 5.21 (dt, *J* = 7.1, 1.9 Hz, 1H), 4.14 (ddd, *J* = 8.8, 7.1, 3.7 Hz, 1H), 3.72 (s, 3H), 2.82 (ddt, *J* = 18.2, 8.7, 2.3 Hz, 1H), 2.53 (ddq, *J* = 18.2, 4.3, 2.3 Hz, 1H).

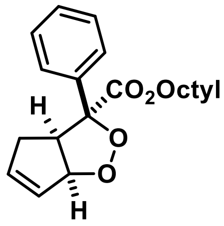
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 138.9, 137.2, 128.5, 128.4, 126.3, 93.1, 90.7, 57.8, 52.8, 36.9.

HR-MS (APCI-MS): m/z calc. for $C_{14}H_{14}NO_4$ $[M+H^+]^+$ 247.0970, found 247.0966.

As further undesired sidereactions may occur, the reaction must not be run longer then until full consumption of starting material.

Octyl (3R*,3aR*,6aS*)-3-phenyl-3,3a,4,6a-tetrahydrocyclopenta[c][1,2]dioxole-3-carboxylate and **Octyl (3S*,3aR*,6aS*)-3-phenyl-3,3a,4,6a-tetrahydrocyclopenta[c][1,2]dioxole-3-carboxylate 2*q***





Following GP4, compound **1q** (75 mg, 0.24 mmol, 1 equiv.) was dissolved in 2 mL MeCN and irradiated with blue light for 12 h in the presence of [MesAcr]ClO_4 (8 mg, 0.02 mmol, 8 mol%). Column chromatography (hexanes:EtOAc 19:1) yielded a colourless oil, (42.3 mg, 0.122 mmol, 51%).; consisting of two inseparable diastereomers.

R_f (hexanes:EtOAc 19:1) = 0.2.

IR (neat): 2956, 2926, 1737, 1597, 1494, 1449, 1347, 1211, 1159, 1091, 1011, 965, 910, 814 cm^{-1}.

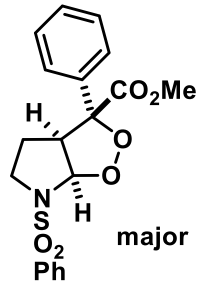
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 2H), 7.39 – 7.33 (m, 3H), 6.11 (dt, *J* = 5.0, 2.2 Hz, 1H), 5.83 – 5.77 (m, 1H), 5.19 (dt, *J* = 7.0, 1.8 Hz, 1H), 4.18 – 4.06 (m, 3H), 2.82 (ddt, *J* = 18.0, 8.7, 2.2 Hz, 1H), 2.55 (ddt, *J* = 15.8, 3.9, 1.9 Hz, 1H), 1.55 (m, 2H), 1.32 – 1.16 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H).

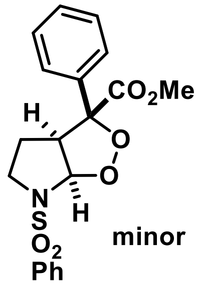
^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 139.0, 137.1, 128.3, 127.5, 126.2, 92.9, 90.6, 65.9, 57.3, 36.8, 31.7, 29.1, 29.0, 28.3, 25.6, 22.6, 14.1.

HR-MS (ESI-MS): m/z calc. for $C_{21}H_{29}O_4$ $[M+H^+]^+$ 345.2060, found 345.2064.

Methyl (3R*,3aS*,6aR*)-3-phenyl-6-(phenylsulfonyl)hexahydro-[1,2]dioxolo[3,4-b]pyrrole-3-carboxylate and

Methyl (3S*,3aS*,6aR*)-3-phenyl-6-(phenylsulfonyl)hexahydro-[1,2]dioxolo[3,4-b]pyrrole-3-carboxylate ***2r***





Following GP4, **1r** (71.5 mg, 0.2 mmol, 1 equiv.) was was dissolved in 10 mL MeCN and irradiated with blue light for 12 h in the presence of [MesAcr]ClO_4 (8.3 mg, 0.02 mmol, 10 mol%). Crude NMR revealed a diastereomeric ratio of 1:1, column chromatography (hexanes:EtOAc 9:1 to 4:1) allowed for separation of the diastereomers, which were isolated as colorless viscous oils. Major: 13.5 mg, 0.034 mmol, 17% Minor: 13.2 mg, 0.034 mmol, 17%; combined: 26.7 mg, 0.068 mmol, 34%

Major

R_f (hexanes:EtOAc 4:1) = 0.14.

IR (neat): 2944, 2840, 1707, 1584, 1453, 1412, 1274, 1237, 1121, 1006, 913, 853, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.59 (dt, *J* = 26.4, 7.3 Hz, 3H), 7.37 – 7.31 (m, 3H), 7.20 – 7.13 (m, 2H), 6.25 (d, *J* = 5.9 Hz, 1H), 4.64 – 4.49 (m, 1H), 3.75 (s, 3H), 3.43 (t, *J* = 8.7 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.04 – 1.89 (m, 1H), 1.50 (d, *J* = 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 139.1, 137.4, 133.1, 129.2, 129.1, 128.9, 128.8, 128.6, 127.8, 126.1, 94.4, 92.7, 60.2, 53.1, 47.5, 28.4.

HR-MS (EI-MS): m/z calc. for $C_{19}H_{20}NO_6S$ $[M+H^+]^+$ 390.1011, found 390.1015.

<u>Minor</u>

R_f (hexanes:EtOAc 4:1) = 0.17.

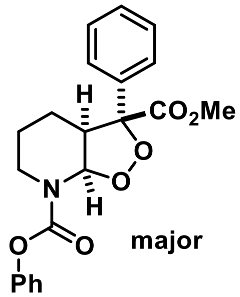
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.89 (m, 2H), 7.63 – 7.51 (m, 5H), 7.43 – 7.35 (m, 3H), 6.00 (d, *J* = 5.9 Hz, 1H), 4.16 – 4.09 (m, 1H), 3.69 (s, 3H), 3.63 – 3.57 (m, 1H), 3.38 (td, *J* = 8.9, 7.1 Hz, 1H), 2.36 (dq, *J* = 13.7, 8.8 Hz, 1H), 2.09 (ddt, *J* = 13.9, 7.3, 3.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.6, 139.1, 137.4, 133.1, 129.2, 129.1, 128.9, 128.8, 128.6, 127.8, 126.1, 94.4, 92.7, 60.2, 53.1, 47.5, 28.4.

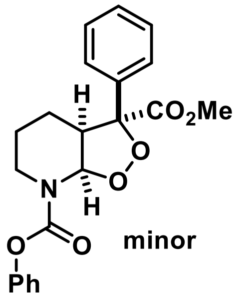
HR-MS (EI-MS): m/z calc. for $C_{19}H_{20}NO_6S$ $[M+H^+]^+$ 390.1011, found 390.1011.

3-methyl 7-phenyl (3R*,3aS*,7aR*)-3-phenyltetrahydro-3H-[1,2]dioxolo[3,4-b]pyridine-3,7(4H)-dicarboxylate and

3-methyl 7-phenyl (3S*,3aS*,7aR*)-3-phenyltetrahydro-3H-[1,2]dioxolo[3,4-b]pyridine-3,7(4H)-dicarboxylate ***2s***



major



minor

Following GP4, **1s** (154 mg, 0.44 mmol, 1 equiv.) was dissolved in 10 mL MeCN and irradiated with blue light for 15 h in the presence of $[MesAcr]ClO_4$ (14 mg, 0.035 mmol, 8 mol%). Crude NMR revealed a diastereomeric ratio of 5.3:1. Column chromatography (hexanes:EtOAc 9:1 to 2:1) yielded the major diastereomer as colourless crystalline solid, (52.7 mg, 0.137 mmol, 31%); The minor diastereomer could not be purified, the total yield was calculated based on the diastereomeric ratio determined from the crude NMR as 37%;

R_f (hexanes:EtOAc 9:1) = 0.1.

m.p.: 153 °C

IR (neat): 2967, 1735, 1591, 1445, 1413, 1287, 1247, 1193, 1100, 1052, 960, 909, 793 cm^{-1}.

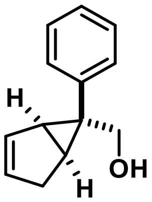
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 6.9 Hz, 2H), 7.46 – 7.29 (m, 6H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.02 (s, 2H), 6.05 (d, *J* = 4.7 Hz, 1H), 4.17 – 4.03 (m, 1H), 3.75 (s, 3H), 3.34 – 3.08 (m, 2H), 2.25 – 2.15 (m, 1H), 1.99 – 1.80 (m, 2H), 1.60 (s, 1H); broadened signals due to rotamers.

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8, 150.9, 137.3, 129.3, 129.0, 128.8, 125.8, 125.7, 121.7, 92.2, 84.8, 52.9, 50.3, 40.2, 39.8, 22.1, 21.9.

HR-MS (APCI-MS): m/z calc. for $C_{21}H_{22}NO_6$ $[M+H^+]^+$ 384.1442, found 384.1443.

Synthesis of hydroperoxides

((1R*,5S*,6R*)-6-phenylbicyclo[3.1.0]hex-2-en-6-yl)methanol ***S1k***



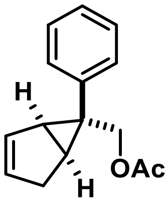
Compound **1p** (108.4 mg, 0.5 mmol, 1 equiv.) was reduced to the alcohol by stirring it in 10 mL MeOH and slowly adding $NaBH_4$ (45.9 mg, 1.2 mmol, 2.4 equiv.) to the solution. When the gas evolution ceased, stirring was continued for 3 h, then water was added dropwise to quench the remaining $NaBH_4$. The reaction mixture was acidified using 1M HCl_{aq} and then extracted with EtOAc. The organic phases were combined and dried over $MgSO_4$, filtered over a plug of silica and used in the next step without further purification, yielding 80.4 mg (0.43 mmol, 86%) of clear viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.20 (dd, *J* = 19.2, 7.8 Hz, 3H), 5.76 – 5.67 (m, 1H), 5.11 (dq, *J* = 5.5, 2.1 Hz, 1H), 3.65 (dd, *J* = 11.1, 4.0 Hz, 1H), 3.43 (dd, *J* = 11.2, 5.2 Hz, 1H), 2.55 (dd, *J* = 18.4, 7.5 Hz, 1H), 2.31 (dt, *J* = 5.4, 2.2 Hz, 1H), 2.04 (dq, *J* = 18.4, 3.3 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.39 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 136.5, 132.2, 130.9, 130.7, 128.1, 126.6, 71.4, 39.1, 35.1, 33.1, 26.6.

HR-MS (EI-MS): m/z calc. for $C_{13}H_{14}O$ $[M^{+}]^+$ 186.1039, found 186.1036.

((1S*,5R*,6R*)-6-phenylbicyclo[3.1.0]hex-2-en-6-yl)methyl acetate ***1x***



Compound **S1k** (70.0 mg, 0.37 mmol, 1 equiv.) was dissolved in DCM and acetic anhydride (50 µL, 0.49 mmol, 1.3 equiv.) was added. The reaction was cooled to 0°C using an ice-bath, and NEt_3 (70 µL, 0.49 mmol, 1.3 equiv.) was added slowly. After stirring for 2 h, the mixture was quenched by adding water, and consecutively washed with water, $NaHCO_{3aq,\,sat}$ and 1M HCl. Upon drying over $MgSO_4$ the solvent was removed and the crude further purified by column chromatography, yielding 80.9 mg clear viscous oil (0.35 mmol, 96%).

R$_f$ (hexanes:EtOAc 9:1) = 0.4.

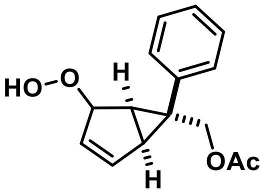
IR (neat): 3057, 3026, 2903, 2837, 1736, 1602, 1496, 1445, 1361, 1223, 1027, 957, 767 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (s, 5H), 5.71 (dq, *J* = 5.6, 2.2 Hz, 1H), 5.12 (dtd, *J* = 5.6, 2.2, 1.2 Hz, 1H), 4.10 (d, *J* = 11.2 Hz, 1H), 3.98 (d, *J* = 11.2 Hz, 1H), 2.61 – 2.49 (m, 1H), 2.39 – 2.34 (m, 1H), 2.09 – 1.95 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 136.3, 132.2, 131.2, 130.4, 127.8, 126.5, 72.3, 35.5, 35.4, 33.2, 27.0, 21.1.

HR-MS (EI-MS): m/z calc. for $C_{15}H_{16}O_2$ $[M^{+}]^{+}$ 228.1144, found 228.1147.

((1S*,5R*,6R*)-4-hydroperoxy-6-phenylbicyclo[3.1.0]hex-2-en-6-yl)methyl acetate ***3***



Following GP 4 compound **1x** (73 mg, 0.32 mmol, 1 equiv.) was dissolved in MeCN and [MesAcr]ClO_4 (12.3 mg, 0.03 mmol, 0.1 equiv.) was added. The reaction was irradiated with a 455 nm LED and progress monitored by TLC. The reaction was terminated after 3 h and the mixture directly subjected to column chromatography. Hydroperoxide **3** was obtained as 52.6 mg beige solid (0.20 mmol, 63%).

R$_f$ (hexanes:EtOAc 7:1) = 0.2.

m.p.: decomposes upon heating above 80 °C. Compound turns dark brown

IR(neat): 3400, 3061, 2925, 2855, 1710, 1602, 1495, 1455, 1379, 1222, 1157, 972, 759, 723, 699 cm^{-1}.

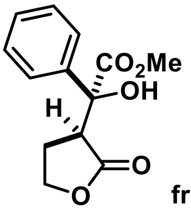
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.29 – 7.08 (m, 5H), 6.17 (d, *J* = 5.5 Hz, 1H), 5.26 (d, *J* = 5.5 Hz, 1H), 4.55 (s, 1H), 4.18 (d, *J* = 11.3 Hz, 1H), 4.05 (d, *J* = 11.3 Hz, 1H), 2.51 (dt, *J* = 5.1, 2.4 Hz, 1H), 2.42 (d, *J* = 5.7 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 138.6, 135.0, 131.7, 127.9, 127.7, 126.9, 88.6, 70.8, 42.5, 33.6, 32.0, 20.9.

HR-MS (APCI-MS): m/z calc. for $C_{15}H_{17}O_4$ $[M+H^{+}]^{+}$ 261.1121, found 261.1121.

Synthesis of butyrolactones from endoperoxides

Methyl (S*)-2-hydroxy-2-((S*)-2-oxotetrahydrofuran-3-yl)-2-phenylacetate *4a*



from 2a-minor

2a-minor (33.8 mg, 0.13 mmol, 1 equiv.) was dissolved in 5 mL MeOH and $HNEt_2$ (15 µL, 0.14 mmol, 1.1 equiv.) was added while stirring. The reaction was stirred over night for 16 h and the solvent evaporated under reduced pressure. Column chromatography (hexanes:EtOAc 1:1) yielded the product was white amorphous solid (32.1 mg, 12.8 mmol, 95%).

R_f (hexanes:EtOAc 1:1) = 0.2.

m.p.: 130-133 °C

IR (neat): 3482, 2962, 2925, 2856, 2360, 1765, 1719, 1497, 1449, 1224, 1256, 1180, 1143, 1111, 1021, 932, 895, 842 cm^{-1}.

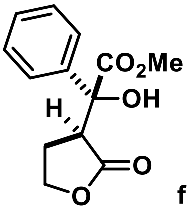
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.36 (dt, *J* = 15.7, 7.1 Hz, 3H), 4.34 (td, *J* = 8.9, 3.1 Hz, 1H), 4.17 (q, *J* = 8.9 Hz, 1H), 4.13 (s, 1H), 3.87 (s, 3H), 3.77 (t, *J* = 9.7 Hz, 1H), 2.25 – 2.13 (m, 1H), 2.05 – 1.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.98, 174.02, 139.18, 128.71, 128.43, 125.86, 77.29, 66.93, 53.98, 48.48, 23.84.

HR-MS (APCI-MS): m/z calc. for $C_{13}H_{15}O_5$ $[M+H^+]^+$ 251.0914, found 251.0916.

Crystals suitable for X-ray analysis (CDC 1980429) were obtained by recrystallization from DCM/Et_2O.

Methyl (R*)-2-hydroxy-2-((S*)-2-oxotetrahydrofuran-3-yl)-2-phenylacetate *4b*



from 2a-major

2a-major (48.9 mg, 0.19 mmol, 1 equiv.) was dissolved in 5 mL MeOH and $HNEt_2$ (20 µL, 0.19 mmol, 1 equiv.) was added while stirring. The reaction was stirred over night for 16 h and the solvent evaporated under reduced pressure. Column chromatography (hexanes:EtOAc 1:1) yielded the product was white very viscous oil (46.4 mg, 18.5 mmol, 95%).

R_f (hexanes:EtOAc 1:1) = 0.2.

IR (neat): 3524, 3064, 3004, 2952, 1766, 1722, 1449, 1427, 1375, 1254, 1132, 1077, 1027, 968 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.49 (m, 2H), 7.45 – 7.29 (m, 3H), 4.60 – 4.35 (m, 2H), 4.20 (q, *J* = 8.2 Hz, 1H), 3.82 (s, 3H), 3.32 (t, *J* = 9.3 Hz, 1H), 2.45 (dq, *J* = 12.7, 8.8 Hz, 1H), 2.20 (dddd, *J* = 12.8, 9.5, 7.6, 4.0 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 176.2, 173.4, 138.6, 128.5 (2C), 125.4, 79.4, 66.7, 53.6, 48.0, 25.6.

HR-MS (APCI-MS): m/z calc. for $C_{13}H_{15}O_5$ $[M+H^+]^+$ 251.0914, found 251.0916.

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Chiral HPLC

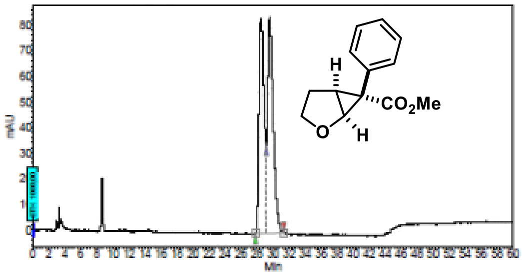
HPLC chromatograms are shown below.

Rac methyl 6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate

Vail : 54
Method : Phex-Cel1_99-1
Run time : 60,00 min
Inj. vol. : 10,000 µl

λ : 215 nm

Column : Phenomenex Lux Cellulose-1,
4.6 x 250 mm, 5 µm
Eluents : A = n-Heptane
B = i-Propanol
Flow : 1.0 ml/min



Peak Results :

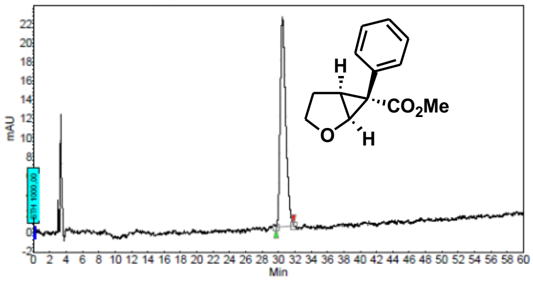
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	28,52	45,03	83,7	59,4	45,029
2	UNKNOWN	29,59	54,97	84,4	72,5	54,971
Total			100,00	168,1	131,8	100,000

Methyl (1S,5S,6R)-6-phenyl-2-oxabicyclo[3.1.0]hexane-6-carboxylate

Vail : 117
Method : Phex-Cel1_99-1
Run time : 60,00 min
Inj. vol. : 10,000 µl

λ : 215 nm

Column : Phenomenex Lux Cellulose-1,
4.6 x 250 mm, 5 µm
Eluents : A = n-Heptane
B = i-Propanol
Flow : 1.0 ml/min



Peak Results :

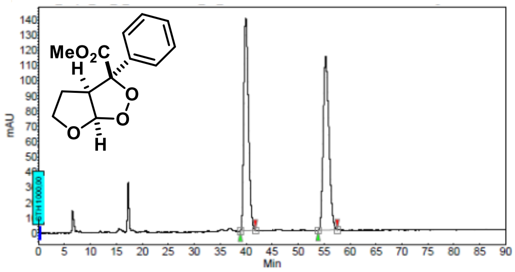
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	30,49	100,00	22,1	17,4	100,000
Total			100,00	22,1	17,4	100,000

Rac Methyl 3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate

Vail : 54
Method : AS-H_95-5_0.5
Run time : 90,00 min
Inj. vol. : 10,000 µl

λ : 215 nm

Column : Chiralpak AS-H, 4.6 x 250 mm, 10 µm
Eluents : A = n-Heptane
B = i-Propanol
Flow : 0.5 ml/min



Peak Results :

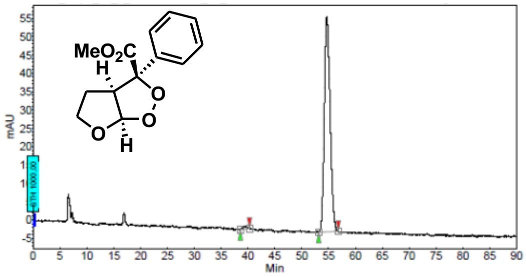
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	39,93	49,70	139,8	145,0	49,696
2	UNKNOWN	55,32	50,30	114,2	146,8	50,304
Total			100,00	254,0	291,8	100,000

Methyl (3R,3aS,6aR)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate

Vail : 117
Method : AS-H_95-5_0.5
Run time : 90,00 min
Inj. vol. : 20,000 µl

λ : 215 nm

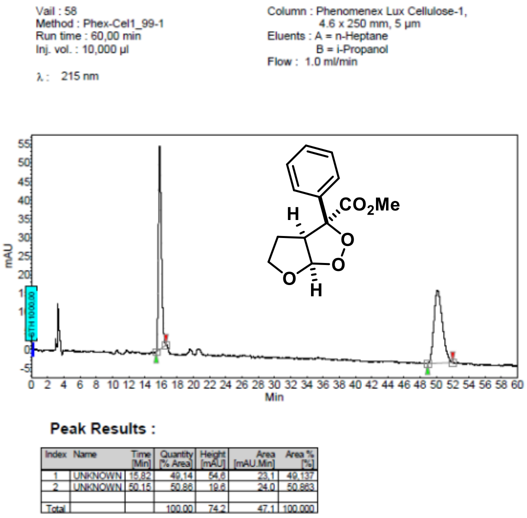
Column : Chiralpak AS-H, 4.6 x 250 mm, 10 µm
Eluents : A = n-Heptane
B = i-Propanol
Flow : 0.5 ml/min



Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	39,43	0,77	0,8	0,6	0,771
2	UNKNOWN	54,70	99,23	58,8	73,5	99,229
Total			100,00	59,6	74,1	100,000

rac Methyl 3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate



Vail : 58
Method : Phex-Cel1_99-1
Run time : 60,00 min
Inj. vol. : 10,000 µl

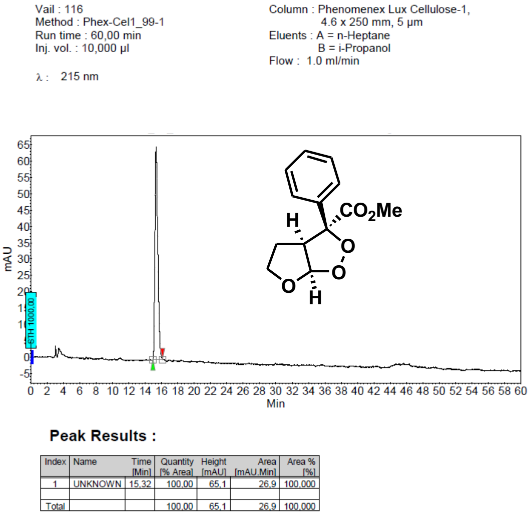
λ : 215 nm

Column : Phenomenex Lux Cellulose-1,
4.6 x 250 mm, 5 µm
Eluents : A = n-Heptane
B = i-Propanol
Flow : 1.0 ml/min

Peak Results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15,82	49,14	54,6	23,1	49,137
2	UNKNOWN	50,15	50,86	19,6	24,0	50,863
Total			100,00	74,2	47,1	100,000

Methyl (3S,3aS,6aR)-3-phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole-3-carboxylate



Vail : 116
Method : Phex-Cel1_99-1
Run time : 60,00 min
Inj. vol. : 10,000 µl

λ : 215 nm

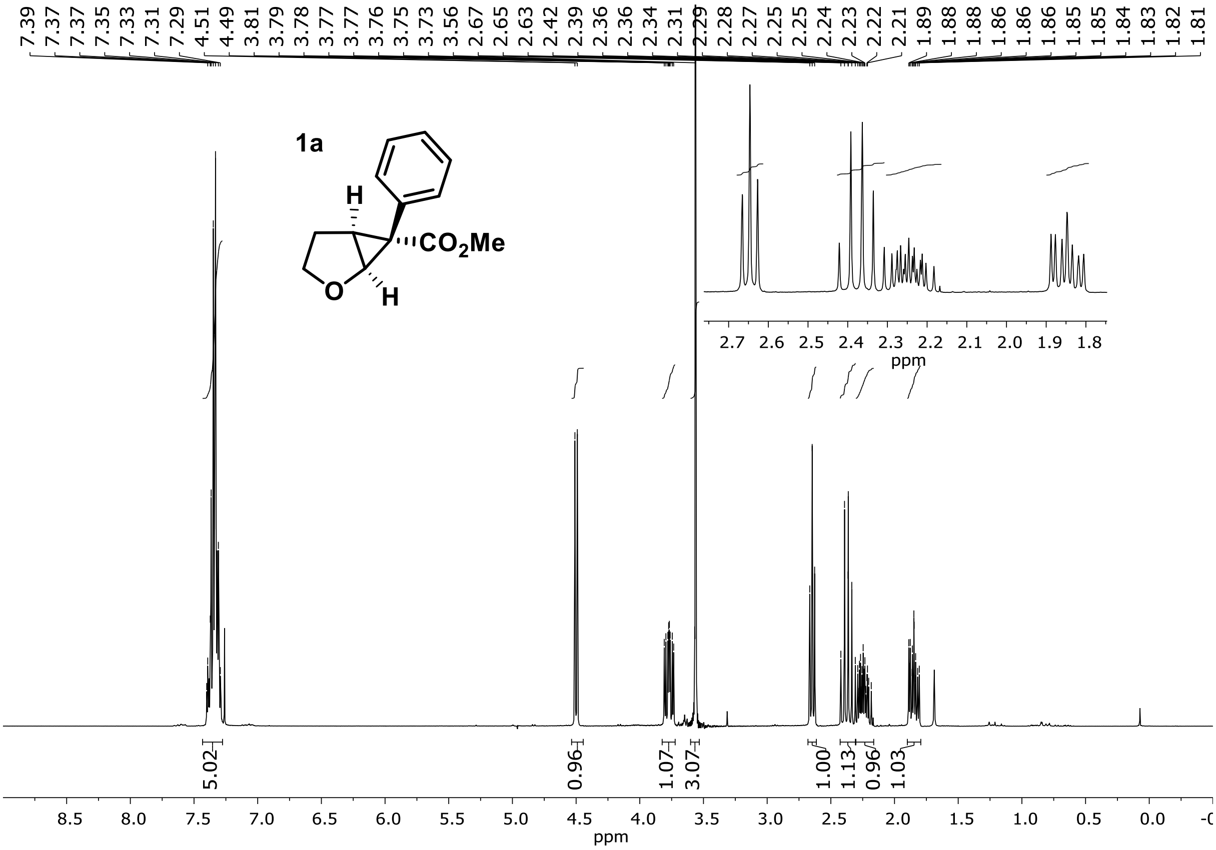
Column : Phenomenex Lux Cellulose-1,
4.6 x 250 mm, 5 µm
Eluents : A = n-Heptane
B = i-Propanol
Flow : 1.0 ml/min

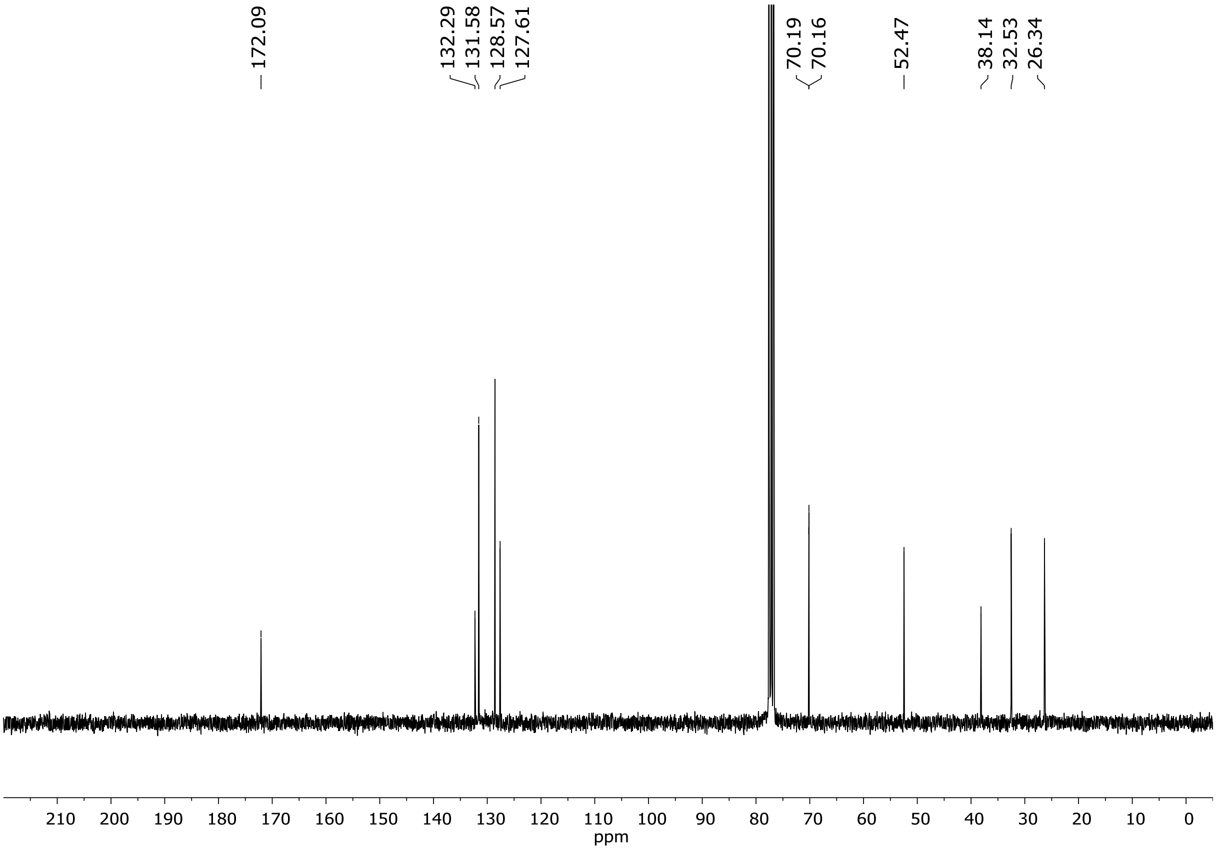
Peak Results :

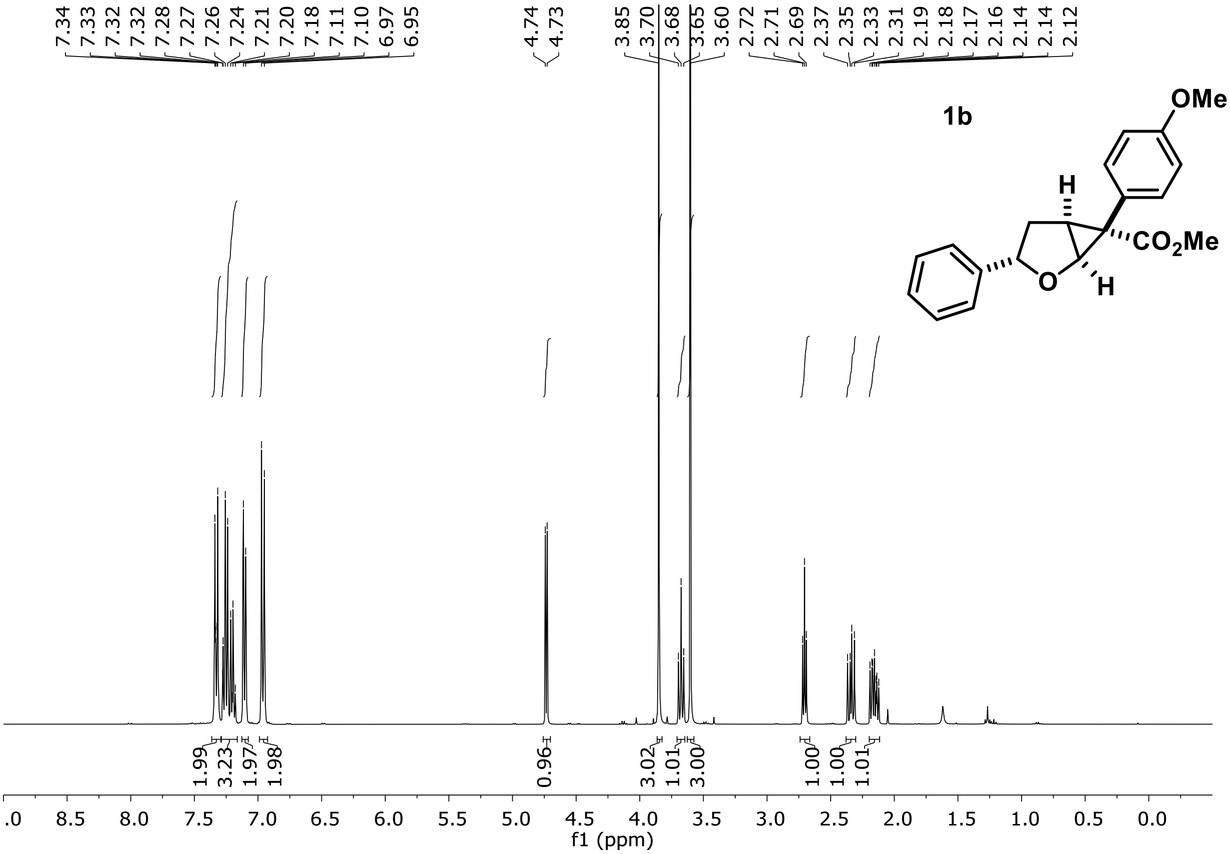
Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	15,32	100,00	65,1	26,9	100,000
Total			100,00	65,1	26,9	100,000

NMR spectra

Starting Materials 1



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7.24
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7.20
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7.11
7.10
6.97
6.95
4.74
4.73
3.85
3.70
3.68
3.65
3.60
2.72
2.71
2.69
2.37
2.35
2.33
2.31
2.19
2.18
2.17
2.16
2.14
2.14
2.12
1b
OMe
H
CO_2Me
O
H
1.99
3.23
1.97
1.98
0.96
3.02
1.01
3.00
1.00
1.00
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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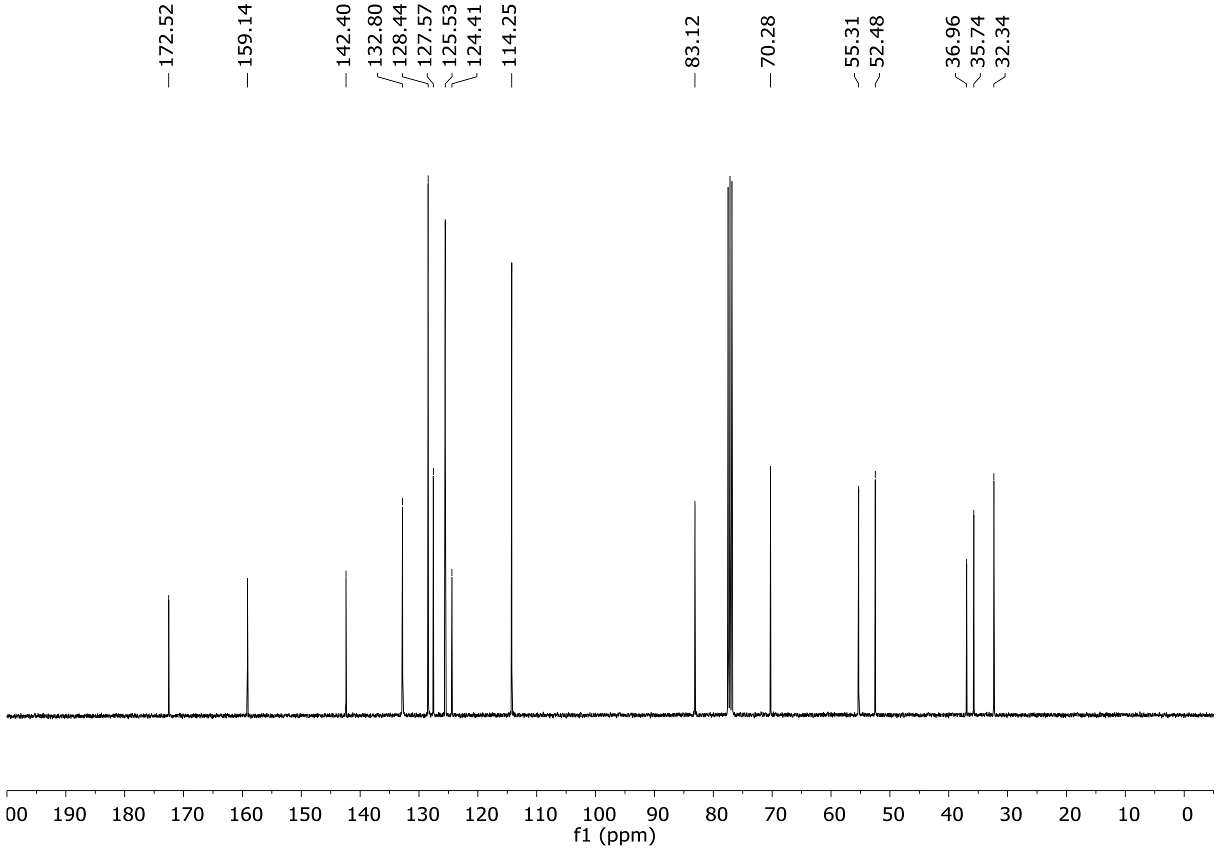
0.0
f1 (ppm)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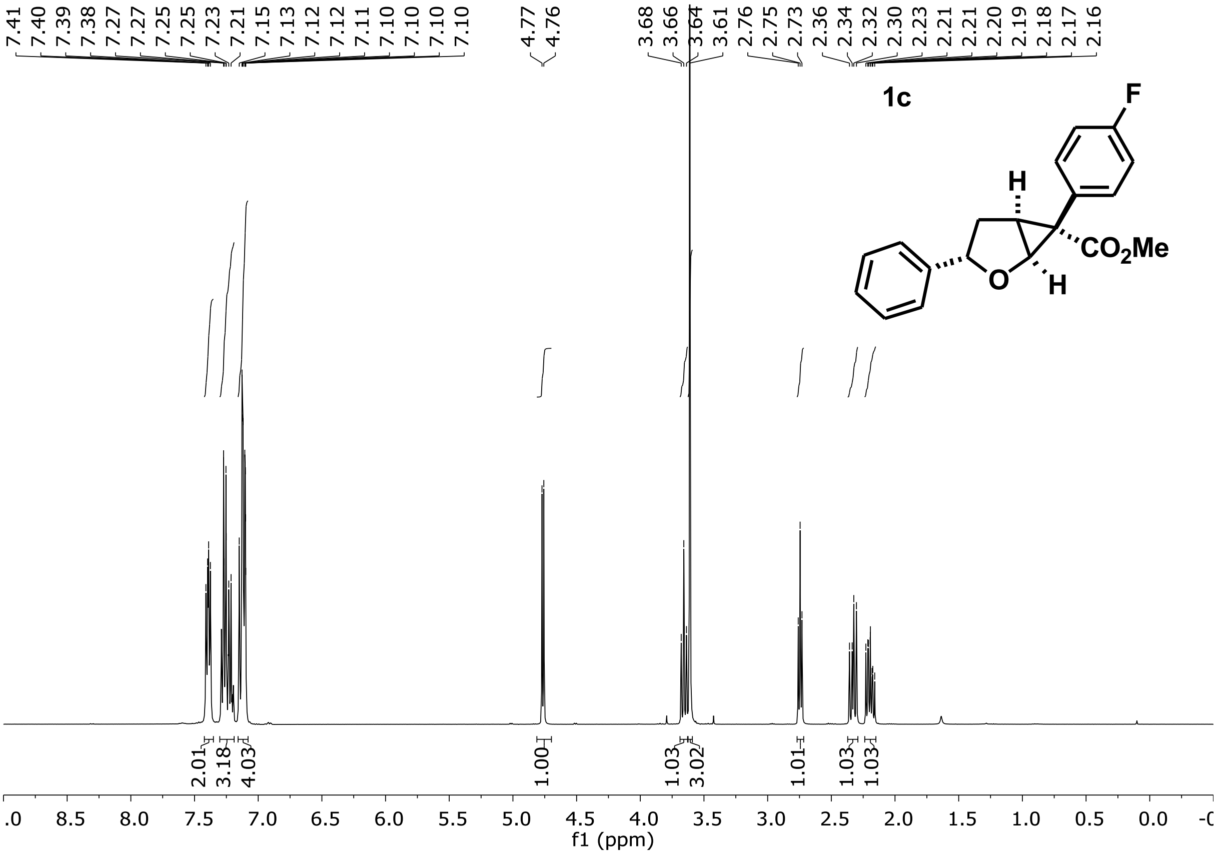
52.48
36.96
35.74
32.34
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.25
7.25
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7.13
7.12
7.12
7.11
7.10
7.10
7.10
4.77
4.76
3.68
3.66
3.64
3.61
2.76
2.75
2.73
2.36
2.34
2.32
2.30
2.23
2.21
2.21
2.20
2.19
2.18
2.17
2.16
1c
F
H
CO_2Me
O
H
2.01
3.18
4.03
1.00
1.03
3.02
1.01
1.03
1.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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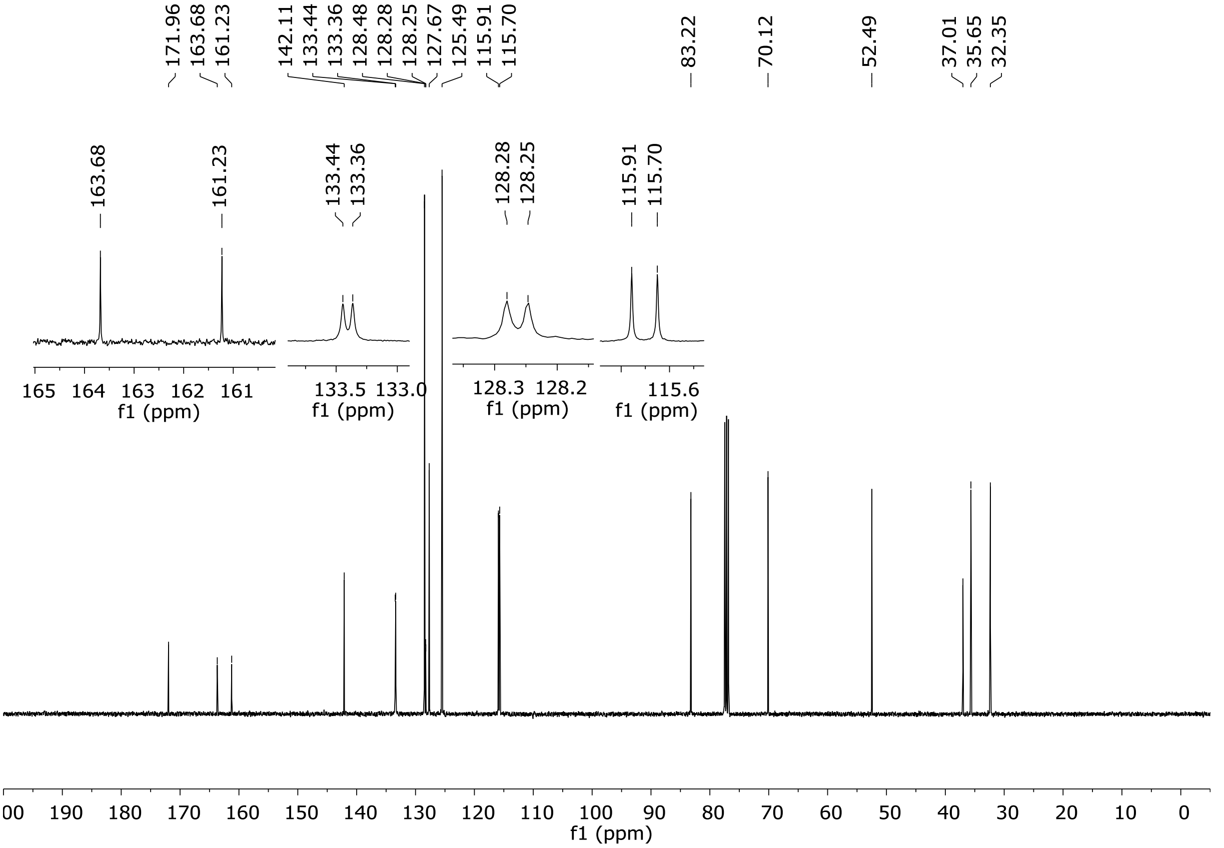
1.5
1.0
0.5
0.0
-(
f1 (ppm)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127.67
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115.70
83.22
70.12
52.49
37.01
35.65
32.35
163.68
161.23
165
164
163
162
161
f1 (ppm)
133.44
133.36
133.5
133.0
f1 (ppm)
128.28
128.25
128.3
128.2
f1 (ppm)
115.91
115.70
115.6
f1 (ppm)
00
190
180
170
160
150
140
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120
110
100
90
80
70
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50
40
30
20
10
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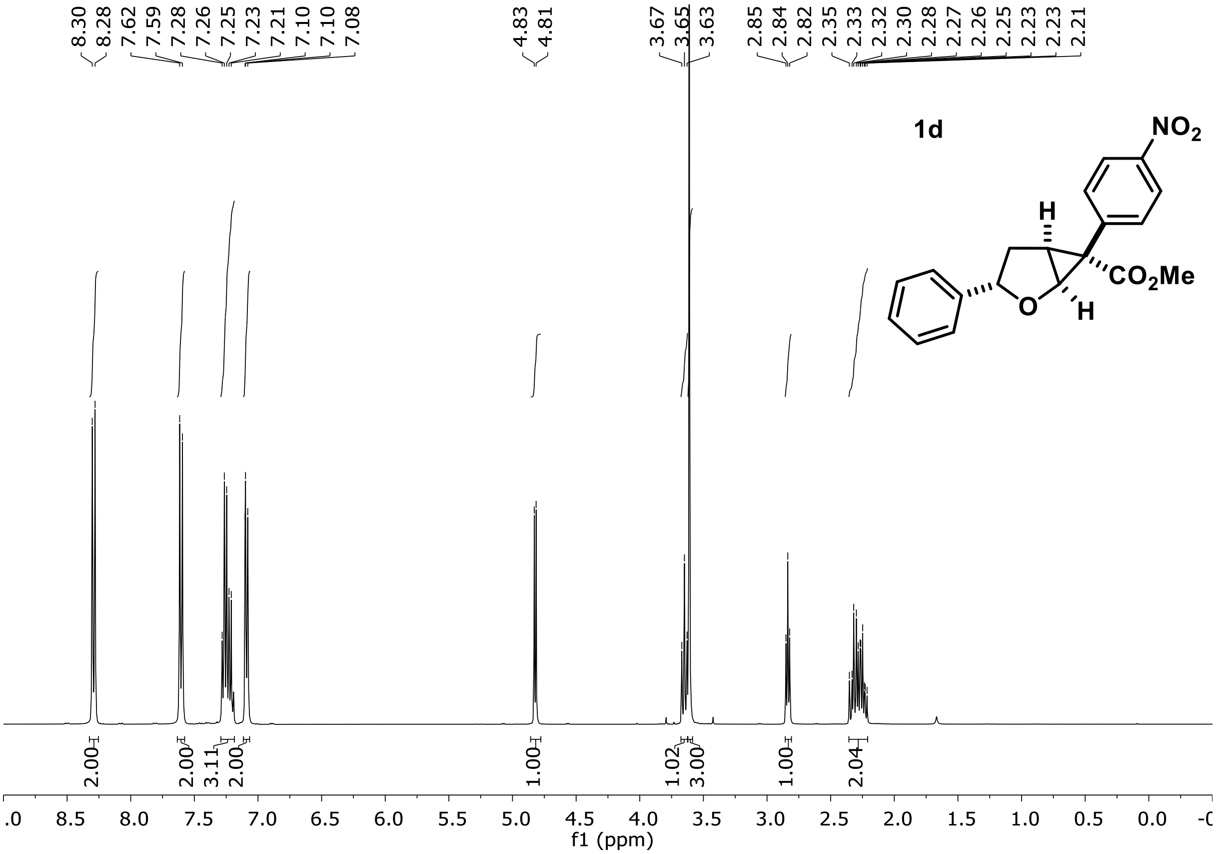
f1 (ppm)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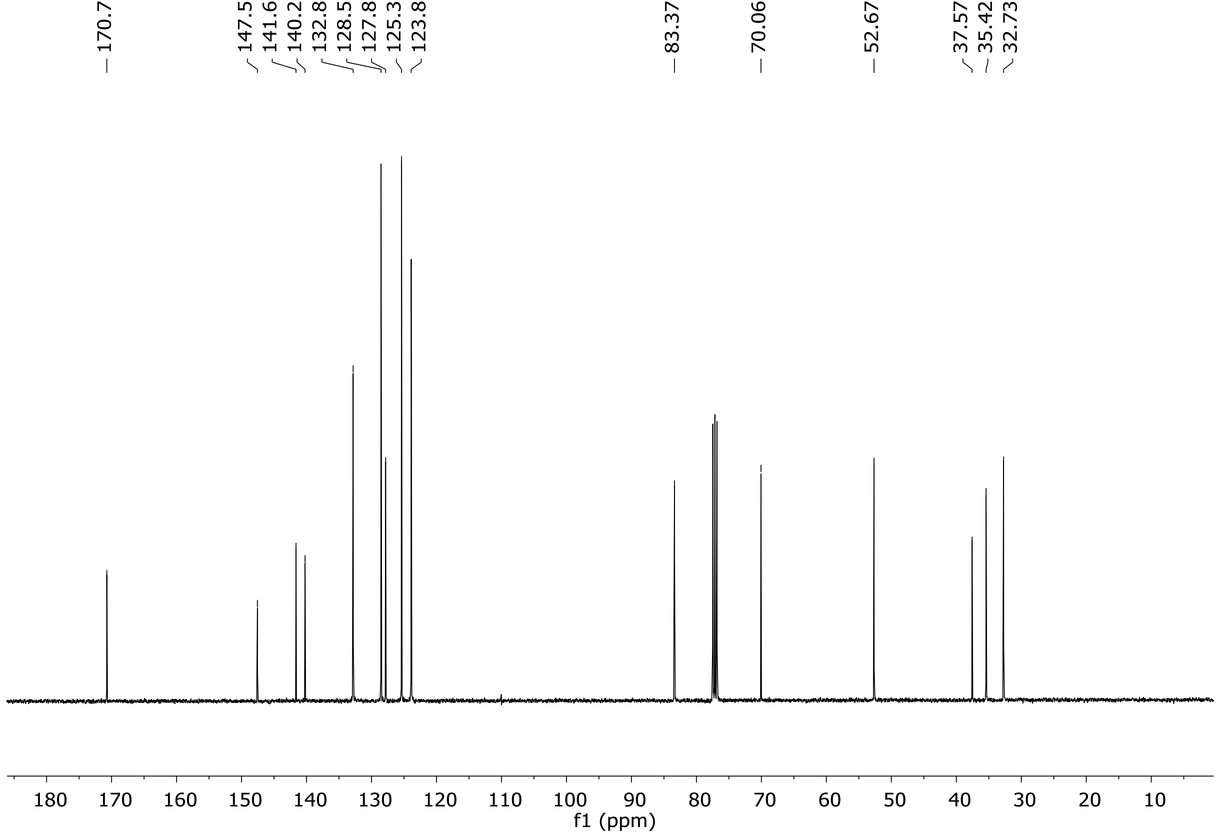
7.23
7.21
7.10
7.10
7.08
4.83
4.81
3.67
3.65
3.63
2.85
2.84
2.82
2.35
2.33
2.32
2.30
2.28
2.27
2.26
2.25
2.23
2.23
2.21
1d
NO2
H
CO2Me
O
H
2.00
2.00
3.11
2.00
1.00
1.02
3.00
1.00
2.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)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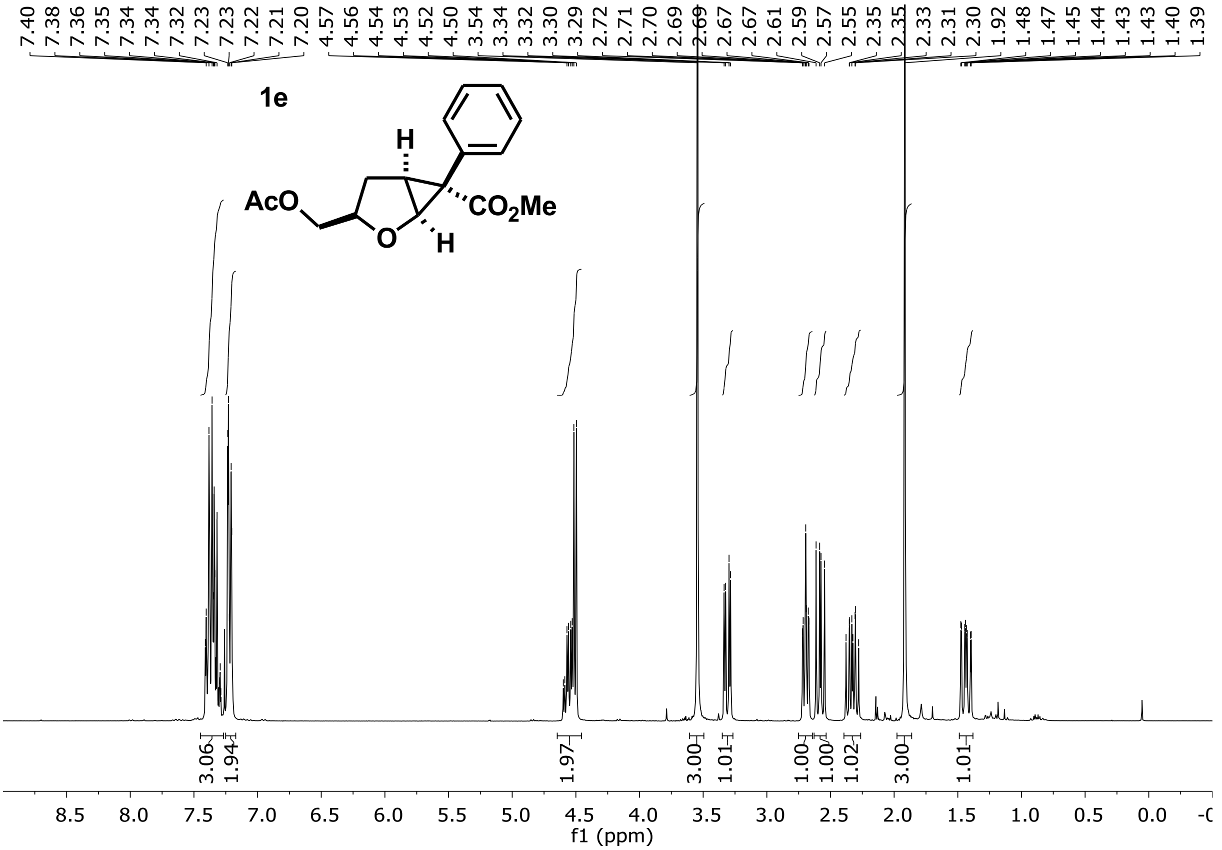
147.56
141.62
140.22
132.82
128.53
127.83
125.38
123.89
83.37
70.06
52.67
37.57
35.42
32.73
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

1e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7.38
7.36
7.35
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7.34
7.32
7.23
7.23
7.22
7.21
7.20
4.57
4.56
4.54
4.53
4.52
4.50
3.54
3.34
3.32
3.30
3.29
2.72
2.71
2.70
2.69
2.69
2.67
2.67
2.61
2.59
2.57
2.55
2.35
2.35
2.33
2.31
2.30
1.92
1.48
1.47
1.45
1.44
1.43
1.43
1.40
1.39
AcO
O
H
H
CO2Me
3.06
1.94
1.97
3.00
1.01
1.00
1.00
1.00
1.02
3.00
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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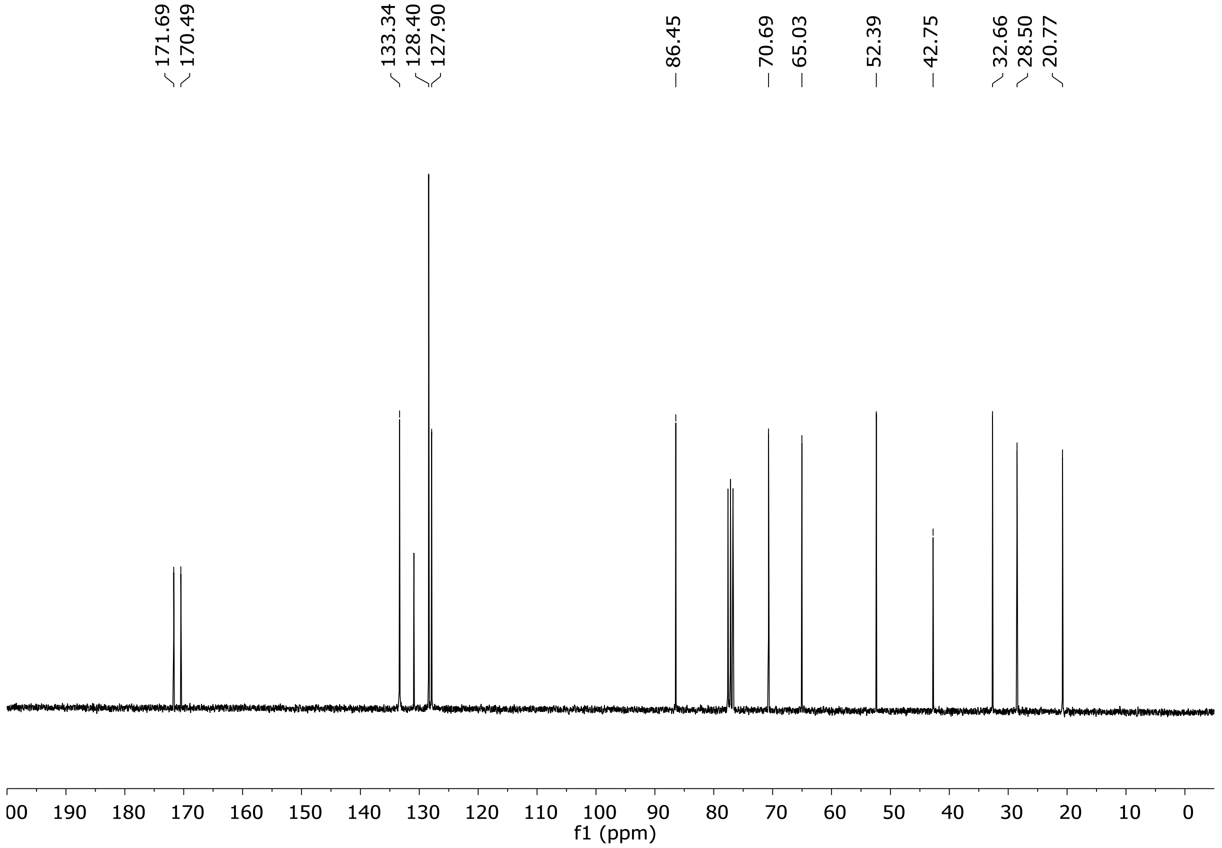
f1 (ppm)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65.03
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42.75
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28.50
20.77
190
180
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150
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120
110
100
90
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70
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50
40
30
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10
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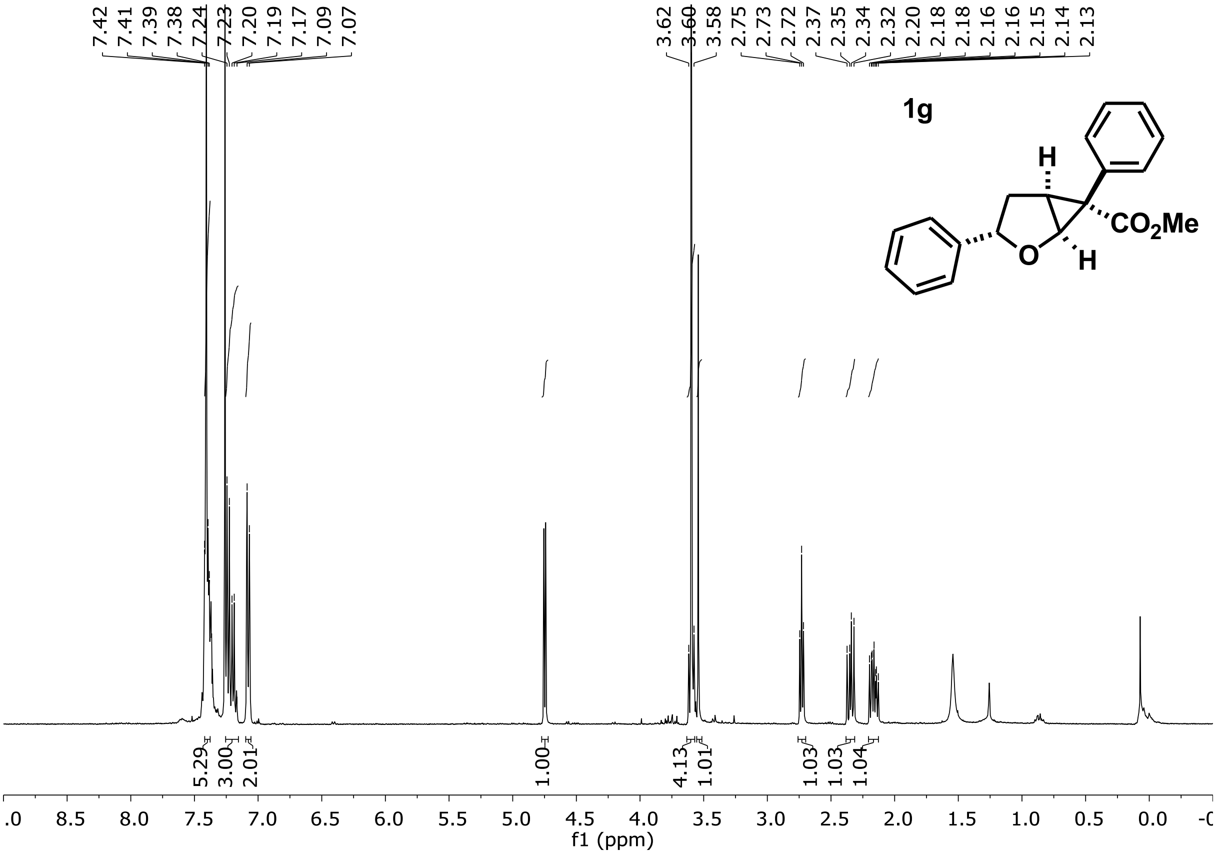
f1 (ppm)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7.17
7.09
7.07
3.62
3.60
3.58
2.75
2.73
2.72
2.37
2.35
2.34
2.32
2.20
2.18
2.18
2.16
2.16
2.15
2.14
2.13
H
H
O
CO2Me
5.29
3.00
2.01
1.00
4.13
1.01
1.03
1.03
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
1.5
1.0
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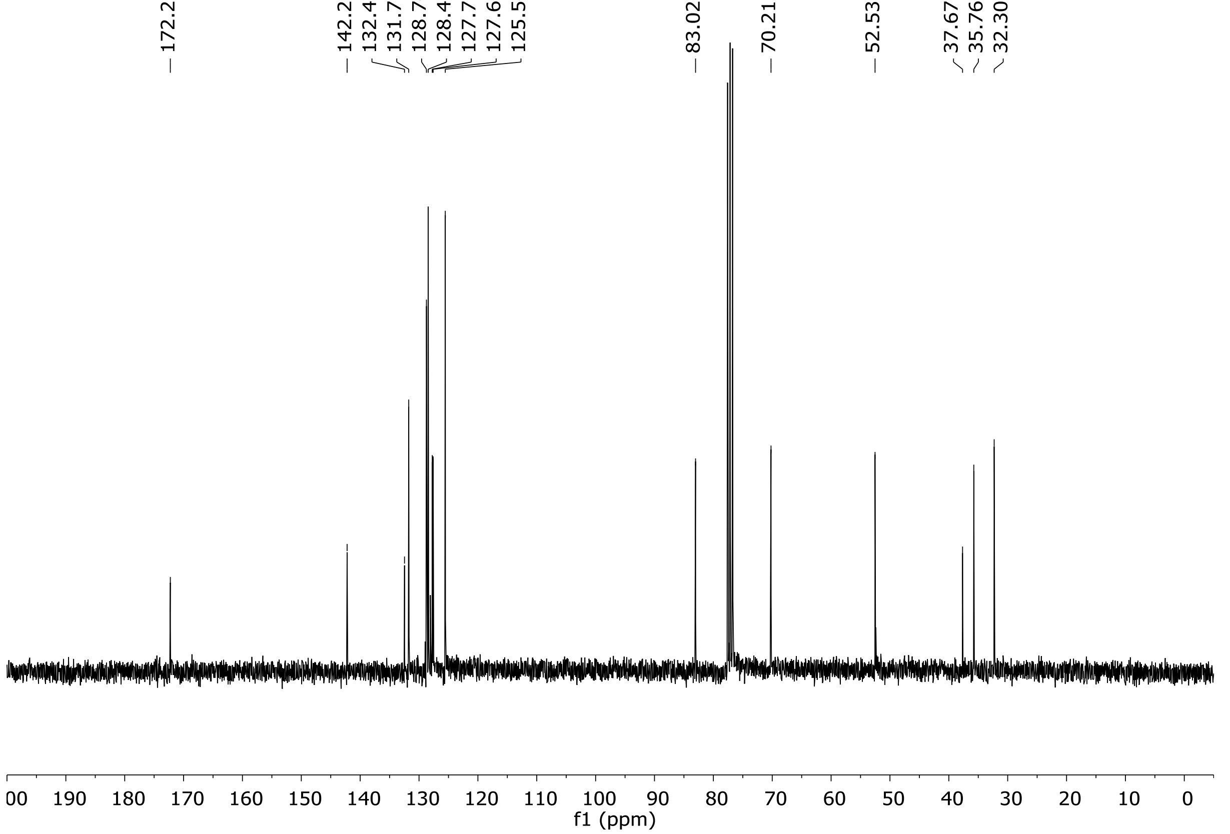
0.0
-(
f1 (ppm)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132.47
131.75
128.74
128.45
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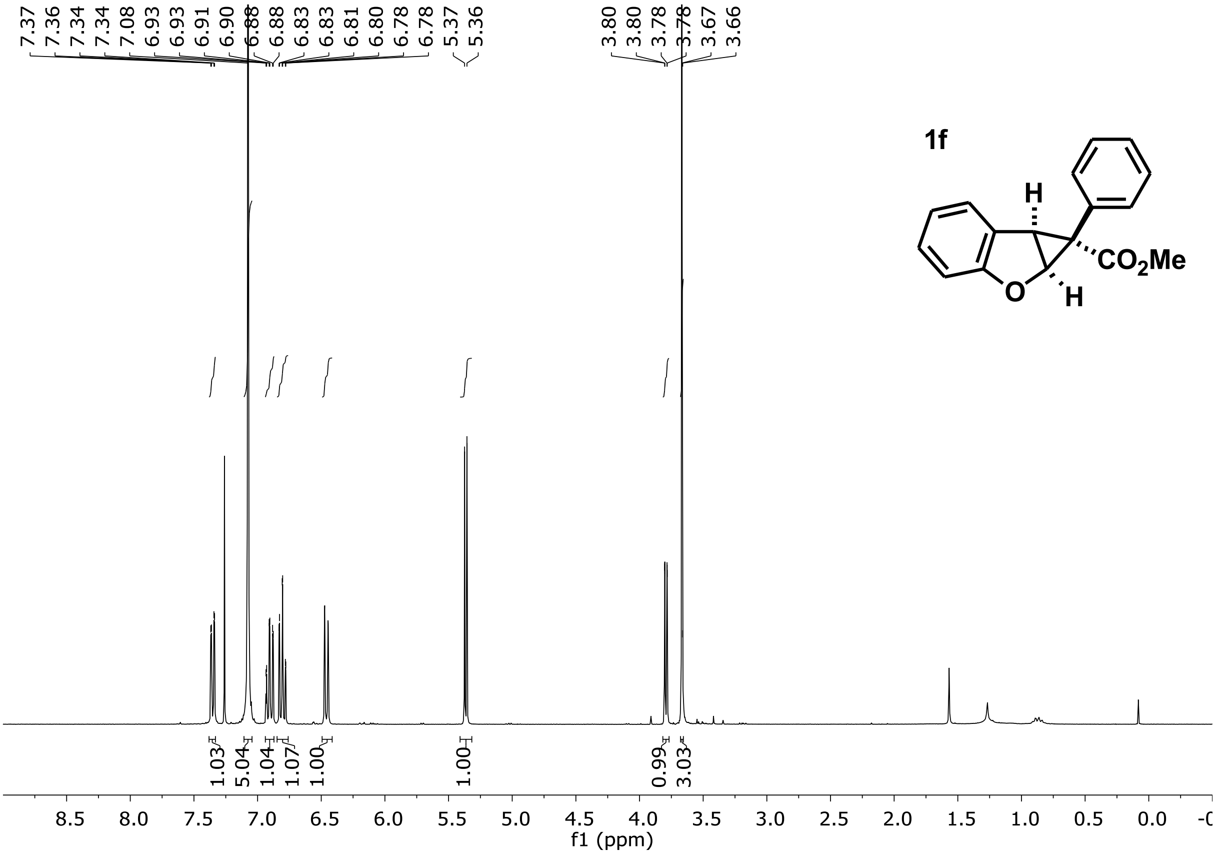
127.61
125.54
83.02
70.21
52.53
37.67
35.76
32.30
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1f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6.88
6.83
6.83
6.81
6.80
6.78
6.78
5.37
5.36
3.80
3.80
3.78
3.78
3.67
3.66
H
H
O
CO2Me
1.03
5.04
1.04
1.07
1.00
1.00
0.99
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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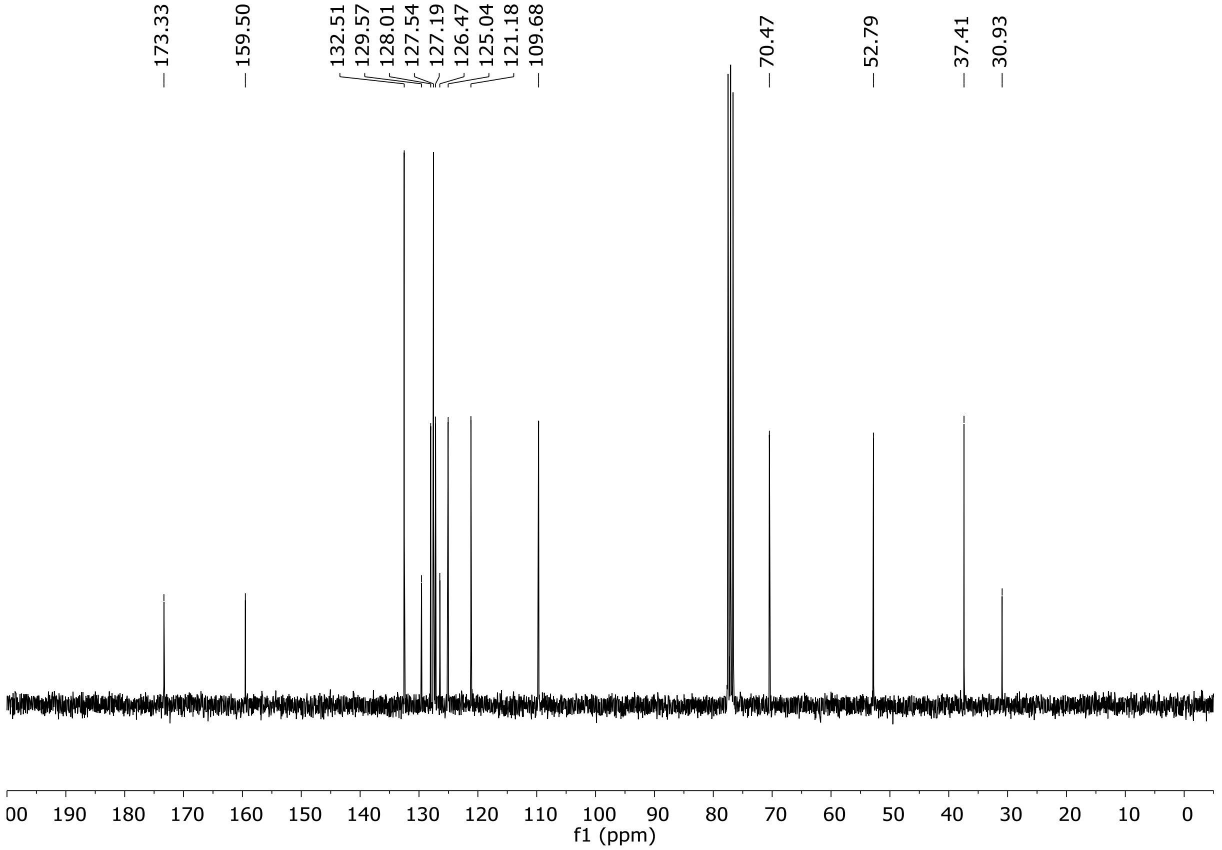
0.0
f1 (ppm)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37.41
30.93
190
180
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50
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20
10
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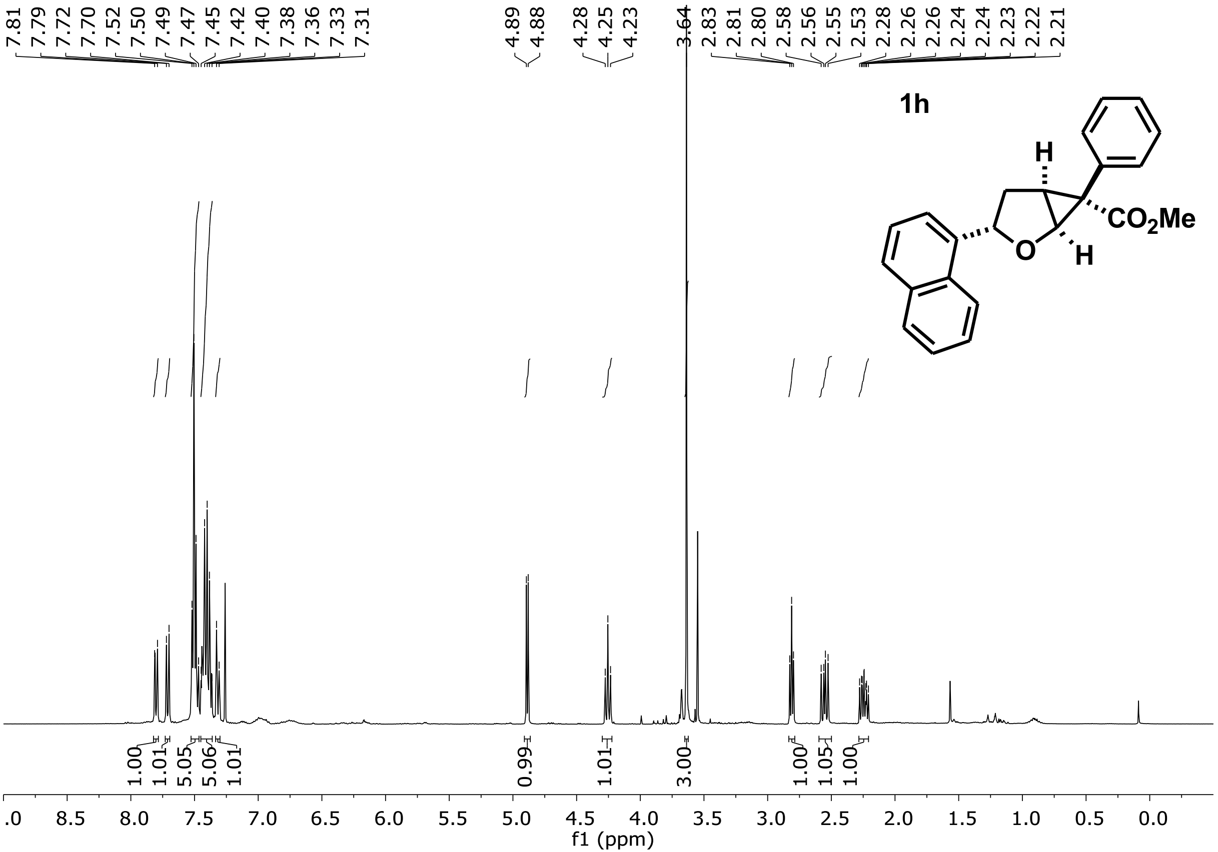
f1 (ppm)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7.36
7.33
7.31
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4.88
4.28
4.25
4.23
3.64
2.83
2.81
2.80
2.58
2.56
2.55
2.53
2.28
2.26
2.26
2.24
2.24
2.23
2.22
2.21
1h
H
H
O
CO2Me
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1.01
5.05
5.06
1.01
0.99
1.01
3.00
1.00
1.05
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
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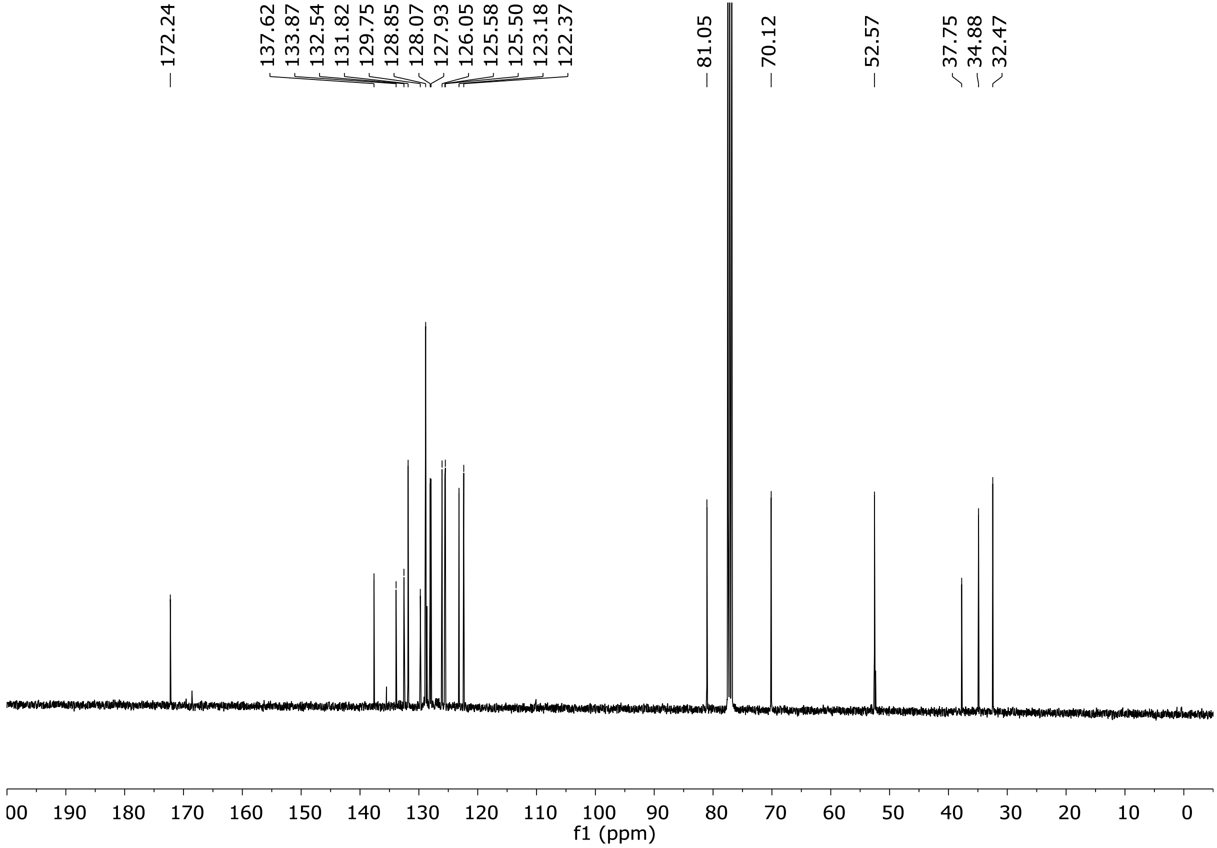
1.0
0.5
0.0
f1 (ppm)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123.18
122.37
81.05
70.12
52.57
37.75
34.88
32.47
00
190
180
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120
110
100
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50
40
30
20
10
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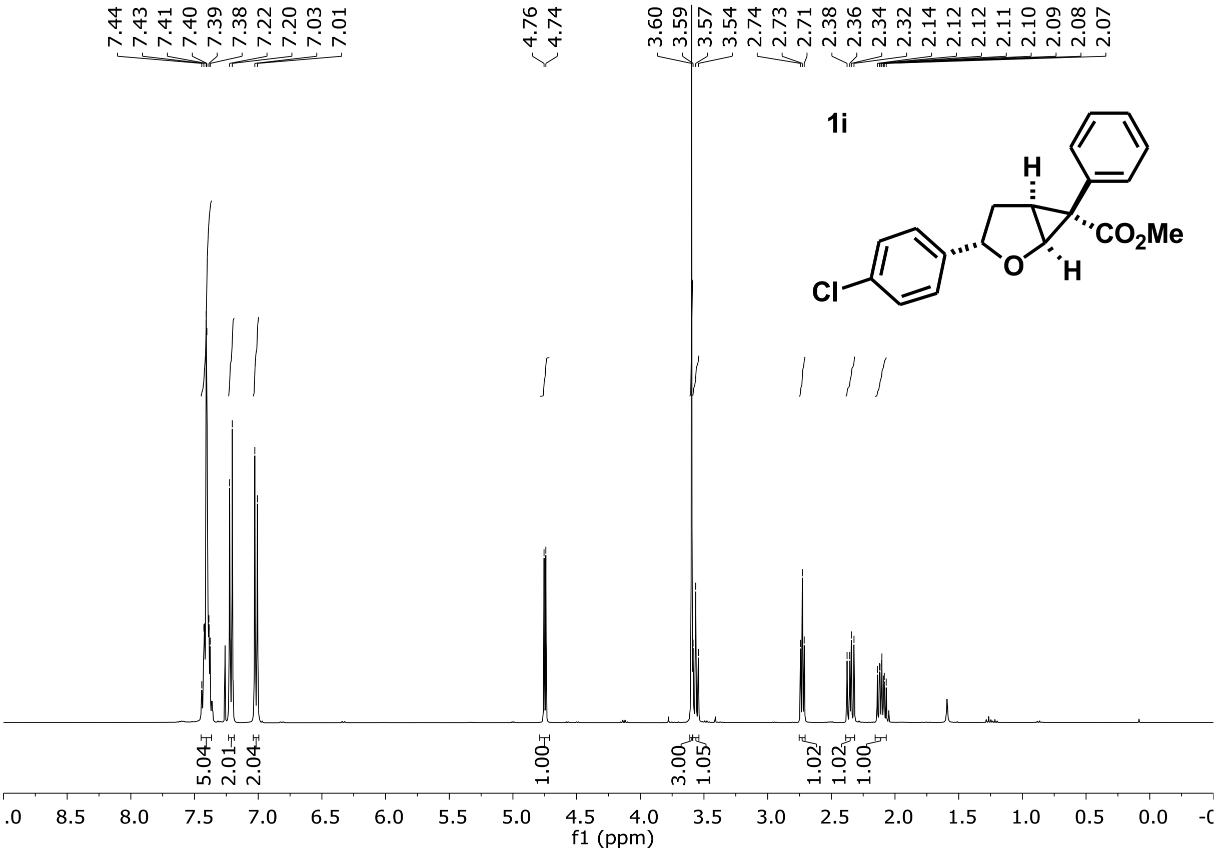
f1 (ppm)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3.59
3.57
3.54
2.74
2.73
2.71
2.38
2.36
2.34
2.32
2.14
2.12
2.12
2.11
2.10
2.09
2.08
2.07
1i
H
CO2Me
H
O
Cl
5.04
2.01
2.04
1.00
3.00
1.05
1.02
1.02
1.00
.0
8.5
8.0
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7.0
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6.0
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3.0
2.5
2.0
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1.0
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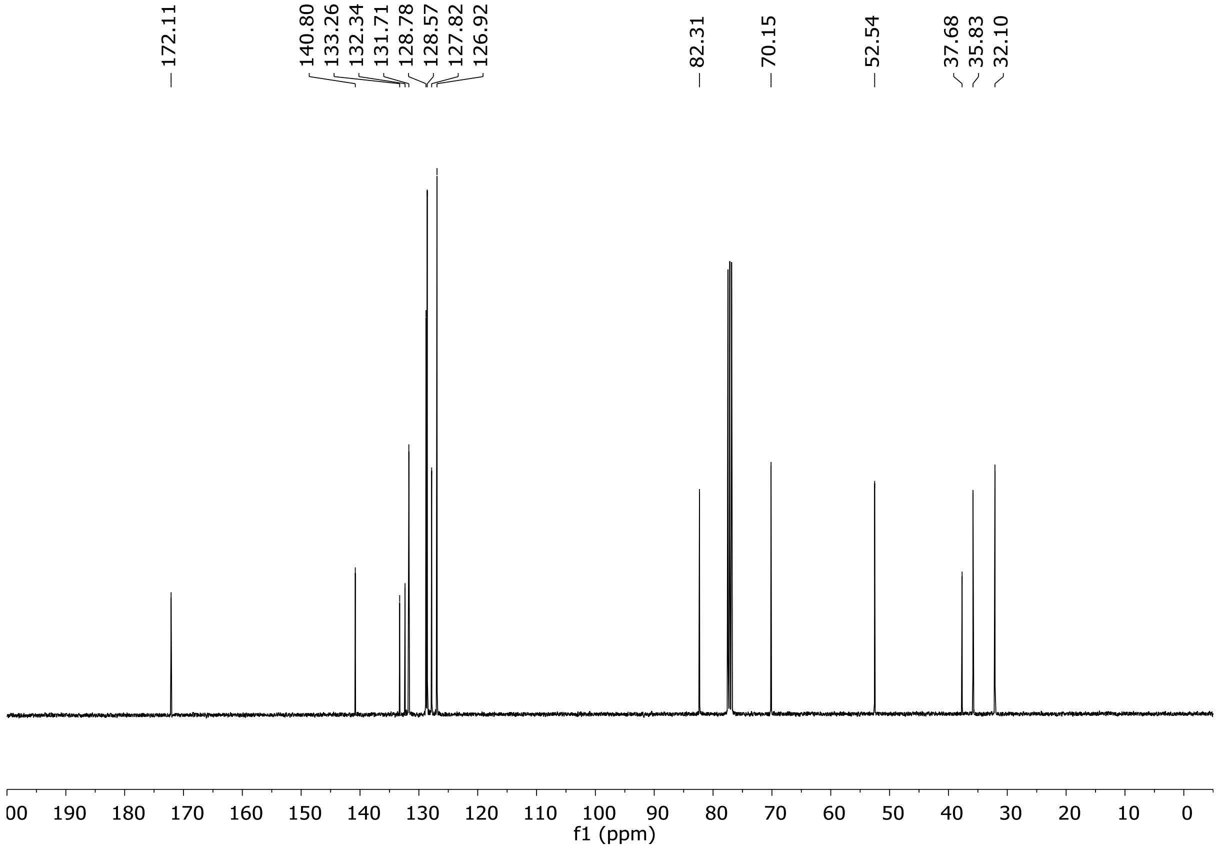
f1 (ppm)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35.83
32.10
00
190
180
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160
150
140
130
120
110
100
90
80
70
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50
40
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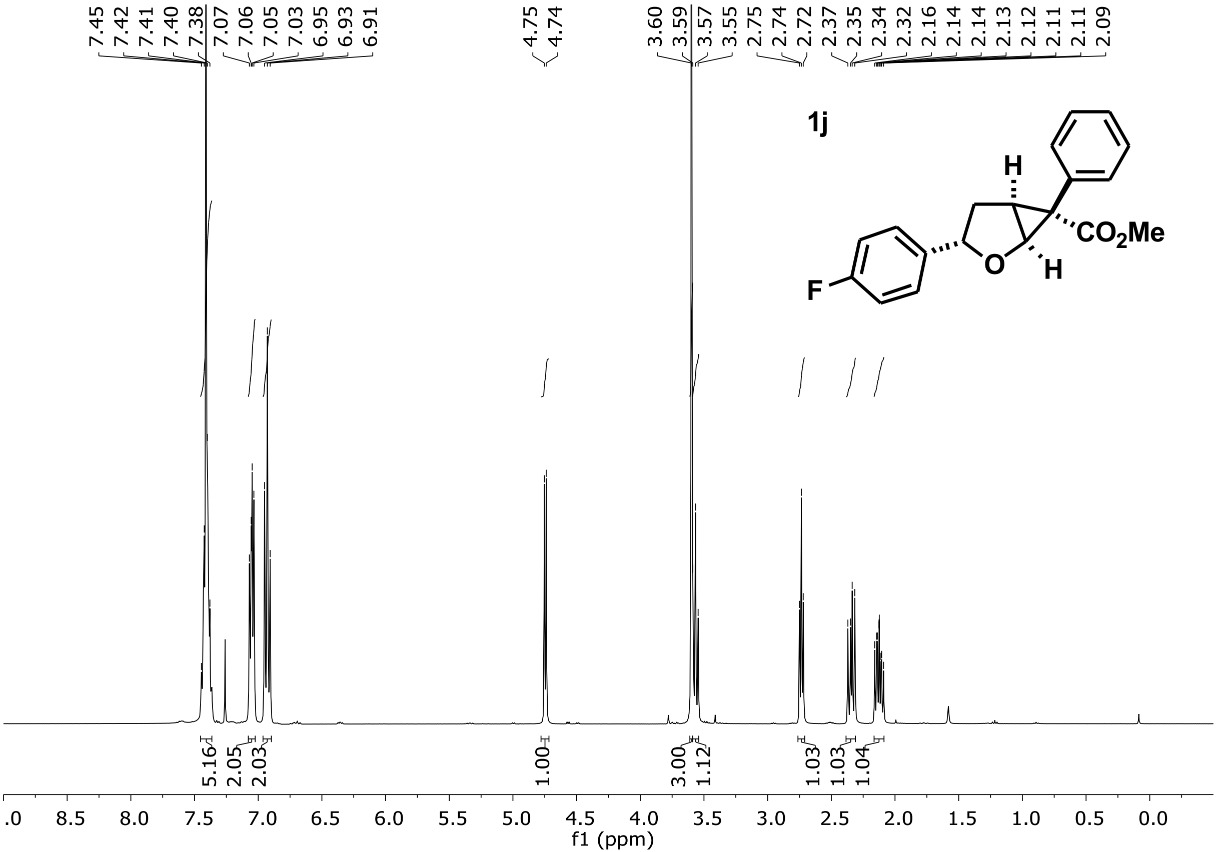
20
10
0
f1 (ppm)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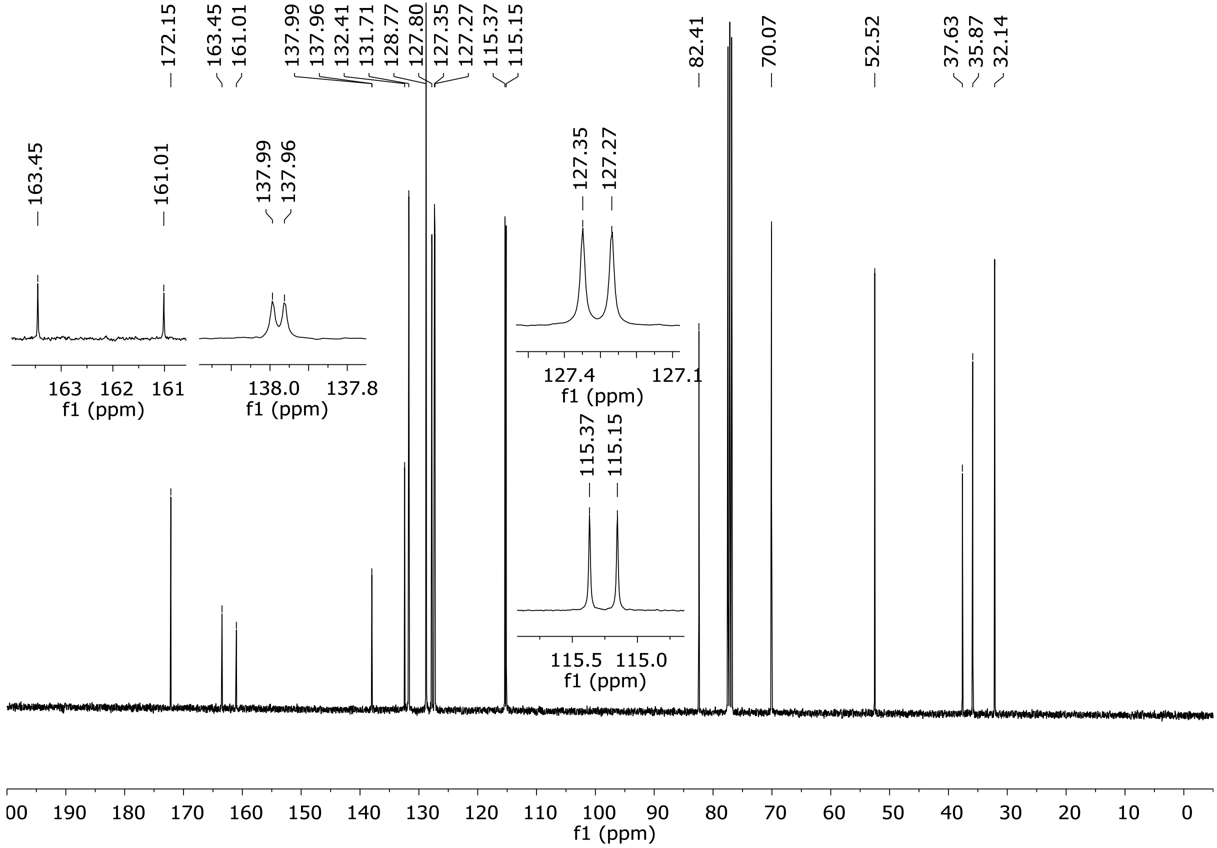
6.91
4.75
4.74
3.60
3.59
3.57
3.55
2.75
2.74
2.72
2.37
2.35
2.34
2.32
2.16
2.14
2.14
2.13
2.12
2.11
2.11
2.09
1j
H
H
CO2Me
O
F
5.16
2.05
2.03
1.00
3.00
1.12
1.03
1.03
1.04
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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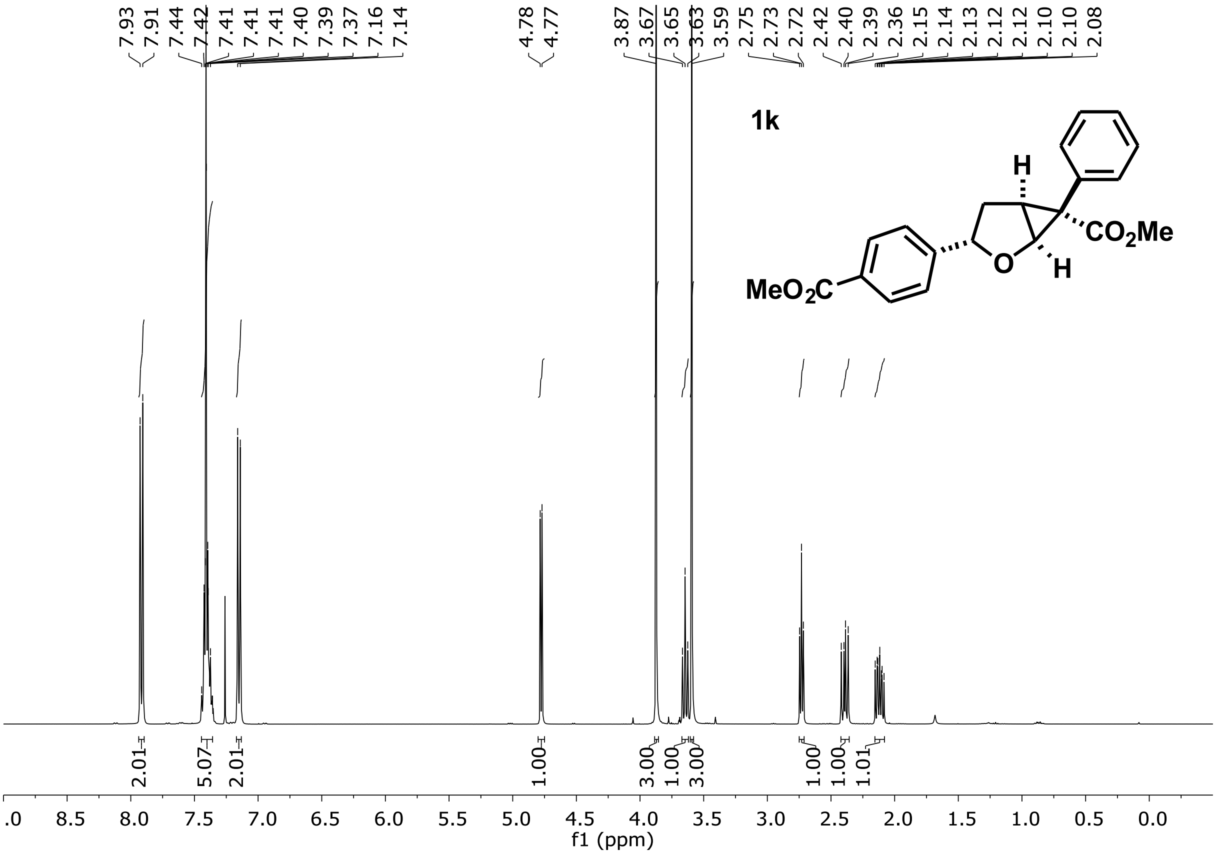
127.35
127.27
115.37
115.15
82.41
70.07
52.52
37.63
35.87
32.14
163.45
161.01
163 162 161
f1 (ppm)
137.99
137.96
138.0 137.8
f1 (ppm)
127.35
127.27
127.4 127.1
f1 (ppm)
115.37
115.15
115.5 115.0
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.41
7.41
7.40
7.39
7.37
7.16
7.14
4.78
4.77
3.87
3.67
3.65
3.63
3.59
2.75
2.73
2.72
2.42
2.40
2.39
2.36
2.15
2.14
2.13
2.12
2.12
2.10
2.10
2.08
1k
H
H
CO2Me
MeO2C
O
2.01
5.07
2.01
1.00
3.00
1.00
3.00
1.00
1.00
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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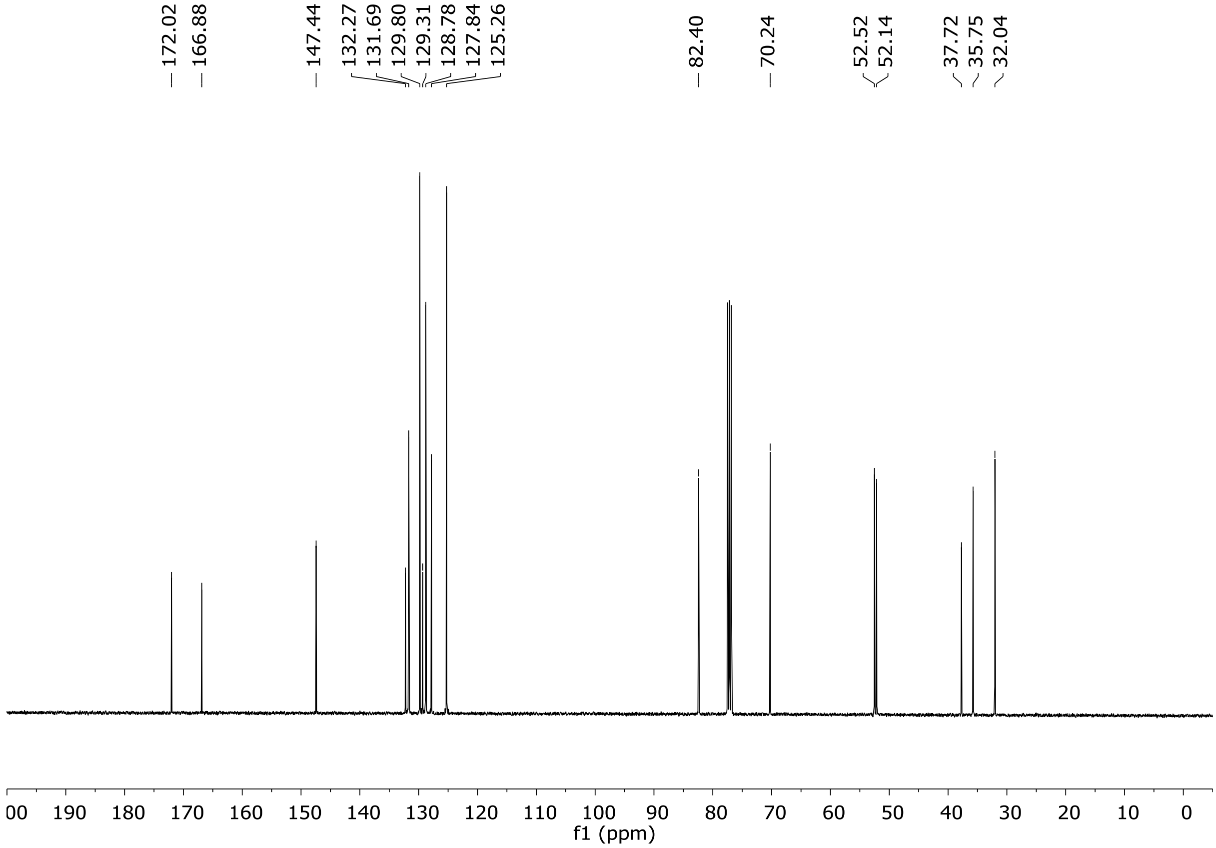
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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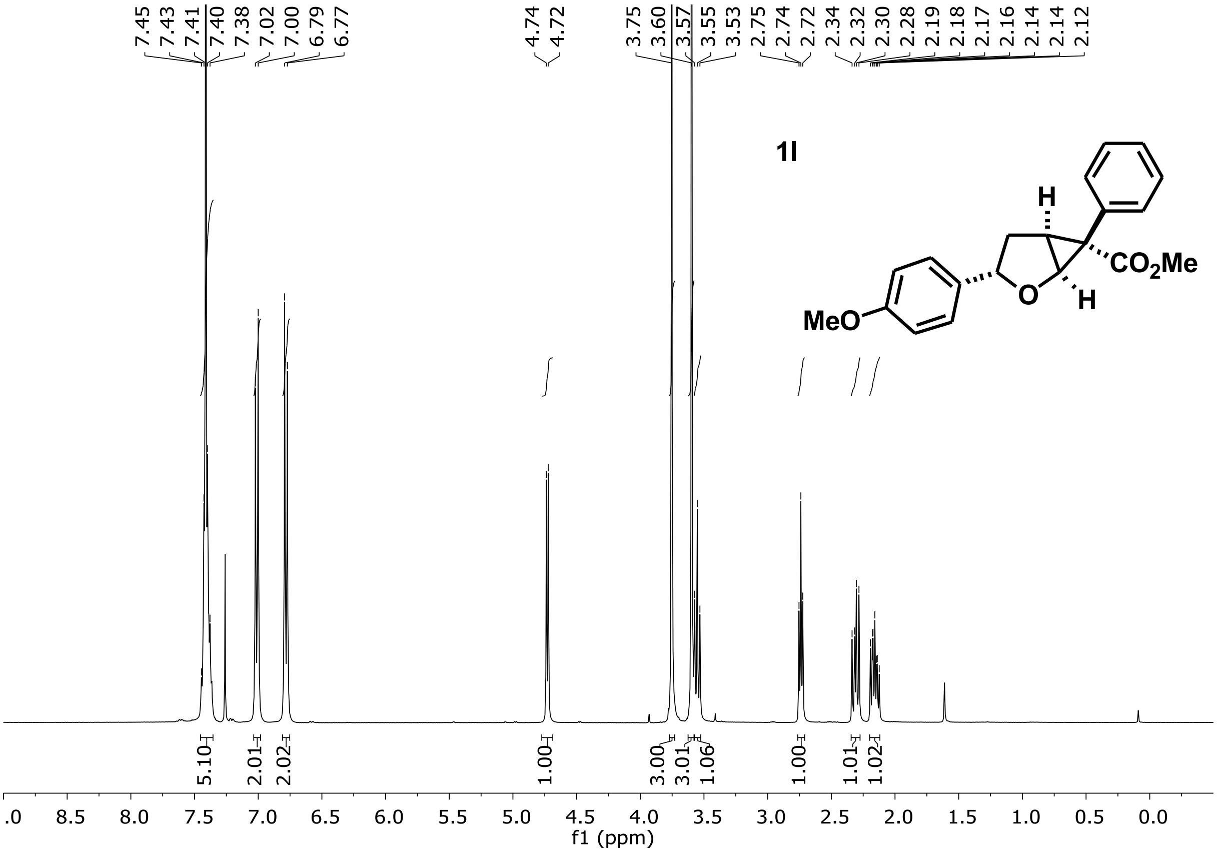
128.78
127.84
125.26
82.40
70.24
52.52
52.14
37.72
35.75
32.04
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.41
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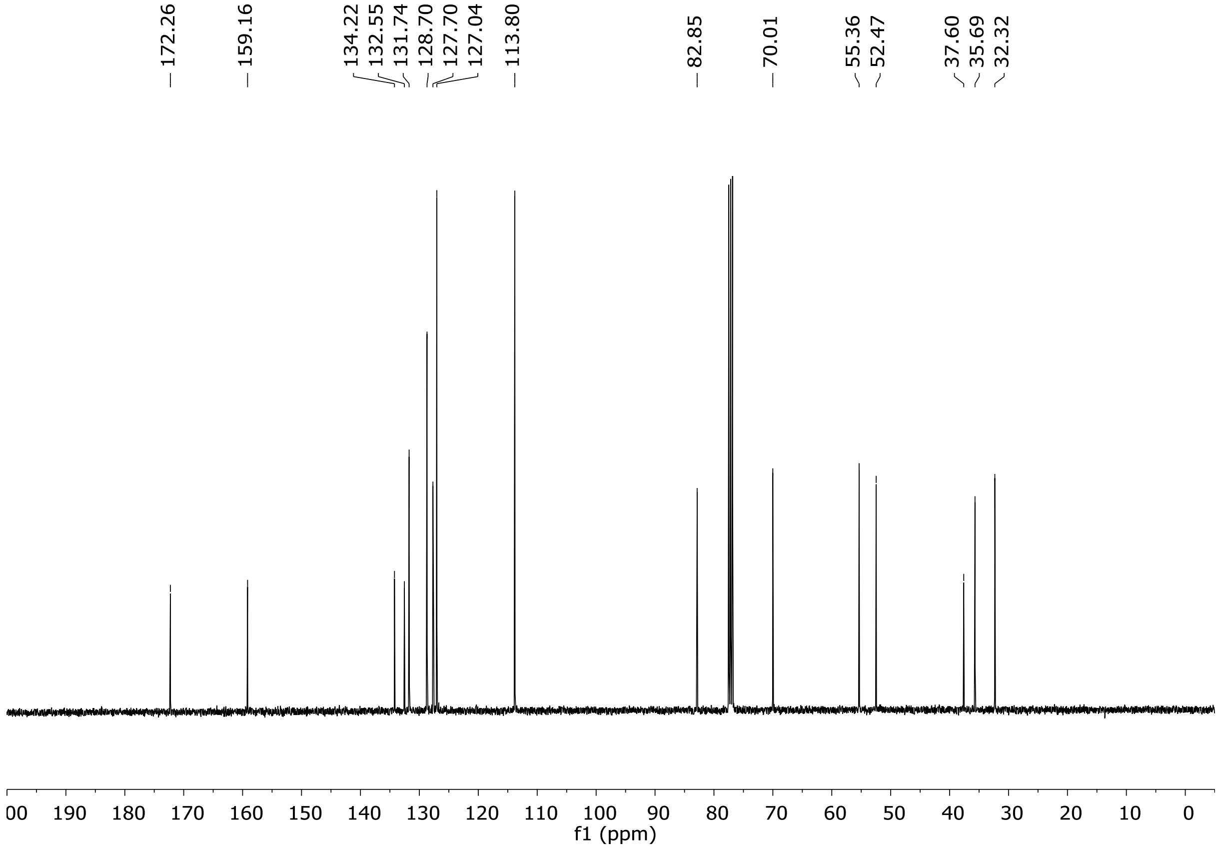
7.02
7.00
6.79
6.77
4.74
4.72
3.75
3.60
3.57
3.55
3.53
2.75
2.74
2.72
2.34
2.32
2.30
2.28
2.19
2.18
2.17
2.16
2.14
2.14
2.12
1l
H
CO2Me
H
O
MeO
5.10
2.01
2.02
1.00
3.00
3.01
1.06
1.00
1.01
1.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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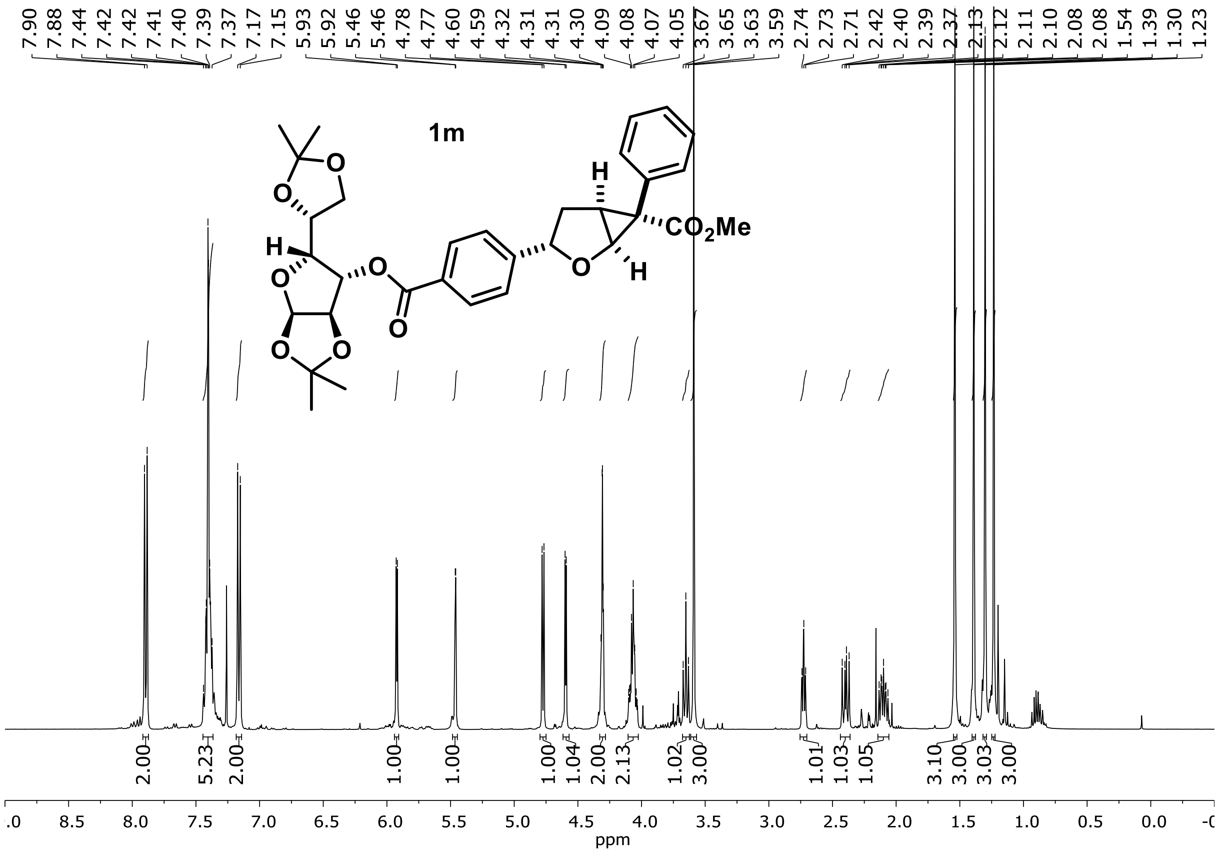
131.74
128.70
127.70
127.04
113.80
82.85
70.01
55.36
52.47
37.60
35.69
32.32
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.42
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7.39
7.37
7.17
7.15
5.93
5.92
5.46
5.46
4.78
4.77
4.60
4.59
4.32
4.31
4.31
4.30
4.09
4.08
4.07
4.05
3.67
3.65
3.63
3.59
2.74
2.73
2.71
2.42
2.40
2.39
2.37
2.13
2.12
2.11
2.10
2.08
1.54
1.39
1.30
1.23
1m
H
H
CO2Me
O
O
O
H
O
O
O
O
O
2.00
5.23
2.00
1.00
1.00
1.00
1.04
2.00
2.13
1.02
3.00
1.01
1.03
1.05
3.10
3.00
3.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
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1.5
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0.5
0.0
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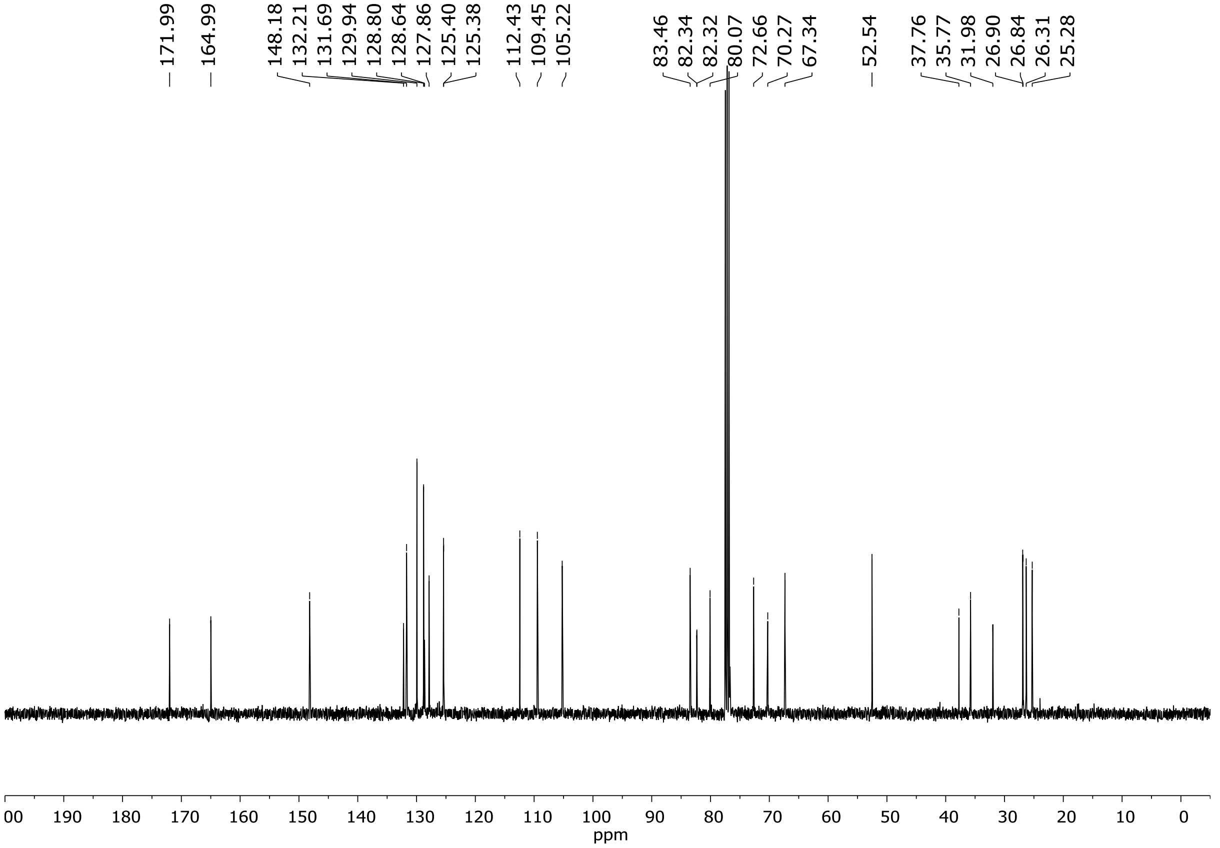
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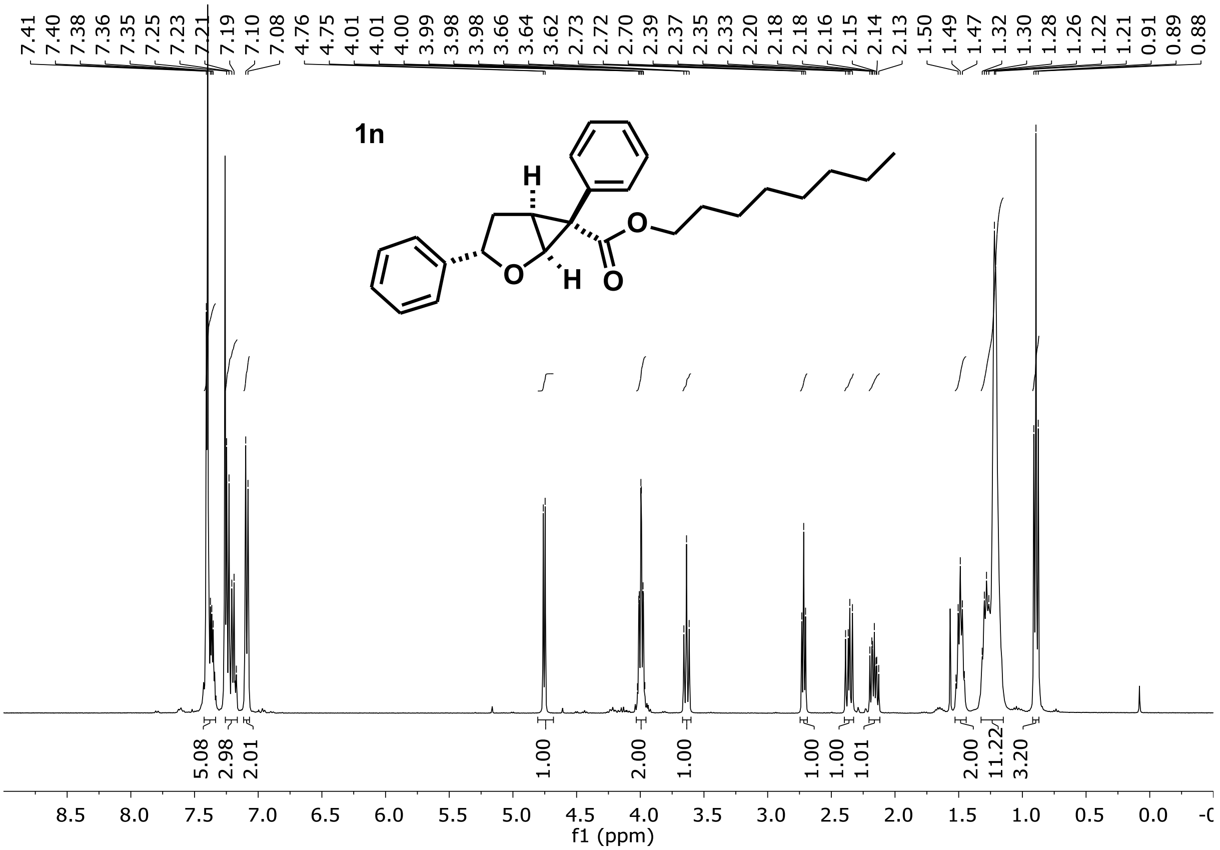
125.38
112.43
109.45
105.22
83.46
82.34
82.32
80.07
72.66
70.27
67.34
52.54
37.76
35.77
31.98
26.90
26.84
26.31
25.28
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.40
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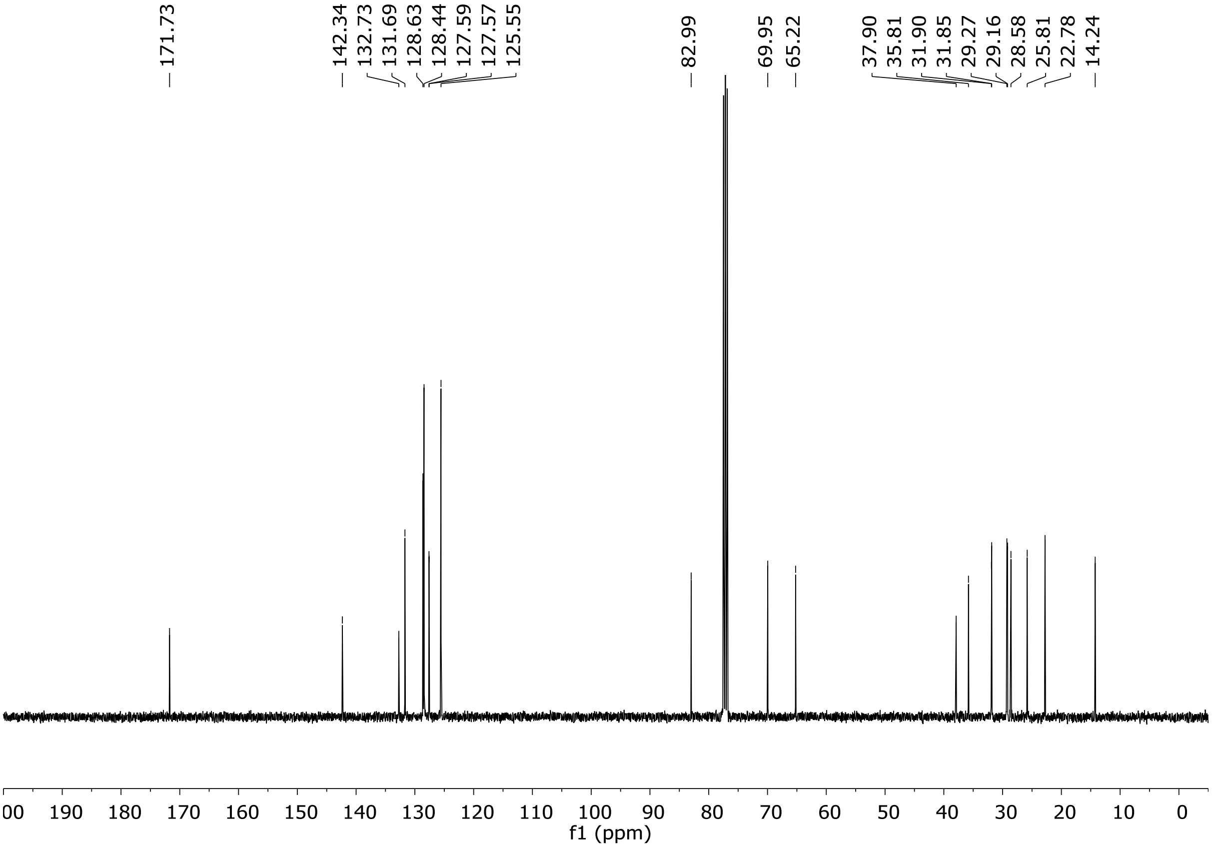
7.36
7.35
7.25
7.23
7.21
7.19
7.10
7.08
4.76
4.75
4.01
4.01
4.00
3.99
3.98
3.98
3.66
3.64
3.62
2.73
2.72
2.70
2.39
2.37
2.35
2.33
2.20
2.18
2.18
2.16
2.15
2.14
2.13
1.50
1.49
1.47
1.32
1.30
1.28
1.26
1.22
1.21
0.91
0.89
0.88
1n
H
O
H
O
O
5.08
2.98
2.01
1.00
2.00
1.00
1.00
1.00
1.01
2.00
11.22
3.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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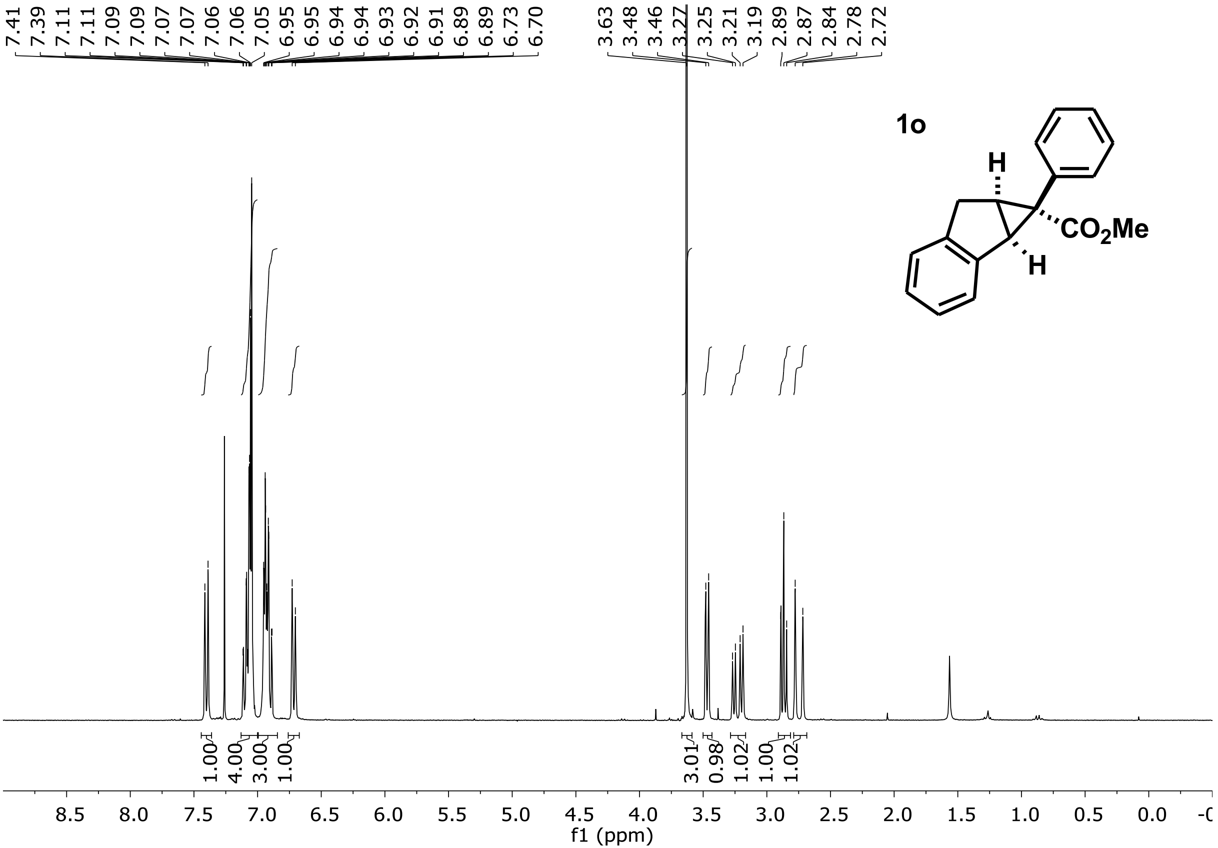
142.34
132.73
131.69
128.63
128.44
127.59
127.57
125.55
82.99
69.95
65.22
37.90
35.81
31.90
31.85
29.27
29.16
28.58
25.81
22.78
14.24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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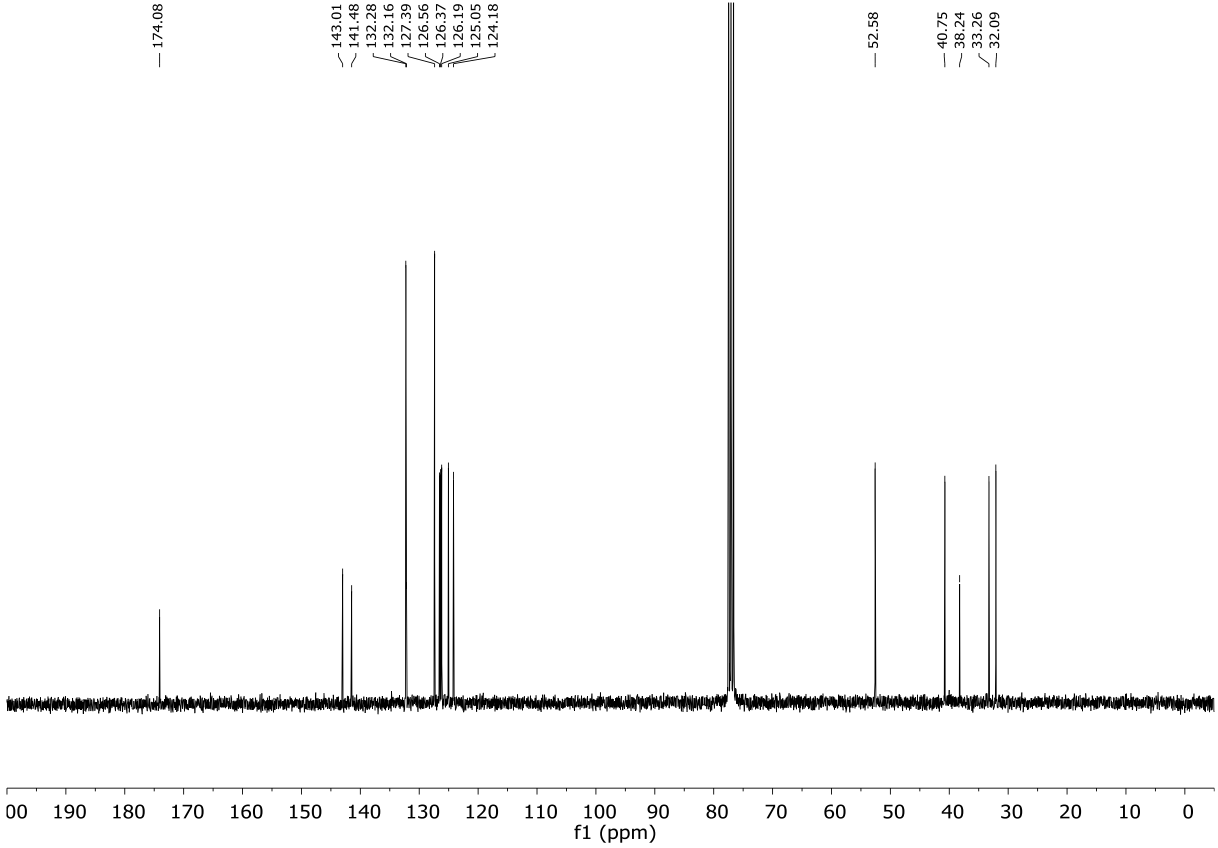
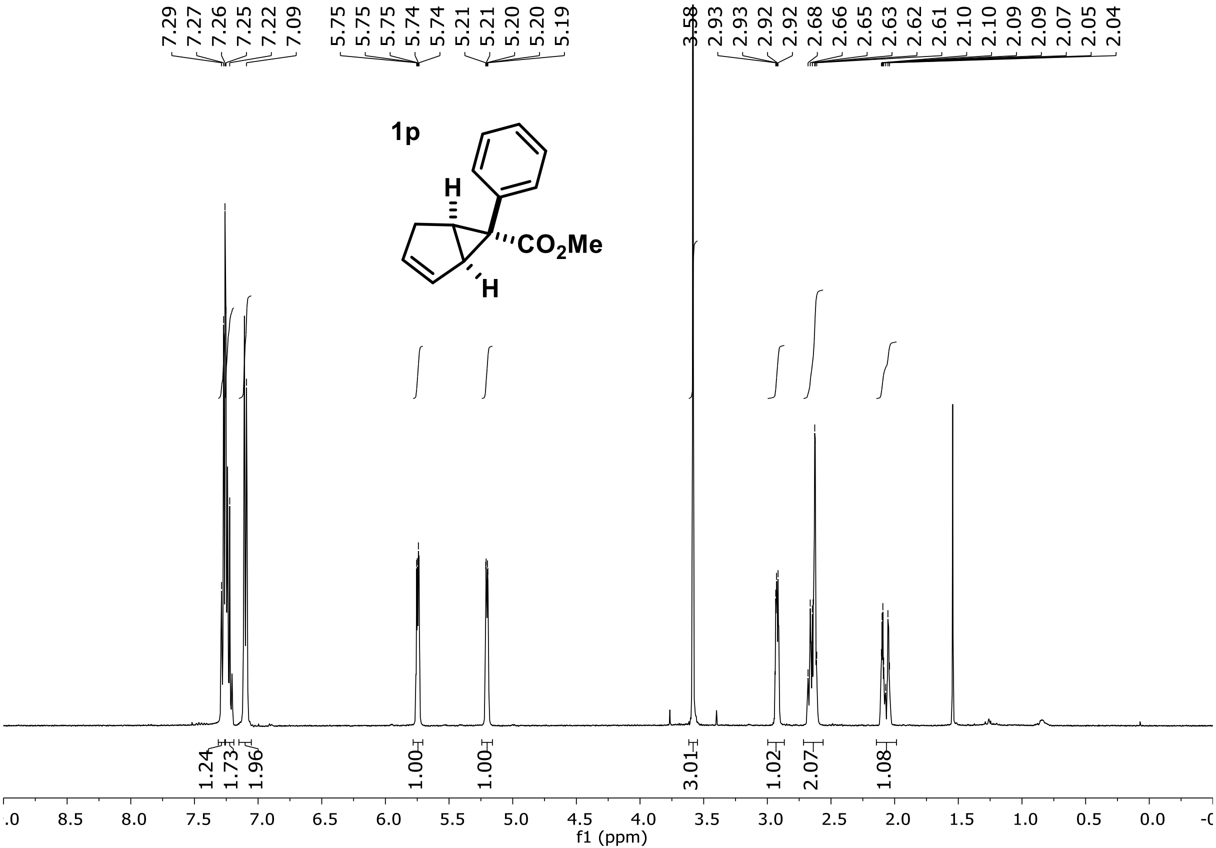
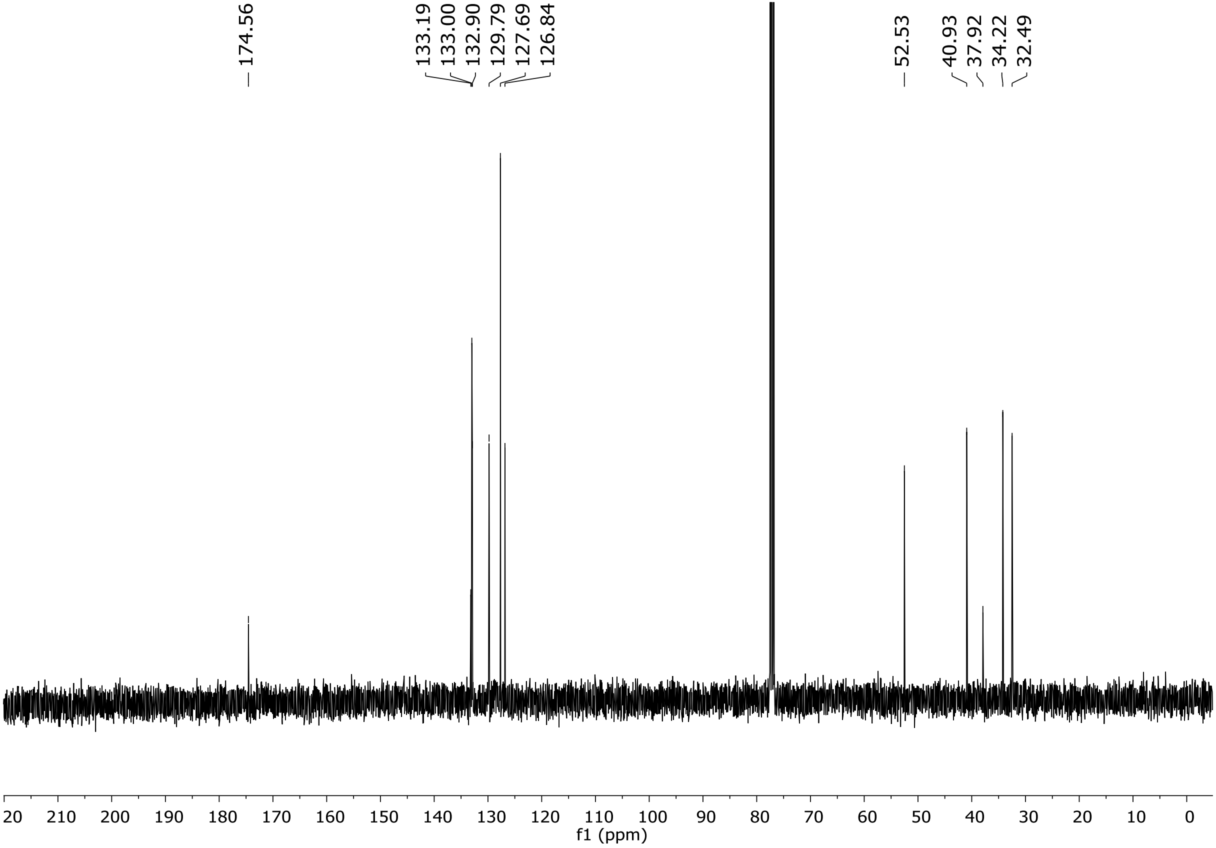
7.39
7.11
7.11
7.09
7.09
7.07
7.07
7.06
7.06
7.05
6.95
6.95
6.94
6.94
6.93
6.92
6.91
6.89
6.89
6.73
6.70
3.63
3.48
3.46
3.27
3.25
3.21
3.19
2.89
2.87
2.84
2.78
2.72
1o
H
H
CO$_2$Me
1.00
4.00
3.00
1.00
3.01
0.98
1.02
1.00
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


174.08
143.01
141.48
132.28
132.16
127.39
126.56
126.37
126.19
125.05
124.18
52.58
40.75
38.24
33.26
32.09
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1p

7.29
7.27
7.26
7.25
7.22
7.09
5.75
5.75
5.75
5.74
5.74
5.21
5.21
5.20
5.20
5.19
3.58
2.93
2.93
2.92
2.92
2.68
2.66
2.65
2.63
2.62
2.61
2.10
2.10
2.09
2.09
2.07
2.05
2.04
H
CO2Me
H
1.24
1.73
1.96
1.00
1.00
3.01
1.02
2.07
1.08
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)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133.19
133.00
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129.79
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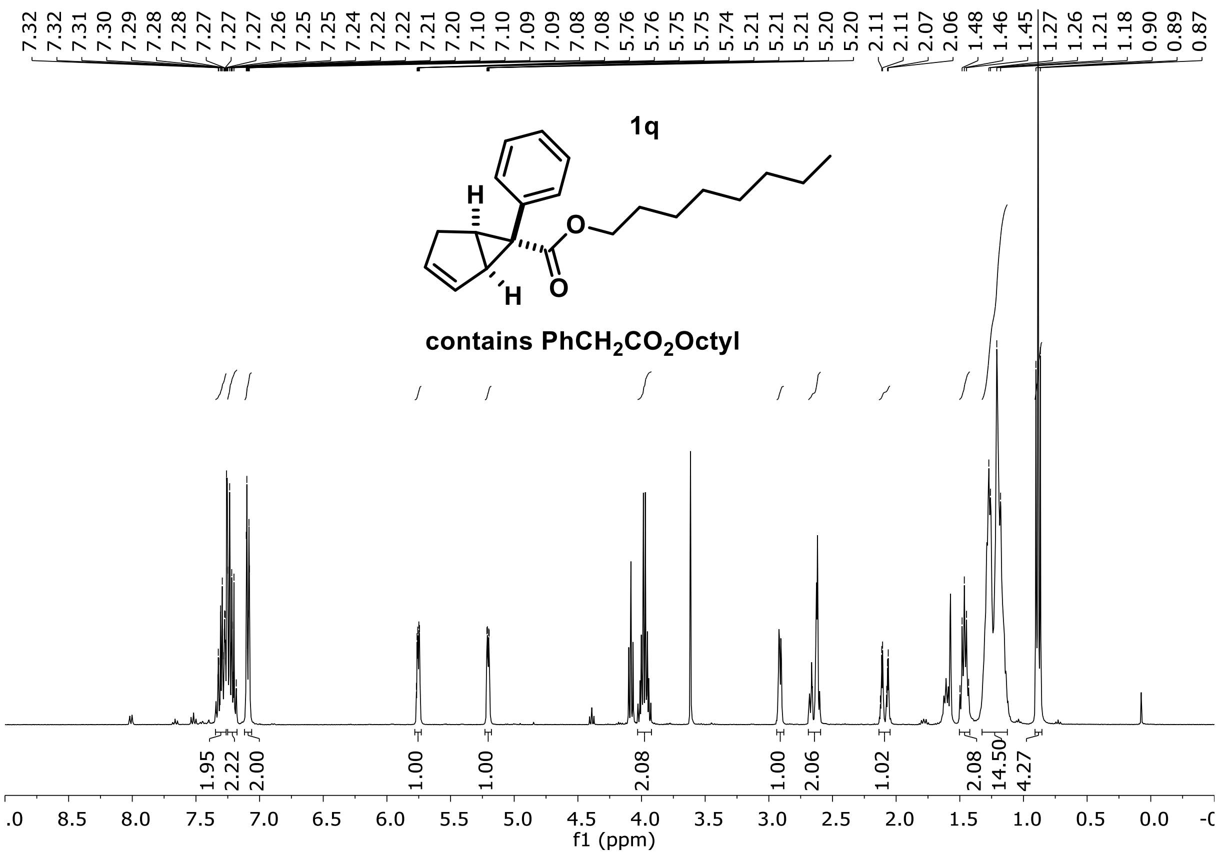
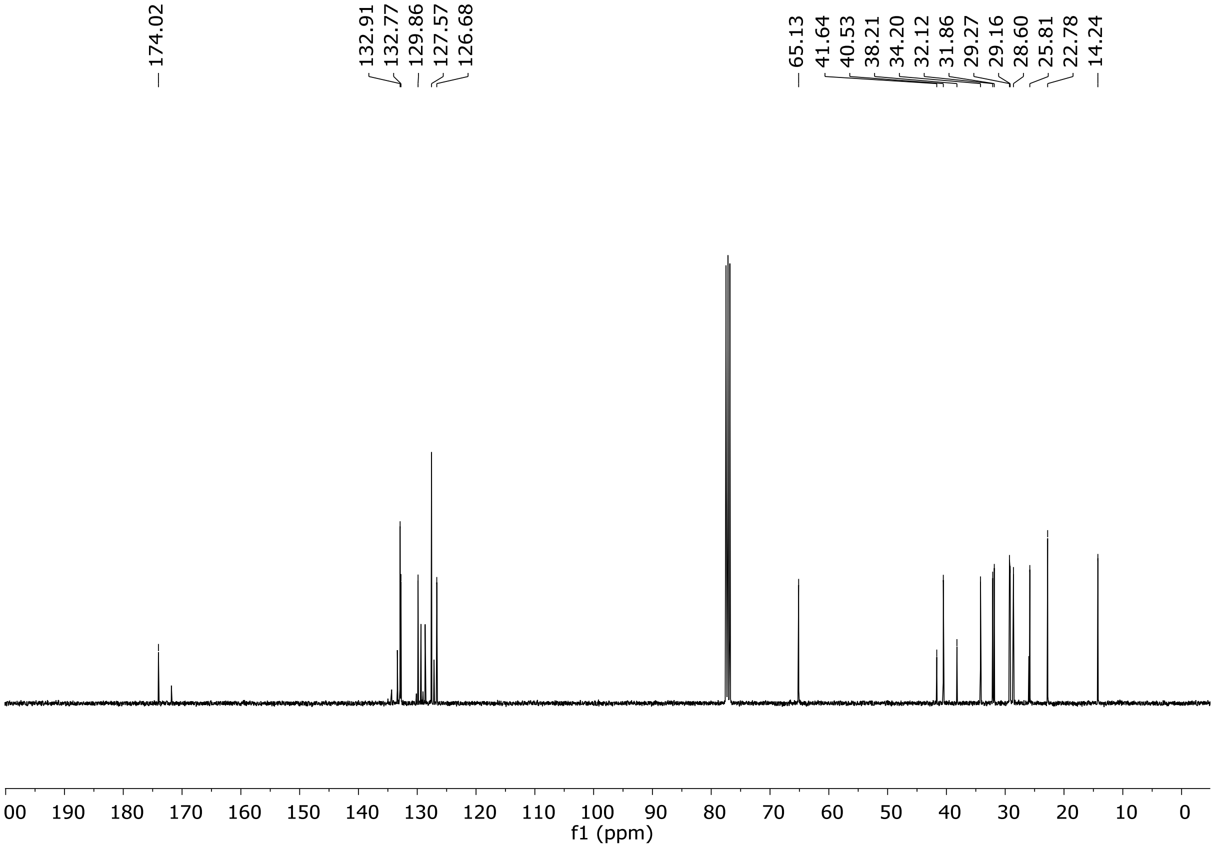
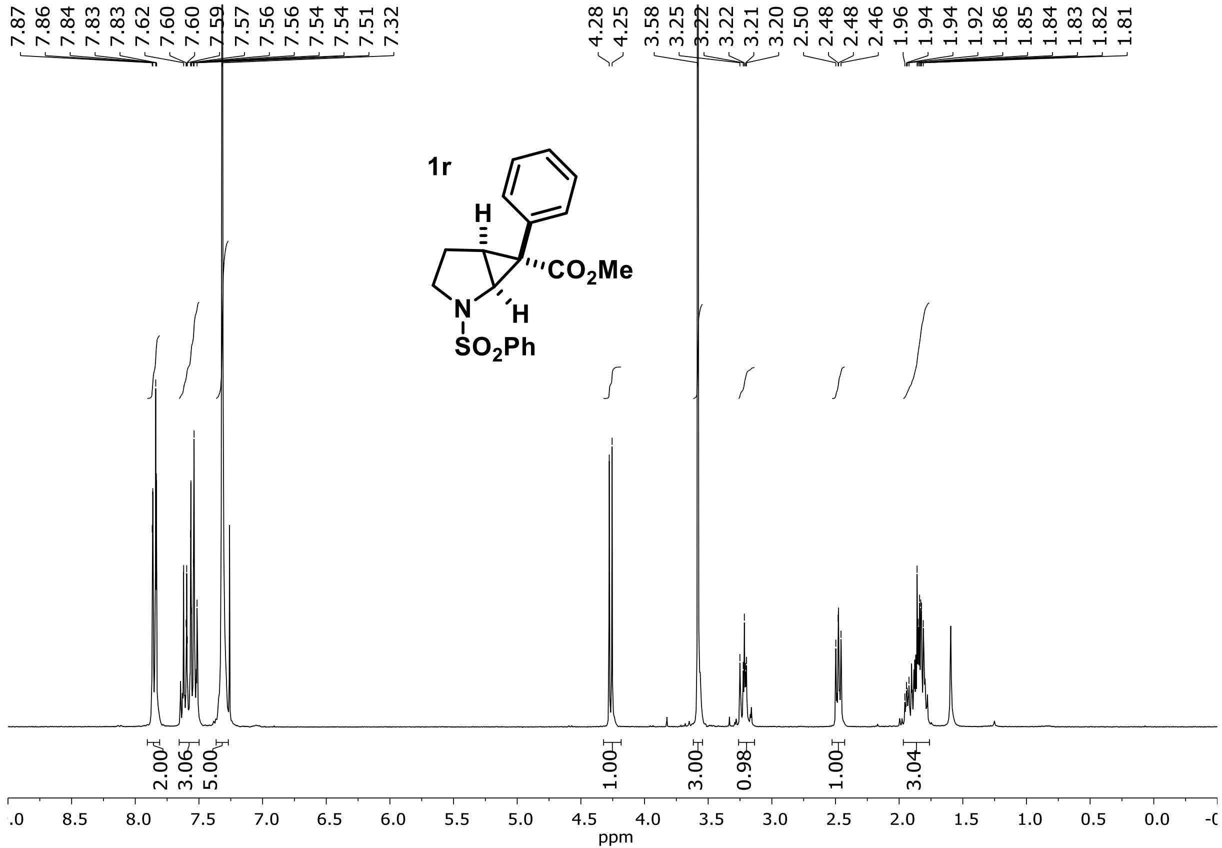
126.84
52.53
40.93
37.92
34.22
32.49
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1q

contains $PhCH_2CO_2Octyl$

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7.84
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7.83
7.62
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7.60
7.59
7.57
7.56
7.56
7.54
7.54
7.51
7.32
4.28
4.25
3.58
3.25
3.22
3.22
3.21
3.20
2.50
2.48
2.48
2.46
1.96
1.94
1.94
1.92
1.86
1.85
1.84
1.83
1.82
1.81
1r
H
CO2Me
N
H
SO2Ph
2.00
3.06
5.00
1.00
3.00
0.98
1.00
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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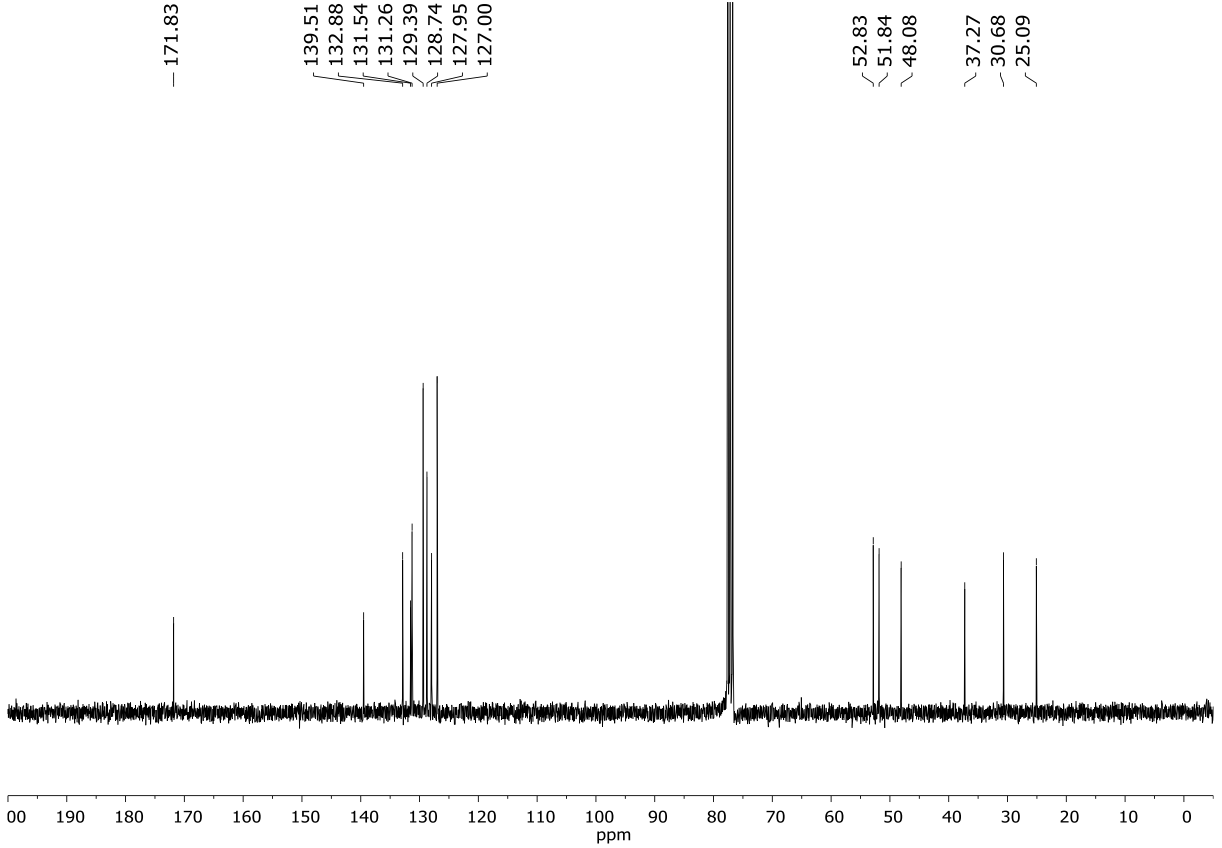
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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127.95
127.00
52.83
51.84
48.08
37.27
30.68
25.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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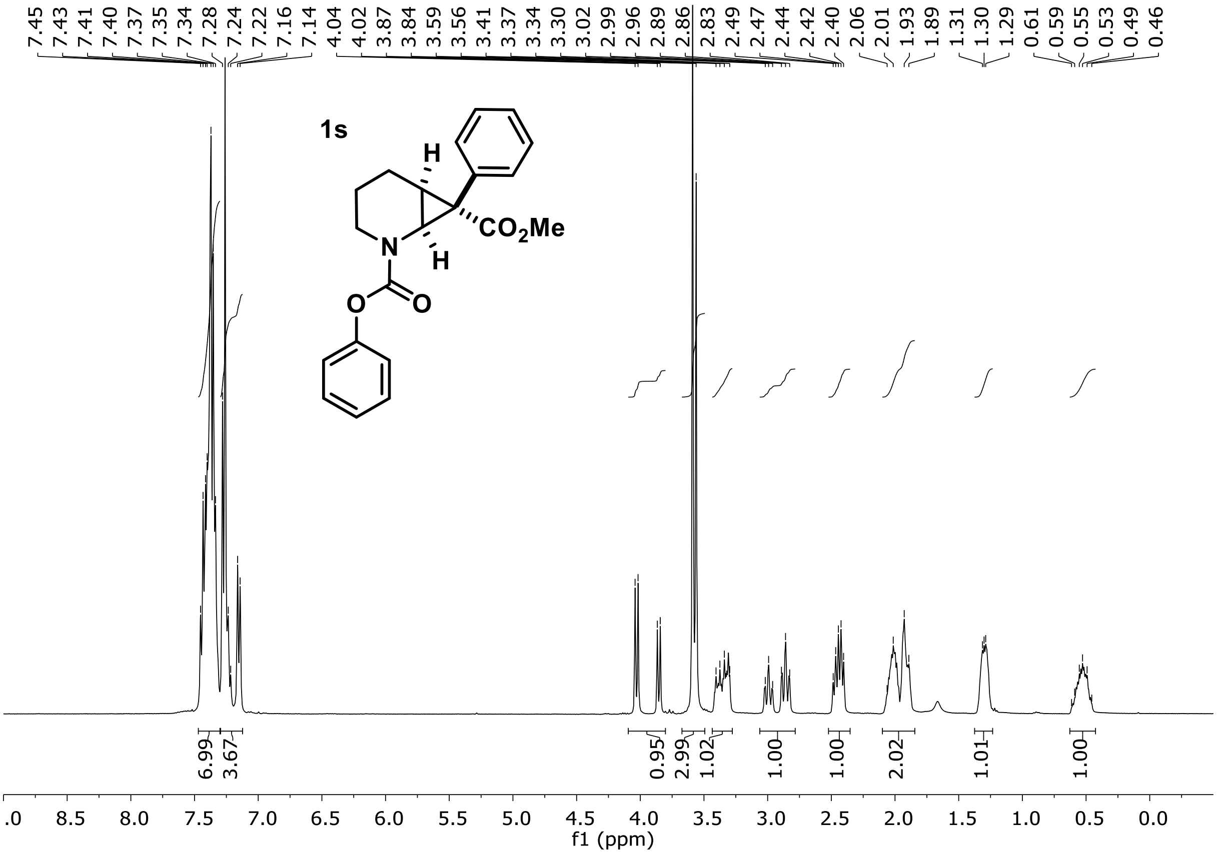
30
20
10
0
ppm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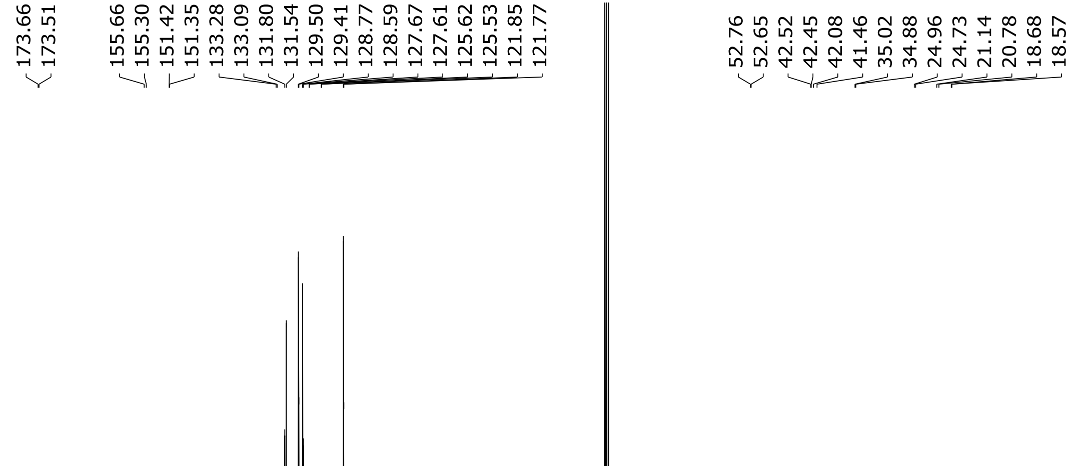
7.34
7.28
7.24
7.22
7.16
7.14
4.04
4.02
3.87
3.84
3.59
3.56
3.41
3.37
3.34
3.30
3.02
2.99
2.96
2.89
2.86
2.83
2.49
2.47
2.44
2.42
2.40
2.06
2.01
1.93
1.89
1.31
1.30
1.29
0.61
0.59
0.55
0.53
0.49
0.46
1s
H
H
N
O
O
CO$_2$Me
6.99
3.67
0.95
2.99
1.02
1.00
1.00
2.02
1.01
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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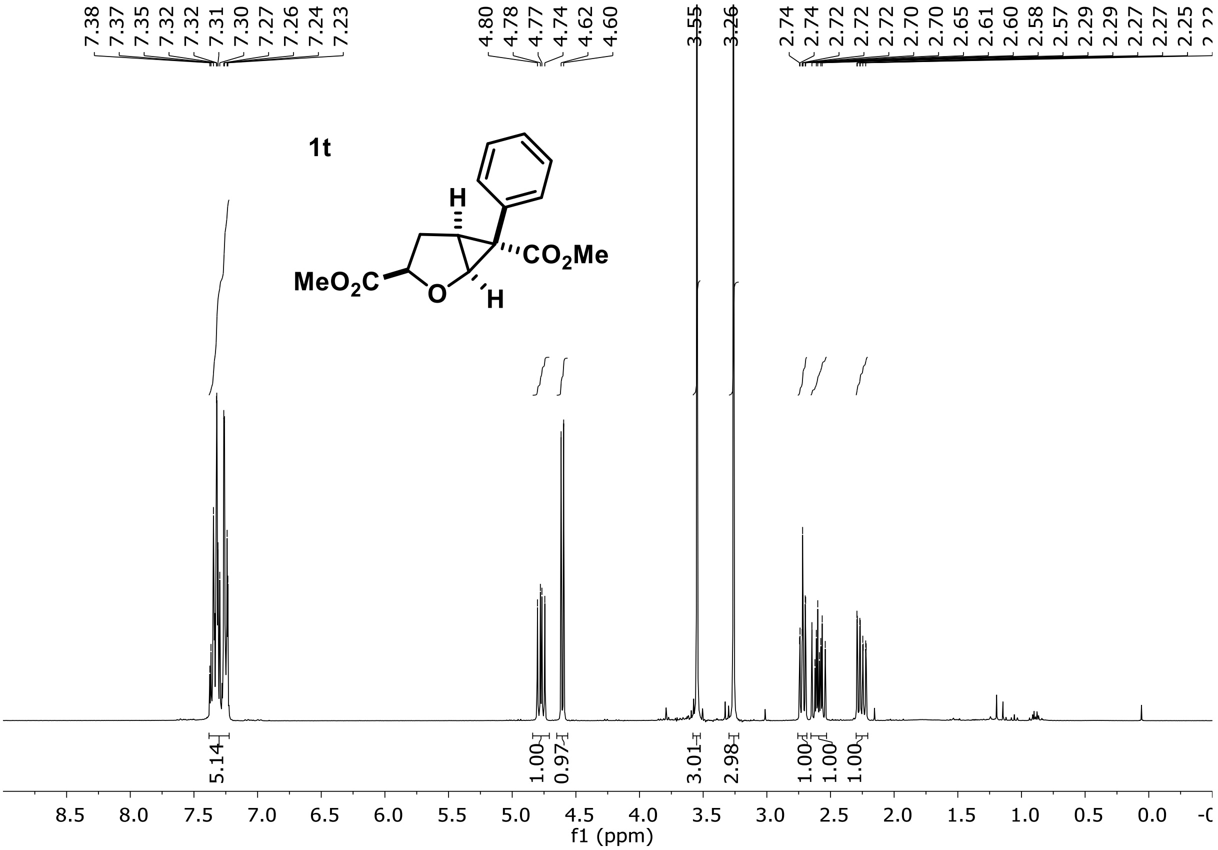
173.51
155.66
155.30
151.42
151.35
133.28
133.09
131.80
131.54
129.50
129.41
128.77
128.59
127.67
127.61
125.62
125.53
121.85
121.77
52.76
52.65
42.52
42.45
42.08
41.46
35.02
34.88
24.96
24.73
21.14
20.78
18.68
18.57
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.38
7.37
7.35
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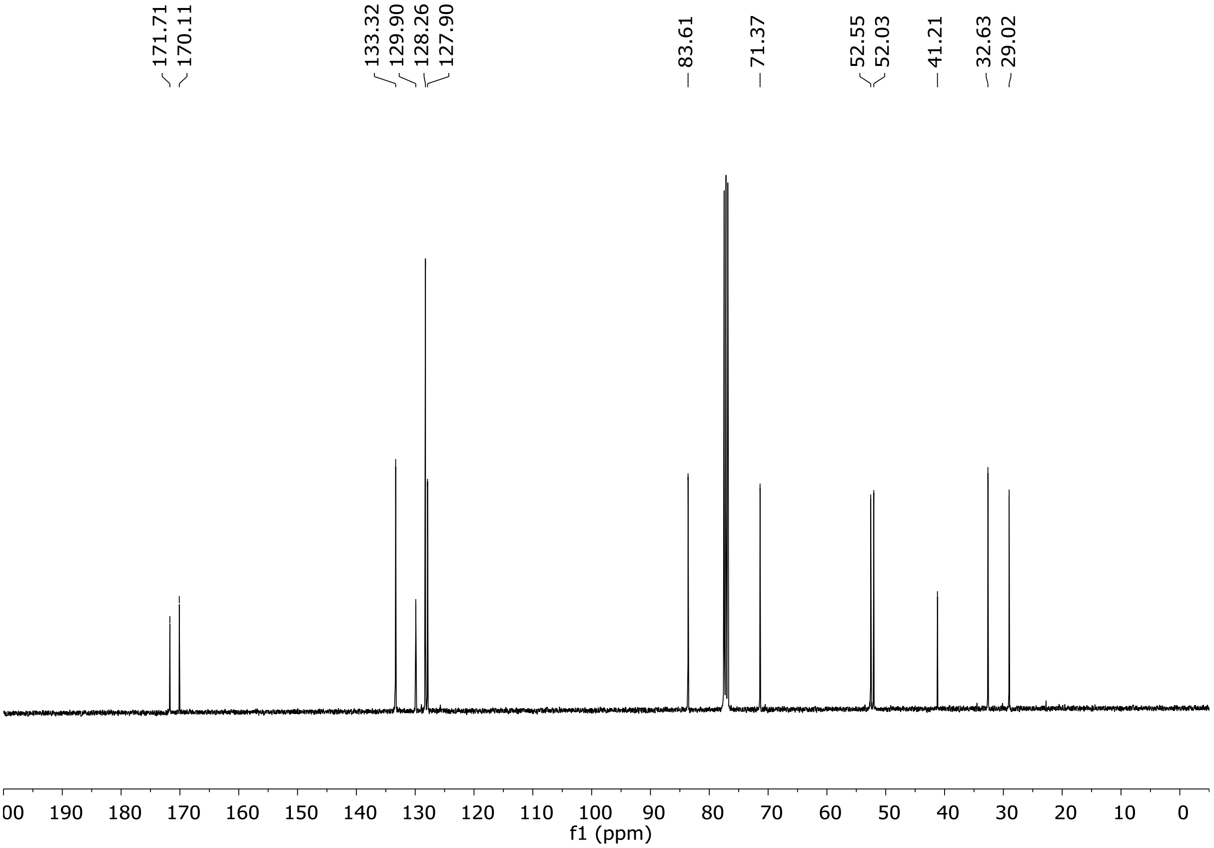
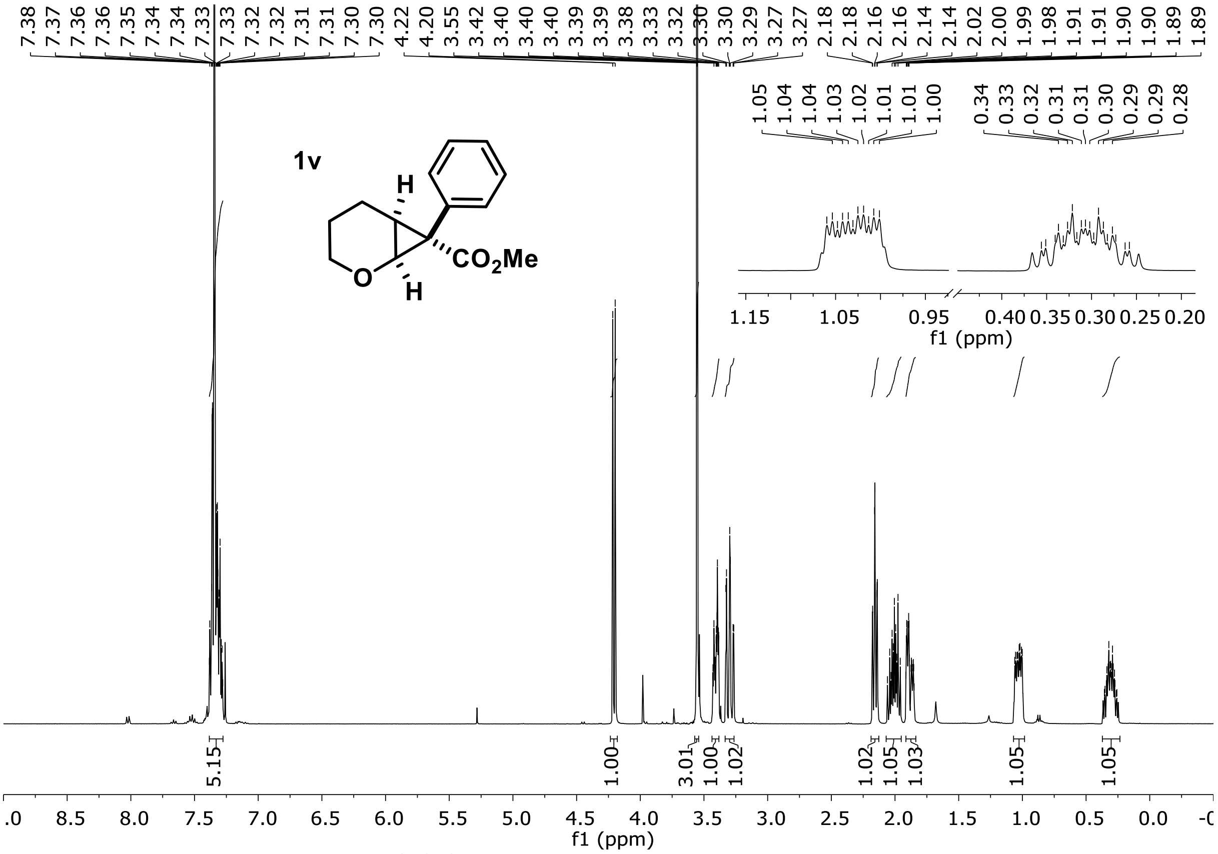
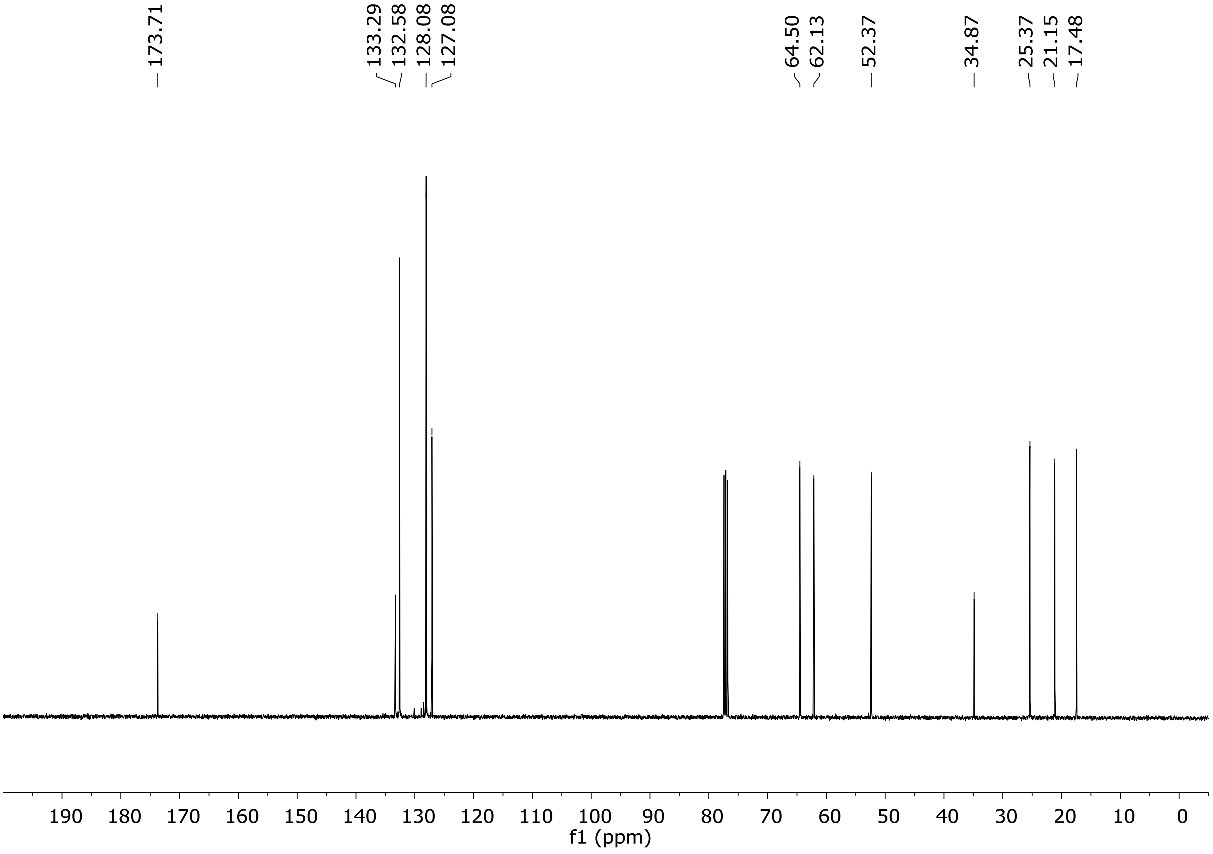
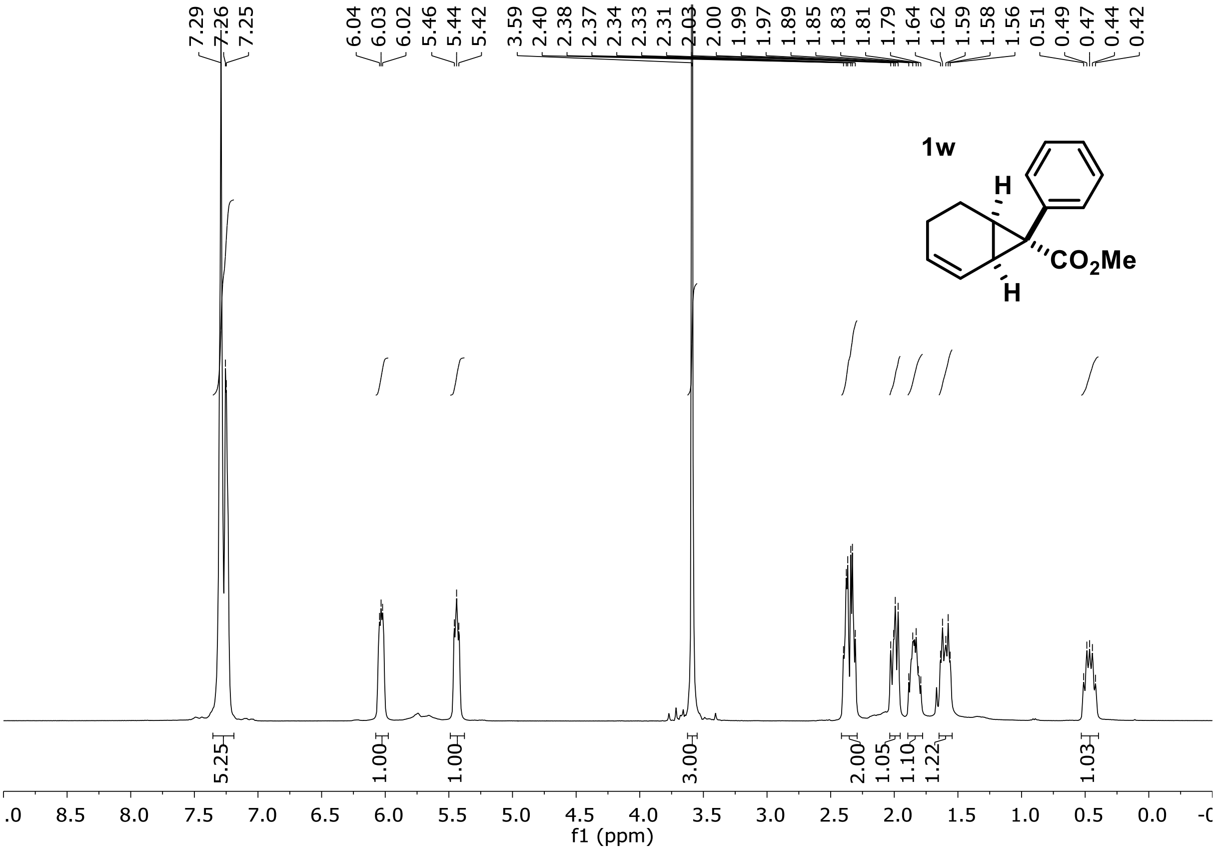
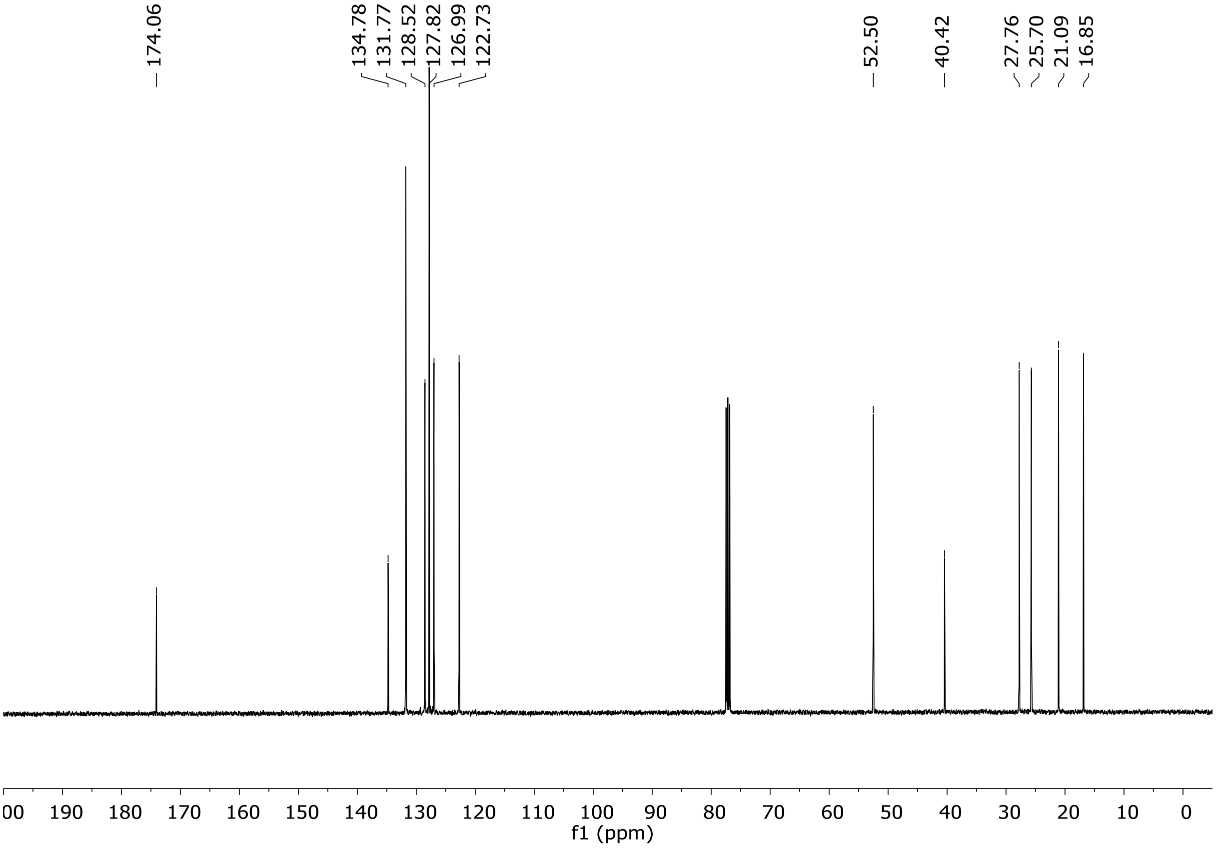
7.32
7.31
7.30
7.27
7.26
7.24
7.23
4.80
4.78
4.77
4.74
4.62
4.60
3.55
3.26
2.74
2.74
2.72
2.72
2.72
2.70
2.70
2.65
2.61
2.60
2.58
2.57
2.29
2.29
2.27
2.27
2.25
1t
H
CO2Me
MeO2C
O
H
5.14
1.00
0.97
3.01
2.98
1.00
1.00
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

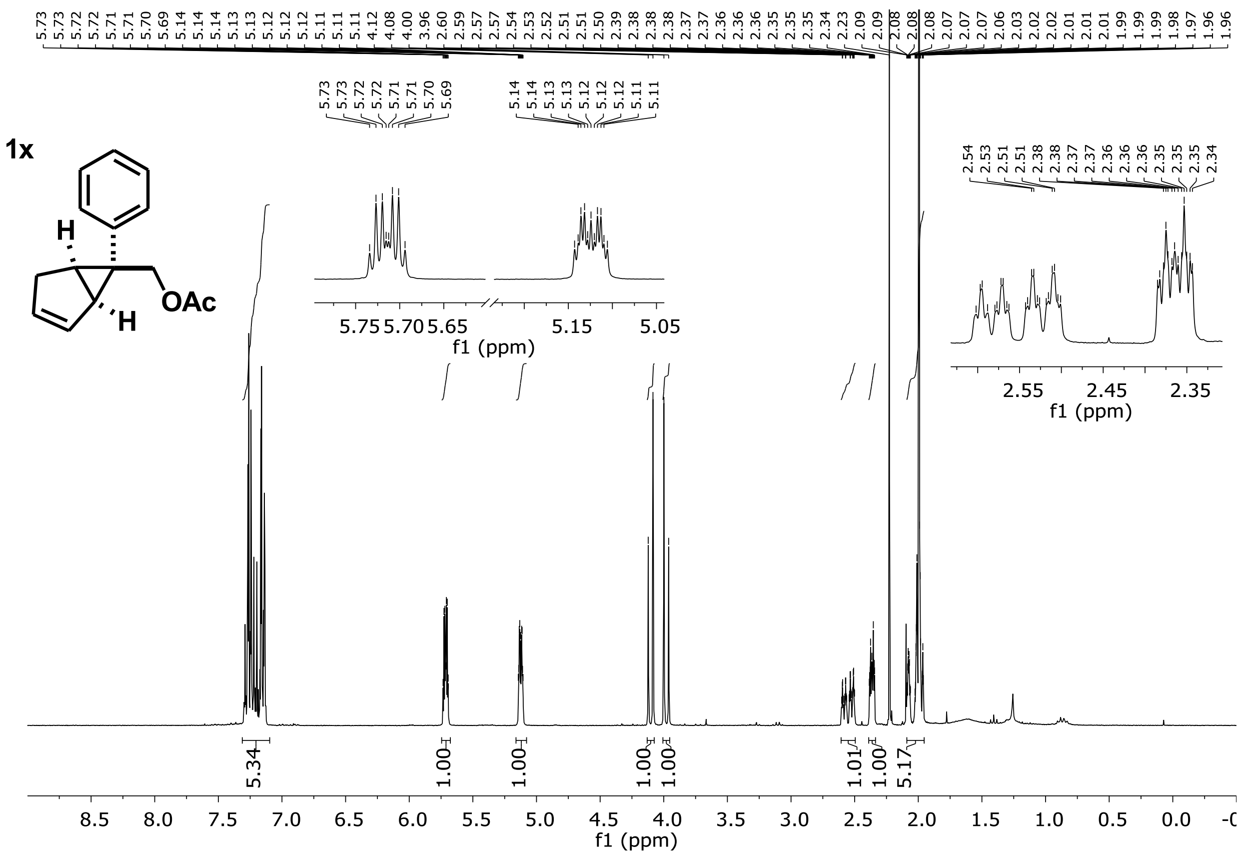

171.71
170.11
133.32
129.90
128.26
127.90
83.61
71.37
52.55
52.03
41.21
32.63
29.02
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

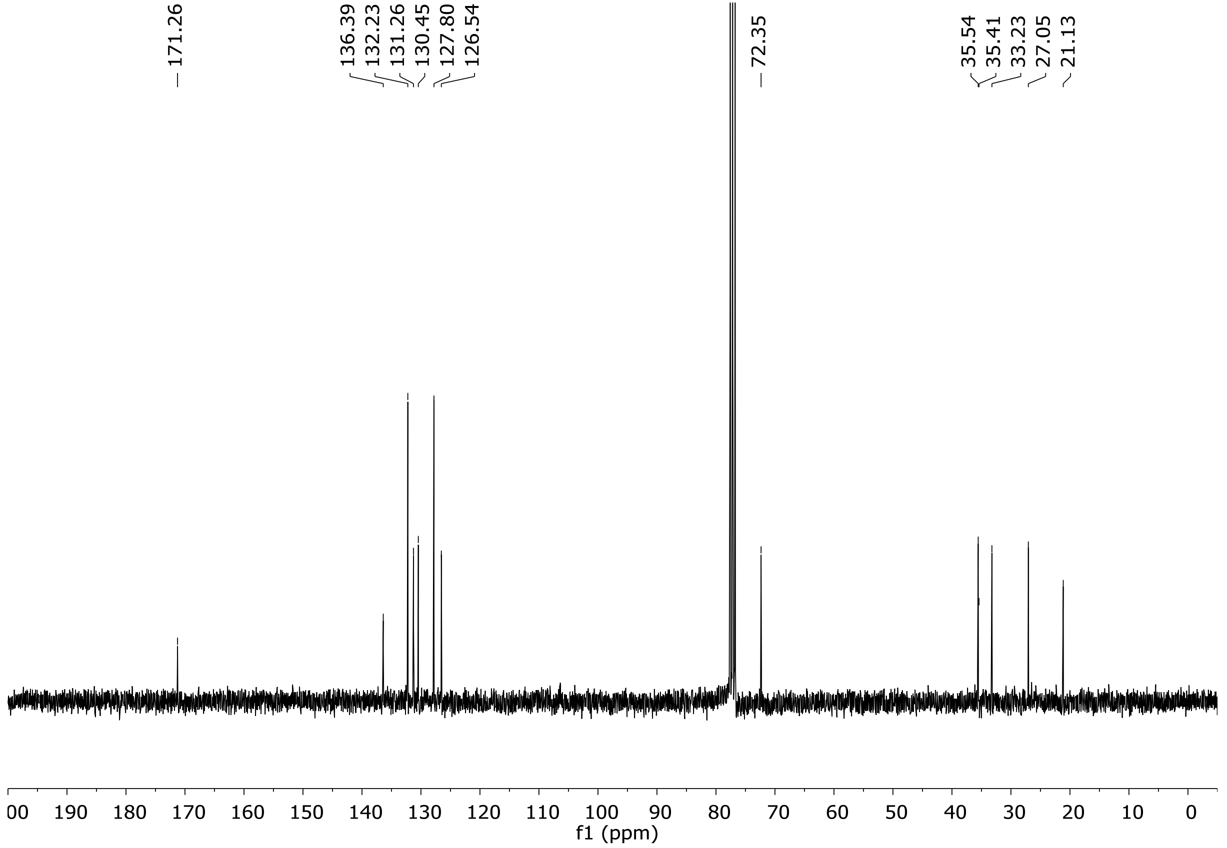

7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 4.22 4.20 3.55 3.42 3.40 3.40 3.40 3.39 3.39 3.38 3.33 3.32 3.30 3.30 3.29 3.27 3.27 2.18 2.18 2.16 2.16 2.14 2.14 2.02 2.00 1.99 1.98 1.91 1.91 1.90 1.90 1.89 1.89
1.05 1.04 1.04 1.03 1.02 1.01 1.01 1.00
0.34 0.33 0.32 0.31 0.31 0.30 0.29 0.29 0.28
1v
H
CO2Me
O
H
1.15 1.05 0.95 0.40 0.35 0.30 0.25 0.20
f1 (ppm)
5.15
1.00
3.01
1.00
1.02
1.02
1.05
1.03
1.05
1.05
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)


173.71
133.29 132.58 128.08 127.08
64.50 62.13
52.37
34.87
25.37 21.15 17.48
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

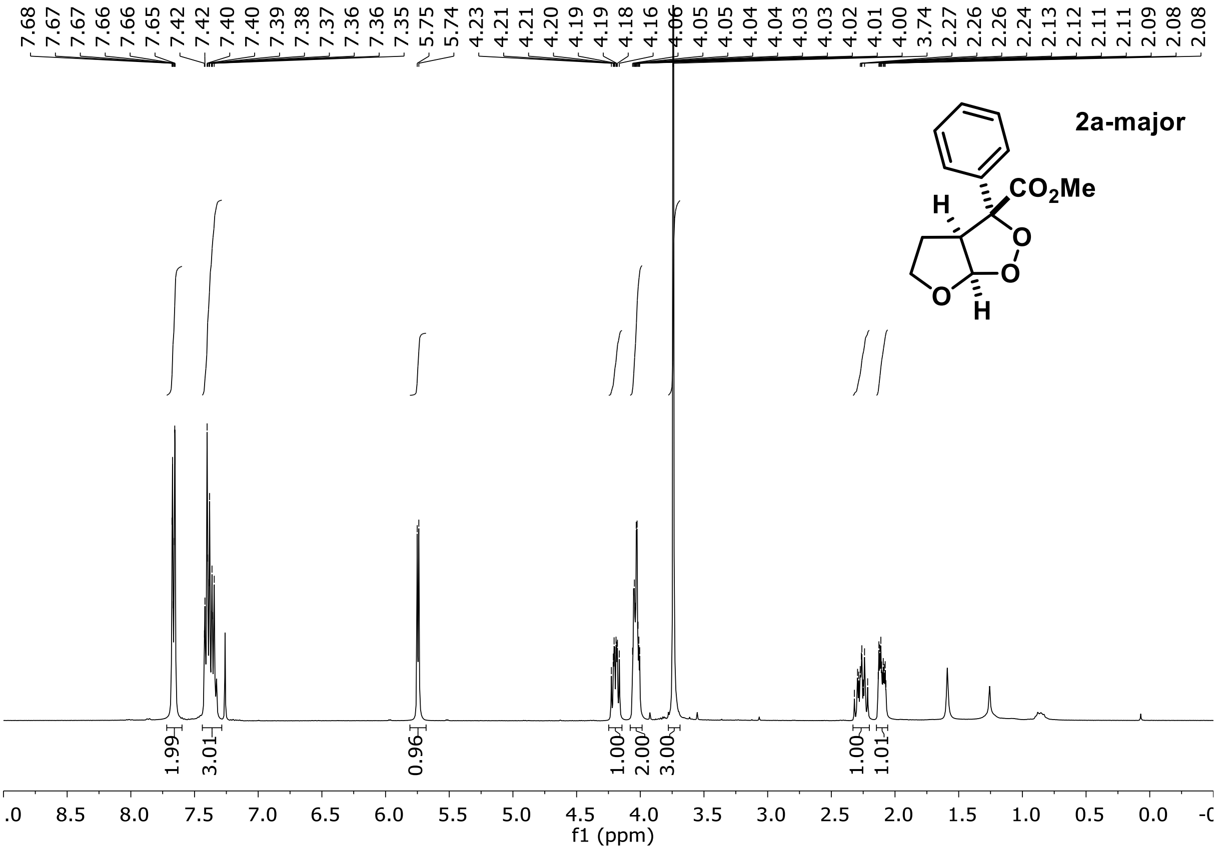

7.29
7.26
7.25
6.04
6.03
6.02
5.46
5.44
5.42
3.59
2.40
2.38
2.37
2.34
2.33
2.31
2.03
2.00
1.99
1.97
1.89
1.85
1.83
1.81
1.79
1.64
1.62
1.59
1.58
1.56
0.51
0.49
0.47
0.44
0.42
1w
H
H
CO$_2$Me
5.25
1.00
1.00
3.00
2.00
1.05
1.10
1.22
1.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

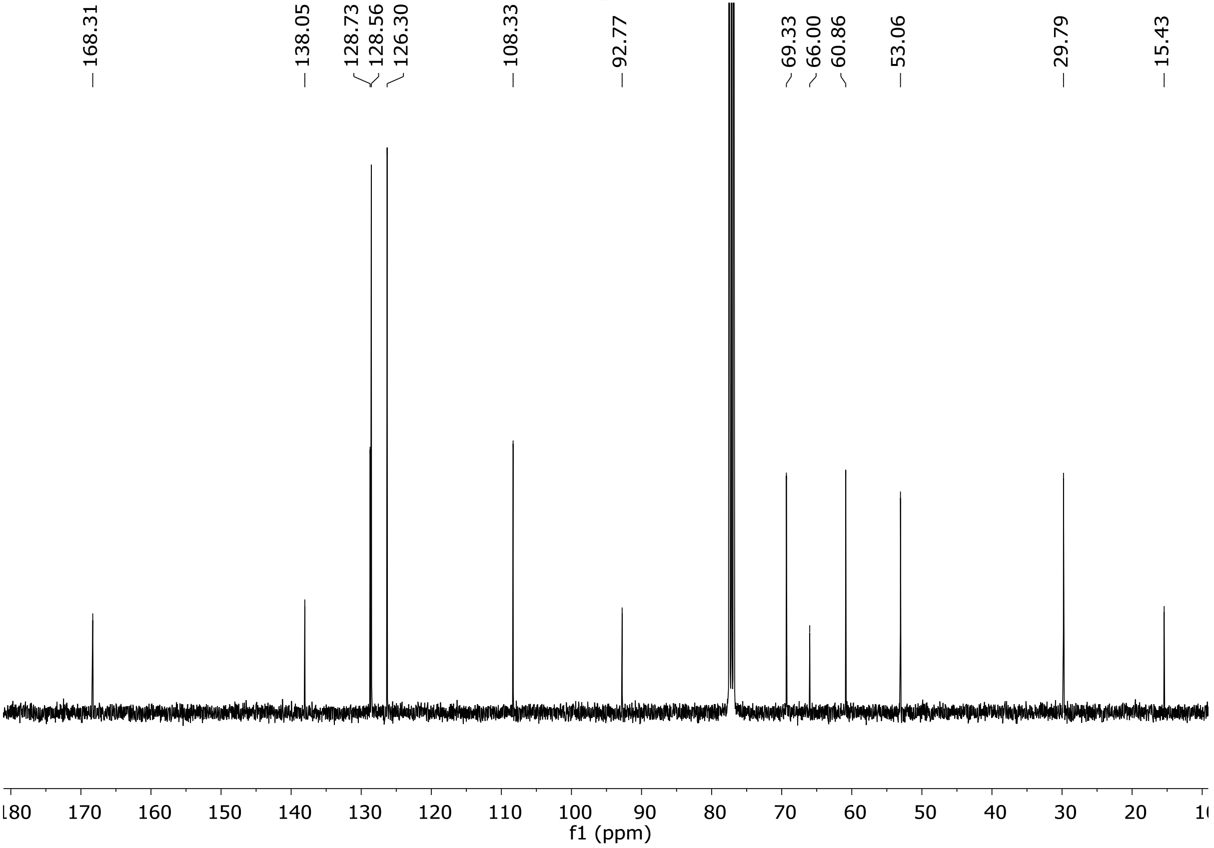

174.06
134.78
131.77
128.52
127.82
126.99
122.73
52.50
40.42
27.76
25.70
21.09
16.85
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

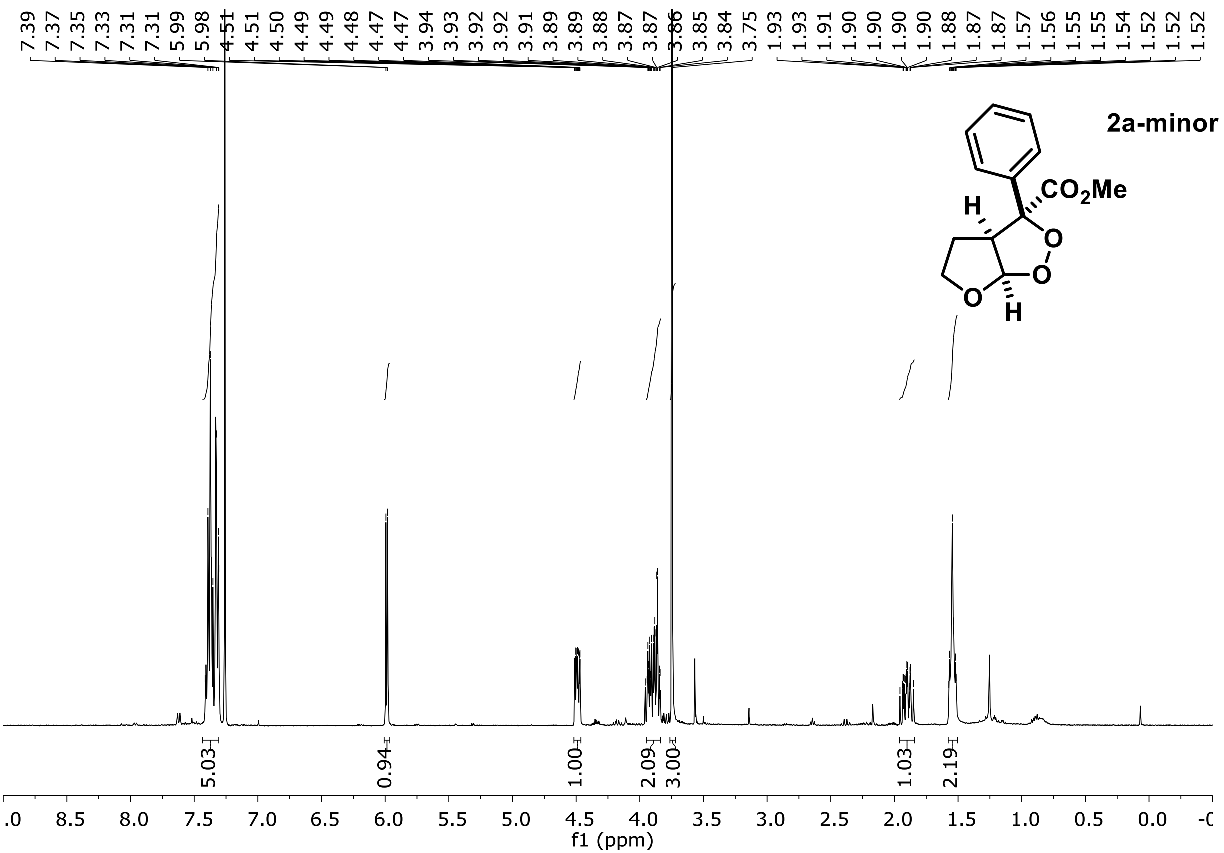

1x
H
H
OAc
5.73 5.73 5.72 5.72 5.71 5.71 5.70 5.69 5.14 5.14 5.14 5.13 5.13 5.12 5.12 5.12 5.11 5.11 5.11 4.12 4.08 4.00 3.96 2.60 2.59 2.57 2.57 2.54 2.53 2.52 2.51 2.51 2.50 2.39 2.38 2.38 2.38 2.37 2.37 2.36 2.36 2.36 2.35 2.35 2.34 2.23 2.09 2.09 2.08 2.08 2.08 2.07 2.07 2.06 2.03 2.02 2.02 2.01 2.01 1.99 1.99 1.99 1.98 1.97 1.96 1.96
5.73 5.73 5.72 5.72 5.71 5.71 5.70 5.69
5.14 5.14 5.13 5.13 5.12 5.12 5.12 5.11 5.11
5.75 5.70 5.65
5.15
5.05
f1 (ppm)
2.54 2.53 2.51 2.51 2.38 2.38 2.37 2.37 2.36 2.36 2.36 2.35 2.35 2.35 2.34
2.55
2.45
2.35
f1 (ppm)
5.34
1.00
1.00
1.00
1.00
1.01
1.00
5.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.26
136.39
132.23
131.26
130.45
127.80
126.54
72.35
35.54
35.41
33.23
27.05
21.13
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Peroxides 2

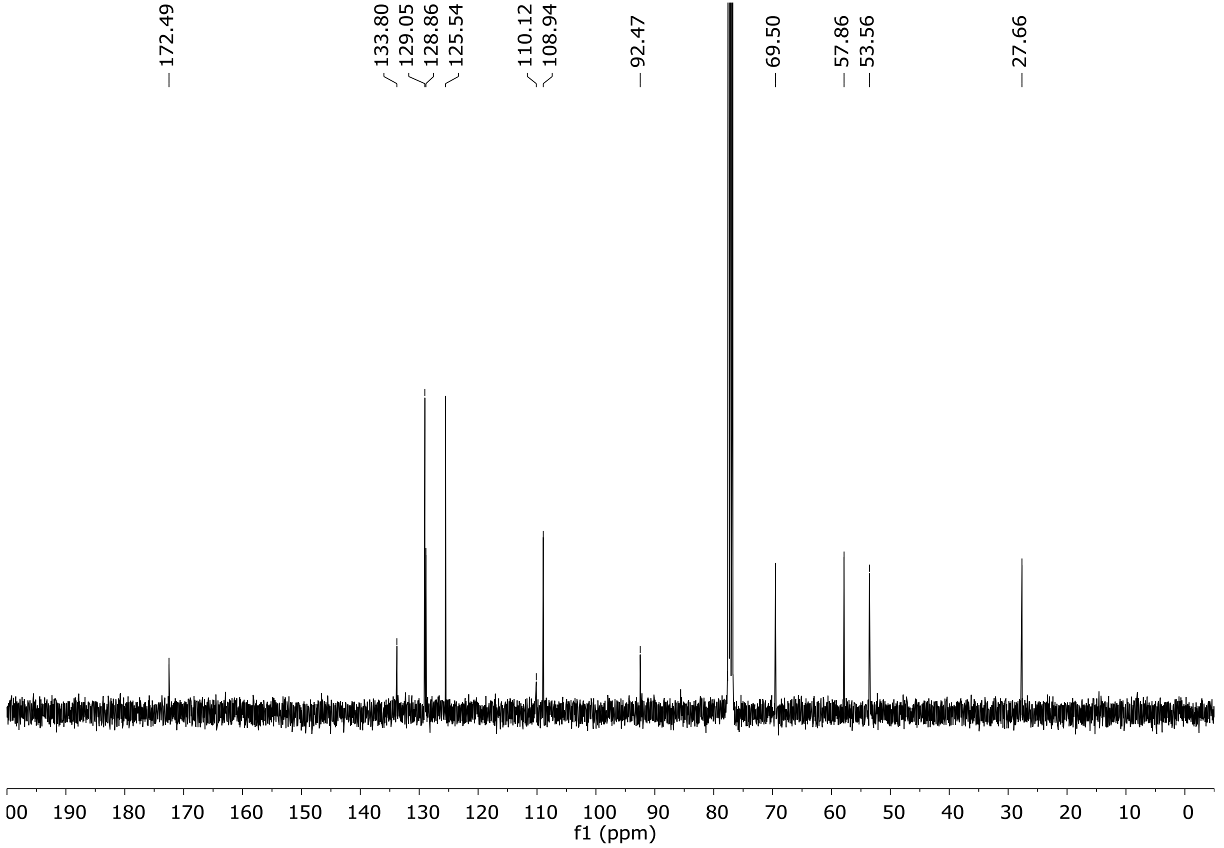

2a-major



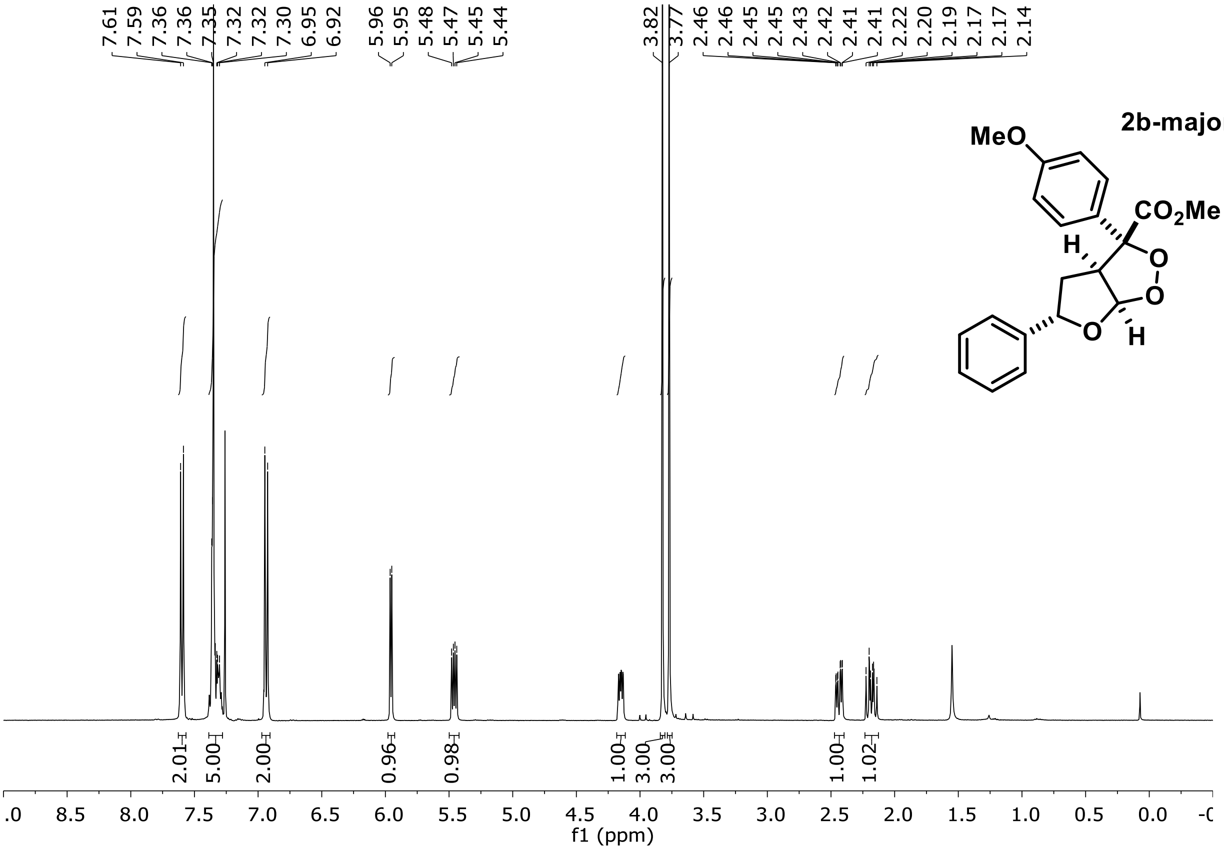


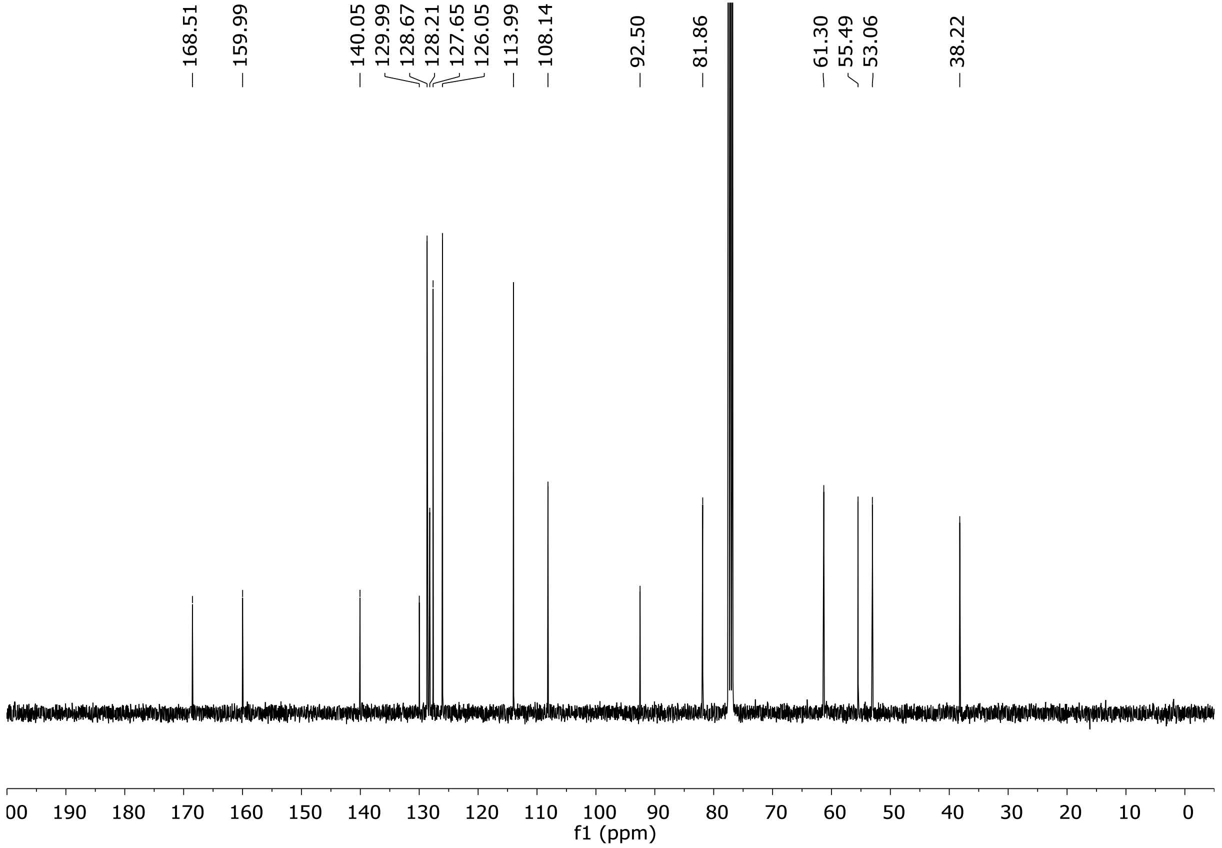
2a-minor

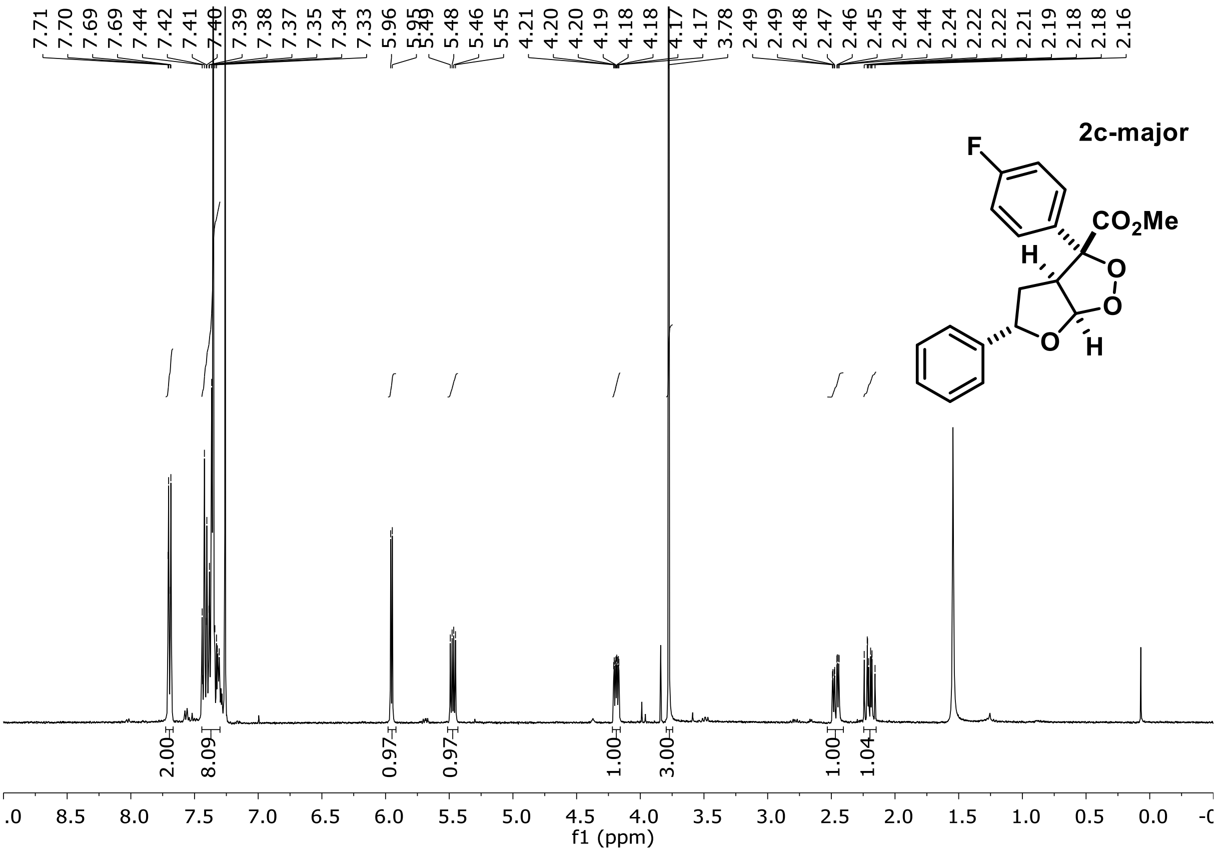
7.39
7.37
7.35
7.33
7.31
7.31
5.99
5.98
4.51
4.51
4.50
4.49
4.49
4.48
4.47
4.47
3.94
3.93
3.92
3.92
3.91
3.89
3.89
3.88
3.87
3.87
3.86
3.85
3.84
3.75
1.93
1.93
1.91
1.90
1.90
1.90
1.90
1.88
1.87
1.87
1.57
1.56
1.55
1.55
1.54
1.52
1.52
1.52
H
CO2Me
O
O
O
H
5.03
0.94
1.00
2.09
3.00
1.03
2.19
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

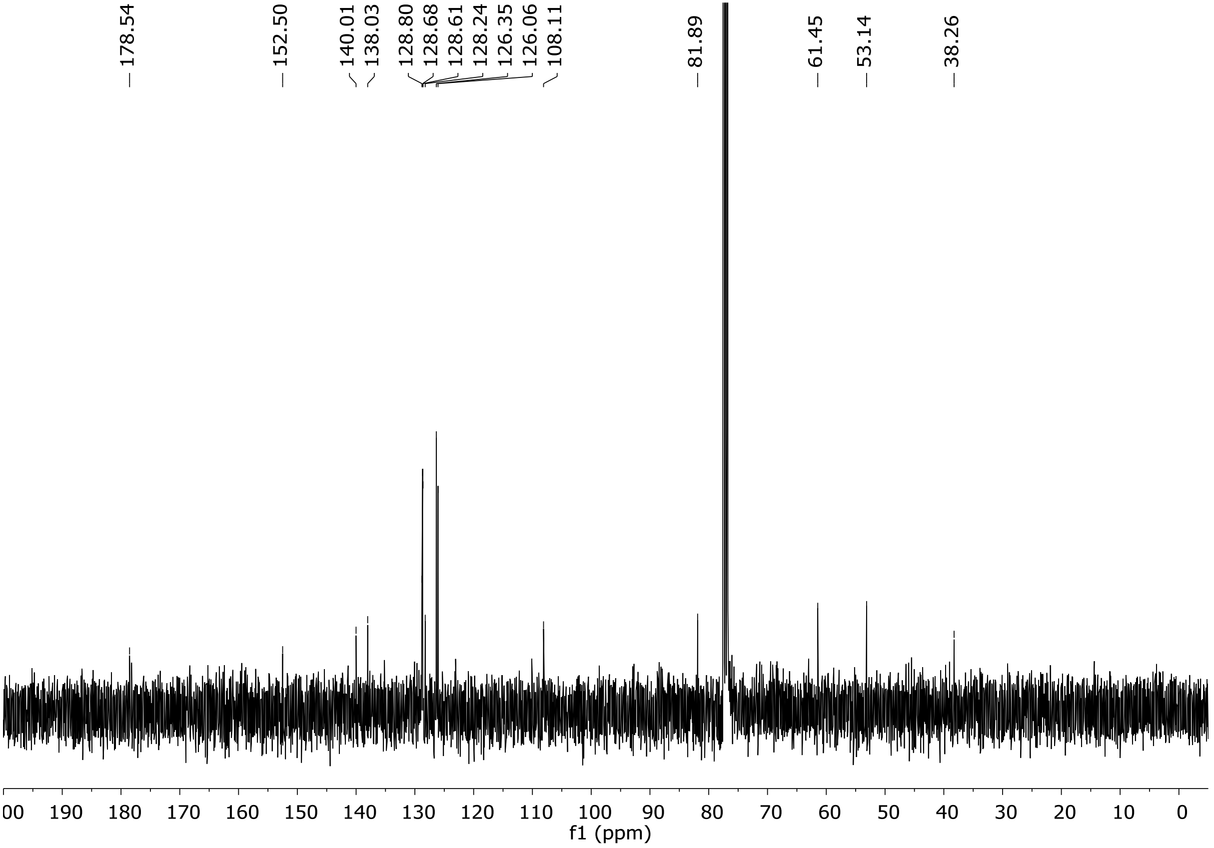


172.49
133.80
129.05
128.86
125.54
110.12
108.94
92.47
69.50
57.86
53.56
27.66
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

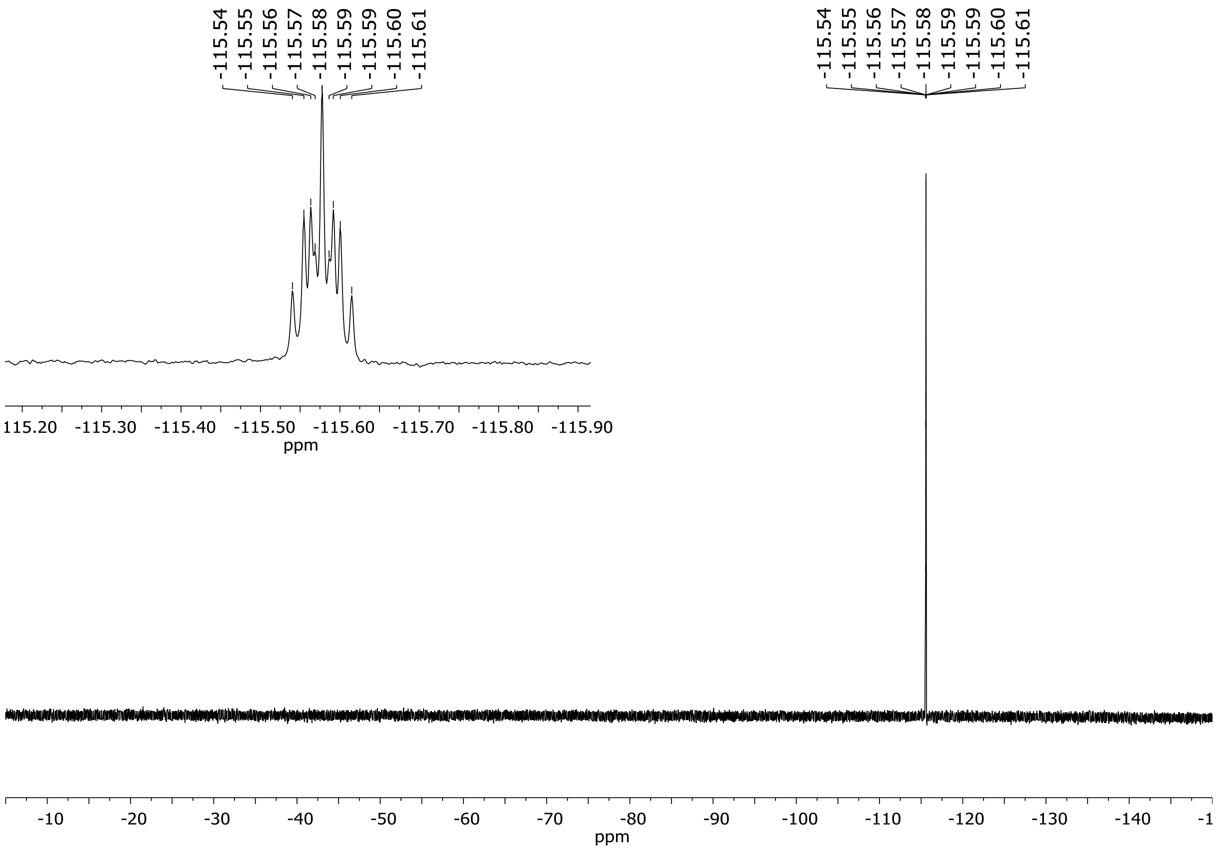

7.61
7.59
7.36
7.36
7.35
7.32
7.32
7.30
6.95
6.92
5.96
5.95
5.48
5.47
5.45
5.44
3.82
3.77
2.46
2.46
2.45
2.45
2.43
2.42
2.41
2.41
2.22
2.20
2.19
2.17
2.17
2.14
MeO
CO2Me
H
O
O
O
H
2b-major
2.01
5.00
2.00
0.96
0.98
1.00
3.00
3.00
1.00
1.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.51
159.99
140.05
129.99
128.67
128.21
127.65
126.05
113.99
108.14
92.50
81.86
61.30
55.49
53.06
38.22
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

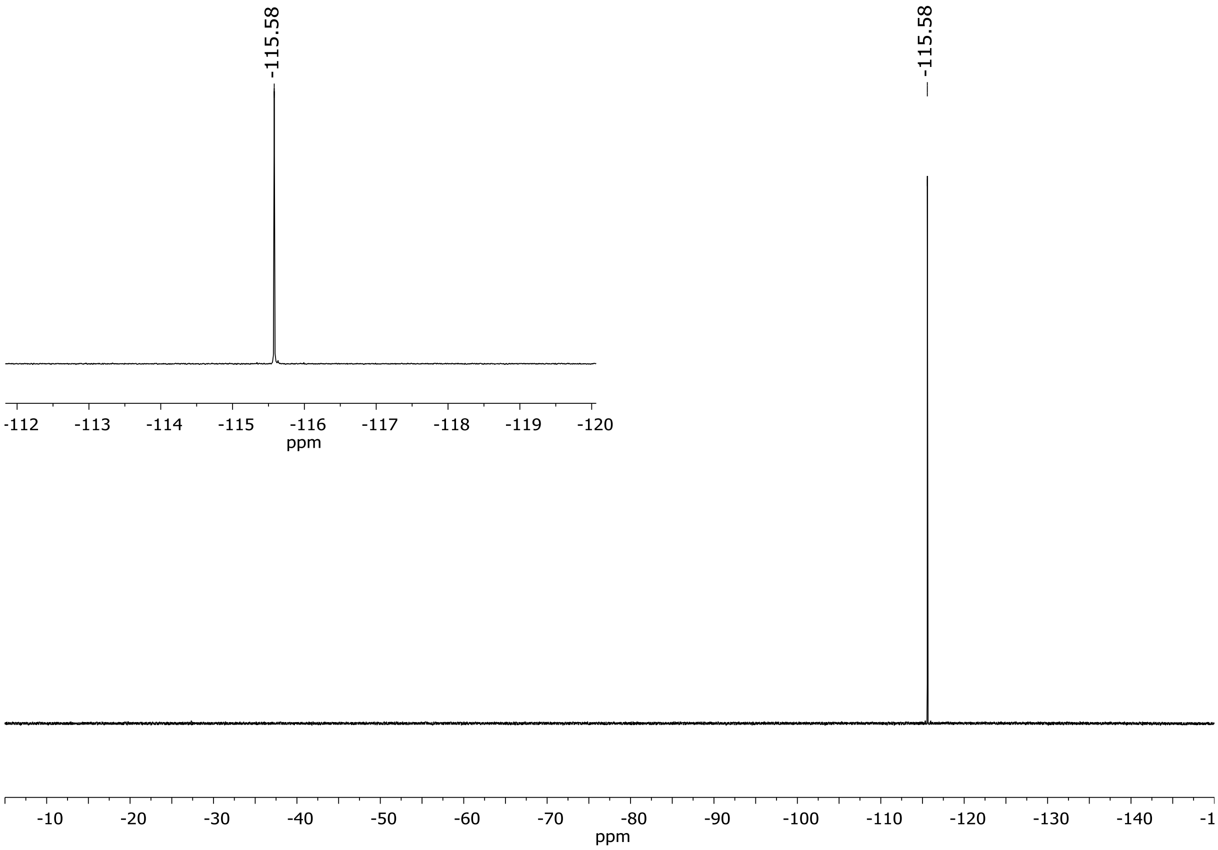

2c-major
F
CO2Me
H
O
O
O
H
7.71
7.70
7.69
7.69
7.44
7.42
7.41
7.40
7.39
7.38
7.37
7.35
7.34
7.33
5.96
5.95
5.49
5.48
5.46
5.45
4.21
4.20
4.19
4.18
4.18
4.17
4.17
3.78
2.49
2.49
2.48
2.47
2.46
2.45
2.44
2.44
2.24
2.22
2.22
2.21
2.19
2.18
2.18
2.16
2.00
8.09
0.97
0.97
1.00
3.00
1.00
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

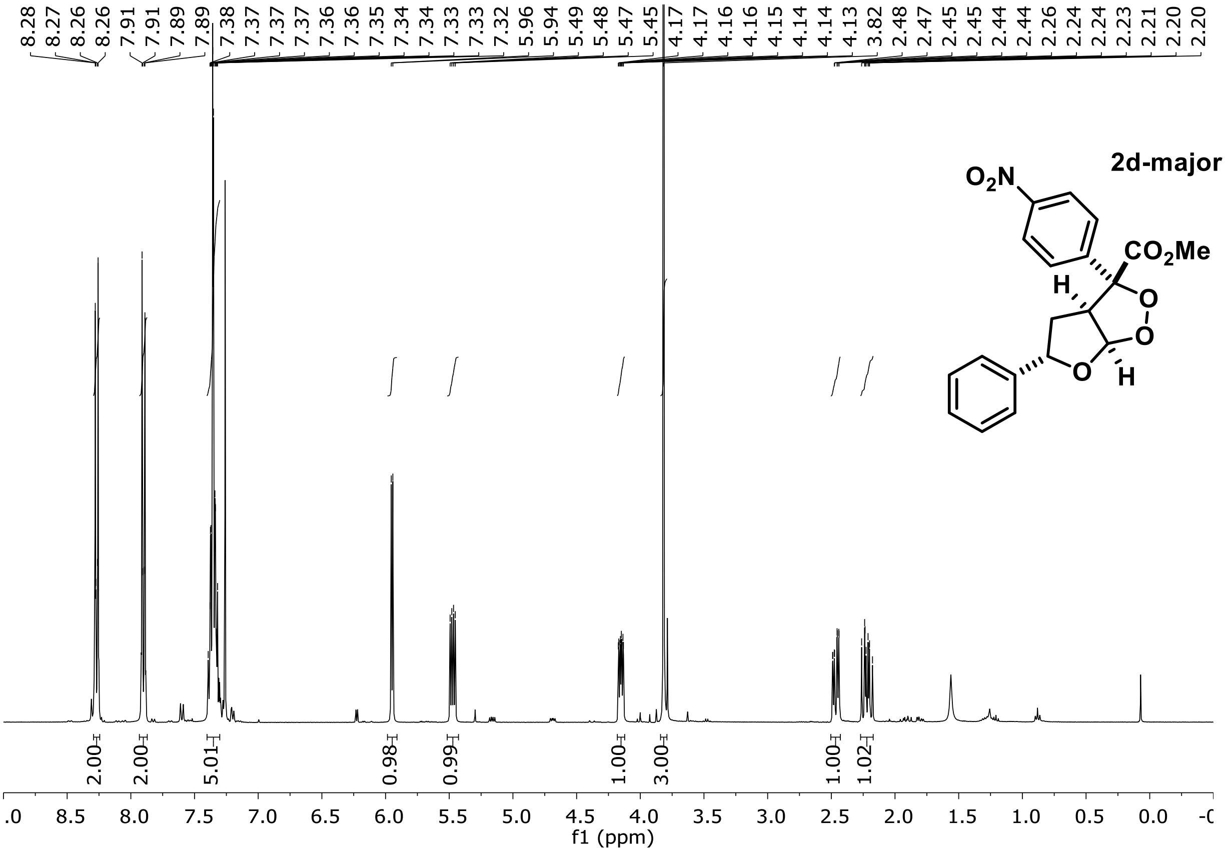

178.54
152.50
140.01
138.03
128.80
128.68
128.61
128.24
126.35
126.06
108.11
81.89
61.45
53.14
38.26
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

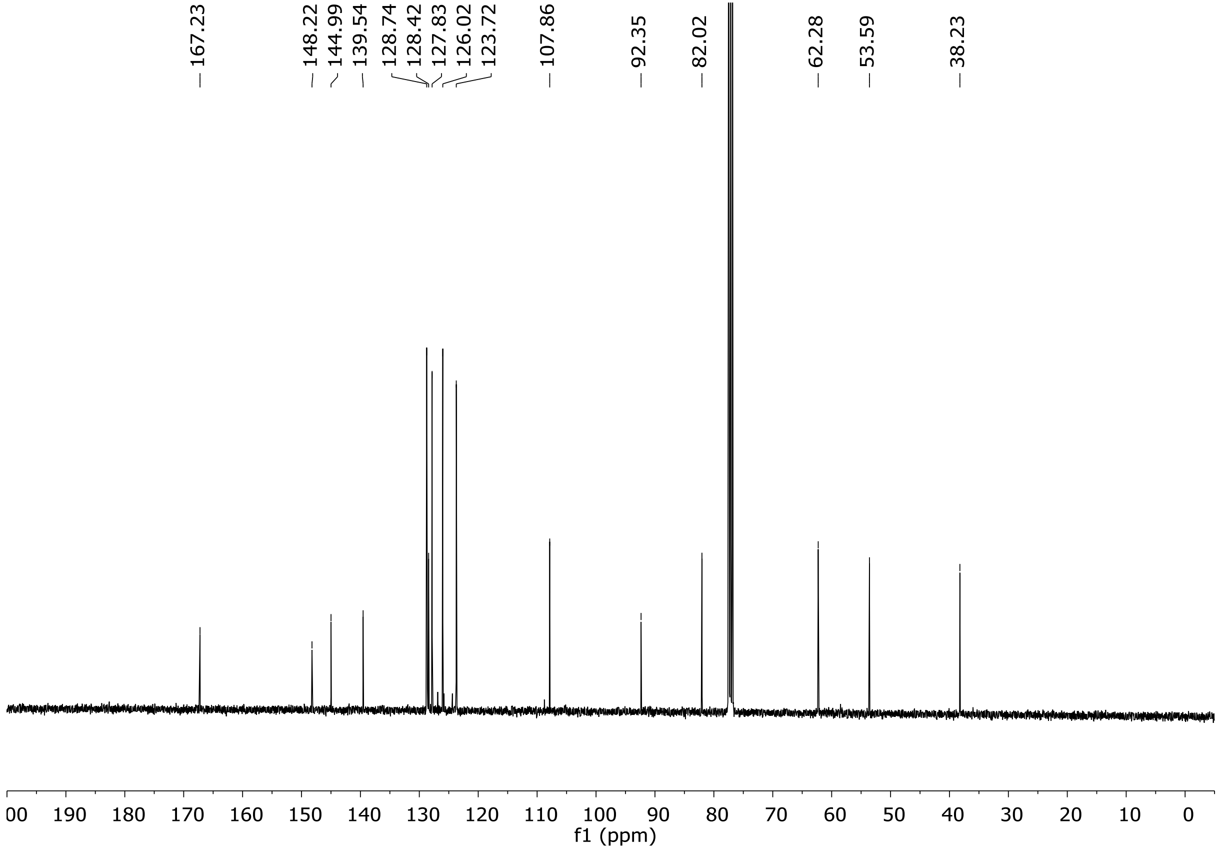
2c-major ^{19}F

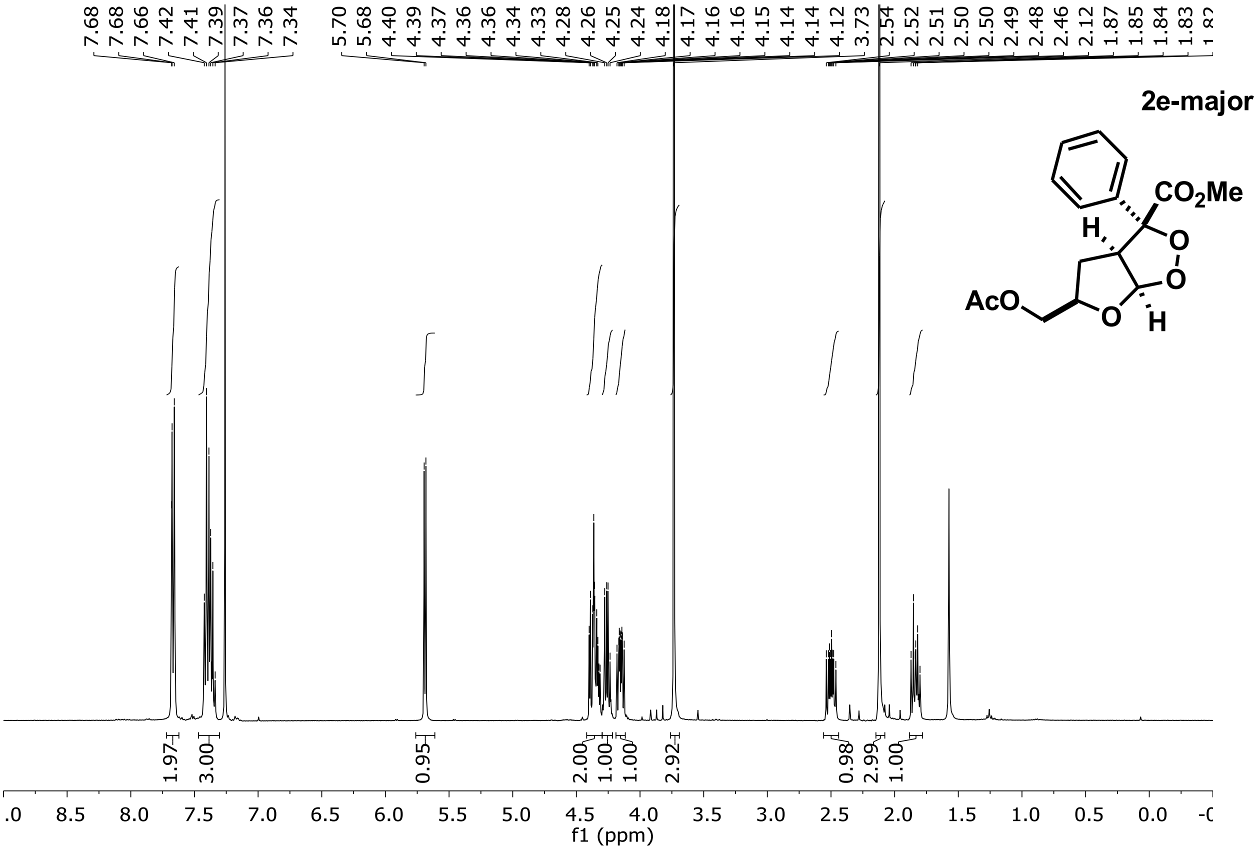


2c-major ^{19}F-CPD

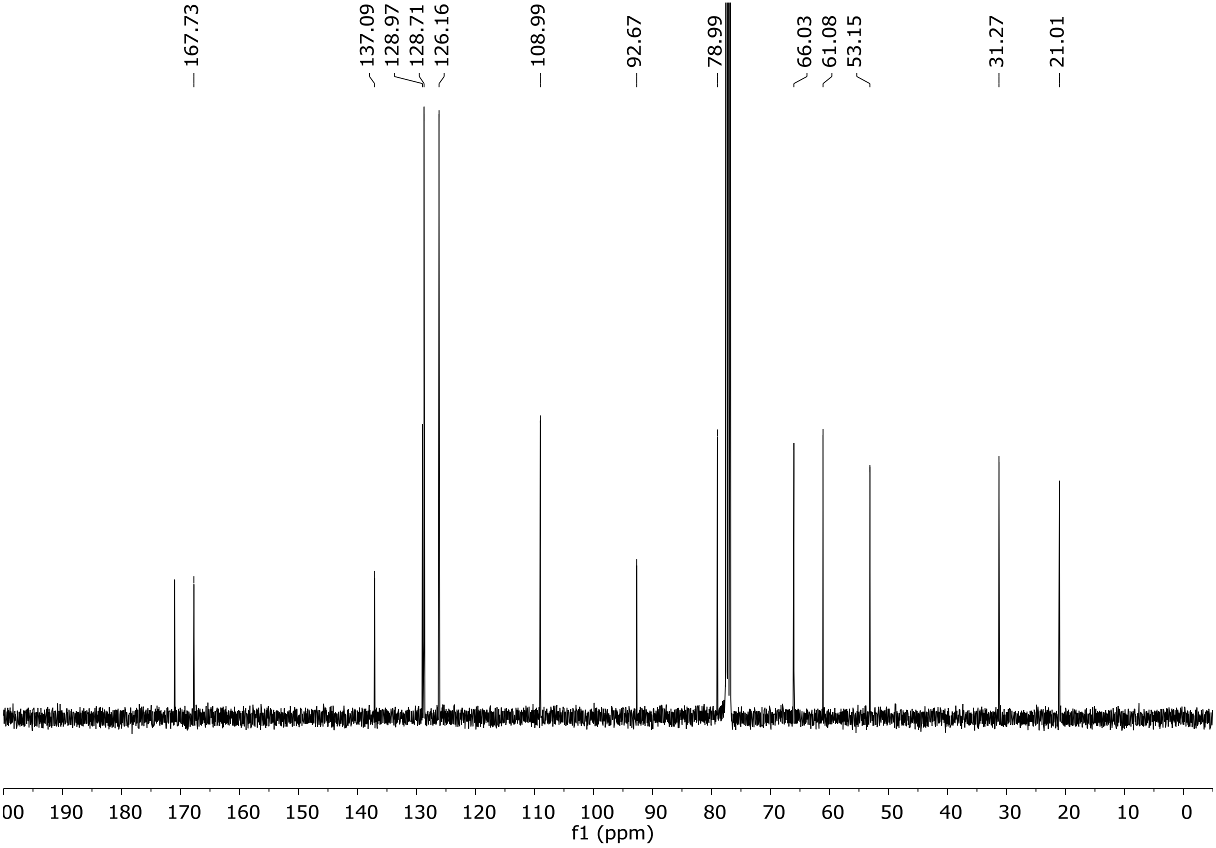


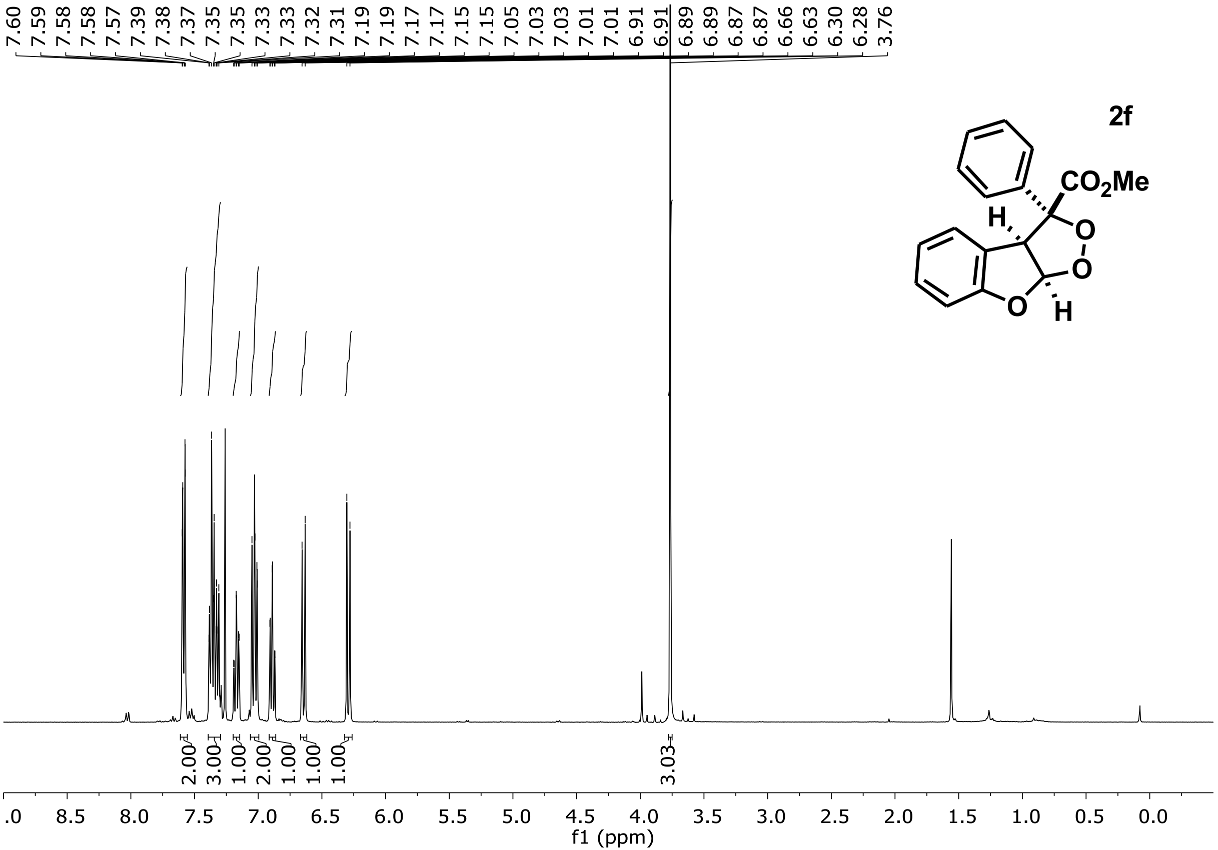

8.28
8.27
8.26
8.26
7.91
7.91
7.89
7.89
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
5.96
5.94
5.49
5.48
5.47
5.45
4.17
4.17
4.16
4.16
4.15
4.14
4.14
4.13
3.82
2.48
2.47
2.45
2.45
2.44
2.44
2.26
2.24
2.24
2.23
2.21
2.20
2.20
2d-major
O2N
CO2Me
H
O
O
O
H
2.00
2.00
5.01
0.98
0.99
1.00
3.00
1.00
1.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.23
148.22
144.99
139.54
128.74
128.42
127.83
126.02
123.72
107.86
92.35
82.02
62.28
53.59
38.23
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

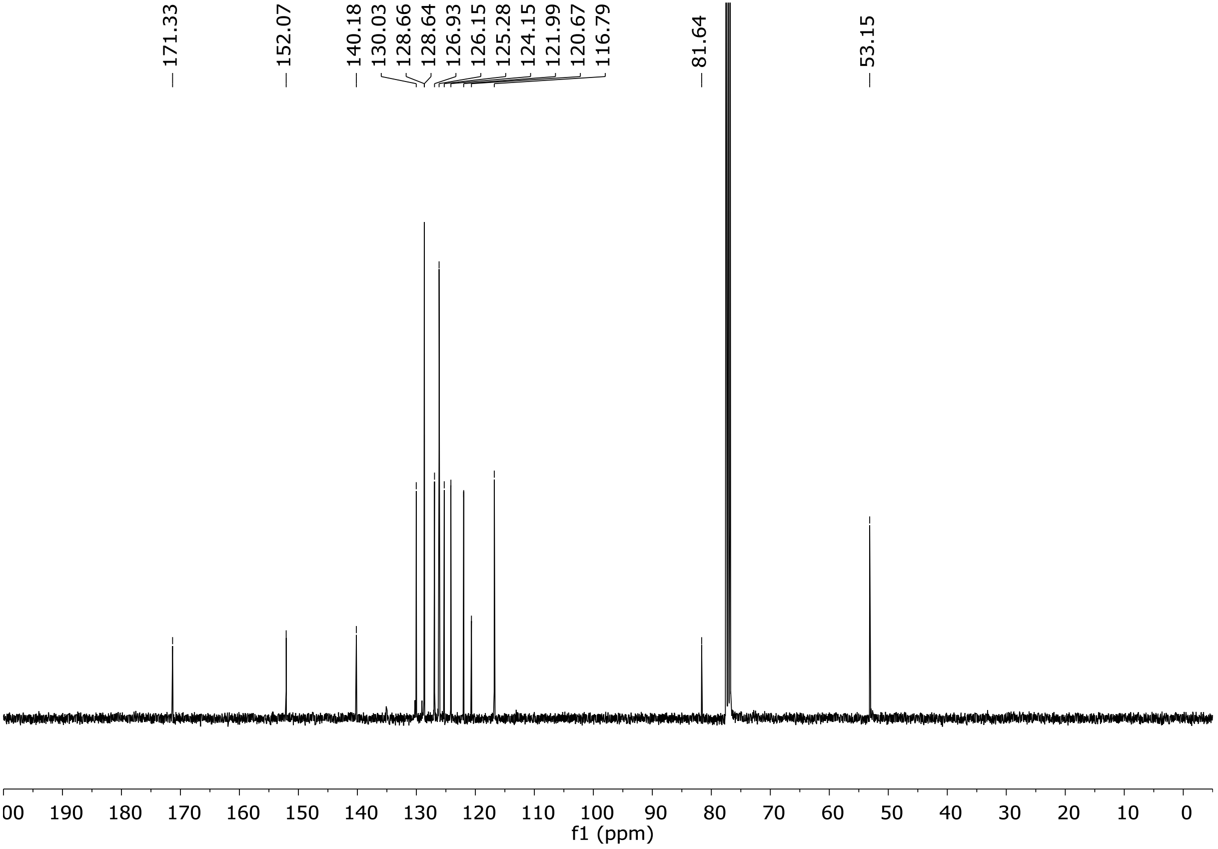

7.68
7.68
7.66
7.42
7.41
7.39
7.37
7.36
7.34
5.70
5.68
4.40
4.39
4.37
4.36
4.36
4.34
4.33
4.28
4.26
4.25
4.24
4.18
4.17
4.16
4.16
4.15
4.14
4.14
4.12
3.73
2.54
2.52
2.51
2.50
2.50
2.49
2.48
2.46
2.12
1.87
1.85
1.84
1.83
1.97
3.00
0.95
2.00
1.00
1.00
2.92
0.98
2.99
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
CO2Me
H
O
O
AcO
O
H

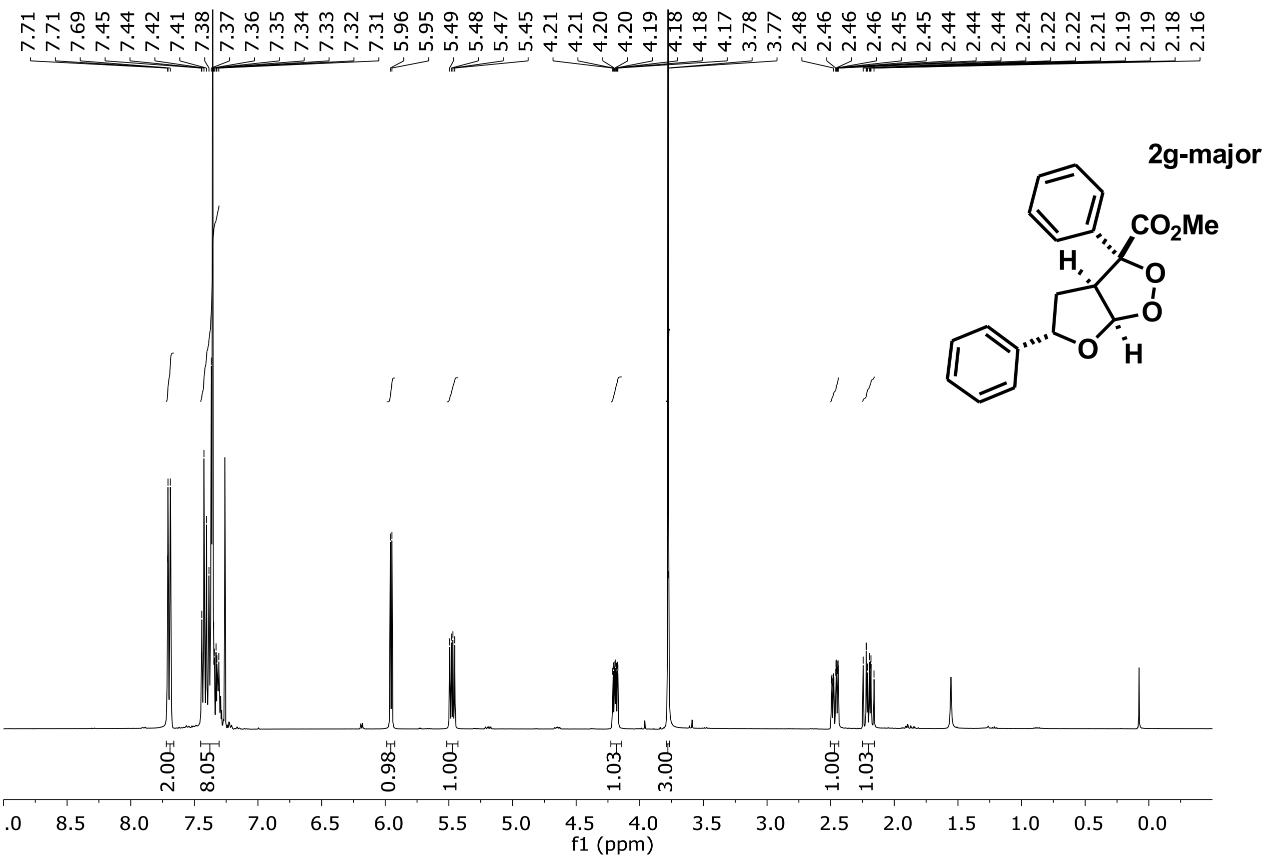
2e-major

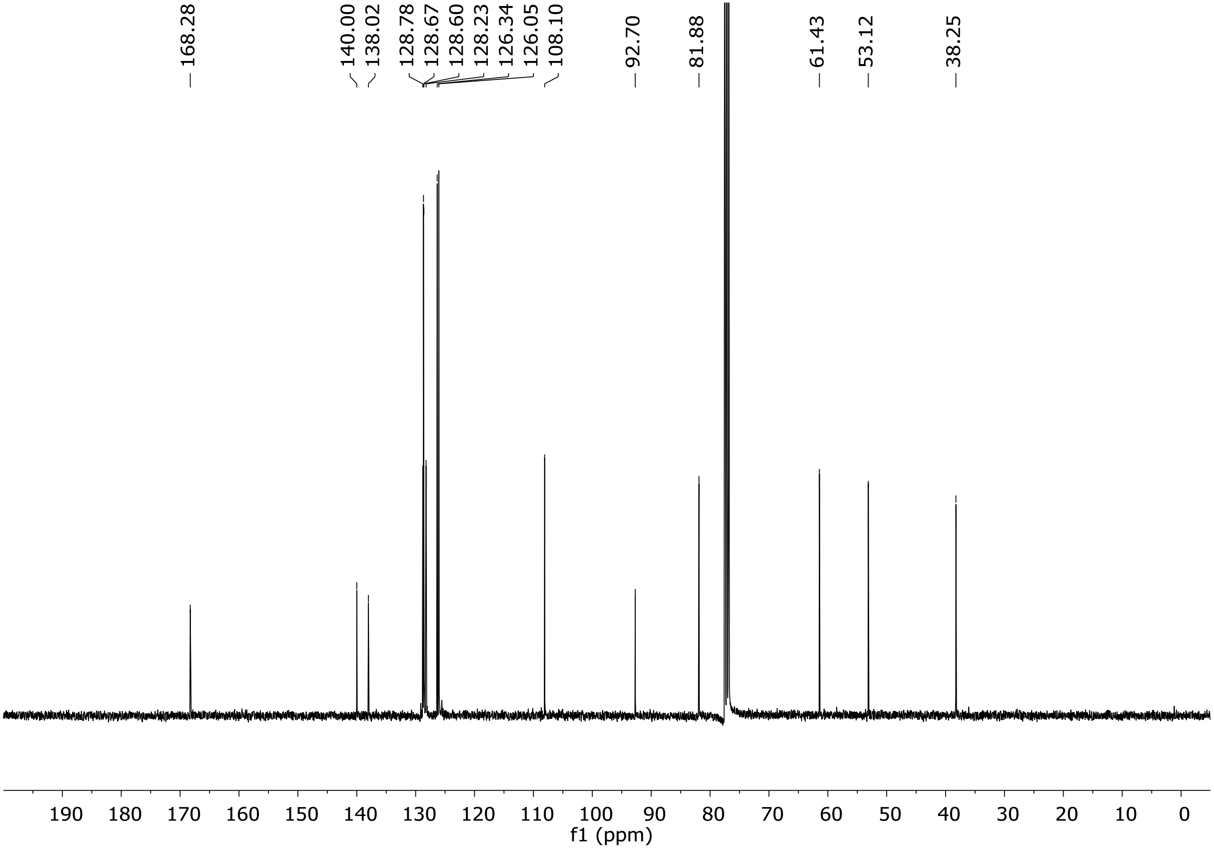

167.73
137.09
128.97
128.71
126.16
108.99
92.67
78.99
66.03
61.08
53.15
31.27
21.01
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

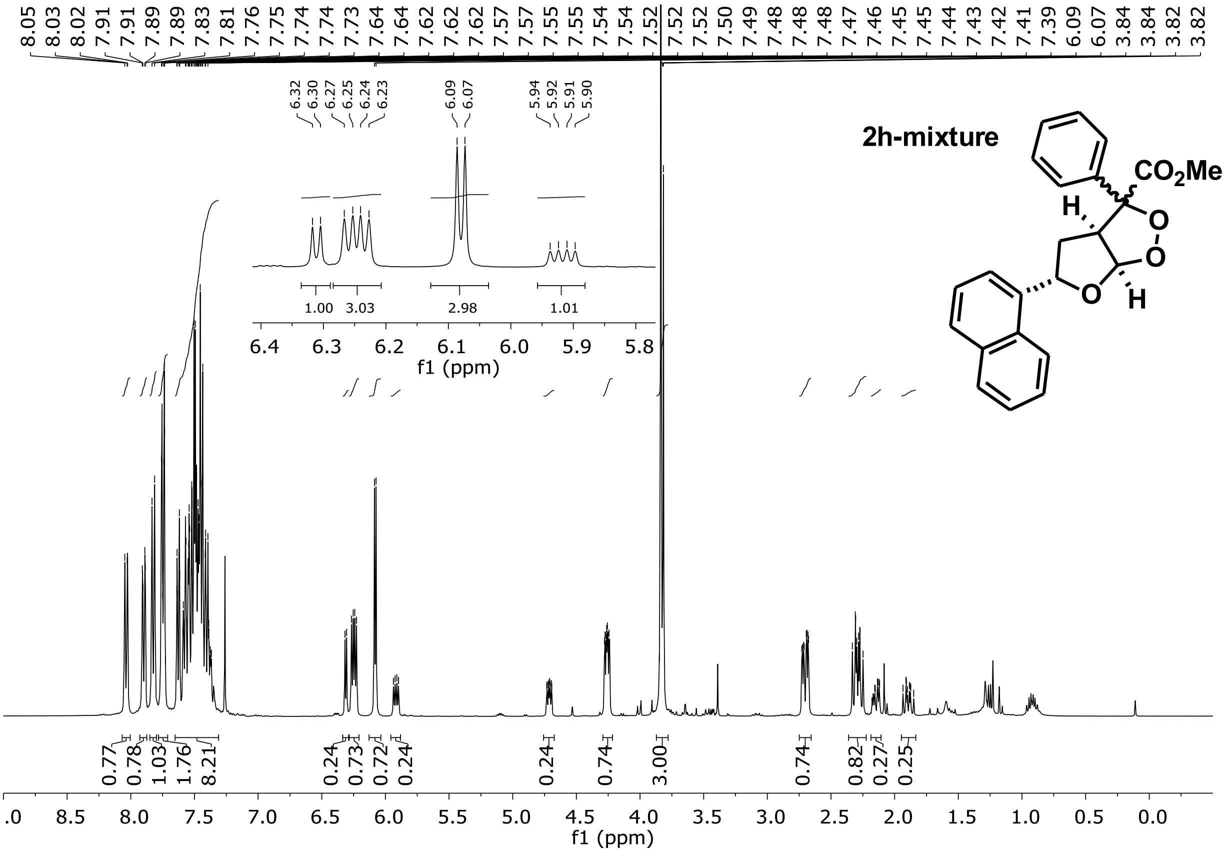

7.60
7.59
7.58
7.58
7.57
7.39
7.38
7.37
7.35
7.35
7.33
7.33
7.32
7.31
7.19
7.17
7.17
7.15
7.15
7.05
7.03
7.03
7.01
7.01
6.91
6.91
6.89
6.89
6.87
6.87
6.66
6.63
6.30
6.28
3.76
CO2Me
H
O
O
O
H
2.00
3.00
1.00
2.00
1.00
1.00
1.00
3.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2f


171.33
152.07
140.18
130.03
128.66
128.64
126.93
126.15
125.28
124.15
121.99
120.67
116.79
81.64
53.15
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.71
7.71
7.69
7.45
7.44
7.42
7.41
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.31
5.96
5.95
5.49
5.48
5.47
5.45
4.21
4.21
4.20
4.20
4.19
4.18
4.18
4.17
3.78
3.77
2.48
2.46
2.46
2.46
2.45
2.45
2.44
2.44
2.44
2.24
2.22
2.22
2.21
2.19
2.19
2.18
2.16
2g-major
CO2Me
H
O
O
O
H
2.00
8.05
0.98
1.00
1.03
3.00
1.00
1.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.28
140.00
138.02
128.78
128.67
128.60
128.23
126.34
126.05
108.10
92.70
81.88
61.43
53.12
38.25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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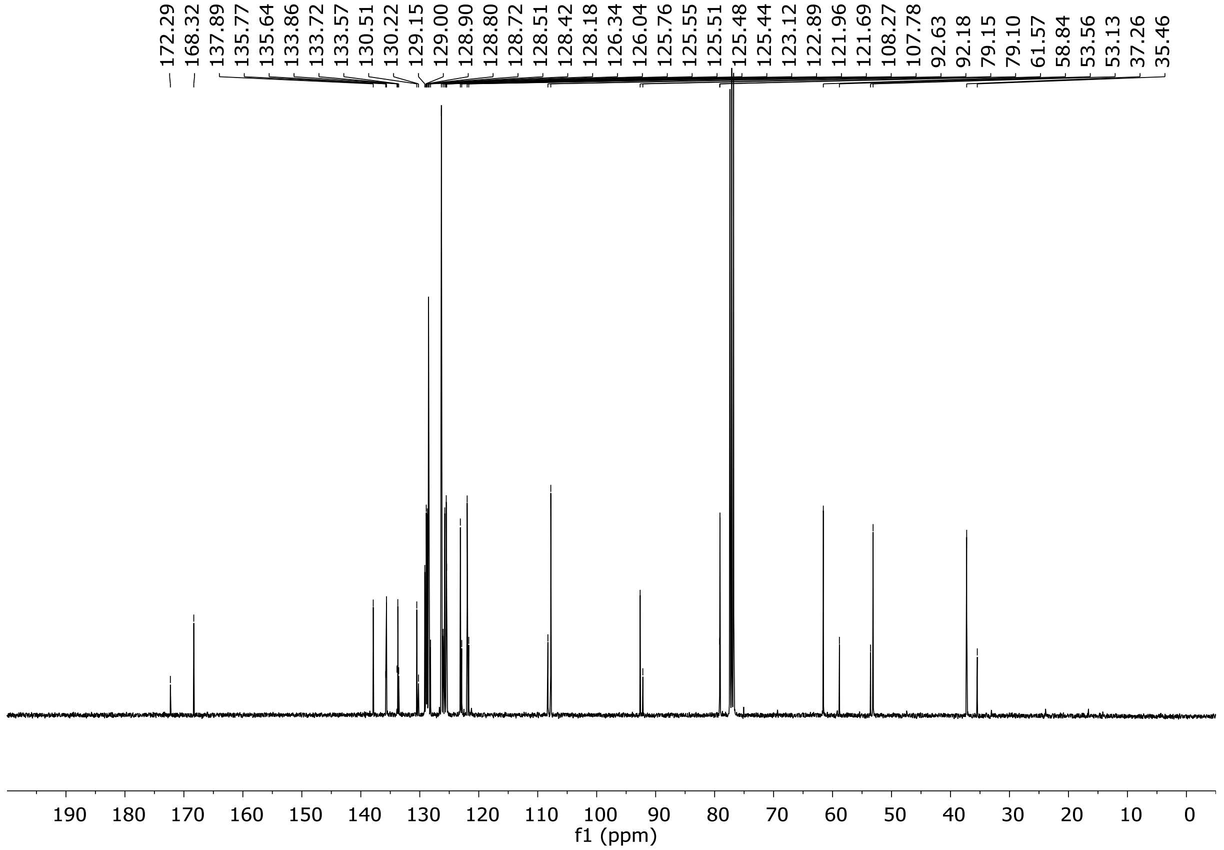
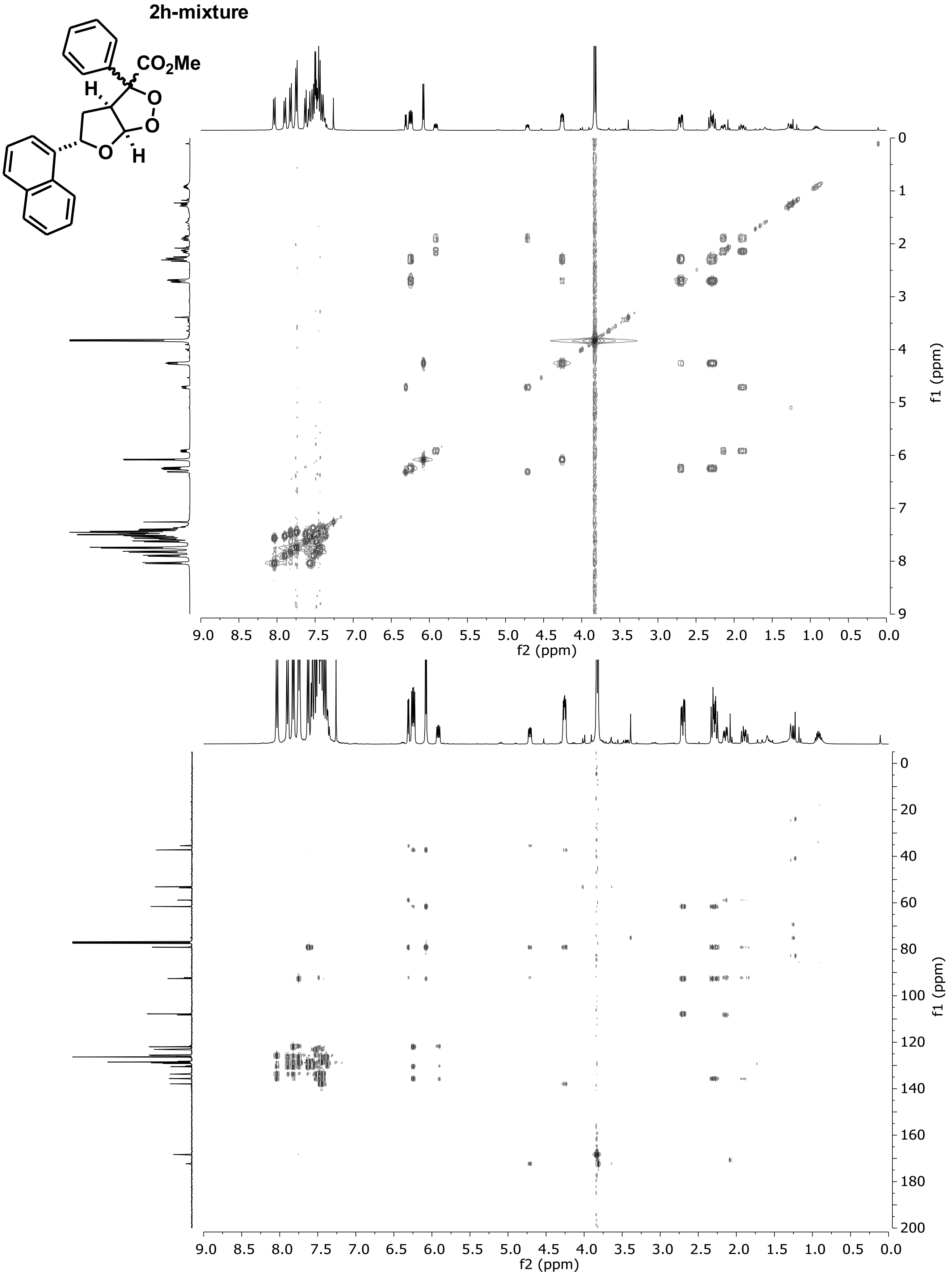
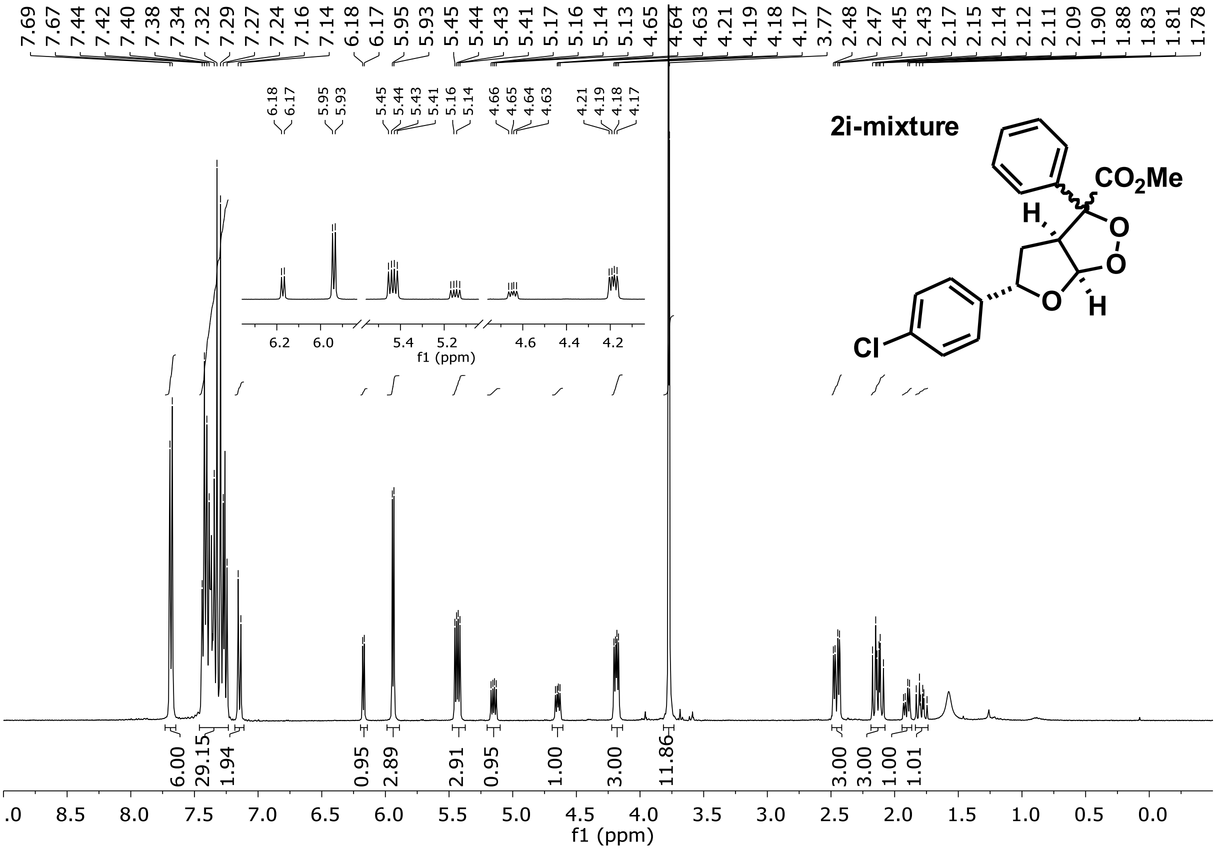
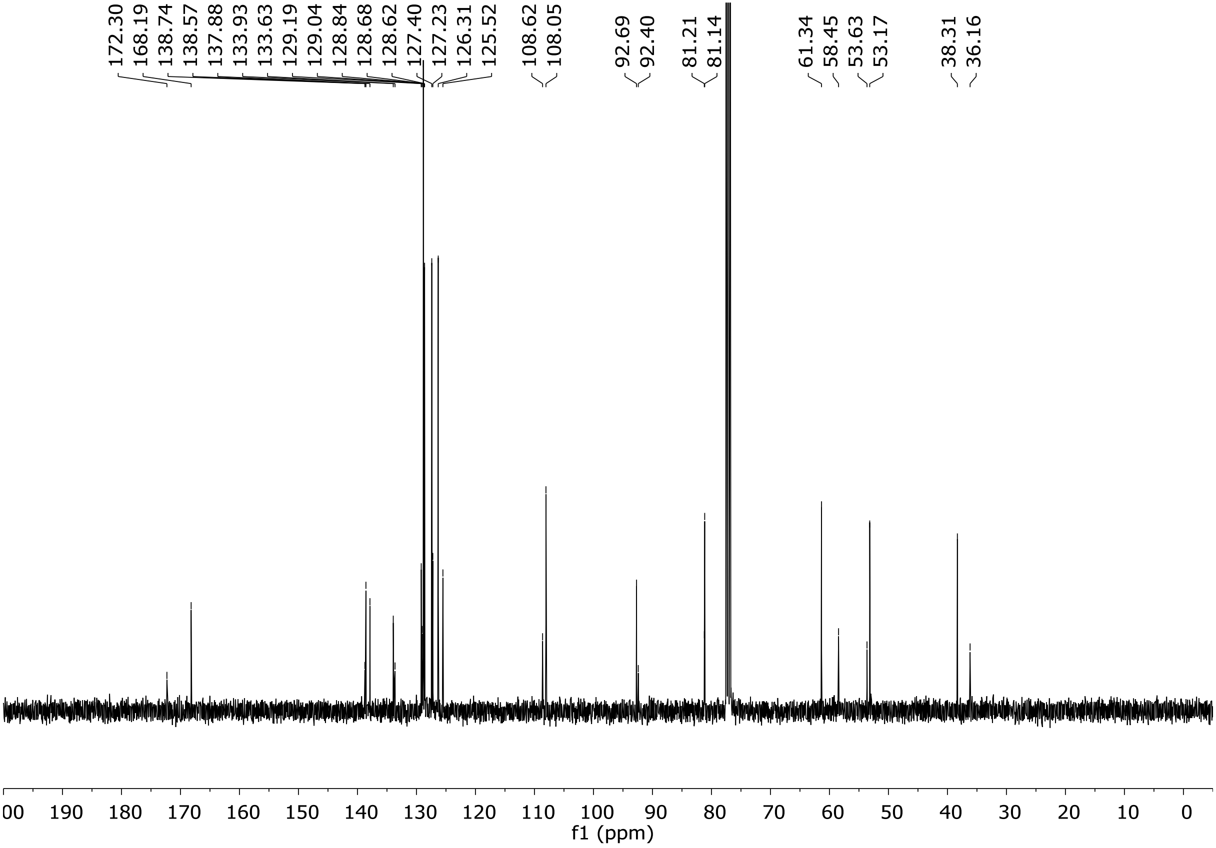
8.03
8.02
7.91
7.91
7.89
7.89
7.83
7.81
7.76
7.75
7.74
7.74
7.73
7.64
7.64
7.62
7.62
7.62
7.57
7.57
7.55
7.55
7.54
7.54
7.52
7.52
7.52
7.50
7.49
7.48
7.48
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.41
7.39
6.09
6.07
3.84
3.84
3.82
3.82
6.32
6.30
6.27
6.25
6.24
6.23
6.09
6.07
5.94
5.92
5.91
5.90
1.00
3.03
2.98
1.01
6.4
6.3
6.2
6.1
6.0
5.9
5.8
f1 (ppm)
2h-mixture
CO2Me
H
O
O
H
O
0.77
0.78
1.03
1.76
8.21
0.24
0.73
0.72
0.24
0.24
0.74
3.00
0.74
0.82
0.27
0.25
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

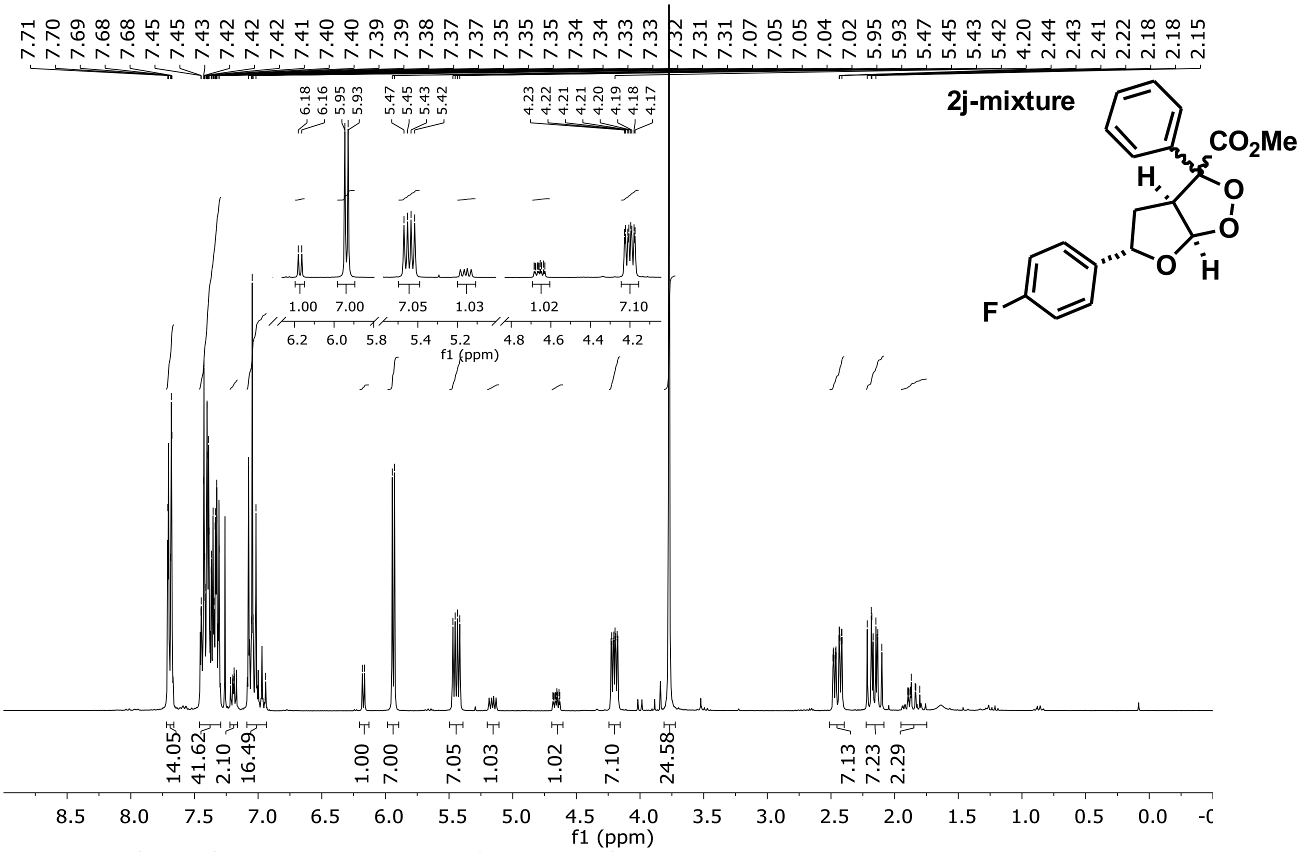

172.29
168.32
137.89
135.77
135.64
133.86
133.72
133.57
130.51
130.22
129.15
129.00
128.90
128.80
128.72
128.51
128.42
128.18
126.34
126.04
125.76
125.55
125.51
125.48
125.44
123.12
122.89
121.96
121.69
108.27
107.78
92.63
92.18
79.15
79.10
61.57
58.84
53.56
53.13
37.26
35.46
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

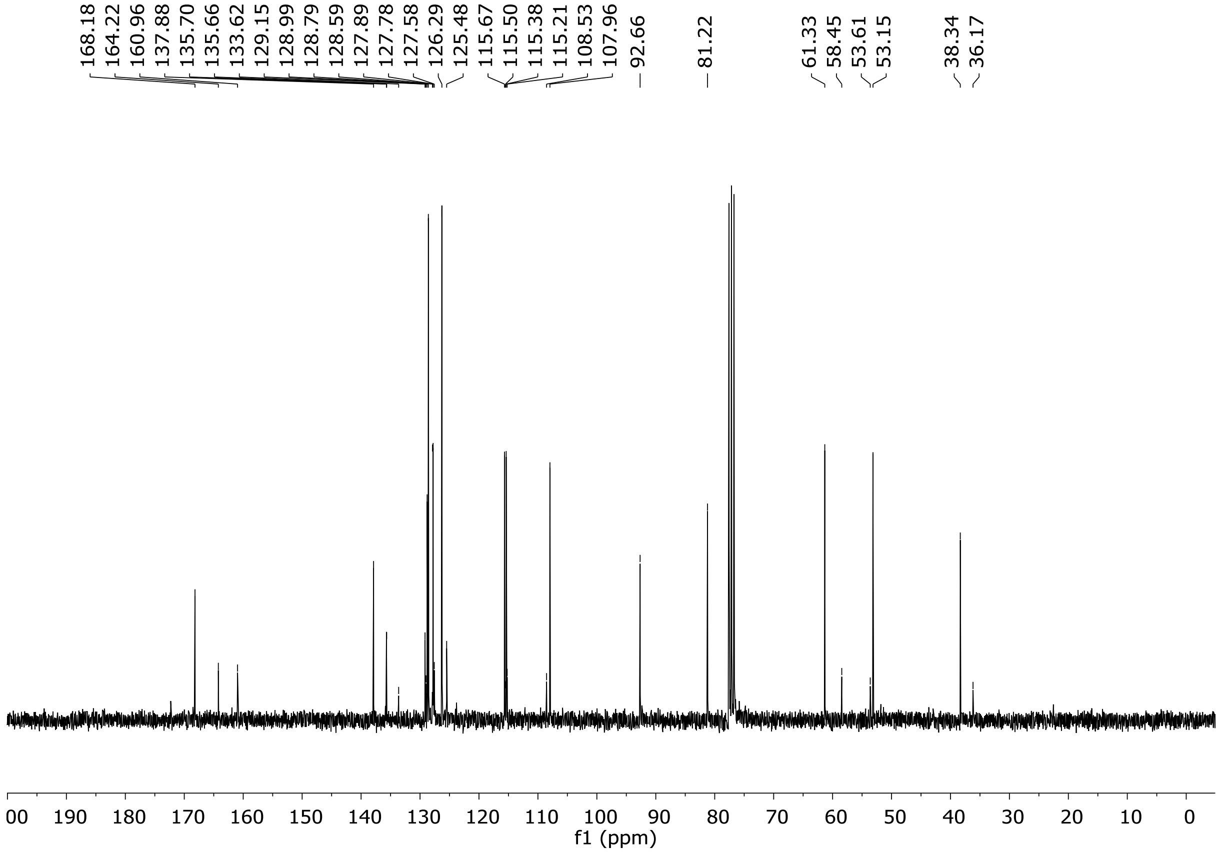
2h-mixture


CO2Me
H
O
O
O
H
f2 (ppm)
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8 9
0 20 40 60 80 100 120 140 160 180 200

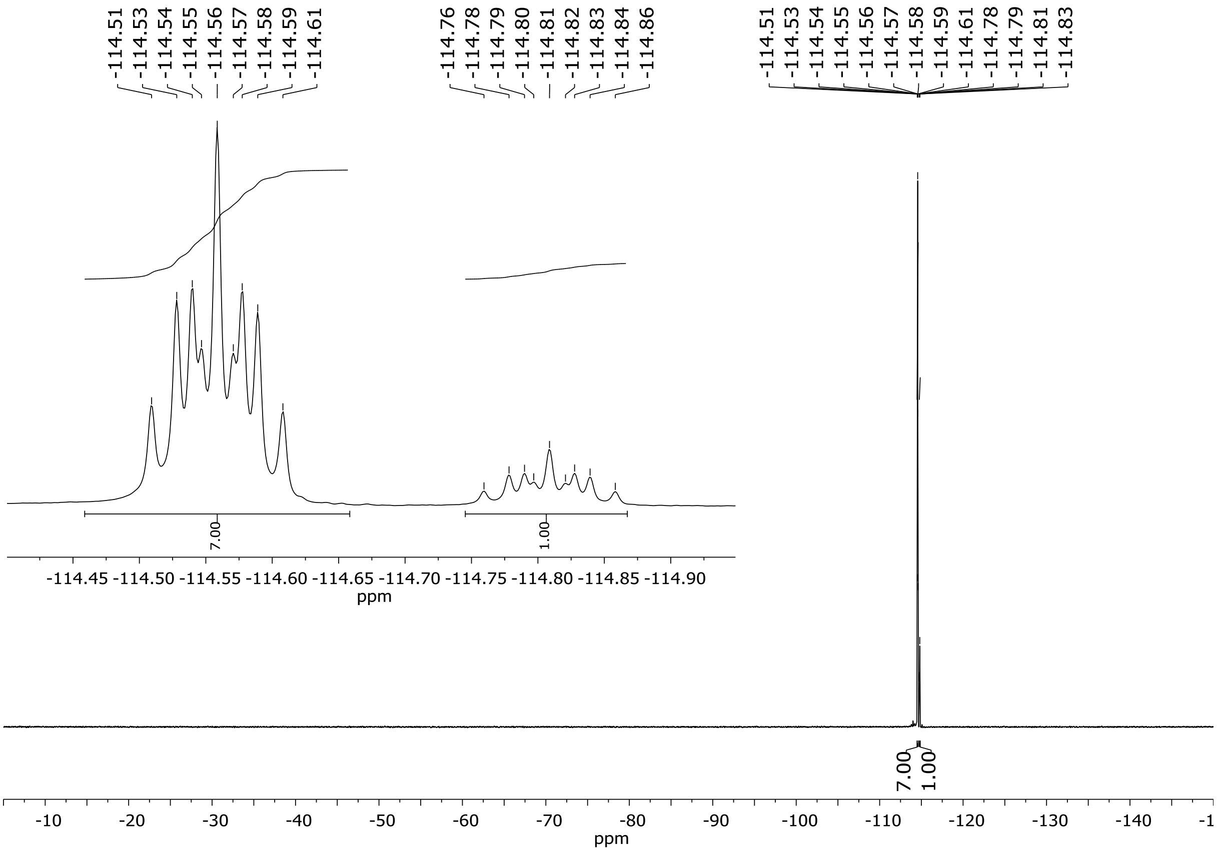

2i-mixture
CO2Me
H
O
O
O
H
Cl
7.69 7.67 7.44 7.42 7.40 7.38 7.34 7.32 7.29 7.27 7.24 7.16 7.14 6.18 6.17 5.95 5.93 5.45 5.44 5.43 5.41 5.17 5.16 5.14 5.13 4.65 4.64 4.63 4.21 4.19 4.18 4.17 3.77 2.48 2.47 2.45 2.43 2.17 2.15 2.14 2.12 2.11 2.09 1.90 1.88 1.83 1.81 1.78
6.18 6.17 5.95 5.93 5.45 5.44 5.43 5.41 5.16 5.14 4.66 4.65 4.64 4.63 4.21 4.19 4.18 4.17
6.2 6.0 5.4 5.2 4.6 4.4 4.2
f1 (ppm)
6.00 29.15 1.94 0.95 2.89 2.91 0.95 1.00 3.00 11.86 3.00 3.00 1.00 1.01
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.30 168.19 138.74 138.57 137.88 133.93 133.63 129.19 129.04 128.84 128.68 128.62 127.40 127.23 126.31 125.52 108.62 108.05 92.69 92.40 81.21 81.14 61.34 58.45 53.63 53.17 38.31 36.16
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

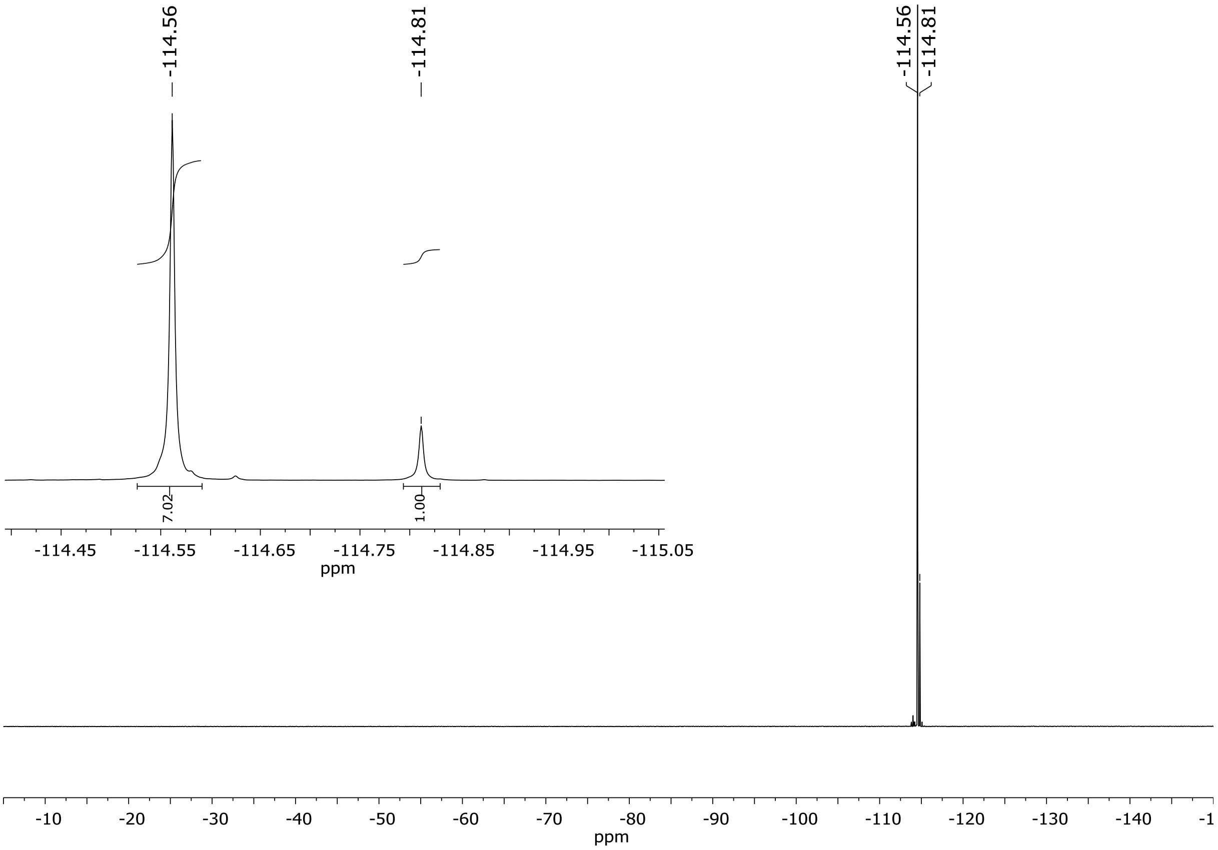

7.71 7.70 7.69 7.68 7.68 7.45 7.45 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.37 7.37 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.31 7.07 7.05 7.05 7.04 7.02 5.95 5.93 5.47 5.45 5.43 5.42 4.20 2.44 2.43 2.41 2.22 2.18 2.15
6.18 6.16 5.95 5.93 5.47 5.45 5.43 5.42 4.23 4.22 4.21 4.21 4.20 4.19 4.18 4.17
1.00 7.00 7.05 1.03 1.02 7.10
6.2 6.0 5.8 5.4 5.2 4.8 4.6 4.4 4.2
f1 (ppm)
2j-mixture
CO2Me
H
O
O
O
H
F
14.05 41.62 2.10 16.49 1.00 7.00 7.05 1.03 1.02 7.10 24.58 7.13 7.23 2.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)

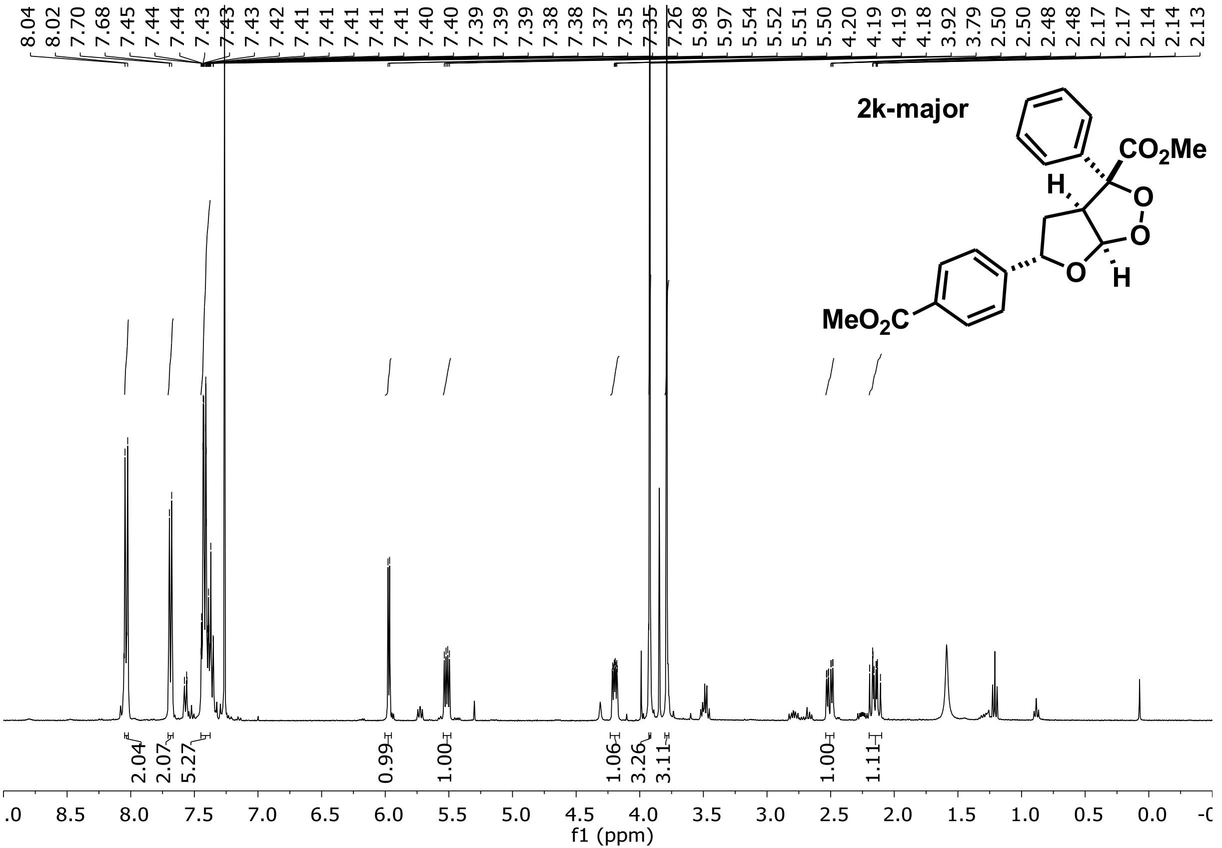

168.18 164.22 160.96 137.88 135.70 135.66 133.62 129.15 128.99 128.79 128.59 127.89 127.78 127.58 126.29 125.48 115.67 115.50 115.38 115.21 108.53 107.96 92.66 81.22 61.33 58.45 53.61 53.15 38.34 36.17
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2j ^{19}F



2j ^{19}F-CPD

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7.42
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7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.35
7.35
7.26
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5.97
5.54
5.52
5.51
5.50
4.20
4.19
4.19
4.18
3.92
3.79
2.50
2.50
2.48
2.48
2.17
2.17
2.14
2.14
2.13
2k-major
CO2Me
H
O
O
O
H
MeO2C
2.04
2.07
5.27
0.99
1.00
1.06
3.26
3.11
1.00
1.11
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
1.5
1.0
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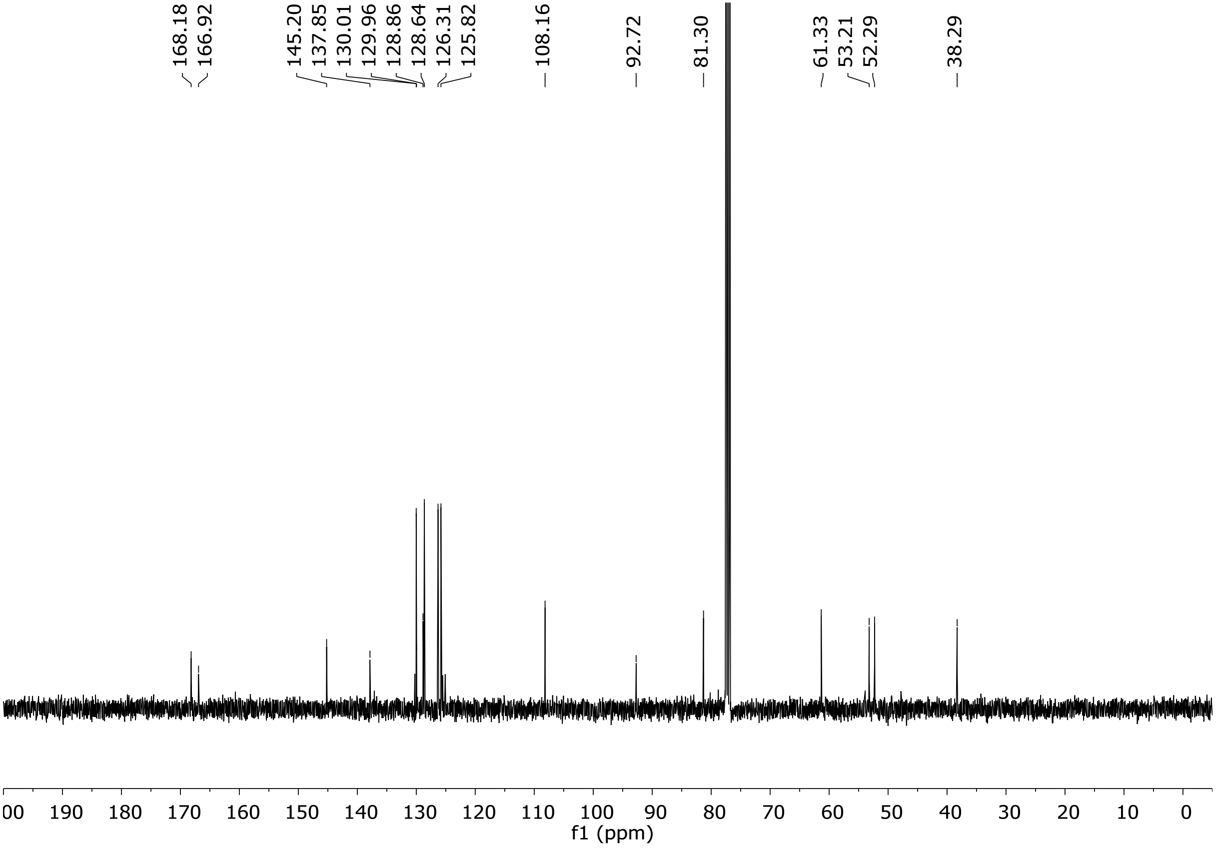
f1 (ppm)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128.64
126.31
125.82
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81.30
61.33
53.21
52.29
38.29
00
190
180
170
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150
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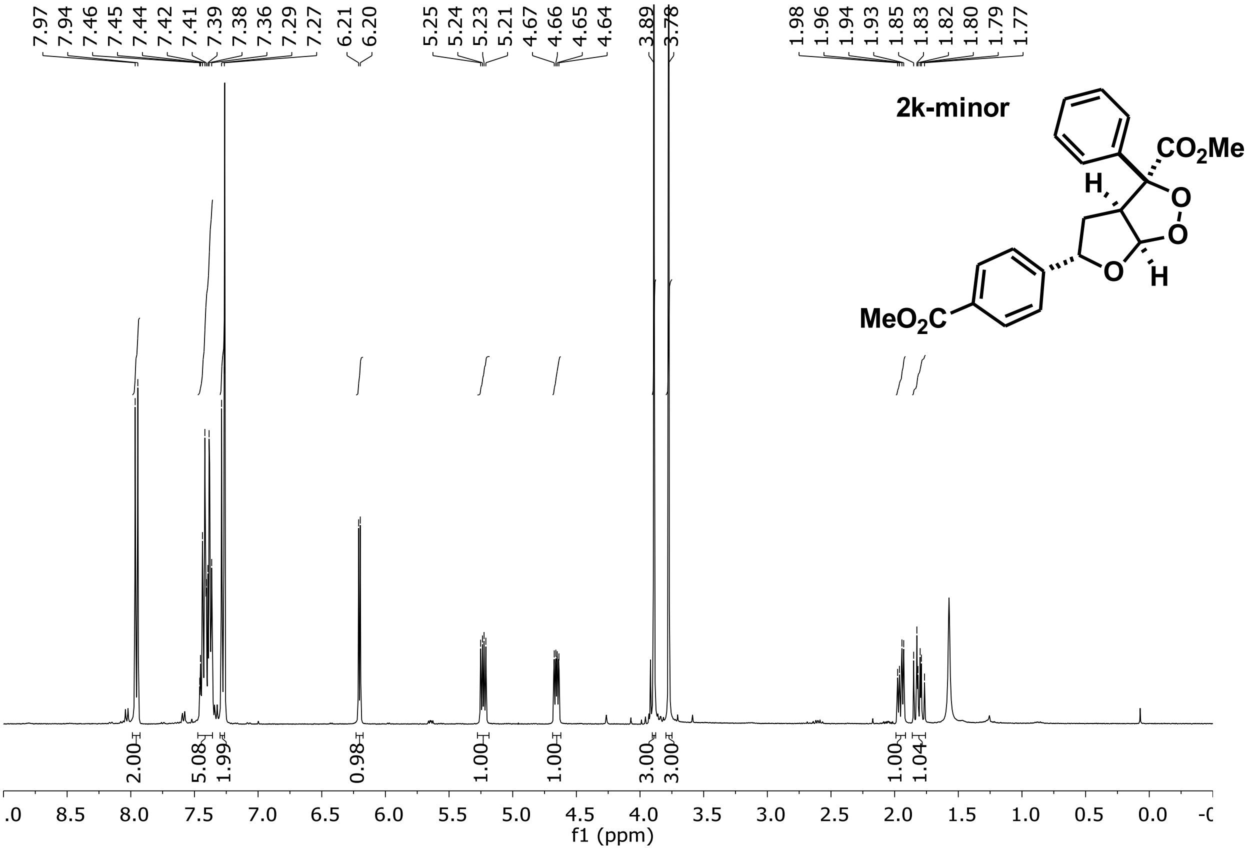
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.20
5.25
5.24
5.23
5.21
4.67
4.66
4.65
4.64
3.89
3.78
1.98
1.96
1.94
1.93
1.85
1.83
1.82
1.80
1.79
1.77
2k-minor
CO2Me
H
O
O
H
O
MeO2C
2.00
5.08
1.99
0.98
1.00
1.00
3.00
3.00
1.00
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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1.5
1.0
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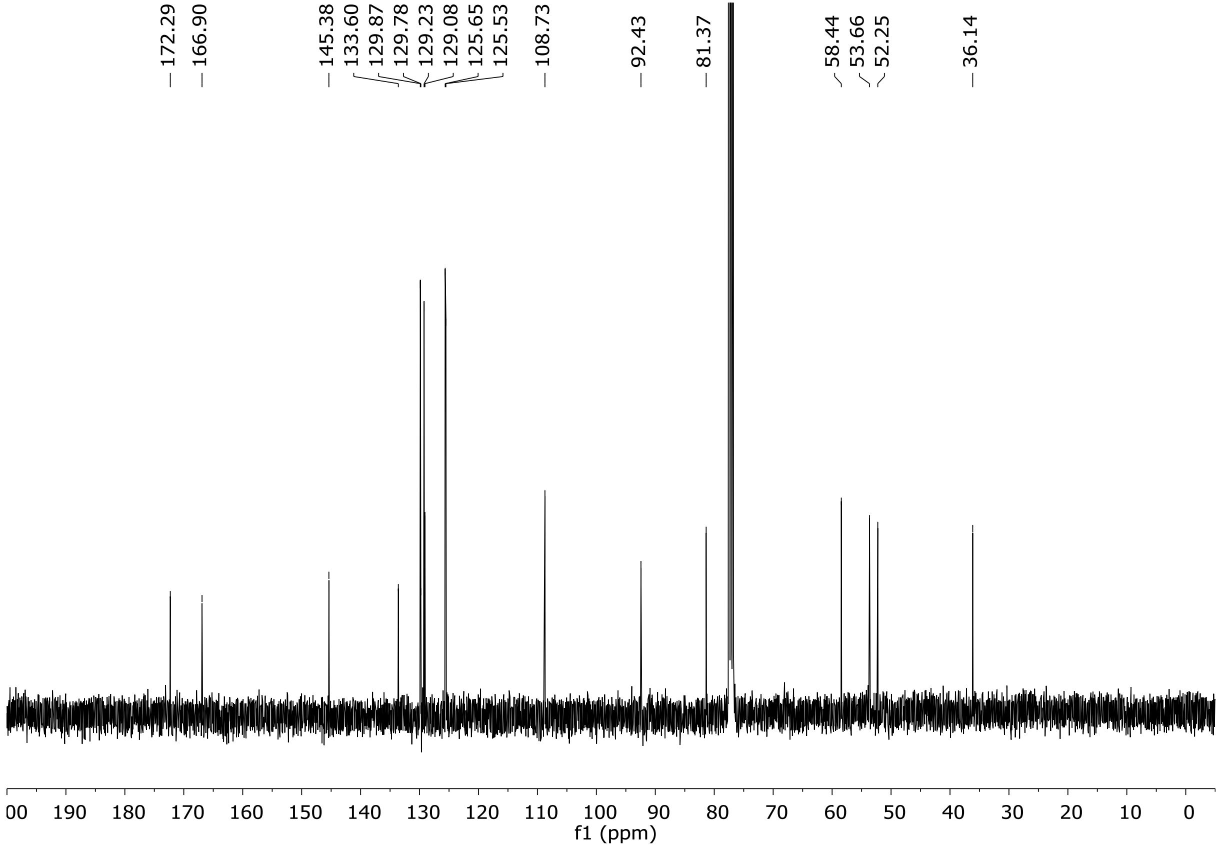
f1 (ppm)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129.78
129.23
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108.73
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52.25
36.14
00
190
180
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90
80
70
60
50
40
30
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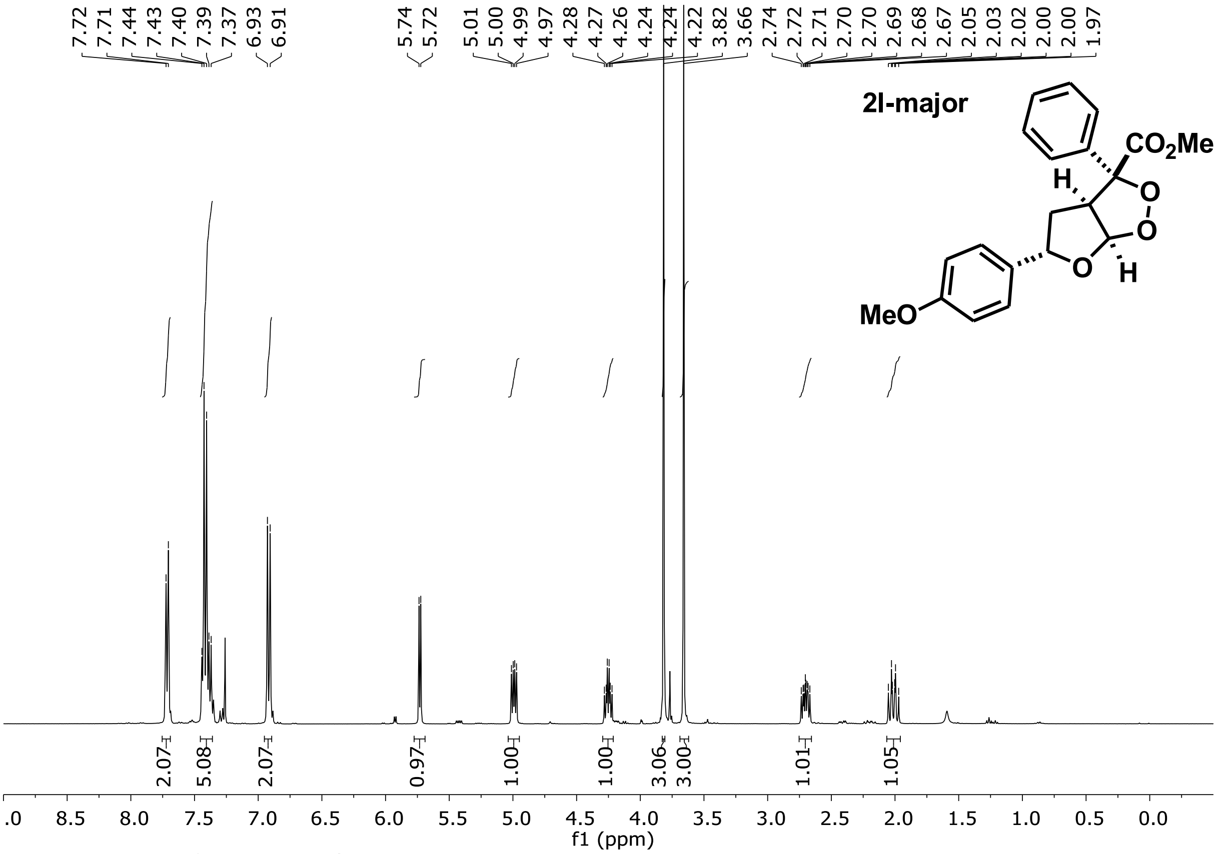
10
0
f1 (ppm)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7.71
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7.40
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7.37
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6.91
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5.72
5.01
5.00
4.99
4.97
4.28
4.27
4.26
4.24
4.24
4.22
3.82
3.66
2.74
2.72
2.71
2.70
2.70
2.69
2.68
2.67
2.05
2.03
2.02
2.00
2.00
1.97
CO$_2$Me
H
O
O
O
H
MeO
2.07
5.08
2.07
0.97
1.00
1.00
3.06
3.00
1.01
1.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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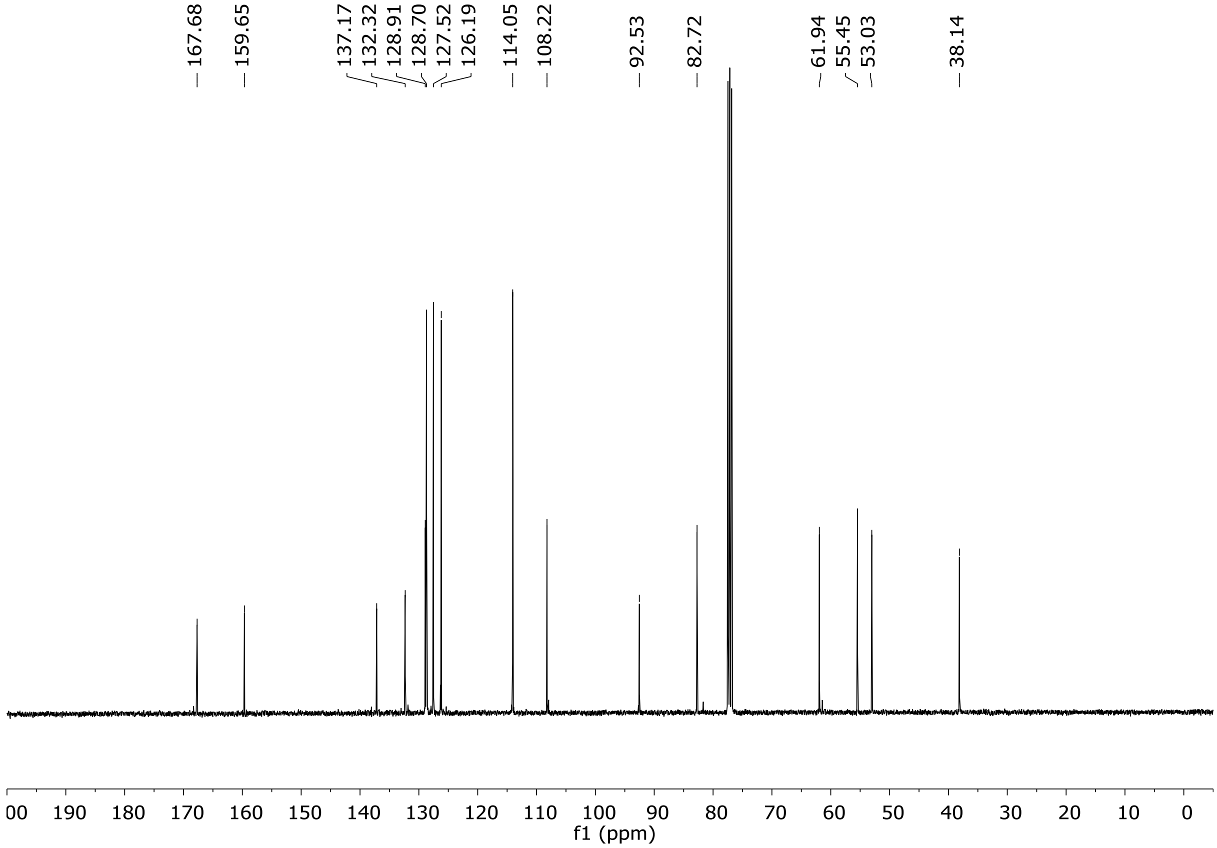
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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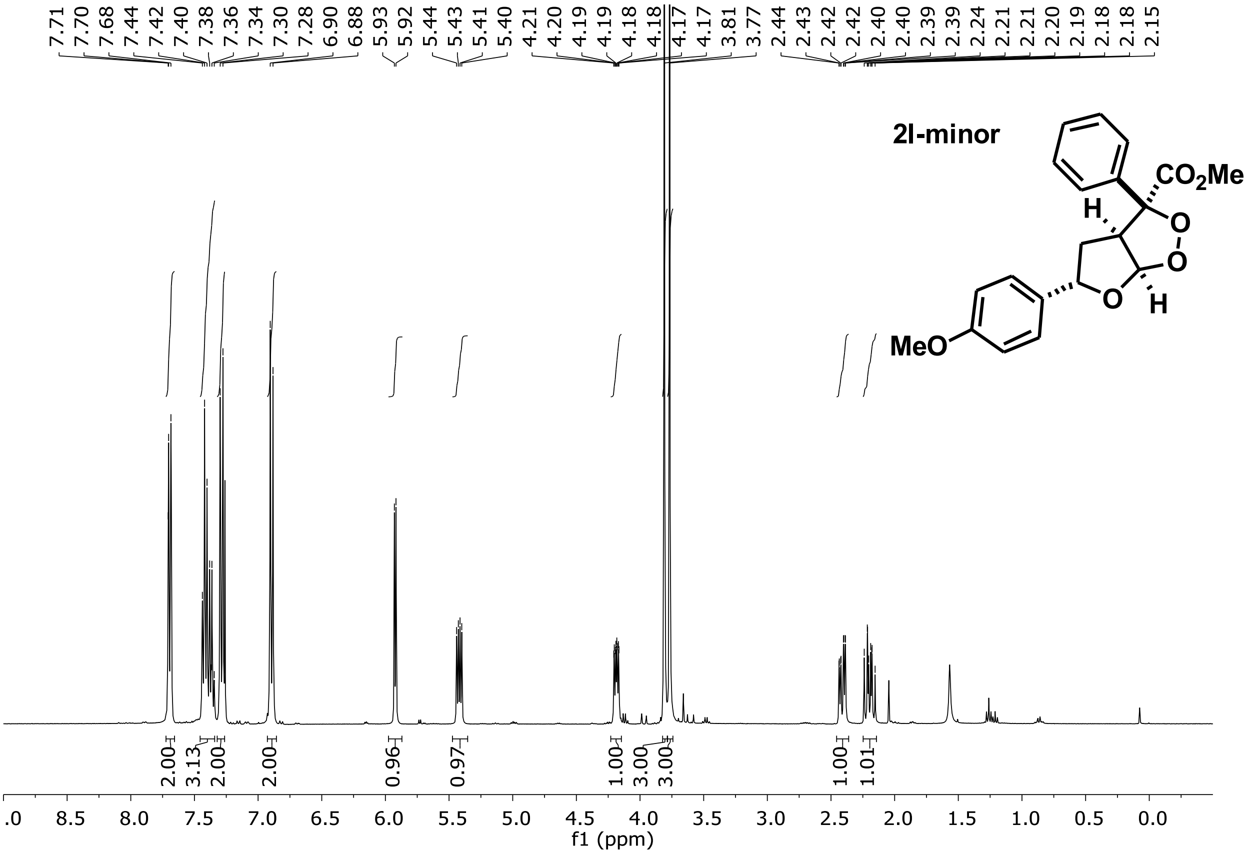
128.70
127.52
126.19
114.05
108.22
92.53
82.72
61.94
55.45
53.03
38.14
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.30
7.28
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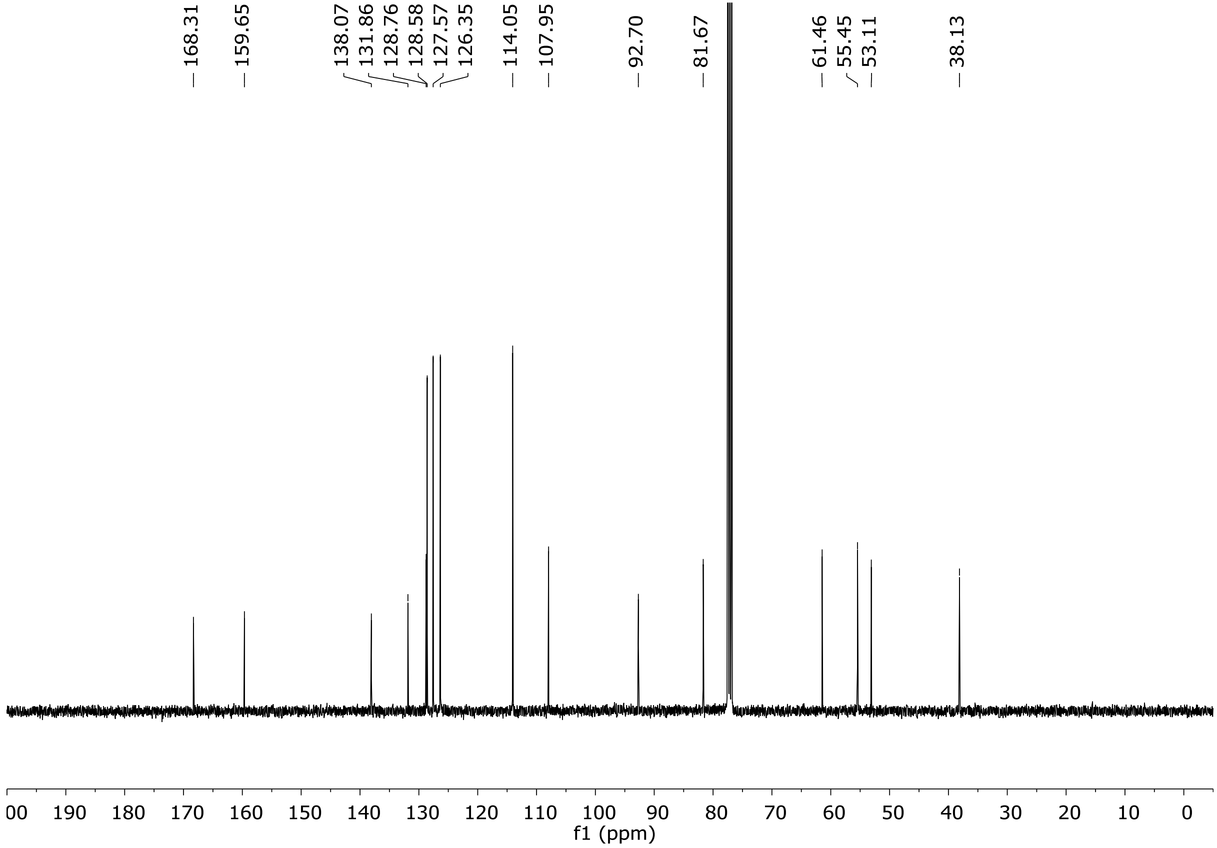
6.88
5.93
5.92
5.44
5.43
5.41
5.40
4.21
4.20
4.19
4.19
4.18
4.18
4.17
4.17
3.81
3.77
2.44
2.43
2.42
2.42
2.40
2.40
2.39
2.39
2.24
2.21
2.21
2.20
2.19
2.18
2.18
2.15
2l-minor
CO$_2$Me
H
O
O
O
H
MeO
2.00
3.13
2.00
2.00
0.96
0.97
1.00
3.00
3.00
1.00
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.76
128.58
127.57
126.35
114.05
107.95
92.70
81.67
61.46
55.45
53.11
38.13
00
190
180
170
160
150
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120
110
100
90
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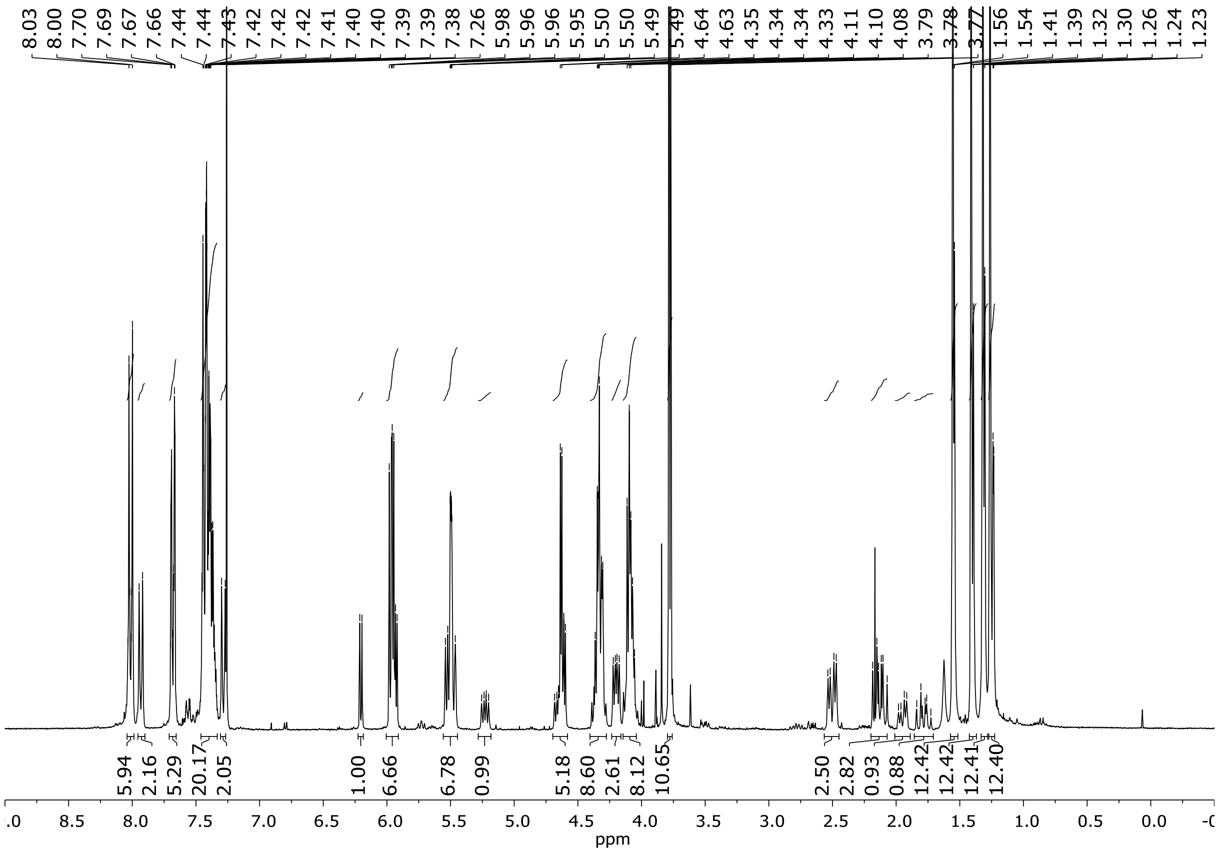
30
20
10
0
f1 (ppm)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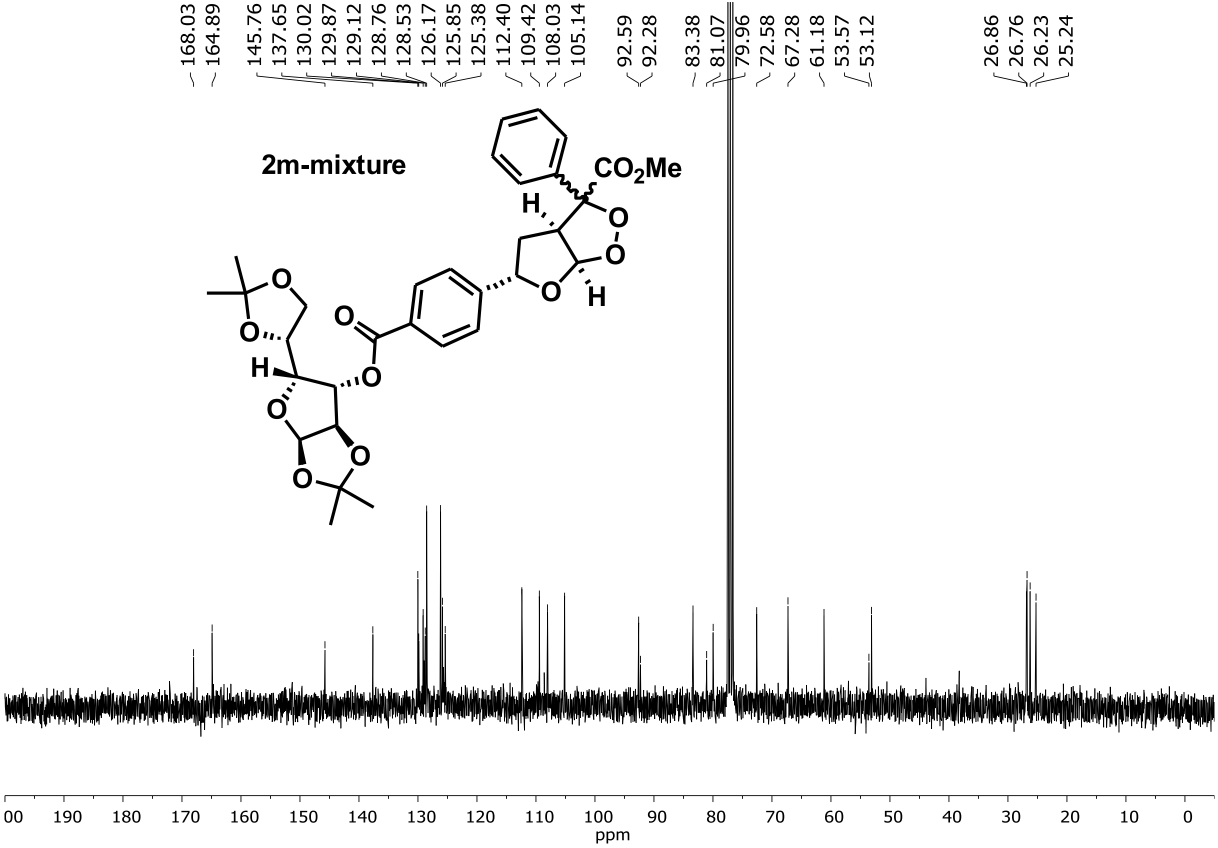
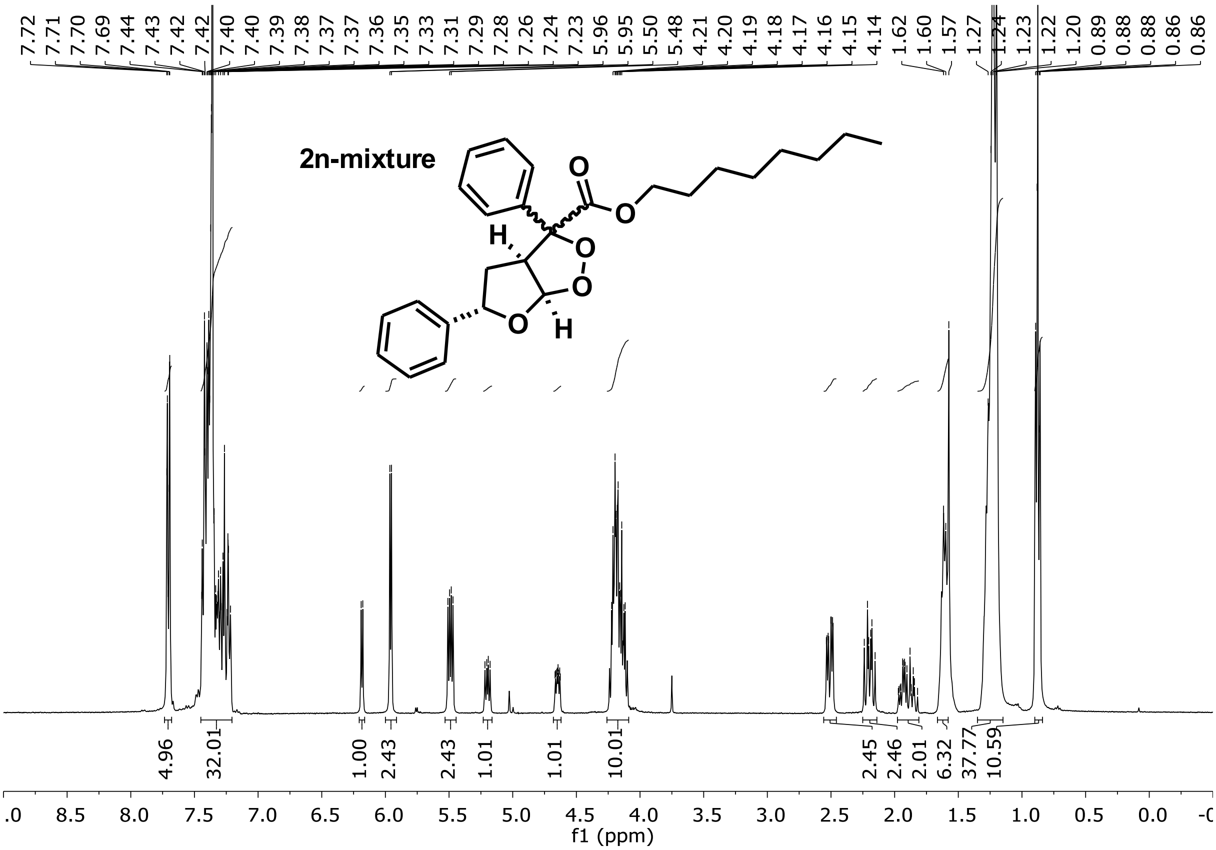
5.94 2.16 5.29 20.17 2.05 1.00 6.66 6.78 0.99 5.18 8.60 2.61 8.12 10.65 2.50 2.82 0.93 0.88 12.42 12.42 12.41 12.40
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
ppm


2m-mixture

168.03 164.89 145.76 137.65 130.02 129.87 129.12 128.76 128.53 126.17 125.85 125.38 112.40 109.42 108.03 105.14 92.59 92.28 83.38 81.07 79.96 72.58 67.28 61.18 53.57 53.12 26.86 26.76 26.23 25.24
CO2Me
H
O
O
O
H
O
O
H
O
O
O
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.37
7.37
7.36
7.35
7.33
7.31
7.29
7.28
7.26
7.24
7.23
5.96
5.95
5.50
5.48
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
1.62
1.60
1.57
1.27
1.24
1.23
1.22
1.20
0.89
0.88
0.88
0.86
0.86
2n-mixture
O
O
O
O
O
H
H
4.96
32.01
1.00
2.43
2.43
1.01
1.01
10.01
2.45
2.46
2.01
6.32
37.77
10.59
.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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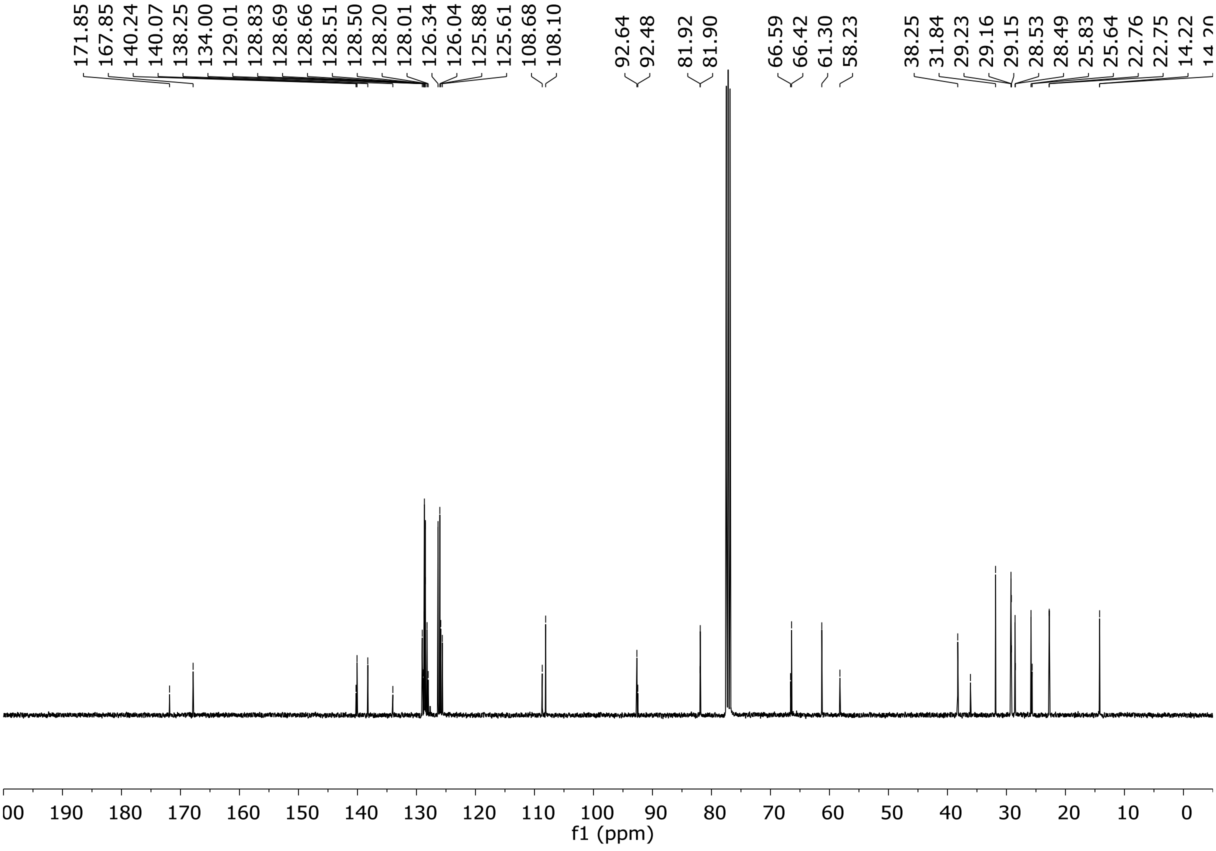
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)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128.20
128.01
126.34
126.04
125.88
125.61
108.68
108.10
92.64
92.48
81.92
81.90
66.59
66.42
61.30
58.23
38.25
31.84
29.23
29.16
29.15
28.53
28.49
25.83
25.64
22.76
22.75
14.22
14.20
00
190
180
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160
150
140
130
120
110
100
90
80
70
60
50
40
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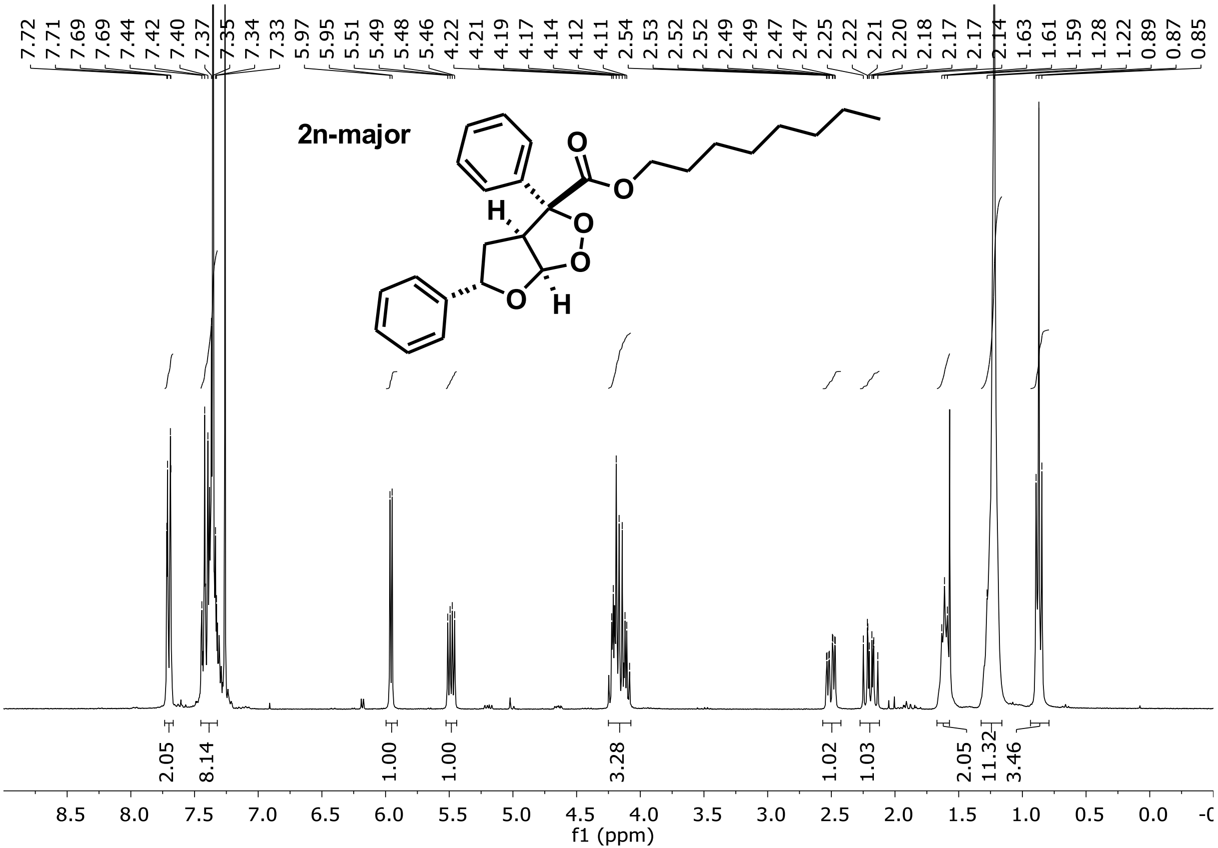
20
10
0
f1 (ppm)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7.42
7.40
7.37
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7.34
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5.95
5.51
5.49
5.48
5.46
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4.21
4.19
4.17
4.14
4.12
4.11
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2.20
2.18
2.17
2.17
2.14
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1.61
1.59
1.28
1.22
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0.87
0.85
2n-major
O
O
O
O
O
H
H
2.05
8.14
1.00
1.00
3.28
1.02
1.03
2.05
11.32
3.46
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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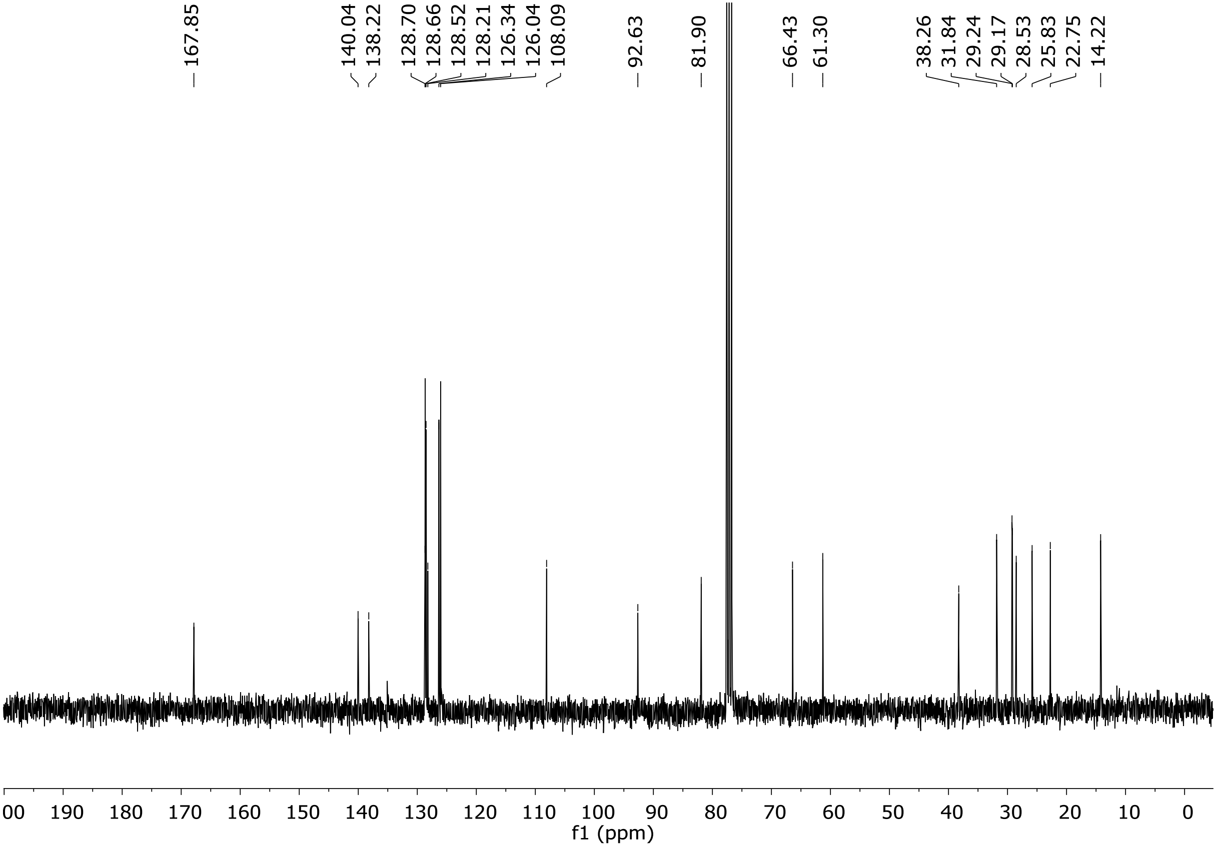
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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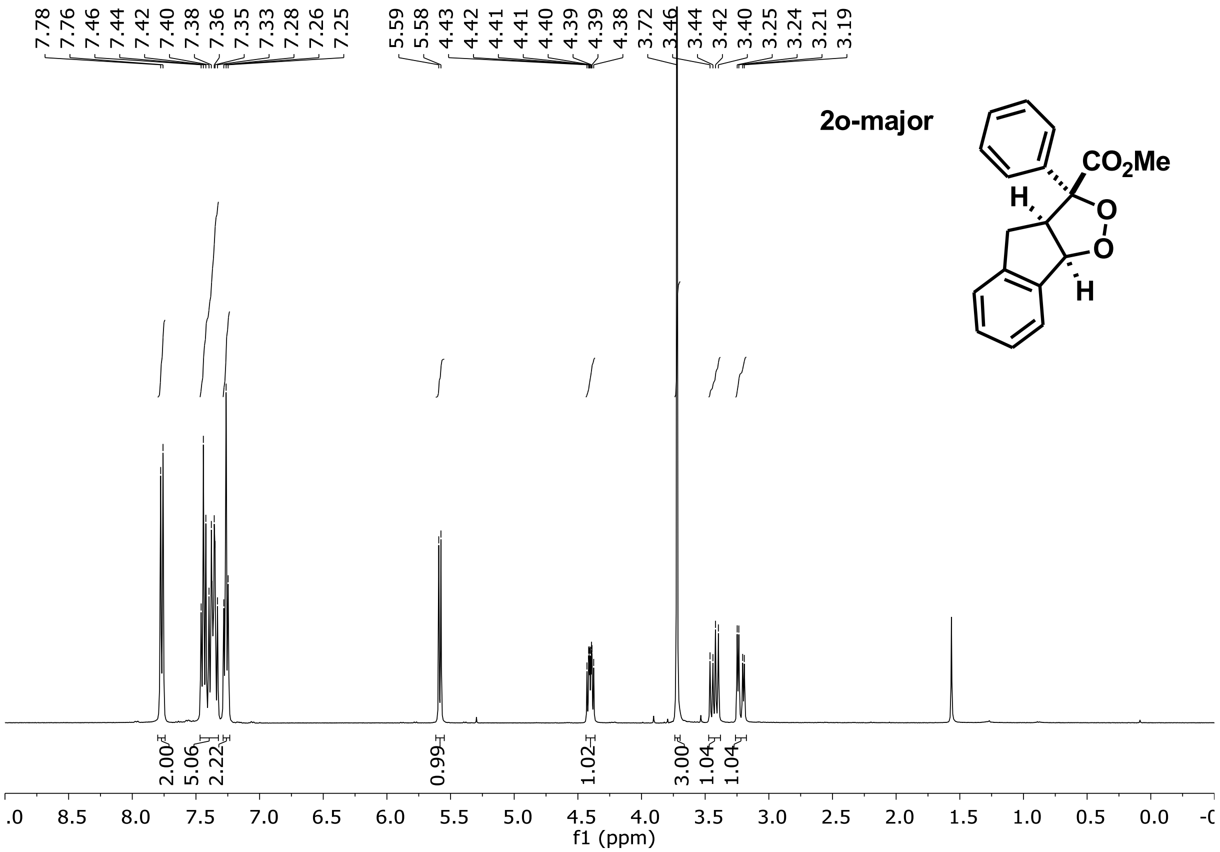
128.52
128.21
126.34
126.04
108.09
92.63
81.90
66.43
61.30
38.26
31.84
29.24
29.17
28.53
25.83
22.75
14.22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.25
5.59
5.58
4.43
4.42
4.41
4.41
4.40
4.39
4.39
4.38
3.72
3.46
3.44
3.42
3.40
3.25
3.24
3.21
3.19
2o-major
CO2Me
H
O
O
H
2.00
5.06
2.22
0.99
1.02
3.00
1.04
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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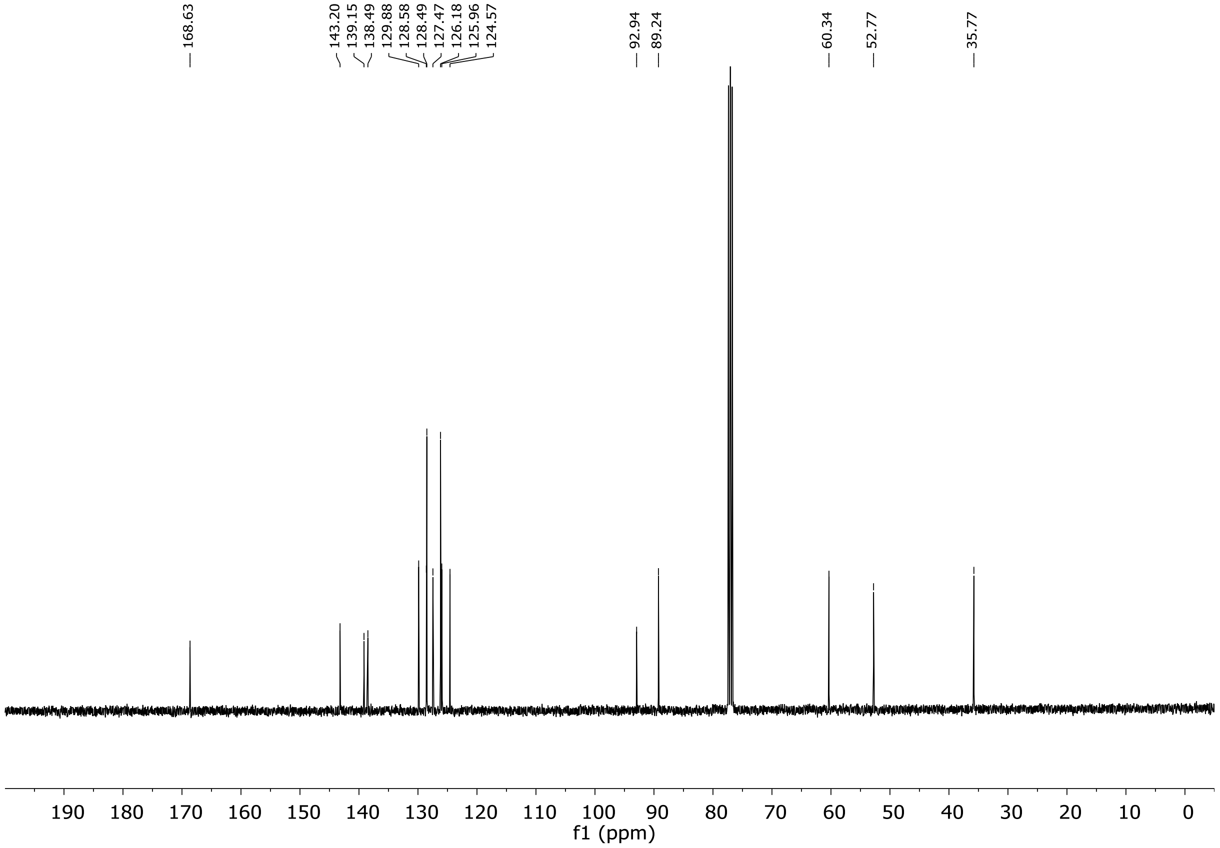
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)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126.18
125.96
124.57
92.94
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60.34
52.77
35.77
190
180
170
160
150
140
130
120
110
100
90
80
70
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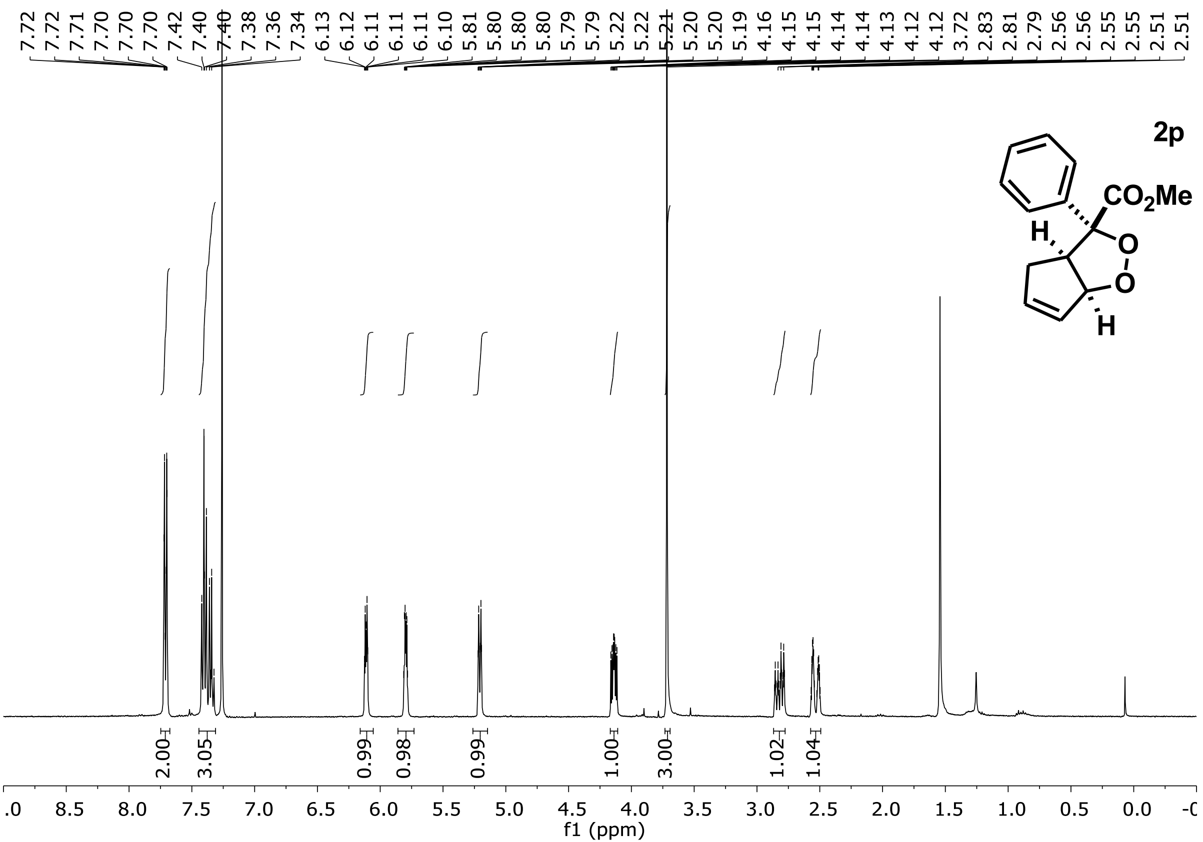
50
40
30
20
10
0
f1 (ppm)


2p
CO2Me
H
O
O
H
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7.72
7.71
7.70
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7.70
7.42
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7.40
7.38
7.36
7.34
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6.12
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6.11
6.11
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5.20
5.20
5.19
4.16
4.15
4.15
4.14
4.14
4.13
4.12
4.12
3.72
2.83
2.81
2.79
2.56
2.56
2.55
2.55
2.51
2.51
2.00
3.05
0.99
0.98
0.99
1.00
3.00
1.02
1.04
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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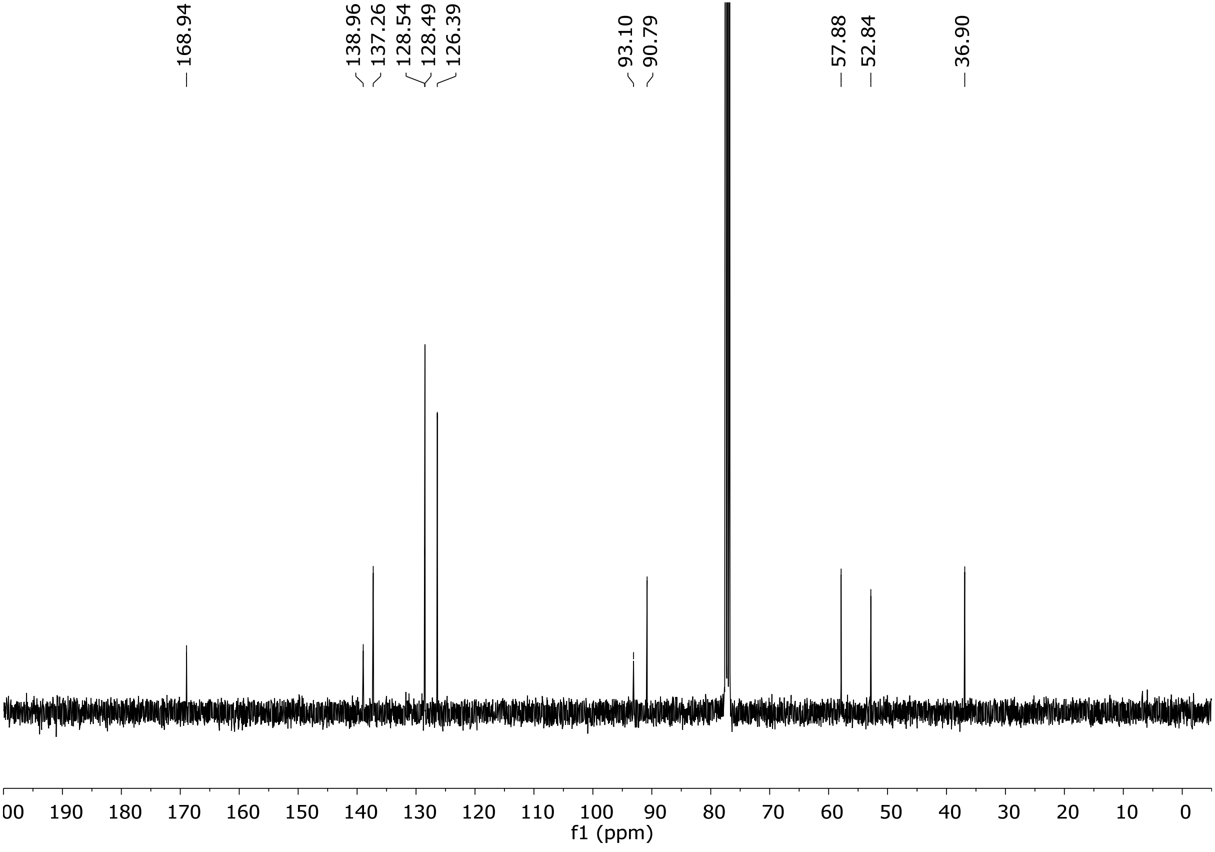
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)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00
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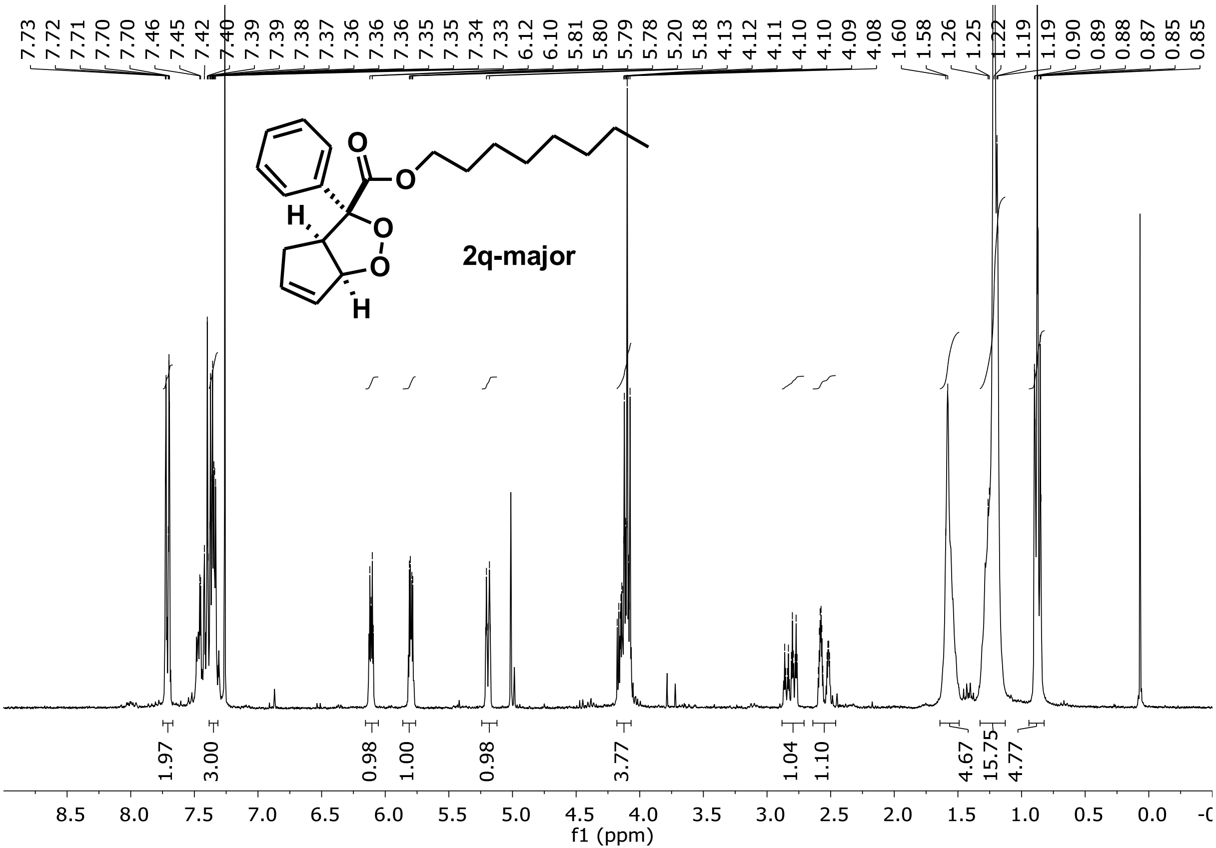
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.34
7.33
6.12
6.10
5.81
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5.78
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5.18
4.13
4.12
4.11
4.10
4.10
4.09
4.08
1.60
1.58
1.26
1.25
1.22
1.19
1.19
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0.89
0.88
0.87
0.85
0.85
O
O
H
O
O
H
2q-major
1.97
3.00
0.98
1.00
0.98
3.77
1.04
1.10
4.67
15.75
4.77
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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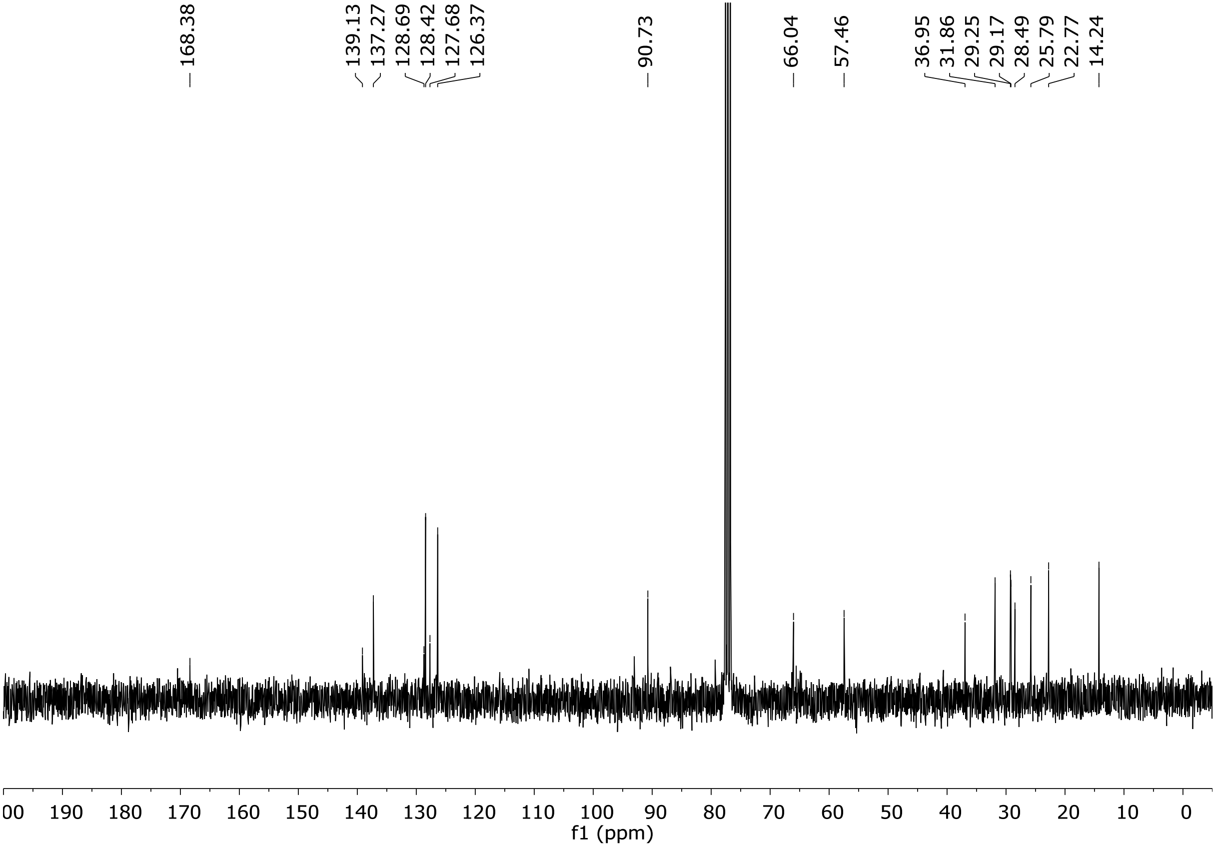
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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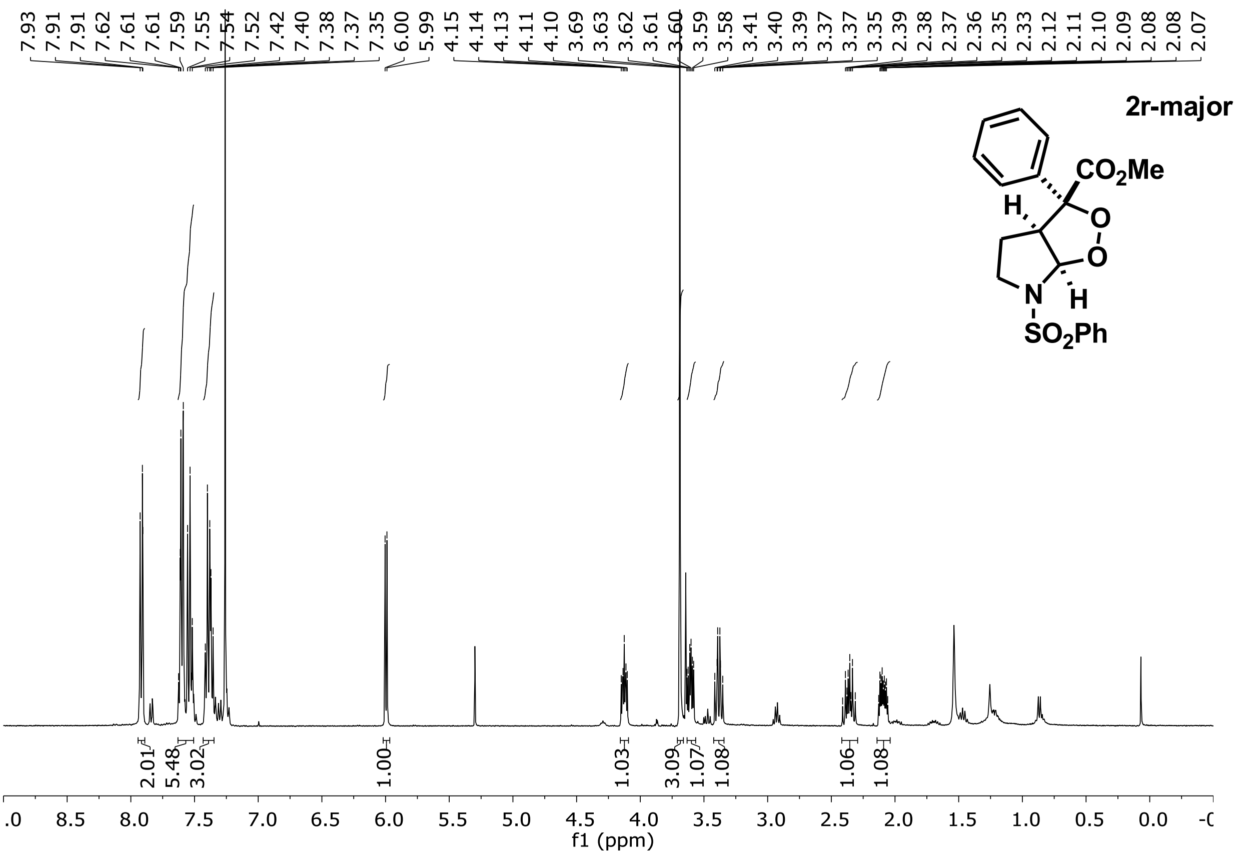
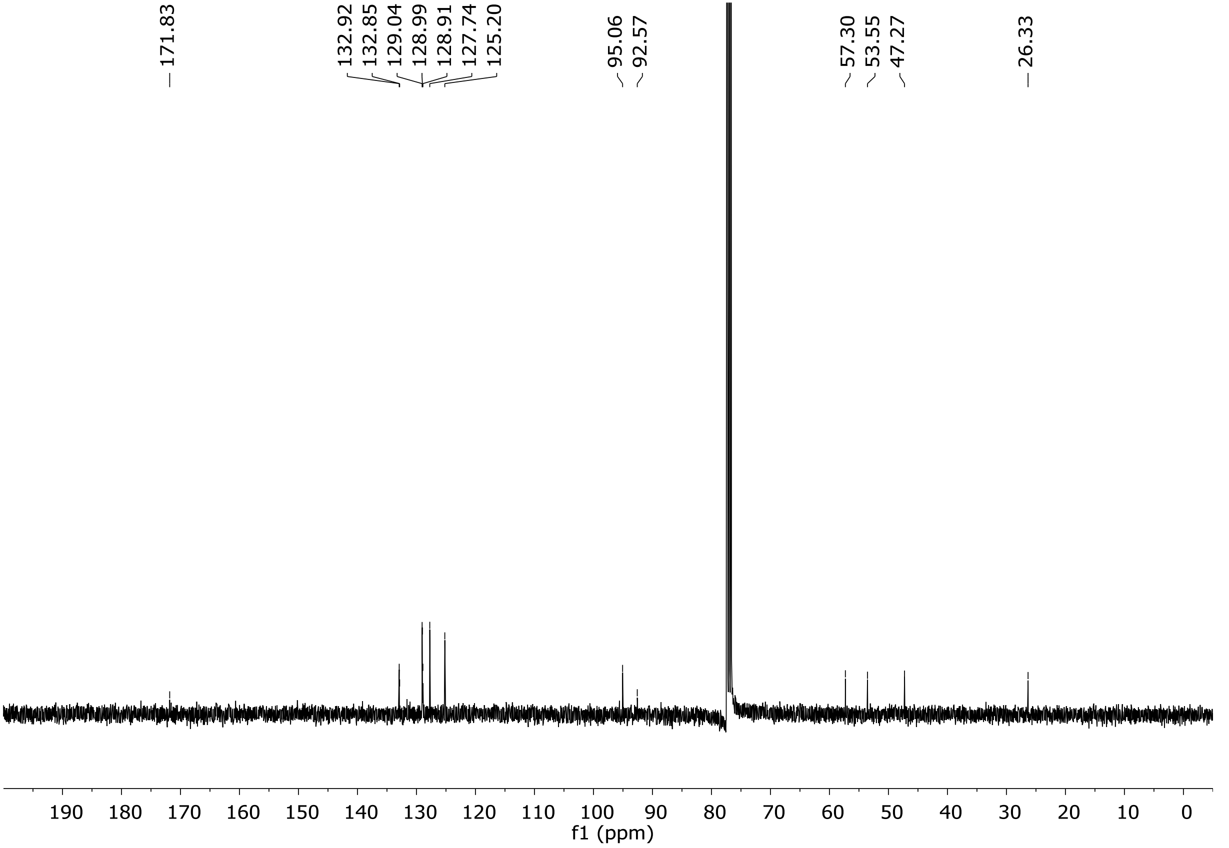
128.69
128.42
127.68
126.37
90.73
66.04
57.46
36.95
31.86
29.25
29.17
28.49
25.79
22.77
14.24
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.93
7.91
7.91
7.62
7.61
7.61
7.59
7.55
7.54
7.52
7.42
7.40
7.38
7.37
7.35
6.00
5.99
4.15
4.14
4.13
4.11
4.10
3.69
3.63
3.62
3.61
3.60
3.59
3.58
3.41
3.40
3.39
3.37
3.37
3.35
2.39
2.38
2.37
2.36
2.35
2.33
2.12
2.11
2.10
2.09
2.08
2.08
2.07
CO2Me
H
O
O
N
H
SO2Ph
2.01
5.48
3.02
1.00
1.03
3.09
1.07
1.08
1.06
1.08
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

2r-major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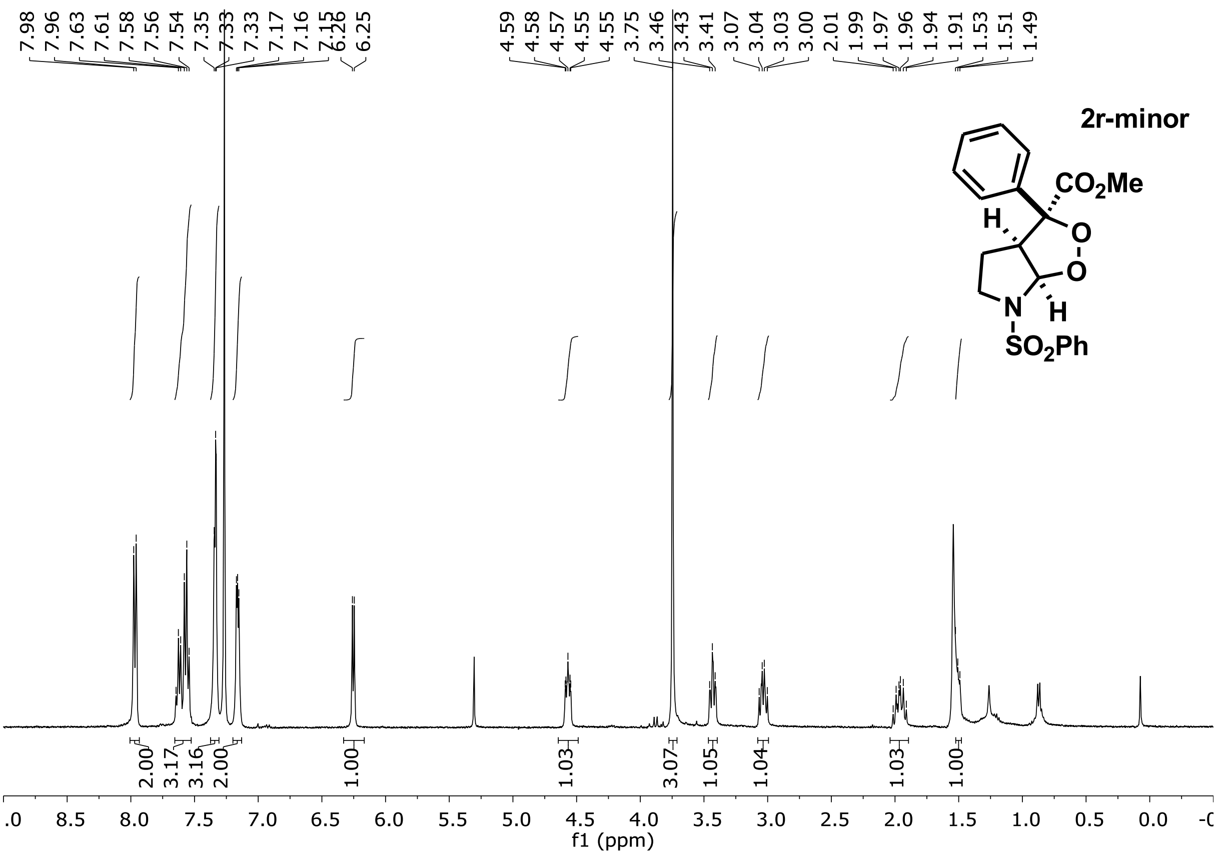
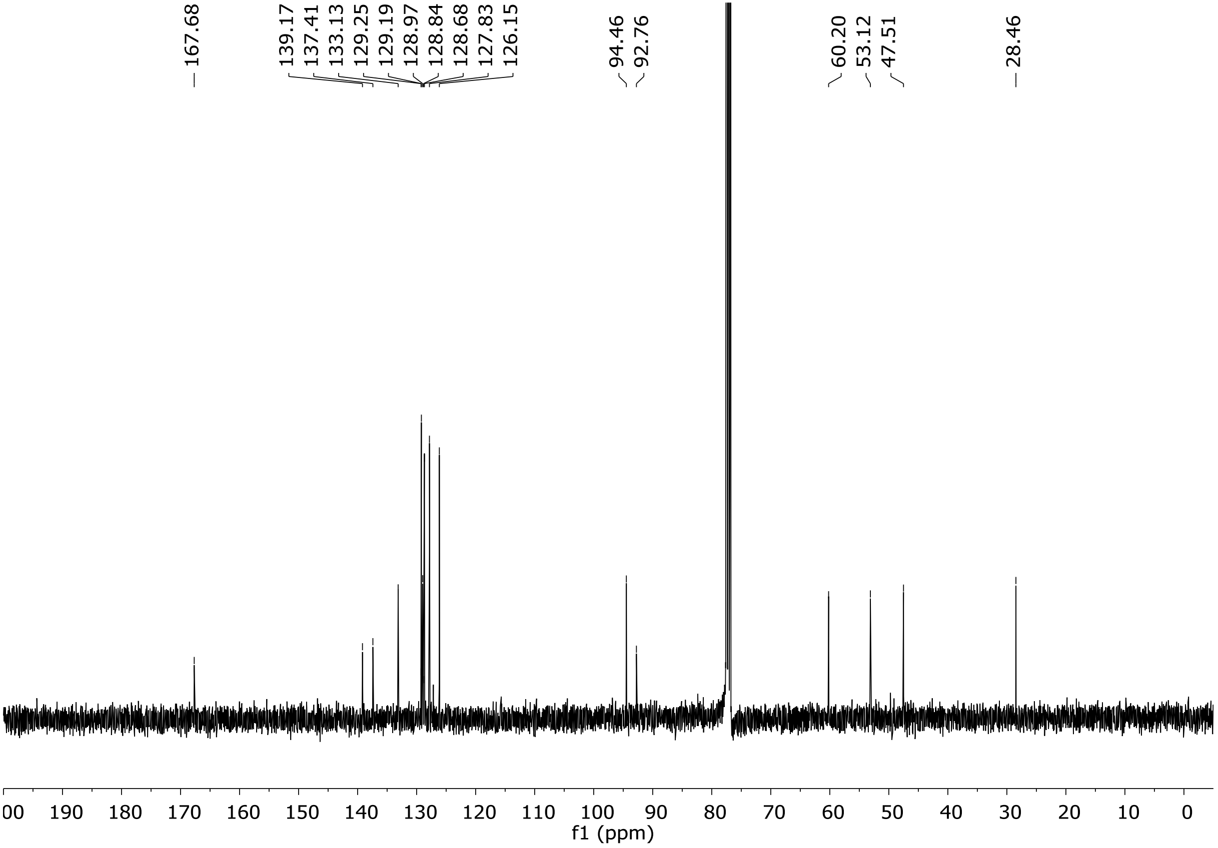
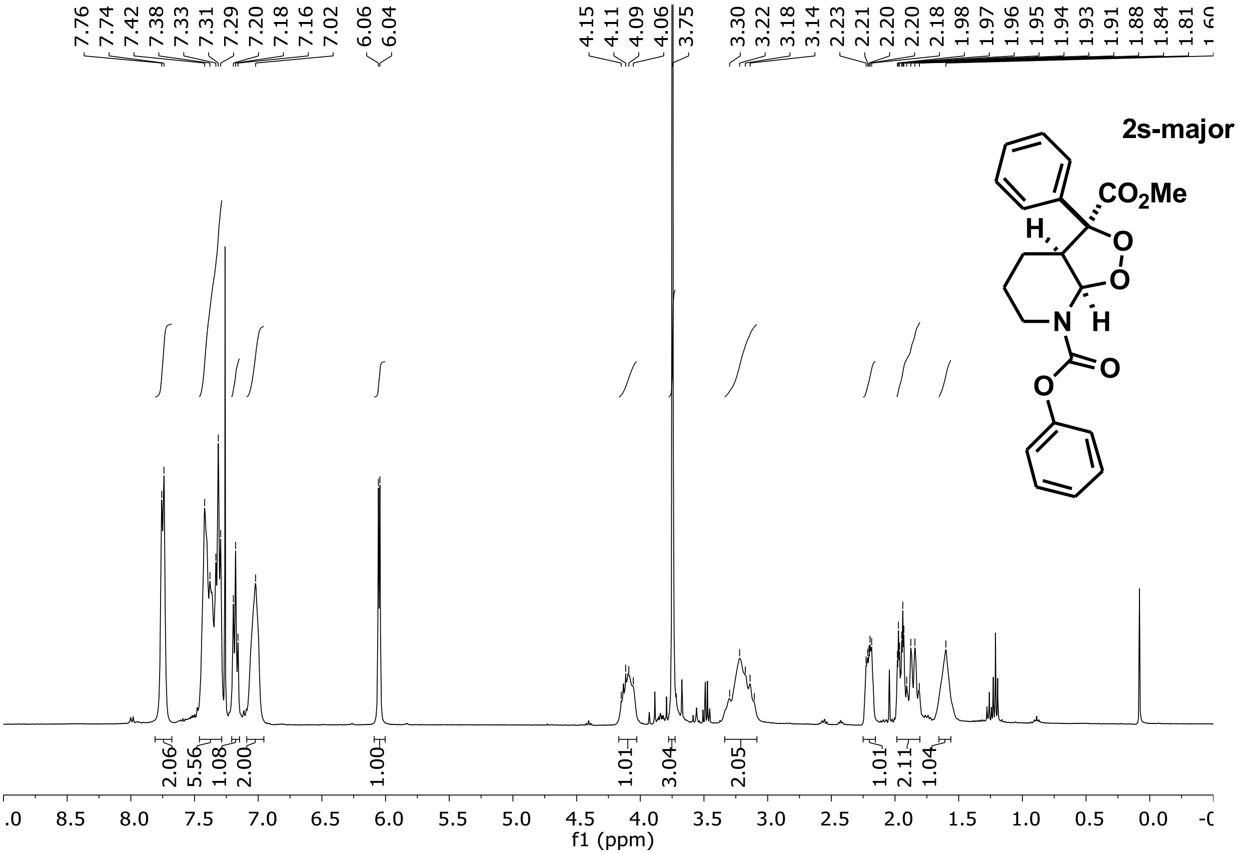
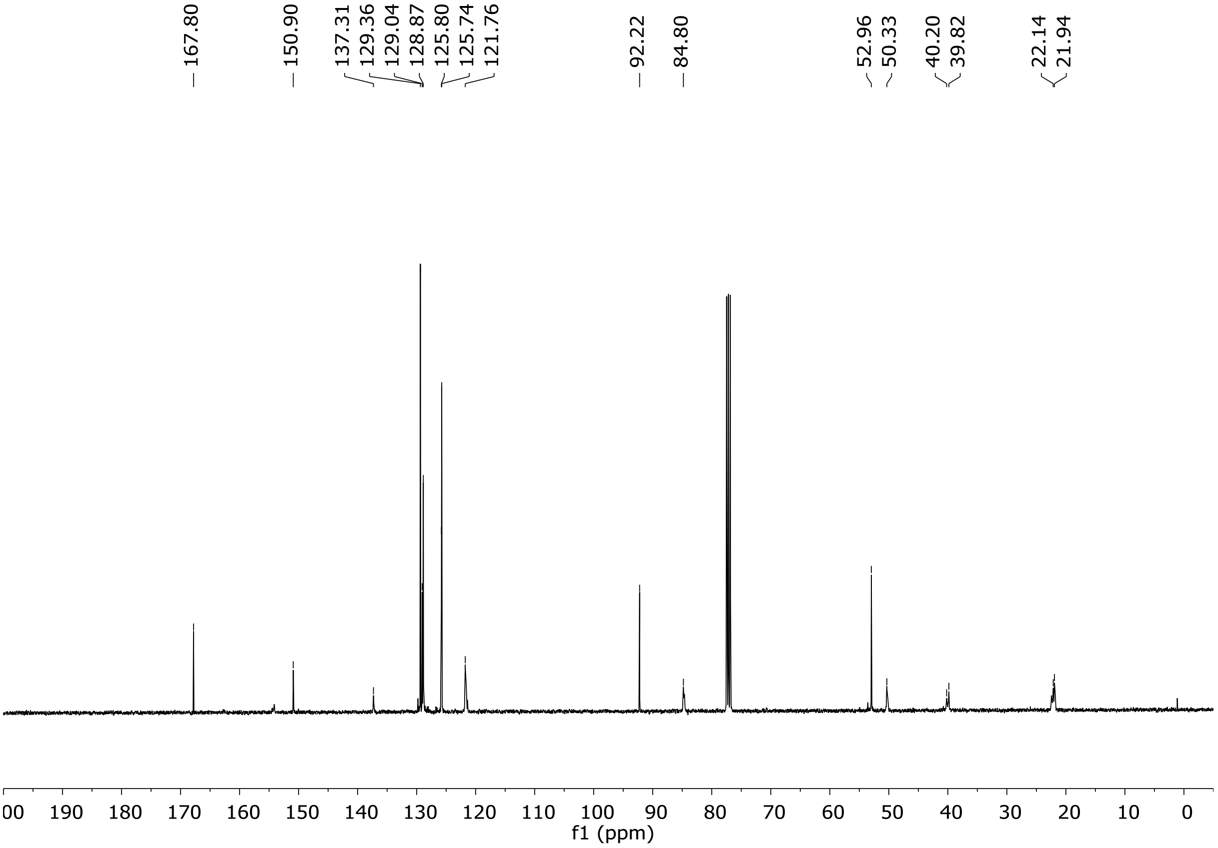
132.92
132.85
129.04
128.99
128.91
127.74
125.20
95.06
92.57
57.30
53.55
47.27
26.33
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.98
7.96
7.63
7.61
7.58
7.56
7.54
7.35
7.33
7.33
7.17
7.16
7.15
6.26
6.25
4.59
4.58
4.57
4.55
4.55
3.75
3.46
3.43
3.41
3.07
3.04
3.03
3.00
2.01
1.99
1.97
1.96
1.94
1.91
1.53
1.51
1.49
2r-minor
CO2Me
H
O
O
N
H
SO2Ph
2.00
3.17
3.16
2.00
1.00
1.03
3.07
1.05
1.04
1.03
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)


167.68
139.17
137.41
133.13
129.25
129.19
128.97
128.84
128.68
127.83
126.15
94.46
92.76
60.20
53.12
47.51
28.46
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.76
7.74
7.42
7.38
7.33
7.31
7.29
7.20
7.18
7.16
7.02
6.06
6.04
4.15
4.11
4.09
4.06
3.75
3.30
3.22
3.18
3.14
2.23
2.21
2.20
2.20
2.18
1.98
1.97
1.96
1.95
1.94
1.93
1.91
1.88
1.84
1.81
2s-major
CO2Me
H
O
O
N
H
O
O
2.06
5.56
1.08
2.00
1.00
1.01
3.04
2.05
1.01
2.11
1.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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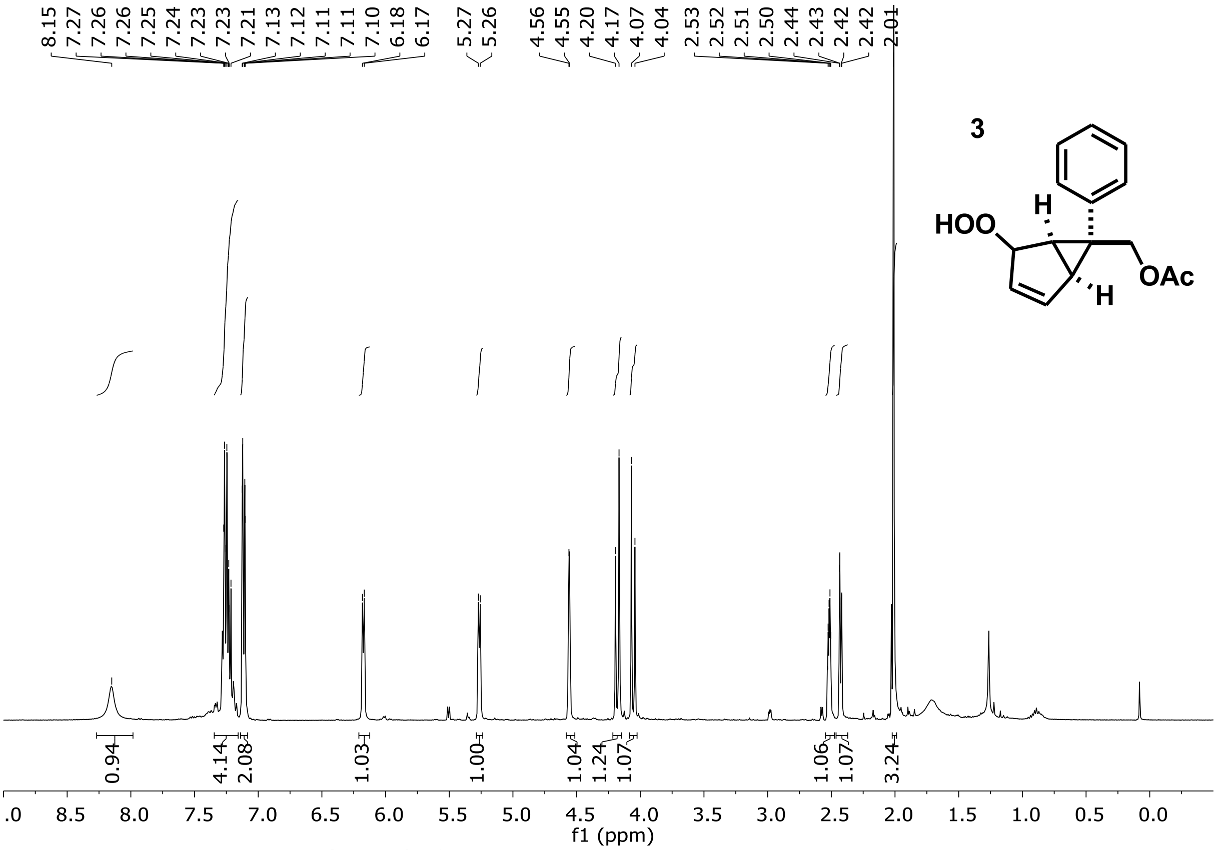
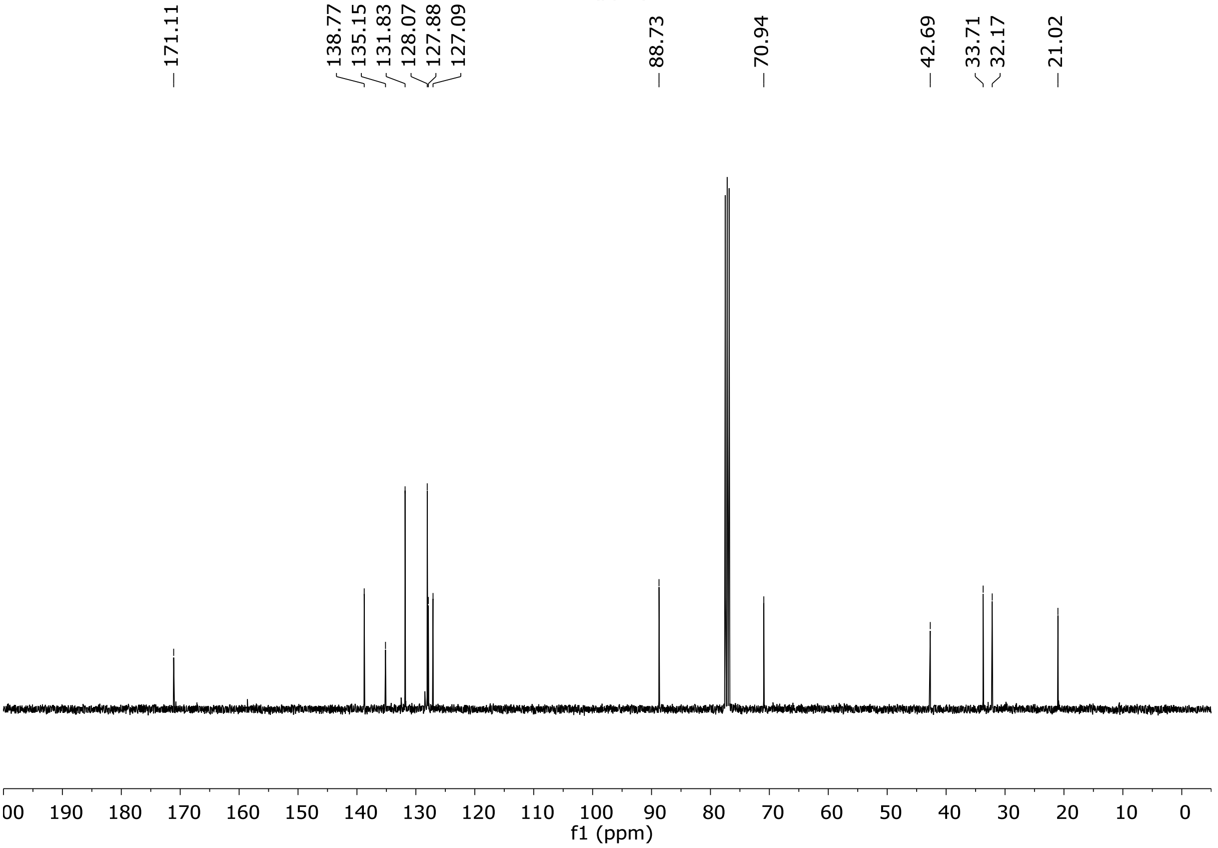
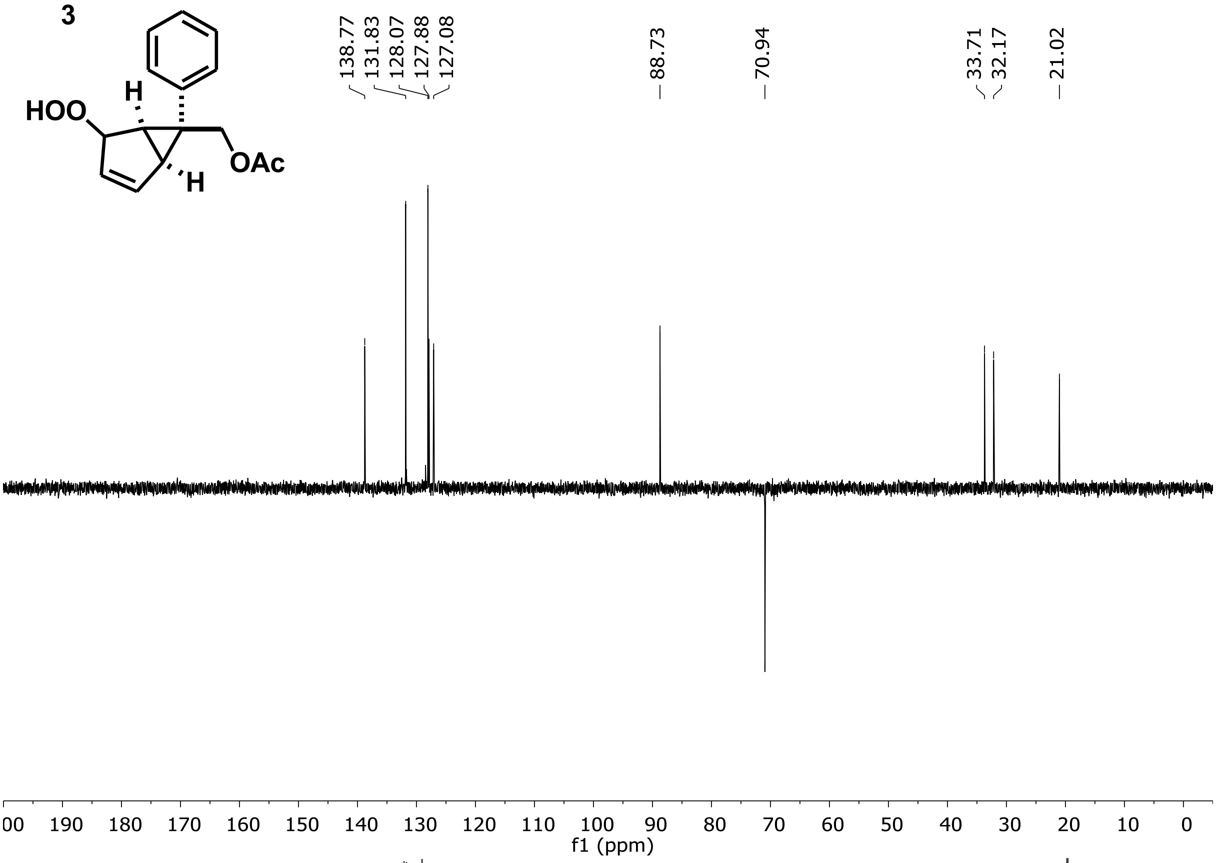
150.90
137.31
129.36
129.04
128.87
125.80
125.74
121.76
92.22
84.80
52.96
50.33
40.20
39.82
22.14
21.94
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

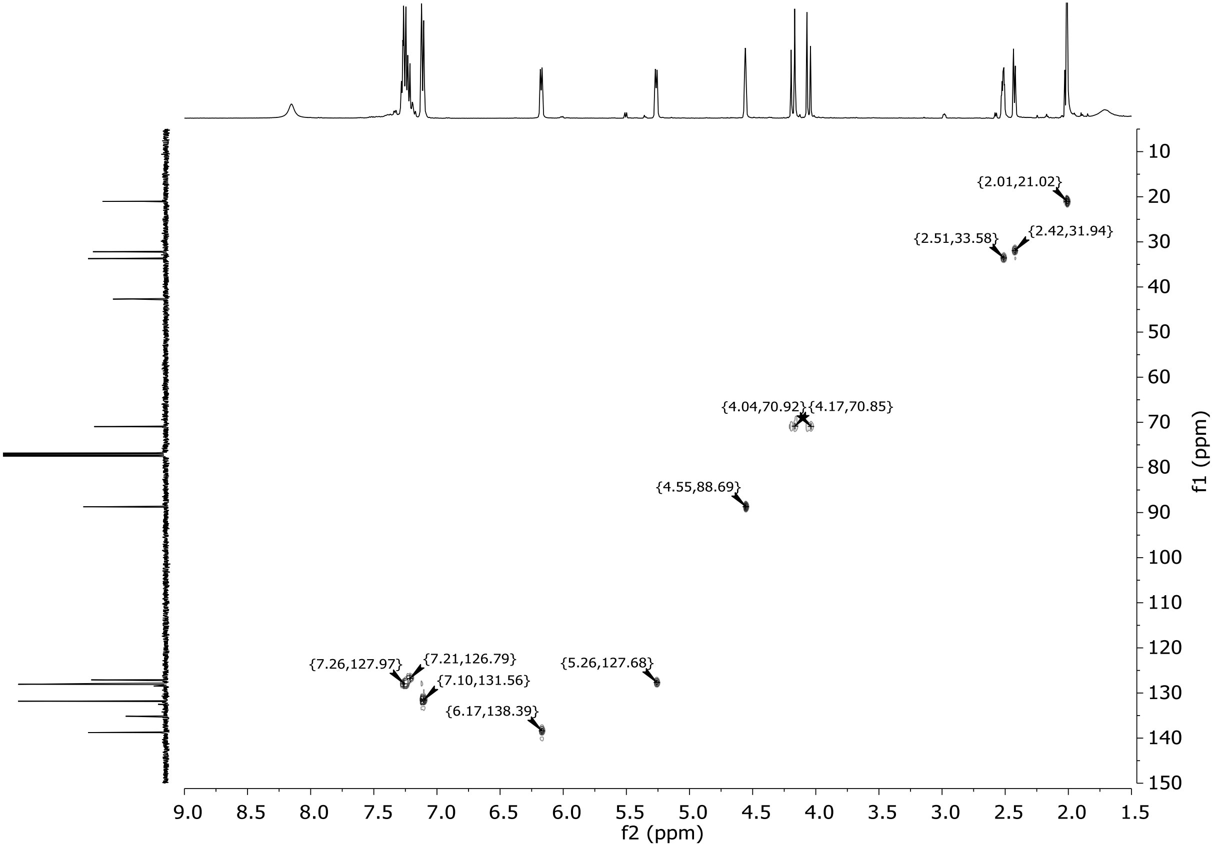
Others

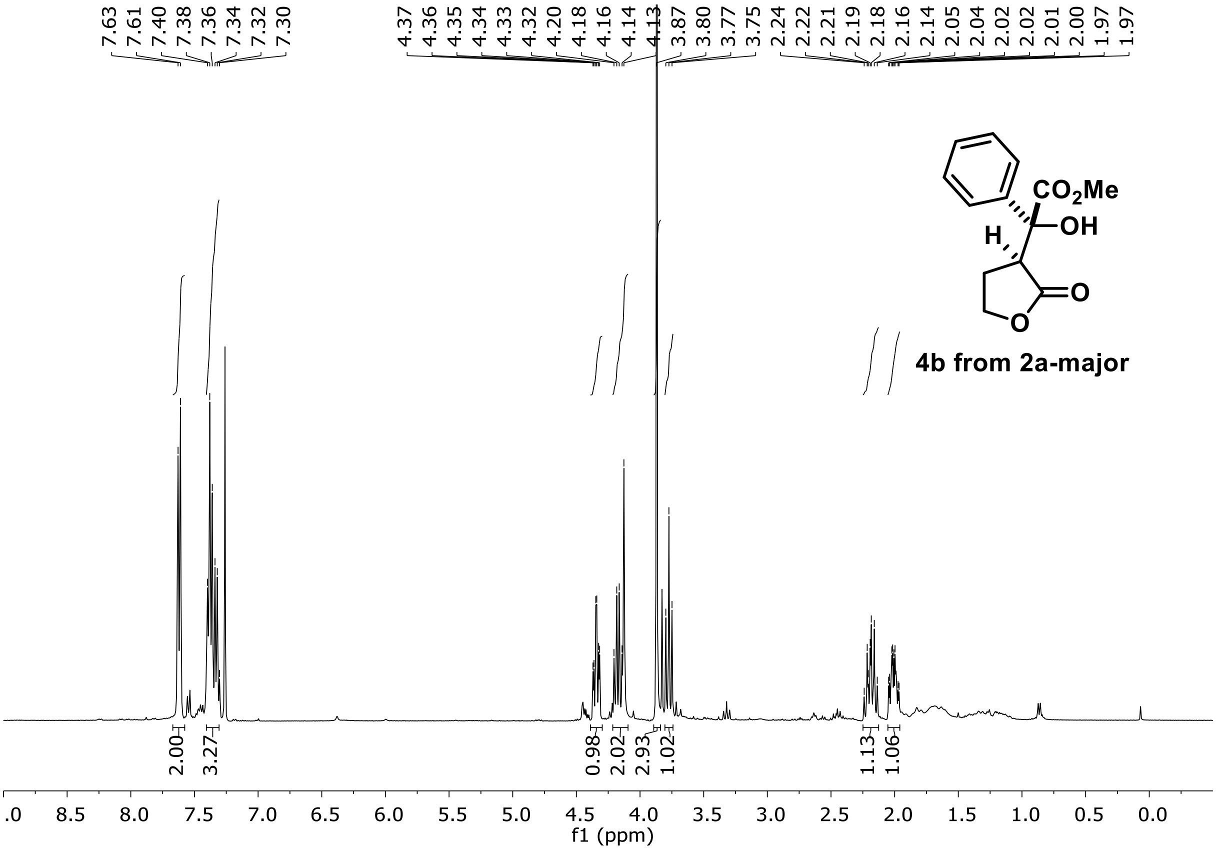

8.15
7.27
7.26
7.26
7.25
7.24
7.23
7.23
7.21
7.13
7.12
7.11
7.11
7.10
6.18
6.17
5.27
5.26
4.56
4.55
4.20
4.17
4.07
4.04
2.53
2.52
2.51
2.50
2.44
2.43
2.42
2.42
2.01
3
H
HOO
OAc
H
0.94
4.14
2.08
1.03
1.00
1.04
1.24
1.07
1.06
1.07
3.24
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

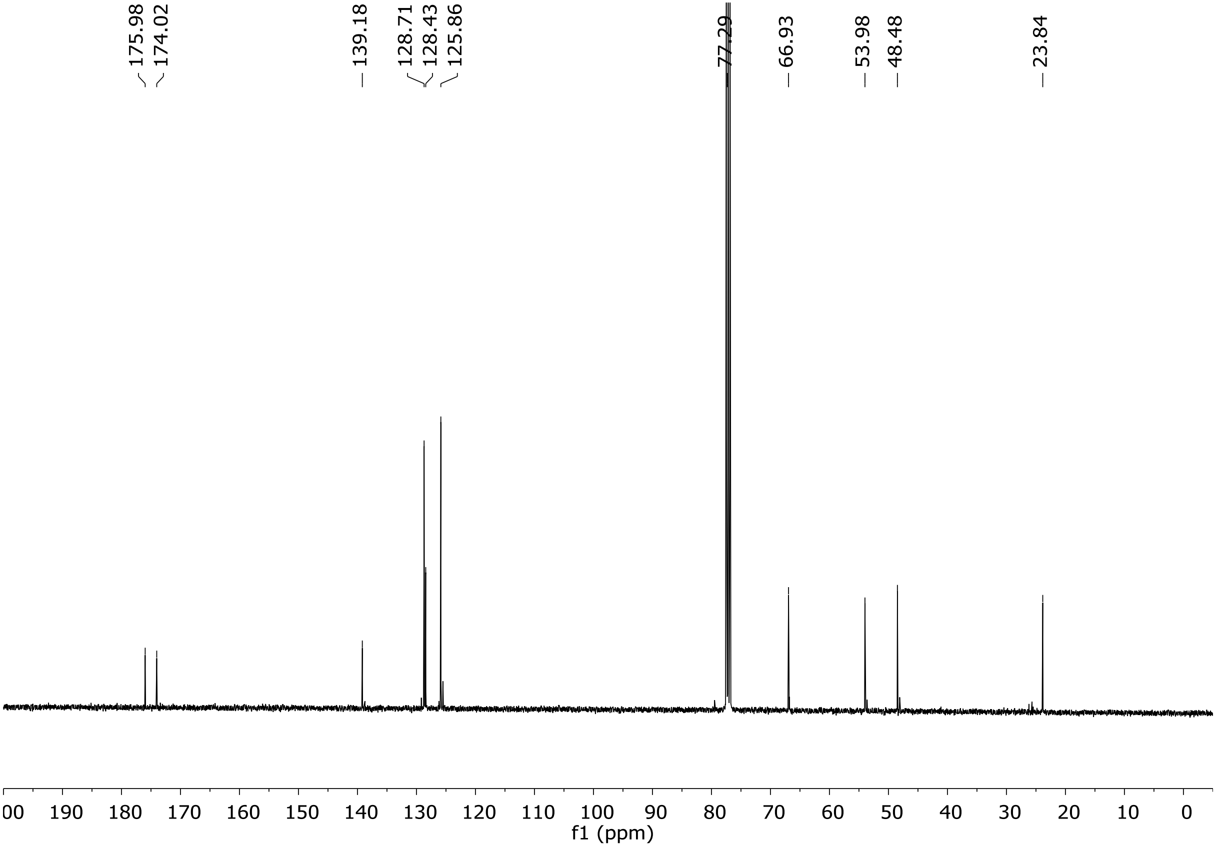

171.11
138.77
135.15
131.83
128.07
127.88
127.09
88.73
70.94
42.69
33.71
32.17
21.02
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

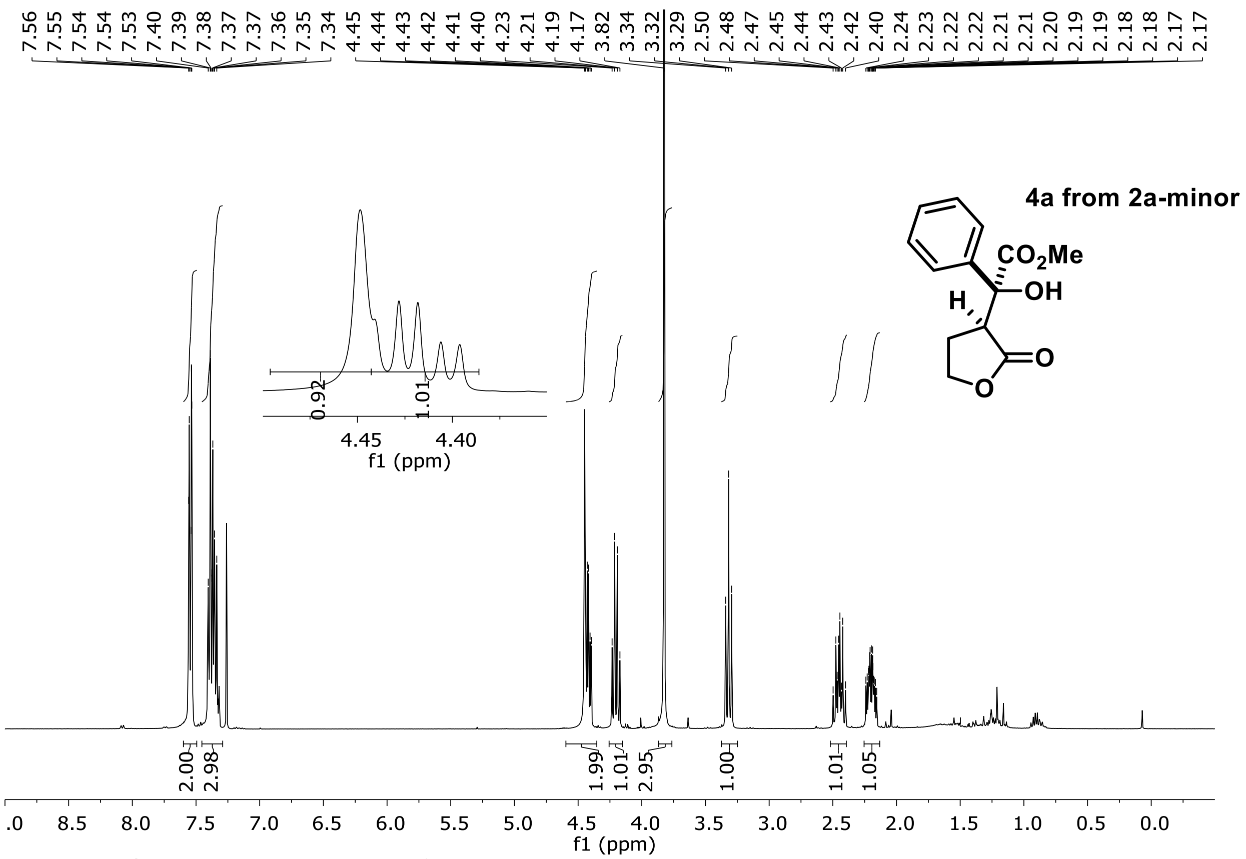
3

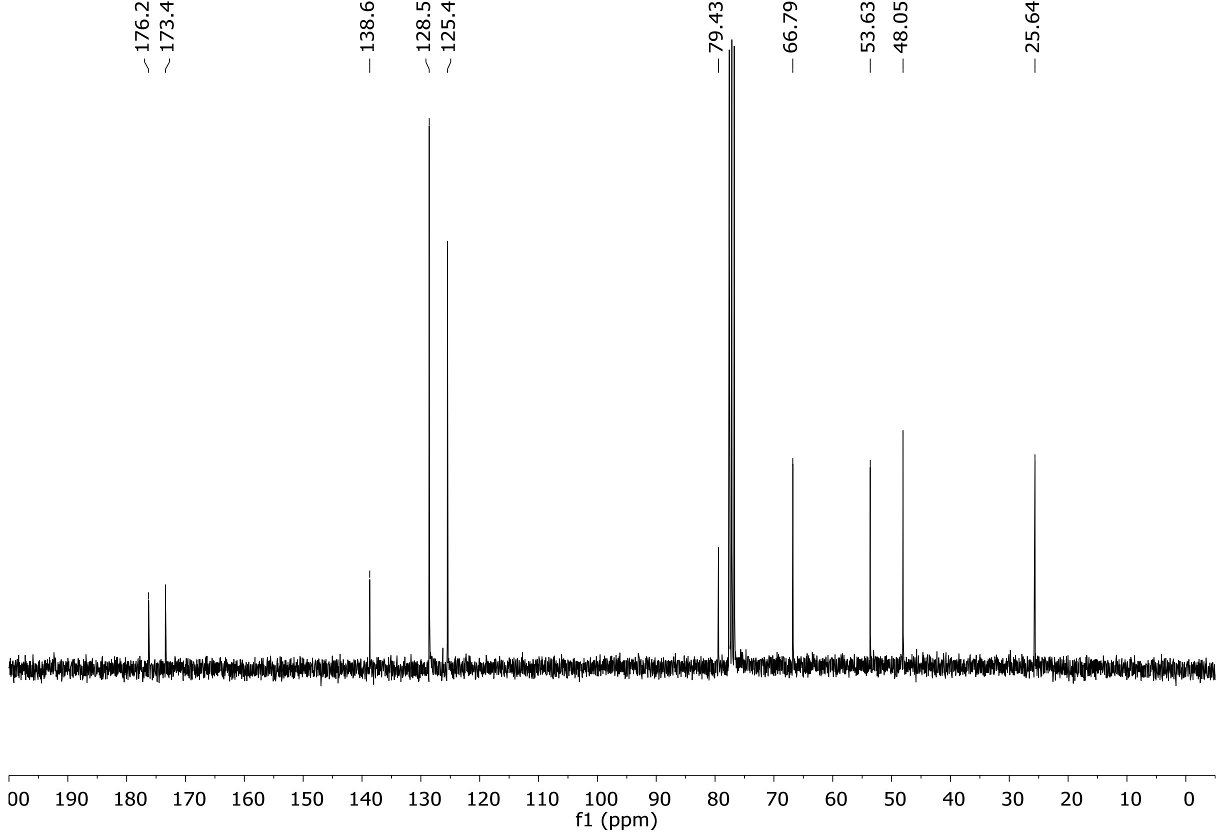

HOO
H
H
OAc
138.77
131.83
128.07
127.88
127.08
88.73
70.94
33.71
32.17
21.02
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


{2.01,21.02}
{2.51,33.58}
{2.42,31.94}
{4.04,70.92}
{4.17,70.85}
{4.55,88.69}
{7.26,127.97}
{7.21,126.79}
{7.10,131.56}
{5.26,127.68}
{6.17,138.39}
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)


7.63
7.61
7.40
7.38
7.36
7.34
7.32
7.30
4.37
4.36
4.35
4.34
4.33
4.32
4.20
4.18
4.16
4.14
4.13
3.87
3.80
3.77
3.75
2.24
2.22
2.21
2.19
2.18
2.16
2.14
2.05
2.04
2.02
2.02
2.01
2.00
1.97
1.97
CO2Me
OH
H
O
O
4b from 2a-major
2.00
3.27
0.98
2.02
2.93
1.02
1.13
1.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.98
174.02
139.18
128.71
128.43
125.86
77.29
66.93
53.98
48.48
23.84
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.56
7.55
7.54
7.54
7.53
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.34
4.45
4.44
4.43
4.42
4.41
4.40
4.23
4.21
4.19
4.17
3.82
3.34
3.32
3.29
2.50
2.48
2.47
2.45
2.44
2.43
2.42
2.40
2.24
2.23
2.22
2.22
2.21
2.21
2.20
2.19
2.19
2.18
2.18
2.17
2.17
4a from 2a-minor
CO2Me
OH
H
O
O
0.92
1.01
4.45
4.40
f1 (ppm)
2.00
2.98
1.99
1.01
2.95
1.00
1.01
1.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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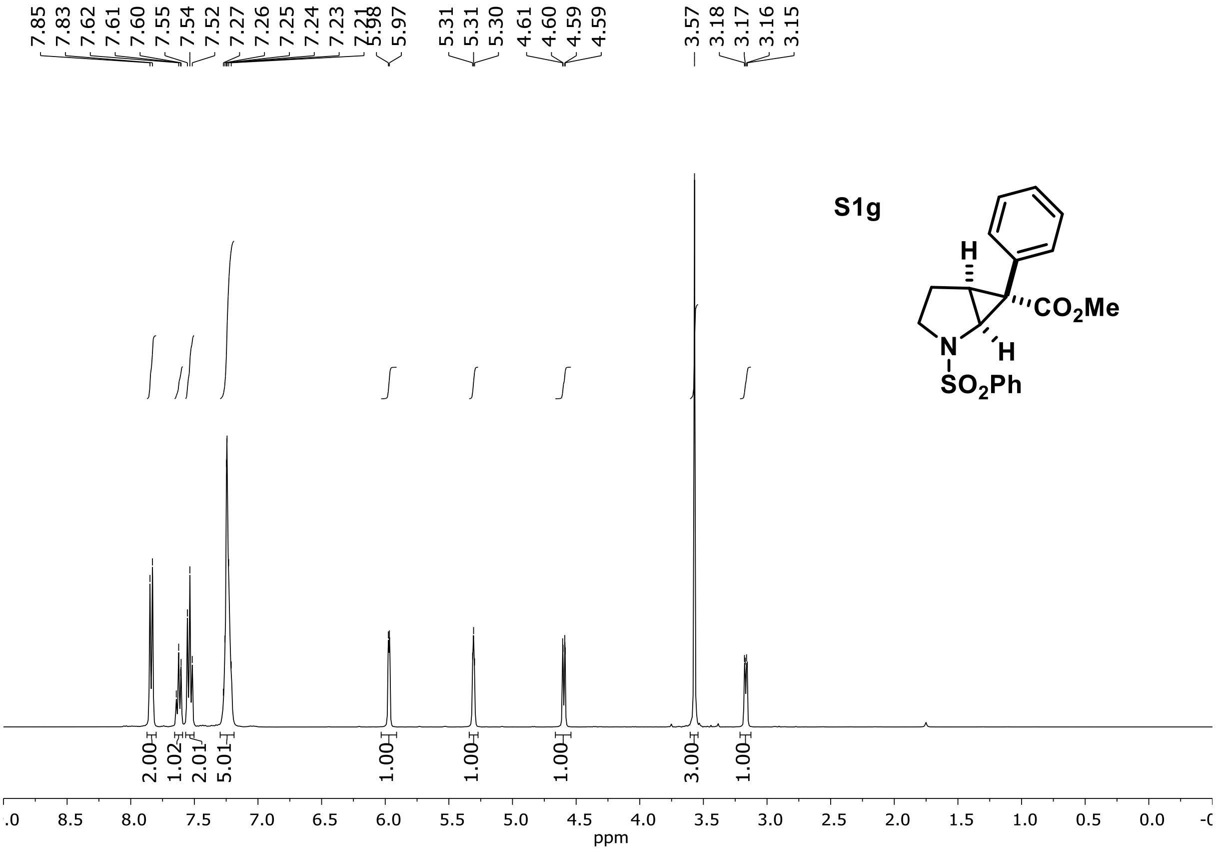
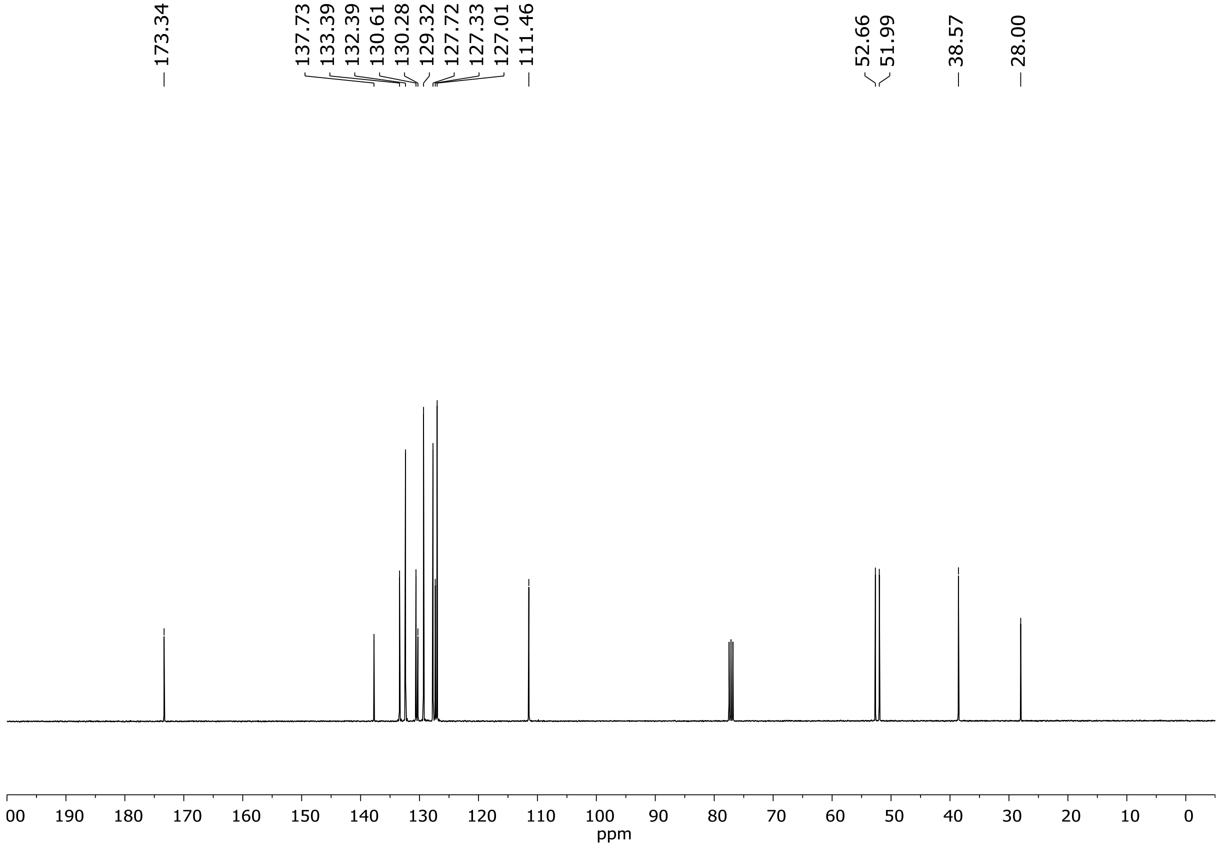
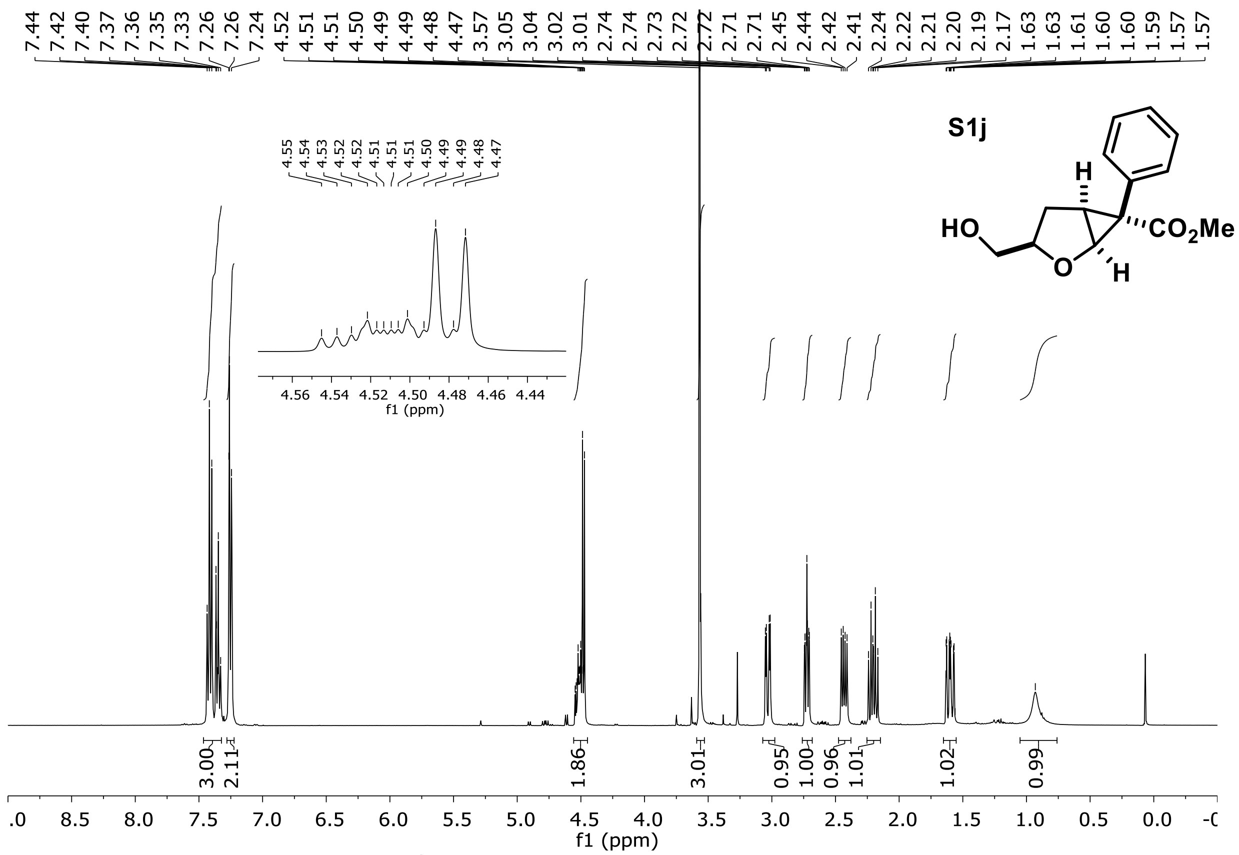
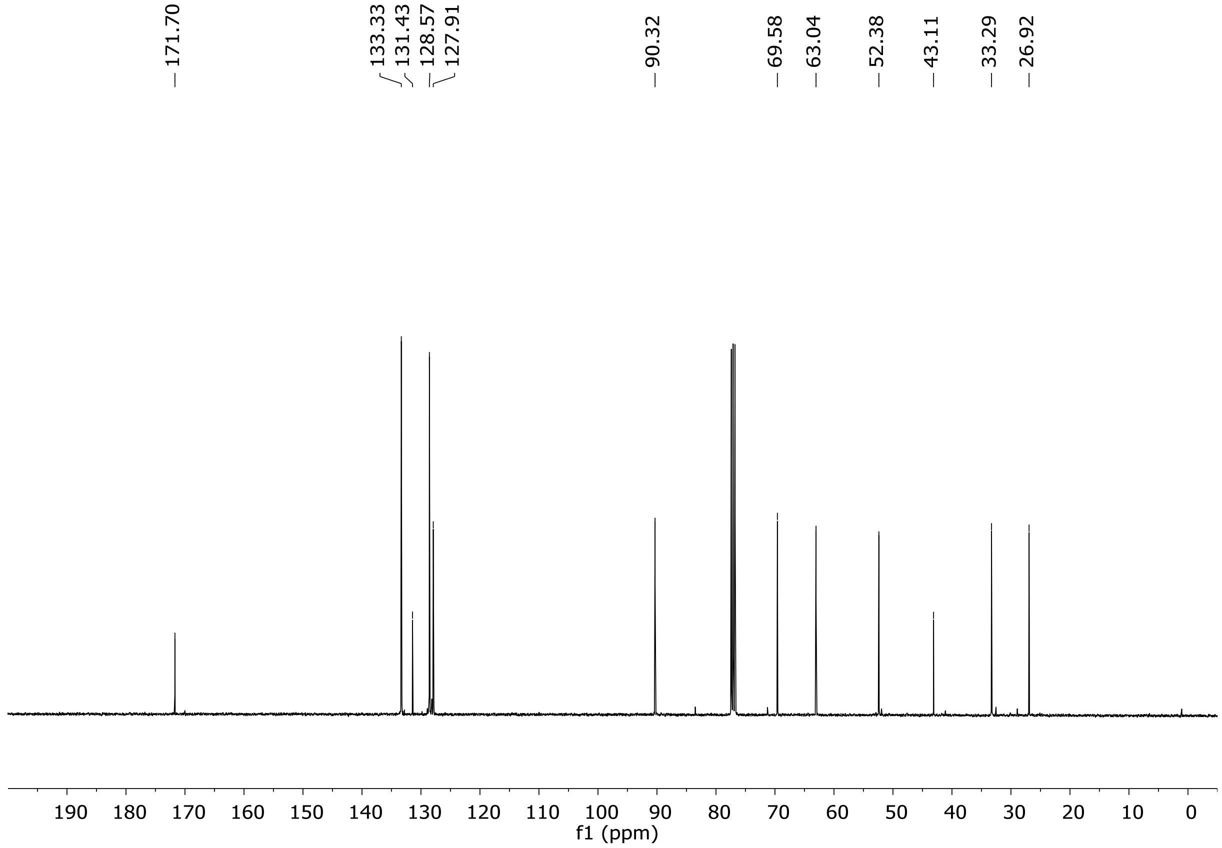
173.41
138.69
128.58
125.49
79.43
66.79
53.63
48.05
25.64
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

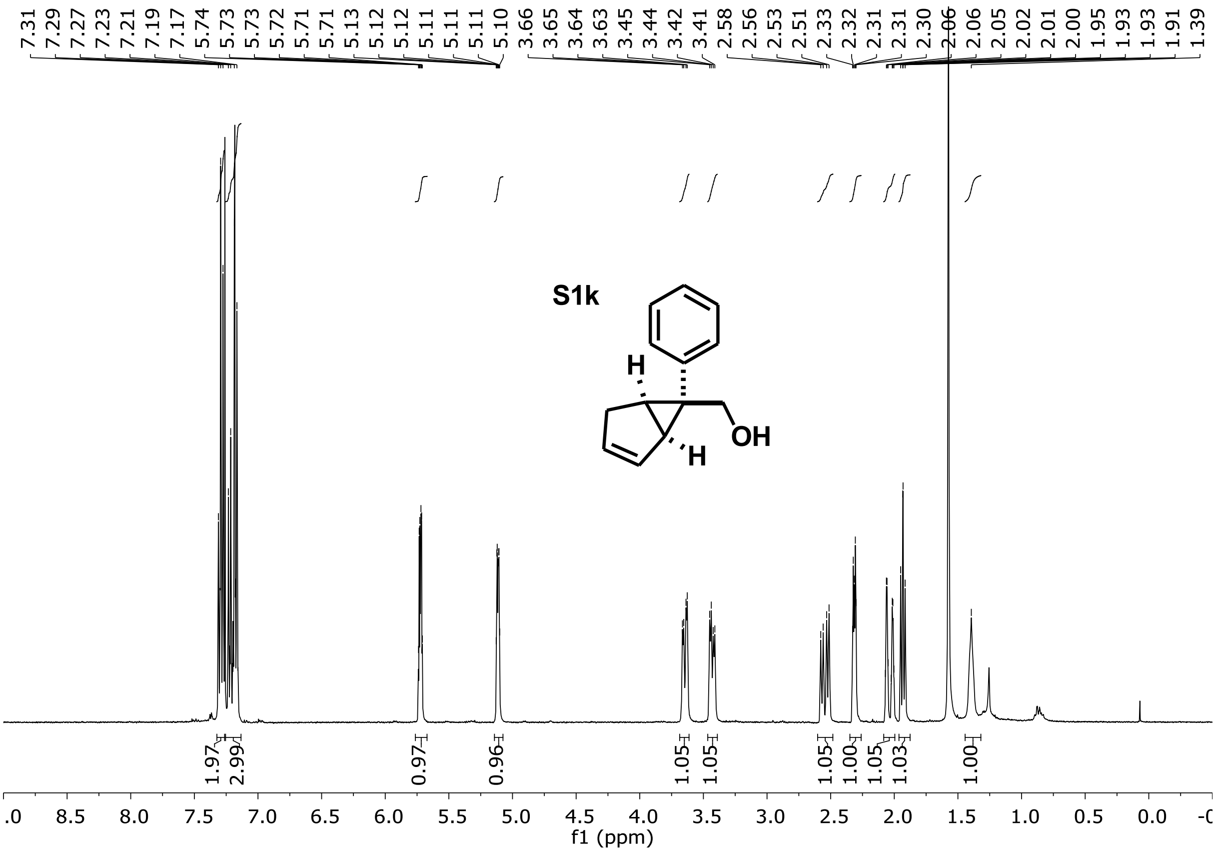

7.85
7.83
7.62
7.61
7.60
7.55
7.54
7.52
7.27
7.26
7.25
7.24
7.23
7.21
5.98
5.97
5.31
5.31
5.30
4.61
4.60
4.59
4.59
3.57
3.18
3.17
3.16
3.15
S1g
H
CO2Me
N
H
SO2Ph
2.00
1.02
2.01
5.01
1.00
1.00
1.00
3.00
1.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
ppm

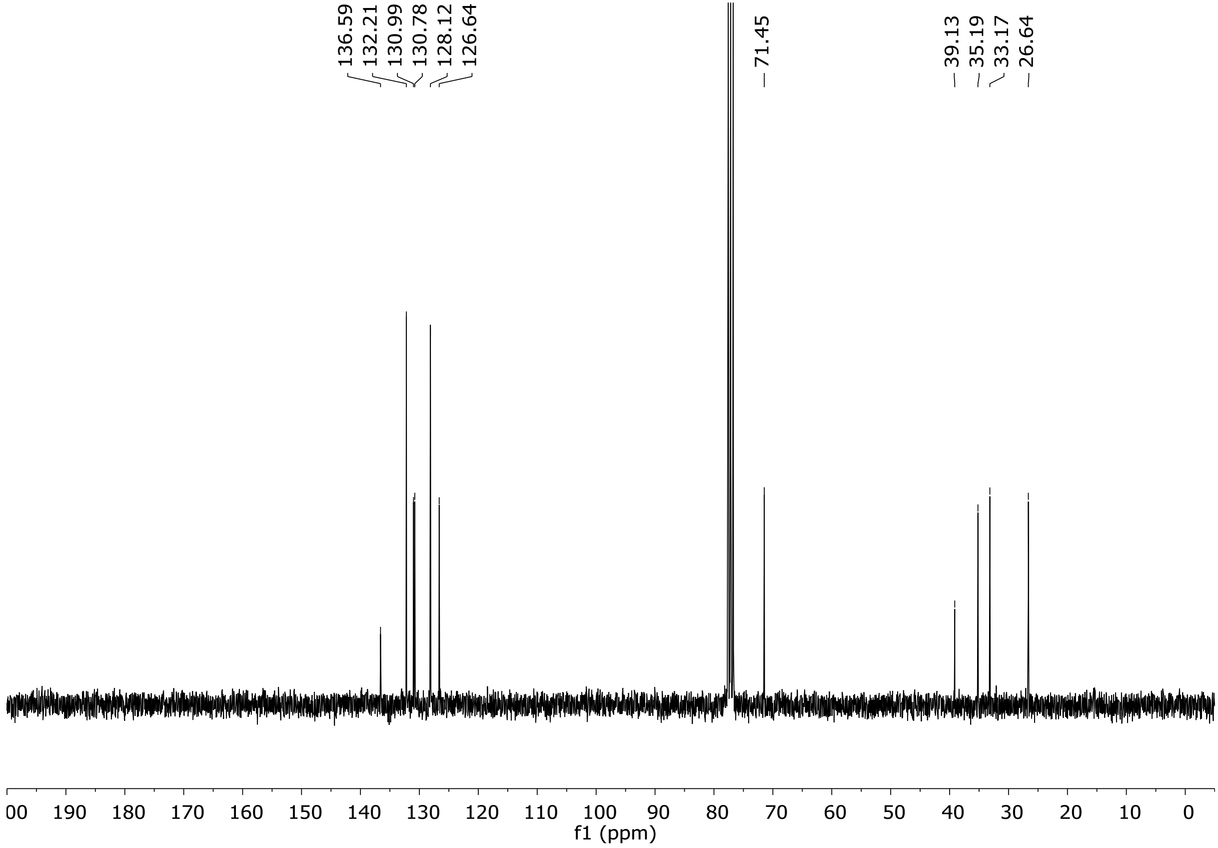

173.34
137.73
133.39
132.39
130.61
130.28
129.32
127.72
127.33
127.01
111.46
52.66
51.99
38.57
28.00
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


S1j
7.44
7.42
7.40
7.37
7.36
7.35
7.33
7.26
7.26
7.24
4.52
4.51
4.51
4.50
4.49
4.49
4.48
4.47
3.57
3.05
3.04
3.02
3.01
2.74
2.74
2.73
2.72
2.72
2.71
2.71
2.45
2.44
2.42
2.41
2.24
2.22
2.21
2.20
2.19
2.17
1.63
1.63
1.61
1.60
1.59
1.57
1.57
4.55
4.54
4.53
4.52
4.52
4.51
4.51
4.50
4.49
4.49
4.48
4.47
4.56 4.54 4.52 4.50 4.48 4.46 4.44
f1 (ppm)
H
HO
O
H
CO2Me
3.00
2.11
1.86
3.01
0.95
1.00
0.96
1.01
1.02
0.99
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -(
f1 (ppm)


171.70
133.33
131.43
128.57
127.91
90.32
69.58
63.04
52.38
43.11
33.29
26.92
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S1k


7.31 7.29 7.27 7.23 7.21 7.19 7.17 5.74 5.73 5.73 5.72 5.71 5.71 5.13 5.12 5.12 5.11 5.11 5.11 5.10 3.66 3.65 3.64 3.63 3.45 3.44 3.42 3.41 2.58 2.56 2.53 2.51 2.33 2.32 2.31 2.31 2.30 2.06 2.06 2.05 2.02 2.01 2.00 1.95 1.93 1.93 1.91 1.39
H
H
OH
1.97
2.99
0.97
0.96
1.05
1.05
1.05
1.00
1.05
1.03
1.00
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


136.59 132.21 130.99 130.78 128.12 126.64
71.45
39.13 35.19 33.17 26.64
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)