

Electronic Supplementary Data

Expeditious approach to the *Amarylidaceae* alkaloids, crinasiadine and its analogues, via a palladium-catalyzed intramolecular direct C-H arylation

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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 (Et₂O) was distilled over sodium/benzophenone ketyl. *N,N*-dimethylacetamide (DMA) was distilled over calcium hydride. All other solvents such as DMF, dichloromethane, toluene and reagents such as aniline, *o*-anisidine, *p*-anisidine, *N*-ethylaniline, 3,4-methylenedioxybenzaldehyde, 3,4-dimethoxybenzaldehyde, 3-methoxybenzaldehyde, 2-bromobenzylalcohol, 2-bromobenzoic acid, 2-iodobenzoic acid, thionyl chloride, *N*-bromosuccinimide, iodine, LiAlH₄, methylchloroformate, acetyl chloride, triethylamine, potassium carbonate, Pd(OAc)₂, Triphenylphosphine, Pd(PPh₃)₄, 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, anisaldehyde stain and other stains. Silicagel from Merck (particle size 100-200 mesh) 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. ¹H and ¹³C NMR spectra were recorded on Bruker 400, 500 MHz spectrometers with ¹³C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for ¹H NMR and δ = 77.0 for ¹³C NMR). Data for ¹H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). 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 spectra and X-ray crystal data were obtained from the Central Instrumentation Facility (CIF) at the Indian Institute of Science Education and Research (IISER) Bhopal.

General procedure for synthesis of amides (2c, 3a-f and 3j-k) for direct biaryl-coupling:

Step 1:

An oven-dried round-bottom flask was charged with 2-halo substituted benzoic acid [1.0 equiv. (generally in 1 g scale)] in toluene (5 mL per mmol) and cooled to 0 °C on an ice-bath. To this reaction mixture was added thionyl chloride (1.2 equiv) drop-wise over a period of 5 minutes. After stirring at 0 °C for additional 5 minutes, the reaction mixture was warmed to 23 °C and stirring continued for another 10 minutes. Then, the reaction mixture was placed on an oil-bath maintaining the temperature to 100 °C and stirring continued another 2.5 h at same temperature. Upon completion of the reaction (monitoring by TLC), it was cooled to the reaction mixture and directly used for coupling reaction, without isolation of acid chloride.

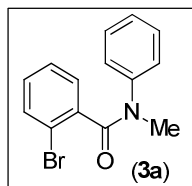
Step 2:

In a two-necked flame-dried round-bottom flask was charged with aniline derivatives (1.0 equiv.) and triethylamine (3.0 equiv) in dichloromethane (10 mL per mmol) and cooled to 0 °C on an ice-bath. After 5 minutes of stirring at same temperature, a toluene solution of acid chloride (1.0 equiv as prepared earlier) was added drop-wise to the reaction mixture by a glass syringe and allowed to warm to RT. The stirring was continued till TLC showed complete consumption of starting materials. The reaction mixture was poured into a separatory funnel and washed with water (20 mL). The aqueous layer was further extracted with CH₂Cl₂ (10 mL X 2). The combined organic extracts were dried over MgSO₄ and concentrated under vacuum. The crude product was purified by flash chromatography (2:1 hexanes/EtOAc) to afford pure amides.

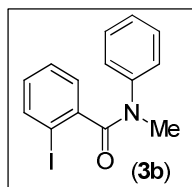
Step 3:

In an oven-dried round-bottom flask, the benzamide (1.0 equiv as prepared earlier) was taken in *N, N*-dimethylformamide (5 mL) under inert atmosphere and the reaction vessel was cooled to 0 °C. To this reaction mixture NaH (1.2 equiv) was added portion-wise and it was stirred for another 5 min. Then MeI (1.2 equiv) was added drop-wise to the reaction mixture at 0 °C. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH₄Cl (3 mL) and then diluted with 10 mL of EtOAc. The whole

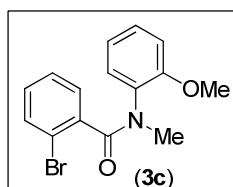
reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over Na₂SO₄ and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (1:1 hexanes/EtOAc) to afford amides **2c**, **3**, **9**.



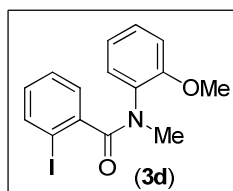
2-bromo-N-methyl-N-phenylbenzamide (3a): 95% yield as yellow gel, R_f = 0.64 (40% EtOAc in hexane). ¹H NMR (400 MHz, CDCl₃) δ : 7.45-7.42 (m, 1H), 7.36 (d, J = 7.86 Hz, 1H), 7.19-7.15 (m, 4H), 7.09 (m, 2H), 7.01 (m, 1H), 3.50 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 143.2, 138.5, 132.6, 129.8, 129.0, 128.9, 127.2, 126.9, 126.7, 119.8, 37.2; IR (film) $\nu_{\max}$ 3064, 2925, 1652, 1594, 1495, 1373, 1301, 1107, 1024, 765, 698 cm⁻¹; HRMS (ESI) m/z 290.0186 [M + H]⁺; calculated for [C₁₄H₁₂BrNO + H]⁺: 290.0175.



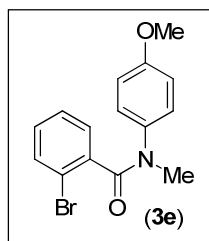
2-iodo-N-methyl-N-phenylbenzamide (3b): 91% yield as grey color solid, R_f = 0.32 (30% EtOAc in hexane). ¹H NMR (400 MHz, CDCl₃) δ : 7.64 (d, J = 7.92 Hz, 1H), 7.18-7.17 (m, 4H), 7.12-7.10 (m, 2H), 7.04-7.02 (m, 1H), 6.84 (t, J = 6.67 Hz, 1H), 3.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 143.3, 142.4, 139.1, 129.7, 129.0, 128.6, 127.3, 127.1, 127.0, 93.7, 37.4; IR (film) $\nu_{\max}$ 3064, 2923, 1651, 1595, 1494, 1423, 1372, 1303, 1105, 1017, 764, 744, 697, 666 cm⁻¹; HRMS (ESI) m/z 388.0050 [M + H]⁺; calculated for [C₁₄H₁₂INO + H]⁺: 388.0036; MP 62–63 °C.



2-bromo-*N*-(2-methoxyphenyl)-*N*-methylbenzamide (3c): 94% yield as light yellow color solid, $R_f = 0.31$ (20% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.36 (d, $J = 7.43$ Hz, 1H), 7.24 (d, $J = 7.60$ Hz, 1H), 7.14-7.10 (m, 2H), 7.03-6.96 (m, 2H), 6.76-6.72 (m, 2H), 3.83 (s, 3H), 3.38 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.2, 154.5, 138.6, 132.4, 131.8, 129.7, 129.3, 128.7, 127.5, 126.3, 120.6, 119.8, 111.3, 55.3, 36.0; **IR** (film) ν_{max} 2929, 1651, 1590, 1502, 1463, 1375, 1278, 1097, 1025, 747, 667 cm^{-1} ; **HRMS** (ESI) m/z 320.0282 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{14}\text{BrNO}_2 + \text{H}]^+$: 320.0281; **MP** 114–116 $^{\circ}\text{C}$.

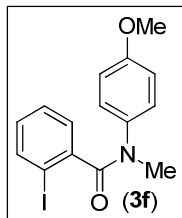


2-iodo-*N*-(2-methoxyphenyl)-*N*-methylbenzamide (3d): 94% yield as white solid, $R_f = 0.28$ (20% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.64 (d, $J = 7.76$ Hz, 1H), 7.29 (d, $J = 7.63$ Hz, 1H), 7.12 (d, $J = 7.78$ Hz, 1H), 7.04-7.00 (m, 2H), 6.82-6.79 (m, 1H), 6.77-6.73 (m, 2H), 3.85 (s, 3H), 3.38 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.1, 154.5, 142.4, 139.0, 132.0, 129.7, 129.3, 128.9, 127.1, 126.9, 120.6, 111.3, 93.7, 55.3, 36.2; **IR** (film) ν_{max} 2937, 2838, 1651, 1596, 1501, 1465, 1418, 1374, 1278, 1250, 1161, 1127, 1096, 1049, 1020, 746, 661 cm^{-1} ; **HRMS** (ESI) m/z 368.0142 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{14}\text{INO}_2 + \text{H}]^+$: 368.0142; **MP** 110–113 $^{\circ}\text{C}$.

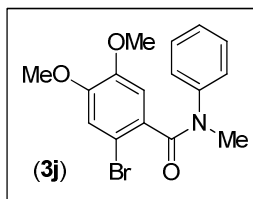


2-bromo-*N*-(4-methoxyphenyl)-*N*-methylbenzamide (3e): 95% yield as brown color solid, $R_f = 0.30$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.38 (d, $J = 7.83$ Hz, 1H), 7.10 (s, 3H), 7.08 (s, 1H), 7.02 (m, 1H), 6.69 (d, $J = 8.08$ Hz, 2H), 3.71 (s, 3H), 3.47 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.0, 158.3, 138.8, 136.1, 132.6, 129.7, 128.8, 128.1, 126.7, 119.6, 114.1, 55.3, 37.4; **IR** (film) ν_{max} 2932, 1651, 1511, 1374, 1302, 1248, 1181, 1107, 1027, 836, 767 cm^{-1} ;

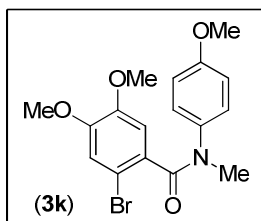
HRMS (ESI) m/z 320.0293 $[M + H]^+$; calculated for $[C_{15}H_{14}BrNO_2 + H]^+$: 320.0281; **MP** 54–57 °C.



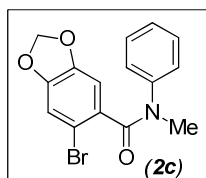
2-iodo-N-(4-methoxyphenyl)-N-methylbenzamide (3f): 94% yield as yellow gel, R_f = 0.39 (20% EtOAc in hexane). **^1H NMR** (400 MHz, $CDCl_3$) δ : 7.66 (d, J = 7.91 Hz, 1H), 7.14–7.12 (m, 3H), 7.05 (d, J = 7.36 Hz, 1H), 6.86 (t, J = 7.33 Hz, 1H), 6.70 (d, J = 8.12 Hz, 2H), 3.72 (s, 3H), 3.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 158.3, 142.6, 139.1, 136.1, 129.6, 128.2, 127.3, 127.1, 114.6, 114.1, 55.3, 37.6; **IR** (film) ν_{max} 2925, 1674, 1510, 1375, 1247, 1018, 836 cm^{-1} ; **HRMS** (ESI) m/z 368.0153 $[M + H]^+$; calculated for $[C_{15}H_{14}INO_2 + H]^+$: 368.0142.



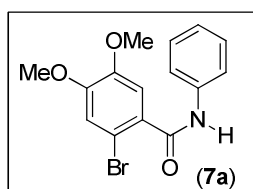
2-bromo-4,5-dimethoxy-N-methyl-N-phenylbenzamide (3j): 96% yield as white crystalline solid, R_f = 0.20 (40% EtOAc in hexane). **^1H NMR** (400 MHz, $CDCl_3$) δ : 7.20–7.12 (m, 5H), 6.82 (s, 1H), 6.59 (s, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 3.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 149.5, 147.7, 143.5, 130.4, 129.0, 127.0, 126.7, 125.2, 121.9, 110.6, 56.1, 56.0, 37.3; **IR** (film) ν_{max} 2931, 1651, 1596, 1506, 1388, 1358, 1256, 1214, 1164, 1110, 1018, 699 cm^{-1} ; **HRMS** (ESI) m/z 350.0401 $[M + H]^+$; calculated for $[C_{16}H_{16}BrNO_3 + H]^+$: 350.0386; **MP** 115–118 °C.



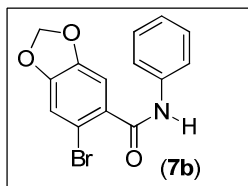
2-bromo-4,5-dimethoxy-*N*-(4-methoxyphenyl)-*N*-methylbenzamide (3k): 72% yield as white color solid, $R_f = 0.16$ (40% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.08-7.05 (m, 2H), 6.82 (s, 1H), 6.72-6.69 (m, 2H), 6.60 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 3.45 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.0, 158.2, 149.4, 147.7, 136.3, 130.6, 127.9, 115.1, 114.1, 111.7, 110.4, 56.02, 56.01, 55.3, 37.5; **IR** (film) ν_{max} 2932, 2845, 1651, 1601, 1512, 1389, 1256, 1213, 1165, 1109, 1027, 852 cm^{-1} ; **HRMS** (ESI) m/z 380.0503 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{17}\text{H}_{18}\text{BrNO}_4 + \text{H}]^+$: 380.0492; **MP** 80–83 °C.



6-bromo-*N*-methyl-*N*-phenylbenzo[d][1,3]dioxole-5-carboxamide (2c): 93% yield, White solid, $R_f = 0.39$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.22-7.16 (m, 5H), 6.79 (s, 1H), 6.56 (s, 1H), 5.86 (s, 2H), 3.45 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.5, 148.4, 146.8, 143.3, 131.7, 129.0, 127.1, 126.8, 112.7, 111.1, 108.7, 101.9, 37.4; **IR** (film) ν_{max} 3057, 2906, 1651, 1596, 1480, 1428, 1394, 1361, 1298, 1280, 1037, 930, 866, 852, 763, 732, 699 cm^{-1} ; **HRMS** (ESI) m/z 334.0111 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{12}\text{BrNO}_3 + \text{H}]^+$: 334.0073; **MP** 112–114 °C.



2-bromo-4,5-dimethoxy-*N*-phenylbenzamide (7a): 74% yield as yellow solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.13 (s, 1H), 7.67 (d, $J = 7.85$ Hz, 2H), 7.38 (t, $J = 7.64$ Hz, 2H), 7.26 (s, 1H), 6.72-7.16 (m, 1H), 7.02 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.9, 151.1, 148.5, 137.7, 129.2, 129.1, 124.7, 120.0, 115.8, 113.0, 109.9, 56.3, 56.2.



6-bromo-N-phenylbenzo[d][1,3]dioxole-5-carboxamide (7b): 69% yield as white solid. ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (s, 1H), 7.59 (d, J = 8.08 Hz, 2H), 7.31 (t, J = 7.82 Hz, 2H), 7.12 (t, J = 7.47 Hz, 1H), 6.98 (s, 1H), 6.92 (s, 1H), 5.97 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 149.8, 147.4, 137.7, 131.1, 129.0, 124.8, 120.2, 113.2, 110.9, 109.5, 102.4.

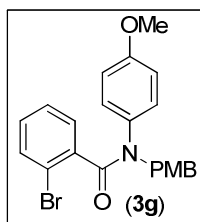
General procedure for synthesis of amides (3g-i and 3p) for dehydrohalide coupling:

Step 1:

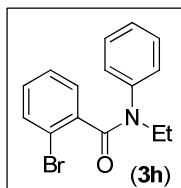
See the general procedure shown in S3.

Step 2:

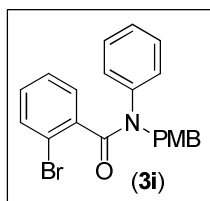
See the general procedure shown in S4. The crude products were purified by flash chromatography (3:1 hexanes/EtOAc) to afford amides (**3g-i** and **3p**).



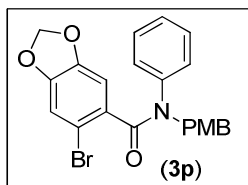
2-bromo-N-(4-methoxybenzyl)-N-(4-methoxyphenyl)benzamide (3g): 75% yield as yellow gel, R_f = 0.47 (30% EtOAc in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.35 (d, J = 7.98 Hz, 1H), 7.25-7.23 (m, 2H), 7.06 (d, J = 4.24 Hz, 2H), 7.00-6.94 (m, 1H), 6.88-6.86 (m, 2H), 6.83-6.80 (m, 2H), 6.58-6.56 (m, 2H), 5.00 (s, 2H), 3.78 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 159.0, 158.5, 138.7, 134.1, 132.6, 130.4, 129.6, 129.3, 129.2, 128.6, 126.7, 119.6, 113.9, 113.8, 55.2, 55.19, 52.4; IR (film) ν_{max} 3060, 3001, 2931, 2838, 1645, 1590, 1514, 1469, 1434, 1395, 1321, 1301, 1249, 1177, 1109, 1028, 975, 837, 765, 741 cm^{-1} ; HRMS (ESI) m/z 426.0718 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{22}\text{H}_{20}\text{BrNO}_3 + \text{H}]^+$: 426.0699.



2-bromo-N-ethyl-N-phenylbenzamide (3h): 94% yield as white solid, $R_f = 0.31$ (20% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.37 (d, $J = 7.95$ Hz, 1H), 7.22-7.10 (m, 5H), 7.06 (d, $J = 4.17$ Hz, 2H), 7.02-6.97 (m, 1H), 4.00 (q, $J = 7.05$ Hz, 2H), 1.26 (t, $J = 7.08$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.2, 141.6, 138.7, 132.6, 129.6, 128.9, 128.7, 128.0, 127.4, 126.6, 119.8, 44.2, 12.9; **IR** (film) ν_{max} 3063, 2975, 2936, 1651, 1594, 1494, 1429, 1397, 1307, 1258, 1118, 1025, 878, 766, 746, 699, 672 cm^{-1} ; **HRMS** (ESI) m/z 304.0345 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{14}\text{BrNO} + \text{H}]^+$: 304.0332 ; **MP** 74–76 $^{\circ}\text{C}$.



2-bromo-N-(4-methoxybenzyl)-N-phenylbenzamide (3i): 84% yield as yellow gel, $R_f = 0.54$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.35 (d, $J = 7.84$ Hz, 1H), 7.26-7.25 (m, 1H), 7.24 (m, 1H), 7.08-7.04 (m, 5H), 6.99-6.95 (m, 3H), 6.83-6.79 (m, 2H), 5.06 (s, 2H), 3.78 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.6, 159.0, 141.5, 138.5, 132.6, 130.3, 129.7, 129.2, 128.8, 128.2, 127.5, 126.6, 119.8, 113.8, 55.2, 52.3; **IR** (film) ν_{max} 3061, 2934, 2836, 1651, 1614, 1594, 1513, 1495, 1430, 1393, 1321, 1303, 1248, 1177, 1109, 1075, 1030, 973, 817, 759, 739, 698, 671, 609 cm^{-1} ; **HRMS** (ESI) m/z 396.0610 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{21}\text{H}_{18}\text{BrNO}_2 + \text{H}]^+$: 396.0594.



6-bromo-N-(4-methoxybenzyl)-N-phenylbenzo[d][1,3]dioxole-5-carboxamide (3p): 91% yield as yellow solid, $R_f = 0.43$ (40% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.20 (d,

$J = 8.34$ Hz, 2H), 7.12-7.07 (m, 3H), 6.97 (s, 1H), 6.94 (s, 1H), 6.78 (d, $J = 8.66$ Hz, 2H), 6.76 (s, 1H), 6.52 (s, 1H), 5.83 (s, 2H), 5.00 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.0, 148.3, 146.7, 141.5, 131.7, 130.3, 129.2, 128.9, 128.1, 127.5, 113.7, 112.7, 111.1, 108.6, 101.9, 55.2, 52.4; IR (film) ν_{max} 3056, 2908, 2837, 1644, 1595, 1483, 1415, 1373, 1300, 1242, 1176, 1152, 1112, 1036, 936, 863, 832, 735, 699 cm^{-1} ; HRMS (ESI) m/z 440.0530 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{22}\text{H}_{18}\text{BrNO}_4 + \text{H}]^+$: 440.0492; MP 86–88 °C.

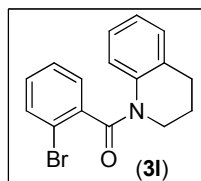
General procedure for synthesis of tricyclic amide substrates (**3l** and **3m**) for dehydrohalide coupling:

Step 1:

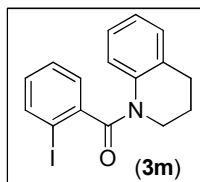
See the general procedure shown in S3.

Step 2:

See the general procedure shown in S4. The crude product was purified by flash chromatography (2:1 hexanes/EtOAc) to afford pure amides (**3l** and **3m**).



2-Bromo-N-tetrahydroquinolyl-benzamide (3l): 71% yield, $R_f = 0.30$ (4:1 hexanes/EtOAc). ^1H NMR (400 MHz, CDCl_3) (rotameric mixture) δ 7.58-8.12 (m, 1H for major + minor rotamers), 6.94-7.39 (m, 2H for major + minor rotamers), 6.47-6.74 (m, 1H for major + minor rotamers), 3.48-4.11 (m, 1H for major + minor rotamers), 2.84 (br, s, 1H for major + minor rotamers), 2.02-2.14 (br, 2H for major + minor rotamers); ^{13}C NMR (100 MHz, CDCl_3) (rotameric mixture) δ 168.19 (another C missing for minor rotamer), 138.85, 138.62, 138.18, 138.14, 132.98, 132.88, 130.31, 130.25, 129.72, 129.52, 128.47, 128.30, 127.86, 127.64, 127.44, 127.25, 125.89, 125.78, 125.00, 124.98, 124.50, 124.48, 120.05, 120.04, 47.11, 46.95, 43.42, 43.31, 27.19, 26.88; IR (film) ν_{max} 2946, 2361, 1652, 1600, 1492, 1430, 1386, 1304, 1154, 1025, 941, 760 cm^{-1} ; HRMS (ESI) m/z 316.0344 $[(\text{M} + \text{H})^+]$; calculated for $[\text{C}_{16}\text{H}_{15}\text{BrNO}]^+$: 316.0332; MP 137–139 °C.



2-Iodo-*N*-tetrahydroquinolyl-benzamide (3m): 68% yield, $R_f = 0.35$ (4:1 hexanes/EtOAc). **¹H NMR** (500 MHz, CDCl₃ + 1 drop DMSO-*d*₆) (rotameric mixture) δ 7.82-8.08 (br, m, 1H for major + minor rotamers), 7.39-7.69 (br, m, 1H for major + minor rotamers), 7.22 (br, s, 1H for major + minor rotamers), 7.10 (br, s, 2H for major + minor rotamers), 7.82-8.08 (br, m, 1H for major + minor rotamers), 6.96 (br, s, 1H for major + minor rotamers), 6.44-6.72 (br, m, 1H for major + minor rotamers), 3.98 (br, s, 1H for major rotamer), 3.45 (br, s, 1H for minor rotamer), 2.85 (br, s, 2H for major + minor rotamers), 2.03 (br, m, 2H for major + minor rotamers); **IR** (film) $\nu_{\max}$ 2946, 2360, 1651, 1648, 1581, 1492, 1456, 1385, 1256, 1154, 1015, 940, 759, 741 cm⁻¹; **HRMS** (ESI) m/z 364.0198 [(M+H)⁺; calculated for [C₁₆H₁₅INO]⁺: 364.0193]; **MP** 133–135 °C.

Synthesis of methyl *N*-(2-bromobenzyl)-*N*-phenylacetamide derivatives (5a-d):

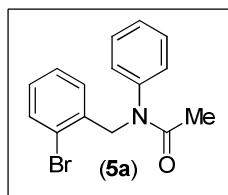
Step 1:

An oven-dried round-bottom flask was charged with aniline [1.0 equiv (generally in 5 g scale)] and triethylamine (3.0 equiv) in dichloromethane (40 mL) and cooled to 0 °C on an ice-bath. After 5 minutes of stirring at same temperature, acetyl chloride (1.2 equiv) was added dropwise to the reaction mixture by a glass syringe and allowed to warm to room temperature. The stirring was continued till TLC showed complete consumption of starting materials. The reaction mixture was washed with water (50 mL) and stirred with 2(*N*) HCl solution. The aqueous layer was further extracted with CH₂Cl₂ (30 mL X 2). The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was directly treated for next step (without isolation).

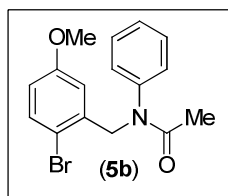
Step 2:

In an oven-dried round-bottom flask, the crude acetamide [1.0 equiv (generally in 500 mg scale)] as prepared earlier was taken in *N,N*-dimethylformamide (15 mL) under inert atmosphere and the reaction vessel was cooled to 0 °C. To this reaction mixture NaH (1.2 equiv) was added

portion-wise and it was stirred for another 5 min. A solution of 2-bromobenzylbromides derivatives (1.1 equiv) in *N,N*-dimethylformamide (5 mL) was added drop-wise to the reaction mixture at 0 °C. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH₄Cl (5 mL) and then diluted with 20 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 30 mL of water. The organic filtrate was dried over Na₂SO₄ and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (1:1 hexanes/EtOAc) to afford **5a-d**.

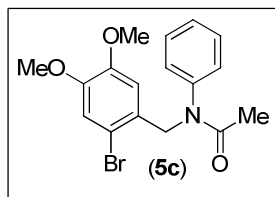


***N*-(2-bromobenzyl)-*N*-phenylacetamide (5a)**: 87% yield as yellow gel, $R_f = 0.54$ (40% EtOAc in hexane). ¹H NMR (400 MHz, CDCl₃) δ : 7.47 (d, $J = 8.02$ Hz, 1H), 7.38 (dd, $J = 7.67$ Hz, 1.31 Hz 1H), 7.35-7.24 (m, 4H), 7.12-7.07 (m, 3H), 5.07 (s, 2H), 1.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 142.6, 136.3, 132.7, 130.2, 129.6, 128.8, 128.0, 127.5, 123.8, 121.1, 52.4, 22.7; IR (film) $\nu_{\max}$ 3062, 2923, 1662, 1595, 1495, 1391, 1299, 1277, 1231, 1025, 779, 738, 700 cm⁻¹; HRMS (ESI) m/z 304.0347 [M + H]⁺; calculated for [C₁₅H₁₄BrNO + H]⁺: 304.0332.

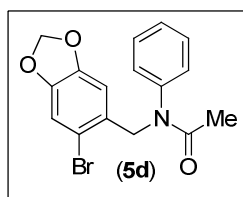


***N*-(2-bromo-5-methoxybenzyl)-*N*-phenylacetamide (5b)**: 79% yield as white solid, $R_f = 0.46$ (30% EtOAc in hexane). ¹H NMR (400 MHz, CDCl₃) δ : 7.35-7.28 (m, 4H), 7.09 (s, 1H), 7.07 (s, 1H), 6.94 (d, $J = 3.08$ Hz, 1H), 6.65 (dd, $J = 8.71$ Hz, 2.98 Hz, 1H), 5.00 (s, 2H), 3.75 (s, 3H), 1.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.6, 159.1, 142.6, 137.4, 133.2, 129.6, 128.0, 115.8, 114.5, 114.2, 55.5, 52.5, 22.7; IR (film) $\nu_{\max}$ 2921, 2852, 1655, 1595, 1467, 1384,

1294, 1274, 1237, 1161, 1019, 805, 778, 698 cm^{-1} ; **HRMS** (ESI) m/z 334.0441 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{16}\text{H}_{16}\text{BrNO}_2 + \text{H}]^+$: 334.0437; **MP** 53–55 $^{\circ}\text{C}$.



***N*-(2-bromo-4,5-dimethoxybenzyl)-*N*-phenylacetamide (5c)**: 87% yield as White solid, R_f = 0.43 (50% EtOAc in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.35–7.30 (m, 3H), 7.02–6.99 (m, 2H), 6.96 (s, 1H), 6.89 (s, 1H), 5.01 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 148.8, 148.5, 142.3, 129.5, 128.6, 128.3, 128.0, 115.0, 114.4, 113.5, 56.1, 56.06, 51.5, 22.7; **IR** (film) ν_{max} 2935, 1659, 1596, 1506, 1439, 1381, 1258, 1223, 1206, 1162, 1030, 801, 700 cm^{-1} ; **HRMS** (ESI) m/z 364.0560 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{17}\text{H}_{18}\text{BrNO}_3 + \text{H}]^+$: 364.0543; **MP** 111–112 $^{\circ}\text{C}$.



***N*-((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-phenylacetamide (5d)**: 90% yield as white solid, R_f = 0.65 (50% EtOAc in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 7.36–7.31 (m, 3H), 7.06 (d, J = 6.56 Hz, 2H), 6.94 (s, 1H), 6.89 (s, 1H), 5.96 (s, 2H), 4.97 (s, 2H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 147.6, 147.57, 142.4, 129.7, 129.6, 128.1, 128.0, 114.4, 112.4, 110.0, 101.7, 52.0, 22.6; **IR** (film) ν_{max} 2926, 1661, 1595, 1495, 1479, 1396, 1242, 1112, 1038, 931, 699 cm^{-1} ; **HRMS** (ESI) m/z 348.0247 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{16}\text{H}_{14}\text{BrNO}_3 + \text{H}]^+$: 348.0230; **MP** 83–84 $^{\circ}\text{C}$.

Synthesis of methyl 2-bromobenzyl(phenyl)carbamate derivatives (7c-d):

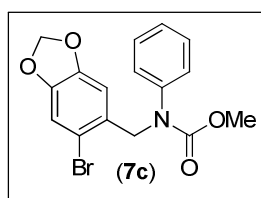
Step 1:

A round-bottom flask was charged with aniline (2.0 mmol; 1.0 equiv) in toluene : NaHCO_3 (1:1) (10 mL) at room temperature. To this reaction mixture methyl chloroformate (3.0

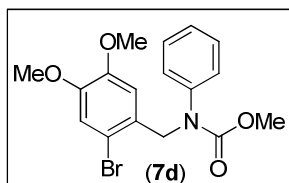
mmol; 1.5 equiv) was added drop-wise and it was stirred for 4 h at room temperature. Upon completion of the reaction (monitoring by TLC), it was diluted by 10 mL EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 10 mL of water. The organic filtrate was dried over anhydrous Na₂SO₄ and concentrated in a rotary evaporator under vacuum. Without isolation the crude material was directly treated for next step.

Step 2:

In an oven-dried round-bottom flask, the crude carbamate (1.0 equiv as prepared earlier) was taken in *N,N*-dimethylformamide (5 mL) under inert atmosphere and the reaction vessel was cooled to 0 °C. To this reaction mixture NaH (2.40 mmol; 1.2 equiv) was added portion-wise and it was stirred for another 5 min. A solution of 2-bromobenzyld bromide derivatives (2.20 mmol; 1.1 equiv) in *N,N*-dimethylformamide (2 mL) was added drop-wise to the reaction mixture at 0 °C. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH₄Cl (3 mL) and then diluted with 10 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 15 mL of water. The organic filtrate was dried over anhydrous Na₂SO₄ and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (3:1 hexanes/EtOAc) to afford **7c** and **7d**.



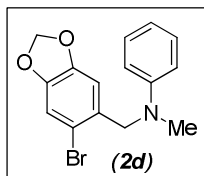
Methyl ((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)(phenyl)carbamate (7c): 86% yield as Yellow crystalline solid, $R_f = 0.41$ (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ : 7.30-7.26 (m, 2H), 7.21-7.17 (m, 1H), 7.17-7.13 (m, 2H), 6.92 (s, 1H), 6.87 (s, 1H), 5.93 (s, 2H), 4.87 (s, 2H), 3.72 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 156.3, 147.6, 147.5, 141.6, 130.0, 129.0, 128.9, 126.6, 112.7, 108.9, 108.86, 101.8, 53.9, 53.2; **IR** (film) $\nu_{\max}$ 2956, 2923, 1713, 1598, 1501, 1480, 1447, 1383, 1295, 1242, 1108, 1038, 932, 763, 699 cm⁻¹; **HRMS** (ESI) m/z 364.0174 [M + H]⁺; calculated for [C₁₆H₁₄BrNO₄ + H]⁺: 364.0179; **MP** 70–73 °C.



methyl 2-bromo-4,5-dimethoxybenzyl(phenyl)carbamate (7d): 94% yield as White solid, R_f = 0.50 (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.29-7.25 (m, 2H), 7.30-7.17 (m, 1H), 7.11 (d, J = 7.56 Hz, 2H), 6.92 (s, 1H), 6.84 (s, 1H), 4.91 (s, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 156.3, 148.8, 148.5, 141.5, 141.46, 128.9, 128.8, 126.9, 126.8, 126.7, 115.4, 56.1, 56.06, 53.5, 53.2; **IR** (film) ν_{max} 2954, 2930, 2852, 1710, 1599, 1505, 1444, 1378, 1260, 1227, 1208, 1164, 1139, 1030, 858, 767, 701 cm^{-1} ; **HRMS** (ESI) m/z 380.0507 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{17}\text{H}_{18}\text{BrNO}_4 + \text{H}]^+$: 380.0492; **MP** 116–118 $^\circ\text{C}$.

General Procedure for the synthesis of (2d):

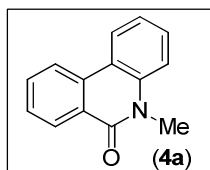
In an oven-dried round-bottom flask, *N*-methylaniline derivatives (5.00 mmol; 1.0 equiv) was taken in *N,N*-dimethylformamide (20 mL) under inert atmosphere and the reaction vessel was cooled to 0 $^\circ\text{C}$. To this reaction mixture NaH (6.00 mmol; 1.2 equiv) was added portion-wise and it was stirred for another 5 min. A solution of 2-bromo (3,4-methylenedimethoxy)benzylbromides (5.50 mmol; 1.1 equiv) in *N,N*-dimethylformamide (2 mL) was added drop-wise to the reaction mixture at 0 $^\circ\text{C}$. Then it was warmed to room temperature and stirred for another 2 h. Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was quenched with saturated NH_4Cl (5 mL) and then diluted with 30 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 30 mL of water. The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford **2d**.



***N*-((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)-*N*-methylaniline (2d):** Light yellow solid, R_f = 0.65 (10% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 (m, 2H), 7.07 (s, 1H), 6.76 (m, 1H), 6.69 (m, 3H), 5.95 (s, 2H), 4.47 (s, 2H), 3.10 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 149.16, 147.76, 147.25, 130.93, 129.26, 116.75, 112.92, 112.53, 112.05, 108.00, 101.62, 57.32, 38.74; **IR** (film) ν_{max} 2896, 1599, 1505, 1479, 1358, 1240, 1102, 1038, 932, 860, 749, 692 cm^{-1} ; **MP** 72-74 $^\circ\text{C}$.

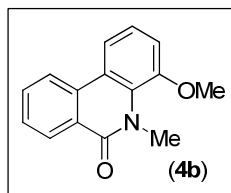
General Procedure for Biaryl-Coupling:

In an oven-dried Schlenk flask, 2-halide aromatic substrates (0.50 mmol; 1.0 equiv), potassium carbonate (1.0 mmol; 2.0 equiv) and Tetrakis(triphenylphosphine)palladium(0) (0.05 mmol; 10 mol%) [In some cases 10 mol% of $\text{Pd}(\text{OAc})_2$ and 20 mol% of PPh_3] were taken in *N,N*-dimethyl acetamide (5 mL) under argon atmosphere and the reaction mixture was purged with argon for approximately 5 min. The Schlenk flask was closed and heated at 140 $^\circ\text{C}$ for indicated time (3-10h). Upon completion of the reactions, (TLC showed complete consumption of starting material) the reaction mixture was diluted with 10 mL of 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 cyclized products were purified by flash chromatography (1:1 hexanes/EtOAc) to afford pure biaryl-coupling products.

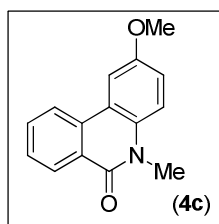


5-methylphenanthridin-6(5H)-one (4a): Brown solid, R_f = 0.47 (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.55 (d, J = 7.93 Hz, 1H), 8.25 (dd, J = 7.79 Hz, 2.31 Hz, 2H), 7.75 (td, J = 8.10 Hz, 1.03 Hz, 1H), 7.58 (t, J = 7.69 Hz, 1H), 7.54 (td, J = 8.31 Hz, 1.03 Hz, 1H),

7.39 (d, $J = 8.40$ Hz, 1H), 7.31 (t, $J = 7.82$ Hz, 1H), 3.81 (s, $J = 7.05$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.6, 138.0, 133.5, 132.3, 129.5, 128.9, 127.9, 125.5, 123.2, 122.4, 121.6, 119.2, 115.0, 30.0; **IR** (film) ν_{max} 2924, 1651, 1609, 1588, 1439, 1351, 1101, 1018, 748, 724 cm^{-1} ; **HRMS** (ESI) m/z 210.0918 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{14}\text{H}_{11}\text{NO} + \text{H}]^+$: 210.0913; **MP** 105–107 °C [lit. (Majumdar, K. C.; Chattopadhyay, S. K.; Gupta, A. K.; *Indian Journal of Chemistry, Section B: Organic Chemistry Including Medicinal Chemistry* **1990**, 29B, 1138): 106 °C].

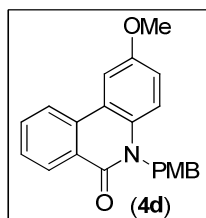


4-methoxy-5-methylphenanthridin-6(5H)-one (4b): White color solid, $R_f = 0.41$ (30% EtOAc in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 8.53 (dd, $J = 7.92$ Hz, 0.67 Hz, 1H), 8.20 (d, $J = 8.20$ Hz, 1H), 7.86 (d, $J = 7.89$ Hz, 1H), 7.72 (td, $J = 8.13$ Hz, 1.33 Hz, 1H), 7.57 (t, $J = 7.35$ Hz, 1H), 7.23 (q, $J = 8.7$ Hz, 1H), 7.06 (d, $J = 7.8$ Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 149.4, 133.5, 132.3, 129.4, 128.6, 128.0, 125.7, 123.1, 122.1, 121.8, 115.8, 113.1, 56.5, 36.8; **IR** (film) ν_{max} 2922, 1644, 1590, 1444, 1341, 1253, 1086, 1016, 743 cm^{-1} ; **HRMS** (ESI) m/z 240.1014 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{13}\text{NO}_2 + \text{H}]^+$: 240.1019; **MP** 125–127 °C [lit. (Ferraccioli, R.; Carenzi, D.; Rombola, O.; Catellani, M.; *Org. Lett.* **2004**, 6, 4759): 128–129 °C].

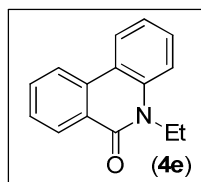


2-methoxy-5-methylphenanthridin-6(5H)-one (4c): Yellow crystalline solid, $R_f = 0.47$ (40% EtOAc in hexane). ^1H NMR (400 MHz, CDCl_3) δ : 8.54 (dd, $J = 8.0$ Hz, 1.12 Hz, 1H), 8.16 (d, $J = 8.25$ Hz, 1H), 7.73 (td, $J = 8.20$ Hz, 1.51 Hz, 1H), 7.68 (d, $J = 2.86$ Hz, 1H), 7.58 (td, $J = 8.09$ Hz, 1.09 Hz, 1H), 7.29 (d, $J = 9.03$ Hz, 1H), 7.11 (dd, $J = 9.22$ Hz, 2.88 Hz, 1H), 3.92 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.1, 155.0, 133.1, 132.3, 132.2, 128.9, 128.0,

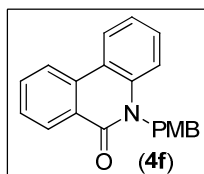
125.8, 121.6, 120.1, 116.4, 116.1, 107.0, 55.7, 30.0; **IR** (film) $\nu_{\max}$ 2925, 1636, 1613, 1516, 1471, 1380, 1319, 1271, 1232, 1209, 1036, 755 cm^{-1} ; **HRMS** (ESI) m/z 240.1062 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{13}\text{NO}_2 + \text{H}]^+$: 240.1019; **MP** 123–125 °C [lit. (Guofu Z., Xiaobao Z., Yunbing Y., Chengrong D.; *Eur. J. Org. Chem.* **2012**, 4, 669): 121–122 °C].



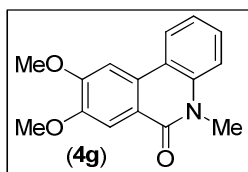
2-methoxy-5-(4-methoxybenzyl)phenanthridin-6(5H)-one (4d): Light yellow color solid, R_f = 0.42 (30% EtOAc in hexane). **^1H NMR** (400 MHz, CDCl_3) δ : 8.62 (dd, J = 7.98 Hz, 0.99 Hz, 1H), 8.22 (d, J = 7.98 Hz, 1H), 7.79–7.75 (m, 1H), 7.72 (d, J = 2.83 Hz, 1H), 7.63–7.59 (m, 1H), 7.26 (d, J = 8.23 Hz, 1H), 7.19 (d, J = 8.74 Hz, 1H), 6.99 (dd, J = 9.20 Hz, 2.83 Hz, 1H), 6.84–6.81 (m, 2H), 5.57 (s, 2H), 3.88 (s, 3H), 3.74 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 161.4, 158.7, 155.1, 133.5, 132.5, 131.6, 129.3, 128.8, 128.2, 127.9, 125.8, 121.7, 120.5, 117.2, 116.5, 114.2, 107.2, 55.7, 55.3, 46.0; **IR** (film) $\nu_{\max}$ 2997, 2929, 2837, 1645, 1584, 1513, 1451, 1423, 1360, 1300, 1248, 1176, 1110, 1026, 987, 806, 772, 689 cm^{-1} ; **HRMS** (ESI) m/z 346.1456 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{22}\text{H}_{19}\text{NO}_3 + \text{H}]^+$: 346.1438; **MP** 107–110 °C.



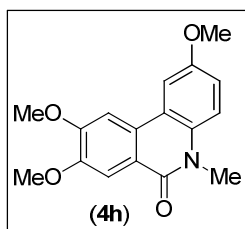
5-ethylphenanthridin-6(5H)-one (4e): 88% yield as light yellow color solid, R_f = 0.41 (20% EtOAc in hexane). **^1H NMR** (400 MHz, CDCl_3) δ : 8.57 (dd, J = 8.1 Hz, 1.08 Hz, 1H), 8.31–8.26 (m, 2H), 7.78–7.74 (m, 1H), 7.61–7.53 (m, 2H), 7.44 (d, J = 7.89 Hz, 1H), 7.33–7.29 (m, 1H), 4.48 (q, J = 7.37 Hz, 2H), 1.44 (t, J = 7.39 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 161.1, 136.9, 133.6, 132.4, 129.6, 128.8, 127.9, 125.6, 123.5, 122.3, 121.6, 119.5, 115.0, 37.7, 12.7; **IR** (film) $\nu_{\max}$ 3072, 2978, 2933, 1644, 1609, 1586, 1439, 1373, 1359, 1315, 1182, 1109, 878, 748, 725, 692 cm^{-1} ; **HRMS** (ESI) m/z 224.1092 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{13}\text{NO} + \text{H}]^+$: 224.1070; **MP** 91–92 °C.



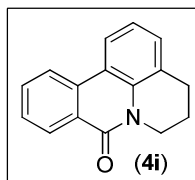
5-(4-methoxybenzyl)phenanthridin-6(5H)-one (4f): White solid, $R_f = 0.57$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.62 (dd, $J = 7.99$ Hz, 0.99 Hz, 1H), 8.30-8.26 (m, 2H), 7.80-7.75 (m, 1H), 7.63-7.59 (m, 1H), 7.42-7.34 (m, 2H), 7.28-7.24 (m, 1H), 7.23-7.20 (m, 2H), 6.84-6.82 (m, 2H), 5.60 (s, 2H), 3.75 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.9, 158.8, 137.4, 133.8, 132.7, 129.5, 129.2, 128.7, 128.0, 127.9, 125.5, 123.3, 122.5, 121.7, 119.5, 116.0, 114.2, 55.3, 45.9; **IR** (film) ν_{max} 3068, 2958, 2932, 1644, 1609, 1587, 1513, 1490, 1456, 1439, 1360, 1315, 1248, 1176, 1111, 1034, 987, 810, 746, 725, 685 cm^{-1} ; **HRMS** (ESI) m/z 316.1346 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{21}\text{H}_{17}\text{NO}_2 + \text{H}]^+$: 316.1332; **MP** 131–134 $^{\circ}\text{C}$.



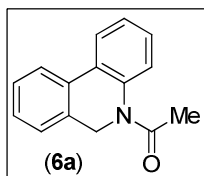
8,9-dimethoxy-5-methylphenanthridin-6(5H)-one (4g): White solid, $R_f = 0.49$ (40% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.13-8.11 (m, 1H), 7.90 (s, 1H), 7.55 (s, 1H), 7.53-7.49 (m, 1H), 7.39 (d, $J = 8.31$ Hz, 1H), 7.32-7.28 (m, 1H), 4.08 (s, 3H), 4.03 (s, 3H), 3.80 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.1, 153.2, 149.7, 137.5, 128.6, 128.2, 122.6, 122.2, 119.6, 119.1, 115.0, 109.0, 102.5, 56.2, 56.1, 29.9; **IR** (film) ν_{max} 2919, 1639, 1607, 1521, 1441, 1316, 1211, 1143, 1025, 752, cm^{-1} ; **HRMS** (ESI) m/z 270.1136 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{16}\text{H}_{15}\text{NO}_3 + \text{H}]^+$: 270.1125; **MP** 220–222 $^{\circ}\text{C}$ [lit. (Harayama, T.; Nagura, C.; Miyagoe, T.; Kawata, Y.; Abe, H.; Takeuchi, Y.; *Heterocycle*, **2010**, 81, 2609): 221.5-222.5 $^{\circ}\text{C}$].



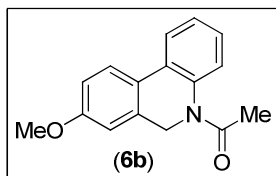
2,8,9-trimethoxy-5-methylphenanthridin-6(5H)-one (4h): 82% yield as white solid, $R_f = 0.47$ (50% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.87 (s, 1H), 7.53 (d, $J = 2.78$ Hz, 1H), 7.44 (s, 1H), 7.27 (d, $J = 9.11$ Hz, 1H), 7.04 (dd, $J = 9.06$ Hz, 2.78 Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H), 3.87 (s, 3H), 3.73 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 160.7, 155.0, 153.1, 150.0, 132.0, 127.8, 120.2, 120.0, 116.1, 114.9, 109.3, 107.3, 102.7, 56.2, 56.1, 55.9, 30.0; **IR** (film) ν_{max} 2925, 1636, 1613, 1516, 1471, 1380, 1319, 1271, 1232, 1209, 1036 cm^{-1} ; **HRMS** (ESI) m/z 300.1249 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{17}\text{H}_{17}\text{NO}_4 + \text{H}]^+$: 300.1230; **MP** 194–196 °C.



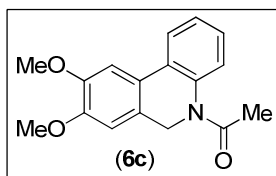
5,6-Dihydropyrido[3,2,1-de]phenanthridin-8(4H)-one (4i): White solid, $R_f = 0.30$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.56 (dd, $J = 7.97$ Hz, 1.04 Hz, 1H), 8.26 (d, $J = 8.15$ Hz, 1H), 8.12 (d, $J = 7.90$ Hz, 1H), 7.77-7.72 (m, 1H), 7.60-7.56 (m, 1H), 7.31-7.28 (m, 1H), 7.20 (t, $J = 7.67$ Hz, 1H), 4.33 (t, $J = 5.89$ Hz, 2H), 3.02 (t, $J = 6.28$ Hz, 2H), 2.14 (p, $J = 6.17$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.1, 134.5, 133.6, 132.2, 129.4, 128.5, 127.8, 125.6, 125.4, 121.9, 121.8, 121.3, 119.1, 42.8, 28.2, 20.8; **IR** (film) ν_{max} 2927, 2852, 1645, 1590, 1421, 1340, 1158, 752, 694 cm^{-1} ; **HRMS** (ESI) m/z 236.1075 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{16}\text{H}_{14}\text{NO}]^+$: 236.1070; **MP** 87–89 °C.



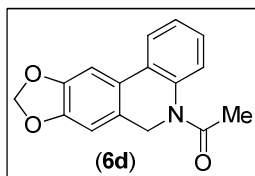
1-(phenanthridin-5(6H)-yl)ethanone (6a): 92% yield as yellow solid, $R_f = 0.37$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.83-7.79 (m, 2H), 7.42-7.37 (m, 1H), 7.35-7.31 (m, 5H), 4.96 (s, 2H), 2.21 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.4, 138.1, 135.2, 131.8, 129.8, 129.5, 128.8, 128.1, 127.8, 126.3, 124.7, 124.5, 123.3, 45.0, 22.3; **IR** (film) ν_{max} 2926, 2891, 1660, 1603, 1488, 1443, 1376, 1342, 1236, 1205, 1092, 1017, 764, 739, 617 cm^{-1} ; **HRMS** (ESI) m/z 224.1071 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{15}\text{H}_{13}\text{NO} + \text{H}]^+$: 224.1070; **MP** 100–103 °C.



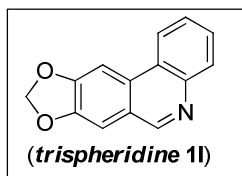
1-(8-methoxyphenanthridin-5(6H)-yl)ethanone (6b): Yellow solid, $R_f = 0.38$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.75-7.70 (m, 2H), 7.31-7.27 (m, 3H), 6.94 (dd, $J = 8.54$ Hz, 2.56 Hz 1H), 6.86 (d, $J = 1.98$ Hz, 1H), 4.92 (s, 2H), 3.86 (s, 3H), 2.20 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.6, 159.6, 137.3, 136.7, 129.8, 129.5, 126.8, 126.3, 124.7, 124.6, 123.8, 114.1, 111.2, 55.4, 45.2, 22.2; **IR** (film) ν_{max} 3054, 2928, 2848, 1659, 1609, 1485, 1378, 1338, 1278, 1230, 1158, 1090, 1042, 820, 762 cm^{-1} ; **HRMS** (ESI) m/z 254.1184 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{16}\text{H}_{15}\text{NO}_2 + \text{H}]^+$: 254.1176; **MP** 103–105 $^\circ\text{C}$.



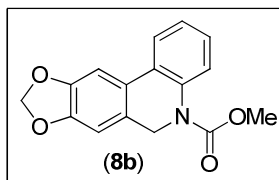
1-(8,9-dimethoxyphenanthridin-5(6H)-yl)ethanone (6c): Yellow solid, $R_f = 0.37$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.71 (d, $J = 8.22$ Hz, 1H), 7.34-7.23 (m, 4H), 6.83 (s, 1H), 4.88 (s, 2H), 3.97 (s, 3H), 3.92 (s, 3H), 2.19 (s, 3H); **IR** (film) ν_{max} 2926, 2854, 1659, 1652, 1609, 1519, 1492, 1448, 1378, 1265, 1227, 1147, 1027, 858, 819, 763, 606 cm^{-1} ; **HRMS** (ESI) m/z 284.1284 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{17}\text{H}_{17}\text{NO}_3 + \text{H}]^+$: 284.1281; **MP** 133–135 $^\circ\text{C}$.



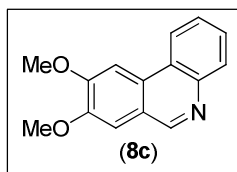
1-([1,3]dioxolo[4,5-j]phenanthridin-5(6H)-yl)ethanone (6d): White solid, $R_f = 0.36$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.63-7.61 (m, 1H), 7.28-7.27 (m, 3H), 7.21 (s, 1H), 6.77 (s, 1H), 5.96 (s, 2H), 4.81 (s, 2H), 2.17 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.4, 147.8, 147.5, 137.3, 129.9, 129.5, 127.0, 126.3, 125.7, 124.5, 123.9, 106.8, 103.9, 101.3, 44.8, 22.1; **IR** (film) ν_{max} 2899, 1659, 1485, 1458, 1374, 1339, 1280, 1220, 1037, 935, 861, 766, 752 cm^{-1} ; **HRMS** (ESI) m/z 268.0975 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{16}\text{H}_{13}\text{NO}_3 + \text{H}]^+$: 268.0968.



[1,3]dioxolo[4,5-j]phenanthridine (1l): 35% yield as white crystalline solid, $R_f = 0.29$ (20% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.07 (s, 1H), 8.35 (d, $J = 8.03$ Hz, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 7.98 (s, 1H), 7.70-7.65 (m, 1H), 7.63-7.59 (m, 1H), 7.32 (s, 1H), 6.15 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 151.7, 151.5, 148.2, 144.0, 130.3, 130.0, 128.0, 126.7, 124.3, 123.0, 122.0, 105.5, 101.9, 100.0; **IR** (film) ν_{max} 2921, 1485, 1464, 1395, 1256, 1226, 1198, 1095, 1036, 940, 857, 755 cm^{-1} ; **HRMS** (ESI) m/z 224.0718 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{14}\text{H}_9\text{NO}_2 + \text{H}]^+$: 224.0706; **MP** 121–123 $^\circ\text{C}$.

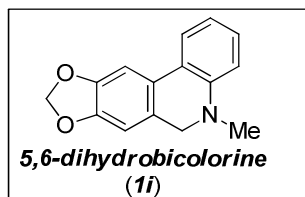


Methyl [1,3]dioxolo[4,5-j]phenanthridine-5(6H)-carboxylate (8b): Brown color solid, $R_f = 0.51$ (20% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.59-7.57 (m, 2H), 7.27-7.24 (m, 1H), 7.22-7.19 (m, 2H), 6.74 (s, 1H), 5.95 (s, 2H), 4.70 (s, 2H), 3.75 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 154.4, 147.8, 147.3, 136.4, 128.8, 128.3, 127.1, 126.0, 125.3, 124.7, 123.4, 106.3, 104.0, 101.2, 53.1, 47.0; **IR** (film) ν_{max} 2923, 2854, 1710, 1484, 1464, 1381, 1257, 1226, 1197, 1038, 942, 853, 931, 758 cm^{-1} ; **HRMS** (ESI) m/z 284.0924 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{16}\text{H}_{13}\text{NO}_4 + \text{H}]^+$: 284.0917; **MP** 105–107 $^\circ\text{C}$.

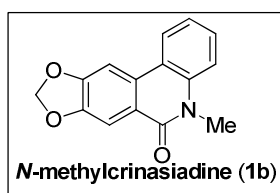


8,9-dimethoxyphenanthridine (8c): White crystalline solid, $R_f = 0.25$ (50% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 9.13 (s, 1H), 8.39 (d, $J = 8.03$ Hz, 1H), 8.13 (d, $J = 8.03$ Hz, 1H), 7.83 (s, 1H), 7.68-7.59 (m, 2H), 7.31 (s, 1H), 4.10 (s, 3H), 4.03 (s, 3H); $^{13}\text{C NMR}$ (100

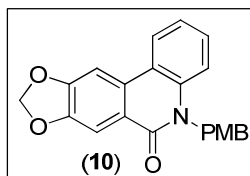
MHz, CDCl₃) δ 153.0, 151.6, 150.0, 143.6, 137.2, 129.8, 128.3, 127.8, 126.7, 123.8, 121.7, 107.8, 101.8, 56.2, 56.1; **IR** (film) $\nu_{\max}$ 3008, 2935, 2868, 1701, 1614, 1594, 1505, 1470, 1442, 1394, 1293, 1266, 1222, 1202, 1159, 1037, 1023, 847, 811, 762, 733 cm⁻¹; **HRMS** (ESI) m/z 240.1027 [M + H]⁺; calculated for [C₁₅H₁₃NO₂ + H]⁺: 240.1019; **MP** 163–165 °C [lit. (Narasimhan, N. S.; Chandrachood, P. S.; Shete, N. R.; *Tetrahedron*, **1981**, 37, 825): 164 °C].



5-methyl-5,6-dihydro-[1,3]dioxolo[4,5-j]phenanthridine (1i): Light yellow solid, R_f = 0.38 (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.57 (dd, J = 7.7 Hz, 1.5 Hz, 1H), 7.23 (m, 2H), 6.88 (dt, J = 7.5 Hz, 1.1 Hz, 1H), 6.76 (dd, J = 8.1 Hz, 0.8 Hz, 1H), 6.65 (s, 1H), 5.99 (s, 2H), 4.10 (s, 2H), 2.93 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 147.56, 146.78, 146.50, 128.40, 127.21, 126.25, 123.64, 122.99, 118.72, 112.22, 106.10, 103.17, 100.97, 55.12, 38.57; **IR** (film) $\nu_{\max}$ 2923, 1600, 1503, 1377, 1290, 1238, 1207, 1096, 1038, 936, 861, 746 cm⁻¹; **HRMS** (ESI) m/z 240.1032 [(M+H)⁺]; calculated for [C₁₅H₁₄NO₂]⁺: 240.1019; **MP** 80-82 °C.



5-methyl-[1,3]dioxolo[4,5-j]phenanthridin-6(5H)-one (1b): White color solid, R_f = 0.47 (30% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ : 8.07 (d, J = 7.95 Hz, 1H), 7.90 (s, 1H), 7.60 (s, 1H), 7.52-7.48 (m, 1H), 7.38 (d, J = 8.26 Hz, 1H), 7.30-7.26 (m, 1H), 6.11 (s, 2H), 3.79 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 161.0, 152.2, 148.4, 137.5, 130.4, 128.9, 122.9, 122.3, 121.3, 119.2, 115.0, 107.0, 101.9, 100.4, 30.0; **IR** (film) $\nu_{\max}$ 2919, 2852, 1626, 1466, 1343, 1314, 1286, 1241, 1206, 1089, 1032, 932, 874, 848, 750, 733 cm⁻¹; **HRMS** (ESI) m/z 254.0807 [M + H]⁺; calculated for [C₁₅H₁₁NO₃ + H]⁺: 254.0812; **MP** 240–242 °C [lit. (Cahiez, G.; Chaboche, C.; Mahuteau-Betzer, F.; Ahr, M.; (2) Cahiez, Gerard; *Org. Lett.* **2005**, 7, 1943): 241-243 °C].

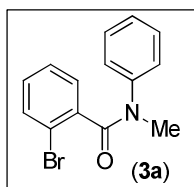


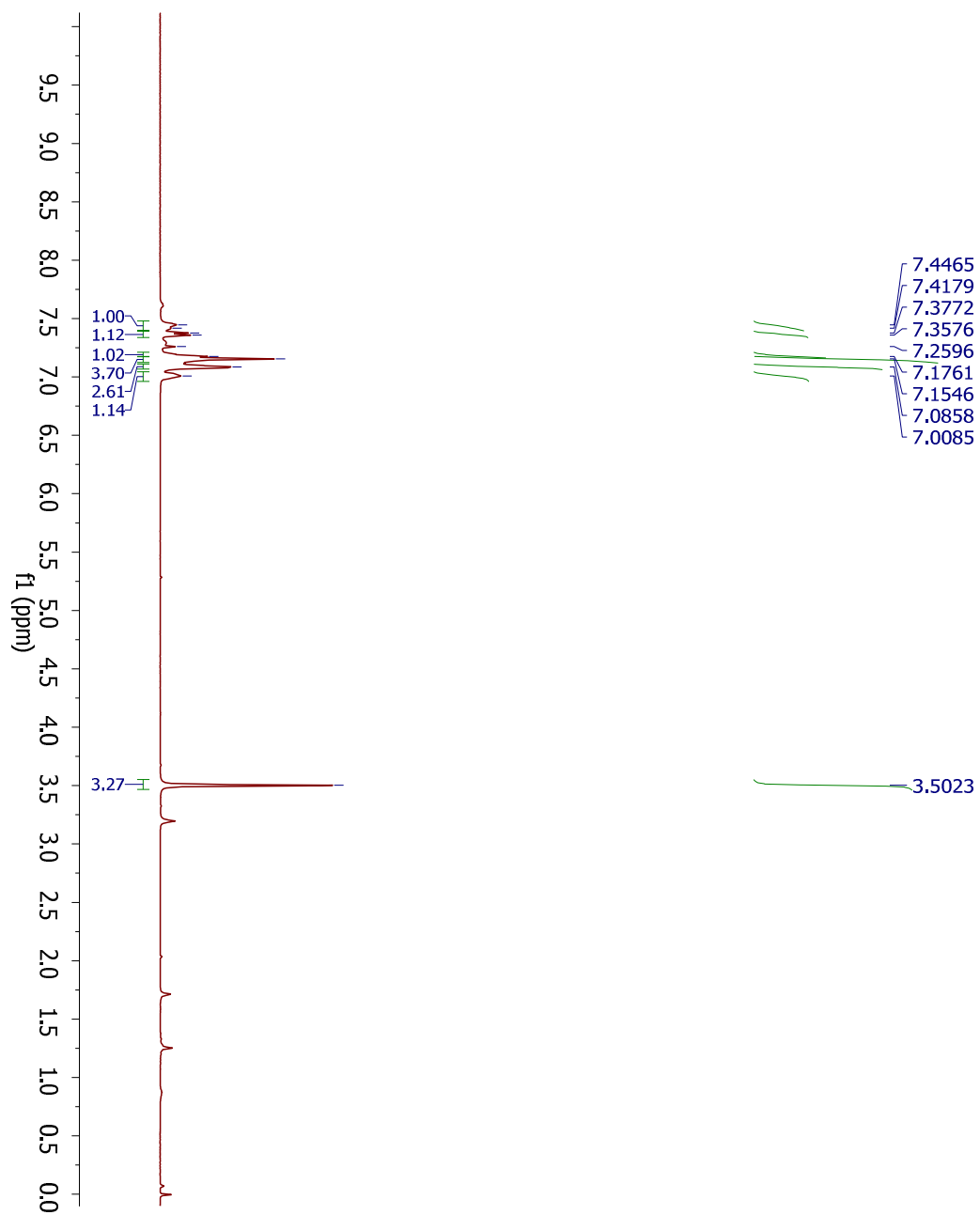
5-(4-methoxybenzyl)-[1,3]dioxolo[4,5-j]phenanthridin-6(5H)-one (10): White solid, $R_f = 0.46$ (30% EtOAc in hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.05 (d, $J = 7.95$ Hz, 1H), 7.95 (s, 1H), 7.61 (s, 1H), 7.37-7.30 (m, 2H), 7.24-7.19 (m, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 6.80 (d, $J = 8.67$ Hz, 2H), 6.11 (s, 2H), 5.56 (s, 2H), 3.73 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 161.2, 158.7, 152.4, 148.5, 136.8, 130.7, 128.8, 128.7, 127.9, 123.0, 122.4, 121.2, 119.4, 115.9, 114.2, 107.2, 102.0, 100.5, 55.2, 46.0; **IR** (film) ν_{max} 2925, 2855, 1644, 1601, 1513, 1483, 1463, 1312, 1246, 1177, 1037, 935, 808, 738, 699 cm^{-1} ; **HRMS** (ESI) m/z 360.1339 $[\text{M} + \text{H}]^+$; calculated for $[\text{C}_{22}\text{H}_{17}\text{NO}_4 + \text{H}]^+$: 360.1230; **MP** 170–173 $^\circ\text{C}$.

Procedure for synthesis of 5, 6-dihydrobicolorine (1i):

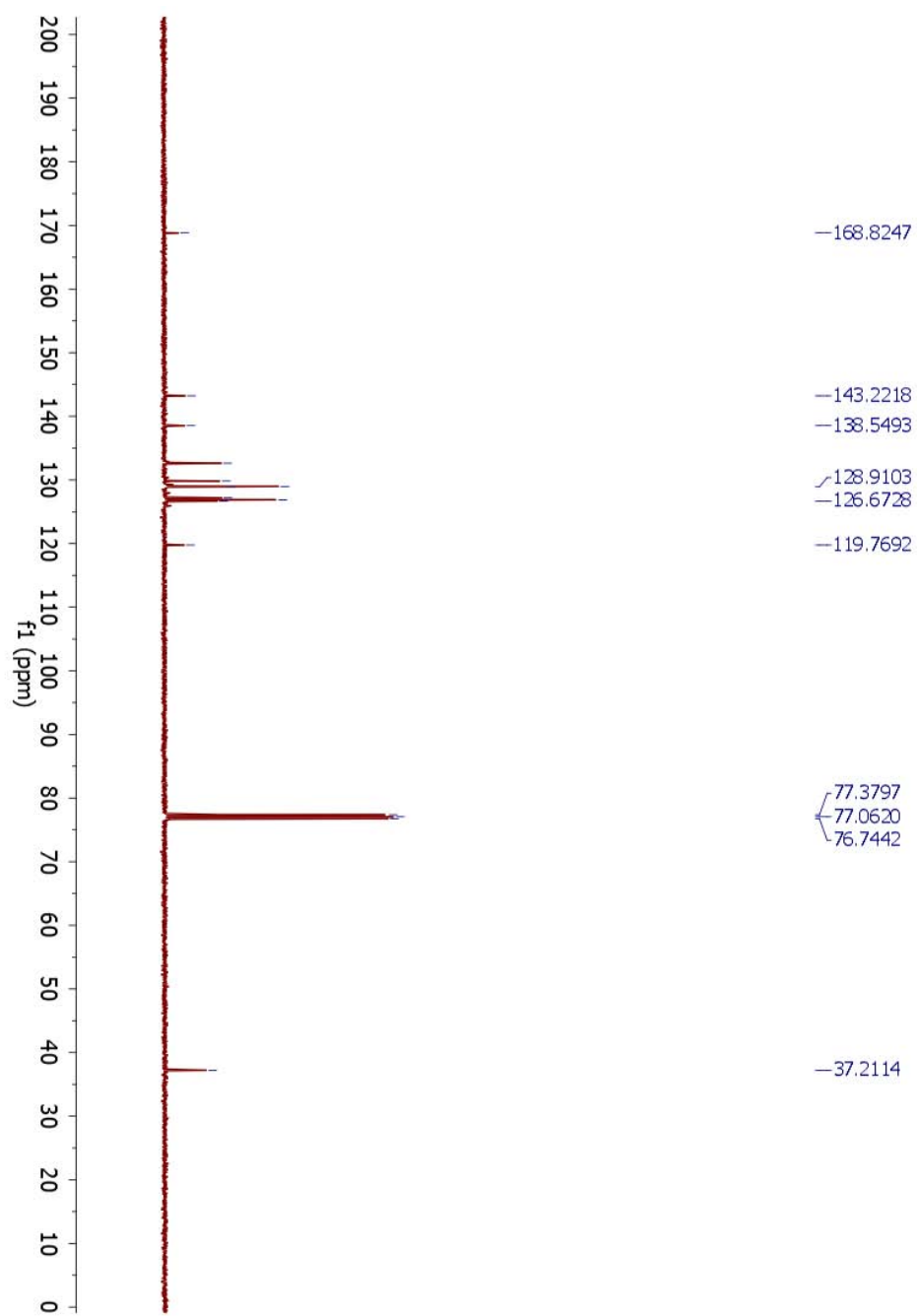
A round-bottom flask was charged with **8b** (0.20 mmol; 1.0 equiv) in dry THF (5 mL) under inert atmosphere and the reaction vessel was cooled to 0 $^\circ\text{C}$. To this reaction mixture LiAlH_4 (0.40 mmol; 2.0 equiv) was added portion-wise and it was stirred for another 5 min. After stirring at 0 $^\circ\text{C}$ for additional 5 minutes, the reaction mixture was warmed to 23 $^\circ\text{C}$ and stirring continued for another 10 minutes. Then, the reaction mixture was refluxed on an oil-bath maintaining the temperature to 80 $^\circ\text{C}$ and stirring continued for 3 h. Upon completion of the reaction (monitoring by TLC), it was cooled to room temperature and then to 0 $^\circ\text{C}$ and quenched with EtOAc, basified with 4(N) NaOH solution and extracted with EtOAc (2 X 15 mL). The combined organic extracts were washed with saturated aq. NaCl (5 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The crude products were purified by flash chromatography (10:1 hexanes/EtOAc) to afford pure **1i**.

^1H -NMR, ^{13}C -NMR, and Mass Spectra

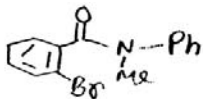




^1H NMR (400 MHz, CDCl_3) compound **(3a)**



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



Display Report

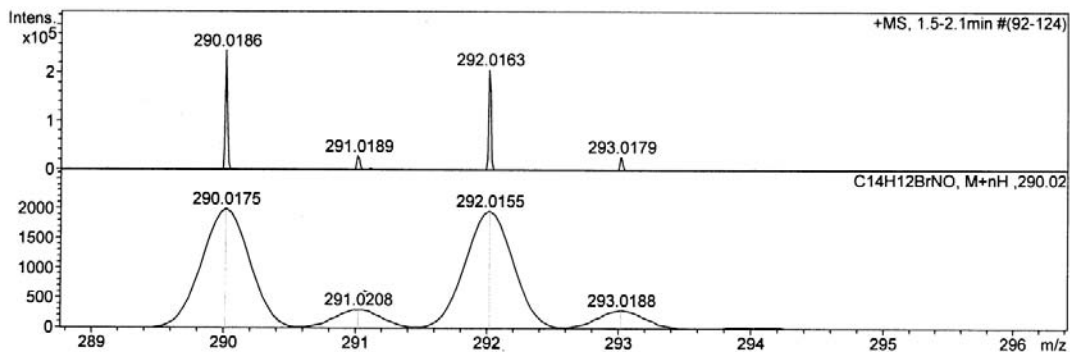
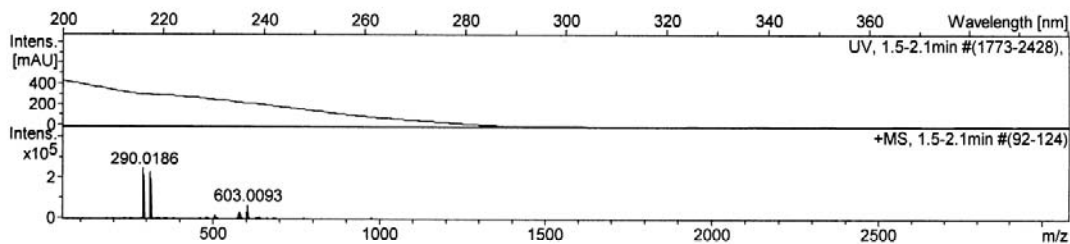
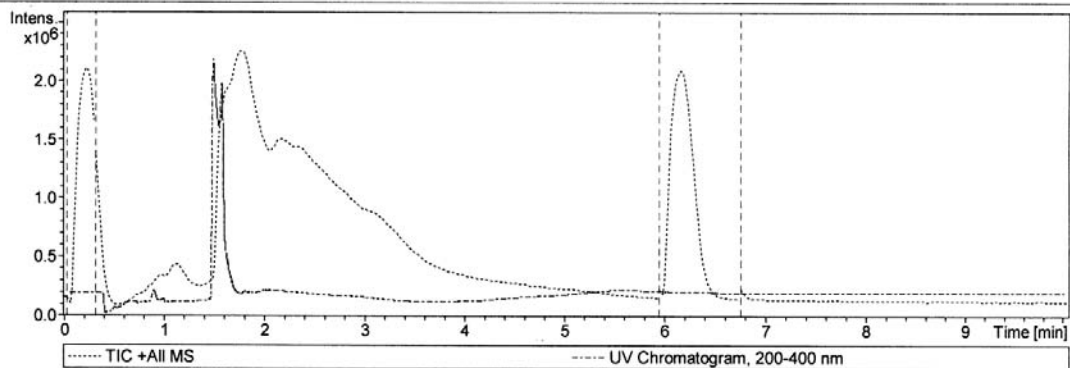
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 Sample Name: Dr. A. Bisai- SD-3-7
 Comment:

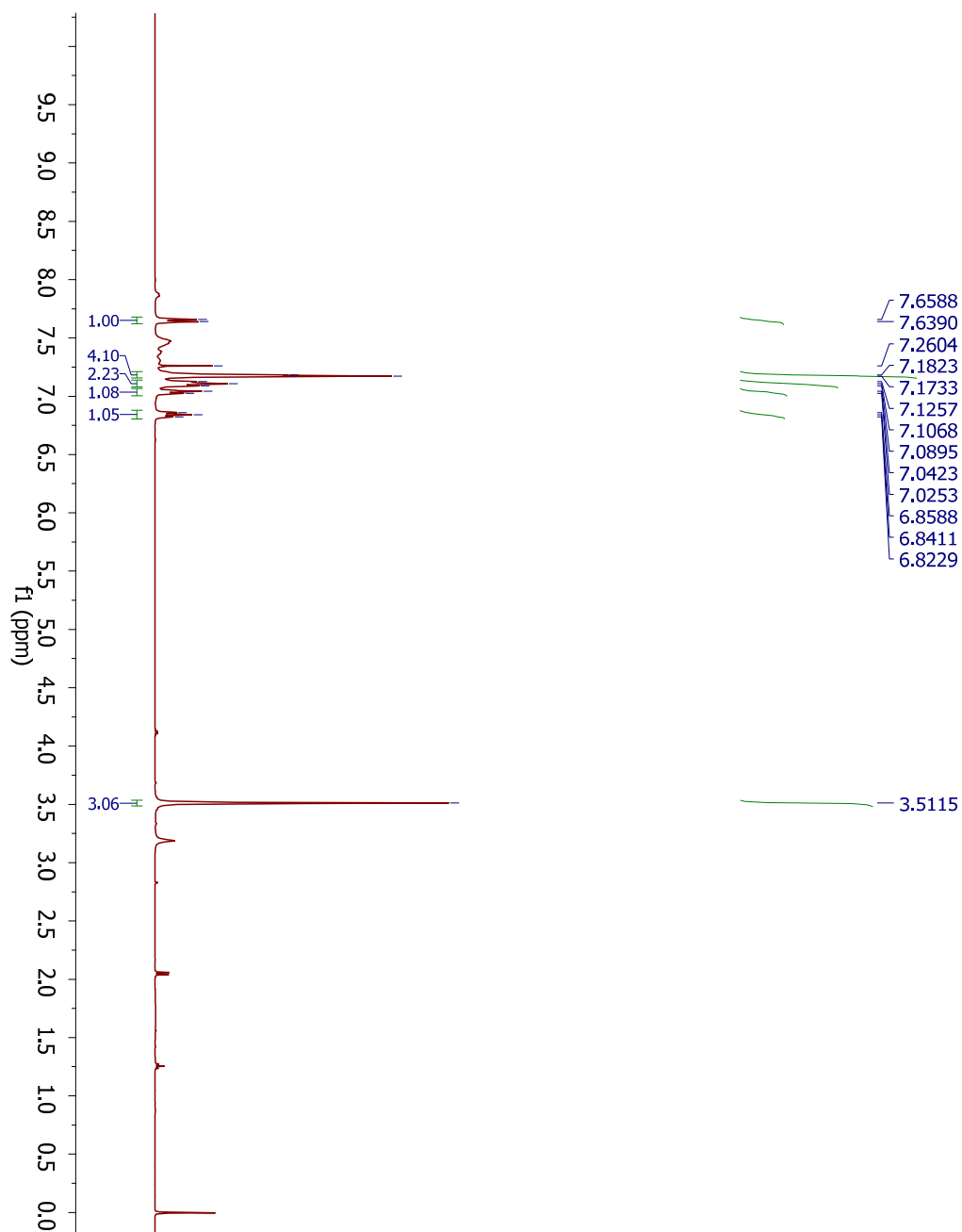
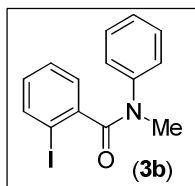
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

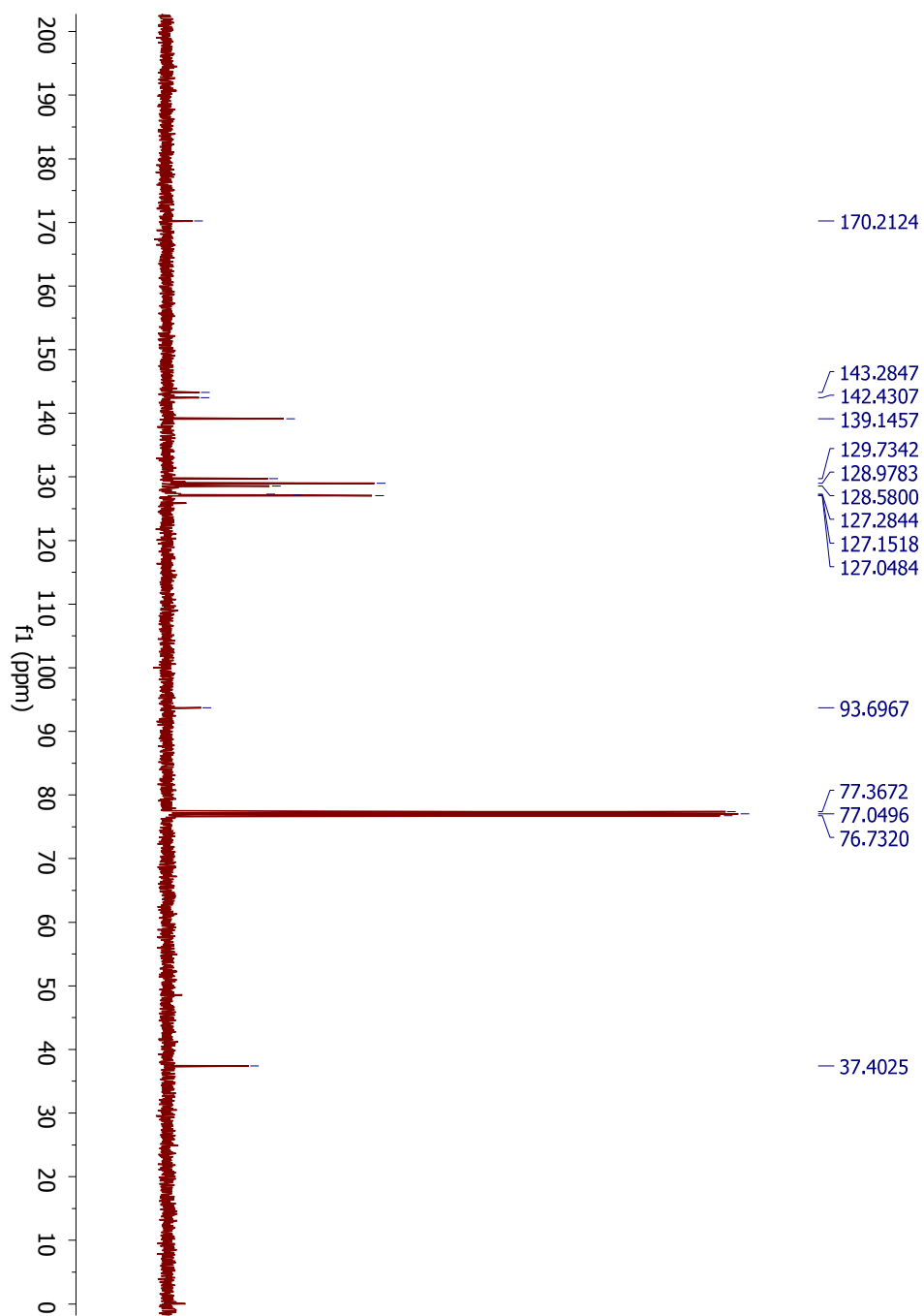
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



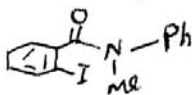
Scanned copy of mass spectrum of (3a)



¹H NMR (400 MHz, CDCl₃) compound **(3b)**



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



Display Report

Analysis Info

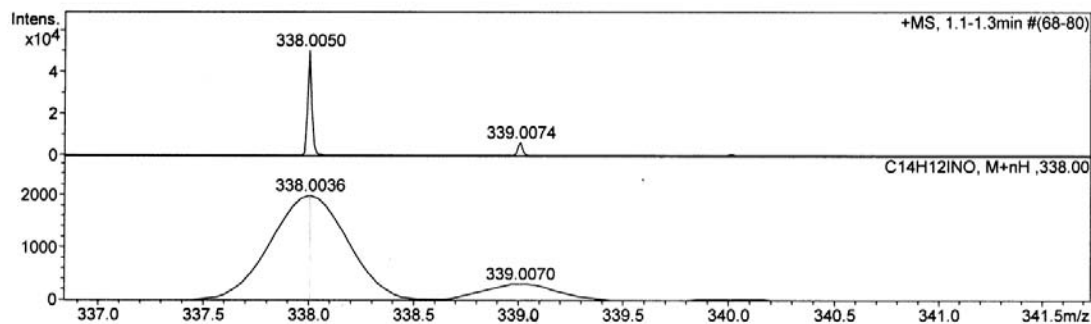
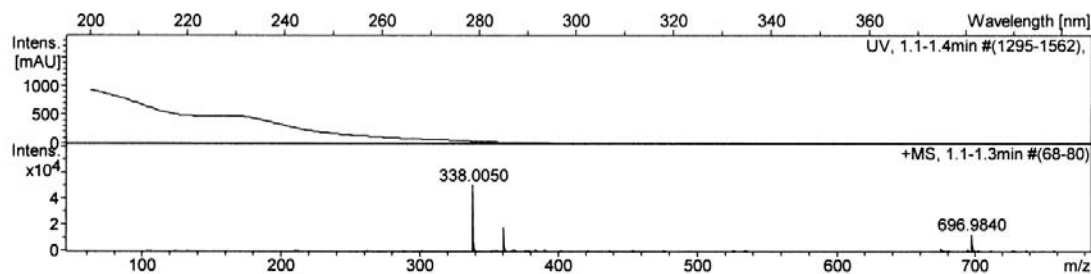
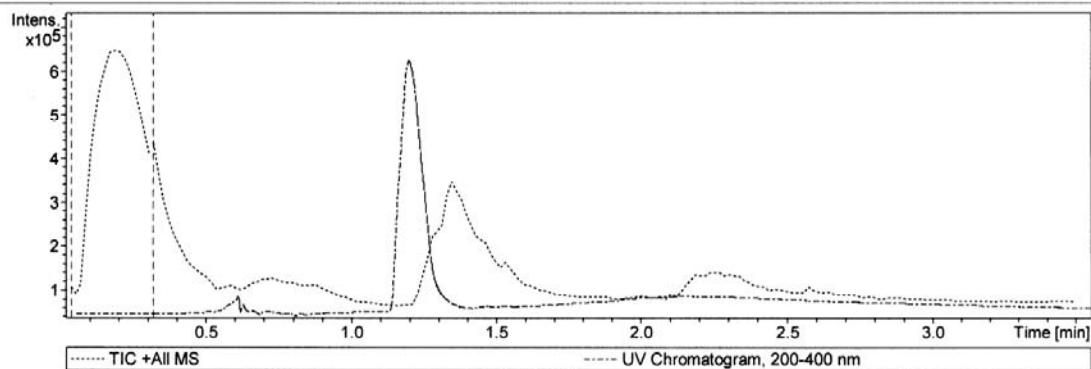
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Sample Name Dr. A. Bisai-SD-2-171
Comment

Acquisition Date 2/22/2012 4:53:08 PM

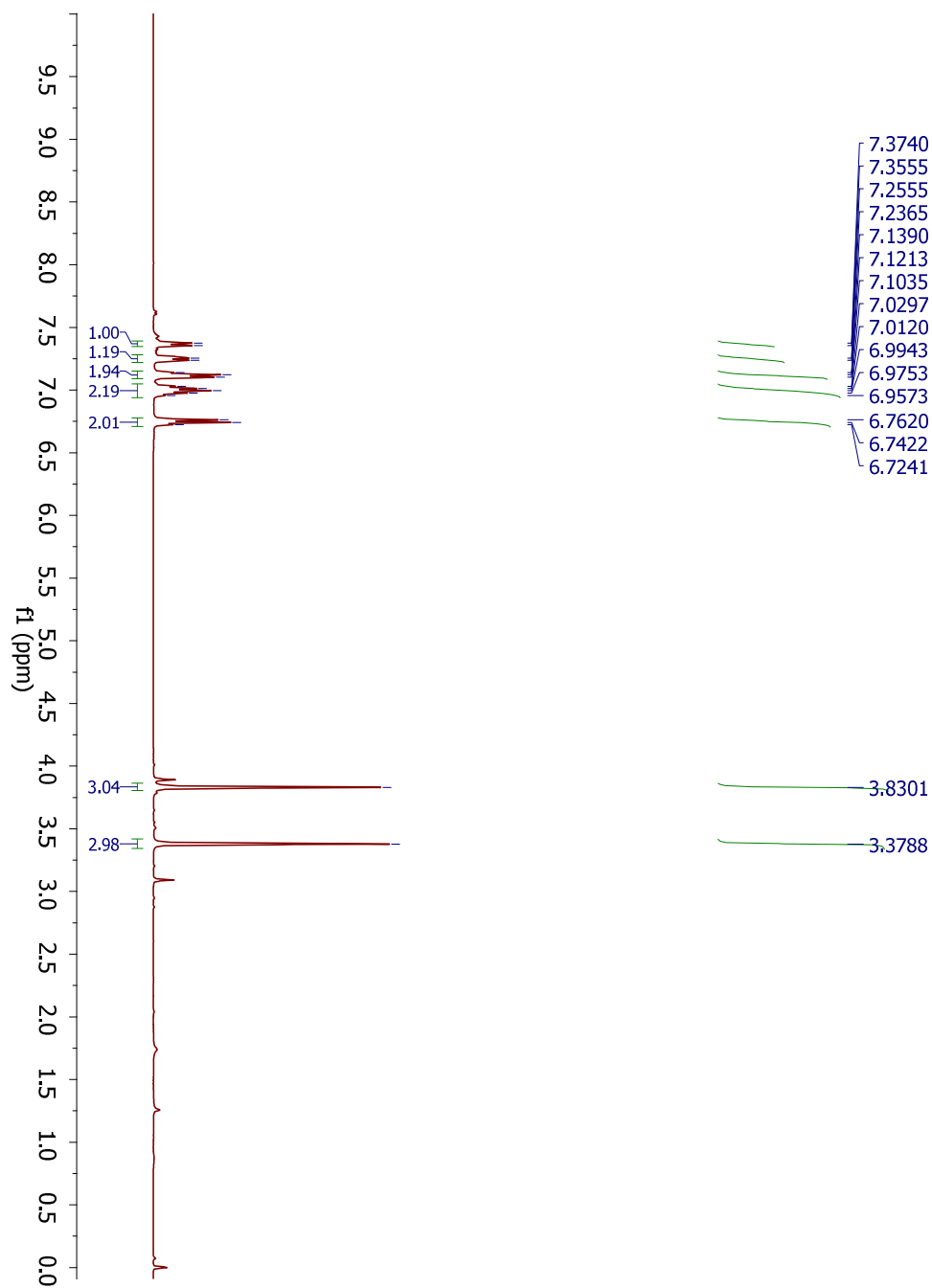
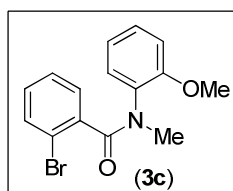
Operator Meena Sharma
Instrument micrOTOF-Q II 10330

Acquisition Parameter

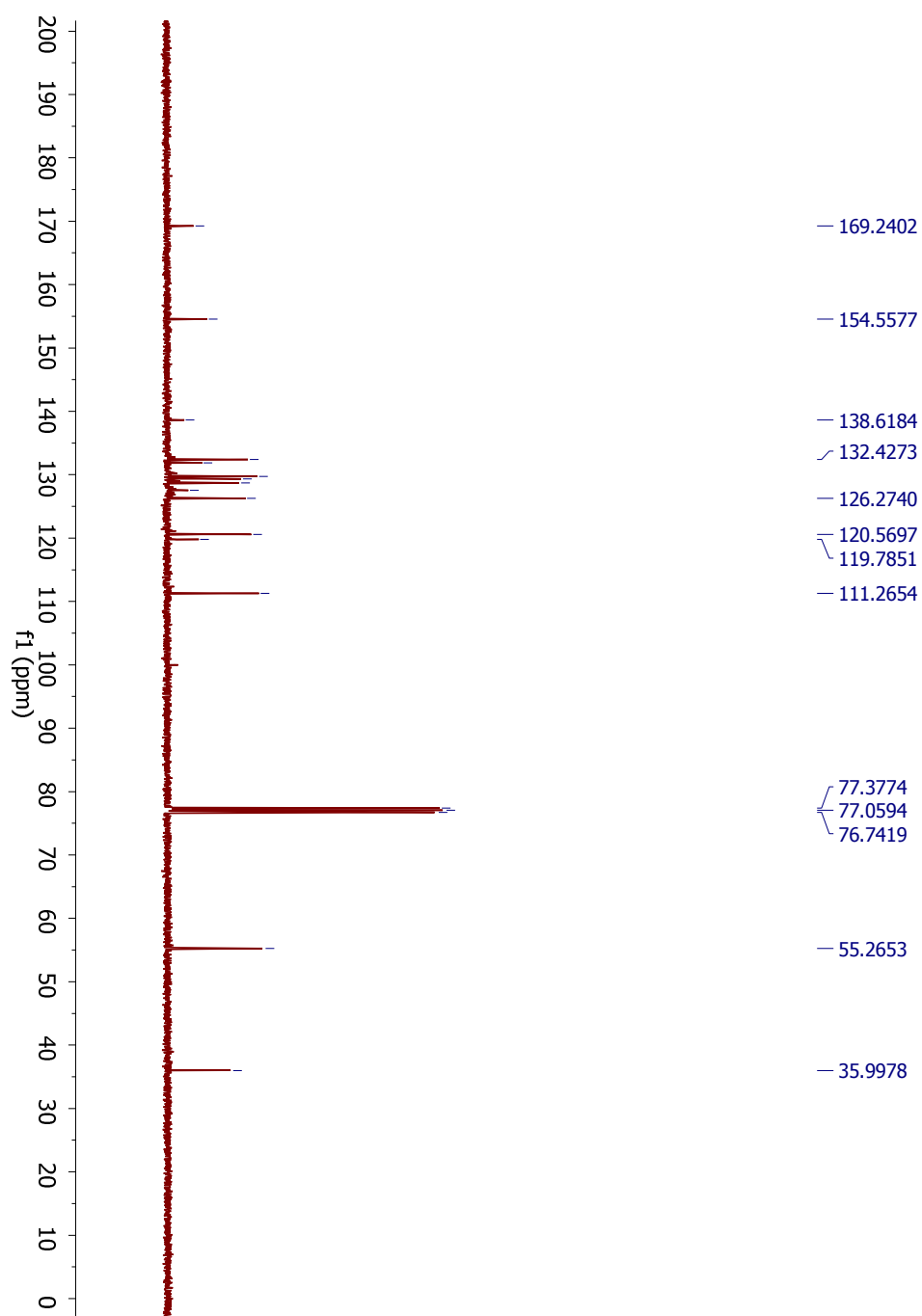
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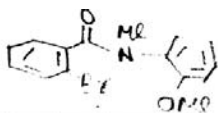
Scanned copy of mass spectrum of (3b)



^1H NMR (400 MHz, CDCl_3) compound **(3c)**



^{13}C NMR (100 MHz, CDCl_3) compound **(3c)**



Display Report

Analysis Info

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 Sample Name Dr. A. Bisai- SD-3-8
 Comment

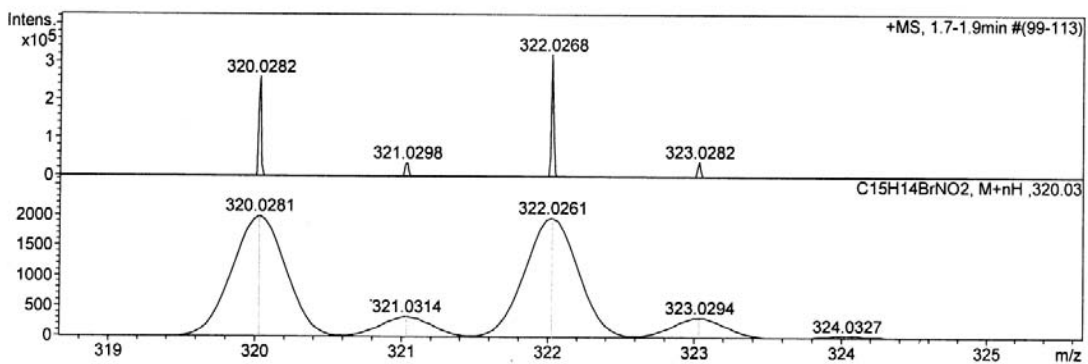
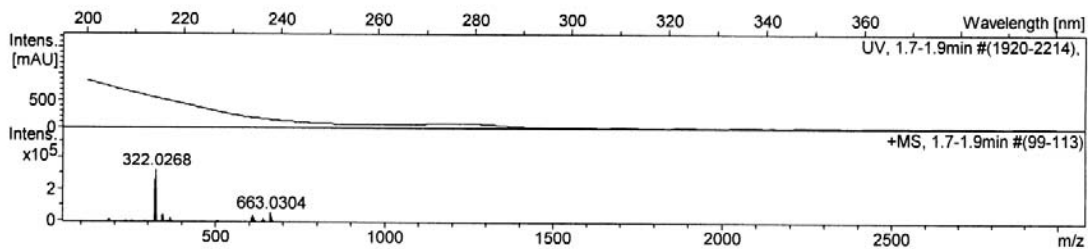
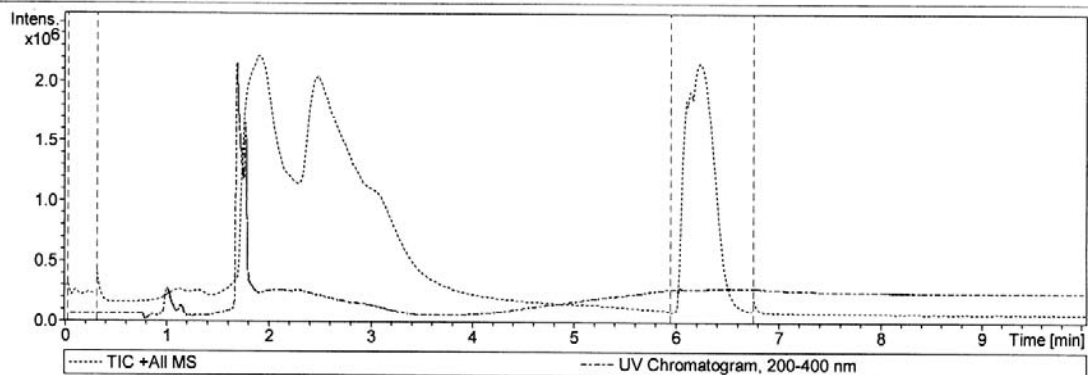
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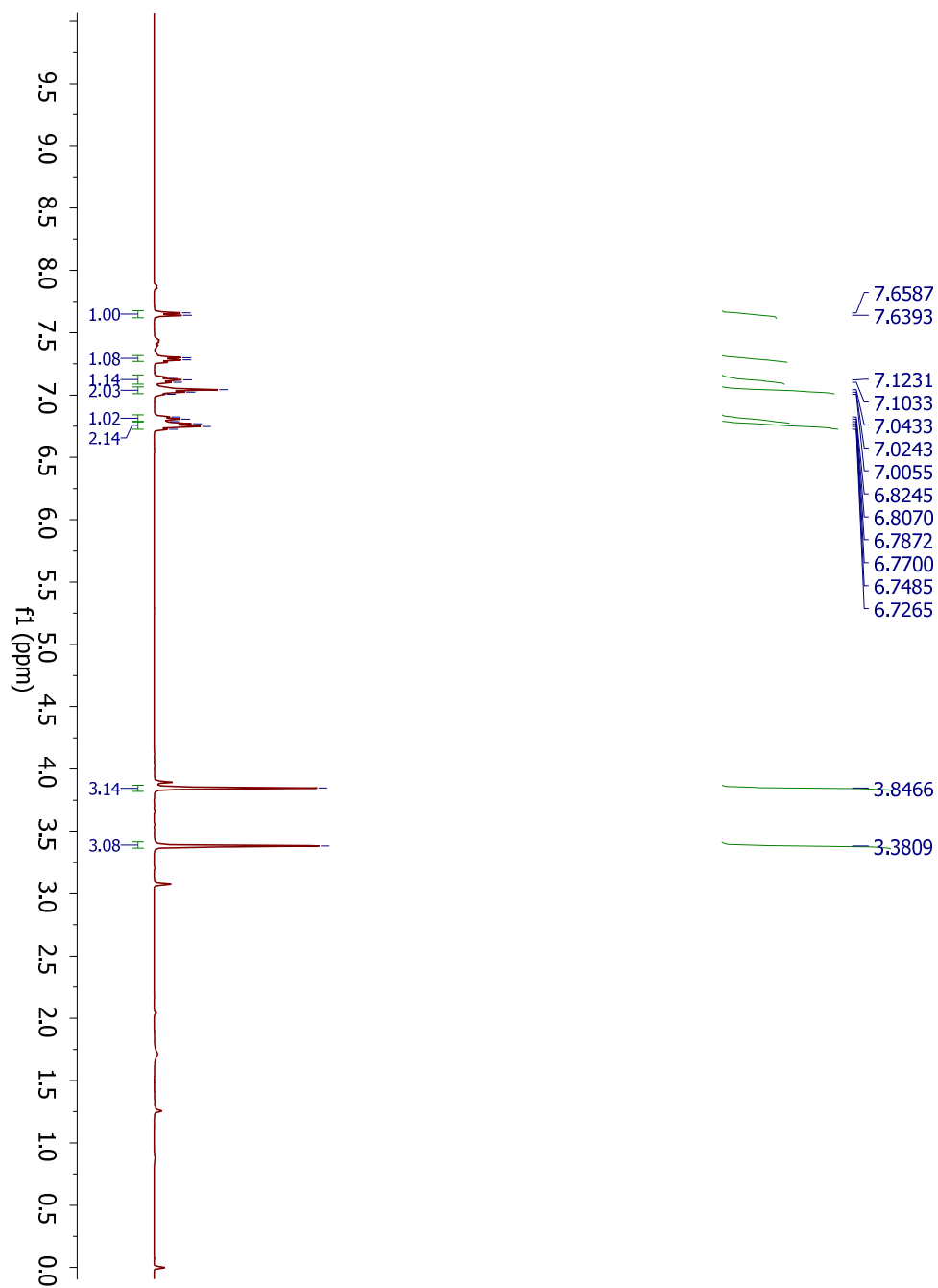
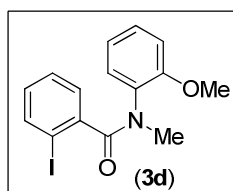
Operator Meena Sharma

Instrument micrOTOF-Q II 10330

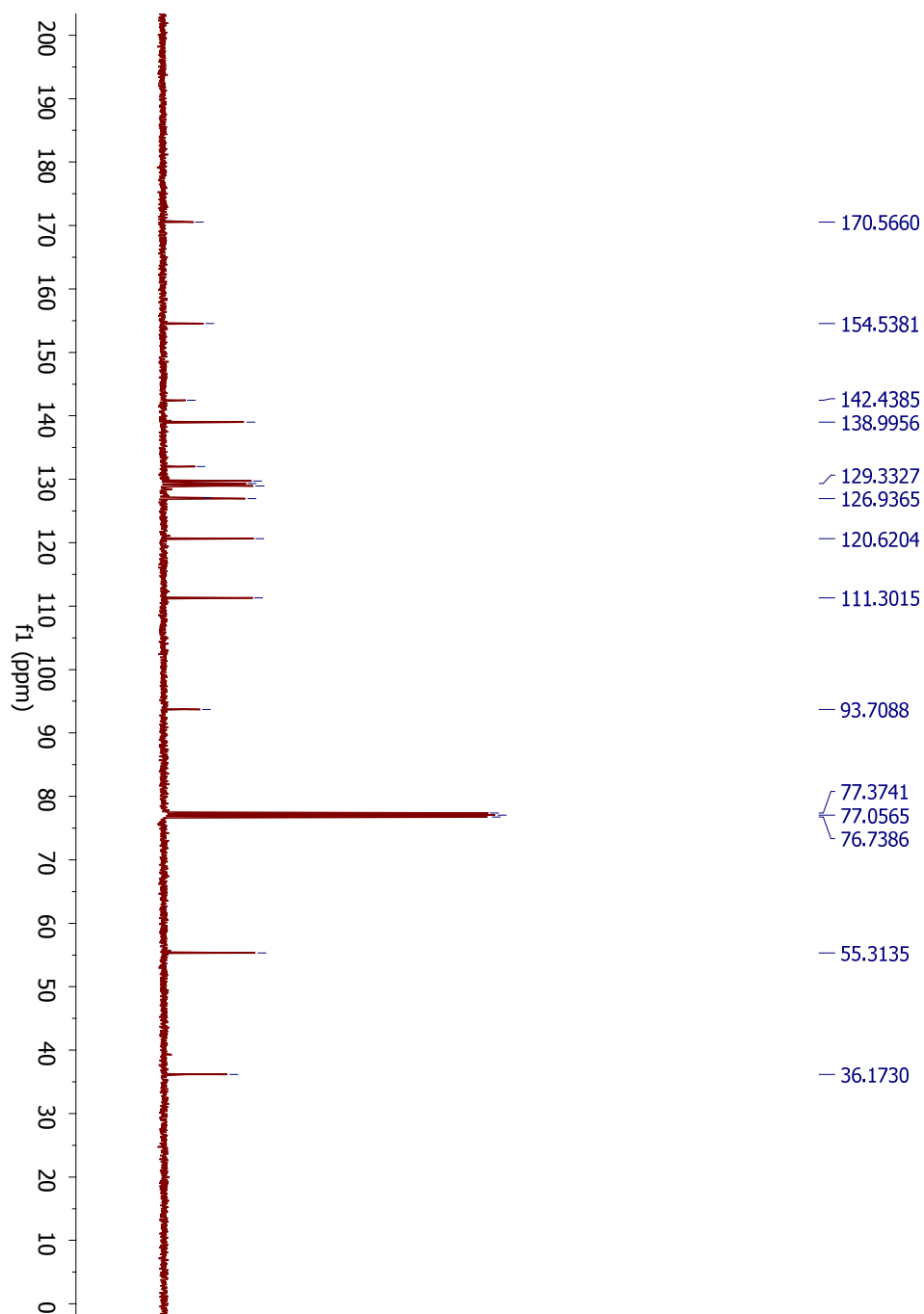
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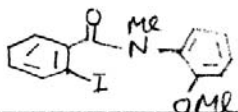




^1H NMR (400 MHz, CDCl_3) compound (3d)



^{13}C NMR (100 MHz, CDCl_3) compound **(3d)**



Display Report

Analysis Info

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 Sample Name Dr. A. Bisai- SD-3-19
 Comment

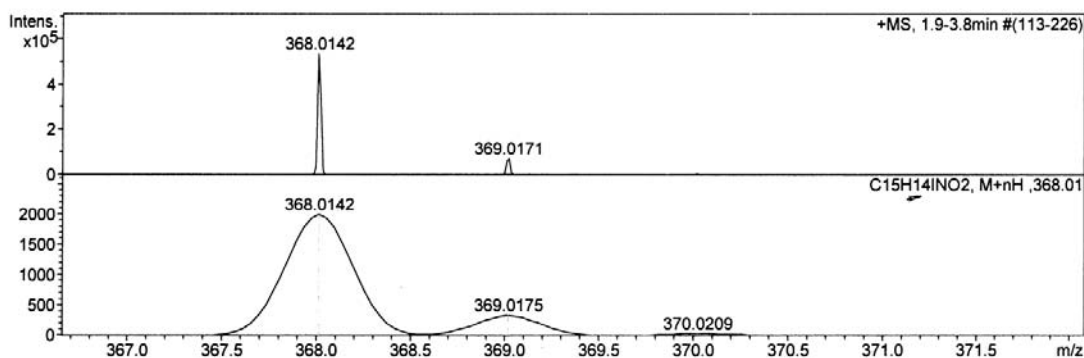
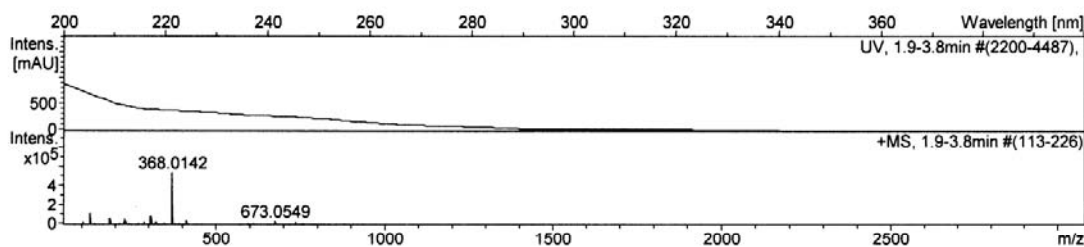
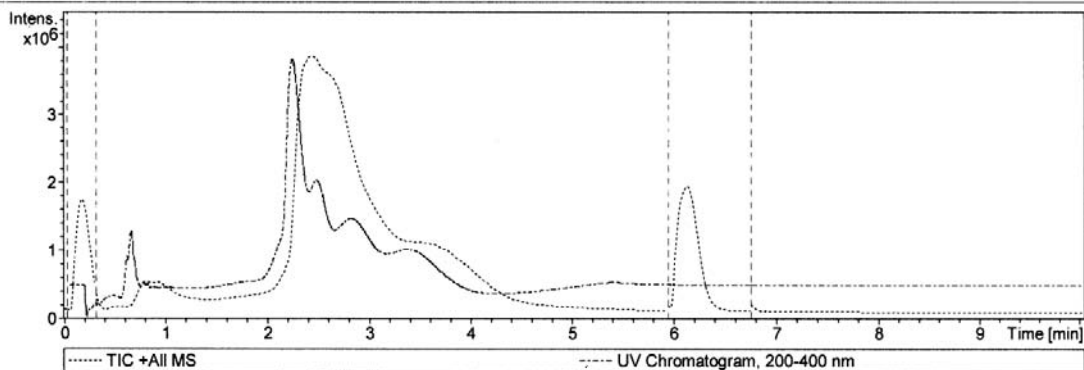
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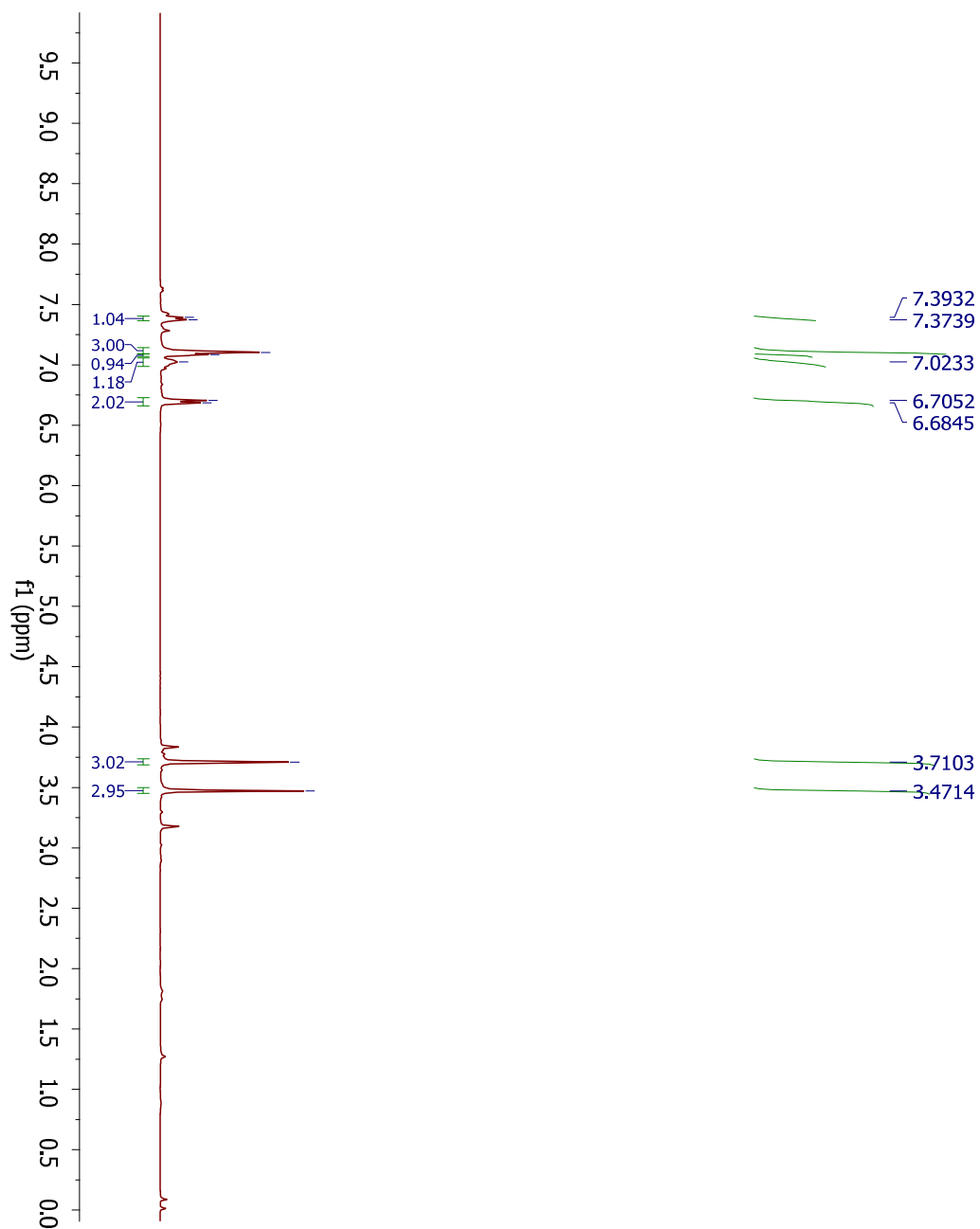
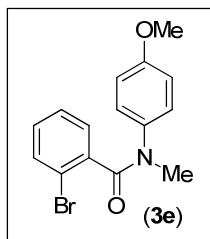
Operator Meena Sharma

Instrument microTOF-Q II 10330

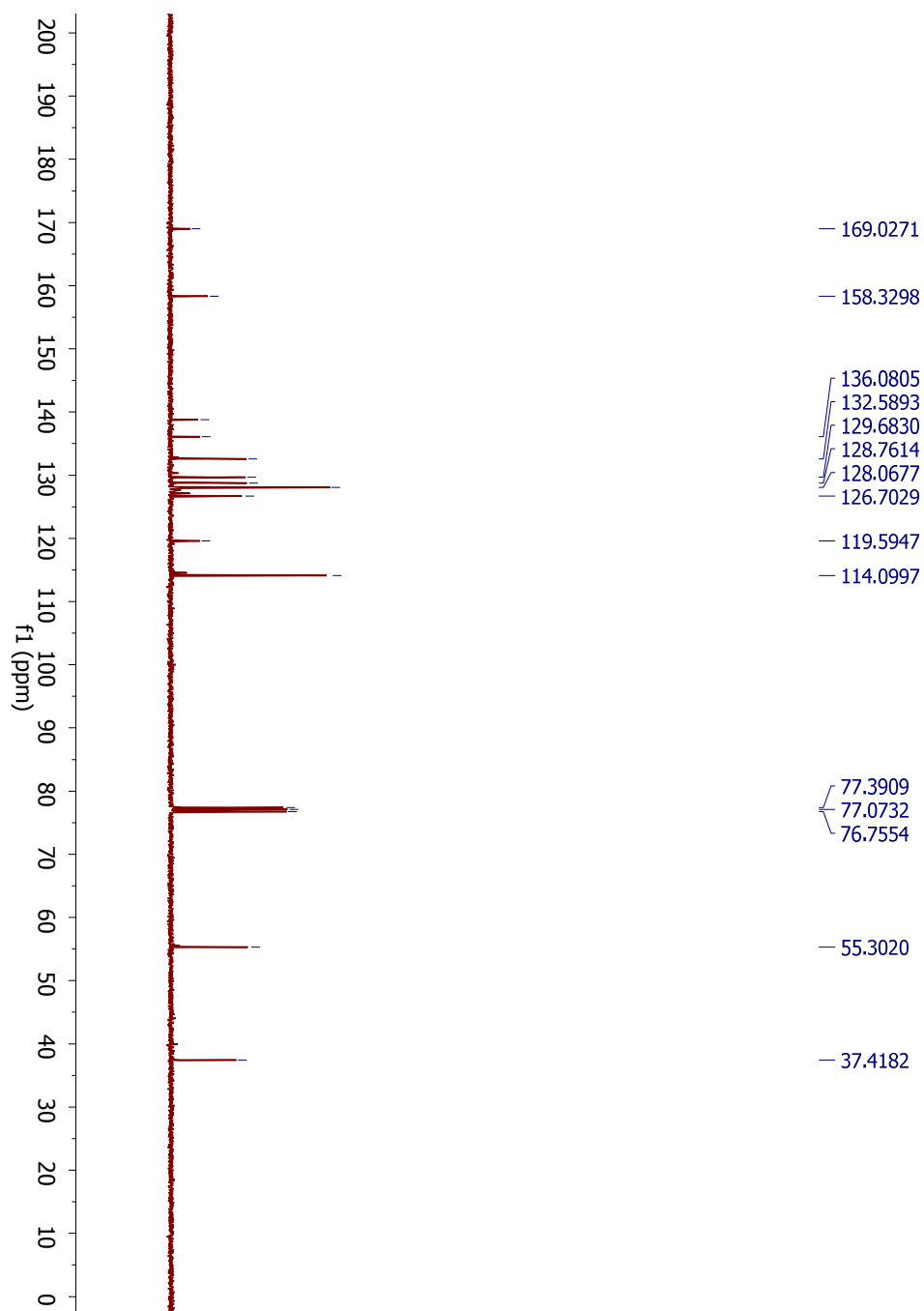
Acquisition Parameter

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

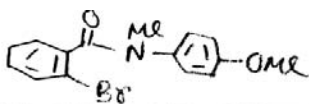




¹H NMR (400 MHz, CDCl₃) compound (3e)



^{13}C NMR (100 MHz, CDCl_3) compound **(3e)**



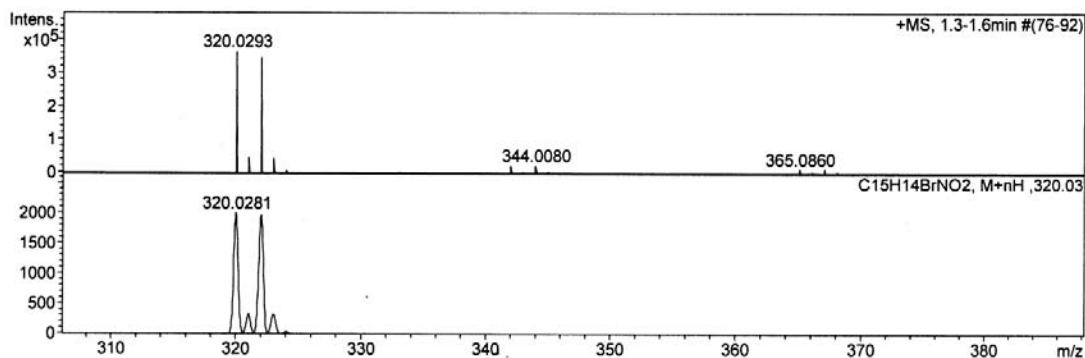
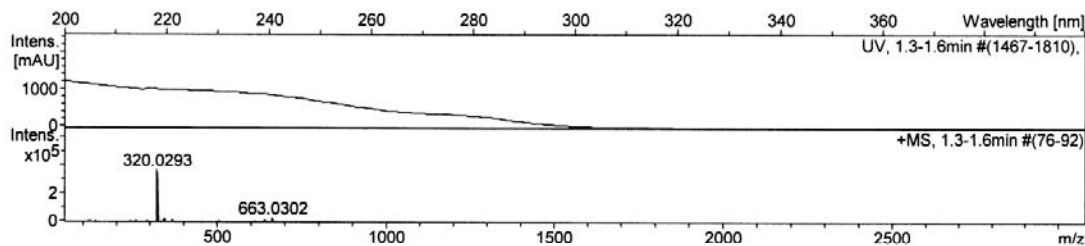
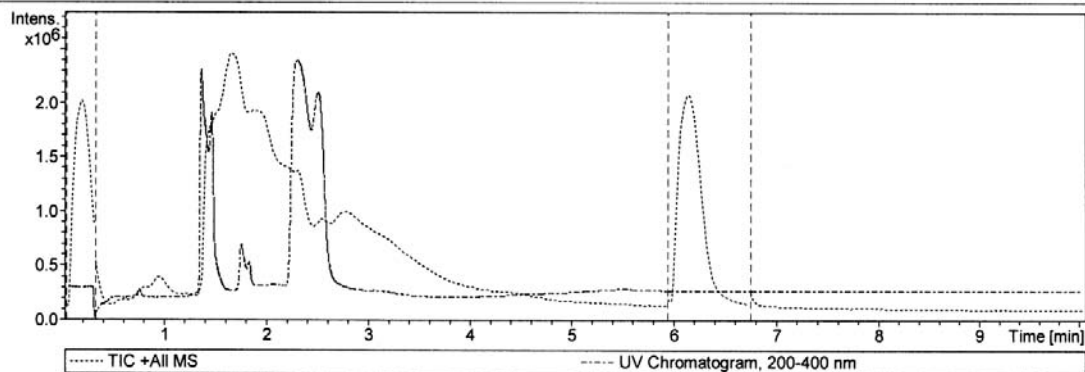
Display Report

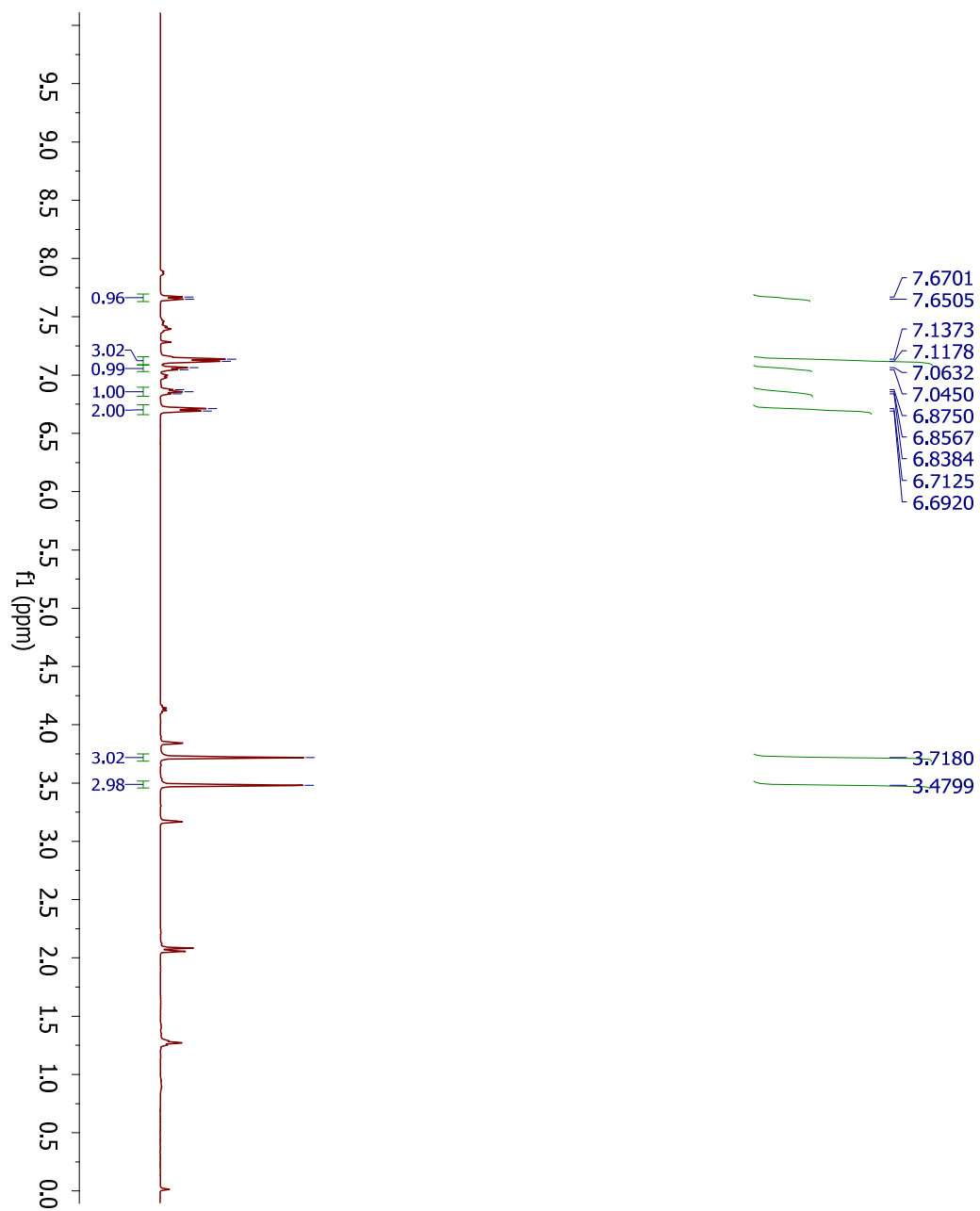
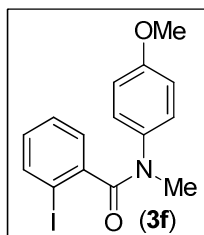
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 Sample Name: Dr. A. Bisai- SD-3-10
 Comment:
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

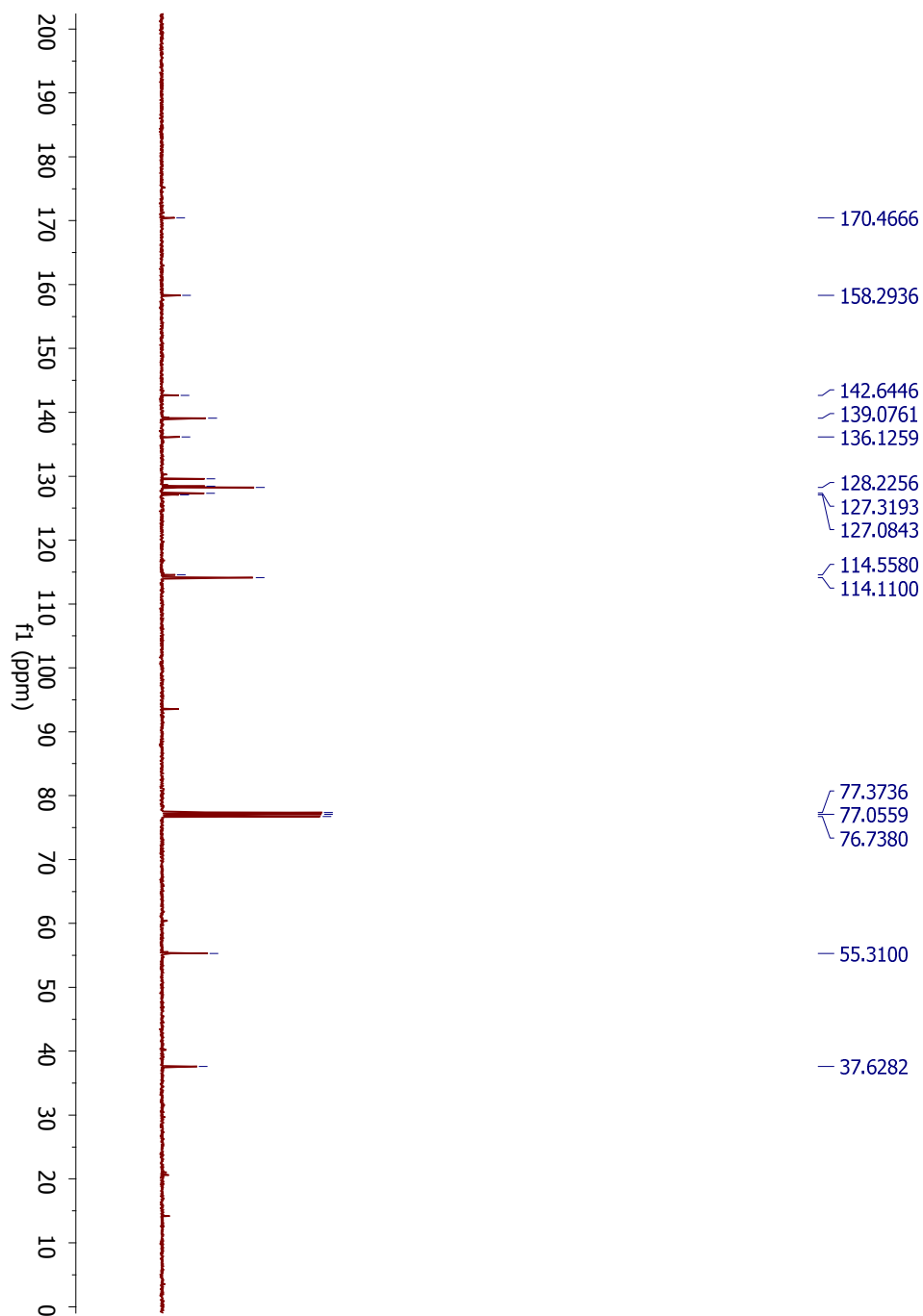
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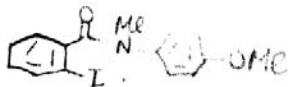




^1H NMR (400 MHz, CDCl_3) compound (3f)



^{13}C NMR (100 MHz, CDCl_3) compound **(3f)**



Display Report

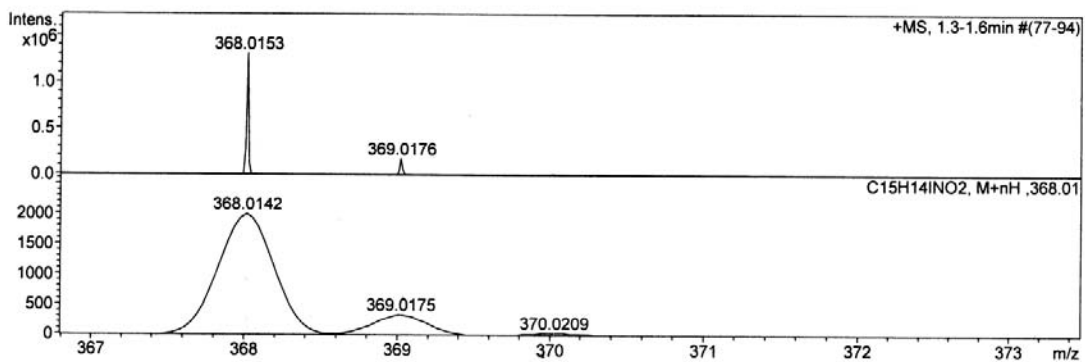
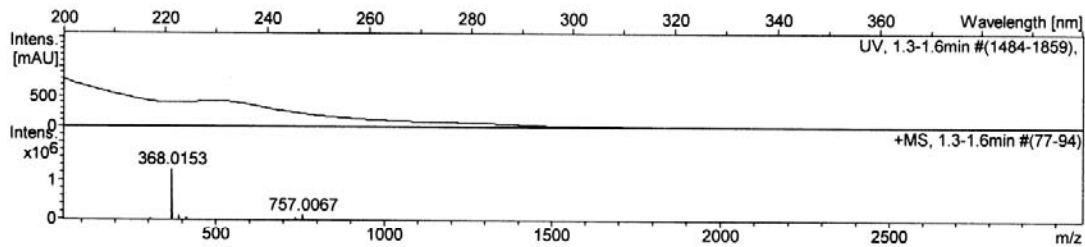
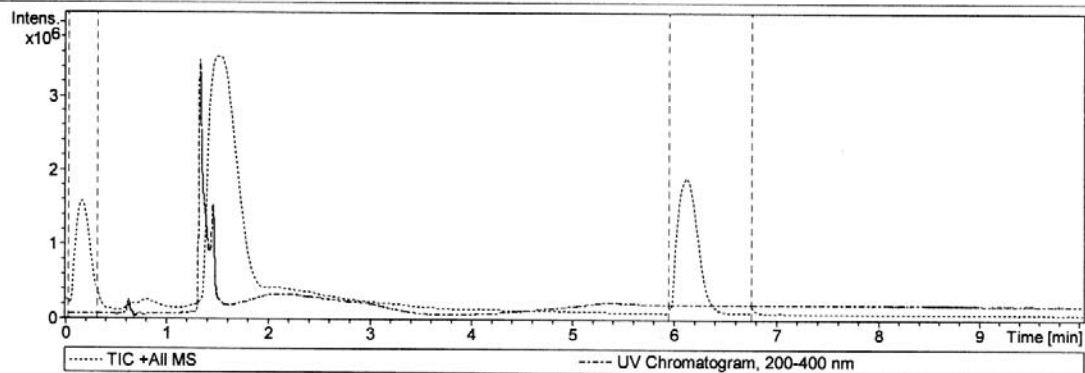
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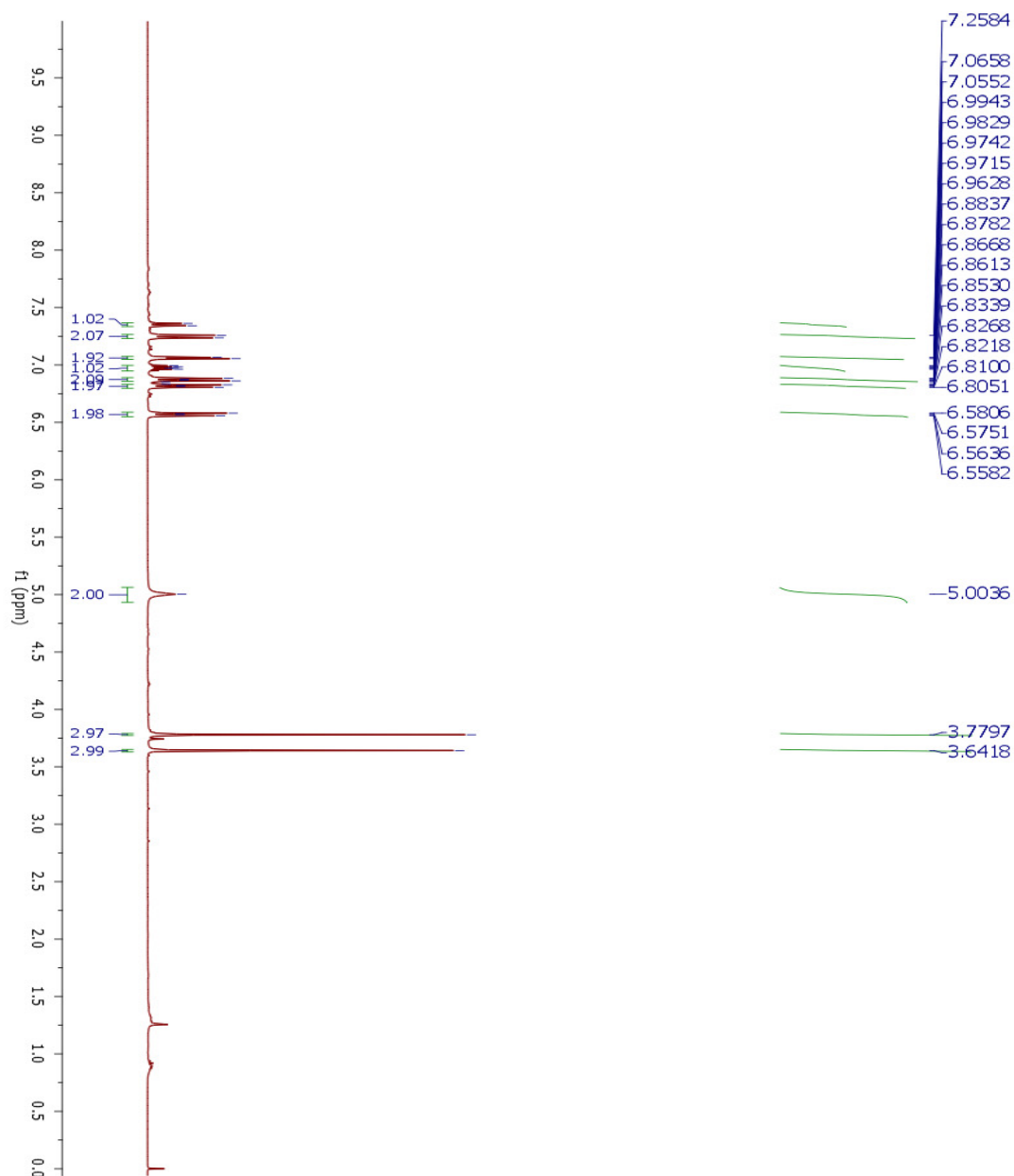
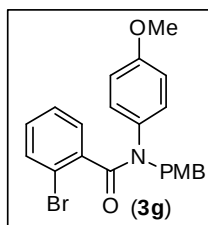
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 Sample Name Dr. A. Bisai- SD-3-20
 Comment

Acquisition Date 5/8/2012 3:53:02 PM
 Operator Meena Sharma
 Instrument microTOF-Q II 10330

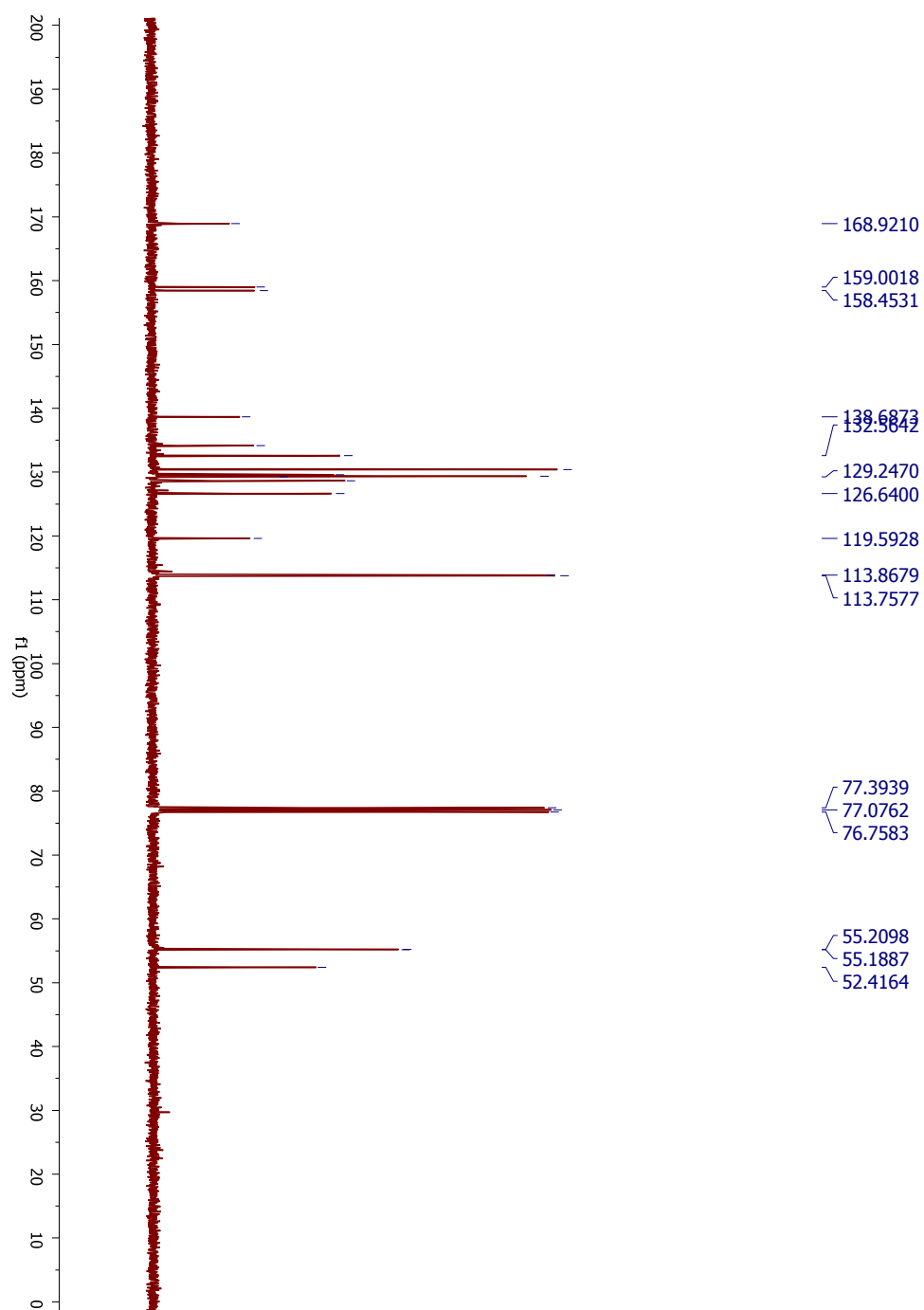
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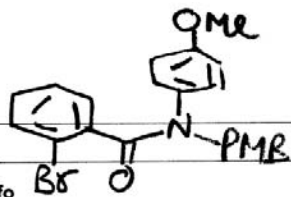




^1H NMR (400 MHz, CDCl_3) compound (3g)



^{13}C NMR (100 MHz, CDCl_3) compound **(3g)**



Display Report

Analysis Info

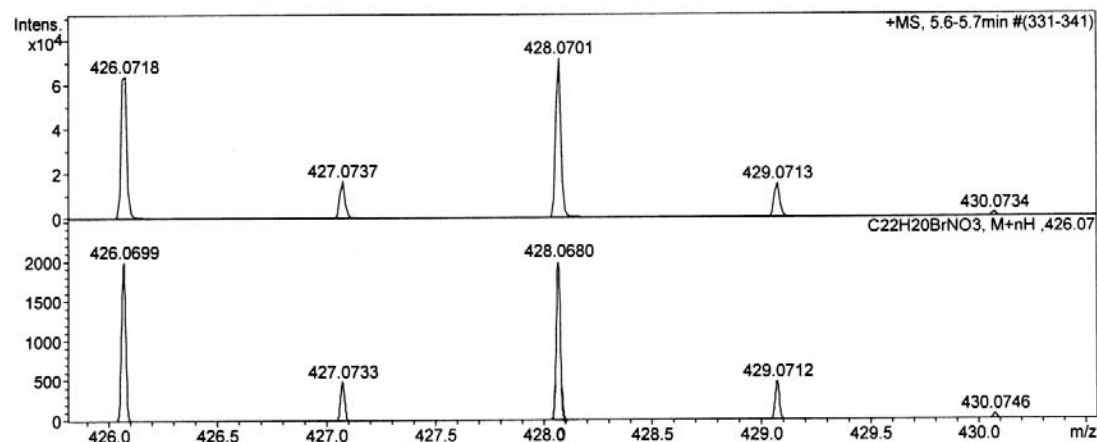
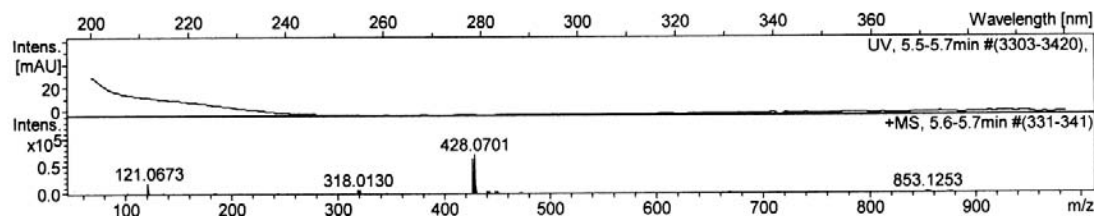
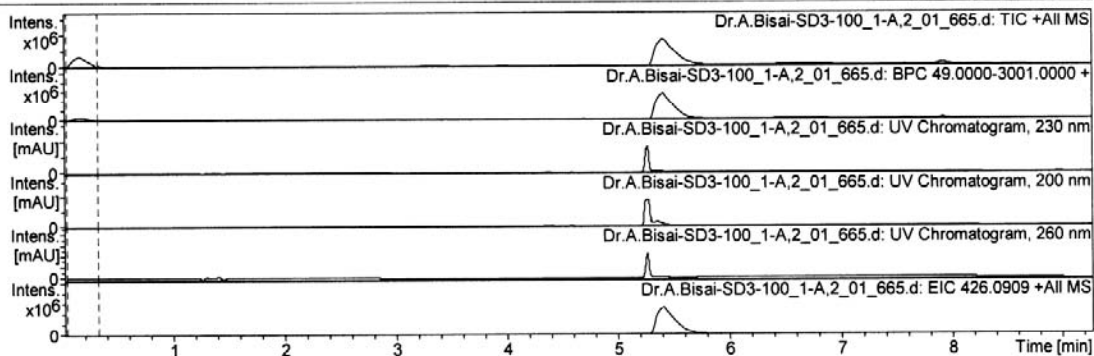
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 Sample Name Dr.A.Bisai-SD3-100
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Acquisition Date 3/18/2013 2:51:45 PM

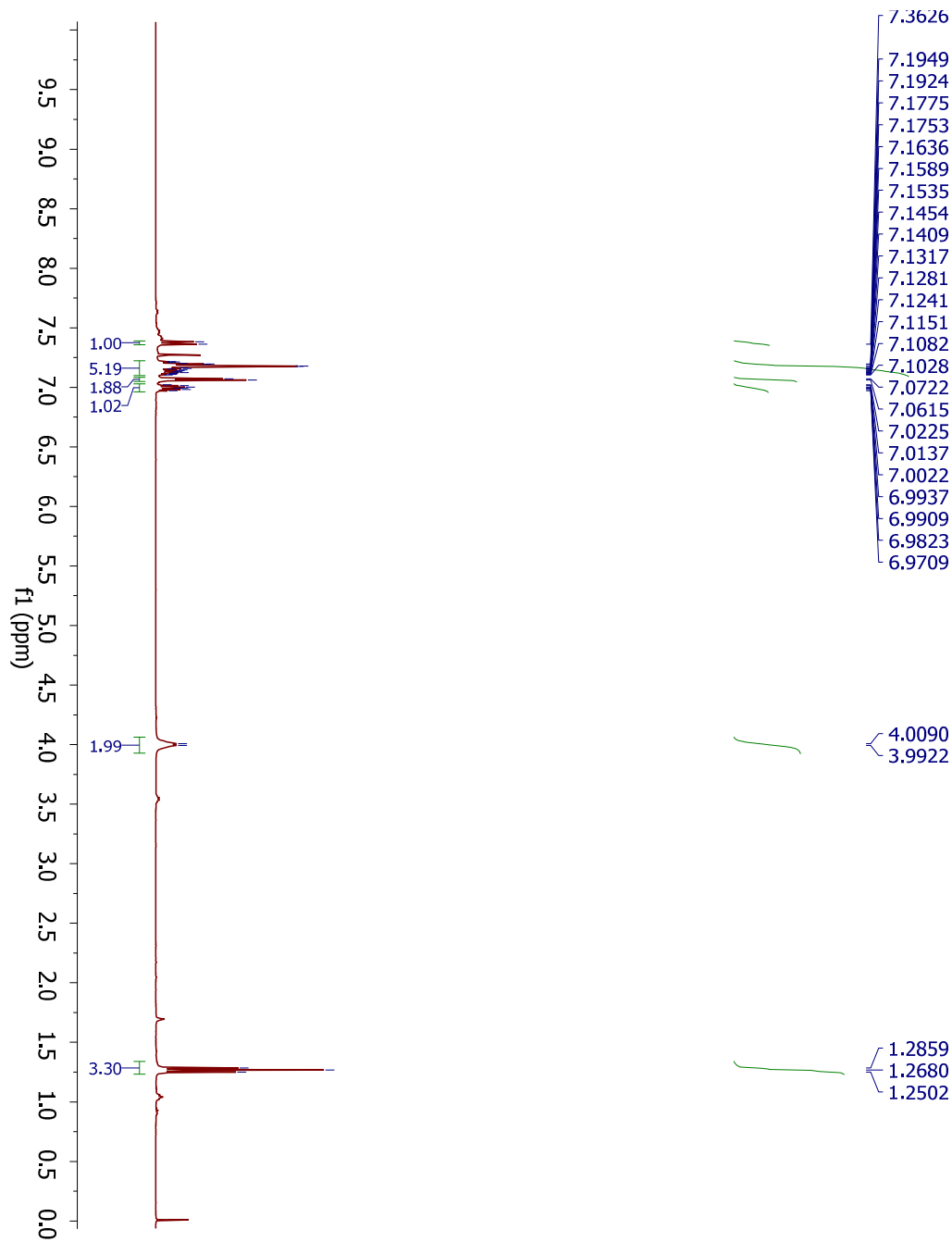
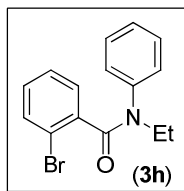
Operator Amit
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

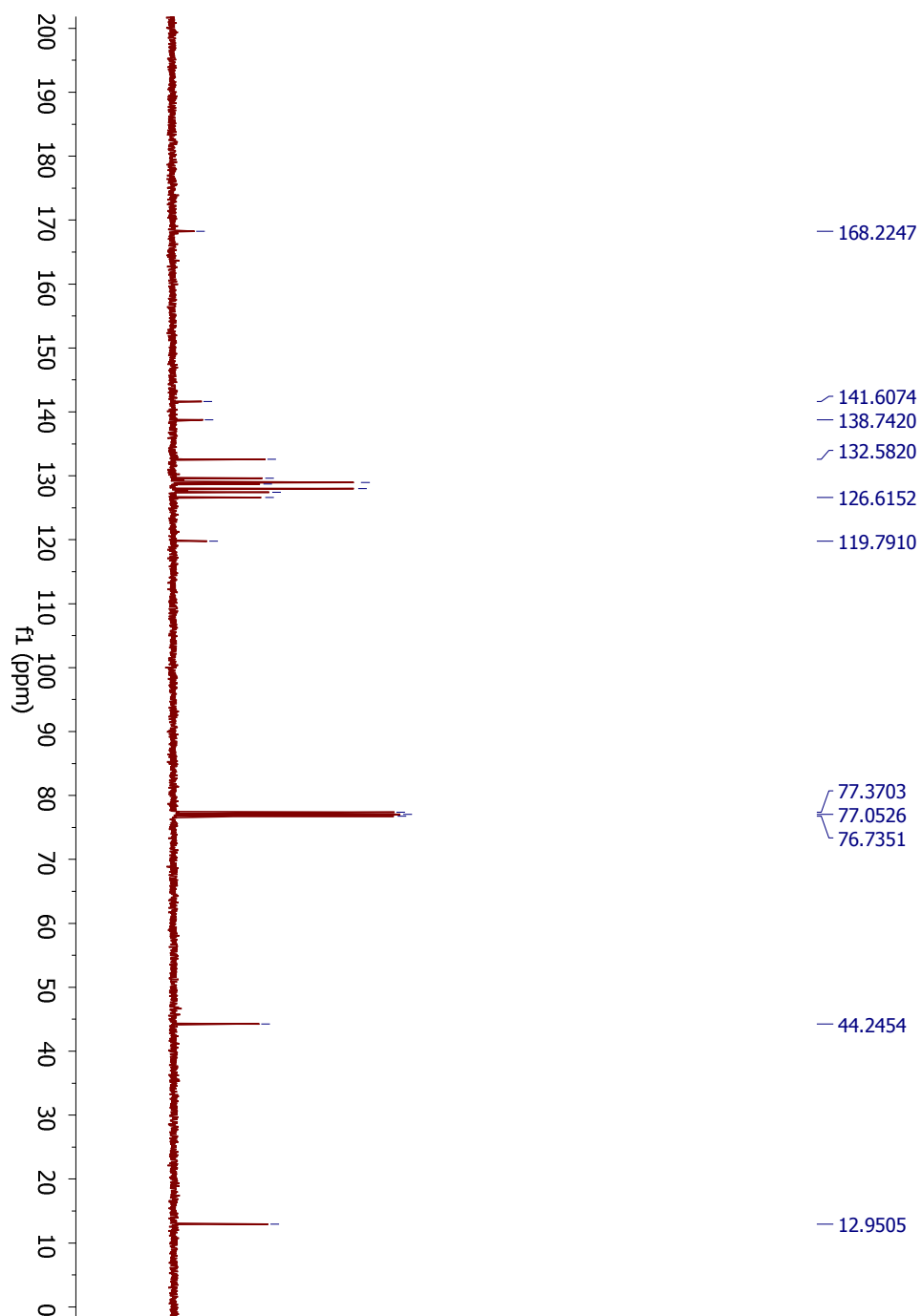
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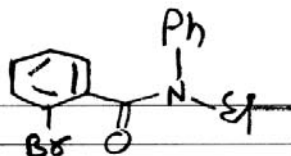
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¹H NMR (400 MHz, CDCl₃) compound (3h)



^{13}C NMR (100 MHz, CDCl_3) compound **(3h)**



Display Report

Analysis Info

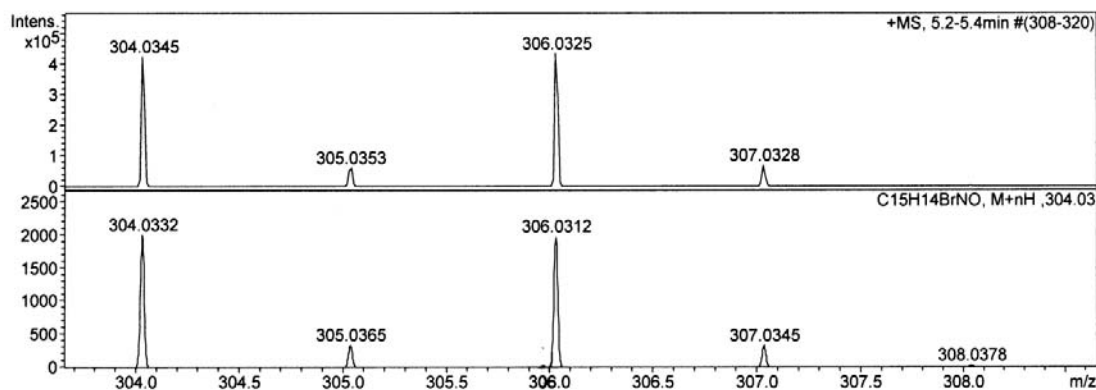
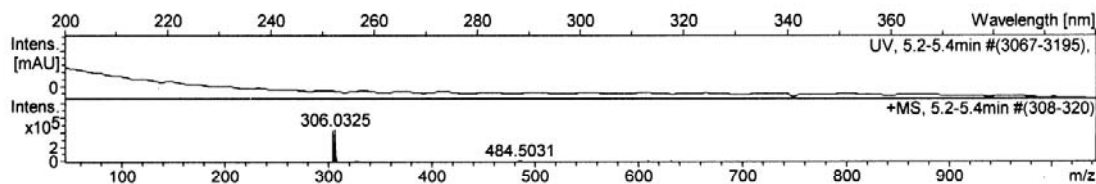
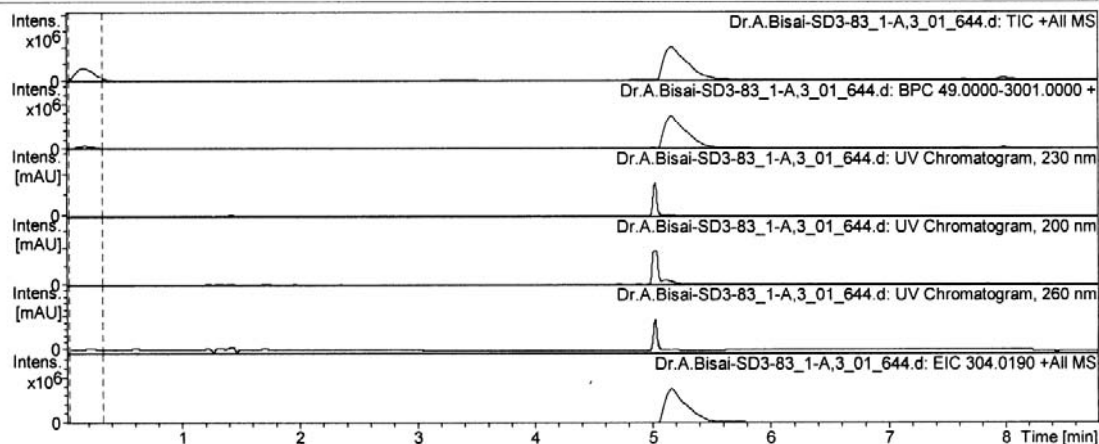
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 Sample Name Dr.A.Bisai-SD3-83
 Comment

Acquisition Date 3/18/2013 10:49:55 AM

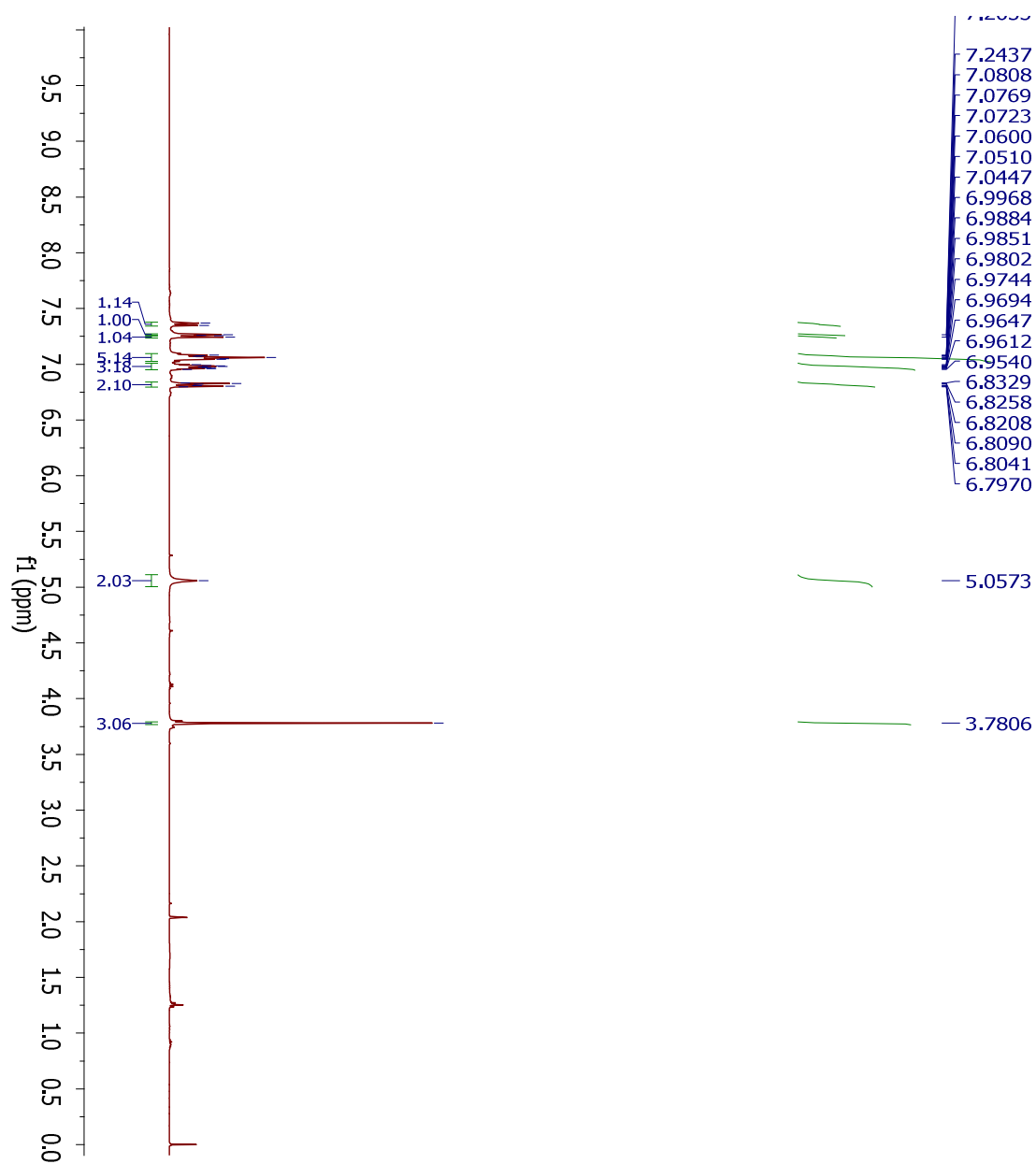
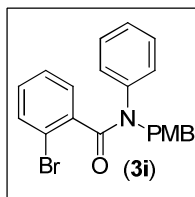
Operator Amit
 Instrument microTOF-Q II 10330

Acquisition Parameter

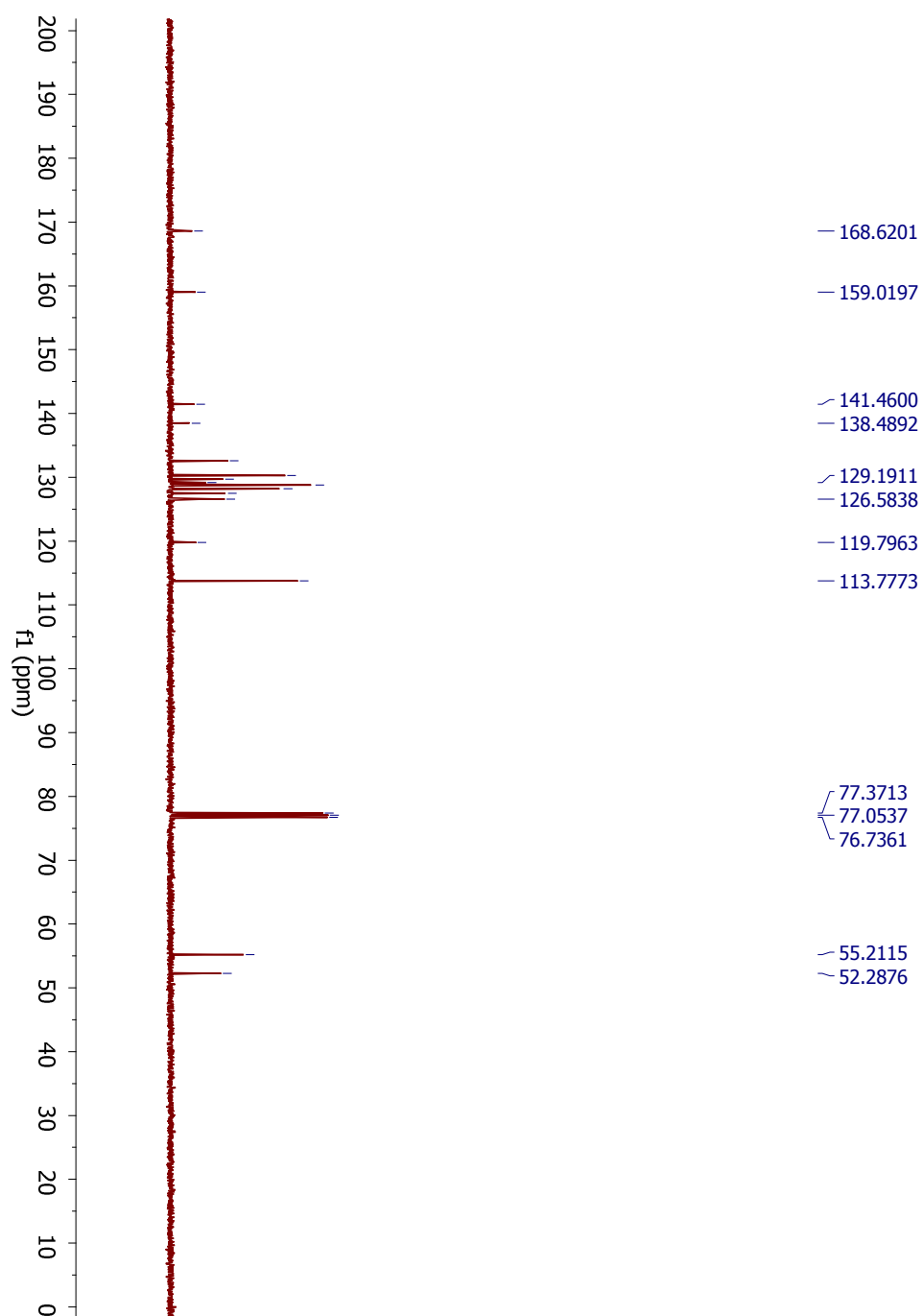
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



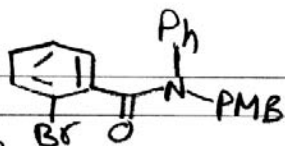
Scanned copy of mass spectrum of (3h)



¹H NMR (400 MHz, CDCl₃) compound (3i)



^{13}C NMR (100 MHz, CDCl_3) compound **(3i)**



Display Report

Analysis Info

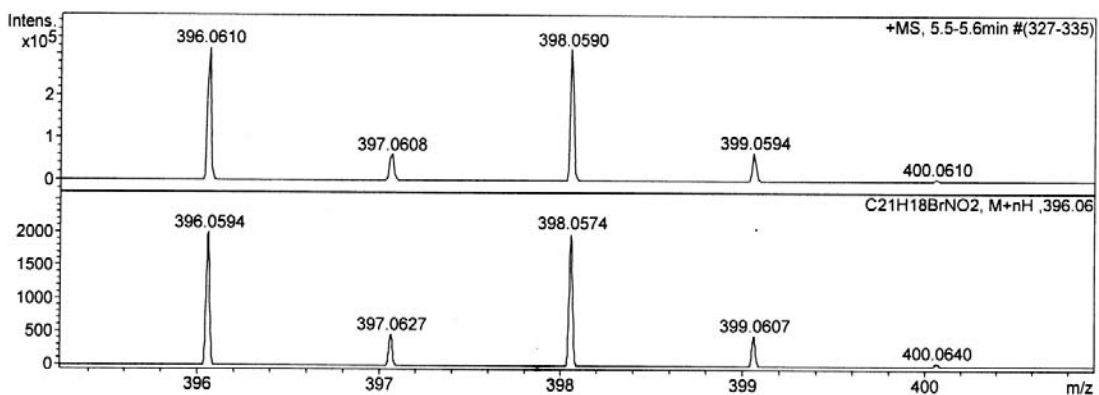
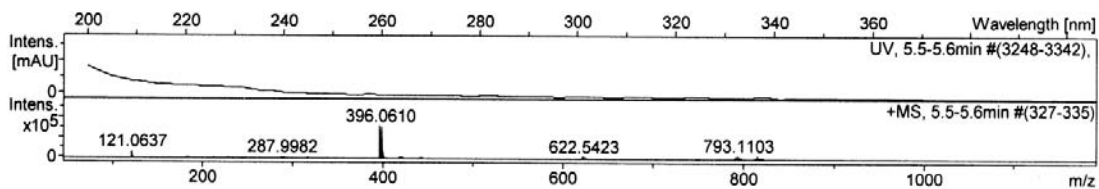
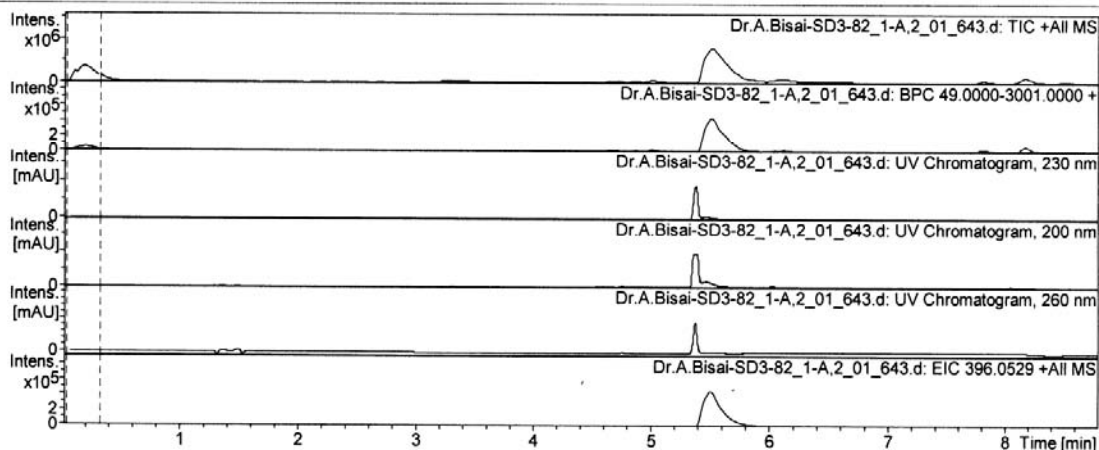
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 Method HRLCMS-20 Sept.m
 Sample Name Dr.A.Bisai-SD3-82
 Comment

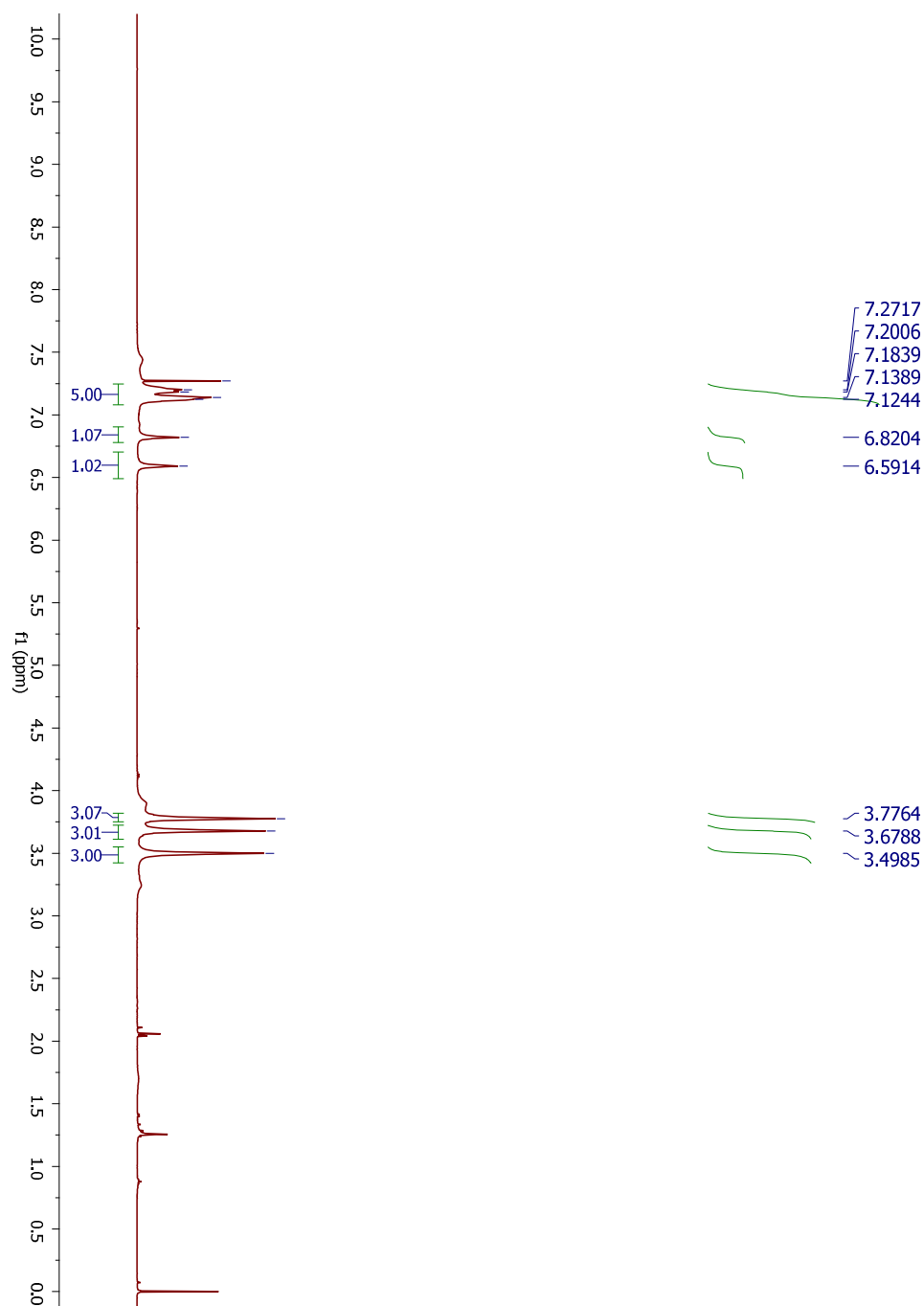
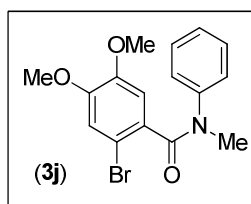
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Operator Amit
 Instrument micrOTOF-Q II 10330

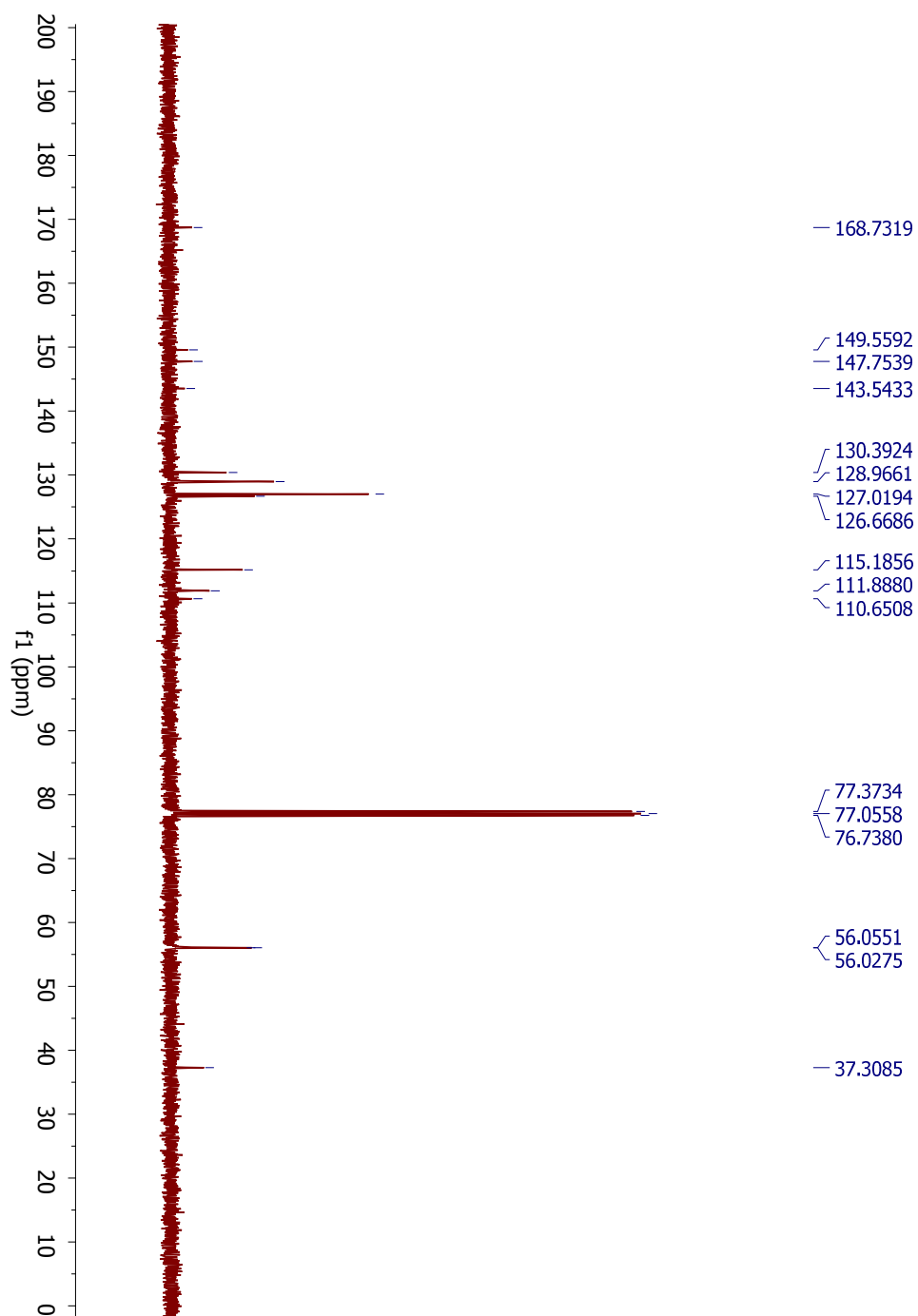
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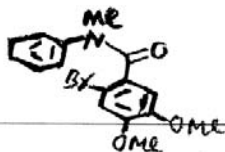




¹H NMR (400 MHz, CDCl₃) compound **(3j)**



^{13}C NMR (100 MHz, CDCl_3) compound **(3j)**



Display Report

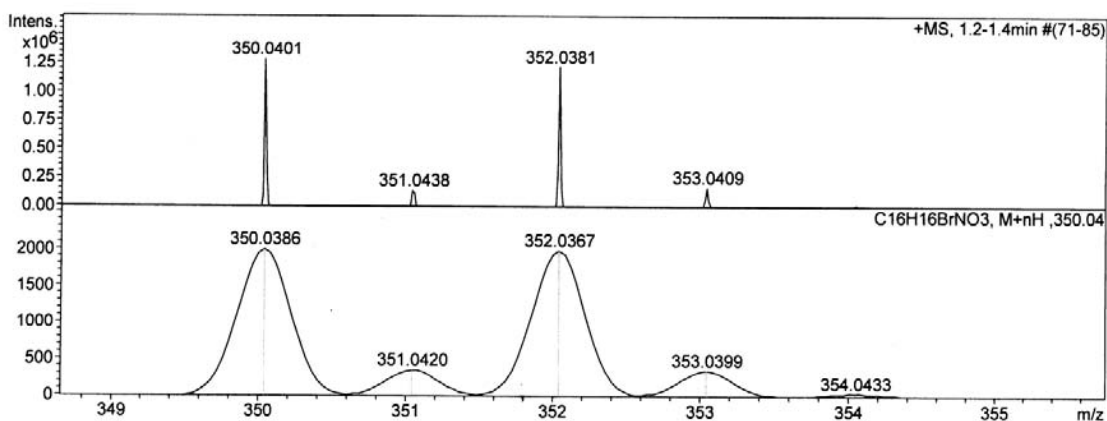
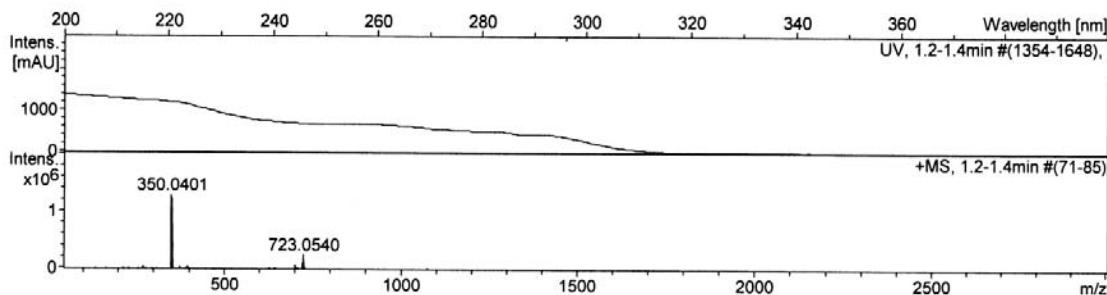
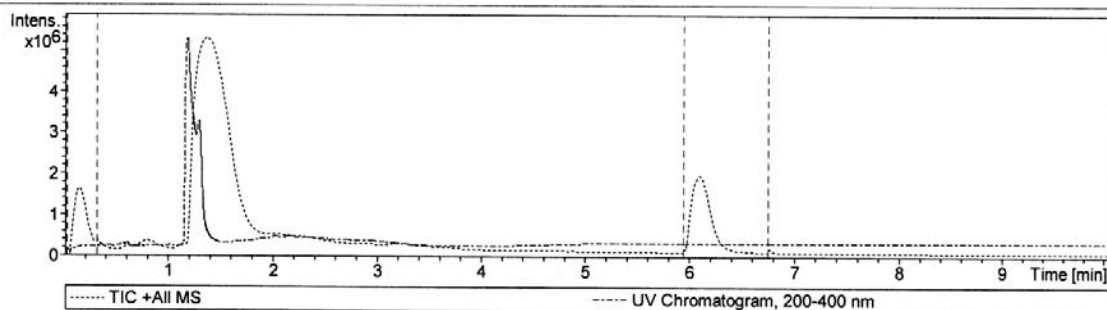
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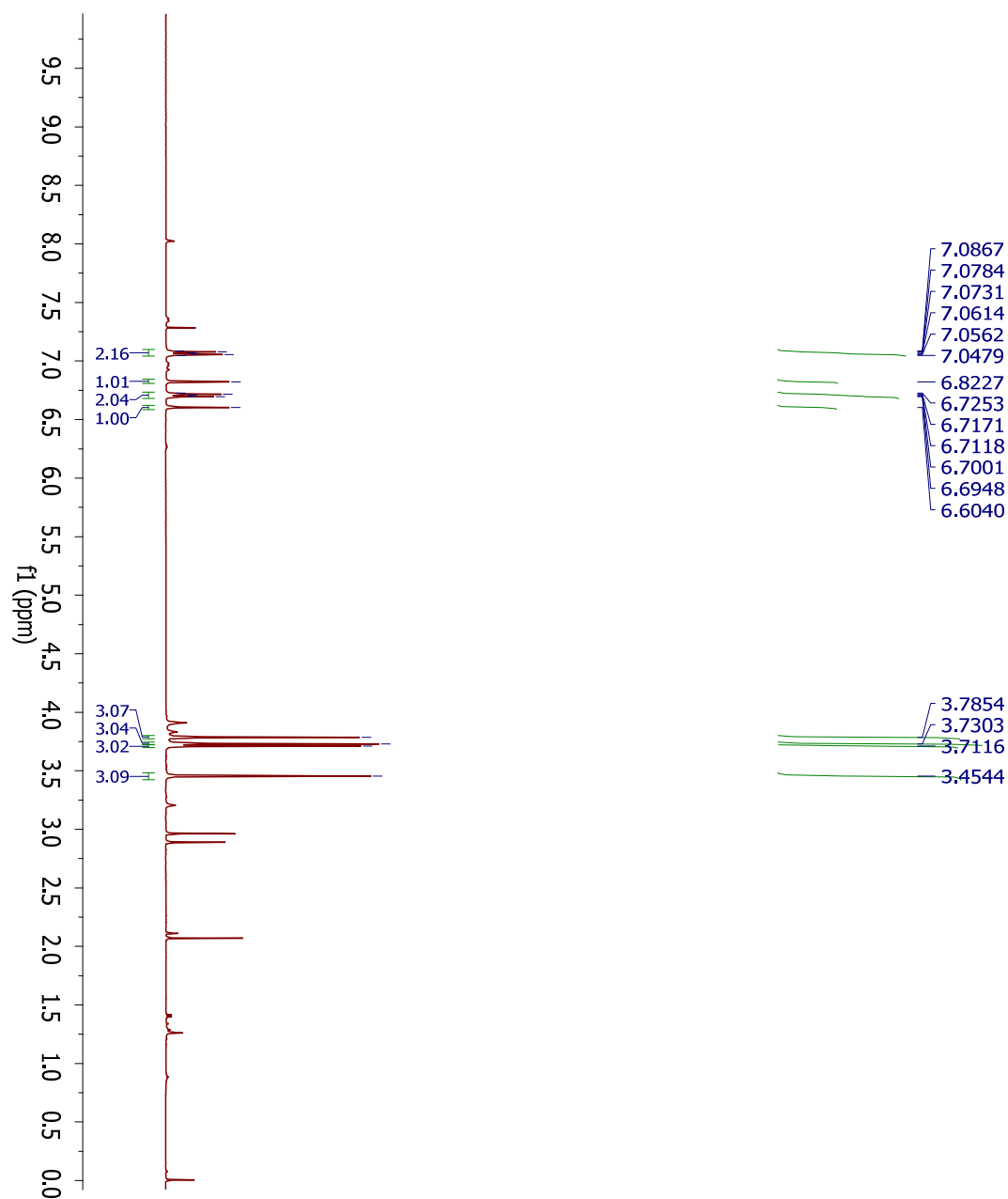
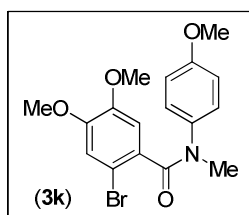
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

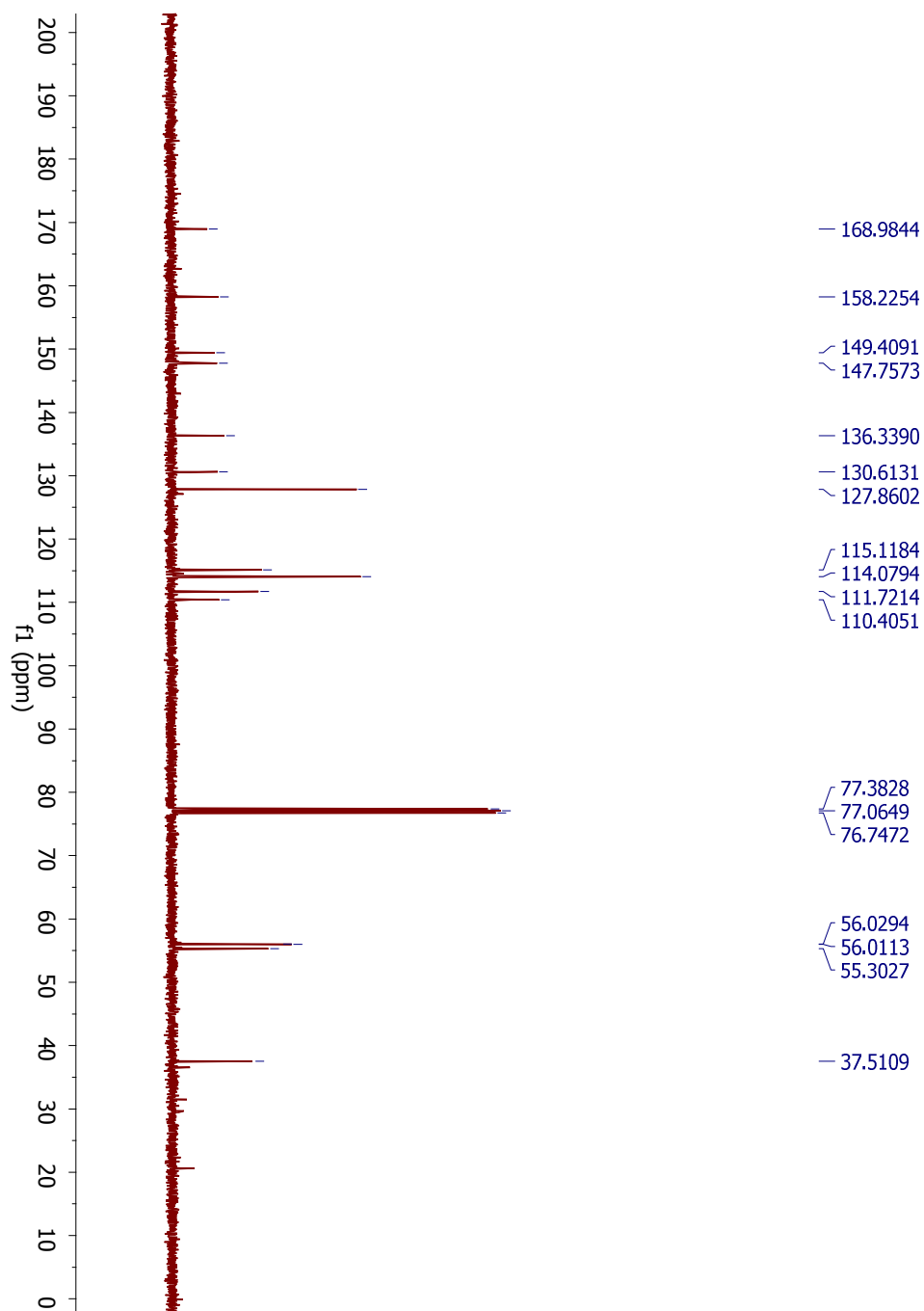
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^1H NMR (400 MHz, CDCl_3) compound **(3k)**



Display Report

Analysis Info

Analysis Name D:\Data\user data\may2012\14 may\Dr. A. Bisai- SD-3-32_1-A_2_01_2195.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SD-3-32
 Comment

Acquisition Date 5/14/2012 10:30:00 AM

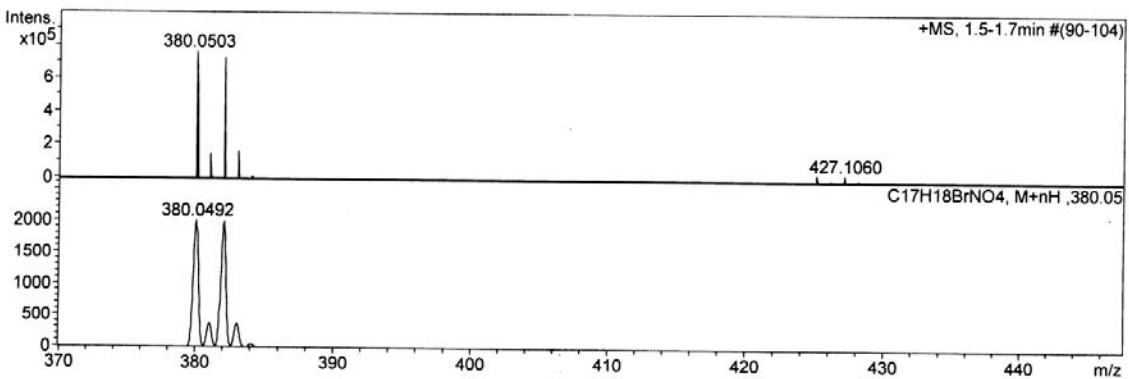
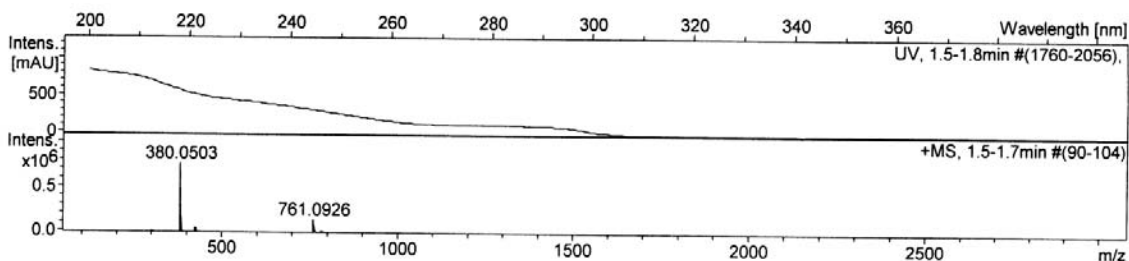
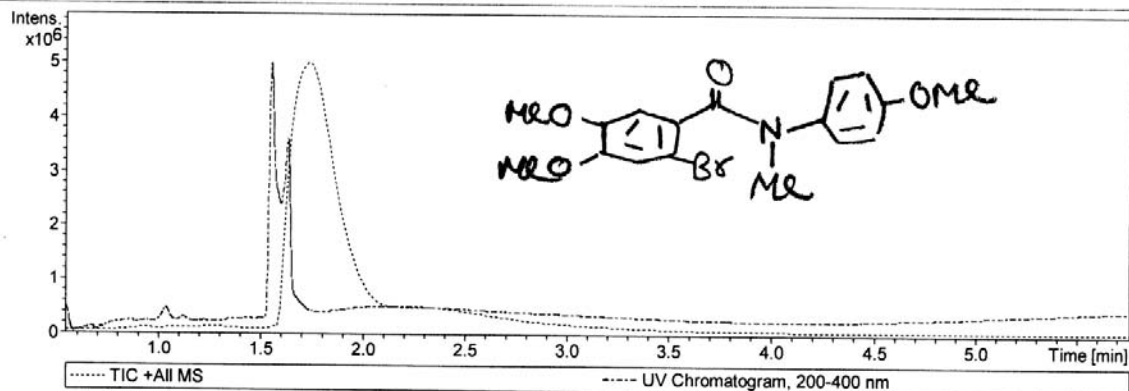
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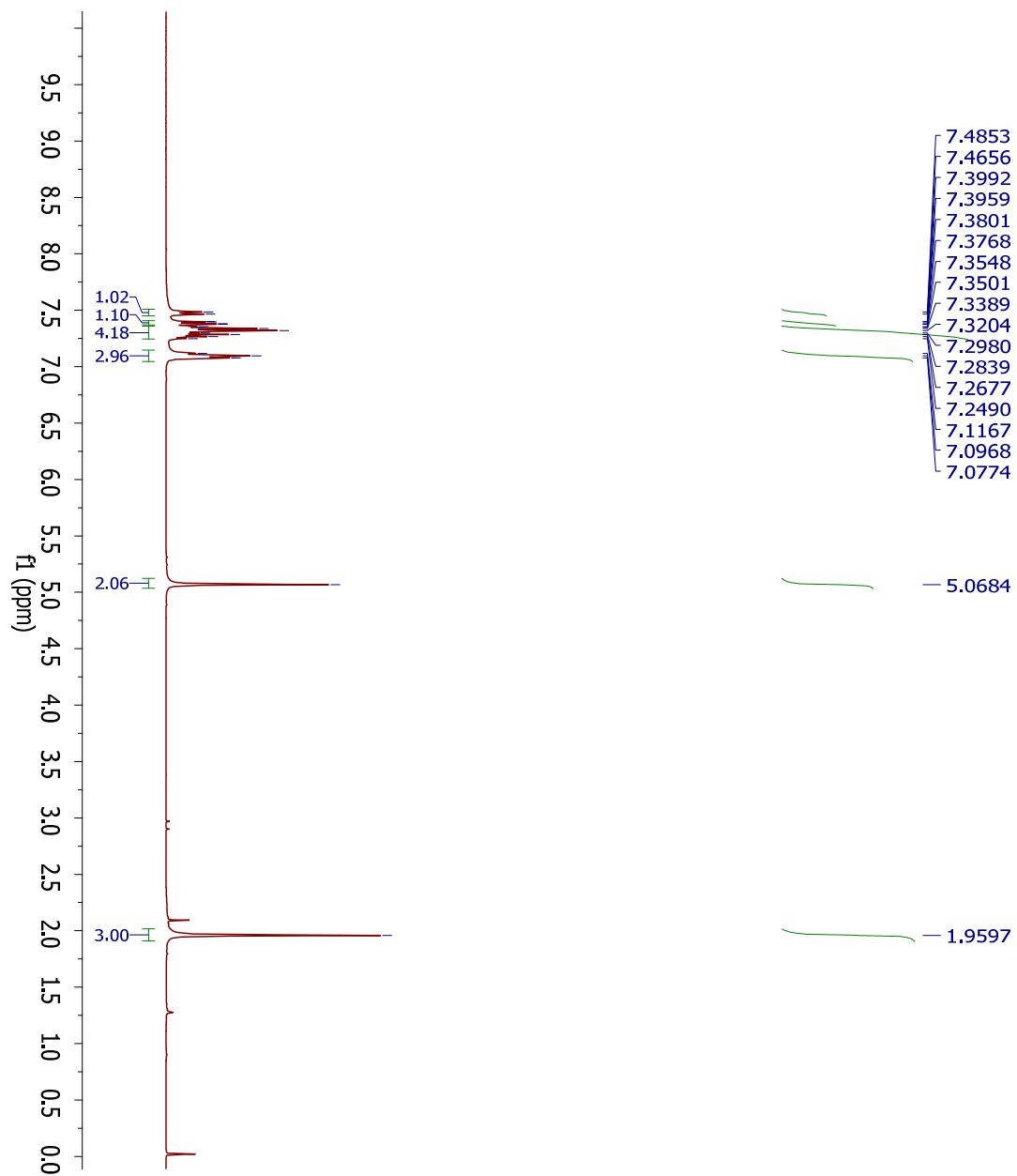
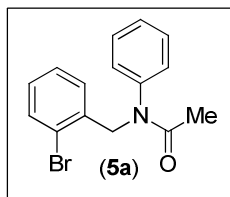
Meena Sharma

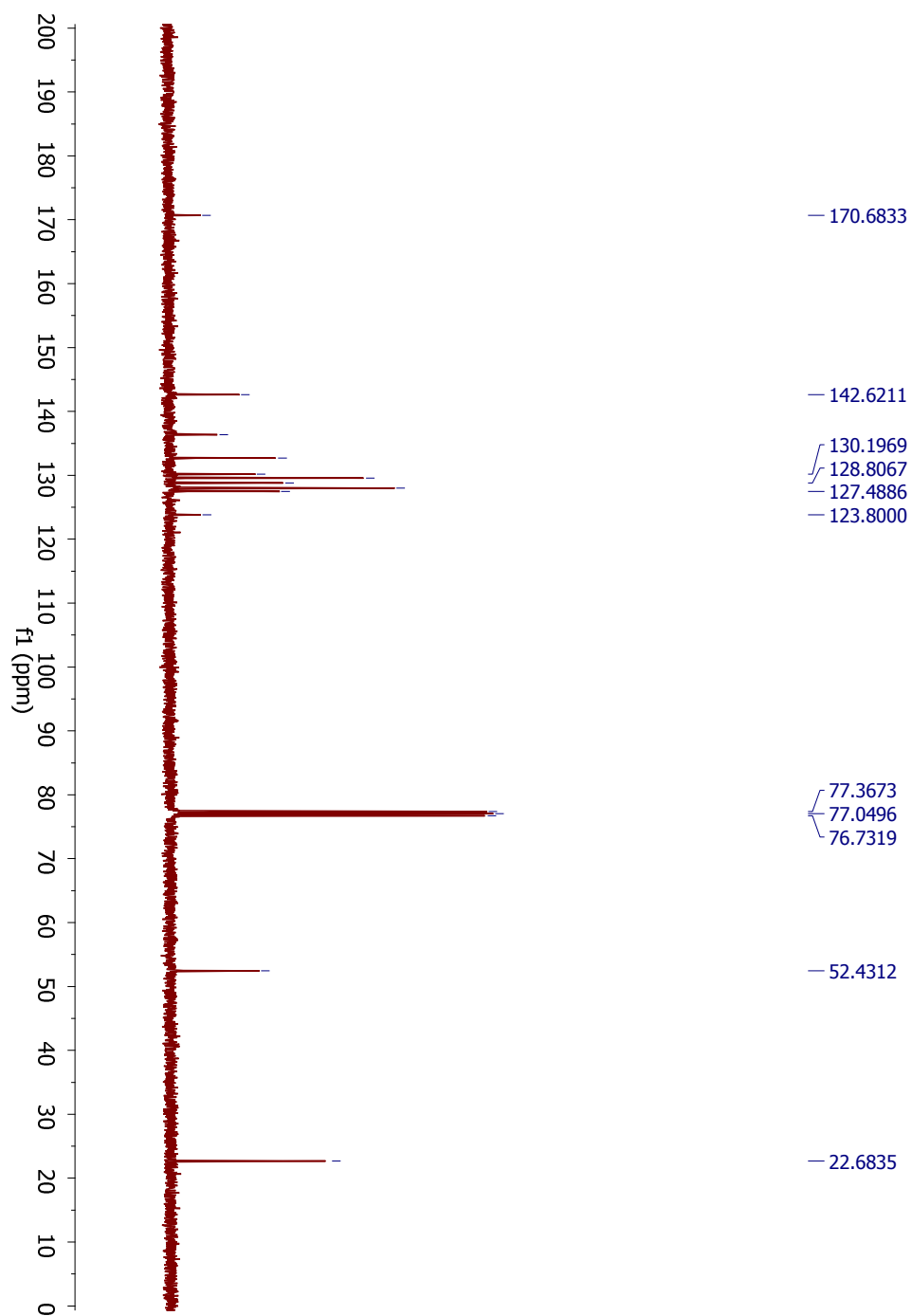
Instrument micrOTOF-Q II 10330

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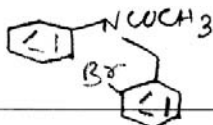
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^{13}C NMR (100 MHz, CDCl_3) compound **(5a)**



Display Report

Analysis Info

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 Sample Name Dr. A. Bisai- SD-2-388
 Comment

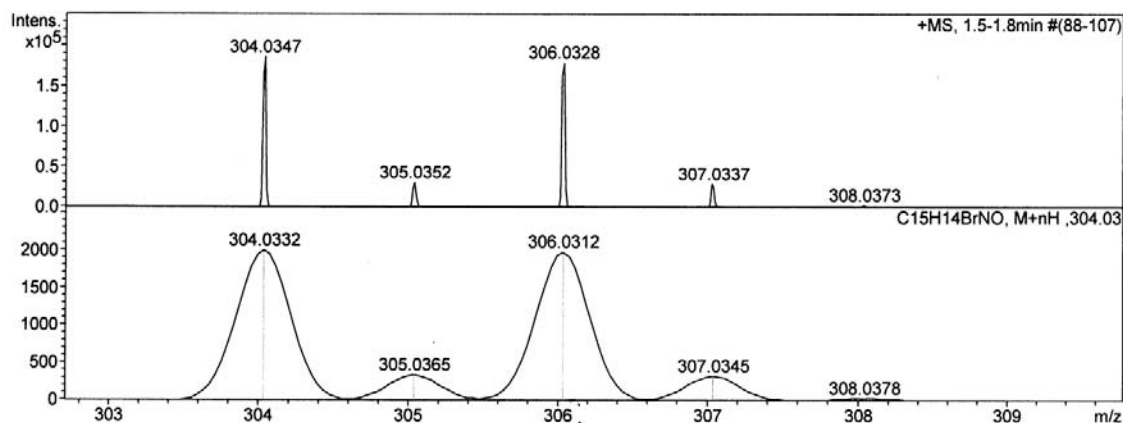
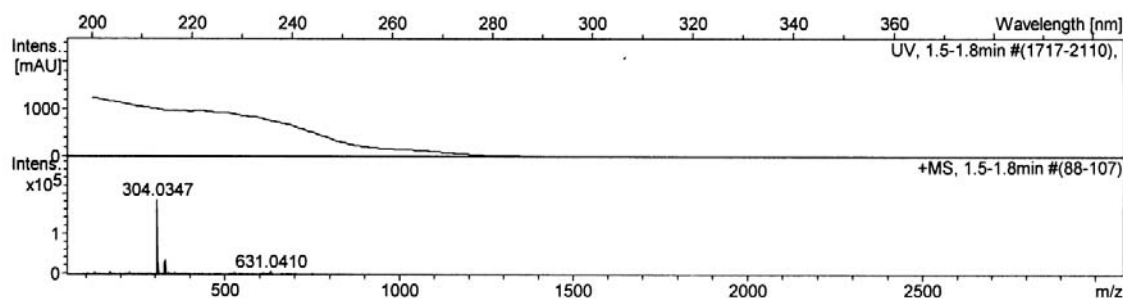
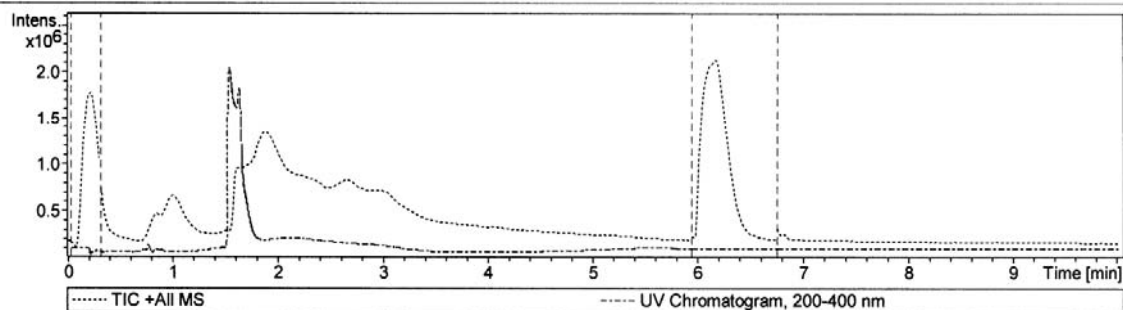
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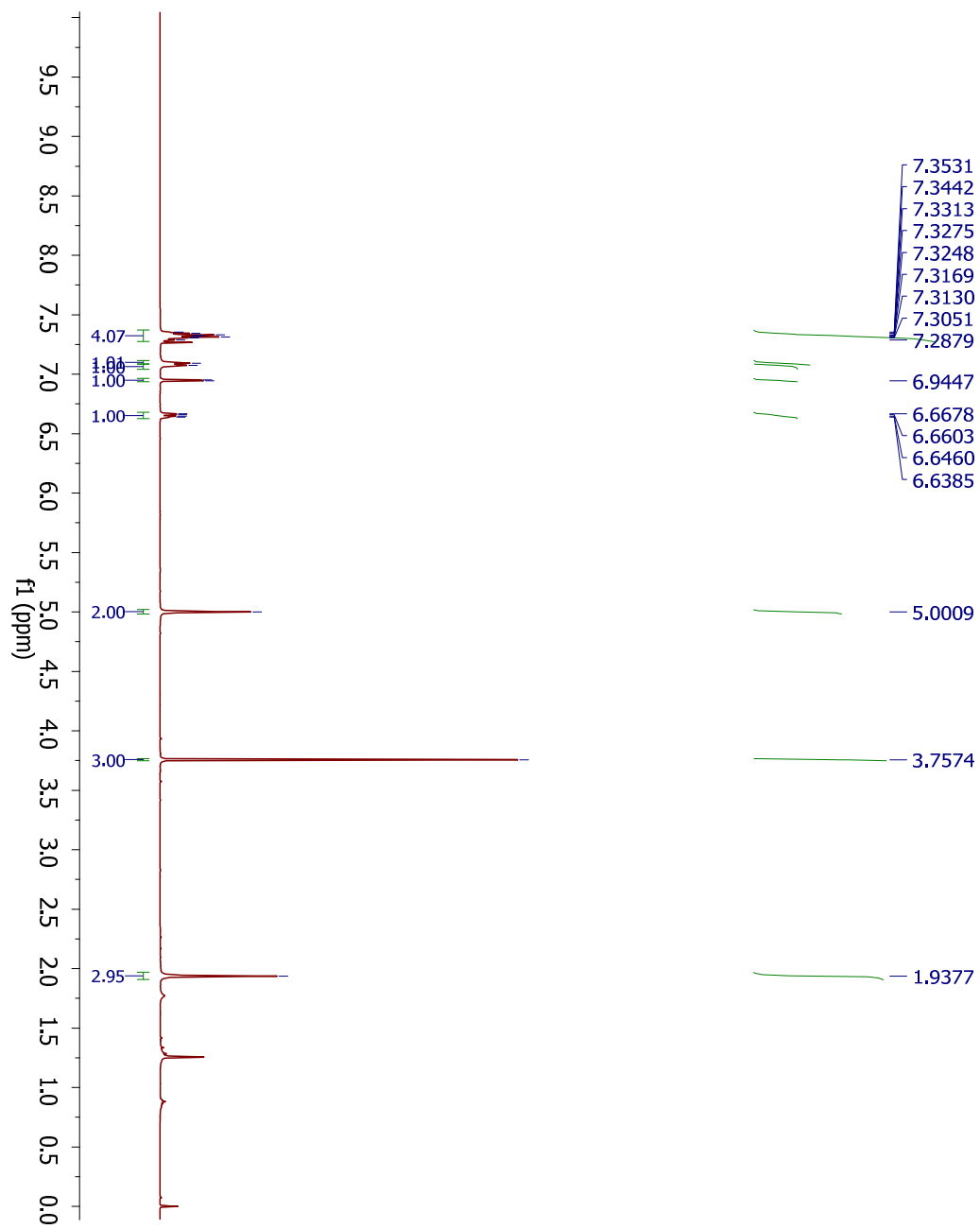
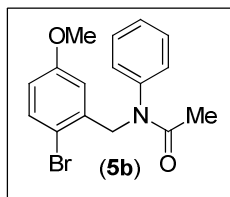
Operator Meena Sharma

Instrument microTOF-Q II 10330

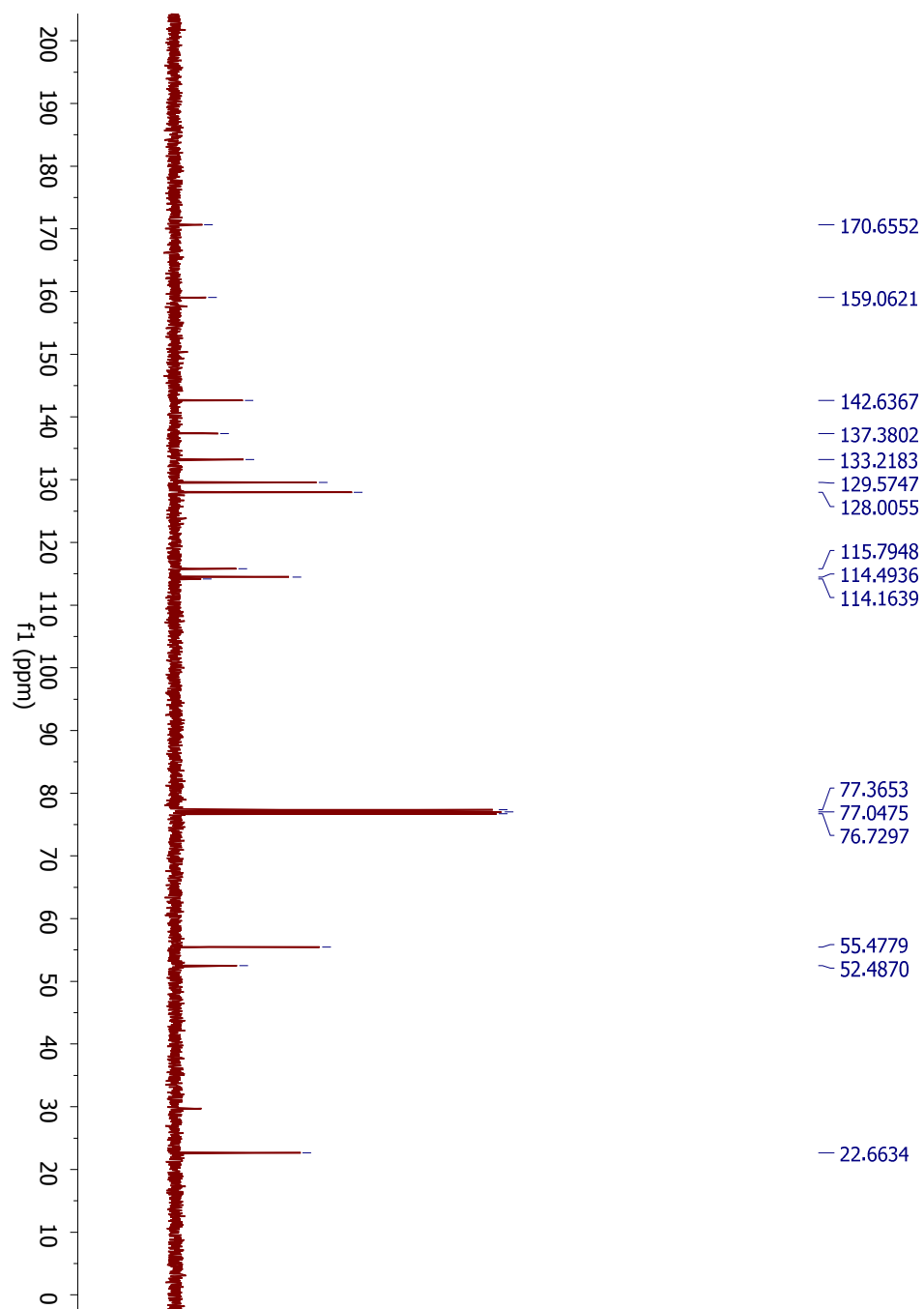
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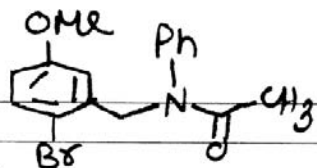




¹H NMR (400 MHz, CDCl₃) compound **(5b)**



^{13}C NMR (100 MHz, CDCl_3) compound **(5b)**



Display Report

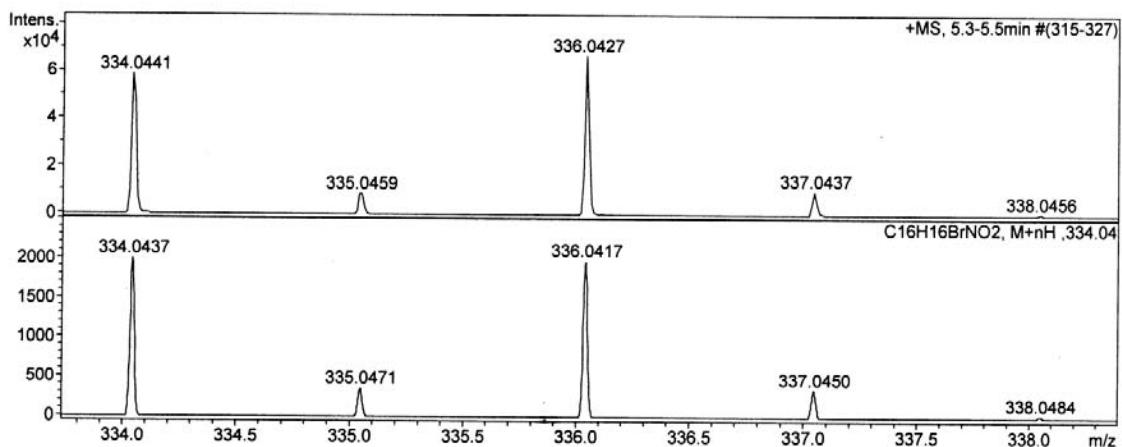
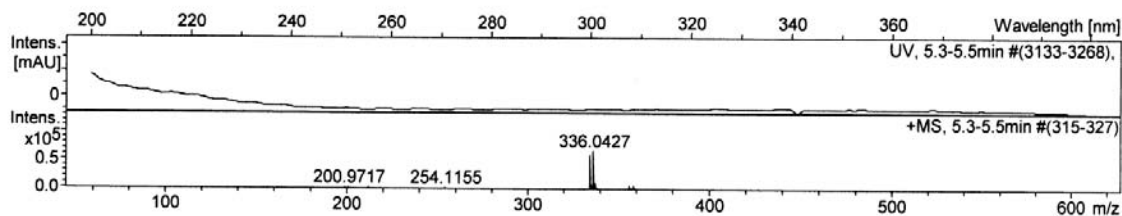
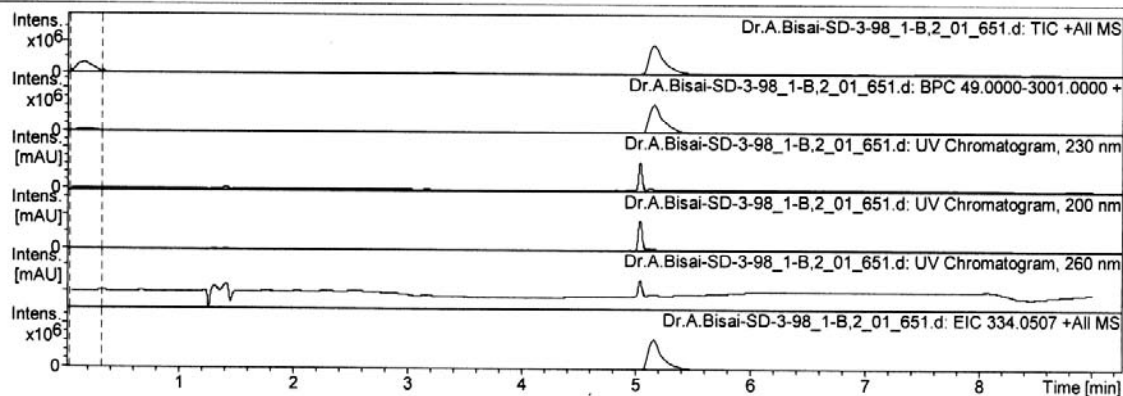
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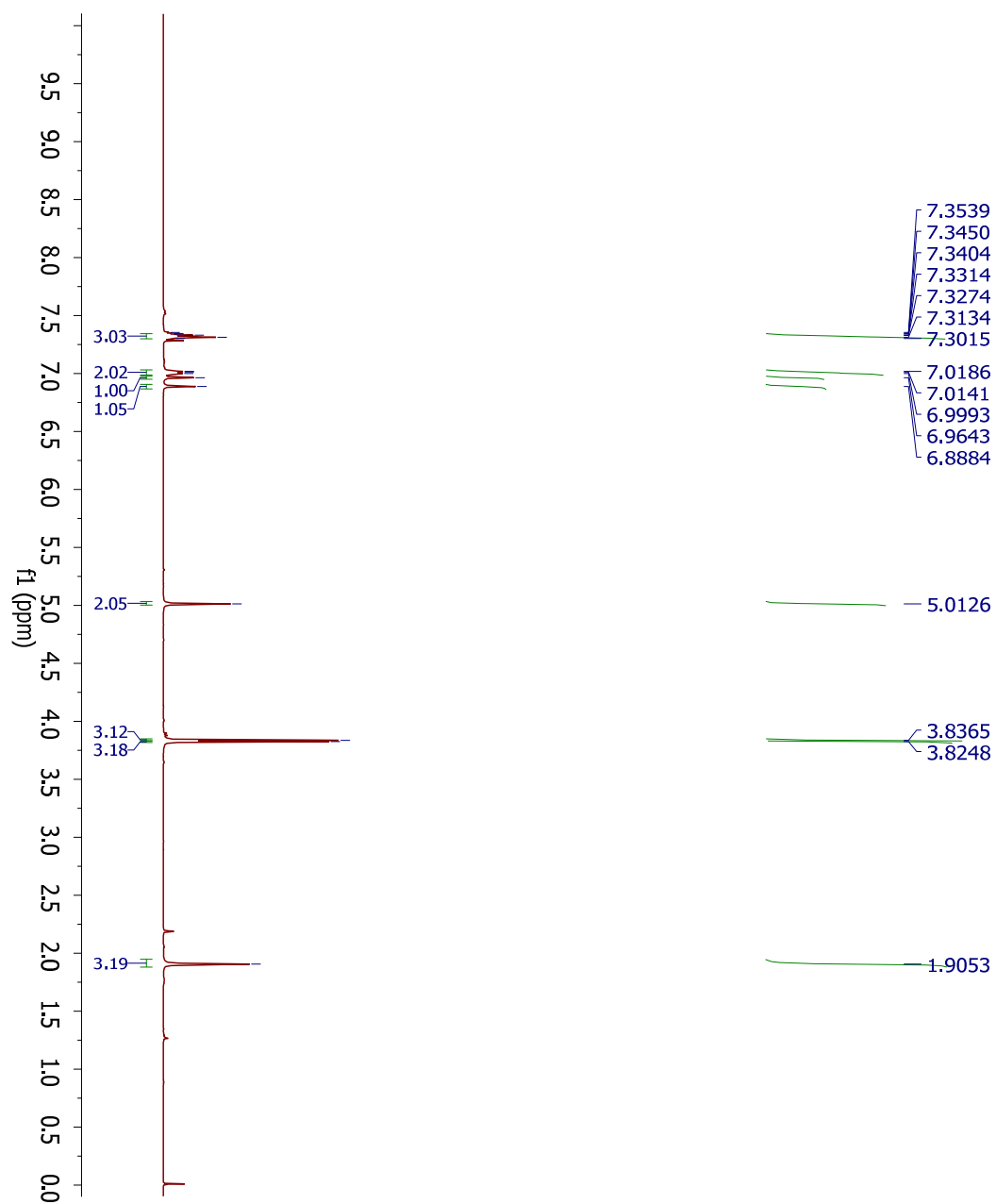
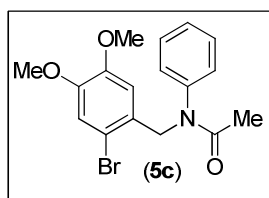
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 Method HRLCMS-20 Sept.m
 Sample Name Dr.A.Bisai-SD-3-98
 Comment

Acquisition Date 3/18/2013 12:01:02 PM
 Operator Amit
 Instrument microTOF-Q II 10330

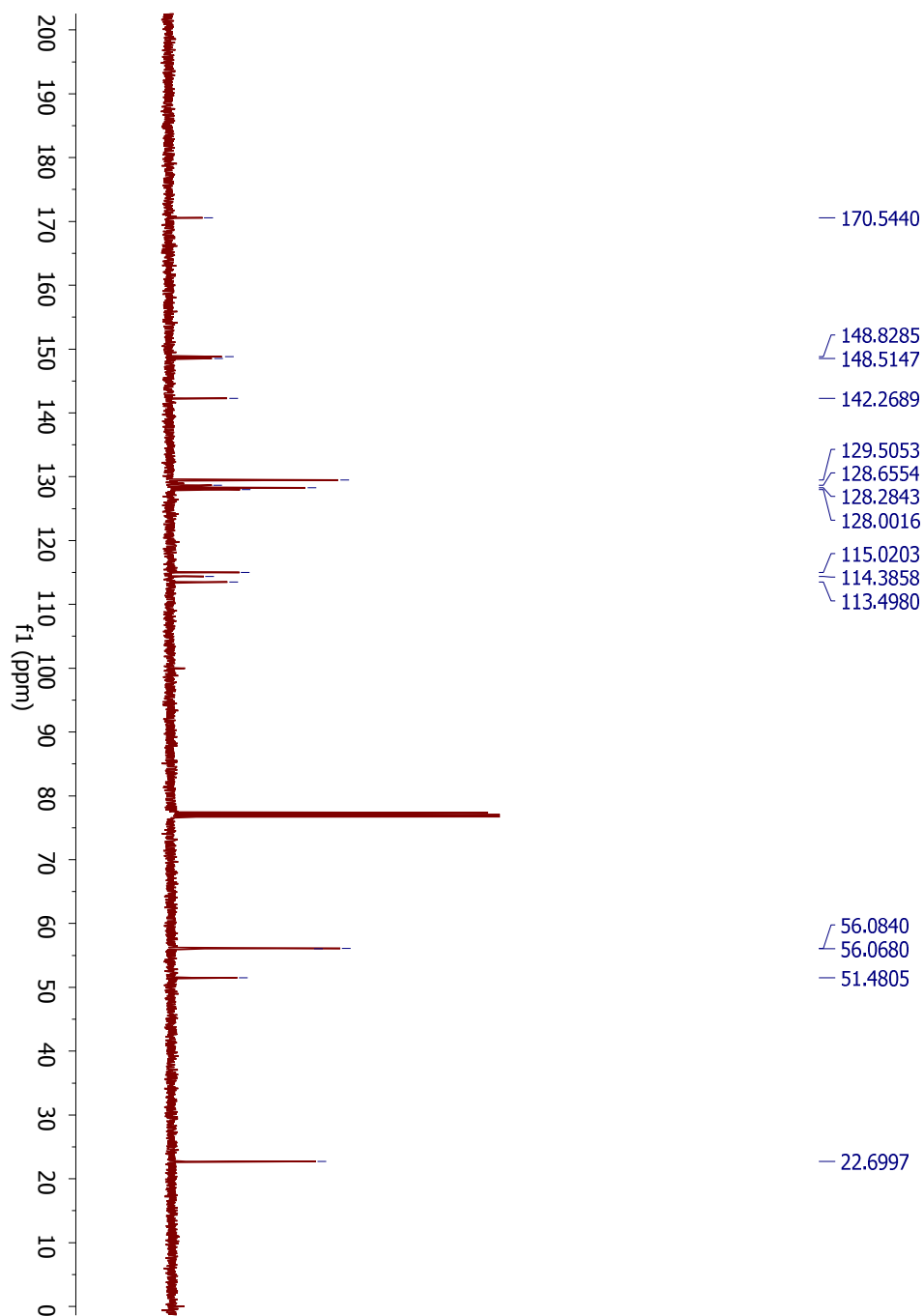
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

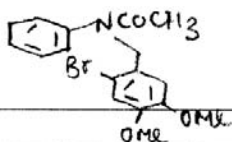




^1H NMR (400 MHz, CDCl_3) compound (5c)



^{13}C NMR (100 MHz, CDCl_3) compound **(5c)**



Display Report

Analysis Info

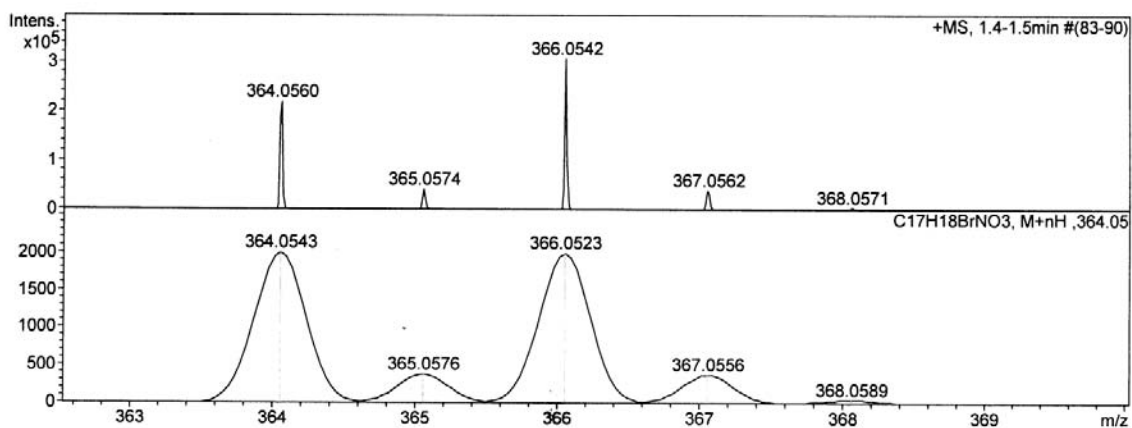
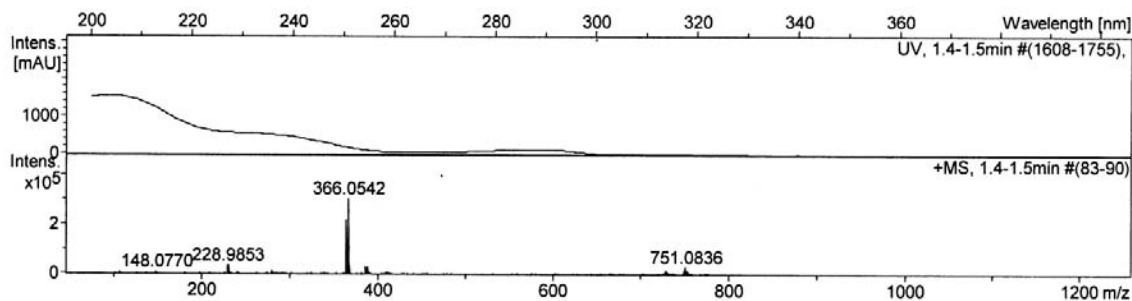
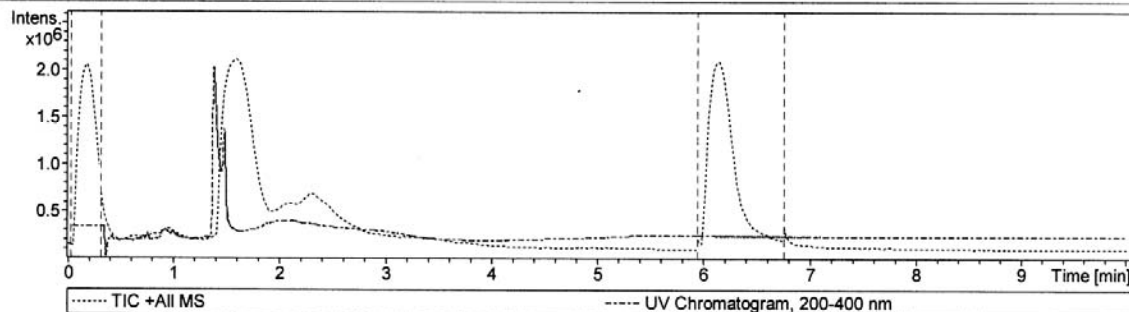
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 Sample Name Dr. A. Bisai- SD-2-392
 Comment

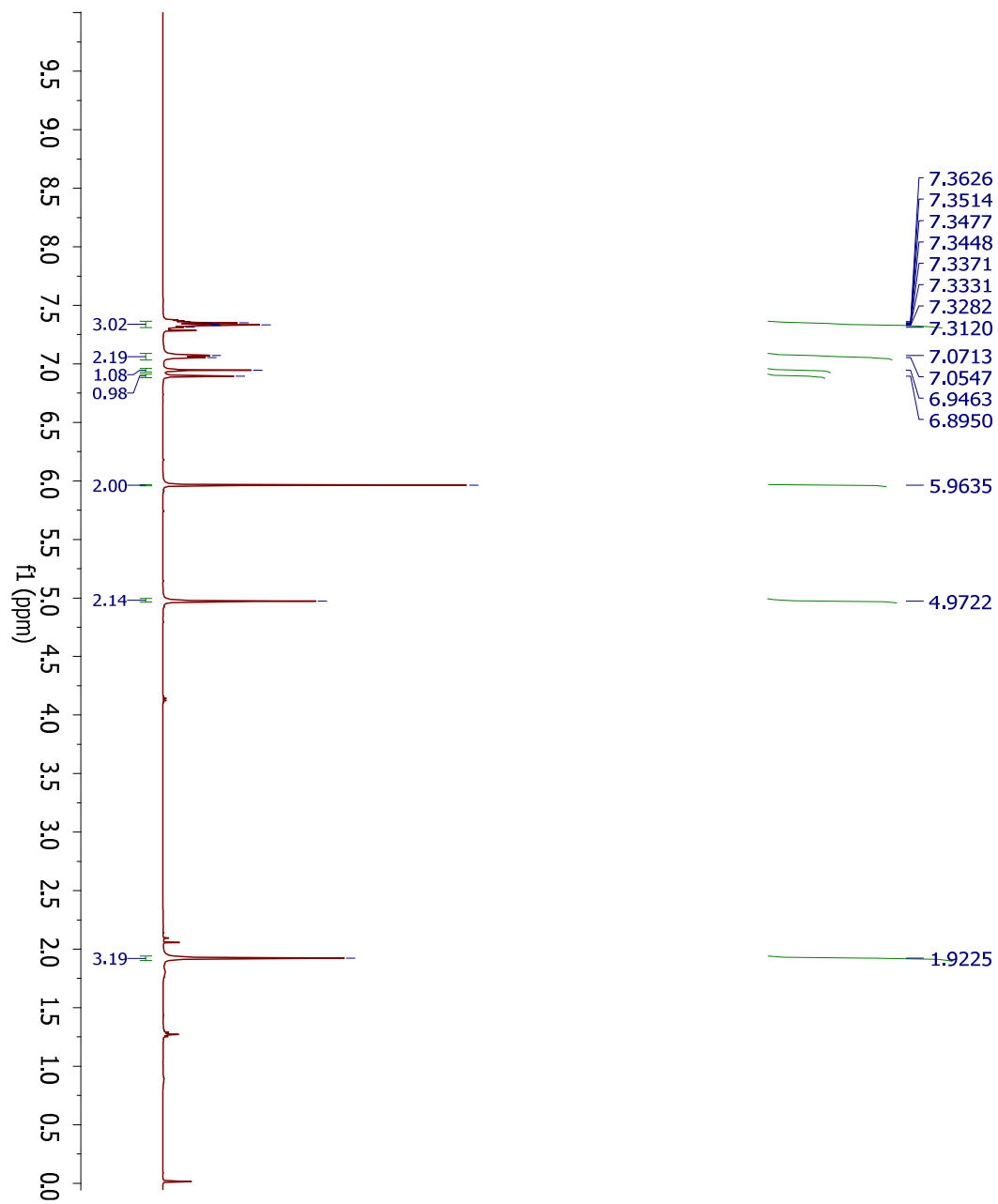
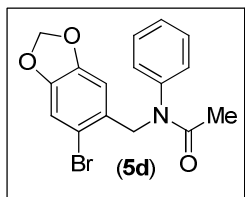
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Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

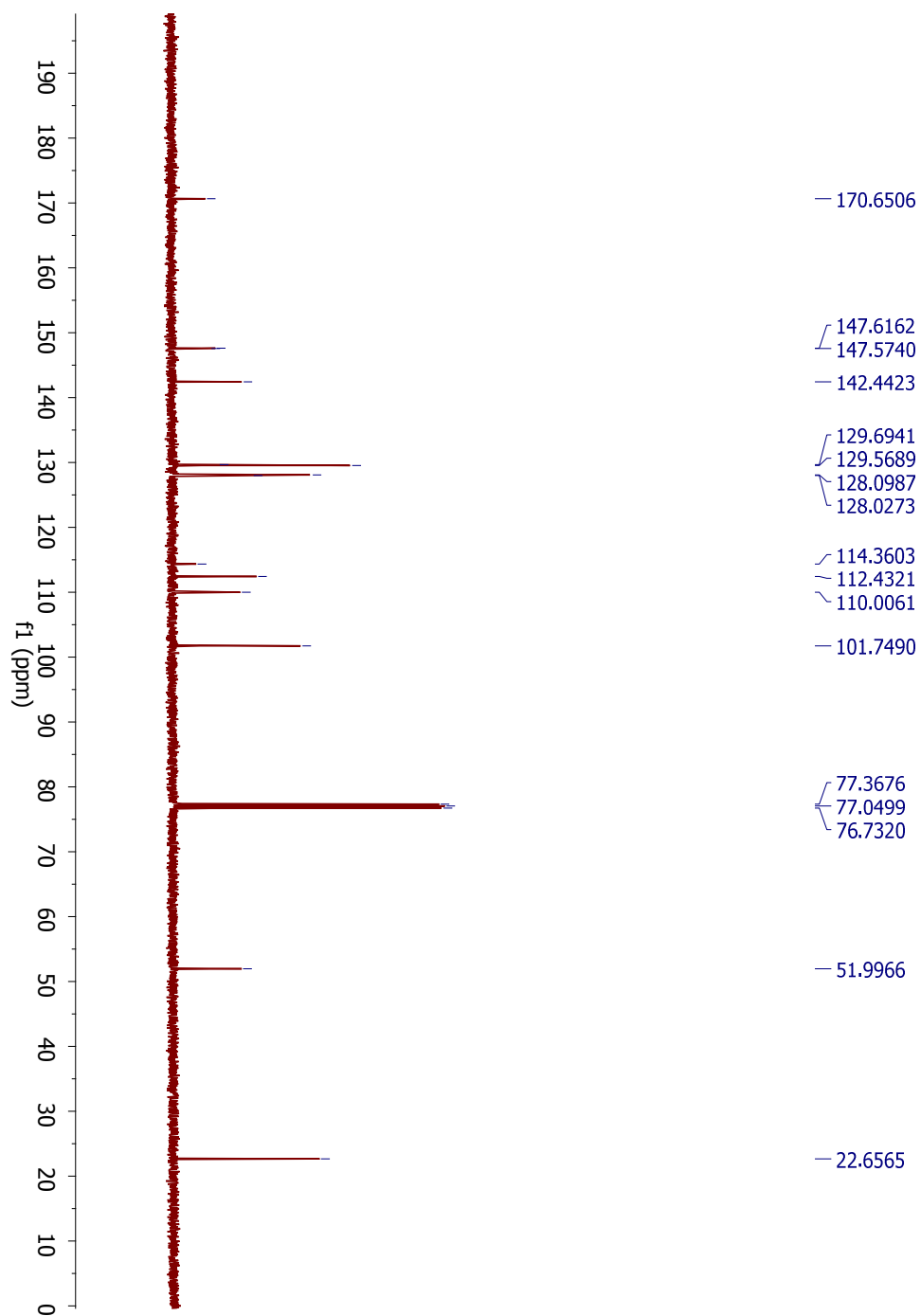
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





¹H NMR (400 MHz, CDCl₃) compound **(5d)**



^{13}C NMR (100 MHz, CDCl_3) compound **(5d)**



Display Report

Analysis Info

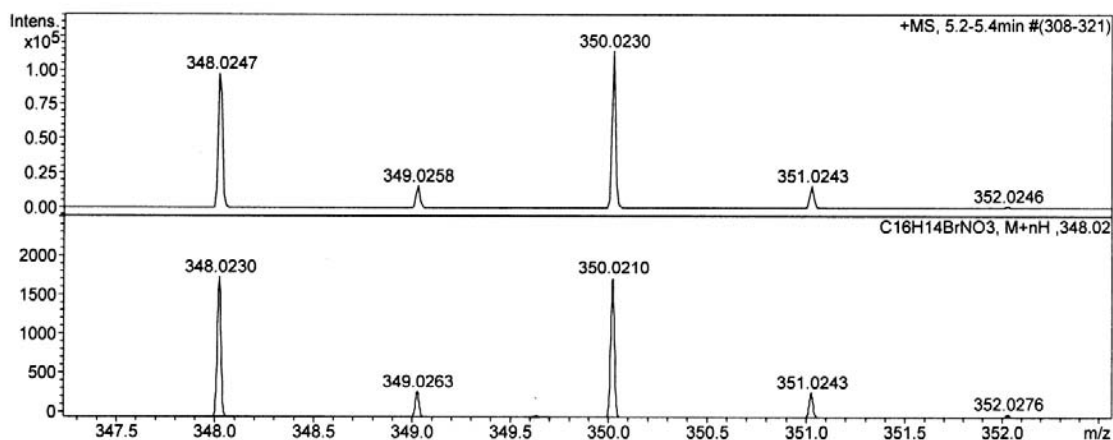
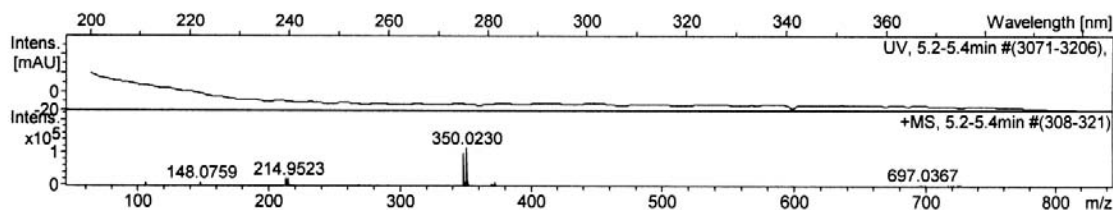
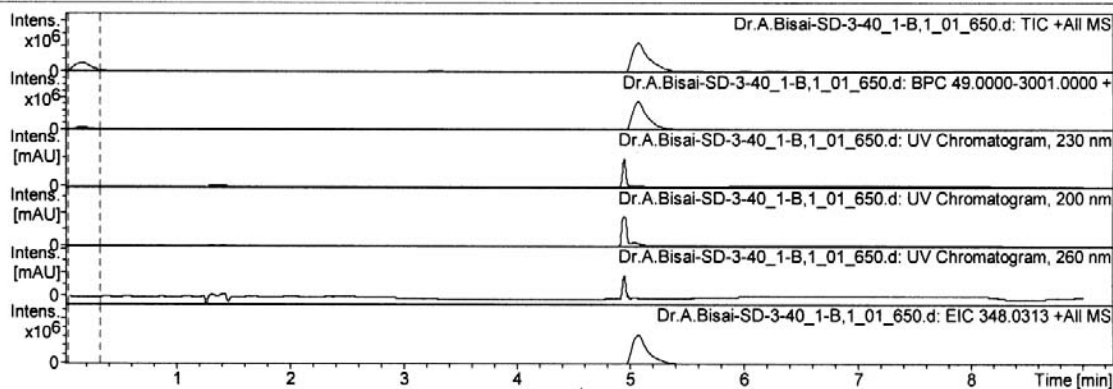
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Sample Name Dr.A.Bisai-SD-3-40
Comment

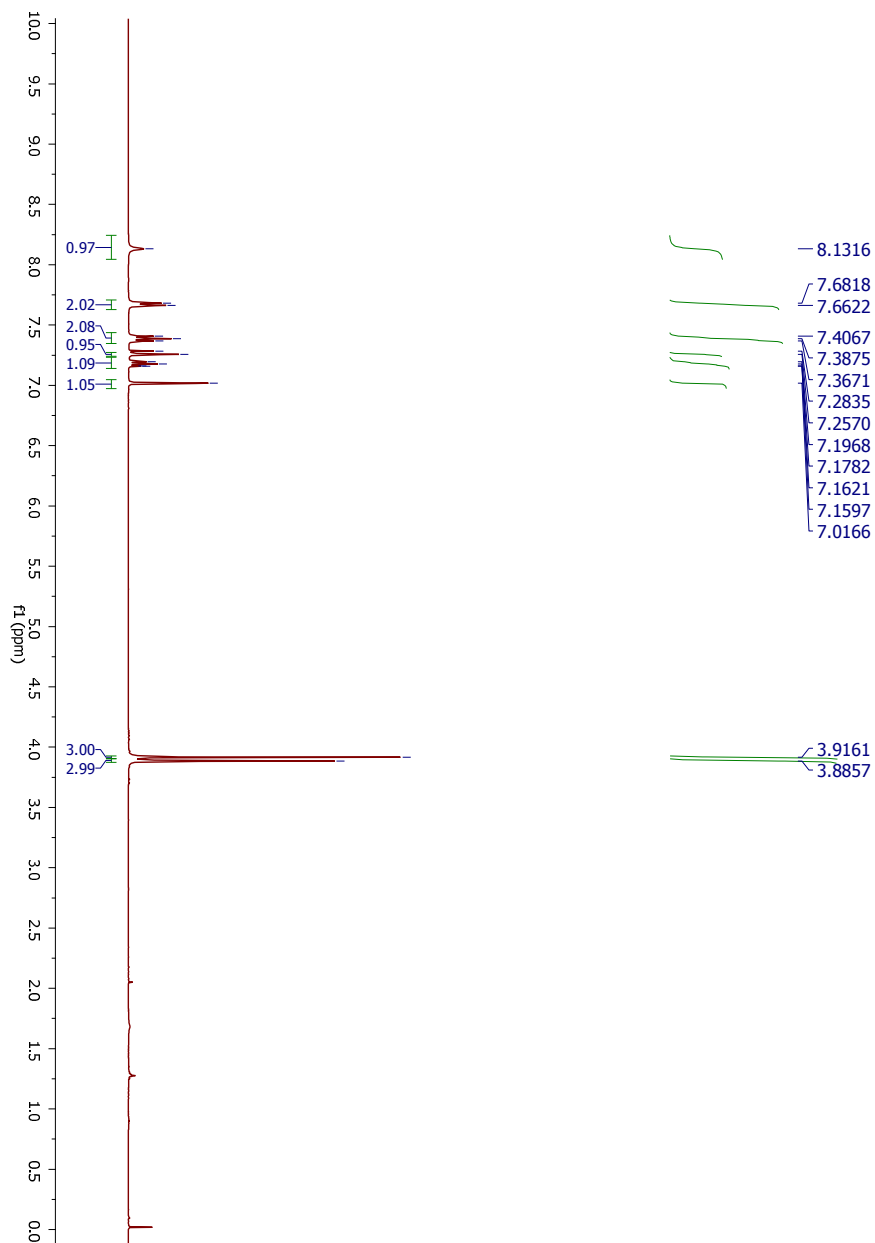
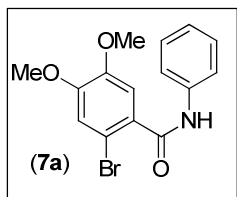
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Operator Amit
Instrument micrOTOF-Q II 10330

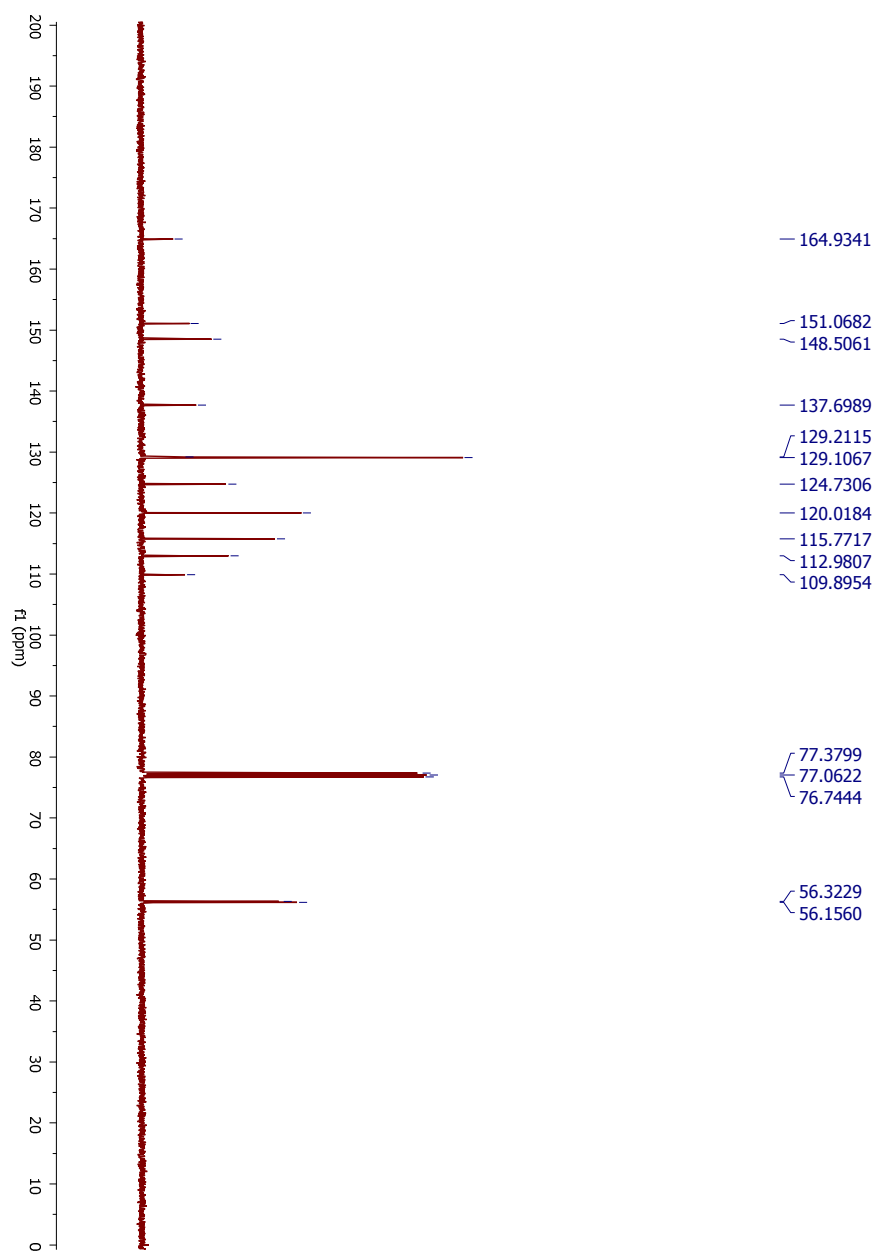
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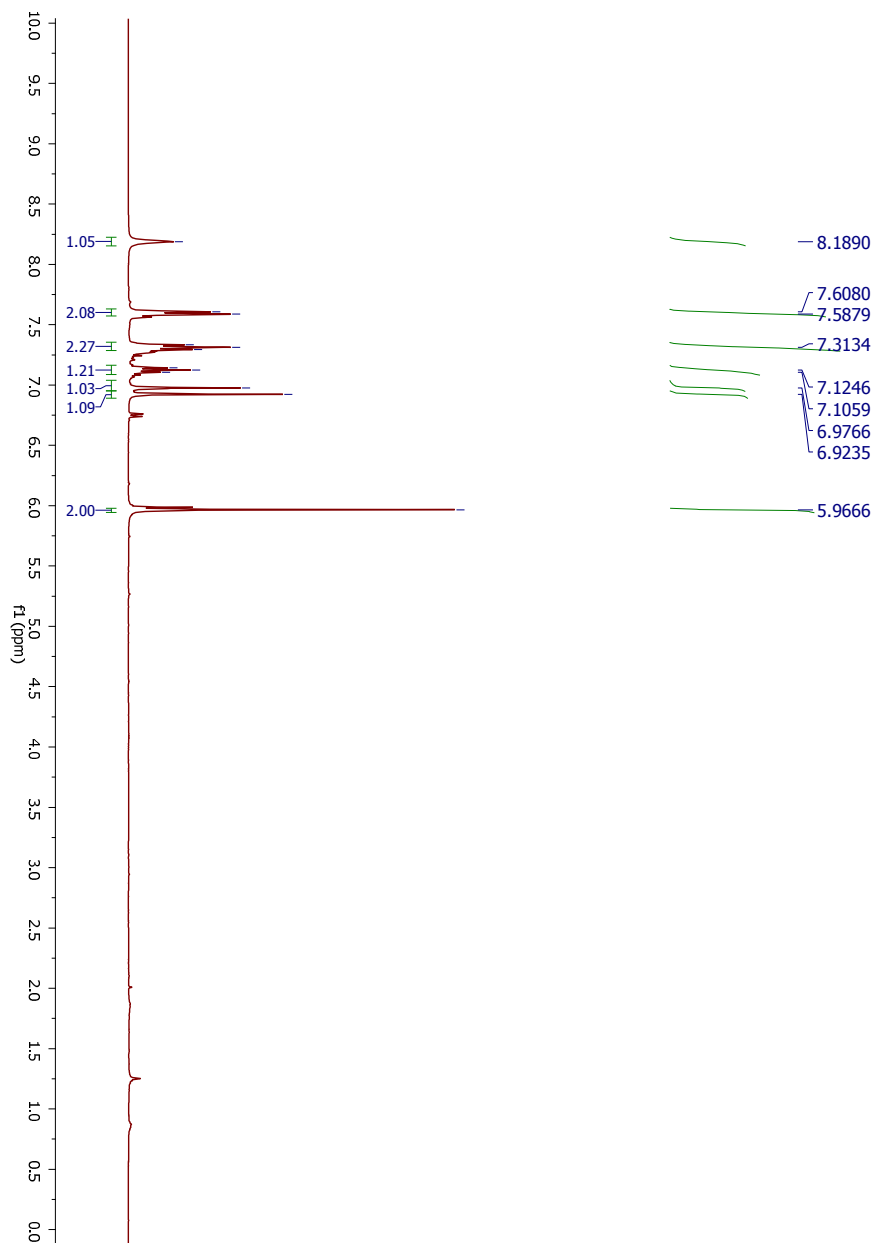
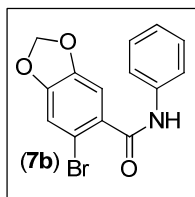




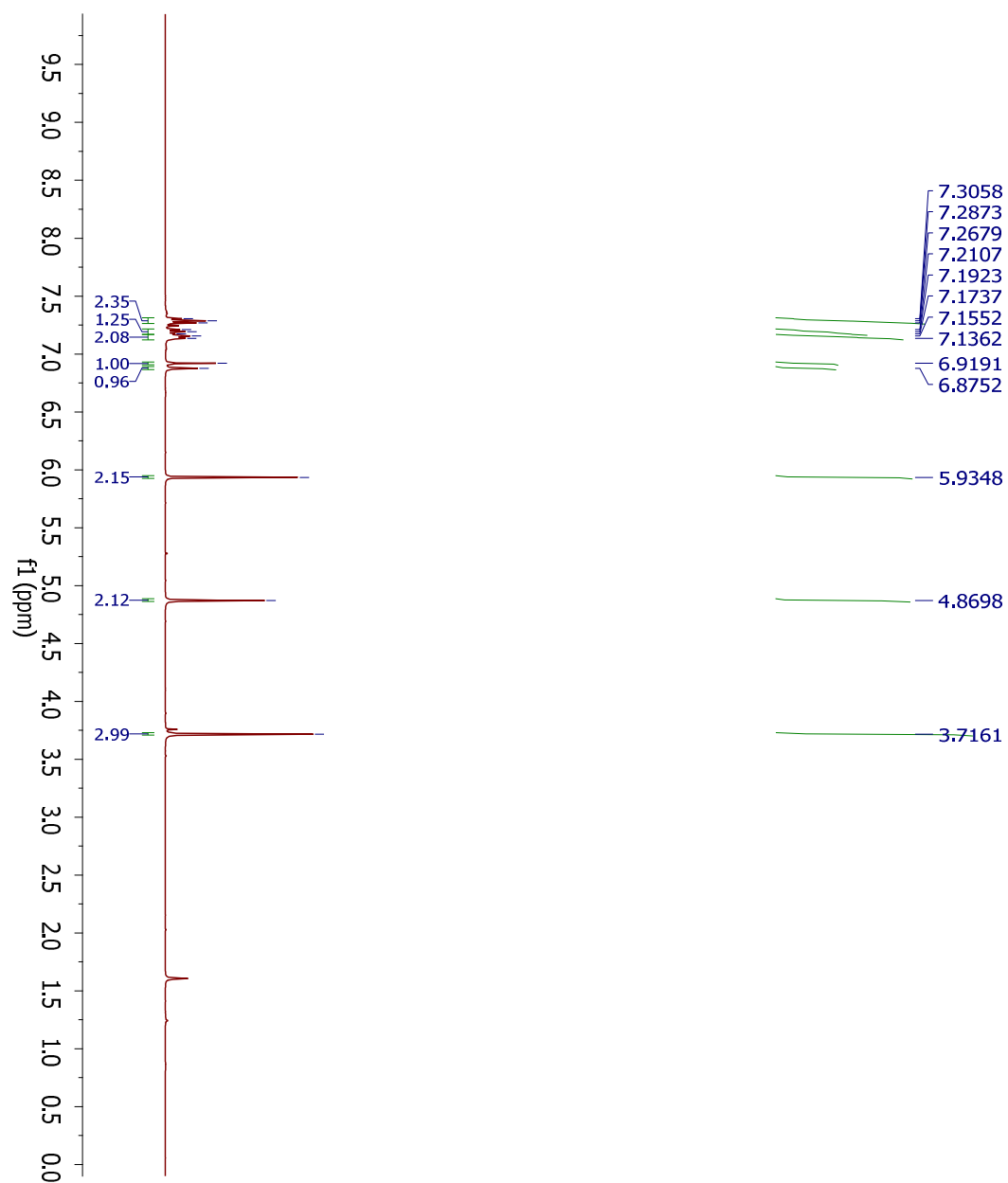
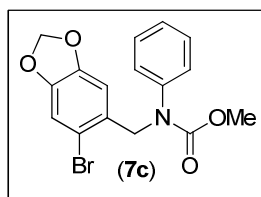
¹H NMR (400 MHz, CDCl₃) compound **(7a)**



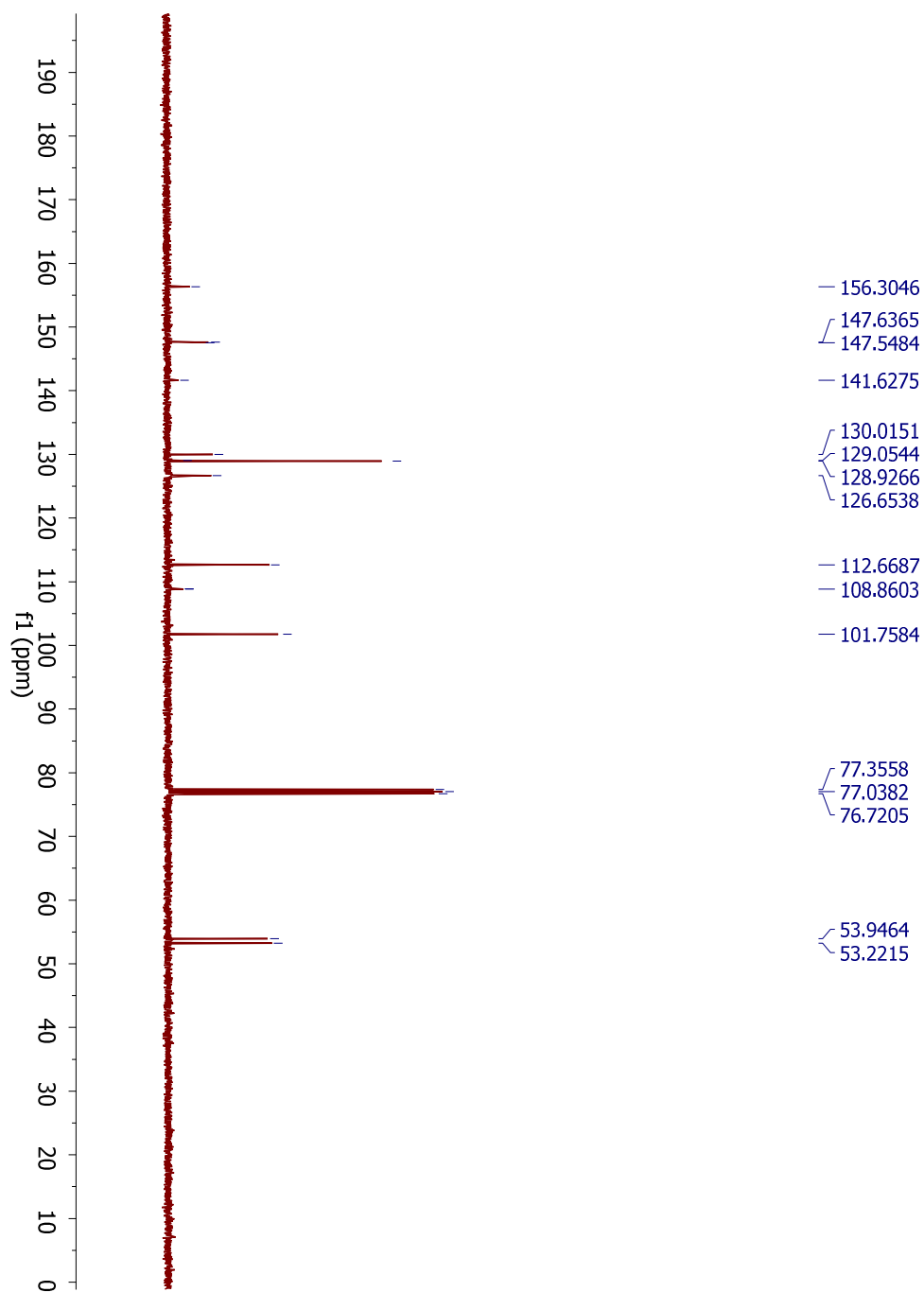
^{13}C NMR (100 MHz, CDCl_3) compound **(7a)**



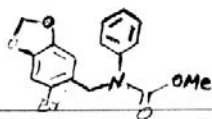
¹H NMR (400 MHz, CDCl₃) compound **(7b)**



^1H NMR (400 MHz, CDCl_3) compound **(7c)**



^{13}C NMR (100 MHz, CDCl_3) compound **(7c)**



Display Report

Analysis Info

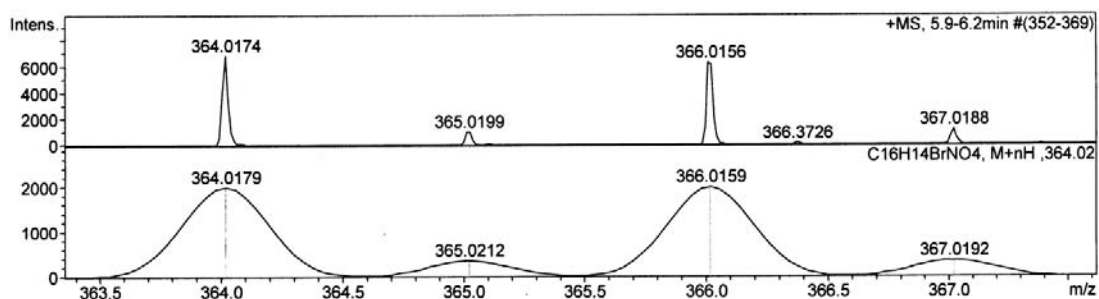
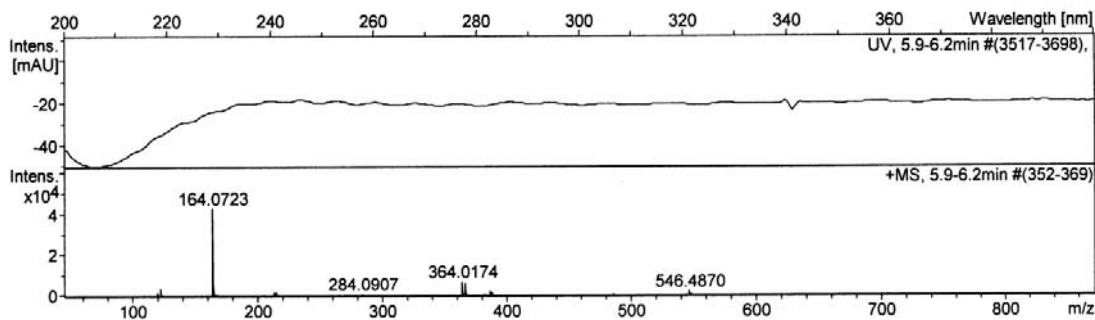
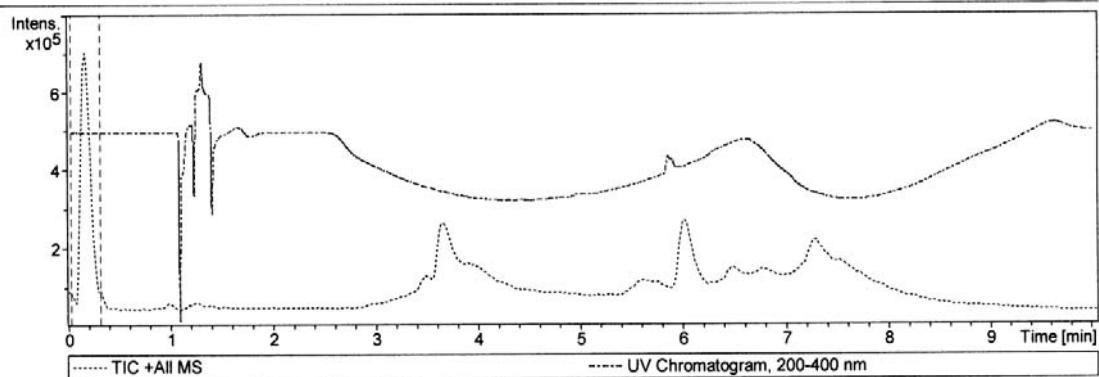
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Method HRLCMS-20 Sept.m
Sample Name Dr.A.Bisai-SM-1-45
Comment

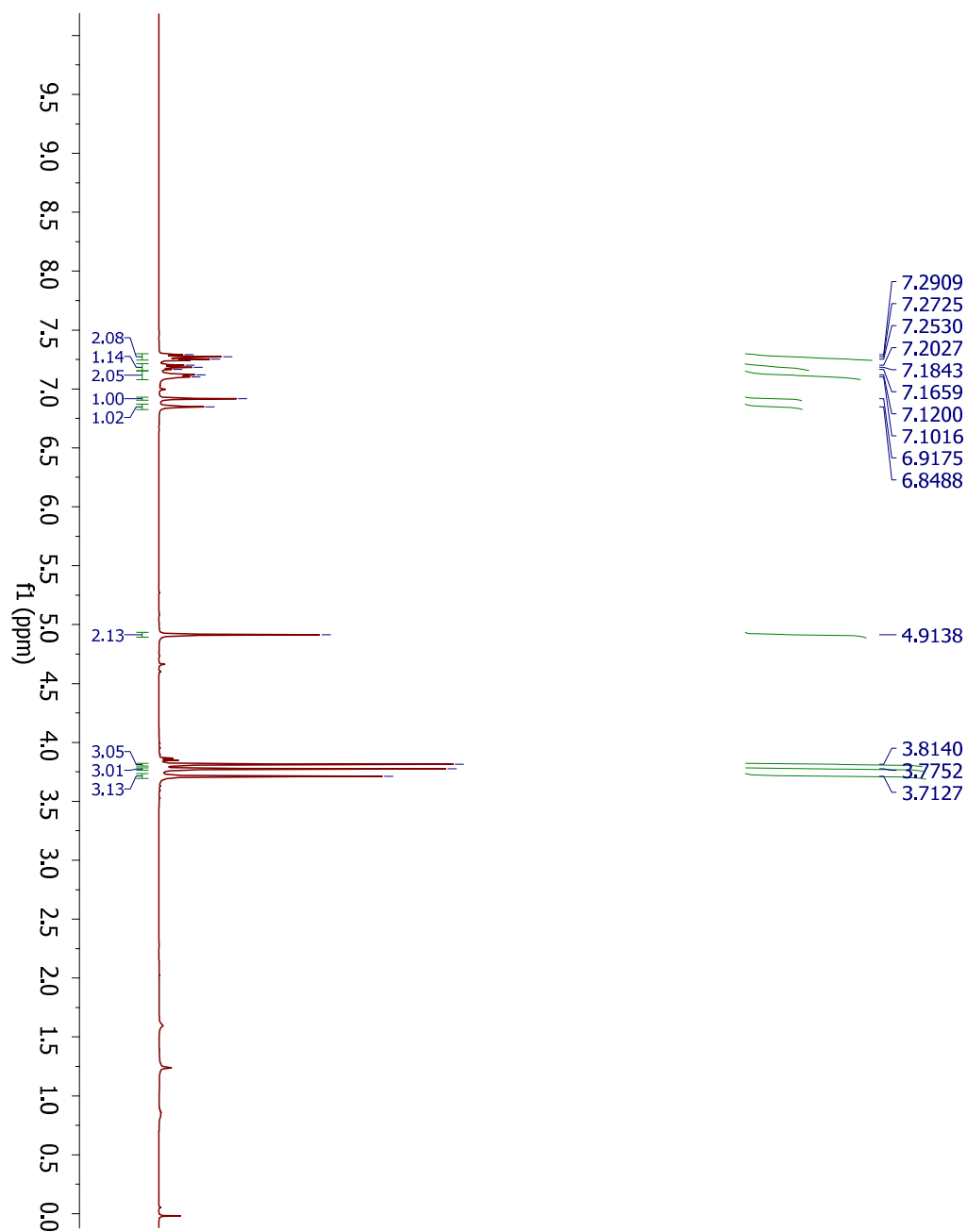
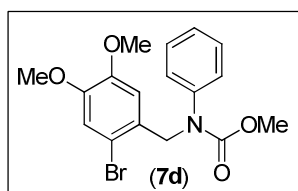
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Operator Meena Sharma
Instrument microTOF-Q II 10330

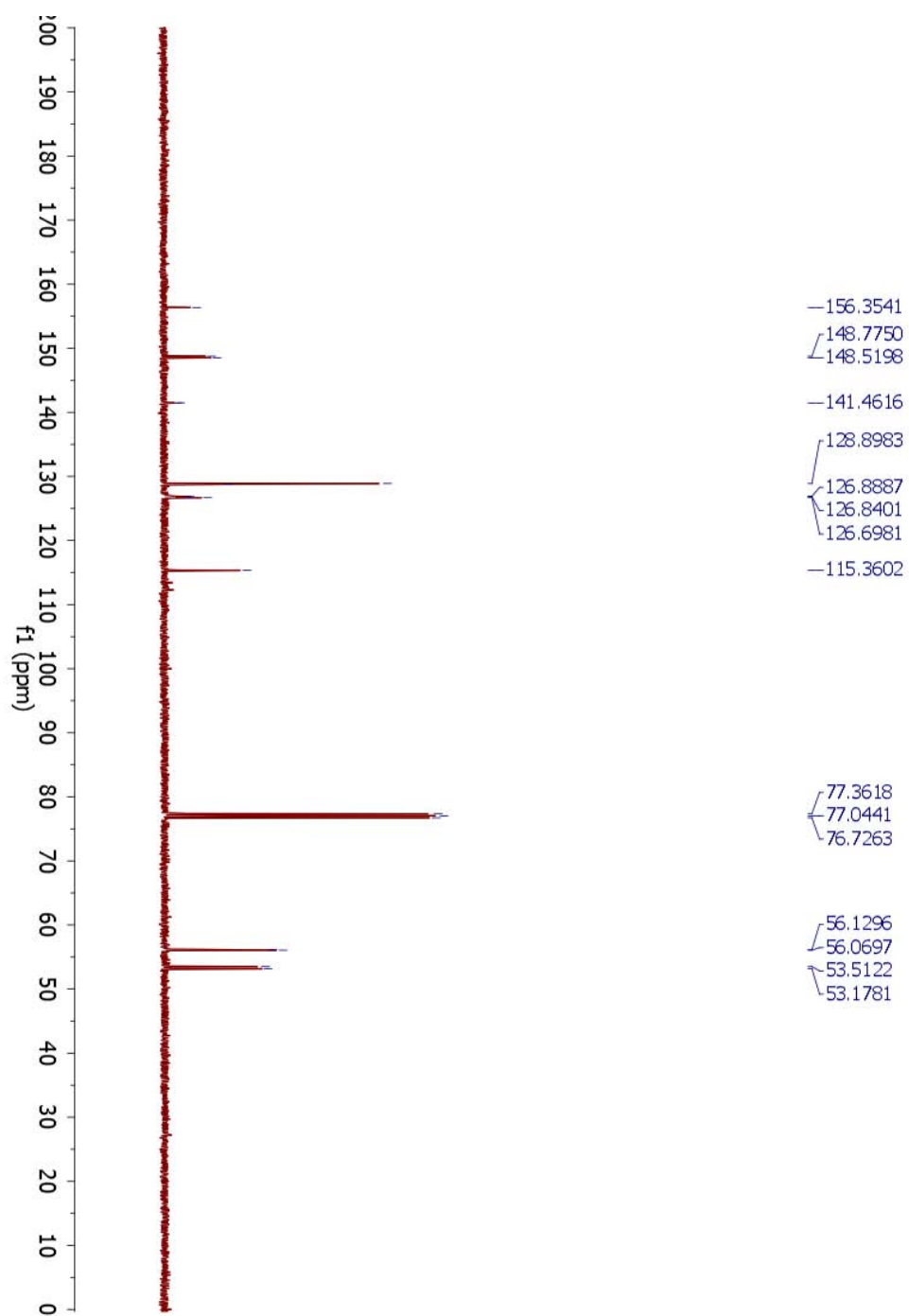
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





^1H NMR (400 MHz, CDCl_3) compound **(7d)**



^{13}C NMR (100 MHz, CDCl_3) compound **(7d)**



Display Report

Analysis Info

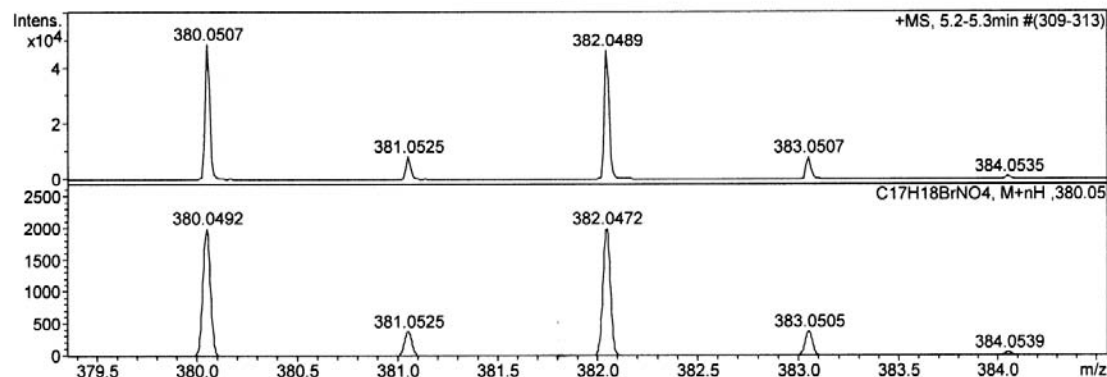
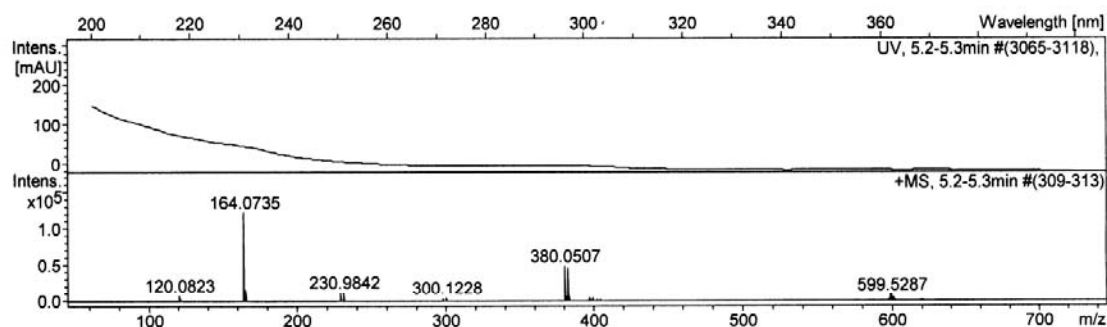
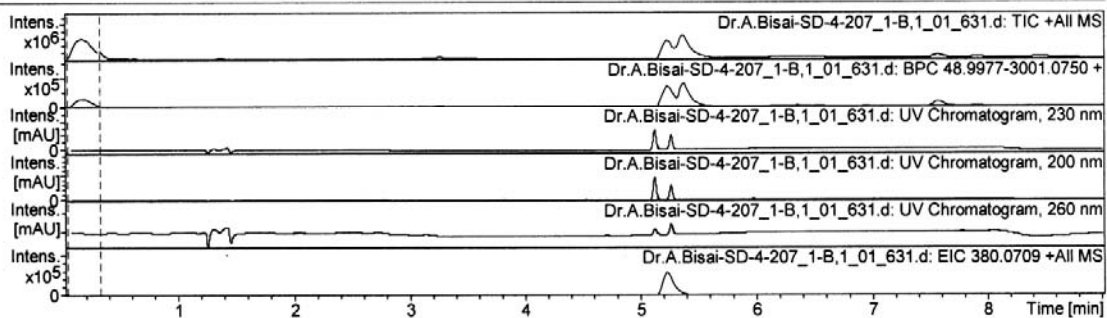
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 Comment

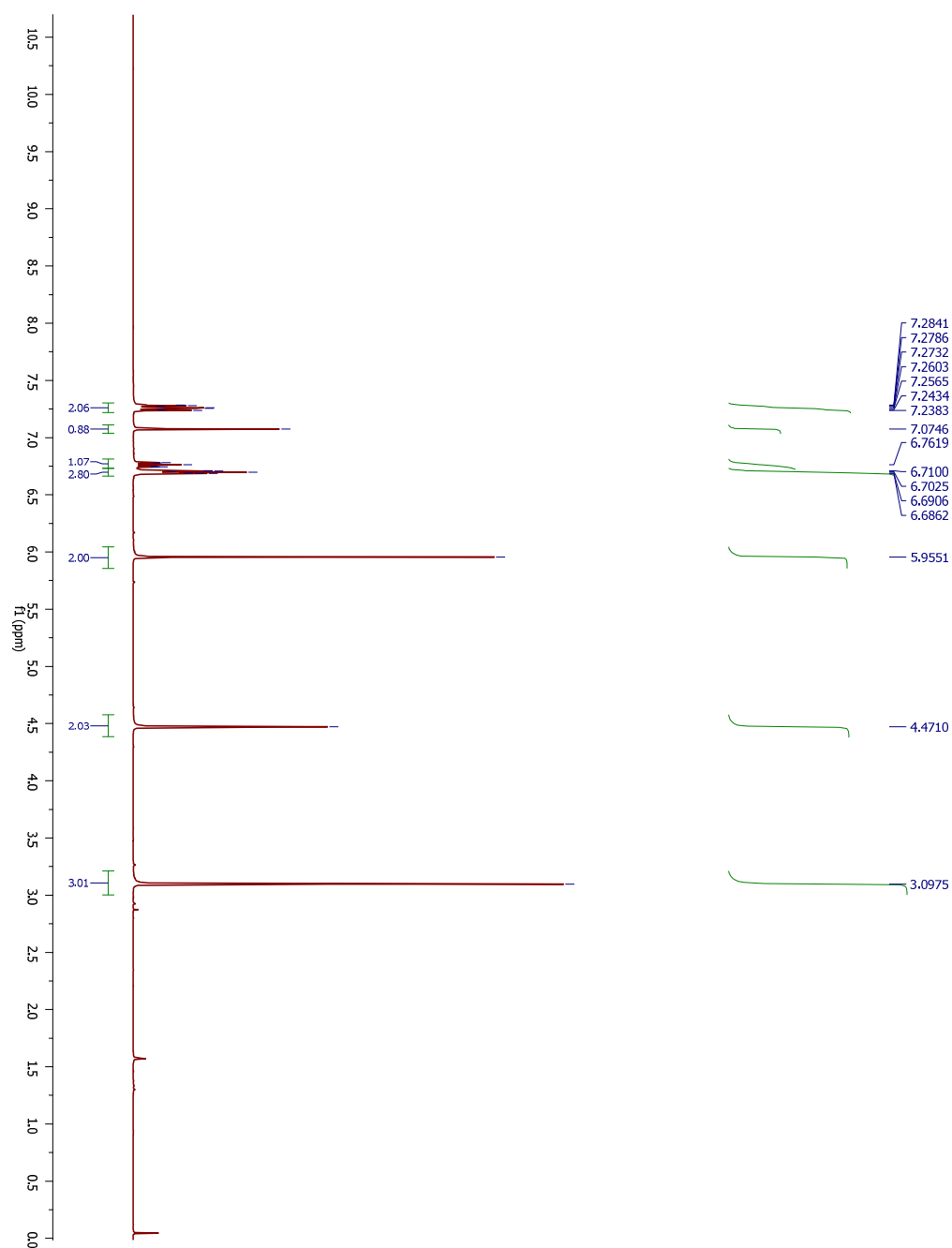
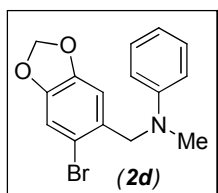
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Operator Amit
 Instrument micrOTOF-Q II 10330

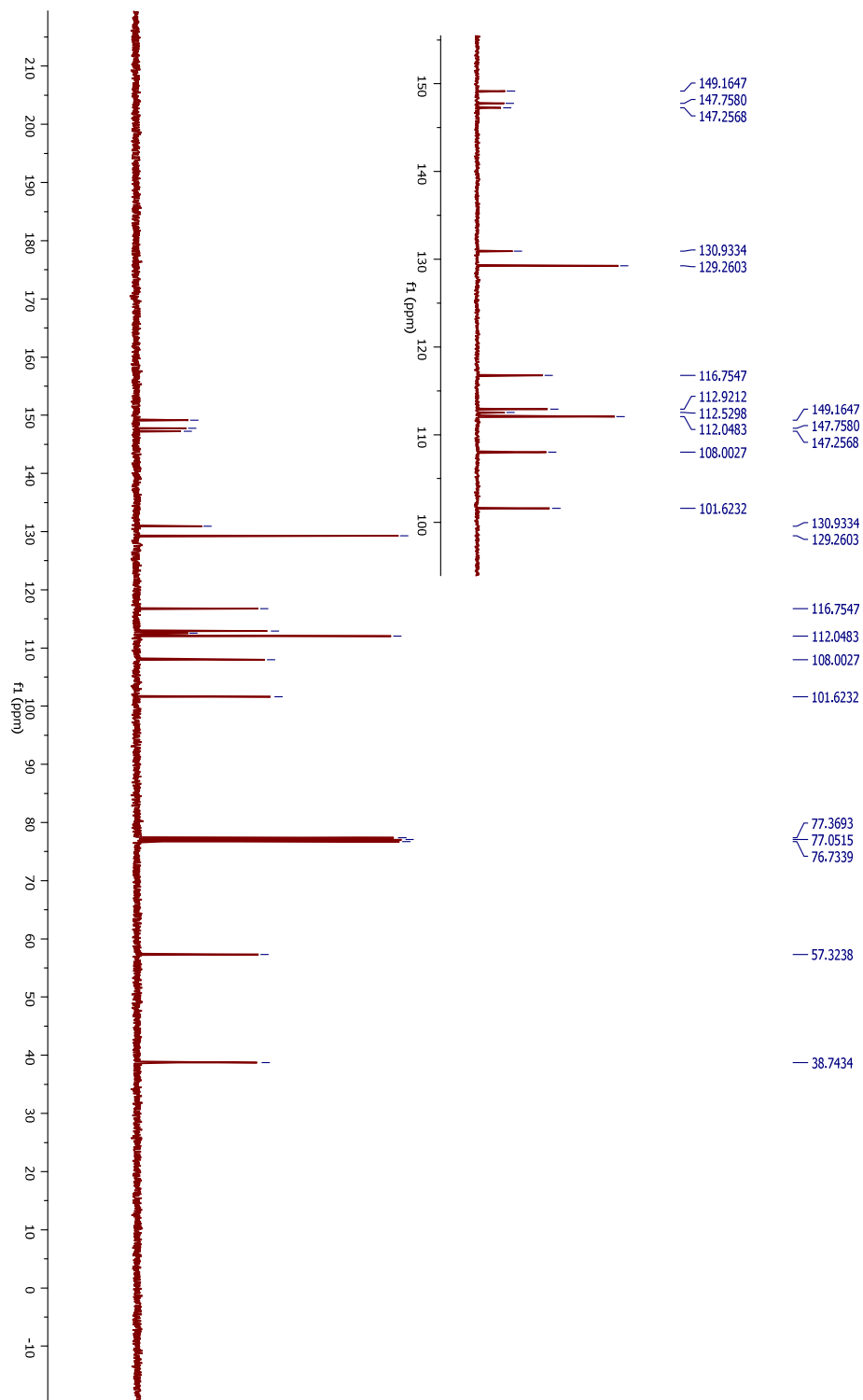
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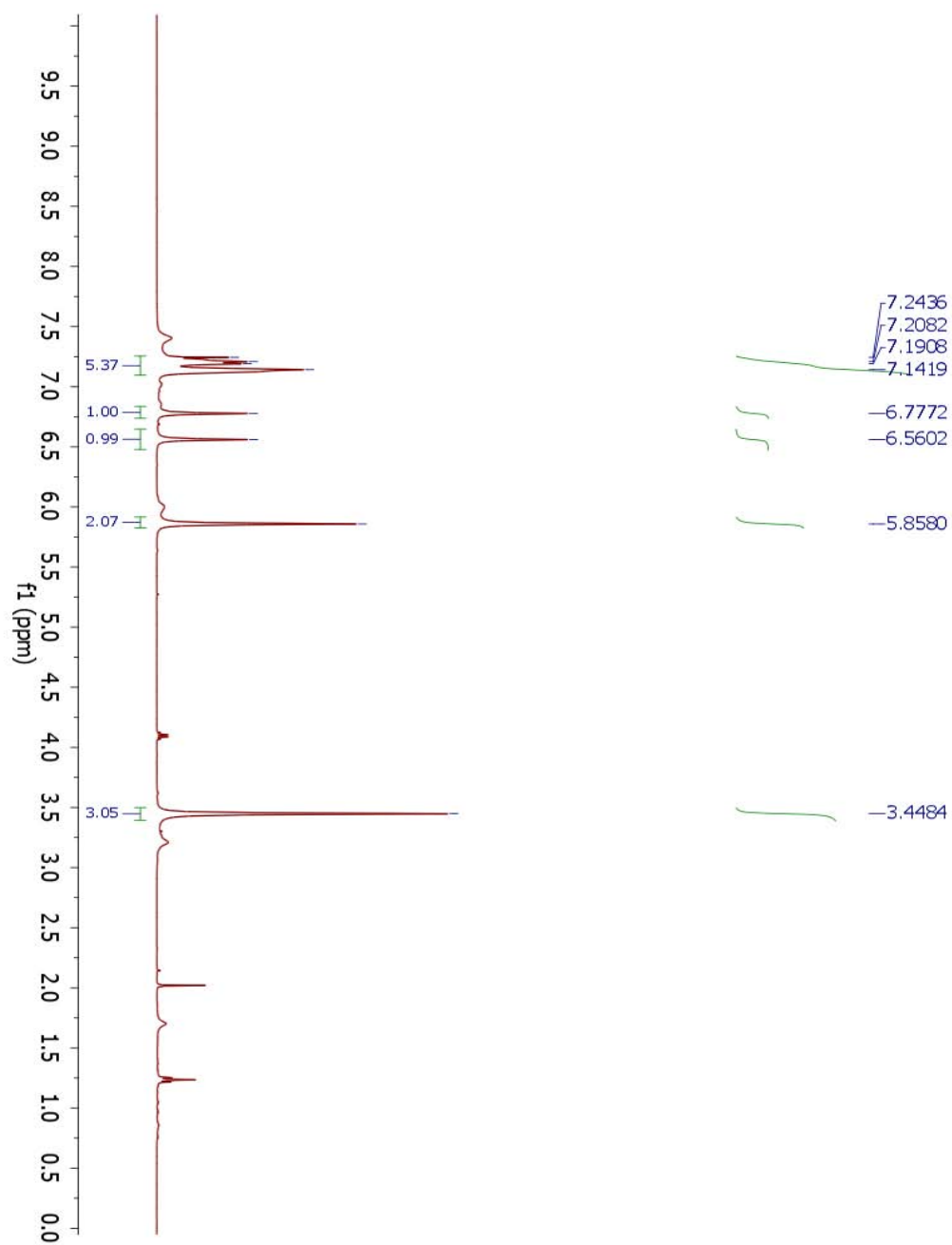
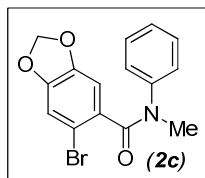
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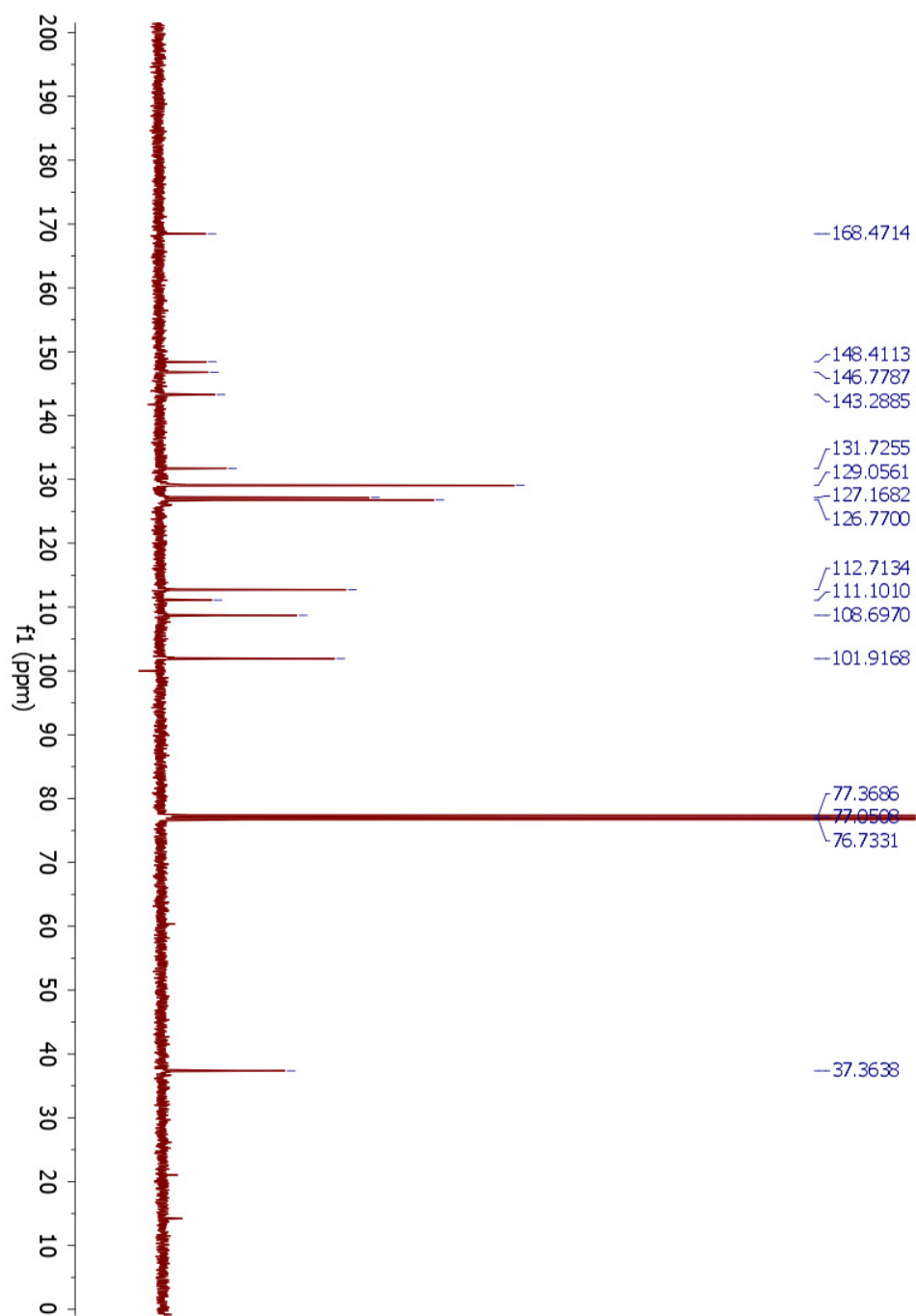


^1H NMR (400 Hz, CDCl_3) compound **(2d)**





^1H NMR (400 MHz, CDCl_3) compound (2c)



^{13}C NMR (100 MHz, CDCl_3) compound **(2c)**

Display Report

Analysis Info

Analysis Name	D:\Data\user data\NOV 2012\16 NOV\Dr.A.Bisai-SM-1-83_1-A,3_01_4416.d
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Comment	

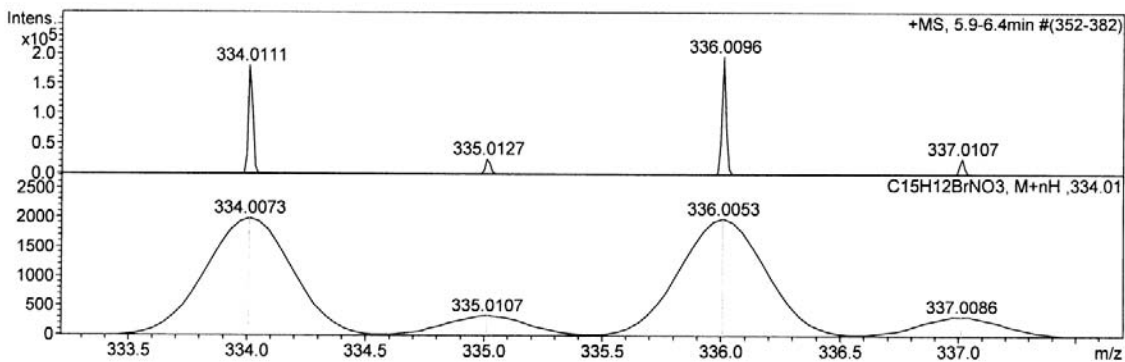
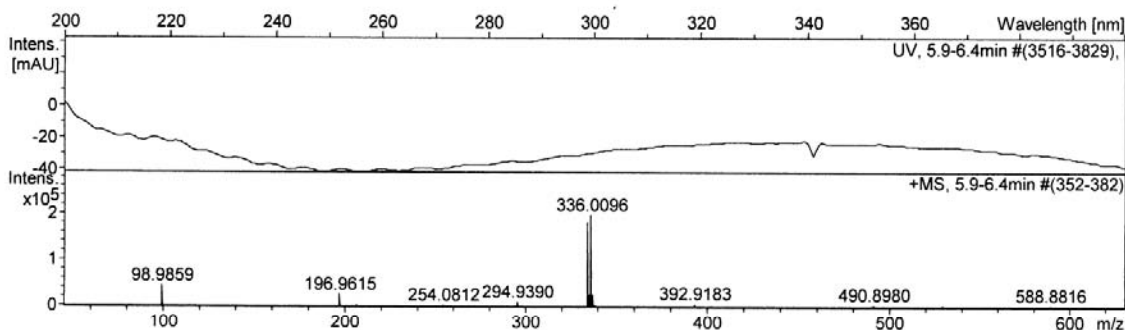
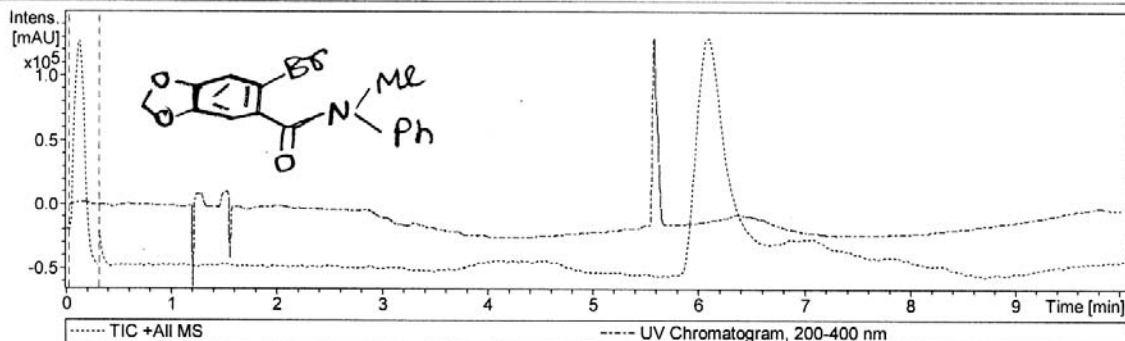
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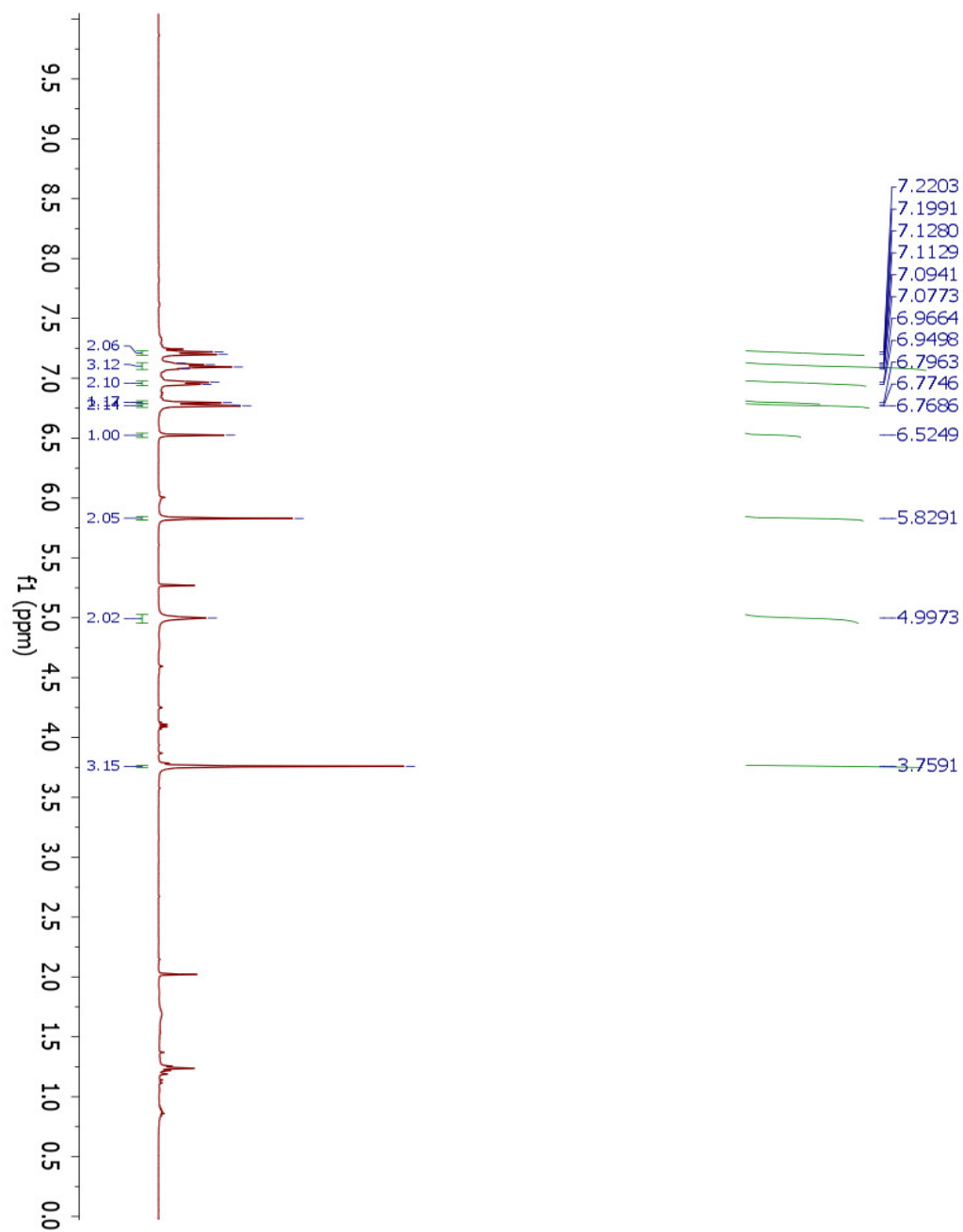
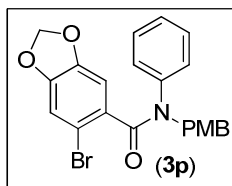
Operator Meena Sharma

Instrument micrOTOF-Q II 10330

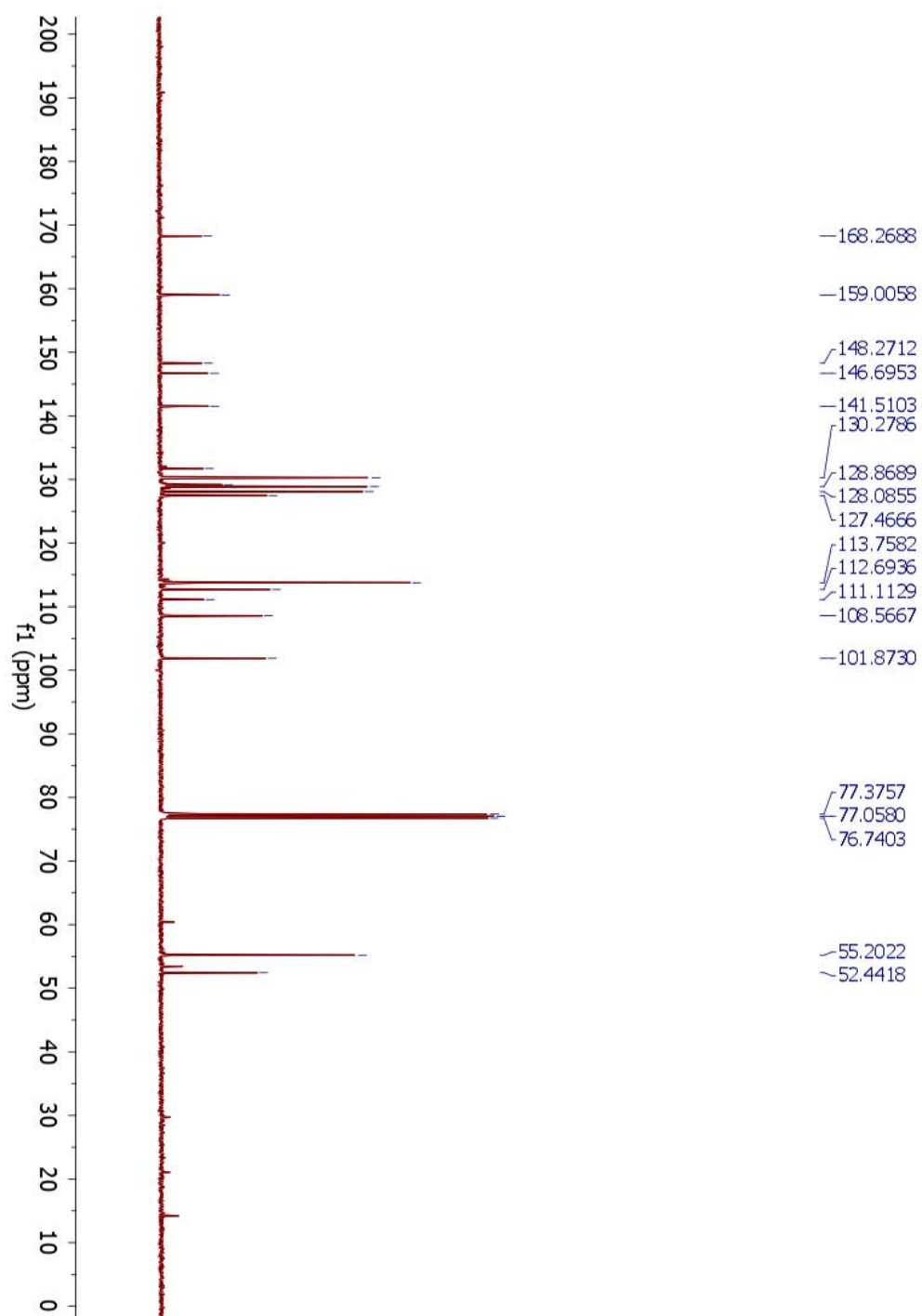
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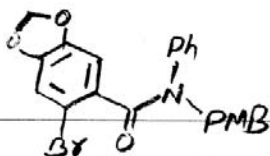




^1H NMR (400 MHz, CDCl_3) compound **(3p)**



^{13}C NMR (100 MHz, CDCl_3) compound **(3p)**



Display Report

Analysis Info

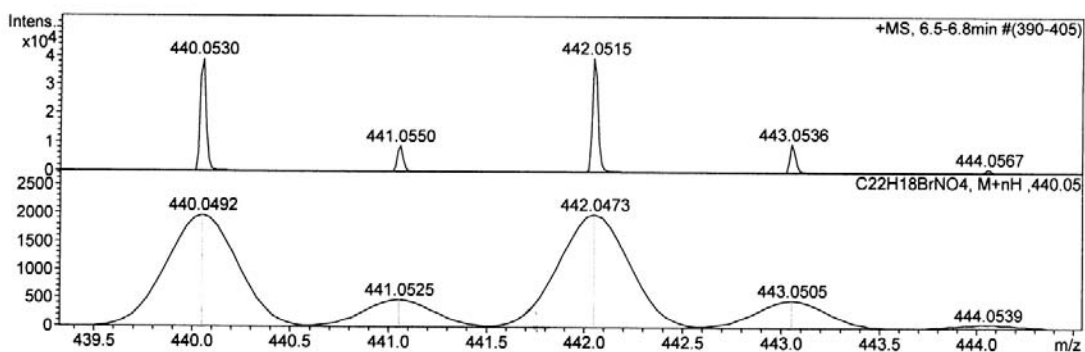
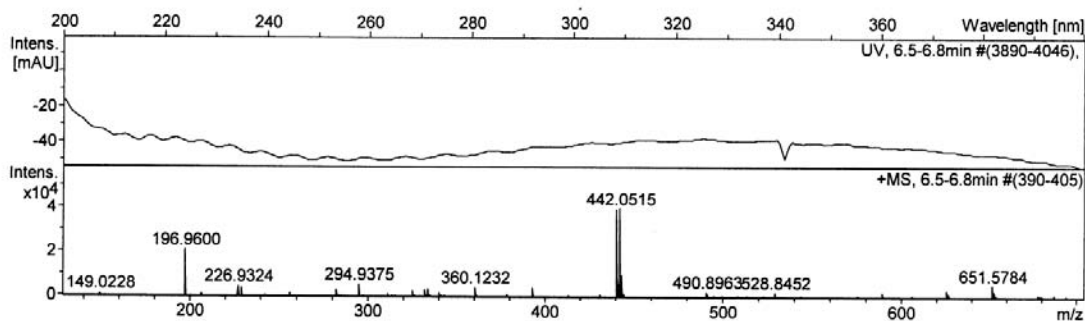
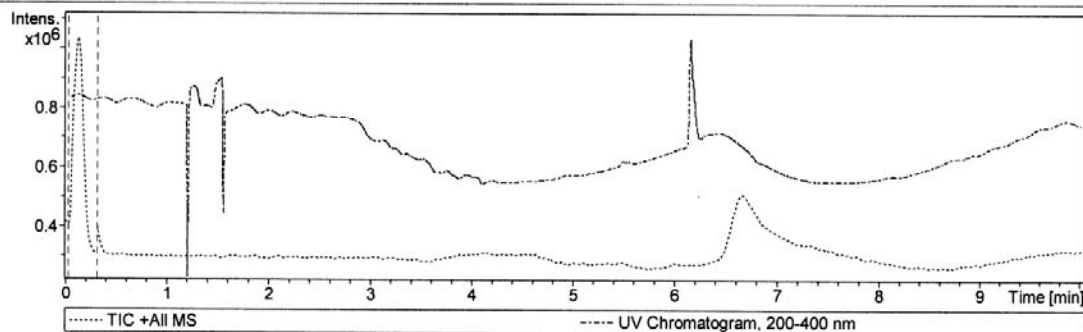
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Method HRLCMS-20 Sept.m
Sample Name Dr.A.Bisai-SM-1-82
Comment

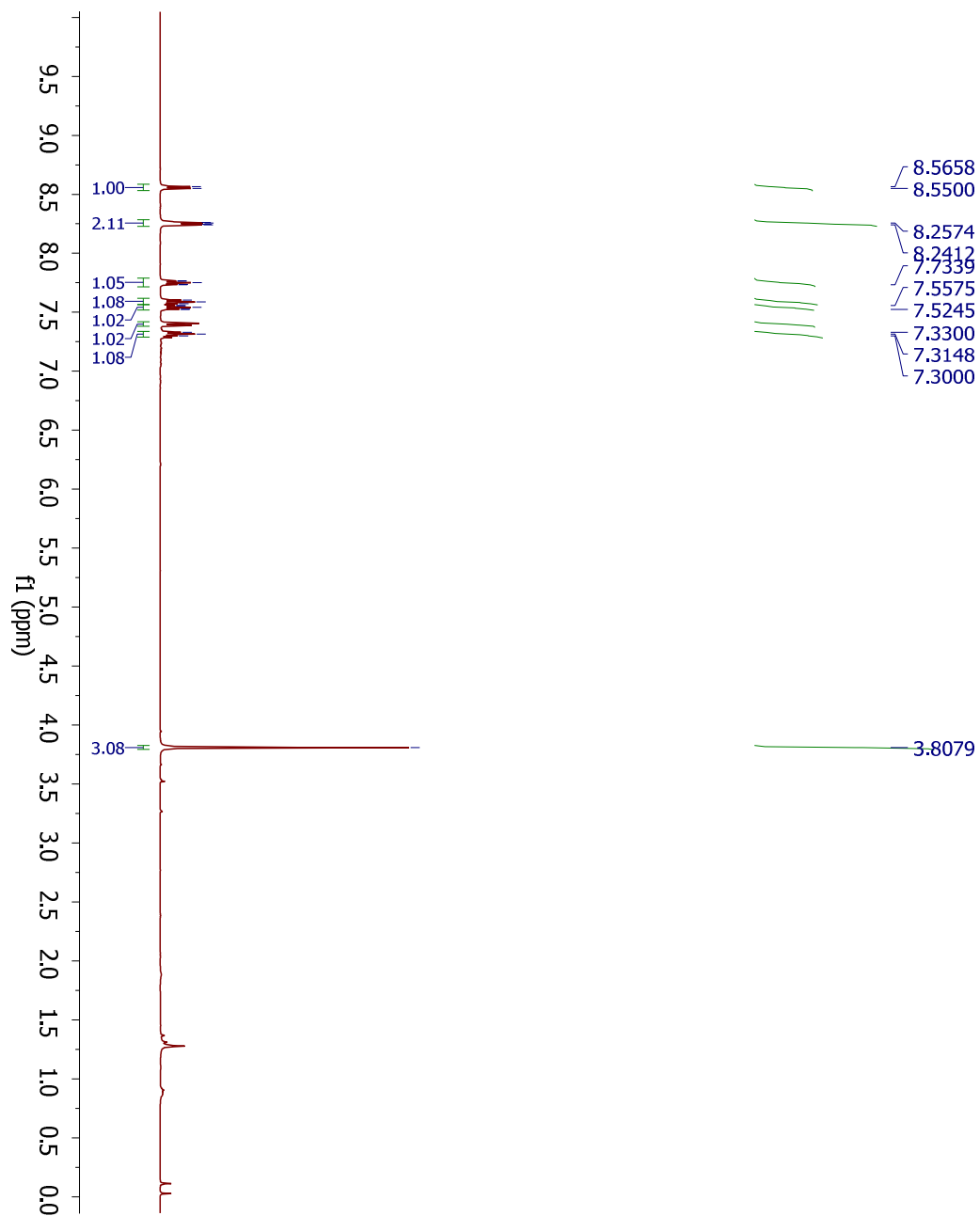
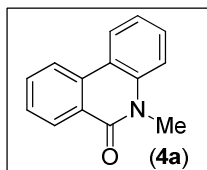
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Operator Meena Sharma
Instrument micrOTOF-Q II 10330

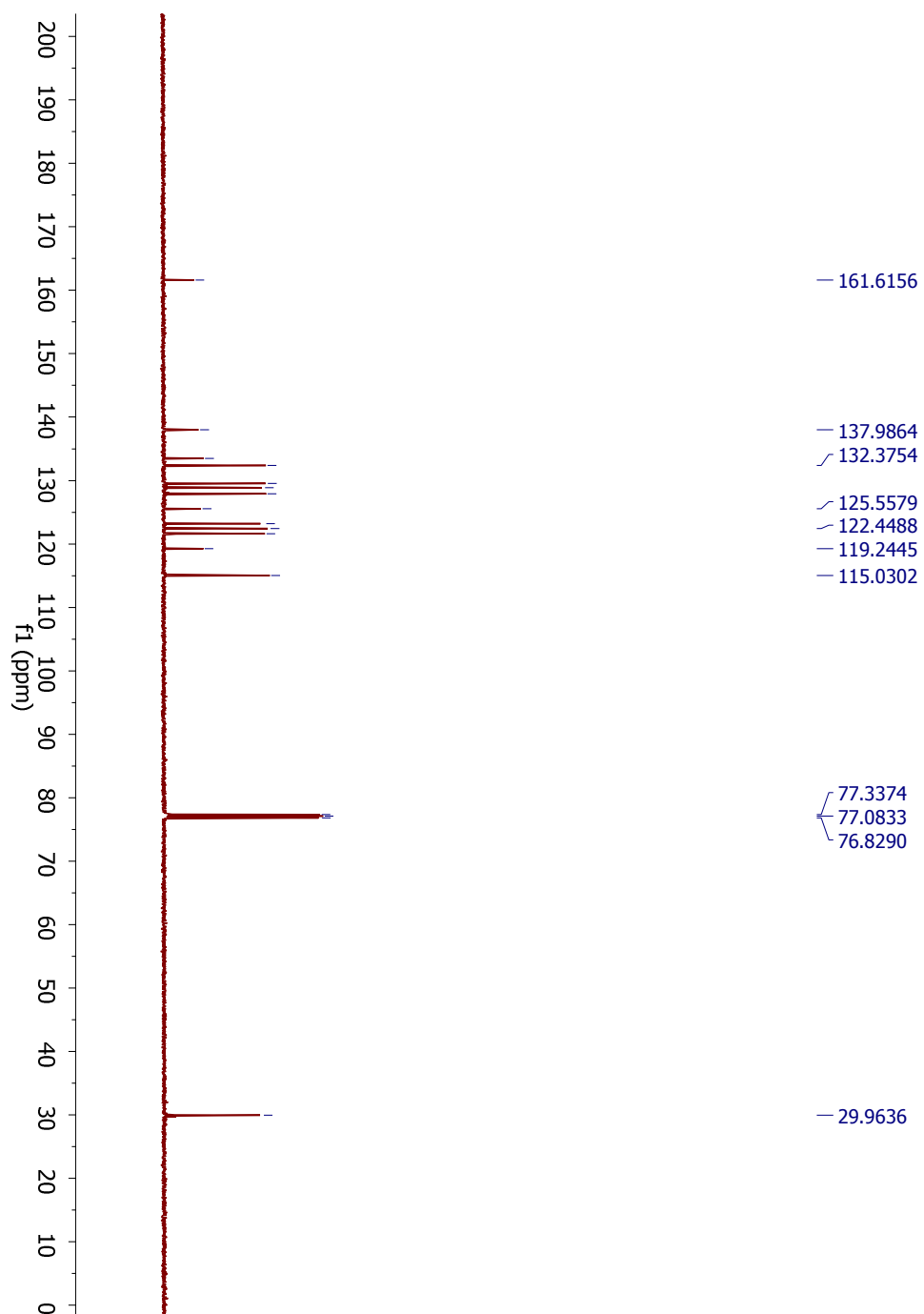
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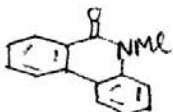




¹H NMR (400 MHz, CDCl₃) compound **(4a)**



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



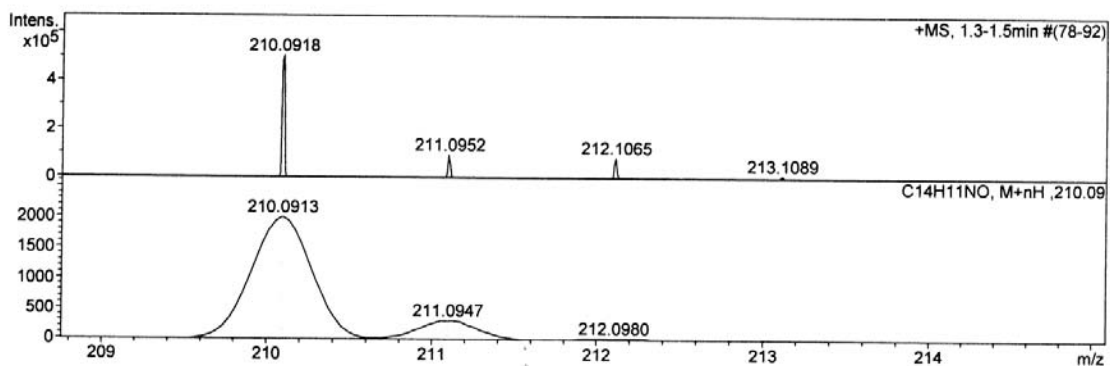
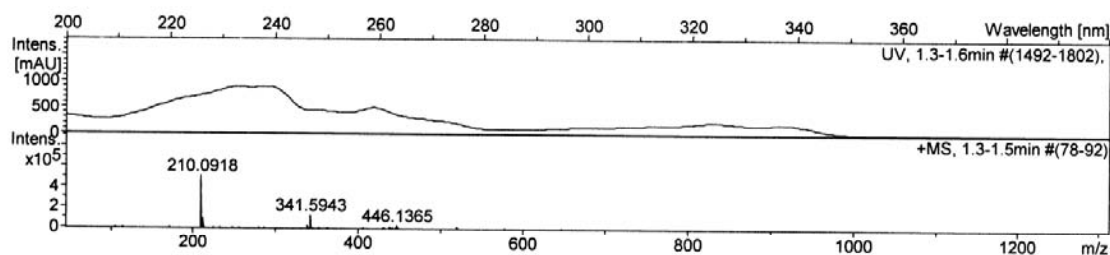
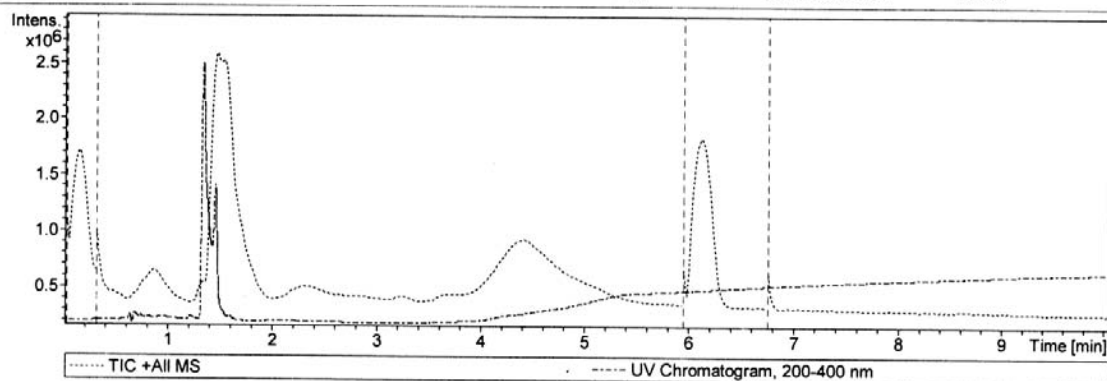
Display Report

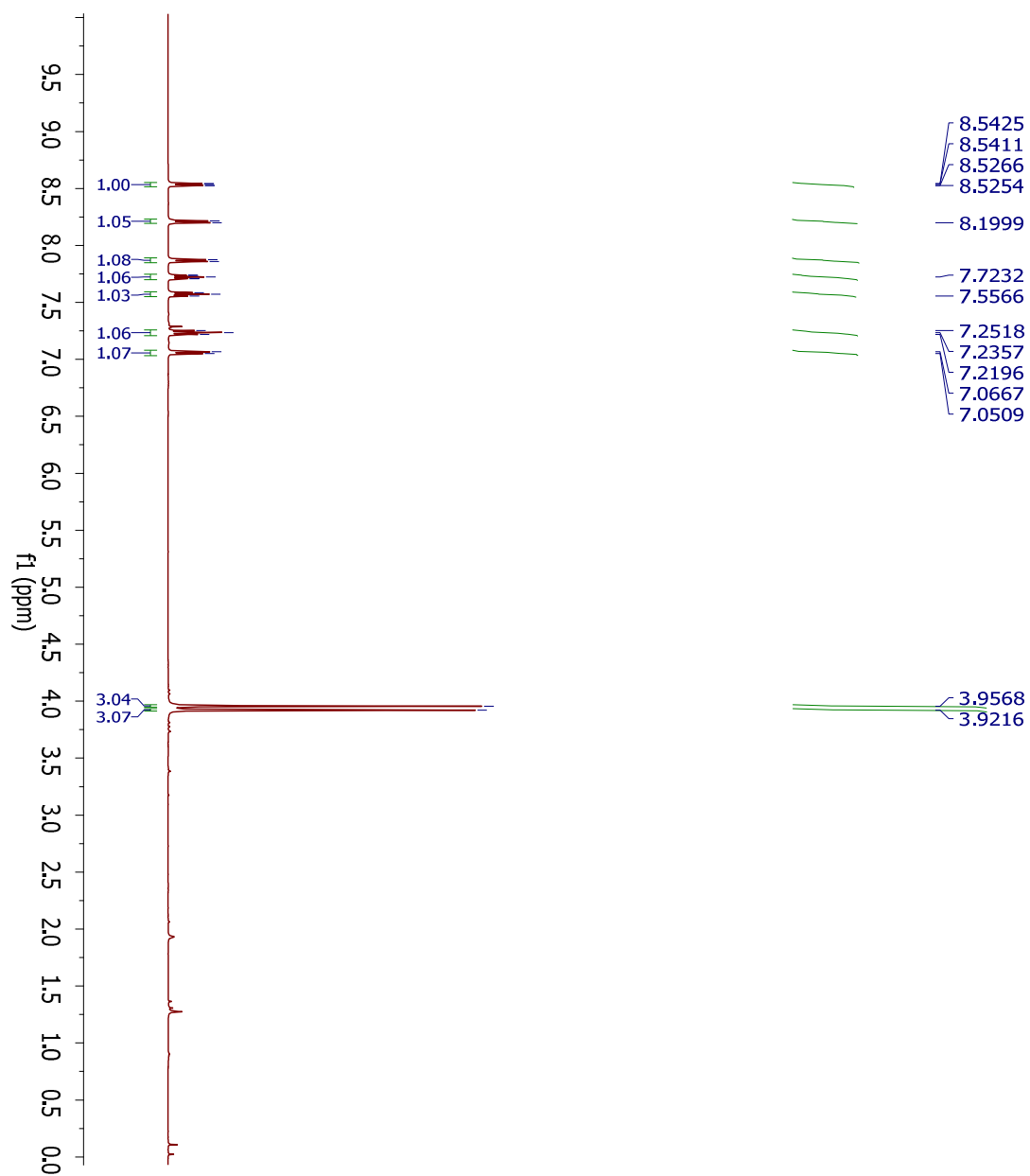
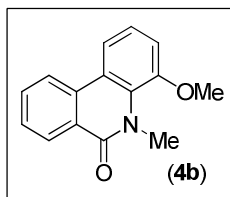
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 Comment:
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 Operator: Meena Sharma
 Instrument: microTOF-Q II 10330

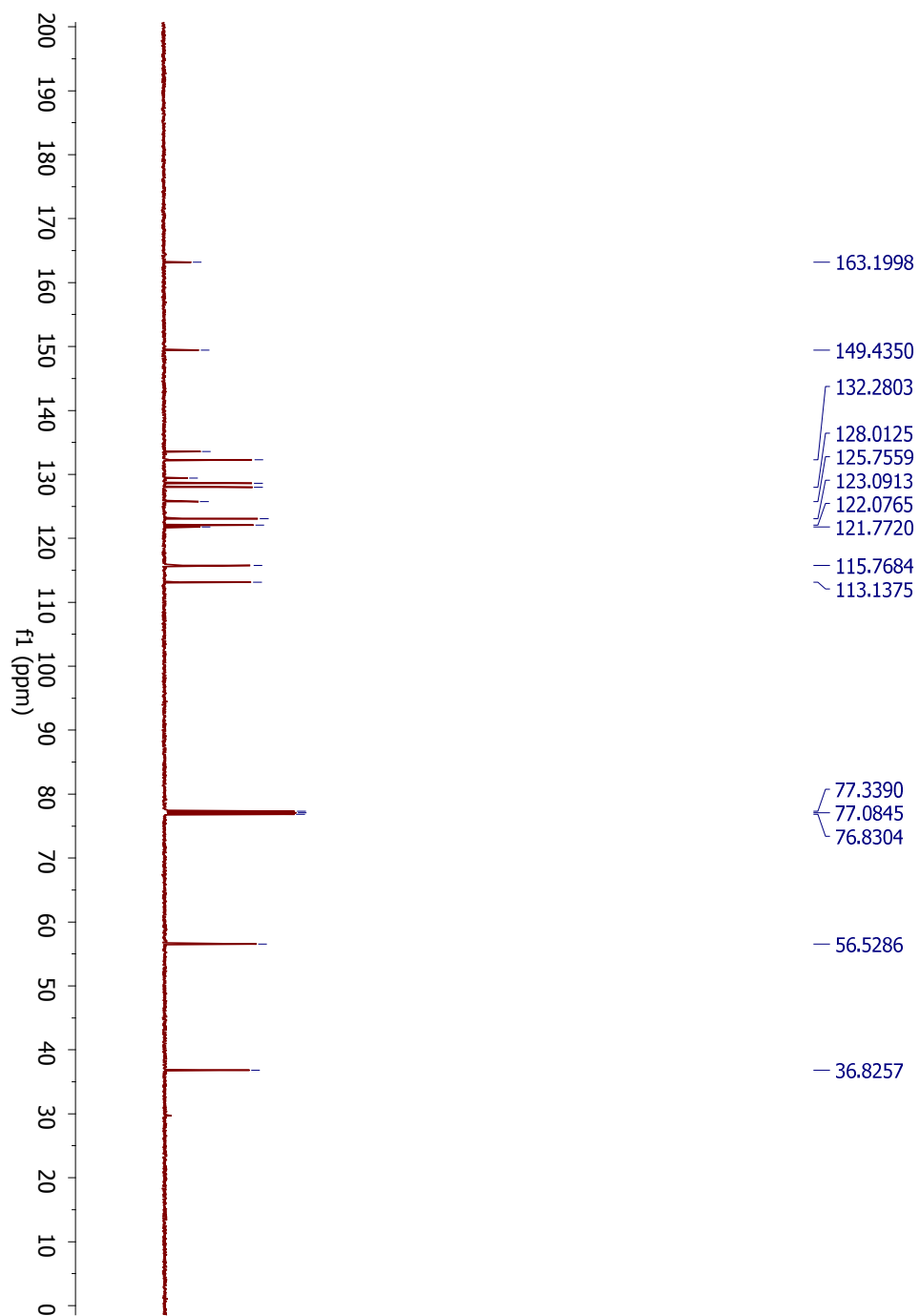
Acquisition Parameter

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

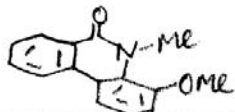




^1H NMR (400 MHz, CDCl_3) compound **(4b)**



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



Display Report

Analysis Info

Analysis Name D:\Data\user data\may2012\10 may\Dr. A. Bisai--SD-3-24_1-A,4_01_2168.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai--SD-3-24
 Comment

Acquisition Date 5/10/2012 11:25:30 AM

Operator

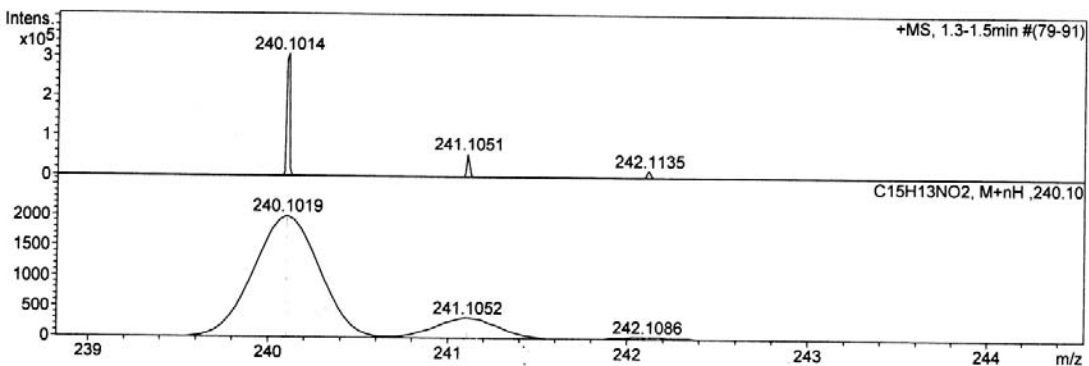
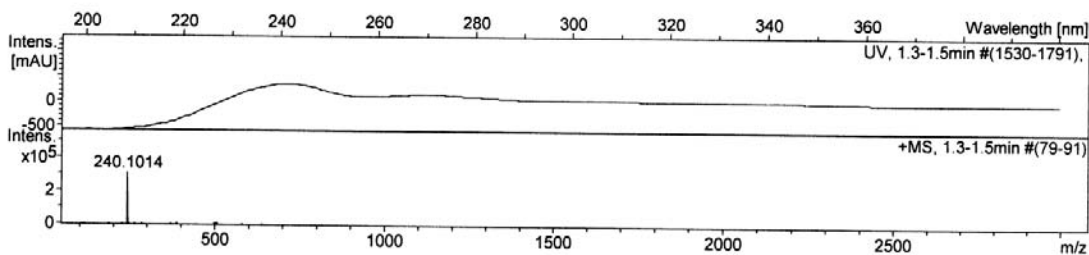
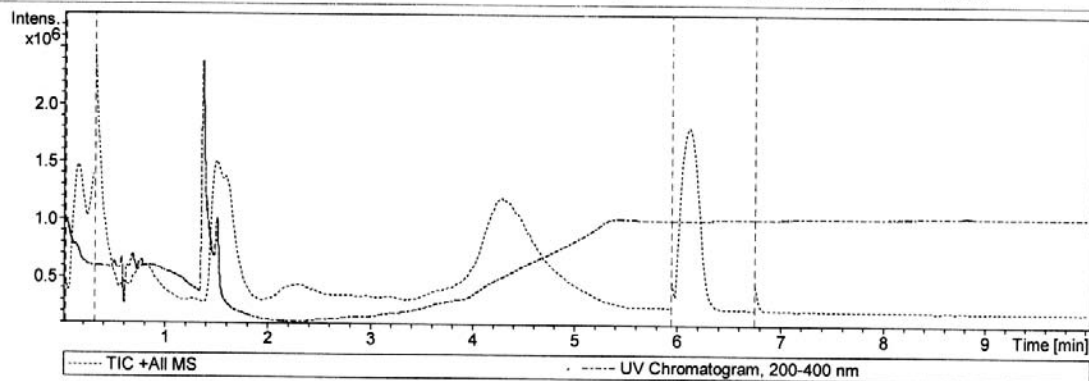
Meena Sharma

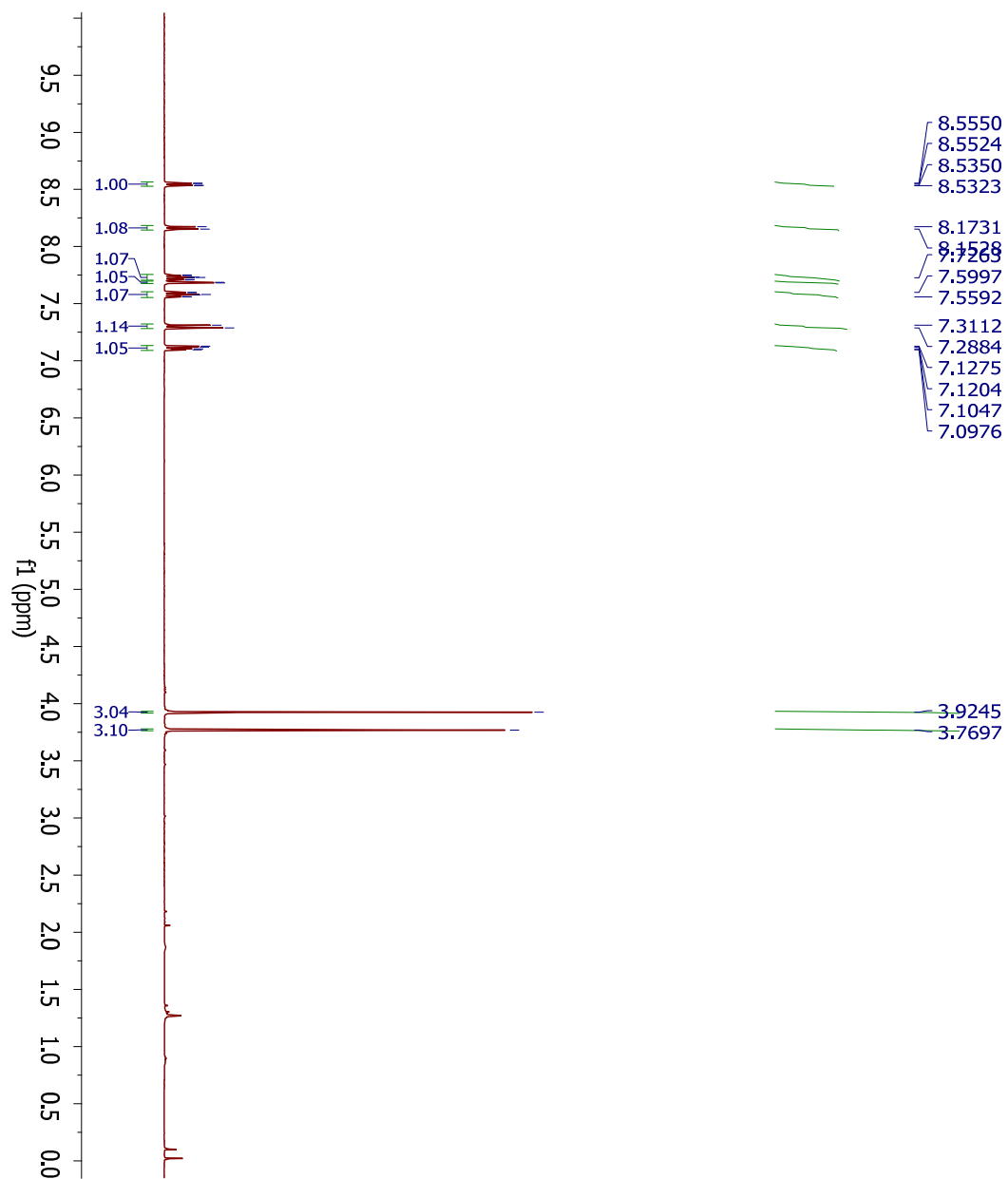
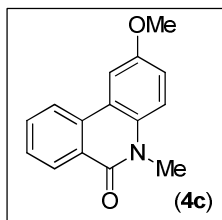
Instrument

micrOTOF-Q II 10330

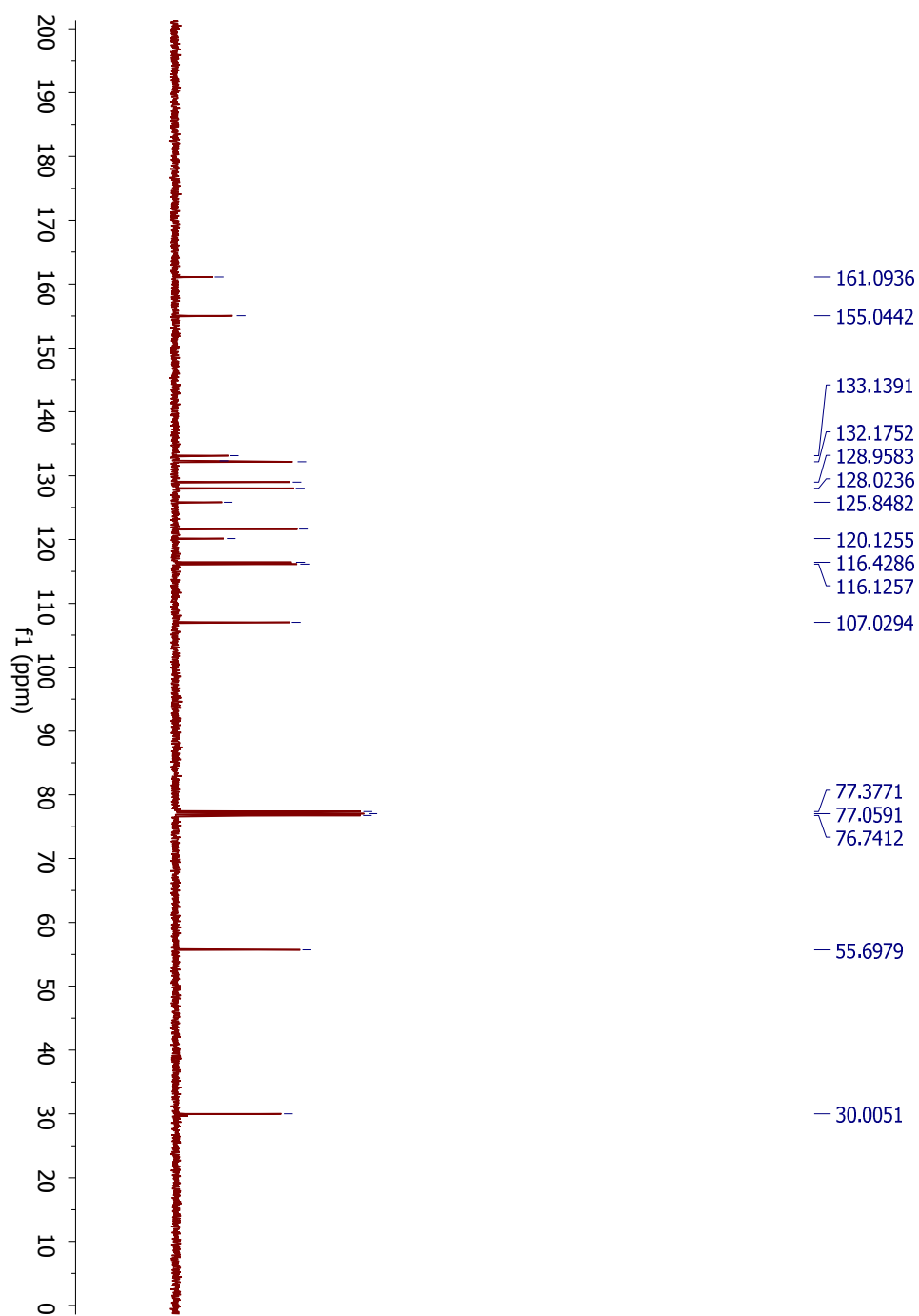
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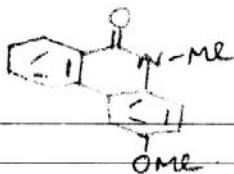




^1H NMR (400 MHz, CDCl_3) compound (4c)



^{13}C NMR (100 MHz, CDCl_3) compound **(4c)**



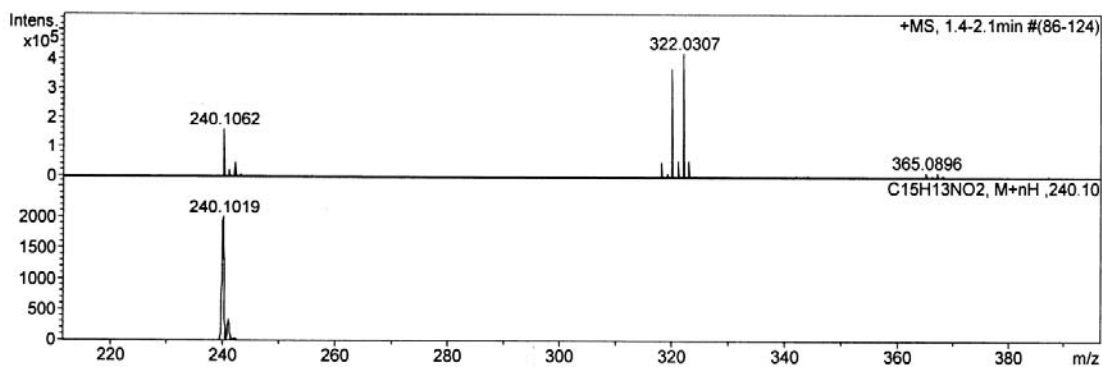
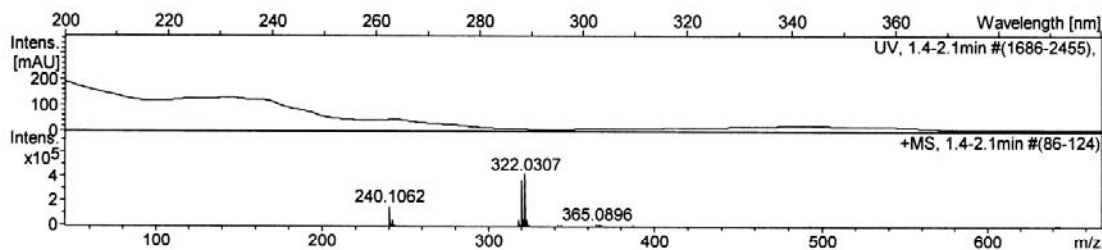
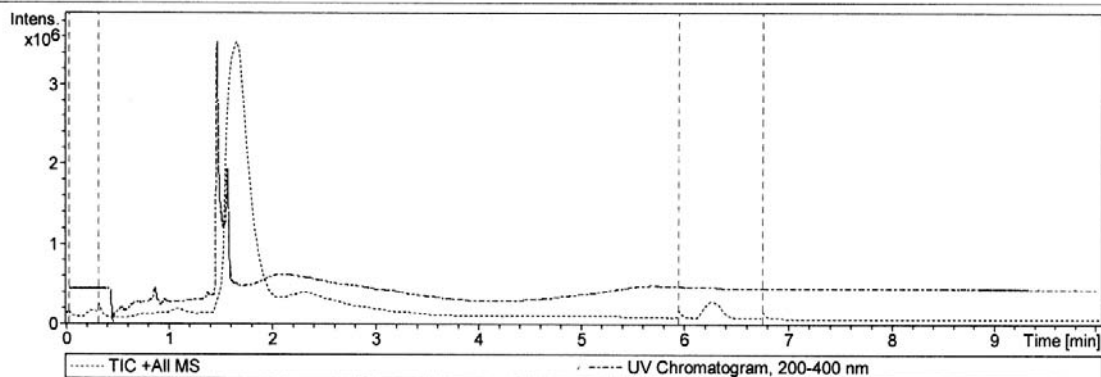
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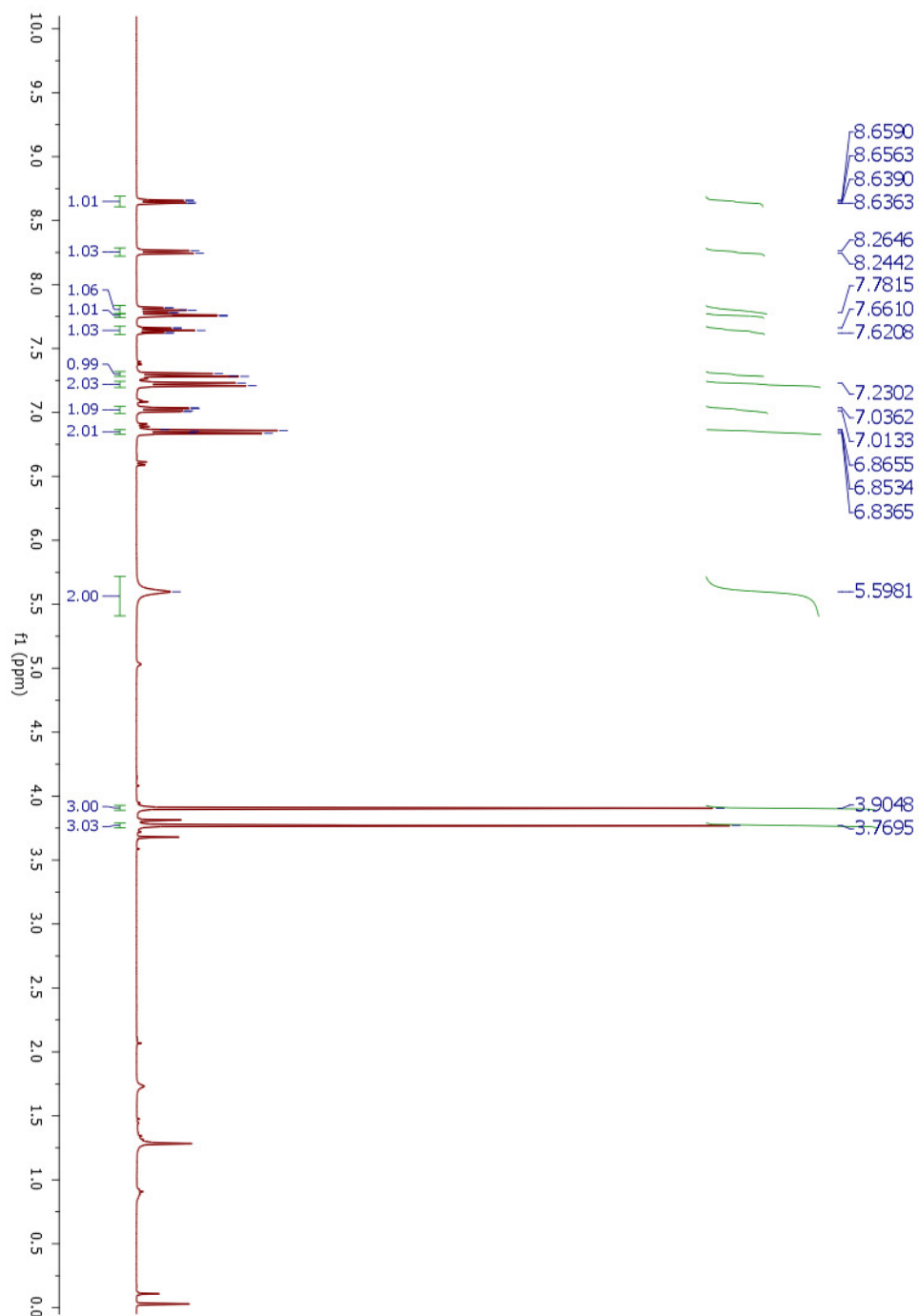
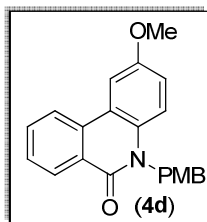
Analysis Info

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 Sample Name: Dr. A. Bisai- SD-3-27
 Comment:
 Acquisition Date: 5/11/2012 4:54:47 PM
 Operator: Meena Sharma
 Instrument: microTOF-Q II 10330

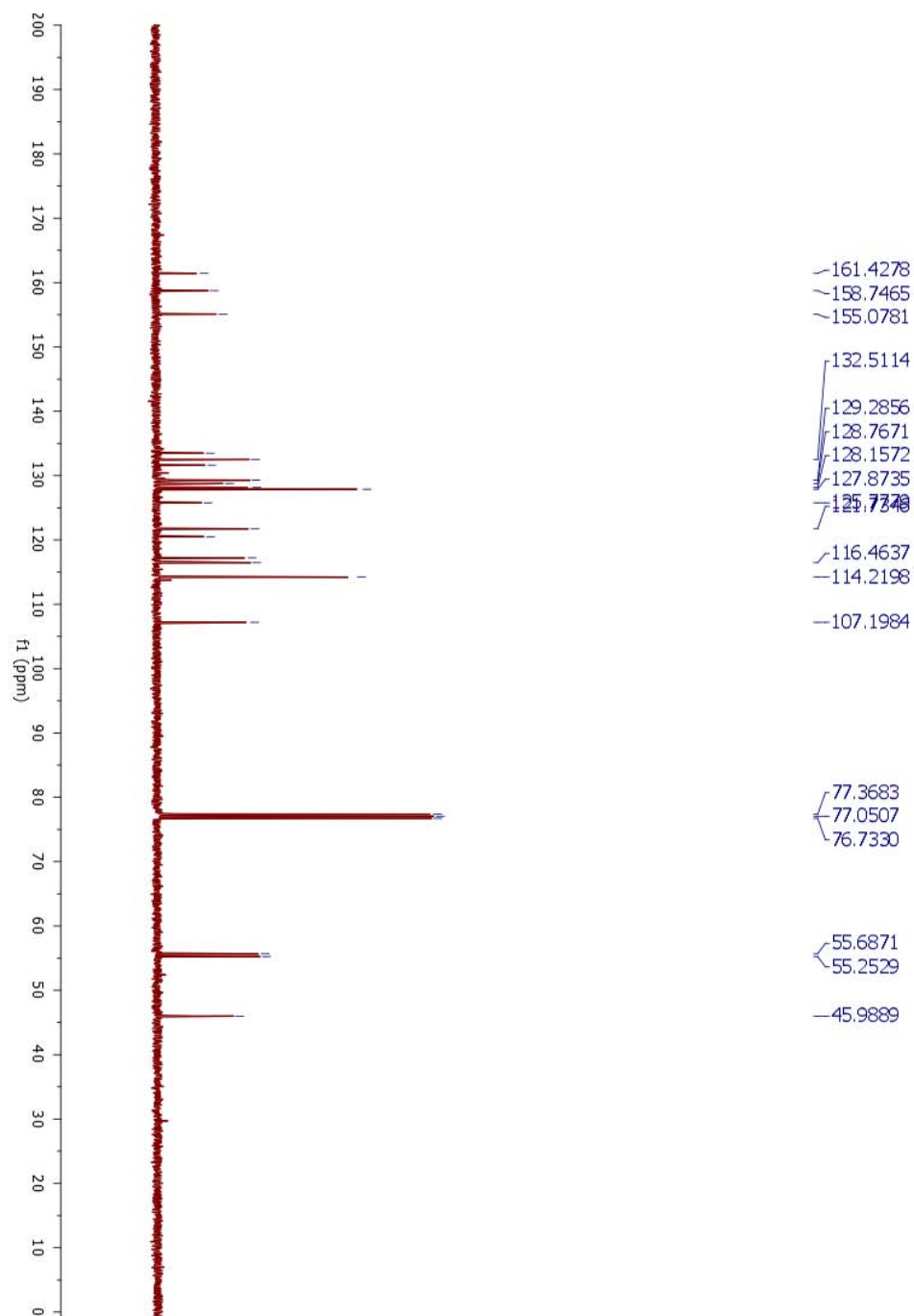
Acquisition Parameter

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





^1H NMR (400 MHz, CDCl_3) compound **4d**



^{13}C NMR (100 MHz, CDCl_3) compound **(4d)**

Display Report

Analysis Info

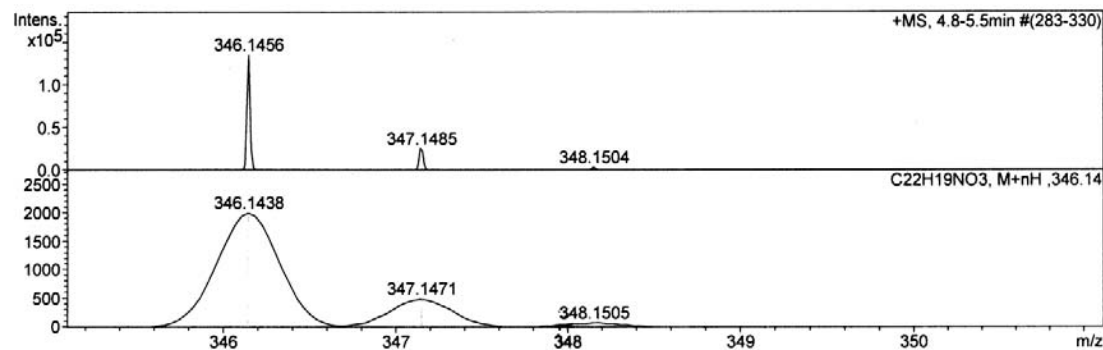
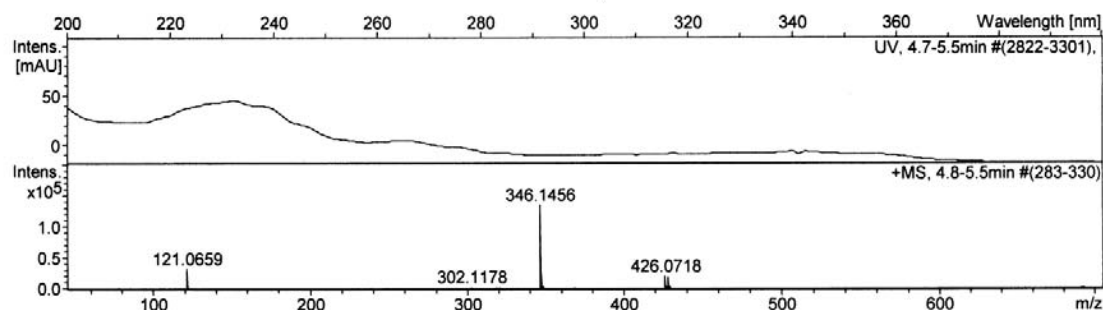
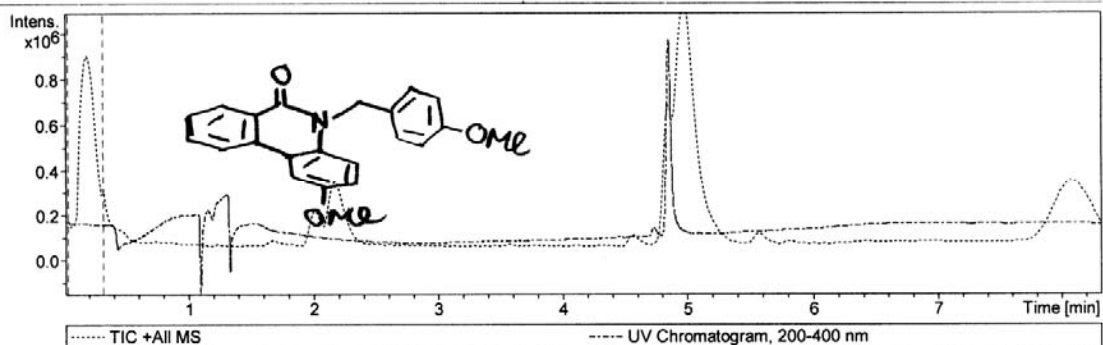
Analysis Name D:\Data\user data\JUNE 2012\4 jun\Dr. A. Bisai-SD-109_1-A,4_01_2515.d
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 Sample Name Dr. A. Bisai-SD-109
 Comment SD-3-109

Acquisition Date 6/4/2012 5:09:10 PM

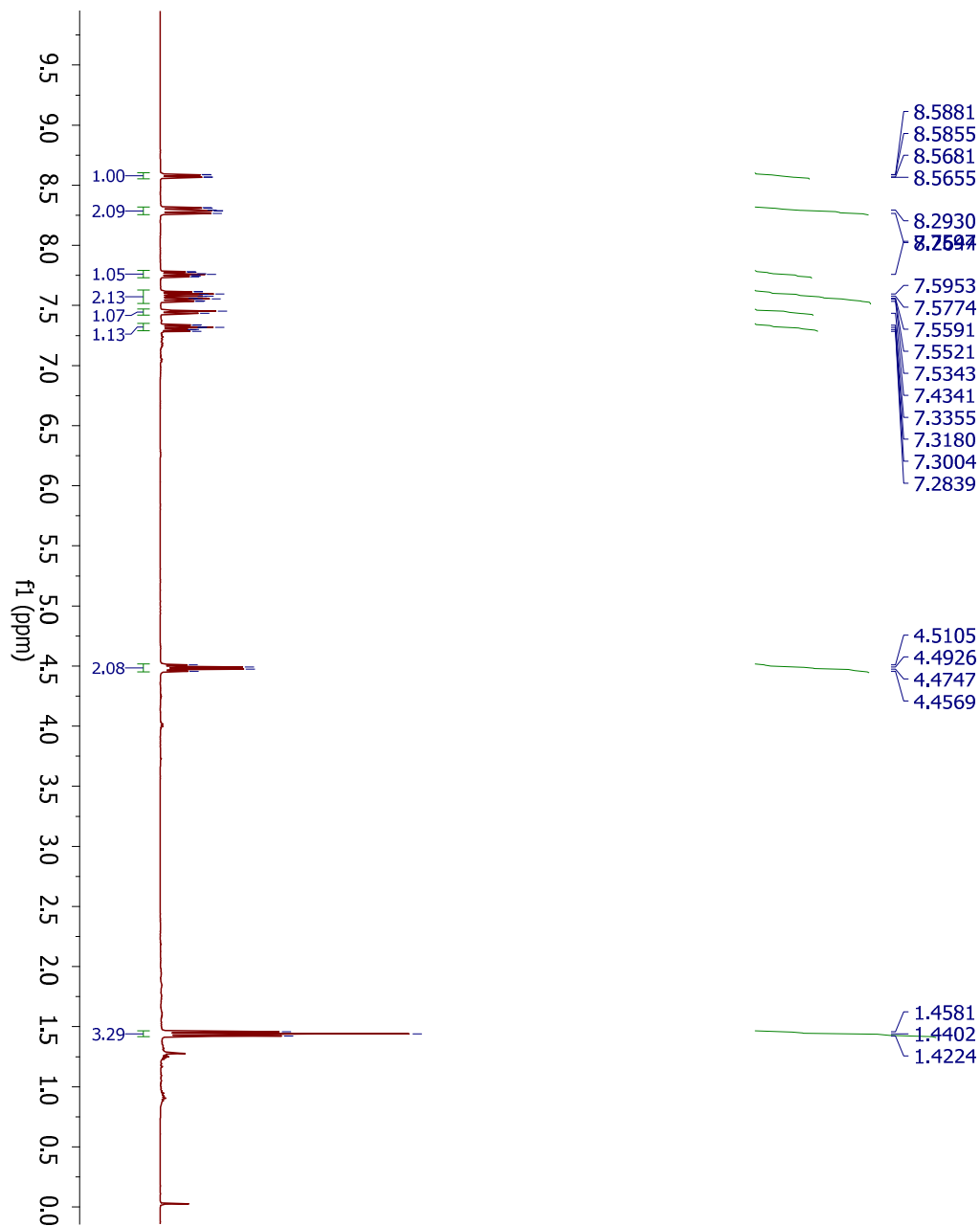
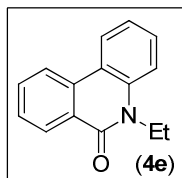
Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

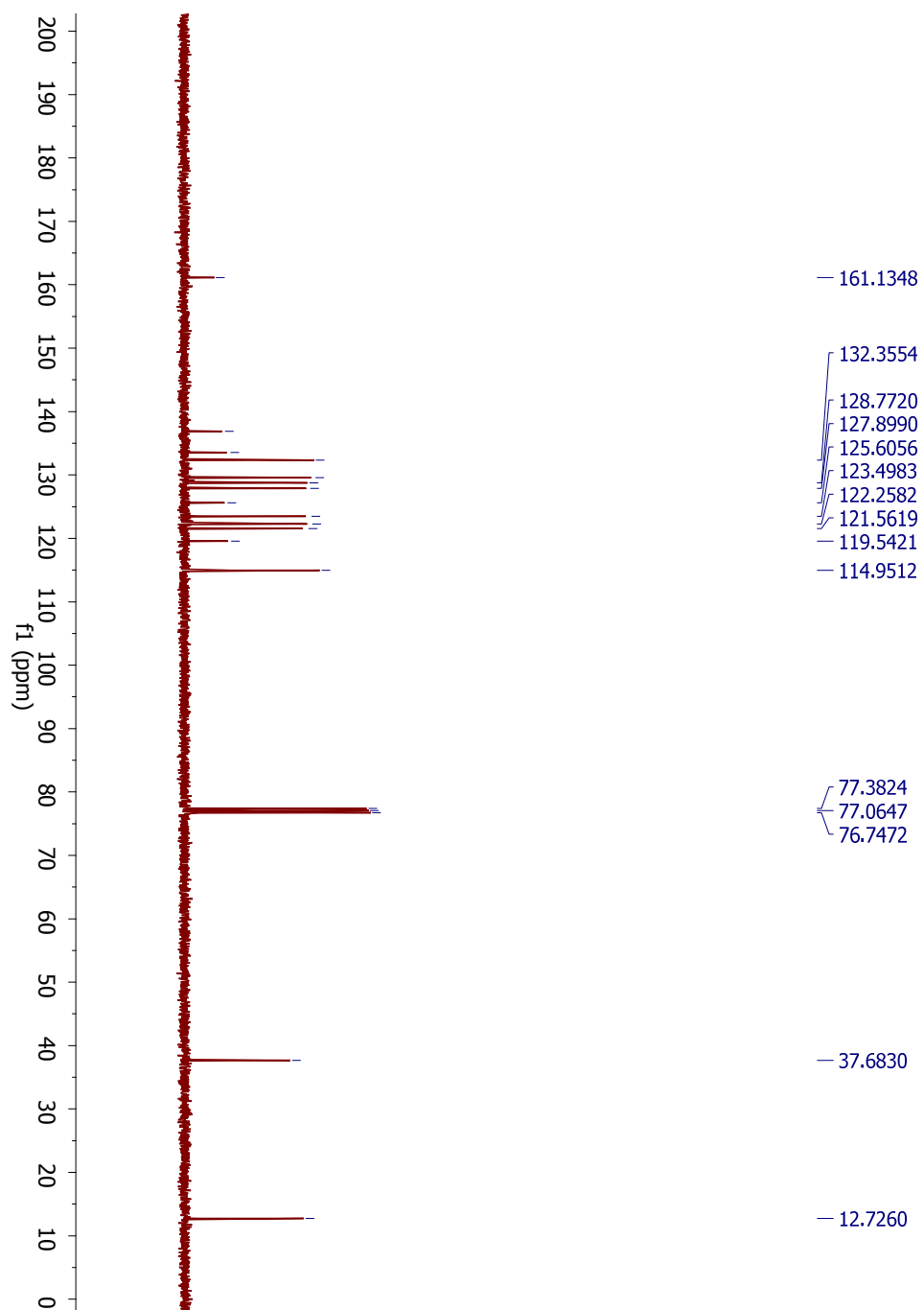
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



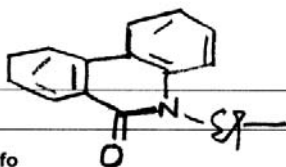
Scanned copy of mass spectrum of (4d)



^1H NMR (400 MHz, CDCl_3) compound (4e)



^{13}C NMR (100 MHz, CDCl_3) compound **(4e)**



Display Report

Analysis Info

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Method HRLCMS-20 Sept.m
Sample Name Dr.A.Bisai-SD3-86
Comment

Acquisition Date 3/18/2013 11:10:13 AM

Operator

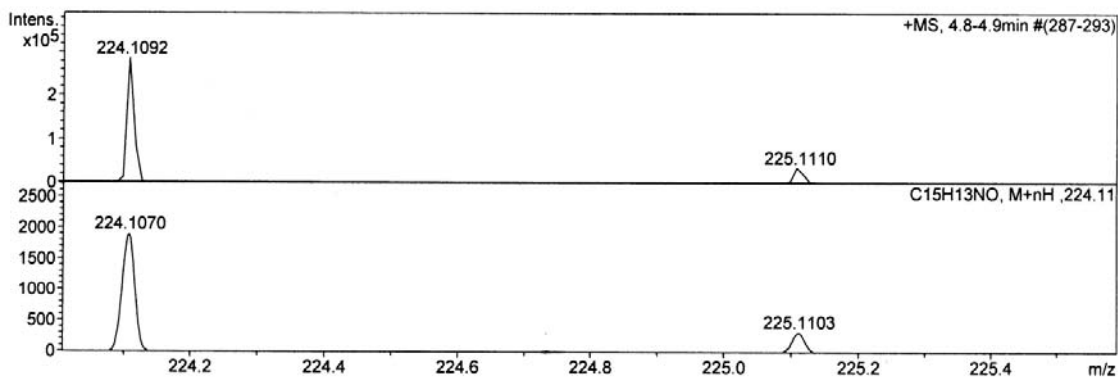
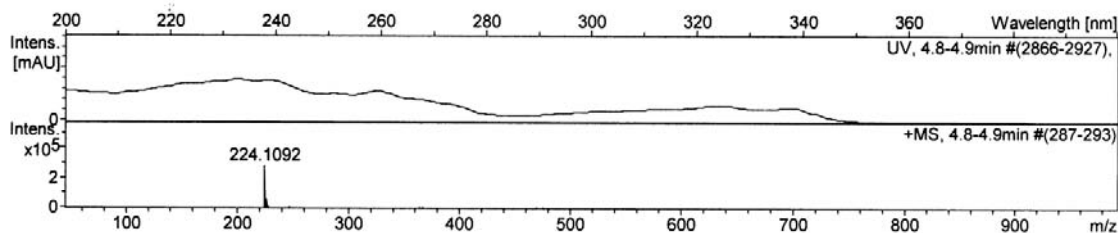
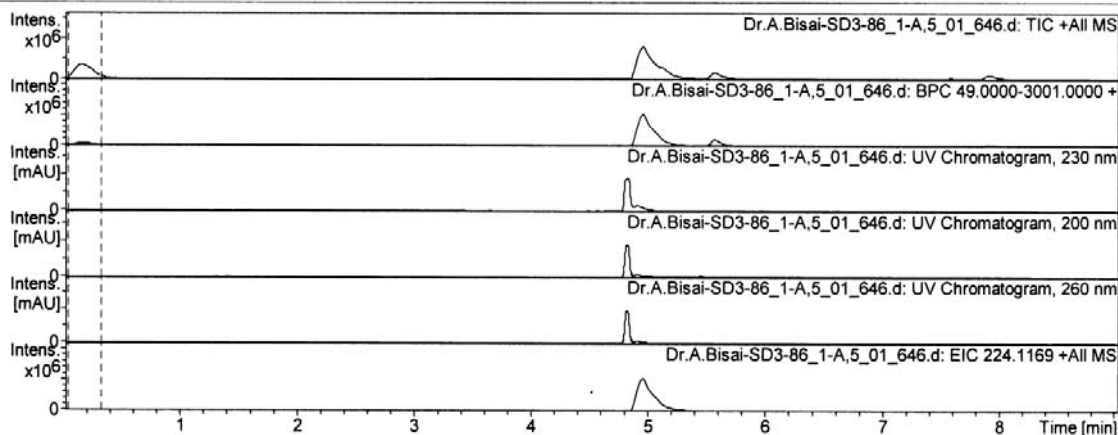
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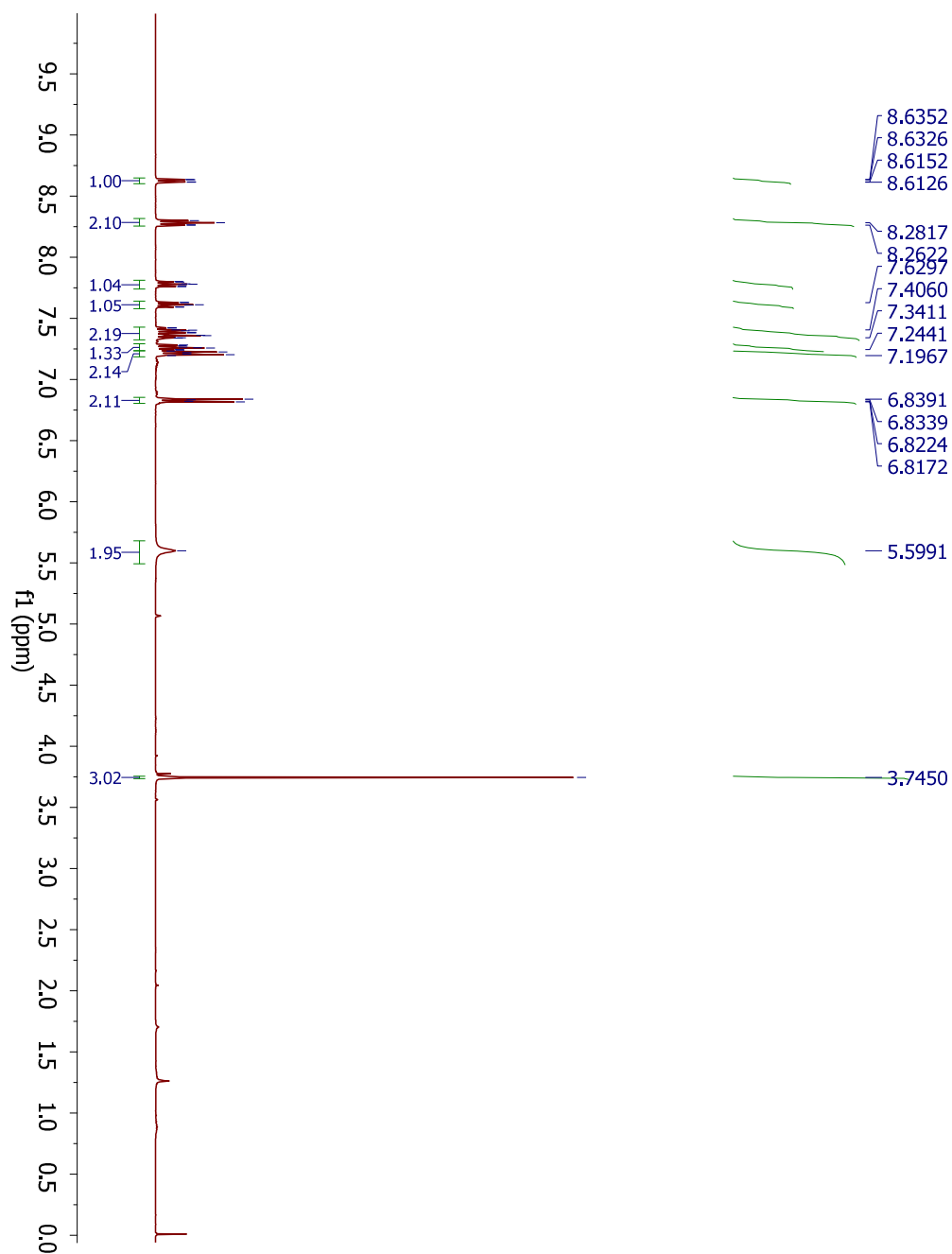
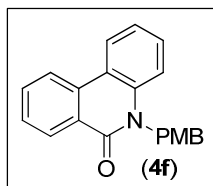
Instrument

microTOF-Q II 10330

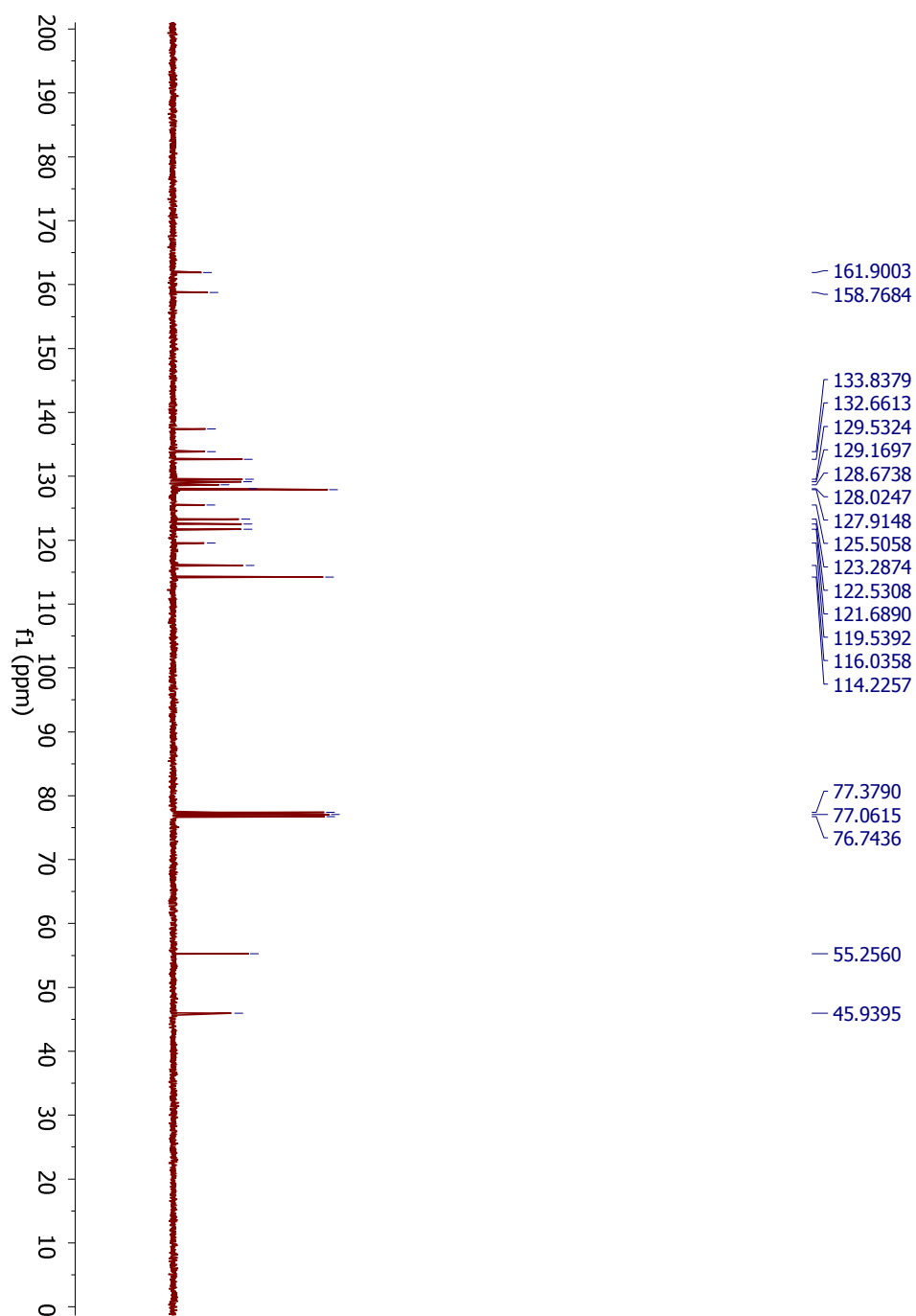
Acquisition Parameter

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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





^1H NMR (400 MHz, CDCl_3) compound **(4f)**





Display Report

Analysis Info

Analysis Name D:\Data\user data\2013\MARCH\18 MAR\Dr.A.Bisai-SD3-85_1-A,4_01_645.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr.A.Bisai-SD3-85
 Comment

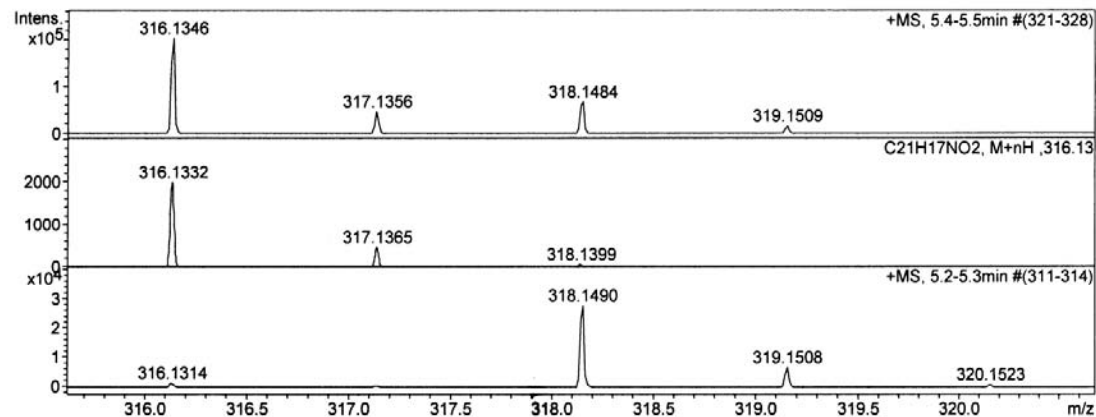
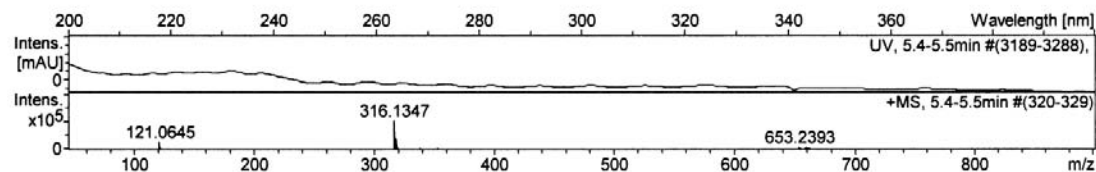
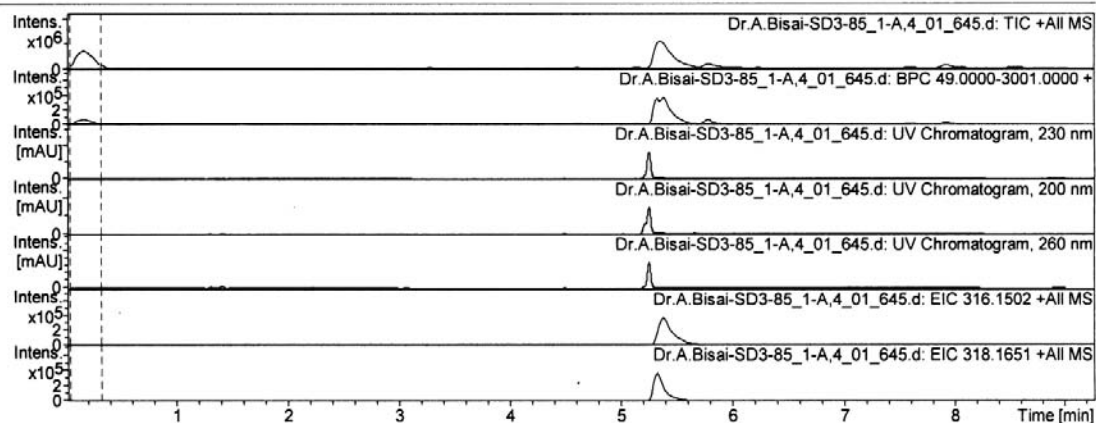
Acquisition Date 3/18/2013 11:00:03 AM

Operator Amit

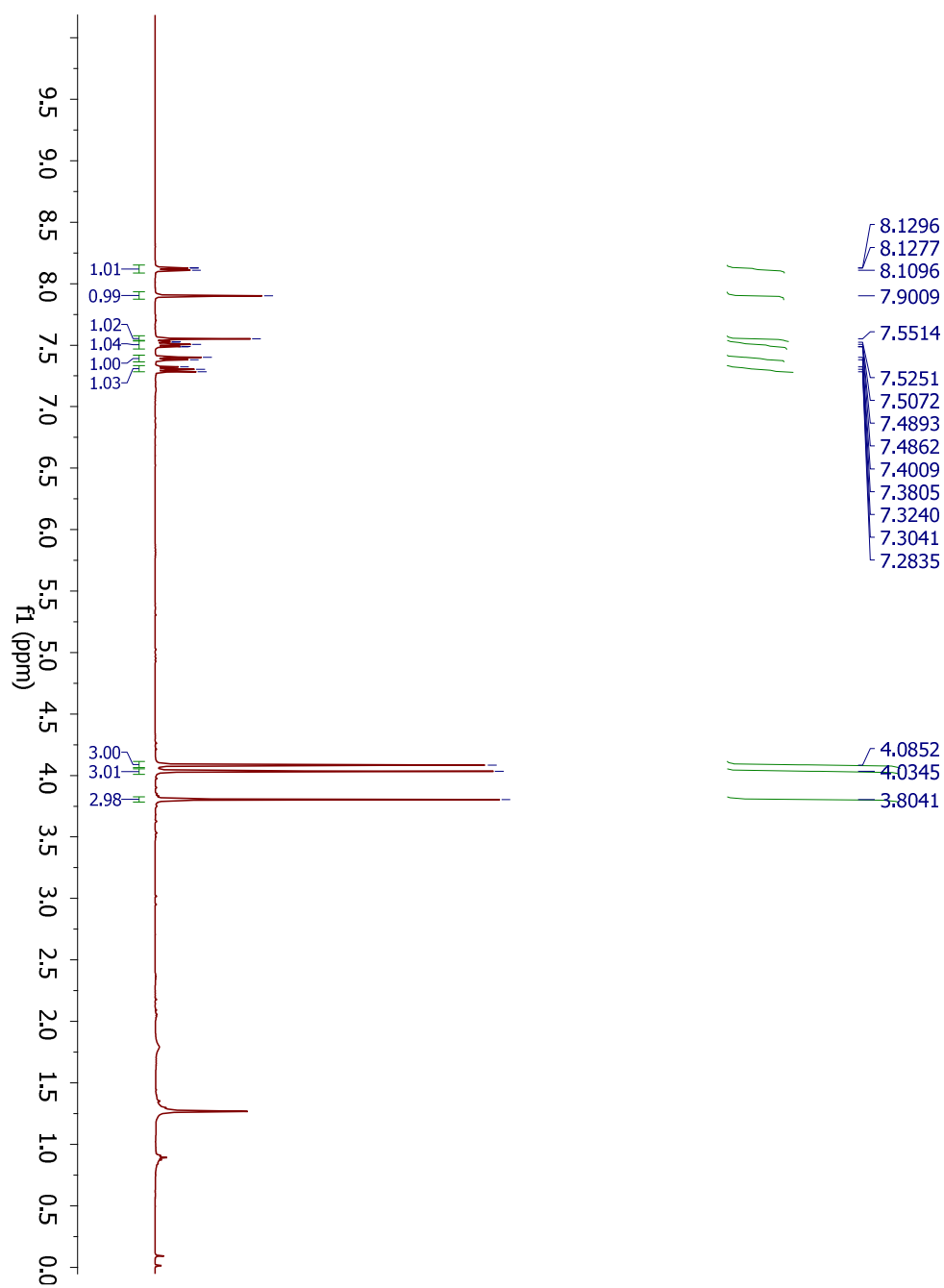
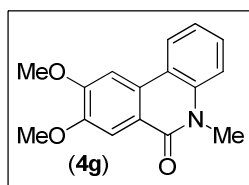
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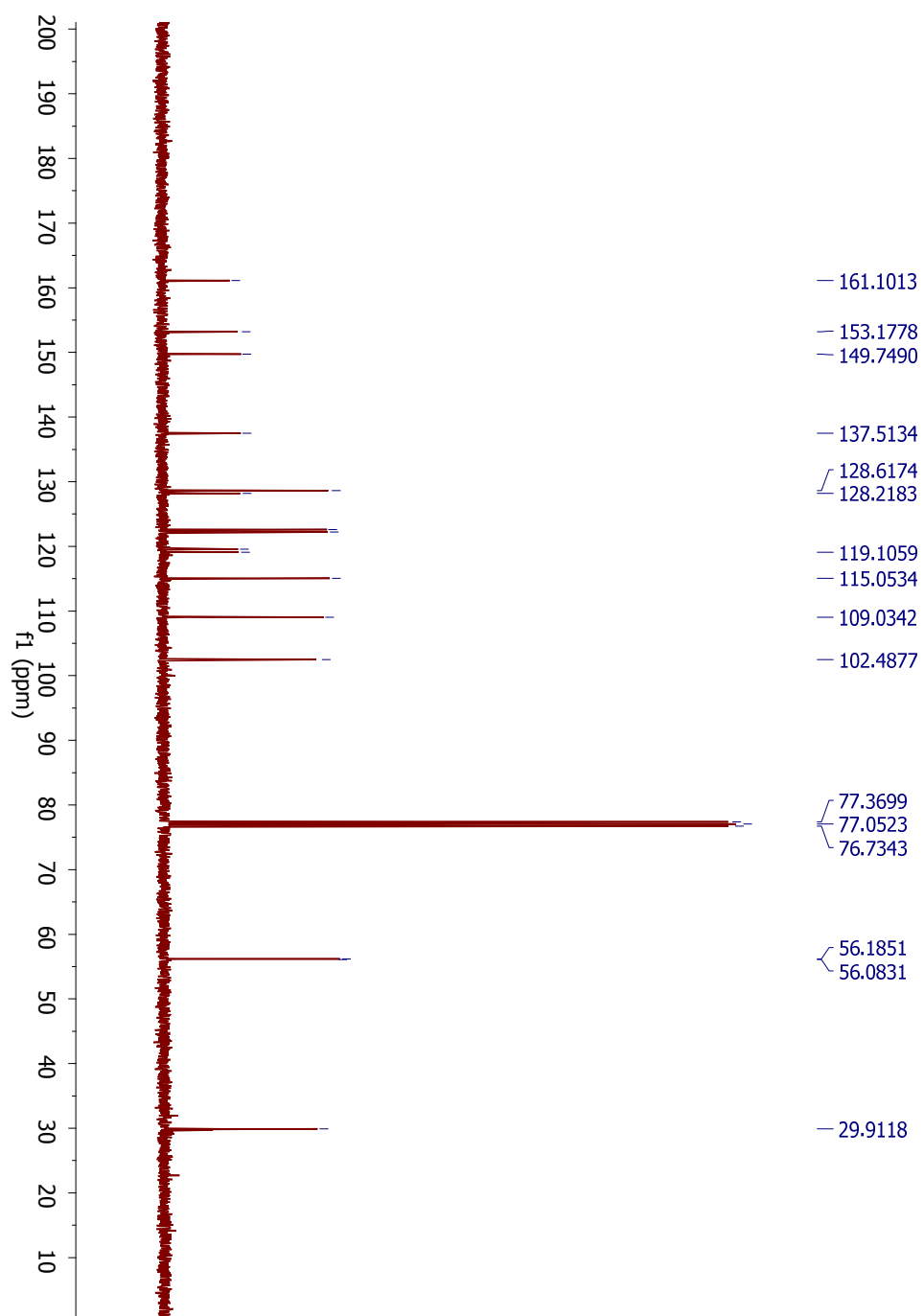
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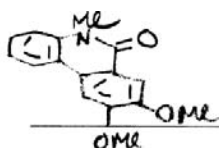
Scanned copy of mass spectrum of (4f)



¹H NMR (400 MHz, CDCl₃) compound **(4g)**



^{13}C NMR (100 MHz, CDCl_3) compound **(4g)**



Display Report

Analysis Info

Analysis Name D:\Data\user data\April 2012\23 apr\Dr. A. Bisai- SD-2-371(PS)_1-A,6_01_1857.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SD-2-371(PS)
 Comment SD-3-33

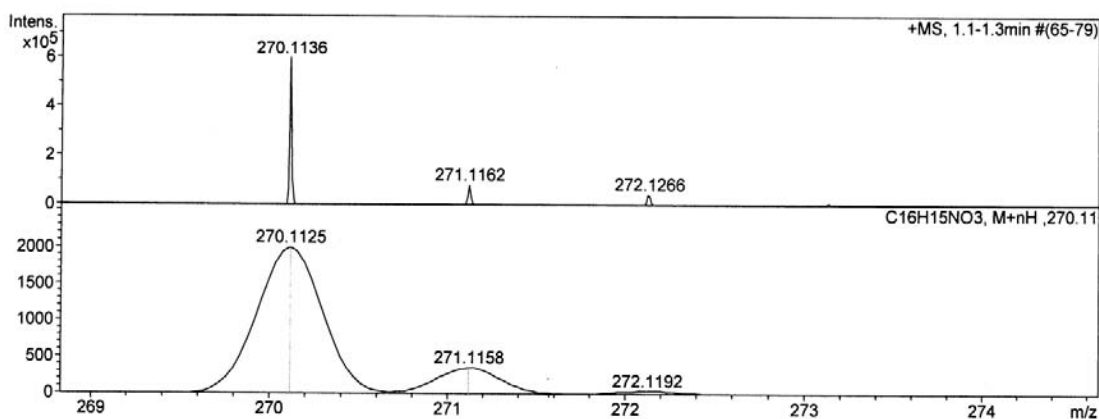
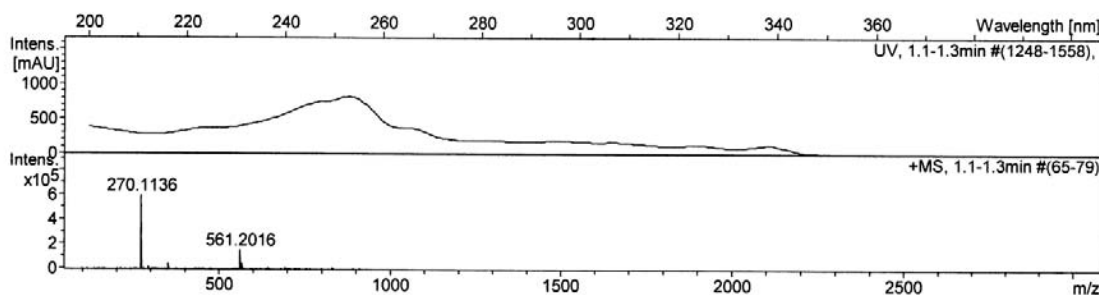
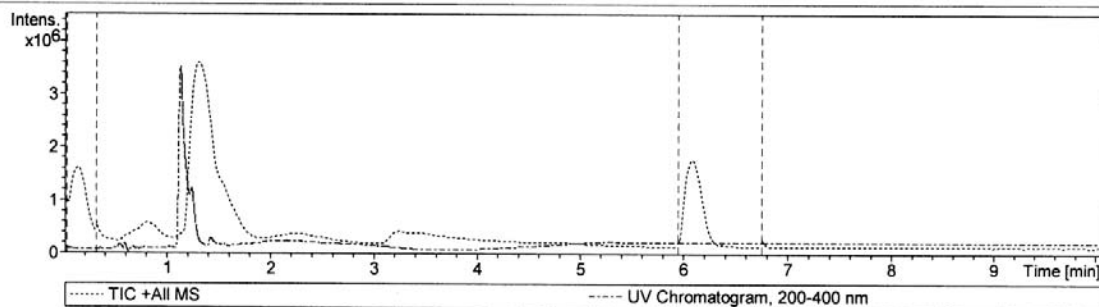
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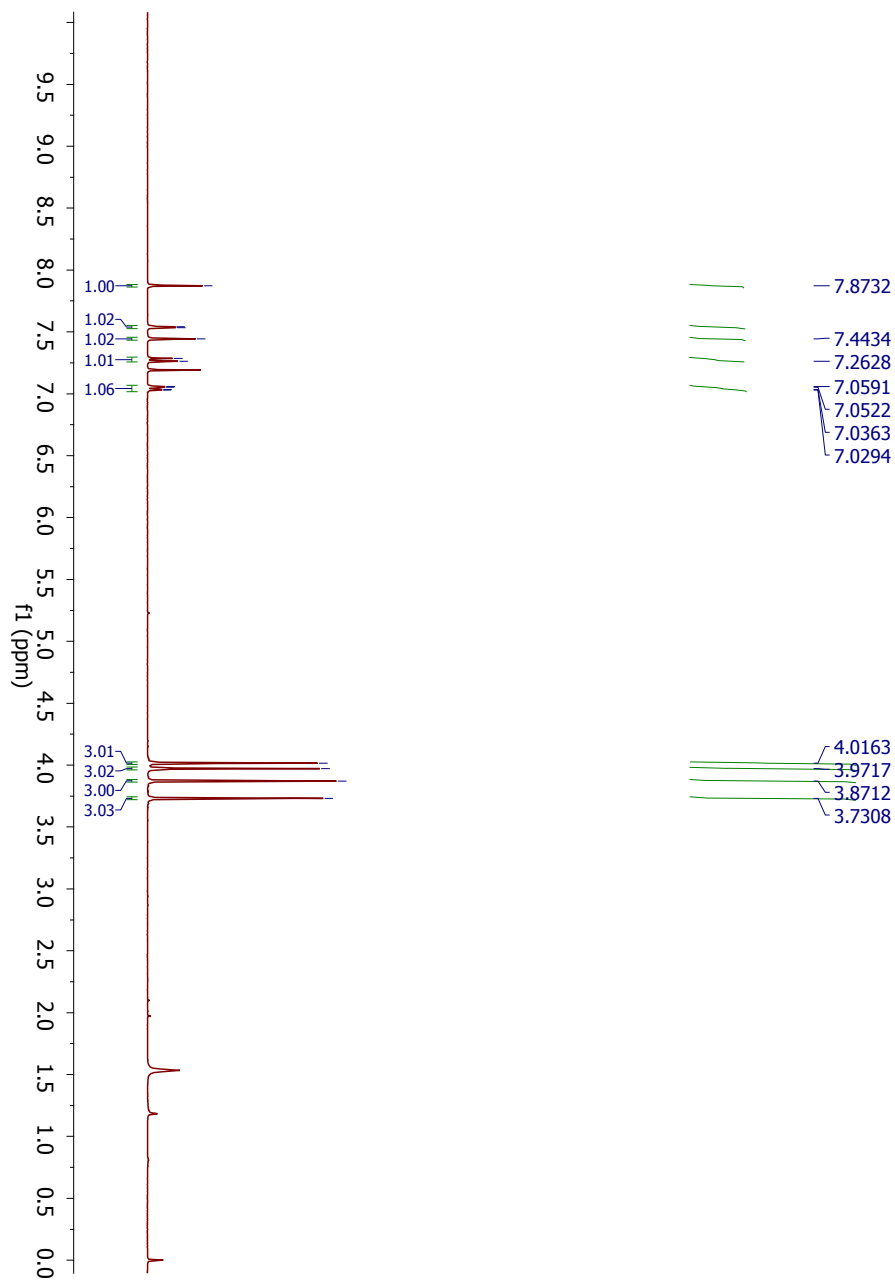
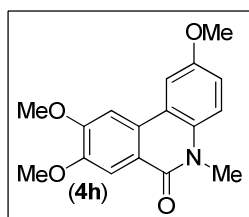
Operator Meena Sharma

Instrument micrOTOF-Q II 10330

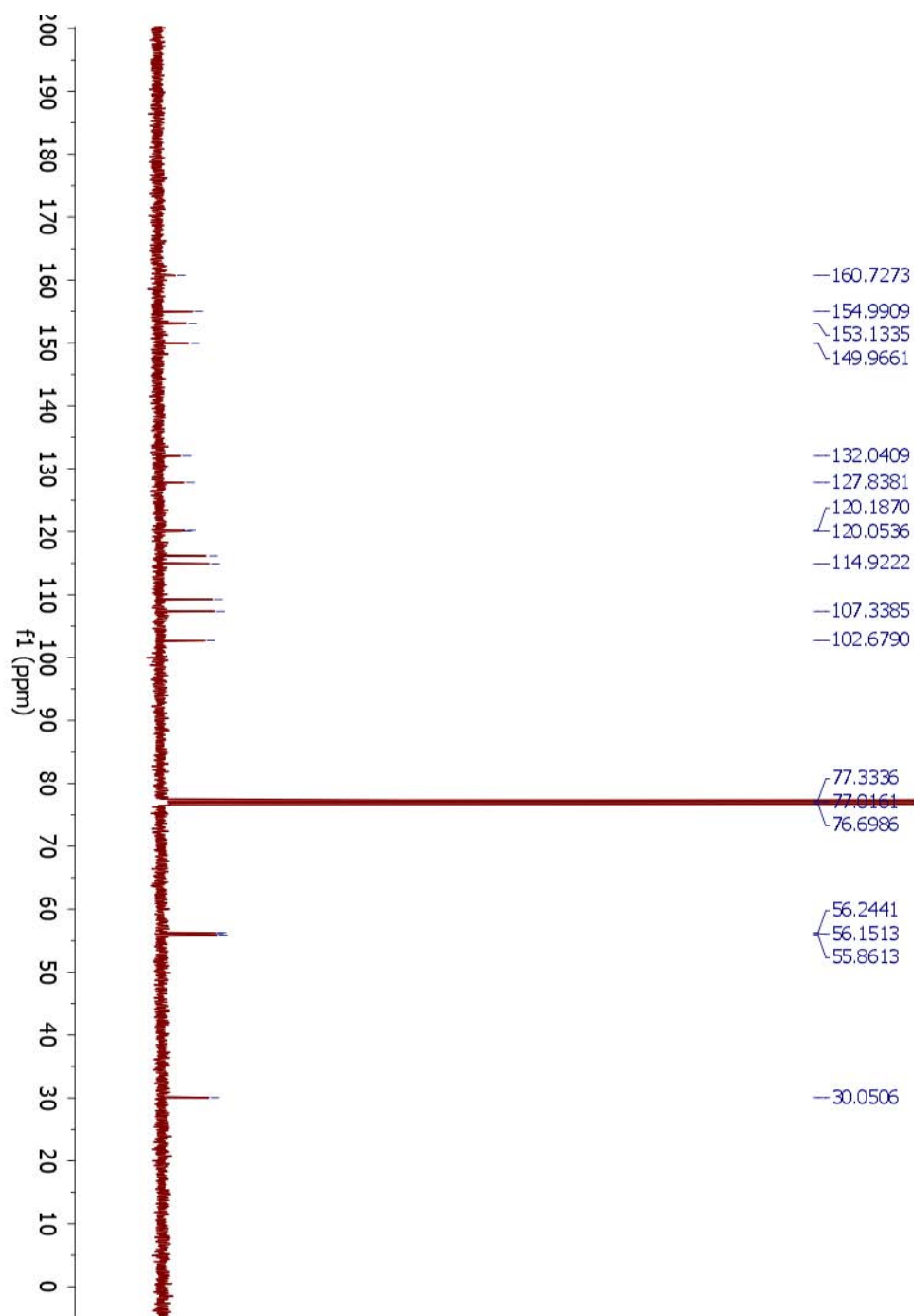
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





^1H NMR (400 MHz, CDCl_3) compound (**4h**)



^{13}C NMR (100 MHz, CDCl_3) compound (**4h**)

Display Report

Analysis Info

Analysis Name D:\Data\user data\JULY-2012\23 JUL\Dr.A.Bisai-SM-123_1-A,6_01_2851.d
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 Sample Name Dr.A.Bisai-SM-123_1 - 2 3
 Comment

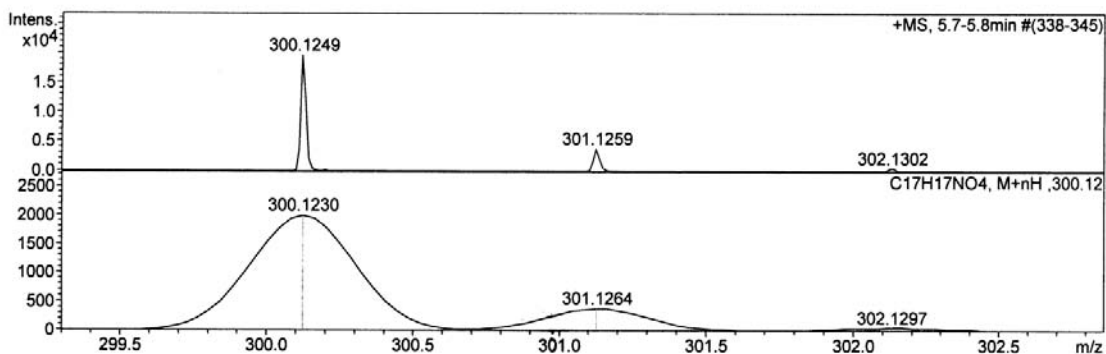
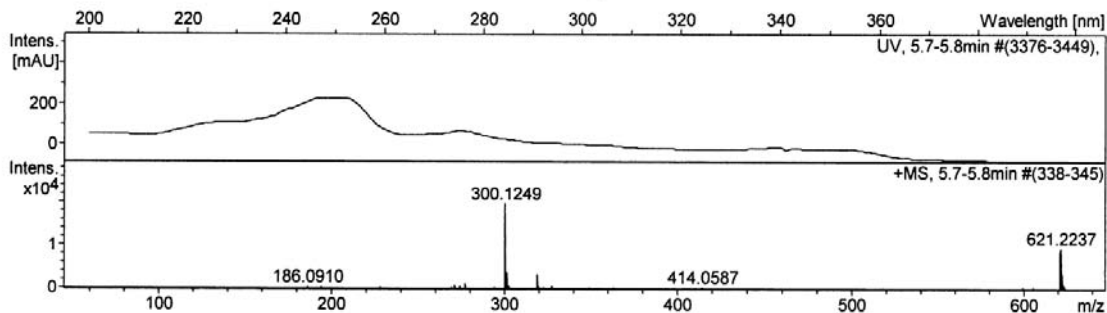
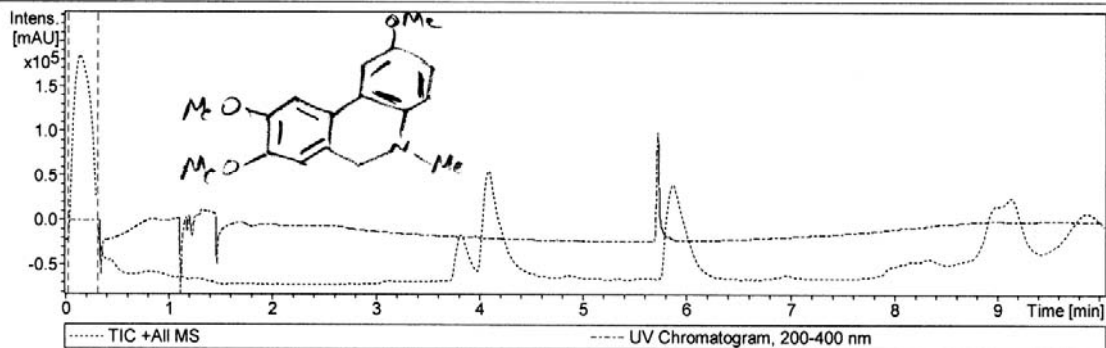
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Operator Meena Sharma

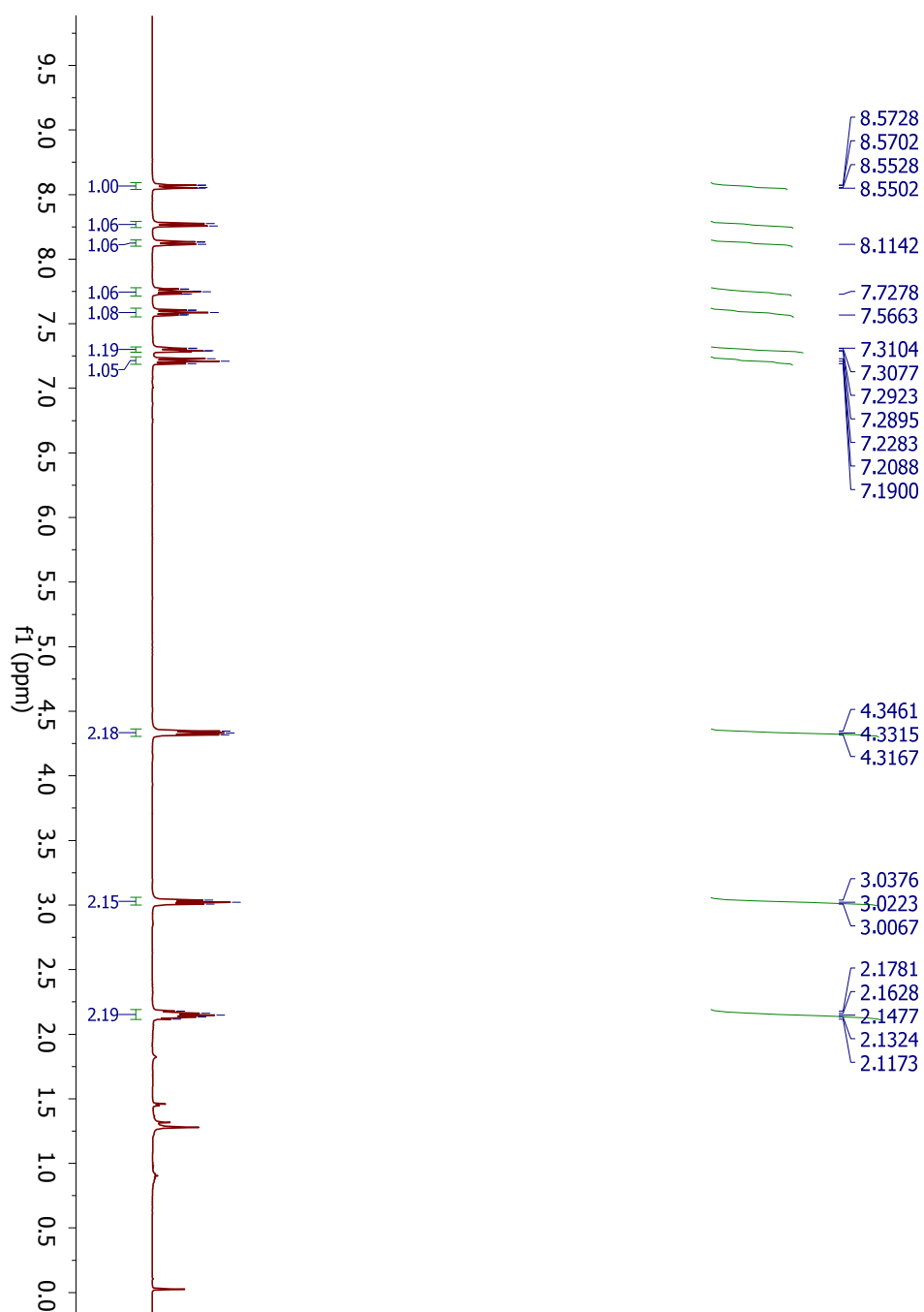
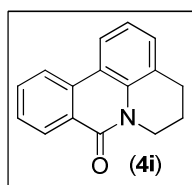
Instrument micrOTOF-Q II 10330

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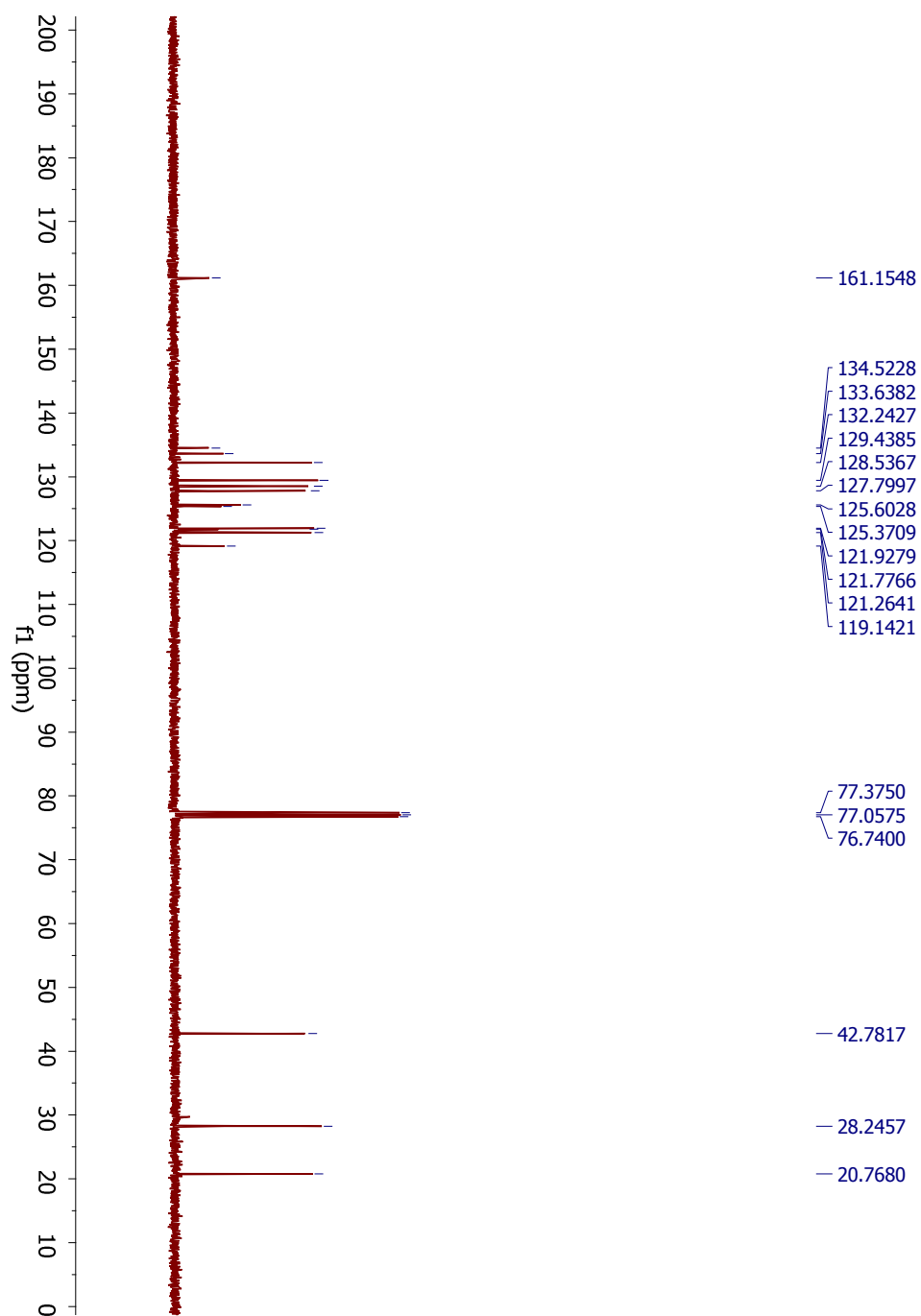
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of (4h)



¹H NMR (400 MHz, CDCl₃) compound **(4i)**



^{13}C NMR (100 MHz, CDCl_3) compound **(4i)**



Display Report

Analysis Info

Analysis Name D:\Data\user data\Aprail 2012\7 APR\Dr. A. Bisai-SD-2-318_1-A_8_01_1685.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai-SD-2-318
 Comment

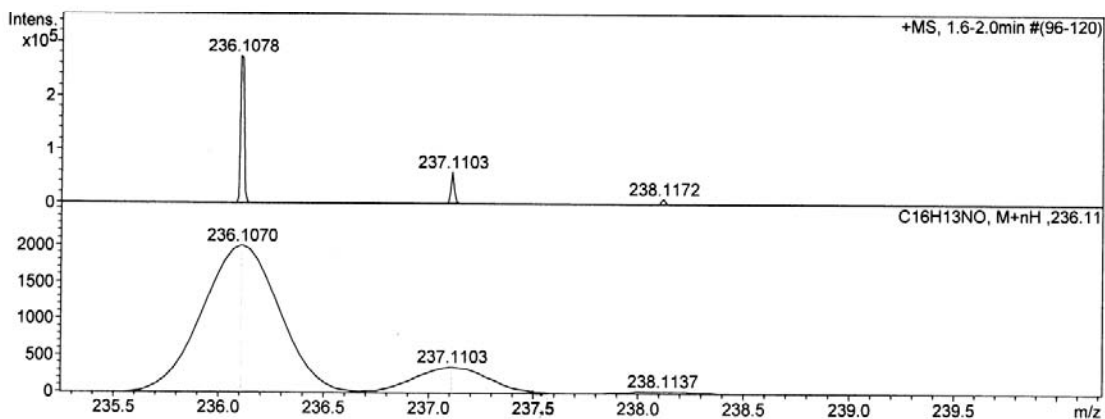
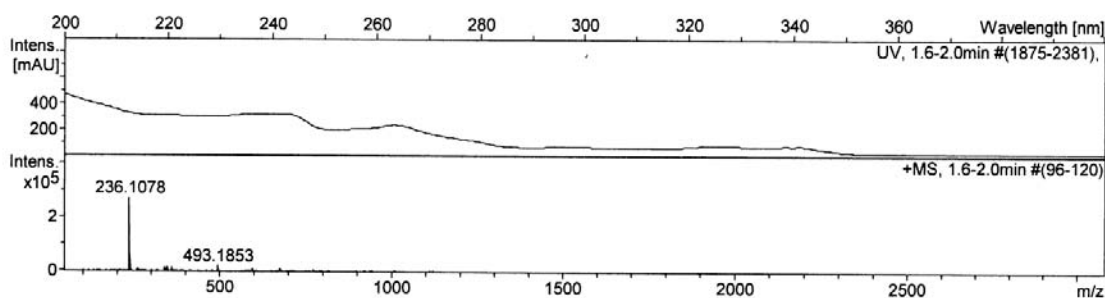
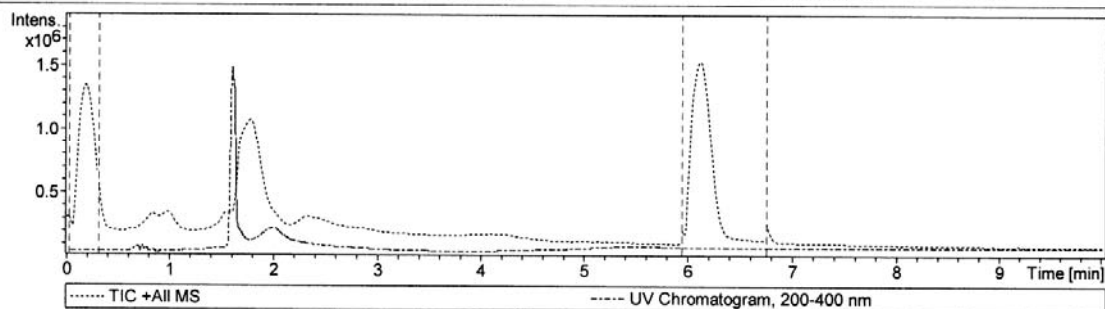
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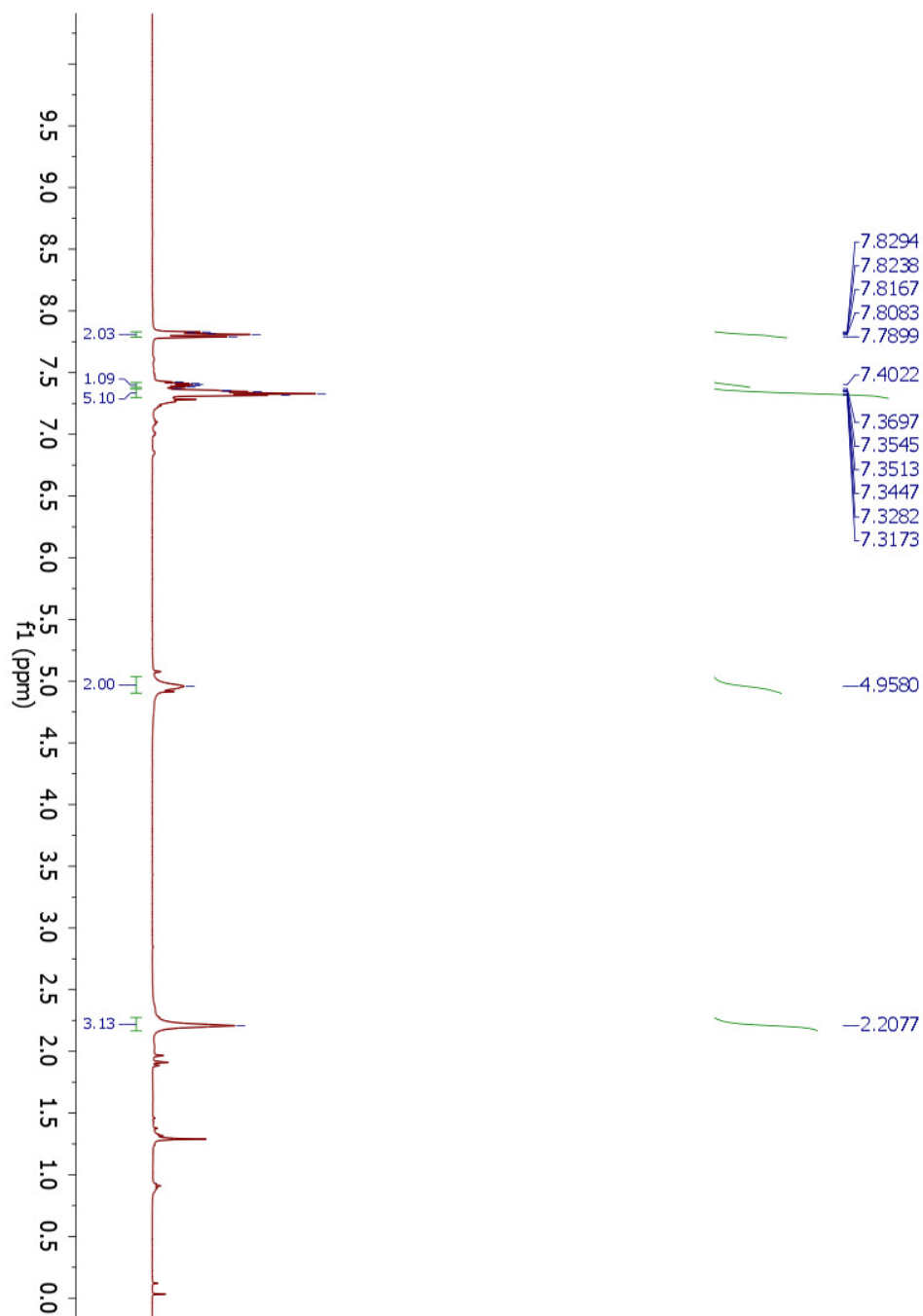
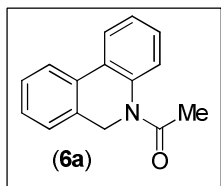
Operator Meena Sharma

Instrument microTOF-Q II 10330

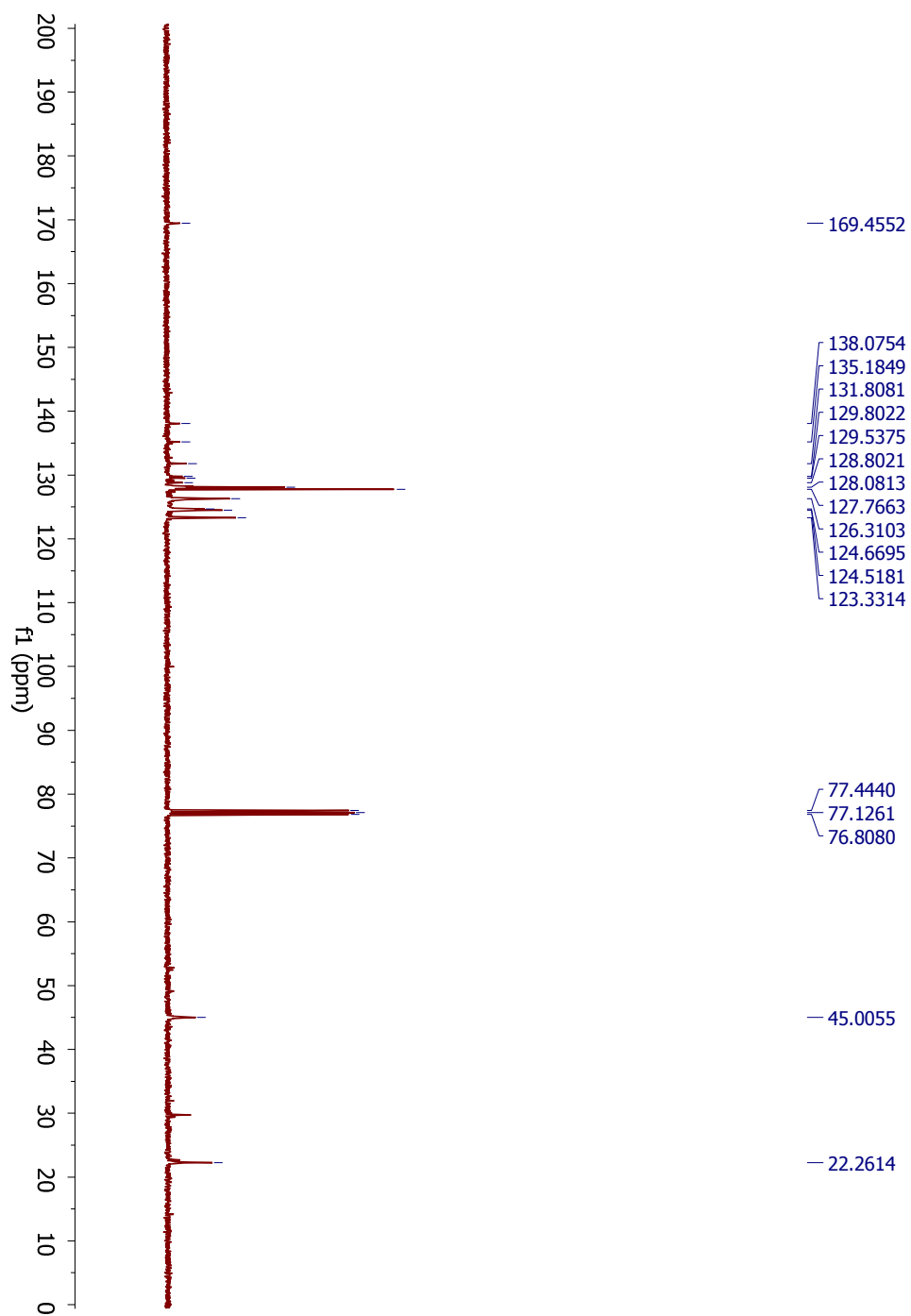
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





^1H NMR (400 MHz, CDCl_3) compound **(6a)**



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

Display Report

Analysis Info

Analysis Name D:\Data\user data\may2012\16 may\Dr. A. Bisai- SD-3-41_1-A_2_01_2254.d
Method HRLCMS-20 Sept.m
Sample Name Dr. A. Bisai- SD-3-41
Comment

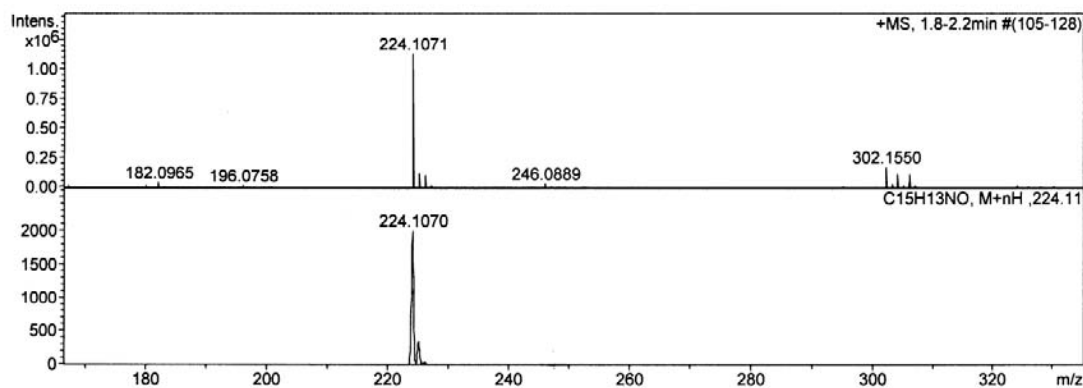
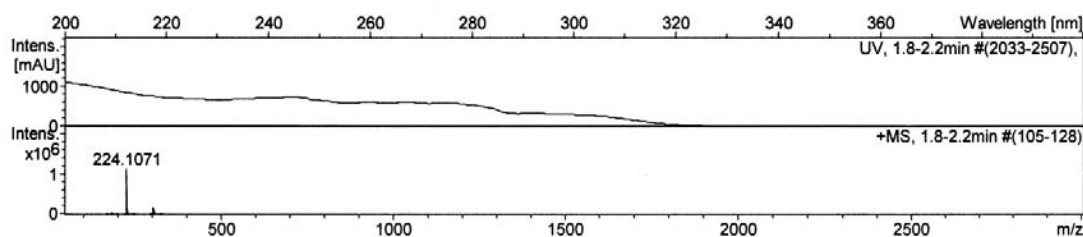
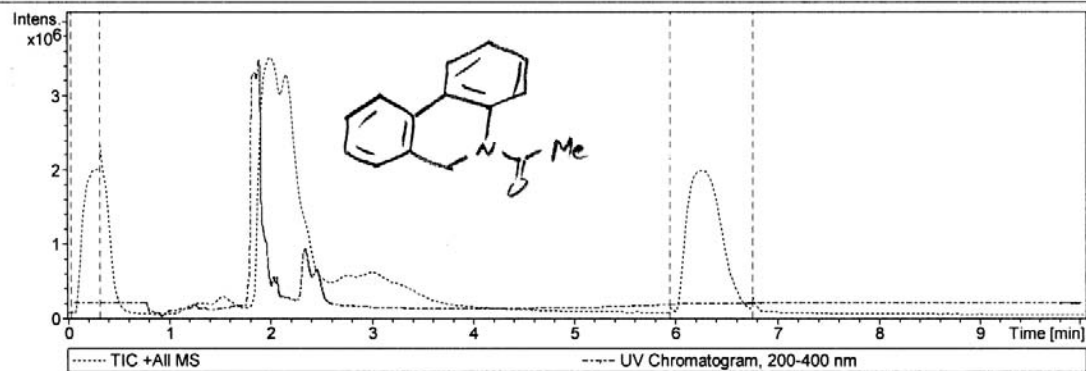
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Operator Meena Sharma

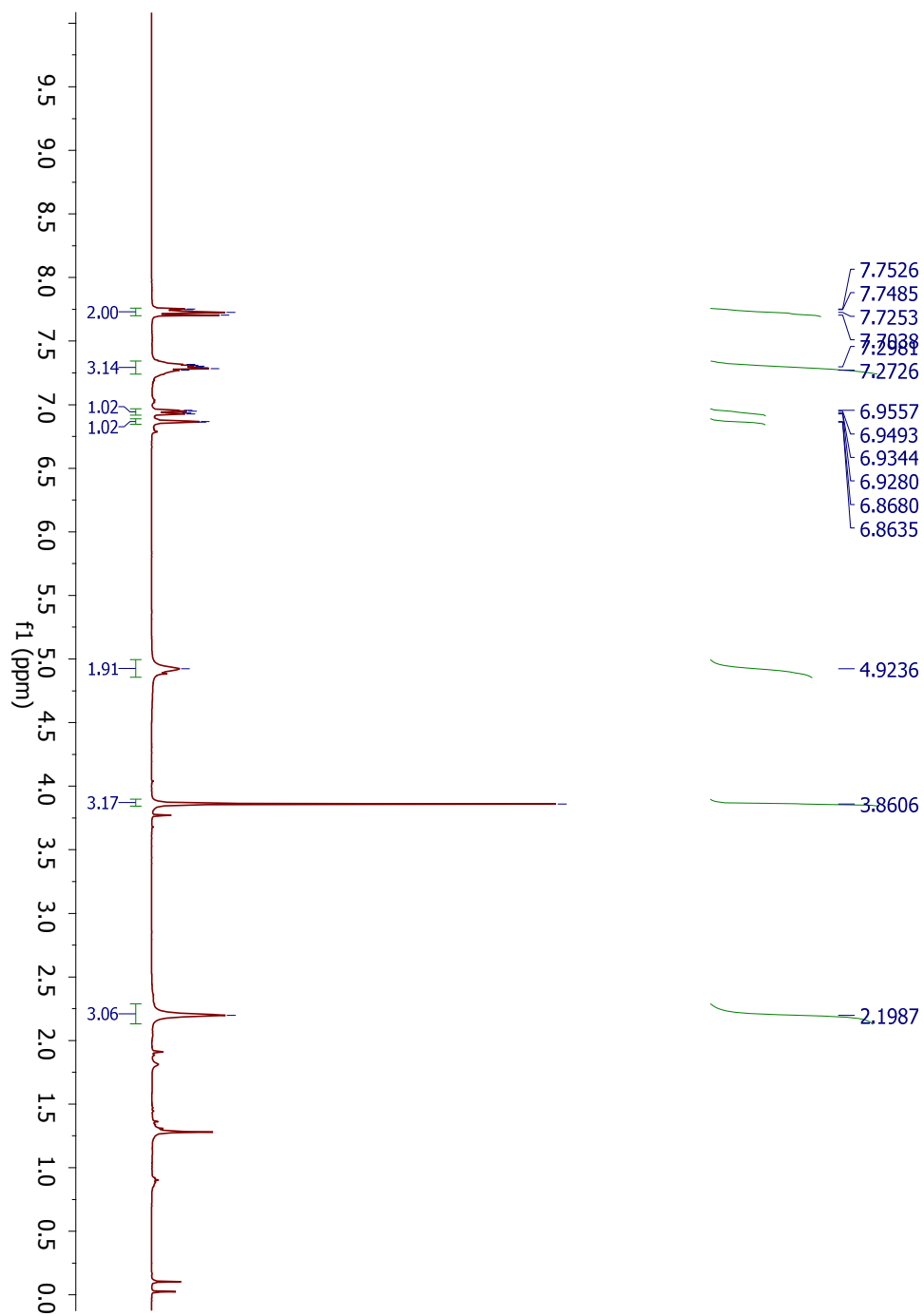
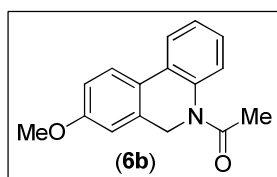
Instrument micrOTOF-Q II 10330

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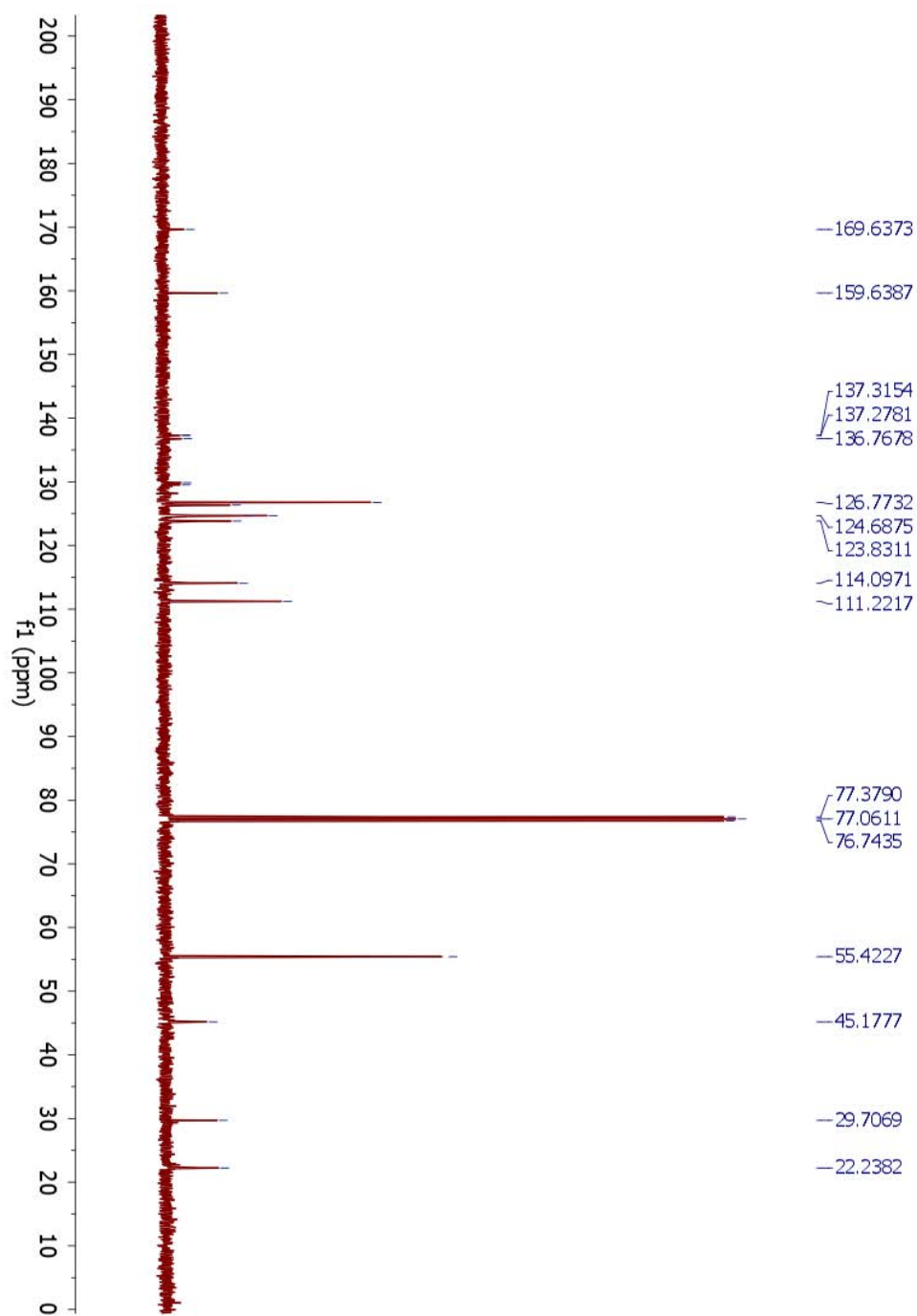
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of (6a)



¹H NMR (400 MHz, CDCl₃) compound **(6b)**



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

Display Report

Analysis Info

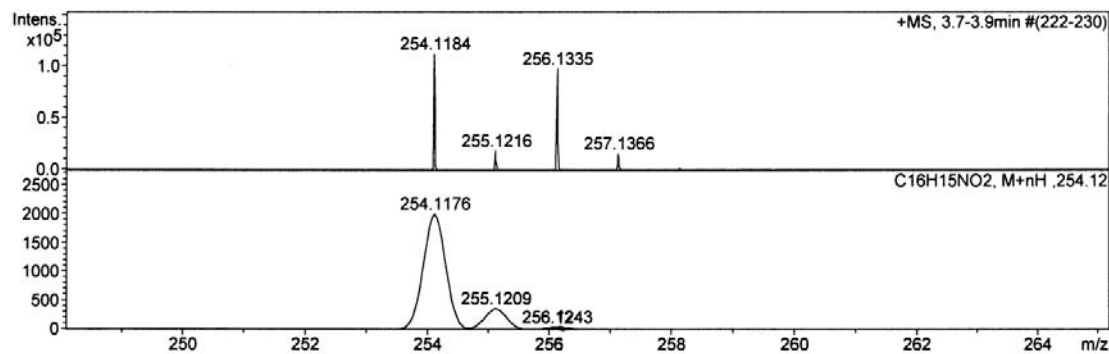
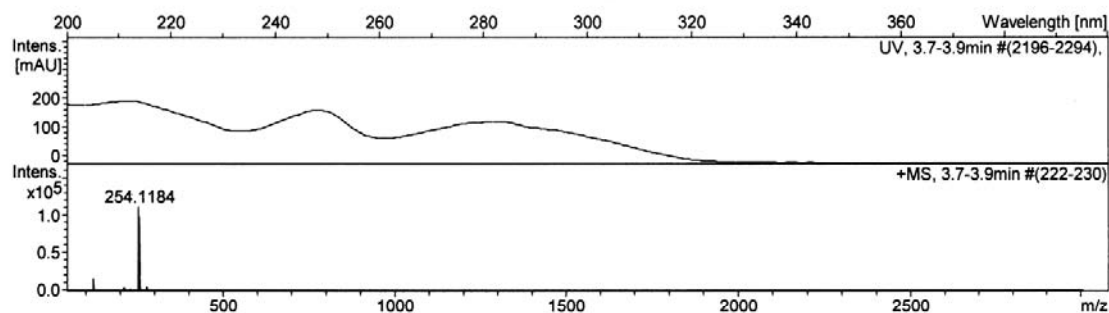
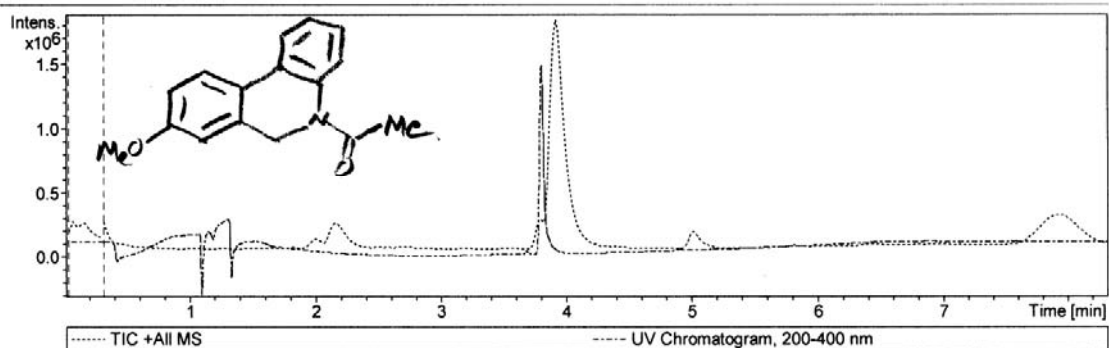
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Sample Name Dr. A. Bisai-SD-108
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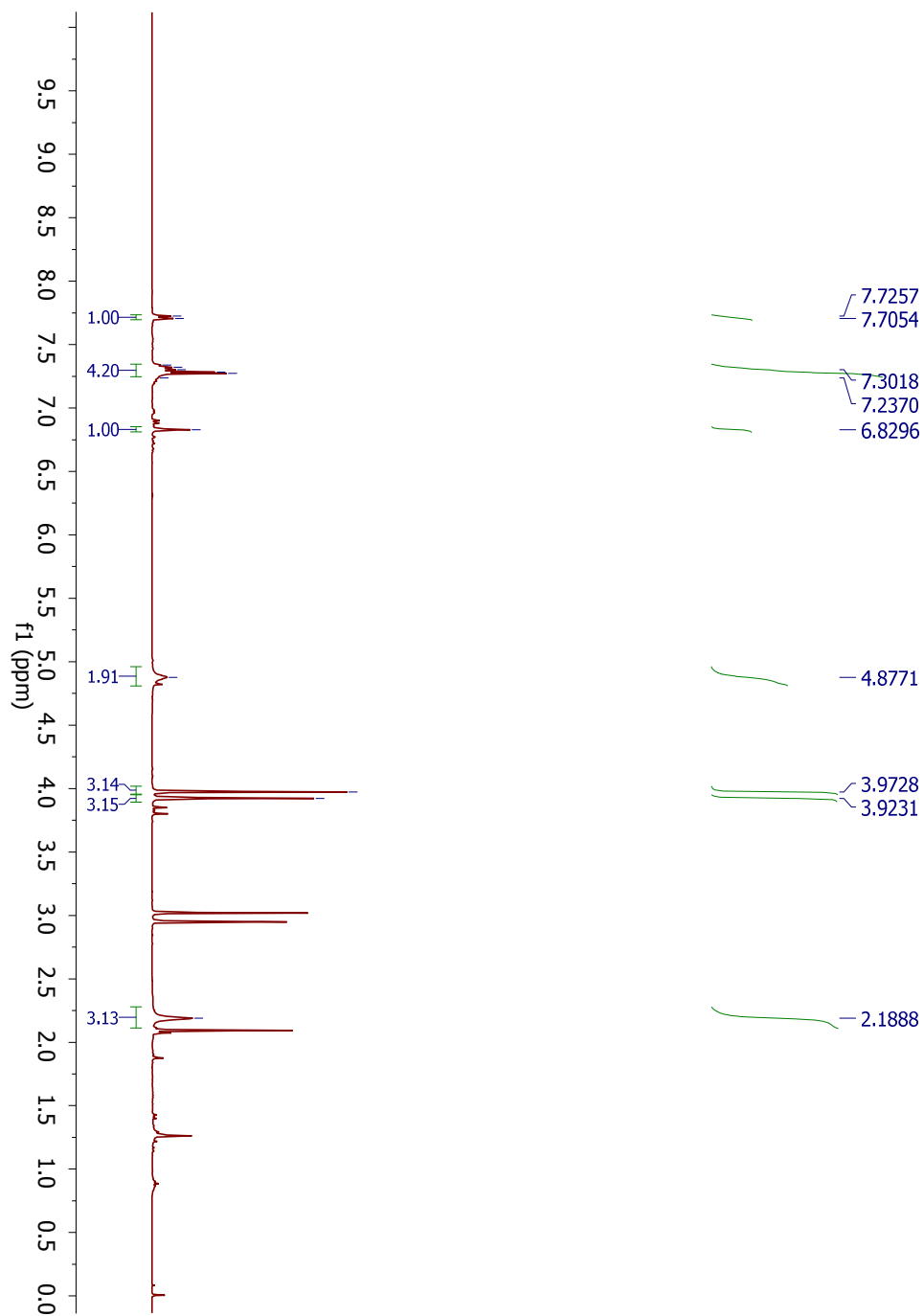
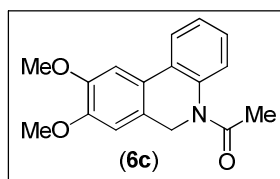
Operator Meena Sharma
Instrument micrOTOF-Q II 10330

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



Scanned copy of mass spectrum of (6b)



¹H NMR (400 MHz, CDCl₃) compound **(6c)**

Display Report

Analysis Info

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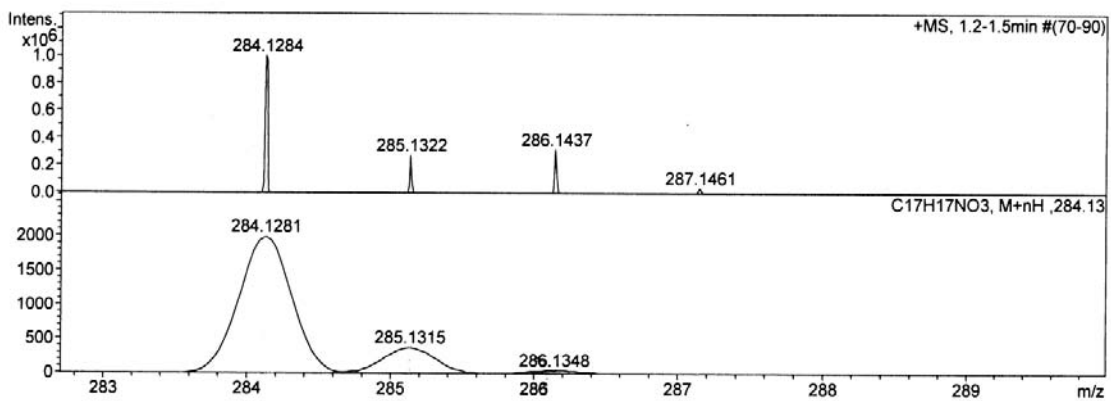
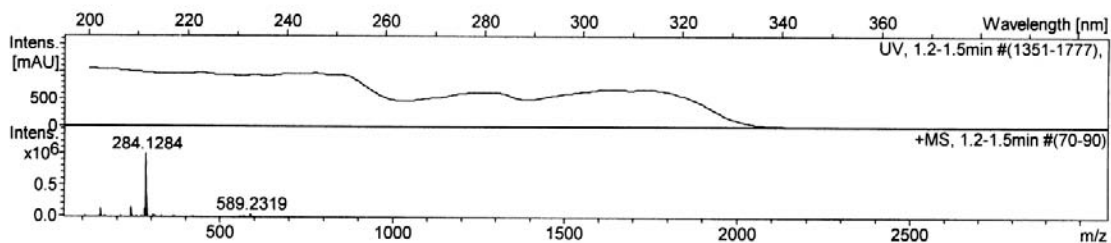
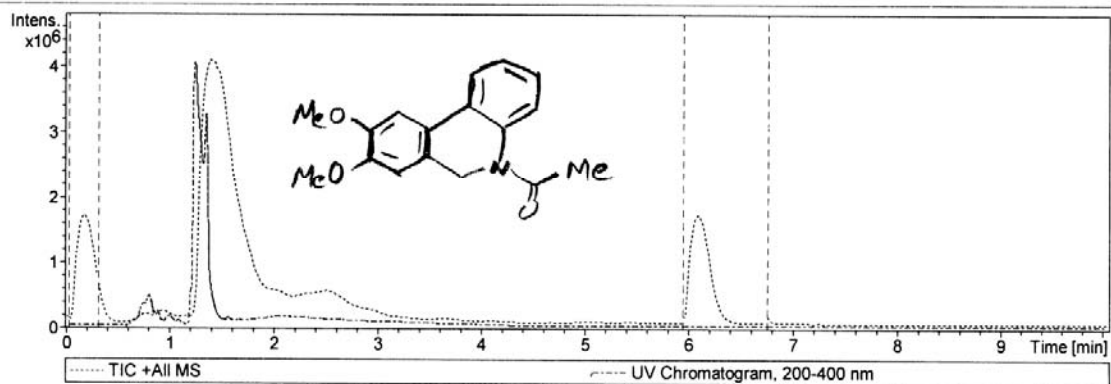
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Operator Meena Sharma

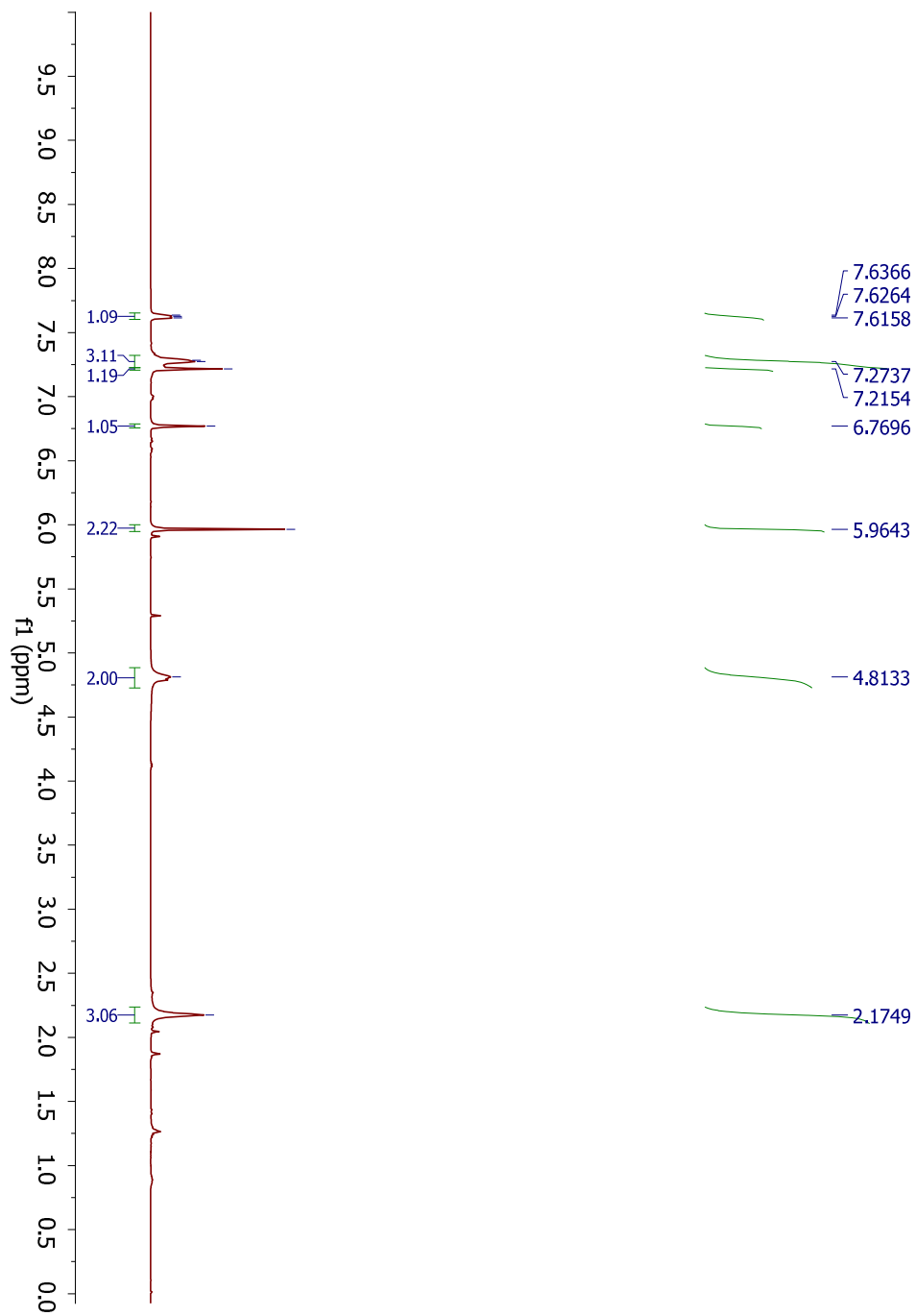
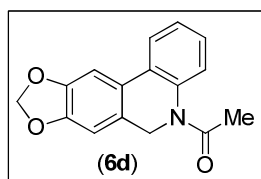
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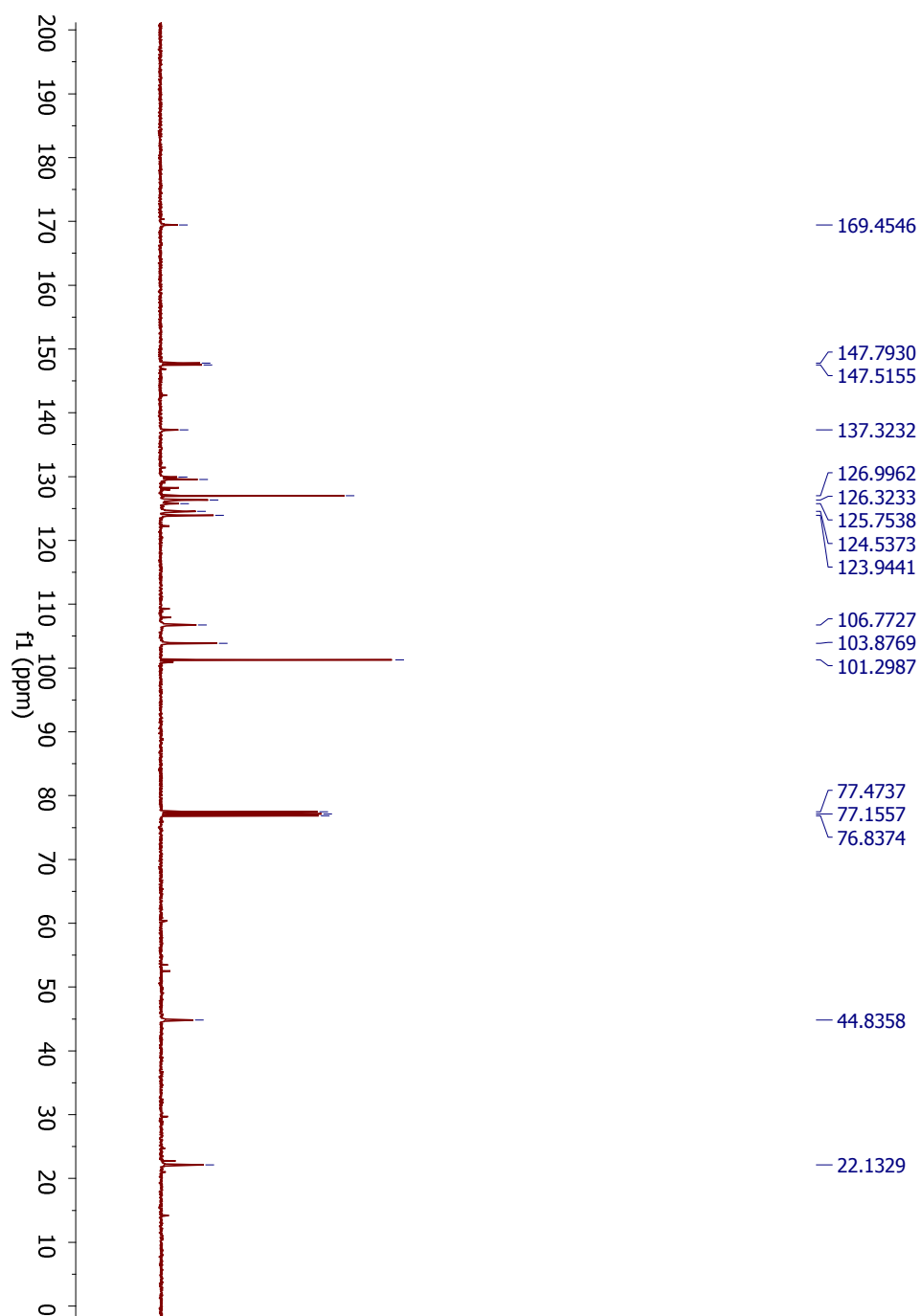
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Scanned copy of mass spectrum of (6c)



^1H NMR (400 MHz, CDCl_3) compound (6d)



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

Display Report

Analysis Info

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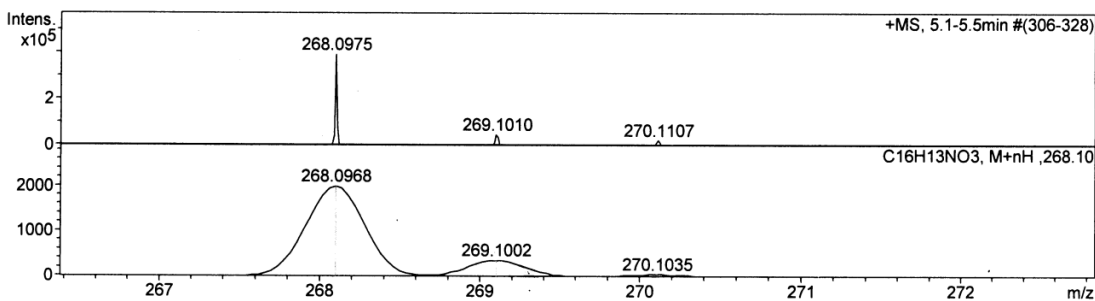
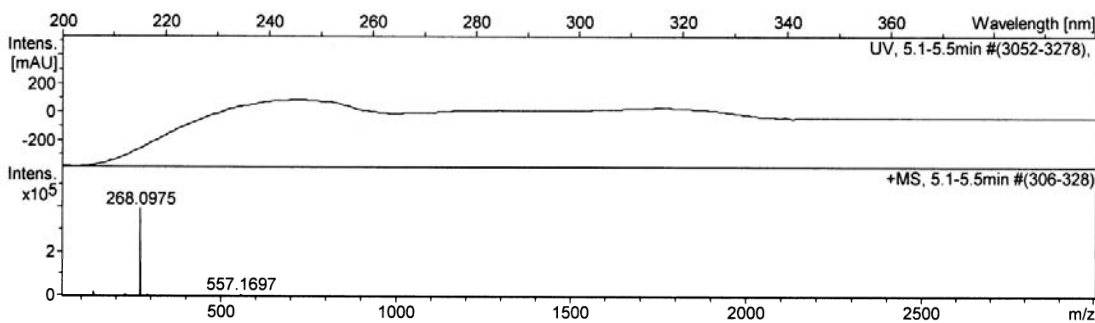
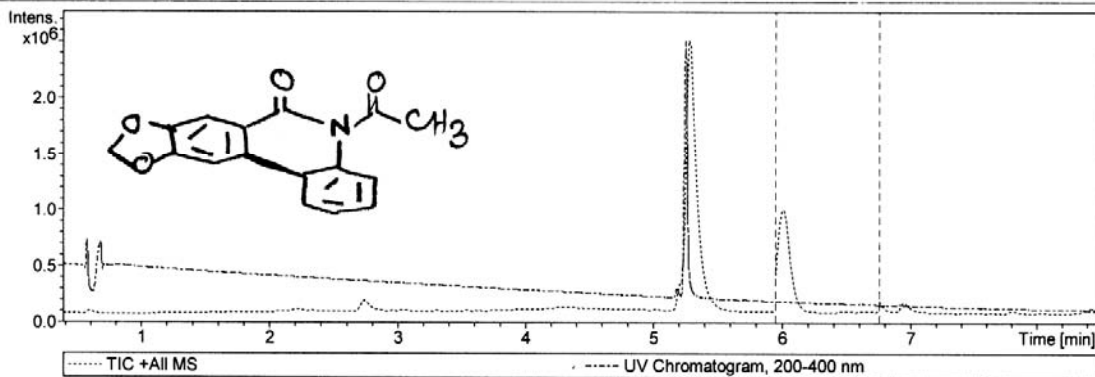
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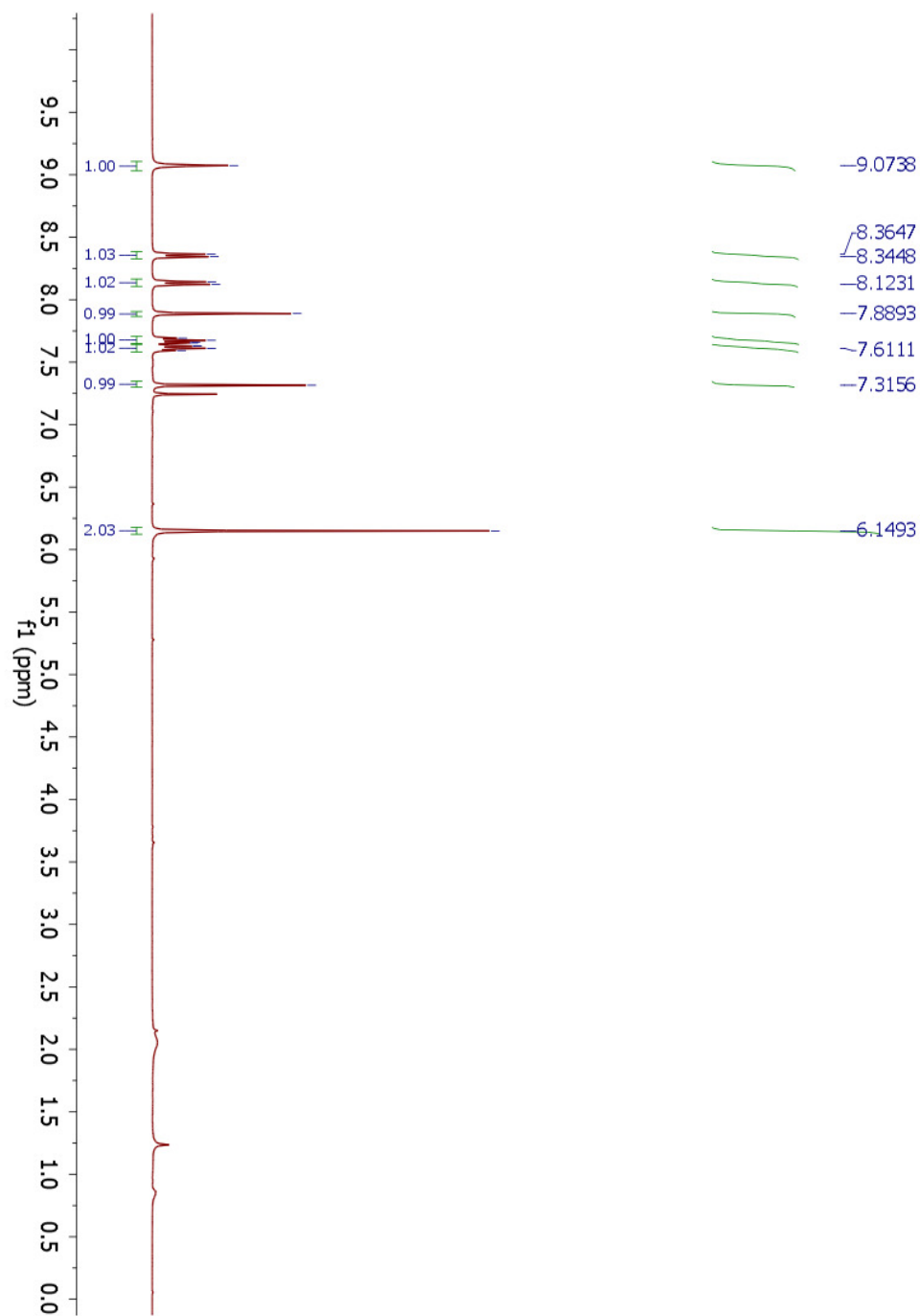
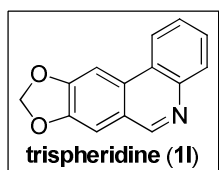
Operator Meena Sharma

Instrument microTOF-Q II 10330

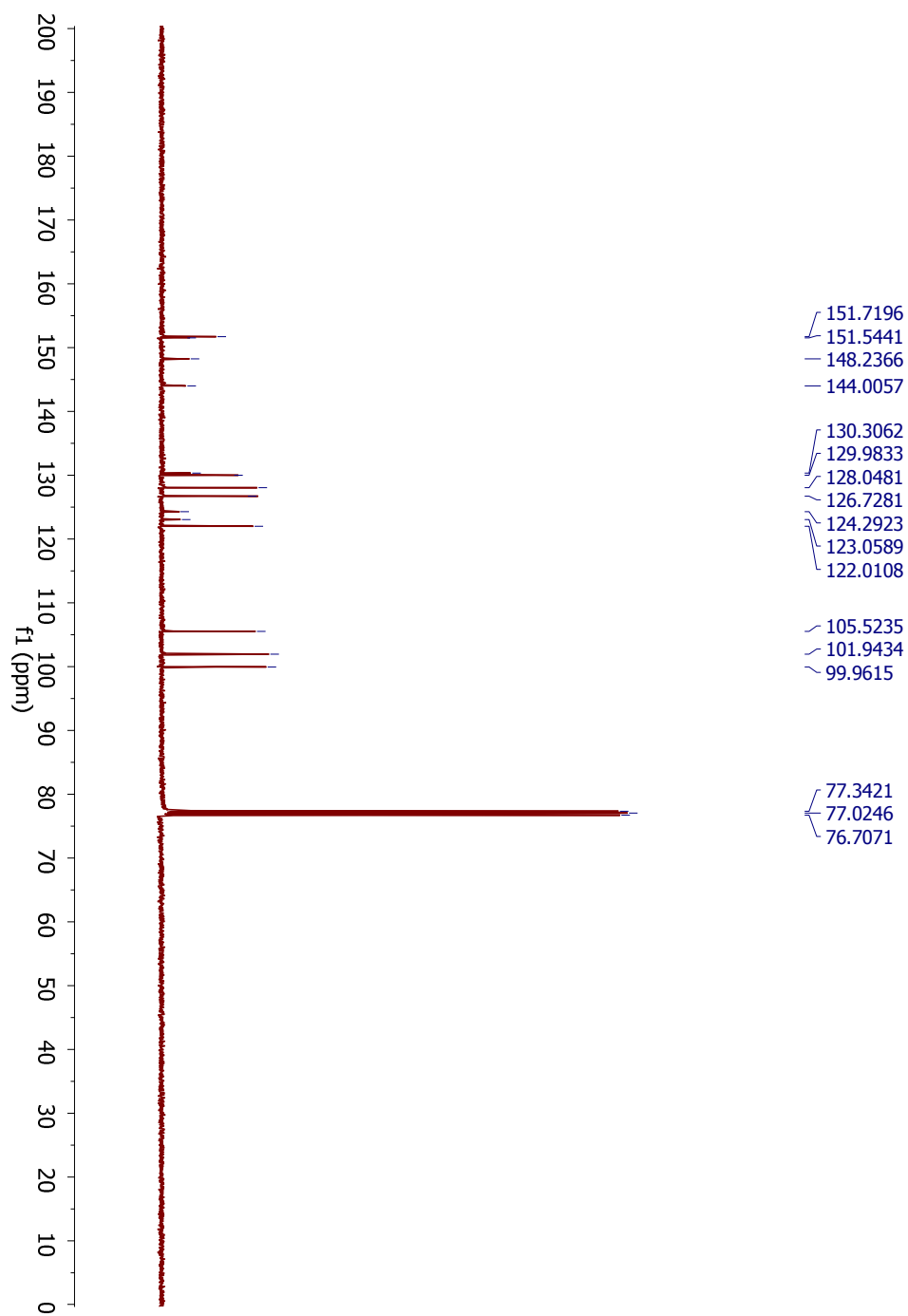
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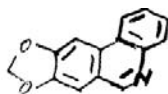
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^1H NMR (400 MHz, CDCl_3) compound (1I)





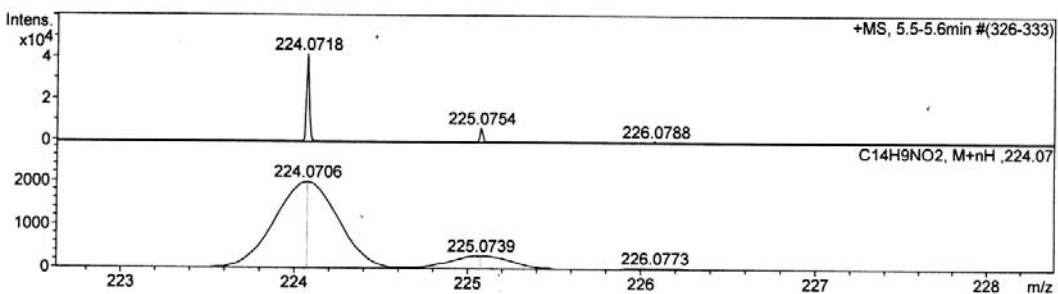
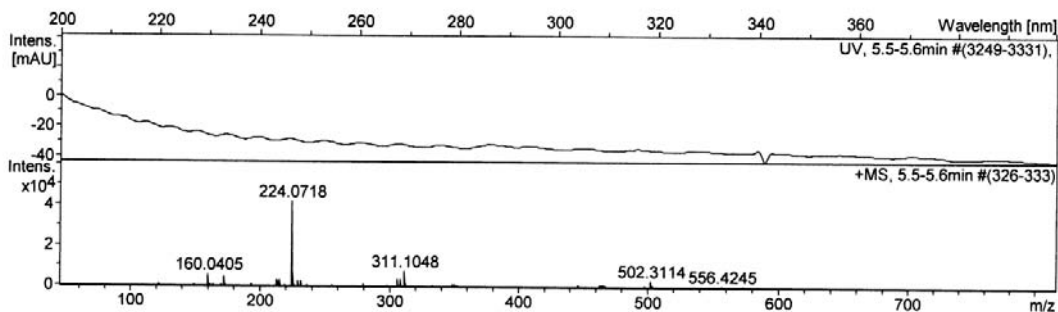
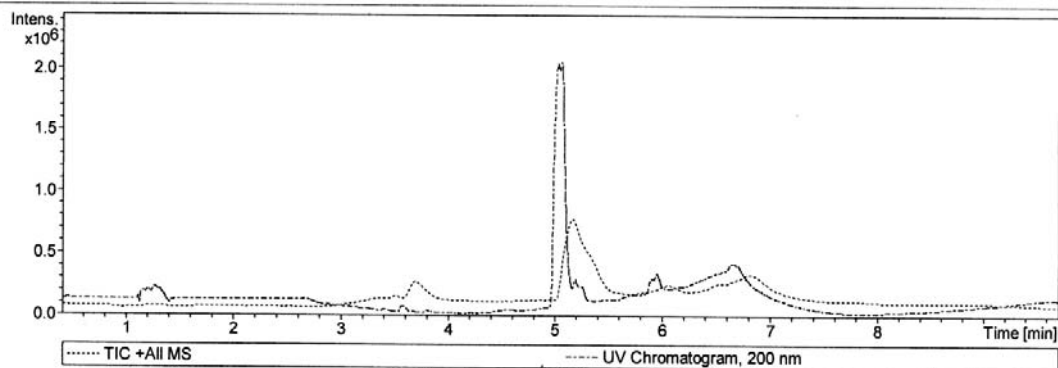
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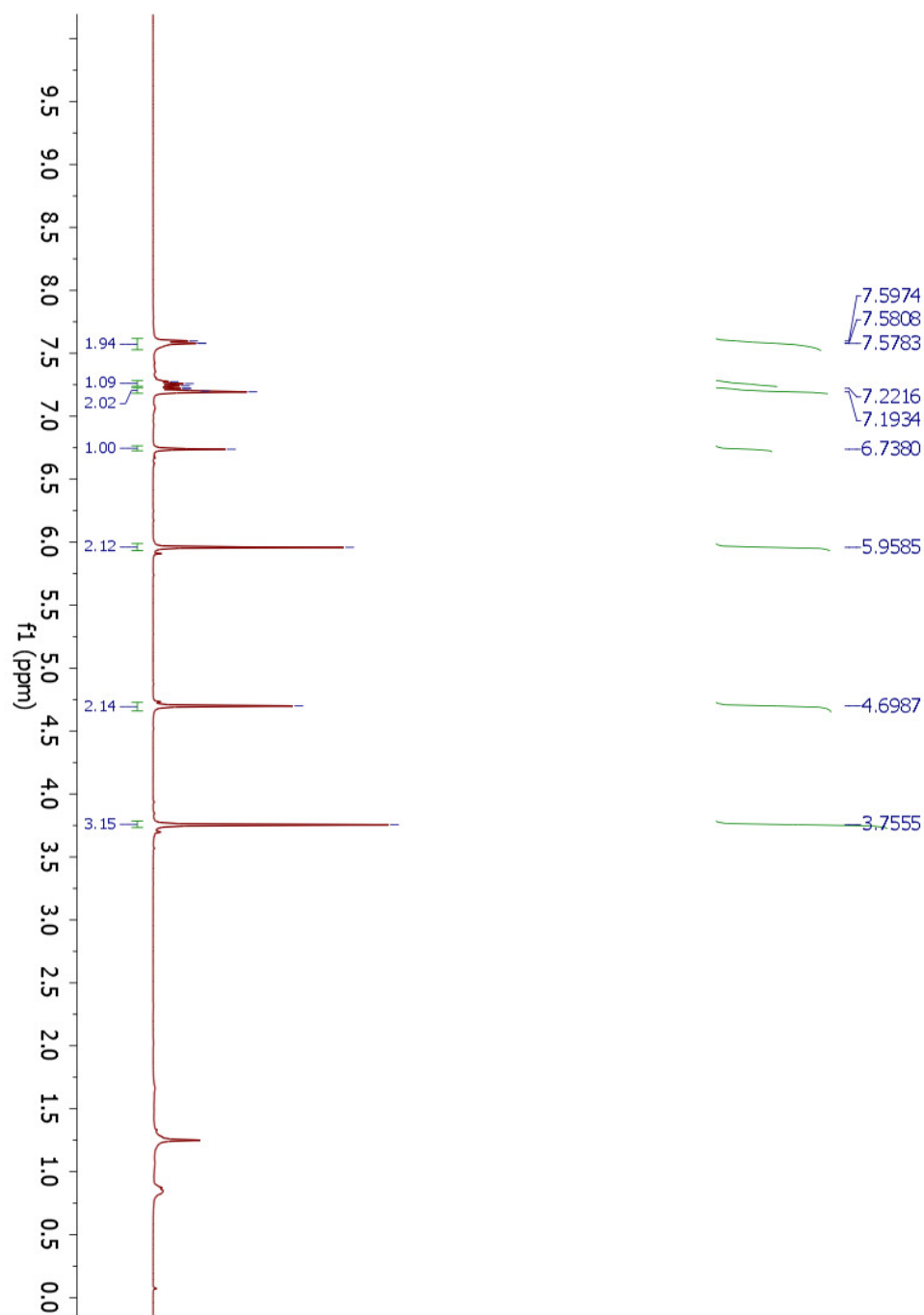
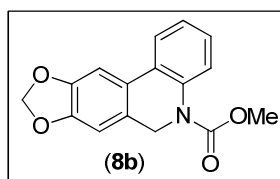
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

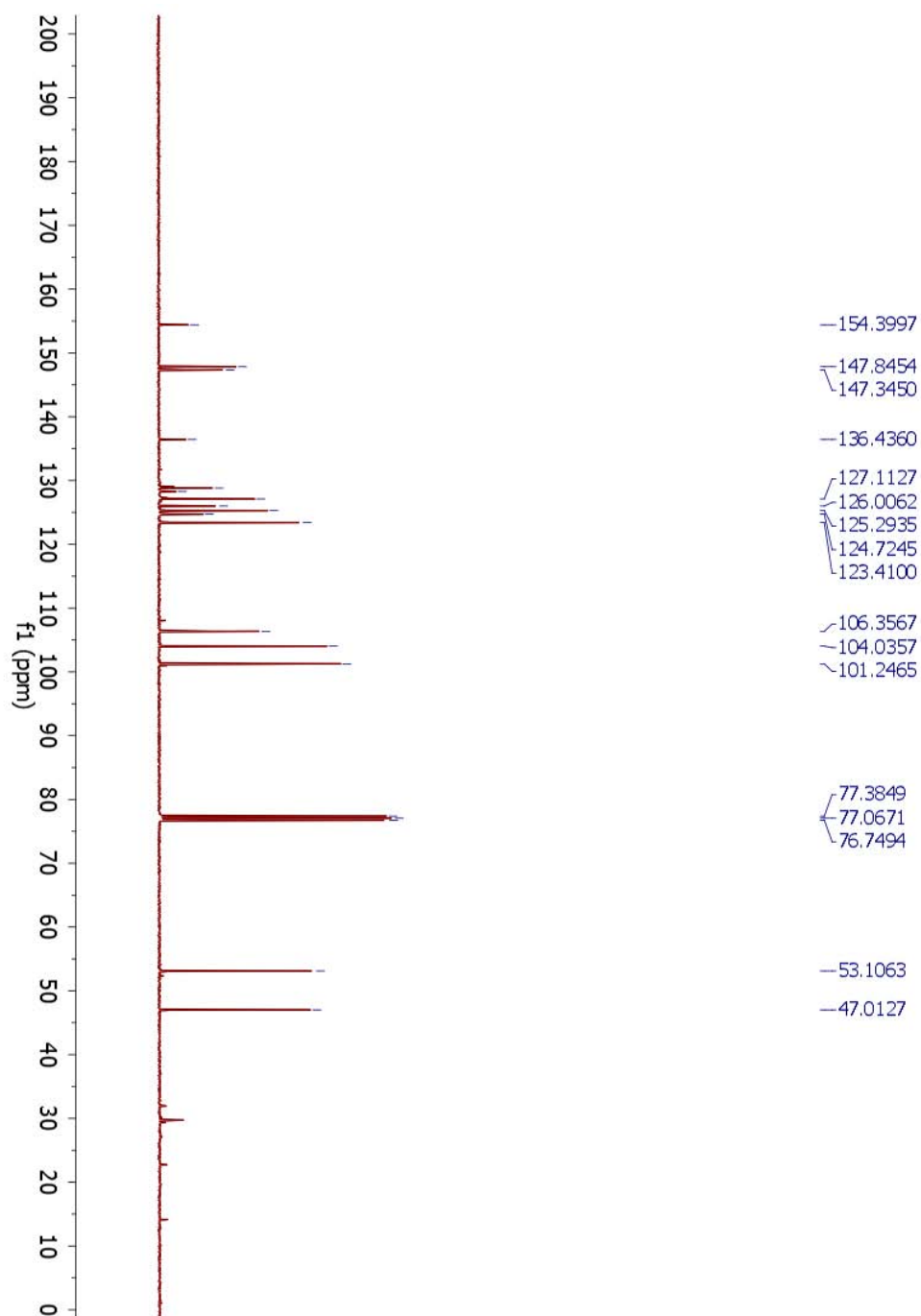
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





^1H NMR (400 MHz, CDCl_3) compound (8b)



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

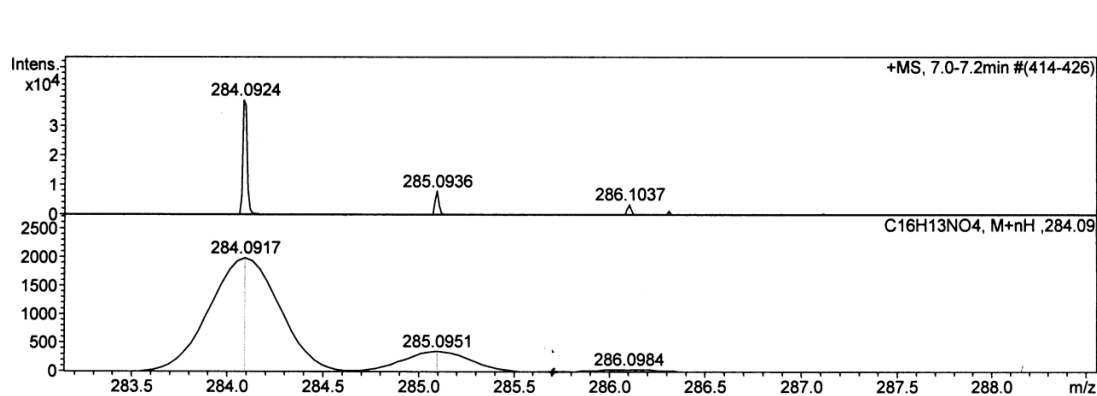
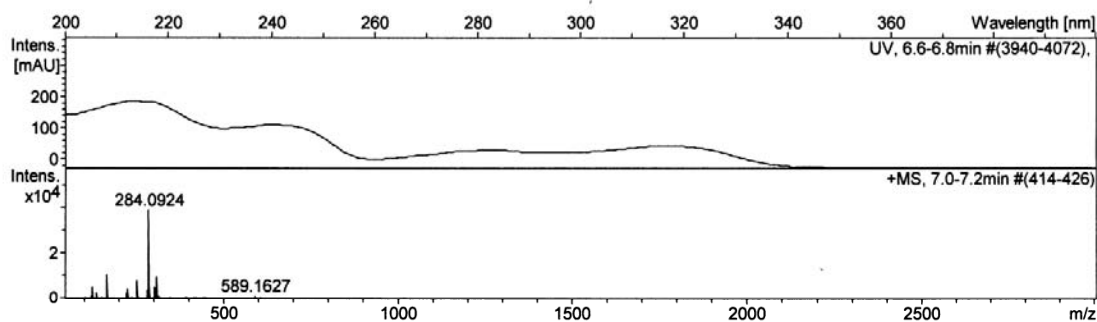
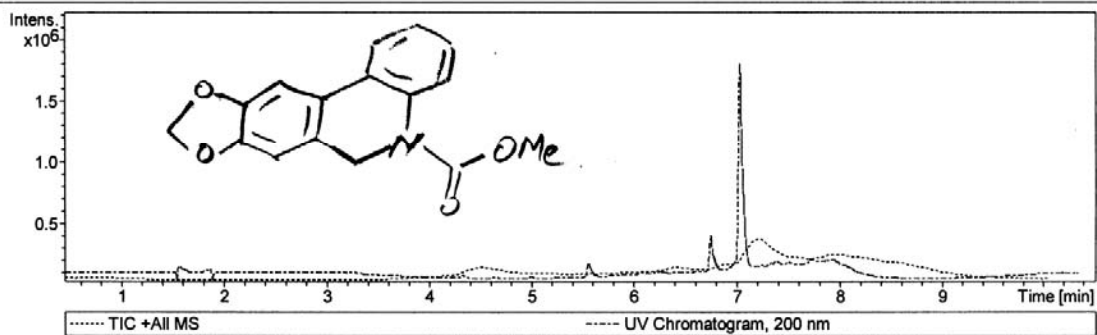
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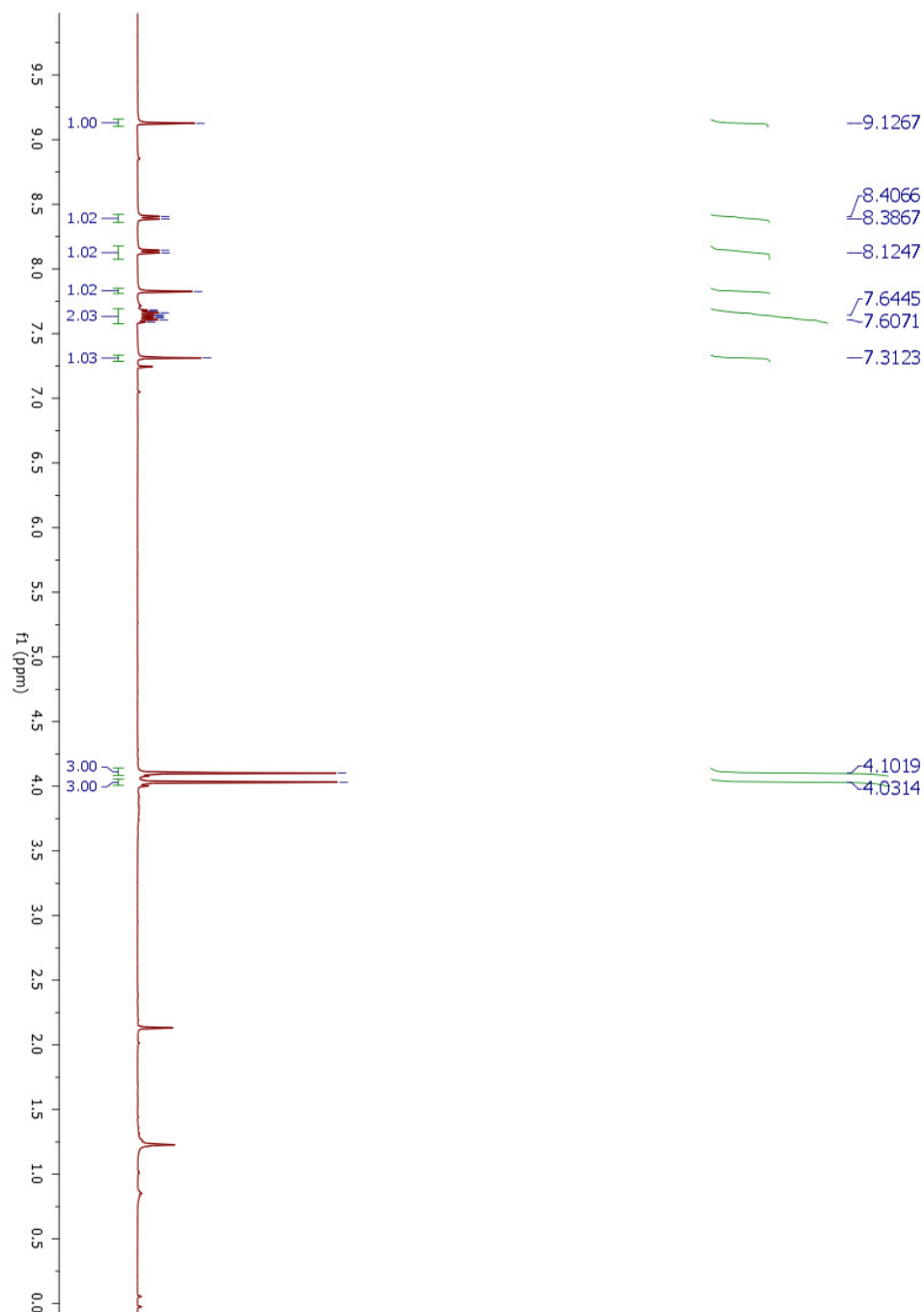
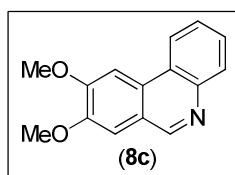
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Operator Meena Sharma
Instrument microTOF-Q II 10330

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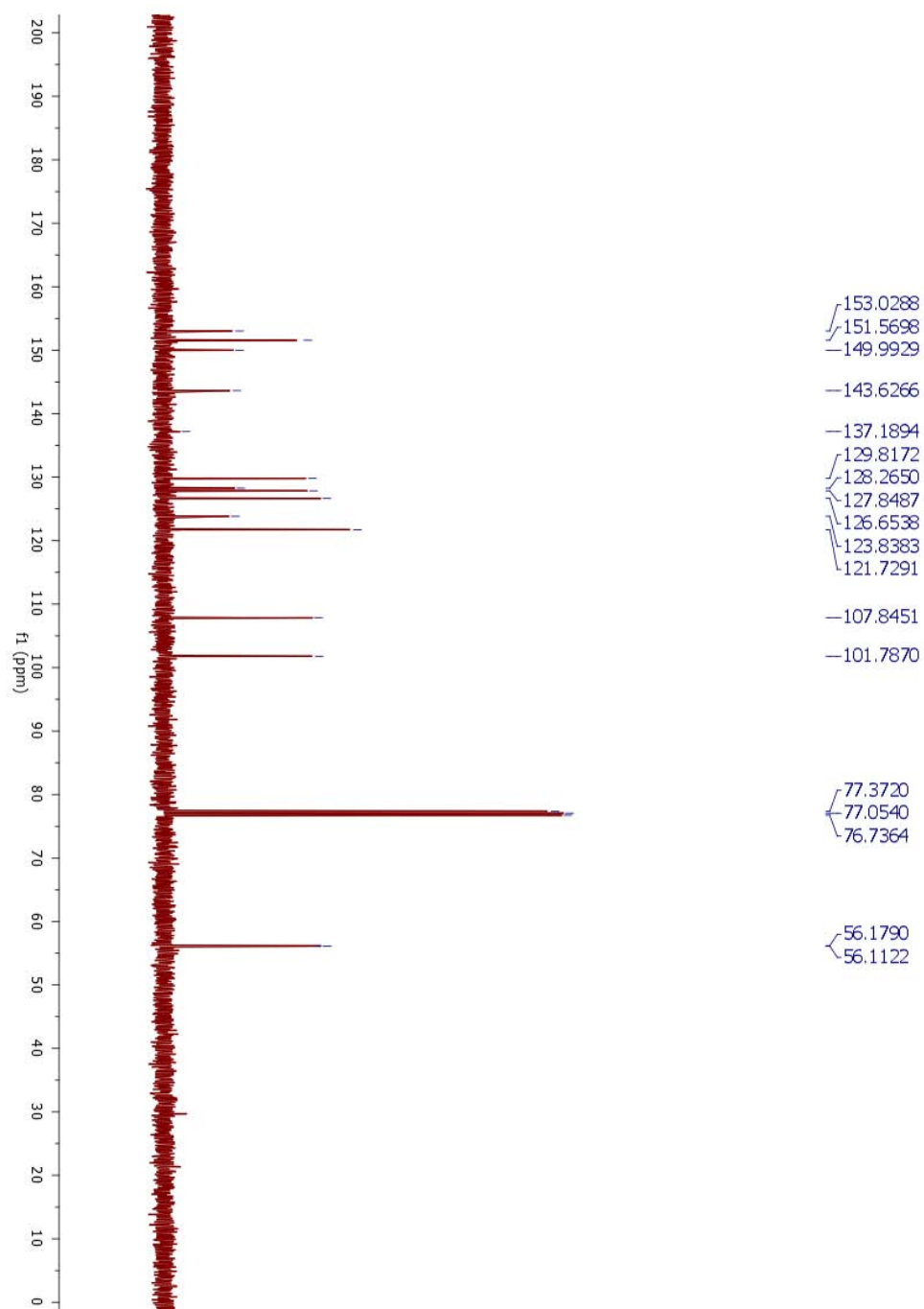
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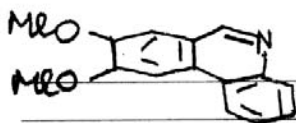
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¹H NMR (400 MHz, CDCl₃) compound **(8c)**



^{13}C NMR (100 MHz, CDCl_3) compound **(8c)**



Display Report

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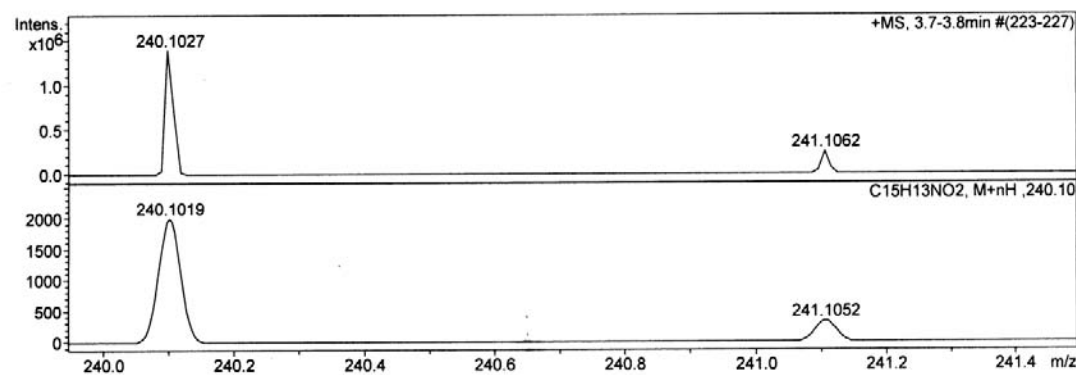
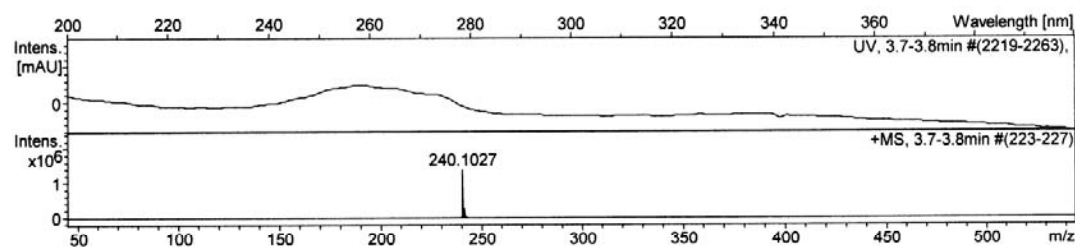
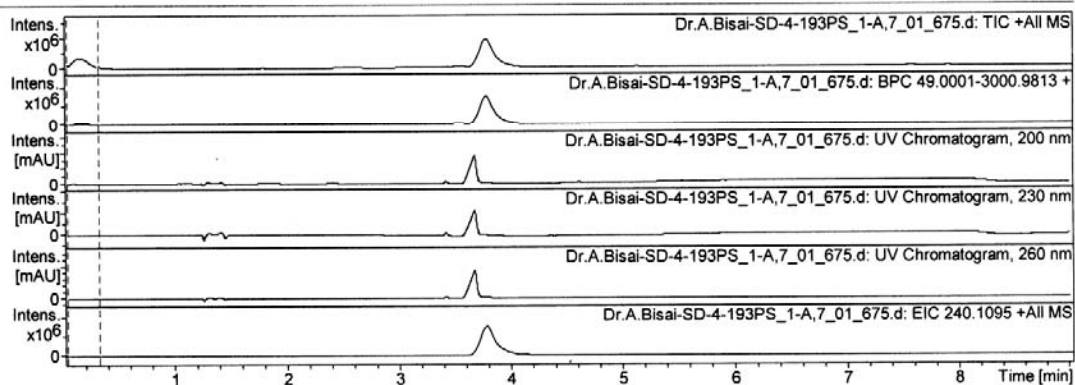
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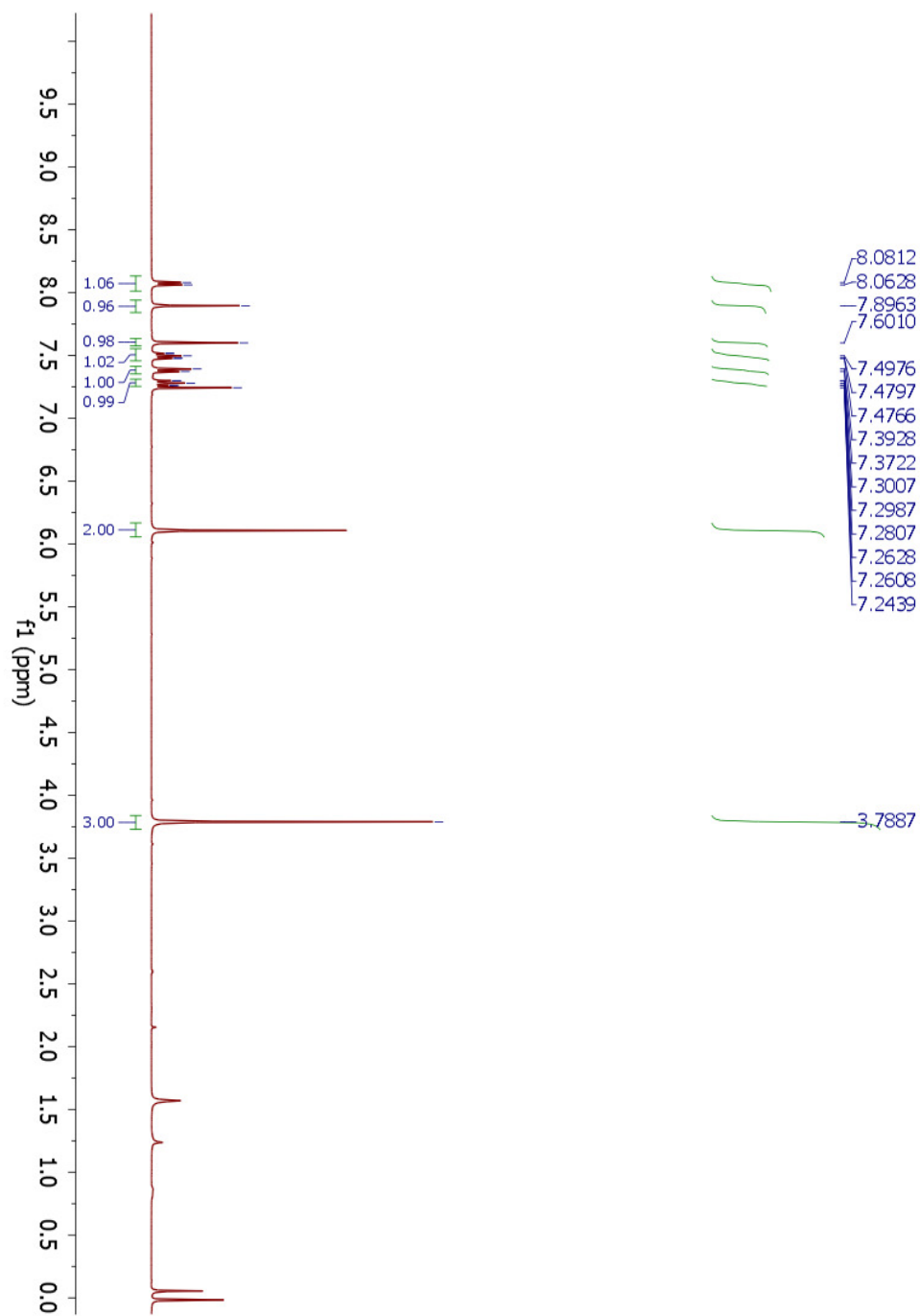
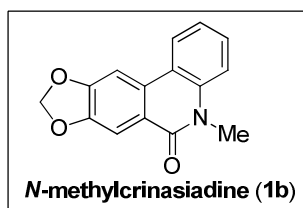
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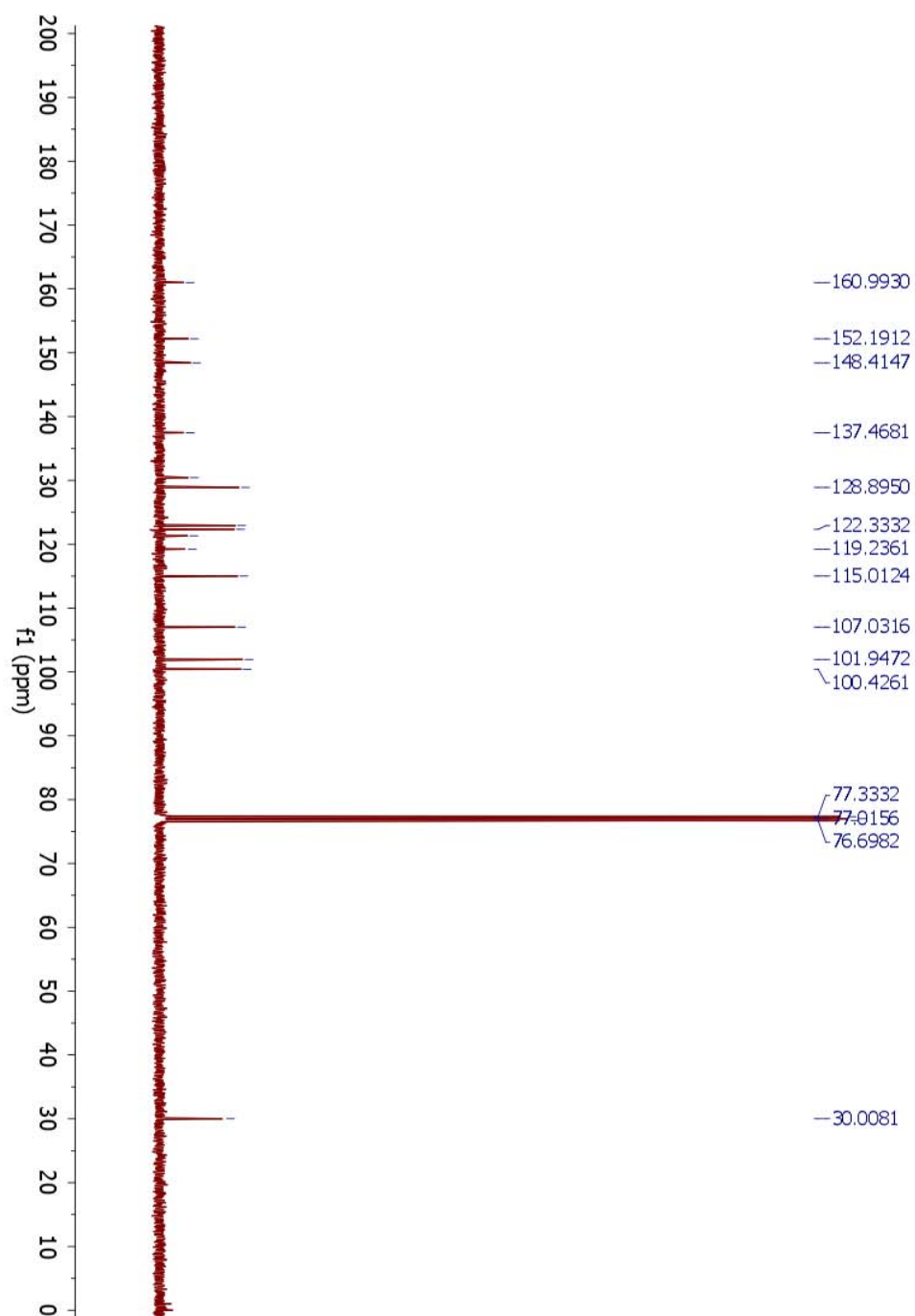
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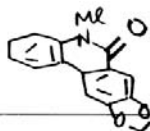




¹H NMR (400 MHz, CDCl₃) compound **(1b)**



^{13}C NMR (100 MHz, CDCl_3) compound **(1b)**



Display Report

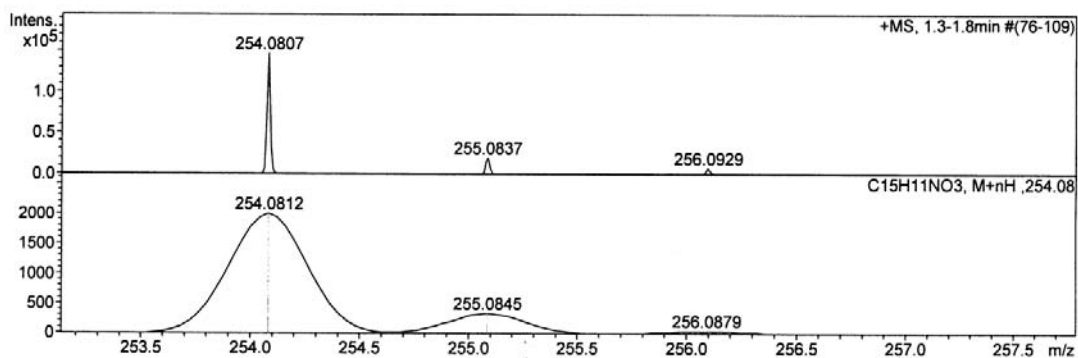
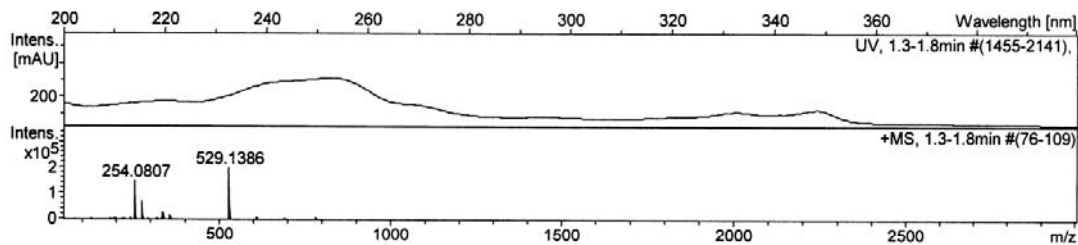
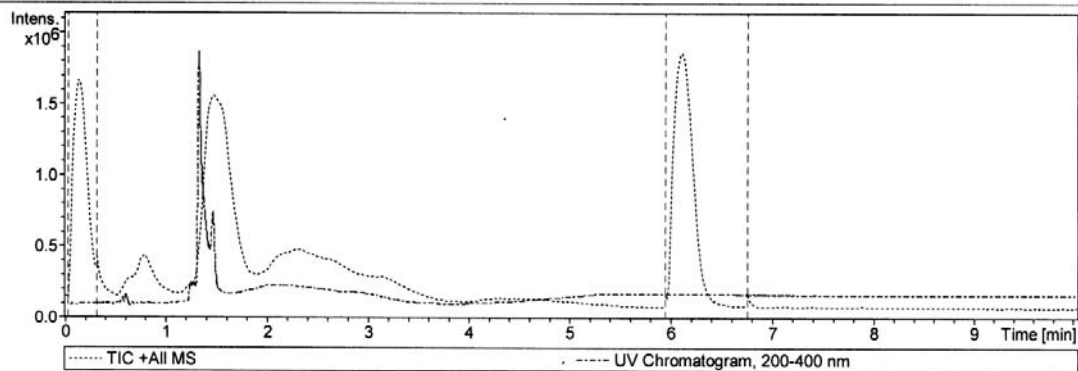
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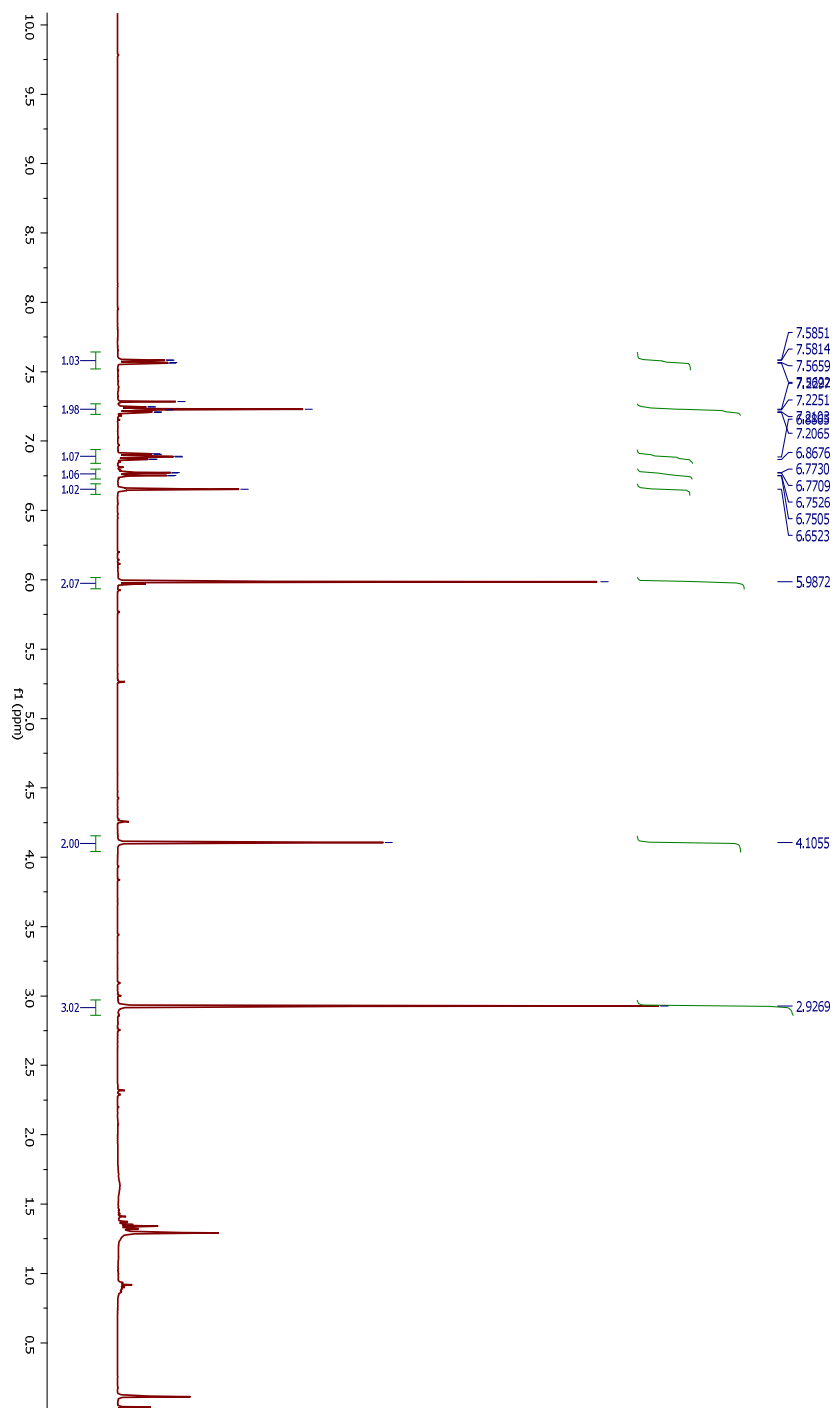
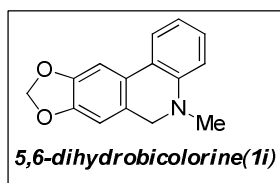
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Method HRLCMS-20 Sept.m
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Instrument micrOTOF-Q II 10330

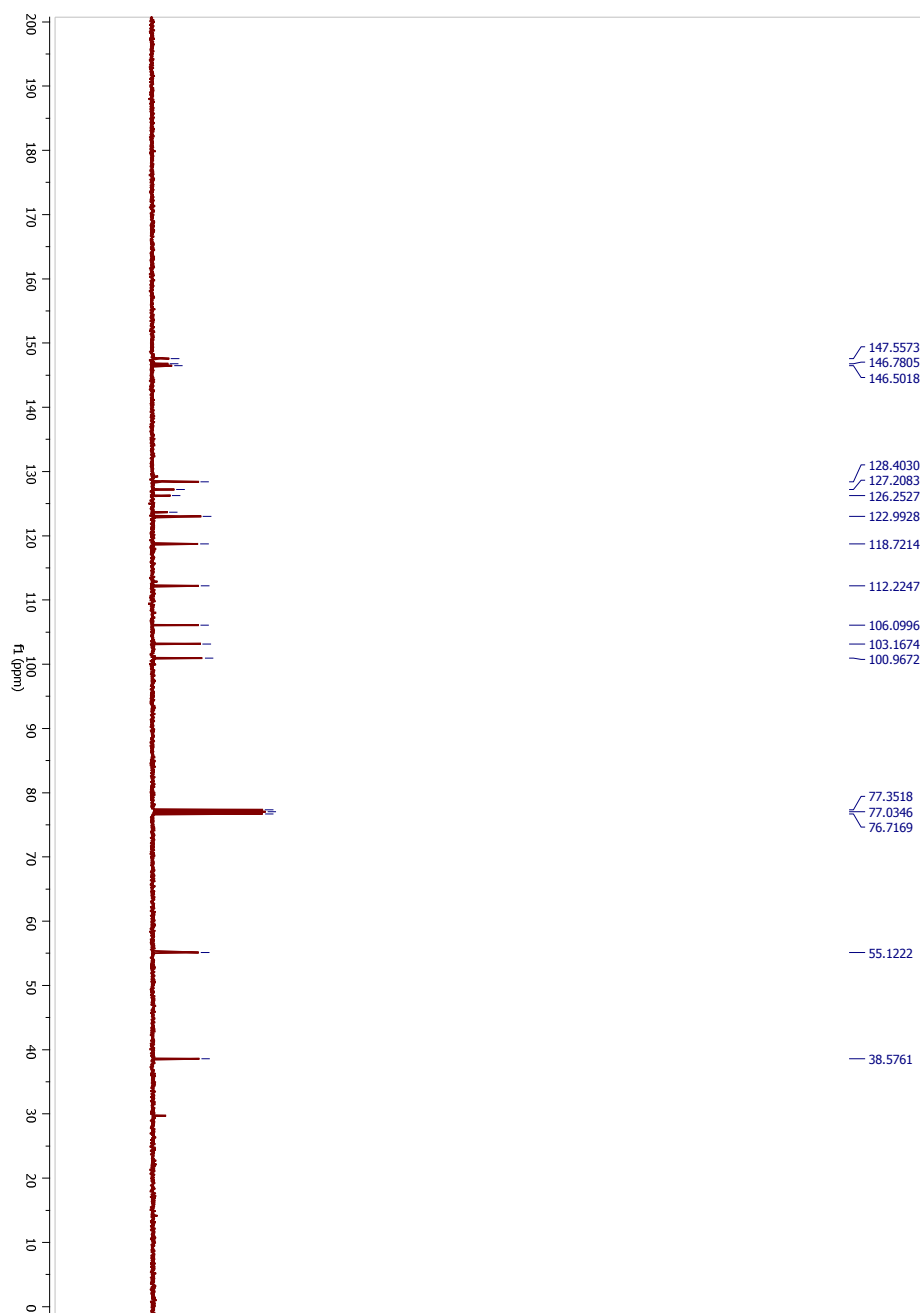
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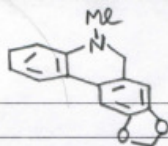




¹H NMR (400 MHz, CDCl₃) compound **(1i)**



^{13}C NMR (100 MHz, CDCl_3) compound **(1i)**



Display Report

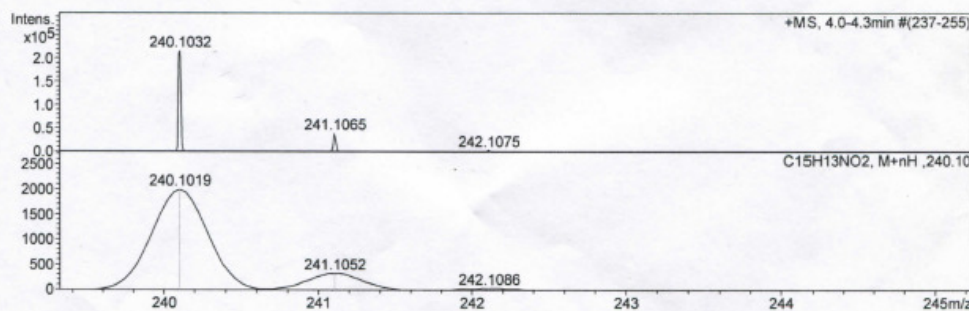
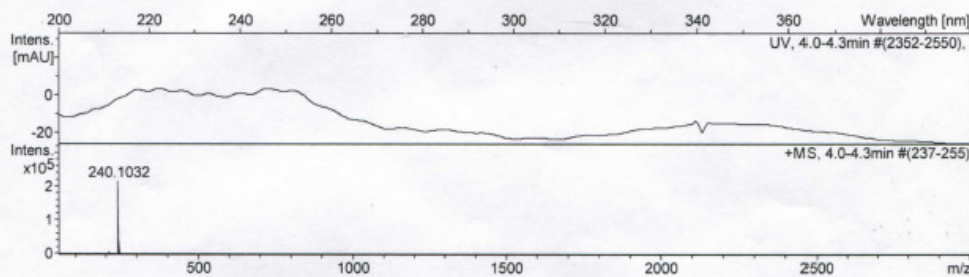
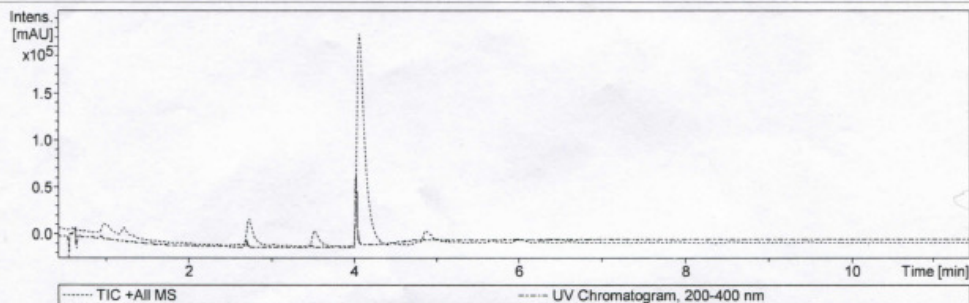
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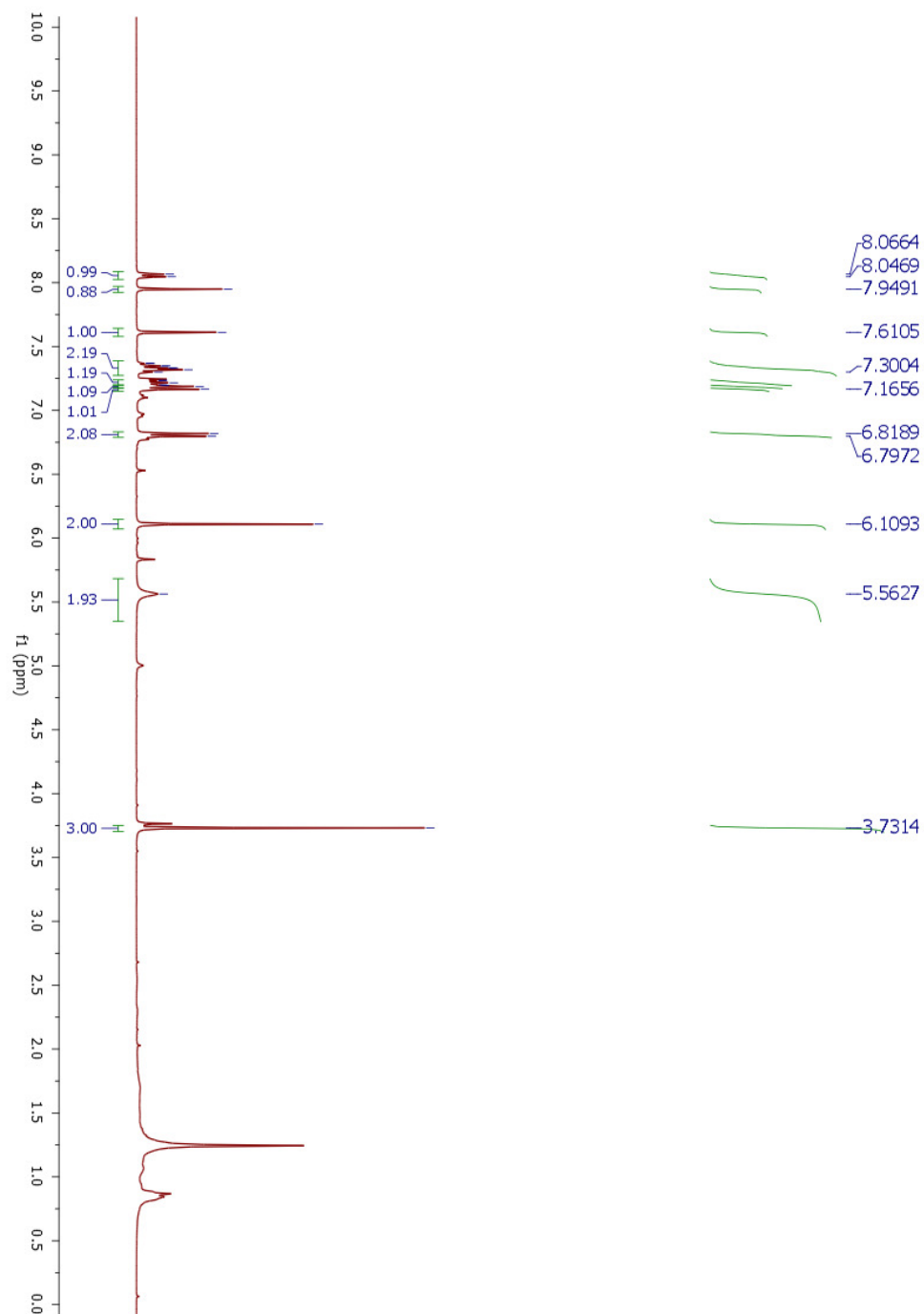
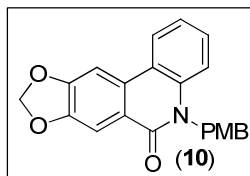
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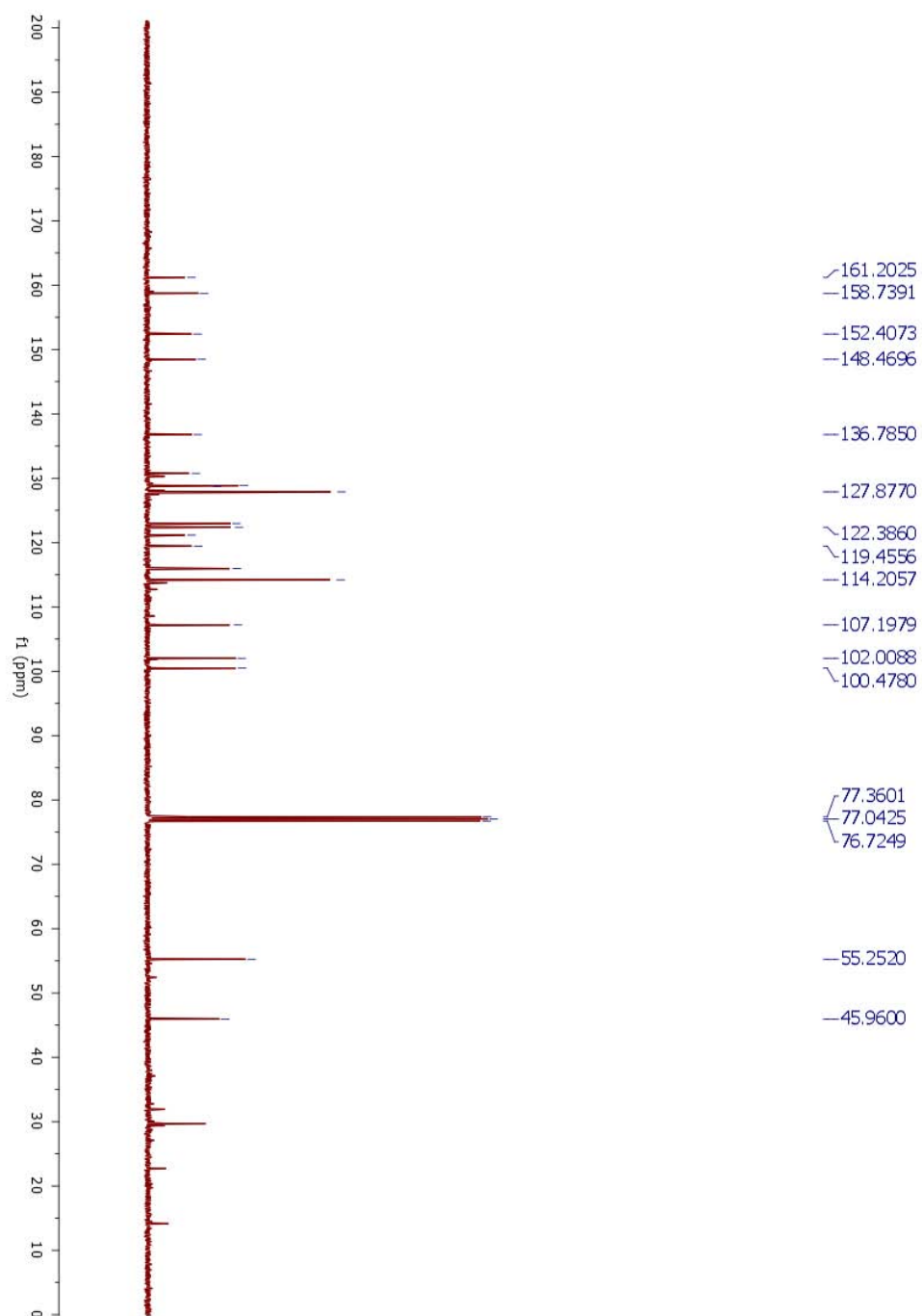
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¹H NMR (400 MHz, CDCl₃) compound **(10)**



^{13}C NMR (100 MHz, CDCl_3) compound **(10)**

Display Report

Analysis Info

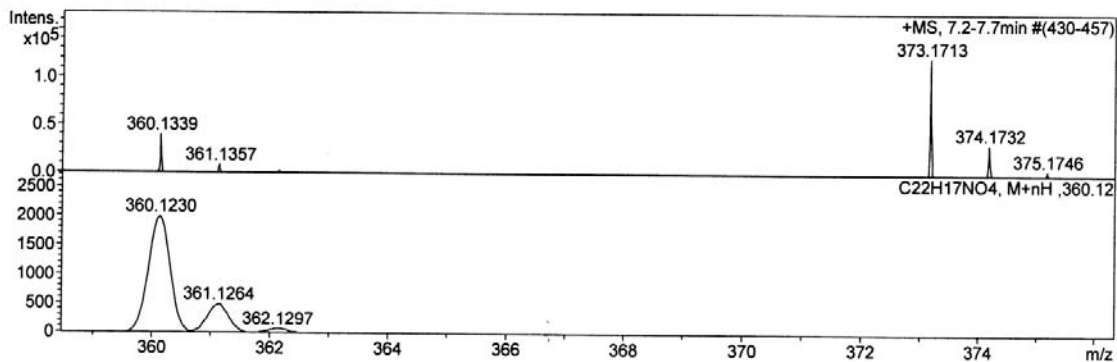
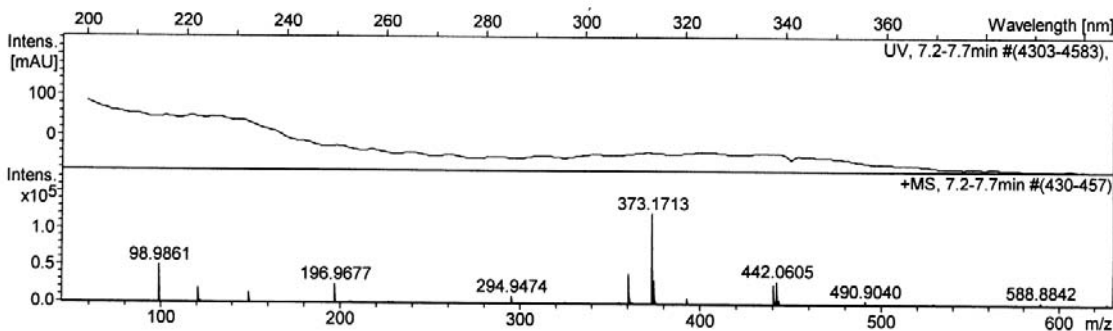
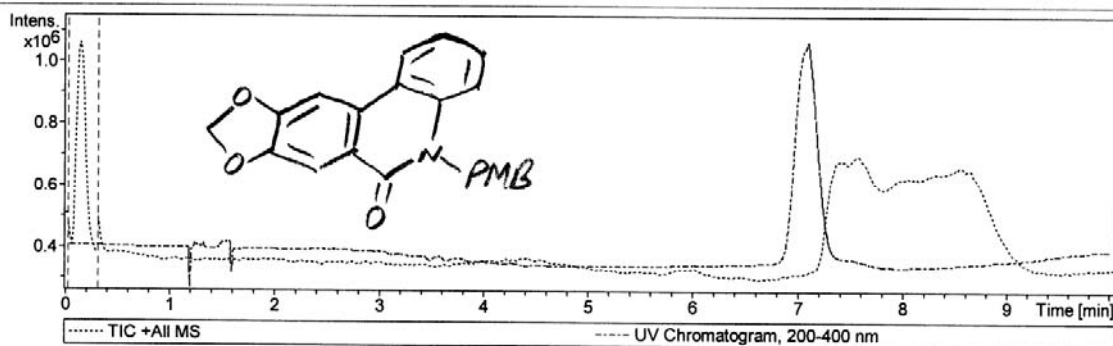
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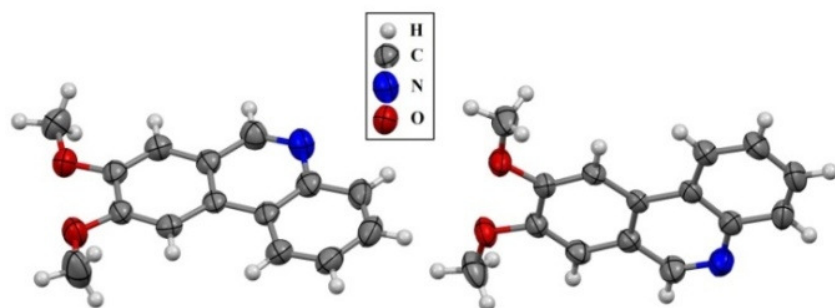
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Instrument micrOTOF-Q II 10330

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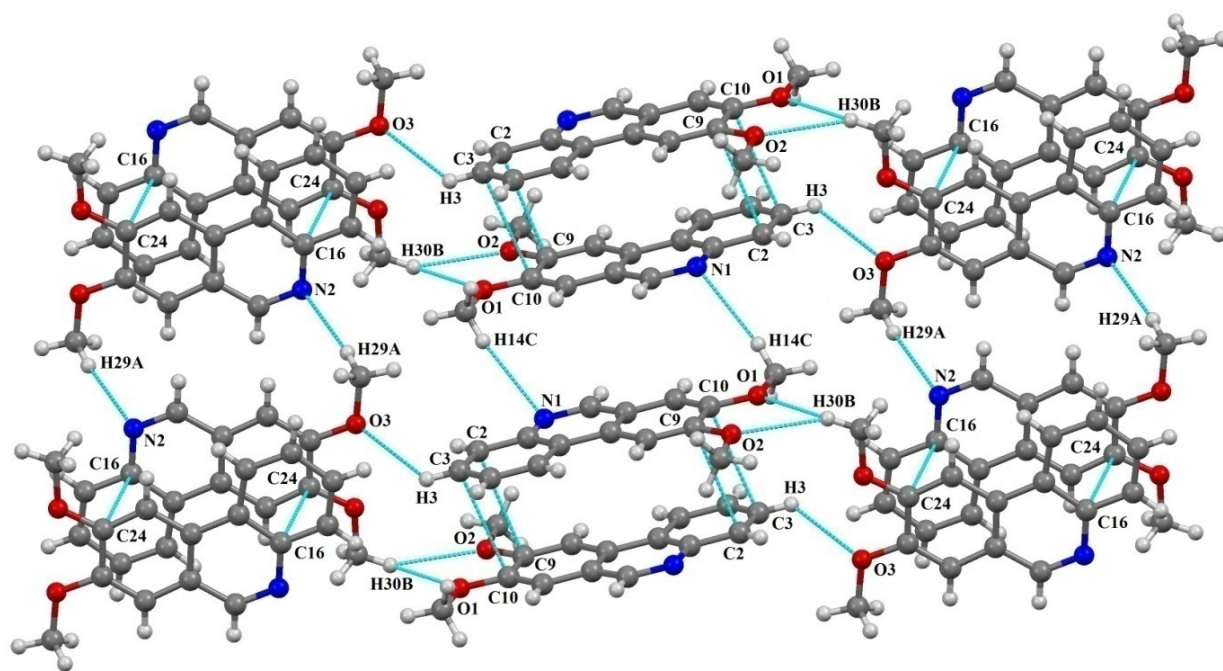


X-Ray structure of compound (8c):



[CCDC 931413]

Figure 2: ORTEP diagram of phenanthridine **8c** (asymmetric unit contains two molecules).



[CCDC 931413]

Figure 3: Intermolecular H-bonding and π -stacking in the crystal packing of compound **8c** using Mercury.

checkCIF/PLATON (standard)

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found.

[CIF dictionary](#)

Please wait while processing

[Interpreting this report](#)

Datablock: SD4193

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	alpha=111.398(1)	beta=90.236(2)	gamma=104.613(2)
Temperature: 298 K			
Volume	Calculated	Reported	
	1195.06(9)	1195.06(9)	
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Hall group	-P 1	-P 1	
Moiety formula	C15 H13 N O2	?	
Sum formula	C15 H13 N O2	C15 H13 N O2	
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F000	504.0	504.0	
F000'	504.23		
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R(reflections)= 0.0642(2784)	WR2(reflections)= 0.1914(3225)		
S = 1.078	Npar= 330		

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.5455

Alert level C

REFNR01_ALERT_3_C Ratio of reflections to parameters is < 10 for a centrosymmetric structure

sine(theta)/lambda 0.5455
Proportion of unique data used 1.0000
Ratio reflections to parameters 9.7727

RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.156

PLAT088_ALERT_3_C Poor Data / Parameter Ratio 9.77

Alert level G

PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.11
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum ?

- 1 **ALERT level A** = Most likely a serious problem - resolve or explain
- 0 **ALERT level B** = A potentially serious problem, consider carefully
- 3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
- 2 **ALERT level G** = General information/check it is not something unexpected

- 1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
- 1 ALERT type 2 Indicator that the structure model may be wrong or deficient
- 4 ALERT type 3 Indicator that the structure quality may be low
- 0 ALERT type 4 Improvement, methodology, query or suggestion
- 0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out

additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

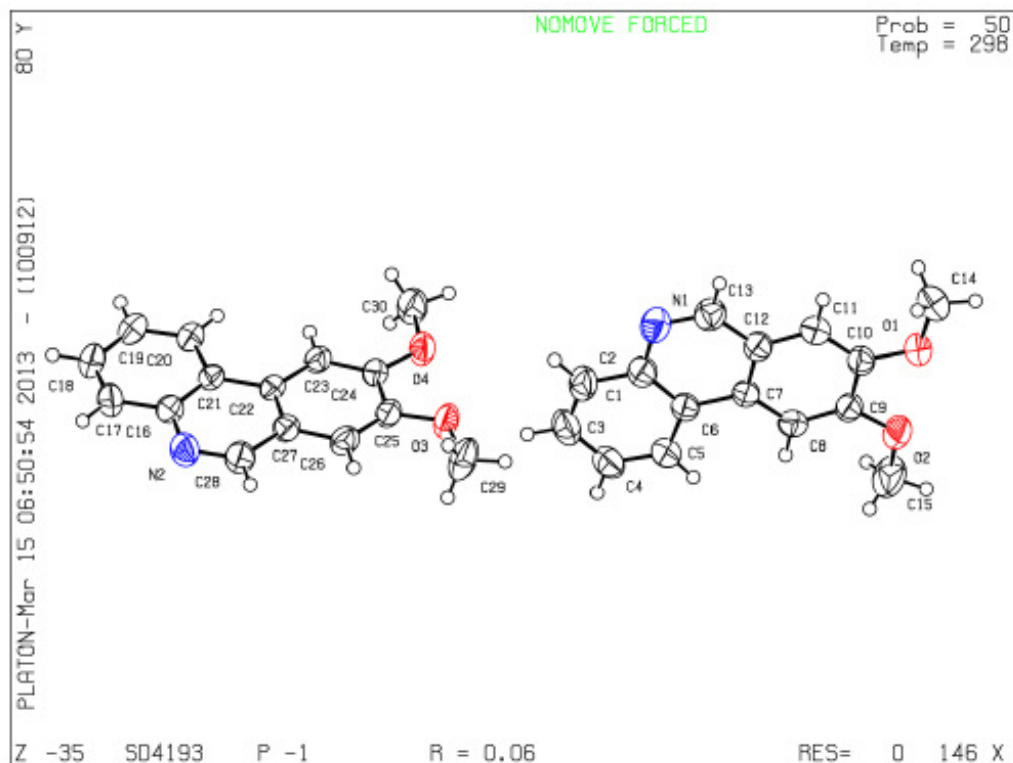
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section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

Publication of your CIF in other journals

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

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock SD4193 - ellipsoid plot



Serial No.	D-H...A	D...H(Å)	D...A(Å)	H...A(Å)	∠D-H...A(°)	Symmetry
1	C3-H3...O3	1.08	3.302(3)	2.64	118	x, y, z
2	C30-H30B...O2	1.08	3.596(3)	2.62	150	-x+1, -y+2, -z+2
3	C30-H30B...O1	1.08	3.340(4)	2.64	137	-x+1, -y+2, -z+2
4	C14-H14C...N1	1.08	3.751(4)	2.68	169	-x+2, -y+2, -z+2
5	C29-H29A...N2	1.08	3.712(4)	2.64	173	-x+1, -y, -z+1
6	C9...C2 C10...C3	3.47 Å (Molecular Stacking) 3.49 Å (Molecular Stacking)				-x+1, -y+2, -z+2
7	C24...C16	3.47 Å (Molecular Stacking)				x+1, y+2, z+1

Table S1: List of intermolecular hydrogen bonds and molecular stacking (–) of phenanthridine **8c**.