Supporting Information for "Cloud Activation Potentials for Atmospheric α-Pinene and β-Caryophyllene Ozonolysis Products"

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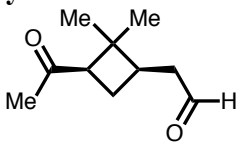
Supporting Information

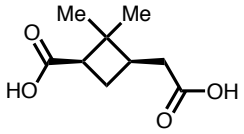
1. General Methods

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. THF, Et_2O and CH_2Cl_2 were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Armarego and Chai.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and anisaldehyde stain, ceric ammonium molybdate stain, or potassium permanganate stain followed by heating. Infrared spectra were recorded at 0.6 cm^{-1} resolution using a Bruker Tensor ATR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) or a Varian Inova 400 (400 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm or CD_3OD at 3.31 ppm). Data are reported as (app = apparent, obs = obscured, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, sep = septet, o = octet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on a Bruker Avance III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm or CD_3OD at 49.00 ppm). Mass spectrometric data were obtained on an Agilent 6210 Time-of-Flight LC/MS and a Thermo Finnegan Mat 900 XL High Resolution Magnetic Sector.

2. Experimental Procedures for the Synthesis of Oxidation Products

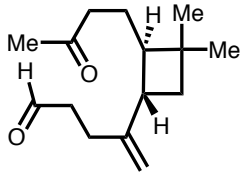


2-((1*R*,3*R*)-3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde [pinonaldehyde] (1): Ozone (generated at 110 V) was bubbled through a solution of (–)-α-pinene (10.0 g, 73.4 mmol) in dichloromethane (250 mL) at –78 ºC for 35 minutes. At this time, O_2 was bubbled through solution for an additional 20 minutes. After addition of dimethyl sulfide (60 mL, 832 mmol), mixture was then allowed to warm to room temperature and stirred for an additional 16 hours. The mixture was then diluted with H_2O (100 mL) and transferred to a separatory funnel. The resulting mixture was extracted with CH_2Cl_2 (3 x 100 mL) and washed with brine (100 mL). The combined organics were dried using $MgSO_4$ and solvent concentrated under reduced pressure to afford the crude product as a light yellow oil. Flash column chromatography on silica gel using 10% → 30% EtOAc in hexanes as the eluent afforded the title compound (8.3 g, 49.3 mmol, 67% yield) as a clear oil. A small amount of material (1.19 g, 7.07 mmol) was further purified by distillation (80 → 120 ºC) under reduced pressure to obtain higher purity samples for analytical measurements: IR (neat) 2954, 2826, 2724, 1720, 1701, 1369, 1181 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 2.92 (dd, J = 10.0, 7.7 Hz, 1H), 2.53 – 2.37 (m, 3H), 2.04 (s, 3H), 2.02 – 1.90 (m, 2H), 1.34 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.5, 201.5, 54.5, 45.3, 43.4, 35.9, 30.5, 30.3, 22.9, 17.8; HRMS (ESI): Exact mass calcd for $C_{10}H_{16}O_2$ $[M+H]^+$, 169.1229. Found 169.1223.

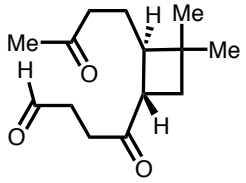


(1'*R*,3'*R*)-2-(3'-carboxy-2',2'-dimethylcyclobutyl)acetic acid [pinic acid] (3): Ozone (generated at 110 V) was bubbled through a solution of (–)-myrtenal (2.1 g, 14.0 mmol) in dichloromethane (125 mL) at –78 ºC for 30 minutes. At this time, O_2 was bubbled through solution for an additional 20 minutes. The resulting reaction mixture was then allowed to warm to room temperature and solvent concentrated under reduced pressure. After diluting with EtOH (100 mL), $AgNO_3$ (2.7 g, 15.9 mmol) added and mixture was allowed to stir at room temperature until $AgNO_3$ was dissolved. At this time, aqueous NaOH solution (4.6 M, 15 mL) was added dropwise and mixture was then allowed to stir at room temperature for an additional 16 hours. The reaction mixture was then vacuum filtered, rinsing with EtOH (25 mL), and filtrate concentrated under reduced pressure. Resulting residue was then diluted with EtOAc (100 mL) and 2 M HCl (100 mL) and transferred to a separatory funnel. The mixture was extracted with EtOAc (3 x 100 mL) and dried over $MgSO_4$. Subsequent concentration under reduced pressure afforded the crude product as a light yellow oil. Flash column chromatography on silica gel using 50% EtOAc in hexanes as the eluent afforded the title compound (2.50 g, 13.4 mmol, 96% yield). A small amount of material (90 mg, 0.48 mmol) was further purified via flash column chromatography on silica gel with 5% MeOH in CH_2Cl_2 as the eluent to obtain higher purity samples for analytical measurements: IR (neat) 3384-2537, 2962, 1719, 1689, 1407, 1246, 906 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 2.75 (dd, J = 10.4, 7.8 Hz, 1H), 2.41 – 2.31 (m, 2H), 2.31 – 2.21 (m, 1H), 2.11 – 2.02 (m, 1H), 1.91 – 1.83 (m, 1H), 1.23 (s, 3H), 0.98 (s, 3H); ^{13}C NMR

(125 MHz, CD_3OD) δ 176.6, 176.5, 47.3, 43.4, 39.6, 36.2, 30.3, 25.6, 17.9; HRMS (ESI): Exact mass calcd for $C_9H_{14}O_4$ $[M+Na]^+$, 209.0790. Found 209.0786.

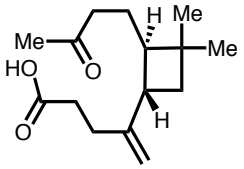


4-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enal [β-caryophyllene aldehyde] (4): Ozone (generated at 70 V) was bubbled through a solution of β-caryophyllene (3.0 g, 14.7 mmol) in dichloromethane (250 mL) at -78 ºC for 10 minutes. At this time, O_2 was bubbled through solution for an additional 20 minutes. After addition of dimethyl sulfide (18 mL, 250 mmol), mixture was then allowed to warm to room temperature and stirred for an additional 16 hours. The mixture was then diluted with H_2O (100 mL) and transferred to a separatory funnel. The resulting mixture was extracted with CH_2Cl_2 (3 x 100 mL) and washed with brine (100 mL). The combined organics were dried using $MgSO_4$ and solvent concentrated under reduced pressure to afford the crude product as a light yellow oil. Flash column chromatography on silica gel using 10% EtOAc in hexanes as the eluent afforded the title compound (422 mg, 1.8 mmol, 12% yield) as a clear oil: IR (neat) 3082, 2950, 2863, 2721, 1714, 1643, 1364, 889 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 1H), 4.80 – 4.76 (m, 1H), 4.68 (d, *J* = 1.7 Hz, 1H), 2.56 (td, *J* = 7.8, 7.4, 1.7 Hz, 2H), 2.45 – 2.27 (m, 5H), 2.11 (s, 3H), 1.88 (dt, *J* = 9.6, 7.6 Hz, 1H), 1.81 (dd, *J* = 10.4, 8.5 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.44 (t, *J* = 10.2 Hz, 1H), 1.05 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 202.3, 150.8, 107.7, 47.9, 42.1, 42.0, 41.8, 39.9, 33.8, 31.2, 30.1, 26.7, 24.7, 22.5. HRMS (ESI): Exact mass calcd for $C_{15}H_{24}O_2$ $[M+H]^+$, 237.1855. Found 237.1851.

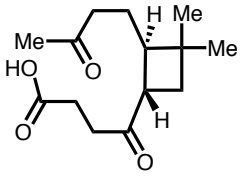


4-[(1*S*,2*R*)-3,3-dimethyl-2-(3-oxidanylidenebutyl)cyclobutyl]-4-oxidanylidene-butanal (β-nocaryophyllone aldehyde) (5): Ozone (generated at 110 V) was bubbled through a solution of β-caryophyllene (6.3 g, 24.5 mmol) in methanol (85 mL) at -78 ºC for 30 minutes. At this time, O_2 was bubbled through solution for an additional 20 minutes. After addition of dimethyl sulfide (26.3 g, 31 mL, 0.423 mol), mixture was then allowed to warm to room temperature and stirred for an additional 16 hours. The mixture was then diluted with H_2O (100 mL) and transferred to a separatory funnel. The resulting mixture was extracted with CH_2Cl_2 (3 x 100 mL) and washed with brine (100 mL). The combined organics were dried using $MgSO_4$ and solvent concentrated under reduced pressure to afford the crude product as a light yellow oil. Flash column chromatography on silica gel using 20% EtOAc in hexanes as the eluent afforded the title compound (2.8 g, 11.7 mmol, 48% yield) as a clear oil. A small amount of material (0.763 g, 3.20 mmol) was further purified by flash column chromatography on silica gel using 10% to 30% EtOAc in hexanes as the eluent to obtain higher purity samples for analytical measurements: IR (neat) 2951, 2865, 2727, 1703, 1363, 1165, 1113 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$) δ 9.80 (s, 1H), 2.89 – 2.58 (m, 5H), 2.42 – 2.30 (m, 2H), 2.17 – 2.12 (m, 1H), 2.11 (s, 3H), 1.88 (ddd, *J* = 10.7, 9.0, 0.8 Hz, 1H), 1.74 (t, *J* = 10.2 Hz, 1H), 1.70 – 1.56 (m, 2H), 1.06 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.0, 208.9, 200.6, 46.9, 46.0, 41.7, 37.5, 36.9, 34.1, 32.9, 30.2, 30.1, 23.9, 22.6; HRMS (ESI): Exact mass calcd for $C_{14}H_{22}O_3$ $[M+H]^+$, 239.1647. Found 239.1644.



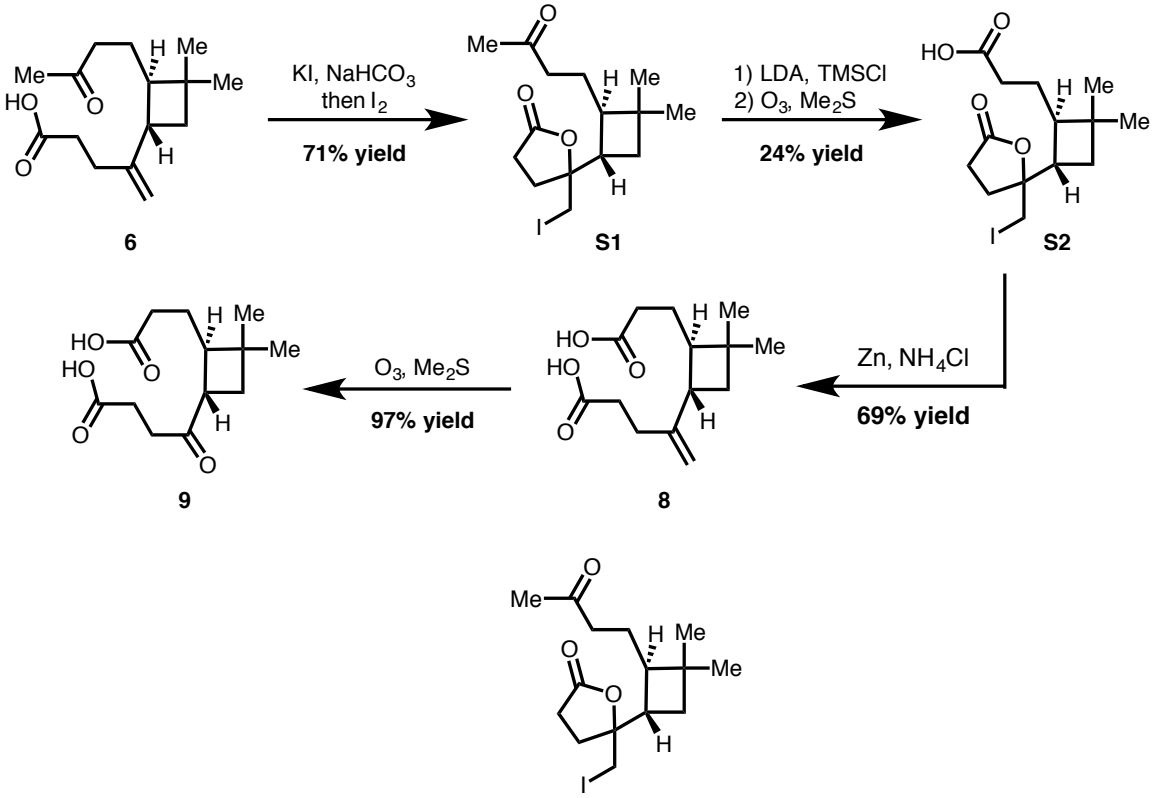
4-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enoic acid [β-caryophyllonic acid] (6): Ozone (generated at 70 V) was bubbled through a solution of β-caryophyllene (3.0 g, 14.7 mmol) in dichloromethane (250 mL) at -78 ºC for 10 minutes. At this time, O_2 was bubbled through solution for an additional 20 minutes. Resulting reaction mixture was then allowed to warm to room temperature and solvent concentrated under reduced pressure. After diluting with EtOH (200 mL), $AgNO_3$ (3.0 g, 17.6 mmol) added and mixture was allowed to stir at room temperature until $AgNO_3$ was dissolved. At this time, aqueous NaOH solution (4.6 M, 17 mL) was added dropwise and mixture was then allowed to stir at room temperature for an additional 16 hours. The reaction mixture was then vacuum filtered, rinsing with EtOH (50 mL), and filtrate concentrated under reduced pressure. The resulting residue was then diluted with EtOAc (150 mL) and 1 M HCl (150 mL) and transferred to a separatory funnel. The mixture was extracted with EtOAc (3 x 100 mL) and dried over $MgSO_4$. Subsequent concentration under reduced pressure afforded the crude product as a viscous yellow oil. Flash column chromatography on silica gel using 20% EtOAc in hexanes as the eluent afforded the title compound (1.9 g, 7.5 mmol, 51% yield): IR (neat) 3100-2665, 3081, 2950, 1707, 1643, 1382, 1161, 887 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.71 (s, 1H), 2.52 – 2.47 (m, 2H), 2.41 – 2.27 (m, 5H), 2.11 (s, 3H), 1.88 (dt, *J* = 9.6, 7.7 Hz, 1H), 1.81 (dd, *J* = 2.0, 1.5, 1.3 Hz, 1H), 1.69 – 1.59 (m, 2H), 1.45 (t, *J* = 10.2 Hz, 1H), 1.05 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.1, 178.8, 150.7, 107.5, 47.9, 42.1, 41.8, 39.8, 33.8, 32.5, 31.2, 30.0, 29.1, 24.7, 22.5; HRMS (ESI): Exact mass calcd for $C_{15}H_{24}O_3$ $[M+Na]^+$, 275.1623. Found 275.1626.



4-oxo-4-[(1*S*)-3,3-dimethyl-2*t*-(3-oxo-butyl)-cyclobutyl-(*r*)]-butyric acid [β-nocaryophyllonic acid] (7): Ozone (generated at 110 V) was bubbled through a solution of β-caryophyllene (3.5 g, 17.1 mmol) in dichloromethane (250 mL) at -78 ºC for 1 hour. At this time, O_2 was bubbled through solution for an additional 20 minutes. Resulting reaction mixture was then allowed to warm to room temperature and solvent concentrated under reduced pressure. After diluting with EtOH (60 mL), $AgNO_3$ (3.4 g, 19.8 mmol) added and mixture was allowed to stir at room temperature until $AgNO_3$ was dissolved. At this time, aqueous NaOH solution (4.6 M, 13 mL) was added dropwise and mixture was then allowed to stir at room temperature for an additional 16 hours. Reaction mixture was then vacuum filtered, rinsing with EtOH (50 mL), and filtrate

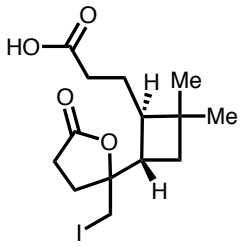
concentrated under reduced pressure. The resulting residue was then diluted with EtOAc (150 mL) and 1 M HCl (150 mL) and transferred to a separatory funnel. The mixture was extracted with EtOAc (3 x 100 mL) and dried over $MgSO_4$. Subsequent concentration under reduced pressure afforded the crude product as a highly viscous oil. Flash column chromatography on silica gel using 20% to 40% EtOAc in hexanes as the eluent afforded the title compound (3.9 g, 14.5 mmol, 85% yield): IR (neat) 3038-2654, 2951, 2865, 1737, 1701, 1366, 1163 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.83 – 2.57 (m, 5H), 2.41 – 2.27 (m, 2H), 2.15 – 2.10 (m, 1H), 2.09 (s, 3H), 1.85 (dd, J = 10.7, 9.1 Hz, 1H), 1.71 (t, J = 10.2 Hz, 1H), 1.67 – 1.52 (m, 2H), 1.04 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.1, 209.3, 178.6, 46.8, 45.9, 41.7, 36.8, 35.0, 34.0, 30.2, 30.1, 27.8, 23.9, 22.6; HRMS (ESI): Exact mass calcd for $C_{14}H_{22}O_4$ $[M+Na]^+$, 277.1416. Found 277.1413.

Scheme S1. Synthetic outline of β-caryophyllinic acid (**8**) and β-nocaryophyllinic acid (**9**).



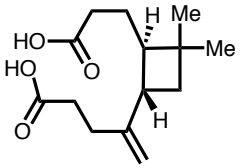
5-[(1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl](iodomethyl)oxolan-2-one (S1): To a solution of KI (7.9 g, 47.6 mmol) and $NaHCO_3$ (2.0 g, 23.8 mmol) in H_2O (40 mL) at room temperature was added dropwise 4-((1S,2R)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enoic acid (**6**) (2.0 g, 7.9 mmol) in CH_2Cl_2 (8 mL) by cannula. Reaction mixture was allowed to stir vigorously for 20 minutes and then I_2 (1.2 g, 9.5 mmol) was added. After 10 minutes, an additional portion of I_2 (0.50 g, 2.0 mmol) was added and reaction was allowed to stir at room temperature for 16 hours. The reaction mixture was then transferred to a separatory funnel. The organic phase was collected and the aqueous layer extracted with dichloromethane (3 x 50 mL). The combined organics were washed with 10% $Na_2S_2O_3$ (3 x 50 mL) and dried with $MgSO_4$. Concentration under reduced pressure and flash column chromatography on silica gel using 20%

EtOAc in hexanes as the eluent afforded the corresponding compound (2.1 g, 5.6 mmol, 71% yield) as a viscous yellow oil. The product was isolated as a mixture of diastereomers and both diastereomers were carried forward to the subsequent reaction: IR (neat) 2952, 2864, 1764, 1702, 1245, 1159, 915 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, mixture of diastereomers) δ ^1H NMR (500 MHz, $CDCl_3$, mixture of diastereomers) δ 3.43 (d, *J* = 10.7 Hz), 3.32 (d, *J* = 10.6 Hz), 3.25 (d, *J* = 10.7 Hz), 3.21 (d, *J* = 10.6 Hz), 2.78 – 2.61 (m), 2.60 – 2.50 (m), 2.47 – 2.28 (m), 2.27 – 2.14 (m), 2.12 (s), 2.11 – 1.99 (m), 1.92 (td, *J* = 9.2, 6.2 Hz), 1.78 (dt, *J* = 9.2, 7.4 Hz), 1.73 – 1.54 (m), 1.41 (t, *J* = 10.2 Hz), 1.07 (s), 1.04 (s); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of diastereomers) δ 208.3, 208.1, 176.5, 176.4, 86.7, 86.2, 44.6, 44.6, 42.3, 42.2, 41.9, 41.7, 34.3, 34.0, 33.7, 33.5, 31.2, 31.0, 30.3, 30.2, 30.1, 29.7, 29.6, 29.5, 25.1, 25.0, 22.7, 22.6, 14.0, 13.4; HRMS (ESI): Exact mass calcd for $C_{15}H_{23}IO_3$ $[M+H]^+$, 379.0770. Found 379.0771.

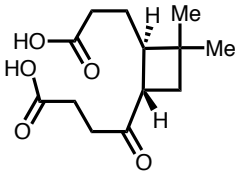


3-[(1*R*,4*S*)-4-[2-iodomethyl)-5-oxooxolan-2-yl]-2,2dimethylcyclobutyl]propanoic acid (S2): To a solution of freshly distilled diisopropylamine (1.0 mL, 7.4 mmol) in THF (30 mL) at 0 ºC was added *n*-BuLi (3.6 mL, 5.9 mmol, 1.62 M in hexanes) under N_2. After 5 minutes, reaction was cooled to –20 ºC and TMSCl (1.3 mL, 9.8 mmol) was added. 5-[(1S,2R)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl](iodomethyl)oxolan-2-one (**S1**) (1.9 g, 4.9 mmol) in THF (20 mL) was then added dropwise via cannula. After stirring at –20 ºC for 2 hours, the reaction was quenched with triethylamine (5 mL) and diluted with $NaHCO_3$ (50 mL). After transferring to a separatory funnel, the mixture was extracted with EtOAc (3 x 100 mL) and washed with brine (50 mL). The combined organics were dried using $MgSO_4$ and solvent concentrated under reduced pressure to afford crude 5-[(1S,2R)-3,3-dimethyl-2-{(3-[(trimethylsilyl)oxy]but-3-en-1-yl}cyclobutyl](iodomethyl)oxolan-2-one (2.2 g, 4.9 mmol) as a light yellow oil, which was directly carried over to the next step without further purification. Ozone (generated at 110 V) was bubbled through a solution of 5-[(1S,2R)-3,3-dimethyl-2-{(3-[(trimethylsilyl)oxy]but-3-en-1-yl}cyclobutyl](iodo-methyl)oxolan-2-one (2.2 g, 4.9 mmol) in dichloromethane (125 mL) at –78 ºC for 6 minutes. At this time, O_2 was bubbled through solution for an additional 15 minutes. After addition of dimethyl sulfide (3.9 mL, 53.7 mmol), mixture was then allowed to warm to room temperature and stir for an additional 16 hours. The mixture was then diluted with H_2O (75 mL) and transferred to a separatory funnel. The resulting mixture was extracted with CH_2Cl_2 (3 x 75 mL) and washed with brine (75 mL). The combined organics were dried using $MgSO_4$ and solvent concentrated under reduced pressure to afford the crude product as a light yellow oil. Flash column chromatography on silica gel using 10% to 15% EtOAc in hexanes as the eluent afforded the title compound (444.2 mg, 1.2 mmol, 24% yield over the two steps) as a light yellow oil. Due to incomplete conversion, the original starting material, 5-[(1S,2R)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl](iodomethyl)oxolan-2-one (**S1**), was recovered (1.35 g, 3.57 mmol) and subsequently cycled through the reaction sequence a second time for an overall yield of the product (**S2**) of 39% (655.4 mg, 1.72 mmol) over the two steps. The product was isolated

as a mixture of diastereomers and both diastereomers were carried forward to the subsequent reaction: IR (neat) 3358-2553, 2951, 2864, 1770, 1706, 1154, 915, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, mixture of diastereomers) δ 3.43 (d, *J* = 10.7 Hz), 3.33 (d), 3.25 (d, *J* = 10.7 Hz), 3.21 (d, *J* = 10.6 Hz), 2.79 – 2.60 (m), 2.58 – 2.47 (m), 2.43 – 2.30 (m), 2.30 – 1.95 (m), 1.91 – 1.69 (m), 1.68 – 1.57 (m), 1.44 (t, *J* = 10.2 Hz), 1.09 (s), 1.08 (s); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of diastereomers) δ 178.2, 178.1, 176.5, 176.4, 86.8, 86.2, 77.2, 44.4, 44.3, 42.2, 42.0, 34.3, 34.1, 33.8, 33.5, 32.3, 32.2, 31.1, 31.0, 30.2, 29.7, 29.7, 29.5, 26.3, 26.2, 22.6, 22.6, 13.6, 13.3; HRMS (ESI): Exact mass calcd for $C_{14}H_{21}IO_4$ $[M+H]^+$, 381.0563. Found 381.0560.



4-[(1*S*,2*R*)-2-(3-hydroxy-3-oxopropyl)-3,3-dimethyl-cyclobutyl]pent-4-enoic acid (β-caryophyllinic acid) (8): Zn dust (1.2 g, 17.8 mmol) and NH_4Cl (0.95 g, 17.8 mmol) were added to a solution of 3-[(1R,4S)-4-[2-iodomethyl)-5-oxooxolan-2-yl]-2,2dimethylcyclobutyl]propanoic acid (**S2**) (444.2 mg, 1.2 mmol) in EtOH (19 mL). The reaction mixture was heated under reflux for 1 hour. After cooling to room temperature, the reaction mixture was vacuum filtered, rinsing with acetone (25 mL), and solvent concentrated under reduced pressure to afford the crude product as a dark yellow oil. The reaction was repeated on the same scale and crude products were combined prior to purification. Flash column chromatography on silica gel with 5% MeOH and 0.1% AcOH in CH_2Cl_2 as the eluent afforded the title compound (383.2 mg, 1.5 mmol, 69% yield from combined crude product) as a yellow oil: IR (neat) 3391-2344, 3080, 2950, 2864, 1704, 1644, 1438, 888 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 4.81 (s, 1H), 4.74 (s, 1H), 2.51 – 2.38 (m, 3H), 2.35 – 2.15 (m, 4H), 1.98 (dt, *J* = 9.6, 7.6 Hz, 1H), 1.83 (dd, *J* = 10.4, 8.5 Hz, 1H), 1.76 – 1.63 (m, 2H), 1.46 (t, *J* = 10.2 Hz, 1H), 1.08 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 177.4, 177.1, 152.5, 107.8, 42.7, 40.8, 34.6, 33.6, 33.4, 31.5, 30.5, 27.1, 22.7; HRMS (ESI): Exact mass calcd for $C_{14}H_{22}O_4$ $[M+Na]^+$, 277.1416. Found 277.1421.



4-[(1*S*,2*R*)-2-(2-carboxyethyl)-3,3-dimethylcyclobutyl]-4-oxobutanoic acid (β-nocaryophyllinic acid) (9): Ozone (generated at 110 V) was bubbled through a solution of 4-[(1S,2R)-2-(3-hydroxy-3-oxopropyl)-3,3-dimethyl-cyclobutyl]pent-4-enoic acid (#) (121.2 mg, 0.5 mmol) in MeOH (22 mL) at –78 ºC for 5 minutes. At this time, O_2 was bubbled through solution for an additional 15 minutes. After addition of dimethyl sulfide (385 μL, 5.2 mmol), the mixture was allowed to warm to room temperature and stir for an additional 16 hours. The mixture was then diluted with 2 M HCl (10 mL) and transferred to a separatory funnel. The resulting mixture was extracted with EtOAc (3 x 25 mL). The combined organics were dried using $MgSO_4$ and solvent concentrated under reduced pressure to afford the crude product as a light yellow oil. Flash column chromatography on silica gel with 5% MeOH in CH_2Cl_2 as the

eluent afforded the title compound (118 mg, 0.5 mmol, 97% yield) as a white solid: IR (neat) 2955-2561, 2917, 2866, 1696, 1384, 1286, 951 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD) δ 2.97 – 2.86 (m, 1H), 2.78 – 2.61 (m, 2H), 2.59 – 2.45 (m, 2H), 2.28 – 2.13 (m, 3H), 1.86 (dd, *J* = 10.7, 9.0 Hz, 1H), 1.78 – 1.60 (m, 3H), 1.09 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 212.6, 177.2, 176.4, 47.5, 47.2, 37.3, 36.3, 34.7, 33.2, 30.6, 28.6, 26.6, 22.7. HRMS (ESI): Exact mass calcd for $C_{13}H_{20}O_5$ $[M+H]^+$, 257.1389. Found 257.1384 .

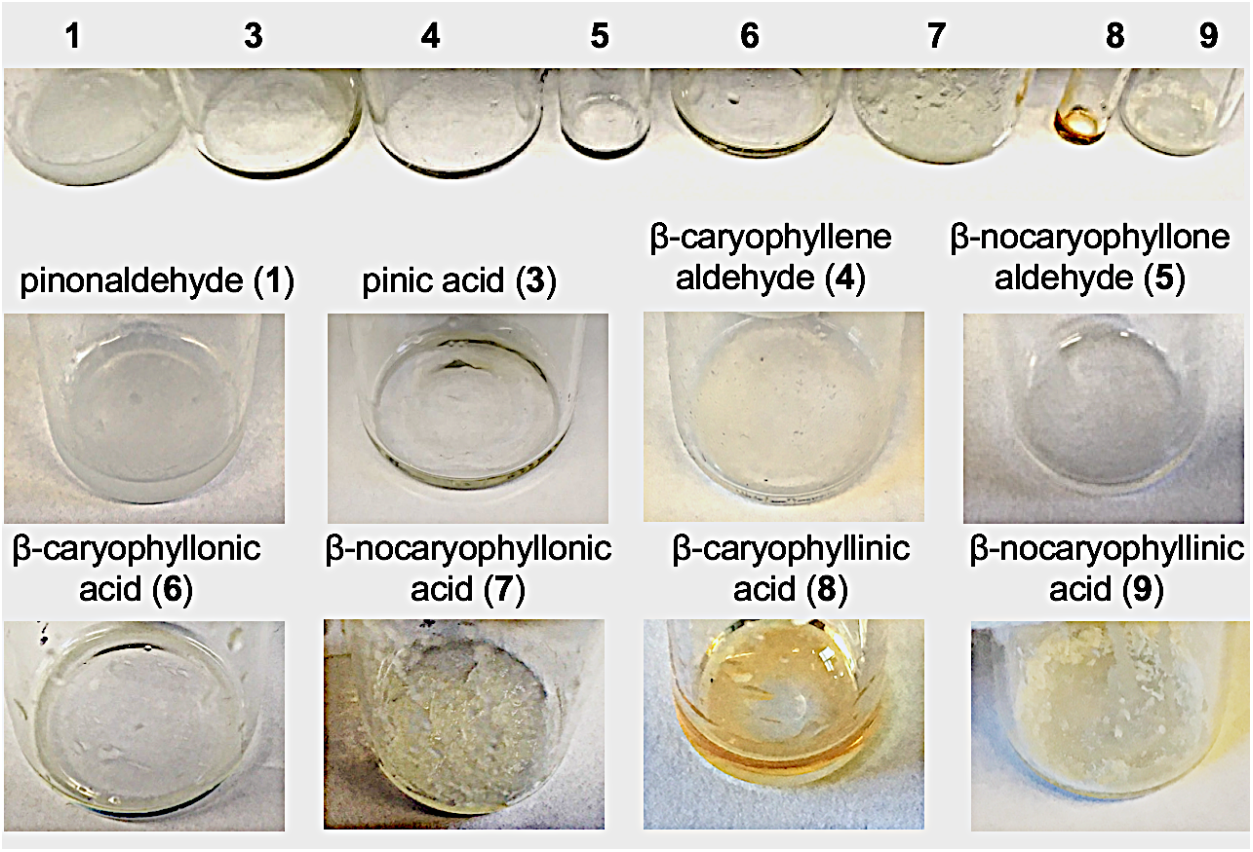
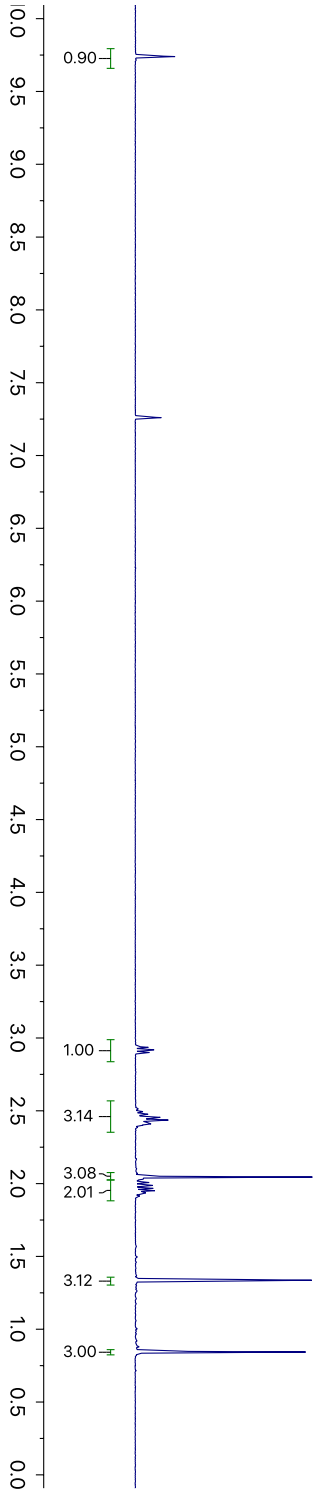
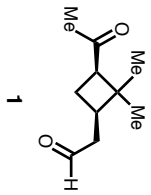


Figure S1. Sample pictures highlighting the phase states of all compounds synthesized in this study.

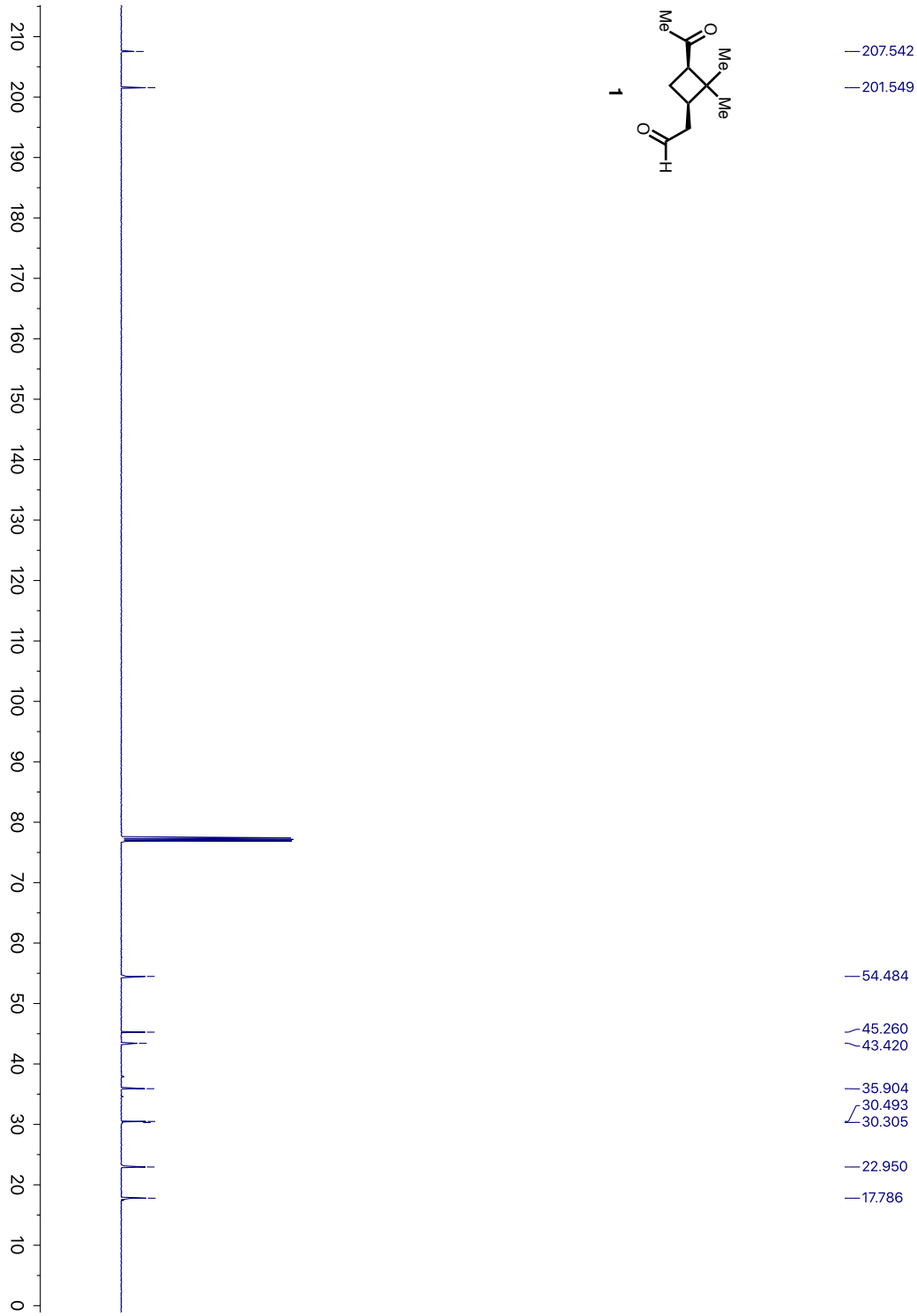
3. ^{1}H and ^{13}C NMR Spectra

3.1 ^{1}H and ^{13}C NMR Spectra of Synthesized Compounds





1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O
Me
Me
O
H
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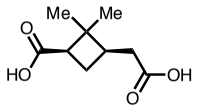
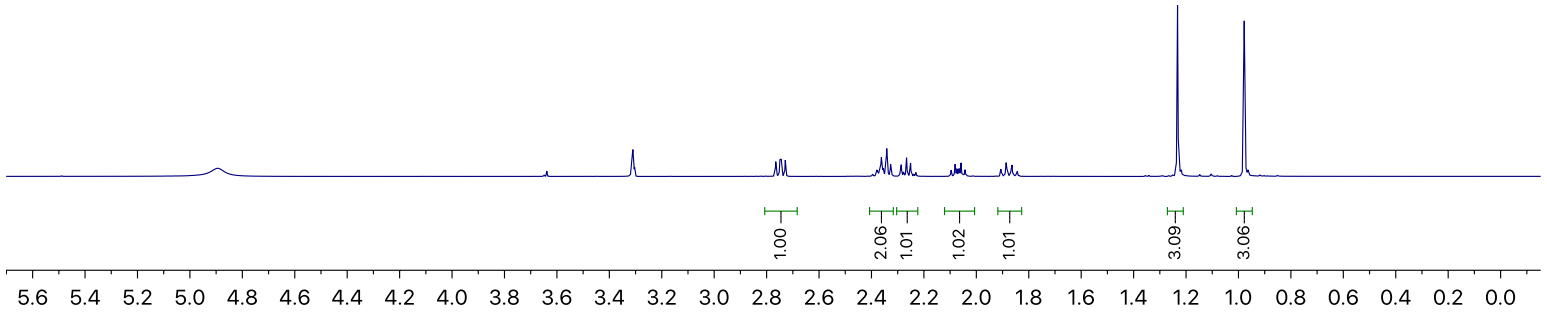
201.549
54.484
45.260
43.420
35.904
30.493
30.305
22.950
17.786
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
Me
O
HO
OH
O

3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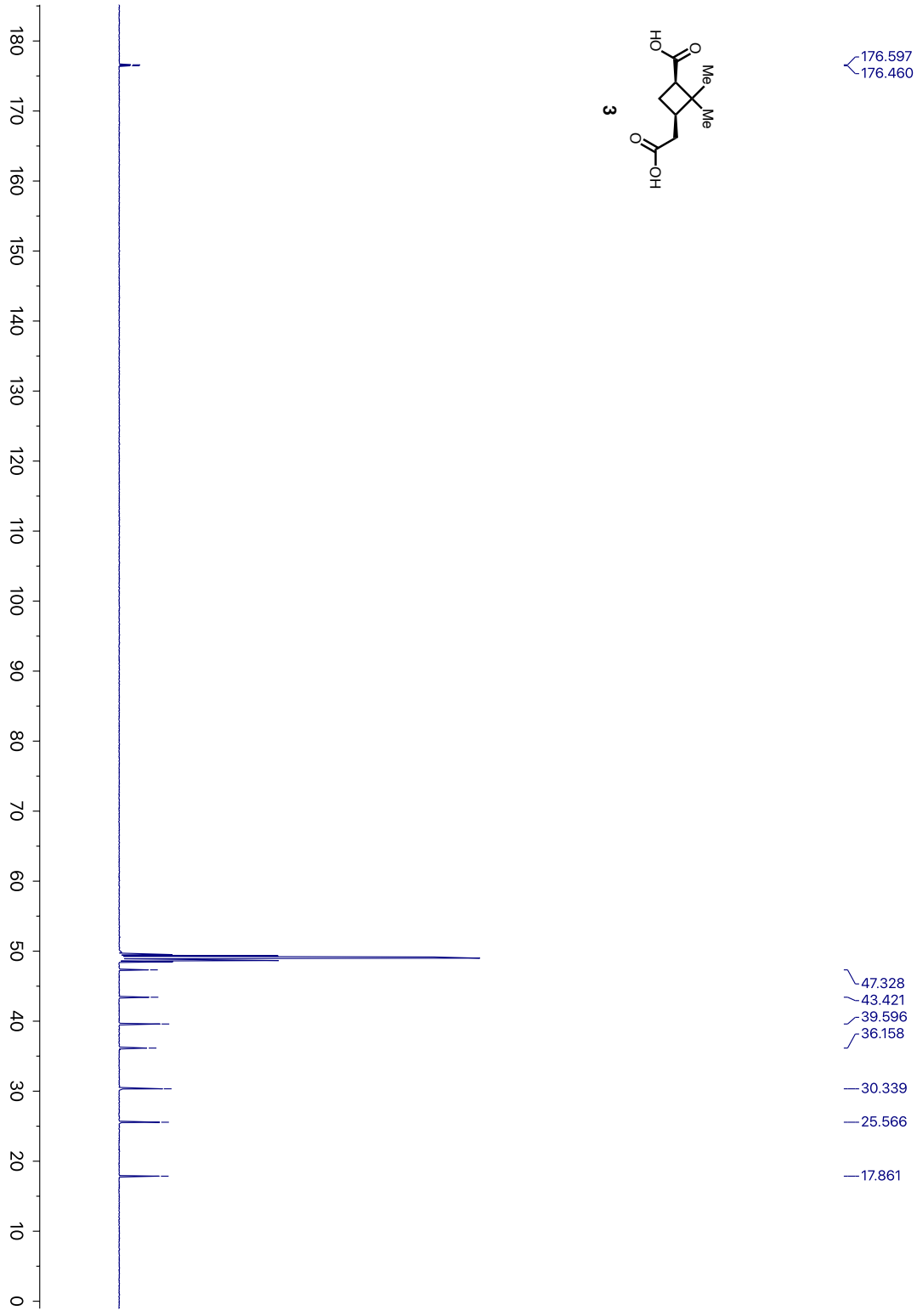
2.06
1.01
1.02
1.01
3.09
3.06
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0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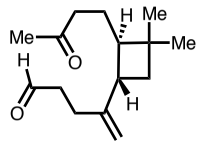
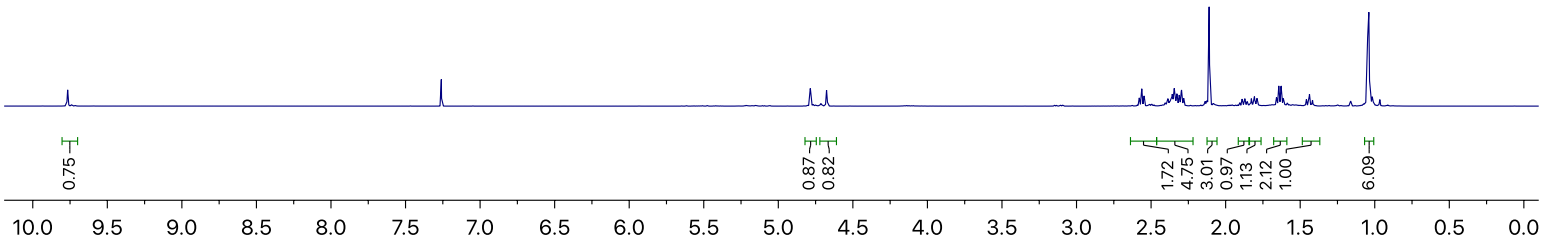
176.460
47.328
43.421
39.596
36.158
30.339
25.566
17.861
3
HO
O
Me
Me
O
OH


Me
H
O
O
H
Me
Me
H

4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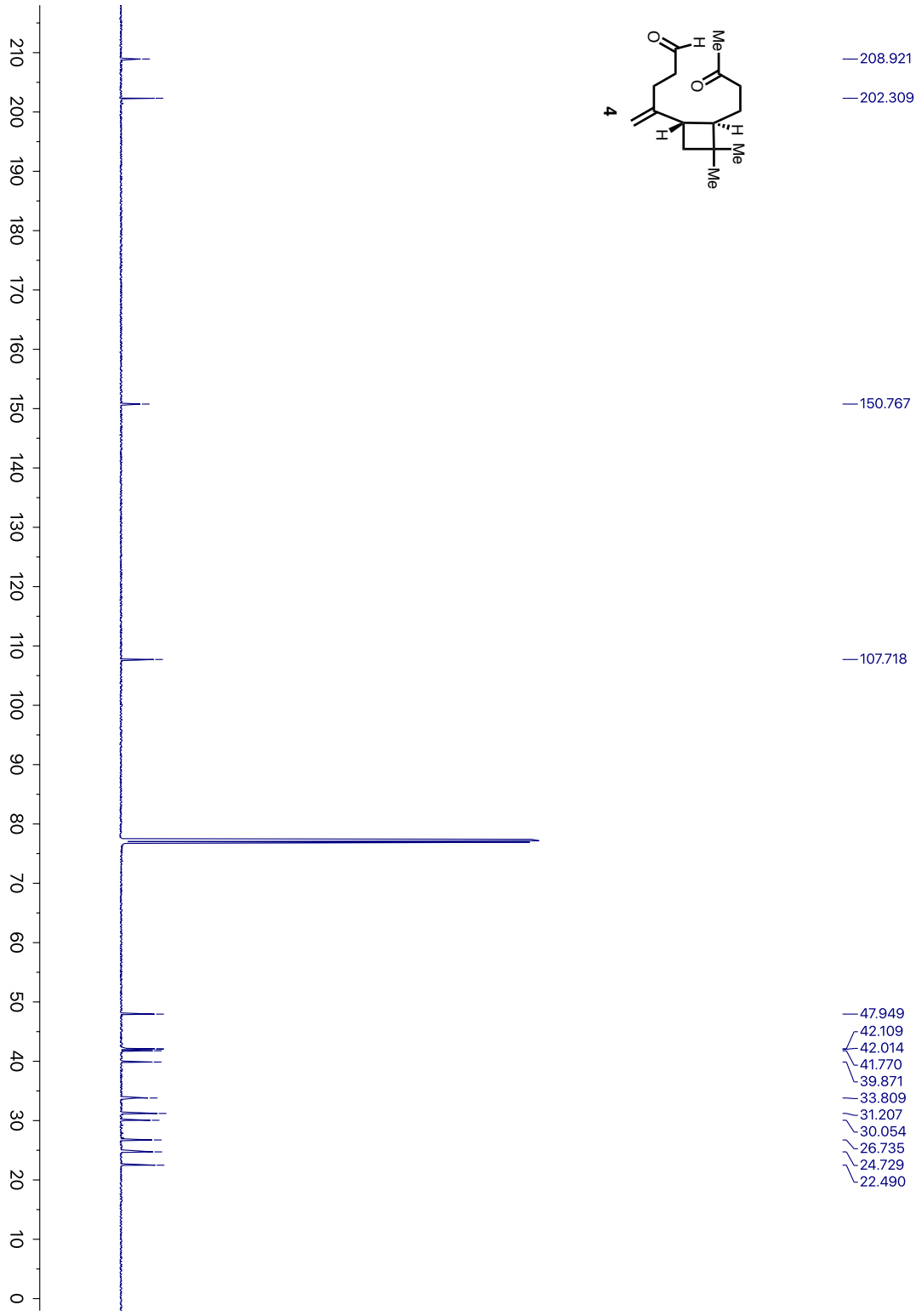
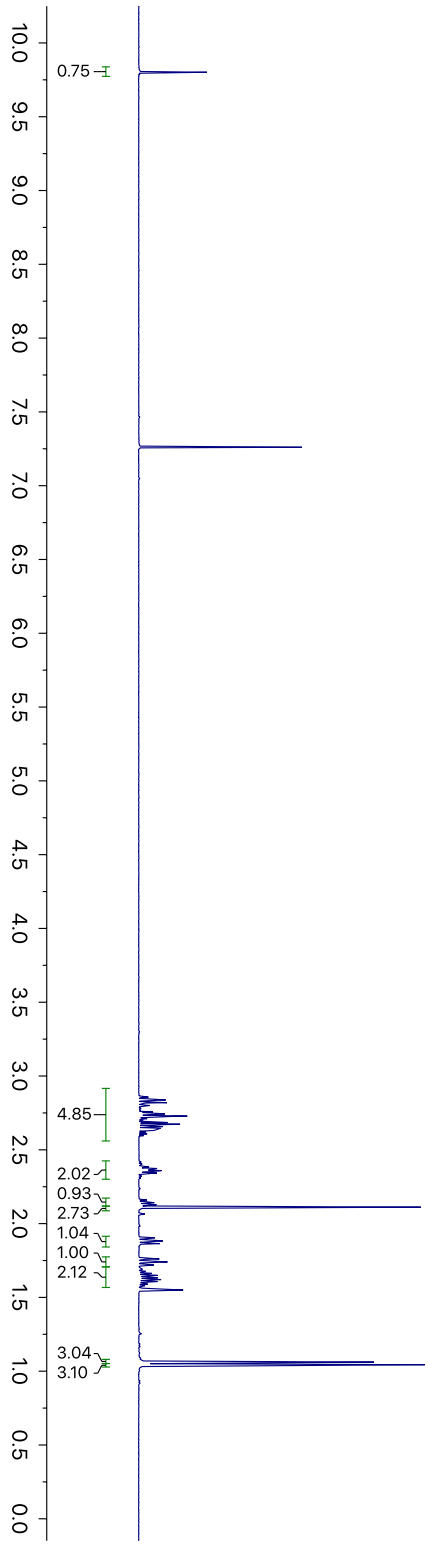
0.87
0.82
1.72
4.75
3.01
0.97
1.13
2.12
1.00
6.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


4
208.921
202.309
150.767
107.718
47.949
42.109
42.014
41.770
39.871
33.809
31.207
30.054
26.735
24.729
22.490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9.0
8.5
8.0
7.5
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6.5
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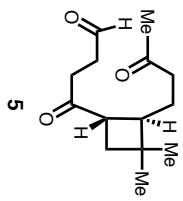
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.75
4.85
2.02
0.93
2.73
1.04
1.00
2.12
3.04
3.10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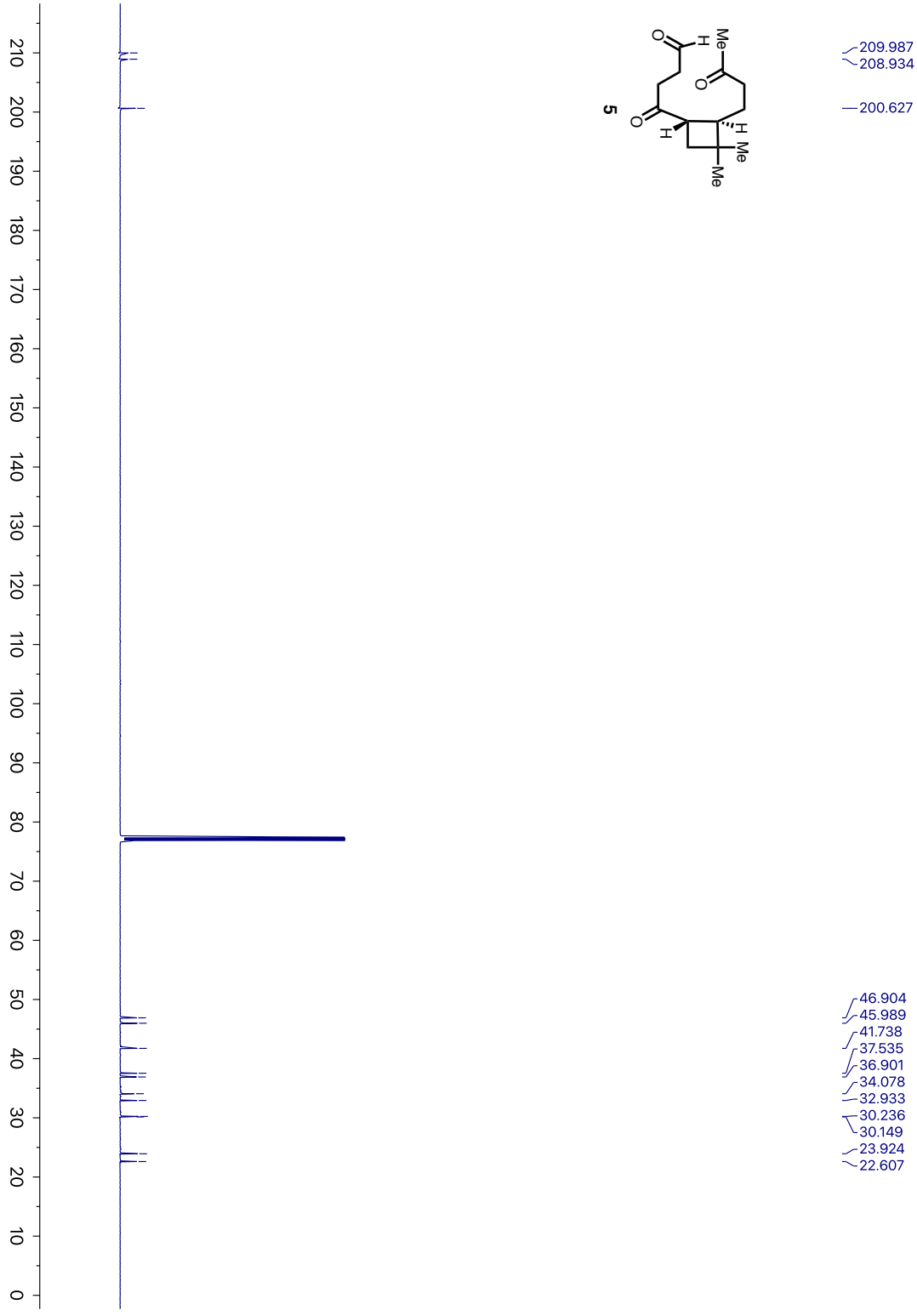
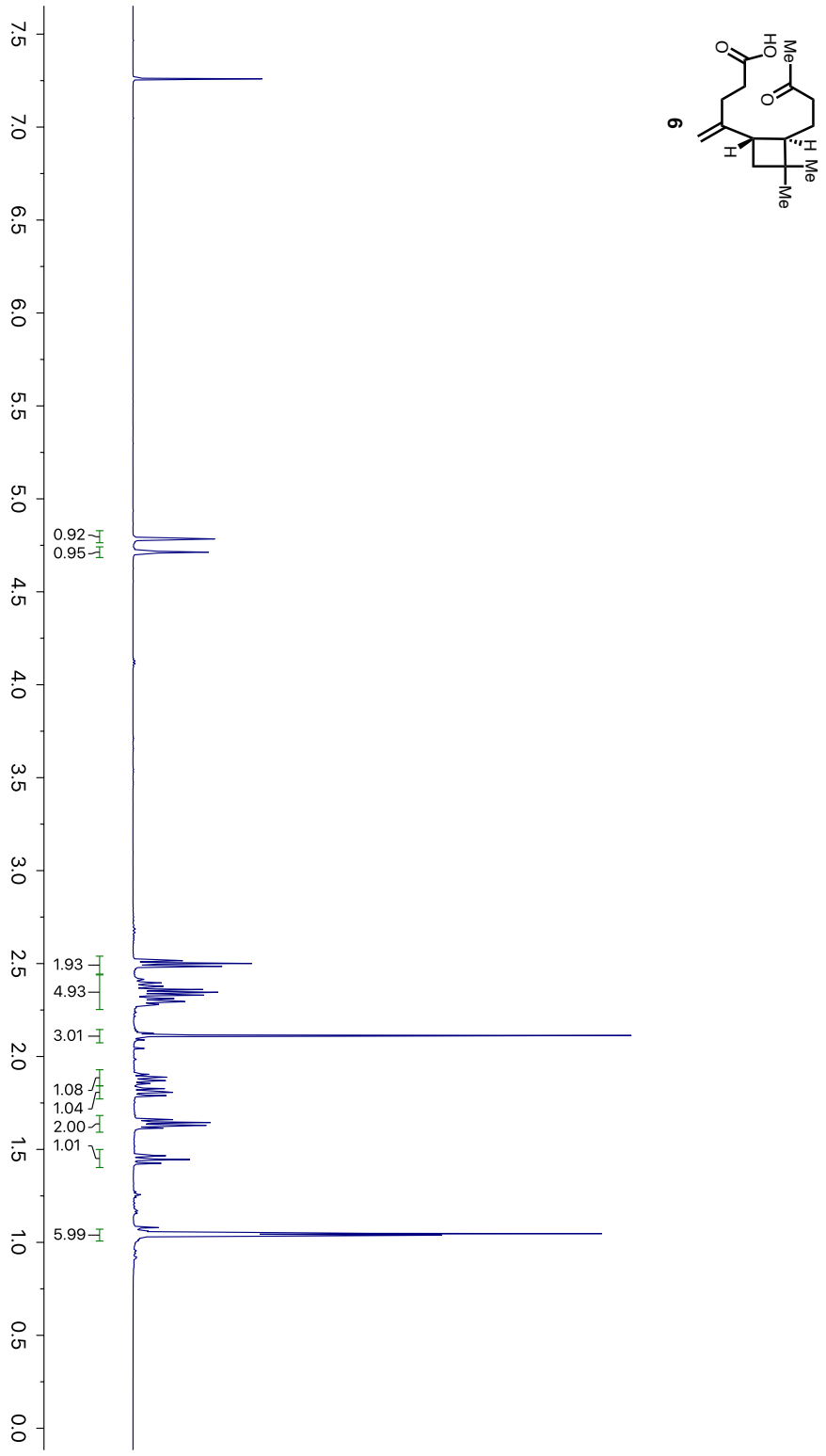
H
O
O
O
H
H
Me
Me

5


5
209.987
208.934
200.627
46.904
45.989
41.738
37.535
36.901
34.078
32.933
30.236
30.149
23.924
22.607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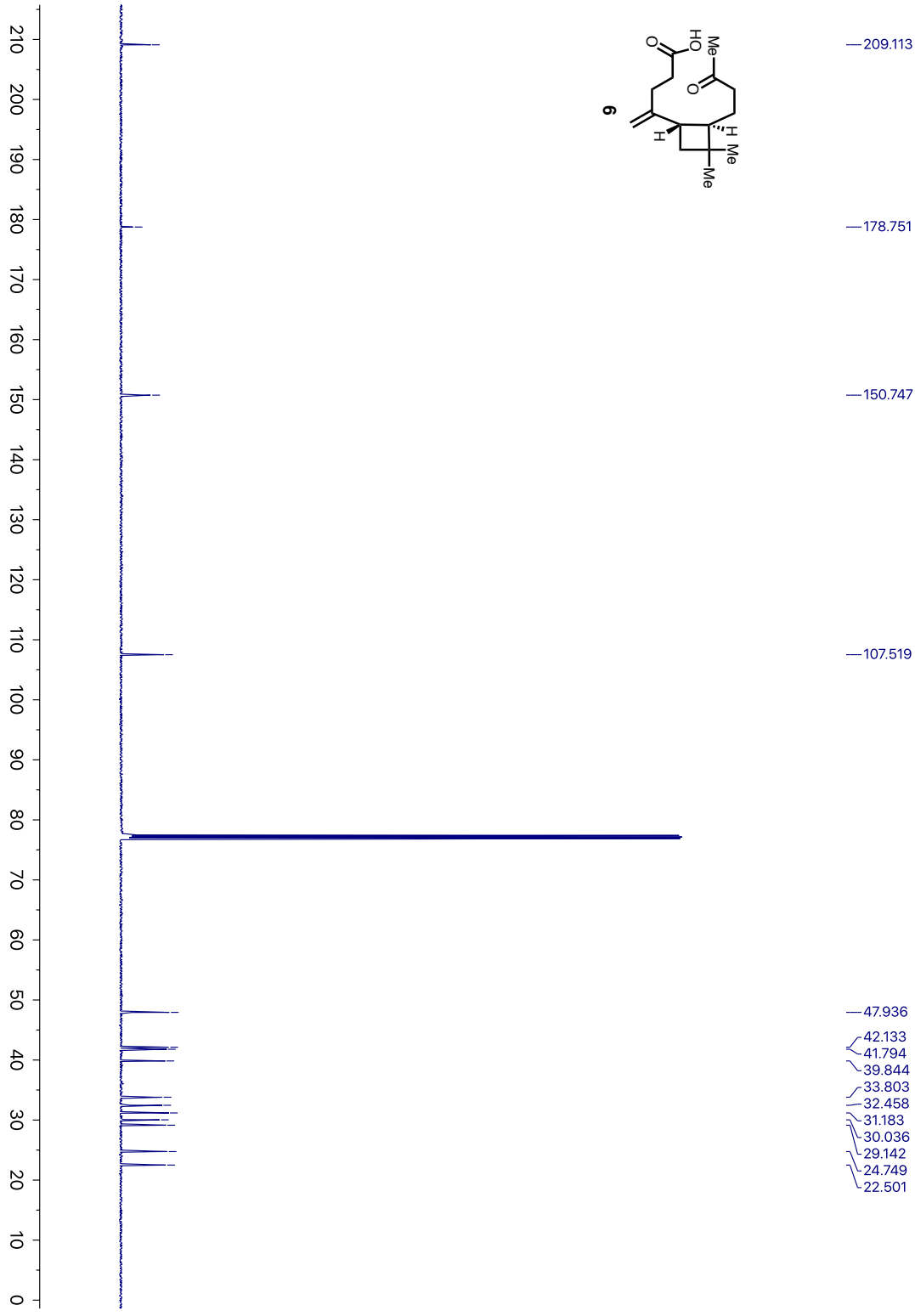
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.92
0.95
1.93
4.93
3.01
1.08
1.04
2.00
1.01
5.99
HO
Me
O
O
H
H
Me
Me
6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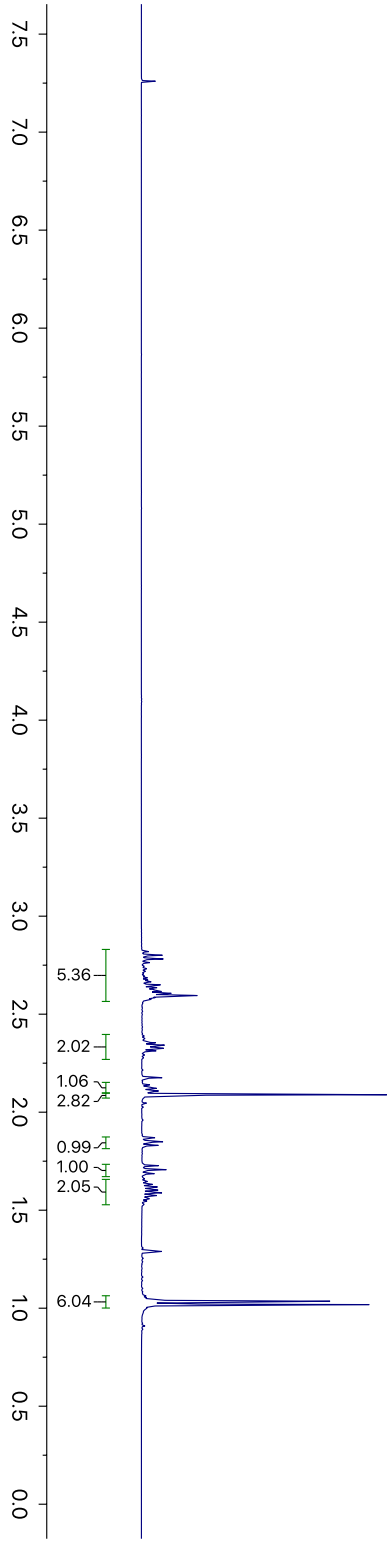
41.794
39.844
33.803
32.458
31.183
30.036
29.142
24.749
22.501
6


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
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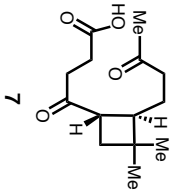
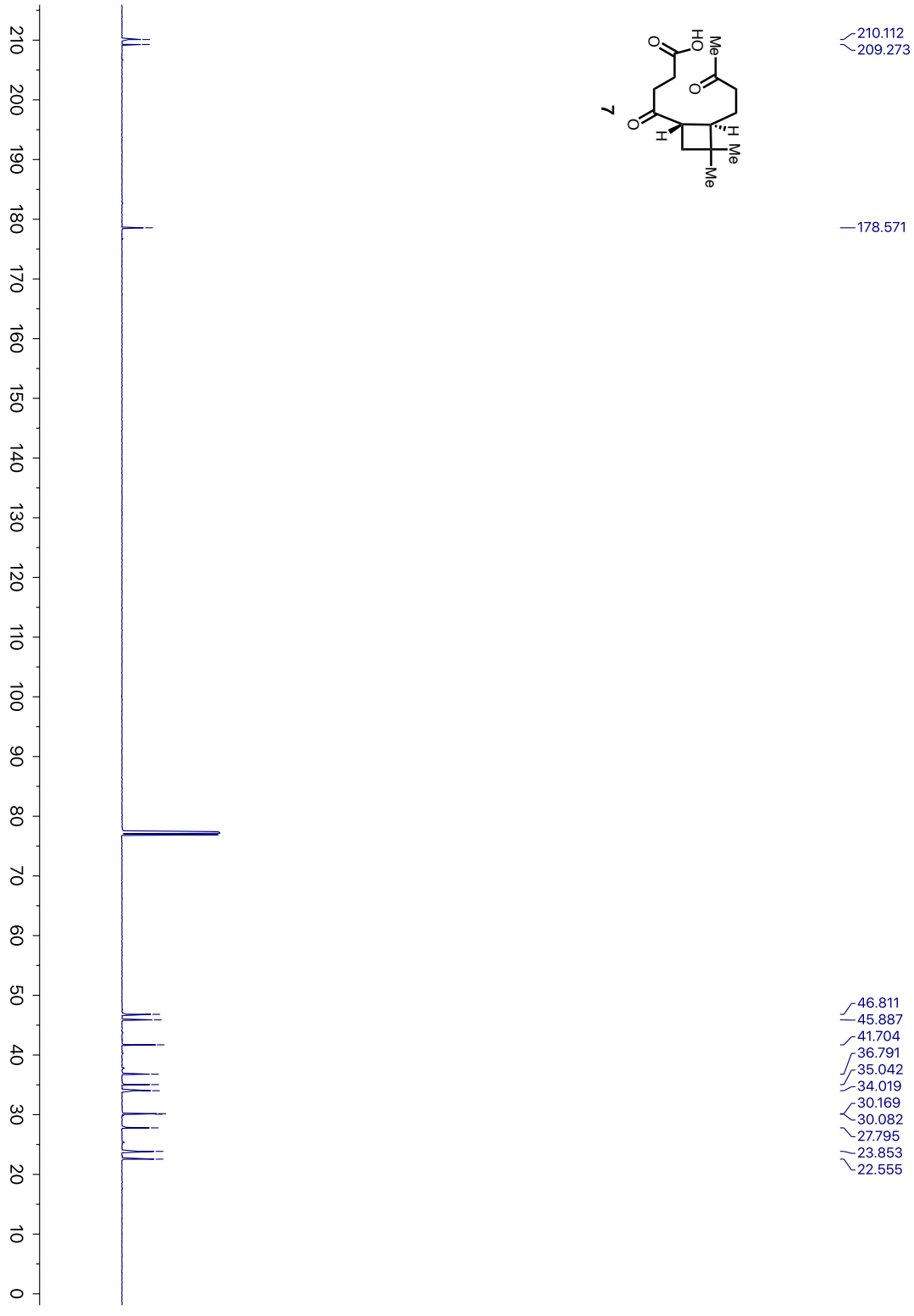
2.02
1.06
2.82
0.99
1.00
2.05
6.04


HO
Me
O
O
O
H
H
Me
Me

7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41.704
36.791
35.042
34.019
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30.082
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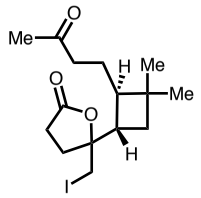
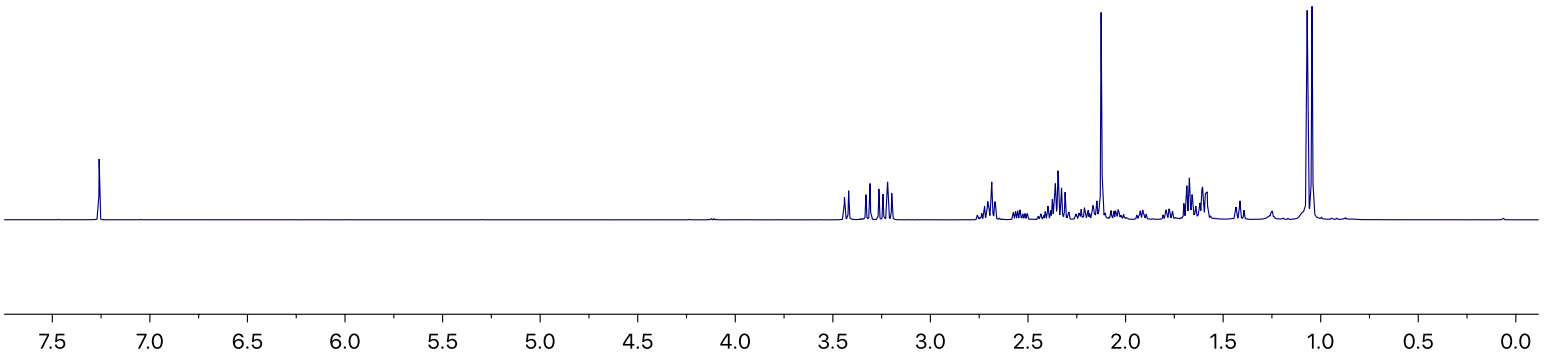
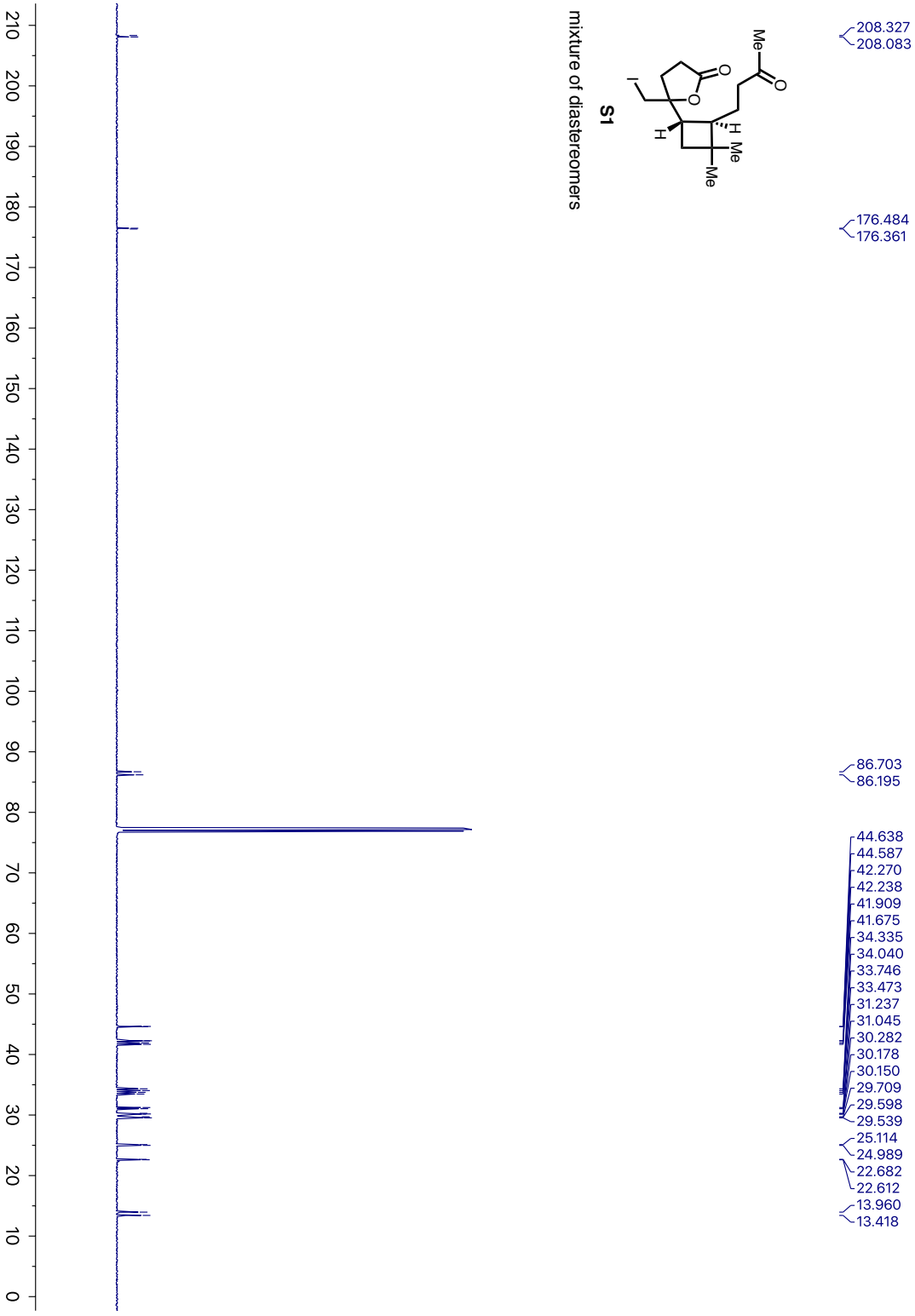
23.853
22.555
7



S1

mixture of diastereomers

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mixture of diastereomers
Me
O
O
I
O
H
H
Me
Me
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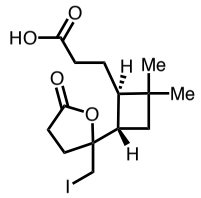
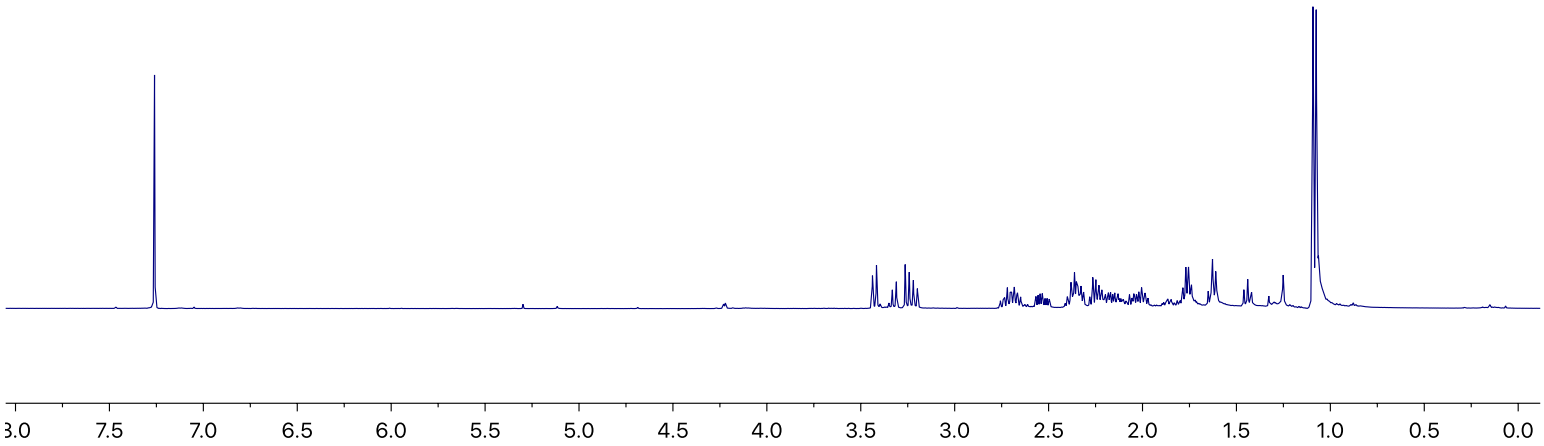
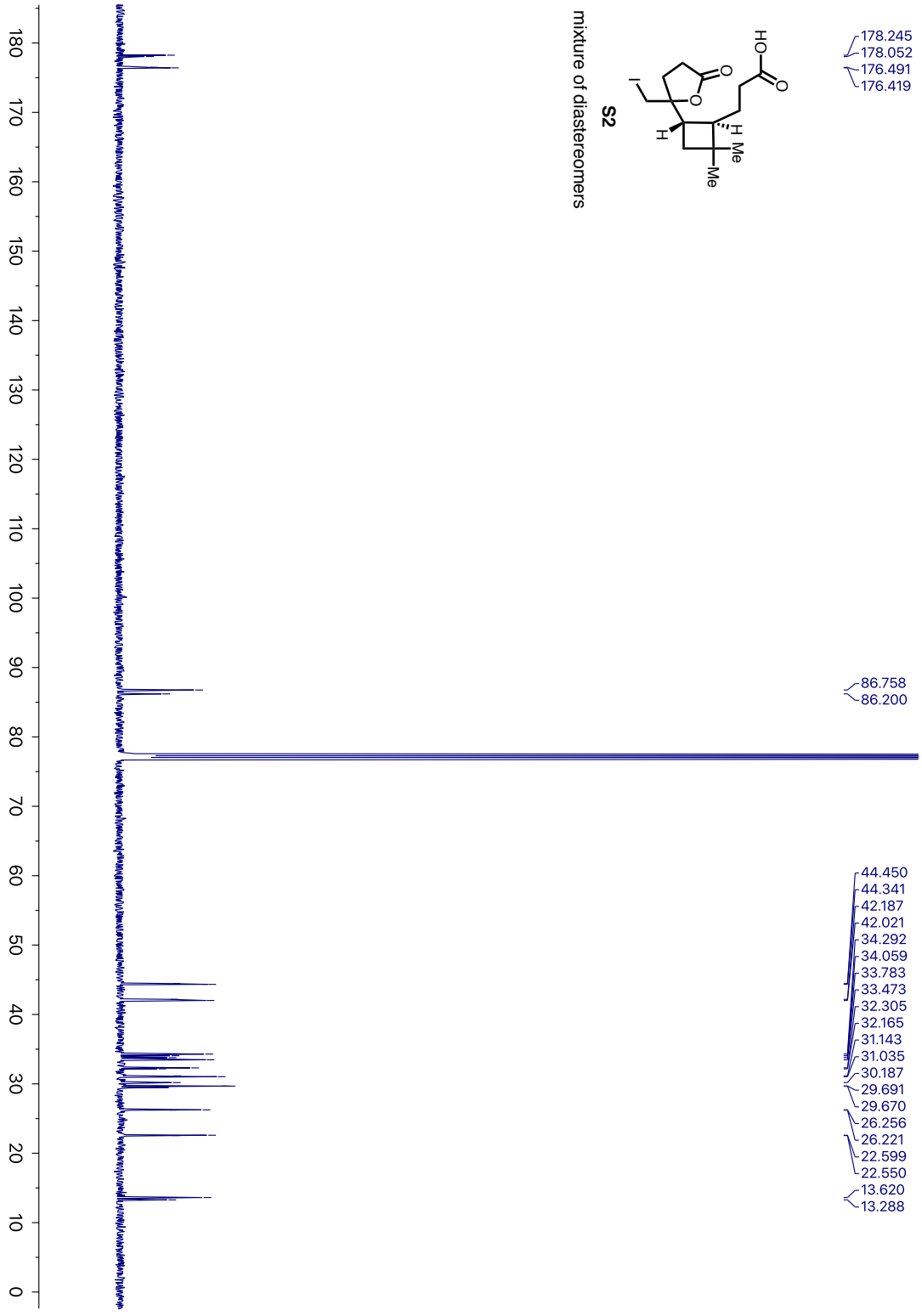
208.083
176.484
176.361
86.703
86.195
44.638
44.587
42.270
42.238
41.909
41.675
34.335
34.040
33.746
33.473
31.237
31.045
30.282
30.178
30.150
29.709
29.598
29.539
25.114
24.989
22.682
22.612
13.960
13.418
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



S2

mixture of diastereomers




S2
mixture of diastereomers
HO
O
O
O
I
H
H
Me
Me
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178.052
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176.419
86.758
86.200
44.450
44.341
42.187
42.021
34.292
34.059
33.783
33.473
32.305
32.165
31.143
31.035
30.187
29.691
29.670
26.256
26.221
22.599
22.550
13.620
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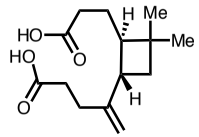
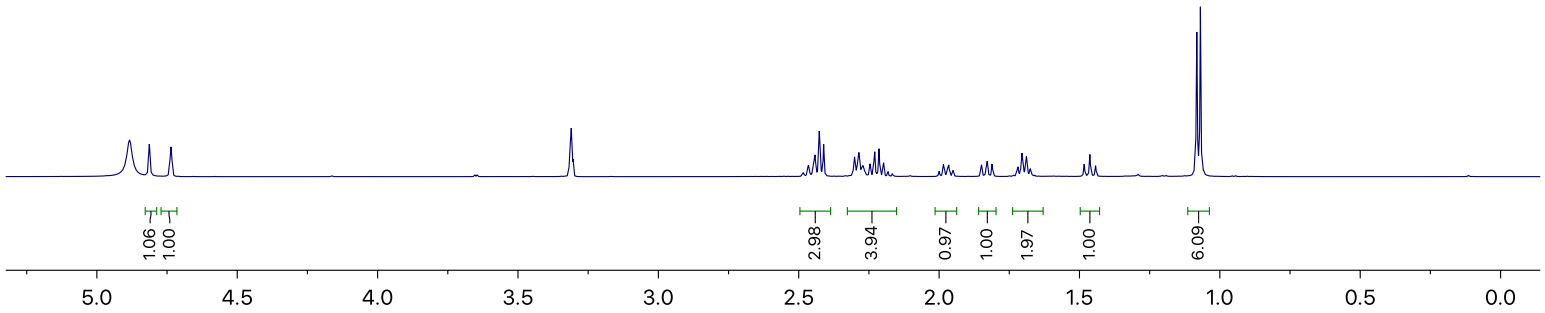
70
60
50
40
30
20
10
0


HO
HO
O
O
H
Me
Me
H

8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1.00
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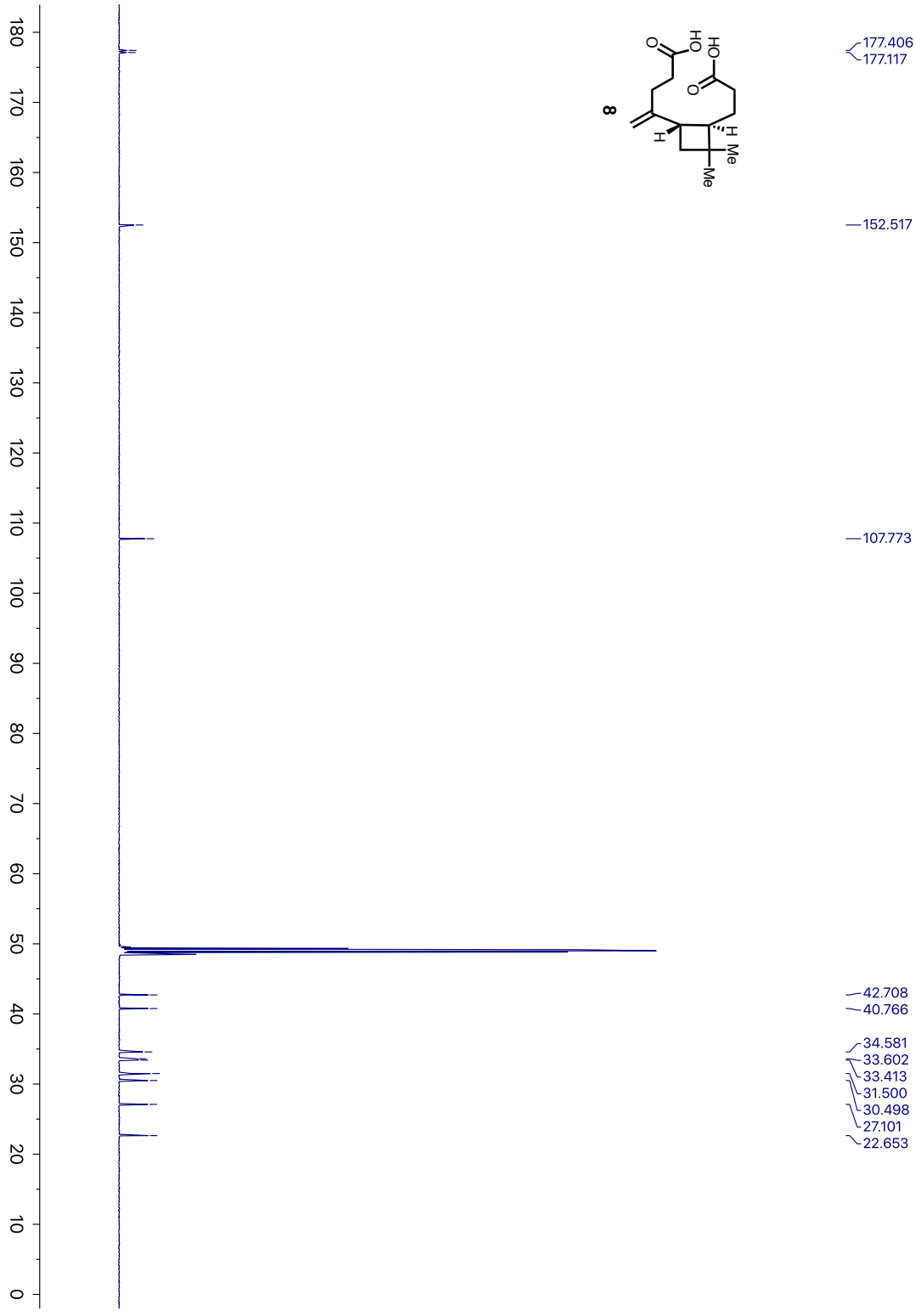
3.0
2.5
2.0
1.5
1.0
0.5
0.0


8
HO
O
HO
O
H
H
Me
Me
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152.517
107.773
42.708
40.766
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33.602
33.413
31.500
30.498
27.101
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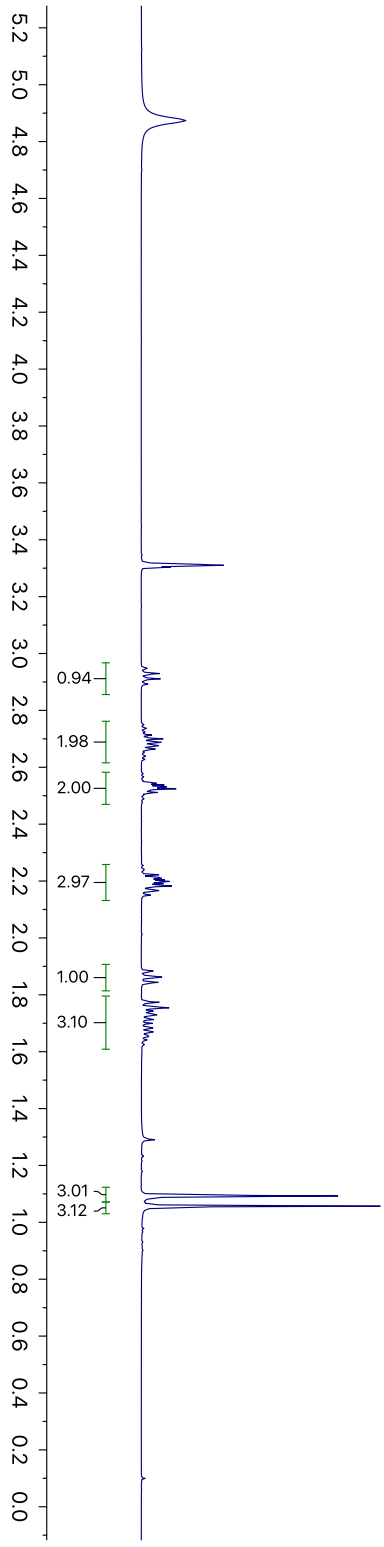
90
80
70
60
50
40
30
20
10
0


5.2
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4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
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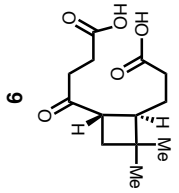
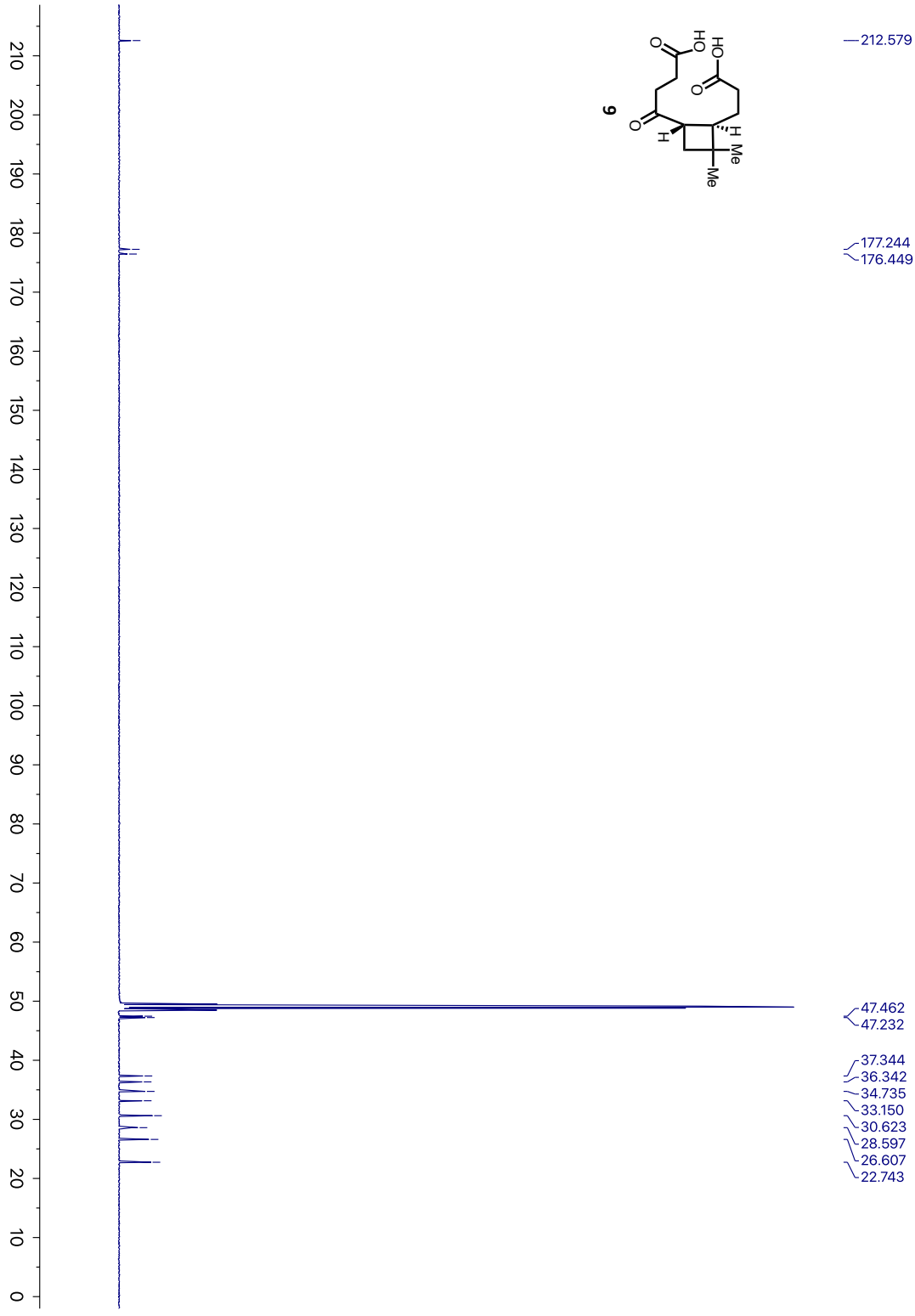
0.0
0.94
1.98
2.00
2.97
1.00
3.10
3.01
3.12


HO
HO
O
O
O
O
H
H
Me
Me

9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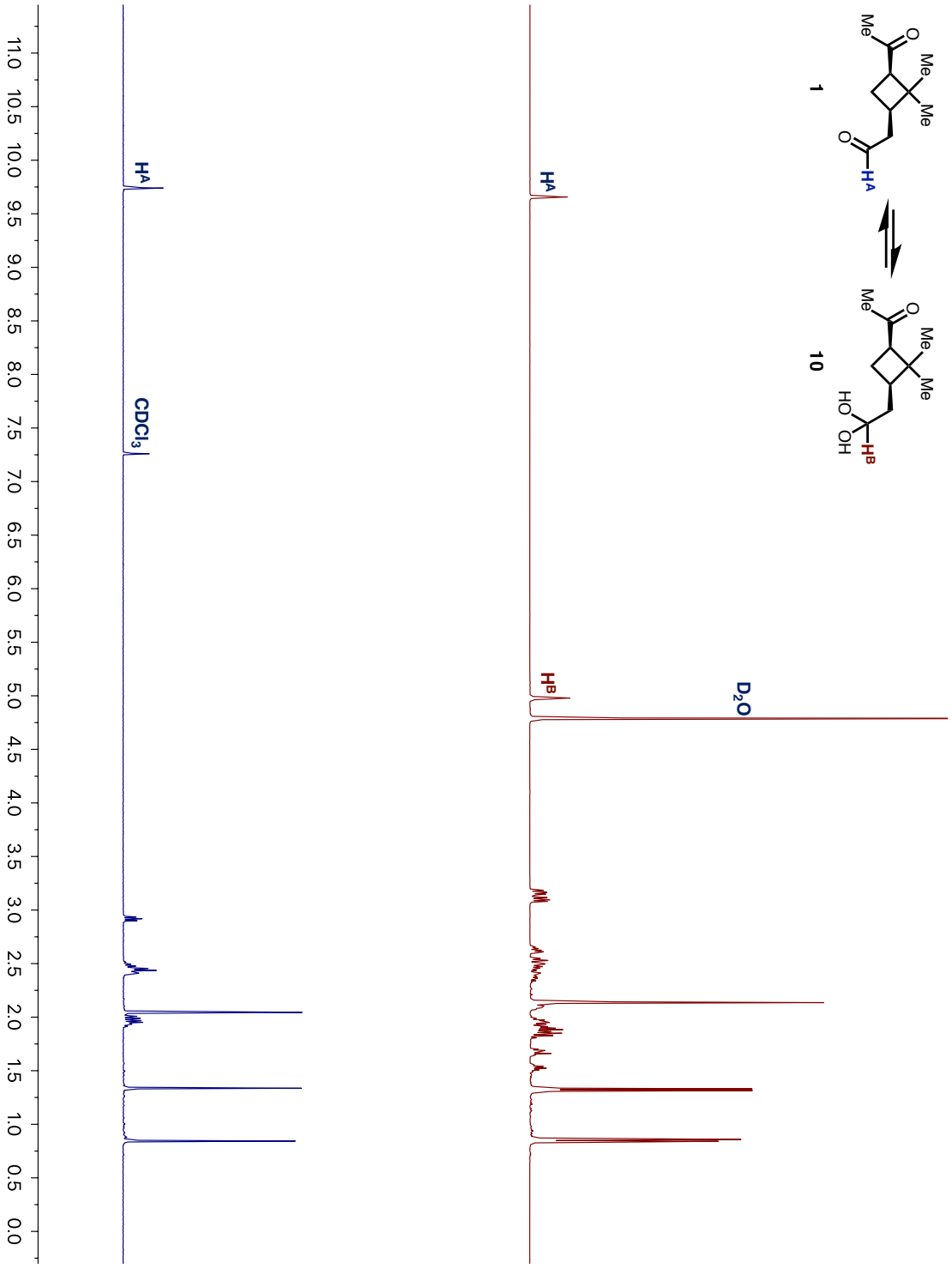
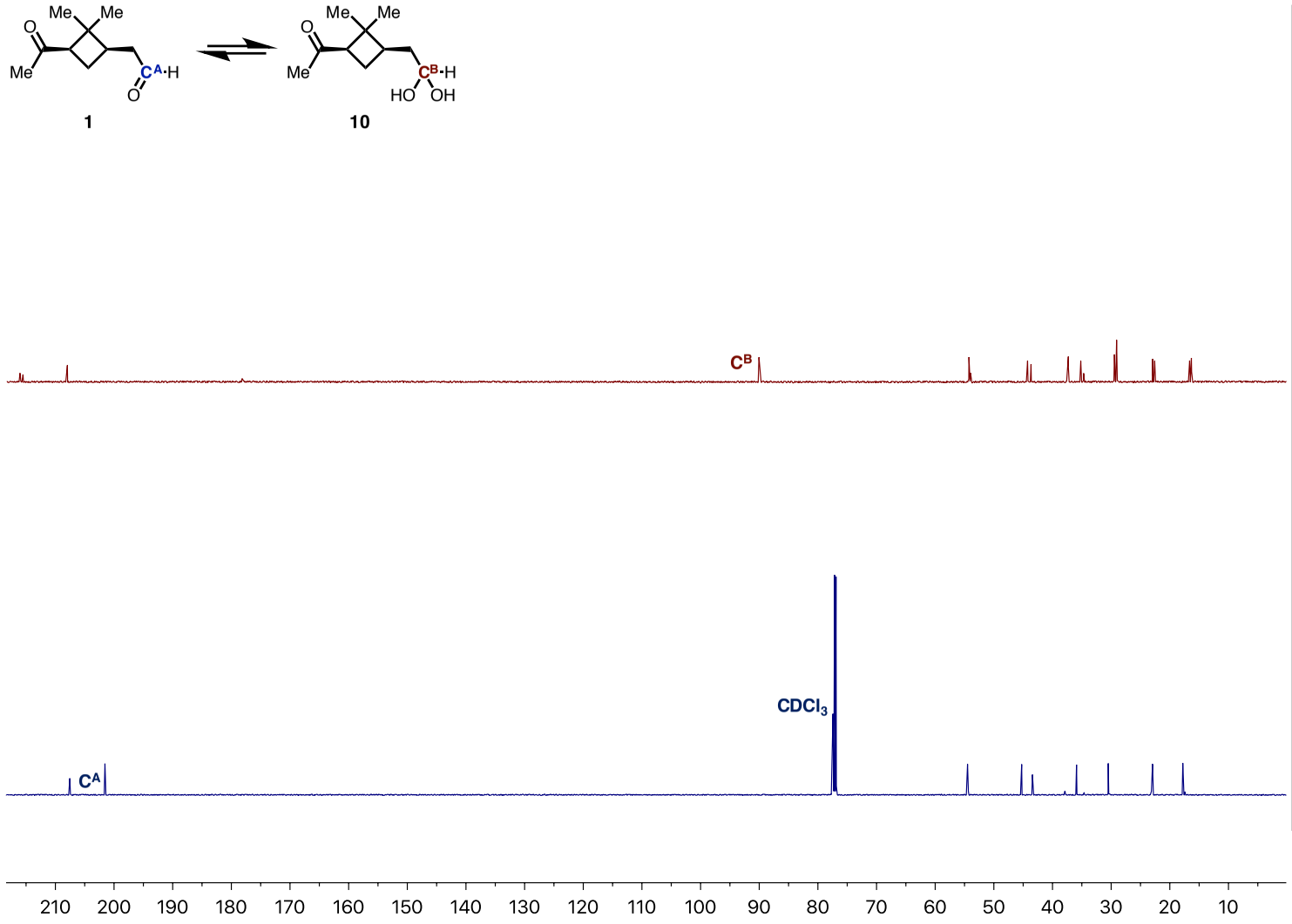
177.244
176.449
47.462
47.232
37.344
36.342
34.735
33.150
30.623
28.597
26.607
22.743
9

3.2 ^{1}H and ^{13}C NMR Spectra Revealing Aldehyde to Hydrate Conversion




Me
Me
O
Me
C^A·H
O
1
Me
Me
O
Me
C^B·H
HO
OH
10
C^B
CDCl3
C^A
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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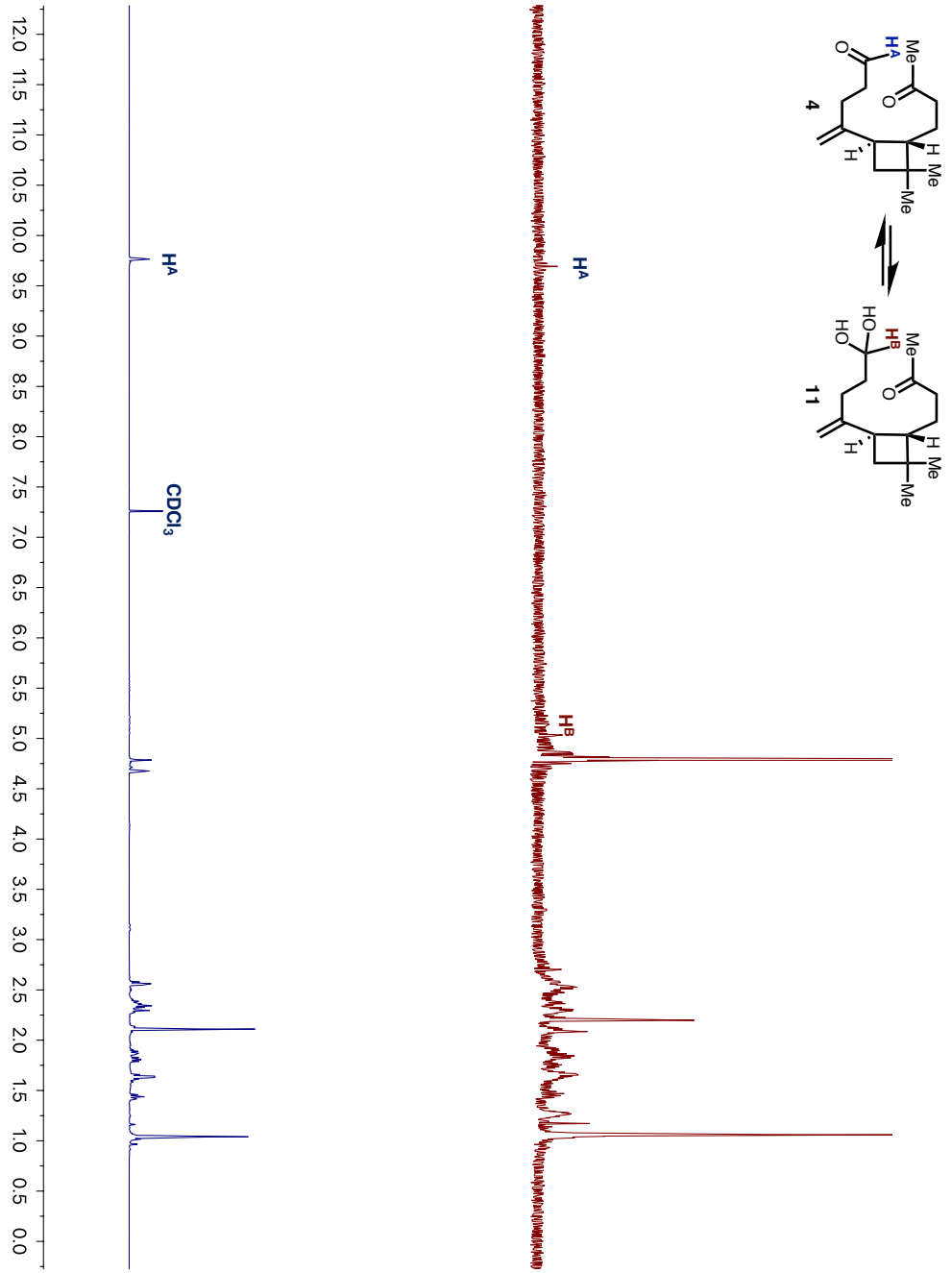
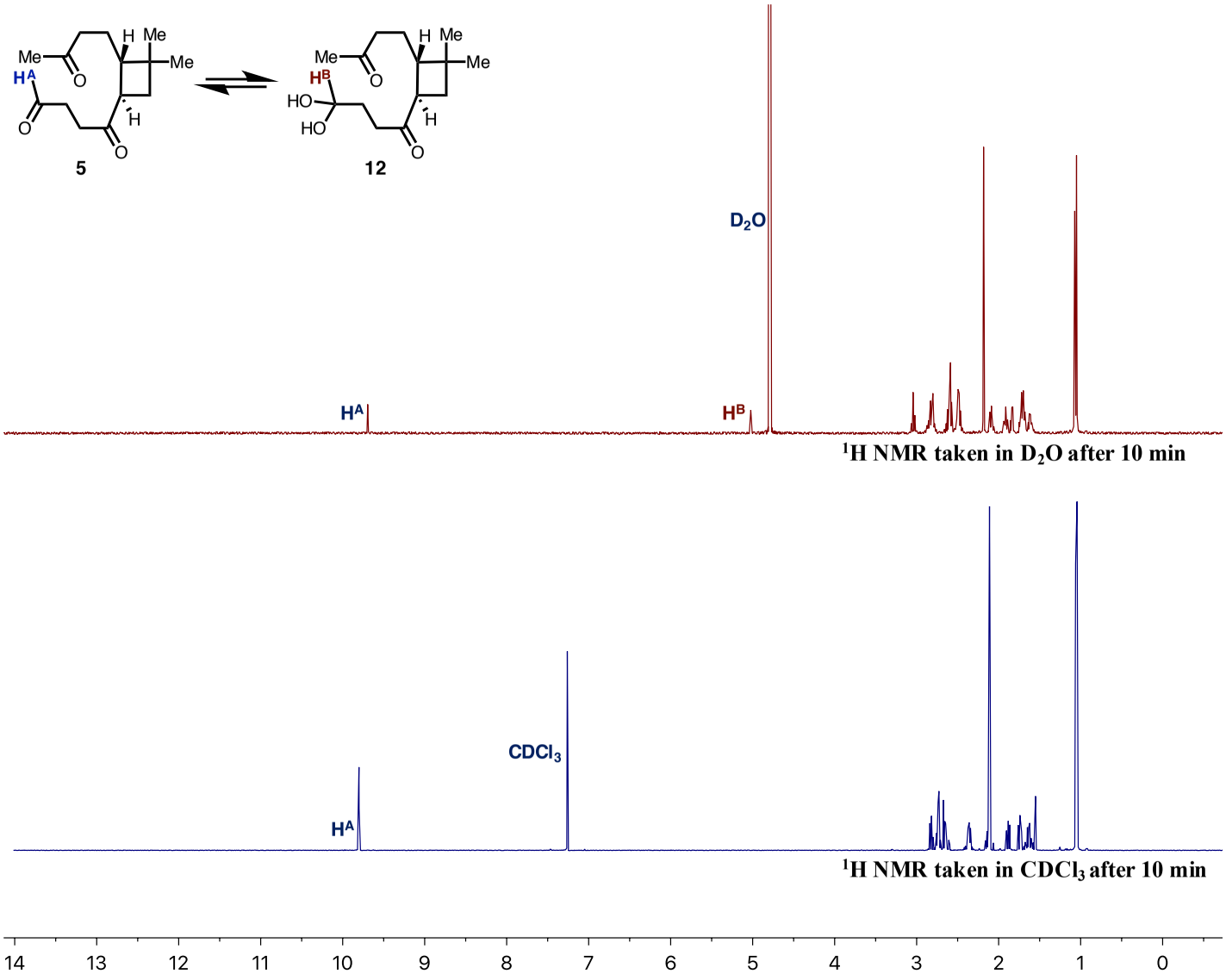
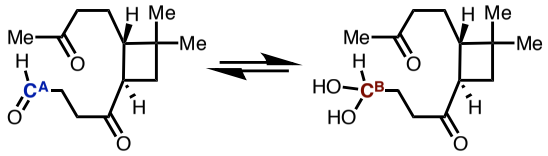
10

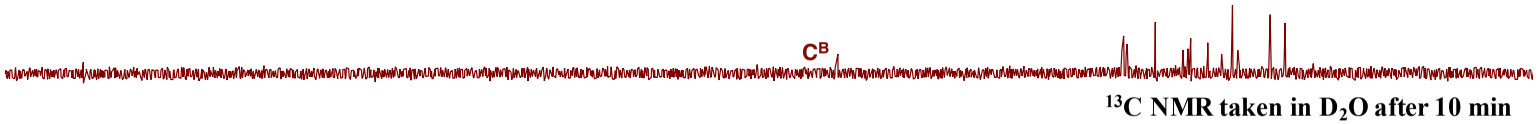


Note that the sparing solubility of β-caryophyllene aldehyde (**4**) in D_2O resulted in low signal-to-noise in the NMR spectra obtained for this compound and therefore the ^{13}C NMR data is not included.


Me
H
Me
Me
HA
O
O
H
O
5
Me
H
Me
Me
HB
O
HO
HO
H
O
12
D2O
HA
HB
1H NMR taken in D2O after 10 min
CDCl3
HA
1H NMR taken in CDCl3 after 10 min
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0

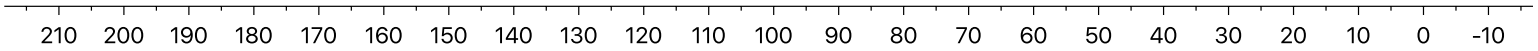


5 **12**



^{13}C NMR taken in D_2O after 10 min

^{13}C NMR taken in $CDCl_3$ after 10 min



4. Dynamic Surface Tension Experimental Details and Supplementary Data

4.1 Dynamic Surface Tension Experimental Details. The procedure and experimental setup for interfacial tension measurements using PDT have been described in detail previously.[3] Briefly, surface tension was measured on a FTA125 goniometer by capturing images of droplets over the course of ten minutes at 20 ± 2 °C for solutions prepared in either deionized H_2O or 1.0 M $(NH_4)_2SO_4$ solution. The pH of the $(NH_4)_2SO_4$ solutions were approximately 5.0–6.0 and the pH of solutions prepared in water were approximately 6.0–7.5. Measurements are reported as an average of 3–5 successive runs (replicates). Interfacial tension measurements reported previously from our labs were performed using a 1 mL plastic syringe.[3] Due to the increased hydrophobicity of compounds measured here relative to those studied previously,[3] a consistent reduction in surface tension was noticed when comparing successive data acquisitions on the same solution collected using a plastic syringe without refreshing the solution volume in the syringe between runs (Figure S2). Potentially due to the solute molecules partitioning to the interior walls of the plastic syringe over time, this "dipping effect" was first noticed for oxidation products derived from β-caryophyllene and was especially pronounced for the more hydrophobic compounds that exhibit lower solubility in water and 1.0 M $(NH_4)_2SO_4$. This "dipping effect" was not observed in our previous study,[3] likely due to the highly hydrophilic nature of the isoprene-derived oxidation products compared to the compounds analysed in this study. Use of a clean and oven-dried 1 mL glass syringe eliminated the "dipping effect" for all compounds studied here.

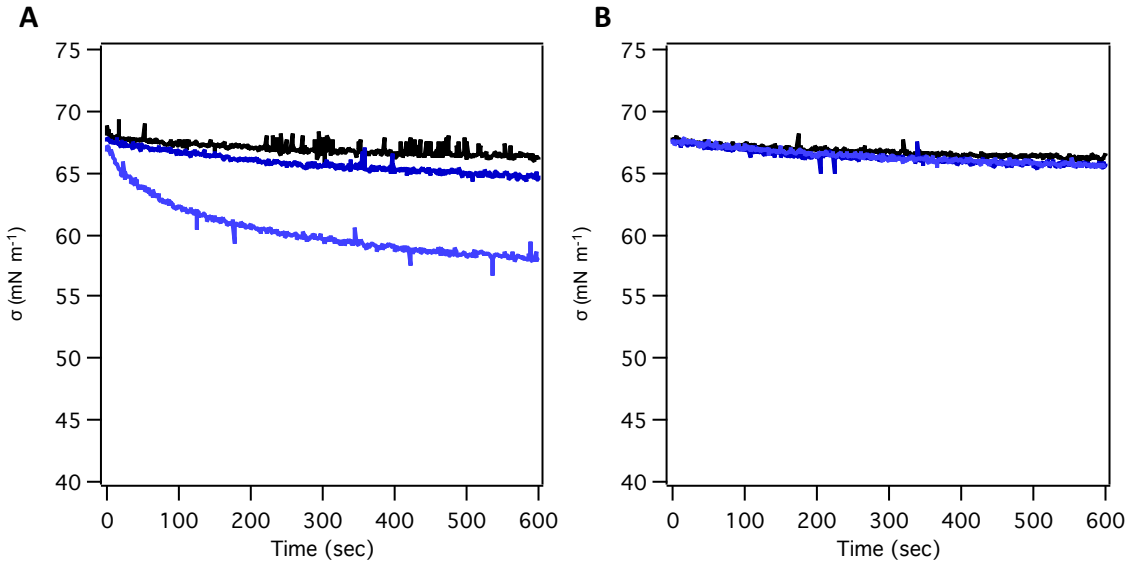


Figure S2. A) Example of "dipping effect" in surface tension data observed upon measuring a β-caryophyllene-derived oxidation product when volume in syringe was not refreshed and a plastic syringe was used. B) "Dipping effect" not observed when volume in syringe was refreshed each time using a plastic syringe and when volume in syringe was not refreshed using a glass syringe.

4.2 Dynamic Surface Tension Supplementary Data

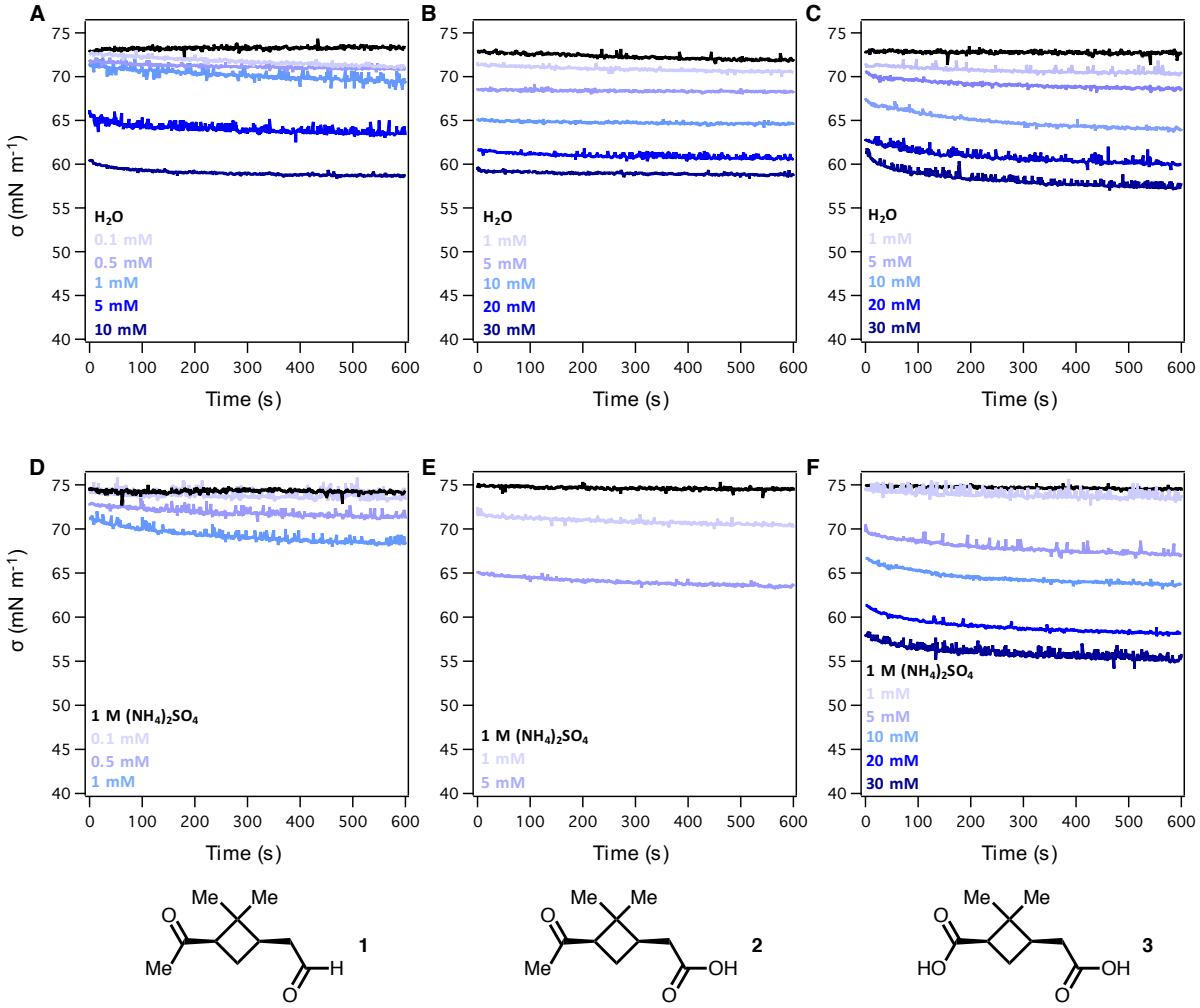


Figure S3 Dynamic surface tension measurements for pinonaldehyde **1** (**A, D**), pinonic acid **2** (**B, E**), and pinic acid **3** (**C, F**) in water (**top**) and 1.0 M ammonium sulfate (**bottom**). Pinonaldehyde **1** (**A**) was insoluble at concentrations greater than 10 mM in dH$_2$O. Pinonaldehyde **1** (**D**) and pinonic acid **2** (**E**) were insoluble at concentrations greater than 1 mM and 5 mM in 1.0 M ammonium sulfate, respectively.

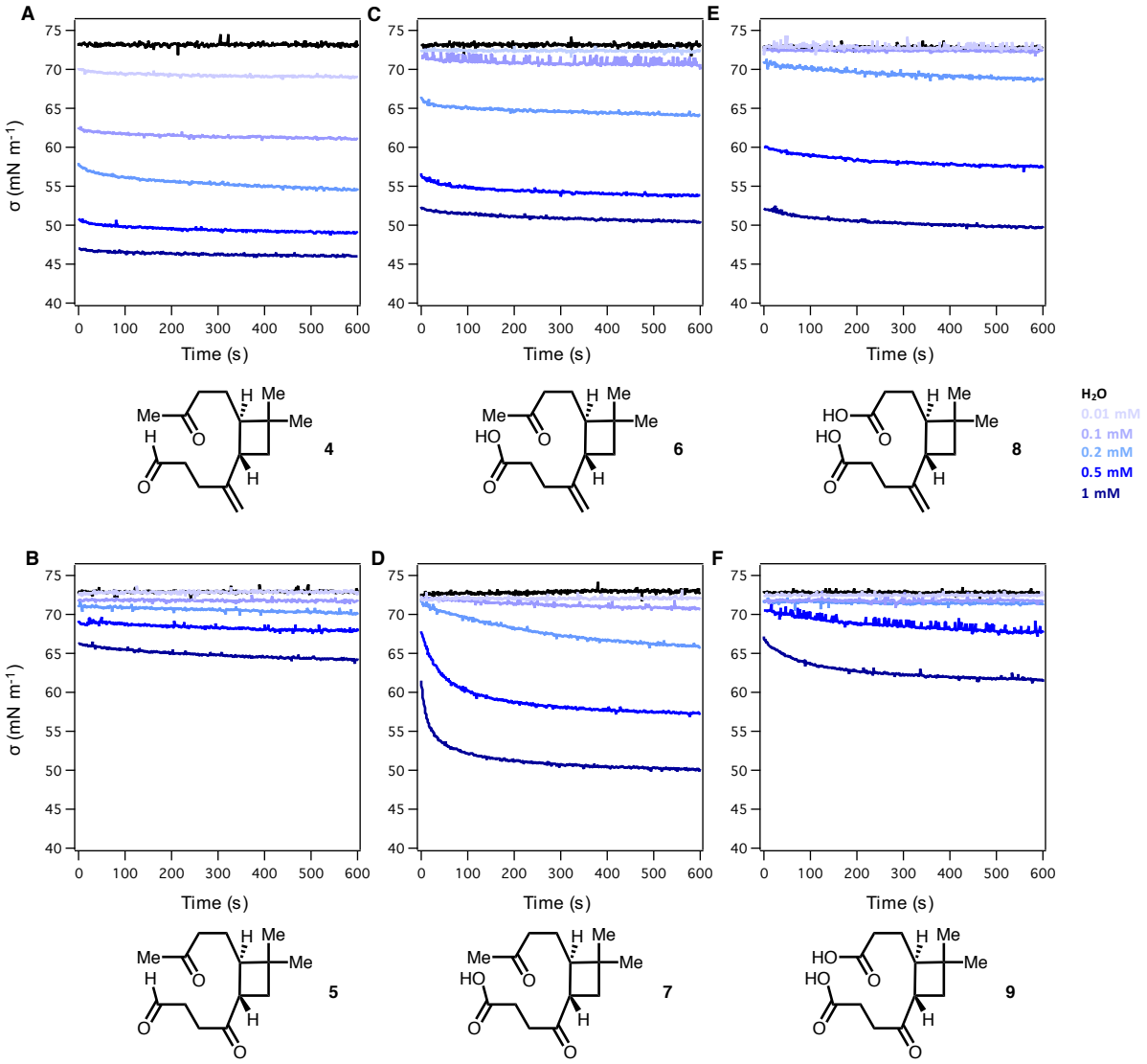


Figure S4. Dynamic surface tension measurements for β-caryophyllene aldehyde **4** (**A**), β-nocaryophyllone aldehyde **5** (**B**), β-caryophyllonic acid **6** (**C**), β-nocaryophyllonic acid **7** (**D**), β-caryophyllinic acid **8** (**E**), and β-nocaryophyllinic acid **9** (**F**) in water.

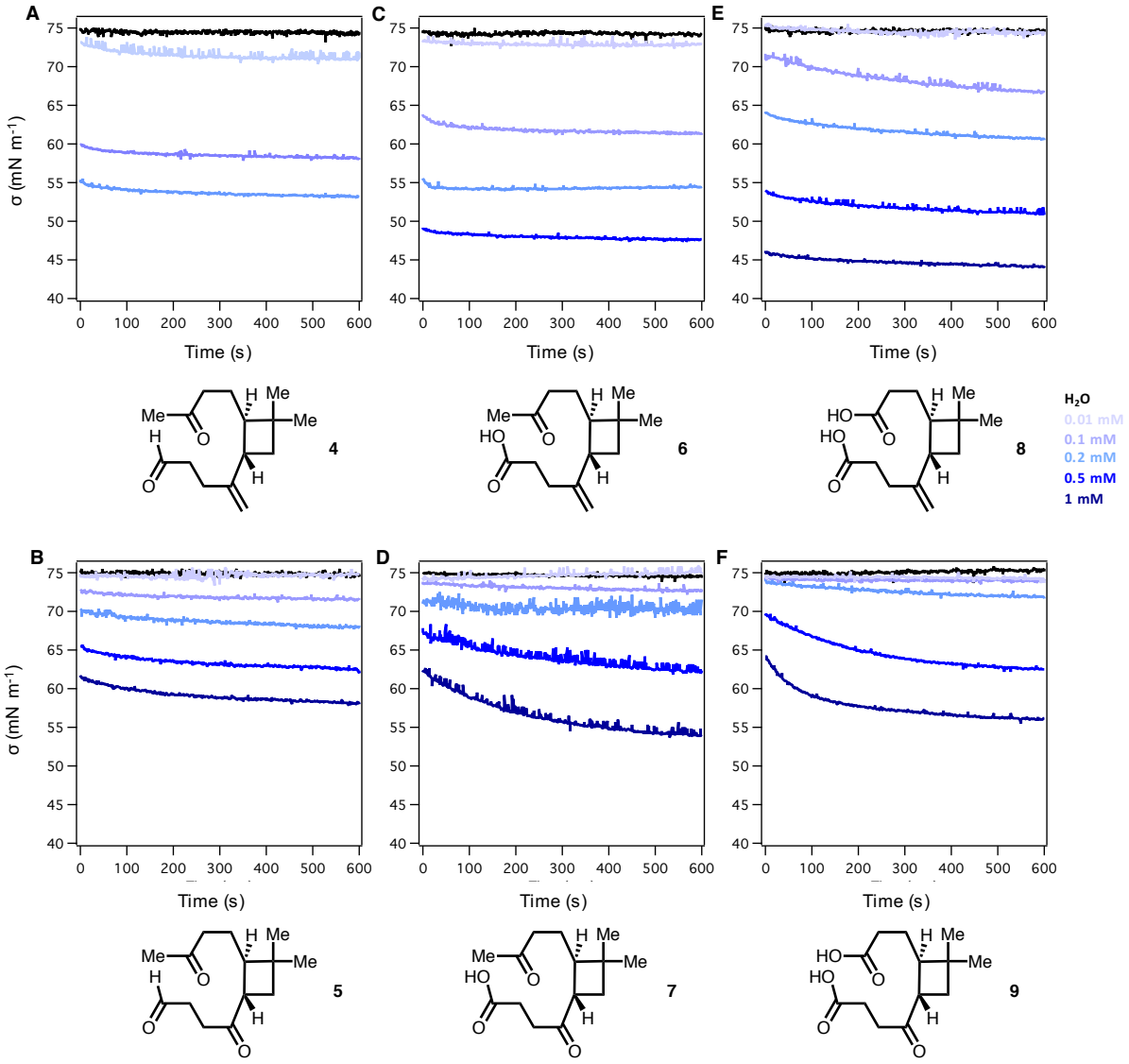
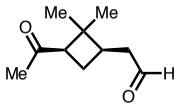
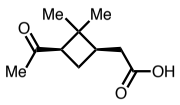
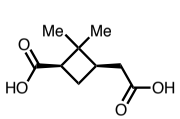
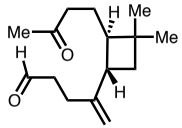
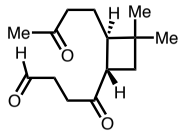


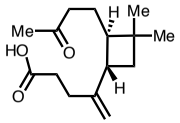
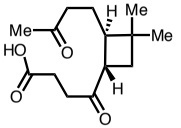
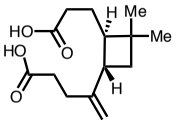
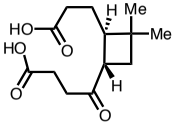
Figure S5. Dynamic surface tension measurements for β-caryophyllene aldehyde **4** (**A**), β-nocaryophyllone aldehyde **5** (**B**), β-caryophyllonic acid **6** (**C**), β-nocaryophyllonic acid **7** (**D**), β-caryophyllinic acid **8** (**E**), and β-nocaryophyllinic acid **9** (**F**) in 1.0 M ammonium sulfate. β-Caryophyllene aldehyde **4** (**A**) and β-caryophyllonic acid **6** (**C**) were insoluble at concentrations above 0.2 mM and 0.5 mM, respectively.

Table S1. Optimized fitting parameters for kinetics of interfacial tension and equilibration timescale calculations.

compound	conc. (mM)	n	σ_0 (mN m^{-1})	σ_m (mN m^{-1})	t_{m_lab} (s)	D_{drop} (mm)	$t_{eq\_1\ \mu m}$ (s)
pinonaldehyde 1 	0.1	1.06±0.25 (0.75±1.69)	72.63±0.07 (74.30±0.46)	68.94±1.91 (73.32±1.86)	841±716 (n.d.*)	2.21±0.03 (2.18±0.04)	3.20x10^{-4} (n.d.*)
	0.5	1.00±0.34 (0.98±0.46)	71.77± 0.08 (72.83±0.17)	70.54±0.32 (70.45±1.22)	257±123 (395±382)	2.29±0.01 (2.15±0.02)	1.03x10^{-4} (1.71x10^{-4})
	1	0.82±0.55 (0.98±0.24)	71.30±0.25 (71.21±0.20)	64.68±12.55 (67.10±0.81)	n.d.* (269±99)	2.24±0.02 (2.14±0.06)	n.d.* (1.18x10^{-4})
	5	n.d.*	66.05±1.53	60.09±12.96	n.d.*	2.21±0.02	n.d.*
	10	0.49±0.14	60.87±0.32	57.75±0.46	101±34	2.13±0.02	4.42x10^{-5}
pinonic acid 2 	1	1.05±0.34 (0.78±0.33)	71.40±0.06 (71.65±0.12)	69.94±0.59 (68.53±2.75)	453±324 (n.d.*)	2.27±0.02 (2.04±0.09)	1.99x10^{-4} (5.05x10^{-4})
	5	1.20±0.93 (0.86±0.19)	68.55±0.05 (65.04±0.08)	68.15±0.30 (62.08±0.89)	n.d.* (538±344)	2.23±0.04 (2.04±0.08)	n.d.* (2.59x10^{-4})
	10	0.82±0.52	65.09±0.09	64.26±0.58	n.d.*	2.19±0.04	n.d.*
	20	0.65±0.53	61.71±0.27	60.02±1.34	n.d.*	2.16±0.04	n.d.*
	30	0.61±0.46	59.39±0.14	58.28±0.96	n.d.*	2.13±0.07	n.d.*
pinic acid 3 	1	1.81±0.53 (1.65±1.06)	71.28±0.07 (74.49±0.15)	70.32±0.13 (73.43±0.37)	200±32 (222±96)	2.26±0.02 (2.19±0.07)	7.85x10^{-5} (9.25x10^{-5})
	5	0.59±0.20 (0.79±0.22)	70.50±0.20 (69.76±0.22)	66.75±1.54 (65.27±1.35)	n.d.* (386±264)	2.22±0.02 (2.13±0.14)	n.d.* (1.70x10^{-4})
	10	1.27±0.10 (1.00±0.09)	67.04±0.07 (66.62±0.09)	63.28±0.16 (62.98±0.17)	192±12 (156±13)	2.11±0.05 (2.10±0.03)	8.61x10^{-5} (7.10x10^{-5})
	20	0.98±0.23 (0.67±0.08)	62.87±0.21 (61.57±0.16)	59.16±0.54 (56.44±0.47)	194±12 (211±46)	2.04±0.05 (2.04±0.02)	8.95x10^{-5} (1.01x10^{-4})
	30	0.44±0.20 (0.55±0.36)	62.13±0.90 (58.32±0.69)	53.41±3.71 (52.72±3.93)	n.d.* (n.d.*)	2.08±0.04 (1.94±0.08)	n.d.* (n.d.*)
β-caryophyllene aldehyde 4 	0.01	0.56±0.23 (1.24±0.35)	70.16±0.21 (73.12±0.21)	68.46±0.47 (70.87±0.21)	173±122 (105±20)	2.25±0.04 (2.10±0.04)	6.84x10^{-5} (4.75x10^{-5})
	0.1	0.59±0.20 (0.51±0.19)	62.44±0.15 (60.12±0.30)	60.02±0.88 (57.06±0.86)	n.d.* (231±190)	2.18±0.08 (2.03±0.01)	n.d.* (1.13x10^{-4})
	0.2	0.47±0.09 (0.51±0.13)	57.98±0.21 (55.40±0.22)	48.55±3.57 (51.55±0.91)	n.d.* (353±265)	2.08±0.11 (1.95±0.03)	n.d.* (1.86x10^{-4})
	0.5	0.47±0.15	50.93±0.22	46.83±1.72	n.d.*	1.99±0.14	n.d.*
	1	0.65±0.22	47.03±0.11	45.24±0.66	425±423	1.95±0.01	2.24x10^{-4}
β-nocaryophyllone aldehyde 5 	0.01	n.d.* (n.d.*)	72.55± 1.44 (74.50±0.07)	73.21±4.64 (74.97±1.44)	n.d.* (n.d.*)	2.23±0.05 (2.17±0.10)	n.d.* (n.d.*)
	0.1	n.d.* (0.75±0.27)	71.86±0.06 (72.71±0.14)	71.61±0.69 (71.02±0.46)	n.d.* (232±142)	2.17±0.07 (2.15±0.05)	n.d.* (1.00x10^{-4})
	0.2	1.22±0.47 (0.73±0.22)	71.01±0.05 (70.17±0.16)	68.45±3.04 (64.72±3.13)	n.d.* (n.d.*)	2.18±0.05 (2.07±0.04)	n.d.* (n.d.*)
	0.5	1.83±0.37 (0.70±0.11)	68.94±0.04 (65.56±0.15)	67.62± 0.18 (60.53±0.75)	293±47 (349±130)	2.14±0.02 (2.03±0.02)	1.27x10^{-4} (1.69x10^{-4})
	1	0.88±0.12 (0.90±0.08)	66.21±0.07 (61.52±0.09)	62.52±0.64 (56.76±0.30)	488±177 (229±28)	2.14±0.02 (2.03±0.03)	2.12x10^{-4} (1.12x10^{-4})

* = due to large uncertainties on the point estimates

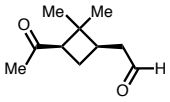
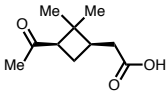
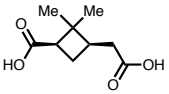
Table S1 (continued). Optimized fitting parameters for kinetics of interfacial tension and equilibration timescale calculations.

compound	conc. (mM)	n	σ_0 (mN m^{-1})	σ_m (mN m^{-1})	t_{m_lab} (s)	D_{drop} (mm)	$t_{eq\_1\ \mu m}$ (s)
β-caryophyllonic acid 6 	0.01	n.d.* (1.80±0.91)	72.45±0.05 (73.32±0.10)	72.18±1.11 (72.82±0.05)	n.d.* (83±25)	2.17±0.05 (2.13±0.07)	n.d.* (3.65x10^{-5})
	0.1	1.99±1.13 (0.50±0.13)	71.49±0.14 (64.18±0.42)	70.74±0.10 (60.39±0.48)	114±32 (77±21)	2.25±0.01 (2.02±0.05)	4.80x10^{-5} (3.75x10^{-5})
	0.2	0.44±0.20 (n.d.*)	66.21±0.29 (54.51±1.96)	60.44±4.90 (54.11±2.96)	n.d.* (n.d.*)	2.18±0.03 (1.97±0.05)	n.d.* (n.d.*)
	0.5	0.51±0.11 (0.55±0.20)	56.62±0.25 (49.09±0.18)	51.93±0.85 (46.04±1.39)	272±148 (n.d.*)	2.01±0.03 (1.87±0.03)	1.34x10^{-4} (n.d.*)
	1	0.71±0.15	52.14±0.09	48.43±1.20	774±623	1.97±0.02	3.97x10^{-4}
β-nocaryophyllonic acid 7 	0.01	n.d.* (1.23±0.70)	71.96±0.24 (74.21±0.09)	72.23±2.03 (n.d.*)	n.d.* (n.d.*)	2.21±0.05 (2.14±0.10)	n.d.* (n.d.*)
	0.1	1.08±0.28 (0.93±0.37)	72.11±0.08 (73.68±0.09)	69.82± 0.72 (71.55±1.40)	441±241 (n.d.*)	2.25±0.06 (2.08±0.01)	1.74x10^{-4} (n.d.*)
	0.2	1.07±0.06 (2.00±1.21)	71.37±0.07 (71.39±0.26)	63.09±0.39 (70.33±0.10)	314±26 (71±26)	2.25±0.01 (2.07±0.05)	1.29x10^{-4} (3.31x10^{-5})
	0.5	0.95±0.02 (0.95±0.23)	68.12±0.14 (67.30±0.29)	56.41±0.06 (58.48±2.56)	45±1 (460±259)	2.09±0.01 (2.02±0.01)	2.07x10^{-5} (2.26x10^{-4})
	1	0.64±0.02 (1.17±0.09)	63.50±0.38 (62.20±0.19)	48.89±0.09 (51.60±0.52)	14±1 (209±16)	2.00±0.03 (1.99±0.01)	7.21x10^{-6} (1.05x10^{-4})
β-caryophyllinic acid 8 	0.01	n.d.* (2.00±0.65)	72.98±0.09 (75.18±0.09)	72.75±0.08 (74.35±0.06)	137±86 (113±18)	2.29±0.01 (2.16±0.02)	5.22x10^{-5} (4.84x10^{-5})
	0.1	n.d.* (0.99±0.11)	72.46± 0.03 (71.49±0.13)	n.d.* (63.09±1.19)	n.d.* (453±120)	2.23±0.05 (2.13±0.06)	n.d.* (2.00x10^{-4})
	0.2	0.84±0.20 (0.68±0.09)	70.88±0.13 (64.10±0.12)	66.70±1.41 (56.18±1.66)	569±413 (881±479)	2.20±0.06 (2.08±0.06)	2.36x10^{-4} (4.08x10^{-4})
	0.5	0.94±0.09 (0.68±0.16)	60.05±0.07 (53.95±0.20)	56.40±0.26 (48.47±1.58)	242±32 (519±391)	2.07±0.03 (1.92±0.05)	1.12x10^{-4} (2.81x10^{-4})
	1	0.78±0.10 (0.60±0.14)	52.29±0.10 (46.10±0.13)	48.44±0.37 (41.36±1.91)	249±52 (n.d.*)	1.99±0.04 (1.84±0.20)	1.26x10^{-4} (n.d.*)
β-nocaryophyllinic acid 9 	0.01	n.d.* (n.d.*)	72.49±0.03 (74.47±0.03)	72.34±3.31 (73.28±9.14)	n.d.* (n.d.*)	2.21±0.01 (2.15±0.02)	n.d.* (n.d.*)
	0.1	n.d.* (0.95±0.91)	71.77±0.84 (74.30±0.15)	71.81±2.16 (73.96±0.10)	n.d.* (66±55)	2.18±0.02 (2.20±0.03)	n.d.* (2.82x10^{-5})
	0.2	2.00±1.20 (0.99±0.18)	71.69±0.05 (73.81±0.08)	71.37±0.07 (70.05±0.97)	180±51 (546±259)	2.16±0.01 (2.17±0.01)	7.73x10^{-5} (2.36x10^{-4})
	0.5	0.91±0.27 (1.29±0.04)	70.62±0.22 (69.41±0.06)	65.48±1.85 (60.95±0.13)	456±332 (185±4)	2.10±0.04 (2.11±0.02)	2.07x10^{-4} (8.33x10^{-5})
	1	0.93±0.05 (0.89±0.03)	66.89±0.12 (64.52±0.12)	60.72±0.13 (54.64±0.12)	91±4 (83±2)	2.07±0.02 (1.97±0.03)	4.21x10^{-5} (4.28x10^{-5})

* = due to large uncertainties on the point estimates

Table S2. A) Equilibrium surface tension for α-pinene-derived oxidation products at 0–30 mM in H_2O and 1.0 M $(NH_4)_2SO_4$ (values in parentheses). All values have units of mN m^{-1}. [Asterisk (*) notes that value was not obtained due to insolubility at the indicated concentration.] B) Fitting parameters, a and b, cross-sectional area of the surfactant molecules at the surface (ω), and free energy of adsorption (ΔG°_{ads}) for the α-pinene-derived oxidation products obtained from Szyszkowski-Langmuir equation,[4-6] where T is the laboratory temperature, σ_{blank} is the average surface tension of the blank solution, and σ is the minimum surface tension at each concentration C (in mM) measured. [SEP denotes standard error exceeds point estimate.]

A

Conc. (mM)	 pinonaldehyde 1	 pinonic acid 2	 pinic acid 3
0	73.29±0.15 (74.16±0.13)	71.90±0.11 (74.52±0.09)	72.66±0.28 (74.52±0.09)
1	69.40±0.33 (68.54±0.36)	70.57±0.07 (70.42±0.12)	70.31±0.08 (73.51±0.30)
5	63.61±0.31 (N/A*)	68.27±0.10 (63.48±0.11)	68.63±0.14 (67.16±0.28)
10	58.66±0.10 (N/A*)	64.59±0.08 (N/A*)	64.00±0.16 (63.71±0.11)
20	N/A* (N/A*)	60.68±0.17 (N/A*)	60.02±0.12 (58.16±0.08)
30	N/A* (N/A*)	58.79±0.19 (N/A*)	57.46±0.29 (55.21±0.28)

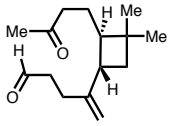
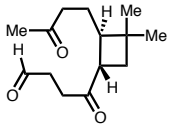
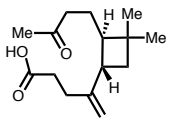
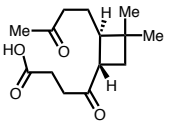
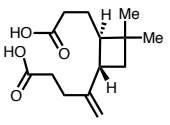
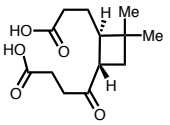
B

Szyszkowski-Langmuir equation fit parameters: $\sigma = \sigma_{blank} - aTln(1 + bC)$ where $a = R/\omega$ and $b = K_{ads}$

a (mN m^{-1} K^{-1})	0.026 ± 0.007 (0.067 ± SEP)	0.024 ± 0.004 (0.022± N/A)	0.030 ± 0.008 (0.034 ± 0.004)
b (L $mmol^{-1}$)	0.53± 0.30 (0.36 ± SEP)	0.21 ± 0.08 (0.89 ± N/A)	0.16 ± 0.08 (0.21 ± 0.05)
ω (Å^2 $molec^{-1}$)	54.0 ± 15.5 (20.7 ± SEP)	57.2 ± 10.7 (61.8 ± N/A)	45.7 ± 12.4 (40.8 ± 4.7)
$-\Delta G^{\circ}_{ads}$ (kJ mol^{-1})	25.1 ± 1.4 (24.1 ± SEP)	22.9 ± 0.9 (26.3 ± N/A)	22.1 ± 1.2 (22.8 ± 0.6)

Table S3. A) Equilibrium surface tension for β-caryophyllene-derived oxidation products at 0–1 mM in H_2O and 1.0 M $(NH_4)_2SO_4$ (values in parentheses). All values have units of mN m^{-1}. [Asterisk (*) notes that value was not obtained due to insolubility at the indicated concentration.] B) Fitting parameters, a and b, cross-sectional area of the surfactant molecules at the surface (ω), and free energy of adsorption (ΔG°_{ads}) for the β-caryophyllene-derived oxidation products obtained from Szyszkowski-Langmuir equation,[4-6] where T is the laboratory temperature, σ_{blank} is the average surface tension of the blank solution, and σ is the minimum surface tension at each concentration C (in mM) measured. [SEP denotes standard error exceeds point estimate.]

A

Conc. (mM)	 β-caryophyllene aldehyde 4	 β-nocaryophyllone aldehyde 5	 β-caryophyllonic acid 6	 β-nocaryophyllonic acid 7	 β-caryophyllinic acid 8	 β-nocaryophyllinic acid 9
0	73.14±0.20 (74.33±0.21)	72.90±0.14 (74.78±0.19)	73.08±0.37 (74.16±0.13)	73.01±0.16 (74.52±0.09)	72.78±0.17 (74.65±0.13)	72.76±0.09 (75.33±0.09)
0.01	68.99±0.08 (71.13±0.35)	72.87±0.16 (74.77±0.07)	72.31±0.10 (72.88±0.07)	72.11±0.08 (74.97±0.30)	72.77±0.14 (74.33±0.16)	72.48±0.14 (74.18±0.22)
0.1	61.04±0.08 (58.18±0.07)	71.72±0.11 (71.54±0.11)	70.69±0.39 (61.38±0.07)	70.76±0.11 (72.69±0.09)	72.32±0.16 (66.72±0.10)	71.69±0.16 (73.98±0.13)
0.2	54.58±0.08 (53.19±0.06)	70.14±0.14 (67.96±0.13)	64.13±0.10 (54.47±0.06)	65.91±0.14 (70.50±0.69)	68.73±0.09 (60.68±0.07)	71.41±0.13 (71.85±0.10)
0.5	49.04±0.06 (N/A*)	67.94±0.15 (62.49±0.16)	53.81±0.07 (47.62±0.06)	57.32±0.07 (62.33±0.34)	57.52±0.08 (51.14±0.34)	67.84±0.40 (62.56±0.13)
1	46.01±0.05 (N/A*)	64.19±0.12 (58.10±0.09)	50.46±0.08 (N/A*)	50.10±0.07 (54.07±0.27)	49.72±0.09 (44.10±0.06)	61.60±0.10 (56.08±0.09)

B

Szyszkowski-Langmuir equation fit parameters: $\sigma = \sigma_{blank} - aTln(1 + bC)$ where $a = R/\omega$ and $b = K_{ads}$

a (mN m^{-1} K^{-1})	0.022 ± 0.003 (0.030 ± 0.003)	4.099 ± SEP (0.033 ± 0.005)	0.050 ± 0.025 (0.034 ± 0.005)	0.077 ± 0.029 (0.178 ± 0.131)	0.197 ± SEP (0.047 ± 0.004)	6.047 ± SEP (0.203 ± SEP)
b (L mmol^{-1})	64.6 ± 24.8 (51.4 ± 10.4)	0.007 ± SEP (4.7 ± 1.4)	4.0 ± 3.5 (28.3 ± 9.3)	1.8 ± 0.9 (0.5 ± 0.4)	0.508 ± SEP (8.5 ± 1.6)	0.006 ± SEP (0.4 ± SEP)
ω (Å^2 molec^{-1})	61.7 ± 7.1 (45.5 ± 3.9)	0.3 ± SEP (42.0 ± 7.0)	27.6 ± 13.7 (40.1 ± 5.5)	17.9 ± 6.7 (7.8 ± 5.7)	7.0 ± SEP (29.5 ± 2.7)	0.2 ± SEP (6.8 ± SEP)
$-\Delta G^{\circ}_{ads}$ (kJ mol^{-1})	36.8 ± 0.9 (36.2 ± 0.6)	14.7 ± SEP (30.4 ± 0.8)	30.0 ± 2.1 (34.8 ± 0.8)	28.0 ± 1.3 (24.9 ± 2.1)	25.0 ± SEP (31.9 ± 0.5)	14.2 ± SEP (24.2 ± SEP)

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