Supplemental material for:

Total Synthesis of Atropisomeric Indolosesquiterpenoids by N–N Bond Formation: Dixiamycins A and B

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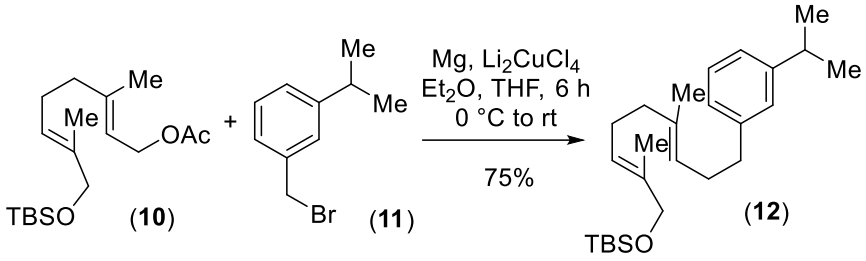
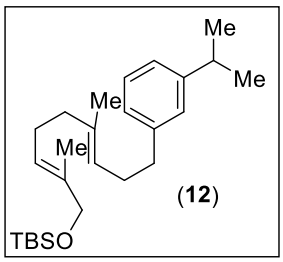
Materials and Methods

Unless otherwise stated, reactions were carried out using oven dried glass ware with Teflon coated magnetic stirring bars were used to stir the reactions. The Syringe was used to transfer the solvents and liquid reagents. Tetrahydrofuran (THF) Diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane CH_2Cl_2) was distilled over calcium hydride. All other solvents like MeOH, EtOAc, DMF, Dichloroethane (DCE) and reagents were used as received. Reaction temperatures above 25 °C were maintained by using oil bath on a magnetic stirrer. Thin layer chromatography (TLC) analysis was performed by using silica gel precoated plates (0.25 mm) 60 (F-254), Visualized by UV irradiation, yellow dip stain and other stains. Silica gel of particle size 230-400 and 100-200 mesh were used to perform flash chromatography. Digital melting point apparatus is used to record the melting points. ^{1}H-NMR spectra was recorded by using 400, 500 MHz spectrometers, ^{13}C-NMR operating frequencies are 100, 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvents ($CDCl_3$) signal (δ = 7.29 for 1H NMR and δ = 77.0 for ^{13}C NMR) and (CD_3OD) signal (δ = 3.33 for ^{1}H NMR and δ = 49.0 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 was recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. Optical rotations were measured on an automatic polarimeter. Enantiomeric excess was determined by chiral HPLC analysis performed on HPLC system with Daicel Chiralpak IC-3 column.

Cu-catalyzed Csp^3-Csp^3 bond formation (12):



In oven-dried round bottom flask Mg turnings (221 mg, 9.18 mmol, 1.5 equiv.) was taken in 8 mL diethyl ether solvent. To this solution, isopropyl benzyl bromide **11** (1.96 g, 9.18 mmol, 1.5 equiv.) in 10 mL Et_2O solvent was added drop wise manner and stirred the mixture for 1.5 h at room temperature. Then the mixture was cooled at 0 ^oC and Li_2CuCl_4 (6.12 mL, 0.612 mmol, 0.1 equiv.) was added slowly to it and stirred for another 10 min at the same temperature. Then acetate **10** (2 g, 6.12 mmol, 1.0 equiv.) in 8 mL THF solvent was added to the mixture drop wise manner over 10 minutes and stirred the reaction mixture for another 4 h at room temperature. After completion of the reaction (monitored by TLC), saturated aqueous NH_4Cl solution (10 mL) was added to the reaction mixture. The reaction mixture was then partitioned and extracted with EtOAc (15 mL X 2). The combined organic layers were concentrated in a rotary evaporator under reduced pressure and crude product was purified by flash column chromatography with 1.5% EtOAc in *n*-Hexane to afford **12** as light-yellow liquid (1.84 g, 75% yield).



***tert*-Butyl(((2*E*,6*E*)-9-(3-isopropylphenyl)-2,6-dimethylnona-2,6-dien-1 yl)oxy)dimethylsilane** [**12**]: **12** was obtained as light yellow liquid (6.12 mmol scale of reaction; 1.84 g; 75% yield). R_f = 0.6 (in *n*-hexane).

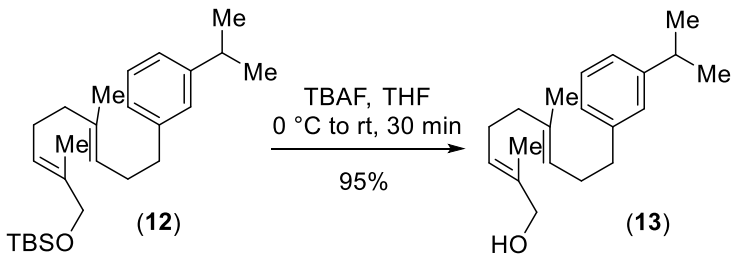
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 3.3 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 5.43 – 5.37 (m, 1H), 5.23 (t, *J* = 7.1 Hz, 1H), 4.03 (s, 2H), 2.90 (p, *J* = 6.9 Hz, 1H), 2.65 (t, *J* = 7.9 Hz, 2H), 2.33 (q, *J* = 7.6 Hz, 2H), 2.15 (q, *J* = 7.4 Hz, 2H), 2.04 (t, *J* = 7.7

Hz, 2H), 1.63 (s, 3H), 1.59 (s, 3H), 1.28 (d, *J* = 1.2 Hz, 3H), 1.27 (d, *J* = 1.1 Hz, 3H), 0.94 (d, *J* = 1.1 Hz, 9H), 0.09 (d, *J* = 1.1 Hz, 6H).

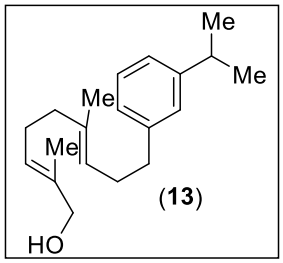
^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 142.4, 135.5, 134.3, 128.2, 126.6, 125.8, 124.4, 123.9,123.7, 68.7, 39.4, 36.2, 34.1, 30.0, 26.2, 25.9(2C), 24.1, 18.4, 15.9, 13.4, -5.2(3C).

IR (neat) υ_{max} 2858, 2785, 1683, 1498, 1095, 812 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{26}H_{44}OSi + Na]^+$ 423.3054, found 423.3086.

Synthesis of allyl alcohol compound 13 from compound 12:



In over-dried round bottom flask compound **12** (10.25 g, 25.60 mmol, 1.0 equiv.) was taken in 35 mL dry THF solvent and cooled at 0 °C. To the solution TBAF 1(M) in THF solution (28.16 mL, 28.16 mmol, 1.1 equiv.) was added drop wise at the same temperature and stirred the reaction mixture at room temperature for 30 minutes. After completion of reaction (monitored by TLC) purification of the crude mixture was completed using flash column chromatography with 10-20% EtOAc in *n*-Hexane to afford **13** as colorless liquid (6.96 g, 95% yields).



(*2E,6E***)-9-(3-Isopropylphenyl)-2,6-dimethylnona-2,6-dien-1-ol** [**13**]**: 13** was obtained as colorless liquid (25.6 mmol scale of reaction; 6.96 g; 95%). R_f = 0.2 (10% EtOAc in *n*-hexane).

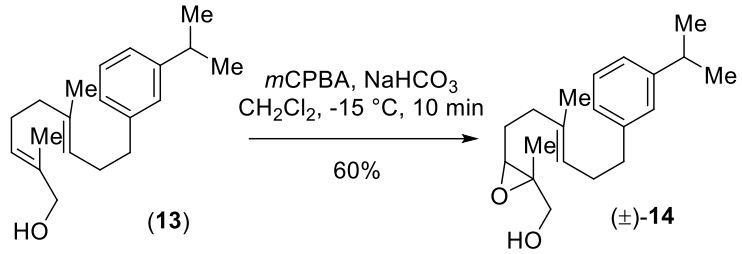
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 6.0 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 5.45 – 5.38 (m, 1H), 5.23 (t, *J* = 7.2 Hz, 1H), 4.02 (s, 2H), 2.91 (p, *J* = 6.9 Hz,

1H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.34 (q, *J* = 7.6 Hz, 2H), 2.16 (q, *J* = 7.6 Hz, 2H), 2.05 (t, *J* = 7.8 Hz, 2H), 1.70 (s, 3H), 1.60 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 142.3, 135.3, 134.7, 128.2, 126.6, 126.1, 125.8, 124.0,123.7, 69.0, 39.3, 36.2, 34.1, 29.9, 26.2, 24.1 (2C), 15.9, 13.7.

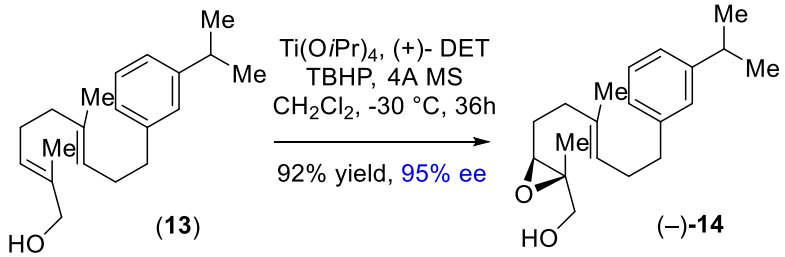
IR (neat) υ_{max} 3405, 2843, 1695, 1668, 1501, 1120 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{20}H_{30}O + Na]^+$ 309.2189, found 309.2199.

Synthesis of racemic epoxy-alcohol (±)**-14:**

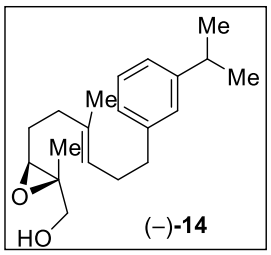


In an oven-dried round bottom flask allyl alcohol **13** (500 mg, 1.75 mmol, 1.0 equiv.) was taken in 6 mL CH_2Cl_2 and cooled to –15 °C. To this solution $NaHCO_3$ (147 mg, 3.5 mmol, 2.0 equiv.) was added followed by *m*CPBA (332 mg, 1.93 mmol, 1.1 equiv.) as solids. The reaction mixture was stirred at that temperature for 10 minutes. After completion of reaction (monitored by TLC), reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (2 mL). The biphasic layers were separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL X 2). The Organic layer was collected and dried over Na_2SO_4 and evaporated under reduced pressure. Now the crude product was purified by flash chromatography with 25% EtOAc in *n*-Hexane to afford epoxy alcohol (±)-**14** as light yellow coloured liquid (318 mg, 60% yield).

Synthesis of enantioselective epoxy-alcohol (–)**-14:**



In an oven-dried long neck round bottom flask 4Å MS was taken in 12 mL CH_2Cl_2. To it $Ti(o^{i}pr)_4$ (679 μL, 2.27 mmol, 0.1 equiv.) and (+)-diethyl-L-tartrate (467 μL, 2.72 mmol, 0.12 equiv.) were added at – 30 °C followed by addition of *t*-BuOOH (8.25 mL, 45.38 mmol, 2 equiv., 5.5 M in decane) simultaneously. The mixture was stirred vigorously at the same temperature for 20 min. Then allyl alcohol **13 (**6.5 g, 22.69 mmol, 1.0 equiv.) in 12 mL CH_2Cl_2 was added to this mixture drop wise manner and stirred for 36 h at the same temperature. After completion of reaction (monitored by TLC), reaction mixture was quenched with saturated aq. Na_2SO_3 solution (10 mL). Then the biphasic layer was extracted with CH_2Cl_2 (15 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 25% EtOAc in *n*-Hexane to afford epoxy alcohol (–)-**14** as light yellow colored liquid (6.31 g, 92% yield).



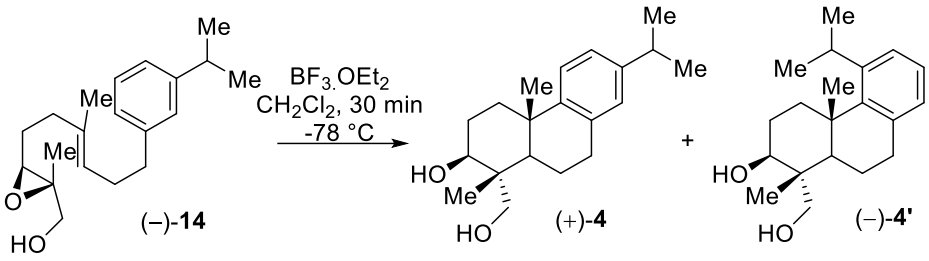
((*2S,3S***)-3-((***E***)-6-(3-Isopropylphenyl)-3-methylhex-3-en-1-yl)-2-methyloxiran-2-yl)methanol** [(–)-**14**]**:** (–)-**14** was obtained as light yellow coloured liquid (22.69 mmol scale of reaction; 6.31 g; 92%). R_f = 0.2 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 5.27 (t, *J* = 7.2 Hz, 1H), 3.69 (dd, *J* = 12.1, 3.9 Hz, 1H), 3.58 (dd, *J* = 12.2, 8.3 Hz, 1H), 3.04 (t, *J* = 6.3 Hz, 1H), 2.90 (p, *J* = 6.9 Hz, 1H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.34 (q, *J* = 7.6 Hz, 2H), 2.15 (dq, *J* = 21.9, 7.1 Hz, 2H), 1.70 (dt, *J* = 15.0, 7.8 Hz, 2H), 1.60 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 142.1, 134.5, 128.2, 126.6, 125.9, 124.6, 123.8, 65.4, 60.9, 59.9, 36.3, 36.1, 34.1, 29.9, 26.8, 24.1(2C), 15.9, 14.3.

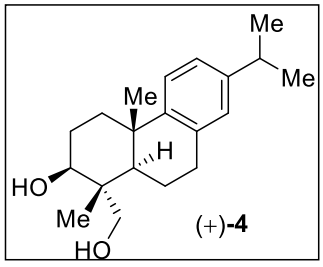
IR (neat) υ_{max} 3451, 2938, 1720, 1558, 1457, 1243, 915, 728 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{20}H_{30}O_2 + Na]^+$ 325.2138, found 325.2145.

Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IC-3 column; solvent: *n*-hexane/2-propanol = 99.5/0.5; flow rate: 1.00 mL/min; detection: at 270.0 nm: ^{t}Rmajor = 17.416 min, ^{t}Rminor = 18.554 min (ee = 95%); $[\alpha]^{20}_{589}$ = – 8.0 (*c* = 1.26, $CHCl_3$).

Total Synthesis of 4-*epi*-Triptobenzene L [(+)-4]:



In an oven-dried round bottom flask epoxy alcohol compound (–)-**14** (540 mg, 1.79 mmol, 1.0 equiv.) was taken in 8 mL CH_2Cl_2 and cooled at – 78 °C. To the solution 3 M solution of $BF_3.OEt_2$ (717 µL, 2.15 mmol, 1.2 equiv.) was added in a drop wise manner. The mixture was stirred at that temperature for 30 minutes and after completion of reaction (monitored by TLC) was quenched with saturated aqueous $NaHCO_3$ solution (5 mL). The biphasic layers were separated and the aqueous layer was extracted with CH_2Cl_2 (6 mL X 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash column chromatography with 22-30% EtOAc in *n*-Hexane to afford (+)-**4** (341 mg, 63% yields) along with (+)-**4'** (92 mg, 17% yield) as white foam.



(1*R*,2*S*,4a*S*,10a*R*)-**1-(Hydroxymethyl)-7-*i*sopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-ol** [(+)-**4**]: (+)-**4** was obtained as colourless gel (1.79 mmol scale of reaction; 341 mg; 63%). R_f = 0.23 (40% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.87 (s, 1H), 3.80 (d, *J* = 10.3 Hz, 1H), 3.70 (dd, *J* = 9.1, 7.1 Hz, 1H), 3.47 (d, *J* = 10.3 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.82 (m, 2H), 2.29 (dt, *J* = 13.1, 3.4 Hz, 1H), 1.83 – 1.76 (m, 3H), 1.74 – 1.69 (m, 1H), 1.57 – 1.49 (m, 1H), 1.44 (dd, *J* = 12.0, 2.6 Hz, 1H), 1.22 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H), 1.0 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 145.9, 134.6, 126.8, 124.4, 124.1, 76.9, 72.3, 44.7, 42.1, 37.3, 36.7, 33.5, 30.4, 27.6, 25.3, 24.0, 24.0, 19.2, 11.2.

IR (neat) ν_{max} 3654, 3340, 2845, 1671, 1541, 1481, 1250, 832 cm^{-1}.
HRMS (ESI) *m*/*z*: $[M+ Na]^+$ calcd. for $[C_{20}H_{30}O_2 + Na]^+$ 325.2138, found 325.2142.

$[\alpha]^{25}_{589}$ = +41.50 (*c* = 0.7, $CHCl_3$); lit.[1] $[\alpha]_D^{26}$= +52.1 (*c* = 1.0, $CHCl_3$), lit.[2] $[\alpha]_D^{20}$ = +50.9 (*c* = 0.31, $CHCl_3$).

Comparison of NMR Data of 4-*epi*-triptobenzene L [(+)-**4**] of this report with literature of (+)-**4** by Kanokmedhakul[1] and Carter[2]:

Comparison of ^{1}H-NMR Data:

Isolation report: (+)-4-*epi*-triptobenzene L [(+)-**4**] (^{1}H-NMR, 400 MHz, $CDCl_3$)[1]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.15	1H	d	*J* = 8.2 Hz
7.00	1H	dd	*J* = 8.2, 1.6 Hz
6.89	1H	d	*J* = 1.6 Hz
3.80	1H	ABd	*J* = 10.4 Hz
3.70	1H	dd	*J* = 9.2, 6.8 Hz

3.50	1H	ABd	*J* = 10.4 Hz
2.90	1H	m	-
2.83	1H	m	-
2.80	1H	sept	*J* = 6.8 Hz
2.30	1H	dt	*J* = 13.2, 3.4 Hz
1.80	3H	m	-
1.76	1H	m	-
1.53	1H	m	-
1.46	1H	dd	*J* = 11.8, 2.6 Hz
1.22	3H	d	*J* = 6.8 Hz
1.22	3H	d	*J* = 6.8 Hz
1.21	3H	s	-
1.00	3H	s	-

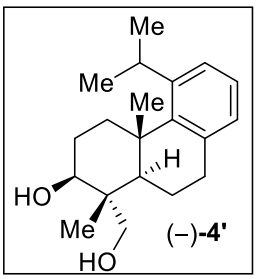
Carter's report (+)-4-*epi*-triptobenzene L [(+)-**4**] (^{1}H-NMR, 700 MHz, $CDCl_3$)[2]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.16	1H	d	*J* = 8.2 Hz
6.99	1H	d	*J* = 8.2 Hz
6.89	1H	s	-
3.82	1H	d	*J* = 10.3 Hz
3.71	1H	t	*J* = 8.1Hz
3.48	1H	d	*J* = 10.3 Hz
2.92	1H	dd	*J* = 17.0, 6.2 Hz
2.87 - 2.79	2H	m	-
2.31	1H	dt	*J* = 13.2, 3.4 Hz
1.84 - 1.76	1H	m	-
1.84 - 1.76	1H	m	-
1.84 - 1.76	1H	m	-

1.52-1.57	1H	m	-
1.44	1H	dd	J = 12.3, 2.0 Hz
1.22	3H	d	J = 6.8 Hz
1.22	3H	d	J = 6.8 Hz
1.21	3H	s	-
1.0	3H	s	-

This report (+)-4-*epi*-triptobenzene L [(+)-**4**] (^{1}H-NMR, 400 MHz, $CDCl_3$)			
δ (ppm)	Int.	mult.	J (Hz)
7.14	1H	d	J = 8.1 Hz
6.98	1H	d	J = 8.1 Hz
6.87	1H	s	-
3.80	1H	d	J = 10.3 Hz
3.70	1H	dd	J = 9.1, 7.1 Hz
3.47	1H	d	J = 10.3 Hz
2.95 – 2.87	1H	m	-
2.82	2H	m	-
2.29	1H	dt	J = 13.1, 3.4 Hz
1.83 – 1.76	3H	m	-
1.74 – 1.69	1H	m	-
1.57 – 1.49	1H	m	-
1.44	1H	dd	J = 12.0, 2.6 Hz
1.22	3H	s	-
1.21	3H	s	-
1.20	3H	s	-
1.0	3H	s	-

Comparison of ^{13}C-NMR Data:

Isolation report on (+)-4-*epi*-triptobenzene L [(+)-**4**] (^{13}C NMR, 100 MHz, $CDCl_3$)[1]	Carter's report on (+)-4-*epi*-triptobenzene L [(+)-**4**] (^{13}C NMR, 175 MHz, $CDCl_3$)[2]	This report: (+)-4-*epi*-triptobenzene L [(+)-**4**] (^{13}C NMR, 100 MHz, $CDCl_3$)
146.5	146.5	146.6
145.8	145.9	145.9
134.2	134.5	134.6
126.7	126.8	126.8
124.3	124.3	124.4
123.9	124.0	124.1
76.8	76.9	76.9
72.2	72.4	72.3
44.6	44.6	44.7
42.1	42.1	42.1
37.2	37.2	37.3
36.8	36.6	36.7
33.4	33.5	33.5
30.3	30.4	30.4
27.5	27.6	27.6
25.2	25.2	25.3
23.9	24.0	24.0
23.9	24.0	24.0
19.1	19.1	19.1
11.1	11.1	11.2



(–)-**4'**

(1*R*,2*S*,4a*S*)-**1-(Hydroxymethyl)-5-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-ol** [(–)-**4'**]: (–)-**4'** was obtained as white foam (1.79 mmol scale of reaction; 92 mg; 17%). R_f = 0.25 (40% EtOAc in *n*-hexane).

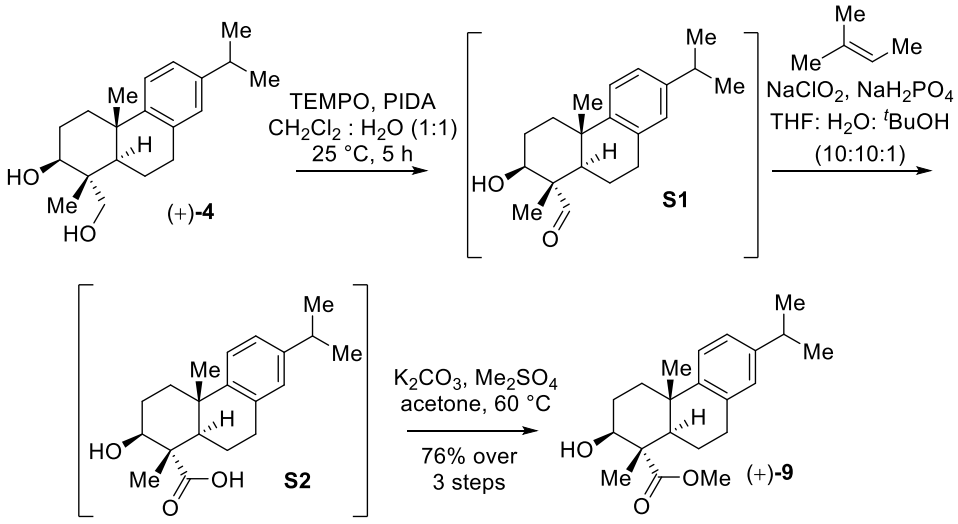
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dt, *J* = 7.5, 4.6 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 10.8 Hz, 1H), 3.97 (d, *J* = 11.0 Hz, 1H), 3.86 (d, *J* = 10.5 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 2.91 (p, *J* = 7.1 Hz, 1H), 2.64 (t, *J* = 8.7 Hz, 2H), 2.27 (dtt, *J* = 34.6, 17.1, 8.3 Hz, 4H), 2.09 – 2.01 (m, 1H), 1.86 – 1.77 (m, 1H), 1.75 (s, 3H), 1.71 (s, 1H), 1.30 – 1.27 (m, 6H), 1.10 (d, *J* = 2.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 142.4, 132.2, 131.0, 128.5, 126.4, 125.5, 123.9, 73.8, 69.8, 45.1, 36.2, 34.1, 31.0, 27.0, 24.1, 19.9, 15.9.

IR (neat) υ_{max} 3362, 3349, 2954, 1665, 1501, 1460, 1071, 821 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{20}H_{30}O_2 + Na]^+$ 325.2138, found 325.2140.

$[\alpha]^{25}_{589}$ = –36.67 (*c* = 0.63, $CHCl_3$).

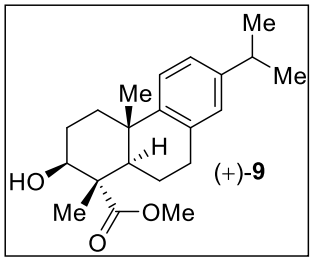
Synthesis of β-hydroxy ester (+)-**9:**



Diol (+)-**4** (4.85 g, 16.04 mmol, 1.0 equiv.) was taken in a mixture of CH_2Cl_2: H_2O (1:1, 20 mL) at room temperature. To this solution was added TEMPO (3.23 g, 20.85 mmol, 1.3 equiv.) and stirred for 5 minutes. Next, PIDA (6.71 g, 20.85 mmol, 1.3 equiv.) was added portion wise to the reaction mixture. The resulting orange-brown mixture was vigorously stirred for an additional 5 h at the same temperature. After completion of reaction (monitored by TLC) saturated aqueous $NaHCO_3$ (8 mL) was added and excess oxidants were quenched with $Na_2S_2O_3$ (8 mL) and stirred for 5 more minutes. The mixture was extracted with dichloromethane (15 mL X 2). The organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum to afford crude β-hydroxy aldehyde **S1** which was taken for next step without further purification.

β-hydroxy aldehyde **S1** (16.04 mmol, 1.0 equiv.) was taken in a mixture of tetrahydrofuran, *tert*-butanol and water [THF: H_2O: ^{t}BuOH (10:10:1)] at 25 °C and 2-methyl-2-butene (17 mL, 160.4 mmol, 10.0 equiv.) was added to the reaction vessel. After 5 minutes of stirring, NaH_2PO_4 (9.62 g, 80.2 mmol, 5.0 equiv.) was added to the reaction mixture and it was cooled to 0 °C. Then $NaClO_2$ (4.35 g, 48.12 mmol, 3.0 equiv.) was added portion wise over a period of 10 minutes. The reaction mixture was allowed to warm to 25 °C and stirring was continued for an additional 2 h. After complete consumption of the starting material (as judged by TLC), it was diluted with water and pH<3 was maintained by addition of 2(*N*) HCl. Next, mixture was extracted with EtOAc (15 mL X 3) and organic layer was dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum to afford β-hydroxy acid **S2** which was taken for the next step without further purification.

In an oven-dried round-bottom flask, crude **S2** (16.04 mmol, 1.0 equiv.) was dissolved in acetone (18 mL) and Me_2SO_4 (1.82 mL, 19.25 mmol, 1.2 equiv.) was added at 25 °C. Next, K_2CO_3 (2.7 g, 19.25 mmol, 1.2 equiv.) was added to the reaction mixture portion wise over a period of 5 minutes and it was placed on a pre-hated oil bath maintaining temperature at 60 ^{o}C and stirring was continued for 2 h. After completion of the reaction (monitored by TLC), 8 mL water was added and it was filtered through a celite bed and solids were washed with 40% EtOAc in *n*-hexane (20 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The residue was purified by flash column chromatography using 20% EtOAc in *n*-hexane to afford β-hydroxy ester (+)-**9** as white foam (4.03 g, 76% yield over 3 steps).



Methyl (1*S*,2*S*,4a*S*,10a*R*)-**2-hydroxy-7-*i*sopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**9**]: (+)-**9** was obtained as white foam (16.04 mmol scale; 4.03 g; 76% yield). R_f = 0.20 (20% EtOAc in *n*-hexane).

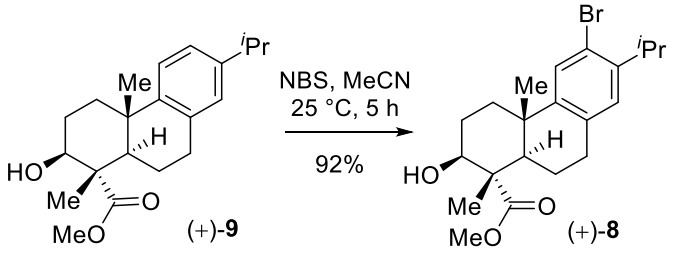
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.1 Hz, 1H), 7.02 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 4.06 (dd, *J* = 11.7, 4.6 Hz, 1H), 3.75 (s, 3H), 2.90 (dt, *J* = 9.9, 4.6 Hz, 2H), 2.84 (m, *J* = 6.9 Hz, 1H), 2.36 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.15 (dd, *J* = 12.5, 2.2 Hz, 1H), 1.96 – 1.86 (m, 2H), 1.86 – 1.80 (m, 1H), 1.67 (dd, *J* = 13.3, 3.9 Hz, 1H), 1.44 (ddt, *J* = 13.0, 5.6, 2.6 Hz, 1H), 1.28 (s, 3H), 1.25 (s, 3H), 1.23 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 146.1, 146.0, 134.5, 126.8, 124.3, 124.1, 75.2, 53.8, 52.2, 45.5, 36.7, 36.6, 33.5, 30.1, 27.3, 25.2, 23.9 (2C), 21.4, 10.7.

IR (neat) υ_{max} 3350, 1703, 1665, 1480, 1121, 885, 718 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{21}H_{30}O_3 + Na]^+$ 353.2087, found 353.2096.

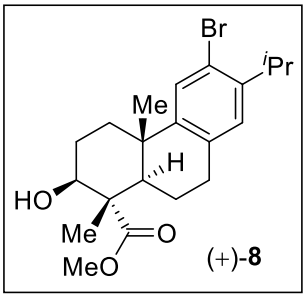
$[\alpha]^{20}_{589}$ = +40.5 (*c* = 0.87, $CHCl_3$).

Aromatic Electrophilic Bromination of (+)**-9:**



In an oven dried round-bottom flask compound (+)-**9** (3.5 g, 10.6 mmol, 1.0 equiv.) was taken in CH_3CN (30 mL) at 25 °C under an argon atmosphere. To this solution was added a recrystallized *N*-bromo succinimide [NBS (2.26 g, 12.72 mmol, 1.2 equiv.)] at 25 °C and stirred for an additional 5 h. After completion of the reaction (confirmed by TLC analysis), it was

quenched with saturated aqueous $Na_2S_2O_3$ solution (5 mL). The reaction mixture was then extracted with 50% EtOAc in *n*-hexane (30 mL X 2). The organic layers were collected, dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. It was purified by flash chromatography using 25% EtOAc in *n*-hexane to afford (+)-**8** as white foam (4 g, 92% yield).



Methyl (1*R*,2*S*,4a*S*,10a*R*)-**6-bromo-2-hydroxy-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**8**]**:** (+)-**8** was obtained as white foam (10.6 mmol scale; 4 g; 92% yield). R_f = 0.37 (30% EtOAc in *n*-hexane).

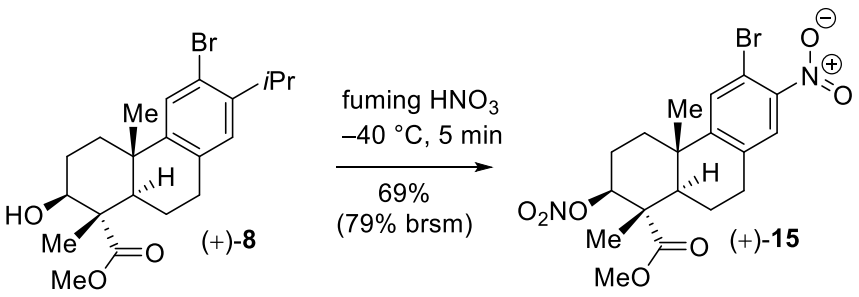
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.91 (s, 1H), 4.02 (dd, *J* = 11.8, 4.6 Hz, 1H), 3.72 (s, 3H), 3.25 (h, *J* = 6.8 Hz, 1H), 2.87 (ddd, *J* = 12.2, 6.4, 2.6 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.28 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.88 (dt, *J* = 11.6, 4.3 Hz, 2H), 1.82 – 1.75 (m, 1H), 1.64 (dd, *J* = 13.4, 3.6 Hz, 1H), 1.42 (ddq, *J* = 12.5, 7.9, 3.1, 2.6 Hz, 1H), 1.24 (s, 3H), 1.22 (d, *J* = 3.2 Hz, 3H), 1.20 (d, *J* = 2.4 Hz, 3H), 1.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6, 148.1, 144.3, 134.2, 128.7, 127.0, 121.6, 75.1, 53.6, 52.3, 45.2, 36.8, 36.4, 32.3, 29.6, 27.1, 25.1, 22.9, 22.8, 21.1, 10.7.

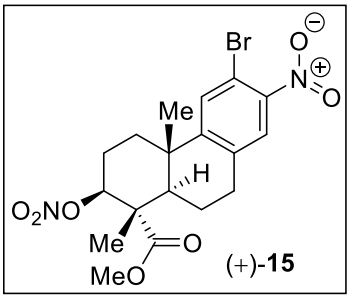
IR (neat) υ_{max} 3347, 1710, 1690, 1520, 1147, 1025, 785 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{21}H_{29}O_3Br + Na]^+$ 431.1192, found 431.1170.

$[\alpha]^{25}_{589}$ = +37.2 (*c* = 0.82, $CHCl_3$).

***ipso*-Nitration of** (+)-**8:**



An oven-dried round-bottom flask was charged with 2 mL of fuming nitric acid and it was cooled to – 40 °C. Then compound (+)-**8** (800 mg, 1.95 mmol, 1.0 equiv.) was directly charged into the reaction vessel and scratched well with a spatula (5 minutes) maintaining the – 40 °C temperature. After 5 minutes (TLC analysis showed product formation), the reaction mixture was quenched with water (5 mL) and saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (20 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure and purified by column chromatography 10% EtOAc in *n*-hexane to afford compound (+)-**15** as yellow foam [615 mg, 69% yield (79% BRSM)].



Methyl (1*S*,2*S*,4a*S*,10a*R*)-**6-bromo-1,4a-dimethyl-7-nitro-2-(nitrooxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**15**]**:** (+)-**15** was obtained as a yellow foam. (1.95 mmol scale, 615 mg, 69% yield); R_f = 0.31 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.57 (s, 1H), 5.45 (dd, *J* = 12.2, 4.3 Hz, 1H), 3.76 (s, 3H), 2.99 (dd, *J* = 17.9, 6.9 Hz, 1H), 2.89 (dt, *J* = 18.1, 9.3 Hz, 1H), 2.45 (d, *J* = 13.3 Hz, 1H), 2.19 (dd, *J* = 18.6, 12.8 Hz, 2H), 2.04 – 1.90 (m, 2H), 1.82 (t, *J* = 13.6 Hz, 1H), 1.52 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.34 (s, 3H), 1.28 (s, 3H).

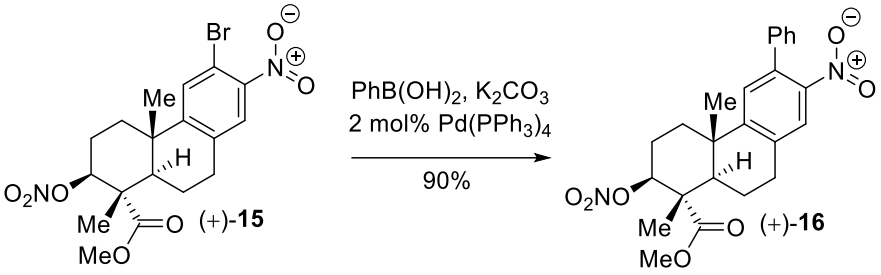
^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 153.9, 147.3, 135.7, 131.3, 126.3, 111.6, 85.2, 77.2, 52.9, 51.3, 45.8, 37.5, 35.9, 29.1, 24.8, 22.6, 20.1, 11.7.

IR (neat) υ_{max} 3310, 2234, 1759, 1558, 1417, 1236, 1183, 998, 801 cm^{-1}.

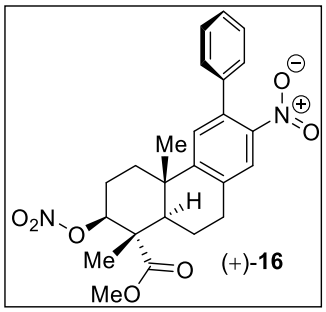
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{18}H_{21}BrN_2O_7 + Na]^+$ 479.0424, found 479.0403.

$[\alpha]^{25}_{589}$ = +24.9 (*c* = 0.9, $CHCl_3$).

Suzuki Coupling of (+)-**15:**



A round-bottom flask was charged with (+)-**15** (2.45 g, 5.36 mmol, 1.0 equiv.) and benzene boronic acid (784 mg, 6.43 mmol, 1.2 equiv.) in a mixture of benzene (18 mL), EtOH (6 mL), and water (6 mL) at room temperature under argon atmosphere. Next, potassium carbonate (1.5 g, 10.72 mmol, 2.0 equiv.) was added to the reaction mixture followed by the addition of catalyst, tetrakis(triphenylphosphine)palladium(0) (124 mg, 0.107 mmol, 0.02 equiv.) at the same temperature. Then the reaction mixture was placed on a pre-heated oil bath maintaining temperature of 80 °C. Upon completion of the reaction (10 h), as monitored by TLC analysis, it was extracted with 20% EtOAc in *n*-hexane (25 mL X 2). The combined organic layers were washed with brine (15 mL X 1) and dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography with 10% EtOAc in *n*-hexane to furnish (+)-**16** as a yellow solid (2.19 g, 90% yield).



Methyl (1*S*,2*S*,4a*S*,10a*R*)-**1,4a-dimethyl-7-nitro-2-(nitrooxy)-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**16**]**:** (**+**)-**16** was obtained as a yellow solid after

recrystallization (mp: 146-150 ˚C); (5.36 mmol scale, 2.19 g, 90% yield); R_f = 0.3 (10% EtOAc in *n*-hexane).

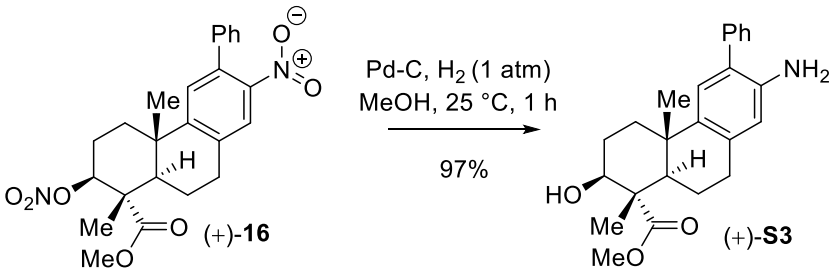
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.1 Hz, 1H), 7.46 – 7.41 (m, 3H), 7.32 – 7.28 (m, 3H), 5.48 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.77 (s, 3H), 3.12 – 3.04 (m, 1H), 3.03 – 2.94 (m, 1H), 2.48 (dt, *J* = 13.3, 3.5 Hz, 1H), 2.24 (dd, *J* = 12.6, 2.3 Hz, 1H), 2.21 – 2.15 (m, 1H), 2.06 – 1.94 (m, 2H), 1.85 (td, *J* = 13.6, 3.7 Hz, 1H), 1.55 (ddt, *J* = 13.6, 7.7, 2.0 Hz, 1H), 1.36 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 152.5, 146.9, 137.8, 135.3, 134.3, 128.6, 128.3, 128.1, 127.9 (2C), 124.7, 85.5, 77.2, 52.9, 51.4, 46.2, 37.5, 36.0, 29.3, 24.9, 22.6, 20.3, 11.7.

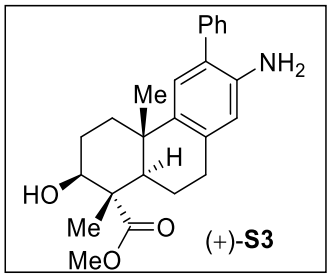
IR (neat) υ_{max} 3323, 2180, 1710, 1565, 1456, 1236, 890, 725 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{24}H_{26}O_7N_2 + Na]^+$ 477.1632, found 477.1653.

$[\alpha]^{25}_{589}$ = +40.5 (*c* = 0.8, $CHCl_3$).

Synthesis of (+)-**S3:**



In an oven-dried round-bottom flask compound (+)-**16** (2.1 g, 4.62 mmol, 1.0 equiv.) was taken in MeOH (25 mL) and degassed with N_2 balloon for 10 minutes. To this solution was added Pd/C (10% w/w) (210 mg) and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (1 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure, and it was purified by column chromatography with 30% EtOAc in *n*-hexane to afford (+)-**S3** as a white foam (1.7 g, 97% yield).



Methyl (1*S*,2*S*,4a*S*,10a*R*)**-7-amino-2-hydroxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S3**]**:** (+)-**S3** was obtained as a white foam (4.62 mmol scale, 1.7 g, 97% yield); R_f = 0.25 (30% EtOAc in *n*-hexane).

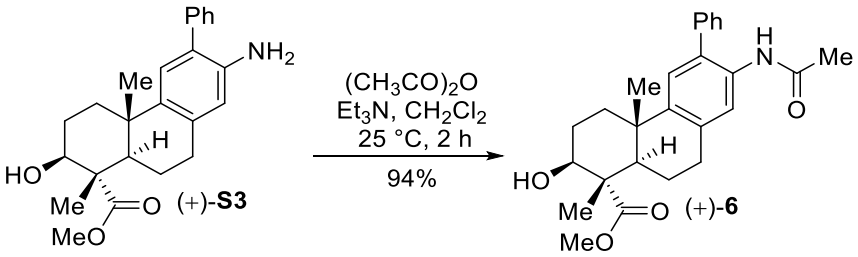
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 4.3 Hz, 4H), 7.32 (dq, *J* = 8.6, 4.6, 4.0 Hz, 1H), 6.99 (s, 1H), 6.50 (s, 1H), 4.03 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.72 (s, 3H), 2.89 – 2.76 (m, 2H), 2.28 (dt, *J* = 12.9, 3.3 Hz, 1H), 2.13 (dd, *J* = 12.5, 2.2 Hz, 1H), 1.94 – 1.79 (m, 2H), 1.75 (dd, *J* = 11.6, 3.2 Hz, 1H), 1.64 (dd, *J* = 12.9, 3.8 Hz, 1H), 1.41 (ddd, *J* = 14.1, 6.1, 3.1 Hz, 1H), 1.23 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 140.7, 139.9, 139.7, 135.2, 129.1 (2C), 128.8 (2C), 127.1, 126.6, 126.4, 115.6, 75.3, 53.8, 52.2, 45.8, 36.8, 36.5, 29.9, 27.3, 25.3, 21.4, 10.7.

IR (neat) υ_{max} 3395, 3343, 2810, 1707, 1615, 1460, 1281, 1065, 985, 764, 650 cm^{-1}.
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{24}H_{30}O_3N + H]^+$ 380.2226, found 380.2218.

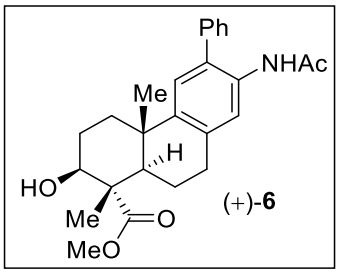
$[\alpha]^{25}_{589}$ = +47.0 (*c* = 0.73, $CHCl_3$).

Synthesis of Acetanilide derivative (+)**-6:**



In an oven-dried round-bottom flask, compound (+)-**S3** (500 mg, 1.32 mmol., 1.0 equiv.) was taken in dry CH_2Cl_2 (15 mL) and Et_3N (0.55 mL, 3.95 mmol., 3.0 equiv.) was added to the

reaction mixture. Next, acetic anhydride (0.15 mL, 1.58 mmol., 1.2 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of starting material. Upon completion (2 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2 (15 mL X 1). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 45% EtOAc in *n*-hexane to afford (+)-**6** as yellow foam (523 mg, 94% yield).



Methyl (1*S*,2*S*,4a*S*,10a*R*)**-7-acetamido-2-hydroxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**6**]**:** (+)-**6** was obtained as a yellow foam (1.32 mmol scale, 523 mg, 94% yield); R_f = 0.25 (50% EtOAc in *n*-hexane).

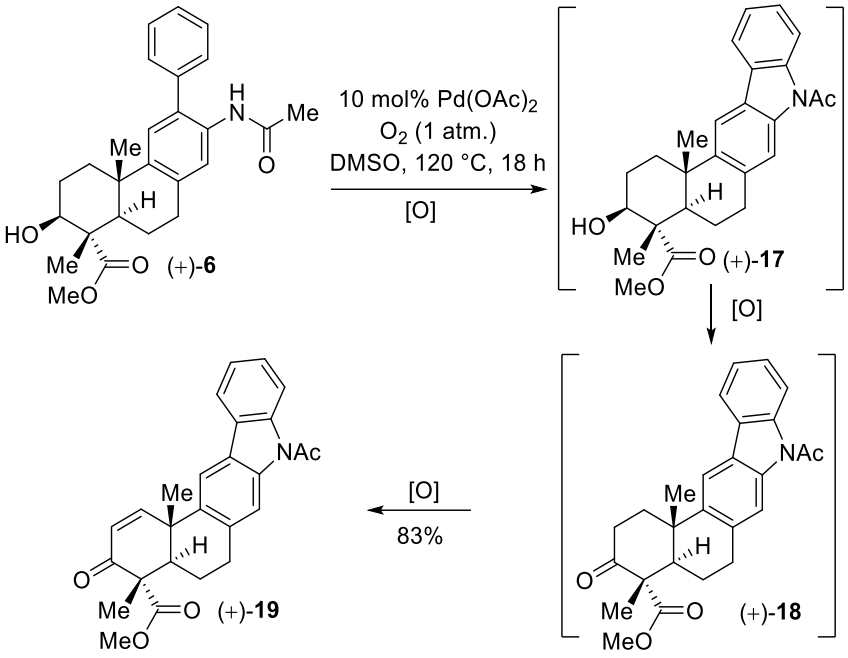
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.11 (s, 1H), 7.08 (s, 1H), 4.05 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.75 (s, 3H), 2.97 (pd, *J* = 10.2, 2.7 Hz, 2H), 2.31 (dt, *J* = 13.3, 3.4 Hz, 1H), 2.16 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.03 (s, 3H), 1.97 – 1.92 (m, 1H), 1.91 – 1.85 (m, 1H), 1.80 (qd, *J* = 13.2, 3.2 Hz, 1H), 1.65 (td, *J* = 13.2, 3.9 Hz, 1H), 1.46 (ddd, *J* = 16.2, 8.0, 5.8 Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 168.5, 145.3, 138.5, 135.3, 132.0, 130.6, 129.3, 129.0, 127.8, 126.2, 122.2, 75.1, 53.7, 52.3, 45.5, 36.8, 36.6, 30.0, 27.2, 25.2, 24.5, 21.5, 10.7.

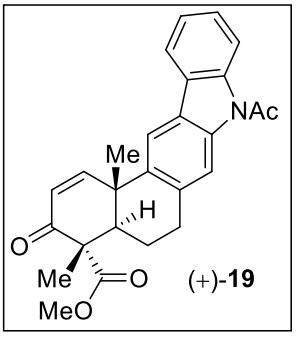
IR (neat) υ_{max} 3307, 2987, 2705, 1843, 1757, 1602, 1187, 1059, 915 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{26}H_{31}O_4N + Na]^+$ 444.2145, found 444.2138.

$[\alpha]^{25}_{589}$= +68.35 (*c* = 0.52, MeOH).

Buchwald's Oxidative C-N Coupling of (+)-6:



2-Phenyl acetanilide derivative (+)-**6** (350 mg, 0.83 mmol, 1.0 equiv.) was taken in DMSO (6 mL) under argon atmosphere and $Pd(OAc)_2$ (18.6 mg, 0.083 mmol, 0.1 equiv.) was added to it. The reaction mixture was sonicated and degassed and refilled with O_2 from the double manifold (this sequence was carried out 3 times). The sealed tube was set into a pre-heated oil bath at 120 °C and stirred for 18 h (complete consumption of starting materials). After cooling it to room temperature, the reaction mixture was diluted with water (10 mL) and extracted with 40% EtOAc in *n*-hexane (10 mL X 2). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in a rotary evaporator under reduced pressure. The residue was purified by silica gel column chromatography with 25% EtOAc in *n*-hexane to afford to provide (+)-**19** as colorless oil (286 mg, 83% yield).



Methyl (4*S*,4a*R*,13b*S*)**-8-acetyl-4,13b-dimethyl-3-oxo-4,4a,5,6,8,13b-hexahydro-3H-naphtho[2,1-*b*] carbazole-4-carboxylate** [(+)-**19**]**:** (+)-**19** was obtained as a colorless oil (0.83 mmol scale, 286 mg, 83% yield); R_f = 0.3 (20% EtOAc in *n*-hexane).

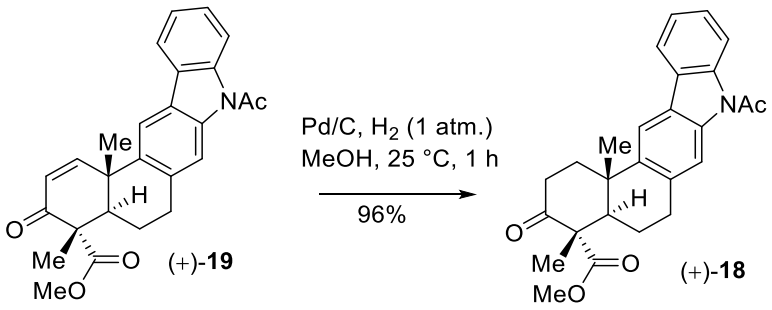
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 8.07 (s, 1H), 8.05 – 8.01 (m, 2H), 7.88 (d, *J* = 10.5 Hz, 1H), 7.50 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.42 (td, *J* = 7.5, 0.9 Hz, 1H), 6.22 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 3H), 3.25 – 3.15 (m, 2H), 3.11 (dd, *J* = 13.0, 2.7 Hz, 1H), 2.89 (s, 3H), 2.13 (tdd, *J* = 13.2, 10.2, 7.7 Hz, 1H), 1.72 (ddt, *J* = 10.5, 7.5, 2.8 Hz, 1H), 1.55 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 173.4, 170.0, 157.1, 139.8, 138.9, 137.6, 135.1, 127.3, 126.2, 124.8, 123.8, 119.6, 117.6, 116.1, 114.7, 58.3, 44.4, 39.9, 30.3, 29.7, 28.0, 27.7, 20.2, 16.6.

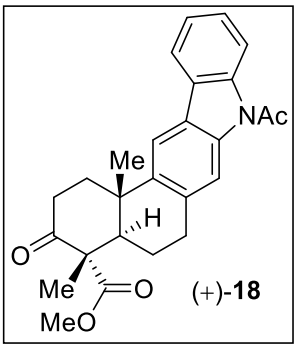
IR (neat) υ_{max} 2890, 2816, 1681, 1422, 1206, 1124, 1009, 789 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{26}H_{25}O_4N + Na]^+$ 438.1676, found 438.1645.

$[\alpha]^{25}_{589}$ = +62.08 (*c* = 0.78, $CHCl_3$).

Hydrogenation of Enone (+)-19:



In an oven-dried round-bottom flask under an inert (argon) atmosphere, enone (+)-**19** (152 mg, 0.365 mmol, 1.0 equiv.) was taken in MeOH (4 mL). To this solution, 10% Pd–C (w/w) (15 mg) was added, and purged with nitrogen gas (3 times). Next, a hydrogen balloon (having 1 atm. hydrogen pressure) was connected with the septum. Upon completion of the reaction (confirmed by TLC analysis), the reaction mixture was filtered and purified with 50% EtOAc in *n*-hexane to afford pure keto (+)-**18** as yellow gel (146 mg, 96% yield).



Methyl (4*S*,4a*R*,13b*S*)**-8-acetyl-4,13b-dimethyl-3-oxo-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**18**]**:** (+)-**18** was obtained as yellow gel (0.365 mmol scale of reaction, 146 mg of product, 96% yield); R_f = 0.28 (30% EtOAc in *n*-hexane).

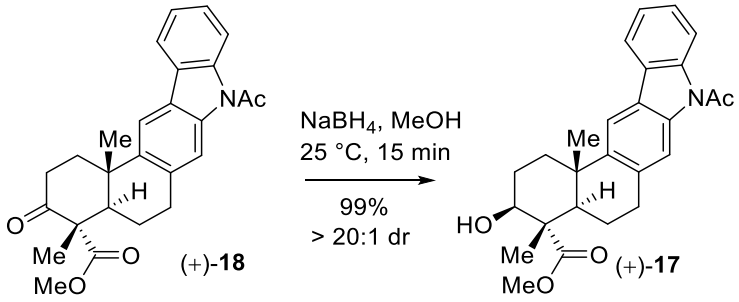
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.99 – 7.96 (m, 2H), 7.91 (s, 1H), 7.47 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.40 (td, *J* = 7.5, 1.0 Hz, 1H), 3.77 (s, 3H), 3.21 – 3.12 (m, 2H), 2.93 – 2.89 (m, 1H), 2.88 (s, 3H), 2.80 – 2.73 (m, 2H), 2.24 – 2.15 (m, 1H), 2.01 (tdd, *J* = 12.9, 11.2, 7.0 Hz, 1H), 1.69 – 1.60 (m, 2H), 1.52 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 173.5, 170.0, 142.9, 138.9, 137.4, 134.7, 127.1, 126.5, 125.1, 123.7, 119.5, 116.5, 116.2, 116.1, 61.0, 52.7, 46.8, 37.3, 36.9, 35.3, 31.4, 27.7, 24.8, 21.5, 16.8.

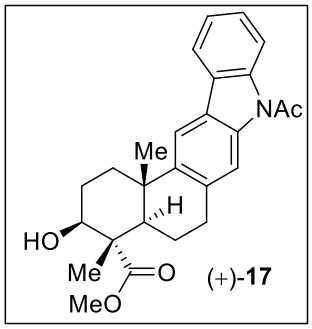
IR (neat) υ_{max} 3021, 2798, 1712, 1696, 1665, 1587, 1388, 1102, 885, 714 cm^{-1}.
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{26}H_{27}O_4N + Na]^+$ 440.1832, found 440.1852.

$[\alpha]^{25}_{589}$ = +86.7 (*c* = 0.68, $CHCl_3$).

Synthesis of *N*-Acetyl Xiamycin A Methyl ester (+)-17:



Ketone (+)-**18** (140 mg, 0.335 mmol, 1.0 equiv.) was taken in MeOH (4 mL) at 0 °C, $NaBH_4$ (14 mg, 0.335 mmol, 1.0 equiv.) was added portion wise and the reaction mixture was stirred at room temperature for 15 min. After complete consumption of starting material (judged by TLC analysis), it was quenched with saturated NH_4Cl (5 mL) and extracted with EtOAc (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. The crude products were purified by flash chromatography with 50% EtOAc in *n*-hexane to afford (+)-**17** as yellow oil (138 mg, 99% yield), R_f = 0.32 (40% EtOAc in *n*-hexane).



Methyl (3*S*,4*S*,4a*R*,13b*S*)**-8-acetyl-3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*] carbazole-4-carboxylate** [(+)-**17**]**:** (+)-**17** was obtained as yellow oil (0.335 mmol scale, 138 mg, 99% yield); R_f = 0.32 (40% EtOAc in *n*-hexane).

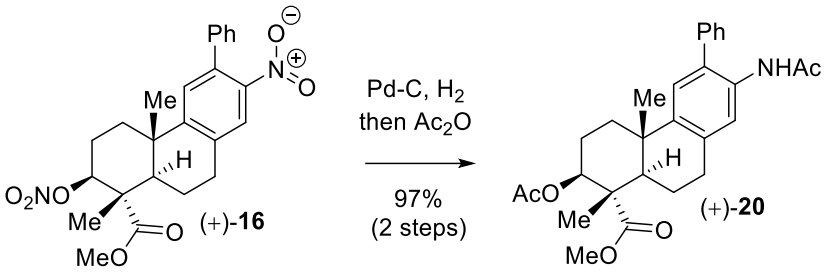
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.96 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.90 (s, 1H), 7.86 (s, 1H), 7.46 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.38 (td, *J* = 7.5, 0.9 Hz, 1H), 4.11 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.78 (s, 3H), 3.18 – 3.08 (m, 2H), 2.87 (s, 3H), 2.57 (dt, *J* = 12.8, 3.4 Hz, 1H), 2.22 (dd, *J* = 12.6, 2.3 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.93 – 1.88 (m, 1H), 1.81 (dd, *J* = 13.1, 3.7 Hz, 1H), 1.54 (ddt, *J* = 12.5, 7.0, 2.4 Hz, 1H), 1.32 (d, *J* = 3.1 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 170.0, 145.0, 138.9, 137.1, 134.8, 126.9, 126.7, 124.8, 123.6, 119.5, 116.3, 115.3, 75.2, 53.7, 52.3, 45.6, 37.3, 37.03, 31.06, 27.67, 27.29, 25.56, 21.4, 10.8.

IR (neat) υ_{max} 3351, 2823, 1632, 1522, 1470, 1356, 954 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{26}H_{29}O_4N + Na]^+$ 442.1989, found 442.1984.

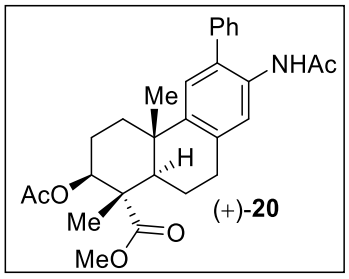
$[\alpha]^{25}_{589}$ = +85.42 (*c* = 0.69, $CHCl_3$).

Procedure for the synthesis of (+)-**20:**



In an oven-dried round-bottom flask, (+)-**16** (2.1 g, 4.62 mmol, 1.0 equiv.) was taken in MeOH (25 mL) under inert atmosphere and degassed with N_2 balloon for 10 minutes. Next, 105 mg of Pd/C (5% w/w) was added to the reaction mixture at 25 °C. Then, H_2 gas was purged constantly at 25 ºC using a H_2 gas balloon (1 atm. pressure) until the full consumption of starting material (2 h) [as monitored by TLC analysis]. Next, the reaction mixture was filtered through celite pad and concentrated under the reduced pressure and charged for the next step without purification.

The crude reaction mixture from the above reaction (4.62 mmol., 1 equiv.) was taken in dry CH_2Cl_2 (25 mL). To the solution was added Et_3N (1.35 ml, 9.7 mmol., 2.1 equiv.) and catalytic amount of DMAP (57 mg, 0.462 mmol., 0.1 equiv.) at 25 °C. Acetic anhydride (0.92 ml, 9.7 mmol., 2.1 equiv.) was added at 25 ºC and it was allowed to stir until the full consumption of starting material (2 h). Upon completion of the reaction (as monitored by TLC analysis), water (20 mL) was added and then extracted with CH_2Cl_2 (20 mL X 1). The organic layers were separated and dried over Na_2SO_4 and concentrated on a rotary evaporator under the reduced pressure. The crude bis-acetate was purified by flash column chromatography with 45% EtOAc in *n*-hexane to afford (+)-**20** as yellow foam (2.1 g, 97% yield).



Methyl (1*S*,2*S*,4a*S*,10a*R*)-**7-acetamido-2-acetoxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**20**]**:** (+)-**20** was obtained as a yellow foam (4.65 mmol scale, 2.1 g, 97% yield); R_f = 0.2 (30% EtOAc in *n*-hexane).

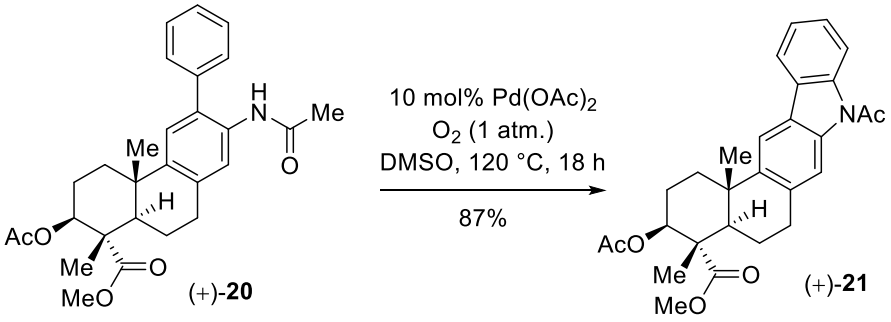
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.11 (s, 1H), 7.04 (s, 1H), 5.24 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.70 (s, 3H), 2.97 (dtd, *J* = 21.0, 10.9, 10.2, 6.6 Hz, 2H), 2.35 – 2.26 (m, 2H), 2.03 (s, 6H), 2.00 – 1.90 (m, 3H), 1.82 (dd, *J* = 12.4, 3.0 Hz, 1H), 1.76 (dd, *J* = 12.8, 3.1 Hz, 1H), 1.44 – 1.40 (m, 1H), 1.33 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 170.1, 168.3, 144.9, 138.5, 135.2, 132.2, 129.3, 129.0, 127.8, 126.1, 122.0, 52.4, 52.1, 45.6, 36.7, 36.3, 29.9, 29.7, 25.1, 24.5, 24.0, 21.1, 21.1, 11.7.

IR (neat) υ_{max} 2987, 2745, 1823, 1745, 1605, 1178, 1095, 965, cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{28}H_{33}O_5N + Na]^+$ 486.2251, found 486.2283.

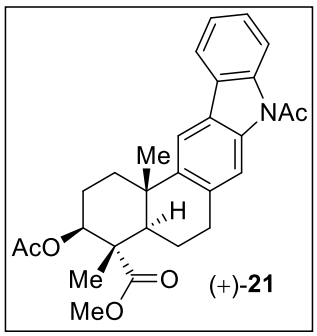
$[\alpha]^{25}_{589}$= +94.0 (*c* = 0.87, MeOH).

Buchwald's Oxidative C–N bond formation of (+)-20:



2-Phenyl acetanilide derivative (+)-**20** (300 mg, 0.65 mmol, 1.0 equiv.) was taken in DMSO (6 mL) under argon atmosphere and $Pd(OAc)_2$ (15 mg, 0.065 mmol, 0.1 equiv.) was added to it. The reaction mixture was sonicated and degassed and refilled with O_2 from the double manifold (this sequence was carried out 3 times). The sealed tube was set into a pre-heated oil bath at 120 °C and stirred for 18 h (complete consumption of starting materials). After cooling it to room temperature, the reaction mixture was diluted with water (15 mL) and extracted with 50% EtOAc in *n*-hexane (15 mL X 2). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in a rotary evaporator under reduced pressure. The residue was purified by silica gel column chromatography with 25% EtOAc in *n*-hexane to

afford to provide (+)-**21** as white foam (259 mg, 87% yield). Later, compound (+)-**21** was prepared in 1.8 g following several batches.



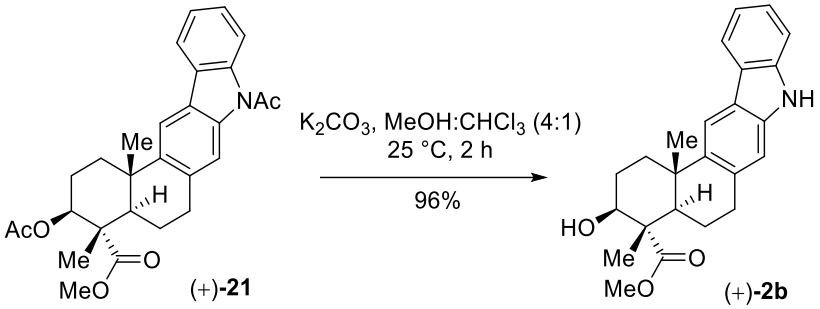
Methyl (3*S*,4*S*,4a*R*,13b*S*)-**3-acetoxy-8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**21**]**:** (+)-**21** was obtained as a white foam (0.65 mmol scale, 259 mg, 87% yield); R_f = 0.25 (20% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.91 (m, 1H), 7.87 (s, 1H), 7.82 (s, 1H), 7.45 – 7.40 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 5.30 – 5.21 (m, 1H), 3.68 (s, 3H), 3.13 – 3.04 (m, 2H), 2.83 (s, 3H), 2.59 – 2.50 (m, 1H), 2.30 (dd, *J* = 12.8, 2.4 Hz, 1H), 2.07 – 2.02 (m, 1H), 2.01 (s, 3H), 2.00 – 1.92 (m, 1H), 1.91 – 1.82 (m, 2H), 1.48 – 1.41 (m, 1H), 1.34 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 170.2, 170.1, 144.8, 138.9, 137.2, 134.8, 127.0, 126.8, 124.9, 123.7, 119.6, 116.4, 115.3, 76.9, 52.5, 52.2, 45.8, 37.2, 36.8, 31.0, 27.8, 25.5, 24.2, 21.3, 21.2, 11.8.

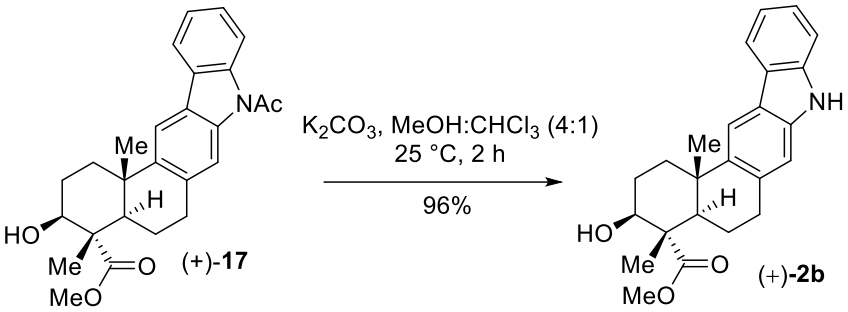
IR (neat) υ_{max} 3257, 2130, 1703, 1653, 1507, 1152, 965, 795 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{28}H_{31}O_5N + Na]^+$ 484.2094, found 484.2055.
$[\alpha]^{25}_{589}$ = +56.7 (*c* = 0.93, $CHCl_3$).

Total Synthesis of (+)-**Xiamycin A Methyl Ester** [(+)-**2b**]**:**



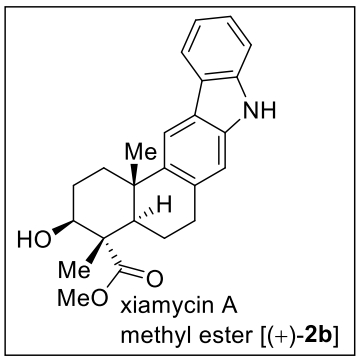
In an oven dried round-bottom flask, (+)-**21** (780 mg, 1.69 mmol, 1.0 equiv.) was taken in a mixture of methanol and chloroform [MeOH: $CHCl_3$ (4:1)] solvent (15 mL). To this solution was added K_2CO_3 (934 mg, 6.76 mmol, 4.0 equiv.) at 25 ºC and stirring was continued for an additional 2 h. After completion of the reaction (judged by TLC analysis), the reaction mixture was diluted with water (10 mL). Next, it was extracted with dichloromethane (10 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. Next, the crude methyl ester was purified by flash column chromatography with 30% EtOAc in *n*-hexane to afford the naturally occurring xiamycin A methylester (+)-**2b** as a white foam (612 mg, 96% yield).

Synthesis of xiamycin A methylester (+)-**2b** from (+)-**17**:



In an oven dried round-bottom flask (+)-**17** (387 mg, 0.922 mmol, 1.0 equiv.) was taken in a mixture of methanol and chloroform [MeOH: $CHCl_3$ (4:1)] solvent (8 mL). To this solution was added K_2CO_3 (510 mg, 3.69 mmol, 4.0 equiv.) at 25 ºC and stirring was continued for an additional 2 h. After completion of the reaction (judged by TLC analysis), the reaction mixture was diluted with water. Next, it was extracted with dichloromethane. The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. The crude methyl ester was purified by flash column chromatography with 35% EtOAc in *n*-hexane to

afford the naturally occurring xiamycin A methylester (+)-**2b** as a white foam (334 mg, 96% yield).



Methyl (3*S*,4*S*,4a*R*,13b*S*)-**3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**2b**]**:** Natural product xiamycin A methylester (+)-**2b** was obtained as white foam (1.69 mmol scale, 612 mg, 96% yield). R_f = 0.2 (30% EtOAc in *n*-hexane)

^{1}H NMR (500 MHz, CD_3OD) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.95 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 4.08 (dd, *J* = 9.4, 6.9 Hz, 1H), 3.73 (s, 3H), 3.10 (dd, *J* = 17.0, 6.8 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.64 (dq, *J* = 13.3, 3.3 Hz, 1H), 2.18 – 2.11 (m, 1H), 2.04 (ddt, *J* = 20.0, 9.7, 5.9 Hz, 1H), 1.91 (td, *J* = 10.6, 9.6, 5.5 Hz, 2H), 1.74 (td, *J* = 12.6, 11.8, 4.6 Hz, 1H), 1.40 (ddd, *J* = 13.6, 7.5, 2.0 Hz, 1H), 1.30 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 179.6, 141.9, 141.6, 140.1, 133.8, 125.9, 124.6, 123.0, 120.5, 119.3, 116.2, 111.4, 110.7, 76.2, 55.4, 52.5, 47.9, 38.8, 38.3, 31.8, 28.4, 26.2, 22.5, 11.2.

IR (neat) υ_{max} 3389, 2930, 2866, 1710, 1602, 1455, 1243, 915, 788, 540 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{24}H_{27}O_3N + Na]^+$ 400.1883, found 400.1885.

$[\alpha]^{25}_{589}$ = +112.6 (*c* = 0.79, CH_3OH); lit.[3] $[\alpha]_D^{21}$ = +162.4 (*c* = 1.3, CH_3OH).

Comparison of ^{1}H-NMR Data of (+)-Xiamycin A methylester [(+)-**2b**] of this report with natural (+)-**2b** by Hertweck[3]:

Hertweck's isolation of (+)-xiamycin A methyl ester [(+)-**2b**] (^{1}H-NMR, 300 MHz, CD_3OD)[3]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.96	1H	dd	*J* = 7.7, 1.1 Hz
7.92	1H	s	-
7.34	1H	dd	*J* = 8.0, 1.1 Hz
7.27	1H	ddd	*J* = 8.0, 7.4, 1.1Hz
7.08	1H	ddd	*J* = 8.1, 7.3, 1.1Hz
7.05	1H	s	-
4.05	1H	dd	*J* = 9.1, 7.1 Hz
3.71	3H	s	-
3.09	1H	dd	*J* = 16.7, 6.1
2.98	1H	m	-
2.61	1H	td	*J* = 13.1, 3.0 Hz
2.13	1H	dd	*J* = 12.5, 2.0 Hz
2.00	1H	ddd	*J* = 13.4, 12.8, 7.0 Hz
1.88	2H	m	-
1.74	1H	m	-
1.38	1H	m	-
1.29	3H	s	-
1.23	3H	s	-

This Synthesis: (+)-xiamycin A methyl ester [(+)-**2b**] (^{1}H-NMR, 500 MHz, CD_3OD)			
δ (ppm)	Int.	mult.	*J* (Hz)
8.00	1H	d	*J* = 7.8 Hz
7.95	1H	s	-
7.37	1H	d	*J* = 8.0 Hz
7.31	1H	t	*J* = 7.6 Hz
7.11	1H	t	*J* = 7.5 Hz
7.07	1H	s	-

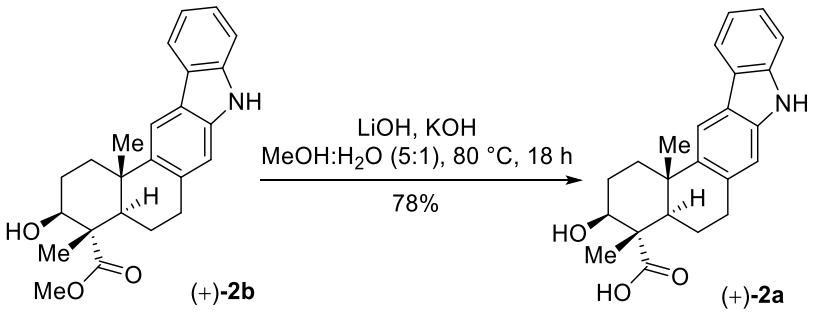
4.08	1H	dd	J = 9.4, 6.9 Hz
3.73	3H	s	-
3.10	1H	dd	J = 17.0, 6.8 Hz
3.06 – 2.96	1H	m	-
2.64	1H	dq	J = 13.3, 3.3 Hz
2.18 – 2.11	1H	m	-
2.04	1H	ddt	J = 20.0, 9.7, 5.9 Hz
1.91	2H	td	J = 10.6, 9.6, 5.5 Hz
1.74	1H	td	J = 12.6, 11.8, 4.6 Hz
1.40	1H	ddd	J = 13.6, 7.5, 2.0 Hz
1.30	3H	s	-
1.28	3H	s	-

Comparison of ^{13}C-NMR Data:

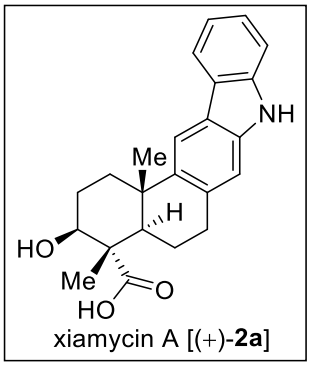
Hertweck's report on isolation of (+)-xiamycin A methyl ester [(+)-**2b**] (^{13}C-NMR, 125.76 MHz, CD_3OD)[3]	This Synthesis: (+)-xiamycin A methyl ester [(+)-**2b**] (^{13}C-NMR, 125 MHz, CD_3OD)
179.8	179.6
142.0	141.9
141.8	141.6
140.2	140.1
133.9	133.8
126.1	125.9
124.6	124.6
123.1	123.0
120.5	120.5
119.4	119.3
116.3	116.2
111.5	111.4
110.8	110.7

76.3	76.2
55.4	55.4
52.6	52.5
48.1	47.9
39.0	38.8
38.4	38.3
31.9	31.8
28.5	28.4
26.3	26.2
22.6	22.5
11.3	11.2

Total Synthesis of Xiamycin A [(+)-**2a**]**:**



In an oven dried round-bottom flask xiamycin A methyl ester [(+)-**2b**] (58 mg, 0.153 mmol, 1.0 equiv.) was taken in a mixture of methanol and water [MeOH: H_2O (5:1)] at 25 ℃. Next, KOH (259 mg, 4.61 mmol, 30 equiv.) and LiOH (128 mg, 3.06 mmol, 20 equiv.) were added subsequently and the reaction mixture was heated under reflux at 80 ºC. After completion of the reaction as confirmed by TLC analysis (18 h), the reaction mixture was quenched with 6(*N*) HCl at 0 ºC and the pH of the reaction mixture was adjusted to ~1-2. Then whole reaction mixture was extracted with EtOAc (8 mL X 2). The combined organic layers were collected, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography with ~80-90% EtOAc to afford the naturally occurring xiamycin A [(+)-**2a**] as white foam (43 mg, 78% yield).



xiamycin A [(+)-**2a**]

(3*S*,4*S*,4a*R*,13b*S*)-**3-Hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylic acid** [(+)-**2a**]**:** Natural product xiamycin A [(+)-**2a**] was obtained as white foam (0.153 mmol scale, 43 mg, 78% yield). R_f = 0.2 (70% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, CD_3OD): δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.09 (s, 1H), 4.12 (dd, *J* = 9.4, 7.0 Hz, 1H), 3.13 (dd, *J* = 16.9, 6.7 Hz, 1H), 3.05 (ddd, *J* = 17.3, 11.0, 7.4 Hz, 1H), 2.64 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.18 (d, *J* = 12.4 Hz, 1H), 2.04 (qd, *J* = 12.3, 7.2 Hz, 1H), 1.92 (dt, *J* = 10.7, 5.5 Hz, 2H), 1.81 – 1.73 (m, 1H), 1.57 (dd, *J* = 13.3, 7.4 Hz, 1H), 1.32 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD): δ 181.3, 142.0, 141.8, 140.1, 134.0, 126.0, 124.6, 123.1, 120.5, 119.3, 116.3, 111.4, 110.8, 76.3, 54.9, 47.9, 38.9, 38.3, 31.9, 28.6, 26.3, 22.6, 11.4.

IR (neat) υ_{max} 3350, 2935, 2263, 1670, 1415, 1013, 917, 837 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{23}H_{25}O_3N + Na]^+$ 386.1727, found 386.1717.

$[\alpha]^{25}_{589}$ = +107 (*c* = 0.69, CH_3OH); lit.[3] $[\alpha]_D^{21}$ = +137.6 (*c* = 5.3, CH_3OH).

Comparison of ^{1}H-NMR Data of (+)-Xiamycin A [(+)-**2a**] of this report with natural (+)-**2a** by Hertweck[3] and with literature by Baran[4] and Sarpong[5]:

Hertweck's report on isolation of (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 300 MHz, CD_3OD)[3]			
δ (ppm)	Int.	mult.	*J* (Hz)

7.96	1H	dd	*J* = 7.7, 1.1 Hz
7.92	1H	s	-
7.34	1H	dd	*J* = 8.0, 1.1 Hz
7.27	1H	ddd	*J* = 8.0, 7.4, 1.1Hz
7.08	1H	ddd	*J* = 8.1, 7.3, 1.1Hz
7.05	1H	s	-
4.09	1H	dd	*J* = 9.1, 7.1 Hz
3.09	1H	dd	*J* = 16.7, 6.1
3.02	1H	m	-
2.61	1H	td	*J* = 13.1, 3.0 Hz
2.15	1H	dd	*J* = 12.5, 2.0 Hz
2.00	1H	ddd	*J* = 13.4, 12.8, 7.0 Hz
1.89	2H	m	-
1.74	1H	m	-
1.53	1H	m	-
1.29	3H	s	-
1.23	3H	s	-

Baran's Total Synthesis of (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 600 MHz, CD_3OD)[4]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.97	1H	dt	*J* = 7.8, 1.0 Hz
7.94	1H	s	-
7.35	1H	dt	*J* = 8.1, 0.9 Hz
7.29	1H	ddd	*J* = 8.1, 7.1, 1.2 Hz
7.09	1H	t	*J* = 7.9, 7.1, 1.0 Hz
7.06	1H	s	-
4.10	1H	dd	*J* = 9.3, 7.1 Hz
3.14 – 3.07	1H	m	-
3.06 – 2.98	1H	m	-
2.63	1H	dt	*J* = 13.1, 3.5 Hz

2.16	1H	dd	*J* = 12.6, 2.2 Hz
2.01	1H	tdd	*J* = 12.8, 11.3, 6.9
1.94 – 1.86	2H	m	-
1.78 – 1.70	1H	m	-
1.57 – 1.52	1H	m	-
1.29	3H	s	-
1.24	3H	s	-

Sarpong's Total Synthesis of (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 700 MHz, CD_3OD)[5]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.97	1H	d	*J* = 8.0 Hz
7.94	1H	s	-
7.35	1H	d	*J* = 8.0 Hz
7.29	1H	t	*J* = 7.9 Hz
7.09	1H	t	*J* = 7.5 Hz
7.07	1H	s	-
4.10	1H	dd	*J* = 10.5, 7.5 Hz
3.15-3.08	1H	m	-
3.08-2.99	1H	m	-
2.64	1H	d	*J* = 12.8 Hz
2.14	1H	d	*J* = 11.8 Hz
2.08-1.98	1H	m	-
1.93-1.88	2H	m	-
1.78-1.72	1H	m	-
1.58-1.53	1H	m	-
1.30	3H	s	-
1.25	3H	s	-

This Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 500 MHz, CD_3OD)			
δ (ppm)	Int.	mult.	*J* (Hz)

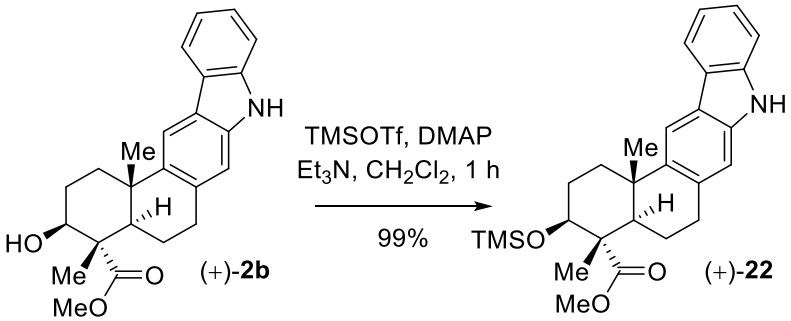
8.00	1H	d	*J* = 7.8 Hz
7.96	1H	s	-
7.37	1H	d	*J* = 8.0 Hz,
7.31	1H	t	*J* = 7.6 Hz,
7.12	1H	d	*J* = 7.5 Hz
7.09	1H	s	-
4.12	1H	dd	*J* = 9.4, 7.0 Hz
3.13	1H	dd	*J* = 16.9, 6.7 Hz
3.05	1H	ddd	*J* = 17.3, 11.0, 7.4 Hz
2.64	1H	dd	*J* = 13.2, 3.6 Hz
2.18	1H	d	*J* = 12.4 Hz
2.04	1H	qd	*J* = 12.3, 7.2 Hz
1.92	2H	dt	*J* = 10.7, 5.5 Hz
1.81-1.73	1H	m	-
1.57	1H	dd	*J* = 13.3, 7.4 Hz
1.32	3H	s	-
1.27	3H	s	-

Comparison of ^{13}C-NMR Data:

Hertweck's isolation of (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 125.77 MHz, CD_3OD)[3]	Baran's Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 151 MHz, CD_3OD)[4]	Sarpong's Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 176 MHz, CD_3OD)[5]	This Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 125 MHz, CD_3OD)
181.3	181.4	181.3	181.3
142.0	142.0	142.0	142.0
141.8	141.8	141.8	141.8
140.1	140.1	140.1	140.1
134.0	134.0	134.0	134.0
126.0	126.1	126.0	126.0
124.7	124.7	124.6	124.6

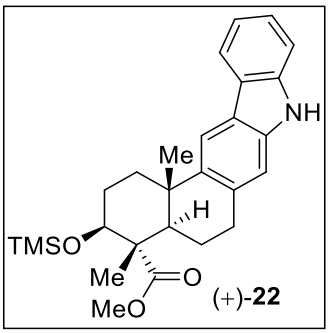
123.1	123.1	123.1	123.1
120.5	120.6	120.6	120.5
119.3	119.3	119.3	119.3
116.3	116.4	116.4	116.3
111.5	111.4	111.4	111.4
110.8	110.8	110.8	110.8
76.3	76.3	76.3	76.3
54.9	54.9	54.9	54.9
47.9	47.9	47.9	47.9
39.0	39.0	39.0	38.9
38.3	38.3	38.3	38.3
32.0	32.0	32.1	31.9
28.6	28.6	28.7	28.6
26.3	26.3	26.3	26.3
22.6	22.6	22.6	22.6
11.4	11.4	11.4	11.4

Synthesis of Xiamycin A methyl ester TMS ether [(+)-**22**]**:**



Xiamycin A methyl ester [(+)-**2b**] (1.1 g, 2.91 mmol., 1 equiv.) was taken in dry CH_2Cl_2 (12 mL) at 25 °C. Triethylamine (0.943 ml, 7.27 mmol., 2.5 equiv.) was added to the reaction mixture followed by the addition of catalytic amount of DMAP (36 mg, 0.291 mmol., 0.1 equiv.) at the same temperature. Next, TMSOTf (0.633 ml, 3.49 mmol., 1.2 equiv.) was added to it at 25 ºC and stirring was continued until the complete consumption of starting material. Upon completion of the reaction (judged by TLC analysis), water (10 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (10 mL X 2). The combined organic layers were

dried over Na_2SO_4 and concentrated under reduced pressure and purified by flash column chromatography with 10% EtOAc in *n*-hexane to afford xiamycin A methyl ester TMS ether (+)-**22** as yellow foam (1.29 g, 99% yield).



Methyl (3*S*,4*S*,4a*R*,13b*S*)-**4,13b-dimethyl-3-((trimethylsilyl)oxy)-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**22**]**:** Xiamycin A methyl ester TMS ether [(+)-**22**] was obtained as yellow foam (2.91 mmol scale, 1.29 g, 99% yield). R_f = 0.2 (10% EtOAc in *n*-hexane).

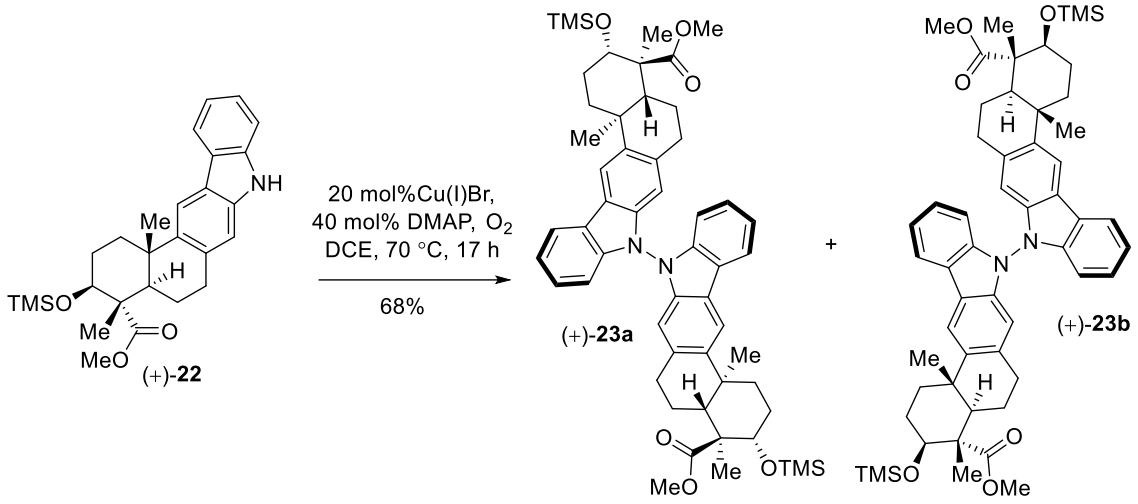
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.96 (s, 1H), 7.85 (s, 1H), 7.38 (d, *J* = 3.6 Hz, 2H), 7.22 (dt, *J* = 8.0, 3.9 Hz, 1H), 7.07 (s, 1H), 4.16 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.72 (s, 3H), 3.13 – 3.05 (m, 2H), 2.60 – 2.53 (m, 1H), 2.24 (dd, *J* = 12.5, 2.5 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.95 – 1.81 (m, 3H), 1.42 (ddt, J = 12.7, 7.3, 2.3 Hz, 1H), 1.32 (s, 3H), 1.30 (s, 3H), 0.09 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.9, 141.4, 140.0, 138.2, 133.5, 125.4, 123.7, 121.9, 119.9, 119.1, 115.6, 110.5, 109.8, 76.0, 54.7, 51.9, 46.3, 37.5, 37.1, 30.7, 28.3, 25.7, 21.5, 10.9, 0.2.

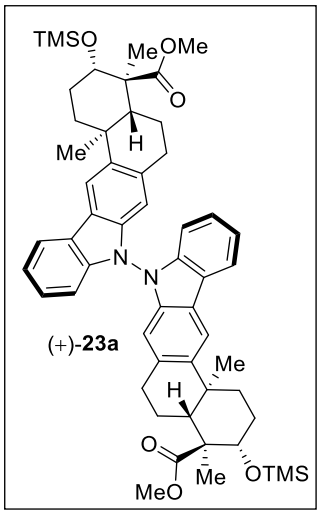
IR (neat) υ_{max} 3375, 2932, 2852, 1707, 1615, 1442, 1213, 1042, 778, 534 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{27}H_{35}O_3NSi + Na]^+$ 472.2278, found 472.2255.

$[\alpha]^{25}_{589}$ = +98.21 (*c* = 0.95, CH_3OH).

Cu(I)-Catalyzed Aerobic Oxidative *N–N* bond formation of [(+)-**23**]**:**



In an oven-dried sealed tube equipped with a septum and magnetic bar, (+)-**22** (300 mg, 0.67 mmol, 1.0 equiv.) was taken in 1,2-dichloroethane (8 mL) and 4-*N*,*N*-dimethylamino pyridine (DMAP, 32.7 mg, 0.27 mmol, 0.40 eq.) was added. This reaction mixture was purged with O_2 gas (using an O_2 balloon having 1 atm. pressure) for 10 minutes. Next, Cu(I)Br (27.5 mg, 0.134 mmol, 0.2 eq.) was added and capped the sealed tube tightly and placed on a pre-heated oil bath at 70 ºC and stirring was continued. Upon completion of the reaction (monitored by TLC analysis), most of the volatiles were evaporated under reduced pressure and purified by column chromatography using 5% EtOAc in *n*-hexane to afford 126 mg (42% yield) dixiamycin A methyl ester TMS ether **23a** and 78 mg (26% yield) dixiamycin B methyl ester TMS ether **23b**.



Dimethyl (3*S*,3'*S*,4a*R*,4'*S*,4'a*R*,8*R*,13b*S*,13'b*S*)**-4,4',13b,13'b-tetramethyl-3,3'-bis((trimethylsilyl)oxy)-1,1',2,2',3,3',4,4a,4',4'a,5,5',6,6',13b,13'b-hexadecahydro-[8,8'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylate** [(+)-**23a**]: Dixiamycin A methyl ester TMS

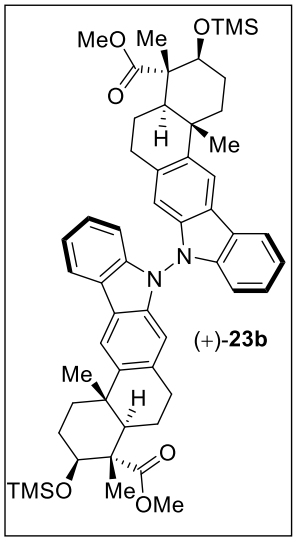
ether [(+)-**23a**] was obtained as colorless gel (0.67 mmol scale, 126 mg, 42% yield). R_f = 0.28 (5% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.11 (m, 2H), 8.07 (s, 2H), 7.32 – 7.29 (m, 2H), 7.27 (d, *J* = 9.3 Hz, 2H), 6.81 – 6.76 (m, 2H), 6.63 (s, 2H), 4.15 (dt, *J* = 11.0, 3.4 Hz, 2H), 3.67 (s, 6H), 2.94 – 2.84 (m, 4H), 2.61 (dd, *J* = 9.4, 3.3 Hz, 2H), 2.20 (dt, *J* = 12.7, 2.7 Hz, 2H), 1.96 – 1.90 (m, 4H), 1.89 – 1.82 (m, 4H), 1.35 (s, 6H), 1.31 – 1.30 (m, 2H), 1.28 (s, 6H), 0.09 (s, 18H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 143.0, 140.0, 138.4, 134.5, 126.0, 122.2, 120.8, 120.3, 120.1, 116.1, 109.0, 108.3, 76.0, 54.6, 51.9, 46.1, 37.5, 37.2, 30.5, 28.2, 25.7, 21.3, 10.9, 0.2.

IR (neat) υ_{max} 3313, 2891, 2812, 1692, 1591, 1586, 1442, 1248, 1197, 1074, 807 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{54}H_{68}O_6N_2Si_2 + Na]^+$ 919.4508, found 919.4522.

$[\alpha]^{25}_{589}$ = +67.7 (*c* = 0.42, CH_3OH).



Dimethyl (3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)**-4,4',13b,13'b-tetramethyl-3,3'-bis((trimethylsilyl)oxy)-1,1',2,2',3,3',4,4a,4',4'a,5,5',6,6',13b,13'b-hexadecahydro-[8,8'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylate** [(+)-**23b**]**:** Dixiamycin B methyl ester TMS ether [(+)-**23b**] was obtained as colorless gel (0.67 mmol scale, 78 mg, 26% yield). R_f = 0.3 (5% EtOAc in *n*-hexane).

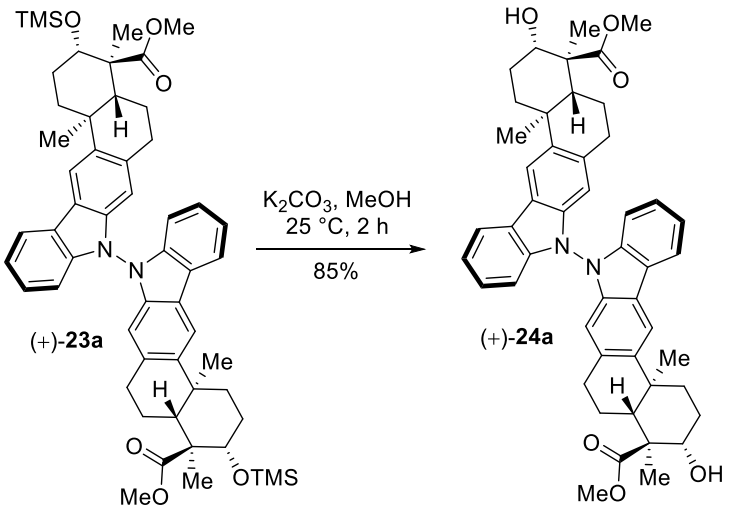
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.4, 2.3 Hz, 2H), 8.07 (s, 2H), 7.31 (ddd, *J* = 6.7, 4.1, 1.7 Hz, 4H), 6.93 – 6.87 (m, 2H), 6.52 (s, 2H), 4.16 (dd, *J* = 11.1, 4.1 Hz, 2H), 3.68 (s, 6H), 2.92 – 2.83 (m, 4H), 2.61 (dq, *J* = 8.7, 5.6, 4.0 Hz, 2H), 2.20 (dd, *J* = 12.6, 2.5 Hz, 2H), 1.98 – 1.91 (m, 4H), 1.91 – 1.83 (m, 4H), 1.35 (s, 6H), 1.33 – 1.31 (m, 2H), 1.28 (s, 6H), 0.10 (s, 18H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 143.0, 140.2, 138.3, 134.5, 126.0, 122.2, 120.8, 120.3, 120.1, 116.1, 109.0, 108.3, 76.0, 54.6, 51.9, 46.1, 37.5, 37.2, 30.5, 28.2, 25.7, 21.3, 10.9, 0.2.

IR (neat) υ_{max} 3321, 2899, 2841, 1697, 1601, 1591, 1437, 1245, 1201, 1072, 796 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{54}H_{68}O_6N_2Si_2 + Na]^+$ 919.4508, found 919.4527.

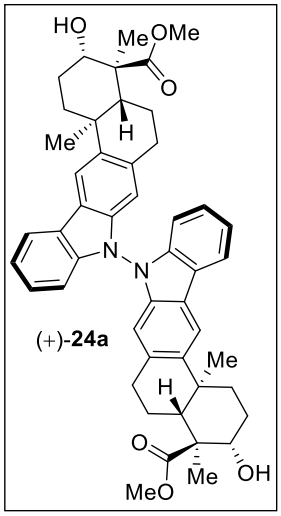
$[\alpha]^{25}_{589}$ = +30.0 (*c* = 0.32, CH_3OH).

Total Synthesis of Dixiamycin A Methyl Ester [(+)-**24a**]**:**



In an oven dried round-bottom flask, (+)-**23a** (36 mg, 0.04 mmol, 1.0 equiv.) was taken in MeOH (3 mL) at 25 ºC. K_2CO_3 (28 mg, 0.2 mmol, 5.0 equiv.) was added to it and stirring continued for 2 h. Upon completion of the reaction (monitored by TLC analysis), water (3 mL) was added to the reaction mixture the whole mixture was extracted with ethyl acetate (5 mL X 4). The organic layers were collected and dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. The crude product was purified by flash column

chromatography with 25% EtOAc in *n*-hexane to afford (+)-**24a** as white foam (25 mg, 85% yield).



Dimethyl (3*S*,3'*S*,4a*R*,4'*S*,4'a*R*,8*R*,13b*S*,13'b*S*)-**3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-1,1',2,2',3,3',4,4a,4',4'a,5,5',6,6',13b,13'b-hexadecahydro-[8,8'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylate** [(+)-**24a**]: Dixiamycin A methyl ester [(+)-**24a**] was obtained as white foam (0.04 mmol scale, 25 mg, 85% yield). R_f = 0.23 (50% EtOAc in *n*-hexane).

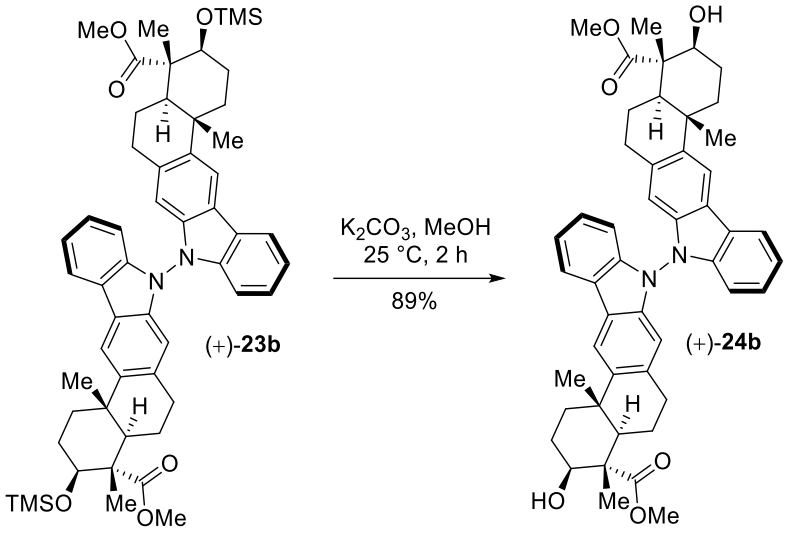
^{1}H NMR (500 MHz, CD_3OD): δ 8.12 (s, 2H), 8.09 (d, *J* = 7.0 Hz, 2H), 7.18 (td, *J* = 7.5, 1.2 Hz, 2H), 7.13 (td, *J* = 7.6, 1.3 Hz, 2H), 6.66 – 6.61 (m, 2H), 6.36 (s, 2H), 4.09 – 4.02 (m, 2H), 3.60 (s, 6H), 2.70 – 2.62 (m, 6H), 2.07 (dd, *J* = 12.5, 2.5 Hz, 2H), 1.94 – 1.81 (m, 6H), 1.80 – 1.72 (m, 2H), 1.30 (s, 2H), 1.28 (s, 6H), 1.23 (s, 6H).

^{13}C NMR (125 MHz, CD_3OD): δ 179.4, 144.4, 141.5, 139.7, 135.6, 127.2, 123.5, 122.1, 121.8, 121.4, 117.5, 109.7, 109.1, 76.2, 55.4, 52.6, 47.7, 38.8, 38.5, 31.5, 28.4, 26.17, 22.26, 11.3.

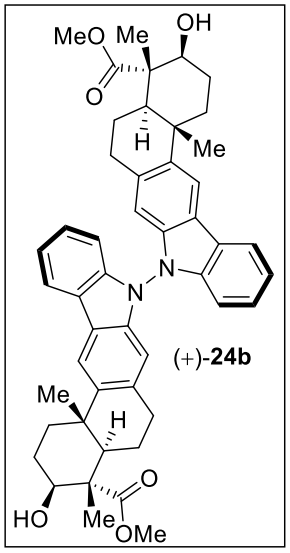
IR (neat) υ_{max} 3342, 3325, 2882, 1706, 1674, 1568, 1461, 1253, 1057, 912 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{48}H_{52}O_6N_2 + Na]^+$ 775.3718, found 775.3721.

$[\alpha]^{25}_{589}$ = +59.50 (*c* = 0.36, CH_3OH).

Total Synthesis of Dixiamycin B Methyl Ester [(+)-**24b**]**:**



In an oven dried round-bottom flask, (+)-**23b** (60 mg, 0.066 mmol, 1.0 equiv.) was taken in MeOH (4 mL) at 25 ºC. K_2CO_3 (47 mg, 0.33 mmol, 5.0 equiv.) was added to it and stirring continued for 2 h. Upon completion of the reaction (monitored by TLC analysis), water (5 mL) was added to the reaction mixture the whole mixture was extracted with ethyl acetate (5 mL X 4). The organic layers were collected and dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 25% EtOAc in *n*-hexane to afford (+)-**24b** as white foam (44 mg, 89% yield).



Dimethyl (3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-1,1',2,2',3,3',4,4a,4',4'a,5,5',6,6',13b,13'b-hexadecahydro-[8,8'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylate** [(+)-**24b**]**:** Dixiamycin B methyl ester [(+)-**24b**] was

obtained as white foam (0.066 mmol scale, 44 mg, 89% yield). R_f = 0.2 (50% EtOAc in *n*-hexane).

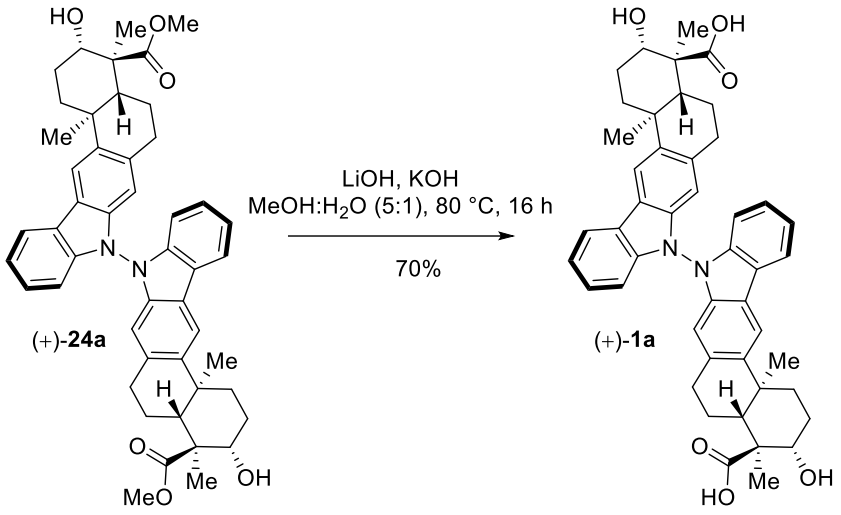
^{1}H NMR (500 MHz, CD_3OD): δ 8.15 (d, *J* = 6.9 Hz, 2H), 7.23 (p, *J* = 7.3 Hz, 2H), 6.71 (d, *J* = 7.7 Hz, 2H), 6.41 (s, 2H), 4.08 (t, *J* = 8.1 Hz, 2H), 3.65 (s, 6H), 2.81 – 2.74 (m, 4H), 2.69 (d, *J* = 13.2 Hz, 2H), 2.10 (d, *J* = 12.4 Hz, 2H), 1.92 (d, *J* = 9.8 Hz, 6H), 1.83 – 1.74 (m, 2H), 1.39 (s, 2H), 1.32 (s, 6H), 1.25 (s, 6H).

^{13}C NMR (125 MHz, CD_3OD): δ 179.4, 144.4, 141.6, 139.7, 135.7, 127.2, 123.5, 122.1, 121.9, 121.4, 117.5, 109.7, 109.1, 76.2, 55.4, 52.5, 47.8, 38.9, 38.5, 31.6, 28.4, 26.14, 22.3, 11.3.

IR (neat) υ_{max} 3101, 2932, 2861, 1709, 1667, 1641, 1417, 1401, 1373, 1227, 973, 761 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ K]^+$ calcd. for $[C_{48}H_{52}O_6N_2 + K]^+$ 791.3457, found 791.3474.

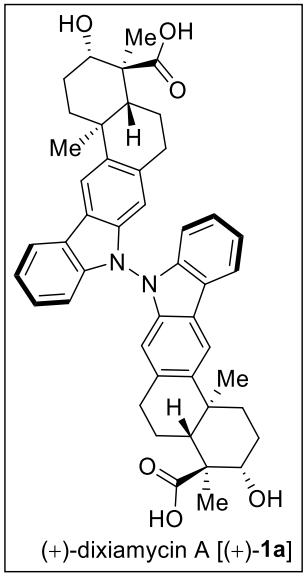
$[\alpha]^{25}_{589}$ = +80.5 (*c* = 0.41, CH_3OH).

Total Synthesis of Dixiamycin A [(+)-**1a**]**:**



In a round-bottom flask dixiamycin A methyl ester [(+)-**24a**] (9 mg, 0.012 mmol, 1.0 equiv.) was taken in a 5 mL mixture of methanol and water [MeOH: H_2O (5:1)] at 25 °C. KOH (34 mg, 0.6 mmol, 50 equiv.) and LiOH (15 mg, 0.36 mmol, 30 equiv.) were added successively to the reaction mixture at the same temperature. Next, this was placed on a pre-heated oil bath maintaining temperature at 80 ºC. After completion of the reaction (16 h), as confirmed by

TLC analysis, it was quenched with 6(*N*) HCl at 0 ºC and the pH of the reaction mixture was adjusted to ~1-2 and extracted with ethyl acetate (6 mL X 4). The organic layers were collected, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography with 10% MeOH in CH_2Cl_2 to afford dixiamycin A [(+)-**1a**] as white solid (6 mg, 70% yield).



(+)-dixiamycin A [(+)-**1a**]

(3*S*,3'*S*,4a*R*,4'*S*,4'a*R*,8*R*,13b*S*,13'b*S*)-**3,3'-Dihydroxy-4,4',13b,13'b-tetramethyl-1,1',2,2',3,3',4,4a,4',4'a,5,5',6,6',13b,13'b-hexadecahydro-[8,8'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylic acid** [(+)-**1a**]**:** Dixiamycin A [(+)-**1a**] was obtained as white solid (0.012 mmol scale, 6 mg, 70% yield). R_f = 0.27 (10% MeOH in CH_2Cl_2).

^{1}H NMR (500 MHz, CD_3OD) δ 8.16 (d, *J* = 6.6 Hz, 4H), 7.28 – 7.23 (m, 4H), 6.73 – 6.68 (m, 2H), 6.45 (s, 2H), 4.10 (q, *J* = 7.4, 5.6 Hz, 2H), 2.84 – 2.73 (m, 4H), 2.74 – 2.65 (m, 2H), 2.12 (d, *J* = 12.1 Hz, 2H), 1.96 – 1.87 (m, 6H), 1.78 (dt, *J* = 18.0, 8.9 Hz, 2H), 1.46 – 1.42 (m, 2H), 1.31 (s, 6H), 1.22 (s, 6H).

^{13}C NMR (125 MHz, CD_3OD) δ 180.1, 144.4, 141.4, 139.6, 135.7, 127.1, 123.4, 122.0, 121.7, 121.3, 117.4, 109.6, 108.9, 76.1, 54.7, 47.5, 38.8, 38.4, 31.7, 28.4, 26.1, 22.1, 11.3.

IR (neat) υ_{max} 3365, 2917, 2845, 1693, 1480, 1204, 1099, 851 cm^{-1}.
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{46}H_{47}O_6N_2 + Na]^+$ 747.3405, found 747.3431.

$[\alpha]^{25}_{589}$ = +77.5 (*c* = 0.34, CH_3OH); lit.[6] $[\alpha]_D^{21}$ = +90 (*c* = 0.4, CH_3OH).

Comparison of ^{1}H-NMR Data of Dixiamycin A [(+)-**1a**] of this report with natural Dixiamycin A [(+)-**1a**] by Zhang[6]:

Zhang's report Dixiamycin A [(+)-**1a**] (^{1}H-NMR, 500 MHz, CD_3OD)[6]			
δ (ppm)	Int.	mult.	*J* (Hz)
8.13	1H	d	*J* = 7.0 Hz
8.10	1H	s	-
7.26	1H	t	*J* = 7.0 Hz
7.24	1H	t	*J* = 7.0 Hz
6.73	1H	d	*J* = 7.0 Hz
6.53	1H	s	-
4.10	1H	dd	*J* = 9.0, 6.5 Hz
2.87	2H	-	-
2.66	1H	dt	*J* = 12.3, 2.0 Hz
2.17	1H	dd	*J* = 12.5, 1.6 Hz
1.95	2H	-	-
1.91	1H	-	-
1.84	1H	ddd	*J* = 12.3, 9.0, 1.0 Hz
1.47	1H	m	-
1.35	3H	s	-
1.25	3H	s	-

Li's isolation of Dixiamycin A [(+)-**1a**] (^{1}H-NMR, 600 MHz, CD_3OD)[7]		
δ (ppm)	Int.	mult.
8.16 – 8.14	2H	m
7.27 – 7.22	2H	m
6.72 - 6.71	1H	q
6.44	1H	s

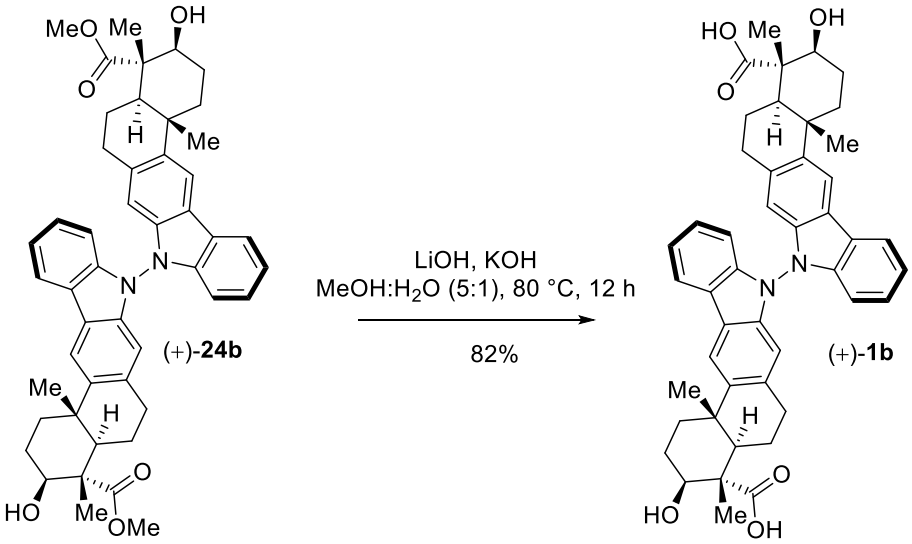
4.10 – 4.07	1H	t
2.86 – 2.80	2H	m
2.69 – 2.66	1H	m
2.13 – 2.11	1H	d
1.95 – 1.89	3H	m
1.80 – 1.75	1H	m
1.47 – 1.44	1H	m
1.32	3H	s
1.21	3H	s

This synthesis: Dixiamycin A [(+)-**1a**] (^{1}H-NMR, 500 MHz, CD_3OD)			
δ (ppm)	Int.	mult.	*J* (Hz)
8.16	4H	d	*J* = 6.6 Hz
7.28 – 7.23	4H	m	-
6.73 – 6.68	2H	m	-
6.45	2H	s	-
4.10	2H	q	*J* = 7.4, 5.6 Hz
2.84 – 2.73	4H	m	-
2.74 – 2.65	2H	m	-
2.12	2H	d	*J* = 12.1 Hz
1.96 – 1.87	6H	m	-
1.78	2H	dt	*J* = 18.0, 8.9 Hz
1.46 – 1.42	2H	m	-
1.31	6H	s	-
1.22	6H	s	-

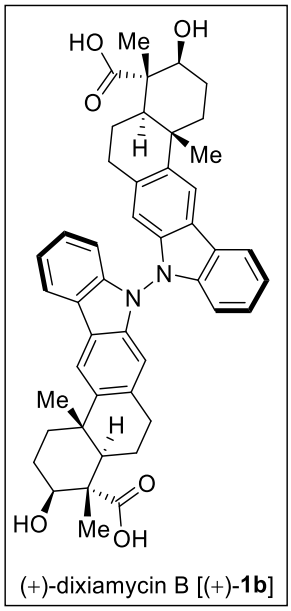
Comparison of ^{13}C-NMR Data:

Zhang's isolation of Dixiamycin A [(+)-**1a**] (^{13}C-NMR, 125.77 MHz, CD_3OD)[6]	This synthesis: Dixiamycin A [(+)-**1a**] (^{13}C-NMR, 125 MHz, CD_3OD)
180.0	180.1
144.2	144.4
141.2	141.4
139.5	139.6
135.6	135.7
126.9	127.1
123.3	123.4
121.9	122.0
121.5	121.7
121.1	121.3
117.2	117.4
109.7	109.6
109.1	108.9
76.0	76.1
54.6	54.7
47.2	47.5
38.8	38.8
38.3	38.4
31.7	31.7
28.3	28.4
26.4	26.1
22.1	22.1
11.4	11.3

Total Synthesis of (+)-Dixiamycin B [(+)-**1b**]**:**



In a round-bottom flask dixiamycin B methylester [(+)-**24b**] (20 mg, 0.027 mmol, 1.0 equiv.) was taken in a 5 mL mixture of methanol and water [MeOH: H_2O (5:1)] at 25 °C. KOH (75 mg, 1.33 mmol, 50 equiv.) and LiOH (34 mg, 0.81 mmol, 30 equiv.) were added successively to the reaction mixture at the same temperature. Next, this was placed on a pre-heated oil bath maintaining temperature at 80 ºC. After completion of the reaction (16 h), as confirmed by TLC analysis, it was quenched with 6(*N*) HCl at 0 ºC and the pH of the reaction mixture was adjusted to ~1-2 and extracted with ethyl acetate (6 mL X 4). The organic layers were collected, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography with 10% MeOH in CH_2Cl_2 to afford dixiamycin B [(+)-**1b**] as white solid (15 mg, 82% yield).



(+)-dixiamycin B [(+)-**1b**]

(3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-**3,3'-Dihydroxy-4,4',13b,13'b-tetramethyl-1,1',2,2',3,3',4,4a,4',4'a,5,5',6,6',13b,13'b-hexadecahydro-[8,8'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylic acid** [(+)-**1b**]**:** Dixiamycin B [(+)-**1b**] was obtained as white solid (0.027 mmol scale, 15 mg, 82% yield). R_f = 0.2 (10% MeOH in CH_2Cl_2).

^{1}H NMR (500 MHz, CD_3OD) δ 8.17 (d, *J* = 8.8 Hz, 4H), 7.26 (p, *J* = 7.3 Hz, 4H), 6.73 (d, *J* = 7.5 Hz, 2H), 6.46 (s, 2H), 4.14 – 4.08 (m, 2H), 2.83 (t, *J* = 8.5 Hz, 4H), 2.75 – 2.67 (m, 2H), 2.14 (d, *J* = 12.2 Hz, 2H), 1.95 (m, 6H), 1.82 (d, *J* = 13.7 Hz, 2H), 1.49 – 1.44 (m, 2H), 1.34 (s, 6H), 1.24 (s, 6H).

^{13}C NMR (125 MHz, CD_3OD) δ 181.4, 144.5, 141.5, 139.7, 135.8, 127.2, 123.5, 122.1, 121.8, 121.4, 117.5, 109.7, 109.1, 76.2, 54.8, 47.6, 38.9, 38.5, 31.8, 28.6, 26.2, 22.3, 11.4.

IR (neat) υ_{max} 3283, 2916, 2843, 1701, 1654, 1417, 1171, 905, 763 cm^{-1}
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd for $[C_{46}H_{47}O_6N_2 + Na]^+$: 747.3405, found: 747.3399.

$[\alpha]^{25}_{589}$ = +55.12 (*c* = 0.29, CH_3OH); lit.[6] $[\alpha]_D^{21}$ = +20 (*c* = 0.32, CH_3OH), lit.[4] $[\alpha]_D$ = +66 (*c* = 0.085, CH_3OH).

Comparison of ^{1}H-NMR Data of Dixiamycin B [(+)-**1b**] of this report with natural Dixiamycin B [(+)-**1b**] by Hertweck[8] and with literature by Baran[4]:

Hertweck's isolation of Dixiamycin B [(+)-**1b**] (^{1}H-NMR, 600 MHz, CD_3OD)[8]			
δ (ppm)	Int.	mult.	*J* (Hz)
8.17	2H	d	*J* = 7.7 Hz
8.16	2H	s	-
7.27	2H	t	*J* = 6.8 Hz
7.25	2H	t	*J* = 6.8 Hz
6.73	2H	d	*J* = 6.8 Hz
6.45	2H	s	-
4.09	2H	dd	*J* = 8.6, 7.1 Hz
2.86	2H	m	-
2.83	2H	m	-
2.69	2H	td	*J* = 13.1, 3.0 Hz
2.13	2H	dd	*J* = 12.5, 2.0 Hz
1.93	4H	m	-
1.92	2H	m	-
1.80	2H	m	-
1.45	2H	m	-
1.33	6H	s	-
1.22	6H	s	-

Baran's synthesis of Dixiamycin B [(+)-**1b**] (^{1}H-NMR, 600 MHz, CD_3OD)[4]			
δ (ppm)	Int.	mult.	*J* (Hz)
8.18 – 8.15	2H	m	-
8.14	2H	s	-
7.28 – 7.24	4H	m	-
6.72 – 6.70	2H	m	-
6.47	2H	s	-
4.10	2H	dd	*J* = 9.3, 7.0 Hz
2.89 – 2.80	4H	m	-

2.70	2H	td	J = 13.0, 3.5 Hz
2.12	2H	dd	J = 12.6, 2.3 Hz
1.94 – 1.88	6H	m	-
1.82 – 1.75	2H	m	-
1.54 – 1.48	2H	m	-
1.32	6H	s	-
1.22	6H	s	-

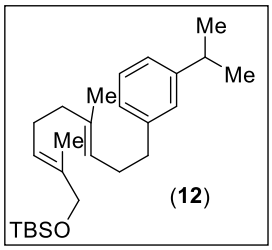
This synthesis: Dixiamycin B [(+)-**1b**] (^{1}H-NMR, 500 MHz, CD_3OD)			
δ (ppm)	Int.	mult.	J (Hz)
8.17	4H	d	J = 8.8 Hz
7.26	4H	p	J = 7.3 Hz
6.73	2H	d	J = 7.5 Hz
6.46	2H	s	-
4.14 – 4.08	2H	m	-
2.83	4H	t	J = 8.5 Hz
2.75 – 2.67	2H	m	-
2.14	2H	d	J = 12.2 Hz
1.95	6H	m	-
1.82	2H	d	J = 13.7 Hz
1.49 – 1.44	2H	m	-
1.34	6H	s	-
1.24	6H	s	-

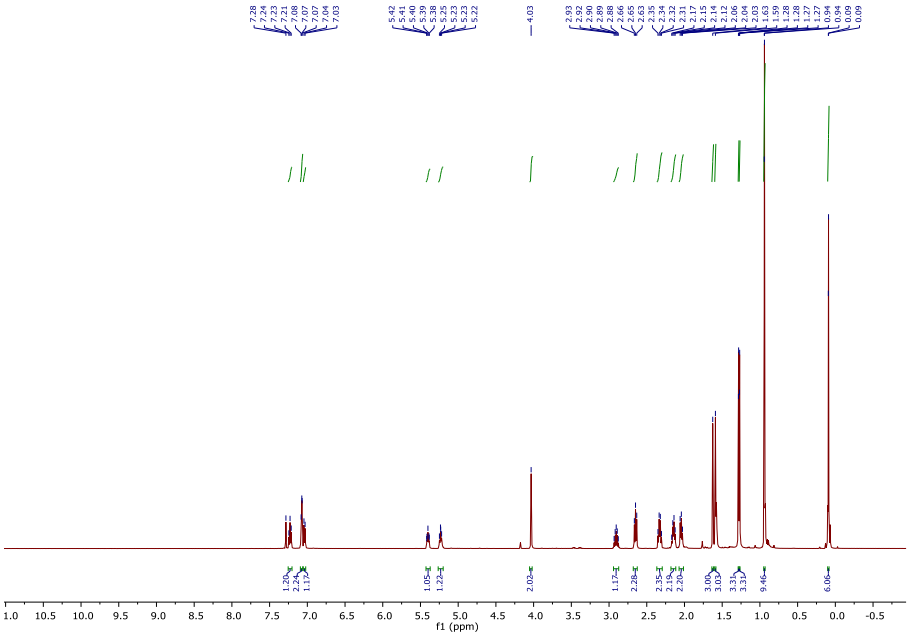
Comparison of ^{13}C-NMR Data:

Hertweck's isolation of Dixiamycin B [(+)-**1b**] (^{13}C-NMR, 125.77 MHz, CD_3OD)[8]	Baran's synthesis of Dixiamycin B [(+)-**1b**] (^{13}C-NMR, 151 MHz, CD_3OD)[4]	This synthesis: Dixiamycin B [(+)-**1b**] (^{13}C-NMR, 125 MHz, CD_3OD)

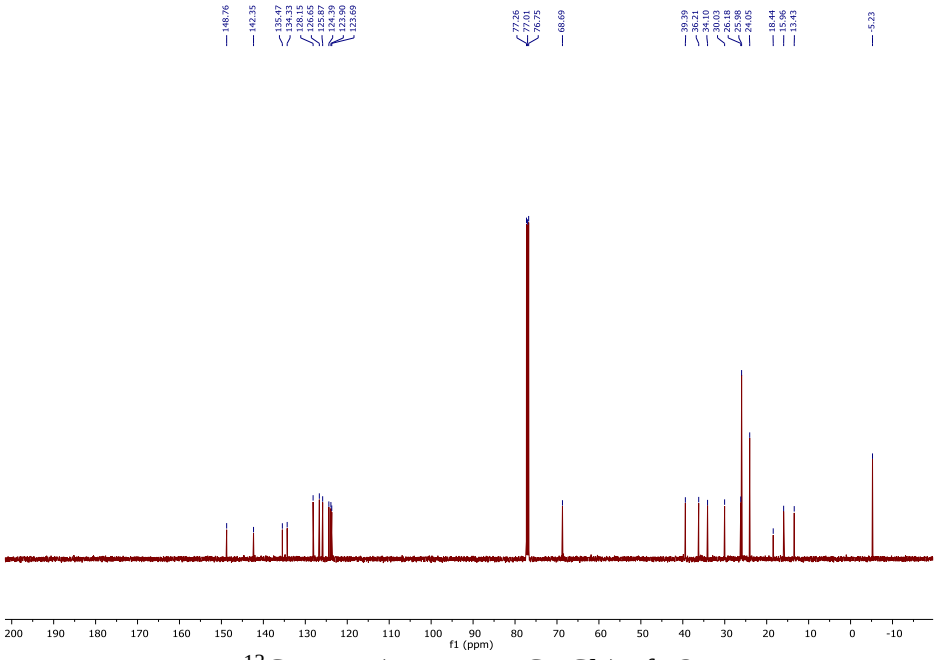
181.2	181.1	181.4
144.5	144.5	144.5
141.6	141.5	141.5
139.7	139.7	139.7
135.8	135.8	135.8
127.2	127.2	127.2
123.6	123.6	123.5
122.1	122.1	122.1
121.8	121.8	121.8
121.4	121.4	121.4
117.6	117.6	117.5
109.7	109.7	109.7
109.1	109.0	109.1
76.2	76.2	76.2
54.8	54.8	54.8
47.7	47.7	47.6
38.9	38.9	38.9
38.5	38.5	38.5
31.8	31.8	31.8
28.6	28.6	28.6
26.2	26.2	26.2
22.3	22.3	22.3
11.4	11.4	11.4

Spectral Traces





^{1}H NMR (500 MHz, $CDCl_3$) of **12**



^{13}C NMR (125 MHz, $CDCl_3$) of **12**

Display Report

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Sample Name	ab_rn_0105	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

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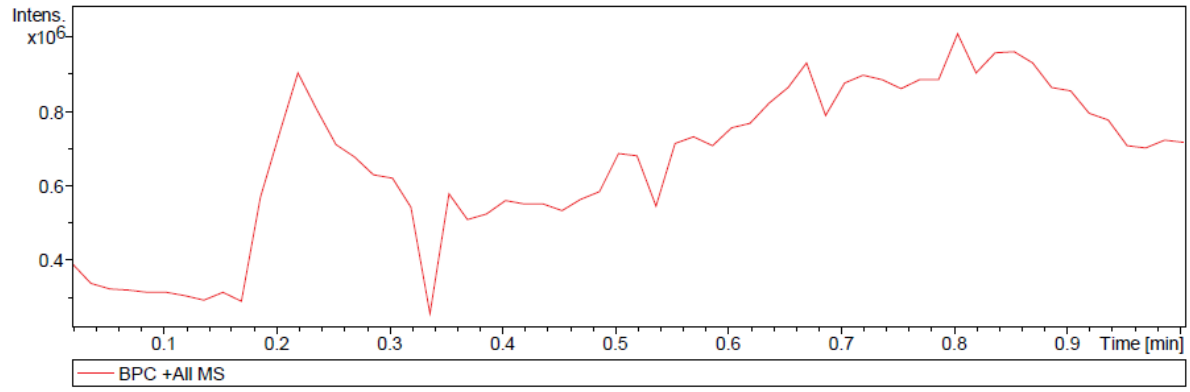
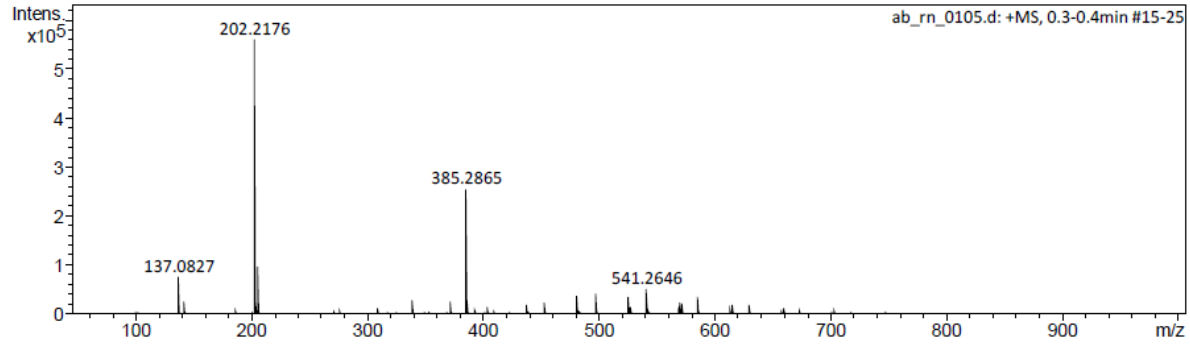
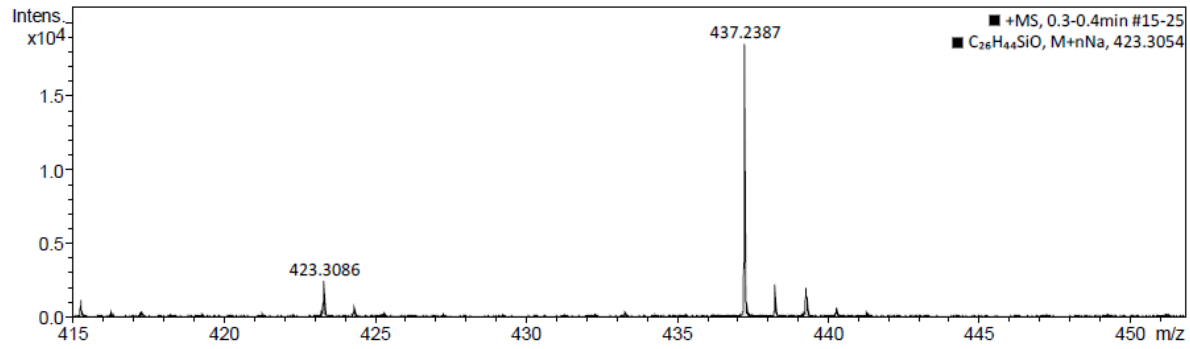
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



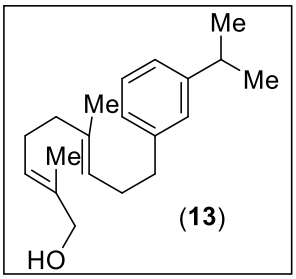


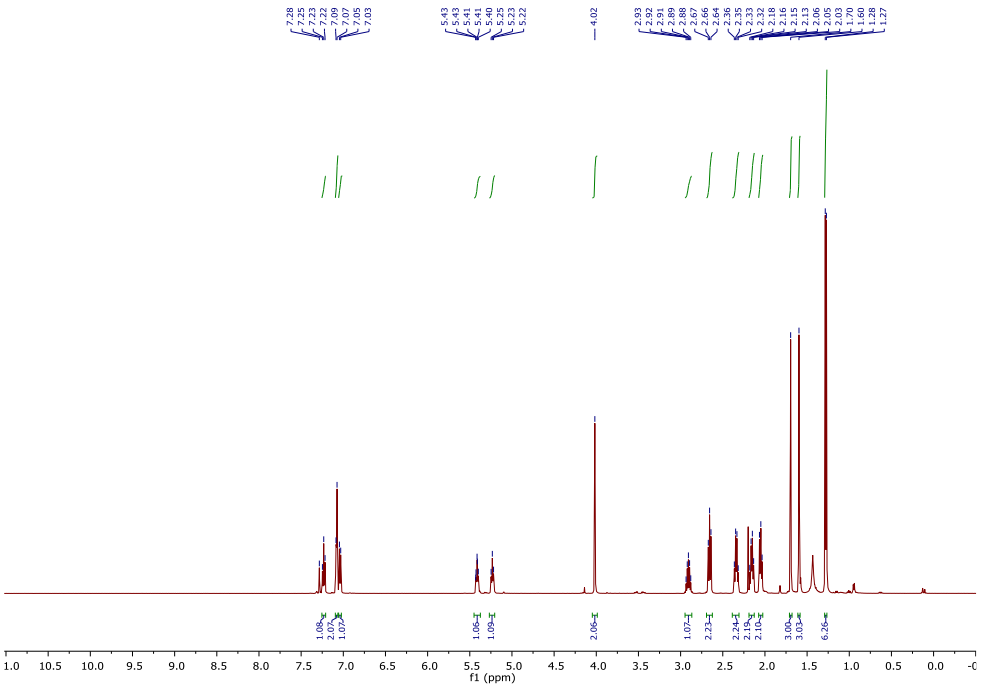


ab_rn_0105.d

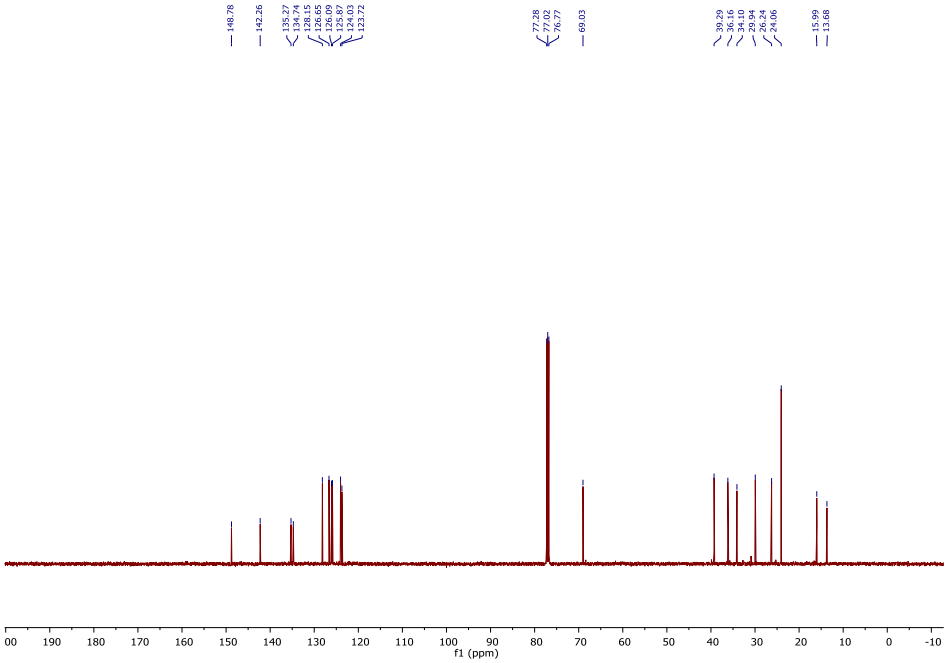
Bruker Compass DataAnalysis 4.1 printed: 5/9/2022 2:26:23 PM by: IISER Kolkata Page 1 of 1

HRMS data of **12**





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



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

Display Report

Analysis Info

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Comment			

Acquisition Parameter

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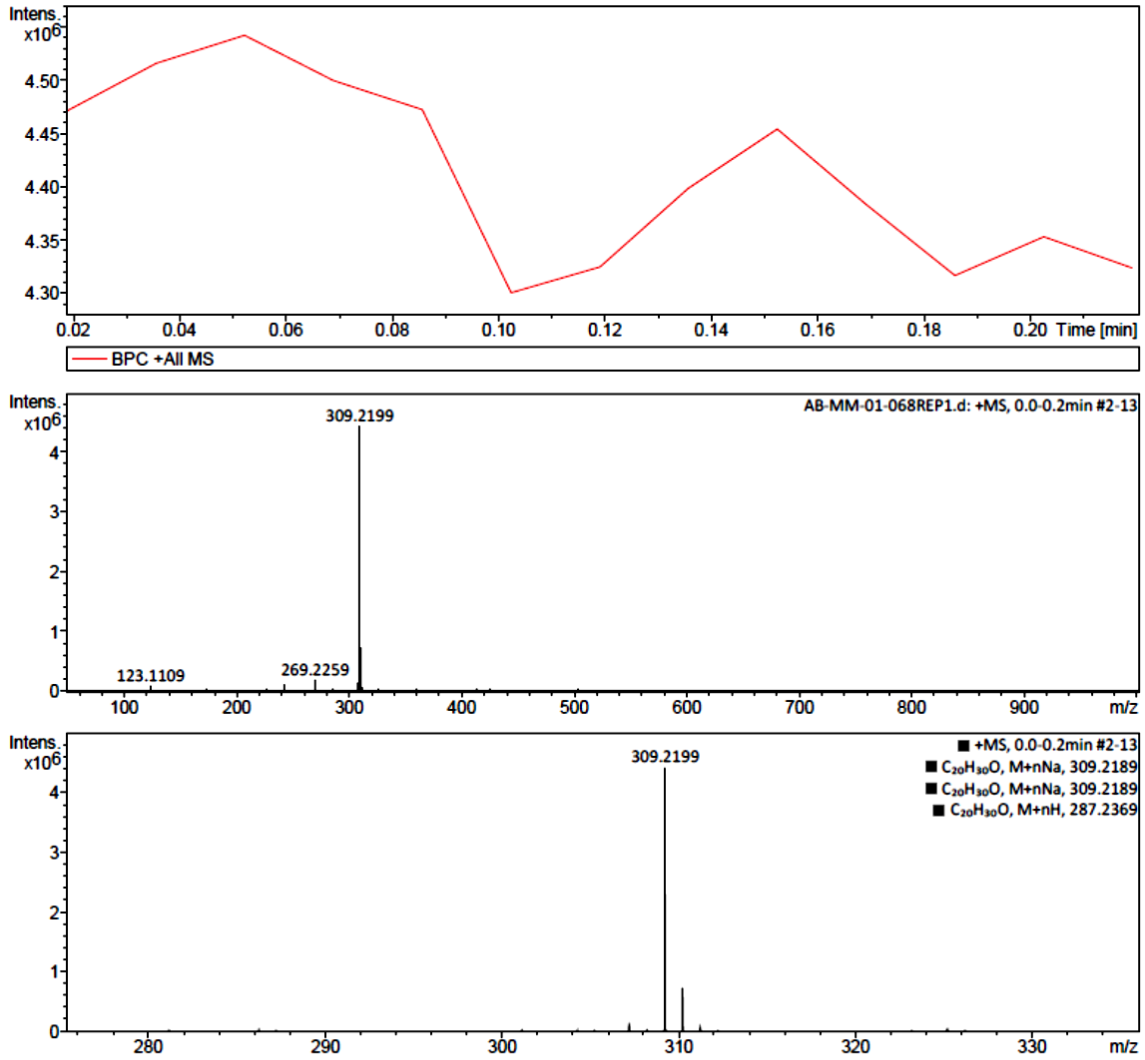
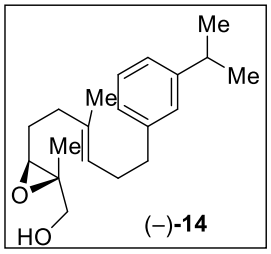
		Set Corona	0 nA	Set APCI Heater	0 °C



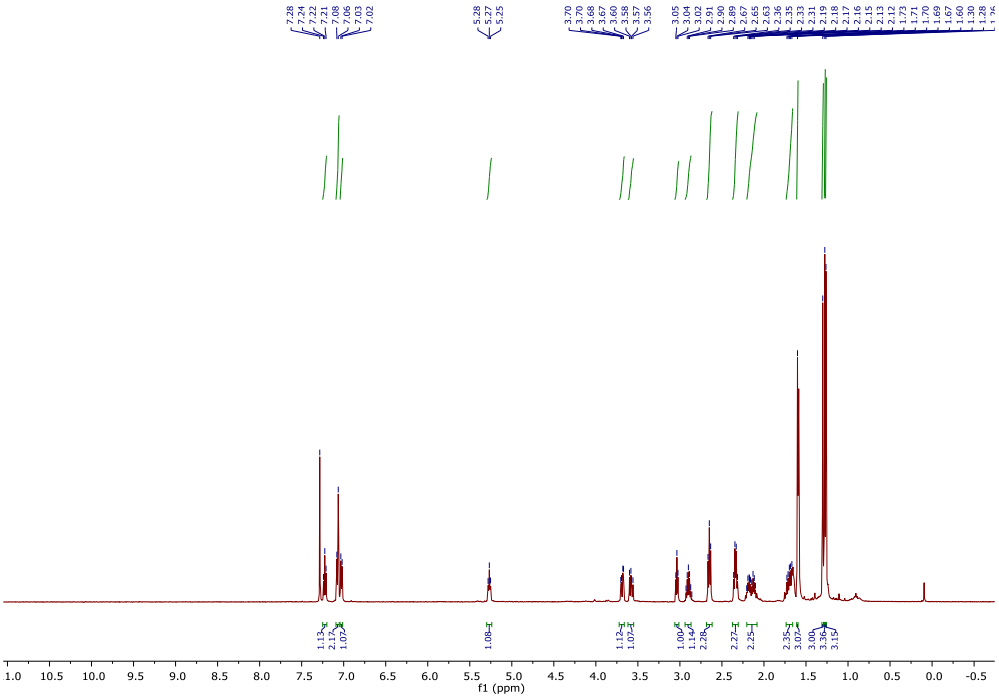
AB-MM-01-068REP1.d

Bruker Compass DataAnalysis 4.1 printed: 12/21/2020 11:45:24 AM by: IISER Kolkata Page 1 of 1

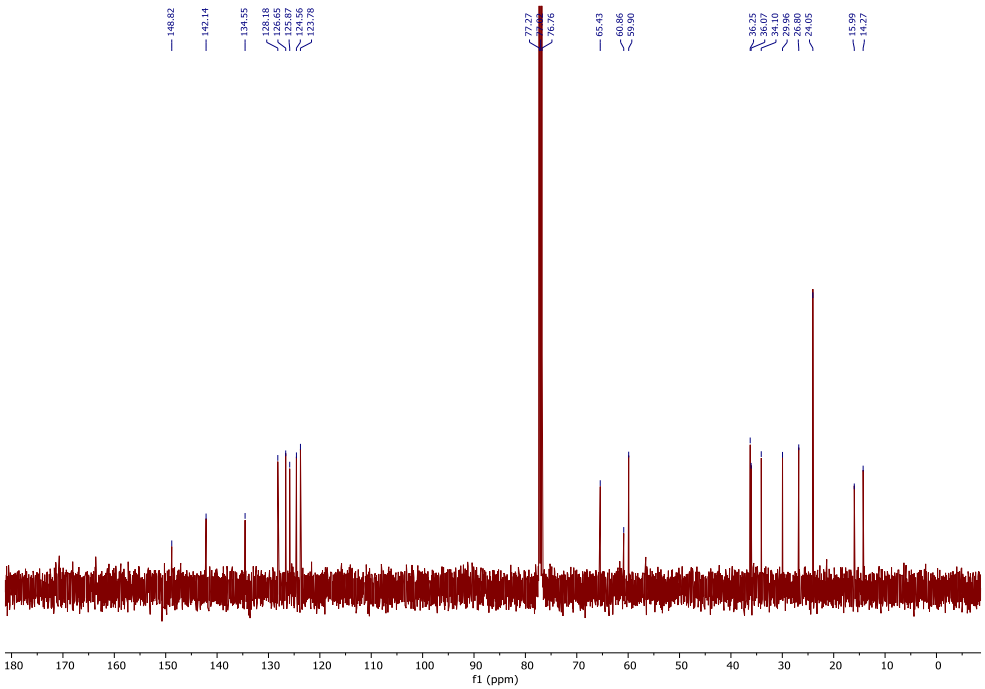
HRMS data of **13**



(–)-**14**



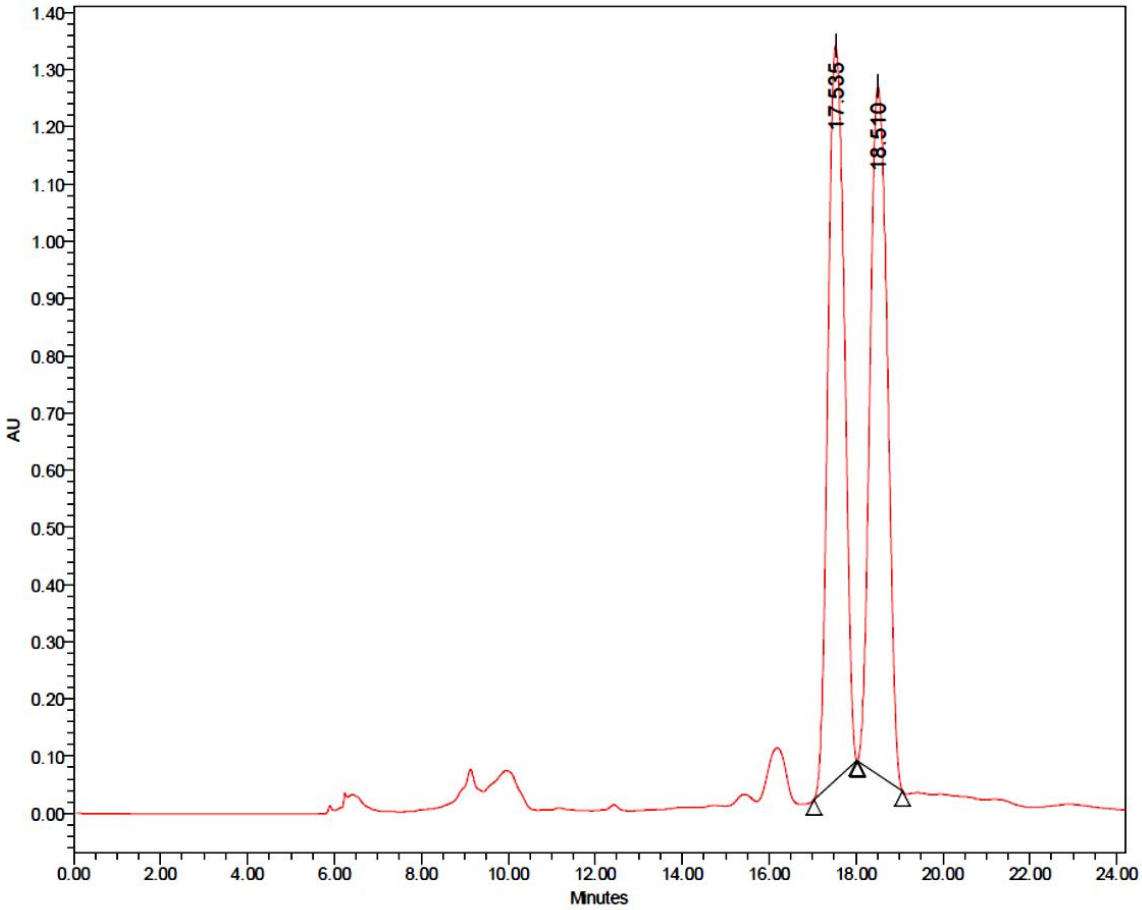
^{1}H NMR (500 MHz, $CDCl_3$) of (–)-**14**



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

Empower 3 SOFTWARE

Peak Summary Report



Sample Name: AB_RN_IC-3_HEX_0p5_0324; Date Acquired: 30-12-2021 18:53:20 IST; Vial: 1; Injection 1

Peak Summary with Statistics

Name:

	Sample Name	Vial	Inj	Retention Time (min)	Area	% Area	Height
1	AB_RN_IC-3_HEX_0p5_0324	1	1	18.510	33519938	49.94	1203537
2	AB_RN_IC-3_HEX_0p5_0324	1	1	17.535	33603619	50.06	1284144
Mean				18.022			
Std. Dev.				0.690			

Reported by User: System
Report Method: Peak Summary Report
Report Method ID 1009
Page: 1 of 2

Project Name: AB Research Group
Date Printed:
09-07-2022
11:02:25 Asia/Calcutta

HPLC data for (±)-**14**

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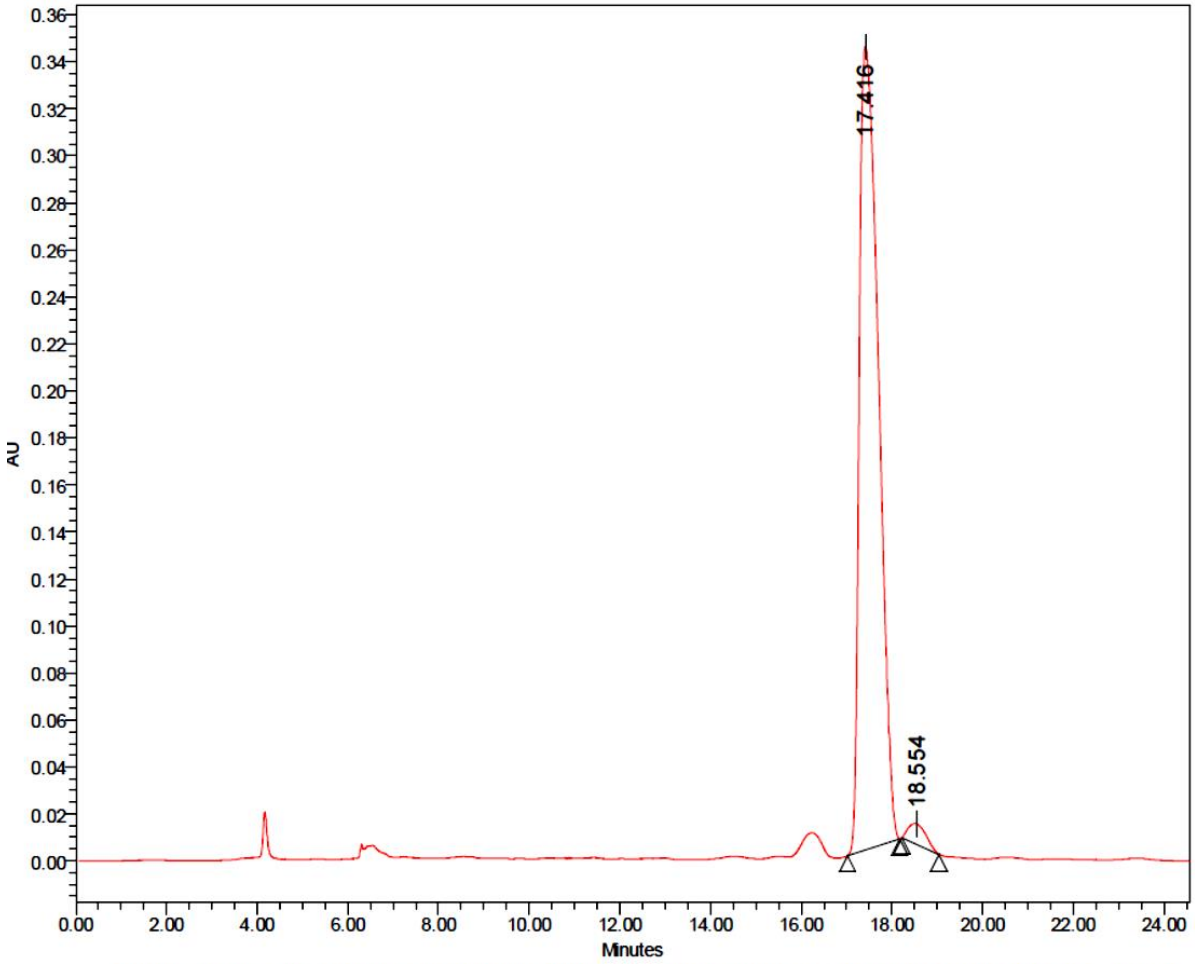
Peak Summary Report



Sample Name: AB_RN_IC-3_HEX_0p5_0285_CHI; Date Acquired: 30-12-2021 19:19:05 IST; Vial: 1
Injection: 2

Peak Summary with Statistics
Name:

	Sample Name	Vial	Inj	Retention Time (min)	Area	% Area	Height
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2	AB_RN_IC-3_HEX_0p5_0285_CHI	1	2	17.416	9977366	97.66	341559
Mean				17.985			
Std. Dev.				0.804			

Reported by User: System
Report Method: Peak Summary Report
Report Method ID 1009
Page: 1 of 2

Project Name: AB Research Group
Date Printed:
02-01-2022
16:05:25 Asia/Calcutta

HPLC data for (–)-**14**

Display Report

Analysis Info

Analysis Name	D:\Data\User data\2021\JAN\AB-AYA-RN-0107R.d	Acquisition Date	1/13/2021 11:46:36 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB-AYA-RN-0107R	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

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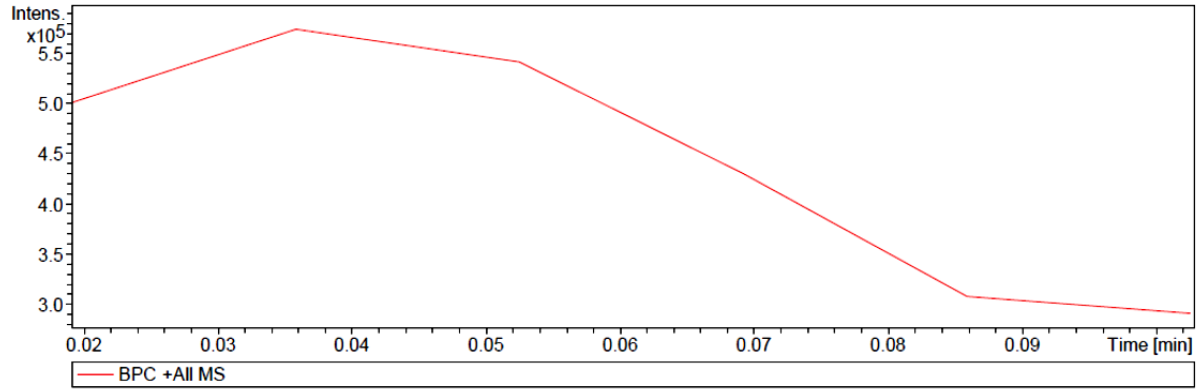
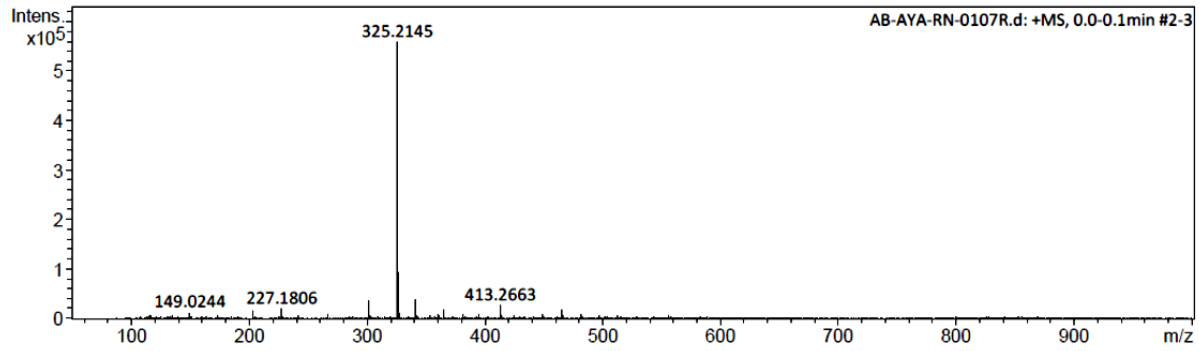
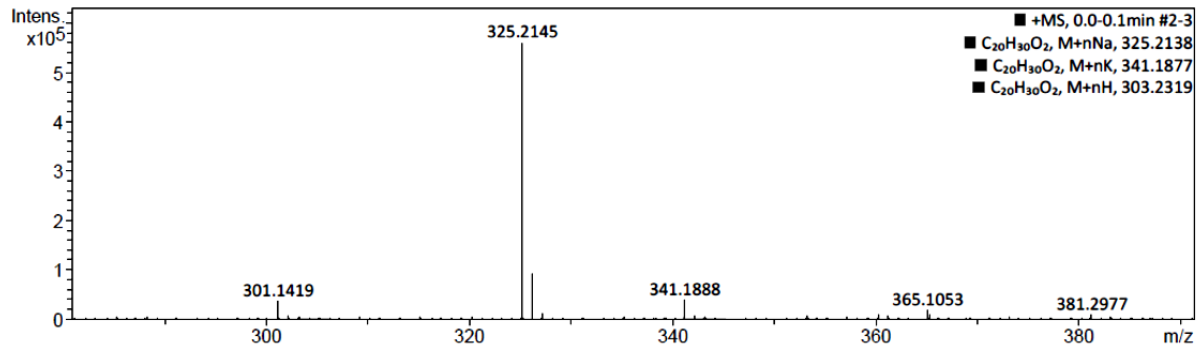
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



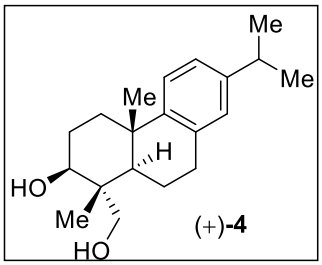


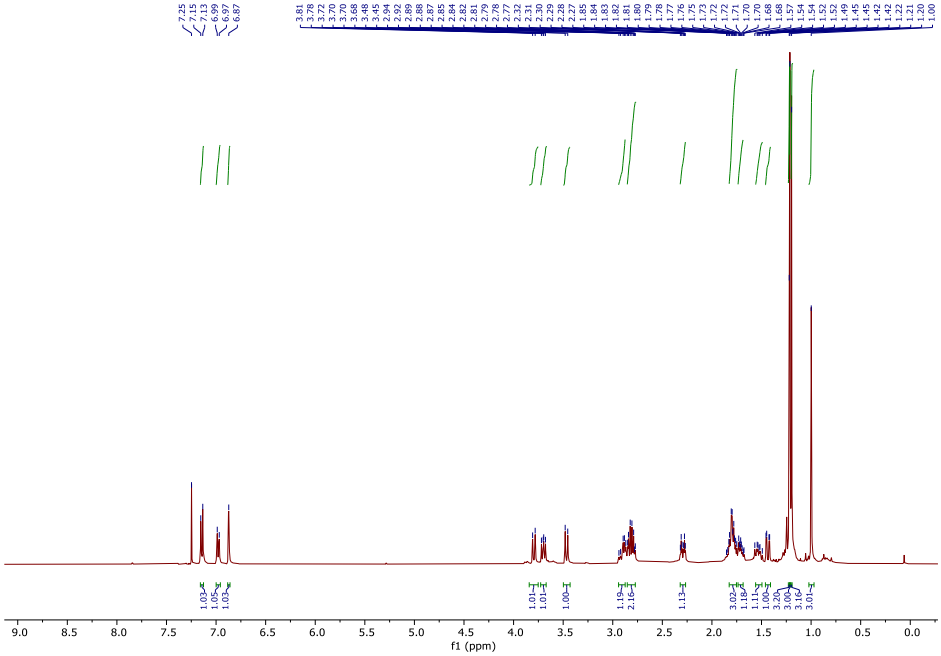


AB-AYA-RN-0107R.d

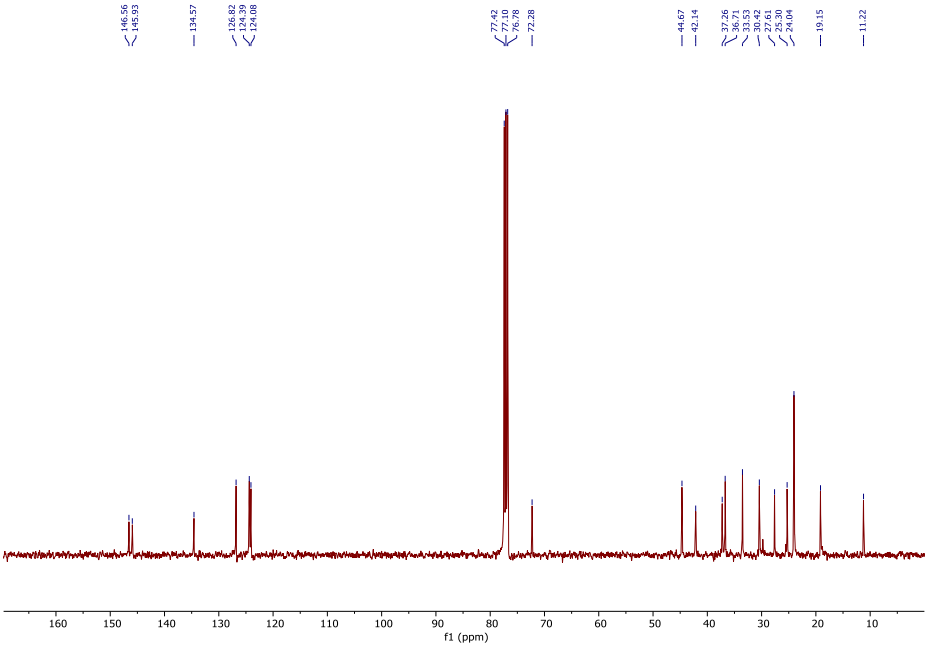
Bruker Compass DataAnalysis 4.1 printed: 1/13/2021 11:50:22 AM by: IISER Kolkata Page 1 of 1

HRMS Data of (−)-**14**





^{1}H NMR (400 MHz, $CDCl_3$) of (+)-**4**



^{13}C NMR (100 MHz, $CDCl_3$) of (+)-**4**

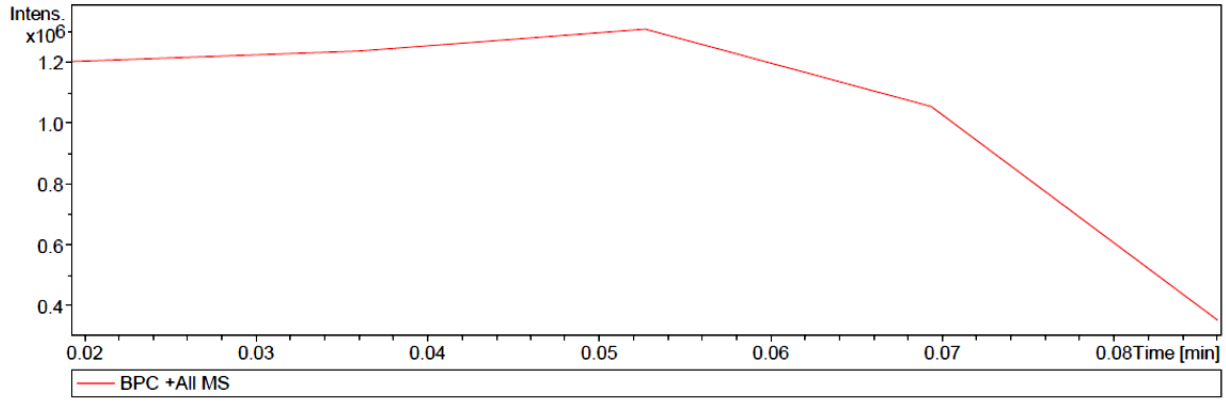
Display Report

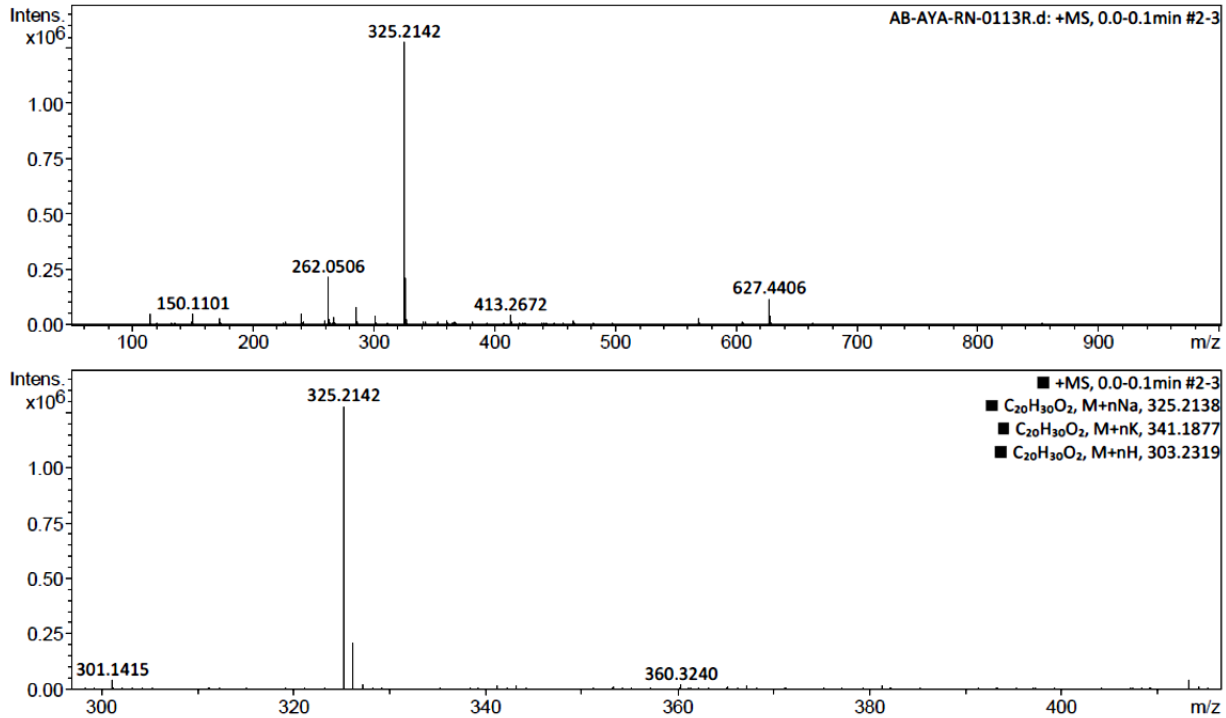
Analysis Info

Analysis Name	D:\Data\User data\2021\JAN\AB-AYA-RN-0113R.d	Acquisition Date	1/18/2021 1:37:04 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB-AYA-RN-0113R	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

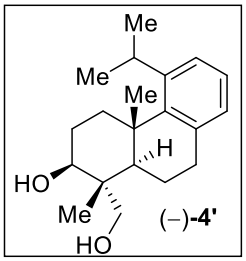


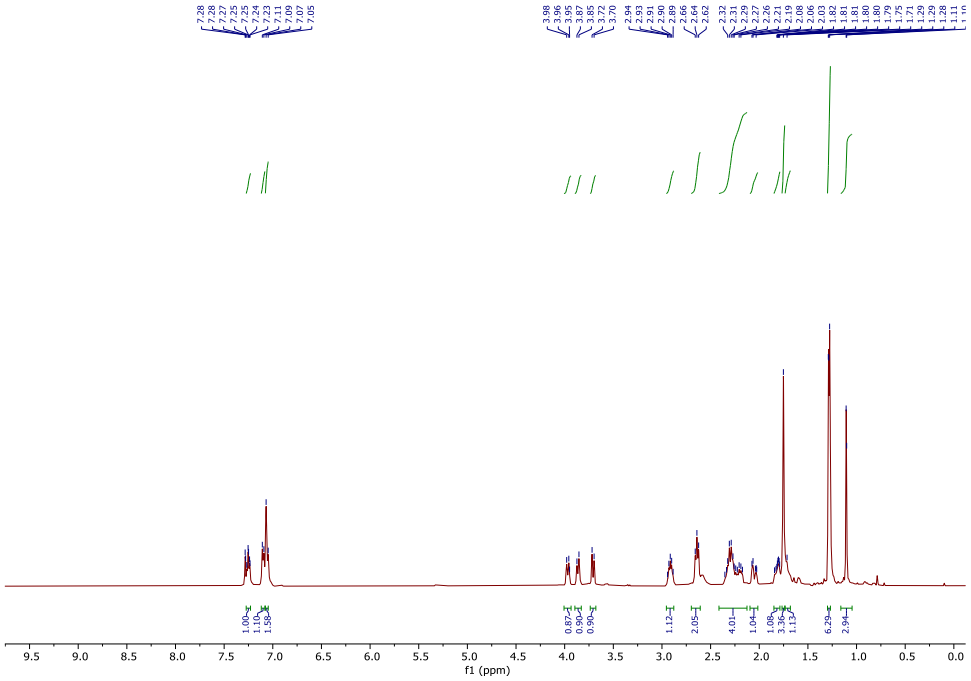


AB-AYA-RN-0113R.d

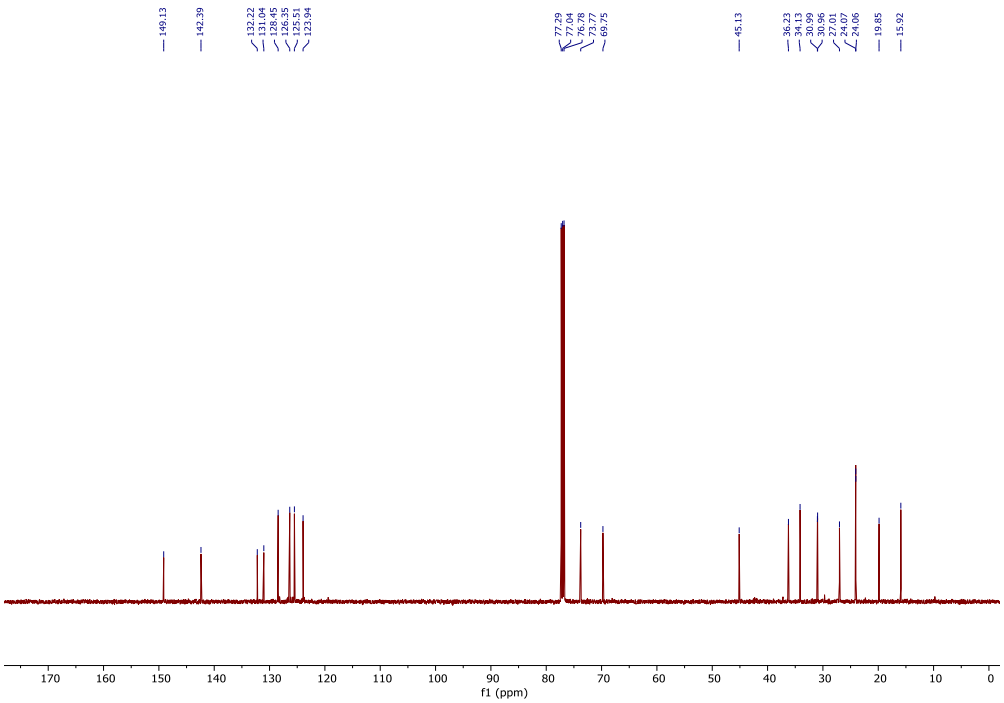
Bruker Compass DataAnalysis 4.1 printed: 1/18/2021 1:40:01 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**4**





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



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

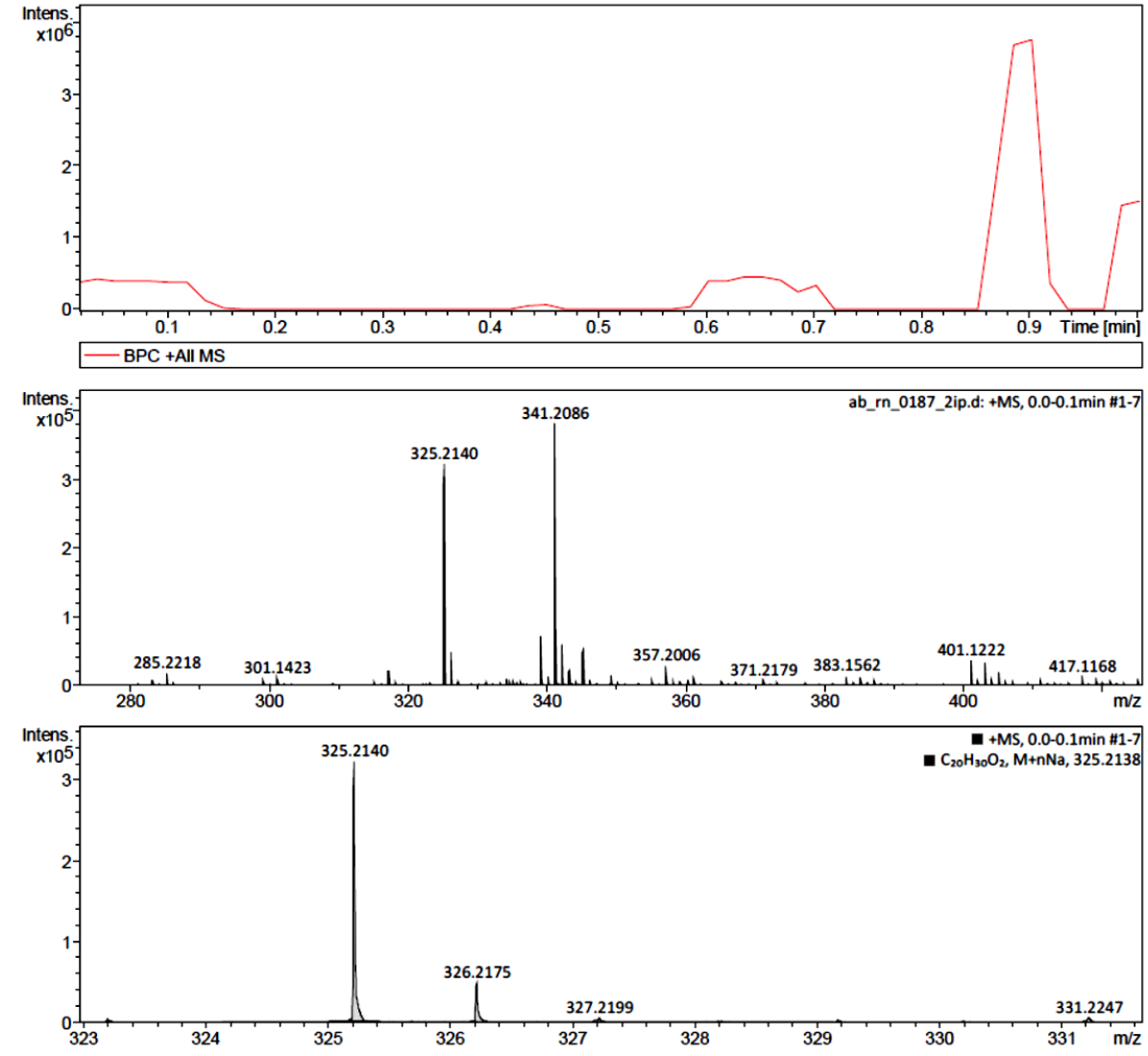
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2022\JULY\ab_rn_0187_2ip.d	Acquisition Date	7/18/2022 10:26:57 AM
Method	Tune_pos_Standard_July2022.m	Operator	IISER Kolkata
Sample Name	ab_rn_0187_2ip	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

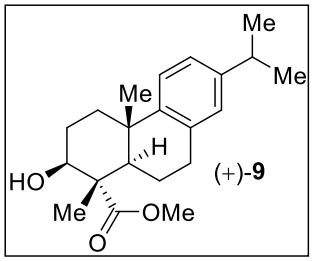
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

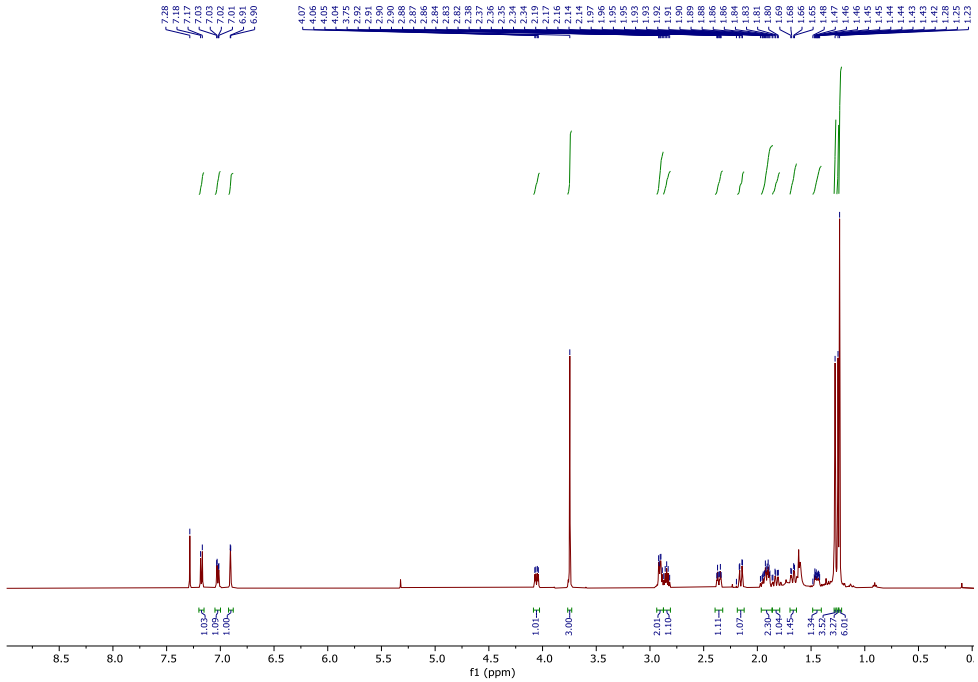


ab_rn_0187_2ip.d

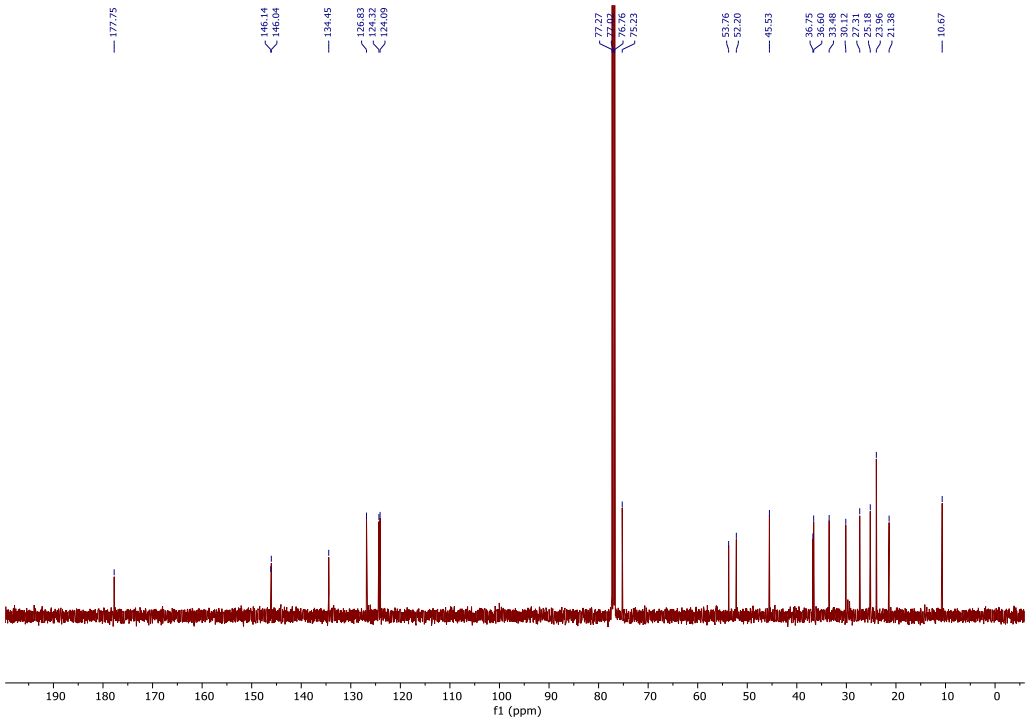
Bruker Compass DataAnalysis 4.1 printed: 7/18/2022 10:31:48 AM by: IISER Kolkata Page 1 of 1

HRMS data of (−)-**4'**





^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**9**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**9**

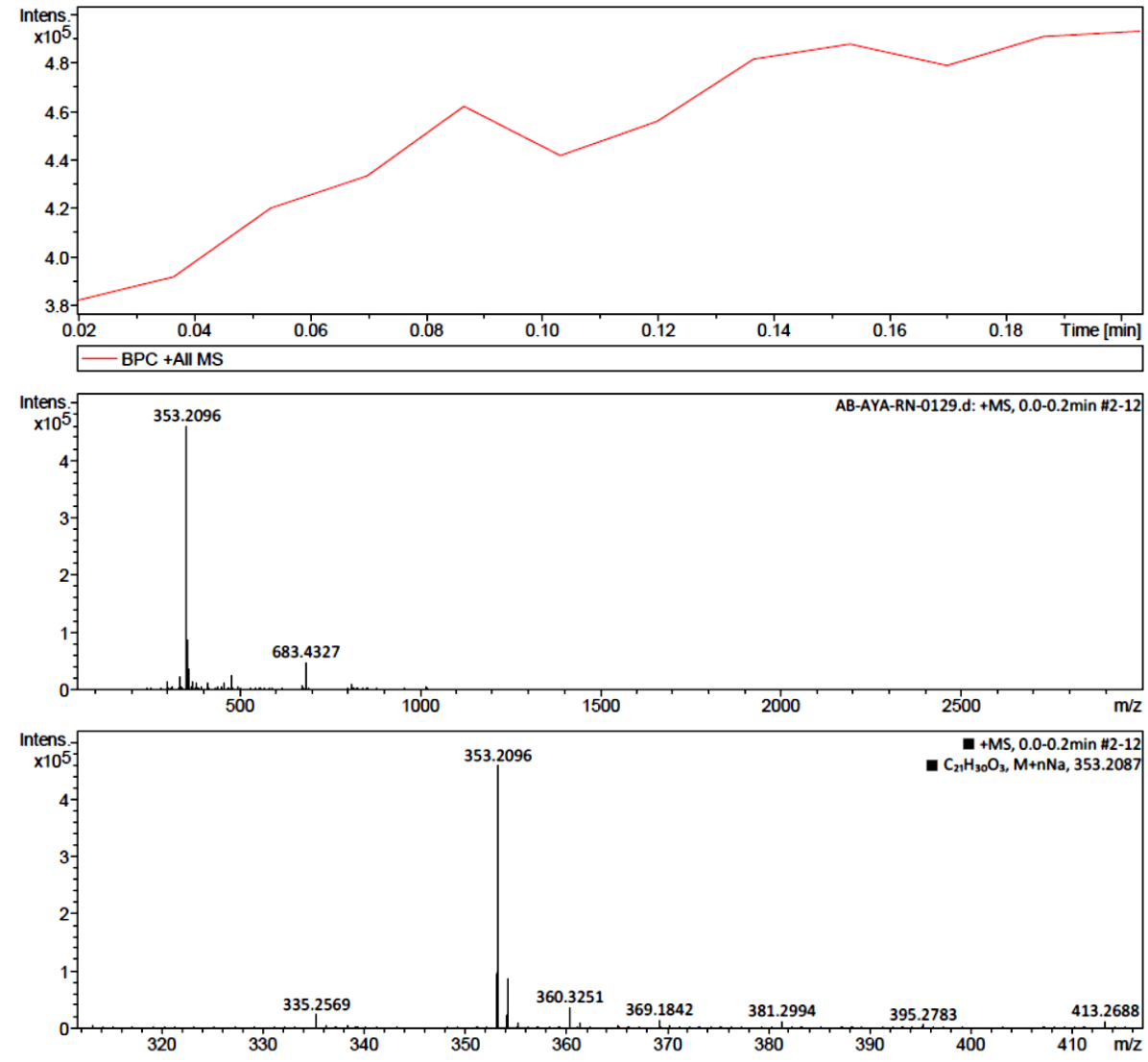
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2021\JAN\AB-AYA-RN-0129.d	Acquisition Date	1/27/2021 2:42:29 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB-AYA-RN-0129	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

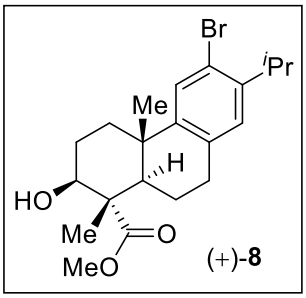
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

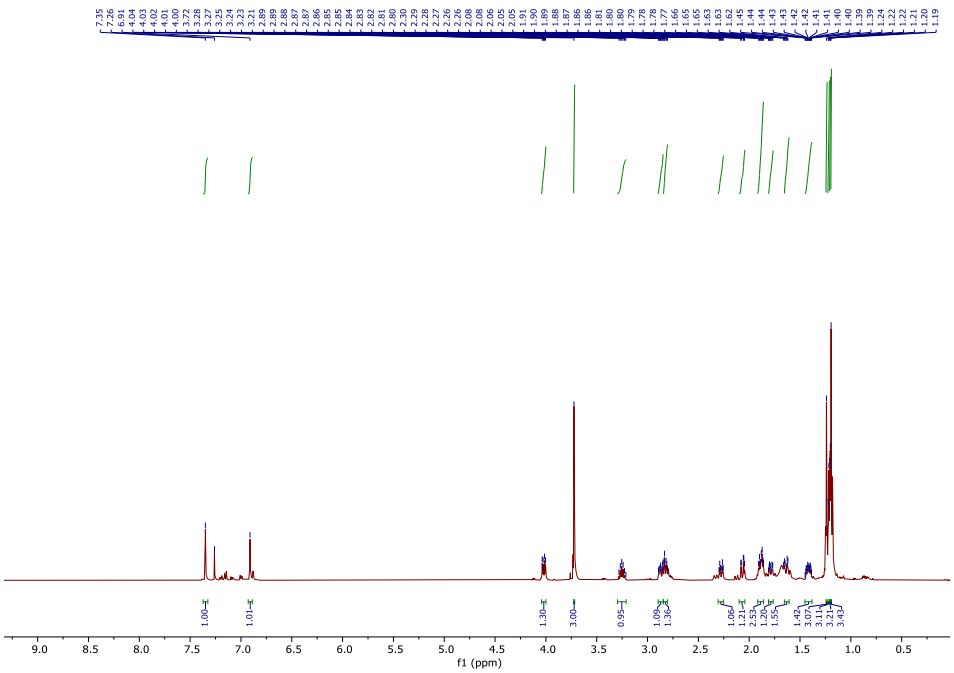


AB-AYA-RN-0129.d

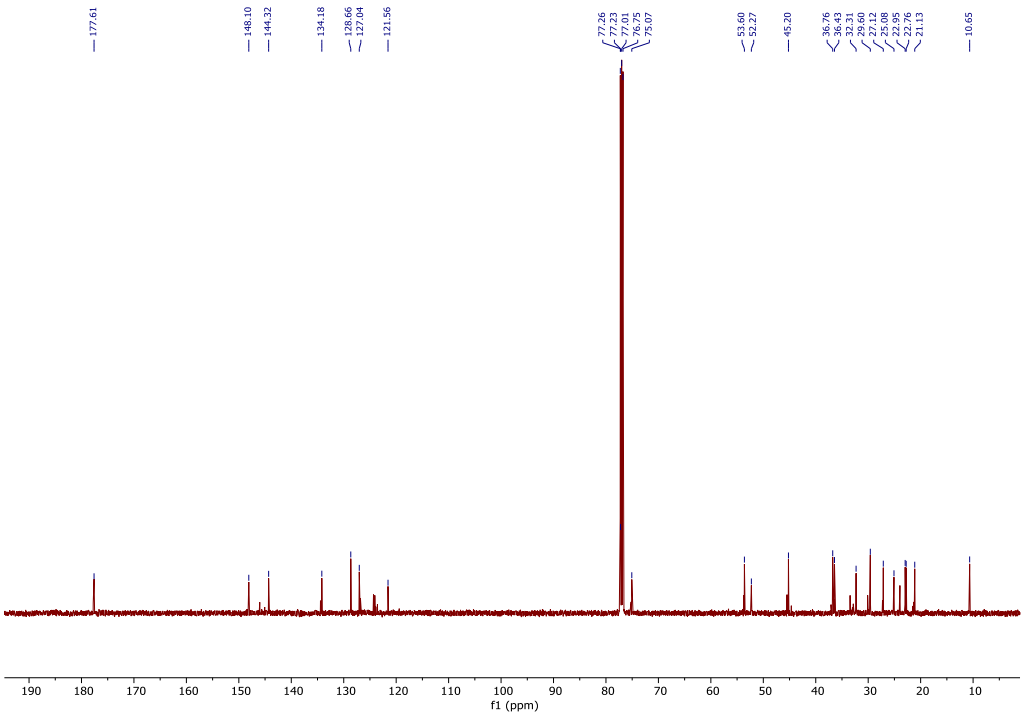
Bruker Compass DataAnalysis 4.1 printed: 1/27/2021 2:48:40 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**9**





^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**8**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**8**

Display Report

Analysis Info

Analysis Name	D:\Data\User data\2022\JAN\ab_rn_0348.d	Acquisition Date	1/25/2022 10:56:53 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_rn_0348	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
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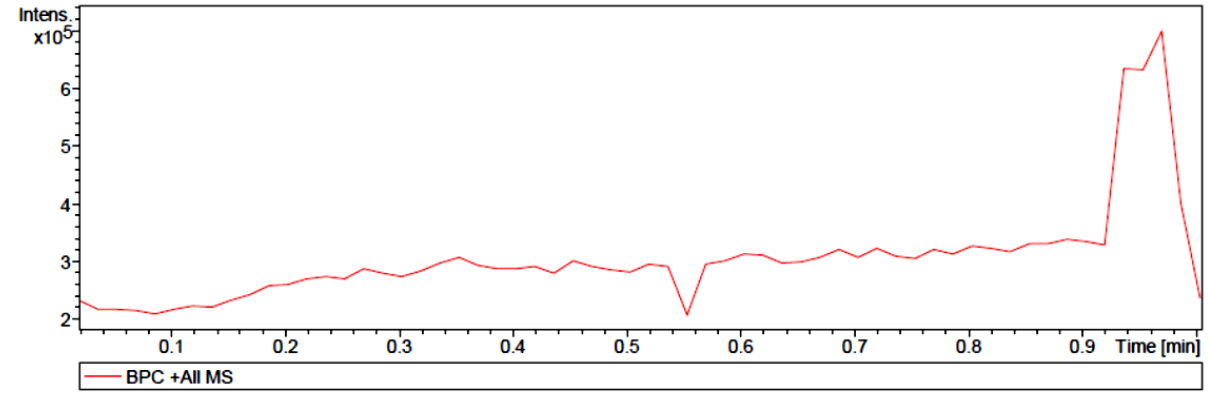
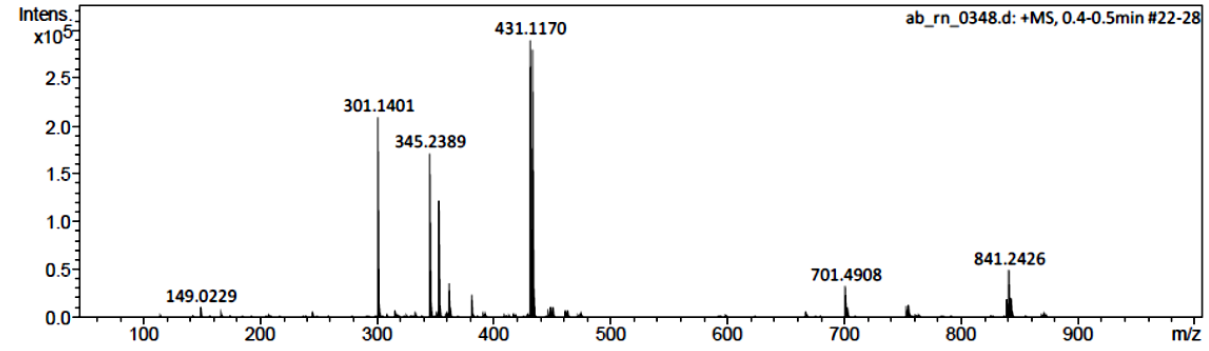
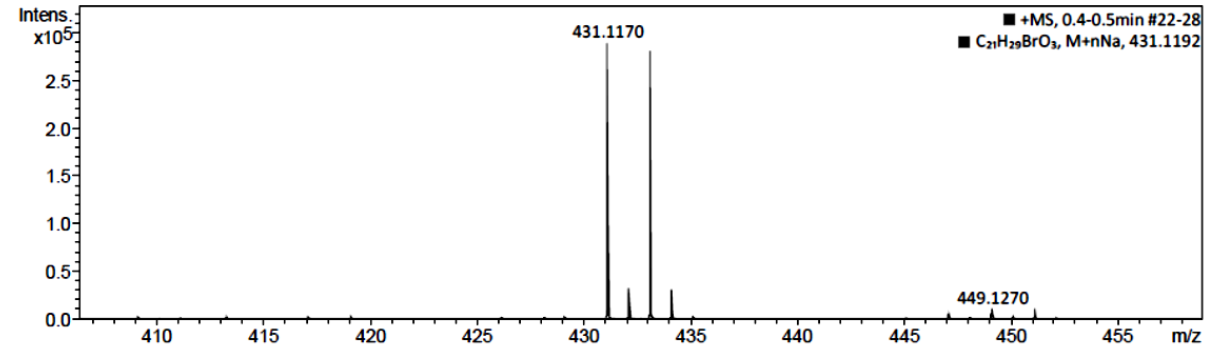


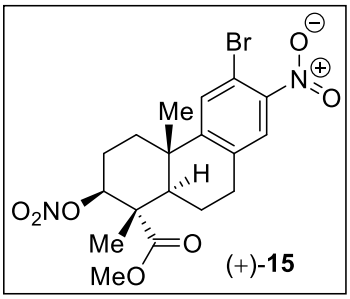


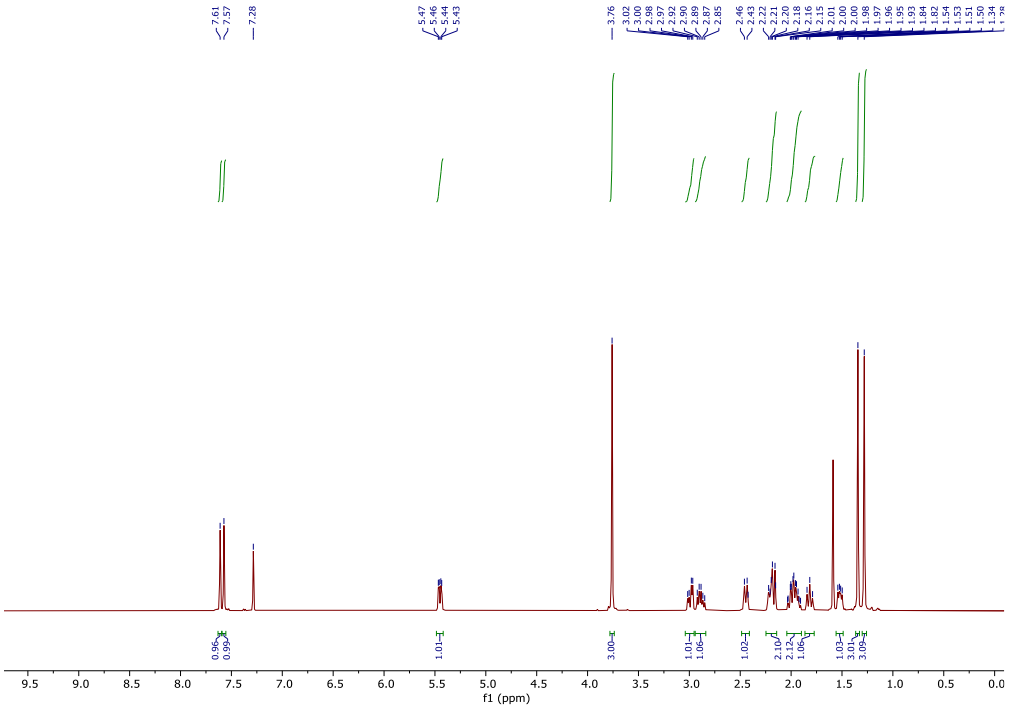


ab_rn_0348.d

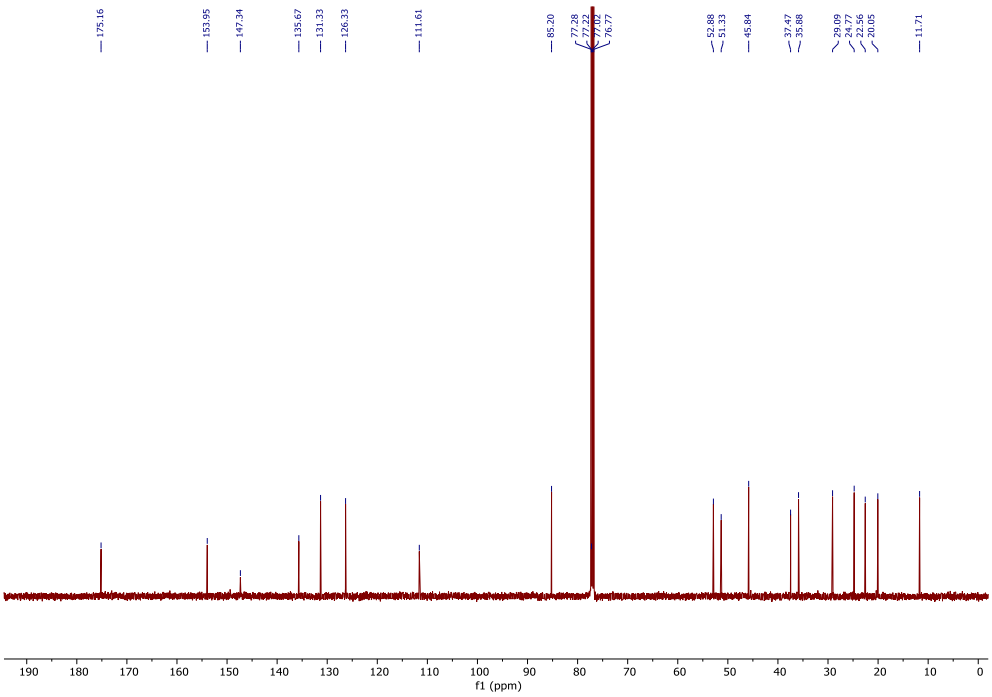
Bruker Compass DataAnalysis 4.1 printed: 1/25/2022 11:36:09 AM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**8**





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



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

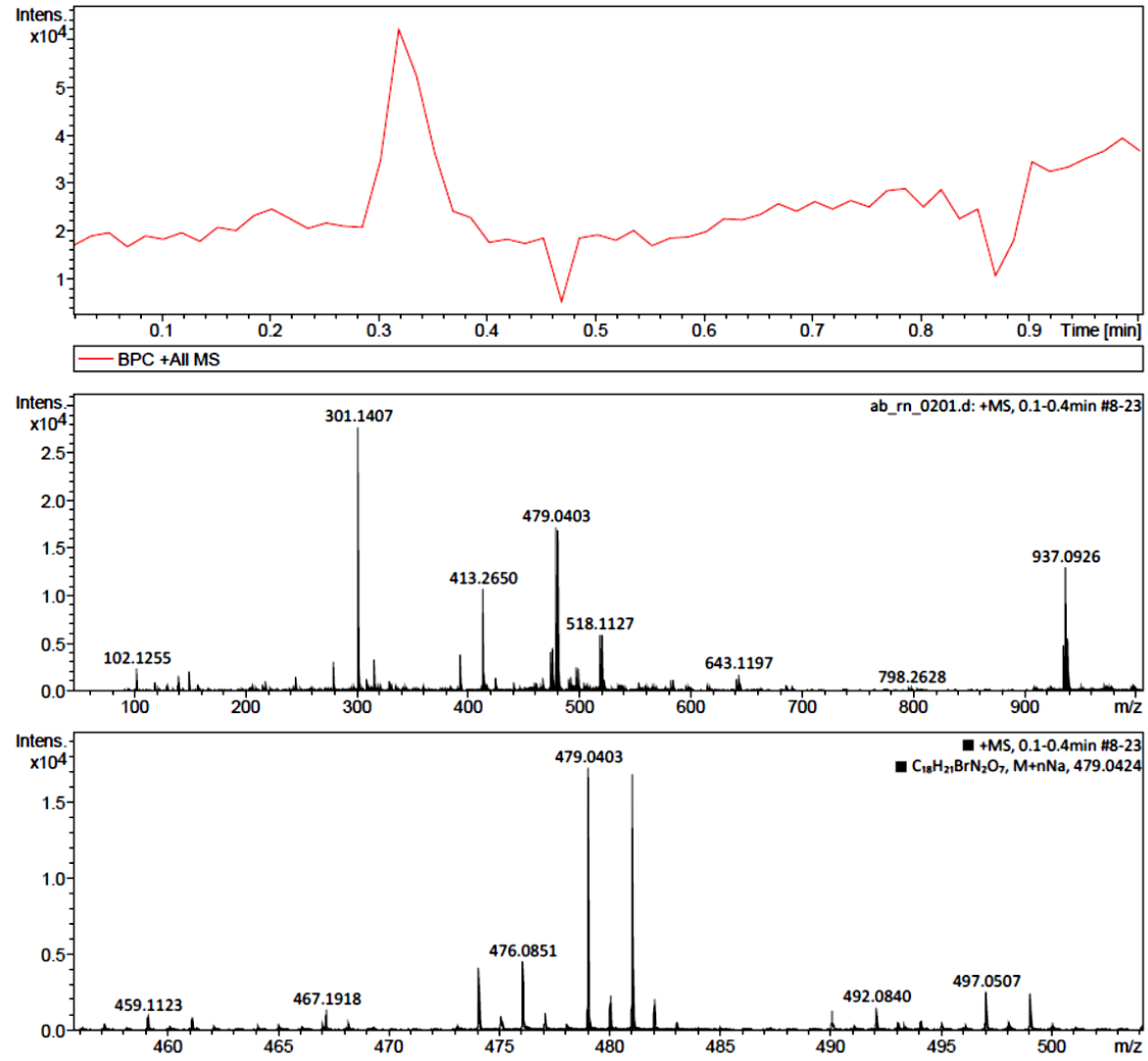
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2022\FEB\ab_rn_0201.d	Acquisition Date	2/21/2022 10:50:15 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_rn_0201	Instrument	maXis impact 8282001.00127
Comment	signal dropping issue		

Acquisition Parameter

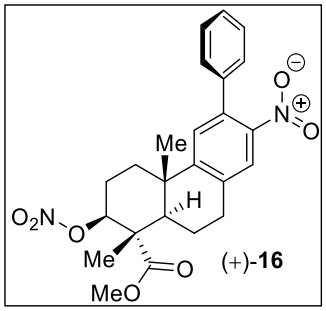
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

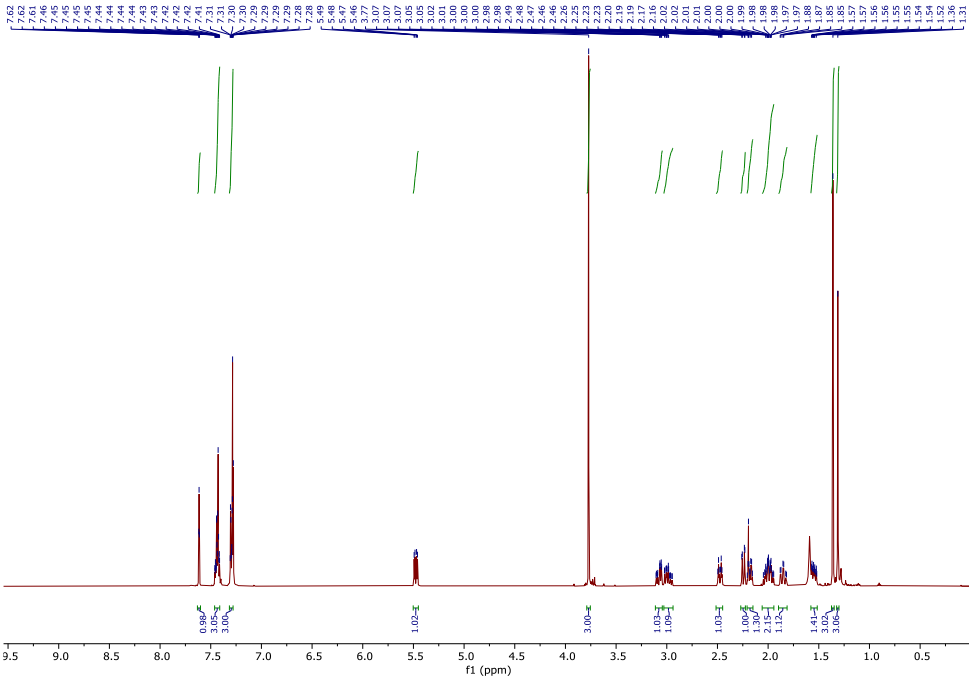


ab_rn_0201.d

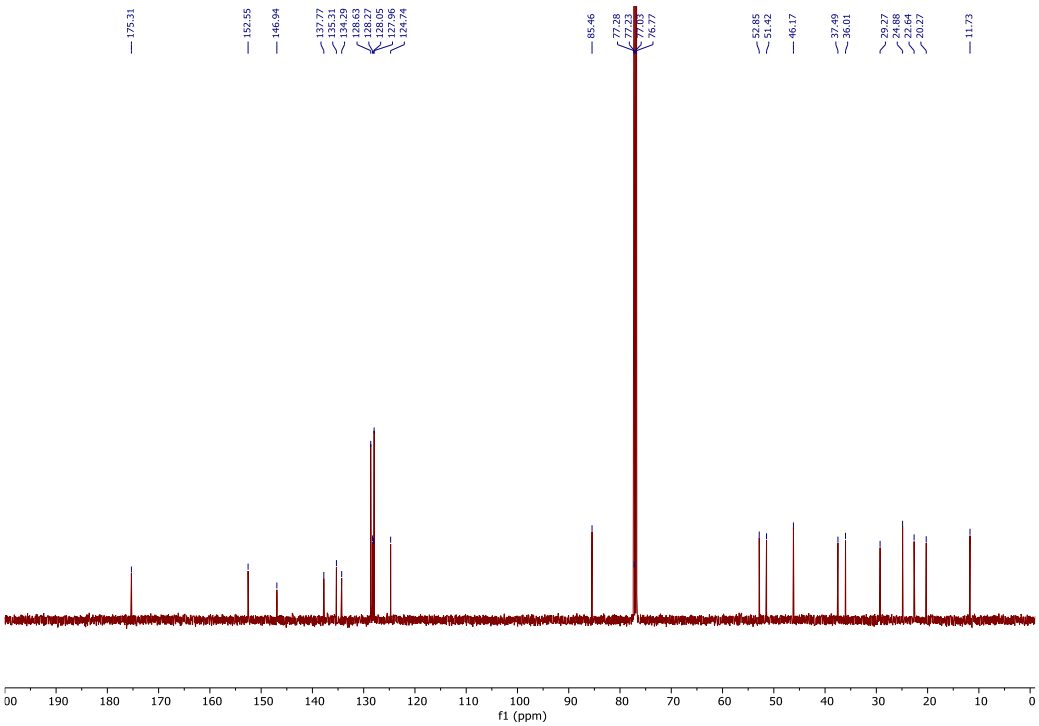
Bruker Compass DataAnalysis 4.1 printed: 2/21/2022 10:53:45 AM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**15**





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



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

Display Report

Analysis Info

Analysis Name	D:\Data\User data\2022\FEB\AB_RN_0202.d	Acquisition Date	2/18/2022 11:59:02 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_RN_0202	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
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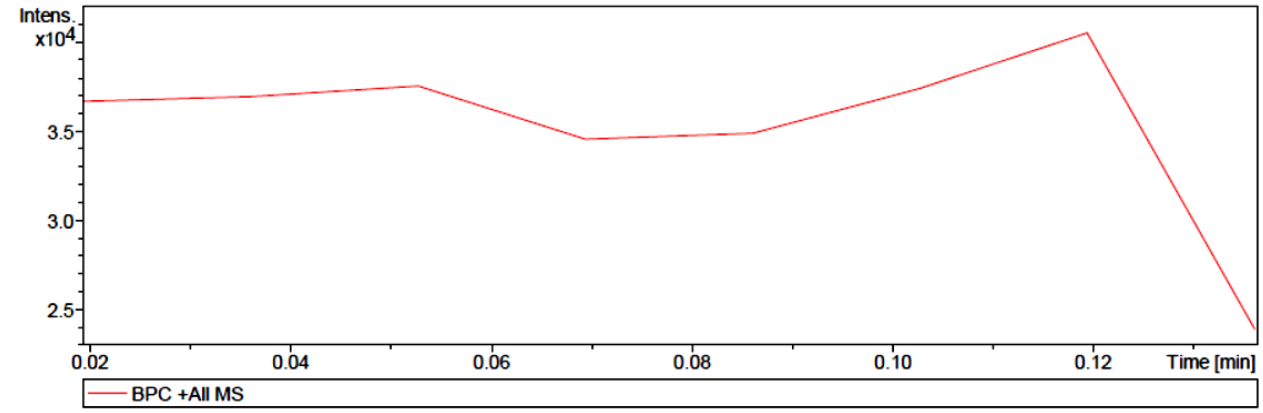
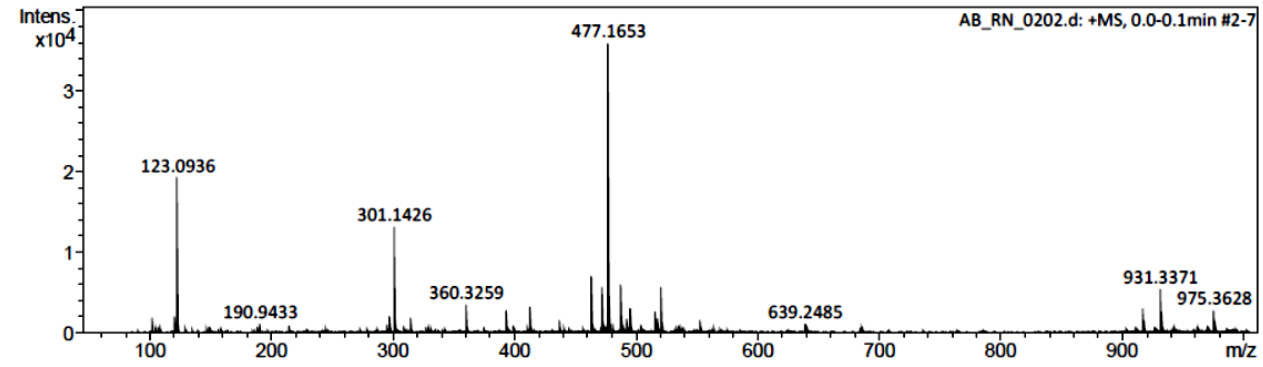
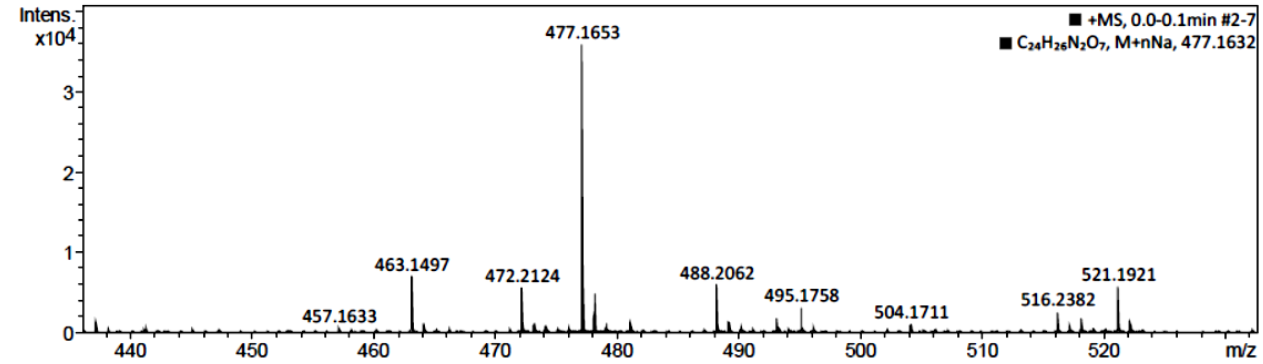


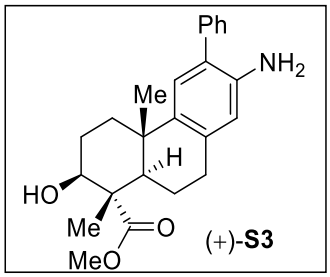


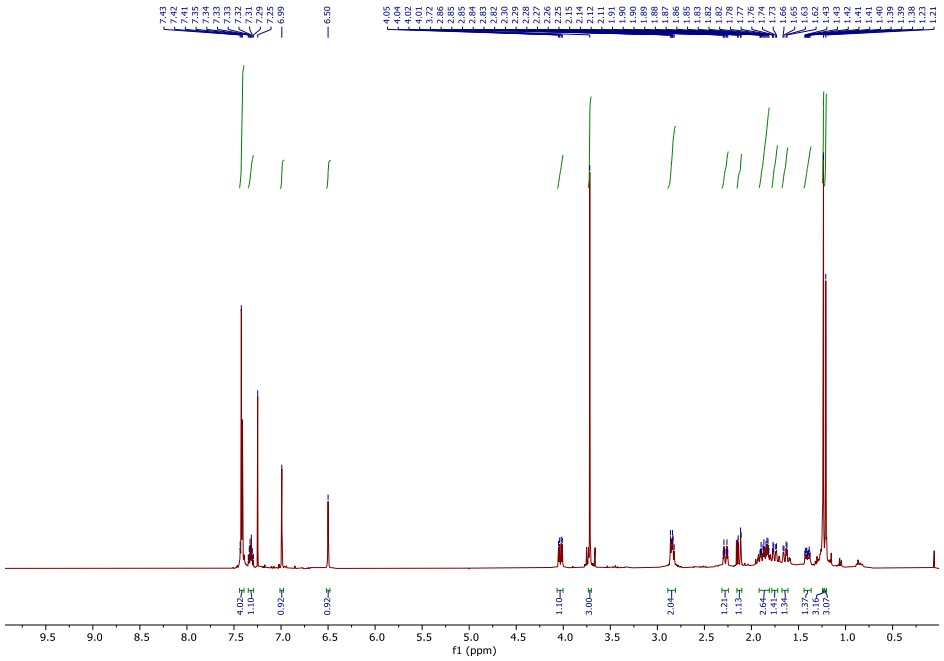


AB_RN_0202.d

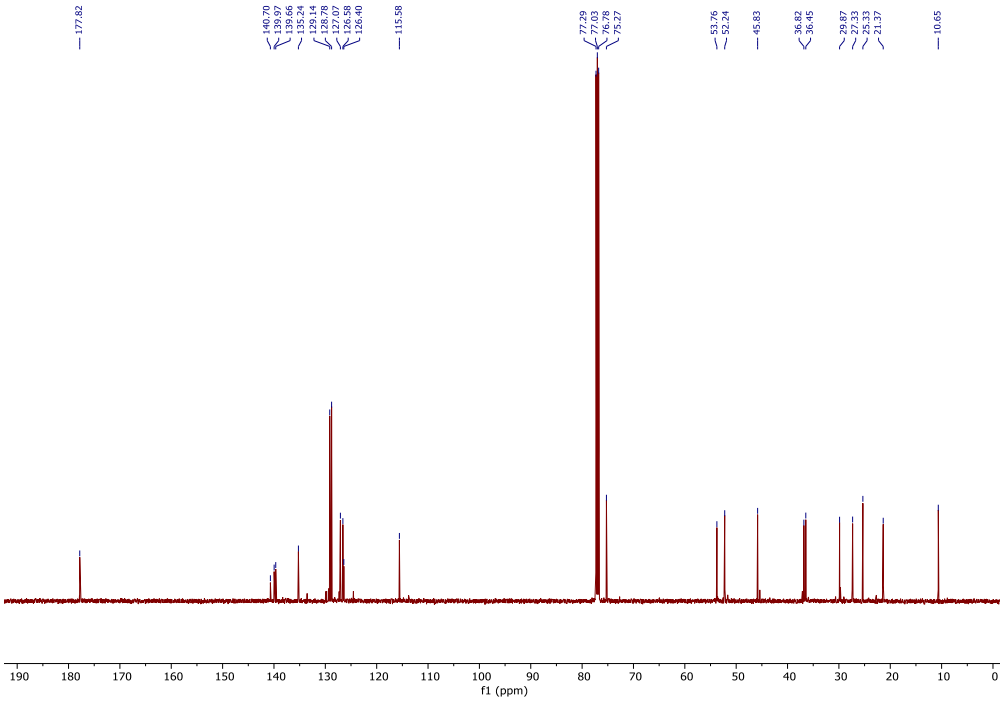
Bruker Compass DataAnalysis 4.1 printed: 2/18/2022 12:02:53 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**16**





^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**S3**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**S3**

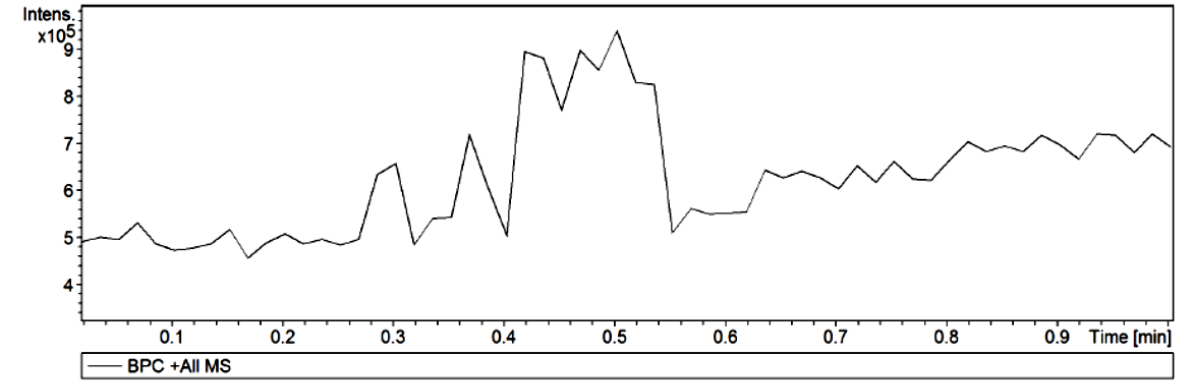
Display Report

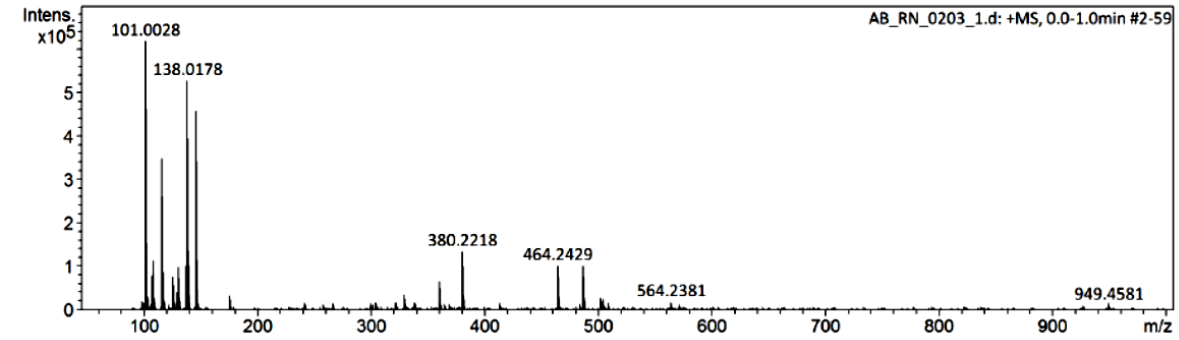
Analysis Info

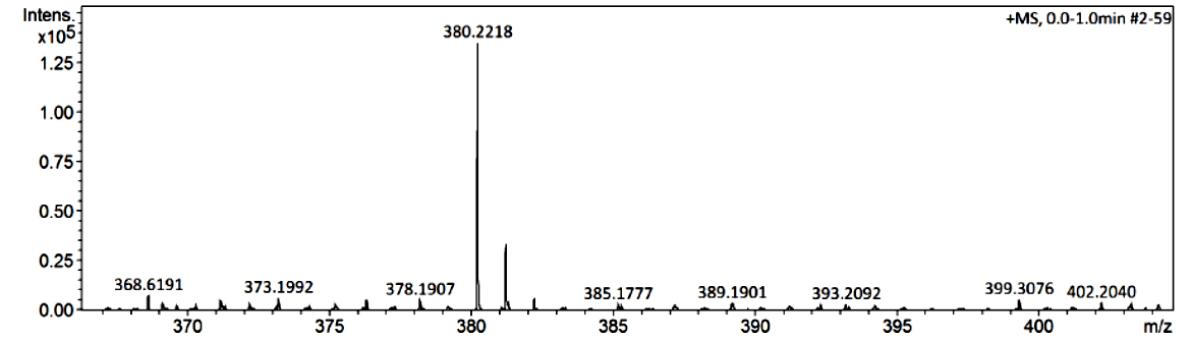
Analysis Name	D:\Data\User data\2021\JULY\AB_RN_0203_1.d	Acquisition Date	7/16/2021 6:44:03 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	RN_0203	Instrument	maXis impact 8282001.00127
Comment			

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



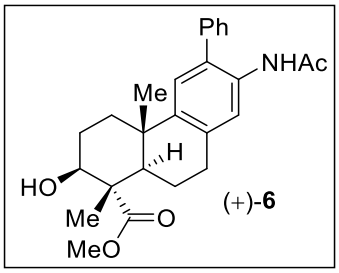




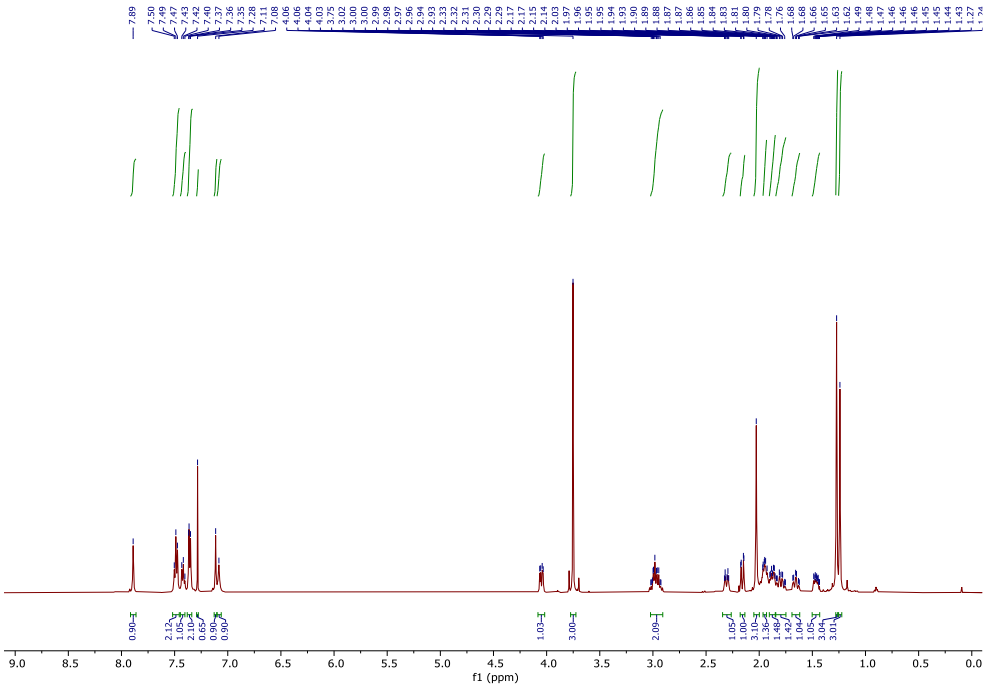
AB_RN_0203_1.d

Bruker Compass DataAnalysis 4.1 printed: 7/19/2021 6:08:00 PM by: IISER Kolkata Page 1 of 1

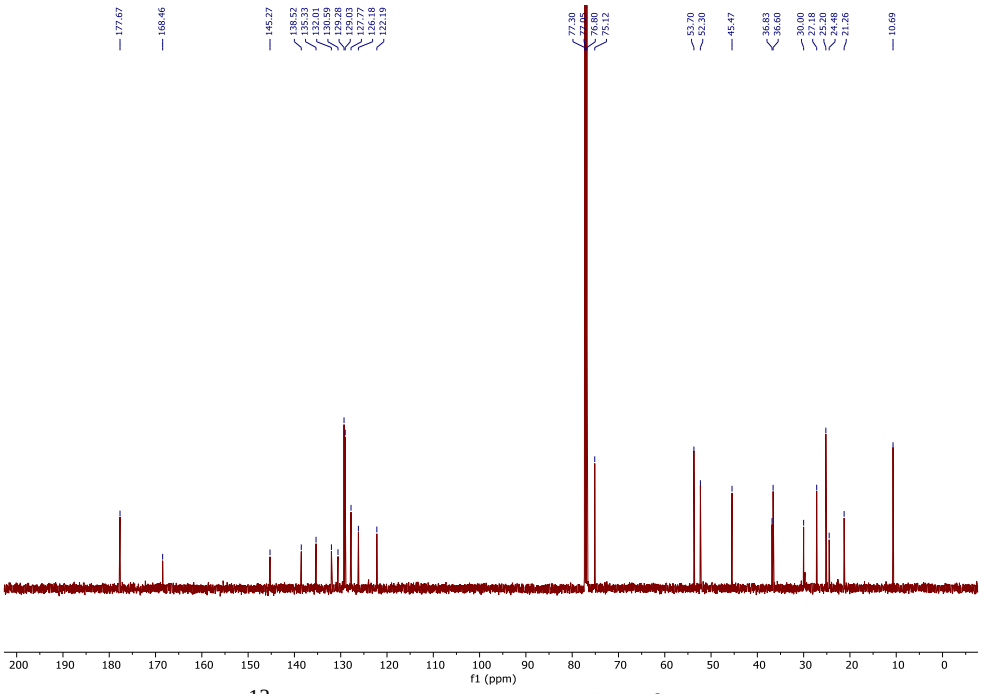
HRMS data of (+)-**S3**



(+)-**6**



^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**6**



^{13}C NMR (125 MHz, $CDCl_3$) of (+)-**6**

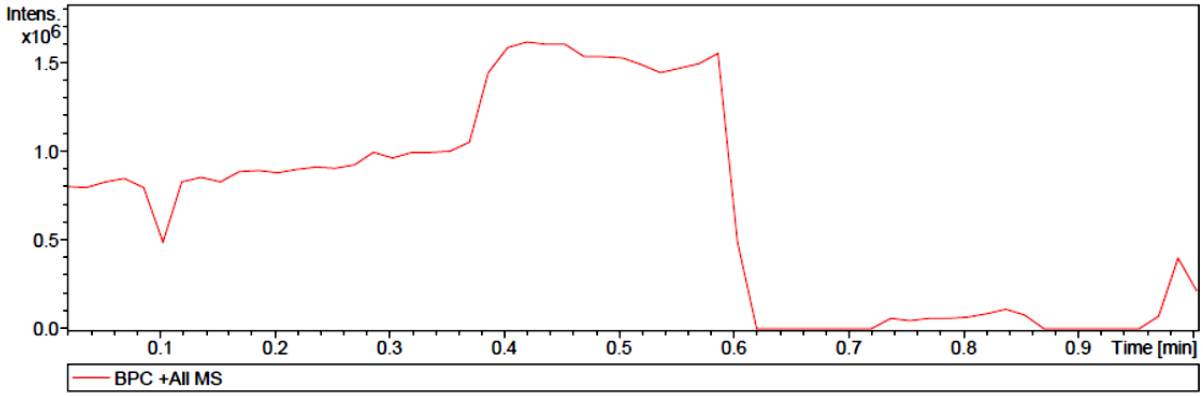
Display Report

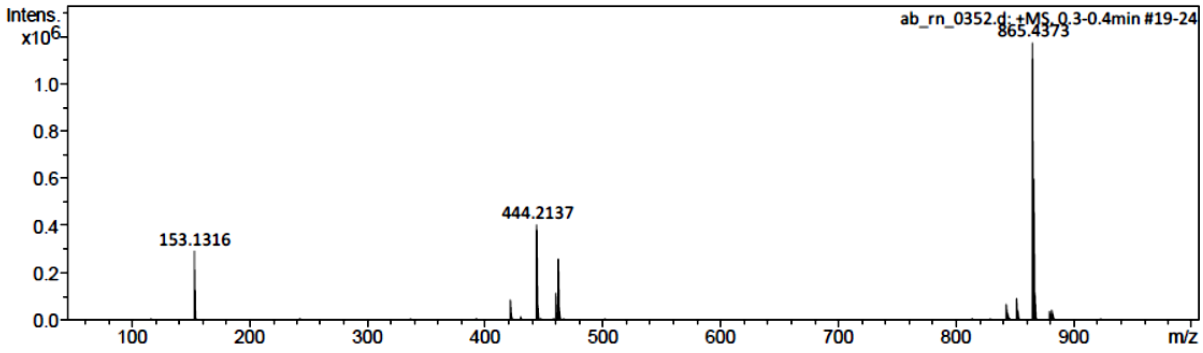
Analysis Info

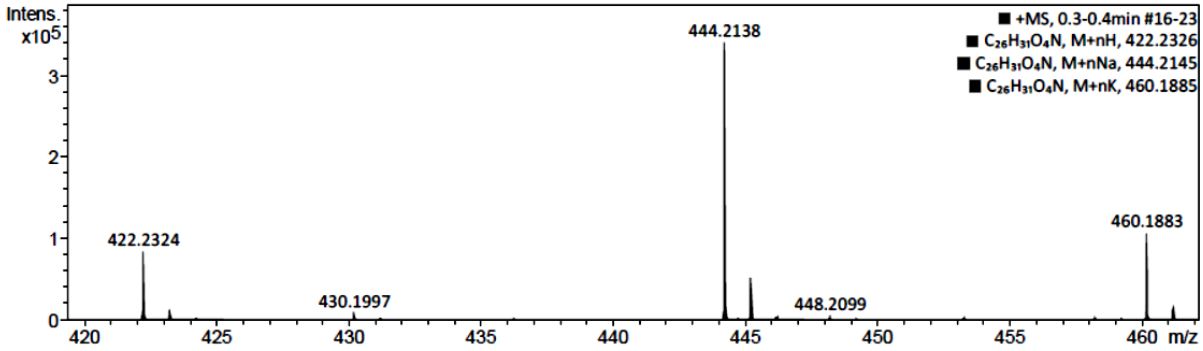
Analysis Name	D:\Data\User data\2022\JAN\ab_rn_0352.d	Acquisition Date	1/31/2022 1:03:25 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_rn_0352	Instrument	maXis impact 8282001.00127
Comment	hydrolyzed to aldhyde using quantitative TFA		

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



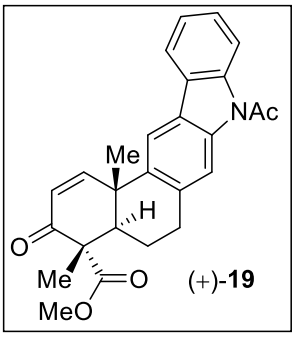




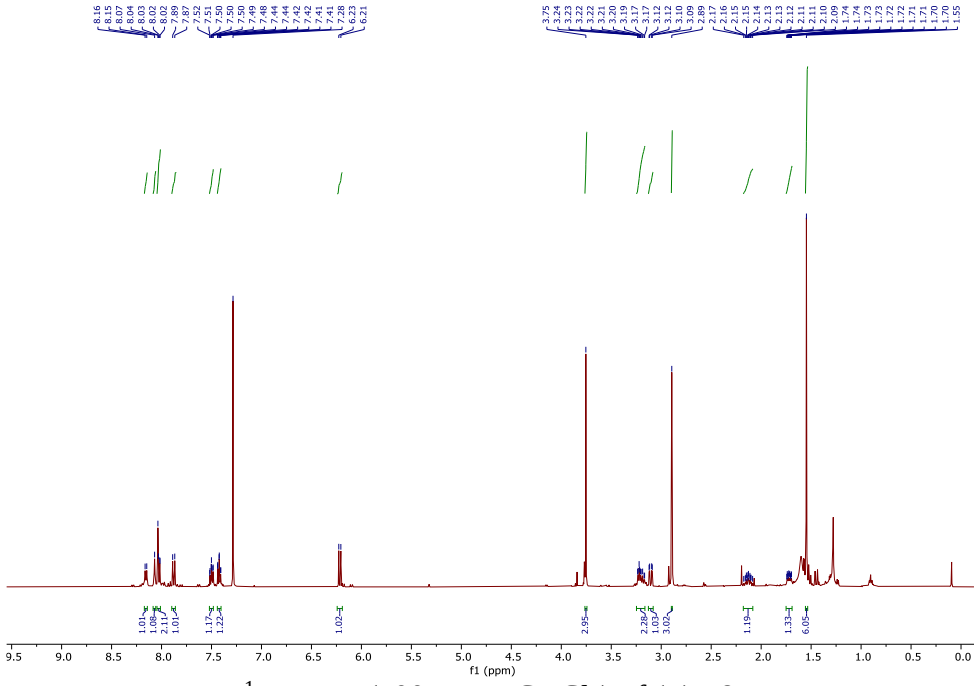
ab_rn_0352.d

Bruker Compass DataAnalysis 4.1 printed: 1/31/2022 2:28:25 PM by: IISER Kolkata Page 1 of 1

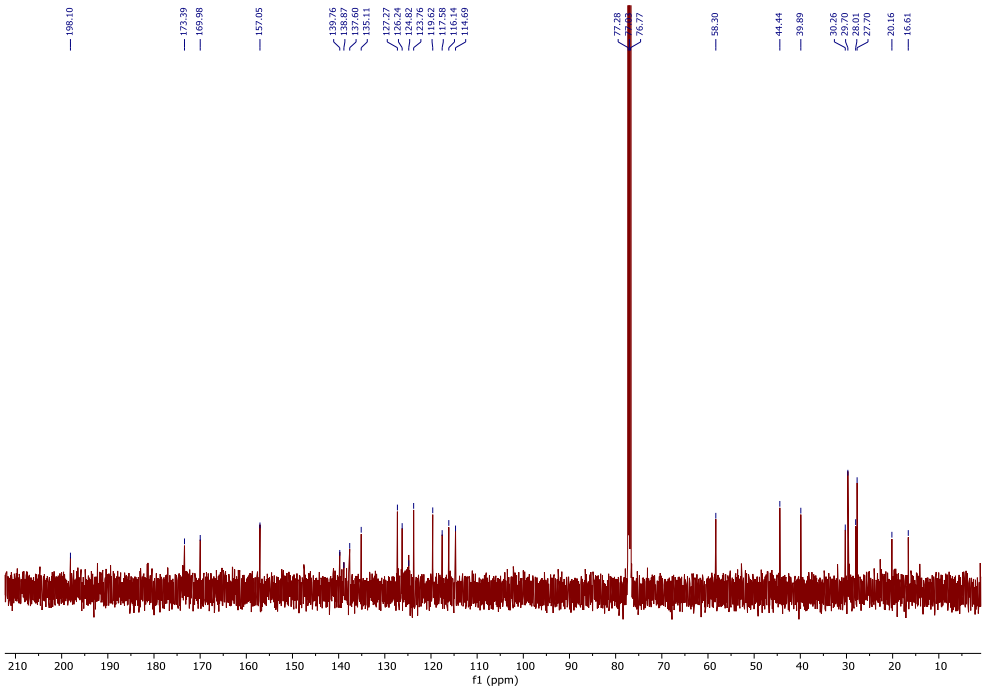
HRMS data of (+)-**6**



(+)-**19**



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



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

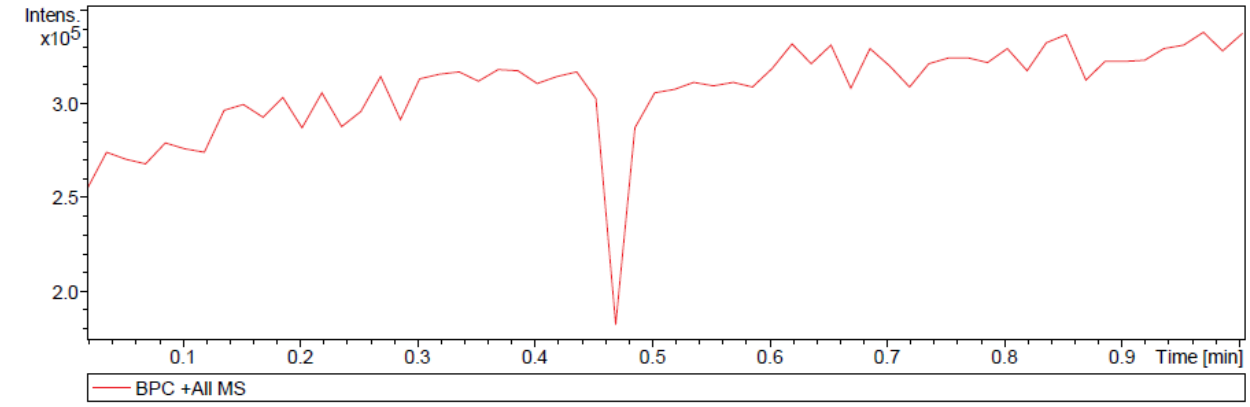
Display Report

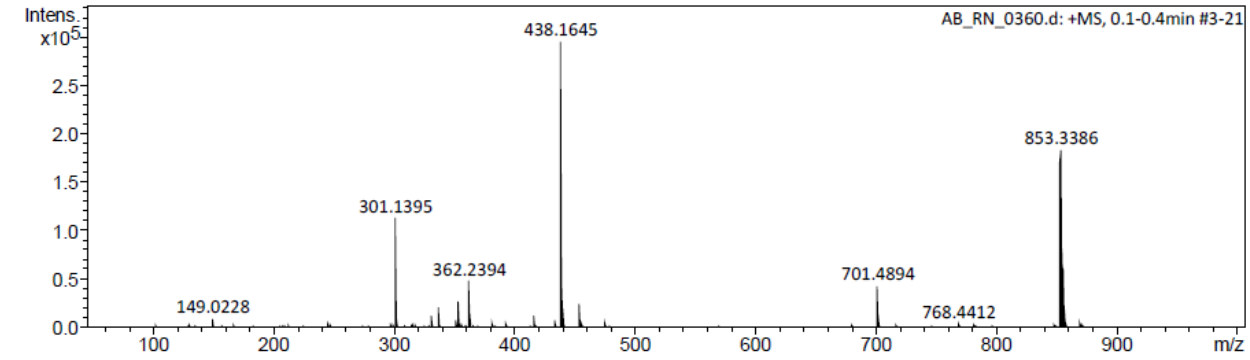
Analysis Info

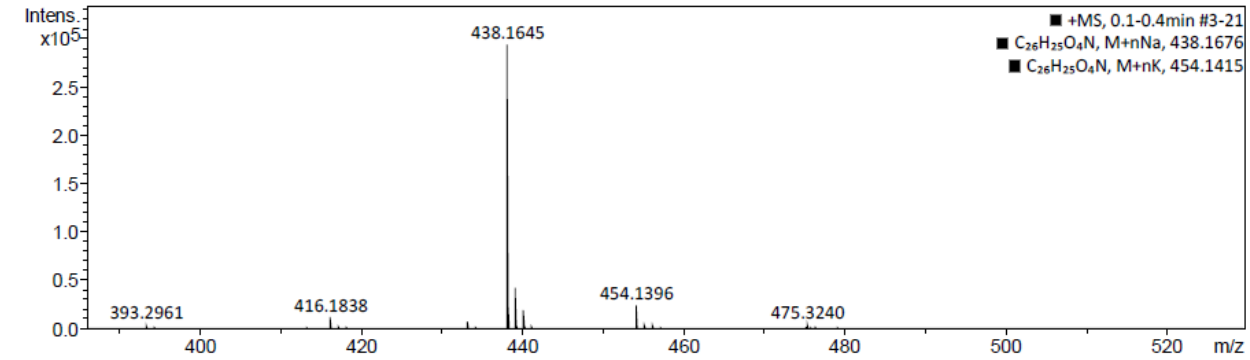
Analysis Name	D:\Data\User data\2022\FEB\AB_RN_0360.d	Acquisition Date	2/2/2022 1:14:20 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_RN_0360	Instrument	maXis impact 8282001.00127
Comment	hydrolyzed to aldhyde using quantitative TFA		

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



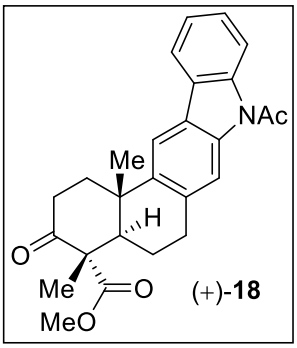


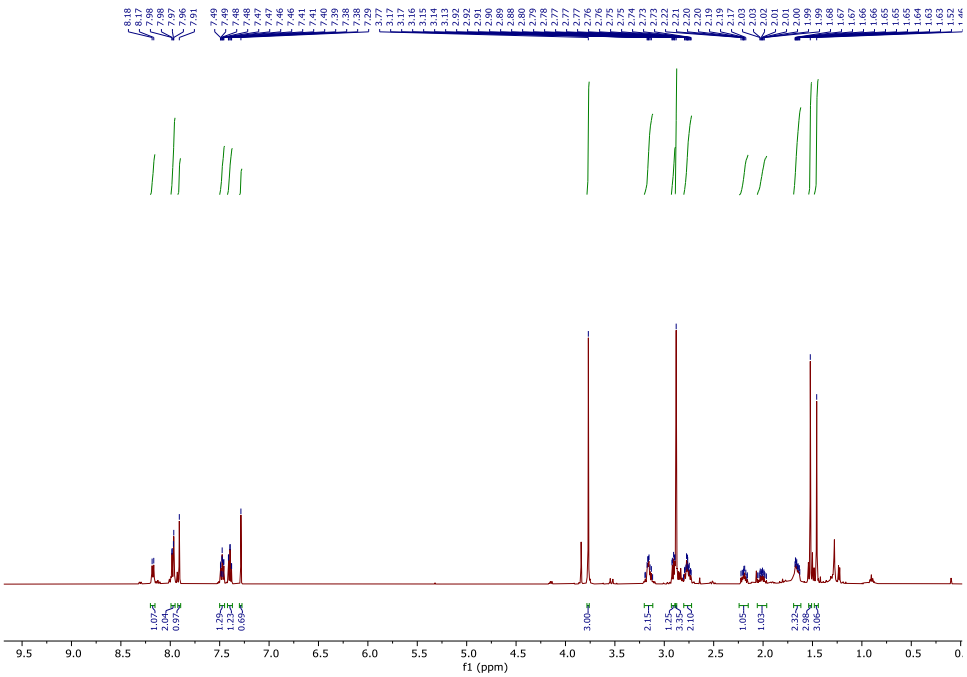


AB_RN_0360.d

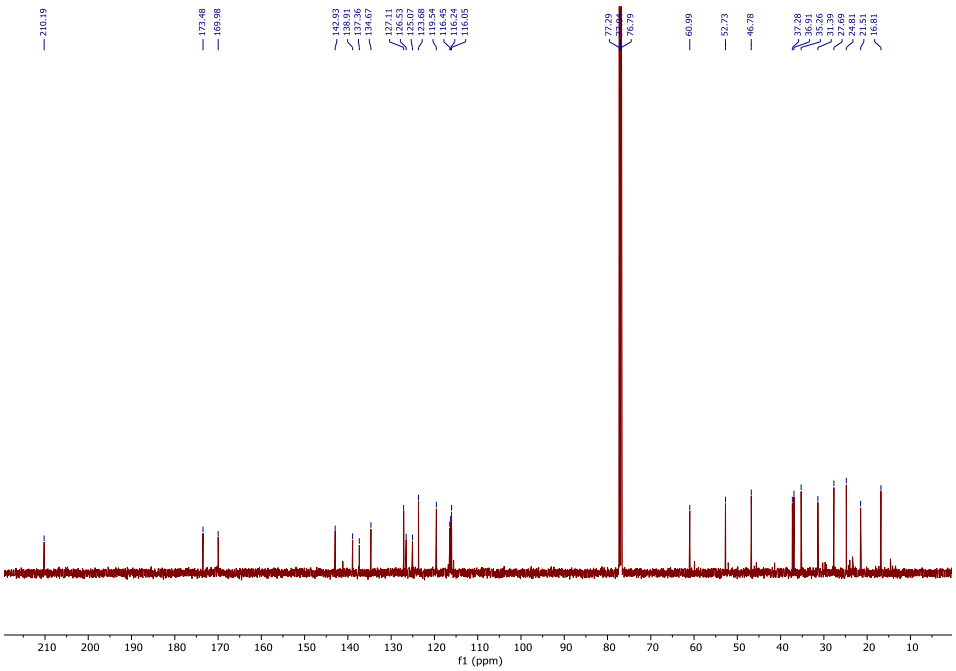
Bruker Compass DataAnalysis 4.1 printed: 2/2/2022 1:19:03 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**19**





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



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

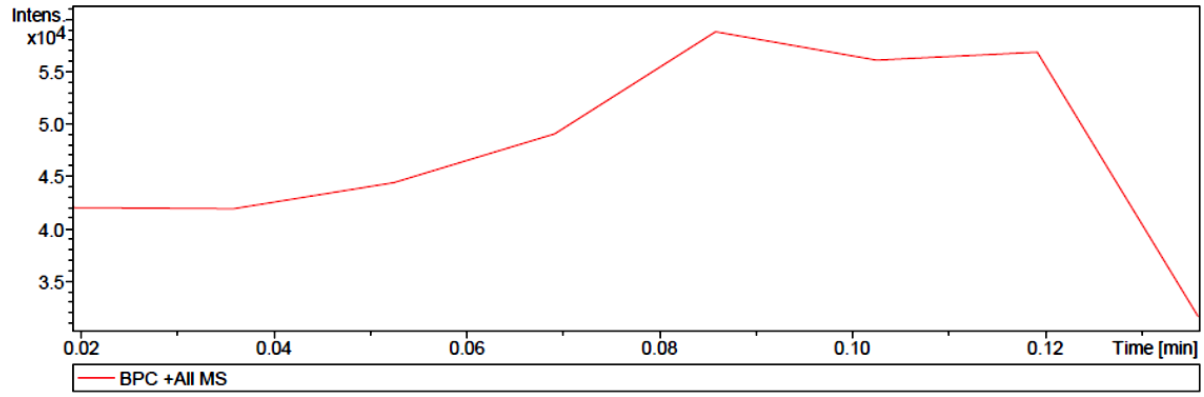
Display Report

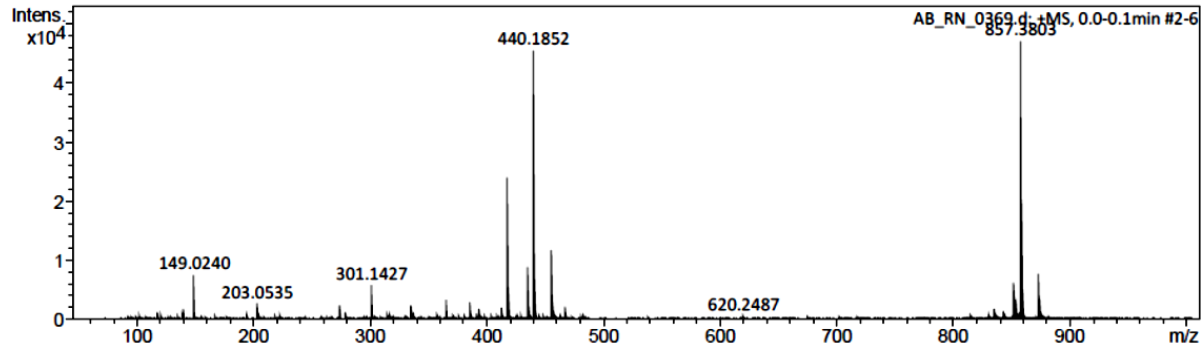
Analysis Info

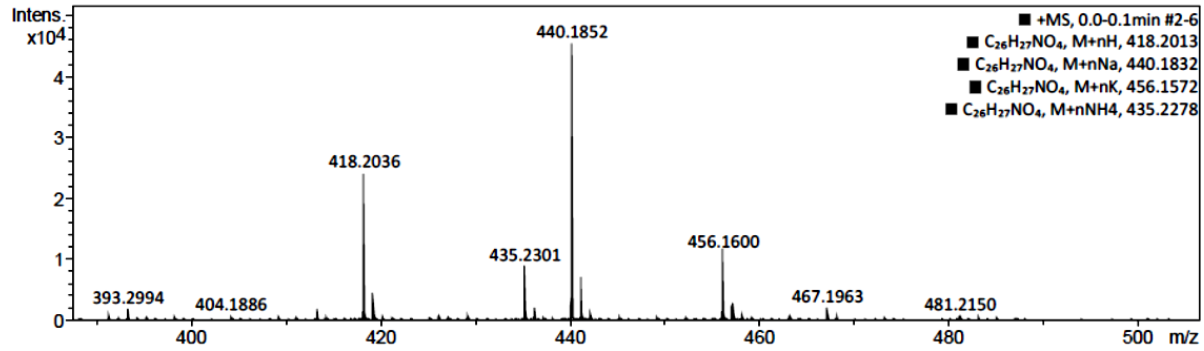
Analysis Name	D:\Data\User data\2022\FEB\AB_RN_0369.d	Acquisition Date	2/17/2022 6:48:52 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_RN_0369	Instrument	maXis impact 8282001.00127
Comment			

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



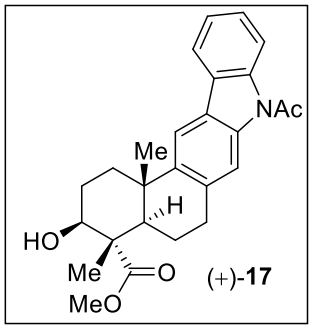


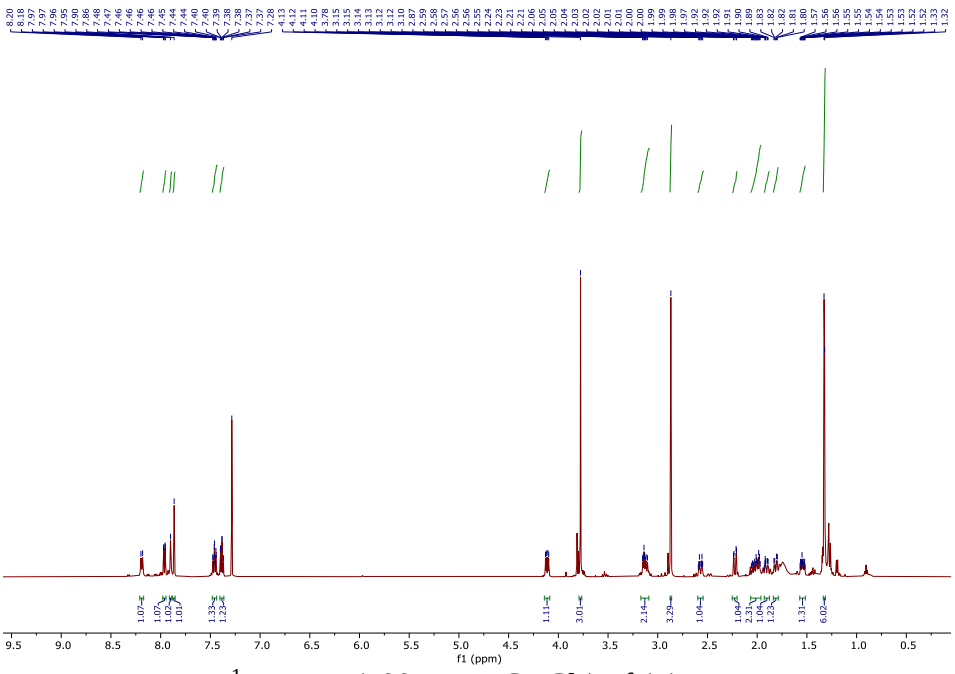


AB_RN_0369.d

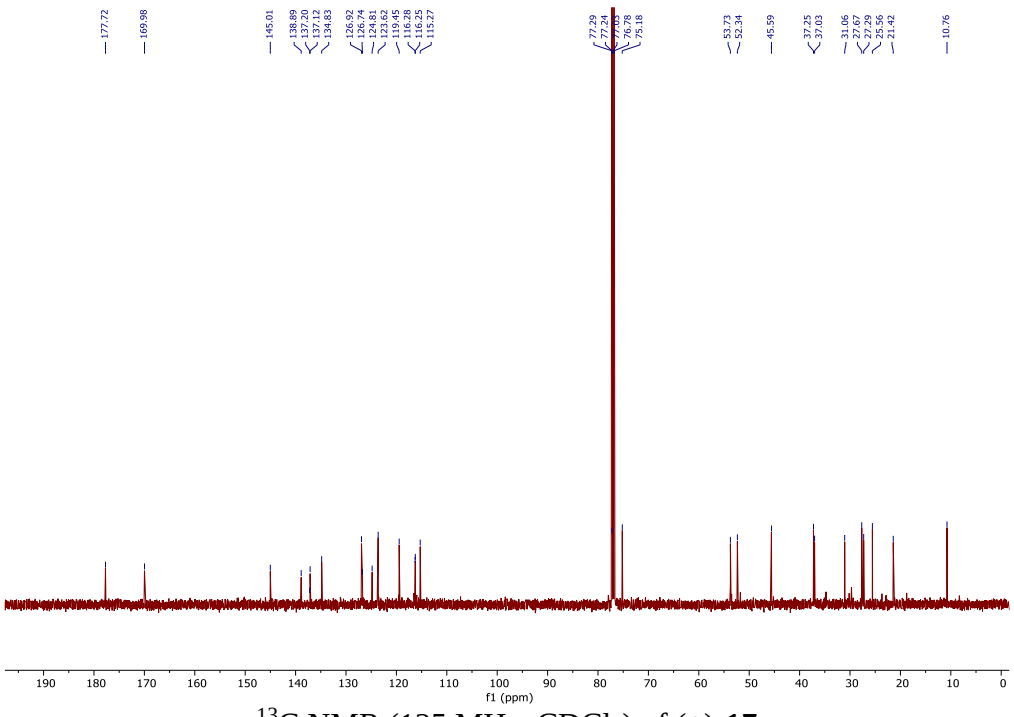
Bruker Compass DataAnalysis 4.1 printed: 2/17/2022 6:56:31 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**18**





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



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

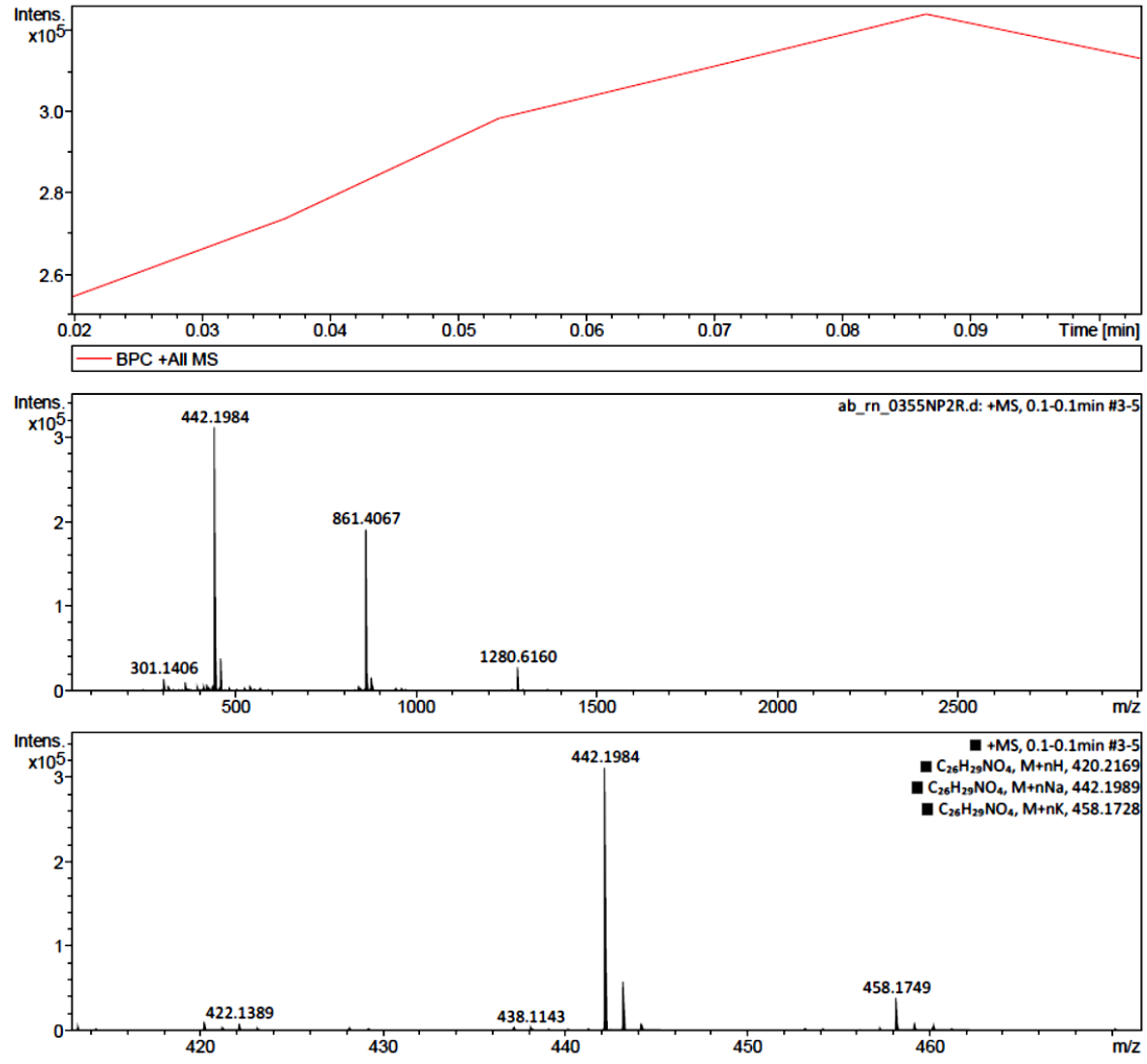
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2022\FEB\ab_rn_0355NP2R.d	Acquisition Date	2/3/2022 1:40:59 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	ab_rn_0355NP2R	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

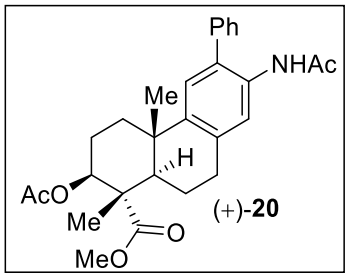
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

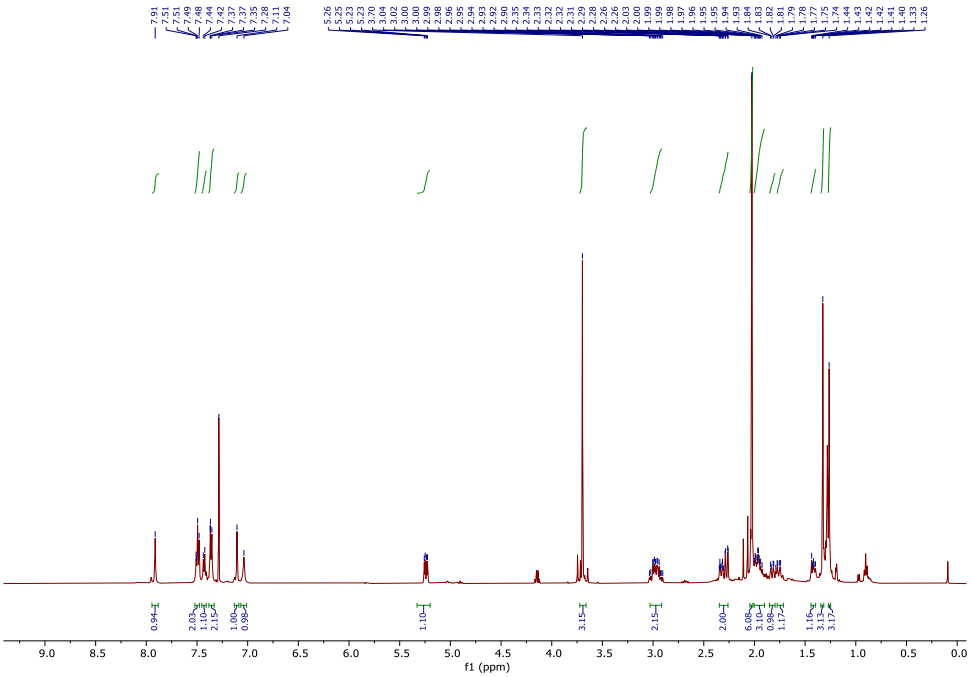


ab_rn_0355NP2R.d

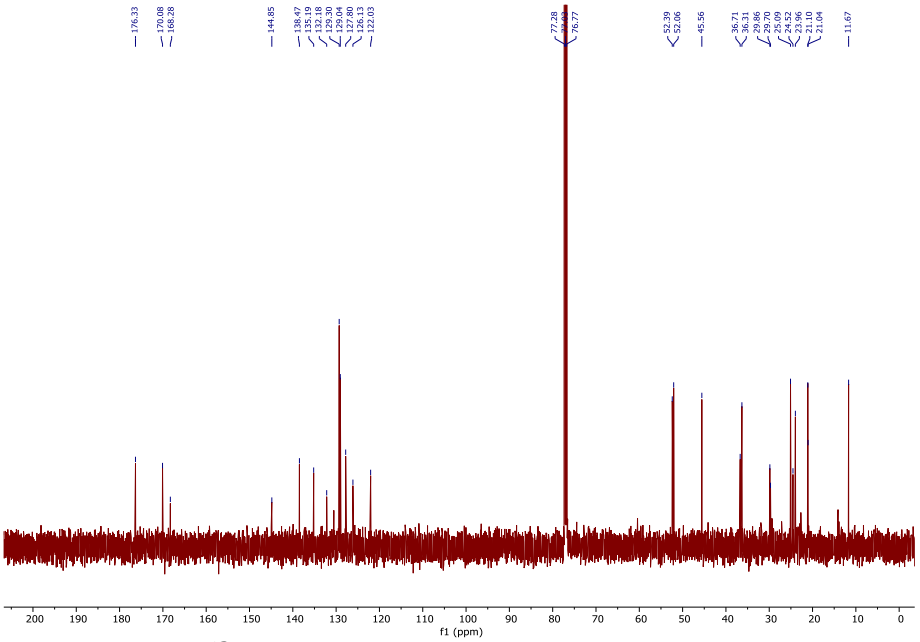
Bruker Compass DataAnalysis 4.1 printed: 2/3/2022 1:42:58 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**17**





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



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

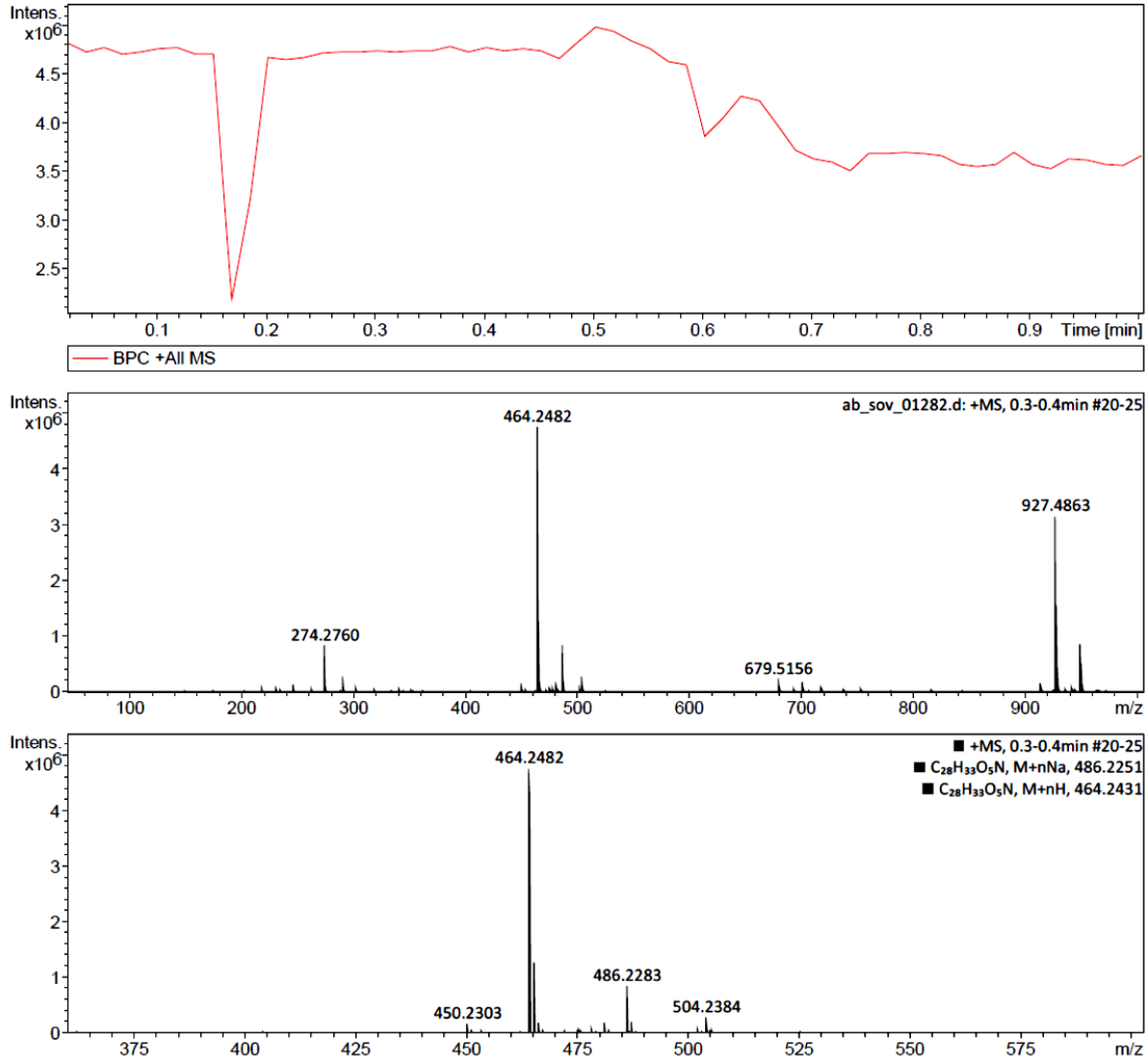
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2021\DEC\ab_sov_01282.d	Acquisition Date	12/15/2021 1:14:12 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_sov_01282	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

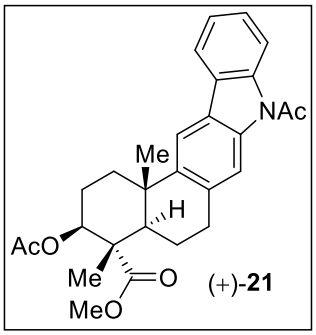
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

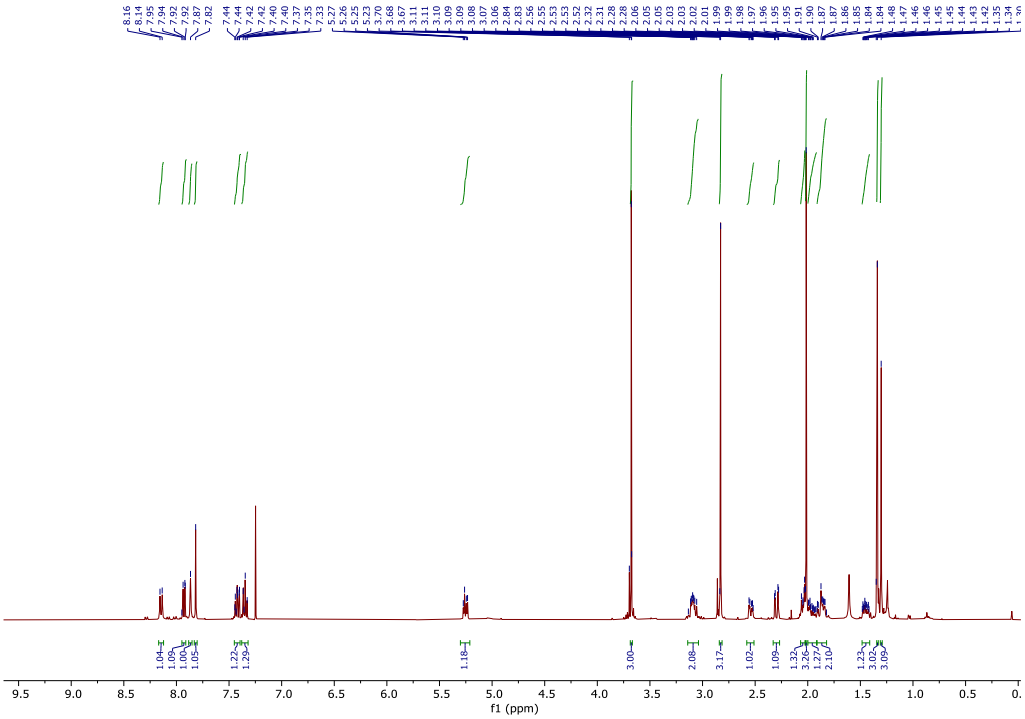


ab_sov_01282.d

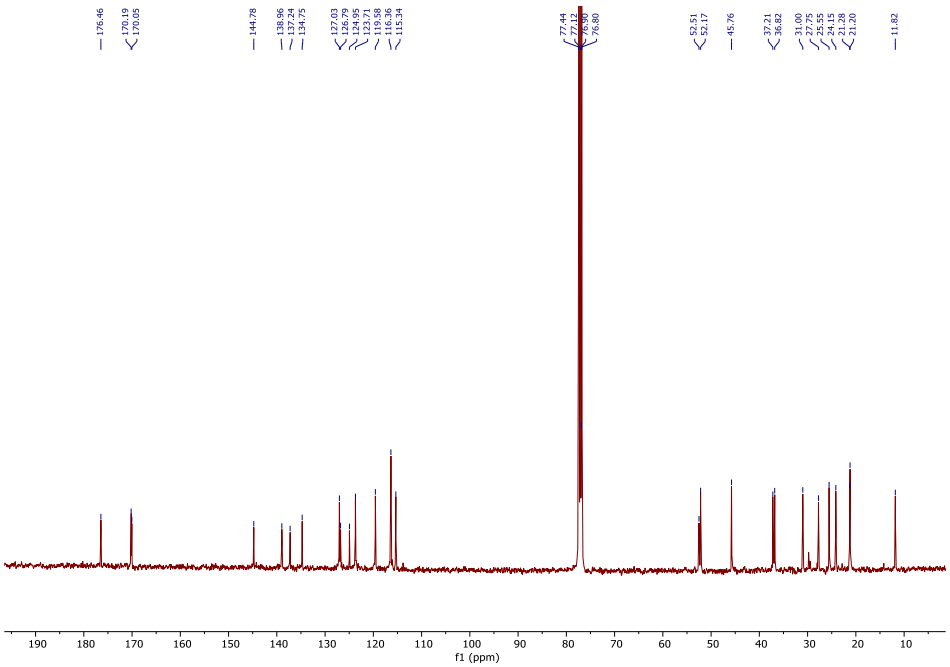
Bruker Compass DataAnalysis 4.1 printed: 12/15/2021 1:16:39 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**20**





^{1}H NMR (400 MHz, $CDCl_3$) of (+)-**21**



^{13}C NMR (100 MHz, $CDCl_3$) of (+)-**21**

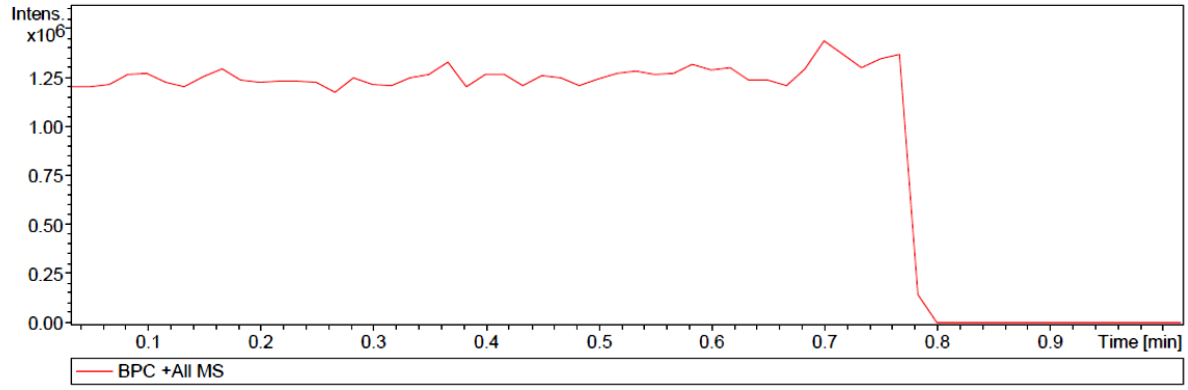
Display Report

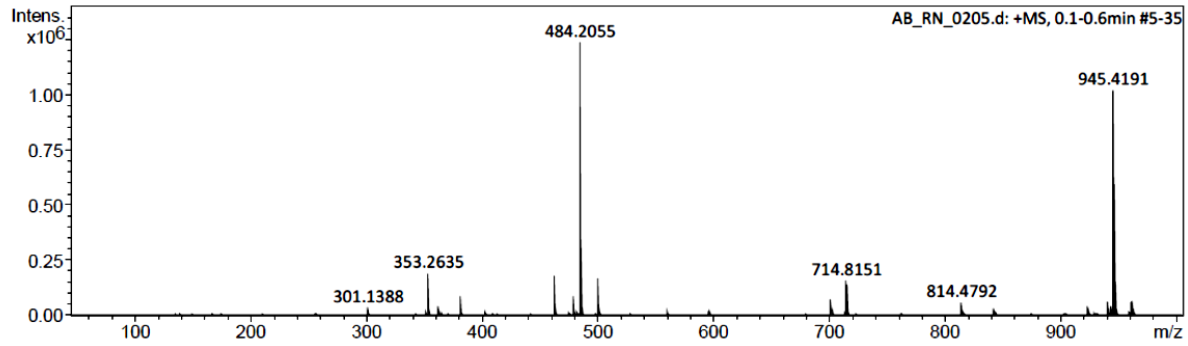
Analysis Info

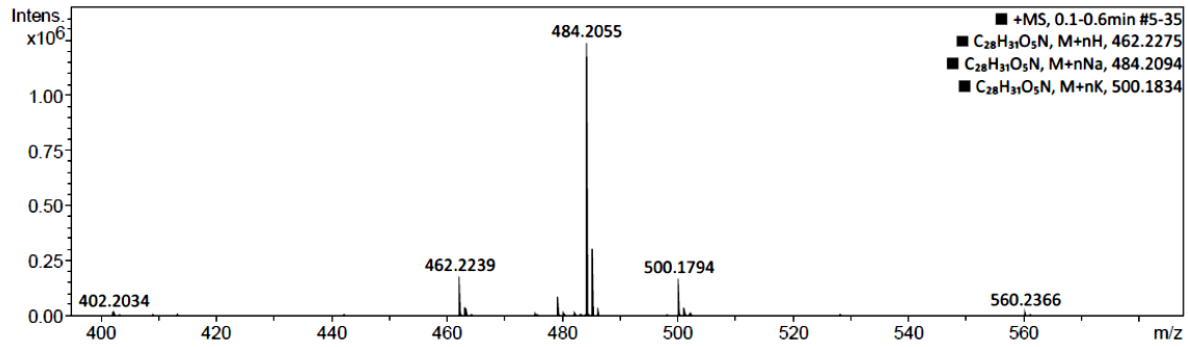
Analysis Name	D:\Data\User data\2021\AUGUST\AB_RN_0205.d	Acquisition Date	8/24/2021 12:39:41 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_RN_0205	Instrument	maXis impact 8282001.00127
Comment			

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



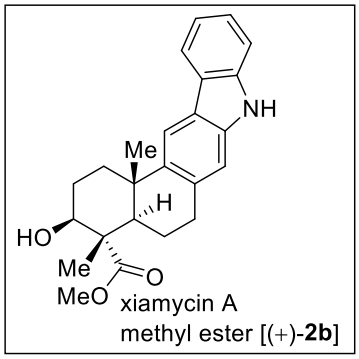


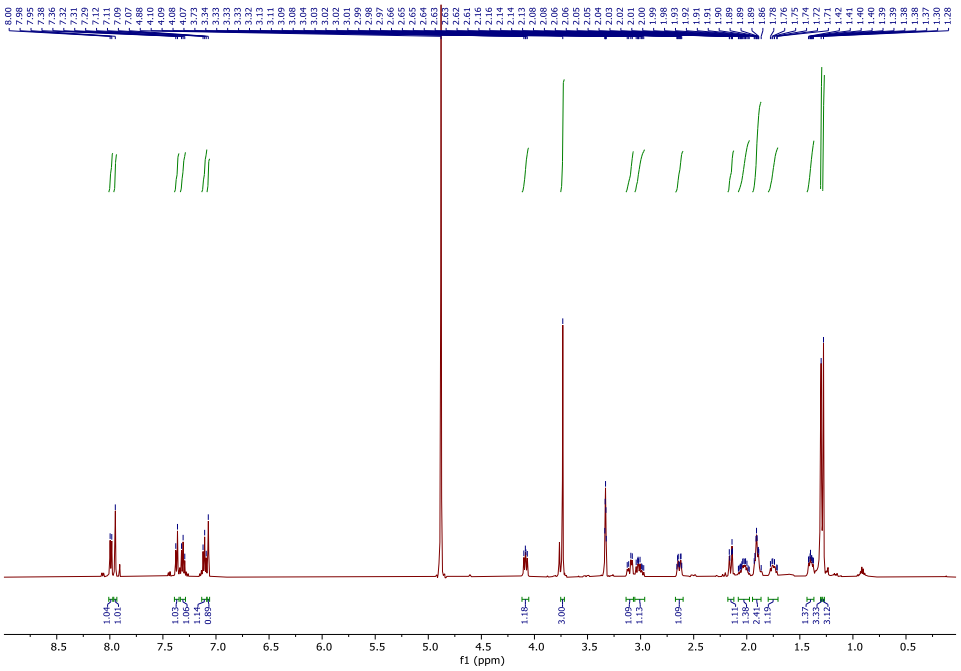


AB_RN_0205.d

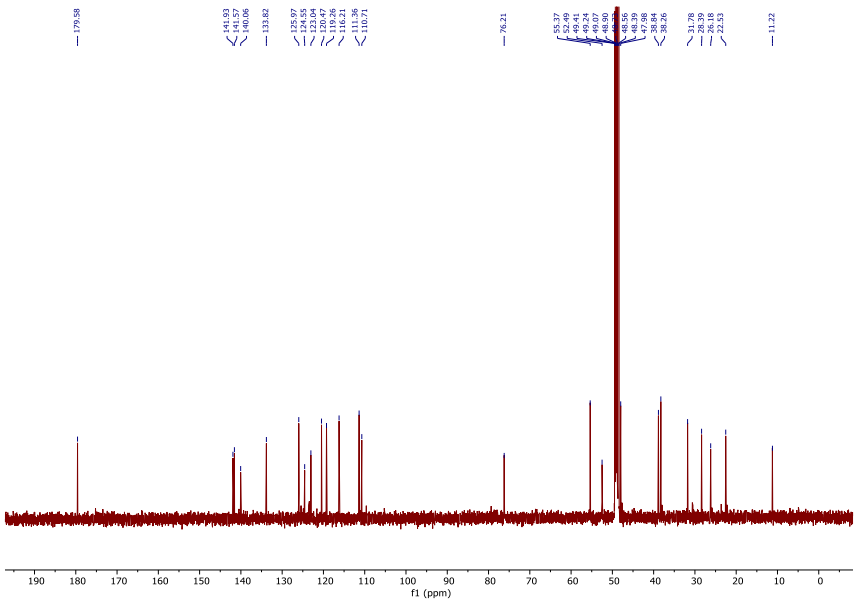
Bruker Compass DataAnalysis 4.1 printed: 8/24/2021 12:44:18 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**21**





^{1}H NMR (500 MHz, CD_3OD) of Xiamycin A methylester [(+)-**2b**]



^{13}C NMR (125 MHz, CD_3OD) of Xiamycin A methylester [(+)-**2b**]

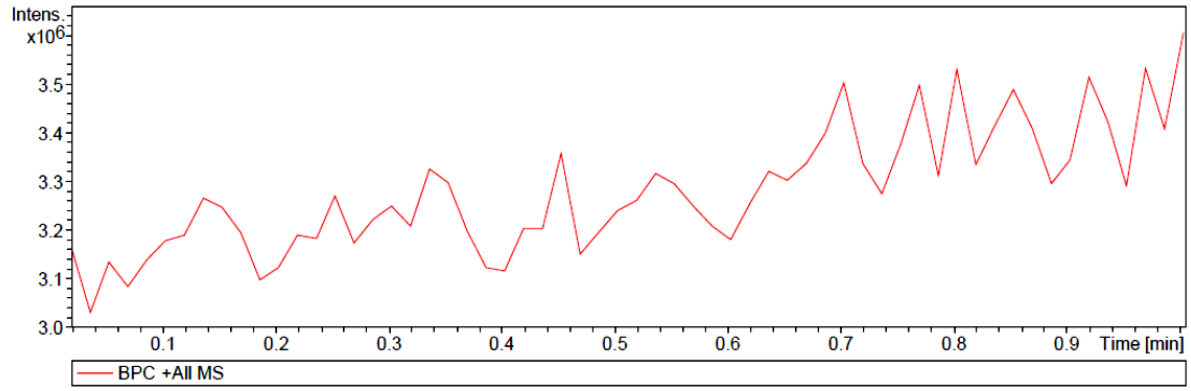
Display Report

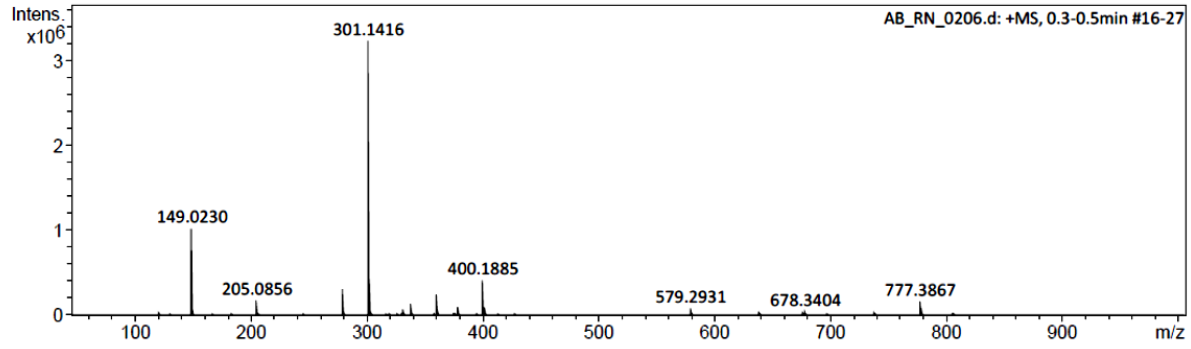
Analysis Info

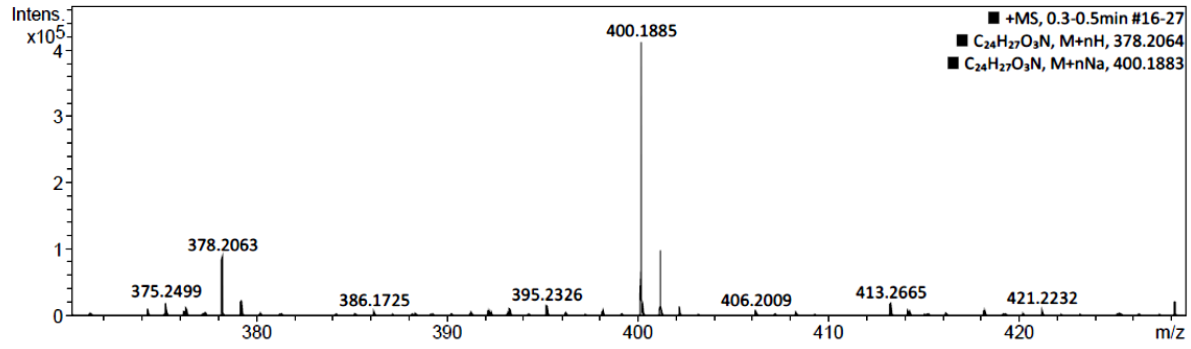
Analysis Name	D:\Data\User data\2021\JULY\AB_RN_0206.d	Acquisition Date	7/16/2021 5:23:48 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	RN_0206	Instrument	maXis impact 8282001.00127
Comment			

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



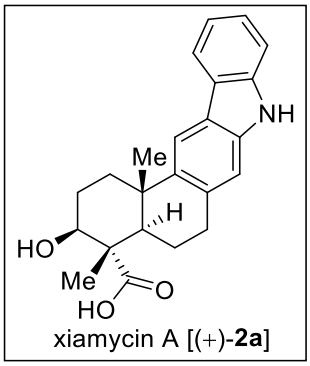




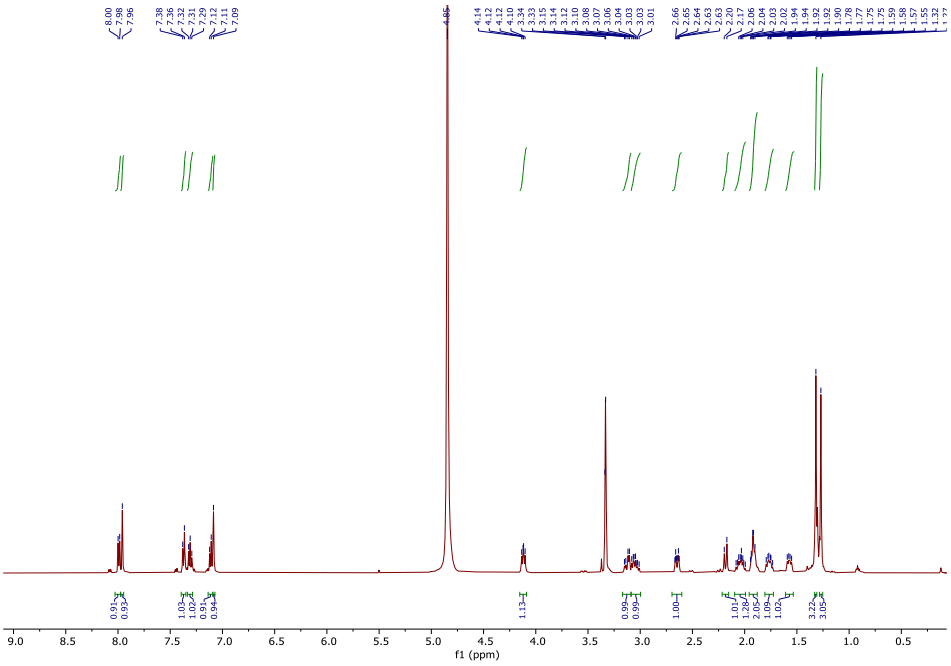
AB_RN_0206.d

Bruker Compass DataAnalysis 4.1 printed: 8/24/2021 4:31:10 PM by: IISER Kolkata Page 1 of 1

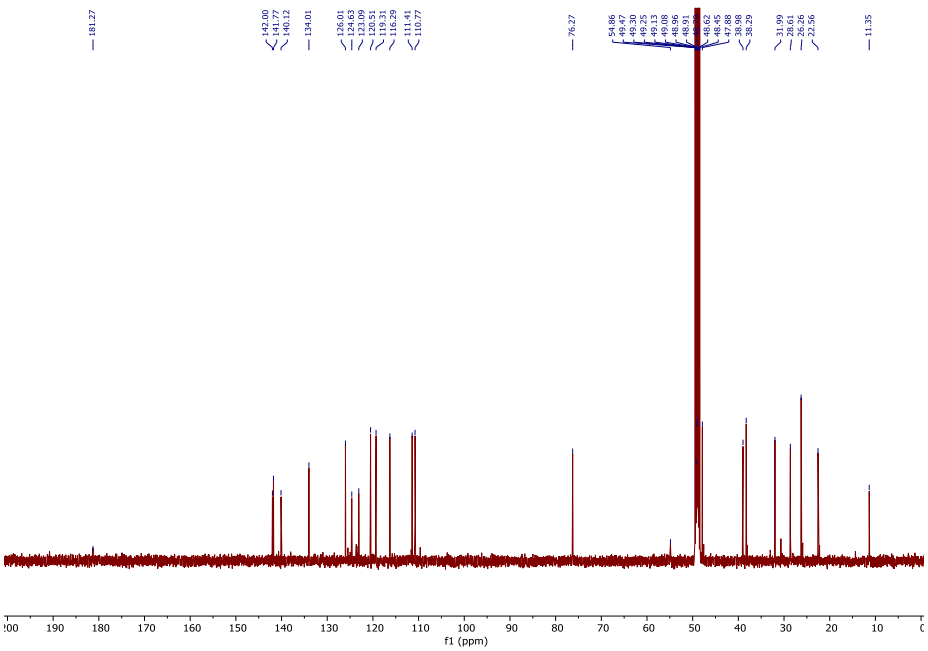
HRMS data of Xiamycin A methylester [(+)-**2b**]



xiamycin A [(+)-**2a**]



^{1}H NMR (500 MHz, CD_3OD) of Xiamycin A [(+)-**2a**]



^{13}C NMR (125 MHz, CD_3OD) of Xiamycin A [(+)-**2a**]

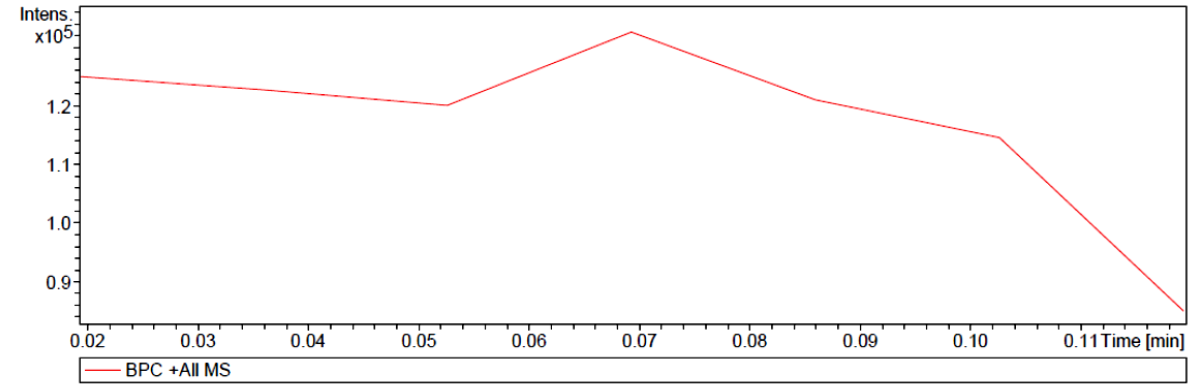
Display Report

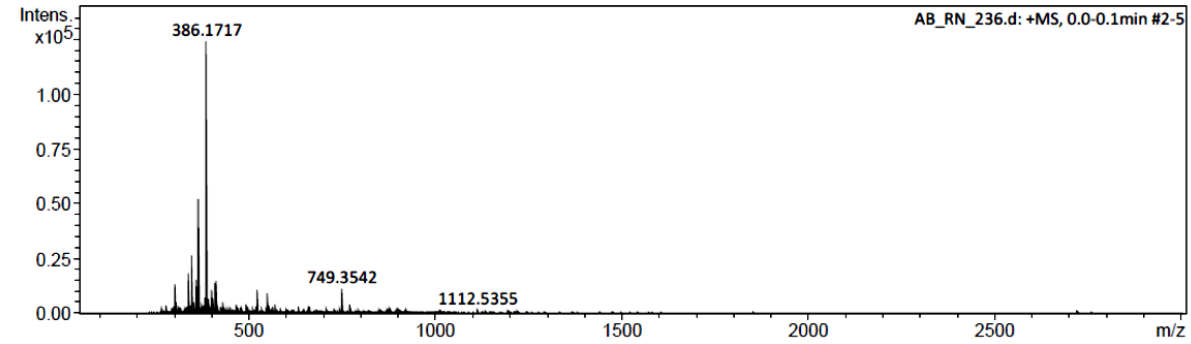
Analysis Info

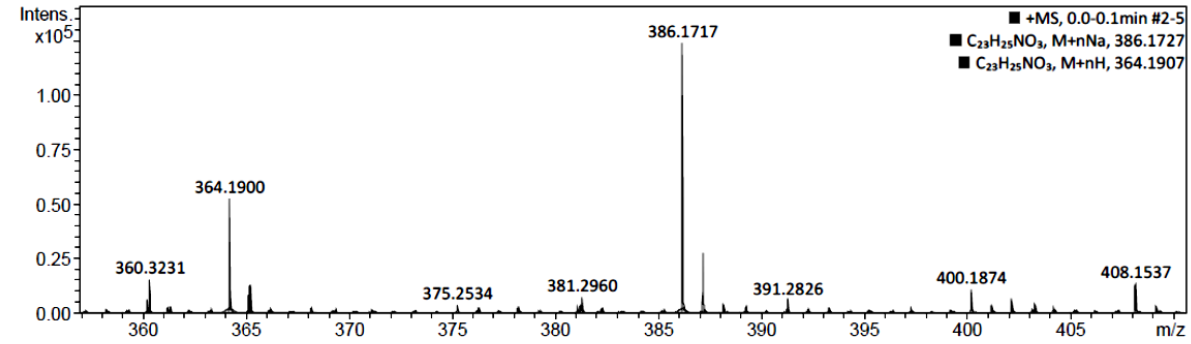
Analysis Name	D:\Data\User data\2021\AUGUST\AB_RN_236.d	Acquisition Date	8/21/2021 11:36:08 AM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_RN_236	Instrument	maXis impact 8282001.00127
Comment			

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



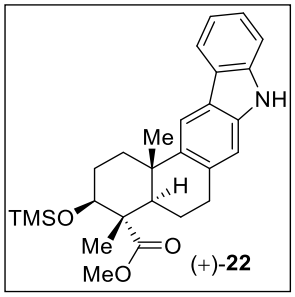


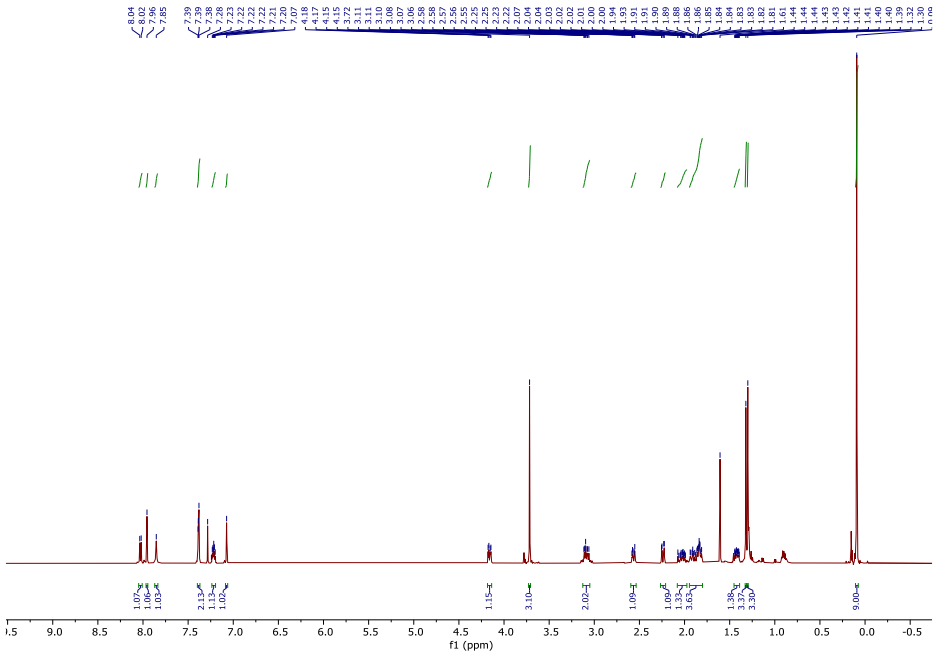


AB_RN_236.d

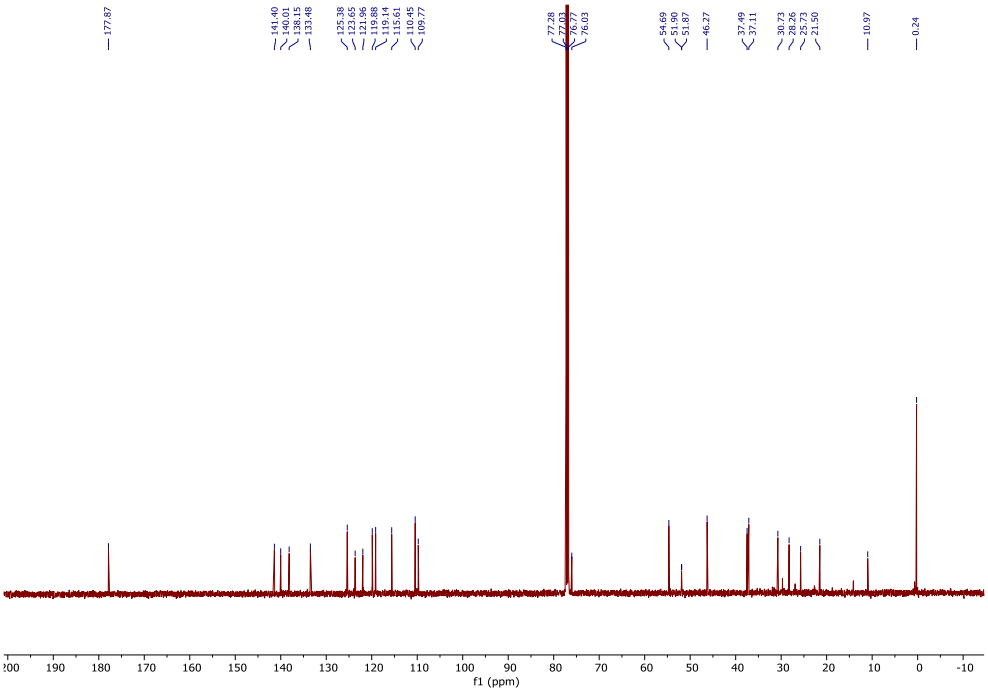
Bruker Compass DataAnalysis 4.1 printed: 8/21/2021 4:55:12 PM by: IISER Kolkata Page 1 of 1

HRMS data of Xiamycin A [(+)-**2a**]





^{1}H NMR (500 MHz, $CDCl_3$) xiamycin A methyl ester TMS ether [(+)-**22**]



^{13}C NMR (125 MHz, $CDCl_3$) xiamycin A methyl ester TMS ether [(+)-**22**]

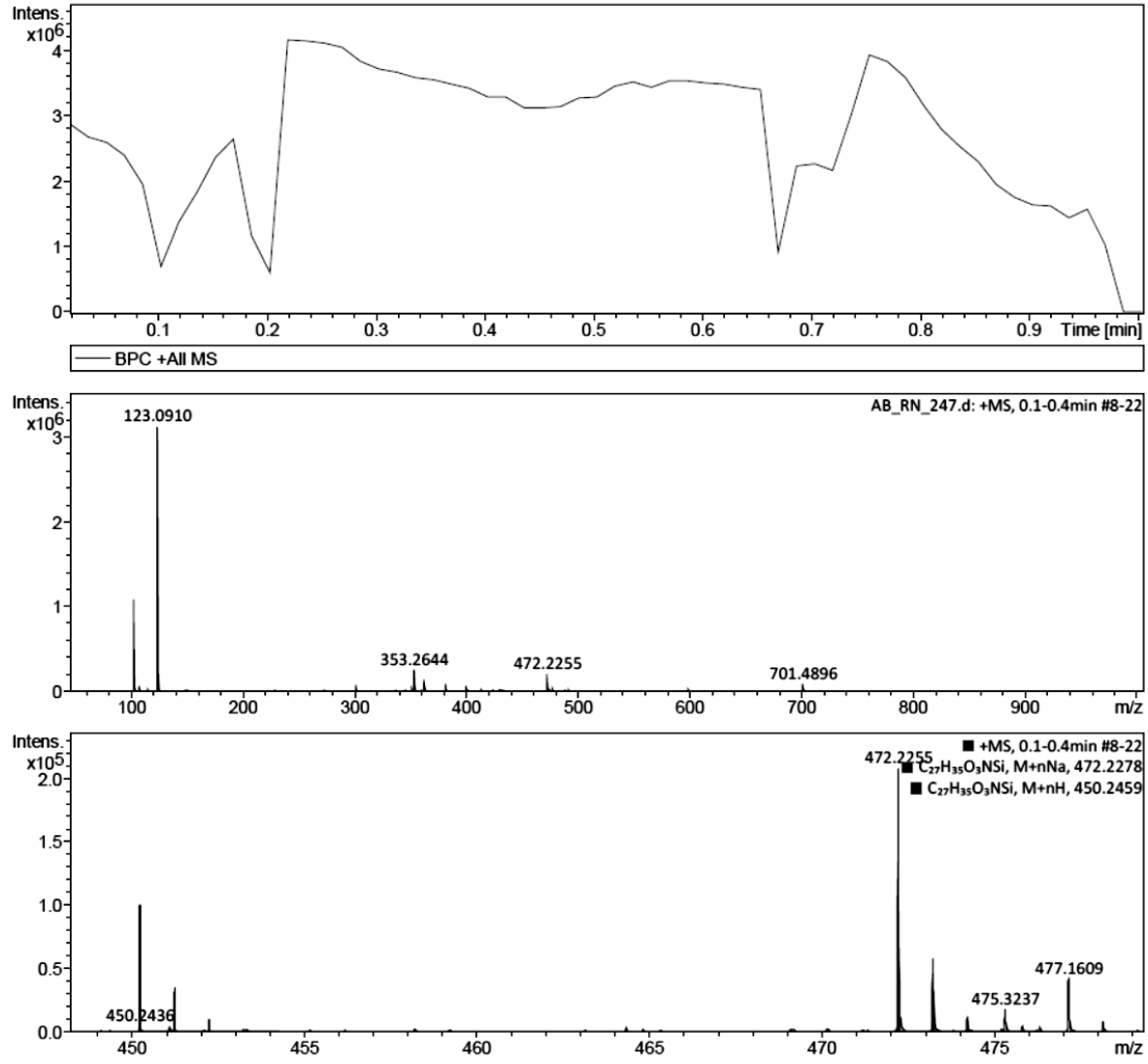
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2021\SEPT\AB_RN_247.d	Acquisition Date	9/14/2021 1:02:36 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_RN_247	Instrument	maXis impact 8282001.00127
Comment	A PEAK AT 273 CONSTANTLY COMING FROM YESTERDAY CAME FROM SAMPLE DM_SUD_MCOO4		

Acquisition Parameter

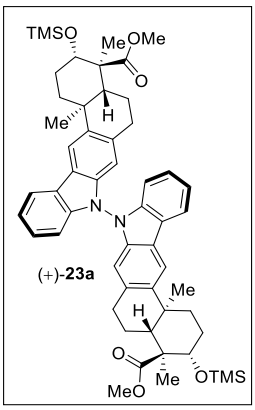
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

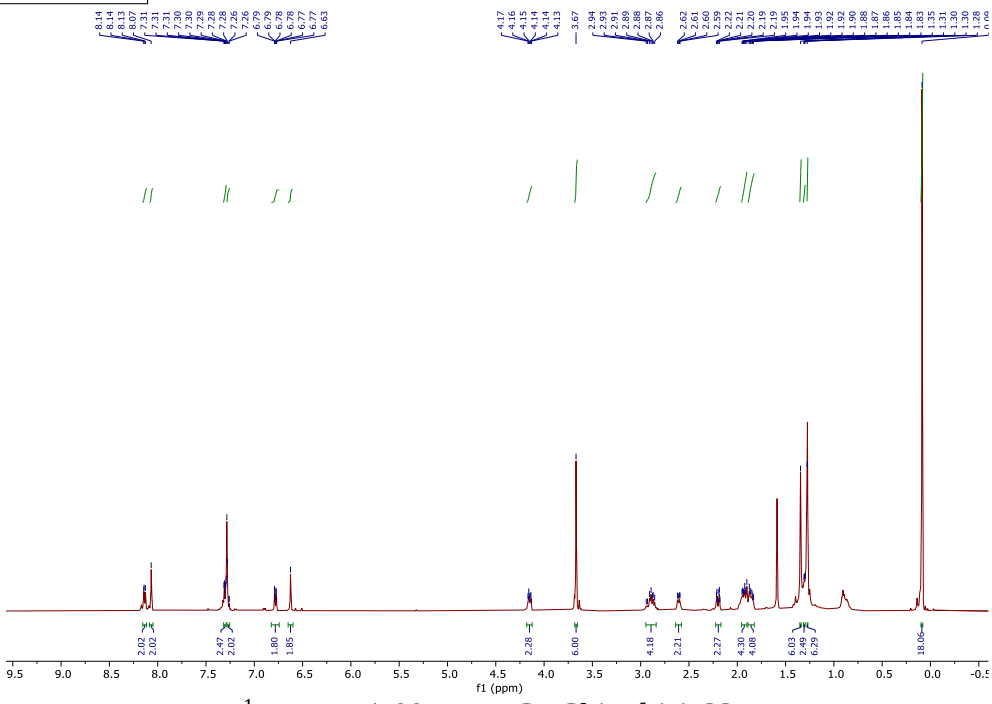


AB_RN_247.d

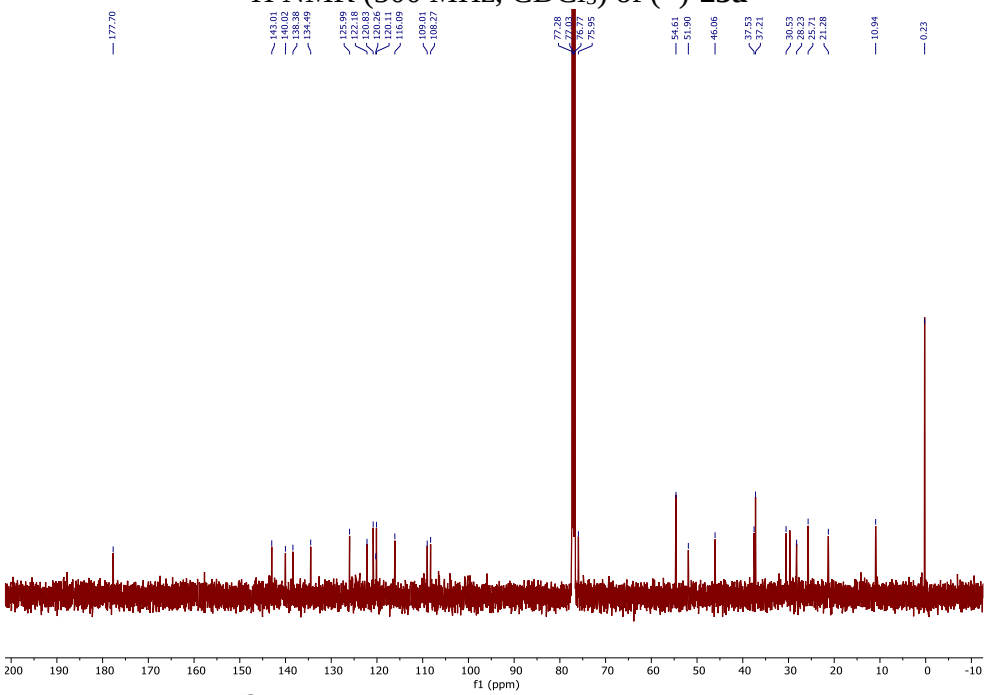
Bruker Compass DataAnalysis 4.1 printed: 9/14/2021 1:07:47 PM by: IISER Kolkata Page 1 of 1

HRMS data of xiamycin A methyl ester TMS ether [(+)-**22**]





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



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

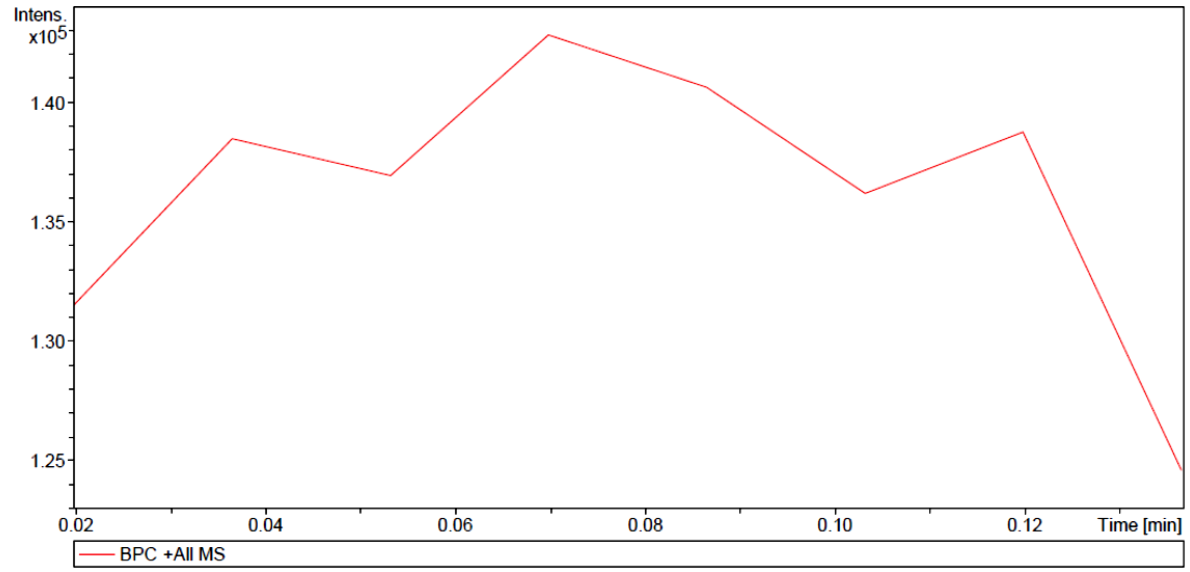
Display Report

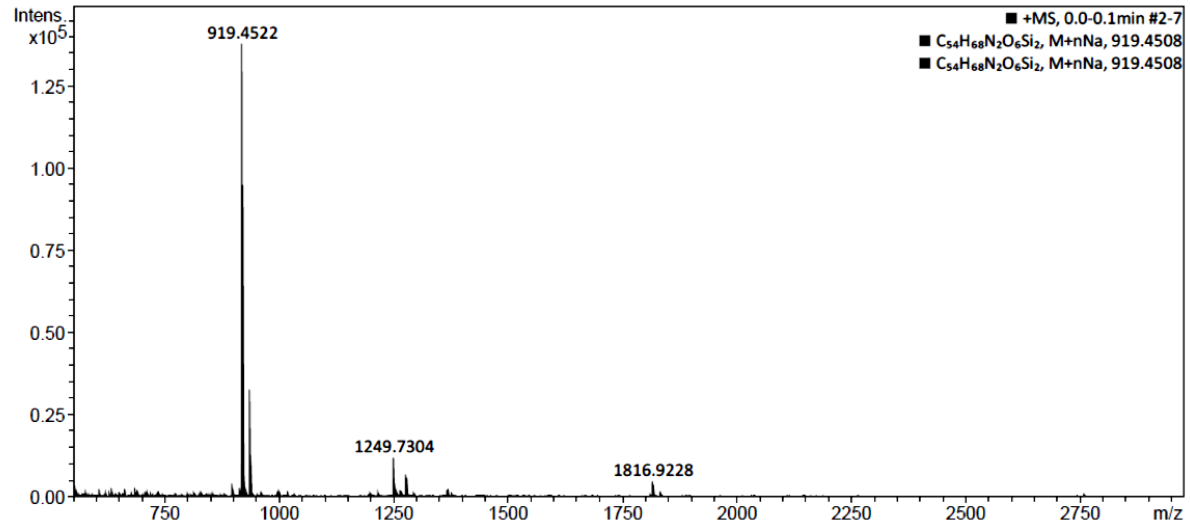
Analysis Info

Analysis Name	D:\Data\User data\2021\SEPT\AB_RN_0250NP2.d	Acquisition Date	9/9/2021 10:33:59 AM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_RN_0250NP2	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

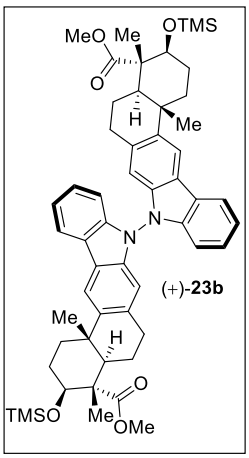


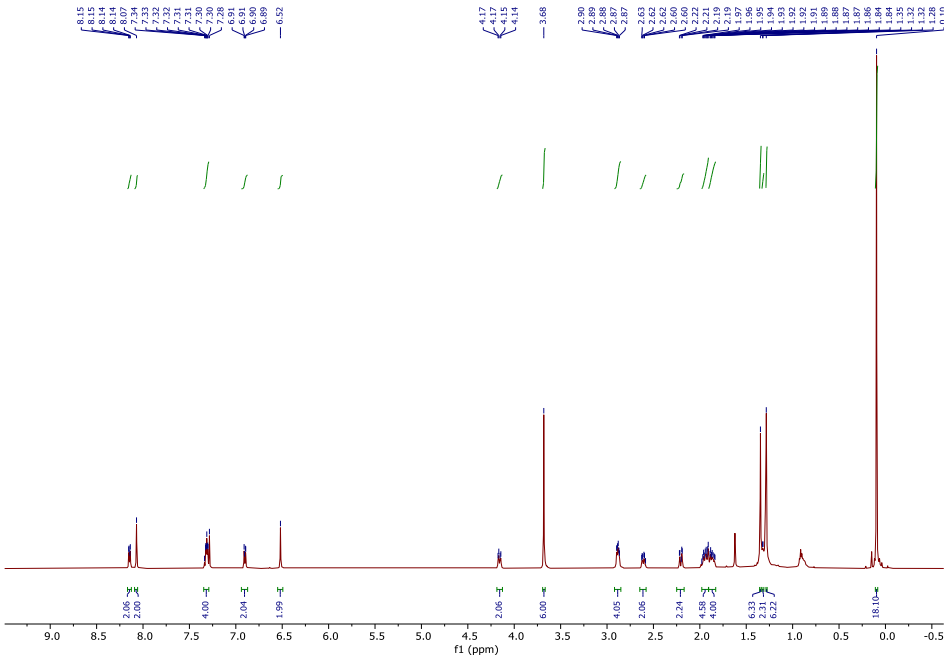


AB_RN_0250NP2.d

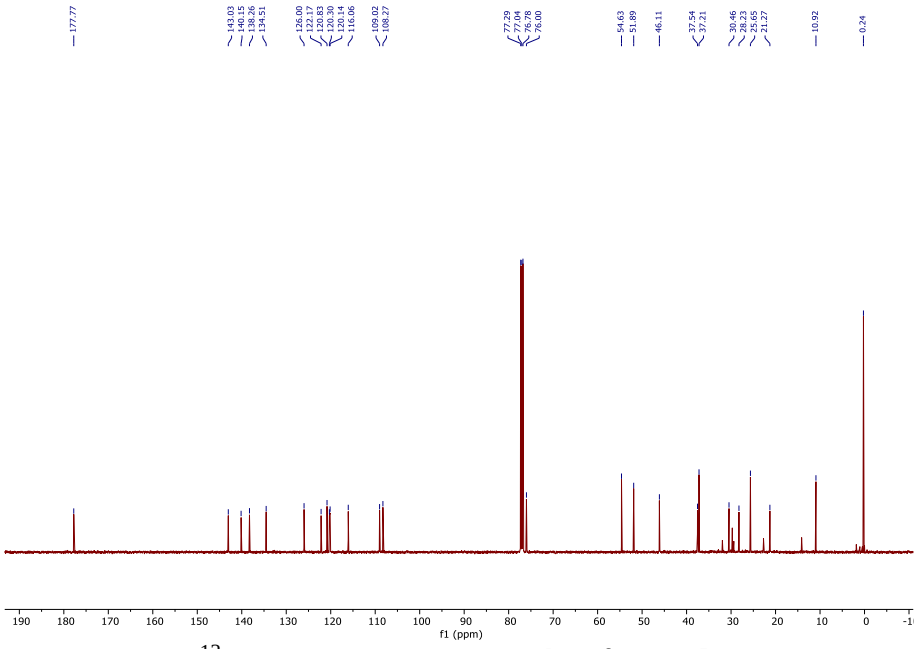
Bruker Compass DataAnalysis 4.1 printed: 9/9/2021 10:41:42 AM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**23a**





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



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

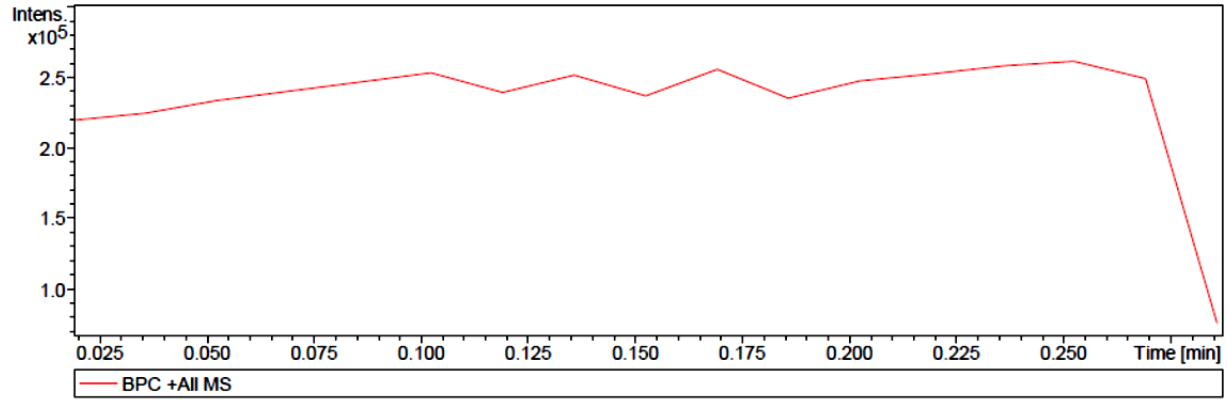
Display Report

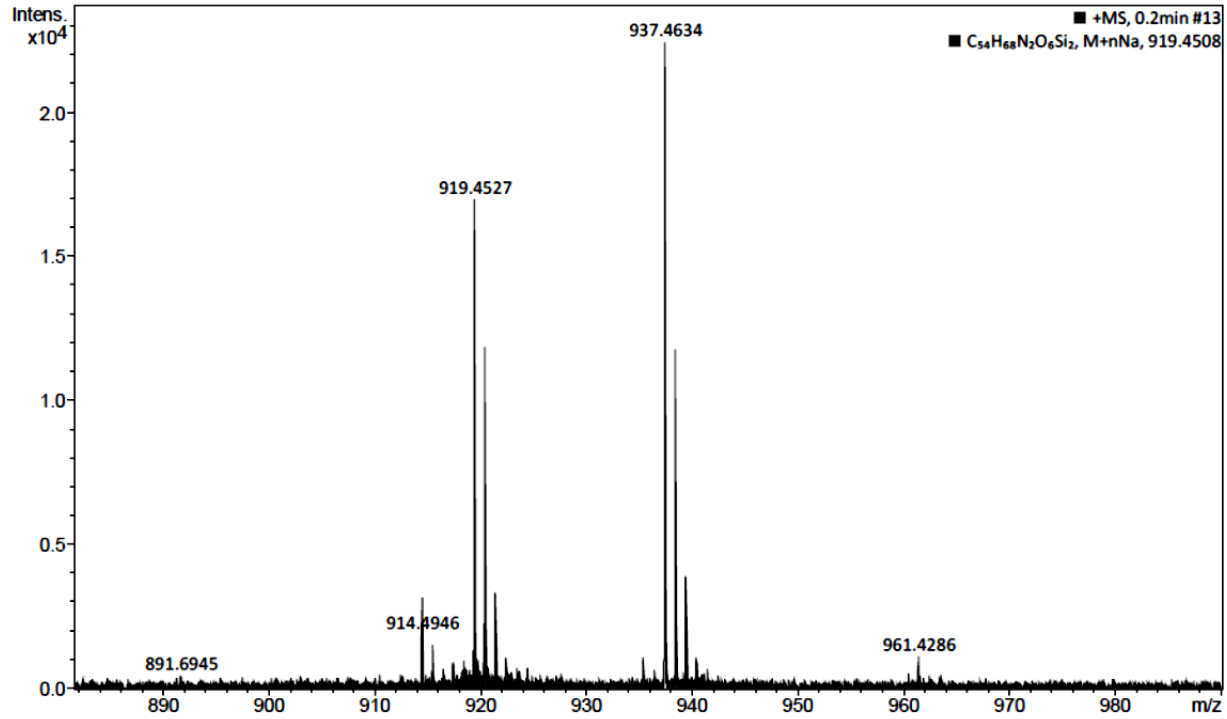
Analysis Info

Analysis Name	D:\Data\User data\2022\FEB\AB_RN_0373NP1.d	Acquisition Date	2/25/2022 12:17:00 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_RN_0373NP1	Instrument	maXis impact 8282001.00127
Comment	signal dropping issue		

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

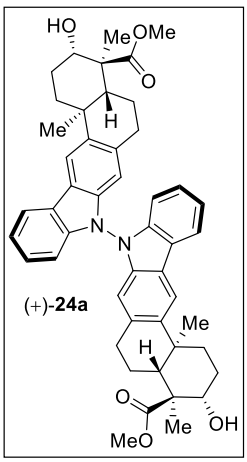


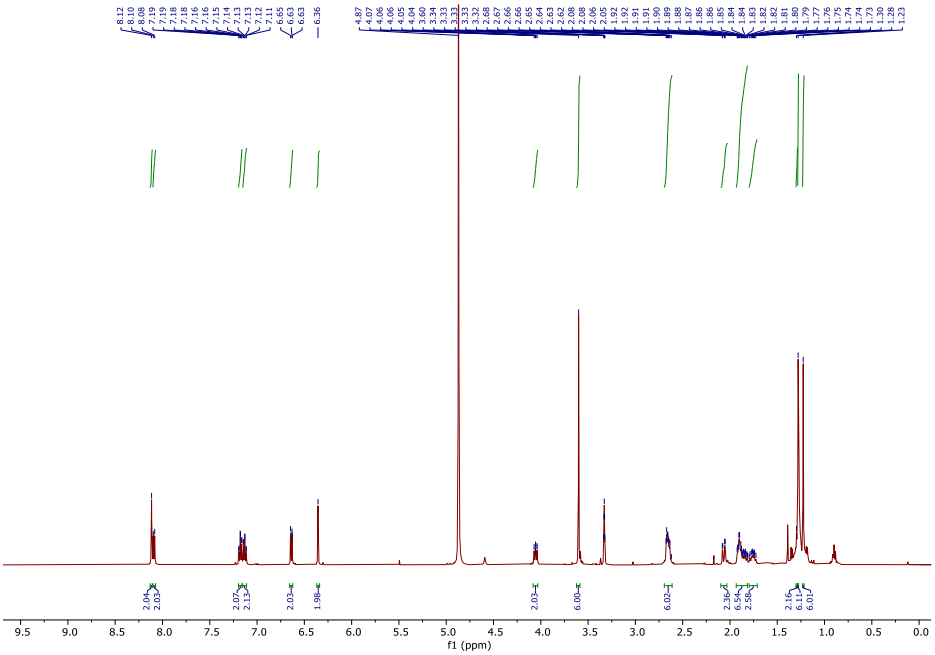


AB_RN_0373NP1.d

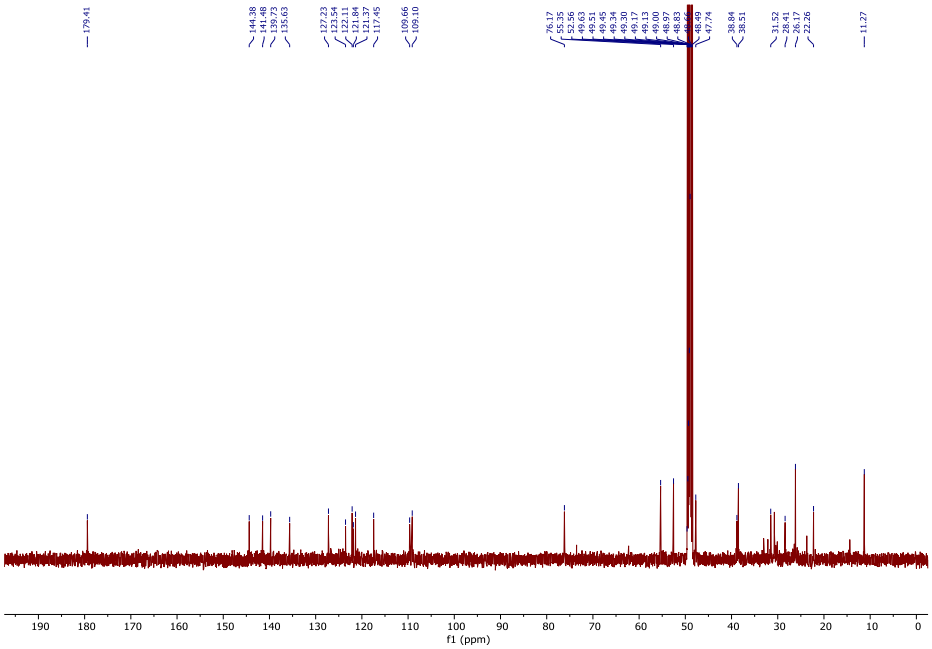
Bruker Compass DataAnalysis 4.1 printed: 2/25/2022 12:19:46 PM by: IISER Kolkata Page 1 of 1

HRMS data of (+)-**23b**





^{1}H NMR (500 MHz, CD_3OD) of (+)-**24a**



^{13}C NMR (125 MHz, CD_3OD) of (+)-**24a**

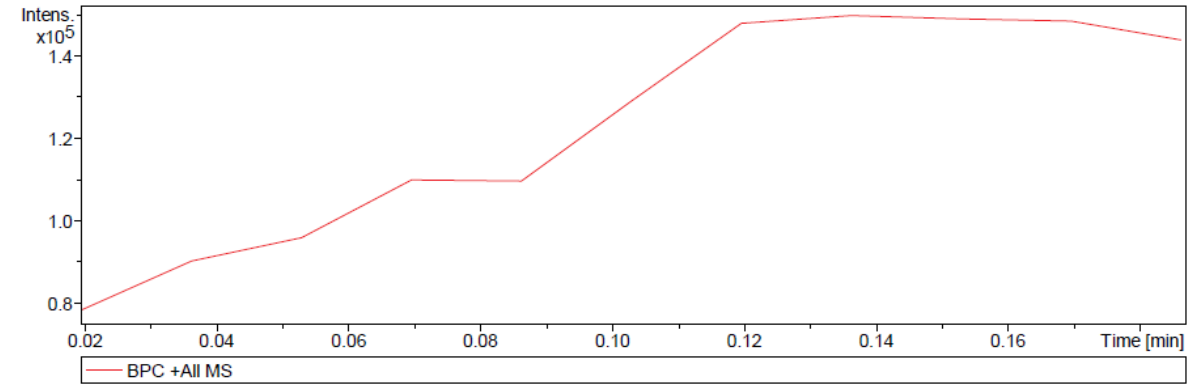
Display Report

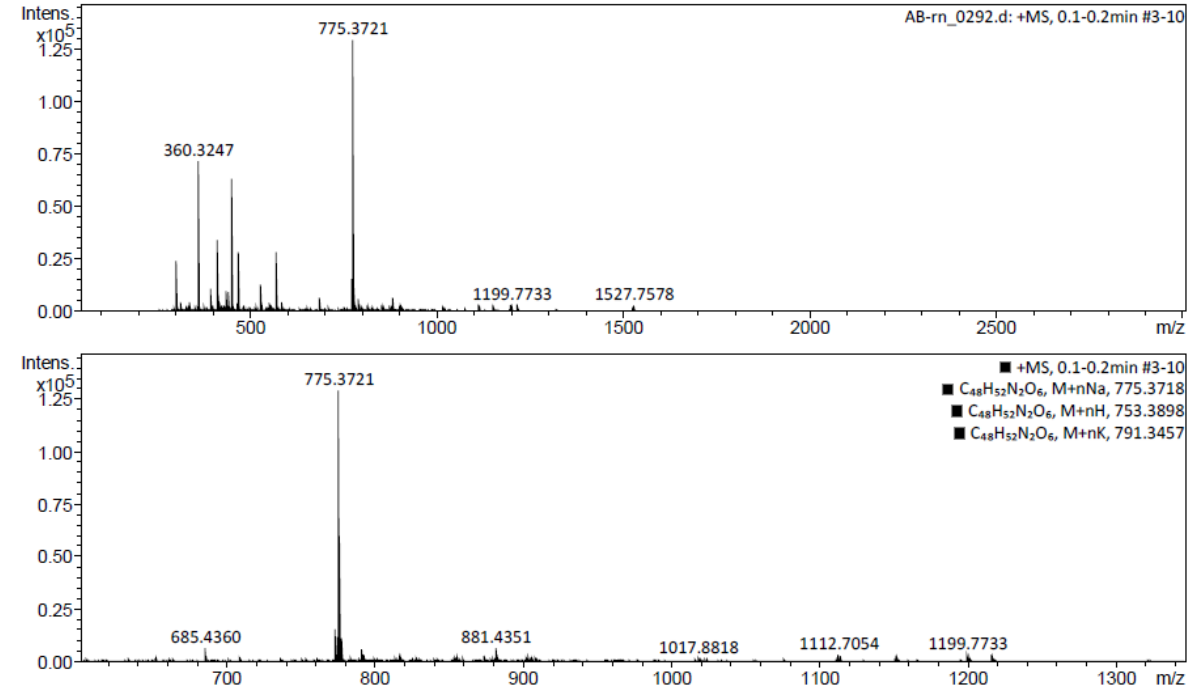
Analysis Info

Analysis Name	D:\Data\User data\2021\NOV\AB-rn_0292.d	Acquisition Date	11/12/2021 1:55:58 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB-rn_0292	Instrument	maXis impact 8282001.00127
Comment			

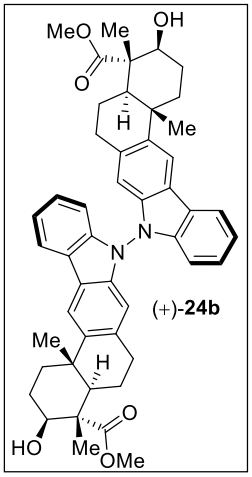
Acquisition Parameter

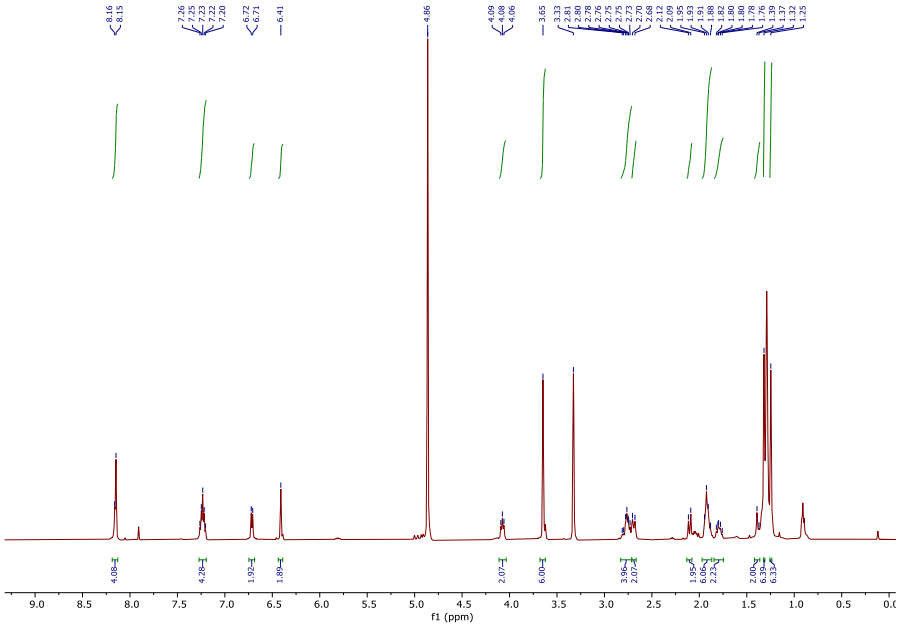
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



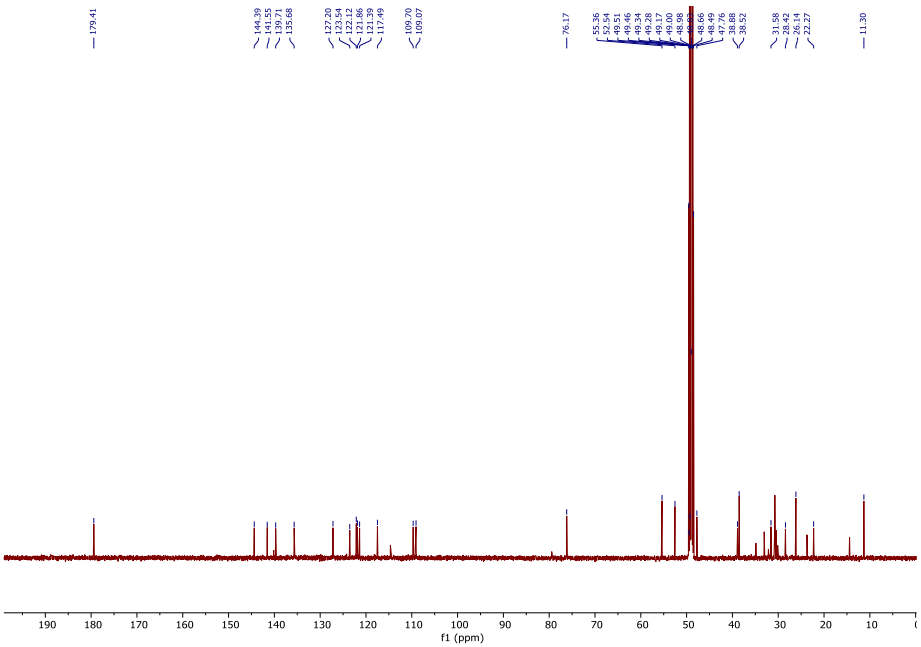


HRMS data of (+)-**24a**





^{1}H NMR (500 MHz, CD_3OD) of (+)-**24b**



^{13}C NMR (125 MHz, CD_3OD) of (+)-**24b**

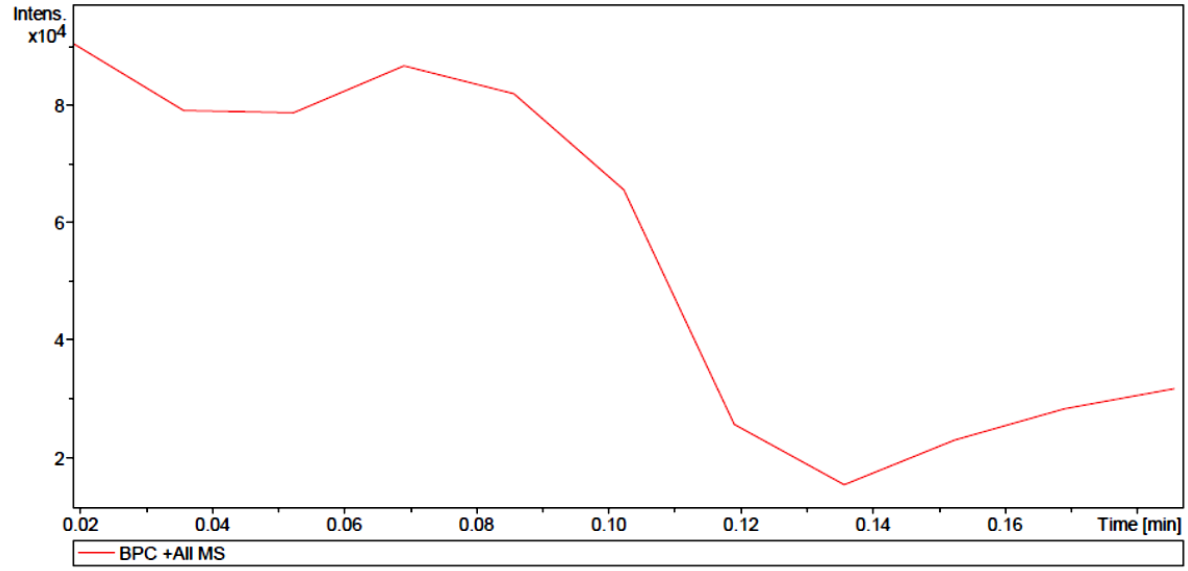
Display Report

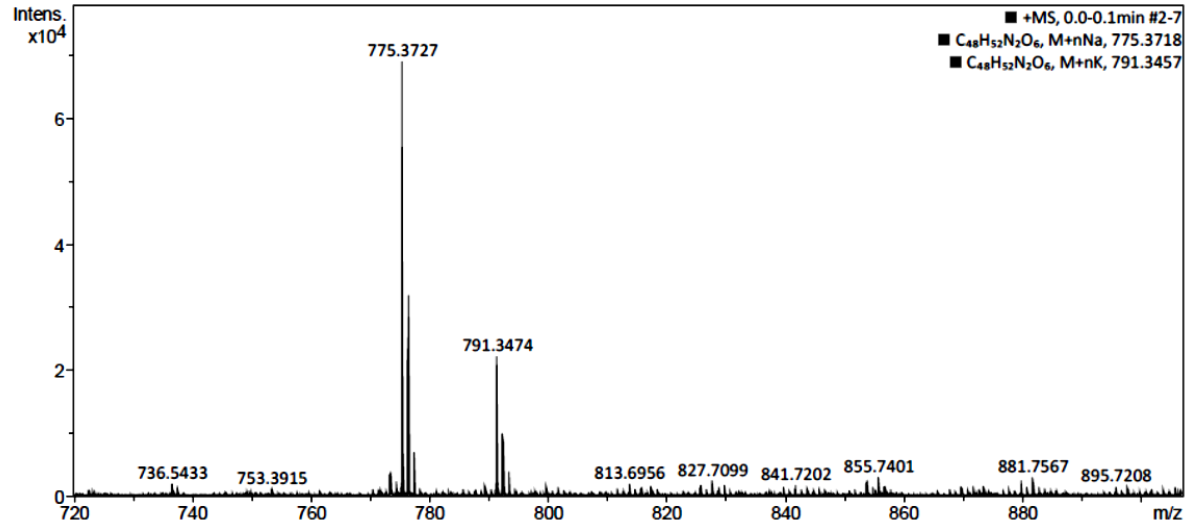
Analysis Info

Analysis Name	D:\Data\User data\2021\SEPT\AB_RN_0261.d	Acquisition Date	9/28/2021 2:19:27 PM
Method	Tune_pos_Mid.m	Operator	IISER Kolkata
Sample Name	AB_RN_0261	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_RN_0261.d

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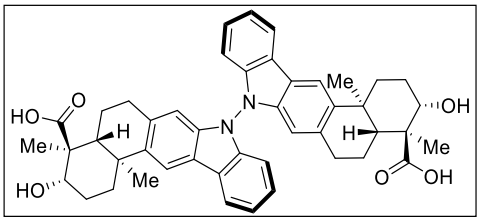
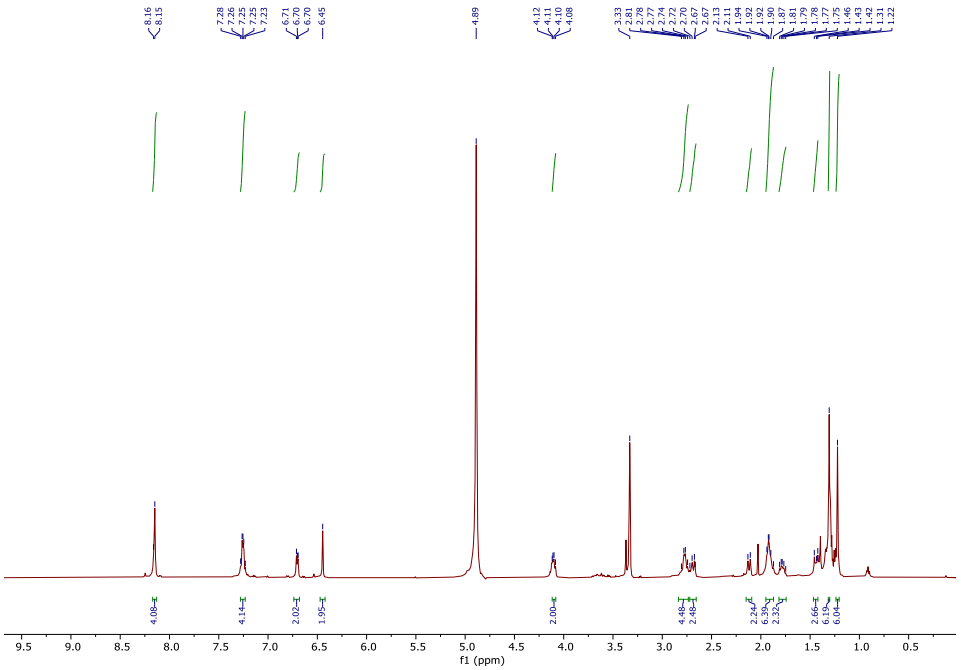
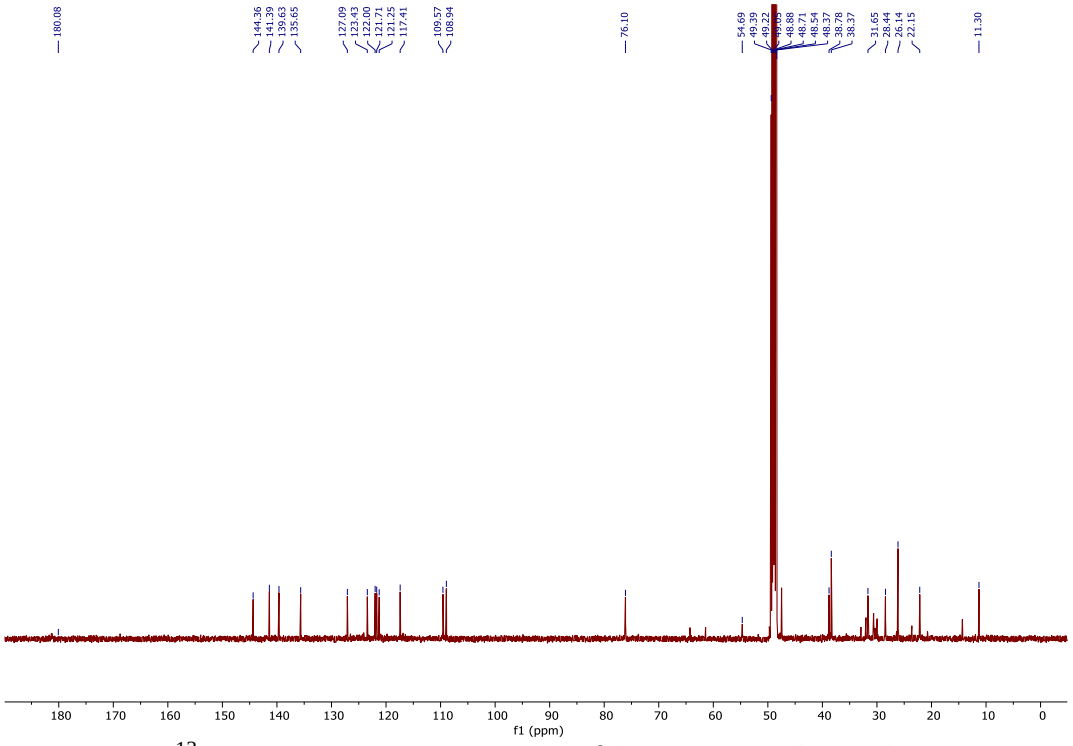
HRMS data of (+)-**24b**



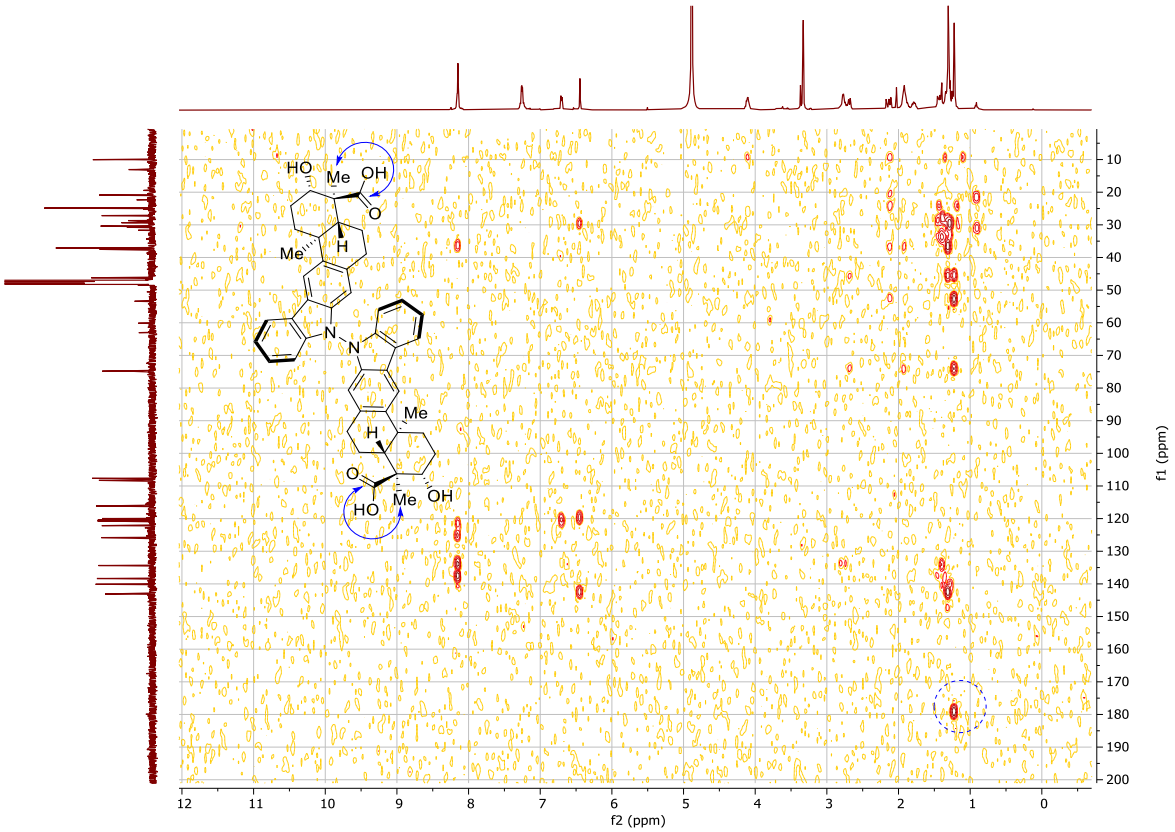
(+)-dixiamycin A [(+)-**1a**]



^{1}H NMR (500 MHz, CD_3OD) of dixiamycin A [(+)-**1a**]



^{13}C NMR (125 MHz, CD_3OD) of dixiamycin A [(+)-**1a**]



HMBC Data of dixiamycin A [(+)-**1a**]

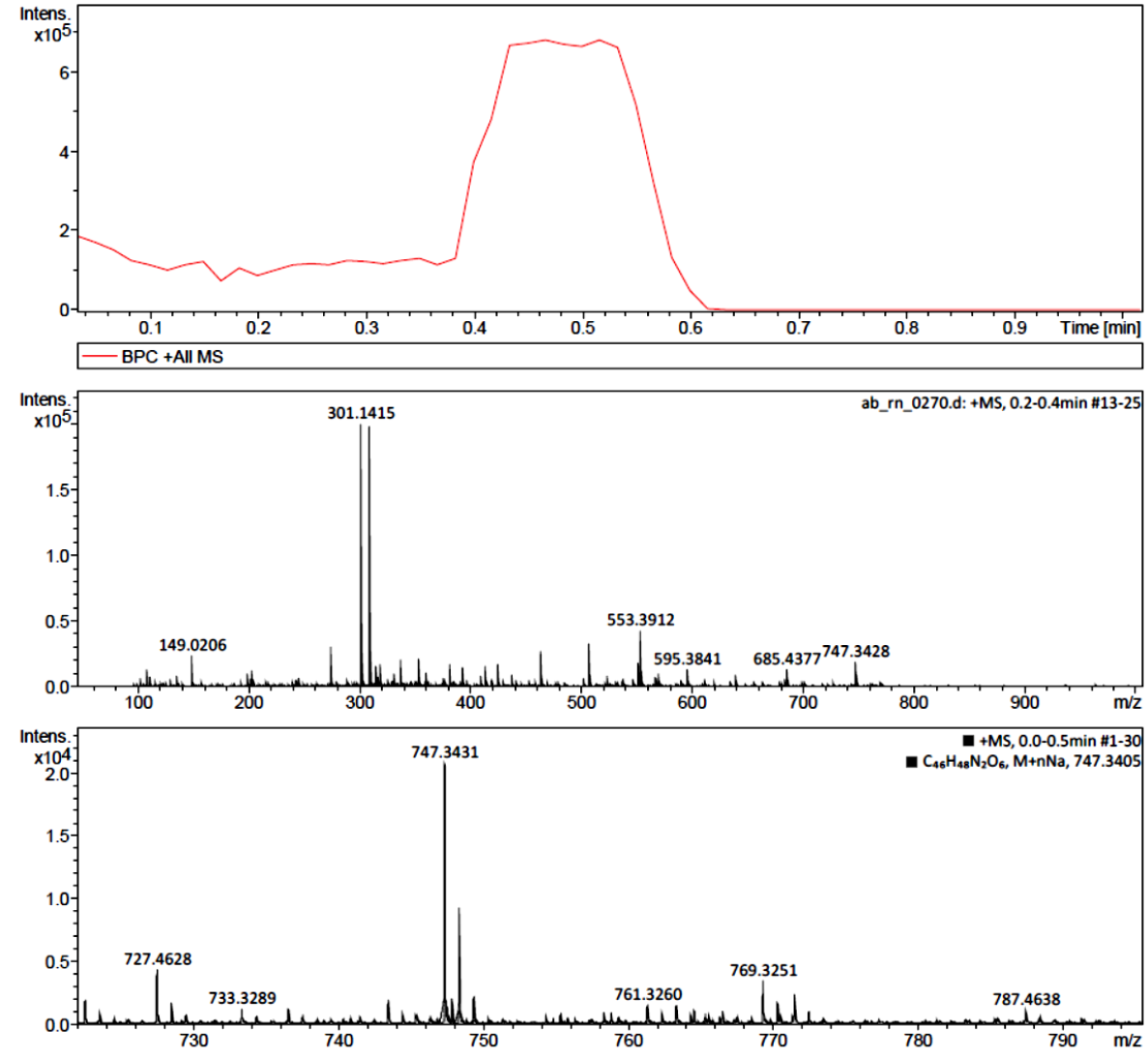
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2021\OCTOBER\ab_rn_0270.d	Acquisition Date	10/25/2021 10:49:19 AM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	ab_rn_0270	Instrument	maXis impact 8282001.00127
Comment			

Acquisition Parameter

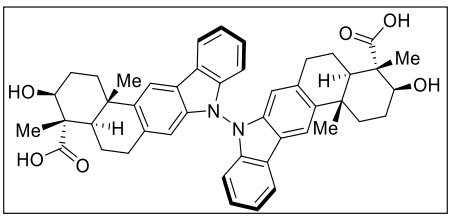
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Active	Set Capillary	3400 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



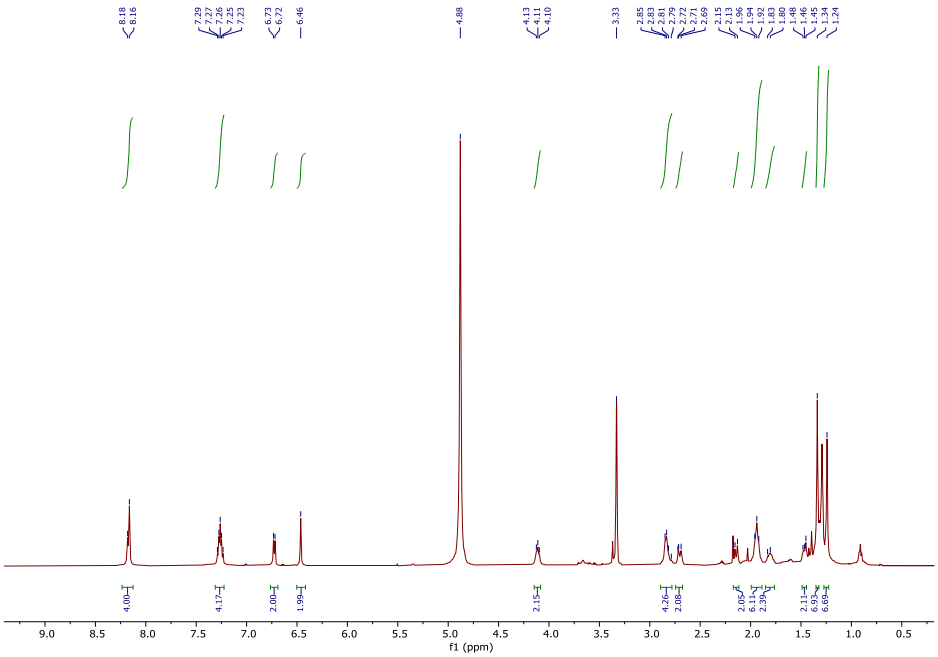
ab_rn_0270.d

Bruker Compass DataAnalysis 4.1 printed: 7/20/2022 4:47:39 PM by: IISER Kolkata Page 1 of 1

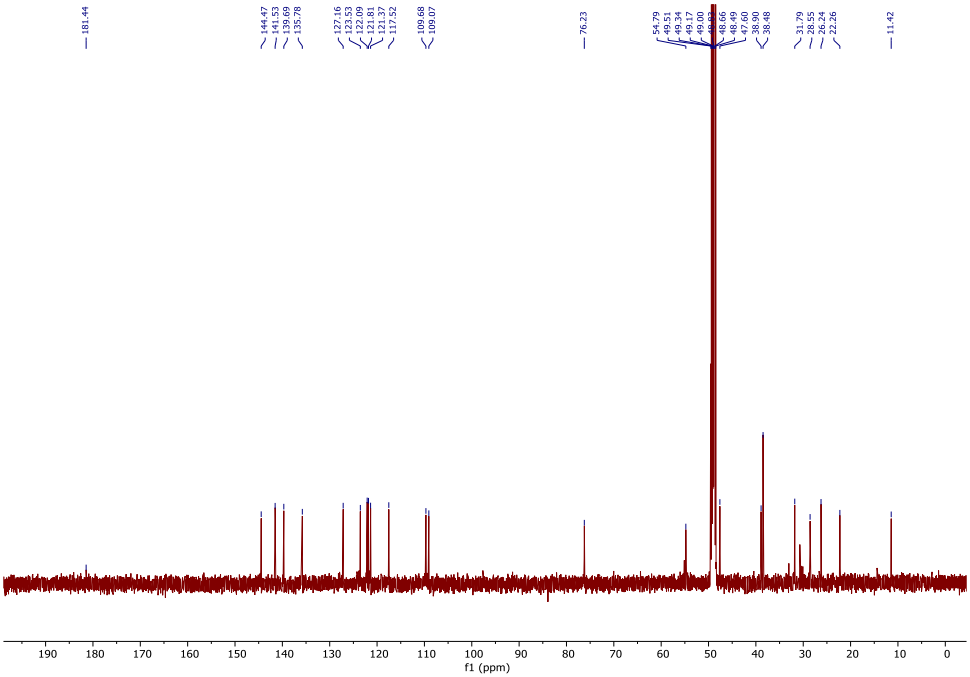
HRMS data of dixiamycin A [(+)-**1a**]



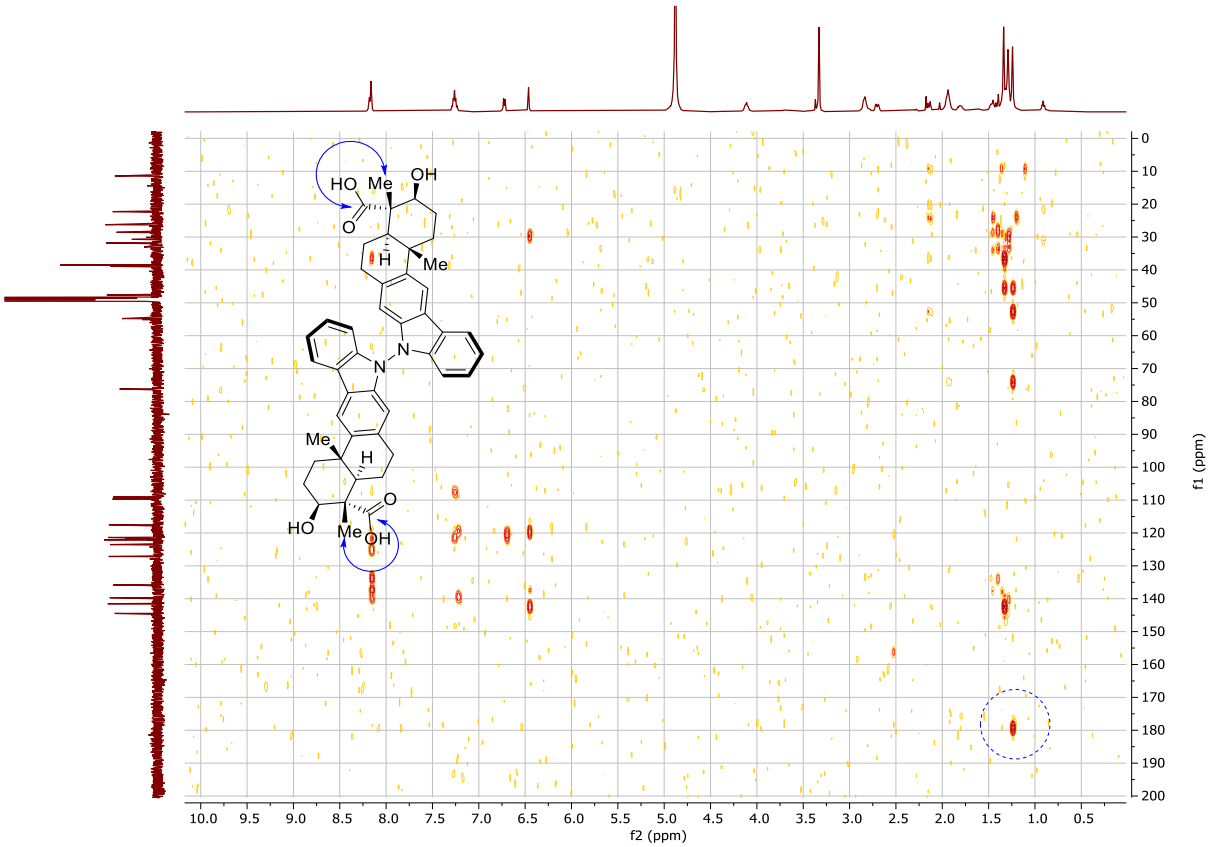
(+)-dixiamycin B [(+)-**1b**]



^{1}H NMR (500 MHz, CD_3OD) of dixiamycin B [(+)-**1b**]



^{13}C NMR (125 MHz, CD_3OD) of dixiamycin B [(+)-**1b**]



HMBC data of dixiamycin B [(+)-**1b**]

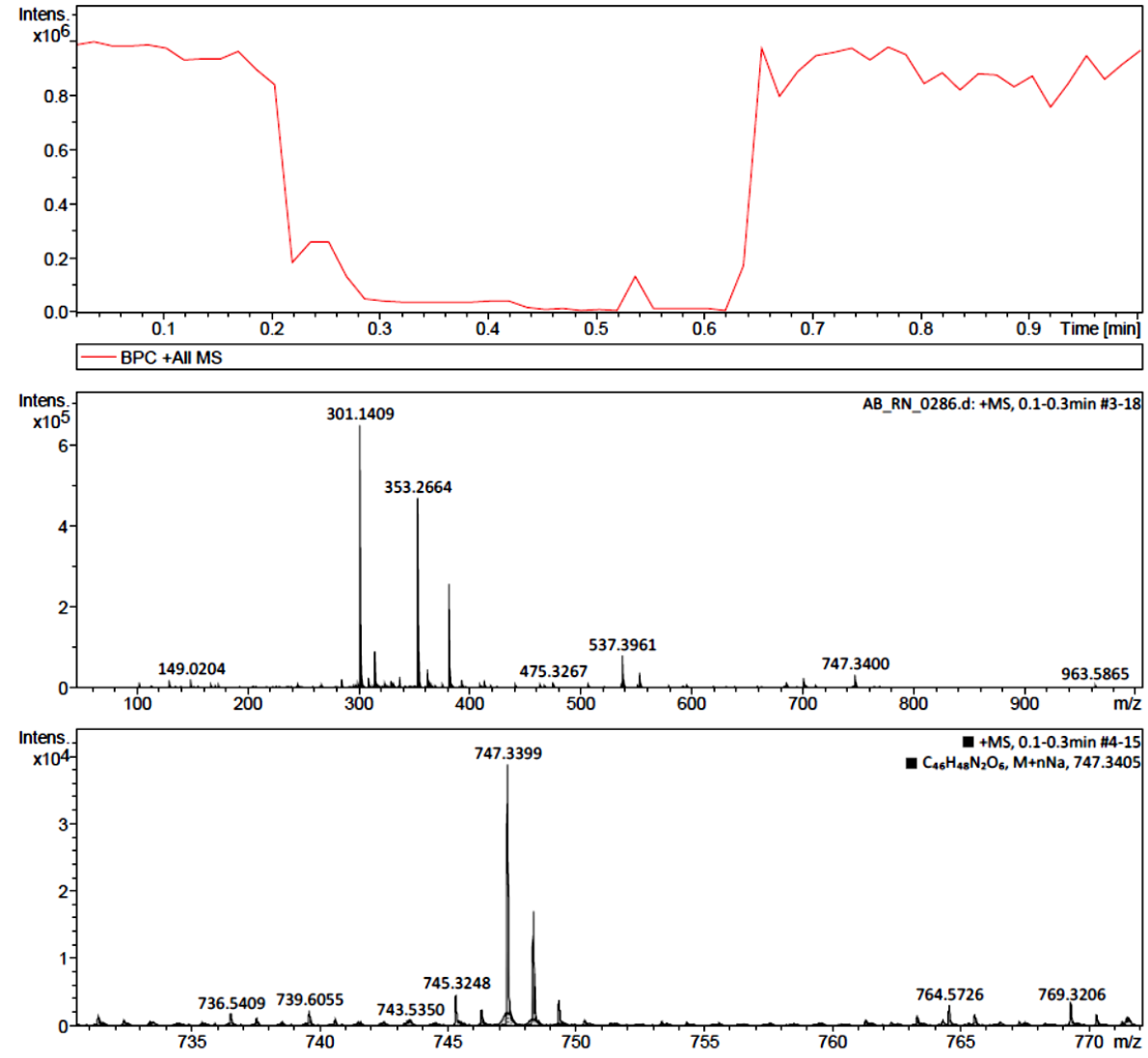
Display Report

Analysis Info

Analysis Name	D:\Data\User data\2021\NOV\AB_RN_0286.d	Acquisition Date	11/1/2021 1:18:46 PM
Method	Tune_pos_Standard.m	Operator	IISER Kolkata
Sample Name	AB_RN_0286	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_RN_0286.d

Bruker Compass DataAnalysis 4.1 printed: 7/20/2022 4:50:20 PM by: IISER Kolkata Page 1 of 1

HRMS data of dixiamycin B [(+)-**1b**]

Crystal Data and Structure Refinement of (+)**-16 (CCDC 2218312):**

A colorless block 0.22 × 0.18 × 0.12 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100.15 K using omega scans. Crystal-to-detector distance was 43.92 mm and exposure time was 0.50 seconds per frame at low angles and 2.00 seconds at high angles, using a scan width of 0.5°. The 2Θ range for data collection /° 7.252 to 136.454. A total of 14987 reflections were collected covering the indices $-5 \leq h \leq 7$, $-15 \leq k \leq 15$, $-37 \leq l \leq 36$. 4258 reflections were founded to be symmetry independent, with an R_{int} of 0.0298. Indexing and unit cell refinement indicated a primitive, orthorhombic lattice. The space group was found to be $P2_12_12_1$. CrysAlis^{Pro} 1.171.41.115a (Rigaku Oxford Diffraction, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2018/2) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by least-squares (SHELXL-2018/3). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2018/3.

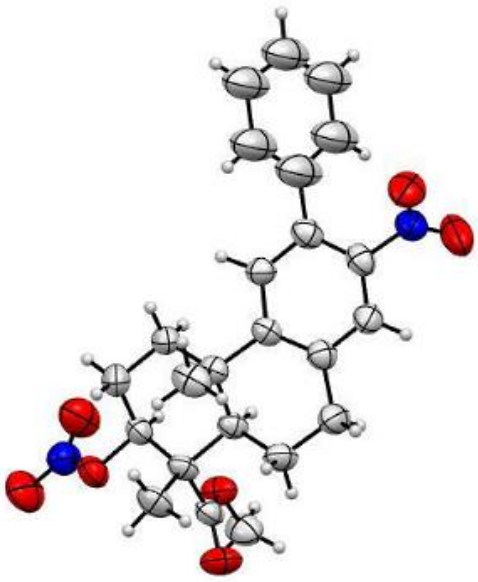


Figure S1. Single crystal XRD structure of compound (+)**-16**. ORTEP drawn at 50% probability level.

Table 1 Crystal data and structure refinement for (+)-16 (CCDC 2218312).

Identification code	rn202
Empirical formula	$C_{26}H_{27}N_2O_9$
Formula weight	511.49
Temperature/K	100.15

Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.08080(10)
b/Å	13.2575(2)
c/Å	31.0012(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2499.20(7)
Z	4
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	0.870
F(000)	1076.0
Crystal size/mm^3	0.22 × 0.18 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.252 to 136.454
Index ranges	$-5 \leq h \leq 7$, $-15 \leq k \leq 15$, $-37 \leq l \leq 36$
Reflections collected	14987
Independent reflections	4258 [R_{int} = 0.0298, R_{sigma} = 0.0276]
Data/restraints/parameters	4258/0/309
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0748, wR_2 = 0.2050
Final R indexes [all data]	R_1 = 0.0861, wR_2 = 0.2139
Largest diff. peak/hole / e Å^{-3}	0.78/-0.34
Flack parameter	-0.33(18)

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rn202
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.
No syntax errors found. CIF dictionary Interpreting this report

Datablock: rn202

```
Bond precision: C-C = 0.0108 A Wavelength=1.54184
Cell: a=6.0808(1) b=13.2575(2) c=31.0012(5)
alpha=90 beta=90 gamma=90
Temperature: 100 K
Calculated Reported
Volume 2499.20(7) 2499.20(7)
Space group P 21 21 21 P 21 21 21
Hall group P 2ac 2ab P 2ac 2ab
Moiety formula C24 H26 N2 O7, C2 H O2 C24 H26 N2 O7, C2 H O2
Sum formula C26 H27 N2 O9 C26 H27 N2 O9
Mr 511.50 511.49
```

```
Dx,g cm-3 1.359 1.359
Z 4 4
Mu (mm-1) 0.870 0.870
F000 1076.0 1076.0
F000' 1079.75
h,k,lmax 7,15,37 7,15,37
Nref 4576[ 2660] 4258
Tmin,Tmax 0.829,0.901 0.724,1.000
Tmin' 0.826
Correction method= # Reported T Limits: Tmin=0.724 Tmax=1.000
AbsCorr = EMPIRICAL
Data completeness= 1.60/0.93 Theta(max)= 68.227
R(reflections)= 0.0748( 3637)
wR2(reflections)=
0.2139( 4258)
S = 1.042 Npar= 309
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01081 Ang.
PLAT420_ALERT_2_B D-H Bond Without Acceptor O --H . Please Check
PLAT780_ALERT_1_B Coordinates do not Form a Properly Connected Set Please Do !

Alert level C

DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
STRVA01_ALERT_4_C Flack parameter is too small
From the CIF: _refine_ls_abs_structure_Flack -0.330
From the CIF: _refine_ls_abs_structure_Flack_su 0.180
PLAT031_ALERT_4_C Refined Extinction Parameter Within Range of ... 2.800 Sigma
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.26 Report
PLAT097_ALERT_2_C Large Reported Max. (Positive) Residual Density 0.78 eA-3
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C19 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N1 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C16 Check
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C26 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C25 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including O 0.211 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 2.597 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 6 Report

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 1 Info
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1 Report
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) O --C26_a . 5.7 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) O8 --C25 . 21.4 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) O8 --C26 . 8.5 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) O8 --C26_a . 8.8 s.u.
PLAT231_ALERT_4_G Hirshfeld Test (Solvent) C25 --C26 . 5.0 s.u.
PLAT344_ALERT_2_G Unusual Angle Range in Solvent/Ion for C26 Check
PLAT367_ALERT_2_G Long? C(sp?)-C(sp?) Bond C25 - C26 . 1.66 Ang.
PLAT773_ALERT_2_G Check long C-C Bond in CIF: C25 --C26 2.04 Ang.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle(s) in CIF ... 38.90 Deg.
O8 -C26 -C25 1_555 1_555 1_555 ..... # 124 Check
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle(s) in CIF ... 32.60 Deg.
O8 -C26 -C25 4_546 1_555 4_546 ..... # 126 Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 15 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File 4 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 3 Info

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0 ALERT level A = Most likely a serious problem - resolve or explain
3 ALERT level B = A potentially serious problem, consider carefully
13 ALERT level C = Check. Ensure it is not caused by an omission or oversight
17 ALERT level G = General information/check it is not something unexpected
2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
12 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
13 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

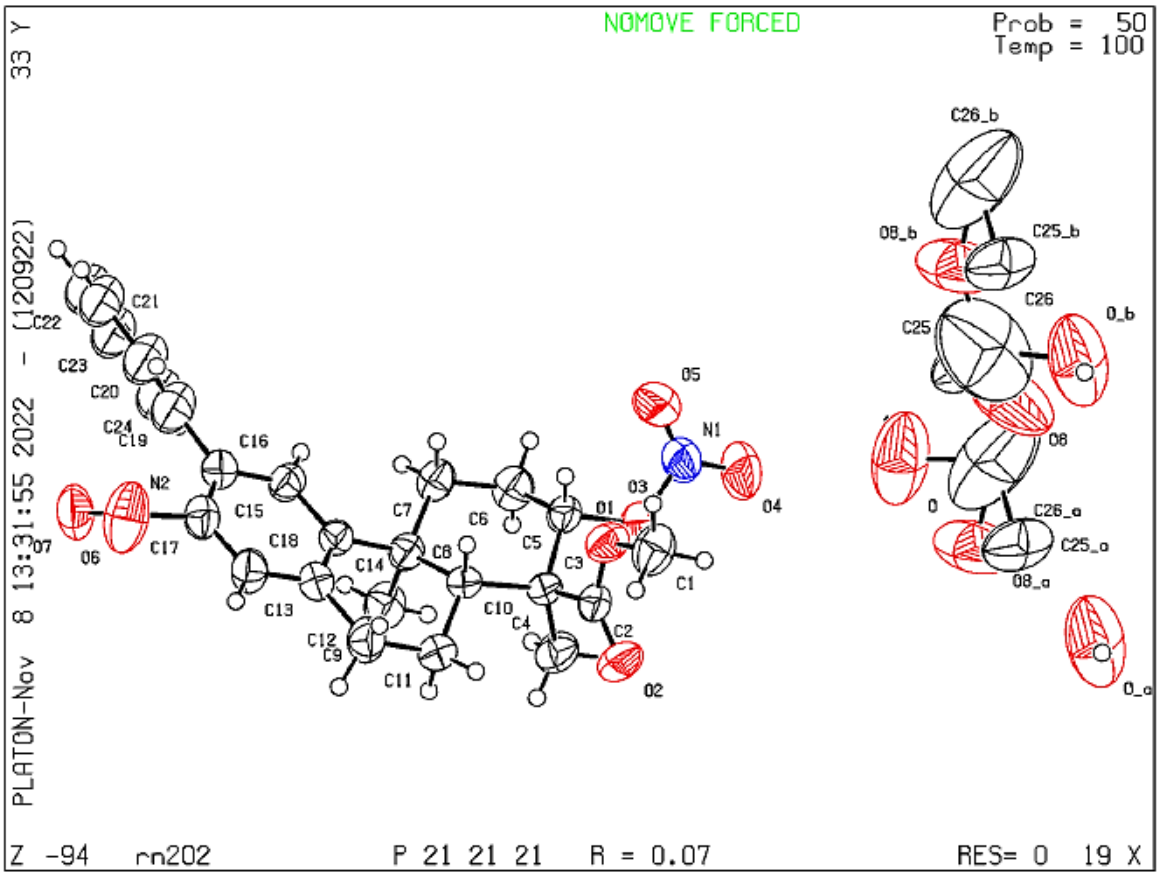
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

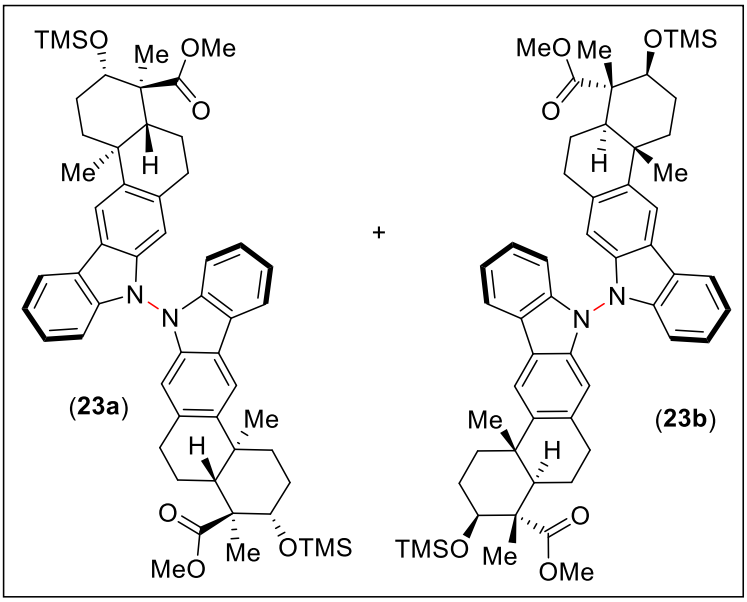
Publication of your CIF in other journals

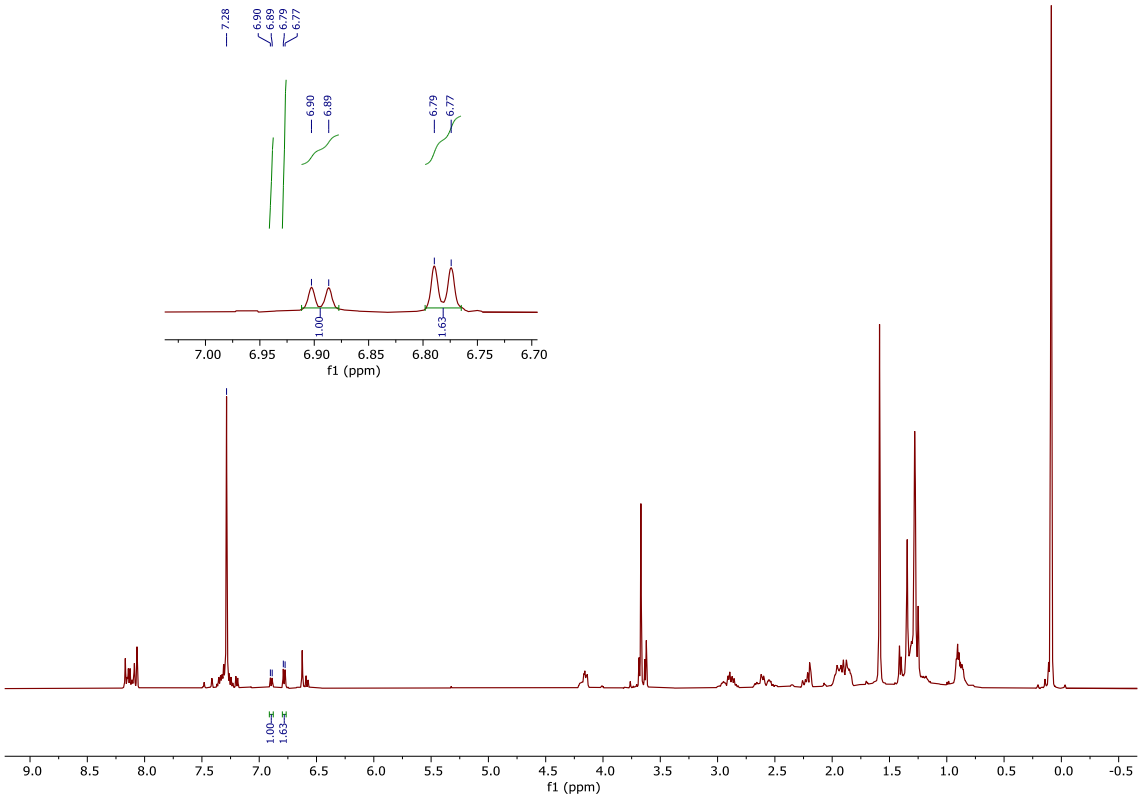
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 12/09/2022; check.def file version of 09/08/2022

Datablock rn202 - ellipsoid plot

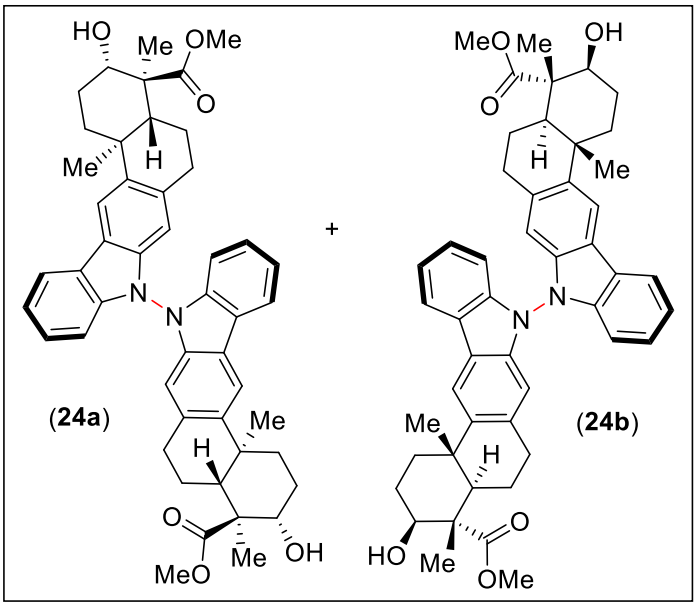


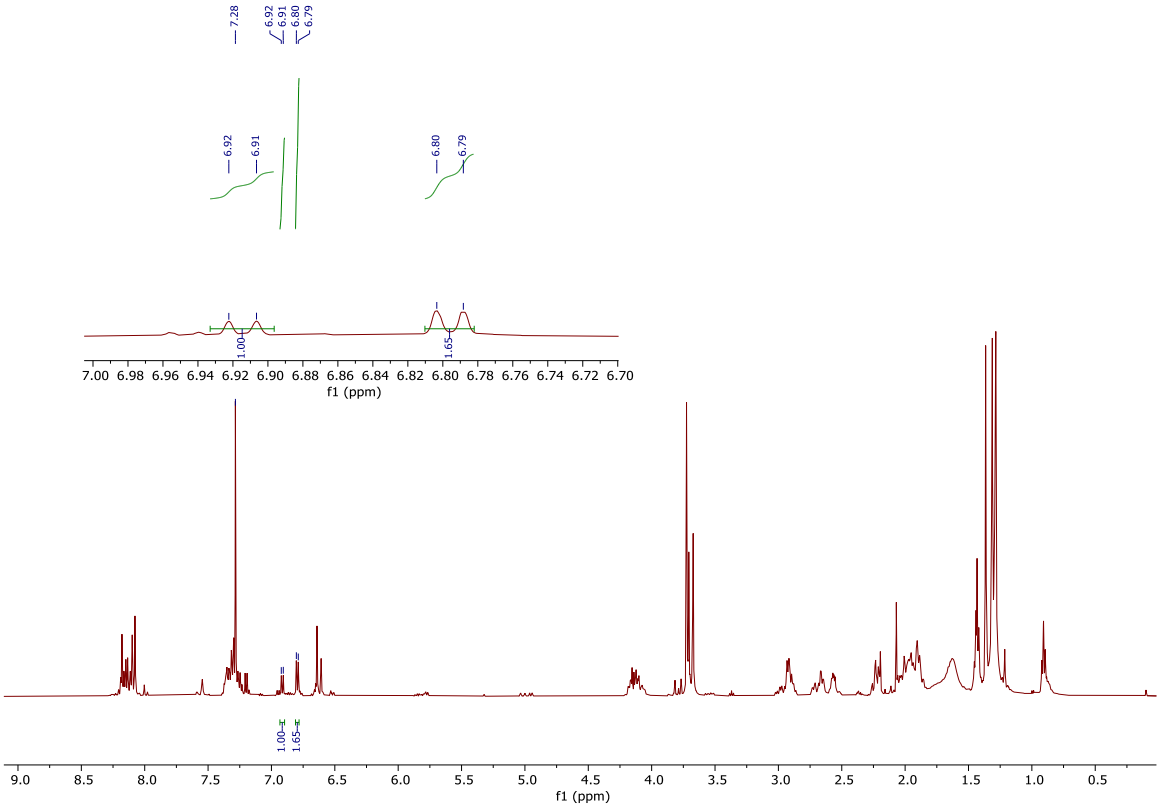




^{1}H NMR (500 MHz, $CDCl_3$) of reaction mixture of **23a** and **23b**

Atropo-diastereomeric ratio: **23a: 23b** = ~1.6:1



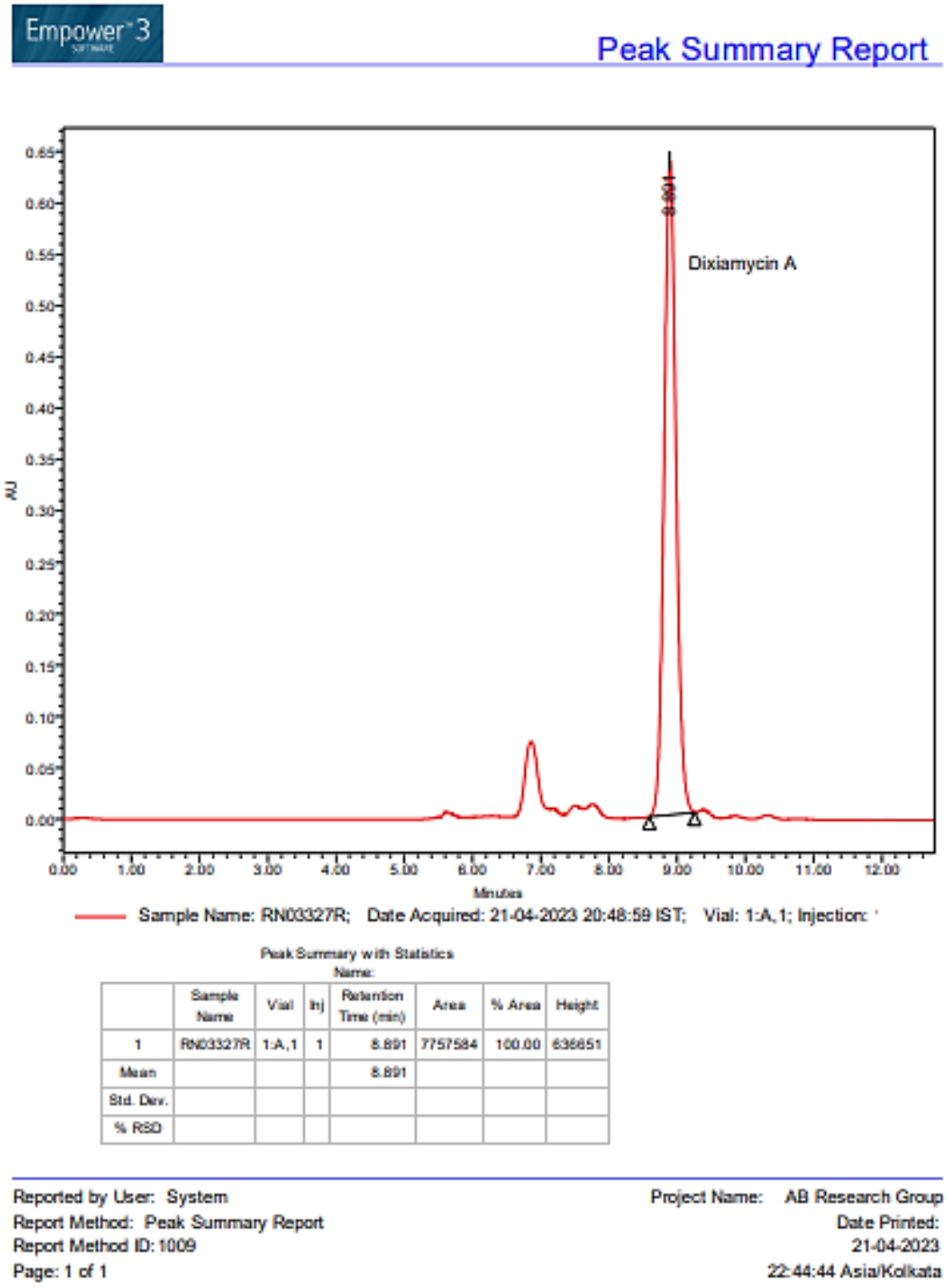


^{1}H NMR (500 MHz, $CDCl_3$) of reaction mixture of **24a** and **24b**

Atropo-diastereomeric ratio: **24a: 24b** = ~1.6:1

Retention time of dixiamycin A (**1a**) was determined via a reverse phase HPLC analysis using a Spherisorb ODS-2 C18 5µm column;
Solvent: Acetonitrile/Methanol = 90/10; Flow rate: 0.50 mL/min; Detection: at 295.0 nm:

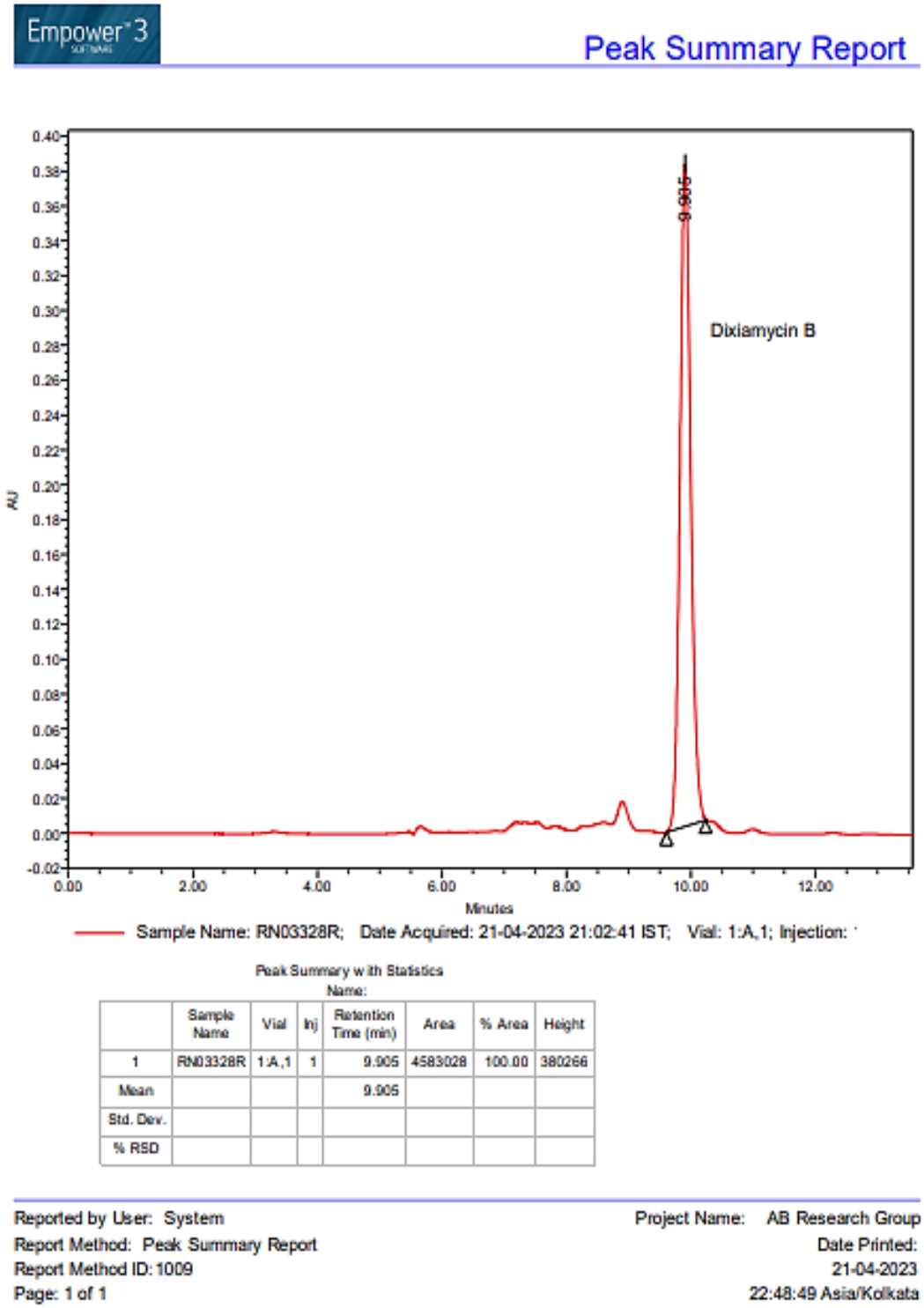
^{t}R of dixiamycin A (**1a**) = 8.891 min.



HPLC traces of dixiamycin A (**1a**)

Retention time of dixiamycin B (**1b**) was determined via a reverse phase HPLC analysis using a Spherisorb ODS-2 C18 5µm column;
Solvent: Acetonitrile/Methanol = 90/10; Flow rate: 0.50 mL/min; Detection: at 295.0 nm

^{t}R of dixiamycin B (**1b**) = 9.905 min.

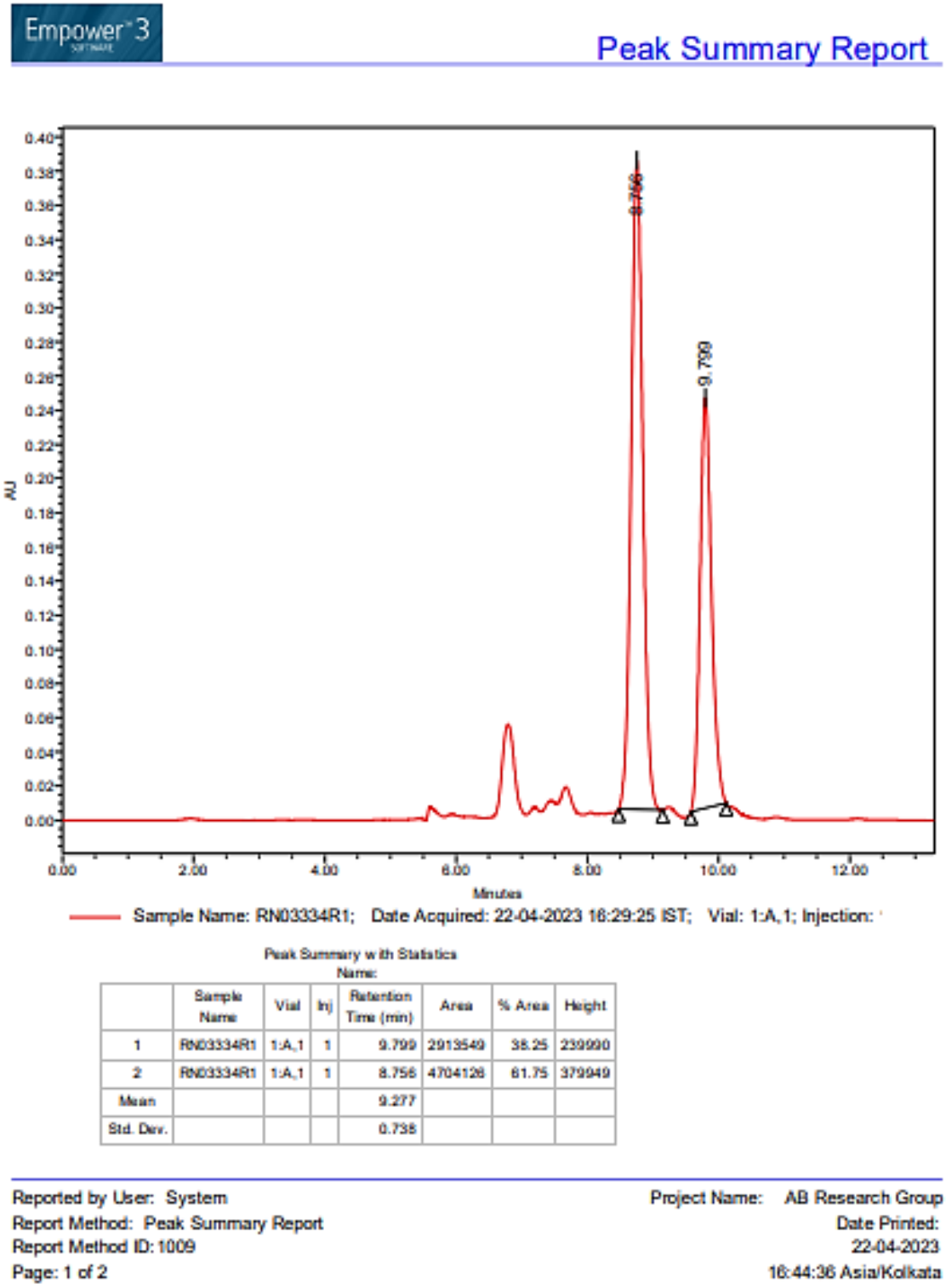


HPLC traces of dixiamycin B (**1b**)

Retention time of atropo-diastereomeric ratio of dixiamycin A (**1a**) and dixiamycin B (**1b**) were determined via reverse phase HPLC analysis using a Spherisorb ODS-2 C18 5µm column;

Solvent: Acetonitrile/Methanol = 90/10; Flow rate: 0.50 mL/min; Detection: at 295.0 nm

^{t}R of dixiamycin A (**1a**) = 8.756 min and ^{t}R of dixiamycin B (**1b**) = 9.799 min



Peak Summary with Statistics
Name:

	Sample Name	Vial	Inj	Retention Time (min)	Area	% Area	Height
1	RN03334R1	1:A,1	1	9.799	2913549	38.25	239990
2	RN03334R1	1:A,1	1	8.756	4704126	61.75	379949
Mean				9.277			
Std. Dev.				0.738			

Reported by User: System
Report Method: Peak Summary Report
Report Method ID: 1009
Page: 1 of 2

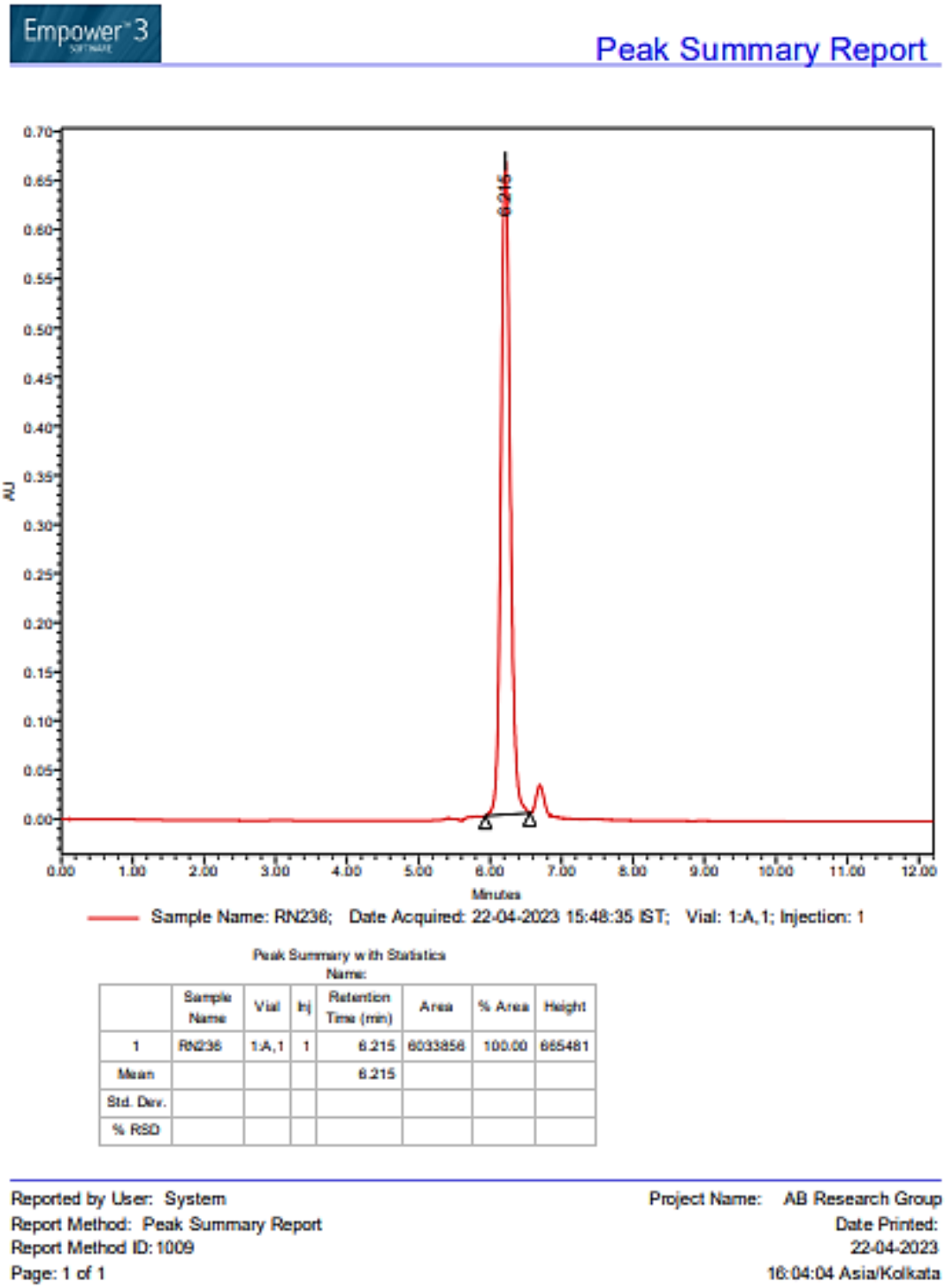
Project Name: AB Research Group
Date Printed:
22-04-2023
16:44:36 Asia/Kolkata

HPLC traces of dixiamycin A (**1a**) and dixiamycin B (**1b**)

Retention time of xiamycin A (**2a**) was determined via reverse phase HPLC analysis using a Spherisorb ODS-2 C18 5µm column;

Solvent: Acetonitrile/Methanol = 90/10; Flow rate: 0.50 mL/min; Detection: at 295 nm:

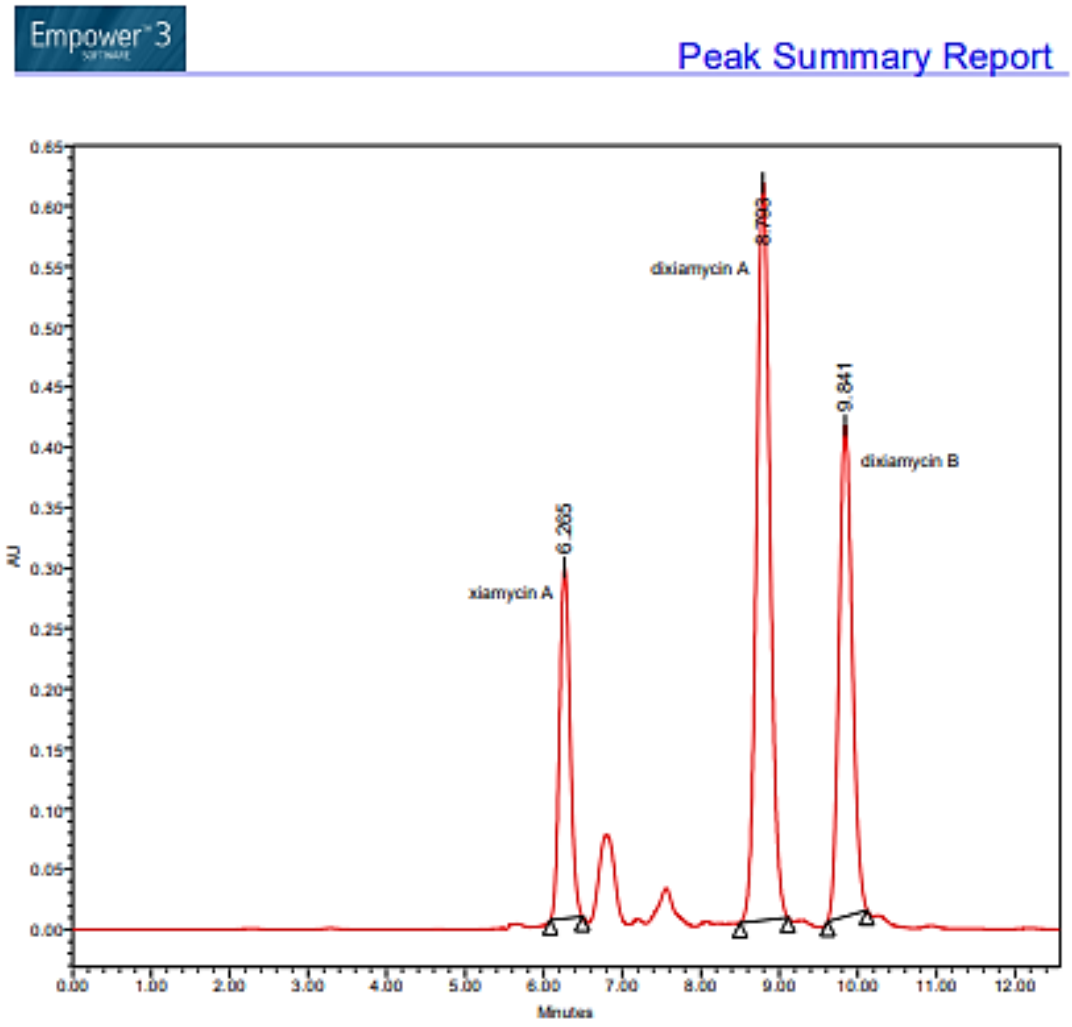
^{t}R of xiamycin A (**2a**) = 6.215 min.



HPLC traces of xiamycin A (**2a**)

Comparison of the retention time of xiamycin A (**2a**), dixiamycin A (**1a**) and dixiamycin B (**1b**) were determined via reverse phase HPLC analysis using a Spherisorb ODS-2 C18 5µm column;
Solvent: Acetonitrile/Methanol = 90/10; Flow rate: 0.50 mL/min; Detection: at 295.0 nm.

^{t}R of xiamycin A (**2a**) = 6.265 min,
^{t}R of dixiamycin A (**1a**) = 8.793 min
^{t}R of dixiamycin B (**1b**) = 9.841 min.



Peak Summary with Statistics
Name:

	Sample Name	Vial	Inj	Retention Time (min)	Area	% Area	Height
1	RN03335R	1:A,1	1	9.841	4755359	32.10	407371
2	RN03335R	1:A,1	1	8.793	7360640	49.69	611626
3	RN03335R	1:A,1	1	6.265	2697794	18.21	291571
Mean				8.300			

Reported by User: System
Report Method: Peak Summary Report
Report Method ID: 1009
Page: 1 of 2

Project Name: AB Research Group
Date Printed:
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18:31:49 Asia/Kolkata

HPLC traces of xiamycin A (**2a**), dixiamycin A (**1a**) and dixiamycin B (**1b**)

References:

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