Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Table of contents

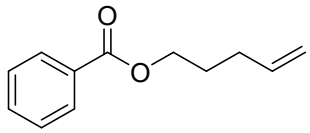
General remarks

Catalytic reactions were carried out in undivided electrochemical cells using pre-dried glassware under argon atmosphere, if not noted otherwise. The fluorinated carbon electrodes (15 mm × 10 mm × 0.2 mm, obtained from SIGRACET® Fuel Cell Components) and platinum electrodes (15 mm × 10 mm × 0.125 mm, 99.9%, obtained from ChemPur® Karlsruhe, Germany) were connected using stainless steel adapters. Electrocatalysis was conducted using an AXIOMET AX-3003P potentiostat in constant current mode. Cyclic Voltammetry studies were performed using a Gamry 1010E interface workstation. Yields refer to isolated compounds, estimated to be >95% pure as determined by 1H NMR. Chromatography: Spectrochem silica gel 60-200 mesh. NMR: Spectra were recorded on Bruker AV 400 and Bruker AV 500 in the solvent indicated; chemical shifts (δ) are given in ppm relative to the residual solvent peak. FT-IR was analyzed in Bruker ALPHA instrument and reported as cm^{-1}. High-resolution (HRMS) mass spectral analyses were recorded by a Hybrid Quadrupole Orbitrap Mass Spectrometer coupled to the UHPLC system. The Field Emission Scanning Electron Microscope (FESEM) analysis was conducted utilizing the FEI Nova Nano SEM 450 FESEM microscope. Sample preparation for FESEM involved applying a thin coating of the isopropyl alcohol (IPA)-dispersed sample (5 mg of the sample in 5 mg IPA) onto a silicon wafer. Subsequently, the samples underwent a 30-minute drying process under an infrared (IR) lamp to eliminate the IPA. Elemental inspection was performed using Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) employing a Quanta 200 3D FEI instrument connected to the TEAMTM EDS analysis system.

Starting materials:

For the substrate scope, alkenes **1a**-**1z** and **1a′** were either purchased from commercial sources or prepared by following the reported procedure: pent-4-en-1-yl benzoate (**1a**), 3-methylbut-3-en-1-yl benzoate (**1a´**), pent-4-en-1-yl acetate (**1b**), (pent-4-en-1-yloxy)methylbenzene (**1c**), allylbenzene (**1d**, CAS: 300-57-2), 1-allyl-2-methylbenzene (**1e**, CAS: 1587-04-8), 1-allyl-3-methylbenzene (**1f**, CAS: 3333-20-8) 1-allyl-4-methoxybenzene (**1g**, CAS: 140-67-0), 4-allyl-1,2-dimethoxybenzene (**1h**, CAS: 93-15-2), but-3-en-1-ylbenzene (**1i**, CAS: 768-56-9), 2-(oct-7-en-1-yl)oxirane (**1j**, CAS: 85721-25-1), (but-3-en-1-yloxy)(tert-butyl)dimethylsilane (**1k**), oct-1-ene (**1l**, CAS: 111-66-0), dec-1-ene (**1m**, CAS: 872-05-9), vinylcyclohexane (**1n**, CAS: 695-12-5), allylcyclohexane (**1o**, CAS: 2114-42-3), pent-4-en-1-yloxy)benzene (**1p**), 1-ethyl-4-(pent-4-en-1-yloxy)benzene (**1q**), pent-4-en-1-yl(phenyl)sulfane (**1r**), ethyl undec-10-enoate (**1s,** CAS: 692-86-4), N,N-diisopropylundec-10-enamide (**1t**), 6-bromohex-1-ene (**1u**, CAS: 2695-47-8), 10-bromodec-1-ene (**1v**, CAS: 62871-09-4), (Z)-cyclooctene (**1w**, CAS: 931-87-3), styrene (**1x**, CAS: 100-42-5), 1H-indene (**1y**, CAS: 95-13-6), (E)-prop-1-en-1-ylbenzene (**1z**, CAS: 873-66-5), (3-methylbut-3-en-1-yl)benzene (**1i′**) 5,5-dimethylcyclohexane-1,3-dione (**2a**, CAS: 126-81-8), cyclohexane-1,3-dione (**2b**, CAS: 504-02-9), pentane 2,4-dione (**2c**, CAS: 123-54-6), heptane 3,5-dione (**2d**, CAS: 7424-54-6), ethyl 3-oxobutanoate (**2e**, CAS: 141-97-9).

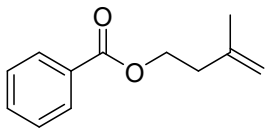
Preparation of starting materials



Pent-4-en-1-yl benzoate (1a) was prepared by following the literature procedure given by Miranda/Padrón and coworkers.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 – 8.00 (m, 2H), 7.61 – 7.51 (m, 1H), 7.52 – 7.38 (m, 2H), 5.85 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.12 – 4.98 (m, 2H), 4.34 (t, J = 6.6 Hz, 2H), 2.23 (ddd, J = 7.7, 6.8, 1.2 Hz, 2H), 1.93 – 1.83 (m, 2H).

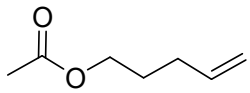
^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7 (C_q), 137.6 (CH), 133.0 (CH), 130.6 (C_q), 129.7 (CH), 128.5 (CH), 115.5 (CH_2), 64.5 (CH_2), 30.3 (CH_2), 28.1 (CH_2).



3-Methylbut-3-en-1-yl benzoate (1a´) was prepared by following the literature procedure given by Xu/Loh and coworkers.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.01 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 4.83 (d, J = 11.0 Hz, 2H), 4.44 (t, J = 6.8 Hz, 2H), 2.49 (t, J = 6.8 Hz, 2H), 1.82 (s, 3H).

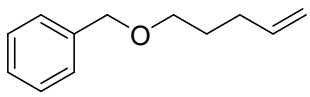
^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7 (C_q), 141.9 (C_q), 133.0 (CH), 130.5 (C_q), 129.7 (CH), 128.5 (CH), 112.6 (CH_2), 63.3 (CH_2), 37.0 (CH_2), 22.7 (CH_3).



Pent-4-en-1-yl acetate (1b) was prepared by following the literature procedure given by Harrity and coworkers.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.79 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.95 (m, 2H), 4.06 (t, J = 6.7 Hz, 2H), 2.11 (dd, J = 14.8, 6.8 Hz, 2H), 2.04 (s, 3H), 1.72 (dt, J = 13.8, 6.8 Hz, 2H).

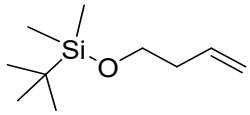
^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.3 (C_q), 137.6 (CH), 115.4 (CH_2), 64.0 (CH_2), 30.2 (CH_2), 27.9 (CH_2), 21.1 (CH_3).



(Pent-4-en-1-yloxy) methyl) benzene (**1c)** was prepared by following the literature procedure given by Berkowitz and coworkers.[4]

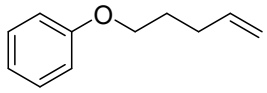
1H NMR (400 MHz, $CDCl_3$) δ = 7.40 – 7.37 (m, 4H), 7.36 – 7.29 (m, 1H), 5.88 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.09 (ddd, J = 17.1, 3.3, 1.6 Hz, 1H), 5.03 (d, J = 10.2 Hz, 1H), 4.56 (s, 2H), 3.54 (t, J = 6.5 Hz, 2H), 2.22 (dd, J = 14.7, 6.9 Hz, 2H), 1.83 – 1.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.7 (C_q), 138.3 (CH), 128.4 (CH), 127.7 (CH), 127.6 (CH), 114.8 (CH_2), 72.9 (CH_2), 69.8 (CH_2), 30.4 (CH_2), 29.1 (CH_2).



(But-3-en-1-yloxy)(tert-butyl)dimethylsilane (1k) was prepared by following the literature procedure given by Wu and coworkers.[5]

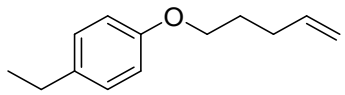
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.82 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 5.13 – 4.96 (m, 2H), 3.66 (t, J = 6.8 Hz, 2H), 2.28 (qt, J = 6.8, 1.3 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 135.6 (CH), 116.4 (CH_2), 63.0 (CH_2), 37.6 (CH_2), 26.1 (CH_3), 18.5 (C_q), 5.1 (CH_3).



(Pent-4-en-1-aryloxy) benzene. (**1p)** was prepared by following the literature procedure given by Song and coworkers.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.31 (dd, J = 7.9, 7.9 Hz, 2H), 7.00 – 6.90 (m, 3H), 5.89 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.11 (d, J = 17.1 Hz, 1H), 5.04 (d, J = 10.2 Hz, 1H), 4.00 (t, J = 6.4 Hz, 2H), 2.30 – 2.25 (m, 2H), 1.95 – 1.90 (m, 2H).

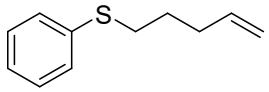
^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.2 (C_q), 138.0 (CH), 129.5 (CH), 120.7 (CH), 115.3 (CH_2), 114.6 (CH), 67.1 (CH_2), 30.3 (CH_2), 28.6 (CH_2).



1-Ethyl-4-(pent-4-en-1-yloxy) benzene (**1q)** was prepared by following the literature procedure given by Wang and coworkers.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.87 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.07 (dd, J = 17.1, 1.2 Hz, 1H), 5.00 (dd, J = 10.2, 1.1 Hz, 1H), 3.96 (t, J = 6.4 Hz, 2H), 2.60 (q, J = 7.6 Hz, 2H), 2.25 (q, J = 7.1 Hz, 2H), 1.94 – 1.82 (m, 2H), 1.22 (t, J = 7.6 Hz, 3H).

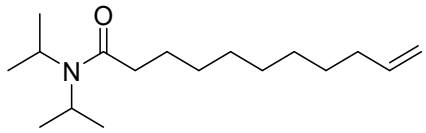
^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.2 (C_q), 138.1 (CH), 136.4 (C_q), 128.8 (CH), 115.2 (CH_2), 114.5 (CH), 67.4 (CH_2), 30.3 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 16.0 (CH_3).



Pent-4-en-1-yl (phenyl) sulfane. (**1r)** was prepared by following the literature procedure given by Dussault and coworkers.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 7.20 – 7.15 (m, 1H), 5.79 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.10 – 4.97 (m, 2H), 2.96 – 2.89 (m, 2H), 2.21 (dd, J = 14.5, 6.9 Hz, 2H), 1.80 – 1.71 (m, 2H).

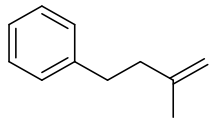
^{13}C NMR (101 MHz, $CDCl_3$) δ = 137.7 (CH), 136.9 (C_q), 129.2 (CH), 129.0 (CH), 125.9 (CH), 115.5 (CH_2), 33.1 (CH_2), 32.8 (CH_2), 28.4 (CH_2).



N, N-Diisopropylundec-10-enamide (1t) was prepared by following the literature procedure given by Coates and coworkers.[9]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.98 (ddd, J = 17.1, 3.6, 1.6 Hz, 1H), 4.91 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 3.95 (dt, J = 13.3, 6.6 Hz, 1H), 3.47 (bs, 1H), 2.30 – 2.20 (m, 2H), 2.06 – 1.96 (m, 2H), 1.58 (dd, J = 14.9, 7.3 Hz, 2H), 1.36 (d, J = 6.7 Hz, 6H), 1.29 (bs, 10H), 1.19 (d, J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.2 (C_q), 139.4 (CH), 114.2 (CH_2), 48.3 (CH), 45.6 (CH), 35.6 (CH_2), 33.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 25.6 (CH_2), 21.2 (CH_3), 20.9 (CH_3).

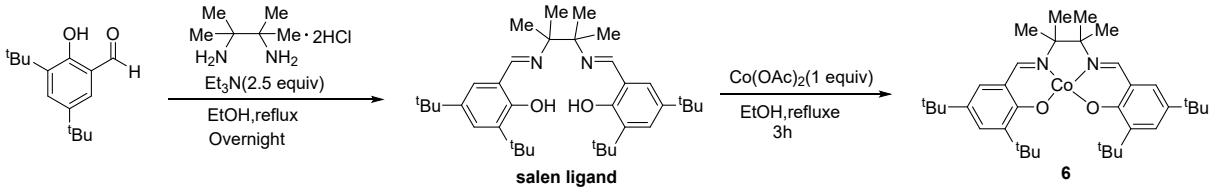


(3-methylbut-3-en-1-yl)benzene (1i′) was prepared by following the literature procedure given by Carreira and coworkers.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.76 (d, J = 10.5 Hz, 2H), 2.78 (dd, J = 9.4, 6.9 Hz, 2H), 2.42 – 2.30 (m, 2H), 1.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.5 (C_q), 142.4 (C_q), 128.5 (CH), 128.4 (CH), 125.9 (CH), 110.4 (CH_2), 39.8 (CH_2), 34.4 (CH_2), 22.8 (CH_3).

Preparation of Cobalt-Complex



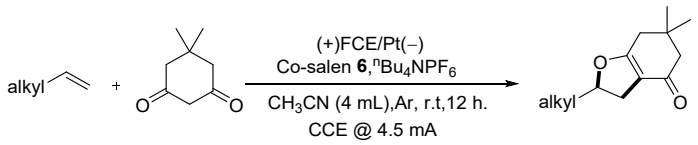
6,6'-((1E,1'E)-((2,3-Dimethylbutane-2,3-diyl)bis(azaneylylidene))bis(methaneylylidene))bis(2,4-di-tert-butylphenol) (Salen ligand) and **Cobalt-salen complex 6** were prepared by following the literature procedure given by Lin and coworkers.[11]

<u>(Salen Ligand)</u> ^{1}H NMR (400 MHz, $CDCl_3$) δ = 14.32 (s, 2H), 8.40 (s, 2H), 7.36 (d, J = 2.4 Hz, 2H), 7.10 (d, J = 2.4 Hz, 2H), 1.44 (s, 18H), 1.40 (s, 12H), 1.30 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.8 (CH), 158.6 (C_q), 139.9 (C_q), 136.8 (C_q), 126.9 (CH), 126.4 (CH), 118.1 (C_q), 65.1 (C_q), 35.2 (C_q), 34.3 (C_q), 31.7 (CH_3), 29.6 (CH_3), 23.4 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{36}H_{57}N_2O_2$ [M+H] + 549.4415 found 549.4413.
FT-IR (cm^{-1}): 3686, 3020, 2403, 1623.1471, 1216, 1036, 928, 763.

General procedure for electrochemical (3+2) cycloaddition (A)

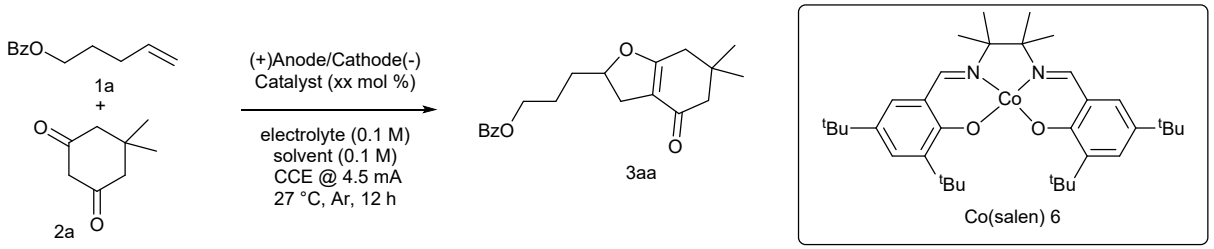


The electrochemical (3+2) cycloaddition was carried out in an undivided cell with a fluorinated carbon electrode (FCE) (15 x 10 x 0.2 mm) anode and Pt plate (15 x 10 x 0.125 mm) cathode. To a 10 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added 1,3-dione (0.80mmol, 2.0 equiv), $^{n}Bu_4NPF_6$ (0.40 mmol, 1.0 equiv.), alkene (0.40 mmol, 1.0 equiv.) and Co-salen **6** catalyst (10 µmol, 0.025 equiv.) under argon atmosphere. Then CH_3CN (4 mL) was added and the reaction mixture was stirred for five minutes before the electrolysis at a constant current of 4.5 mA for 12 h (5 F/mole). at room temperature. The reaction mixture was transferred to a separating funnel and H_2O (15 mL) was added. The resulting mixture was extracted with EtOAc (15 mL× 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography using pet ether/EtOAc to furnish the desired product.

Electrochemical reaction in 1 mmol scale

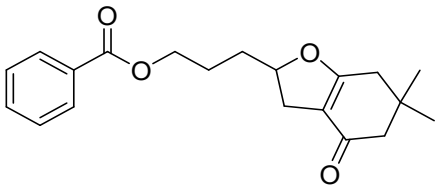
The electrochemical (3+2) cycloaddition was carried out in an undivided cell with a fluorinated carbon electrode (FCE) (25 x 10 x 0.2 mm) anode and Pt plate (25 x 10 x 0.125 mm) cathode. To a 25 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added 5,5-dimethylcyclohexane-1,3-dione **2a** (2.0 mmol, 2.0 equiv), $^{n}Bu_4NPF_6$ (1.0 mmol, 1.0 equiv.), but-3-en-1-ylbenzene **1i** (1.0 mmol, 1.0 equiv.) and Co-salen catalyst (25 µmol, 0.025 equiv.) under argon atmosphere. Then CH_3CN (10 mL) was added and the reaction mixture was stirred for five minutes before the electrolysis at a constant current of 10.0 mA for 12 h. at room temperature. The reaction mixture was concentrated in a vacuum and the crude reaction mixture was purified by silica gel column chromatography using pet ether/EtOAc to furnish the desired product **3ia** (167.6 mg, 62% yield) as a colourless oil.

Reaction Optimization for electrochemical (3+2) cycloaddition



Entry	Electrode/Mediator	Solvent	Supporting Electrolyte	Yield 3aa (%)a
1	glassy carbon/Pt	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	0
2	RVC/Pt	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	trace
3	graphite plate/Pt	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	15
4	graphite felt/Pt	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	19
5	carbon fiber/Pt	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	17
6	FCE/Pt	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	58
7	FCE/Pt, ferrocene (2.5 / 5 / 10 mol %)	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	58 / 45 / 13
8	FCE/Pt, Tempo (2.5 / 5 mol %)	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	22 / 39
9	FCE/Pt, $^nBu_4NI$ (2.5 / 5 mol %)	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	37 / 45
10	FCE/Pt, Co(salen) 6 (1.25 / 2.5 / 5 mol %)	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	66 / 72 / 63
11	FCE/Pt, Co(salen) (2.5 mol %) / NaOAc (0.5 equiv) / 4.5 mA	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	40
12	FCE/Pt, Co(salen) (2.5 mol %) / 3 mA, 18 h	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	59
13	FCE/Pt, Co(salen) (2.5 mol %) / 6 mA, 9 h	CH_3CN	$^nBu_4NPF_6$ (0.1 M)	65
14	FCE/Pt, Co(salen) (2.5 mol %)	CH_3CN	$^nBu_4NBF_4$ (0.1 M)	69
15	FCE/Pt, Co(salen) (2.5 mol %)	CH_3CN	$^nBu_4NI$ (0.1 M)	0
16	FCE/Pt, Co(salen) (2.5 mol %)	CH_3CN	$LiClO_4$ (0.1 M)	56
17	FCE/Pt, Co(salen) (2.5 mol %)	DMF	$^nBu_4NPF_6$ (0.1 M)	66
18	FCE/Pt, Co(salen) (2.5 mol %)	DMA	$^nBu_4NPF_6$ (0.1 M)	71
19	FCE/Pt, Co(salen) (2.5 mol %)	CH_3CN / HFIP	$^nBu_4NPF_6$ (0.1 M)	73

Characterization data for compounds:



3-(6,6-Dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl)propyl benzoate (3aa)

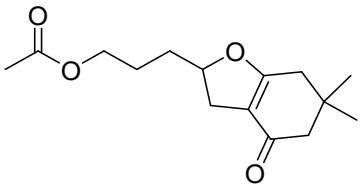
General procedure **A** was followed using pent-4-en-1-yl benzoate (**1a)** (76.1mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a)** (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =1:1) yielded **3aa** (94.6 mg, 72%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, J = 7.4 Hz, 2H), 7.54 (dd, J = 7.5, 7.5 Hz, 1H), 7.42 (dd, J = 7.5, 7.5 Hz, 2H), 4.93 – 4.80 (m, 1H), 4.35 (d, J = 5.1 Hz, 2H), 2.98 – 2.88 (m, 1H), 2.48 (dd, J = 14.1, 7.0 Hz, 1H), 2.24 (s, 2H), 2.20 (s, 2H), 2.01 – 1.72 (m, 4H), 1.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.2 (C_q), 166.6 (C_q), 133.1 (CH), 130.3 (C_q), 129.6 (CH), 128.5 (CH), 111.5 (C_q), 85.7 (CH), 64.4 (CH_2), 51.0 (CH_2), 37.9 (CH_2), 34.1 (C_q), 32.9 (CH_2), 31.4 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 24.7 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{20}H_{25}O_4$ $[M+H]^+$ 329.1747 found 329.1750.

FT-IR (cm^{-1}): 3021, 2964, 1714, 1628, 1274, 1113, 931, 767.



3-(6,6-Dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl)propyl acetate (3ba)

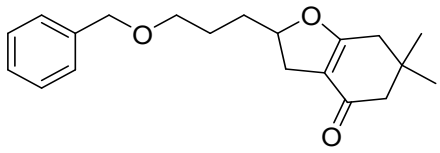
General procedure **A** was followed using pent-4-en-1-yl acetate (**1b)** (51.3 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether /EtOAc =2:1) yielded **3ba** (71.4 mg, 67%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.86 – 4.71 (m, 1H), 4.10 – 4.00 (m, 2H), 2.98 – 2.84 (m, 1H), 2.43 (dd, J = 14.3, 7.2 Hz, 1H), 2.22 (s, 2H), 2.17 (s, 2H), 2.01 (s, 3H), 1.83 – 1.63 (m, 4H), 1.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.2 (C_q), 171.1 (C_q), 111.4 (C_q), 85.6 (CH), 63.9 (CH_2), 50.9 (CH_2), 37.9 (CH_2), 34.1 (C_q), 32.7 (CH_2), 31.3 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 24.4 (CH_2), 21.0 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{15}H_{23}O_4$ $[M+H]^+$ 267.1591 found 267.1591.

FT-IR (cm^{-1}): 3021, 2927, 1726, 1630, 1216, 1036, 927, 759.



2-(3-(Benzyloxy)propyl)-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ca)

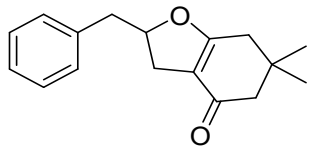
General procedure **A** was followed using (pent-4-en-1-yloxy)methylbenzene (**1c)** (70.5mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ca** (89.3 mg, 71%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 – 7.22 (m, 4H), 7.22 – 7.17 (m, 1H), 4.79 – 4.72 (m, 1H), 4.42 (s, 2H), 3.43 (t, J = 5.8 Hz, 2H), 2.83 (dd, J = 14.2, 10.0 Hz, 1H), 2.39 (ddt, J = 14.3, 7.3, 1.7 Hz, 1H), 2.17 (s, 2H), 2.13 (s, 2H), 1.84 – 1.54 (m, 4H), 1.01 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.3 (C_q), 138.4 (C_q), 128.4 (CH), 127.6 (CH), 111.4 (C_q), 86.1 (CH), 72.9 (CH_2), 69.7 (CH_2), 50.9 (CH_2), 37.9 (CH_2), 34.1 (C_q), 33.0 (CH_2), 31.2 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 25.4 (CH_2). One carbon signal is missing due to the resonance of the signals.

HRMS (ESI) (m/z): calcd for $C_{20}H_{27}O_3$ $[M+H]^+$ 315.1955 found 315.1957.

FT-IR (cm^{-1}): 3021, 2957, 1715, 1626, 1216, 1100, 928, 768.



2-Benzyl-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3da)

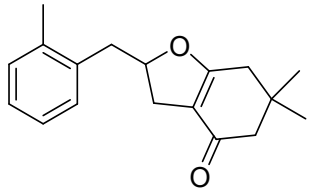
General procedure **A** was followed using allylbenzene (**1d)** (47.3mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3da** (68.7 mg, 67%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 5.09 – 5.01 (m, 1H), 3.01 (dd, J = 14.0, 6.5 Hz, 1H), 2.93 (dd, J = 14.0, 6.5 Hz, 1H), 2.90 – 2.82 (m, 1H), 2.59 (ddt, J = 14.0, 6.5, 1.6 Hz, 1H), 2.24 (s, 2H), 2.16 (d, J = 4.8 Hz, 2H), 1.06 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.8 (C_q), 176.2 (C_q), 136.4 (C_q), 129.5 (CH), 128.6 (CH), 126.9 (CH), 111.5 (C_q), 86.1 (CH), 50.9 (CH_2), 42.0 (CH_2), 37.9 (CH_2), 34.1 (C_q), 30.7 (CH_2), 28.9 (CH_3), 28.6 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{17}H_{21}O_2$ $[M+H]^+$ 257.1536 found 257.1538.

FT-IR (cm^{-1}): 3019, 2960, 1628, 1510, 1217, 1101, 927, 769.



6,6-Dimethyl-2-(2-methylbenzyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ea)

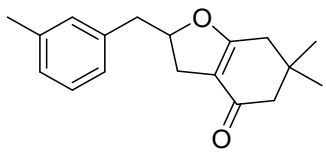
General procedure **A** was followed using 1-allyl-2-methylbenzene (**1e)** (52.9 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ea** (64.9 mg, 60%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 – 7.15 (m, 4H), 5.23 – 4.99 (m, 1H), 3.08 (dd, J = 14.4, 7.4 Hz, 1H), 2.96 – 2.84 (m, 2H), 2.62 (ddd, J = 14.4, 8.2, 4.5 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 2H), 2.21 (s, 2H), 1.08 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.1 (C_q), 136.5 (C_q), 135.0 (C_q), 130.5 (CH), 129.9 (CH), 127.0 (CH), 126.1 (CH), 111.5 (C_q), 85.7 (CH), 51.0 (CH_2), 39.3 (CH_2), 37.9 (CH_2), 34.2 (C_q), 31.1 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 19.8 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{23}O_2$ $[M+H]^+$ 271.1693 found 271.1695.

FT-IR (cm^{-1}): 3019, 2965, 1627, 1521, 1217, 1104, 928, 758.



6,6-Dimethyl-2-(3-methylbenzyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3fa)

General procedure **A** was followed using 1-allyl-3-methylbenzene (**1f)** (52.9 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol,

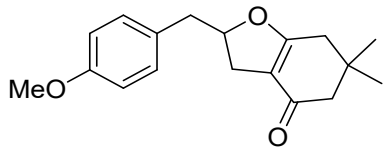
1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =4:1) yielded **3fa** (58.4 mg, 54%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (dd, J = 7.4, 7.4 Hz, 1H), 7.05 –7.00 (m, 3H), 5.09 – 5.01 (m, 1H), 3.00 (dd, J = 13.9, 6.5 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.59 (dd, J = 14.4, 7.0 Hz, 1H), 2.33 (s, 3H), 2.26 (s, 2H), 2.18 (d, J = 4.1 Hz, 2H), 1.08 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.2 (C_q), 138.2 (C_q), 136.4 (C_q), 130.3 (CH), 128.5 (CH), 127.7 (CH), 126.5 (CH), 111.6 (C_q), 86.3 (CH), 51.0 (CH_2), 42.0 (CH_2), 38.0 (CH_2), 34.2 (C_q), 30.7 (CH_2), 28.9 (CH_3), 28.6 (CH_3), 21.5 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{23}O_2$ $[M+H]^+$ 271.1693 found 271.1695.

FT-IR (cm^{-1}): 3020, 2964, 1625, 1523, 1216, 1101, 928, 761.



2-(4-Methoxybenzyl)-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ga)

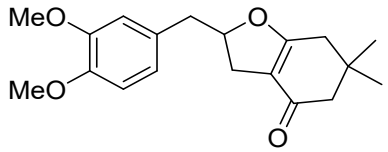
General procedure **A** was followed using 1-allyl-4-methoxybenzene (**1g)** (59.3 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethylcyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ga** (74.5 mg, 65%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.05 – 4.98 (m, 1H), 3.78 (s, 3H), 2.95 (dd, J = 14.1, 6.4 Hz, 1H), 2.91 – 2.82 (m, 2H), 2.58 (dd, J = 14.4, 7.0 Hz, 1H), 2.24 (d, J = 1.1 Hz, 2H), 2.17 (d, J = 4.4 Hz, 2H), 1.07 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.3 (C_q), 158.6 (C_q), 130.5 (CH), 128.4 (C_q), 114.1 (CH), 111.6 (C_q), 86.4 (CH), 55.4 (CH_3), 51.0 (CH_2), 41.2 (CH_2), 37.9 (CH_2), 34.2 (C_q), 30.6 (CH_2), 28.9 (CH_3), 28.7 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1642 found 287.1643.

FT-IR (cm^{-1}): 3019, 2960, 1626, 1514, 1218, 1102, 928, 762.



2-(3,4-Dimethoxybenzyl)-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ha)

General procedure **A** was followed using 4-allyl-1,2-dimethoxybenzene (**1h)** (71.3 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1

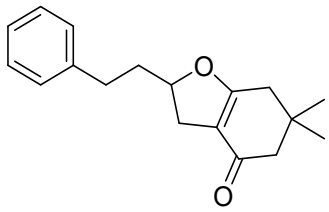
mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =1:1) yielded **3ha** (75.9 mg, 60%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6. 80 – 6.76 (m, 1H), 6.76 – 6.69 (m, 2H), 5.06 – 4.99 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.95 (dd, J = 14.1, 6.4 Hz, 1H), 2.91 – 2.78 (m, 2H), 2.58 (dd, J = 14.4, 7.1 Hz, 1H), 2.27 – 2.21 (m, 2H), 2.17 (d, J = 4.0 Hz, 2H), 1.06 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.2 (C_q), 149.0 (C_q), 148.1 (C_q), 128.9 (C_q), 121.6 (CH), 112.7 (CH), 111.6 (C_q), 111.4 (CH), 86.3 (CH), 56.0 (CH_3), 56.0 (CH_3), 50.9 (CH_2), 41.6 (CH_2), 38.0 (CH_2), 34.1 (C_q), 30.6 (CH_2), 28.9 (CH_3), 28.6 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1747 found 317.1750.

FT-IR (cm^{-1}): 3020, 2962, 1627, 1517, 1218, 1151, 927, 765.



6,6-Dimethyl-2-phenethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ia)

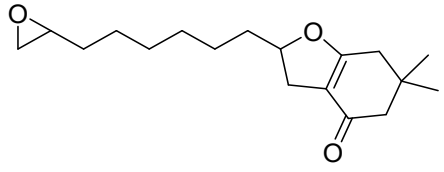
General procedure **A** was followed using but-3-en-1-ylbenzene (**1i)** (52.9 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ia** (71.4 mg, 66%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 – 7.28 (m, 2H), 7.24–7.21 (m, 3H), 4.86 – 4.79 (m, 1H), 2.95 (dd, J = 14.2, 10.0 Hz, 1H), 2.84 – 2.70 (m, 2H), 2.54 (dd, J = 14.3, 7.3 Hz, 1H), 2.30 (s, 2H), 2.24 (s, 2H), 2.13 – 2.04 (m, 1H), 2.01 – 1.92 (m, 1H), 1.12 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.4 (C_q), 141.0 (C_q), 128.6 (CH), 128.5 (CH), 126.2 (CH), 111.5 (C_q), 85.3 (CH), 51.0 (CH_2), 37.9 (CH_2), 37.9 (CH_2), 34.2 (C_q), 31.4 (CH_2), 31.2 (CH_2), 28.8 (CH_3), 28.8 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{23}O_2$ $[M+H]^+$ 271.1693 found 271.1689.

FT-IR (cm^{-1}): 3014, 2957, 1716, 1629, 1220, 1102, 920, 756.



6,6-Dimethyl-2-(6-(oxiran-2-yl)hexyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ja)

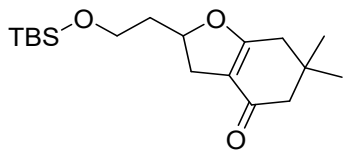
General procedure **A** was followed using 2-(oct-7-en-1-yl) oxirane (**1j)** (61.7 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ja** (77.2 mg, 66%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.78 (ddd, J = 13.2, 9.9, 7.2 Hz, 1H), 2.92 – 2.83 (m, 2H), 2.74 – 2.69 (m, 1H), 2.47 – 2.39 (m, 2H), 2.24 (s, 2H), 2.19 (s, 2H), 1.70 (ddd, J = 13.3, 8.2, 5.9 Hz, 1H), 1.65 – 1.56 (m, 1H), 1.55 – 1.27 (m, 10H), 1.07 (s, 3H), 1.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.4 (C_q), 111.5 (C_q), 86.4 (CH), 52.4 (CH), 51.0 (CH_2), 47.2 (CH_2), 38.0 (CH_2), 36.2 (CH_2), 34.1 (C_q), 32.5 (CH_2), 31.3 (CH_2), 29.4 (CH_2), 28.9 (CH_3), 28.7 (CH_3), 26.0 (CH_2), 24.9 (CH_2). One carbon signal is missing due to the resonance of the signals.

HRMS (ESI) (m/z): calcd for $C_{18}H_{29}O_3$ $[M+H]^+$ 293.2111 found 293.2113.

FT-IR (cm^{-1}): 3018, 2962, 1745, 1624, 1296, 1143, 926, 770.



2-{2-[(tert-Butyldimethylsilyl)oxy]ethyl}-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ka)

General procedure **A** was followed using (but-3-en-1-yloxy) (*tert*-butyl) dimethyl silane (**1k)** (74.5 mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ka** (70.1 mg, 54%) as a colourless oil.

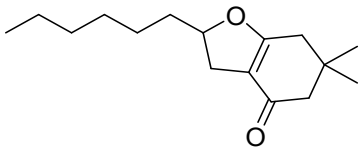
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.00 – 4.91 (m, 1H), 3.78 – 3.67 (m, 2H), 2.92 (dd, J = 14.2, 10.0 Hz, 1H), 2.47 (dd, J = 14.2, 7.3 Hz, 1H), 2.24 (d, J = 1.6 Hz, 2H), 2.20 (s, 2H), 1.98 – 1.89 (m, 1H), 1.84 – 1.73 (m, 1H), 1.08 (s, 3H), 1.07 (s, 3H), 0.87 (s, 9H), 0.04 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.3 (C_q), 111.5 (C_q), 83.3 (CH), 59.2 (CH_2), 51.0 (CH_2), 39.4 (CH_2), 38.0 (CH_2), 34.2 (C_q), 31.4 (CH_2), 28.9 (CH_3), 28.8 (CH_3), 26.0 (CH_3), 18.4 (C_q), -5.3 (Si-CH_3).

^{29}Si NMR (79 MHz, $CDCl_3$) δ = 19.6.

HRMS (ESI) (m/z): calcd for $C_{18}H_{33}O_3Si$ $[M+H]^+$ 325.2193 found 325.2190.

FT-IR (cm^{-1}): 3018, 2955, 1627, 1521, 1217, 1101, 926, 768.



2-Hexyl-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3la)

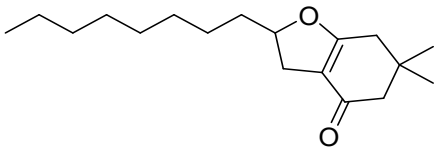
General procedure **A** was followed using oct-1-ene (**1l)** (44.9 mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3la** (58.1 mg, 58%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.83 – 4.75 (m, 1H), 2.93 – 2.84 (m, 1H), 2.45 (dd, J = 14.2, 7.3 Hz, 1H), 2.24 (s, 2H), 2.20 (s, 2H), 1.73 – 1.68 (m, 1H), 1.66 – 1.55 (m, 1H), 1.49 – 1.16 (m, 8H), 1.08 (s, 6H), 0.87 (t, J = 5.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.4 (C_q), 111.6 (C_q), 86.5 (CH), 51.0 (CH_2), 38.0 (CH_2), 36.3 (CH_2), 34.2 (C_q), 31.8 (CH_2), 31.3 (CH_2), 29.1 (CH_2), 28.9 (CH_3), 28.7 (CH_3), 25.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{16}H_{27}O_2$ $[M+H]^+$ 251.2006 found 251.2007.

FT-IR (cm^{-1}): 3021, 2960, 1624, 1522, 1216, 1039, 927, 771.



6,6-Dimethyl-2-octyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ma)

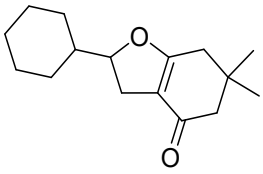
General procedure **A** was followed using dec-1-ene (**1m)** (56.1 mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ma** (69.1 mg, 62%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.83 – 4.74 (m, 1H), 2.87 (dd, J = 14.2, 9.9 Hz, 1H), 2.43 (dd, J = 14.2, 7.4 Hz, 1H), 2.23 (s, 2H), 2.19 (s, 2H), 1.79 – 1.66 (m, 1H), 1.64 – 1.54 (m, 1H), 1.46 – 1.15 (m, 12H), 1.07 (s, 3H), 1.06 (s, 3H), 0.85 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.4 (C_q), 111.5 (C_q), 86.5 (CH), 51.0 (CH_2), 38.0 (CH_2), 36.2 (CH_2), 34.1 (C_q), 31.9 (CH_2), 31.2 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.9 (CH_3), 28.7 (CH_3), 25.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{31}O_2$ $[M+H]^+$ 279.2319 found 279.2320.

FT-IR (cm^{-1}): 3018, 2931, 1625, 1521, 1217, 1155, 926, 770.



2-Cyclohexyl-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3na)

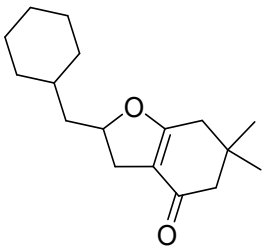
General procedure **A** was followed using vinylcyclohexane (**1n)** (44.1 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =4:1) yielded **3na** (55.6 mg, 56%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.59 – 4.53 (m, 1H), 2.82 – 2.75 (m, 1H), 2.56 (dd, J = 14.3, 8.0 Hz, 1H), 2.26 (d, J = 1.5 Hz, 2H), 2.20 (d, J = 4.9 Hz, 2H), 1.83 (d, J = 12.8 Hz, 1H), 1.79 – 1.51 (m, 5H), 1.32 – 1.12 (m, 3H), 1.09 (s, 3H), 1.07 (s, 3H), 1.05 – 0.93 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.7 (C_q), 111.8 (C_q), 90.6 (CH), 51.0 (CH_2), 43.1 (CH), 37.9 (CH_2), 34.2 (C_q), 29.0 (CH_3), 28.8 (CH_2), 28.6 (CH_3), 28.1 (CH_2), 28.0 (CH_2), 26.5 (CH_2), 25.9 (CH_2), 25.8 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{16}H_{25}O_2$ $[M+H]^+$ 249.1849 found 249.1851.

FT-IR (cm^{-1}): 3020, 2932, 1624, 1521, 1217, 1098, 931, 761.



2-(Cyclohexylmethyl)-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3oa)

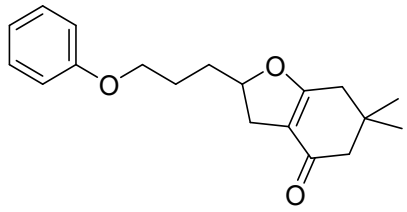
General procedure **A** was followed using allylcyclohexane (**1o)** (49.7 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3oa** (61.9 mg, 59%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.93 – 4.85 (m, 1H), 2.89 (dd, J = 14.1, 9.8 Hz, 1H), 2.41 (dd, J = 14.2, 7.5 Hz, 1H), 2.24 (s, 2H), 2.19 (s, 2H), 1.77 (d, J = 11.2 Hz, 1H), 1.73 – 1.58 (m, 5H), 1.51 – 1.38 (m, 2H), 1.30 – 1.11 (m, 3H), 1.07 (s, 3H), 1.07 (s, 3H), 1.02 – 0.85 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.4 (C_q), 111.5 (C_q), 84.6 (CH), 51.0 (CH_2), 44.2 (CH_2), 38.1 (CH_2), 34.4 (CH), 34.2 (C_q), 33.7 (CH_2), 33.1 (CH_2), 31.9 (CH_2), 28.9 (CH_3), 28.8 (CH_3), 26.5 (CH_2), 26.3 (CH_2), 26.2 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{17}H_{27}O_2$ $[M+H]^+$ 263.2006 found 263.2007.

FT-IR (cm^{-1}):3020, 2932, 2403, 1624, 1521, 1098, 931, 761.



6,6-Dimethyl-2-(3-phenoxypropyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3pa)

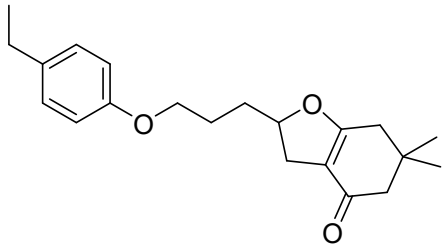
General procedure **A** was followed using (pent-4-en-1-yloxy) benzene (**1p)** (64.9 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3pa** (78.1 mg, 65%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (dd, J = 8.0, 7.3 Hz, 2H), 6.94 (dd, J = 8.0, 7.3 Hz, 1H), 6.89 (d, J = 8.0 Hz, 2H), 4.95 – 4.83 (m, 1H), 3.99 (t, J = 9.5 Hz, 2H), 3.00 – 2.89 (m, 1H), 2.51 (dd, J = 14.1, 7.3 Hz, 1H), 2.26 (s, 2H), 2.22 (s, 2H), 2.01 – 1.74 (m, 4H), 1.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.3 (C_q), 158.9 (C_q), 129.6 (CH), 120.8 (CH), 114.6 (CH), 111.6 (C_q), 86.0 (CH), 67.2 (CH_2), 51.0 (CH_2), 38.0 (CH_2), 34.2 (C_q), 33.0 (CH_2), 31.4 (CH_2), 28.9 (CH_3), 28.8 (CH_3), 25.1 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{19}H_{25}O_3$ $[M+H]^+$ 301.1798 found 301.1800.

FT-IR (cm^{-1}): 3019, 2960, 1713, 1627, 1217, 1041, 929, 769.



2-[3-(4-Ethylphenoxy)propyl]-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3qa)

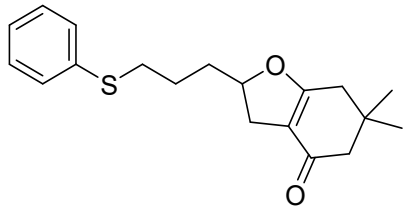
General procedure **A** was followed using 1-ethyl-4-(pent-4-en-1-yloxy) benzene (**1q)** (76.1 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3qa** (86.7 mg, 66%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 7.9 Hz, 2H), 4.96 – 4.80 (m, 1H), 4.06 – 3.90 (m, 2H), 3.00 – 2.91 (m, 1H), 2.58 (q, J = 7.3 Hz, 2H), 2.50 (dd, J = 14.1, 7.2 Hz, 1H), 2.26 (s, 2H), 2.22 (s, 2H), 2.02 – 1.72 (m, 4H), 1.20 (t, J = 7.4 Hz, 3H), 1.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.3 (C_q), 156.9 (C_q), 136.5 (C_q), 128.8 (CH), 114.4 (CH), 111.5 (C_q), 85.9 (CH), 67.3 (CH_2), 51.0 (CH_2), 37.9 (CH_2), 34.1 (C_q), 32.9 (CH_2), 31.3 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 28.0 (CH_2), 25.1 (CH_2), 15.9 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{21}H_{29}O_3$ $[M+H]^+$ 329.2111 found 329.2112.

FT-IR (cm^{-1}): 3019, 2961, 1626, 1513, 1218, 1109, 928, 769.



6,6-Dimethyl-2-(3-(phenylthio)propyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ra)

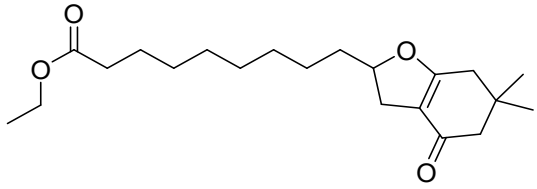
General procedure **A** was followed using pent-4-en-1-yl (phenyl) sulfane (**1r)** (71.3 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ra** (72.2 mg, 57%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.18 (tt, J = 8.4, 2.0 Hz, 1H), 4.81 (dtd, J = 10.0, 7.3, 4.9 Hz, 1H), 3.00 – 2.86 (m, 3H), 2.45 (ddt, J = 14.3, 7.3, 1.7 Hz, 1H), 2.24 (d, J = 1.5 Hz, 2H), 2.21 (s, 2H), 1.90 – 1.66 (m, 4H), 1.09 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.3 (C_q), 136.3 (C_q), 129.5 (CH), 129.0 (CH), 126.2 (CH), 111.5 (C_q), 85.7 (CH), 51.0 (CH_2), 37.9 (CH_2), 35.2 (CH_2), 34.2 (C_q), 33.6 (CH_2), 31.3 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 24.8 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{19}H_{25}O_2S$ $[M+H]^+$ 317.1570 found 317.1572.

FT-IR (cm^{-1}): 3014, 2958, 1714, 1627, 1218, 1097, 1031, 925, 766.



Ethyl 9-(6,6-dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl)nonanoate (3sa)

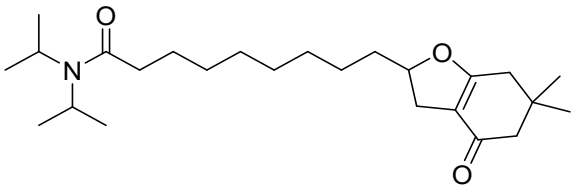
General procedure **A** was followed using ethyl undec-10-enoate (**1s)** (84.9 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3sa** (86.9 mg, 62%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.77 (dt, J = 13.3, 7.1 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.86 (dd, J = 14.2, 9.9 Hz, 1H), 2.42 (dd, J = 14.2, 7.4 Hz, 1H), 2.29 – 2.21 (m, 4H), 2.18 (s, 2H), 1.77 – 1.65 (m, 1H), 1.63 – 1.53 (m, 3H), 1.44 – 1.24 (m, 10H), 1.22 (t, J = 7.1 Hz, 3H), 1.06 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 176.4 (C_q), 173.9 (C_q), 111.5 (C_q), 86.5 (CH), 60.2 (CH_2), 51.0 (CH_2), 38.0 (CH_2), 36.2 (CH_2), 34.4 (CH_2), 34.1 (C_q), 31.2 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 25.0 (CH_2), 25.0 (CH_2), 14.3 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{21}H_{35}O_4$ $[M+H]^+$ 351.2530 found 351.2531.

FT-IR (cm^{-1}): 3022, 2934, 1723, 1625, 1216, 1105, 927, 774.



9-(6,6-Dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl)-N,N-diisopropylnonanamide (3ta)

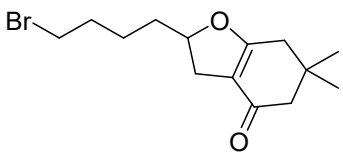
General procedure **A** was followed using N, N-diisopropylundec-10-enamide (**1t)** (107.0 mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =1:1) yielded **3ta** (99.0 mg, 61%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.79 – 4.72 (m, 1H), 3.92 (dt, J = 13.2, 6.6 Hz, 1H), 3.43 (bs, 1H), 2.85 (dd, J = 14.1, 10.0 Hz, 1H), 2.41 (dd, J = 14.2, 7.4 Hz, 1H), 2.24 – 2.20 (m, 4H), 2.17 (s, 2H), 1.75 – 1.62 (m, 1H), 1.62 – 1.47 (m, 3H), 1.32 (d, J = 6.7 Hz, 6H), 1.28 – 1.20 (bs, 10H), 1.15 (d, J = 6.7 Hz, 6H), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.4 (C_q), 172.0 (C_q), 111.5 (C_q), 86.4 (CH), 50.9 (CH_2), 48.3 (CH), 45.5 (CH), 37.9 (CH_2), 36.2 (CH_2), 35.4 (CH_2), 34.1 (C_q), 31.2 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 25.5 (CH_2), 25.0 (CH_2), 21.1 (CH_3), 20.8 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{25}H_{44}NO_3$ $[M+H]^+$ 406.3316 found 406.3305.

FT-IR (cm^{-1}): 3022, 2934, 1723, 1625, 1216, 1105, 927, 774.



2-(4-Bromobutyl)-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ua)

General procedure **A** was followed using 6-bromohex-1-ene (**1u)** (65.2 mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg,

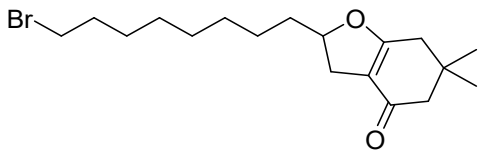
10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ua** (72.3 mg, 60%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.83 – 4.75 (m, 1H), 3.39 (t, J = 6.7 Hz, 2H), 2.89 (dd, J = 14.3, 10.0 Hz, 1H), 2.44 (dd, J = 14.3, 7.4 Hz, 1H), 2.23 (s, 2H), 2.18 (s, 2H), 1.92 – 1.84 (m, 2H), 1.79 – 1.47 (m, 4H), 1.06 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.3 (C_q), 111.5 (C_q), 85.9 (CH), 50.9 (CH_2), 37.9 (CH_2), 35.3 (CH_2), 34.1 (C_q), 33.4 (CH_2), 32.4 (CH_2), 31.3 (CH_2), 28.8 (CH_3), 28.7 (CH_3), 23.8 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{14}H_{22}BrO_2$ $[M+H]^+$ 301.0798 found 301.0803.

FT-IR (cm^{-1}): 3021, 2967, 1717,1625, 1216, 1037, 927, 769.



2-(8-Bromooctyl)-6,6-dimethyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3va)

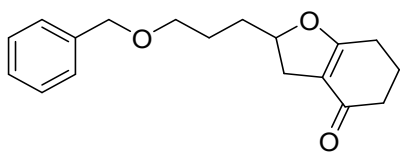
General procedure **A** was followed using 10-bromodec-1-ene (**1v)** (87.7 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3va** (91.5 mg, 64%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.85 – 4.70 (m, 1H), 3.37 (t, J = 6.8 Hz, 2H), 2.95 – 2.84 (m, 1H), 2.43 (ddd, J = 12.6, 5.4, 3.8 Hz, 1H), 2.23 (s, 2H), 2.18 (s, 2H), 1.81 (dd, J = 14.6, 7.0 Hz, 2H), 1.77 – 1.65 (m, 1H), 1.65 – 1.53 (m, 1H), 1.39 (d, J = 6.1 Hz, 4H), 1.33 – 1.24 (m, 6H), 1.07 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.4 (C_q), 111.5 (C_q), 86.4 (CH), 51.0 (CH_2), 38.0 (CH_2), 36.2 (CH_2), 34.1 (C_q), 34.0 (CH_2), 32.8 (CH_2), 31.2 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 28.9 (CH_3), 28.7 (CH_3), 28.7 (CH_2), 28.2 (CH_2), 24.9 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{18}H_{30}BrO_2$ $[M+H]^+$ 357.1424 found 357.1431.

FT-IR (cm^{-1}): 3020, 2933, 1624, 1525, 1031, 927, 758, 668.



2-[3-(Benzyloxy)propyl]-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3cb)

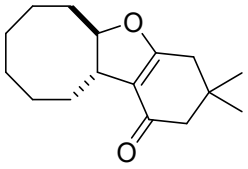
General procedure **A** was followed using **1e (**pent-4-en-1-yloxy) methyl benzene (**1c)** (70.5 mg, 0.40 mmol, 1.0 equiv.), cyclohexane-1,3-dione (**2b**) (89.7 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =1:1) yielded **3cb** (75.6 mg, 66%) as a colourless oil.

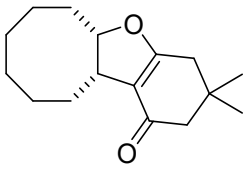
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 – 7.23 (m, 4H), 7.22 – 7.17 (m, 1H), 4.81 – 4.68 (m, 1H), 4.43 (s, 2H), 3.43 (t, J = 5.7 Hz, 2H), 2.83 (dd, J = 14.2, 10.0 Hz, 1H), 2.39 (dd, J = 14.3, 7.4 Hz, 1H), 2.31 (t, J = 6.1 Hz, 2H), 2.28 – 2.22 (m, 2H), 2.02 – 1.90 (m, 2H), 1.81 – 1.56 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.6 (C_q), 177.4 (C_q), 138.5 (C_q), 128.4 (CH), 127.6 (CH), 113.0 (C_q), 85.9 (CH), 73.0 (CH_2), 69.7 (CH_2), 36.4 (CH_2), 33.0 (CH_2), 31.5 (CH_2), 25.5 (CH_2), 24.0 (CH_2), 21.7 (CH_2). One carbon signal is missing due to the resonance of the signals.

HRMS (ESI) (m/z): calcd for $C1_8H_{23}O_3$ $[M+H]^+$ 287.1642 found 287.1644

FT-IR (cm^{-1}): 3017, 2949, 1624, 1219, 1101, 1101, 931, 770.





***anti*-3,3-Dimethyl-3,4,5a,6,7,8,9,10,11,11a-decahydrocycloocta[b]benzofuran-1(2H)-one (4wa-*anti*)**

***syn*-3,3-Dimethyl-3,4,5a,6,7,8,9,10,11,11a-decahydrocycloocta[b]benzofuran-1(2H)-one (4wa-*syn*)**

General procedure **A** was followed using (Z)-cyclooctene (**1w)** (44.1 mg, 0.40 mmol, 1.0 equiv.), 5, 5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =3:1) yielded **4wa-*anti*** (35.8 mg, 36%) as a colourless oil and **4wa-*syn*** (17.9 mg,18%) as white solid.

(4wa-*anti*)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.71 – 4.64 (m, 1H), 3.13 (t, J = 10.0 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.29 – 2.19 (m, 3H), 2.14 (t, J = 15.6 Hz, 2H), 1.88 – 1.59 (m, 5H), 1.58 – 1.39 (m, 3H), 1.35 – 1.24 (m, 1H), 1.19 (td, J = 13.3, 3.2 Hz, 1H), 1.09 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 195.3 (C_q), 175.4 (C_q), 115.5 (C_q), 92.1 (CH), 51.6 (CH_2), 44.5 (CH), 38.0 (CH_2), 34.8 (CH_2), 34.1 (C_q), 33.4 (CH_2), 29.0 (CH_3), 28.6 (CH_3), 27.0 (CH_2), 24.4 (CH_2), 22.6 (CH_2). One carbon signal is missing due to the resonance of the signals.

HRMS (ESI) (m/z): calcd for $C_{16}H_{25}O_2$ $[M+H]^+$ 249.1849 found 249.1850

FT-IR (cm^{-1}):3021, 2931, 1624, 1522, 1216, 1118, 926, 770.

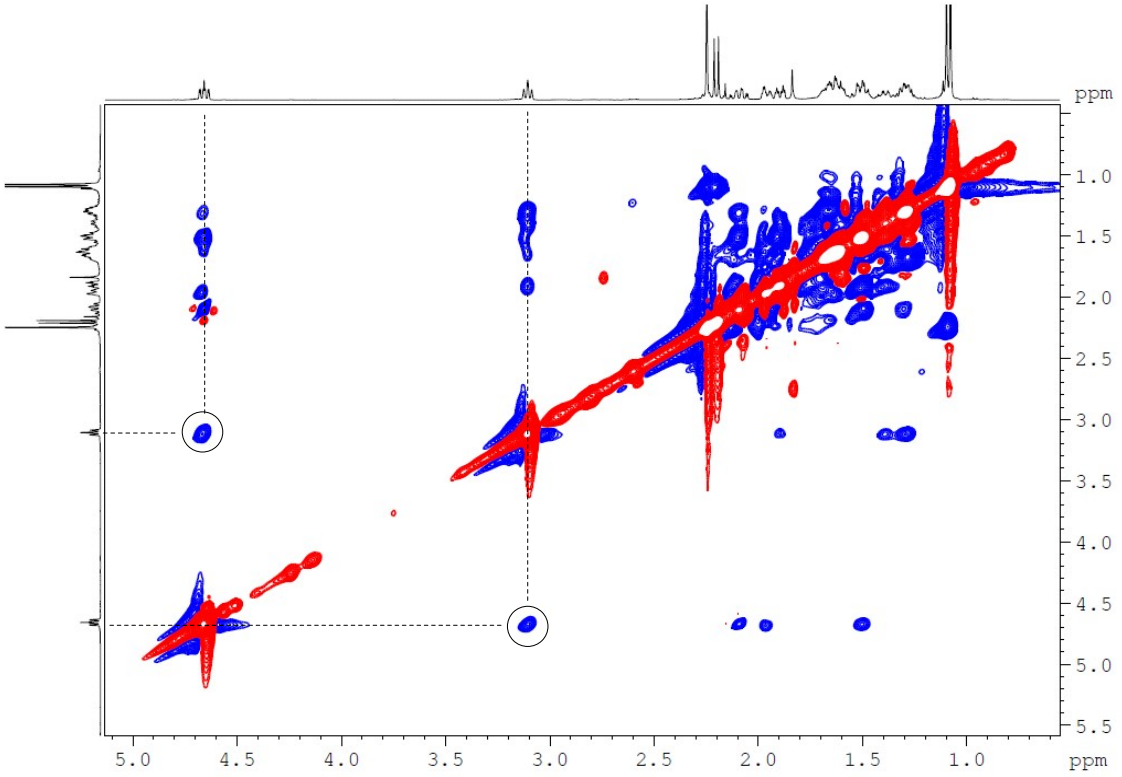
(4wa-*syn*)

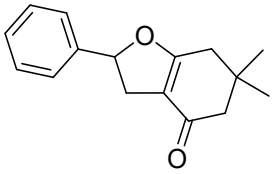
^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.63 (ddd, J = 11.6, 9.5 2.3 Hz, 1H), 3.08 (t, J = 9.5 Hz, 1H), 2.22 (s, 2H), 2.17 (d, J = 10.4 Hz, 2H), 2.12 – 2.01 (m, 1H), 1.98 – 1.90 (m, 1H), 1.87 (dt, J = 14.7, 3.7 Hz, 1H), 1.71 – 1.53 (m, 4H), 1.53 – 1.42 (m, 2H), 1.42 – 1.32 (m, 1H), 1.32 – 1.19 (m, 2H), 1.07 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.8 (C_q), 174.7 (C_q), 117.4 (C_q), 90.6 (CH), 51.4 (CH_2), 43.1 (CH), 37.9 (CH_2), 34.0 (C_q), 29.9 (CH_2), 29.2 (CH_3), 28.2 (CH_3), 26.8 (CH_2), 26.4 (CH_2), 26.2 (CH_2), 25.9 (CH_2), 25.4 (CH_2).

HRMS (ESI) (m/z): calcd for $C_{16}H_{25}O_2$ $[M+H]^+$ 249.1849 found 249.1849.

FT-IR (cm^{-1}): 3022, 2929, 1627, 1522, 1216, 1028, 926, 773.





6,6-Dimethyl-2-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3xa)

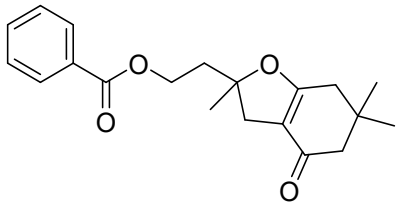
General procedure **A** was followed using styrene (**1x)** (41.7 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3xa** (75.6 mg, 78%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (dd, J = 7.2, 7.2 Hz, 2H), 7.36 – 7.28 (m, 3H), 5.76 (dd, J = 10.5, 7.8 Hz, 1H), 3.43 – 3.19 (m, 1H), 2.88 (dd, J = 14.6, 7.8 Hz, 1H), 2.37 (s, 2H), 2.27 (d, J = 3.4 Hz, 2H), 1.14 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 194.9 (C_q), 176.2 (C_q), 140.9 (C_q), 128.9 (CH), 128.6 (CH), 125.9 (CH), 111.6 (C_q), 86.7 (CH), 51.1 (CH_2), 37.9 (CH_2), 34.3 (C_q), 34.0 (CH_2), 29.0 (CH_3), 28.7 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{16}H_{19}O_2$ $[M+H]^+$ 243.1380 found 243.1381.

FT-IR (cm^{-1}):3013, 2958, 1630, 1218, 1154, 1102, 926, 761.



2-(2,6,6-Trimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl)ethyl benzoate (5a´a)

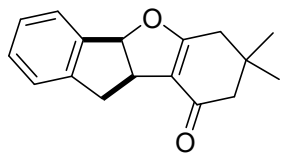
General procedure **A** was followed using 3-methylbut-3-en-1-yl benzoate (**1a´)** (76.1 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **5a´a** (106.4 mg, 81%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (dd, J = 8.0, 1.4 Hz, 2H), 7.53 (dd, J = 8.0, 7.8 Hz, 1H), 7.41 (dd, J = 8.0, 7.8 Hz, 2H), 4.42 (td, J = 6.8, 2.2 Hz, 2H), 2.81 (dt, J = 14.4, 1.7 Hz, 1H), 2.62 (dt, J = 14.4, 1.7 Hz, 1H), 2.21 (d, J = 1.3 Hz, 2H), 2.19 – 2.15 (m, 4H), 1.47 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 175.0 (C_q), 166.5 (C_q), 133.1 (CH), 130.1 (C_q), 129.6 (CH), 128.5 (CH), 111.1 (C_q), 91.1 (C_q), 60.8 (CH_2), 50.9 (CH_2), 39.6 (CH_2), 37.9 (CH_2), 37.8 (CH_2), 34.1 (C_q), 28.8 (CH_3), 28.7 (CH_3), 27.1 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{20}H_{25}O_4$ $[M+H]^+$ 329.1747 found 329.1749

FT-IR (cm^{-1}): 3021, 2402, 2970, 1715, 1626, 1271, 1114, 926, 769.



7,7-Dimethyl-4b,6,7,8,9b,10-hexahydro-9H-indeno[1,2-b]benzofuran-9-one (4ya)

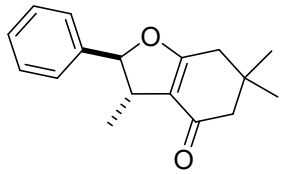
General procedure **A** was followed using 1H-indene (**1y)** (46.5 mg, 0.40 mmol, and 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN (4 mL) for 12 h, purification by column chromatography using (pet ether/EtOAc =2:1) yielded **4ya** (81.4 mg, 80%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, J = 7.1 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.29 – 7.26 (m, 2H), 6.20 (d, J = 8.8 Hz, 1H), 4.17 – 3.92 (m, 1H), 3.35 (dd, J = 17.1, 8.4 Hz, 1H), 3.16 (dd, J = 17.1, 2.3 Hz, 1H), 2.24 (dd, J = 4.9, 1.7 Hz, 2H), 2.19 (s, 2H), 1.09 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.0 (C_q), 175.6 (C_q), 143.5 (C_q), 139.5 (C_q), 129.9 (CH), 127.2 (CH), 125.9 (CH), 125.7 (CH), 115.4 (C_q), 93.7 (CH), 51.3 (CH_2), 41.8 (CH), 38.0 (CH_2), 37.5 (CH_2), 34.1 (C_q), 29.1 (CH_3), 28.4 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{17}H_{19}O_2$ $[M+H]^+$ 255.1380 found 255.1381

FT-IR (cm^{-1}): 3019, 2962, 1716, 1626, 1216, 1096, 927, 762.



3,6,6-Trimethyl-2-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (4za)

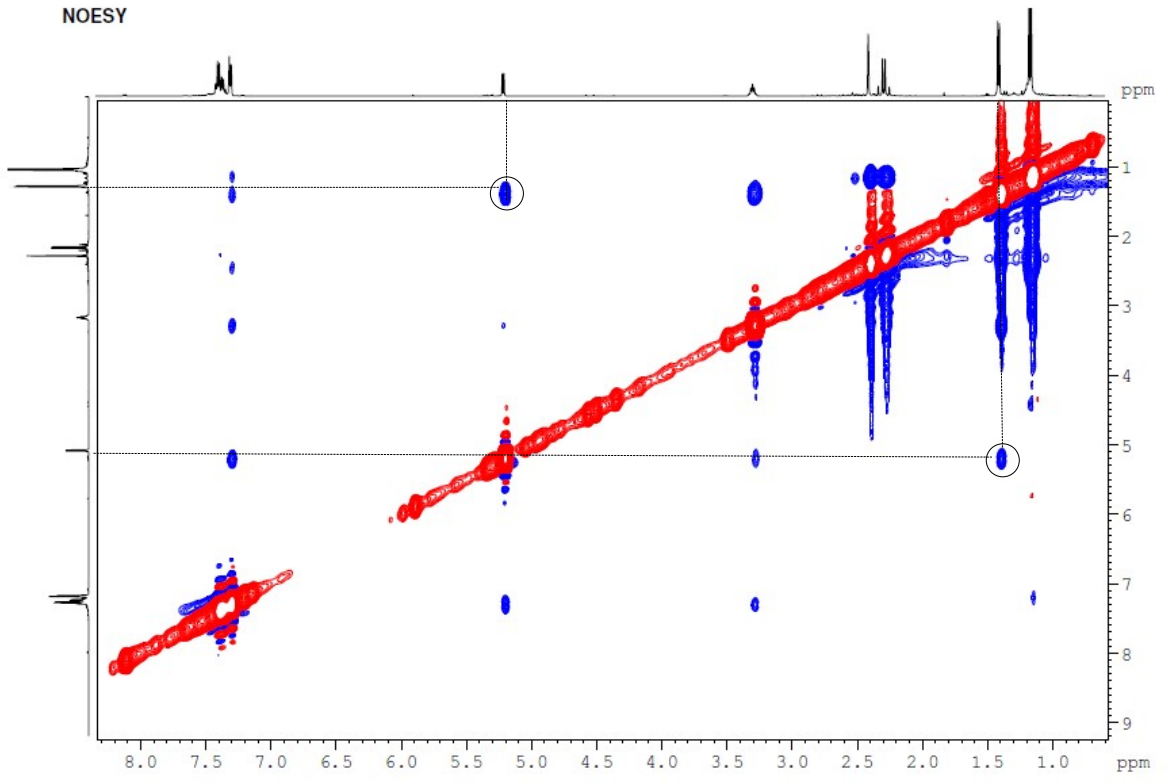
General procedure **A** was followed using (E)-prop-1-en-1-ylbenzene (**1z)** (47.3 mg, 0.40 mmol, 1.0 equiv.), 5,5-dimethyl cyclohexane-1,3-dione (**2a**) (112 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.) and tetrabutylammonium hexafluorophosphate (155 mg, 0.40 mmol,1.0 equiv.) in CH_3CN (4 mL)for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **4za** (84.1 mg, 82%) as a colourless oil.

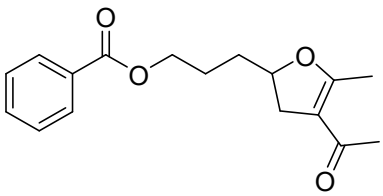
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.23 (m, 3H), 7.21 – 7.15 (m, 2H), 5.08 (d, J = 6.5 Hz, 1H), 3.23 – 3.12 (m, 1H), 2.28 (s, 2H), 2.16 (d, J = 7.0 Hz, 2H), 1.29 (d, J = 6.8 Hz, 3H), 1.05 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.8 (C_q), 175.4 (C_q), 140.4 (C_q), 128.8 (CH), 128.5 (CH), 125.6 (CH), 115.8 (C_q), 94.0 (CH), 51.4 (CH_2), 42.9 (CH), 37.9 (CH_2), 34.2 (C_q), 28.7 (CH_3), 28.6 (CH_3), 19.4 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{17}H_{21}O_2$ $[M+H]^+$ 257.1536 found 257.1538.

FT-IR (cm^{-1}): 3018, 2964, 1633, 1506, 1217, 1113, 937, 774.





3-(4-Acetyl-5-methyl-2,3-dihydrofuran-2-yl)propyl benzoate (3ac)

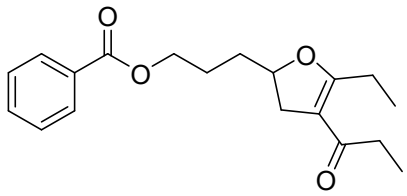
General procedure **A** was followed using pent-4-en-1-yl benzoate (**1a)** (76.1mg, 0.40 mmol, 1.0 equiv.), pentane-2,4-dione (**2c)** (80.1 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.), sodium acetate (16.4 mg, 0.20 mmol, 0.5 equiv.) and tetrabutylammonium tetrafluoroborate (132 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN/HFIP (3.5/0.5 mL) for 12 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ac** (70.4 mg, 61%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (dd, J = 8.1, 1.0 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.5, 7.5 Hz, 2H), 4.66 (tt, J = 14.6, 7.2 Hz, 1H), 4.35 (td, J = 5.9, 2.2 Hz, 2H), 3.04 (ddd, J = 13.8, 10.1, 1.1 Hz, 1H), 2.60 (ddd, J = 14.0, 7.9, 1.1 Hz, 1H), 2.19 (s, 3H), 2.18 (s, 3H), 1.96 – 1.72 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.6 (C_q), 167.6 (C_q), 166.6 (C_q), 133.0 (CH), 130.3 (C_q), 129.6 (CH), 128.4 (CH), 112.1 (C_q), 82.0 (CH), 64.5 (CH_2), 36.1 (CH_2), 32.7 (CH_2), 29.4 (CH_3), 24.7 (CH_2), 15.1 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{17}H_{21}O_4$ $[M+H]^+$ 289.1434 found 289.1438.

FT-IR (cm^{-1}): 3068, 2956, 2253, 1714, 1596, 1315, 909, 735, 650.



3-(5-Ethyl-4-propionyl-2,3-dihydrofuran-2-yl)propyl benzoate (3ad)

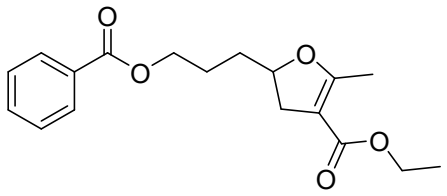
General procedure **A** was followed using pent-4-en-1-yl benzoate (**1a)** (76.1mg, 0.40 mmol, 1.0 equiv.), heptane-3,5-dione (**2d)** (102.5 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.), sodium acetate (16.4 mg, 0.20 mmol, 0.5 equiv.) and tetrabutylammonium tetrafluoroborate (132 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN/HFIP (3.5/0.5 mL) for 16 h. Purification by column chromatography using (pet ether/EtOAc =2:1) yielded **3ad** (69.7 mg, 55%) as a colourless oil.

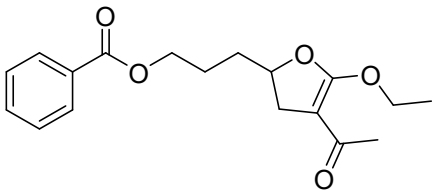
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (dd, J = 7.1, 1.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.5, 7.5 Hz, 2H), 4.71 – 4.64 (m, 1H), 4.42 – 4.29 (m, 2H), 3.06 (dd, J = 13.8, 10.2 Hz, 1H), 2.69 – 2.57 (m, 3H), 2.42 (q, J = 7.3 Hz, 2H), 1.98 – 1.71 (m, 4H), 1.12 (t, J = 7.5 Hz, 3H), 1.07 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.5 (C_q), 171.9 (C_q), 166.5 (C_q), 132.9 (CH), 130.2 (C_q), 129.5 (CH), 128.4 (CH), 109.6 (C_q), 81.7 (CH), 64.5 (CH_2), 35.8 (CH_2), 34.5 (CH_2), 32.7 (CH_2), 24.6 (CH_2), 22.0 (CH_2), 11.1 (CH_3), 7.9 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{19}H_{25}O_4$ $[M+H]^+$ 317.1747 found 317.1745.

FT-IR (cm^{-1}): 2975, 2940, 1717, 1595, 1456, 1276, 1115, 756, 713.





Ethyl 5-(3-(benzoyloxy)propyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3ae) and **3-(4-acetyl-5-ethoxy-2,3-dihydrofuran-2-yl)propyl benzoate (3ae-R)**

General procedure **A** was followed using pent-4-en-1-yl benzoate (**1a)** (76.1mg, 0.40 mmol, 1.0 equiv.), ethyl 3-oxobutanoate (**2e)** (104.1 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.), sodium acetate (16.4 mg, 0.20 mmol, 0.5 equiv.) and tetrabutylammonium tetrafluoroborate (132 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN/HFIP (3.5/0.5 mL) for 6 h. Purification by column

chromatography using (pet ether/EtOAc =2:1 to 1:2) yielded **3ae** (47.0 mg, 37%) and **3ae-R** (11.5 mg, 9%) as a colourless oil.

3ae

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 – 8.00 (m, 2H), 7.57 – 7.52 (m, 1H), 7.45 – 7.40 (m, 2H), 4.70 – 4.60 (m, 1H), 4.40 – 4.30 (m, 2H), 4.27 – 4.07 (m, 2H), 2.99 (t, J = 12.1 Hz, 1H), 2.63 – 2.45 (m, 1H), 2.17 (s, 3H), 1.95 – 1.70 (m, 4H), 1.30 – 1.20 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.8 (C_q), 166.7 (C_q), 166.4 (C_q), 133.1 (CH), 130.4 (C_q), 129.7 (CH), 128.5 (CH), 101.7 (C_q), 81.9 (CH), 64.6 (CH_2), 59.5 (CH_2), 35.4 (CH_2), 32.8 (CH_2), 24.7 (CH_2), 14.6 (CH_3), 14.2 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{22}NaO_5$ $[M+Na]^+$ 341.1359 found 341.1352.

FT-IR (cm^{-1}): 2958, 2255, 1794, 1645, 1321, 1278, 909, 740, 651.

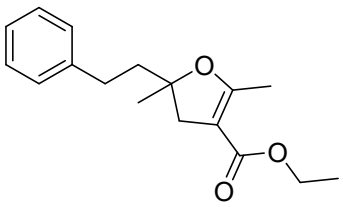
3ae-R

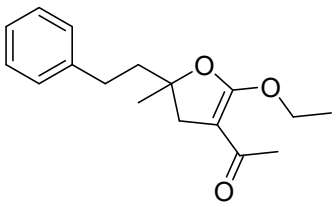
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.5, 7.5 Hz, 2H), 4.80 – 4.65 (m, 1H), 4.37 (t, J = 5.2 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 3.05 (dd, J = 13.4, 9.7 Hz, 1H), 2.61 (dd, J = 13.4, 7.2 Hz, 1H), 2.25 (s, 3H), 1.94 – 1.80 (m, 4H), 1.37 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.5 (C_q), 167.2 (C_q), 166.7 (C_q), 133.2 (CH), 130.3 (C_q), 129.7 (CH), 128.6 (CH), 90.0 (C_q), 82.0 (CH), 66.5 (CH_2), 64.4 (CH_2), 33.5 (CH_2), 32.7 (CH_2), 27.8 (CH_3), 24.7 (CH_2), 15.1 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{18}H_{23}O_5$ $[M+H]^+$ 319.1540 found 319.1541.

FT-IR (cm^{-1}): 3015, 1715, 1584, 1443, 1276, 1217, 951, 757, 667.





Ethyl 2,5-dimethyl-5-phenethyl-4,5-dihydrofuran-3-carboxylate (5i′e) and **1-(2-ethoxy-5-methyl-5-phenethyl-4,5-dihydrofuran-3-yl)ethan-1-one (5i′e-R)**

General procedure **A** was followed using (3-methylbut-3-en-1-yl)benzene (**1i′)** (58.5mg, 0.40 mmol, 1.0 equiv.), ethyl 3-oxobutanoate (**2e)** (104.1 mg, 0.80 mmol, 2.0 equiv.), Co-salen (**6**) (6.1 mg, 10 µmol, 0.025 equiv.), sodium acetate (16.4 mg, 0.20 mmol, 0.5 equiv.) and tetrabutylammonium tetrafluoroborate (132 mg, 0.40 mmol, 1.0 equiv.) in CH_3CN/HFIP (3.5/0.5 mL) for 6 h. Purification by column chromatography using (pet ether/EtOAc =2:1 to 1:2) yielded **5i′e** (35.5 mg, 32%) and **5i′e-R** (35.0 mg, 32%) as a colourless oil.

5i′e

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25 – 7.17 (m, 2H), 7.15 – 7.08 (m, 3H), 4.10 (q, J = 7.1 Hz, 2H), 2.76 (dd, J = 14.4, 1.5 Hz, 1H), 2.65 – 2.52 (m, 3H), 2.11 (t, J = 1.4 Hz, 3H), 1.93 – 1.79 (m, 2H), 1.33 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.0 (C_q), 166.6 (C_q), 142.0 (C_q), 128.6 (CH), 128.4 (CH), 126.0 (CH), 101.3 (C_q), 87.9 (C_q), 59.5 (CH_2), 43.2 (CH_2), 40.9 (CH_2), 30.3 (CH_2), 26.9 (CH_3), 14.6 (CH_3), 14.5 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{17}H_{23}O_3$ $[M+H]^+$ 275.1642 found 275.1638.

FT-IR (cm^{-1}): 2980, 2933, 2254, 1683, 1642, 1381, 910, 743, 651.

5i′e-R

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 7.2 Hz, 2H), 7.21 – 7.17 (m, 3H), 4.21 (dtd, J = 10.3, 7.1, 3.6 Hz, 2H), 2.90 (d, J = 13.5 Hz, 1H), 2.73 – 2.66 (m, 3H), 2.26 (s, 3H), 2.05 – 1.96 (m, 2H), 1.46 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.5 (C_q), 166.3 (C_q), 141.5 (C_q), 128.6 (CH), 128.4 (CH), 126.1 (CH), 90.1 (C_q), 88.9 (C_q), 66.1 (CH_2), 42.9 (CH_2), 39.1 (CH_2), 30.2 (CH_2), 27.8 (CH_3), 26.7 (CH_3), 15.1 (CH_3).

HRMS (ESI) (m/z): calcd for $C_{17}H_{23}O_3$ $[M+H]^+$ 275.1642 found 275.1643.

FT-IR (cm^{-1}): 3017, 2935, 1727, 1582, 1436, 1216, 1053, 765, 668.

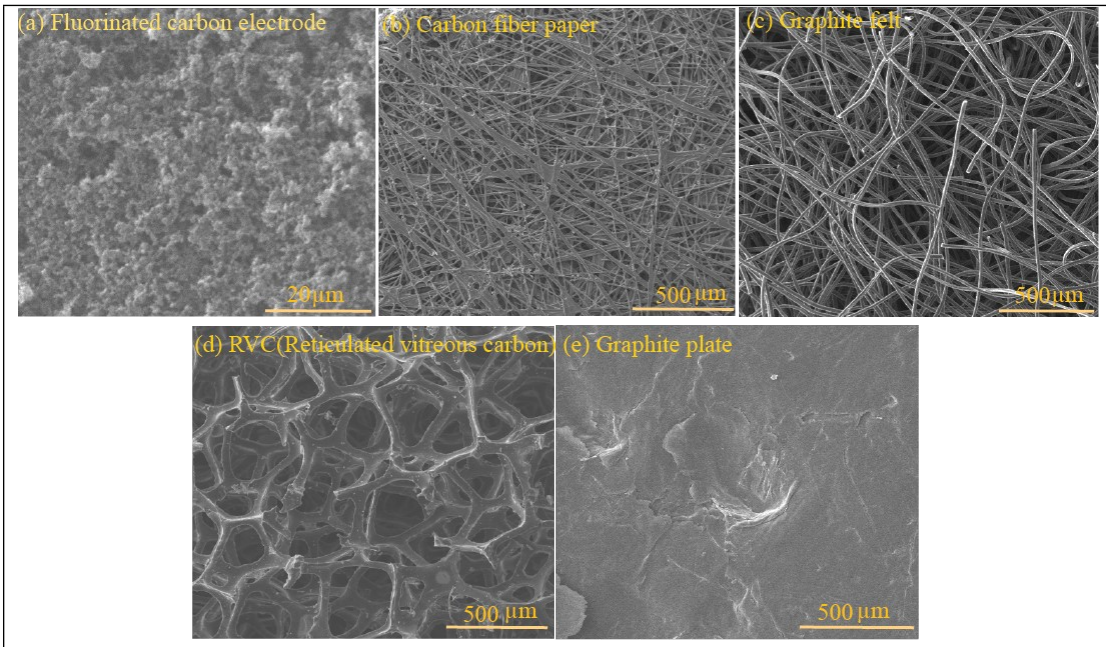


Figure-S1: (a) Polytetrafluoroethylene (PTFE)-coated carbon electrode (fluorinated carbon electrode), revealing a uniformly porous structure on the electrode surface; (b) ESEM image of PTFE-coated carbon fiber paper electrodes; (c) ESEM images of graphite felt; (d ESEM image of reticulated vitreous carbon (RVC); (e) ESEM image of the graphite plate, which exhibits an almost flat 2D graphene structure, resulting in significantly lower porosity.

Characterization of electrode materials

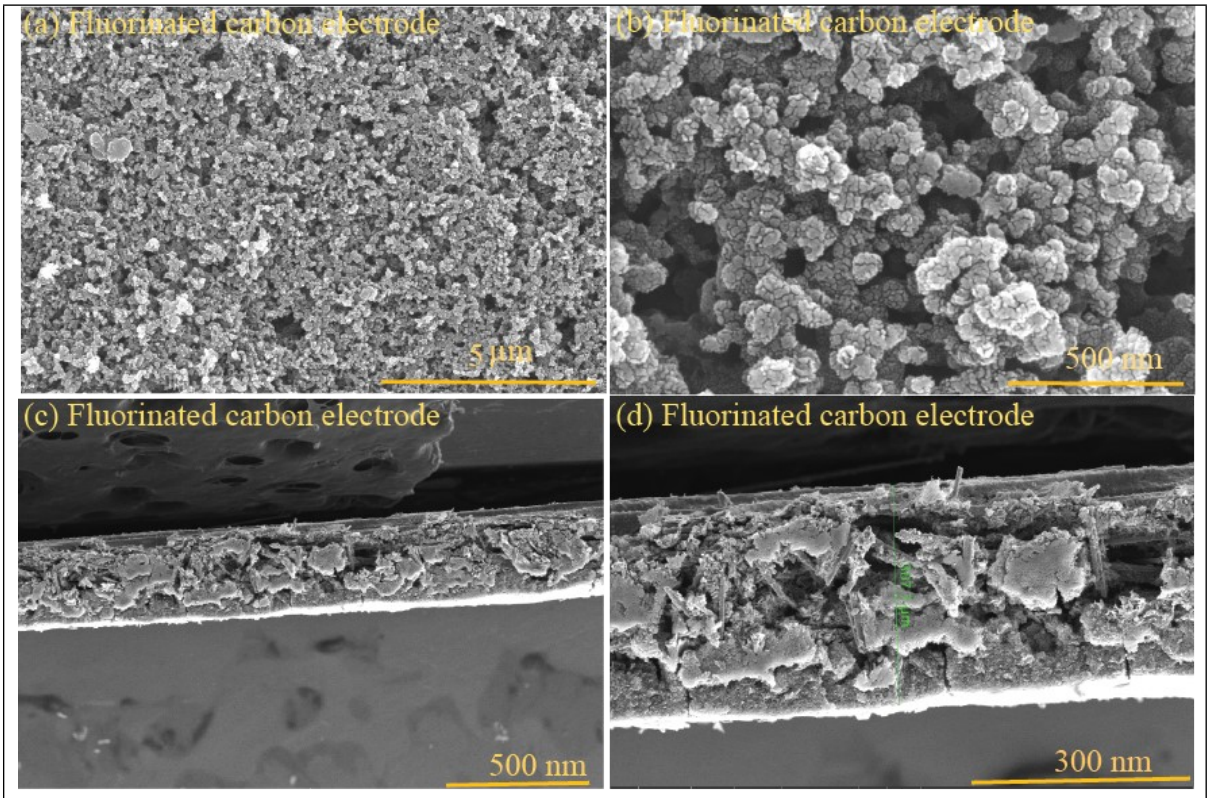


Figure-S2: (a)-(b) Field-emission scanning electron microscopy (FESEM) images of (PTFE)-coated carbon electrode (fluorinated carbon electrode), elucidating the microporous architecture; (c)-(d) cross-sectional FESEM images of the (PTFE)-coated carbon electrode displaying the heterojunction interface with an overall thickness of 200 uM.

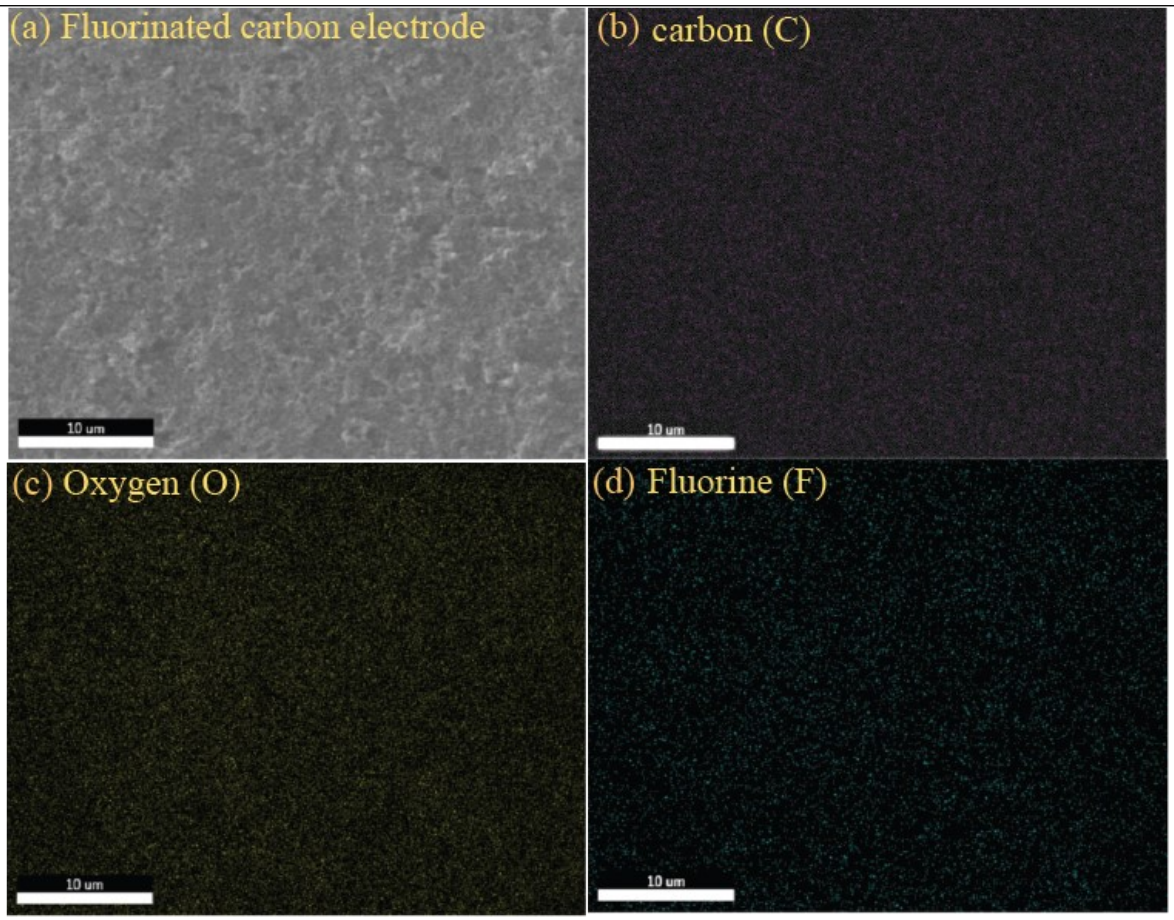
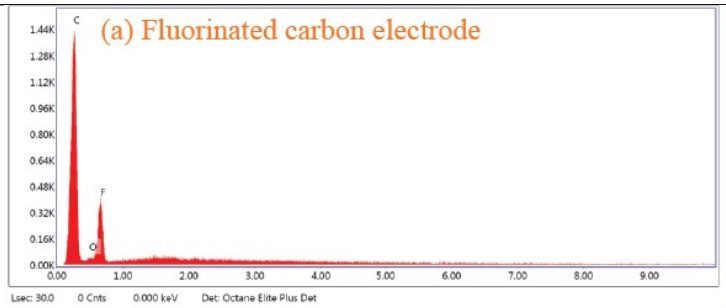
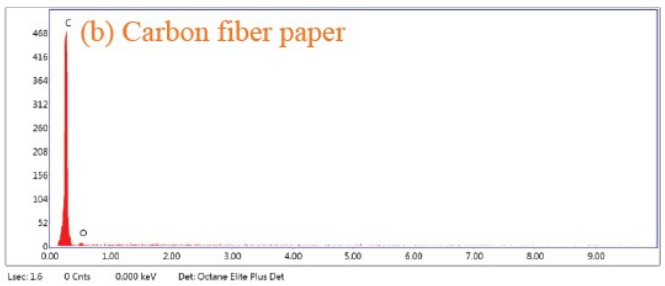


Figure-S3: (a–d) Elemental mapping was conducted for carbon (C), oxygen (O), and fluorine (F) on a polytetrafluoroethylene (PTFE)-coated carbon electrode.



Element	Weight %	Atomic %
C K	76.63	83.50
O K	3.08	2.52
F K	20.29	13.98



Element	Weight %	Atomic %
C K	91.78	93.91
O K	6.42	4.93
F K	1.80	1.16

Figure-S4: Energy-dispersive X-ray spectroscopy (EDS) mapping was performed to analyze the elemental distribution in two systems: (a) PTFE-coated carbon electrode, and (b) PTFE-coated carbon fiber paper electrode.

Cyclic Voltammetry

Cyclic voltammetry A glassy-carbon electrode (3 mm diameter, disc-electrode) was used as the working electrode, a Pt–wire as auxiliary electrode and an Ag–AgCl as reference electrode.

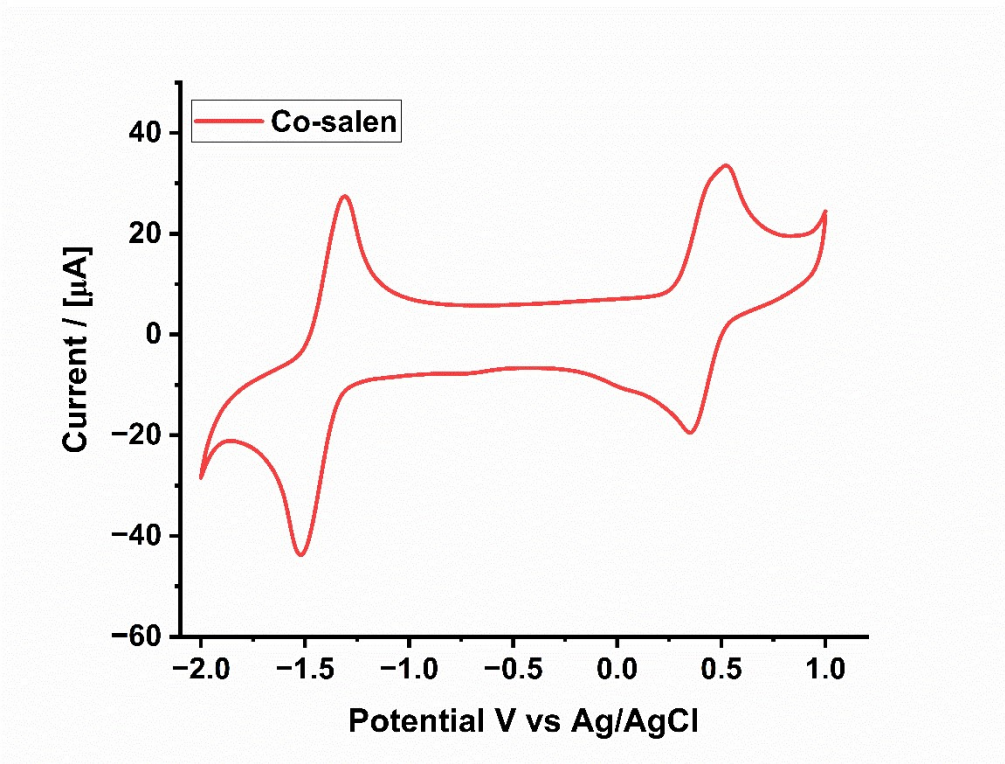


Figure S5 Cyclic voltammetry was performed in CH_3CN using $^{n}Bu_4NPF_6$ (0.1 M) at 100 mV/Sec scan rate vs Ag/AgCl. Cyclic voltammetry of Co-salen.

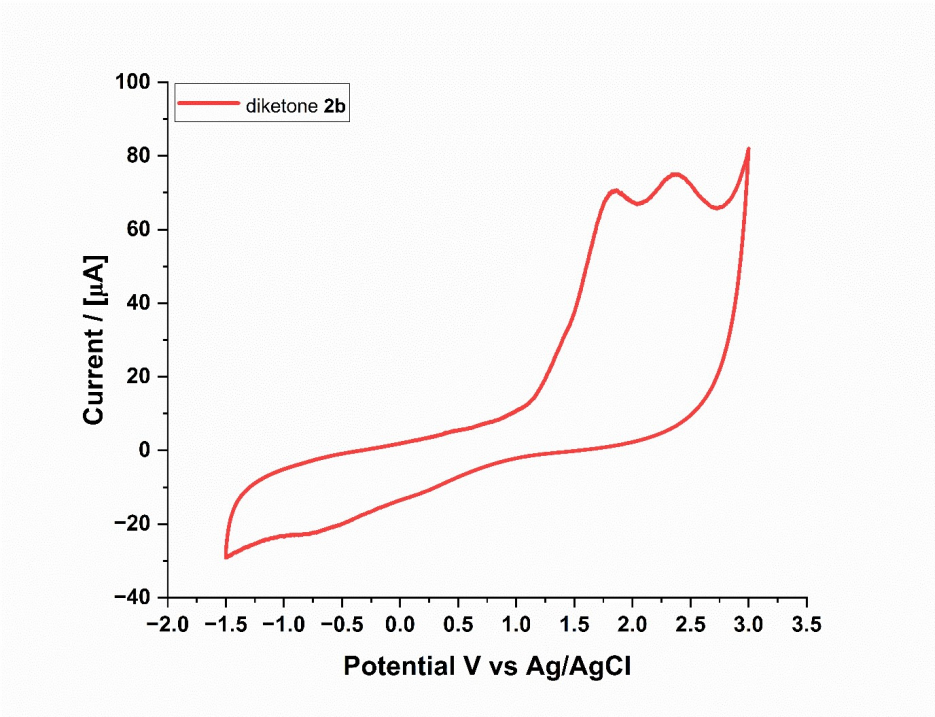


Figure S6 Cyclic voltammetry was performed in CH_3CN using $^nBu_4NPF_6$ (0.1 M) at 100 mV/Sec scan rate vs Ag/AgCl. Cyclic voltammetry of cyclohexane-1,3-dione **2b**

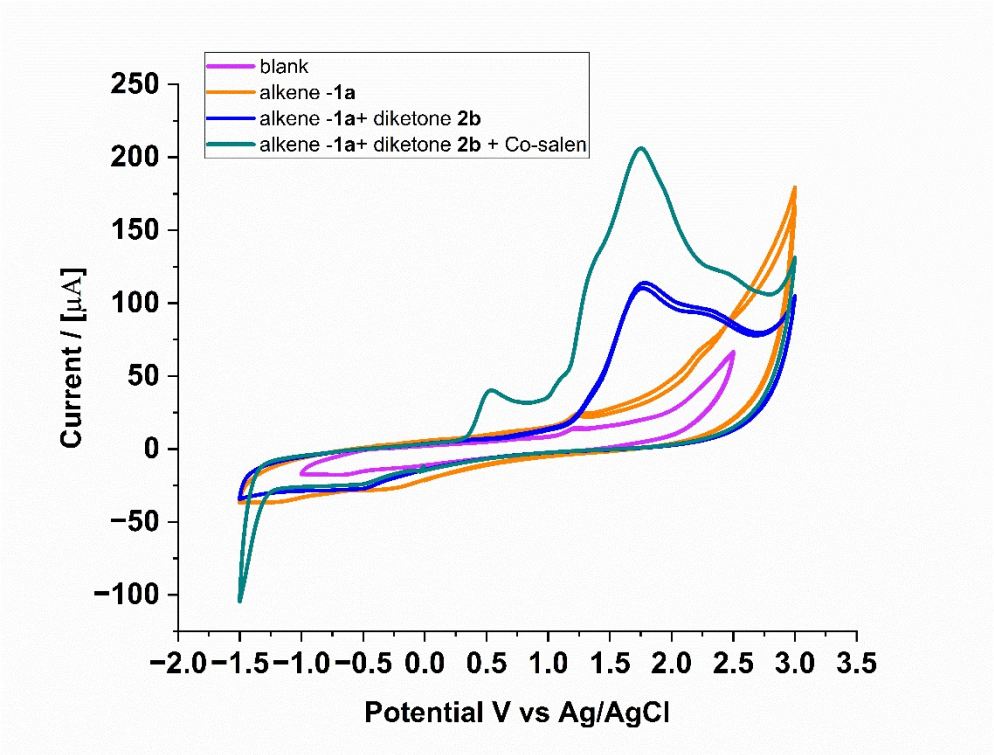


Figure S7 Cyclic voltammetry was performed in CH_3CN $^nBu_4NPF_6$ (0.1 M) using glassy-carbon (3 mm diameter, disc-electrode) working electrode and Pt wire counter electrode at 100 mV/Sec scan rate *vs* Ag/AgCl. Blank (majenta), alkene-**1a** (orange), alkene-**1a** + diketone **2b** (blue) and alkene-**1a** + diketone **2b** + Co-salen (green)

References:

[1] Cruz, D. A.; Sinka, V.; de Armas, P.; Steingruber, H. S.; Fernández, I.; Martín, V. S.; Miranda, P. O.; Padrón, J. I., Iron(II) and Copper(I) Control the Total Regioselectivity in the Hydrobromination of Alkenes. *Org. Lett.* **2021**, *23*, 6105-6109.

[2] Liang, Q.-J.; Yang, C.; Meng, F.-F.; Jiang, B.; Xu, Y.-H.; Loh, T.-P., Chelation versus Non-Chelation Control in the Stereoselective Alkenyl sp2 C−H Bond Functionalization Reaction. *Angew. Chem., Int. Ed.* **2017**, *56*, 5091-5095.

[3] García-Vázquez, V.; Hoteite, L.; Lakeland, C. P.; Watson, D. W.; Harrity, J. P. A., A Pd-Catalyzed [4 + 2] Annulation Approach to Fluorinated N-Heterocycles. *Org. Lett.* **2021**, *23*, 2811-2815.

[4] Ginotra, S. K.; Friest, J. A.; Berkowitz, D. B., Halocarbocyclization Entry into the Oxabicyclo[4.3.1]decyl Exomethylene-δ-Lactone Cores of Linearifolin and Zaluzanin A: Exploiting Combinatorial Catalysis. *Org. Lett.* **2012**, *14*, 968-971.

[5] Wu, F.-P.; Yuan, Y.; Schünemann, C.; Kamer, P. C. J.; Wu, X.-F., Copper-Catalyzed Regioselective Borocarbonylative Coupling of Unactivated Alkenes with Alkyl Halides: Synthesis of β-Boryl Ketones. *Angew. Chem., Int. Ed.* **2020**, *59*, 10451-10455.

[6] Li, X.; He, S.; Song, Q., Diethylzinc-Mediated Radical 1,2-Addition of Alkenes and Alkynes. *Org. Lett.* **2021**, *23*, 2994-2999.

[7] Hou, Z.-W.; Li, L.; Wang, L., Organocatalytic electrochemical amination of benzylic C–H bonds. *Org. Chem. Front.* **2021**, *8*, 4700-4705.

[8] Horn, A.; Dussault, P. H., Synthesis of α-Cyano and α-Sulfonyl Cyclic Ethers via Intramolecular Reactions of Peroxides with Sulfone- and Nitrile-Stabilized Carbanions. *J. Org. Chem.* **2019**, *84*, 14611-14626.

[9] Lamb, J. R.; Jung, Y.; Coates, G. W., Meinwald-type rearrangement of monosubstituted epoxides to methyl ketones using an [Al porphyrin]+[Co(CO)4]− catalyst. *Org. Chem. Front.* **2015**, *2*, 346-349.

[10] Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M., Hydrazines and Azides via the Metal-Catalyzed Hydrohydrazination and Hydroazidation of Olefins. *J. Am. Chem. Soc.* **2006**, *128*, 11693-11712.

[11] Wu, X.; Gannett, C. N.; Liu, J.; Zeng, R.; Novaes, L. F. T.; Wang, H.; Abruña, H. D.; Lin, S., Intercepting Hydrogen Evolution with Hydrogen-Atom Transfer: Electron-Initiated Hydrofunctionalization of Alkenes. *J. Am. Chem. Soc.* **2022**, *144*, 17783-17791.

Crystal data: 6,6-Dimethyl-2-(3-(phenylthio)propyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ra)

A specimen of $C_{19}H_{24}O_2S$, approximate dimensions 0.040 mm x 0.090 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The integration of the data using a monoclinic unit cell yielded a total of 31647 reflections to a maximum θ angle of 28.72° (0.74 Å resolution), of which 4463 were independent (average redundancy 7.091, completeness = 99.9%, R_{int} = 7.47%, R_{sig} = 4.75%) and 3384 (75.82%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 11.5620(8) Å, $\underline{b}$ = 5.6279(4) Å, $\underline{c}$ = 26.4527(18) Å, β = 92.458(3)°, volume = 1719.7(2) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6037 and 0.7458.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21/n , with Z = 4 for the formula unit, $C_{19}H_{24}O_2S$. The final anisotropic full-matrix least-squares refinement on F^2 with 201 variables converged at R1 = 5.19%, for the observed data and wR2 = 13.12% for all data. The goodness-of-fit was 1.031. The largest peak in the final difference electron density synthesis was 0.929 $e^-/Å^3$ and the largest hole was -0.407 $e^-/Å^3$ with an RMS deviation of 0.065 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.222 g/cm^3 and F(000), 680 e^-.

Table 1. Sample and crystal data for RCS_003

Identification code	RCS_003	
Chemical formula	$C_{19}H_{24}O_2S$	
Formula weight	316.44 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.090 x 0.180 mm	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 11.5620(8) Å	α = 90°
	b = 5.6279(4) Å	β = 92.458(3)°
	c = 26.4527(18) Å	γ = 90°
Volume	1719.7(2) $Å^3$	
Z	4	
Density (calculated)	1.222 g/cm^3	
Absorption coefficient	0.193 mm^{-1}	
F(000)	680	

Table 2. Data collection and structure refinement for RCS_003.

Theta range for data collection	1.95 to 28.72°	
Index ranges	-15<=h<=15, -7<=k<=7, -35<=l<=34	
Reflections collected	31647	
Independent reflections	4463 [R(int) = 0.0747]	
Max. and min. transmission	0.7458 and 0.6037	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4463 / 0 / 201	
Goodness-of-fit on F^2	1.031	
Δ/σ_{max}	0.001	
Final R indices	3384 data; I>2σ(I)	R1 = 0.0519, wR2 = 0.1167

	all data	R1 = 0.0764, wR2 = 0.1312
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0444P)^2+1.8655P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.929 and -0.407 eÅ^{-3}	
R.M.S. deviation from mean	0.065 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for RCS_003.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S1	0.04810(4)	0.02826(9)	0.57327(2)	0.02416(14)
O1	0.55577(12)	0.0399(3)	0.40601(5)	0.0234(3)
O2	0.24633(13)	0.5449(3)	0.43276(5)	0.0292(4)
C1	0.42477(16)	0.5942(3)	0.32042(7)	0.0186(4)
C2	0.52893(16)	0.7113(4)	0.34876(8)	0.0226(4)
C3	0.49906(16)	0.8612(3)	0.39414(7)	0.0193(4)
C4	0.40183(17)	0.7810(4)	0.42156(7)	0.0222(4)
C5	0.33682(17)	0.5968(4)	0.40441(7)	0.0222(4)
C6	0.25076(18)	0.7070(4)	0.47741(7)	0.0243(4)
C7	0.35256(19)	0.8786(4)	0.46931(8)	0.0283(5)
C8	0.26266(18)	0.5525(4)	0.52384(8)	0.0242(4)
C009	0.35477(17)	0.4524(3)	0.35845(7)	0.0204(4)
C9	0.15833(17)	0.3877(4)	0.52854(7)	0.0225(4)
C10	0.17393(16)	0.2196(3)	0.57340(7)	0.0207(4)
C11	0.07533(16)	0.8337(3)	0.62458(7)	0.0183(4)
C12	0.17575(17)	0.8340(4)	0.65568(7)	0.0232(4)
C13	0.18912(18)	0.6661(4)	0.69392(8)	0.0278(5)
C14	0.10458(18)	0.4973(4)	0.70149(8)	0.0284(5)
C15	0.00506(18)	0.4967(4)	0.67040(8)	0.0259(4)
C16	0.99007(17)	0.6640(4)	0.63227(7)	0.0219(4)
C17	0.34809(18)	0.7823(4)	0.29415(8)	0.0264(4)
C18	0.46911(19)	0.4248(4)	0.28057(8)	0.0290(5)

	x/a	y/b	z/c	U(eq)

Table 4. Bond lengths (Å) for RCS_003.

S1-C11	1.7618(19)	S1-C10	1.8099(19)
O1-C3	1.234(2)	O2-C5	1.345(2)
O2-C6	1.491(2)	C1-C18	1.526(3)
C1-C17	1.529(3)	C1-C2	1.539(3)
C1-C009	1.541(3)	C2-C3	1.519(3)
C3-C4	1.436(3)	C4-C5	1.348(3)
C4-C7	1.511(3)	C5-C009	1.484(3)
C6-C8	1.507(3)	C6-C7	1.545(3)
C8-C9	1.531(3)	C9-C10	1.523(3)
C11-C16	1.394(3)	C11-C12	1.394(3)
C12-C13	1.388(3)	C13-C14	1.384(3)
C14-C15	1.385(3)	C15-C16	1.385(3)

Table 5. Bond angles (°) for RCS_003.

C11-S1-C10	104.55(9)	C5-O2-C6	107.92(15)
C18-C1-C17	108.90(17)	C18-C1-C2	108.96(16)
C17-C1-C2	110.57(16)	C18-C1-C009	109.22(16)
C17-C1-C009	110.17(16)	C2-C1-C009	109.00(16)
C3-C2-C1	115.03(15)	O1-C3-C4	123.12(18)
O1-C3-C2	121.16(17)	C4-C3-C2	115.72(16)
C5-C4-C3	120.59(18)	C5-C4-C7	109.65(17)
C3-C4-C7	129.72(18)	O2-C5-C4	114.52(18)
O2-C5-C009	118.52(17)	C4-C5-C009	126.96(18)
O2-C6-C8	106.94(16)	O2-C6-C7	105.85(15)
C8-C6-C7	115.51(18)	C4-C7-C6	101.85(16)
C6-C8-C9	111.78(17)	C5-C009-C1	110.33(16)
C10-C9-C8	111.85(17)	C9-C10-S1	107.45(13)
C16-C11-C12	119.41(18)	C16-C11-S1	115.74(15)
C12-C11-S1	124.80(15)	C13-C12-C11	119.55(19)
C14-C13-C12	121.0(2)	C13-C14-C15	119.29(19)
C16-C15-C14	120.38(19)	C15-C16-C11	120.32(19)

Table 6. Anisotropic atomic displacement parameters (Å²) for RCS_003.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0214(2)	0.0233(3)	0.0273(3)	0.0072(2)	-0.00455(18)	-0.0051(2)
O1	0.0219(7)	0.0237(7)	0.0245(7)	-0.0037(6)	0.0005(5)	-0.0076(6)
O2	0.0329(8)	0.0347(8)	0.0205(7)	-0.0071(6)	0.0076(6)	-0.0157(7)
C1	0.0184(8)	0.0184(9)	0.0192(9)	-0.0042(7)	0.0022(7)	-0.0013(7)
C2	0.0164(9)	0.0254(10)	0.0263(10)	-0.0056(8)	0.0035(7)	-0.0027(8)
C3	0.0175(8)	0.0203(9)	0.0200(9)	-0.0007(8)	-0.0016(7)	-0.0027(7)
C4	0.0238(9)	0.0225(10)	0.0204(9)	-0.0031(8)	0.0016(7)	-0.0070(8)
C5	0.0223(9)	0.0258(10)	0.0188(9)	-0.0005(8)	0.0038(7)	-0.0058(8)
C6	0.0272(10)	0.0257(10)	0.0202(9)	-0.0042(8)	0.0041(8)	-0.0048(8)
C7	0.0317(11)	0.0292(11)	0.0244(10)	-0.0045(9)	0.0057(9)	-0.0114(9)
C8	0.0272(10)	0.0238(10)	0.0217(10)	-0.0036(8)	0.0031(8)	-0.0052(8)
C009	0.0228(9)	0.0174(9)	0.0211(9)	-0.0031(8)	0.0022(7)	-0.0042(7)
C9	0.0266(10)	0.0219(10)	0.0190(9)	0.0004(8)	0.0027(8)	-0.0038(8)
C10	0.0203(9)	0.0176(9)	0.0245(10)	-0.0004(8)	0.0031(7)	-0.0027(7)
C11	0.0192(9)	0.0186(9)	0.0172(9)	-0.0006(7)	0.0013(7)	-0.0010(7)
C12	0.0202(9)	0.0252(10)	0.0241(10)	0.0015(8)	-0.0009(8)	-0.0043(8)
C13	0.0235(10)	0.0366(12)	0.0231(10)	0.0031(9)	-0.0016(8)	-0.0020(9)
C14	0.0292(10)	0.0339(12)	0.0224(10)	0.0094(9)	0.0045(8)	-0.0001(9)
C15	0.0265(10)	0.0274(11)	0.0245(10)	0.0042(9)	0.0079(8)	-0.0063(8)
C16	0.0183(9)	0.0262(10)	0.0214(9)	-0.0008(8)	0.0011(7)	-0.0035(8)
C17	0.0289(10)	0.0249(10)	0.0250(10)	0.0004(9)	-0.0029(8)	0.0003(8)
C18	0.0295(11)	0.0290(11)	0.0291(11)	-0.0120(9)	0.0100(9)	-0.0059(9)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for RCS_003.

	x/a	y/b	z/c	U(eq)
H2A	0.5834	0.5849	0.3604	0.027000
H2B	0.5696	0.8130	0.3247	0.027000

	x/a	y/b	z/c	U(eq)
H6	0.1770	0.7995	0.4781	0.029000
H7A	0.3252	1.0441	0.4645	0.034000
H7B	0.4102	0.8729	0.4981	0.034000
H8A	0.2704	0.6546	0.5543	0.029000
H8B	0.3339	0.4556	0.5222	0.029000
H00A	0.2788	0.4076	0.3425	0.024000
H00B	0.3968	0.3047	0.3680	0.024000
H9A	0.0879	0.4847	0.5325	0.027000
H9B	0.1473	0.2937	0.4971	0.027000
H10A	0.1808	0.3109	0.6054	0.025000
H10B	0.2450	0.1236	0.5703	0.025000
H12	0.2346	-0.0517	0.6507	0.028000
H13	0.2574	-0.3330	0.7152	0.033000
H14	0.1147	-0.6171	0.7277	0.034000
H15	-0.0532	-0.6190	0.6753	0.031000
H16	-0.0787	-0.3370	0.6113	0.026000
H17A	0.3939	0.8737	0.2706	0.040000
H17B	0.3175	0.8893	0.3196	0.040000
H17C	0.2837	0.7044	0.2754	0.040000
H18A	0.5150	0.5138	0.2567	0.043000
H18B	0.4033	0.3497	0.2623	0.043000
H18C	0.5175	0.3022	0.2971	0.043000

Crystal data: *syn*-3,3-Dimethyl-3,4,5a,6,7,8,9,10,11,11a-decahydrocycloocta[b]benzofuran-1(2H)-one (4wa-*syn*)

A specimen of $C_{16}H_{24}O_2$, approximate dimensions 0.030 mm x 0.080 mm x 0.110 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The total exposure time was 4.33 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 18011reflections to a maximum θ angle of 28.37° (0.75 Å resolution), of which 3472 were independent (average redundancy 5.188, completeness = 99.8%, R_{int} = 13.88%, R_{sig} = 12.10%) and 2070 (59.62%) were greater than $2\sigma(F^2)$. The final cell constants

of a = 10.399(2) Å, b = 13.561(3) Å, c = 9.8880(18) Å, volume = 1394.4(5) Å^3, are based upon the refinement of the XYZ-centroids of 1935 reflections above 20 σ(I) with 4.936° < 2θ < 42.32°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.801. The calculated minimum and maximum transmission coefficients (based on crystal size) are0.9920 and 0.9980.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P c a 21, with Z = 4 for the formula unit, $C_{16}H_{24}O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 166variables converged at R1 = 6.37%, for the observed data and wR2 = 13.52% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.282 e^-/Å^3 and the largest hole was-0.251 e^-/Å^3 with an RMS deviation of 0.062 e^-/Å^3. On the basis of the final model, the calculated density was 1.183 g/cm^3 and F(000), 544 e^-.

Table 1. Sample and crystal data for RCS_A_024_180124.

Identification code	RCS_A_024_180124	
Chemical formula	$C_{16}H_{24}O_2$	
Formula weight	248.35 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.030 x 0.080 x 0.110 mm	
Crystal system	orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 10.399(2) Å	α = 90°
	b = 13.561(3) Å	β = 90°
	c = 9.8880(18) Å	γ = 90°
Volume	1394.4(5) Å^3	
Z	4	
Density (calculated)	1.183 g/cm^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	544	

Table 2. Data collection and structure refinement for RCS_A_024_180124.

Theta range for data collection	2.47 to 28.37°
Index ranges	-13<=h<=13, -18<=k<=17, -13<=l<=13
Reflections collected	18011
Independent reflections	3472 [R(int) = 0.1388]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9980 and 0.9920
Structure solution technique	direct methods
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3472 / 1 / 166
Goodness-of-fit on F^2	1.033

Final R indices	2070 data; I>2σ(I)	R1 = 0.0637, wR2 = 0.1100
	all data	R1 = 0.1378, wR2 = 0.1352
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0447P)^2+0.1240P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.4(10)	
Extinction coefficient	0.0290(40)	
Largest diff. peak and hole	0.282 and -0.251 eÅ^{-3}	
R.M.S. deviation from mean	0.062 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for RCS_A_024_180124.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.7763(3)	0.8380(2)	0.4220(3)	0.0336(8)
O2	0.3553(3)	0.7869(2)	0.5525(3)	0.0271(7)
C1	0.6598(4)	0.8496(3)	0.4007(4)	0.0242(10)
C5	0.4375(4)	0.8260(3)	0.4607(4)	0.0218(10)
C6	0.5612(4)	0.8093(3)	0.4874(4)	0.0230(10)
C7	0.5742(4)	0.7409(3)	0.6083(4)	0.0236(10)
C8	0.4353(4)	0.7482(3)	0.6660(5)	0.0256(10)
C9	0.3682(4)	0.6574(3)	0.7150(5)	0.0292(10)
C10	0.4042(4)	0.6259(3)	0.8578(5)	0.0309(11)
C11	0.5466(4)	0.6063(3)	0.8796(5)	0.0300(11)
C12	0.6013(5)	0.5300(3)	0.7798(5)	0.0364(12)
C13	0.6852(5)	0.5739(3)	0.6673(5)	0.0416(13)
C14	0.6207(4)	0.6399(3)	0.5623(5)	0.0300(10)
C15	0.4916(4)	0.7772(3)	0.1635(5)	0.0336(11)
C16	0.4387(4)	0.9526(4)	0.1207(5)	0.0421(13)
C2	0.6133(4)	0.9106(3)	0.2833(5)	0.0276(10)
C3	0.4813(4)	0.8791(3)	0.2269(4)	0.0261(10)
C4	0.3834(4)	0.8782(3)	0.3429(4)	0.0272(10)

Table 4. Bond lengths (Å) for RCS_A_024_180124.

O1-C1	1.240(5)	O2-C5	1.355(5)
O2-C8	1.493(5)	C1-C6	1.444(6)
C1-C2	1.506(6)	C5-C6	1.332(6)
C5-C4	1.475(6)	C6-C7	1.520(6)
C7-C14	1.522(6)	C7-C8	1.555(6)
C8-C9	1.496(6)	C9-C10	1.522(6)
C10-C11	1.520(6)	C11-C12	1.539(6)
C12-C13	1.535(6)	C13-C14	1.526(6)
C15-C3	1.521(6)	C16-C3	1.514(6)
C2-C3	1.543(6)	C3-C4	1.534(6)

Table 5. Bond angles (°) for RCS_A_024_180124.

C5-O2-C8	106.8(3)	O1-C1-C6	123.1(4)
O1-C1-C2	120.9(4)	C6-C1-C2	116.0(4)
C6-C5-O2	114.3(4)	C6-C5-C4	127.3(4)
O2-C5-C4	118.4(4)	C5-C6-C1	120.3(4)
C5-C6-C7	110.2(4)	C1-C6-C7	129.4(4)
C6-C7-C14	110.0(3)	C6-C7-C8	99.6(3)
C14-C7-C8	117.5(3)	O2-C8-C9	105.8(3)
O2-C8-C7	105.4(3)	C9-C8-C7	120.0(3)
C8-C9-C10	114.6(4)	C11-C10-C9	114.9(4)
C10-C11-C12	112.7(4)	C13-C12-C11	114.5(4)
C14-C13-C12	118.1(4)	C7-C14-C13	117.7(4)
C1-C2-C3	114.3(4)	C16-C3-C15	109.5(4)
C16-C3-C4	109.2(4)	C15-C3-C4	110.4(4)
C16-C3-C2	109.2(3)	C15-C3-C2	109.8(4)
C4-C3-C2	108.8(3)	C5-C4-C3	110.0(3)

Table 6. Torsion angles (°) for RCS_A_024_180124.

C8-O2-C5-C6	7.4(4)	C8-O2-C5-C4	-174.4(3)
O2-C5-C6-C1	-177.8(3)	C4-C5-C6-C1	4.2(6)
O2-C5-C6-C7	5.8(5)	C4-C5-C6-C7	-172.2(4)
O1-C1-C6-C5	178.6(4)	C2-C1-C6-C5	0.8(5)
O1-C1-C6-C7	-5.9(7)	C2-C1-C6-C7	176.3(4)
C5-C6-C7-C14	108.7(4)	C1-C6-C7-C14	-67.2(5)
C5-C6-C7-C8	-15.4(4)	C1-C6-C7-C8	168.7(4)
C5-O2-C8-C9	-145.0(3)	C5-O2-C8-C7	-17.0(4)
C6-C7-C8-O2	18.8(4)	C14-C7-C8-O2	-99.9(4)
C6-C7-C8-C9	137.8(4)	C14-C7-C8-C9	19.1(6)
O2-C8-C9-C10	-159.6(3)	C7-C8-C9-C10	81.6(5)
C8-C9-C10-C11	-57.7(5)	C9-C10-C11-C12	-55.2(5)
C10-C11-C12-C13	105.4(5)	C11-C12-C13-C14	-66.8(6)
C6-C7-C14-C13	158.4(4)	C8-C7-C14-C13	-88.7(5)
C12-C13-C14-C7	69.9(6)	O1-C1-C2-C3	151.2(4)
C6-C1-C2-C3	-31.0(5)	C1-C2-C3-C16	173.6(4)
C1-C2-C3-C15	-66.3(5)	C1-C2-C3-C4	54.5(5)
C6-C5-C4-C3	21.0(5)	O2-C5-C4-C3	-157.0(3)
C16-C3-C4-C5	-166.5(4)	C15-C3-C4-C5	73.1(4)
C2-C3-C4-C5	-47.4(4)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for RCS_A_024_180124.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0150(17)	0.0453(17)	0.0405(19)	0.0054(16)	-0.0032(14)	-0.0001(14)
O2	0.0152(15)	0.0355(16)	0.0307(16)	0.0069(14)	0.0024(14)	0.0041(14)
C1	0.018(2)	0.026(2)	0.028(2)	-0.003(2)	-0.001(2)	-0.0016(18)
C5	0.016(2)	0.022(2)	0.027(3)	-0.0001(19)	0.0024(19)	-0.0014(18)
C6	0.015(2)	0.024(2)	0.030(3)	-0.0046(19)	0.002(2)	0.0024(17)
C7	0.014(2)	0.030(2)	0.027(2)	-0.001(2)	-0.0004(19)	0.0009(18)
C8	0.020(2)	0.030(2)	0.027(2)	0.000(2)	0.000(2)	0.0013(19)
C9	0.014(2)	0.034(2)	0.040(3)	0.006(2)	-0.003(2)	0.0007(19)
C10	0.023(3)	0.034(3)	0.037(3)	0.004(2)	-0.002(2)	-0.003(2)
C11	0.024(3)	0.035(3)	0.032(3)	0.004(2)	-0.005(2)	-0.004(2)
C12	0.030(3)	0.036(3)	0.044(3)	0.012(2)	-0.005(2)	0.012(2)
C13	0.034(3)	0.045(3)	0.046(3)	0.012(3)	0.002(2)	0.016(2)
C14	0.025(3)	0.032(2)	0.033(3)	0.000(2)	-0.002(2)	0.003(2)
C15	0.024(3)	0.048(3)	0.029(2)	-0.006(2)	0.002(2)	-0.012(2)
C16	0.020(3)	0.060(3)	0.047(3)	0.015(3)	0.000(2)	-0.002(2)
C2	0.018(2)	0.032(2)	0.032(2)	-0.001(2)	0.001(2)	-0.003(2)
C3	0.016(2)	0.037(3)	0.025(2)	0.006(2)	-0.0041(19)	-0.0044(19)
C4	0.014(2)	0.030(2)	0.037(3)	0.002(2)	-0.003(2)	0.0006(18)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for RCS_A_024_180124.

	x/a	y/b	z/c	U(eq)
H7	0.6365	0.7694	0.6746	0.028000
H8	0.4351	0.7980	0.7406	0.031000
H9A	0.3878	0.6026	0.6522	0.035000
H9B	0.2742	0.6690	0.7115	0.035000
H10A	0.3764	0.6780	0.9215	0.037000
H10B	0.3558	0.5652	0.8804	0.037000
H11A	0.5599	0.5823	0.9732	0.036000
H11B	0.5945	0.6690	0.8696	0.036000
H12A	0.6531	0.4815	0.8311	0.044000
H12B	0.5288	0.4940	0.7377	0.044000
H13A	0.7547	0.6124	0.7107	0.050000
H13B	0.7266	0.5185	0.6186	0.050000
H14A	0.6822	0.6499	0.4871	0.036000
H14B	0.5460	0.6038	0.5250	0.036000
H15A	0.4079	0.7580	0.1264	0.050000
H15B	0.5180	0.7294	0.2326	0.050000
H15C	0.5556	0.7785	0.0908	0.050000
H16A	0.4993	0.9517	0.0449	0.063000
H16B	0.4364	1.0188	0.1604	0.063000
H16C	0.3527	0.9349	0.0882	0.063000
H2A	0.6776	0.9067	0.2097	0.033000
H2B	0.6081	0.9804	0.3123	0.033000

	x/a	y/b	z/c	U(eq)
H4A	0.3615	0.9467	0.3685	0.033000
H4B	0.3036	0.8449	0.3130	0.033000

Crystal data: 7,7-Dimethyl-4b,6,7,8,9b,10-hexahydro-9H-indeno[1,2-b]benzofuran-9-one (4ya)

A specimen of $C_{17}H_{18}O_2$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 1.54178 Å).

The integration of the data using a monoclinic unit cell yielded a total of 36903 reflections to a maximum θ angle of 74.73° (0.80 Å resolution), of which 2669 were independent (average redundancy 13.827, completeness = 99.4%, R_{int} = 5.88%, R_{sig} = 2.54%) and 2334 (87.45%) were greater than 2σ(F^2). The final cell constants of a = 11.0571(5) Å, b = 10.1834(5) Å, c = 11.8525(6) Å, β = 102.100(2)°, volume = 1304.93(11) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I).

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21/c, with Z = 4 for the formula unit, $C_{17}H_{18}O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 174 variables converged at R1 = 3.94%, for the observed data and wR2 = 12.57% for all data. The goodness-of-fit was 1.180. The largest peak in the final difference electron density synthesis was 0.340 $e^-/Å^3$ and the largest hole was -0.360 $e^-/Å^3$ with an RMS deviation of 0.106 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.294 g/cm^3 and F(000), 544 e^-.

Table 1. Sample and crystal data for SMS_11_18.

Identification code	SMS_11_18	
Chemical formula	$C_{17}H_{18}O_2$	
Formula weight	254.31 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.0571(5) Å	α = 90°
	b = 10.1834(5) Å	β = 102.100(2)°
	c = 11.8525(6) Å	γ = 90°
Volume	1304.93(11) $Å^3$	

Z	4
Density (calculated)	1.294 g/cm^3
Absorption coefficient	0.658 mm^{-1}
F(000)	544

Table 2. Data collection and structure refinement for SMS_11_18.

Theta range for data collection	4.09 to 74.73°	
Index ranges	-13<=h<=13, -12<=k<=12, -14<=l<=14	
Reflections collected	36903	
Independent reflections	2669 [R(int) = 0.0588]	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2669 / 0 / 174	
Goodness-of-fit on F^2	1.180	
Final R indices	2334 data; I>2σ(I)	R1 = 0.0394, wR2 = 0.1105
	all data	R1 = 0.0484, wR2 = 0.1257
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0663P)^2+0.4528P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.340 and -0.360 eÅ^{-3}	
R.M.S. deviation from mean	0.106 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for SMS_11_18.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O001	0.50145(9)	0.68264(10)	0.51516(8)	0.0220(3)
O002	0.26117(8)	0.45969(9)	0.72828(8)	0.0173(2)
C003	0.10256(11)	0.69444(13)	0.54473(11)	0.0166(3)

	x/a	y/b	z/c	U(eq)
C004	0.37940(11)	0.56760(12)	0.62278(11)	0.0150(3)
C005	0.02869(12)	0.80620(13)	0.53881(11)	0.0198(3)
C006	0.46713(11)	0.52361(13)	0.83434(10)	0.0154(3)
C007	0.48896(12)	0.63625(13)	0.60792(11)	0.0162(3)
C008	0.37074(11)	0.51874(12)	0.72601(11)	0.0145(3)
C009	0.59670(11)	0.54449(13)	0.80709(10)	0.0152(3)
C00A	0.64438(12)	0.41839(13)	0.76098(11)	0.0183(3)
C00B	0.09156(11)	0.59435(13)	0.62181(11)	0.0170(3)
C00C	0.00812(12)	0.60418(15)	0.69442(12)	0.0209(3)
C00D	0.19616(12)	0.66097(14)	0.47344(11)	0.0187(3)
C00E	0.94564(12)	0.81625(14)	0.61142(12)	0.0219(3)
C00F	0.58799(12)	0.65504(13)	0.71690(11)	0.0172(3)
C00G	0.68748(12)	0.58561(14)	0.91713(11)	0.0200(3)
C00H	0.18012(11)	0.48417(13)	0.61436(11)	0.0169(3)
C00I	0.93577(12)	0.71654(15)	0.68927(12)	0.0230(3)
C00J	0.26313(12)	0.53834(13)	0.53404(11)	0.0164(3)

Table 4. Bond lengths (Å) for SMS_11_18.

O001-C007	1.2308(16)	O002-C008	1.3578(15)
O002-C00H	1.4768(15)	C003-C00B	1.3909(19)
C003-C005	1.3940(19)	C003-C00D	1.5059(18)
C004-C008	1.3427(18)	C004-C007	1.4411(18)
C004-C00J	1.5102(16)	C005-C00E	1.388(2)
C005-H005	0.950000	C006-C008	1.4877(17)
C006-C009	1.5479(17)	C006-H00A	0.990000
C006-H00B	0.990000	C007-C00F	1.5202(17)
C009-C00G	1.5281(17)	C009-C00A	1.5318(18)
C009-C00F	1.5416(17)	C00A-H00C	0.980000
C00A-H00D	0.980000	C00A-H00E	0.980000
C00B-C00C	1.3909(19)	C00B-C00H	1.5040(18)
C00C-C00I	1.390(2)	C00C-H00F	0.950000

C00D-C00J	1.5494(18)	C00D-H00G	0.990000
C00D-H00H	0.990000	C00E-C00I	1.392(2)
C00E-H00I	0.950000	C00F-H00J	0.990000
C00F-H00K	0.990000	C00G-H00L	0.980000
C00G-H00M	0.980000	C00G-H00N	0.980000
C00H-C00J	1.5554(18)	C00H-H00O	1.000000
C00I-H00P	0.950000	C00J-H00Q	1.000000

Table 5. Bond angles (°) for SMS_11_18.

C008-O002-C00H	106.26(9)	C00B-C003-C005	120.02(12)
C00B-C003-C00D	111.57(11)	C005-C003-C00D	128.38(12)
C008-C004-C007	120.89(11)	C008-C004-C00J	110.41(11)
C007-C004-C00J	128.70(11)	C00E-C005-C003	119.07(13)
C00E-C005-H005	120.500000	C003-C005-H005	120.500000
C008-C006-C009	110.58(10)	C008-C006-H00A	109.500000
C009-C006-H00A	109.500000	C008-C006-H00B	109.500000
C009-C006-H00B	109.500000	H00A-C006-H00B	108.100000
O001-C007-C004	123.36(12)	O001-C007-C00F	120.99(12)
C004-C007-C00F	115.57(11)	C004-C008-O002	114.61(11)
C004-C008-C006	126.80(11)	O002-C008-C006	118.58(11)
C00G-C009-C00A	108.70(11)	C00G-C009-C00F	109.03(11)
C00A-C009-C00F	109.93(10)	C00G-C009-C006	109.31(10)
C00A-C009-C006	111.23(11)	C00F-C009-C006	108.61(10)
C009-C00A-H00C	109.500000	C009-C00A-H00D	109.500000
H00C-C00A-H00D	109.500000	C009-C00A-H00E	109.500000
H00C-C00A-H00E	109.500000	H00D-C00A-H00E	109.500000
C00C-C00B-C003	120.95(12)	C00C-C00B-C00H	127.92(12)
C003-C00B-C00H	111.13(11)	C00I-C00C-C00B	118.84(13)
C00I-C00C-H00F	120.600000	C00B-C00C-H00F	120.600000
C003-C00D-C00J	103.90(10)	C003-C00D-H00G	111.000000
C00J-C00D-H00G	111.000000	C003-C00D-H00H	111.000000
C00J-C00D-H00H	111.000000	H00G-C00D-H00H	109.000000

C005-C00E-C00I	120.76(13)	C005-C00E-H00I	119.600000
C00I-C00E-H00I	119.600000	C007-C00F-C009	115.24(10)
C007-C00F-H00J	108.500000	C009-C00F-H00J	108.500000
C007-C00F-H00K	108.500000	C009-C00F-H00K	108.500000
H00J-C00F-H00K	107.500000	C009-C00G-H00L	109.500000
C009-C00G-H00M	109.500000	H00L-C00G-H00M	109.500000
C009-C00G-H00N	109.500000	H00L-C00G-H00N	109.500000
H00M-C00G-H00N	109.500000	O002-C00H-C00B	110.49(10)
O002-C00H-C00J	107.26(10)	C00B-C00H-C00J	104.26(10)
O002-C00H-H00O	111.500000	C00B-C00H-H00O	111.500000
C00J-C00H-H00O	111.500000	C00C-C00I-C00E	120.35(13)
C00C-C00I-H00P	119.800000	C00E-C00I-H00P	119.800000
C004-C00J-C00D	114.72(11)	C004-C00J-C00H	99.73(10)
C00D-C00J-C00H	106.47(10)	C004-C00J-H00Q	111.700000
C00D-C00J-H00Q	111.700000	C00H-C00J-H00Q	111.700000

Table 6. Anisotropic atomic displacement parameters (Å^2) for SMS_11_18.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	0.0213(5)	0.0258(5)	0.0193(5)	0.0046(4)	0.0051(4)	-0.0020(4)
O002	0.0113(4)	0.0188(5)	0.0210(5)	0.0036(4)	0.0018(4)	-0.0014(4)
C003	0.0135(6)	0.0182(7)	0.0163(6)	-0.0025(5)	-0.0013(5)	-0.0012(5)
C004	0.0137(6)	0.0149(6)	0.0155(6)	-0.0015(5)	0.0013(5)	0.0009(5)
C005	0.0183(6)	0.0185(7)	0.0196(6)	-0.0006(5)	-0.0029(5)	0.0014(5)
C006	0.0155(6)	0.0162(6)	0.0147(6)	0.0004(4)	0.0035(5)	0.0003(5)
C007	0.0169(6)	0.0136(6)	0.0183(6)	-0.0004(5)	0.0041(5)	0.0019(5)
C008	0.0126(6)	0.0114(6)	0.0200(6)	-0.0015(5)	0.0041(5)	0.0005(5)
C009	0.0132(6)	0.0173(7)	0.0148(6)	-0.0006(5)	0.0019(5)	-0.0002(5)
C00A	0.0167(6)	0.0196(7)	0.0187(6)	0.0000(5)	0.0040(5)	0.0017(5)
C00B	0.0120(6)	0.0176(7)	0.0194(6)	-0.0016(5)	-0.0013(5)	-0.0015(5)
C00C	0.0140(6)	0.0267(7)	0.0211(6)	0.0022(5)	0.0016(5)	-0.0022(5)
C00D	0.0169(6)	0.0217(7)	0.0167(6)	0.0008(5)	0.0016(5)	0.0026(5)

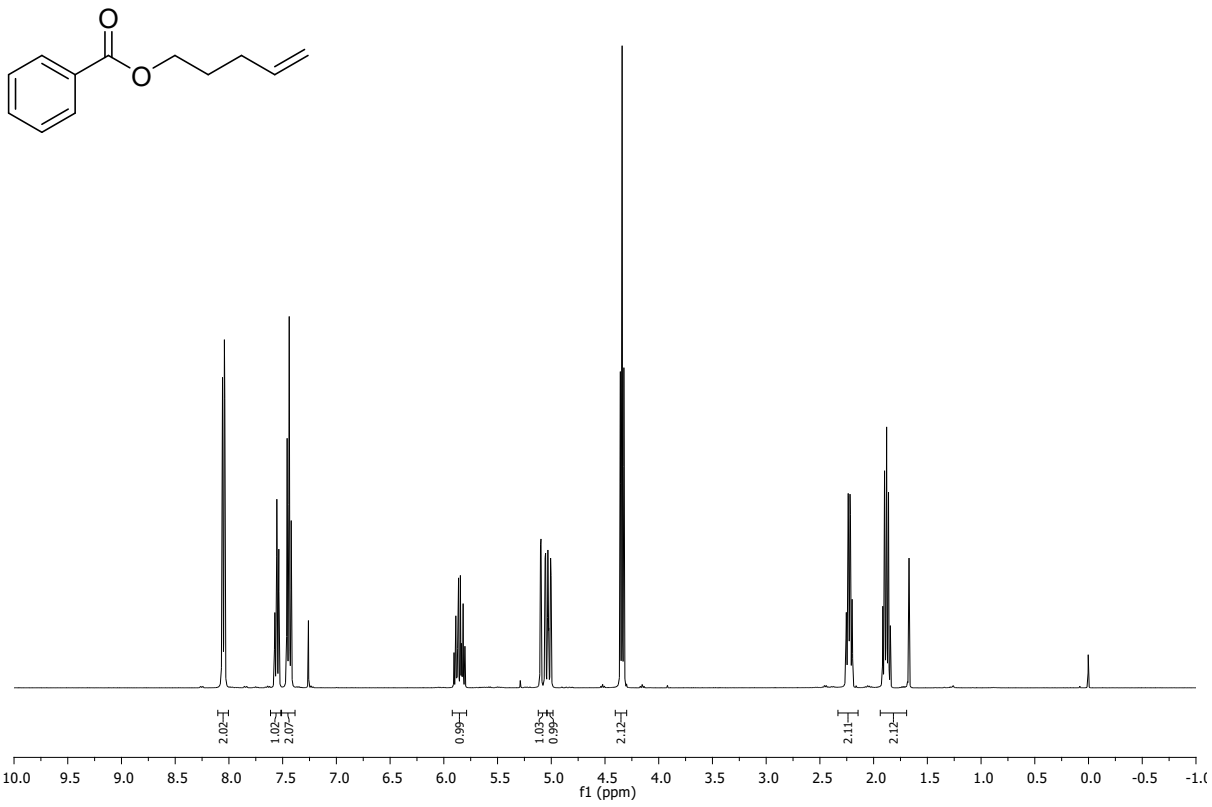
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C00E	0.0164(6)	0.0236(7)	0.0229(7)	-0.0062(5)	-0.0026(5)	0.0059(6)
C00F	0.0146(6)	0.0164(6)	0.0201(6)	0.0003(5)	0.0022(5)	-0.0030(5)
C00G	0.0160(6)	0.0256(7)	0.0172(6)	-0.0024(5)	0.0006(5)	-0.0005(5)
C00H	0.0129(6)	0.0163(6)	0.0198(6)	-0.0006(5)	-0.0007(5)	-0.0012(5)
C00I	0.0140(6)	0.0323(8)	0.0222(7)	-0.0039(6)	0.0030(5)	0.0021(6)
C00J	0.0140(6)	0.0177(6)	0.0168(6)	-0.0025(5)	0.0017(5)	0.0003(5)

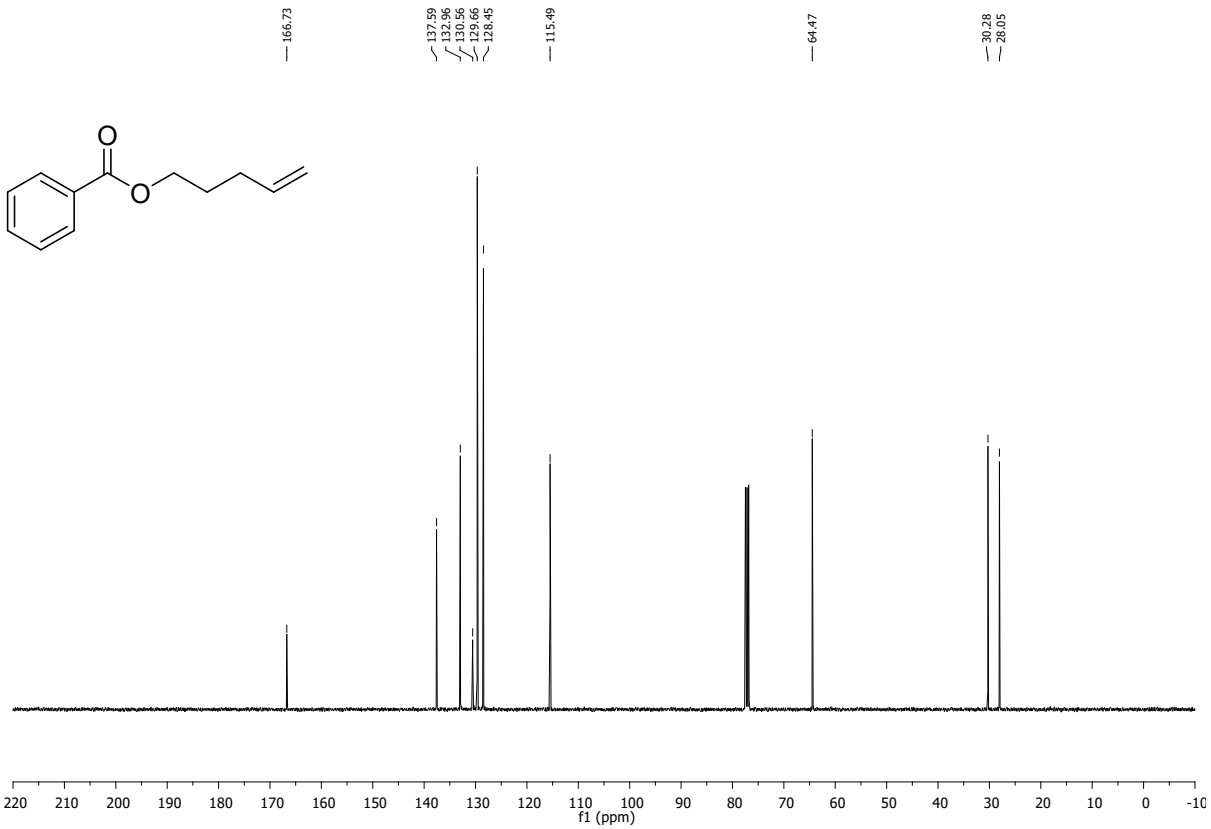
Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for SMS_11_18.

	x/a	y/b	z/c	U(eq)
H005	0.0351	0.8745	0.4858	0.024000
H00A	0.4663	0.4405	0.8774	0.018000
H00B	0.4487	0.5963	0.8835	0.018000
H00C	0.5888	0.3931	0.6885	0.027000
H00D	0.6472	0.3479	0.8177	0.027000
H00E	0.7276	0.4335	0.7472	0.027000
H00F	0.0007	0.5353	0.7466	0.025000
H00G	0.2549	0.7343	0.4734	0.022000
H00H	0.1550	0.6408	0.3928	0.022000
H00I	-0.1051	0.8921	0.6079	0.026000
H00J	0.5719	0.7388	0.7535	0.021000
H00K	0.6692	0.6632	0.6947	0.021000
H00L	0.7689	0.6018	0.8996	0.030000
H00M	0.6940	0.5154	0.9747	0.030000
H00N	0.6577	0.6660	0.9477	0.030000
H00O	0.1355	0.4027	0.5820	0.020000
H00P	-0.1207	0.7253	0.7392	0.028000
H00Q	0.2779	0.4709	0.4771	0.020000

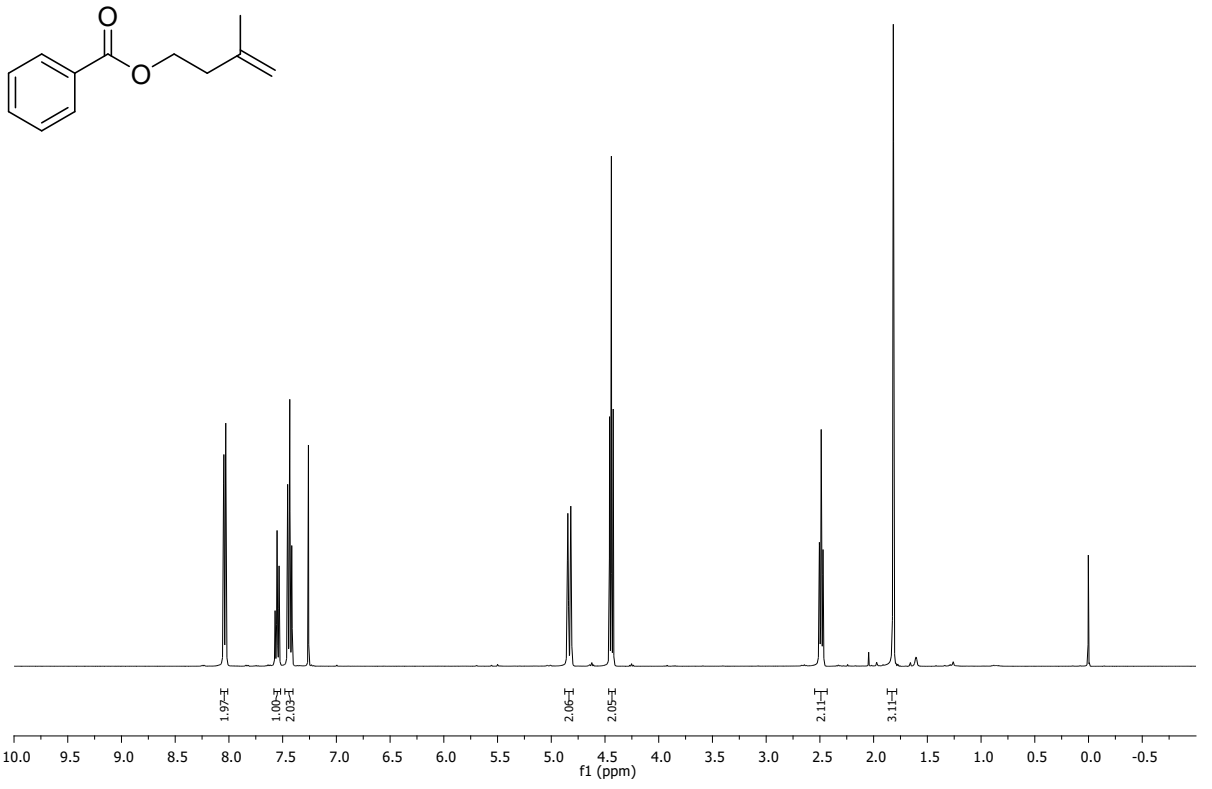
^{1}H and ^{13}C NMR Spectra

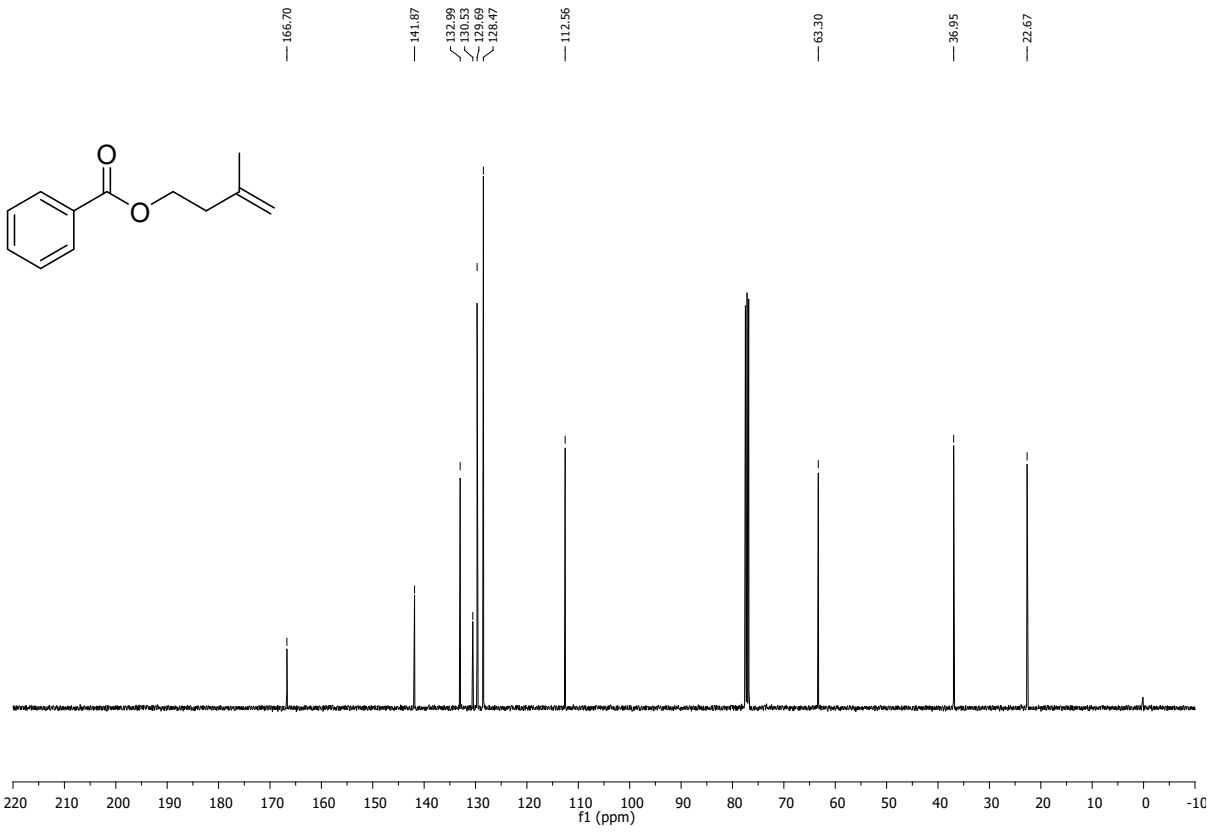
1a



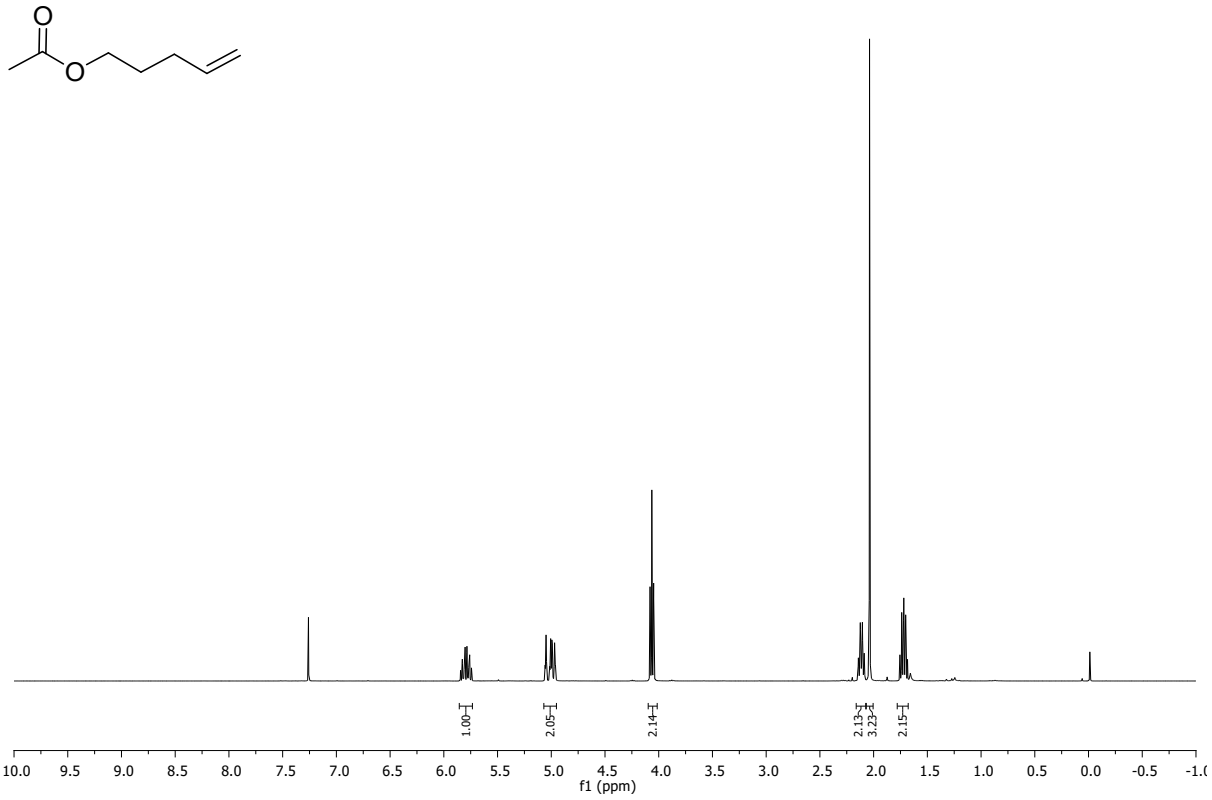

166.73
137.59
132.96
130.56
129.66
128.45
115.49
64.47
30.28
28.05
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

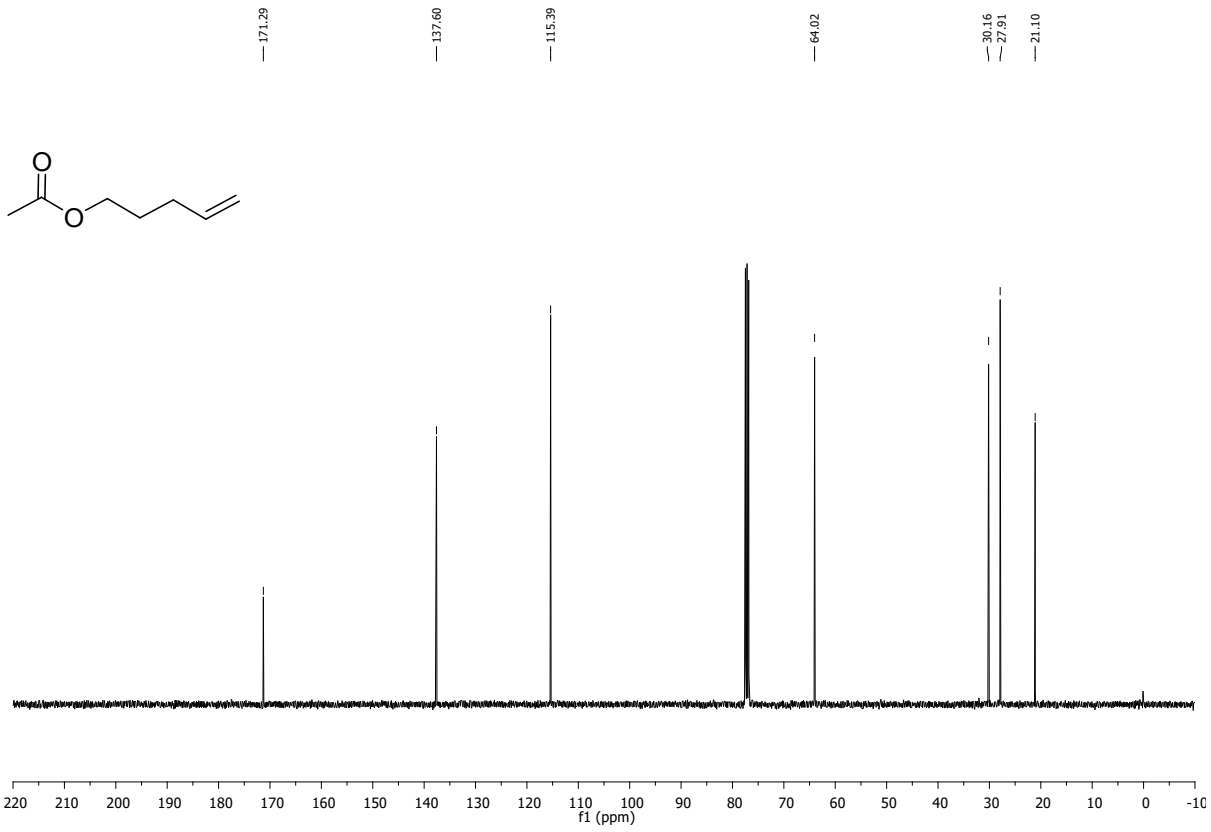
1a´


O
O
1.97
1.00
2.03
2.06
2.05
2.11
3.11
10.0 9.5 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 -0.5
f1 (ppm)

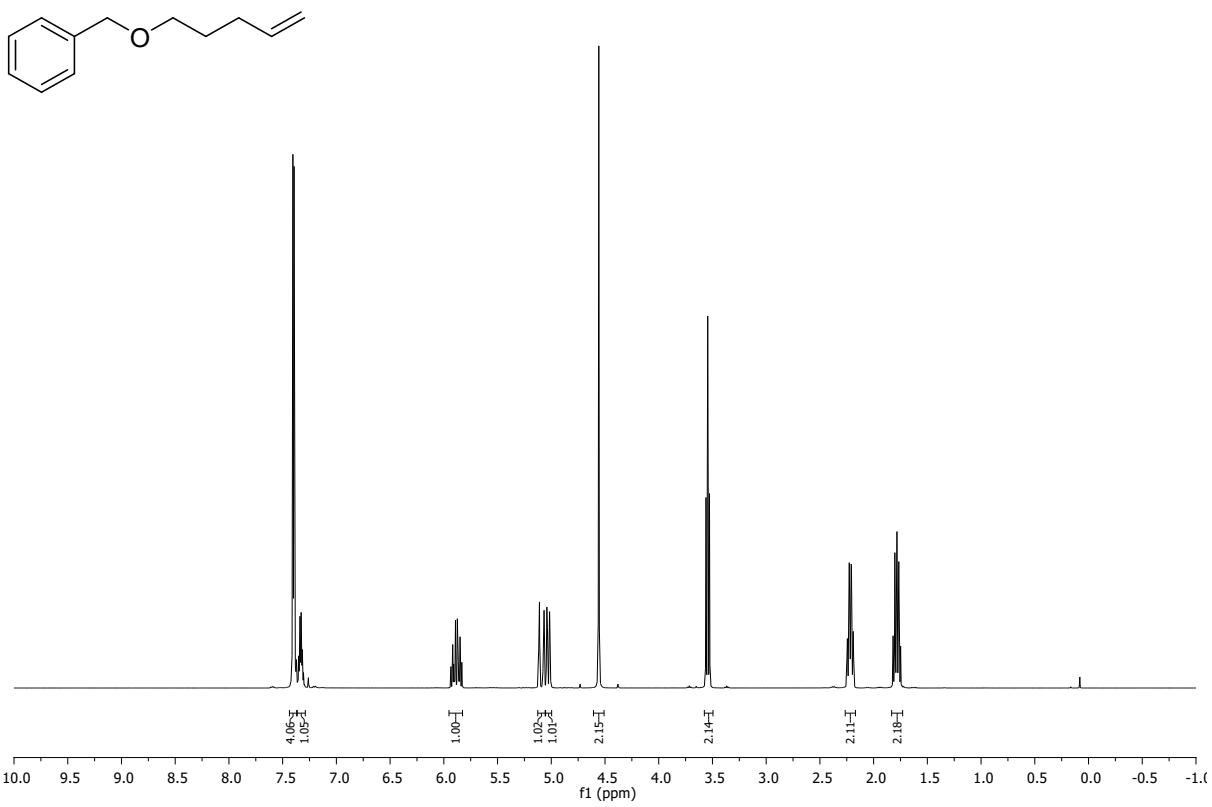

166.70
141.87
132.99
130.53
129.69
128.47
112.56
63.30
36.95
22.67
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

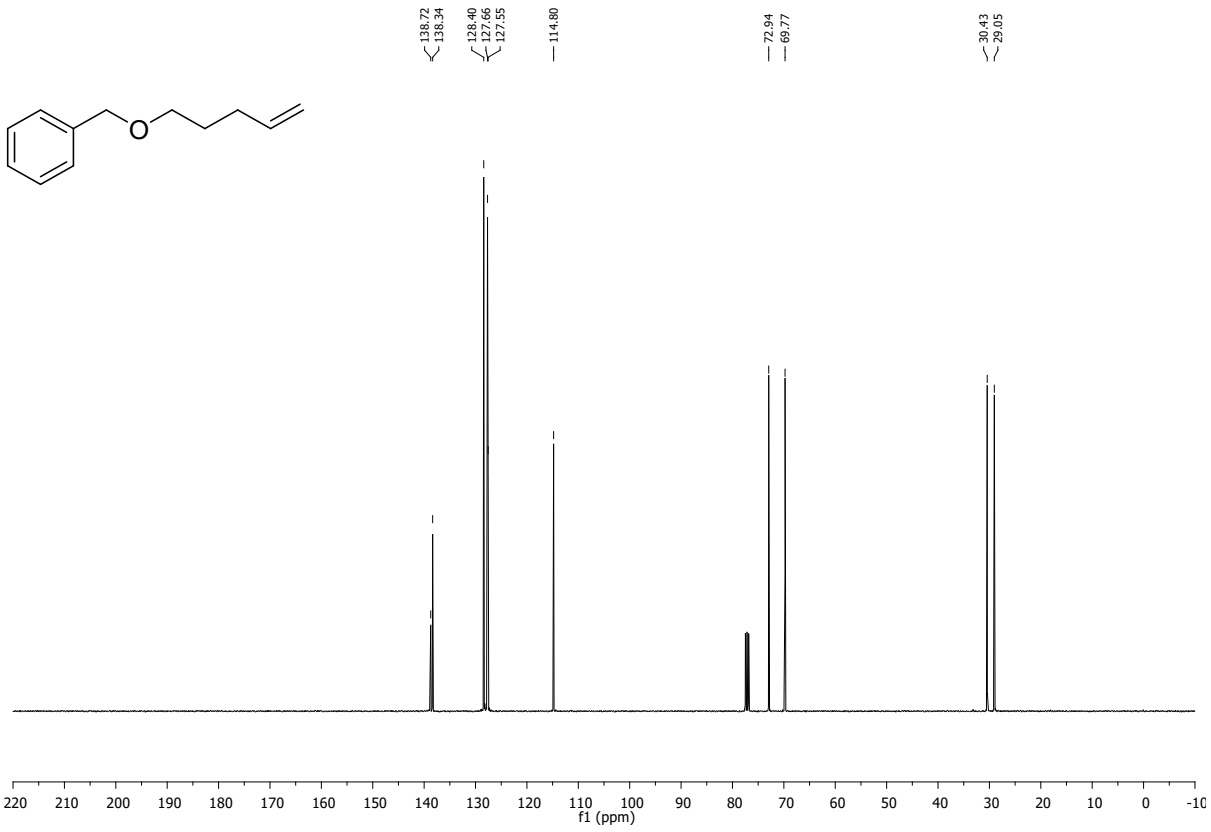
1b


O
O
1.00
2.05
2.14
2.13
3.23
2.15
10.0 9.5 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 -0.5 -1.0
f1 (ppm)

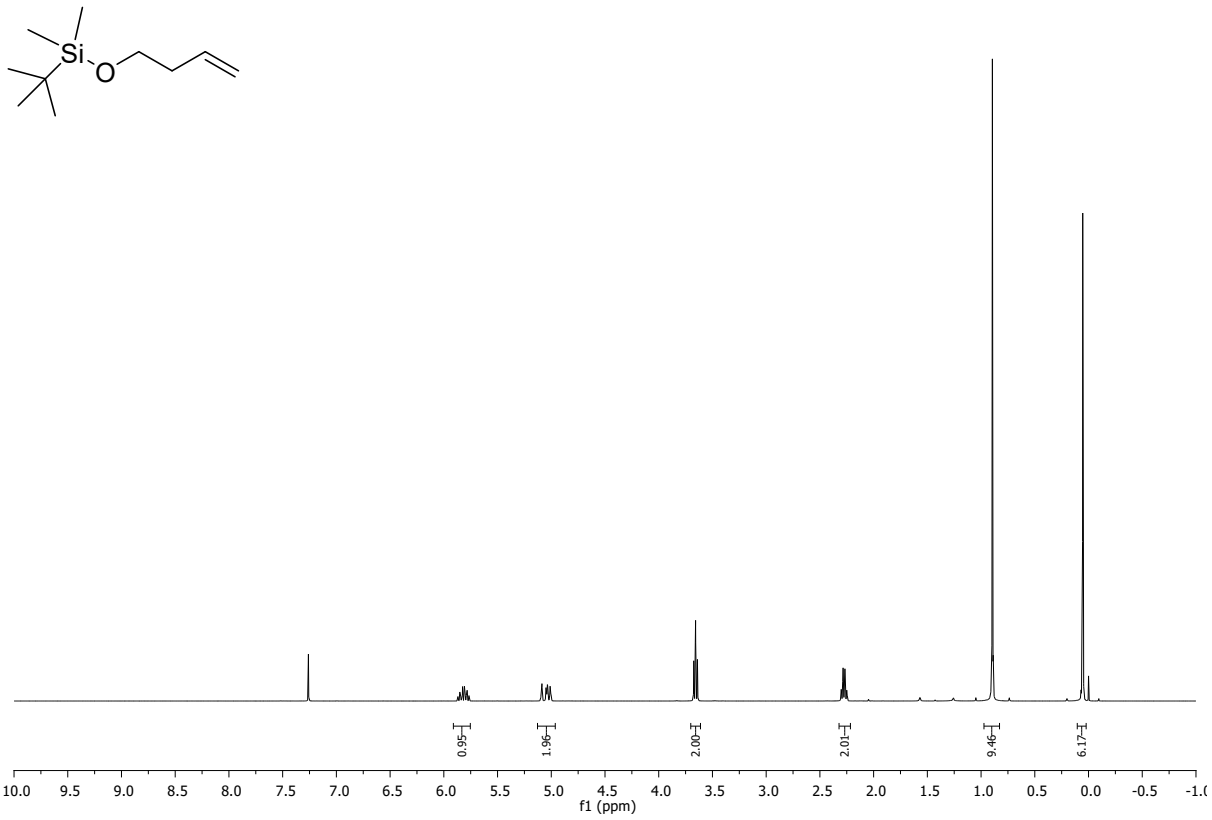

171.29
137.60
115.39
64.02
30.16
27.91
21.10
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

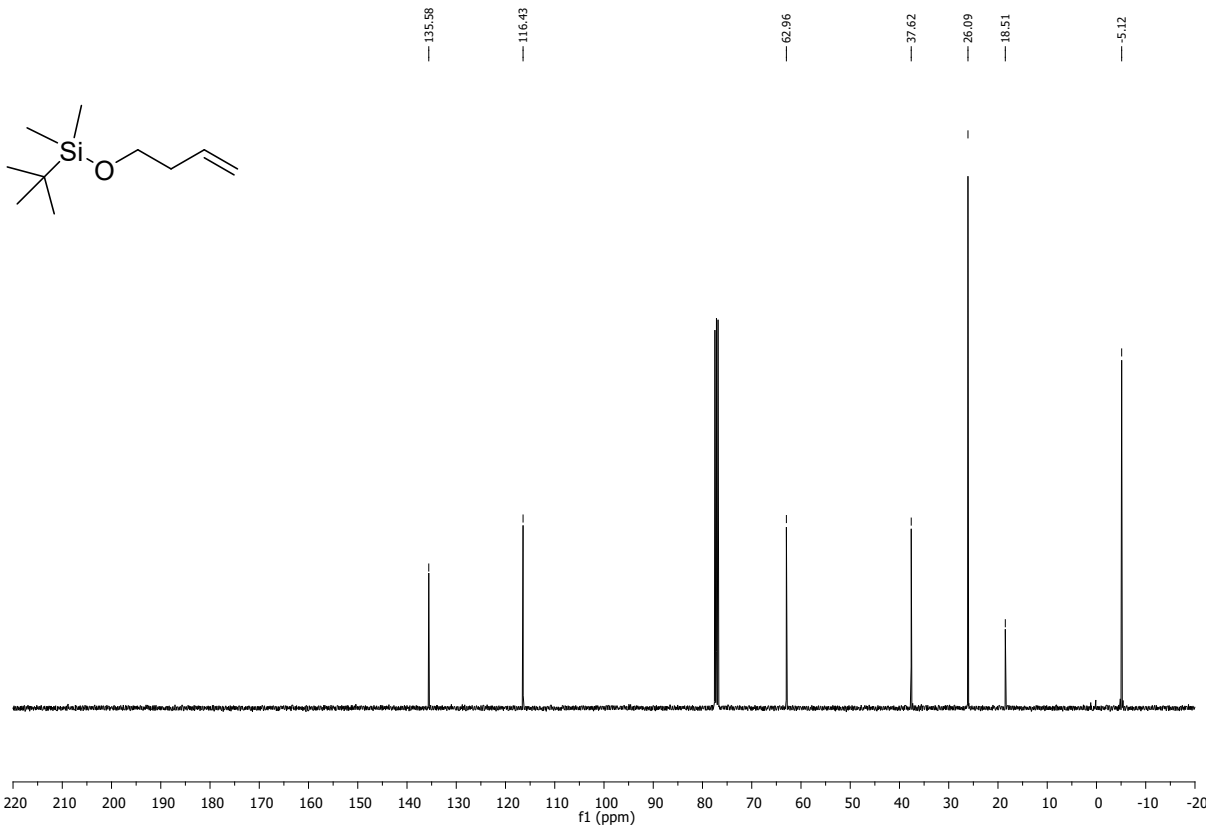
1c


O
4.06
1.05
1.00
1.02
1.01
2.15
2.14
2.11
2.18
10.0 9.5 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 -0.5 -1.0
f1 (ppm)

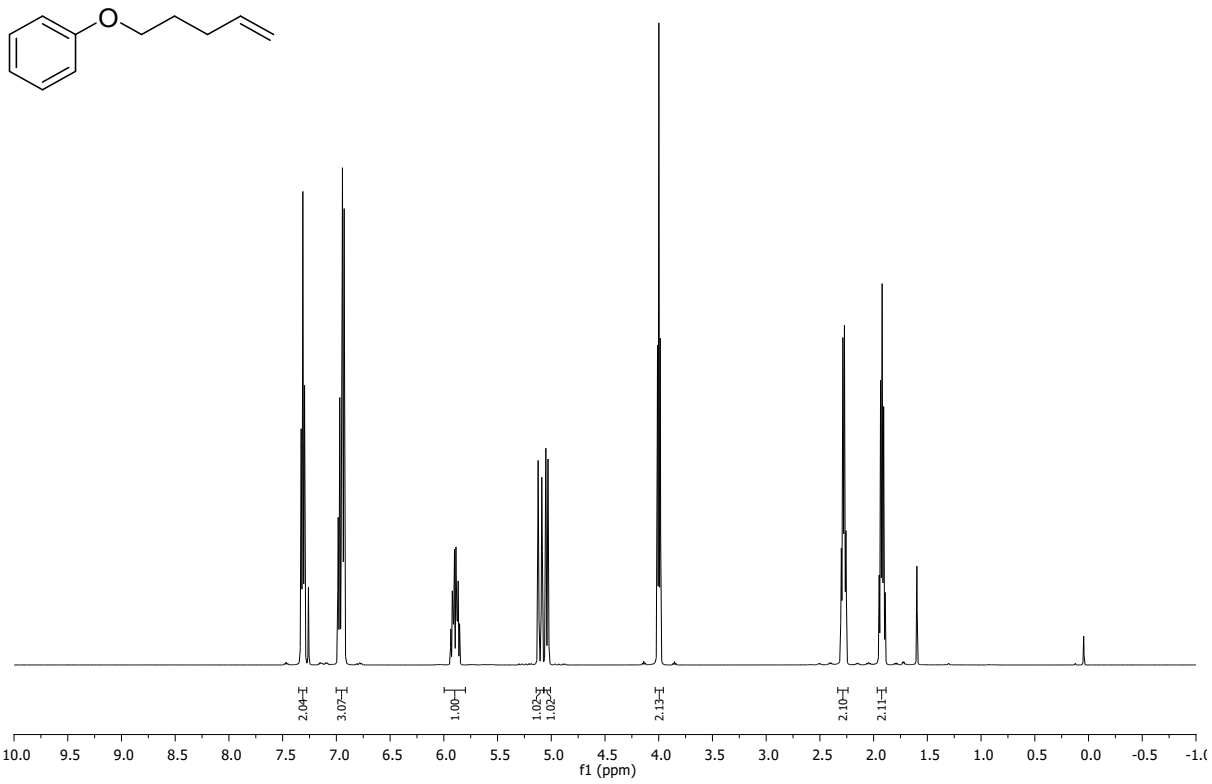

138.72
138.34
128.40
127.66
127.55
114.80
72.94
69.77
30.43
29.05
O
f1 (ppm)

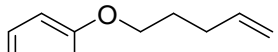
1k

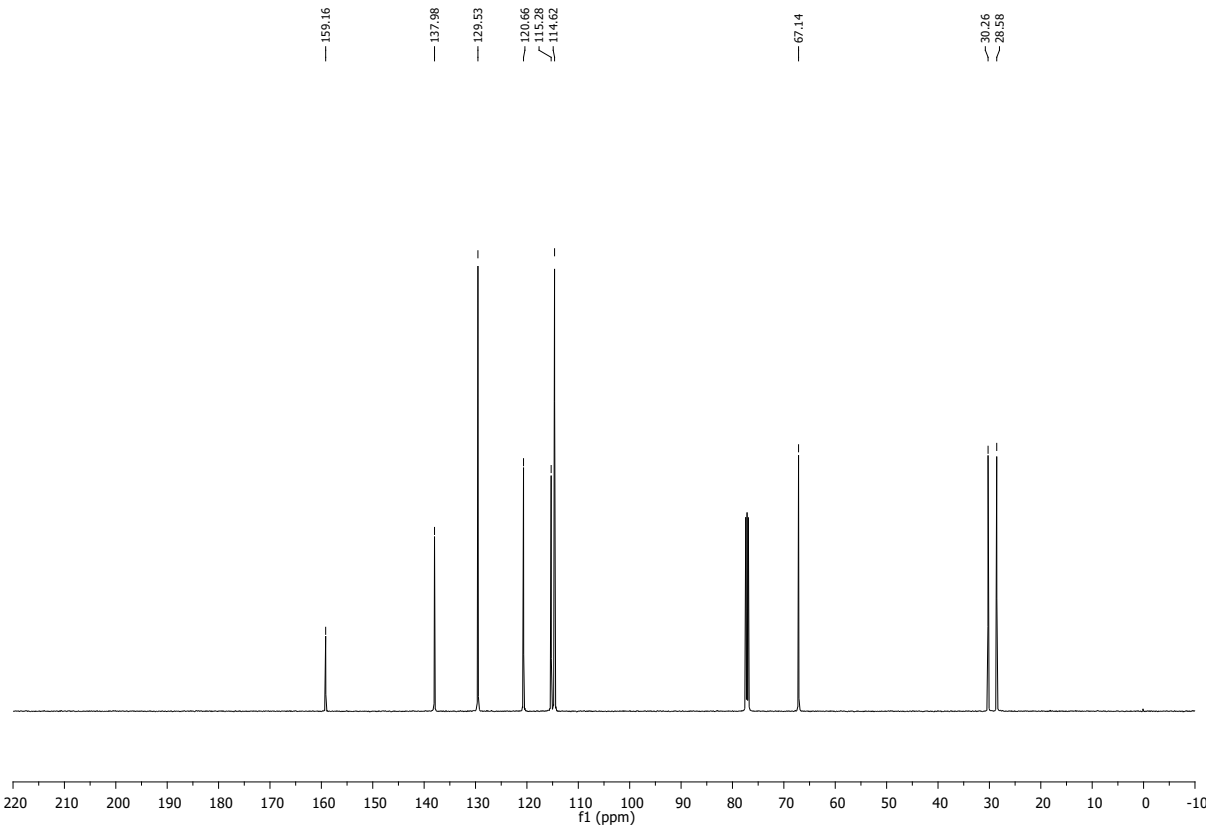

Si
O
0.95
1.96
2.00
2.01
9.46
6.17
f1 (ppm)


135.58
116.43
62.96
37.62
26.09
18.51
-5.12
Si
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

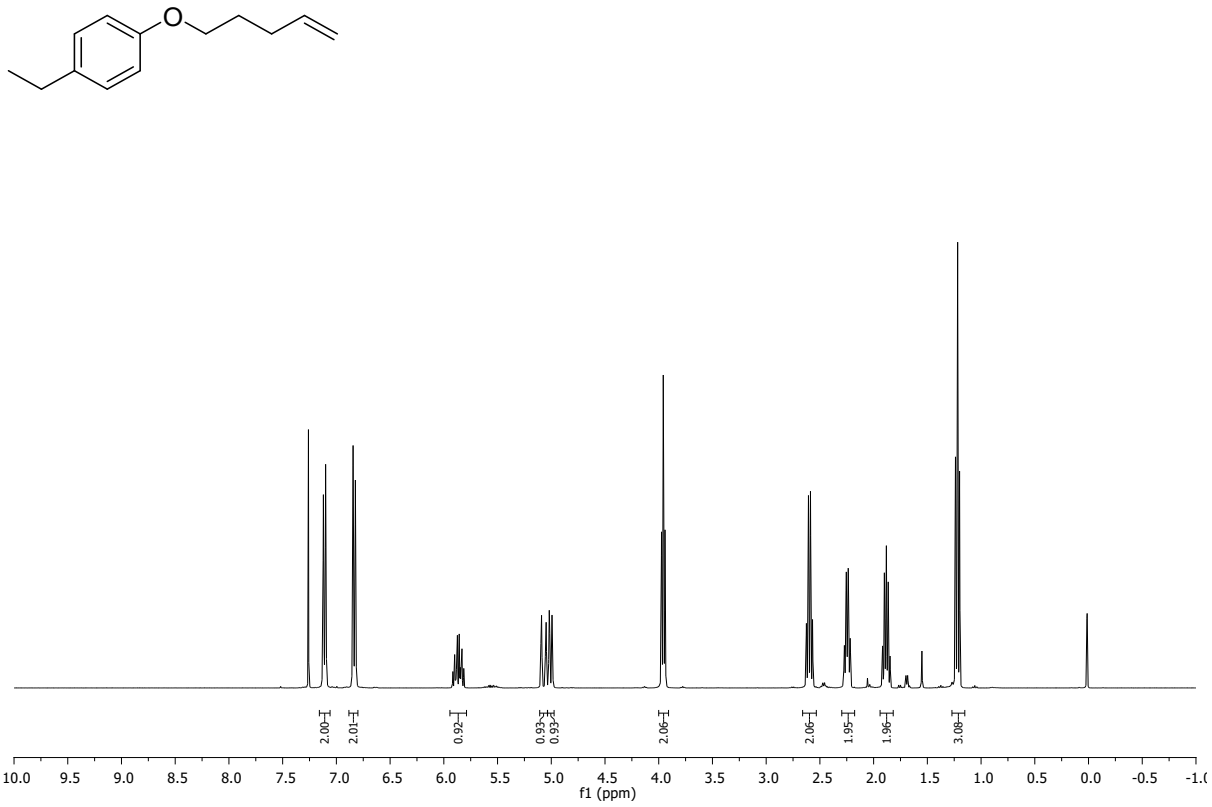
1p

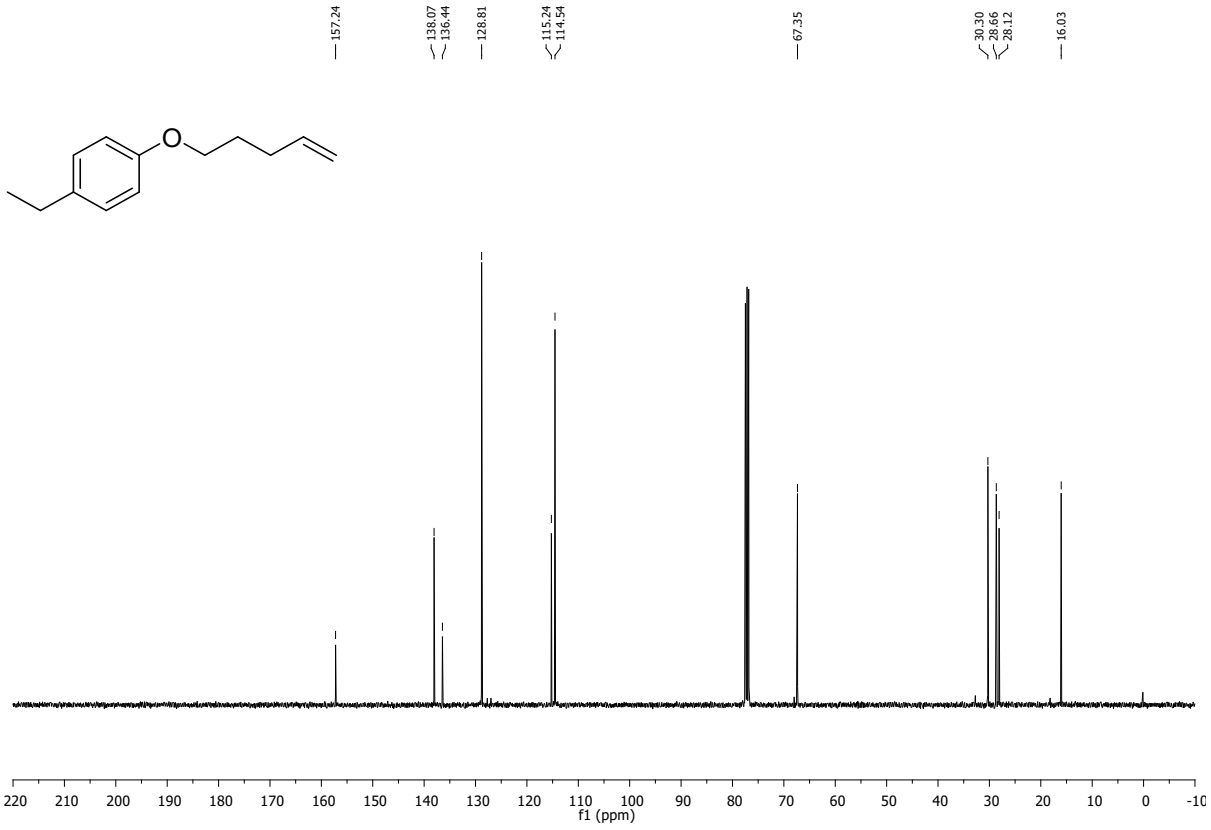

O
2.04
3.07
1.00
1.02
1.02
2.13
2.10
2.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


O

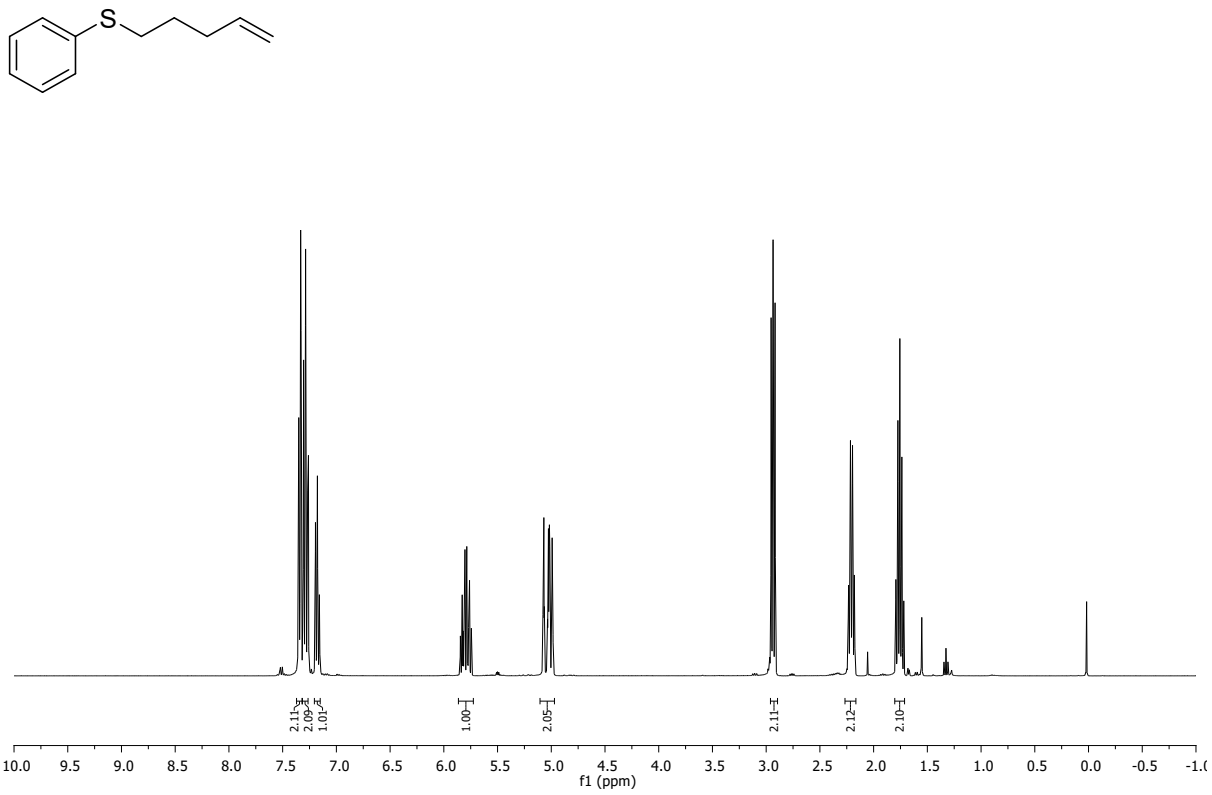

159.16
137.98
129.53
120.66
115.28
114.62
67.14
30.26
28.58
f1 (ppm)

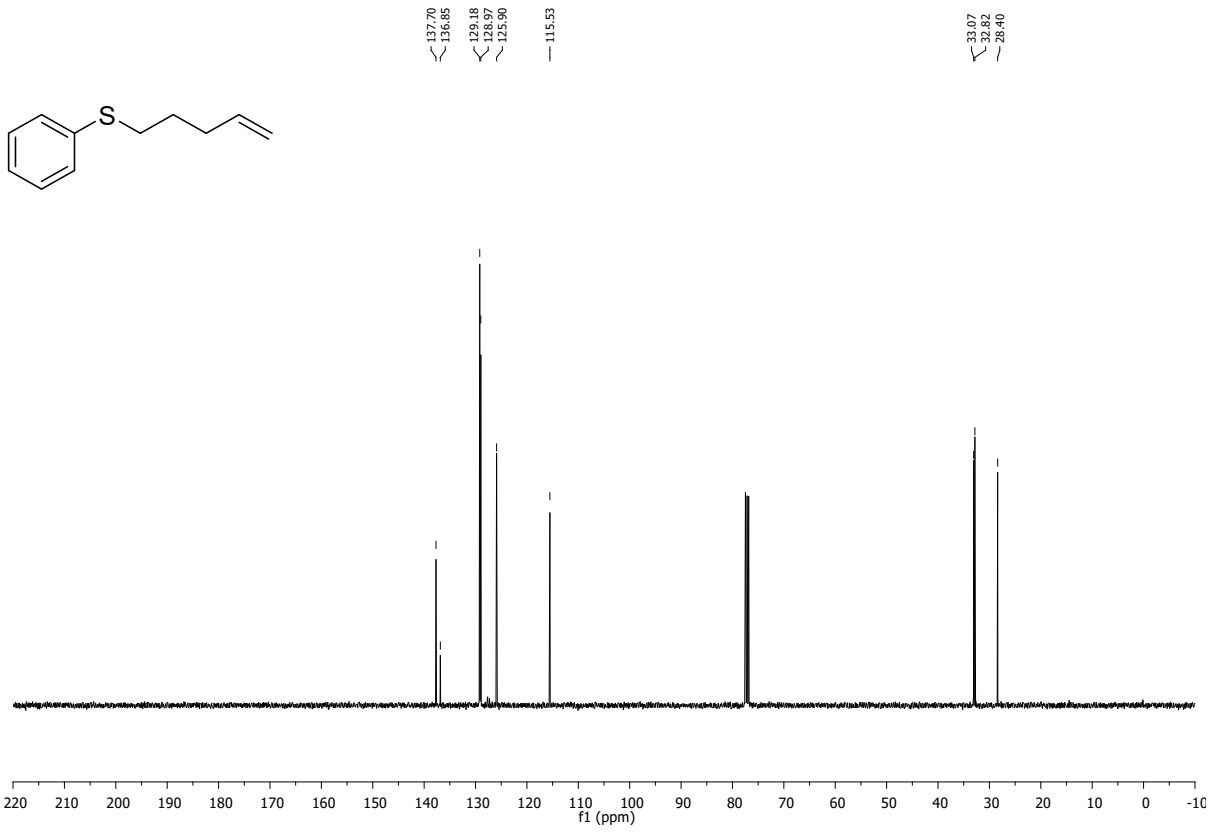
1q


2.00
2.01
0.92
0.93
0.93
2.06
2.06
1.95
1.96
3.08
f1 (ppm)

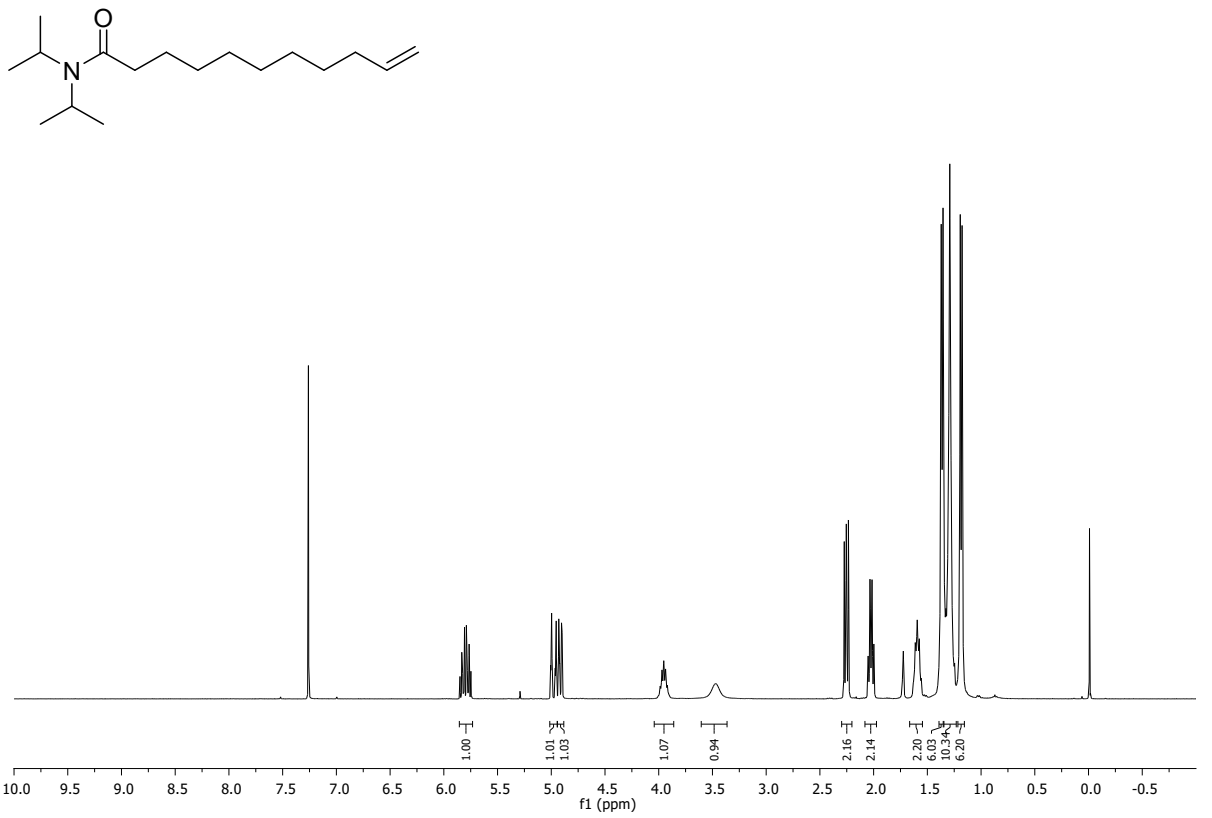

157.24
138.07
136.44
128.81
115.24
114.54
67.35
30.30
28.66
28.12
16.03
O
f1 (ppm)

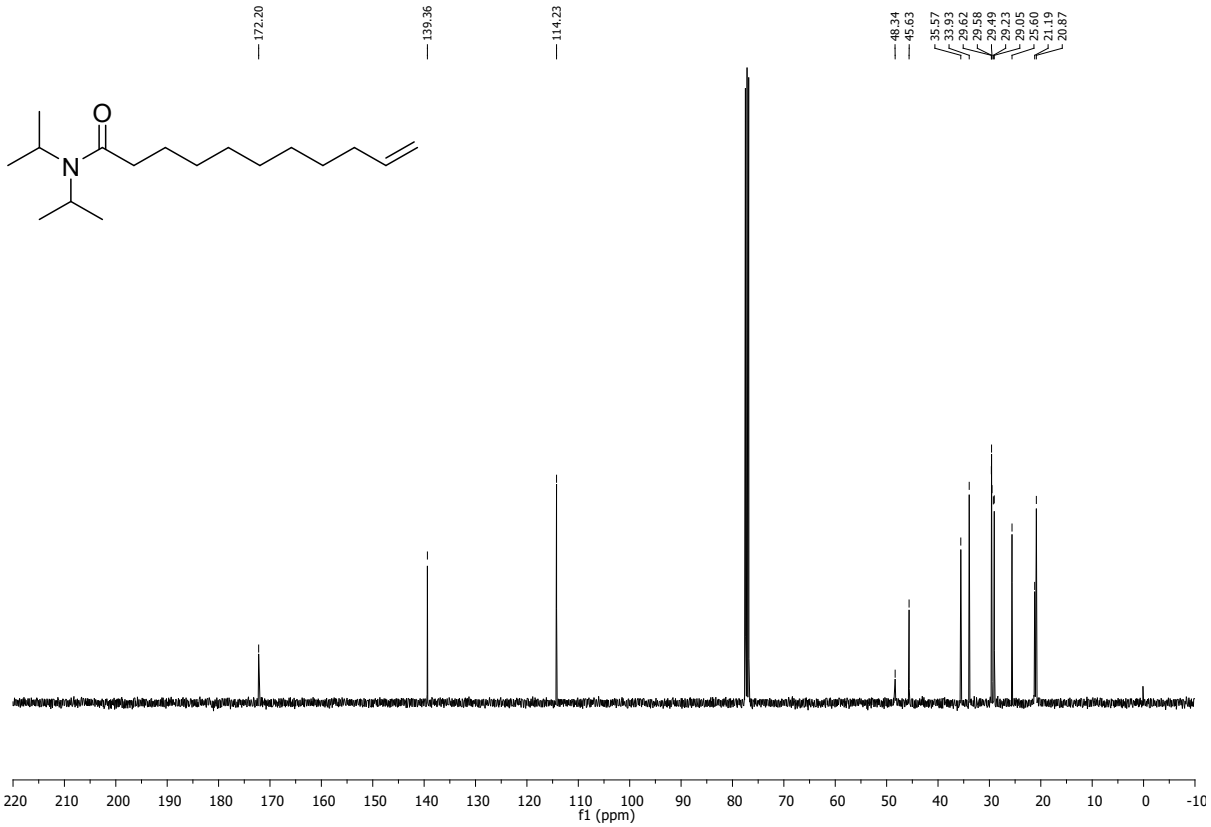
1r


S
2.11
2.09
1.01
1.00
2.05
2.11
2.12
2.10
f1 (ppm)

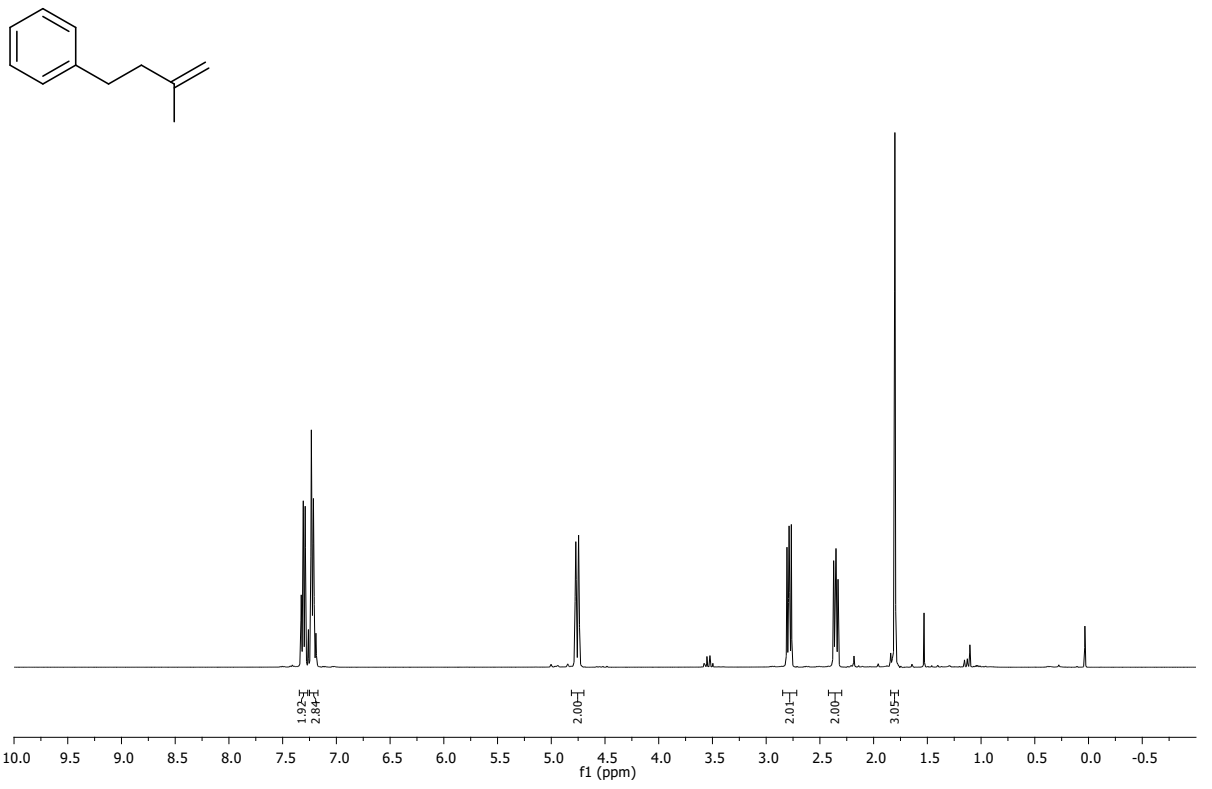

137.70
136.85
129.18
128.97
125.90
115.53
33.07
32.82
28.40
S
f1 (ppm)

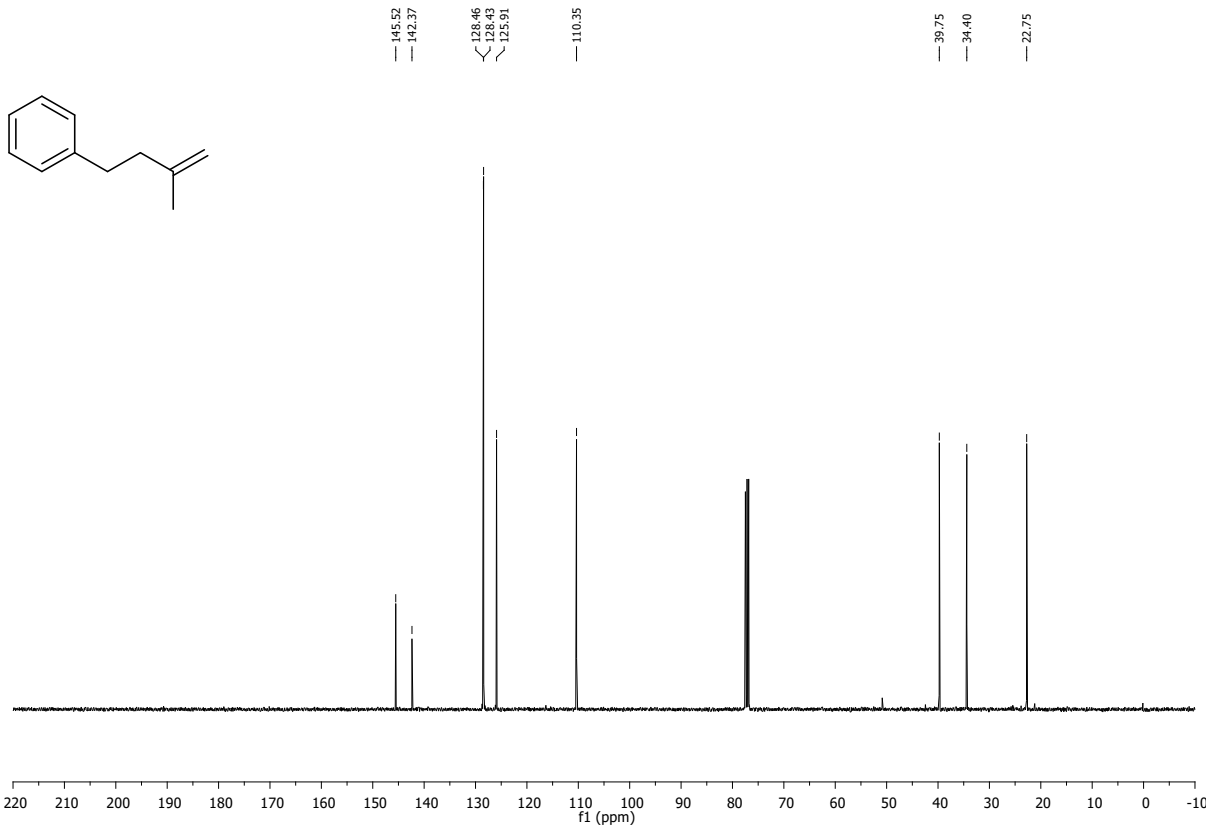
1t


O
N
1.00
1.01
1.03
1.07
0.94
2.16
2.14
2.20
6.03
10.34
6.20
f1 (ppm)

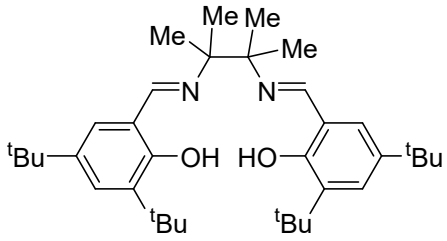

172.20
139.36
114.23
48.34
45.63
35.57
33.93
29.62
29.58
29.49
29.23
29.05
25.60
21.19
20.87
O
N
f1 (ppm)

1i′

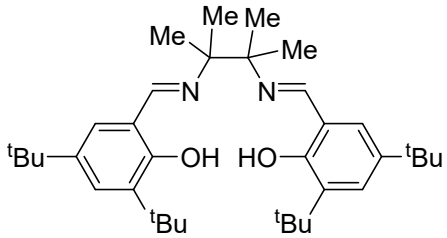

1.92
2.84
2.00
2.01
2.00
3.05
f1 (ppm)



Salen ligand

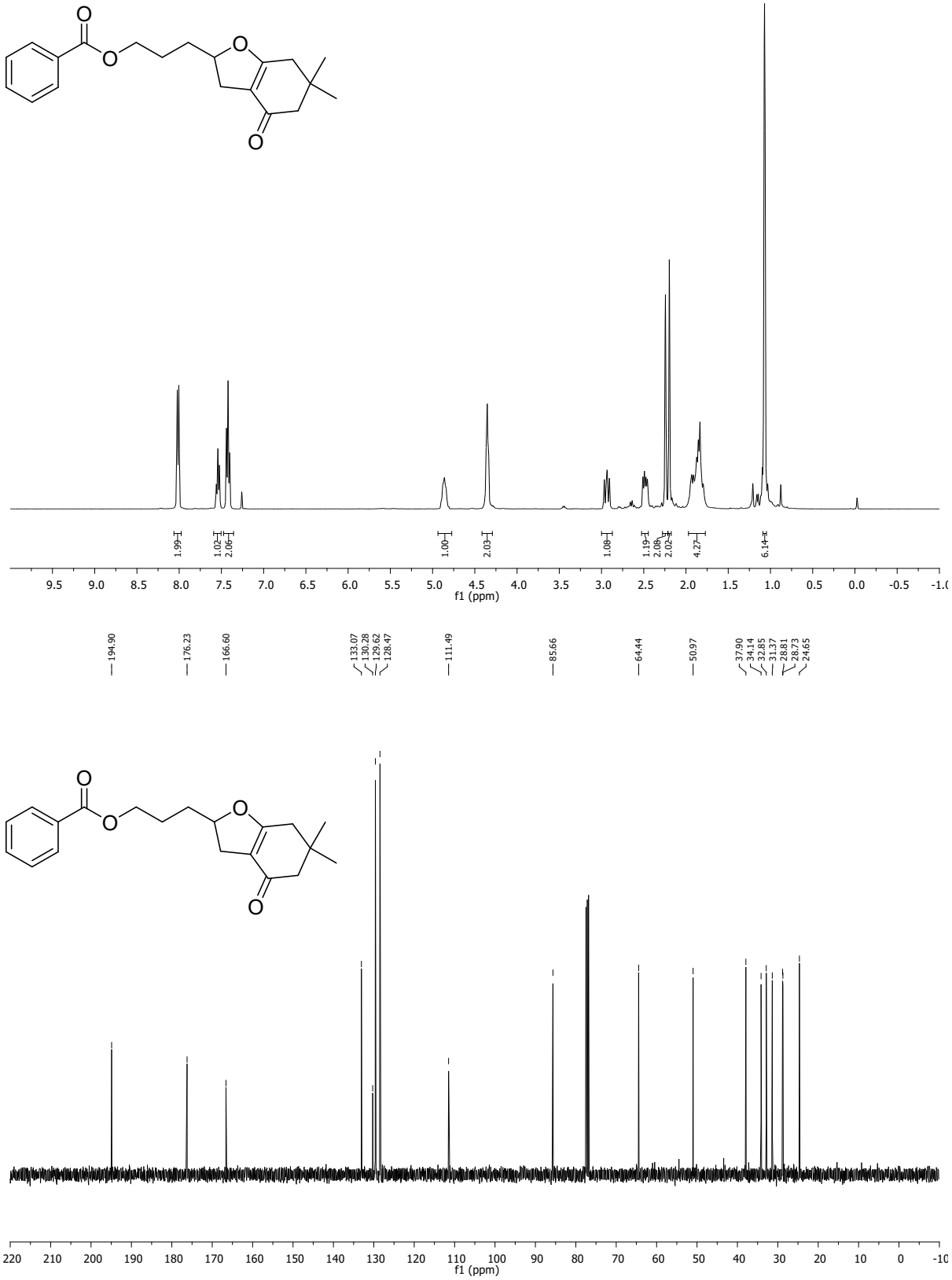

Me
Me
Me
Me
N
N
tBu
OH
HO
tBu
tBu
tBu

0.97
0.99
1.02
1.00
8.90
5.80
8.99
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

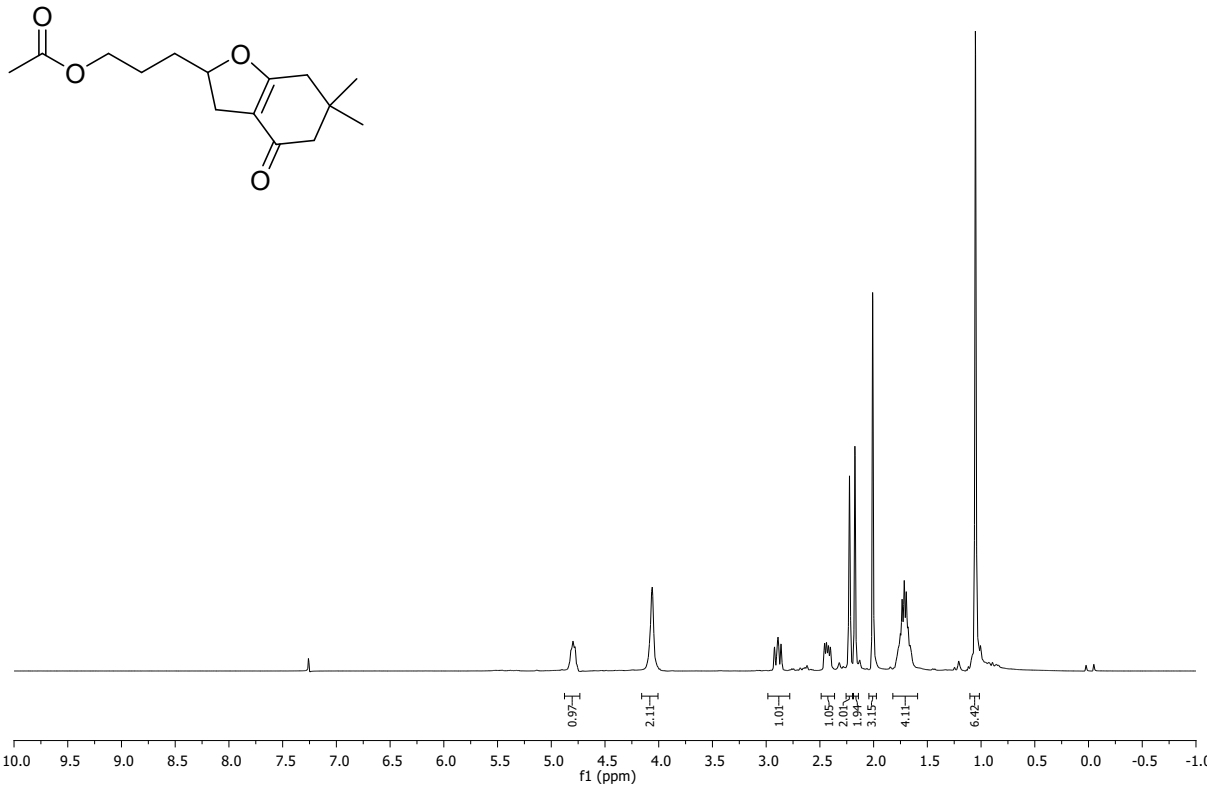

Me
Me
Me
Me
N
N
tBu
OH
HO
tBu
tBu
tBu

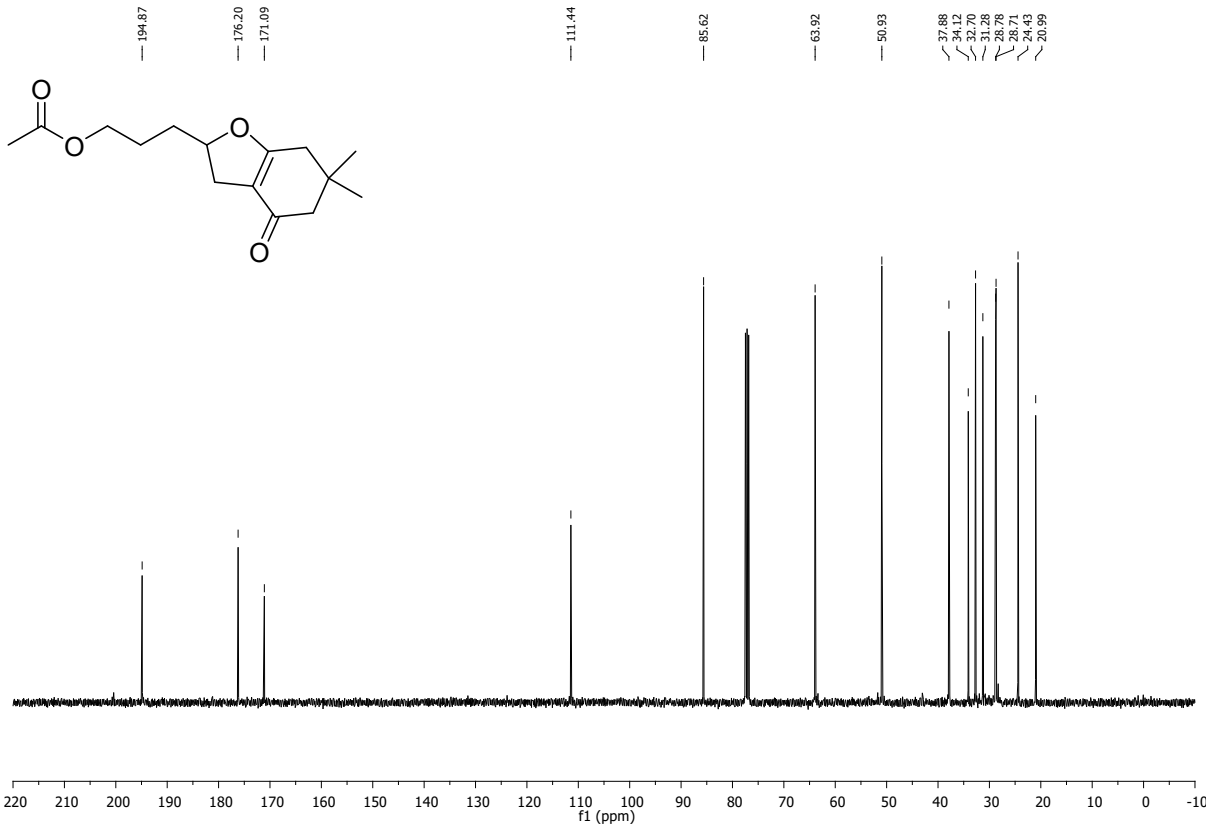
162.78
158.60
139.86
136.78
126.87
126.36
118.12
65.11
35.19
34.26
31.65
29.59
23.40
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3aa

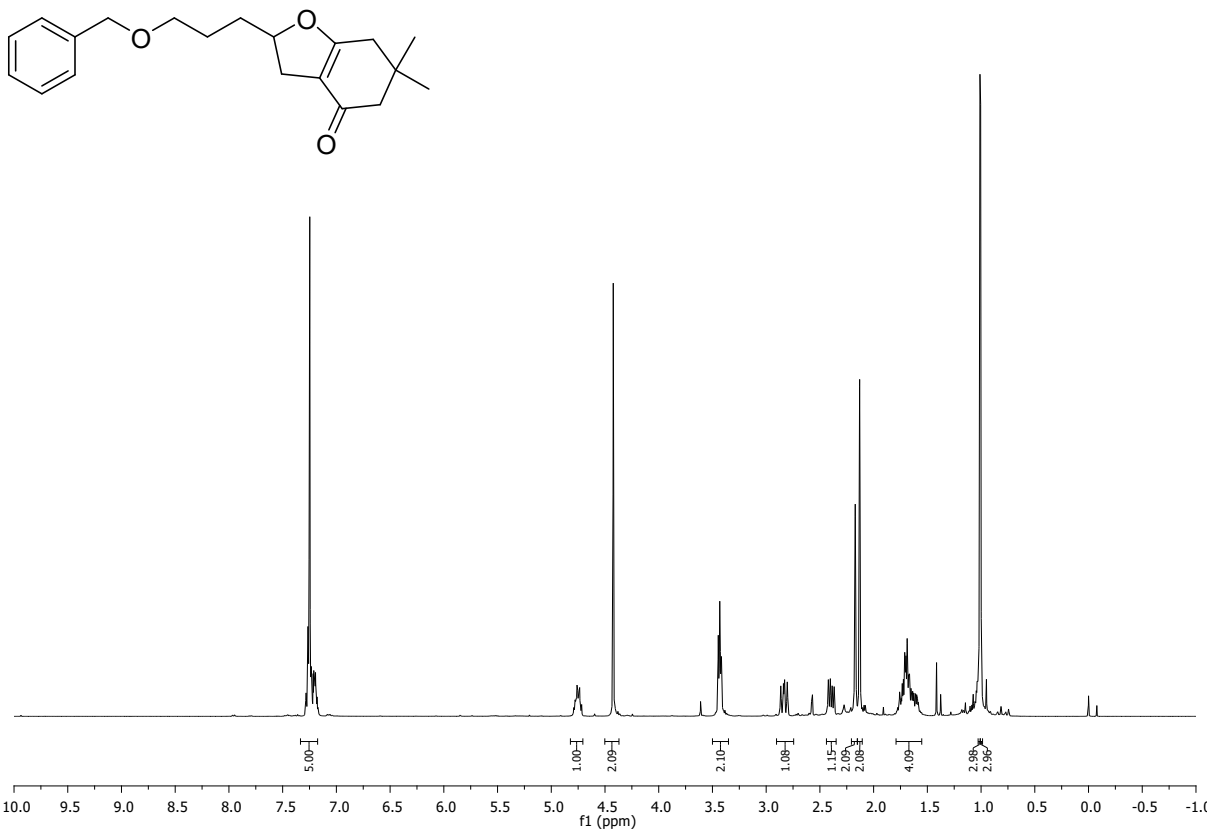

1.99
1.02
2.06
1.00
2.03
1.08
1.19
2.08
2.02
4.27
6.14
f1 (ppm)
194.90
176.23
166.60
133.07
130.28
129.62
128.47
111.49
85.66
64.44
50.97
37.90
34.14
32.85
31.37
28.81
28.73
24.65
f1 (ppm)

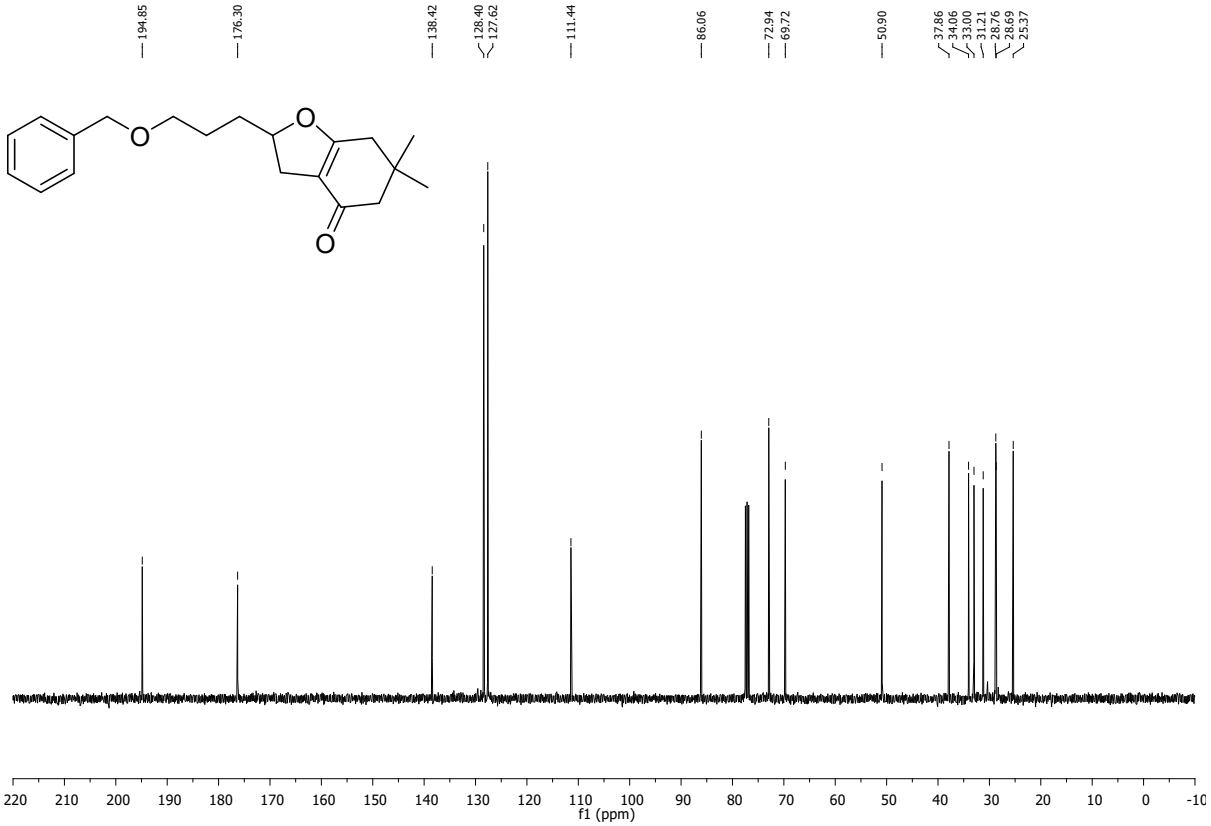
3ba


0.97
2.11
1.01
1.05
2.01
1.94
3.15
4.11
6.42
f1 (ppm)

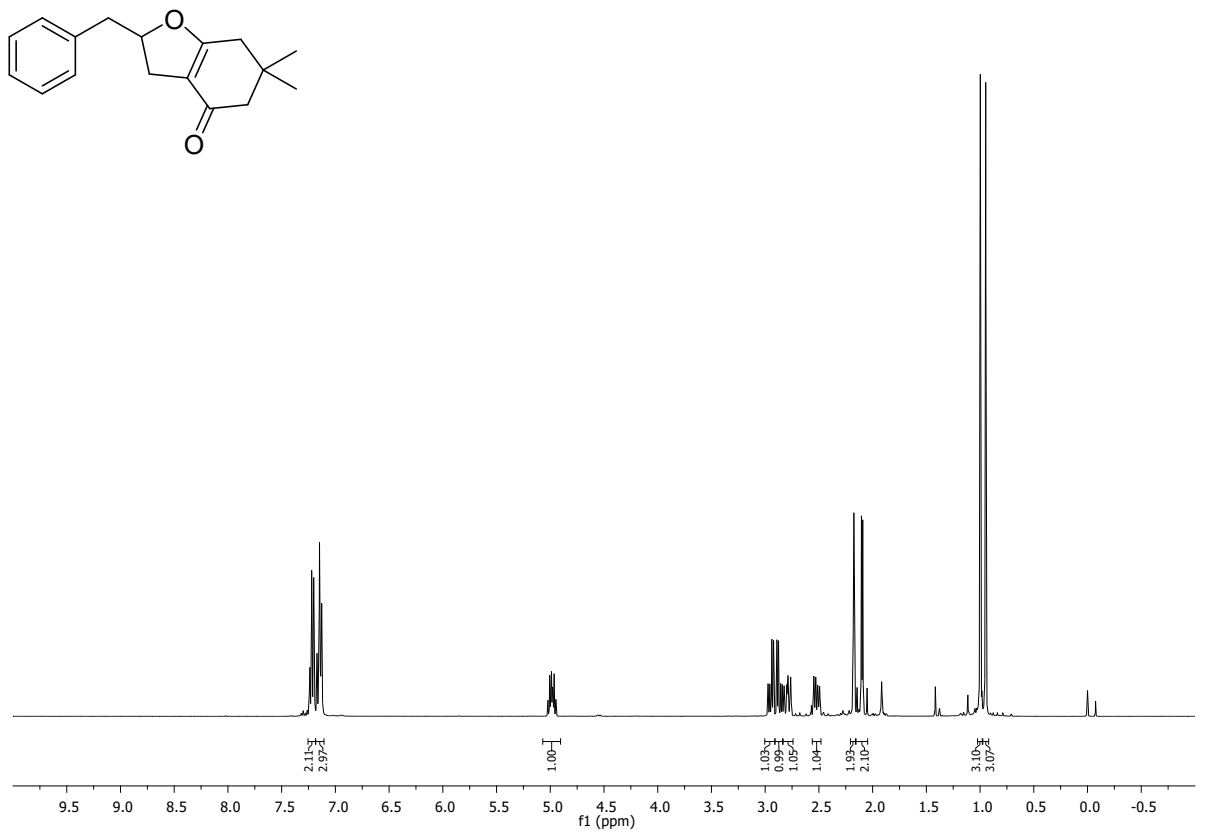

194.87
176.20
171.09
111.44
85.62
63.92
50.93
37.88
34.12
32.70
31.28
28.78
28.71
24.43
20.99
f1 (ppm)

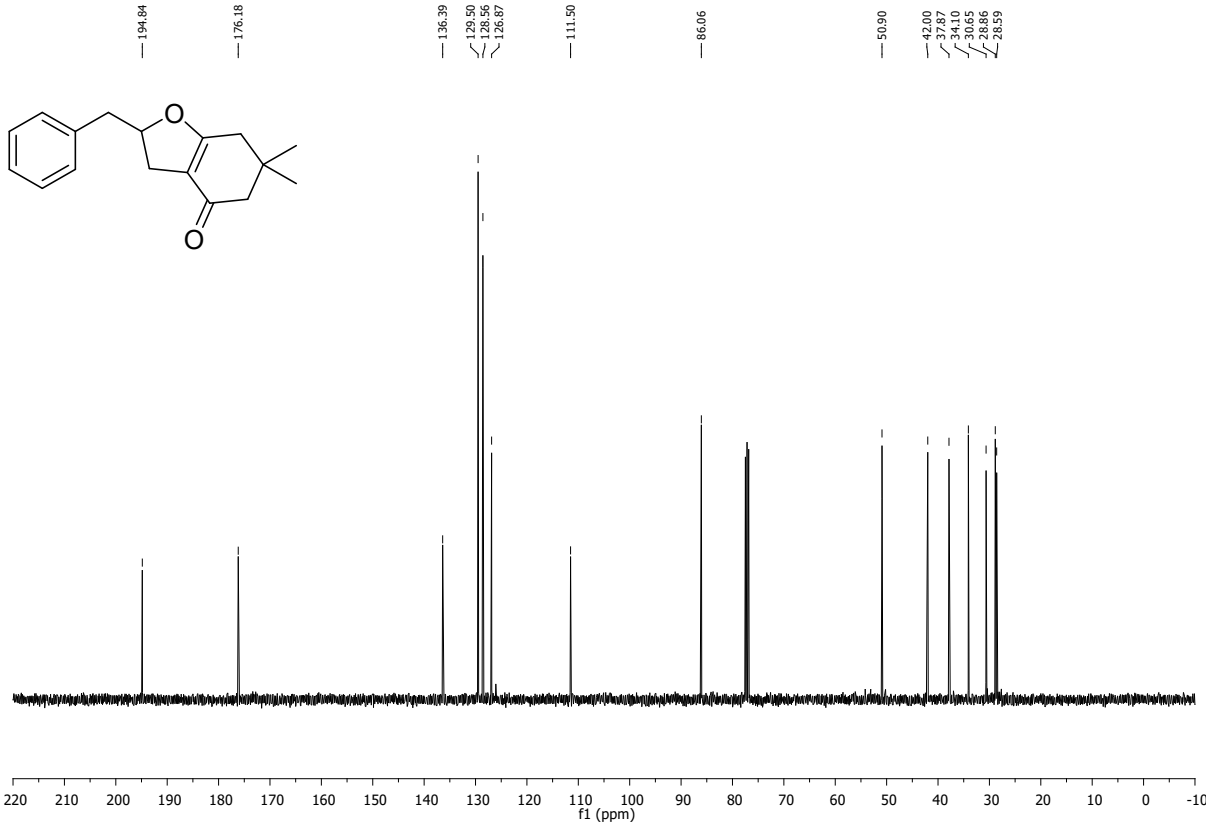
3ca


O
O
O
5.00
1.00
2.09
2.10
1.08
1.15
2.09
2.08
4.09
2.98
2.96
10.0 9.5 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 -0.5
f1 (ppm)

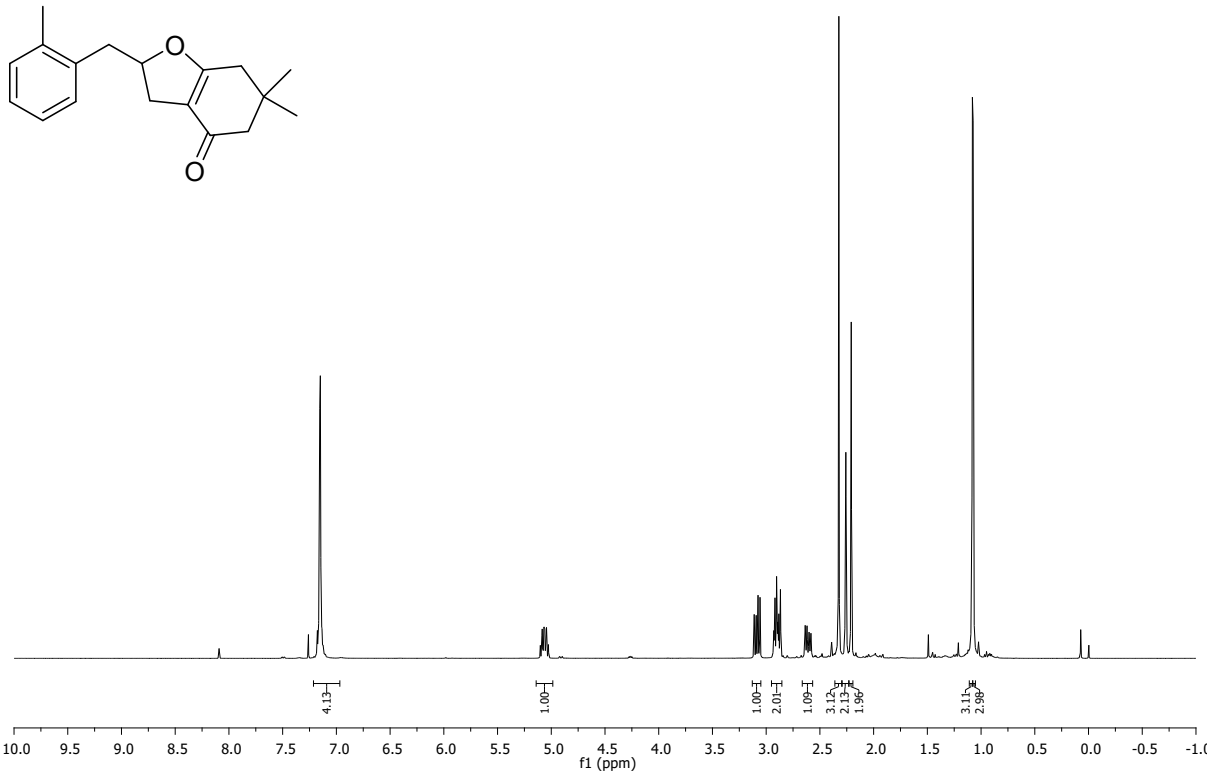

194.85
176.30
138.42
128.40
127.62
111.44
86.06
72.94
69.72
50.90
37.86
34.06
33.00
31.21
28.76
28.69
25.37
O
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

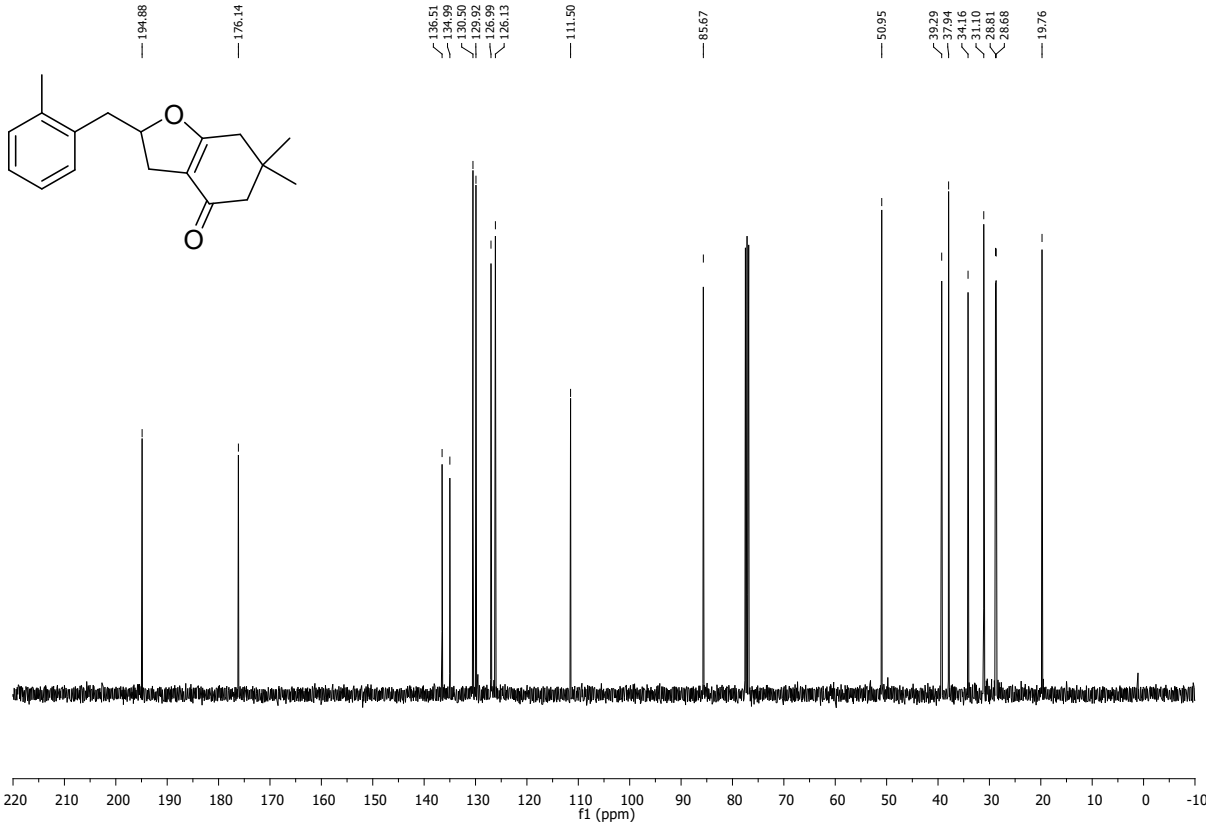
3da


O
O
2.11
2.97
1.00
1.03
0.99
1.05
1.04
1.93
2.10
3.10
3.07
9.5 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 -0.5
f1 (ppm)

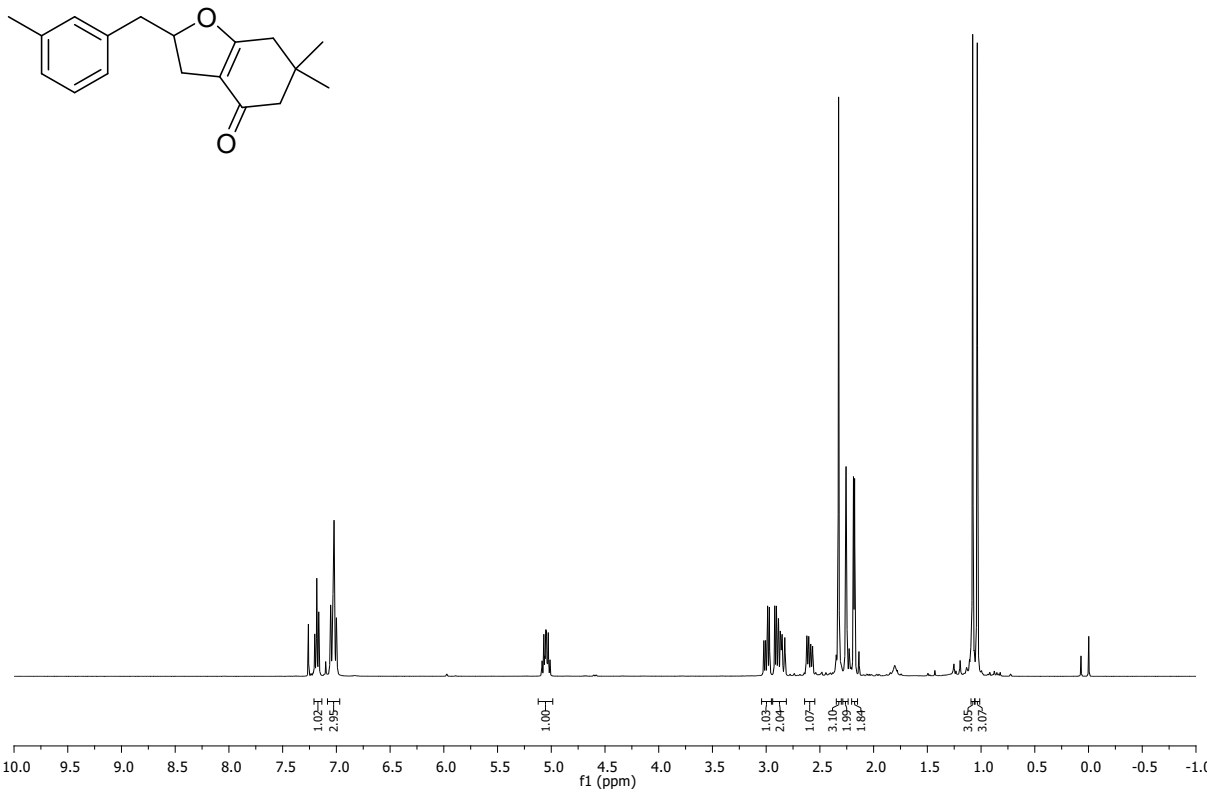

194.84
176.18
136.39
129.50
128.56
126.87
111.50
86.06
50.90
42.00
37.87
34.10
30.65
28.86
28.59
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

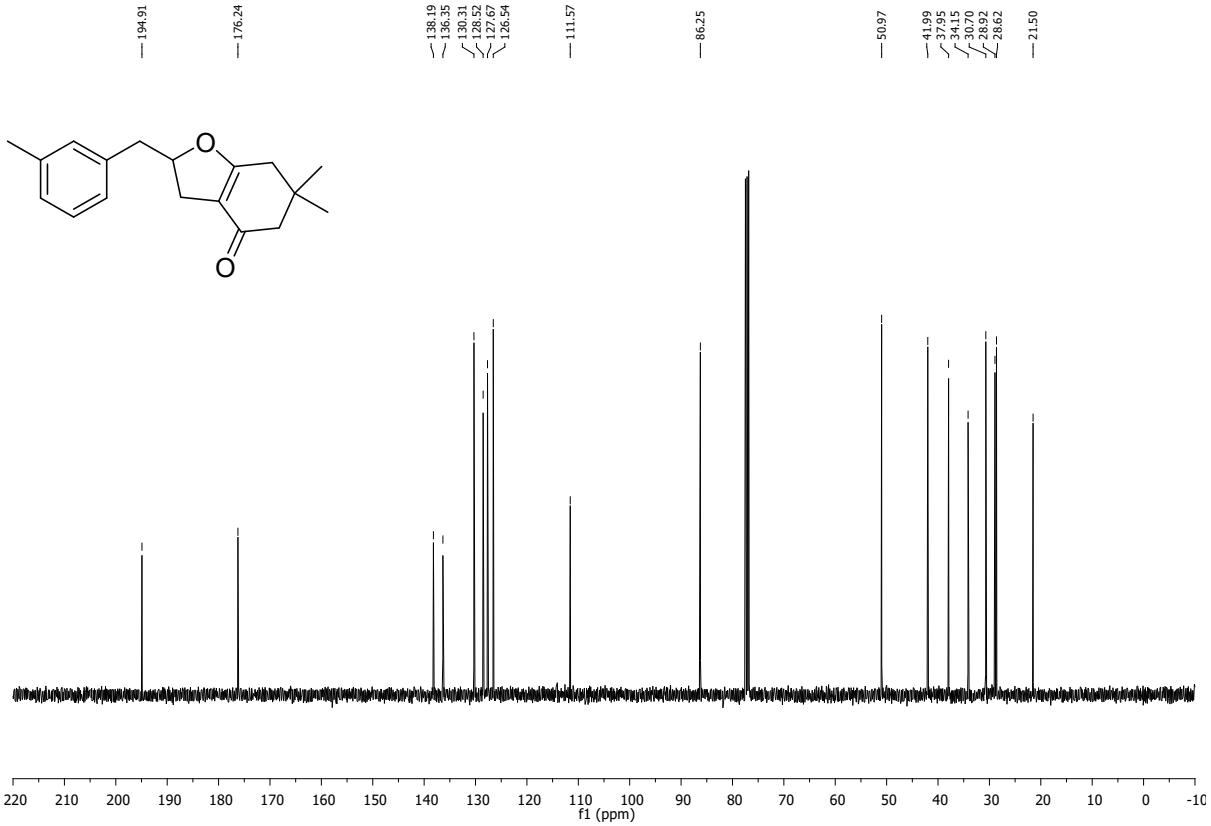
3ea


O
O
4.13
1.00
1.00
2.01
1.09
3.12
2.13
1.96
3.11
2.90
10.0 9.5 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 -0.5
f1 (ppm)

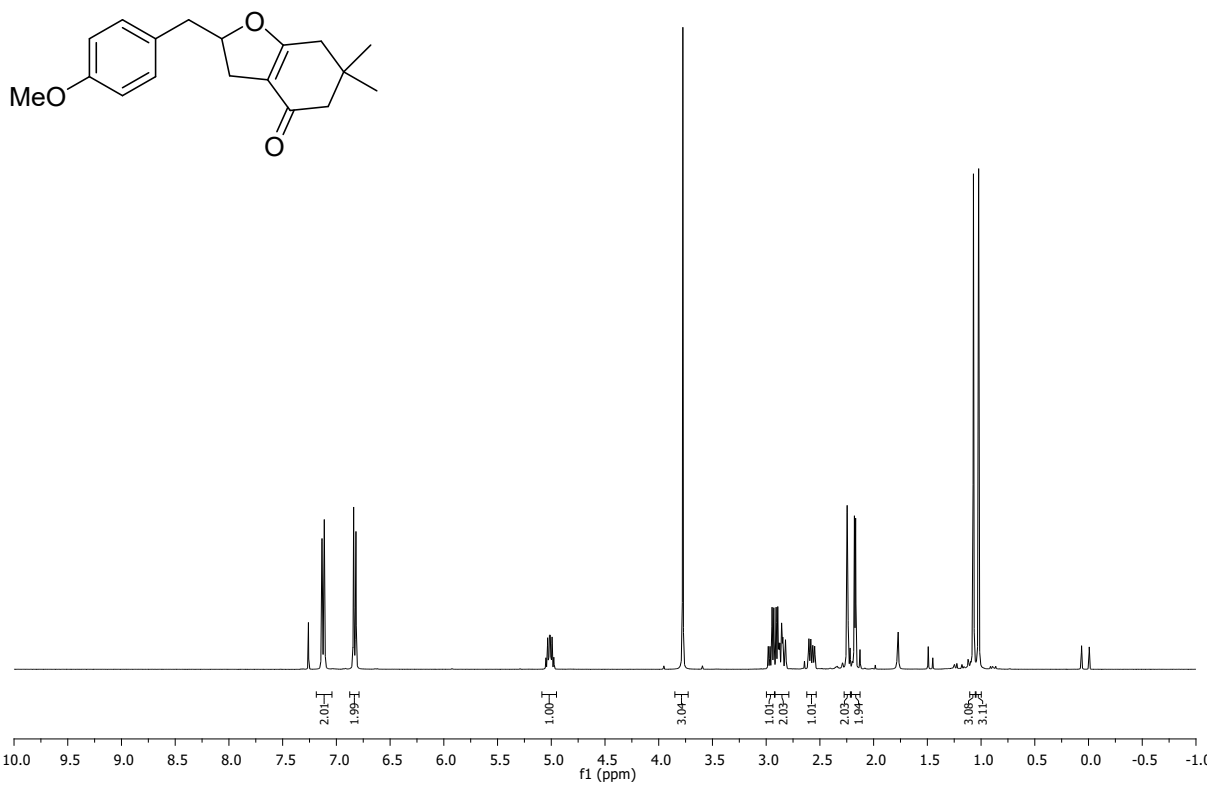

194.88
176.14
136.51
134.99
130.50
129.92
126.99
126.13
111.50
85.67
50.95
39.29
37.94
34.16
31.10
28.81
28.68
19.76
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

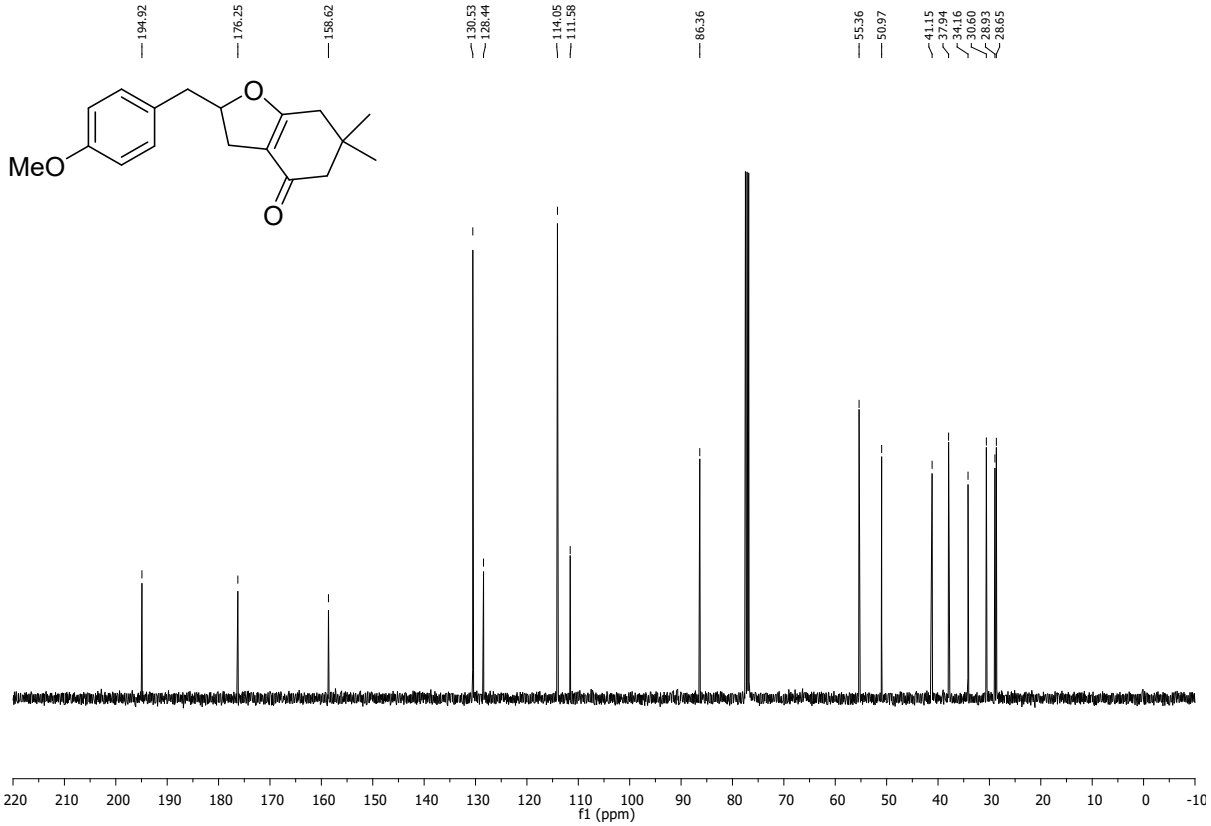
3fa


O
O
1.02
2.95
1.00
1.03
2.04
1.07
3.10
1.99
1.84
3.05
3.07
10.0 9.5 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 -0.5
f1 (ppm)

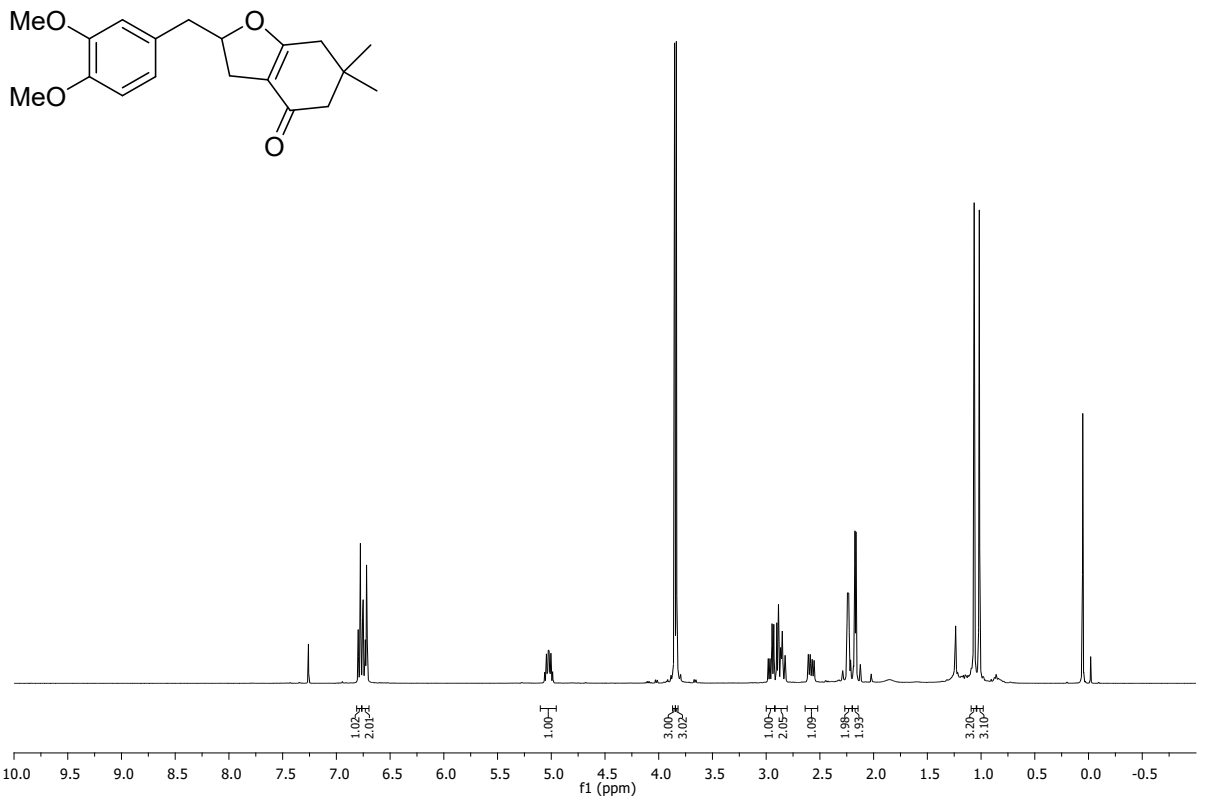

194.91
176.24
138.19
136.35
130.31
128.52
127.67
126.54
111.57
86.25
50.97
41.99
37.95
34.15
30.70
28.92
28.62
21.50
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

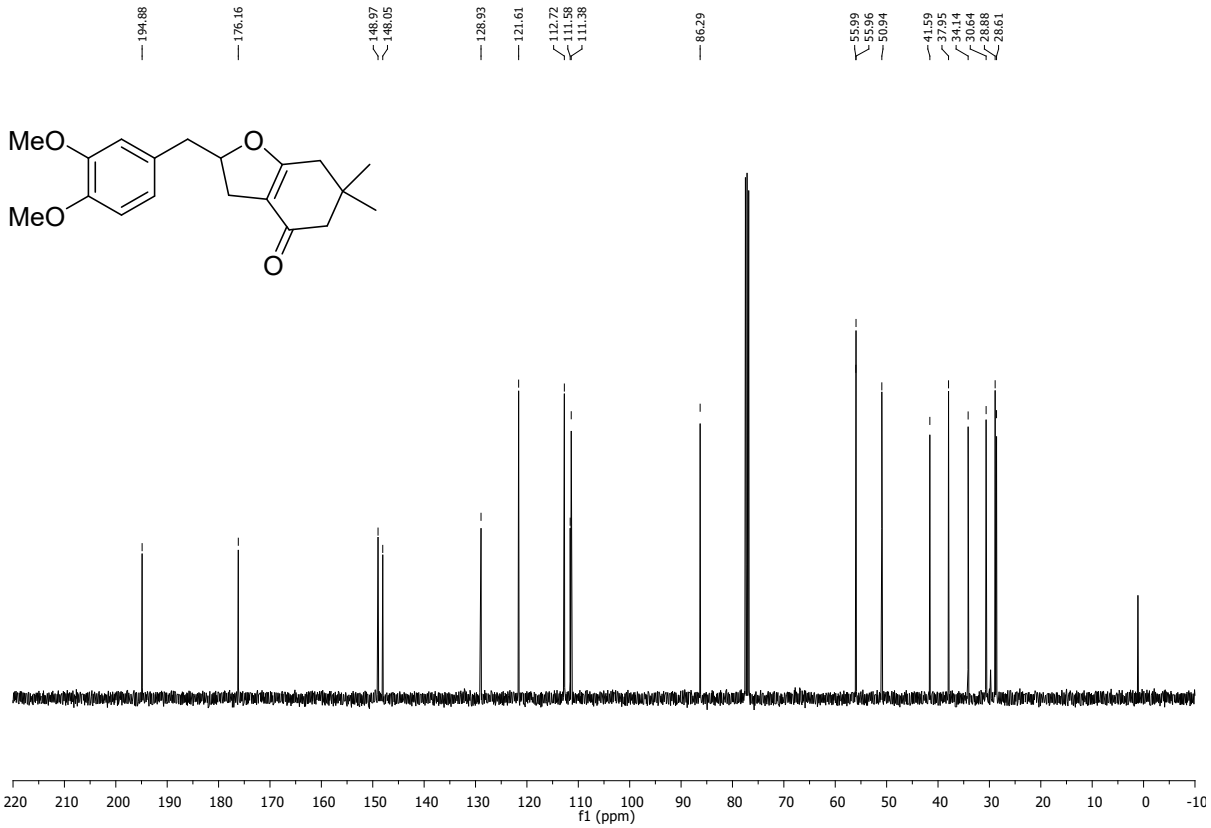
3ga


MeO
O
O
2.01
1.99
1.00
3.04
1.01
2.03
1.01
2.03
1.94
3.08
3.11
10.0 9.5 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 -0.5
f1 (ppm)

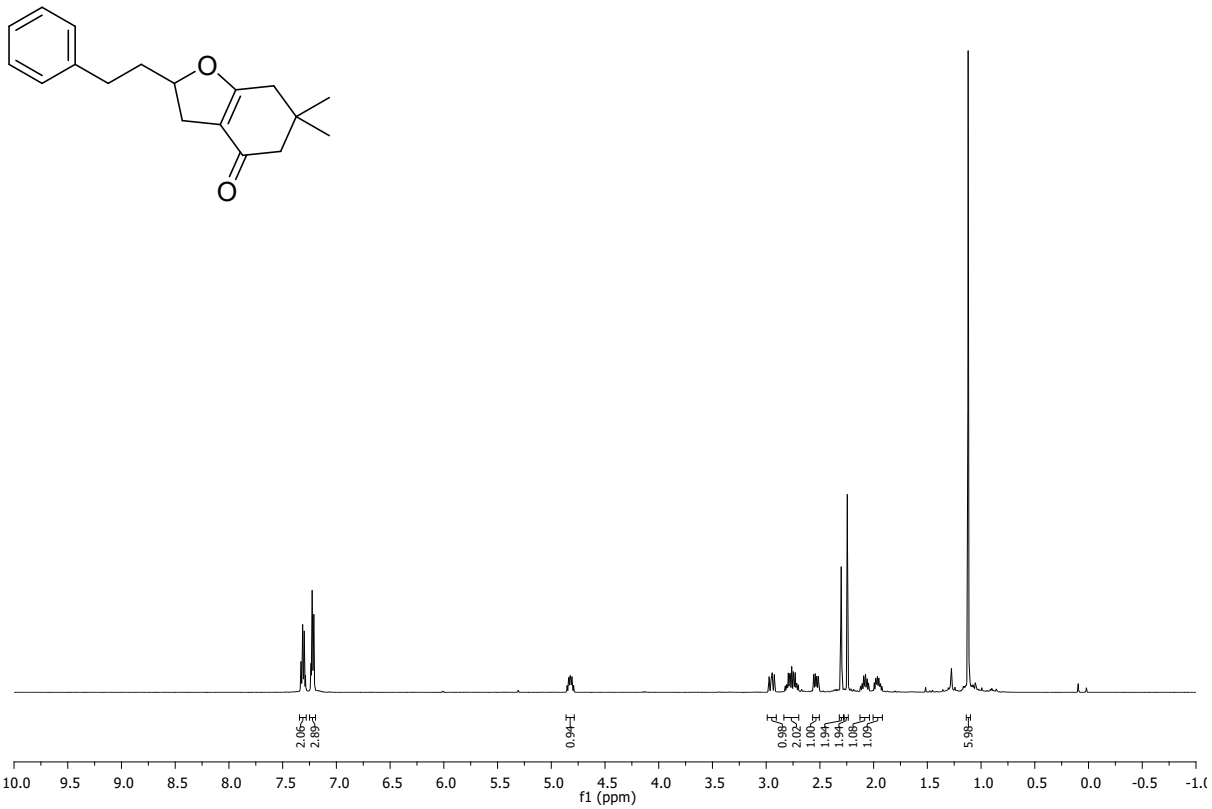

194.92
176.25
158.62
130.53
128.44
114.05
111.58
86.36
55.36
50.97
41.15
37.94
34.16
30.60
28.93
28.65
MeO
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

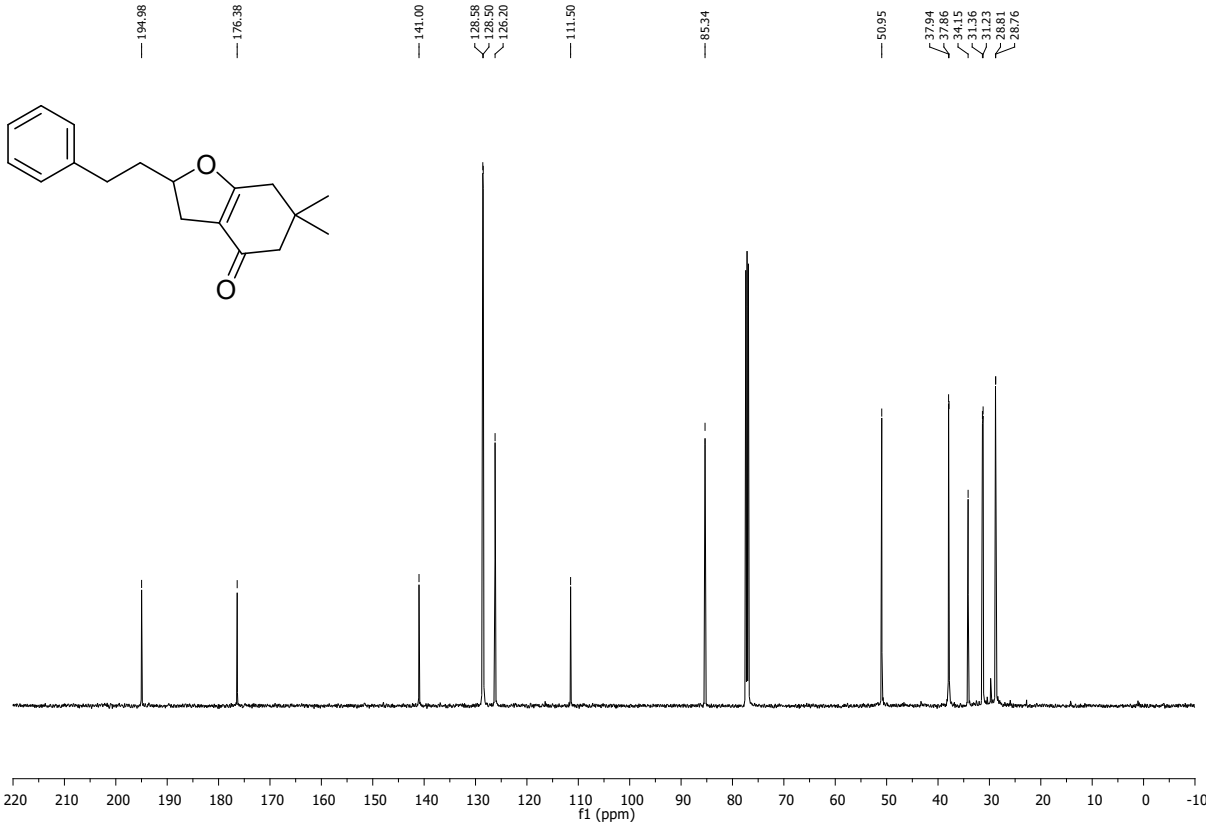
3ha


MeO
MeO
O
O
1.02
2.01
1.00
3.00
3.02
1.00
2.05
1.09
1.98
1.93
3.20
3.10
10.0 9.5 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 -0.5
f1 (ppm)

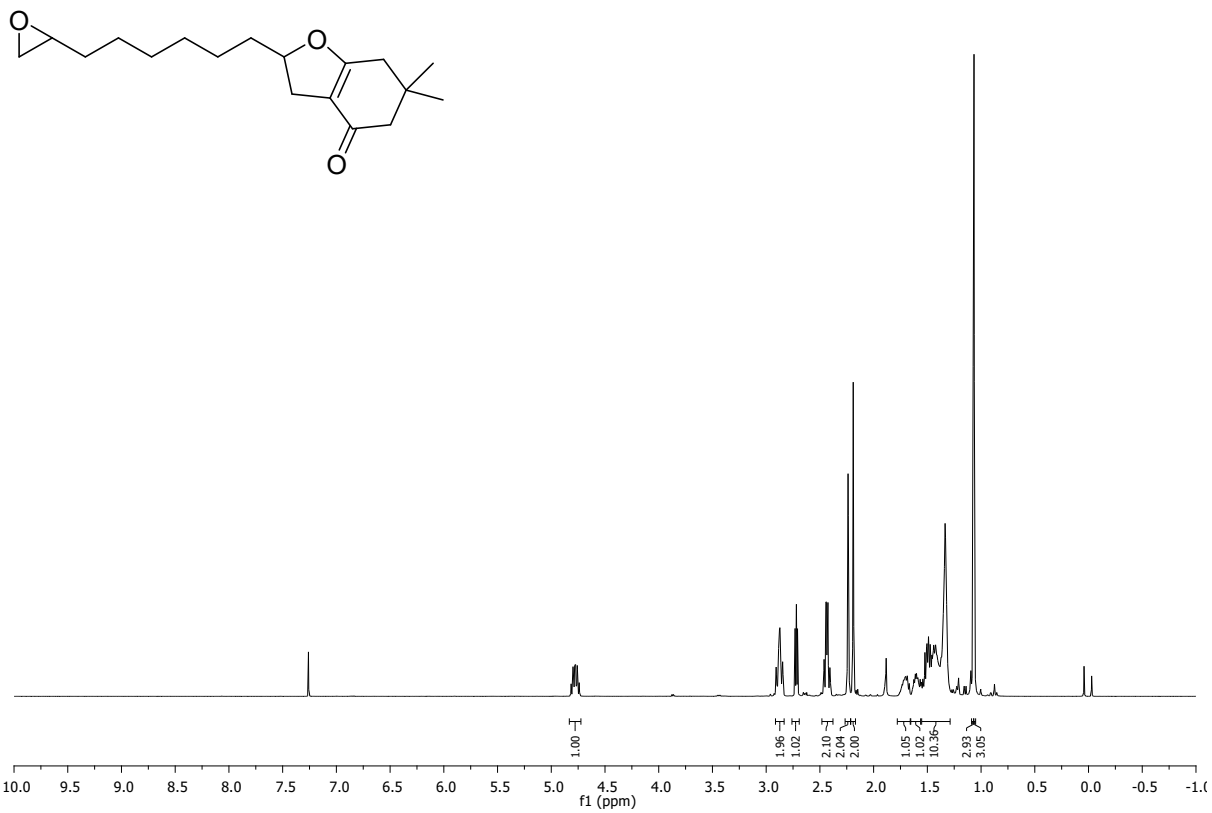

194.88
176.16
148.97
148.05
128.93
121.61
112.72
111.58
111.38
86.29
55.99
55.96
50.94
41.59
37.95
34.14
30.64
28.88
28.61
MeO
MeO
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

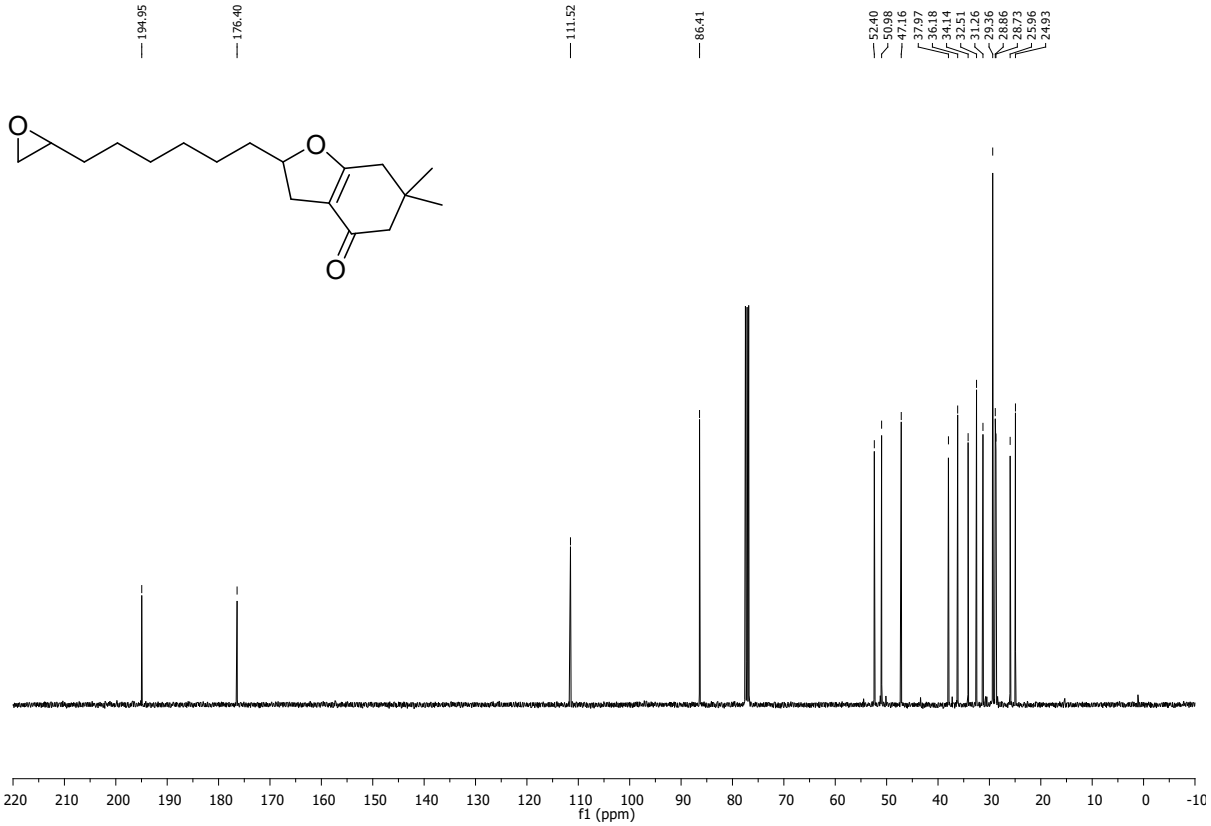
3ia


O
O
2.05
2.89
0.94
0.98
2.02
1.00
1.94
1.94
1.08
1.09
5.98
10.0 9.5 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 -0.5 -1.0
f1 (ppm)

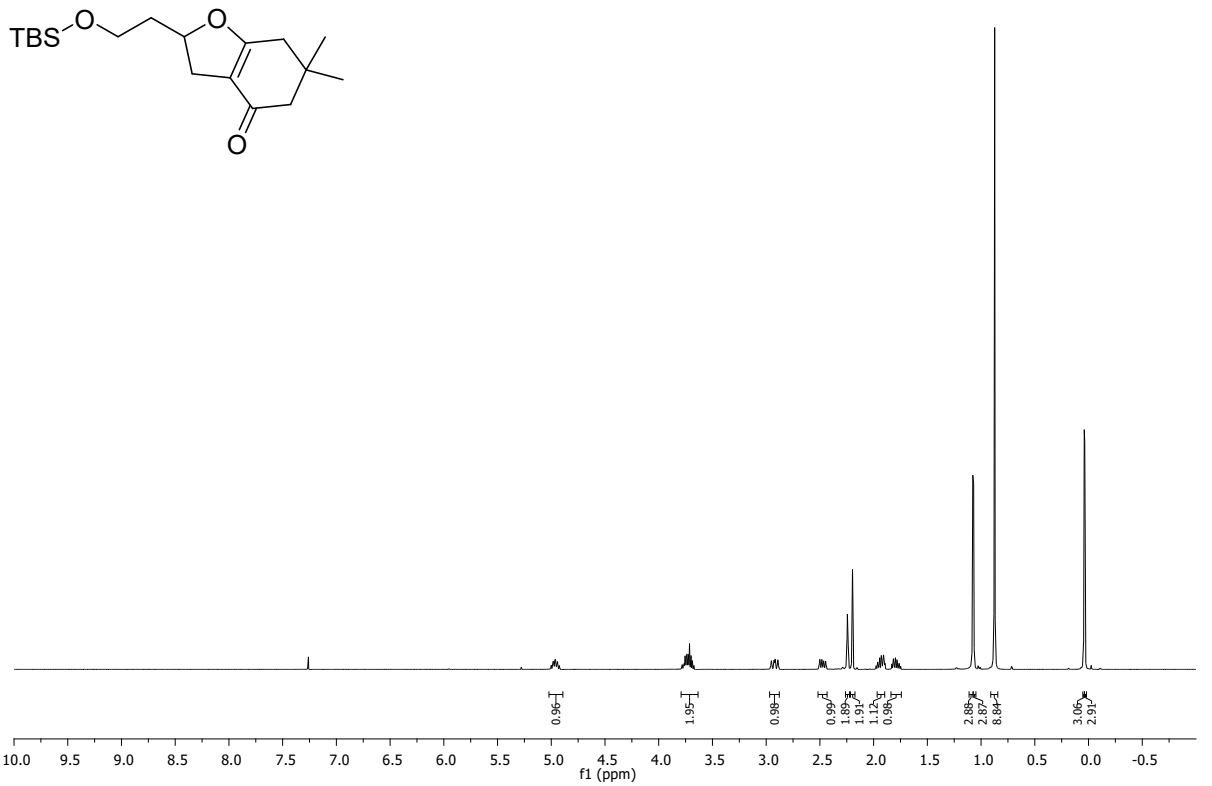

194.98
176.38
141.00
128.58
128.50
126.20
111.50
85.34
50.95
37.94
37.86
34.15
31.36
31.23
28.81
28.76
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

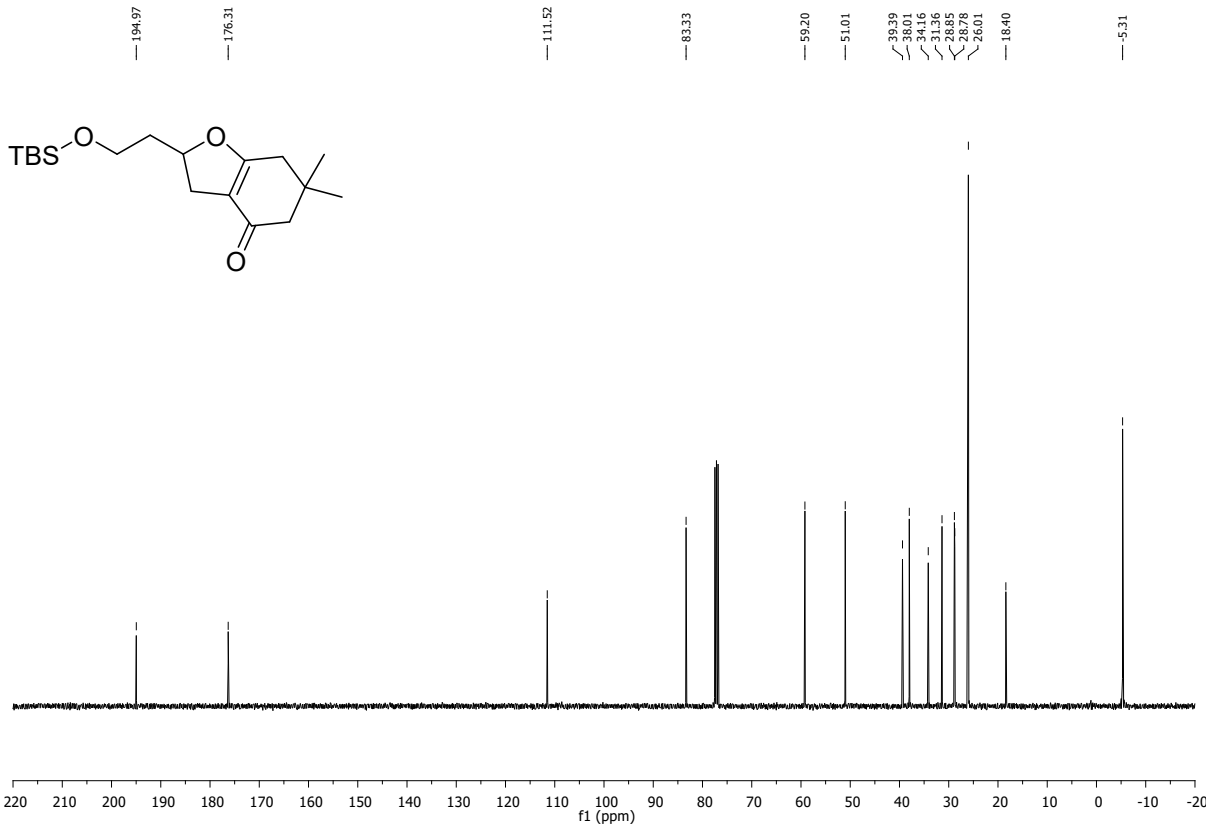
3ja


1.00
1.96
1.02
2.10
2.04
2.00
1.05
1.02
10.36
2.93
3.05
f1 (ppm)

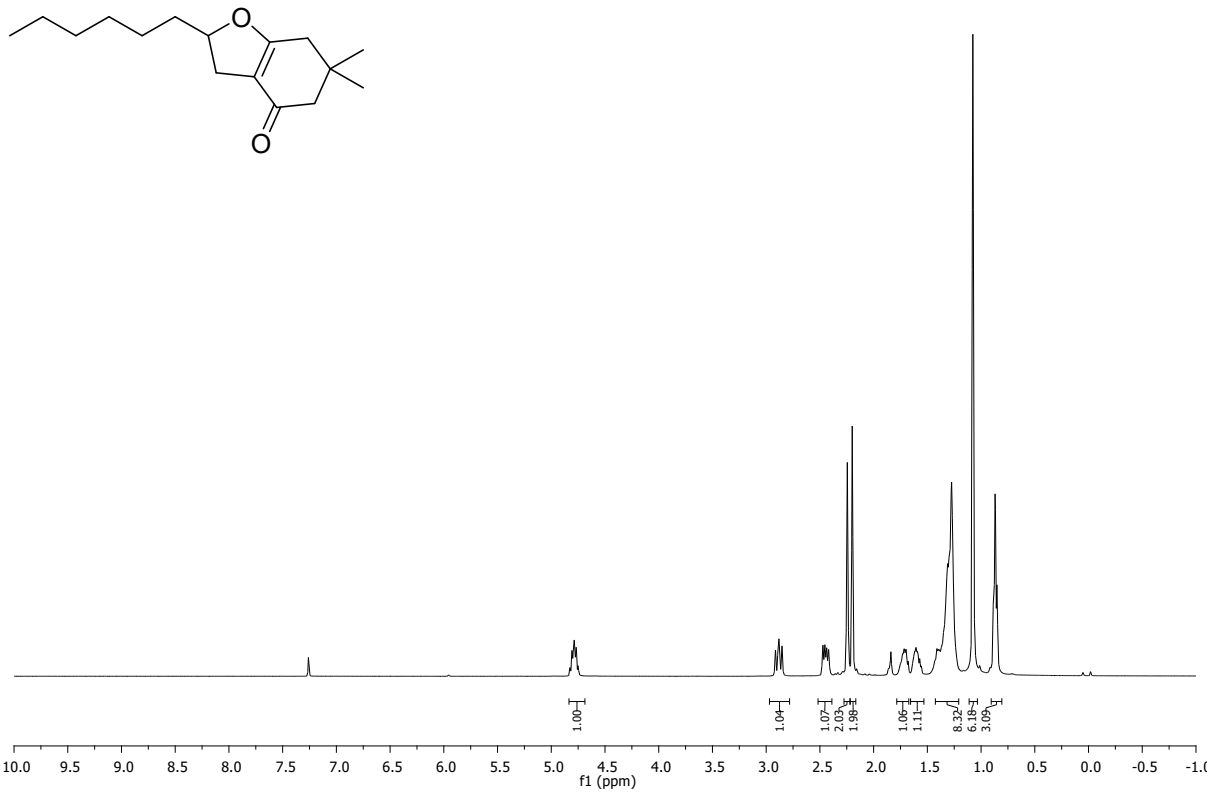

194.95
176.40
111.52
86.41
52.40
50.98
47.16
37.97
36.18
34.14
32.51
31.26
29.36
28.86
28.73
25.96
24.93
f1 (ppm)

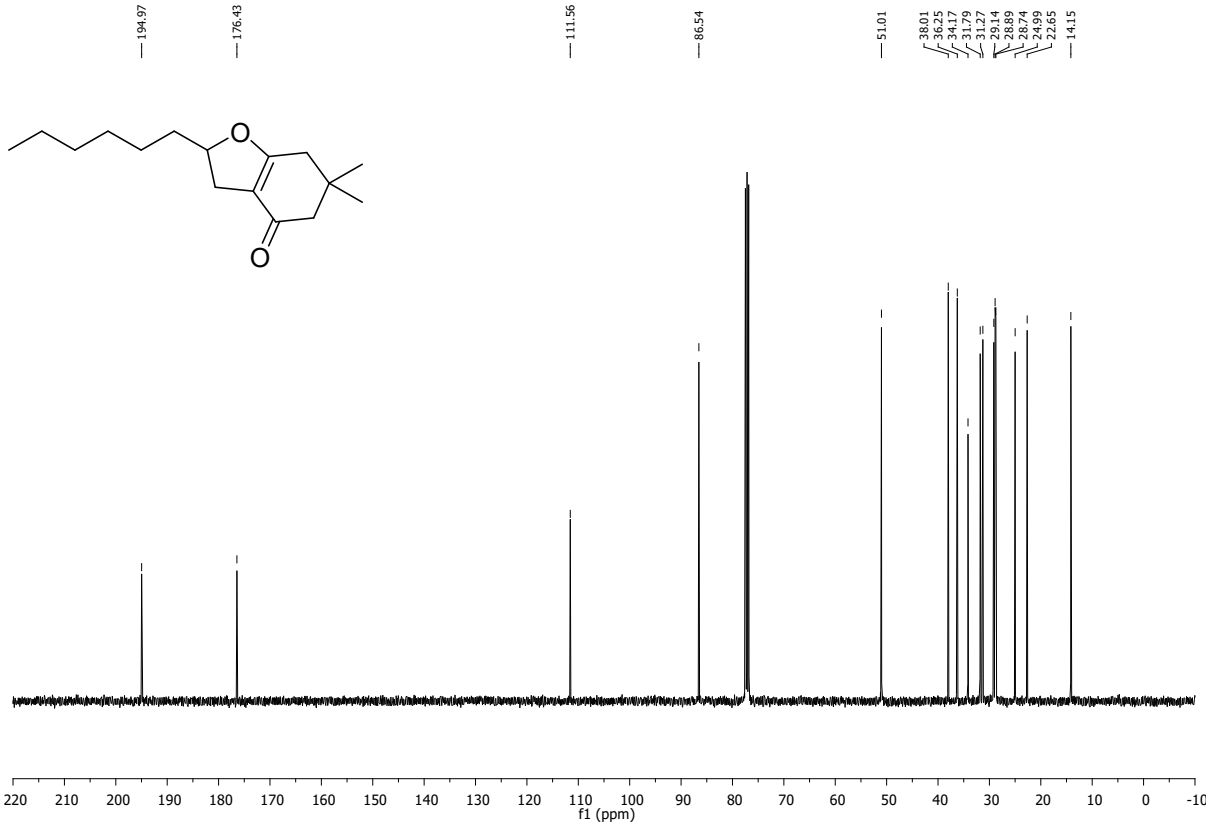
3ka


TBS
O
O
O
0.96
1.95
0.98
0.99
1.89
1.91
1.12
0.98
2.88
2.87
8.84
3.06
2.91
10.0 9.5 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 -0.5
f1 (ppm)

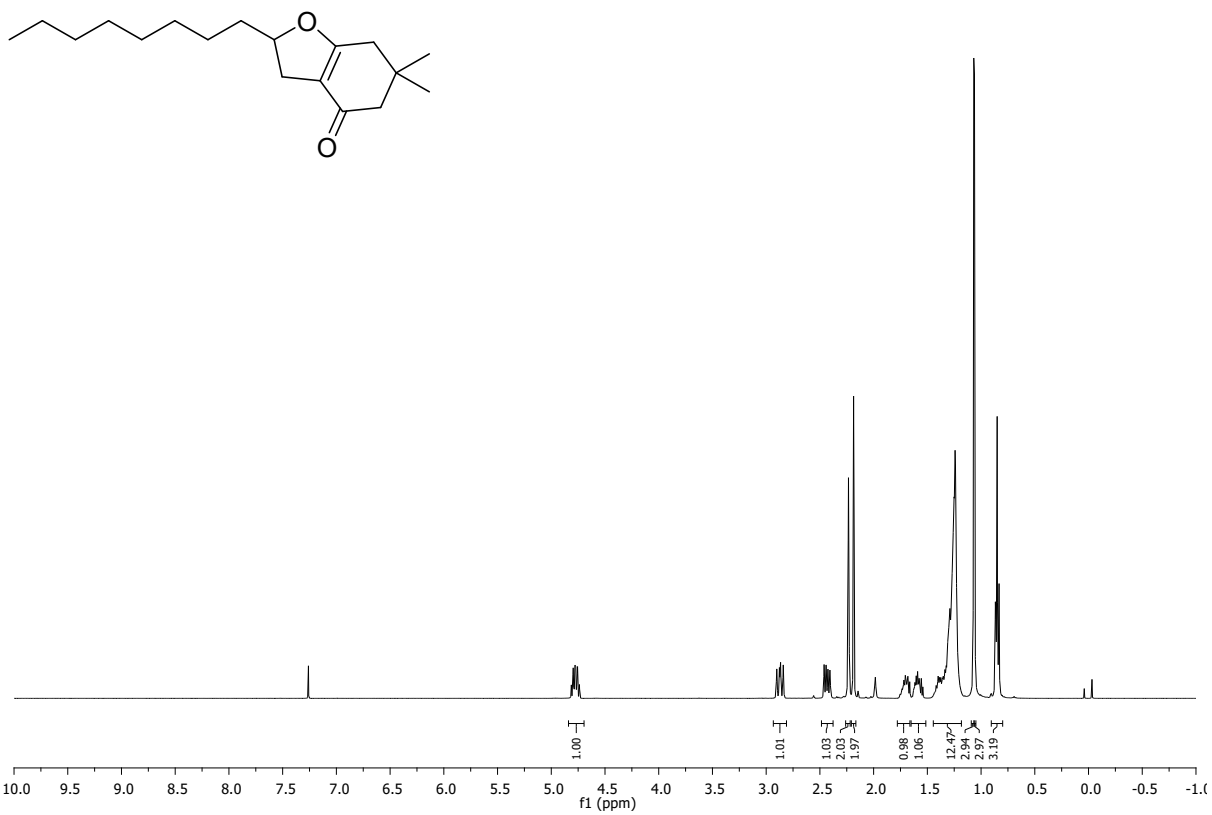

194.97
176.31
111.52
83.33
59.20
51.01
39.39
38.01
34.16
31.36
28.85
28.78
26.01
18.40
-5.31
TBS
O
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

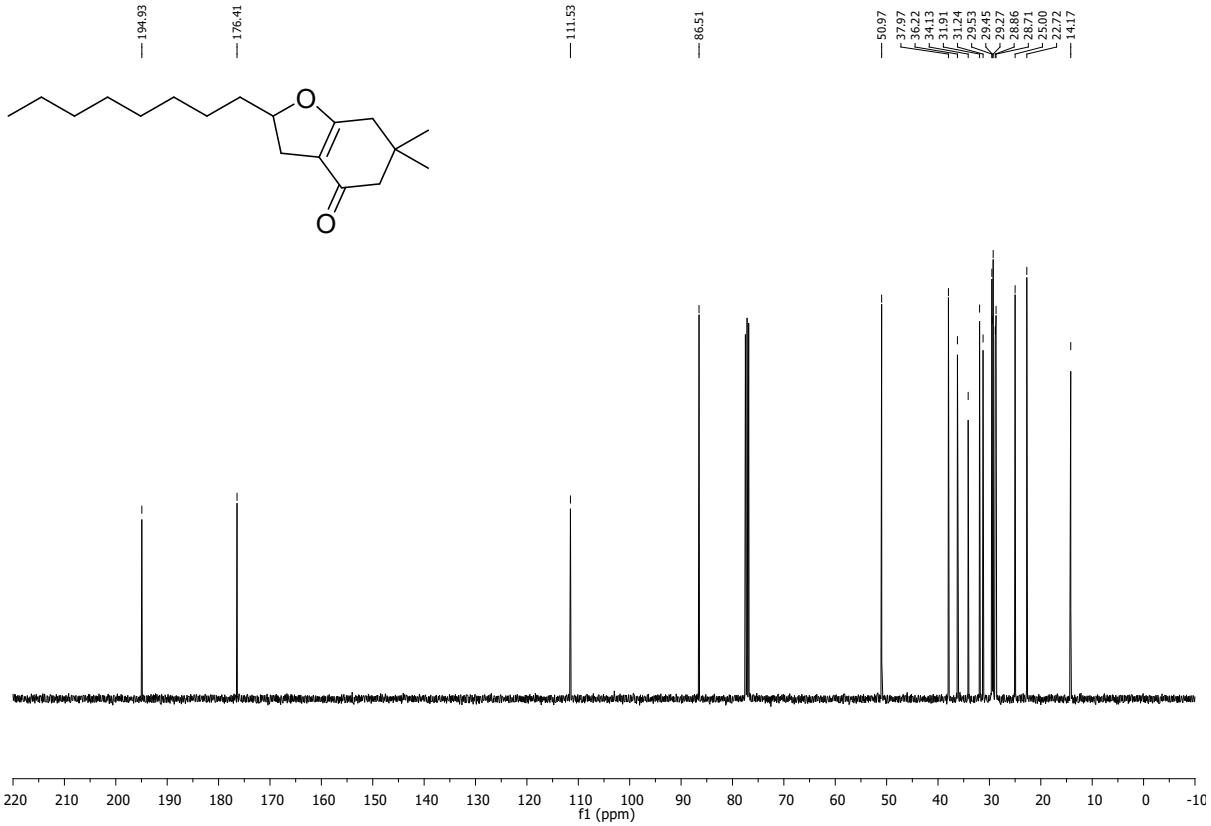
3la


O
O
1.00
1.04
1.07
2.03
1.98
1.06
1.11
8.32
6.18
3.09
10.0 9.5 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 -0.5
f1 (ppm)

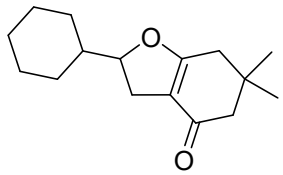

194.97
176.43
111.56
86.54
51.01
38.01
36.25
34.17
31.79
31.27
29.14
28.89
28.74
24.99
22.65
14.15
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ma

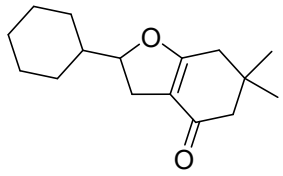

O
O
1.00
1.01
1.03
2.03
1.97
0.98
1.06
12.47
2.94
2.97
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


194.93
176.41
111.53
86.51
50.97
37.97
36.22
34.13
31.91
31.24
29.53
29.45
29.27
28.86
28.71
25.00
22.72
14.17
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3na

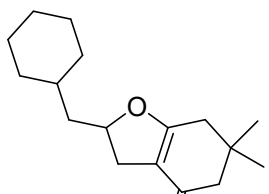


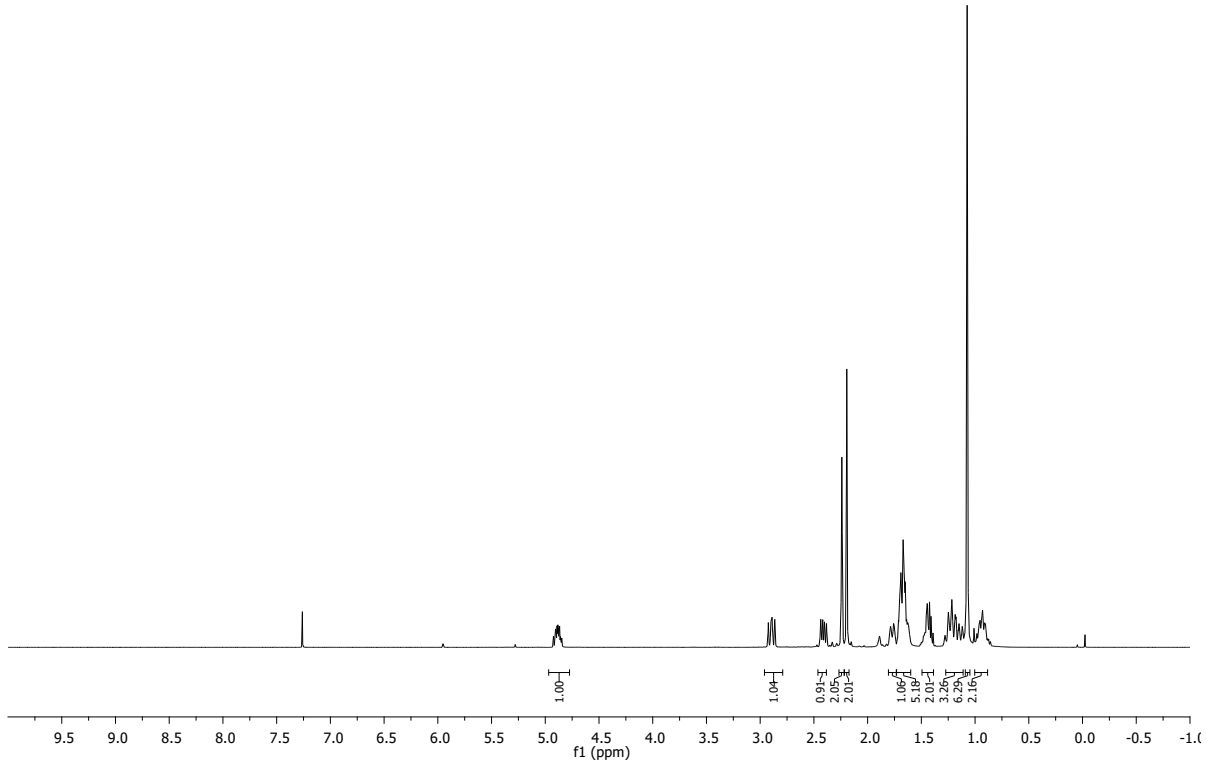
1.00
1.01
1.03
2.02
2.01
1.06
5.49
3.22
3.17
3.05
2.12
f1 (ppm)

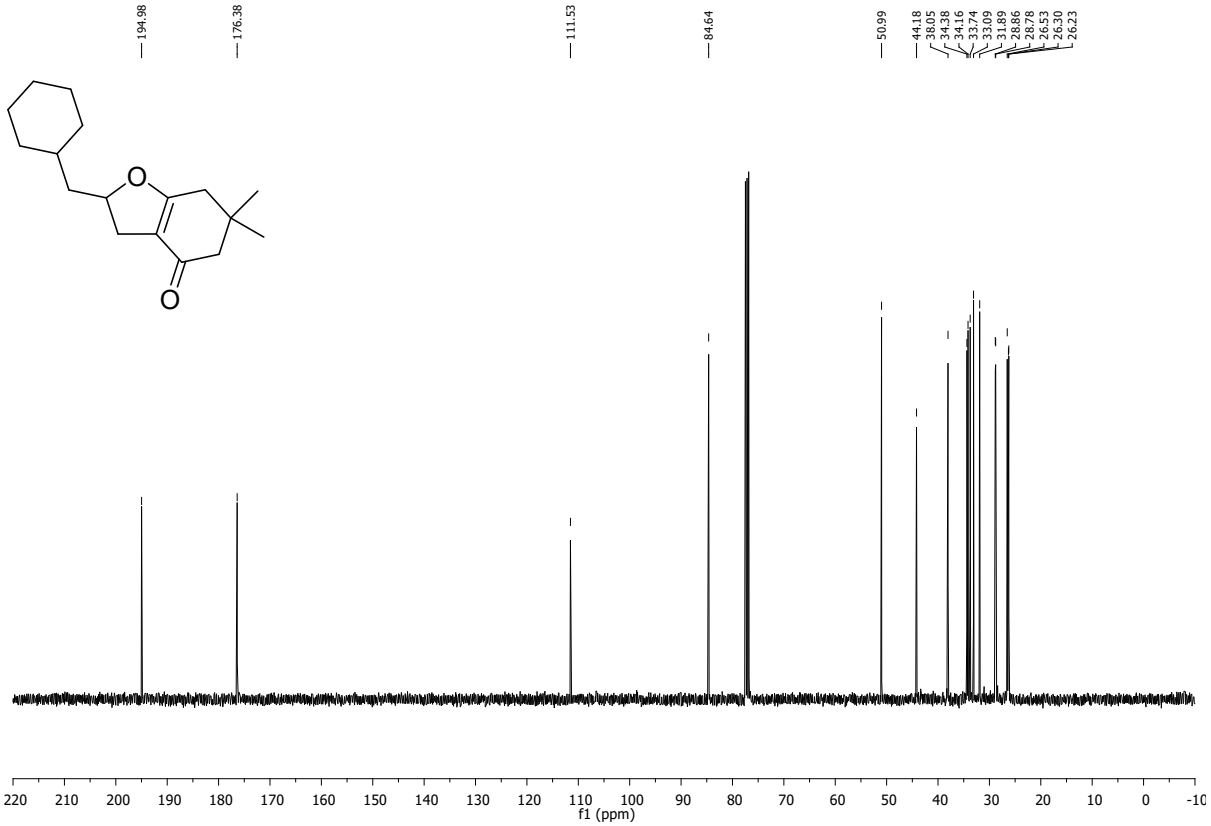


194.89
176.66
111.77
90.56
51.00
43.08
37.93
34.18
29.03
28.76
28.63
28.10
27.97
26.47
25.93
25.79
f1 (ppm)

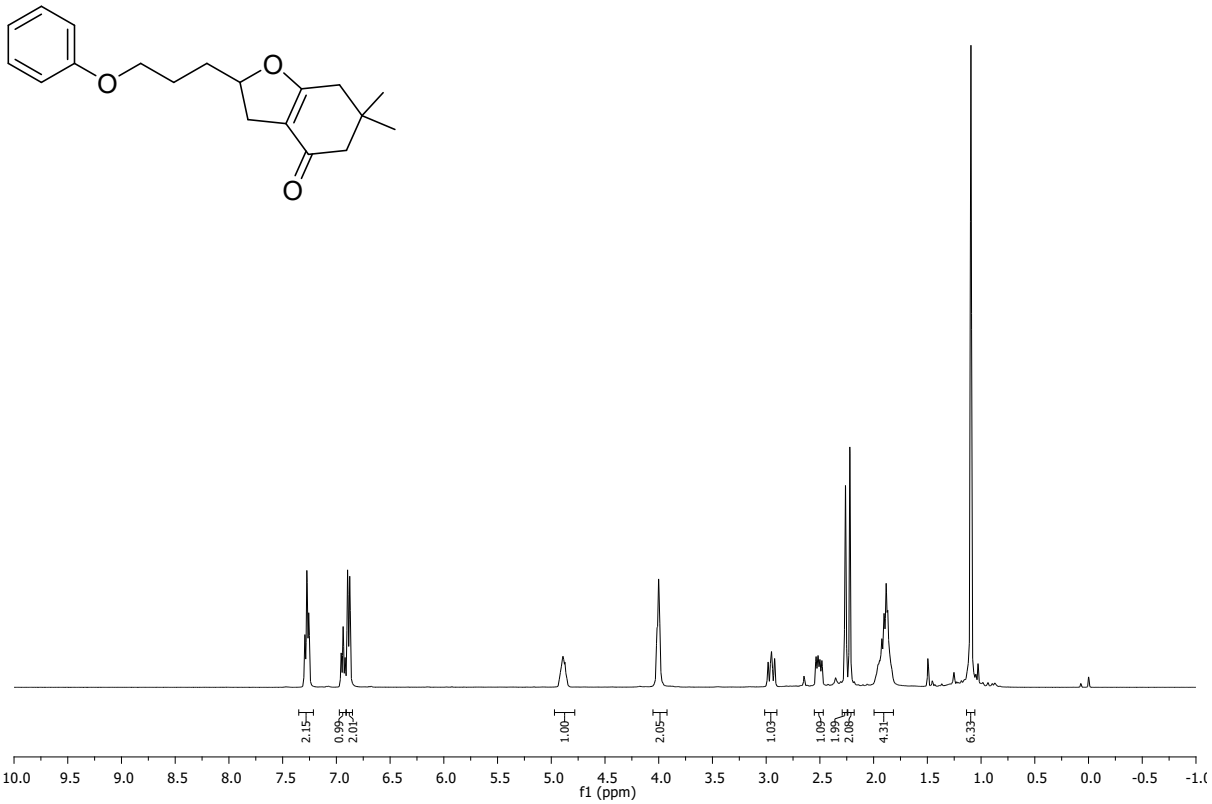
3oa

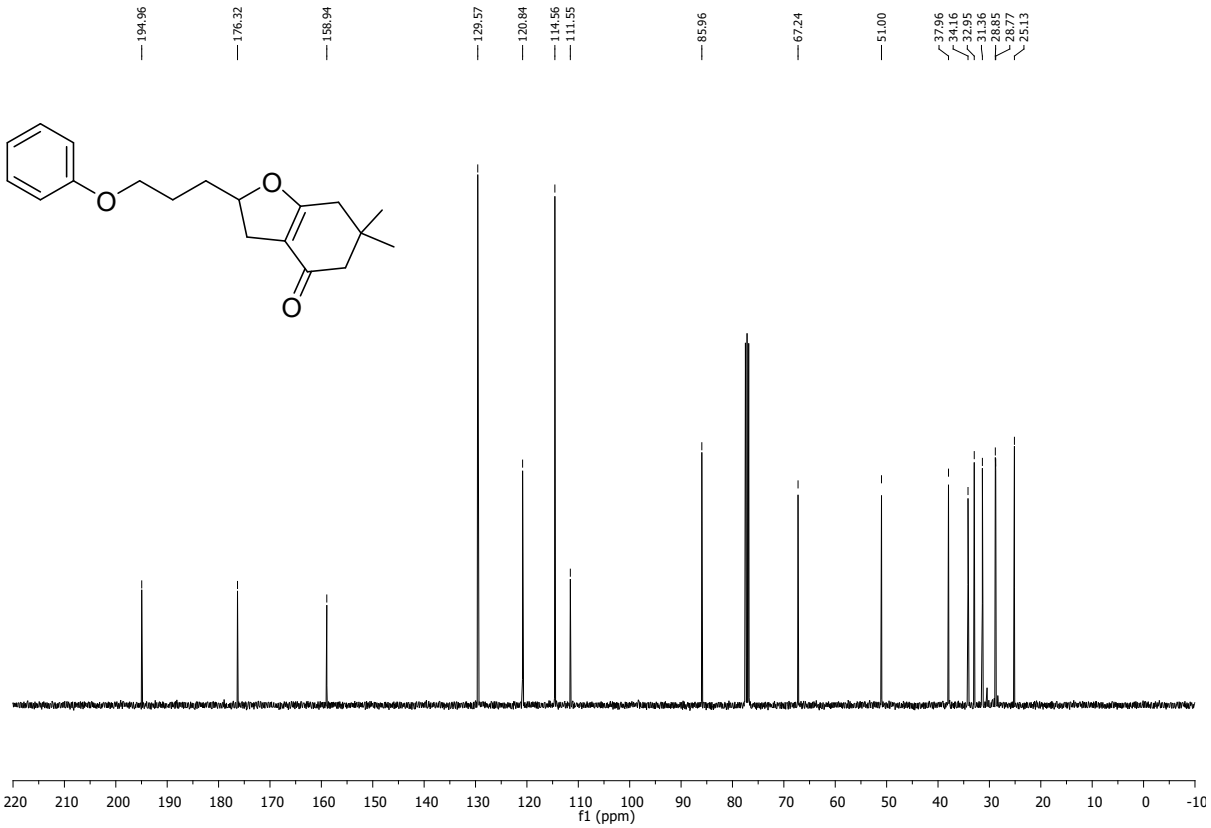



1.00
1.04
0.91
2.05
2.01
1.06
5.18
2.01
3.26
6.29
2.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

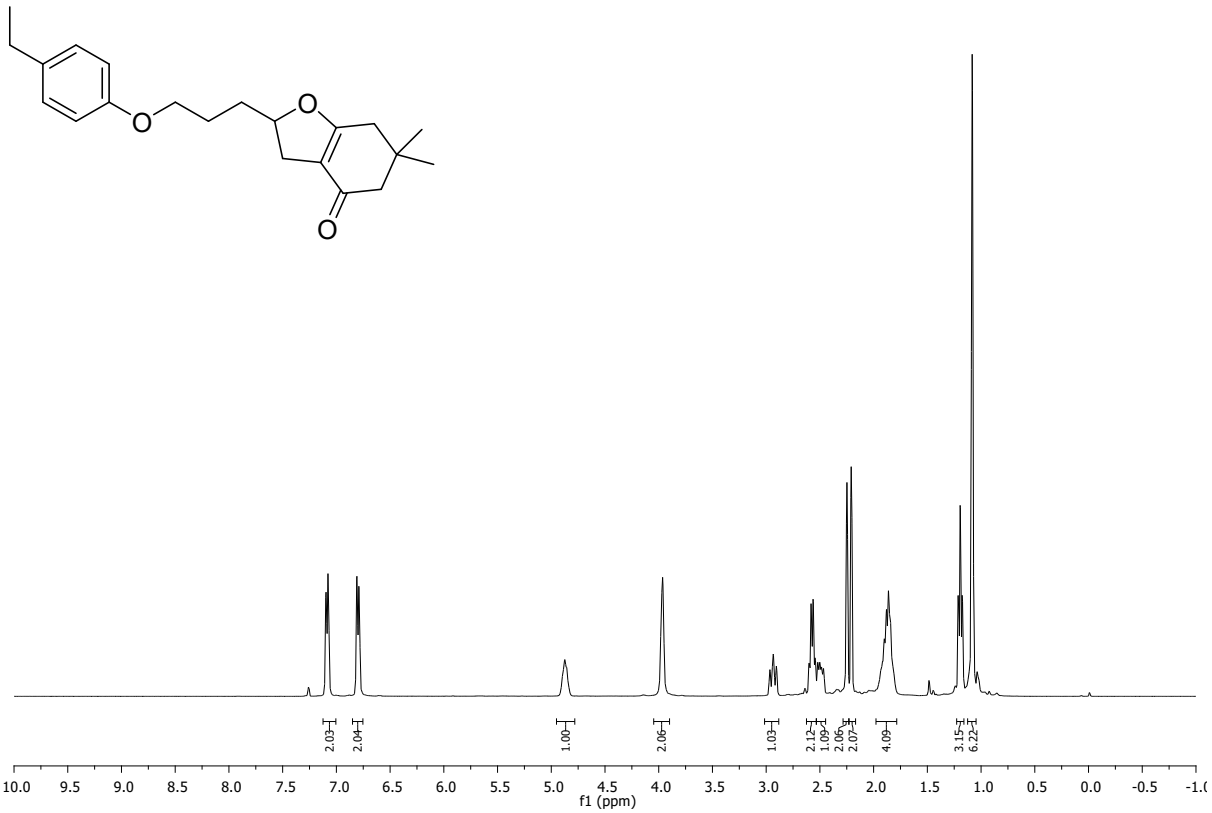

194.98
176.38
111.53
84.64
50.99
44.18
38.05
34.38
34.16
33.74
33.09
31.89
28.86
28.78
26.53
26.30
26.23
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

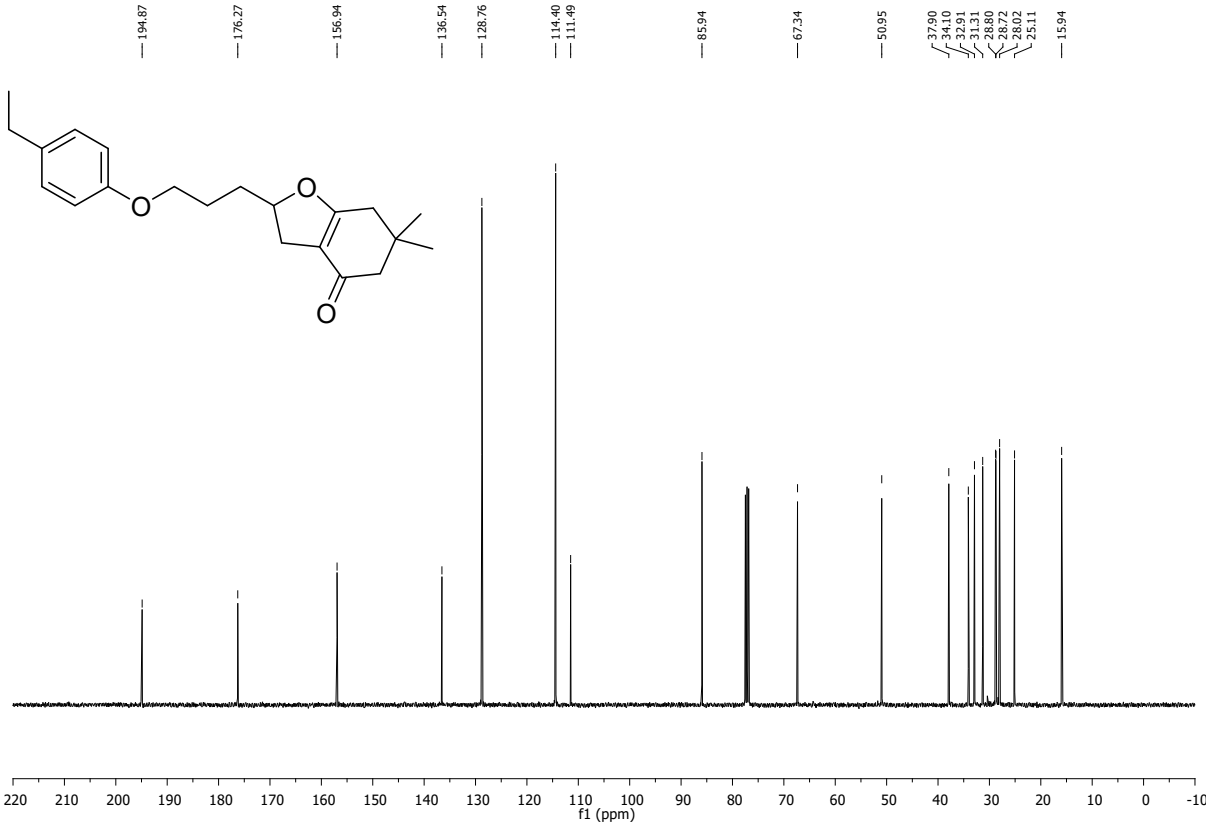
3pa


2.15
0.99
2.01
1.00
2.05
1.03
1.09
1.99
2.08
4.31
6.33
f1 (ppm)

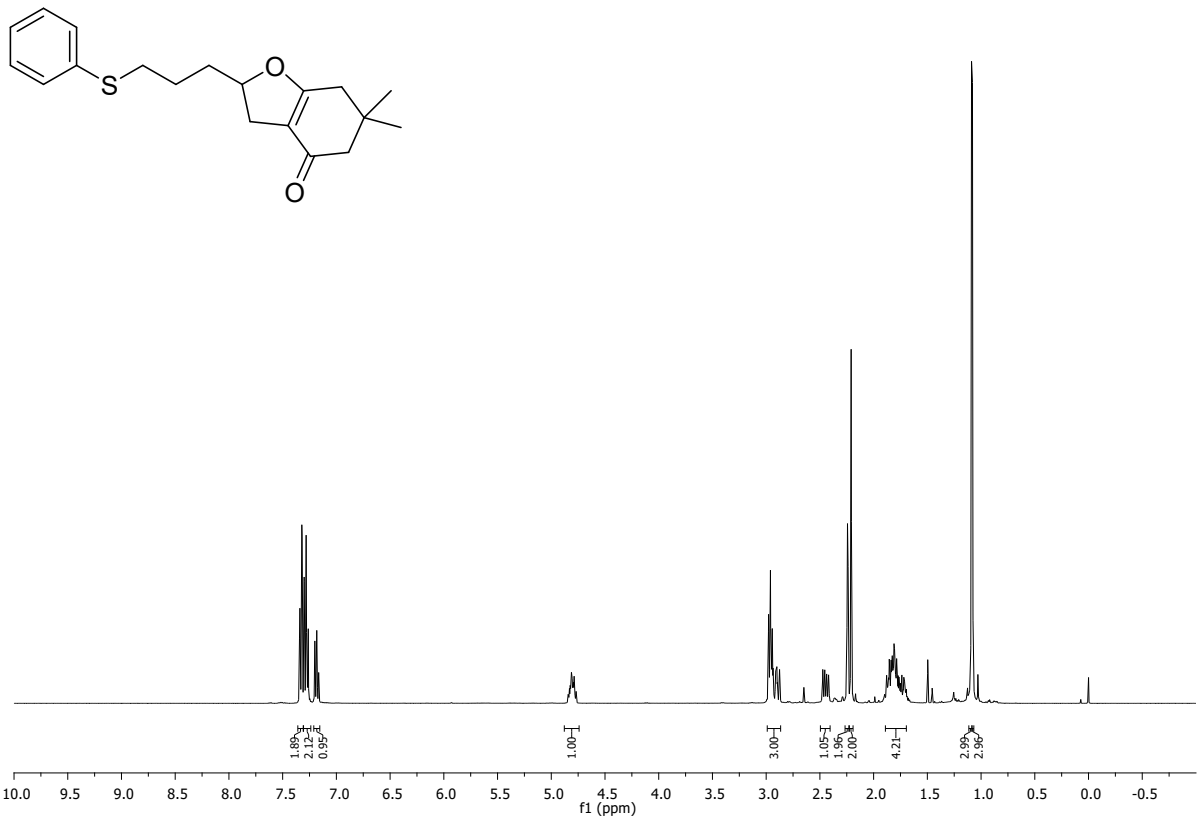

194.96
176.32
158.94
129.57
120.84
114.56
111.55
85.96
67.24
51.00
37.96
34.16
32.95
31.36
28.85
28.77
25.13
f1 (ppm)

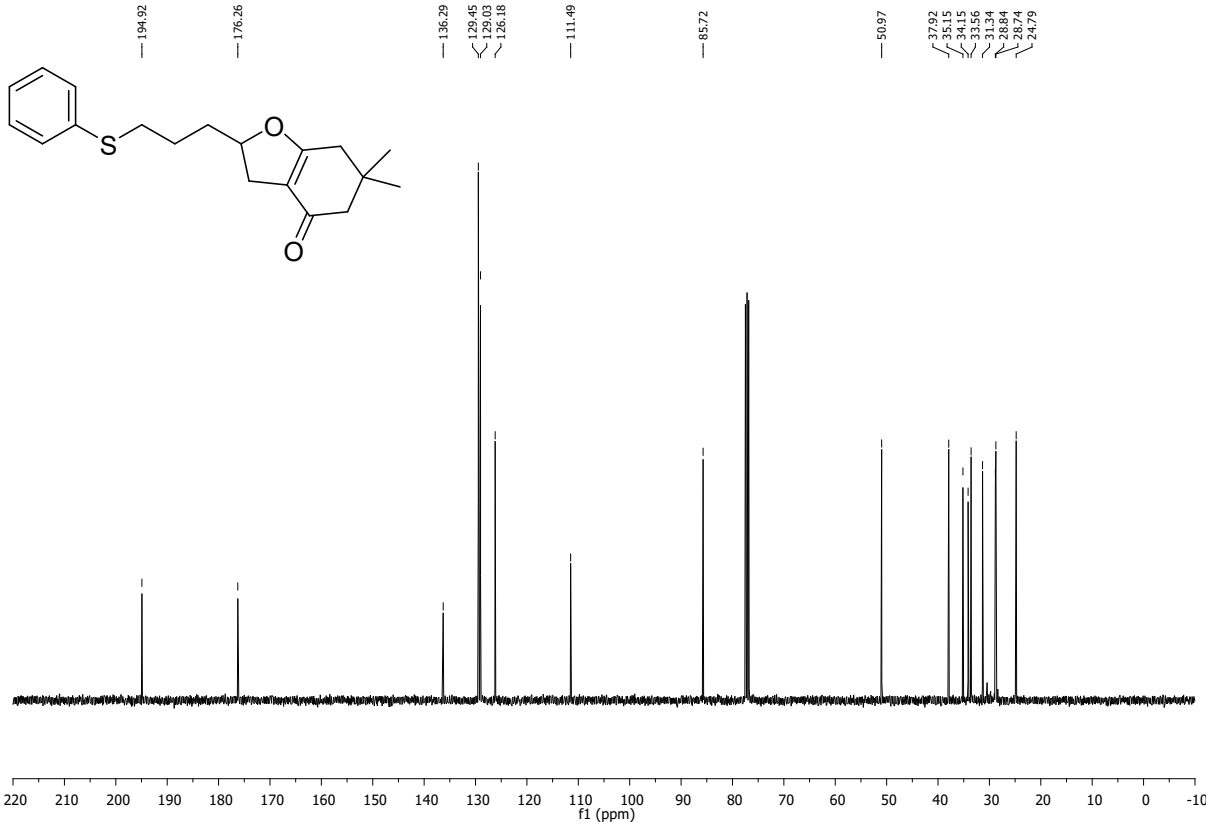
3qa


2.03
2.04
1.00
2.06
1.03
2.12
1.09
2.06
2.07
4.09
3.15
6.22
f1 (ppm)

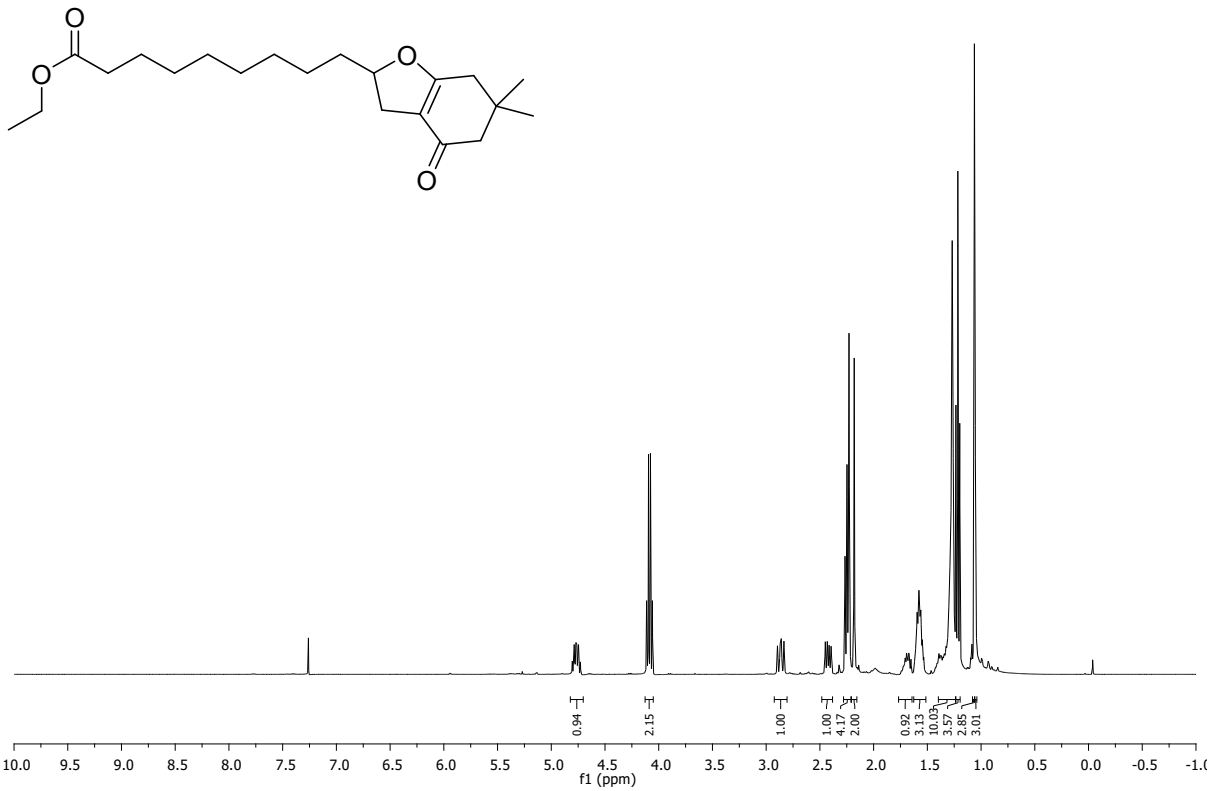

194.87
176.27
156.94
136.54
128.76
114.40
111.49
85.94
67.34
50.95
37.90
34.10
32.91
31.31
28.80
28.72
28.02
25.11
15.94
f1 (ppm)

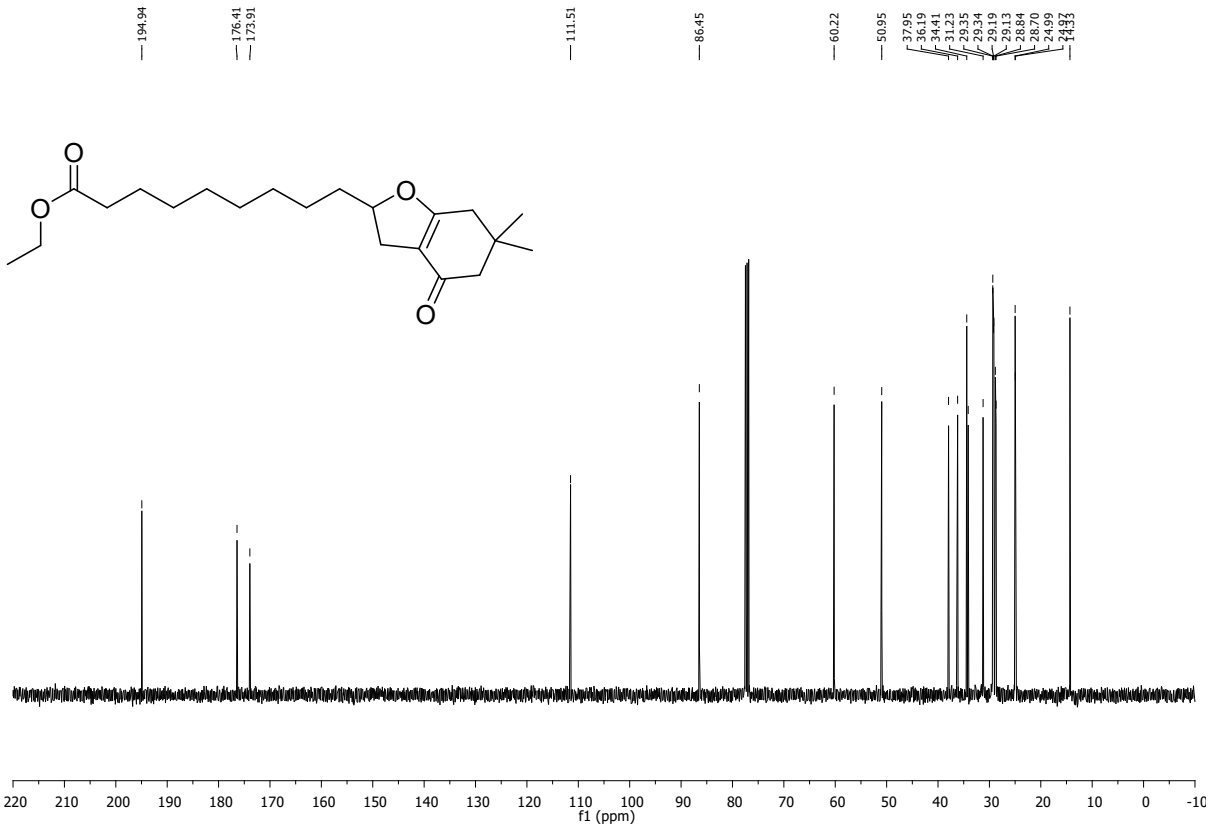
3ra


S
O
O
1.89
2.12
0.95
1.00
3.00
1.05
1.96
2.00
4.21
2.99
2.96
10.0 9.5 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 -0.5
f1 (ppm)

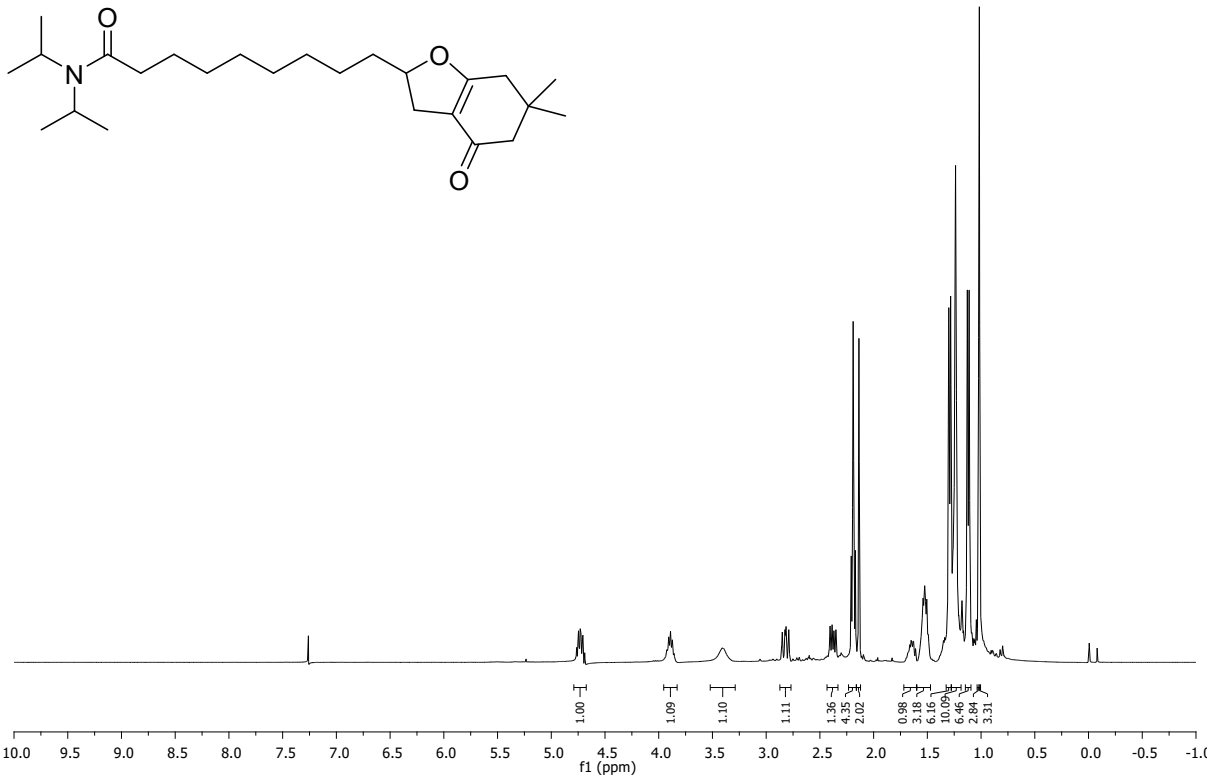

194.92
176.26
136.29
129.45
129.03
126.18
111.49
85.72
50.97
37.92
35.15
34.15
33.56
31.34
28.84
28.74
24.79
S
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

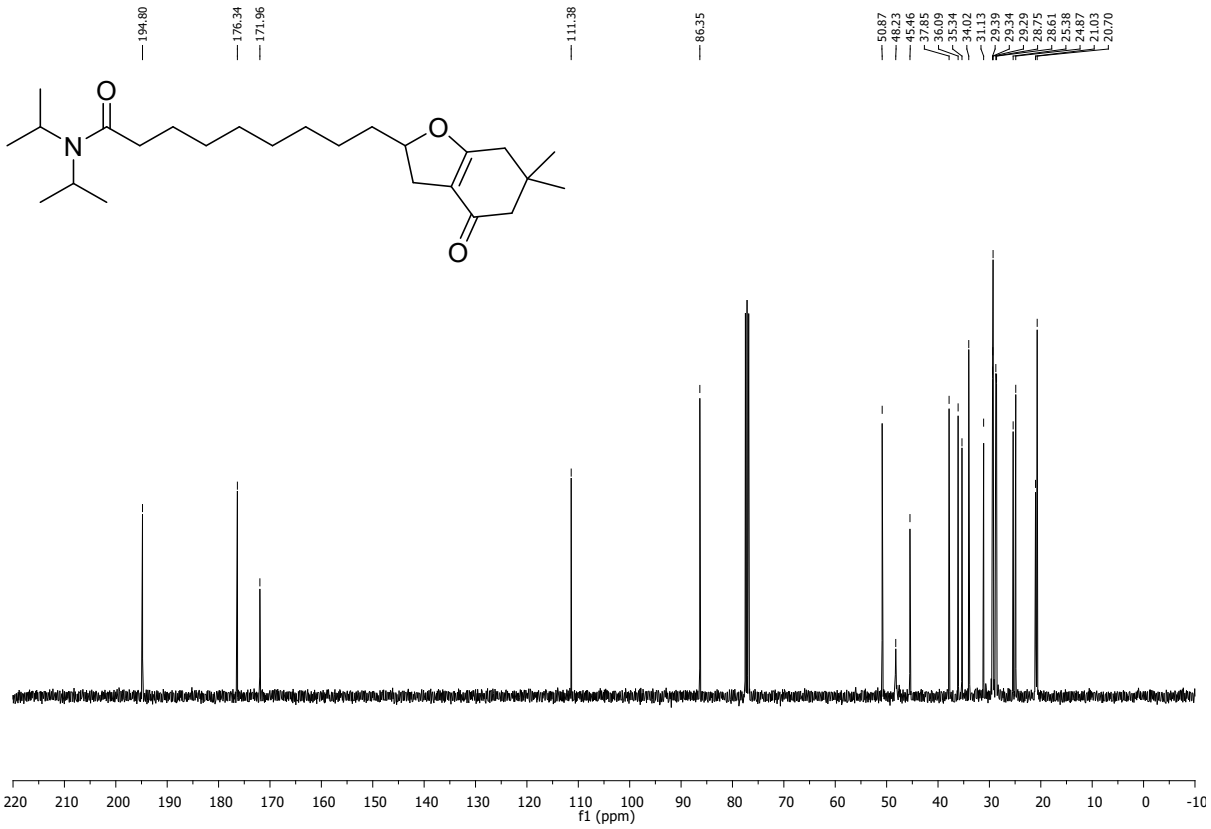
3sa


O
O
O
O
0.94
2.15
1.00
1.00
4.17
2.00
0.92
3.13
10.03
3.57
2.85
3.01
10.0 9.5 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 -0.5
f1 (ppm)

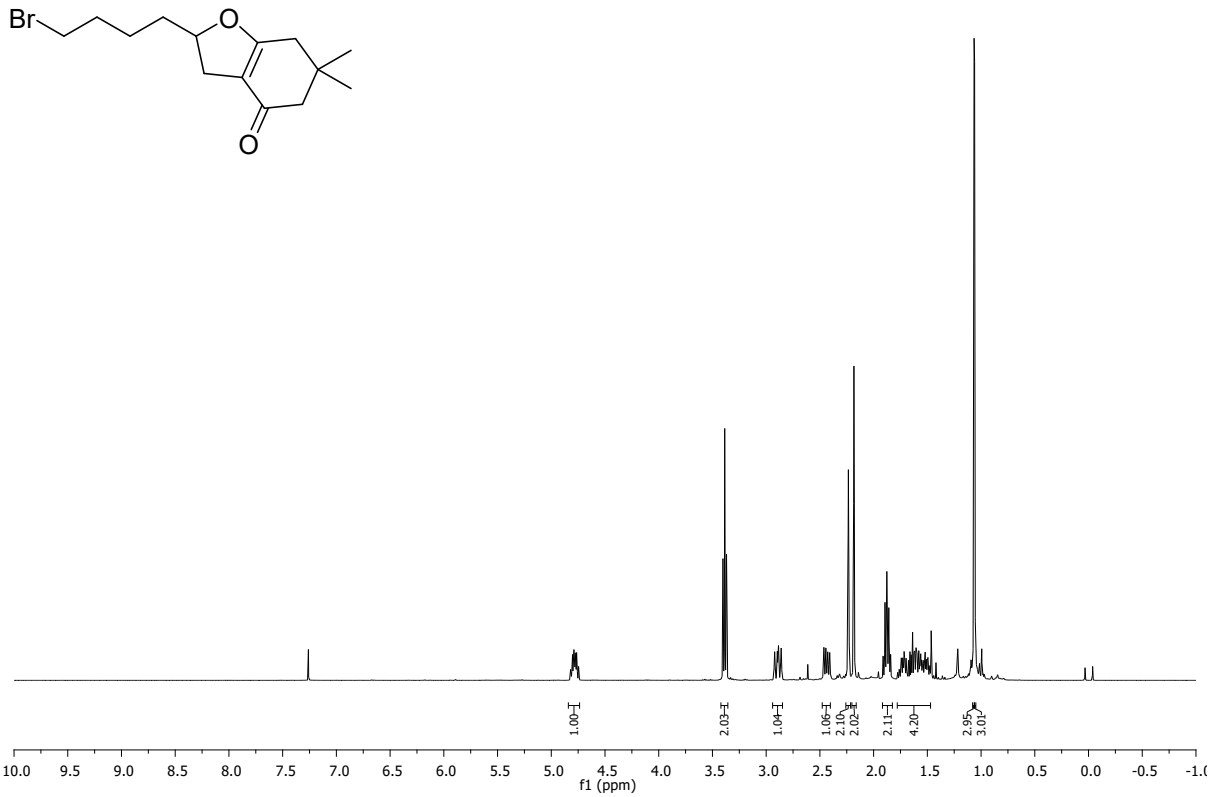

194.94
176.41
173.91
111.51
86.45
60.22
50.95
37.95
36.19
34.41
31.23
29.35
29.34
29.19
29.13
28.84
28.70
24.99
14.33
O
O
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

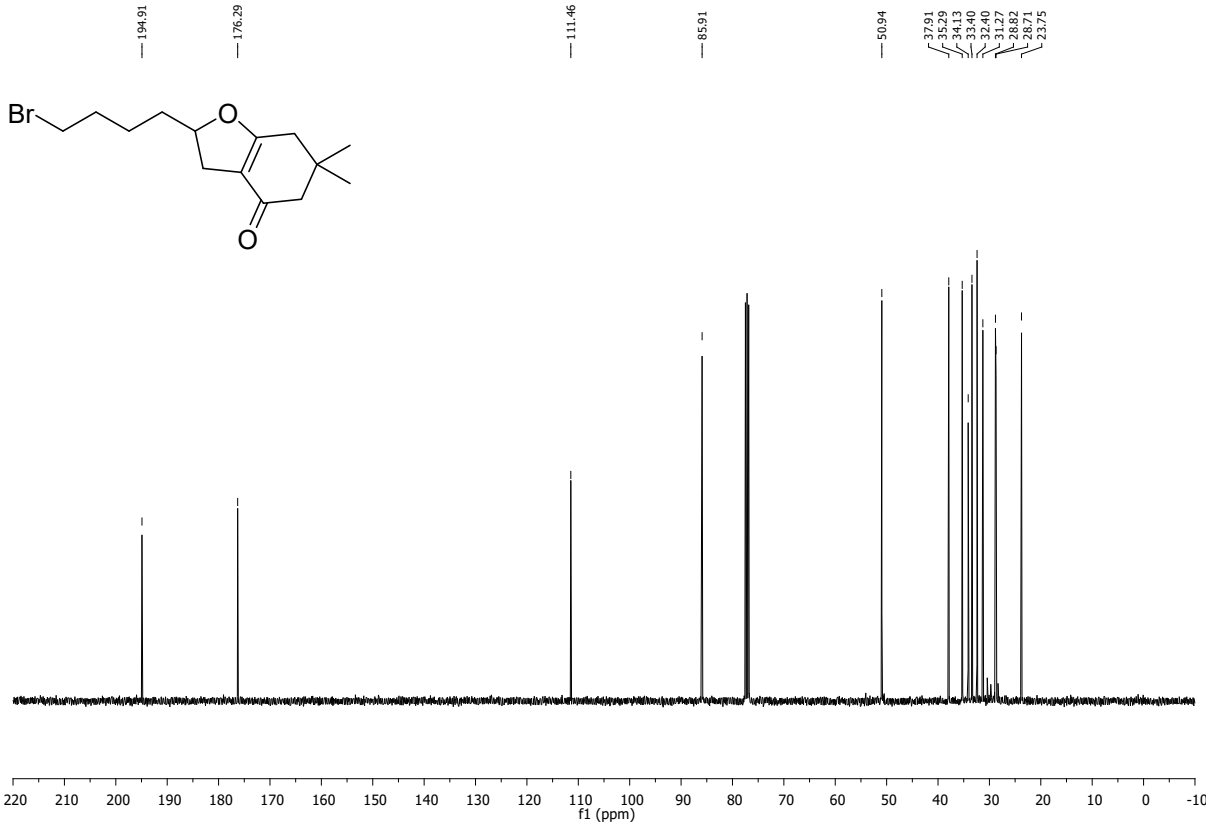
3ta


O
N
O
O
1.00
1.09
1.10
1.11
1.36
4.35
2.02
0.98
3.18
6.16
10.09
6.46
2.84
3.31
10.0 9.5 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 -0.5
f1 (ppm)

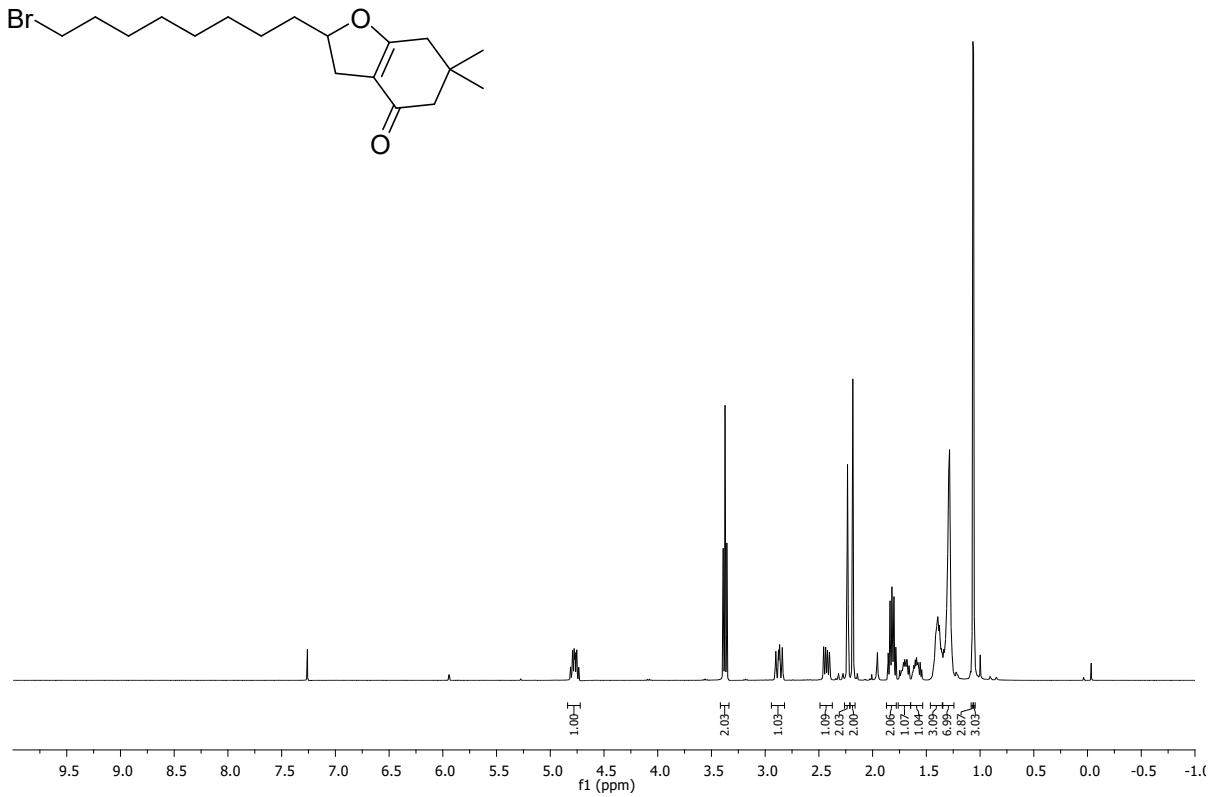

194.80
176.34
171.96
111.38
86.35
50.87
48.23
45.46
37.85
36.09
35.34
34.02
31.13
29.39
29.34
29.29
28.75
28.61
25.38
24.87
21.03
20.70
O
N
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

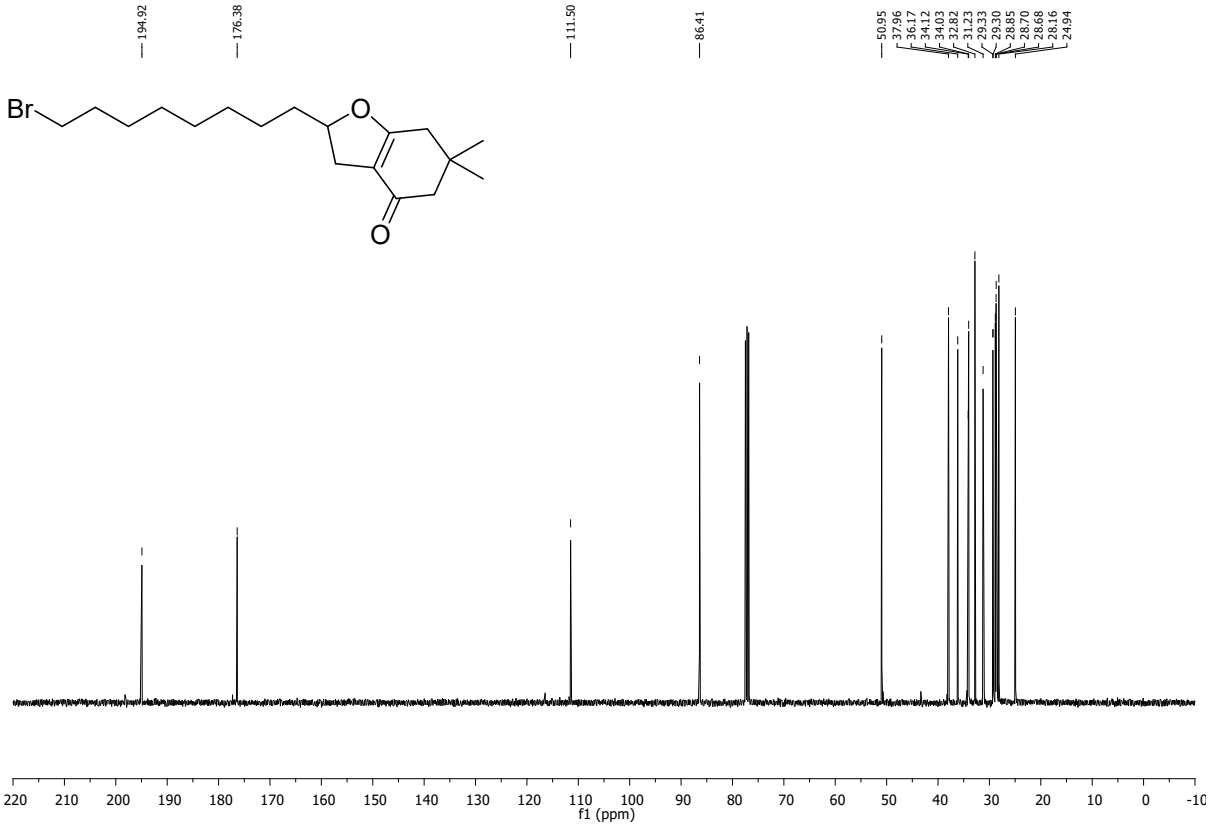
3ua


Br
O
O
1.00
2.03
1.04
1.06
2.10
2.02
2.11
4.20
2.95
3.01
10.0 9.5 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 -0.5
f1 (ppm)

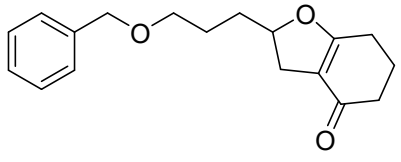

194.91
176.29
111.46
85.91
50.94
37.91
35.29
34.13
33.40
32.40
31.27
28.82
28.71
23.75
Br
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

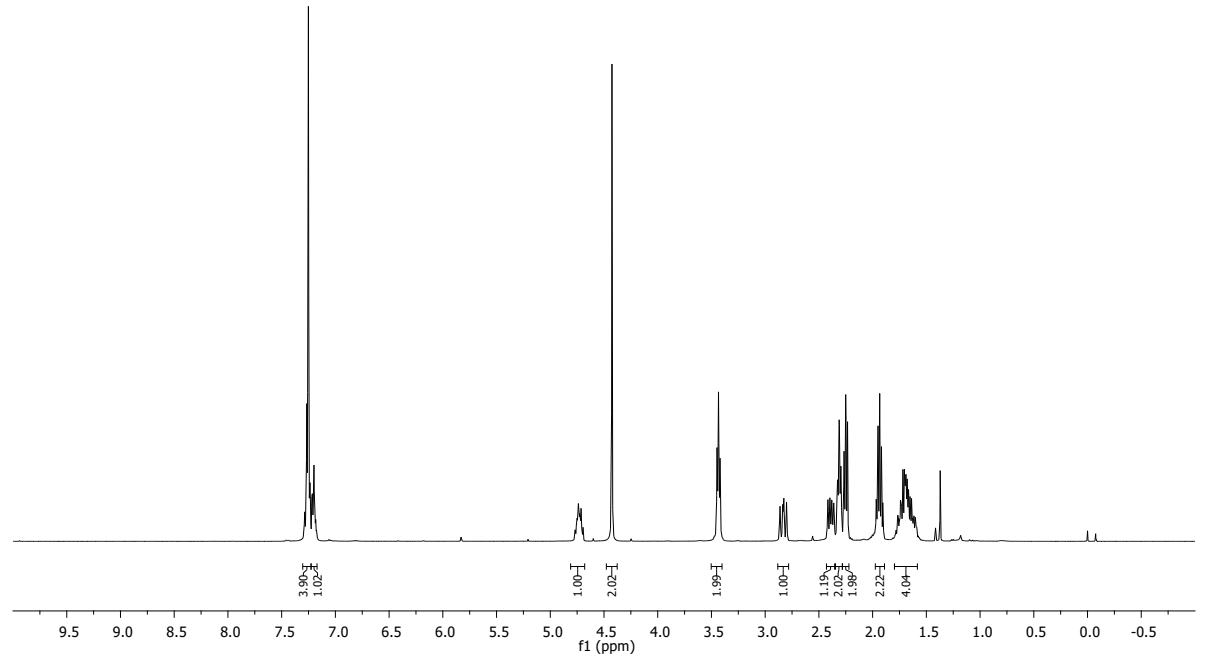
3va

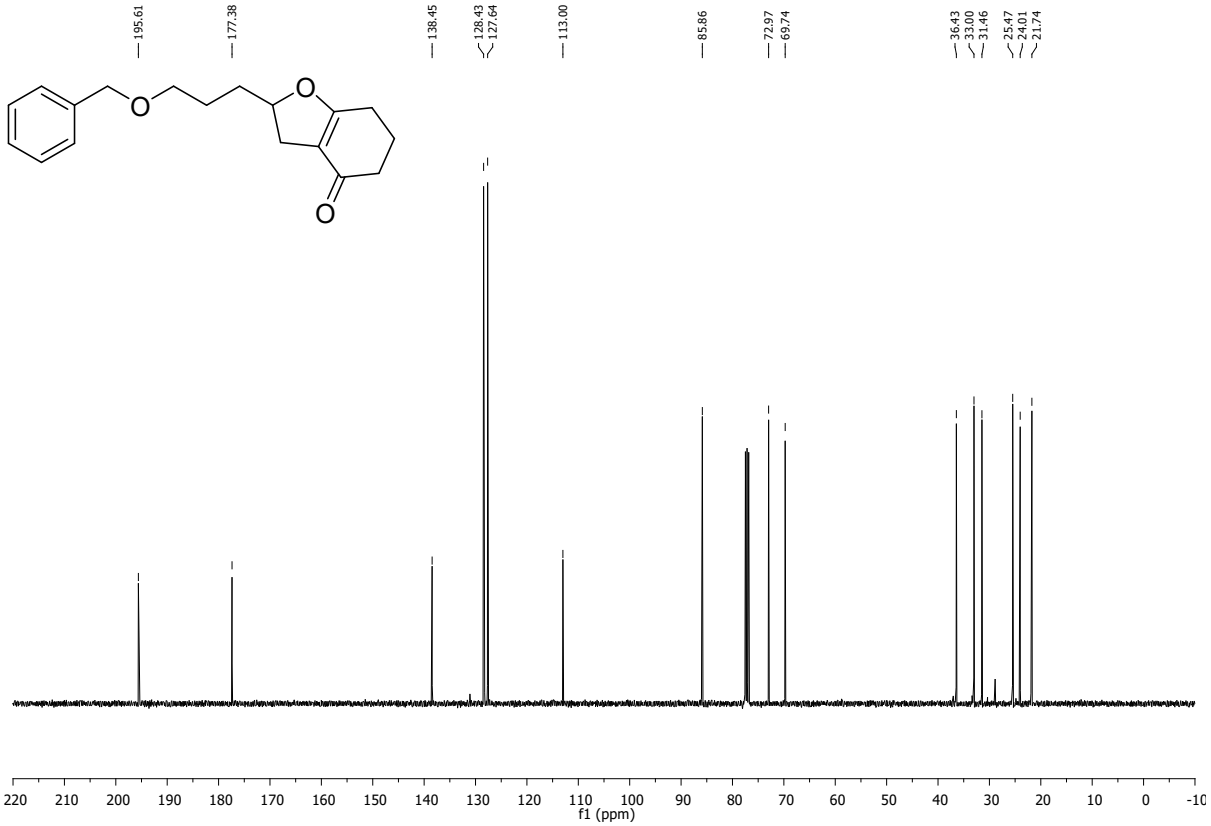

Br
O
O
1.00
2.03
1.03
1.09
2.03
2.00
2.06
1.07
1.04
3.09
6.99
2.87
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


194.92
176.38
111.50
86.41
50.95
37.96
36.17
34.12
34.03
32.82
31.23
29.33
29.30
28.85
28.70
28.68
28.16
24.94
Br
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

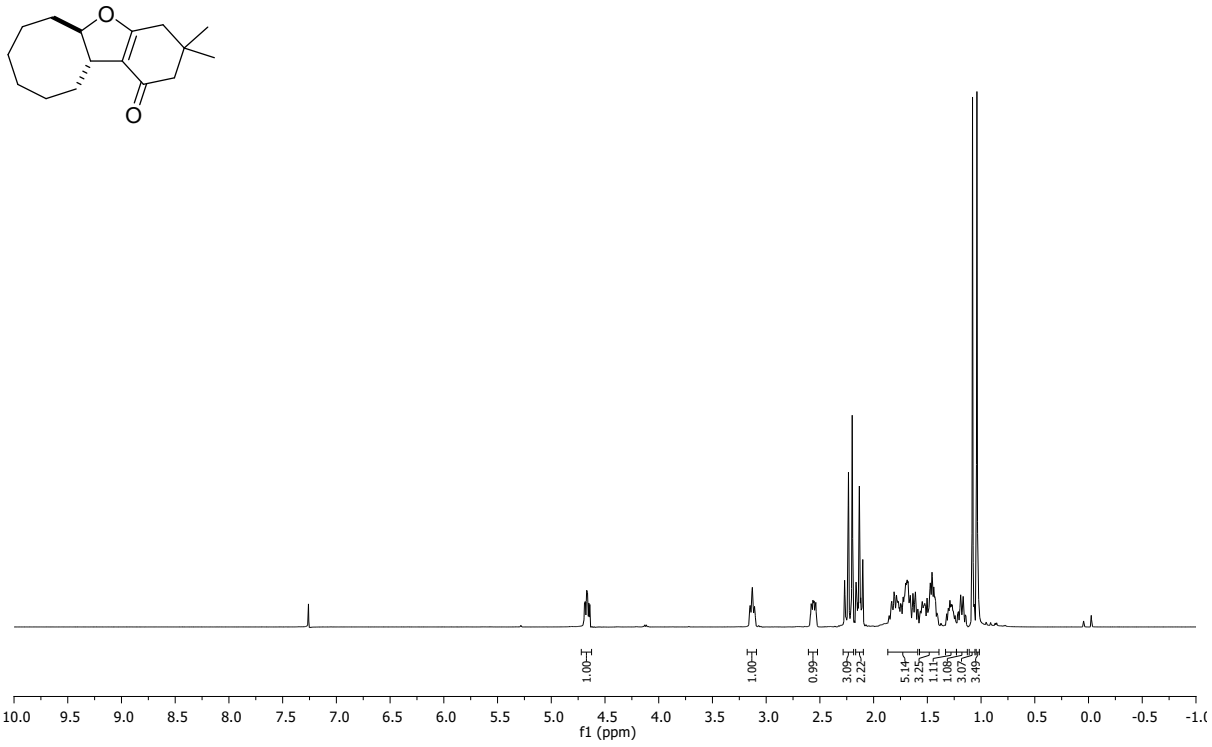
3cb

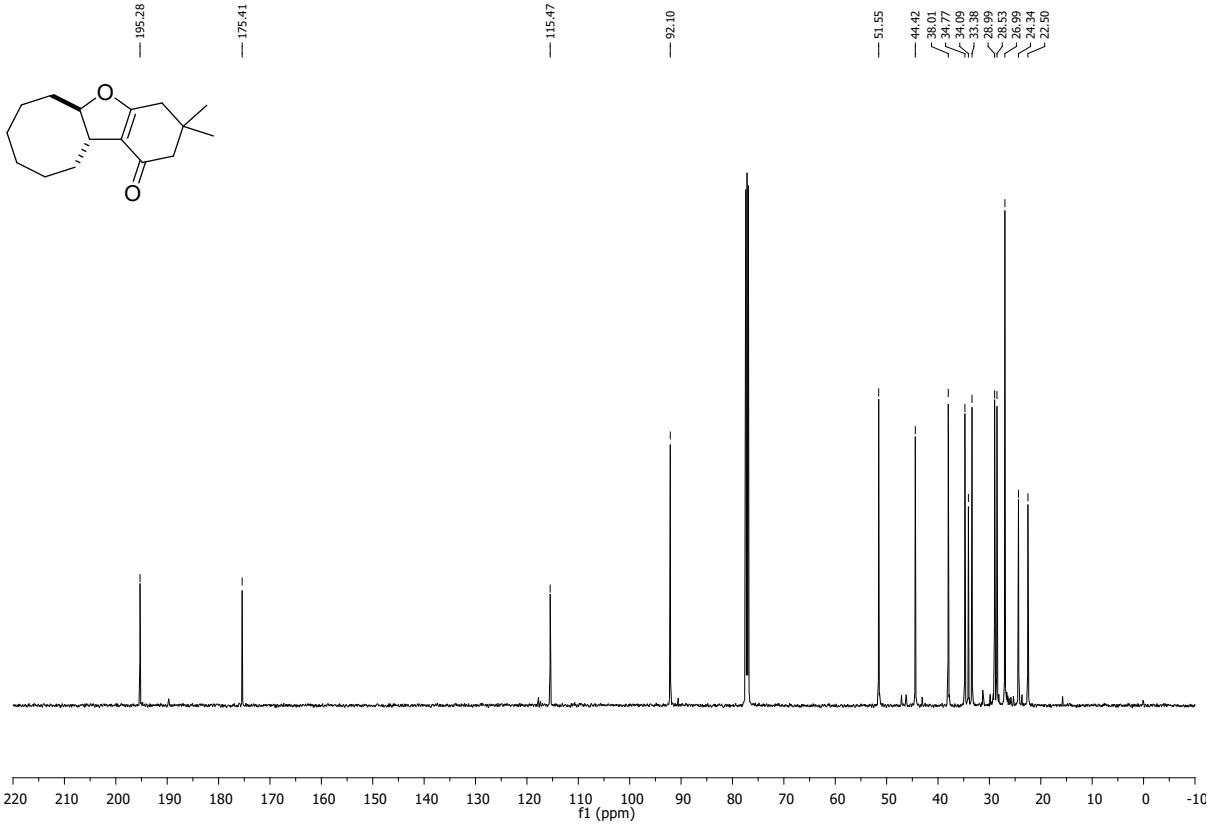

O
O
O


3.90
1.02
1.00
2.02
1.99
1.00
1.19
2.02
1.98
2.22
4.04
f1 (ppm)

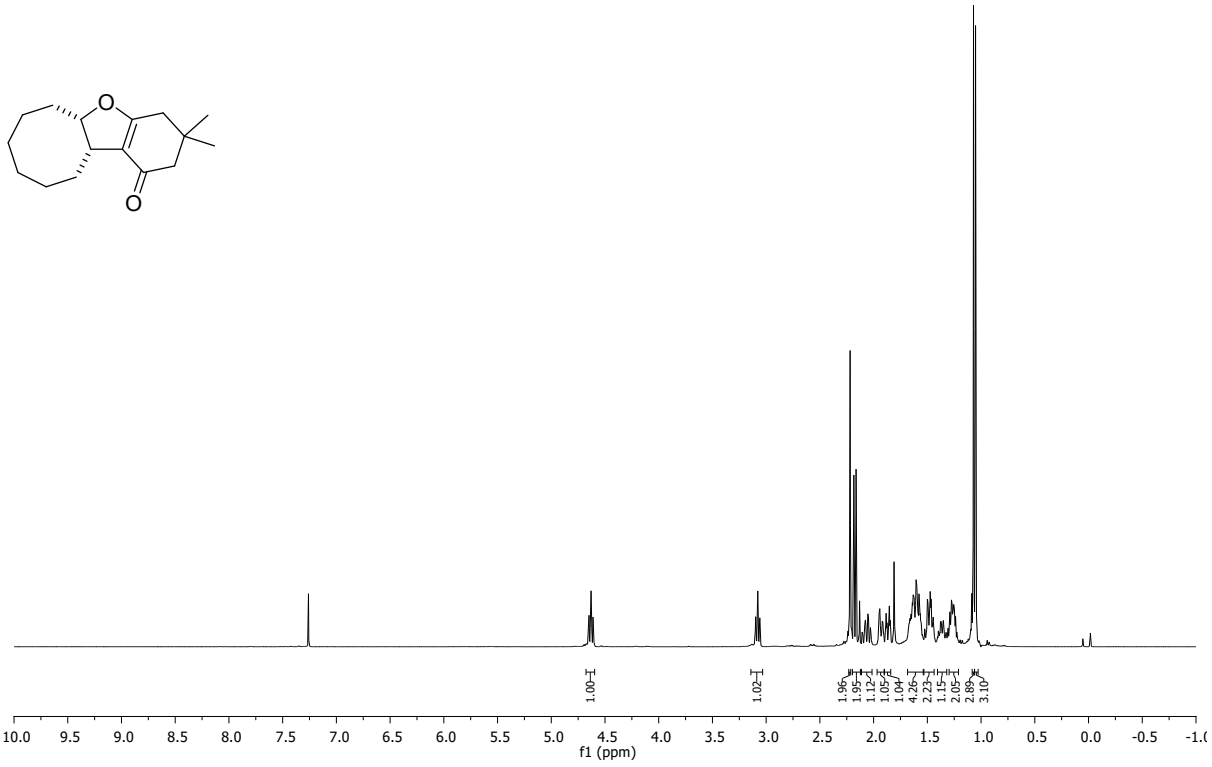

195.61
177.38
138.45
128.43
127.64
113.00
85.86
72.97
69.74
36.43
33.00
31.46
25.47
24.01
21.74
O
O
O
f1 (ppm)

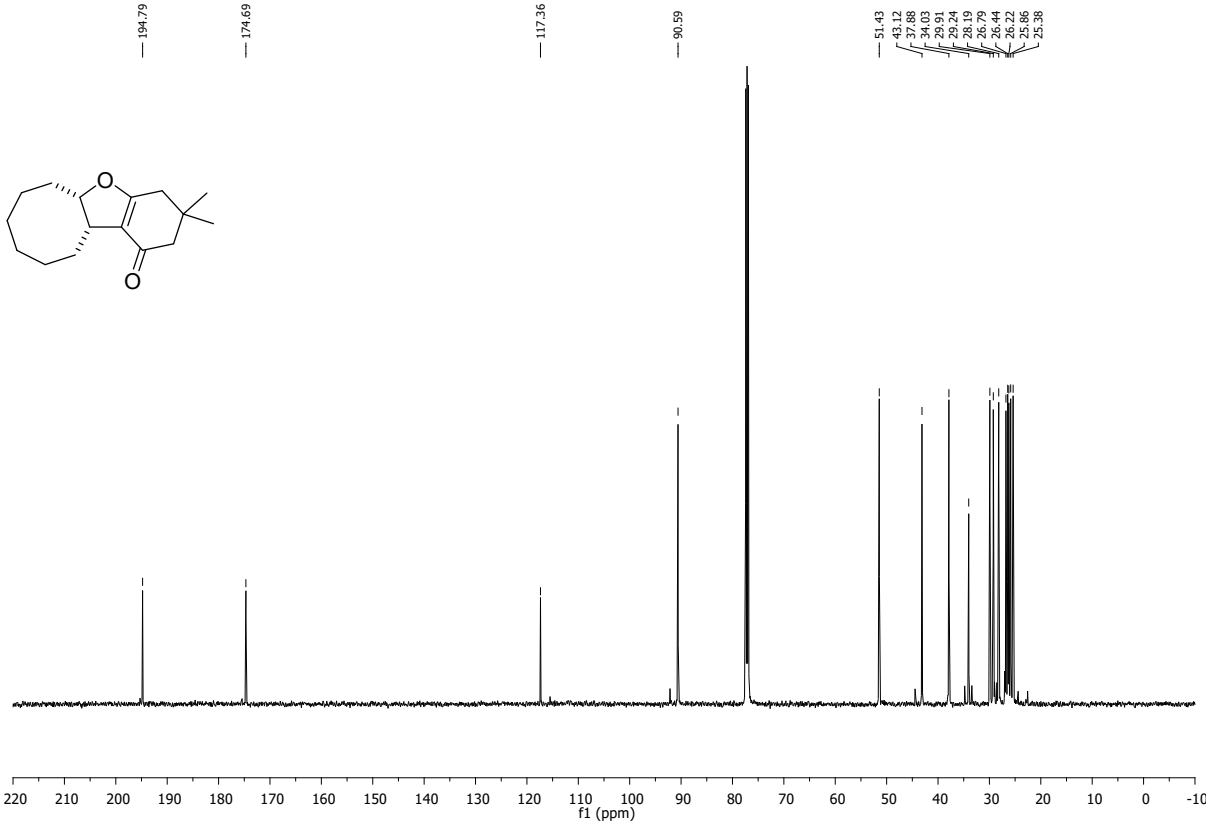
4wa-anti


O
O
1.00
1.00
0.99
3.09
2.22
5.14
3.25
1.11
1.08
3.07
3.49
10.0 9.5 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 -0.5
f1 (ppm)

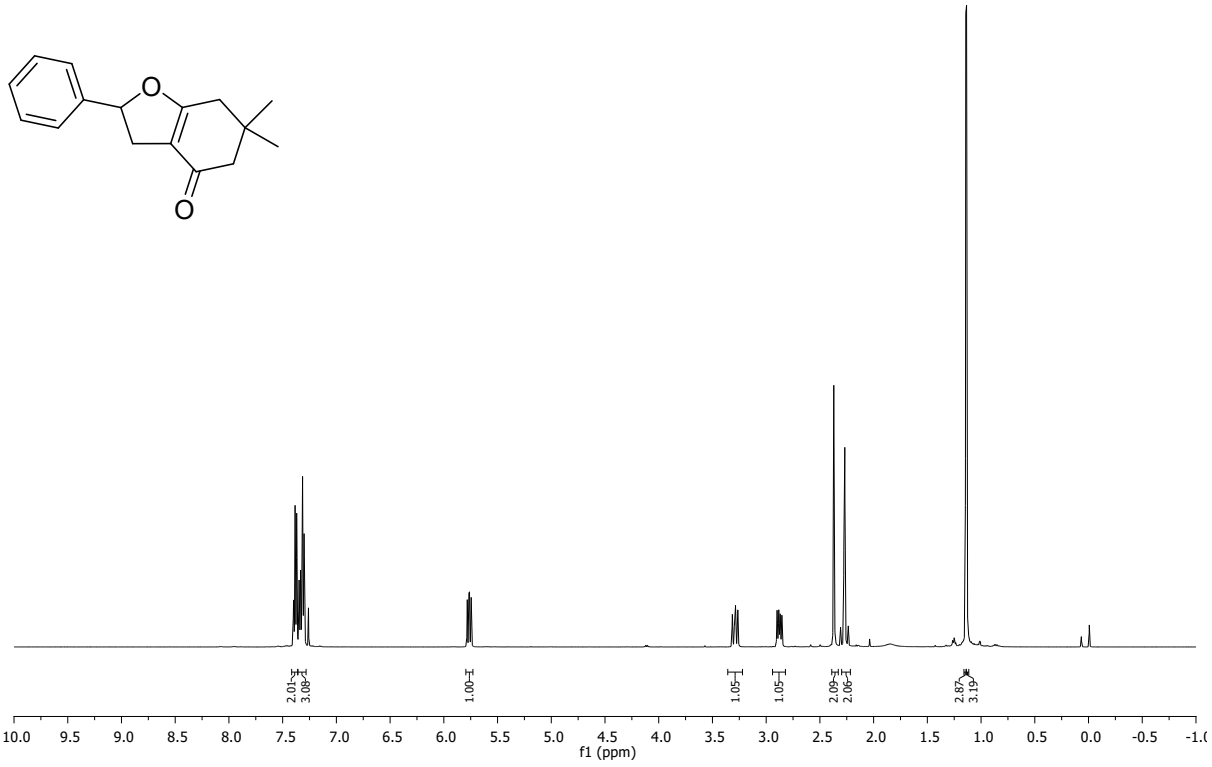

195.28
175.41
115.47
92.10
51.55
44.42
38.01
34.77
34.09
33.38
28.99
28.53
26.99
24.34
22.50
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

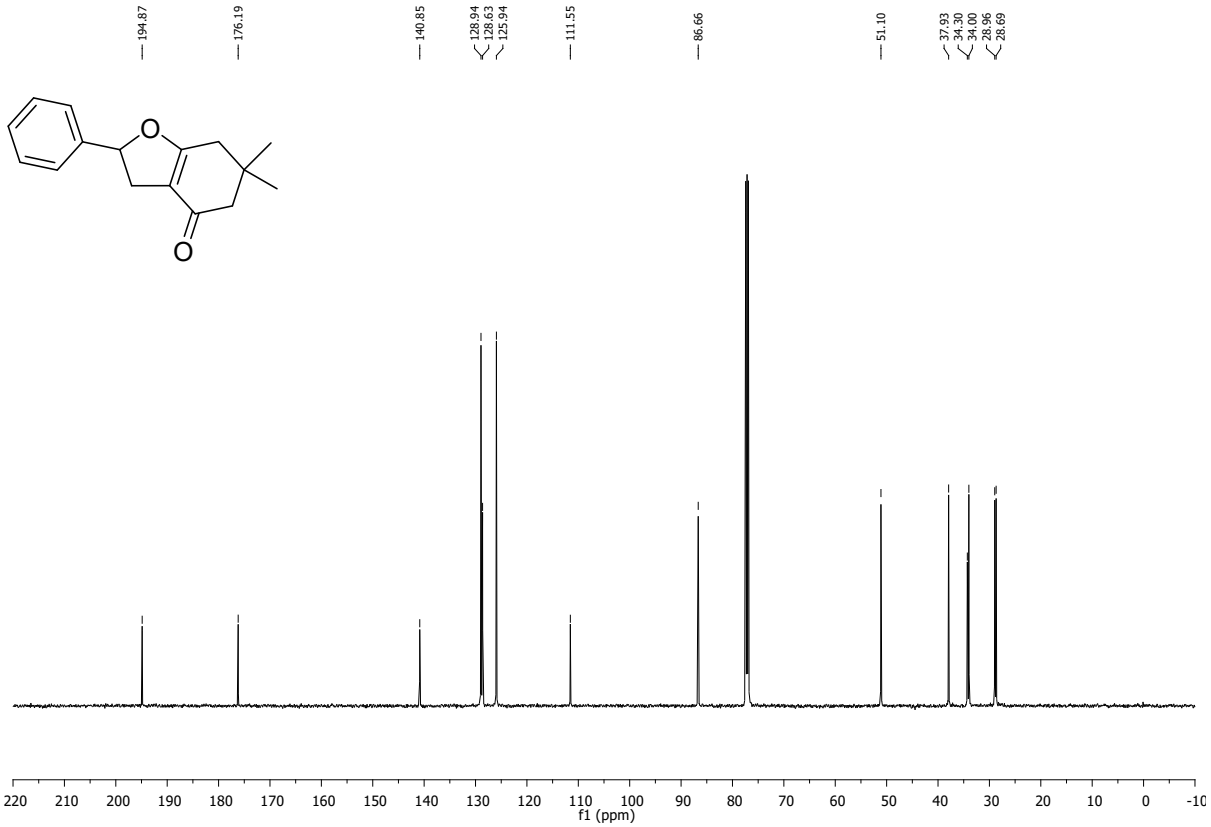
4wa-syn


O
O
1.00
1.02
1.96
1.95
1.12
1.05
1.04
4.26
2.23
1.15
2.05
2.89
3.10
10.0 9.5 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 -0.5
f1 (ppm)

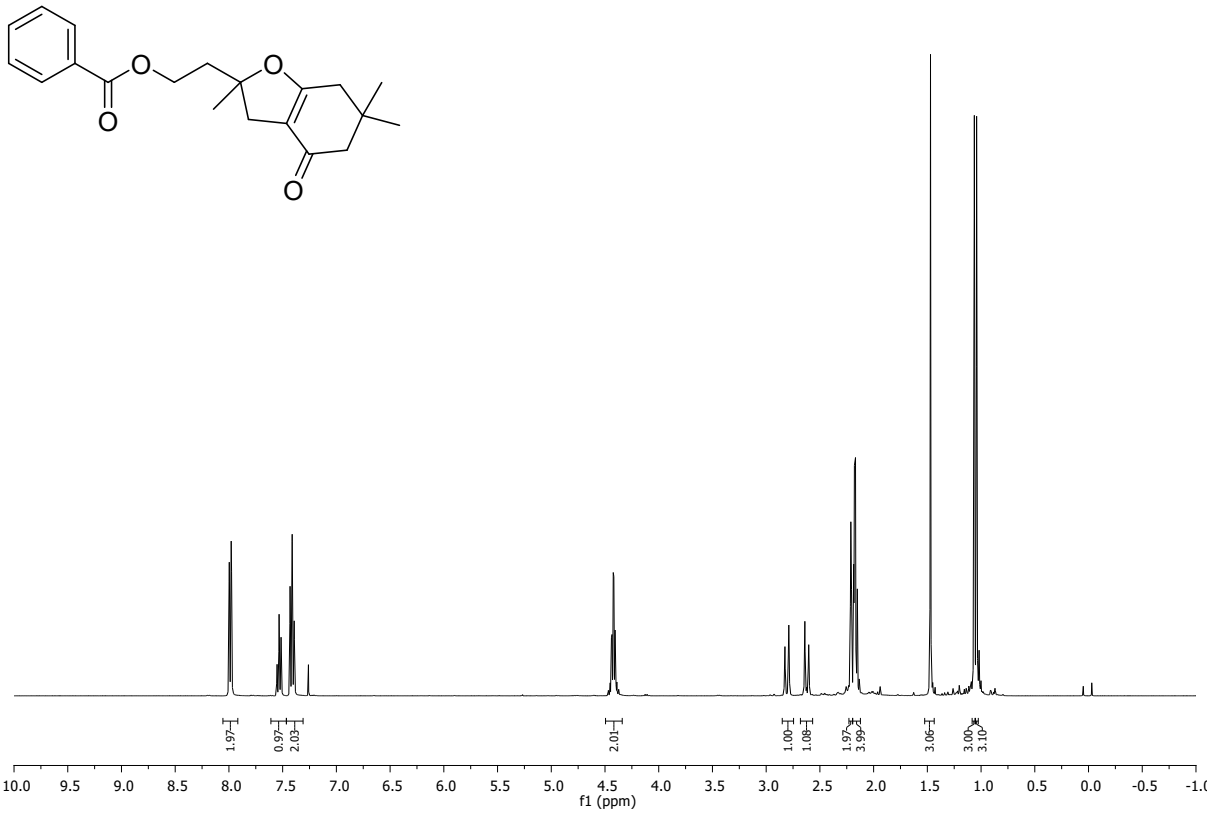

194.79
174.69
117.36
90.59
51.43
43.12
37.88
34.03
29.91
29.24
28.19
26.79
26.44
26.22
25.86
25.38
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

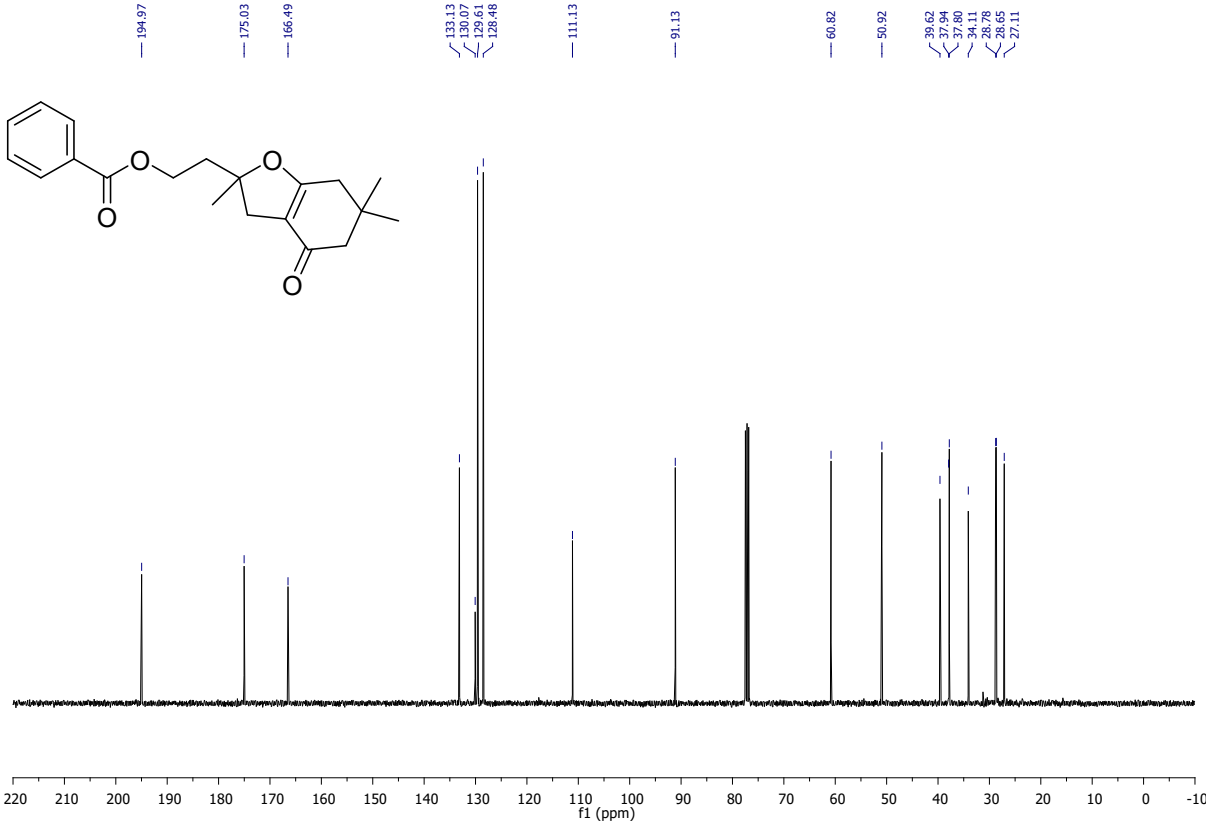
3xa


O
O
2.01
3.08
1.00
1.05
1.05
2.09
2.06
2.87
3.19
10.0 9.5 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 -0.5
f1 (ppm)

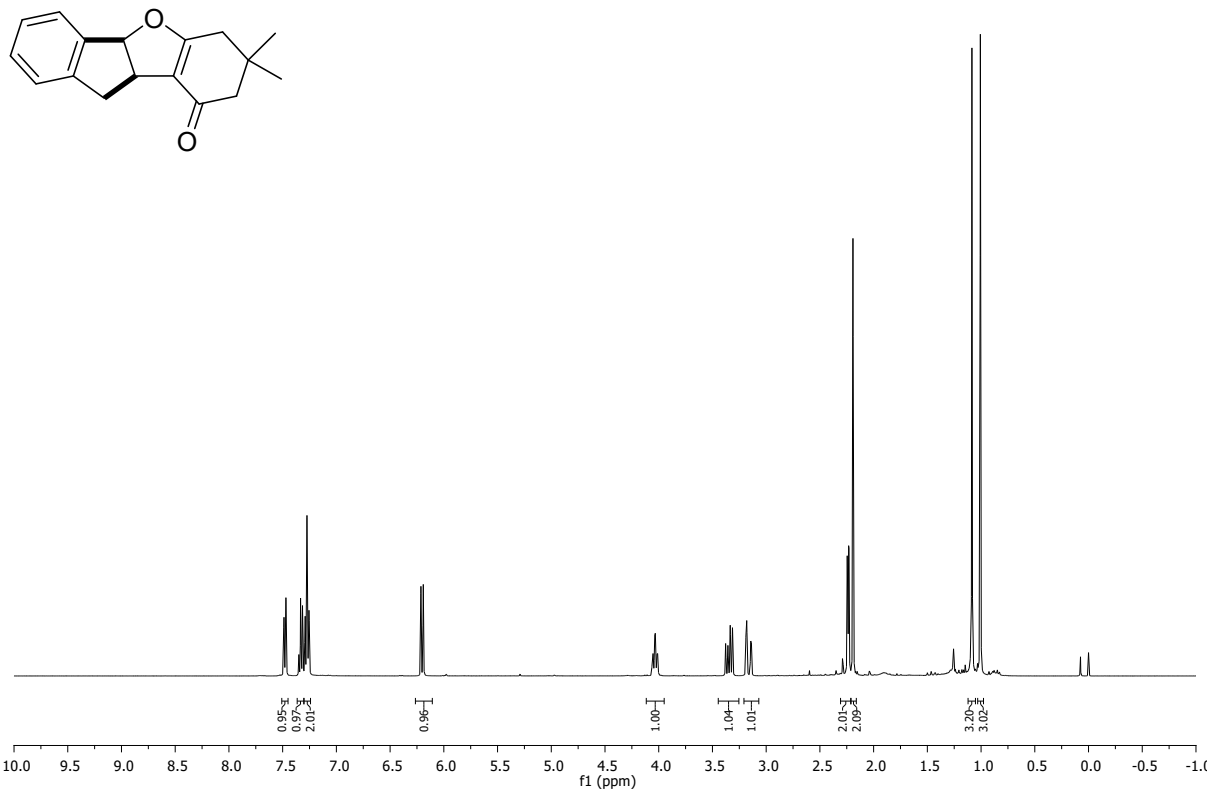

194.87
176.19
140.85
128.94
128.63
125.94
111.55
86.66
51.10
37.93
34.30
34.00
28.96
28.69
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

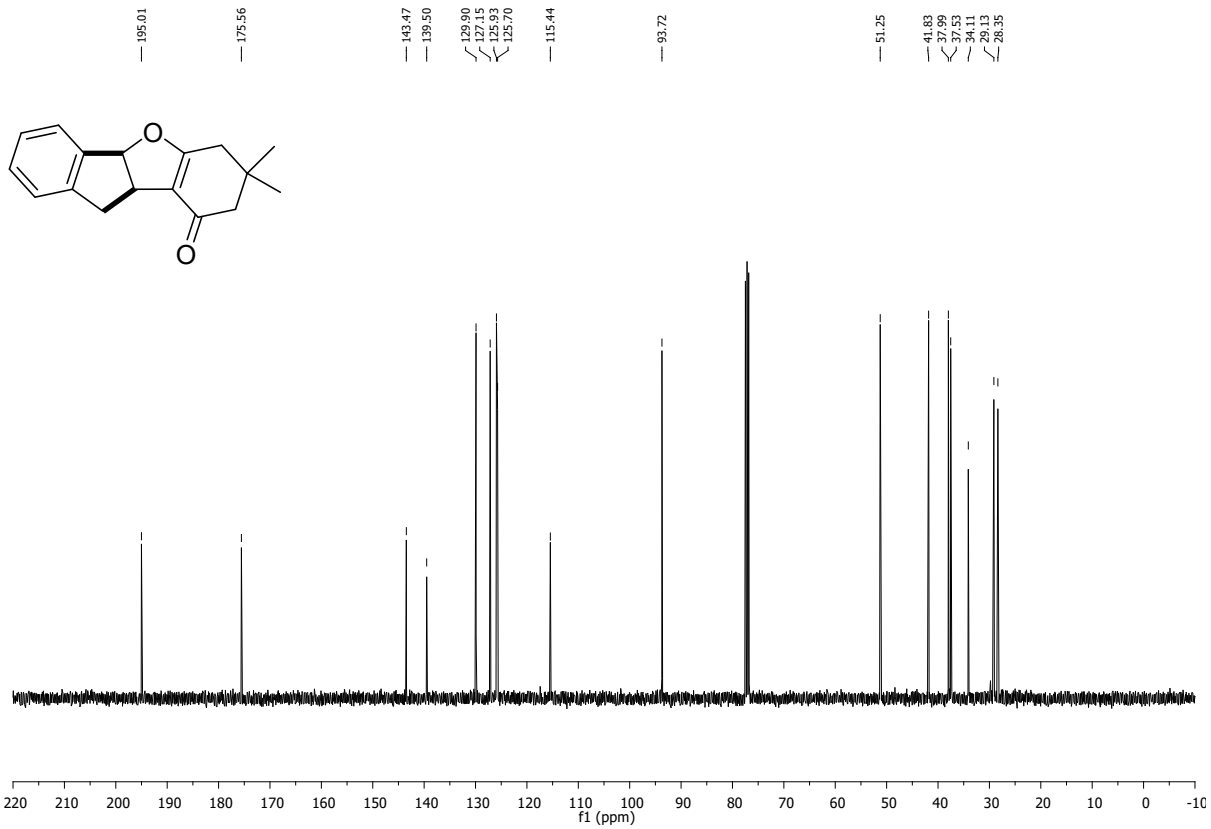
5a′a


1.97
0.97
2.03
2.01
1.00
1.08
1.97
3.99
3.06
3.00
3.10
f1 (ppm)

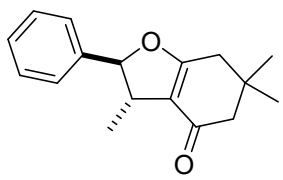

194.97
175.03
166.49
133.13
130.07
129.61
128.48
111.13
91.13
60.82
50.92
39.62
37.94
37.80
34.11
28.78
28.65
27.11
f1 (ppm)

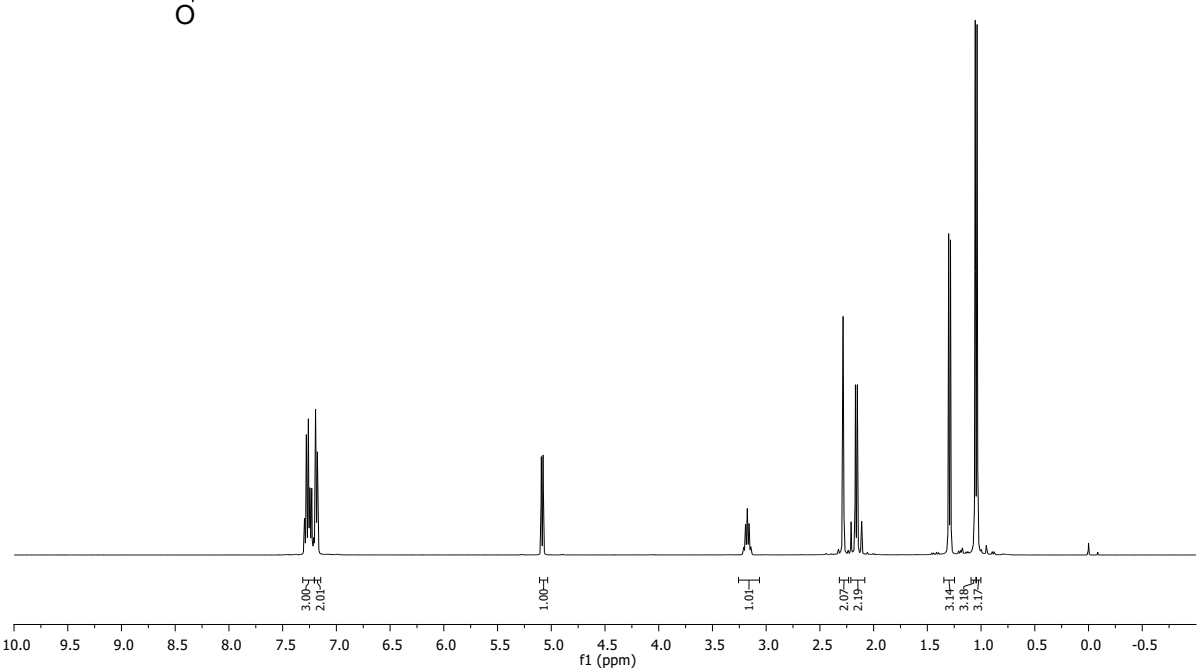
4ya


O
O
0.95
0.97
2.01
0.96
1.00
1.04
1.01
2.01
2.09
3.20
3.02
10.0 9.5 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 -0.5
f1 (ppm)

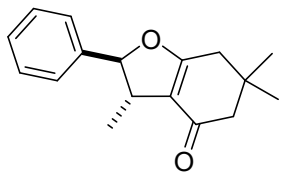

195.01
175.56
143.47
139.50
129.90
127.15
125.93
125.70
115.44
93.72
51.25
41.83
37.99
37.53
34.11
29.13
28.35
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4za


O
O

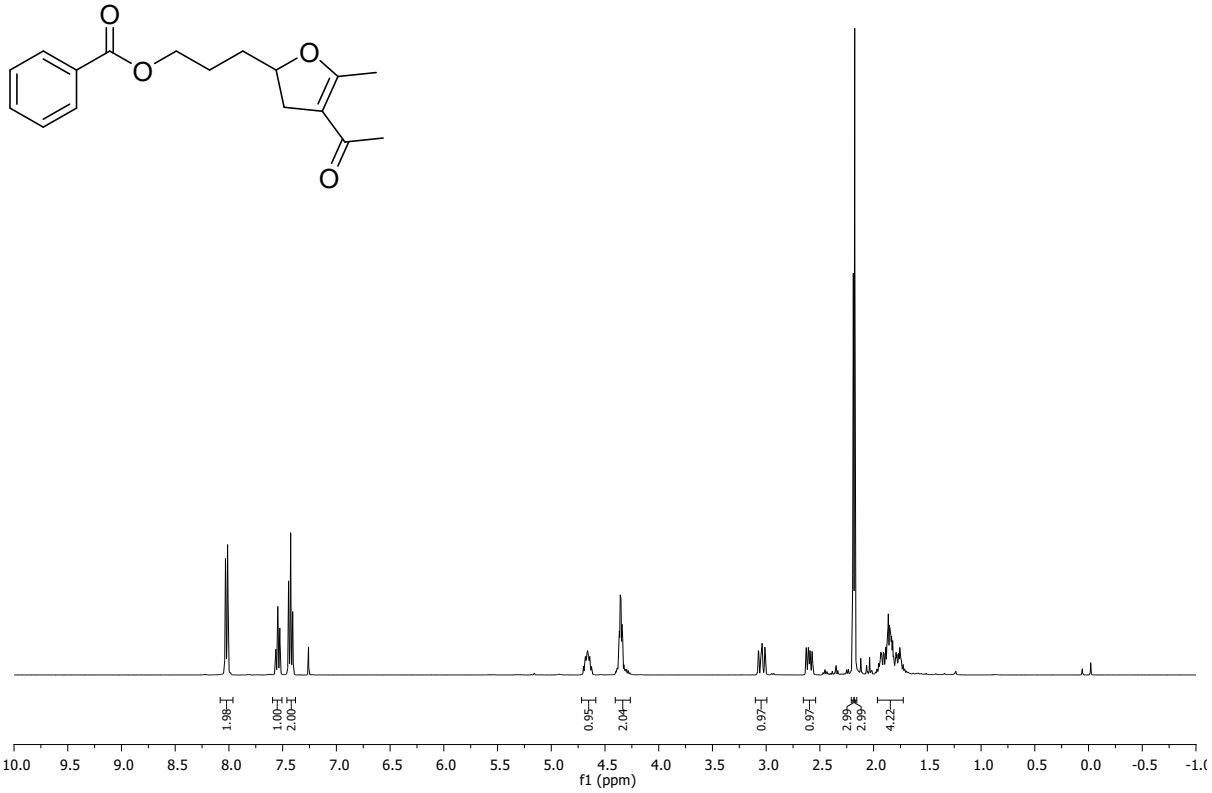

3.00
2.01
1.00
1.01
2.07
2.19
3.14
3.18
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

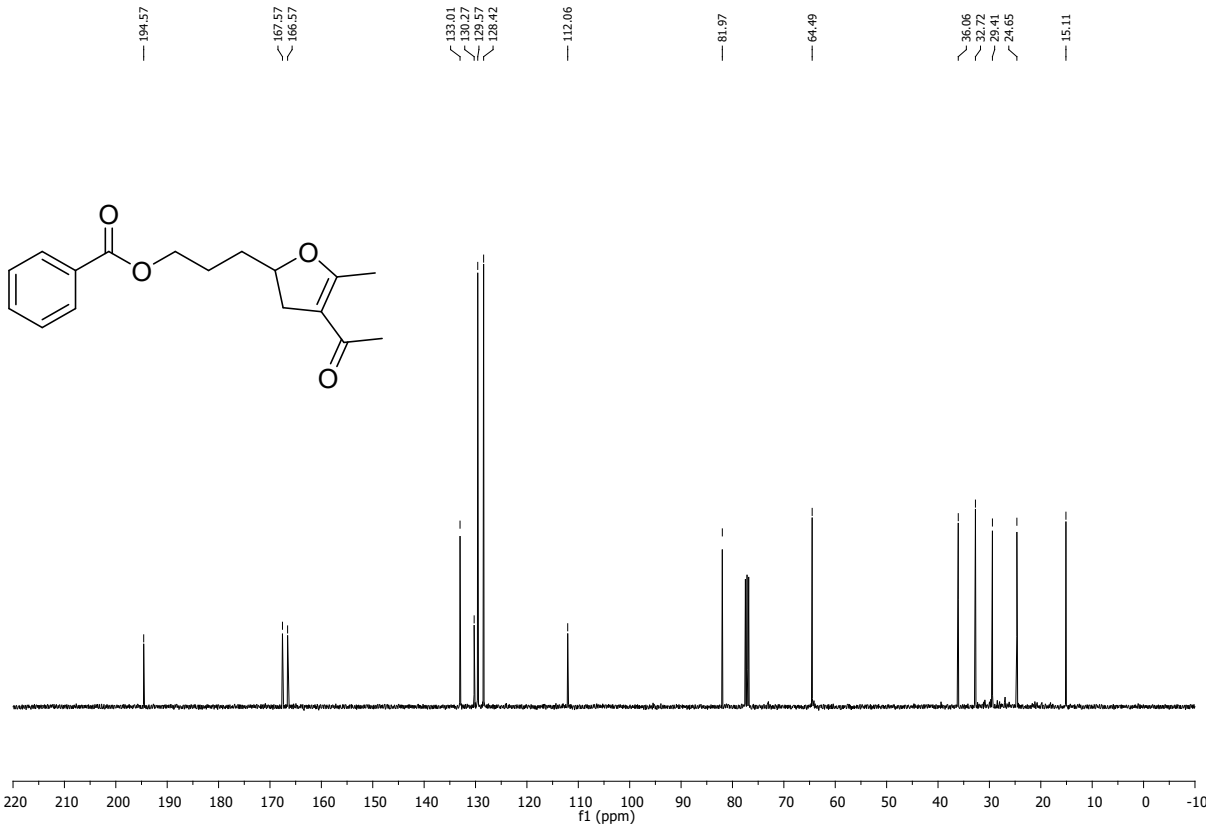

194.79
175.39
140.37
128.78
128.47
125.56
115.81
93.99
51.42
42.94
37.89
34.21
28.67
28.62
19.42


O
O

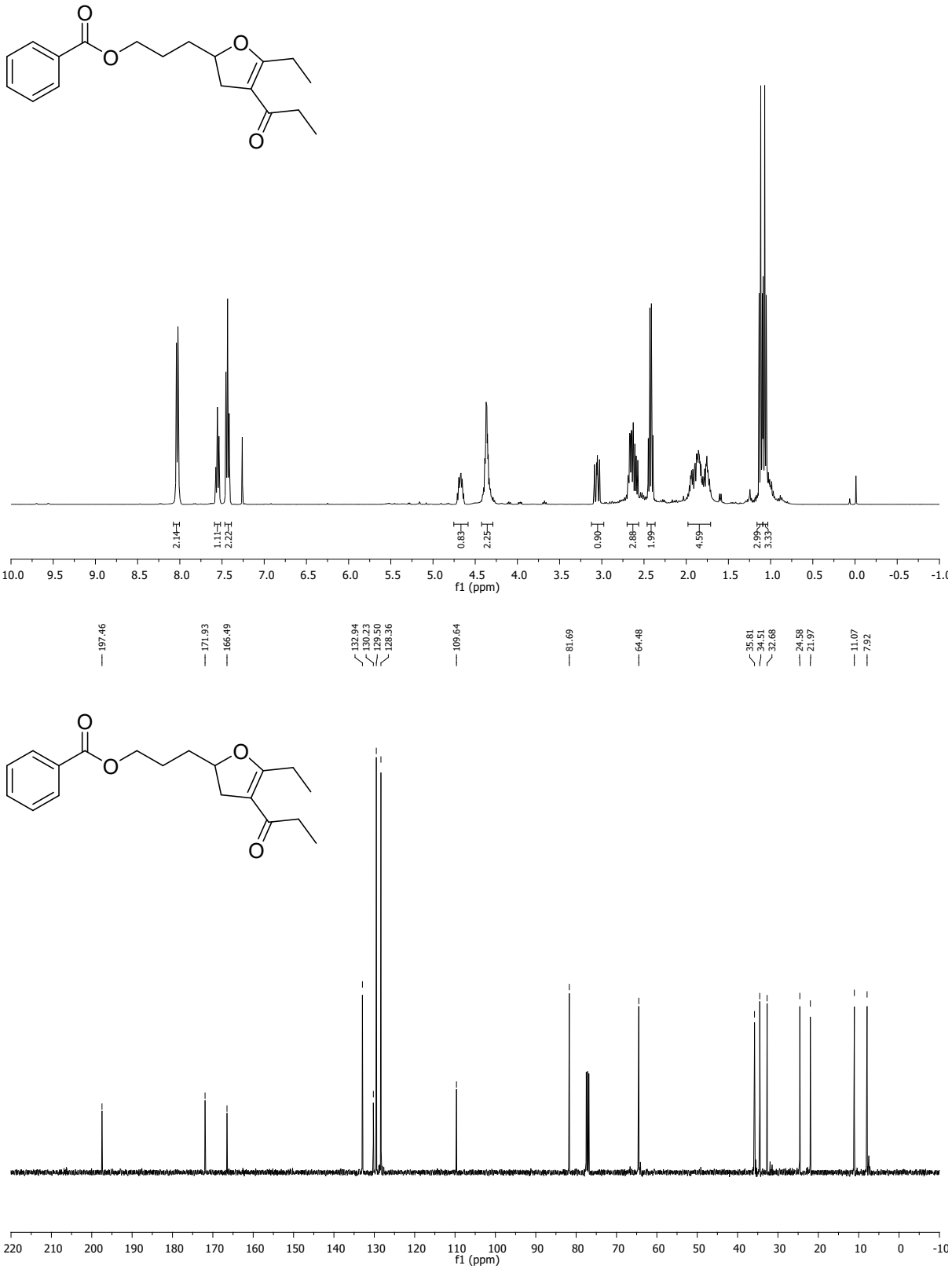
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ac

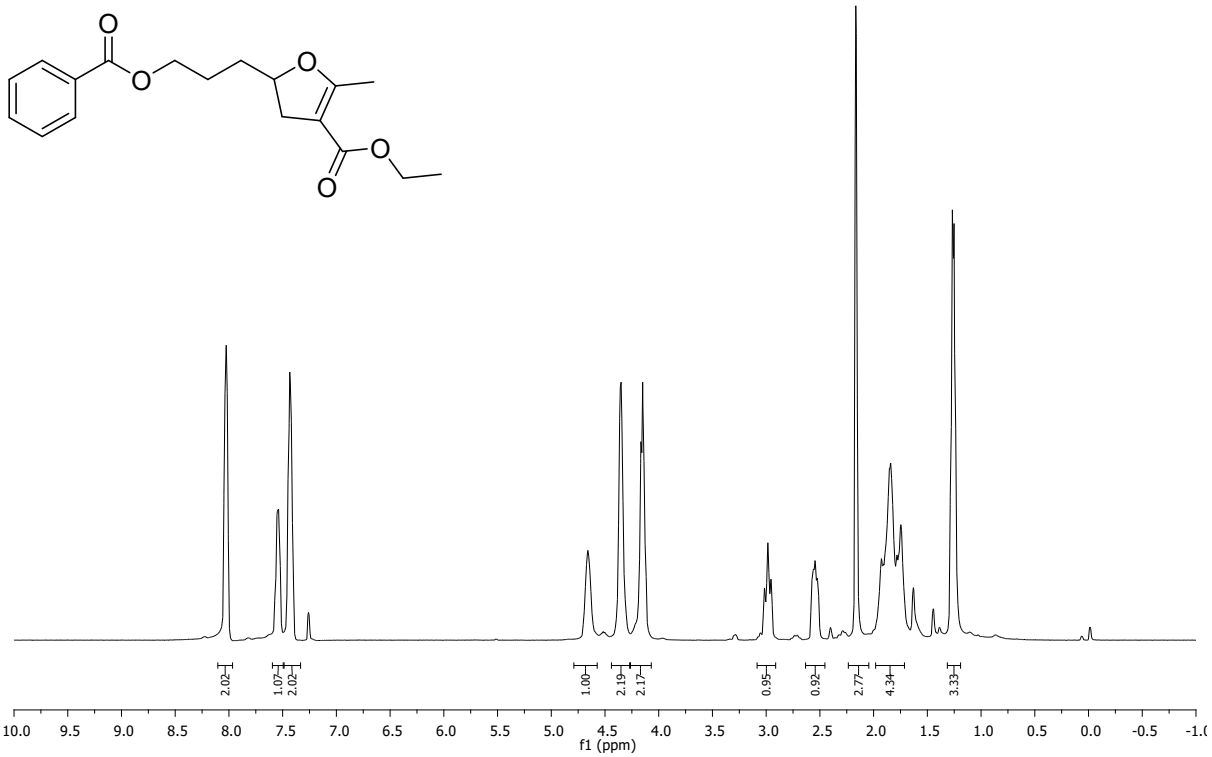

1.98
1.00
2.00
0.95
2.04
0.97
0.97
2.99
2.99
4.22
f1 (ppm)

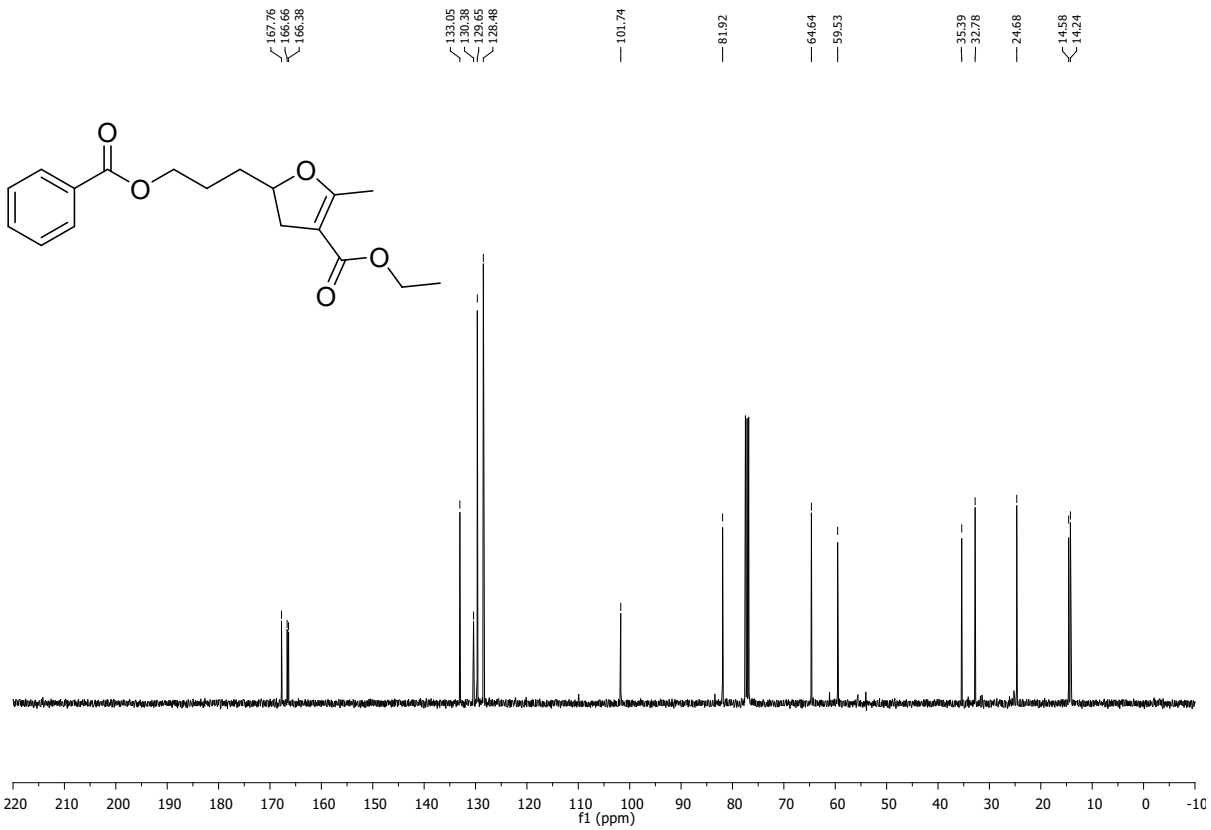

194.57
167.57
166.57
133.01
130.27
129.57
128.42
112.06
81.97
64.49
36.06
32.72
29.41
24.65
15.11
f1 (ppm)

3ad

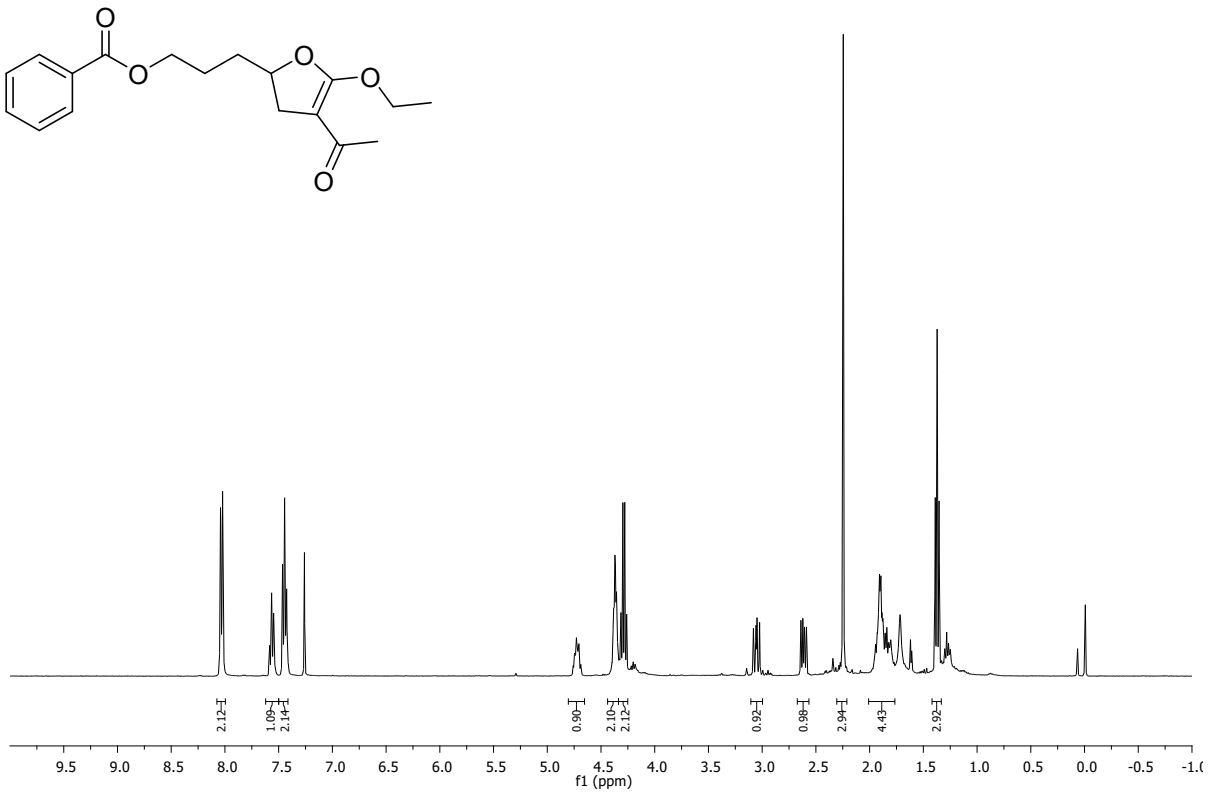

O
O
O
O
2.14
1.11
2.22
0.83
2.25
0.90
2.88
1.99
4.59
2.99
3.33
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
197.46
171.93
166.49
132.94
130.23
129.50
128.36
109.64
81.69
64.48
35.81
34.51
32.68
24.58
21.97
11.07
7.92
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

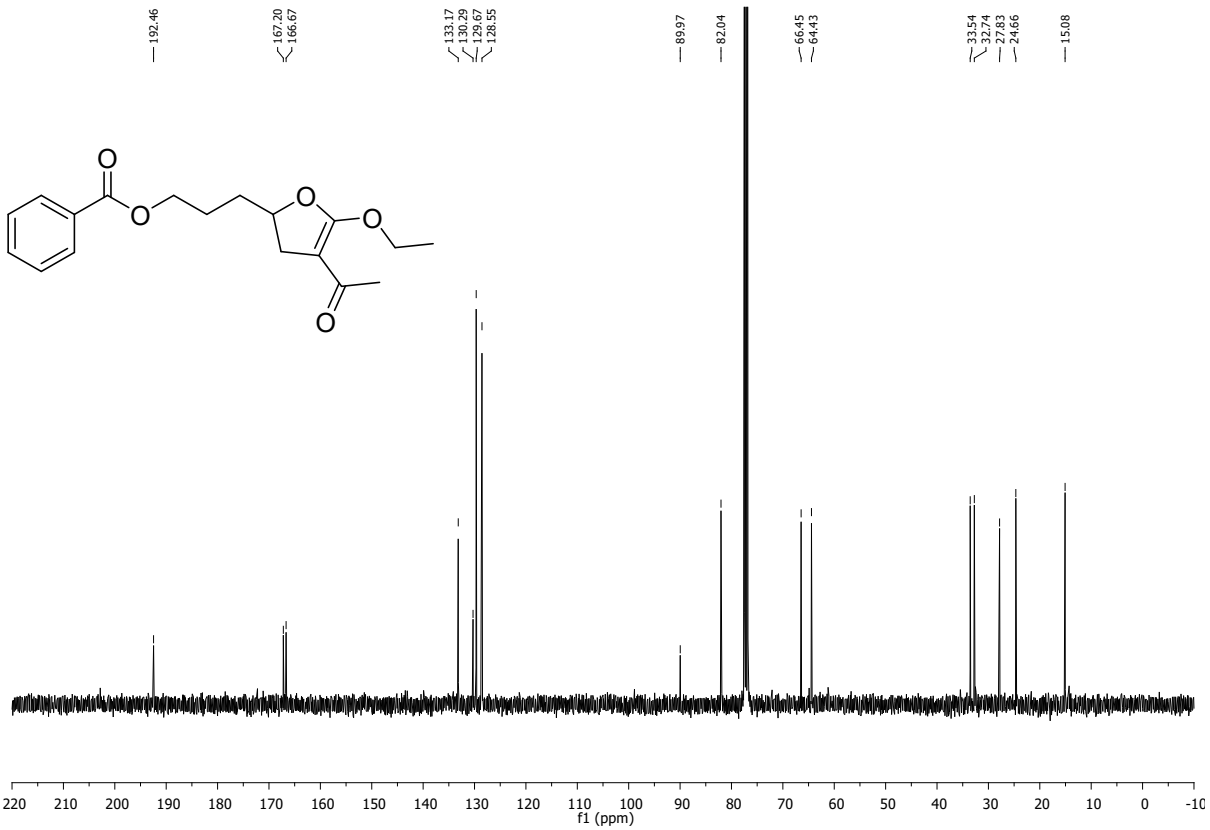
3ae


2.02
1.07
2.02
1.00
2.19
2.17
0.95
0.92
2.77
4.34
3.33
f1 (ppm)

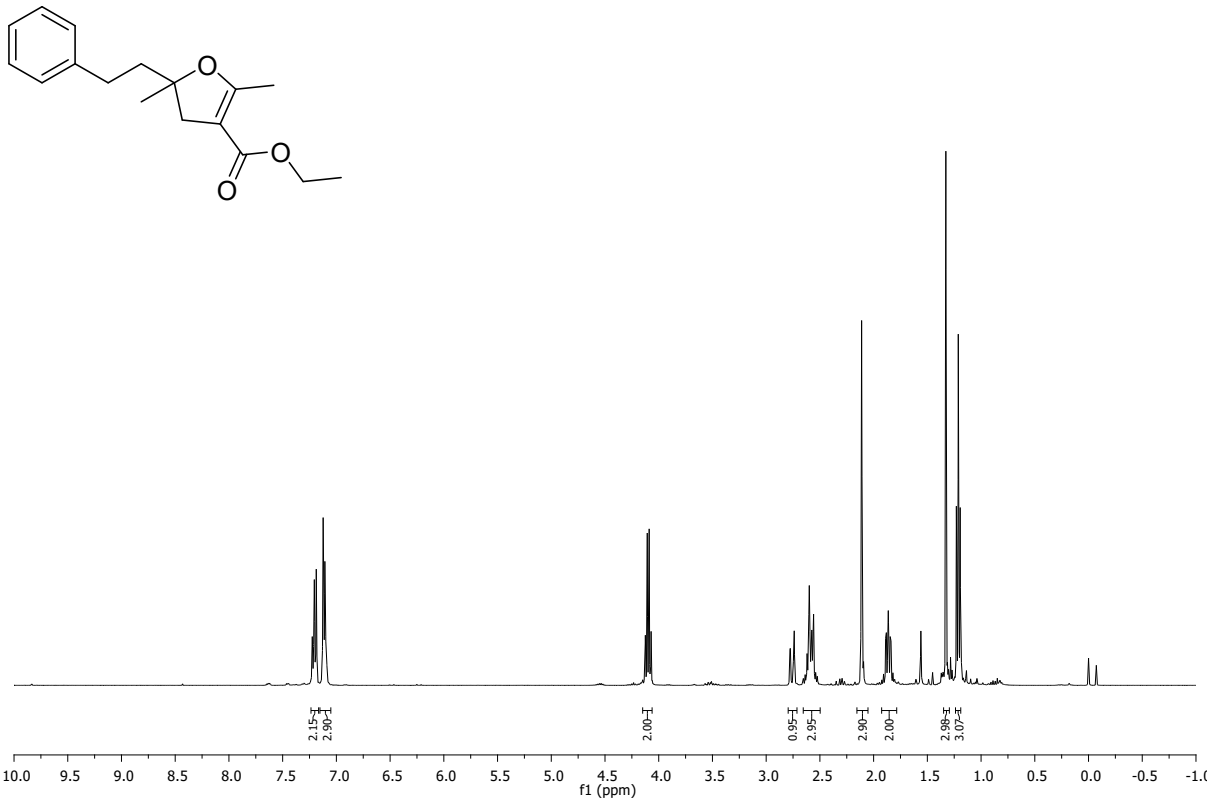

167.76
166.66
166.38
133.05
130.38
129.65
128.48
101.74
81.92
64.64
59.53
35.39
32.78
24.68
14.58
14.24
f1 (ppm)

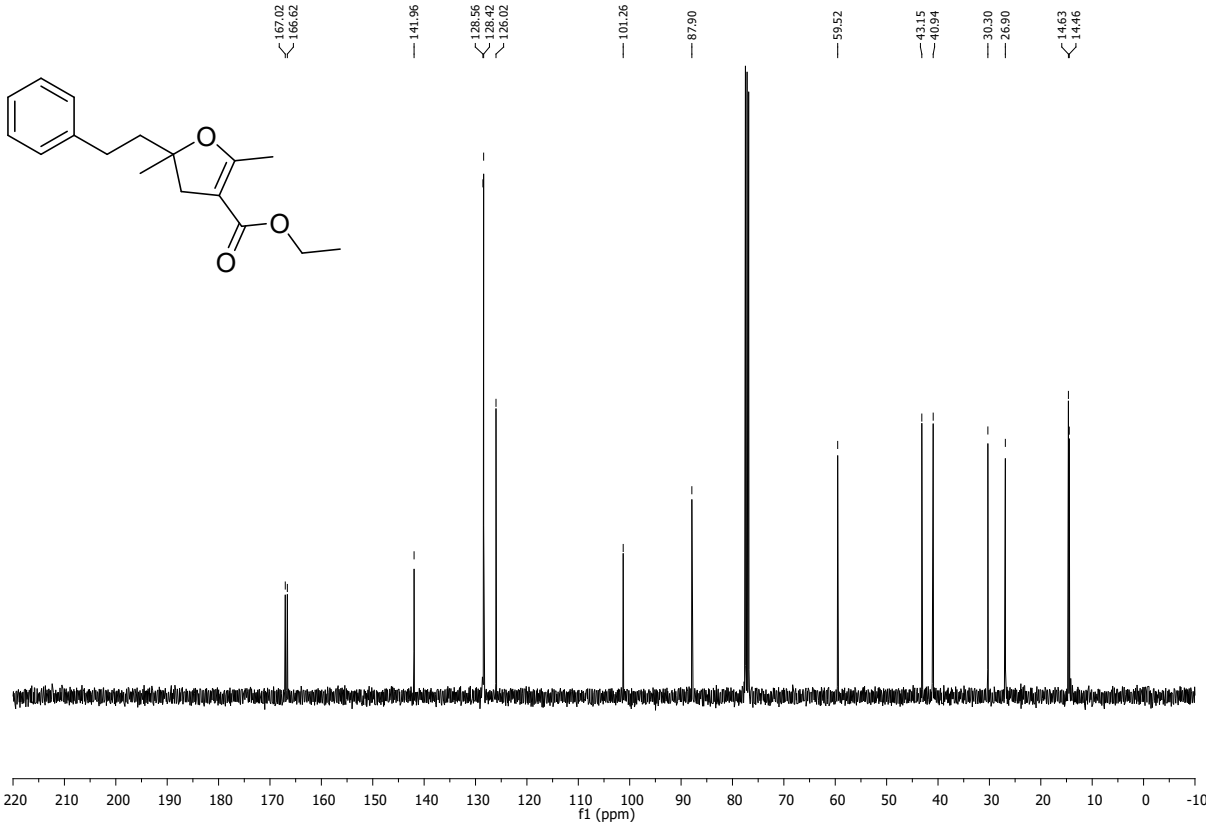
3ae-R


2.12
1.09
2.14
0.90
2.10
2.12
0.92
0.98
2.94
4.43
2.92
f1 (ppm)

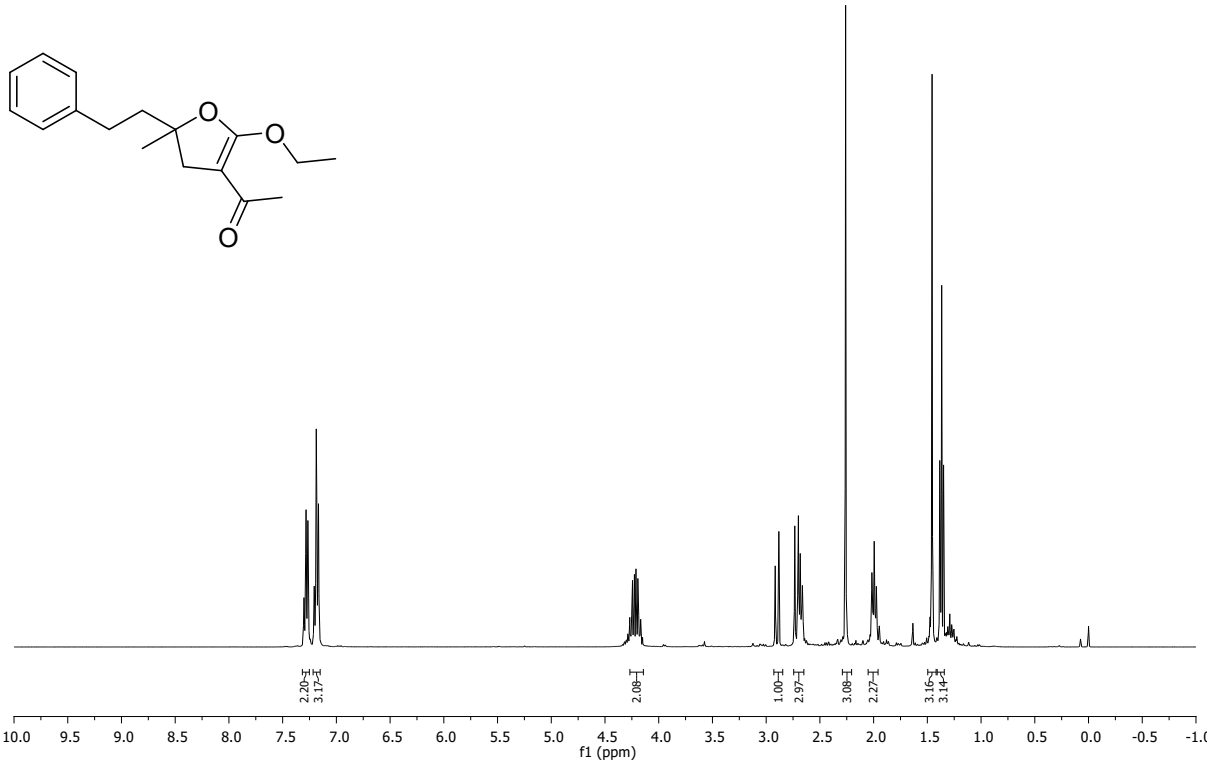

192.46
167.20
166.67
133.17
130.29
129.67
128.55
89.97
82.04
66.45
64.43
33.54
32.74
27.83
24.66
15.08
f1 (ppm)

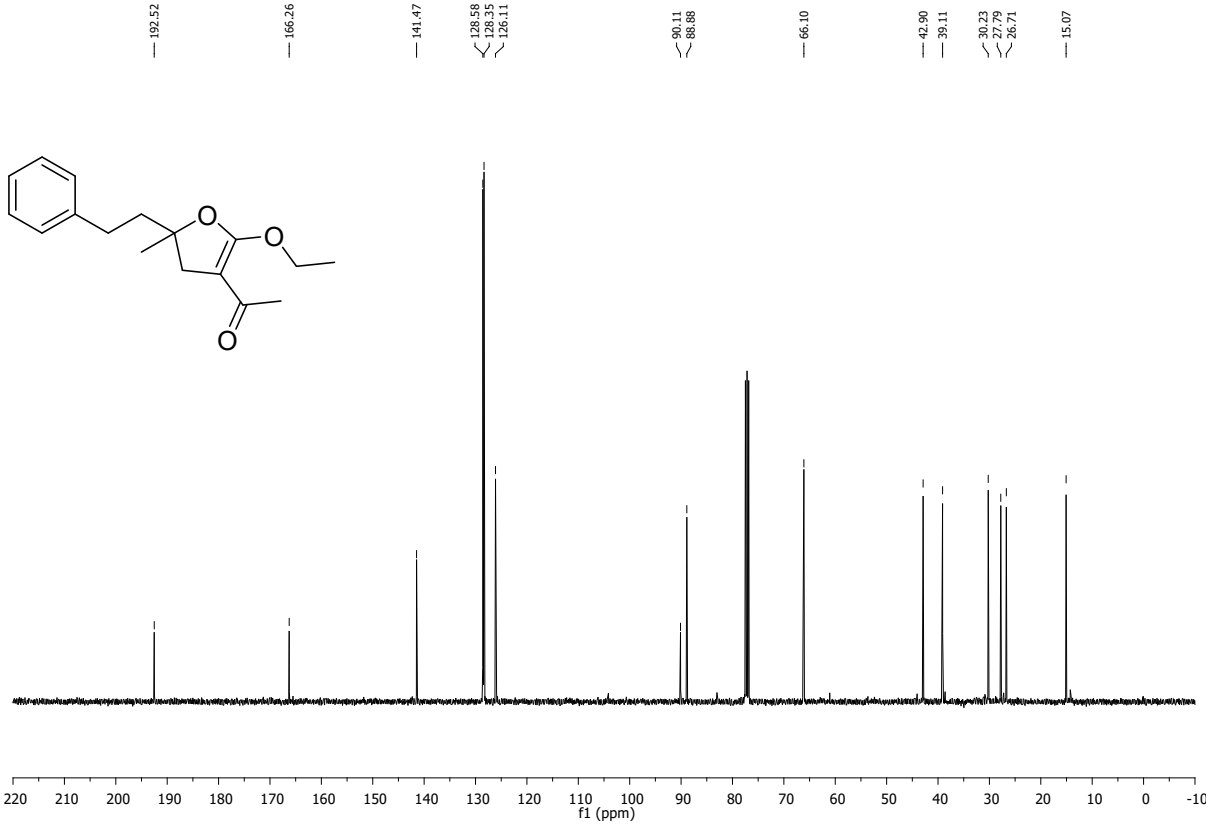
5i′e


O
O
O
2.15
2.90
2.00
0.95
2.95
2.90
2.00
2.08
3.07
10.0 9.5 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 -0.5
f1 (ppm)


167.02
166.62
141.96
128.56
128.42
126.02
101.26
87.90
59.52
43.15
40.94
30.30
26.90
14.63
14.46
O
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5i′e-R


O
O
O
2.20
3.17
2.08
1.00
2.97
3.08
2.27
3.16
3.14
10.0 9.5 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 -0.5
f1 (ppm)


192.52
166.26
141.47
128.58
128.35
126.11
90.11
88.88
66.10
42.90
39.11
30.23
27.79
26.71
15.07
O
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)