Supporting information for

Exploring Volatility Properties of Discrete Secondary Organic Aerosol Constituents of α-Pinene and Polycyclic Aromatic Hydrocarbons

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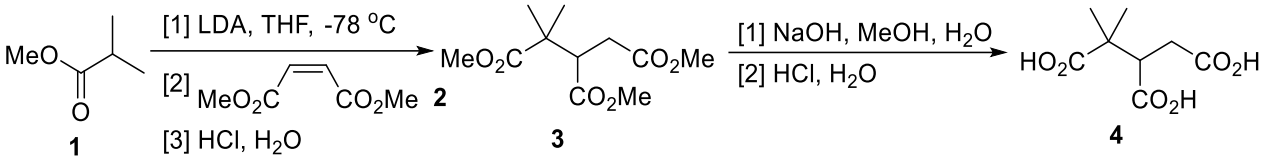
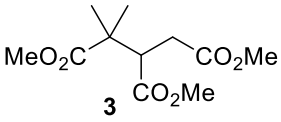
Synthetic Procedures for SOA Constituents

Synthesis of 3-methylbutane-1,2,3-tricarboxylic acid (3-MBTCA) (4) [1]

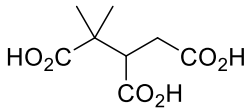


A solution of methyl isobutyrate (**1**) (1.02 g, 10 mmol) in anhydrous tetrahydrofuran (4 mL) was added to a cooled solution of LDA in THF (2.0 M, 5 mL) at –70 °C over 15 min. The colorless solution was stirred for 15 min at –70 °C and a solution of dimethyl maleate (**2**) (1.44 g, 10 mmol) in anhydrous tetrahydrofuran (4 mL) was added dropwise over 15 min. Over the course of addition, the reaction mixture changed from colorless to yellow. The reaction mixture was stirred for 30 min at –70 °C and then poured into a cooled 1 M aqueous HCl solution (22 mL) and extracted with dichloromethane (3 times x 20 mL). Removal of the combined organic solvent under reduced pressure left behind a crude mixture, which was separated by vacuum distillation to give triester **3** (bp 108 °C/15 mmHg, 1.72 g, 70%) as a colorless turbid oil. ***Trimethyl 3-methylbutane-1,2,3-tricarboxylate (3)***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.21 (s, 3H), 2.40 (dd, *J* = 16.8 and 3.3 Hz, 1H), 2.81 (dd, *J* = 16.8 and 11.4 Hz, 1H), 3.32 (dd, *J* = 11.4 and 3.3 Hz, 1H), 3.68 (s, 3H), 3.69 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 23.2, 32.4, 44.0, 48.0, 51.9 (x2), 52.2, 172.5, 173.1, 176.4.



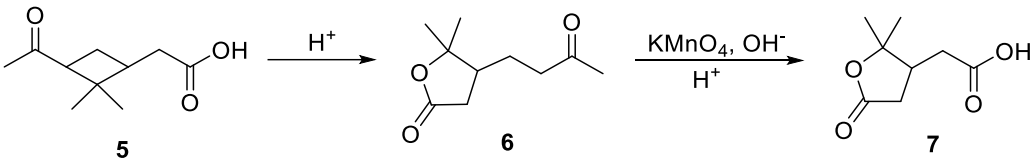
Trimethyl 3-methylbutane-1,2,3-tricarboxylate

Triester **3** (0.74 g, 3 mmol) was added to a solution of NaOH (1.90 g, 48 mol) in H_2O (6 mL) and MeOH (6 mL) and the mixture was stirred for 4 h at reflux. The mixture was cooled in an ice bath and acidified with a 1 M aqueous HCl solution (pH 1) until a white solid was formed. The suspension was extracted with dichloromethane (7 times x 10 mL), dried over Na_2SO_4, and evaporated under reduced pressure to obtain triacid **4** (0.60 g, 98%) as a white solid. ***3-Methylbutane-1,2,3-tricarboxylic acid (4)***. Mp 151-153 °C (154-155 °C[1b]). ^{1}H NMR (500 MHz, CD_3OD) δ 1.12 (s, 3H), 1.13 (s, 3H), 2.53 (dd, *J* = 17.0 and 3.6 Hz, 1H), 2.68 (dd, *J* = 17.0 and 11.5 Hz, 1H), 3.15 (dd, *J* = 11.5 and 3.6 Hz, 1H). ^{13}C NMR (125 MHz, CD_3OD) δ 22.6, 23.2, 32.9, 44.4, 49.1, 177.2, 177.5, 181.5.

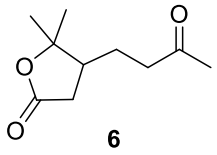


3-Methylbutane-1,2,3-tricarboxylic acid (3-MBTCA)

Synthesis of terpenylic acid (7) [2–4]



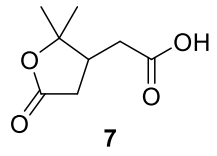
5 6 7



6

5,5-Dimethyl-4-(3-oxobutyl)dihydrofuran-2(3*H*)-one

cis-Pinonic acid **5** (2.0 g, 10.9 mmol) was dissolved in 42.6 g of an aqueous 50% H_2SO_4 solution and the mixture was heated for 30 min at 100 °C. To the resulting brown mixture was added distilled water (60 mL) and the mixture was further saturated with $(NH_4)_2SO_4$. The mixture was extracted with dichloromethane (3 times x 20 mL), dried over Na_2SO_4, and evaporated under reduced pressure to yield homoterpenyl methyl ketone **6** (2.0 g, 100%). ***5,5-Dimethyl-4-(3-oxobutyl)dihydrofuran-2(3H)-one (6)***. Mp 61-63 °C (63-64 °C[2d]). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28 (s, 3H), 1.46 (s, 3H), 1.50-1.58 (m, 1H), 1.78-1.84 (m, 1H), 2.17 (s, 3H), 2.18-2.22 (m, 1H), 2.28 (dd, *J* = 16.9 and 11.6 Hz, 1H), 2.40-2.54 (m, 2H), 2.59 (dd, *J* = 16.9 and 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.9, 23.2, 27.4, 30.1, 34.8, 41.8, 45.1, 86.7, 175.2, 207.2.



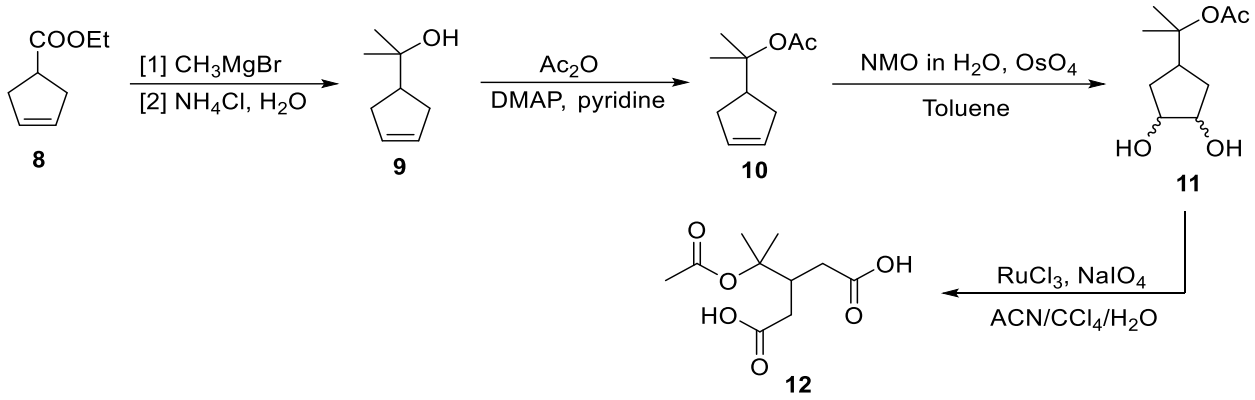
7

2-(2,2-Dimethyl-5-oxotetrahydrofuran-3-yl)acetic acid

To homoterpenyl methyl ketone **6** (1.5 g, 8.1 mmol) dissolved in a 0.93 M aqueous KOH solution (30 mL), a 0.16 M aqueous $KMnO_4$ solution (150 mL) was added over 10 min. After removal of the brown precipitate by filtration, the aqueous mixture was acidified with a 10% aqueous H_2SO_4 solution and extracted with diethyl ether. The organic phase was dried over Na_2SO_4, evaporated, and recrystallized (hexane/diethyl ether) to give terpenylic acid **7** (1.0 g, 72%). ***2-(2,2-Dimethyl-5-oxotetrahydrofuran-3-yl)acetic acid (7)***. Mp 89-91 °C (90 °C[2e]). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.48 (s, 3H), 2.38 (dd, *J* = 10.4 and 17.5 Hz, 1H), 2.40 (dd, *J* = 10.2 and 16.2 Hz, 1H), 2.56 (dd, *J* = 4.7 and 16.2 Hz, 1H), 2.67-2.74 (m, 1H), 2.86 (dd, *J* = 8.2 and 17.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 27.3, 34.4, 35.1, 41.3, 86.0, 175.3, 176.5.

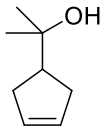
Synthesis of diaterpenylic acid acetate (DTAA) (12)

Procedure A [5,6]



8 **9** **10** **11** **12**

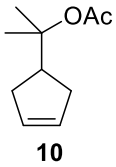
A methyl magnesium bromide solution (6 mL, 3.0 M in diethyl ether) was added dropwise to a solution of ethyl cyclopent-3-ene-1-carboxylate (**8)** (0.76 g, 6 mmol) in diethyl ether (10 mL) at 0 ºC. After the resulting mixture was stirred for 2 h at 45 ºC, a saturated NH_4Cl aqueous solution (20 mL) was slowly added into the mixture. The reaction mixture was extracted with ethyl acetate (3 times x 20 mL), dried oved Na_2SO_4, evaporated, and distilled under reduced pressure to yield tertiary alcohol **9** (bp 79-81 ºC/35 mmHg, 0.62 g, 81%). ***2-(Cyclopent-3-en-1-yl)propan-2-ol (9)***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 6H), 1.46 (s, 1H), 2.22-2.29 (m, 2H), 2.34-2.42 (m, 3H), 5.66 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.70, 34.11, 48.72, 72.28, 129.93.



9

2-(Cyclopent-3-en-1-yl)propan-2-ol

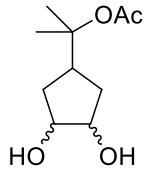
4-Dimethylaminopyridine (DMAP) (0.06 g, 0.49 mmol) was added to a solution of tertiary alcohol **9** (0.62 g, 4.9 mmol) in pyridine (20 mmol) and acetic anhydride (20 mmol), and then stirred overnight at room temperature. The excess acetic anhydride was destroyed by the addition of methanol (5 mL) and the mixture was neutralized by a 1 M aqueous HCl solution. The resulting mixture was extracted with diethyl ether (3 times x 20 mL) and dried over Na_2SO_4. Removal of the solvent left behind a crude mixture, which was separated by vacuum distillation to yield acetate **10** (0.62 g, 76%, bp 84-87 °C/20 mmHg). ***2-(Cyclopent-3-en-1-yl)propan-2-yl acetate (10)***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 (s, 6H), 1.97 (s, 3H), 2.22-2.28 (m, 2H), 2.33-2.40 (m, 2H), 2.70-2.76 (m, 1H). 5.64-5.67 (m, 2H). ^{13}C



10

2-(Cyclopent-3-en-1-yl)propan-2-yl acetate

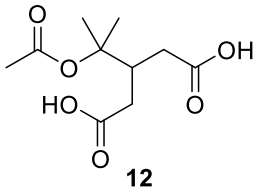
NMR (125 MHz, $CDCl_3$) δ 22.5, 23.6, 33.9, 47.4, 84.0, 129.8, 170.6.



11

2-(3,4-Dihydroxycyclopentyl) propan-2-yl acetate

To the stirred dispersion of acetate **10** (0.62 g, 3.7 mmol) in 20 mL distilled water, *m*CPBA (0.71 g, 4.1 mmol) was slowly added over 10 min at 0 ºC. After the reaction mixture was stirred for 30 min at room temperature, a 10% aqueous H_2SO_4 solution (0.7 mL) was added to the mixture. Additional stirring of the mixture for 2 h at room temperature was followed by adding solid NaOH until the mixture became limpid. The mixture was quenched with a saturated aqueous NaCl solution (15 mL) and extracted with dichloromethane (3 times x 30 mL). Drying the organic phase over Na_2SO_4 and removal of the solvent gave diol **11** (0.49 g, 65%), which was used in the next step without further purification. ***2-(3,4-Dihydroxycyclopentyl)propan-2-yl acetate (11)***. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 6H), 1.75-1.78 (m, 4H), 1.96 (s, 3H), 2.62 (q, *J* = 8.8 Hz, 1H), 3.15 (br s, 2H), 4.11-4.12 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 23.8, 32.6, 45.6, 74.0, 83.5, 170.8.

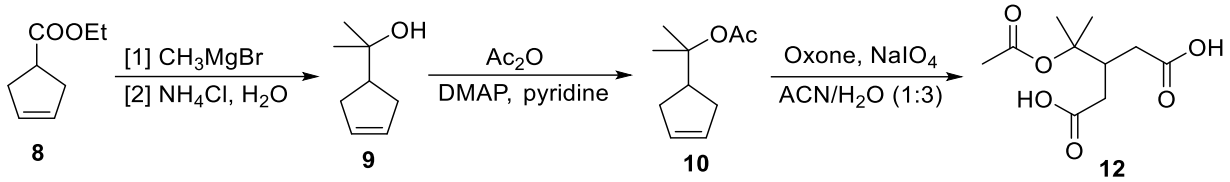


12

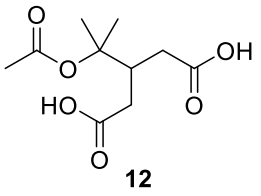
3-(2-Acetoxypropan-2-yl)pentanedioic acid

To a strongly stirred solution of diol **11** (0.69 g, 3.4 mmol) in acetonitrile/CCl_4/H_2O (2:2:3, 40 mL), $NaIO_4$ (2.97 g, 13.9 mmol) was added. The mixture was stirred for 10 min at room temperature. After adding $RuCl_3 \cdot xH_2O$ (0.016 g, 0.075 mmol) to the mixture and stirring for an additional 2 h at room temperature, the reaction mixture was diluted with water, extracted with dichloromethane (3 times x 40 mL), and dried over Na_2SO_4. Removal of the solvent left behind a crude mixture, which was filtered through a short pad of celite using diethyl ether. Purification by recrystallization (hexane/diethyl ether) gave DTAA **12** (0.55 g, 70%). ***3-(2-Acetoxypropan-2-yl)pentanedioic acid (DTAA)*** **(12)**. Mp 166-167 ºC. ^{1}H NMR (500 MHz, DMSO) δ 1.38 (s, 6H), 1.88 (s, 3H), 2.13 (dd, *J* = 15.9 and 7.4 Hz, 2H), 2.37 (dd, *J* = 15.9 and 5.6 Hz, 2H), 2.73-2.80 (m, 1H), 12.11 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.0, 23.0, 35.0, 40.5, 83.2, 169.5, 173.7.

Procedure B [7]

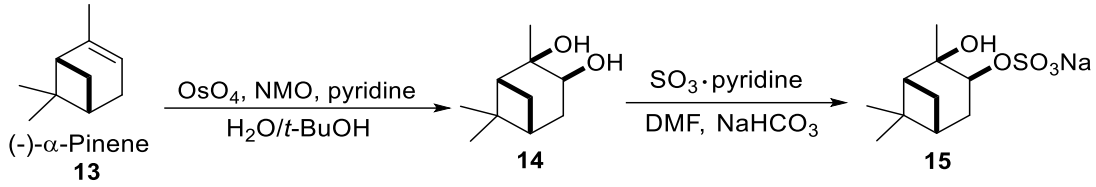


To a stirred solution of acetate **10** (0.5 g, 3.0 mmol) in acetonitrile/H_2O (1:3, 20 mL), oxone (1.84 g, 6 mmol) and sodium periodate (0.96 g, 4.5 mmol) were added. The reaction mixture was vigorously stirred for 24 h at room temperature. The mixture was filtered, extracted with diethyl ether (20 mL x 3 times), and dried over Na_2SO_4. Evaporation of the solvent left behind a crude mixture, which was purified by recrystallization (hexane/diethyl ether) to give DTAA **12** (0.54 g, 77%).

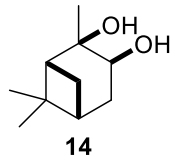


3-(2-Acetoxypropan-2-yl)pentanedioic acid

Synthesis of sodium (1*R*,2*R*,3*S*,5*R*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl sulfate (15) [8–11]



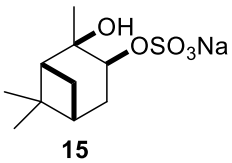
To (-)-α-pinene **13** (1.36 g, 10 mmol) in a 50 mL round-bottom flask was added 4-methylmorpholine-N-oxide (1.76 g, 15 mmol) and pyridine (0.78 mL) in a mixture of water (3.1 mL) and *t*-BuOH (15.4 mL). After adding a solution of OsO_4 (0.34 mL, 2.5% in *t*-BuOH) to the mixture, it was heated for 48 h at reflux. Then, the mixture was quenched with a saturated aqueous solution of $NaHSO_3$ (35 mL) and stirred for 30 min at room temperature. The mixture was extracted with dichloromethane (3 times x 50 mL), dried over Na_2SO_4, and purified by column chromatography using hexane/ethyl acetate (1:8) to yield diol **14** (1.46 g, 85%). ***(1R,2R,3S,5R)-2,6,6-Trimethylbicyclo[3.1.1]heptane-2,3-diol (14)***. Mp 55-56 ºC (52-54 ºC[4d]). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.27 (s, 3H), 1.31 (s, 3H), 1.37 (d, *J* = 10.4 Hz, 1H), 1.64 (ddd, *J* = 2.2, 4.8 and 13.9 Hz, 1H), 1.91-1.94 (m, 1H), 2.01 (t, *J* = 5.8 Hz, 1H), 2.18-2.23 (m, 1H), 2.43-2.63 (m, 1H), 4.00 (dd, *J* = 4.8 and 7.7 Hz, 1H).



14

(1*R*,2*R*,3*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]heptane-2,3-diol

To the dissolved solution of diol **14** (0.90 g, 5 mmol) in dimethylformamide (5 mL) was added SO_3-Py (0.80 g, 5 mmol). After the mixture was stirred for 4 h at room temperature, $NaHCO_3$ (0.84 g, 10 mmol) was added to the mixture. The resulting mixture was further stirred for 12 h at 50 ºC. Removal of the solvent under reduced pressure left behind a crude mixture that was purified by column chromatography using gradient eluents (hexane/ethyl acetate = 2:1 to dichloromethane/methanol = 15:1) to give organosulfate **15** (1.23 g, 90%) as a white solid. ***Sodium (1R,2R,3S,5R)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl sulfate (15)***. Mp >300 ºC. ^{1}H NMR (500 MHz, CD_3OD) δ 1.00 (s, 3H), 1.29 (s, 3H), 1.37 (s, 3H), 1.55 (d, *J* = 10.3 Hz, 1H), 1.87-1.96 (m, 3H), 2.16-2.21 (m, 1H), 2.51-2.56 (m, 1H), 4.74 (dd, *J* = 5.8 and 9.8 Hz, 1H). ^{13}C NMR (125 MHz, CD_3OD) δ 24.6, 28.4, 29.2, 30.1, 36.7, 39.5, 41.8, 55.4, 75.1, 77.5

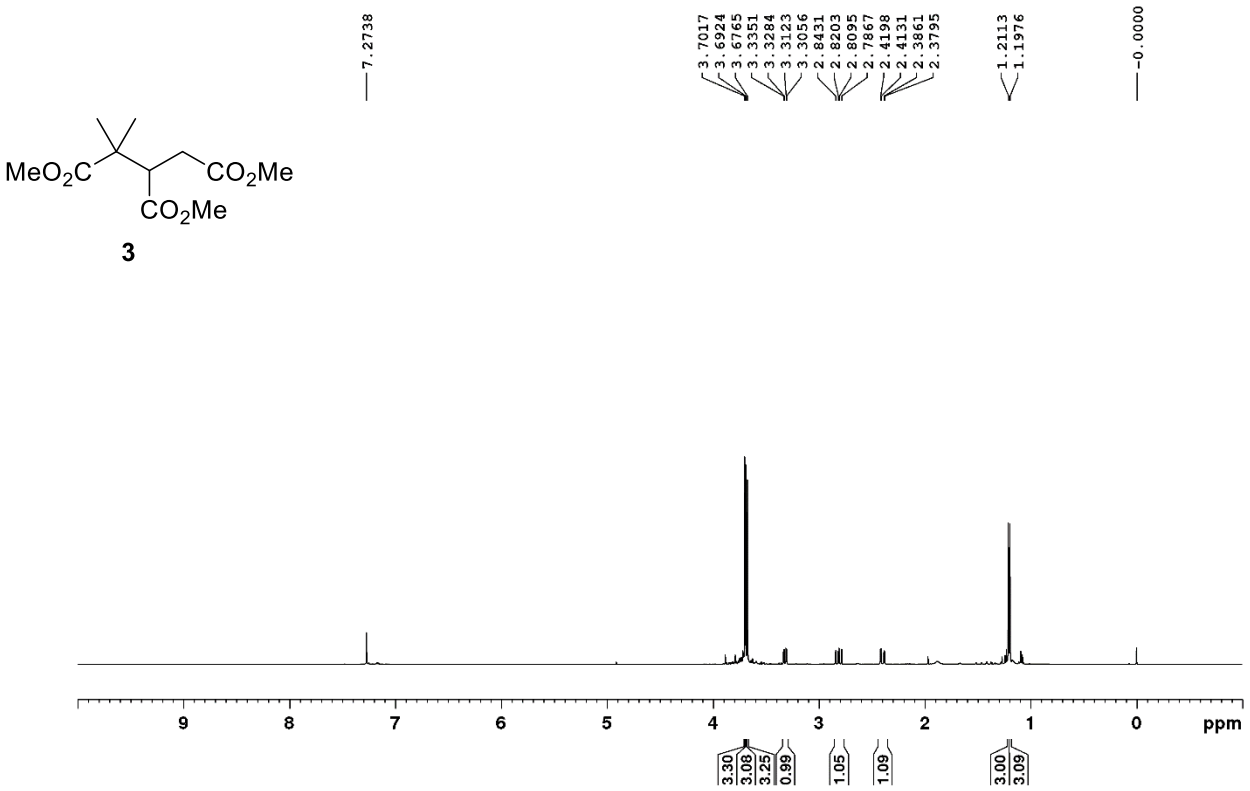


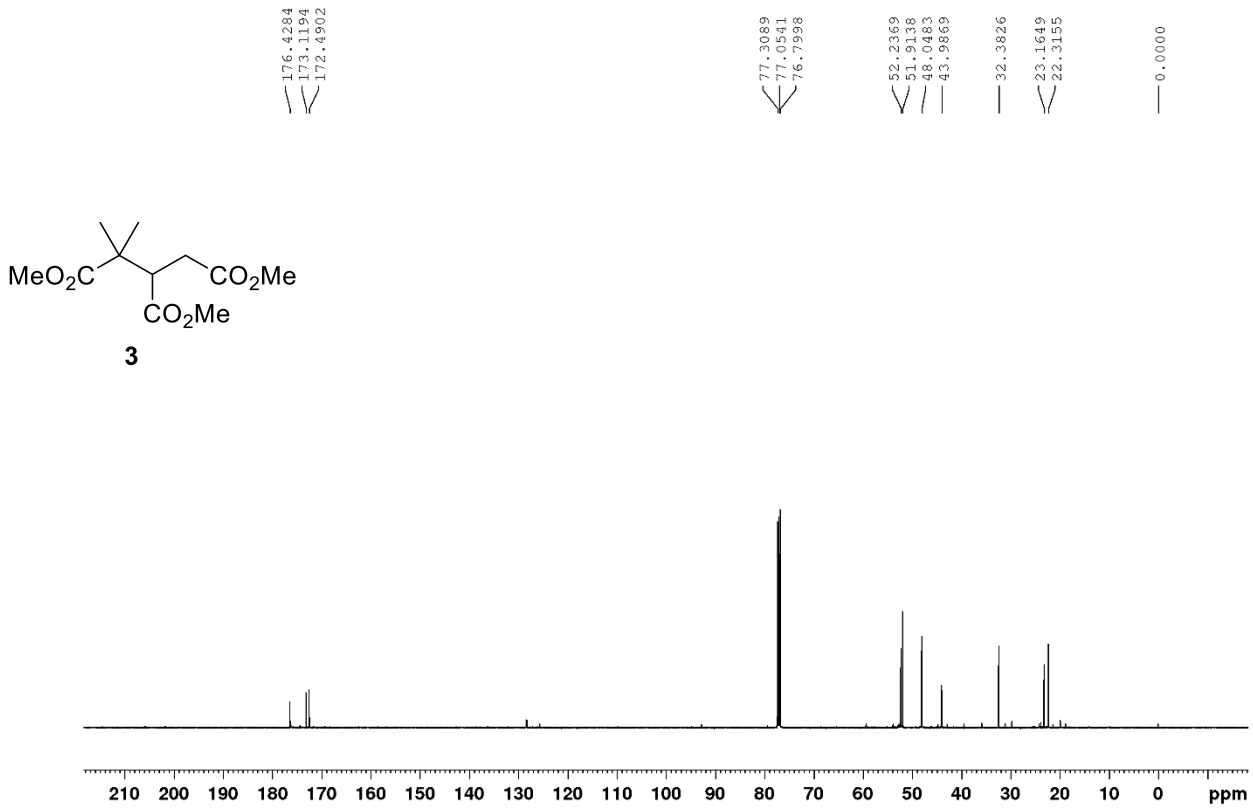
15

Sodium (1*R*,2*R*,3*S*,5*R*)-2-hydroxy-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl sulfate

^{1}H and ^{13}C NMR Spectra of Synthesized SOA Constituents

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker Avance Digital 500 spectrometer using TMS as an internal standard in $CDCl_3$, MeOD, or DMSO-d_6.

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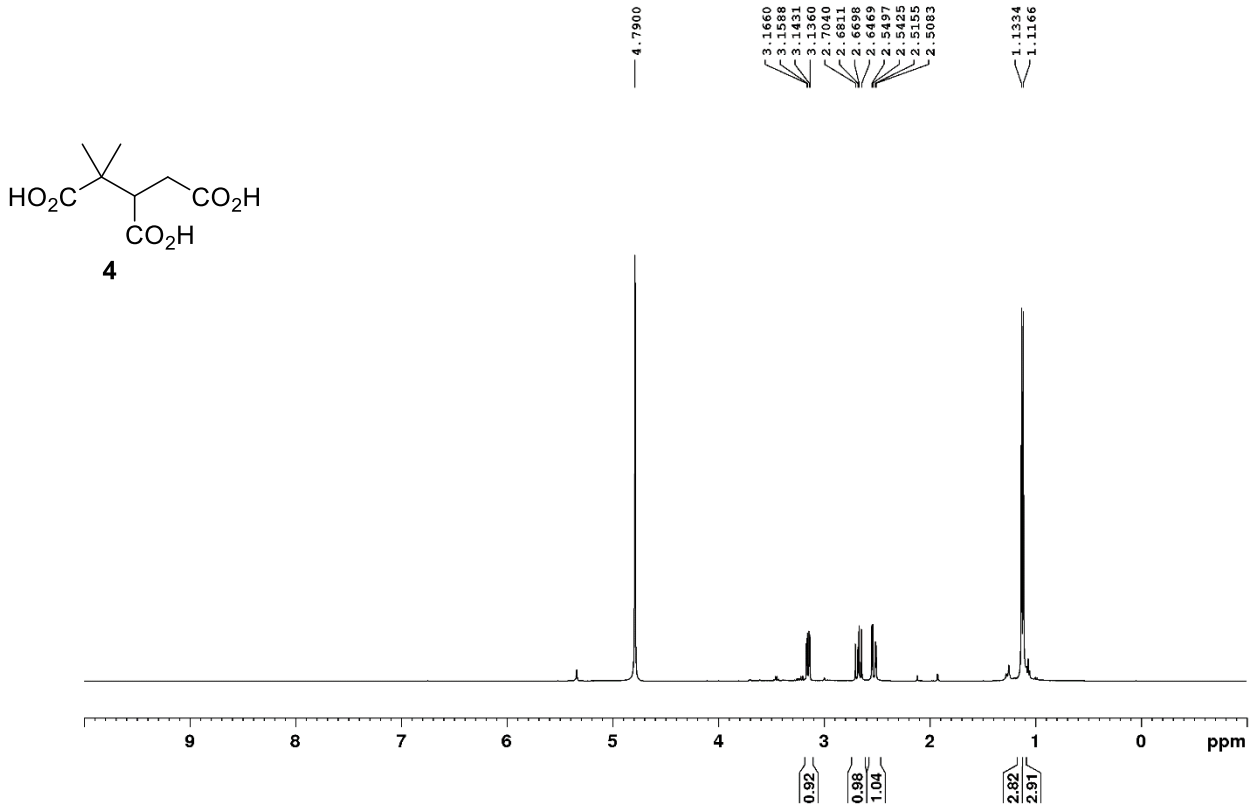
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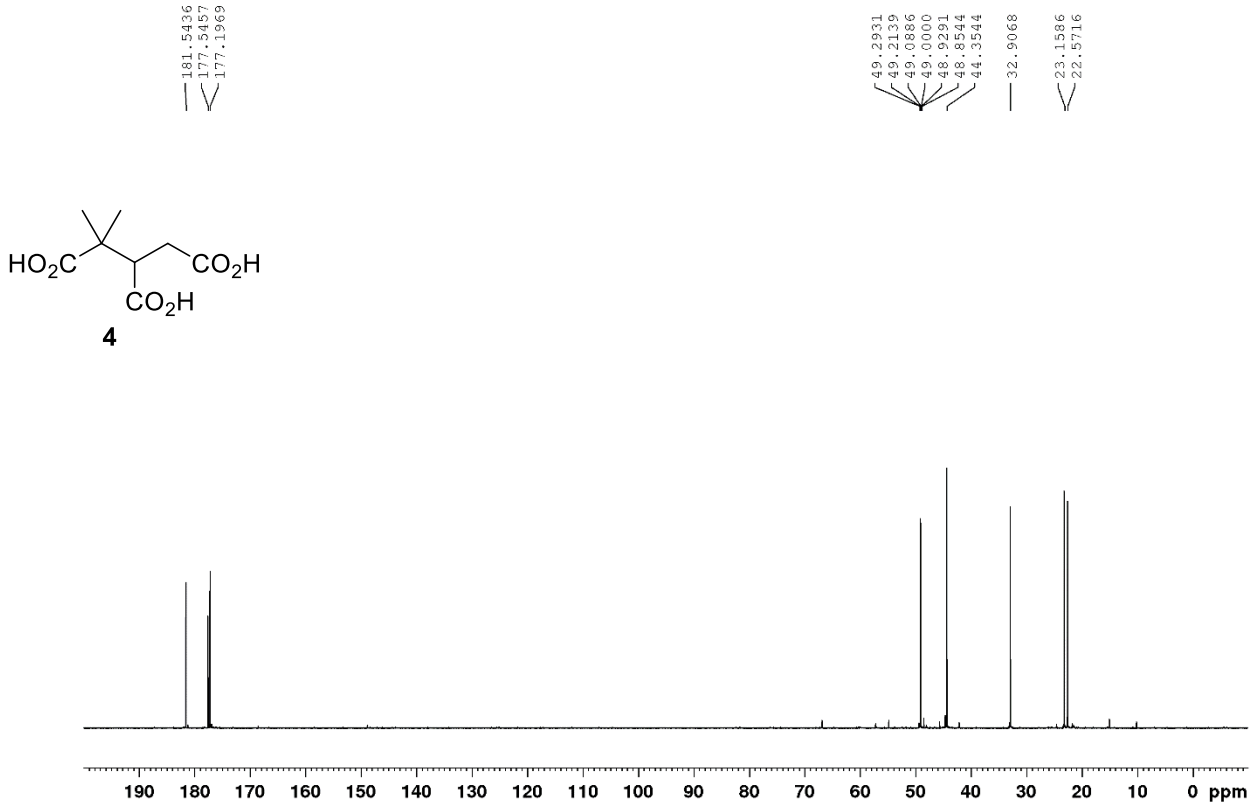
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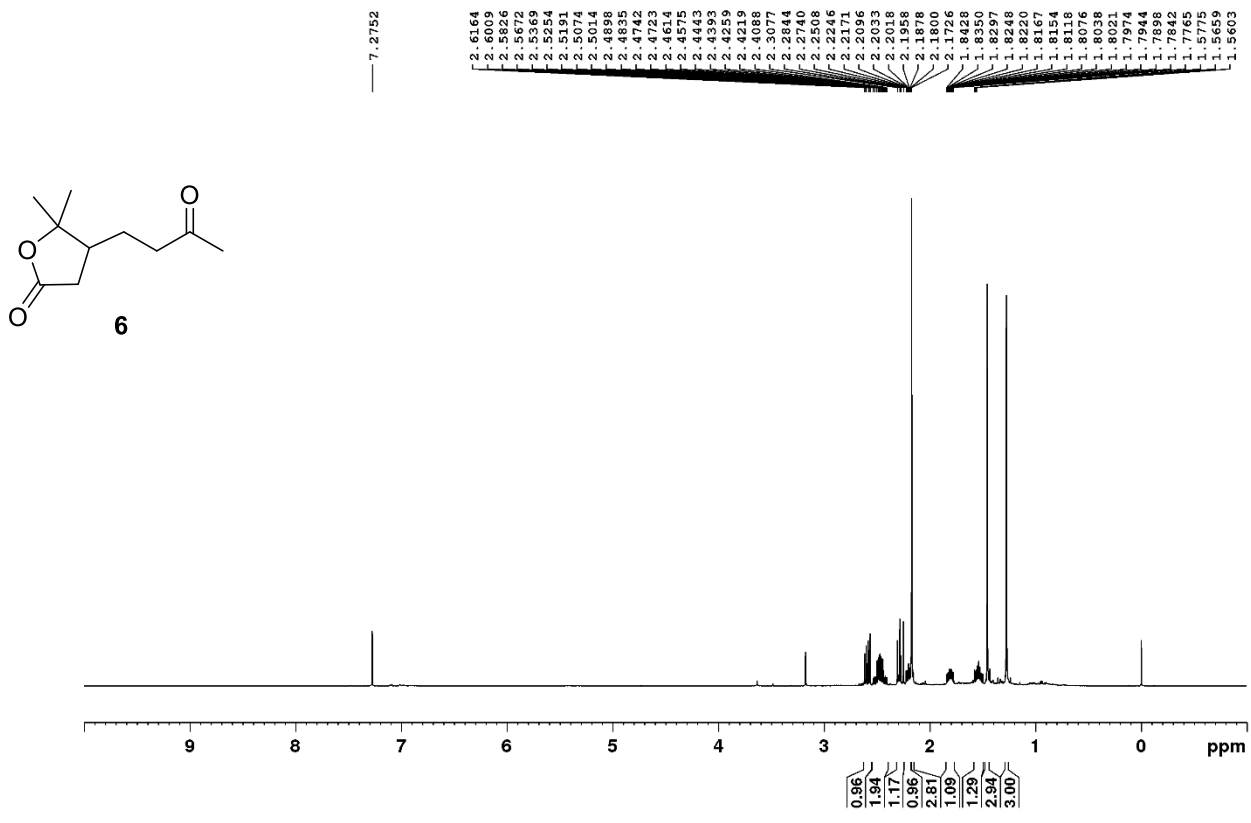
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1.5775
1.5659
1.5603
O
O
O
6
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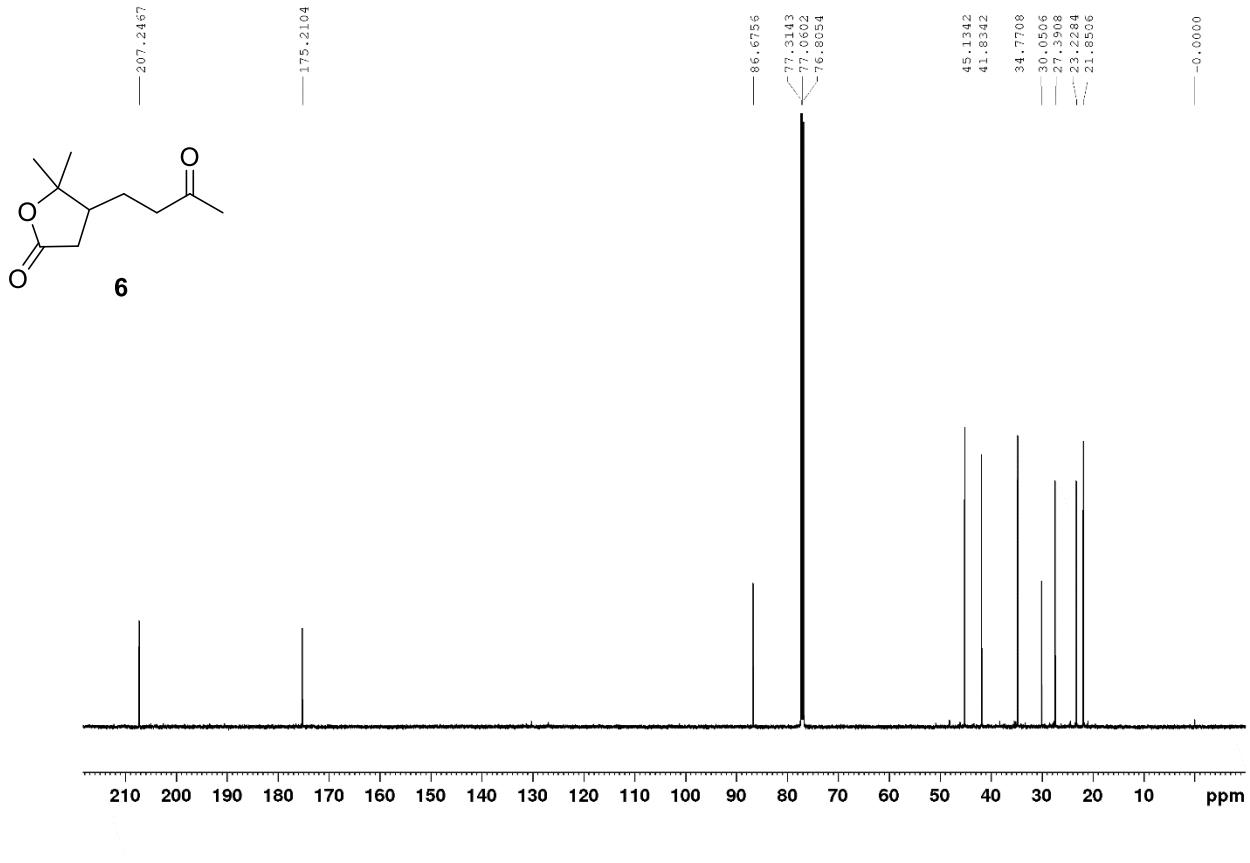
1.94
1.17
0.96
2.81
1.09
1.29
2.94
3.00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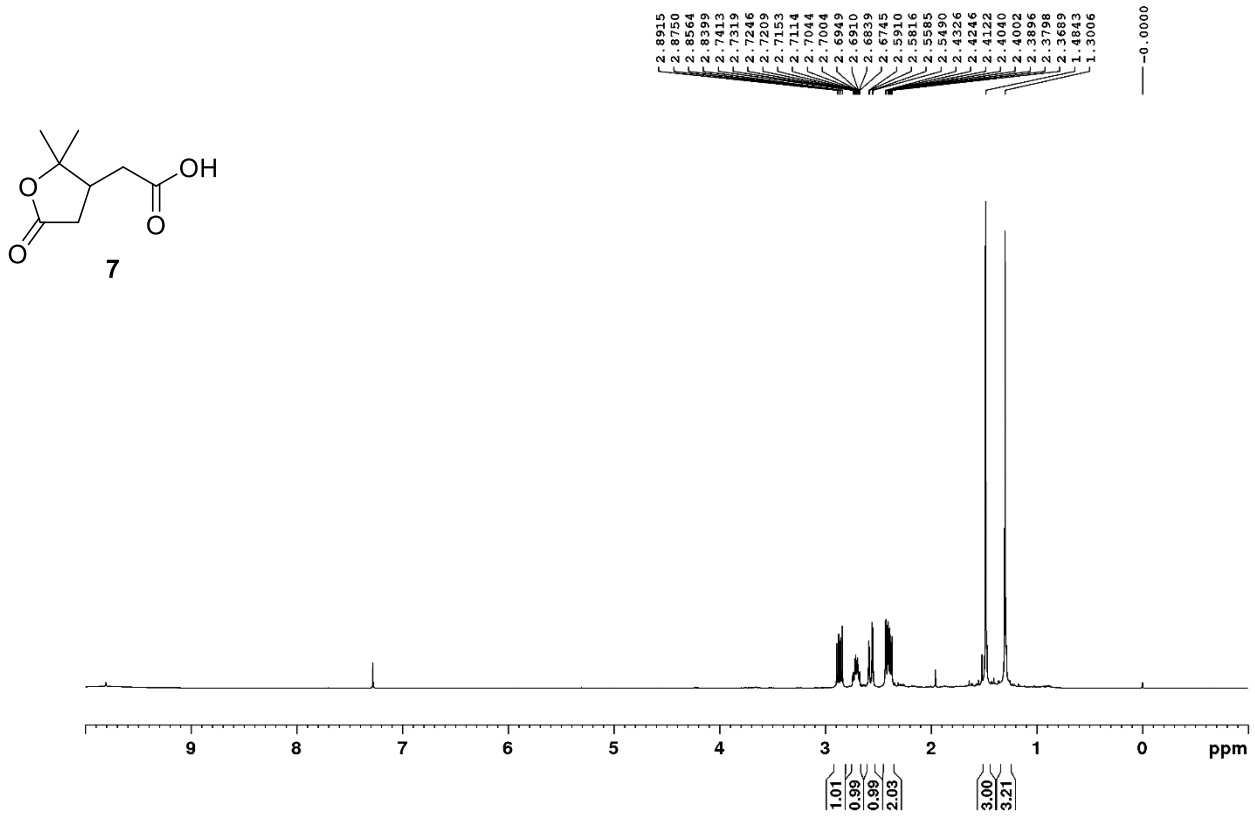
77.0602
76.8054
45.1342
41.8342
34.7708
30.0506
27.3908
23.2284
21.8506
0.0000
O
O
O
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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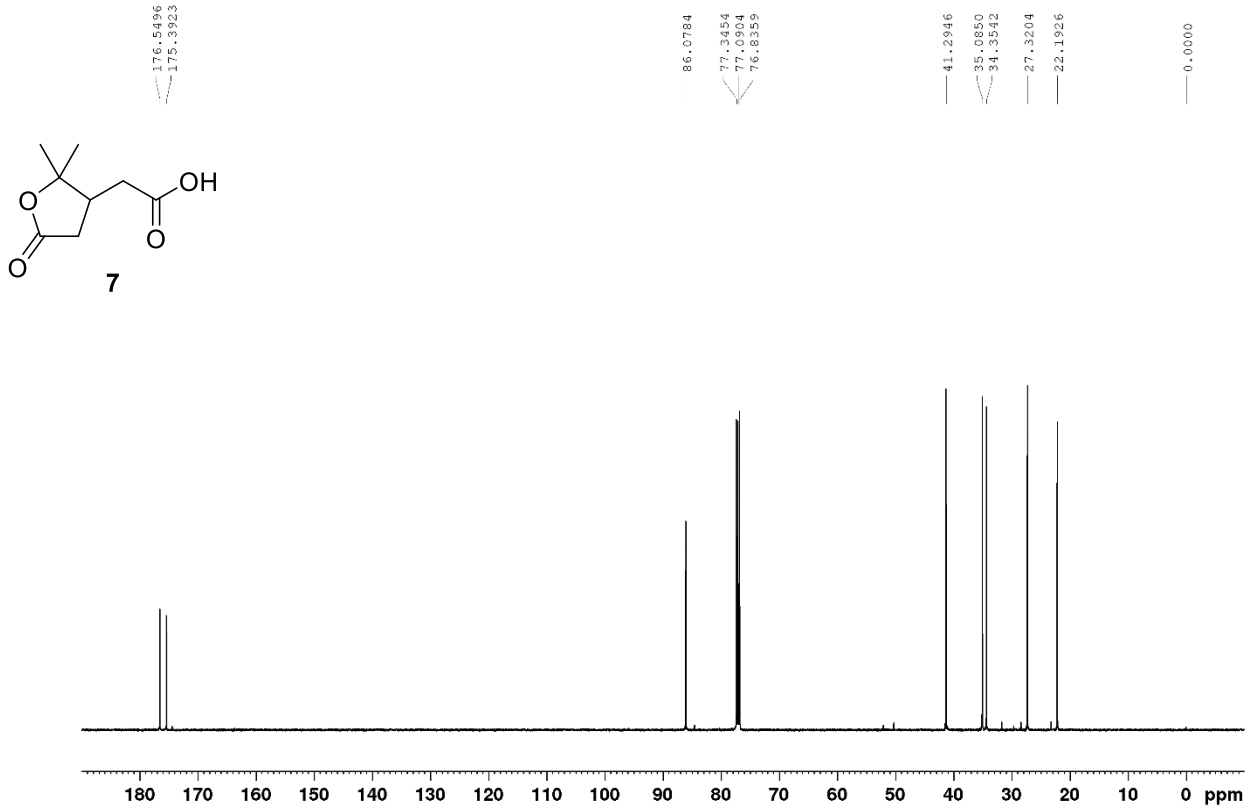
2.8750
2.8564
2.8399
2.7413
2.7319
2.7246
2.7209
2.7153
2.7114
2.7044
2.7004
2.6949
2.6910
2.6839
2.6745
2.5910
2.5816
2.5585
2.5490
2.4326
2.4246
2.4122
2.4040
2.4002
2.3896
2.3798
2.3689
1.4843
1.3006
0.0000
OH
O
O
O
7
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.99
0.99
2.03
3.00
3.21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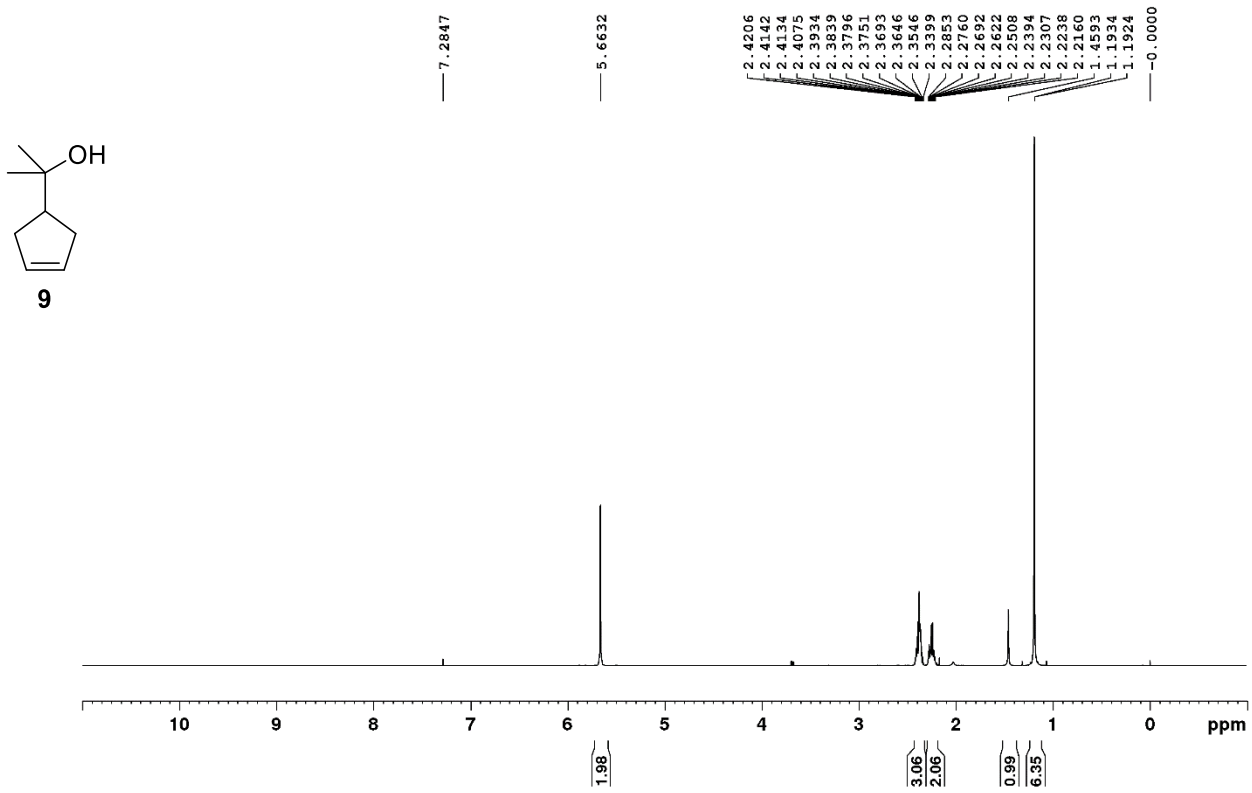
175.3923
86.0784
77.3454
77.0904
76.8359
41.2946
35.0850
34.3542
27.3204
22.1926
0.0000
OH
O
O
O
7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


OH
9
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5.6632
2.4206
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2.4134
2.4075
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2.3839
2.3796
2.3751
2.3693
2.3646
2.3546
2.3399
2.2853
2.2760
2.2692
2.2622
2.2508
2.2394
2.2307
2.2238
2.2160
1.4593
1.1934
1.1924
0.0000
10
9
8
7
6
5
4
3
2
1
0
ppm
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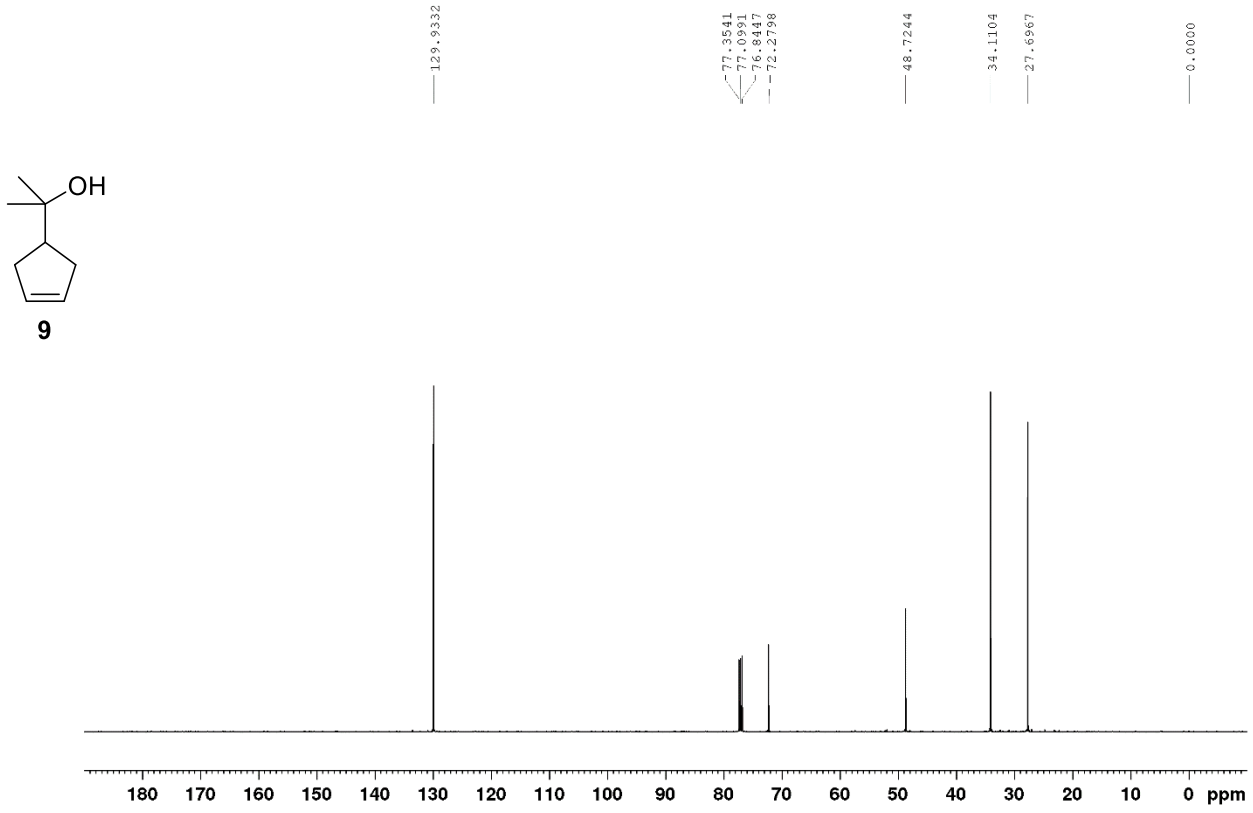
3.06
2.06
0.99
6.35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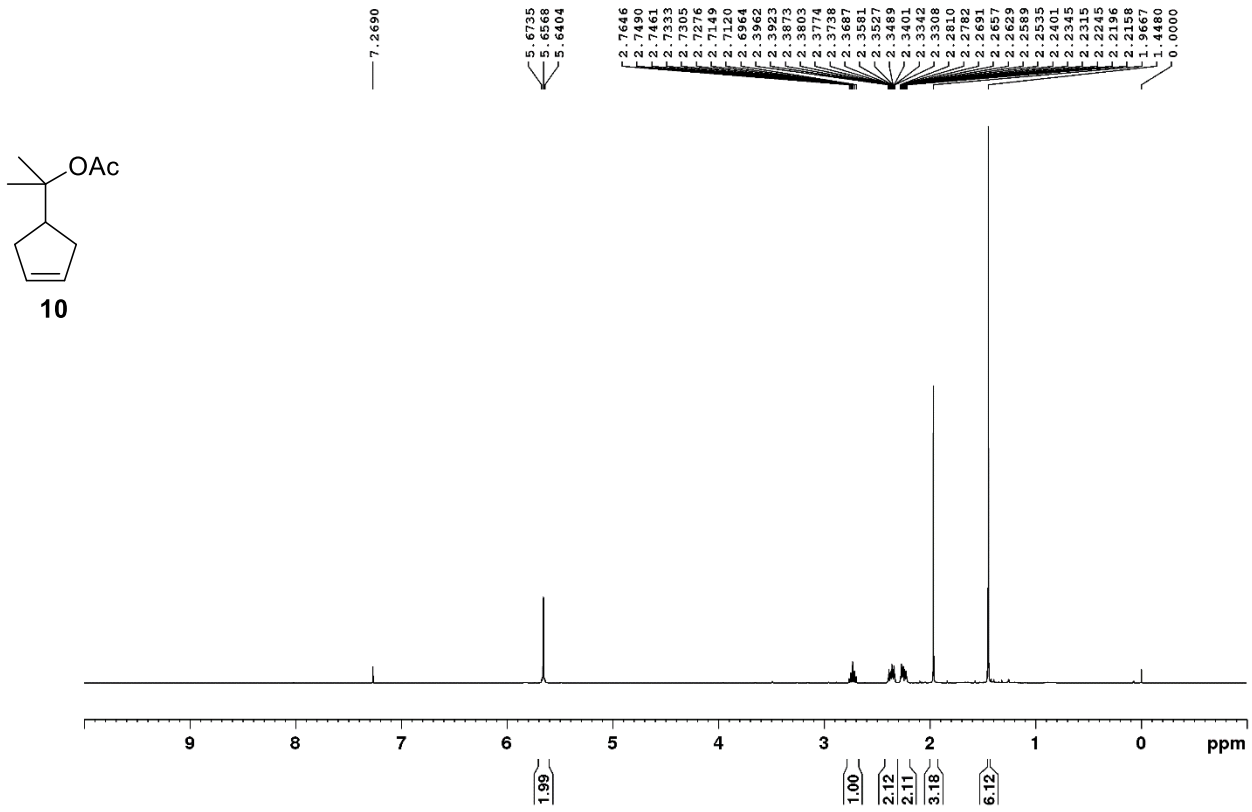
77.0991
76.8447
72.2798
48.7244
34.1104
27.6967
0.0000
OH
9
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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10
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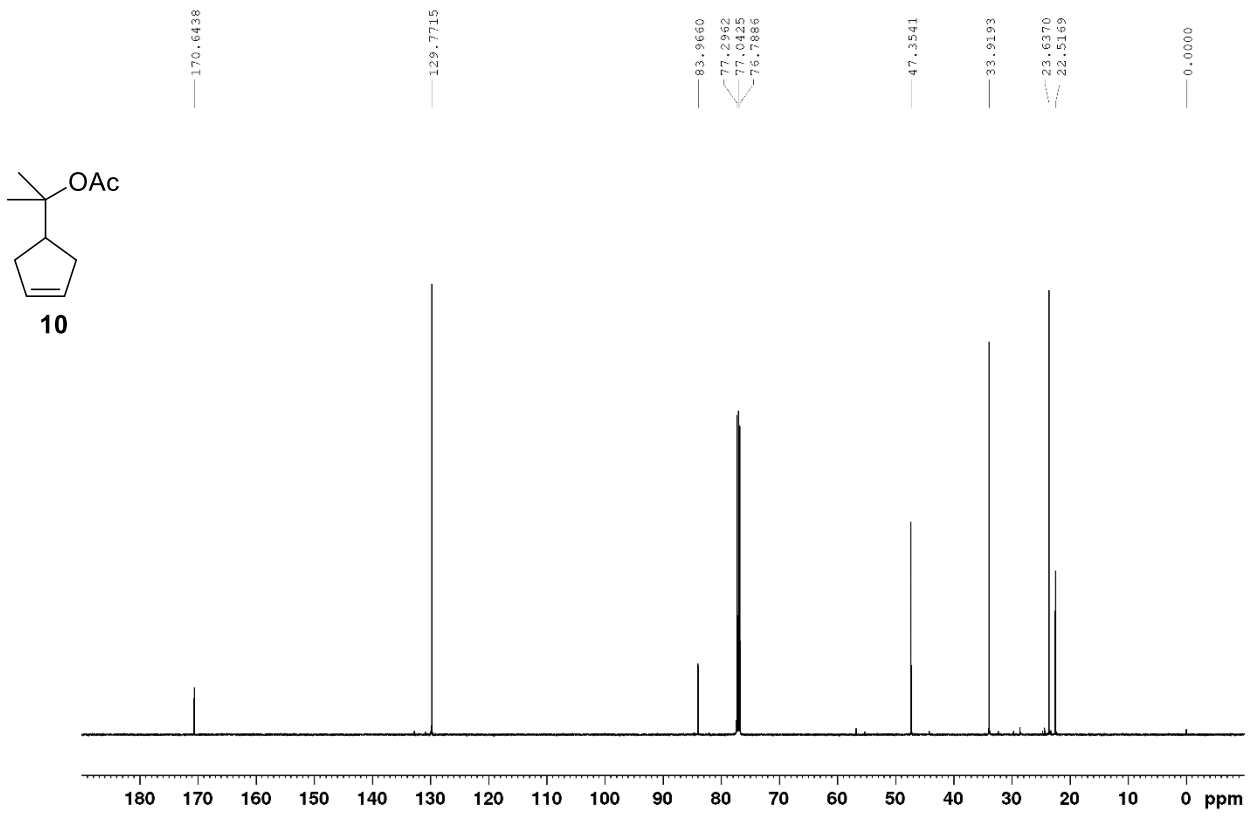
2.7490
2.7461
2.7333
2.7305
2.7276
2.7149
2.7120
2.6964
2.3962
2.3923
2.3873
2.3803
2.3774
2.3738
2.3687
2.3581
2.3527
2.3489
2.3401
2.3342
2.3308
2.2810
2.2782
2.2691
2.2657
2.2629
2.2589
2.2535
2.2401
2.2345
2.2315
2.2245
2.2196
2.2158
1.9667
1.4480
0.0000
9
8
7
6
5
4
3
2
1
0
ppm
1.99
1.00
2.12
2.11
3.18
6.12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129.7715
83.9660
77.2962
77.0425
76.7886
47.3541
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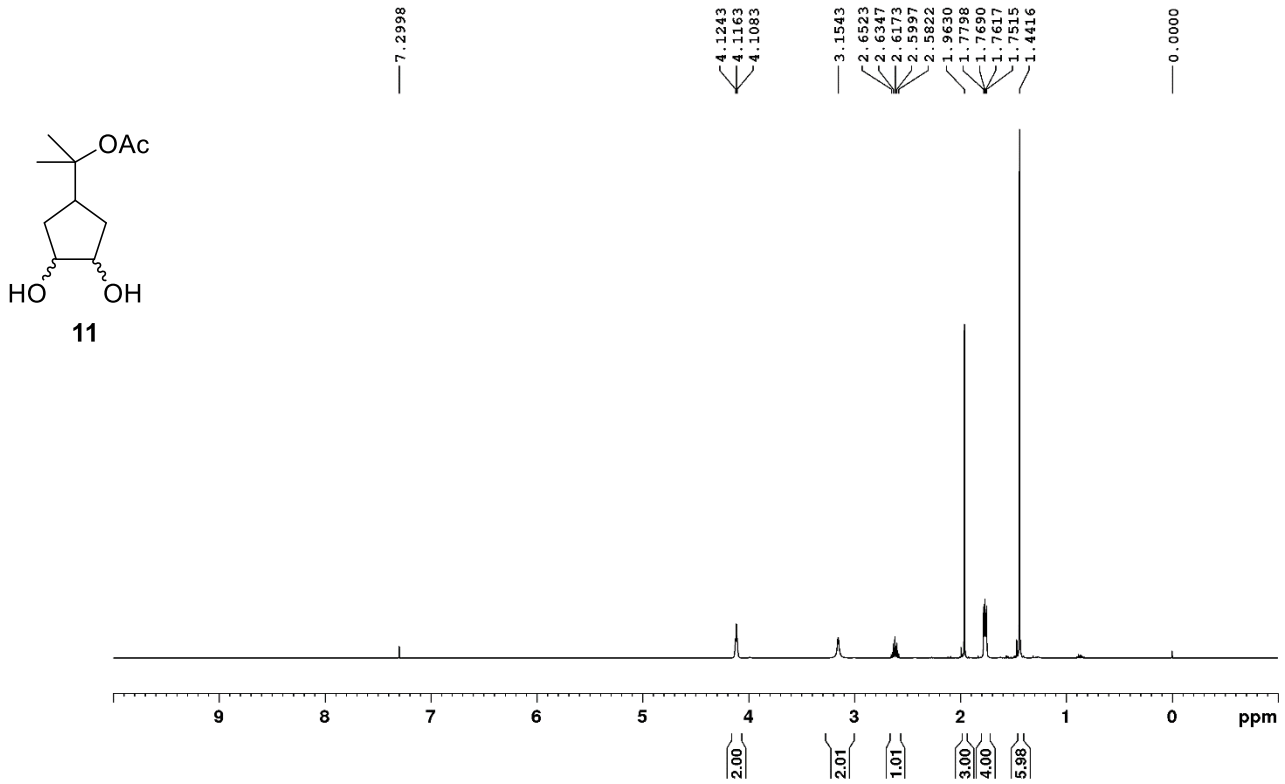
23.6370
22.5169
0.0000
OAc
10
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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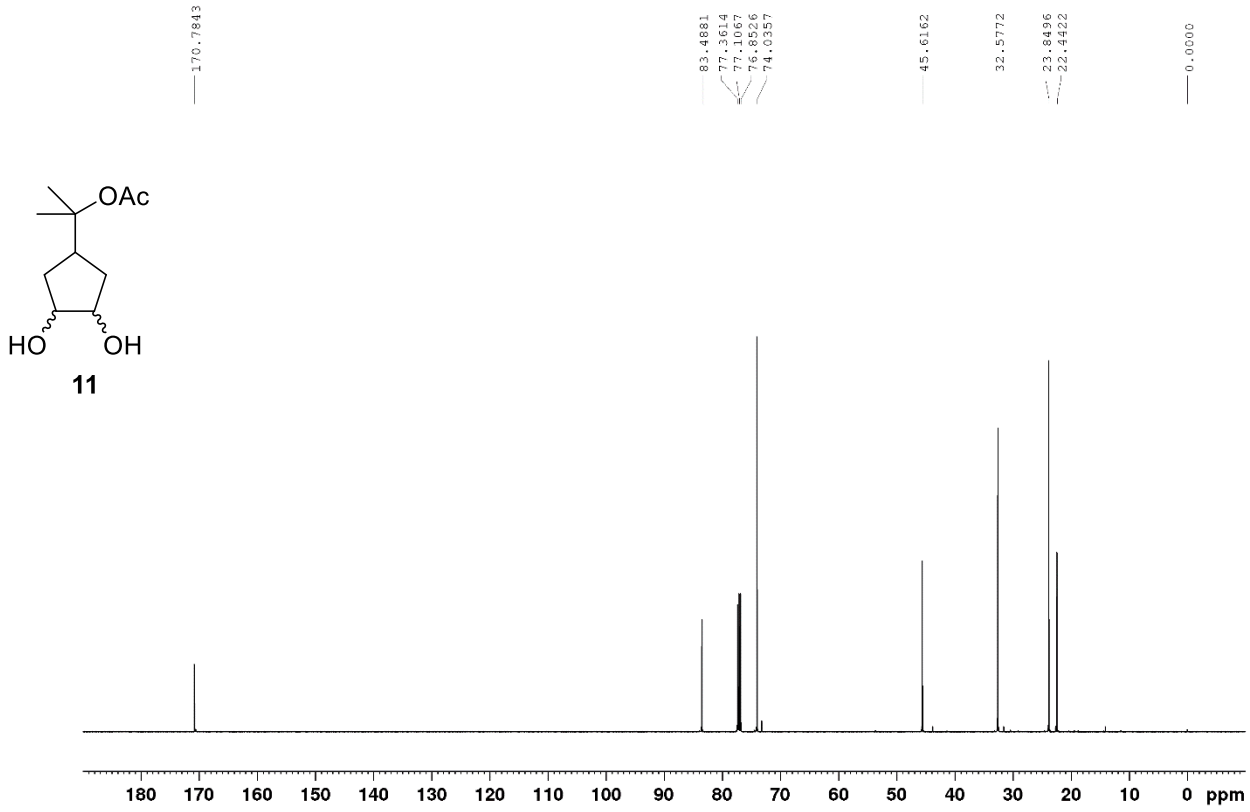
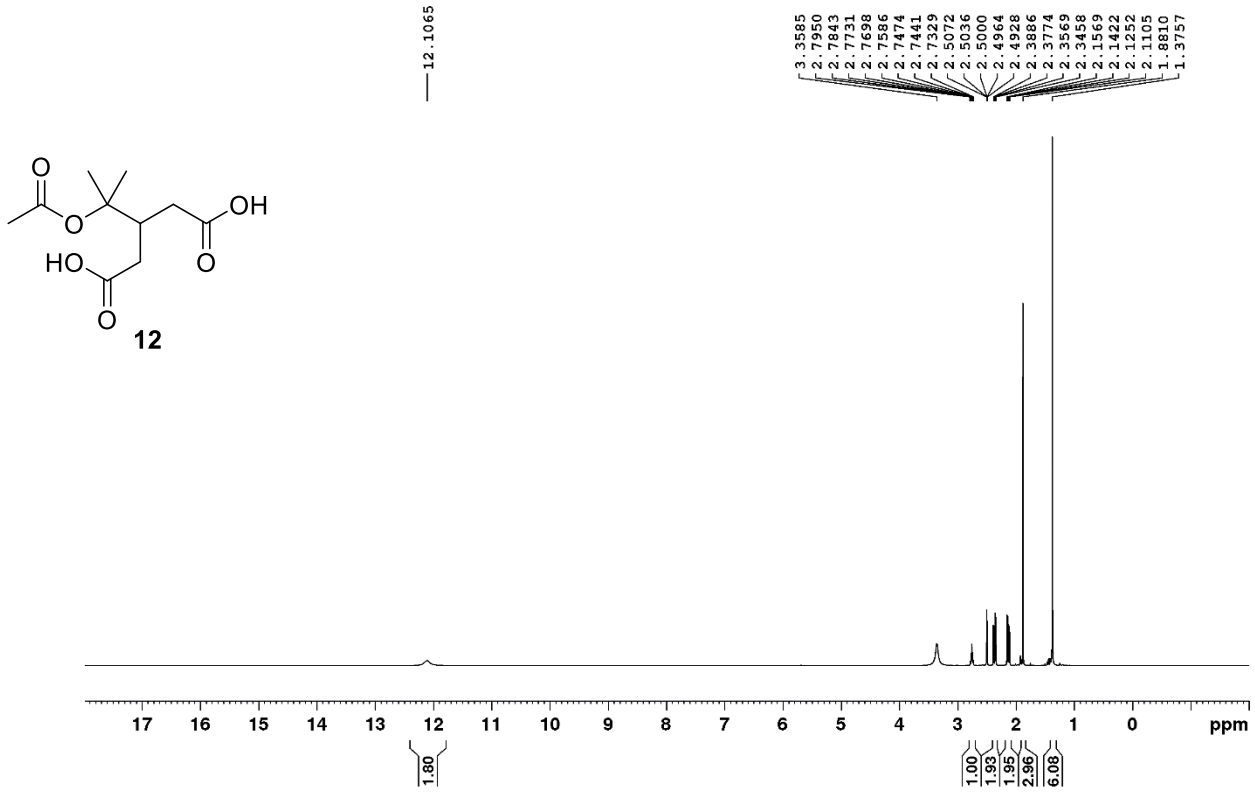
4.1163
4.1083
3.1543
2.6523
2.6347
2.6173
2.5997
2.5822
1.9630
1.7798
1.7690
1.7617
1.7515
1.4416
0.0000
OAc
HO
OH
11
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
1.01
3.00
4.00
5.98


170.7843
83.4881
77.3614
77.1067
76.8526
74.0357
45.6162
32.5772
23.8496
22.4422
0.0000
OAc
HO
OH
11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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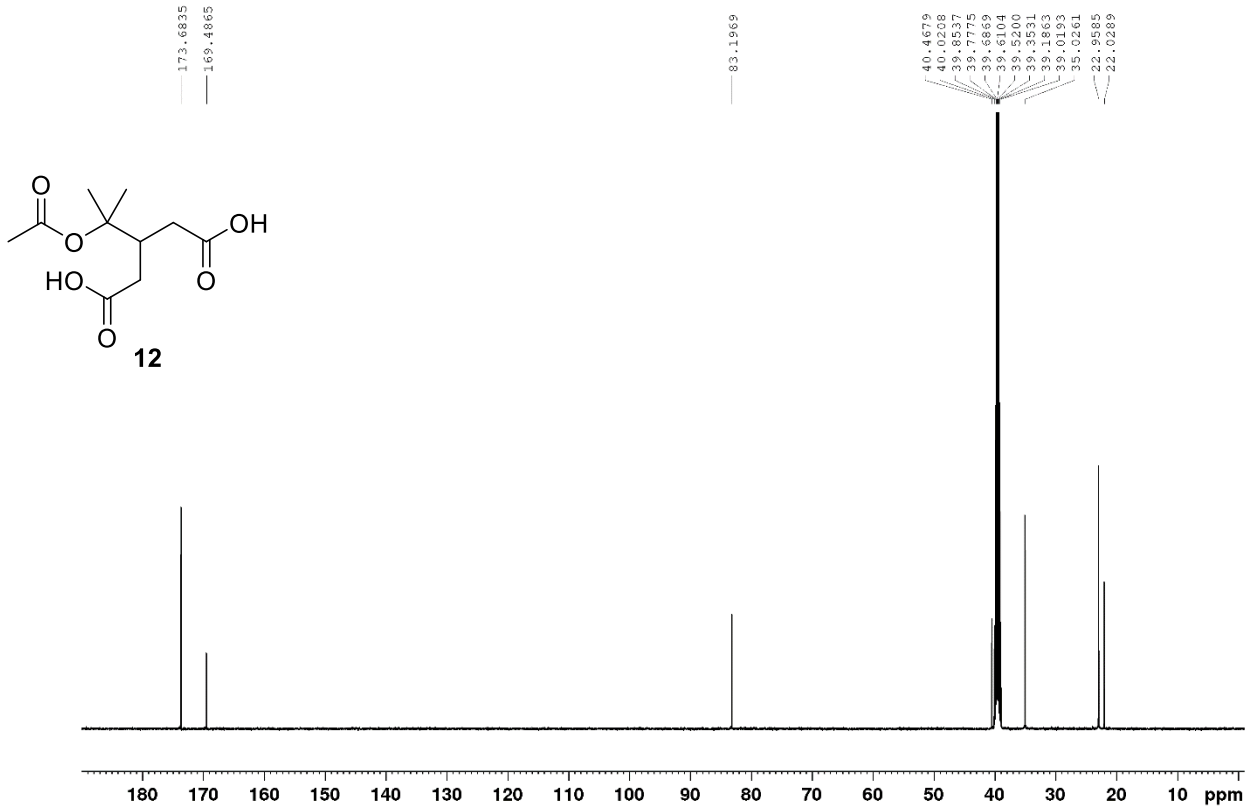
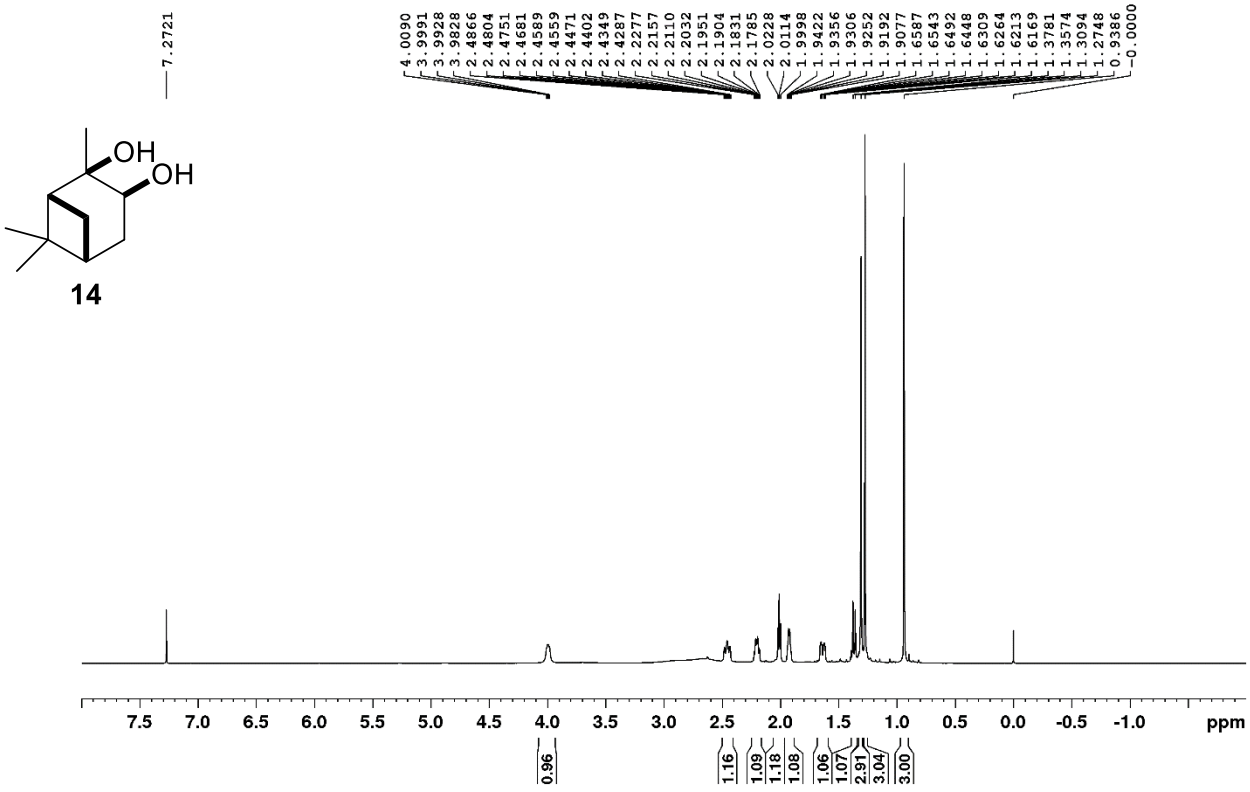
3.3585
2.7950
2.7843
2.7731
2.7698
2.7586
2.7474
2.7441
2.7329
2.5072
2.5036
2.5000
2.4964
2.4928
2.3886
2.3774
2.3569
2.3458
2.1569
2.1422
2.1252
2.1105
1.8810
1.3757
O
O
OH
HO
O
O
12
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.80
1.00
1.93
1.95
2.96
6.08


173.6835
169.4865
83.1969
40.4679
40.0208
39.8537
39.7775
39.6869
39.6104
39.5200
39.3531
39.1863
39.0193
35.0261
22.9585
22.0289
O
O
OH
HO
O
O
12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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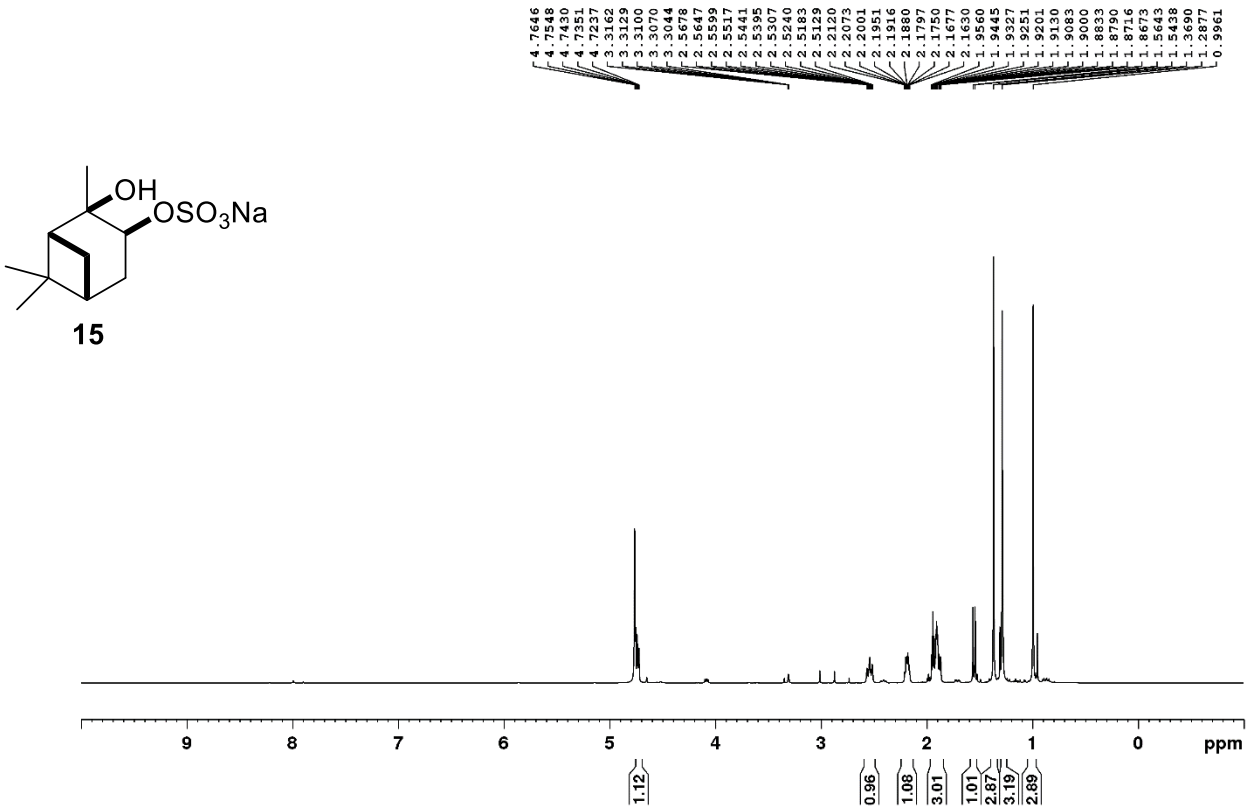
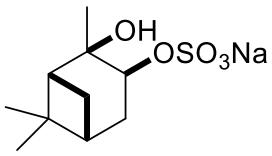
4.0090
3.9991
3.9928
3.9828
2.4866
2.4804
2.4751
2.4681
2.4589
2.4559
2.4471
2.4402
2.4349
2.4287
2.2277
2.2157
2.2110
2.2032
2.1951
2.1904
2.1831
2.1785
2.0228
2.0114
1.9998
1.9422
1.9356
1.9306
1.9252
1.9192
1.9077
1.6587
1.6543
1.6492
1.6448
1.6309
1.6264
1.6213
1.6169
1.3781
1.3574
1.3094
1.2748
0.9386
0.0000
OH
OH
14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm
0.96
1.16
1.09
1.18
1.08
1.06
1.07
2.91
3.04
3.00


OH
OSO3Na
15
4.7646
4.7548
4.7430
4.7351
4.7237
3.3162
3.3129
3.3100
3.3070
3.3044
2.5678
2.5647
2.5599
2.5517
2.5441
2.5395
2.5307
2.5240
2.5183
2.5129
2.2120
2.2073
2.2001
2.1951
2.1916
2.1880
2.1797
2.1750
2.1677
2.1630
1.9560
1.9445
1.9327
1.9251
1.9201
1.9130
1.9083
1.9000
1.8833
1.8790
1.8716
1.8673
1.5643
1.5438
1.3690
1.2877
0.9961
9
8
7
6
5
4
3
2
1
0
ppm
1.12
0.96
1.08
3.01
1.01
2.87
3.19
2.89


OH
OSO3Na

15

77.4851
75.0595
55.3954
49.5105
49.3416
49.1703
49.0000
48.8302
48.6587
48.4898
41.7731
39.4773
36.7018
30.1201
29.2010
28.3787
24.5592
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Particle Transmission Efficiencies of Thermal Denuder

The particle size distribution and size-resolved particle transmission efficiencies at set temperatures of 25 ºC, 40 ºC, 60 ºC, and 100 ºC with an effective RT of 60 s are demonstrated in Figs. S1 (a) and (b). In general, no substantial change in sized-resolved particle number concentration was perceived at aforementioned set temperatures. The particle transmission efficiencies remained the same for particles larger than 25 nm, as large particles possess small diffusivities. Regardless of the set temperature, particles smaller than 25 nm exhibited lower transmission efficiencies than particles larger than 25 nm which might be due to diffusional losses inside the heating section of thermal denuder. Similar observations were also noted in other studies.[12–14]

The particle size distribution and transmission efficiency at the effective RTs of 60 s and 70 s and a set temperature of 100 ºC are demonstrated in Figs. S1 (c) and (d). The particle size distribution and sized-resolved transmission efficiency were nearly same at effective RTs of 60 s and 70 s.

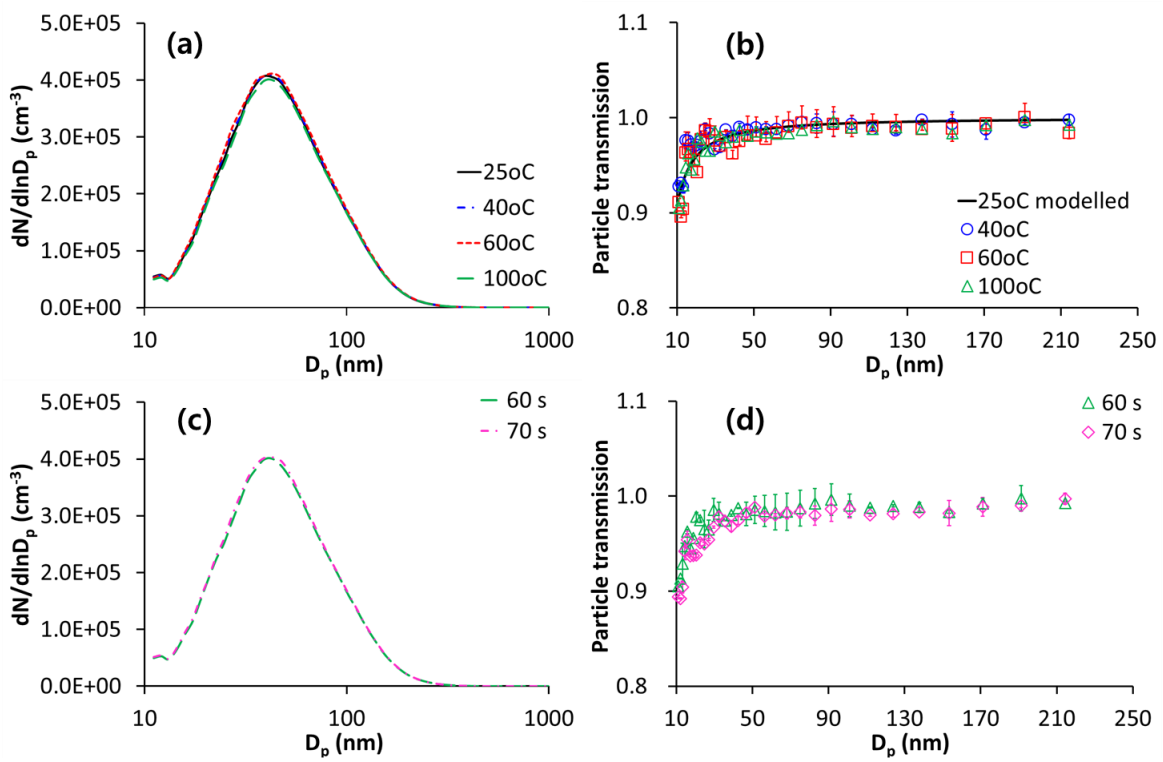


Fig. S1. For NaCl at set temperatures of 25°C, 40°C, 60°C, and 100°C and effective RT of 60 s, (a) particle size distribution and (b) size-resolved particle transmission efficiency. Theoretical diffusional losses of particles at reference temperature of 25 °C is represented by solid line. For NaCl at effective RTs of 60 s and 70 s and set temperature of 100°C, (c) particle size distribution and (d) size-resolved particle transmission efficiency.

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