Electronic Supplementary Information (ESI)

Novel cinnamic Acid Analogues: Synthesis of *Aminotroponyl Acrylates* by Pd(II)-Catalysed C(sp^2)-H Olefination

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1. General Information

Material and Instrumentation. All required materials were purchased from commercial suppliers and used without further purification. Anhydrous DMF was freshly prepared by distilling over calcium hydride. Reactions were monitored by thin layer chromatography, visualized by UV and Ninhydrin. Column chromatography was performed in 230-400 and 100-200 mesh silica. ^{1}H NMR spectra were recorded on Bruker AV-400 instrument (400 MHz) or Bruker AV-700 instrument (700 MHz). ^{13}C NMR spectra were recorded on Bruker AV-400 instrument (100 MHz) or Bruker AV-700 instrument (176 MHz). ^{1}H and ^{13}C NMR chemical shifts were recorded in ppm downfield from tetramethyl silane or relative to the residual solvent ($CDCl_3$) signal. Splitting patterns are abbreviated as: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; dq, doublet of quartet; m, multiplet. Mass spectra were obtained from Bruker MicroTOF-Q II Spectometer and Waters XEVO- G2XSQTOF Spectrometer.

2. Experimental Section

General procedure for synthesis of 2-aminotropone. The synthesis of 2-aminotropone was started from commercially available material tropolone (**1)**. It was first converted into tropolone tosylate by reacting it with tosyl chloride (1.5 equiv.) and triethyl amine (3.0 euiv.) in anhydrous DCM at room temperature for 24 h. Then, tropolone tosylate and amine (pyrrolidine/ piperidine/ morpholine/ 2,6- dimethylmorpholine/ *N*, *N*- diethylamine/ proline- methyl ester) (1.2 equiv.) were refluxed in ethanol in the presence of triethylamine (3.0 euiv.). The completion of the reaction was monitored by TLC. The general reaction time observed for all the reactions was 24–36 h. After completion of the reaction, all the volatiles were removed under reduced pressure. To the crude product, 1.0 N HCl was added and extracted with EtOAc (three times), and then the combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The obtained crude product was purified by silica gel column chromatography by using EtOAc and hexane mixture as the mobile phase.

General procedure for synthesis of troponylated di-peptide. Troponyl proline carboxylic acid derivative was obtained by refluxing tropolone tosylate and proline (1.2 equiv.) in presence of triethyl amine (3.0 equiv.) in ethanol. After the completion of the reaction which was monitored by TLC, all the volatiles were removed under reduced pressure. The crude reaction mixture was dissolved in anhydrous DMF and resultant solution was cooled to 0 ^{o}C. To this EDC. HCl was added and stirred at 0 ^{o}C for 5 minutes.To the resultant mixture, amino acid glycine methyl ester neutralized with triethylamine was added. Then the reaction mixture stirred at 0 ^{o}C for 30-60 minutes and reaction temperature raised to 55 ^{o}C. After the completion of the reaction, DMF was evaporated and the resultant reaction mixture was extracted with EtOAc (three times). and then the combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The obtained crude product was purified by silica gel column chromatography by using EtOAc and hexane mixture as the mobile phase to obtain the desired troponylated *di*-peptide.

Procedure for synthesis of 2- ethoxytropone (**5b**). To a heterogeneous mixture of tropolone (**1**) (8.2 mmol) and K_2CO_3 (32.8 mmol) in Acetonitrile (20 ml.) under nitrogen atmosphere, Iodoethane (24.6 mmol) was added gradually and the resulting suspension was allowed to reflux for 24- 48 h until no starting materials are detected by TLC. After the completion of the reaction, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The obtained crude product was purified by silica gel column chromatography by using EtOAc and hexane mixture as the mobile phase to obtain the desired 2- ethoxytropone (**5b**).

General procedure for Pd-catalyzed olefination of 2-aminotropone/ troponylated di-peptide/ tropone/ ethoxytropone. To a 15 mL sealed reaction tube, the 2-aminotropone/ troponylated *di*-peptide/ tropone/ ethoxytropone substrates were added under the indicated reaction conditions. The reaction was conducted at 130^{o} C for 24 h and cooled to room temperature upon

completion. The resulting sample was diluted with ethyl acetate (5.0 mL), filtered through a pad of Celite, concentrated under reduced pressure and purified by column chromatography with EtOAc/ hexane solvent system and the product was obtained typically as an orange red glutinous liquid in case of olefinated 2-aminotropone/ troponylated *di*-peptide and rosewood glutinous liquid in case of olefinated tropone and ethoxytropone.

General procedure for syntheses of Olefins- modified L- Tyrosine (**3e**) *and L- Threonine* (**3f**) . Boc- protected L- Tyrosine- OMe or L- Threonine- OMe was taken in THF and was allowed to stir at 0 ^{o}C under an Ar atmosphere. Triethylamine (3.0 equiv.) was added slowly followed by addition of acryloyl chloride (1.5 equiv.) at 0 ^{o}C. Then the reaction was allowed to carry out at room temperature for 2 hours. After the completion of the reaction which was monitored by TLC, all the volatiles were evaporated under reduced pressure and the resultant reaction mixture was extracted with EtOAc (three times). and then the combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The obtained crude product was purified by silica gel column chromatography by using EtOAc and hexane mixture as the mobile phase to obtain the desired olefins.

Procedure for synthesis of Olefin (Coupling partner) (**3g**). Acrylic acid was taken in acetonitrile and allowed to stir at 0 ^{o}C.for 5 minutes. To this potassium carbonate (2.0 equiv.) and benzyl chloride (2.0 equiv.) were added. After 30 minutes, the reaction temperature raised to 70 ^{o}C and the resulting reaction mixture was allowed to stir for 24 h. After the completion of the reaction, which was monitored by TLC, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The obtained crude product was purified by silica gel column chromatography by using EtOAc and hexane mixture as the mobile phase to obtain the desired olefin.

General procedure for Pd-catalyzed acetoxylation of 2-aminotropone. A 15 mL sealed reaction tube, equipped with a magnetic stirbar was charged with 2-aminotropone substrates (**2a**/ **2b**/

2e) (1.0 equiv.), Pd $(OAc)_2$ (10 mol%) and (diacetoxyiodo)benzene (2.0 equiv.). Anhydrous toluene was added and the mixture was stirred at 80 °C for 24 h on a heating block. After cooling to room temperature, the resulting sample was diluted with ethyl acetate (5.0 mL), filtered through a pad of Celite, concentrated under reduced pressure and purified by column chromatography with EtOAc/ hexane solvent system to obtain the desired acetoxylated products.

Optimization Studies:

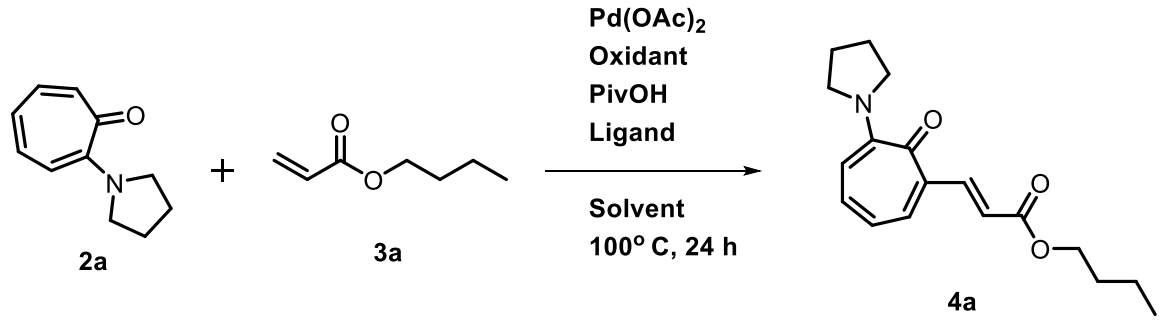
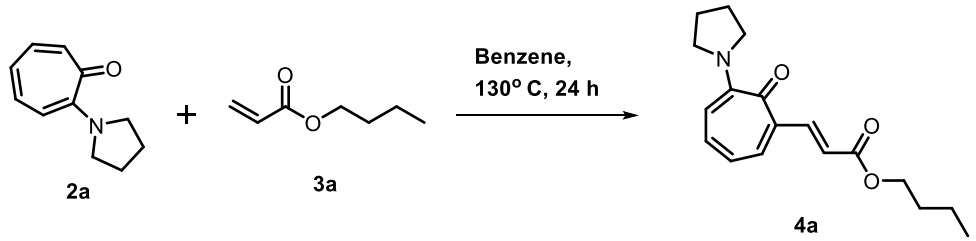


Table S1. Optimization of reaction conditions[a]

Entry	Oxidant	Ligand (0.5 equiv.)	Solvent	Yield (%) [b]
1	AgOAc (2.0 equiv.)	-	^{t}BuOH	13
2	AgOAc (2.0 equiv.)	-	TFE	Trace
3	AgOAc (2.0 equiv.)	-	THF	19
4	AgOAc (2.0 equiv.)	-	DMA	15
5	AgOAc (2.0 equiv.)	-	1,4- Dioxane	27
6	AgOAc (2.0 equiv.)	-	Benzene	31
7	AgOAc (2.0 equiv.)	-	DMF	23
8	AgOAc (2.0 equiv.)	-	Toluene	22
9	AgOAc (2.0 equiv.)	-	NMP	11
10	AgOAc (2.0 equiv.)	-	Isopropanol	05
11	AgOAc (2.0 equiv.)	-	1,2- DCE	29
12	AgOAc (2.0 equiv.)	-	MeCN	17
13	AgOAc (2.0 equiv.)	-	HFIP	n.d.
14	AgOAc (3.0 equiv.)	-	Benzene	43
15	AgOAc (2.0 equiv.) / NaOAc (2.0 equiv.)	-	Benzene	32
16	AgOAc (2.0 equiv.) / Cu (OAc)$_2$ (2.0 equiv.)	-	Benzene	34
17	Ag_2CO_3 (2.0 equiv.)	-	Benzene	47
18	Ag_2CO_3 (3.0 equiv.)	-	1,2- DCE	52
19	Ag_2CO_3 (3.0 equiv.)	-	Benzene	59
20[c]	Ag_2CO_3 (3.0 equiv.)	-	Benzene	78
21	Ag_2CO_3 (3.0 equiv.)	2- Picolinic acid	Benzene	n.d.
22	Ag_2CO_3 (3.0 equiv.)	Boc- Glycine	Benzene	40
23	Ag_2CO_3 (3.0 equiv.)	L- Proline	Benzene	n.d.
24	Ag_2CO_3 (3.0 equiv.)	N- Boc- L- Valine	Benzene	38
25	Ag_2CO_3 (3.0 equiv.)	Salicylic acid	Benzene	31
26	Ag_2CO_3 (3.0 equiv.)	DMAP	Benzene	n.d.

[a]Reaction conditions: **2a** (0.29 mmol), **3a** (0.58 mmol), Pd (OAc)$_2$ catalyst (0.029 mmol), Oxidant (0.58 mmol), PivOH (0.58 mmol), Solvent (2 ml), 100 ^{o}C, 24 h. [b] Isolated Yield. [c] PivOH (0.87 mmol, 3.0 equiv.), **3a** (1.16 mmol, 4.0 equiv.), 130 ^{o}C, 24 h

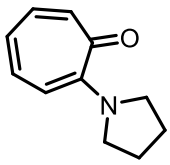
Table S2. The role of catalyst and oxidant additive.[b]



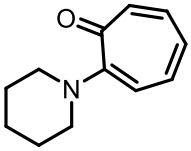
Entry	Oxidant/Additive	$Pd(OAc)_2$	PivOH (3	Yield (%)
1	NaOAc (4.0 equiv.)	-	-	n.d.
2	Ag_2CO_3 (3.0 equiv.)	-	PivOH (3.0 equiv.)	n.d.
3	-	$Pd(OAc)_2$ (1.0 equiv.)	-	Acetoxylation
4	-	$Pd(OAc)_2$ (10 mol%)	-	n.d.
5	-	$Pd(OAc)_2$ (10 mol%)[b]	PivOH (3.0 equiv.)	Trace

[b]Reaction conditions: **2a** (0.29 mmol), **3a** (1.16 mmol, 4.0 equiv.),

2-(Pyrrolidin-1-yl) cyclohepta-2,4,6-trien-1-one (**2a**) . Aminotropone (**2a**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (15:85) as rosewood glutinous liquid (1.0 g, 83% yield); R_f = 0.54 (30% EtOAc in hexane) starting from tropolone tosylate (2.0 g, 7.2 mmol) and pyrrolidine (0.6 g, 9.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.09-6.99 (m, 2H), 6.88 (d, J = 12.0 Hz, 1H), 6.46 (t, J = 10.0 Hz, 1H), 6.32 (d, J = 12.0 Hz, 1H), 3.61 (s, 4H), 1.96 (d, J = 8.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.9, 156.5, 135.6, 134.5, 130.7, 120.7, 111.5, 77.4, 77.1, 76.8, 50.9, 25.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{11}H_{13}NONa$ 198.0889; found 198.0882.

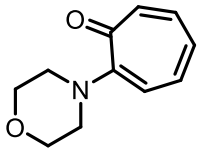

2a

2-(Piperidin-1-yl) cyclohepta-2,4,6-trien-1- one (**2b**) . Aminotropone (**2b**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as rosewood glutinous liquid.(1.0 g, 77% yield); R_f = 0.72 (50% EtOAc in hexane) starting from tropolone tosylate (2.0 g, 7.2 mmol) and piperidine (0.8 g, 9.4 mmol).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.10- 6.98 (m, 3H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.64 (t, *J* = 12.0 Hz, 1H), 3.33 (d, *J* = 4.0 Hz, 4H), 1.71 (dd, *J* = 4.0, 4.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 182.8, 160.6, 135.3, 134.8, 133.8, 125.3, 118.3, 77.4, 77.1, 76.8, 50.3, 25.9, 24.6. ESI-HRMS m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}NONa$ 212.1046; found 212.1040.



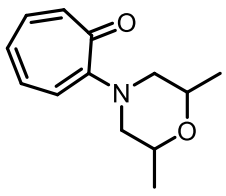
2b

2-Morpholinocyclohepta-2,4,6-trien-1-one (**2c**). Aminotropone (**2c**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (30:70) as rosewood glutinous liquid.(1.1 g, 83 % yield); R_f = 0.43 (50% EtOAc in hexane) starting from tropolone tosylate (2.0 g, 7.2 mmol) and morpholine(0.8 g, 9.4 mmol).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15 – 7.02 (m, 3H), 6.76 – 6.67 (m, 2H), 3.88 (t, *J* = 4.0 Hz, 4H), 3.32 (t, *J* = 4.0 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 182.6, 159.7, 136.0, 135.6, 133.6, 126.9, 118.9, 77.4, 77.1, 76.8, 66.8, 49.1. ESI-HRMS m/z: $[M+H]^+$ Calcd. for $C_{11}H_{14}NO_2$ 192.1019 found 192.1034.



2c

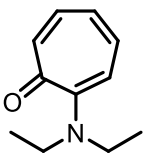
2-(2,6-Dimethylmorpholino) cyclohepta-2,4,6-trien-1- one (**2d**). Aminotropone (**2d**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (25: 75) as rosewood glutinous liquid (1.2 g, 80 % yield); R_f = 0.54 (50% EtOAc in hexane) starting from tropolone tosylate (2.0 g, 7.2 mmol) and 2,6-dimethylmorpholine (1.0 g, 9.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.11 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.04 (t, *J* = 10.0 Hz, 2H), 6.70 (dd, *J* = 12.0, 8.0 Hz, 2H), 3.92 - 3.85 (m, 2H), 3.74 (d, *J* = 16.0 Hz, 2H), 2.46 (t, *J* = 10.0 Hz, 2H), 1.23 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 182.7, 159.4, 135.8, 135.5,



2d

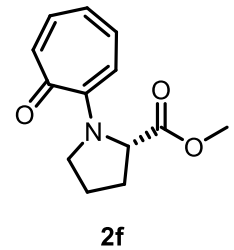
133.7, 126.5, 118.9, 77.4, 77.1, 76.8, 71.5, 54.3,18.9. ESI-HRMS m/z: $[M+H]^+$ Calcd. for $C_{13}H_{18}NO_2$ 220.1332; found 220.1339.

2-(Diethylamino) cyclohepta-2,4,6-trien-1-one (**2e**). Aminotropone (**2e**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (15: 85) as rosewood glutinous liquid (0.5 g, 78 % yield); R_f = 0.45 (30% EtOAc in hexane) starting from tropolone tosylate (1.0 g, 3.6 mmol) and N, N-diethylamine (0.3 g, 5.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.06 - 6.97 (m, 2H), 6.87 (d, *J* = 12.0 Hz, 1H), 6.49 (t, *J* = 10.0 Hz, 2H), 3.54 (q, *J* = 8.0 Hz, 4H), 1.22 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 180.9, 156.9, 134.9, 133.8, 130.9, 121.8, 112.6, 77.4, 77.1, 76.8, 46.1, 12.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{11}H_{15}NONa$ 200.1046; found 200.1051.



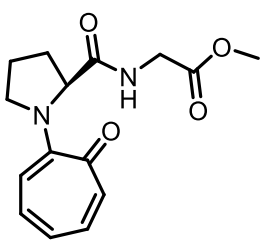
2e

Methyl (7-oxocyclohepta-1,3,5-trien-1-yl)-L-prolinate (**2f**). Troponylated Proline-OMe **(2f)** was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (25:75) as straw yellow glutinous liquid. (0.8 g, 51 % yield); R_f = 0.52 (50% EtOAc in hexane) . ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.05 (q, *J* = 10.0 Hz, 2H), 6.87 (d, *J* = 12.0 Hz, 1H), 6.53 (t, *J* = 10.0 Hz, 1H), 6.44 (d, *J* = 12.0 Hz, 1H), 5.23 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.74 (s, 3H), 3.63 – 3.58 (m, 1H), 3.50 – 3.44 (m, 1H), 2.26 – 2.17 (m, 1H), 2.12 – 1.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 180.6, 173.4, 155.3, 136.1, 134.8, 132.5, 122.7, 113.1, 77.4, 77.1, 76.8, 62.7, 52.02, 51.5, 31.2, 22.6. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{15}NO_3Na$ 256.0944; found 256.0951.



2f

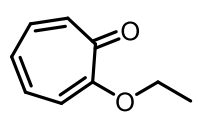
Methyl (7-oxocyclohepta-1,3,5-trien-1-yl)-L-prolylglycinate (**2g**) . Aminotroponyl *di*-peptide (**2g**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (90:10) as rosewood glutinous liquid.(0.6 g, 57 % yield); R_f = 0.30 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.13 -7.02 (m, 2H), 6.92 (d, *J* = 12.0 Hz, 1H), 6.70 (s, 1H), 6.60(t, *J* = 10.0 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 4.95 (t, *J* = 6.0



2g

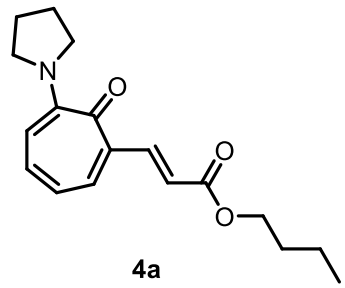
Hz, 1H), 4.01 (qd, *J* = 20.0 Hz, 6.0 Hz, 2H), 3.88- 3.82 (m, 1H), 3.71 (s, 3H), 3.42- 3.36 (m, 1H), 2.26 - 2.09 (m, 2H), 1.99 - 1.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 180.8, 173.1, 170.3, 155.8, 135.9, 134.4, 132.7, 123.6, 113.9, 77.4, 77.1, 76.7, 64.1, 52.2, 51.9, 41.1, 31.5, 23.4. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{15}H_{18}N_2O_4Na$ 313.1159; found 313.1166.

2-ethoxycyclohepta-2,4,6-trien-1-one (**5b**). 2-ethoxytropone (**5b**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (90:10) as rosewood glutinous liquid.(0.6g, 49 % yield); R_f = 0.52 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)7.21 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 10.0 Hz, 1H), 6.87 - 6.82 (m, 1H), 6.74 (d, *J* = 12.0 Hz, 1H), 4.13 (q, *J* = 8.0 Hz, 2H), 1.52 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 180.7, 164.9, 136.9, 136.5, 132.9, 127.8, 113.2, 77.4, 77.1, 76.8, 64.9, 14.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_9H_{10}O_2Na$ 173.0573; found 173.0565.



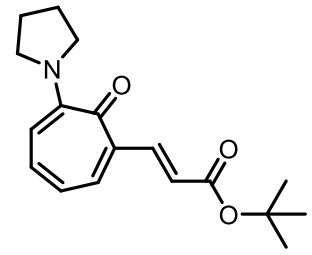
5b

Butyl (E)-3-(7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4a**). Olefinated aminotropone (**4a**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as orange red glutinous liquid. (134 mg, 78 % yield); R_f = 0.45 (30% EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (d, *J* = 16.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 10.0 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.42 (t, *J* = 10.0 Hz, 1H), 6.26 (d, *J* = 12.0 Hz, 1H), 4.20 (t, *J* = 6.0 Hz, 2H), 3.57 (s, 4H), 2.00 (s, 4H), 1.72 - 1.65 (m, 2H), 1.49 - 1.40 (m, 2H), 0.97 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.5, 167.9, 155.3, 144.9, 135.9, 135.8, 132.0, 118.0, 117.9, 109.9, 77.4, 77.1, 76.7, 64.2, 50.8, 30.8, 25.4, 19.2, 13.8. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{23}NO_3Na$ 324.1570; found 324.1594.



4a

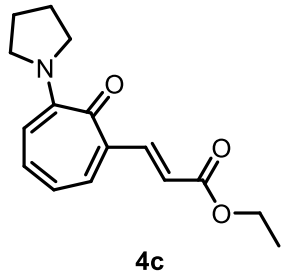
tert-Butyl (E)-3-(7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4b**) .



4b

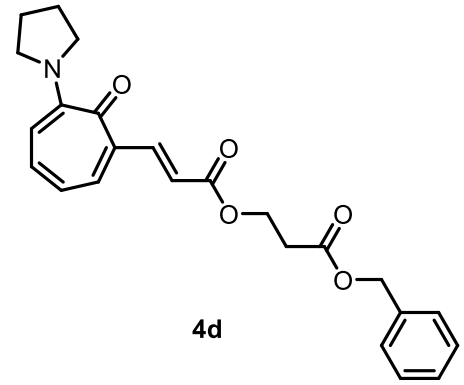
Olefinated aminotropone (**4b**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (10:90) as orange red glutinous liquid. (62 mg, 72 % yield); R_f = 0.67 (50% EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, *J* = 16.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 10.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.40 (t, *J* = 10.0 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 4H), 2.01 - 1.97 (m, 4H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.7, 167.1, 155.1, 143.9, 135.7, 135.6, 132.4, 120.0, 118.1, 109.8, 80.0, 77.4, 77.1, 76.7, 50.8, 28.3, 25.4. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{23}NO_3Na$ 324.1570; found 324.1543.

Ethyl (E)-3-(7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4c**). Olefinated aminotropone (**4c**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as orange red glutinous liquid. (116 mg, 75% yield); R_f = 0.64 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 10.0 Hz, 1H), 6.62 (d, *J* = 12.0 Hz, 1H), 6.41 (t, *J* = 10.0 Hz, 1H), 6.25 (d, *J* = 12.0 Hz, 1H), 4.24 (q, *J* = 8.0 Hz, 2H), 3.56 (s, 4H), 1.99 (s, 4H), 1.32 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.5, 167.8, 155.3, 144.9, 135.9, 135.8, 132.0, 118.1, 117.9, 109.9, 77.4, 77.1, 76.8, 60.3, 50.9, 25.4, 14.4. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{19}NO_3Na$ 296.1257; found 296.1242.



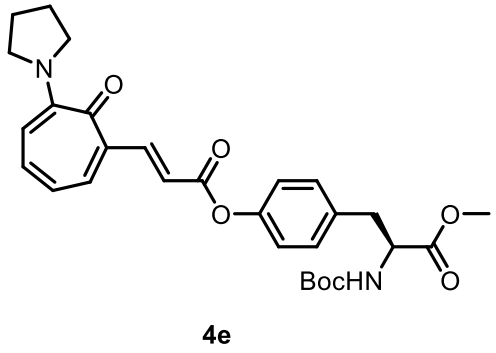
4c

3-(Benzyloxy)-3-oxopropyl (E)-3-(7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4d**). Olefinated aminotropone (**4d**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (148 mg, 64 % yield); R_f = 0.63 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, *J* = 16.0 Hz, 1H), 7.40 - 7.27 (m, 6H), 7.04 (t, *J* = 10.0 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.40 (t, *J* = 10.0 Hz, 1H), 6.24 (d, *J* = 12.0 Hz, 1H), 5.17 (s, 2H), 4.48 (t, *J* = 6.0 Hz, 2H), 3.55 (s, 4H), 2.77 (t, *J* = 6.0 Hz, 2H), 1.98 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.4, 170.8, 167.5, 155.4, 145.7, 136.17, 136.16, 135.7, 131.7, 128.6, 128.28, 128.25, 117.9, 117.1, 109.9, 77.4, 77.1, 76.7, 66.6, 59.7, 50.9, 34.1, 25.4. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{25}NO_5Na$ 430.1625; found 430.1602.



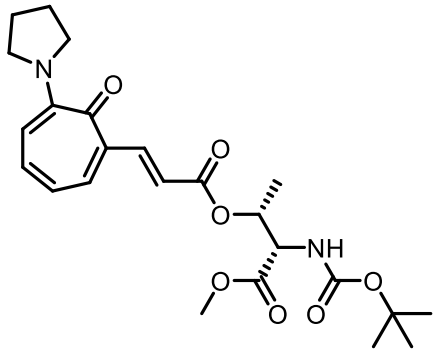
4d

(S)-4-(2-((tert-butoxycarbonyl) amino)-3-methoxy-3- oxopropyl) phenyl (E)-3-(7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4e**). Olefinated aminotropone (**4e**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (128 mg, 43% yield); R_f = 0.18 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, *J* = 16.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.16 - 7.05 (m, 5H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.42 (t, *J* = 10.0 Hz, 1H), 6.27 (d, *J* = 12.0 Hz, 1H), 5.03 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 3.59 (s, 4H), 3.14 - 3.03 (m, 2H), 2.00 (s, 4H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.3, 172.3, 166.2, 155.6, 155.1, 150.1, 147.1, 136.6, 136.5, 133.2, 131.4, 130.2, 121.8, 117.9, 116.5, 110.1, 80.0, 77.4, 77.1, 76.8, 54.4, 52.3, 50.9, 37.7, 28.3, 25.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{29}H_{34}N_2O_7Na$ 545.2258 found 545.2202.



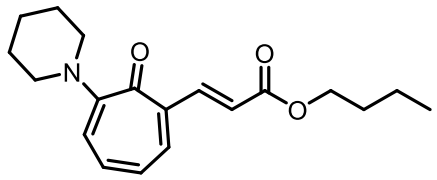
4e

Methyl *N*-(*tert*-butoxycarbonyl)-*O*-((*E*)-3-(7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acryloyl)-L-threoninate (**4f**). Olefinated aminotropone (**4f**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (25:75) as orange red glutinous liquid. (107 mg, 41 % yield); R_f = 0.48 (50% EtOAc in hexane).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 16.0 Hz, 1H), 7.38 (d, *J* = 12.0 Hz, 1H), 7.05 (t, *J* = 10.0 Hz, 1H), 6.61 (d, *J* = 12.0 Hz, 1H), 6.40 (t, *J* = 10.0 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 5.36 (d, *J* = 8.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 3.73 (s, 3H), 3.57 (s, 4H), 2.00 (s, 4H), 1.48 (s, 9H), 1.36 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.3, 170.8, 166.6, 155.9, 155.4, 146.2, 136.7, 136.4, 131.5, 117.9, 116.8, 110.0, 80.2, 77.4, 77.1, 76.8, 70.3, 57.3, 52.7, 50.9, 28.3, 25.4, 17.2.ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{24}H_{32}N_2O_7Na$ 483.2107; found 483.2099.



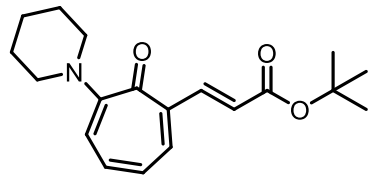
4f

Butyl (*E*)-3-(7-oxo-6-(piperidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4g**). Olefinated aminotropone (**4g**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as orange red glutinous liquid. (116 mg, 70 % yield); R_f = 0.59 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, *J* = 16.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 10.0 Hz, 1H), 6.53 -6.49 (m, 2H), 6.41 (t, *J* = 10.0 Hz, 1H), 4.11 (t, *J* = 8.0 Hz, 2H), 3.34 (s, 4H), 1.63 - 1.58 (m, 8H), 1.35 (dd, *J* = 16.0, 8.0 Hz, 2H), 0.88 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.4, 167.6, 158.4, 144.9, 135.6, 135.4, 134.2, 121.3, 119.2, 113.6, 77.4, 77.1, 76.8, 64.3, 50.1, 30.8, 25.8, 24.5, 19.2, 13.8. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{25}NO_3Na$ 338.1727; found 338.1751.



4g

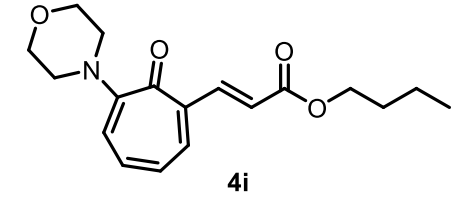
tert-Butyl (*E*)-3-(7-oxo-6-(piperidin-1-yl) cyclohepta-1,3,5-trien-1-yl) acrylate (**4h**).



4h

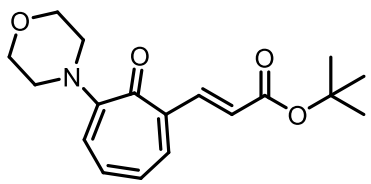
Olefinated aminotropone (**4h**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as orange red glutinous liquid. (108 mg, 65 % yield); R_f = 0.67 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.78 (d, *J* = 16.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 10.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.52- 6.47 (m, 2H), 3.40 (t, *J* = 4.0 Hz, 4H), 1.73 - 1.70 (m, 6H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.6, 166.7, 158.4, 143.9, 135.4, 135.1, 134.7, 121.5, 121.3, 113.8, 80.3, 77.4, 77.1, 76.8, 50.1, 28.2, 25.8, 24.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{25}NO_3Na$ 338.1727; found 338.1716.

Butyl (*E*)-3-(6-morpholino-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4i**). Olefinated aminotropone (**4i**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (165 mg, 67 % yield); R_f = 0.68 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 12.0 Hz, 1H), 6.66 - 6.58 (m, 3H), 4.19 (t, *J* = 8.0 Hz, 2H), 3.87 (t, *J* = 6.0 Hz, 4H), 3.35 (t, *J* = 4.0 Hz, 4H), 1.71 -1.64 (m, 2H), 1.47 -1.40 (m, 2H), 0.95 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.6, 167.2, 158.3, 144.4, 136.6, 135.8, 134.9, 123.8, 120.6, 115.5, 77.4, 77.1, 76.7, 66.6, 64.4, 48.9, 30.8, 19.2, 13.8. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{23}NO_4Na$ 340.1519; found 340.1487.



4i

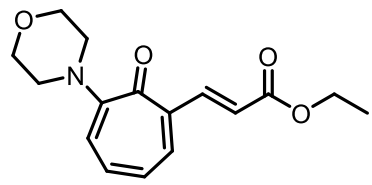
tert-Butyl (*E*)-3-(6-morpholino-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4j**). Olefinated aminotropone (**4j**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (107 mg, 65 % yield); R_f = 0.59 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 16.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 10.0 Hz, 1H), 6.67 - 6.59 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 3.89 (t, *J* =4.0 Hz, 4H), 3.34 (t, *J* = 4.0 Hz, 4H), 1.53 (s,



4j

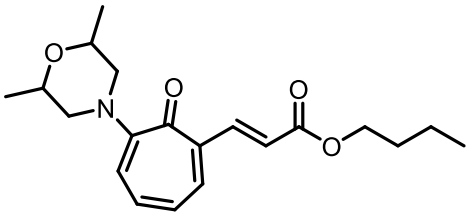
9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.7, 166.4, 158.2, 143.5, 137.0, 135.6, 134.7, 123.9, 122.6, 115.6, 80.5, 77.4, 77.1, 76.7, 66.6, 48.9, 28.2. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{23}NO_4Na$ 340.1519; found 340.1505.

Ethyl (*E*)-3-(6-morpholino-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4k**). Olefinated aminotropone (**4k**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (107 mg, 71 % yield); R_f = 0.37 (50% EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 10.0 Hz, 1H), 6.66 - 6.57 (m, 3H), 4.25 (q, *J* = 6.0 Hz, 2H), 3.88 (t, *J* = 4.0 Hz, 4H), 3.35 (t, *J* = 4.0 Hz, 4H), 1.32 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.6, 167.1, 158.3, 144.4, 136.5, 135.7, 134.9, 123.8, 120.5, 115.4, 77.4, 77.1, 76.8, 66.6, 60.5, 48.9, 14.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{19}NO_4Na$ 312.1206; found 312.1180.



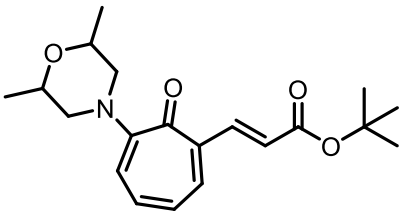
4k

Butyl (*E*)-3-(6-(2,6-dimethylmorpholino)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4l**). Olefinated aminotropone (**4l**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (98 mg, 62 % yield); R_f = 0.71 (50% EtOAc in hexane) ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 7.92 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 1H), 7.03 (t, *J* = 6.0 Hz, 1H), 6.63 - 6.57 (m, 3H), 4.19 (t, *J* = 4.0 Hz, 2H), 3.87 - 3.83 (m, 2H), 3.71 (d, *J* = 8.0 Hz, 2H), 2.54 (t, *J* = 6.0 Hz, 2H), 1.70 - 1.66 (m, 2H), 1.43 (dd, *J* = 8.0, 4.0 Hz, 2H), 1.24 (d, *J* = 4.0 Hz, 6H), 0.96 (t, *J* = 4.0 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ (ppm) 181.5, 167.3, 158.1, 144.6, 136.5, 135.5, 135.0, 123.4, 120.4, 115.6, 77.2, 77.0, 76.9, 71.4, 64.4, 54.1, 30.8, 19.2, 18.9, 13.8. ESI-HRMS m/z: $[M+H]^+$ Calcd. for $C_{20}H_{28}NO_4$ 346.2013; found 346.2023.



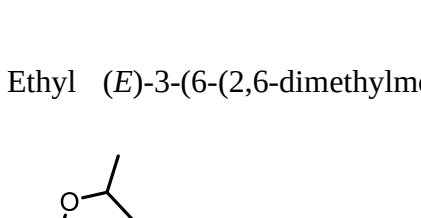
4l

tert-Butyl (*E*)-3-(6-(2,6-dimethylmorpholino)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4m**). Olefinated aminotropone (**4m**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (100 mg, 64 % yield); R_f = 0.76 (50% EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 12.0 Hz, 1H), 6.65 - 6.59 (m, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 3.89 - 3.83 (m, 2H), 3.71 (d, *J* = 12.0 Hz, 2H), 2.56 - 2.50 (m, 2H), 1.53 (s, 9 H), 1.25 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.6, 166.4, 158.1, 143.6, 136.9, 135.3, 134.8, 123.7, 122.4, 115.8, 80.5, 77.4, 77.0, 76.7, 71.4, 54.1, 28.2, 18.9. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{27}NO_4Na$ 368.1832; found 368.1816.



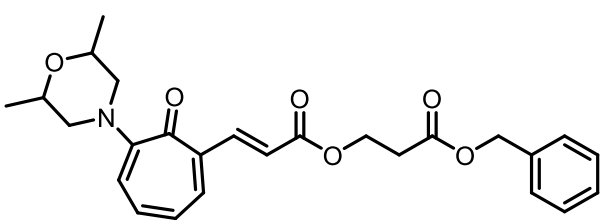
4m

Ethyl (*E*)-3-(6-(2,6-dimethylmorpholino)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4n**). Olefinated aminotropone (**4n**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (99 mg, 69 % yield); R_f = 0.63 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (d, *J* = 16.0 Hz, 1H), 7.38 (d, *J* = 12.0 Hz, 1H), 6.97 (t, *J* = 10.0 Hz, 1H), 6.58 - 6.47 (m, 3H), 4.18 (q, *J* = 8.0 Hz, 2H), 3.78 (tt, *J* = 12.0, 6.0 Hz, 2H), 3.64 (d, *J* = 12.0 Hz, 2H), 2.46 (t, *J* = 10.0 Hz, 2H), 1.26 (t, *J* = 4.0 Hz, 3H), 1.17 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.4, 167.1, 158.2, 144.6, 136.5, 135.5, 135.1, 123.5, 120.4, 115.7, 77.4, 77.1, 76.7, 71.4, 60.5, 54.1, 27.0, 18.9, 14.4. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{23}NO_4Na$ 340.1519; found 340.1515.



4n

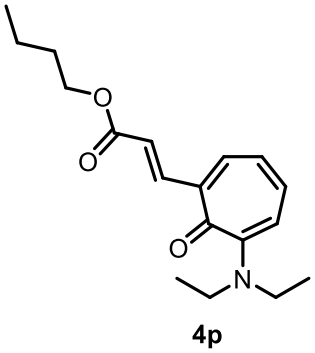
3-(benzyloxy)-3-oxopropyl (*E*)-3-(6-(2,6-dimethylmorpholino)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4o**). Olefinated aminotropone (**4o**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as orange red glutinous liquid. (107 mg, 52 % yield); R_f = 0.69 (50% EtOAc in hexane). ^{1}H



4o

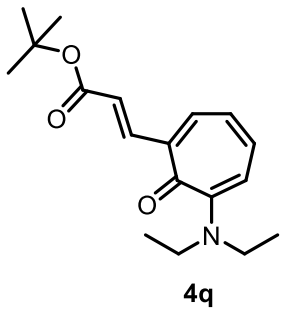
NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.37–7.31 (m, 5H), 7.04 (t, *J* = 10.0 Hz, 1H), 6.64 – 6.54 (m, 3H), 5.17 (s, 2H), 4.49 (t, *J* = 6.0 Hz, 2H), 3.88 - 3.83 (m, 2H), 3.71 (d, *J* = 12.0 Hz, 2H), 2.78 (t, *J* = 6.0Hz, 2H), 2.54 (t, *J* = 12.0 Hz, 2H), 1.24 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.4, 170.7, 166.8, 158.2, 145.3, 136.1, 135.8, 135.7, 135.3, 128.6, 128.3, 128.2, 123.3, 119.6, 115.5, 77.4, 77.1, 76.7, 71.4, 66.6, 59.9, 54.1, 34.1, 18.9. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{29}NO_6Na$ 474.1893; found 474.1913.

Butyl (*E*)-3-(6-(diethylamino)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4p**). Olefinated aminotropone (**4p**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as orange red glutinous liquid. (124 mg, 73 % yield); R_f = 0.54 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 16.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 10.0 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.40 - 6.34 (m, 2H), 4.18 (t, *J* = 8.0 Hz, 2H), 3.57 (q, *J* = 8.0 Hz, 4H), 1.67 (dd, *J* = 16.0, 8.0 Hz, 2H), 1.47 - 1.38 (m, 2H), 1.20 (t, *J* = 6.0 Hz, 6H), 0.95 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.2, 167.9, 154.3, 144.8, 135.7, 135.3, 130.6, 117.9, 117.7, 108.4, 77.4, 77.0, 76.7, 64.2, 46.7, 30.8, 19.2, 13.8, 12.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{25}NO_3Na$ 326.1727; found 326.1706.



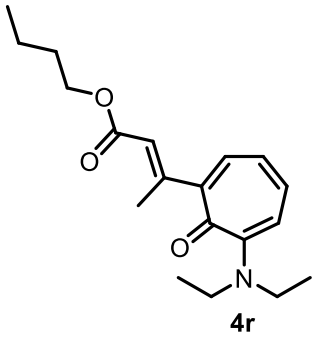
4p

tert-Butyl (*E*)-3-(6-(diethylamino)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4q**) Olefinated aminotropone (**4q**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as orange red glutinous liquid. (116 mg, 68 % yield); R_f = 0.64 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.66 (d, *J* = 16.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 10.0Hz, 1H), 6.49 (d, *J* = 16.0Hz, 1H), 6.36 (t, *J* = 12.0 Hz, 2H), 3.56 (q, *J* = 8.0 Hz, 4H), 1.52 (s, 9H), 1.19 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 167.1, 154.3, 143.8, 135.4, 135.1, 131.0, 119.7, 118.0, 108.5, 80.1, 77.4, 77.1, 76.8, 46.7, 28.2, 12.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{25}NO_3Na$ 326.1727; found 326.1708.



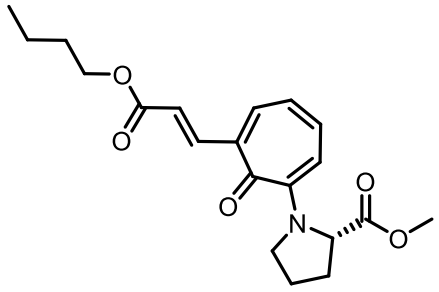
4q

Butyl (*E*)-3-(6-(diethylamino)-7-oxocyclohepta-1,3,5-trien-1-yl) but-2-enoate (**4r**). Olefinated aminotropone (**4r**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (10:90) as orange red glutinous liquid. (123 mg, 69 % yield); R_f = 0.61 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 10.0 Hz, 1H), 6.44 (t, *J* = 10.0 Hz, 2H), 4.19 (t, *J* = 8.0 Hz, 2H), 3.53 (q, *J* = 8.0 Hz, 4H), 2.02 (d, *J* = 1.4 Hz, 3H), 1.73 - 1.66 (m, 2H), 1.43 (dd, *J* = 12.0, 8.0 Hz, 2H), 1.22 (t, *J* = 8.0 Hz, 6H), 0.96 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.7, 168.7, 155.4, 140.1, 135.7, 135.2, 134.1, 128.2, 119.1, 110.7, 77.4, 77.0, 76.7, 64.7, 46.5, 30.8, 19.3, 14.4, 13.8, 12.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{27}NO_3Na$ 340.1883; found 340.1854.



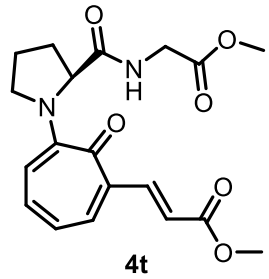
4r

Methyl (*E*)-(6-(3-butoxy-3-oxoprop-1-en-1-yl)-7-oxocyclohepta-1,3,5-trien-1-yl)-L-prolinate (**4s**). Olefinated aminotropone (**4s**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (20: 80) as orange red glutinous liquid. (95 mg, 62 % yield); R_f = 0.64 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.73 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 10.0 Hz, 1H), 6.57 - 6.48 (m, 2H), 6.37 (d, *J* = 12.0 Hz, 1H), 5.15 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.17 (t, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 3.65 - 3.53 (m, 2H), 2.38 - 2.29 (m, 1H), 2.14 - 2.02 (m, 3H), 1.70 - 1.63 (m, 3H), 1.42 (dd, *J* = 12.0, 4.0 Hz, 2H), 0.95 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.7, 172.4, 167.7, 153.7, 145.0, 136.2, 135.9, 133.9, 120.0, 118.8, 111.4, 77.4, 77.0, 76.7, 64.2, 62.5, 52.5, 51.2, 31.1, 30.8, 23.1, 19.2, 13.8. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{25}NO_5Na$ 382.1625; found 382.1601.



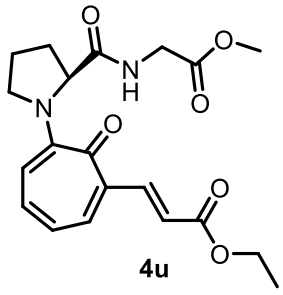
4s

Methyl (*S*, *E*)-3-(6-(2-((2-methoxy-2-oxoethyl) carbamoyl) pyrrolidin-1-yl)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4t**) Olefinated aminotroponyl *di*- peptide (**4t**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate: Hexane (50:50) as orange red glutinous liquid. (36 mg, 56 % yield); R_f = 0.61 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, *J* = 16.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 10.0 Hz, 1H), 6.66 (t, *J* = 6.0 Hz, 1H), 6.54 (m, 2H), 6.38 (d, *J* = 8.0 Hz, 1H), 4.84 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.99 (dd, *J* = 8.0, 4.0 Hz, 2H), 3.86 - 3.81 (m, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.46 - 3.40 (m, 1H), 2.32 - 2.11 (m, 3H), 2.06 - 1.96 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.7, 172.0, 170.1, 167.8, 154.4, 144.9, 135.9, 135.8, 133.9, 120.6, 118.5, 111.9, 77.4, 77.1, 76.7, 64.1, 52.3, 51.7, 51.6, 41.2, 31.6, 23.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{22}N_2O_6Na$ 397.1370; found 397.1391.



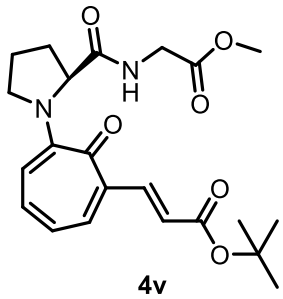
4t

Ethyl (*S*, *E*)-3-(6-(2-((2-methoxy-2-oxoethyl) carbamoyl) pyrrolidin-1-yl)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4u**). Olefinated aminotroponyl *di*- peptide (**4u**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (50:50) as orange red glutinous liquid. (35 mg, 53 % yield); R_f = 0.67 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 12.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 10.0 Hz, 1H), 6.61 (t, *J* = 4.0 Hz, 1H), 6.54 (dd, *J* = 16.0, 8.0 Hz, 2H), 6.37 (d, *J* = 12.0 Hz, 1H), 4.82 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.23 (q, *J* = 6.0 Hz, 2H), 4.01 - 3.99 (m, 2H), 3.87 - 3.81 (m, 1H), 3.72 (s, 3H), 3.45 - 3.39 (m, 1H), 2.32 - 2.16 (m, 2H), 2.15 - 2.11 (m, 1H), 2.03 - 1.95 (m, 2H), 1.31 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.8, 172.0, 170.1, 167.4, 154.3, 144.5, 135.9, 135.7, 134.1, 120.7, 119.1, 111.9, 77.4, 77.0, 76.7, 64.1, 60.3, 52.3, 51.7, 41.2, 31.5, 23.5, 14.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{24}N_2O_6Na$ 411.1527; found 411.1497.



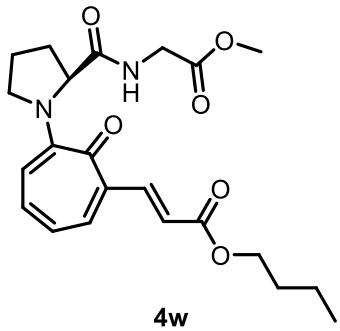
4u

tert-Butyl (*S, E*)-3-(6-(2-((2-methoxy-2-oxoethyl) carbamoyl) pyrrolidin-1-yl)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4v**). Olefinated aminotroponyl *di*- peptide (**4v**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (50:50) as orange red glutinous liquid. (35 mg, 49 % yield); R_f = 0.64 (EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 (d, *J* = 16.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 10.0 Hz, 1H), 6.69 (t, *J* = 6.0 Hz, 1H), 6.54 - 6.46 (m, 2H), 6.36 (d, *J* = 8.0 Hz, 1H), 4.82 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.01 - 3.98 (m, 2H), 3.86 - 3.80 (m, 1H), 3.71 (s, 3H), 3.44 - 3.38 (m, 1H), 2.27 - 2.10 (m, 3H), 2.04 - 1.91 (m, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.8, 172.1, 170.1, 166.7, 154.1, 143.6, 135.8, 135.4, 134.3, 121.1, 120.7, 111.8, 80.2, 77.4, 77.1, 76.8, 64.0, 52.3, 51.7, 41.2, 31.5, 28.2, 23.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{28}N_2O_6Na$ 439.1840; found 439.1860.



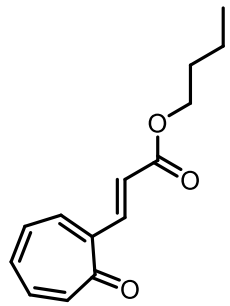
4v

Butyl (*S, E*)-3-(6-(2-((2-methoxy-2-oxoethyl) carbamoyl) pyrrolidin-1-yl)-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**4w**). Olefinated aminotroponyl *di*- peptide (**4w**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (50:50) as orange red glutinous liquid. (37 mg, 51 % yield); R_f = 0.69 (EtOAc). ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 14.0 Hz, 1H), 7.43 (d, *J* = 14.0 Hz, 1H), 7.06 (t, *J* = 10.5 Hz, 1H), 6.68 (s, 1H), 6.57 - 6.51 (m, 2H), 6.38 (d, *J* = 7.0 Hz, 1H), 4.83 (dd, *J* = 7.0, 7.0 Hz, 1H), 4.17 (t, *J* = 7.0 Hz, 2H), 3.99 (qd, *J* = 35.0, 7.0 Hz, 2H), 3.85 -3.82 (m, 1H), 3.72 (s, 3H), 3.44 - 3.41 (m, 1H), 2.31 - 2.27 (m, 1H), 2.23 - 2.19 (m, 1H), 2.16 - 2.12 (m, 1H), 2.01 - 1.98 (m, 1H), 1.69 - 1.64 (m, 2H), 1.43 - 1.40 (m, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 179.7, 172.1, 170.2, 167.6, 154.4, 144.6, 136.0, 135.8, 134.0, 120.7, 119.1, 111.9, 77.4, 77.1, 76.8, 64.3, 52.3, 41.1, 31.6, 30.8, 29.7, 27.2, 23.6, 19.2, 13.8. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{22}H_{29}N_2O_6$ 417.2020; found 417.2029.



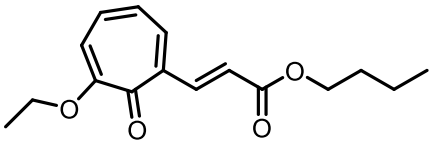
4w

Butyl (*E*)-3-(7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**6a**). Olefinated tropone (**6a**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as rosewood glutinous liquid. (16 mg, 7 % yield); R_f = 0.41 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, *J* = 16.0 Hz, 1H), 7.52 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.17 - 7.09 (m, 2H), 7.05 - 7.02 (m, 2H), 6.79 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.0 Hz, 2H), 1.68 - 1.64 (m, 2H), 1.41 (ddd, *J* = 16.0, 8.0, 4.0 Hz, 2H), 0.95 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ (ppm) 186.0, 166.8, 145.5, 142.7, 141.8, 136.5, 135.4, 135.2, 133.2, 123.9, 77.2, 77.0, 76.9, 64.7, 30.7, 19.2, 13.7. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{16}O_3Na$ 255.0992; found 255.0990.



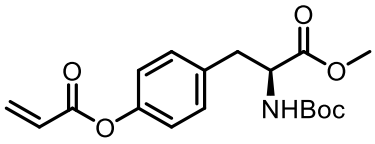
6a

Butyl (*E*)-3-(6-ethoxy-7-oxocyclohepta-1,3,5-trien-1-yl) acrylate (**6b**). Olefinated 2-ethoxytropone (**6b**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (35:65) as rosewood glutinous liquid. (33mg, 18 % yield); R_f = 0.48 (70% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 16.0 Hz, 1H), 7.46 (dd, *J* = 12.0, 4.0 Hz, 1H), 7.23 - 7.17 (m, 2H), 6.73 (d, *J* = 12.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.23 - 4.16 (m, 4H), 1.69 (dt, *J* = 16.0, 8.0 Hz, 2H), 1.55 (t, *J* = 8.0 Hz, 3H), 1.43 (dd, *J* = 16.0, 8.0 Hz, 2H), 0.96 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ (ppm) 180.2, 166.7, 164.7, 145.6, 136.6, 135.4, 133.9, 133.4, 118.9, 112.4, 77.2, 77.0, 76.8, 65.4, 64.7, 30.7, 19.2, 14.2, 13.7. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{20}O_4Na$ 299.1254; found 299.1261.



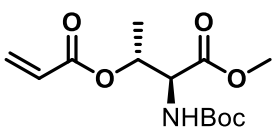
6b

(*S)*-4-(2-((*tert*-butoxycarbonyl) amino)-3-methoxy-3-oxopropyl) phenyl acrylate (**3e**). Olefin-modified Tyrosine (**3e**) was synthesized by the above mentioned procedure and purified by column chromatography with solvent system Ethylacetate:Hexane (15:85) as colourless glutinous liquid. R_f = 0.75 (40% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.30 (dd, *J* = 18.0, 10.0 Hz, 1H), 5.99 (d, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 8.0 Hz, 1H), 4.57 (d, *J* = 8.0 Hz, 1H), 3.70 (s, 3H), 3.08 (ddd, *J* = 32.0, 12.0, 4.0 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 172.2, 164.4, 155.1, 149.6, 133.8, 132.6, 130.2, 127.9, 121.5, 79.9, 77.5, 77.2, 76.9, 54.4, 52.2, 37.6, 28.3. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{18}H_{23}NO_6Na$ 372.1418; found 372.1407.



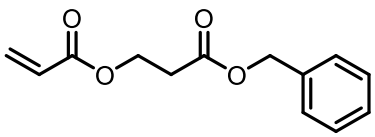
3e

Methyl *O*-acryloyl-*N*-(*tert*-butoxycarbonyl)-L-threoninate (**3f**). Olefin- modified Threonine (**3f**) was synthesized by the above mentioned procedure and purified by column chromatography with solvent system Ethylacetate:Hexane (10:90) as colourless glutinous liquid. R_f = 0.50 (20% EtOAc in hexane). ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 6.39 (dd, *J* = 17.5, 3.5 Hz, 1H), 6.07 (dd, *J* = 17.5, 10.5 Hz, 1H), 5.84 (d, *J* = 7.0 Hz, 1H), 5.46 (dd, *J* = 7.0, 2.3 Hz, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 4.47 (dd, *J* = 7.0, 2.2 Hz, 1H), 3.72 (s, 3H), 1.47 (s, 9H), 1.34 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ (ppm) 170.7, 164.9, 155.8, 131.5, 127.9, 80.3, 77.2, 77.0, 76.9, 70.83, 57.1, 52.6, 28.3, 16.9. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{21}NO_6Na$ 310.1261; found 310.1259.



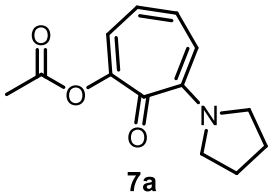
3f

3-(benzyloxy)-3-oxopropyl acrylate (**3g**). Olefin (Coupling partner) (**3g**) was synthesized by the above mentioned procedure and purified by column chromatography with solvent system Ethylacetate:Hexane (25:75) as colourless glutinous liquid. (1.4 g, 46 % yield). R_f = 0.68 (30% EtOAc in hexane). ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 7.37 - 7.26 (m, 5H), 6.37 (d, *J* = 14.0 Hz, 1H), 6.08 (dd, *J* = 14.0, 7.0 Hz, 1H), 5.81 (d, *J* = 7.0 Hz, 1H), 5.16 (s, 2H), 4.45 (t, *J* = 7.0 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ (ppm) 170.5, 165.9, 135.7, 131.2, 128.6,128.4, 128.3, 128.1, 77.2, 77.0, 76.9, 66.6, 59.9, 33.9. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{14}O_4Na$ 257.0784; found 257.0760.



3g

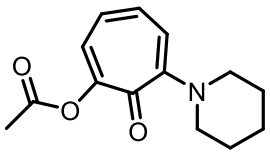
7-oxo-6-(pyrrolidin-1-yl) cyclohepta-1,3,5-trien-1-yl acetate (**7a**). Acetoxylated aminotropone



7a

(**7a**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as rosewood glutinous liquid. (30 mg, 45 % yield); R_f = 0.43 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.85 - 6.84 (m, 2H), 6.75 (dd, *J* = 12.0, 4.0 Hz, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 3.60 (t, *J* = 6.0 Hz, 4H), 2.25 (s, 3H), 1.96 - 1.93 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.8, 170.3, 155.5, 143.7, 130.9, 129.4, 126.4, 109.0, 77.4, 77.0, 76.7, 50.9, 25.5, 21.0. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{15}NO_3Na$ 256.0944; found 256.0925.

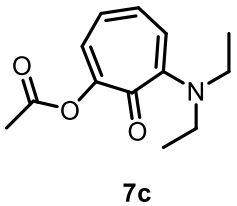
7-oxo-6-(piperidin-1-yl) cyclohepta-1,3,5-trien-1-yl acetate (**7b**). Acetoxylated aminotropone



7b

(**7b**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (20:80) as rosewood glutinous liquid. (29 mg, 44 % yield). R_f = 0.36 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.97 (d, *J* = 12.0 Hz, 1H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.75 (d, *J* = 12.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 3.32 - 3.29 (m, 4H), 2.27 (s, 3H), 1.73 - 1.68 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 181.7, 169.9, 159.5, 147.1, 133.9, 131.4, 124.9, 116.3, 77.4, 77.0, 76.7, 50.4, 25.9, 24.6, 21.0. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{14}H_{17}NO_3Na$ 270.1101; found 270.1133.

6-(diethylamino)-7-oxocyclohepta-1,3,5-trien-1-yl acetate (**7c**). Acetoxylated aminotropone



7c

(**7c**) was synthesized by the general procedure (the above mentioned procedure) and purified by column chromatography with solvent system Ethylacetate:Hexane (25:75) as rosewood glutinous liquid. (28 mg, 42 % yield); R_f = 0.45 (50% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.84 (d, *J* = 1.0 Hz, 2H), 6.74 (dt, *J* = 12.0, 1.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 3.52 (q, *J* = 8.0 Hz, 4H), 2.26 (s, 3H), 1.22 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.9, 170.1, 155.9, 144.6, 130.5, 130.0, 125.4, 110.7, 77.3, 77.0, 76.7, 46.1, 21.0, 12.5. ESI-HRMS m/z: $[M+Na]^+$ Calcd. for $C_{13}H_{17}NO_3Na$ 258.1101; found 258.1103.

3. NMR and Mass spectra of aminotropones/ troponylated amino acid/ peptide (**2a**- **2g**) / 2-ethoxy tropone (**5b**)

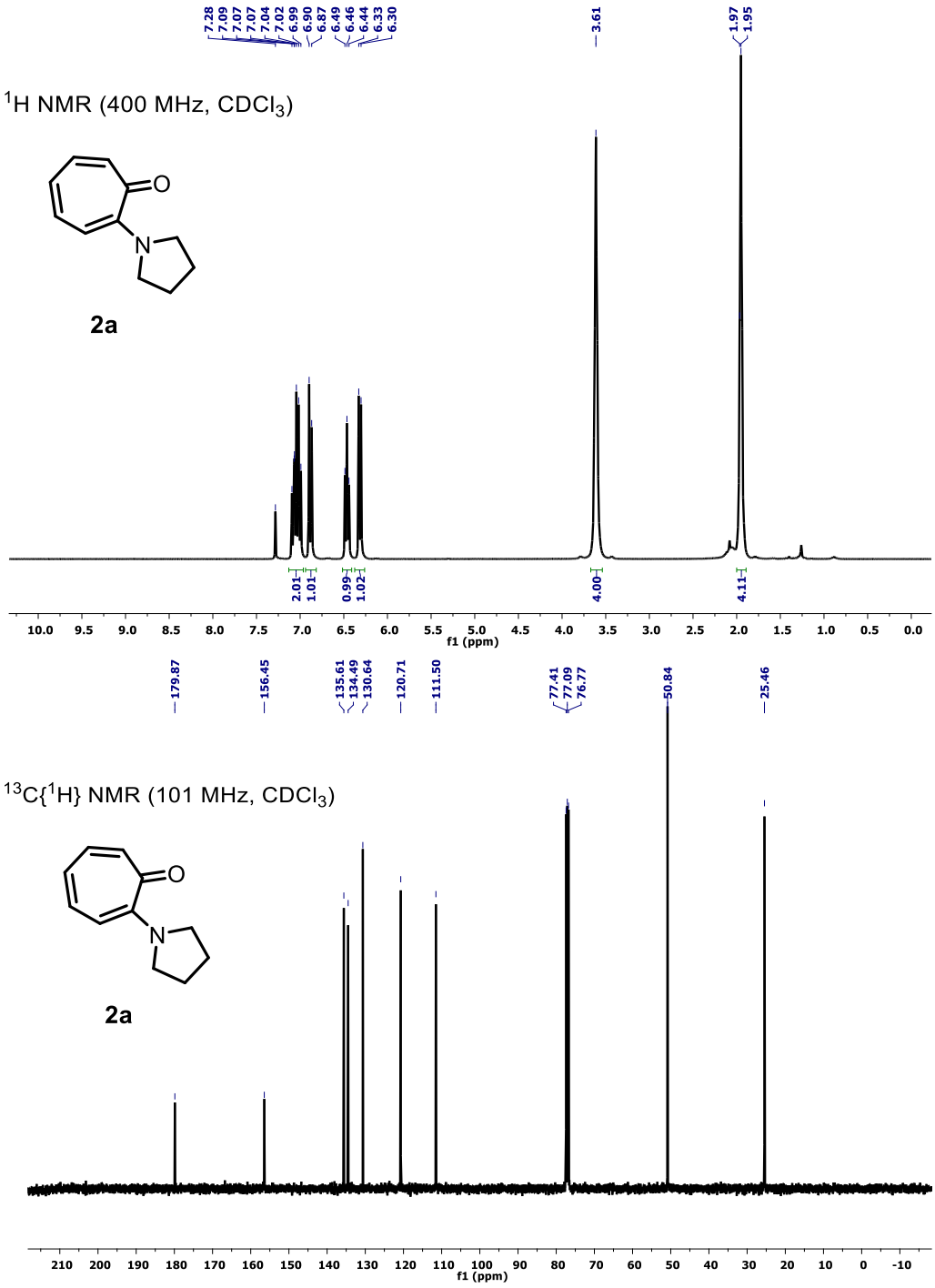


Fig S1. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of aminotropone **2a**

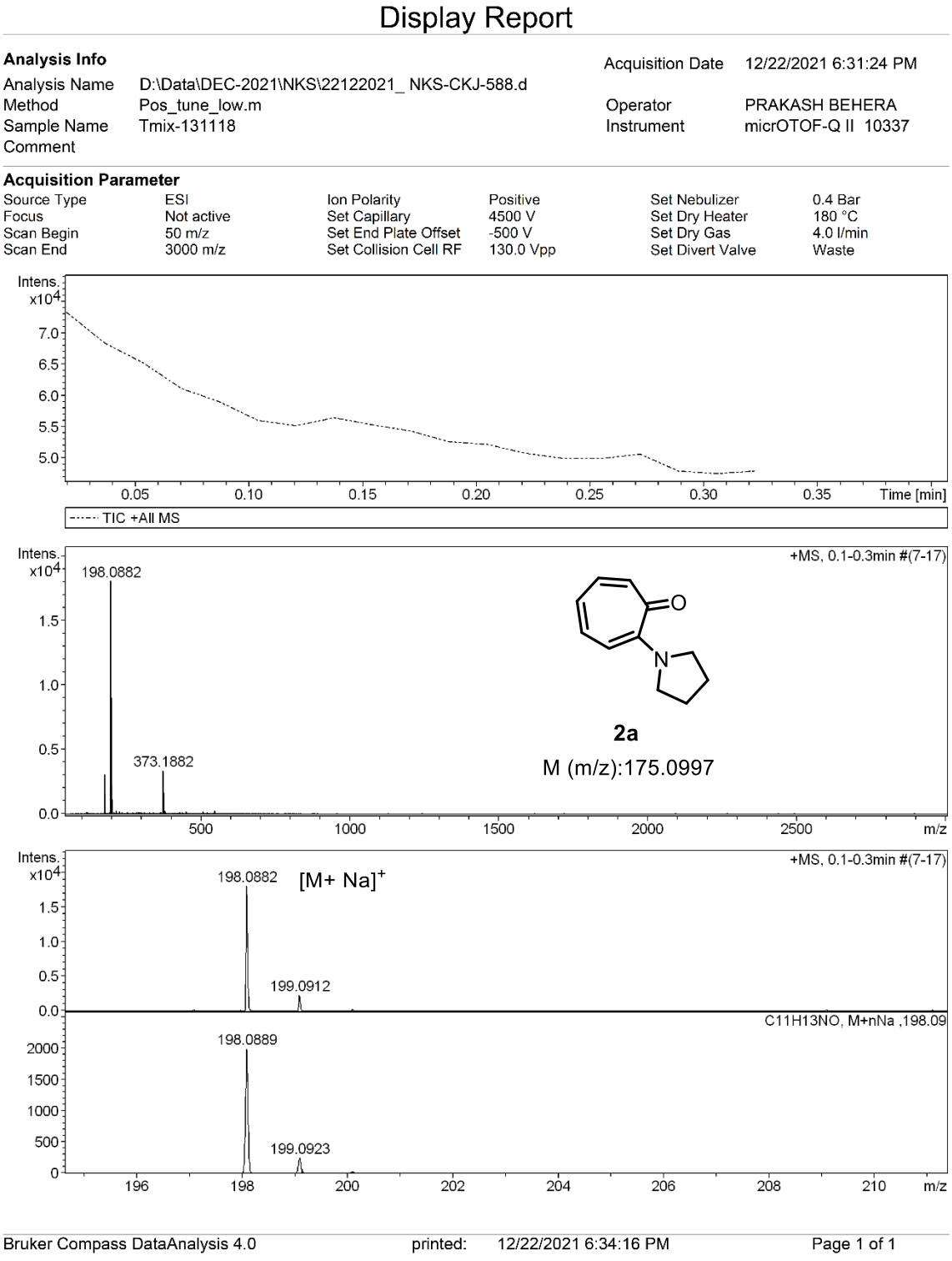


Fig S2. ESI-HRMS spectra of aminotropone **2a**

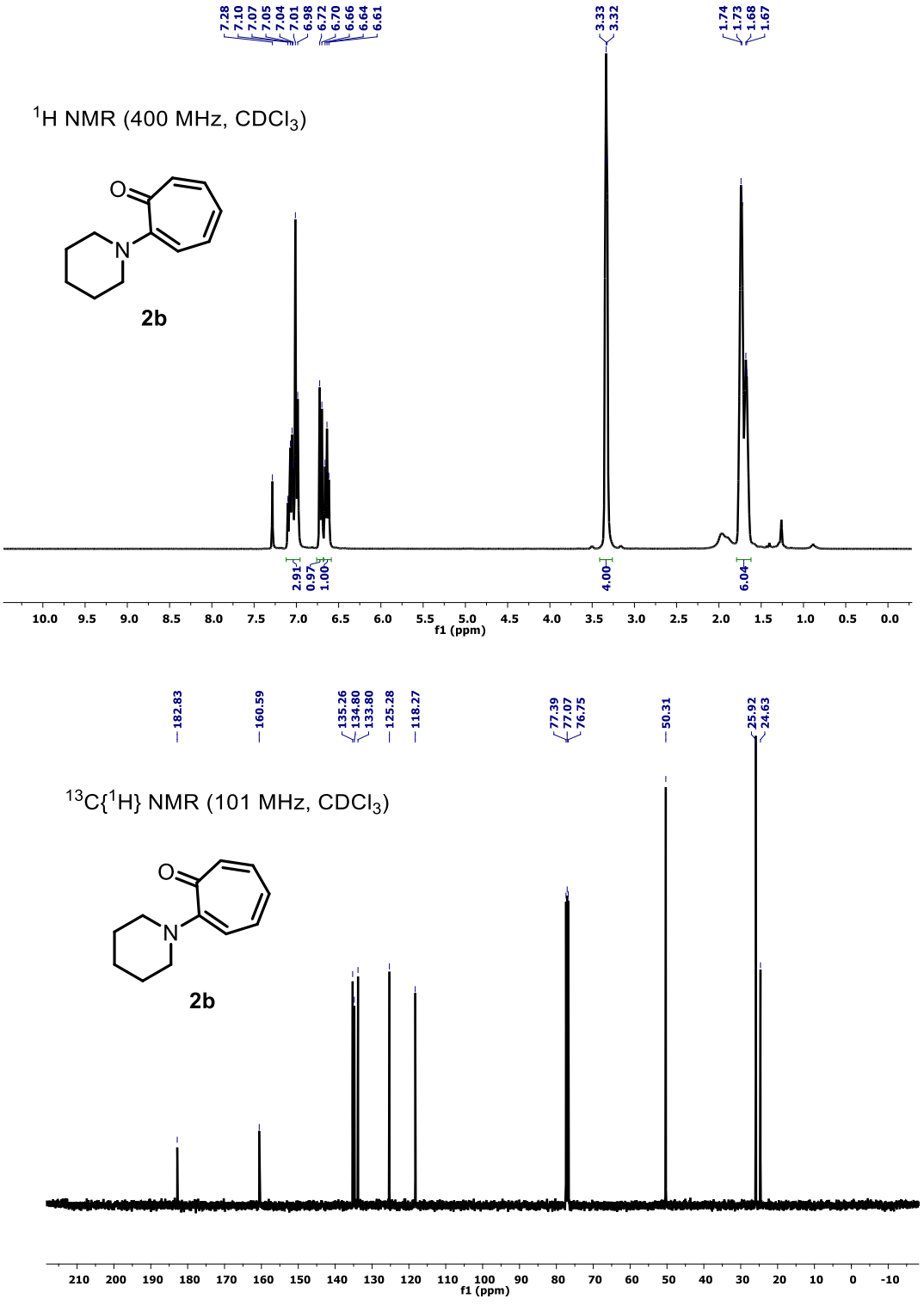


Fig S3. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of aminotropone **2b**

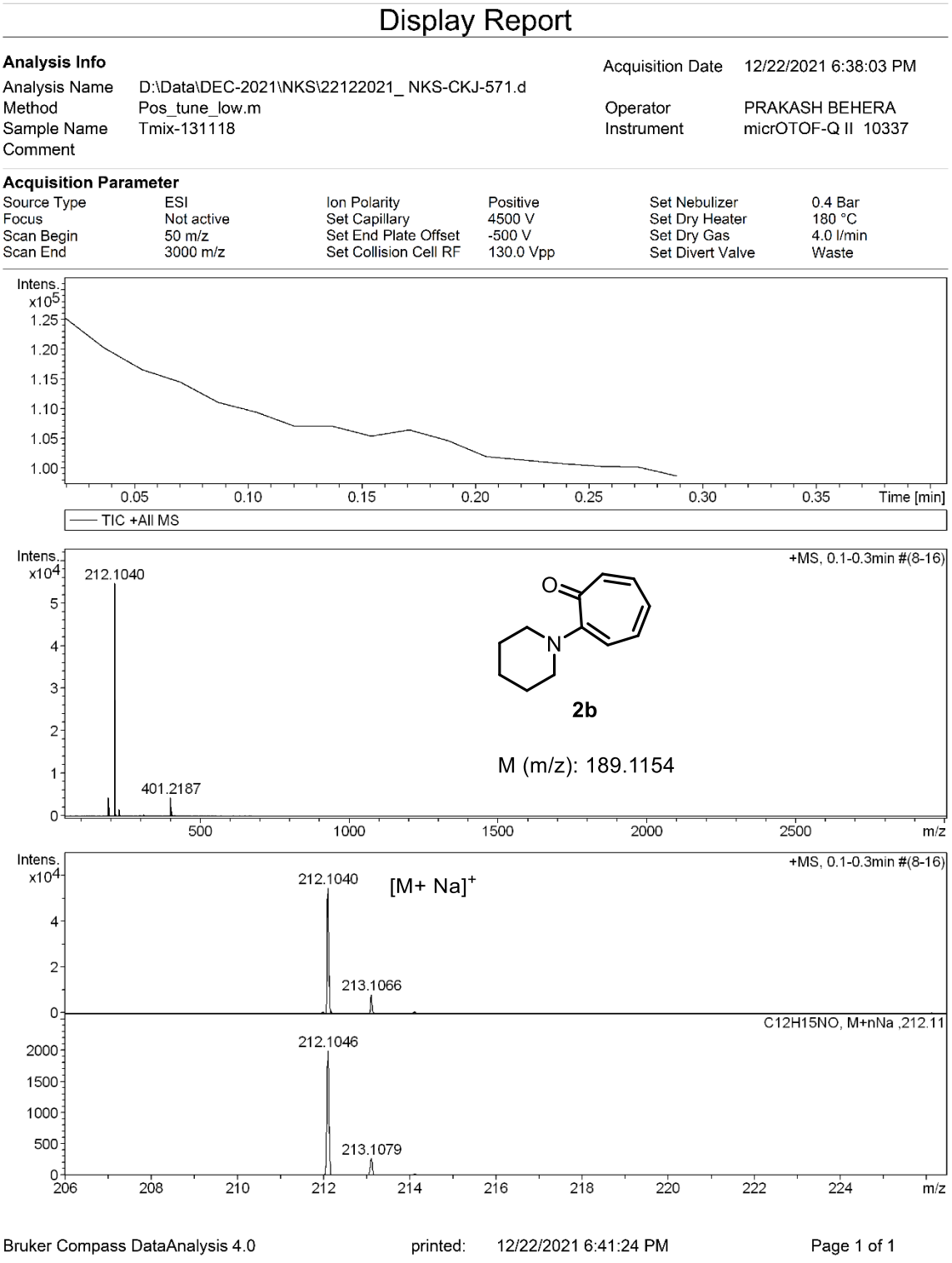


Fig S4. ESI-HRMS spectra of aminotropone **2b**

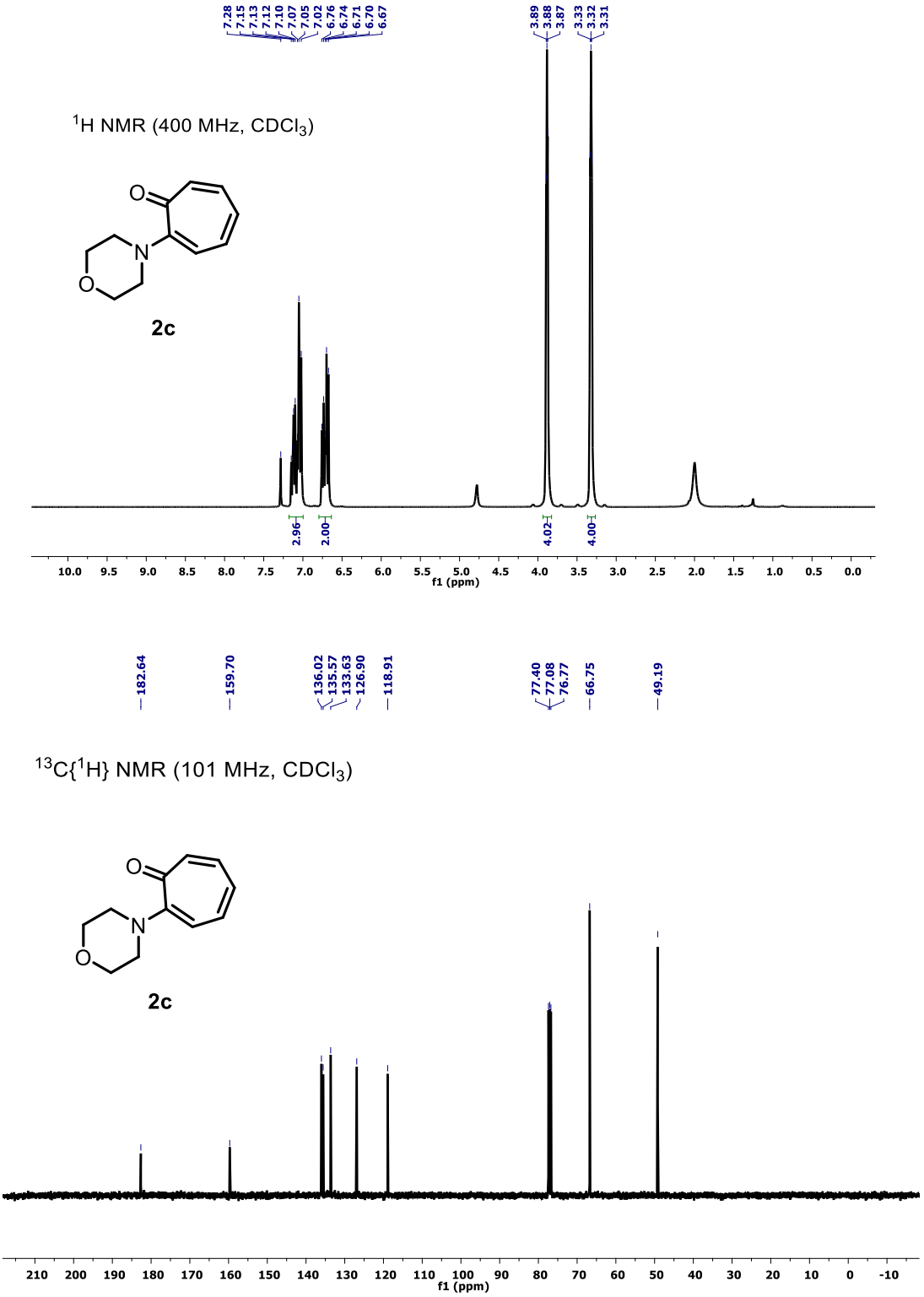


Fig S5. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of aminotropone **2c**

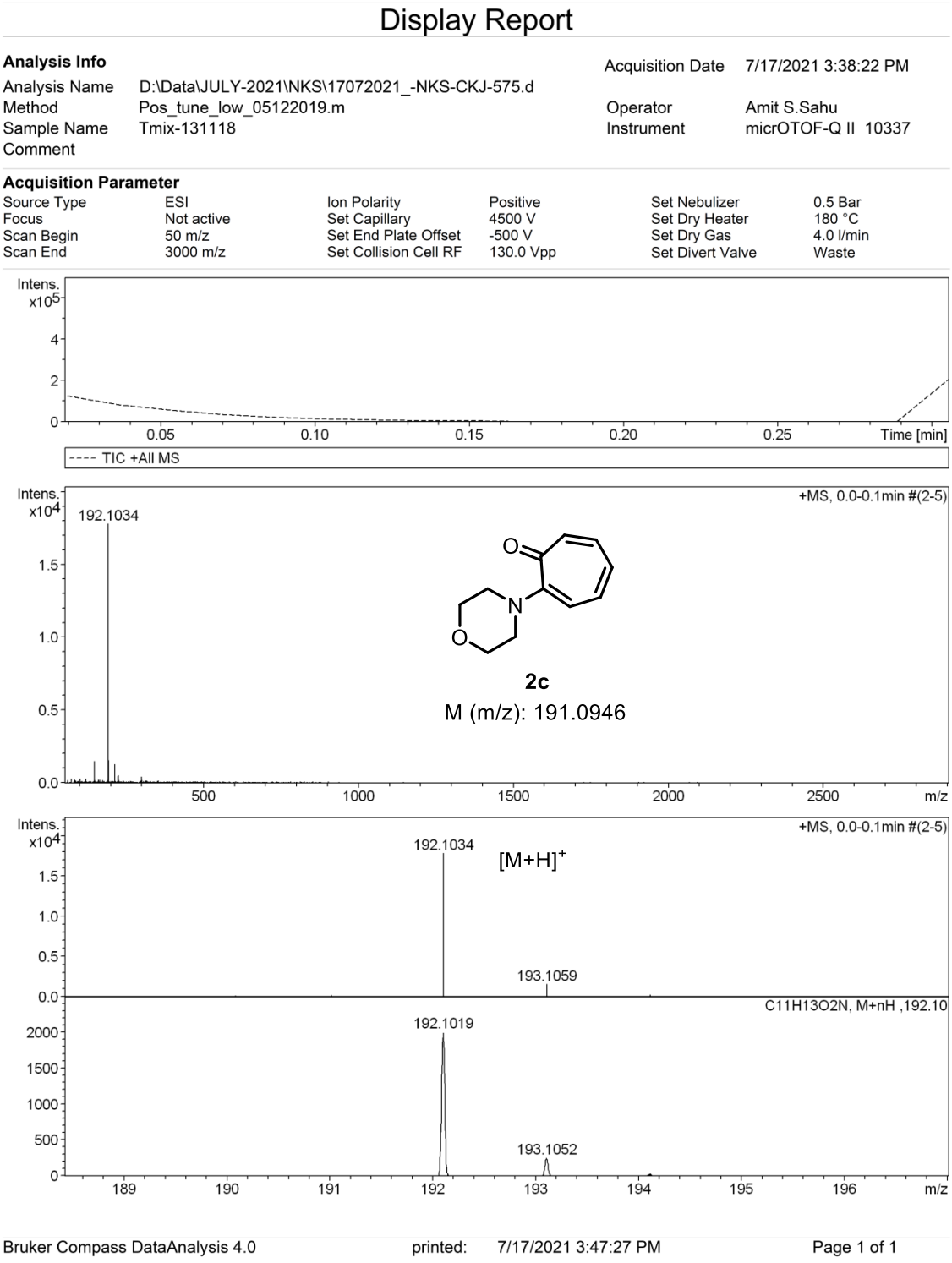


Fig S6. ESI-HRMS spectra of aminotropone **2c**

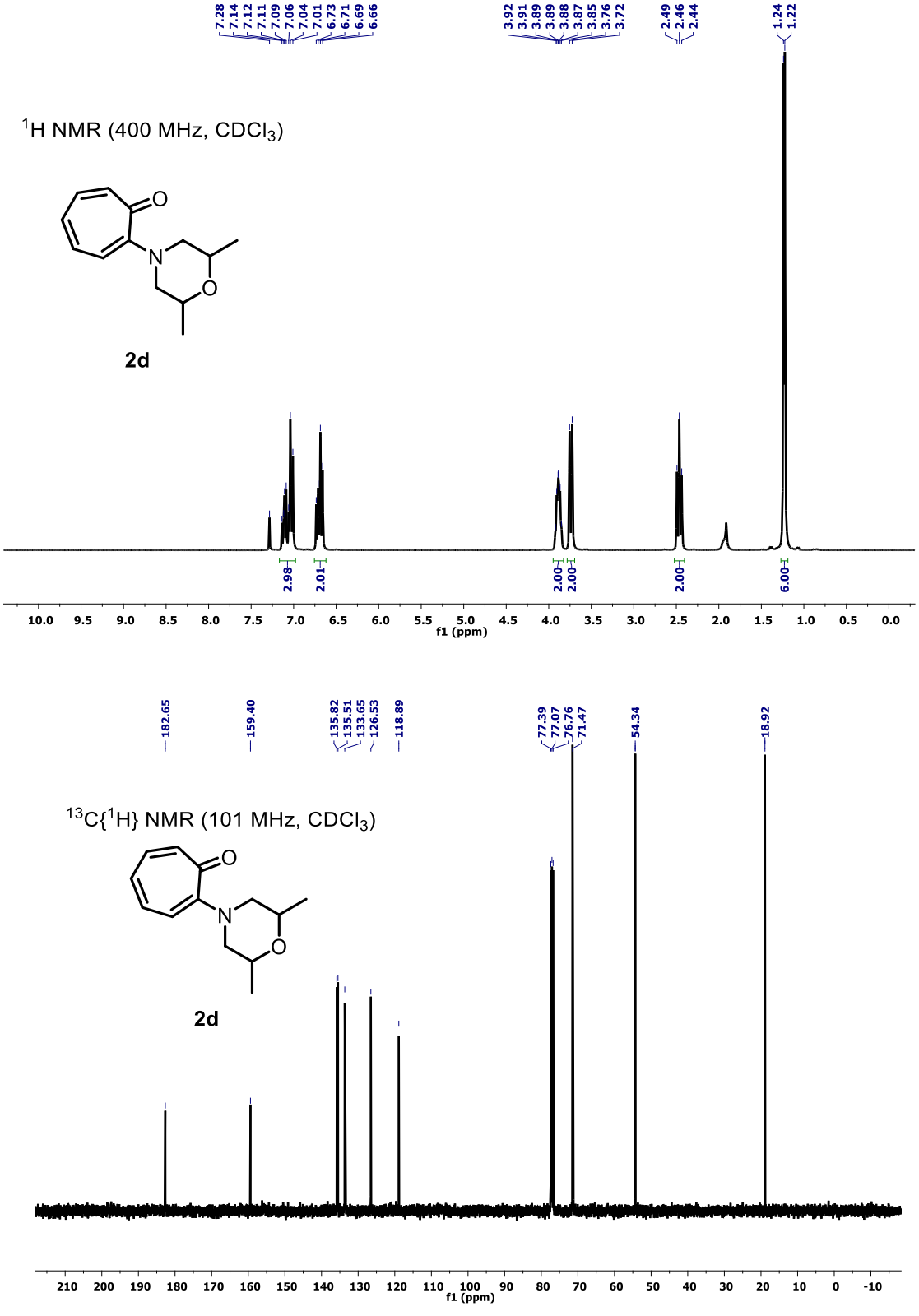


Fig S7. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of aminotropone **2d**

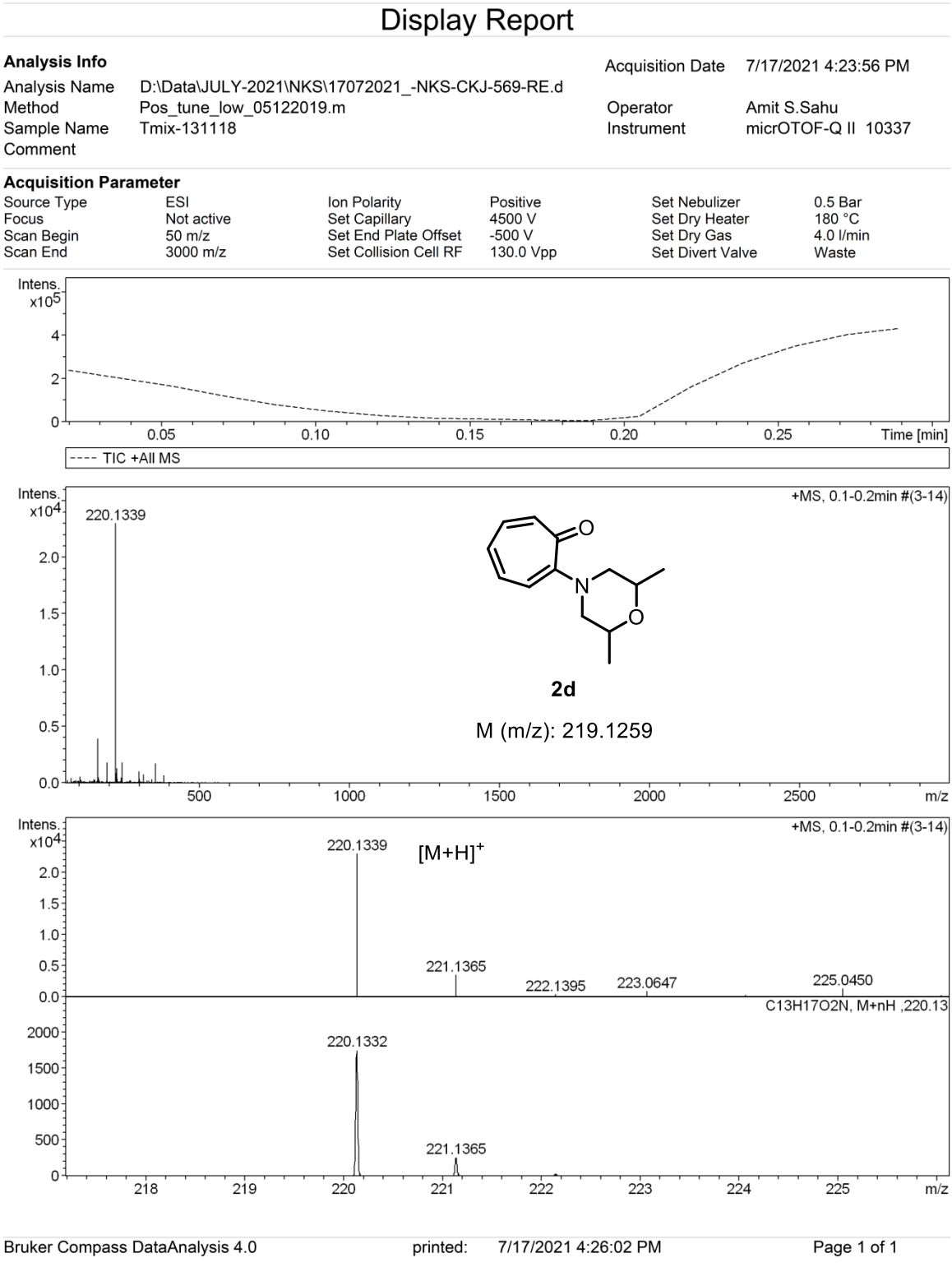


Fig S8. ESI-HRMS spectra of aminotropone **2d**

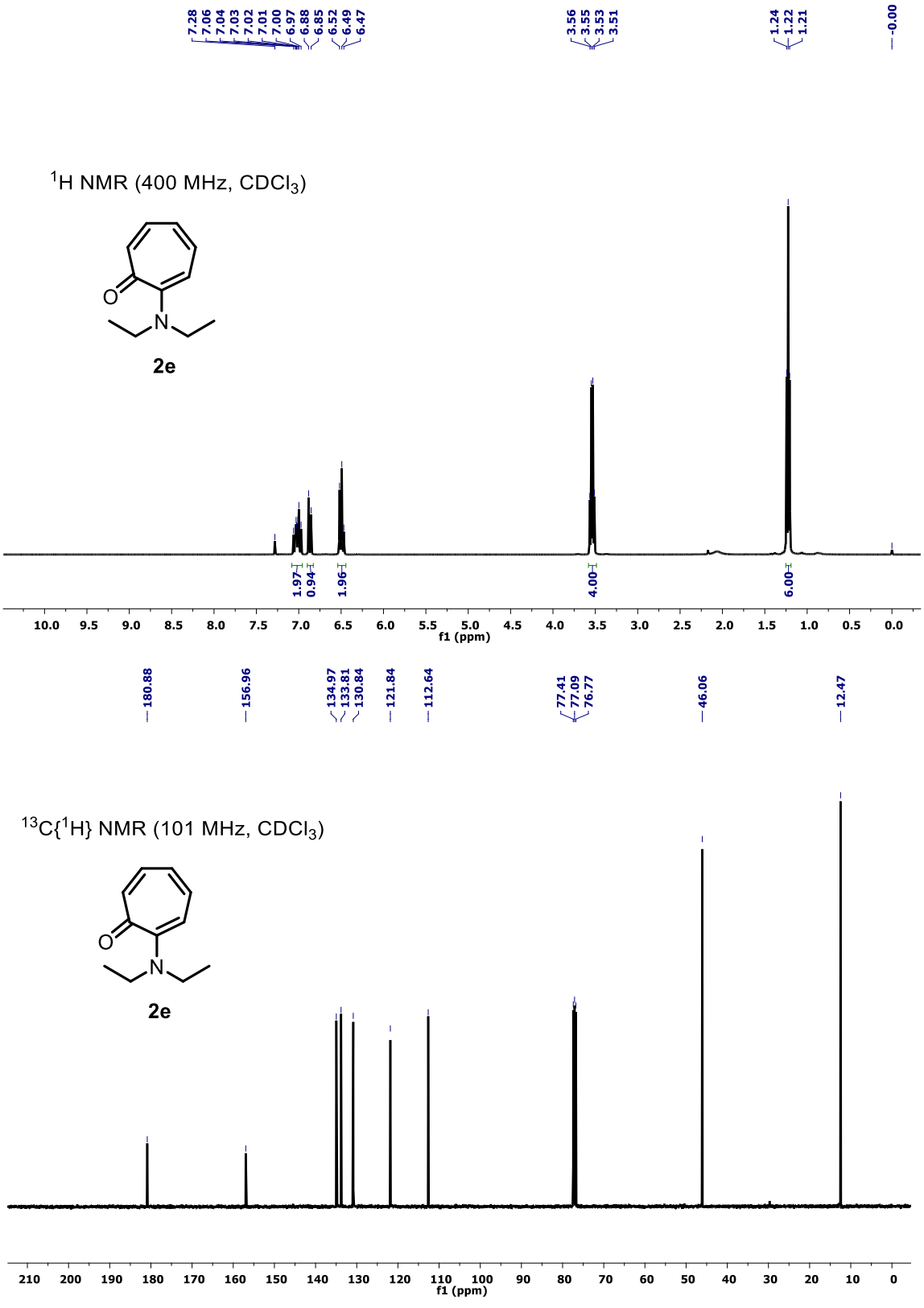


Fig S9. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of aminotropone **2e**

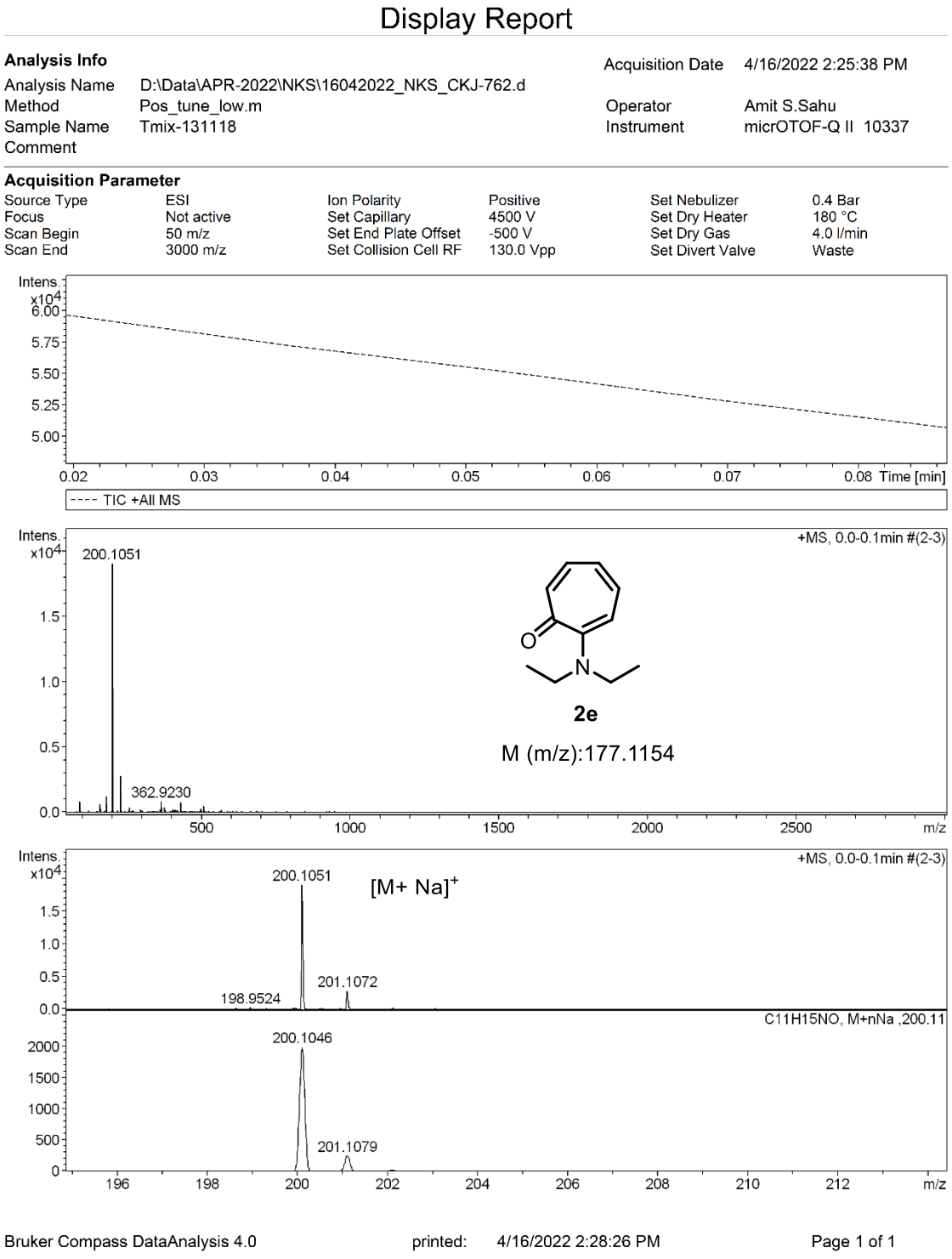


Fig S10. ESI-HRMS spectra of aminotropone **2e**

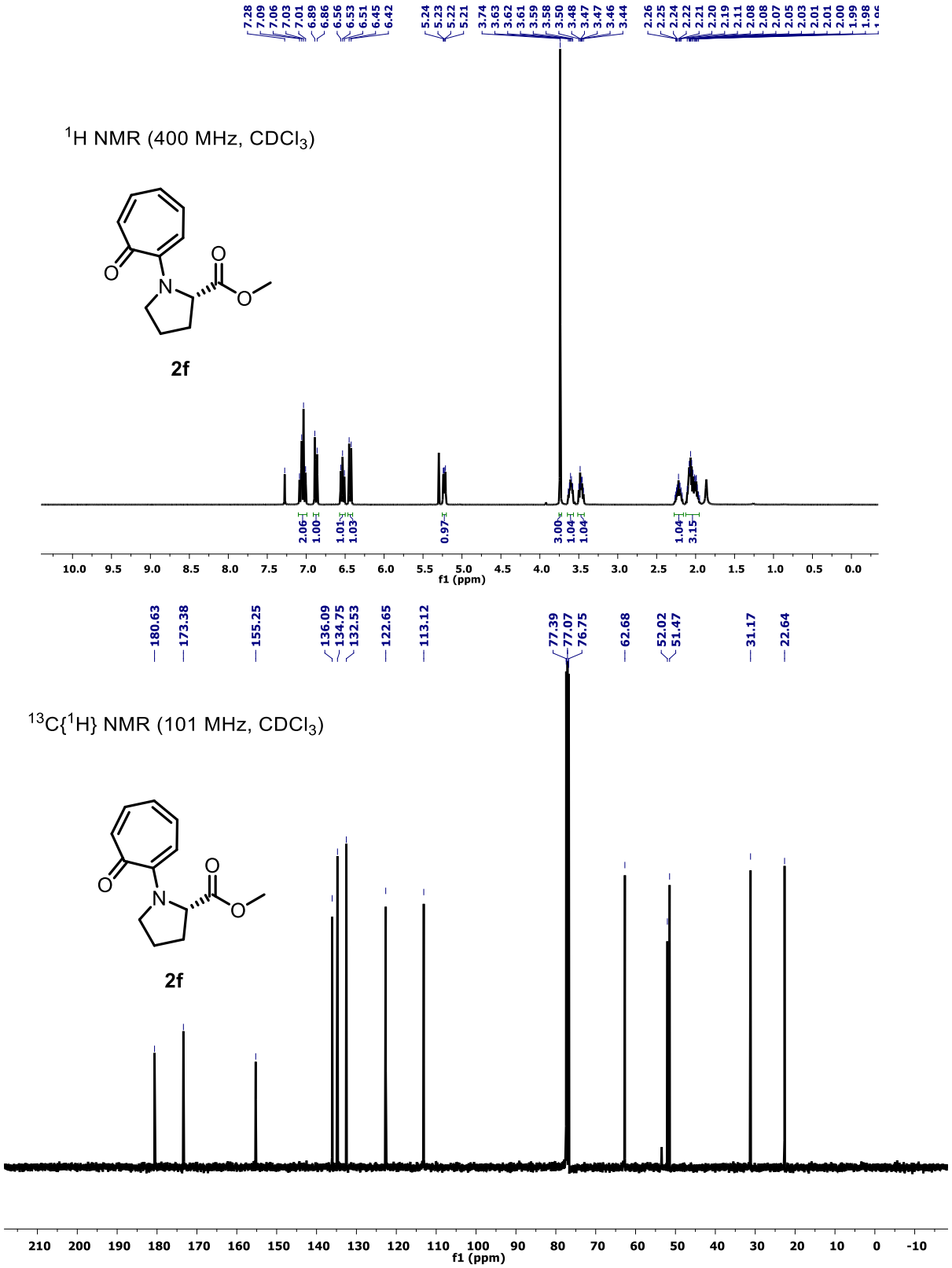


Fig S11. ^{1}H, ^{13}C {^{1}H} NMR spectra of troponylated aminoacid ester **2f**

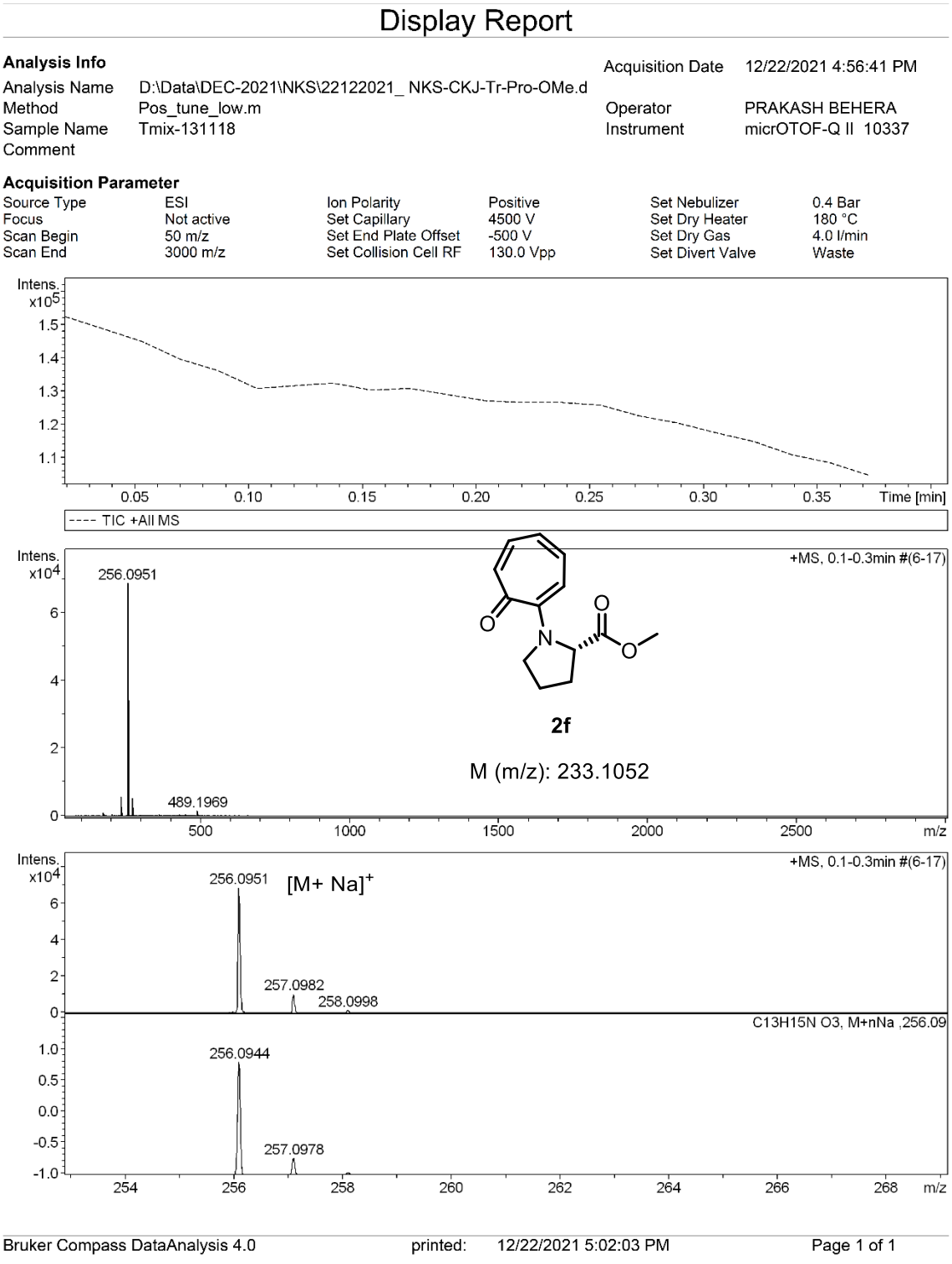


Fig S12. ESI-HRMS spectra of troponylated aminoacid ester **2f**

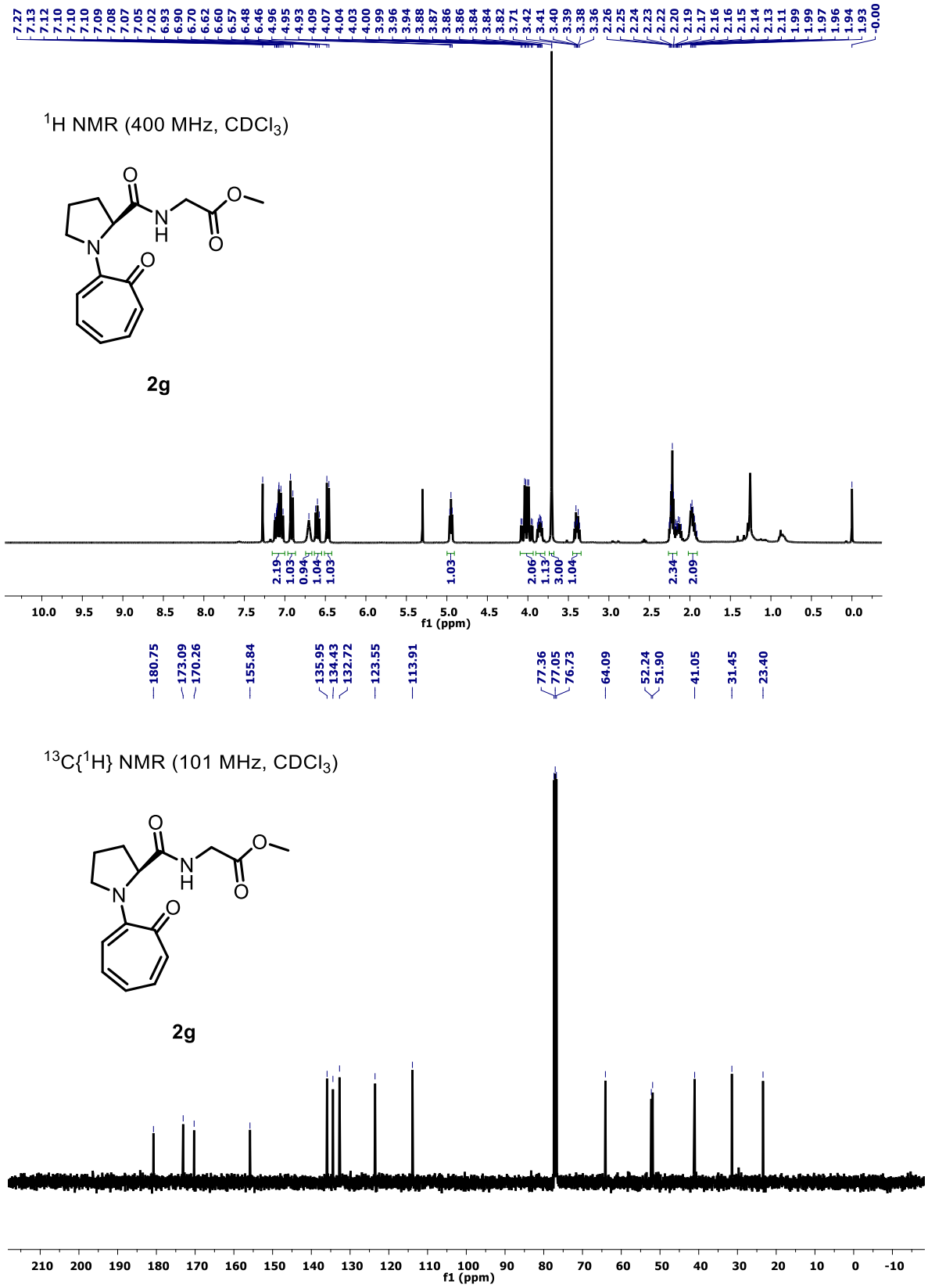


Fig S13. ^{1}H, ^{13}C {^{1}H} NMR spectra of troponylated *di*- peptide **2g**

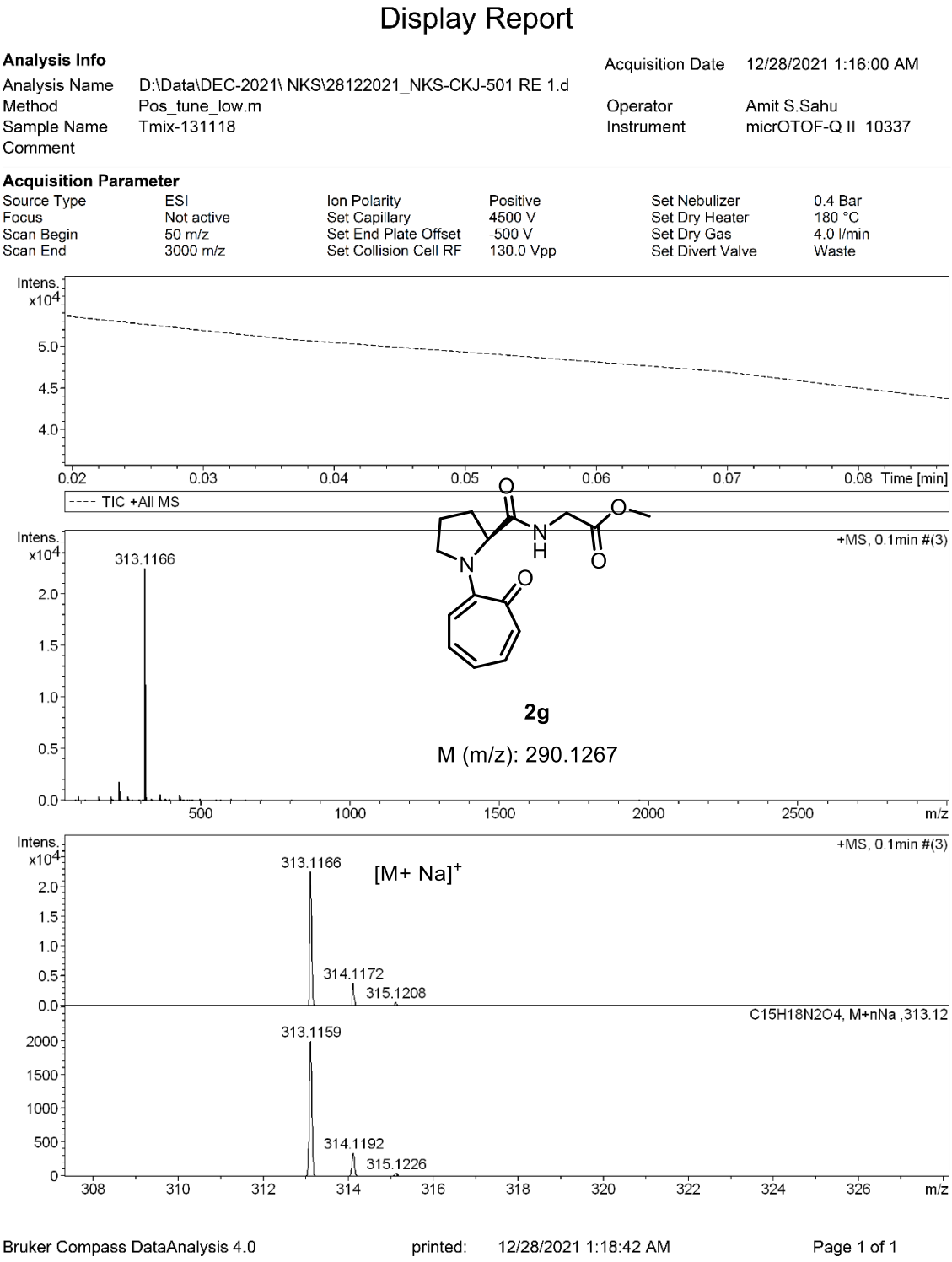


Fig S14. ESI-HRMS spectra of troponylated *di*- peptide **2g**

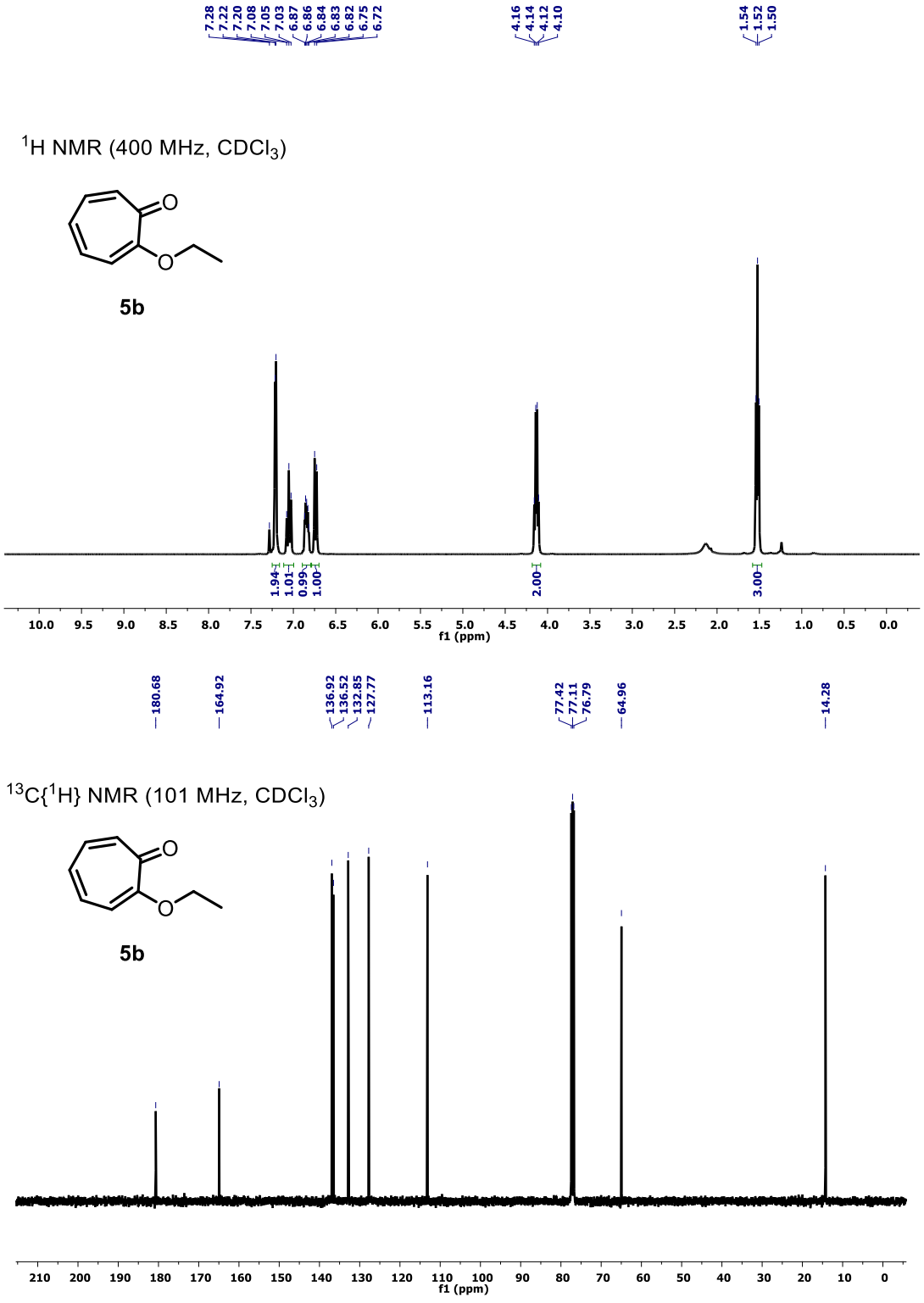


Fig S15. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of 2- ethoxytropone **5b**

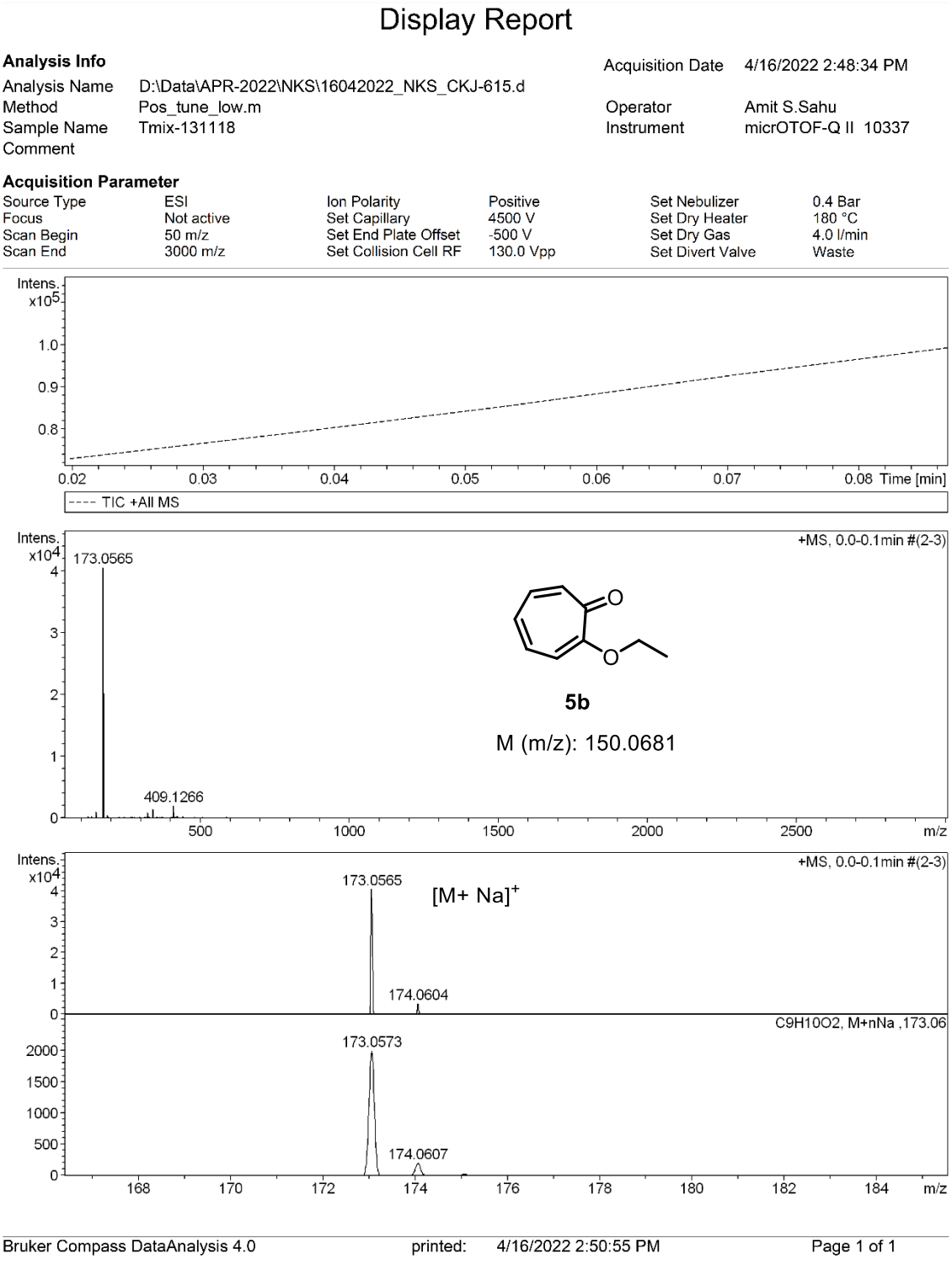


Fig S16. ESI-HRMS spectra of 2-ethoxytropone **5b**

4. NMR and Mass spectra of Olefinated aminotropones/ troponyl amino acid/ peptides (**4a**- 4**w**)/ tropone (**6a**)/ 2-ethoxytropone (**6b**)

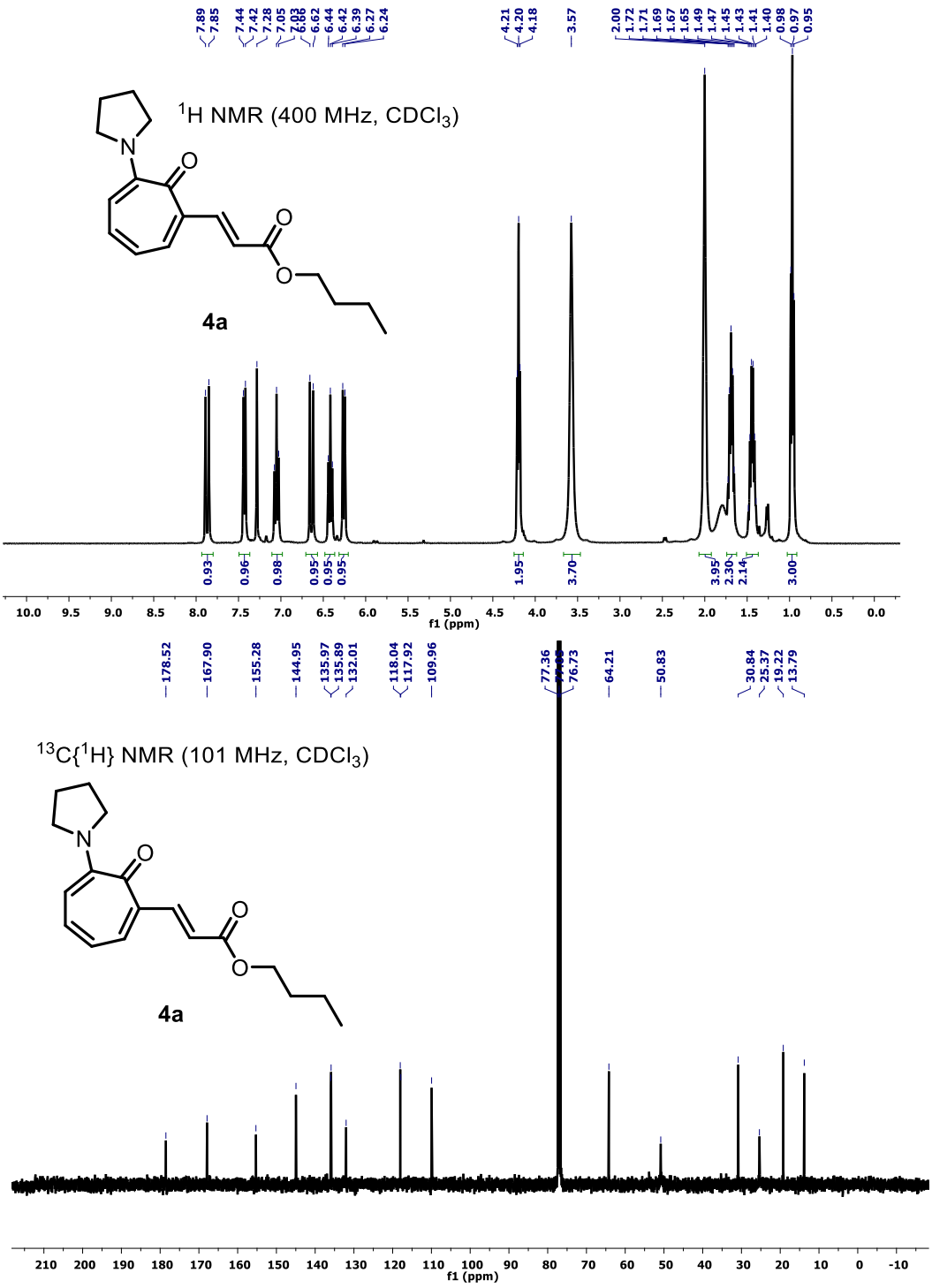


Fig S17. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated aminotropone **4a**

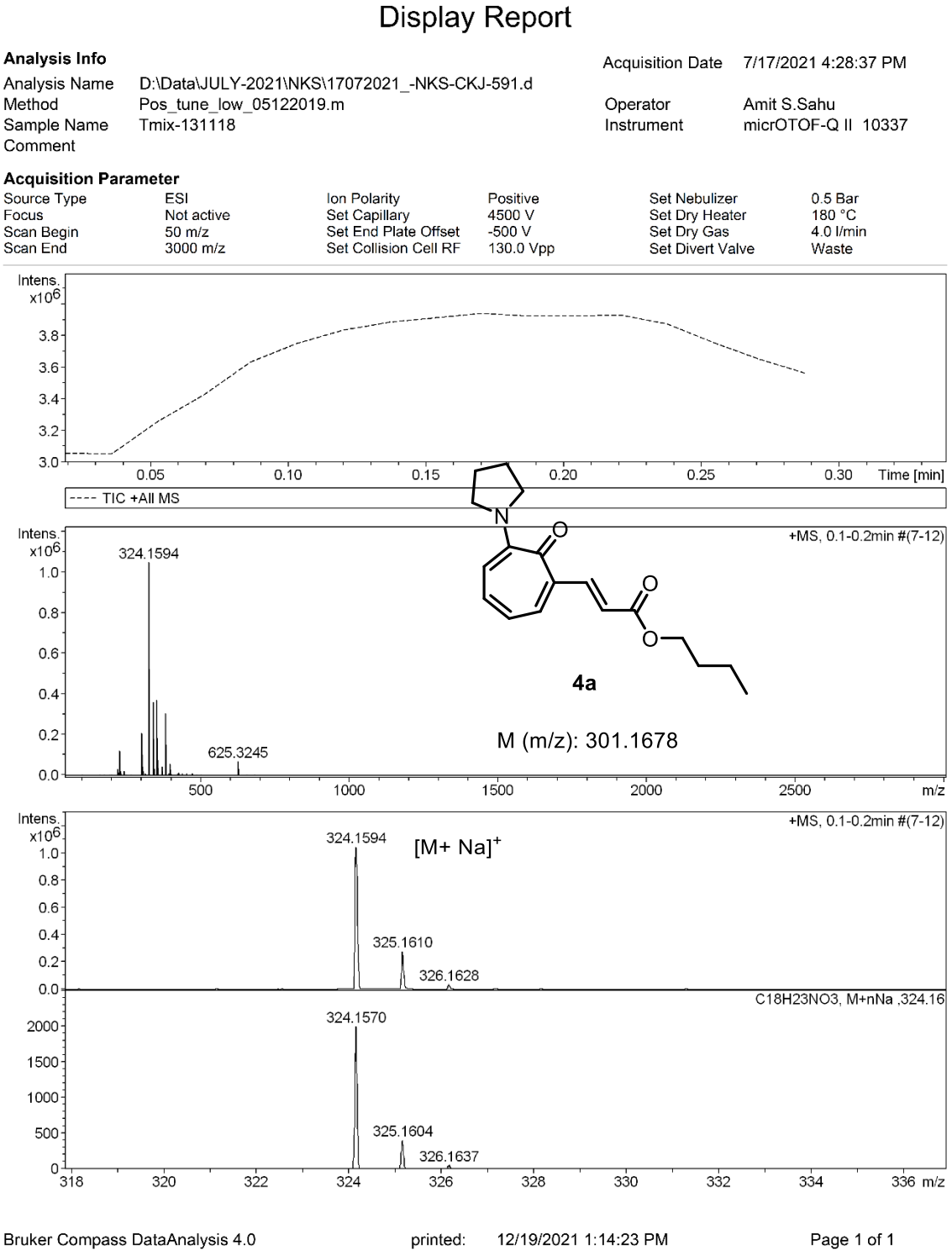


Fig S18. ESI-HRMS spectra of olefinated aminotropone **4a**

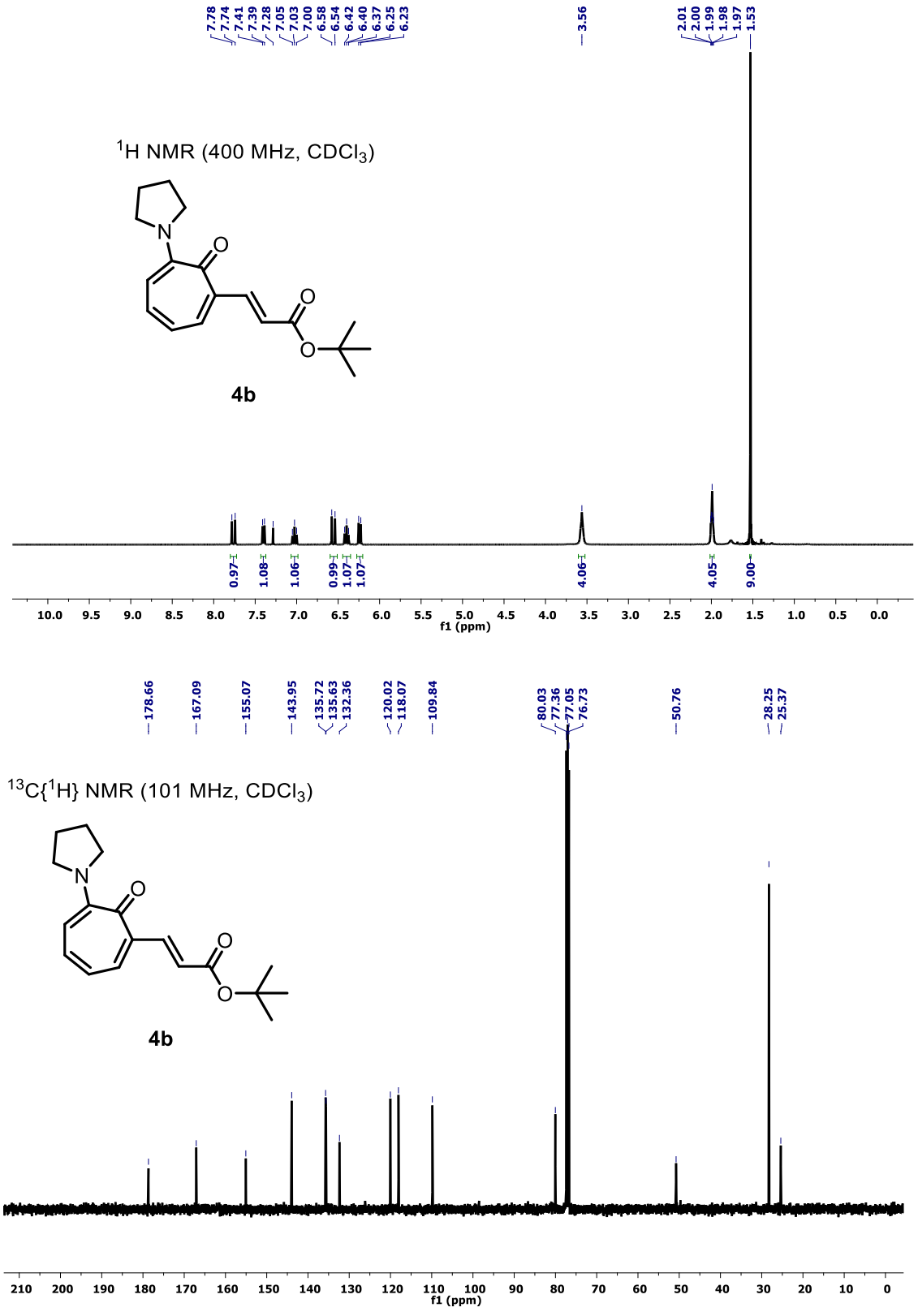


Fig S19. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4b**

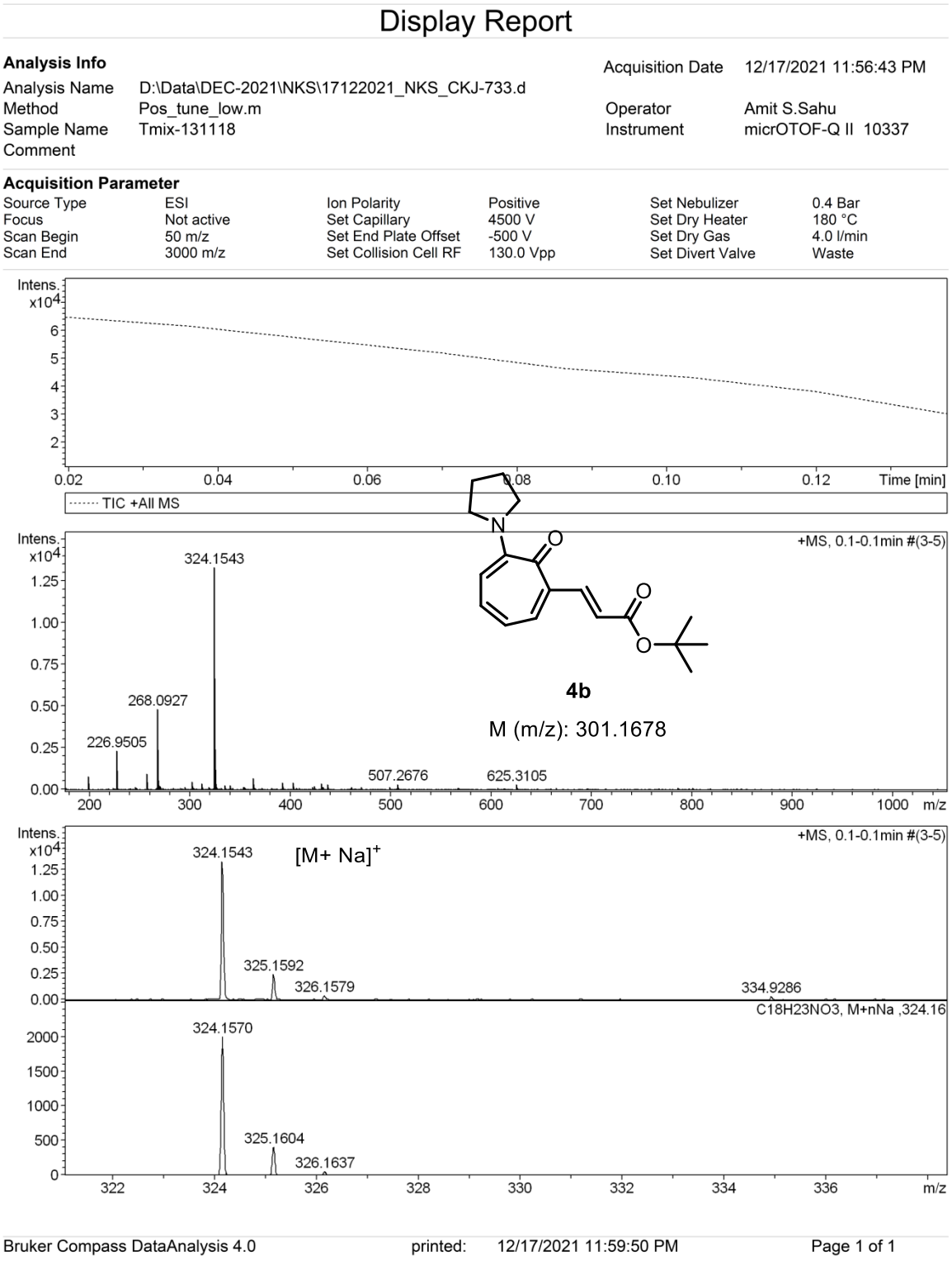


Fig S20. ESI-HRMS spectra of olefinated aminotropone **4b**

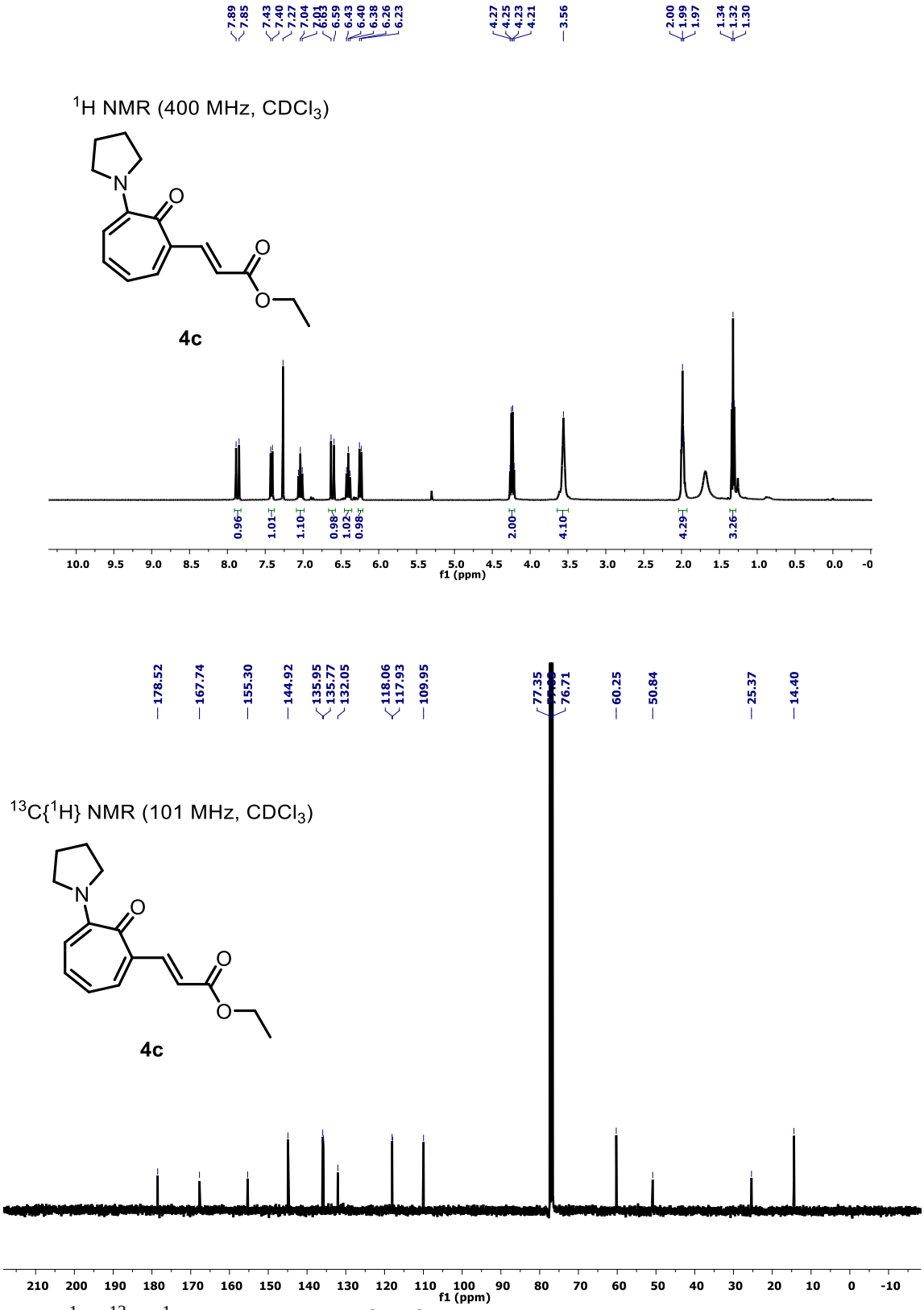


Fig S21. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4c**

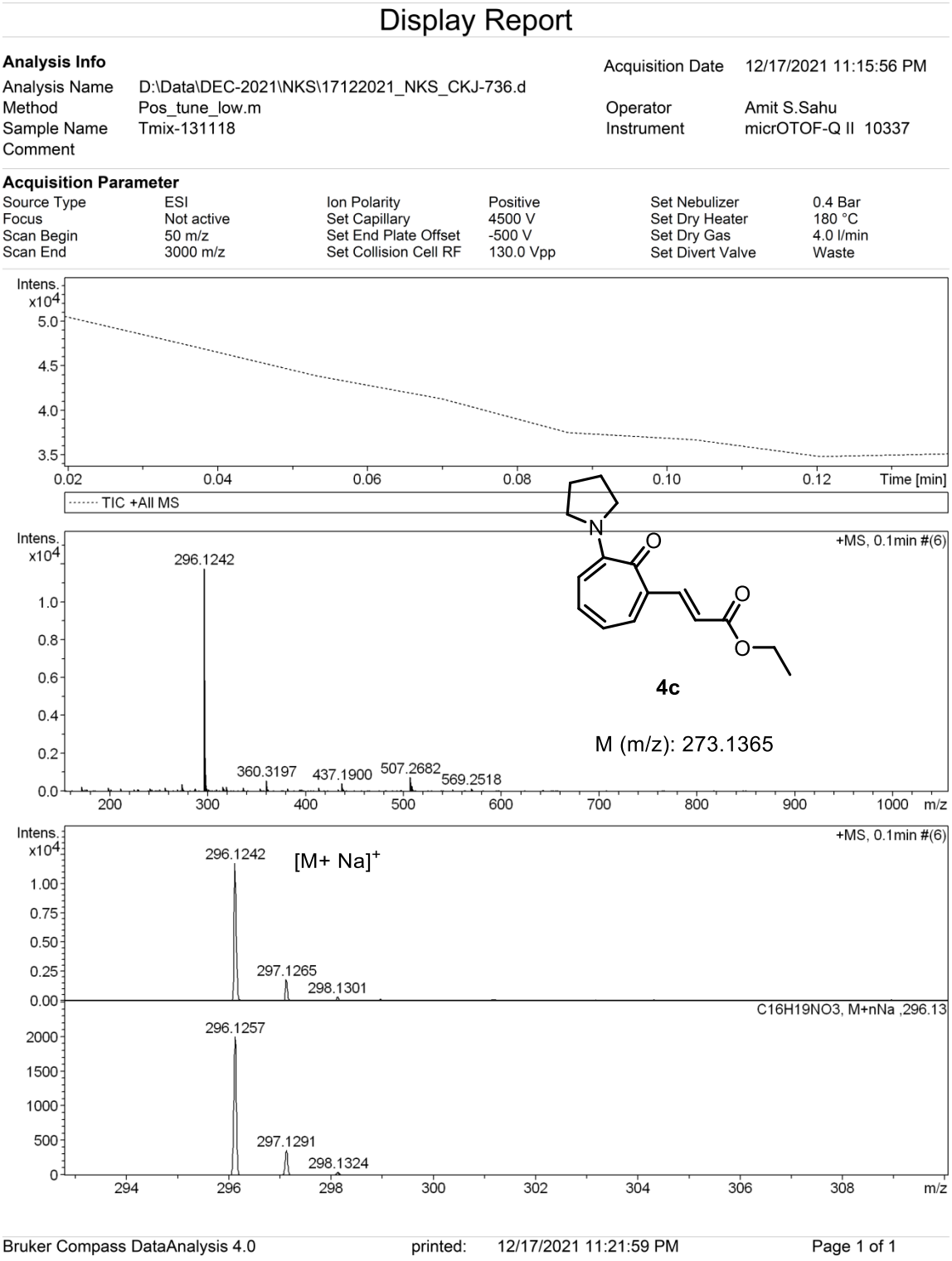


Fig S22. ESI-HRMS spectra of olefinated aminotropone **4c**

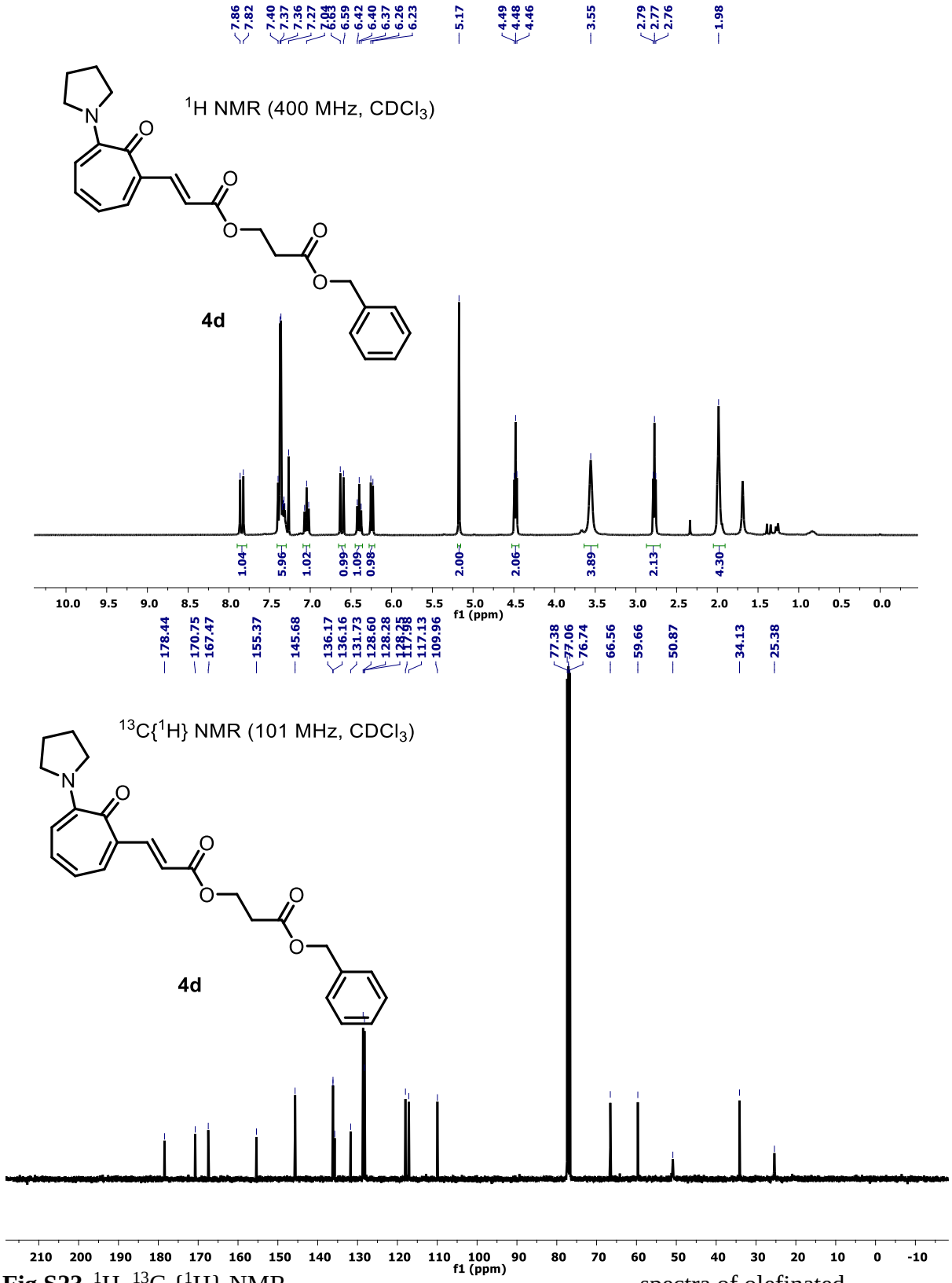


Fig S23. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4d**

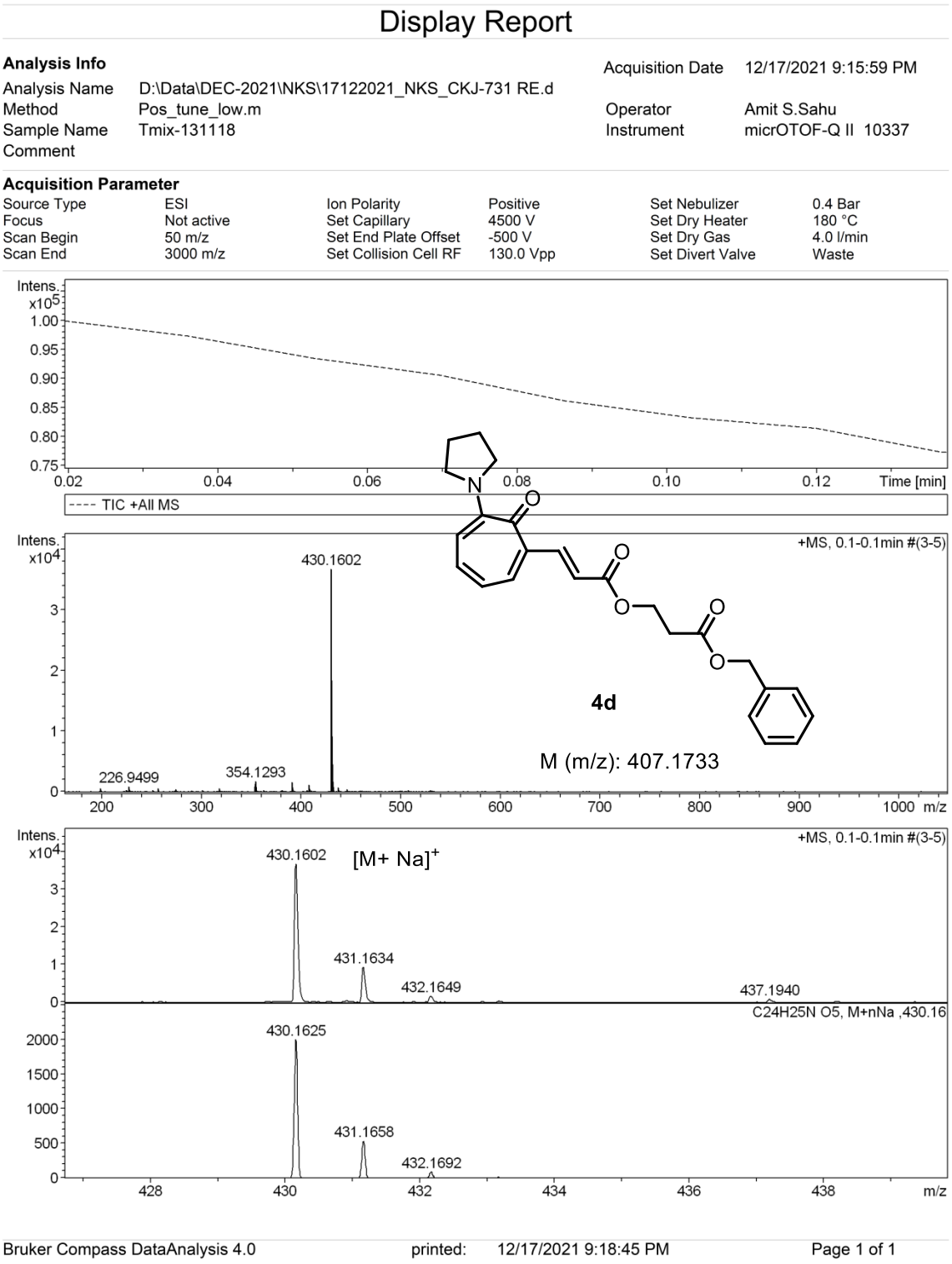


Fig S24. ESI-HRMS spectra of olefinated aminotropone **4d**

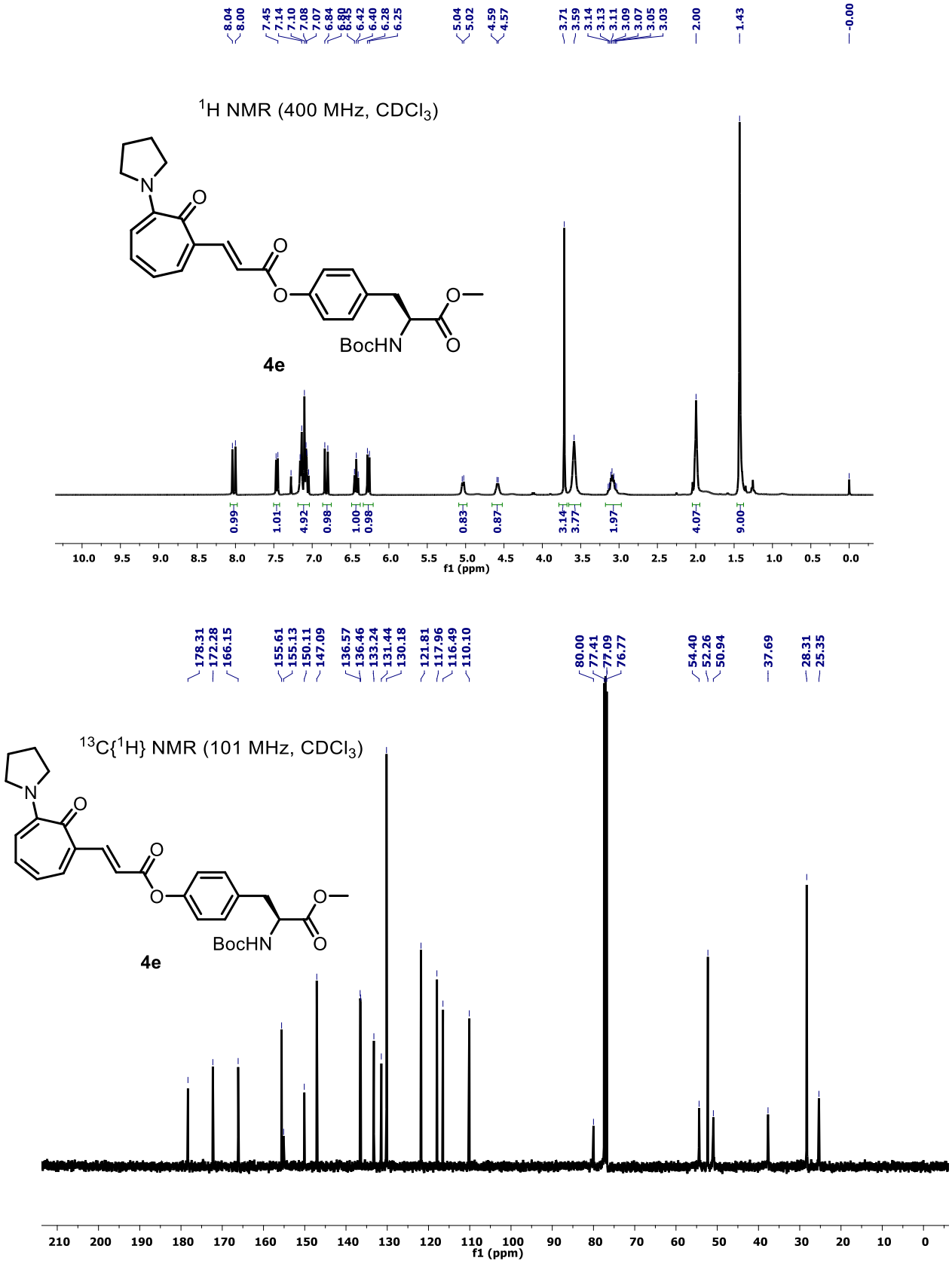


Fig S25. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4e**

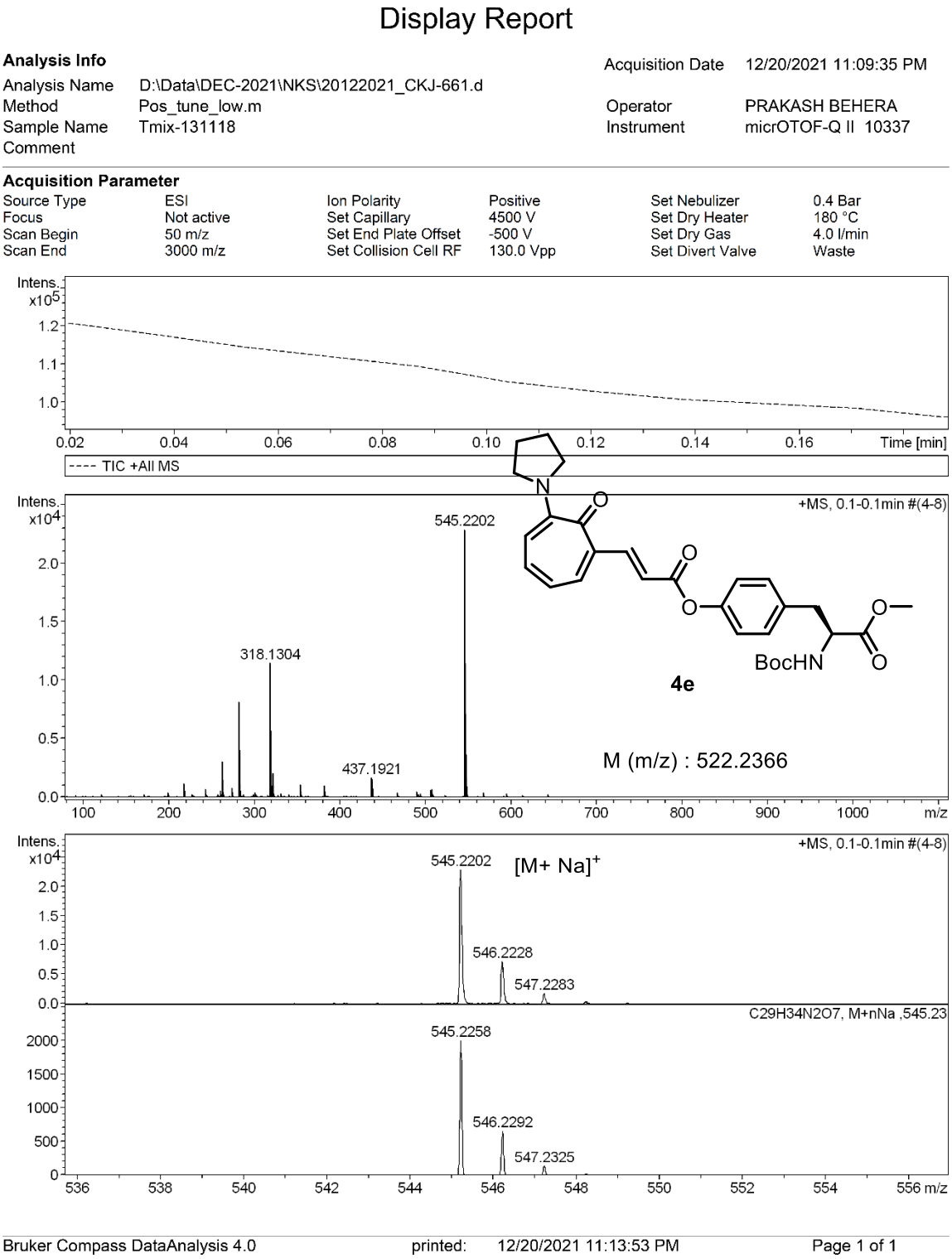


Fig S26. ESI-HRMS spectra of olefinated aminotropone **4e**

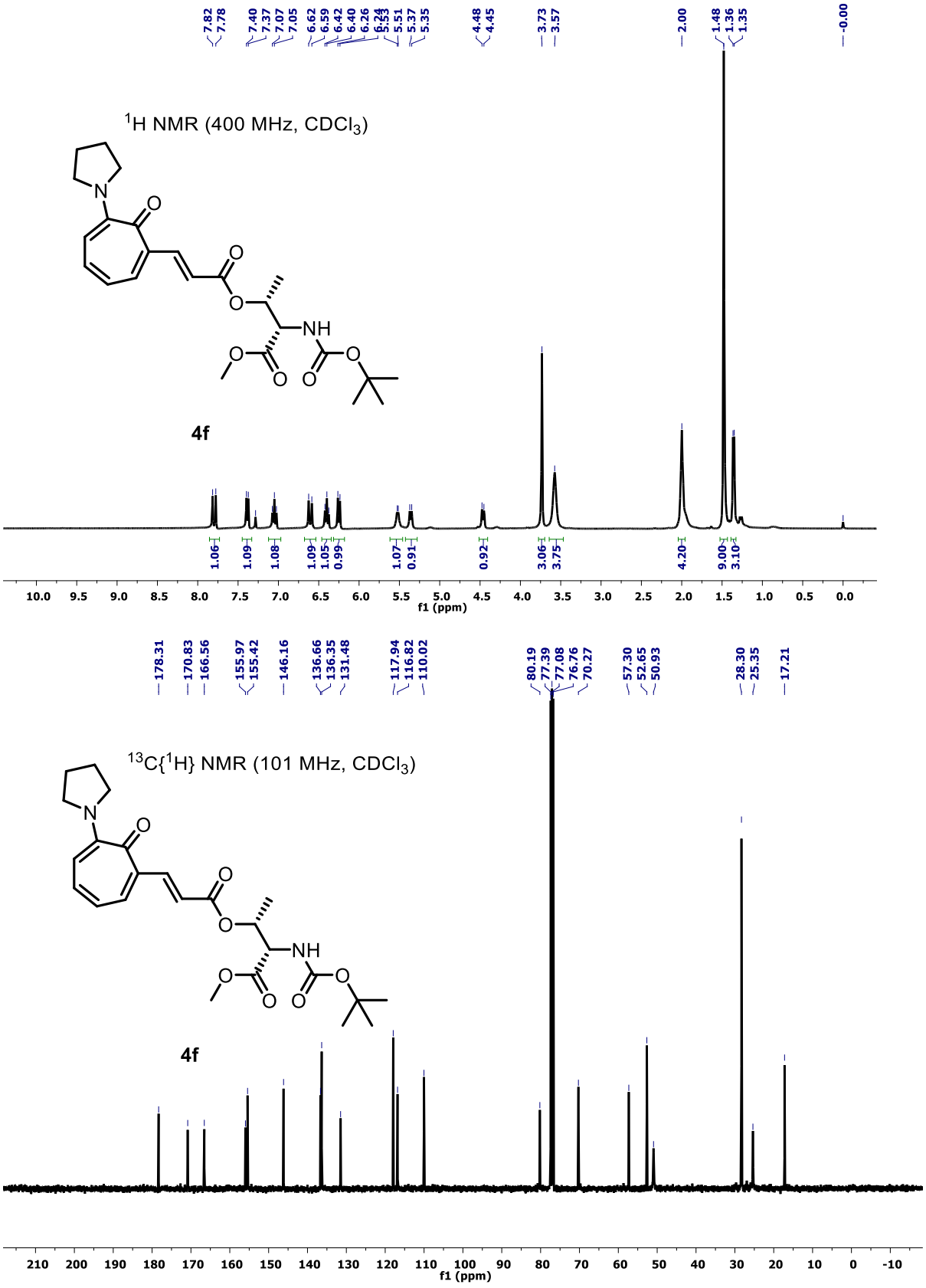


Fig S27. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4f**

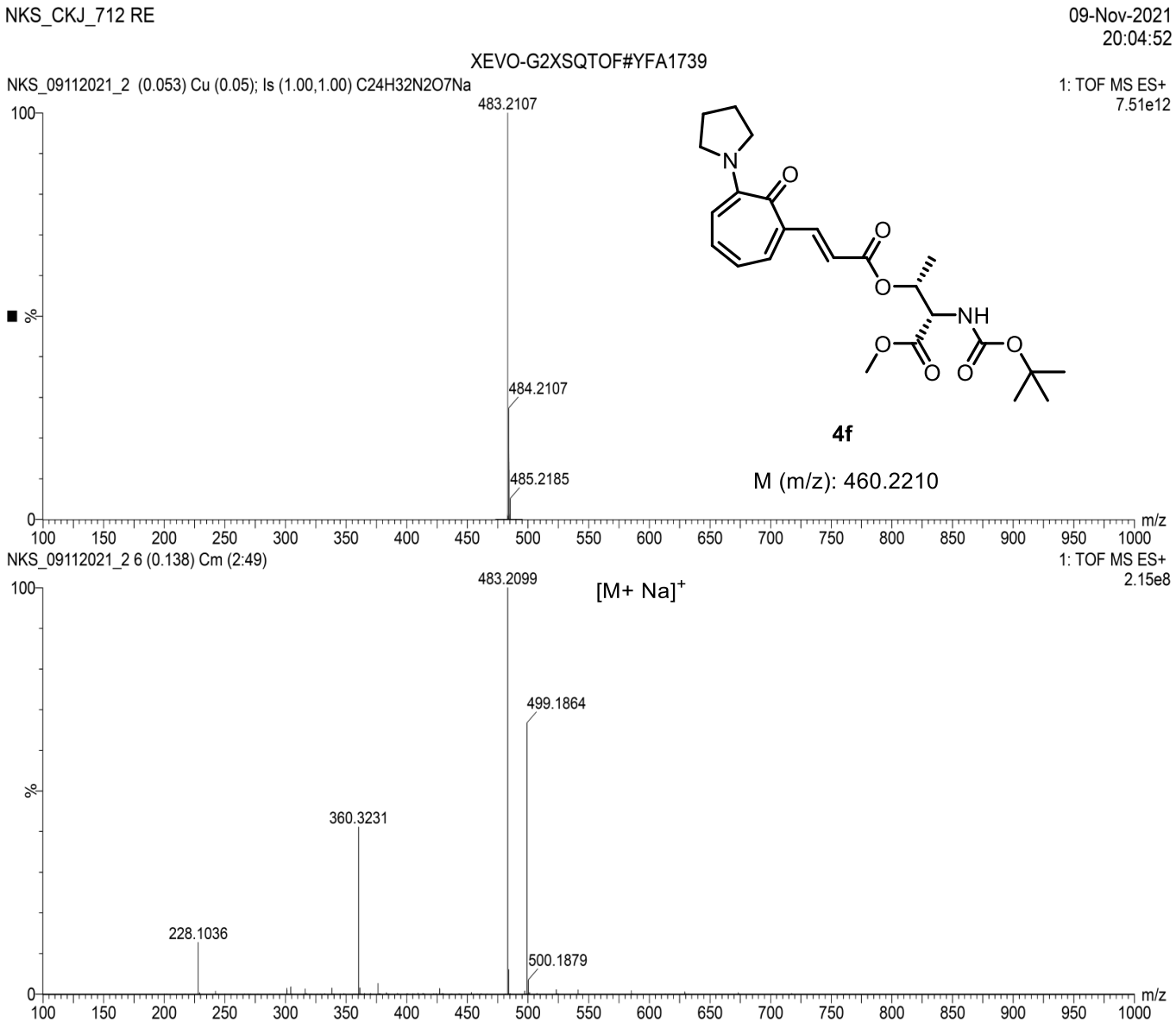


Fig S28. ESI-HRMS spectra of olefinated aminotropone **4f**

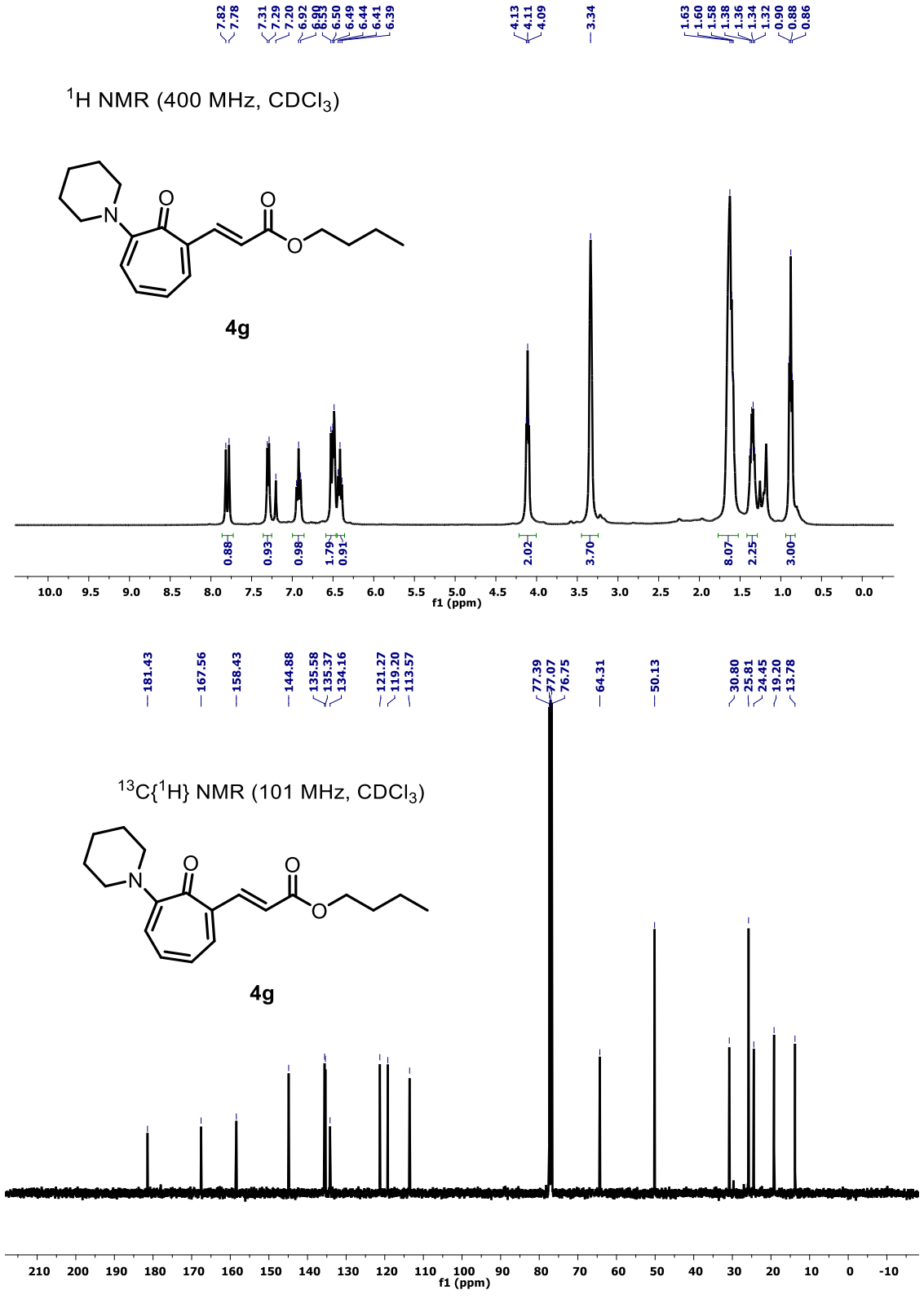


Fig S29. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4g**

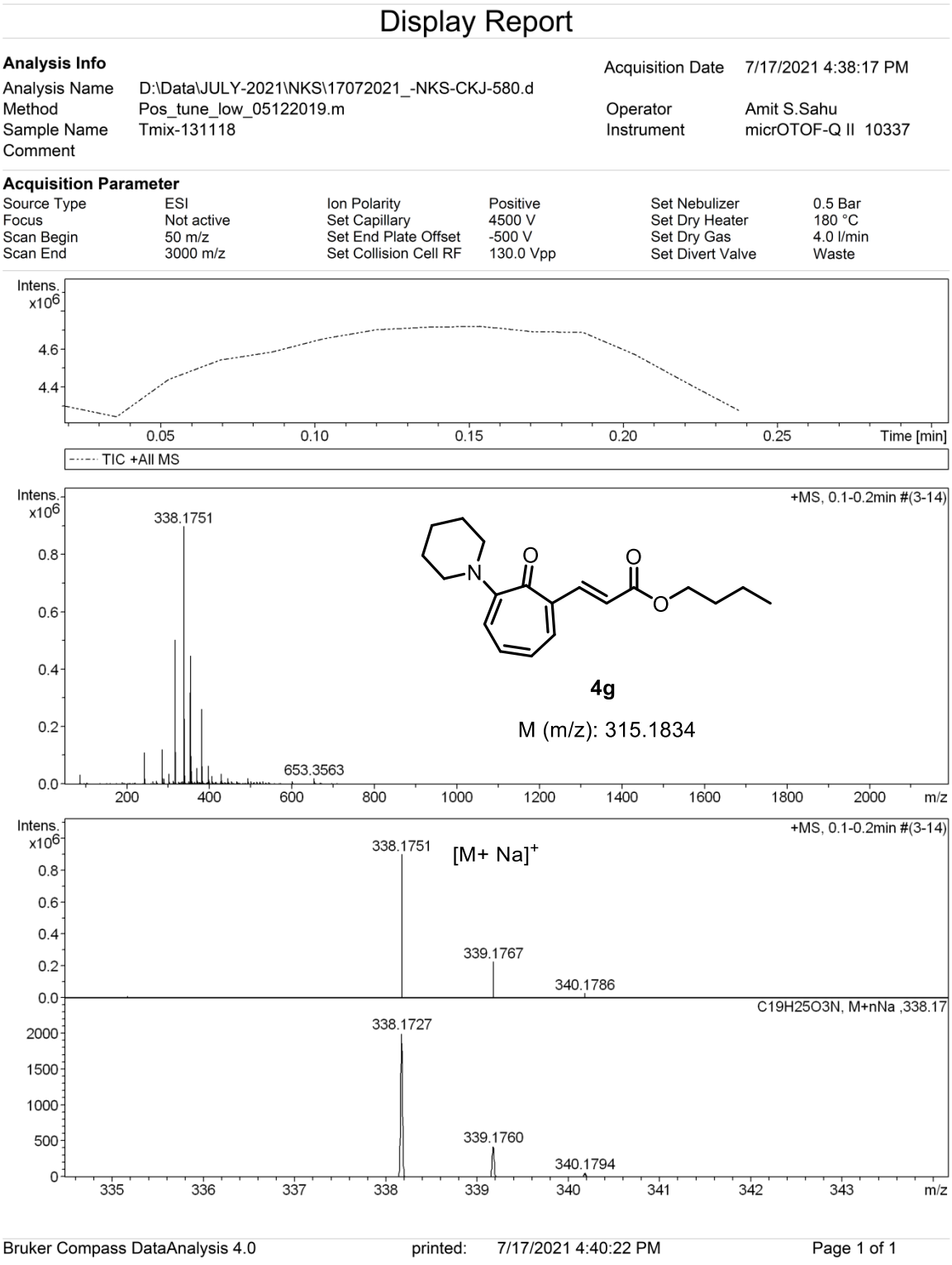


Fig S30. ESI-HRMS spectra of olefinated aminotropone **4g**

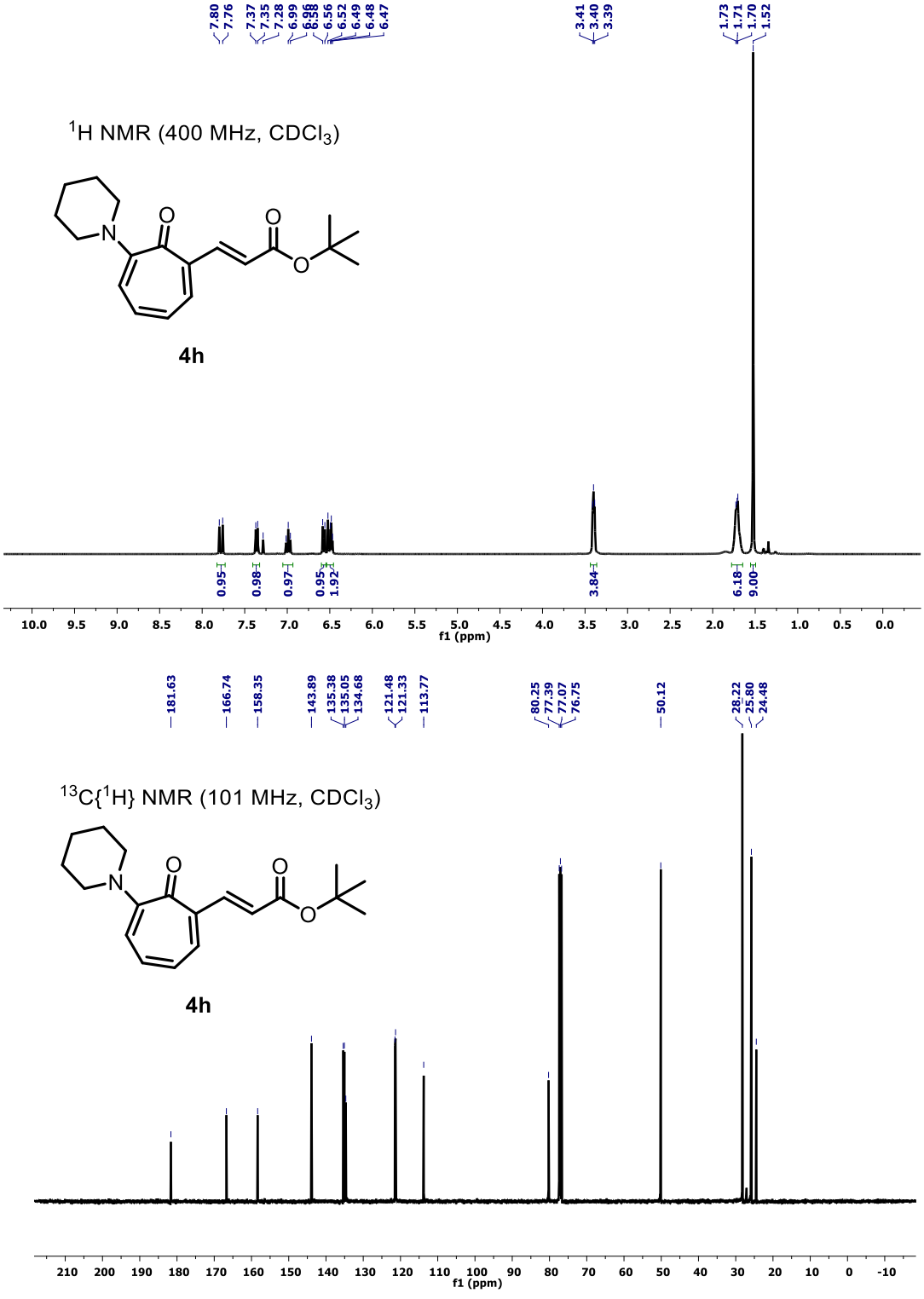


Fig S31. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated aminotropone **4h**

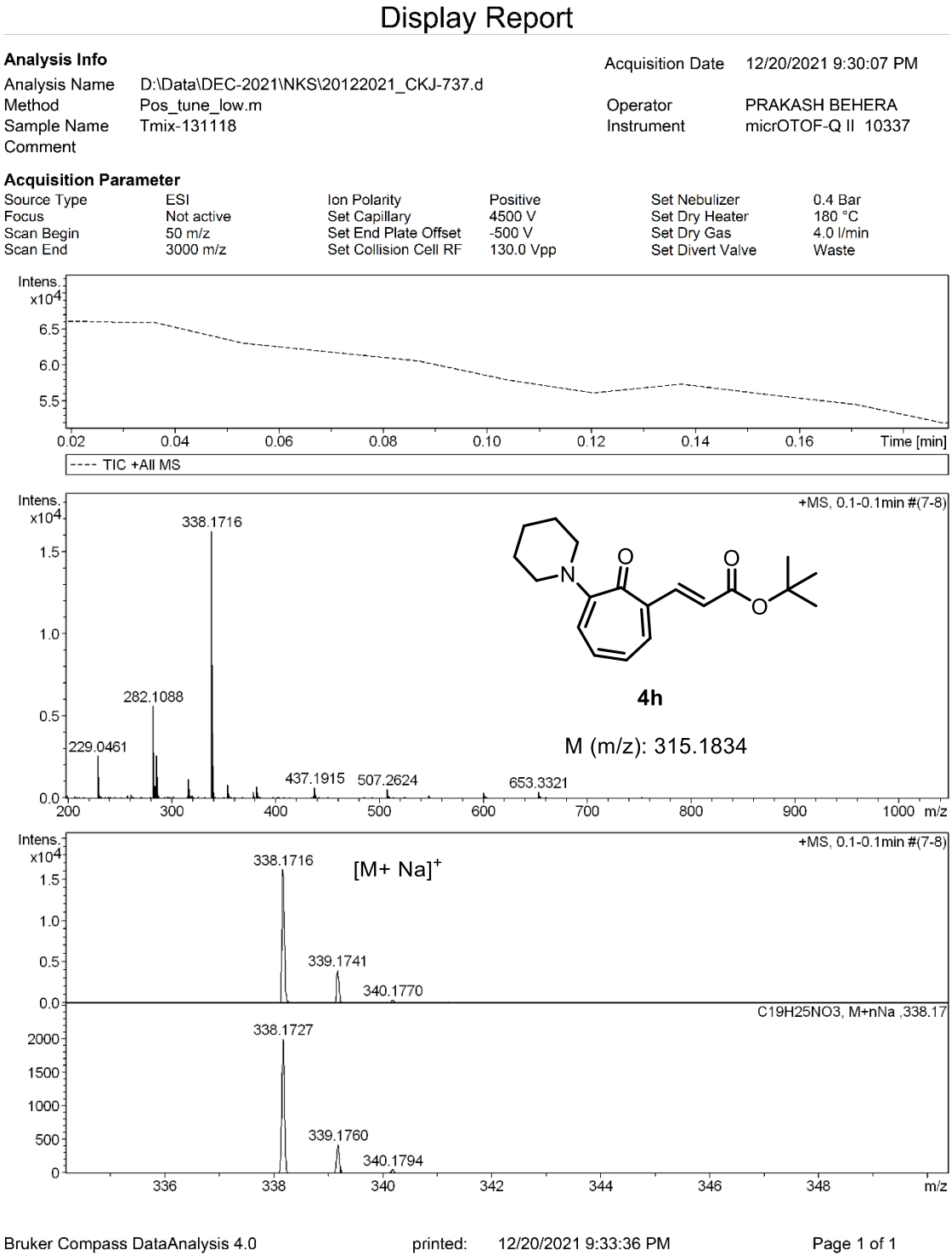


Fig S32. ESI-HRMS spectra of olefinated aminotropone **4h**

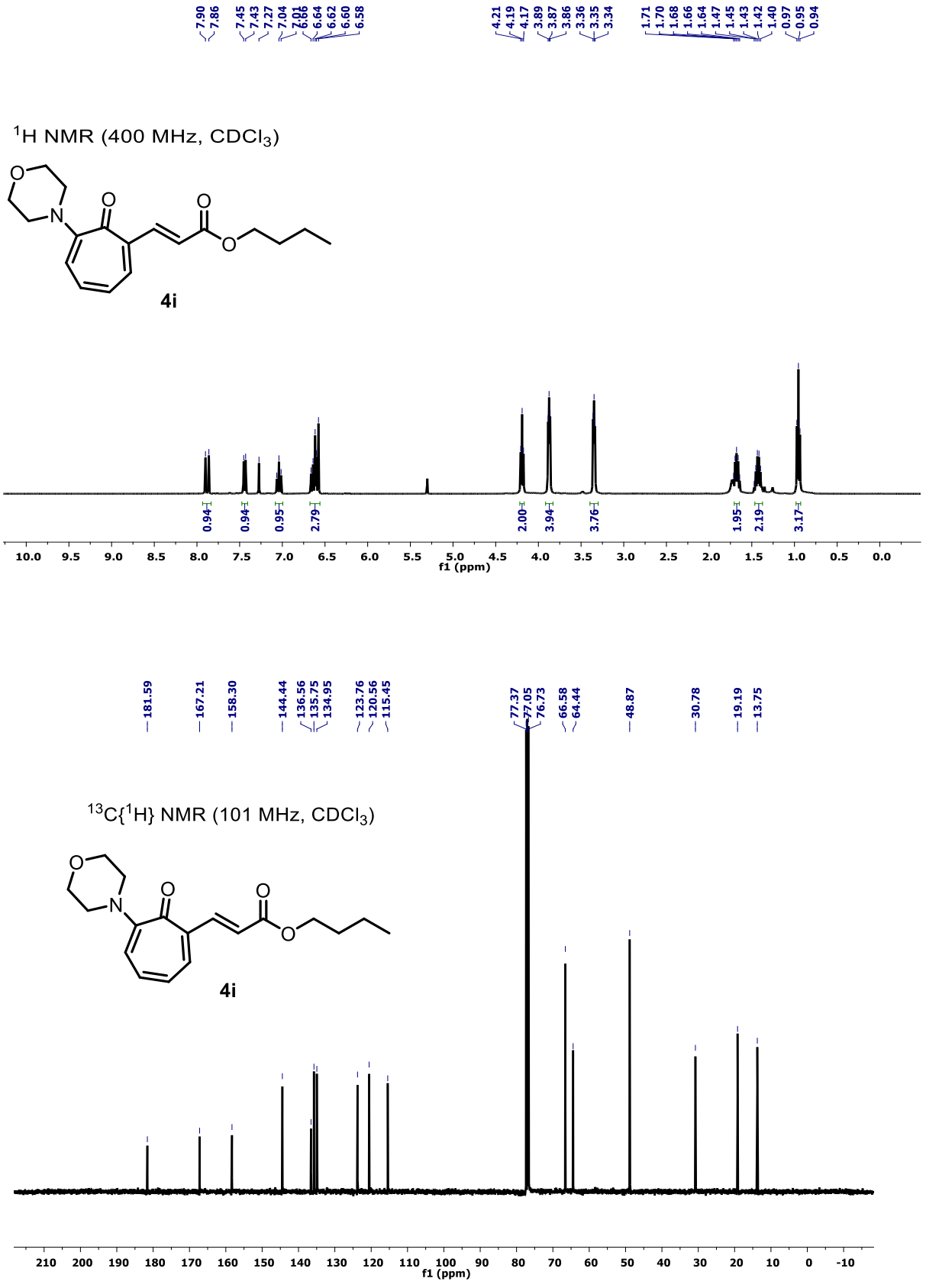


Fig S33. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4i**

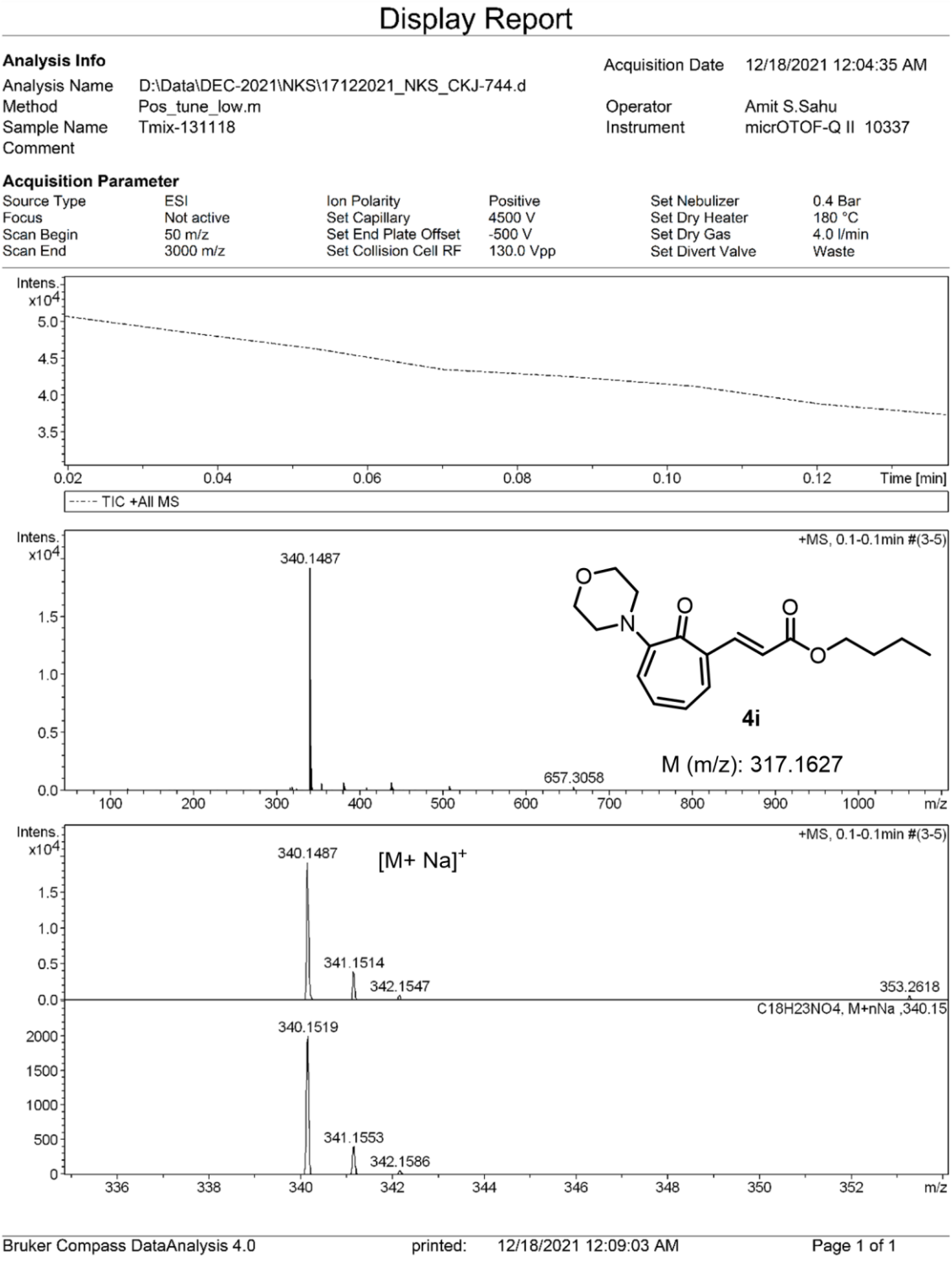


Fig S34. ESI-HRMS spectra of olefinated aminotropone **4i.**

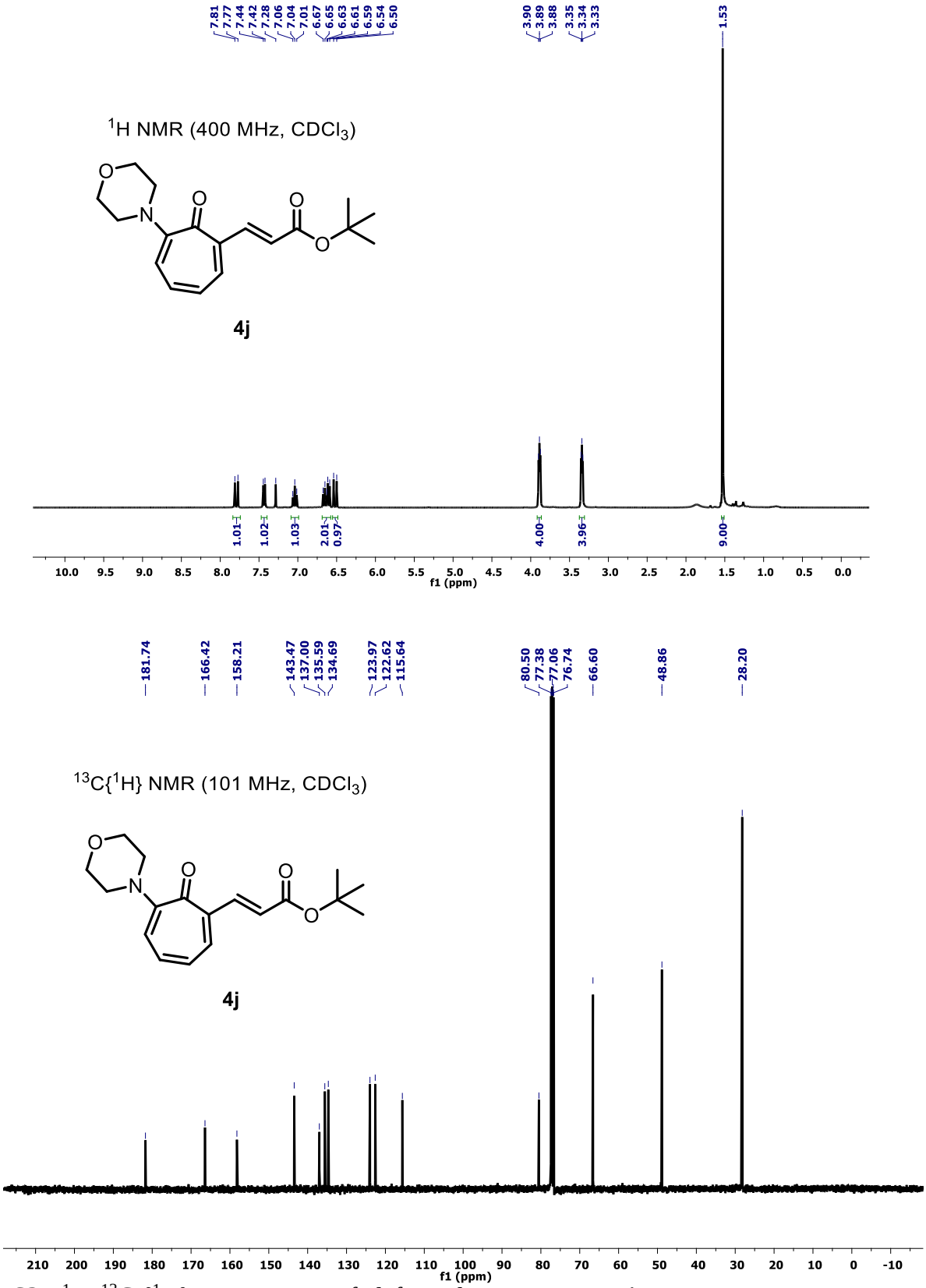


Fig S35. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4j**

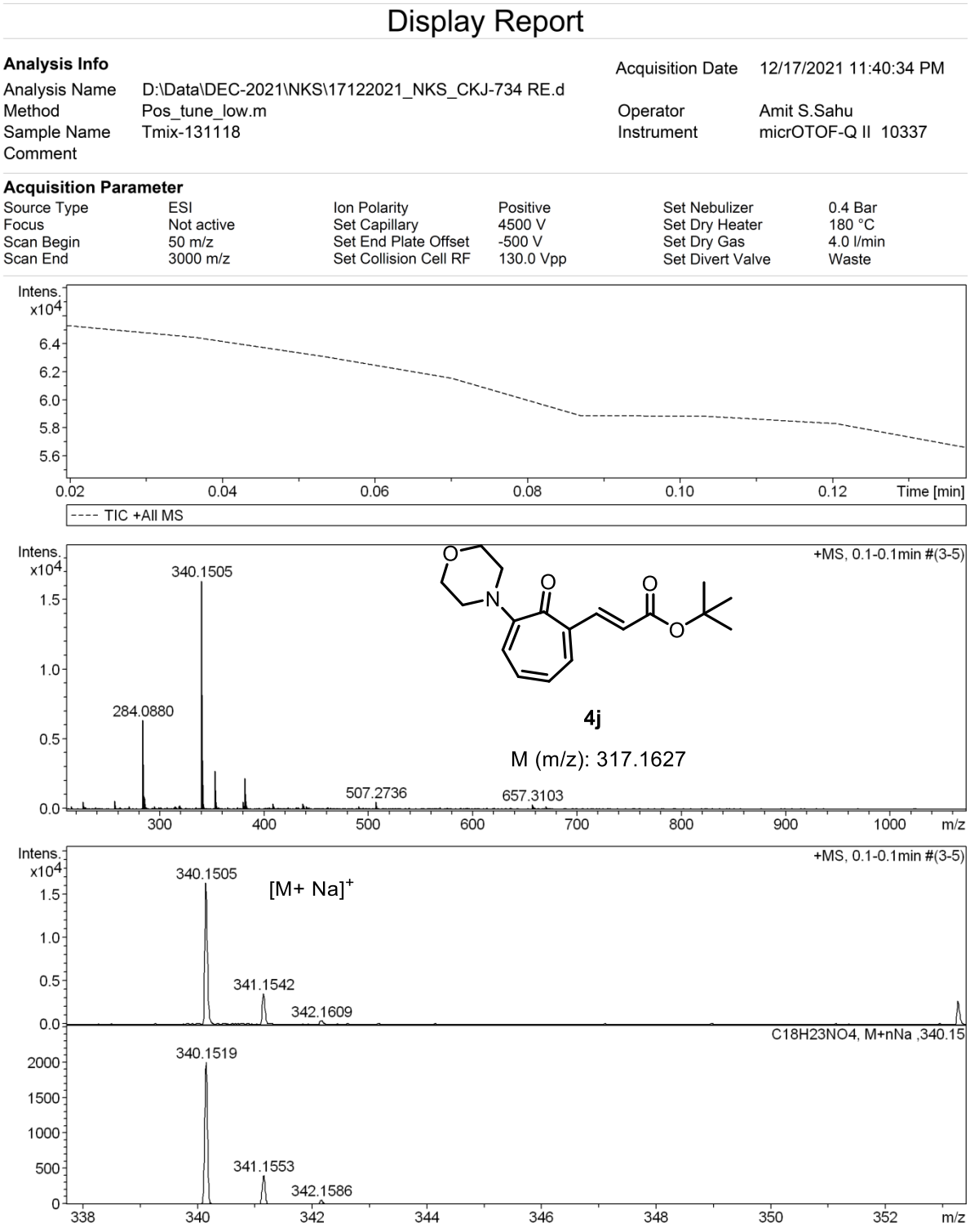


Fig S36. ESI-HRMS spectra of olefinated aminotropone **4j**

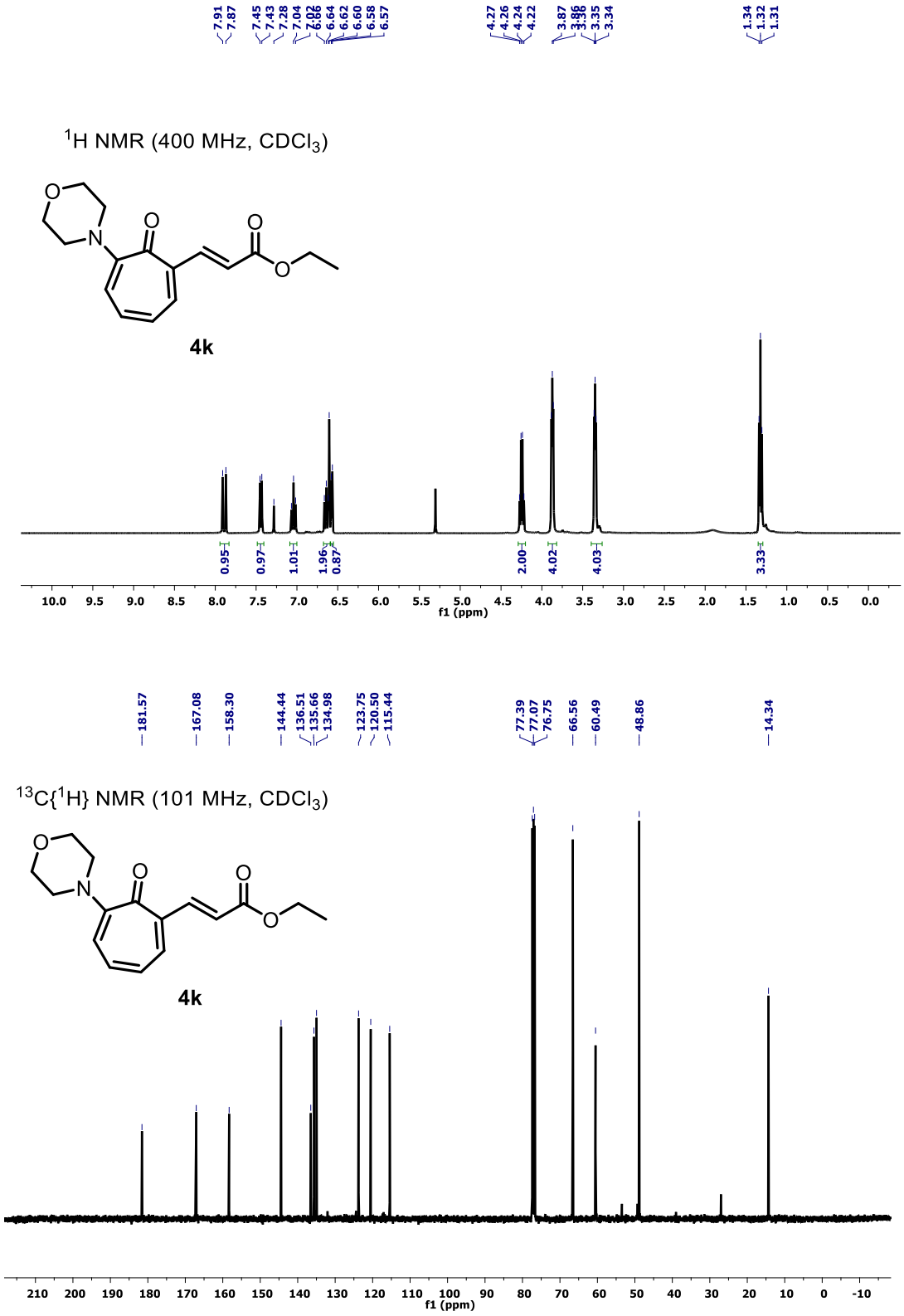


Fig S37. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated aminotropone **4k**

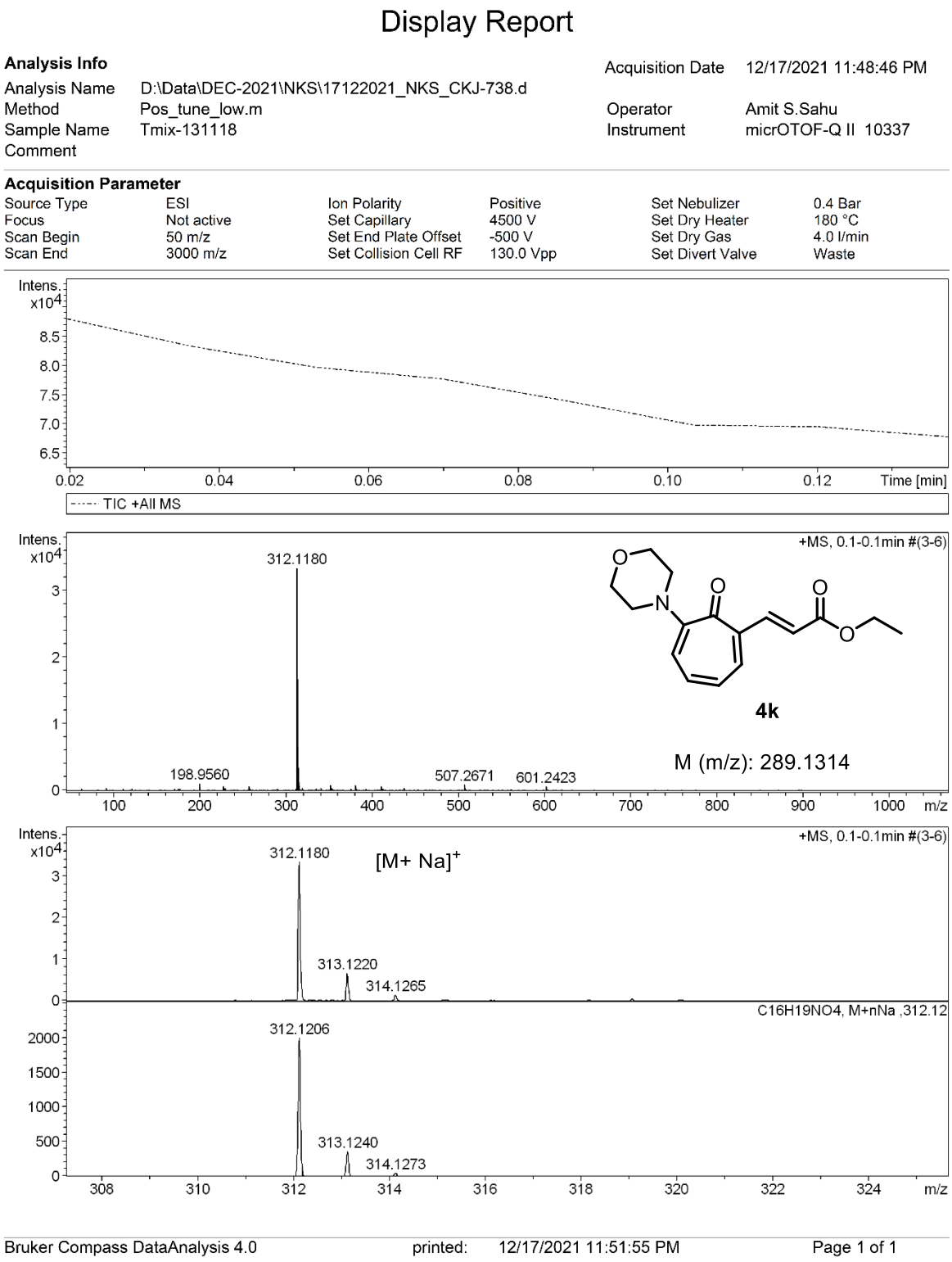


Fig S38. ESI-HRMS spectra of olefinated aminotropone **4k**

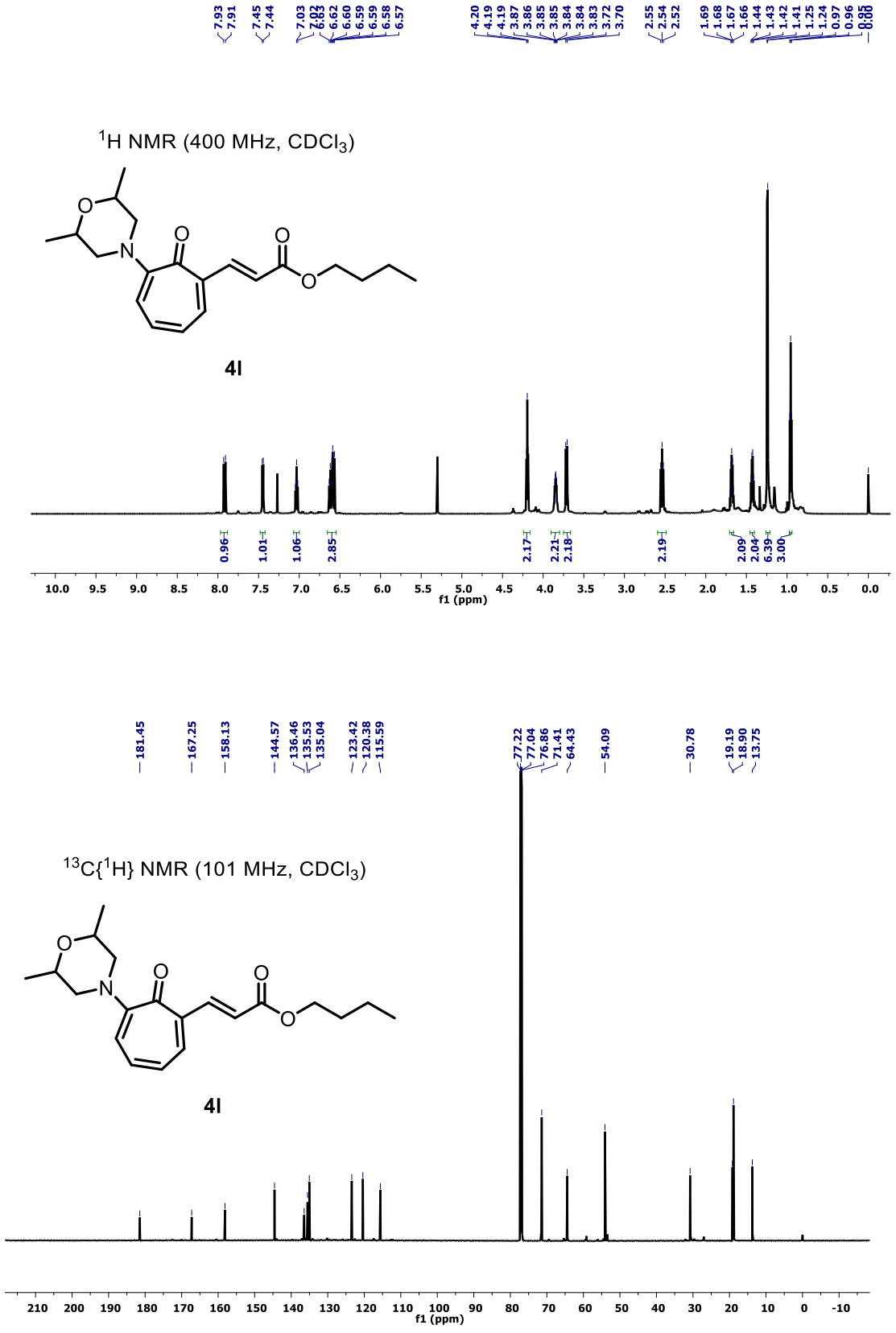


Fig S39. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated aminotropone **4l**

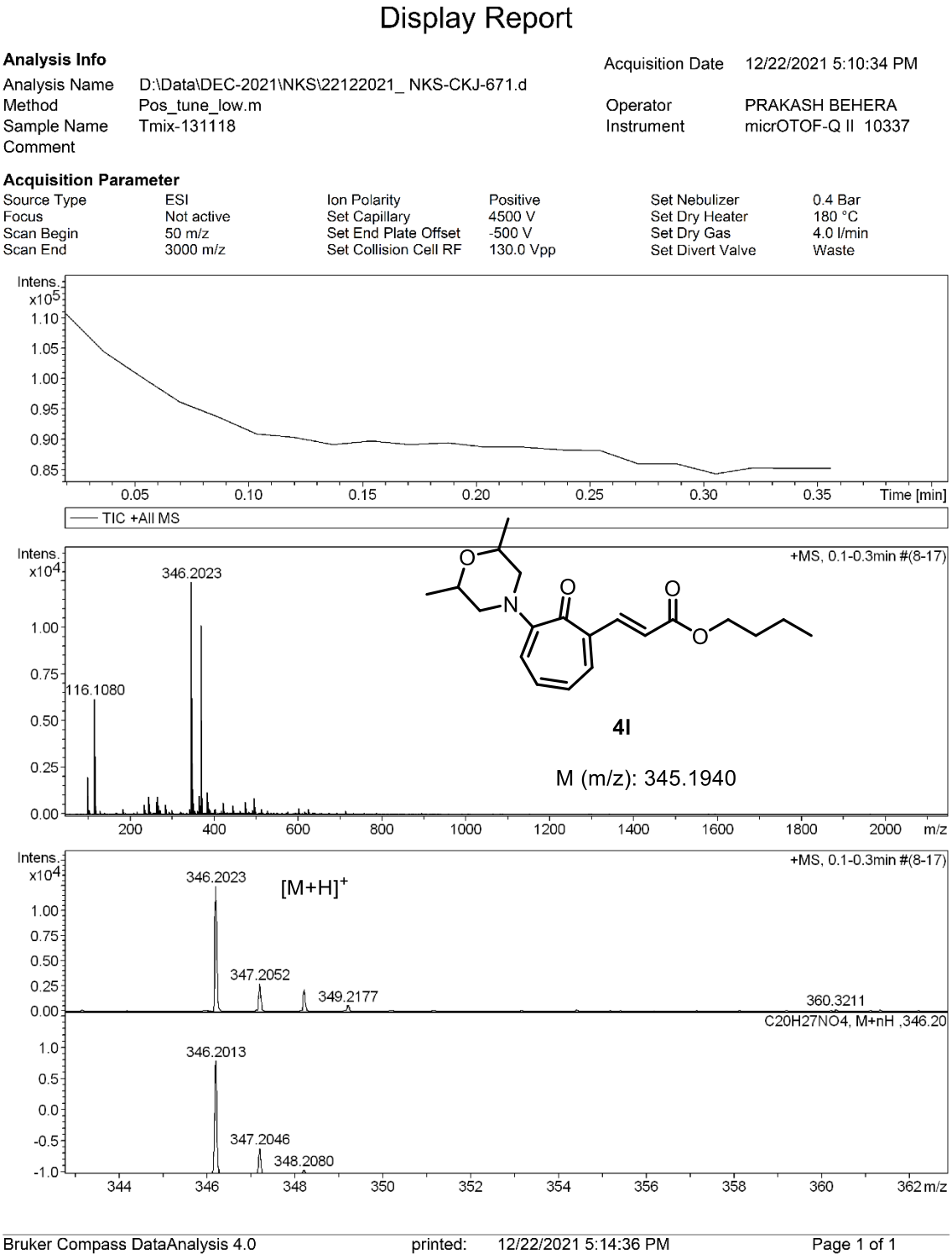


Fig S40. ESI-HRMS spectra of olefinated aminotropone **4l**

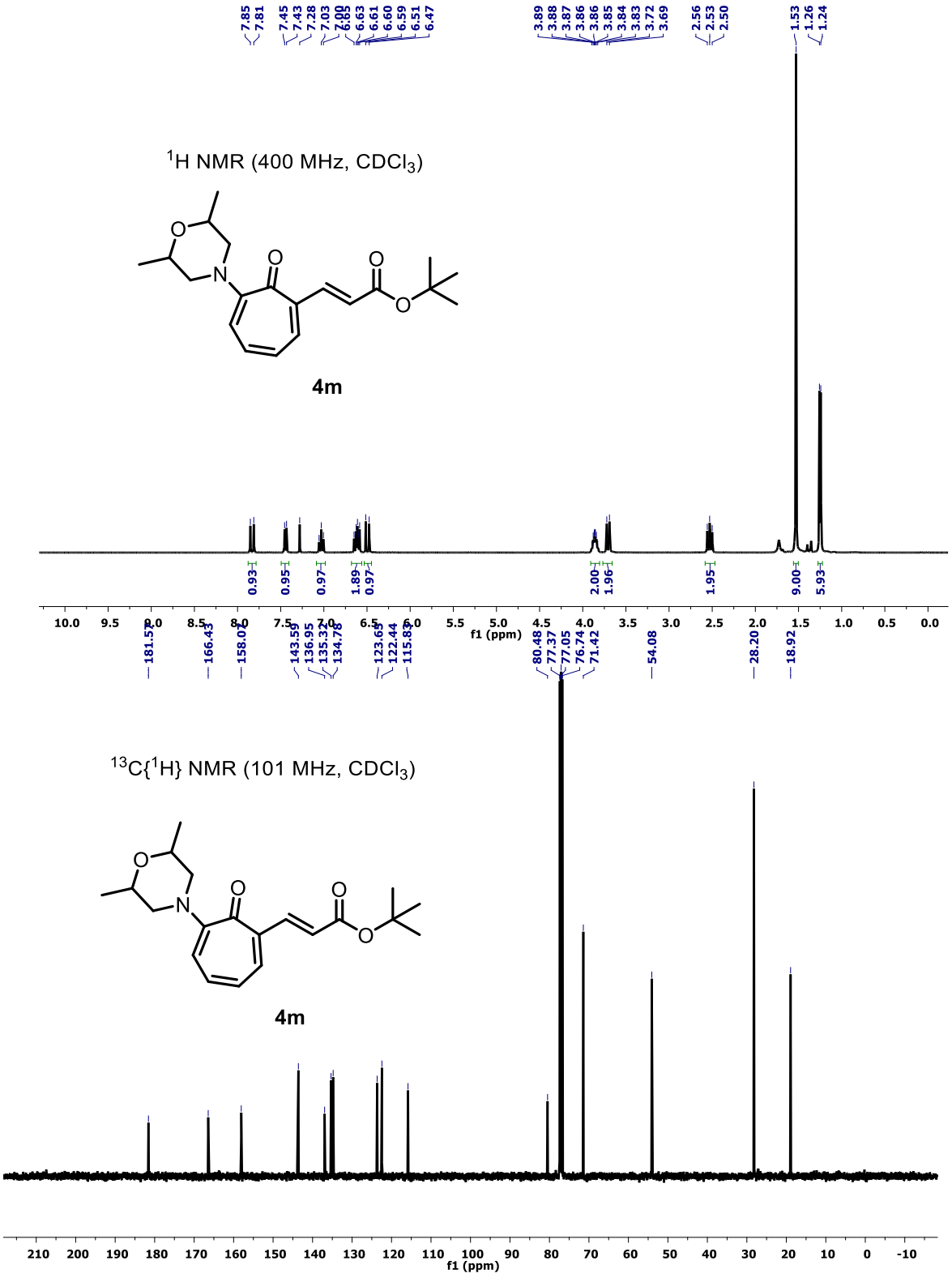


Fig S41. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated aminotropone **4m**

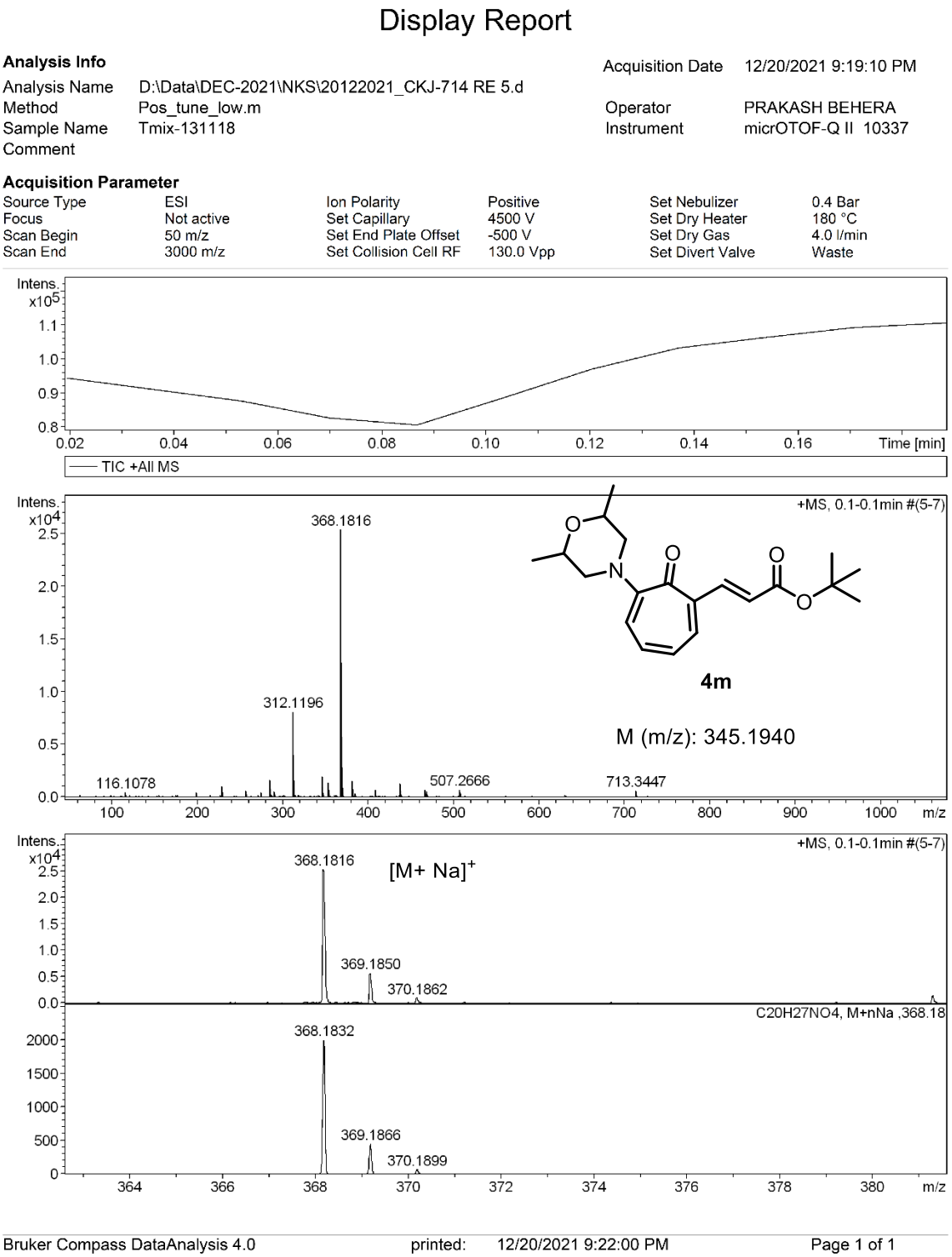


Fig S42. ESI-HRMS spectra of olefinated aminotropone **4m**

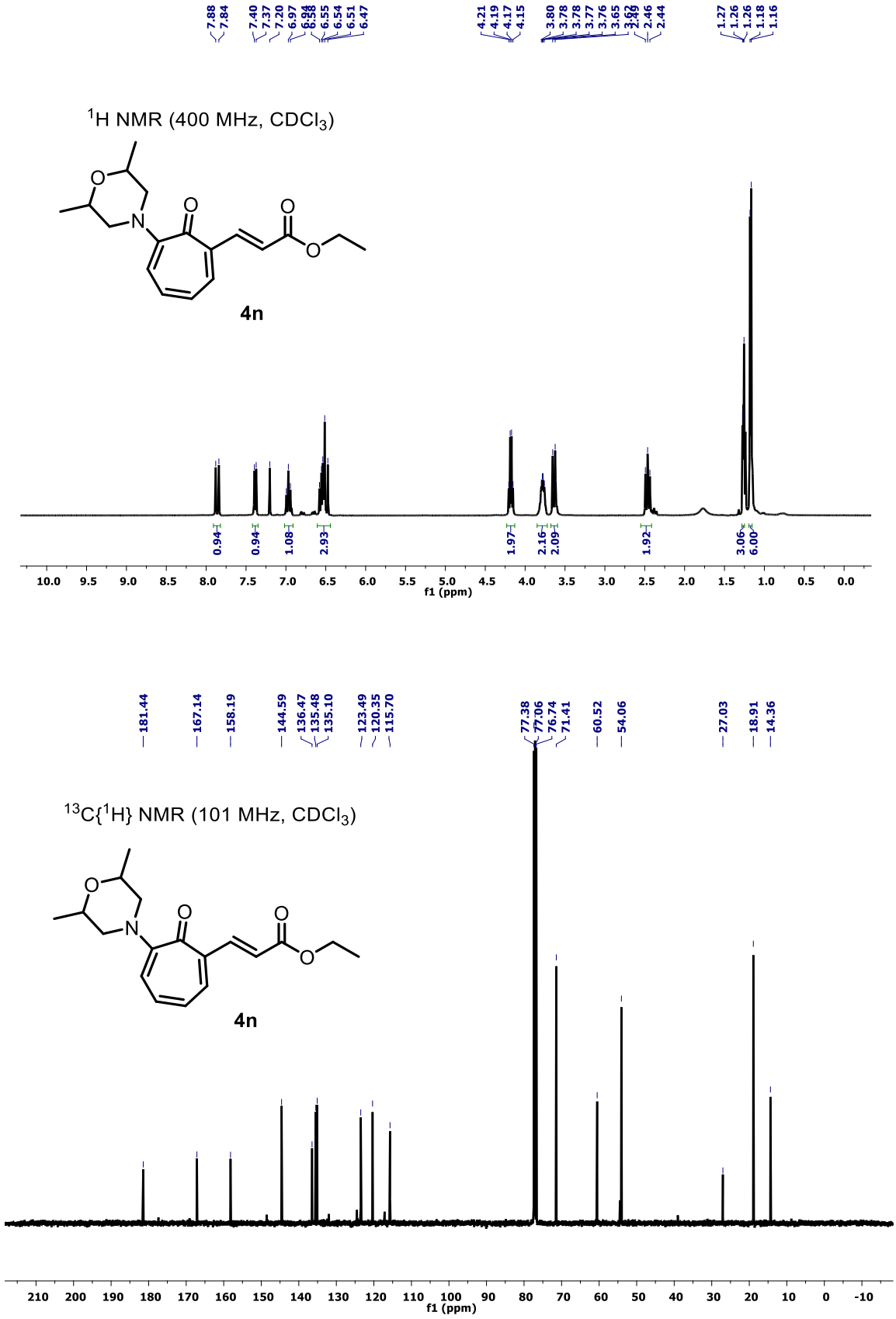


Fig S43. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4n**

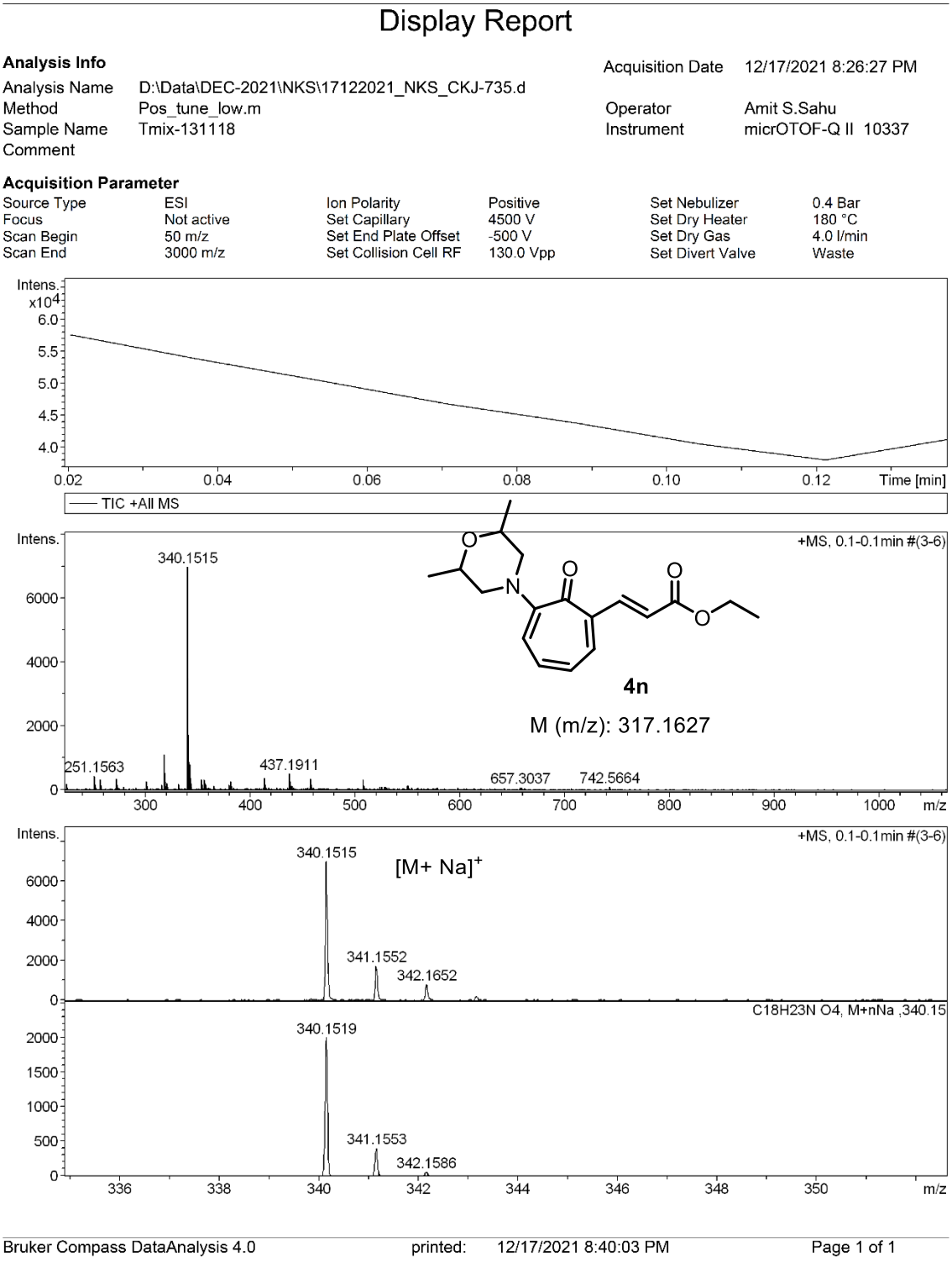


Fig S44. ESI-HRMS spectra of olefinated aminotropone **4n**

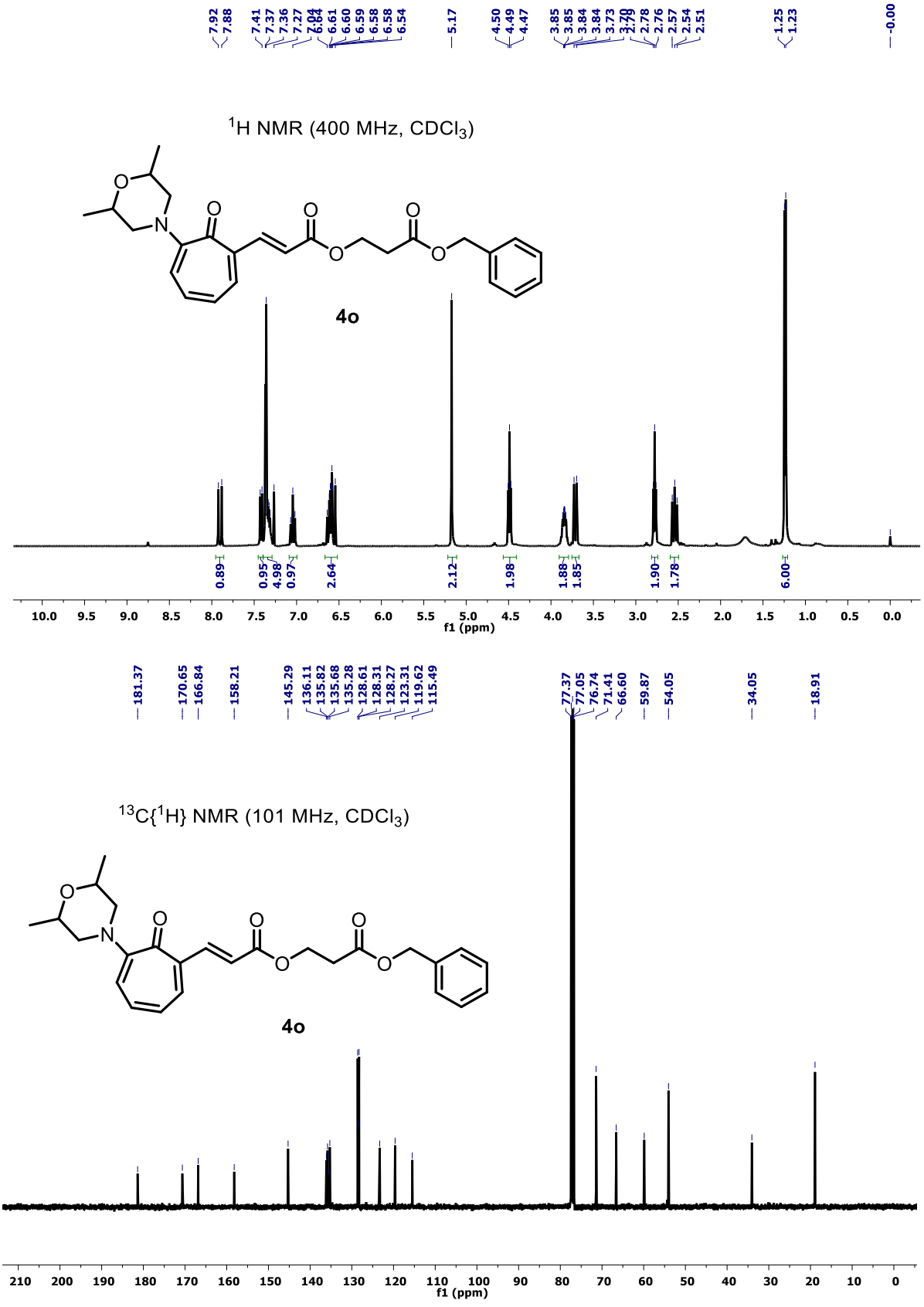


Fig S45. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4o**

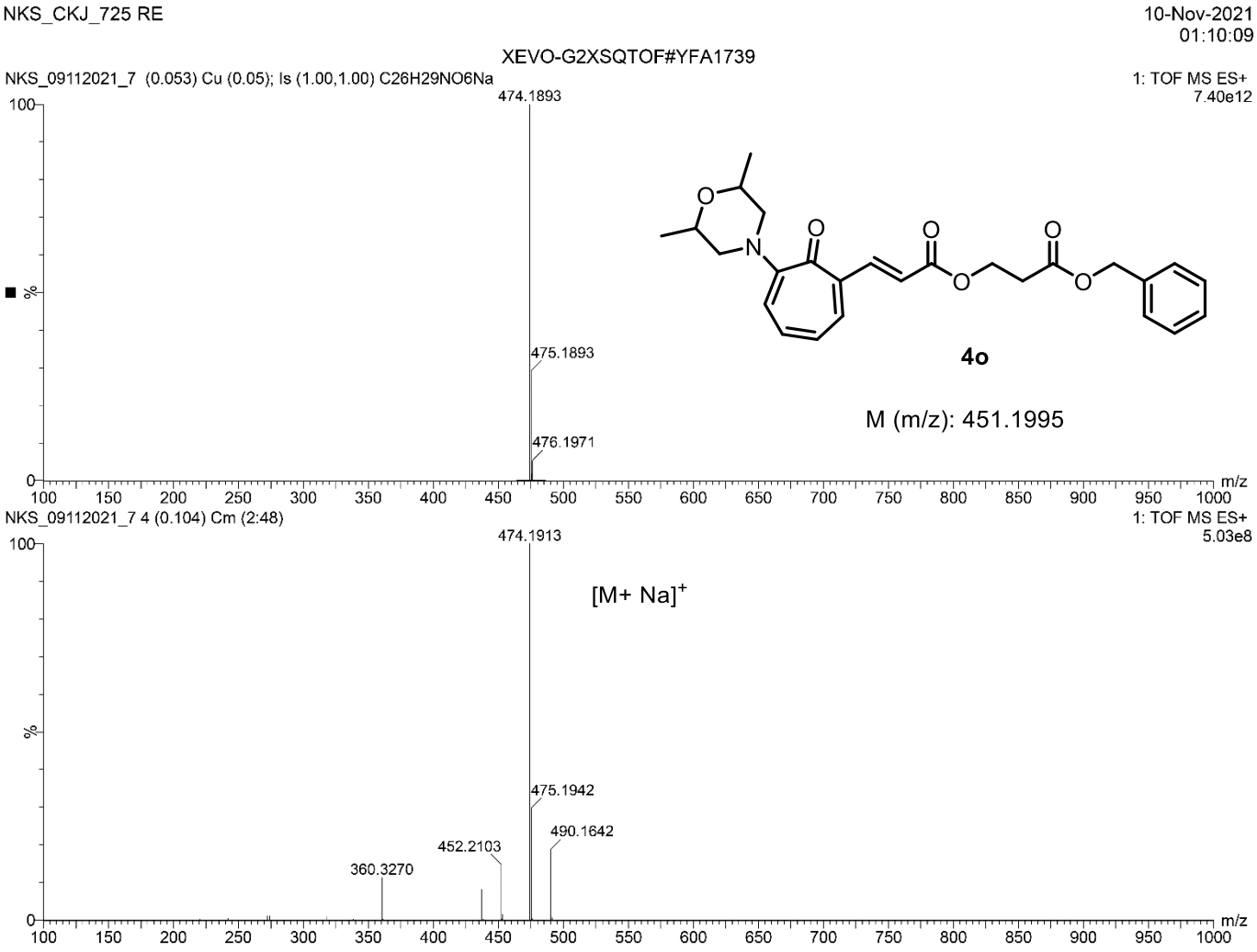


Fig S46. ESI-HRMS spectra of olefinated aminotropone **4o**

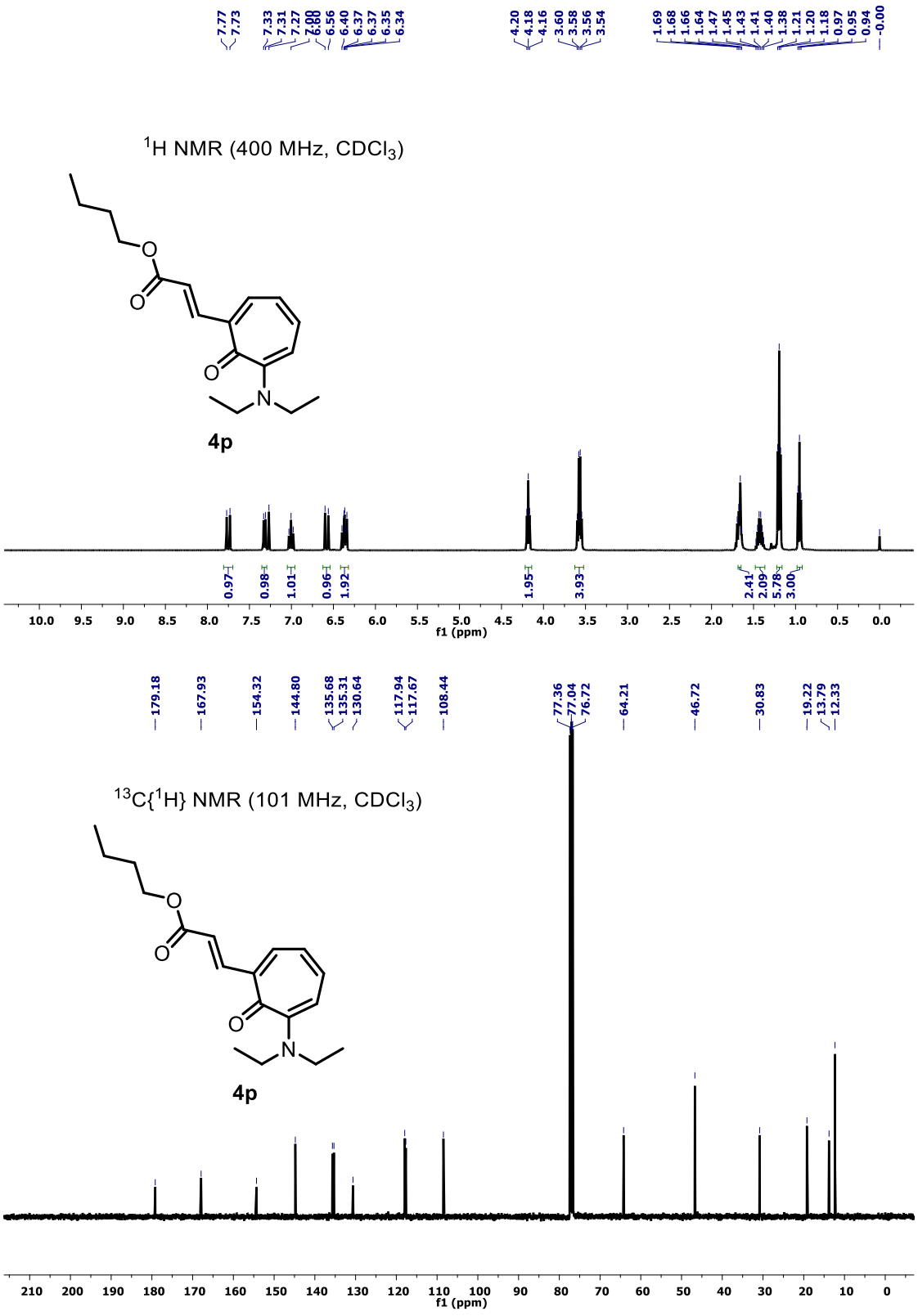


Fig S47. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4p**

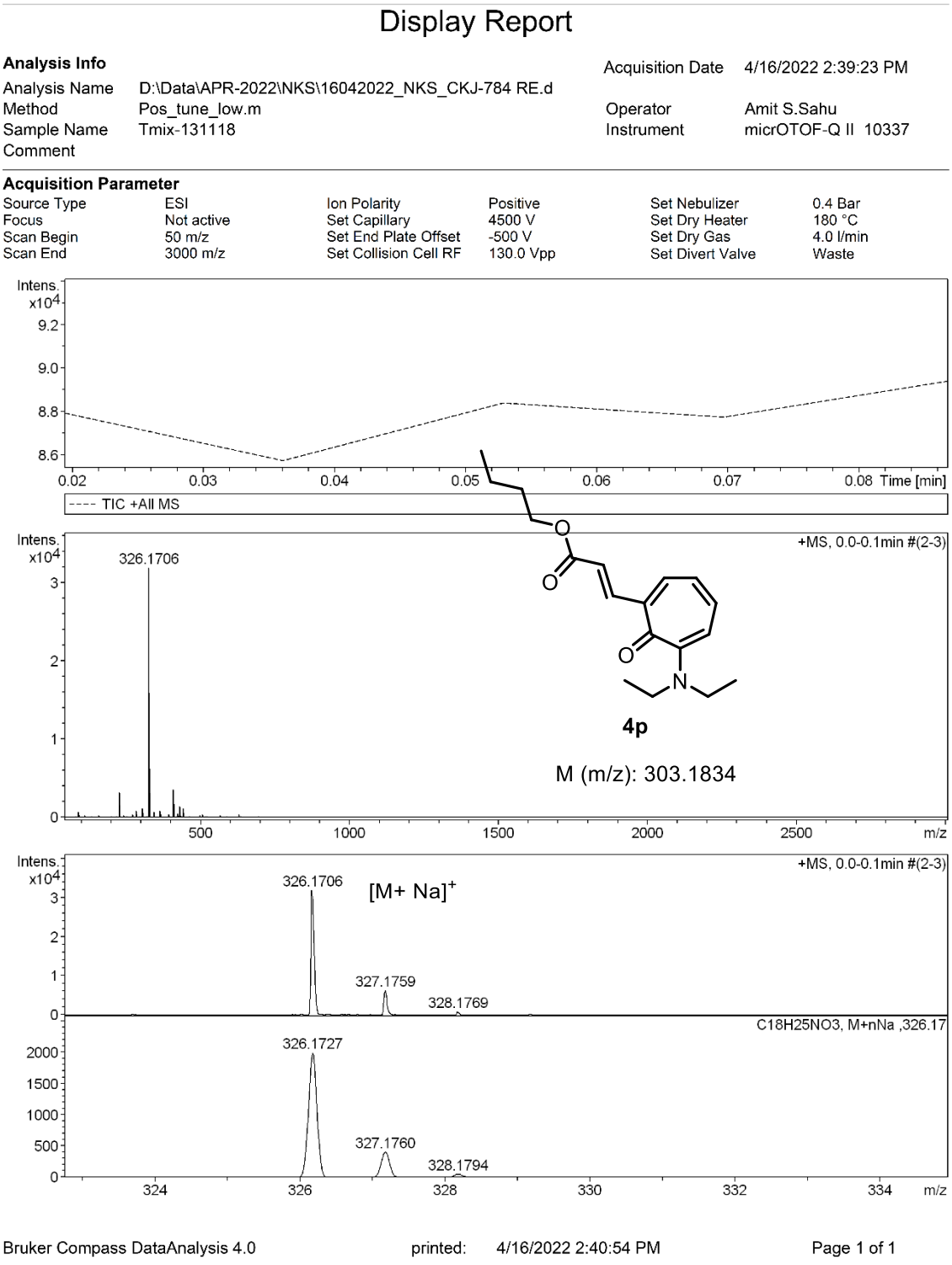


Fig S48. ESI-HRMS spectra of olefinated aminotropone **4p**

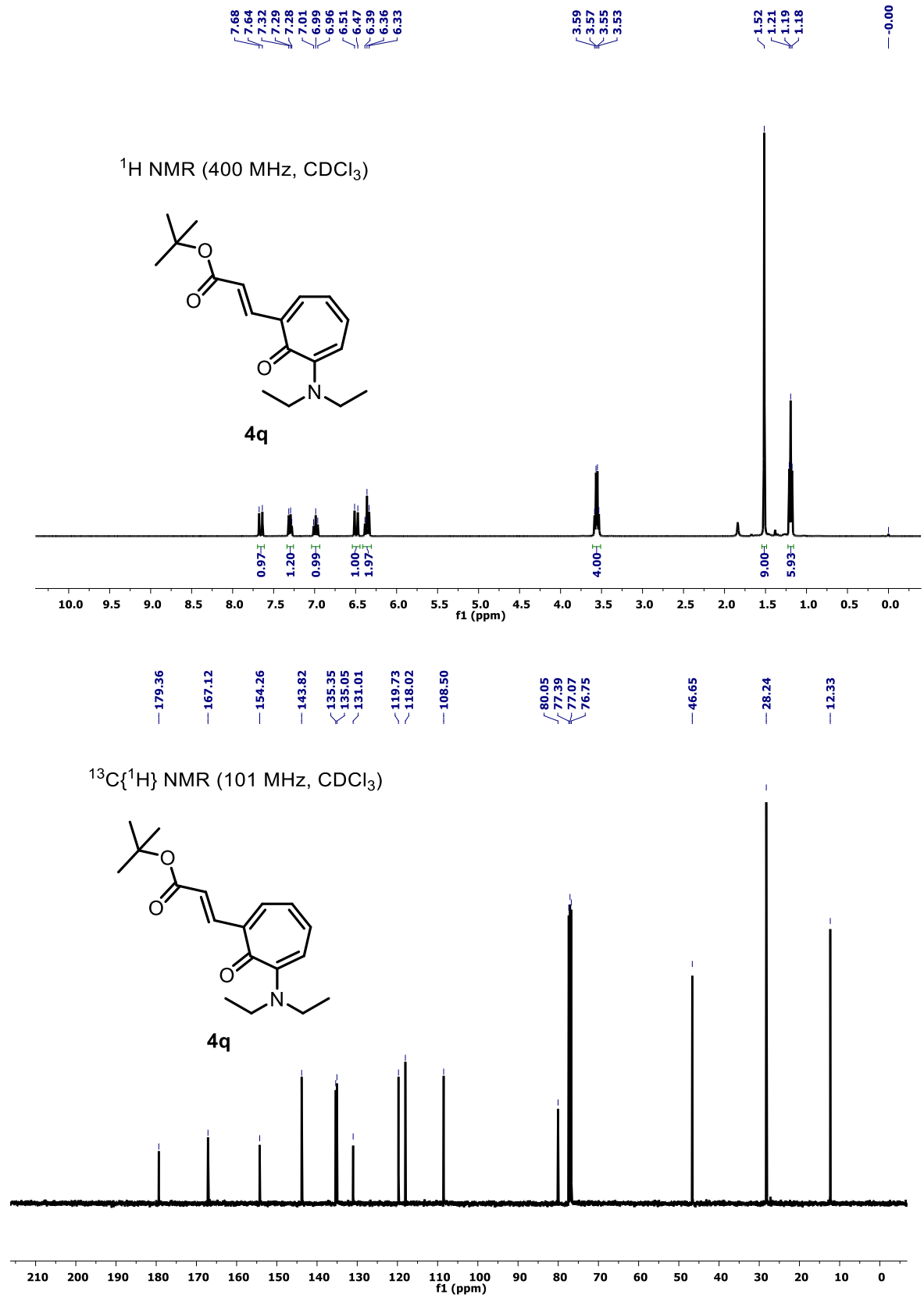


Fig S49. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated aminotropone **4q**

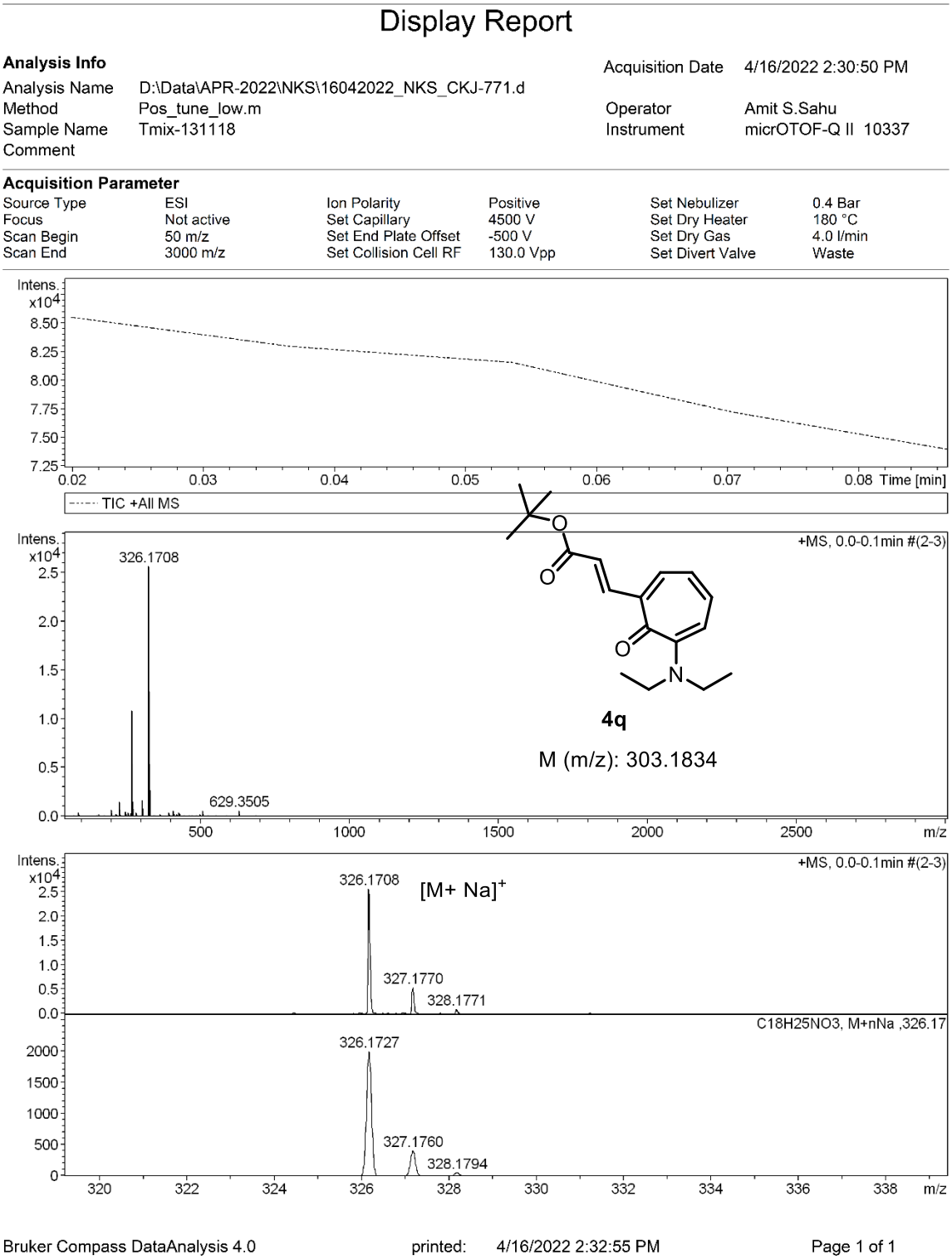


Fig S50. ESI-HRMS spectra of olefinated aminotropone **4q**

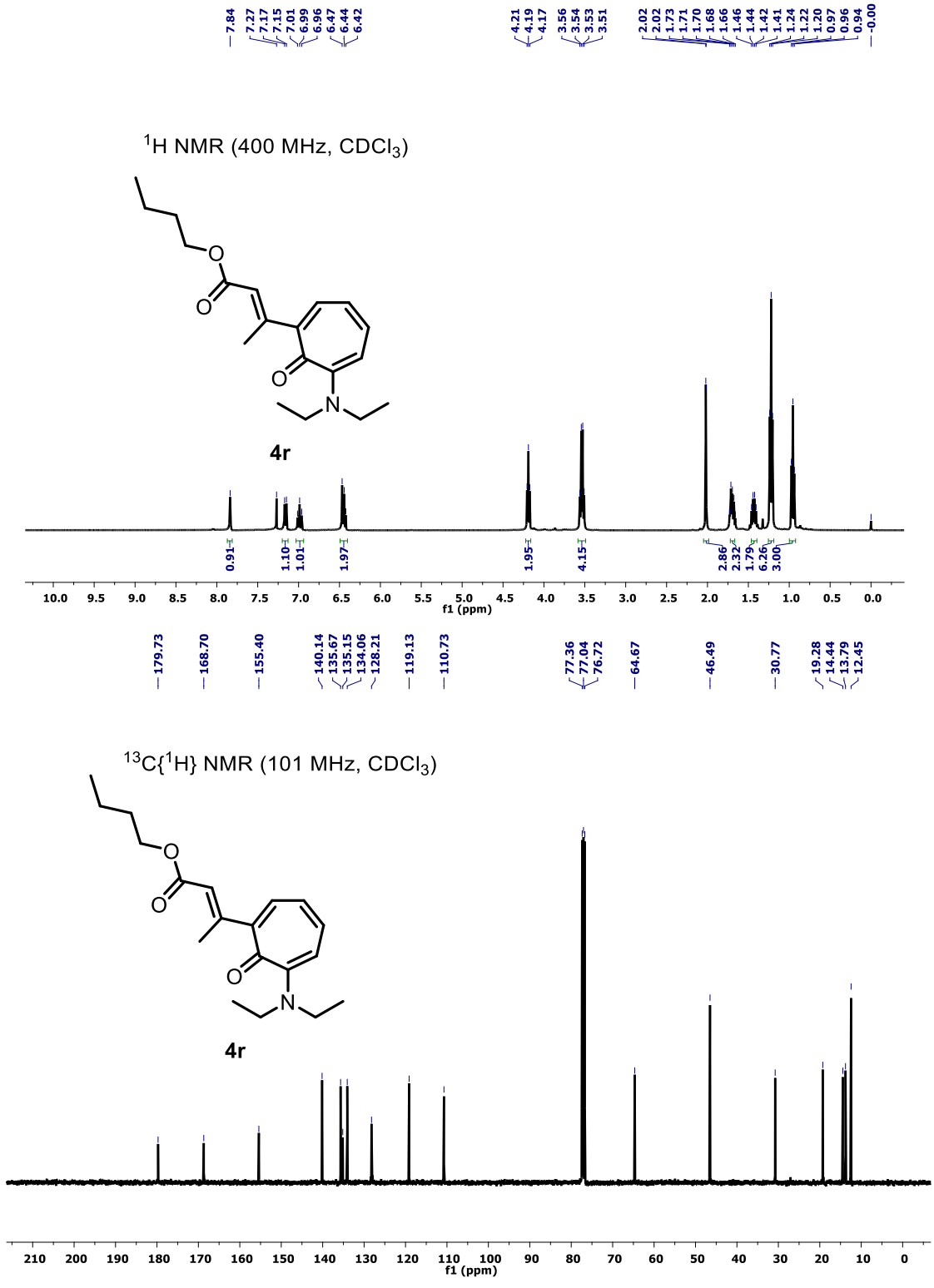


Fig S51. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated aminotropone **4r**

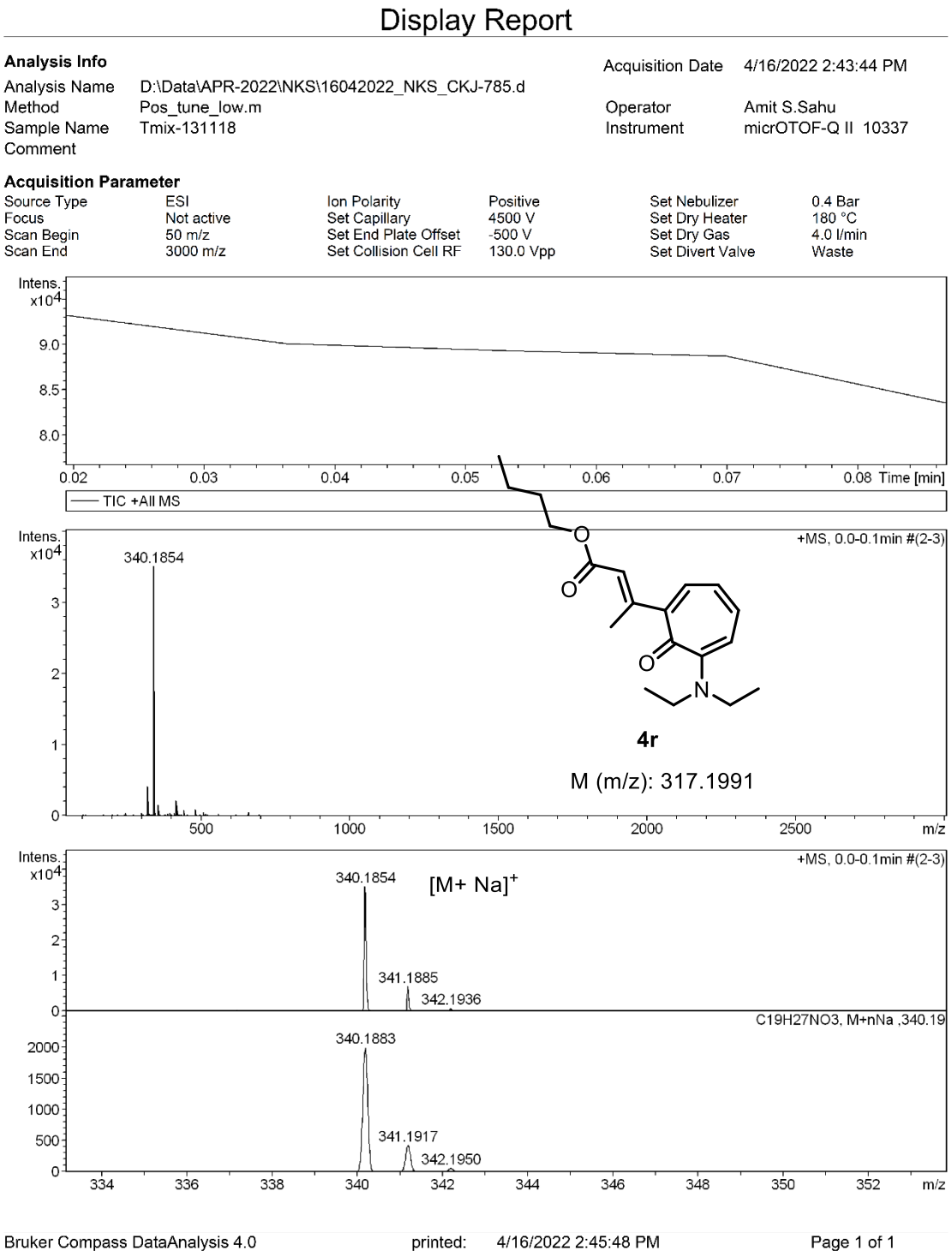


Fig S52. ESI-HRMS spectra of olefinated aminotropone **4r**

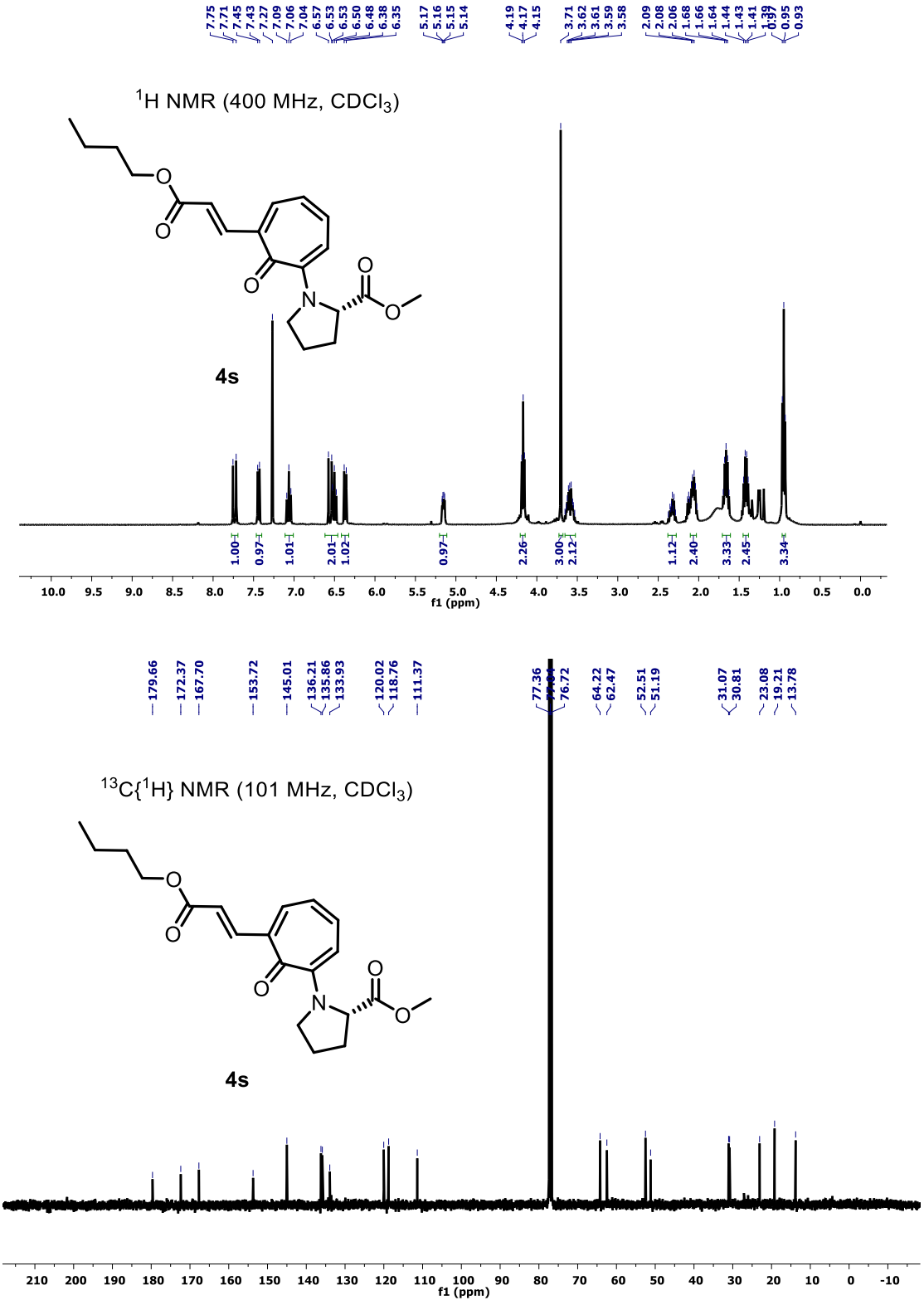


Fig S53. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated troponylproline ester **4s**

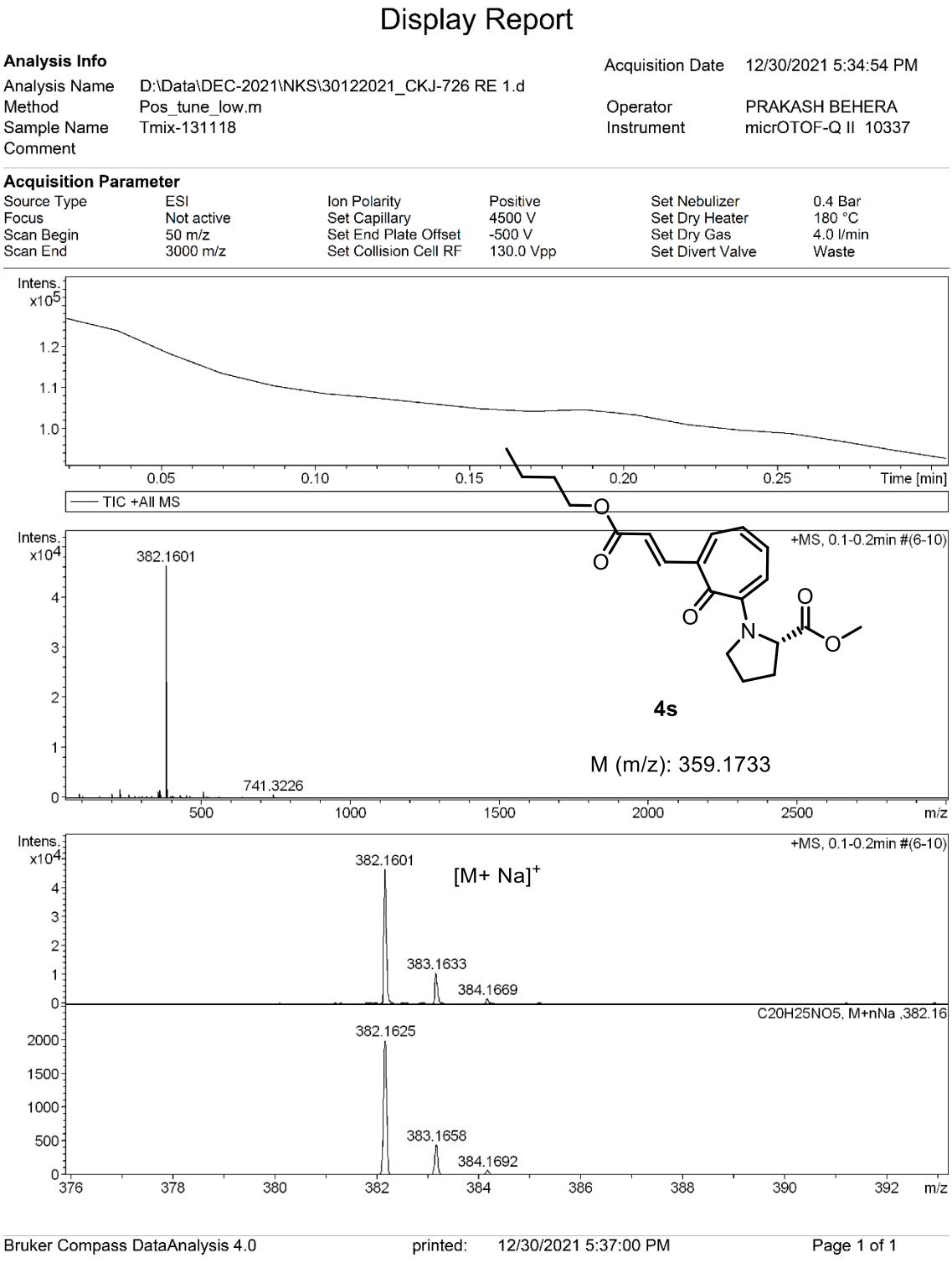


Fig S54. ESI-HRMS spectra of olefinated troponylproline ester **4s**

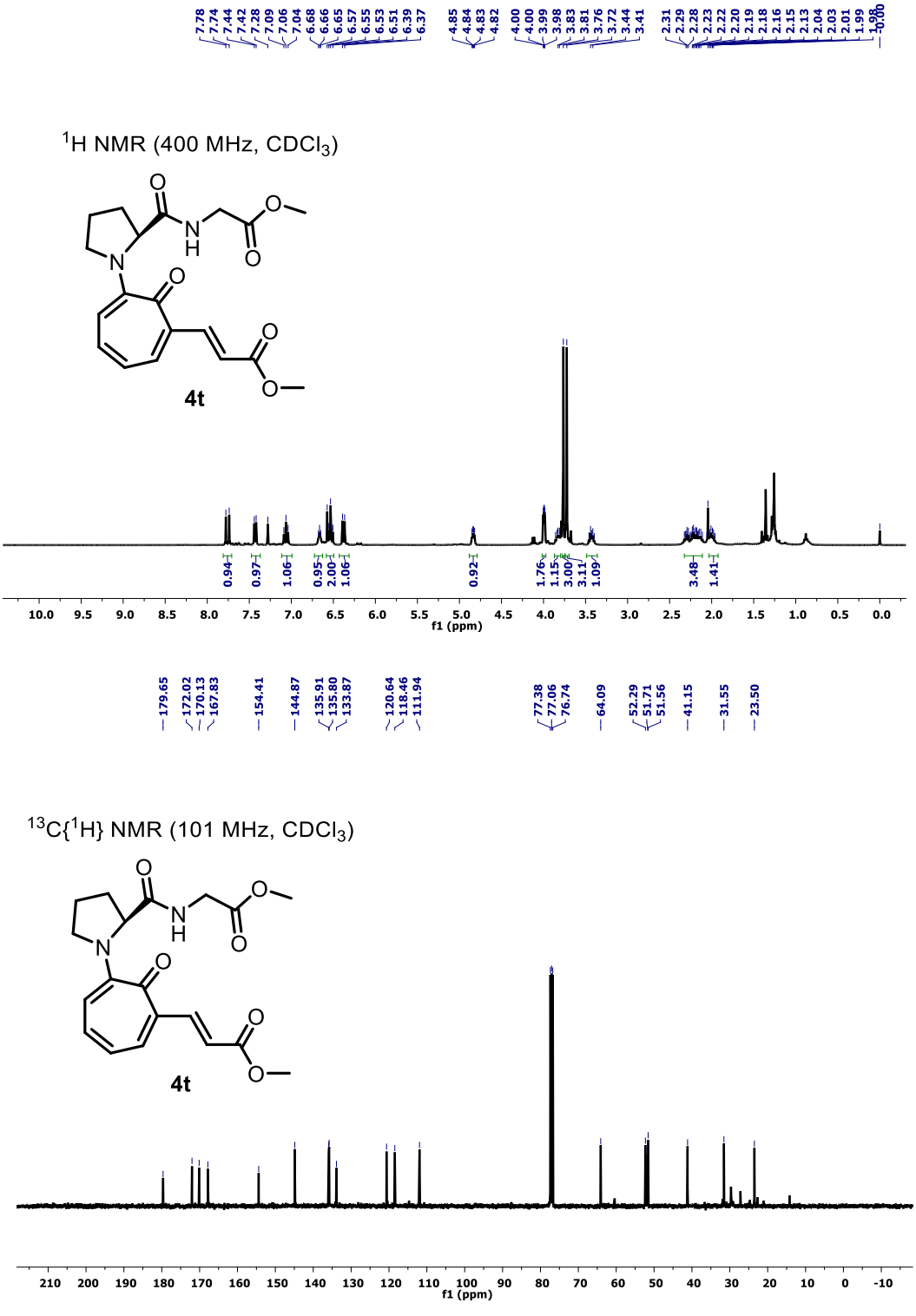


Fig S55. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated troponyl *di*- peptide **4t**

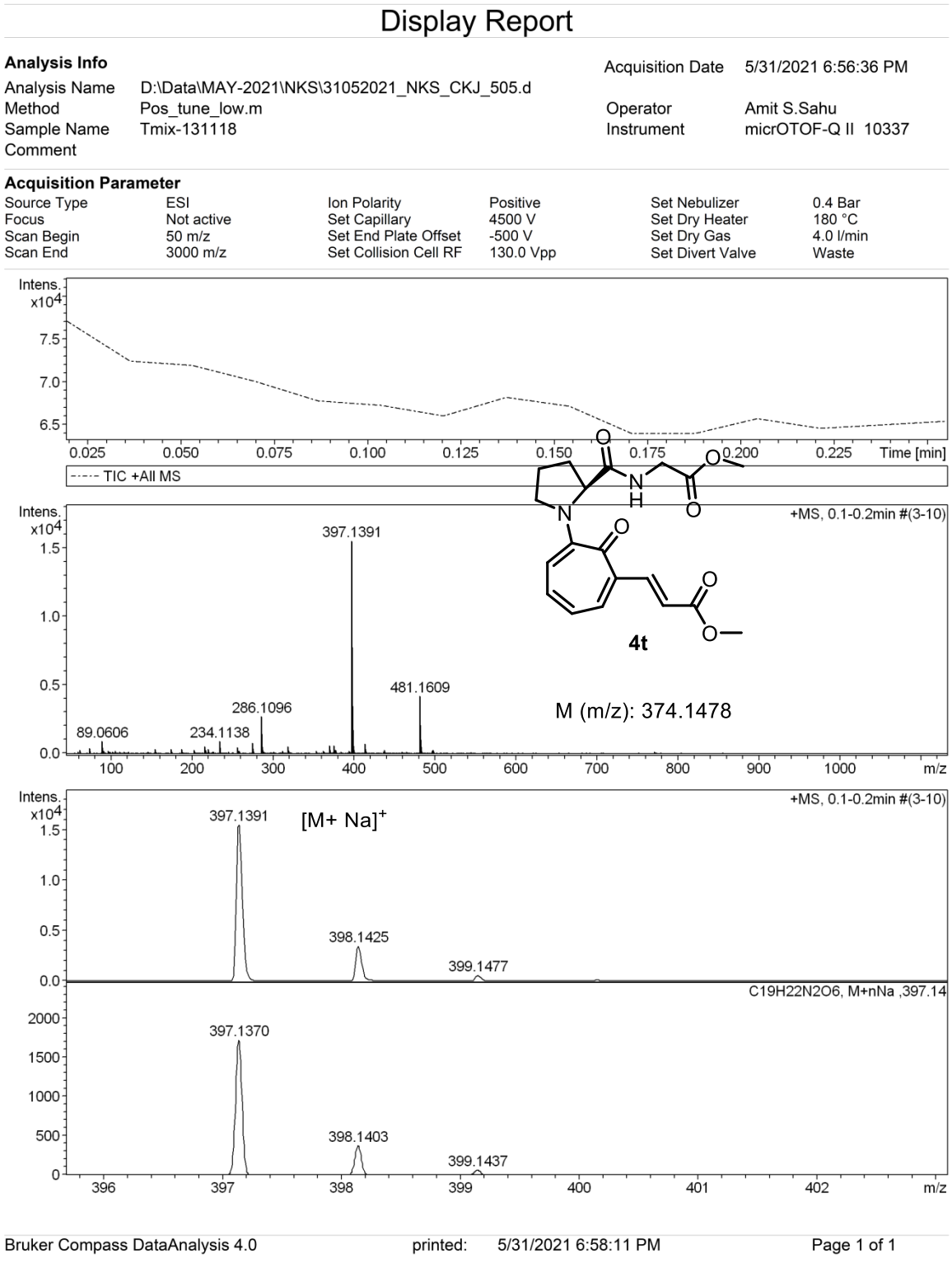


Fig S56. ESI-HRMS spectra of olefinated troponyl *di*- peptide **4t**

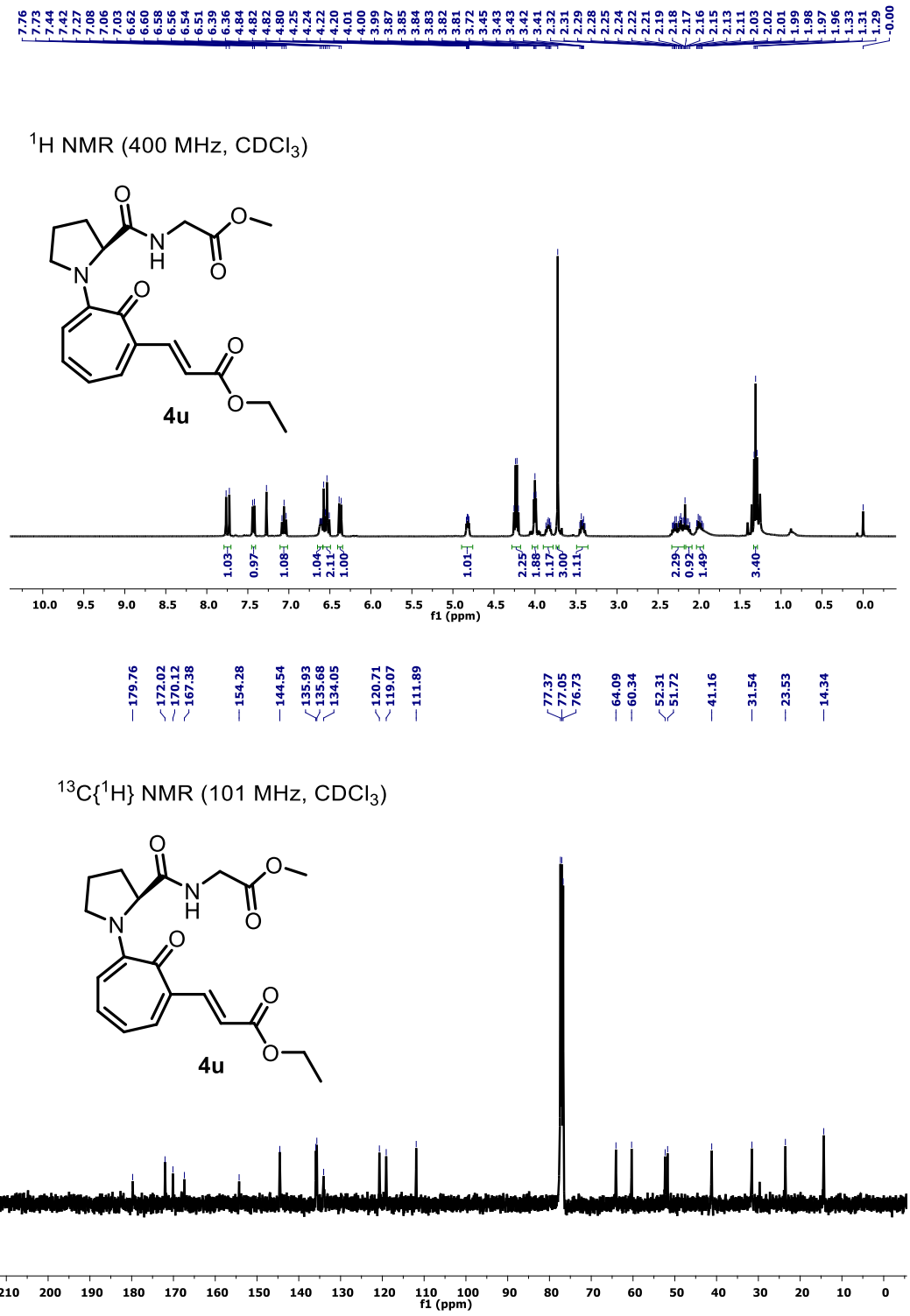


Fig S57. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated troponyl *di*- peptide **4u**

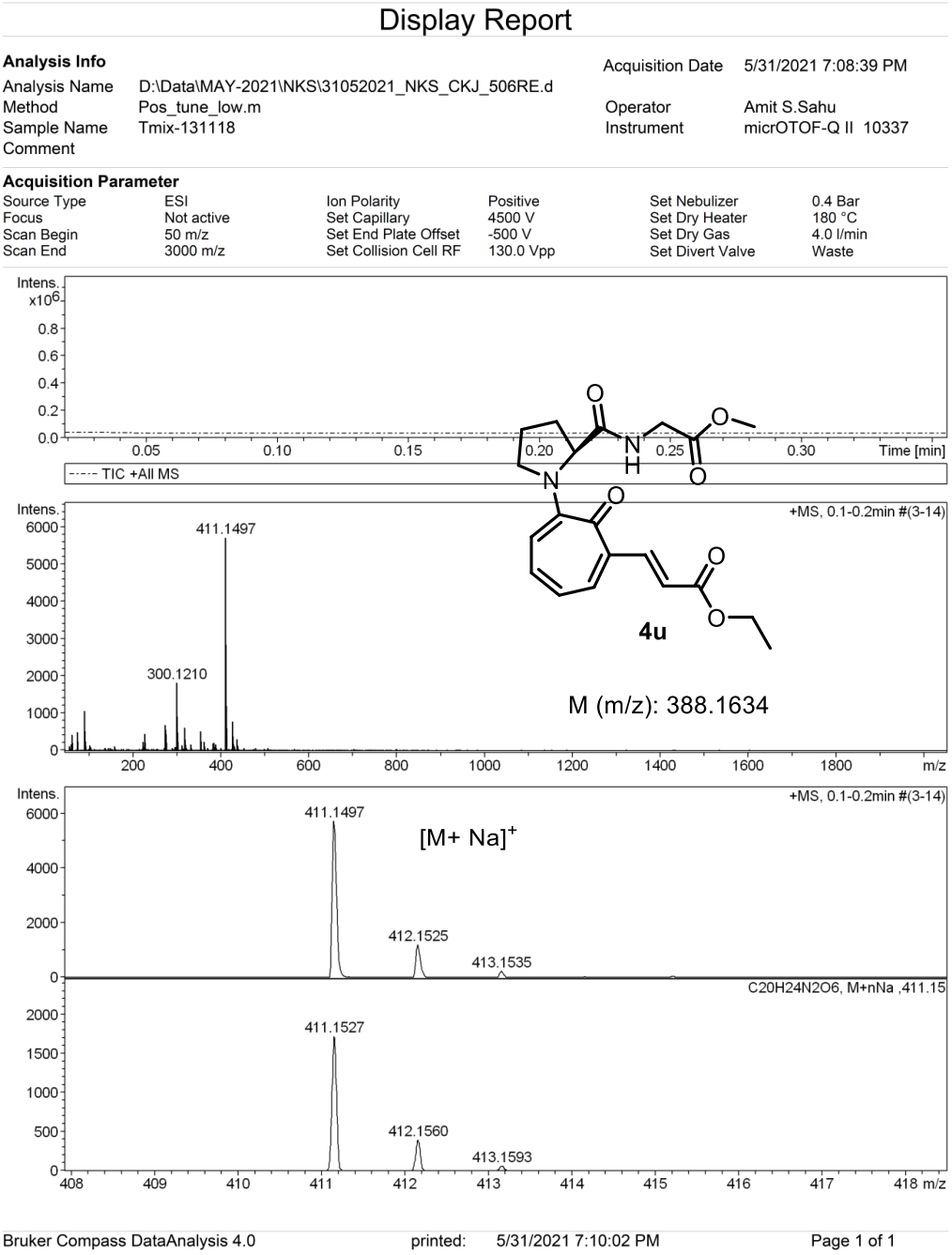


Fig S58. ESI-HRMS spectra of olefinated troponyl *di*- peptide **4u**

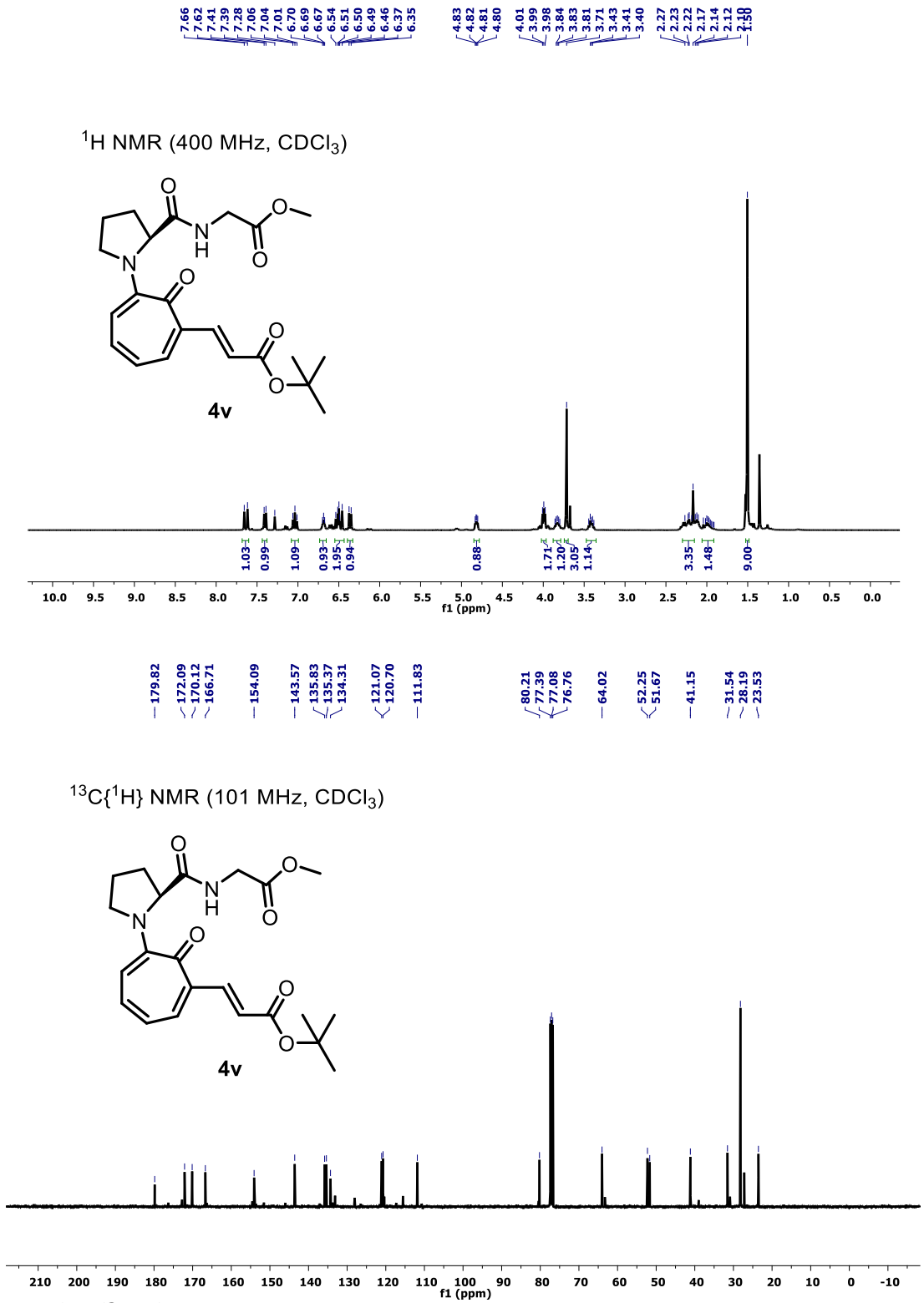


Fig S59. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated troponyl *di*- peptide **4v**

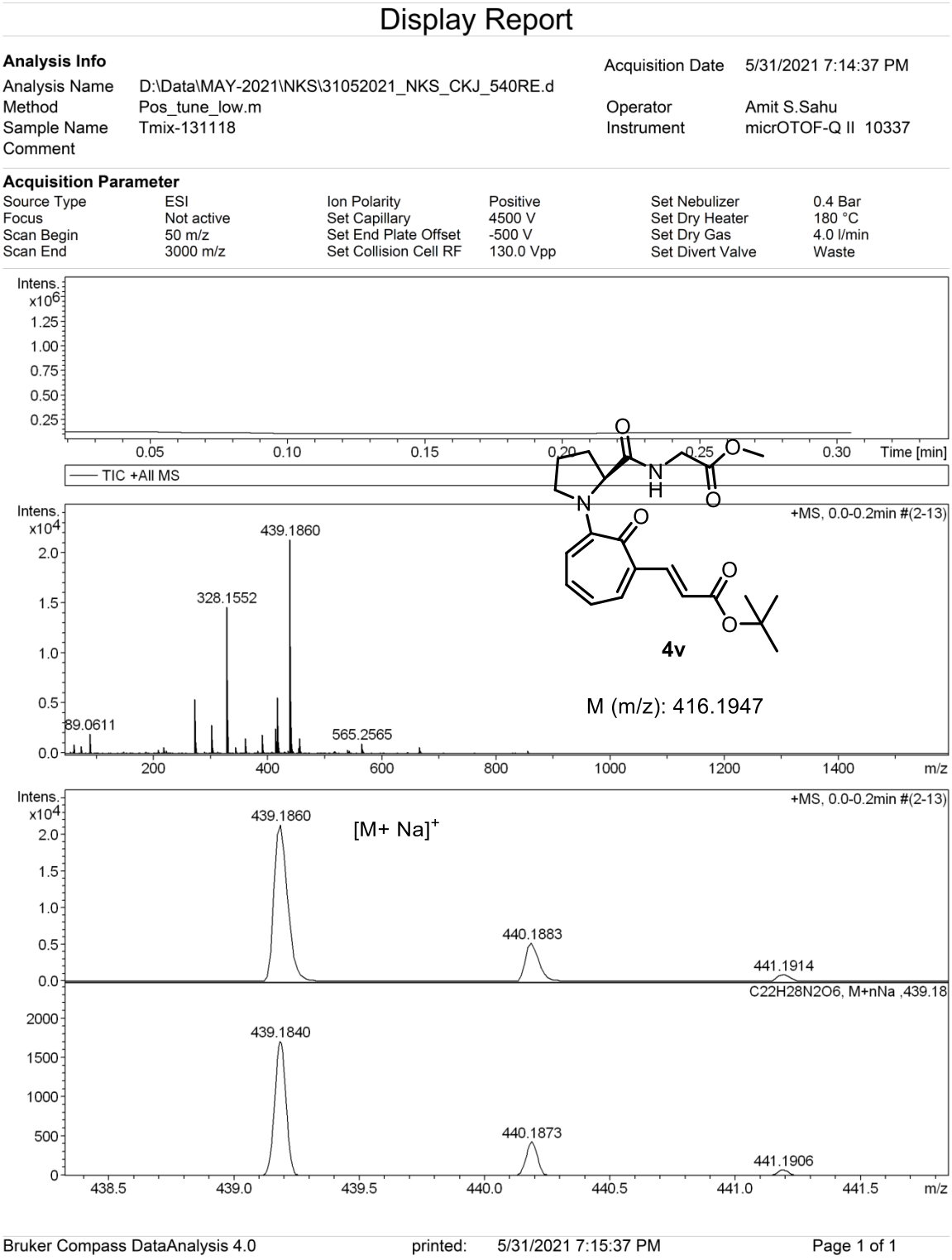


Fig S60. ESI-HRMS spectra of olefinated troponyl *di*- peptide **4v**

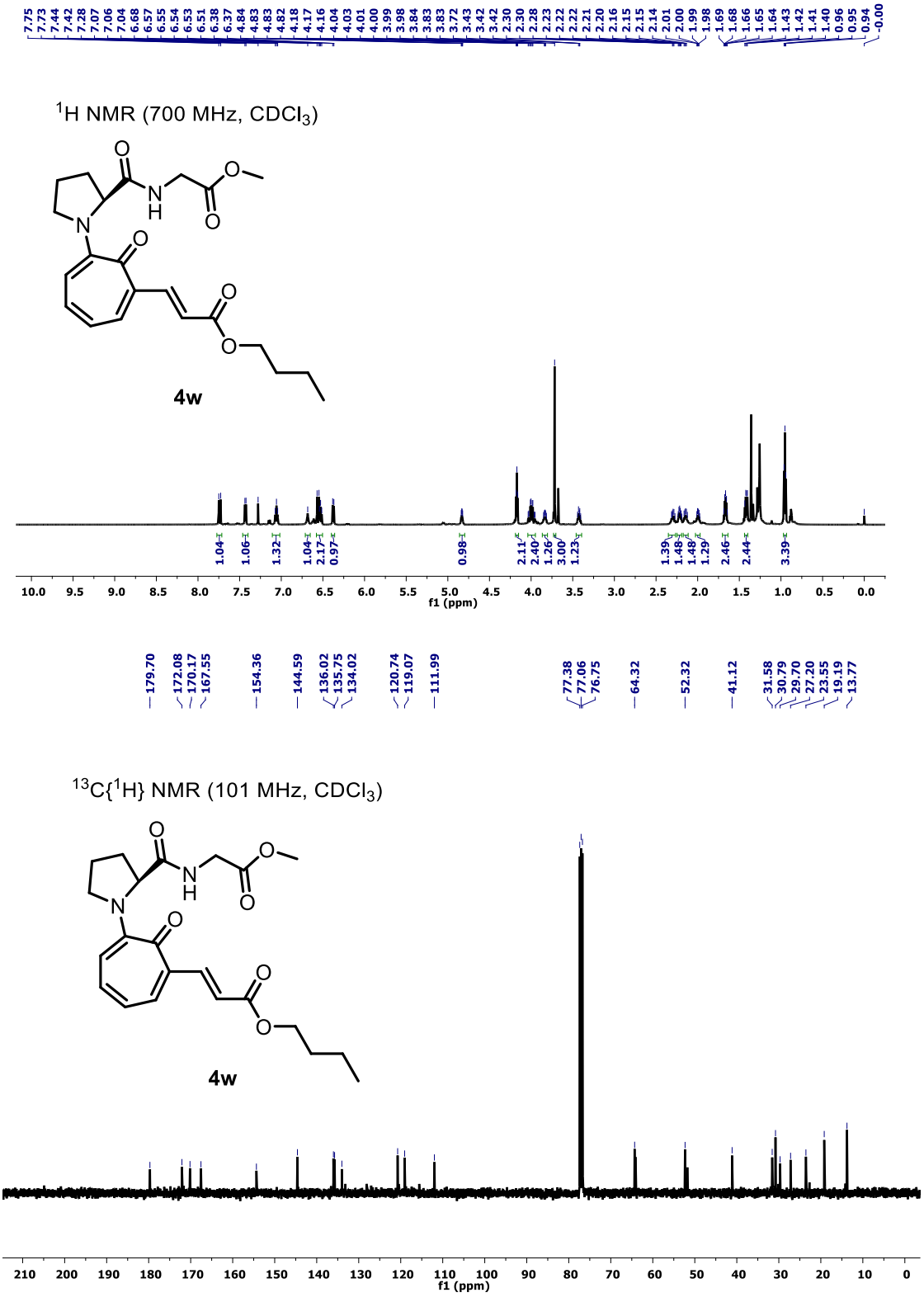


Fig S61. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefinated troponyl *di*- peptide **4w**

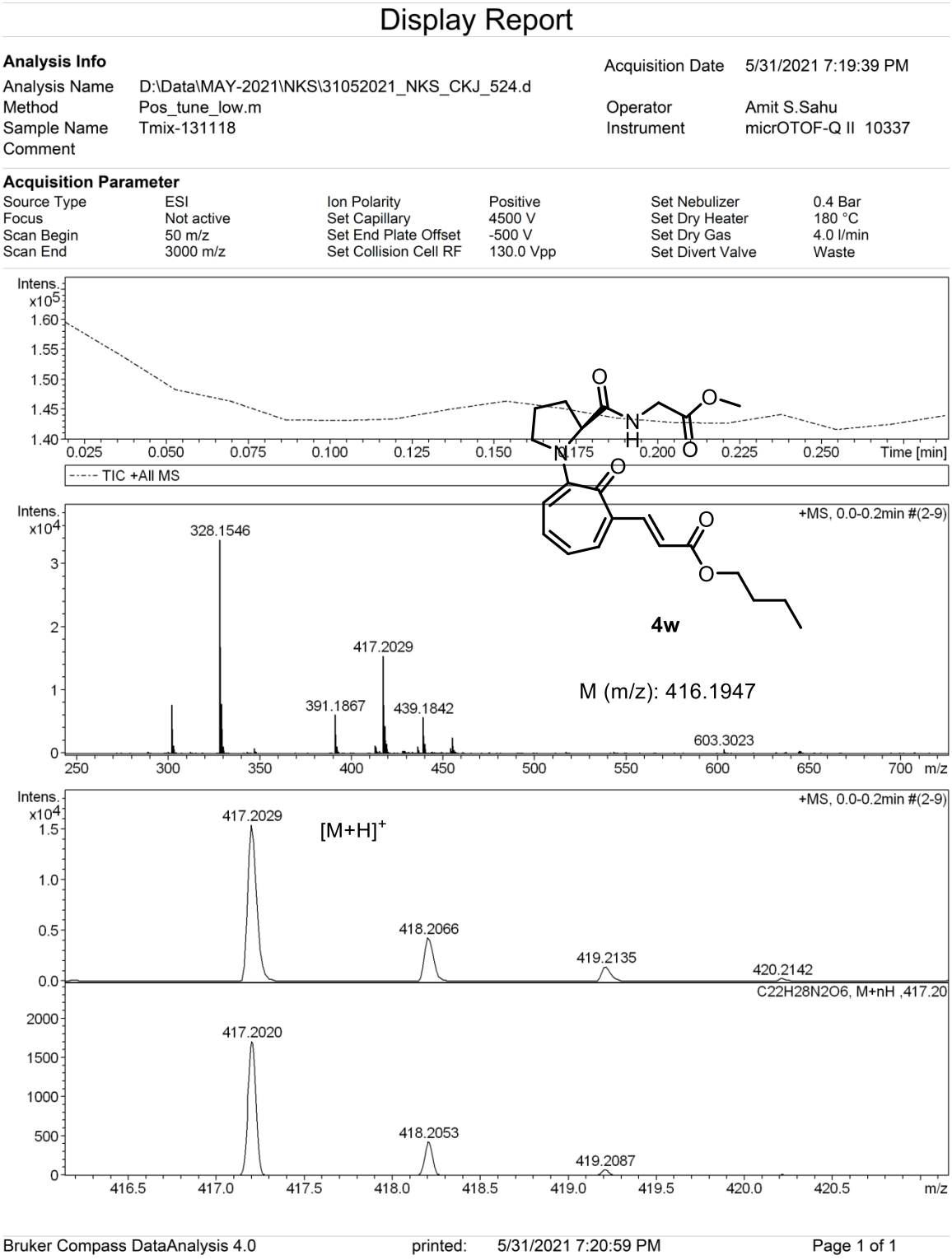


Fig S62. ESI-HRMS spectra of olefinated troponyl *di*- peptide **4w**

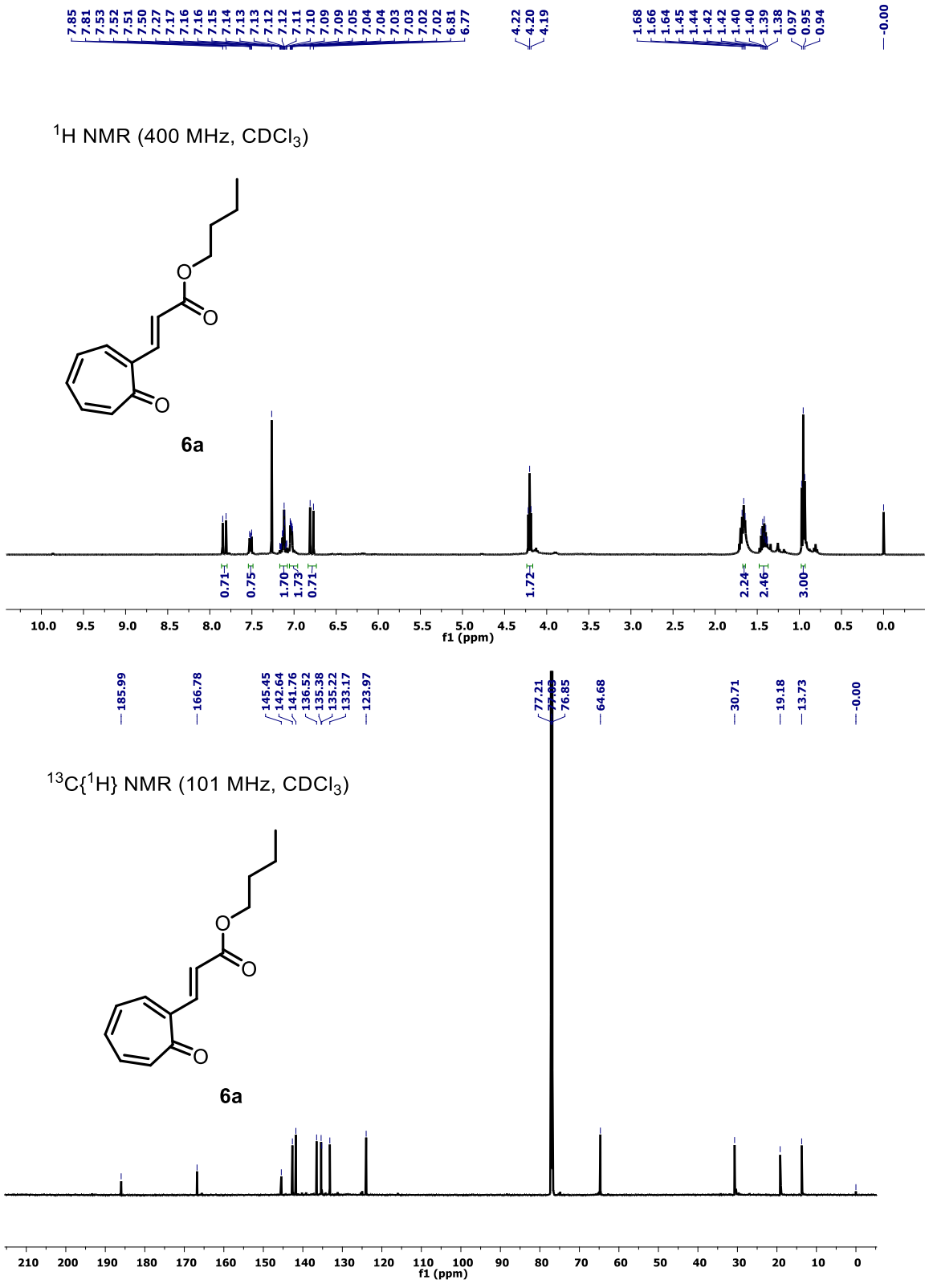


Fig S63. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated tropone **6a**

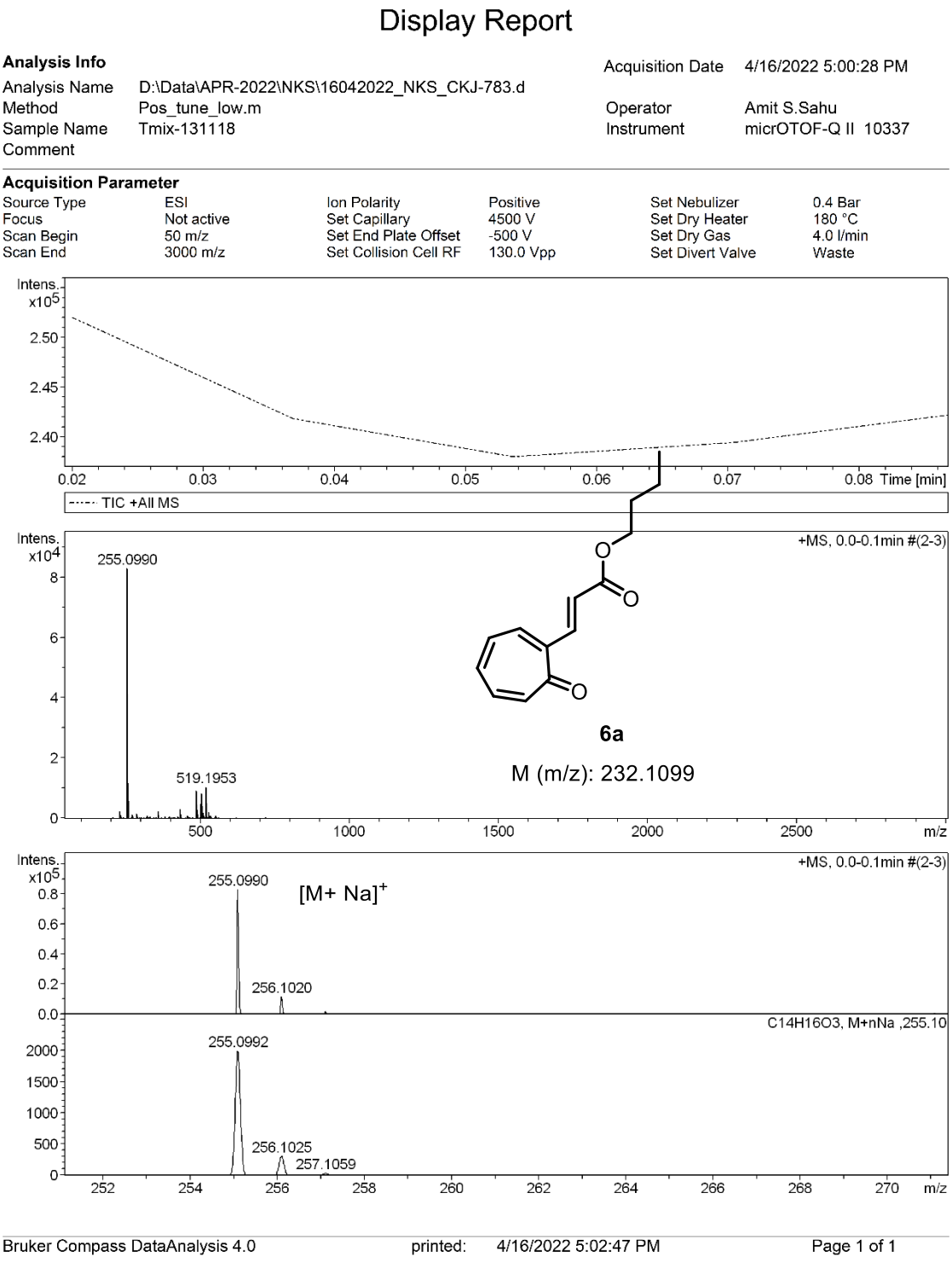


Fig S64. ESI-HRMS spectra of olefinated tropone **6a**

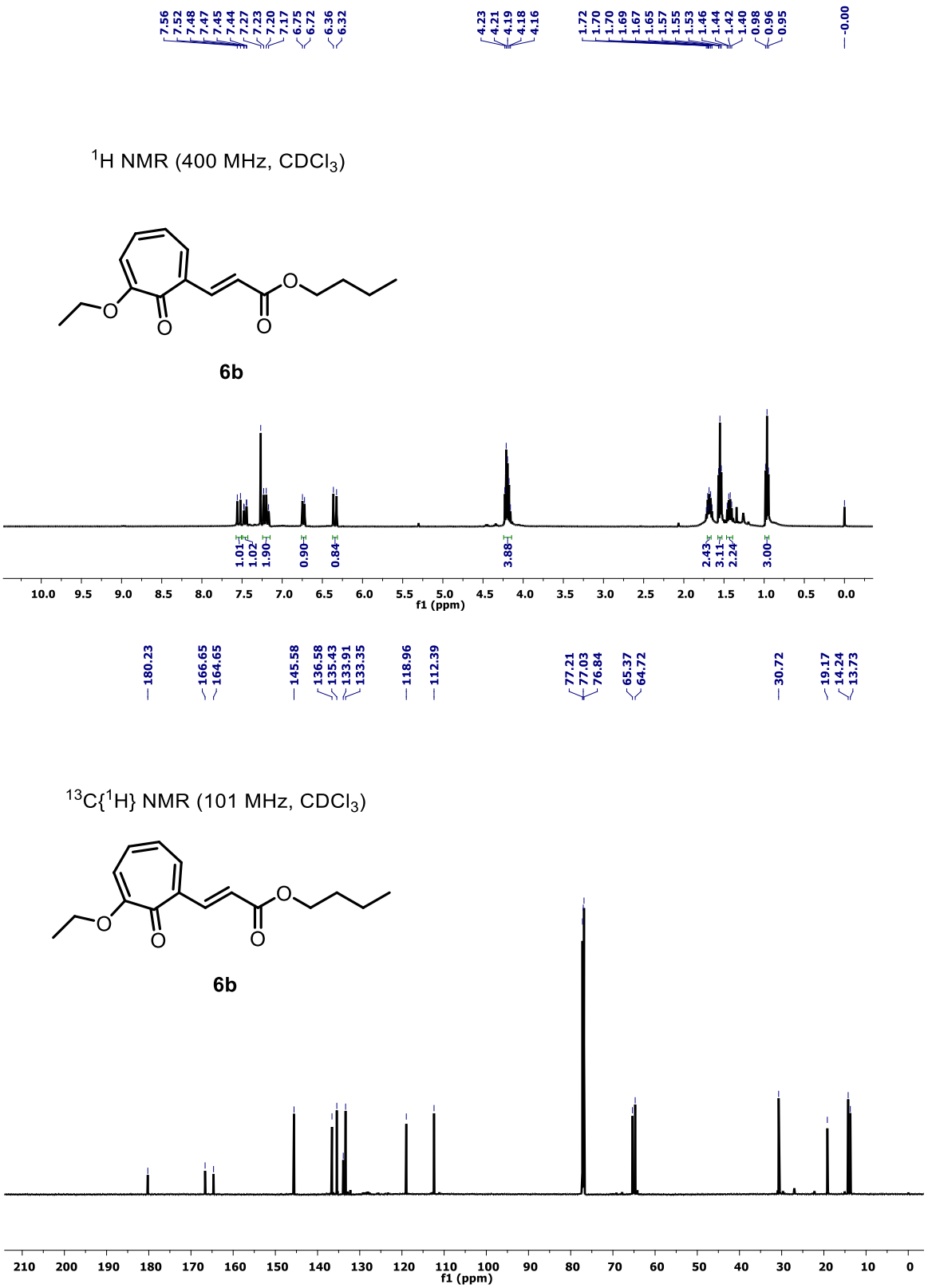


Fig S65. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefinated ethoxy tropone **6b**

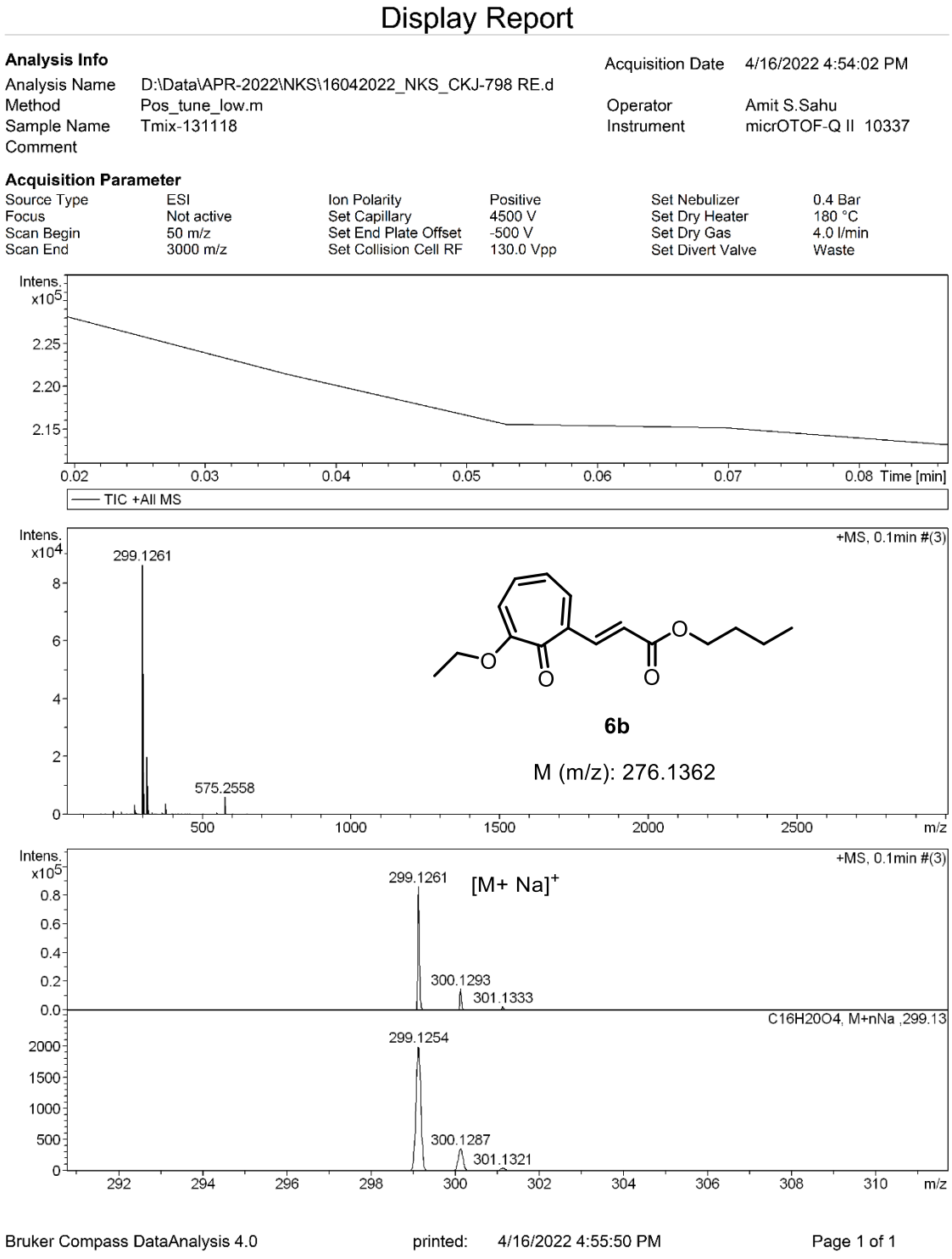


Fig S66. ESI-HRMS spectra of olefinated ethoxy tropone **6b**

5. NMR and Mass spectra of Olefins (Coupling Partners) (**3e/ 3f/ 3g)**

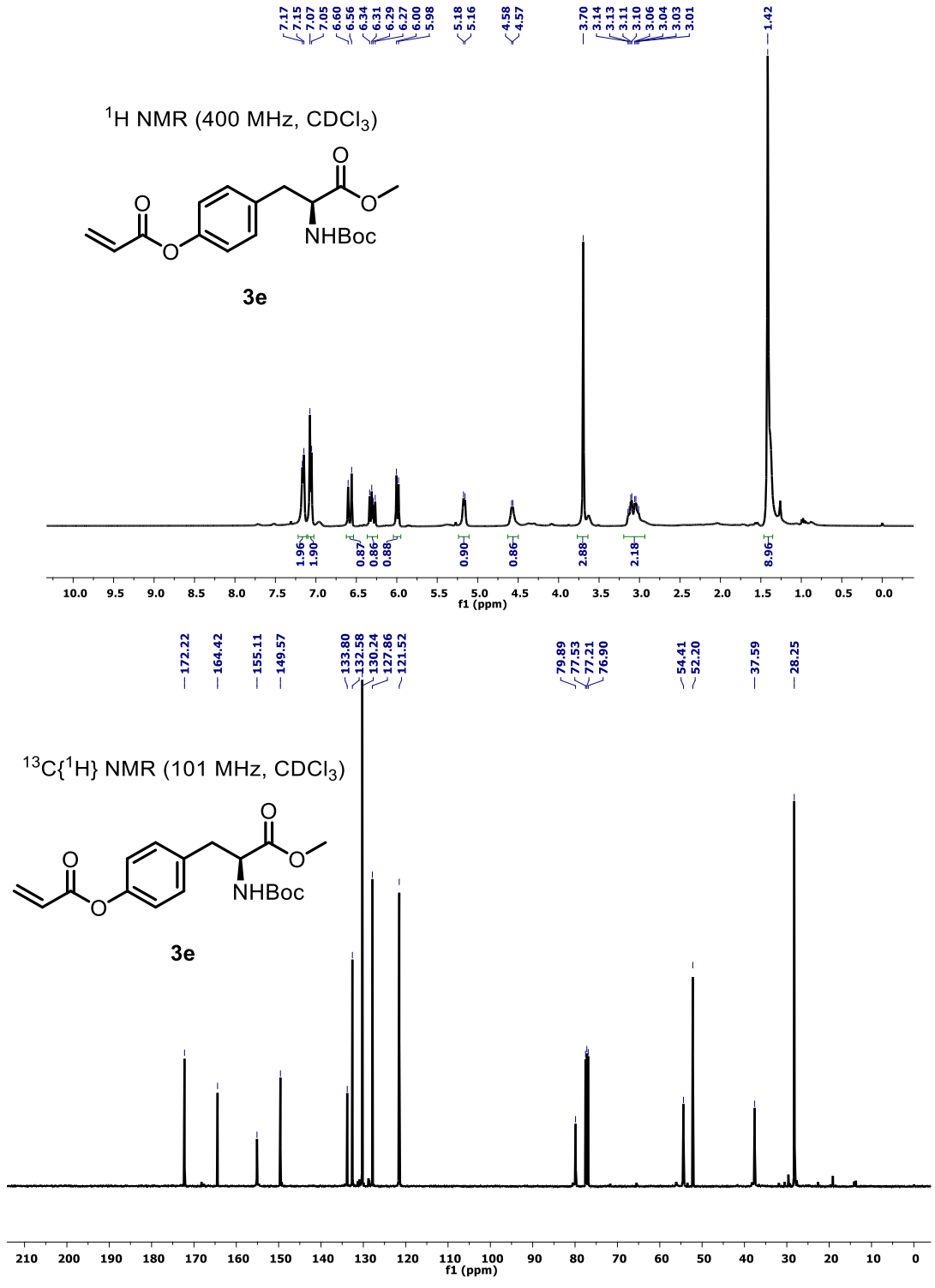


Fig S67. ^{1}H, ^{13}C {^{1}H} NMR spectra of olefin- modified Tyrosine **3e**

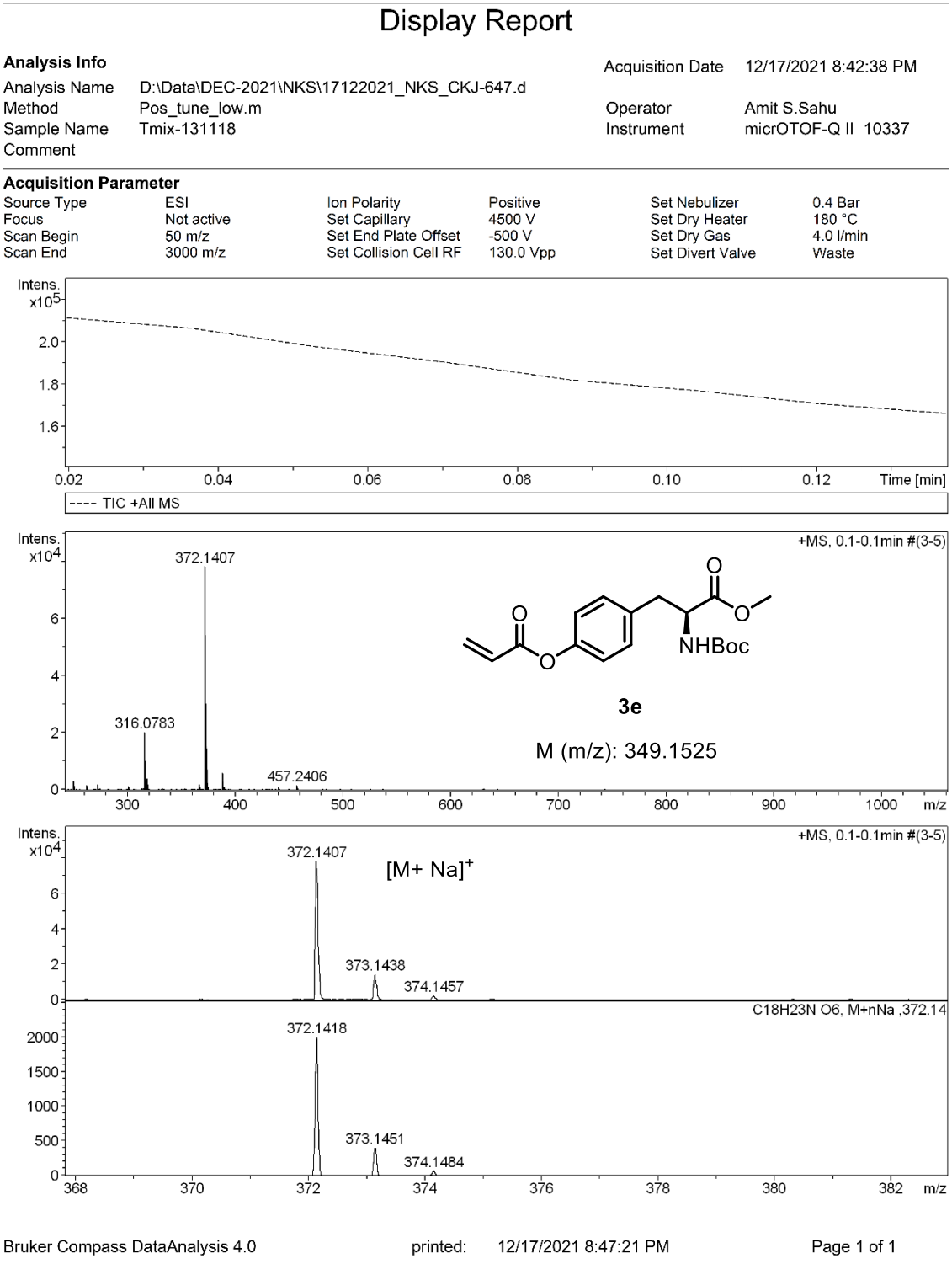


Fig S68. ESI-HRMS spectra of olefin- modified Tyrosine **3e**

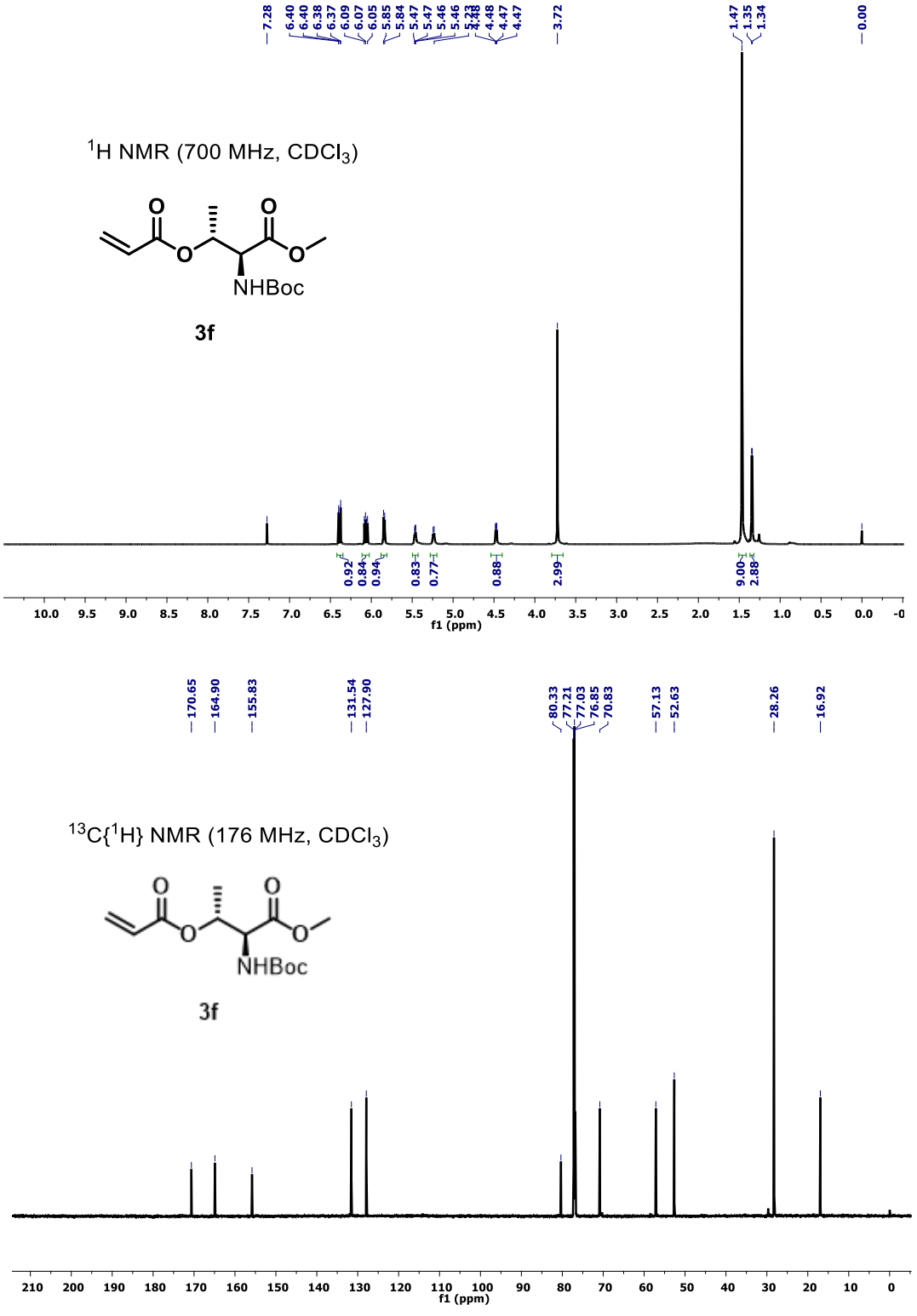


Fig S69. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefin- modified Threonine **3f**

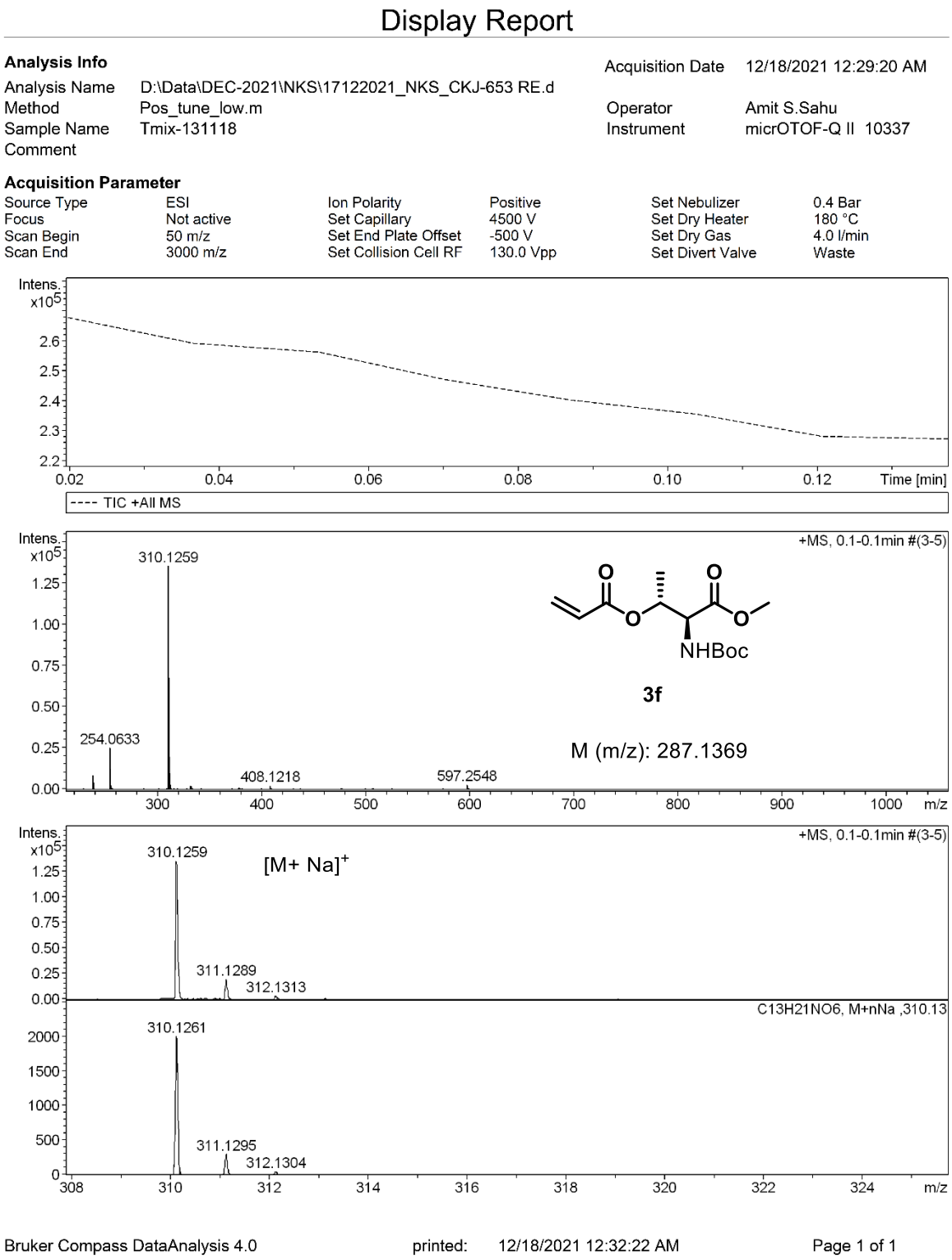


Fig S70. ESI-HRMS spectra of olefin- modified Threonine **3f**

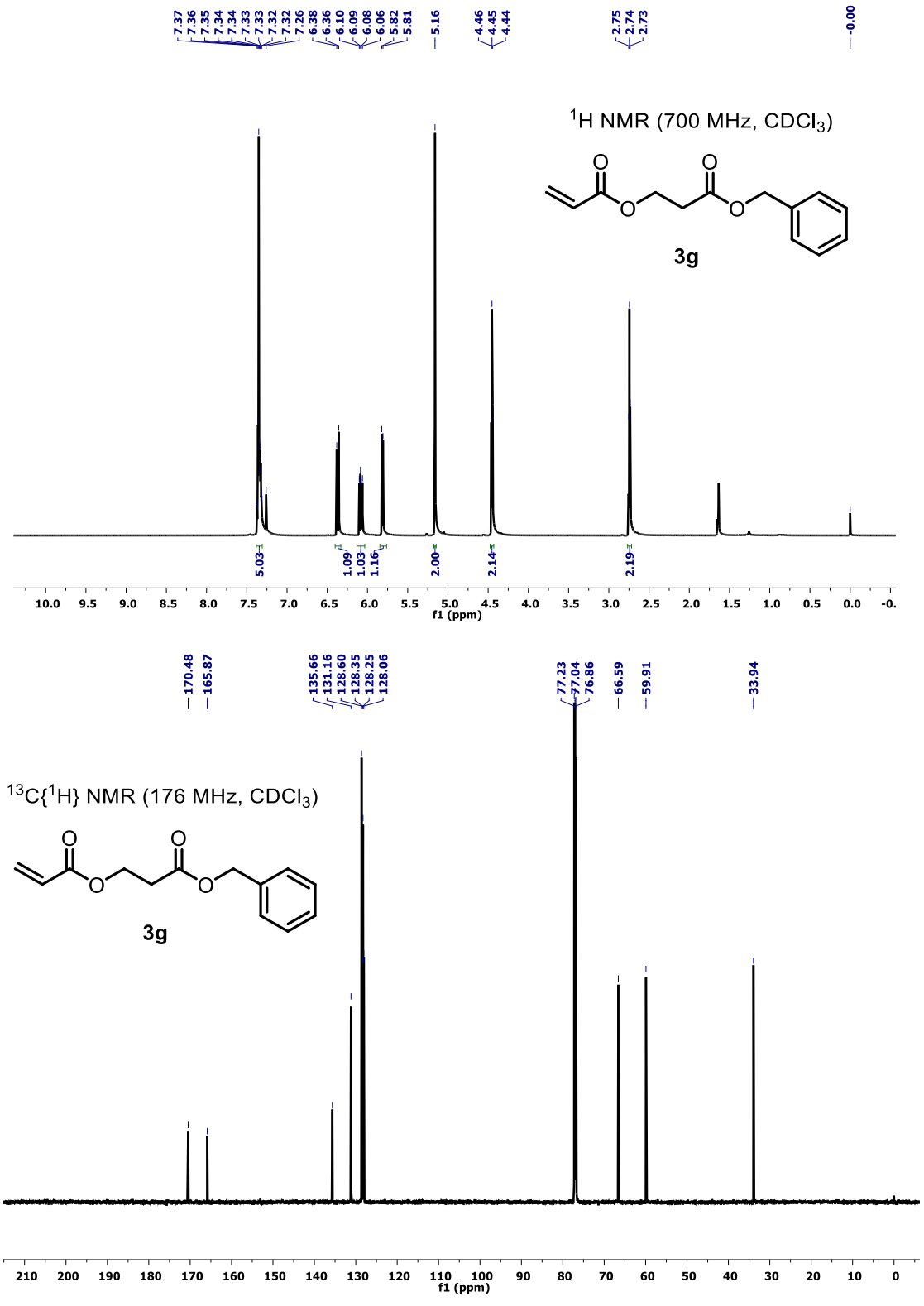


Fig S71. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of olefin (Coupling partner) **3g**

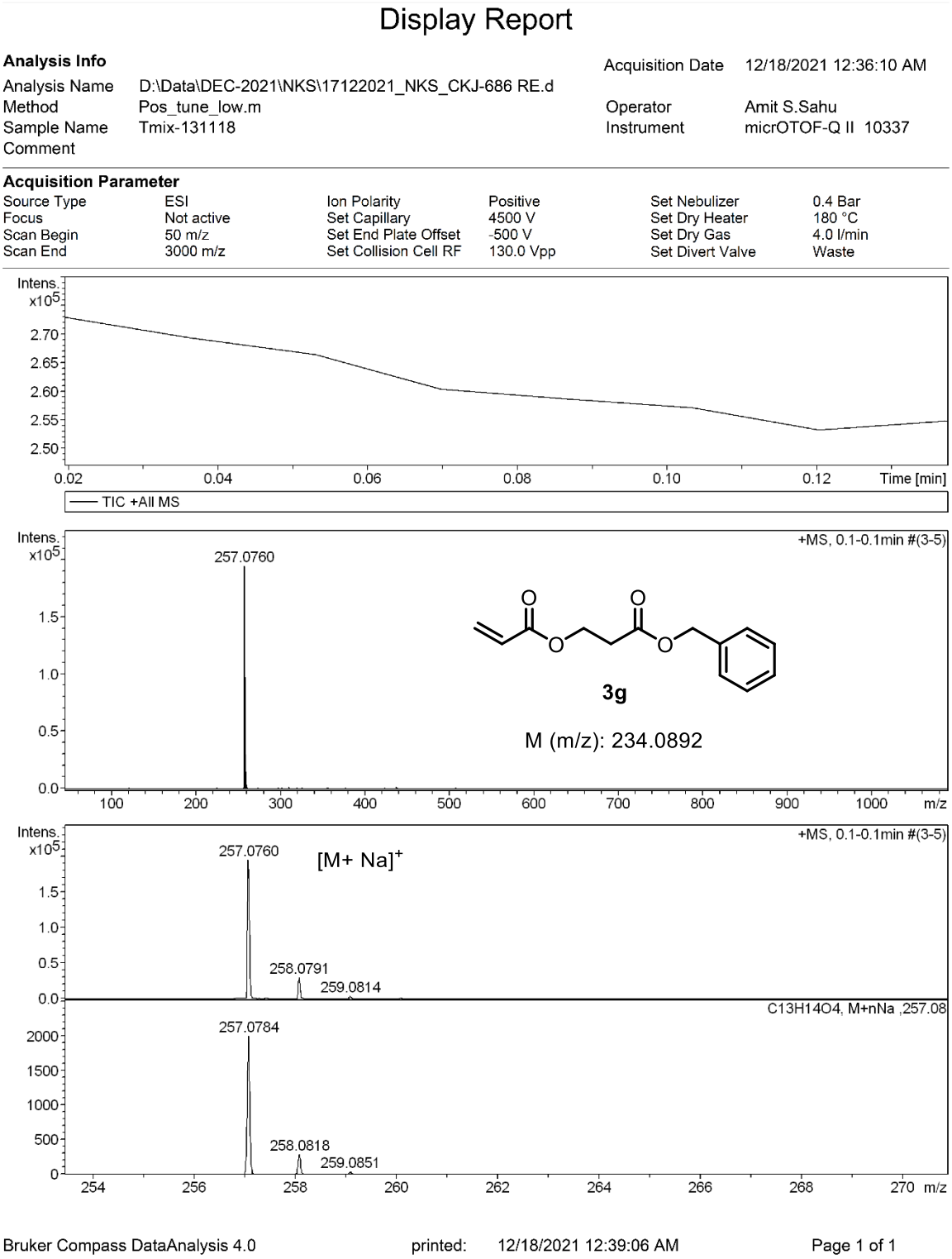


Fig S72. ESI-HRMS spectra of olefin (Coupling partner) **3g**

6. NMR and Mass spectra of Acetoxylated aminotropones (**7a**/ **7b**/ **7c**)

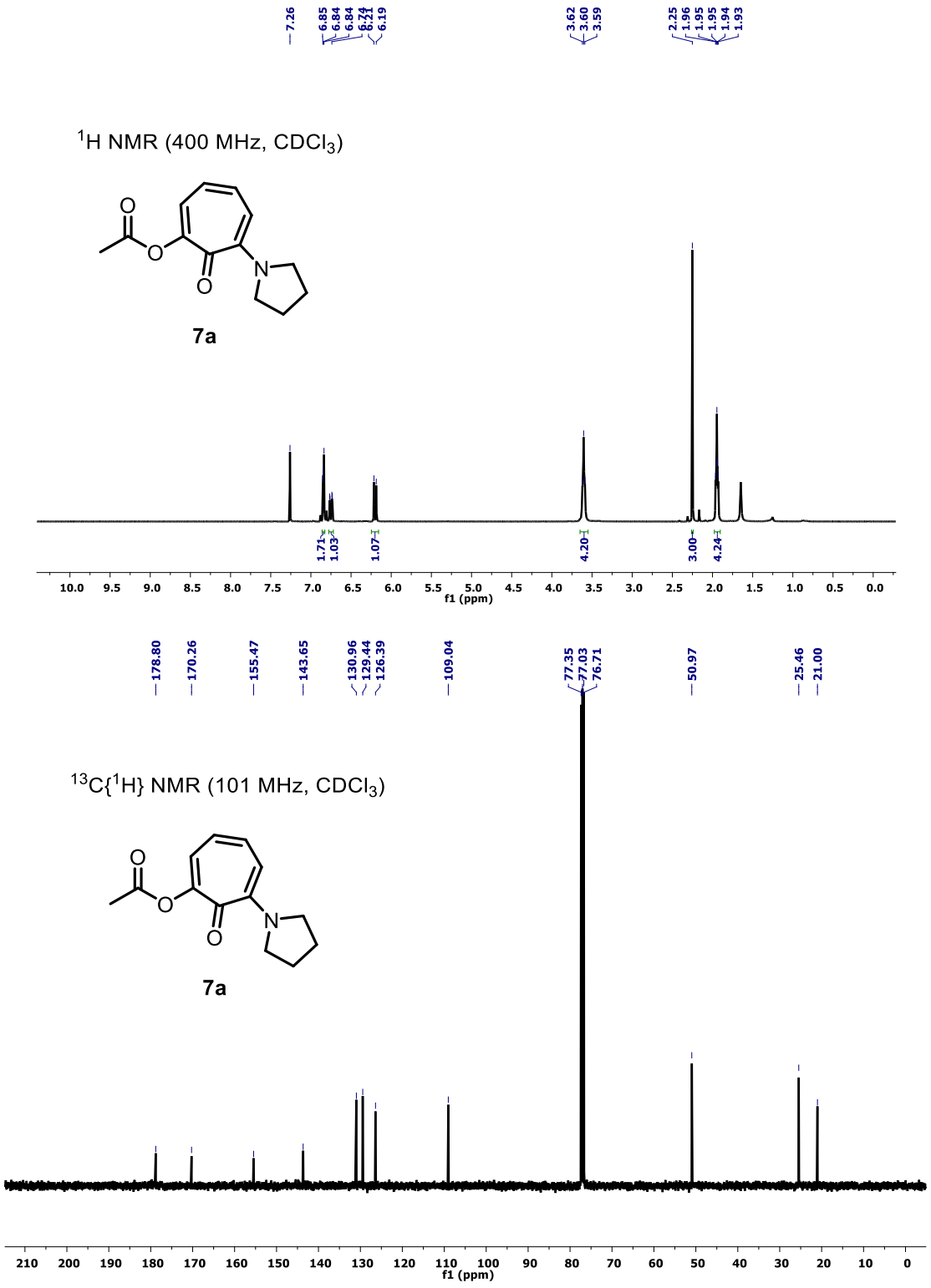


Fig S73. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of acetoxylated aminotropone **7a**

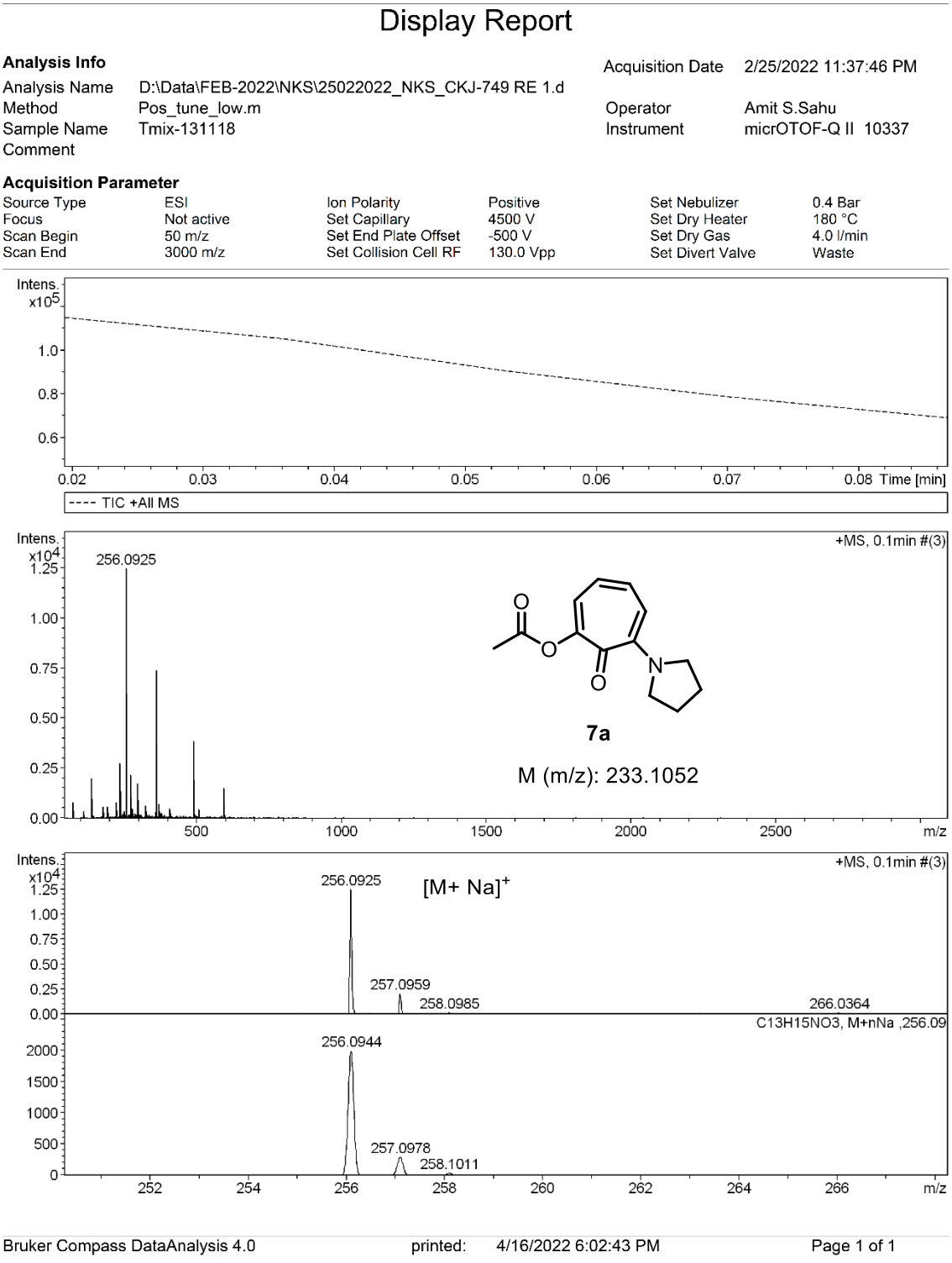


Fig S74. ESI-HRMS spectra of acetoxylated aminotropone **7a**

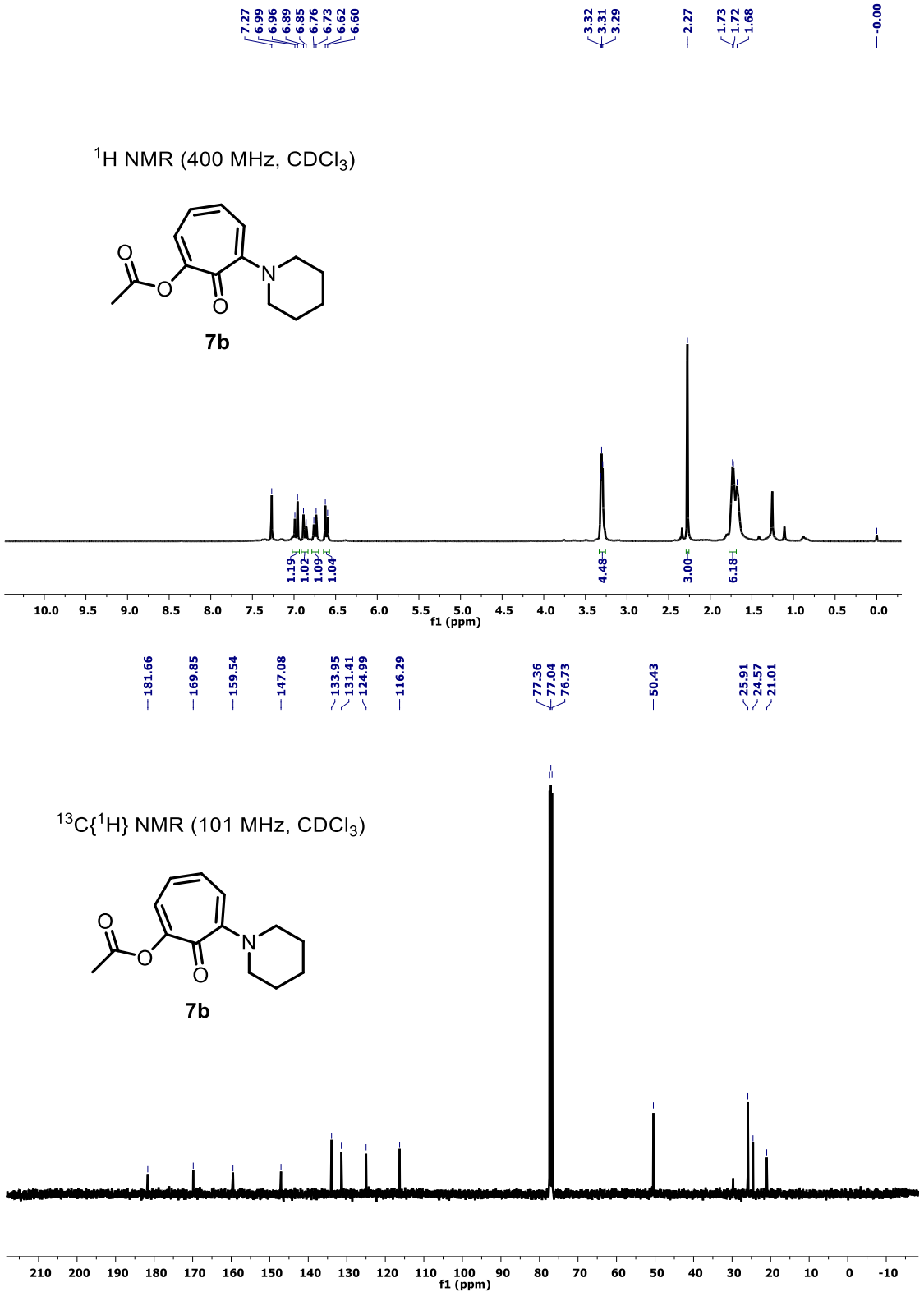


Fig S75. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of acetoxylated aminotropone **7b**

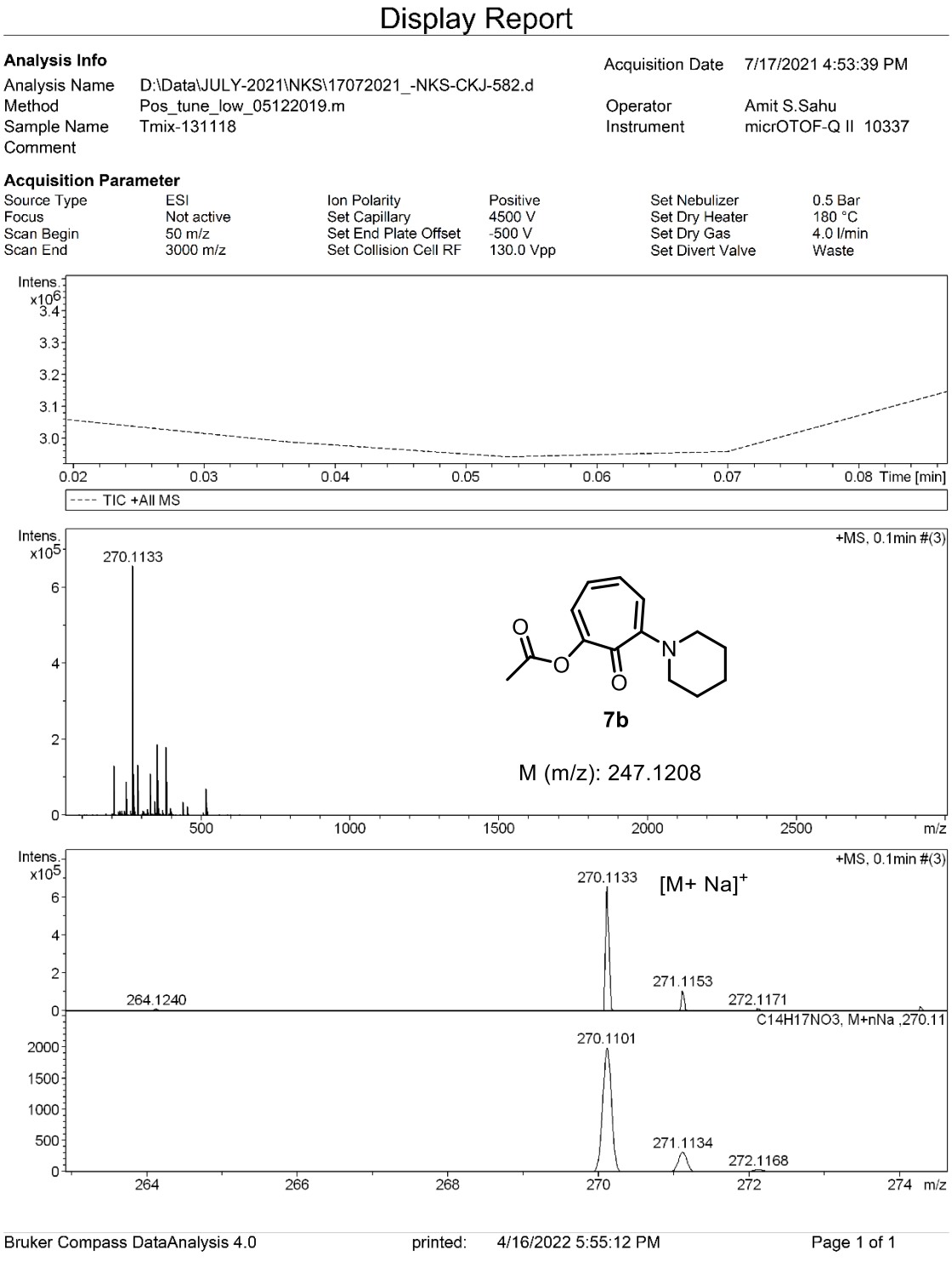


Fig S76. ESI-HRMS spectra of acetoxylated aminotropone **7b**

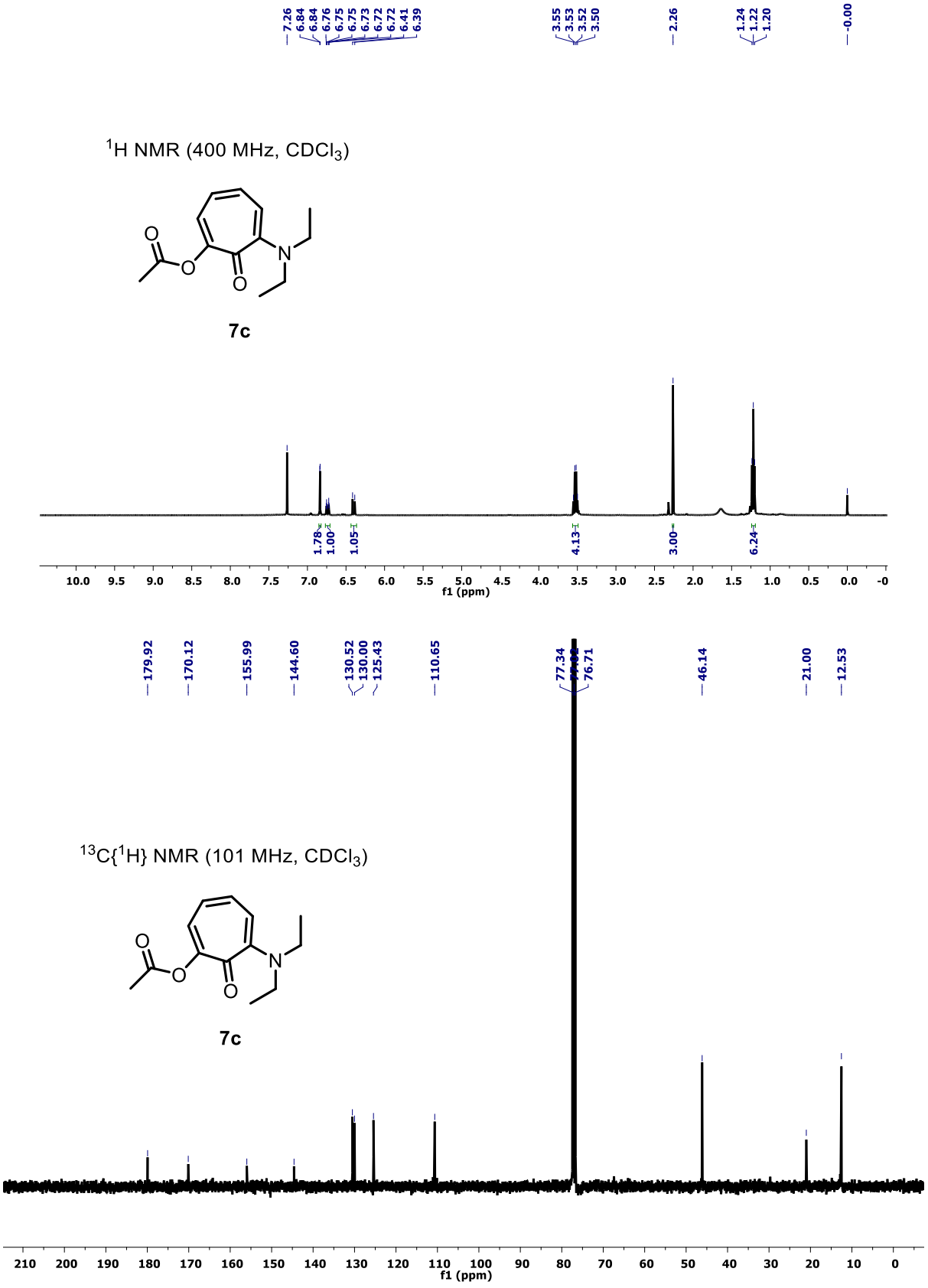


Fig S77. ^{1}H, ^{13}C $\{^{1}H\}$ NMR spectra of acetoxylated aminotropone **7c**

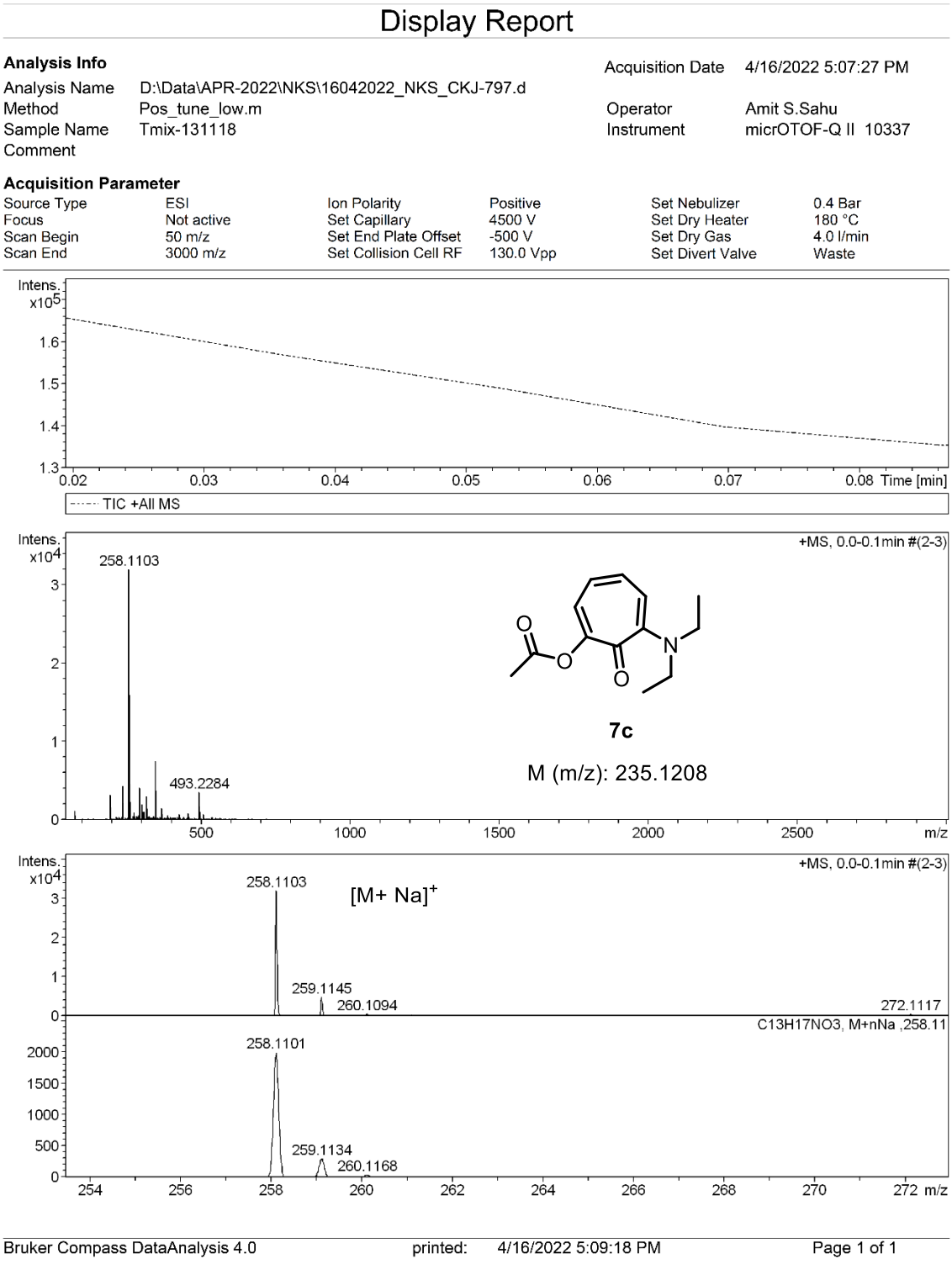


Fig S78. ESI-HRMS spectra of acetoxylated aminotropone **7c**

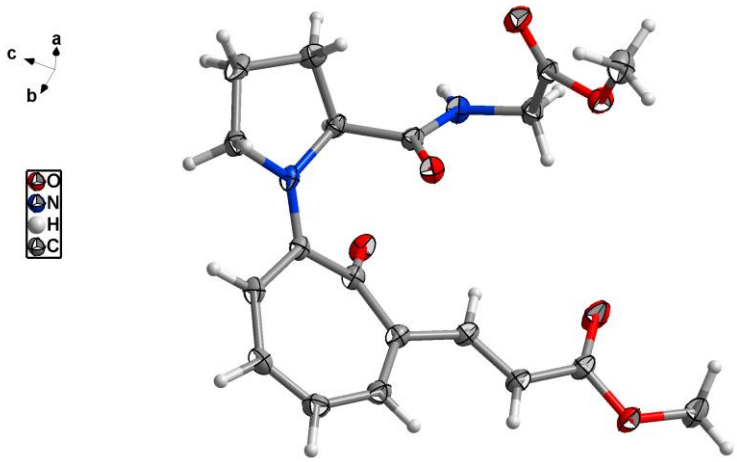
7. X-Ray Studies of Single Crystal of Olefinated Troponyl *di*- Peptide (**4t**)

Single crystal of olefinated troponyl *di*- peptide was obtained in solvent mixture ethylacetate and hexane by slow evaporation method. The crystal data of peptide derivative (**4t**) was collected on a Rigaku Oxford diffractometer at 293 K. Selected - collection parameters and other crystallographic results are summarized below. The program package SHELXTL1 and Olex2 was used for structure solution and ORTEP diagram carried out by DIAMOND 3.2.

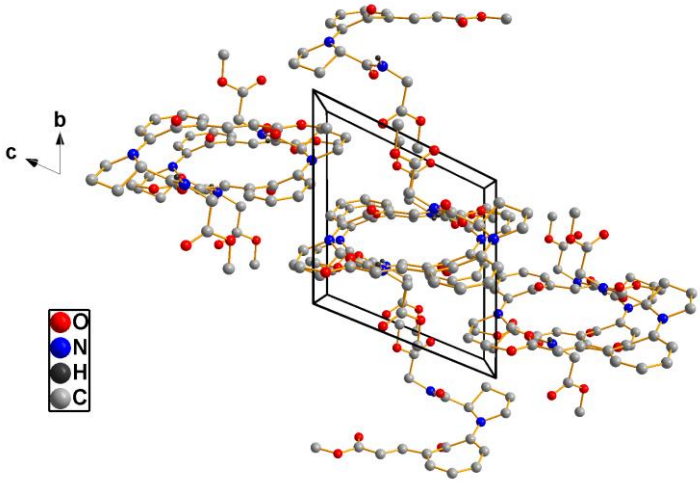
Table S3 Crystal data and structure refinement for 4t

Identification code	**4t**
Empirical formula	$C_{19}H_{22}N_2O_6$
Formula weight	374.38
Temperature/K	300.47(15)
Crystal system	triclinic
Space group	P-1
a/Å	10.1306(9)
b/Å	10.1315(8)
c/Å	11.0192(9)
α/°	67.839(7)
β/°	63.570(8)
γ/°	88.924(7)
Volume/Å^3	922.68(15)
Z	2
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.101
F (000)	396.0
Crystal size/mm^3	0.01 × 0.01 × 0.001
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.898 to 60.452
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-13 \leq l \leq 15$
Reflections collected	16378
Independent reflections	4416 [R_{int} = 0.0397, R_{sigma} = 0.0351]
Data/restraints/parameters	4416/0/246
Goodness-of-fit on F^2	1.183
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1670
Final R indexes [all data]	R_1 = 0.0818, wR_2 = 0.1799
Largest diff. peak/hole / e Å^{-3}	0.26/-0.15

(a)



(b)



(c)

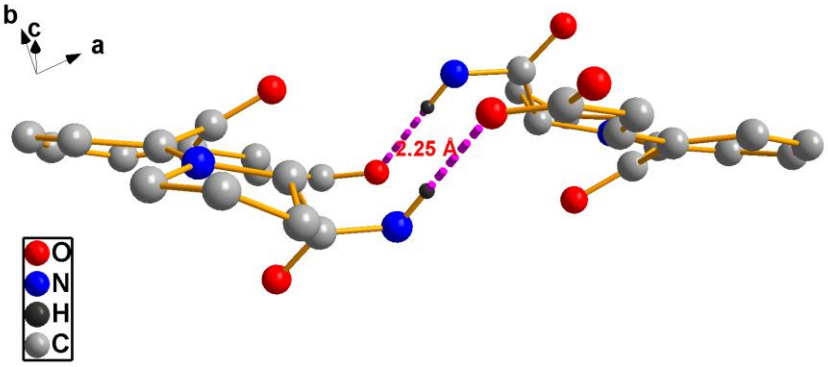


Fig S79. (a) ORTEP diagram of olefinated troponyl *di*- peptide (**4t**) [ellipsoid contour probability: 50%] (b) Packing Diagram of(**4t**) (c) hydrogen bonding of (**4t**)

8. Cell Proliferation Assay

We performed cell proliferation assay to examine cell viability by using versatile in vitro by MTT assay.[1-3] In order to analyse the effect of Compounds **4a, 4c, 4e, 4i, 4k, 4l, 4n, 4s** on cell viabilty, cell proliferation assay (MTT assay) was conducted. Human embryonic kidney derived cell line Hek293T and human cervical carcinoma derived cell line Hela cells were used for the assay. $2*10^4$ cells/ mL in 10% DMEM were seeded in 96 well microtitre plate and incubated for 10 h. After incubation cells were observed for its shape and confluency and media as carefully aspirated. Different concentrations of respective compounds were prepared in DMEM medium and each concentration was added in triplicate along with only media and DMSO (exact concentration used for making the compound solution) control. The 96 well plate was incubated under standard conditions (humidified incubator with 5% CO_2 under 37°C) for 24 h. The CellTiter 96® AQueous One Solution as used to analyse the cell proliferation ability in presence of different compounds. 10µl of CellTiter 96® AQueous One Solution Reagent into each well of the 96-well assay plate containing the samples in 190µl of culture medium followed by incubation for 1h at standard condition. After incubation absorbance was recorded using Various scan at 490 nm.

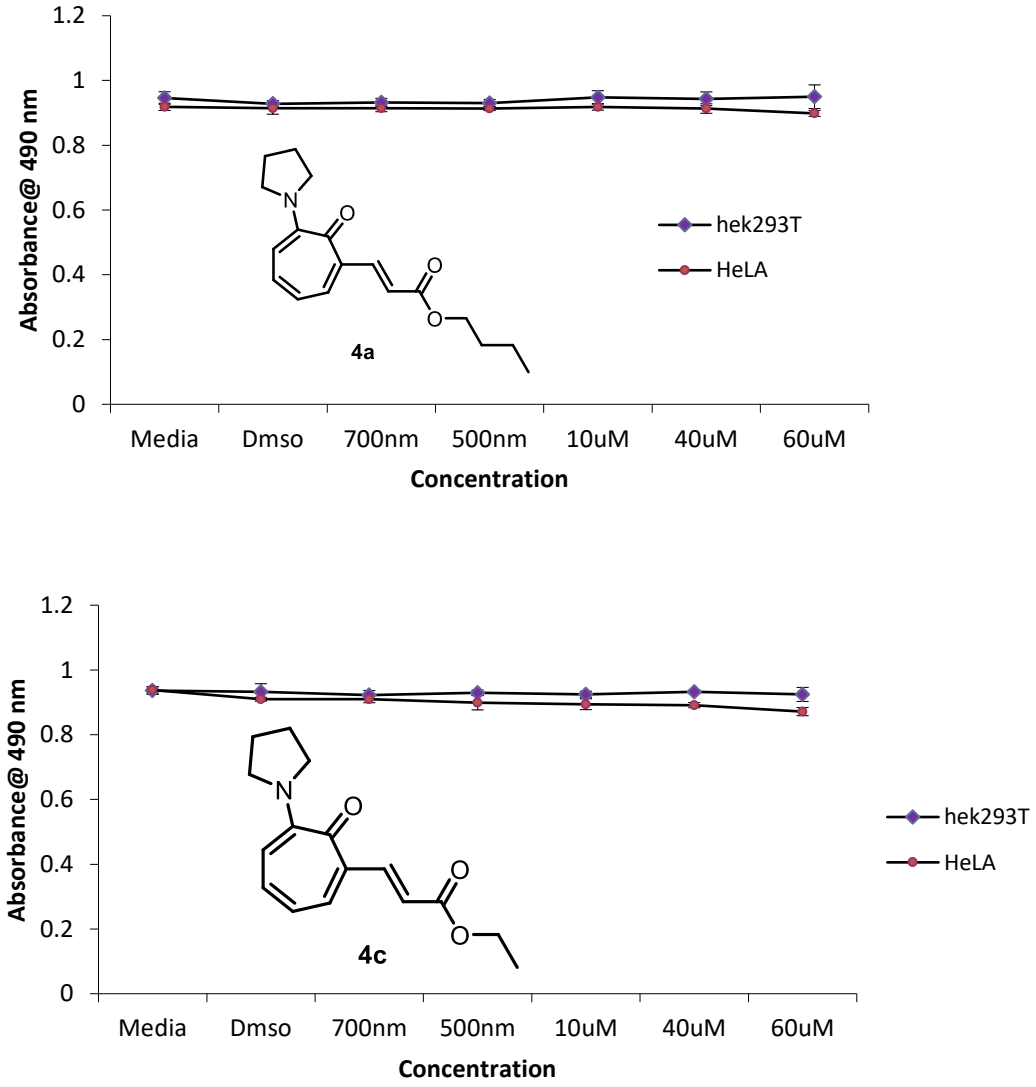


Fig S80. Cell Proliferation Assay of olefinated aminotropone **4a**(Above) and **4c** (Below)

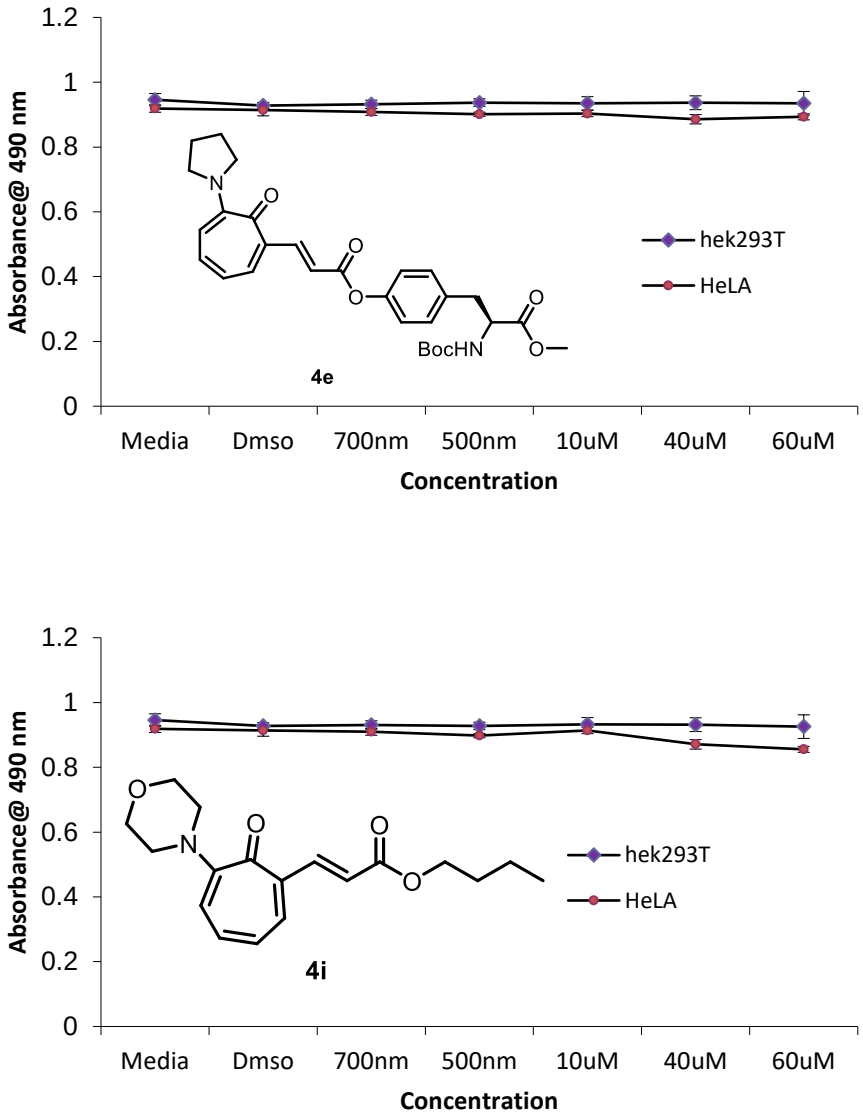


Fig S81. Cell Proliferation Assay of olefinated aminotropone **4e** (Above) and **4i**(Below)

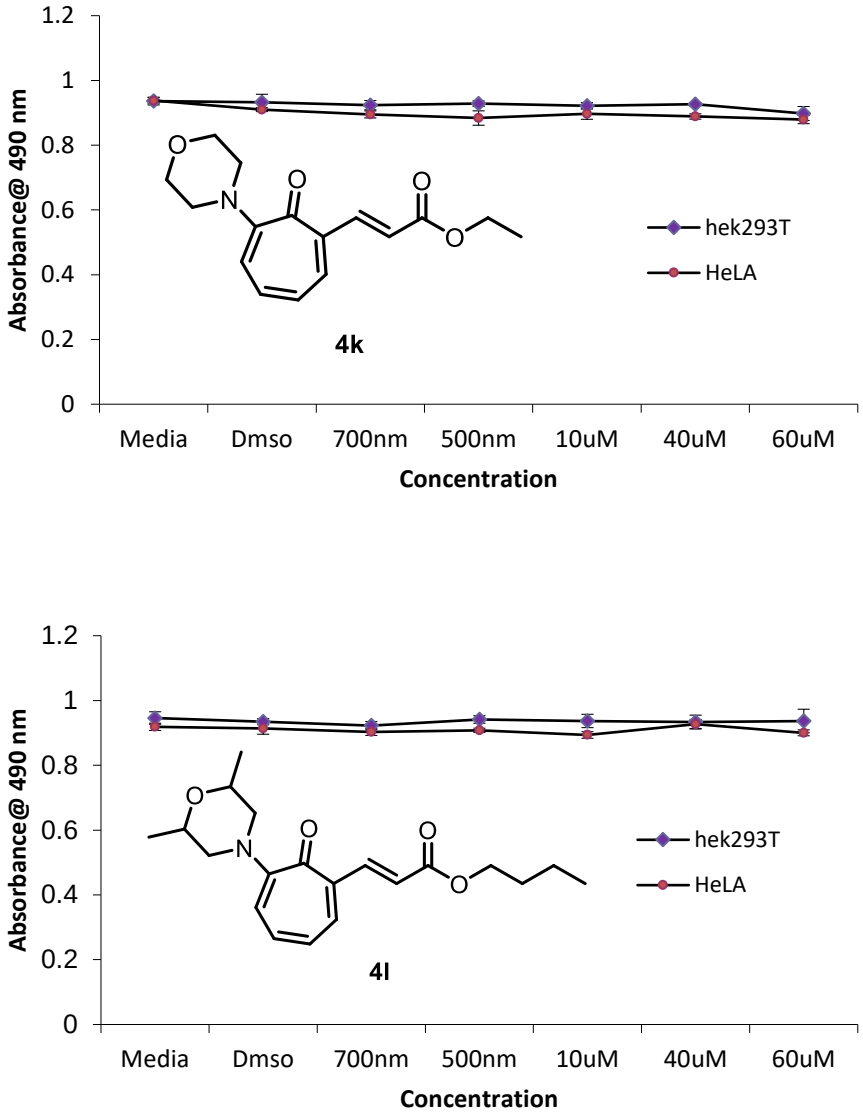


Fig S82. Cell Proliferation Assay of olefinated aminotropone **4k**(Above) and **4l** (Below)

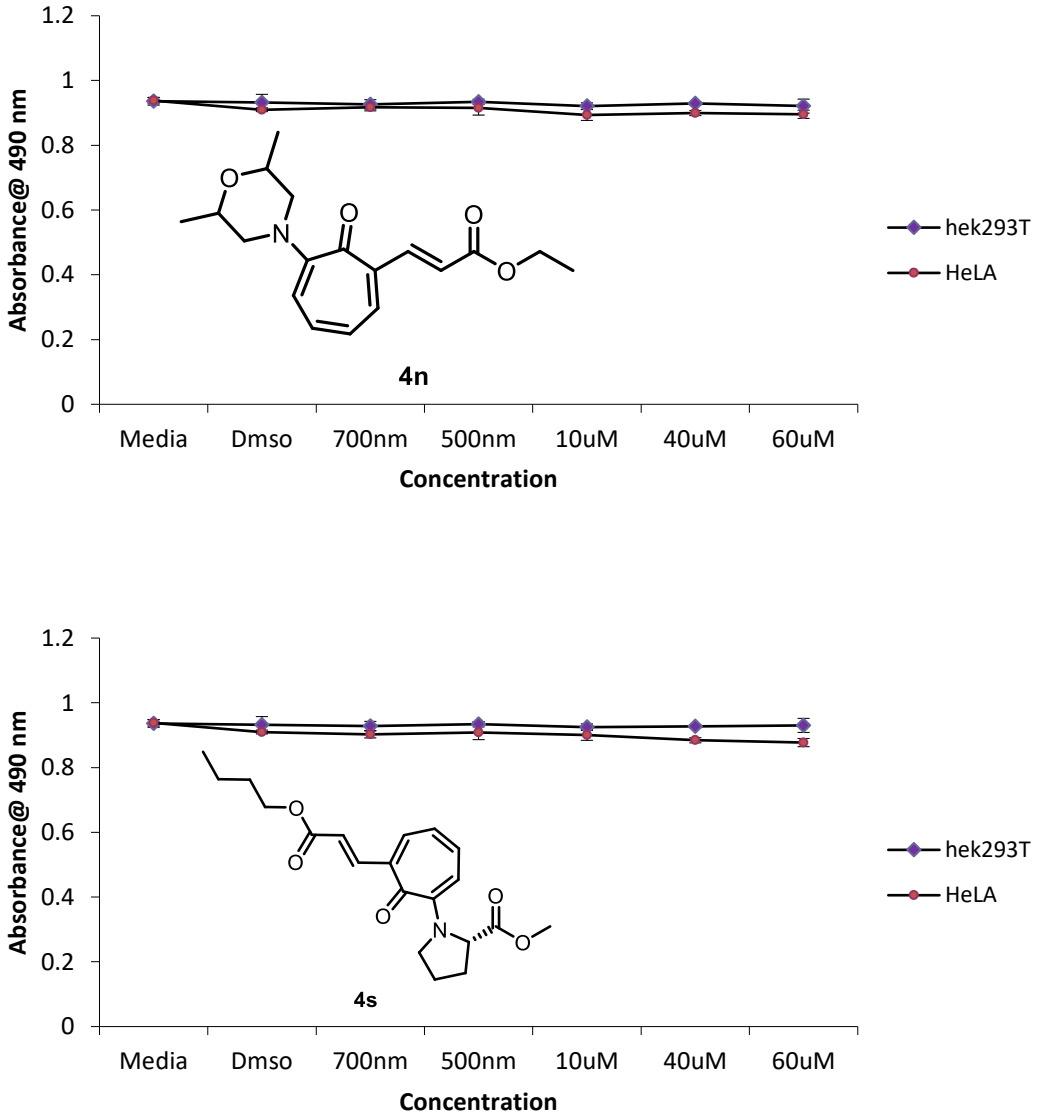


Fig S83. Cell Proliferation Assay of olefinated aminotropone **4n** (Above) and **4s** (Below)

9. References

1. D. C. Marks, L. Belov, M. W. Davey, R. A. Davey and A. D. Kidman, *Leukemia research*, 1992, **16**, 1165-1173.
2. T. L. Riss, R. A. Moravec, A. L. Niles, S. Duellman, H. A. Benink, T. J. Worzella and L. Minor, *Assay Guidance Manual [Internet]*, 2016.
3. C. Karthikeyan, H. Amawi, C. R. Ashby Jr, V. M. Khare, V. Jones, N. H. N. Moorthy, P. Trivedi and A. K. Tiwari, *Heliyon*, 2019, **5**, e01603.