Supplemental material for:

Concise Total Syntheses of (±)-Mesembrane and (±)-Crinane

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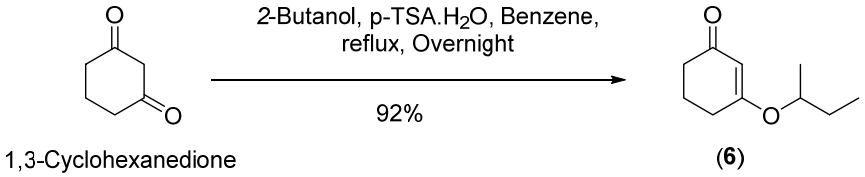
EXPERIMENTAL SECTION

Materials and Methods

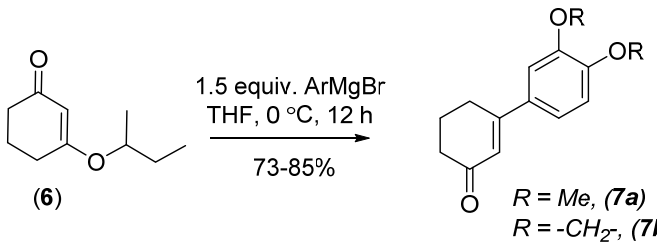
Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O) was distilled over sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2), toluene, and benzene were distilled over calcium hydride. All other solvents such as chloroform, methanol, ethanol, *p*-xylene, DMSO and reagents such as 1,3-cyclohexanedione, *p*-TSA.H_2O, 2-butanol, veratrole, 4-bromoveratrole, 4-bromo-1,2-(methylenedioxy)benzene, cerium(III) chloride heptahydrate, sodium borohydride, *N*,*N*-dimethylacetamide dimethyl acetal, methyl chloroformate, $LiAlH_4$, iodine, DBU, oxalyl chloride, triethylamine, sodium cyanoborohydride, acetic acid, trifluoroacetic acid, benzyl chloroformate, ammonium acetate, methylamine, Eschenmoser's salt etc. were used as received, unless otherwise noted. Thin layer chromatography was performed using Merck Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, 2,4-DNP, anisaldehyde stain and other stains. Silicagel from Merck (particle size 100-200 mesh), basic alumina was used for flash chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (AN ISO 9001:2000) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, 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) from PerkinElmer spectrometer and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-resolution mass spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent. High resolution mass spectra and NMR data were obtained from the Central Instrumentation Facility (CIF) at the Indian Institute of Science Education and Research (IISER) Bhopal.

Synthesis of vinylogous ester (**6**):



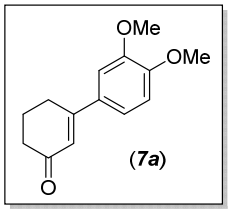
A mixture of 1,3-cyclohexanedione (20.0 g, 178.36 mmol, 1.0 equiv.), *p*-toluenesulfonic acid monohydrate (1.69 g, 8.92 mmol) and 2-butanol (50 mL) in benzene (150 mL) was held at reflux in dean-stark apparatus for 12 h and then cooled to RT. Most of the solvent was removed under vacuum and the resulting residue was poured into brine and extracted with ether. The organic phase was dried (anhydrous Na_2SO_4), filtered and concentrated to give a crude residue which on purification by flash chromatography afforded 27.6 g (92% yields) of compound **6** as yellow oil. R_f = 0.49 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.30 (s, 1H), 4.18-4.11 (m, 1H), 2.33-2.27 (m, 4H), 1.91 (p, *J* = 6.49 Hz, 2H), 1.66-1.57 (m, 1H), 1.56-1.46 (m, 1H), 1.19 (d, *J* = 6.10 Hz, 3H), 0.85 (t, *J* = 7.46 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 177.5, 102.9, 75.9, 36.6, 29.5, 28.6, 21.2, 18.6, 9.5; **IR** (film) υ_{max} 2945, 2882, 1634, 1377, 1330, 1222, 1186, 1137, 1099, 1029, 995, 930, 875, 826, 759 cm^{-1}; **HRMS** (ESI) m/z 191.1063 $[M + Na]^+$; calculated for $[C_{10}H_{16}O_2 + Na]^+$: 191.1043.

General Procedure for Stork-Danheiser's Sequence of Vinylogous Esters ±-(7a-b):

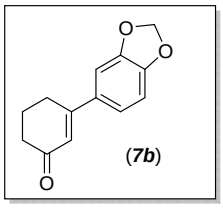


A flame-dried round-bottom flask was charged with vinylogous ester **6** (20.0 mmol), dry THF (30 mL) and cooled to 0 ºC. To this solution, aryl magnesium bromide (24.0 mmol) in dry THF (20 mL) was added dropwise *via* syringe over 10 min. After stirring

for 6-8 h at RT, the reaction mixture was quenched by the addition of 1(*N*) HCl (20 mL) at 0 ºC. The reaction mixture was stirred for 3 h while it was allowed to warm to room temperature and then neutralized by the addition of saturated $NaHCO_3$ solution. The resulting mixture was extracted with EtOAc (4 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (hexanes and EtOAc as eluents) to give 3-aryl-cyclohexenone **7**.

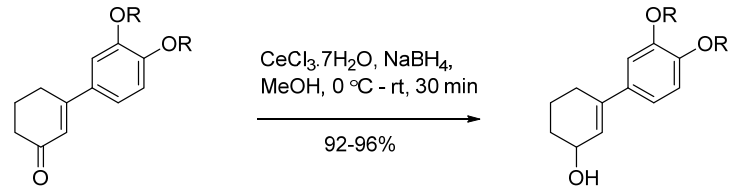


3',4'-Dimethoxy-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (**7a**): 3.4 g, 73% yield as yellow solid, R_f = 0.30 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.41 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 2.77 (t, *J* = 5.7 Hz, 2H), 2.48 (t, *J* = 6.4 Hz, 2H), 2.15 (t, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 159.4, 150.9, 149.0, 131.1, 123.9, 119.5, 110.9, 108.9, 55.97, 55.94, 37.2, 27.9, 22.8; **IR** (film) υ_{max} 3322, 2943, 2844, 1650, 1597, 1519, 1455, 1255, 1185, 1024, 964, 885, 440 cm^{-1}; **HRMS** (ESI) m/z 255.0994 [$(M + Na)^+$; calculated for $[C_{14}H_{16}O_3 + Na]^+$: 255.0992]; mp 118−120 °C.



3-(Benzo[*d*][1,3]dioxol-5-yl)cyclohex-2-enone (**7b**): 3.7 g, 85% yield as colorless crystalline solid, R_f = 0.45 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.98 (d, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.29 (s, 1H), 5.97 (s, 2H), 2.69-2.66 (m, 2H), 2.44-2.40 (m, 2H), 2.09 (p, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.8, 159.1, 149.3, 148.2, 132.8, 124.2, 120.7, 108.4, 106.2, 101.6, 37.2, 28.1, 22.8; **IR** (film) υ_{max} 2916, 1660, 1649, 1591, 1445, 1254, 1110, 1035, 879 cm^{-1}; mp 102-104 °C, [lit. (G. E. Keck and R. R. Webb, *J. Am. Chem. Soc.,* 1981, **103**, 3173) 100-103 °C].

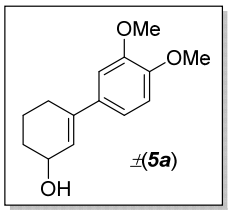
General Procedure for Synthesis of 3-Aryl-cyclohexenol (±)-5a-b:



*R = Me, (**7a**)*
*R = -CH_2-, (**7b**)*

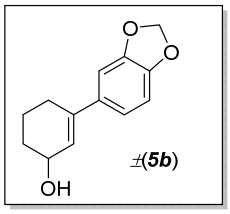
*R = Me, (**5a**)*
*R = -CH_2-, (**5b**)*

In a round-bottom flask, 3-aryl-cyclohexenone **7** (15.0 mmol, 1.0 equiv) was dissolved in MeOH (40 mL). To this solution was added $CeCl_3.7H_2O$ (6.7 g, 18.0 mmol, 1.2 equiv). The reaction mixture was stirred at RT for 15 minutes and then was cooled to 0 ºC. $NaBH_4$ (681 mg, 18.0 mmol, 1.2 equiv) was added to the reaction mixture over 15 minutes. The reaction mixture was continued stirring. At the completion of the reaction (TLC, 30 min), it was quenched with saturated aq. NH_4Cl (10 mL) and aq. $NaHCO_3$ (10 mL). After stirring vigorously for 30 mins, the solvent was removed under reduced pressure. Water (20 mL) was added to the crude reaction mixture and it was extracted with CH_2Cl_2 (3 X 30 mL). The combined organic extracts were washed with saturated aq. NaCl (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography to provide of allylic alcohol **5**.



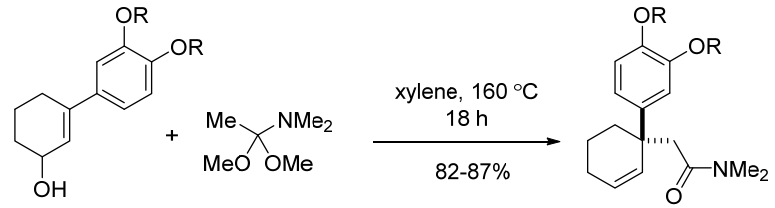
3',4'-Dimethoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol ±(**5a**): 3.2 g, 92% yield as colorless crystalline solid, R_f = 0.25 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94-6.93 (m, 2H), 6.82-6.79 (m, 1H), 6.054-6.051 (m, 1H), 4.37 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.44-2.31 (m, 2H), 1.94-1.84 (m, 2H), 1.77-1.61 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 148.6, 139.7, 134.3, 125.3, 117.8, 110.9, 108.7, 66.4, 55.9, 55.8, 31.8, 27.6, 19.4; **IR** (film) υ_{max} 3445, 2921, 2840, 1615, 1458, 1406,1259,

1175, 1029, 743 cm^{-1}; mp 96−98 °C, [lit.(G. E. Keck and R. R. Webb, *J. Org. Chem.*,1982, **47**, 1302) 97-98 °C].

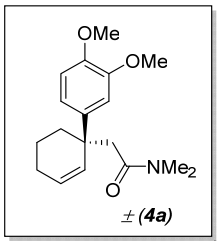


3-(Benzo[*d*][1,3]dioxol-5-yl)cyclohex-2-enol (**5b**): 3.1 g, 96% yield as white solid, R_f = 0.40 (50% EtOAc in hexane). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.92 (d, *J* = 1.8 Hz, 1H), 6.88 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.04-6.02 (m, 1H), 5.95 (s, 2H), 4.37-4.36 (m, 1H), 2.43-2.36 (m, 1H), 2.33-2.26 (m, 1H), 2.18 (brs, 1H), 1.96-1.86 (m, 2H), 1.76-1.62 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 147.7, 146.9, 139.4, 135.8, 125.7, 118.9, 108.0, 106.0, 101.0, 66.3, 31.6, 27.7, 19.5; **IR** (film) υ_{max} δ 3402, 2932, 1720, 1650, 1606, 1505, 1486, 1372, 1247, 1160, 1104, 1040, 970, 936, 865, 807, 738, 703, 634 cm^{-1}; mp 105-108 °C.

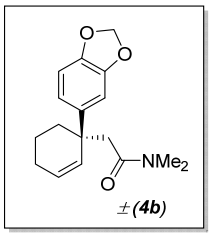
General Procedure For Eschenmoser-Claisen Rearrangement:



An oven-dried Schlenk flask was charged with a solution of alcohol (±)-**5** (generally in 3.0 mmol scale, 1.0 equiv) in *p*-xylene followed by addition of *N*, *N*-dimethylacetamide dimethyl acetal (3.07 mL, 21.0 mmol, 7.0 equiv). The solution was sparged with N_2 and then sealed and heated at 160 ºC for 18 h. The reaction mixture was allowed to cool to room temperature and concentrated. The crude product was purified by flash chromatography to give of amide **4**.

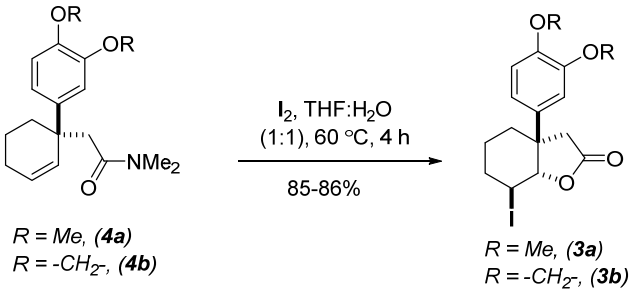


2-(3',4'-Dimethoxy-1,2,3,4-tetrahydro-[1,1'-biphenyl]-1-yl)-*N*,*N*-imethylacetamide ±(4a): 746 mg, 82% yield as yellow gel, R_f = 0.20 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87-6.85 (m, 2H), 6.78-6.76 (m, 1H), 6.14 (d, *J* = 10.2 Hz, 1H), 5.89- 5.85 (m, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.81 (s, 3H), 2.71 (s, 3H), 2.69-2.67 (m, 2H), 2.10-1.90 (m, 4H), 1.59-1.54 (m, 1H), 1.41-1.33 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 148.4, 147.0, 140.3, 133.1, 128.0, 118.8, 110.7, 110.5, 55.9, 55.8, 45.1, 41.8, 37.8, 36.5, 35.4, 25.3, 18.8; **IR** (film) υ_{max} 2934, 1640, 1519, 1258, 1238, 1179, 1145, 1028, 757 cm^{-1}; **HRMS** (ESI) m/z 304.1905 $[(M + H)^+$; calculated for $[C_{18}H_{25}NO_3 + H]^+$: 304.1907].

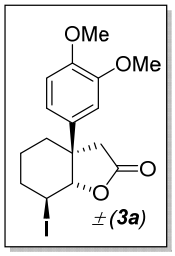


2-(1-(Benzo[*d*][1,3]dioxol-5-yl)cyclohex-2-en-1-yl)-N,N-dimethylacetamide ±(4b): 750 mg, 87% yield as yellow gel, R_f = 0.25 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 (m, 1H), 6.76 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.10 (d, *J* = 10.7 Hz, 1H), 5.87 (s, 2H), 5.85-5.82 (m, 1H), 2.8 (s, 3H), 2.79 (s, 3H), 2.66 (ABq, *J* =14.7 Hz, 2H), 2.0-1.95 (m, 3H), 1.89-1.82 (m, 1H), 1.55-1.48 (m, 1H), 1.39-1.33 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 147.4, 145.3, 141.8, 143.0, 128.1, 119.8, 107.6, 107.4, 100.8, 44.8, 42.0, 37.8, 37.2, 35.3, 25.2, 18.7; **IR** (film) υ_{max} 2931, 1643, 1487, 1433, 1238, 1143, 1101, 1039, 935, 812, 745 cm^{-1}; **HRMS** (ESI) m/z 288.1607 $[(M + H)^+$; calculated for $[C_{17}H_{21}NO_3 + H]^+$: 288.1594].

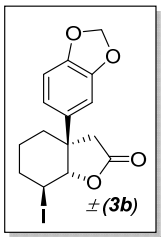
General Procedure for Synthesis of Iodolactone Intermediates (±)-3a-b:



A solution of amide **4** (5 mmol, 1 equiv), in 1:1 mixture of THF:Water (20 mL) was added iodine (1.5 g, 6 mmol, 1.2 equiv) and the reaction mixture was heated at 60 ºC for 4h and cooled to room temperature. This was followed by reductive work up with saturated aqueous sodium bisulphate solution. The reaction mixture was extracted with EtOAc (3 X 20 mL). The combined organic extracts were washed with saturated aq. NaCl (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography to provide of **3** as a solid.

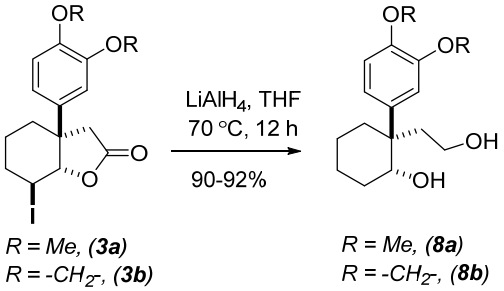


(3,4-Dimethoxyphenyl)-7-iodohexahydrobenzofuran-2(3H)-one ±(**3a**)**:** 1.73 g, 86% yield as white solid, R_f = 0.35 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91-6.89 (m, 1H), 6.84-6.80 (m, 2H), 5.0 (d, *J* = 6.8 Hz, 1H), 4.23- 4.18 (m, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.71 (ABq, *J* = 17.2 Hz, 2H), 2.76-2.24 (m, 1H), 2.08-1.93 (m, 3H), 1.79-1.75 (m, 1H), 1.62-1.53 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 149.2, 148.4, 135.5, 118.2, 111.2, 109.6 ,88.5, 56.2, 55.9, 46.7, 41.7, 34.1, 32.6, 25.6, 21.9; **IR** (film) υ_{max} 2920, 2838, 1770, 1590, 1519, 1455, 1251, 1098, 1028, 946, 914, 806, 739 cm^{-1}; **HRMS** (ESI) m/z 403.0418 $[(M + H)^+$; calculated for $[C_{16}H_{19}IO_4 + H]^+$: 403.0401]; mp 125-127 °C.

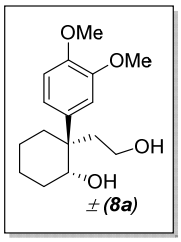


(Benzo[*d*][1,3]dioxol-5-yl)-7-iodohexahydrobenzofuran-2(3H)-one ±(**3b**)**:** 1.64 g, 85% yield as white solid, R_f = 0.35 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.86-6.82 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 2H), 4.97 (d, *J* = 6.8 Hz, 1H), 4.25-4.2 (m, 1H), 2.71 (ABq, *J* = 21.8 Hz, 2H), 2.31-2.24 (m, 1H), 2.1-1.92 (m, 3H), 1.84-1.75 (m, 1H), 1.63-1.53 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 148.3, 146.8, 136.9, 119.1 ,108.3, 106.6, 101.4, 88.5, 46.8, 42.0, 34.0, 32.7, 25.3, 21.8; **IR** (film) υ_{max} 2930, 2859, 1783, 1489, 1447, 1238, 1204, 1169, 1040, 1017, 935, 812, 735 cm^{-1}; **HRMS** (ESI) m/z 387.0069 $[(M + H)^+$; calculated for $[C_{15}H_{15}IO_4 + H]^+$: 387.0088]; mp 171-173 °C.

General Procedure for Synthesis of diols (±)-8a-b:

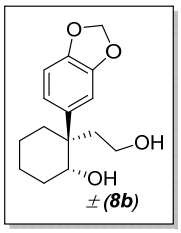


To a suspension of lithium aluminium hydride, (605 mg, 16.0 mmol, 4.0 equiv) in THF (30 mL) at 0 °C was added a solution of compound **3** (4.0 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was allowed to warm to room temperature, fitted with a water condenser, heated to 80 ºC and held at reflux for 20h. The reaction mixture was cooled to RT and then to 0 ºC and quenched with EtOAc, basified with 4(*N*) NaOH solution and extracted with EtOAc (3 X 25 mL). The combined organic extracts were washed with saturated aq. NaCl (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography to provide **8**.



± (8a)

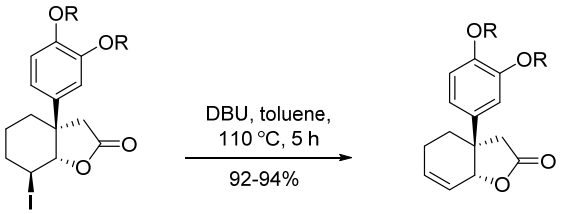
2-(3,4-Dimethoxyphenyl)-2-(2-hydroxyethyl)cyclohexanol ±(**8a**)**:** 1.004 g, 90% yield as yellow gel, R_f = 0.15 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94-6.93 (m, 2H), 6.83-6.81 (m, 1H), 4.23 (brs, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.58-3.53 (m, 1H), 3.49-3.43 (m, 1H), 2.78 (brs, 2H), 2.25-2.18 (m, 1H), 1.82-1.73 (m, 6H), 1.5-1.49 (m, 1H), 1.38-1.36 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 147.1, 137.9, 119.2, 111.0, 110.6, 72.7, 59.3, 56.0, 55.8, 45.4, 29.8, 29.7, 22.7, 21.6, 20.6; **IR** (film) υ_{max} 3352, 2935, 2110, 1781, 1649, 1506, 1454, 1355, 1238, 1204, 1169, 1109, 1039, 1017, 935, 808, 736 cm^{-1}; **HRMS** (ESI) m/z 303.1601 [$(M + Na)^+$; calculated for $[C_{16}H_{24}O_4 + Na]^+$: 303.1567].



± (8b)

2-(Benzo[*d*][1,3]dioxol-5-yl)-2-(2-hydroxyethyl)cyclohexanol ±(**8b**)**:** 973 mg, 92% yield as white solid, R_f = 0.2 (50% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 1.7 Hz, 1H), 6.84 (dd, *J* = 6.5, 1.7 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.91 (s, 2H), 4.16-4.14 (m, 1H), 3.54-3.49 (m, 1H), 3.45-3.39 (m, 1H), 3.05 (brs, 2H), 2.22-2.14 (m, 1H), 1.83-1.64 (m, 6H), 1.52-1.44 (m, 1H), 1.39-1.32 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 145.4, 139.5, 119.9, 108.0, 107.6, 100.9, 72.5, 59.1, 45.7, 38.8, 35.8, 29.8, 22.7, 21.5; **IR** (film) υ_{max} 3351, 2935, 2866, 1612, 1489, 1437, 1240, 1040, 937, 913, 738, 431 cm^{-1}; **HRMS** (ESI) m/z 287.1254 [$(M + Na)^+$; calculated for $[C_{15}H_{20}O_4 + Na]^+$: 287.1254]; mp 90-92 °C.

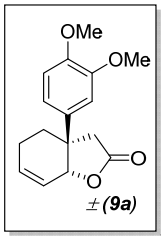
General Procedure for Synthesis of (±)-9a-b:



R = Me,± ***(3a)***
*R = -CH2-, ±****(3b)***

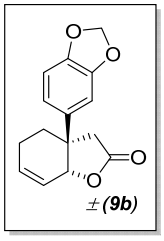
R = Me,± ***(9a)***
R = -CH2-,± ***(9b)***

A solution of iodolactone **3** (0.5 mmol, 1 equiv), in toluene (7 mL) was added DBU (112 µL, 0.75 mmol, 1.5 equiv) and the reaction mixture was refluxed at 110 ºC for 5h. Upon completion of the reaction (monitoring by TLC), it was diluted by 10 mL EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 10 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography to provide **9.**



± ***(9a)***

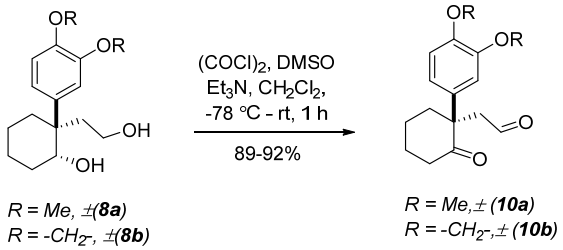
3a-(3,4-Dimethoxyphenyl)-3,3a,4,5-tetrahydrobenzofuran-2(7aH)-one ±(9a): 129 mg, 94% yield as colorless gel, R_f = 0.30 (20% EtOAc in hexane). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.82 (d, *J* = 8.3 Hz, 1H), 6.70-6.67 (m, 2H), 6.28-6.25 (m, 1H), 6.16-6.13 (m, 1H), 4.94 (d, *J* = 4.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.89 (ABq, *J* = 16.9 Hz, 2H), 2.10-2.04 (m, 1H), 1.85-1.73 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 149.0, 148.1, 135.9, 135.0, 122.8, 118.0, 111.1, 109.4, 78.2, 56.0, 55.9, 44.6, 44.2, 31.6, 22.0; **IR** (film) υ_{max} 2921, 1780, 1592, 1520, 1468, 1255, 1201, 1150, 1027, 978, 809 cm^{-1}; **HRMS** (ESI) m/z 313.0839 $[(M + K)^+$; calculated for $[C_{16}H_{18}O_4 + K]^+$: 313.0837].



± ***(9b)***

3a-(Benzo[*d*][1,3]dioxol-5-yl)-3,3a,4,5-tetrahydrobenzofuran-2(7aH)-one ±(**9b**)**:** 119 mg, 92% yield as white solid, R_f = 0.40 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 8.1 Hz, 1H), 6.62 (d, *J* = 1.8 Hz, 1H), 6.56 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.25-6.21 (m, 1H), 6.12-6.09 (m, 1H), 5.93 (s, 2H), 4.86 (d, *J* = 4.2 Hz, 1H), 2.83 (ABq, *J* = 13.2 Hz, 2H), 2.08-2.0 (m, 1H), 1.85-1.61 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 148.0, 146.5, 136.3, 136.0, 122.7, 118.9, 108.3, 106.6, 101.2, 78.1, 44.8, 44.4, 31.7, 21.9; **IR** (film) υ_{max} 2920, 2856, 2343, 1775, 1460, 1237, 1196, 1106, 1037, 810 cm^{-1}; **HRMS** (ESI) m/z 259.0983 [$(M + H)^+$; calculated for $[C_{15}H_{14}O_4 + H]^+$: 259.0965]; mp 96-98 °C.

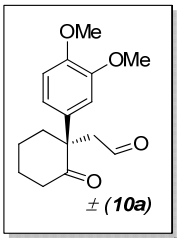
General Procedure for Synthesis of ketoaldehyde (±)-10a-b:



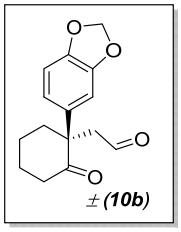
*R = Me, ±(**8a**)*
*R = -CH_2-, ±(**8b**)*

*R = Me,± (**10a**)*
*R = -CH_2-,± (**10b**)*

A flame-dried round-bottom flask was charged with DMSO (528 µL, 10.0 mmol, 10 equiv), CH_2Cl_2 (8 mL) and cooled to -78 ºC. In a separate flask, oxalyl chloride (257 µL 3.0 mmol, 3 equiv) was dissolved in CH_2Cl_2 (6 mL). The oxalyl chloride solution was added dropwise to the DMSO/ CH_2Cl_2 solution at -78 ºC *via* syringe over 15 mins. After stirring for 30 mins at -78 ºC, diol (±)-**8** (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added dropwise over 30 mins and the reaction mixture was stirred at -78 ºC for an additional 2.5 h. Triethylamine (1.4 mL, 10.0 mmol, 10 equiv) was added dropwise and then the reaction mixture was stirred at that temperature for an hour and then allowed to slowly warm to RT. After stirring at RT for 1 h, the reaction mixture was poured into a separatory funnel and washed with water (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 X 20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography to afford of (±)-**10.**

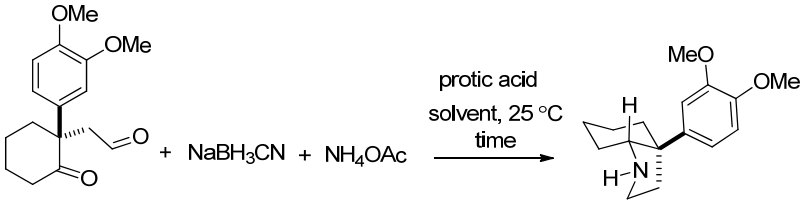


2-(1-(3,4-Dimethoxyphenyl)-2-oxocyclohexyl)acetaldehyde ±(**10a**)**:** 246 mg, 89% yield as colorless gel, R_f = 0.56 (40% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.76 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.64 (s,1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.70-2.65 (m, 3H), 2.46-2.33 (m, 2H), 2.02-1.89 (m, 2H), 1.79-1.65 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.0, 201.7, 149.6, 148.3, 131.7, 118.9, 111.6, 109.7, 56.0, 55.9, 55.7, 53.4, 39.5, 35.9, 27.7, 21.3; **IR** (film) υ_{max} 2939, 2865, 1707, 1589, 1519, 1465, 1259, 1153, 1026, 811 cm^{-1}; **HRMS** (ESI) m/z 299.1249 [$(M + Na)^+$; calculated for $[C_{16}H_{20}O_4 + Na]^+$: 299.1254].



2-(1-(Benzo[*d*][1,3]dioxol-5-yl)-2-oxocyclohexyl)acetaldehyde ±(**10b**)**:** 239 mg, 92% yield as white solid, R_f = 0.35 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.72-6.69 (m, 1H), 6.63-6.61 (m, 1H), 5.95 (s, 2H), 2.66-2.57 (m, 3H), 2.47-2.33 (m, 2H), 1.98-1.89 (m, 2H), 1.77-1.68 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.8, 201.6, 148.7, 146.9, 133.3, 120.0, 108.9, 106.9, 101.3, 55.8, 53.4, 39.5, 36.1, 27.8, 21.3; **IR** (film) υ_{max} 2939, 2866, 1713, 1706, 1610, 1489, 1345, 1241, 1039, 934, 814 cm^{-1}; **HRMS** (ESI) m/z 261.1122 [$(M + H)^+$; calculated for $[C_{15}H_{16}O_4 + H]^+$: 261.1121], mp 38-40 ºC.

Optimization of reductive amination of (±)-10:

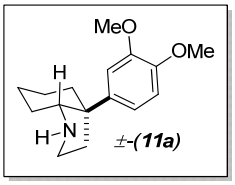


±-(**10a**) ±-(**11a**)

entry	acid	solvent	temp.	time	%yield[a, b]
1.	TFA (1 equiv.)	MeOH	0 - 25 °C	12 h	72%
2.	AcOH (1 equiv.)	MeOH	0 - 25 °C	12 h	75%
3.	TFA (1 equiv.)	EtOH	0 - 25 °C	10 h	89%
4.	AcOH (1 equiv.)	EtOH	0 - 25 °C	10 h	88%
5.	TFA (1 equiv.)	THF	0 - 25 °C	18 h	35%
6.	AcOH (1 equiv.)	THF	0 - 25 °C	18 h	32%
7.	TFA (10 mol%)	EtOH	0 - 25 °C	16 h	83%
8.	AcOH (10 mol%)	EtOH	0 - 25 °C	16 h	85%

[a]2.0 equiv. of NH_4OAc and 3.0 equiv. $NaBH_3CN$ were used in each case and all the reactions were performed on a 0.20 mmol of (±)-**10a** in 2 mL of solvent under inert atmosphere. [b]isolated yields after column chromatography.

An oven-dried round-bottom flask was charged with ketoaldehyde (±)-**10a** (50 mg, 0.181 mmol, 1.0 equiv) in EtOH (3 mL), followed by addition of NH_4OAc (28 mg, 0.362 mmol, 2.0 equiv), $NaBH_3CN$ (45 mg, 0.724 mmol, 4.0 equiv) and protic acid (0.087 mmol, 0.1 equiv) respectively. The reaction mixture was stirred at room temperature for indicated time. The reaction mixture was then basified with 2(*N*) NaOH and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous K_2CO_3 and concentrated under vacuum. The crude product was purified by flash chromatography to give amine **11a** as a light yellow gel.

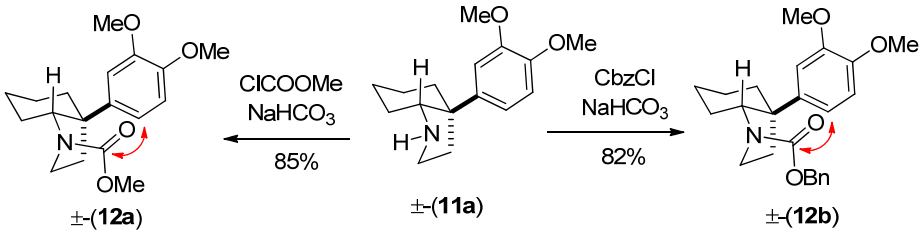


±-(**11a**)

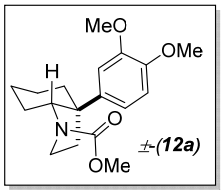
3a-(3,4-dimethoxyphenyl)octahydro-1*H*-indole ±(11a): 42 mg, 89% yield as colorless gel, R_f = 0.3 (1 mL MeOH + 30 mL CH_2Cl_2 + 1 mL Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.95-6.91 (m, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.48 (t, *J* = 4.3 Hz, 1H), 3.2-3.13 (m, 1H), 3.07-3.00 (m, 1H), 2.08-2.02 (m, 2H), 1.99-1.87 (m, 3H), 1.82-1.67 (m, 3H), 1.55-1.48 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

149.1, 147.8, 134.7, 118.3, 111.2, 109.7, 61.0, 56.1, 55.9, 46.9, 41.3, 40.3, 23.7, 22.7, 21.1, 19.7; **IR** (film) υ_{max} 3400, 2982, 2853, 1501, 1473, 1231, 1099, 1011, 911 cm^{-1}; **HRMS** (ESI) m/z 262.1818 $[(M + H)^+$; calculated for $[C_{16}H_{23}NO_2 + H]^+$: 262.1802].

Synthesis of Amine Derivatives ±(12a-b):

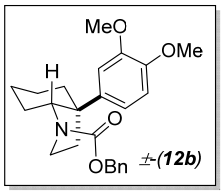


A round-bottom flask was charged with amine **(±)-11a** (0.25 mmol; 1.0 equiv.) in toluene : $NaHCO_3$ (1:1) (7 mL) at room temperature. To this reaction mixture chloroformate (0.3 mmol, 1.2 equiv) was added dropwise and it was stirred for 30 min at room temperature. Upon completion of the reaction (monitoring by TLC), it was diluted by 10 mL EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 5 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography to give product **12** as a light yellow gel.



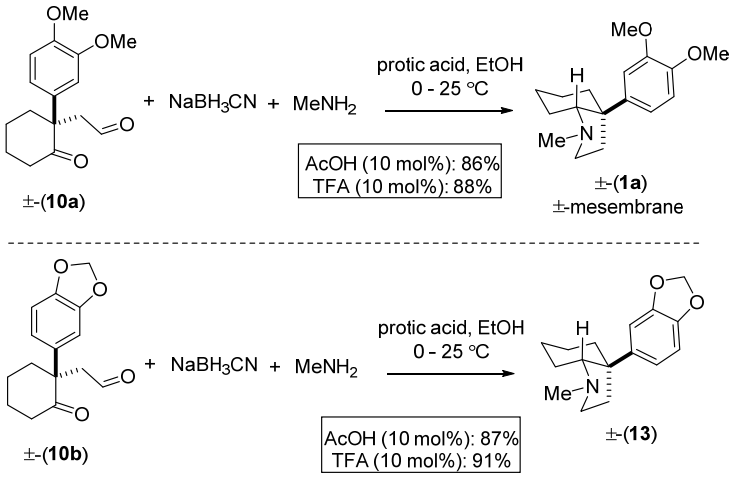
Methyl 3a-(3,4-dimethoxyphenyl)octahydro-1*H*-indole-1-carboxylate ±(12a): 68 mg, 85% yield as colorless gel, R_f = 0.30 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.83-6.77 (m, 3H), 4.25-4.11 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.69-3.62 (m, 3H), 3.39-3.34 (m, 1H), 3.09-3.07 (m, 1H), 2.39-2.31 (m, 1H), 2.15-2.02 (m, 3H), 1.92-1.90 (m, 1H), 1.66-1.55 (m, 4H), 1.49-1.43 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 148.7, 147.2, 140.1, 117.7, 111.0, 109.3, 59.6, 55.9, 55.8, 52.1, 57.1, 43.3, 35.6, 33.3, 29.7, 23.2, 22.3; **IR** (film) υ_{max} 2928, 2856, 1696, 1520, 1454, 1392, 1256, 1155,

1029, 769 cm^{-1}; **HRMS** (ESI) m/z 320.1859 $[(M + H)^+$; calculated for $[C_{18}H_{25}NO_4 + H]^+$: 320.1856].

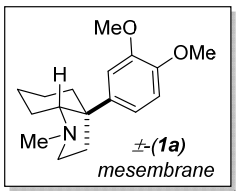


Benzyl 3a-(3,4-dimethoxyphenyl)octahydro-1*H*-indole-1-carboxylate ±(12b): 81 mg, 82% yield as yellow gel, R_f = 0.55 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 5H), 6.86-6.71 (m, 3H), 5.19-5.03 (m, 2H), 4.29-4.16 (m, 1H), 3.84 (s, 3H), 3.78-3.75 (m, 3H), 3.41 (t, *J* = 9.4 Hz, 1H), 3.18-3.12 (m, 1H), 2.40-2.32 (m, 1H), 2.17-2.04 (m, 2H), 1.97-1.89 (m, 1H), 1.66-1.43 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) (rotameric mixture) δ 154.64, 154.61, 148.73, 148.71, 147.28, 147.22, 140.14, 140.11, 137.19, 137.17, 128.47, 128.39, 127.86, 127.75, 127.65, 127.52, 117.68, 117.48, 111.05, 111.01, 109.25, 109.23, 66.59, 66.33, 59.67, 59.60, 55.84, 55.80, 47.86, 47.12, 43.57, 43.42, 35.93, 35.54, 33.38, 31.92, 31.58, 29.70, 29.32, 28.37, 23.54, 23.24, 22.35, 22.28; **IR** (film) υ_{max} 3055, 2929, 2855, 1696, 1519, 1454, 1416, 1348, 1265, 1154, 1029, 805 cm^{-1}; **HRMS** (ESI) m/z 396.2179 $[(M + H)^+$; calculated for $[C_{24}H_{29}NO_4 + H]^+$: 396.2169].

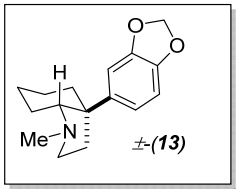
Total Synthesis of (±)-*mesembrane*:



An oven-dried round-bottom flask was charged with ketoaldehyde (±)-**10a** (20 mg, 0.072 mmol, 1.0 equiv) in EtOH (3 mL), followed by addition of methylamine in THF (364 μL, 0.72 mmol, 10.0 equiv), $NaBH_3CN$ (19 mg, 0.291 mmol, 4.0 equiv) and protic acid (0.0072 mmol, 0.1 equiv) respectively. The reaction mixture was stirred at room temperature for indicated time. The reaction mixture was then basified with 2(*N*) NaOH and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous K_2CO_3 and concentrated under vacuum. The crude product was purified by flash chromatography to give amine **1a** and **13** as a light yellow gel.



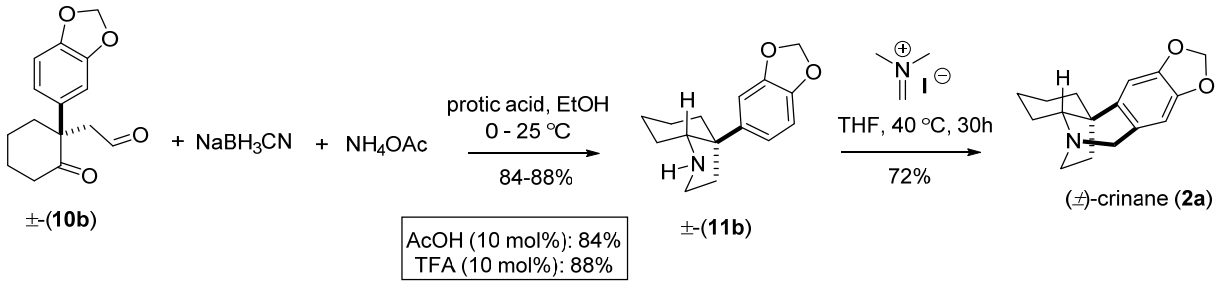
3a-(3,4-dimethoxyphenyl)-1-methyloctahydro-1*H*-indole ±(**1a**)**:** 17 mg, 88% yield as colorless gel, R_f = 0.45 (1 mL MeOH + 30 mL CH_2Cl_2 + 1 mL Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94-6.90 (m, 2H), 6.84-6.81 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.28-3.23 (m, 1H), 2.59 (brs, 1H), 2.33 (s, 3H), 2.32-2.29 (m, 1H), 1.96-1.80 (m, 4H), 1.67-1.65 (m, 3H), 1.50-1.45 (m, 2H), 1.39-1.36 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.6, 146.8, 140.3, 118.9, 110.7, 110.6, 68.7, 55.9, 55.8, 54.4, 47.5, 41.0, 40.7, 36.1, 23.7, 22.9, 20.4; **IR** (film) υ_{max} 2932, 2856, 1589, 1519, 1464, 1410, 1326, 1257, 1148, 1030, 805 cm^{-1}; **HRMS** (ESI) m/z 276.1965 [$(M + H)^+$; calculated for [$C_{17}H_{25}NO_2$ + H]$^+$: 276.1958].

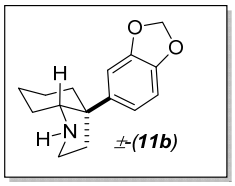


3a-(Benzo[*d*][1,3]dioxol-5-yl)-1-methyloctahydro-1*H*-indole ±(**13**)**:** 23 mg, 91% yield as colorless gel, R_f = 0.50 (1 mL MeOH + 30 mL CH_2Cl_2 + 1 mL Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 1.7 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 5.90 (s, 2H), 3.31-3.25 (m, 1H), 2.59 (brs, 1H), 2.33 (s, 3H), 2.32- 2.28 (m, 1H), 1.91-1.73 (m, 5H), 1.60-1.57 (m, 2H), 1.47-1.44 (m, 1H), 1.36-1.34 (m, 1H), 1.16-1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 145.2, 141.3, 119.6, 107.7,

107.6, 100.8, 68.9, 54.2, 47.7, 40.9, 40.7, 35.9, 23.5, 22.7, 20.3; **IR** (film) υ_{max} 2920, 2857, 2787, 1726, 1612, 1505, 1485, 1455, 1360, 1340, 1265, 1237, 1191, 1110, 1082, 976 cm^{-1}; **HRMS** (ESI) m/z 260.1650 $[(M + H)^+$; calculated for $[C_{16}H_{21}NO_2 + H]^+$: 260.1645].

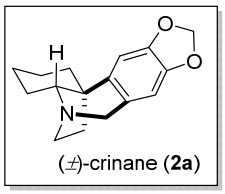
Total Synthesis of Crinane ±(2a):





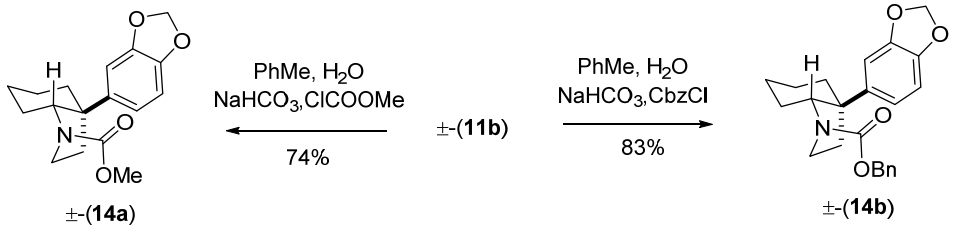
Same procedure as reductive amination of **11a.**

3a-(Benzo[*d*][1,3]dioxol-5-yl)octahydro-1*H*-indole ±(11b): 21 mg, 88% yield as yellow gel, R_f = 0.40 (1 mL MeOH + 30 mL CH_2Cl_2 + 1 mL Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 1.8 Hz, 1H), 6.80 (dd, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 5.91 (s, 2H), 3.40 (s, 1H), 3.16-3.09 (m, 1H), 3.02-2.96 (m, 1H), 2.5 (brs, 1H), 2.02-1.96 (m, 1H), 1.91-1.85 (m, 1H), 1.77-1.73 (m, 3H), 1.69-1.62 (m, 1H), 1.55-1.39 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 145.3, 140.6, 119.4, 107.8, 107.5, 100.8, 60.9, 47.9, 42.9, 41.2, 33.8, 29.7, 26.1, 22.0; **IR** (film) υ_{max} 3382, 2924, 2857, 1472, 1234, 1119, 1040, 936, 808 cm^{-1}; **HRMS** (ESI) m/z 246.1469 $[(M + H)^+$; calculated for $[C_{15}H_{19}NO_2 + H]^+$: 246.1489.



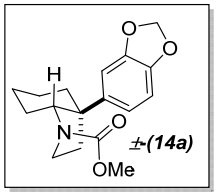
2,3,4,4a-Tetrahydro-1*H*,6*H*-5,11b-ethano[1,3]dioxolo[4,5-*j*]phenanthridine ±(2a): An oven-dried round-bottom flask was charged with (±)-**11b** (21 mg, 0.082 mmol, 1.0 equiv) in dry THF (7 mL). To the reaction mixture, **Eschenmoser's salt** (23 mg, 0.124 mmol, 1.5 equiv) was added and heated the reaction mixture at 40 °C for 30h. Upon completion of the reaction (monitoring by TLC), THF was removed under vacuum and then 10 ml EtOAc and 1(*N*) NaOH was added until the solution became basic. The organic phases were combined and dried over anhydrous K_2CO_3 and concentrated under vacuum. The crude product was purified by flash chromatography with basic alumina to give amine **2a** as a light yellow gel. 16 mg, 72% yield as light yellow gel, R_f = 0.40 (10% MeOH in CH_2Cl_2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.43 (s, 1H), 5.86 (s, 2H), 4.31 (d, *J* = 16.8 Hz, 1H), 3.72 (d, *J* = 16.8 Hz, 1H), 3.27-3.34 (m, 1H), 2.74-2.83 (m, 2H), 2.31-2.34 (m, 1H), 2.15-2.22 (m, 1H), 1.70-1.84 (m, 1H), 1.56-1.61 (m, 1H), 1.47-1.51 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.1, 145.5, 142.3, 126.2, 106.2, 103.3, 100.6, 57.3, 62.1, 51.9, 42.8, 37.9, 29.0, 27.6, 24.4, 21.8; **IR** (film) υ_{max} 2929, 2916, 2881, 1649, 1484, 1454, 1238, 1040, 935, 867 cm^{-1}; **HRMS** (ESI) m/z 258.1501 [$(M + H)^+$; calculated for $[C_{167}H_{19}NO_2 + H]^+$: 258.1489].

Synthesis of Amine Derivatives 14a-b:

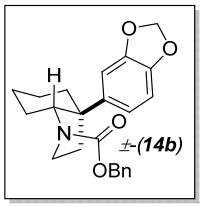


A round-bottom flask was charged with amine **(±)-11b** (0.03 mmol; 1.0 equiv.) in toluene : $NaHCO_3$ (1:1) (5 mL) at room temperature. To this reaction mixture chloroformate (0.036 mmol, 1.2 equiv) was added dropwise and it was stirred for 30

min at room temperature. Upon completion of the reaction (monitoring by TLC), it was diluted by 10 mL EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 7 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography to give product **14** as a light yellow gel.



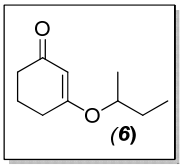
Methyl 3a-(benzo[*d*][1,3]dioxol-5-yl)octahydro-1*H*-indole-1-carboxylate ±(**14a**)**:** 7 mg, 74% yield as light yellow gel, R_f = 0.40 (30% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.84-6.72 (m, 3H), 5.93 (s, 2H), 4.19-4.08 (m, 1H), 3.70-3.64 (m, 3H), 3.41-3.37 (m, 1H), 3.13 (m, 1H), 2.38-2.30 (m, 1H), 2.17-2.12 (m, 1H), 2.04-1.92 (m, 2H), 1.68-1.29 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) (rotameric mixture) δ 155.32, 155.26, 147.79, 145.68, 141.61, 141.45, 118.38, 107.98, 106.63, 106.47, 100.93, 59.82, 52.26, 52.08, 48.21, 47.45, 43.53, 43.31, 36.26, 35.91, 33.09, 31.51, 29.14, 28.24, 23.45, 23.17, 22.31; **IR** (film) υ_{max} 2928, 2862, 2357, 2321, 1695, 1649, 1454, 1394, 1266, 1236, 1193, 1155, 1116, 1041, 939, 807, 770, 738, 705 cm^{-1}; **HRMS** (ESI) m/z 304.1562 $[(M + H)^+$; calculated for $[C_{17}H_{21}NO_4 + H]^+$: 304.1543].

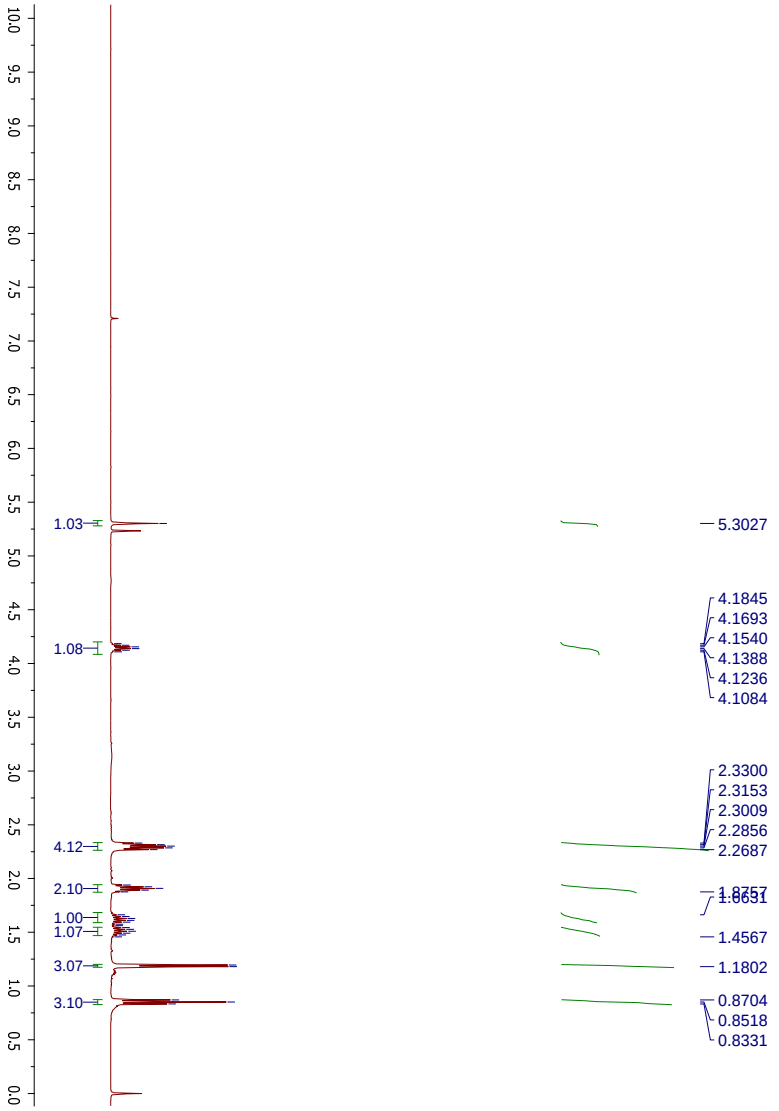


Benzyl 3a-(benzo[*d*][1,3]dioxol-5-yl)octahydro-1*H*-indole-1-carboxylate ±(**14b**)**:** 9 mg, 83% yield as colorless gel, R_f = 0.50 (20% EtOAc in hexane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 5H), 6.86-6.67 (m, 3H), 5.94 (s, 2H), 5.20-5.07 (m, 2H), 4.25-4.12 (m, 1H), 3.46-3.41 (m, 1H), 3.23-3.16 (m, 1H), 2.40-2.32 (m, 1H), 2.19-1.92 (m, 3H), 1.69-1.37 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) (rotameric mixture) δ 154.63, 154.44, 147.82, 145.69, 141.41, 141.38, 140.94, 137.22, 128.56, 128.48, 128.39, 127.83, 127.74, 127.64, 127.48, 126.98, 118.38, 118.30, 107.95, 106.69, 106.56, 106.46, 100.94, 100.93, 66.59, 66.34, 59.88, 59.82, 48.21, 47.47, 43.59, 43.40, 37.17, 35.81, 33.16,

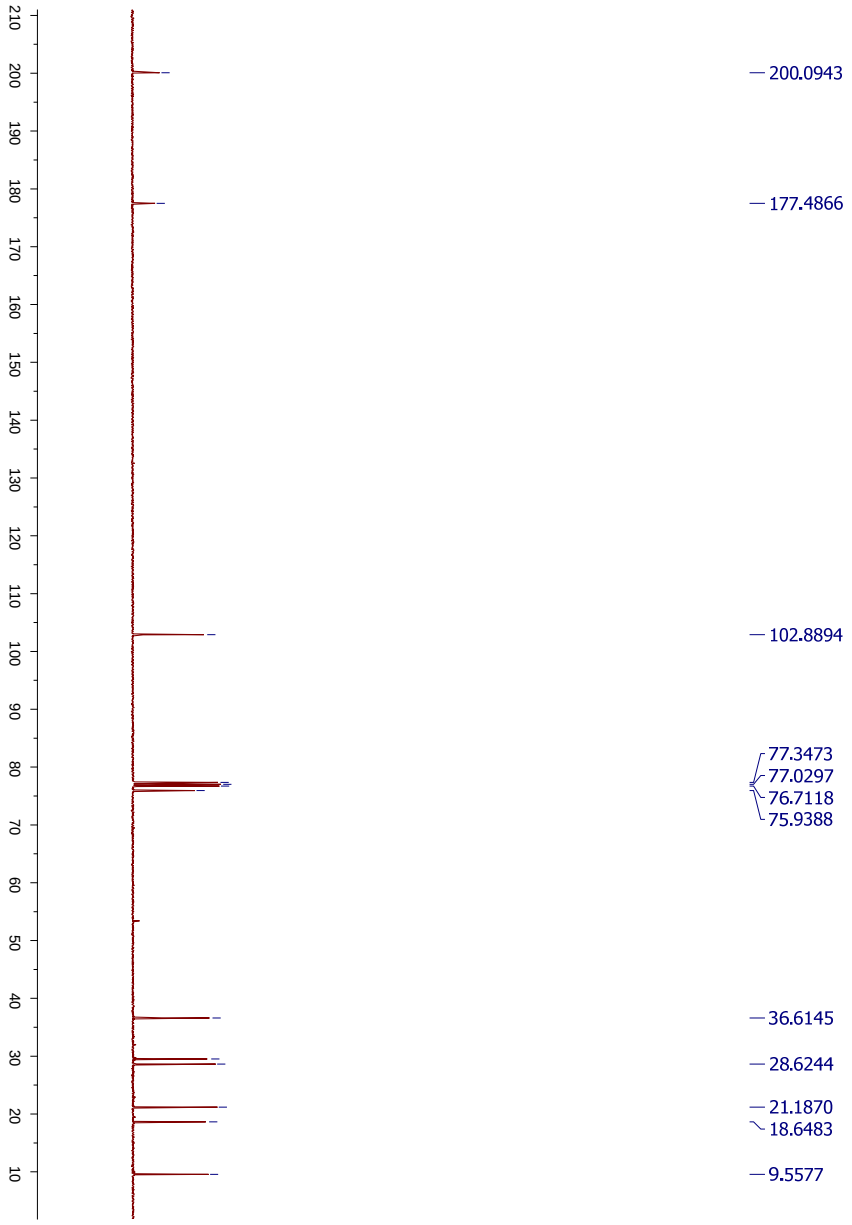
31.49, 29.70, 29.27, 23.50, 23.16, 22.33, 22.28; **IR** (film) υ_{max} 2929, 2857, 1696, 1649, 1415, 1348, 1265, 1236, 1154, 1098, 1040, 938, 808, 739, 700 cm^{-1}; **HRMS** (ESI) m/z 380.1856 $[(M + H)^+$; calculated for $[C_{23}H_{25}NO_4 + H]^+$: 380.1856].

^{1}H, ^{13}C and Mass spectral traces

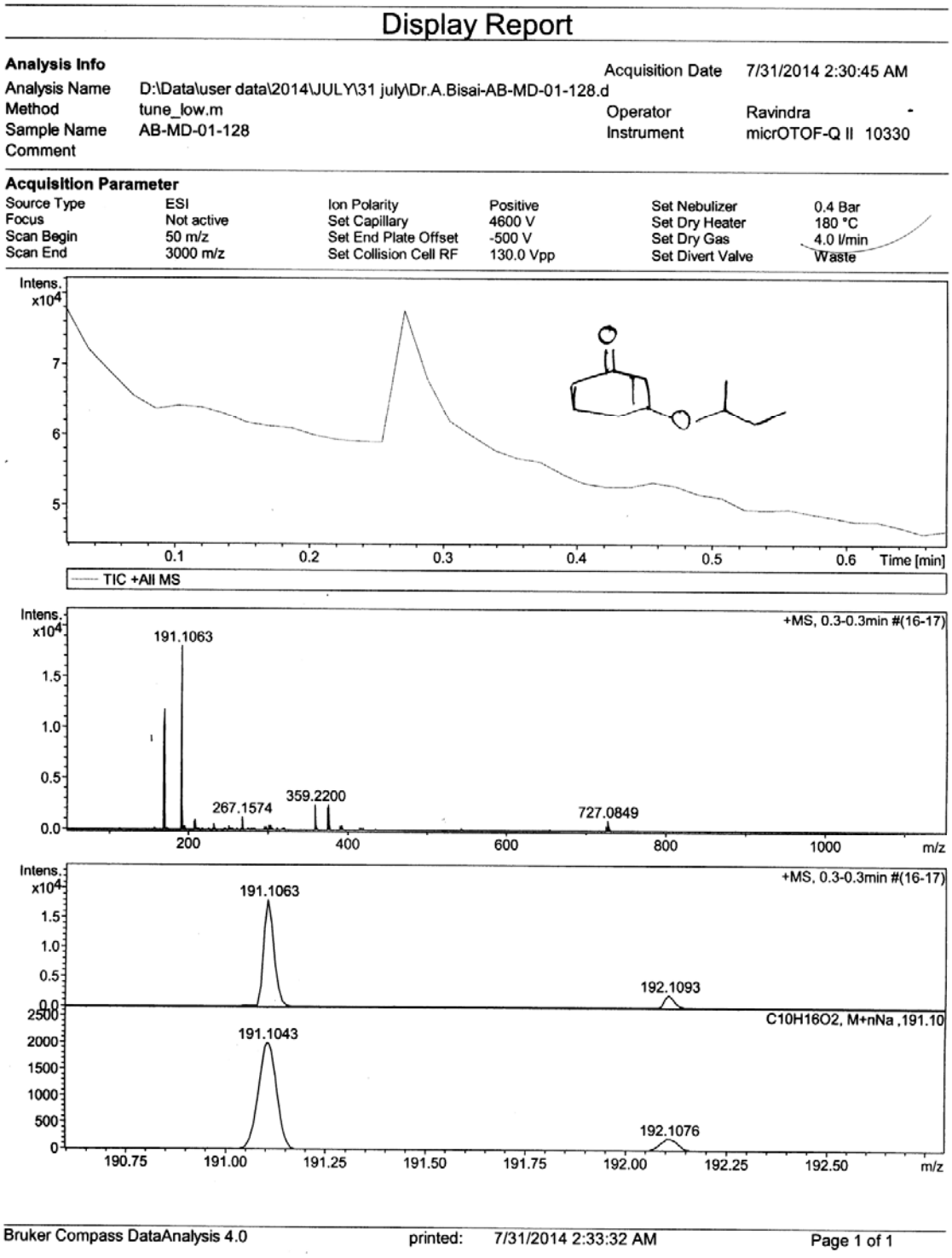




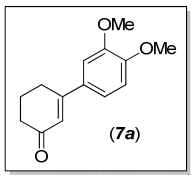
^{1}H NMR (400 MHz, $CDCl_3$) of compound **(6)**

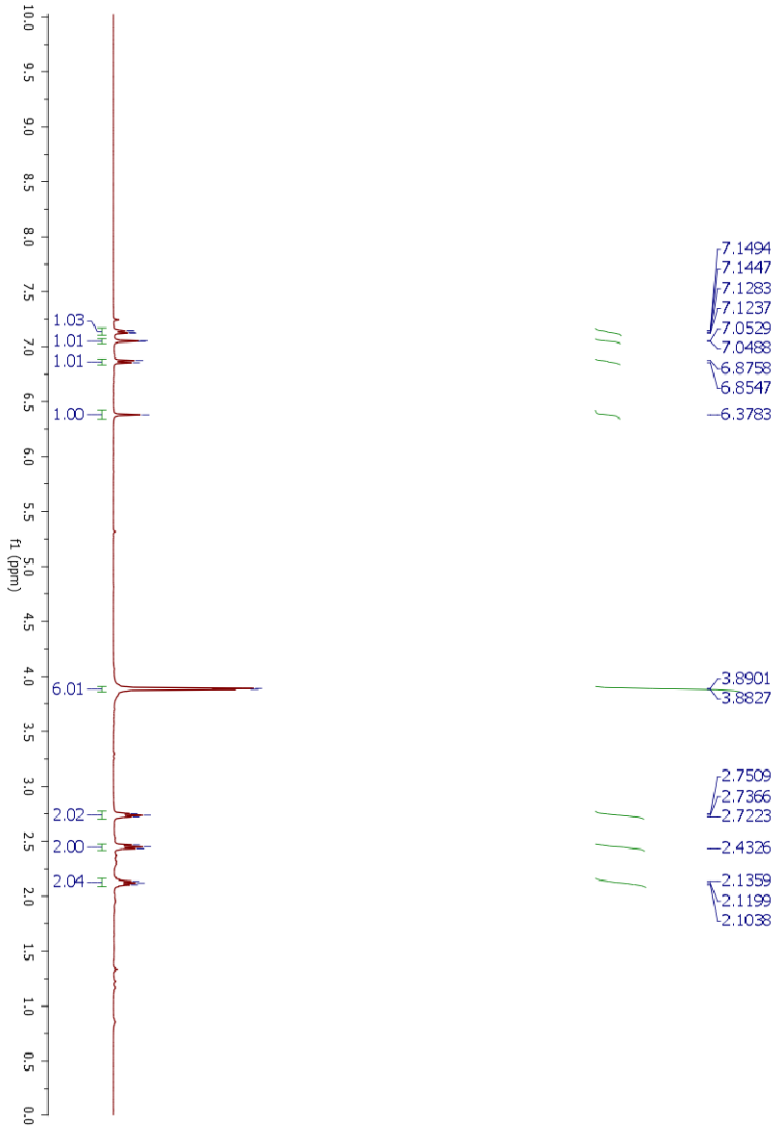


^{13}C NMR (100 MHz, $CDCl_3$) of compound **(6)**

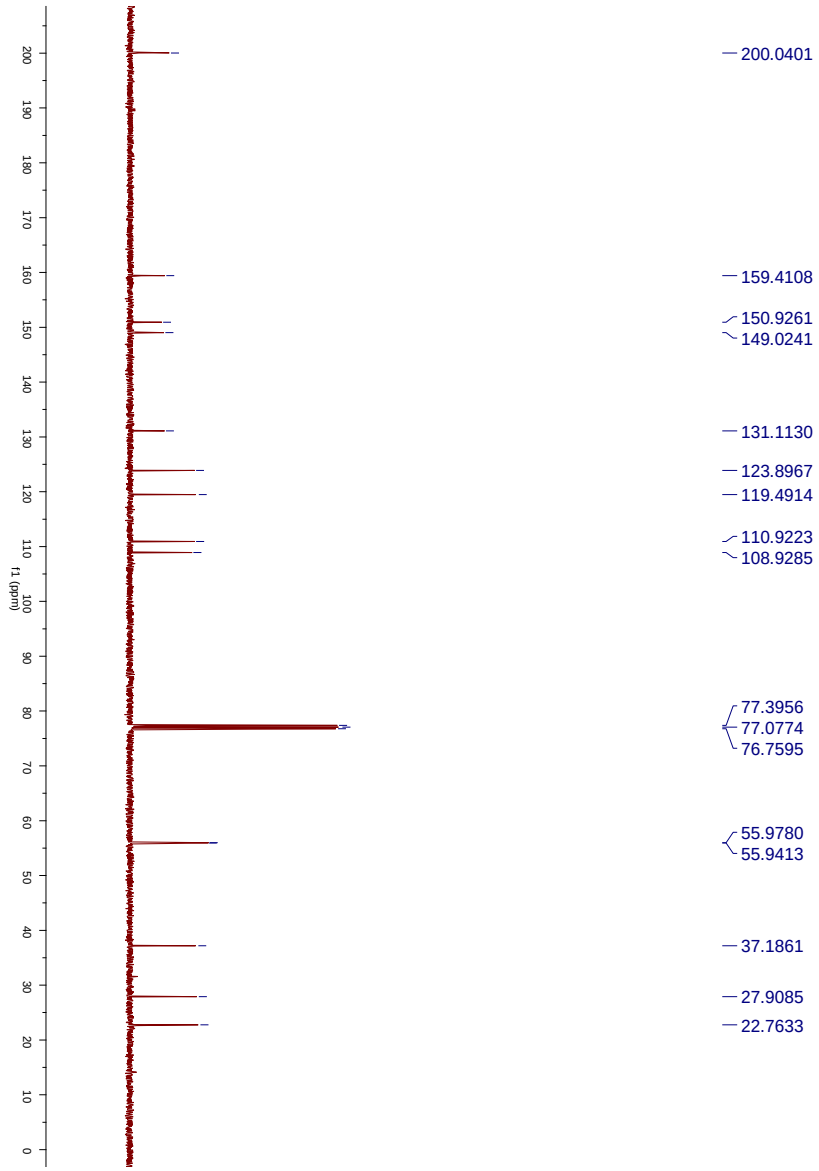


Scanned copy of mass spectrum of (**6**)

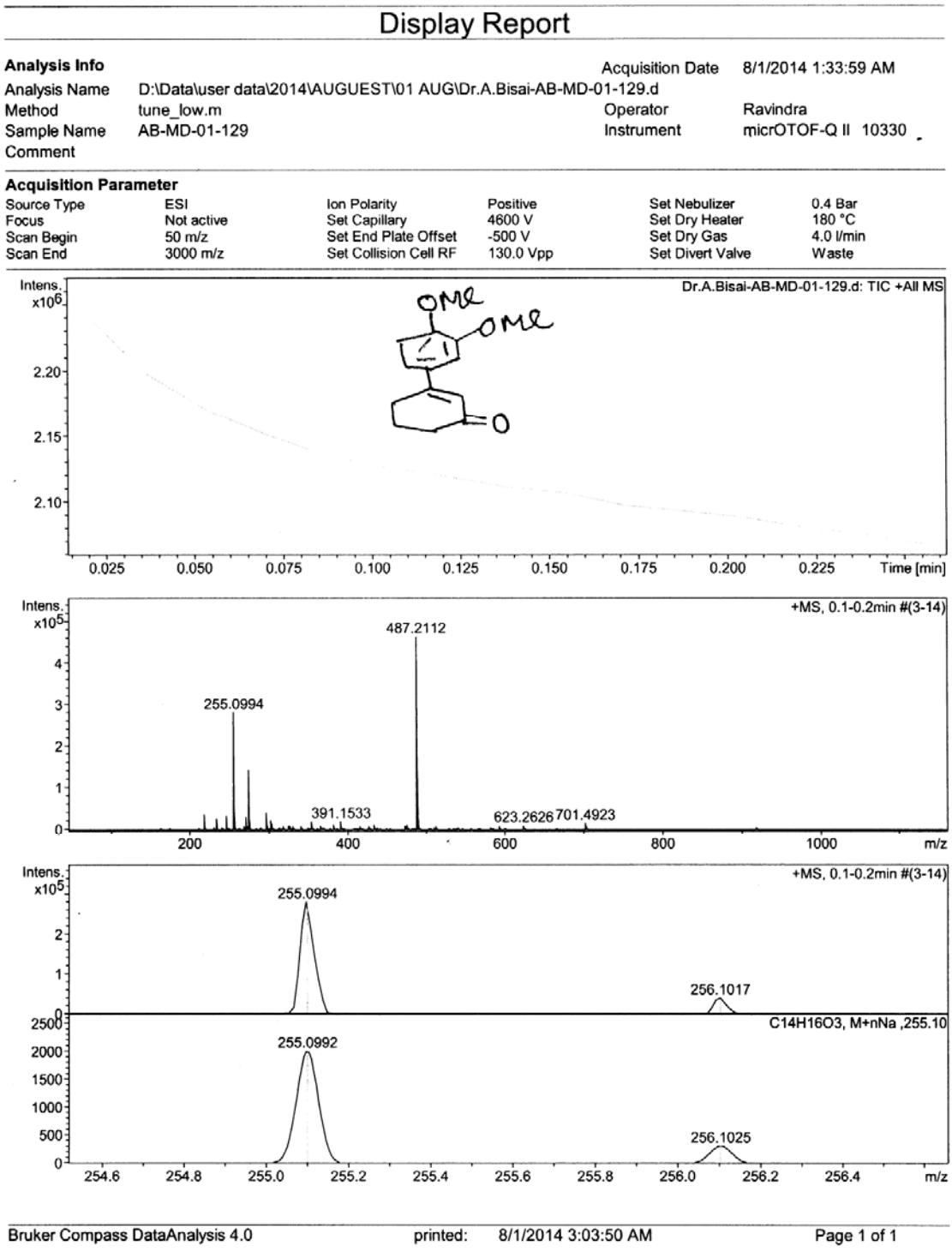




^{1}H NMR (400 MHz, $CDCl_3$) of compound **(7a)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **(7a)**



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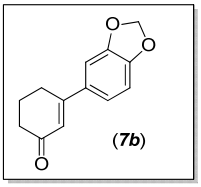
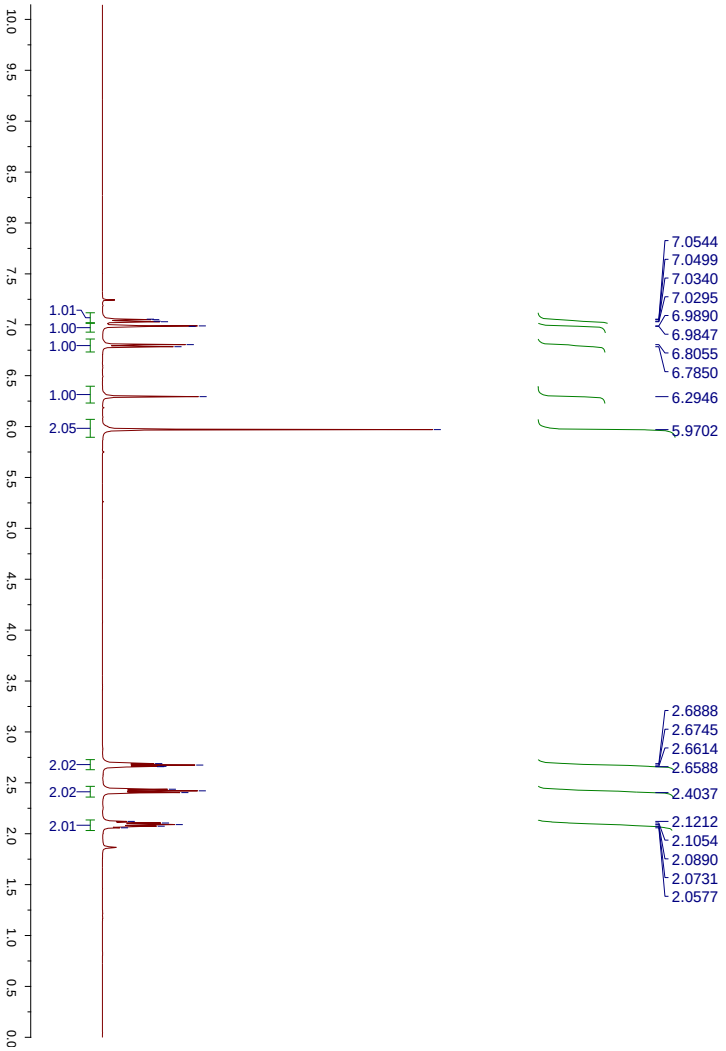
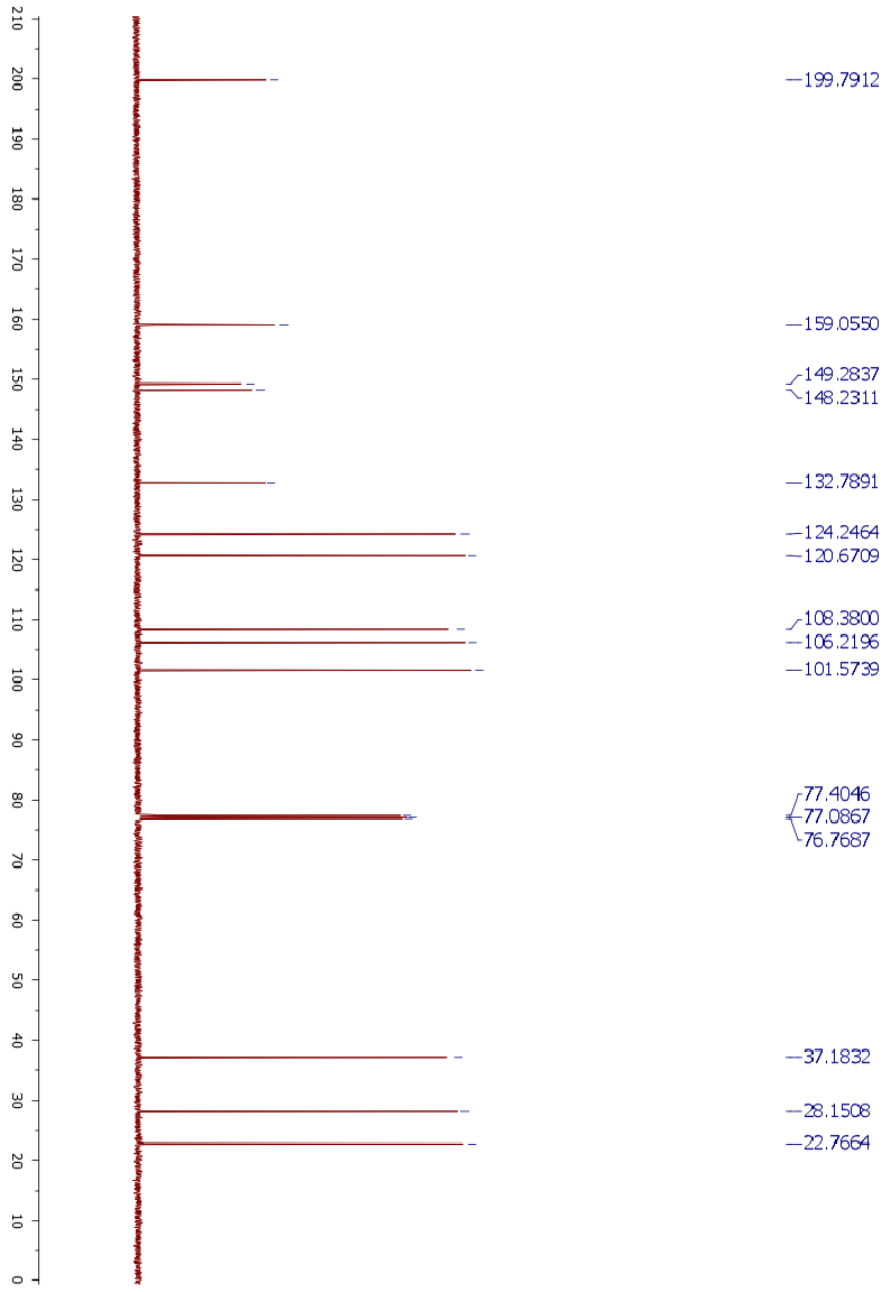
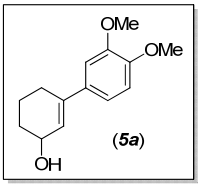


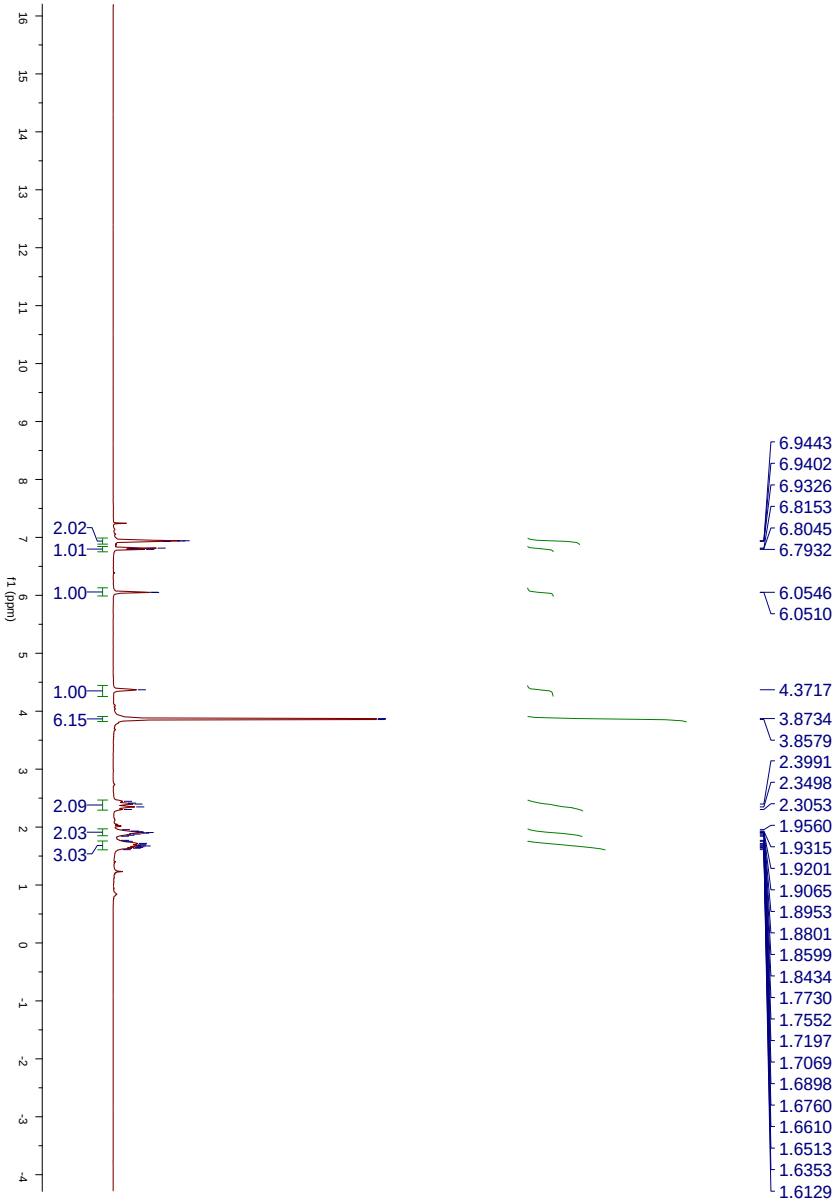


^{1}H NMR (400 MHz, $CDCl_3$) of compound **(7b)**

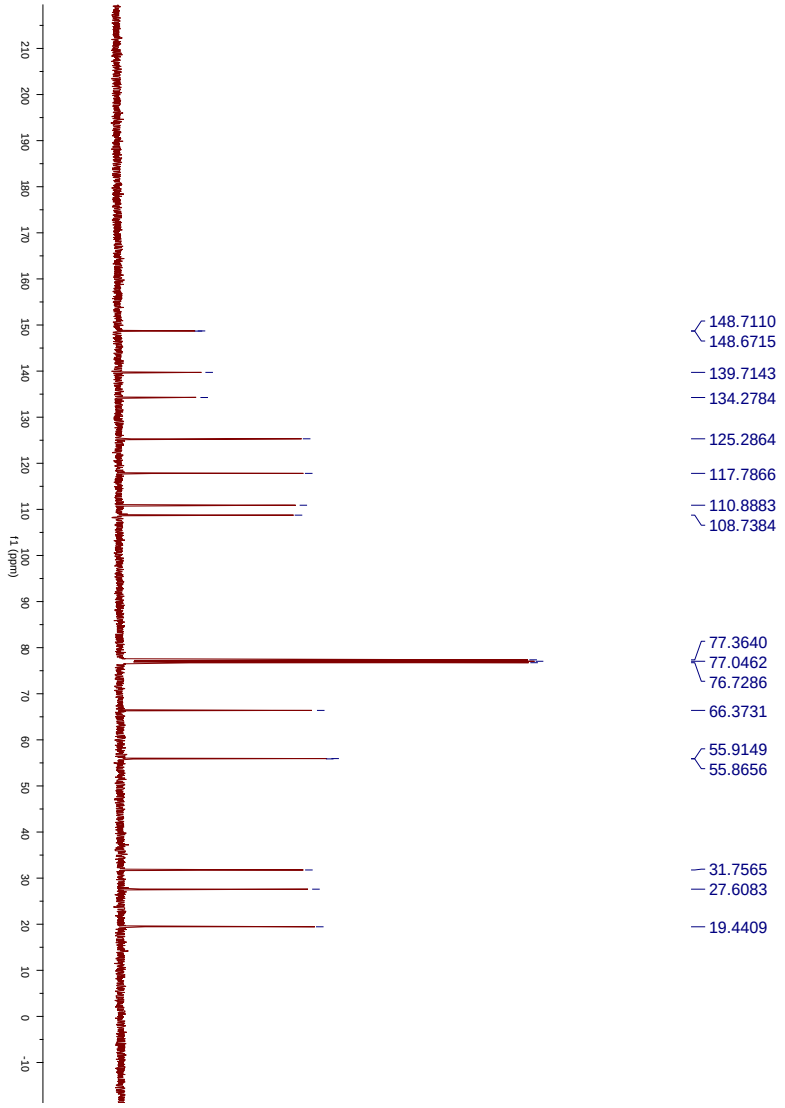


^{13}C NMR (100 MHz, $CDCl_3$) of compound **(7b)**

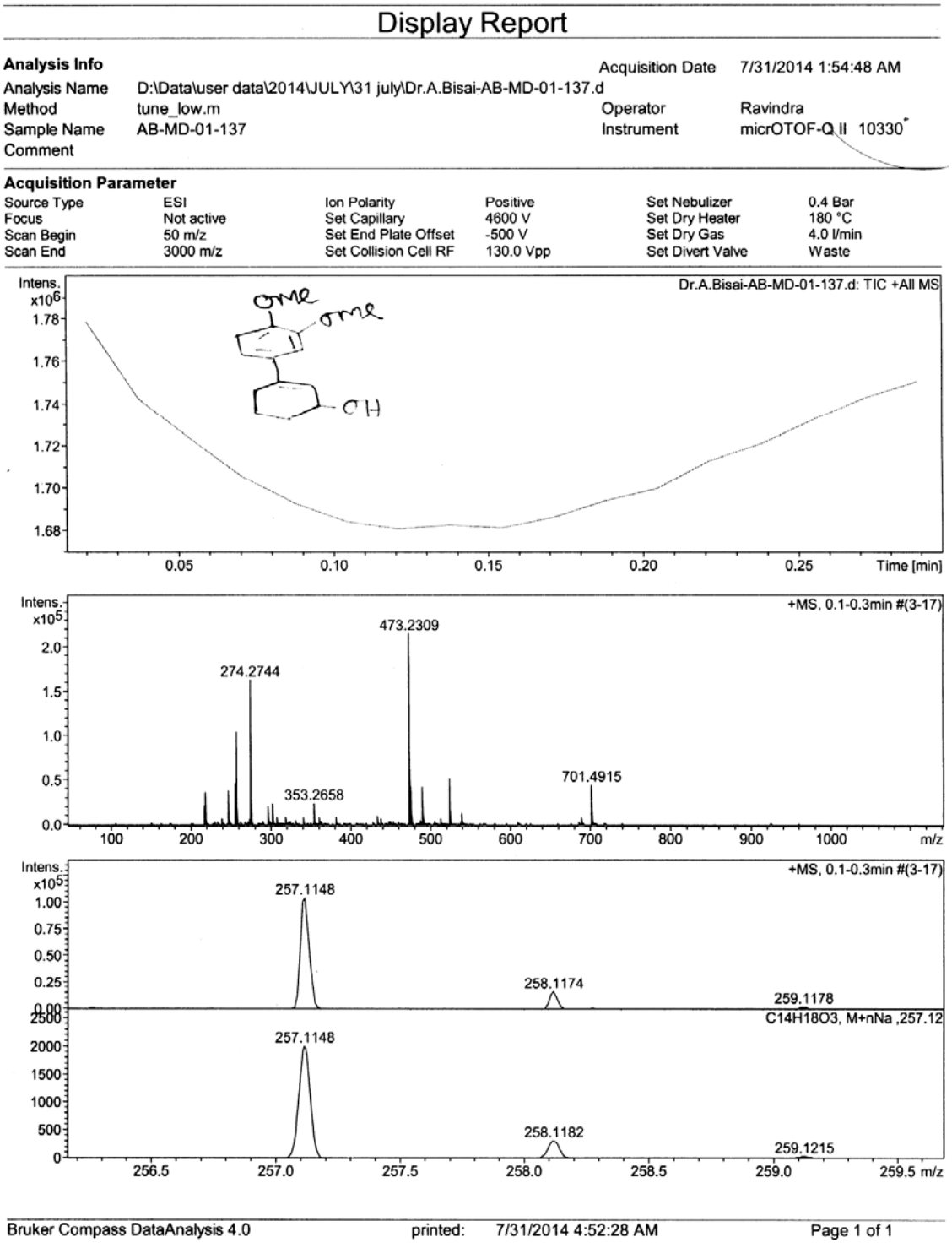




^{1}H NMR (400 MHz, $CDCl_3$) of compound **(5a)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound **(5a)**



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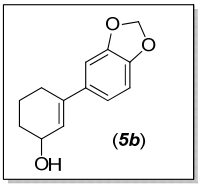
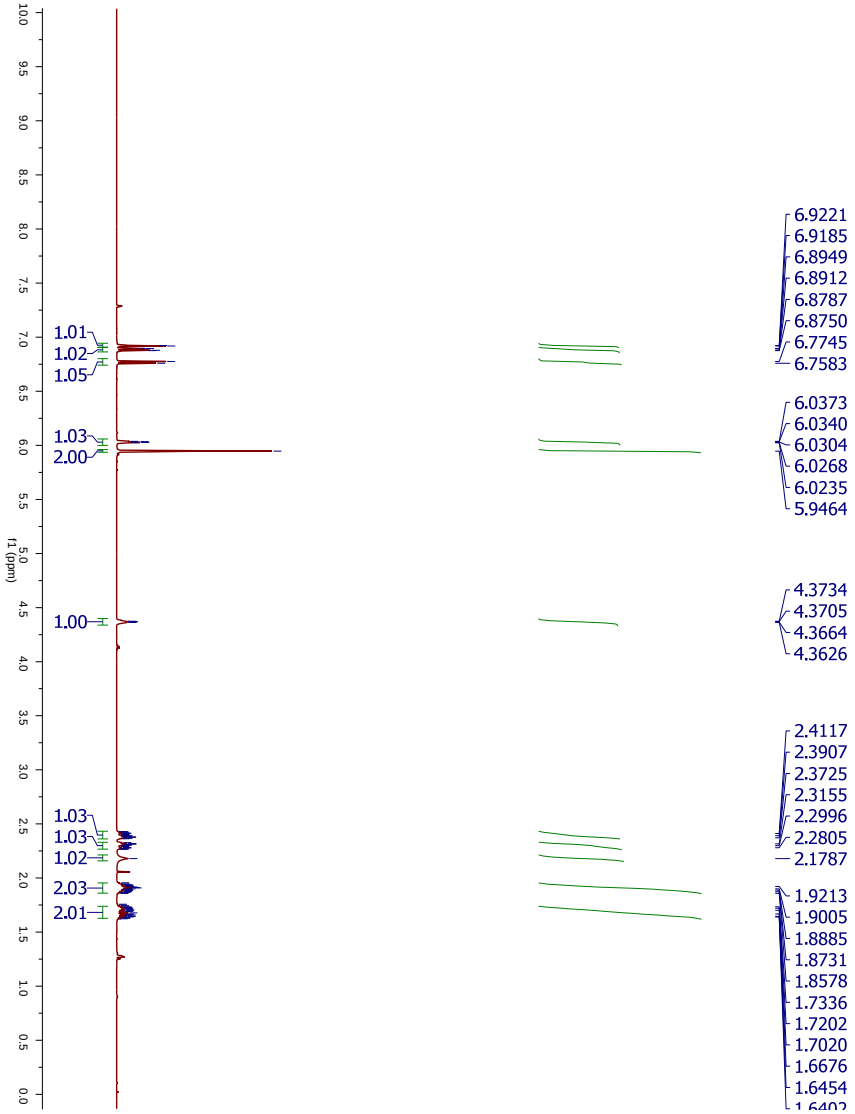
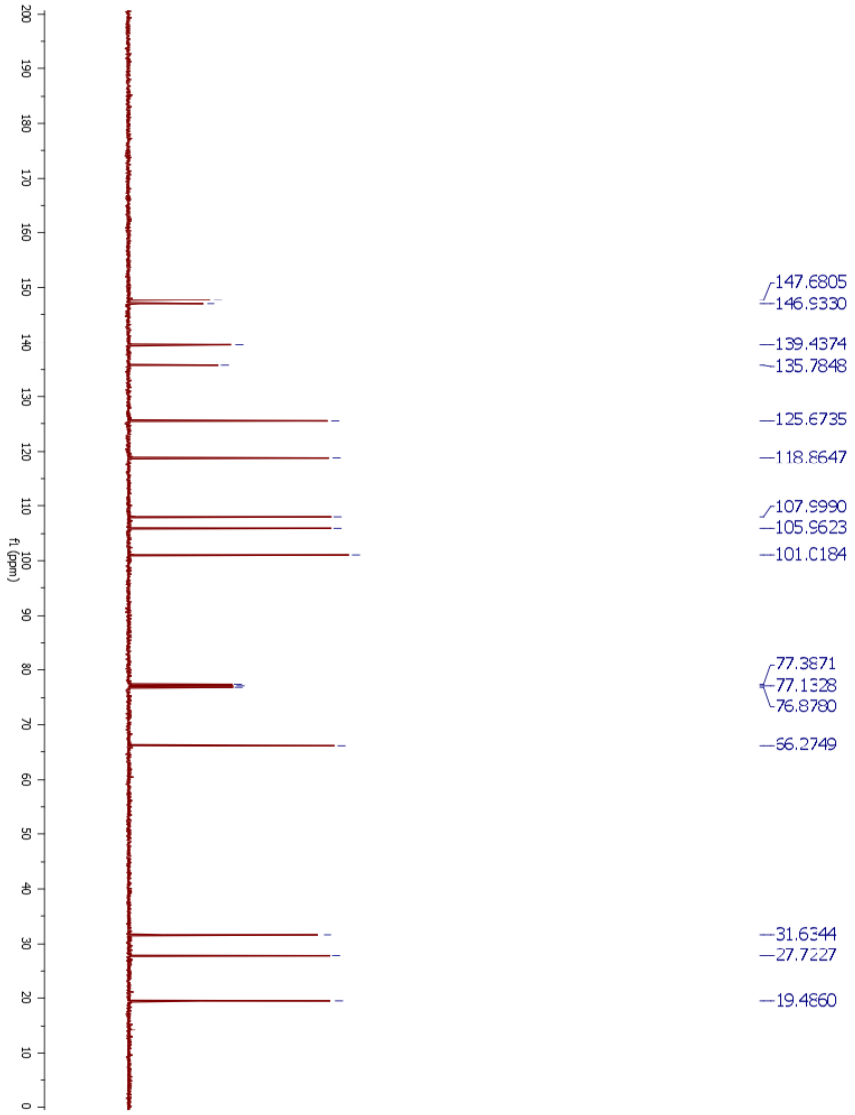
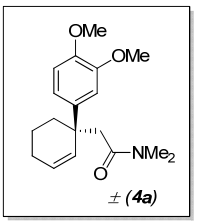


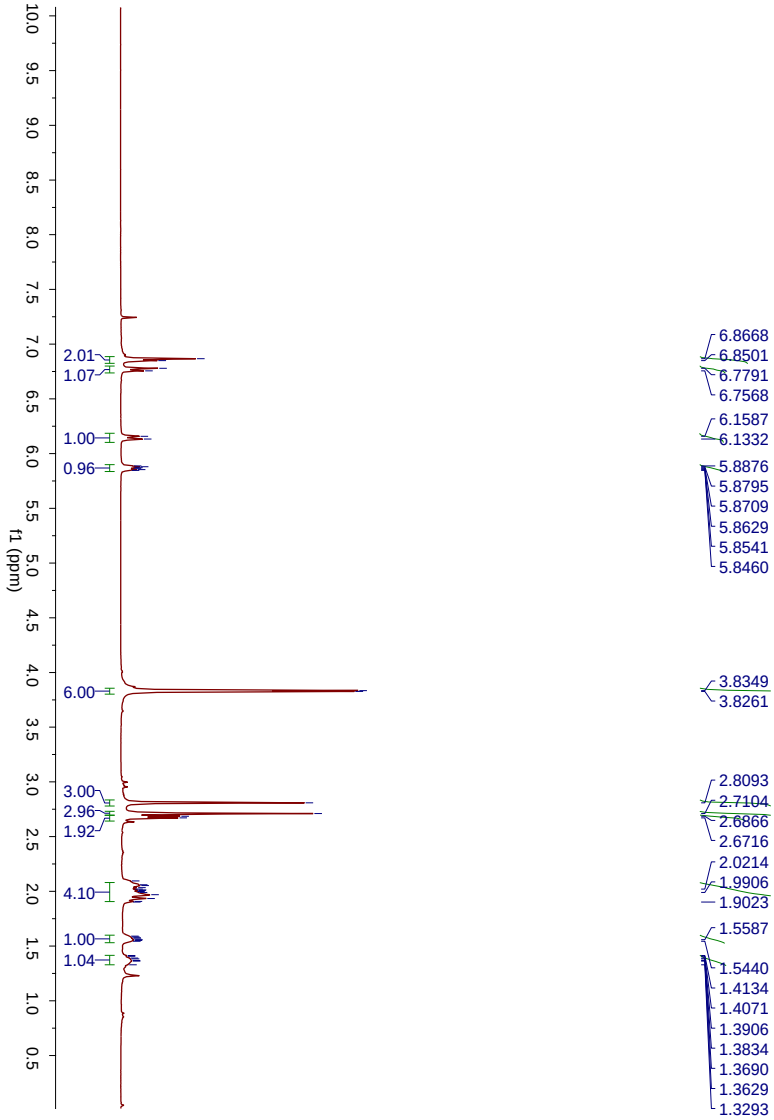


^{1}H NMR (500 MHz, $CDCl_3$) of compound **(5b)**

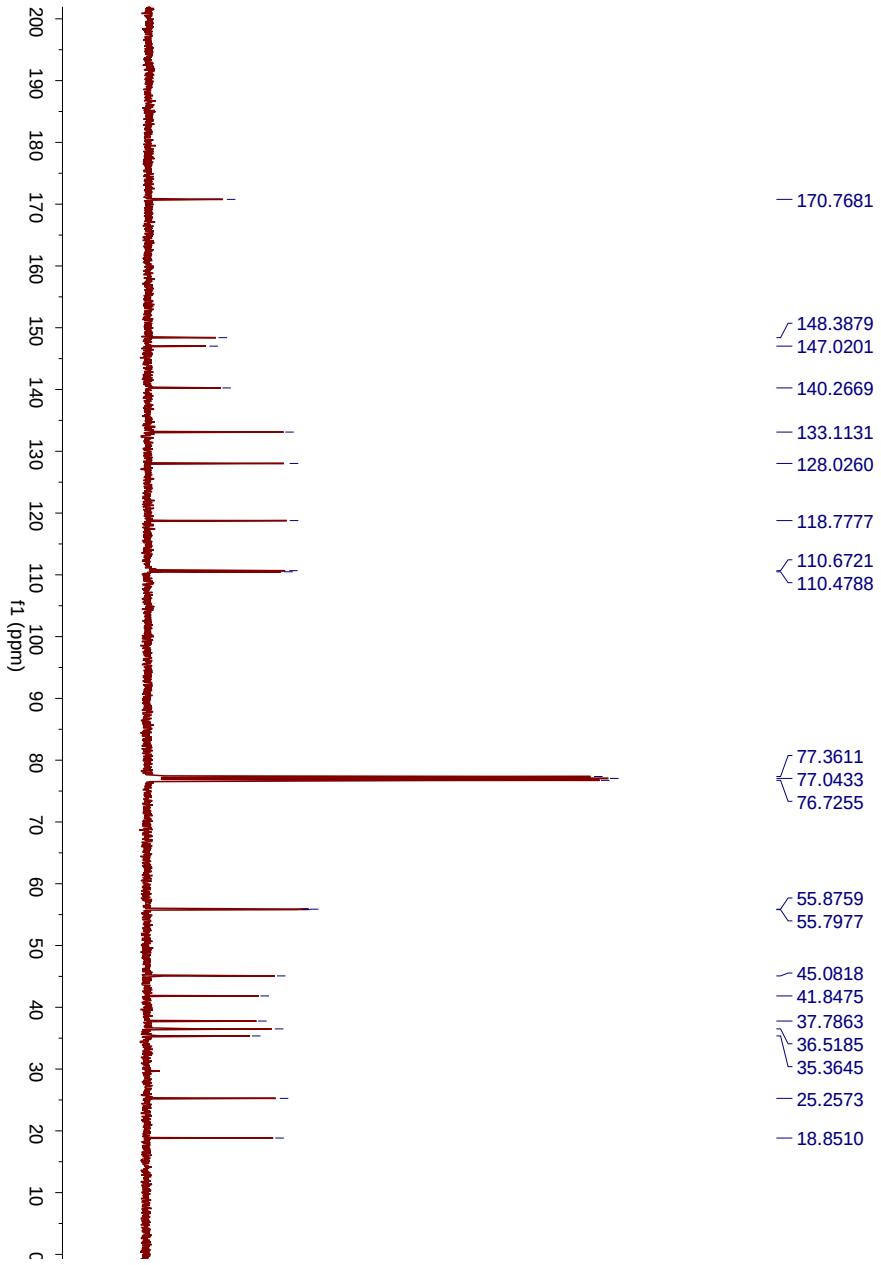


^{13}C NMR (125 MHz, $CDCl_3$) of compound **(5b)**

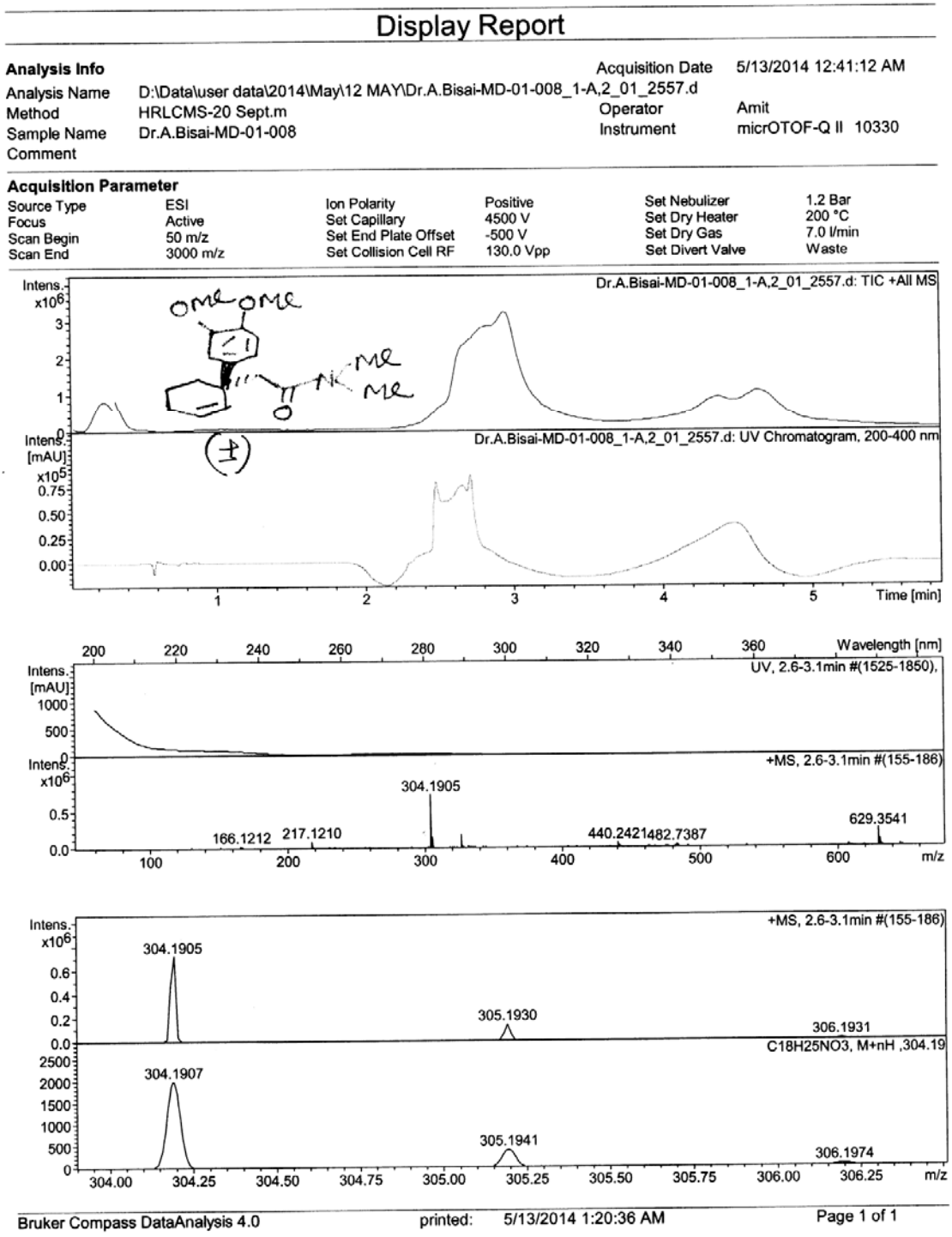




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(4a)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(4a)**



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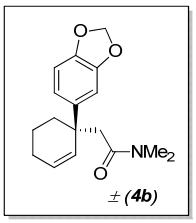
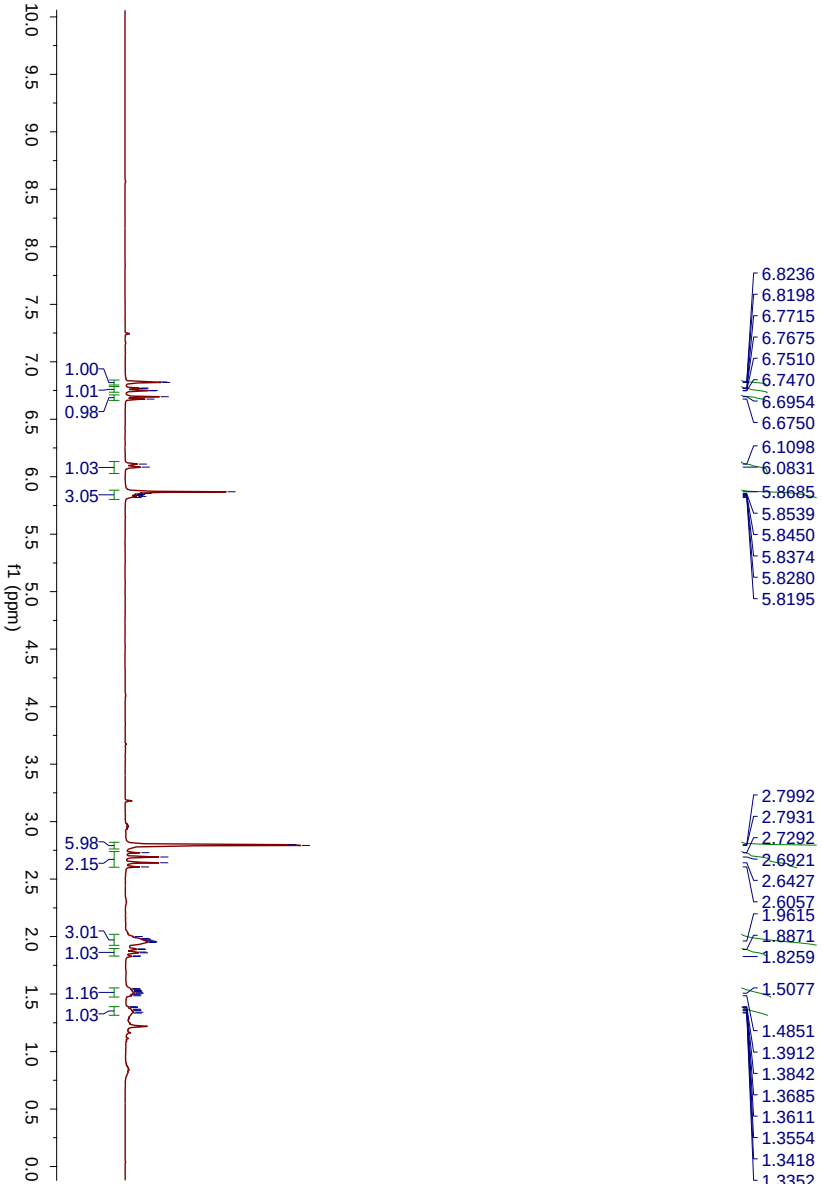
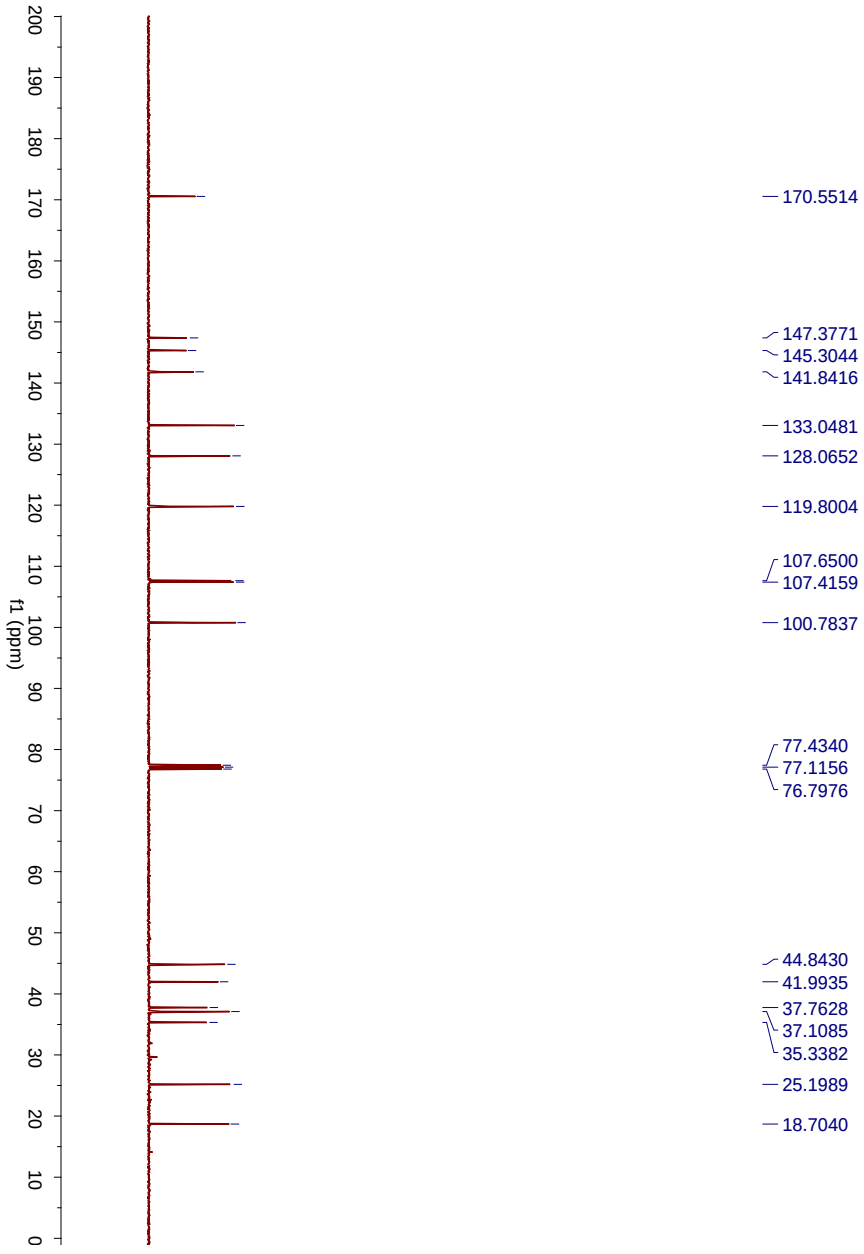
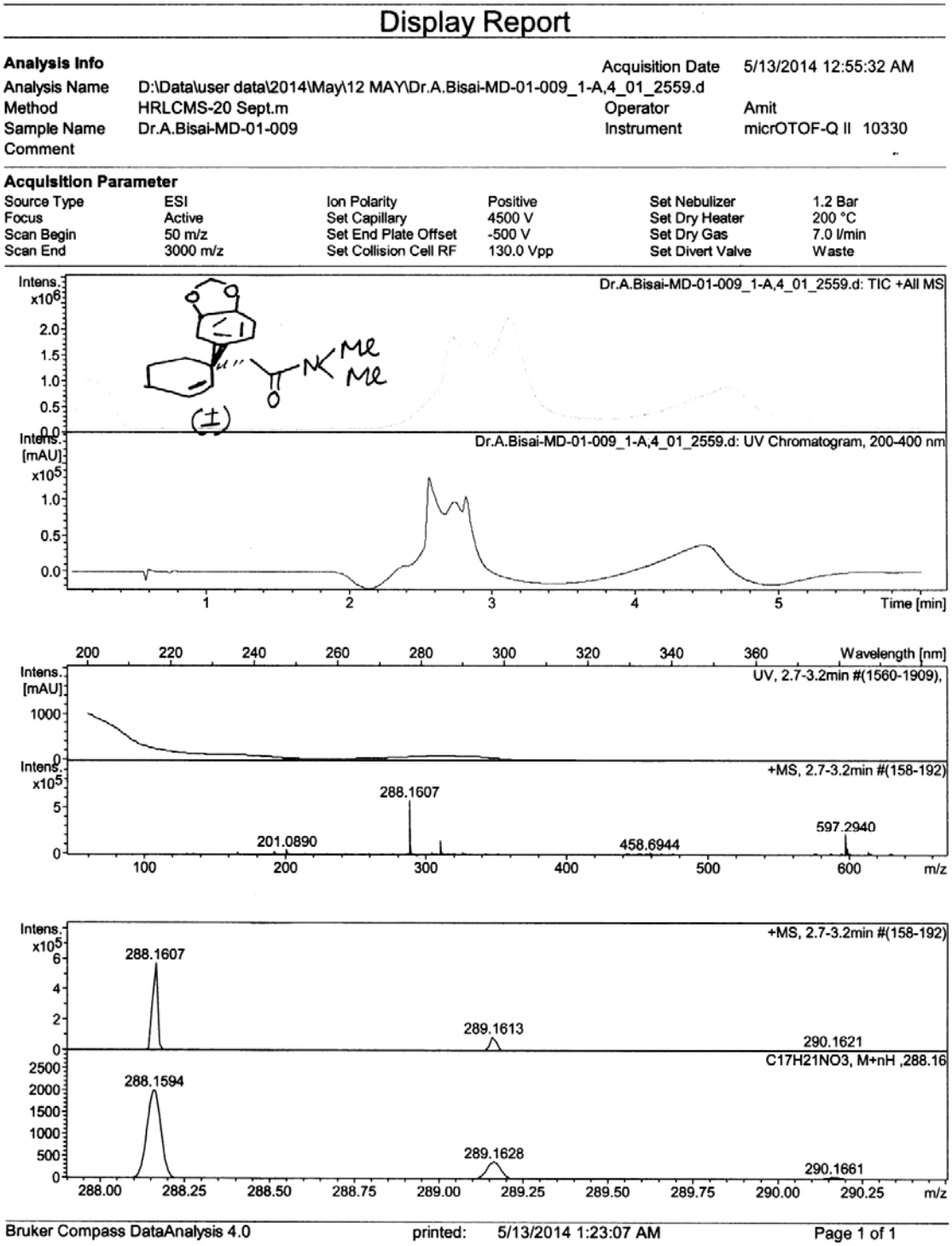




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(4b)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(4b)**



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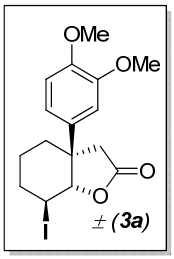
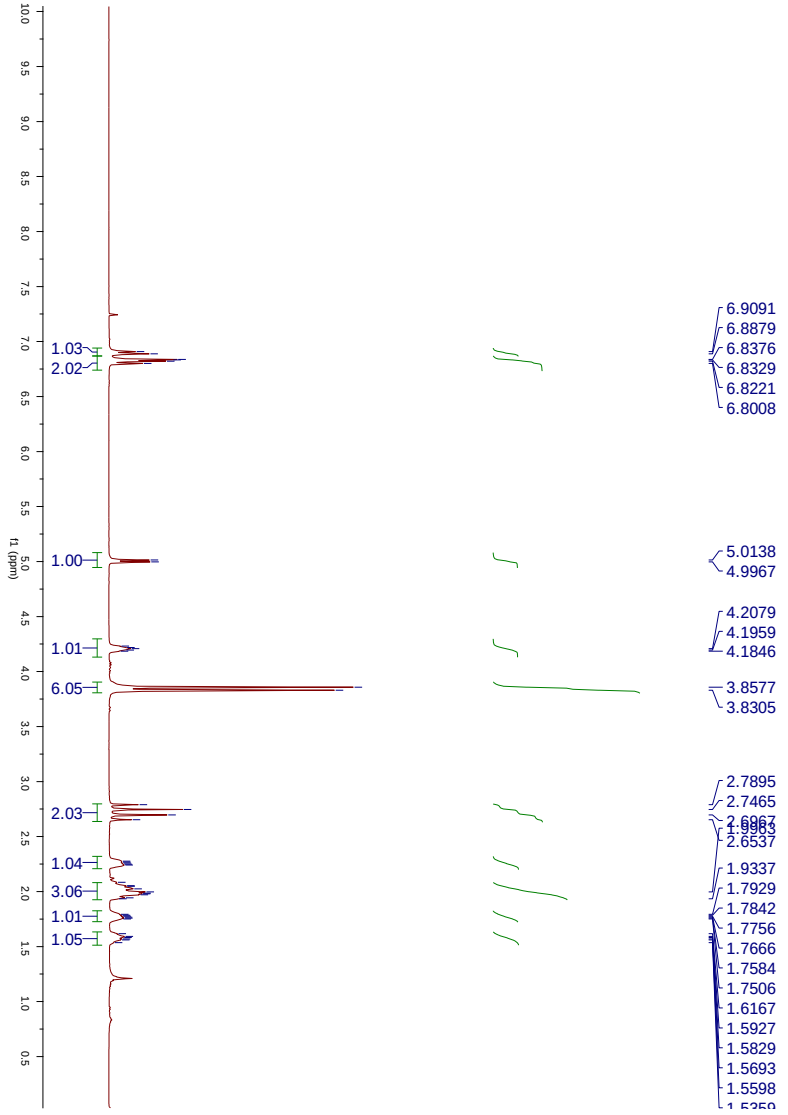
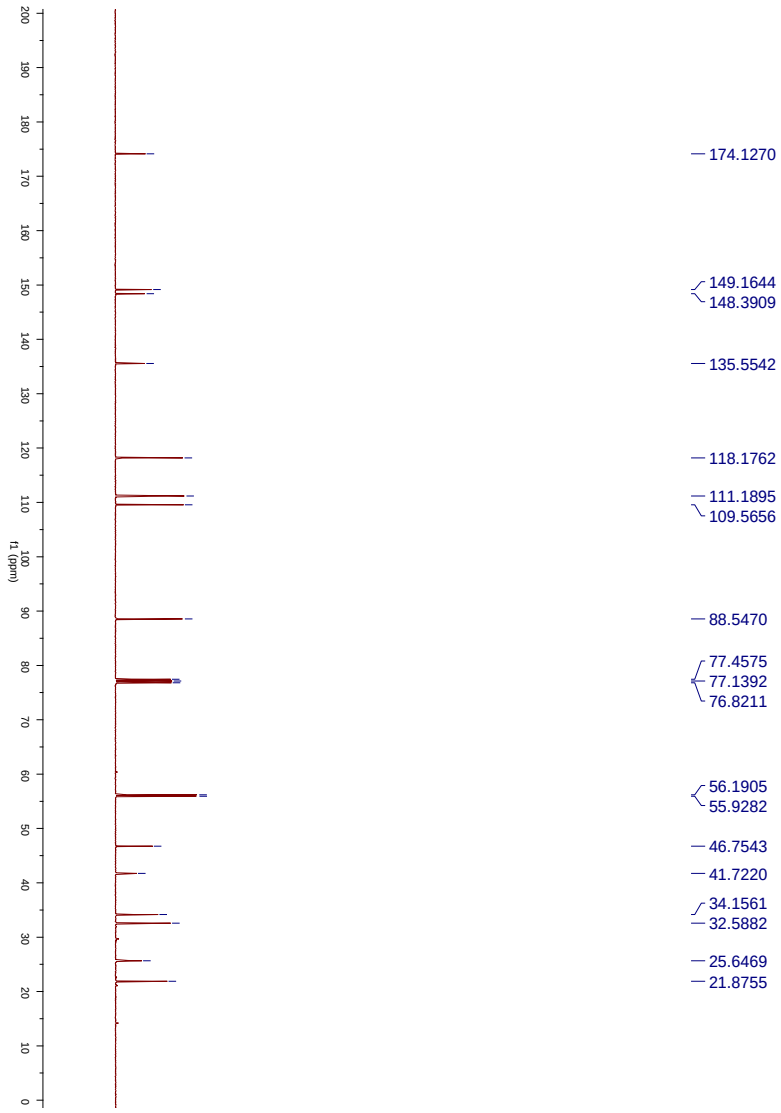
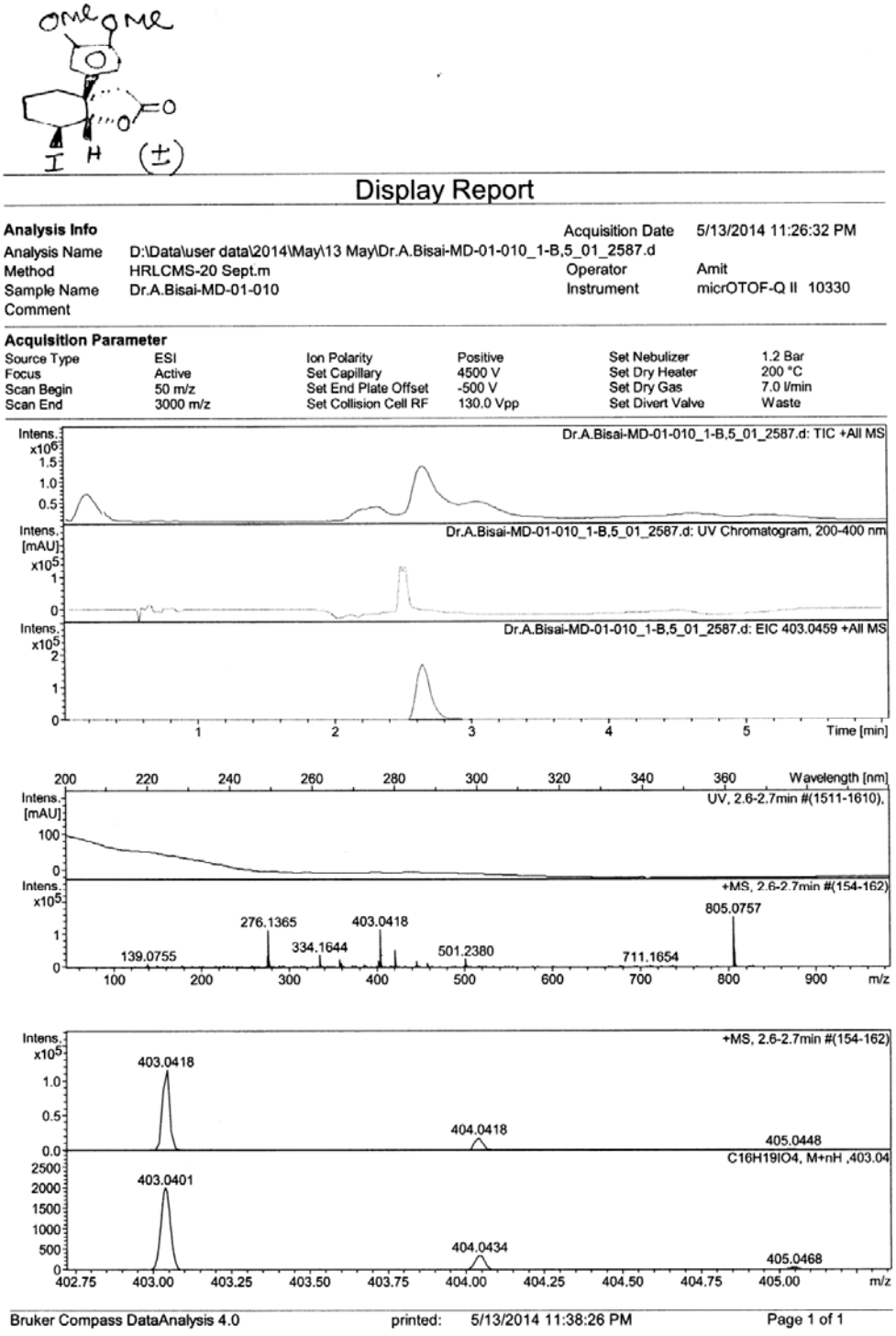




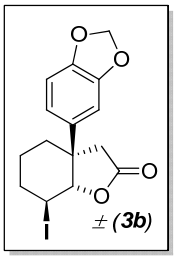
^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(3a)**

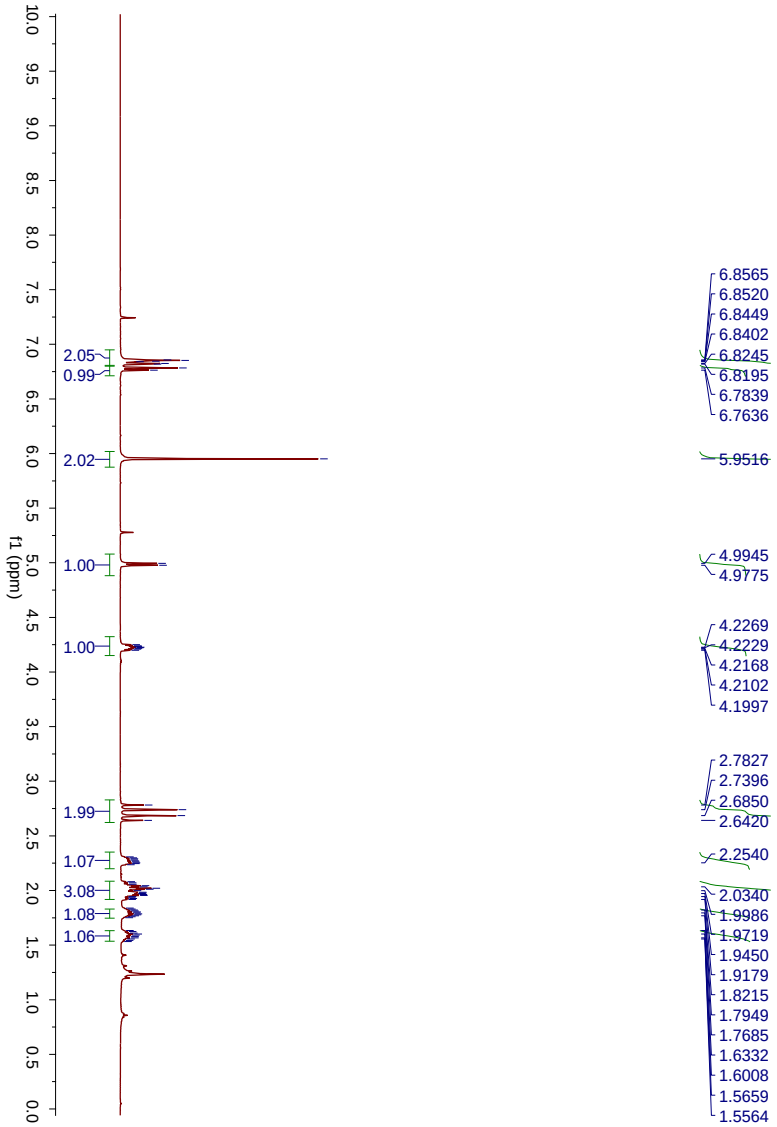


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(3a)**

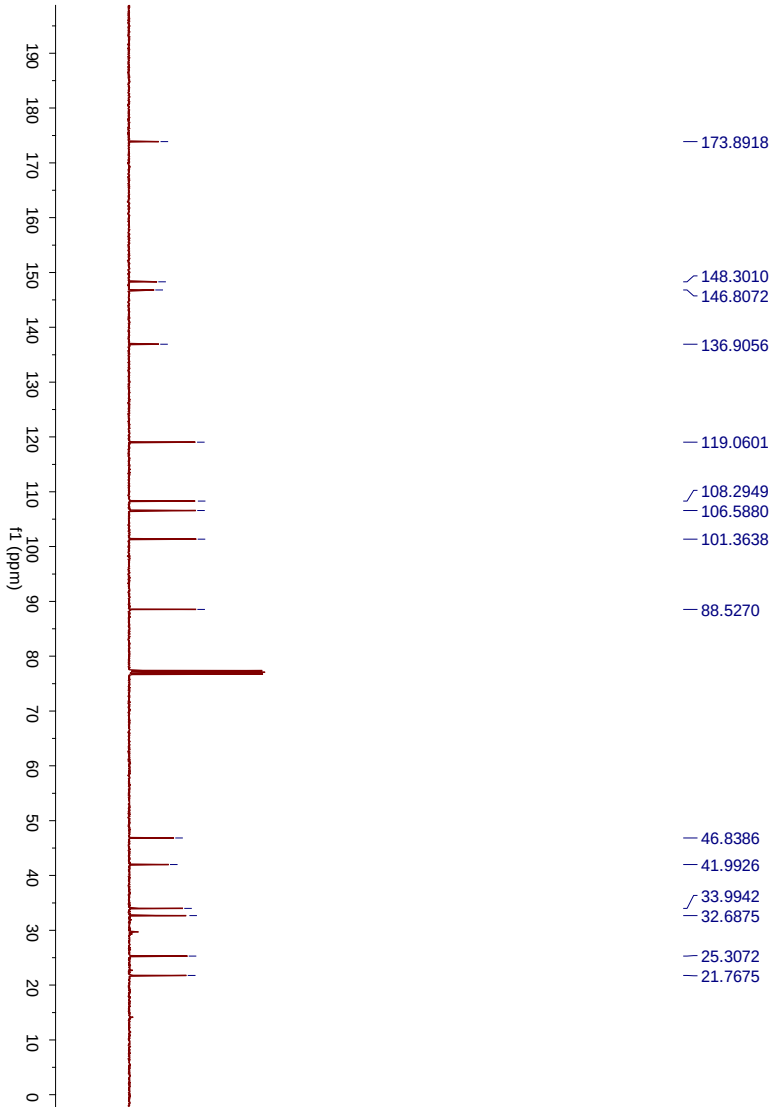


Scanned copy of mass spectrum of ±(**3a**)

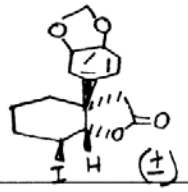




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(3b)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(3b)**



Display Report

Analysis Info

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Sample Name	Dr.A.Bisai-MD-01-011	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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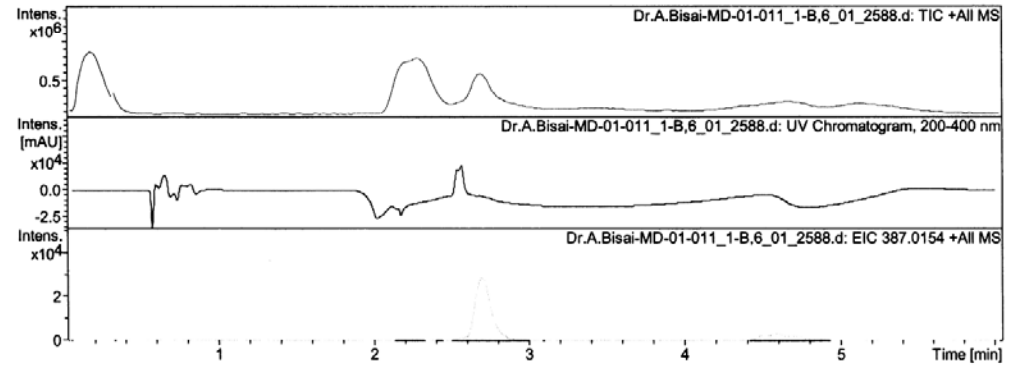
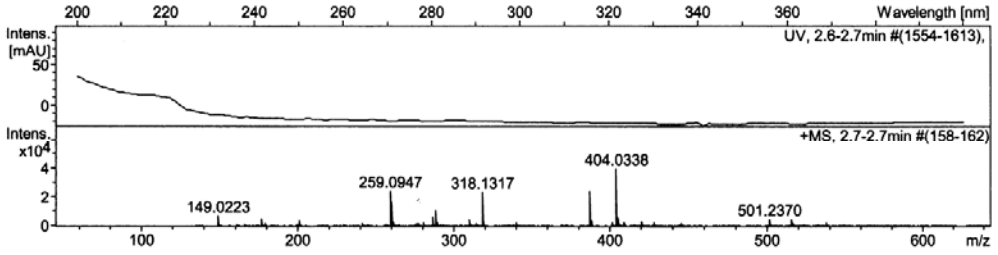
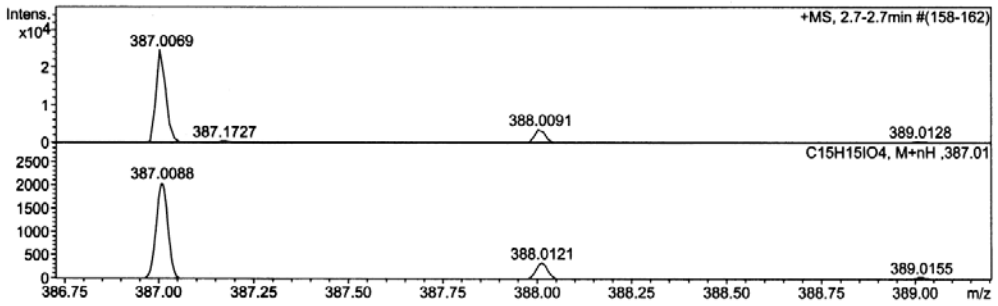
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

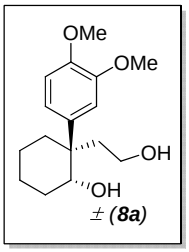




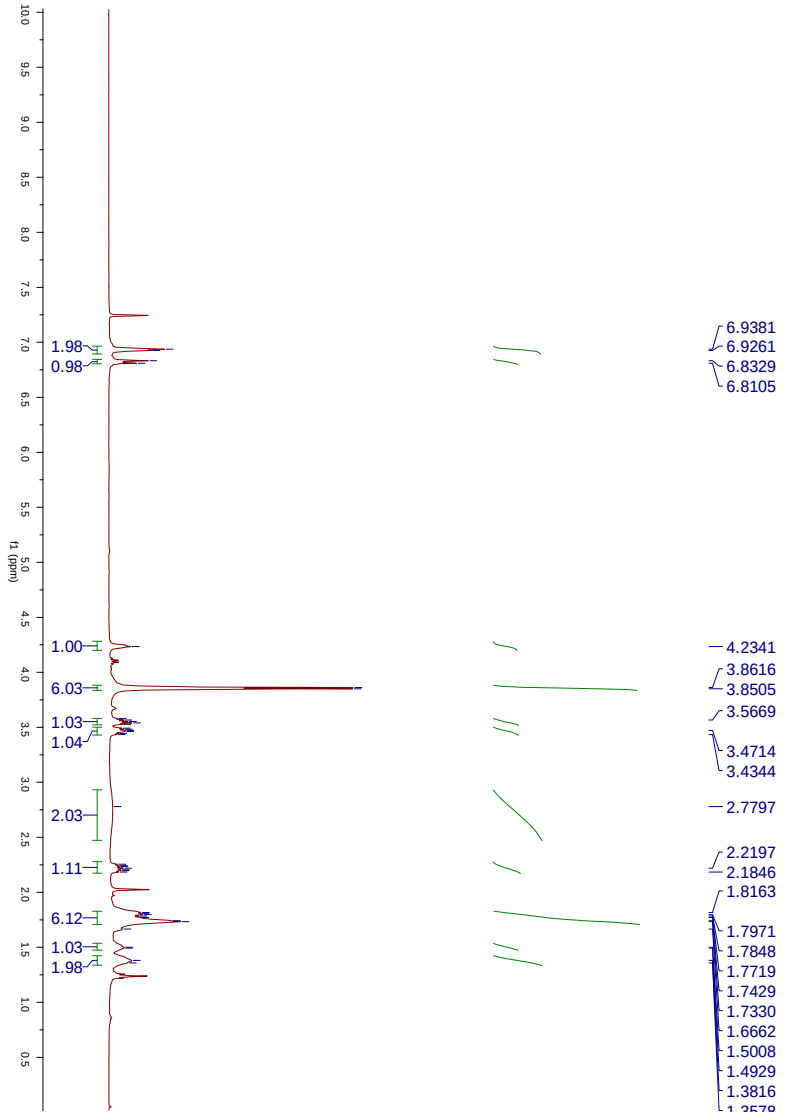


Bruker Compass DataAnalysis 4.0 printed: 5/14/2014 12:18:39 AM Page 1 of 1

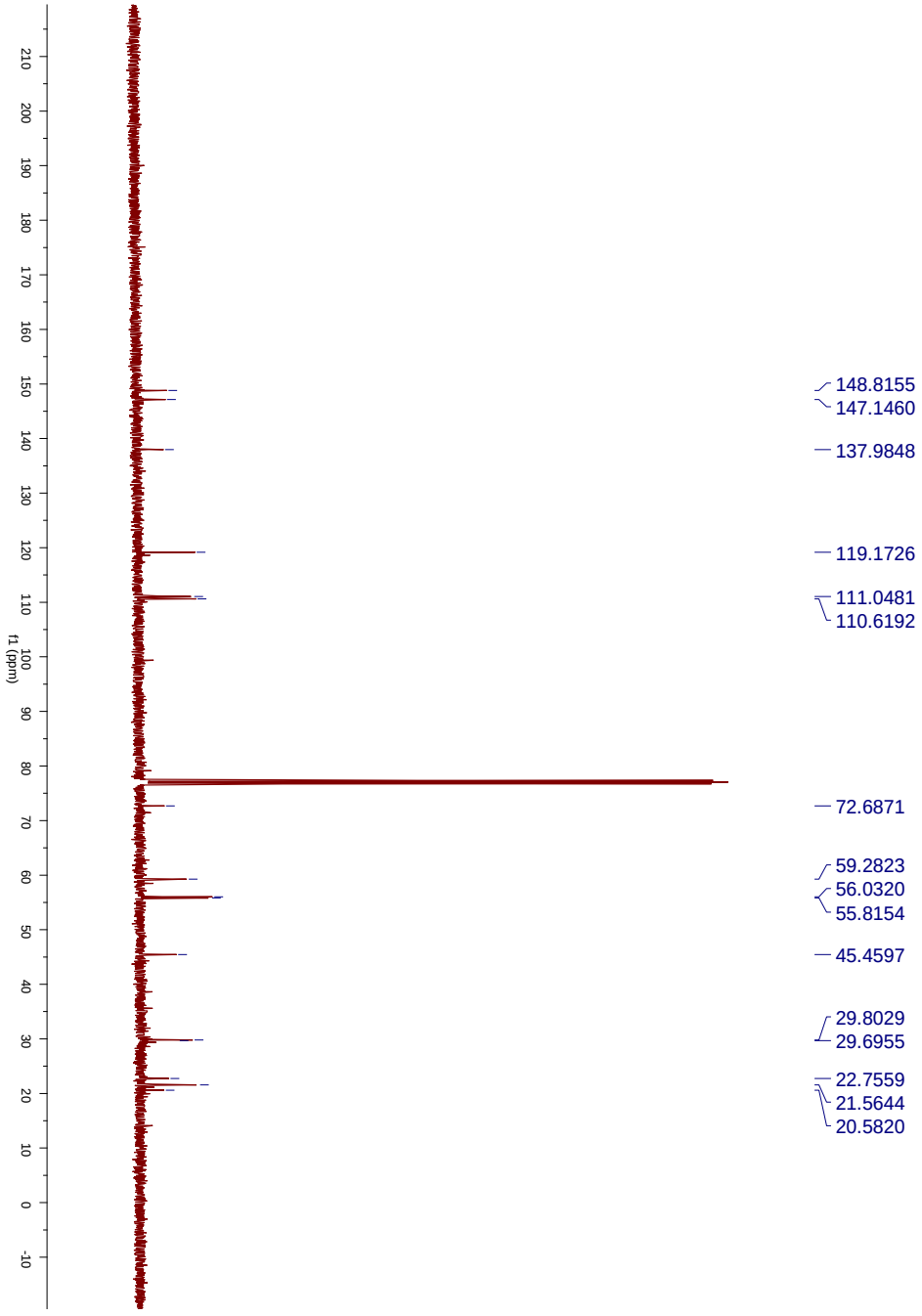
Scanned copy of mass spectrum of ±(**3b**)



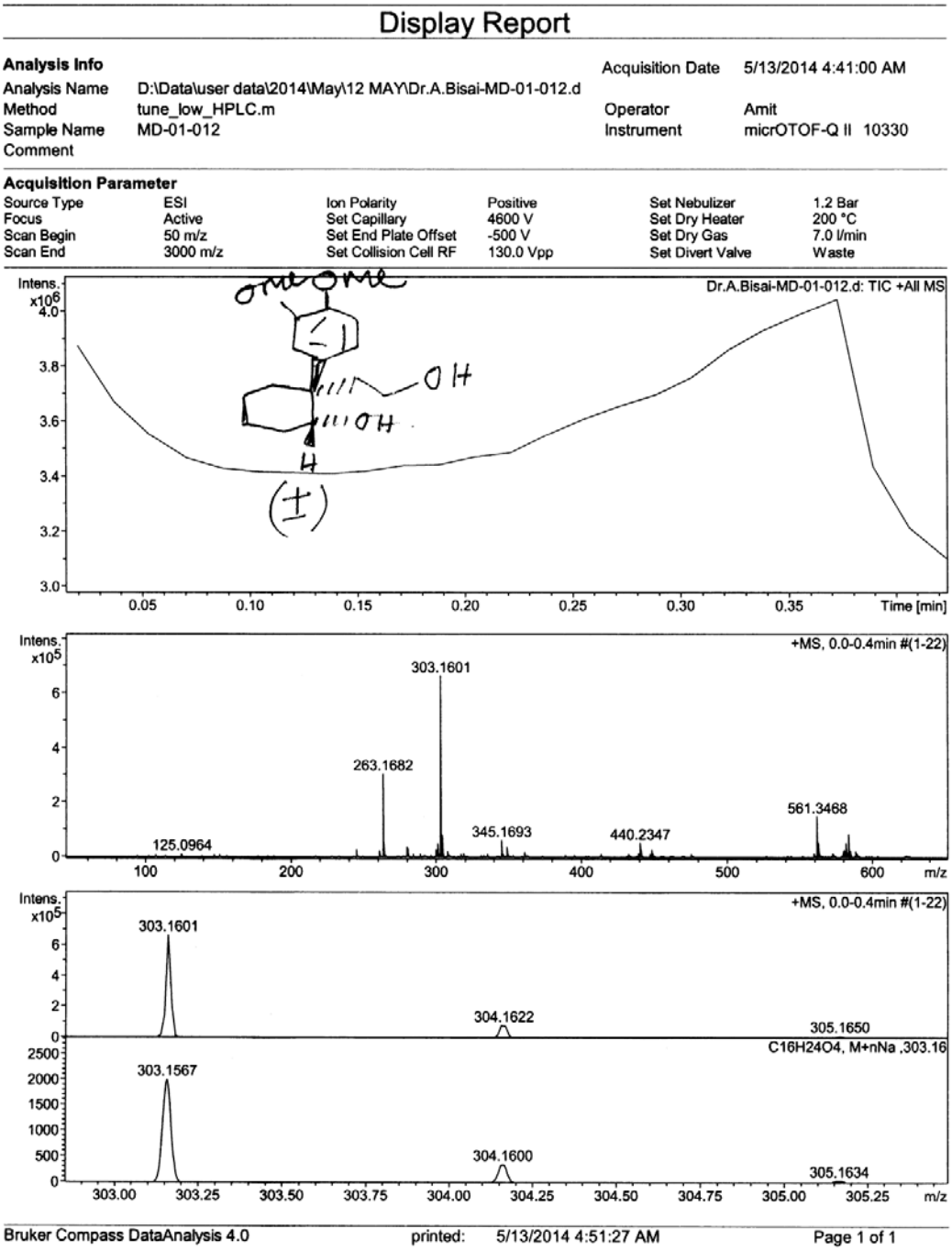
± ***(8a)***



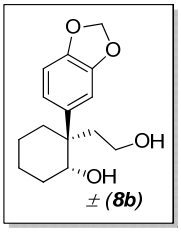
^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(8a)**

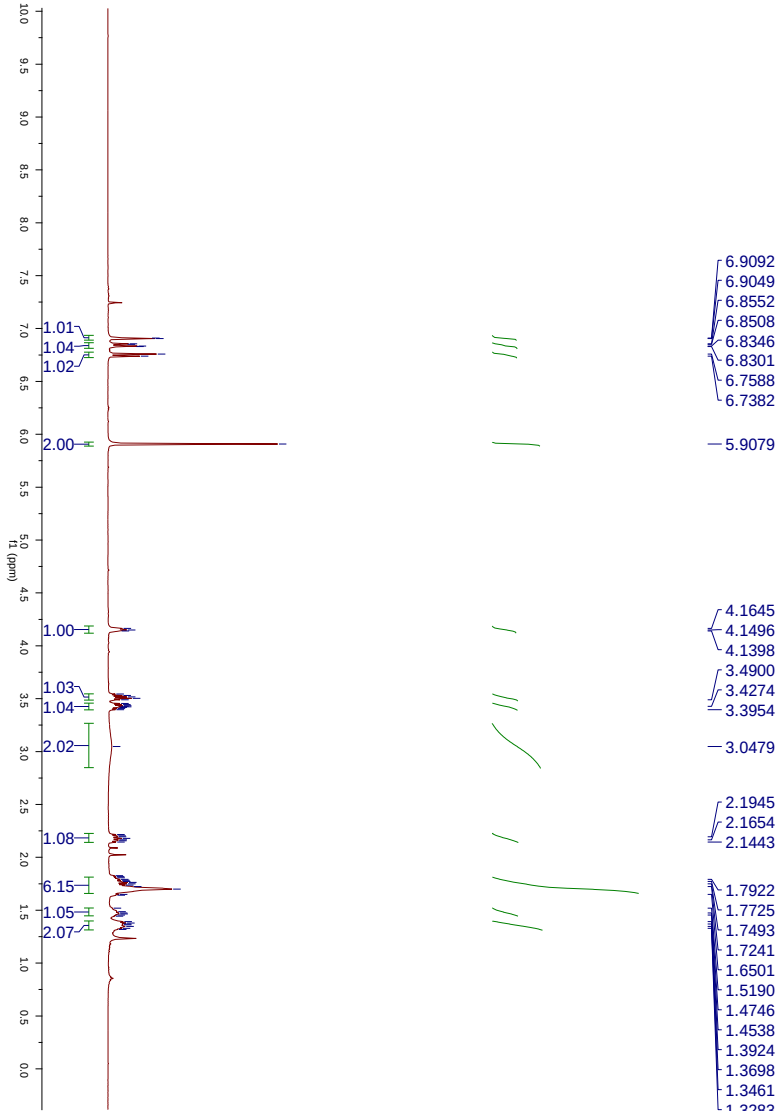


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(8a)**

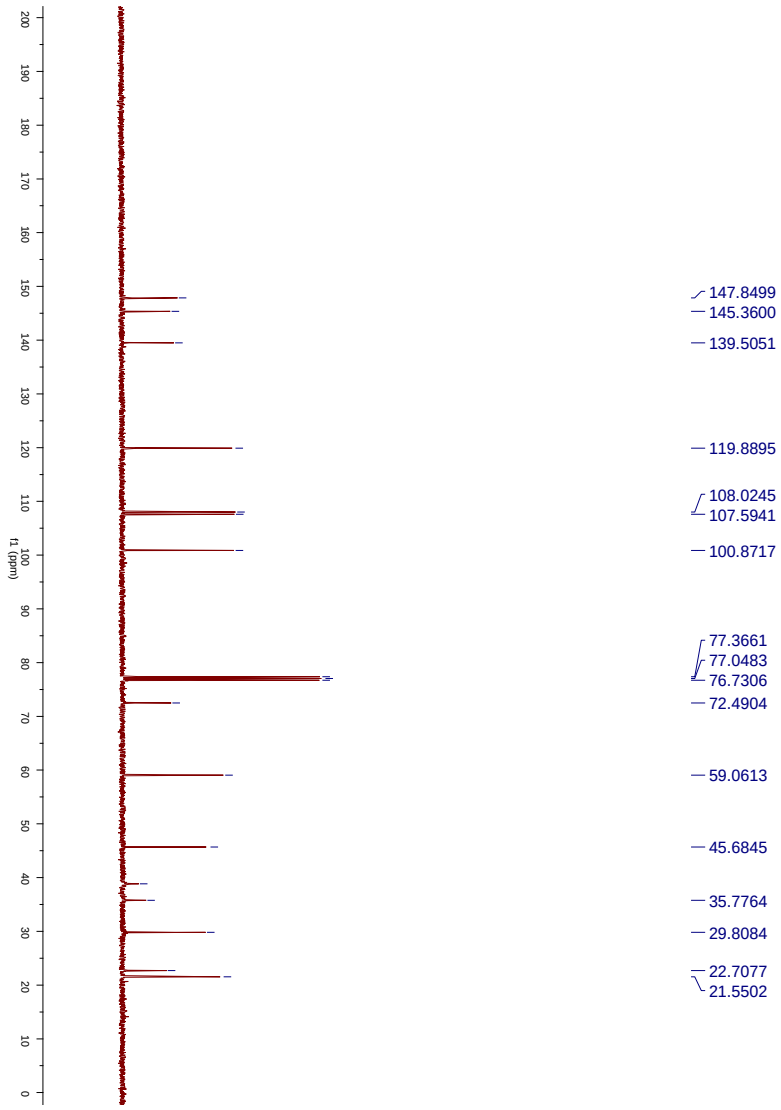


Scanned copy of mass spectrum of ±(**8a**)

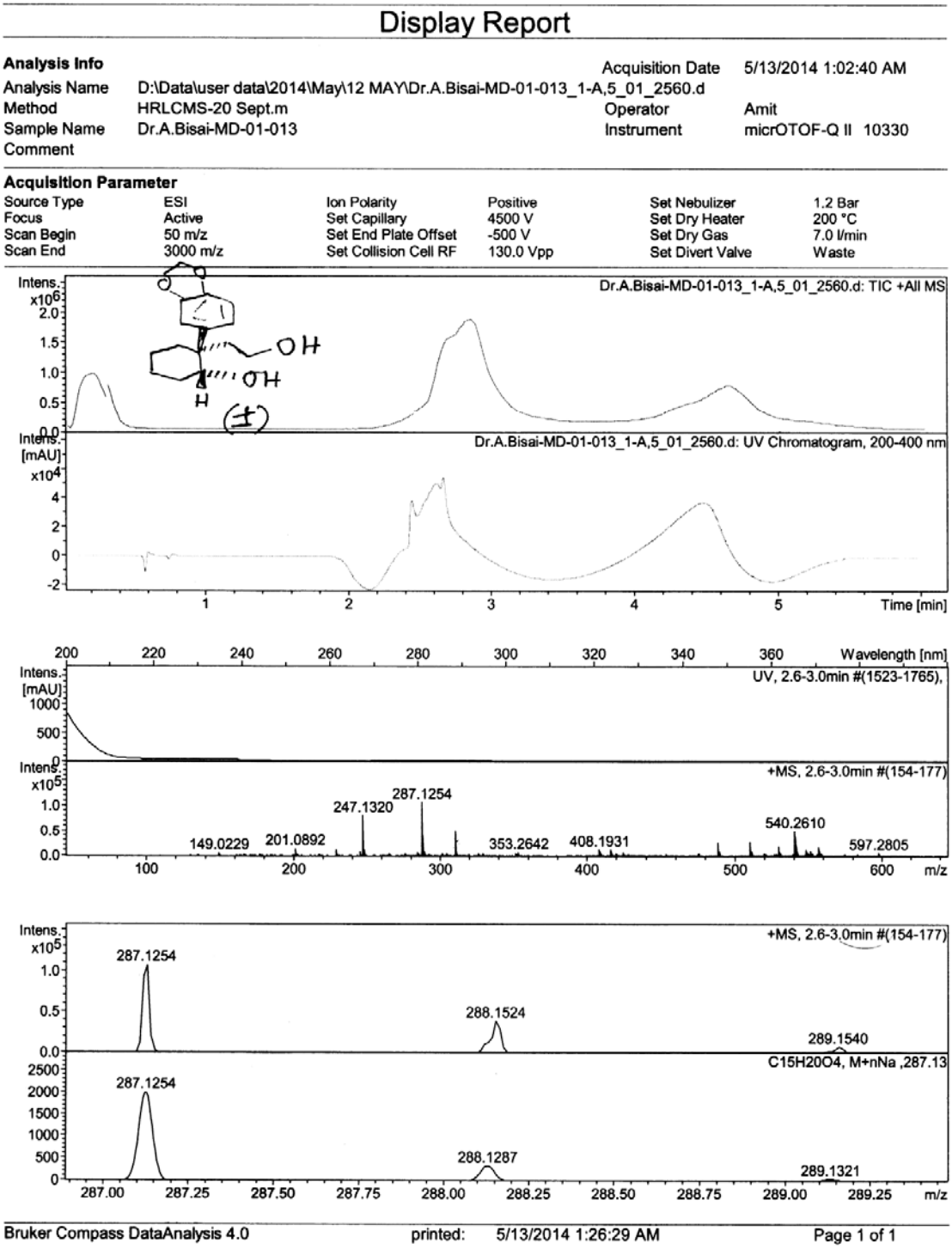




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(8b)**



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



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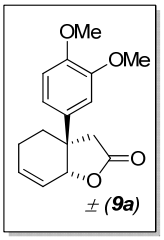
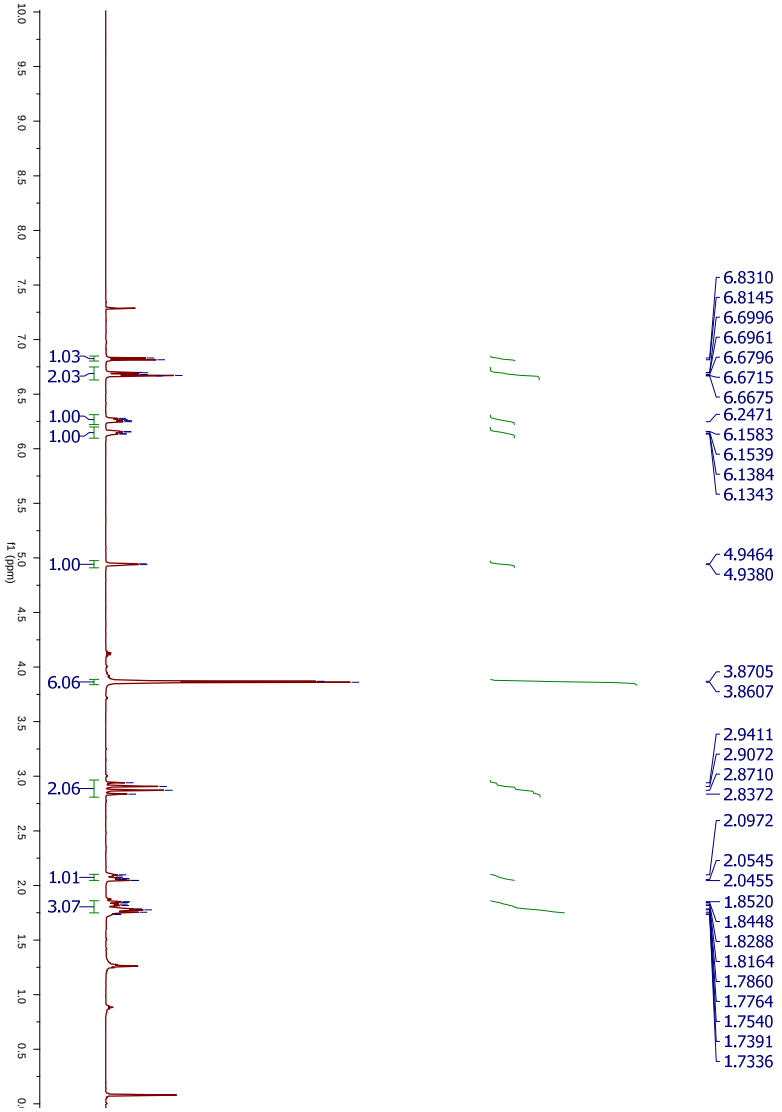
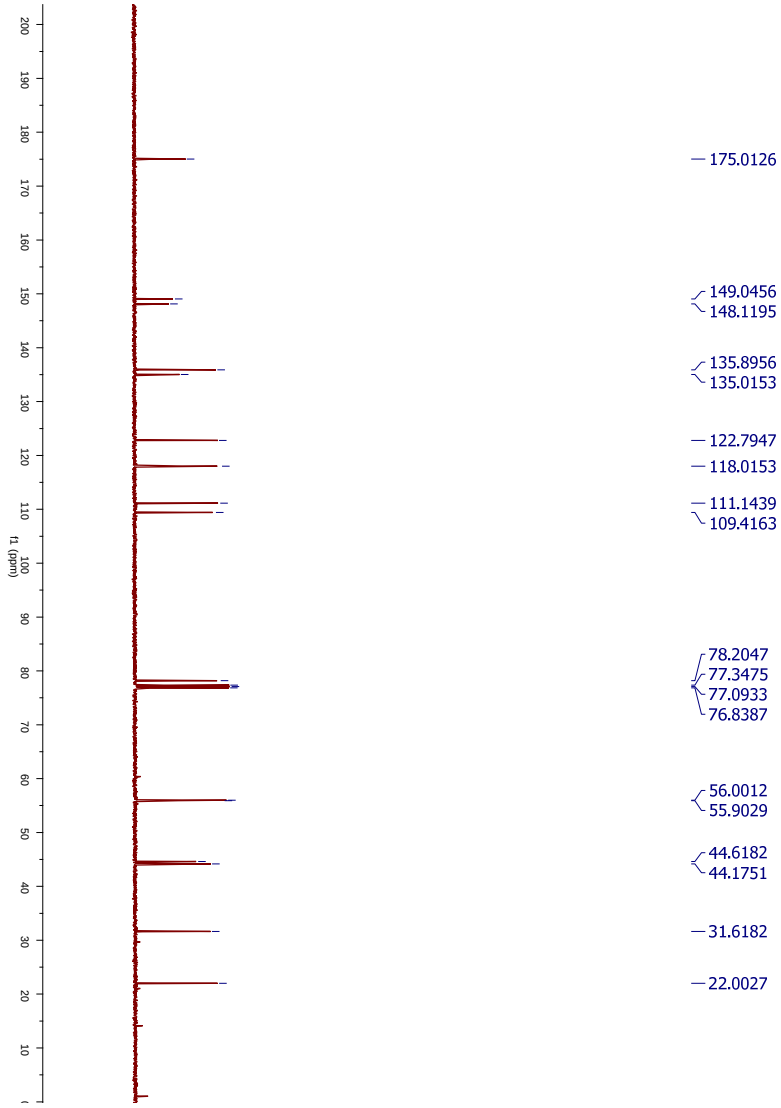
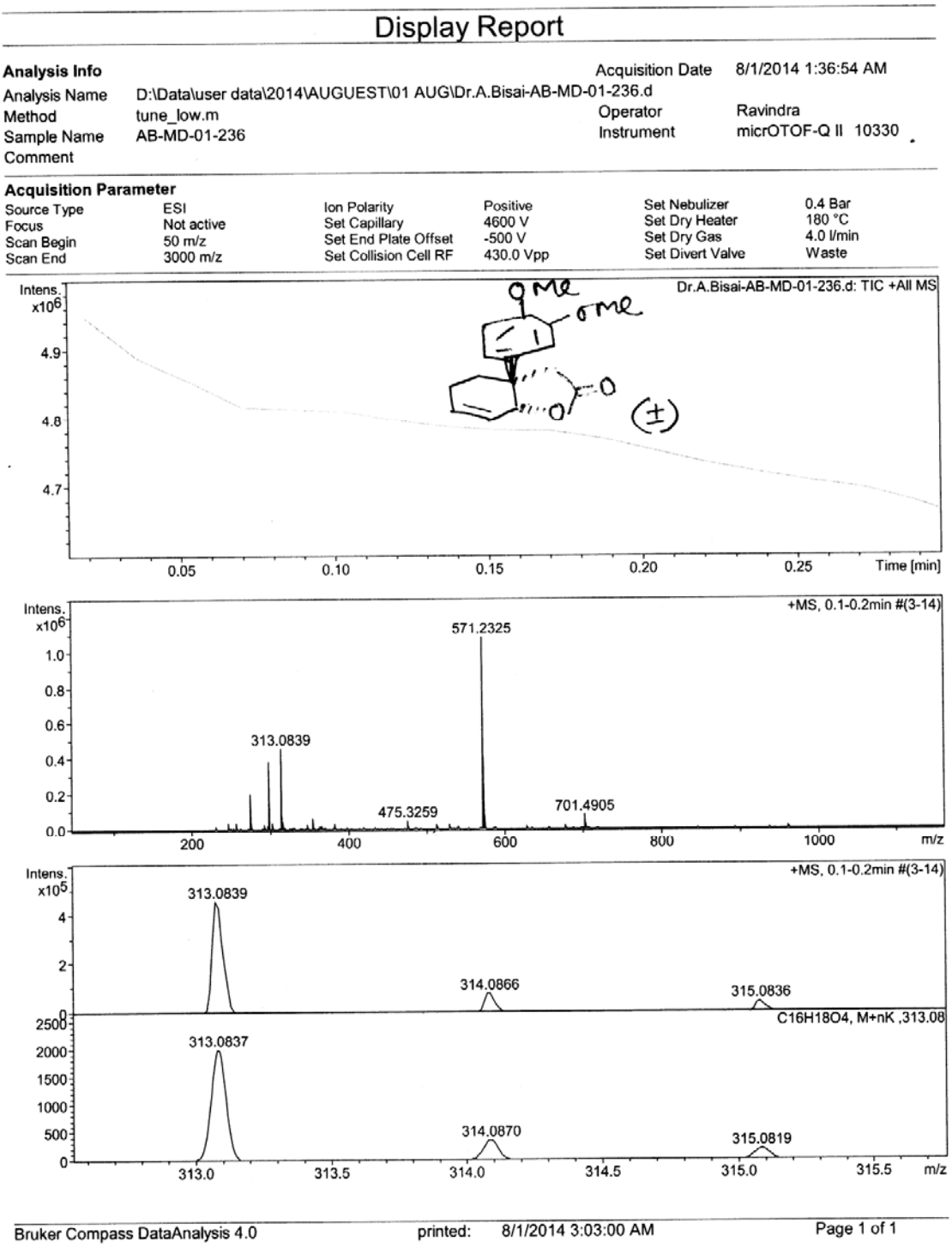




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(9a)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(9a)**



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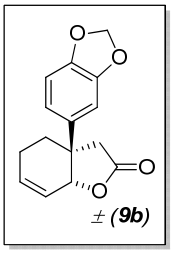
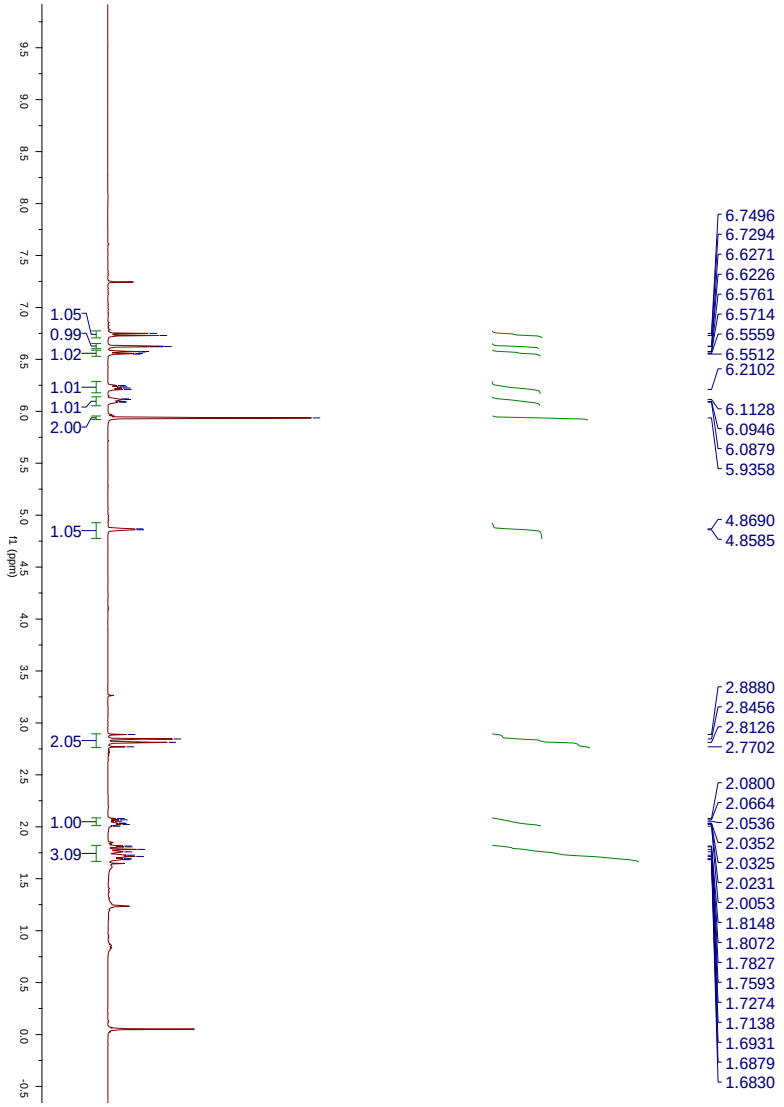
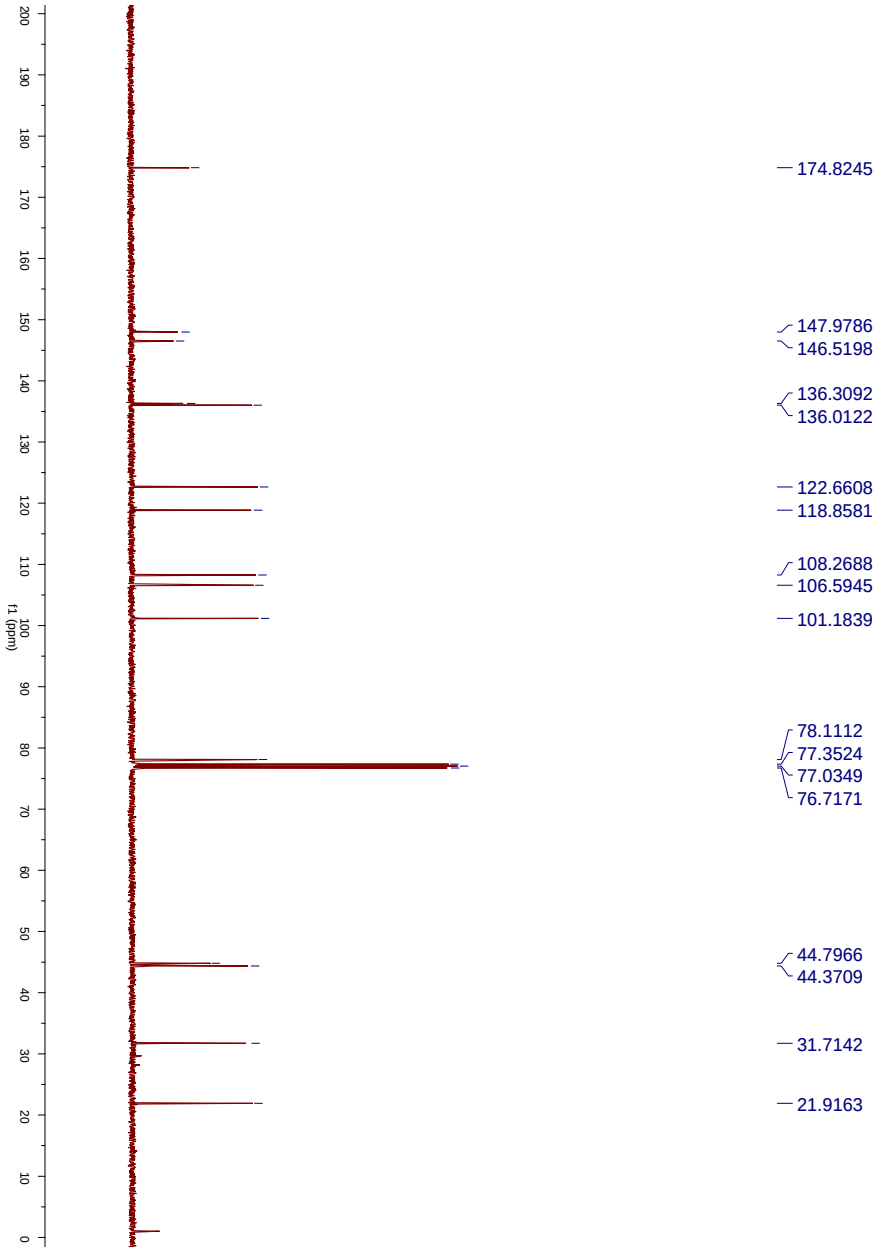
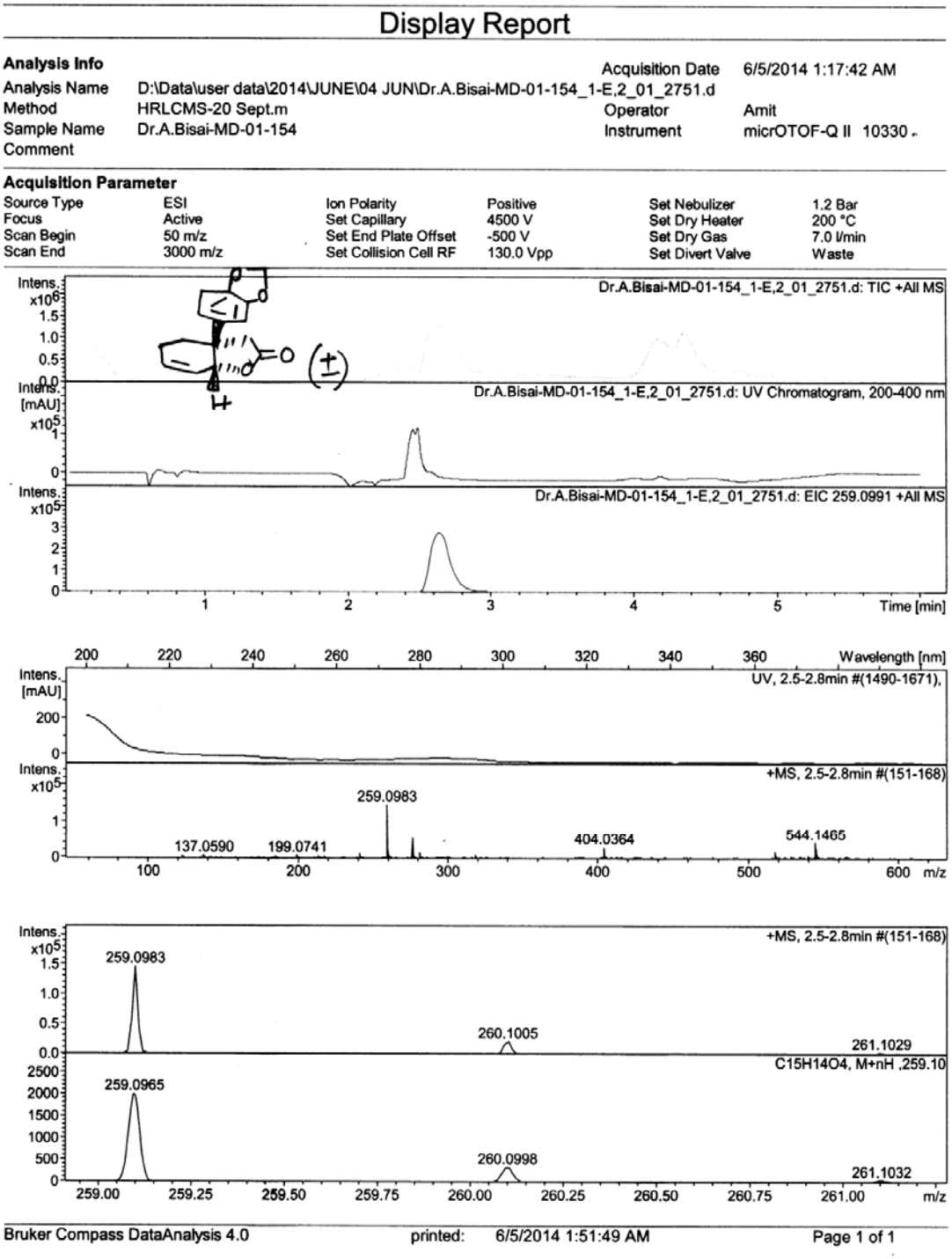




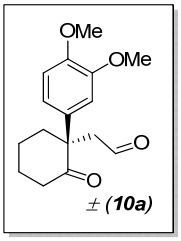
^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(9b)**

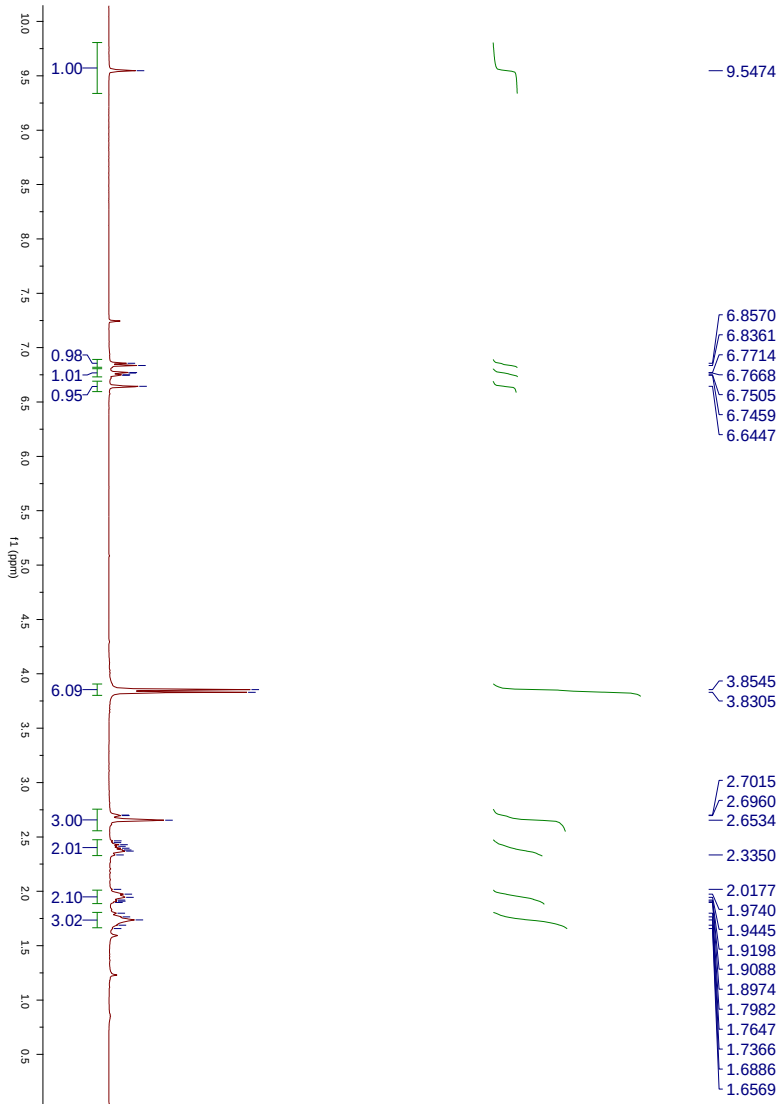


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(9b)**

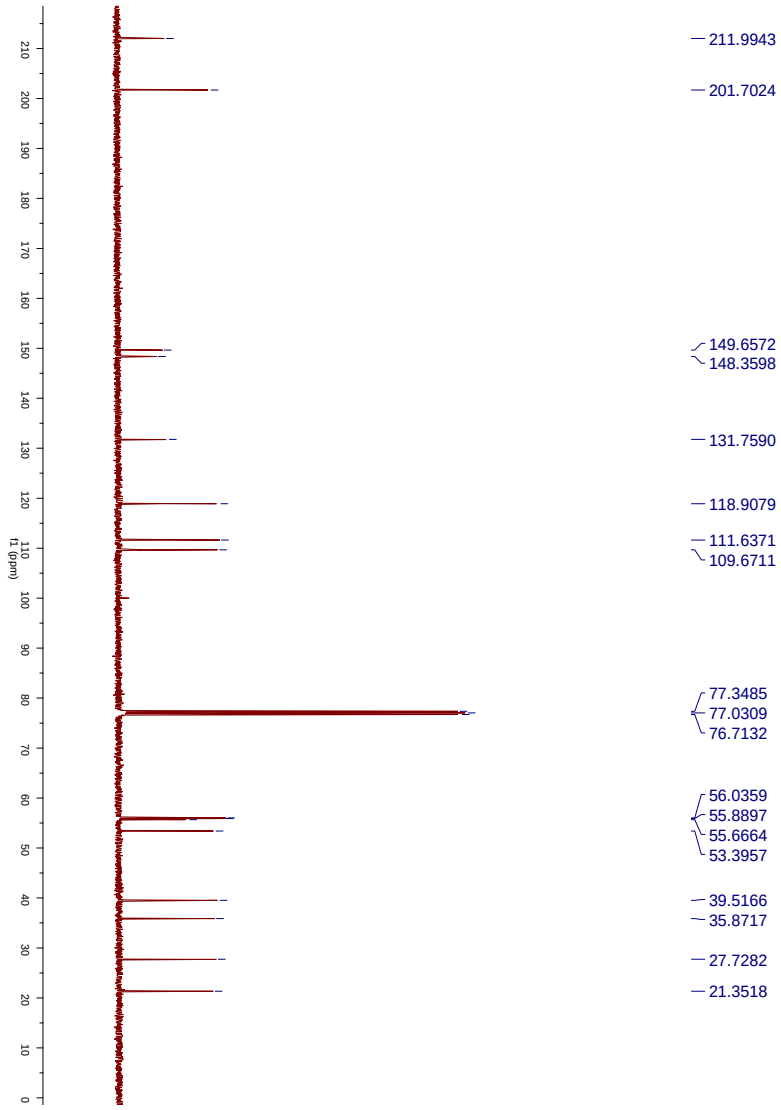


Scanned copy of mass spectrum of ±(**9b**)

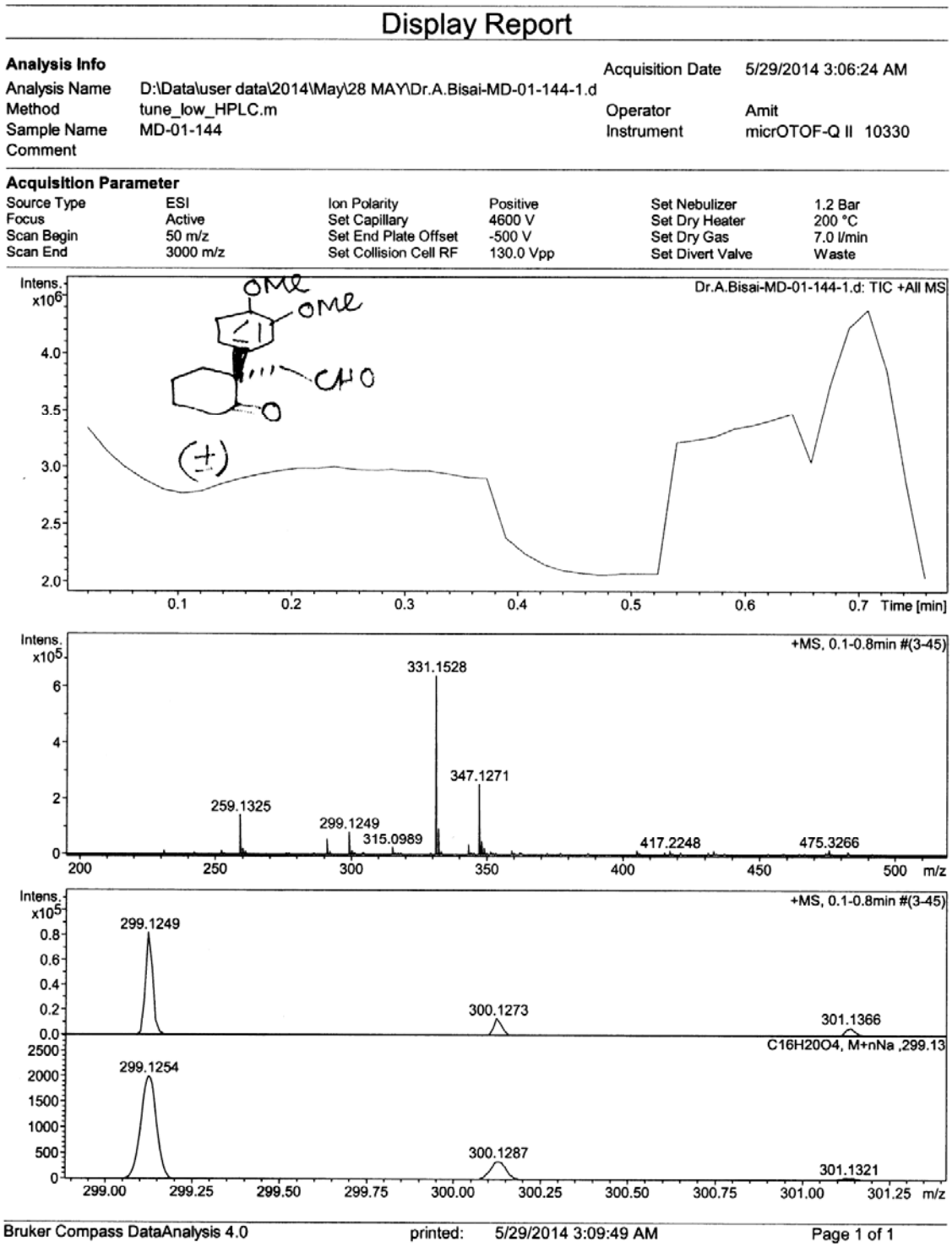




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(10a)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(10a)**



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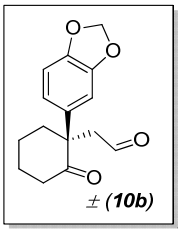
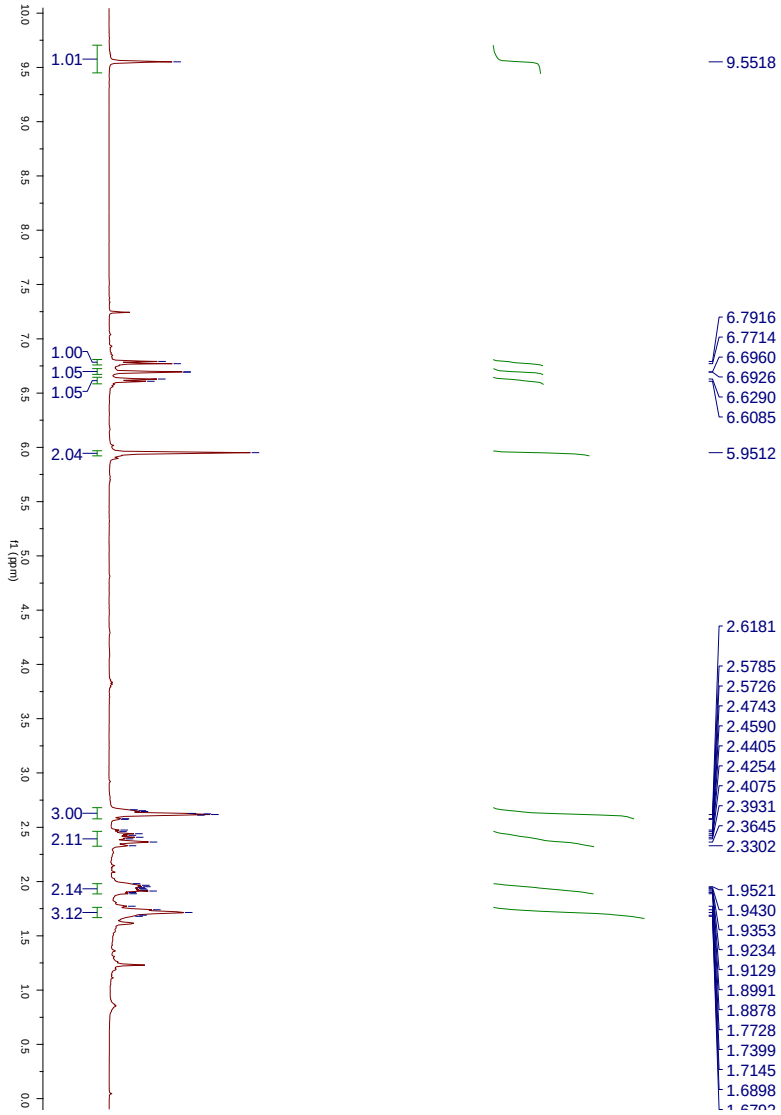
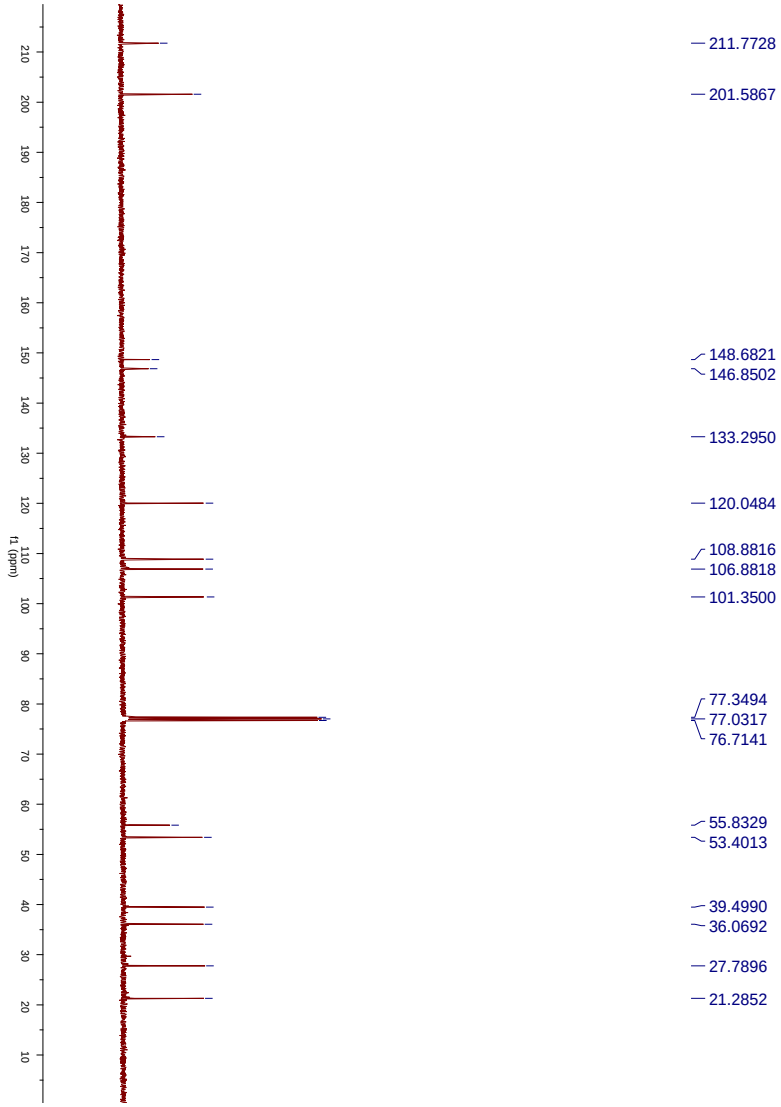
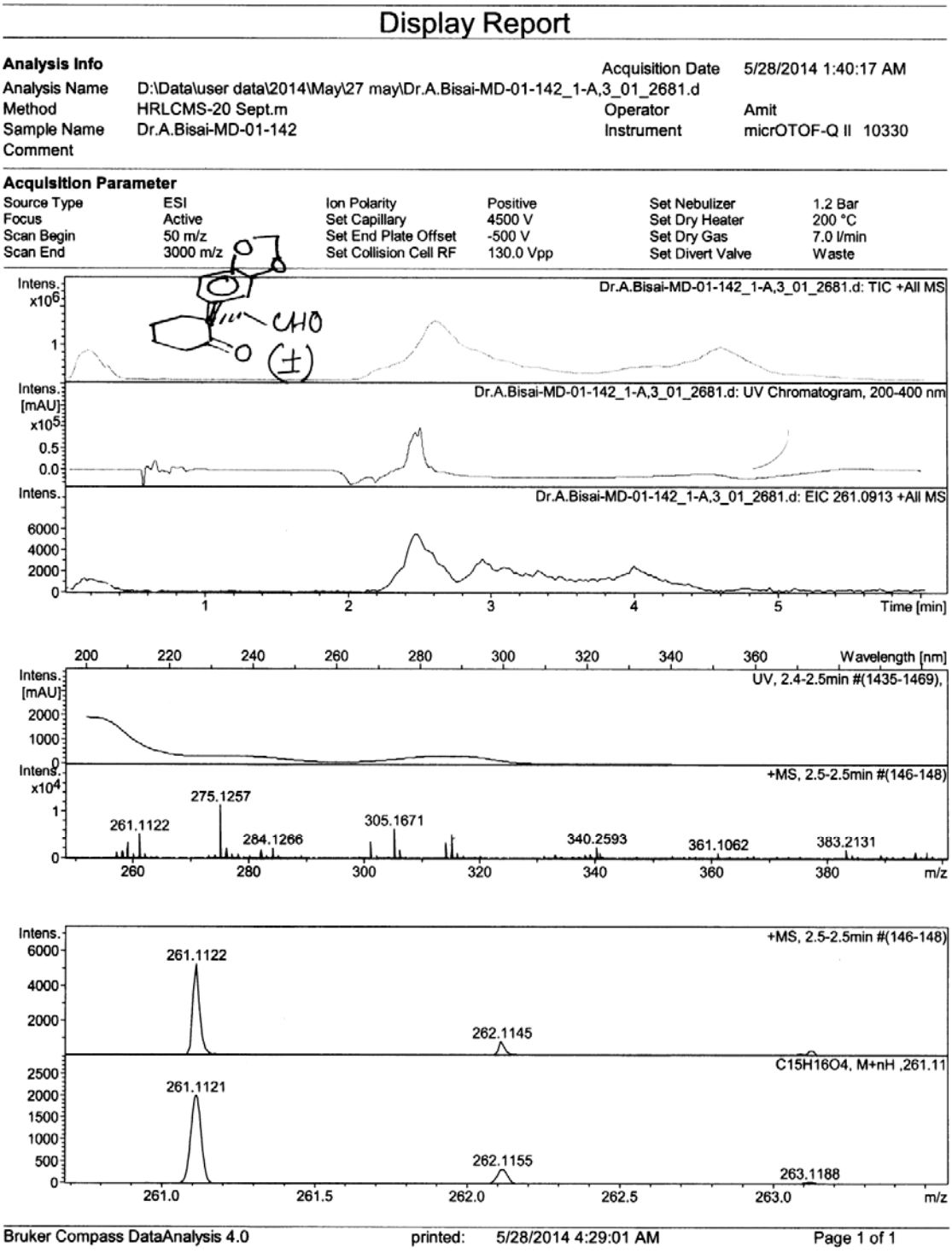




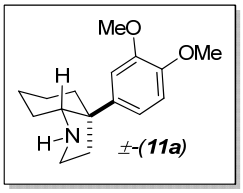
^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(10b)**

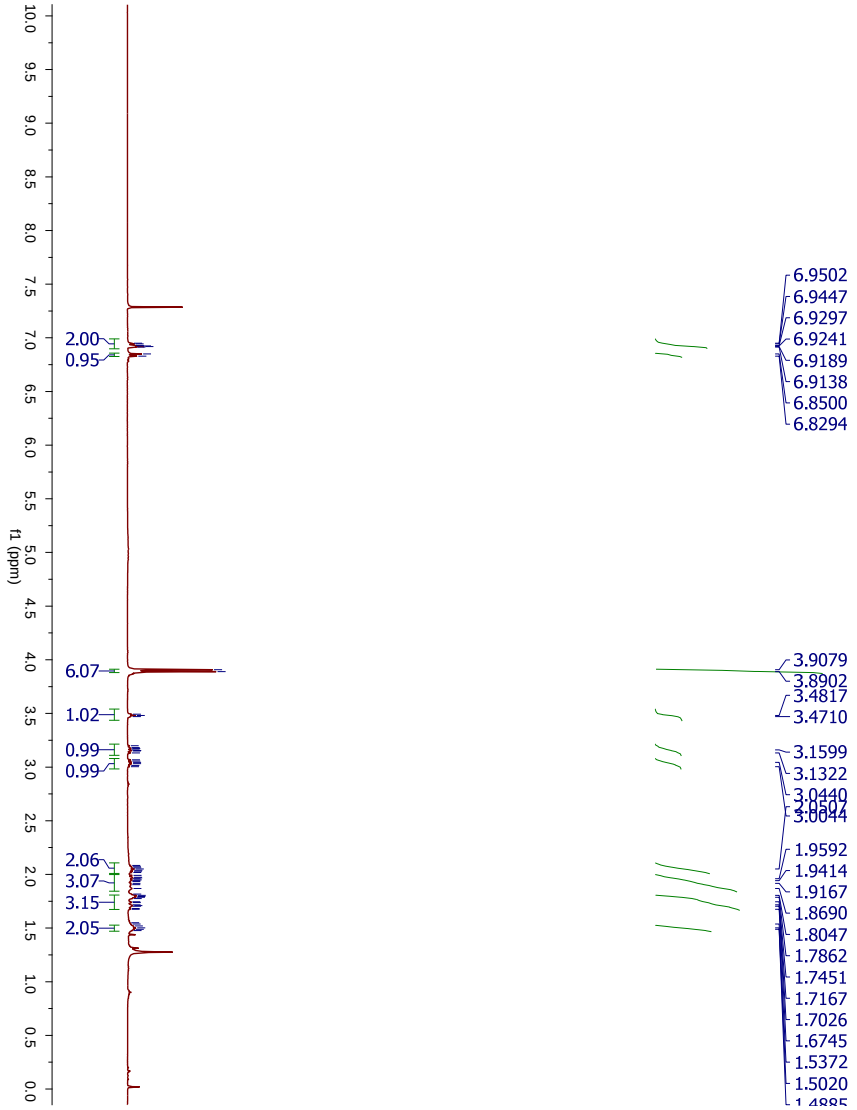


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(10b)**

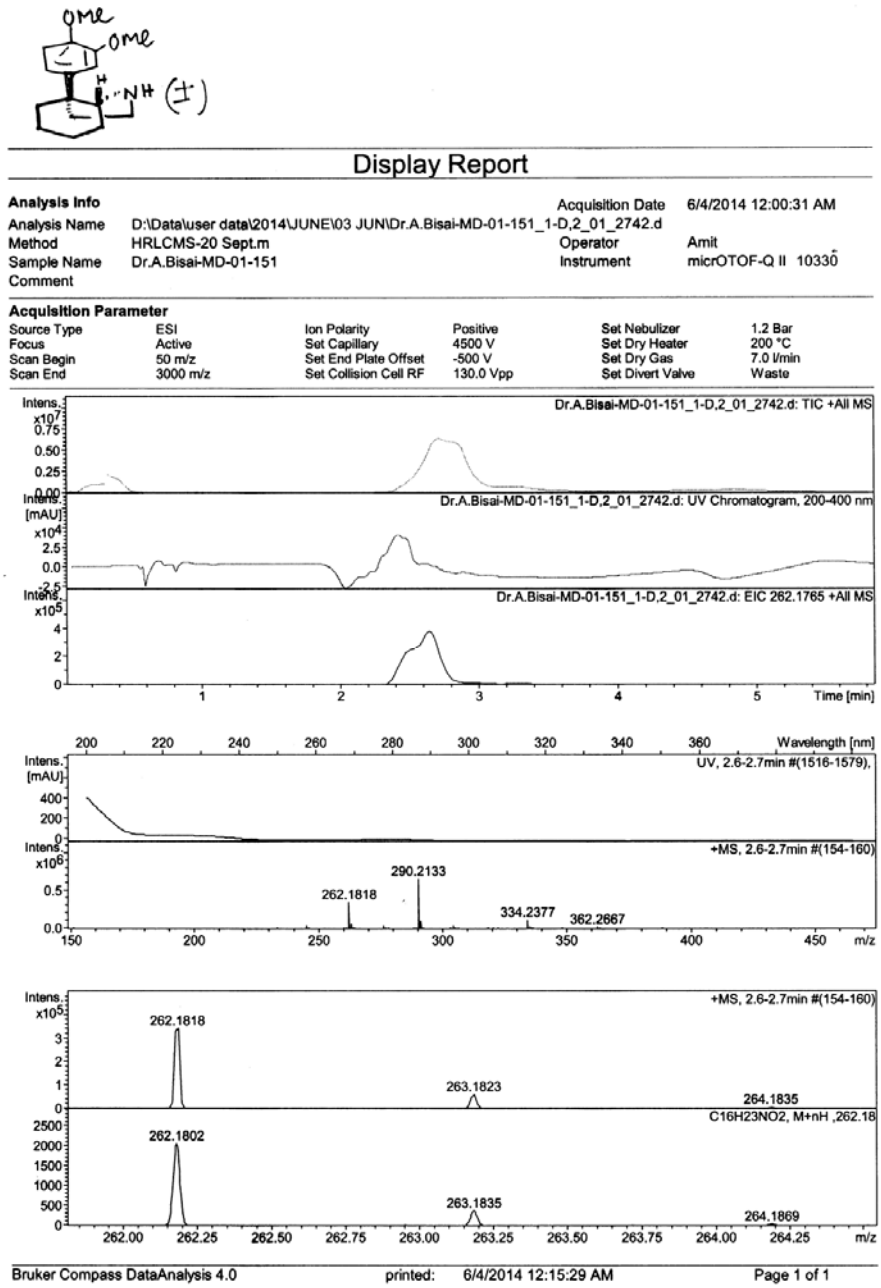


Scanned copy of mass spectrum of ±(**10b**)

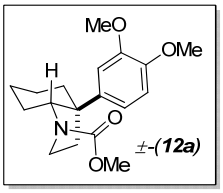


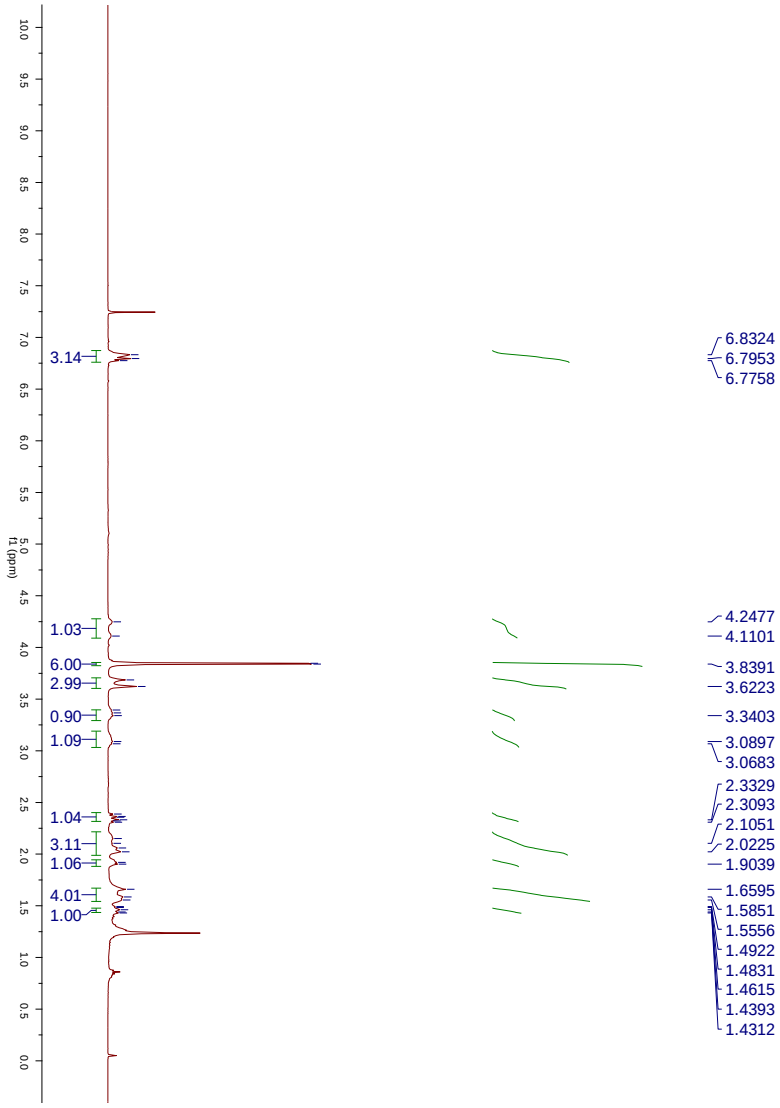


^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(11a)**



Scanned copy of mass spectrum of ±(**11a**)





^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(12a)**

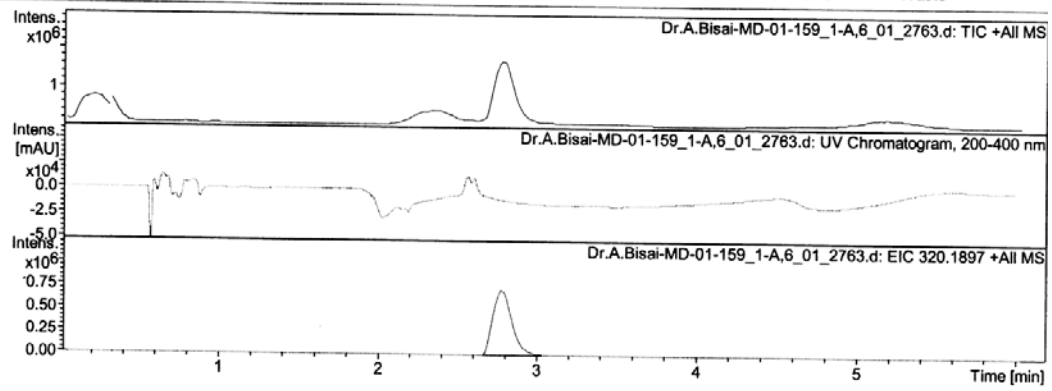
Display Report

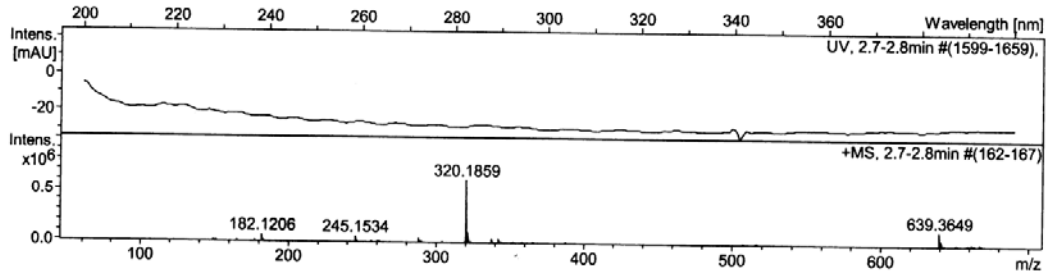
Analysis Info

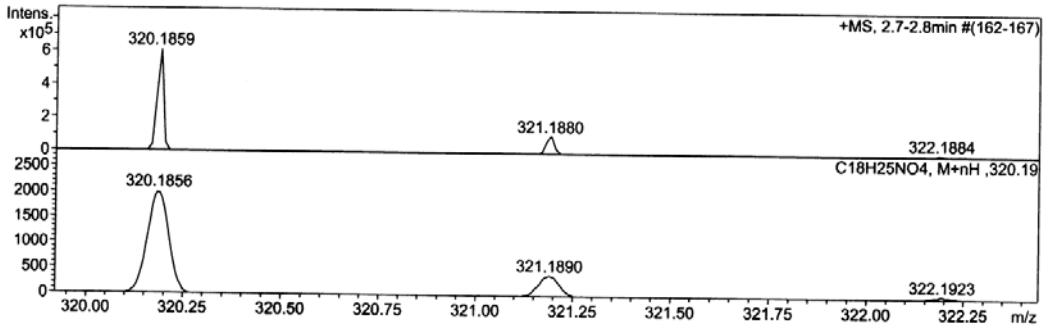
Analysis Name	D:\Data\user data\2014\JUNE\05 JUN\Dr.A.Bisai-MD-01-159_1-A,6_01_2763.d	Acquisition Date	6/6/2014 1:31:31 AM
Method	HRLCMS-20 Sept.m	Operator	Amit
Sample Name	Dr.A.Bisai-MD-01-159	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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

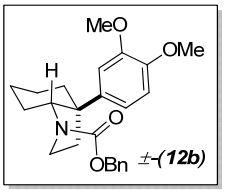


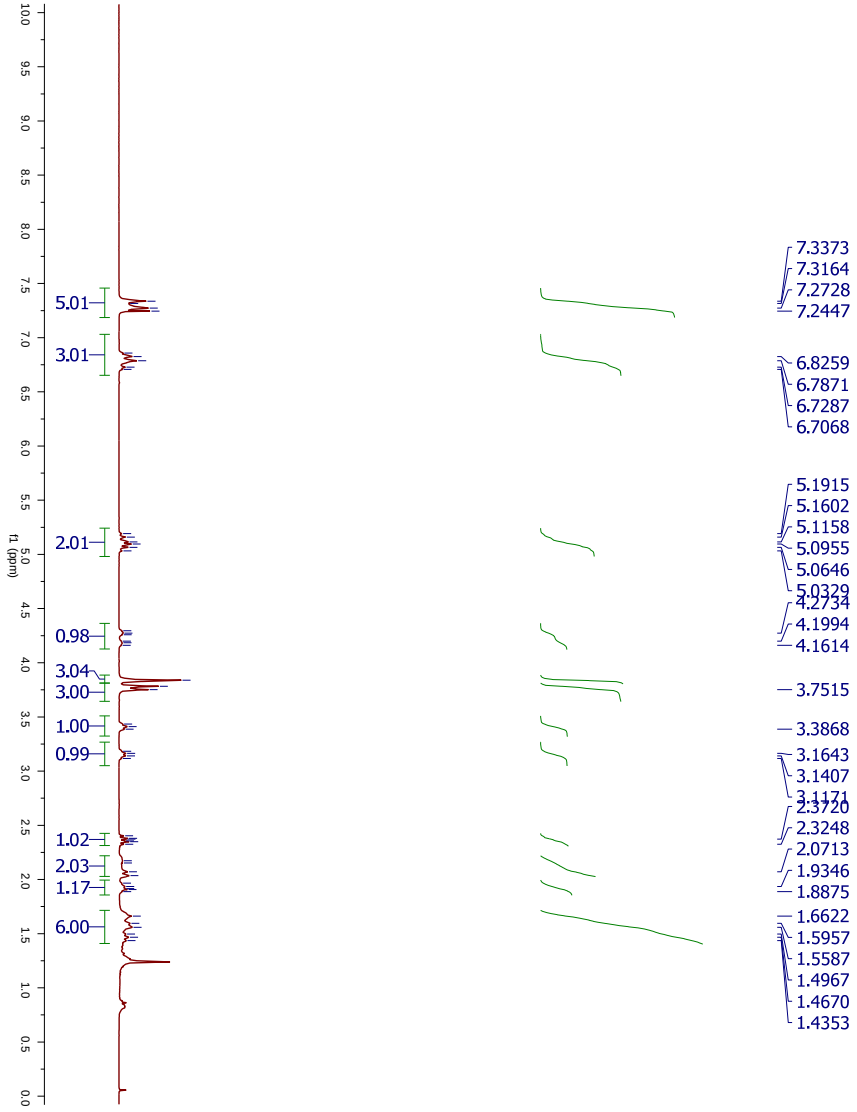




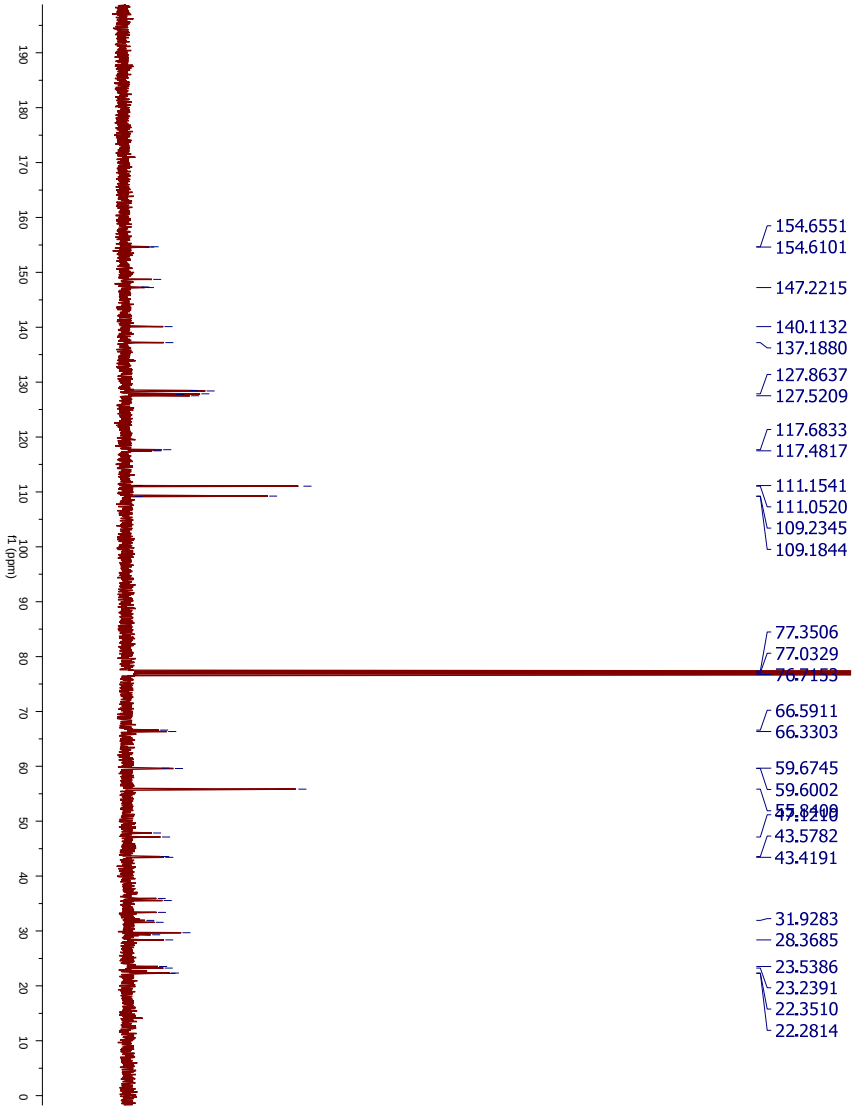
Bruker Compass DataAnalysis 4.0 printed: 6/6/2014 2:04:07 AM Page 1 of 1

Scanned copy of mass spectrum of ±(**12a**)

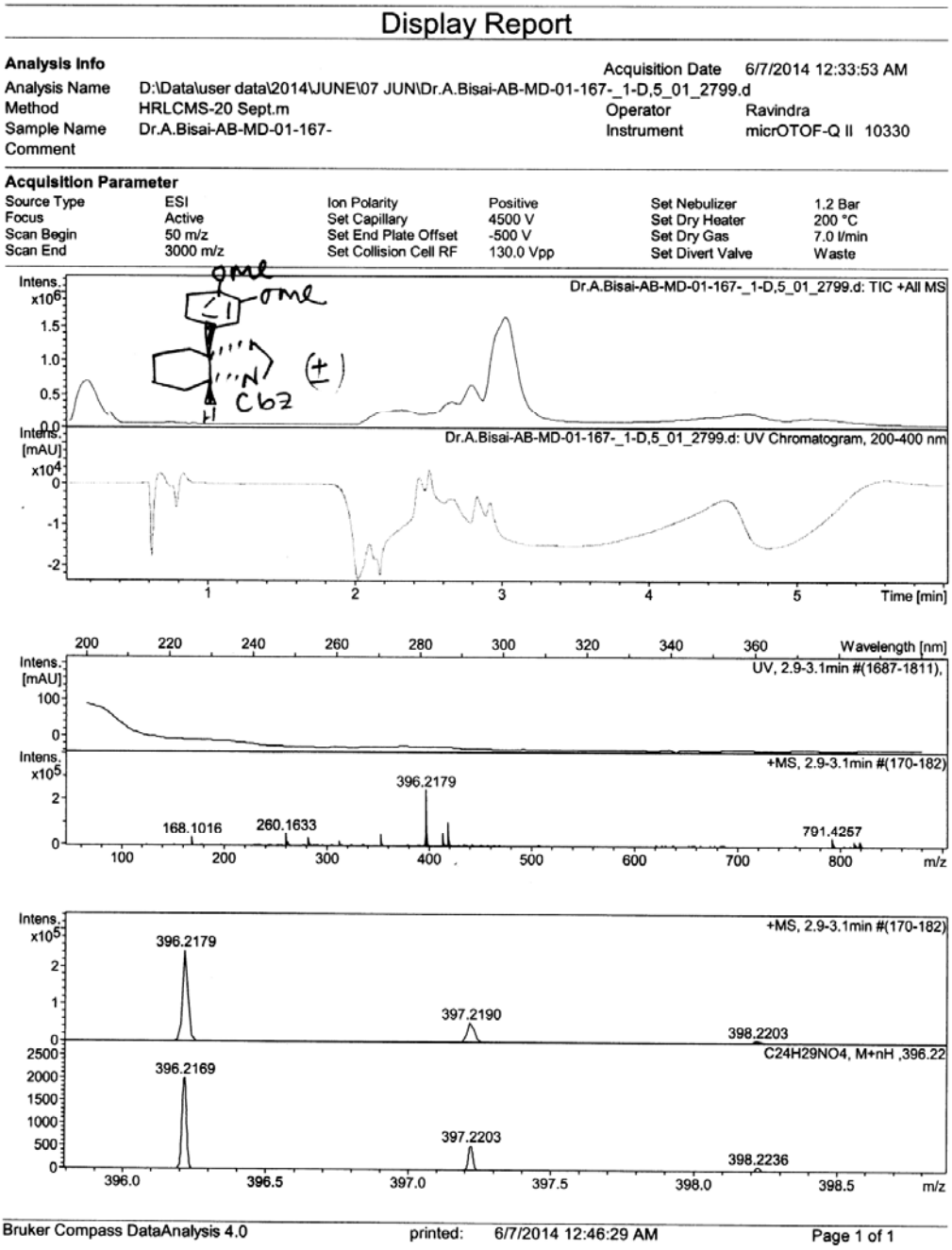




^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(12b)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(12b)**



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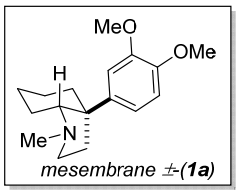
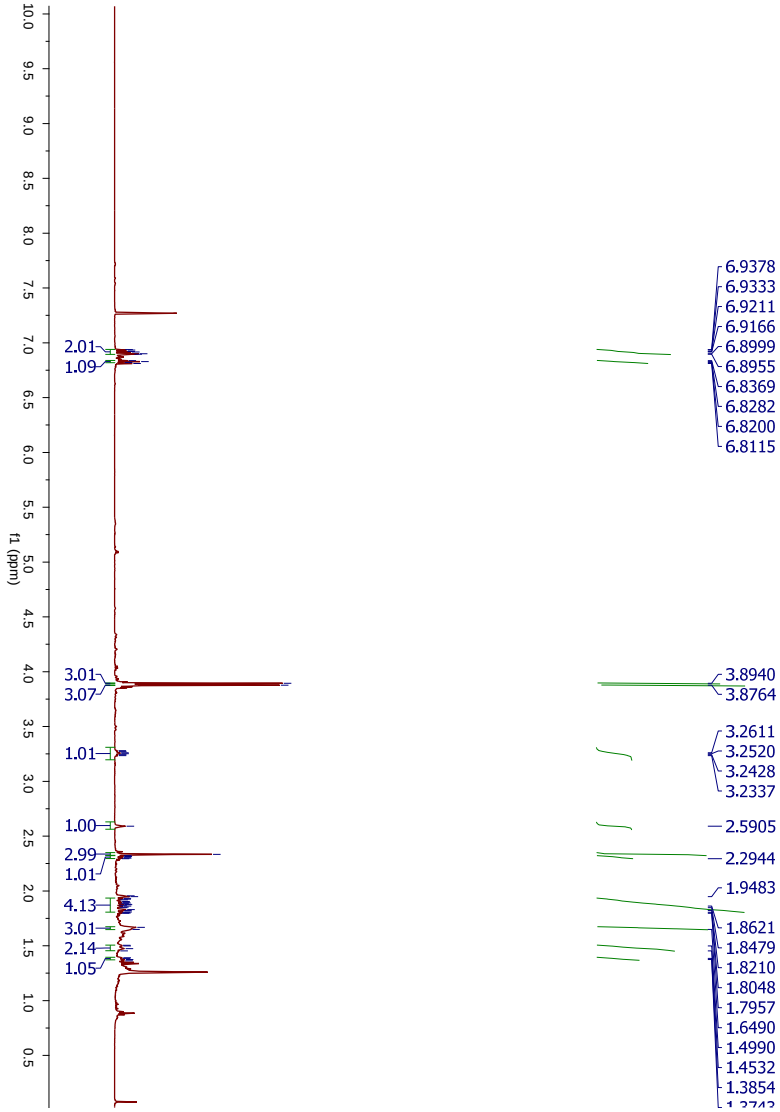




^{1}H NMR (400 MHz, $CDCl_3$) of compound ± **(1a)**

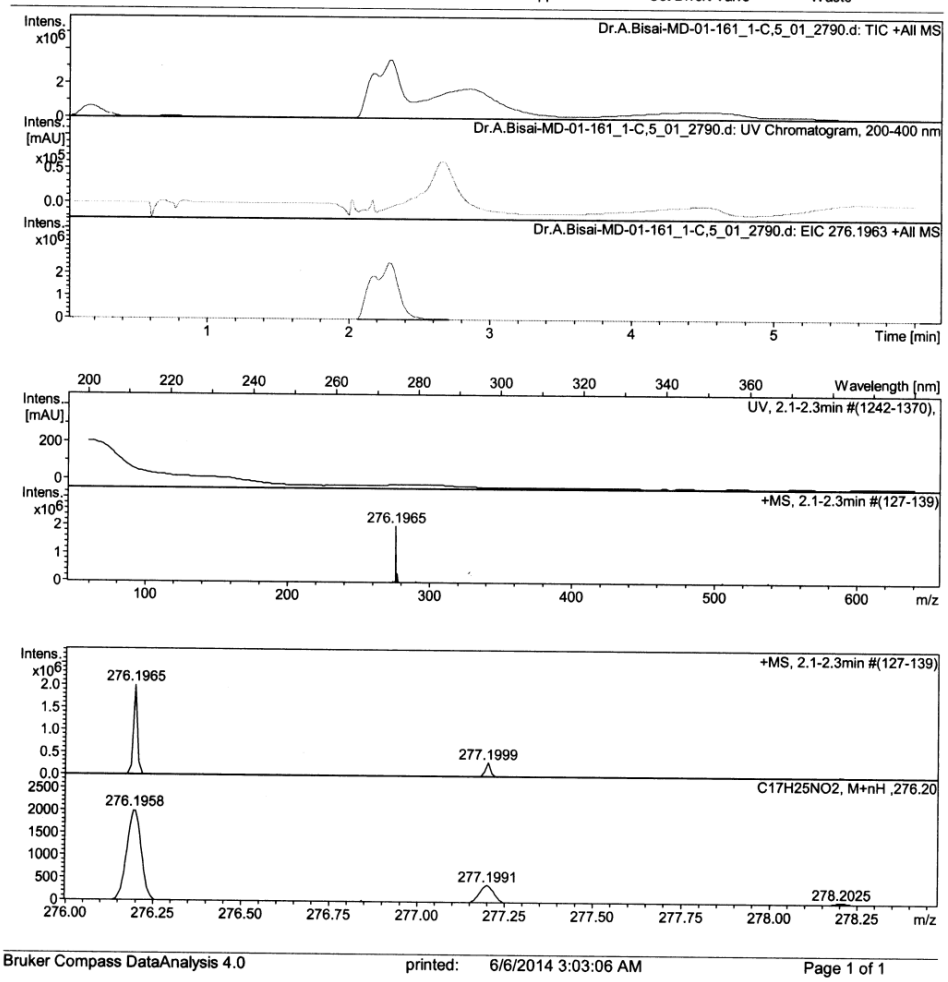
Display Report

Analysis Info

Analysis Name	D:\Data\user data\2014\JUNE\06 JUN\Dr.A.Bisai-MD-01-161_1-C,5_01_2790.d	Acquisition Date	6/6/2014 2:56:02 AM
Method	HRLCMS-20 Sept.m	Operator	Ravindra
Sample Name	Dr.A.Bisai-MD-01-161	Instrument	micrOTOF-Q II 10330
Comment			

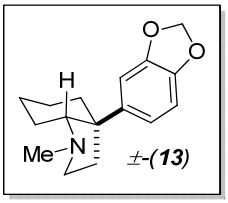
Acquisition Parameter

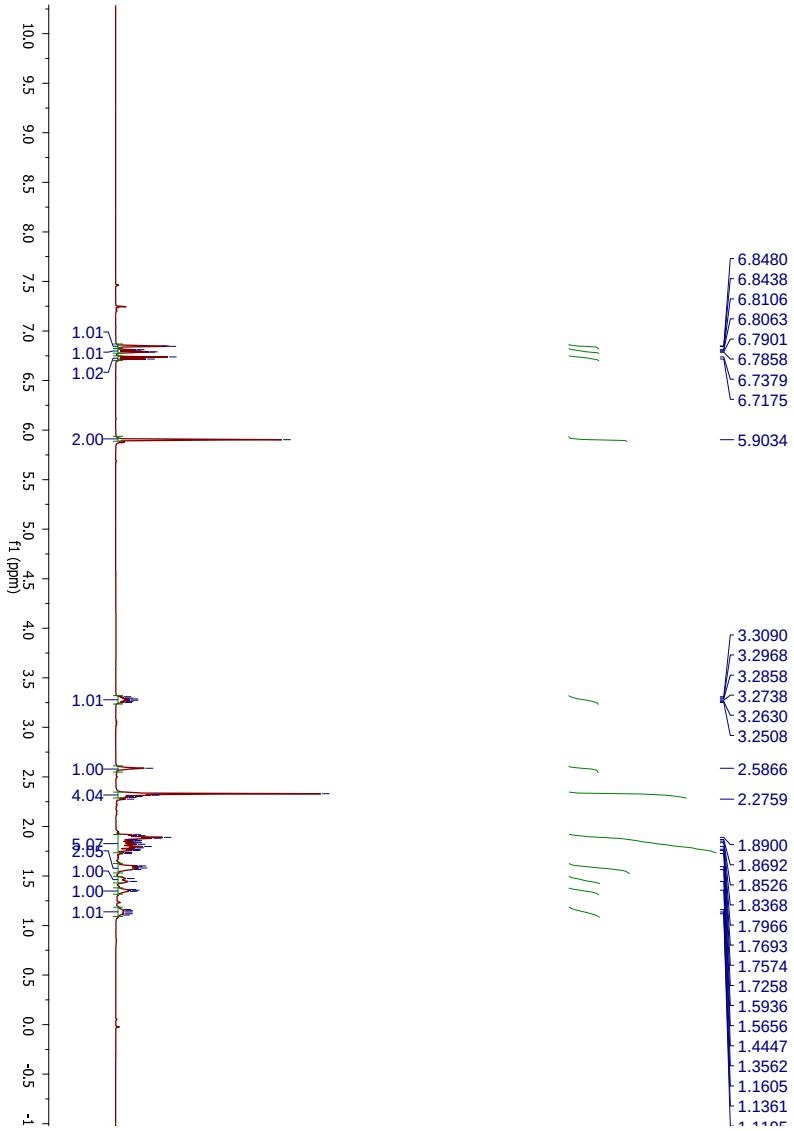
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



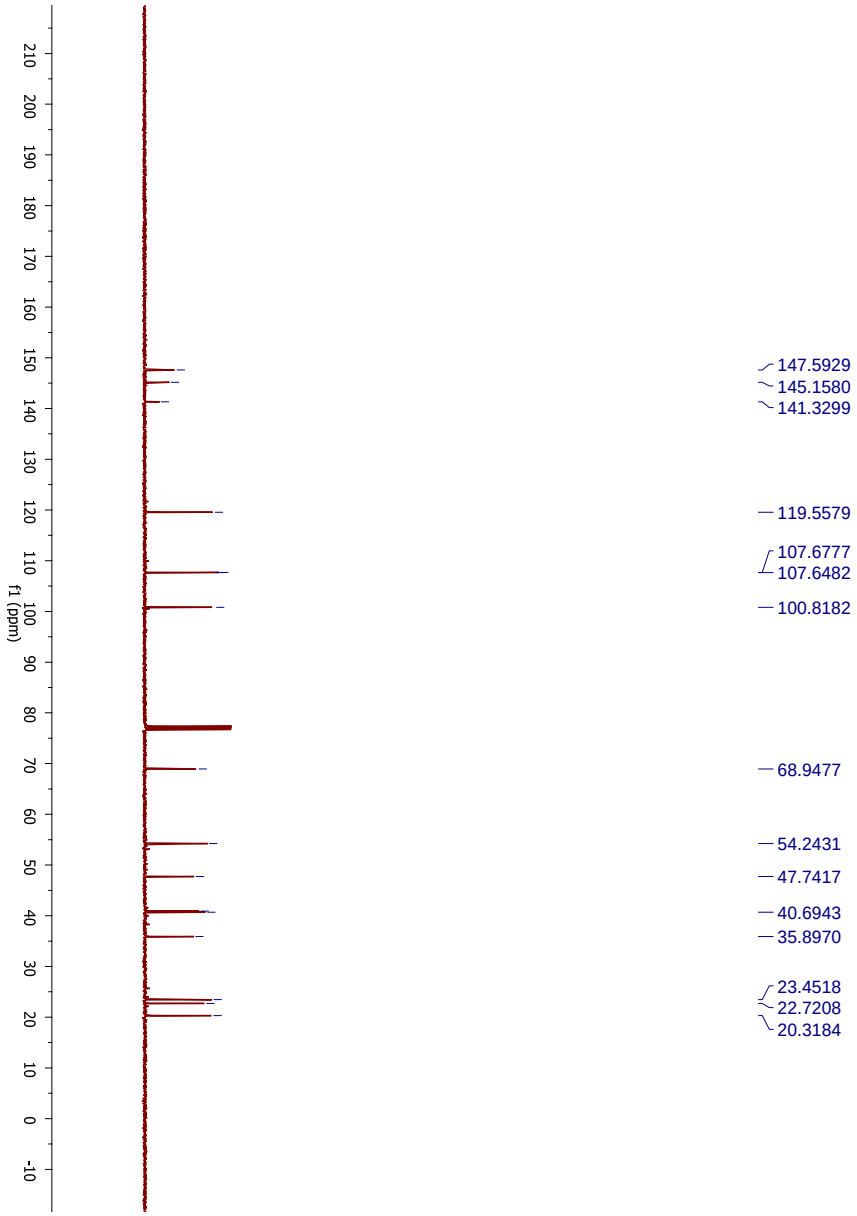
Bruker Compass DataAnalysis 4.0 printed: 6/6/2014 3:03:06 AM Page 1 of 1

Scanned copy of mass spectrum of ±(**1a**)

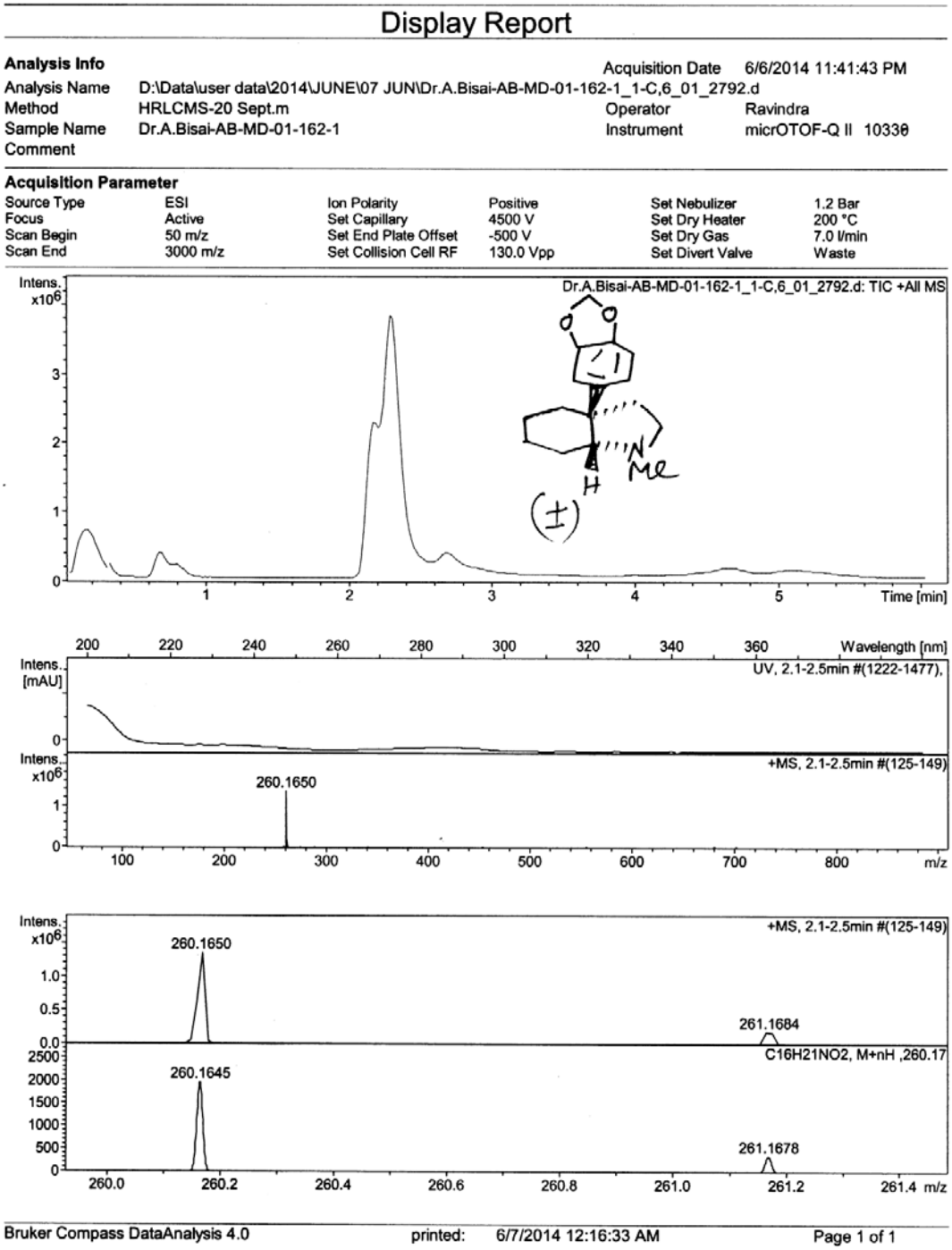




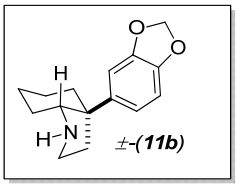
^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(13)**

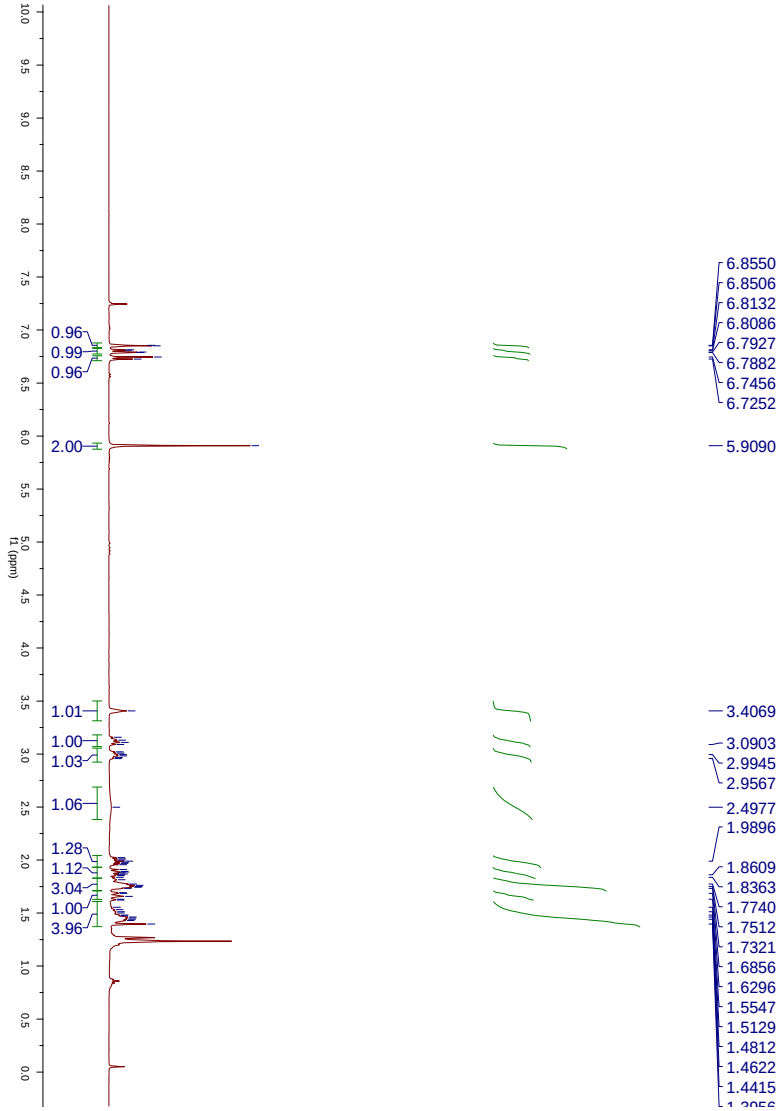


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(13)**

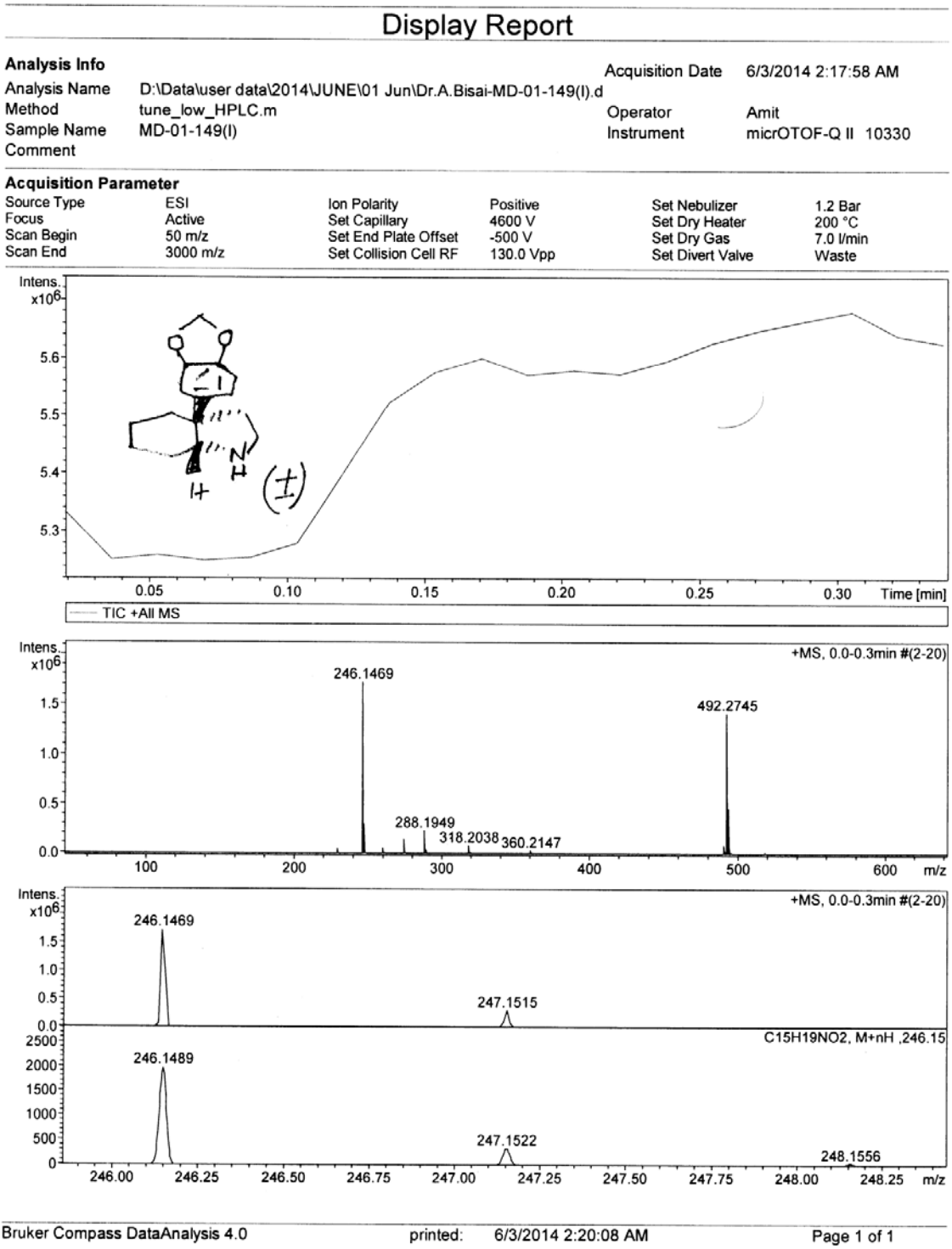


Scanned copy of mass spectrum of ±(**13**)

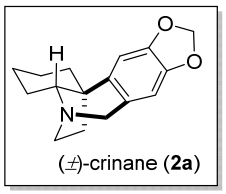


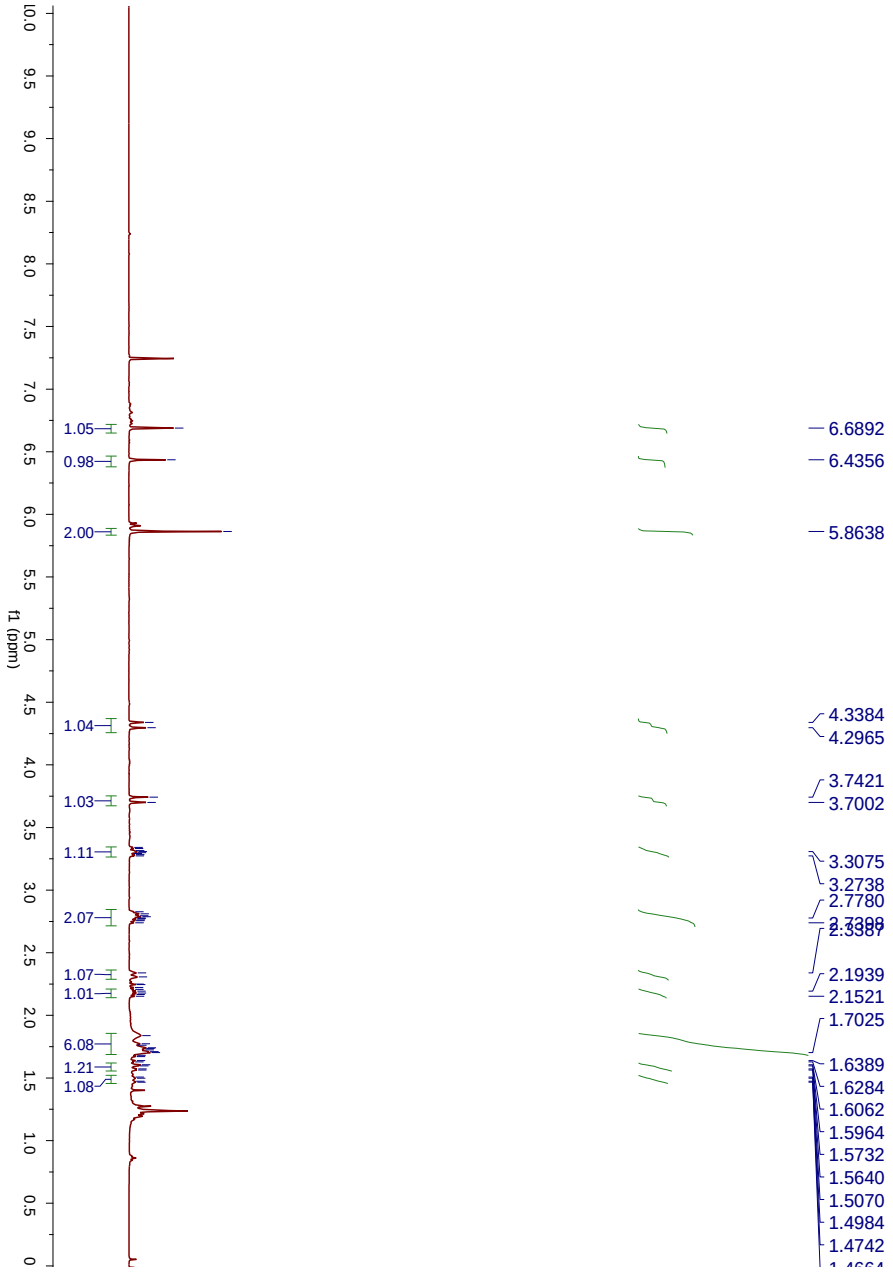


^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(11b)**

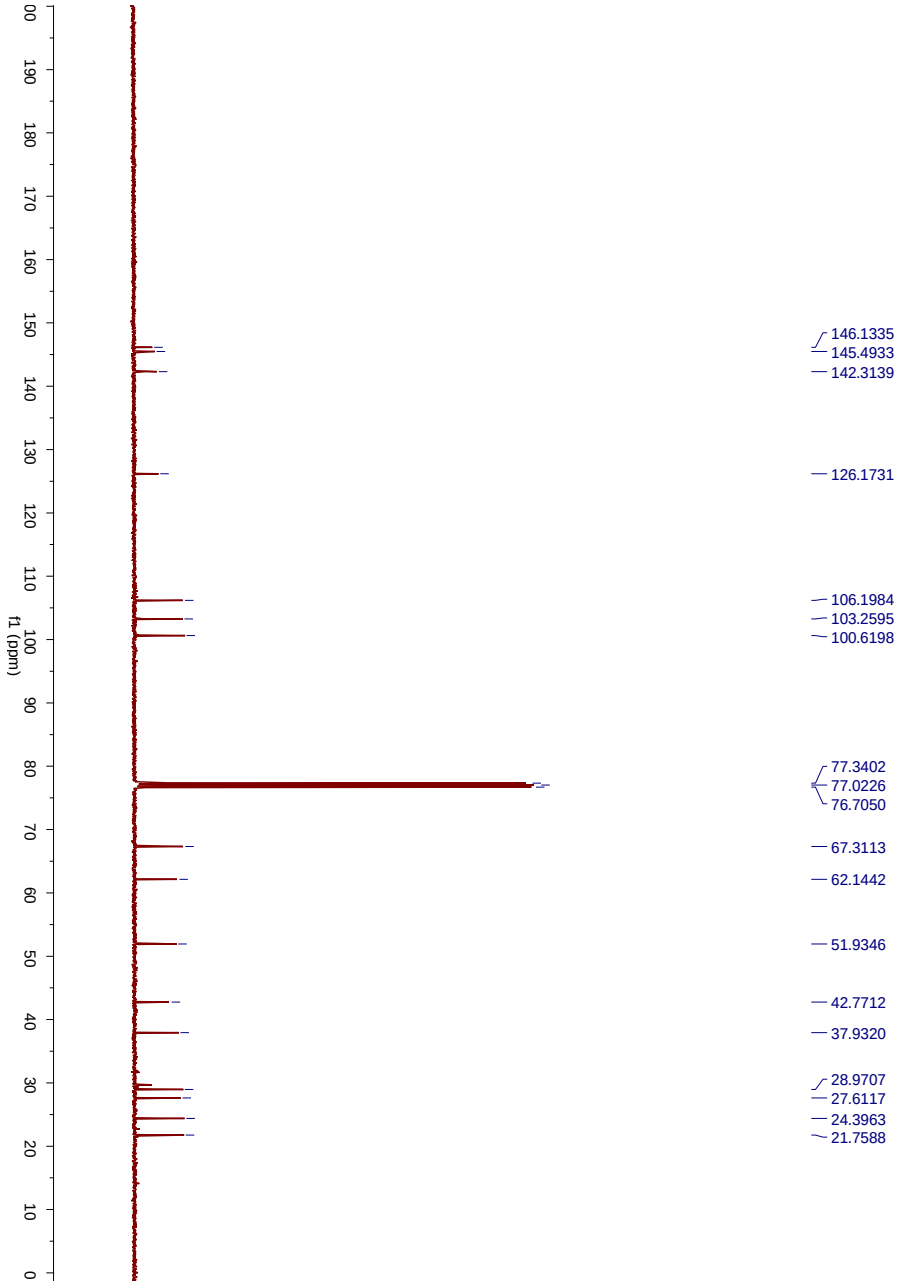


Scanned copy of mass spectrum of ±(**11b**)

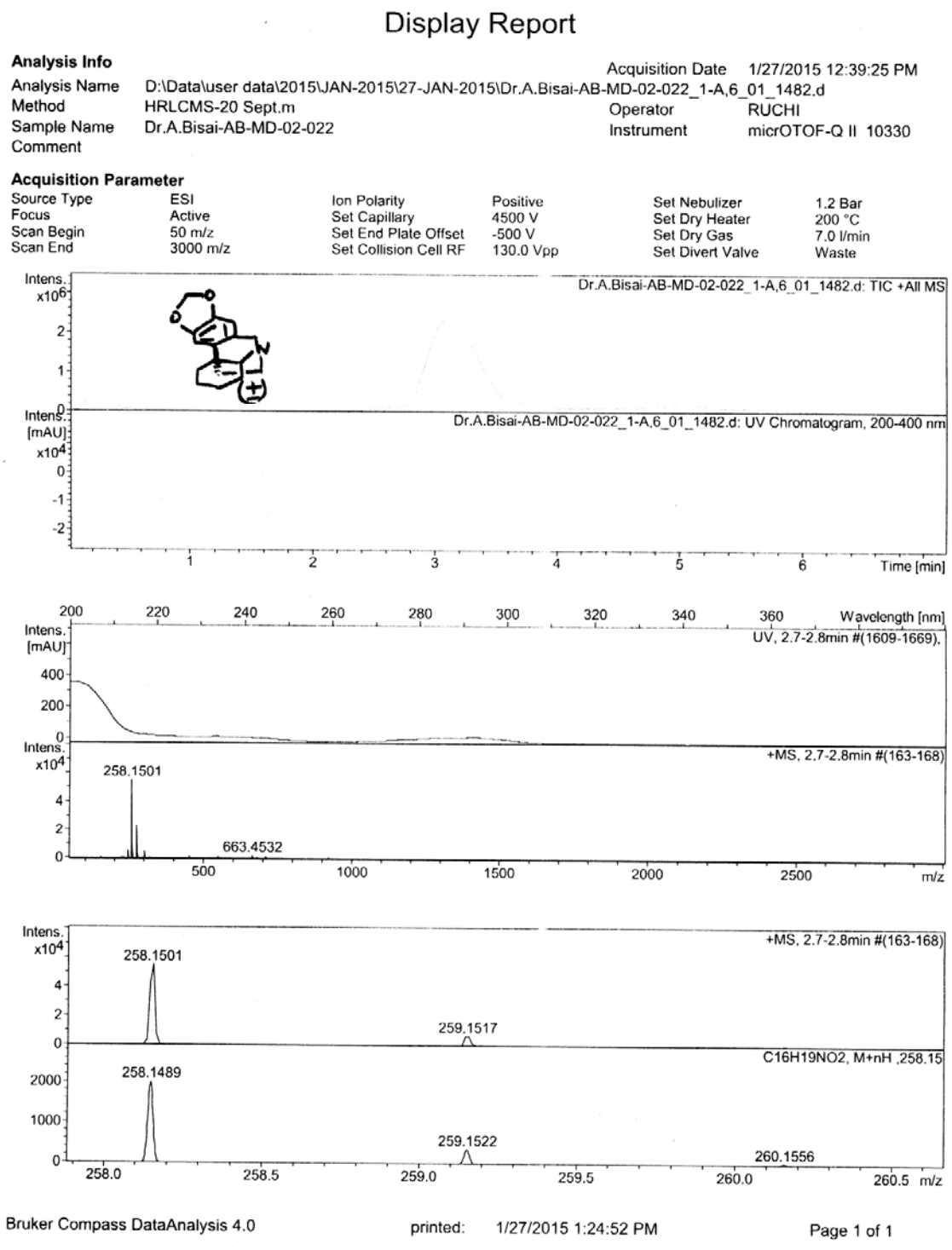




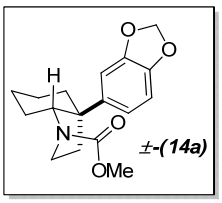
^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(2a)**

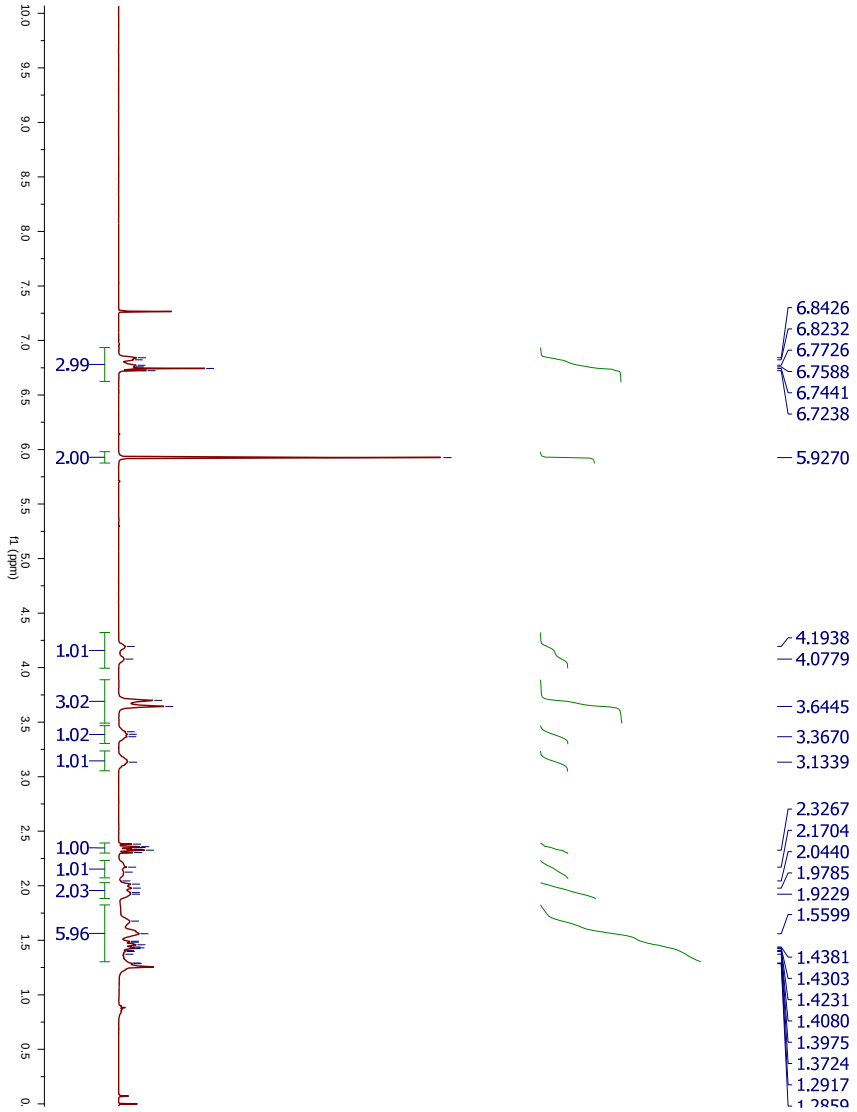


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(2a)**

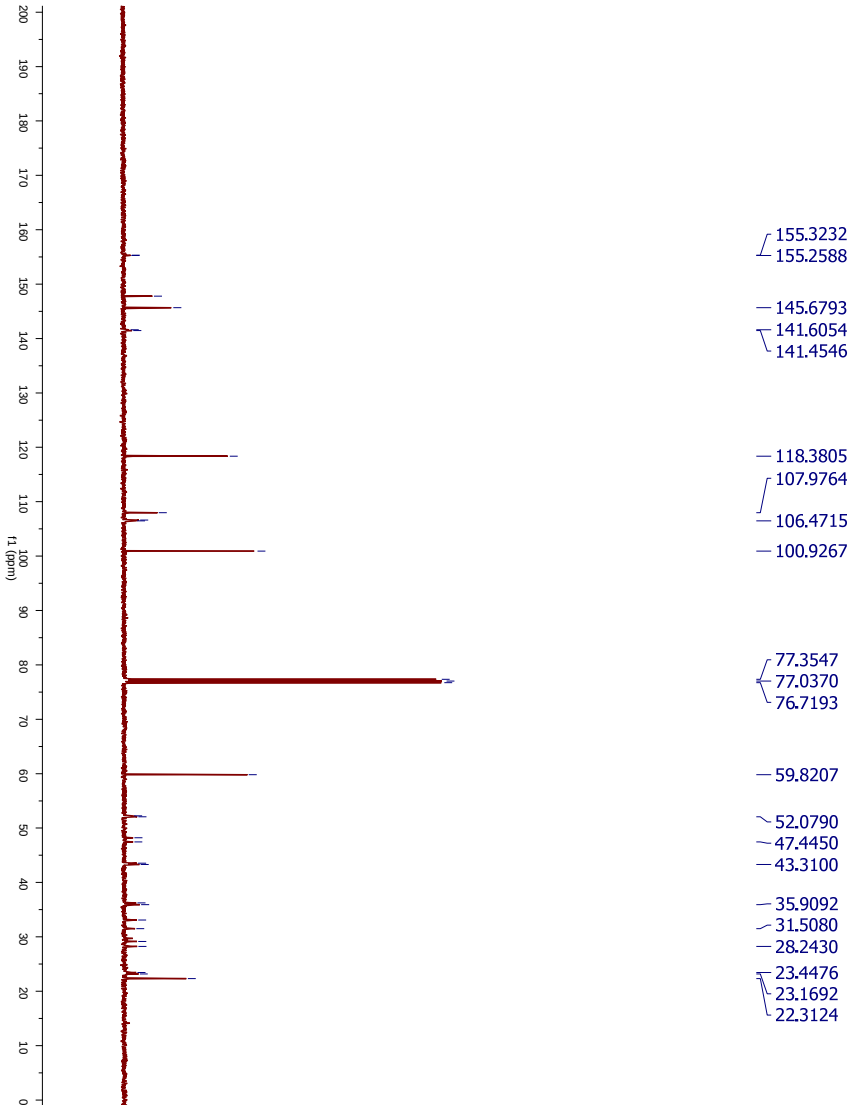


Scanned copy of mass spectrum of ±(**2a**)

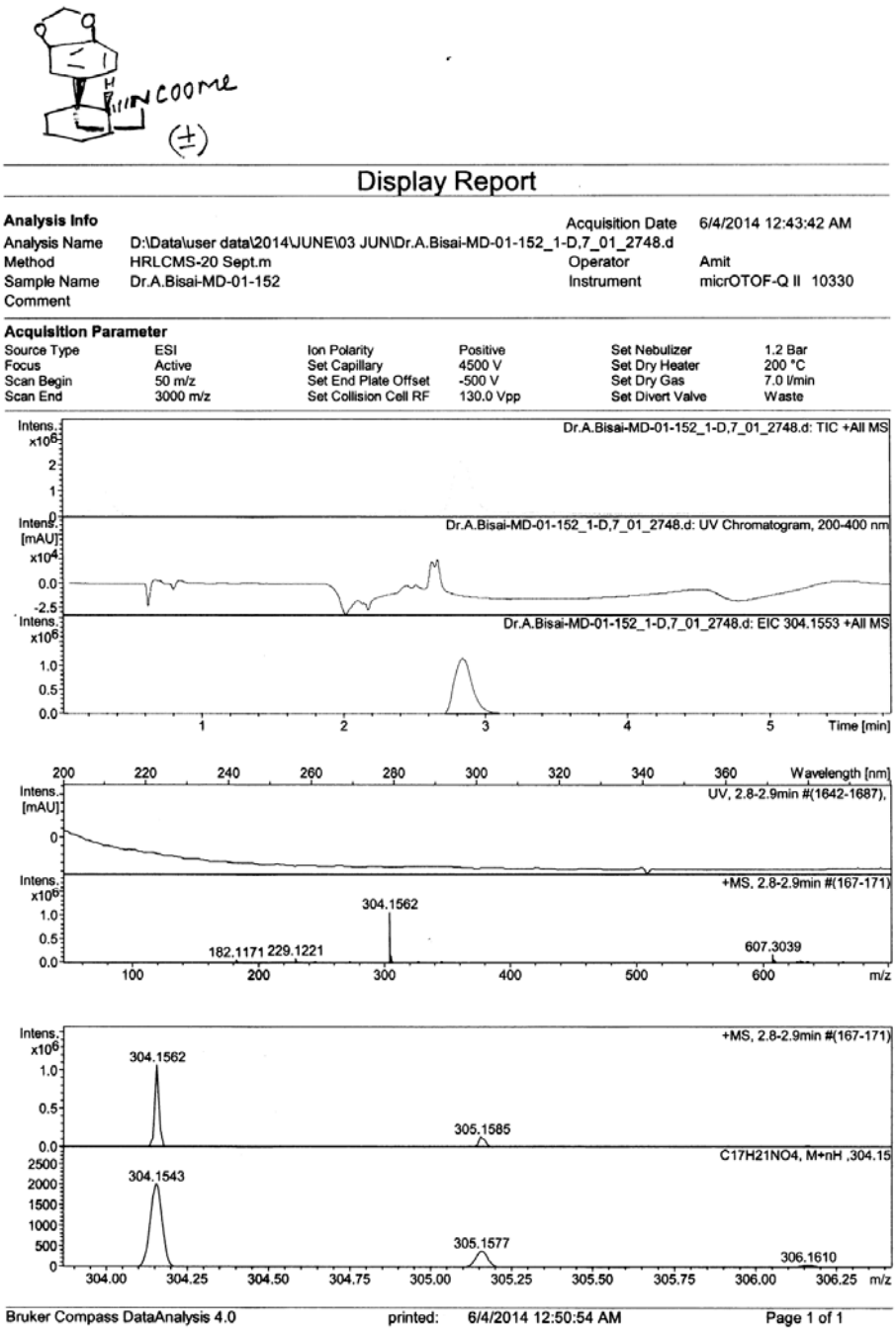




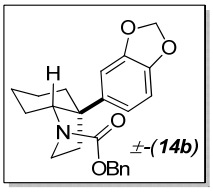
^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(14a)**

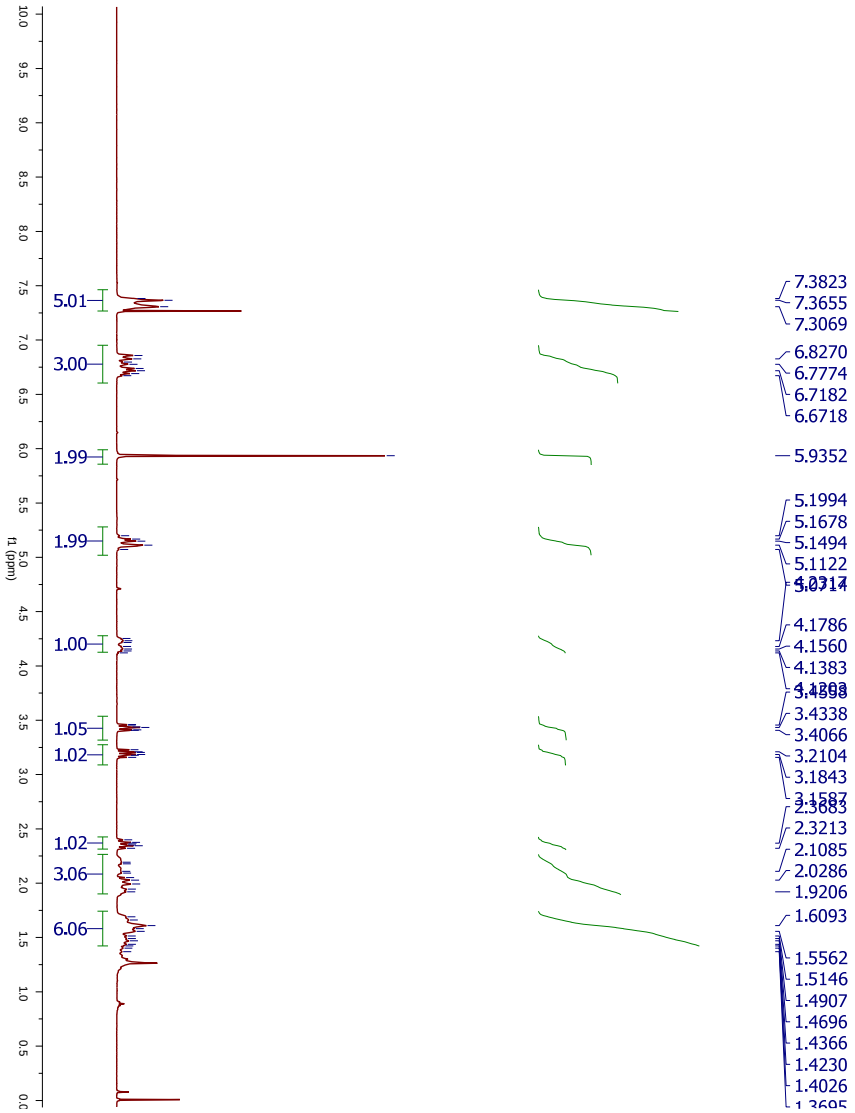


^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(14a)**

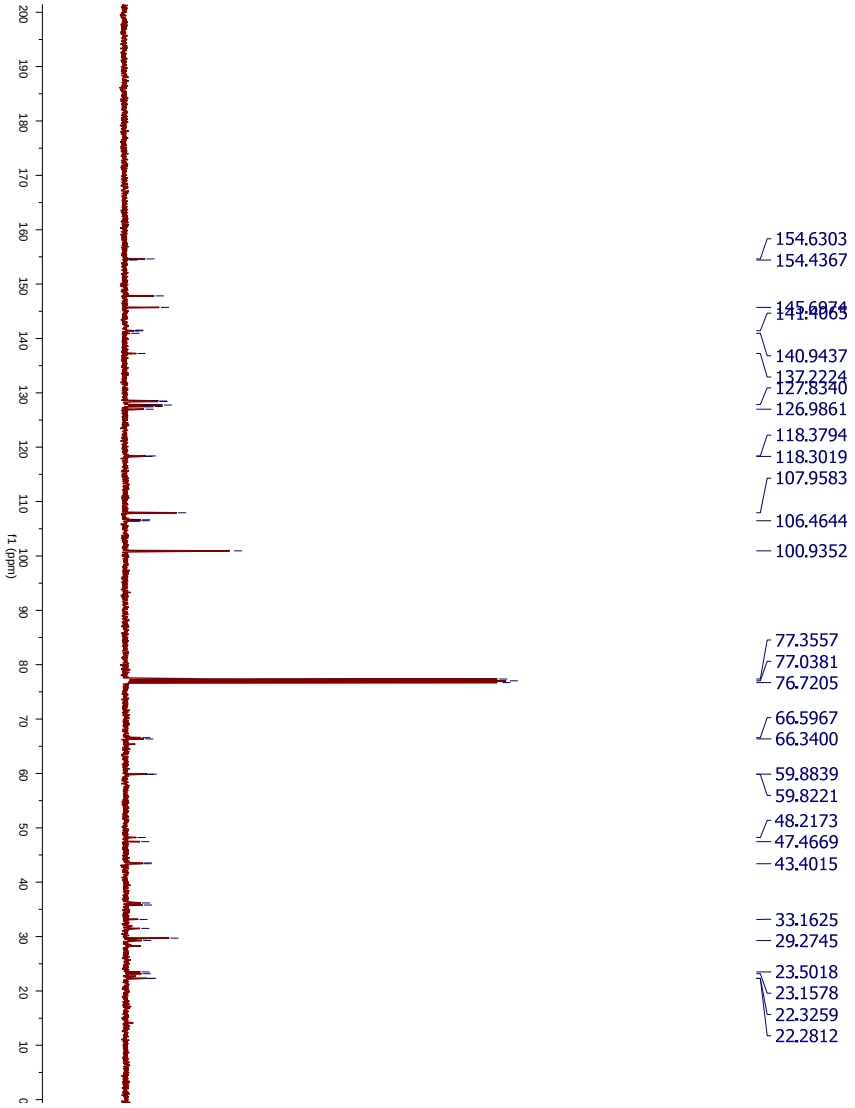


Scanned copy of mass spectrum of ±(**14a**)





^{1}H NMR (400 MHz, $CDCl_3$) of compound ±**(14b)**



^{13}C NMR (100 MHz, $CDCl_3$) of compound ±**(14b)**

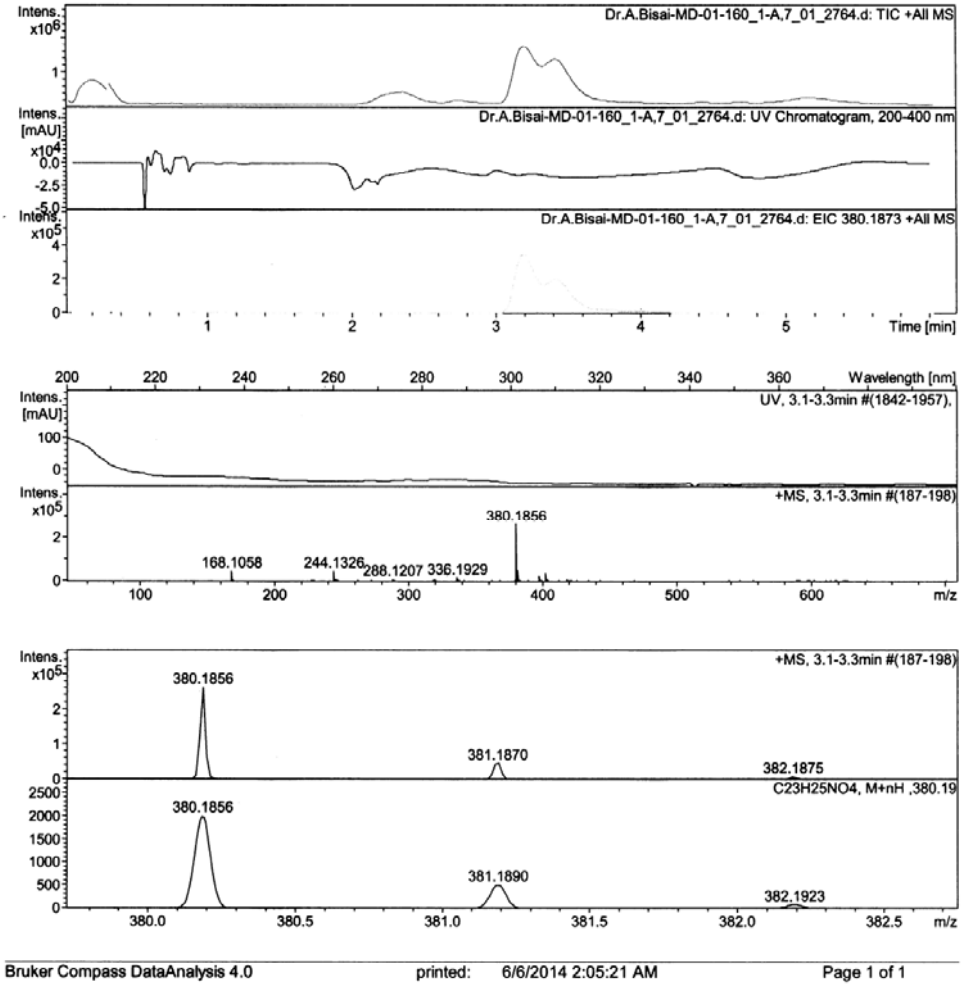
Display Report

Analysis Info

Analysis Name	D:\Data\user data\2014\JUNE\05 JUN\Dr.A.Bisai-MD-01-160_1-A,7_01_2764.d	Acquisition Date	6/6/2014 1:38:42 AM
Method	HRLCMS-20 Sept.m	Operator	Amit
Sample Name	Dr.A.Bisai-MD-01-160	Instrument	micrOTOF-Q II 10339
Comment			

Acquisition Parameter

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



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Scanned copy of mass spectrum of ±(**14b**)