SUPPLEMENTARY INFORMATION

Chemical proteomic analysis of palmostatin beta-lactone analogs that affect N-Ras palmitoylation

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Biological Methods

Cell lines and tissue culture

OCI-AML3 (DSMZ: ACC-582) cells were grown in RPMI supplemented with 10% fetal bovine serum (FBS), L-glutamine (2 mM), penicillin (100 U/mL), streptomycin (100 µg/mL), and 50 µM β-mercaptoethanol and grown at densities between 3 x 10^6 and 2 x 10^6 cells/mL. HEK293T (ATCC: CRL-3216) were grown in DMEM supplemented with 10% fetal bovine serum (FBS), L-glutamine (2 mM), penicillin (100 U/mL), and streptomycin (100 µg/mL). All cells were maintained at 37 °C with 5% CO_2.

Generation and validation of OCI-AML3 sublines ("ON" and "ONK") and ABHD17B stably transduced HEK293Ts was previously described[1].

Activity-based protein profiling (ABPP) screen of beta-lactone analogs by gel

HEK293T cells stably transduced to express ABHD17B were incubated with inhibitors or DMSO control for 4 h *in situ.* Samples were then processed for analysis by gel as previously described[1].

Dynamic palmitoylation assay

Dynamic palmitoylation assay, including immunoprecipitation, western blotting and on-bead click chemistry were done as previously described[1].

MS-ABPP sample preparation

MS-ABPP samples treated with FP-biotin were prepared as previously described[1]. For samples treated with Palm M-yne (which was synthesized as previously described[2]), conjugation with biotin-N_3 was performed with previously described click chemistry conditions[1].

MS-ABPP data analysis

Mass spectrometry experiments were performed using a Thermo Orbitrap Velos mass spectrometer. Samples were analyzed using a five-step multidimensional LC/MS MudPIT protocol with conditions as previously described[3].

Spectrum raw files were extracted into MS2 files using RawConverter (version 1.1.0.22 from http://fields.scripps.edu/rawconv/) and searched using the ProLuCID (version 1.4) algorithm[4] against a human reverse concatenated nonredundant Uniprot database (2012 version), with static modifications for cysteine residues to account for alkylation by iodoacetamide (+57.0215 m/z), and standard static modifications for reductive dimethylation: lysine and N-terminus (+28.0313 m/z for light, +34.06312 m/z for heavy). Data was assembled using DTASelect version 2.0,[5] and ratio quantification was performed using in-house CIMAGE software. Peptides were required to be fully tryptic, unique, to have an envelope correlation score of $R^2 \geq 0.5$, and ratios were capped to a maximum value of 20. Ratios (R) for each protein were calculated from the median of all quantified peptide ratios. In cases where a protein had exactly one peptide with a ratio of 20, and at least one other peptide with a ratio below 2, the 20 value was discarded. Peptides with a ratio of 20 were also manually reviewed and filtered.

Synthetic Methods and Compound Characterization

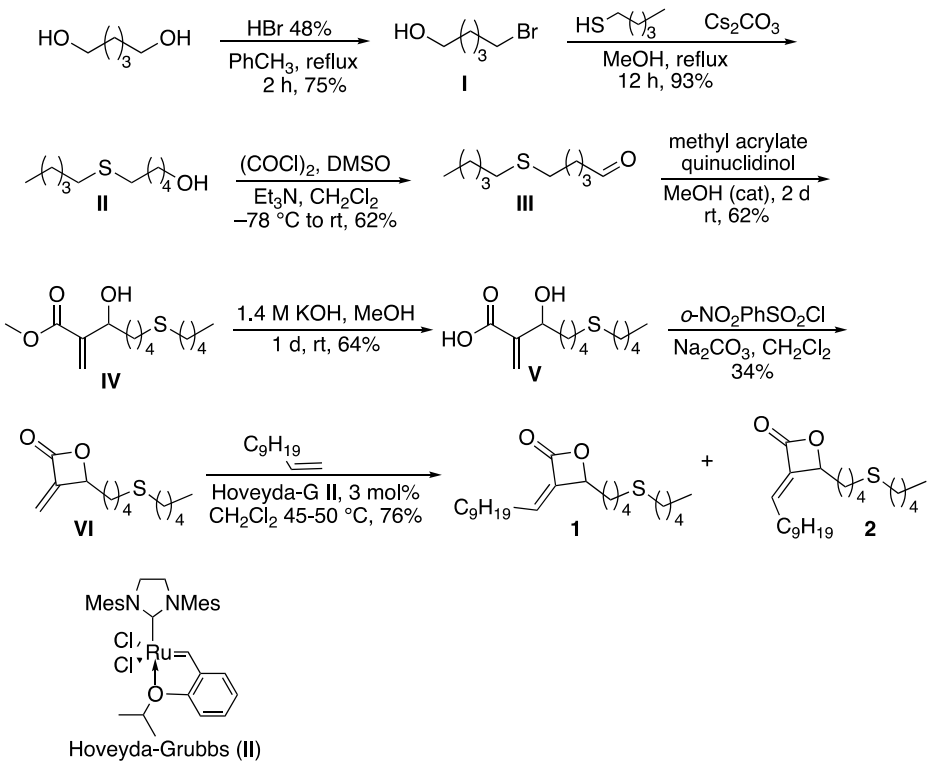
Experimental procedures for preparation of compounds 1-13:

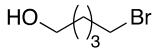
All moisture sensitive reactions were run in a flame-dried flask under N_2. THF was dried using a J. C. Meyer Solvent Dispensing System (SDS) and dispensed under N_2. All other solvents were dried over CaH_2 or 4 Å molecular sieves. Deuterated chloroform ($CDCl_3$) was dried over 4 Å molecular sieves. All starting materials and reagents were purchased from commercial sources and used as received. ^{1}H NMR experiments were recorded on a 500 or 400 MHz spectrometer. All ^{13}C NMR experiments were recorded at 125 or 100 MHz. Chemical shifts (δ) are given in ppm,

and coupling constants (*J*) are given in Hz. The 7.26 resonance of residual $CHCl_3$ for ^1H NMR spectra or the residual CD_3OH proton at 3.34 ppm and the 77.23 ppm resonance of $CDCl_3$ or the 49.5 ppm resonance of CD_3OD for ^{13}C NMR spectra were used as internal references. High resolution mass spectroscopy (HRMS) was performed on a TOF instrument with ESI in a positive or negative ionization mode.

Unless otherwise stated, reaction progress was monitored by thin layer chromatography (TLC) performed on glass plates coated with silica gel UV254. Visualization was achieved by ultraviolet light (254 nm), 0.5% $KMnO_4$ in 0.1 M aqueous NaOH solution and/or 5% phosphomolybdic acid in ethanol. Column chromatography was performed using silica gel, 40 microns flash silica.

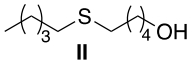
Preparation of β-lactones 1 and 2:





I

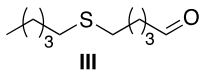
5-Bromo-1-pentanol (I). 1,5-Pentanediol (5.20 g, 49.9 mmol) was transferred to a round bottom flask equipped with a magnetic stir bar. Toluene (120 mL) was added, and the solution was stirred. HBr (48% in H_2O, 6.0 mL) was diluted with H_2O (10 mL) and added, and a Dean-Stark apparatus was connected. The mixture was heated at reflux for 2 h; during this time ~15 mL of H_2O were collected. The light orange solution was allowed to cool to rt. It was then washed with aqueous NaOH (1.0 M, 2 × 50 mL), H_2O (50 mL) and brine (50 mL) and dried ($MgSO_4$). The organic solvent was removed, and the resulting yellow oil was purified by flash column chromatography on silica gel (petroleum ether/EtOAc 90:10—to remove 1,5-dibromopentane—then petroleum ether/EtOAc 50:50) to give **I** as a pale yellow oil (6.24 g, 75%):[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (t, J = 6.2 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 1.97–1.81 (m, 2H), 1.67–1.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.7, 33.9, 32.7, 31.9, 24.6.



II

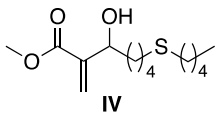
5-(Pentylthio)pentan-1-ol (II). 5-Bromo-1-pentanol (**I**) (5.20 g, 31.1 mmol) was transferred to a round bottom flask and dissolved in CH_3OH (100 mL). The solution was bubbled with N_2 for 15 min, followed by the addition of Cs_2CO_3 (10.1 g, 31.0 mmol). 1-Pentanethiol (4.1 mL, 33.1 mmol) was added dropwise under positive N_2 and at rt. The mixture was then heated at reflux overnight under N_2. The mixture was gravity filtered, and CH_3OH was removed, resulting in a yellow oil. H_2O (100 mL) and Et_2O (200 mL) were added to the residue, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and brine (2 × 50 mL) and dried ($MgSO_4$). The solvent was removed to provide **II** as a yellow oil (5.5 g, 93%): IR (neat) 3336, 2921, 2852, 1691, 1459, 1274, 1054 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.64 (t, J = 6.5 Hz, 2H), 2.52 (t, J = 7.3 Hz, 2H), 2.50 (t, J = 7.4 Hz, 2H), 1.65–1.55 (m, 7H), 1.49–1.43 (m, 2H), 1.39–1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 62.7, 32.3, 32.2, 32.1, 31.1, 29.5, 29.4, 25.1, 22.3, 14.0; HRMS (ESI) calcd for $C_{10}H_{23}OS$ $(M + H)^+$ *m/z* 191.1470, found 191.1485.



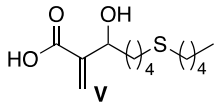
III

5-(Pentylthio)pentanal (III). Oxalyl chloride (1.8 mL, 21 mmol) was added to CH_2Cl_2 (20 mL) at rt and under N_2. The solution was immersed in a cooling bath at –78 °C; then, a solution of DMSO (2.7 mL, 38 mmol) in CH_2Cl_2 (10 mL) was added dropwise over a period of 10 min. The solution was stirred for 20 min at –78 °C. Then, 5-(pentylthio)pentan-1-ol (**II**) (3.31 g, 17.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise over 10 min. Stirring was continued for 20 min at –78 °C. Et_3N (8.7 mL, 62 mmol) was added dropwise over 10 min, and a white suspension resulted. The mixture was stirred for 10 min at –78 °C. The cooling bath was removed, and stirring was continued for 45 min. The reaction was diluted with CH_2Cl_2 (50 mL), and H_2O (50 mL) was added. The mixture was stirred at rt until two clear layers formed. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with H_2O (2 × 50 mL) and brine (2 × 50 mL) and dried ($MgSO_4$). The organic solvent was removed, and the resulting yellow oil was purified by column chromatography on silica gel (petroleum ether/EtOAc 95:5) to give **III** as a yellow oil (2.02 g, 62%): IR (neat) 2926, 2857, 2718, 1722, 1457, 1261, 1072, 732, 523 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.7 Hz, 1H), 2.53–2.43 (m, 6H), 1.77–1.70 (m, 2H), 1.65–1.53 (m, 4H), 1.39–1.26 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 43.6, 32.4, 32.0, 31.3, 29.6, 29.2, 22.5, 21.5, 14.2; HRMS (ESI) calcd for $C_{10}H_{19}OS$ $(M - H)^-$ *m/z* 187.1157, found 187.1160.



IV

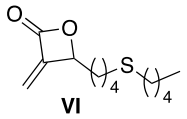
Methyl 3-hydroxy-2-methylene-7-(pentylthio)heptanoate (**IV**)**.** 5-(Pentylthio)pentanal (**III**) (4.7 g, 25 mmol) was transferred to a round bottom flask. Methyl acrylate (4.5 mL, 50 mmol) and 3-quinuclidinol (0.79 g, 6.2 mmol) were added. Methanol (1.0 mL, 25 mmol) was added, and the mixture was stirred for 3 d. Then, excess methyl acrylate was removed in *vacuo*, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 90:10) to give **IV** as a pale yellow oil (4.22 g, 62%): IR (neat) 3400, 2927, 2857, 1717, 1438, 1260, 1194, 1157, 1075, 954 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (s, 1H), 5.81 (s, 1H), 4.40 (ddd, *J* = 6.4, 6.4, 6.4 Hz, 1H), 3.78 (s, 3H), 2.57 (d, J = 6.7 Hz, 1H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 1.74–1.51 (m, 7H), 1.51-1.40 (m, 1H), 1.34–1.29 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 142.4, 125.1, 71.6, 51.9, 35.8, 32.2, 32.0, 31.1, 29.5, 29.4, 25.1, 22.3, 14.0; HRMS(ESI) calcd for $C_{14}H_{27}O_3S$ $(M + H)^+$ *m/z* 275.1675, found 275.1670.



V

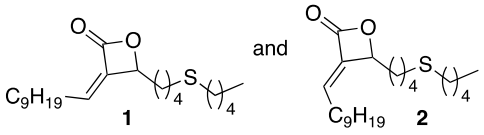
3-Hydroxy-2-methylene-7-(pentylthio)heptanoic acid (V). Methyl 3-hydroxy-2-methylene-7-(pentylthio)heptanoate (**IV**) (4.0 g, 15 mmol) was transferred to a round bottom flask equipped with a stir bar. CH_3OH (50 mL) was added. Then, aqueous NaOH (1.3 M, 25 mL) was added, and the solution was stirred for 1 d. The reaction mixture was concentrated in *vacuo* and diluted with aqueous HCl (2 M, 100 mL). It was then extracted with Et_2O (3 × 100 mL), and the combined organic extracts were washed with H_2O (100 mL) and brine (2 × 50 mL), dried ($MgSO_4$) and concentrated to give a yellow, viscous oil which was purified by column chromatography on silica gel (petroleum ether/EtOAc 70:30) to provide **V** as a pale yellow oil (2.44 g, 64%): IR (neat) 2927, 2858, 1694, 1627, 1250, 1169, 1071, 1047, 960, 736 cm^{-1}; ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 6.39 (s, 1H), 5.93 (s, 1H), 4.44 (dd, *J* = 7.7, 5.1 Hz, 1H), 2.51 (t, *J* = 7.4 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H),

1.80-1.54 (m, 7H), 1.53-1.28 (m, 5H), 0.90 (t, J = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 142.0, 127.6, 71.4, 35.9, 32.4, 32.2, 31.3, 29.6, 29.6, 25.2, 22.5, 14.1; HRMS **(**ESI) calcd for $C_{13}H_{25}O_3S$ $(M + H)^+$ *m/z* 261.1524, found 261.1499.



VI

3-Methylene-4-(4-(pentylthio)butyl)oxetan-2-one (VI). 3-Hydroxy-2-methylene-7-(pentylthio)-heptanoic acid (**V**) (1.13 g, 4.34 mmol) was dissolved in CH_2Cl_2 (50 mL). Na_2CO_3 (4.01 g, 37.8 mmol) was added, and the mixture was stirred for 30 min. Then, 2-nitrobenzenesuflonyl chloride (1.47 g, 6.63 mmol) was added, and the mixture was stirred for 1 d, resulting in a white suspension. It was gravity filtered, and the solvent was removed, resulting in a yellow oil which was purified by column chromatography on silica gel (hexanes/EtOAc 95:5) to give **VI** as a colorless oil (0.363 g, 35%): IR (neat) 2928, 2858, 1816, 1080, 816 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (dd, J = 2.0, 2.0 Hz, 1H), 5.44 (dd, J = 1.8, 1.8 Hz, 1H), 4.97 (tt, J = 6.4, 1.7 Hz, 1H), 2.57 (t, J = 7.0 Hz, 2H), 2.53 (t, J = 7.5 Hz, 2H), 1.95–1.81 (m, 2H), 1.71–1.59 (m, 6H), 1.43–1.33 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ163.6, 146.4, 115.2, 79.5, 33.1, 32.4, 31.9, 31.3, 29.5, 29.3, 24.0, 22.5, 14.1; HRMS/ESI calcd for $C_{13}H_{23}O_2S$ $(M + H)^+$ *m/z* 243.1419, found 243.1407.

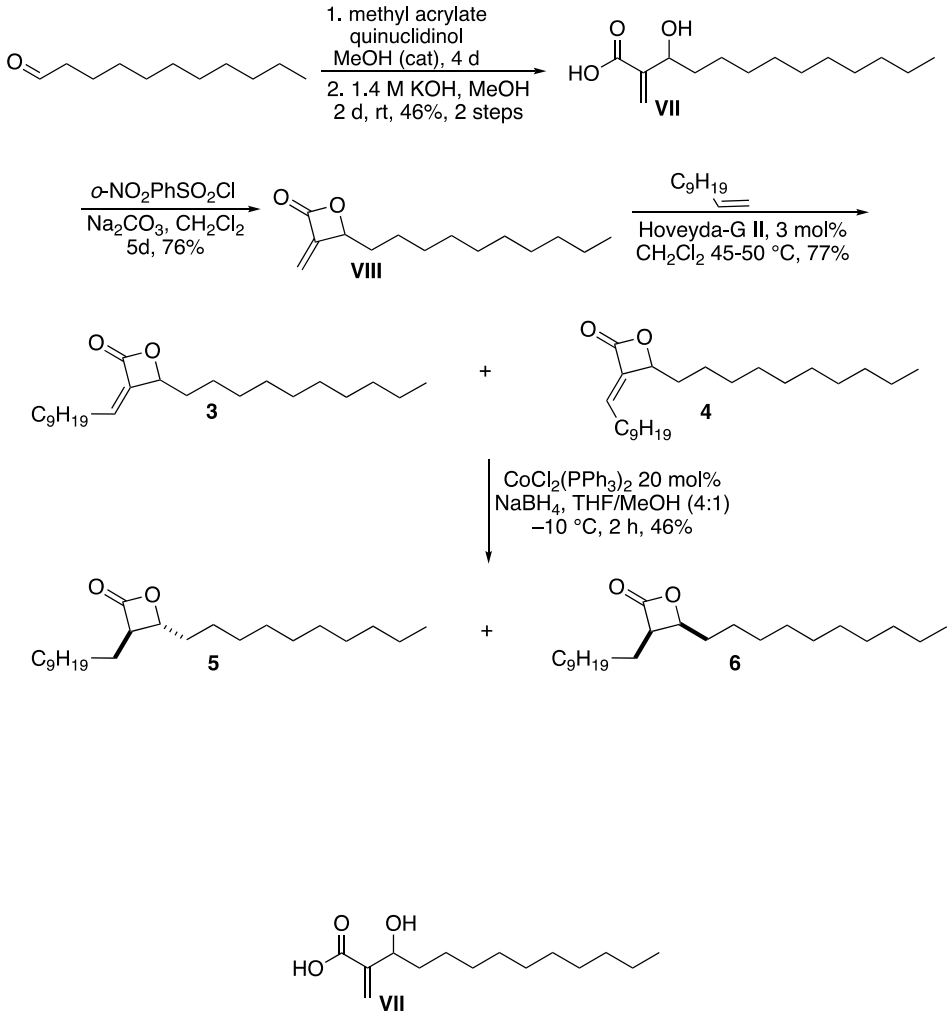


1 and **2**

(*Z/E*)-3-Decylidene-4-(4-(pentylthio)butyl)oxetan-2-one (1/2). **3**-Methylene-4-(4-(pentylthio)-butyl)oxetan-2-one (**VI**) (0.25 g, 1.0 mmol), Hoveyda-Grubbs-2nd generation catalyst (34.3 mg, 0.0548 mmol) and undecene (0.50 mL, 2.4 mmol) were dissolved in CH_2Cl_2 (5 mL). A green solution resulted. It was heated at 40 °C under N_2 overnight. The resulting brown solution was allowed to cool to rt and was filtered through celite. The filtrate was concentrated and the residue

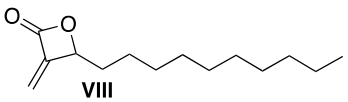
purified by column chromatography on silica gel (petroleum ether/EtOAc 96:4) to provide **1/2** as a colorless oil (290 mg, 76% *Z*:*E* ratio 3.8:1). The two isomers were separated by column chromatography using the same conditions. (*Z*)-**1**: IR (neat) 2922, 2853, 1805, 1464, 1066, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (td, *J* = 7.9, 1.4 Hz, 1H), 4.85 (td, *J* = 6.4, 1.3 Hz, 1H), 2.54–2.48 (m, 6H), 1.82 (dt, *J* = 7.0, 7.0 Hz, 2H), 1.68–1.62 (m, 2H), 1.60–1.54 (m, 4H), 1.47–1.42 (m, 2H), 1.38–1.26 (m, 16H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 137.3, 136.5, 78.3, 33.4, 32.2, 31.9, 31.8, 31.1, 29.5, 29.4, 29.3, 29.3, 29.0, 28.9, 28.8, 23.9, 22.7, 22.3, 14.1, 14.0; HRMS (ESI) calculated for $C_{22}H_{41}O_2S$ $(M + H)^+$ *m/z* 369.2827, found 369.2814. (*E*)-**2**: IR (neat) 2923, 2853, 1810, 1458, 731cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (td, *J* = 8.0, 1.8 Hz, 1H), 4.99 (m, 1H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.50 (t, *J* = 6.0 Hz, 2H), 2.11 (m, 2H), 1.99–1.92 (m, 1H), 1.83–1.76 (m, 1H), 1.71–1.52 (m, 7H), 1.47 (p, *J* = 7.5 Hz, 2H), 1.38–1.27 (m, 15H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 137.4, 134.2, 78.8, 32.9, 32.2, 31.9, 31.1, 29.5, 29.4, 29.3, 29.3, 29.3, 29.2, 28.9, 28.4, 24.0, 22.7, 22.3, 14.1, 13.9; HRMS **(**ESI) calculated for $C_{22}H_{41}O_2S$ $(M + H)^+$ m/z 369.2827, found 369.2812.

Preparation of β-lactones 3-6:



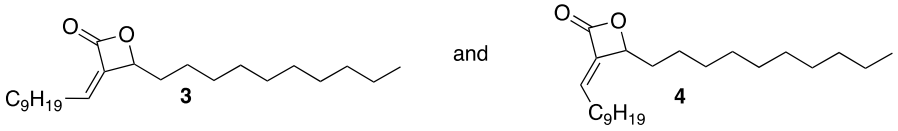
3-Hydroxy-2-methylenetridecanoic acid (VII). Undecanal (5.0 g, 0.029 mol) and methyl acrylate (5.3 mL, 0.059 mol) were transferred to a round bottom flask equipped with a stir bar. 3-quinuclidinol (940 mg, 7.4 mmol) and MeOH (0.9 mL) were added, and the mixture was stirred at rt for 4 d. Then, excess methyl acrylate was removed in *vacuo* to provide methyl 3-hydroxy-2-methylenetridecanoate as a yellow oil which was used for the next step without purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (s, 1H), 5.79 (s, 1H), 4.37 (dd, J = 6.5, 6.5 Hz, 1H), 3.77 (s, 3H), 1.67 (m, 2H), 1.43 (m, 1H), 1.25 (brs, 15H), 0.87 (t, J = 6.3 Hz, 3H). A solution of methyl 3-hydroxy-2-methylenetridecanoate in MeOH (100 mL) and KOH (3.81g, 68 mmol) dissolved in H_2O (50 mL) was stirred for 2 d at rt. MeOH was removed, and aqueous 2M HCl (100 mL) was added

to the residue. The solution was then extracted with Et_2O (200 mL, then 2 × 100 mL). The combined organic extracts were washed with brine (2 × 100 mL) and dried ($MgSO_4$). The solvent was removed, and the crude yellow oil was purified by column chromatography on silica gel (petroleum ether/EtOAc 80:20) to provide **VII** as a pale yellow oil (3.3 g, 46%): IR (neat) 3321 (br), 2917, 2849, 1690, 1634, 1284 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.39 (s, 1H), 5.91 (s, 1H), 4.42 (dd, *J* = 6.6, 6.6 Hz, 1H), 1.67 (m, 2H), 1.43 (m, 1H), 1.26 (brs, 15H), 0.87 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 142.1, 127.7, 71.8, 36.4, 32.1, 29.8, 29.8, 29.6, 29.5, 26.0, 22.9, 14.3; HRMS (ESI) calcd for $C_{14}H_{27}O_3$ $(M + H)^+$ *m/z* 243.1960, found 243.1927.

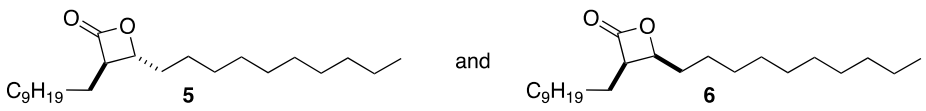


VIII

4-Decyl-3-methyleneoxetan-2-one (VIII). 3-Hydroxy-2-methylenetridecanoic acid (**VII**) (1.33 g, 5.49 mmol) was transferred to a round bottom flask and dissolved in CH_2Cl_2 (50 mL). Anhydrous Na_2CO_3 (3.0 g, 0.028 mol) was added, and the mixture was stirred at rt for 15 min, followed by the addition of 2-nitrobenzenesulfonyl chloride (1.74 g, 7.85 mmol). The mixture was stirred for 5 d at rt, then diluted with CH_2Cl_2 (50 mL) and H_2O (50 mL). The solution was stirred until two clear layers formed. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with H_2O (100 mL) and brine (3 × 50 mL) and dried ($MgSO_4$). The solvent was removed, and the resulting yellow oil was purified by column chromatography on silica gel (petroleum ether/EtOAc 90:10) to afford **VIII** as a pale yellow oil (0.94 g, 76%): IR (neat) 2923, 2854, 1818, 1079 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.90 (t, *J* = 1.9 Hz, 1H), 5.41 (t, *J* = 1.7 Hz, 1H), 5.06-4.85 (m, 1H), 1.87–1.81 (m, 2H), 1.51–1.41 (m, 2H), 1.26 (brs, 14H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 146.7, 115.0, 79.8, 33.5, 32.1, 29.7, 29.8, 29.6, 29.5, 29.4, 24.8, 22.9, 14.3; HRMS (ESI) calcd for $C_{14}H_{25}O_2$ $(M + H)^+$ *m/z* 225.1855, found 225.1850.



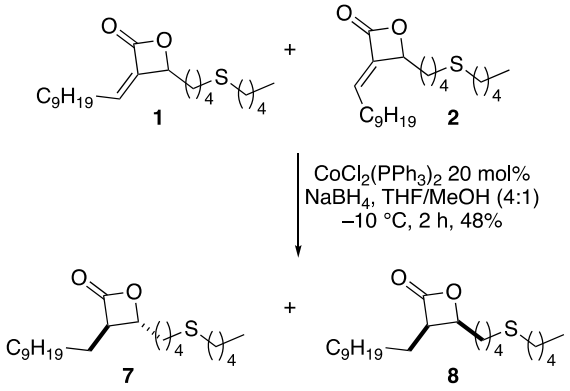
(*Z/E*)-4-Decyl-3-decylideneoxetan-2-one (3/4). 4-Decyl-3-methyleneoxetan-2-one (**VIII**) (509 mg, 2.3 mmol) and undecene (0.70 mL, 3.4 mmol) were transferred to a round bottom flask and dissolved in CH_2Cl_2 (12 mL). Grubbs (II) catalyst (43 mg, 0.069 mmol) was added, and the solution was heated at 40 °C for 12 h. It was then concentrated, and the crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc 98:2) to provide **3/4**, a pale-yellow oil, as a mixture of *Z/E*-isomers (2:1) (613 mg, 77%). The isomers were separated using the same chromatographic conditions. (*Z*)-**3**: IR (neat) 2924, 2855, 1803, 1465, 1215, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (t, *J* = 7.9 Hz, 1H), 4.84 (t, *J* = 6.3 Hz, 1H), 2.51–2.46 (m, 2H), 1.82–1.77 (m, 2H), 1.47–1.41 (m, 4H), 1.26 (brs, 26H), 0.88 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 137.7, 136.4, 78.8, 33.9, 32.1, 32.1, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 29.2, 29.1, 29.1, 24.8, 22.9, 14.3; HRMS (ESI) calcd for $C_{23}H_{43}O_2$ $(M + H)^+$ m/z 351.3263, found 351.3271. (*E*)-**4**: IR (neat) 2922, 2853, 1813, 1464, 1117, 1044, 818, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.38 (td, *J* = 7.9, 1.7 Hz, 1H), 5.03 (m, 1H), 2.18–2.13 (m, 2H), 2.01–1.94 (m, 1H), 1.86–1.78 (m, 1H), 1.56–1.48 (m, 4H), 1.32 (brs, 26H), 0.93 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 137.6, 134.0, 79.2, 33.3, 31.9, 31.9, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 28.9, 28.4, 24.7, 22.7, 22.6, 14.1; HRMS (ESI) calcd for $C_{23}H_{43}O_2$ $(M + H)^+$ *m/z* 351.3263, found 351.3236.

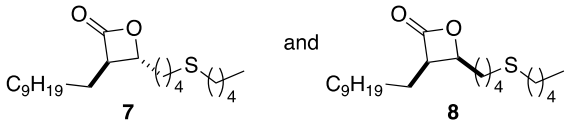


(*trans/cis*)-3,4-Didecyloxetan-2-one (5/6). 4-Decyl-3-decylideneoxetan-2-one (**3/4**) a mixture of *E/Z*-isomers (124 mg, 0.35 mmol) was dissolved in a mixture of THF/MeOH (1.7/0.4 mL) and immersed in a cooling bath at –10 °C. $CoCl_2(PPh_3)_2$ (47 mg, 0.072 mmol) was added, followed by the addition of $NaBH_4$ (18 mg, 0.48 mmol) in portions over 10 min. A dark brown mixture formed

which was stirred at –10 °C for 2 h. It was then filtered through a pad of celite, and the celite was washed with $CHCl_3$ (10 mL). The organic layer was washed with 2 M HCl (2 × 5 mL) and brine (3 × 5 mL) and dried ($MgSO_4$). The solvent was removed, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 96:4) to provide a mixture of isomers (*trans/cis*, 2:1) as a white solid (58 mg, 46%). The mixture was carefully purified using the same chromatographic conditions to obtain individual isomers. *trans*-**5**: IR (neat) 2918, 2851, 1794, 1467, 1140, 857, 816, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.21 (ddd, *J* = 7.3, 6.0, 3.9 Hz, 1H), 3.16 (ddd, *J* = 10.5, 6.5, 3.9 Hz, 1H), 1.89–1.78 (m, 2H), 1.75–1.67 (m, 2H), 1.26 (brs, 32H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 78.2, 56.2, 34.5, 31.9, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 27.9, 27.0, 25.0, 22.7, 14.1; HRMS (ESI) calculated for $C_{23}H_{45}O_2$ $(M + H)^+$ *m/z* 353.3414, found 353.3404. *cis*-**6**: IR (neat) 2918, 2850, 1795, 1467, 1132, 1066, 814, 722 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$) δ 4.53 (ddd, *J* = 10.0, 6.4, 4.0 Hz, 1H), 3.59 (ddd, *J* = 8.9, 7.0, 7.0 Hz, 1H), 1.81–1.70 (m, 2H), 1.68–1.57 (m, 2H), 1.26 (brs, 32H), 0.88 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 75.8, 52.7, 31.9, 30.2, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 27.6, 25.6, 24.0, 22.7, 14.1; HRMS (ESI) calculated for $C_{23}H_{44}O_2Na$ $(M + Na)^+$ *m/z* 375.3234, found 375.3220.

Preparation of β-lactones 7 and 8:



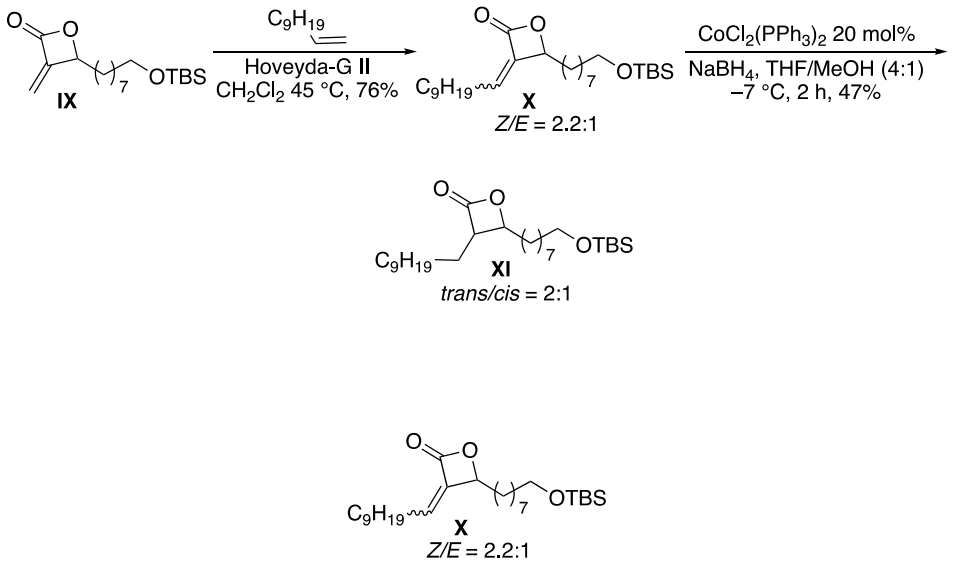


7 **8**

(*trans/cis*)-3-Decyl-4-(4-(pentylthio)butyl)oxetan-2-one (7/8). (*Z/E*)-3-Decylidene-4-(4-(pentylthio)butyl)oxetan-2-one (**1/2**) (174 mg, 0.472 mmol) was transferred to a round bottom flask, and THF/MeOH (2.0ice/0.5 mL) was added. The solution was immersed in a cooling bath at –10 °C, and $CoCl_2(PPh_3)_2$ (63 mg, 0.097 mmol) was added. Then, $NaBH_4$ (21 mg, 0.57 mmol) was added in portions over 10 min, resulting in a dark brown mixture. This was stirred at –10 °C for 2 h. The mixture was then filtered through a pad of celite, and the celite was washed with $CHCl_3$ (10 mL). The filtrate was then washed with 2M HCl (2 × 5 mL), H_2O (5 mL) and brine (3 × 5 mL) and dried ($MgSO_4$). It was concentrated and purified by column chromatography on silica gel (petroleum. ether/EtOAc 96:4) to give **7/8** as a clear oil (83 mg, 48%; *trans/cis* 2:1). The two isomers were separated by column chromatography on silica gel (petroleum. ether/EtOAc 96:4). *trans*-**7** (colorless oil): IR (neat) 2923, 2854, 1819, 1460, 1116 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.23–4.19 (m, 1H), 3.19–3.15 (m, 1H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.89–1.69 (m, 4H), 1.66–1.62 (m, 2H), 1.59–1.55 (m, 2H), 1.38–1.26 (m, 22H), 0.89 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 78.1, 56.4, 34.3, 32.4, 32.1, 32.0, 31.3, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 28.1, 27.2, 24.5, 22.9, 22.5, 14.3, 14.2; HRMS (ESI) calcd for $C_{22}H_{43}O_2S$ $(M + H)^+$ *m/z* 371.2984, found 371.2982. *cis*-**8** (colorless oil): IR (neat) 2923, 2854, 1819, 1461, 1125, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.53 (ddd, *J* = 9.4, 3.8, 3.7 Hz, 1H), 3.62 (ddd, *J* = 8.8, 6.8, 6.8 Hz, 1H), 2.53 (t, *J* = 8.5 Hz, 2H), 2.50 (t, *J* = 9.5 Hz, 2H), 1.82–1.48 (m, 12H), 1.39–1.26 (m, 18H), 0.89 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 75.5, 52.8, 32.2, 31.9, 31.9, 31.1, 29.9, 29.6, 29.5, 29.4, 29.3, 29.3, 27.6, 24.9, 24.0, 22.7, 22.3, 14.1, 14.0; HRMS (ESI) calcd for $C_{22}H_{43}O_2S$ $(M + H)^+$ *m/z* 371.2984, found 371.2993.

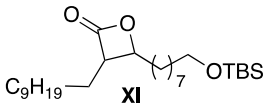
Preparation of β-lactones 9 and 10:

Preparation of key β-lactone precursors (*Z/E*)-**X** and *trans/cis*-**XI**:



(*Z/E*)-4-(8-*tert*-Butyldimethylsilyloxy)octanyl-3-decanylideneoxetan-2-one (X). Hoveyda-Grubbs II catalyst (52 mg, 0.061 mmol) was added to a solution of 4-(8-*tert*-butyldimethylsilyloxy)octanyl-3-methyleneoxetan-2-one (**IX**)[7] (0.40 g, 1.2 mmol) and 1-undecene (0.28 g, 1.8 mmol) in dry DCM (70mL). The mixture was stirred overnight at 40 °C. The reaction mixture was allowed to cool to rt and then concentrated to give a brown residue. The ^{1}H NMR *Z*:*E* ratio of the crude reaction mixture was 2.2:1. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 98:2) provided **X** as a colorless oil (0.42 g, 76%). The isomers were separable by careful column chromatography using the same solvent system. (*Z*)-**X** (colorless oil) (0.23 g, 42%): IR (neat) 2925, 2854, 1808, 1251, 1095, 1073 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ□5.83 (t, *J* = 7.5 Hz, 1H), 4.81 (t, *J* = 6.2 Hz, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.46 (app q, *J* = 7.4 Hz, 2H), 1.77 (app q, *J* = 7.0 Hz, 2H), 1.52–1.37 (m, 4H), 1.36–1.17 (m, 22H), 0.87 (s, 9H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 137.7, 136.3, 78.7, 63.3, 33.9, 33.0, 32.0, 29.6, 29.5, 29.4, 29.4, 29.2, 29.0, 26.1, 25.9, 24.7, 22.8, 18.5, 14.2 –5.1; HRMS (ESI) calcd for $C_{27}H_{53}O_3Si$ $(M + H)^+$ *m/z* 453.3764 found 453.3776. (*E*)-**X** (colorless oil) (51 mg, 9.2%): IR 2926, 2854, 1815, 1463, 1251, 1095 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ□6.32 (ddd, *J* =

7.8, 7.8, 1.5 Hz, 1H), 5.01–4.95 (m, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.10 (app q, *J* = 7.5 Hz, 2H), 1.97–1.86 (m, 1H), 1.84–1.70 (m, 1H), 1.55–1.40 (m, 4H), 1.39–1.23 (m, 22H), 0.87 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 137.8, 134.1, 79.3, 63.5, 33.5, 33.0, 32.1, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 29.0, 28.6, 26.2, 26.0, 24.9, 22.9, 18.6, 14.3, –5.1; HRMS (ESI) calcd for $C_{27}H_{53}O_3Si$ $(M + H)^+$ *m/z* 453.3764, found 453.3750.

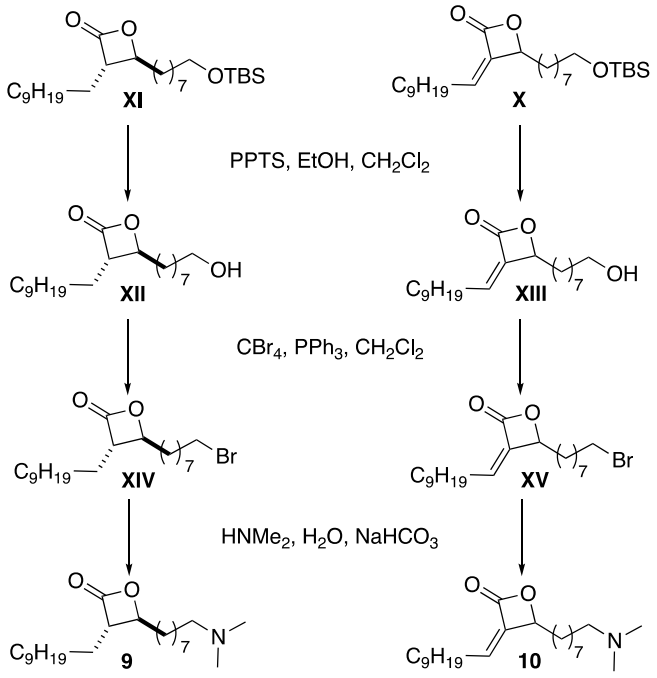


XI

trans/cis = 2:1

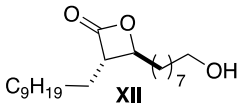
***trans*-4-(8-*tert*-Butyldimethylsilyloxy)octanyl-3-decyloxetan-2-one (XI).** (*Z/E*)-4-(8-*tert*-Butyldimethylsilyloxy)octanyl-3-decanylideneoxetan-2-one (**X**) (0.34 g, 0.77 mmol) was dissolved in THF:MeOH (10.3 mL, 8.5:1.8). This solution was cooled to –10 ºC, followed by the addition of $CoCl_2(PPh_3)_2$ (0.10 g, 0.15 mmol) and then portion-wise addition of $NaBH_4$ (0.17 g, 4.5 mmol) within 10 min. The mixture was vigorously stirred at –7 to −5 ºC for 2 h. The reaction mixture was filtered through a pad of celite, and the celite was washed with $CHCl_3$ (10 mL). The filtrate was washed with 2M HCl (10 mL), dried ($MgSO_4$) and concentrated. The ^{1}H NMR *trans*:*cis* ratio of the crude reaction mixture was 2:1. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc 49:1) provided **XI** as a colorless oil (0.24 g, 71%). The *trans*-isomer was separable by careful column chromatography using the same solvent system. *trans*-**XI** colorless oil (0.16 g, 47%): IR (neat) 2925, 2854, 1822, 1463, 1254, 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (ddd, *J* = 7.2, 6.0, 4.0 Hz, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 3.17 (ddd, *J* = 8.8, 6.6, 4.0 Hz, 1H), 1.91–1.77 (m, 2H), 1.76–1.64 (m, 2H), 1.55–1.46 (m, 2H), 1.45–1.22 (m, 26H), 0.89 (s, 9H), 0.90–0.86 (m, 3H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 78.4, 63.5, 56.4, 34.7, 33.0, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 28.1, 27.2, 26.0, 25.2, 22.9, 18.6, 14.3, –5.1; HRMS (ESI) calcd for $C_{27}H_{55}O_3Si$ $(M + H)^+$ *m/z* 455.3909, found 455.3926.

Preparation of β-lactones **9** and **10**.



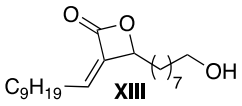
General procedure for cleavage of silyl protecting group.

Pyridinium *p*-toluenesulfonate (PPTS) (0.3 equiv) was added to a solution of silyl ether (1.0 equiv, 0.07 M in EtOH/DCM, 1:1). The resulting mixture was then stirred in a pre-heated oil bath (55 °C) for 3 h. The reaction was allowed to cool to rt. Et_3N (10 volumes) was added, and the reaction mixture was concentrated. The crude product was purified by flash column chromatography on silica gel.



***trans*-3-Decyl-4-(8-hydroxy)octanyloxetan-2-one (XII).** The general procedure was followed using *trans*-4-(8-*tert*-butyldimethylsilyloxy)octanyl-3-decyloxetan-2-one (*trans*-**XI**) (0.13 g, 0.28 mmol). Purification by flash column chromatography on silica gel (hexanes/EtOAc 5:1) provided

XII as a colorless oil (47 mg, 50%): IR (neat) 3332 (br), 2919, 2851, 1794, 1467, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.24–4.17 (m, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 3.19–3.11 (m, 1H), 1.90–1.76 (m, 2H), 1.76–1.61 (m, 2H), 1.60–1.50 (m, 2H), 1.48–1.20 (m, 27H), 0.87 (t, *J* = 5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 78.4, 63.2, 56.4, 34.6, 32.9, 32.1, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 28.1, 27.2, 25.9, 25.2, 22.9, 14.3; HRMS (ESI) calcd for $C_{21}H_{41}O_3$ $(M + H)^+$ *m/z* 341.3056, found 341.3079.



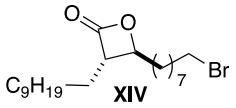
XIII

(*Z*)-3-Decylidene-4-(8-hydroxy)octanyloxetan-2-one (XIII). The general procedure was followed using (*Z*)-4-(8-*tert*-butyldimethylsilyloxy)octanyl-3-decanylideneoxetan-2-one (*Z*-**X**) (0.27 g, 0.59 mmol). Purification by flash column chromatography on silica gel (hexanes/EtOAc 5:1) provided **XIII** as a colorless oil (0.20 g, 98%): IR (neat) 3378 (br), 2923, 2854, 1802, 1464, 1146, 1112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (td, *J* = 7.9, 1.2 Hz, 1H), 4.88–4.82 (m, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.56–2.41 (m, 2H), 1.85–1.75 (m, 2H), 1.61–1.52 (m, 2H), 1.50–1.41 (m, 2H), 1.40–1.17 (m, 23H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 137.6, 136.5, 78.8, 63.2, 33.9, 32.9, 32.1, 29.7, 29.5, 29.5, 29.4, 29.4, 29.2, 29.1, 29.0, 25.9, 24.8, 22.9, 14.3; HRMS (ESI) calcd for $C_{21}H_{39}O_3$ $(M + H)^+$ *m/z* 339.2899, found 339.2895.

General procedure for Appel bromination.

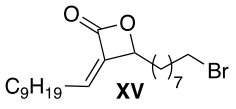
Tetrabromomethane (CBr_4) (1.5 equiv) and triphenylphosphine (PPh_3) (3 equiv) were added to a solution of the alcohol (1 equiv, 0.03 M in DCM) at 0 °C). After 1 h, the reaction mixture was diluted with petroleum ether (~5 volumes). The resultant precipitate was filtered and washed with

petroleum ether, and the filtrate was concentrated. The crude product was adsorbed onto silica gel (dry loaded) and purified by flash column chromatography on silica gel to give the bromide.



XIV

***trans*-4-(8-Bromo)ocatanyl-3-decyloxetan-2-one (XIV).** The general procedure was followed using *trans*-3-decyl-4-(8-hydroxy)octanyloxetan-2-one (**XII**) (0.10 g, 0.31 mmol). Purification by flash column chromatography on silica gel (hexanes/EtOAc 49:1) provided **XIV** as a colorless oil (0.12 g, 95%): IR (neat) 2924, 2854, 1822, 1464, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.19 (ddd, *J* = 7.2, 6.0, 4.1 Hz, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 3.15 (ddd, *J* = 8.8, 6.6, 4.0 Hz, 1H), 1.89–1.77 (m, 4H), 1.76–1.18 (m, 28H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 78.2, 56.3, 34.6, 34.1, 32.9, 32.0, 29.7, 29.7, 29.4, 29.4, 29.3, 28.7, 28.2, 28.0, 27.1, 25.2, 22.8, 14.3; HRMS (ESI) calcd for $C_{21}H_{40}BrO_2$ $(M + Na)^+$ *m/z* 425.2020, found 425.2011.

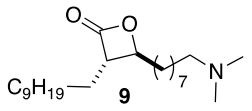


XV

(*Z*)-4-(8-Bromo)octanyl-3-decanylideneoxetan-2-one (XV). The general procedure was followed using (*Z*)-3-decylidene-4-(8-hydroxy)octanyloxetan-2-one (**XIII**) (0.20 g, 0.58 mmol). Purification by flash column chromatography on silica gel (hexanes/EtOAc 98:2) provided **XV** as a colorless oil (96 mg, 41%): IR (neat) 2923, 2854, 1804, 1463, 1115, 1066 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 7.9, 7.9, 1.0 Hz, 1H), 4.87–4.80 (m, 1H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.55–2.40 (m, 2H), 1.88–1.74 (m, 4H), 1.50–1.37 (m, 4H), 1.36–1.18 (m, 20H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 137.6, 136.5, 78.7, 34.1, 33.9, 32.9, 32.0, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.3, 24.7, 22.8, 14.3; HRMS (ESI) calcd for $C_{21}H_{38}BrO_2$ $(M + H)^+$ *m/z* 401.2055, found 401.2033.

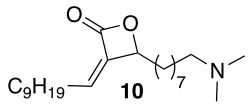
General procedure for nucleophilic substitution with dimethylamine.

Dimethylamine in H_2O (40%, 1.0 equiv) and $NaHCO_3$ (1.0 equiv) were added to a solution of the bromide (1.0 equiv, 0.05 M in DMF), and the mixture was heated at reflux while stirring for 24 h. The mixture was then allowed to cool to rt, concentrated. The crude product was dissolved in DCM (20 volumes relative to bromide solution), and the solution was washed with H_2O (20 volumes relative to bromide solution x 2). The organic layer was dried (Na_2SO_4) and concentrated, and the residue was purified by flash column chromatography on silica gel.



9

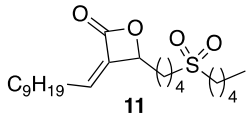
***trans*-3-Decyl-4-(8-dimethylamino)octanyloxetan-2-one (9).** The general procedure was followed using *trans*-4-(8-bromo)ocatanyl-3-decyloxetan-2-one (**XIV**) (0.04 g, 0.099 mmol). Purification by flash column chromatography on silica gel (NH_4OH/MeOH/$CHCl_3$ 2:4.5:175) provided **9** as a brown oil (12 mg, 33%): IR (neat) 2923, 2853, 1823, 1624, 1464, 1118 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.21 (ddd, J = 7.2, 5.9, 4.0 Hz, 1H), 3.16 (t, J = 6.8 Hz, 2H), 3.15 (ddd, J = 8.8, 6.6, 4.0 Hz, 1H), 2.35–2.25 (m, 2H), 2.28 (s, 6H), 1.89–1.77 (m, 2H), 1.76–1.65 (m, 2H), 1.53–1.20 (m, 26H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 78.4, 59.9, 56.4, 45.4, 34.7, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 28.1, 27.5, 27.2, 25.3, 22.9, 14.3; HRMS (ESI) calcd for $C_{23}H_{46}NO_2$ $(M + H)^+$ *m/z* 368.3518, found 368.3525.



10

(*Z*)-3-Decanylidene-4-(8-dimethylamino)octanyloxetan-2-one (10). The general procedure was followed using (*Z*)-4-(8-bromo)octanyl-3-decanylideneoxetan-2-one (**XV**) (0.16 g, 0.41 mmol). Purification by flash column chromatography on silica gel (NH_4OH/MeOH/$CHCl_3$ 2:4.5:175) provided **10** as a brown oil (55 mg, 37%): IR (neat) 2926, 2855, 1806, 1713, 1215 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ□5.84 (ddd, *J* = 7.9, 7.9, 1.1 Hz, 1H), 4.86–4.80 (m, 1H), 2.56–2.41 (m, 2H), 2.44 (s, 6H), 1.78 (app q, *J* = 7.4 Hz, 2H), 1.66–1.55 (m, 2H), 1.49–1.37 (m, 4H), 1.36–1.18 (m, 22H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 137.5, 136.6, 78.8, 59.3, 44.6, 33.9, 32.0, 29.6, 29.5, 29.4, 29.4, 29.2, 29.1, 29.0, 27.2, 26.5, 24.7, 22.8, 14.3; HRMS (ESI) calcd for $C_{23}H_{44}NO_2$ $(M + H)^+$ *m/z* 366.3372, found 366.3375.

Preparation of sulfone 11 and sulfoxides 12 and 13.



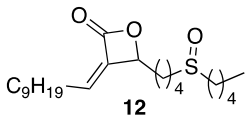
11

(*Z*)-3-Decylidene-4-(4-(pentylsulfonyl)butyl)oxetan-2-one (11). (*Z*)-3-Decylidene-4-(4-(pentyl-thio)butyl)oxetan-2-one (**1**) (12 mg, 0.03 mmol) was transferred into an NMR tube and CD_3OD (~0.6 mL) was added. Peroxyacetic acid (32% in acetic acid, 2.2 eq) was added. The solution was mixed and left overnight. The next day, the reaction was complete based on ^1H NMR. The solution was concentrated, and the residue was purified by a short column chromatography (Pasteur pipette) (CH_2Cl_2/MeOH 98:2) on silica gel. Compound **11** was isolated as a colorless oil (8 mg, 64%): IR (neat) 2954, 2916, 2850, 1800, 1780, 1465, 1126, 804, 767, 593, 498 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.37 (td, *J* = 7.9, 1.5 Hz, 1H), 4.88–4.85 (m, 1H), 2.96 (t, *J* = 6.5 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.55–2.43 (m, 2H), 1.94–1.79 (m, 6H), 1.69–1.61 (m, 2H), 1.47–1.35 (m, 6H), 1.31–1.25 (m, 12H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 163.8, 137.0, 137.0, 77.8, 53.1, 52.2, 33.2, 31.9, 30.6, 29.5, 29.3, 29.3, 29.1, 29.0, 28.8, 23.8, 22.7, 22.2, 21.7, 21.6, 14.1, 13.7; HRMS (ESI) calcd for $C_{22}H_{41}O_4S$ $(M + H)^+$ *m/z* 401.2726, found 401.2718.

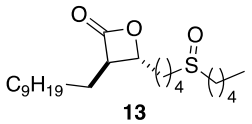
General procedure for the preparation of sulfoxides 12 and 13.

The thioether (~0.03 mmol) was transferred to an NMR tube and CD_3OD (~0.6 mL) was added. H_2O_2 (30% in H_2O, 0.06 mmol) was then added. The reagents were mixed, and the solution was left overnight. The next day, the reaction was complete based on ^1H NMR. The solution was concentrated, and the residue was purified by column chromatography (Pasteur pipette) on silica gel.



12

(*Z*)-3-Decylidene-4-(4-(pentane-1-sulfinyl)butyl)oxetan-2-one (**12**)**.** Purification (CH_2Cl_2/-MeOH 99:1) provided **12** as a light-yellow oil (8 mg, 73% – ~1:1 mixture of diastereomers): IR (neat) 2923, 2854, 1807, 1459, 1407,1080, 908, 816, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.87 (td, 6.2, 1.8 Hz, 1H), 4.89–4.85 (m, 1H), 2.73–2.59 (m, 4H), 2.53–2.45 (m, 2H), 1.94–1.82 (m, 4H), 1.80–1.73 (m, 2H), 1.49–1.35 (m, 6H), 1.33–1.26 (m, 14H), 0.92 (t, *J* = 6.2 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 137.3, 137.2, 137.1, 137.0, 78.2, 78.1, 52.9, 52.8, 52.2, 52.2, 33.6, 33.5, 32.1, 31.2, 29.7, 29.5, 29.5, 29.2, 29.2, 29.0, 24.3, 24.1, 22.9, 22.7, 22.6, 22.5, 22.5, 14.3, 14.0; HRMS (ESI) calcd for $C_{22}H_{41}O_3S$ $(M + H)^+$ *m/z* 385.2776, found 385.2746.



13

(*trans*)-3-Decyl-4-(4-(pentane-1-sulfinyl)butyl)oxetan-2-one (13). Purification (CH_2Cl_2/MeOH 99:1) provided **13** as a white solid (17 mg, 58% – ~1:1 mixture of diastereomers): IR (neat) 2921, 2853, 1806, 1465, 1136, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.23 (ddd, *J* = 7.8, 7.8, 4.2 Hz, 1H), 3.19 (ddd, *J* = 8.7, 6.6, 3.9 Hz, 1H), 2.74–2.66 (m, 2H), 2.65–2.60 (m, 2H), 1.88–1.58 (m, 10H), 1.49–1.35 (m, 6H), 1.34–1.26 (m, 14H), 0.92 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 77.6, 77.5, 56.3, 56.3, 52.7, 52.0, 34.2, 34.1, 31.9, 31.0, 29.6, 29.5, 29.3, 29.3, 27.8, 27.0, 24.6, 24.5, 22.7, 22.4, 22.4, 22.3, 22.3, 14.1, 13.8; HRMS (ESI) calcd for $C_{22}H_{43}O_3S$ $(M + H)^+$ *m/z* 387.2933, found 387.2905.

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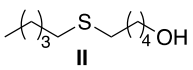
NMR Spectra



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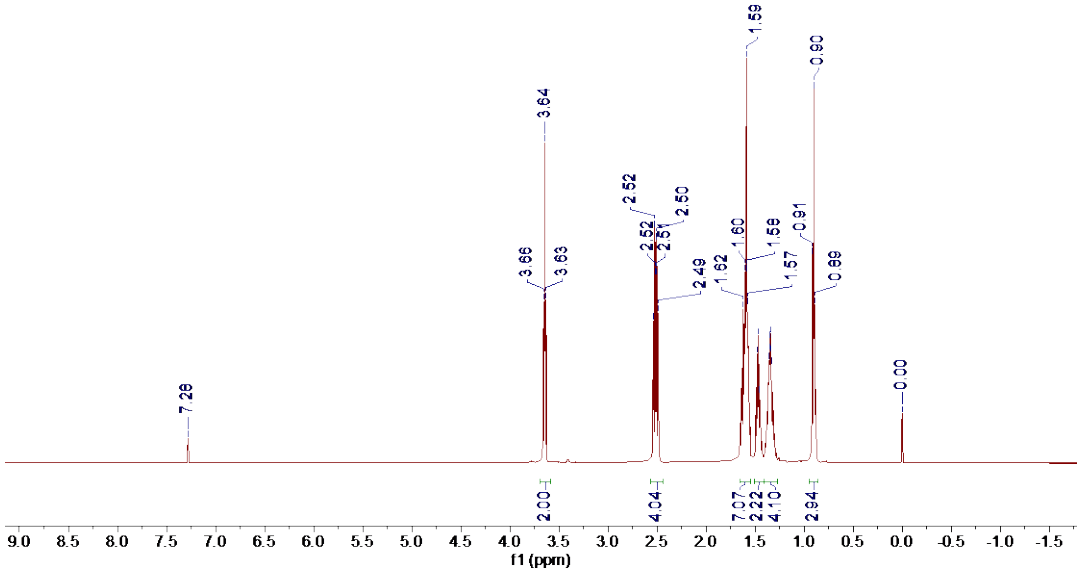

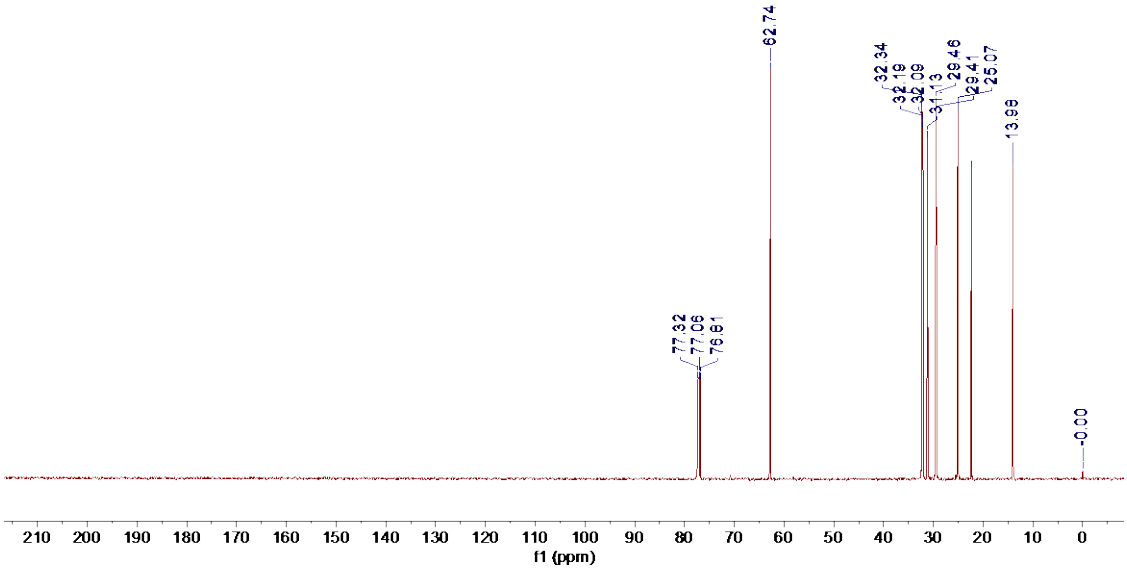

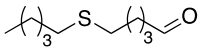

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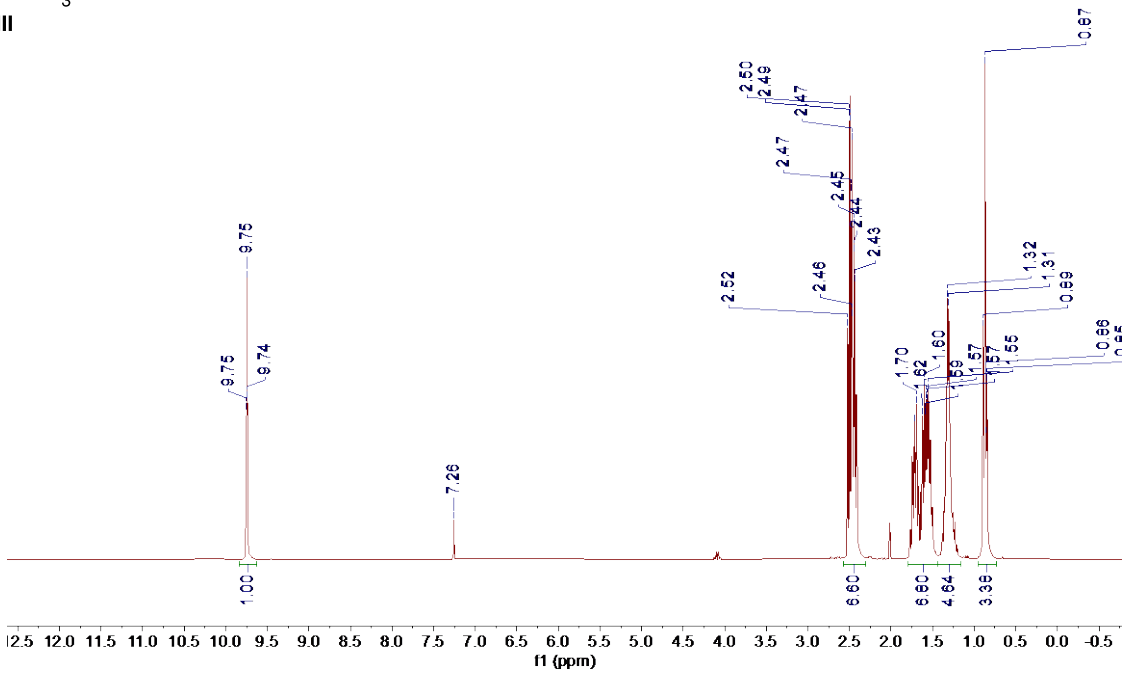
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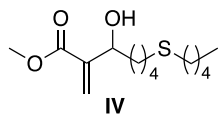
2.50
2.49
2.47
2.47
2.46
2.45
2.44
2.43
1.70
1.62
1.60
1.59
1.57
1.57
1.55
1.32
1.31
0.89
0.87
1.00
6.60
6.80
4.84
3.38
f1 (ppm)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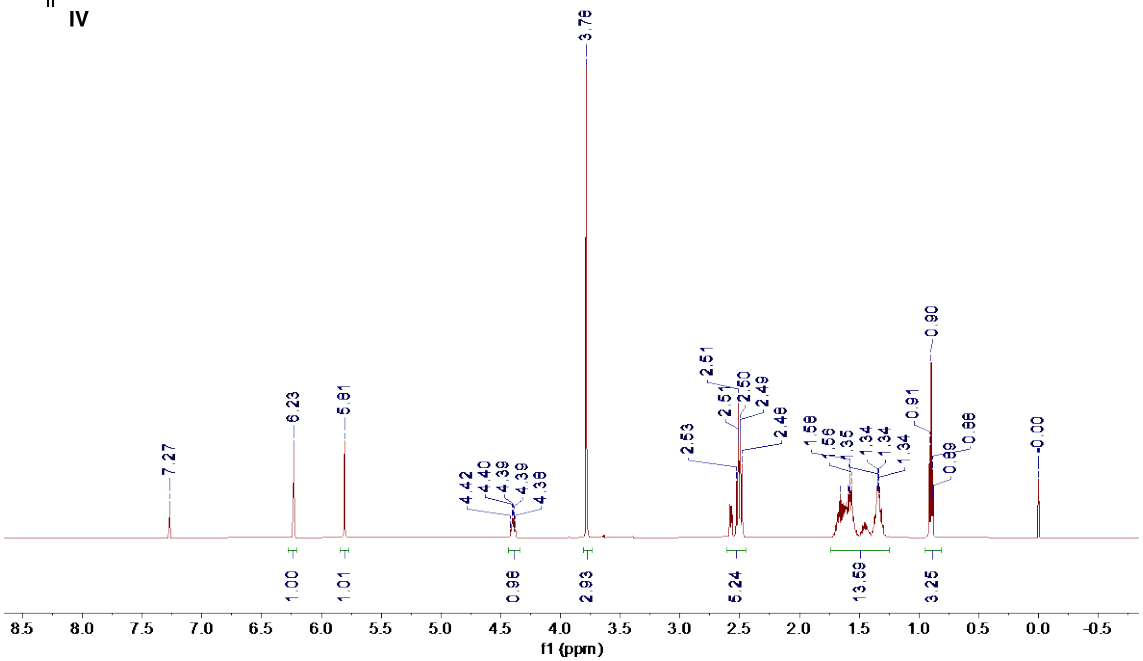
OH
O
S
4
4

IV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4.40
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4.38
3.76
2.53
2.51
2.51
2.50
2.49
2.48
1.59
1.56
1.35
1.34
1.34
1.34
0.91
0.90
0.89
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1.01
0.96
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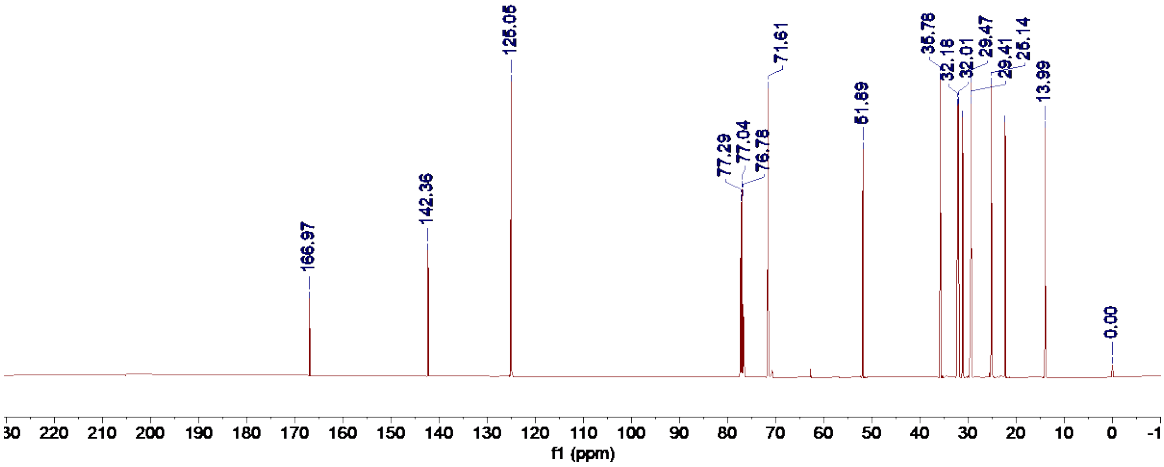
3.25
f1 (ppm)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125.05
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71.61
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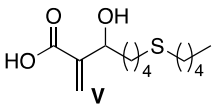
29.47
29.41
25.14
13.99
0.00
f1 (ppm)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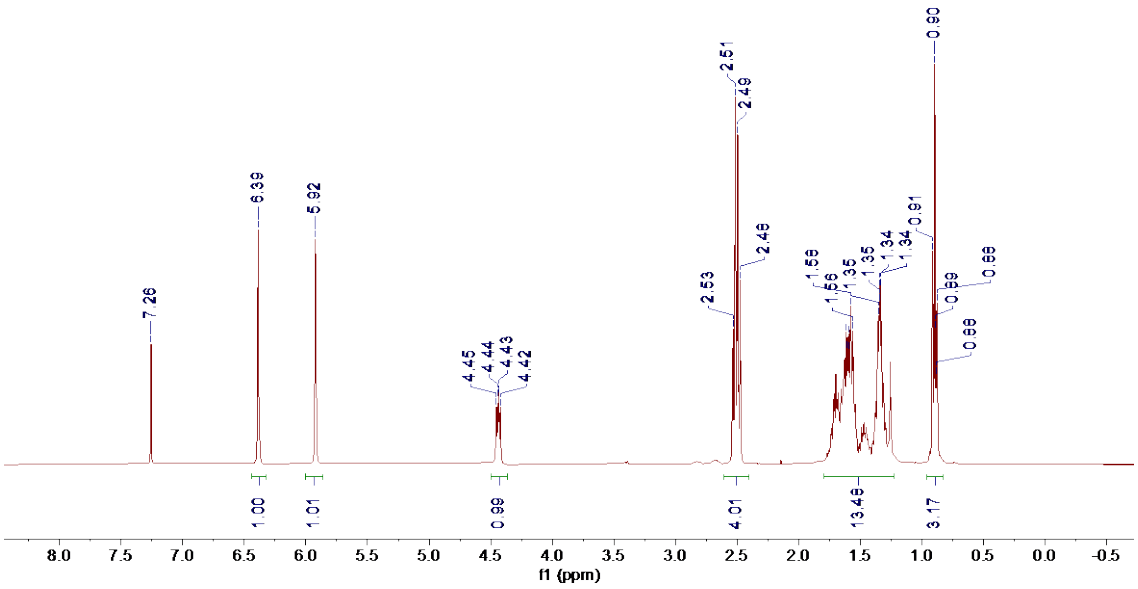
OH
HO
S
4
4

V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1.55
1.35
1.34
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0.89
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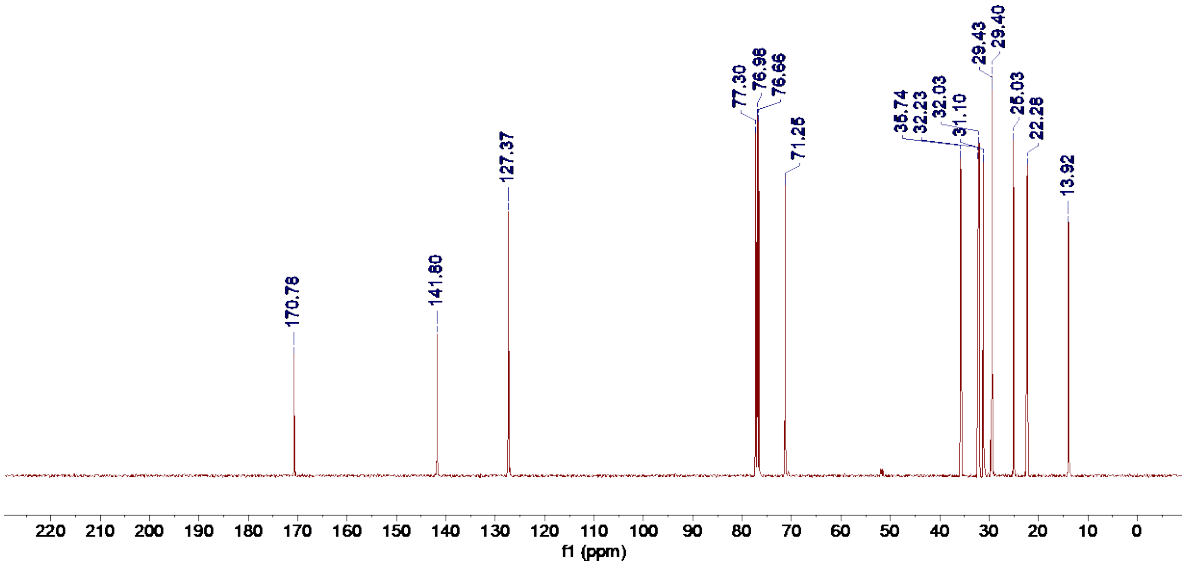
0.99
4.01
13.49
3.17
f1 (ppm)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31.10
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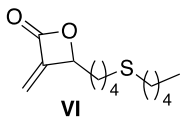
29.40
25.03
22.28
13.92
f1 (ppm)



VI

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5.95
5.48
5.47
5.01
5.00
4.99
4.98
2.57
2.55
2.53
2.52
2.58
1.92
1.91
1.63
1.61
1.38
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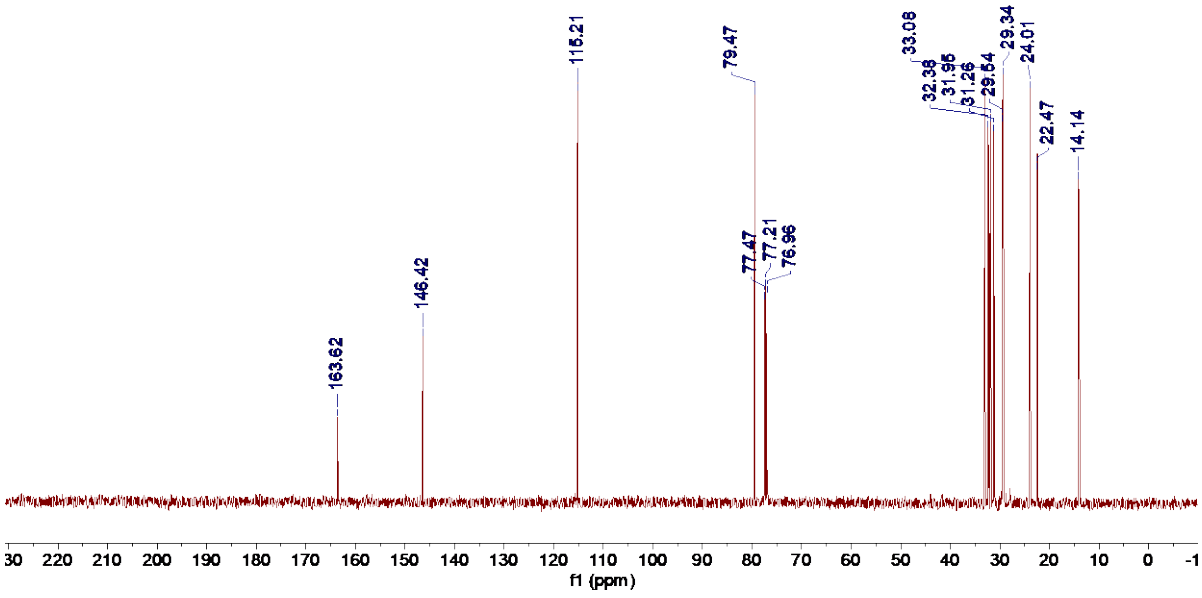
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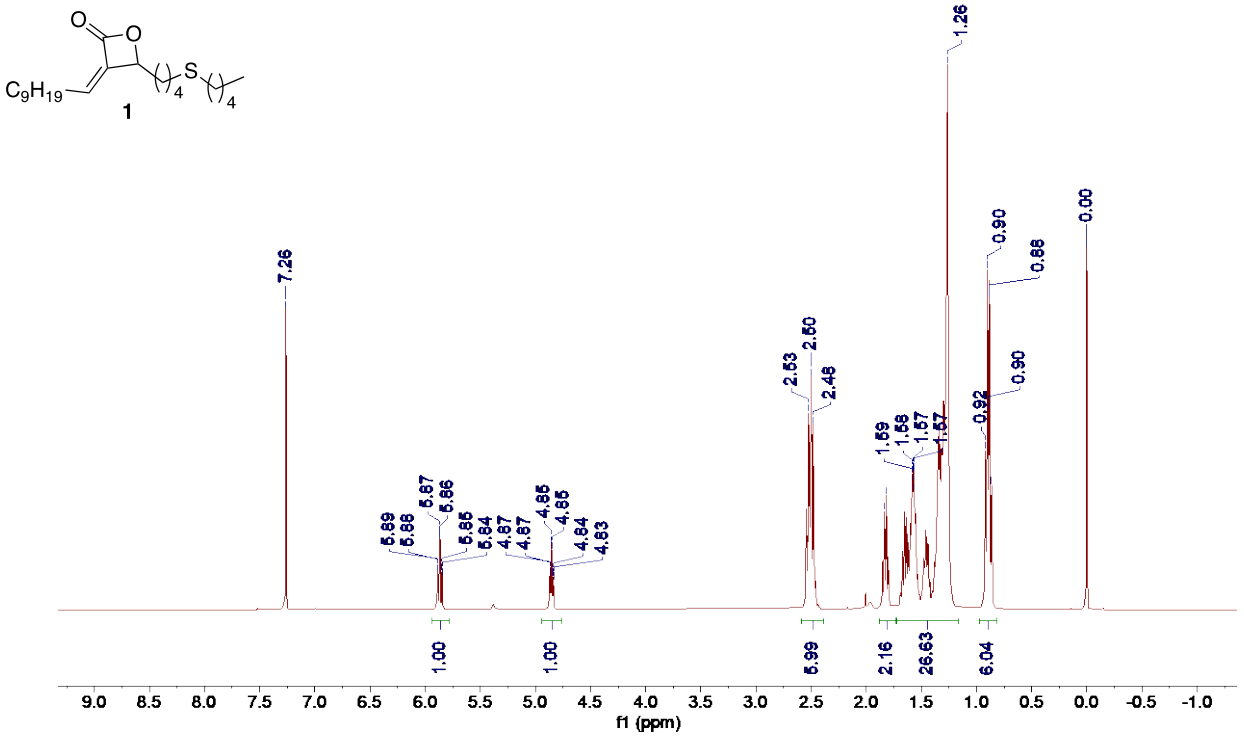
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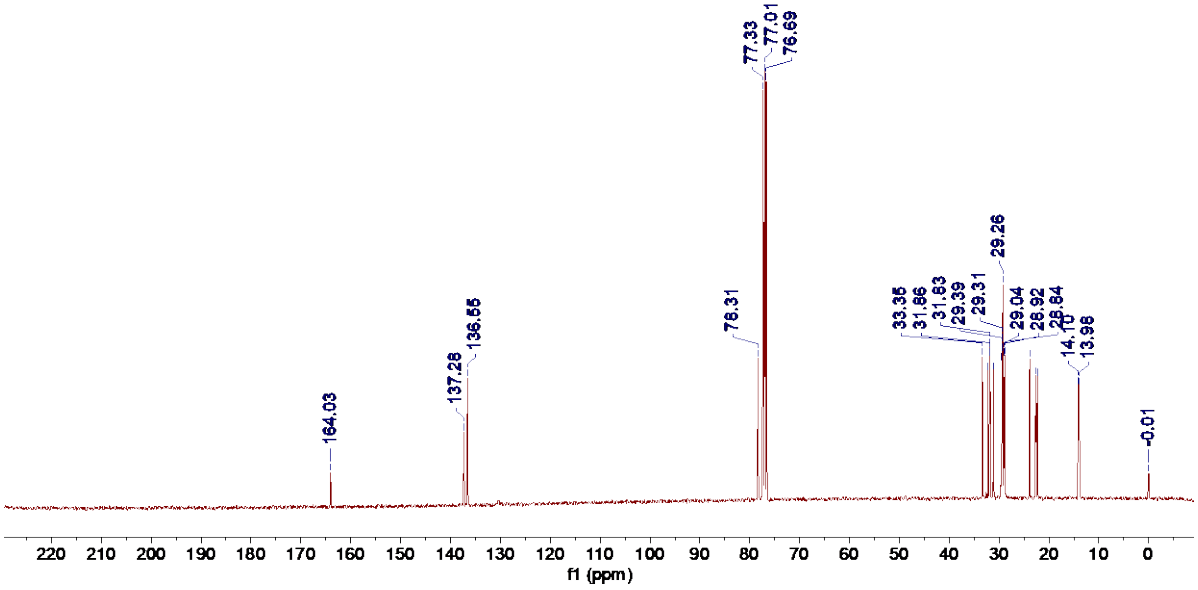
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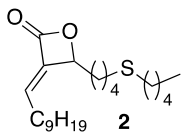
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S
C_9H_{19}

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2.52
2.51
2.50
2.49
2.11
1.60
1.59
1.59
1.58
1.57
1.27
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0.90
0.89
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1.00
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1.08
1.16
6.99
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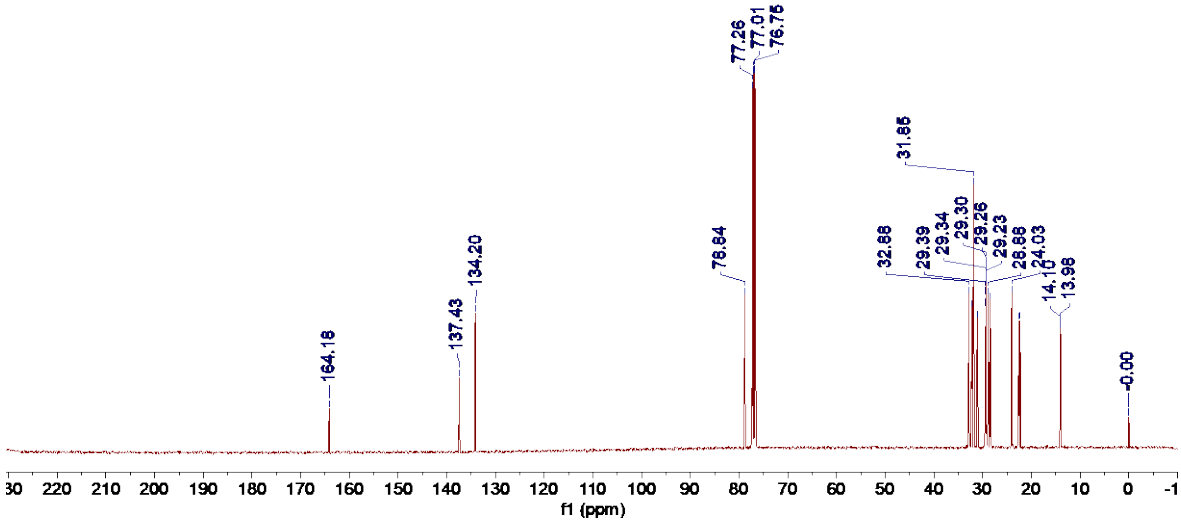
f1 (ppm)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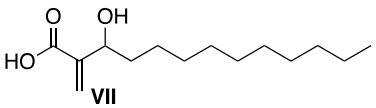
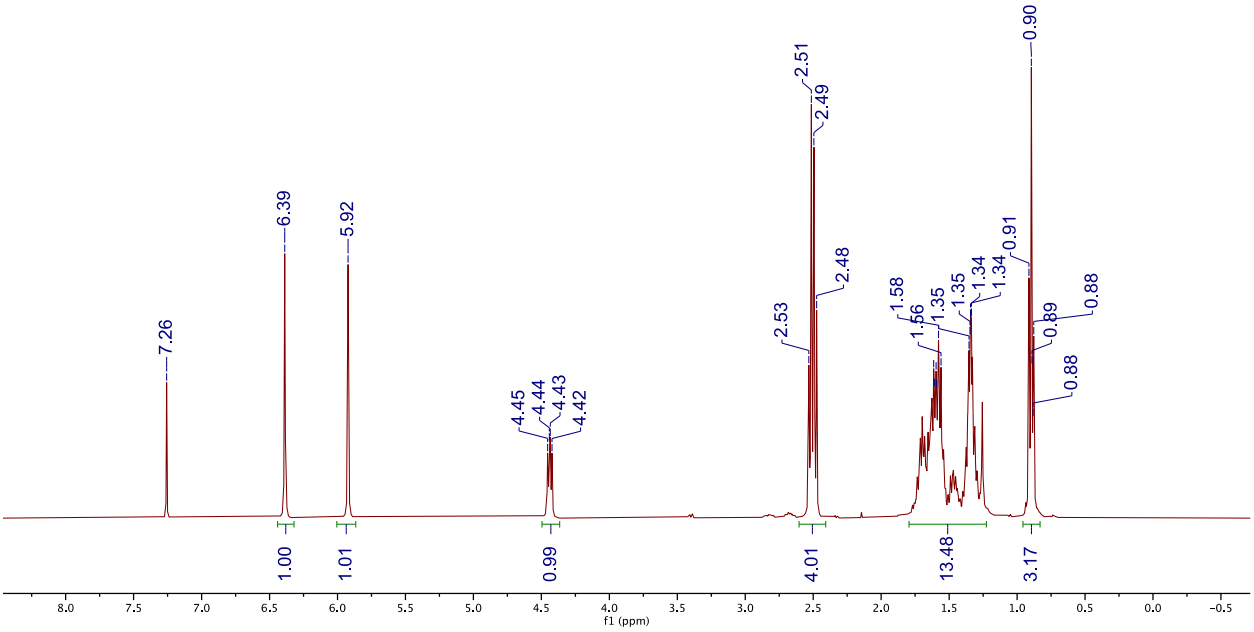
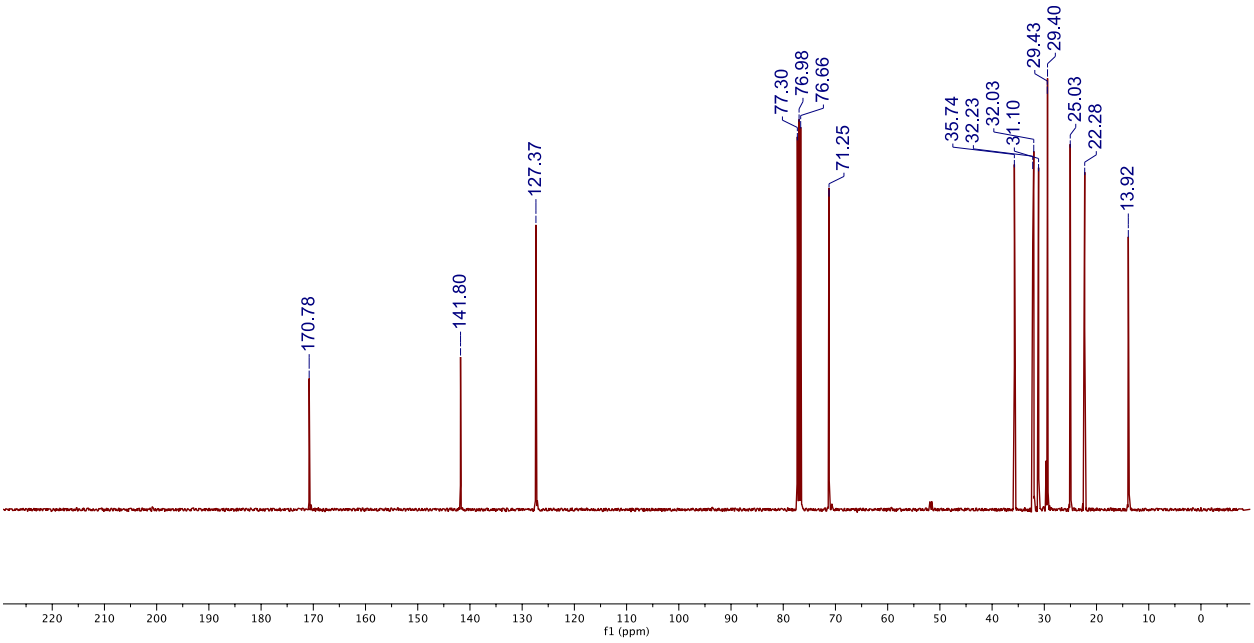
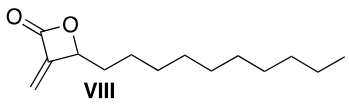
24.03
14.10
13.98
-0.00
f1 (ppm)


O
OH
HO

VII

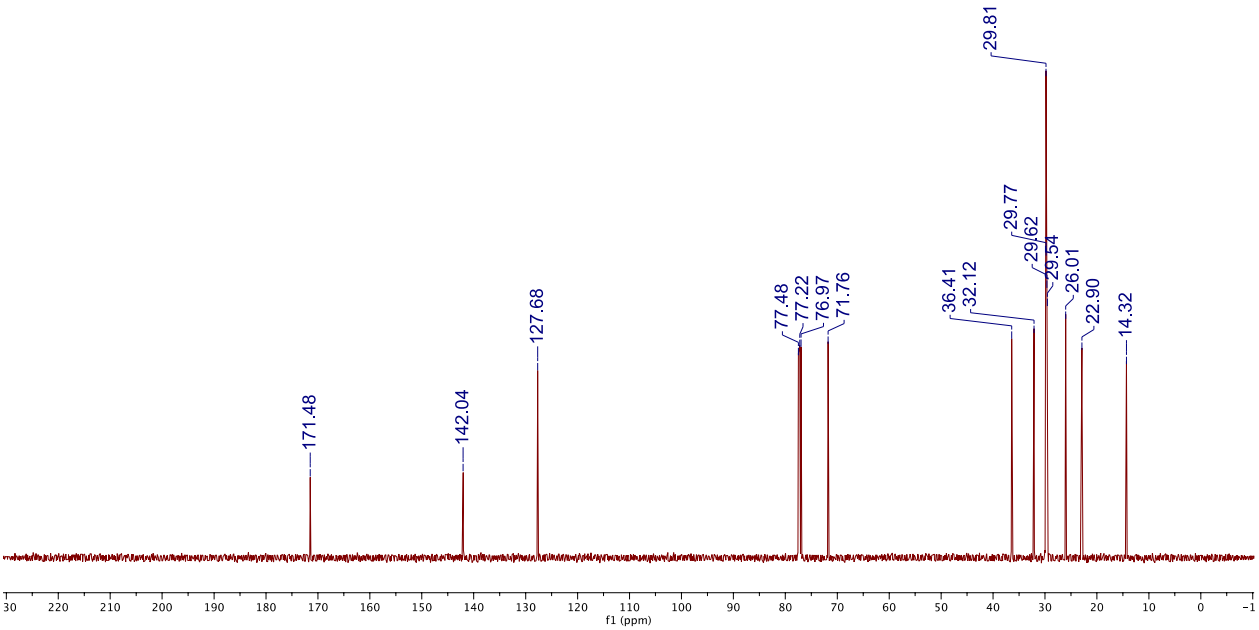

7.26
6.39
5.92
4.45
4.44
4.43
4.42
2.53
2.51
2.49
2.48
1.58
1.56
1.35
1.34
1.34
0.91
0.90
0.89
0.88
0.88
1.00
1.01
0.99
4.01
13.48
3.17
f1 (ppm)


170.78
141.80
127.37
77.30
76.98
76.66
71.25
35.74
32.23
32.03
31.10
29.43
29.40
25.03
22.28
13.92
f1 (ppm)



VIII

1.26
0.87
6.39
5.91
0.89
0.86
7.26
4.44
4.42
4.41
1.68
1.67
1.66
1.43
1.00
1.00
0.96
1.93
1.12
15.20
2.98
f1 (ppm)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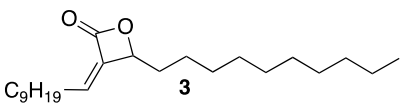
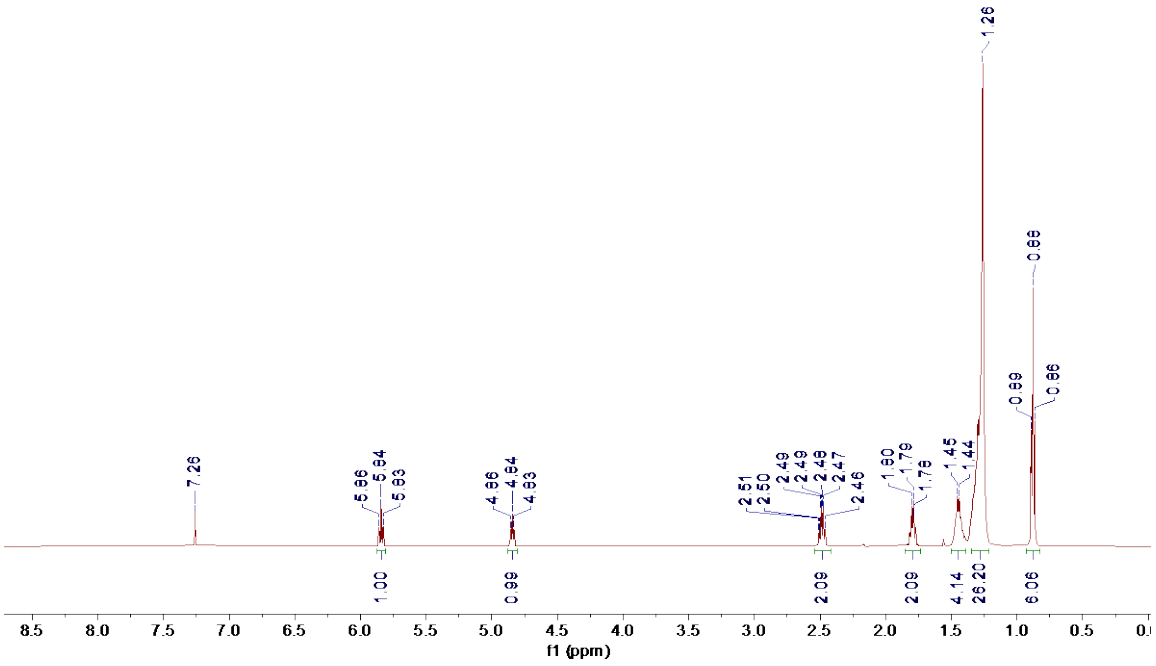
29.77
29.62
29.54
26.01
22.90
14.32
36.41
32.12
77.48
77.22
76.97
71.76
127.68
171.48
142.04
f1 (ppm)


O
O
C_9H_{19}

3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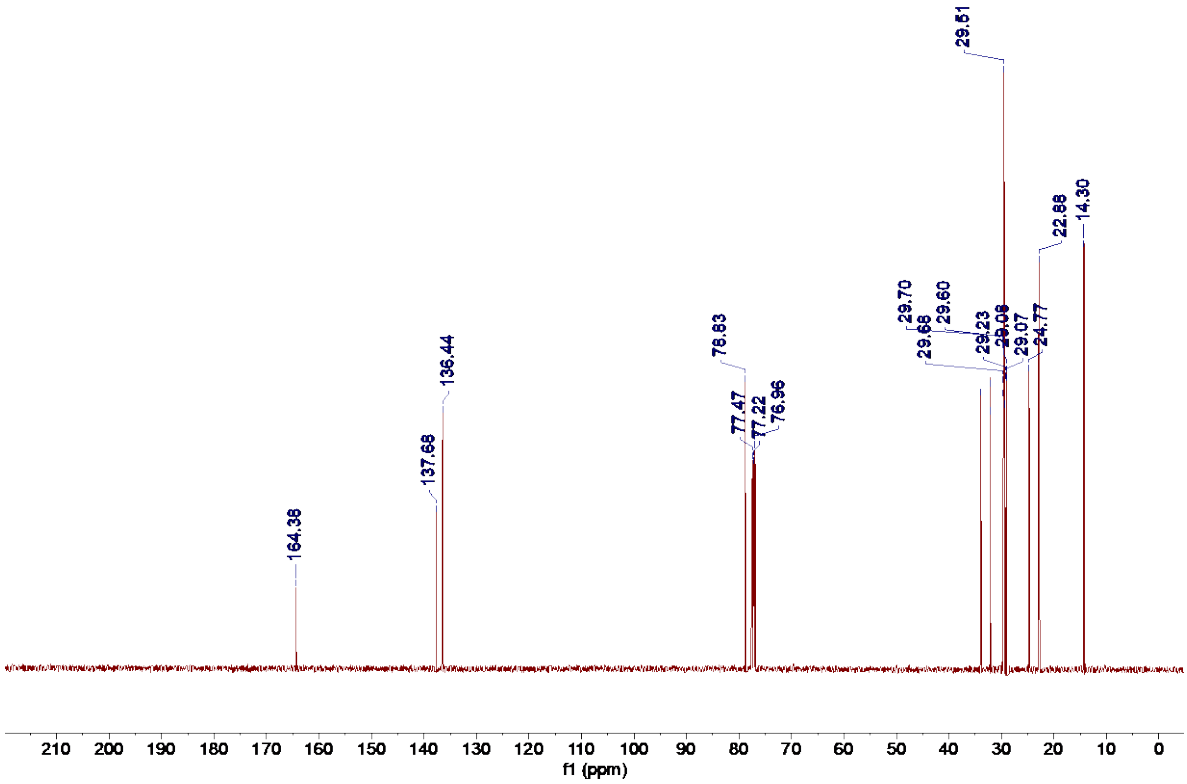
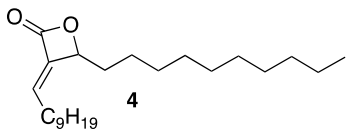
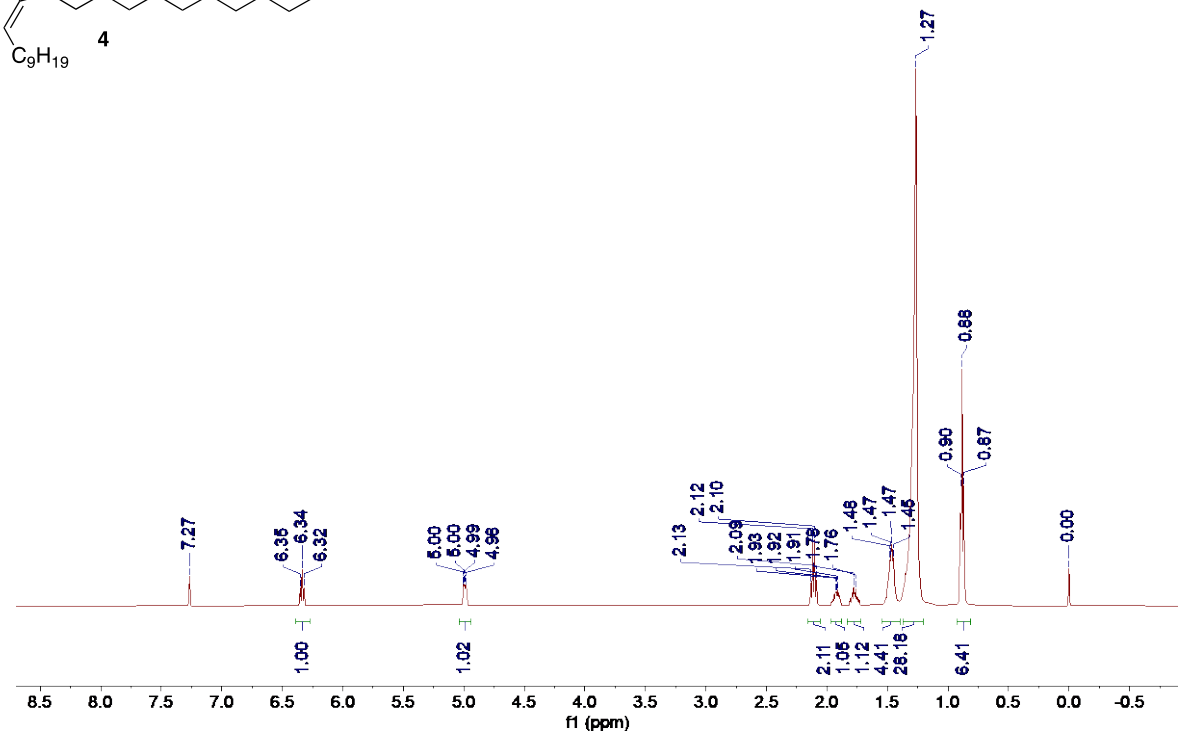
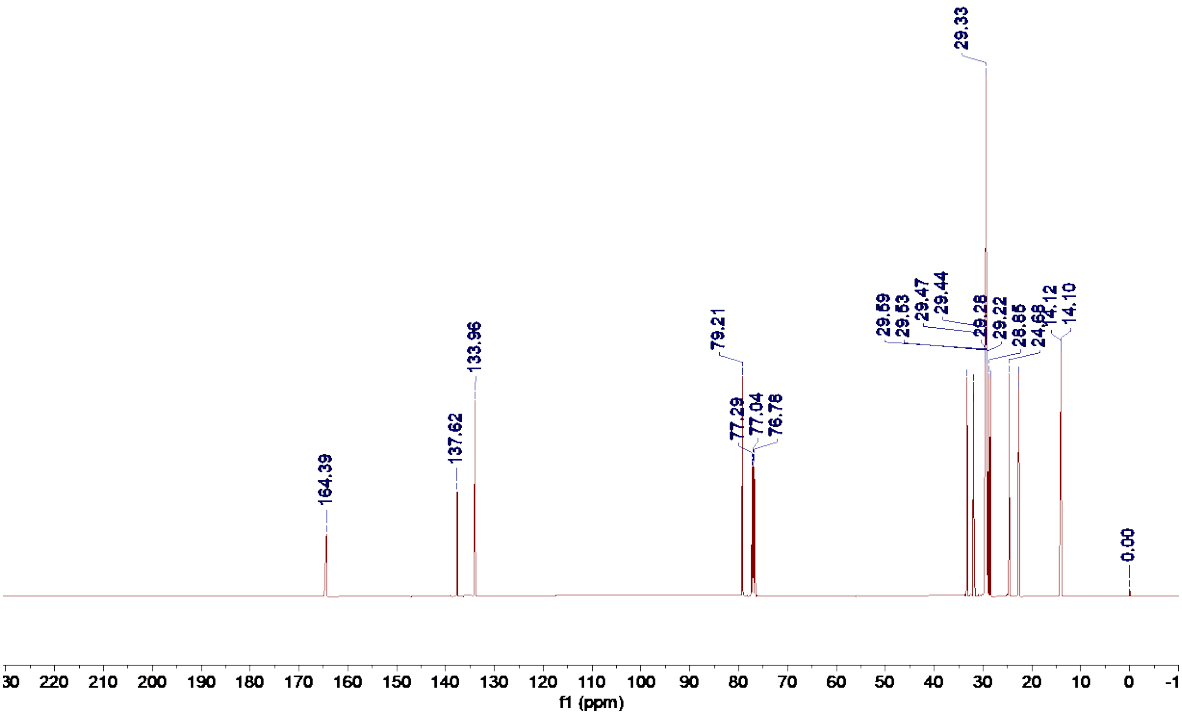
5.96
5.94
5.93
4.96
4.94
4.93
2.51
2.50
2.49
2.49
2.48
2.47
2.46
1.80
1.79
1.78
1.45
1.44
1.26
0.89
0.86
1.00
0.99
2.09
2.09
4.14
26.20
6.06
f1 (ppm)


164.38
137.68
136.44
78.83
77.47
77.22
76.96
29.51
29.70
29.60
29.68
29.23
29.08
29.07
24.77
22.88
14.30
f1 (ppm)


O
O
C9H19

4


7.27
6.35
6.34
6.32
5.00
5.00
4.99
4.98
2.13
2.12
2.10
2.09
1.93
1.92
1.91
1.78
1.76
1.48
1.47
1.47
1.45
1.27
0.90
0.88
0.87
0.00
1.00
1.02
2.11
1.05
1.12
4.41
28.18
6.41
f1 (ppm)


164.39
137.62
133.96
79.21
77.29
77.04
76.78
29.59
29.53
29.47
29.44
29.33
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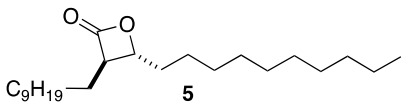
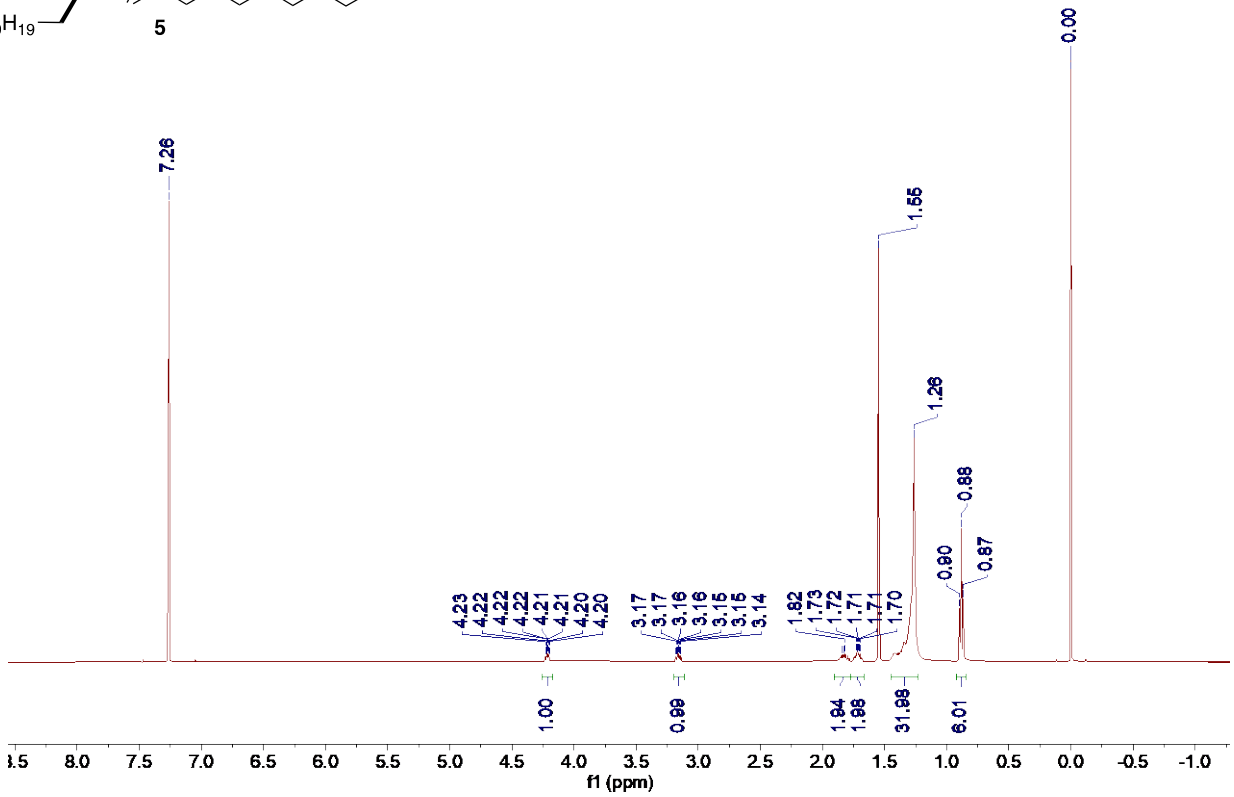
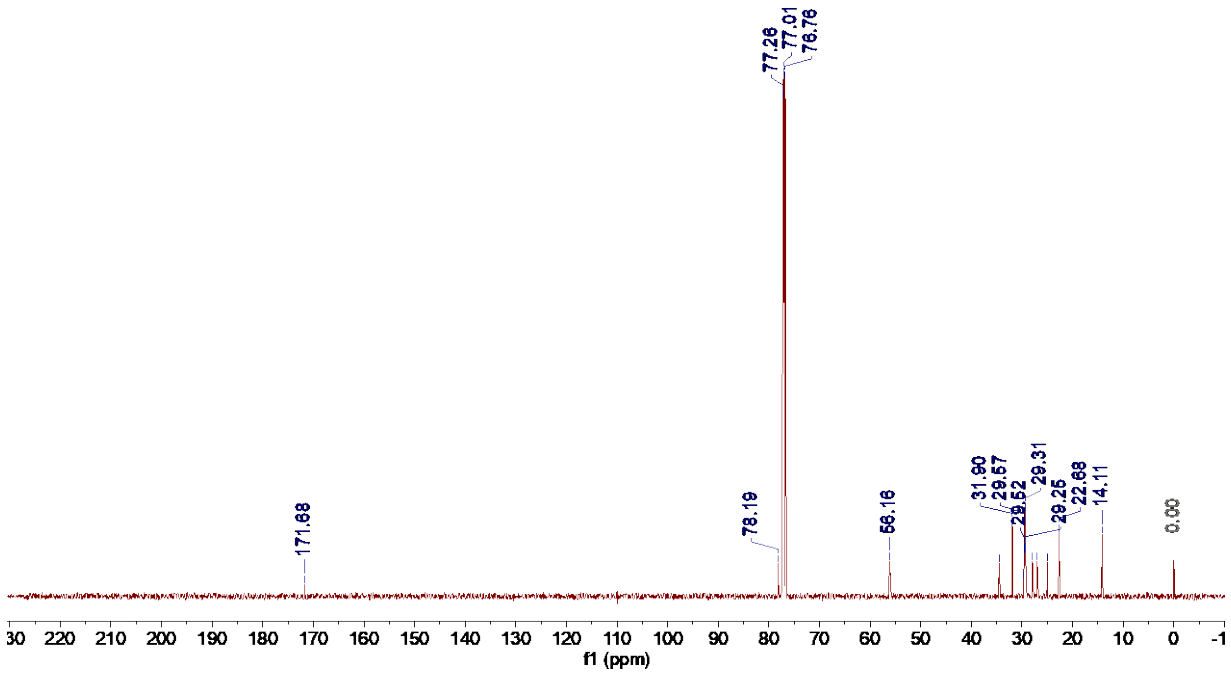
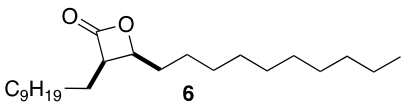
24.88
14.12
14.10
0.00
f1 (ppm)


O
O
C_9H_{19}

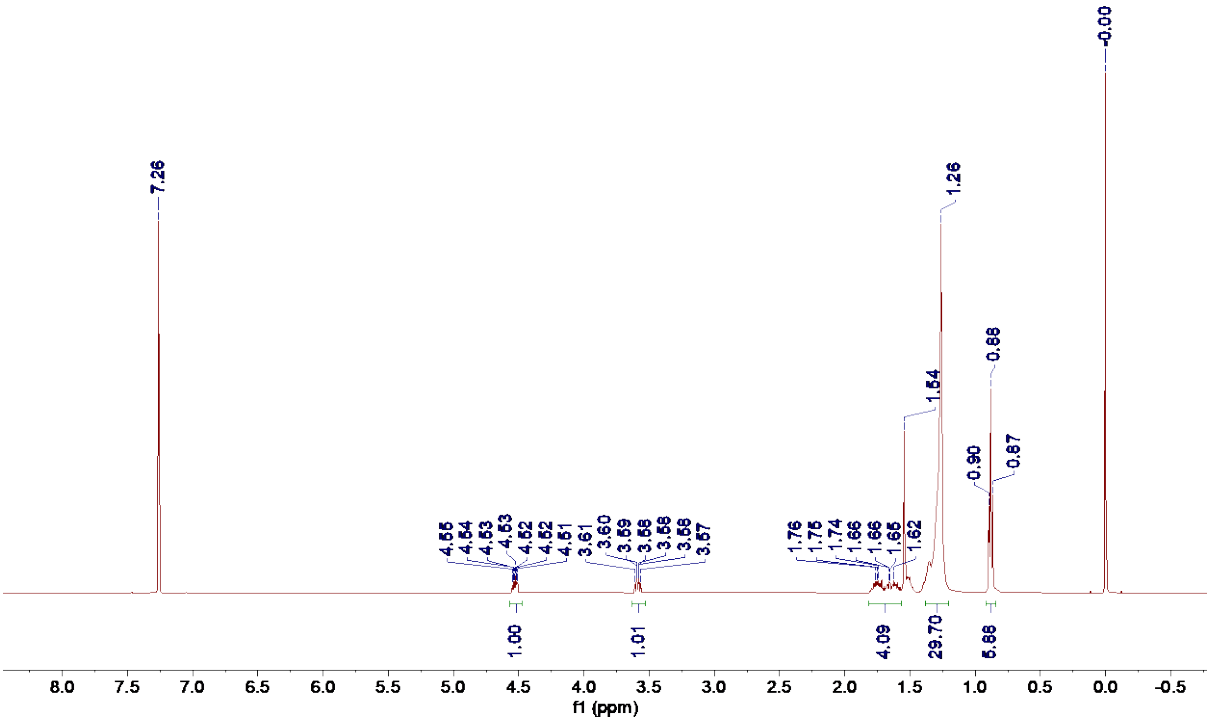
5


7.26
4.23
4.22
4.22
4.22
4.21
4.21
4.20
4.20
3.17
3.17
3.16
3.16
3.15
3.15
3.14
1.82
1.73
1.72
1.71
1.71
1.70
1.55
1.26
0.90
0.88
0.87
0.00
1.00
0.99
1.84
1.98
31.98
6.01
f1 (ppm)


171.68
78.19
77.26
77.01
76.76
56.16
31.90
29.67
29.52
29.31
29.25
22.68
14.11
0.00
f1 (ppm)


O
O
C_9H_{19}

6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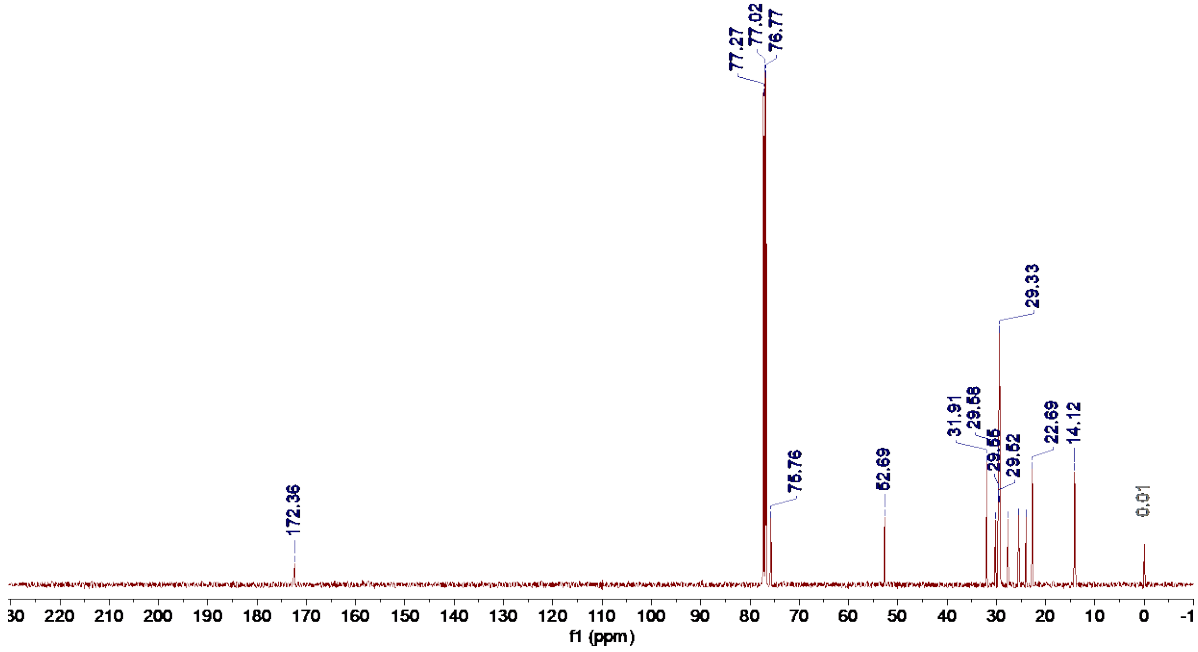
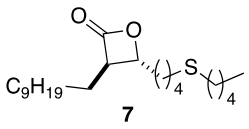
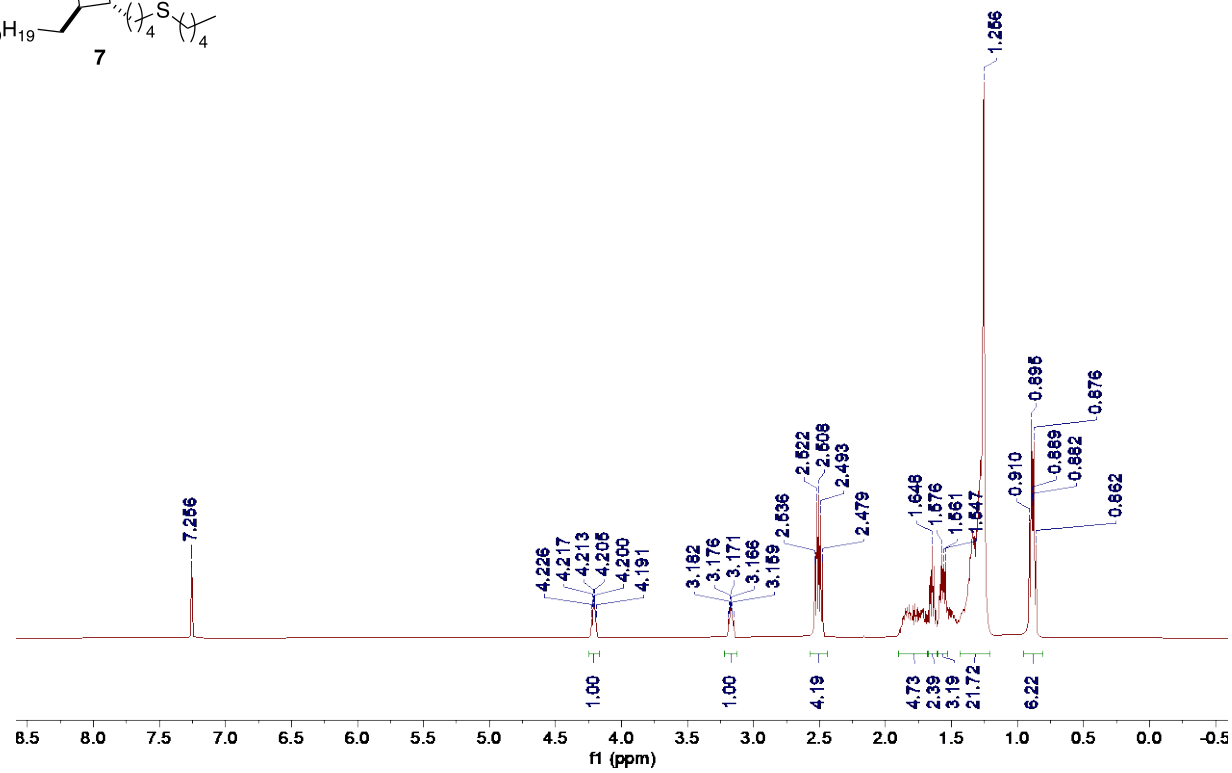
4.55
4.54
4.53
4.53
4.52
4.52
4.51
3.61
3.60
3.59
3.58
3.58
3.57
1.76
1.75
1.74
1.66
1.66
1.65
1.62
1.54
1.26
0.90
0.88
0.87
0.00
1.00
1.01
4.09
29.70
5.88
f1 (ppm)


77.27
77.02
76.77
172.36
76.76
62.69
31.91
29.58
29.55
29.52
29.33
22.69
14.12
0.01
f1 (ppm)


O
O
C_9H_{19}
S
$)_4$
$)_4$

7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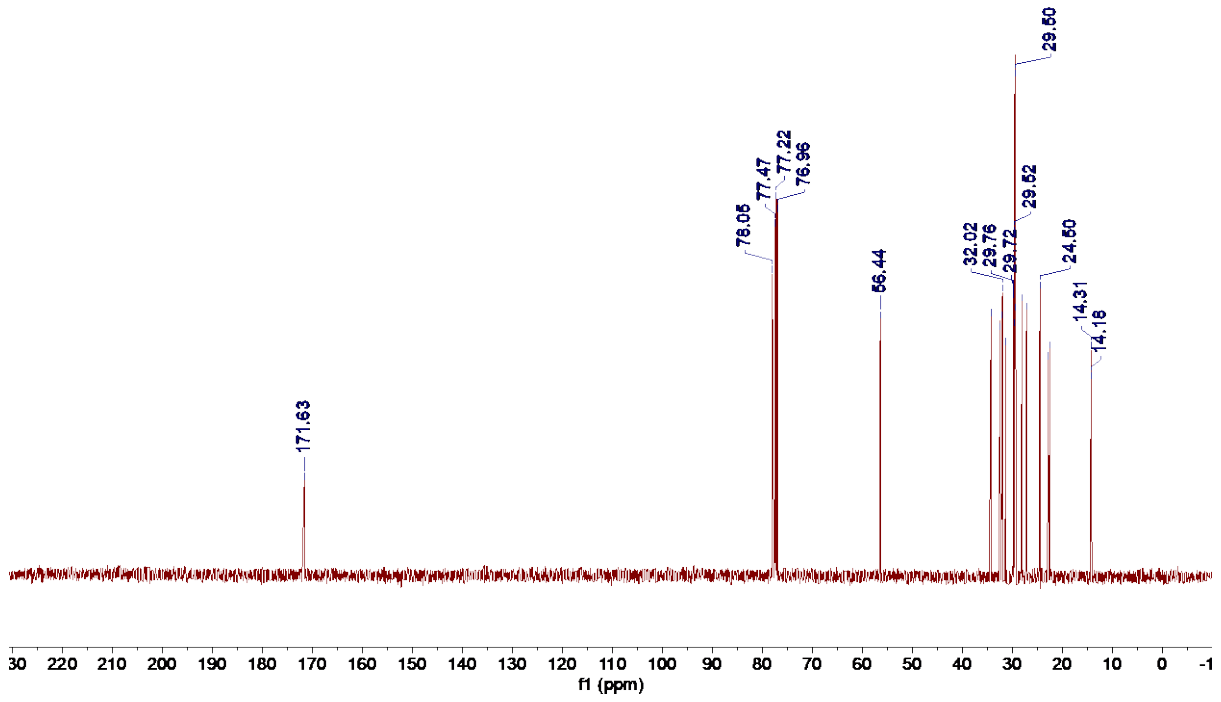
4.217
4.213
4.205
4.200
4.191
3.182
3.176
3.171
3.166
3.159
2.536
2.522
2.508
2.493
2.479
1.646
1.576
1.561
1.547
1.256
0.910
0.895
0.876
0.869
0.862
1.00
1.00
4.19
4.73
2.39
3.19
21.72
6.22
f1 (ppm)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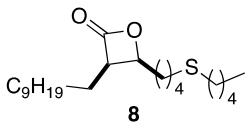
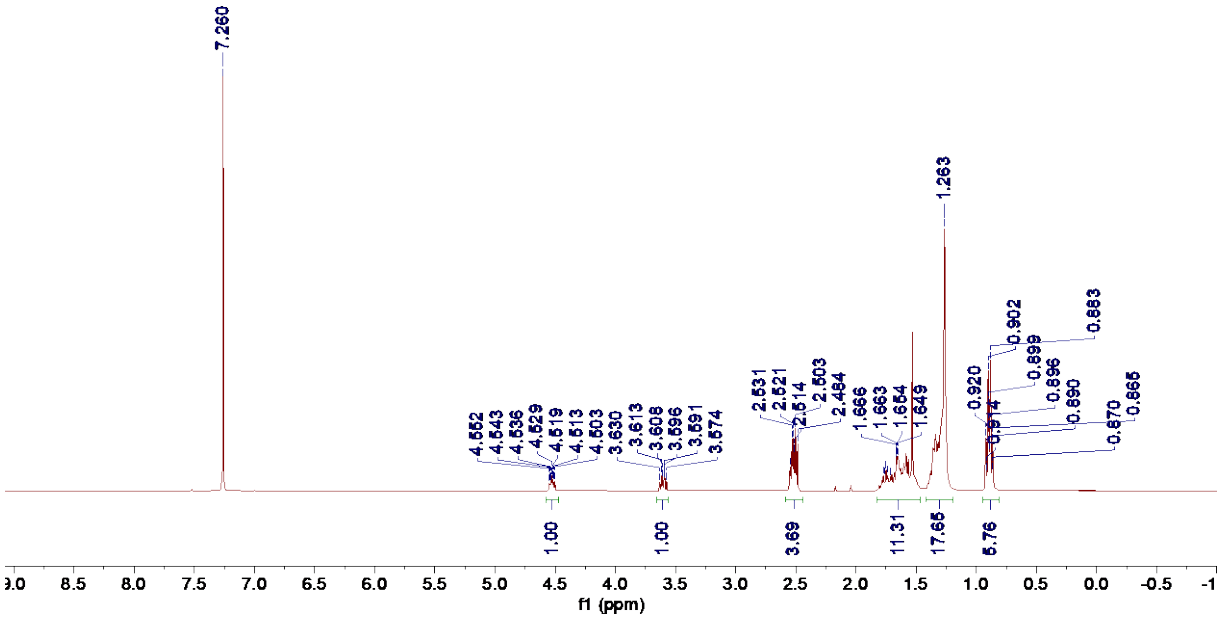
78.05
77.47
77.22
76.96
56.44
32.02
29.76
29.72
29.50
29.52
24.50
14.31
14.18
f1 (ppm)


O
O
S
C_9H_{19}
4
4

8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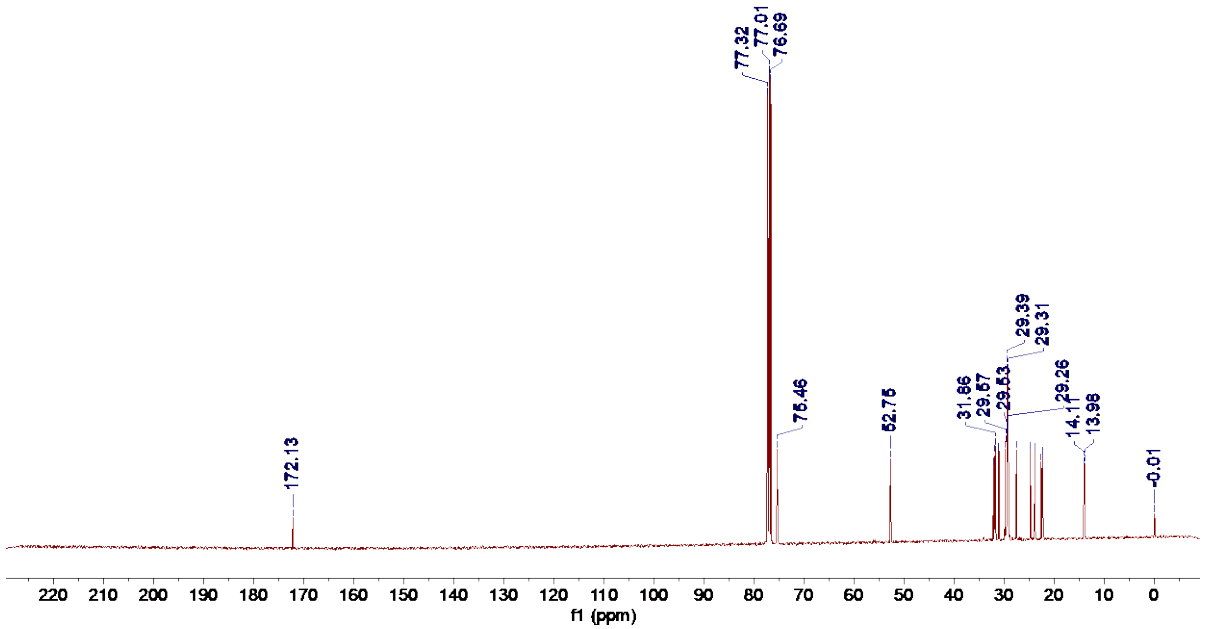
4.543
4.536
4.529
4.519
4.513
4.503
3.630
3.613
3.608
3.596
3.591
3.574
2.531
2.521
2.514
2.503
2.484
1.666
1.663
1.654
1.649
1.263
0.920
0.902
0.899
0.896
0.890
0.883
0.874
0.870
0.865
1.00
1.00
3.69
11.31
17.65
5.76
f1 (ppm)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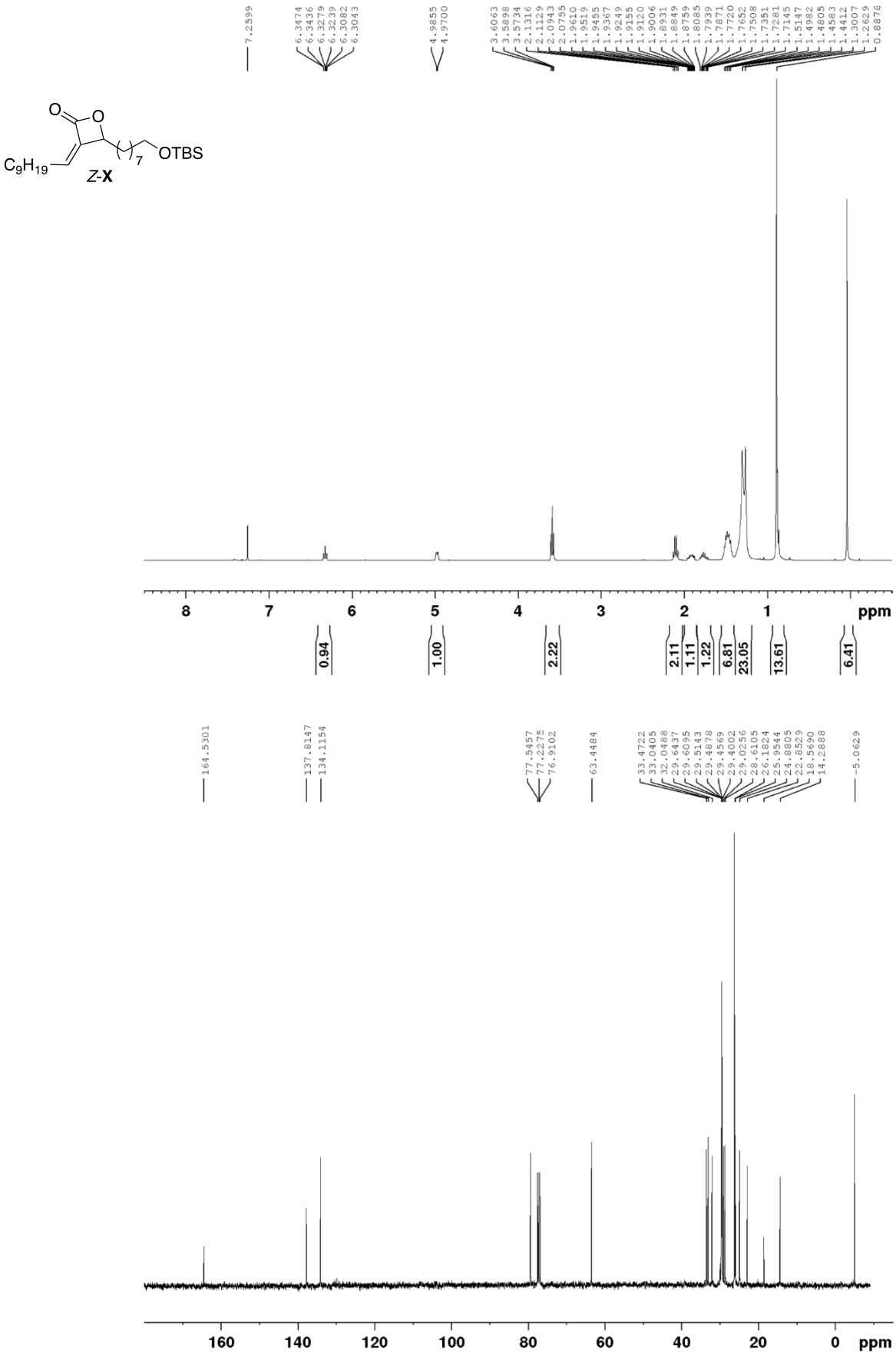
29.57
29.53
29.39
29.31
29.26
14.11
13.98
-0.01
f1 (ppm)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6.3239
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6.3043
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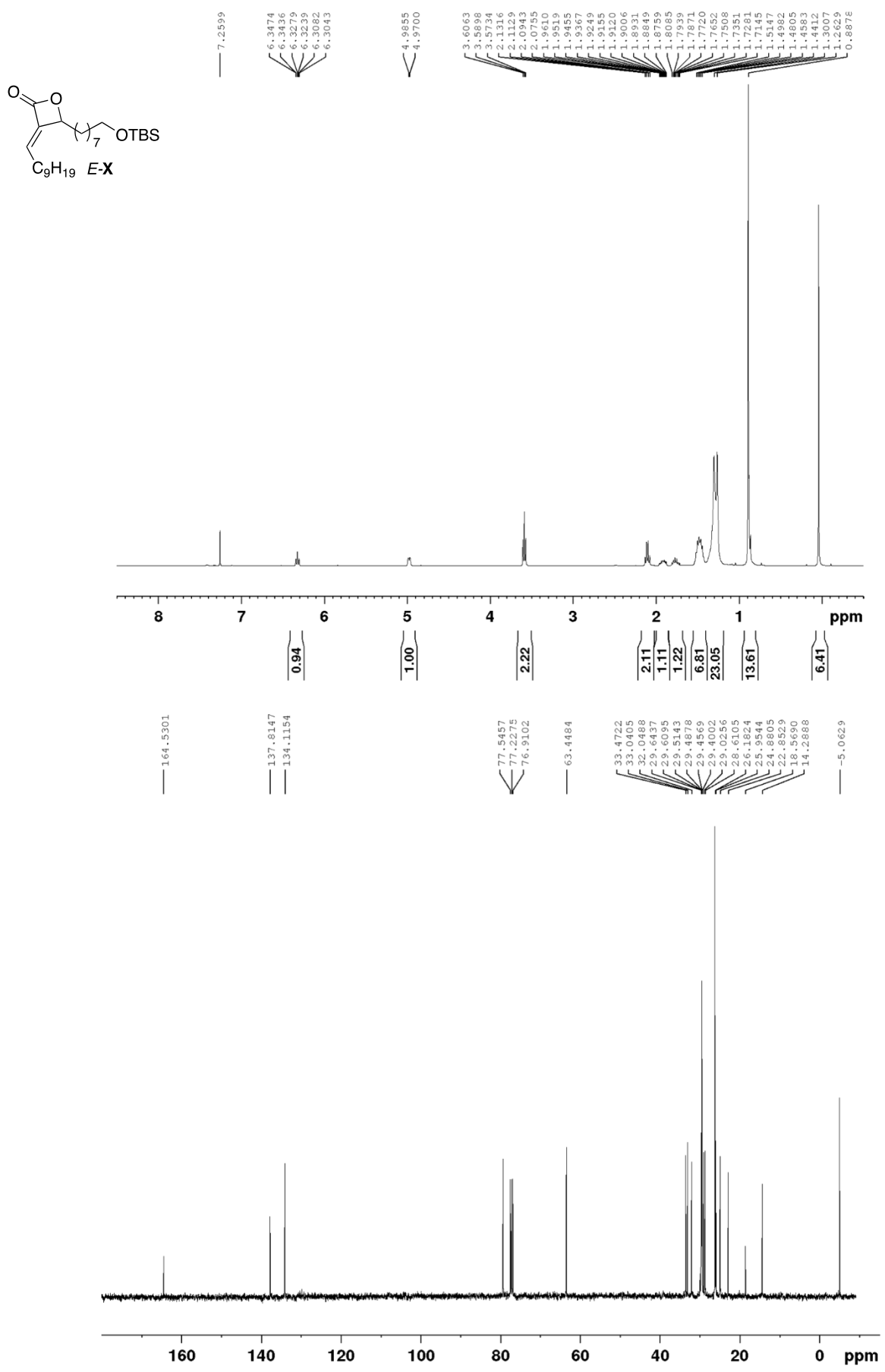
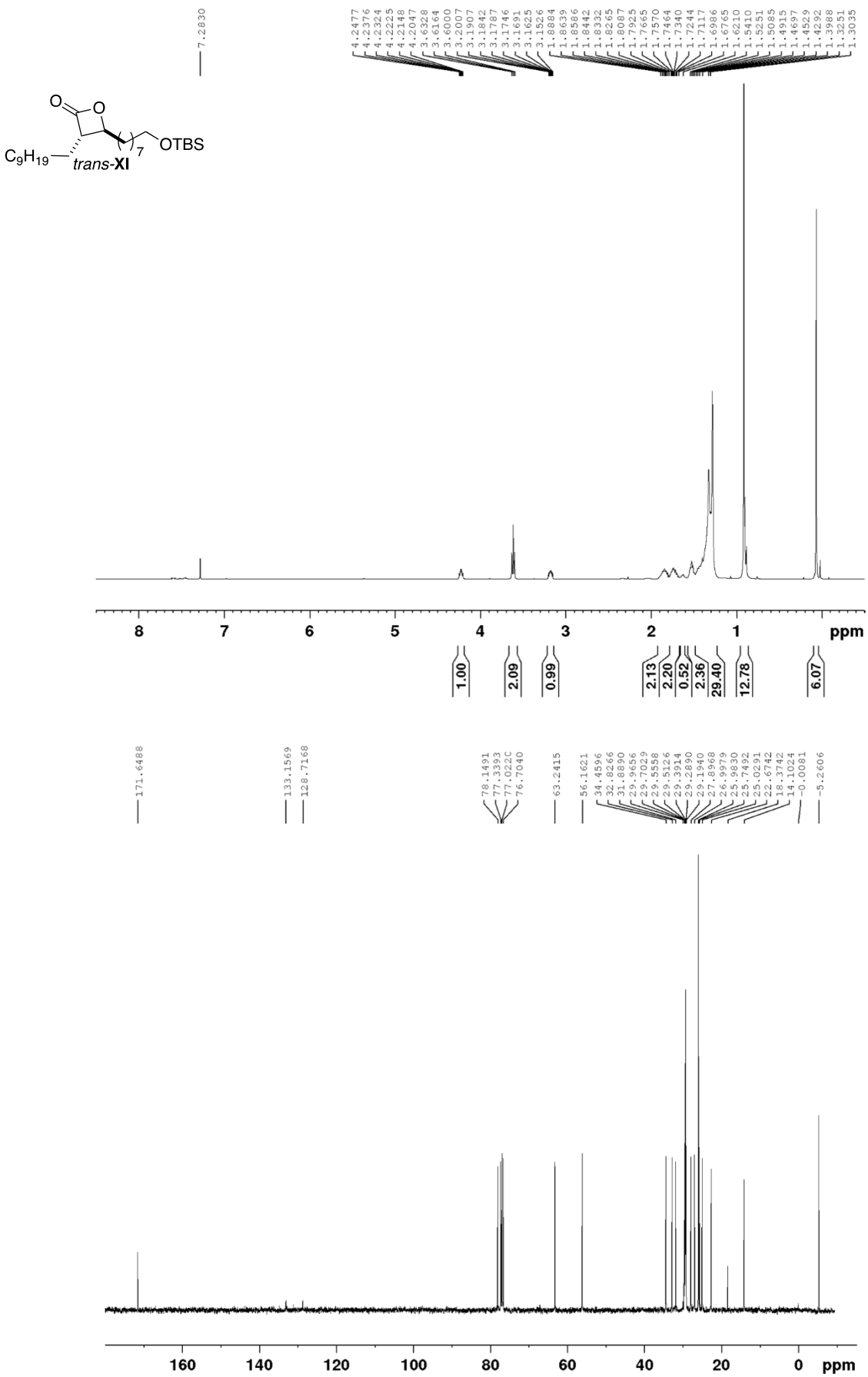
4.9700
3.6063
3.5898
3.5734
2.1316
2.1129
2.0943
2.0755
1.9610
1.9519
1.9455
1.9367
1.9249
1.9155
1.9120
1.9006
1.8931
1.8849
1.8759
1.8085
1.7939
1.7871
1.7720
1.7652
1.7508
1.7351
1.7281
1.7145
1.5147
1.4982
1.4805
1.4583
1.4412
1.3007
1.2629
0.8876
O
O
C9H19
7
OTBS
Z-X
8
7
6
5
4
3
2
1
ppm
0.94
1.00
2.22
2.11
1.11
1.22
6.81
23.05
13.61
6.41
164.5301
137.8147
134.1154
77.5457
77.2275
76.9102
63.4484
33.4722
33.0405
32.0488
29.6437
29.6095
29.5143
29.4678
29.4569
29.4002
29.0256
28.6105
26.1824
25.9544
24.8805
22.8529
18.5690
14.2888
-5.0629
160
140
120
100
80
60
40
20
0
ppm


O
O
7
OTBS
C9H19 E-X
7.2599
6.3474
6.3436
6.3279
6.3239
6.3082
6.3043
4.9855
4.9700
3.6063
3.5898
3.5734
2.1316
2.1129
2.0943
2.0755
1.9610
1.9519
1.9455
1.9367
1.9249
1.9155
1.9120
1.9006
1.8931
1.8849
1.8759
1.8685
1.7939
1.7871
1.7720
1.7652
1.7508
1.7351
1.7281
1.7145
1.5147
1.4982
1.4805
1.4583
1.4412
1.3007
1.2629
0.8878
8
7
6
5
4
3
2
1
ppm
0.94
1.00
2.22
2.11
1.11
1.22
6.81
23.05
13.61
6.41
164.5301
137.8147
134.1154
77.5457
77.2275
76.9102
63.4484
33.4722
33.0405
32.0488
29.6437
29.6095
29.5143
29.4878
29.4569
29.4002
29.0256
28.6105
26.1824
25.9544
24.8805
22.8529
18.5690
14.2888
-5.0629
160
140
120
100
80
60
40
20
0
ppm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4.2225
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3.6164
3.6000
3.2007
3.1907
3.1842
3.1787
3.1746
3.1691
3.1625
3.1526
1.8804
1.8639
1.8586
1.8442
1.8332
1.8265
1.8087
1.7925
1.7765
1.7570
1.7464
1.7340
1.7244
1.7117
1.6986
1.6765
1.6210
1.5410
1.5251
1.5085
1.4915
1.4697
1.4529
1.4292
1.3988
1.3251
1.3035
O
O
OTBS
7
C9H19
trans-XI
8
7
6
5
4
3
2
1
ppm
1.00
2.09
0.99
2.13
2.20
0.52
2.36
29.40
12.78
6.07
171.6488
133.1569
128.7168
78.1491
77.3393
77.0220
76.7040
63.2415
56.1621
34.4596
32.8266
31.8890
29.9656
29.7029
29.5558
29.5126
29.3914
29.2890
29.1940
27.8968
26.9979
25.9830
25.7492
25.0291
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-5.2606
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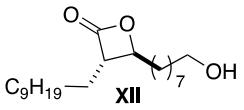
140
120
100
80
60
40
20
0
ppm


O
O
C9H19
7
OH

XII

4.2321
4.2230
3.6731
3.6570
3.6409
3.1999
3.1776
3.1542
1.8415
1.8321
1.7905
1.7453
1.7340
1.7114
1.6981
1.6754
1.6531
1.5669
1.3466
1.2792
0.9133
0.8987
0.8817
8
7
6
5
4
3
2
1
ppm
1.00
2.02
0.99
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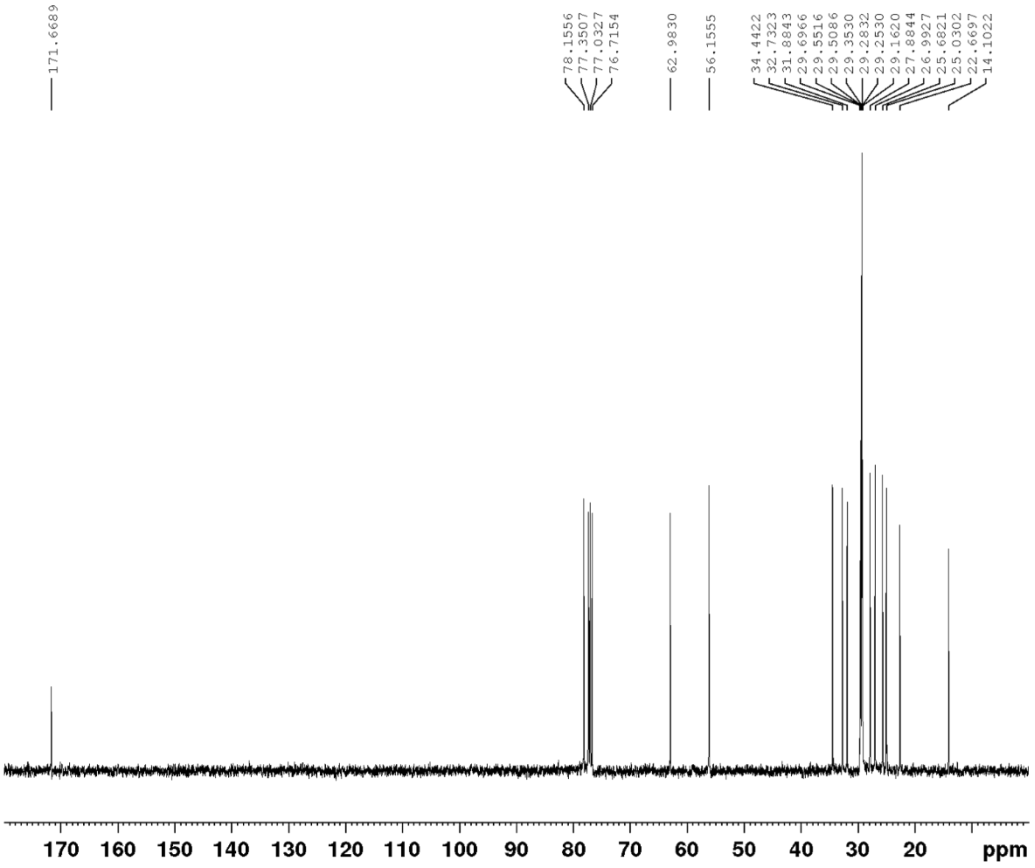
2.26
29.64
3.15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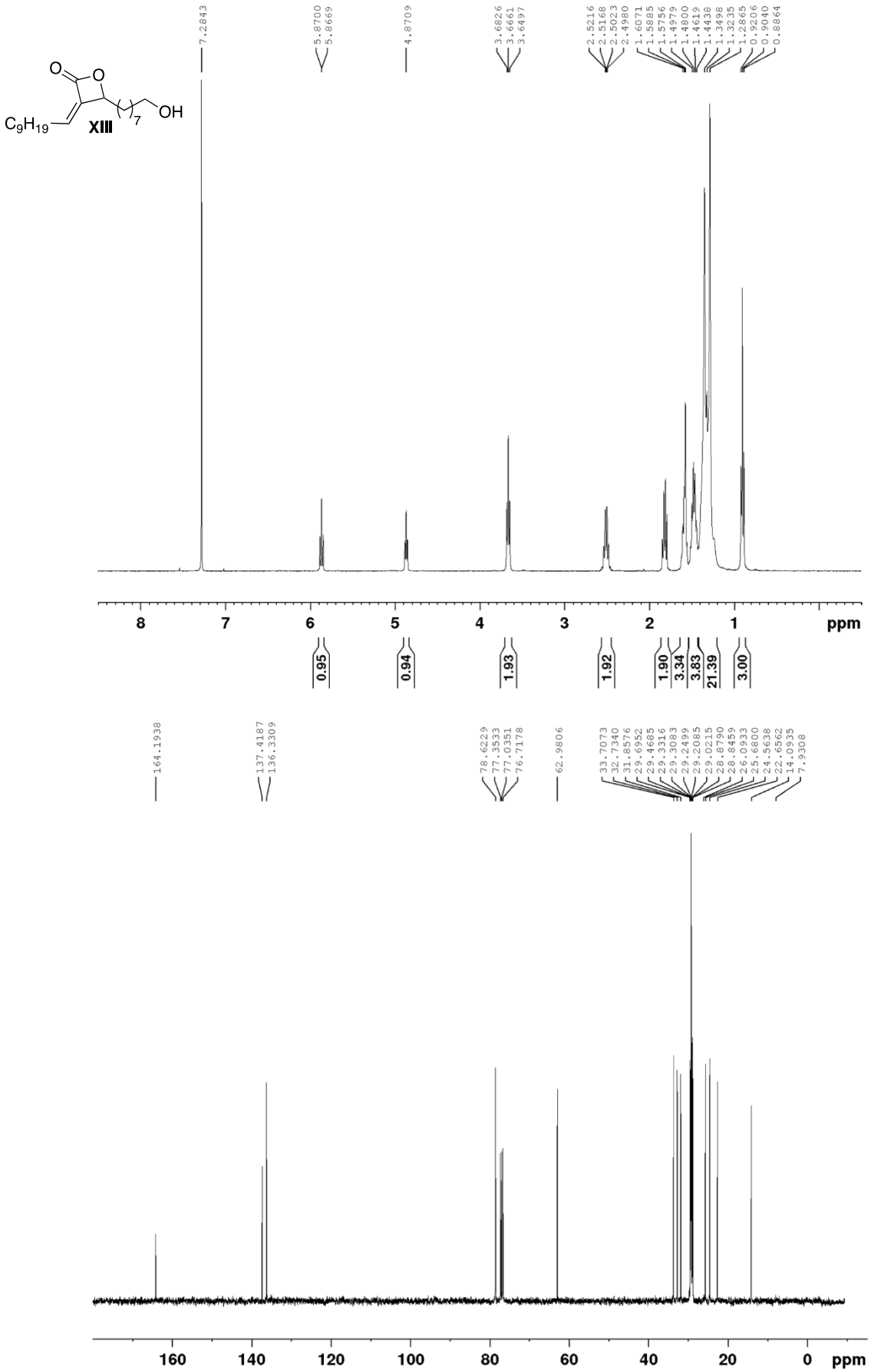
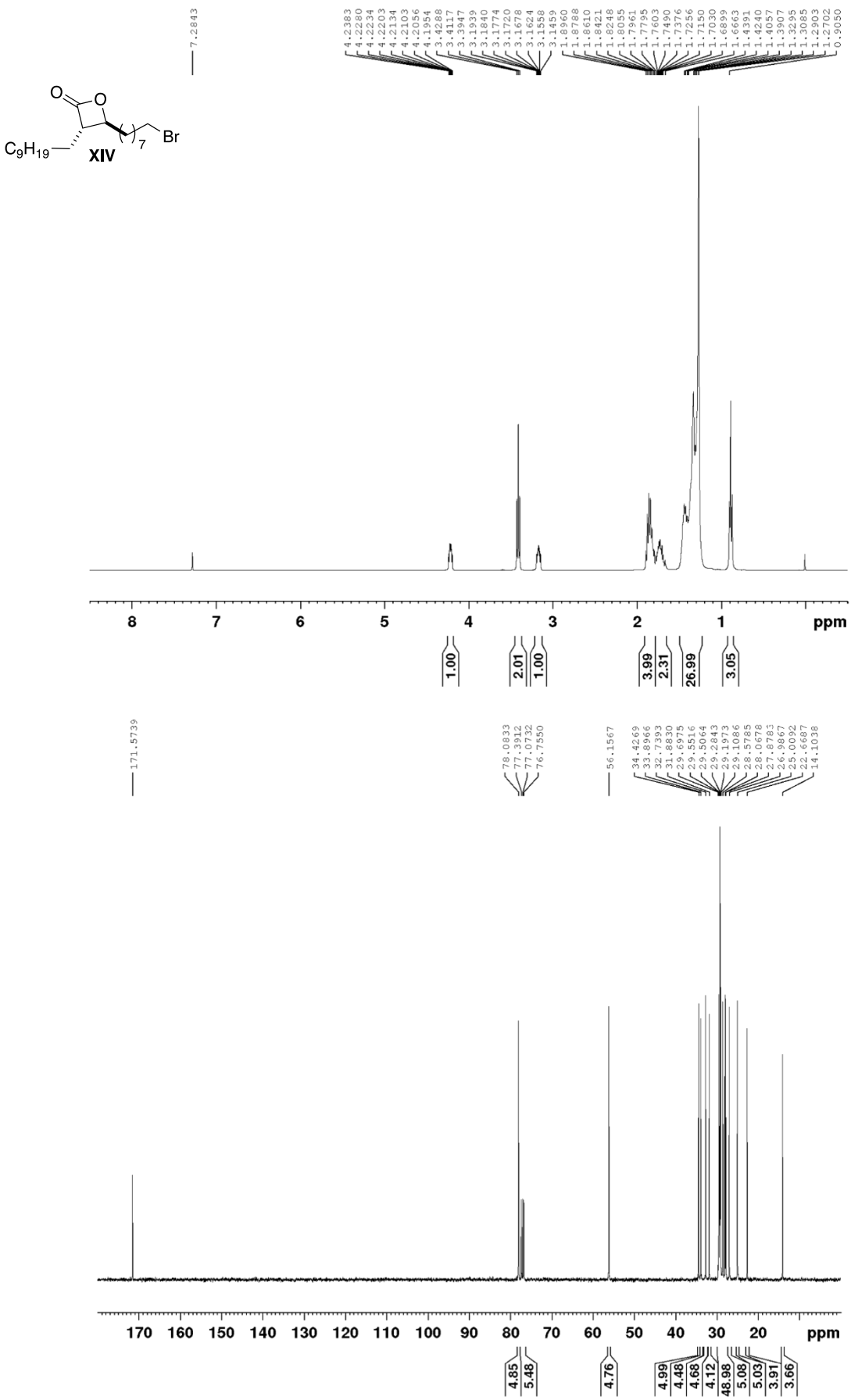
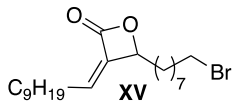
76.7154
62.9830
56.1555
34.4422
32.7323
31.8843
29.6966
29.5516
29.5086
29.3530
29.2832
29.2530
29.1620
27.8844
26.9927
25.6821
25.0302
22.6697
14.1022
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

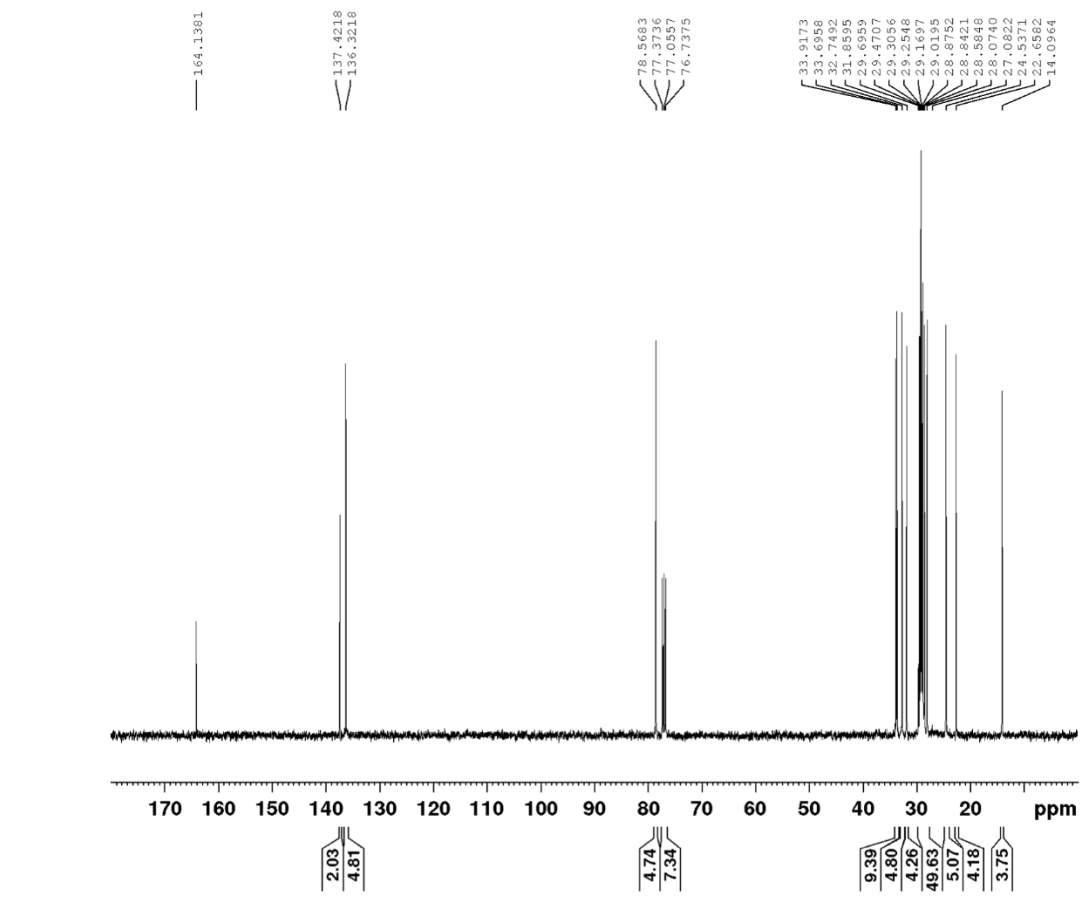

7.2843
5.8700
5.8669
4.8709
3.6826
3.6661
3.6497
2.5216
2.5168
2.5023
2.4980
1.6071
1.5885
1.5756
1.4979
1.4800
1.4619
1.4438
1.3498
1.3235
1.2865
0.9206
0.9040
0.8864
O
O
OH
C_9H_{19}
7
XIII
8
7
6
5
4
3
2
1
ppm
0.95
0.94
1.93
1.92
1.90
3.34
3.83
21.39
3.00
164.1938
137.4187
136.3309
78.6229
77.3533
77.0351
76.7178
62.9806
33.7073
32.7340
31.8576
29.6952
29.4685
29.3316
29.3083
29.2499
29.2085
29.0215
28.8790
28.8459
26.0933
25.6800
24.5638
22.6562
14.0935
7.9308
160
140
120
100
80
60
40
20
0
ppm


XIV
Br
ppm
ppm


O
O
C_9H_{19}
7
Br

XV

7.2843
5.8847
5.8824
5.8651
5.8625
5.8452
4.8740
4.8588
4.8435
3.4323
3.4153
3.3983
2.5247
2.5057
2.4878
2.4684
1.8814
1.8636
1.8447
1.8372
1.8272
1.8187
1.8018
1.7828
1.4865
1.4684
1.4510
1.4339
1.3770
1.3309
1.3190
1.3113
1.2743
0.9073
0.8909
0.8733
8
7
6
5
4
3
2
1
ppm
1.01
0.99
2.04
2.04
4.17
26.81
3.61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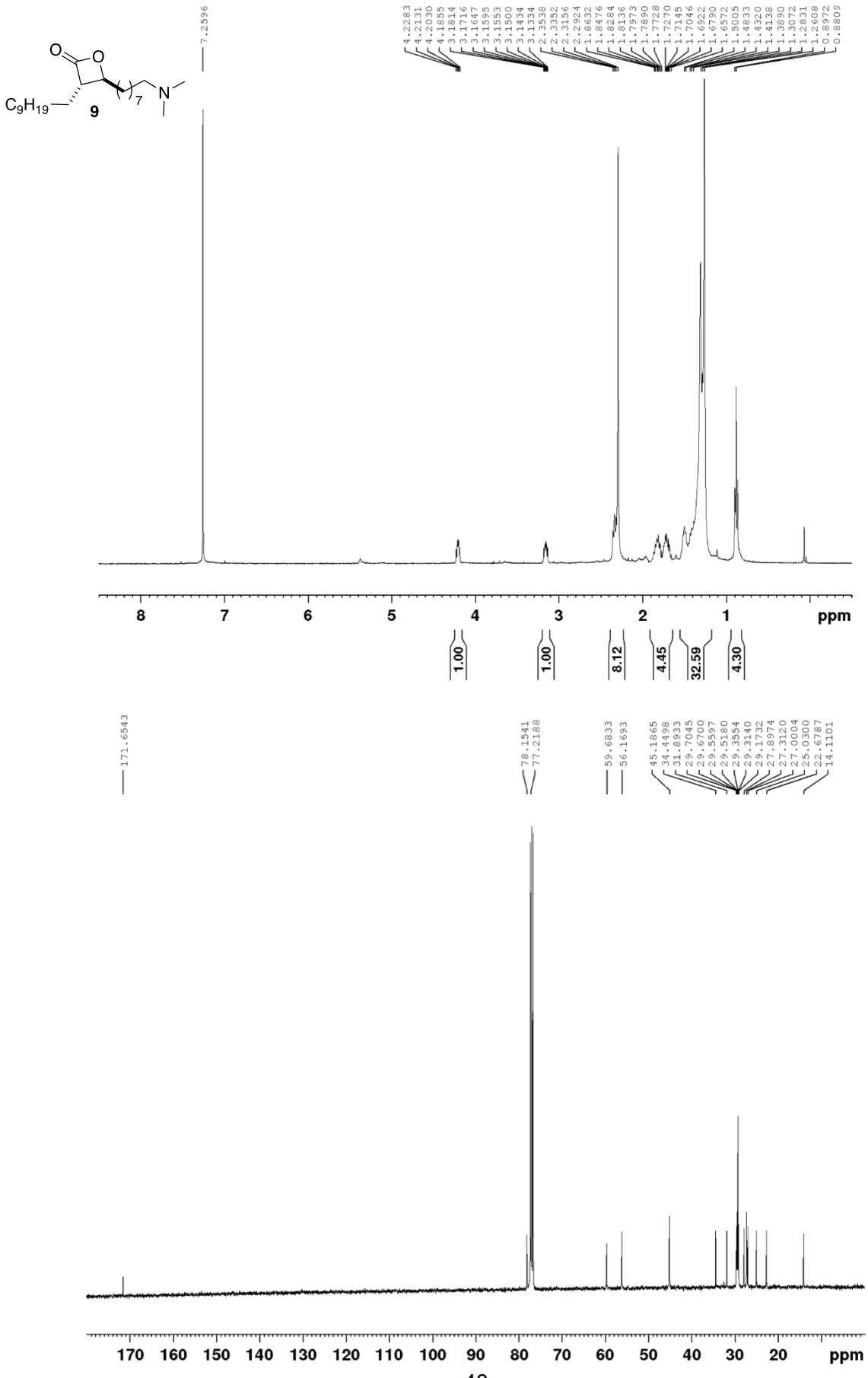
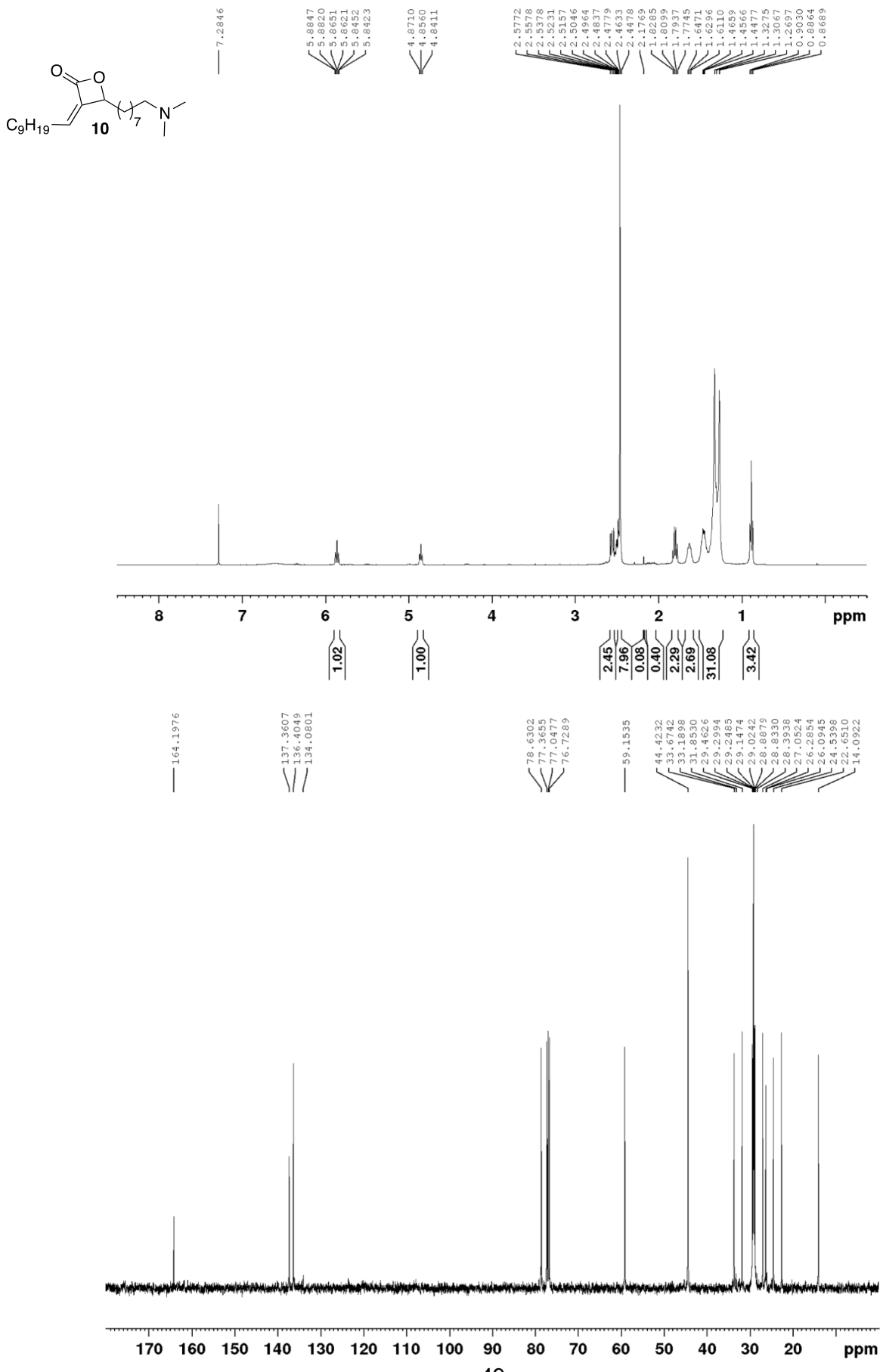
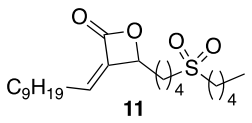
137.4218
136.3218
78.5683
77.3736
77.0557
76.7375
33.9173
33.6958
32.7492
31.8595
29.6959
29.4707
29.3056
29.2548
29.1697
29.0195
28.8752
28.8421
28.5848
28.0740
27.0822
24.5371
22.6582
14.0964
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
2.03
4.81
4.74
7.34
9.39
4.80
4.26
49.63
5.07
4.18
3.75

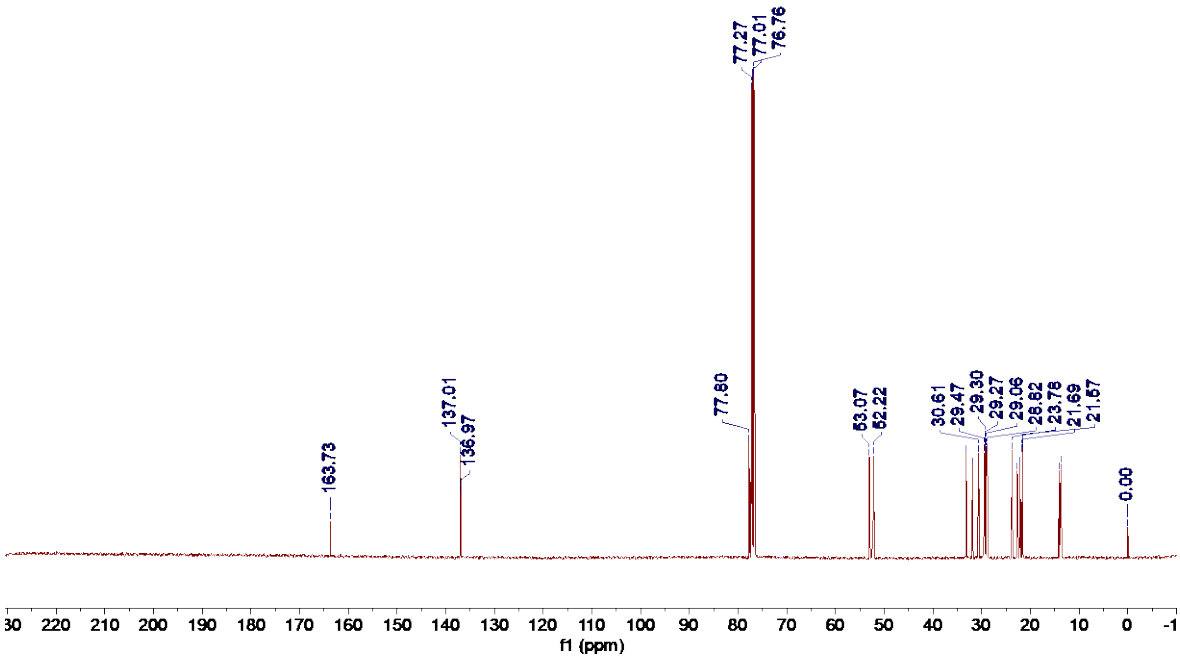

9
7.2596
4.2283
4.2131
4.2030
4.1855
3.1814
3.1716
3.1647
3.1595
3.1553
3.1500
3.1434
3.1334
2.3538
2.3352
2.3156
2.2924
1.8632
1.8476
1.8284
1.8136
1.7973
1.7890
1.7728
1.7270
1.7145
1.7046
1.6922
1.6790
1.6572
1.5005
1.4833
1.4320
1.4138
1.3890
1.3072
1.2831
1.2608
0.8972
0.8809
8 7 6 5 4 3 2 1 ppm
1.00
1.00
8.12
4.45
32.59
4.30
171.6543
78.1541
77.2188
59.6833
56.1693
45.1865
34.4498
31.8933
29.7045
29.6700
29.5597
29.5180
29.3554
29.3140
29.1732
27.8974
27.3120
27.0004
25.0300
22.6787
14.1101
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

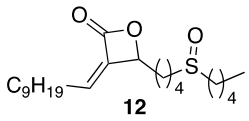

10
7.2846
5.8847
5.8820
5.8651
5.8621
5.8452
5.8423
4.8710
4.8560
4.8411
2.5772
2.5578
2.5378
2.5231
2.5157
2.5046
2.4964
2.4837
2.4779
2.4633
2.4478
2.1769
1.8285
1.8099
1.7937
1.7745
1.6471
1.6296
1.6110
1.4659
1.4566
1.4477
1.3275
1.3067
1.2697
0.9030
0.8864
0.8689
ppm
1.02
1.00
2.45
7.96
0.08
0.40
2.29
2.69
31.08
3.42
164.1976
137.3607
136.4049
134.0801
78.6302
77.3655
77.0477
76.7289
59.1535
44.4232
33.6742
33.1898
31.8530
29.4626
29.2994
29.2485
29.1474
29.0242
28.8879
28.8330
28.3938
27.0524
26.2854
26.0945
24.5398
22.6510
14.0922
ppm


O
O
O
O
S
C_9H_{19}
4
4

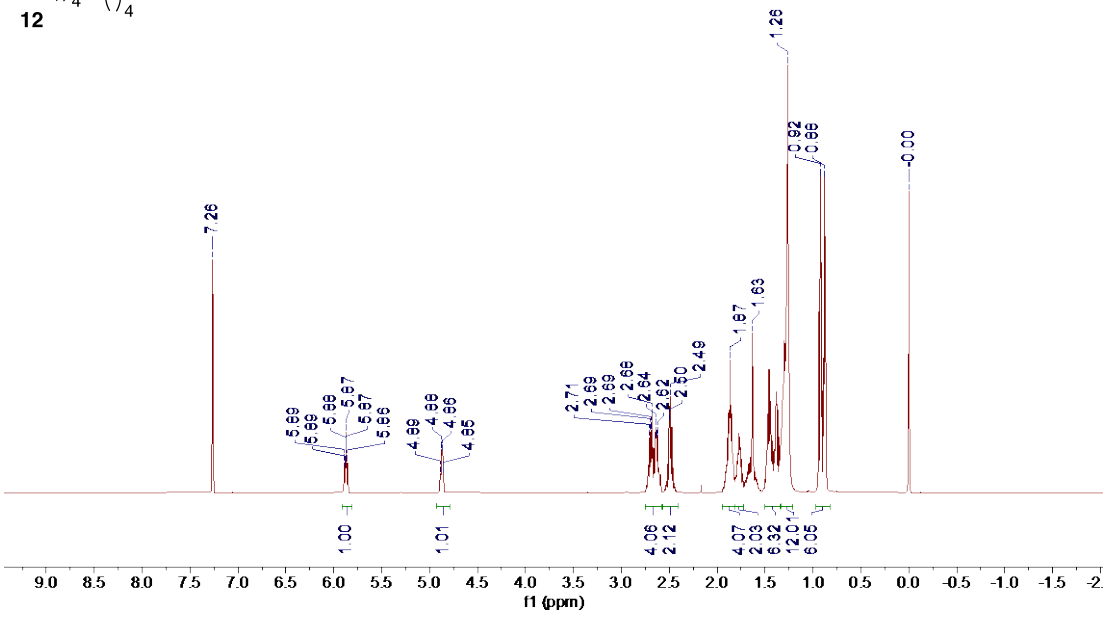
11

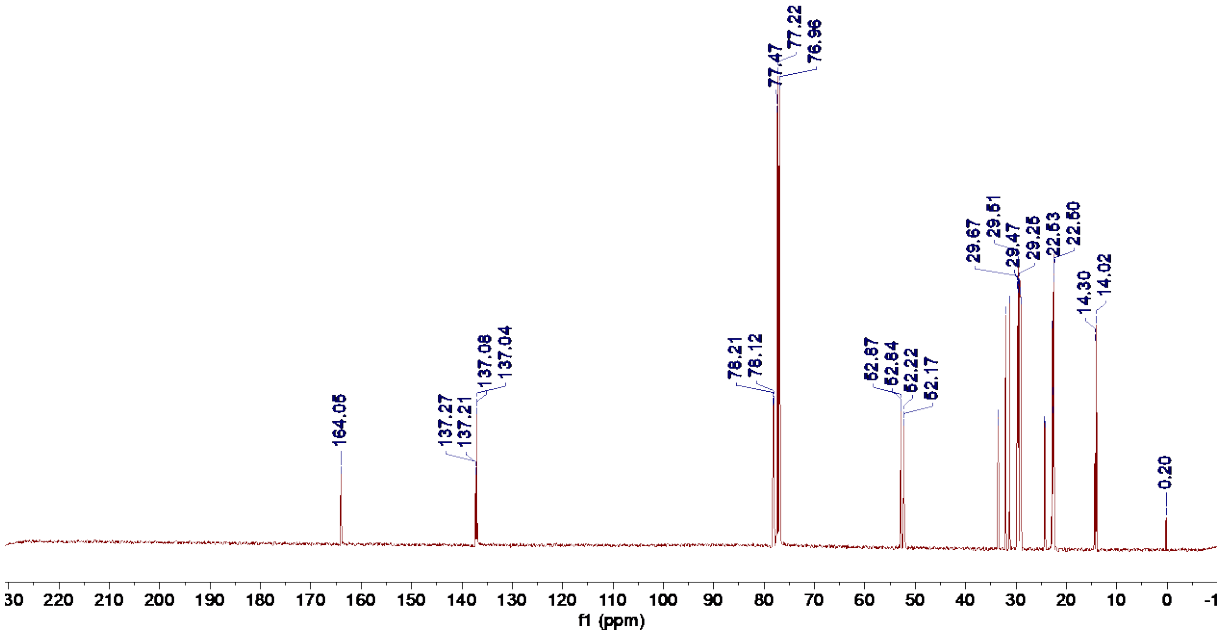
7.262
0.000
1.263
0.927
0.881
0.942
0.913
0.896
0.867
2.965
2.948
2.932
2.960
2.954
2.978
2.490
2.488
1.923
1.459
1.444
5.897
5.895
5.881
5.879
5.866
5.863
4.881
4.878
4.872
4.869
4.866
4.863
4.856
4.854
1.00
0.99
4.09
2.09
6.06
2.03
6.42
13.02
6.28
f1 (ppm)

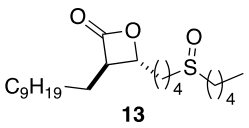

77.27
77.01
76.76
77.60
163.73
137.01
136.97
53.07
52.22
30.61
29.47
29.30
29.27
29.06
28.82
23.78
21.69
21.57
0.00
f1 (ppm)


O
O
O
S
C_9H_{19}
4
4

12

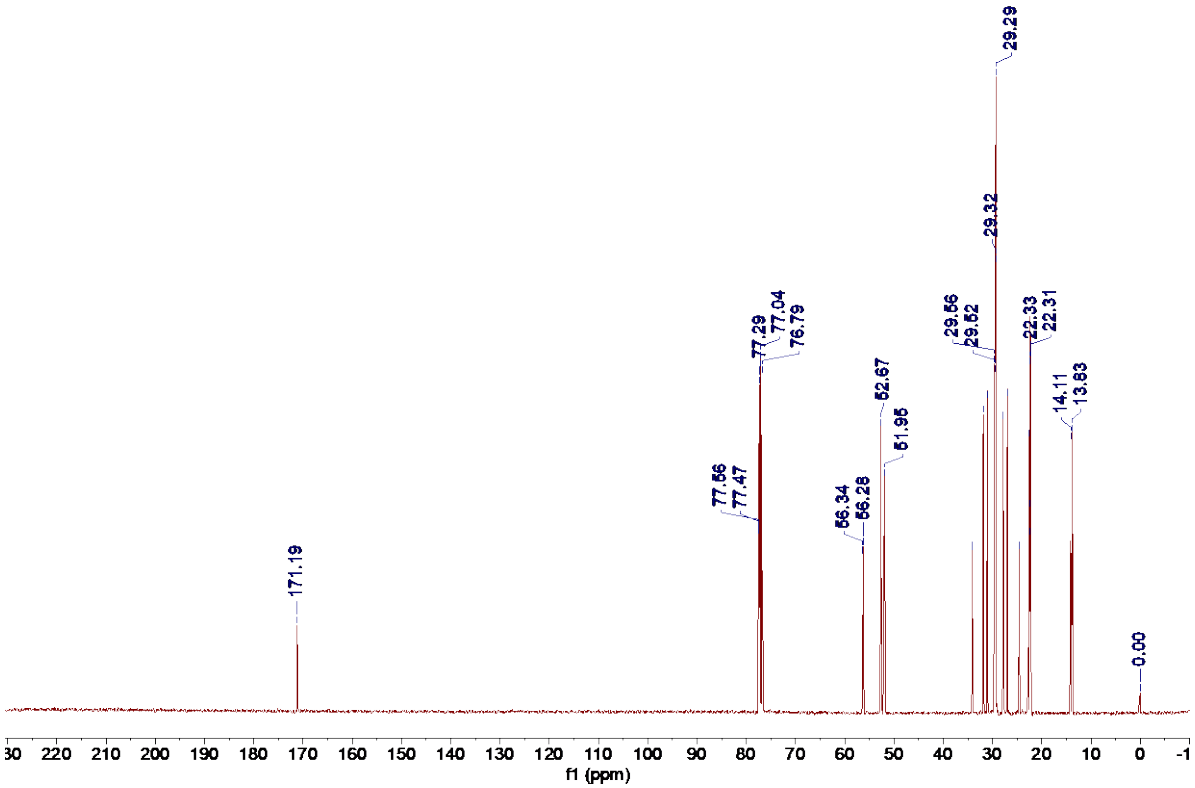

7.26
5.69
5.68
5.67
5.67
5.66
4.99
4.98
4.96
4.95
2.71
2.69
2.69
2.66
2.64
2.62
2.50
2.49
1.97
1.63
1.26
0.92
0.88
0.00
1.00
1.01
4.06
2.12
4.07
2.03
6.32
12.01
6.05
f1 (ppm)


164.05
137.27
137.21
137.08
137.04
78.21
78.12
77.47
77.22
76.96
52.87
52.84
52.22
52.17
29.67
29.51
29.47
29.25
22.53
22.50
14.30
14.02
0.20
f1 (ppm)


O
O
O
S
C_9H_{19}
4
4

13

7.270
4.252
4.243
4.236
4.234
4.228
4.226
4.216
4.210
3.196
3.191
3.166
3.163
2.699
2.693
2.682
2.641
1.871
1.856
1.851
1.263
0.939
0.925
0.882
0.866
0.000
1.00
1.00
4.11
10.22
6.02
14.76
6.17
f1 (ppm)


171.19
77.56
77.47
77.29
77.04
76.79
56.34
56.28
52.67
51.95
29.56
29.52
29.32
29.29
22.33
22.31
14.11
13.83
0.00
f1 (ppm)