Supplemental material for:

Total Synthesis of Naturally Occurring Abietane Diterpenoids *via* a Late-Stage Fe(III)-*b*-TAML Catalysed Csp^3-H Functionalization

Mintu Munda,[a] Debasmita Chatterjee,[b] Moumita Majhi,[b] Souvik Biswas,[b] Debopam Pal,[b] and Alakesh Bisai*[a,b]

[a]Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhopal, MP - 462 066, India.

[b]Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, Nadia, WB - 741 246, India.

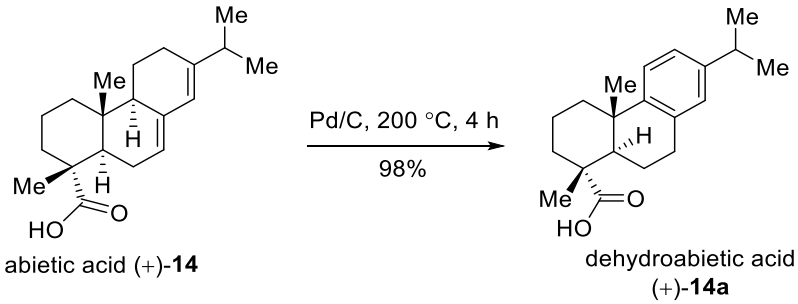
e-Mail: alakesh@iiserkol.ac.in, alakeshb@gmail.com

Table of Contents

Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2), toluene, and benzene were distilled over calcium hydride. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silicagel of particle size 100-200 mesh was used for flash chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent ($CDCl_3$) signal (δ = 7.28 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. Optical rotations were measured on an automatic polarimeter.

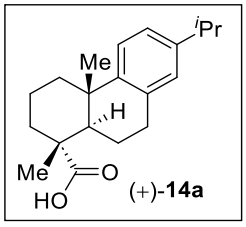
Synthesis of Dehydroabietic acid (+)**-14a**:



abietic acid (+)-**14**

dehydroabietic acid (+)-**14a**

In an oven dried round-bottm flask Abietic acid (+)-**14** (15 g, 49.6 mmol, 1.0 equiv.) and 10% Pd/C (30 mg, 0.1 mmol, 0.002 equiv.) were taken and heated at 200 °C for 4 h. After completing of reaction EtOAc was added to the reaction mixture and Pd/C was removed by filtration and the filtrate was evaporated under reduced pressure. The crude product was purified by flash column chromatography with ~20-30% EtOAc in *n*-Hexane to afford Dehydroabietic acid (+)-**14a** as white foam (14.6 g, 98% yield).



(1*R*,4a*S*,10a*R*)-**7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid** (+)-**14a:** The compound (+)-**14a** was obtained as white foam (49.6 mmol scale of reaction; 14.6 g; 98% yield). R_f = 0.45 (20% EtOAc in *n*-hexane).

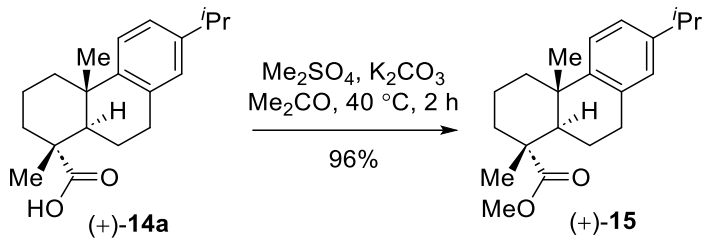
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.1 Hz, 1H), 7.03 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 3.01 – 2.91 (m, 2H), 2.89 – 2.82 (m, 1H), 2.39 – 2.30 (m, 1H), 2.28 (dd, *J* = 12.4, 2.2 Hz, 1H), 1.98 – 1.81 (m, 2H), 1.79 – 1.68 (m, 4H), 1.65–1.50 (m, 1H), 1.32 (s, 3H), 1.27–1.22 (m, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.0, 146.8, 145.7, 134.7, 126.9, 124.1, 123.9, 47.4, 44.6, 37.9, 36.9, 36.7, 33.5, 30.0, 25.1, 24.0, 21.8, 18.5, 16.2.

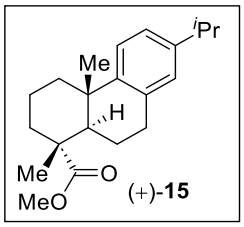
IR (neat) υ_{max} 2946, 2918, 1958, 1861, 1708, 1615, 1409, 1027, 882, 776 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd. for $[C_{20}H_{28}O_2 + H]^+$ 301.2162; found 301.2154.

$[\alpha]_D^{20.0}$ = +39.50 (*c* = 0.1, $CHCl_3$).

Synthesis of compound (+)**-15**:



In an oven-dried round-bottom flask (+)-**14a** (14.6 g, 48.6 mmol, 1.0 equiv.) was taken and dissolved in acetone solvent then K_2CO_3 (7.4 g, 53.5 mmol, 1.1 equiv.) and Me_2SO_4 (5.1 mL, 53.5 mmol, 1.1 equiv.) were added consecutively and stirred for 2 h at 40 °C. Then the reaction mixture was evaporated under reduced pressure and work up was done by CH_2Cl_2/H_2O and the crude product was purified by flash column chromatography with ~5-10% EtOAc in *n*-hexane to afford compound (+)-**15** as colourless gel (14.6 g, 96% yield).



Methyl (1*R*,4a*S*,10a*R*)**-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)**-15:** The compound (+)-**15** was obtained as colourless gel (48.6 mmol scale of reaction; 14.6 g; 96% yield). R_f = 0.60 (5% EtOAc in *n*-hexane).

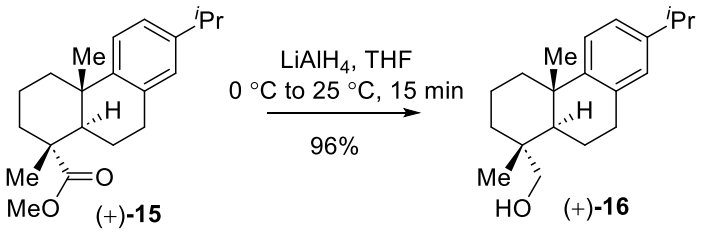
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 1H), 7.07 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 3.72 (s, 3H), 3.05 – 2.90 (m, 2H), 2.90 – 2.85 (m, 1H), 2.40 – 2.34 (m, 1H), 2.32 (dd, *J* = 12.5, 2.3 Hz, 1H), 1.84 (dd, *J* = 4.8, 2.1 Hz, 3H), 1.80 – 1.63 (m, 2H), 1.64 – 1.41 (m, 2H), 1.35 (s, 3H), 1.32 – 1.25 (m, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.1, 146.9, 145.7, 134.7, 126.9, 124.1, 123.9, 51.9, 51.9, 47.7, 44.9, 38.0, 36.9, 36.7, 33.5, 30.0, 25.1, 24.0, 21.8, 18.6, 16.6.

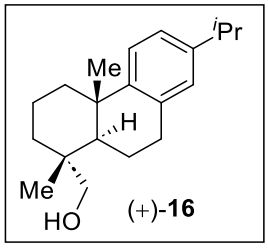
IR (neat) υ_{max} 2958, 2957, 2866, 2369, 1726, 1498, 1243, 1121, 915, 768 cm^{-1}.
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $[C_{21}H_{31}O_2 + H]^+$ 315.2319; found 315.2311.

$[\alpha]_D^{20.0}$ = +32.20 (*c* = 0.1, $CHCl_3$).

Synthesis of compound (+)**-16**:



To a stirred solution (+)-**15** (14.6 g, 46.6 mmol, 1 equiv.) in tetrahydrofuran (120 mL), lithium aluminum hydride (1.8 g, 47.1 mmol, 1.01 equiv.) was added at 0 °C, and the reaction mixture was stirred for 30 min at 25 °C. Distilled water (5 mL), 1M aq. NaOH (1 M, 5 mL), and distilled water (15 mL) was sequentially added at 0 °C and the resulting mixture was warmed to 25 °C. Dried over sodium sulfate and filtered over a pad of celite and washed with ethyl acetate. The combined organic layer was concentrated under reduced pressure, and the resulting crude residue was purified by flash column chromatography on silica gel with ~15-20% EtOAc in *n*-Hexane to provide compound (+)-**16** as yellow oil (12.8 g, 96%).



((1*R*,4a*S*,10a*R*)-**7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanol (+)-16**: The compound (+)-**16** was obtained as yellow oil (46.6 mmol scale of reaction; 12.8 g; 96%). R_f = 0.35 (10% EtOAc in *n*-hexane).

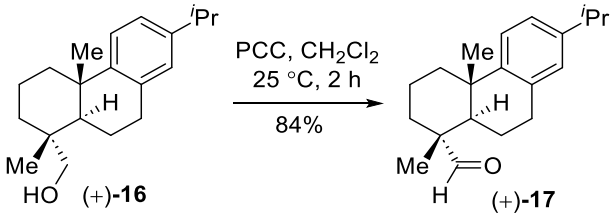
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 3.50 (d, *J* = 10.9 Hz, 1H), 3.26 (d, *J* = 10.9 Hz, 1H), 2.97 – 2.89 (m, 2H), 2.88 – 2.82 (m, 1H), 2.35 – 2.29 (m, 1H), 1.81 (dddd, *J* = 13.5, 10.0, 6.2, 3.4 Hz, 2H), 1.73 (tdd, *J* = 10.1, 4.8, 2.5 Hz, 2H), 1.67 (dd, *J* = 12.2, 2.3 Hz, 1H), 1.46 (d, *J* = 4.1 Hz, 1H), 1.44 – 1.40 (m, 2H), 1.26 (s, 3H), 1.25 (s, 3H), 1.25 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 145.5, 134.8, 126.8, 124.2, 123.8, 72.3, 44.0, 38.5, 37.9, 37.4, 35.1, 33.5, 30.1, 25.3, 24.0, 24.0, 18.9, 18.7, 17.4.

IR (film) υ_{max} 3341, 2942, 2925, 1698, 1512, 1418, 1253, 1230, 1134, 909, 724 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $[C_{20}H_{30}O + H]^+$ 287.2369; Found 287.2374.

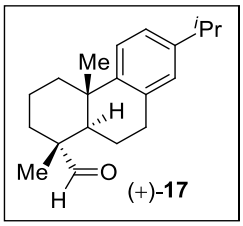
$[\alpha]_D^{25.0}$ = +36.67 (*c* = 0.3, $CHCl_3$).

Synthesis of compound (+)-**17**:



A solution of the alcohol (+)-**16** (12.8 g, 44.7 mmol, 1.0 equiv.) was dissolved in DCM (160 mL) and sequentially added silica gel (14 g), PCC (14.5 g, 67.05 mmol, 1.5 equiv.) and stirred at rt for 2 h. After complete consumption of starting material (monitored by TLC), CH_2Cl_2 was evaporated under reduced pressure. Then the crude product was purified

by column chromatography on silica gel with ~10% EtOAc in *n*-hexane to afford aldehyde (+)-**17** as white solid (10.7 g, 84%).



(1*R*,4a*S*,10a*R*)-**7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbaldehyde (+)-17**: The compound (+)-**17** was obtained as white solid (44.7 mmol scale of reaction; 10.7 g; 84%). R_f = 0.65 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 2.91 (dd, *J* = 8.4, 4.0 Hz, 2H), 2.88 – 2.84 (m, 1H), 2.41 – 2.35 (m, 1H), 1.94 (dd, *J* = 12.8, 2.0 Hz, 1H), 1.88 – 1.85 (m, 1H), 1.82 (td, *J* = 4.6, 2.2 Hz, 2H), 1.54 – 1.47 (m, 2H), 1.40 – 1.34 (m, 2H), 1.26 (s, 6H), 1.25 (s, 3H), 1.19 (s, 3H).

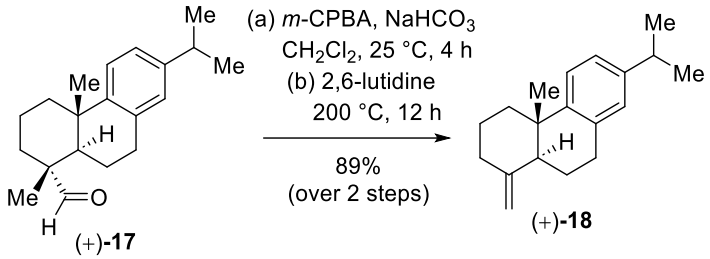
^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 146.2, 146.0, 134.5, 127.0, 124.2, 124.0, 49.8, 42.8, 37.9, 36.3, 33.5, 32.1, 29.8, 25.1, 24.0, 24.0, 21.4, 17.8, 14.0.

IR (film) υ_{max} 2957, 2925, 2822, 2681, 1755, 1482 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $[C_{20}H_{28}O + Na]^+$ 307.2032; Found 307.2038.

$[\alpha]_D^{25.0}$ = +56.50 (*c* = 0.4, $CHCl_3$).

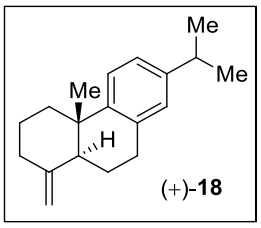
MP = 84-86 °C.

Synthesis of compound (+)-**18**:



To a stirred solution of aldehyde (10.7 g, 37.6 mmol, 1.0 equiv.) in DCM (150 mL) was added recrystallized *m*-CPBA (7.8 g, 45.1 mmol, 1.2 equiv.) and $NaHCO_3$ (6.3 g, 75.2 mmol, 2.0 equiv.) at 0 °C. Then, the mixture was warmed to rt and run for 4 h. Then, the mixture was diluted with DCM (60 mL), washed with saturated aqueous $NaHCO_3$ (3 X 40 mL), brine (2 X 20 mL), dried, and concentrated. The crude product was directly charged for the next step.

A yellowish solution of crude formate (37.6 mmol, 1.0 equiv.) in 2,6-lutidine (40 mL) was heated at 200 °C for 12 h. During this time, the solution became dark orange then cooled to rt and diluted with EtOAc (150 mL). The mixture was washed with 4 (N) HCl (3 X 30 mL) and brine (3 X 30 mL), dried and concentrated. The residue was purified by flash column chromatography (with pure *n*-hexane) to afford exocyclic olefin (+)-**18** as colorless oil (8.5 g, 89% over 2 steps).



(4a*S*,10a*S*)-**7-isopropyl-4a-methyl-1-methylene-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (+)-18**: The compound (+)-**18** was obtained as colorless oil (37.6 mmol scale of reaction; 8.5 g; 89% over 2 steps). R_f = 0.7 (in *n*-hexane).

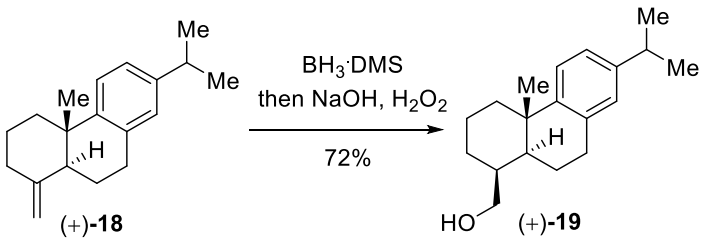
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.2, 2.9 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 4.88 (s, 1H), 4.63 (s, 1H), 2.98 – 2.84 (m, 3H), 2.41 (d, *J* = 13.2 Hz, 1H), 2.28 (dd, *J* = 27.7, 12.6 Hz, 2H), 2.09 (t, *J* = 13.6 Hz, 1H), 1.82 (dddd, *J* = 38.5, 26.7, 12.6, 6.3 Hz, 4H), 1.59 (d, *J* = 3.1 Hz, 1H), 1.30 – 1.25 (m, 6H), 1.04 (d, *J* = 3.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 145.8, 144.7, 134.9, 127.1, 125.4, 123.9, 106.4, 47.9, 39.2, 38.4, 36.4, 33.5, 30.0, 24.0, 24.0, 23.8, 22.8, 21.4.

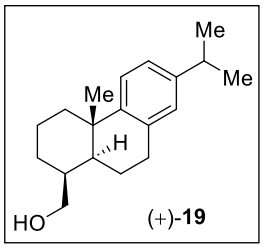
IR (film) υ_{max} 2954, 1735, 1670, 1562, 1140, 1075 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $[C_{19}H_{26} + H]^+$ 255.2107; Found 255.2167.

$[\alpha]_D^{25.0}$ = +165.11 (*c* = 1.0, $CHCl_3$).

Synthesis of compound (+)**-19**:



A solution of borane dimethyl sulfide complex (BDMS) (0.60 equiv.) was added dropwise to the exocyclic olefin (10.7 g, 33.5 mmol, 1.0 equiv.) at 0 °C. After 1 h, the mixture was warmed to room temperature and stirred for 6 h. After addition of NaOH (2 M) and H_2O_2 (35%) stirring was continued for 4 h. The mixture was diluted with EtOAc (90 mL) and washed with 4 (*N*) HCl (3 X 20 mL) and brine (3 X 20 mL), dried and concentrated. After removing the solvent under reduced pressure, the crude product was purified via column chromatography on silica gel with ~20-30% EtOAc in *n*-hexane to afford (+)**-19** as white foam (6.6 g, 72%).



((1*S*,4a*S*,10a*S*)-**7-isopropyl-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanol (+)-19**: The compound **(+)-19** was obtained as white foam (33.5 mmol scale of reaction, 6.6 g, 72%). R_f = 0.35 (20% EtOAc in *n*-hexane).

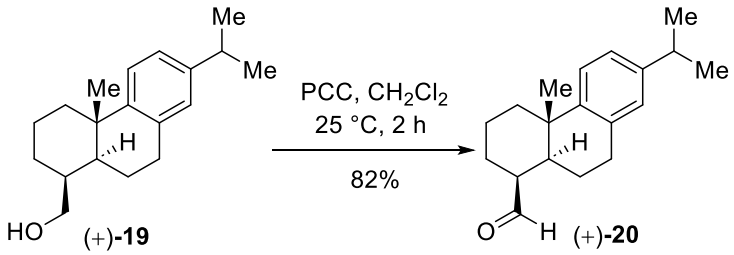
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.1 Hz, 1H), 7.02 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.91 (d, *J* = 2.1 Hz, 1H), 3.90 – 3.60 (m, 2H), 2.92 (dt, *J* = 9.4, 4.7 Hz, 2H), 2.85 (p, *J* = 6.8 Hz, 1H), 2.29 (dt, *J* = 13.3, 3.6 Hz, 1H), 2.03 – 1.91 (m, 3H), 1.86 (ddd, *J* = 12.9, 5.0, 1.9 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.69 – 1.61 (m, 3H), 1.45 (dtd, *J* = 18.8, 9.4, 8.8, 5.1 Hz, 2H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.07 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.1, 145.7, 134.8, 127.0, 124.6, 123.9, 61.8, 44.6, 44.1, 38.6, 37.0, 33.5, 30.7, 27.7, 25.3, 24.4, 24.0, 18.3.

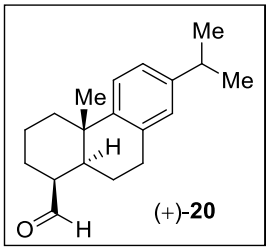
IR (film) υ_{max} 3330, 2906, 2510, 1669, 1500, 1431, 1150, 718, 661 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $[C_{19}H_{28}O + Na]^+$ 295.2032; Found 295.2016.

$[\alpha]_D^{25.0}$ = +79.72 (*c* = 0.2, $CHCl_3$).

Synthesis of compound (+)-20:



A solution of the alcohol (+)**-19** (6.6 g, 24.12 mmol, 1.0 equiv.) was dissolved in DCM (150 mL) and sequentially added silica gel (7 g), PCC (7.8 g, 36.18 mmol, 1.5 equiv.) and stirred at rt for 2 h. After complete consumption of starting material (monitored by TLC), CH_2Cl_2 was evaporated under reduced pressure. Then the crude product was purified by column chromatography on silica gel with ~5-8% EtOAc in *n*-hexane to afford aldehyde (+)**-20** as colorless liquid (5.35 g, 82%).



(1*S*,4a*S*,10a*S*)**-7-isopropyl-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbaldehyde (**+**)-20**: The compound **(**+**)-20** was obtained as colorless liquid (24.1 mmol scale of reaction, 5.35 g, 82%). R_f = 0.7 (10% EtOAc in *n*-hexane).

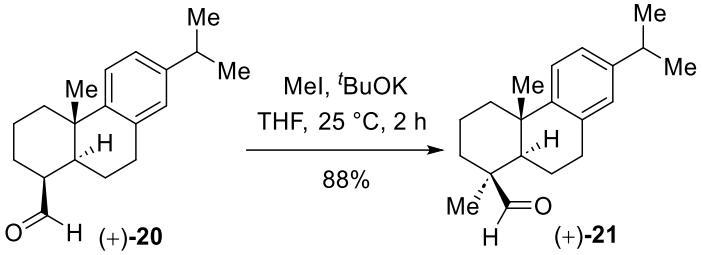
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (d, *J* = 3.8 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.05 (d, *J* = 6.4 Hz, 1H), 6.96 (d, *J* = 3.3 Hz, 1H), 3.00 (d, *J* = 5.4 Hz, 1H), 2.88 (dt, *J* = 12.8, 6.8 Hz, 1H), 2.50 (d, *J* = 5.2 Hz, 1H), 2.45 – 2.27 (m, 3H), 2.15 (d, *J* = 13.2 Hz, 1H), 1.98 (dd, *J* = 12.7, 6.1 Hz, 1H), 1.83 – 1.67 (m, 3H), 1.47 – 1.37 (m, 2H), 1.27 (s, 6H), 1.07 (d, *J* = 3.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 146.1, 144.7, 134.5, 127.1, 124.9, 124.2, 52.3, 45.0, 38.1, 37.6, 33.5, 30.9, 24.8, 24.2, 24.0, 23.7, 19.1.

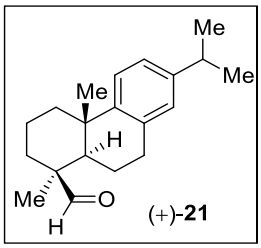
IR (film) υ_{max} 2720, 1985, 1725, 1650, 1375, 776 cm^{-1}.

$[\alpha]_D^{25.0}$ = +45.10 (*c* = 1.0, $CHCl_3$).

Synthesis of compound (+)**-21**:



To a solution of aldehyde (+)-**20** (5.35 g, 19.8 mmol, 1.0 equiv.) in THF (50 mL) at 0 °C was added ^{t}BuOK (3.33 g, 29.7 mmol, 1.5 equiv.), and 10 min later, MeI (1.85 mL, 29.7 mmol, 1.5 equiv.). The reaction was allowed to stirred for 2 h and quenched with H_2O, and aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel with ~5% EtOAc in *n*-hexane to afford callitrisaldehyde (+)-**21** as colorless liquid (4.96 g, 88%).



(1*S*,4a*S*,10a*R*)**-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbaldehyde (+)-21**: The compound **(+)-21** was obtained as a colorless liquid. (19.8 mmol scale of reaction; 4.96 g; 88%). R_f = 0.65 (5% EtOAc in *n*-hexane).

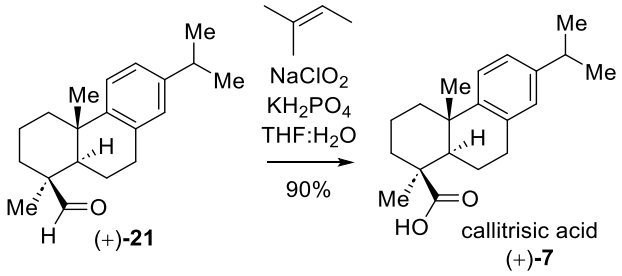
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (d, *J* = 3.4 Hz, 1H), 7.22 (dd, *J* = 8.9, 3.3 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 3.2 Hz, 1H), 3.06 – 2.82 (m, 3H), 2.29 (dd, *J* = 24.3, 13.6 Hz, 3H), 2.06 (qt, *J* = 12.0, 4.5 Hz, 1H), 1.82 – 1.66 (m, 3H), 1.49 – 1.35 (m, 2H), 1.26 (dd, *J* = 6.6, 3.5 Hz, 6H), 1.12 (dd, *J* = 23.3, 3.5 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 146.0, 145.0, 134.4, 126.9, 125.0, 124.2, 52.0, 48.6, 38.4, 37.8, 33.9, 33.5, 31.3, 24.2, 24.1, 24.0, 24.0, 19.3, 18.9.

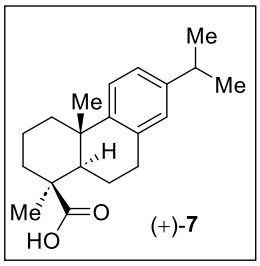
IR (film) υ_{max} 2950, 2965, 2838, 2654, 1730, 1467 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{20}H_{28}O + Na]^+$ 307.2032; Found 307.2022.

$[\alpha]_D^{25.0}$ = +56.61 (*c* = 0.6, $CHCl_3$).

Synthesis of Callitrisic acid (+)-**7**:



To a stirred solution of aldehyde (+)-**21** (4.96 g, 17.4 mmol, 1.0 equiv.) and 2-methyl-2-butene (18.4 mL, 174.0 mmol, 10.0 equiv.) in THF (50 mL) and *tert*-BuOH (5 mL) at rt was added $NaClO_2$ (4.7 g, 52.2 mmol, 3 equiv.) and KH_2PO_4 (11.8 g, 87.0 mmol, 5 equiv.) in H_2O (50 mL). The reaction mixture was capped with a rubber septum with a needle as outlet and stirred for 4 h. Then, the solvent was removed under vacuum (bath temperature 40 °C) and the resulting watery residue was diluted with EtOAc (80 mL) and 10% HCl (40 mL) and brine (20 mL). The phases were separated, and the aqueous layer was extracted with EtOAc (3 X 20 mL) and the combined organic extracts were washed with brine (20 mL), dried and concentrated. The resulting pale oil was chromatographed on silica gel with ~10-15% EtOAc in *n*-hexane to give callitrisic acid (+)-**7** as white solid (4.7 g, 90%).



(1*S*,4a*S*,10a*R*)**-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid (+)-7**: The compound **(+)-7** was obtained as white solid. (17.4 mmol scale of reaction; 4.7 g of product; 90%). R_f = 0.35 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.94 (s, 1H), 2.97 – 2.81 (m, 3H), 2.34 – 2.27 (m, 2H), 2.26 – 2.19 (m, 1H), 2.09 (dtd, *J* = 28.1, 14.5, 13.2, 9.4 Hz, 2H), 1.69 – 1.60 (m, 2H), 1.45 (dt, *J* = 27.0, 8.2 Hz, 2H), 1.38 (d, *J* = 3.0 Hz, 3H), 1.28 (dd, *J* = 7.5, 2.9 Hz, 6H), 1.17 (d, *J* = 3.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 184.5, 145.7, 145.4, 135.1, 126.9, 125.5, 124.1, 53.0, 44.0, 39.3, 38.4, 37.4, 33.5, 32.1, 28.8, 24.0, 23.2, 21.0, 19.9.

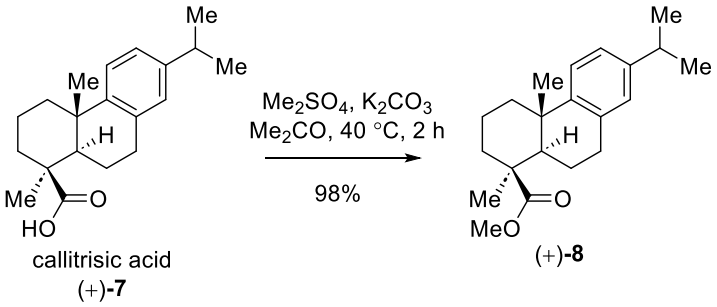
IR (film) υ_{max} 2946, 2918, 1958, 1861, 1708, 1615, 1409, 1027, 882, 776 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $[C_{20}H_{28}O_2 + Na]^+$ 323.1982; Found 323.1996.

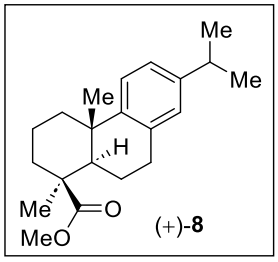
$[\alpha]_D^{25.0}$ = +76.59 (*c* = 1.3, $CHCl_3$).

MP = 198-200 °C.

Synthesis of compound (+)-**8**:



To a solution of callitrisic acid (+)-**7** (4.7 g, 15.7 mmol, 1.0 equiv.) in acetone was added K_2CO_3 (2.4 g, 17.3 mmol, 1.1 equiv.) and Me_2SO_4 (1.7 mL, 17.3 mmol, 1.1 equiv.). The mixture was allowed to reflux for 2 h, cooled to ambient temperature and filtered through a pad Celite. The organic solution was concentrated and purified by flash chromatography on silica gel with ~5% EtOAc in *n*-Hexane to afford (+)-**8** as white solid (4.84 g, 98%).



(1*S*,4a*S*,10a*R*)-**methyl 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (+)-8**: The compound **(+)-8** was obtained as white solid (15.7 mmol scale of reaction; 4.84 g of product; 98%). R_f = 0.80 (10% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 3.67 (s, 3H), 2.95 – 2.76 (m, 3H), 2.29 (td, *J* = 8.6, 4.3 Hz, 2H), 2.24 – 2.17 (m, 1H), 2.07 – 1.95 (m, 2H), 1.64 (dq, *J* = 14.4, 3.6 Hz, 1H), 1.57 (dd, *J* = 12.2, 1.8 Hz, 1H), 1.43 (dd, *J* = 13.4, 4.2 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 1.12 (dd, *J* = 13.7, 4.3 Hz, 1H), 1.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 145.7, 145.6, 135.2, 126.9, 125.6, 124.2, 53.1, 51.3, 44.1, 39.5, 38.3, 37.8, 33.6, 32.3, 28.7, 24.1, 23.1, 21.2, 20.1.

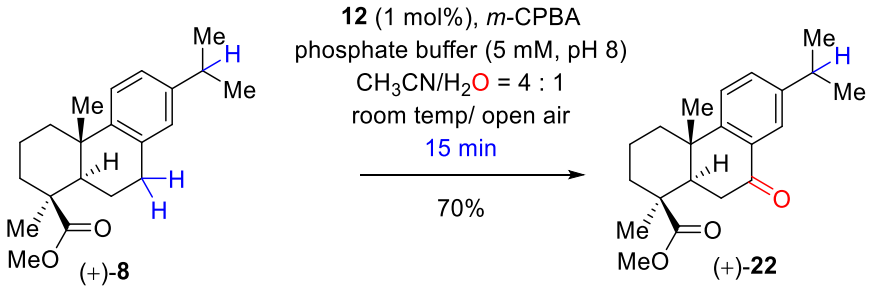
IR (film) υ_{max} 2958, 2957, 2866, 2369, 1726, 1498, 1243, 1121, 915, 768 cm^{-1}.
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $[C_{21}H_{30}O_2 + H]^+$ 315.2319; Found 315.2346.

$[\alpha]_D^{25.0}$ = +73.87 (*c* = 2.1, $CHCl_3$).

MP = 94-96 °C.

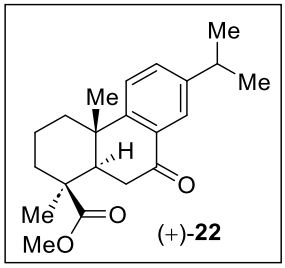
Fe(IV)-*b*-TAML Catalysed Csp^3-H Functionalization:

Synthesis of compound (+)-**22**:



To a 25 mL round-bottom flask containing a magnetic stir bar, NO_2-substituted Fe-*b*TAML catalyst (**12**) (1-2 µmol, 1 mol %), substrate (+)-**8** (100 mg, 0.32 mmol, 1.0 equiv.) and K_2HPO_4 (0.64 mmol, 2 equiv.) in 4 mL CH_3CN-1 mL H_2O were added. A solution of *m*CPBA (1.6 mmol, 5 equiv.) in CH_3CN was added via syringe pump with continuous stirring over a period of 2-12h at room temperature. The reaction was monitored by TLC and/or GC. After completion of the reaction, the solvent (CH_3CN) was removed under reduced pressure (NB: for more volatile substrates slow and careful evaporation was performed at reduced temperatures). Saturated aq. solution of sodium bicarbonate was added to the residual portion and extracted with dichloromethane (2 times). The organic part was dried with anhydrous Na_2SO_4, analysed by GC to estimate substrate conversion

and then further purified by column chromatography on silica gel with ~15% EtOAc in *n*-hexane to obtain the desired product (+)-**22** as yellow foam (73.6 mg, 70%).



(1*S*,4a*S*,10a*R*)-**methyl 7-isopropyl-1,4a-dimethyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)-**22**: The compound (+)-**22** was obtained as yellow foam (0.32 mmol scale of reaction; 73.6 mg of product; 70%). R_f = 0.35 (10% EtOAc in *n*-hexane).

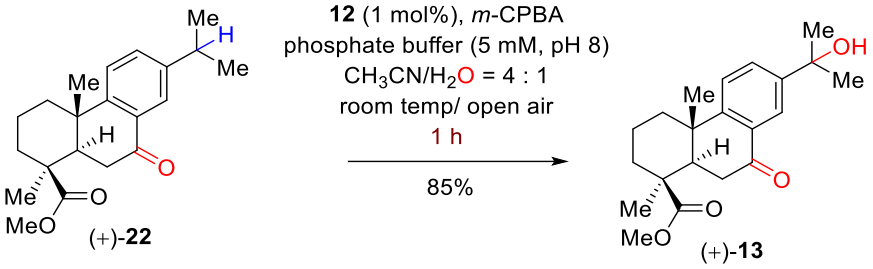
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 3.68 (s, 3H), 3.23 – 3.15 (m, 1H), 2.99 – 2.89 (m, 2H), 2.35 (d, *J* = 13.0 Hz, 1H), 2.32 – 2.28 (m, 1H), 2.06 – 1.99 (m, 2H), 1.72 – 1.63 (m, 2H), 1.53 – 1.46 (m, 1H), 1.24 (s, 6H), 1.22 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 177.2, 152.1, 147.0, 132.7, 130.5, 125.0, 124.7, 51.7, 50.3, 44.0, 38.6, 38.4, 37.8, 37.6, 33.7, 28.1, 23.9, 23.8, 21.4, 19.7.

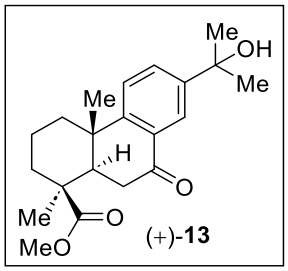
IR (film) υ_{max} 2968, 2946, 2869, 1735, 1695, 1557, 1367, 1238, 1175, 1107, 826 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $[C_{21}H_{28}O_3 + H]^+$ 329.2111; Found 329.2087.

$[\alpha]_D^{25.0}$ = +72.87 (*c* = 0.3, $CHCl_3$).

Synthesis of compound (+)-**13**:



To a 25 mL round-bottom flask containing a magnetic stir bar, NO_2-substituted Fe-*b*TAML catalyst 1 (1-2 µmol, 1 mol %), substrate (73.6 mg, 0.22 mmol, 1.0 equiv.) and K_2HPO_4 (0.44 mmol, 2 equiv.) in 4 mL CH_3CN-1 mL H_2O were added. A solution of *m*-CPBA (0.2-0.5 mmol, 5 equiv.) in CH_3CN was added via syringe pump with continuous stirring over a period of 2-12 h at room temperature. The reaction was monitored by TLC and/or GC. After completion of the reaction, the solvent (CH_3CN) was removed under reduced pressure (NB: for more volatile substrates slow and careful evaporation was performed at reduced temperatures). Saturated aq. solution of sodium bicarbonate was added to the residual portion and extracted with dichloromethane (2 times). The organic part was dried with anhydrous Na_2SO_4, analyzed by GC to estimate substrate conversion and then further purified by column chromatography on silica gel with ~25% EtOAc in *n*-hexane to obtain the desired product (+)-**13** as white solid (64.4 mg, 85%).



(1*S*,4a*S*,10a*R*)-**methyl 7-(2-hydroxypropan-2-yl)-1,4a-dimethyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)-**13**: The compound (+)-**13** was obtained as white solid (0.22 mmol scale of reaction; 64.4 mg of product; 85%). R_f = 0.20 (20% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.4 Hz, 1H), 7.70 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 3.67 (s, 3H), 3.18 (dd, *J* = 17.9, 14.5 Hz, 1H), 2.96 (dd, *J* = 17.9, 3.3 Hz, 1H), 2.32 (ddt, *J* = 25.4, 14.1, 3.7 Hz, 2H), 2.01 (tt, *J* = 11.1, 3.5 Hz, 2H), 1.68 (ddd, *J* = 14.1, 7.0, 3.5 Hz, 1H), 1.55 (d, *J* = 2.8 Hz, 6H), 1.50 (dd, *J* = 13.5, 4.1 Hz, 1H), 1.23 (s, 3H), 1.12 (dd, *J* = 13.6, 4.1 Hz, 1H), 1.08 (s, 3H).

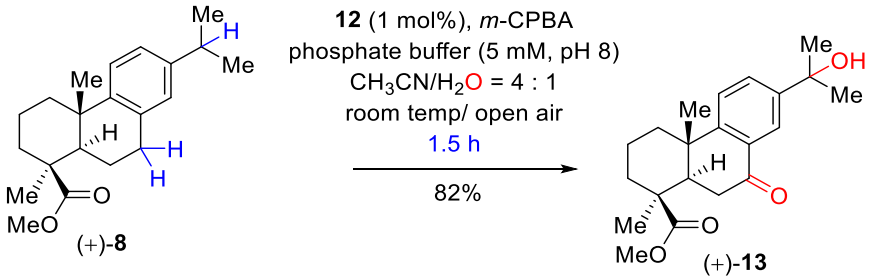
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 177.1, 152.9, 147.4, 130.7, 130.3, 125.1, 122.9, 72.3, 51.7, 50.3, 44.0, 38.5, 38.5, 37.8, 37.5, 31.7, 28.0, 21.4, 19.7.

IR (film) υ_{max} 3000, 2920, 1745, 1680, 1656, 1455, 1360, 1210, 1149, 975, 650 cm^{-1}.
HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{21}H_{28}O_4 + Na]^+$ 367.1880; Found 367.1887.

$[\alpha]_D^{25.0}$ = +51.67 (*c* = 1.1, $CHCl_3$).

MP = 126-128 °C.

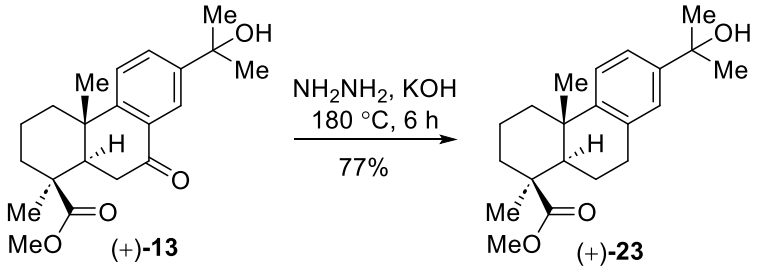
Direct transformation of (+)-**8 into the oxidized abietane** (+)-**13**:



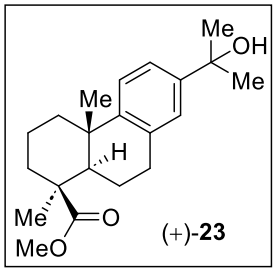
To a 25 mL round-bottom flask containing a magnetic stir bar, NO_2-substituted Fe-*b*TAML catalyst **12** (1-2 µmol, 1 mol %), substrate (100 mg, 0.32 mmol, 1.0 equiv.) and K_2HPO_4 (0.64 mmol, 2 equiv.) in 4 mL CH_3CN-1 mL H_2O were added. A solution of *m*CPBA (1.6 mmol, 5 equiv.) in CH_3CN was added via syringe pump with continuous stirring over a period of 2-12 h at room temperature. The reaction was monitored by TLC and/or GC. After completion of the reaction, the solvent (CH_3CN) was removed under reduced pressure (NB: for more volatile substrates slow and careful evaporation was performed at

reduced temperatures). Saturated aq. solution of sodium bicarbonate was added to the residual portion and extracted with dichloromethane (2 times). The organic part was dried with anhydrous Na_2SO_4, analyzed by GC to estimate substrate conversion and then further purified by column chromatography to obtain the desired product (+)-**13** as white solid (90.4 mg, 82%).

Synthesis of compound (+)-**23:**



In an oven dried round bottom flask (+)-**13** (275 mg, 0.8 mmol, 1.0 equiv.) was taken in Diethylene glycol. To the reaction mixture $NH_2NH_2.H_2O$ (0.37 mL, 12.0 mmol, 15.0 equiv.) was added at rt. Then the reaction was run at 140 °C for 2 h. Then, the reaction mixture was allowed to cool at rt. Then, to the reaction mixture KOH (673.3 mg, 12.0 mmol, 15.0 equiv.) was added at rt and again refluxed at 220 °C for 6 h. After complete consumption of starting material (monitored by TLC), the reaction was quenched by 4(N) HCl. Then the mixture was diluted with EtOAc (20 mL), the organic layer was separated, and the aqueous layer was washed with EtOAc (3 × 8 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography with 20% EtOAc in *n*-hexane to afford (+)-**23** as yellow foam (203.6 mg, 77% yield).



(1*S*,4a*S*,10a*R*)-**methyl 7-(2-hydroxypropan-2-yl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)-**23**: The compound (+)-**23** was obtained as yellow foam. (0.8 mmol scale of reaction, 203.6 mg, 77% yield). R_f = 0.35 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 2H), 7.19 (s, 1H), 3.68 (d, *J* = 2.2 Hz, 3H), 2.94 (dd, *J* = 16.8, 5.5 Hz, 1H), 2.83 (td, *J* = 17.1, 15.0, 6.2 Hz, 1H), 2.30 (d, *J* = 13.6 Hz, 2H), 2.21 (dd, *J* = 14.1, 5.9 Hz, 1H), 2.00 (td, *J* = 14.7, 13.9, 7.3 Hz, 2H), 1.74 (s, 2H), 1.67 – 1.62 (m, 1H), 1.58 (s, 6H), 1.56 – 1.52 (m, 1H), 1.30 (d, *J* = 2.1 Hz, 3H), 1.05 (s, 3H).

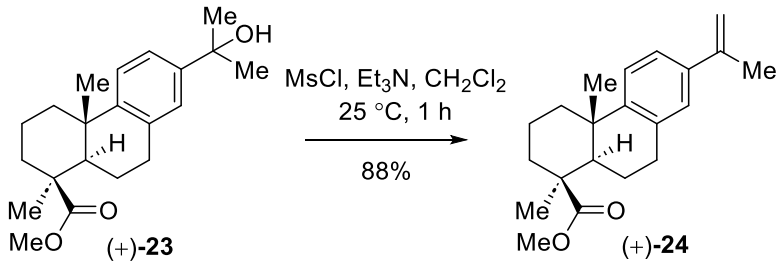
^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9, 146.6, 146.0, 135.1, 125.5, 124.9, 122.1, 72.3, 52.9, 51.2, 44.0, 39.4, 38.2, 37.7, 32.2, 31.6, 28.6, 23.0, 21.0, 20.0.

IR (film) υ_{max} 3300, 2978, 2939, 2855, 1740, 1479, 1235, 1136 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd. for $[C_{21}H_{30}O_3 + Na]^+$ 353.2087; found 353.2083.

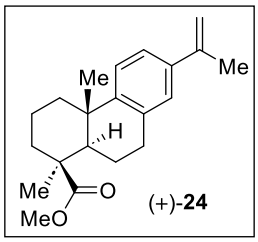
$[\alpha]_D^{25.0}$ = +66.95 (*c* = 0.6, $CHCl_3$).

Synthesis of compound (+)-**24:**



In an oven dried round bottom flask tertiary alcohol (+)-**23** (122 mg, 0.37 mmol, 1.0 equiv.) was taken in CH_2Cl_2. To the reaction mixture triethyl amine (308 μL, 2.22 mmol, 6.0

equiv.) and methane sulfonyl chloride (42.6 μL, 0.55 mmol, 1.5 equiv.) was added at 0 °C consecutively. Then reaction was run at rt for 1 h. After complete consumption of starting material (monitored by TLC), the reaction was quenched by water. Then the mixture was diluted with dichloromethane (6 mL), the organic layer was separated, and the aqueous layer was washed with dichloromethane (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography with 5% EtOAc in *n*-hexane to afford styrene (+)-**24** as white solid (101.7 mg, 88% yield).



(1*S*,4a*S*,10a*R*)-**methyl 1,4a-dimethyl-7-(prop-1-en-2-yl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)-**24**: The compound (+)-**24** was obtained as white solid. (0.37 mmol scale of reaction, 101.7 mg, 88% yield). R_f = 0.65 (5% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.17 (s, 1H), 5.36 (s, 1H), 5.05 (s, 1H), 3.69 (d, *J* = 2.2 Hz, 3H), 2.95 (dd, *J* = 16.9, 5.3 Hz, 1H), 2.84 (td, *J* = 17.0, 14.9, 5.9 Hz, 1H), 2.35 – 2.28 (m, 2H), 2.22 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.15 (s, 3H), 2.03 (td, *J* = 12.8, 12.3, 5.3 Hz, 2H), 1.69 – 1.62 (m, 2H), 1.57 (d, *J* = 12.3 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.31 (d, *J* = 2.2 Hz, 3H), 1.07 (s, 3H).

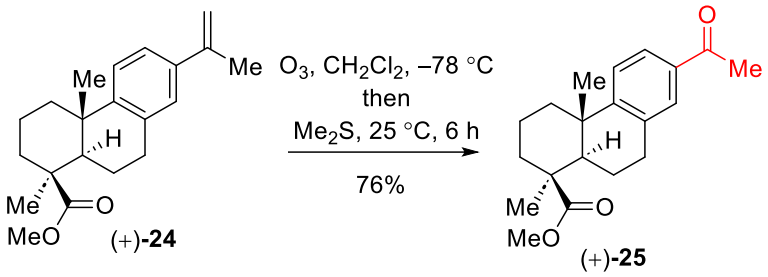
^{13}C NMR (125 MHz, $CDCl_3$) δ 177.9, 147.5, 143.0, 138.2, 135.1, 126.0, 125.5, 123.1, 111.6, 52.9, 51.3, 44.0, 39.4, 38.3, 37.7, 32.2, 28.6, 22.9, 21.8, 21.0, 20.0.

IR (film) υ_{max} 3055, 2935, 2887, 1705, 1650, 1585, 1460, 1305 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd. for $[C_{21}H_{28}O_2 + Na]^+$ 335.1982; found 335.1984.

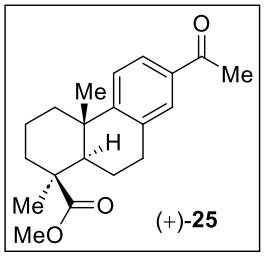
$[\alpha]_D^{25.0}$ = +72.94 (*c* = 0.3, $CHCl_3$).

MP = 112-114 °C.

Synthesis of compound (+)**-25:**



The alkene-ester (+)-**24** (50 mg, 0.16 mmol, 1.0 equiv.) obtained above was dissolved in a 5:1 mixture of CH_2Cl_2:MeOH (6 mL). An ozone stream was bubbled through this suspension at −78 °C until complete consumption of (+)-**24** was observed by TLC analysis. Then Dimethyl sulfide (DMS) (0.16 mmol) was added, and the reaction mixture was warmed to room temperature over four hours. The solvent was removed in vacuo and after evaporation of the solvent the residue was purified by flash chromatography with 10% EtOAc in *n*-hexane to afford product (+)-**25** as white solid (38.24 mg, 76% yield).



(1*S*,4a*S*,10a*R*)-**methyl 7-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)-**25**: The compound (+)-**25** was obtained as

white solid (0.16 mmol scale of reaction, 38.2 mg, 76% yield). R_f = 0.5 (10% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 1H), 7.63 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 3.65 (s, 3H), 2.96 (dd, *J* = 16.8, 5.1 Hz, 1H), 2.87 – 2.77 (m, 1H), 2.54 (s, 3H), 2.27 (d, *J* = 13.9 Hz, 2H), 2.21 (dd, *J* = 13.9, 6.2 Hz, 1H), 2.03 – 1.93 (m, 2H), 1.63 (dd, *J* = 14.2, 3.0 Hz, 1H), 1.53 (d, *J* = 12.3 Hz, 1H), 1.40 – 1.32 (m, 1H), 1.27 (s, 3H), 1.11 – 1.04 (m, 1H), 1.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 177.8, 153.8, 135.9, 134.6, 129.4, 126.1, 125.9, 52.6, 51.4, 44.1, 39.2, 39.0, 37.6, 32.1, 28.6, 26.6, 22.9, 20.9, 20.0.

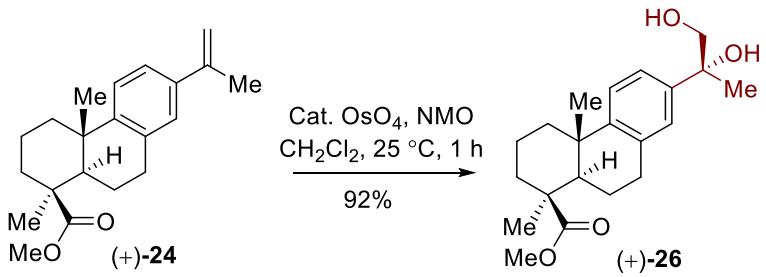
IR (film) υ_{max} 3056, 2945, 2865, 1605, 1340, 1285, 1235, 1165 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd. for $[C_{20}H_{26}O_3 + H]^+$ 315.1960; found 315.1955.

$[\alpha]_D^{25.0}$ = +81.08 (*c* = 2.0, $CHCl_3$).

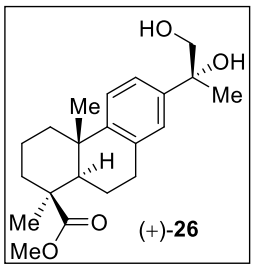
MP = 64-66 °C.

Synthesis of compound (+)-**26:**



Compound (+)-**24** (50 mg, 0.16 mmol, 1.0 equiv.) was taken in dichloromethane (5 mL) at 25 °C. To that solution was added *N*-methyl morpholine *N*-oxide (93.7 mg, 0.80 mmol, 5.0

equiv.) followed by catalytic OsO_4 (20 μL, 4% solution in water). Then the reaction mixture was allowed to stir vigorously at 25 °C unless TLC analysis showed complete consumption of starting materials, the reaction was quenched by saturated Na_2SO_3 solution. Then the mixture was diluted with dichloromethane (5 mL), the organic layer was separated, and the aqueous layer was washed with dichloromethane (2 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography with 60% EtOAc in *n*-hexane to afford diol (+)-**26** as white solid (51.0 mg, 92% yield).



(1*S*,4a*S*,10a*R*)-**methyl 7-((***R***)-1,2-dihydroxypropan-2-yl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** (+)-**26:** The compound (+)-**26** was obtained as white solid. (0.16 mmol scale of reaction; 51.0 mg of product; 92% yield); R_f = 0.5 (40% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 1H), 7.15 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 3.76 – 3.72 (m, 1H), 3.64 (s, 3H), 3.57 (d, *J* = 11.1 Hz, 1H), 2.89 (ddd, *J* = 16.7, 5.5, 1.8 Hz, 1H), 2.78 (ddd, *J* = 17.0, 12.5, 6.0 Hz, 1H), 2.28 – 2.22 (m, 2H), 2.20 – 2.14 (m, 1H), 2.01 – 1.90 (m, 2H), 1.60 (dt, *J* = 14.6, 3.5 Hz, 1H), 1.52 (dd, *J* = 12.5, 2.1 Hz, 1H), 1.48 (s, 3H), 1.37 (dd, *J* = 13.3, 4.3 Hz, 1H), 1.26 (s, 3H), 1.08 (dd, *J* = 13.5, 4.1 Hz, 1H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 147.1, 141.9, 135.5, 125.8, 125.7, 122.7, 74.7, 71.2, 52.9, 51.4, 44.1, 39.4, 38.3, 37.7, 32.3, 28.6, 26.0, 23.1, 21.1, 20.0.

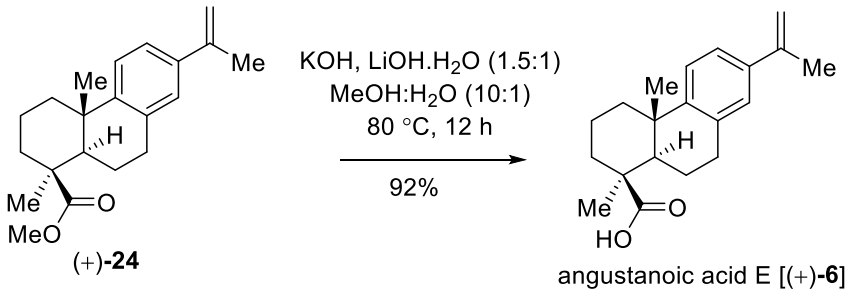
IR (film) υ_{max} 3456, 2936, 2810, 1860, 1620, 1486, 1520, 1225, 1065, 980, cm^{-1}.

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd. for $[C_{21}H_{30}O_4 + Na]^+$ 369.2036; found 369.2048.

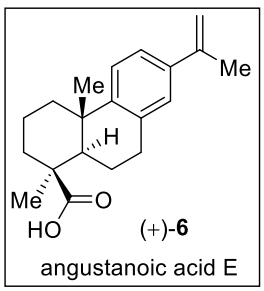
$[\alpha]_D^{25.0}$ = +80.44 (*c* = 0.8, $CHCl_3$).

MP = 112-114 °C.

Synthesis of Angustanoic acid E (+)-**6:**



To a 25 mL round-bottom flask with a magnetic stirring bar was added ester (+)-**24** (78 mg, 0.25 mmol, 1.0 equiv.), KOH (210.4 mg, 3.75 mmol, 15.0 equiv.), $LiOH.H_2O$ (105 mg, 2.5 mmol, 10.0 equiv.), MeOH (10 mL) and water (1 mL). The reaction mixture was heated at reflux for 12 hours before quenching with HCl (0.3 N) at 0 °C. The pH value was adjusted to 1. Then the aqueous layer was extracted with ethyl acetate (3 X 10 mL). The combined organic extracts were washed with water (7 mL), brine (7 mL) and dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residual crude product was purified by flash column chromatography with 20% EtOAc in *n*-hexane to afford angustanoic acid E (+)-**6** as colorless oil (68.64 mg, 92% yield).



(1*S*,4a*S*,10a*R*)**-1,4a-dimethyl-7-(prop-1-en-2-yl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid** (+)-**6**: The compound (+)-**6** was obtained as colorless oil (0.25 mmol scale of reaction; 68.64 mg of product; 92% yield). R_f = 0.6 (20% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 2.0 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 1.9 Hz, 1H), 5.32 (d, *J* = 0.9 Hz, 1H), 5.01 (t, *J* = 1.5 Hz, 1H), 2.91 (dd, *J* = 16.9, 3.8 Hz, 1H), 2.81 (td, *J* = 11.7, 10.8, 6.3 Hz, 1H), 2.28 (d, *J* = 4.0 Hz, 1H), 2.24 (d, *J* = 3.1 Hz, 1H), 2.21 – 2.16 (m, 1H), 2.11 (s, 3H), 2.08 – 2.04 (m, 1H), 2.03 – 1.98 (m, 1H), 1.64 – 1.60 (m, 1H), 1.58 – 1.54 (m, 1H), 1.38 (d, *J* = 4.0 Hz, 1H), 1.33 (s, 3H), 1.12 (s, 3H), 1.07 (dd, *J* = 13.6, 4.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 147.5, 143.0, 138.3, 135.2, 126.1, 125.5, 123.2, 111.8, 52.9, 44.0, 39.3, 38.6, 37.4, 32.2, 28.8, 23.2, 21.8, 21.0, 20.0.

IR (film) υ_{max} 3400-2600 (br), 3055, 2965, 2887, 1705, 1480, 1536, 1217 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $[C_{20}H_{26}O_2 + H]^+$ 299.2006; Found 299.2008.

$[\alpha]_D^{25.0}$ = +76.26 (*c* = 0.7, $CHCl_3$).

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic angustanoic acid E (**6**)

This Report (400 MHz, $CDCl_3$)	Natural[1]
7.24 (d, *J* = 2.0 Hz, 1H)	7.25 (dd, *J* = 8.4, 1.7 Hz, 1H)
7.21 (d, *J* = 8.3 Hz, 1H)	7.20 (d, *J* = 8.4 Hz, 1H)
7.13 (d, *J* = 1.9 Hz, 1H)	7.14 (br d, 1H)
5.32 (d, J=0.9 Hz, 1H)	5.32 (s, 1H)
5.01 (t, *J* = 1.5 Hz, 1H)	5.02 (t, *J* = 1.4 Hz, 1H)
2.91 (dd, *J* = 16.9, 3.8 Hz, 1H)	2.92 (dd, *J* = 16.3, 4.1 Hz, 1H)

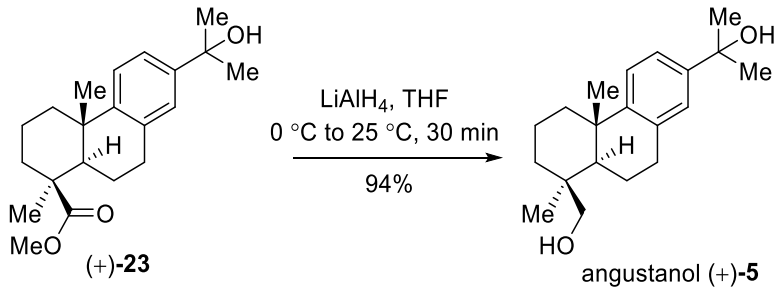
2.81 (td, *J* = 11.7, 10.8, 6.3 Hz, 1H)	2.80 (m, 1H)
2.28 (d, *J* = 4.0 Hz, 1H)	2.28 (m, 1H)
2.24 (d, *J* = 3.1 Hz, 1H)	2.26 (m, 1H)
2.21 – 2.16 (m, 1H)	2.19 (m, 1H)
2.11 (s, 3H)	2.12 (s, 3H)
2.08– 2.04 (m, 1H)	2.06 (m, 1H)
2.03-1.98 (m, 1H)	2.03 (m, 1H)
1.64-1.60 (m, 1H)	1.62 (m, 1H)
1.58-1.54 (m, 1H)	1.57 (m, 1H)
1.38 (d, *J=4.0 Hz*, 1H)	1.38 (m, 1H)
1.33 (s, 3H)	1.33 (s, 3H)
1.12 (s, 3H)	1.12 (s, 3H)
1.07 (dd, *J* = 13.6, 4.3 Hz, 1H)	1.09 (m, 1H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic angustanoic acid E (**6**)

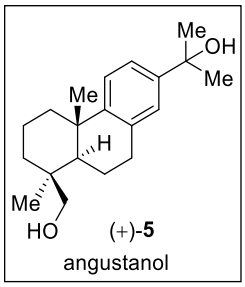
This Report (101 MHz, $CDCl_3$)	Natural[1]
183.9	184.1
147.5	147.4
143.0	143.0
138.3	138.3
135.1	135.1
126.1	126.1
125.5	125.4
123.2	123.1
111.8	111.7
52.9	52.9
44.0	43.9
39.3	39.3
38.6	38.5

37.4	37.4
32.2	32.1
28.8	28.7
23.2	23.1
21.8	21.7
21.0	20.9
20.0	19.9

Synthesis of Angustanol (+)-**5:**



In a flame-dried round-bottom flask, ester (+)-**23** (50 mg, 0.15 mmol, 1.0 equiv.) was taken in dry THF (4 mL) under inert atmosphere at 25 °C. To this reaction mixture was added $LiAlH_4$ (11.4 mg, 0.3 mmol, 2.0 equiv.) portionwise over 5 min, and the reaction mixture was allowed to stir vigorously at 25 °C for 30 min. Upon completion of the reaction as judged by TLC analysis, the reaction mixture was quenched by consecutive addition of EtOAc (6 mL) and saturated aqueous $NaHCO_3$ solution. Then the mixture was filtered through a Celite pad and washed with EtOAc. The separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography with 50% EtOAc in *n*-hexane to afford angustanol (+)-**5** as oil (42.65 mg, 94% yield).



2-((4b*S*,8*S*,8a*R*)**-8-(hydroxymethyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)propan-2-ol** (+)-**5**: The compound (+)-**5** was obtained as oil (0.15 mmol scale of reaction; 42.65 mg of product; 94% yield). R_f = 0.25 (20% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) 7.21 (d, *J* = 1.3 Hz, 2H), 7.14 (s, 1H), 3.85 (d, *J* = 10.9 Hz, 1H), 3.54 (dd, *J* = 11.0, 1.2 Hz, 1H), 2.96 – 2.89 (m, 1H), 2.88 – 2.80 (m, 1H), 2.31 (dq, *J* = 13.6, 2.7, 2.2 Hz, 1H), 2.01 – 1.95 (m, 1H), 1.90 – 1.85 (m, 1H), 1.74 – 1.72 (m, 1H), 1.68 (m, 1H), 1.64 – 1.59 (m, 1H), 1.55 (s, 6H), 1.49 (dd, *J* = 12.8, 2.0 Hz, 1H), 1.45 – 1.39 (m, 1H), 1.17 (s, 3H), 1.04 (s, 3H), 0.99 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 146.0, 134.7, 124.9, 124.6, 122.1, 72.4, 65.3, 51.3, 38.9, 38.8, 37.6, 35.3, 31.7, 31.7, 31.3, 26.9, 25.8, 19.3, 19.1.

IR (film) υ_{max} 3400 (br), 2957, 2927, 2878, 1724, 1470, 1242, 1023 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{20}H_{30}O_2 + Na]^+$ 325.2138; Found 325.2159.

$[\alpha]_D^{25.0}$ = +20.51 (*c* = 1.3, $CHCl_3$).

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic angustanol (**5**)

This Report (400 MHz, $CDCl_3$)	Natural[1]

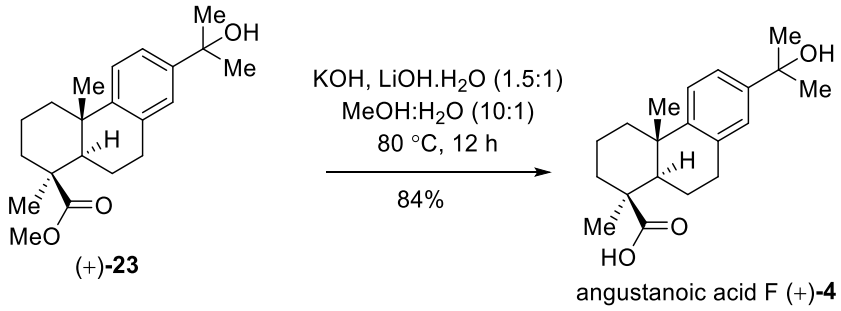
7.21 (d, *J* = 1.3 Hz, 2H)	7.23 (s, 2H)
7.14 (s, 1H)	7.15 (s, 1H)
3.85 (d, *J* = 10.9 Hz, 1H)	3.86 (d, *J* = 10.9 Hz, 1H)
3.54 (dd, *J* = 11.0, 1.2 Hz, 1H)	3.56 (dd, *J* = 10.9, 0.8 Hz, 1H)
2.96-2.89 (m, 1H)	2.93 (dd, *J* = 16.2, 5.6 Hz, 1H)
2.88-2.80 (m, 1H)	2.83 (m, 1H)
2.31 (dq, *J* = 13.6, 2.7, 2.2 Hz, 1H)	2.32 (m, 1H)
2.01-1.95 (m, 1H)	1.99 (m, 1H)
1.90-.1.85 (m, 1H)	1.82 (m, 1H)
1.74 – 1.72 (m, 1H)	1.72 (m, 1H)
1.68 (m, 1H)	1.68 (m, 1H)
1.64– 1.59 (m, 1H)	1.63 (m, 1H)
1.55 (s, 6H)	1.56 (s, 3H), 1.56 (s, 3H)
1.49 (dd, *J* = 12.8, 2.0 Hz, 1H)	1.51 (m, 1H)
1.45-1.39 (m, 1H)	1.43 (m, 1H)
1.17 (s, 3H)	1.18 (s, 3H)
1.04 (s, 3H)	1.05 (s, 3H)
0.99 (m, 1H)	1.02 (m, 1H)

Chemical Shifts of ^{13}C-NMR for natural and synthetic angustanol (**5**)

This Report (101 MHz, $CDCl_3$)	Natural[1]
148.3	148.3
146.0	146.0
134.7	134.6
124.9	124.9
124.6	124.5
122.1	122.0
72.4	72.3

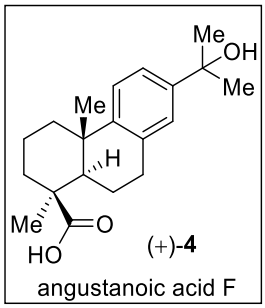
65.3	65.4
51.3	51.3
38.9	39.0
38.8	38.7
37.6	37.6
35.3	35.3
31.7	31.6
31.7	31.6
31.3	31.2
26.9	26.8
25.8	25.7
19.3	19.3
19.1	19.0

Synthesis of Angustanoic acid F (+)-**4:**



To a 25 mL round-bottom flask with a magnetic stirring bar was added ester (+)-**23** (55 mg, 0.17 mmol, 1.0 equiv.), KOH (143.1 mg, 2.55 mmol, 15.0 equiv.), $LiOH.H_2O$ (71.33 mg, 1.7 mmol, 10.0 equiv.), MeOH (8 mL) and water (800 μL). The reaction mixture was heated at reflux for 12 hours before quenching with HCl (0.3 N) at 0 °C. The pH value was adjusted to 1. Then the aqueous layer was extracted with ethyl acetate (3 X 8 mL). The combined organic extracts were washed with water (4 mL), brine (4 mL) and dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residual crude product

was purified by flash column chromatography with 45% EtOAc in *n*-hexane to afford angustanoic acid F (+)-**4** as oil (45.19 mg, 84% yield).



(1*S*,4a*S*,10a*R*)**-7-(2-hydroxypropan-2-yl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid** (+)-**4**: The compound (+)-**4** was obtained as oil (0.17 mmol scale of reaction; 45.19 mg of product; 84% yield). R_f = 0.5 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.18 (s, 1H), 2.94 (dd, *J* = 16.4, 5.5 Hz, 1H), 2.83 (ddd, *J* = 17.1, 12.5, 6.2 Hz, 1H), 2.29 (dq, *J* = 12.6, 3.5 Hz, 2H), 2.21 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.10 – 2.07 (m, 1H), 2.04 (dd, *J* = 13.8, 4.2 Hz, 1H), 1.66 – 1.62 (m, 1H), 1.60 (s, 1H), 1.59 (s, 3H), 1.59 (s, 3H), 1.42 – 1.38 (m, 1H), 1.36 (s, 3H), 1.13 (s, 3H), 1.10 (dd, *J* = 14.2, 4.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 183.5, 146.5, 145.9, 135.1, 125.4, 124.9, 122.1, 72.4, 52.8, 43.9, 39.3, 38.4, 37.4, 32.2, 31.6, 31.6, 28.7, 23.1, 20.9, 19.9.

IR (film) υ_{max} 3416, 3400-2600 (br), 3050, 2978, 2936, 2854, 2868, 1710, 1479, 1230, 1136 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $[C_{20}H_{28}O_3 + Na]^+$ 339.1936; Found 339.1931.

$[\alpha]_D^{25.0}$ = +90.97 (*c* = 0.5, $CHCl_3$).

Chemical Shifts of ^{1}H-NMR for Natural and Synthetic Angustanoic acid F (**4**)

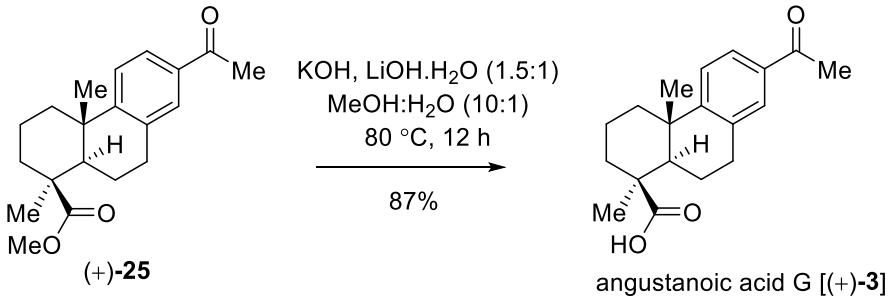
This Report δ (500 MHz, $CDCl_3$)	Natural[1]
δ 7.24 (s, 2H)	**δ** 7.22 (s, 2H)
7.18 (s, 1H)	7.16 (s, 1H)
2.94 (dd, *J* = 16.4, 5.5 Hz, 1H)	2.91 (dd, *J* = 16.0, 5.6 Hz, 1H)
2.83 (ddd, *J* = 17.1, 12.5, 6.2 Hz, 1H)	2.81 (m, 1H)
2.29 (dq, *J* = 12.6, 3.5 Hz, 2H)	2.29-2.26 (m, 2H)
2.21 (dd, *J* = 13.8, 6.0 Hz, 1H)	2.19 (m, 1H)
2.10 – 2.07 (m, 1H)	2.05 (m, 1H)
2.04 (dd, *J* = 13.8, 4.2 Hz, 1H)	2.03 (m, 1H)
1.66 – 1.62 (m, 1H)	1.62 (m, 1H)
1.60 (s, 1H)	1.57 (m, 1H)
1.59 (s, 3H)	1.56 (s, 3H)
1.59 (s, 3H)	1.56 (s, 3H)
1.42 – 1.38 (m, 1H)	1.39 (m, 1H)
1.36 (s, 3H)	1.33 (s, 3H)
1.13 (s, 3H)	1.11 (s, 3H)
1.10 (dd, *J* = 14.2, 4.8 Hz, 1H)	1.08 (m, 1H)

Chemical Shifts of ^{13}C-NMR for Natural and Synthetic Angustanoic acid F (**4**)

This Report δ (125 MHz, $CDCl_3$)	Natural[1]
δ 183.5	**δ** 183.8
146.5	146.5
145.9	146.0
135.1	135.1
125.4	125.5

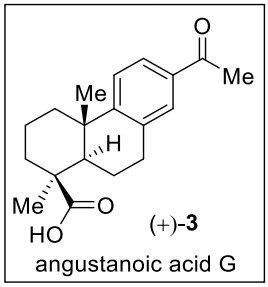
124.9	124.9
122.1	122.1
72.4	72.3
52.8	52.8
43.9	43.9
39.3	39.3
38.4	38.4
37.4	37.5
32.2	32.2
31.6	31.64
31.6	31.62
28.7	28.7
23.1	23.2
20.9	20.9
19.9	19.9

Synthesis of Angustanoic acid G (+)-**3:**



To a 25 mL round-bottom flask with a magnetic stirring bar was added ester (+)-**25** (36 mg, 0.11 mmol, 1.0 equiv.), KOH (92.6 mg, 1.65 mmol, 15.0 equiv.), $LiOH.H_2O$ (46.2 mg, 1.1 mmol, 10.0 equiv.), MeOH (6.5 mL) and water (650 μL). The reaction mixture was heated at reflux for 12 hours before quenching with HCl (0.3 N) at 0 °C. The pH value was adjusted to 1. Then the aqueous layer was extracted with ethyl acetate (3 X 8 mL). The combined organic extracts were washed with water (4 mL), brine (4 mL) and dried over

anhydrous sodium sulfate, filtered and concentrated in vacuo. The residual crude product was purified by flash column chromatography with 35% EtOAc in *n*-hexane to afford angustanoic acid G (+)-**3** as colorless oil (28.75 mg, 87% yield).



(1*S*,4a*S*,10a*R*)**-7-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid** (+)-**3**: The compound (+)-**3** was obtained as colorless oil (0.11 mmol scale of reaction; 28.75 mg of product; 87% yield). R_f = 0.45 (30% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 3.00 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.86 (ddd, *J* = 17.3, 12.7, 6.2 Hz, 1H), 2.58 (s, 3H), 2.29 (ddt, *J* = 22.3, 13.9, 4.8 Hz, 3H), 2.07 (ddd, *J* = 17.9, 9.2, 4.4 Hz, 2H), 1.67 (dq, *J* = 14.5, 3.7 Hz, 1H), 1.59 (dd, *J* = 12.4, 1.8 Hz, 1H), 1.45 – 1.40 (m, 1H), 1.37 (s, 3H), 1.16 (s, 3H), 1.11 (dd, *J* = 13.7, 4.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.2, 183.5, 153.6, 135.8, 134.5, 129.4, 125.9, 125.8, 52.4, 43.9, 39.1, 39.0, 37.2, 31.9, 28.7, 26.5, 22.9, 20.7, 19.8.

IR (film) υ_{max} 3400-2600, 3056, 2945, 2835, 1720, 1605, 1480, 1285, 1235, 1065 cm^{-1}.
HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ Calcd for $[C_{19}H_{24}O_3 + Na]^+$ 323.1618; Found 323.1613.

$[\alpha]_D^{25.0}$ = +81.11 (*c* = 0.4, $CHCl_3$).

Chemical Shifts of ^{1}H-NMR for natural and synthetic angustanoic acid G (**3**)

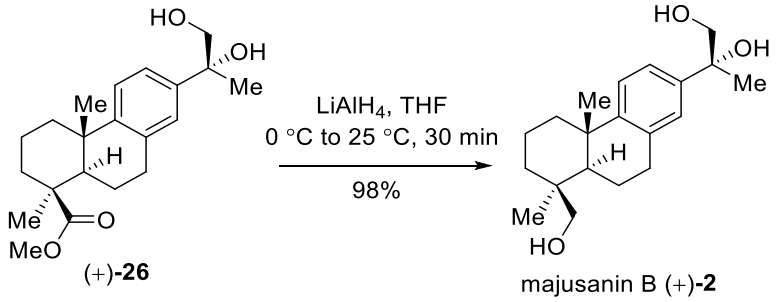
This Report δ (500 MHz, $CDCl_3$)	Natural[1]
δ 7.72 (dd, *J* = 8.3, 2.0 Hz, 1H)	**δ** 7.70 (dd, *J* = 8.4, 1.9 Hz, 1H)
7.67 (d, *J* = 1.9 Hz, 1H)	7.65 (br d, 1H)
7.37 (d, *J* = 8.3 Hz, 1H)	7.35 (d, J = 8.4 Hz, 1H)
3.00 (dd, *J* = 16.8, 5.2 Hz, 1H)	2.99 (dd, *J* = 14.1, 7.0 Hz, 1H)
2.86 (ddd, *J* = 17.3, 12.7, 6.2 Hz, 1H)	2.83 (m, 1H)
2.58 (s, 3H)	2.57 (s, 3H)
2.29 (ddt, *J* = 22.3, 13.9, 4.8 Hz, 3H)	2.30-2.23 (m, 3H)
2.07 (ddd, *J* = 17.9, 9.2, 4.4 Hz, 2H)	2.07-2.04 (m, 2H)
1.67 (dq, *J* = 14.5, 3.7 Hz, 1H)	1.65 (m, 1H)
1.59 (dd, *J* = 12.4, 1.8 Hz, 1H)	1.57 (m, 1H)
1.45 – 1.40 (m, 1H)	1.41 (m, 1H)
1.37 (s, 3H)	1.35 (s, 3H)
1.16 (s, 3H)	1.14 (s, 3H)
1.11 (dd, *J* = 13.7, 4.3 Hz, 1H)	1.11 (m, 1H)

Chemical Shifts of ^{13}C-NMR for natural and synthetic angustanoic acid G (**3**)

This Report δ (125 MHz, $CDCl_3$)	Natural[1]
δ 198.2	**δ** 198.1
183.5	183.0
153.6	153.6
135.8	135.8

134.5	134.6
129.4	129.4
125.9	125.9
125.8	125.8
52.4	52.5
43.9	44.1
39.1	39.1
39.0	38.0
37.2	37.3
31.9	32.0
28.7	28.7
26.5	26.5
22.9	23.0
20.7	20.8
19.8	19.9

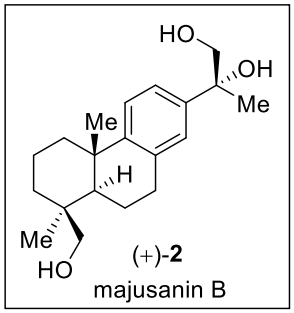
Synthesis of Majusanin B (+)-**2:**



(+)-**26** majusanin B (+)-**2**

In a flame-dried round-bottom flask, ester (+)-**26** (40 mg, 0.12 mmol, 1.0 equiv.) was taken in dry THF (4 mL) under inert atmosphere at 25 °C. To this reaction mixture was added $LiAlH_4$ (6.6 mg, 0.17 mmol, 1.5 equiv.) portionwise over 5 min, and the reaction mixture was allowed to stir vigorously at 25 °C for 30 min. Upon completion of the reaction as judged by TLC analysis, the reaction mixture was quenched by consecutive addition of

EtOAc (6 mL) and saturated aqueous $NaHCO_3$ solution. Then the mixture was filtered through a Celite pad and washed with EtOAc. The separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography with 60% EtOAc in *n*-hexane to afford majusanin B (+)-**2** as white powder (37.46 mg, 98% yield).



(*R*)-**2**-((4b*S*,8*S*,8a*R*)-**8-(hydroxymethyl)-4b,8-dimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)propane-1,2-diol (+)-2**: The compound **(+)-2** was obtained as white powder (0.12 mmol scale of reaction; 37.46 mg of product; 98% yield). R_f = 0.5 (60% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.3 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.10 (d, *J* = 1.9 Hz, 1H), 3.84 (d, *J* = 10.8 Hz, 1H), 3.74 (d, *J* = 11.1 Hz, 1H), 3.58 (d, *J* = 11.1 Hz, 1H), 3.53 (d, *J* = 10.9 Hz, 1H), 2.92 (dd, *J* = 17.1, 6.5 Hz, 1H), 2.83 (ddd, *J* = 17.6, 11.5, 7.2 Hz, 1H), 2.31 (d, *J* = 12.8 Hz, 1H), 1.98 (dd, *J* = 13.3, 7.1 Hz, 1H), 1.87 (d, *J* = 13.6 Hz, 1H), 1.72 – 1.68 (m, 1H), 1.66 (p, *J* = 2.8 Hz, 1H), 1.62 (dt, *J* = 10.4, 3.8 Hz, 1H), 1.49 (s, 3H), 1.48 – 1.46 (m, 1H), 1.44 – 1.37 (m, 1H), 1.16 (s, 3H), 1.04 (s, 3H), 0.99 (dd, *J* = 13.6, 4.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 141.3, 134.4, 125.2, 124.2, 122.1, 74.2, 70.6, 64.8, 50.8, 38.4, 38.2, 37.1, 34.8, 30.7, 26.4, 25.5, 25.3, 18.7, 18.5.

IR (film) υ_{max} 3400, 2986, 2932, 2875, 1795, 1620, 1505, 1486, 1435, 1417, 1225, 1136, 1065, 980, 835 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{20}H_{30}O_3 + Na]^+$ 341.2087; Found 341.2084.

$[\alpha]_D^{25.0}$ = +20.64 (*c* = 0.7, $CHCl_3$).

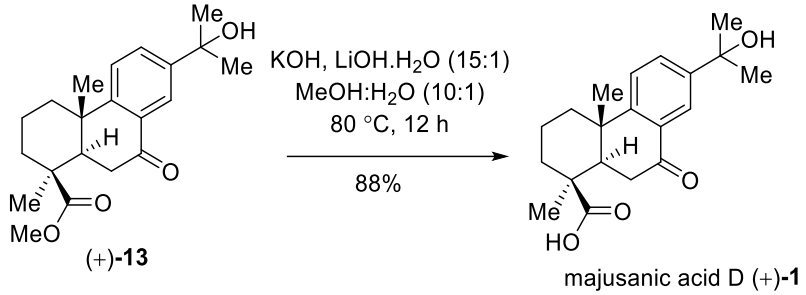
Chemical Shifts of ^{1}H-NMR for natural and synthetic majusanin B (**2**)

This Report δ (500 MHz, $CDCl_3$)	Natural[2] δ (500 MHz, CD_3OD)
δ 7.23 (d, *J* = 8.3 Hz, 1H)	δ 7.15 (d, *J* = 8.0 Hz, 1H)
7.17 – 7.14 (m, 1H)	7.11 (dd, *J* = 8.5, 1.5 Hz, 1H)
7.10 (d, *J* = 1.9 Hz, 1H)	7.05 (br s, 1H)
3.84 (d, *J* = 10.8 Hz, 1H)	3.77 (d, *J* = 11.0 Hz, 1H)
3.74 (d, *J* = 11.1 Hz, 1H)	3.51 (d, *J* = 11.0 Hz, 1H)
3.58 (d, *J* = 11.1 Hz, 1H)	3.48 (d, *J* = 11.0 Hz, 1H)
3.53 (d, *J* = 10.9 Hz, 1H)	3.37 (d, *J* = 11.0 Hz, 1H)
2.92 (dd, *J* = 17.1, 6.5 Hz, 1H)	2.86 (dd, *J* = 17.0, 6.0 Hz, 1H)
2.83 (ddd, *J* = 17.6, 11.5, 7.2 Hz, 1H)	2.75 (m, 1H)
2.31 (d, *J* = 12.8 Hz, 1H)	2.29 (br d, *J* = 13.0 Hz, 1H)
1.98 (dd, *J* = 13.3, 7.1 Hz, 1H)	1.94 (m, 1H)
1.87 (d, *J* = 13.6 Hz, 1H)	1.87 (br d, *J* = 13.5 Hz, 1H)
1.72 – 1.68 (m, 1H)	1.72 (m, 1H)
1.66 (p, *J* = 2.8 Hz, 1H)	1.65 (m, 1H)
1.62 (dt, *J* = 10.4, 3.8 Hz, 1H)	1.54 (m, 1H)
1.49 (s, 3H)	1.40 (s, 3H)
1.48 – 1.46 (m, 1H)	1.38 (dd, *J* = 13.0, 1.5 Hz, 1H)
1.44 – 1.37 (m, 1H)	1.30 (dd, *J* = 13.0, 3.5 Hz, 1H)
1.16 (s, 3H)	1.10 (s, 3H)
1.04 (s, 3H)	0.97 (s, 3H)
0.99 (dd, *J* = 13.6, 4.2 Hz, 1H)	0.92 (dd, *J* = 13.5, 3.5 Hz, 1H)

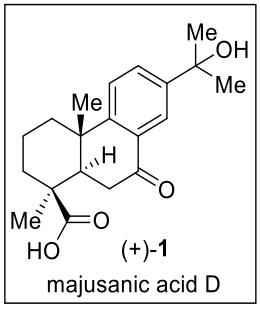
Chemical Shifts of ^{13}C-NMR for natural and synthetic majusanin B (2)

This Report δ (125 MHz, $CDCl_3$)	Natural[2] δ (125 MHz, CD_3OD)
δ 148.2	δ 149.8
141.3	144.3
134.4	135.8
125.2	127.2
124.2	125.5
122.1	124.3
74.2	75.7
70.6	72.1
64.8	65.3
50.8	53.3
38.4	40.6
38.2	40.2
37.1	39.0
34.8	36.7
30.7	32.6
26.4	27.9
25.5	26.6
25.3	26.3
18.7	20.6
18.5	20.4

Synthesis of majusanic acid D (+)-**1:**



To a 25 mL round-bottom flask with a magnetic stirring bar was added ester (+)-**13** (37 mg, 0.11 mmol, 1.0 equiv.), KOH (92.58 mg, 1.65 mmol, 15.0 equiv.), $LiOH.H_2O$ (46.16 mg, 1.1 mmol, 10.0 equiv.), MeOH (6.5 mL) and water (650 μL). The reaction mixture was heated at reflux for 12 hours before quenching with HCl (0.3 N) at 0 °C. The pH value was adjusted to 1. Then the aqueous layer was extracted with ethyl acetate (3 X 7 mL). The combined organic extracts were washed with water (3 mL), brine (3 mL) and dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residual crude product was purified by flash column chromatography with 60% EtOAc in *n*-hexane to afford majusanic acid D (+)-**1** as amorphous powder (32.0 mg, 88% yield).



(1*S*,4a*S*,10a*R*)-**7-(2-hydroxypropan-2-yl)-1,4a-dimethyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid** (+)-**1**: The compound (+)-**1** was obtained as amorphous powder (0.11 mmol scale of reaction; 32.0 mg of product; 88%). R_f = 0.25 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.2 Hz, 1H), 7.71 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 3.26 (dd, *J* = 18.0, 14.5 Hz, 1H), 2.99 (dd, *J* = 18.0, 3.1 Hz, 1H), 2.40 – 2.34 (m, 1H), 2.31 – 2.25 (m, 1H), 2.05 (dt, *J* = 13.9, 3.7 Hz, 2H), 1.70 (dt, *J* = 10.1, 3.6 Hz, 1H), 1.58 (d, *J* = 2.7 Hz, 6H), 1.50 (td, *J* = 13.3, 4.3 Hz, 1H), 1.31 (s, 3H), 1.16 (s, 3H), 1.11 (dd, *J* = 13.6, 4.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 181.9, 152.9, 147.2, 130.8, 130.1, 124.9, 122.9, 72.5, 50.1, 43.7, 38.5, 38.4, 37.5, 37.2, 31.5, 28.1, 21.5, 19.5.

IR (film) υ_{max} 3420, 2985, 2920, 1745, 1697, 1642, 1455, 1388, 1279, 1210, 1149, 975, 620 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $[C_{20}H_{26}O_4 + H]^+$ 331.1904; Found 331.1883.

$[\alpha]_D^{25.0}$ = +40.62 (*c* = 1.7, $CHCl_3$).

Chemical Shifts of ^{1}H-NMR for natural and synthetic majusanic acid D (**1**)

This Report δ (500 MHz, $CDCl_3$)	Natural[3] δ (500 MHz, CD_3COCD_3)
δ 8.09 (d, *J* = 2.2 Hz, 1H)	δ 8.09 (d, *J* = 2.4 Hz, 1H)
7.71 (dd, *J* = 8.4, 2.3 Hz, 1H)	7.74 (dd, *J* = 8.4, 2.4 Hz, 1H)
7.38 (d, *J* = 8.4 Hz, 1H)	7.48 (d, *J* = 8.4 Hz, 1H)
3.26 (dd, *J* = 18.0, 14.5 Hz, 1H)	3.28 (m, 1H)
2.99 (dd, *J* = 18.0, 3.1 Hz, 1H)	2.88 (dd, *J* = 18.0, 3.0 Hz, 1H)
2.40 – 2.34 (m, 1H)	2.45 (br d, *J* = 11.7 Hz, 1H)
2.31 – 2.25 (m, 1H)	2.28 (br d, *J* = 13.0 Hz, 1H)
2.05 (dt, *J* = 13.9, 3.7 Hz, 2H)	2.12 (overlapped, 1H)
1.70 (dt, *J* = 10.1, 3.6 Hz, 1H)	2.09 (overlapped, 1H)
-	1.66 (m, 1H)
1.58 (d, J = 2.7 Hz, 6H)	1.51 (s, 3H), 1.51 (s, 3H)

1.50 (td, *J* = 13.3, 4.3 Hz, 1H)	1.54 (m, 1H)
1.31 (s, 3H)	1.30 (s, 3H)
1.16 (s, 3H)	1.22 (s, 3H)
1.11 (dd, *J* = 13.6, 4.0 Hz, 1H)	1.20 (m, 1H)

Chemical Shifts of ^{13}C-NMR for natural and synthetic majusanic acid D (**1**)

This Report δ (125 MHz, $CDCl_3$)	Natural[3] δ (125 MHz, CD_3COCD_3)
δ 199.3	δ 198.3
181.9	178.3
152.9	153.3
147.2	149.3
130.8	131.3
130.1	131.0
124.9	125.5
122.9	123.3
72.5	71.7
50.1	50.7
43.7	44.1
38.5	39.2
38.4	39.2
37.5	38.3
37.2	38.1
31.5	32.2
31.5	32.2
28.1	28.4
21.5	22.0
19.5	20.5

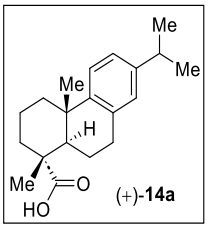
References

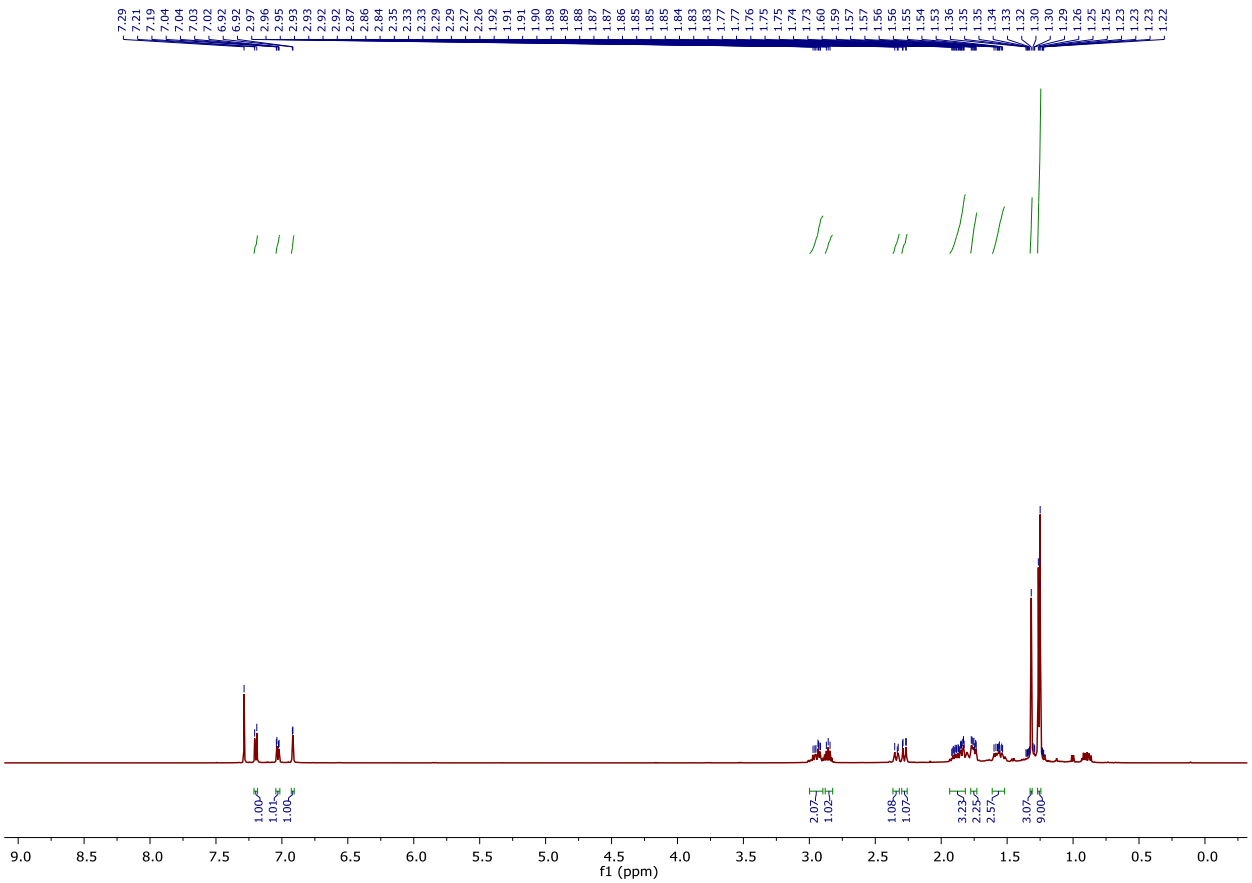
[1] L. Sy and G. Brown, *J. Nat. Prod.*, 1998, **61**, 907–912.

[2] Y-D. Wang, G-J. Zhang, J. Qu, Y-H. Li, J-D. Jiang, Y-B. Liu, S-G. Ma, Y. Li, H-N. Lv and S-S. Yu, *J. Nat. Prod.*, 2013, **76**, 1976–1983.

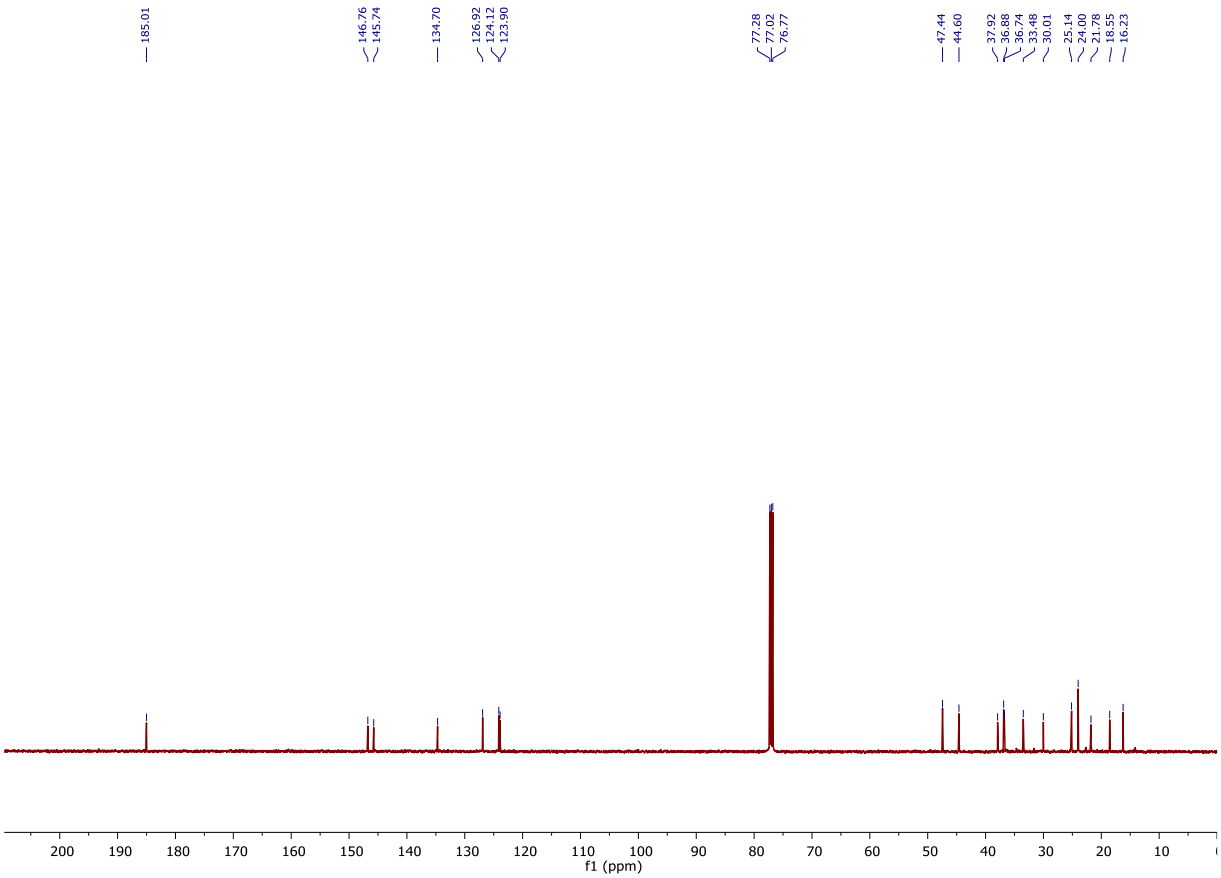
[3] Z-F. Fang, G-J. Zhang, H. Chen, J. Bai, S-S Yu, Y. Liu, W-J Wang, S-G Ma, J. Qu and S. Xu, *Planta. Med.*, 2013, **79**, 142–149.

Spectral graphs

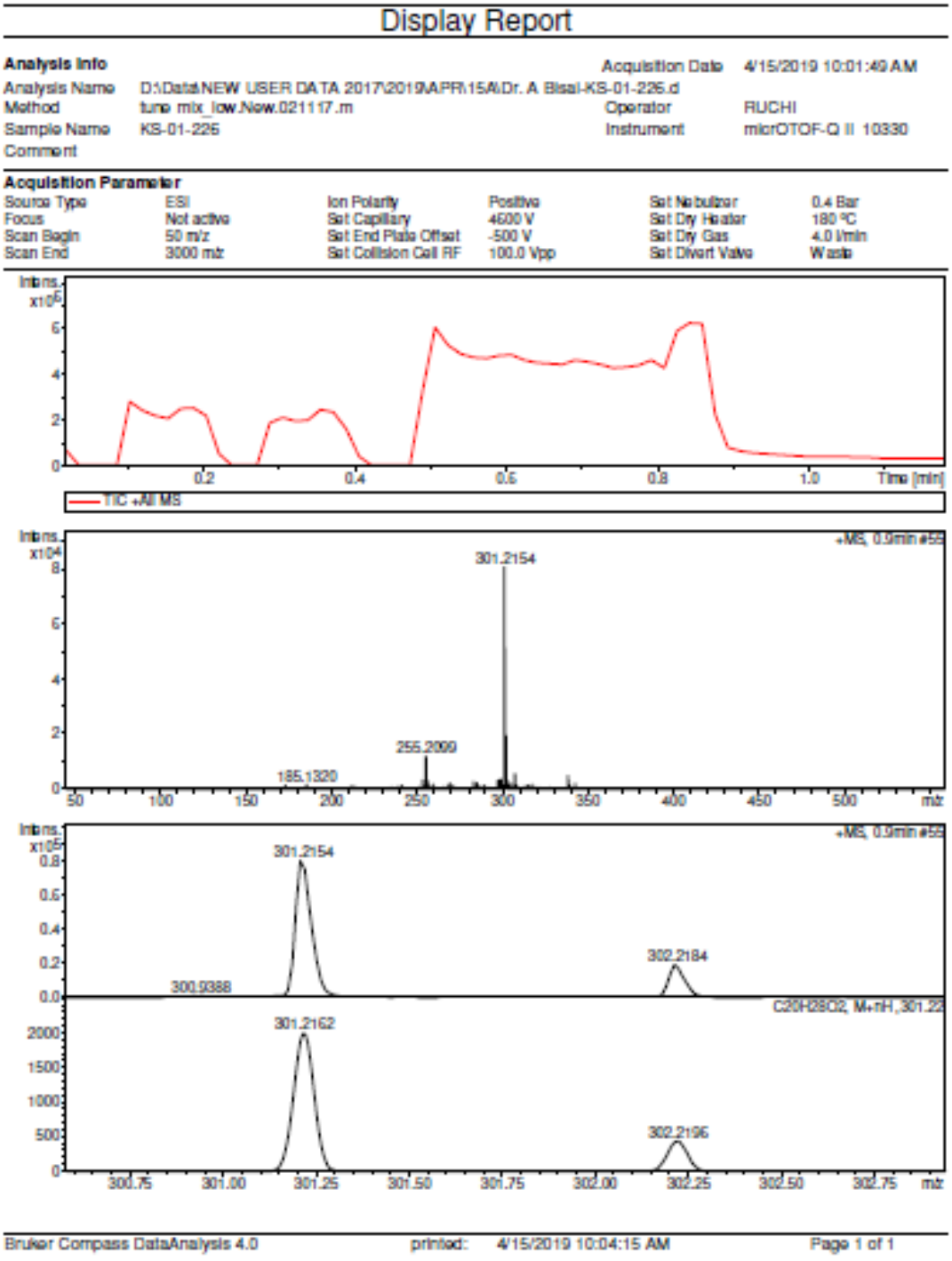




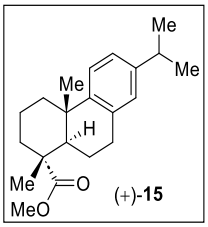
^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**14a**

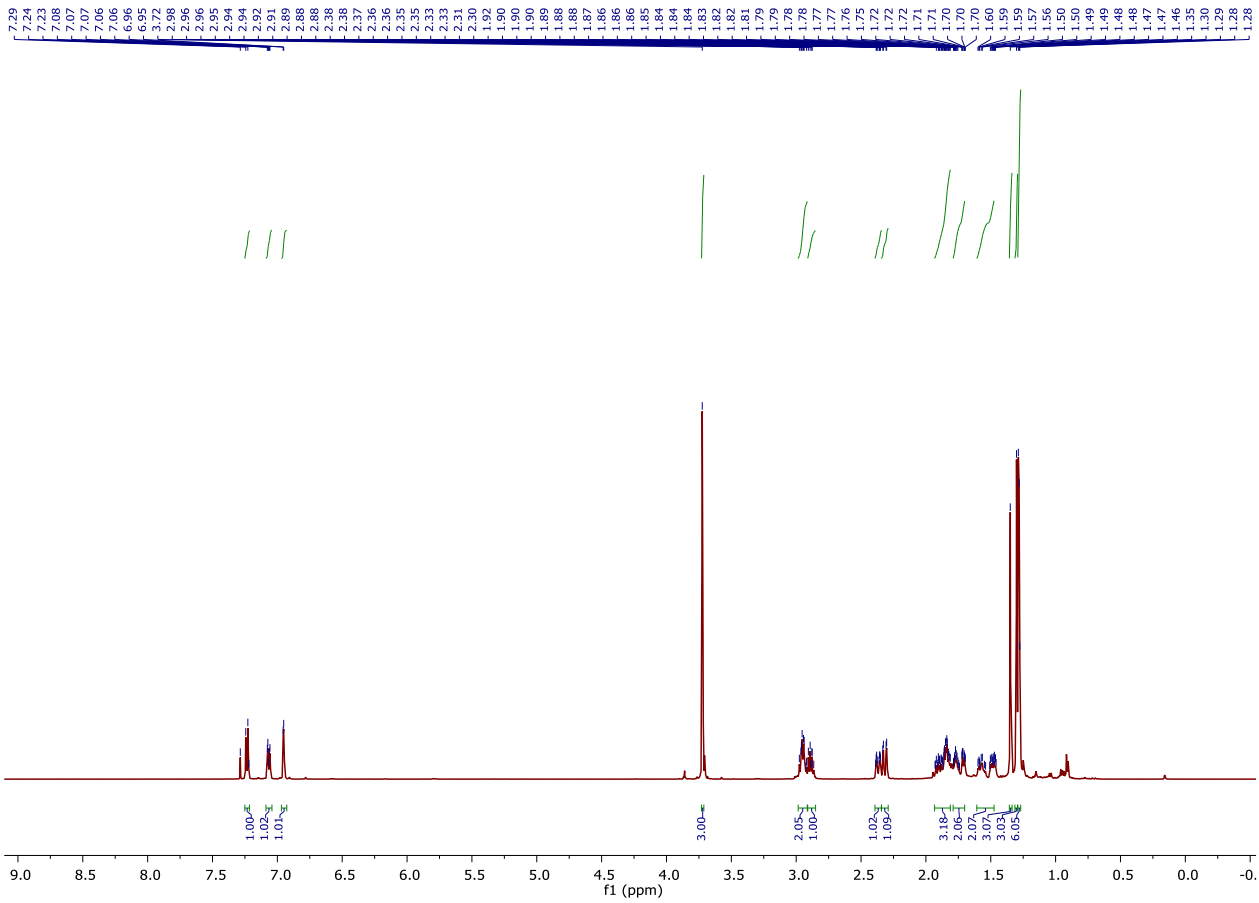


^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**14a**

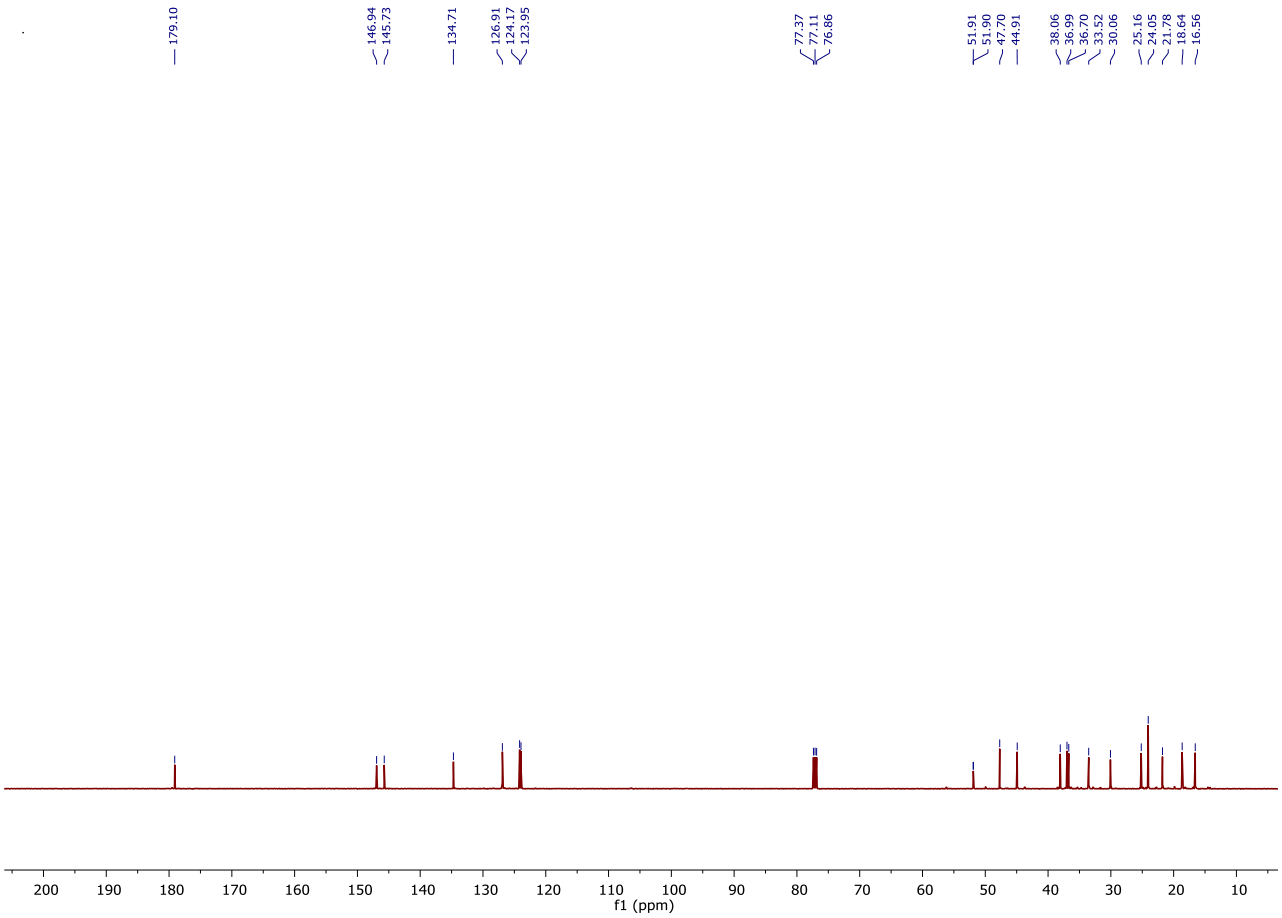


Scanned copy of mass spectrum of (+)-**14a**

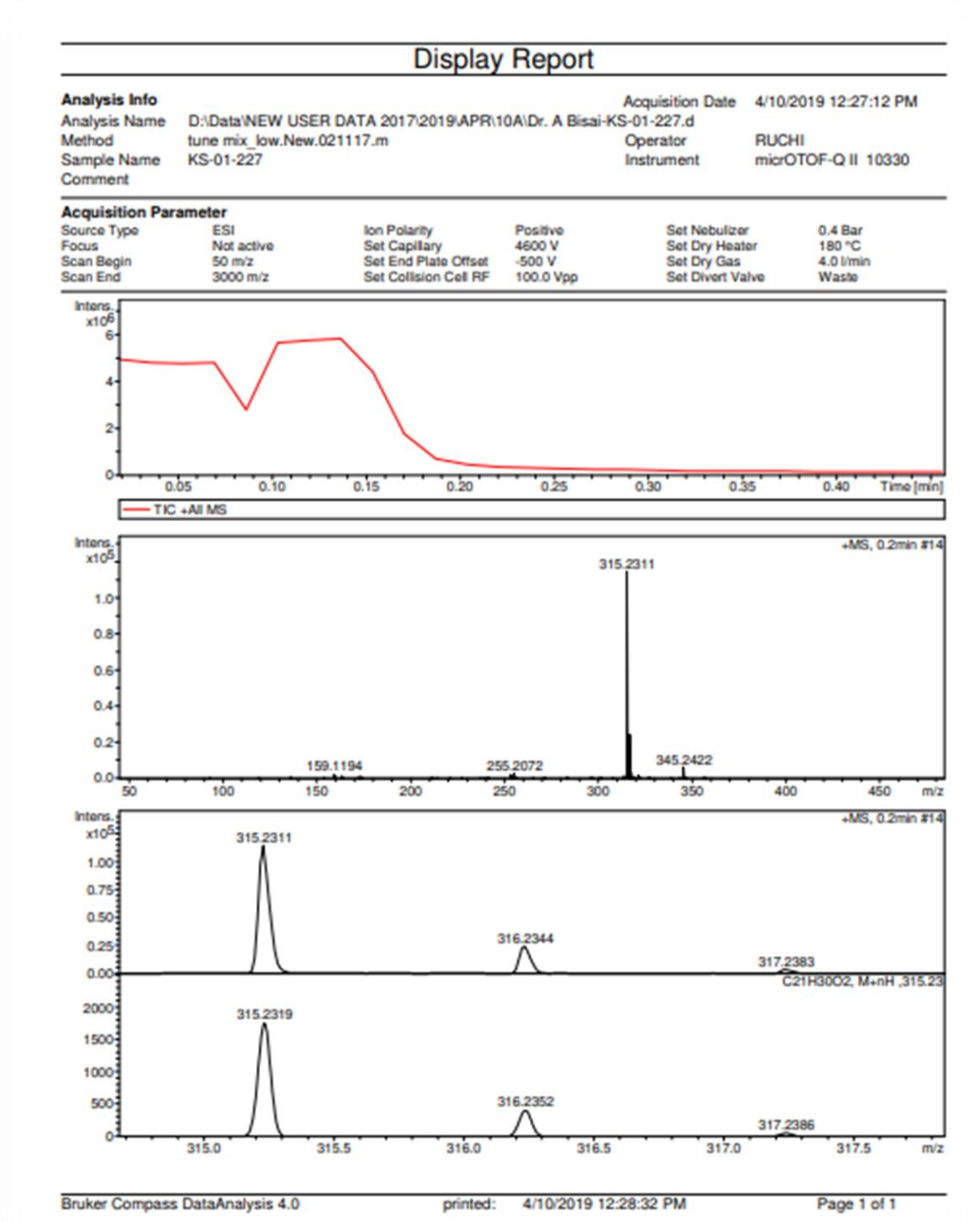




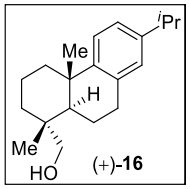
^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**15**

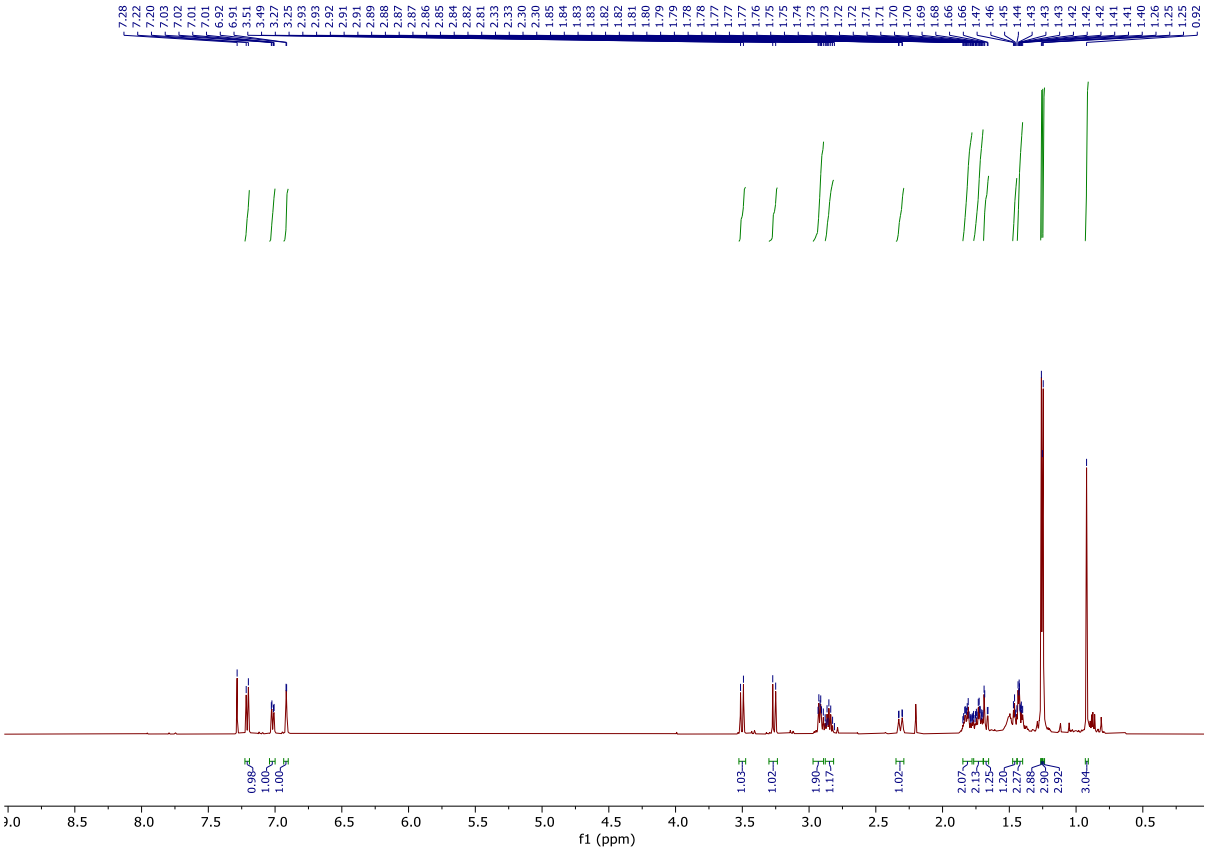


^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**15**

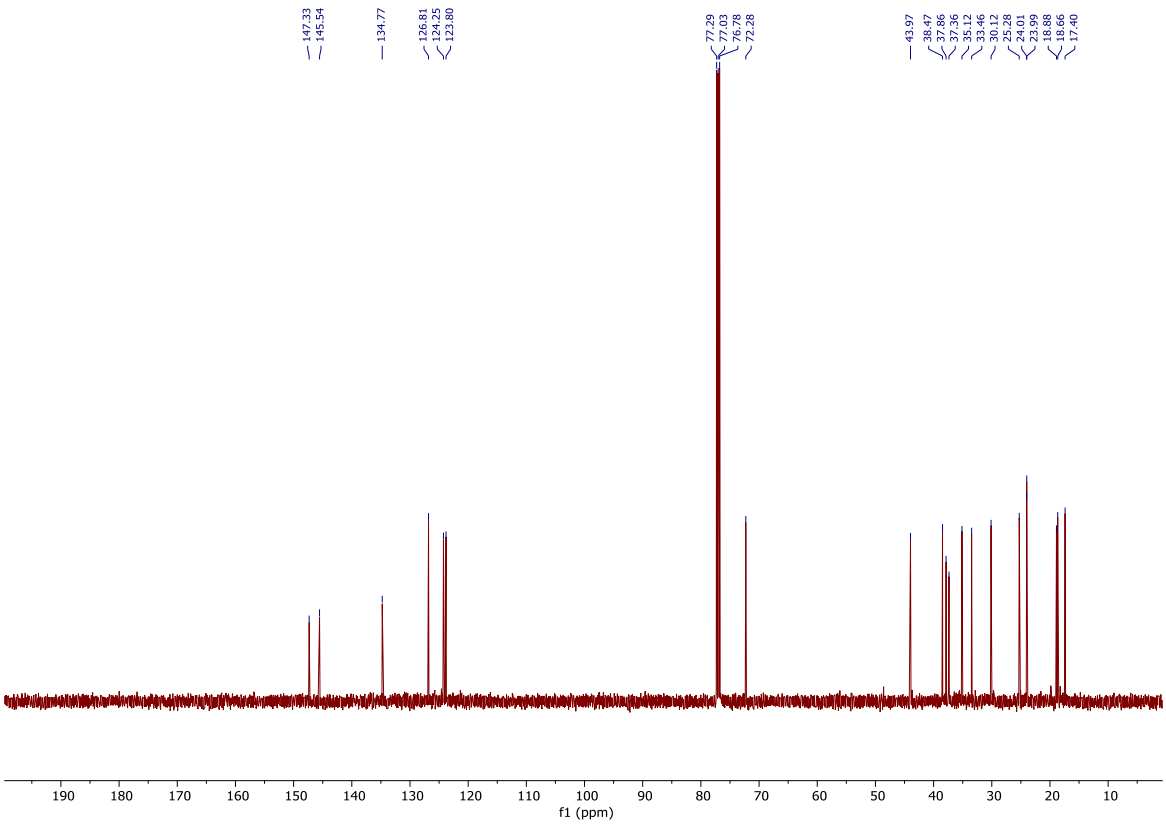


Scanned copy of mass spectrum of (+)-**15**





^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**16**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**16**

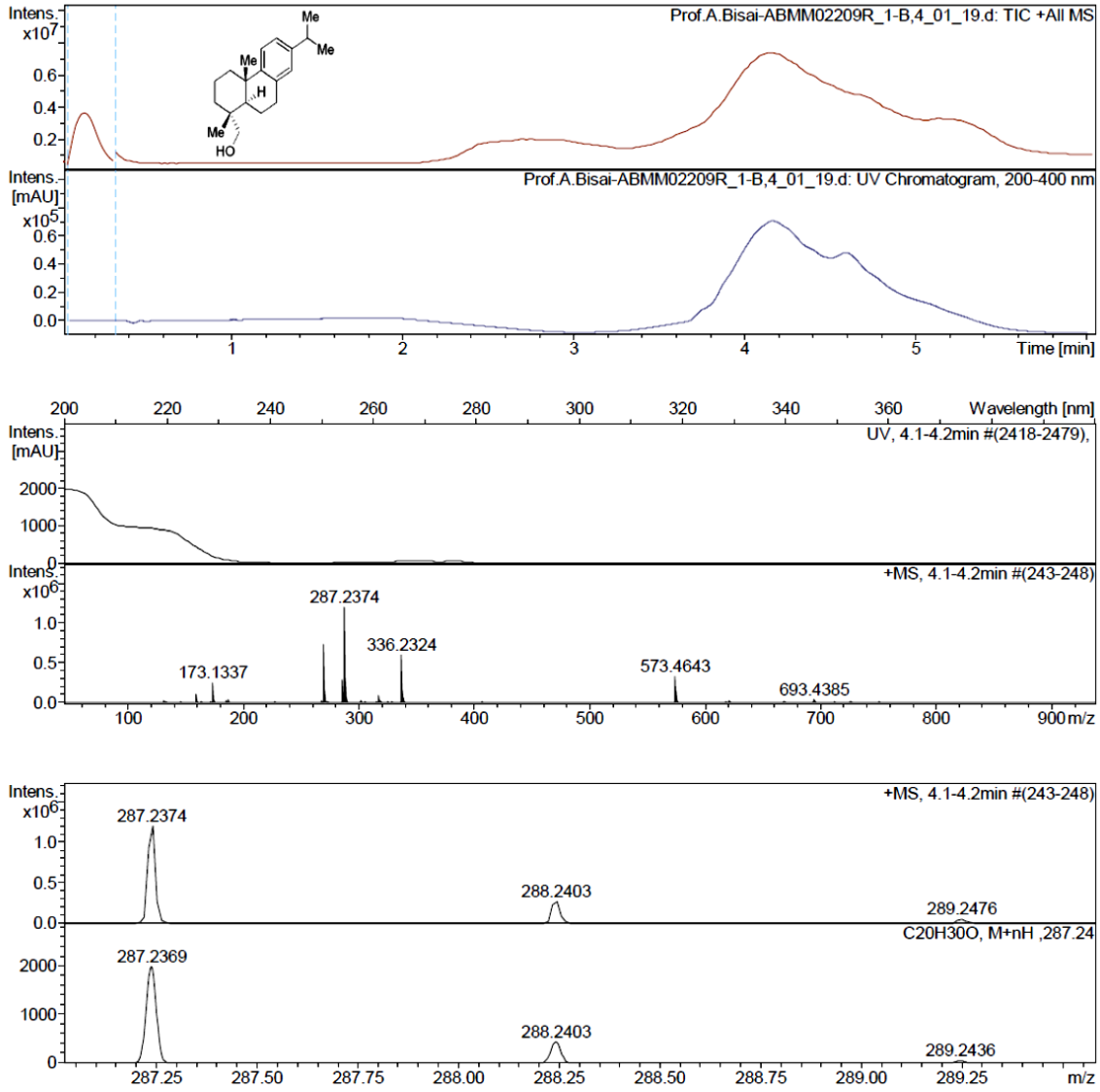
Display Report

Analysis Info

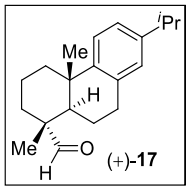
Acquisition Date	5/9/2022 5:11:27 PM		
Analysis Name	D:\Data\USER DATA 2022\MAY 2022\09-05-2022\Prof.A.Bisai-ABMM02209R_1-B,4_01_19.d		
Method	HRLCMS-20 Sept.m	Operator	IISER
Sample Name	Prof.A.Bisai-ABMM02209R	Instrument	micrOTOF-Q II 10330
Comment			

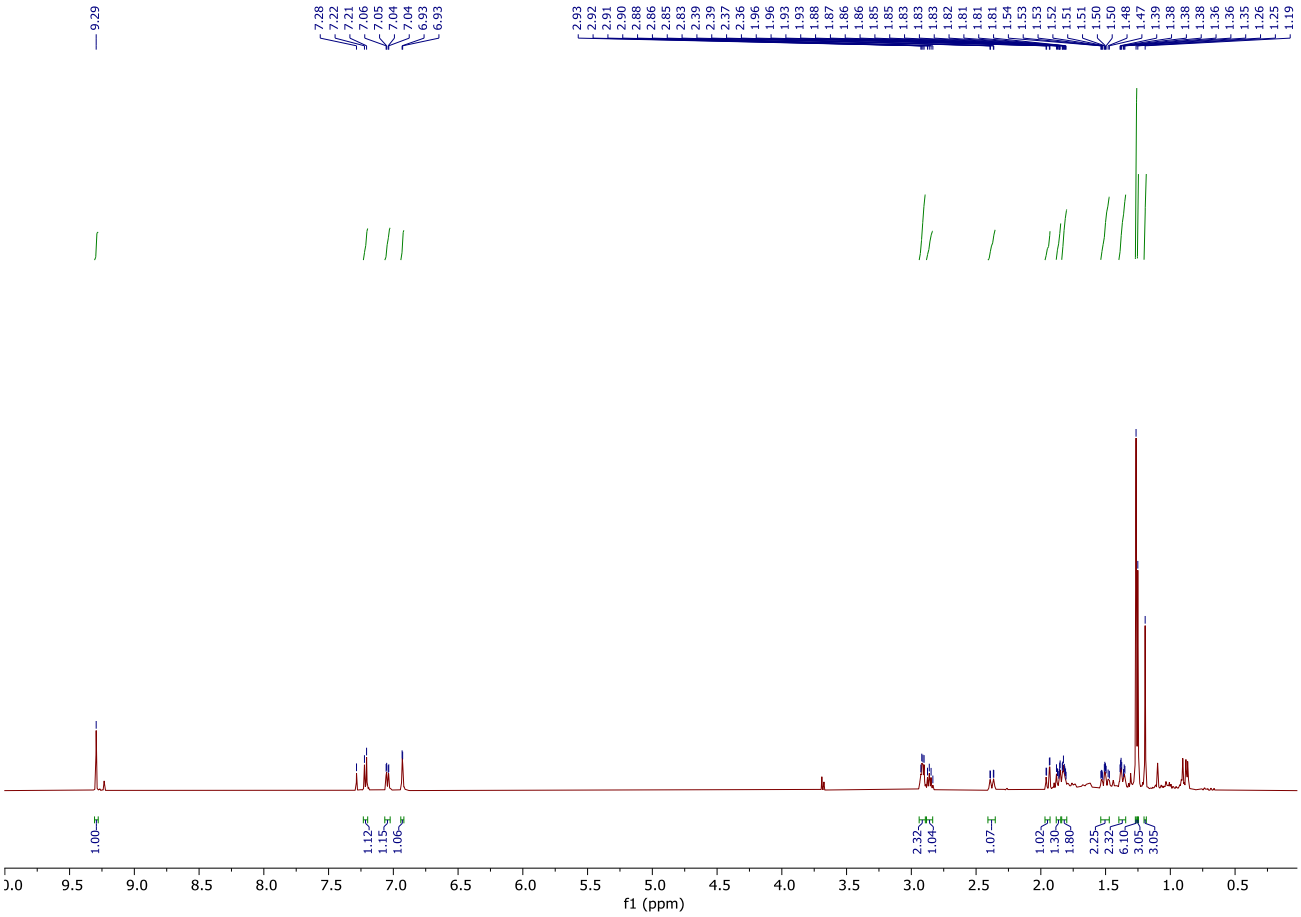
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

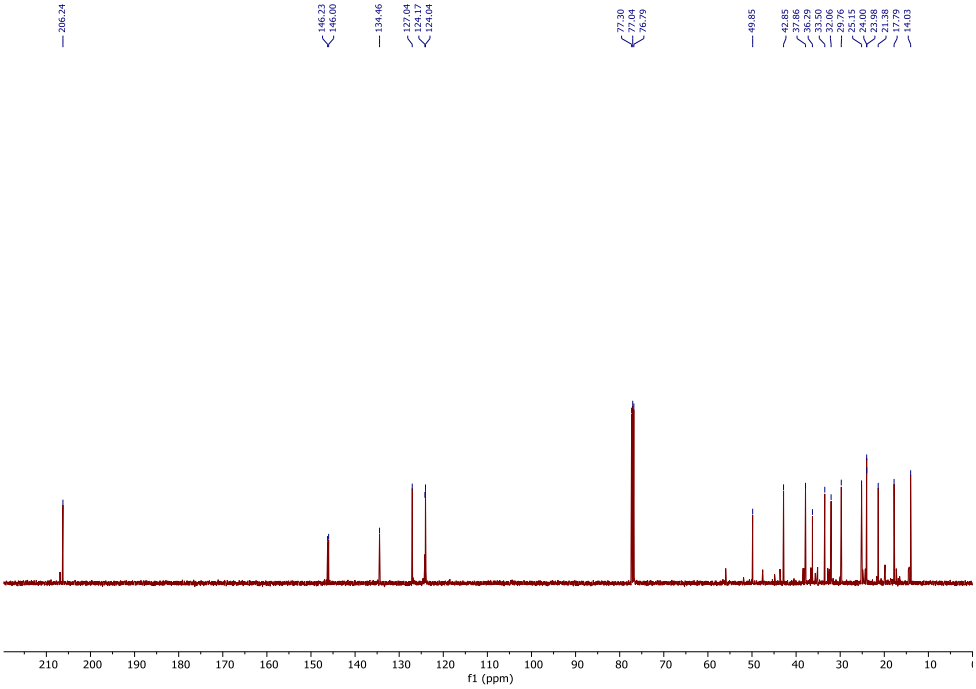


Scanned copy of mass spectrum of (+)-**16**





^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**17**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**17**

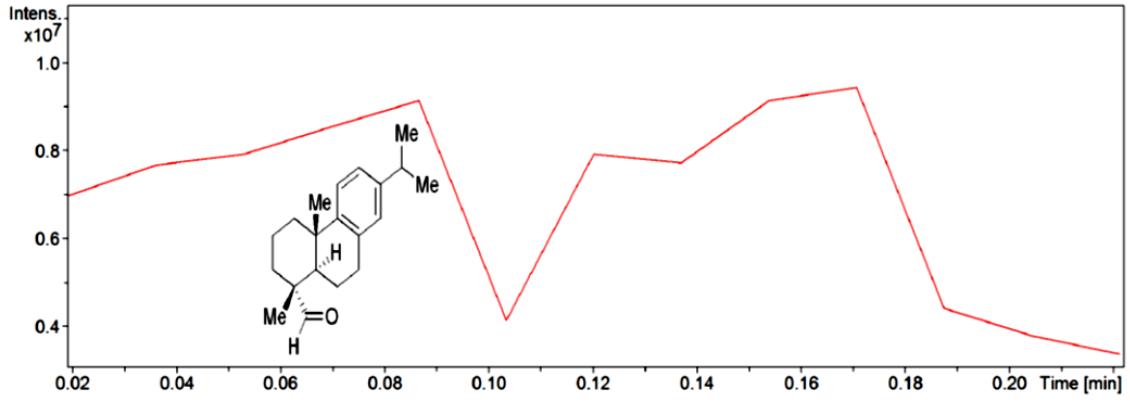
Display Report

Analysis Info

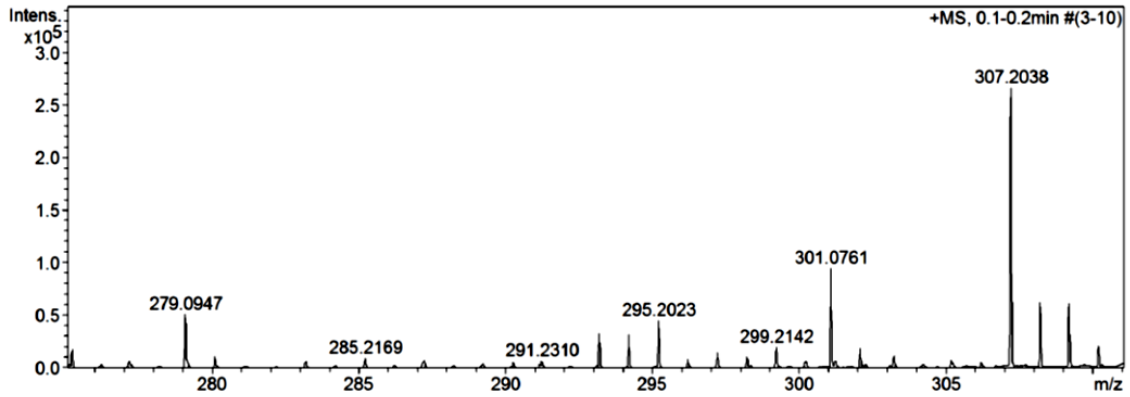
Analysis Name	D:\Data\USER DATA 2022\JUNE2022\27-06-22\Prof A Bisai-MM-01-210-R.d	Acquisition Date	27-06-2022 13:14:45
Method	tune mix_low.New.021117.m	Operator	Bruker
Sample Name	MM-01-210-R	Instrument	micrOTOF-Q 10330
Comment			

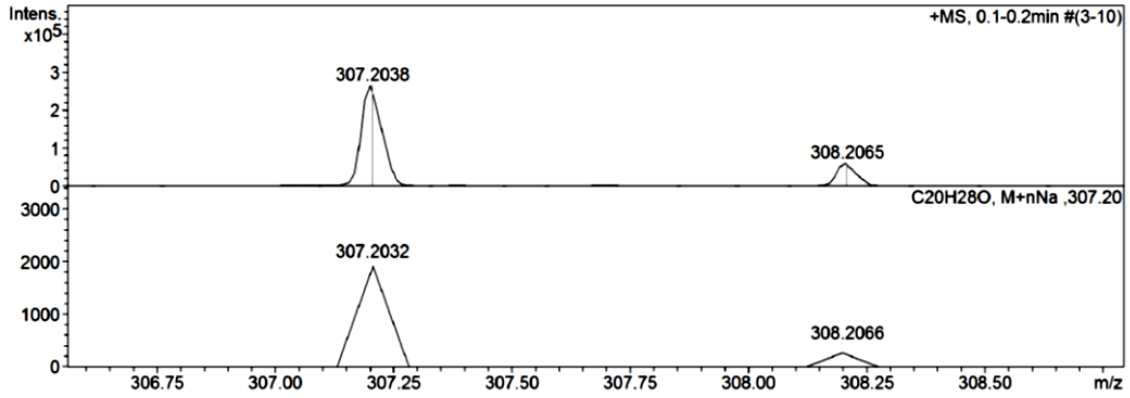
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

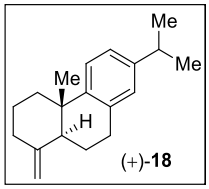


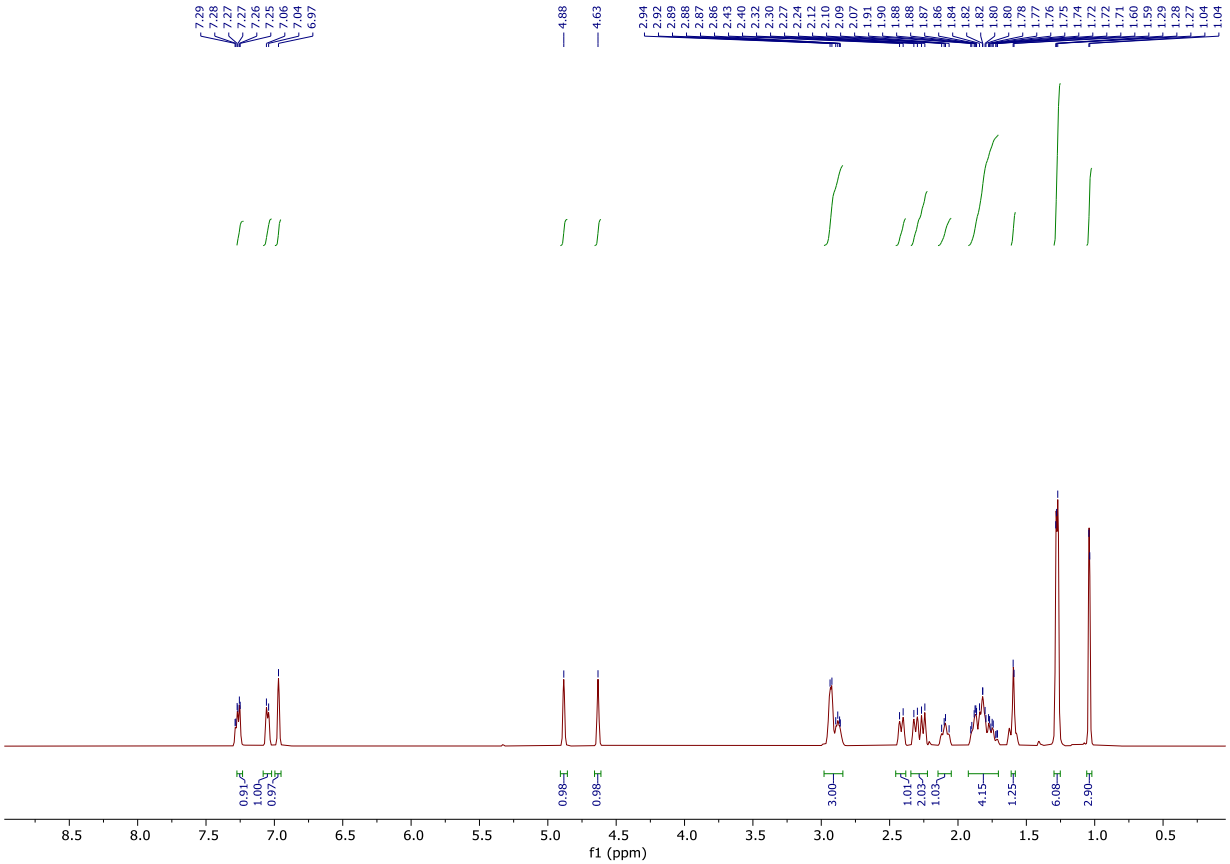
TIC +All MS



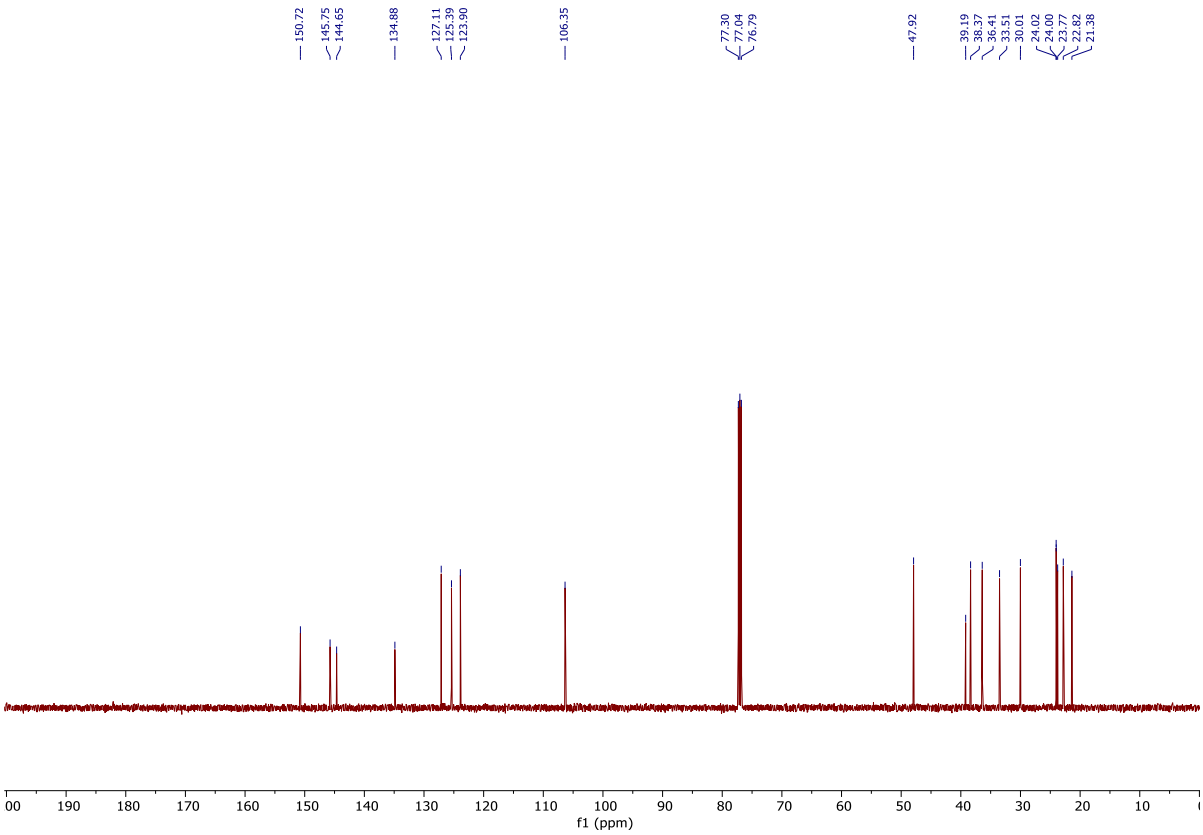


Scanned copy of mass spectrum of (+)-**17**





^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**18**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**18**

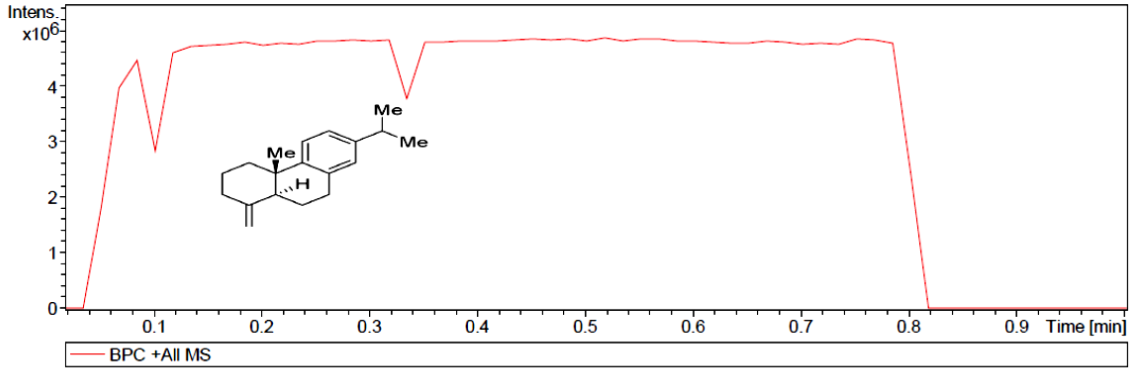
Display Report

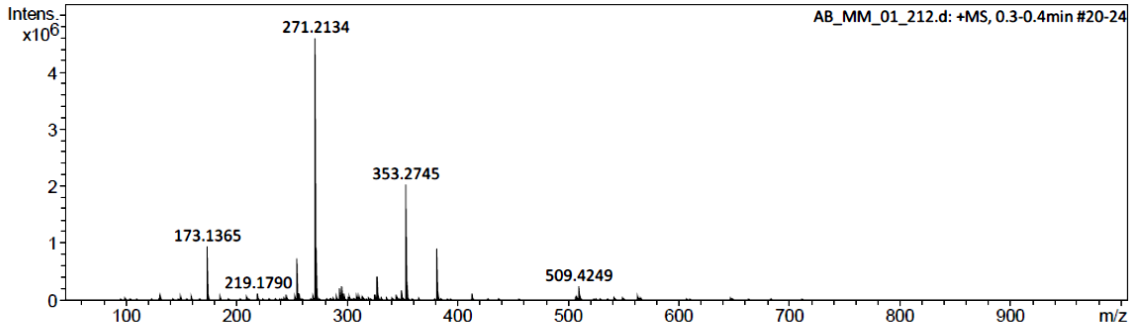
Analysis Info

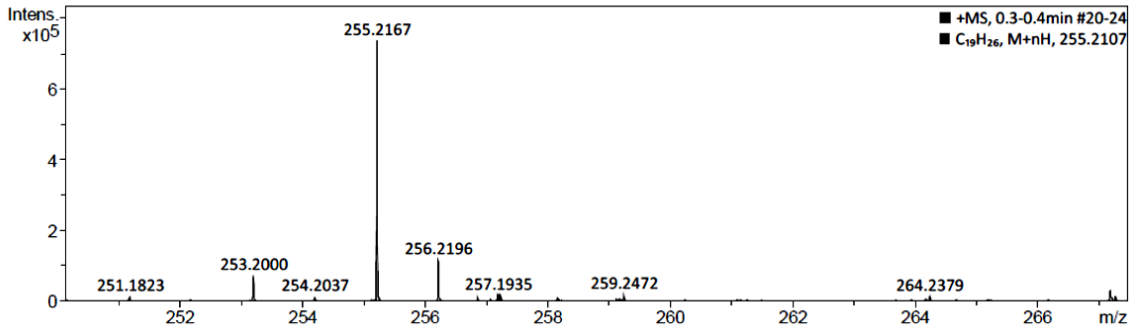
Analysis Name	D:\Data\User data\2021\DEC\AB_MM_01_212.d	Acquisition Date	12/14/2021 3:02:21 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_MM_01_212	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



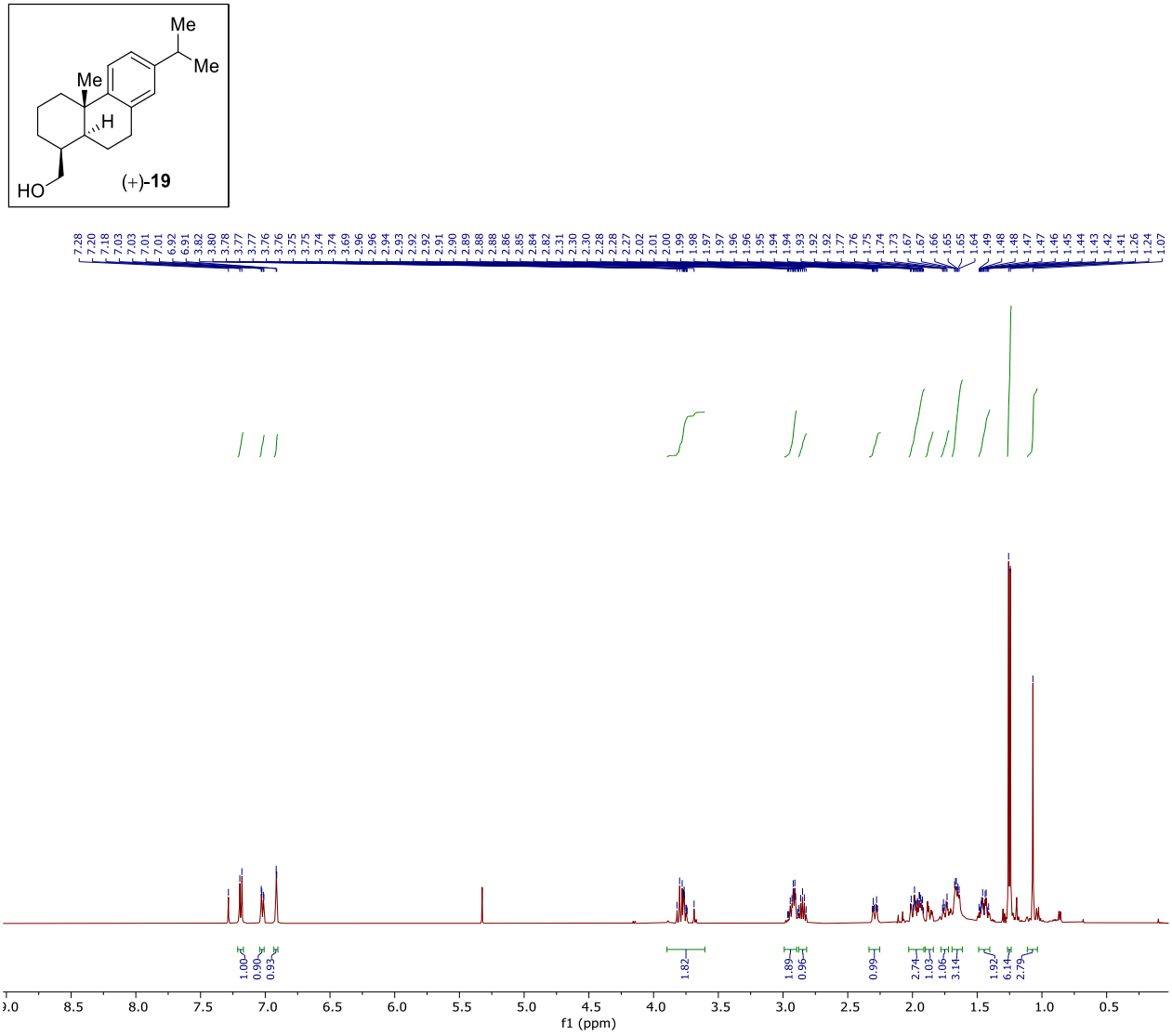




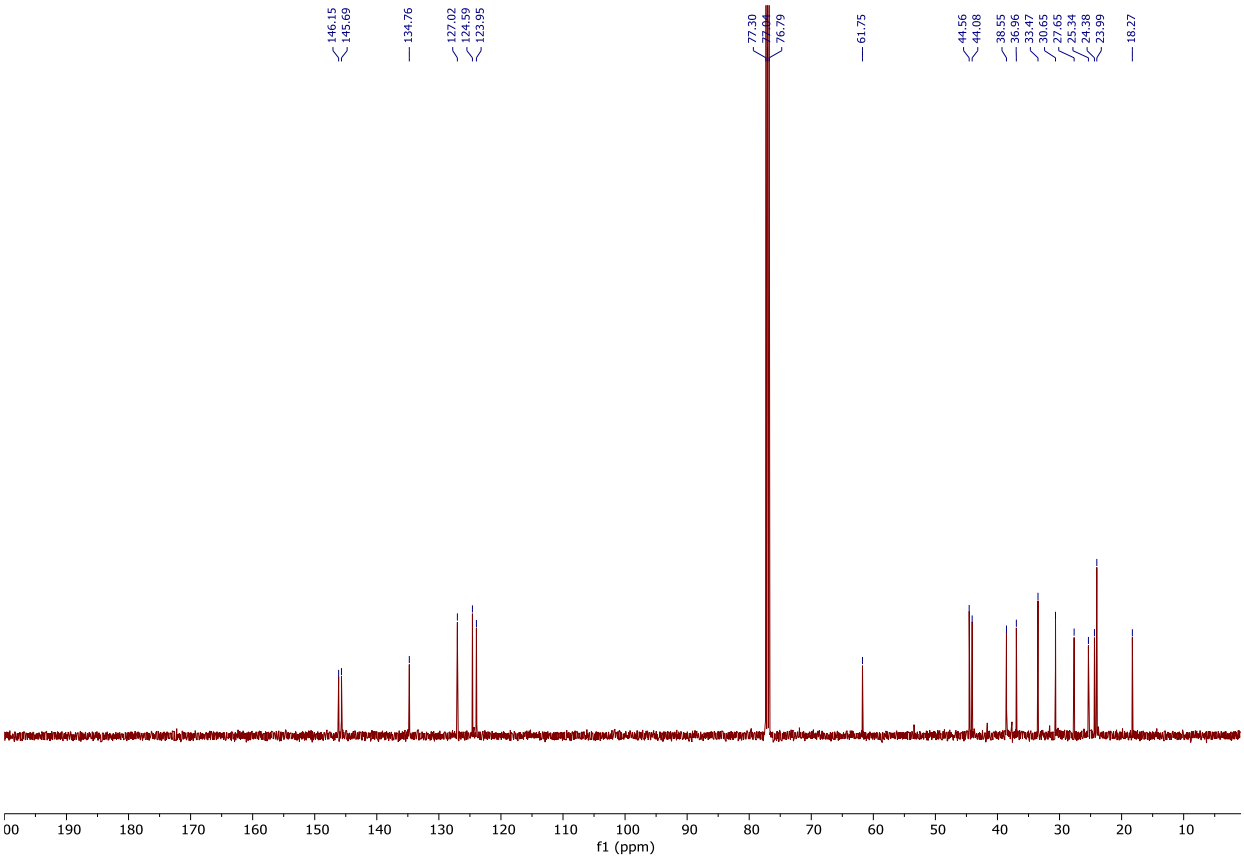
AB_MM_01_212.d

Bruker Compass DataAnalysis 4.1 printed: 12/14/2021 3:06:06 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**18**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**19**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**19**

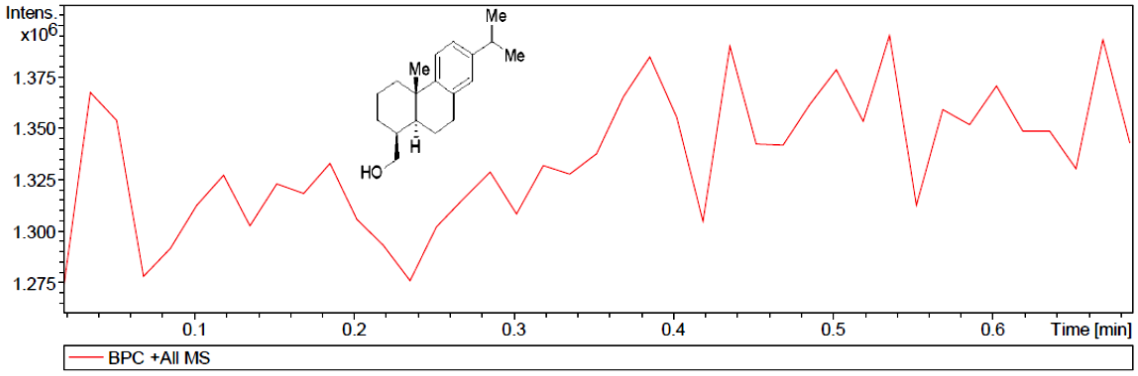
Display Report

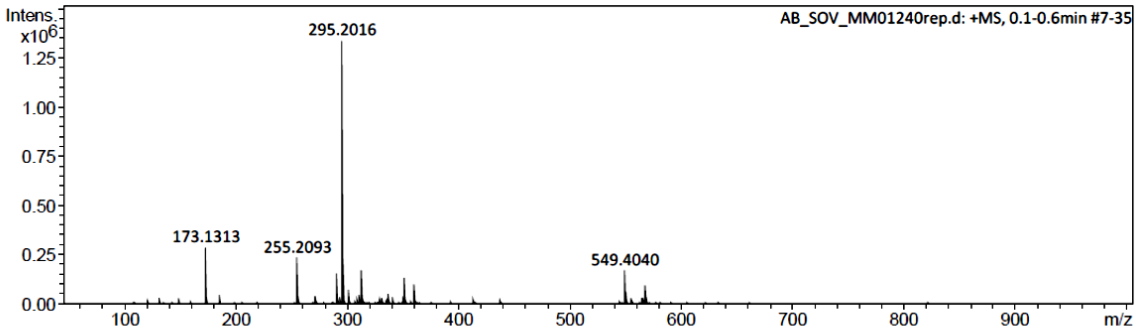
Analysis Info

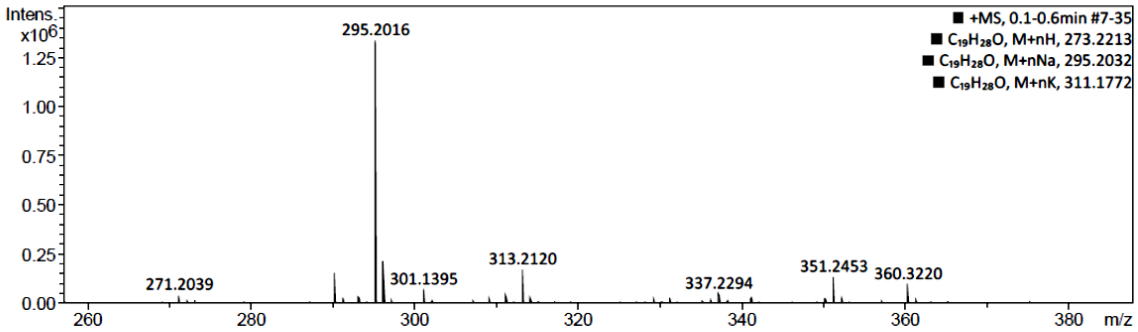
Analysis Name	D:\Data\User data\2021\SEPT\AB_SOV_MM01240rep.d	Acquisition Date	9/9/2021 11:44:46 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_SOV_MM01240	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



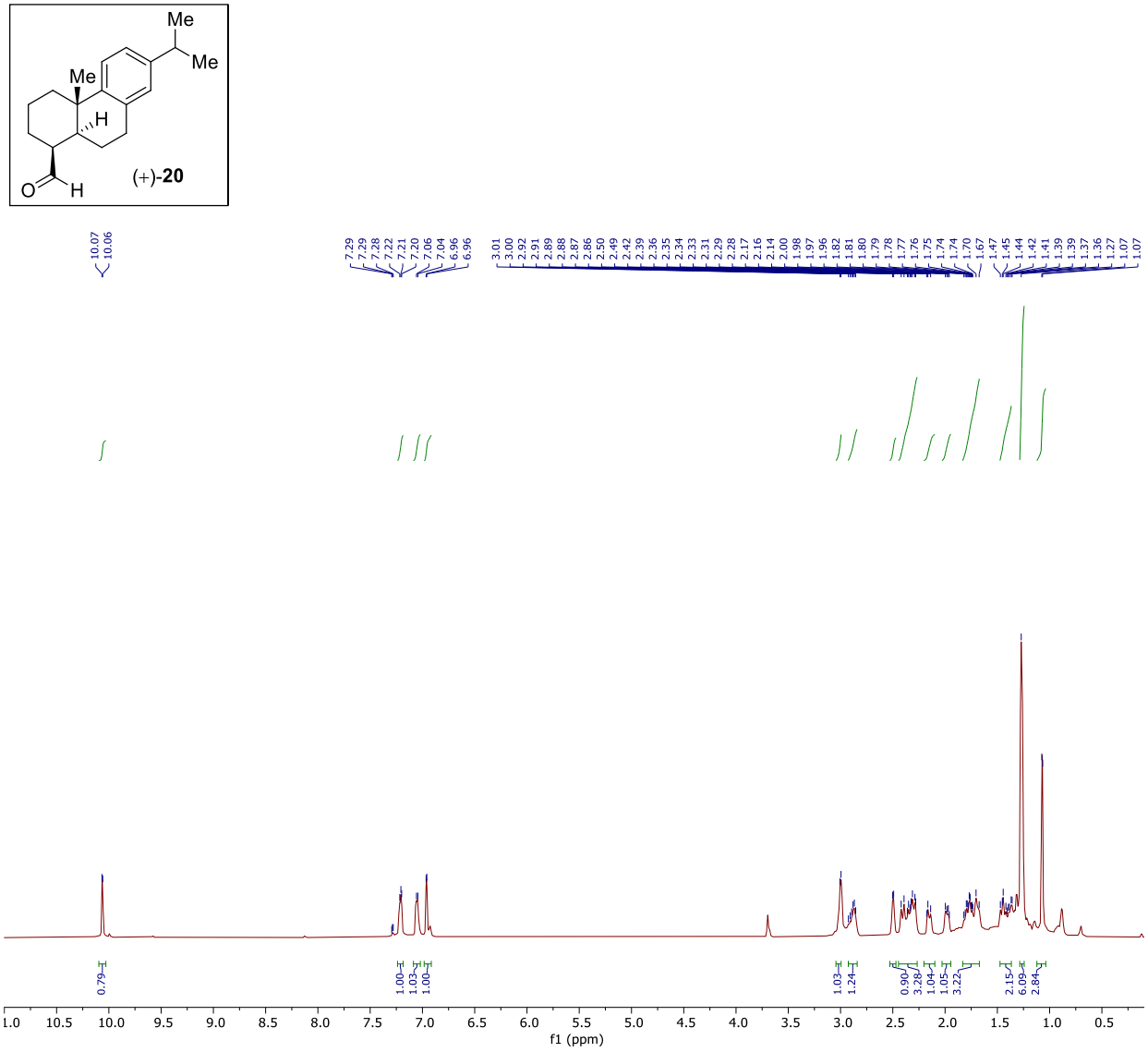




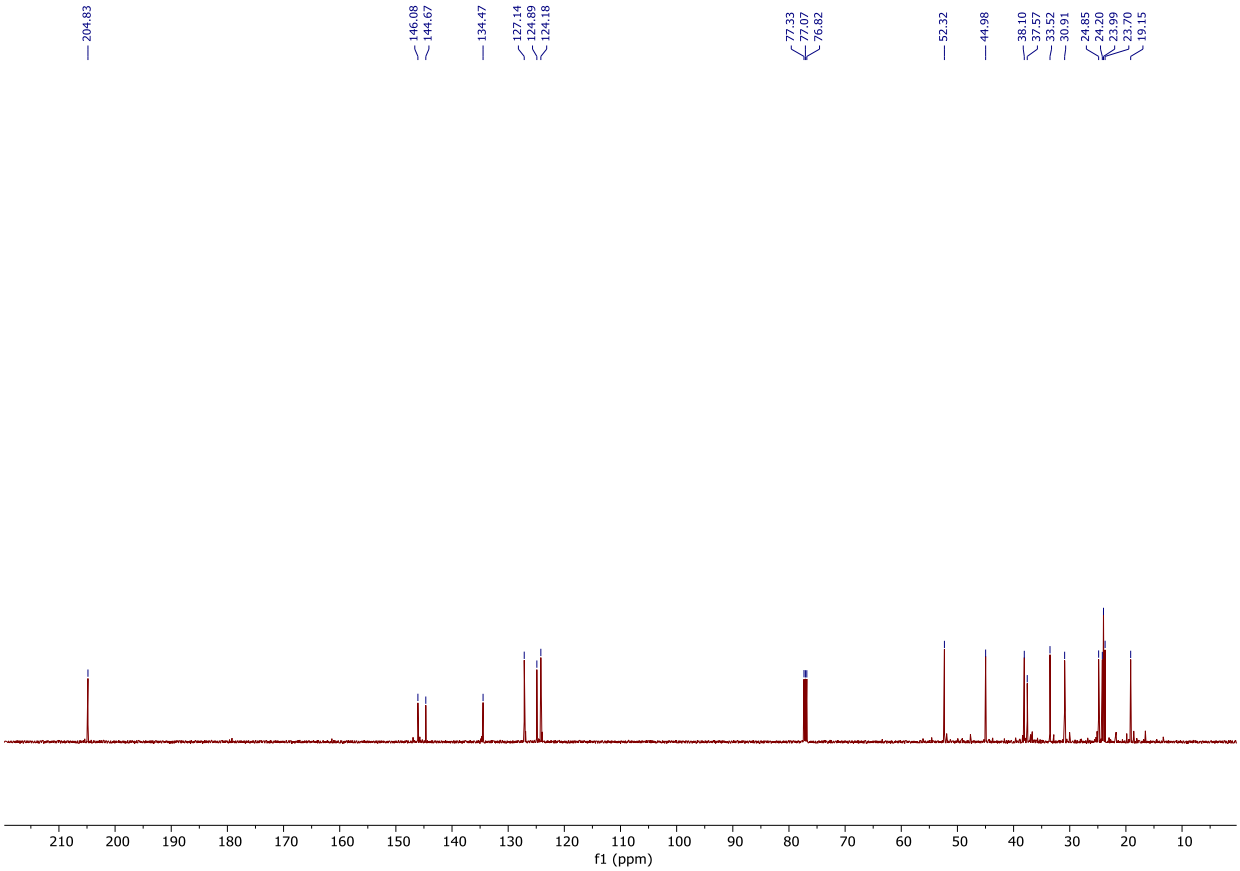
AB_SOV_MM01240rep.d

Bruker Compass DataAnalysis 4.1 printed: 9/9/2021 11:49:57 AM by: IISER Kolkata Page 1 of 1

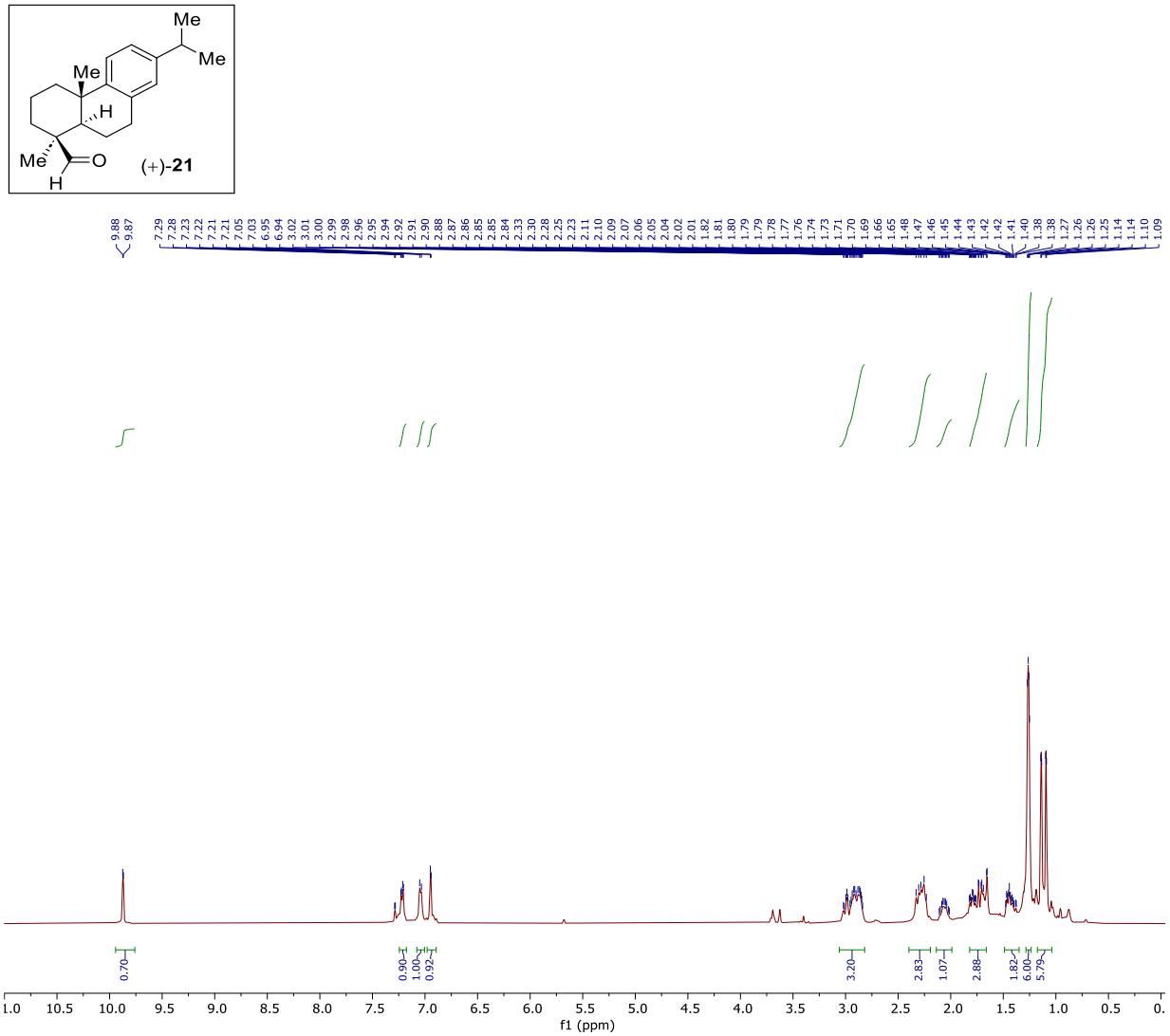
Scanned copy of mass spectrum of (+)-**19**



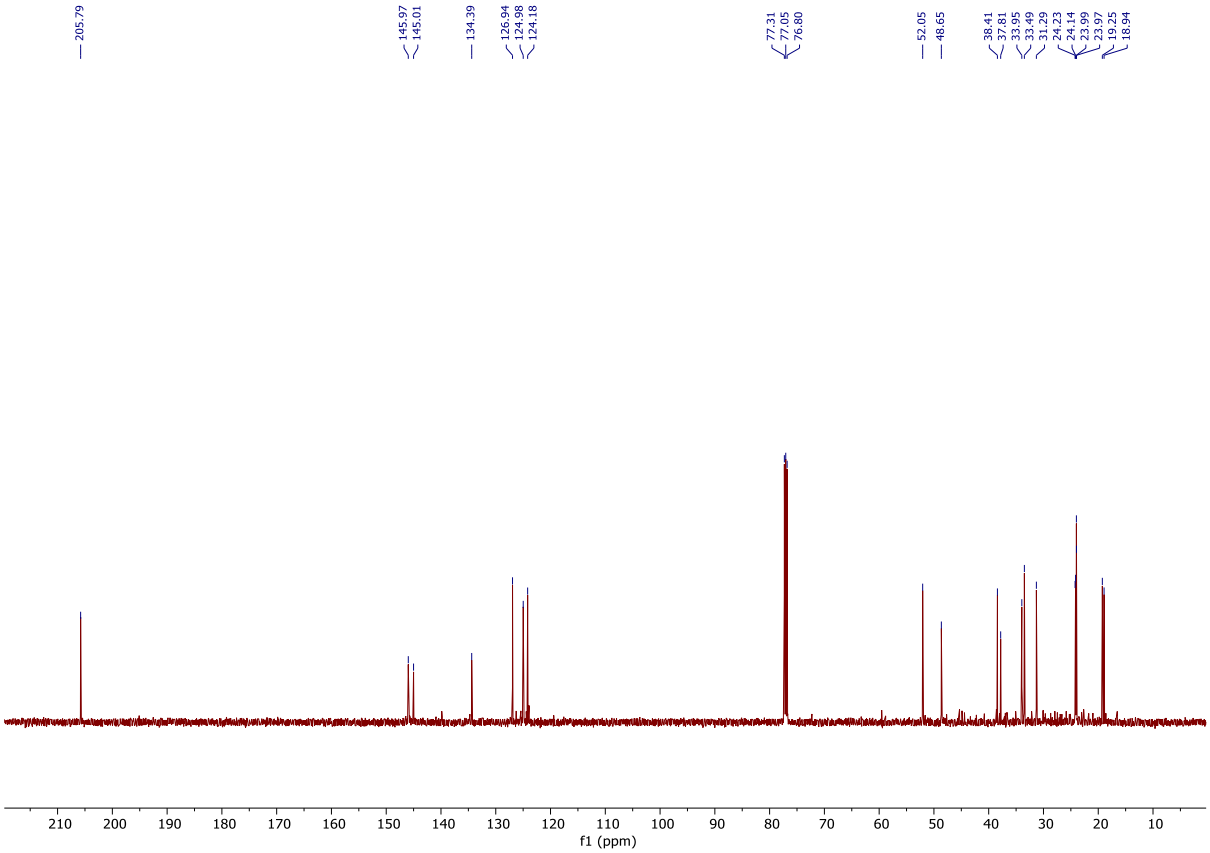
^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**20**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**20**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**21**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**21**

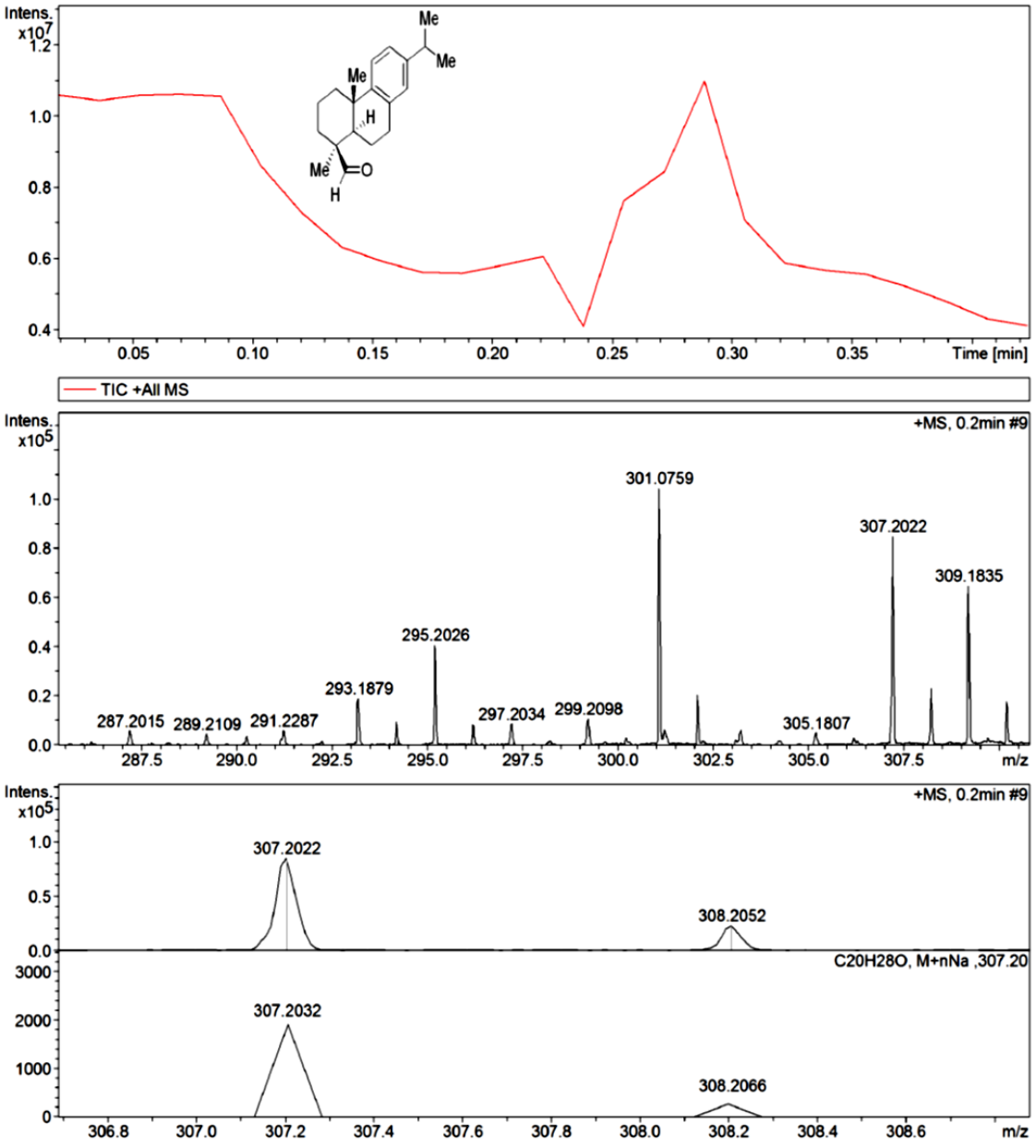
Display Report

Analysis Info

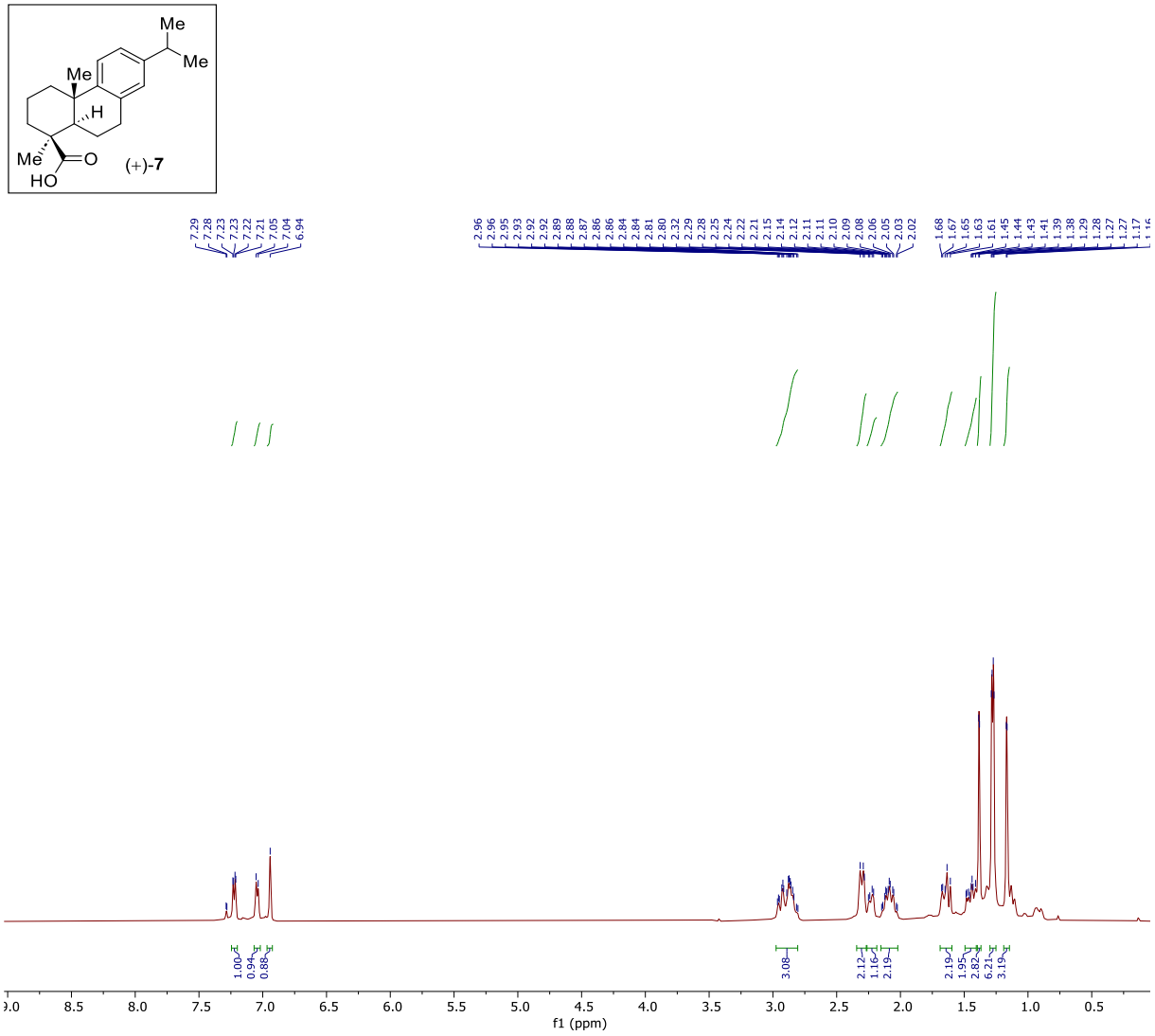
Analysis Name	D:\Data\USER DATA 2022\JUNE2022\27-06-22\Prof A Bisai-MM-01-243.d	Acquisition Date	27-06-2022 12:59:55
Method	tune mix_low.New.021117.m	Operator	Bruker
Sample Name	MM-01-243	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

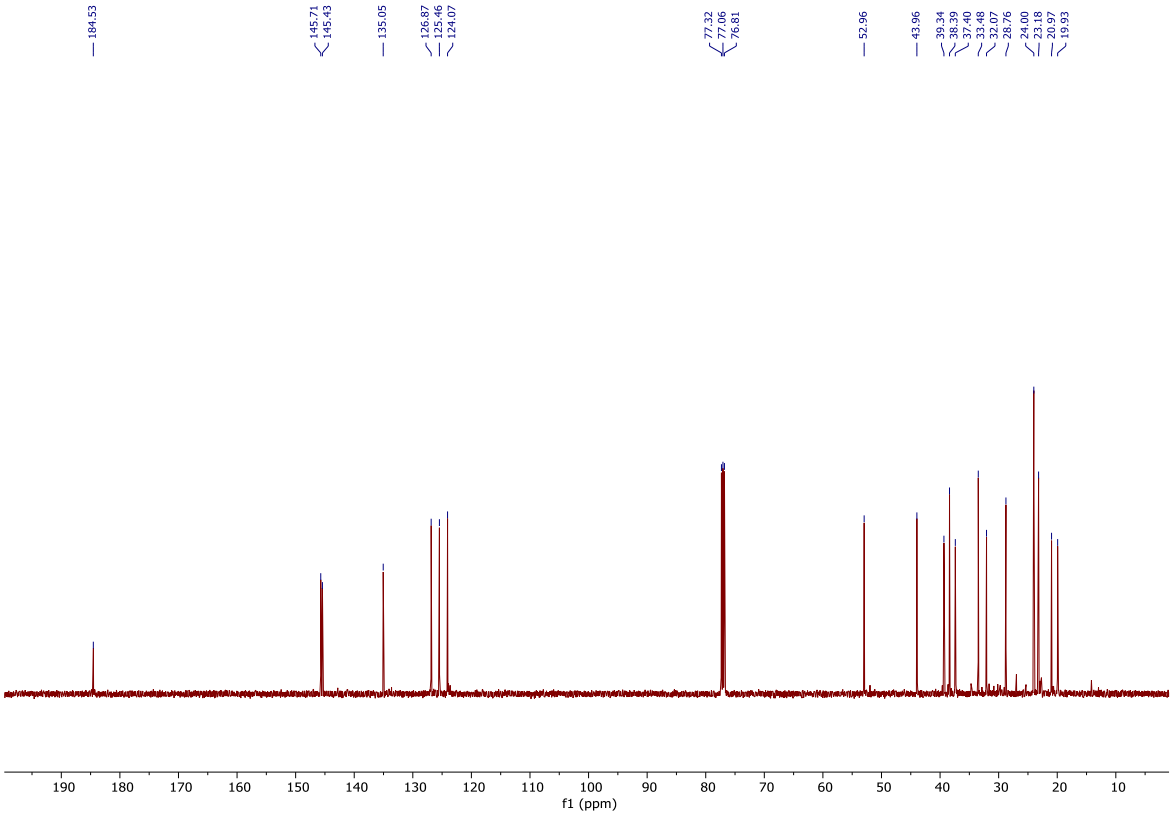
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



Scanned copy of mass spectrum of (+)-**21**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**7**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**7**

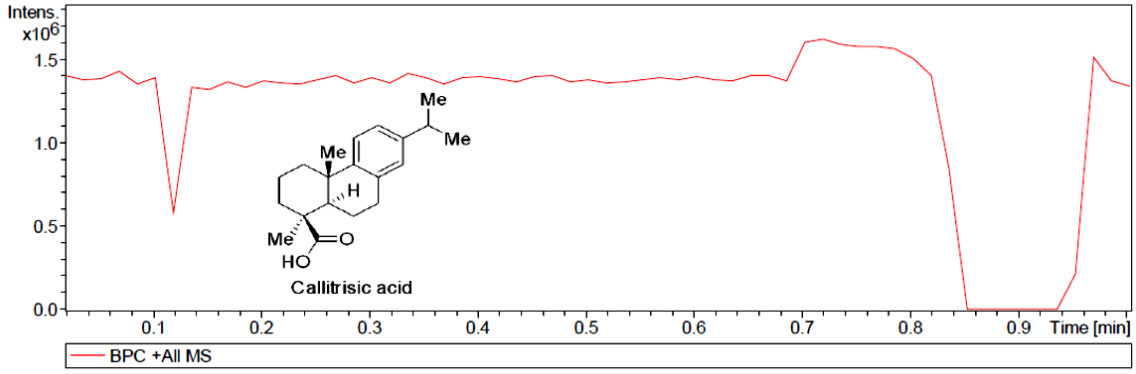
Display Report

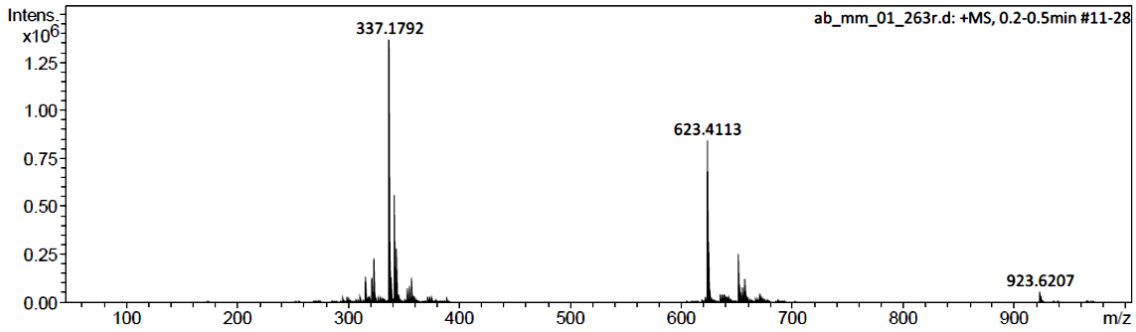
Analysis Info

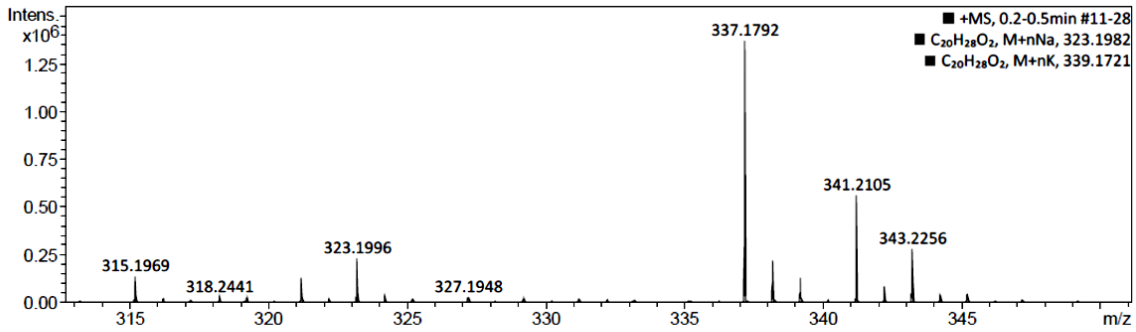
Analysis Name	D:\Data\User data\2021\NOV\ab_mm_01_263r.d	Acquisition Date	11/22/2021 12:37:56 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_mm_01_263r	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



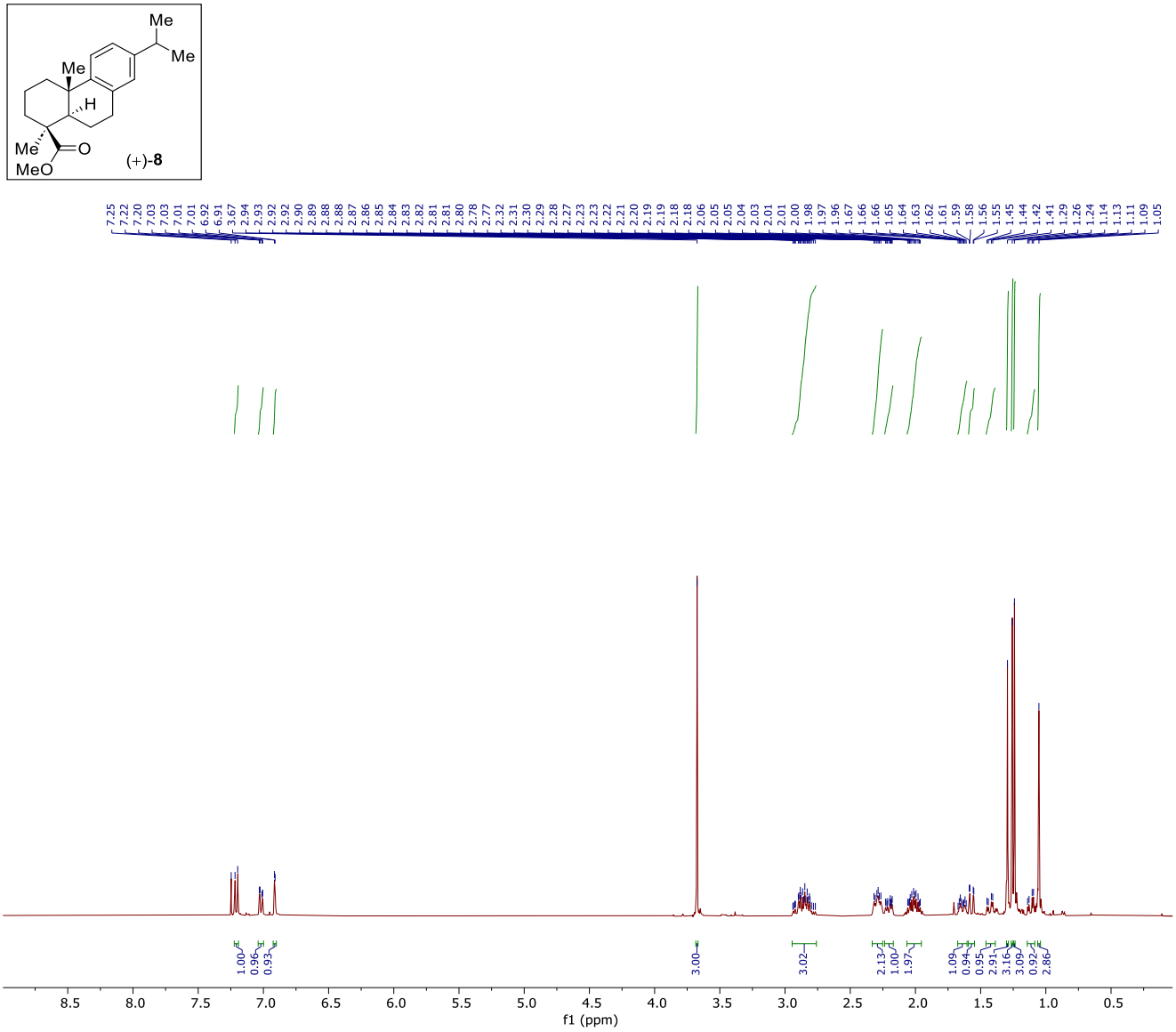




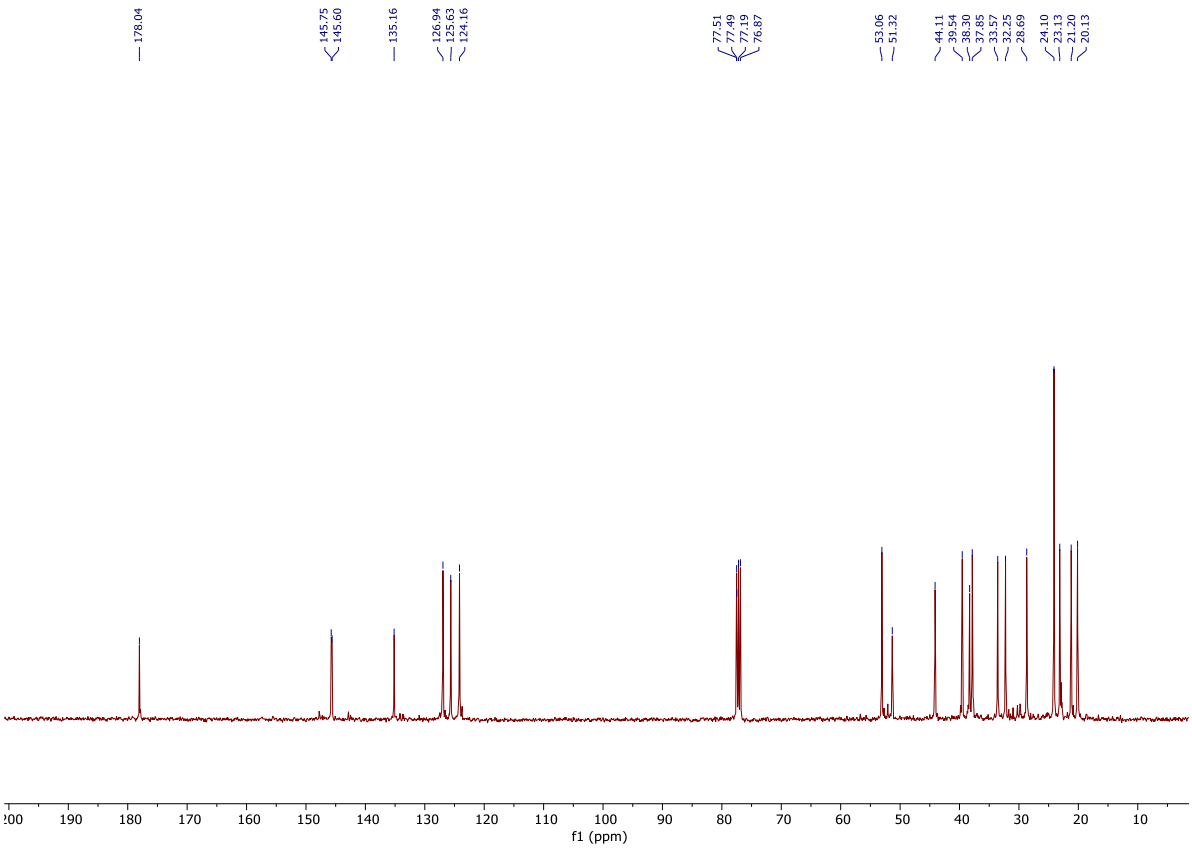
ab_mm_01_263r.d

Bruker Compass DataAnalysis 4.1 printed: 11/22/2021 12:40:44 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**7**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**8**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (+)-**8**

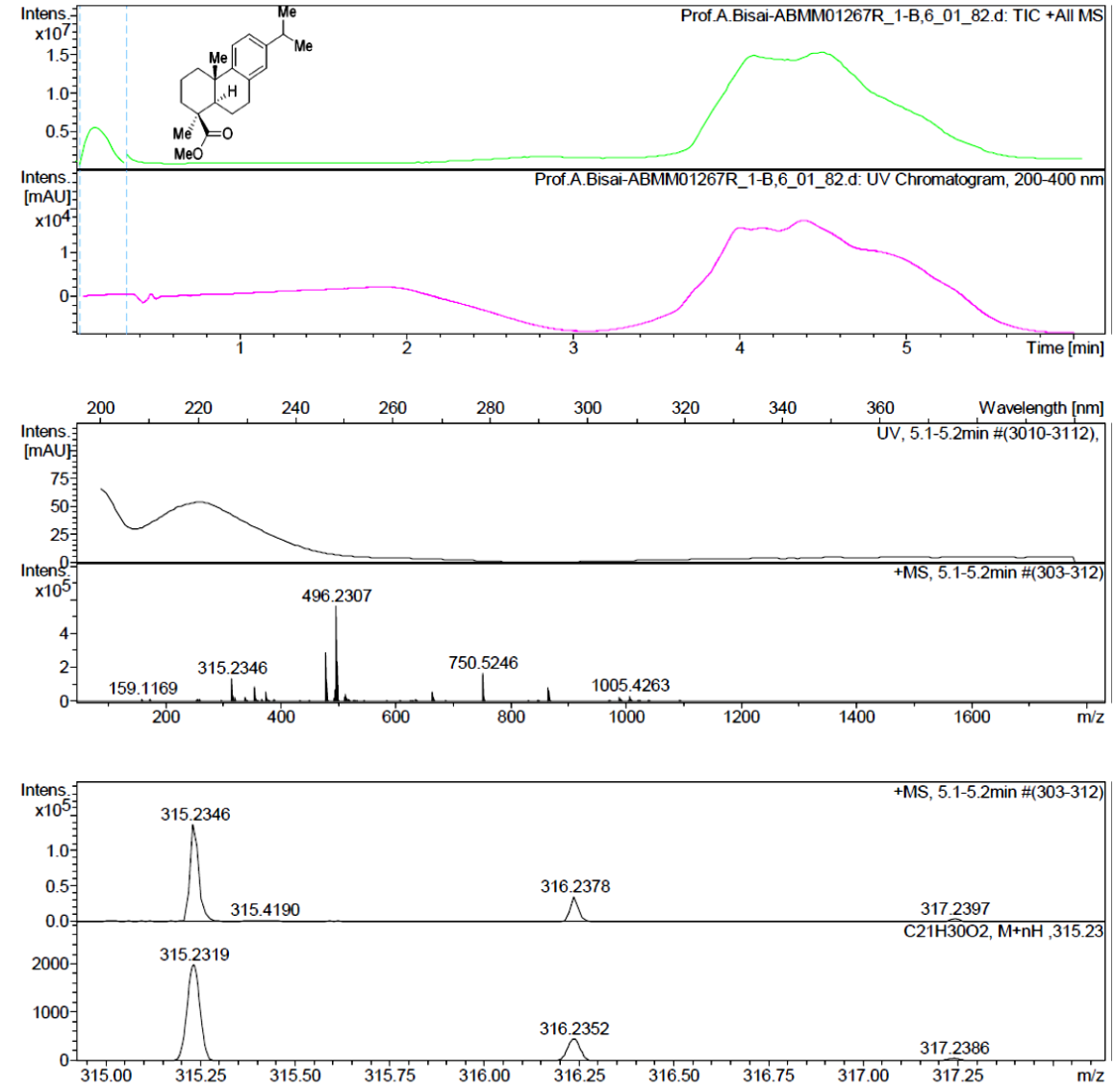
Display Report

Analysis Info

		Acquisition Date	5/11/2022 12:22:31 PM
Analysis Name	D:\Data\USER DATA 2022\MAY 2022\11-05-2022\Prof.A.Bisai-ABMM01267R_1-B,6_01_82.d		
Method	HRLCMS-20 Sept.m	Operator	IISER
Sample Name	Prof.A.Bisai-ABMM01267R	Instrument	micrOTOF-Q II 10330
Comment			

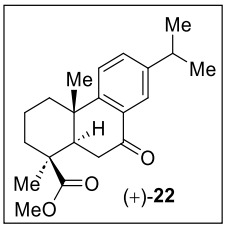
Acquisition Parameter

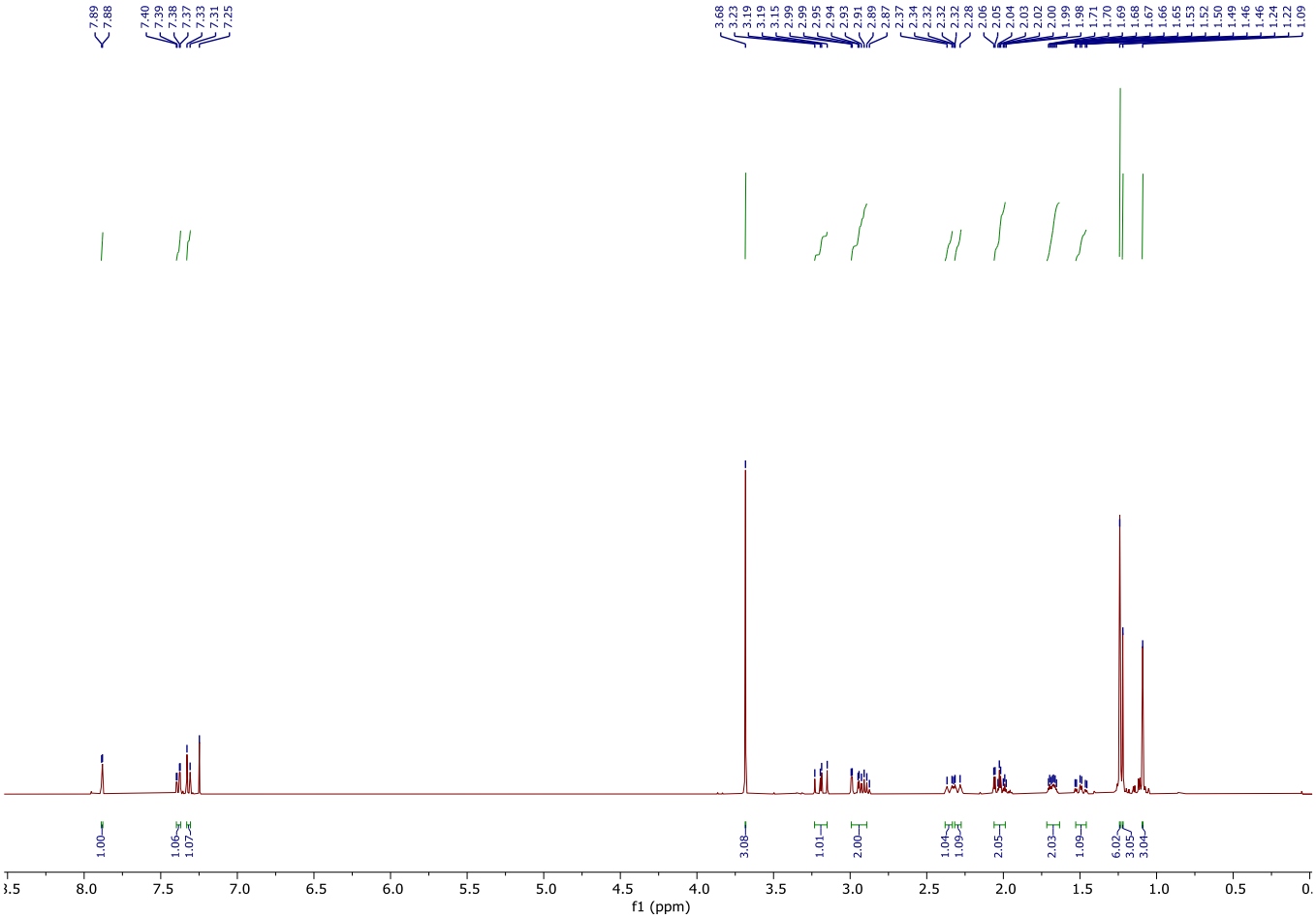
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



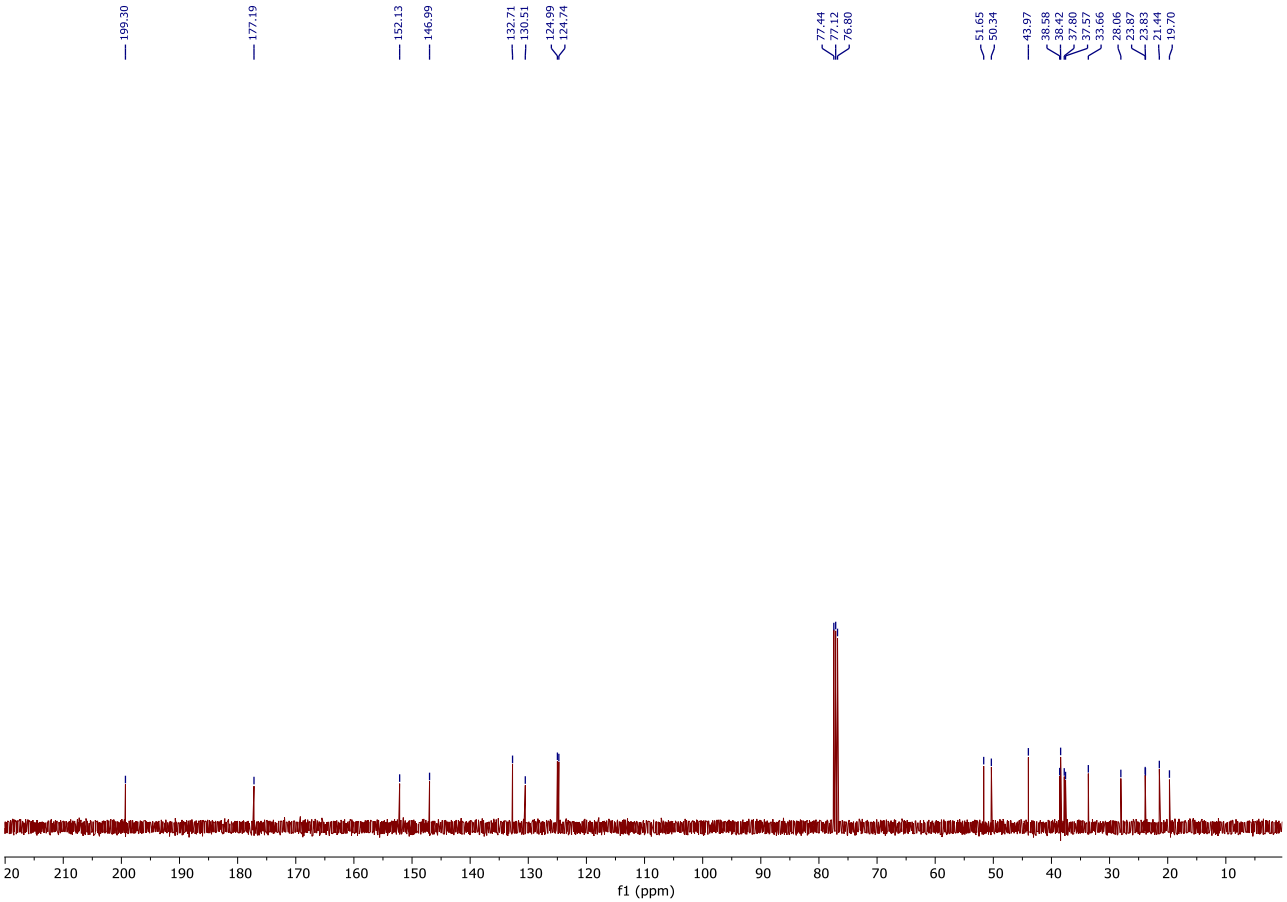
Bruker Compass DataAnalysis 4.0 printed: 5/11/2022 12:46:42 PM Page 1 of 1

Scanned copy of mass spectrum of (+)-**8**





^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**22**



^{13}C NMR (101 MHz, $CDCl_3$) of compound (+)-**22**

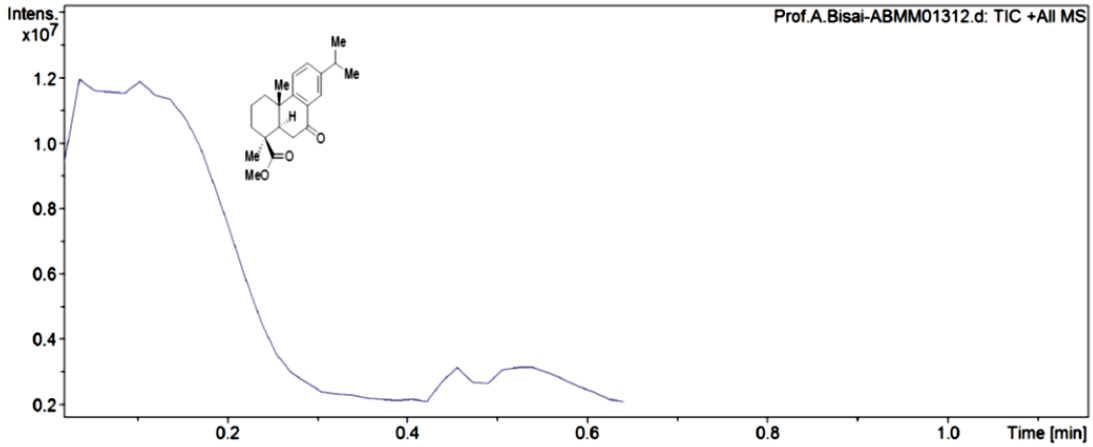
Display Report

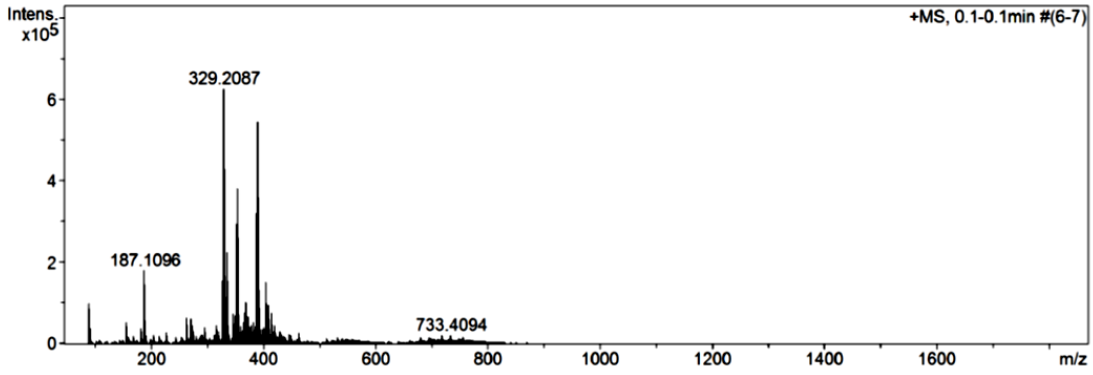
Analysis Info

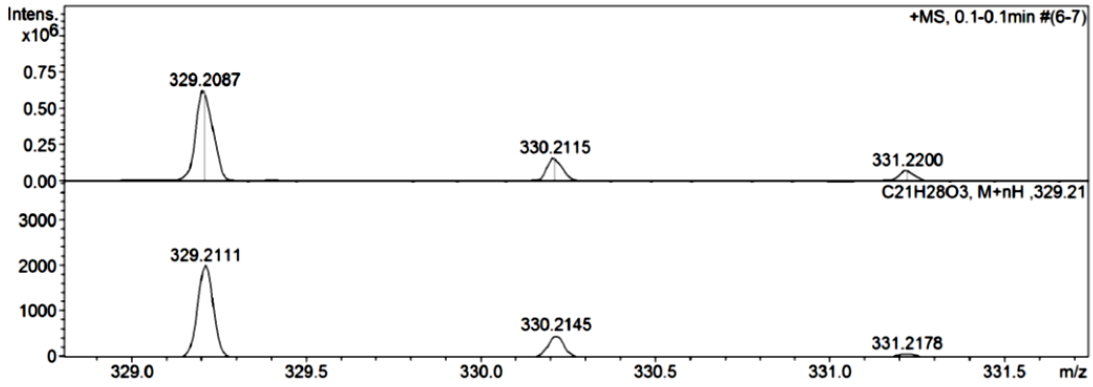
Analysis Name	D:\Data\USER DATA 2022\JUNE2022\29-06-22\Prof.A.Bisai-ABMM01312.d	Acquisition Date	29-06-2022 11:54:44
Method	tune mix_low.New.021117.m	Operator	Bruker
Sample Name	ABMM01312	Instrument	micrOTOF-Q 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4600 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source

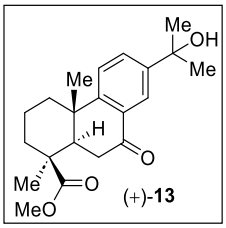


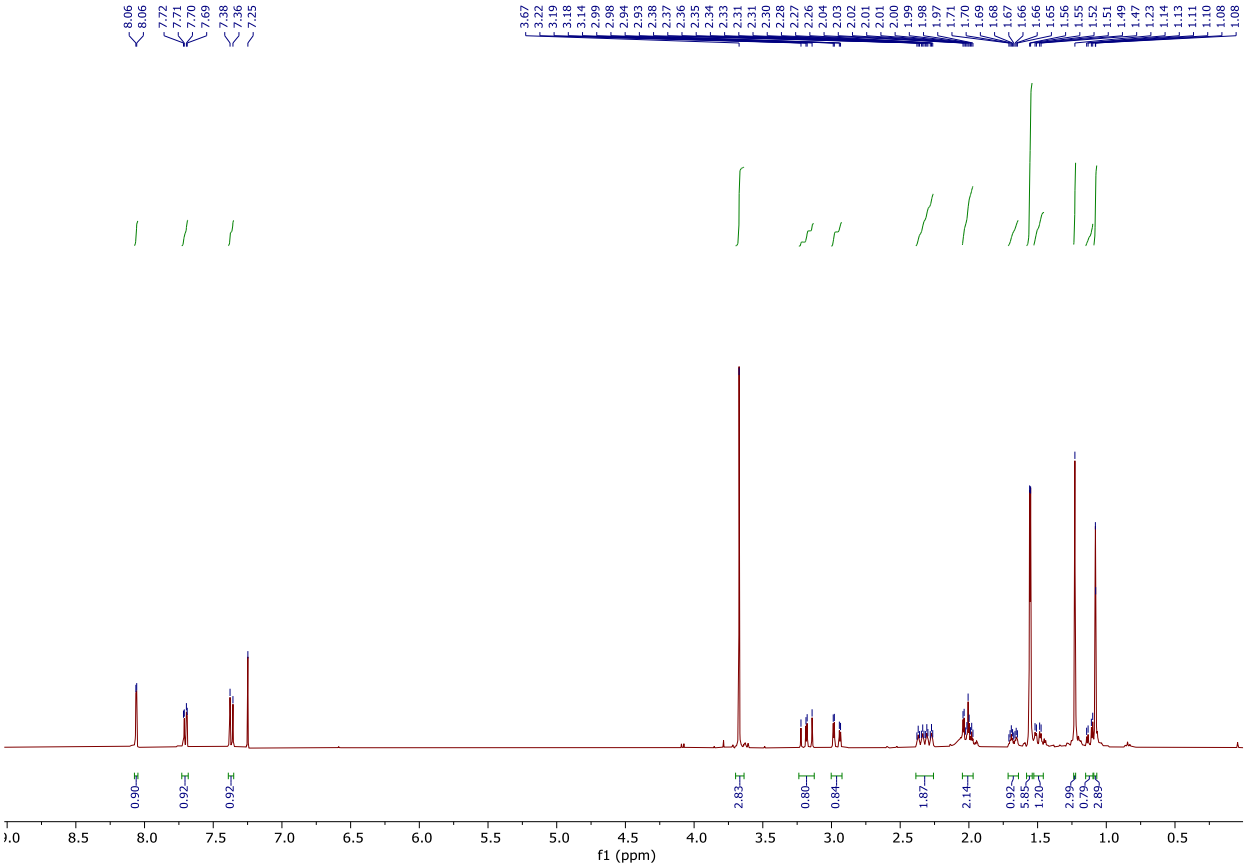




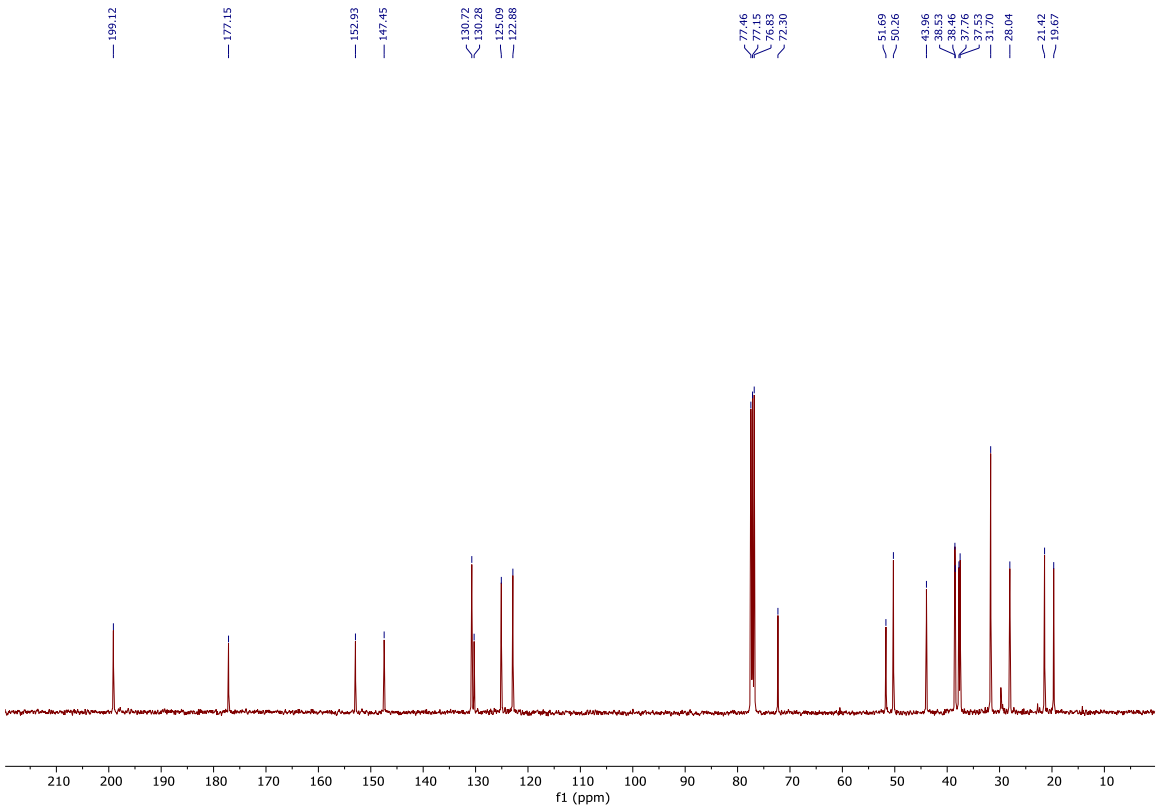
Bruker Compass DataAnalysis 4.0 printed: 29-06-2022 11:56:02 Page 1 of 1

Scanned copy of mass spectrum of (+)-**22**





^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**13**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**13**

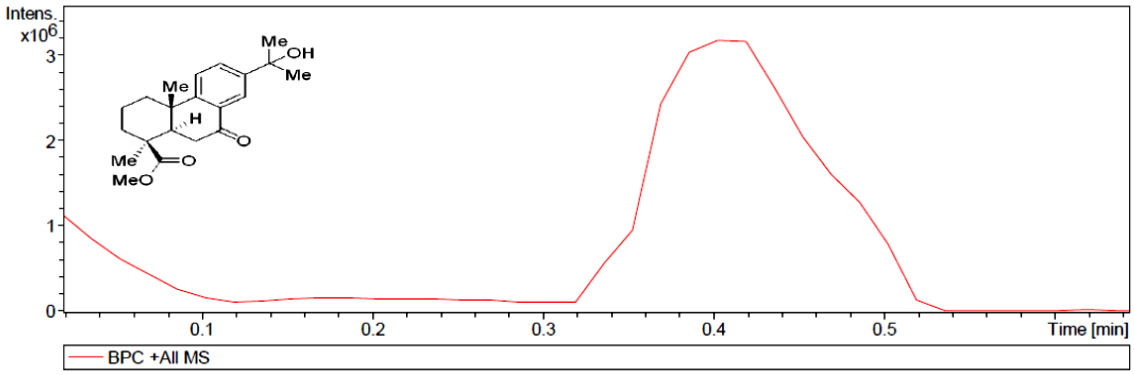
Display Report

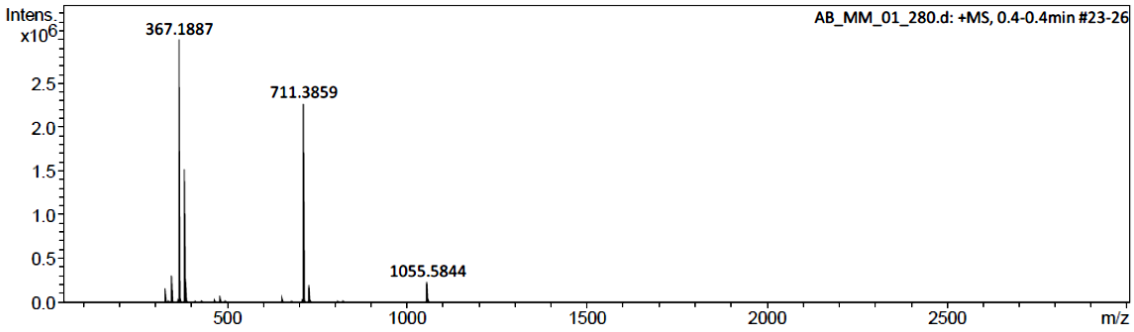
Analysis Info

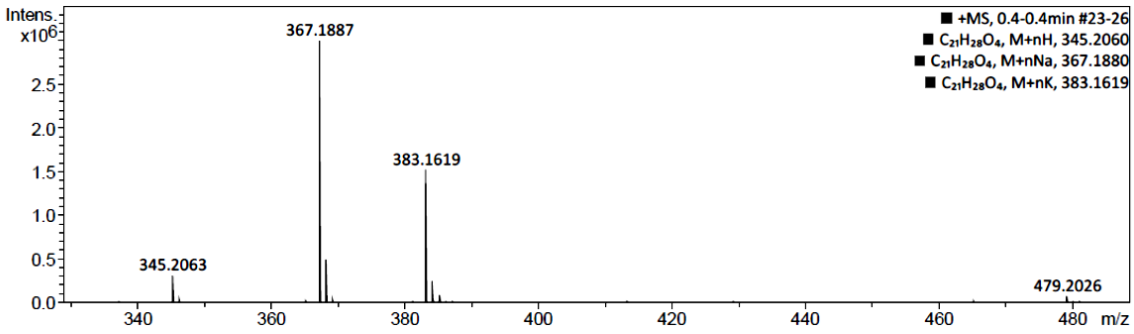
Analysis Name	D:\Data\User data\2021\OCTOBER\AB_MM_01_280.d	Acquisition Date	10/22/2021 12:48:04 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_MM_01_280	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



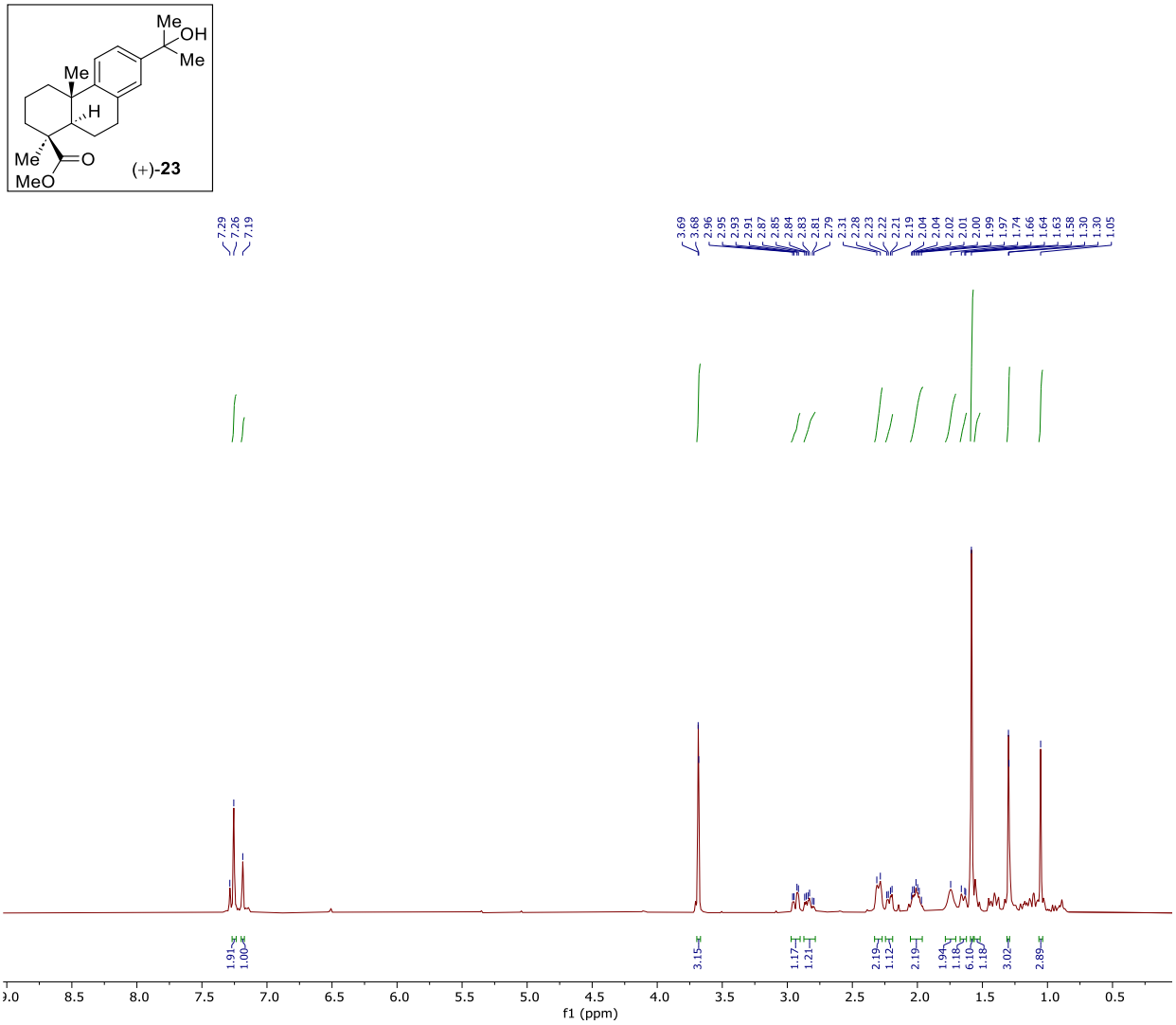




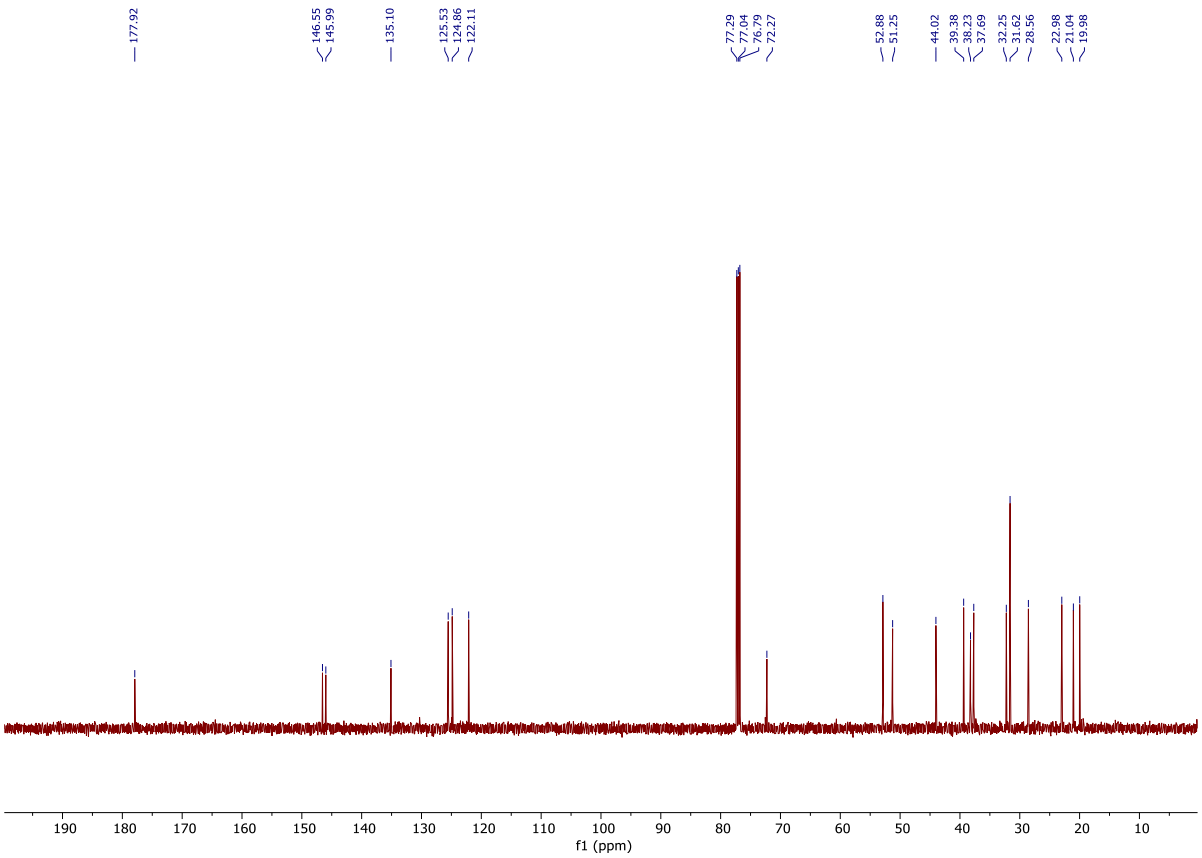
AB_MM_01_280.d

Bruker Compass DataAnalysis 4.1 printed: 10/22/2021 12:50:59 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**13**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**23**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**23**

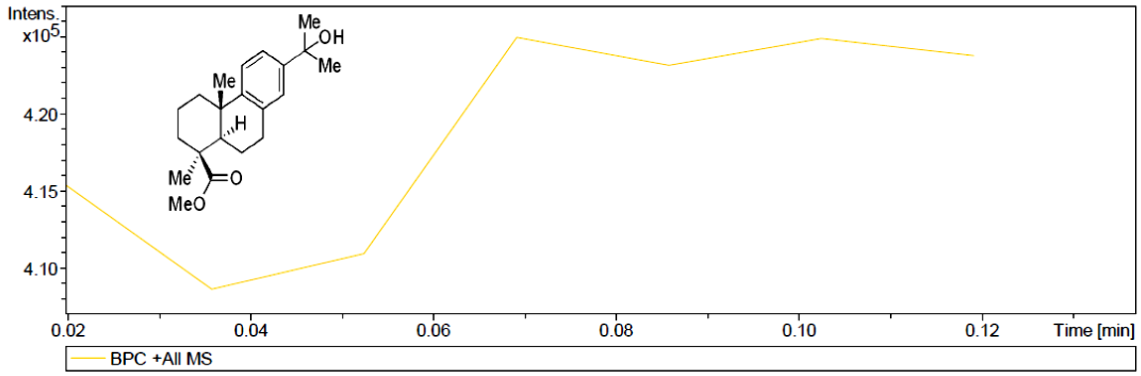
Display Report

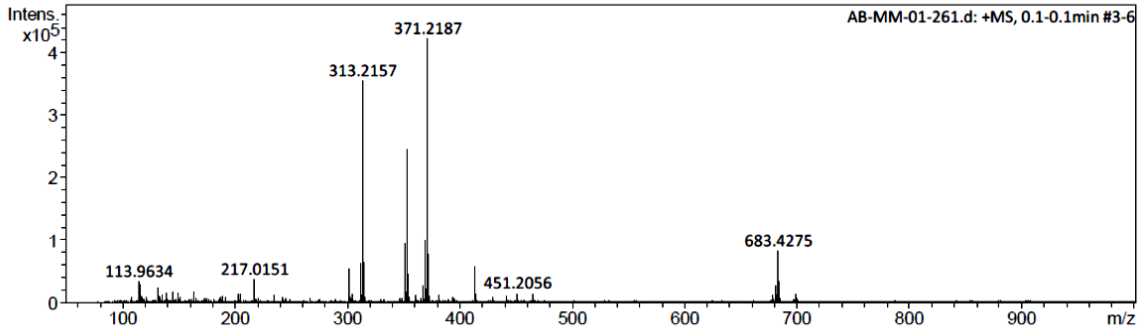
Analysis Info

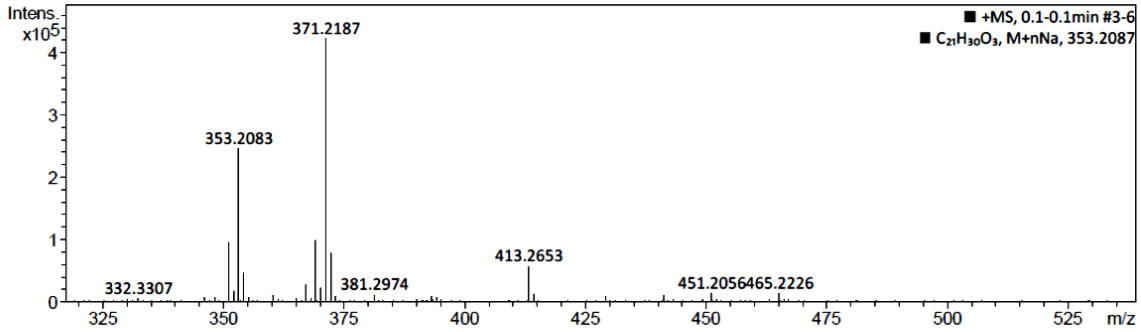
Analysis Name	Y:\2021\SEPT\AB-MM-01-261.d	Acquisition Date	9/15/2021 6:35:59 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB-MM-01-261	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



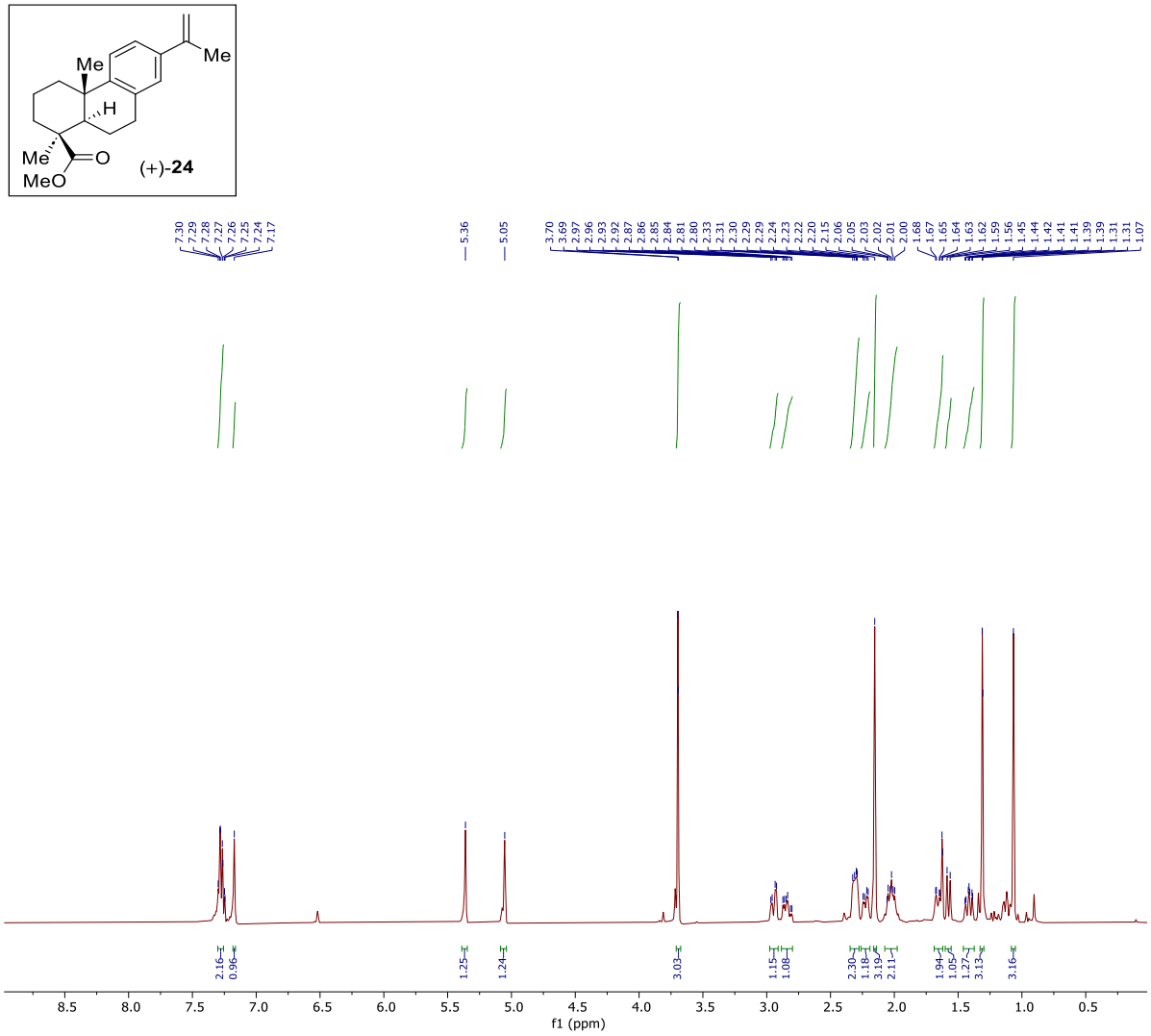




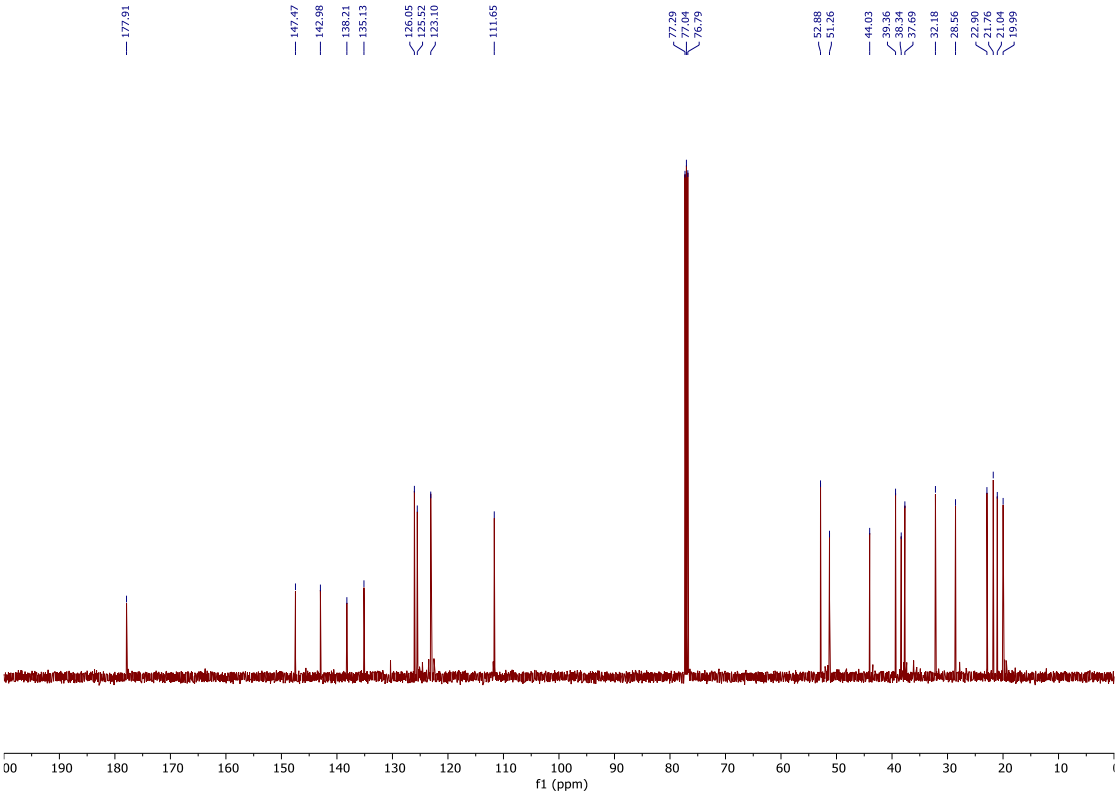
AB-MM-01-261.d

Bruker Compass DataAnalysis 4.1 printed: 9/15/2021 6:40:11 PM by: BDAL@DE Page 1 of 1

Scanned copy of mass spectrum of (+)-**23**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**24**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**24**

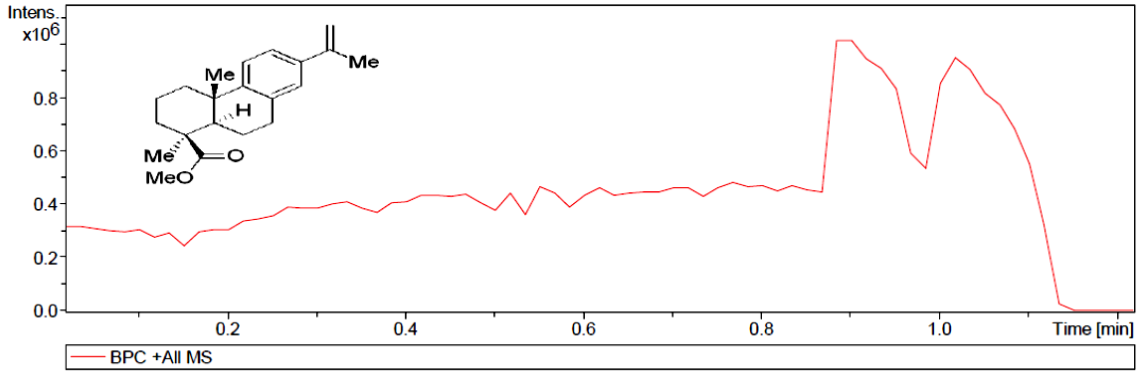
Display Report

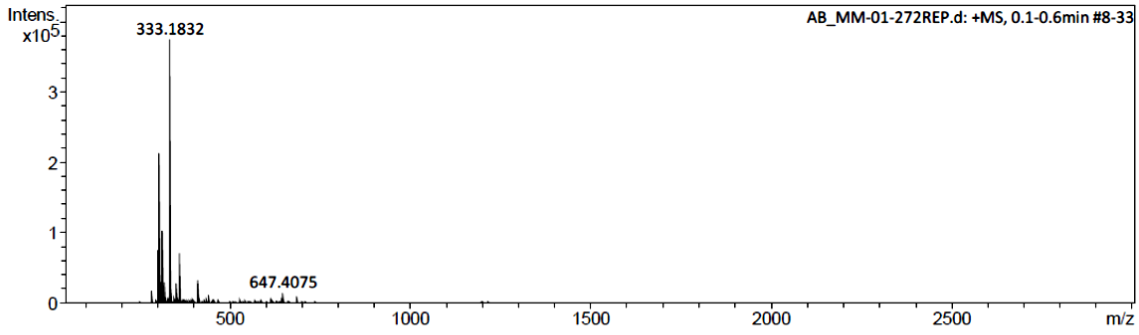
Analysis Info

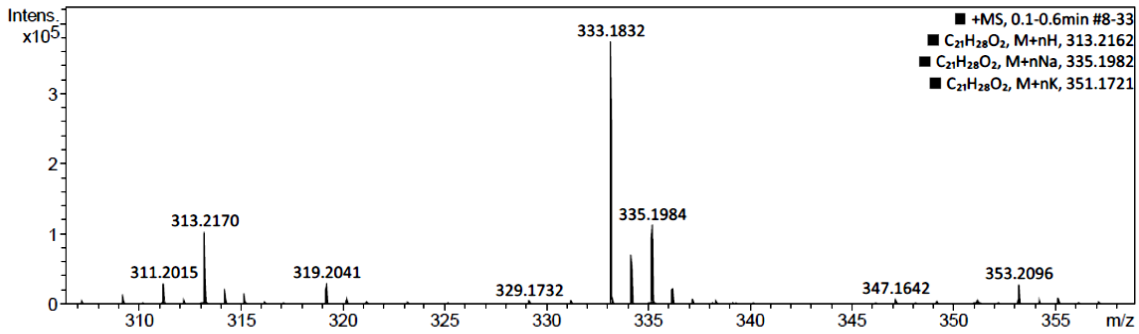
Analysis Name	D:\Data\User data\2021\OCTOBER\AB_MM-01-272REP.d	Acquisition Date	10/8/2021 2:38:09 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_MM-01-272	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



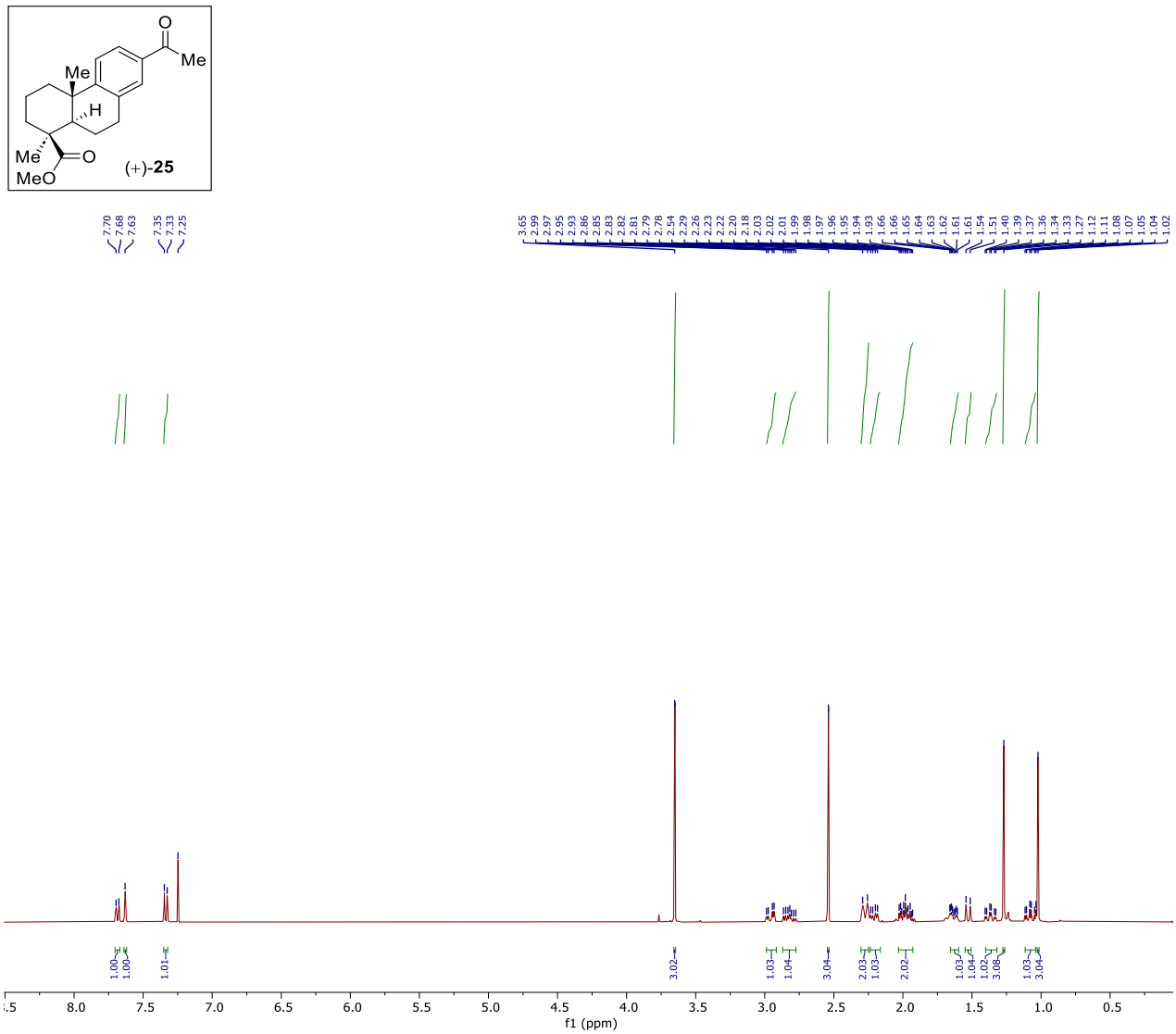




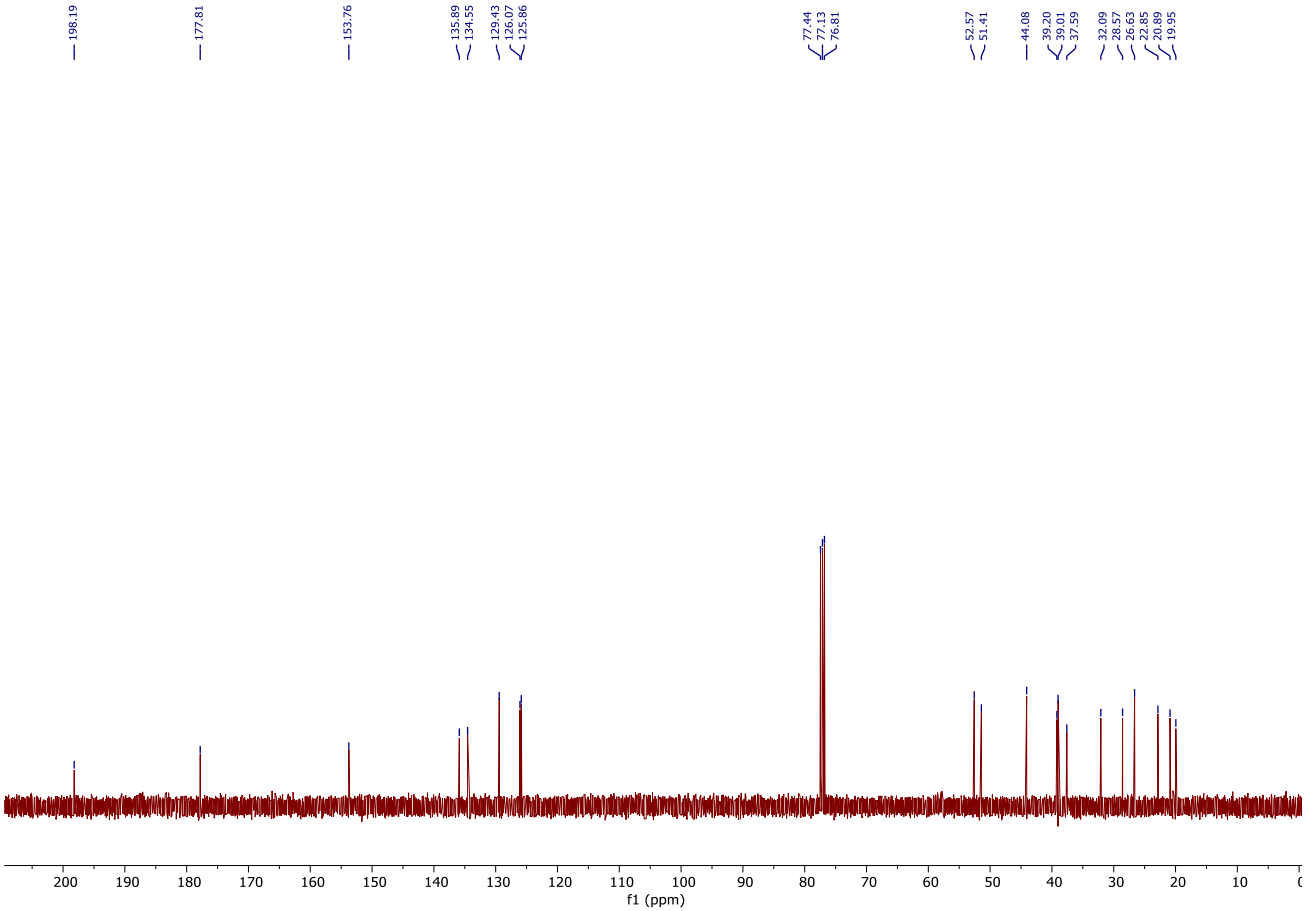
AB_MM-01-272REP.d

Bruker Compass DataAnalysis 4.1 printed: 10/8/2021 2:40:52 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**24**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**25**



^{13}C NMR (101 MHz, $CDCl_3$) of compound (+)-**25**

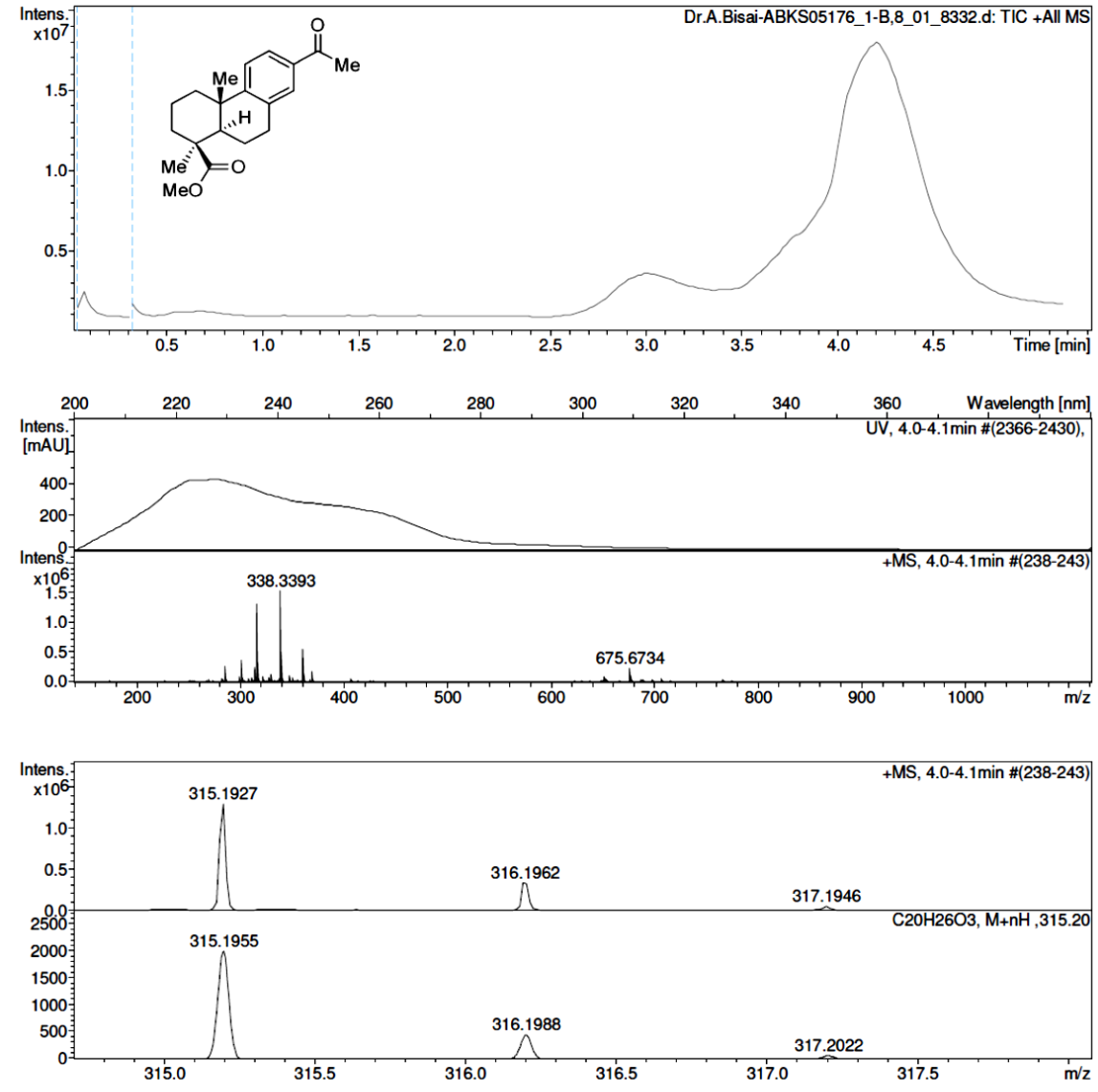
Display Report

Analysis Info

Acquisition Date	8/2/2021 2:33:03 PM		
Analysis Name	D:\Data\new user data 2021\August-2021\02-Aug\Dr.A.Bisai-ABKS05176_1-B,8_01_8332.d		
Method	hrlcms-20 sept.m	Operator	RUCHI
Sample Name	Dr.A.Bisai-ABKS05176	Instrument	micrOTOF-Q II 10330
Comment			

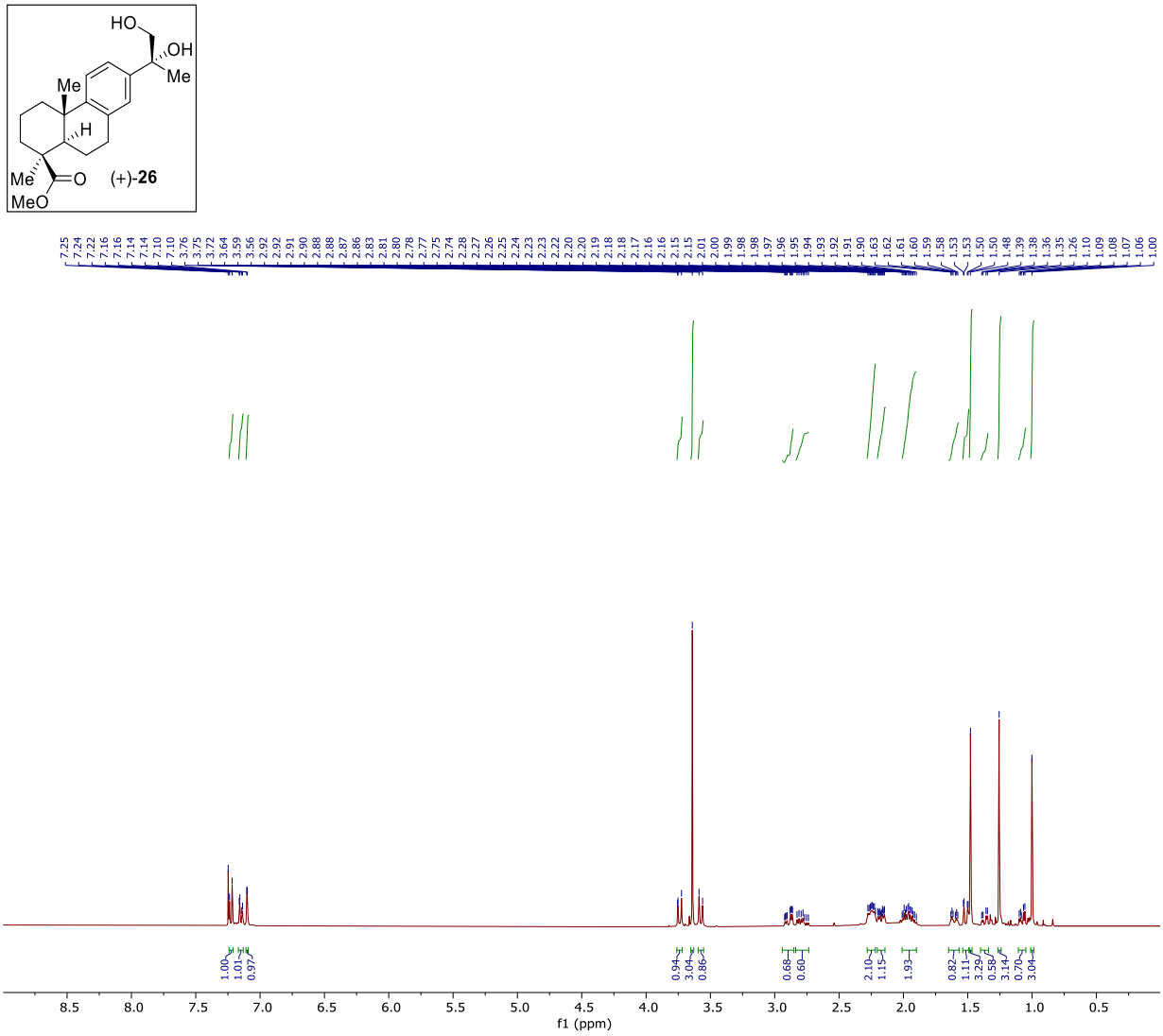
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

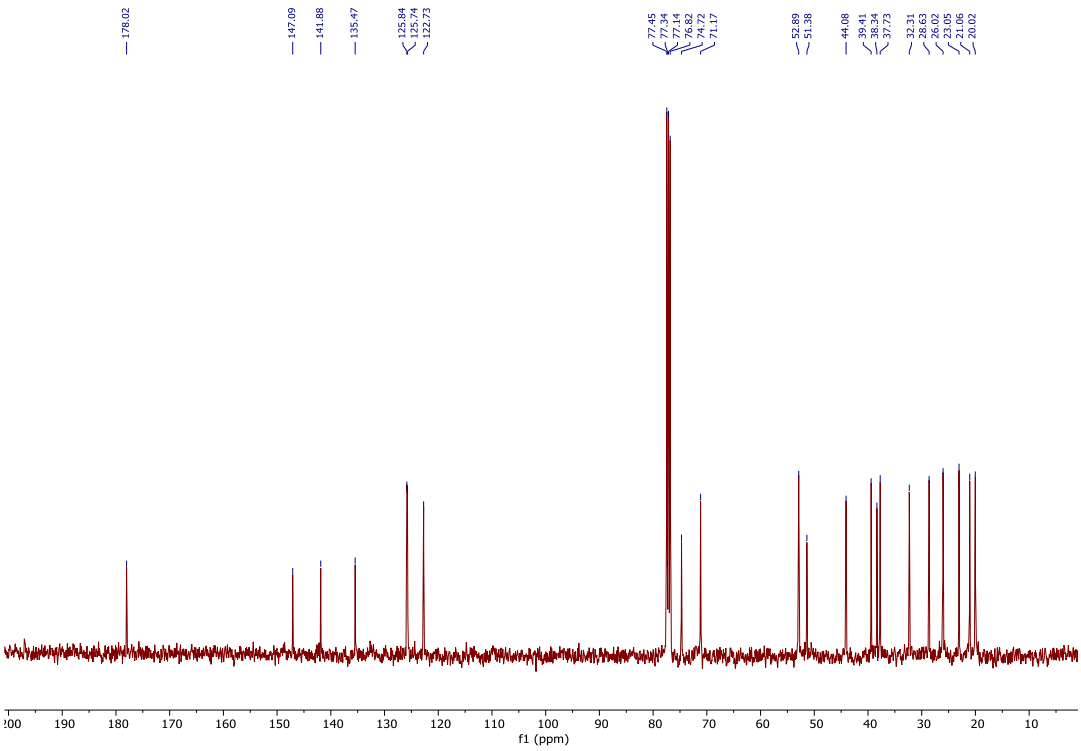


Bruker Compass DataAnalysis 4.0 printed: 8/2/2021 3:54:06 PM Page 1 of 1

Scanned copy of mass spectrum of (+)-**25**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**26**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**26**

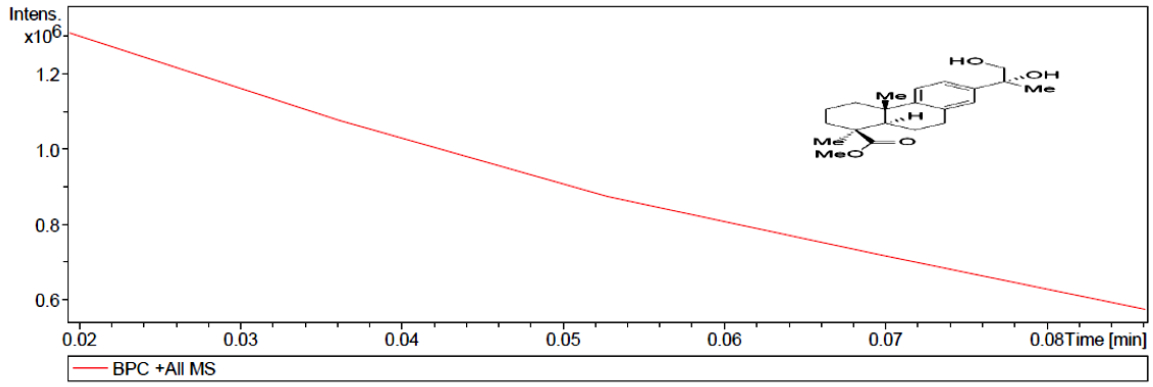
Display Report

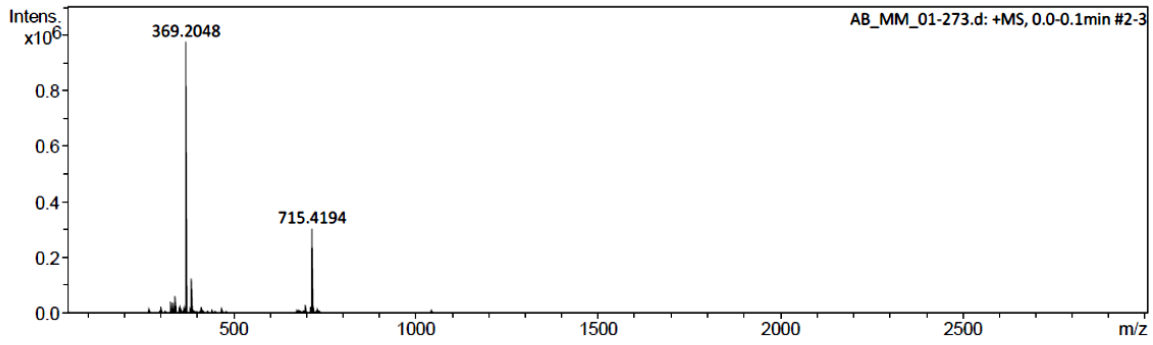
Analysis Info

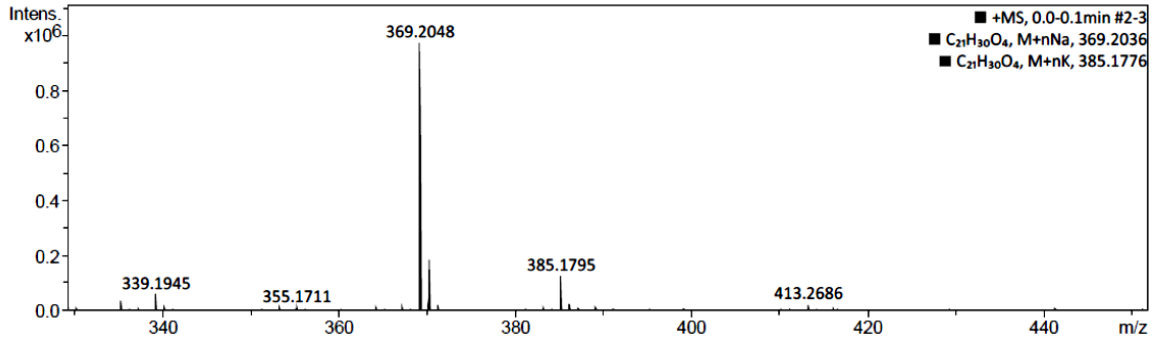
Analysis Name	D:\Data\User data\2021\OCTOBER\AB_MM_01-273.d	Acquisition Date	10/8/2021 4:15:14 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_MM_01-273	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



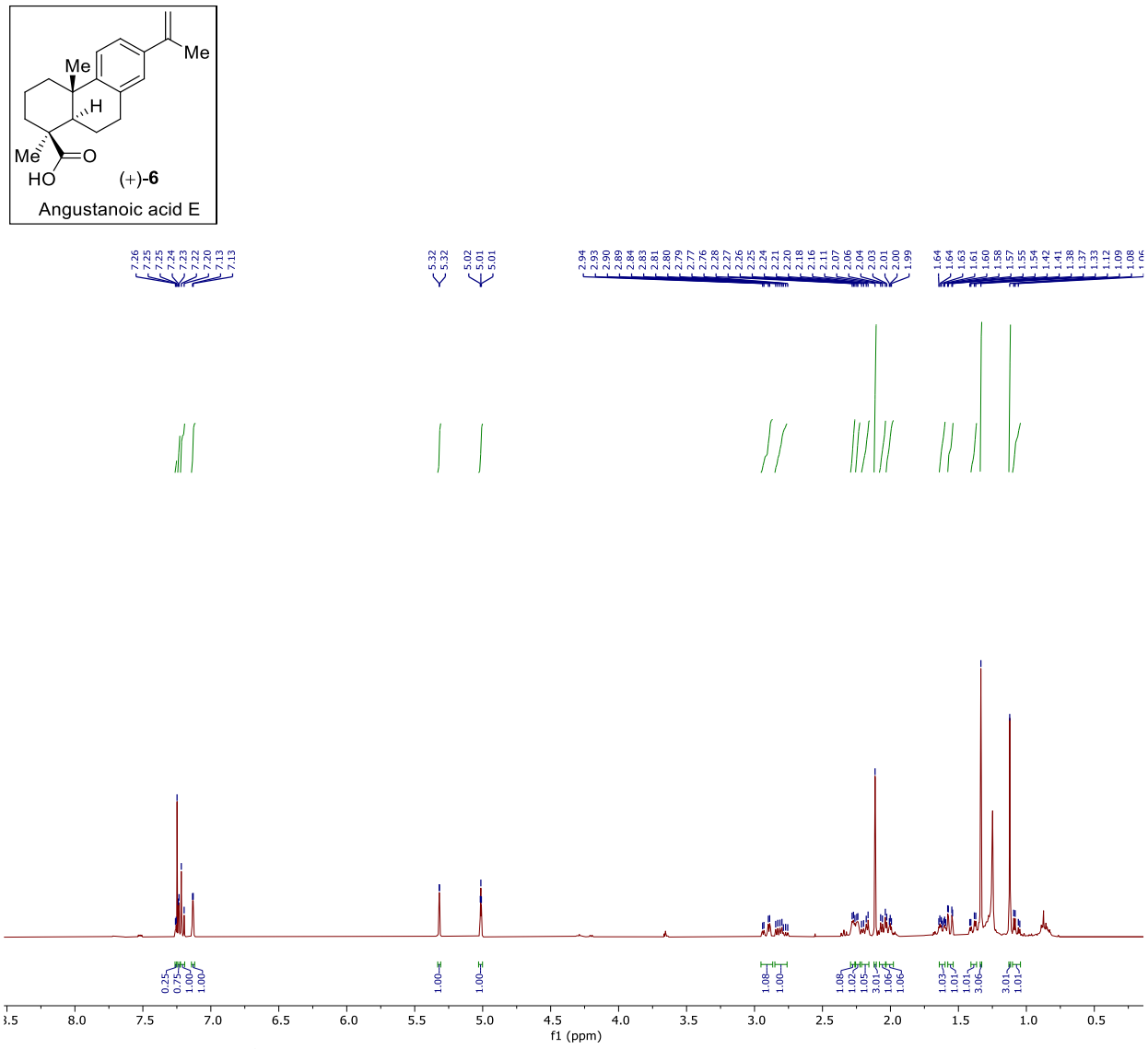




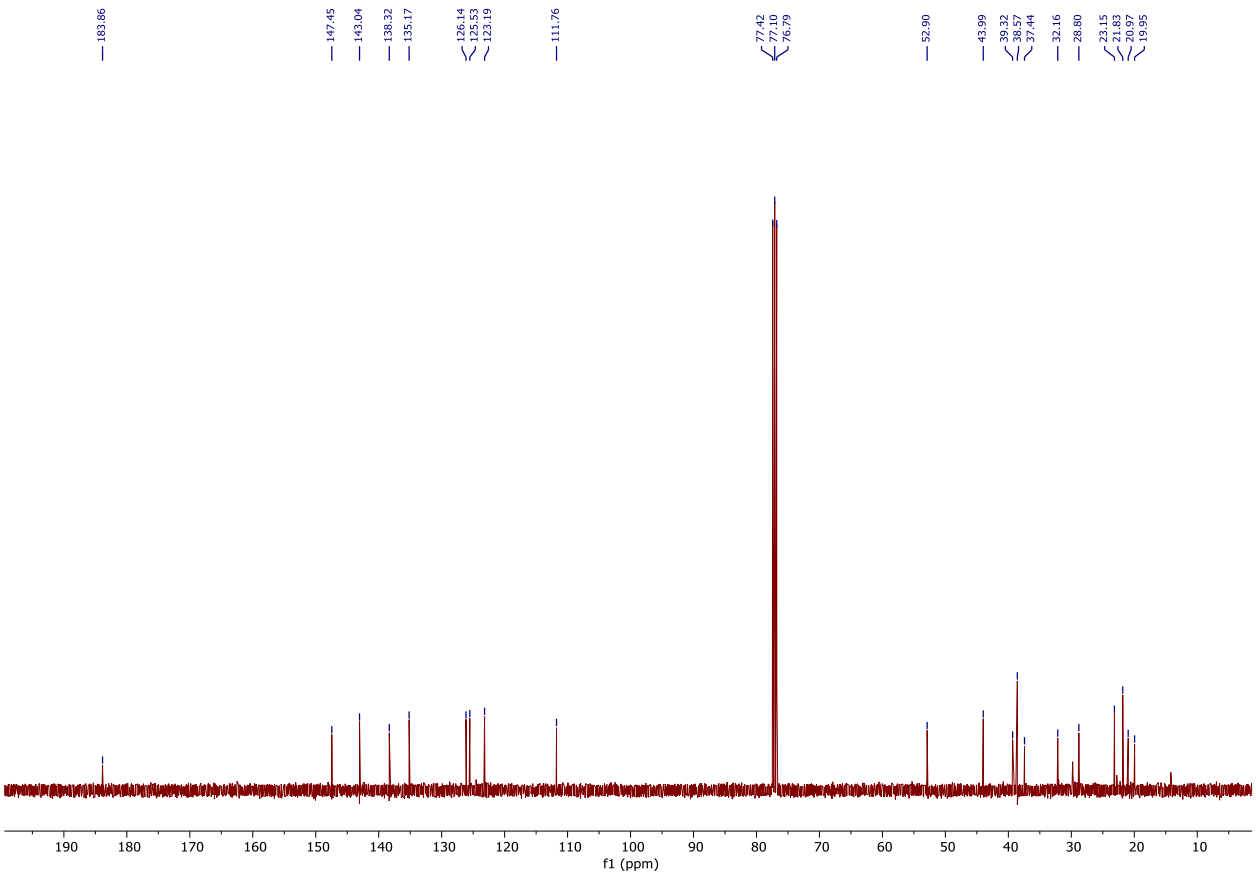
AB_MM_01-273.d

Bruker Compass DataAnalysis 4.1 printed: 10/8/2021 4:19:48 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**26**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**6**



^{13}C NMR (101 MHz, $CDCl_3$) of compound (+)-**6**

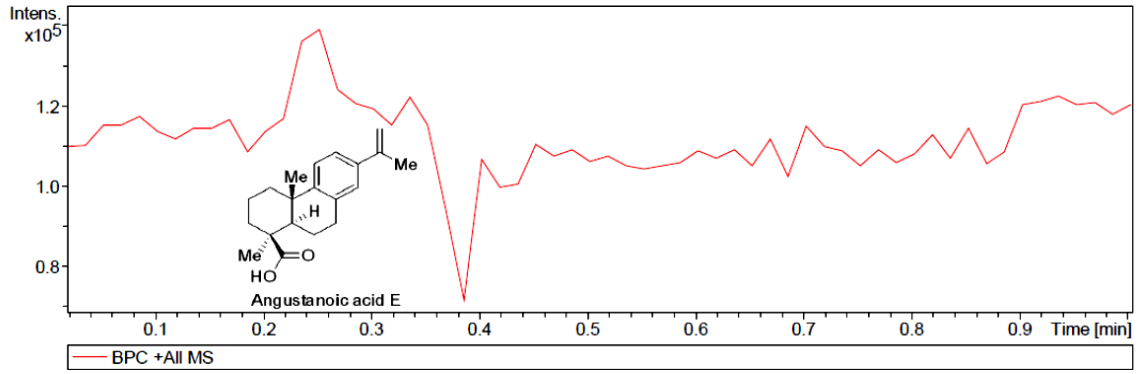
Display Report

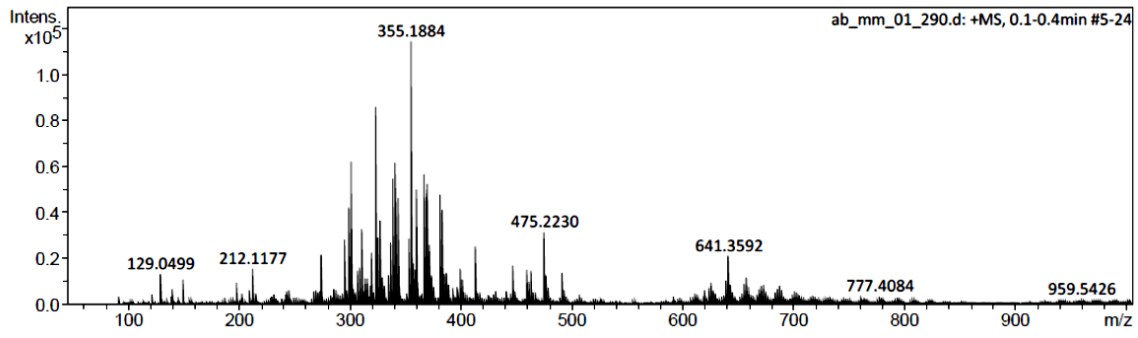
Analysis Info

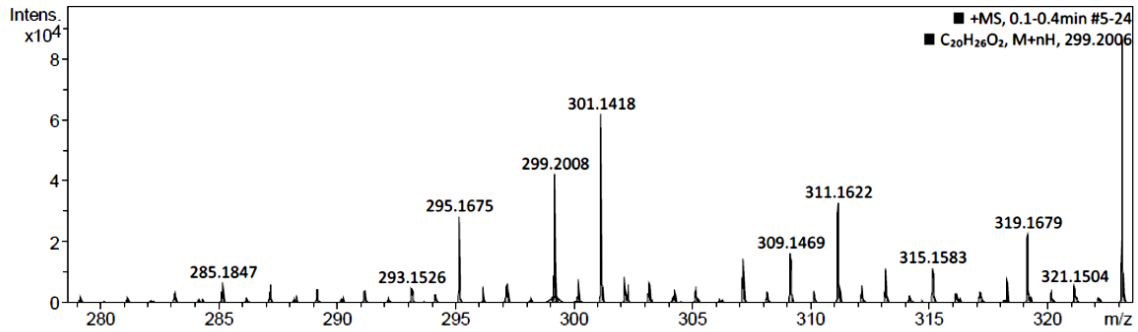
Analysis Name	D:\Data\User data\2021\NOV\ab_mm_01_290.d	Acquisition Date	11/22/2021 12:16:17 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_mm_01_290	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



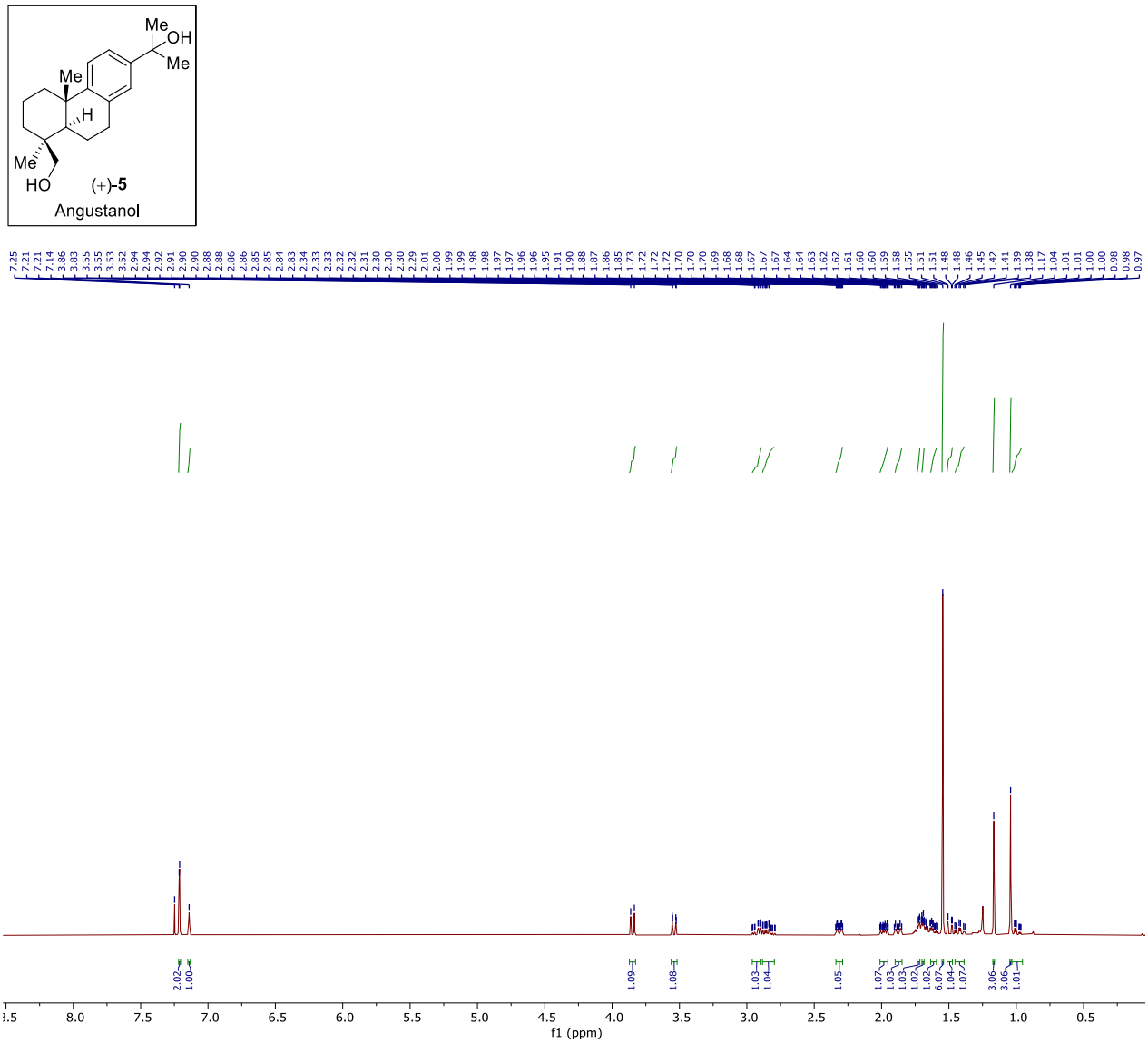




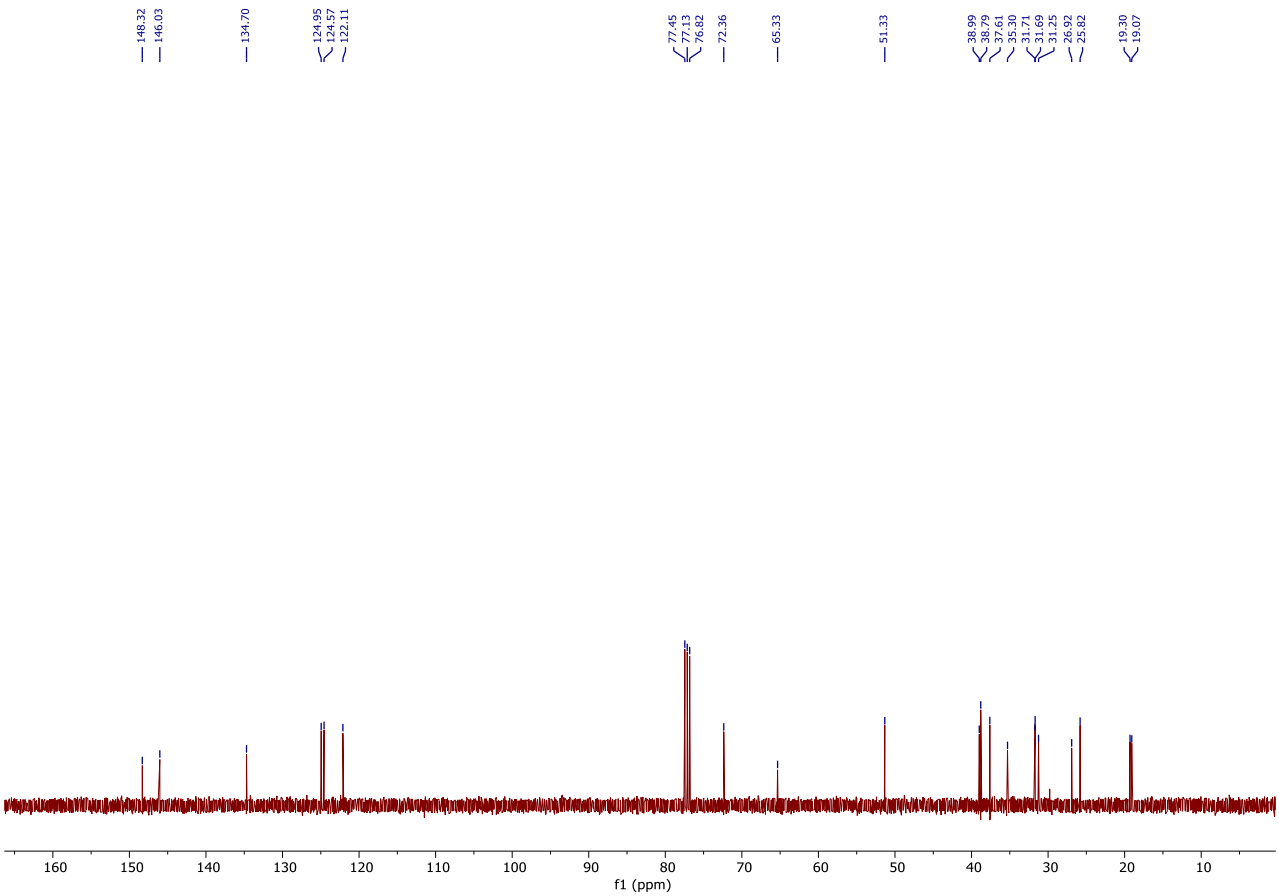
ab_mm_01_290.d

Bruker Compass DataAnalysis 4.1 printed: 11/22/2021 12:19:46 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**6**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (+)-**5**



^{13}C NMR (101 MHz, $CDCl_3$) of compound (+)-**5**

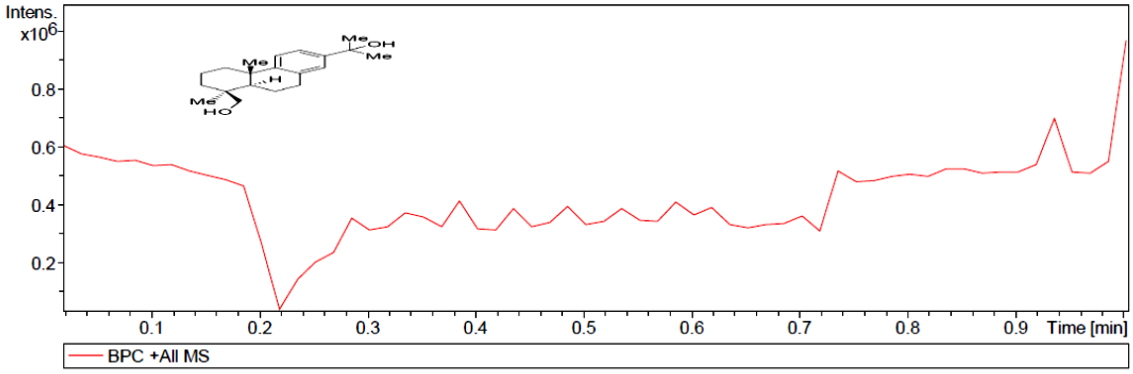
Display Report

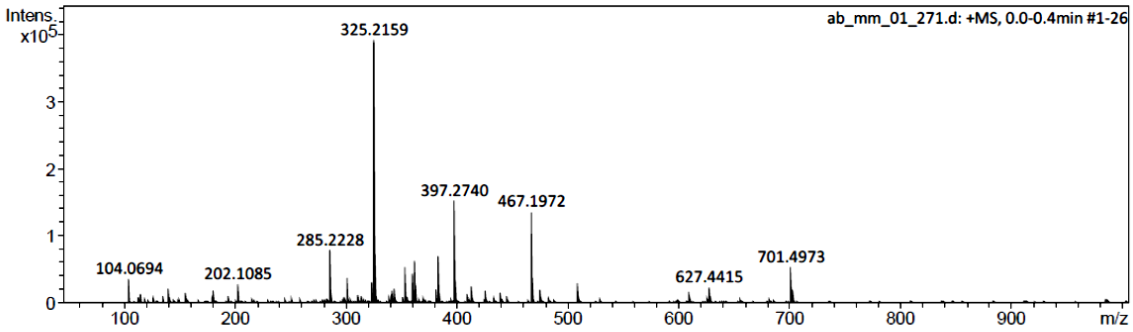
Analysis Info

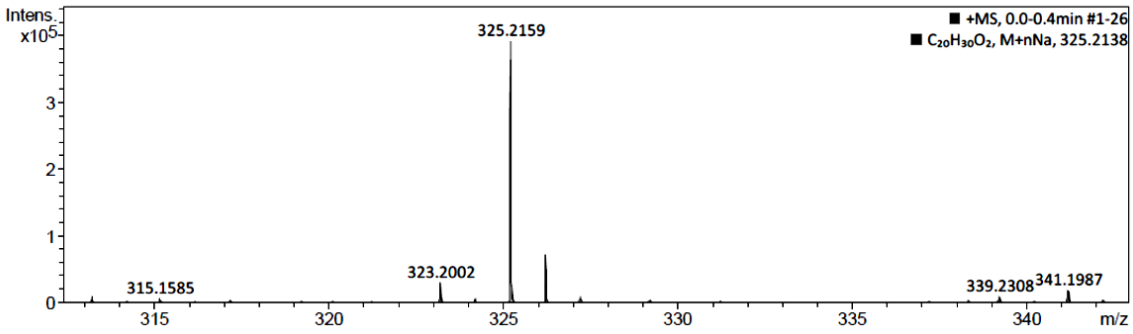
Analysis Name	D:\Data\User data\2021\OCTOBER\ab_mm_01_271.d	Acquisition Date	10/4/2021 12:21:08 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_mm_01_271	Instrument	maXis impact 8282001.00127
Comment	SIGNAL DROPPIN WHILE WASHING WITH MEOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



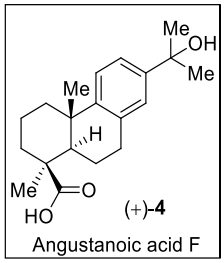


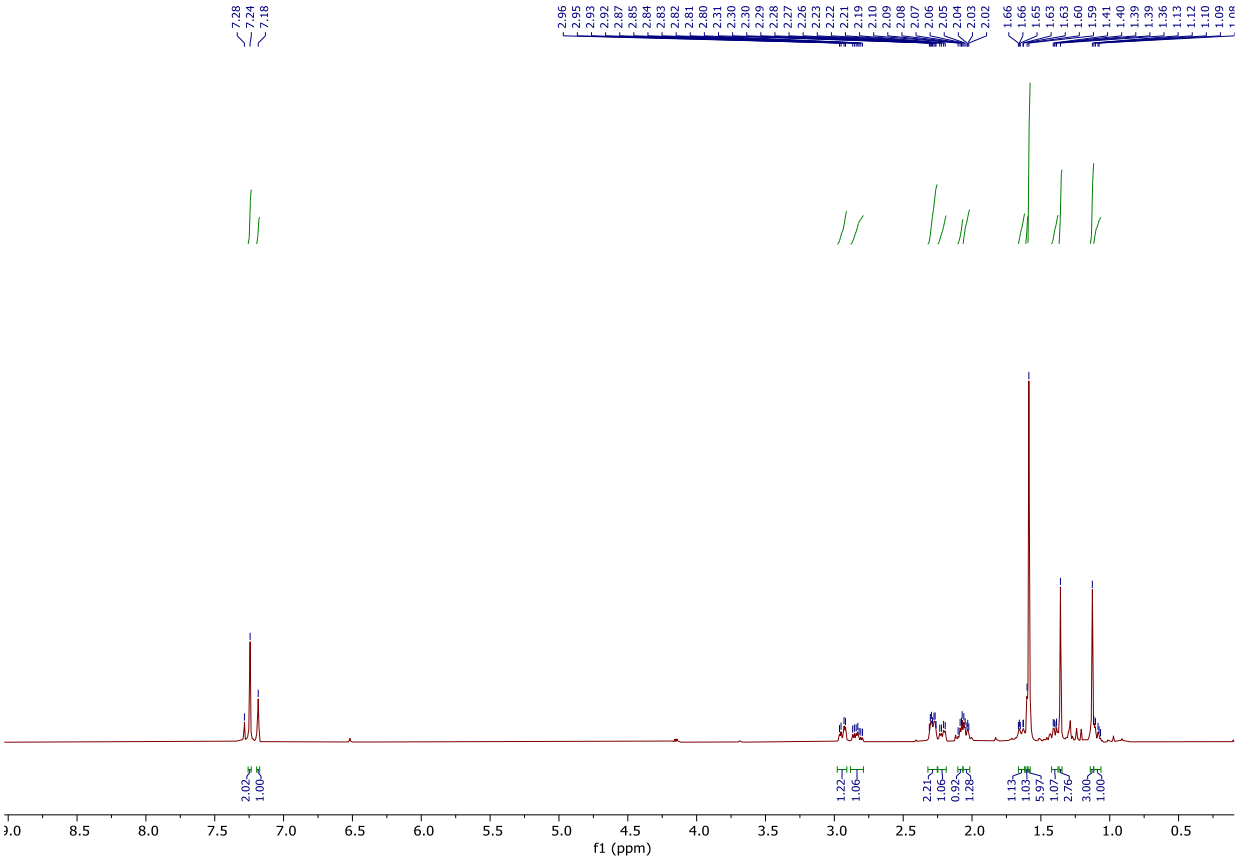


ab_mm_01_271.d

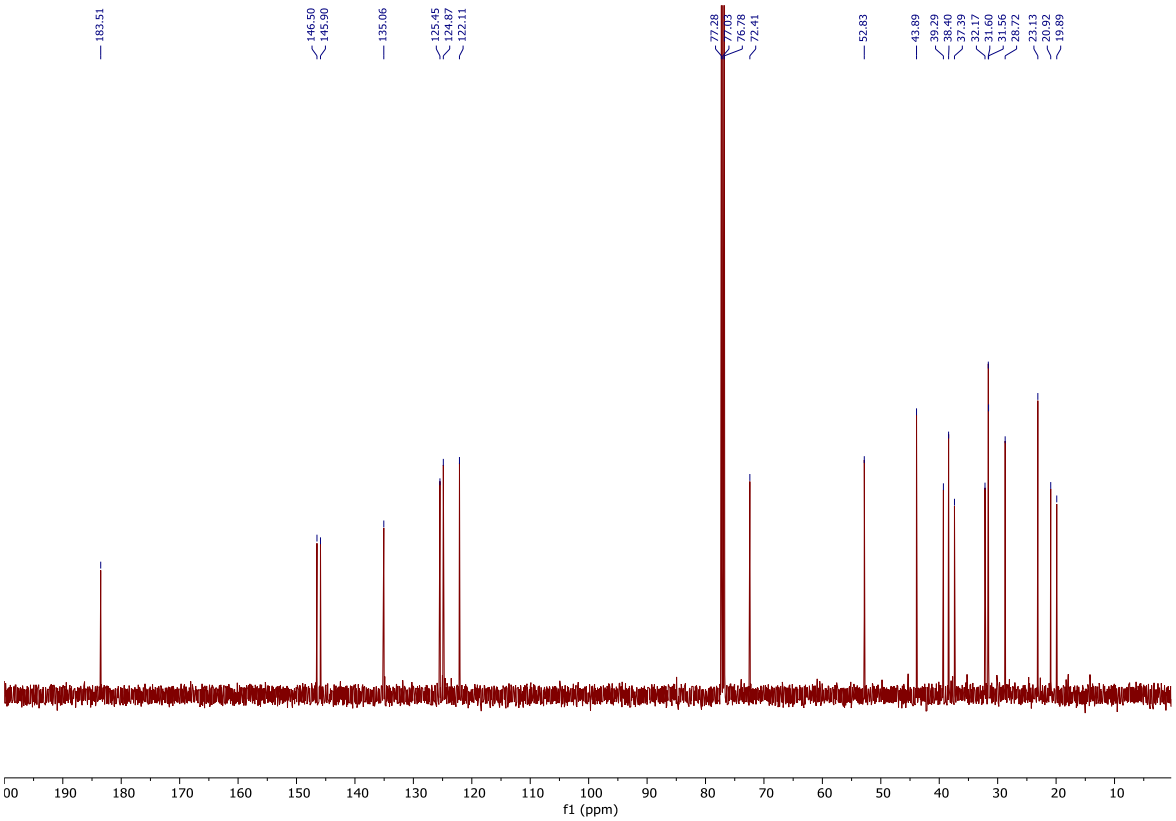
Bruker Compass DataAnalysis 4.1 printed: 10/4/2021 12:24:15 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**5**





^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**4**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**4**

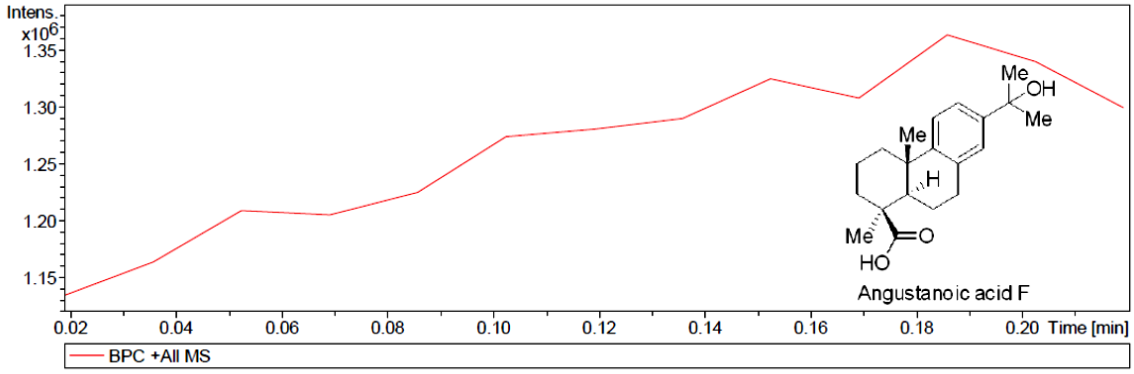
Display Report

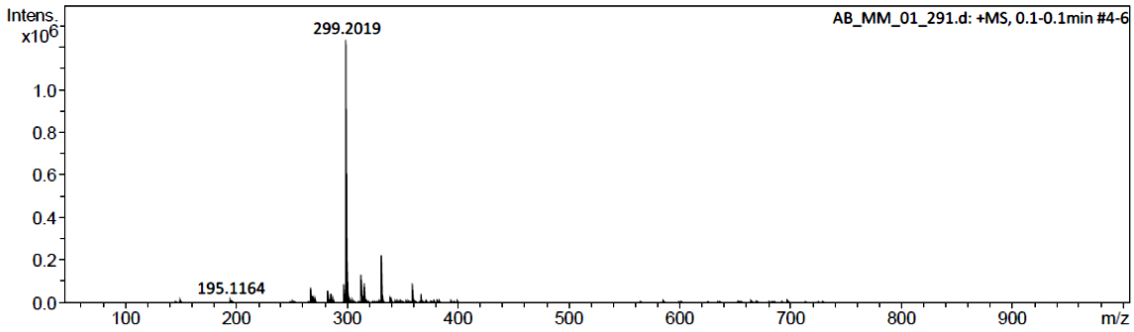
Analysis Info

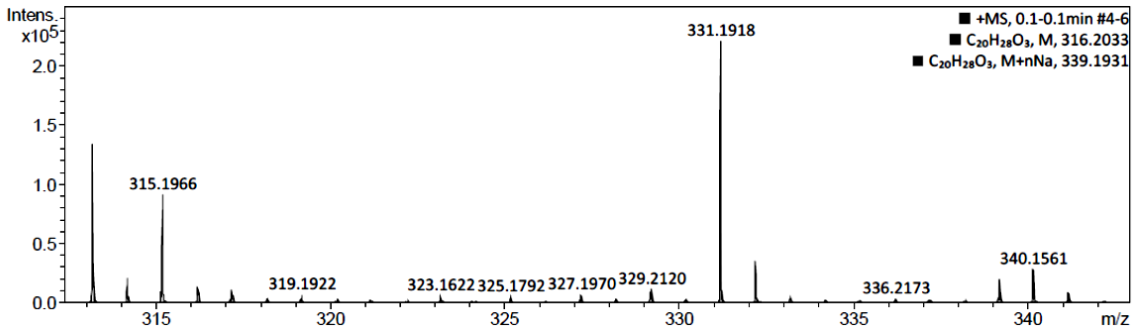
Analysis Name	D:\Data\User data\2022\JAN\AB_MM_01_291.d	Acquisition Date	1/3/2022 1:09:13 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_MM_01_291	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



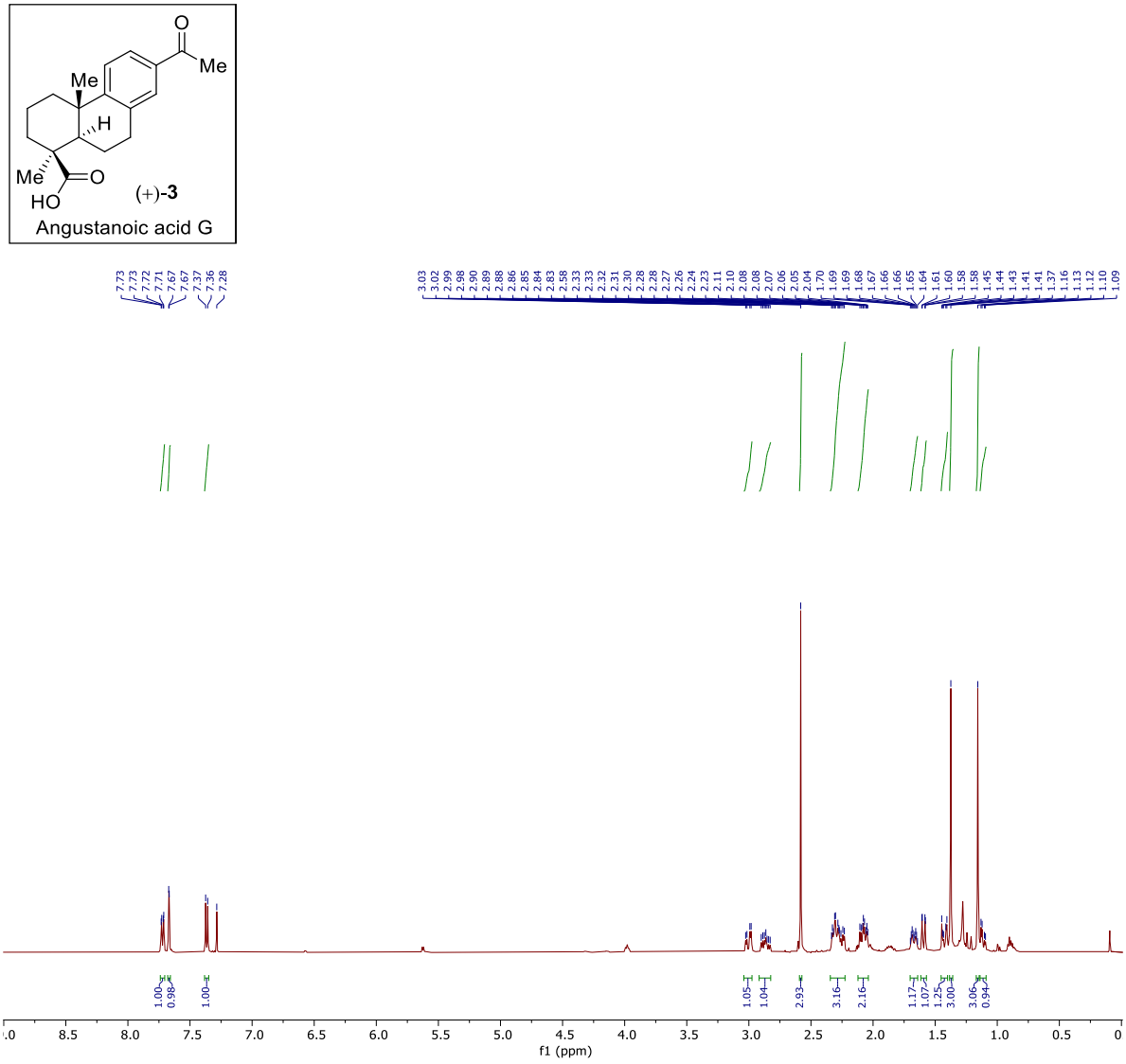




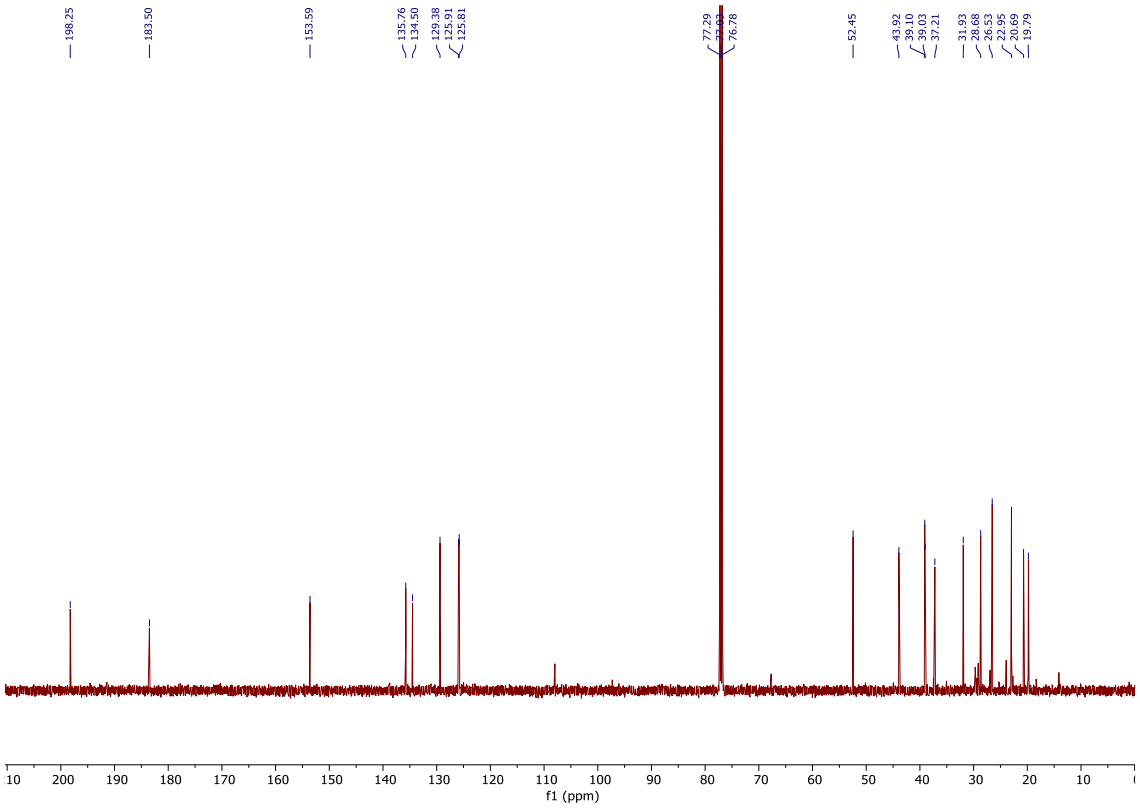
AB_MM_01_291.d

Bruker Compass DataAnalysis 4.1 printed: 1/3/2022 1:11:48 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**4**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**3**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**3**

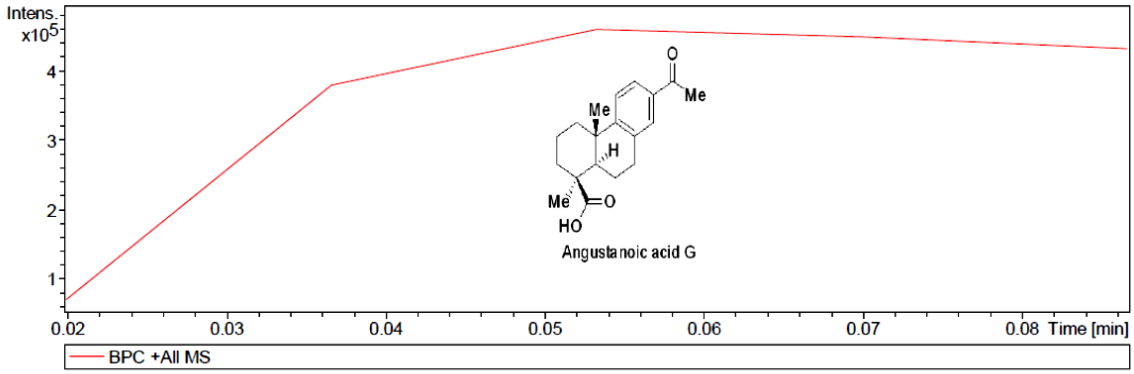
Display Report

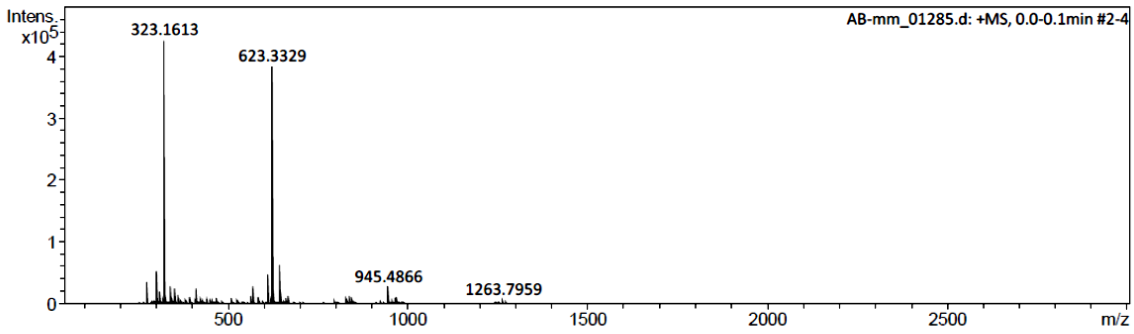
Analysis Info

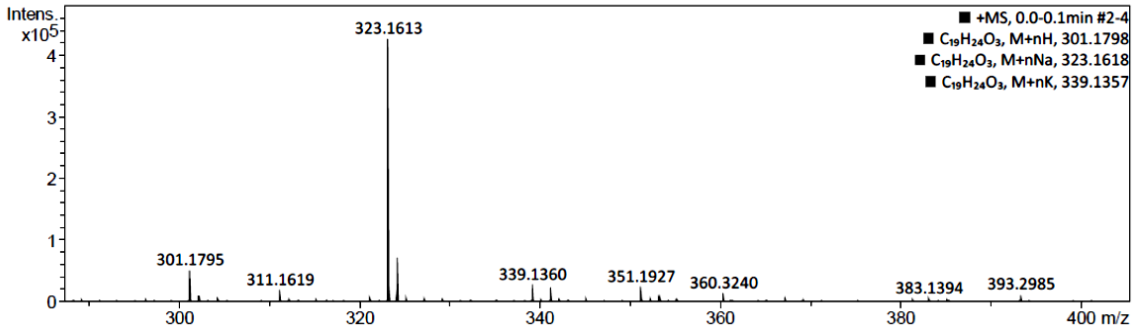
Analysis Name	D:\Data\User data\2021\NOV\AB-mm_01285.d	Acquisition Date	11/8/2021 9:34:37 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB-mm_01285	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



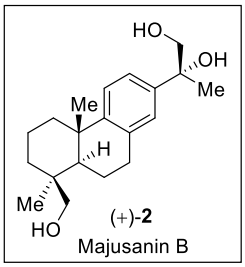


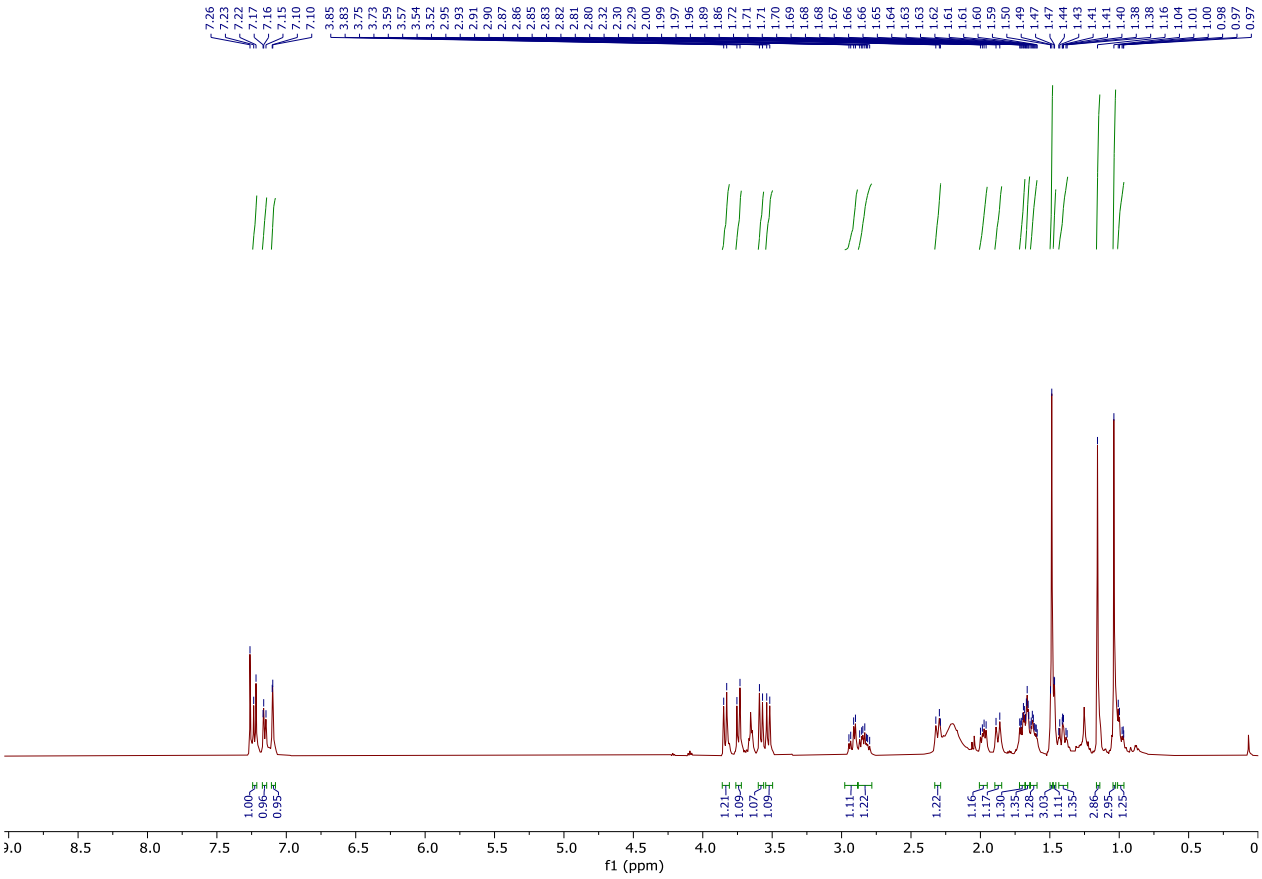


AB-mm_01285.d

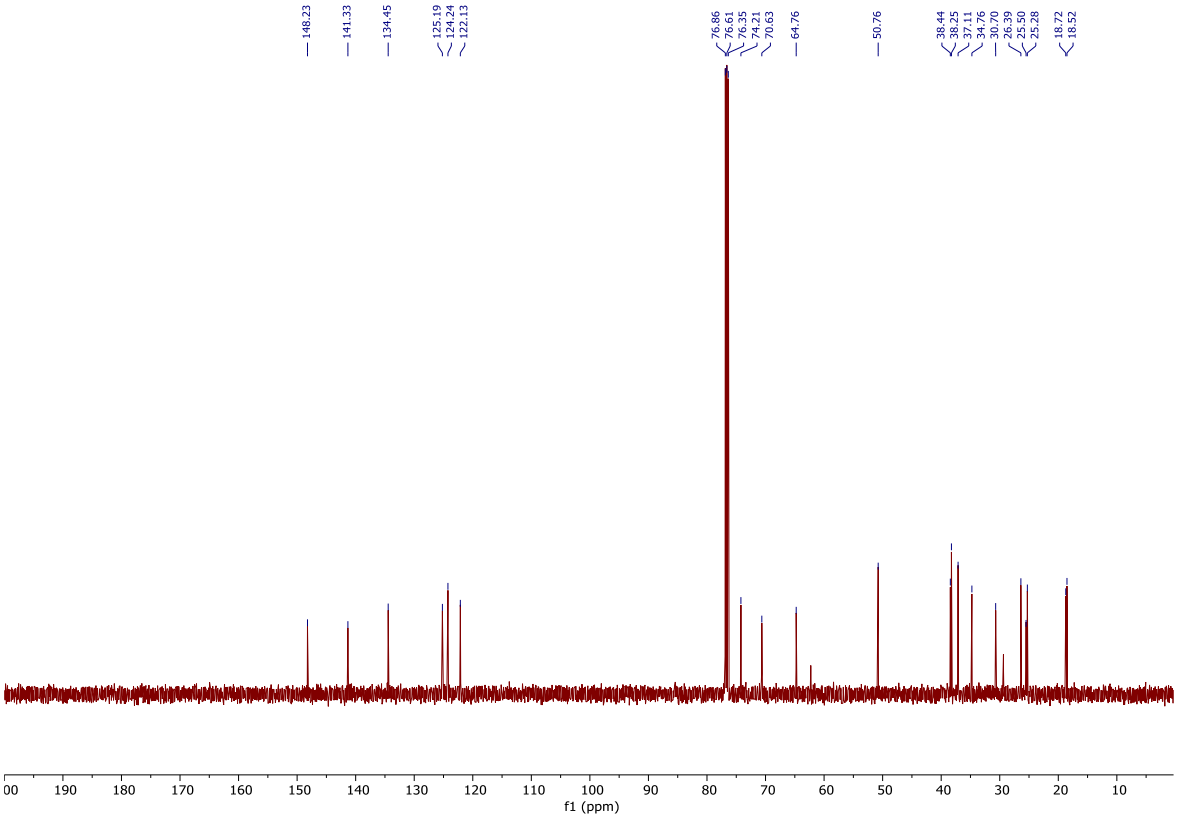
Bruker Compass DataAnalysis 4.1 printed: 11/8/2021 9:36:47 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**3**





^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**2**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**2**

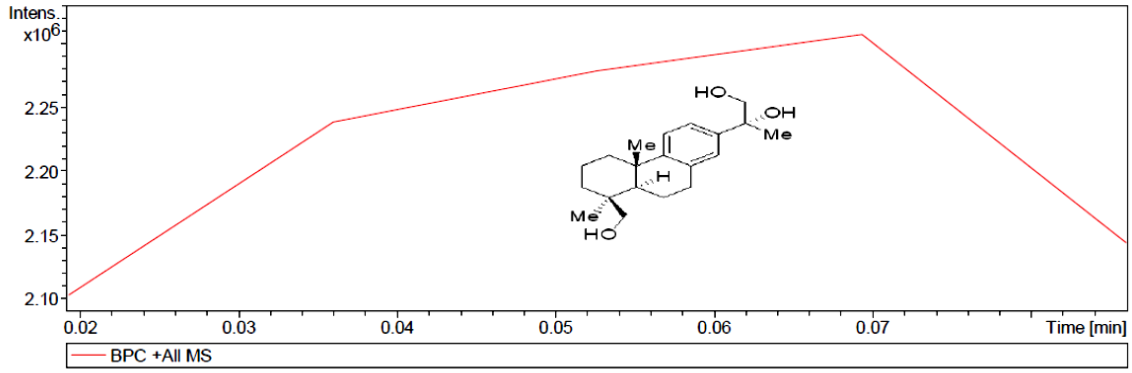
Display Report

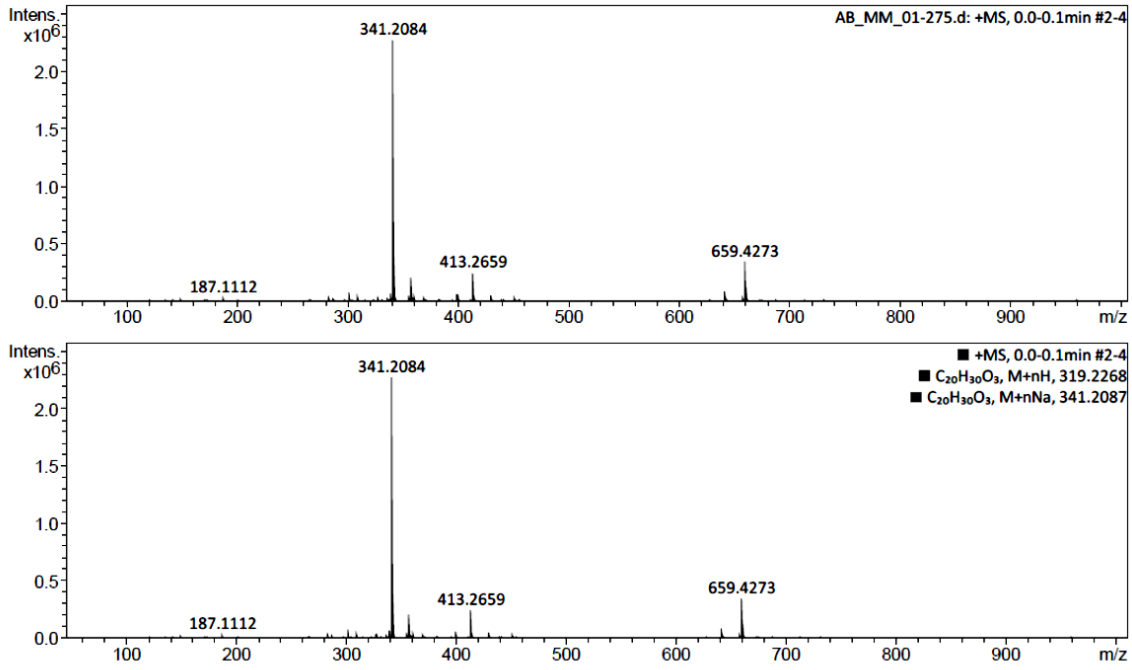
Analysis Info

Analysis Name	D:\Data\User data\2021\OCTOBER\AB_MM_01-275.d	Acquisition Date	10/21/2021 11:41:16 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_MM_01-275	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

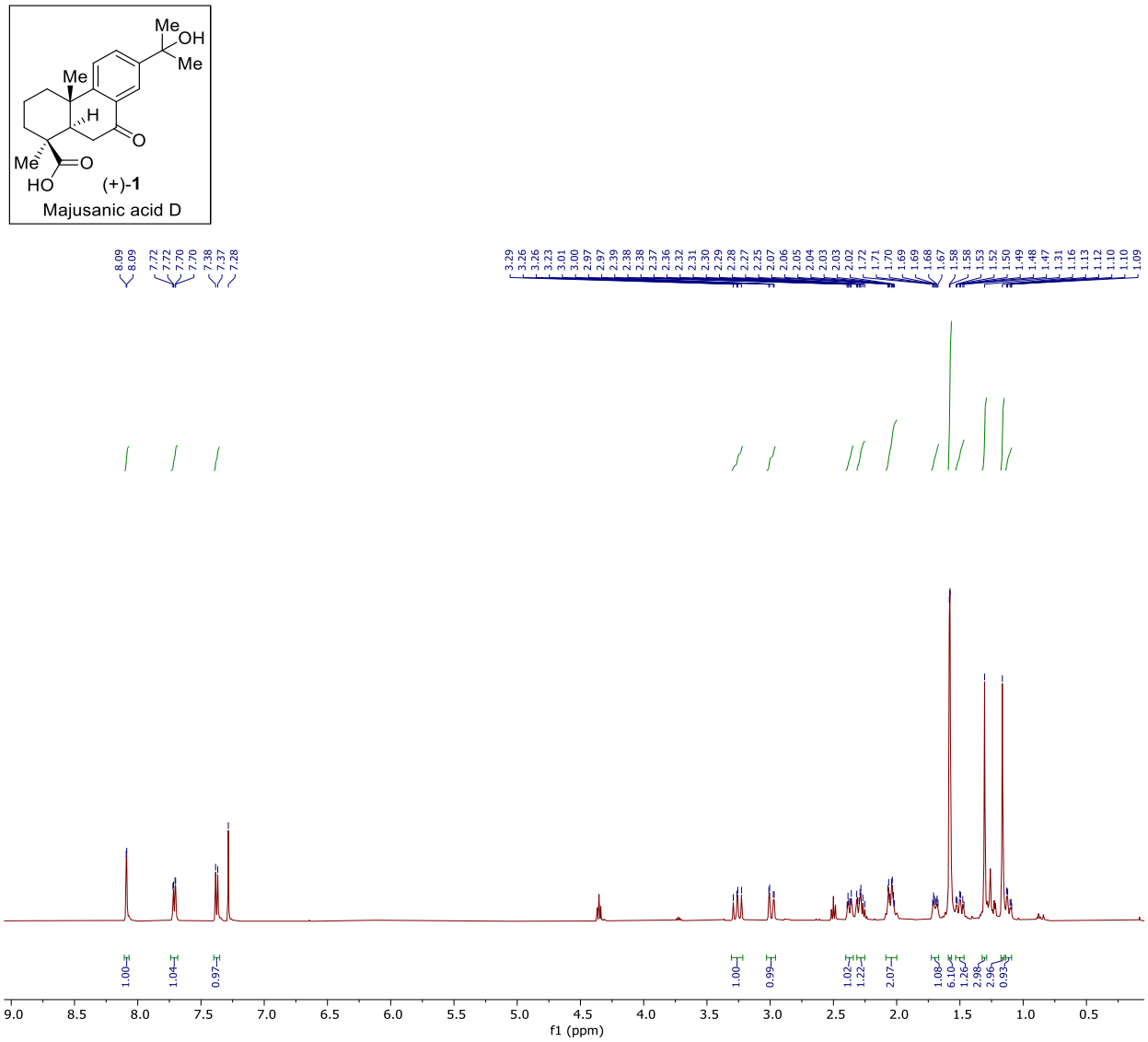




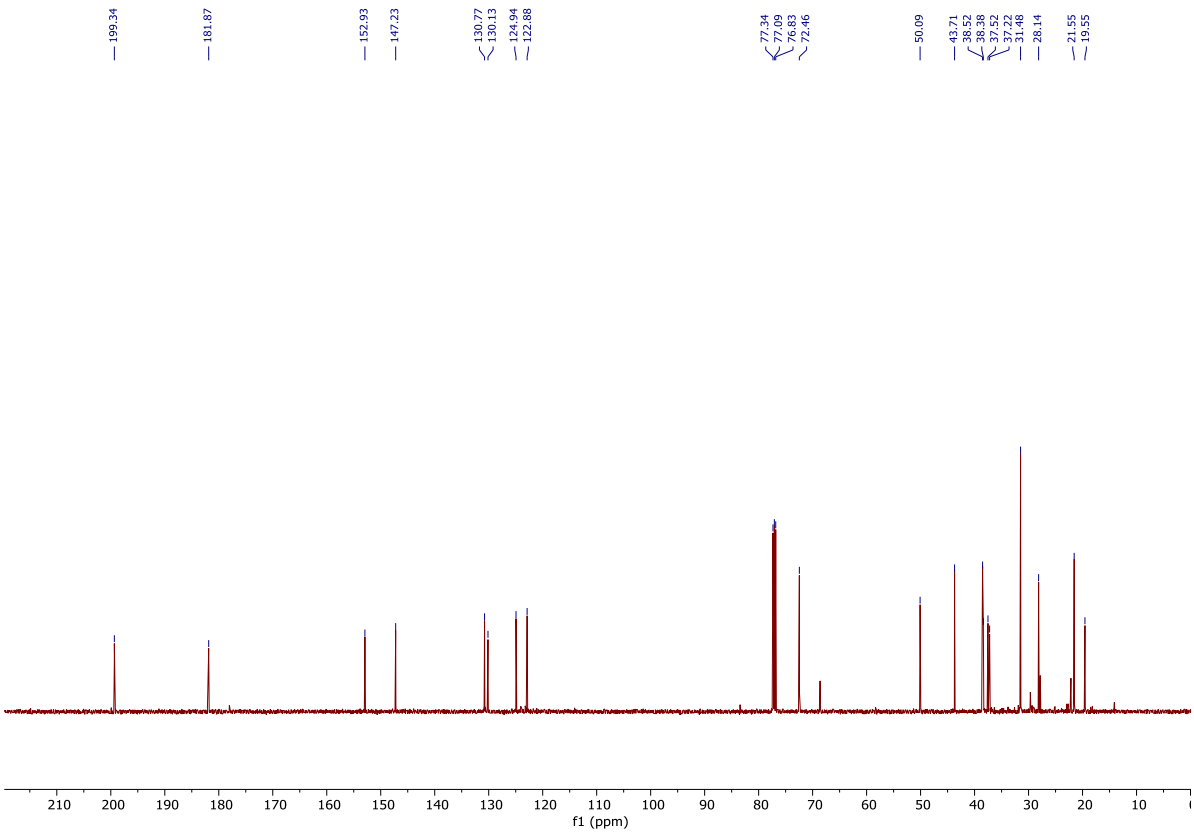
AB_MM_01-275.d

Bruker Compass DataAnalysis 4.1 printed: 10/21/2021 11:43:30 AM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**2**



^{1}H NMR (500 MHz, $CDCl_3$) of compound (+)-**1**



^{13}C NMR (125 MHz, $CDCl_3$) of compound (+)-**1**

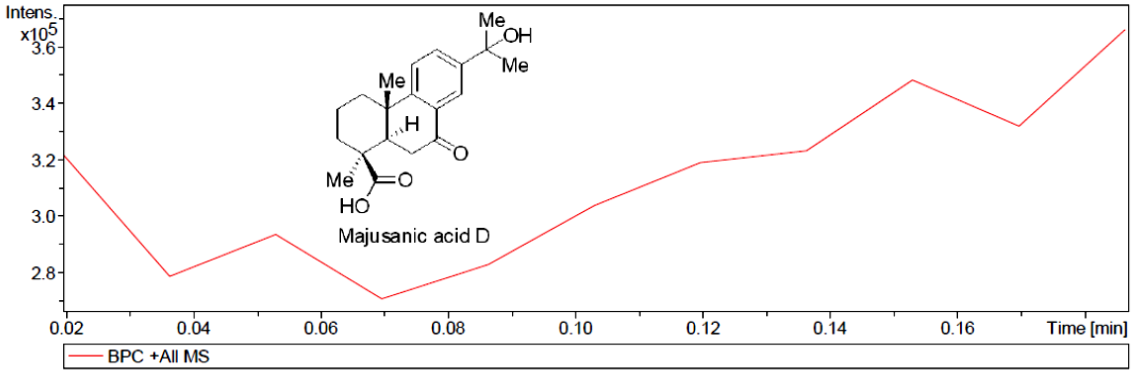
Display Report

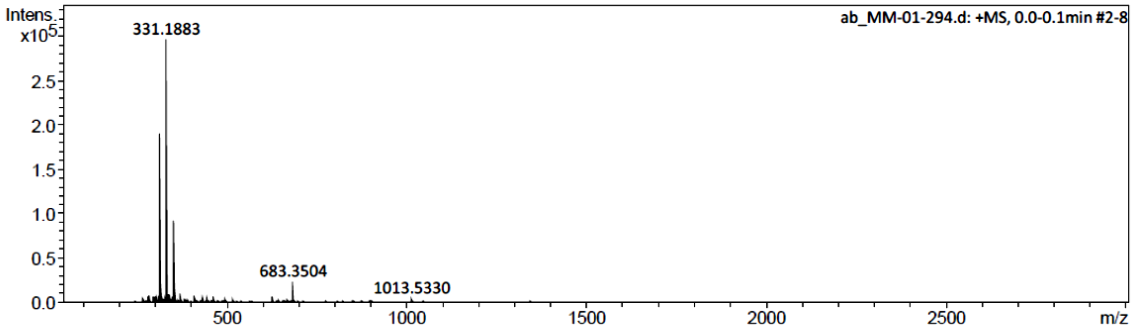
Analysis Info

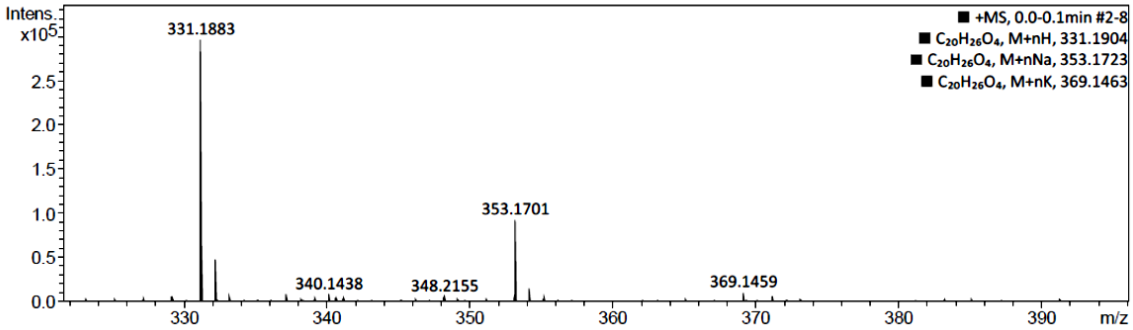
Analysis Name	D:\Data\User data\2022\JAN\ab_MM-01-294.d	Acquisition Date	1/3/2022 7:42:25 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	ab_MM-01-294	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C







ab_MM-01-294.d

Bruker Compass DataAnalysis 4.1 printed: 1/3/2022 7:46:47 PM by: IISER Kolkata Page 1 of 1

Scanned copy of mass spectrum of (+)-**1**