

Supporting Information

Intramolecular-Dehydrogenative-Coupling (IDC) of sp^2 C-H and sp^3 C-H Bonds: An Expeditious Route to 2-Oxindoles

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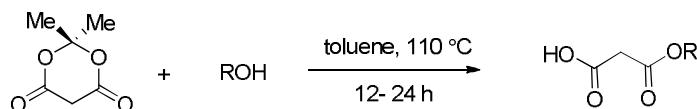
Materials and Methods

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) and diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2), toluene, and benzene were distilled over calcium hydride. All other solvents such as DMSO, DMF, dioxane and reagents such as alkyl halides, *N*-methylaniline, *p*-anisidine etc. were used as received, unless otherwise noted.

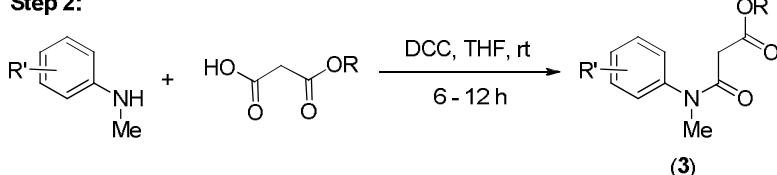
Thin layer chromatography was performed using Merck Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silicagel from Merck (particle size 100-200 mesh) was used for flash chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (AN ISO 9001:2000) and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Bruker 400, 500 MHz spectrometers with ^{13}C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal ($\delta = 7.26$ for ^1H NMR and $\delta = 77.0$ for ^{13}C 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 spectral data were obtained from the Central Instrumentation Facility (CIF) at the Indian Institute of Science Education and Research (IISER) Bhopal.

General procedure for the synthesis of the β -N-arylamido esters:

Step 1:



Step 2:



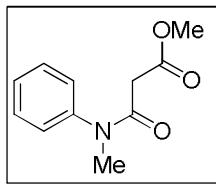
Scheme: Synthesis of β -N-arylamido esters.

Step 1:

A flame-dried round-bottom flask was charged with Meldrum's acid [1.0 equiv. (generally in 10 g scale)] and required alcohol (1.5-10.0 equiv. case to case). The reaction mixture was heated under refluxed at 110 °C for indicated time. Upon completion of the reaction (as judged by TLC), the reaction mixture was cooled to room temperature. Most of the volatile components were evaporated under reduced pressure, without work up. The crude malonic acid monoesters were directly used for coupling reaction without purification.

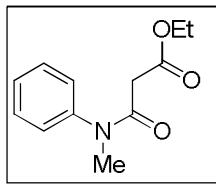
Step 2:

In a flame-dried round-bottom flask, crude malonic acid monoester (1.0 mmol) was taken in dichloromethane (5 mL/mmole) and cooled to 0 °C on an ice-bath. To this reaction mixture was added triethylamine (3 mmol) via a syringe. After 5 minutes of stirring at same temperature, a THF solution of *N*-methylaniline derivatives (1.0 mmol) was added drop wise to the reaction mixture and slowly allowed to warm to rt (over 10 minutes). The stirring was continued till TLC showed complete consumption of starting materials. The reaction mixture was diluted with dichloromethane (approx. 40 mL for 5 mmol scale of a reaction) and then successively washed with water (20 mL), 2(N)-HCl (20 mL), saturated NaHCO₃ (20 mL) and finally with brine (20 mL). The organic extracts were dried over MgSO₄ and concentrated under vacuum. The crude product was purified by flash chromatography (4:1 hexanes/EtOAc) to afford β -N-arylamido esters.



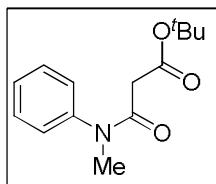
(3a)

Methyl 3-(methyl(phenyl)amino)-3-oxopropanoate (3a): 72% yield (30 mmol scale of a reaction), Colorless gel, $R_f = 0.41$ (50% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.42-7.46 (m, 2H), 7.39 (m, 1H), 7.23-7.25 (m, 2H), 3.68 (s, 3H), 3.32 (s, 3H), 3.23 (s, 2H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 168.14, 165.93, 143.48, 129.97, 128.33, 127.24, 52.28, 41.32, 37.47; **IR** (film) ν_{\max} 2953, 1747, 1651, 1596, 1496, 1435, 1386, 1253, 1160, 1122, 927, 849, 776, 702 cm^{-1} ; **HRMS** (ESI) m/z 230.0800 [(M+Na) $^+$; calculated for $[\text{C}_{11}\text{H}_{13}\text{NO}_3 + \text{Na}]^+$: 230.0788].



(3b)

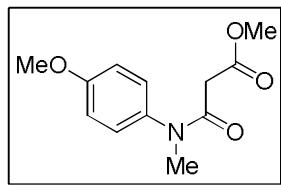
Ethyl 3-(methyl(phenyl)amino)-3-oxopropanoate (3b): 69% yield (20 mmol scale of a reaction), Colorless gel, $R_f = 0.40$ (30% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.42-7.45 (m, 2H), 7.38 (m, 1H), 7.24-7.26 (m, 2H), 4.14 (q, $J = 7.12$ Hz, 2H), 3.32 (s, 3H), 3.21 (s, 2H), 1.24 (t, $J = 7.16$ Hz, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 167.74, 166.06, 143.52, 129.93, 128.27, 127.28, 61.25, 41.57, 37.46, 14.07; **IR** (film) ν_{\max} 2983, 1739, 1661, 1596, 1497, 1423, 1385, 1308, 1248, 1158, 1122, 1030, 927, 776, 702 cm^{-1} ; **HRMS** (ESI) m/z 222.1148 [(M+H) $^+$; calculated for $[\text{C}_{12}\text{H}_{16}\text{NO}_3]^+$: 222.1125].



(3c)

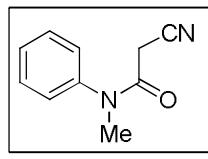
tert-Butyl 3-(methyl(phenyl)amino)-3-oxopropanoate (3c): 75% yield (25 mmol scale of a reaction), Colorless gel, $R_f = 0.51$ (30% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.39-7.43 (m, 2H), 7.33 (m, 1H), 7.22-7.24 (m, 2H), 3.29 (s, 3H), 3.12 (s, 2H), 1.41 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 166.99, 166.42, 143.67, 129.83, 128.14, 127.27, 81.51, 42.70, 37.37, 27.96; **IR** (film) ν_{\max} 2979, 2933, 2360, 1735, 1664, 1596, 1497, 1369, 1328, 1257, 1152, 1121, 960,

853, 765, 702 cm⁻¹; **HRMS** (ESI) m/z 250.1458 [(M+H)⁺; calculated for [C₁₄H₂₀NO₃]⁺: 250.1438].



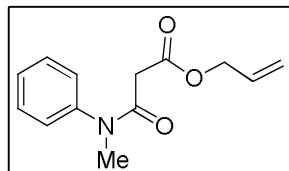
(3d)

Methyl 3-((4-methoxyphenyl)(methyl)amino)-3-oxopropanoate (3d): 61% yield (15 mmol scale of a reaction), Colorless gel, R_f = 0.51 (30% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.12 (d, J = 8.96 Hz, 2H), 6.90 (d, J = 8.96 Hz, 2H), 3.81 (s, 3H), 3.65 (s, 3H), 3.25 (s, 3H), 3.20 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 168.22, 166.28, 159.22, 136.19, 128.32, 115.01, 55.49, 52.22, 41.23, 37.57; **IR** (film) ν_{max} 2954, 2841, 1746, 1660, 1514, 1436, 1386, 1301, 1249, 1171, 1123, 1028, 842 cm⁻¹; **HRMS** (ESI) m/z 238.1080 [(M+H)⁺; calculated for [C₁₂H₁₆NO₄]⁺: 238.1074].



(3e)

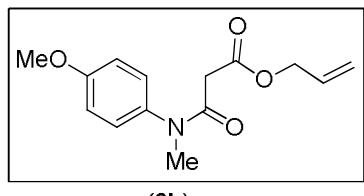
2-Cyano-N-methyl-N-phenylacetamide (3e): 65% yield (20 mmol scale of a reaction), Colorless solid, R_f = 0.62 (40% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (m, 2H), 7.42 (m, 1H), 7.25 (d, J = 8.16 Hz, 2H), 3.31 (s, 3H), 3.25 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 161.77, 142.40, 130.49, 129.04, 127.08, 114.24, 37.91, 25.47; **IR** (film) ν_{max} 2956, 2927, 2258, 1661, 1595, 1497, 1430, 1393, 1309, 1261, 925, 773, 703 cm⁻¹; **HRMS** (ESI) m/z 175.0879 [(M+H)⁺; calculated for [C₁₀H₁₁N₂O]⁺: 175.0866]; **MP** 82–84 °C.



(6a)

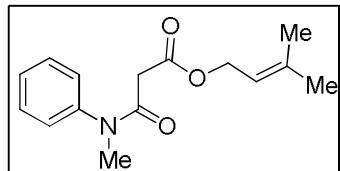
Allyl 3-(methyl(phenyl)amino)-3-oxopropanoate (6a): 60% yield (25 mmol scale of a reaction), Colorless gel, R_f = 0.50 (40% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.43–7.45 (m, 2H), 7.36–7.38 (m, 1H), 7.23–7.25 (m, 2H), 5.82–5.92 (m, 1H), 5.32 (dd, J = 17.20, 1.44

Hz, 1H), 5.22 (dd, J = 10.40, 1.16 Hz, 1H), 4.56 (d, J = 5.72 Hz, 2H), 3.31 (s, 3H), 3.25 (s, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 167.38, 165.86, 143.47, 131.68, 129.96, 128.31, 127.27, 118.59, 65.83, 41.45, 37.46; **IR** (film) ν_{max} 2940, 1744, 1667, 1596, 1496, 1423, 1385, 1309, 1240, 1156, 1122, 992, 930, 775, 702 cm^{-1} ; **HRMS** (ESI) m/z 234.1135 [(M+H) $^+$; calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_3]^+$: 234.1125].



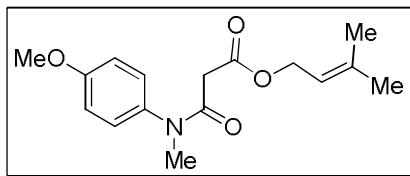
(6b)

Allyl 3-((4-methoxyphenyl)(methyl)amino)-3-oxopropanoate (6b): 67% yield (20 mmol scale of a reaction), Colorless gel, R_f = 0.50 (40% EtOAc in hexane). **^1H NMR** (400 MHz, CDCl_3) δ 7.15 (d, J = 8.88 Hz, 2H), 6.92 (d, J = 8.88 Hz, 2H), 5.83-5.91 (m, 1H), 5.32 (dd, J = 18.60, 1.40 Hz, 1H), 5.23 (dd, J = 10.44, 1.24 Hz, 1H), 4.56 (d, J = 5.76 Hz, 2H), 3.83 (s, 3H), 3.27 (s, 3H), 3.24 (s, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 167.47, 166.22, 159.22, 136.22, 131.72, 128.39, 118.56, 115.00, 65.80, 55.51, 41.40, 37.60; **IR** (film) ν_{max} 2941, 1749, 1666, 1595, 1497, 1383, 1310, 1242, 1159, 1122, 975, 775, 702 cm^{-1} ; **HRMS** (ESI) m/z 264.1241 [(M+H) $^+$; calculated for $[\text{C}_{14}\text{H}_{18}\text{NO}_4]^+$: 264.1230].



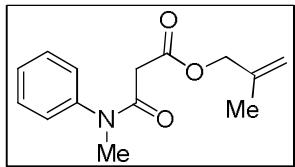
(6c)

3-Methylbut-2-en-1-yl 3-(methyl(phenyl)amino)-3-oxopropanoate (6c): 56% yield (10 mmol scale of a reaction), Colorless gel, R_f = 0.46 (30% EtOAc in hexane). **^1H NMR** (400 MHz, CDCl_3) δ 7.40-7.44 (m, 2H), 7.34-7.38 (m, 1H), 7.22-7.25 (m, 2H), 5.30 (m, 1H), 4.56 (d, J = 7.24 Hz, 2H), 3.31 (s, 3H), 3.21 (s, 2H), 1.75 (s, 3H), 1.69 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 167.74, 166.01, 143.52, 139.40, 129.90, 128.24, 127.29, 118.18, 62.13, 41.57, 37.46, 25.74, 18.01; **IR** (film) ν_{max} 2935, 1738, 1667, 1596, 1496, 1423, 1383, 1310, 1240, 1158, 1122, 975, 775, 702 cm^{-1} ; **HRMS** (ESI) m/z 284.1274 [(M+Na) $^+$; calculated for $[\text{C}_{15}\text{H}_{19}\text{NO}_3 + \text{Na}]^+$: 284.1257].



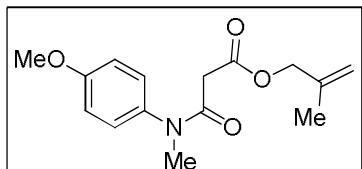
(6d)

3-Methylbut-2-en-1-yl 3-((4-methoxyphenyl)(methyl)amino)-3-oxopropanoate (6d): 52% yield (20 mmol scale of a reaction), Colorless gel, $R_f = 0.52$ (30% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.11 (d, $J = 8.84$ Hz, 2H), 6.87 (d, $J = 8.84$ Hz, 2H), 5.26 (t, $J = 7.24$ Hz, 1H), 4.53 (d, $J = 7.24$ Hz, 2H), 3.80 (s, 3H), 3.23 (s, 3H), 3.18 (s, 2H), 1.72 (s, 3H), 1.66 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 167.85, 166.37, 159.19, 139.37, 136.30, 128.41, 118.21, 114.95, 62.12, 55.50, 41.54, 37.61, 25.75, 18.02; **IR** (film) ν_{\max} 2936, 1738, 1661, 1513, 1445, 1383, 1299, 1248, 1170, 1122, 1030, 978, 840 cm^{-1} ; **HRMS** (ESI) m/z 314.1371 [(M+Na) $^+$; calculated for $[\text{C}_{16}\text{H}_{21}\text{NO}_4 + \text{Na}]^+$: 314.1363].



(6e)

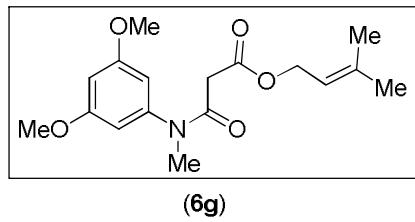
2-Methylallyl 3-(methyl(phenyl)amino)-3-oxopropanoate (6e): 61% yield (15 mmol scale of a reaction), Colorless gel, $R_f = 0.32$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.42-7.46 (m, 2H), 7.37-7.40 (m, 1H), 7.25-7.27 (m, 2H), 4.96 (s, 1H), 4.93 (s, 1H), 4.51 (s, 2H), 3.33 (s, 3H), 3.27 (s, 2H), 1.74 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 167.43, 165.88, 143.53, 139.47, 129.96, 128.31, 127.28, 113.35, 68.42, 41.40, 37.48, 19.46; **IR** (film) ν_{\max} 2943, 1744, 1666, 1596, 1496, 1424, 1385, 1309, 1238, 1157, 1121, 1001, 908, 774, 702 cm^{-1} ; **HRMS** (ESI) m/z 270.1100 [(M + Na) $^+$; calculated for $[\text{C}_{14}\text{H}_{17}\text{NO}_3 + \text{Na}]^+$: 270.1101].



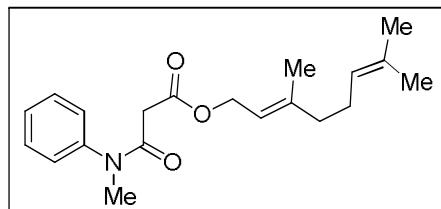
(6f)

2-Methylallyl 3-((4-methoxyphenyl)(methyl)amino)-3-oxopropanoate (6f): 54% yield (10 mmol scale of a reaction), Colorless gel, $R_f = 0.42$ (30% EtOAc in hexane). **$^1\text{H NMR}$** (400

MHz, CDCl₃) δ 7.13 (d, *J* = 8.68 Hz, 2H), 6.89 (d, *J* = 8.68 Hz, 2H), 4.92 (s, 1H), 4.89 (s, 1H), 4.46 (s, 2H), 3.80 (s, 3H), 3.25 (s, 3H), 3.23 (s, 2H), 1.70 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.48, 166.23, 159.21, 139.45, 136.21, 128.35, 114.99, 113.28, 68.33, 55.48, 41.32, 37.57, 19.41; IR (film) ν_{max} 2939, 1744, 1660, 1513, 1445, 1385, 1301, 1249, 1170, 1030, 908, 841 cm⁻¹; HRMS (ESI) m/z 278.1393 [(M+H)⁺; calculated for [C₁₅H₂₀NO₄]⁺: 278.1387].



3-Methylbut-2-en-1-yl 3-((3,5-dimethoxyphenyl)(methyl)amino)-3-oxopropanoate (6g): 57% yield (10 mmol scale of a reaction), Colorless gel, R_f = 0.39 (40% EtOAc in hexane). ¹H NMR (400 MHz, CDCl₃) δ 6.44 (t, *J* = 2.24 Hz, 1H), 6.39 (s, 1H), 6.38 (s, 1H), 5.29-5.34 (m, 1H), 4.59 (d, *J* = 7.24 Hz, 2H), 3.79 (s, 6H), 3.29 (s, 3H), 3.28 (s, 2H), 1.75 (s, 3H), 1.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.93, 165.88, 161.54, 145.18, 139.41, 118.20, 105.39, 100.16, 62.17, 55.50, 41.38, 37.23, 25.73, 18.00; IR (film) ν_{max} 2940, 1738, 1665, 1606, 1462, 1428, 1384, 1351, 1252, 1206, 1157, 1116, 1063, 1044, 981, 847, 703 cm⁻¹; HRMS (ESI) m/z 344.1479 [(M + Na)⁺; calculated for [C₁₇H₂₃NO₅ + Na]⁺: 344.1468].



(E)-3,7-Dimethylocta-2,6-dien-1-yl 3-(methyl(phenyl)amino)-3-oxopropanoate (6h): 58% yield (20 mmol scale of a reaction), Colorless gel, R_f = 0.61 (20% EtOAc in hexane). ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.42 (m, 2H), 7.34 (m, 1H), 7.23-7.25 (m, 2H), 5.30 (dt, *J* = 7.12, 1.08 Hz, 1H), 5.06-5.10 (m, 1H), 4.59 (d, *J* = 7.12 Hz, 2H), 3.32 (s, 3H), 3.23 (s, 2H), 2.10 (m, 2H), 2.04 (m, 2H), 1.69 (s, 6H), 1.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.74, 166.01, 143.54, 142.59, 131.85, 129.90, 128.25, 127.30, 123.70, 117.87, 62.16, 41.57, 39.52, 37.47, 26.28, 25.67, 17.68, 16.47; IR (film) ν_{max} 2926, 1739, 1667, 1596, 1496, 1424, 1383, 1310,

1239, 1156, 1121, 979, 774, 702 cm⁻¹; **HRMS** (ESI) m/z 352.1884 [(M + Na)⁺; calculated for [C₂₀H₂₇NO₃ + Na]⁺: 352.1883].

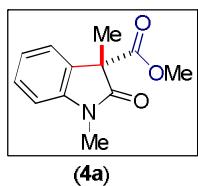
Table 1: Optimization of intramolecular-dehydrogenative-coupling (IDC).

entry	solvent	base	alkylations	oxidants	equiv	time	yield ^{a,b}
1.	DMF	K ^t OBu	20 min	I ₂	1.5 equiv	6 h	65%
2.	DMF	K ^t OBu	20 min	I ₂	1.2 equiv	3 h	62%
3.	THF	K ^t OBu	30 min	I ₂	1.2 equiv	3 h	85%
4.	xylene	K ^t OBu	45 min	I ₂	1.2 equiv	60 min	49% ^c
5.	dioxane	K ^t OBu	20 min	I ₂	1.2 equiv	2 h	88%
6.	benzene	K ^t OBu	50 min	I ₂	1.2 equiv	2 h	43% ^c
7.	toluene	K ^t OBu	45 min	I ₂	1.2 equiv	60 min	45% ^c
8.	DMSO	K ^t OBu	20 min	I ₂	1.5 equiv	30 min	90%
9.	DMSO	NaH	20 min	I ₂	1.5 equiv	30 min	33% ^d
10.	DMSO	NaOMe	120 min	I ₂	1.5 equiv	30 min	---- ^d
11.	DMSO	K ₂ CO ₃	60 min ^e	----	----	----	----
12.	DMSO	Cs ₂ CO ₃	120 min	I ₂	1.5 equiv	30 min	26% ^f
13.	DMSO	Na ^t OBu	30 min	I ₂	1.5 equiv	30 min	---- ^f
14.	DMSO	K ^t OBu	15 min	I ₂	1.2 equiv	30 min	88%
15.	DMSO	K ^t OBu	15 min	I ₂	0.6 equiv	60 min	54%
16.	DMSO	K ^t OBu	15 min	I ₂	0.3 equiv	60 min	29%
17.	DMSO	K ^t OBu	15 min	PIDA	1.2 equiv	30 min	82%
18.	DMSO	K ^t OBu	15 min	DBDMH ^g	1.2 equiv	30 min	16% ^f

^aReactions were carried out on a 0.25 mmol of **3a** with 0.275 mmol of methyl iodide in the presence of 0.30 mmol of base in 1 mL of solvent at 25 °C for specified time for alkylations and 0.30 mmol of oxidant in presence of 0.30 mmol of base under heating at 110 °C for oxidative coupling steps, unless noted otherwise. ^bIsolated yields of **3a** after column chromatography. ^cMixture of products were observed for rest of the mass balance. ^dC-Methylation as major product. ^eStarting material was recovered (92%). ^fDecompositions of starting materials. ^gDBDMH (1,3-dibromo-5,5-dimethyl-hydantoin) as oxidant.

General procedure for one-step alkylations followed by intramolecular oxidative coupling (IDC):

In a flame-dried round-bottom flask, β -amidoester **3** or **6** (0.25 mmol; 1 equiv) was taken in DMSO (0.75 mL) at room temperature. To this reaction mixture was added K'OBu (0.30 mmol; 1.2 equiv) in one portion. After 1-2 minutes of stirring at same temperature, alkyl halide (0.275 mmol, 1.1 equiv) was added and stirring was continued for 5-10 minutes (TLC showed almost complete consumption of starting materials). K'OBu (0.30 mmol; 1.2 equiv) and 1.2 equiv (0.30 mmol) of iodine were added to the reaction mixture at room temperature. Immediately afterwards, the reaction mixture was heated at 110 °C for 30-40 minutes. Upon completion of the oxidative coupling, it was cooled to room temperature and diluted with 5 mL of EtOAc. The reaction mixture was extracted with 5 mL saturated sodium thiosulfate (5 mL X 3 times) and then successively washed with water (5 mL), and brine (5 mL). The organic extracts were dried over MgSO₄ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford 2-oxindole derivatives.



(\pm)-Methyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (**4a**): 88% yield, Colorless solid, R_f = 0.42 (20% EtOAc in hexane). **¹H NMR** (500 MHz, CDCl₃) δ 7.35 (dt, J = 7.70, 1.05 Hz, 1H), 7.29 (m, 1H), 7.10 (dt, J = 7.60, 0.70 Hz, 1H), 6.89 (d, J = 7.80, 1.05 Hz, 1H), 3.68 (s, 3H), 3.28 (s, 3H), 1.70 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 175.15, 170.30, 143.59, 130.03, 129.06, 123.09, 122.94, 108.47, 54.92, 53.04, 26.58, 20.23; **IR** (film) ν_{\max} 2954, 1743, 1716, 1651, 1611, 1494, 1471, 1376, 1349, 1242, 1147, 1119, 1063, 1031, 975, 910 cm⁻¹; **HRMS** (ESI) m/z 220.0975 [(M+H)⁺; calculated for [C₁₂H₁₄NO₃]⁺: 220.0968]; **HRMS** (ESI) m/z 242.0768 [(M+Na)⁺; calculated for [C₁₂H₁₃NO₃ + Na]⁺: 242.0788]; **MP** 83-85 °C.

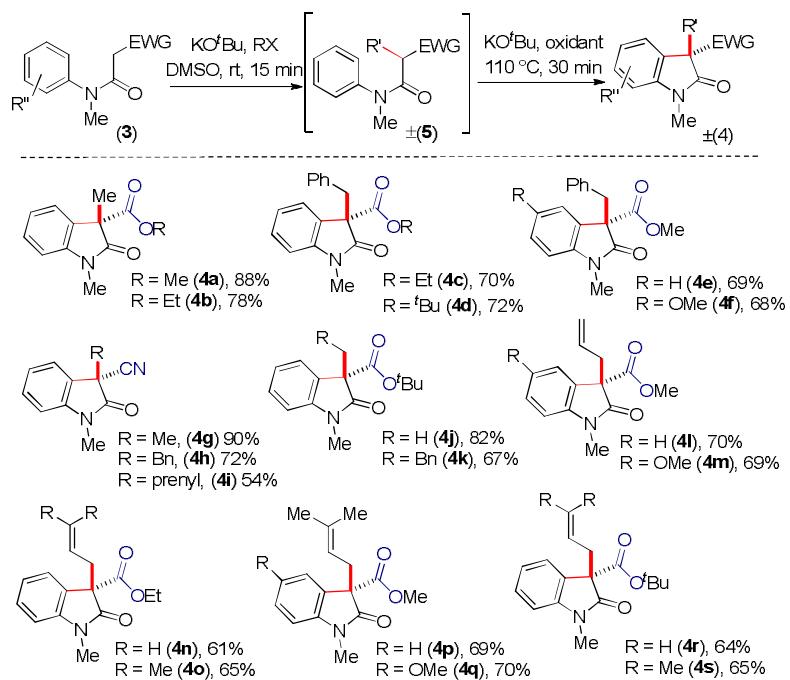
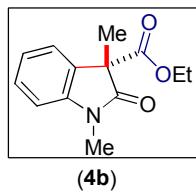
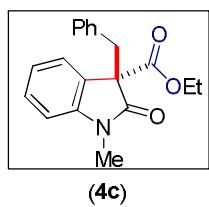


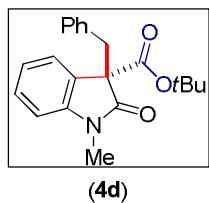
Figure 1: Substrates scope of ‘transition metal-free’ IDC.



(±)-Ethyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (4b): 78% yield, colorless gel, $R_f = 0.47$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ : 7.34 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 7.16$ Hz, 1H), 7.08 (t, $J = 7.28$ Hz, 1H), 6.87 (d, $J = 7.6$ Hz, 1H), 4.10-4.18 (m, 2H), 3.27 (s, 3H), 1.68 (s, 3H), 1.17 (t, $J = 6.96$ Hz, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ : 175.2, 169.7, 143.6, 130.2, 129.0, 123.0, 122.8, 108.4, 62.0, 55.1, 26.5, 20.1, 13.9; **IR** (film) ν_{max} 2984, 2936, 1741, 1721, 1651, 1611, 1494, 1471, 1375, 1349, 1244, 1146, 1106, 1063, 1030, 975, 752 cm^{-1} ; **HRMS** (ESI) m/z 234.1138 [$(\text{M}+\text{H})^+$]; calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}_3]^+$: 234.1125].

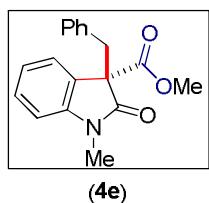


(\pm)-Ethyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (4c): 70% yield, colorless gel, $R_f = 0.56$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.34 (dd, $J = 7.40, 0.76$ Hz, 1H), 7.24 (dd, $J = 7.72, 1.24$ Hz, 1H), 7.08 (dd, $J = 7.60, 1.00$ Hz, 1H), 7.00-7.04 (m, 3H), 6.86 (m, 2H), 6.59 (d, $J = 7.80$ Hz, 1H), 4.21 (m, 2H), 3.56 (s, 2H), 2.97 (s, 3H), 1.22 (t, $J = 7.12$ Hz, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.50, 169.25, 144.06, 134.44, 129.95, 128.97, 127.53, 127.45, 126.70, 123.85, 122.45, 108.11, 62.04, 60.89, 40.04, 26.11, 13.97; **IR** (film) ν_{\max} 2933, 1738, 1715, 1611, 1490, 1471, 1370, 1354, 1233, 1090, 750 cm^{-1} ; **HRMS** (ESI) m/z 310.1424 [$(\text{M}+\text{H})^+$; calculated for $[\text{C}_{19}\text{H}_{20}\text{NO}_3]^+$: 310.1438].



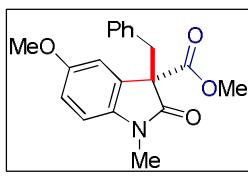
(4d)

(\pm)-tert-Butyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (4d): 72% yield, colorless gel, $R_f = 0.58$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.22-7.35 (m, 3H), 7.02-7.09 (m, 3H), 6.87 (d, $J = 6.32$ Hz, 2H), 6.58 (d, $J = 7.64$ Hz, 1H), 3.52 (m, 2H), 2.96 (s, 3H), 1.41 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.75, 168.15, 144.13, 134.80, 129.94, 128.74, 128.09, 127.51, 126.58, 123.58, 122.29, 107.98, 82.49, 61.79, 39.71, 27.78, 26.02; **IR** (film) ν_{\max} 2980, 2933, 1740, 1720, 1654, 1611, 1494, 1471, 1370, 1351, 1252, 1153, 1022, 751 cm^{-1} ; **HRMS** (ESI) m/z 360.1592 [$(\text{M}+\text{Na})^+$; calculated for $[\text{C}_{21}\text{H}_{23}\text{NO}_3 + \text{Na}]^+$: 360.1570].



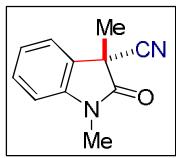
(4e)

(\pm)-Methyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (4e): 69% yield, colorless gel, $R_f = 0.50$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.34 (dd, $J = 7.40, 0.76$ Hz, 1H), 7.25 (dt, $J = 7.72, 1.24$ Hz, 1H), 7.00-7.11 (m, 4H), 6.85-6.87 (m, 2H), 6.60 (d, $J = 7.76$ Hz, 1H), 3.74 (s, 3H), 3.57 (s, 2H), 2.98 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.45, 169.78, 144.01, 134.30, 129.95, 129.09, 127.56, 127.27, 126.76, 123.94, 122.53, 108.18, 60.75, 53.09, 40.07, 26.14; **IR** (film) ν_{\max} 2953, 1741, 1715, 1610, 1494, 1471, 1373, 1353, 1244, 1156, 1128, 1089, 1001, 750 cm^{-1} ; **HRMS** (ESI) m/z 296.1292 [$(\text{M}+\text{nH})^+$; calculated for $[\text{C}_{18}\text{H}_{17}\text{NO}_3 + \text{nH}]^+$: 296.1281].



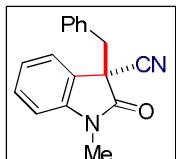
(4f)

(±)-Methyl 3-benzyl-5-methoxy-1-methyl-2-oxoindoline-3-carboxylate (4f): 68% yield, colorless gel, $R_f = 0.54$ (30% EtOAc in hexane). **1H NMR** (400 MHz, CDCl₃) δ 7.02-7.08 (m, 3H), 6.94 (d, $J = 2.52$ Hz, 1H), 6.87-6.90 (m, 2H), 6.76 (dd, $J = 8.52, 2.60$ Hz, 1H), 6.50 (d, $J = 8.48$ Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.55 (s, 2H), 2.95 (s, 3H); **13C NMR** (100 MHz, CDCl₃) δ 173.11, 169.76, 155.88, 133.56, 134.34, 129.97, 128.43, 127.61, 126.78, 113.59, 11.18, 108.55, 61.09, 55.89, 53.11, 40.10, 26.23; **IR** (film) ν_{max} 2101, 1740, 1645, 1498, 1363, 1222, 1032, 758 cm⁻¹; **HRMS** (ESI) m/z 326.1397 [(M+H)⁺]; calculated for [C₁₉H₁₉NO₄]⁺: 326.1387.



(4g)

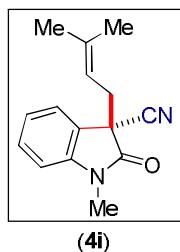
(±)-1,3-Dimethyl-2-oxoindoline-3-carbonitrile (4g): 90% yield, colorless solid, $R_f = 0.42$ (25% EtOAc in hexane). **1H NMR** (500 MHz, CDCl₃) δ 7.42-7.46 (m, 2H), 7.20 (d, $J = 7.65$ Hz, 1H), 6.93 (d, $J = 7.85$ Hz, 1H), 3.29 (s, 3H), 1.84 (s, 3H); **13C NMR** (125 MHz, CDCl₃) δ 171.00, 142.58, 130.34, 126.85, 123.88, 123.78, 117.65, 109.17, 42.12, 27.01, 23.40; **IR** (film) ν_{max} 2937, 2241, 1731, 1651, 1612, 1494, 1472, 1369, 1347, 1239, 1128, 1026, 933, 754 cm⁻¹; **HRMS** (ESI) m/z 187.0884 [(M+H)⁺]; calculated for [C₁₁H₁₁N₂O]⁺: 187.0866; **MP** 78-80 °C.



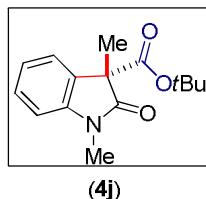
(4h)

(±)-3-Benzyl-1-methyl-2-oxoindoline-3-carbonitrile (4h): 72% yield, colorless solid, $R_f = 0.49$ (20% EtOAc in hexane). **1H NMR** (500 MHz, CDCl₃) δ 7.28 (m, 1H), 7.18-7.24 (m, 3H), 7.11 (d, $J = 4.25$ Hz, 2H), 7.01 (d, $J = 7.25$ Hz, 2H), 6.74 (d, $J = 7.85$ Hz, 1H), 3.57 (d, $J = 13.20$ Hz, 1H), 3.31 (d, $J = 13.20$ Hz, 1H), 3.09 (s, 3H); **13C NMR** (125 MHz, CDCl₃) δ 169.96, 143.00, 132.65, 130.32, 130.30, 128.12, 127.93, 124.97, 124.32, 123.29, 116.92, 108.88, 47.84, 42.77,

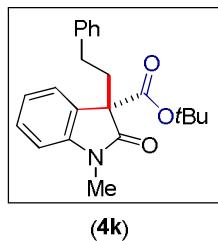
26.72; **IR** (film) ν_{\max} 2926, 2362, 1728, 1611, 1494, 1472, 1371, 1261, 1156, 753, 702 cm^{-1} ; **HRMS** (ESI) m/z 263.1189 [(M+H)⁺; calculated for [C₁₇H₁₅N₂O]⁺: 263.1179; **MP** 127-129 °C.



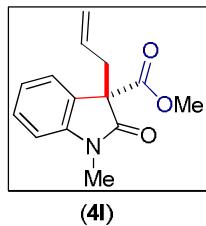
(±)-1-Methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carbonitrile (4i): 54% yield, colorless gel, R_f = 0.51 (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.39-7.41 (m, 2H), 7.14 (dt, J = 7.64, 1.00 Hz, 1H); 6.90 (dd, J = 7.88, 0.56 Hz, 1H), 5.12 (m, 1H), 3.27 (s, 3H), 2.94 (dd, J = 13.96, 7.16 Hz, 1H); 2.73 (dd, J = 14.00, 8.44 Hz, 1H); 1.71 (s, 3H), 1.55 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.36, 142.97, 139.07, 130.16, 125.27, 124.39, 123.45, 116.98, 114.90, 108.90, 46.56, 35.81, 26.88, 25.89, 18.19; **IR** (film) ν_{\max} 2921, 1731, 1612, 1493, 1472, 1371, 1349, 1253, 1129, 753, 696 cm^{-1} ; **HRMS** (ESI) m/z 241.1349 [(M+H)⁺; calculated for [C₁₅H₁₇N₂O]⁺: 241.1335.



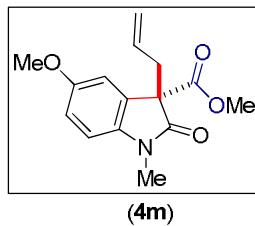
(±)-tert-Butyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (4j): 82% yield, colorless gel, R_f = 0.49 (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.32-7.34 (m, 1H), 7.22-7.25 (m, 1H), 7.07 (dt, J = 7.48, 0.88 Hz, 1H), 6.86 (d, J = 7.76 Hz, 1H), 3.25 (s, 3H), 1.63 (s, 3H), 1.36 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 175.51, 168.66, 143.70, 130.68, 129.30, 128.73, 122.70, 108.24, 82.18, 55.98, 27.90, 26.40, 19.68; **IR** (film) ν_{\max} 2980, 2934, 1738, 1721, 1656, 1611, 1494, 1471, 1369, 1347, 1255, 1158, 1119, 1029, 843, 751 cm^{-1} ; **HRMS** (ESI) m/z 262.1433 [(M+H)⁺; calculated for [C₁₅H₂₀NO₃]⁺: 262.1438.



tert-Butyl 1-methyl-2-oxo-3-phenethylindoline-3-carboxylate (4k): 67% yield, Colorless gel, $R_f = 0.41$ (50% EtOAc in hexane). **1H NMR** (400 MHz, CDCl₃) δ : 7.34-7.38 (td, $J = 7.72, 1.24$ Hz, 1H), 7.32 (dd, $J = 7.48, 0.72$ Hz, 1H), 7.22-7.26 (m, 2H), 7.14-7.18 (m, 1H), 7.08-7.13 (m, 1H), 6.88 (d, $J = 7.76$ Hz, 1H), 3.25 (s, 3H), 2.55-2.63 (m, 1H), 2.38-2.46 (m, 2H), 2.30-2.37 (m, 1H), 1.39 (s, 9H); **13C NMR** (100 MHz, CDCl₃) δ : 174.2, 168.1, 144.3, 141.1, 128.9, 128.4, 128.3, 128.2, 126.0, 123.1, 122.8, 108.2, 82.4, 60.3, 35.7, 30.2, 27.7, 26.4; **IR** (film) ν_{max} 3423, 2978, 1736, 1716, 1610, 1493, 1472, 1346, 1248, 1155, 1091, cm⁻¹; **HRMS** (ESI) m/z 374.1743 [(M+Na)⁺; calculated for [C₂₂H₂₅NO₃ + Na]⁺: 374.1727].

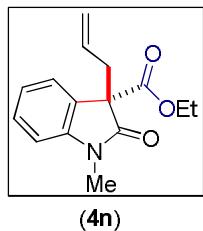


(±)-Methyl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (4l): 70% yield, colorless gel, $R_f = 0.49$ (20% EtOAc in hexane). **1H NMR** (400 MHz, CDCl₃) δ 7.33 (t, $J = 7.72$ Hz, 1H), 7.29 (t, $J = 7.08$ Hz, 1H), 7.09 (t, $J = 7.56$ Hz, 1H), 6.86 (d, $J = 7.80$ Hz, 1H), 5.37 (m, 1H), 5.04 (d, $J = 17.00$ Hz, 1H), 4.93 (d, $J = 10.12$ Hz, 1H), 3.68 (s, 3H), 3.24 (s, 3H), 2.93-3.05 (m, 2H); **13C NMR** (100 MHz, CDCl₃) δ 173.62, 169.56, 144.08, 130.92, 129.11, 127.48, 123.67, 122.80, 119.82, 108.32, 59.11, 53.01, 38.41, 26.44; **IR** (film) ν_{max} 2925, 2852, 1744, 1720, 1651, 1611, 1494, 1471, 1371, 1237, 1124, 923, 752 cm⁻¹; **HRMS** (ESI) m/z 268.0959 [(M+Na)⁺; calculated for [C₁₄H₁₅NO₃ + Na]⁺: 268.0944].

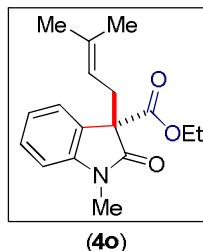


(±)-Methyl 3-allyl-5-methoxy-1-methyl-2-oxoindoline-3-carboxylate (4m): 69% yield, colorless gel, $R_f = 0.51$ (20% EtOAc in hexane). **1H NMR** (400 MHz, CDCl₃) δ 6.89 (d, $J = 2.44$ Hz, 1H), 6.86 (dd, $J = 8.44, 2.56$ Hz, 1H), 6.76 (d, $J = 8.40$ Hz, 1H), 5.33-5.43 (m, 1H), 5.05 (dq, $J = 16.96, 1.28$ Hz, 1H), 4.93 (m, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 3.21 (s, 3H), 2.92-3.03 (m, 2H); **13C NMR** (100 MHz, CDCl₃) δ 173.29, 169.53, 156.11, 137.57, 130.91, 128.69, 119.85, 113.43, 111.00, 108.65, 59.48, 55.84, 53.03, 38.46, 26.52; **IR** (film) ν_{max} 2954, 2359,

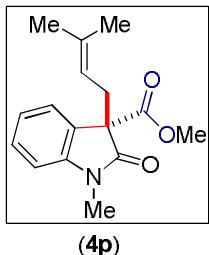
1746, 1715, 1611, 1494, 1471, 1435, 1373, 1351, 1237, 1123, 1082, 1001, 926, 798, 752 cm^{-1} ; **HRMS** (ESI) m/z 298.1048 [(M+Na) $^+$]; calculated for [C₁₅H₁₇NO₄ + Na] $^+$: 298.1050.



(±)-Ethyl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (4n): 61% yield, colorless gel, R_f = 0.51 (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.33 (t, J = 7.64 Hz, 1H), 7.28 (d, J = 6.16 Hz, 1H), 7.08 (t, J = 7.44 Hz, 1H), 6.85 (d, J = 7.72 Hz, 1H), 5.37 (m, 1H), 5.04 (d, J = 17.00 Hz, 1H), 4.93 (d, J = 10.04 Hz, 1H), 4.16 (m, 2H), 3.24 (s, 3H), 2.92-3.04 (m, 2H), 1.81 (t, J = 7.00 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.68, 169.00, 144.12, 131.06, 128.99, 127.67, 123.60, 122.72, 119.70, 108.25, 61.95, 59.25, 38.39, 26.41, 13.93; **IR** (film) ν_{max} 2925, 1740, 1706, 1611, 1494, 1471, 1373, 1350, 1230, 1123, 1020, 925, 751 cm^{-1} ; **HRMS** (ESI) m/z 260.1299 [(M+H) $^+$]; calculated for [C₁₅H₁₈NO₃] $^+$: 260.1281.

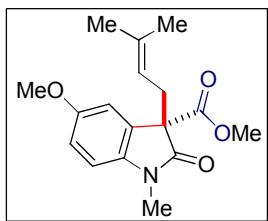


(±)-Ethyl 1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (4o): 65% yield, colorless gel, R_f = 0.48 (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.34 (dt, J = 7.72, 1.24 Hz, 1H), 7.34 (m, 1H), 7.07 (dt, J = 7.56, 0.92 Hz, 1H), 6.84 (d, J = 7.80 Hz, 1H), 4.73 (m, 1H), 4.11-4.17 (m, 2H), 3.24 (s, 3H), 2.94 (d, J = 7.36 Hz, 2H), 1.54 (s, 3H), 1.53 (s, 3H), 1.18 (t, J = 7.12 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 174.08, 169.33, 144.15, 136.19, 128.82, 128.16, 123.60, 122.57, 116.43, 108.08, 61.82, 59.32, 33.02, 26.39, 25.78, 18.05, 13.94; **IR** (film) ν_{max} 2929, 1740, 1720, 1611, 1493, 1471, 1374, 1348, 1230, 1128, 1020, 752 cm^{-1} ; **HRMS** (ESI) m/z 310.1415 [(M+Na) $^+$]; calculated for [C₁₇H₂₁NO₃ + Na] $^+$: 310.1414.



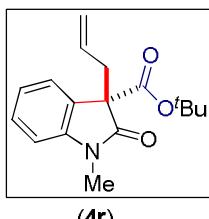
(4p)

(\pm)-Methyl 1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (4p): 69% yield, colorless gel, $R_f = 0.42$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.34 (t, $J = 7.68$ Hz, 1H), 7.28 (d, $J = 7.20$ Hz, 1H), 7.07 (t, $J = 7.52$ Hz, 1H), 6.75 (d, $J = 7.76$ Hz, 1H), 4.72 (t, $J = 6.92$ Hz, 1H), 3.69 (s, 3H), 3.22 (s, 3H), 2.94 (d, $J = 7.32$ Hz, 2H), 1.54 (s, 3H), 1.53 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 174.02, 169.87, 144.12, 136.35, 128.94, 127.97, 123.68, 122.65, 116.27, 108.14, 59.18, 52.92, 33.07, 26.42, 25.78, 18.05; **IR** (film) ν_{max} 2924, 1743, 1715, 1611, 1493, 1471, 1374, 1348, 1306, 1236, 1128, 1087, 1019, 1001, 792, 753 cm^{-1} ; **HRMS** (ESI) m/z 296.1267 ($\text{M}+\text{Na}$) $^+$; calculated for $[\text{C}_{16}\text{H}_{19}\text{NO}_3 + \text{Na}]^+$: 296.1257.



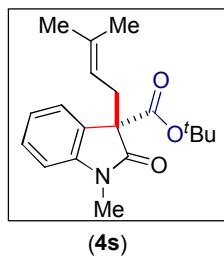
(4q)

(\pm)-Methyl 5-methoxy-1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (4q): 70% yield, colorless gel, $R_f = 0.43$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 6.90 (d, $J = 2.52$ Hz, 1H), 6.86 (dd, $J = 8.60, 2.52$ Hz, 1H), 6.75 (d, $J = 8.44$ Hz, 1H), 4.73 (m, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.22 (s, 3H), 2.94 (d, $J = 7.32$ Hz, 2H), 1.54 (s, 6H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.70, 169.85, 156.00, 137.63, 136.32, 129.16, 116.30, 113.45, 110.91, 108.48, 59.51, 55.83, 52.95, 33.10, 26.51, 25.79, 18.08; **IR** (film) ν_{max} 2962, 2925, 1742, 1715, 1602, 1496, 1435, 1365, 1232, 1162, 1105, 1033, 802 cm^{-1} ; **HRMS** (ESI) m/z 304.1561 ($[\text{M}+\text{H}]^+$); calculated for $[\text{C}_{17}\text{H}_{22}\text{NO}_4]^+$: 304.1543.



(4r)

(\pm)-*tert*-Butyl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (4r**):** 64% yield, colorless gel, $R_f = 0.54$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.26-7.34 (m, 2H), 7.07 (t, $J = 7.48$ Hz, 1H), 6.83 (d, $J = 7.68$ Hz, 1H), 5.40 (m, 1H), 5.03 (d, $J = 17.00$ Hz, 1H), 4.92 (d, $J = 10.08$ Hz, 1H), 3.22 (s, 3H), 2.93 (d, $J = 7.04$ Hz, 2H), 1.38 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.92, 167.88, 144.18, 131.41, 128.78, 128.12, 123.34, 122.55, 119.38, 108.10, 82.38, 60.11, 38.14, 27.96, 26.30; **IR** (film) ν_{\max} 2980, 2929, 1738, 1721, 1611, 1494, 1471, 1370, 1350, 1251, 1157, 993, 842, 750 cm^{-1} ; **HRMS** (ESI) m/z 310.1431 [(M+Na) $^+$; calculated for $[\text{C}_{17}\text{H}_{21}\text{NO}_3 + \text{Na}]^+$: 310.1414].



(\pm)-*tert*-Butyl 1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (4s**):** 65% yield, colorless gel, $R_f = 0.51$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.30 (dt, $J = 7.72, 1.24$ Hz, 1H), 7.25-2.27 (m, 1H), 7.04 (dt, $J = 7.60, 1.00$ Hz, 1H), 6.82 (d, $J = 7.76$ Hz, 1H), 4.75 (m, 1H), 3.21 (s, 3H), 2.87-2.91 (m, 2H), 1.53 (s, 6H), 1.37 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 174.33, 168.23, 144.20, 135.75, 128.61, 128.57, 123.34, 122.41, 116.79, 107.94, 82.16, 60.18, 32.74, 27.73, 26.29, 25.76, 18.05; **IR** (film) ν_{\max} 2978, 2931, 1738, 1721, 1611, 1493, 1471, 1370, 1347, 1250, 1156, 845, 750 cm^{-1} ; **HRMS** (ESI) m/z 338.1739 [(M + Na) $^+$; calculated for $[\text{C}_{19}\text{H}_{25}\text{NO}_3 + \text{Na}]^+$: 338.1727].

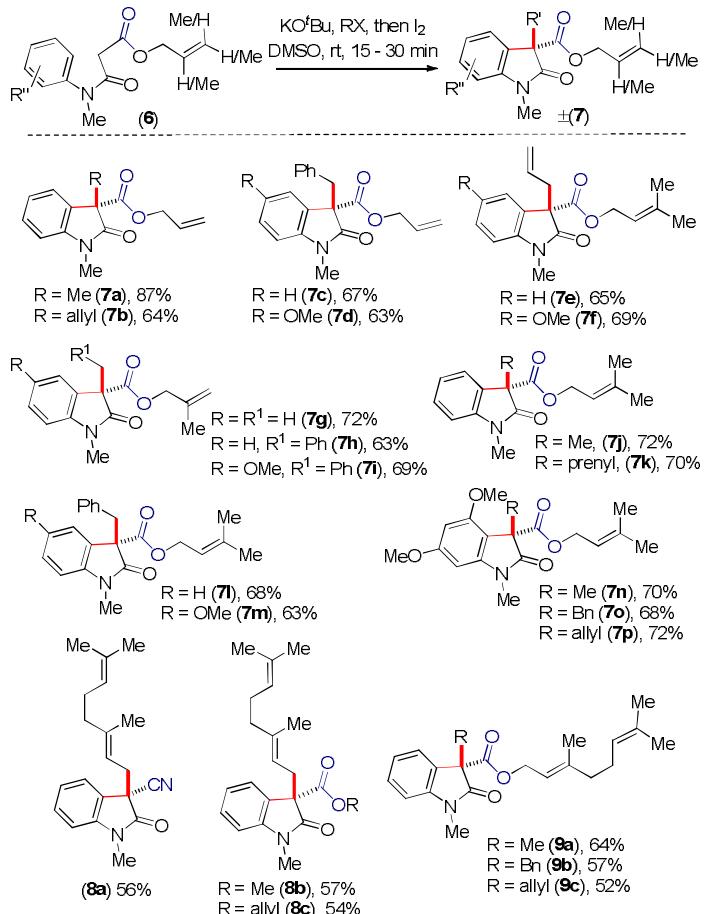
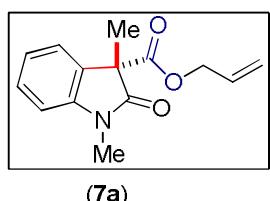
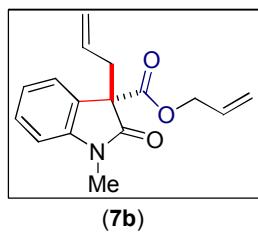


Figure 2: Substrates scope for ‘transition metal-free’ IDC.



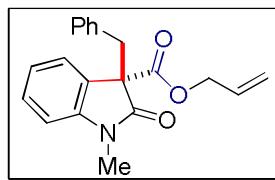
(7a)

(±)-Allyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (7a): 87% yield, colorless solid, $R_f = 0.48$ (20% EtOAc in hexane). **1H NMR** (400 MHz, CDCl₃) δ 7.35 (dt, $J = 7.76, 1.28$ Hz, 1H), 7.26-7.29 (m, 1H), 7.09 (dt, $J = 7.60, 1.00$ Hz, 1H), 6.89 (d, $J = 7.80$ Hz, 1H), 5.74-5.84 (m, 1H), 5.16 (m, 1H), 5.14 (m, 1H), 4.58 (dq, $J = 5.68, 1.52$ Hz, 2H), 3.27 (s, 3H), 1.70 (s, 3H); **13C NMR** (100 MHz, CDCl₃) δ 175.07, 169.40, 143.65, 131.38, 130.06, 129.05, 123.05, 122.89, 117.93, 108.46, 65.99, 55.05, 26.55, 20.07; **IR** (film) ν_{max} 2984, 2936, 1742, 1731, 1651, 1612, 1494, 1471, 1422, 1349, 1225, 1144, 1119, 1030, 974, 932, 752 cm⁻¹; **HRMS** (ESI) m/z 268.0942 [(M+Na)⁺; calculated for [C₁₄H₁₅NO₃ + Na]⁺: 268.0944; **MP** 49-51 °C.



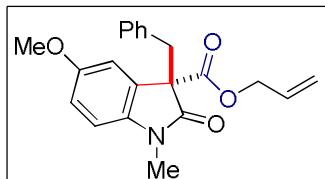
(7b)

(±)-Allyl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (7b): 64% yield, colorless gel, $R_f = 0.43$ (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.35 (dt, $J = 7.72, 1.20$ Hz, 1H), 7.29 (d, $J = 7.04$ Hz, 1H), 7.09 (dt, $J = 7.52, 0.92$ Hz, 1H), 6.86 (d, $J = 7.80$ Hz, 1H), 5.79 (m, 1H), 5.37 (m, 1H), 5.17 (dq, $J = 5.72, 1.52$ Hz, 1H), 5.14 (t, $J = 1.44$ Hz, 1H), 5.05 (dq, $J = 17.00, 1.68$ Hz, 1H), 4.94 (m, 1H), 4.60 (dt, $J = 5.40, 1.48$ Hz, 2H), 3.25 (s, 3H), 3.02 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.54, 168.68, 144.15, 131.36, 130.96, 129.09, 127.52, 123.66, 122.75, 119.81, 118.07, 108.30, 66.06, 59.23, 38.31, 26.44; **IR** (film) ν_{max} 2922, 1690, 1643, 1495, 1384, 1266, 1116, 1040, 785, 712 cm⁻¹; **HRMS** (ESI) m/z 272.1297 [(M+H)⁺; calculated for [C₁₆H₁₈NO₃]⁺: 272.1281].



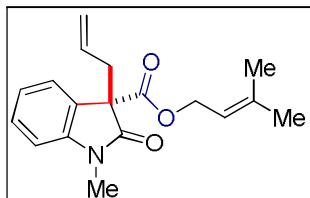
(7c)

(±)-Allyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (7c): 67% yield, colorless gel, $R_f = 0.41$ (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.34 (dd, $J = 7.40, 0.72$ Hz, 1H), 7.24 (dt, $J = 6.48, 1.28$ Hz, 1H), 7.10 (dt, $J = 7.44, 1.00$ Hz, 1H), 7.00-7.05 (m, 3H), 6.86-6.88 (m, 2H), 6.60 (d, $J = 7.76$ Hz, 1H), 5.78-5.88 (m, 1H), 5.22 (m, 1H), 5.17 (m, 1H), 4.64 (dt, $J = 5.36, 1.44$ Hz, 1H), 3.58 (m, 2H), 2.98 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.36, 168.93, 144.08, 134.34, 131.39, 129.97, 129.07, 127.56, 127.29, 126.75, 123.92, 122.49, 118.17, 108.18, 66.15, 60.87, 39.97, 26.14; **IR** (film) ν_{max} 2925, 2360, 1742, 1713, 1604, 1498, 1469, 1436, 1364, 1223, 1161, 1033 cm⁻¹; **HRMS** (ESI) m/z 322.1455 [(M+H)⁺; calculated for [C₂₀H₂₀NO₃]⁺: 322.1438].



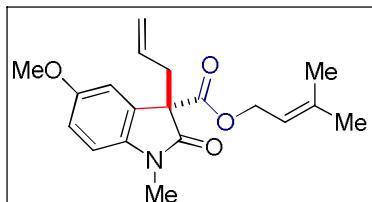
(7d)

(\pm)-Allyl 3-benzyl-5-methoxy-1-methyl-2-oxoindoline-3-carboxylate (7d): 63% yield, colorless solid, $R_f = 0.52$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.02-7.10 (m, 3H), 6.94 (d, $J = 2.48$ Hz, 1H), 6.88 (m, 2H), 6.77 (dd, $J = 8.48, 2.56$ Hz, 1H), 6.51 (d, $J = 8.48$ Hz, 1H), 5.85 (m, 1H), 5.17-5.24 (m, 2H), 4.65 (dd, $J = 5.28, 0.96$ Hz, 2H), 3.81 (s, 3H), 3.55 (s, 2H), 2.95 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.01, 168.89, 155.84, 137.65, 134.38, 131.40, 129.99, 128.44, 127.61, 126.77, 118.22, 113.64, 111.13, 108.54, 66.20, 61.21, 55.91, 40.02, 26.23; **IR** (film) ν_{max} 2934, 1361, 1743, 1713, 1603, 1498, 1469, 1437, 1364, 1289, 1224, 1165, 1032, 810, 702 cm^{-1} ; **HRMS** (ESI) m/z 374.1361 [(M + Na) $^+$]; calculated for [C₂₁H₂₁NO₄ + Na] $^+$: 374.1363]; **MP** 103-105 °C.



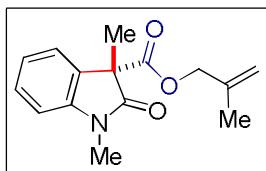
(7e)

(\pm)-3-Methylbut-2-en-1-yl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (7e): 65% yield, colorless gel, $R_f = 0.43$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.35 (dt, $J = 7.72, 1.24$ Hz, 1H), 7.29 (m, 1H), 7.08 (dt, $J = 7.56, 0.96$ Hz, 1H), 6.85 (d, $J = 7.80$ Hz, 1H), 5.33-5.43 (m, 1H), 5.22 (m, 1H), 5.02-5.07 (m, 1H), 4.92 (m, 1H), 4.58 (d, $J = 7.04$ Hz, 2H), 3.24 (s, 3H), 2.99 (m, 2H), 1.70 (s, 3H), 1.61 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.66, 168.96, 144.13, 139.32, 131.10, 128.95, 127.66, 123.67, 122.67, 119.67, 118.00, 108.22, 62.91, 59.33, 38.42, 26.42, 25.66, 18.03; **IR** (film) ν_{max} 2963, 2928, 1744, 1716, 1611, 1493, 1471, 1374, 1348, 1260, 1222, 1088, 934, 799, 752 cm^{-1} ; **HRMS** (ESI) m/z 322.1431 [(M + Na) $^+$]; calculated for [C₁₈H₂₁NO₃ + Na] $^+$: 322.1414].



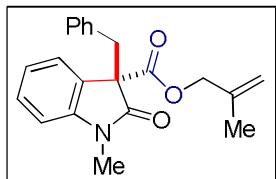
(7f)

(±)-3-Methylbut-2-en-1-yl 3-allyl-5-methoxy-1-methyl-2-oxoindoline-3-carboxylate (7f): 69% yield, colorless gel, $R_f = 0.43$ (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 6.86 (d, $J = 2.40$ Hz, 1H), 6.82 (dd, $J = 8.44, 2.48$ Hz, 1H), 6.71 (d, $J = 8.40$ Hz, 1H), 5.35 (m, 1H), 5.19 (d, $J = 7.04$ Hz, 1H), 5.02 (d, $J = 15.92$ Hz, 1H), 4.90 (d, $J = 10.08$ Hz, 1H), 4.55 (d, $J = 6.96$ Hz, 1H), 3.79 (s, 3H), 3.17 (s, 3H), 2.88-2.98 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.30, 168.91, 156.02, 139.30, 137.65, 131.07, 128.85, 119.68, 118.00, 113.35, 110.97, 108.52, 62.93, 59.68, 55.85, 38.47, 26.50, 25.66, 18.04; **IR** (film) ν_{max} 2935, 1740, 1714, 1602, 1496, 1470, 1362, 1289, 1221, 1167, 1032, 927, 809, 765 cm⁻¹; **HRMS** (ESI) m/z 352.1534 [(M+Na)⁺; calculated for [C₁₉H₂₃NO₄ + Na]⁺: 352.1519].



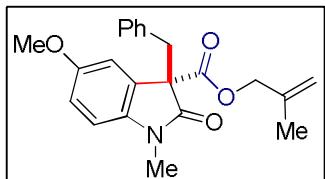
(7g)

(±)-2-Methylallyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (7g): 72% yield, colorless gel, $R_f = 0.58$ (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.35 (dt, $J = 7.72, 1.20$ Hz, 1H), 7.25-7.27 (m, 1H), 7.07 (dt, $J = 7.44, 0.88$ Hz, 1H), 6.88 (d, $J = 7.80$ Hz, 1H), 4.81 (dt, $J = 18.44, 1.40$ Hz, 2H), 4.49 (m, 2H), 3.27 (s, 3H), 1.69 (s, 3H), 1.59 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 175.06, 169.34, 143.69, 139.26, 130.08, 129.06, 123.01, 122.85, 112.60, 108.44, 68.47, 55.08, 26.52, 19.82, 19.08; **IR** (film) ν_{max} 2977, 2936, 1740, 1714, 1651, 1613, 1494, 1470, 1349, 1220, 1108, 1032, 909, 752 cm⁻¹; **HRMS** (ESI) m/z 260.1291 [(M+H)⁺; calculated for [C₁₅H₁₈NO₃]⁺: 260.1281].



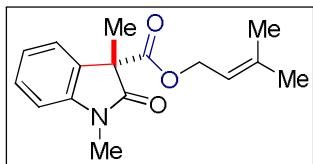
(7h)

(\pm)-2-Methylallyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (7h): 63% yield, colorless gel, $R_f = 0.49$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.40$ Hz, 1H), 7.24 (t, $J = 7.72$ Hz, 1H), 7.01-7.06 (m, 4H), 6.87 (d, $J = 7.28$ Hz, 1H), 6.60 (d, $J = 7.80$ Hz, 1H), 4.83 (d, $J = 10.04$ Hz, 1H), 4.57 (AB quartet, $J = 33.8, 13.28, 7.24$ Hz, 2H), 3.58 (m, 2H), 2.98 (s, 3H), 1.63 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.40, 168.89, 144.12, 139.26, 134.39, 129.97, 129.08, 127.57, 127.32, 126.74, 123.90, 122.46, 112.82, 108.17, 68.63, 60.93, 39.76, 26.13, 19.18; **IR** (film) ν_{max} 2928, 1740, 1714, 1610, 1494, 1470, 1372, 1353, 1262, 1219, 1128, 1089, 1033, 914, 809, 749 cm^{-1} ; **HRMS** (ESI) m/z 336.1599 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{21}\text{H}_{22}\text{NO}_3]^+$: 336.1594].



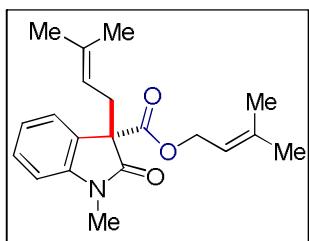
(7i)

(\pm)-2-Methylallyl 3-benzyl-5-methoxy-1-methyl-2-oxoindoline-3-carboxylate (7i): 69% yield, colorless gel, $R_f = 0.46$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.02-7.10 (m, 3H), 6.94 (d, $J = 2.52$ Hz, 1H), 6.90 (dd, $J = 7.40, 1.44$ Hz, 2H), 6.76 (dd, $J = 8.48, 2.56$ Hz, 1H), 6.51 (d, $J = 8.48$ Hz, 1H), 4.85 (d, $J = 7.28$ Hz, 1H), 4.59 (br, s, 2H), 3.81 (s, 3H), 3.56 (d, $J = 1.20$ Hz, 2H), 2.96 (s, 3H), 1.65 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.04, 168.86, 155.82, 139.25, 137.70, 134.43, 130.00, 128.46, 127.62, 126.75, 113.73, 112.84, 111.06, 108.54, 68.66, 61.26, 55.92, 39.82, 26.22, 19.21; **IR** (film) ν_{max} 2924, 2855, 1742, 1713, 1604, 1495, 1469, 1366, 1289, 1216, 1166, 1033, 893, 811, 759 cm^{-1} ; **HRMS** (ESI) m/z 366.1716 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{22}\text{H}_{24}\text{NO}_4]^+$: 366.1700].



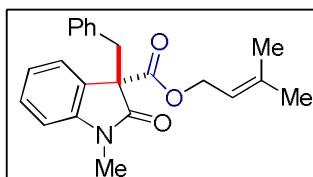
(7j)

(±)-3-methylbut-2-en-1-yl 1,3-dimethyl-2-oxoindoline-3-carboxylate (7j): 72% yield, colorless gel, $R_f = 0.46$ (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 (dt, $J = 7.72, 1.24$ Hz, 1H), 7.24-7.26 (m, 1H), 7.06 (dt, $J = 7.56, 1.00$ Hz, 1H), 6.86 (d, $J = 7.76$ Hz, 1H), 5.20 (m, 1H), 4.55 (d, $J = 7.04$ Hz, 2H), 3.25 (s, 3H), 1.68 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 175.18, 169.68, 143.62, 139.24, 130.21, 128.91, 123.02, 122.79, 118.01, 108.39, 62.85, 55.12, 26.52, 25.64, 20.15, 18.00; **IR** (film) ν_{max} 2978, 2934, 1740, 1723, 1652, 1612, 1494, 1472, 1376, 1348, 1226, 1106, 1030, 942, 751, 703 cm⁻¹; **HRMS** (ESI) m/z 296.1272 [(M+Na)⁺; calculated for [C₁₆H₁₉NO₃ + Na]⁺: 296.1257].



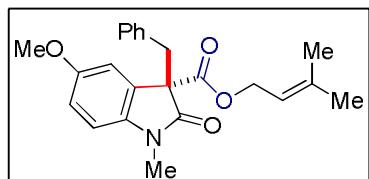
(7k)

(±)-3-Methylbut-2-en-1-yl 1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (7k): 70% yield, colorless gel, $R_f = 0.50$ (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.34 (dt, $J = 7.72, 1.20$ Hz, 1H), 7.28 (d, $J = 5.96$ Hz, 1H), 7.06 (dt, $J = 7.56, 0.88$ Hz, 1H), 6.83 (d, $J = 7.76$ Hz, 1H), 5.23 (m, 1H), 4.73 (m, 1H), 4.56 (d, $J = 7.00$ Hz, 2H), 4.14 (AB quartet, $J = 21.4, 7.12, 7.16$), 3.25 (s, 3H), 2.94 (d, $J = 7.36$ Hz, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.54 (s, 3H), 1.52 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 174.05, 169.28, 144.16, 139.12, 136.15, 128.78, 128.14, 123.68, 122.52, 118.12, 116.47, 108.05, 62.80, 59.38, 33.07, 29.70, 26.39, 25.78, 18.05, 18.03; **IR** (film) ν_{max} 2922, 2359, 1741, 1714, 1612, 1494, 1470, 1374, 1217, 1034, 807, 752 cm⁻¹; **HRMS** (ESI) m/z 328.1910 [(M+H)⁺; calculated for [C₂₀H₂₆NO₃]⁺: 328.1907].



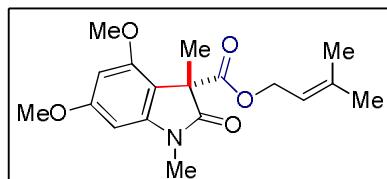
(7l)

(\pm)-3-Methylbut-2-en-1-yl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (7l): 68% yield, colorless gel, $R_f = 0.41$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.34 (m, 1H), 7.23 (dt, $J = 7.76, 1.20$ Hz, 1H), 7.00-7.09 (m, 4H), 6.85-6.88 (m, 2H), 6.58 (d, $J = 7.76$ Hz, 1H), 5.26 (m, 1H), 4.64 (d, $J = 7.04$ Hz, 2H), 3.56 (s, 2H), 2.96 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.46, 169.18, 144.05, 139.36, 134.49, 130.02, 129.96, 128.93, 127.52, 126.69, 123.94, 122.40, 118.05, 108.09, 62.99, 60.96, 40.08, 26.11, 25.69, 18.06; **IR** (film) ν_{max} 2928, 1737, 1715, 1498, 1365, 1225, 1163, 1032, 701 cm^{-1} ; **HRMS** (ESI) m/z 372.1574 [(M+H) $^+$; calculated for $[\text{C}_{22}\text{H}_{23}\text{NO}_3 + \text{Na}]^+$: 372.1570].



(7m)

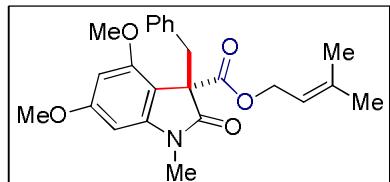
(\pm)-3-Methylbut-2-en-1-yl 3-benzyl-5-methoxy-1-methyl-2-oxoindoline-3-carboxylate (7m): 63% yield, colorless solid, $R_f = 0.41$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 6.98-7.05 (m, 3H), 6.89 (d, $J = 2.48$ Hz, 1H), 6.84 (m, 2H), 6.72-6.74 (dd, $J = 8.48, 1.1$ Hz, 1H), 6.45 (d, $J = 8.44$ Hz, 1H), 5.23 (m, 1H), 4.60 (d, $J = 7.00$ Hz, 1H), 3.77 (s, 3H), 3.50 (s, 2H), 2.90 (s, 2H), 1.69 (s, 3H), 1.60 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 173.13, 169.15, 155.79, 139.39, 137.62, 134.50, 129.98, 128.58, 127.58, 126.73, 118.04, 113.52, 111.12, 108.47, 63.04, 61.29, 55.91, 40.12, 26.23, 25.72, 18.10; **IR** (film) ν_{max} 2925, 2851, 1738, 1715, 1609, 1496, 1469, 1371, 1225, 1032, 807, 754 cm^{-1} ; **HRMS** (ESI) m/z 402.1680 [(M+H) $^+$; calculated for $[\text{C}_{23}\text{H}_{25}\text{NO}_4 + \text{Na}]^+$: 402.1676]; **MP** 109-111 °C.



(7n)

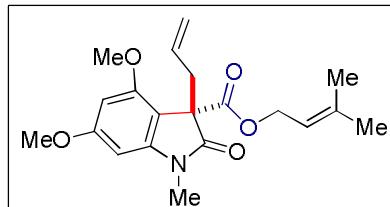
(\pm)-3-Methylbut-2-en-1-yl 4,6-dimethoxy-1,3-dimethyl-2-oxoindoline-3-carboxylate (7n): 70% yield, colorless gel, $R_f = 0.45$ (30% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 6.17 (d, $J = 1.92$ Hz, 1H), 6.12 (d, $J = 1.96$ Hz, 1H), 5.20 (m, 1H), 4.57 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 3.22 (s, 3H), 1.71 (s, 3H), 1.66 (s, 3H), 1.62 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 175.84, 169.30, 161.97, 156.23, 145.62, 138.49, 118.52, 109.26, 92.44, 88.55, 62.53, 55.63,

55.44, 54.21, 26.78, 25.68, 18.33, 17.99; **IR** (film) ν_{max} 2935, 1742, 1716, 1611, 1511, 1456, 1377, 1336, 1258, 1217, 1155, 1106, 1067, 1036, 936, 814, 637 cm^{-1} ; **HRMS** (ESI) m/z 334.166 [(M+H)⁺; calculated for [C₁₈H₂₄NO₅]⁺: 334.1649].



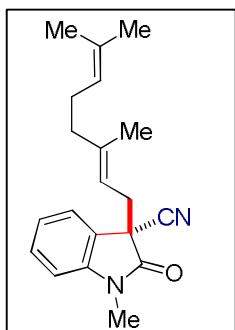
(7o)

(±)-3-Methylbut-2-en-1-yl 3-benzyl-4,6-dimethoxy-1-methyl-2-oxoindoline-3-carboxylate (7o): 68% yield, colorless gel, $R_f = 0.68$ (30% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 6.99-7.04 (m, 3H), 6.85 (dd, $J = 6.92, 1.72$ Hz, 2H), 6.15 (d, $J = 1.92$ Hz, 1H), 5.78 (d, $J = 1.92$ Hz, 1H), 5.24 (m, 1H), 4.60 (m, 2H), 3.89 (s, 3H), 3.78 (s, 3H), 3.64 (dd, $J = 1.92$ Hz, 1H), 3.53-3.67 (m, 2H), 2.90 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 174.25, 168.89, 162.02, 156.25, 145.95, 138.60, 135.60, 129.56, 127.44, 126.36, 118.52, 106.38, 92.20, 88.15, 62.63, 60.16, 55.50, 55.45, 37.21, 26.32, 25.70, 18.02; **IR** (film) ν_{max} 2937, 1744, 1715, 1613, 1511, 1455, 1376, 1336, 1257, 1215, 1153, 1070, 937, 814, 702 cm^{-1} ; **HRMS** (ESI) m/z 410.1991 [(M+H)⁺; calculated for [C₂₄H₂₈NO₅]⁺: 410.1962].



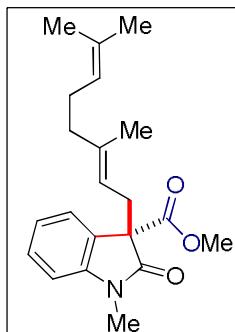
(7p)

(±)-3-methylbut-2-en-1-yl 3-allyl-4,6-dimethoxy-1-methyl-2-oxoindoline-3-carboxylate (7p): 72% yield, colorless gel, $R_f = 0.51$ (30% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 6.17 (d, $J = 1.96$ Hz, 1H), 6.10 (d, $J = 1.96$ Hz, 1H), 5.18-5.24 (m, 2H), 5.02 (m, 1H), 4.84 (m, 1H), 4.56 (m, 2H), 3.86 (s, 3H), 3.80 (s, 3H), 3.18 (s, 3H), 3.15 (m, 1H), 2.98 (m, 1H), 1.70 (s, 3H), 1.62 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 174.43, 168.70, 162.07, 156.34, 146.19, 138.58, 131.99, 118.67, 118.46, 106.45, 92.33, 88.40, 62.56, 58.67, 55.56, 55.44, 35.77, 26.62, 25.67, 17.99; **IR** (film) ν_{max} 2932, 2852, 1745, 1714, 1511, 1455, 1377, 1339, 1260, 1208, 1156, 1060, 935, 804, 701 cm^{-1} ; **HRMS** (ESI) m/z 382.1625 [(M+Na)⁺; calculated for [C₂₀H₂₅NO₅ + Na]⁺: 382.1625].



(8a)

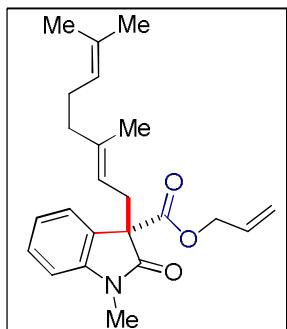
$\pm(E)$ -3-(3,7-dimethylocta-2,6-dien-1-yl)-1-methyl-2-oxoindoline-3-carbonitrile (8a): 56% yield, colorless gel, $R_f = 0.47$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.41 (m, 2H), 7.15 (d, $J = 6.64$ Hz, 1H), 6.89 (d, $J = 6.92$ Hz, 1H), 5.03-5.11 (m, 2H), 3.26 (s, 3H), 2.99 (m, 1H), 2.76 (m, 1H), 2.00 (s, 3H), 1.85-1.94 (m, 1H), 1.69 (s, 3H), 1.59 (s, 3H), 1.53 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.38, 143.01, 142.70, 131.84, 130.15, 125.24, 124.43, 123.75, 123.43, 116.97, 114.74, 108.84, 46.56, 39.77, 35.67, 26.85, 26.50, 25.70, 17.69, 16.57; **IR** (film) ν_{max} 2923, 2856, 1731, 1613, 1493, 1472, 1372, 1257, 1130 cm^{-1} ; **HRMS** (ESI) m/z 309.1960 $[(\text{M}+\text{H})^+;$ calculated for $[\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}]^+$: 309.1961].



(8b)

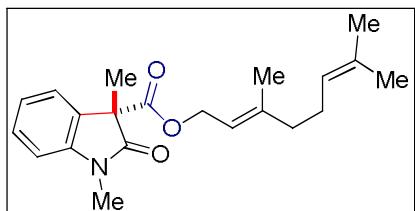
$\pm(E)$ -Methyl 3-(3,7-dimethylocta-2,6-dien-1-yl)-1-methyl-2-oxoindoline-3-carboxylate (8b): 57% yield, colorless gel, $R_f = 0.53$ (10% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.32 (m, 1H), 7.28 (m, 1H), 7.07 (dt, $J = 7.56, 0.96$ Hz, 1H), 6.84 (m, 1H), 4.92 (m, 1H), 4.72 (m, 1H), 3.68 (s, 3H), 3.23 (s, 3H), 2.96-3.00 (m, 2H), 1.82 (s, 3H), 1.68 (m, 1H), 1.64 (s, 3H), 1.59 (m, 1H), 1.52 (s, 3H), 1.51 (s, 3H), 1.51-1.54 (m, 2H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 174.02, 169.87, 144.14, 140.15, 131.36, 128.94, 127.96, 123.96, 123.70, 122.63, 116.17, 108.09, 59.28, 52.91, 39.74, 32.96, 26.72, 26.38, 25.66, 17.60, 16.42; **IR** (film) ν_{max} 2925, 2852, 1744, 1721,

1612, 1494, 1470, 1374, 1348, 1235, 1128, 750 cm^{-1} ; **HRMS** (ESI) m/z 342.2080 [(M+H)⁺; calculated for [C₂₁H₂₈NO₃]⁺: 342.2064].



(8c)

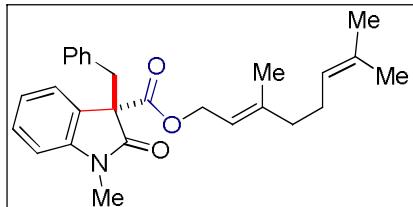
$\pm(E)$ -Allyl 3-(3,7-dimethylocta-2,6-dien-1-yl)-1-methyl-2-oxoindoline-3-carboxylate (8c): 54% yield, colorless gel, $R_f = 0.61$ (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.27-7.34 (m, 2H), 7.07 (d, $J = 6.08$ Hz, 1H), 6.85 (m, 1H), 5.81 (m, 1H), 5.14-5.19 (m, 2H), 4.91 (br, 1H), 4.74 (d, $J = 5.88$ Hz, 1H), 4.59 (m, 2H), 3.23 (s, 3H), 2.97-3.00 (m, 2H), 1.68-1.82 (m, 3H), 1.64 (s, 3H), 1.53 (s, 3H), 1.52 (s, 3H), 1.50-1.64 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.94, 169.00, 144.19, 140.10, 131.36, 131.35, 128.94, 127.96, 123.97, 123.67, 122.60, 117.97, 116.22, 108.10, 65.95, 59.40, 39.75, 32.85, 26.72, 26.38, 25.67, 17.61, 16.44; **IR** (film) ν_{max} 2962, 2926, 2856, 1747, 1731, 1612, 1494, 1471, 1373, 1349, 1223, 1128, 1087, 994, 750 cm^{-1} ; **HRMS** (ESI) m/z 390.2059 [(M+Na)⁺; calculated for [C₂₃H₂₉NO₃ + Na]⁺: 390.2040].



(9a)

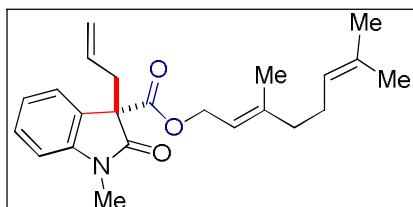
$\pm(E)$ -3,7-Dimethylocta-2,6-dien-1-yl 1,3-dimethyl-2-oxoindoline-3-carboxylate (9a): 64% yield, colorless gel, $R_f = 0.52$ (20% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.35 (dt, $J = 7.72, 1.24$ Hz, 1H), 7.26 (m, 1H), 7.08 (dt, $J = 7.56, 0.96$ Hz, 1H), 6.87 (d, $J = 7.80$ Hz, 1H), 5.21 (m, 1H), 5.07 (m, 1H), 4.55-4.61 (m, 2H), 3.27 (s, 3H), 2.12 (m, 1H), 1.99-2.07 (m, 2H), 1.98 (m, 1H), 1.70 (s, 3H), 1.68 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 175.20, 169.66, 143.64, 142.62, 131.75, 130.24, 128.90, 123.72, 122.79, 117.74, 99.99, 62.81, 59.42, 55.14, 39.42, 26.39,

25.67, 20.12, 17.69, 16.41; **IR** (film) ν_{max} 2925, 1738, 1728, 1612, 1494, 1471, 1375, 1347, 1225, 1105, 1030, 942, 750 cm^{-1} ; **HRMS** (ESI) m/z 364.1901 [(M+Na)⁺; calculated for [C₂₁H₂₇NO₃ + Na]⁺: 364.1883].



(9b)

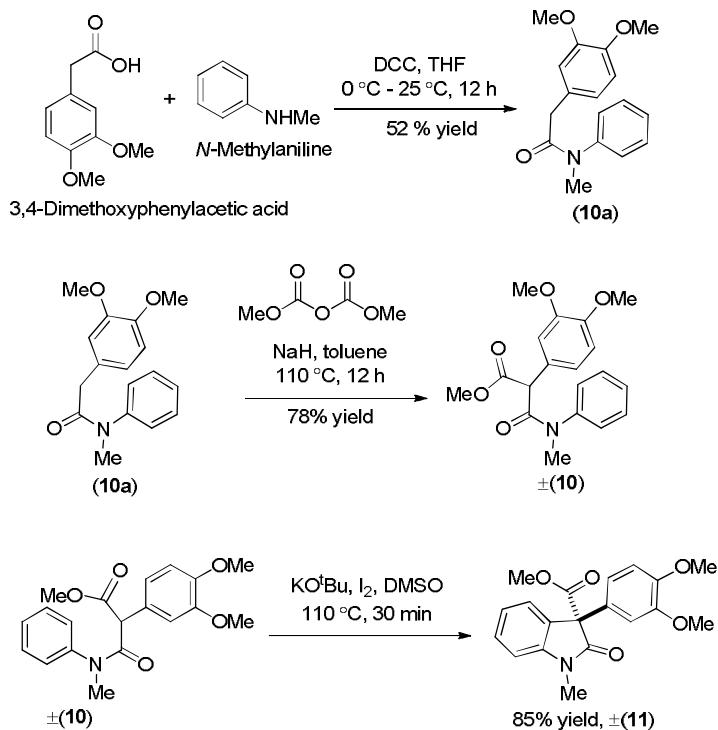
\pm (E)-3,7-Dimethylocta-2,6-dien-1-yl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (9b): 57% yield, colorless gel, R_f = 0.52 (10% EtOAc in hexane). **¹H NMR** (500 MHz, CDCl₃) δ 7.22-7.34 (m, 2H), 7.01-7.04 (m, 4H), 6.86 (d, J = 6.56, 1.12 Hz, 2H), 6.59 (d, J = 6.20 Hz, 1H), 5.26 (dt, J = 5.56, 0.84 Hz, 1H), 5.08 (m, 1H), 4.62-4.71 (m, 2H), 3.57 (s, 2H), 2.97 (s, 3H), 2.07-2.14 (m, 2H), 1.99-2.04 (m, 2H), 1.70 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 173.47, 169.16, 144.06, 142.72, 134.49, 131.80, 129.96, 128.94, 128.14, 127.54, 126.70, 123.92, 123.73, 122.41, 117.77, 108.10, 62.95, 60.96, 40.03, 39.46, 26.28, 26.12, 25.70, 17.71, 16.48; **IR** (film) ν_{max} 2925, 1740, 1721, 1658, 1611, 1494, 1471, 1454, 1375, 1351, 1223, 1106, 998, 749 cm^{-1} ; **HRMS** (ESI) m/z 440.2208 [(M+Na)⁺; calculated for [C₂₇H₃₁NO₃ + Na]⁺: 440.2196].



(9c)

\pm (E)-3,7-Dimethylocta-2,6-dien-1-yl 3-allyl-1-methyl-2-oxoindoline-3-carboxylate (9c): 52% yield, colorless gel, R_f = 0.51 (10% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 (dt, J = 7.72, 1.24 Hz, 1H), 7.26-7.31 (m, 1H), 7.08 (dt, J = 7.56, 0.96 Hz, 1H), 6.86 (d, J = 7.80 Hz, 1H), 5.38-5.44 (m, 1H), 5.20-5.24 (m, 1H), 5.06 (m, 1H), 5.03 (m, 1H), 4.92-4.95 (m, 1H), 4.56-4.66 (m, 2H), 3.24 (s, 3H), 2.94-3.05 (m, 2H), 2.02-2.06 (m, 2H), 1.97-2.00 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.65, 168.92, 144.13, 142.69, 131.77, 131.11, 128.96, 127.67, 123.71, 123.66, 122.66, 119.66, 117.73, 108.21, 62.84, 59.33,

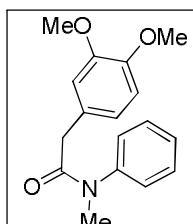
39.42, 38.38, 26.41, 26.26, 25.67, 17.68, 16.43; **IR** (film) ν_{max} 2960, 2924, 2856, 1739, 1722, 1611, 1493, 1471, 1374, 1350, 1225, 1123, 992, 750 cm^{-1} ; **HRMS** (ESI) m/z 390.2043 [(M+Na) $^+$; calculated for [C₂₃H₂₉NO₃ + Na] $^+$: 390.2040].



Scheme 2: Oxidative coupling of compound **±(10)**.

Synthesis of compound **10a**:

In a flame-dried round-bottom flask, 3,4-dimethoxyphenylacetic acid (1.0 equiv.) was taken in tetrahydrofuran (5 mL/mmol) and cooled to 0 °C on an ice-bath. To this reaction mixture was added triethylamine (3.0 equiv.) via a syringe. After 5 minutes of stirring at same temperature, a THF solution (2 mL/mmol) of *N*-methylaniline (1.0 equiv.) was added drop wise to the reaction mixture and slowly allowed to warm to rt (over 10 minutes). The stirring was continued overnight. Upon completion of the reaction (TLC showed complete consumption of starting materials), the reaction mixture was diluted with 10% EtOAc in hexane (15 mL/mmol) and stirred vigorously for 5 minutes. Then the reaction was filtered and the filtrate was evaporated under vacuum to dryness. The crude product was purified by flash chromatography (1:1 hexanes/EtOAc) to afford β -*N*-arylamido esters.

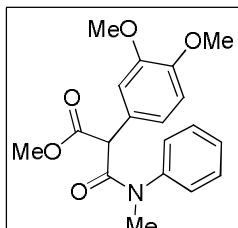


(10a)

2-(3,4-Dimethoxyphenyl)-N-methyl-N-phenylacetamide (10a): 60% yield, colorless gel, $R_f = 0.35$ (50% EtOAc in hexane). **¹H NMR** (400 MHz, CDCl₃) δ 7.32-7.34 (m, 3H), 7.07 (br, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 3.34 (s, 2H), 3.20 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.20, 148.67, 147.72, 143.97, 129.63, 127.89, 127.67, 121.04, 112.33, 111.04, 55.84, 55.71, 40.48, 37.58; **HRMS (ESI)** m/z 286.1456 [(M+H)⁺; calculated for [C₁₇H₁₉NO₃]⁺: 286.1365].

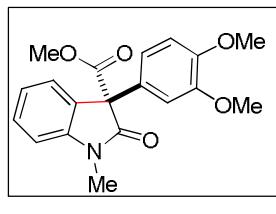
Synthesis of compound (\pm)-10:

In a flame-dried round-bottom flask, amide **10a** (1 g, 3.51 mmol; 1.0 equiv.) was taken in toluene (5 mL/mmol) and cooled to 0 °C in an ice-bath. To this reaction mixture was added NaH (60% dispersion in mineral oil) (421 mg, 10.52 mmol; 3.0 equiv.) portionwise. After 5 minutes of stirring at same temperature, dimethylcarbonate (1.18 mL, 14.03 mmol; 4.0 equiv.) was added drop wise to the reaction mixture and slowly allowed to warm to rt (over 20 minutes of period). The reaction mixture was then placed in an oil-bath maintaining the temperature at 100 °C and heating was continued for overnight. Upon completion of the reaction (TLC showed complete consumption of starting materials), the reaction was cooled to 0 °C and 3 mL glacial acetic acid was added drop wise to the reaction mixture and stirring was continued for 1 h. Then, the reaction was filtered through celite-bed and the filtrate was evaporated under vacuum to dryness. The crude product was purified by flash chromatography (2:1 hexanes/EtOAc) to afford compound (\pm)-**10** in 78% yields.



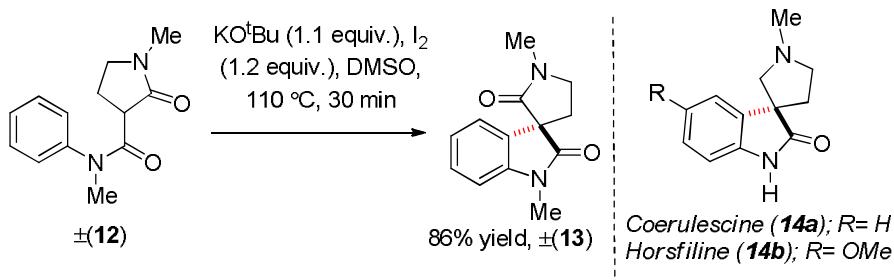
±(10)

Methyl 2-(3,4-dimethoxyphenyl)-3-(methyl(phenyl)amino)-3-oxopropanoate (\pm)-10: 76% yield, colorless gel, $R_f = 0.61$ (50% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.36-7.39 (m, 3H), 7.07 (br, s, 2H), 6.70-6.73 (m, 2H), 6.56 (dd, $J = 8.24, 1.88$ Hz, 1H), 4.51 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 3.25 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 169.58, 168.02, 148.74, 148.70, 143.31, 129.78, 128.33, 127.91, 125.83, 121.80, 112.55, 110.78, 55.83, 55.81, 55.16, 52.63, 37.78; **IR** (film) ν_{max} 2998, 2953, 2838, 1755, 1660, 1594, 1516, 1496, 1464, 1422, 1380, 1302, 1264, 1156, 1027, 774, 702 cm^{-1} ; **HRMS** (ESI) m/z 344.1449 [$(\text{M}+\text{H})^+$]; calculated for $[\text{C}_{19}\text{H}_{22}\text{NO}_5]^+$: 344.1492.

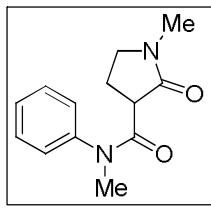


\pm (11)

(\pm)-Methyl 3-(3,4-dimethoxyphenyl)-1-methyl-2-oxoindoline-3-carboxylate (\pm)-11: 85% yield, colorless solid, $R_f = 0.62$ (50% EtOAc in hexane). **$^1\text{H NMR}$** (500 MHz, CDCl_3) δ 7.48 (d, $J = 7.45$ Hz, 1H), 7.44 (t, $J = 7.75$ Hz, 1H), 7.19 (d, $J = 7.55$ Hz, 1H), 7.04 (d, $J = 1.70$ Hz, 1H), 6.94 (d, $J = 7.85$ Hz, 1H), 6.78-6.82 (m, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 3.25 (s, 3H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 173.02, 169.86, 149.18, 148.95, 144.30, 129.69, 127.94, 126.93, 125.95, 122.88, 120.08, 111.53, 110.71, 108.78, 63.23, 55.99, 55.86, 53.37, 26.75; **IR** (film) ν_{max} 2935, 2838, 1745, 1716, 1651, 1609, 1516, 1494, 1469, 1371, 1347, 1259, 1240, 1146, 1131, 1088, 1025, 785, 757 cm^{-1} ; **HRMS** (ESI) m/z 342.1353 [$(\text{M}+\text{H})^+$]; calculated for $[\text{C}_{19}\text{H}_{20}\text{NO}_5]^+$: 342.1336]; **MP** 125-127 °C.

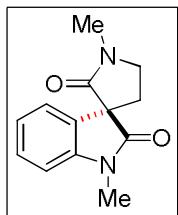


Scheme 3: Spirocyclic products, related to horsfiline (14b) through IDC.



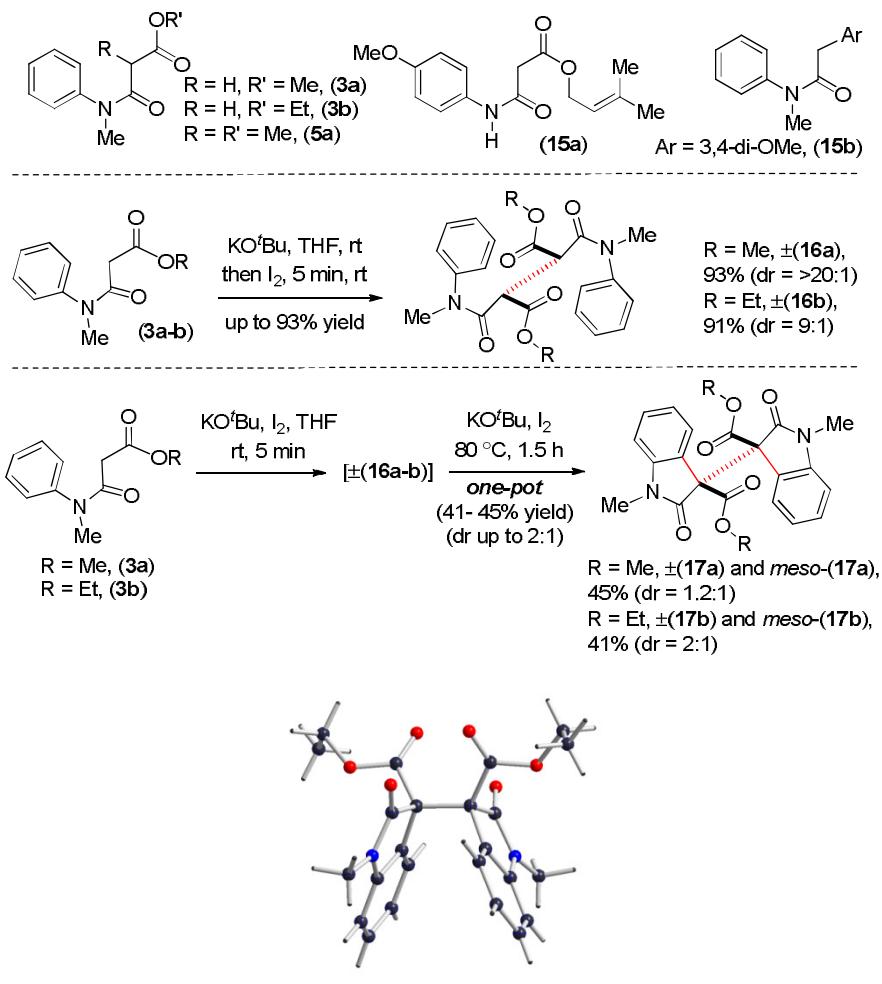
$\pm(12)$

N,N-dimethyl-2-oxo-N-phenylpyrrolidine-3-carboxamide (\pm)-12: 51% yield, colorless solid, $R_f = 0.32$ (75% EtOAc in hexane). **$^1\text{H NMR}$** (500 MHz, CDCl_3) δ 7.40-7.44 (m, 4H), 7.33-7.37 (m, 1H), 3.49-3.52 (m, 1H), 3.45-3.48 (m, 1H), 3.34 (s, 3H), 3.21-3.26 (m, 1H), 2.83 (s, 3H), 2.43-2.50 (m, 1H), 1.97-2.04 (m, 1H); **$^{13}\text{C NMR}$** (125 MHz, CDCl_3) δ 171.31, 170.45, 143.68, 129.71, 127.91, 127.74, 47.98, 45.38, 37.79, 29.87, 23.10; **IR** (film) ν_{max} 2929, 1682, 1651, 1594, 1496, 1454, 1423, 1388, 1303, 1273, 1120, 1045, 776, 703 cm^{-1} ; **HRMS** (ESI) m/z 233.1282 [$(\text{M}+\text{H})^+$; calculated for $[\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2]^+$: 233.1285]; **MP** 120-122 °C.

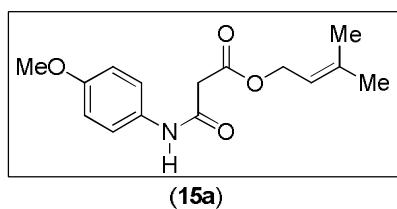


$\pm(13)$

(\pm)-1,1'-dimethylspiro[indoline-3,3'-pyrrolidine]-2,2'-dione (\pm)-13: 86% yield, colorless solid, $R_f = 0.46$ (5% MeOH in dichloromethane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.29 (dt, $J = 7.72, 1.16$ Hz, 1H), 7.13 (d, $J = 6.72$ Hz, 1H), 7.07 (dt, $J = 7.56, 0.60$ Hz, 1H), 6.83 (d, $J = 7.80$ Hz, 1H), 3.74-3.81 (m, 1H), 3.54-3.60 (m, 1H), 3.21 (s, 3H), 2.96 (s, 3H), 2.63-2.70 (m, 1H), 2.34-2.41 (m, 1H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 175.71, 170.48, 144.54, 129.95, 129.00, 123.03, 122.79, 108.54, 57.79, 47.20, 30.56, 29.52, 26.58; **IR** (film) ν_{max} 2919, 2852, 1645, 1261, 1146, 753 cm^{-1} ; **HRMS** (ESI) m/z 253.0950 [$(\text{M}+\text{H})^+$; calculated for $[\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2 + \text{Na}]^+$: 253.0947]; **MP** 172-174 °C.



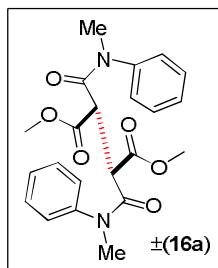
Scheme 4: Substrates scope under IDC.



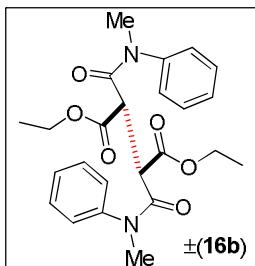
3-Methylbut-2-en-1-yl 3-((4-methoxyphenyl)amino)-3-oxopropanoate (15a): 66% yield, (7 mmol scale of a reaction), Colorless gel, $R_f = 0.45$ (30% EtOAc in hexane). **1H NMR** (400 MHz, CDCl_3) δ : 9.09 (s, 1H), 7.42 (d, $J = 8.96 \text{ Hz}$, 2H), 6.83 (d, $J = 8.96 \text{ Hz}$, 2H), 5.34 (m, 1H), 4.65 (d, $J = 7.32 \text{ Hz}$, 2H), 3.76 (s, 3H), 3.42 (s, 2H), 1.75 (s, 3H), 1.71 (s, 3H); **13C NMR** (100 MHz, CDCl_3) δ : 170.0, 162.8, 156.5, 140.4, 130.7, 121.9, 117.6, 114.1, 62.6, 55.5, 41.4, 25.8, 18.1; **IR** (film) ν_{max} , 3320, 2928, 2851, 1738, 1717, 1661, 1540, 1512, 1442, 1244, 1172, 1034, 830 cm^{-1} ; **HRMS** (ESI) m/z 300.1223 [$(\text{M}+\text{Na})^+$; calculated for $[\text{C}_{15}\text{H}_{19}\text{NO}_4+\text{Na}]^+$: 300.1206].

General procedure for the homodimerization of the β -N-arylamido esters in presence of iodine:

In a flame-dried round-bottom flask, β -amidoester (1.0 mmol; 1.0 equiv.) was taken in dry THF (5 mL) at room temperature. To this reaction mixture was added K'OBu (1.2 mmol; 1.2 equiv.) in one portion. After 2 minutes of stirring at same temperature, Iodine (1.1 mmol, 1.1 equiv.) was added and stirring was continued for 5 minutes (TLC showed complete consumption of starting materials). The reaction mixture wastreated with 5 mL saturated sodium thiosulfate aqueous solution at room temperature and then diluted with 7 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with ethylacetate (7 mL x 2). The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. Finally, the crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford \pm (16a-b).



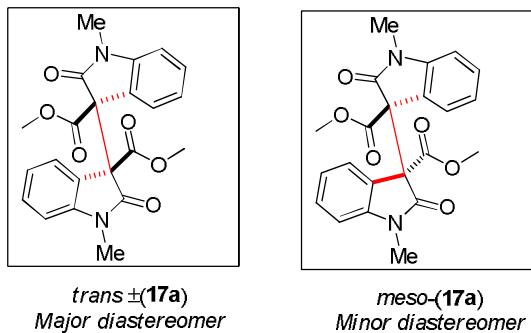
(\pm)-Dimethyl 2,3-bis(methyl(phenyl)carbamoyl)succinate \pm (16a): 93% yield, dr = >20 : 1, R_f = 0.41 (30% EtOAc in hexane), colourless solid. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ : 7.47 (m, 4H), 7.39 (m, 1H), 4.37 (s, 1H), 3.51 (s, 3H), 3.33 (s, 1H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 168.7, 166.6, 143.2, 129.6, 128.2, 128.0, 52.4, 49.9, 38.2; **IR** (film) ν_{max} 2954, 1741, 1661, 1596, 1496, 1435, 1385, 1296, 1162, 1119, 1024, 775, 701 cm^{-1} ; **HRMS** (ESI) m/z 435.1544 [$(\text{M}+\text{Na})^+$; calculated for $[\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_6+\text{Na}]^+$: 435.1527]; **MP** 137–139 °C.



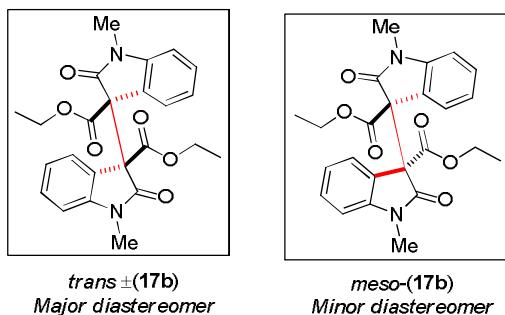
(±)-Diethyl 2,3-bis(methyl(phenyl)carbamoyl)succinate (±)-16b: 91% yield, dr = 9:1, R_f = 0.42 (30% EtOAc in hexane), colorless solid. **^1H NMR** (400 MHz, CDCl_3) δ : (major diastereomer, *trans*-product) 7.51 (m, 1H), 7.46 (m, 3H), 7.37 (m, 1H), 4.39 (s, 1H), 3.97 (m, 2H), 3.33 (s, 3H), 1.12 (t, J = 7.12, 3H), **^{13}C NMR** (100 MHz, CDCl_3) δ : (major diastereomer, *trans*-product) 168.3, 166.8, 143.4, 129.5, 128.1, 128.0, 61.5, 49.9, 38.2, 13.8; **IR** (film) ν_{max} 2984, 1738, 1660, 1596, 1496, 1384, 1296, 1174, 1117, 1027, 775, 701 cm^{-1} ; **HRMS** (ESI) m/z 441.2031 [(M+H) $^+$; calculated for $[\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_6 + \text{H}]^+$: 441.2020]; **MP** 102–105 °C.

General procedure for one-step dimerization followed by intramolecular oxidative coupling (IDC):

In a flame-dried round-bottom flask, β -amidoester **3** (1.0 mmol; 1 equiv.) was taken in dry THF (5 mL). To this reaction mixture was added K^tOBu (1.2 mmol; 1.2 equiv.) at room temperature in one portion. After 2 minutes of stirring at same temperature, Iodine (1.1 mmol, 1.1 equiv.) was added and stirring was continued for 5 minutes (TLC showed complete consumption of starting materials), by which time the dimerization reaction was completed. Then, K^tOBu (1.2 mmol; 1.2 equiv.) was added again to the reaction mixture and immediately afterward Iodine (1.2 mmol; 1.2 equiv.) was added to the reaction mixture at room temperature. Then the reaction mixture was placed in an oil bath pre-heated at 80 °C and stirring was continued for about 1.5 h. Upon completion of the oxidative coupling (TLC showed formation of dimerized 2-oxindole product), it was cooled to room temperature and was treated with 5 mL saturated sodium thiosulfate aqueous solution. Then the reaction mixture was diluted with 7 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with ethylacetate (7 mL x 2). The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude products were purified by flash chromatography (2:1 - 1:1 hexanes/EtOAc) to afford (±)-**17a-b** up to 45% yield.



(±)-Dimethyl 1,1'-dimethyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-dicarboxylate, (±)-17a: 45% yield, dr = (1.2: 1.0), R_f = 0.35 (60% EtOAc in hexane), white solid; **¹H NMR** (400 MHz, CDCl₃) δ: (major diastereomer, *trans*-product) 7.34 (m, 1H), 7.19 (td, J = 1.16, 8.3 Hz, 1H), 6.93 (td, J = 1.06, 7.74 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 3.8 (s, 3H), 3.08 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ: (major diastereomer, *trans*-product) 170.1, 167.8, 144.5, 130.1, 125.9, 123.5, 122.2, 108.1, 61.7, 53.4, 26.5; **¹H NMR** (400 MHz, CDCl₃) δ: (minor diastereomer, *meso*-product) 7.35 (m, 1H), 6.97 (m, 1H), 6.58 (d, J = 7.76 Hz, 1H), 3.79 (s, 3H), 3.15 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ: (minor diastereomer, *meso*-product) 169.1, 166.8, 143.9, 129.8, 125.7, 123.0, 122.2, 107.8, 61.6, 53.3, 26.4; **IR** (film) ν_{max} 2927, 1734, 1608, 1492, 1472, 1371, 1349, 1244, 1029, 756 cm⁻¹; **HRMS** (ESI) m/z 409.1382 [(M + H)⁺]; calculated for [C₂₂H₂₀N₂O₆ + H]⁺: 409.1394]; **MP** 222–224 °C.

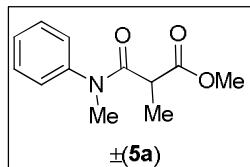


(±)-Diethyl 1,1'-dimethyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-dicarboxylate, (±)-17b: 41% yield, dr = 2:1, R_f = 0.39 (60% EtOAc in hexane), white solid. **¹H NMR** (400 MHz, CDCl₃) δ: (major diastereomer, *trans*-product) 7.31 (m, 1H), 7.19 (td, J = 7.72, 1.20 Hz, 1H), 6.92 (td, J = 7.64, 1.00 Hz, 1H), 6.58 (d, J = 7.64 Hz, 1H), 4.26 (m, 2H), 3.14 (s, 3H), 1.25 (t, J = 7.12, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ: (major diastereomer, *trans*-product) 170.4, 166.4, 144.0, 129.6, 125.9, 123.8, 121.9, 107.7, 62.3, 61.8, 26.4, 13.8; **¹H NMR** (400 MHz, CDCl₃) δ: (minor

diastereomer, *meso*-product) 7.33 (m, 1H), 7.29 (m, 1H), 6.98 (m, 1H), 6.77 (d, $J=7.76$ Hz, 1H), 4.25 (m, 2H), 3.09 (s, 3H), 1.26 (t, $J=7.12$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : (minor diastereomer, *meso*-product) 170.5, 167.1, 144.7, 129.7, 126.1, 123.4, 122.0, 108.0, 62.4, 61.9, 26.5, 13.9; IR (film) ν_{max} 1734, 1609, 1492, 1472, 1372, 1349, 1238, 1028, 754 cm^{-1} ; HRMS (ESI) m/z 459.1525 [(M + Na) $^+$; calculated for $[\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_6 + \text{Na}]^+$: 459.1527]; MP 134–137 °C.

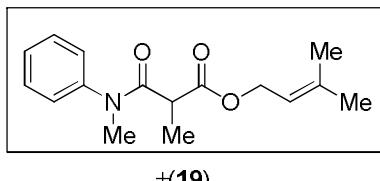
Preparation of C-methylated compound (\pm)-5a:

In a flame-dried round-bottom flask, β -amidoester **3a** (2.0 mmol; 1 equiv.) was taken in DMSO (7 mL) at room temperature. To this reaction mixture was added MeI (2.2 mmol; 1.1 equiv.) via a syringe and stirred at room temperature for 15–20 mins. Upon completion of the reaction (TLC showed complete conversion of starting material) the reaction mixture was quenched with aqueous NH_4Cl solution at room temperature and then diluted with 9 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with ethylacetate (9 mL X 2). The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. Finally, the crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford (\pm)-**5a** (95% yield).



(\pm)-Methyl 2-methyl-3-(methyl(phenyl)amino)-3-oxopropanoate (\pm)-5a: 95% yield, $R_f = 0.40$ (20% EtOAc in hexane), colorless oil, ^1H NMR (500 MHz, CDCl_3) δ : 7.43 (m, 2H), 7.34 (m, 1H), 7.23 (m, 2H), 3.63 (s, 3H), 3.39 (q, $J = 7.04$ Hz, 1H), 3.28 (s, 3H), 1.27 (d, $J = 7.04$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 171.2, 170.1, 143.6, 130.0, 128.3, 127.5, 52.3, 43.5, 37.7, 14.2; IR (film) ν_{max} 2953, 1742, 1716, 1651, 1613, 1497, 1472, 1376, 1347, 1241, 1147, 1118, 1063, 1030, 972, 909 cm^{-1} , HRMS (ESI) m/z 244.0959 [(M + Na) $^+$; calculated for $[\text{C}_{12}\text{H}_{15}\text{NO}_3 + \text{Na}]^+$: 244.0944].

Preparation of C-methylated compound (\pm)-19: The experimental procedure is similar as shown for (\pm)-**5a**.



\pm (19)

3-Methylbut-2-en-1-yl 2-methyl-3-(methyl(phenyl)amino)-3-oxopropanoate (\pm)-19: 89% yield, colorless gel, $R_f = 0.45$ (30% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ : 7.40 (m, 2H), 7.33 (m, 1H), 7.22 (m, 2H), 5.26 (t, $J = 7$ Hz, 1H), 4.56 (m, 1H), 4.47 (m, 1H), 3.37 (q, $J = 7.04$ Hz, 1H), 3.27 (s, 3H), 1.73 (s, 3H), 1.66 (s, 3H), 1.27 (d, $J = 7$ Hz, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ : 170.8, 170.1, 143.6, 139.0, 129.9, 128.2, 127.6, 118.4, 62.1, 43.6, 37.7, 25.7, 18.1, 14.2; **IR** (film) ν_{max} 3443, 2360, 1740, 1734, 1662, 1596, 1496, 1456, 1385, 1187, 775 cm^{-1} ; **HRMS** (ESI) m/z 298.1420 [(M+Na) $^+$; calculated for $[\text{C}_{16}\text{H}_{21}\text{NO}_3+\text{Na}]^+$: 298.1414].

Procedure for the oxidative coupling using *t*-BuOI as a radical generating source (in absence of KO'Bu):

In a flame-dried round-bottom flask, C-methylated- β -amidoester (\pm)-5a (0.5 mmol; 1 equiv) was taken in DMSO (2 mL) at room temperature. To this reaction mixture was added freshly prepared *t*-BuOI (0.6 mmol; 1.2 equiv. in 0.5 mL in benzene) via a syringe. Then, the reaction was placed on a pre-heated oil-bath maintaining the temperature at 100 °C for 45 min. TLC showed incomplete conversion of starting material (most starting material was showed in TLC along with some decomposition). However, the reaction mixture was then treated with 5 mL saturated sodium thiosulfate aqueous solution at room temperature and then diluted with 5 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with ethylacetate (5 mL x 2). The organic filtrate was dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. Finally, the crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford (\pm)-5a (59% yield recovered starting material).

(Preparation of *t*-BuOI: A flame-dried round-bottom flask was charged with 0.6 mmol of *t*-BuONa in 0.5 mL of benzene. To this solution was added 0.6 mmol of I_2 at room temperature.

For reference, see; Montoro, R.; Wirth, T. *Org. Lett.* **2003**, *5*, 4729. This solution was directly used for the oxidative coupling.)

The oxidative coupling of **5a was also conducted with the *t*-BuOI prepared in the following procedure (in absence of KO'Bu):**

(Preparation of *t*-BuOI: A flame-dried round-bottom flask was charged with 0.6 mmol of *t*-BuONa in 0.5 mL of benzene. To this solution was added 1.8 mmol of I₂ at room temperature. For reference, see; Akhtar, M.; Barton, D. H. R. *J. Am. Chem. Soc.* **1964**, *86*, 1528. This solution was directly used for the oxidative coupling.)

Result of Oxidative coupling: When the oxidative coupling was carried out in presence of *t*-BuOI prepared from above procedure, it was observed that 56% of starting material along with decomposition of the rest of the mass balance.

Procedure for the oxidative coupling using *t*-BuOI as a radical generating source (in presence of 1.2 equiv of KO'Bu):

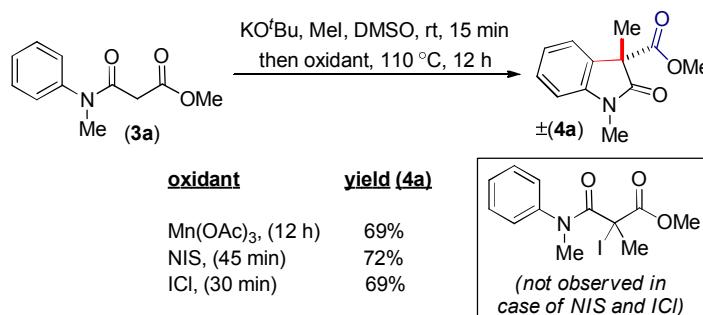
In a flame-dried round-bottom flask, C-methylated-β-amidoester (\pm)-**5a** (0.5 mmol; 1 equiv) was taken in DMSO (2 mL) at room temperature. To this reaction mixture was added KO'Bu (0.6 mmol; 1.2 equiv) in one portion followed by freshly prepared *t*-BuOI (0.6 mmol; 1.2 equiv in 0.5 mL in benzene) via a syringe. Then, the reaction was placed on a pre-heated oil-bath maintaining the temperature at 100 °C for 50 min. TLC showed complete conversion of starting material to product. Then, the reaction mixture was cooled to rt and treated with 5 mL saturated aqueous sodium thiosulfate solution at room temperature and then diluted with 5 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with ethylacetate (5 mL x 2). The organic filtrate was dried over Na₂SO₄ and concentrated in a rotary evaporator under reduced pressure. Finally, the crude products were purified by flash chromatography (4:1 hexanes/EtOAc) to afford oxidative coupling product (\pm)-**4a** in 62% yield.

(Preparation of *t*-BuOI: A flame-dried round-bottom flask was charged with 0.6 mmol of *t*-BuOK in 0.5 mL of benzene. To this solution was added 0.6 mmol of I₂ at room temperature. For reference, see; Montoro, R.; Wirth, T. *Org. Lett.* **2003**, *5*, 4729. This solution was directly used for the oxidative coupling.)

The oxidative coupling of 5a was also conducted with the *t*-BuOI prepared in the following procedure (in presence of 1.2 equiv of KO'Bu):

(Preparation of *t*-BuOI: A flame-dried round-bottom flask was charged with 0.6 mmol of *t*-BuOK in 0.5 mL of benzene. To this solution was added 1.8 mmol of I₂ at room temperature. For reference, see; Akhtar, M.; Barton, D. H. R. *J. Am. Chem. Soc.* **1964**, *86*, 1528. This solution was directly used for the oxidative coupling.)

Result of Oxidative coupling: When the oxidative coupling was carried out in presence of *t*-BuOI prepared from above procedure, the reaction afforded 68% yield of oxidative coupling product (\pm)-4a.



Scheme 6: Intramolecular-dehydrogenative-coupling (IDC) of 3a.

C-Methylation followed by treatment with NIS and ICl (at 110 °C):

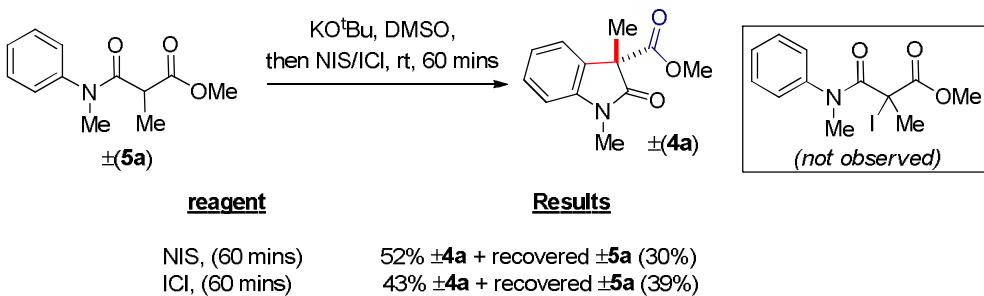
In a flame-dried round-bottom flask, β -amidoester **3a** (0.25 mmol; 1 equiv.) was taken in DMSO (0.75 mL) at room temperature. To this reaction mixture was added K'*O*Bu (0.30 mmol; 1.2 equiv.) in one portion. After 1-2 minutes of stirring at same temperature, MeI (0.275 mmol, 1.1 equiv.) was added and stirring was continued for 10-15 minutes (TLC showed complete

consumption of starting materials). Once methylation is over, K'OBu (0.30 mmol; 1.2 equiv.) and 1.2 equiv. (0.30 mmol) of NIS/ICl were added to the reaction mixture at room temperature. Immediately afterwards, the reaction mixture was heated at 110 °C for 30-45 mins. Upon full conversion of the starting material (TLC showed no starting material left), it was cooled to room temperature and diluted with 5 mL of EtOAc. The reaction mixture was extracted with 5 mL saturated sodium thiosulfate (5 mL X 3 times) and then successively washed with water (5 mL), and brine (5 mL). The organic extracts were dried over MgSO₄ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford 2-oxindole derivatives. (NIS: 72% yield of (\pm)-4a; ICl: 69% yield of (\pm)-4a).

C-Methylation followed by treatment with NIS and ICl (at room temperature):

Once methylation is over, K'OBu (0.30 mmol; 1.2 equiv) and 1.2 equiv (0.30 mmol) of NIS/ICl were added to the reaction mixture at room temperature and stirred for 2 h. After this time, (TLC showed almost 1:1 mixture of starting material and product) the reaction mixture was diluted with 5 mL of EtOAc. The reaction mixture was extracted with 5 mL saturated sodium thiosulfate (5 mL X 3 times) and then successively washed with water (5 mL), and brine (5 mL). The organic extracts were dried over MgSO₄ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford 2-oxindole derivatives and unreacted starting material. However, no iodinated product was observed. (NIS: 45% yield of (\pm)-4a + 36% of starting material; ICl: 36% yield of (\pm)-4a + 47% of starting material).

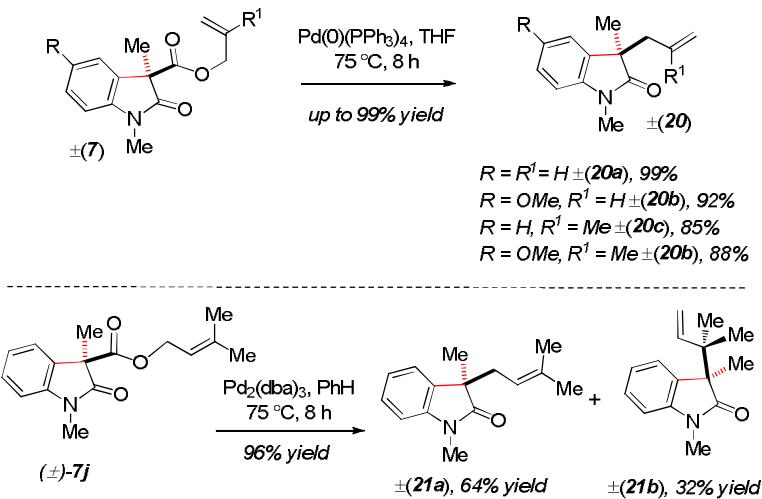
C-Iodination of compound (\pm)-5a was also carried out in presence of K'OBu and NIS or ICl following above procedure, but the reaction led to the formation of (\pm)-4a as major product (see, Scheme below) along with recovered starting material.



Scheme: Intramolecular-dehydrogenative coupling (IDC) of (\pm)-**5a**.

Procedure for one-step alkylations followed by intramolecular oxidative coupling (IDC) using Mn(OAc)₃ (Scheme 6):

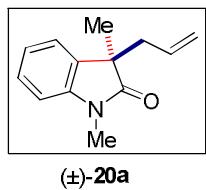
In a flame-dried round-bottom flask, β -amidoester 3a (0.25 mmol; 1 equiv.) was taken in DMSO (0.75 mL) at room temperature. To this reaction mixture was added K'OBu (0.30 mmol; 1.2 equiv.) in one portion. After 1-2 minutes of stirring at same temperature, methyl iodide (0.275 mmol, 1.1 equiv.) was added and stirring was continued for 5-10 minutes (TLC showed complete consumption of starting materials). K'OBu (0.30 mmol; 1.2 equiv.) and 1.1 equiv. (0.275 mmol) of Mn(OAc)₃ were added to the reaction mixture at room temperature. Immediately afterwards, the reaction mixture was heated at 110 °C for 12 h. Upon completion of the oxidative coupling (TLC showed complete consumption of the starting materials), it was cooled to room temperature and diluted with 5 mL of EtOAc. The reaction mixture was extracted with 5 mL saturated sodium thiosulfate (5 mL X 3 times) and then successively washed with water (5 mL), and brine (5 mL). The organic extracts were dried over MgSO₄ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford 2-oxindole derivatives.



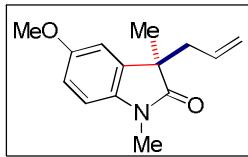
Scheme 7: Synthetic elaboration using Tsuji-Trost reactions.

General procedure for Tsuji-Trost decarboxylative allylation reaction:

In a flame dried sealed tube, 3-alkyl-3-allylester of 2-oxindoles (0.5 mmol, 1 equiv.) was taken in tetrahydrofuran (3 mL of THF) and the reaction vessel was degassed with continuous flow of nitrogen (5 min). To this reaction mixture was added 5 mol% of $\text{Pd}(\text{PPh}_3)_4$ or $\text{Pd}_2(\text{dba})_3$ and it was heated to 75 °C for indicated time. Upon completion of the reaction (TLC showed complete conversion of starting material to product), the reaction mixture was concentrated in a rotary evaporator under reduced pressure. The crude materials were purified by flash chromatography (10:1 hexanes/EtOAc) to afford products (up to 99% yield).

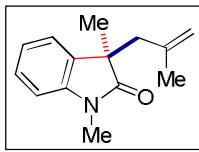


(±)-3-Allyl-1,3-dimethylindolin-2-one (\pm)-20a: 99% yield, colorless gel, $R_f = 0.61$ (20% EtOAc in hexane). **1H NMR** (400 MHz, CDCl_3) δ 7.25 (dt, $J = 7.20, 0.88$ Hz, 1H), 7.17 (d, $J = 7.20$ Hz, 1H), 7.05 (t, $J = 7.52$ Hz, 1H), 6.81 (d, $J = 7.72$ Hz, 1H), 5.38-5.47 (m, 1H), 4.96 (d, $J = 17.00$ Hz, 1H), 4.91 (d, $J = 10.80$ Hz, 1H), 3.18 (s, 3H), 2.49-2.51 (m, 2H), 1.35 (s, 3H); **13C NMR** (100 MHz, CDCl_3) δ 180.2, 143.2, 133.6, 132.6, 127.8, 122.9, 122.3, 118.6, 107.9, 48.3, 42.5, 26.1, 22.7; **IR** (film) ν_{max} 2928, 1722, 1659, 1613, 1595, 1515, 1495, 1469, 1377, 1349, 1263, 1157, 1026, 920, 753 cm^{-1} ; **HRMS** (ESI) m/z 202.1228 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{13}\text{H}_{16}\text{NO}]^+$: 202.1226].



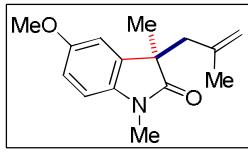
(\pm)-20b

(\pm)-3-Allyl-5-methoxy-1,3-dimethylindolin-2-one (\pm)-20b: 92% yield, colorless gel, $R_f = 0.52$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 6.79-6.84 (m, 2H), 6.74 (d, $J = 8.28$ Hz, 1H), 5.42-5.53 (m, 1H), 5.00 (d, $J = 17.00$ Hz, 1H), 4.94 (d, $J = 10.08$ Hz, 1H), 3.82 (s, 3H), 3.19 (s, 3H), 2.47-2.57 (m, 2H), 1.38 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 179.8, 155.9, 136.8, 135.1, 132.5, 118.7, 111.6, 110.7, 108.1, 55.8, 48.7, 42.4, 26.2, 22.8; **IR** (film) ν_{\max} 2932, 2856, 1740, 1715, 1612, 1494, 1471, 1376, 1348, 1258, 1226, 1105, 1029, 939, 752 cm^{-1} ; **HRMS** (ESI) m/z 232.1341 [(M+H) $^+$; calculated for $[\text{C}_{14}\text{H}_{18}\text{NO}_2]^+$: 232.1332].



(\pm)-20c

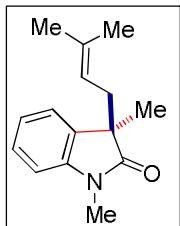
(\pm)-1,3-Dimethyl-3-(2-methylallyl)indolin-2-one (\pm)-20c: 85% yield, colorless gel, $R_f = 0.54$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.28 (d, $J = 7.56$ Hz, 1H), 7.21 (d, $J = 7.24$ Hz, 1H), 7.07 (d, $J = 7.48$ Hz, 1H), 6.84 (d, $J = 7.76$ Hz, 1H), 4.58 (s, 1H), 4.50 (s, 1H), 3.21 (s, 3H), 2.75 (d, $J = 13.48$ Hz, 1H), 2.49 (d, $J = 13.44$ Hz, 1H), 1.40 (s, 3H), 1.35 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 180.4, 143.3, 141.2, 133.7, 127.7, 123.1, 122.2, 114.2, 107.9, 48.7, 45.7, 26.1, 24.7, 23.6; **IR** (film) ν_{\max} 2925, 2856, 1739, 1721, 1609, 1495, 1471, 1376, 1121, 750 cm^{-1} ; **HRMS** (ESI) m/z 216.1397 [(M+H) $^+$; calculated for $[\text{C}_{14}\text{H}_{18}\text{NO}]^+$: 216.1383].



(\pm)-20d

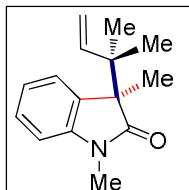
(\pm)-5-Methoxy-1,3-dimethyl-3-(2-methylallyl)indolin-2-one (\pm)-20d: 88% yield, colorless gel, $R_f = 0.53$ (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 6.83 (d, $J = 2.20$ Hz, 1H), 6.78-6.81 (m, 1H), 6.74 (m, 1H), 4.59 (m, 1H), 4.52 (m, 1H), 3.82 (s, 3H), 3.19 (s, 3H), 2.74 (d, $J = 13.04$ Hz, 1H), 2.47 (d, $J = 13.12$ Hz, 1H), 1.38 (s, 3H), 1.28 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz,

CDCl_3) δ 180.0, 155.9, 141.2, 136.9, 135.1, 114.2, 110.9, 108.1, 55.8, 49.0, 45.6, 29.7, 26.2, 24.8, 23.6; **IR** (film) ν_{max} 2926, 1715, 1651, 1614, 1494, 1470, 1377, 1350, 1257, 1143, 1123, 1040, 897, 753 cm^{-1} ; **HRMS** (ESI) m/z 246.1487 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{15}\text{H}_{20}\text{NO}_2]^+$: 246.1489].



$\pm(21\text{a})$

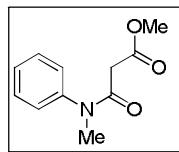
(±)-1,3-Dimethyl-3-(3-methylbut-2-en-1-yl)indolin-2-one (±)-21a: 64% yield, colorless gel, R_f = 0.72 (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.24 (dt, J = 7.72, 1.12 Hz, 1H), 7.16 (d, J = 7.28 Hz, 1H), 7.02 (dt, J = 8.16, 0.72 Hz, 1H), 6.80 (d, J = 7.76 Hz, 1H), 4.79-4.83 (m, 1H), 3.18 (s, 3H), 2.44 (d, J = 7.48 Hz, 2H), 1.55 (s, 3H), 1.49 (s, 3H), 1.34 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 180.7, 143.2, 135.1, 134.1, 127.6, 122.9, 122.2, 118.2, 107.8, 48.4, 36.7, 26.1, 25.8, 22.4, 18.0; **IR** (film) ν_{max} 2966, 2926, 1715, 1613, 1493, 1470, 1453, 1377, 1348, 1312, 1252, 1124, 1095, 1062, 1033, 930, 751 cm^{-1} ; **HRMS** (ESI) m/z 230.1353 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{15}\text{H}_{20}\text{NO}]^+$: 230.1359].



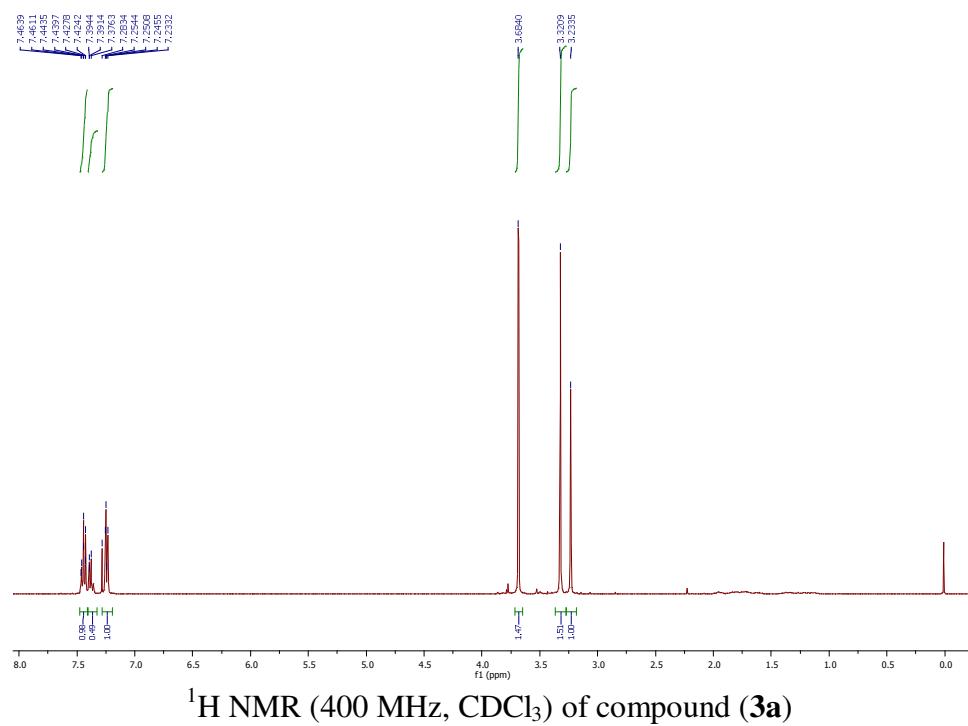
$\pm(21\text{b})$

(±)-1,3-Dimethyl-3-(2-methylbut-3-en-2-yl)indolin-2-one (±)-21b: 32% yield, colorless gel, R_f = 0.81 (20% EtOAc in hexane). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.24 (m, 1H), 7.20 (m, 1H), 6.98 (t, J = 7.52 Hz, 1H), 6.77 (d, J = 7.72 Hz, 1H), 6.00 (dd, J = 17.44, 10.80 Hz, 1H), 5.03 (dd, J = 10.80, 1.04 Hz, 1H), 4.95 (dd, J = 17.44, 0.92 Hz, 1H), 3.16 (s, 3H), 1.32 (s, 3H), 0.98 (s, 3H); **IR** (film) ν_{max} 2969, 2927, 1709, 1652, 1614, 1610, 1494, 1462, 1375, 1341, 1188, 1101, 982, 765, 750 cm^{-1} ; **HRMS** (ESI) m/z 230.1544 $[(\text{M}+\text{H})^+]$; calculated for $[\text{C}_{15}\text{H}_{20}\text{NO}]^+$: 230.1539].

Scanned Copies of Selected $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and Mass Spectra



(3a)



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- 1659314

- 1434751

- 1239722

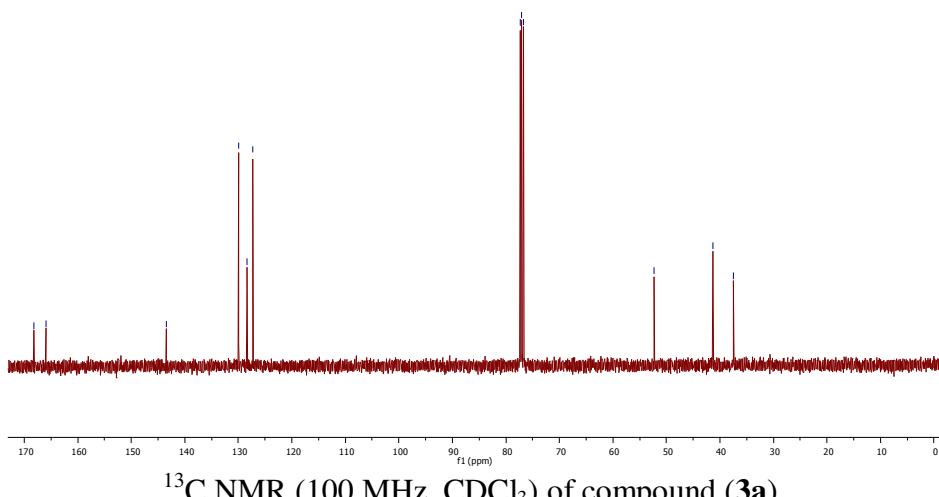
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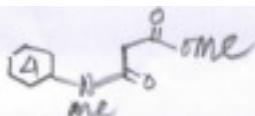
- 773614 -

- 374695

- 374695



¹³C NMR (100 MHz, CDCl₃) of compound (**3a**)



Display Report

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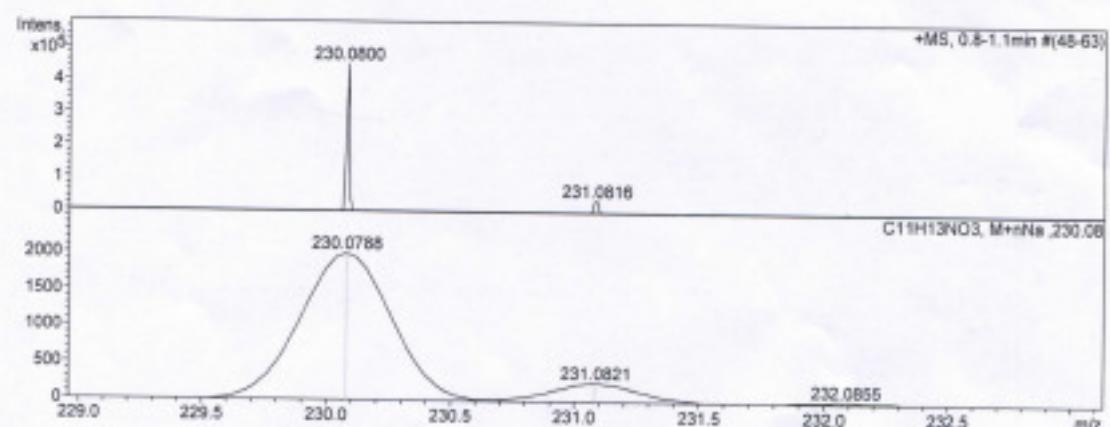
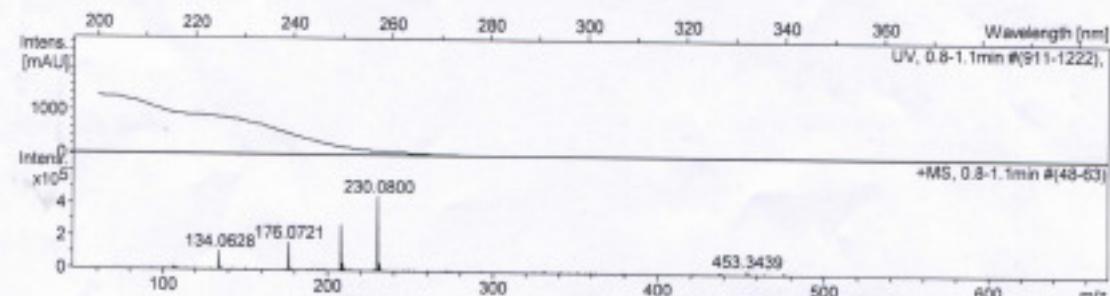
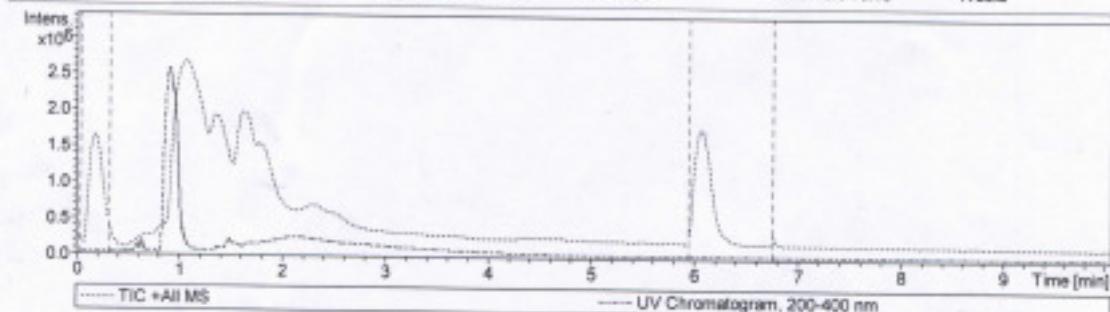
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Operator: Meena Sharma

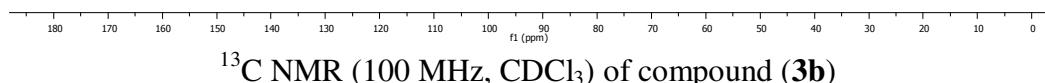
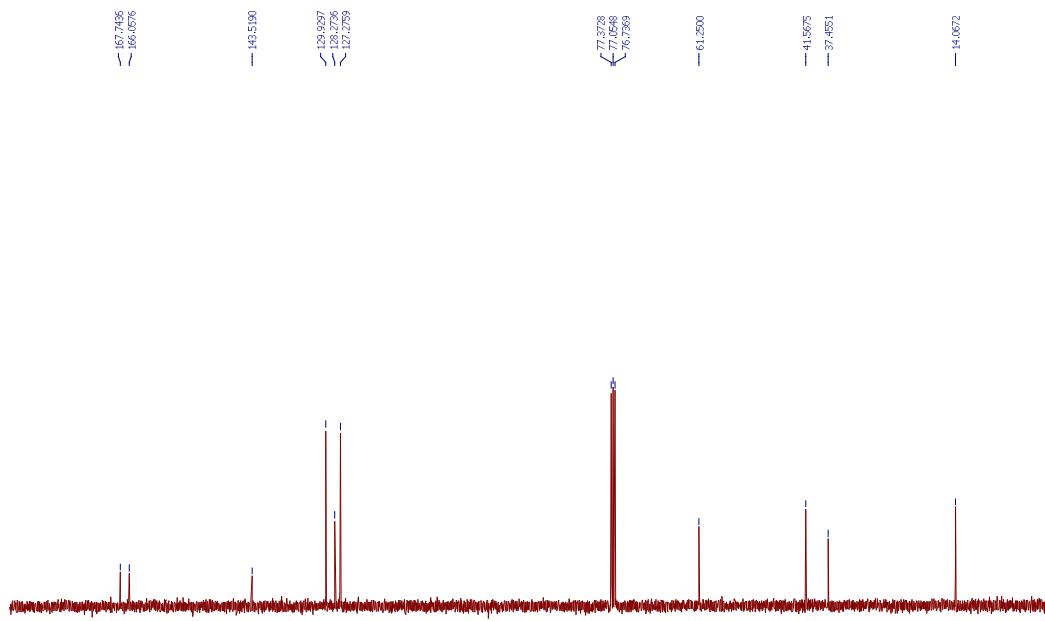
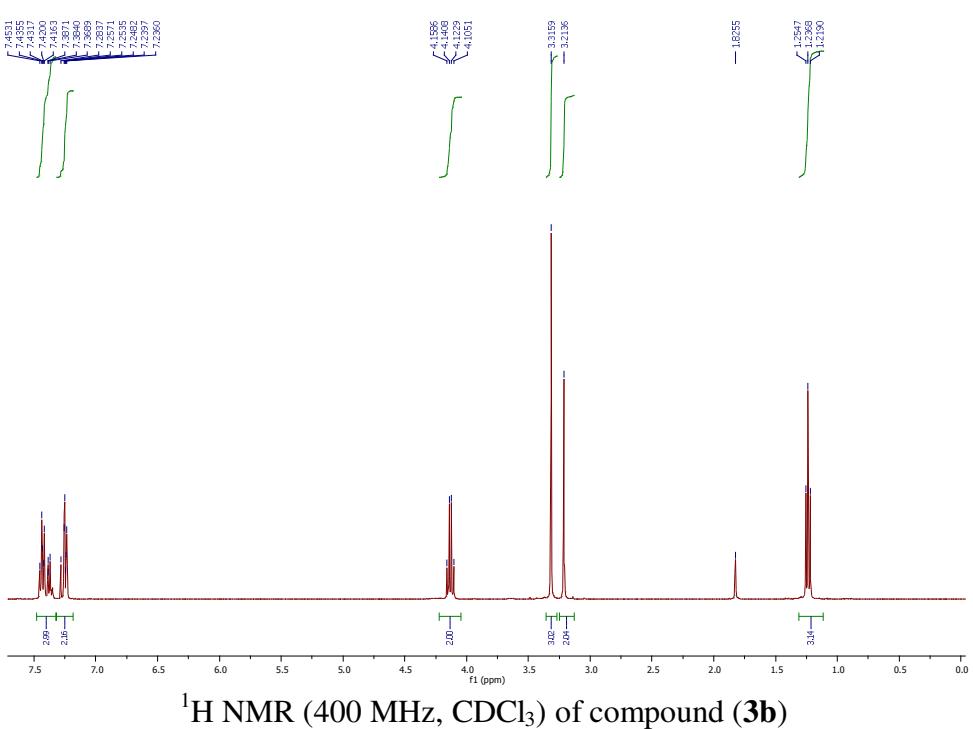
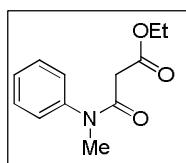
Instrument: micrOTOF-Q II 10330

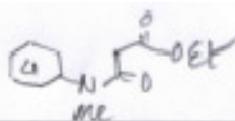
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Scanned copy of mass spectrum of compound 3a





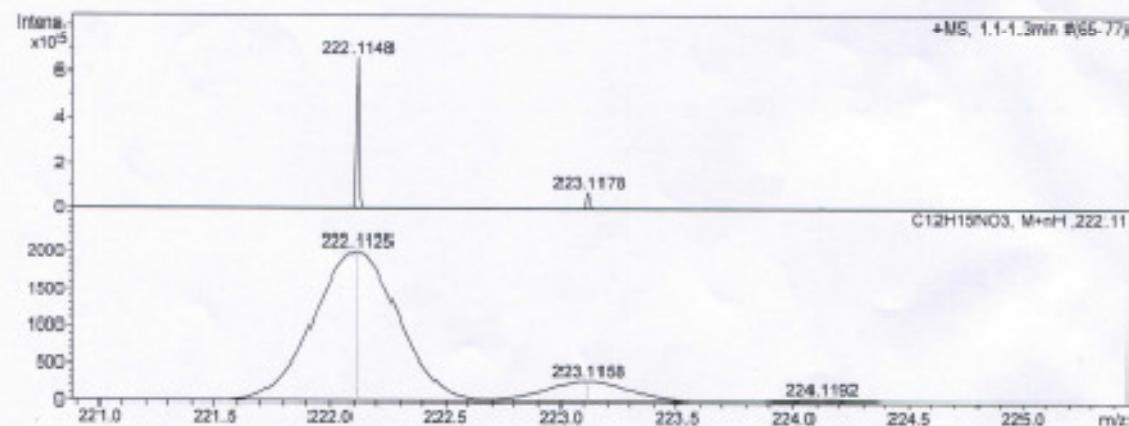
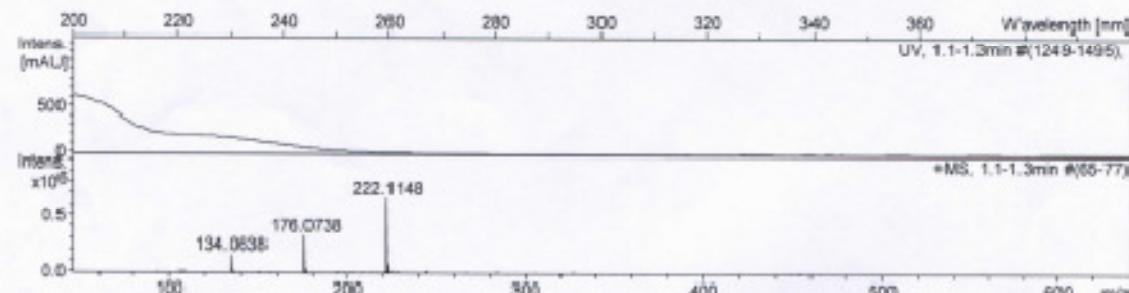
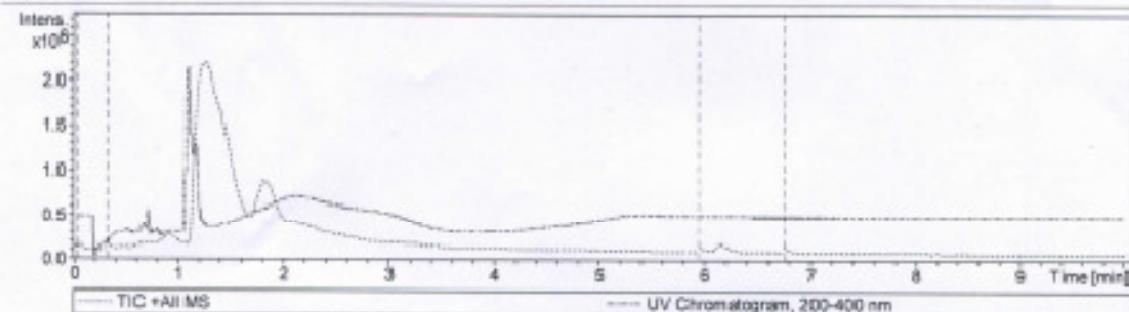
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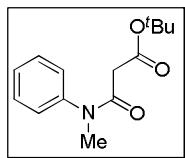
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Sample Name	Dr. A. Bisai- SB-1-295	Instrument	micrOTOF-Q II 10330
Comment			

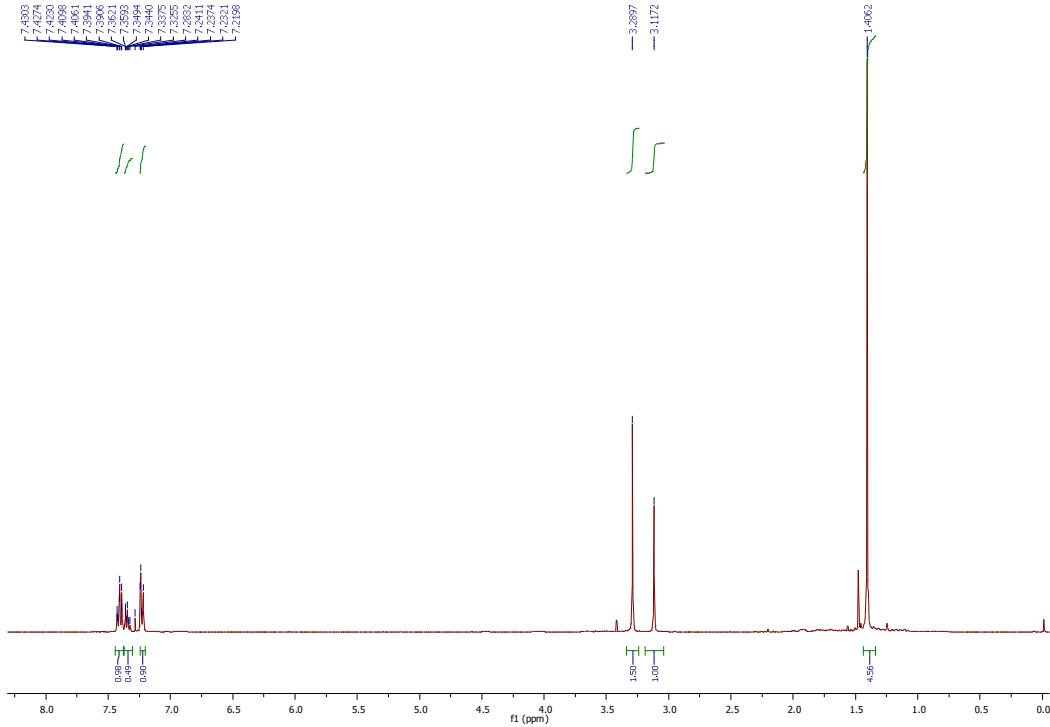
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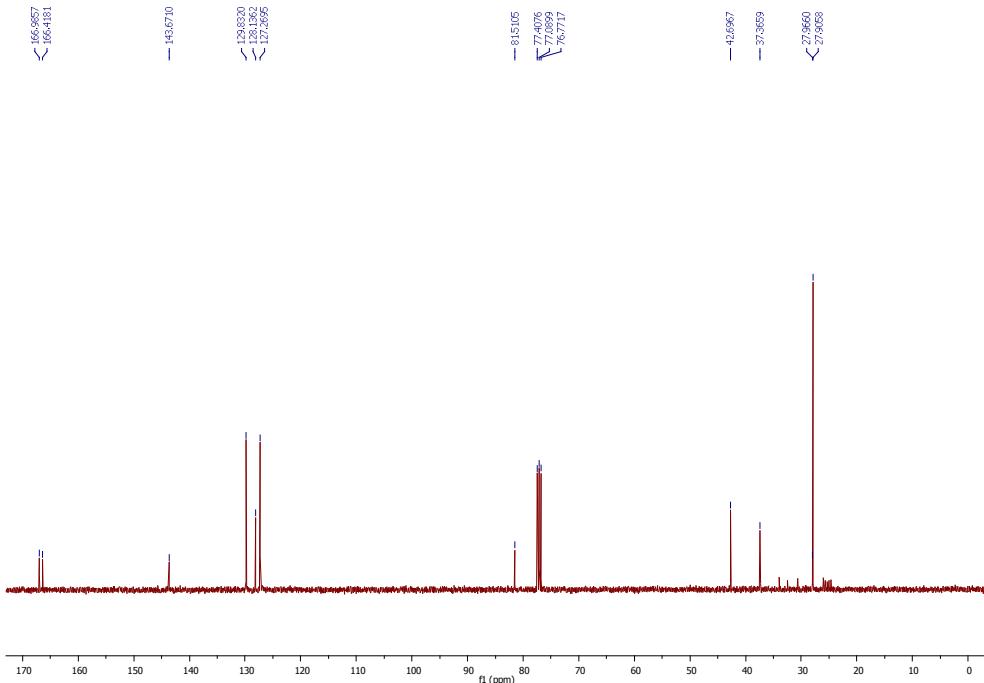




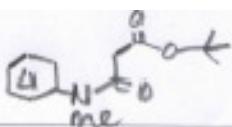
(3c)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**3c**)



Display Report

Analysis Info

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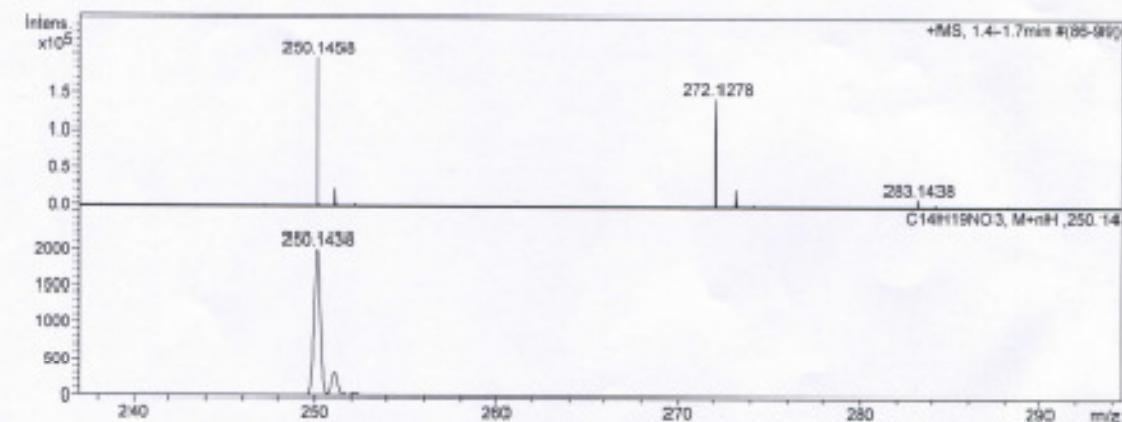
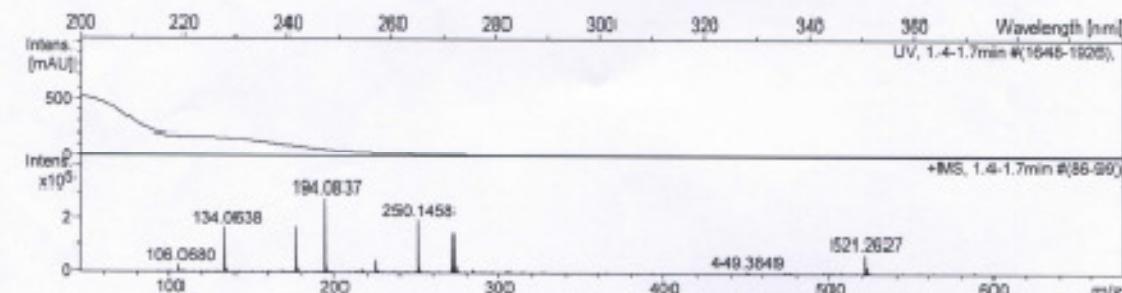
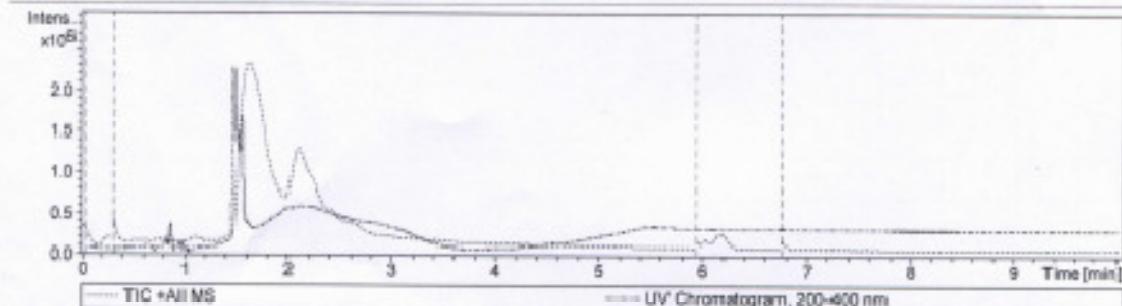
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Operator: Meena Sharma

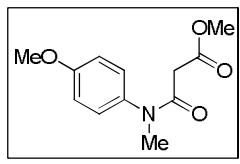
Instrument: micrOTOF-Q II 10330

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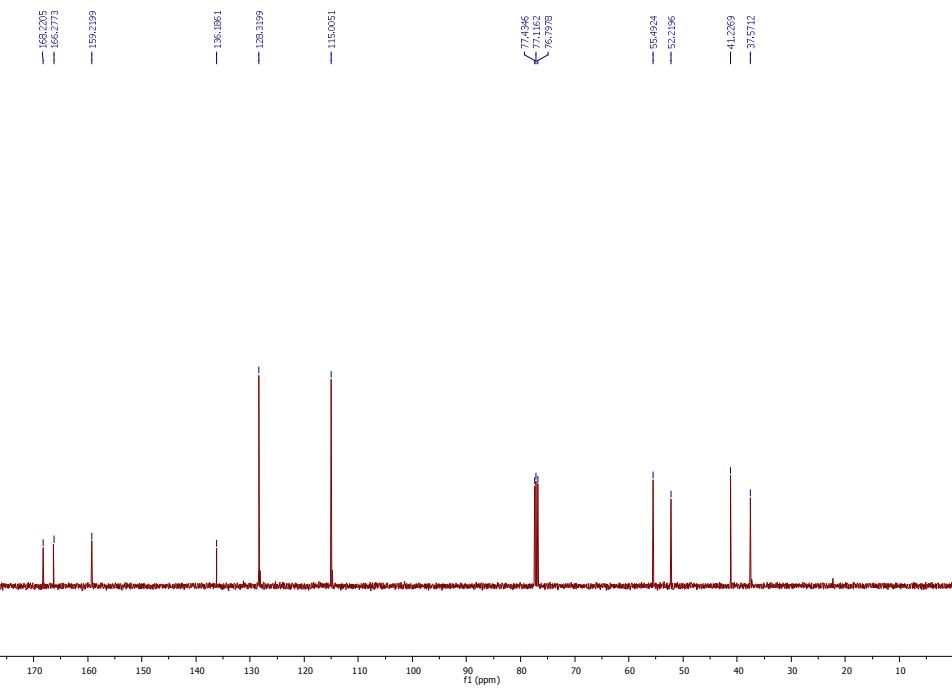
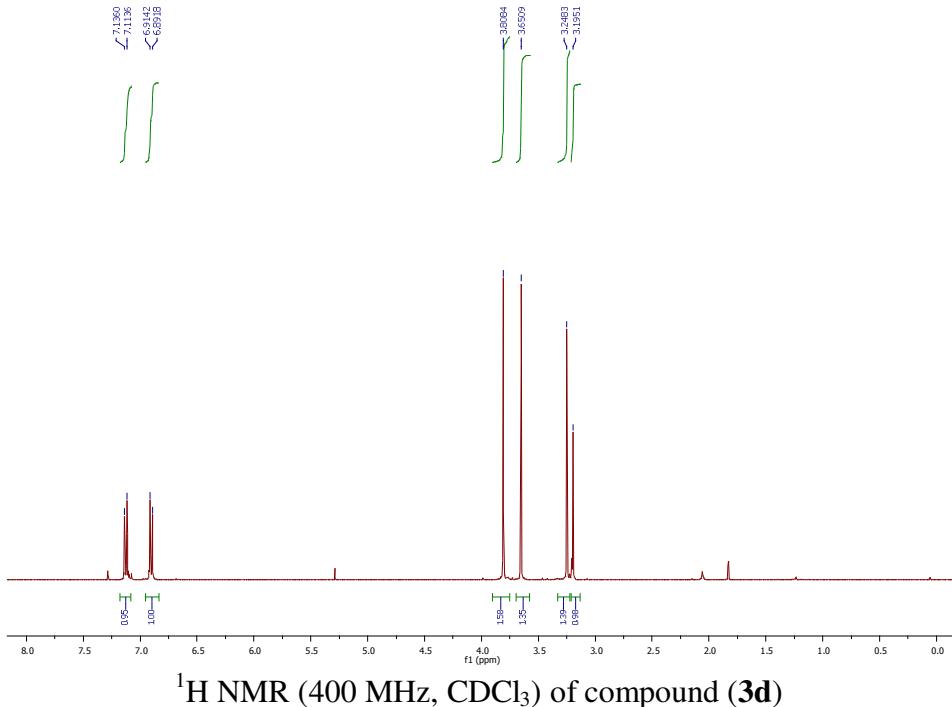
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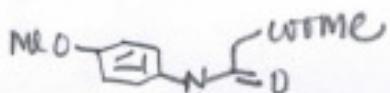


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(3d)





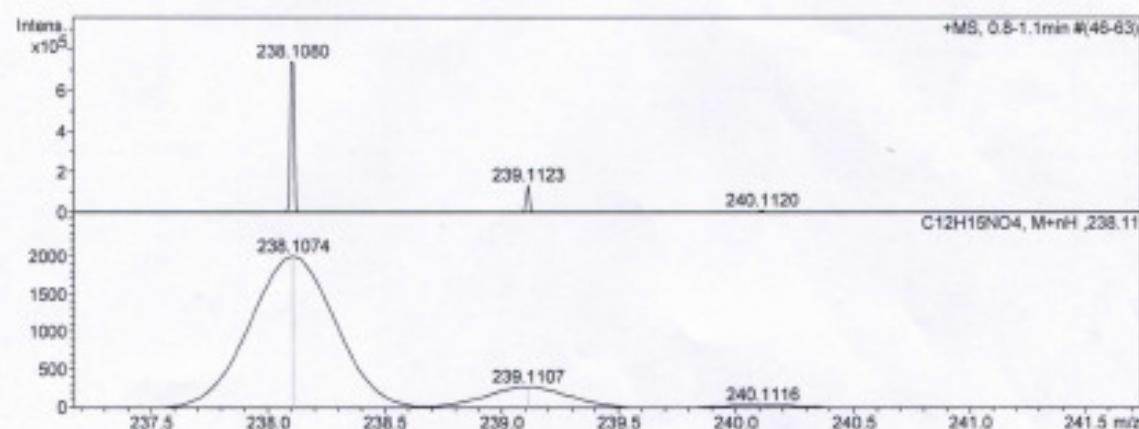
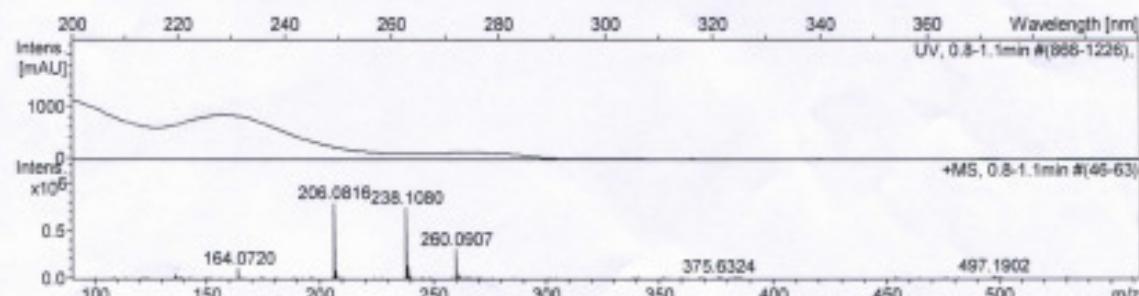
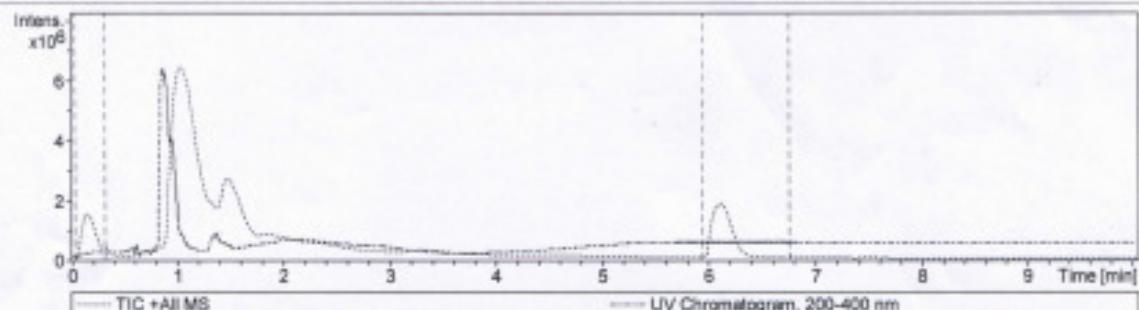
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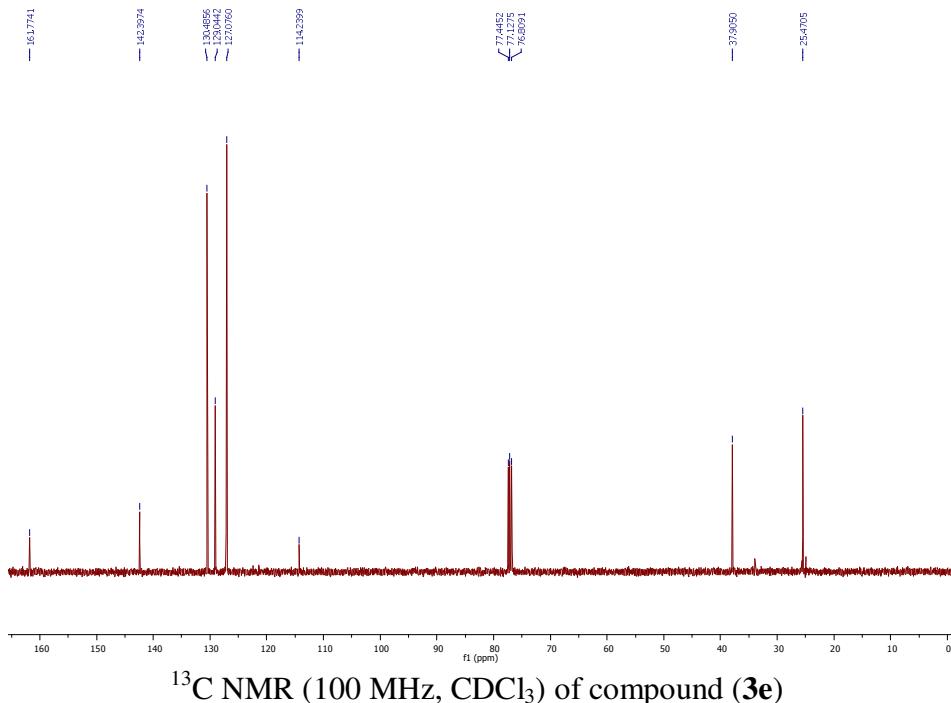
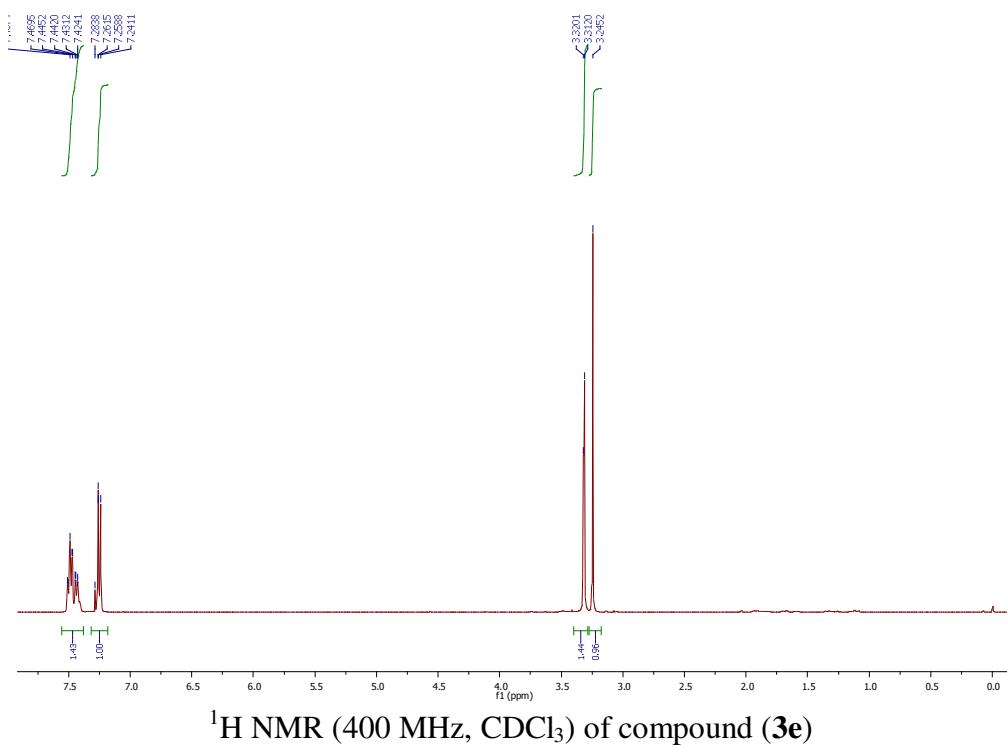
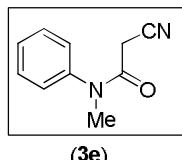
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Sample Name	Dr. A. Bisai- SG4-59	Instrument	micrOTOF-Q II 10330
Comment			

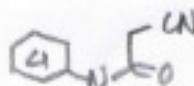
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Scanned copy of mass spectrum of compound 3d





Display Report

Analysis Info

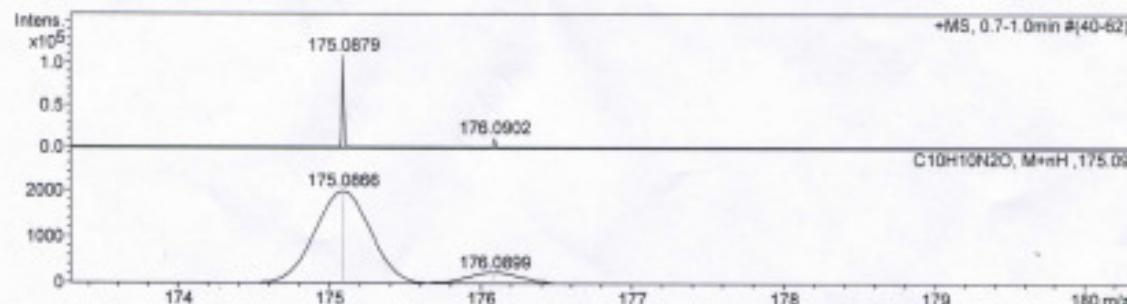
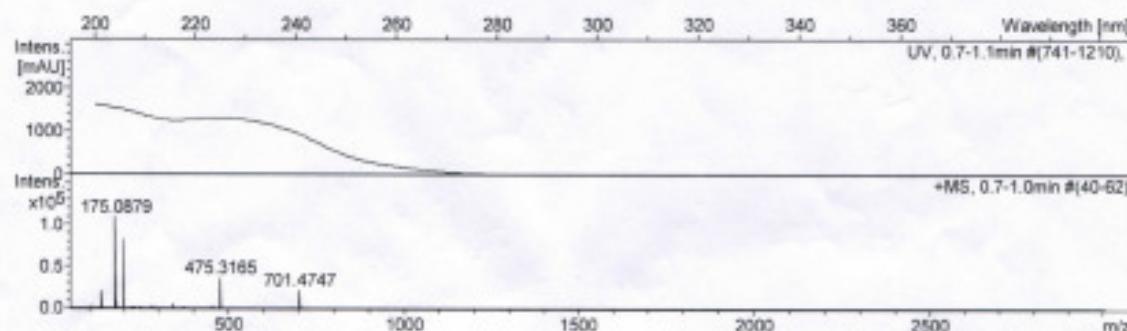
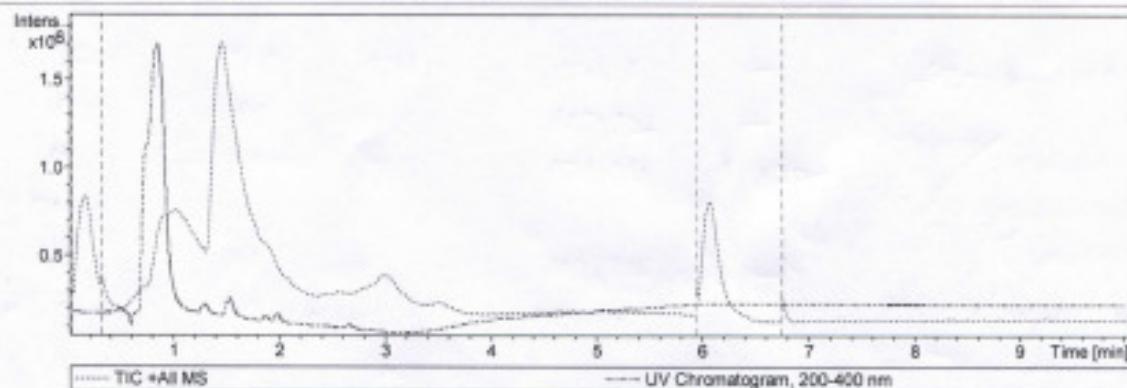
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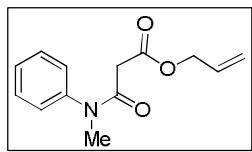
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

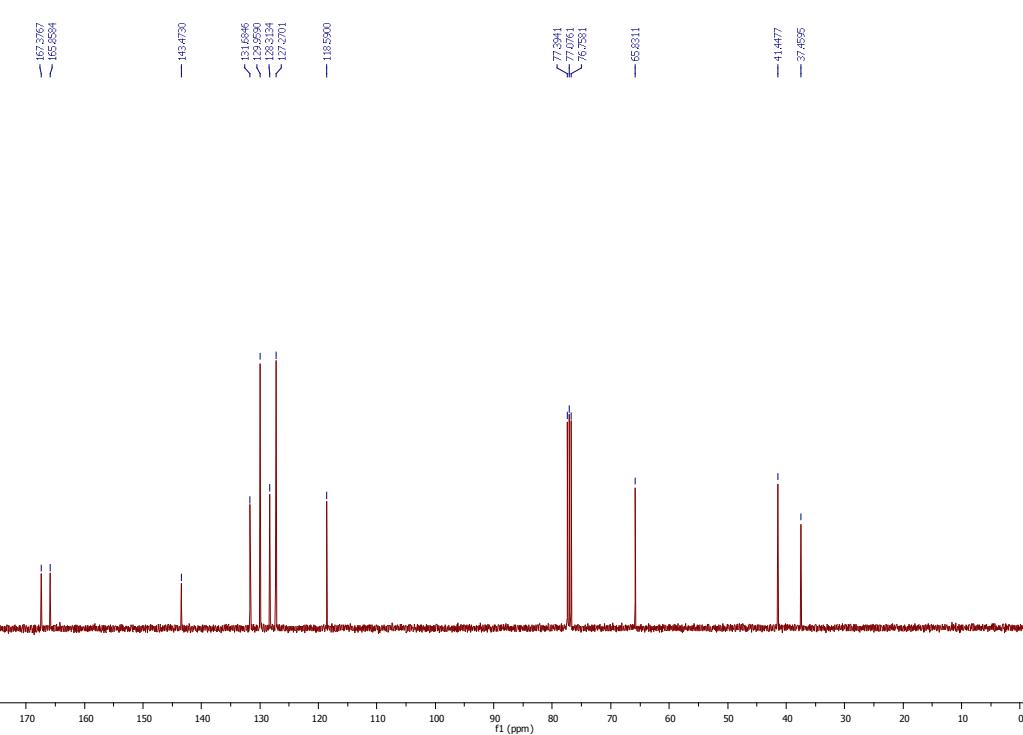
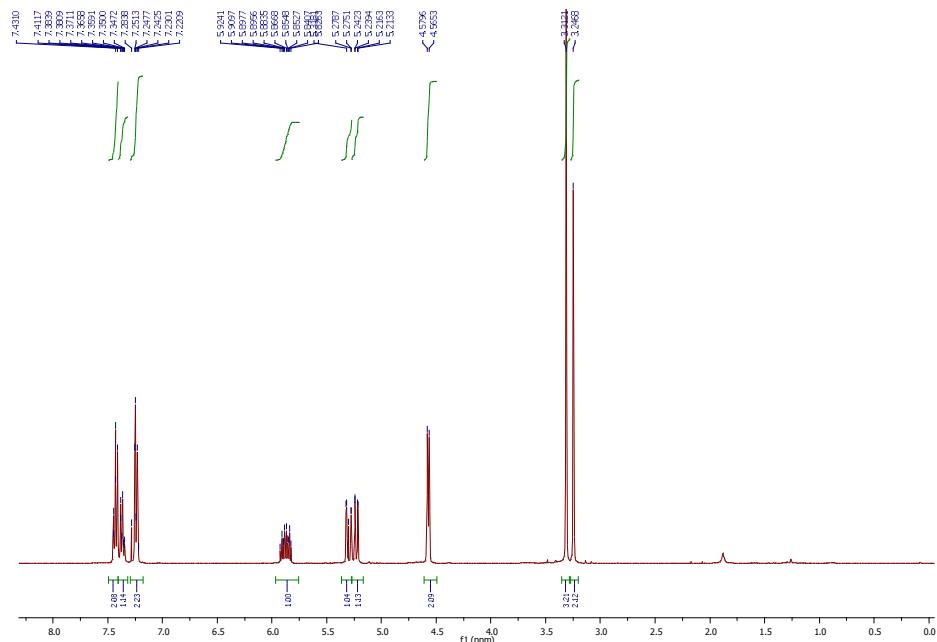
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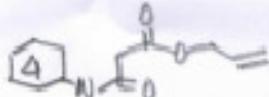
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(6a)





MS

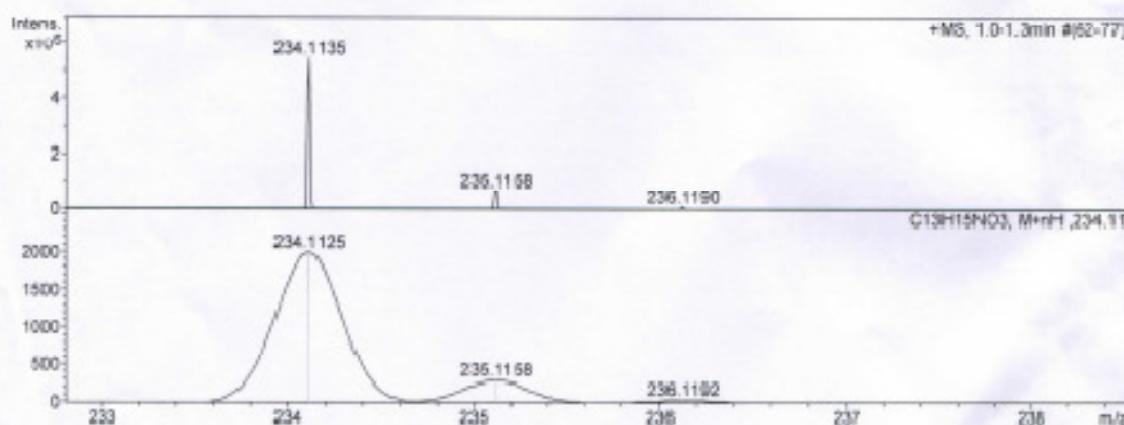
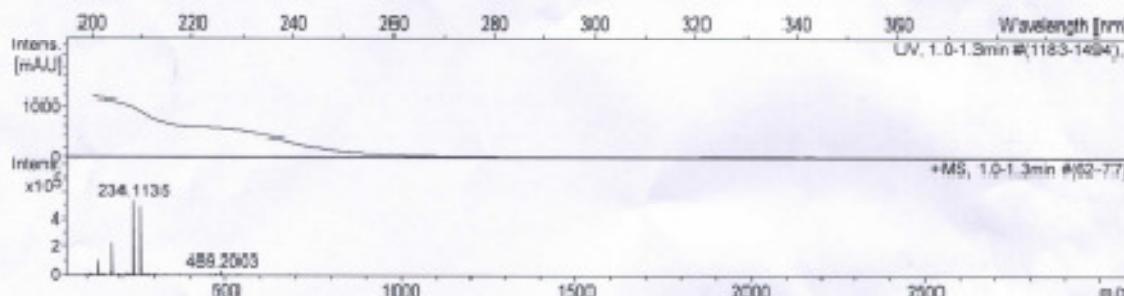
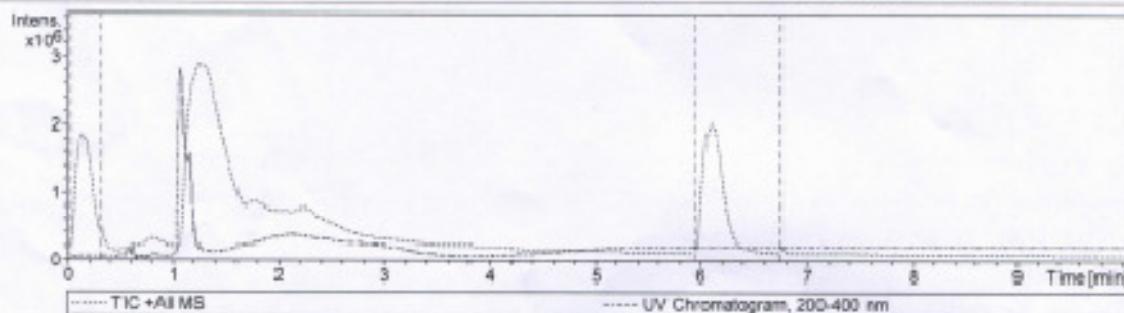
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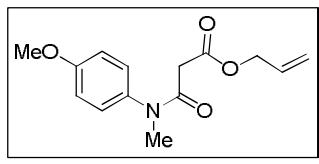
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Sample Name	Dr. A. Bisai- SG3-213	Instrument	microTOF-Q II 10330
Comment			

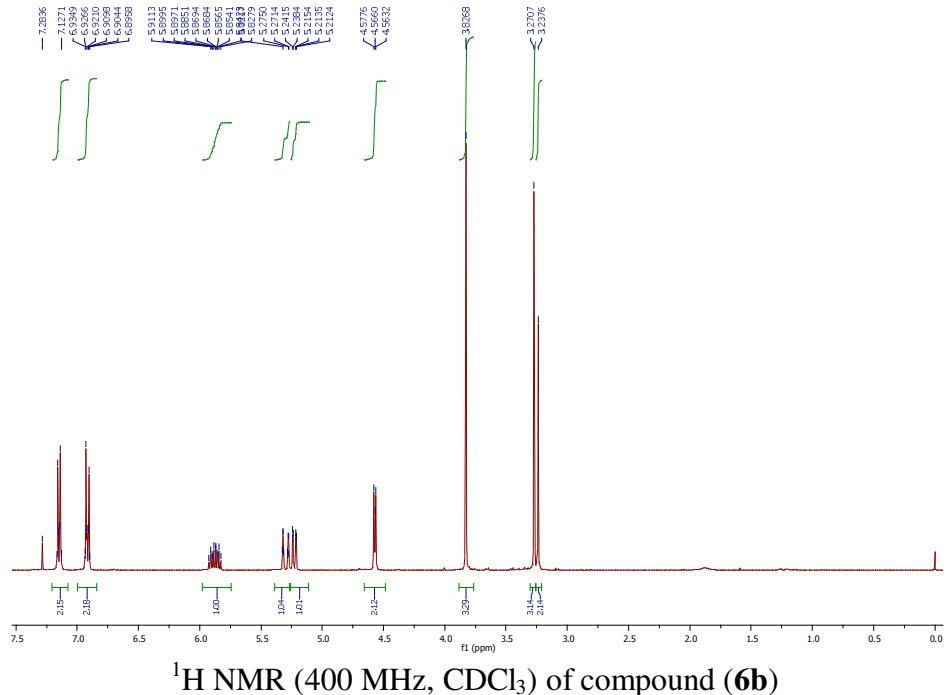
Acquisition Parameter

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

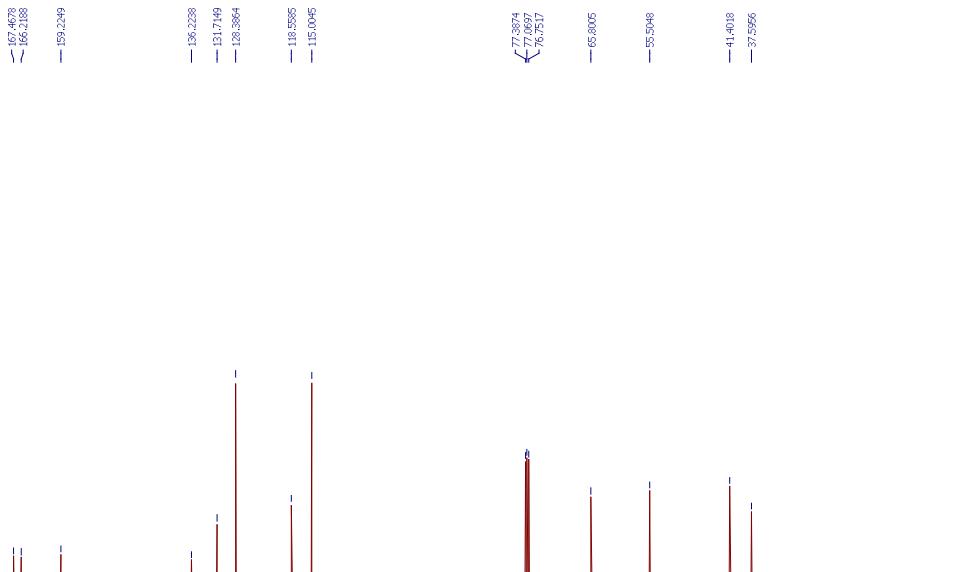




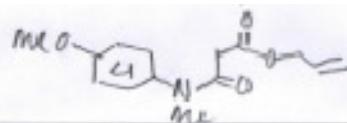
(6b)



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



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



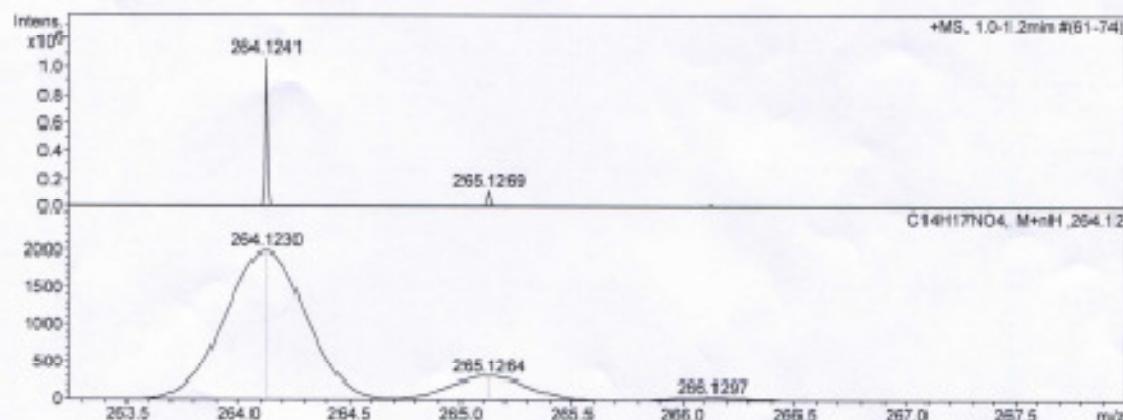
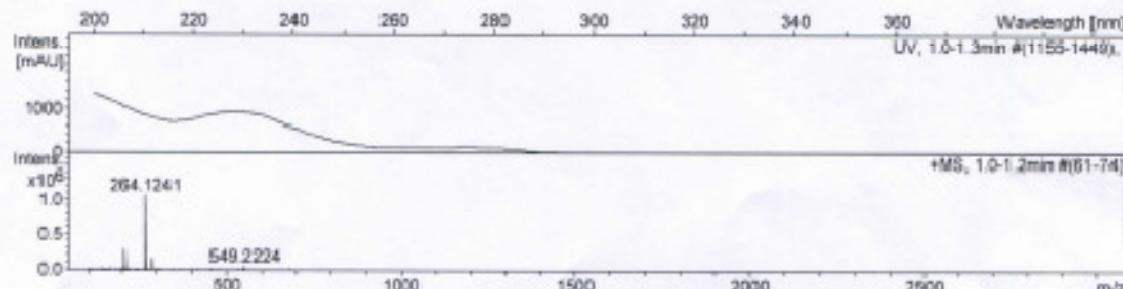
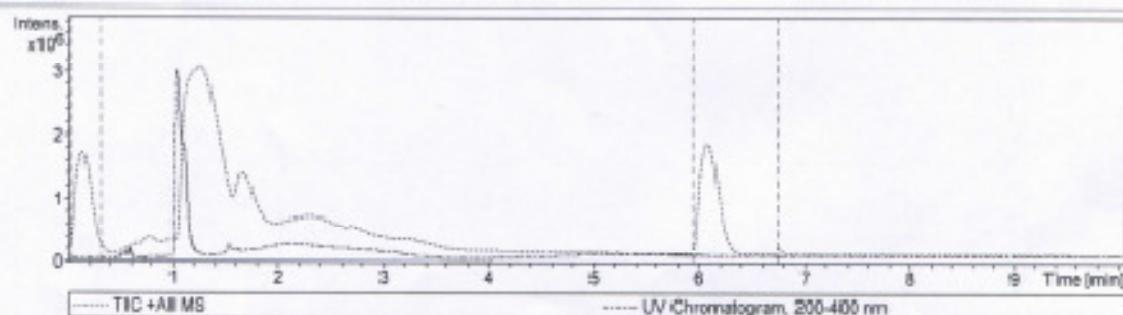
Display Report

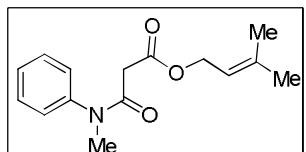
Analysis Info

Analysis Name: D:\Data\user data\April 2012\17 apr\Dr. A. Bisai- SG4-49_1-A,B_01_1816.d Acquisition Date: 4/17/2012 2:59:36 PM
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 Sample Name: Dr. A. Bisai- SG4-49 Instrument: microTOF-Q II 10330
 Comment:

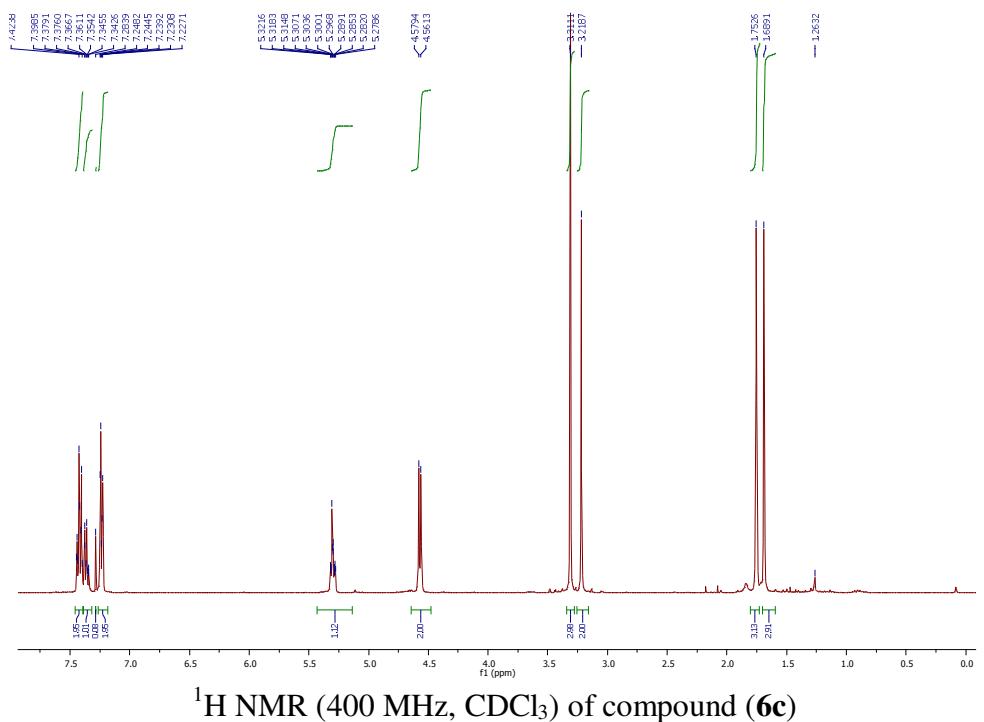
Acquisition Parameter

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

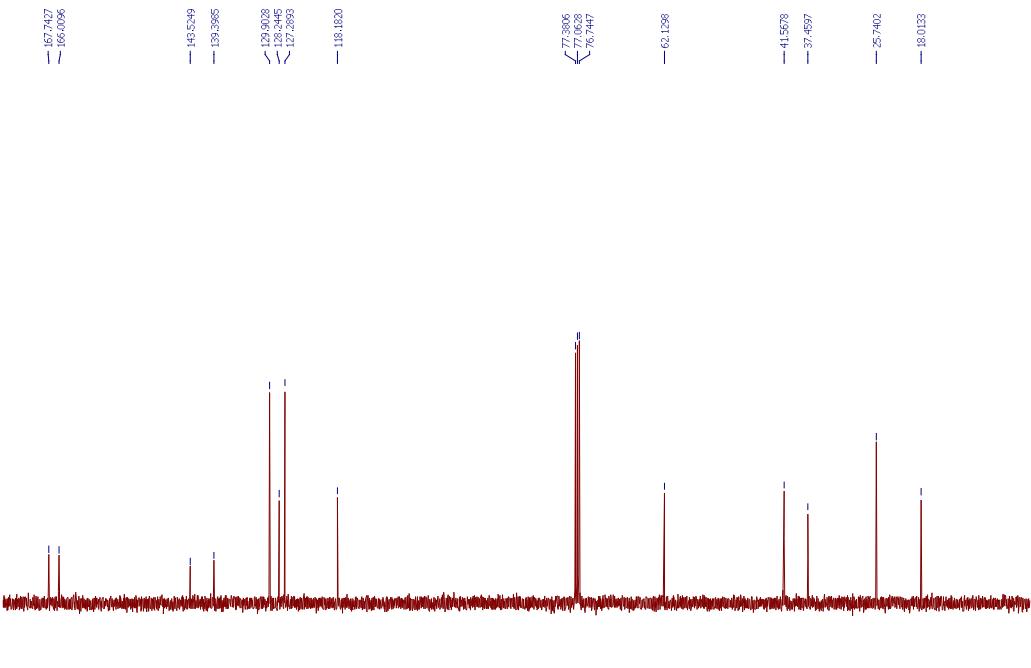




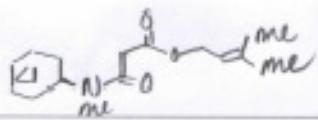
(6c)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**6c**)



Display Report

Analysis Info

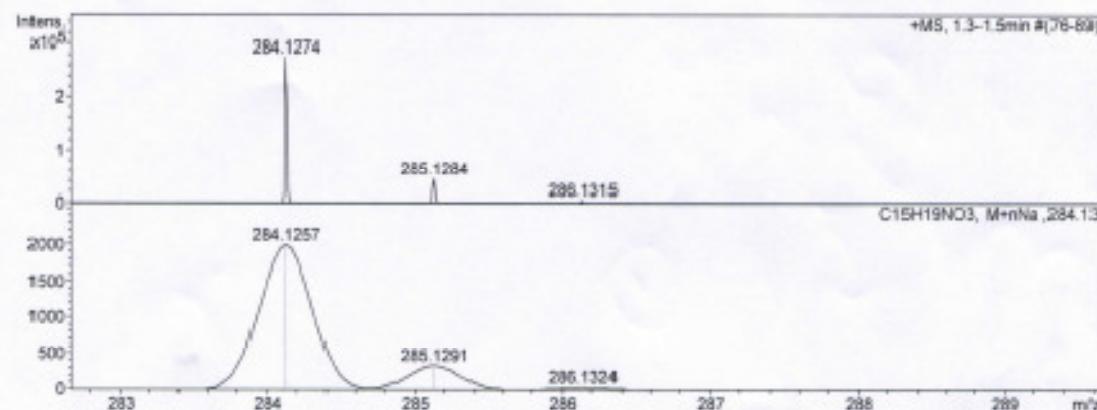
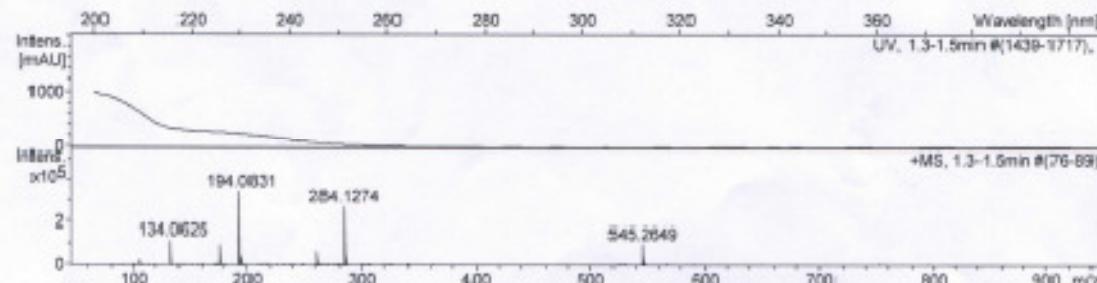
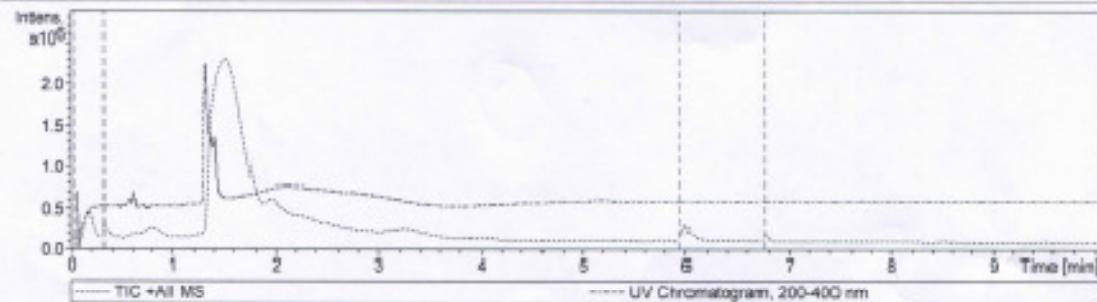
Analysis Name D:\Data\user data\April 2012\17 apr\Dr. A. Bisai- SG3-214_1-A_4_01_1810.d
 Method HRLCMS-20 Sept.mn
 Sample Name Dr. A. Bisai- SG3-214
 Comment

Acquisition Date 4/17/2012 1:10:59 PM

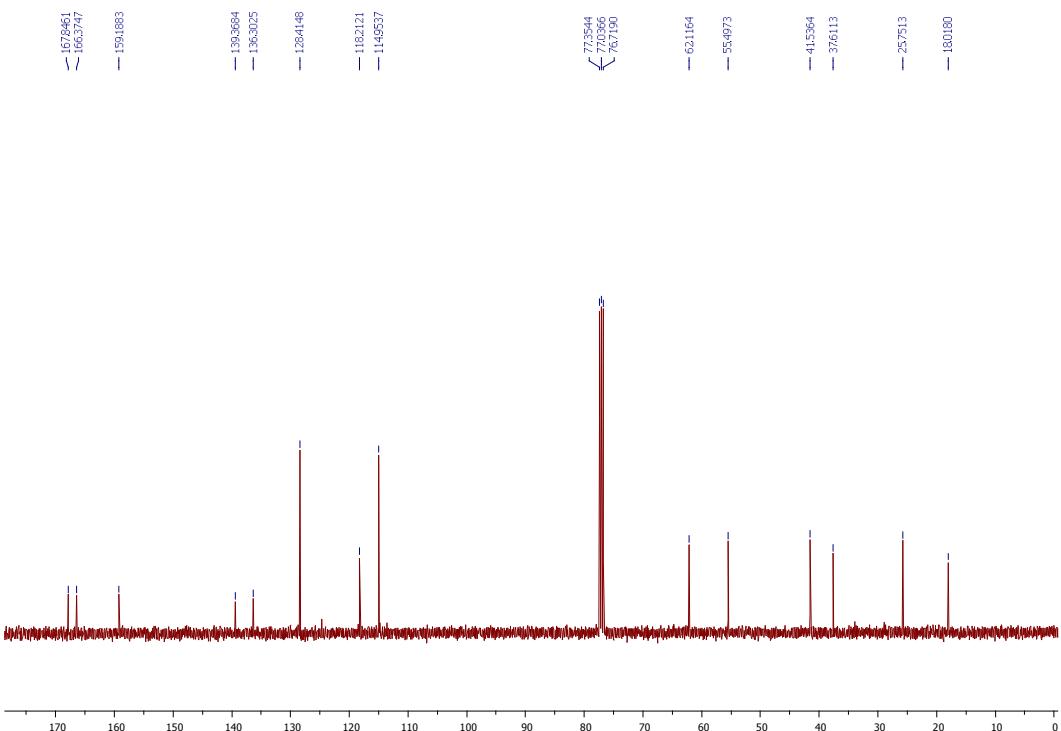
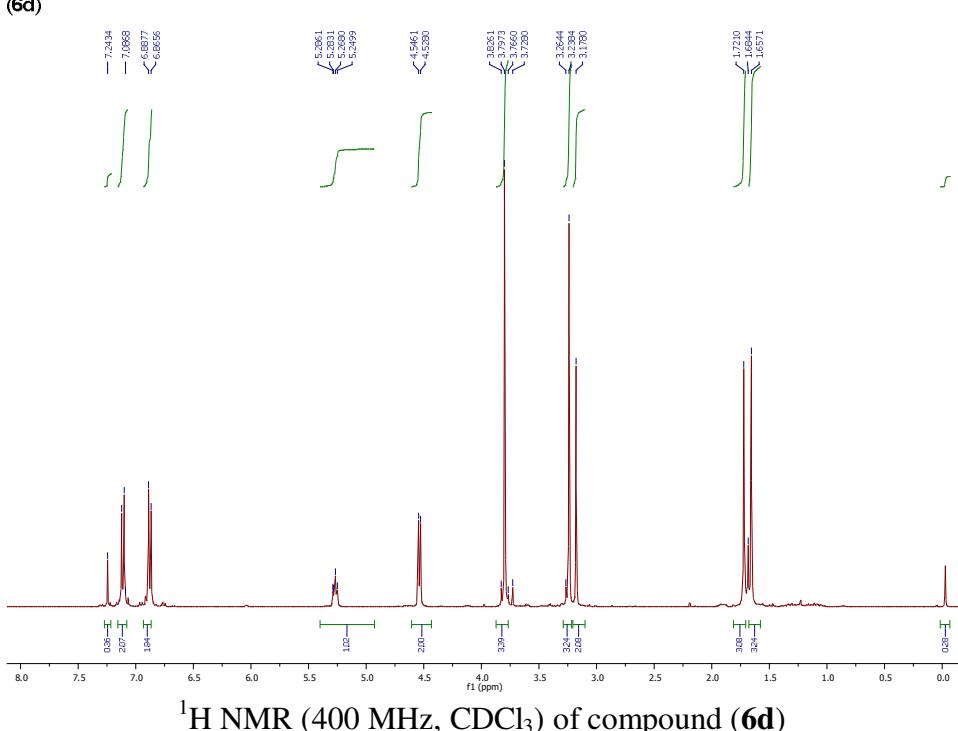
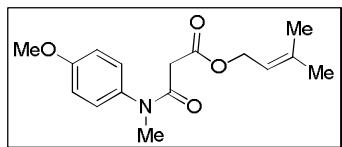
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

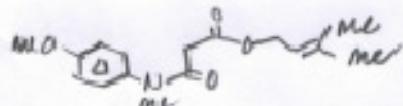
Acquisition Parameter

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



Scanned copy of mass spectrum of compound 6c





Display Report

Analysis Info

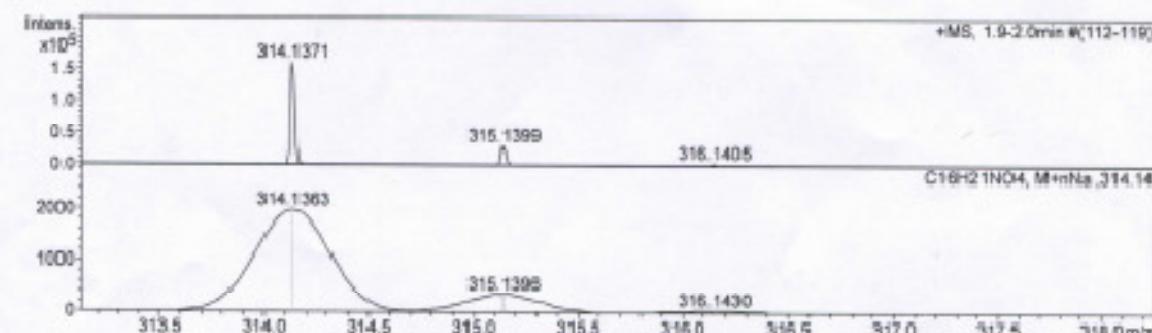
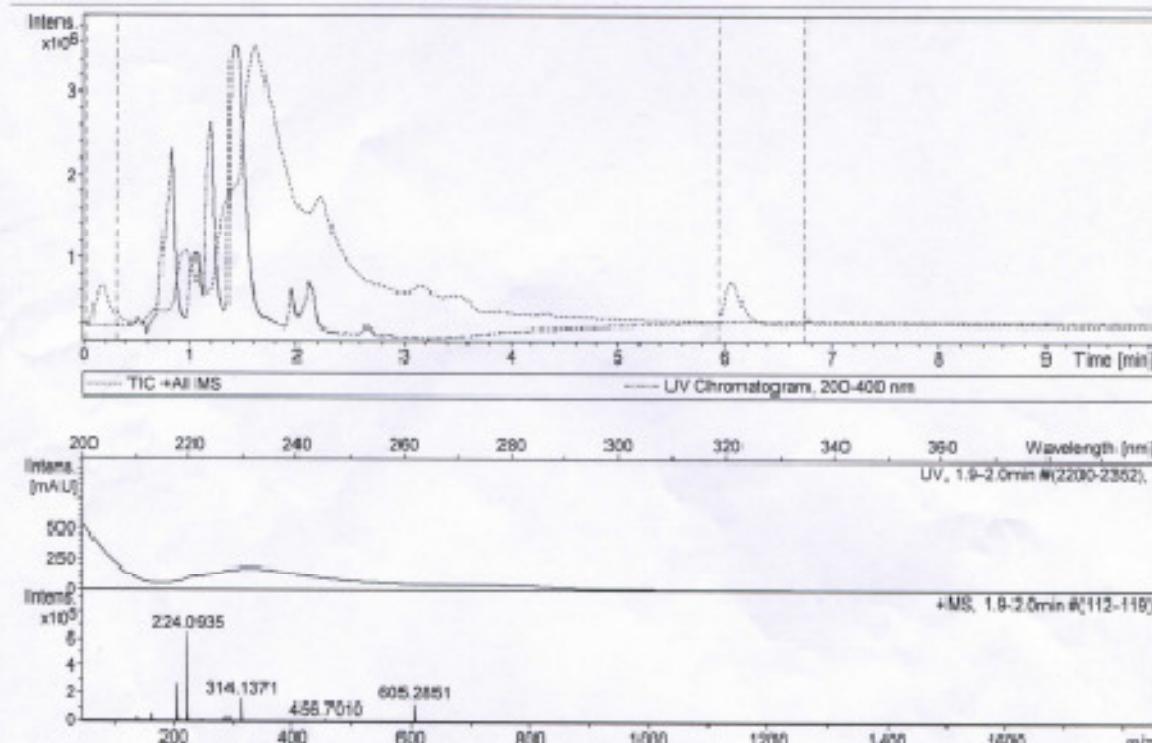
Analysis Name: D:\Data\user data\DEC 17\Dr. A. Bisal- SG3-329_1-A.6_01_587.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisal- SG3-329
 Comment:

Acquisition Date: 12/17/2011 3:05:24 PM

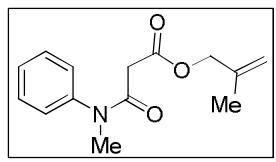
 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

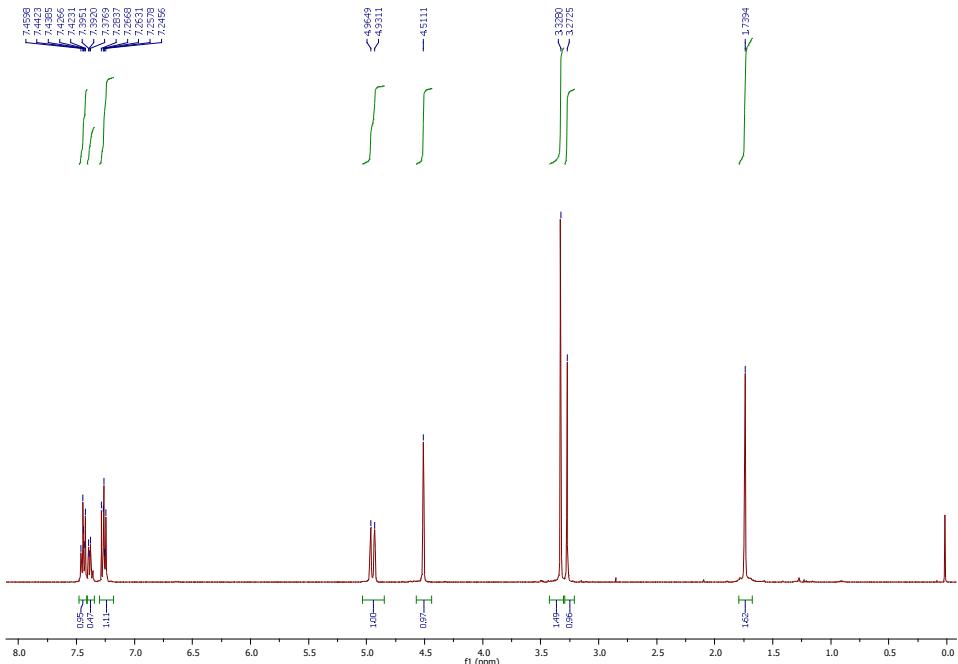
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °G
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



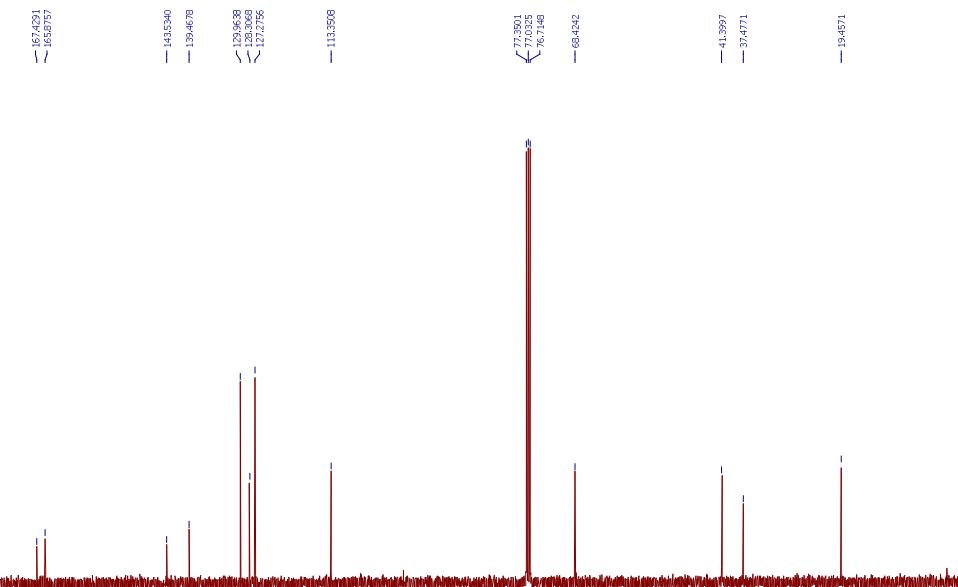
Scanned copy of mass spectrum of compound **6d**



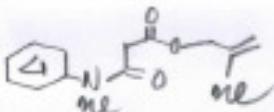
(6e)



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



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



Display Report

Analysis Info

Analysis Name: D:\Data\user data\April 2012\17_april\Dr. A. Bisal- AB-SG4-15_1-A,3_01_1807.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisal- AB-SG4-15
 Comment:

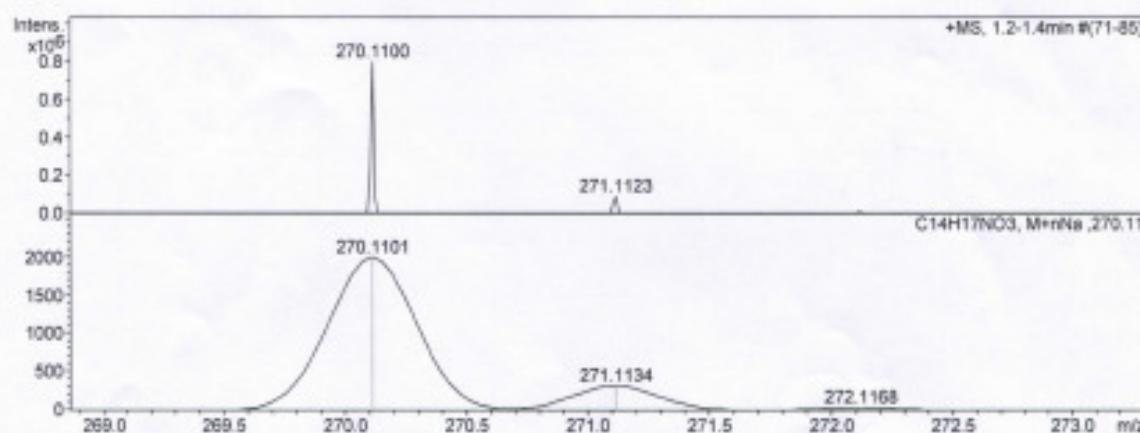
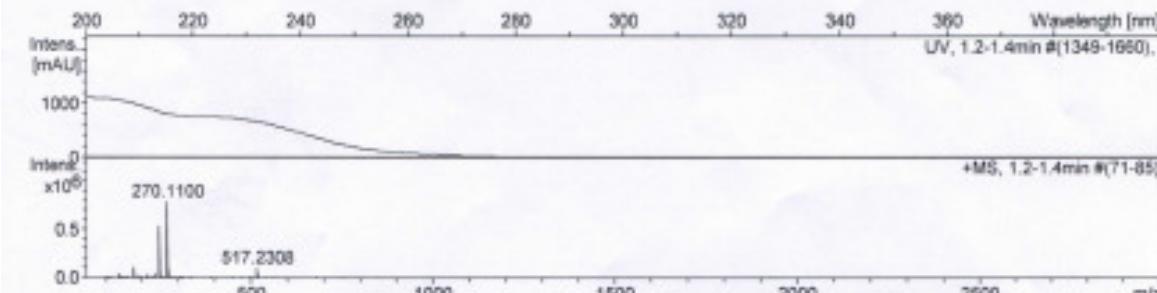
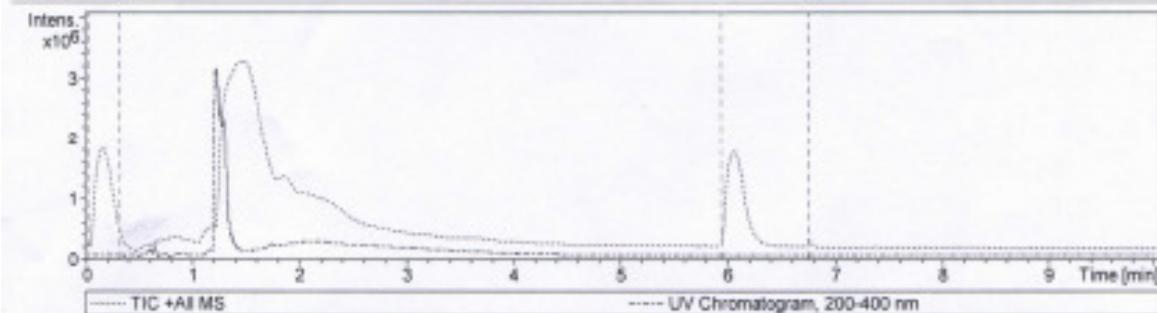
Acquisition Date: 4/17/2012 12:12:06 PM

Operator: Meena Sharma

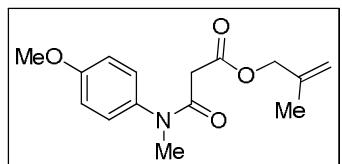
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

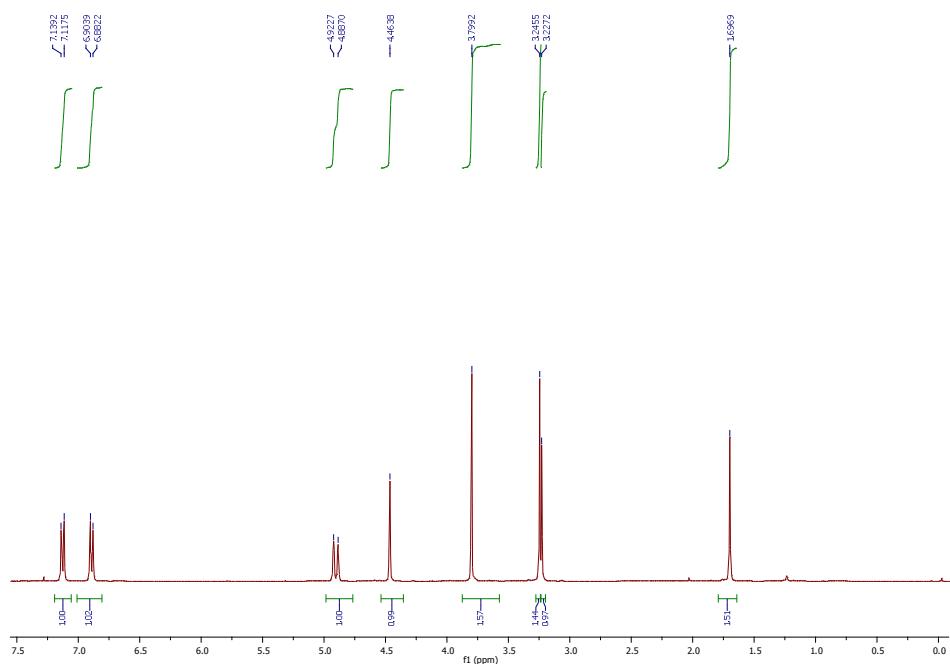
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of compound **6e**

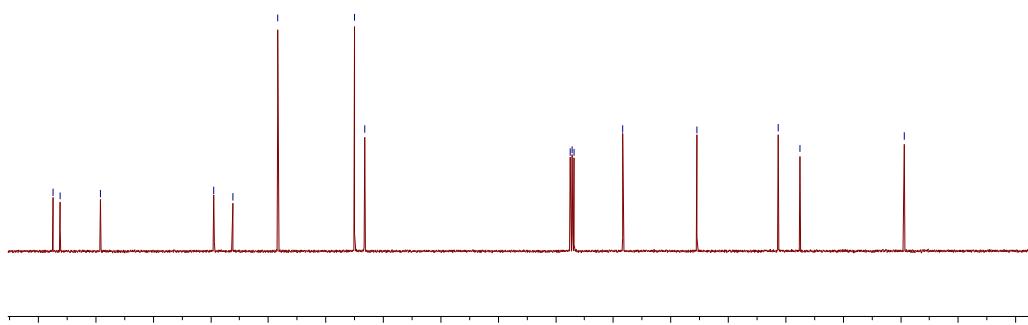


(6f)

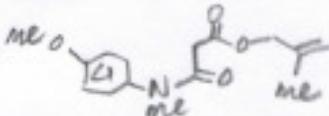


^1H NMR (400 MHz, CDCl_3) of compound (6f)

— 167.059
— 166.257
— 159.2070
— 159.4952
— 156.4141
— 128.5559
— 114.9920
— 113.2753
— 77.4560
— 77.1575
— 76.8190
— 68.3296
— 55.4751
— 41.3200
— 37.5055
— 19.4132



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



Display Report

Analysis Info

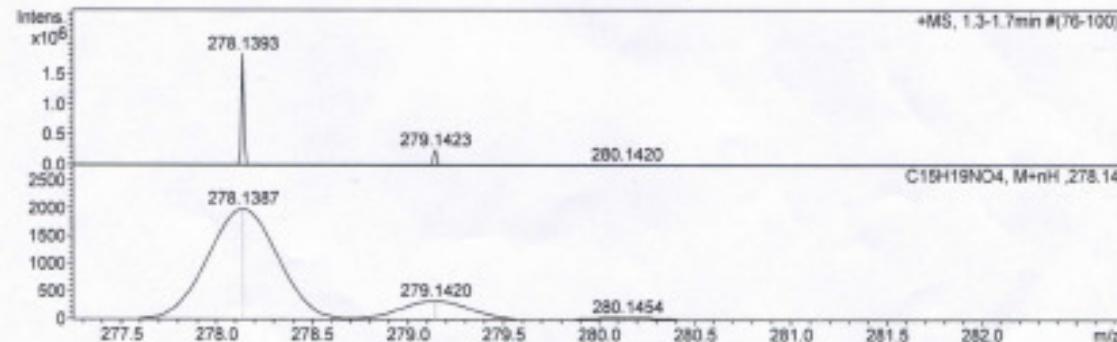
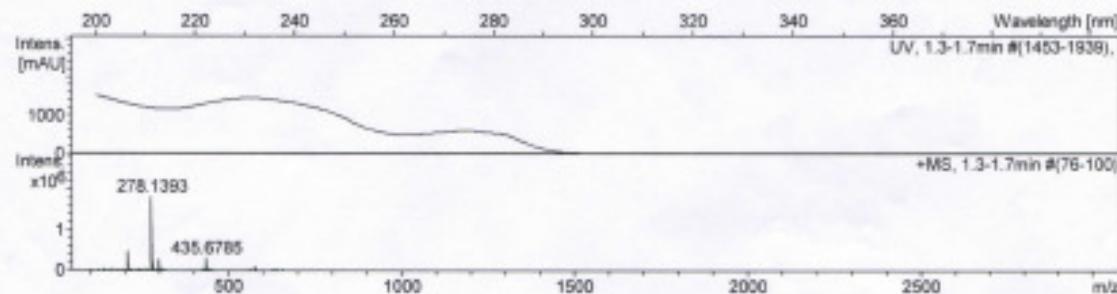
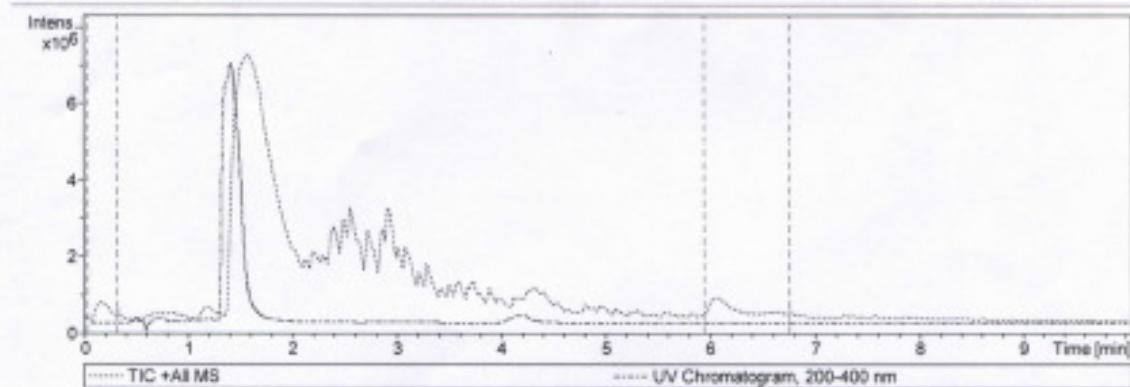
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-SG4-20
 Comment:

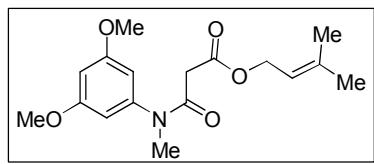
Acquisition Date: 1/6/2012 4:30:58 PM

 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

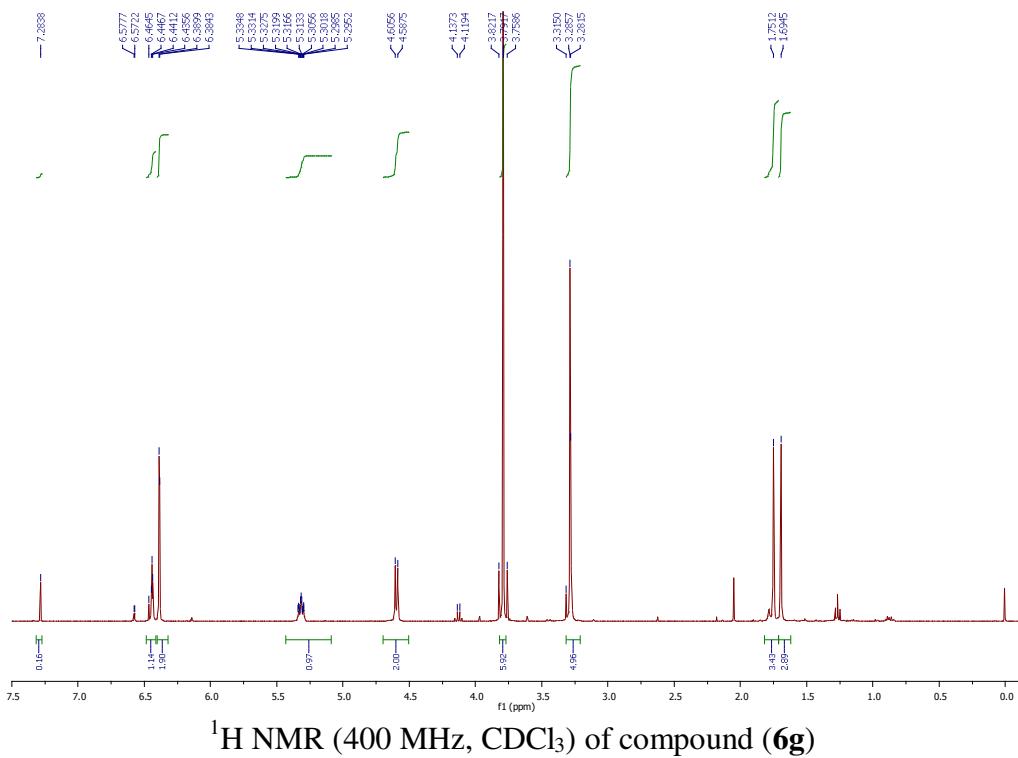
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

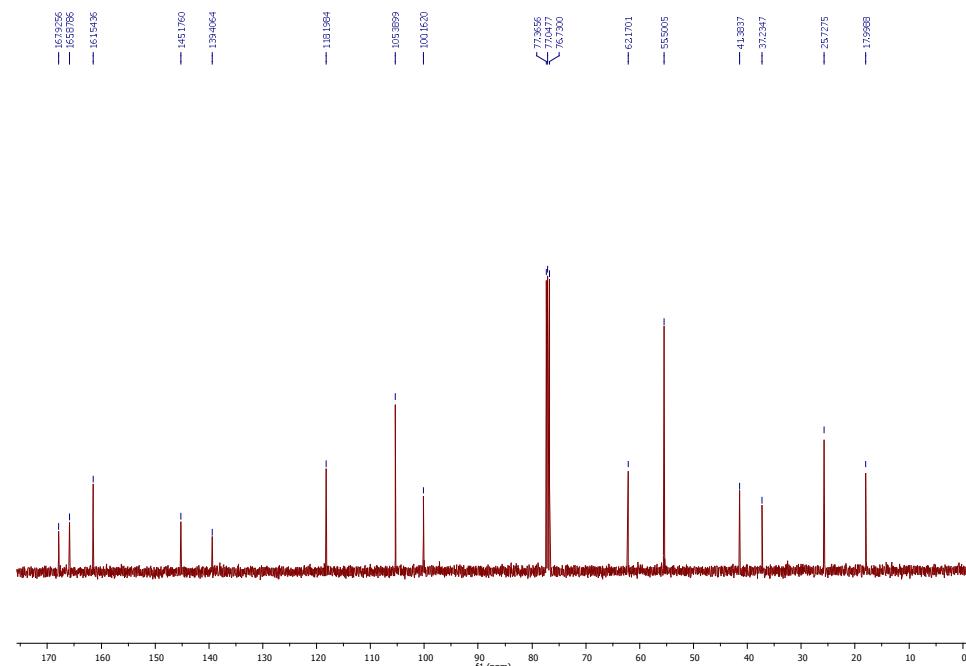




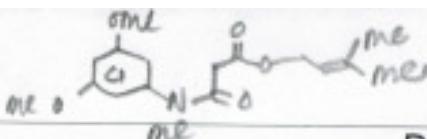
(6g)



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



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



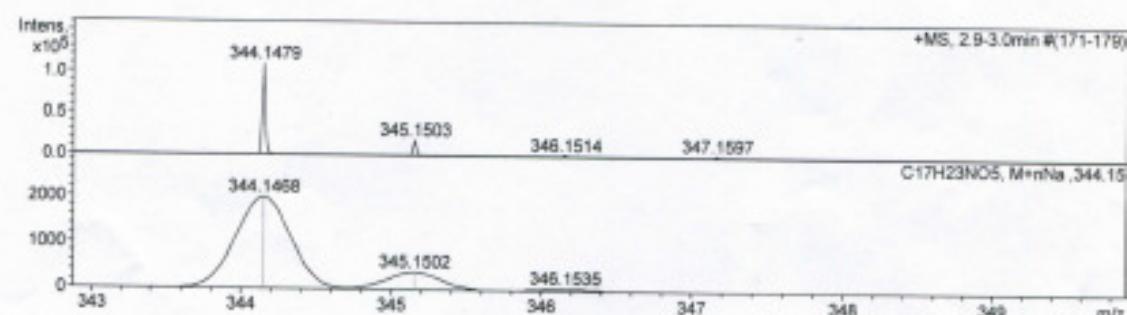
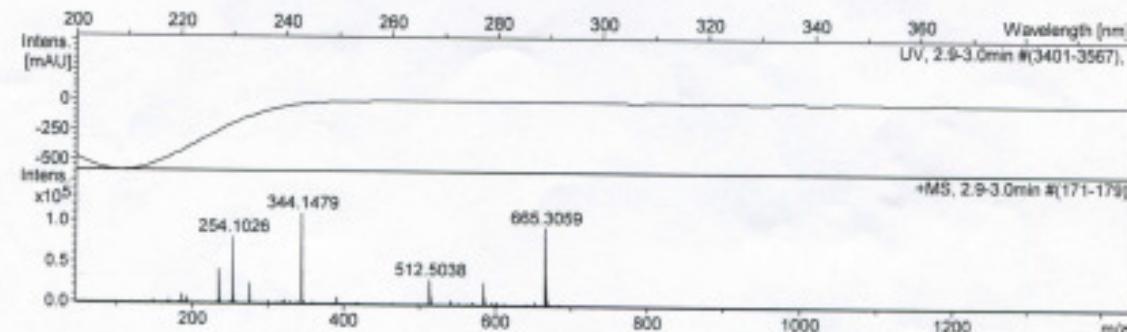
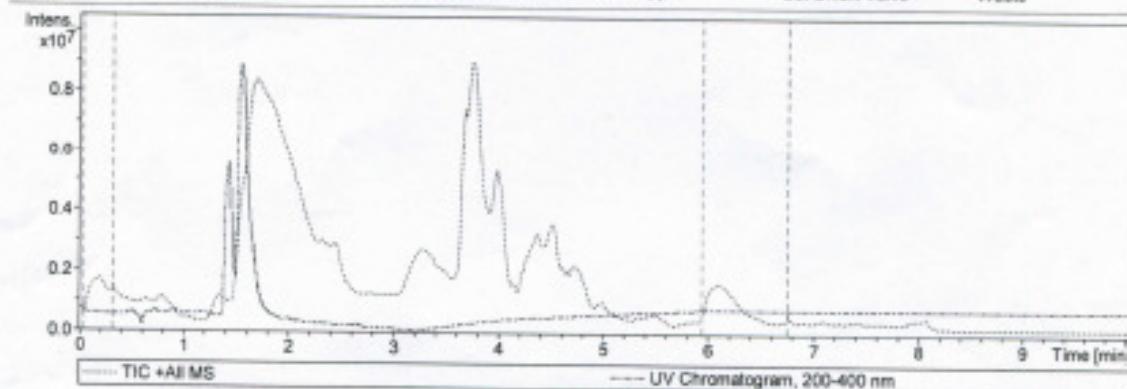
Display Report

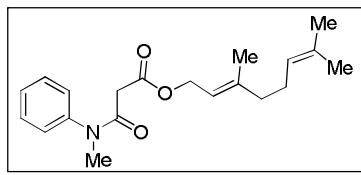
Analysis Info

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Method	HRLCMS-20 Sept.m	Operator	Meena Sharma
Sample Name	Dr. A. Bisal-SG3-278	Instrument	micrOTOF-Q II 10330
Comment			

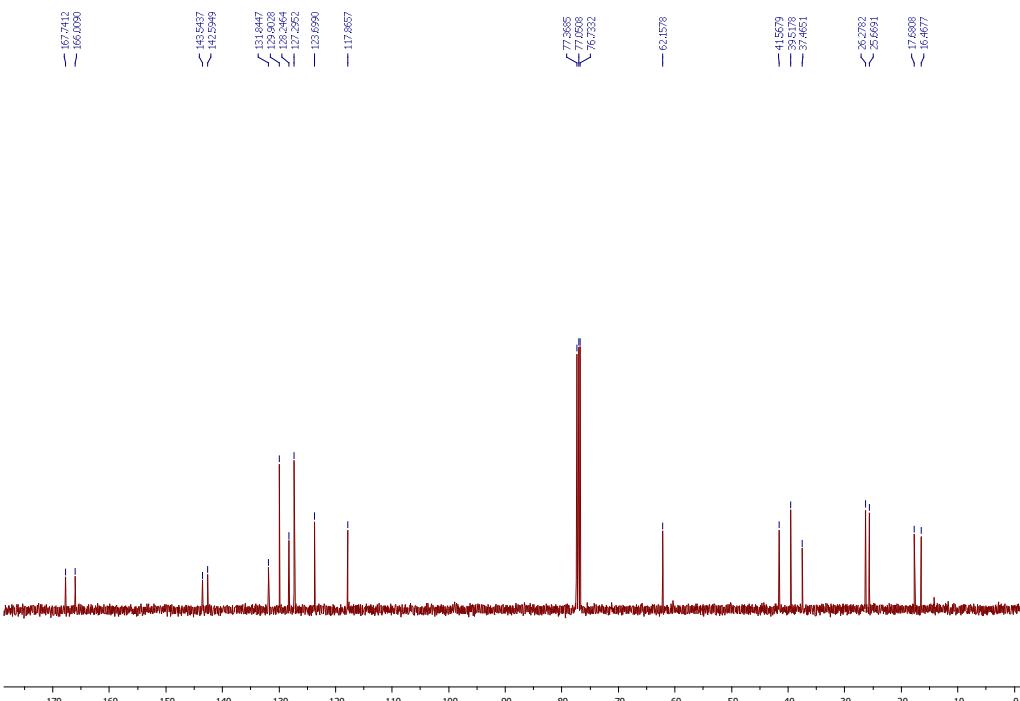
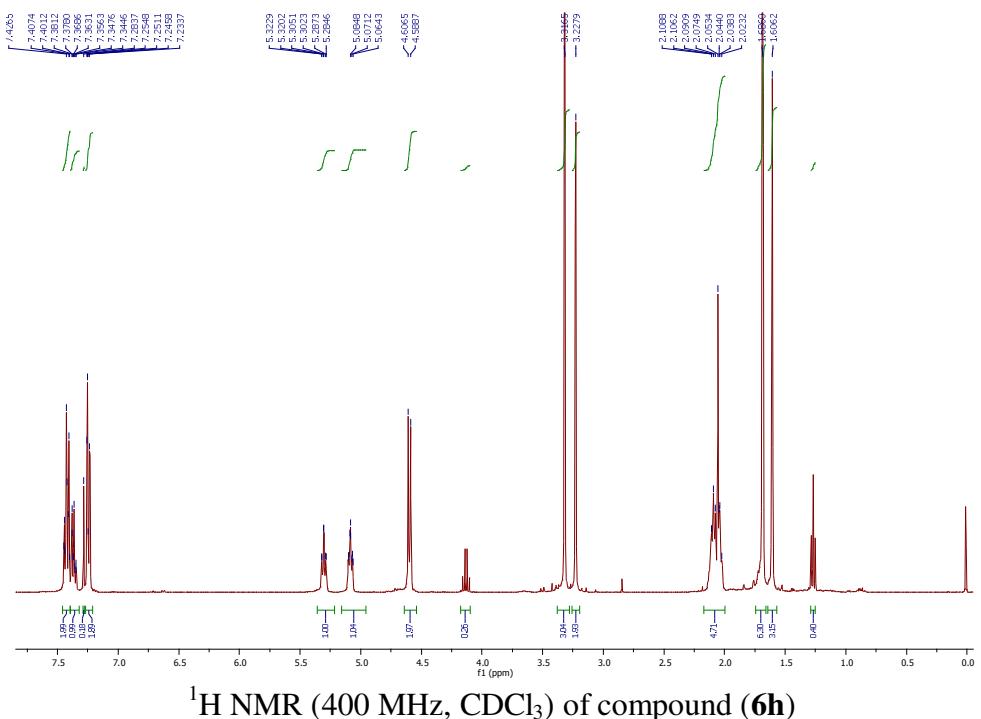
Acquisition Parameter

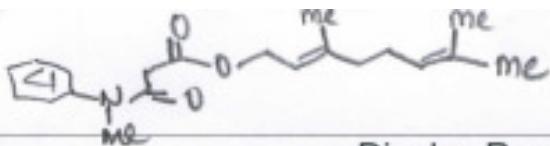
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
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 Scanned copy of mass spectrum of compound **6g**



(6h)





Display Report

Analysis Info

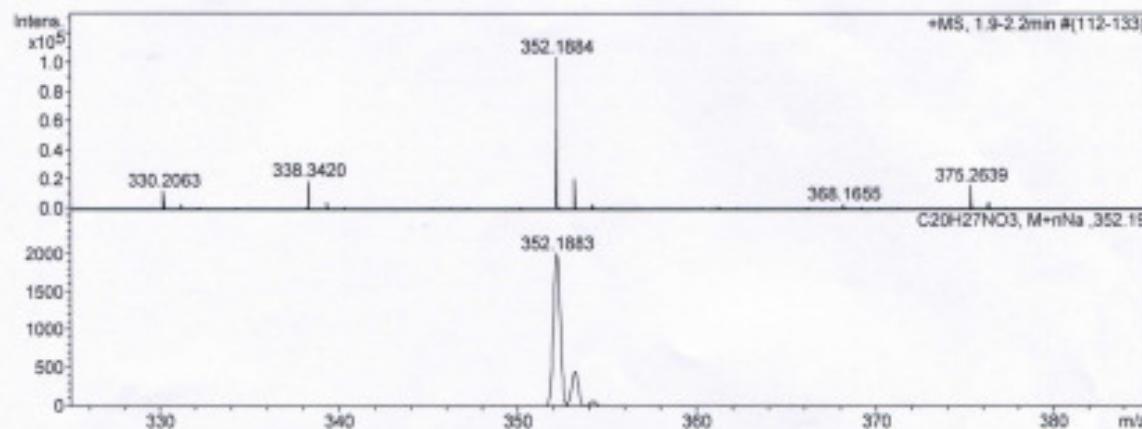
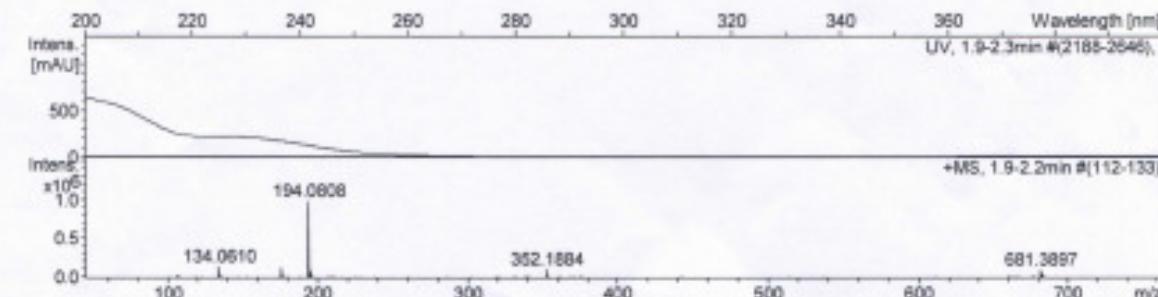
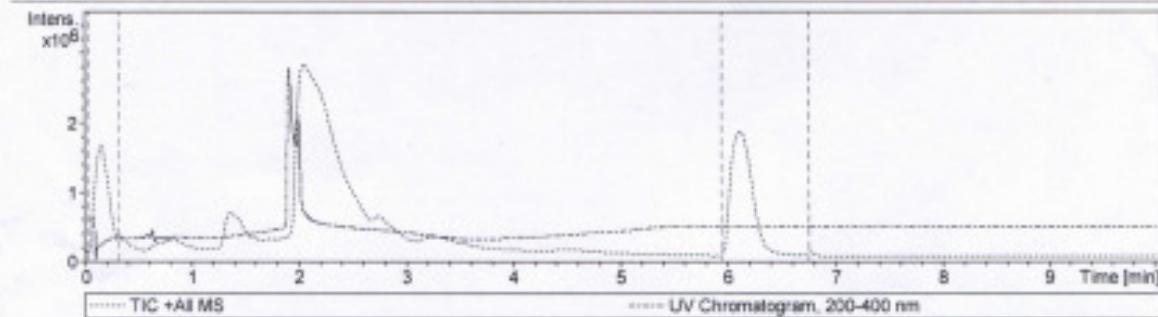
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG4-60
 Comment:

Acquisition Date: 4/25/2012 4:09:09 PM

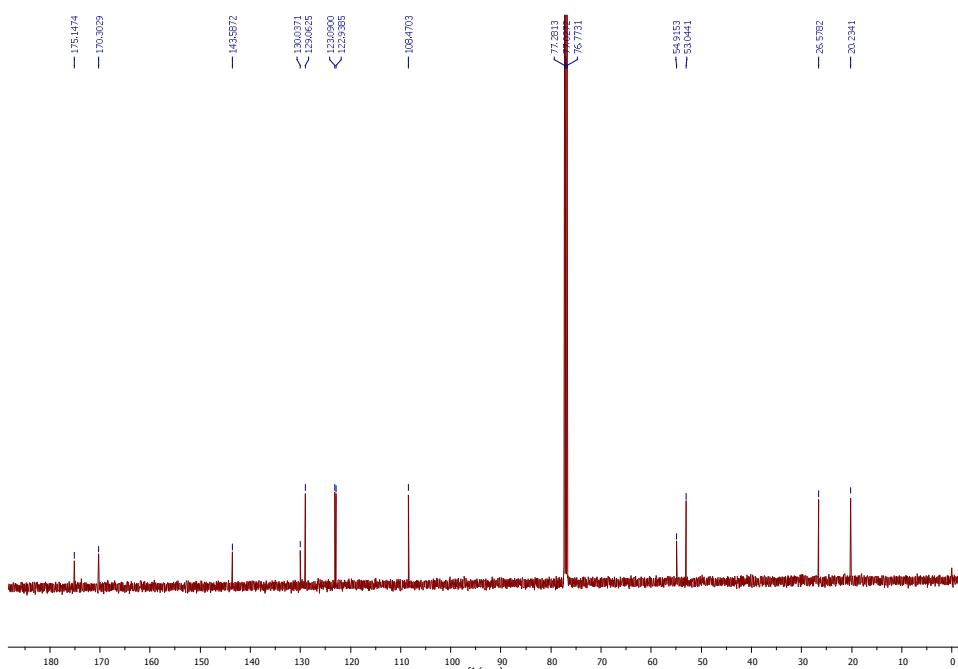
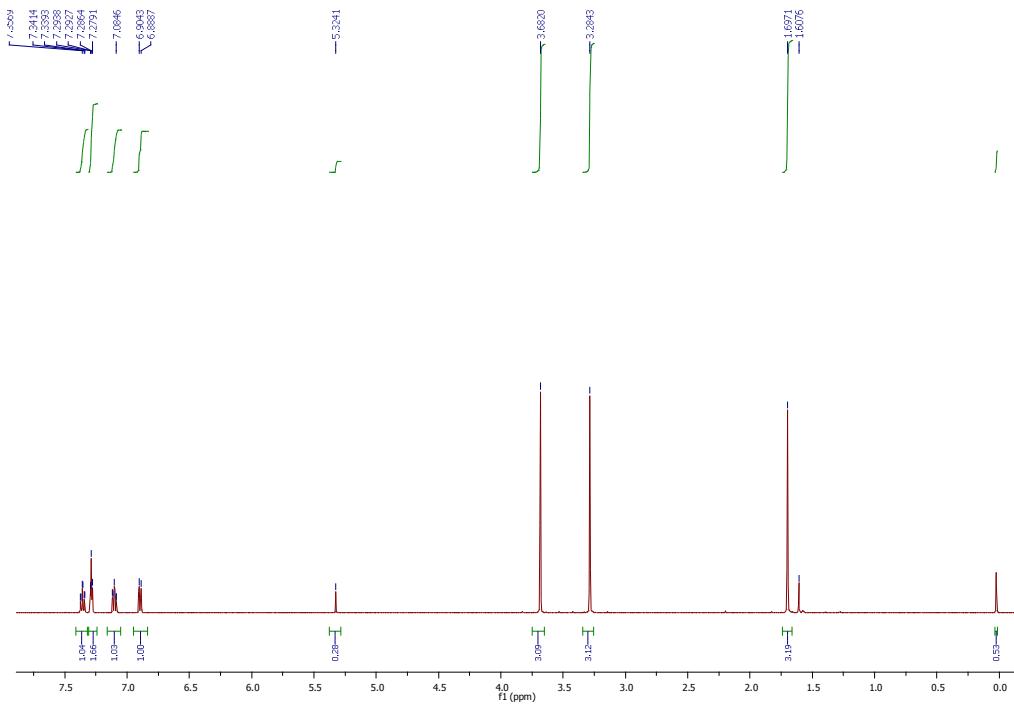
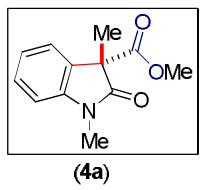
Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

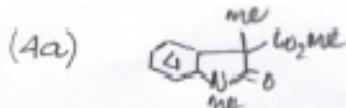
Acquisition Parameter

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



Scanned copy of mass spectrum of compound 6h





Display Report

Analysis Info

Analysis Name: D:\Data\user data\April 2012\10_apr\Dr. A. Bisal- SG4-335_1-A,5_01_1715.d
 Method: HIRLCMS-2D Sept.m
 Sample Name: Dr. A. Bisal- SG4-335
 Comment:

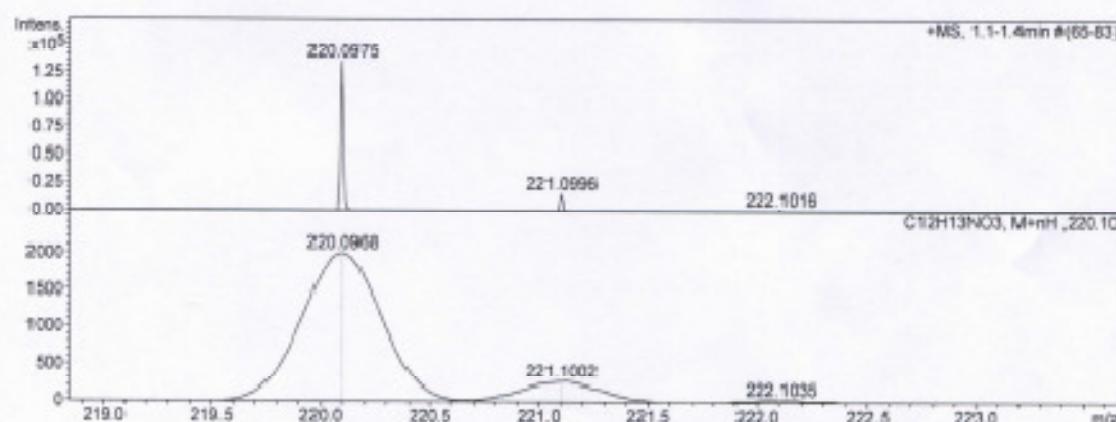
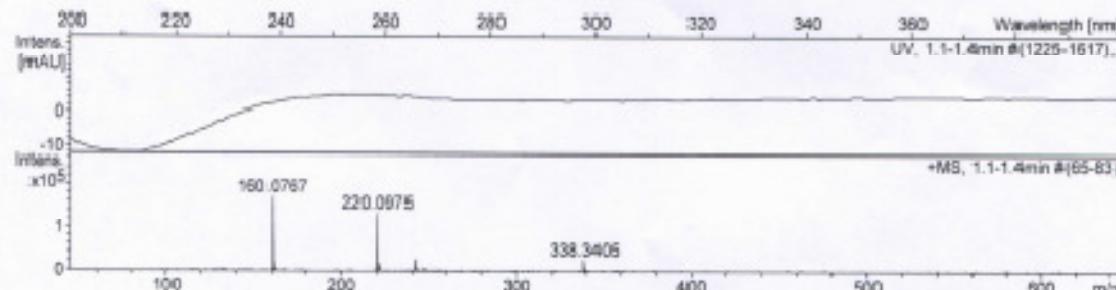
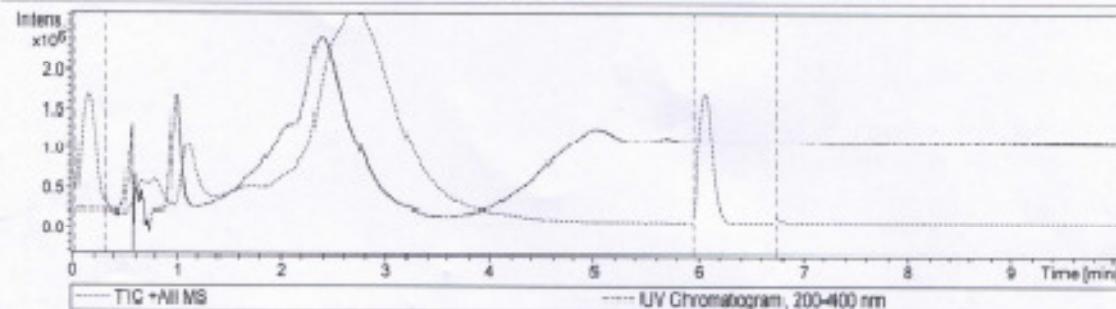
Acquisition Date: 4/10/2012 4:52:01 PM

Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

Acquisition Parameter

Source Type	EI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	300-0 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

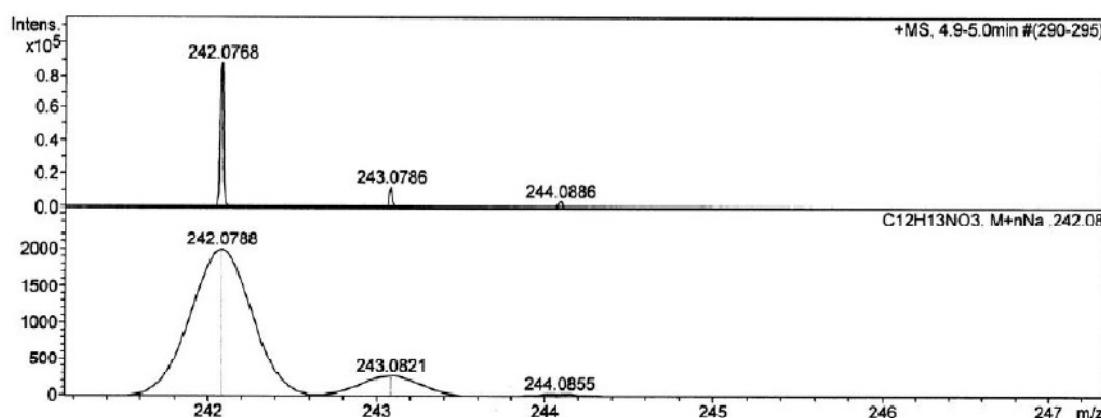
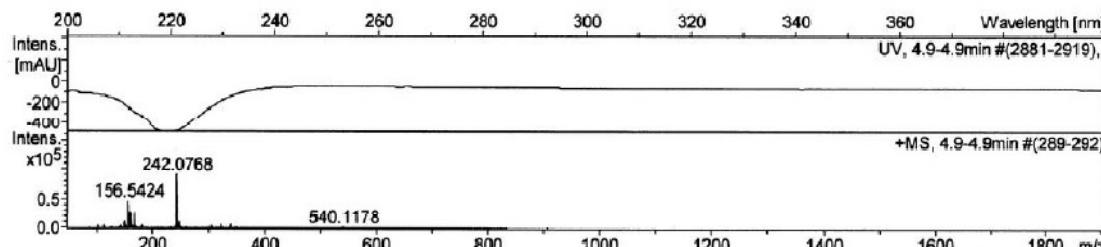
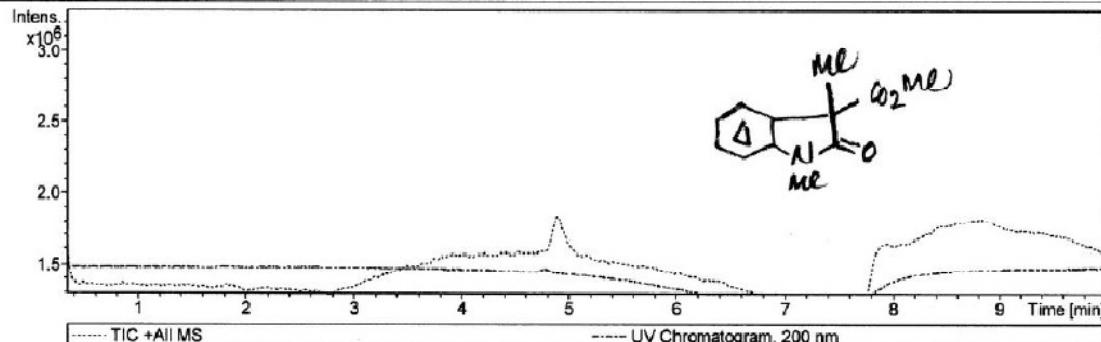


Display Report

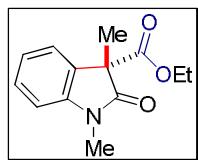
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Analysis Name	D:\Data\user data\OCT 2012\29 oct\Dr. A. Bisai- SG5-268_1-A,6_01_4267.d		
Method	HRLCMS-20 Sept.m	Operator	Meena Sharma
Sample Name	Dr. A. Bisai- SG5-268	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

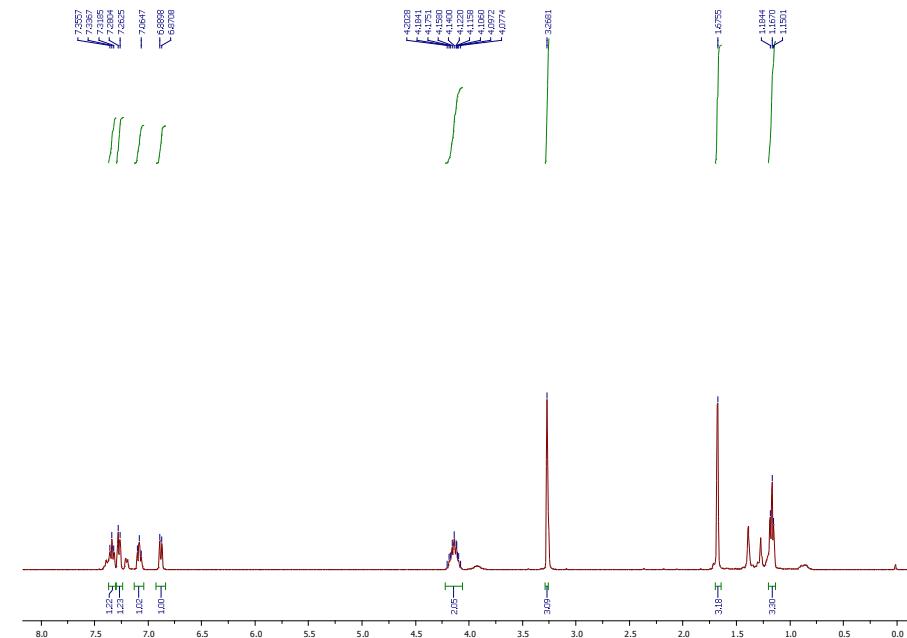


Scanned copy of mass spectrum of compound $\pm(4a)$



(4b)

73537
73567
73585
73604
73625
76647
63888
46778



^1H NMR(400 MHz, CDCl_3) of compound \pm (4b)

—175.221
—169.749

—145.643

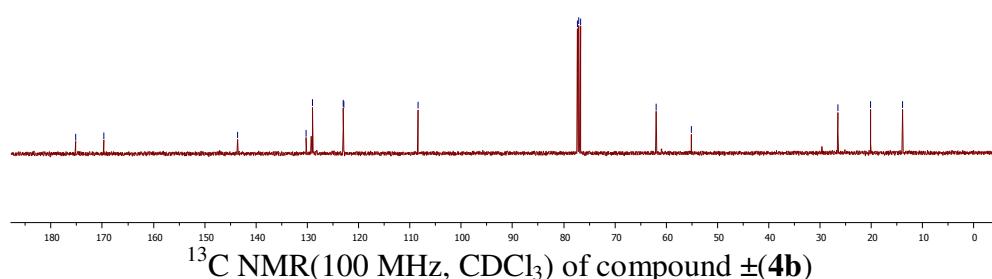
—130.239
—128.964
—122.976
—121.247

—108.404

—77.2543
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—61.9039
—55.0640

—26.5232
—20.1951
—13.8967



Display Report

Analysis Info

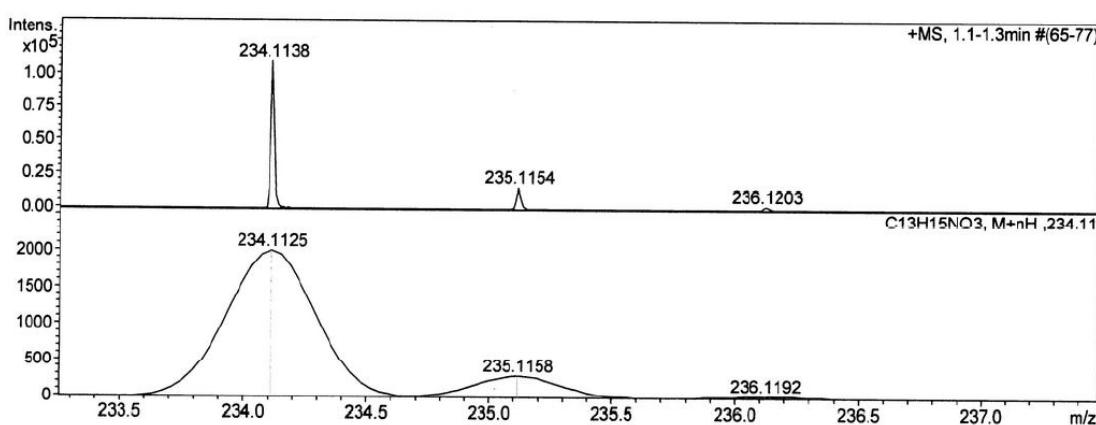
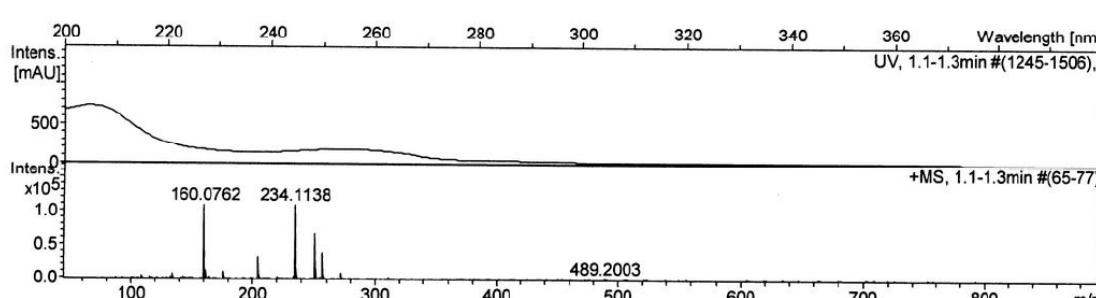
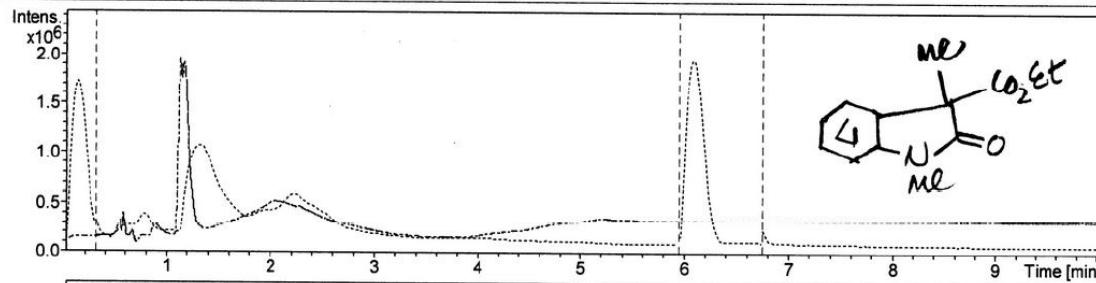
Analysis Name D:\Data\user data\April 2012\13 apr\Dr. A. Bisai- SG4-342_1-A,5_01_1761.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG4-342
 Comment

Acquisition Date 4/13/2012 1:16:05 PM

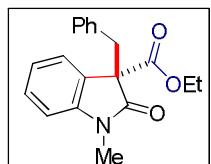
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

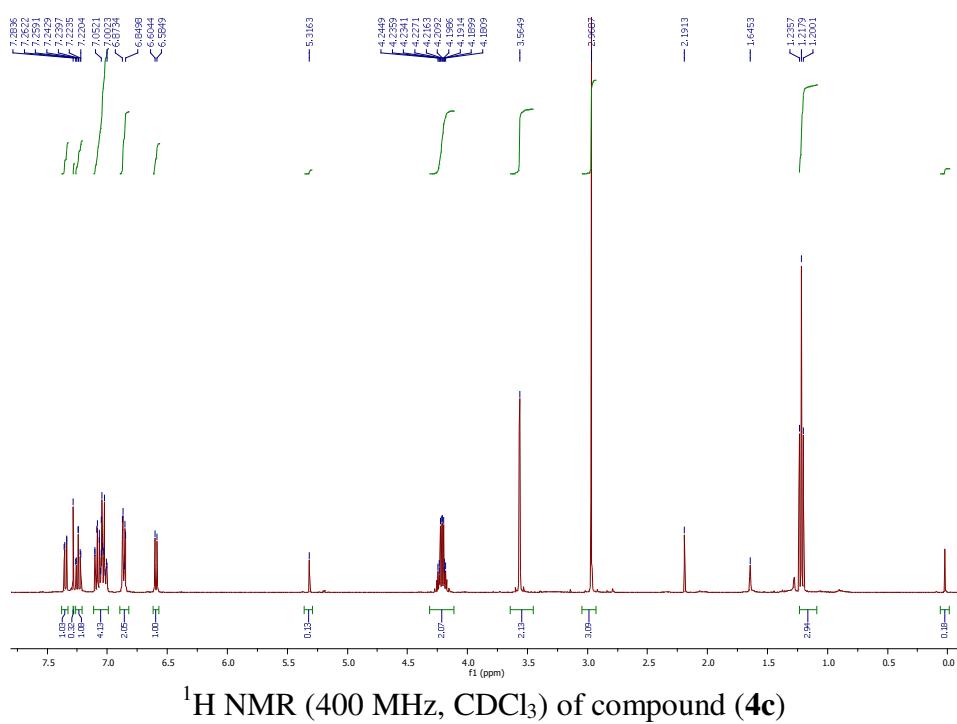
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



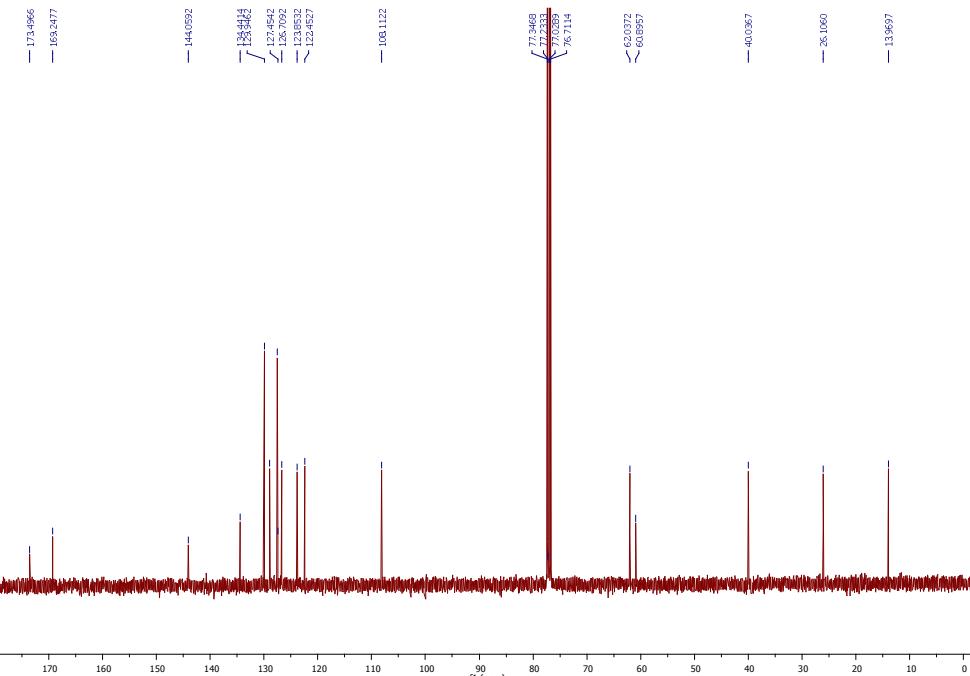
Scanned copy of mass spectrum of compound (\pm)-4b



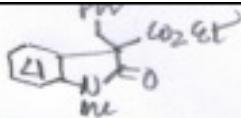
(4c)



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



^1H NMR (100 MHz, CDCl_3) of compound (4c)



Display Report

Analysis Info

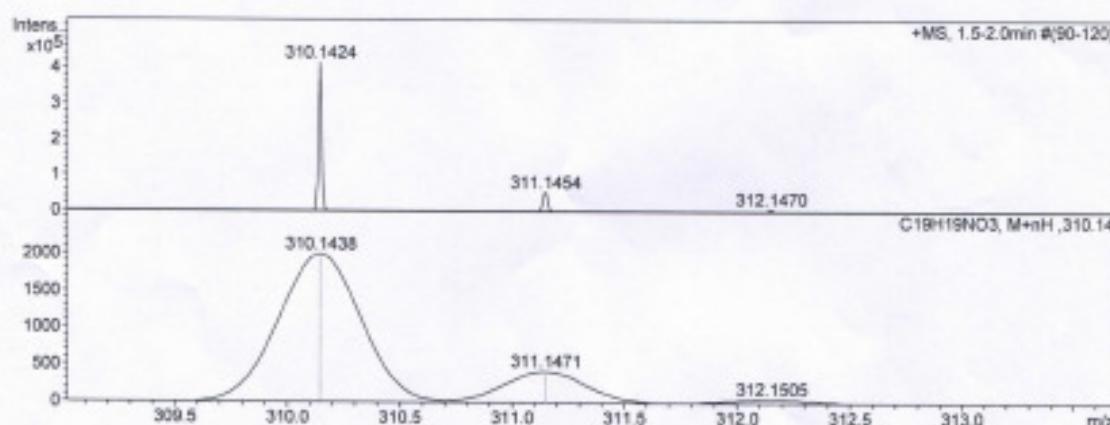
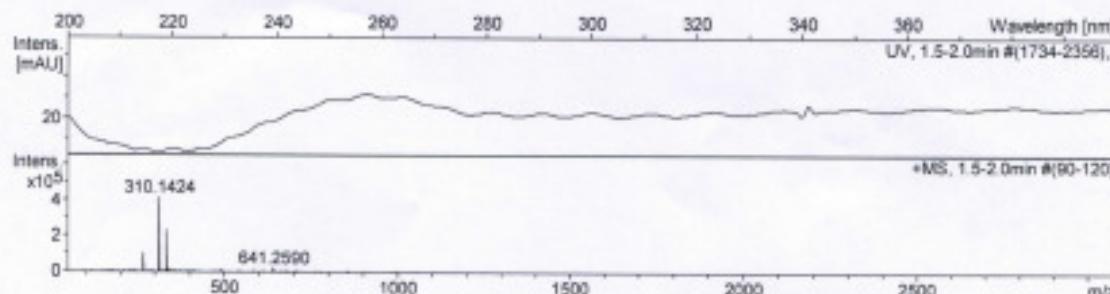
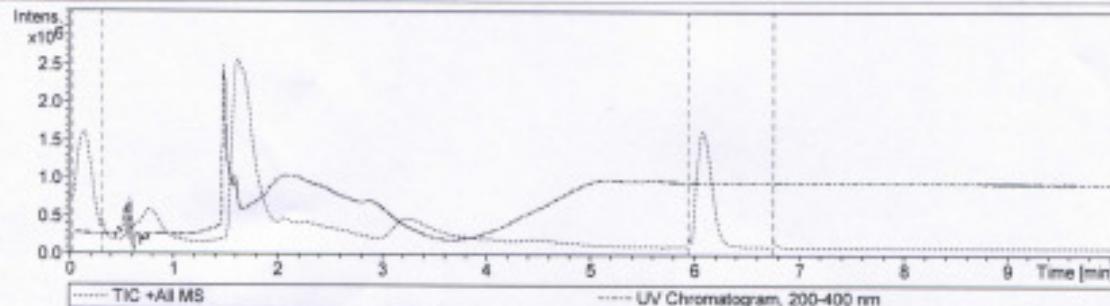
Analysis Name D:\Data\user data\April 2012\23 apr\Dr. A. Bisai- SG4-359_1-A_8_01_1861.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG4-359
 Comment

Acquisition Date 4/23/2012 1:22:42 PM

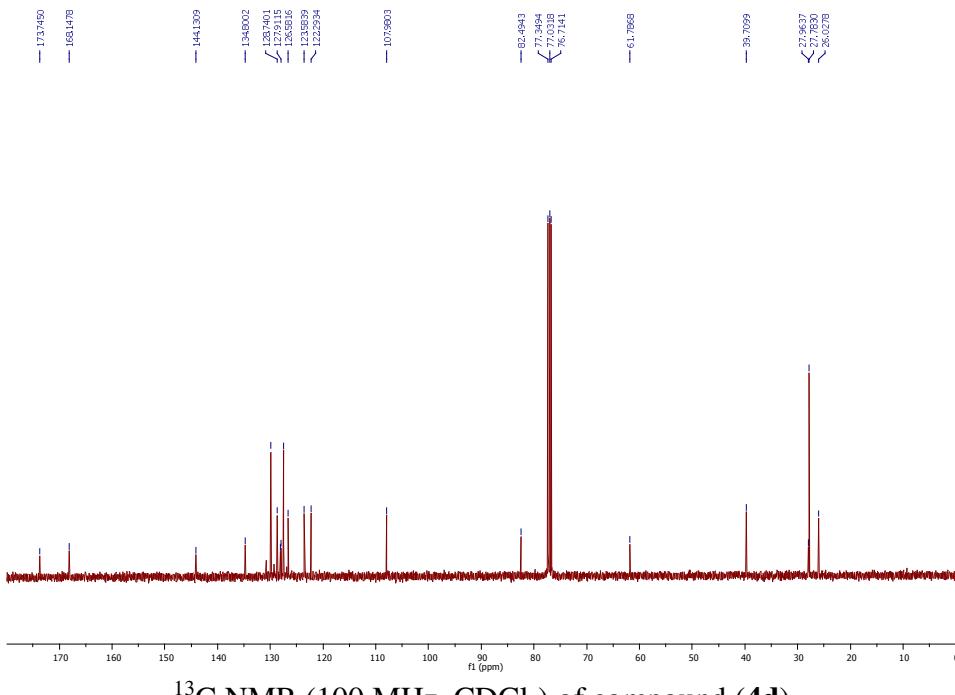
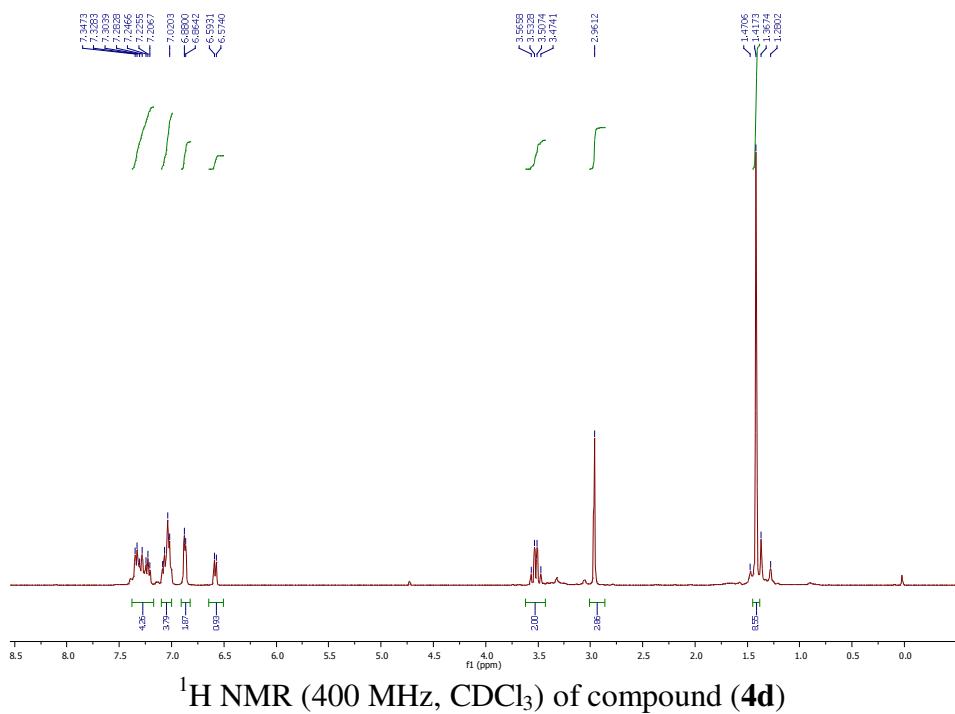
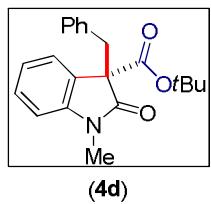
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

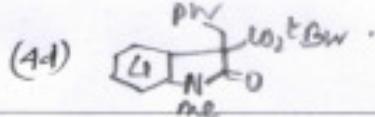
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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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 compound (\pm)-4c





Display Report

Analysis Info

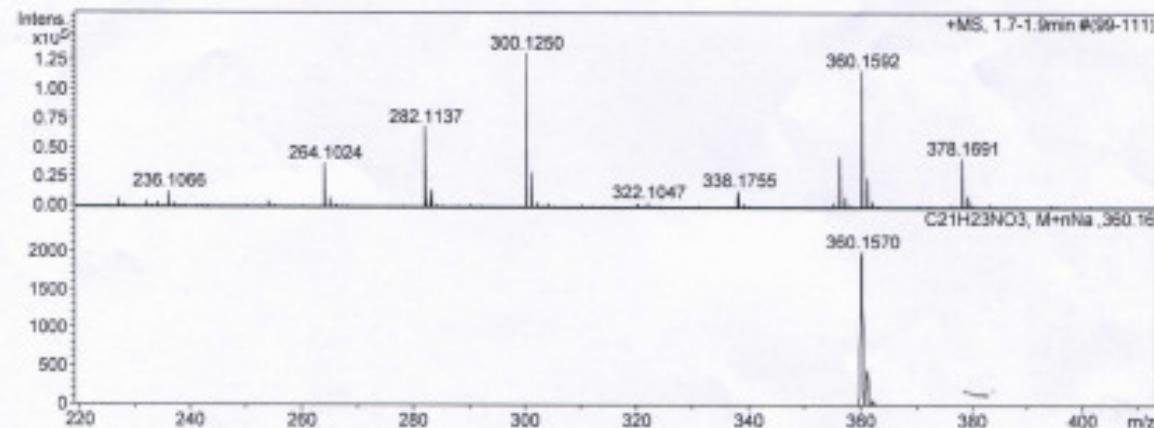
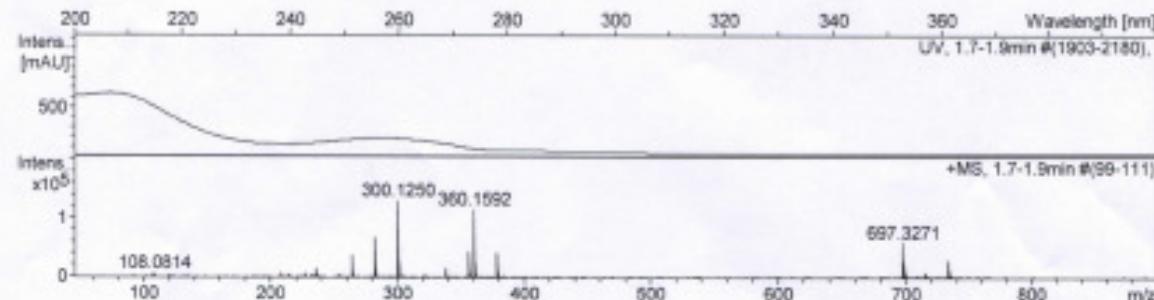
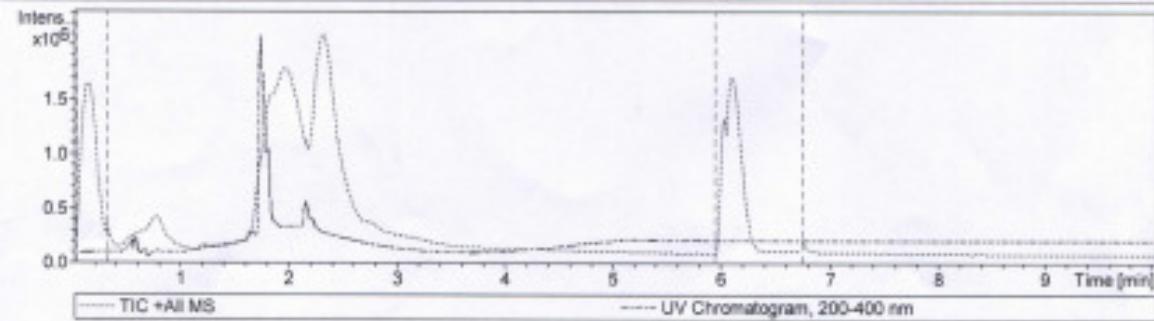
Analysis Name: D:\Data\user data\April 2012\13_april\Dr. A. Bisai- SB4-347R_1-A_2_01_1763.d
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 Sample Name: Dr. A. Bisai- SB4-347R
 Comment:

Acquisition Date: 4/13/2012 2:14:26 PM

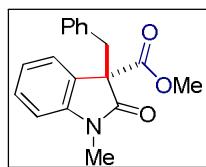
 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

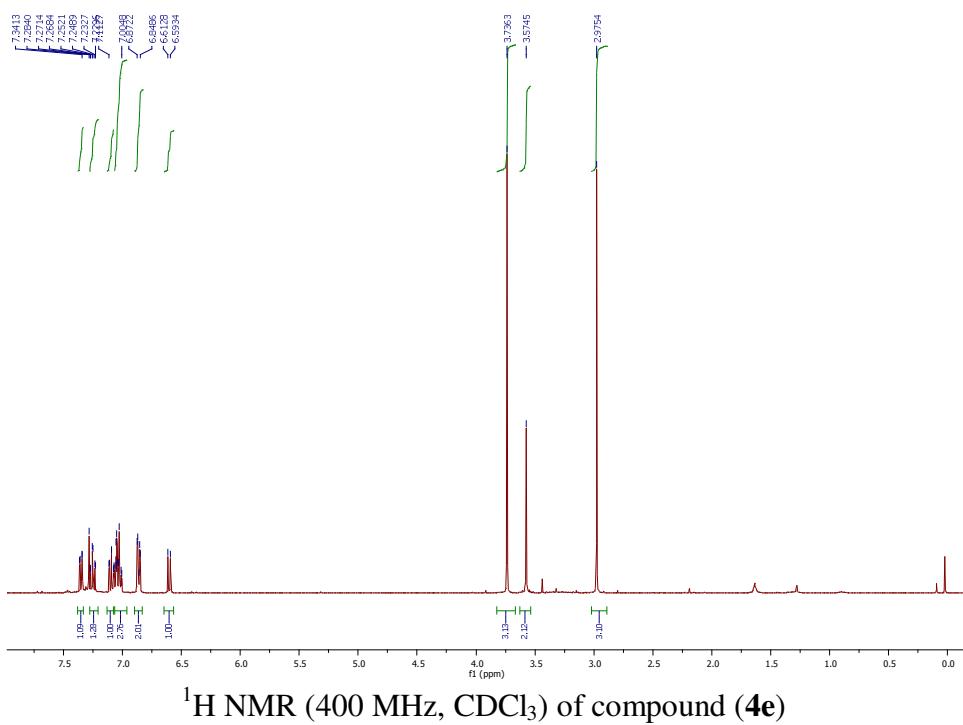
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



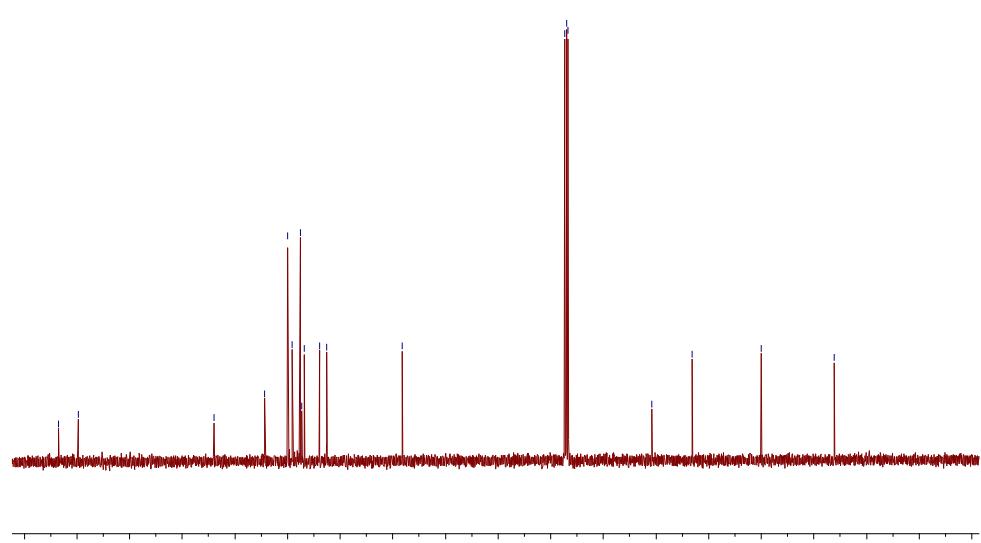
Scanned copy of mass spectrum of compound (\pm)-4d

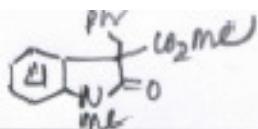


(4e)



— 1734529
— 1637969
— 1440155
— 1343023
— 1275607
— 1267638
— 129445
— 125370
— 1081798
— 773495
— 767123
— 607475
— 530966
— 4010692
— 261371





Display Report

Analysis Info

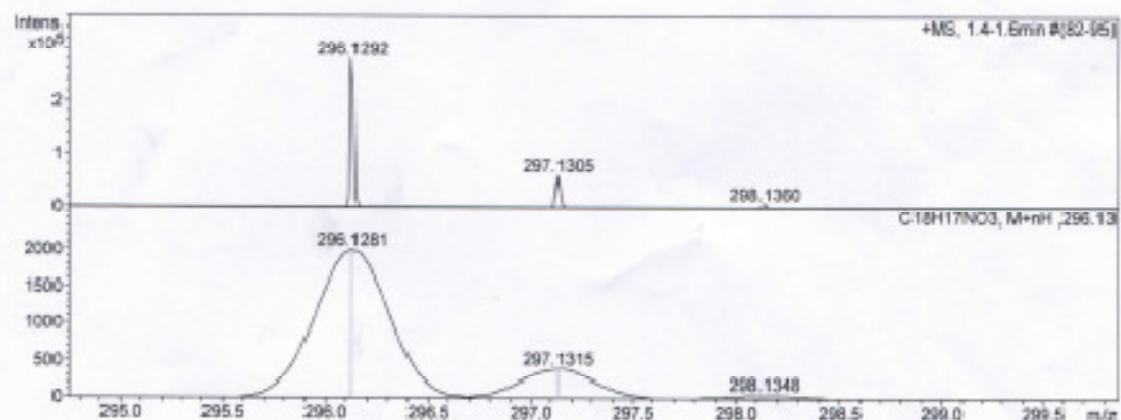
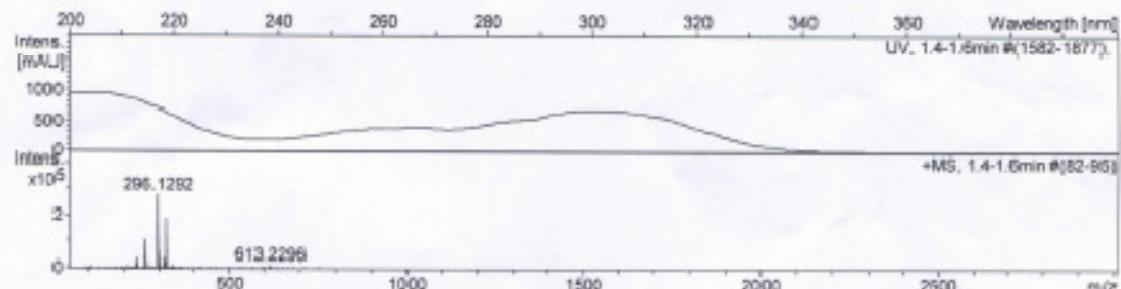
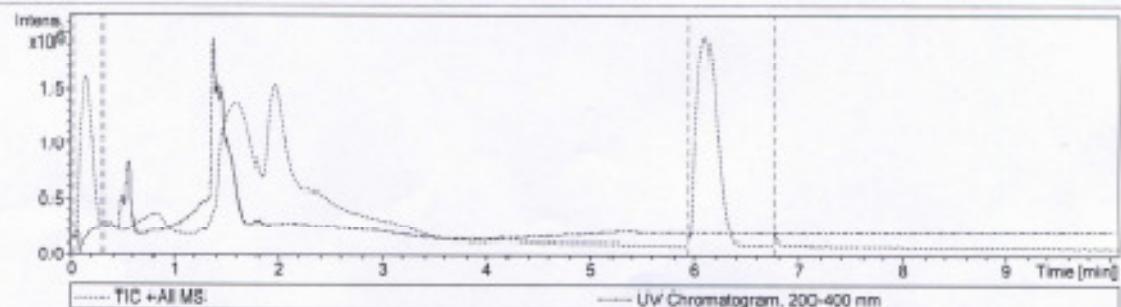
Analysis Name: D:\Data\user data\April 2012\18 apr\Dr. A. Bisai- SD-2-21_1-A_4_01_1789.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SD-2-21
 Comment:

Acquisition Date: 4/16/2012 1:53:17 PM

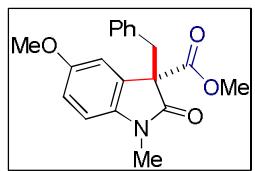
 Operator: Meena Sharma
 Instrument: microTOF-Q II 10330

Acquisition Parameter

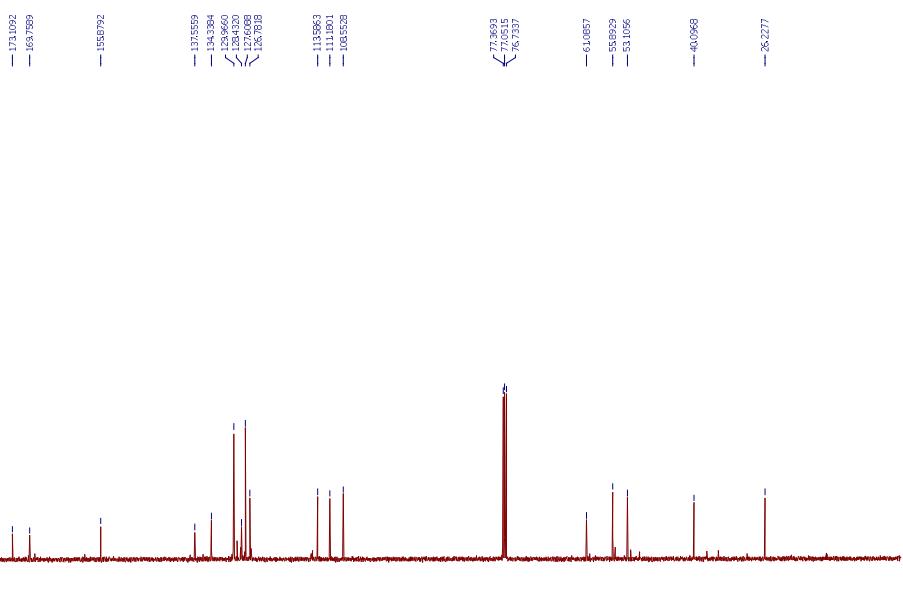
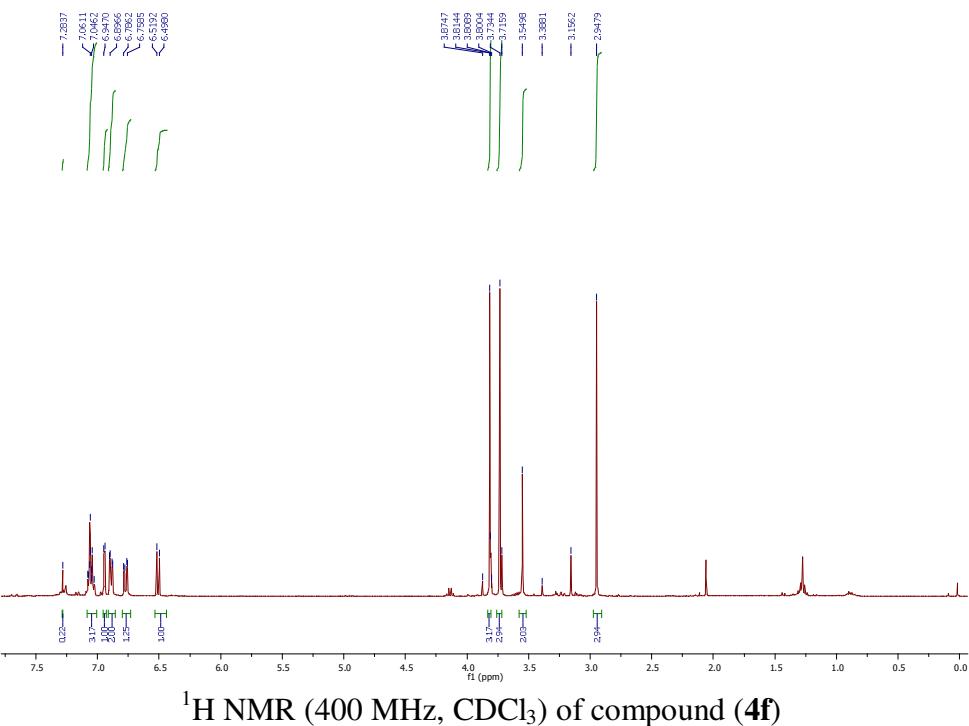
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set: Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set: End Plate Offset	-500 V	Set Dry Gas:	7.0 l/min
Scan End	3000 m/z	Set: Collision Cell R ^o	130.0 Vpp	Set Divert Valve	Waste



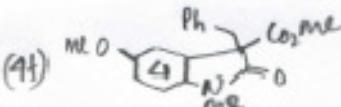
Scanned copy of mass spectrum of compound (\pm)-4e



(4f)



¹³C NMR (100 MHz, CDCl₃) of compound (4f)



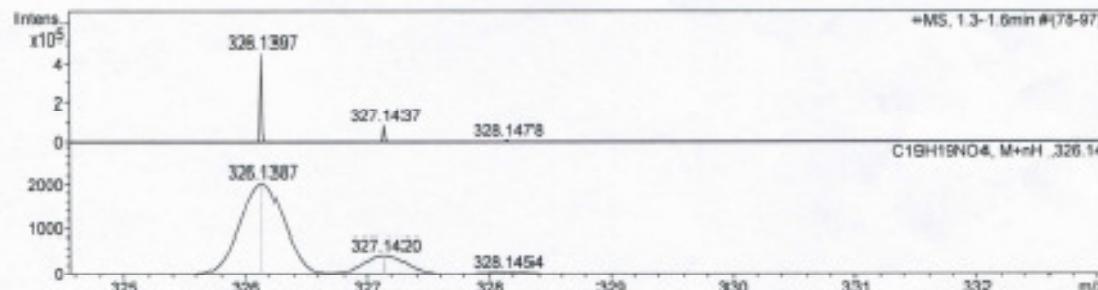
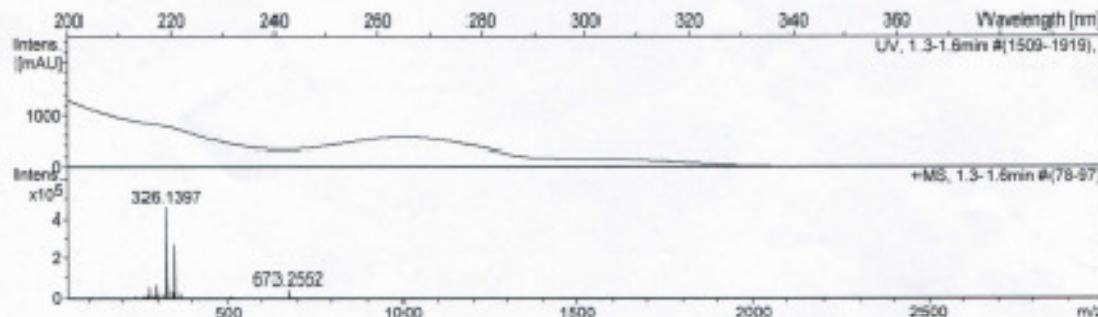
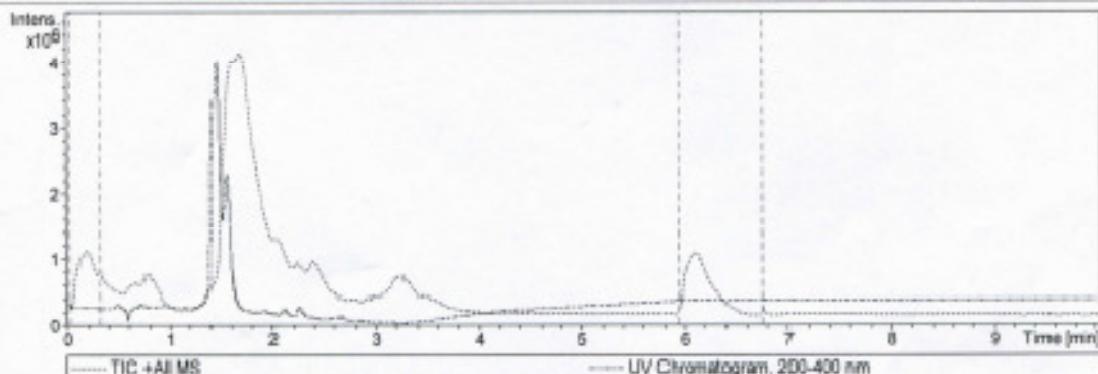
Display Report

Analysis Info

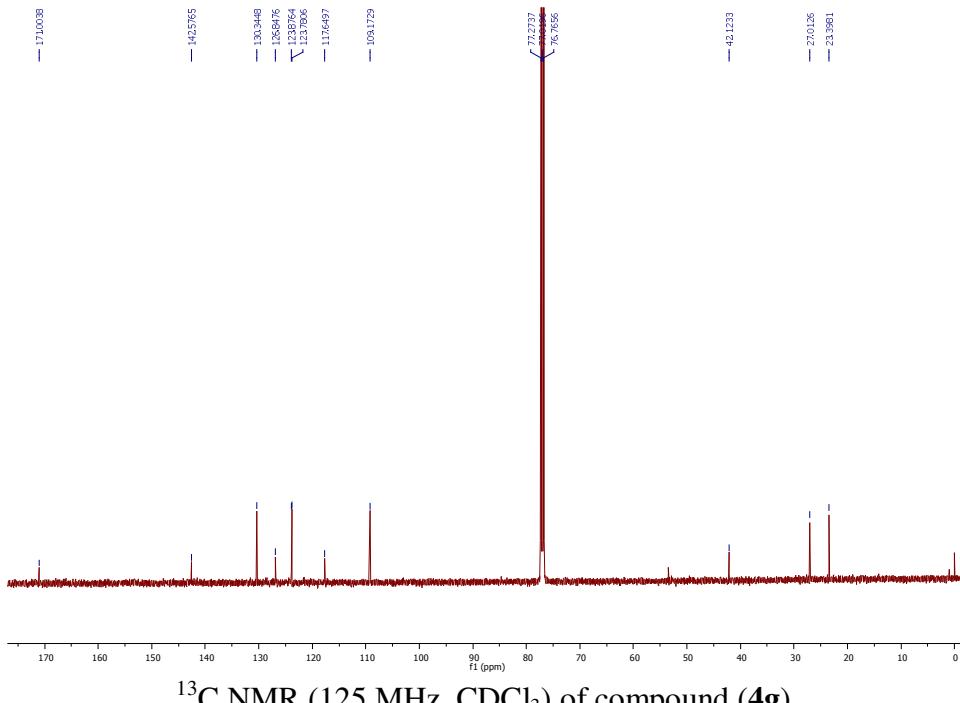
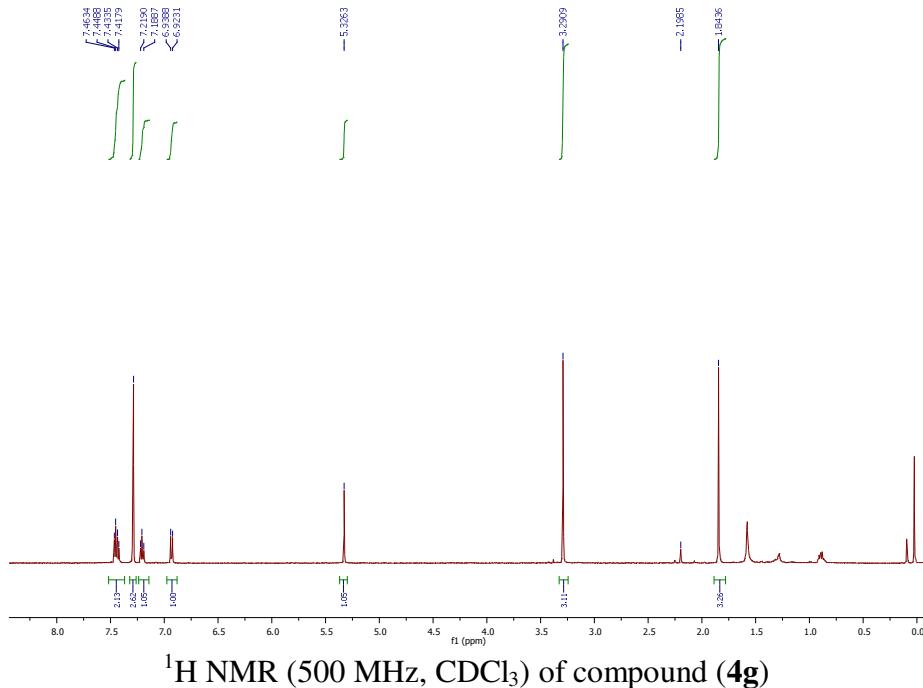
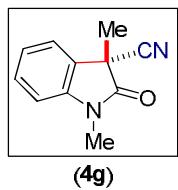
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 Method: HRLCMS-20 Sept.m Operator: Meena Sharma
 Sample Name: Dr. A. Bisai-SG3-281 Instrument: micrOTOF-Q II 10330
 Comment:

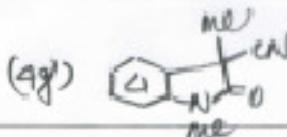
Acquisition Parameter

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



Scanned copy of mass spectrum of compound (\pm)-4f





Display Report

Analysis Info

Analysis Name: D:\Data\user\data\DEC 07\Dr. A. Bisai-AB-SG3-293_1-A,1_01_448.d
 Method: IHR LCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-AB-SG3-293
 Comment:

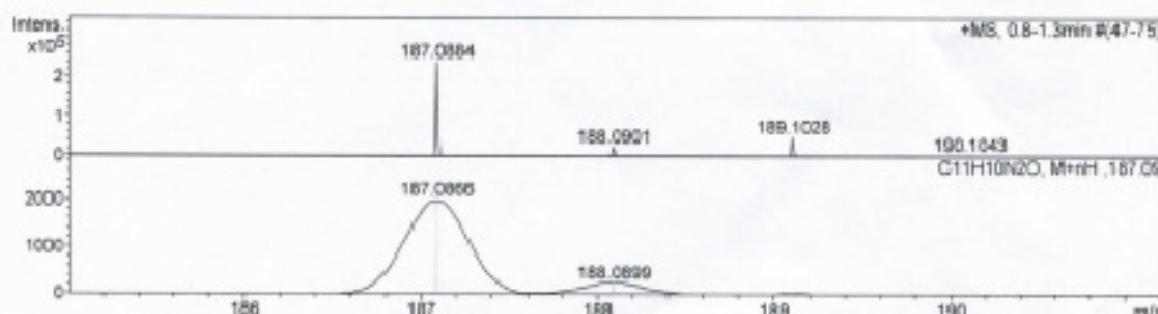
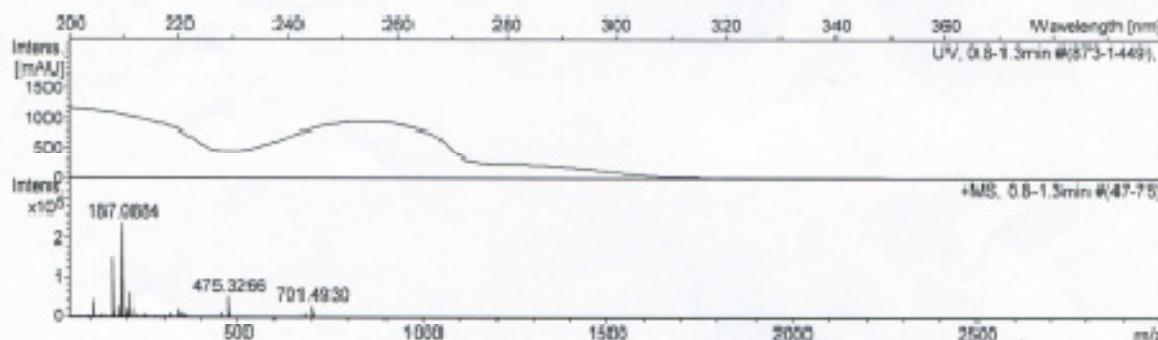
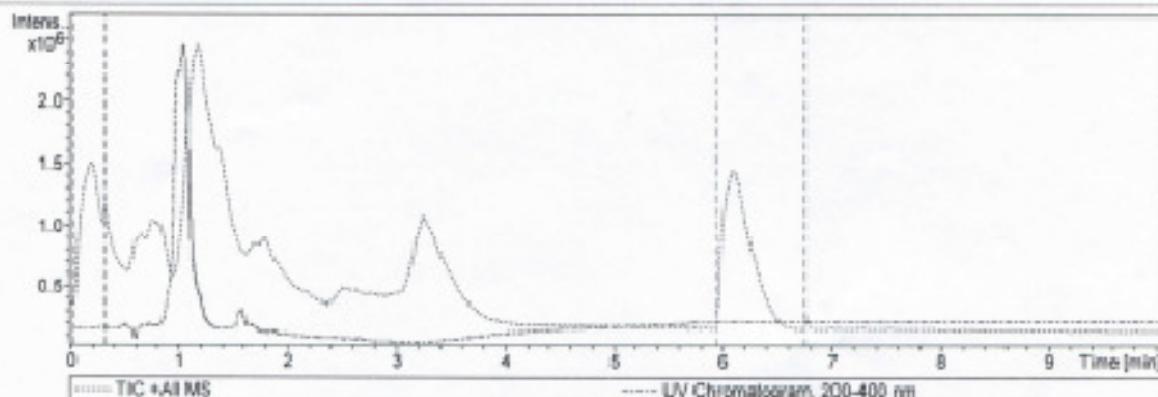
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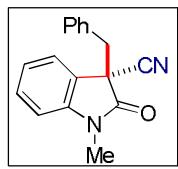
Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

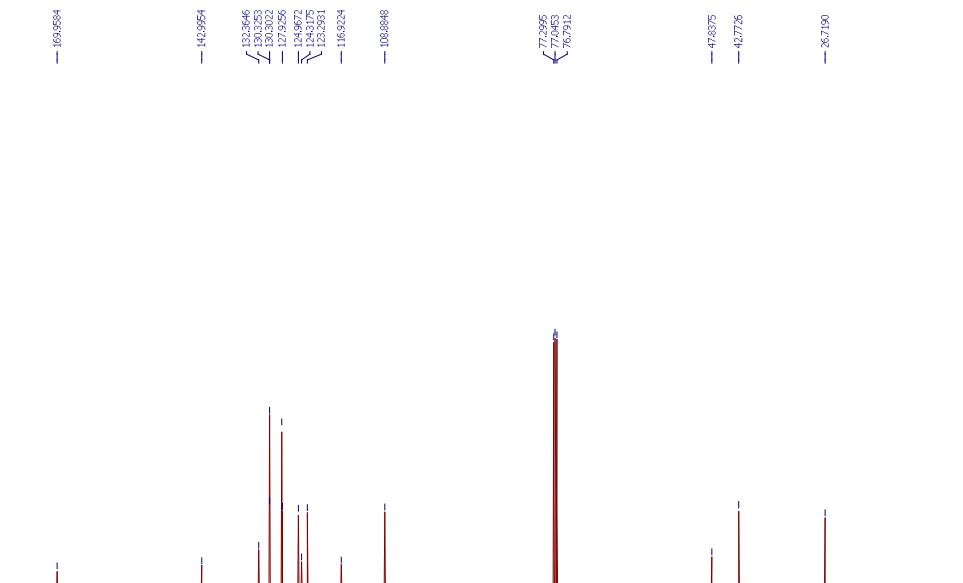
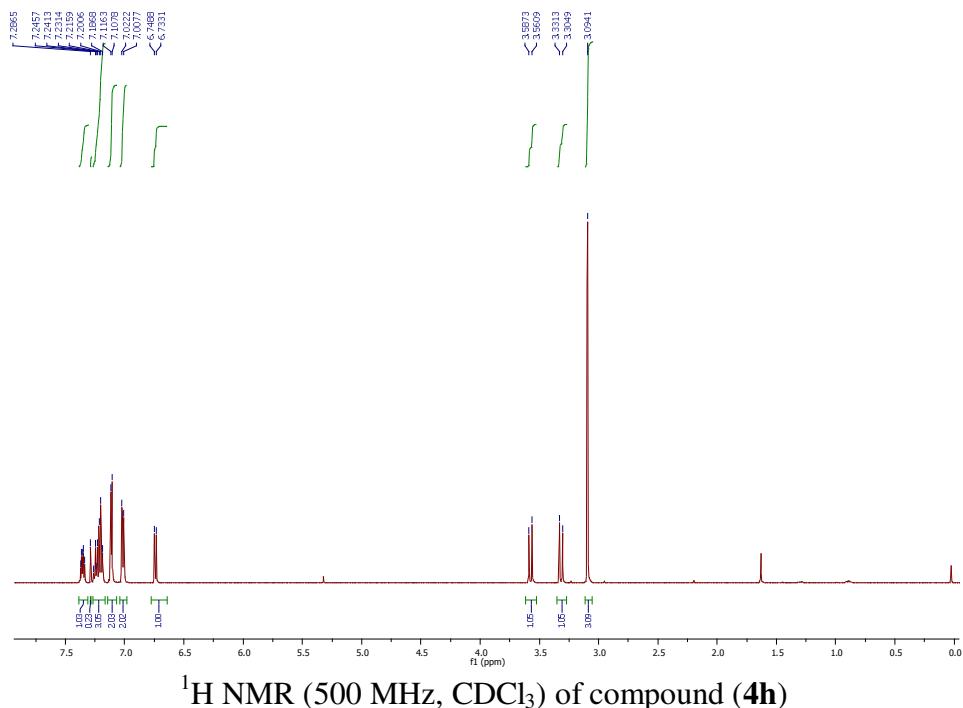
Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	120.0 Vps	Set Diverter Valve	Waste

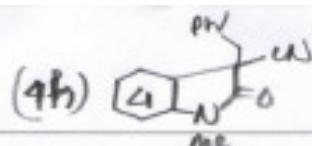




(4h)



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



Display Report

Analysis Info

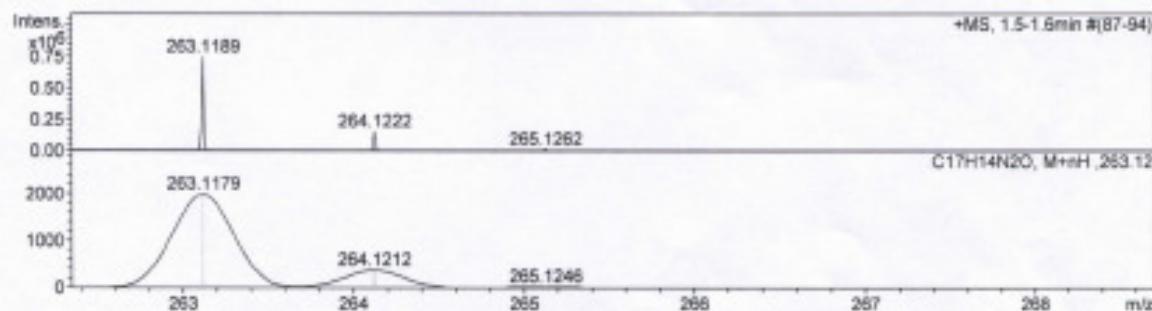
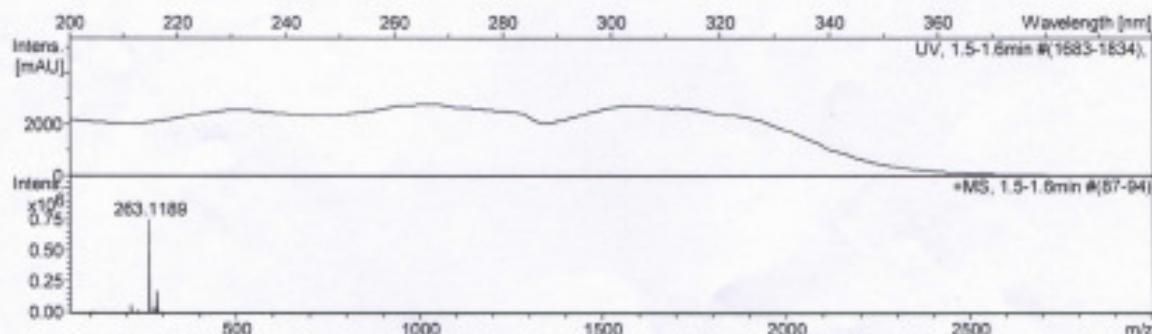
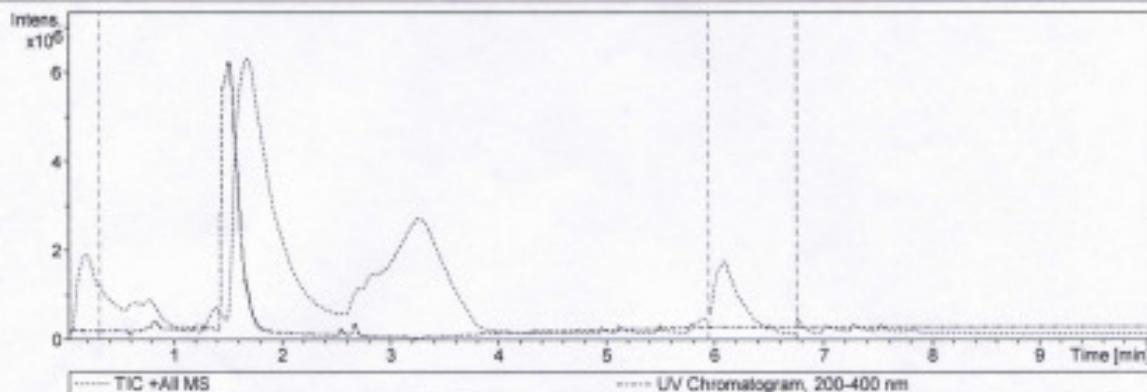
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 Sample Name: Dr. A. Bisal-SG3-298
 Comment:

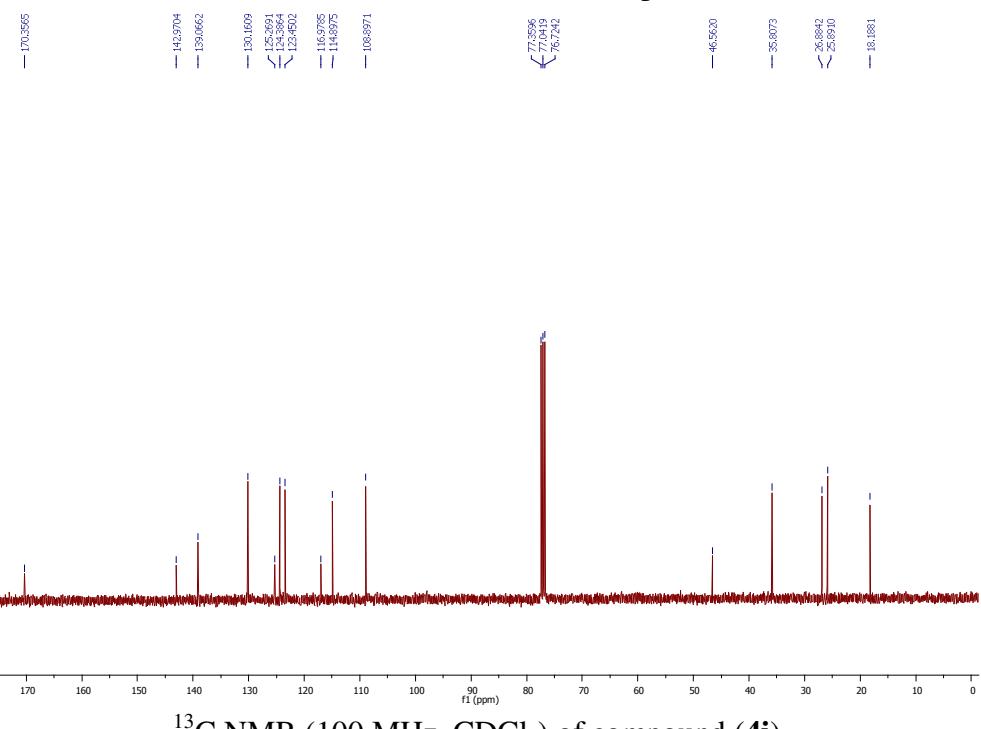
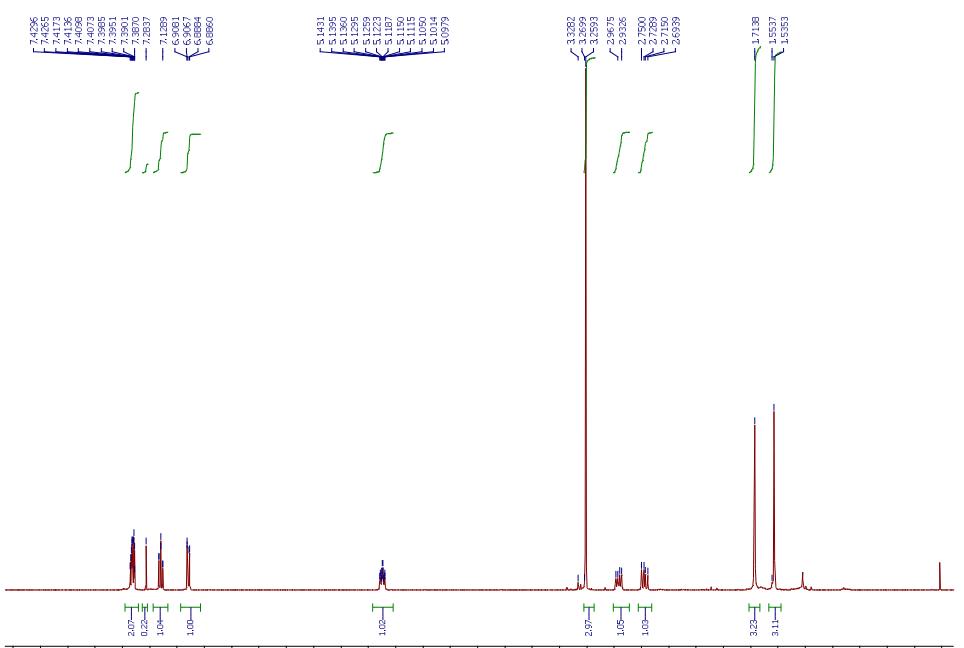
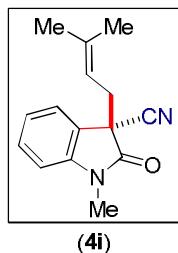
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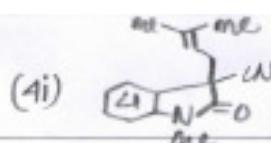
 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

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







Display Report

Analysis Info

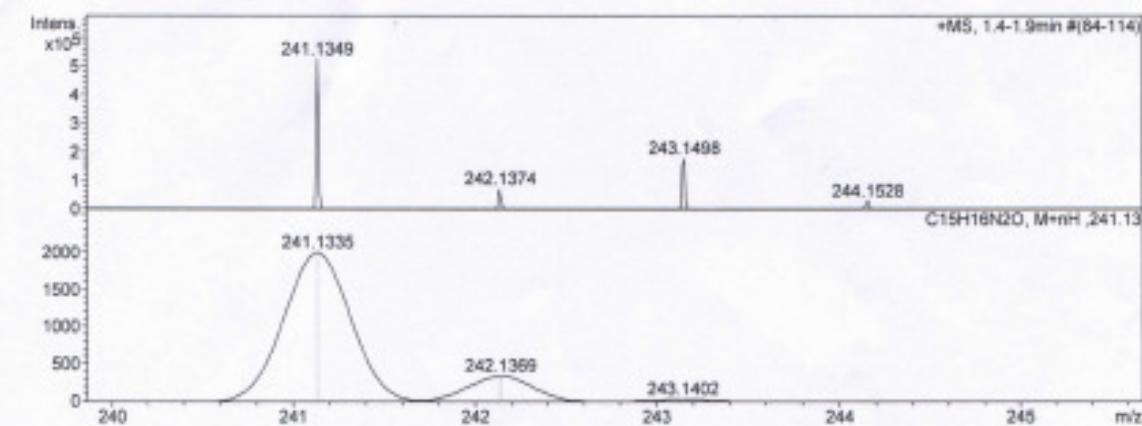
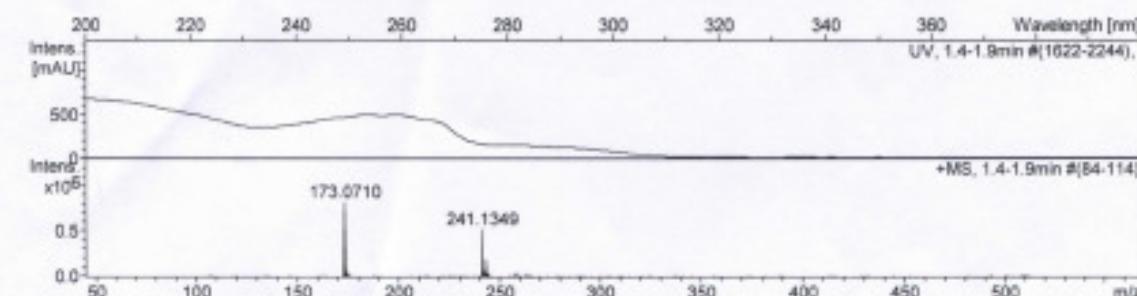
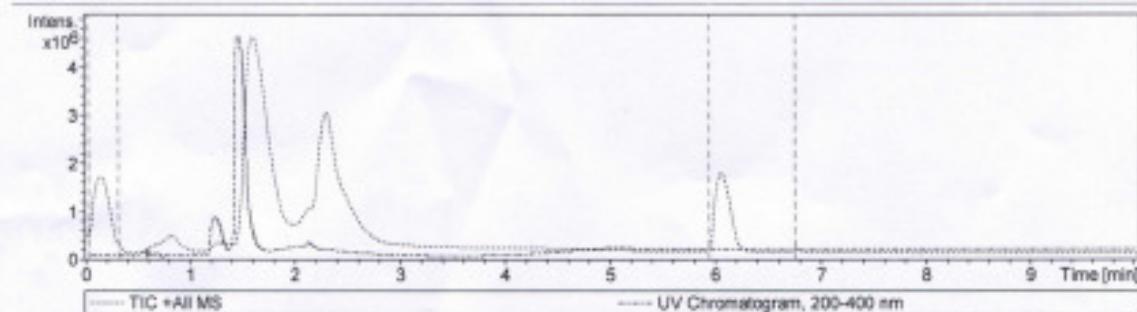
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG4-337
 Comment:

Acquisition Date: 4/11/2012 2:36:56 PM

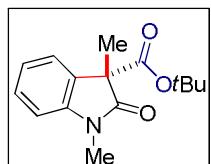
Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

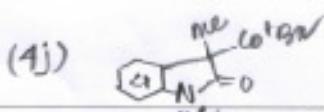
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Focus: Active	Set Capillary: 4500 V	Set Dry Heater: 200 °C
Scan Begin: 50 mHz	Set End Plate Offset: -500 V	Set Dry Gas: 7.0 l/min
Scan End: 3000 mHz	Set Collision Cell RF: 130.0 Vpp	Set Divert Valve: Waste



Scanned copy of mass spectrum of compound (±)-4i



(4j)



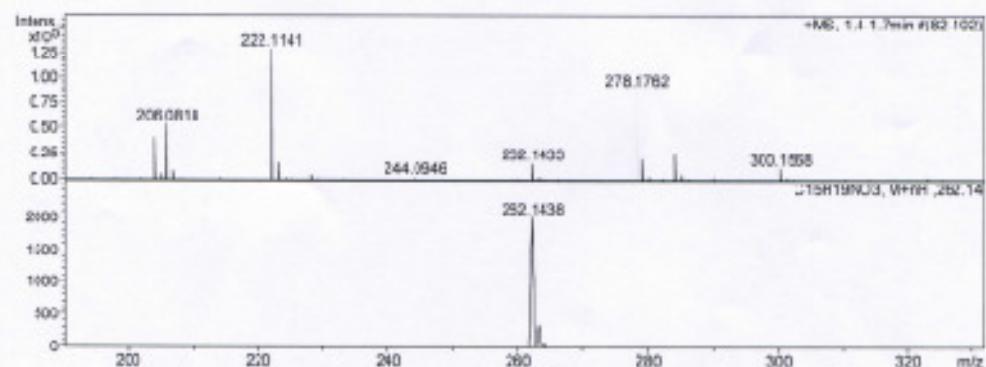
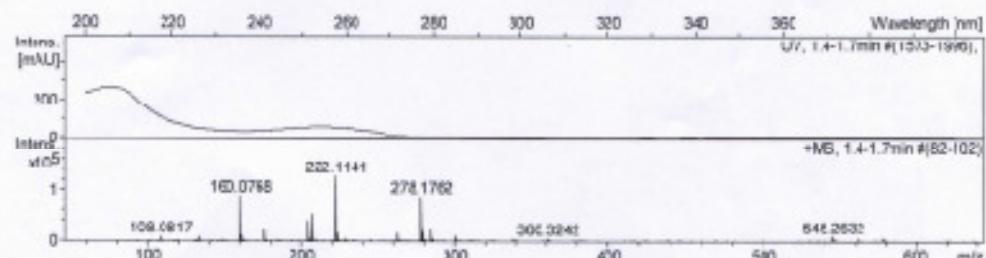
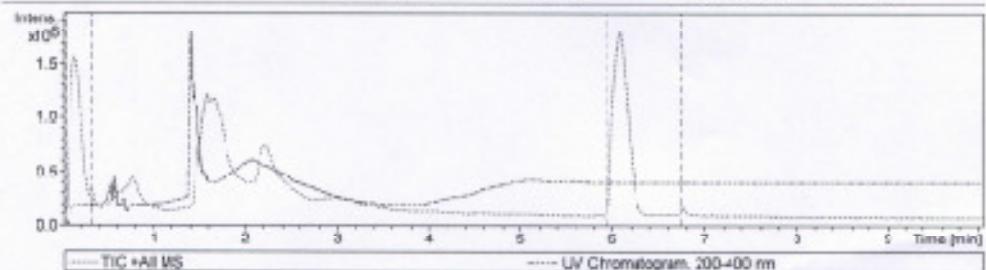
Display Report

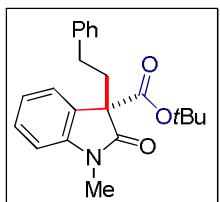
Analysis Info

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Method	HRLCNS-20 Sept.n	Operator	Meena Sharma
Sample Name	Dr. A. Bisai- SG4-345	Instrument	microTOF Q II 10330
Comment			

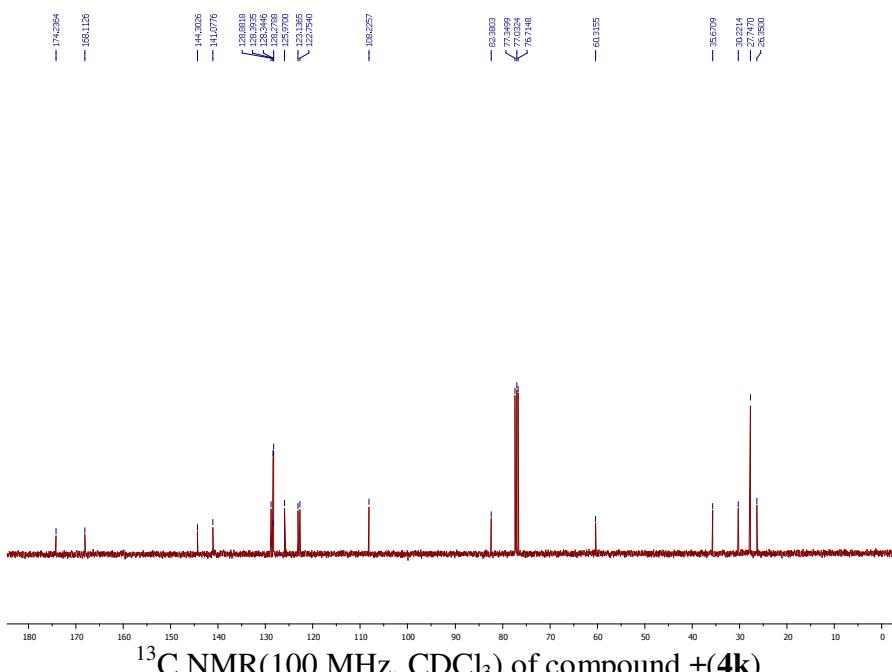
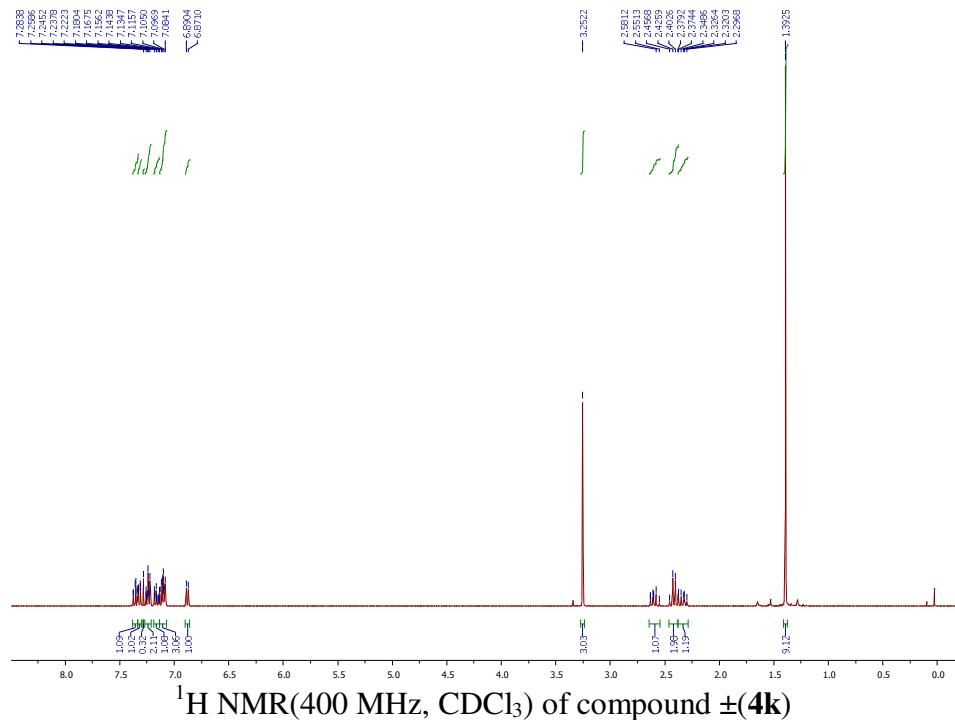
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	+600 V	Set Dry Heater	300 °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	100.0 Vpp	Set Direct Valve	Waste

Scanned copy of mass spectrum of compound (\pm)-4j



(4k)



Display Report

Analysis Info

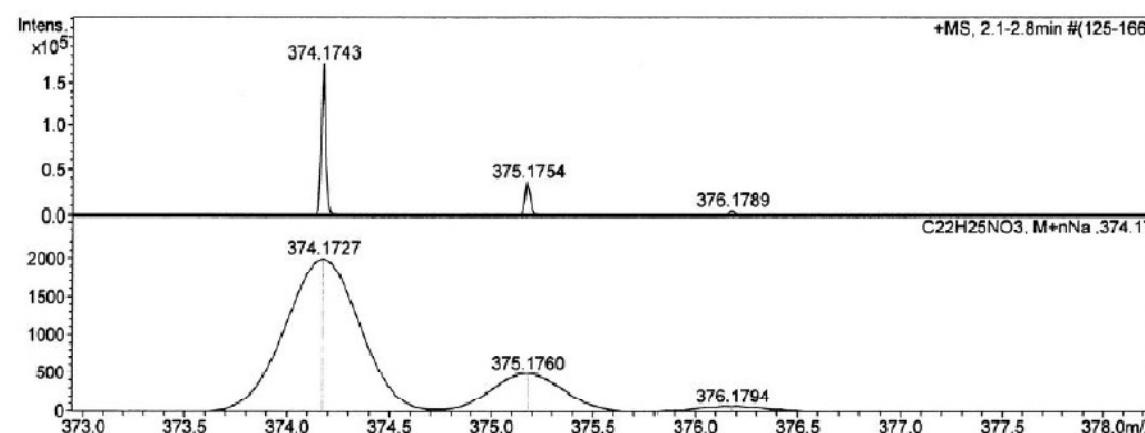
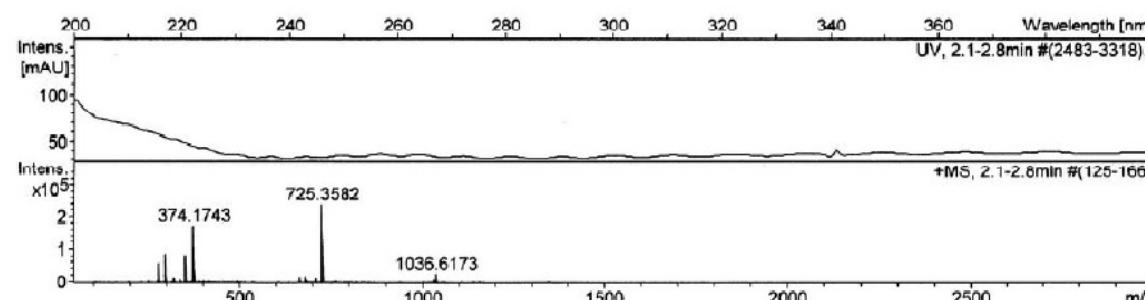
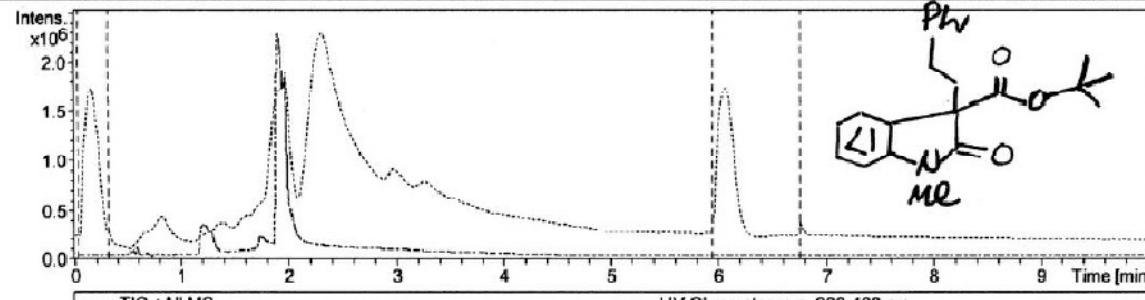
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG4-348
 Comment:

Acquisition Date: 4/14/2012 3:47:43 PM

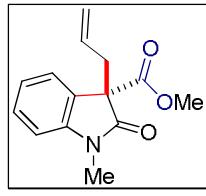
 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

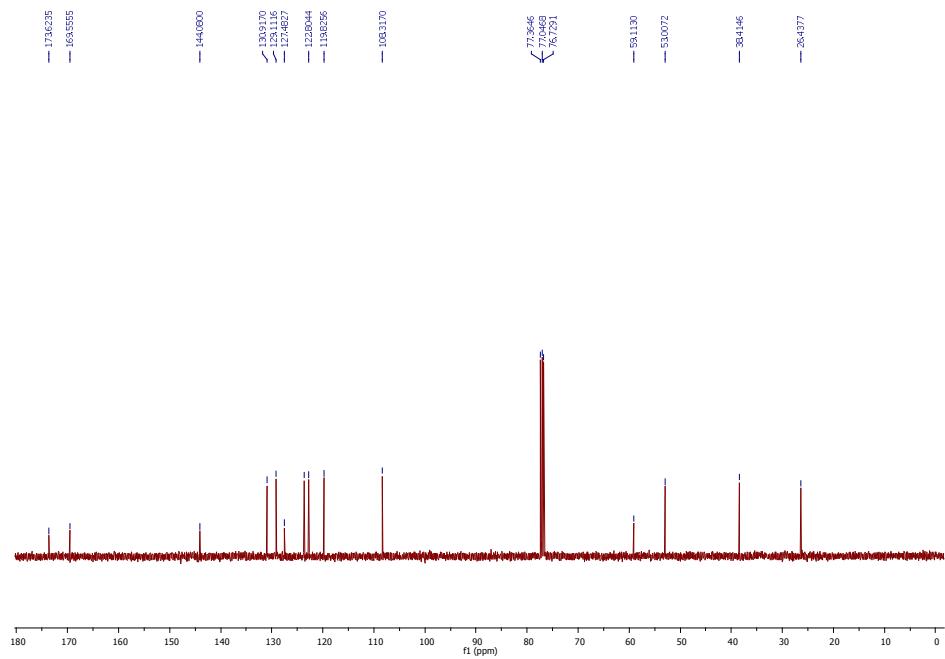
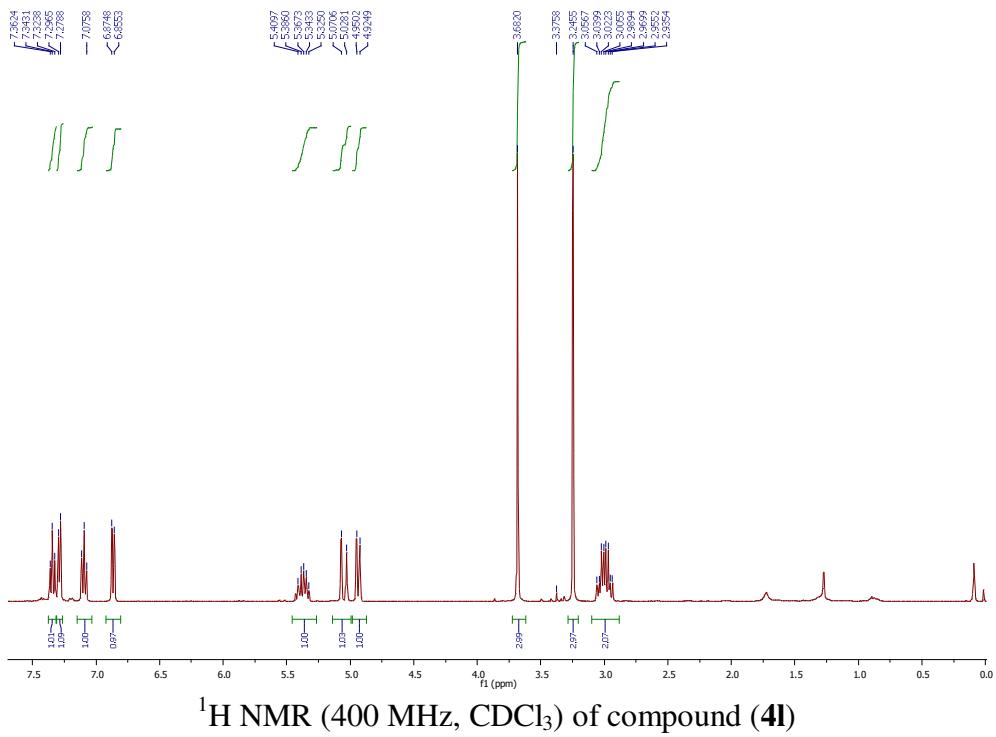
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



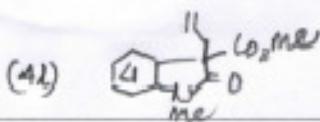
Scanned copy of mass spectrum of compound (\pm)-4k



(41)



¹³C NMR (100 MHz, CDCl₃) of compound (**4l**)



Display Report

Analysis Info

Analysis Name: D:\Data\user_data\DEC_17\Dr. A. Bisai- SD-2-09_1-A,3_01_581.d
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 Sample Name: Dr. A. Bisai- SD-2-09
 Comment:

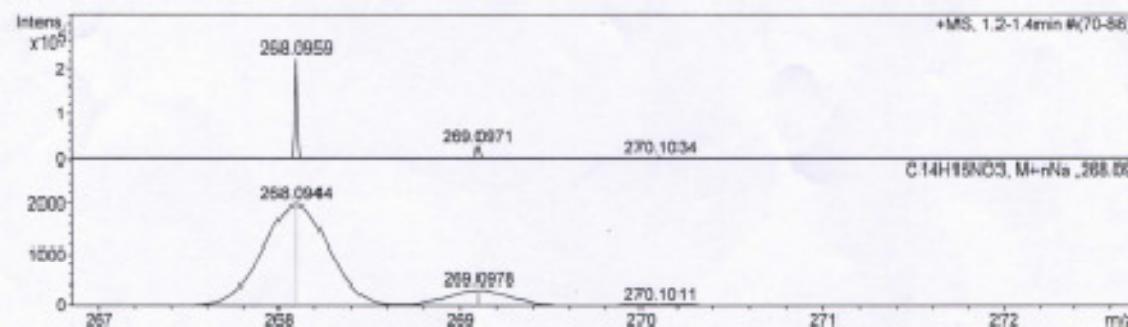
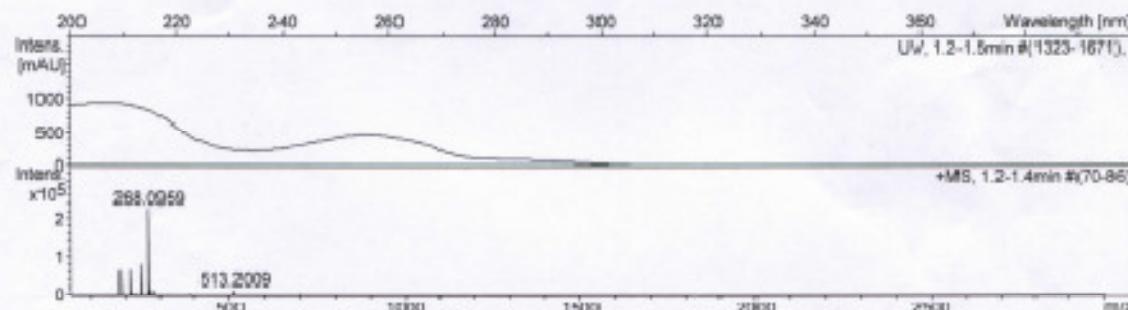
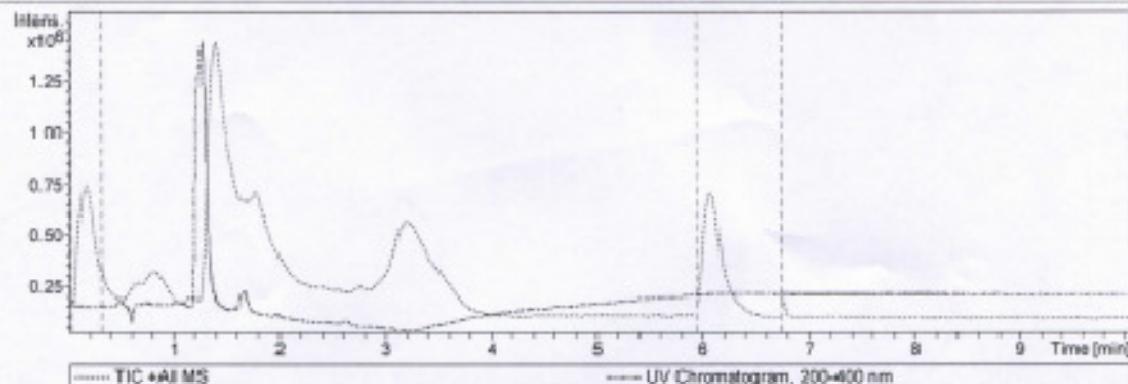
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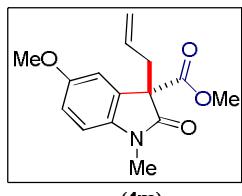
Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

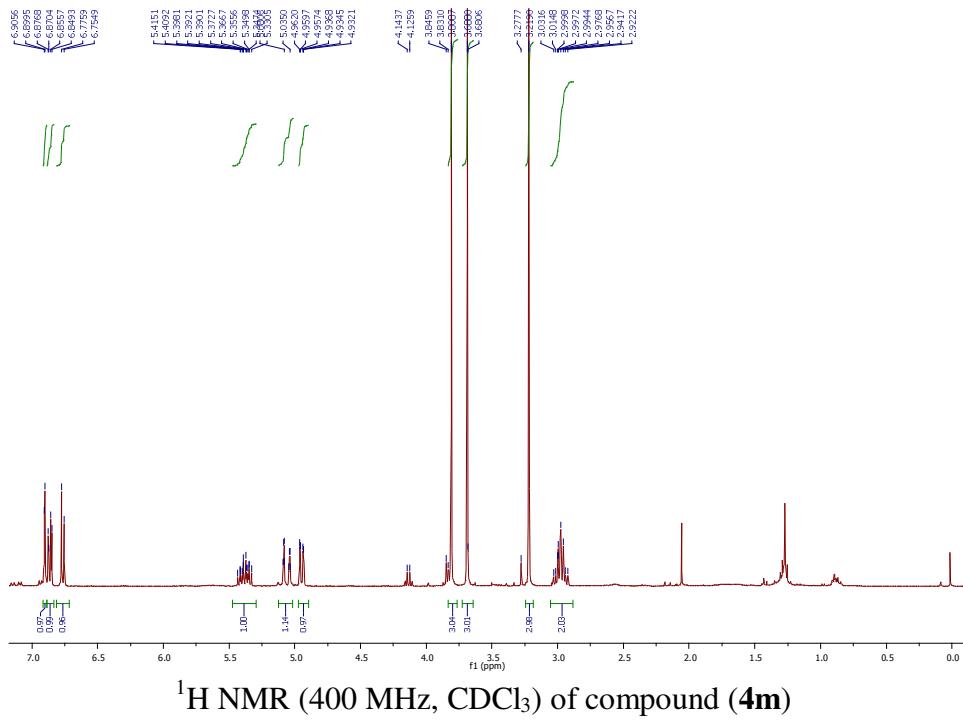
Acquisition Parameter

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

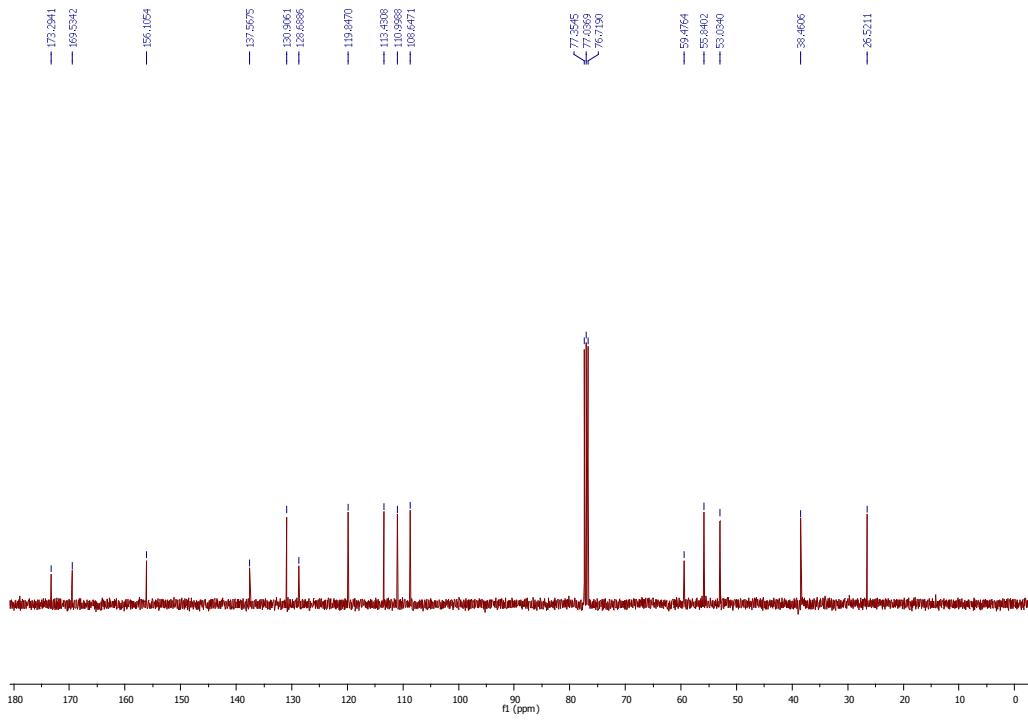




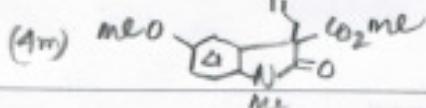
(4m)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**4m**)



Display Report

Analysis Info

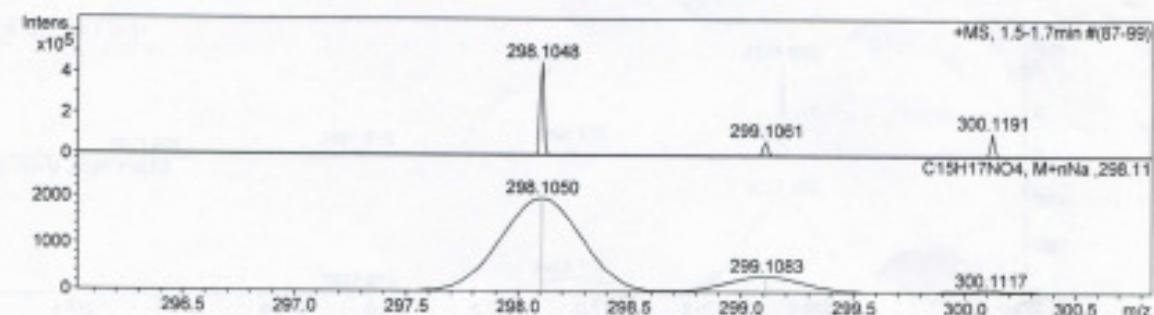
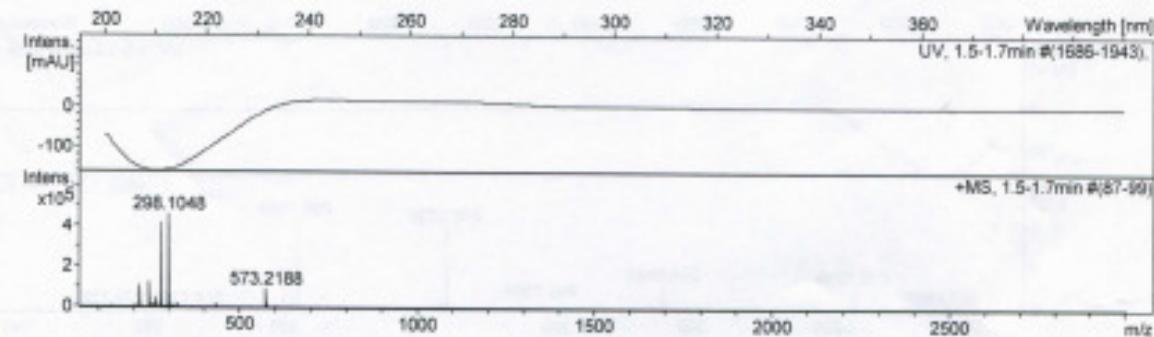
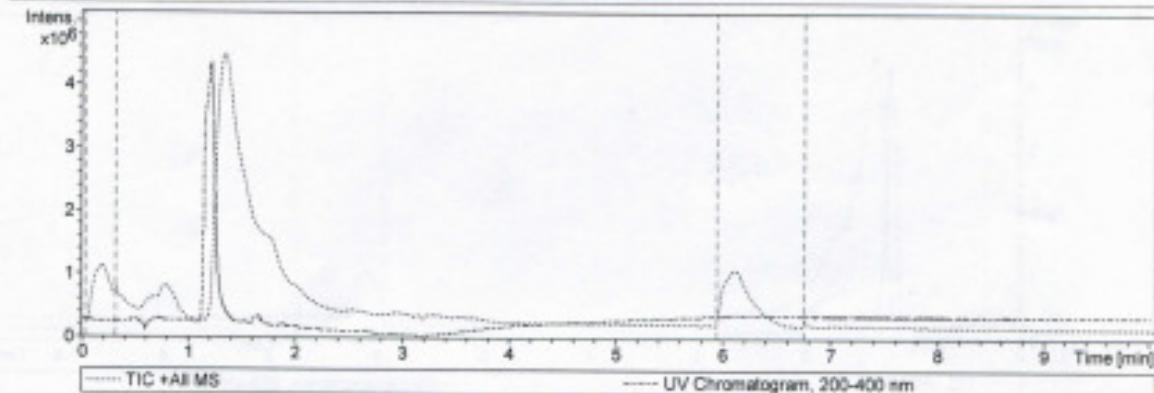
Analysis Name D:\Data\user data\DC\02\Dr. A. Bisai-SG3-280_1-A,5_01_426.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai-SG3-280
 Comment

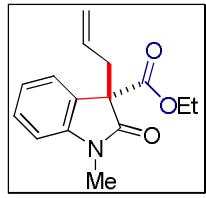
Acquisition Date 12/2/2011 2:43:57 PM

 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

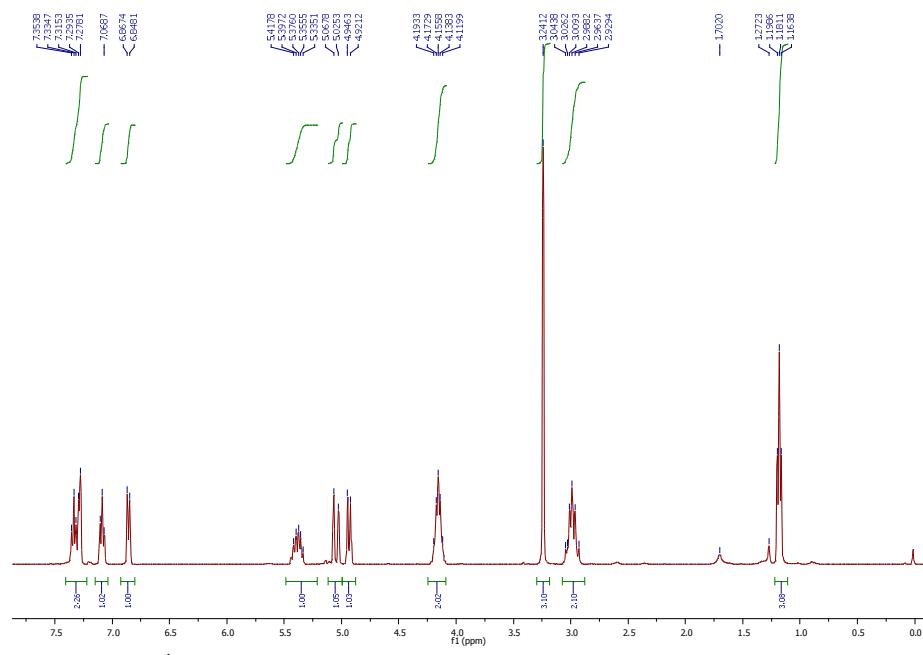
Acquisition Parameter

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

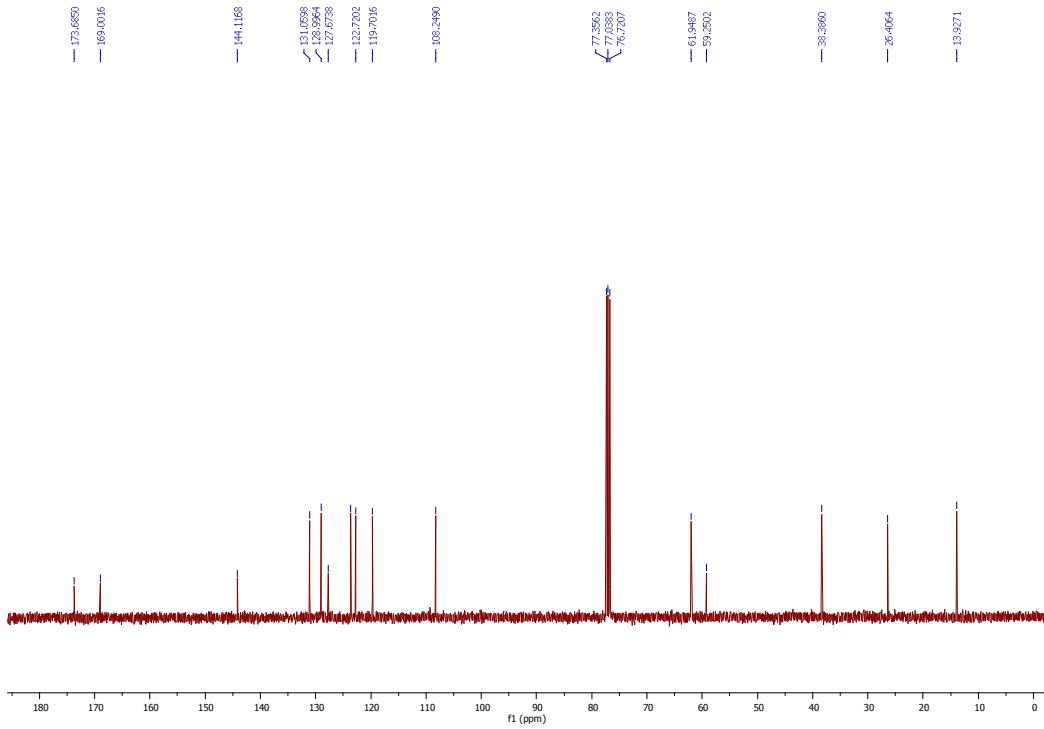




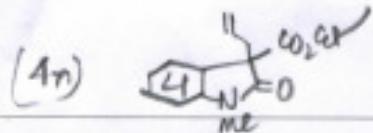
(4n)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**4n**)



Display Report

Analysis Info

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 Sample Name: Dr. A. Bisai- SG4-343
 Comment:

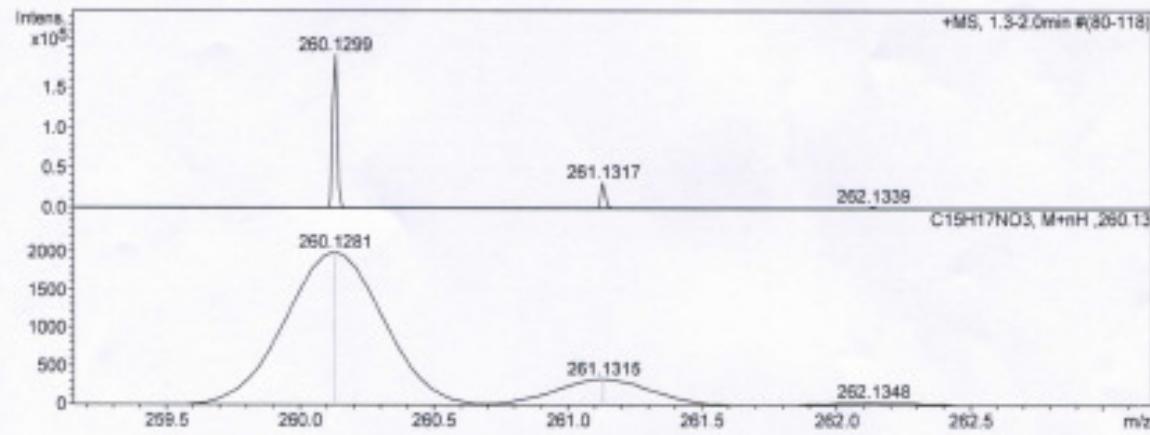
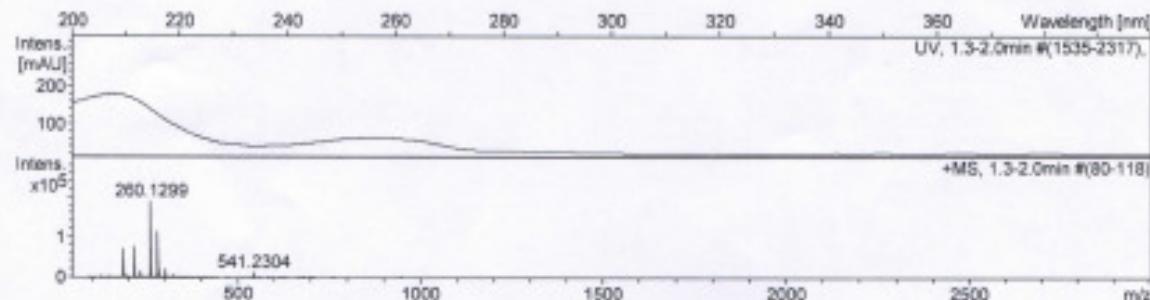
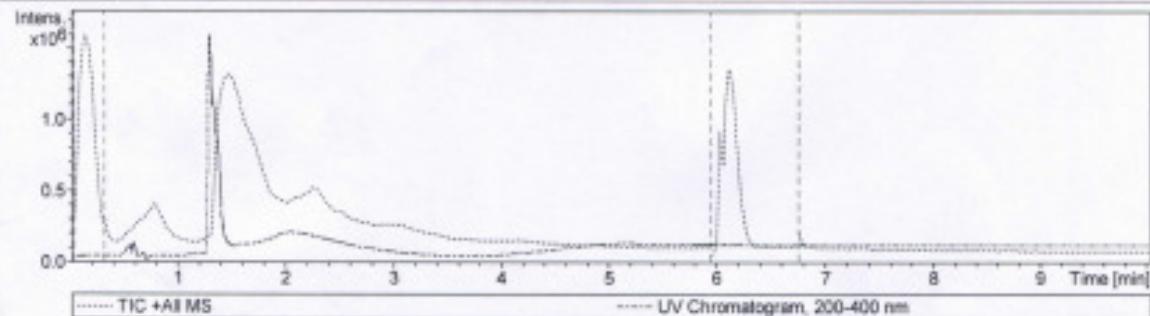
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Operator: Meena Sharma

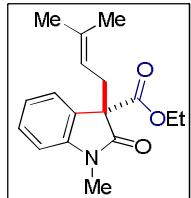
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

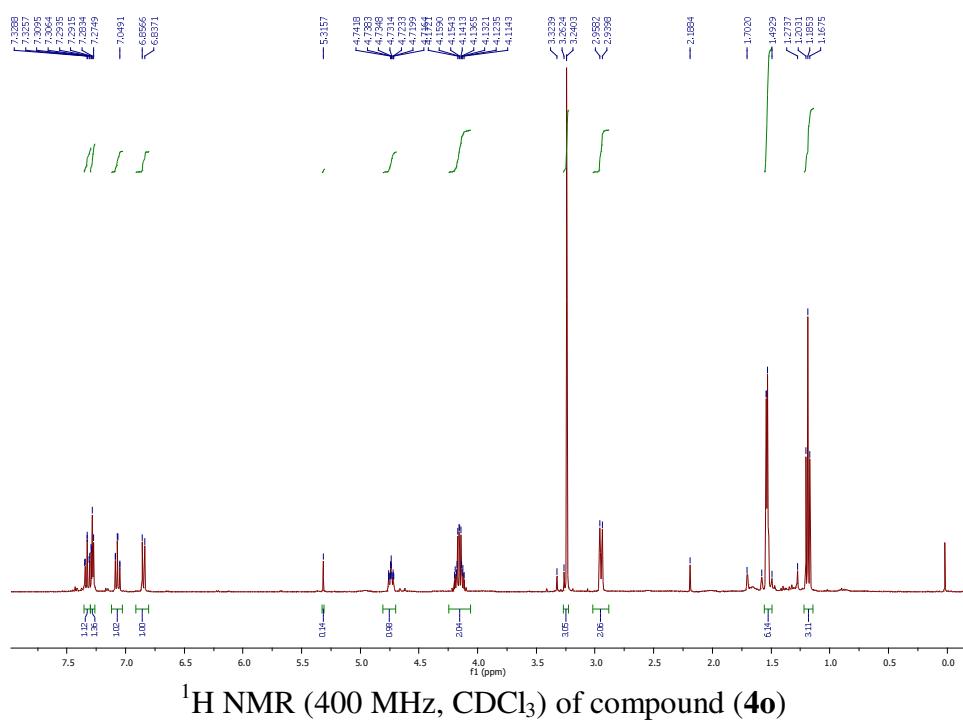
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	60 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



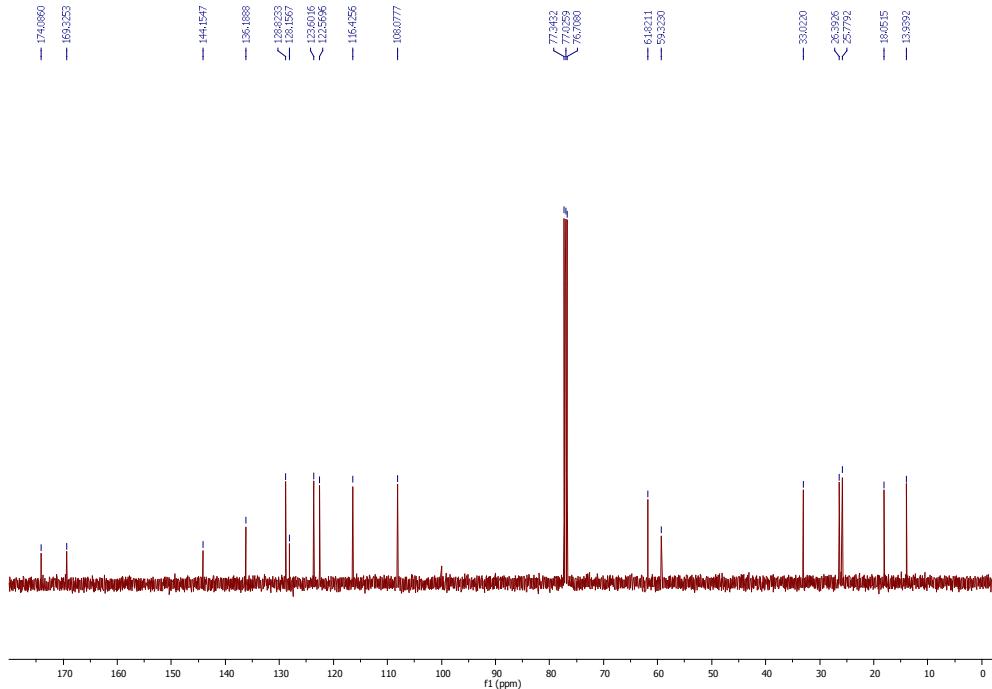
Scanned copy of mass spectrum of compound (\pm)-4n



(40)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**4o**)



Display Report

Analysis Info

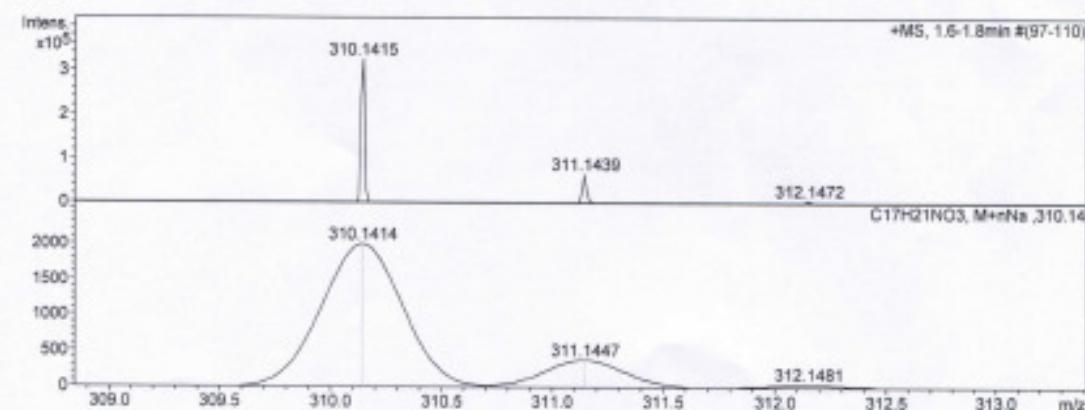
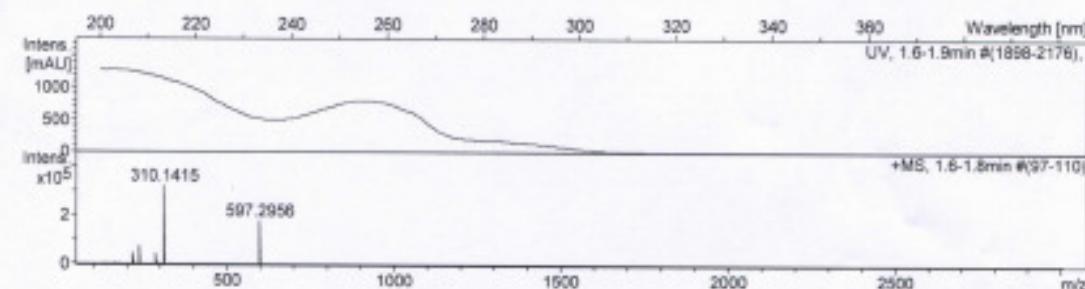
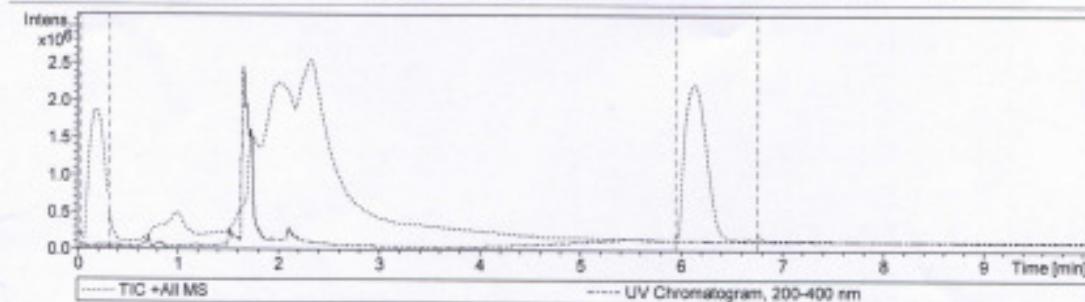
Analysis Name D:\Data\user data\April 2012\14 APR\Dr. A. Bisai- SG4-351_1-A,2_01_1774.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG4-351
 Comment

Acquisition Date 4/14/2012 12:59:36 PM

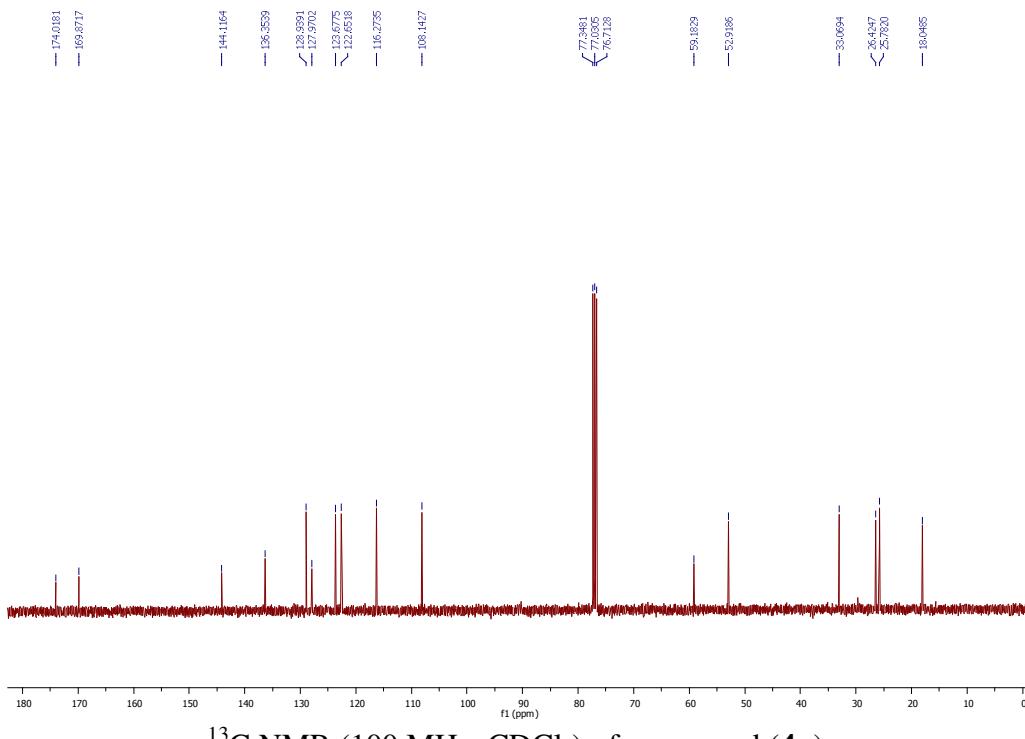
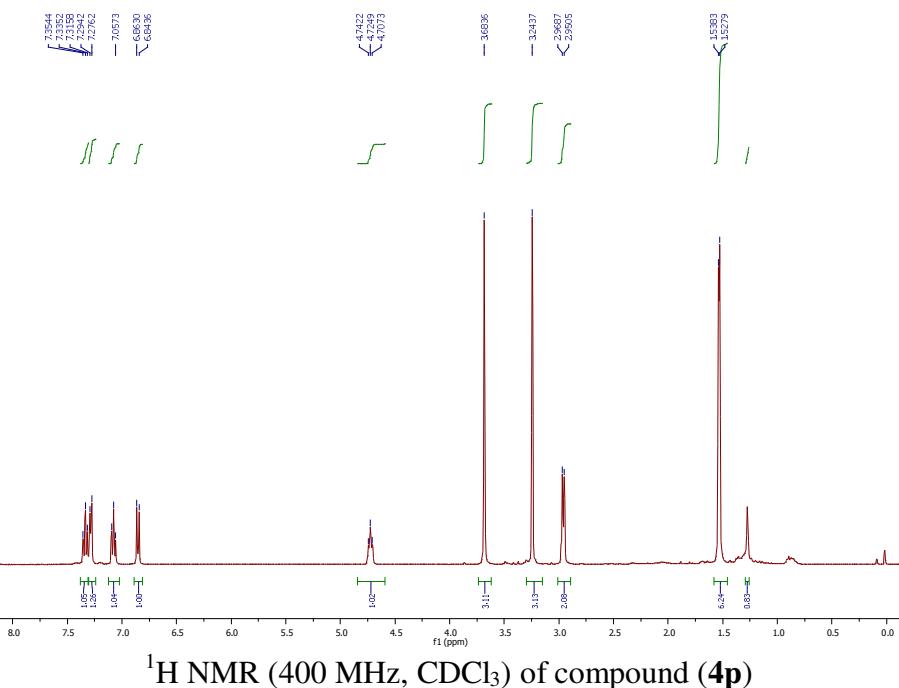
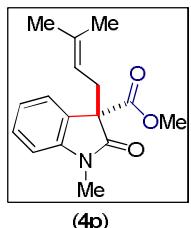
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

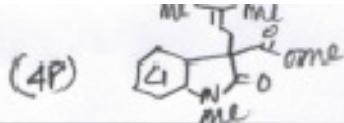
Acquisition Parameter

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



Scanned copy of mass spectrum of compound (\pm)-4o





Display Report

Analysis Info

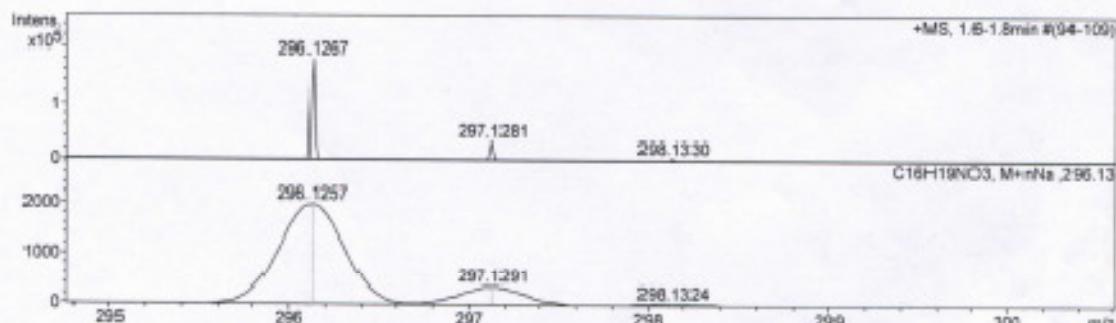
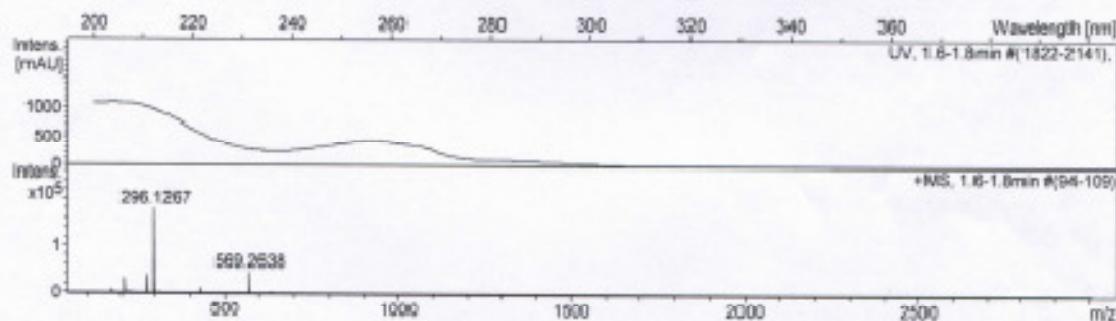
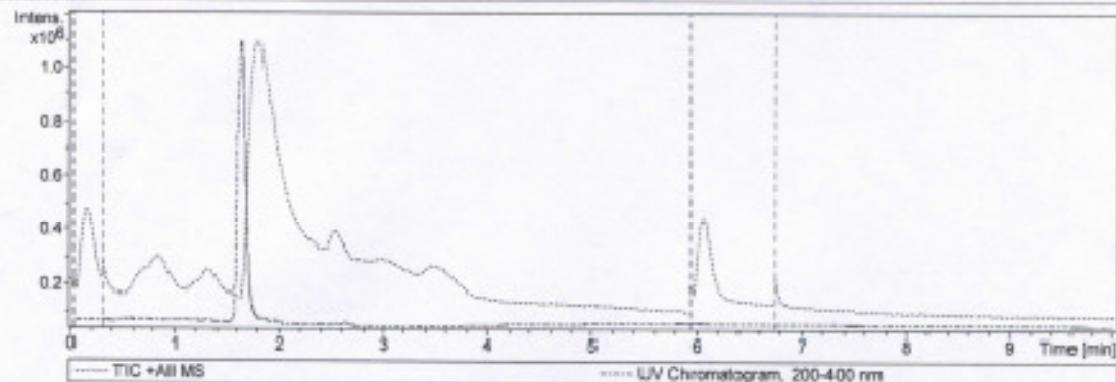
Analysis Name D:\Data\user-data\DEC 23\Dr. A. Bisai-SG3-348_1-A,4_01_668.d
 Method HIRLCMS-2Q Sept.m
 Sample Name Dr. A. Bisai-SG3-348
 Comment

Acquisition Date 12/23/2011 3:48:42 PM

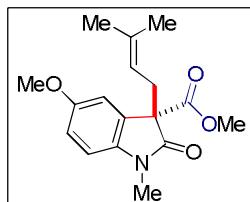
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

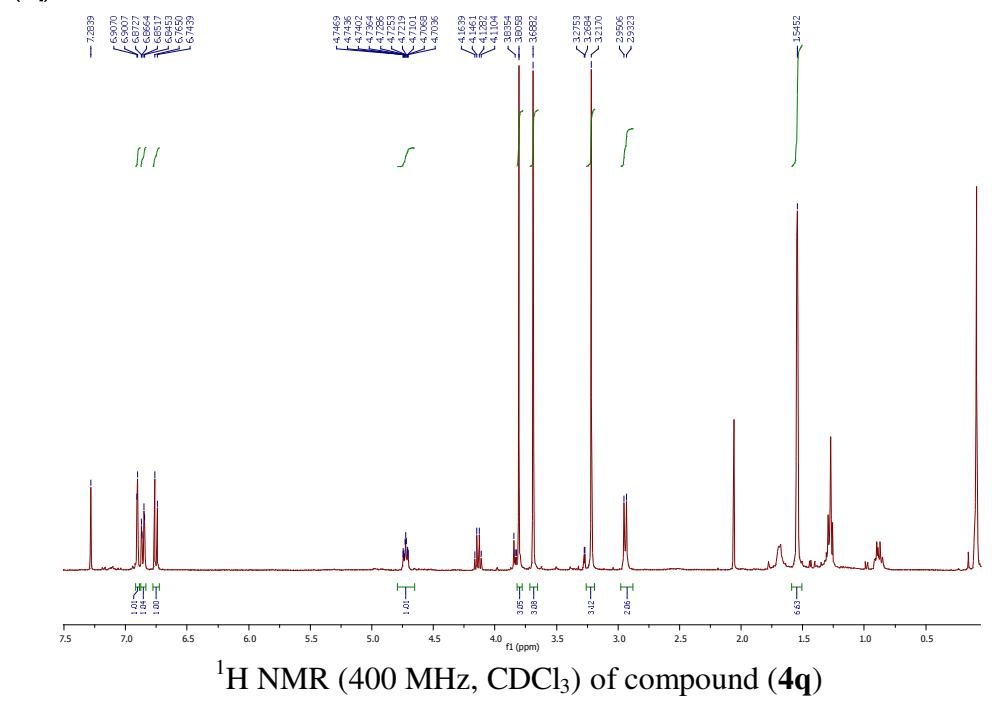
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



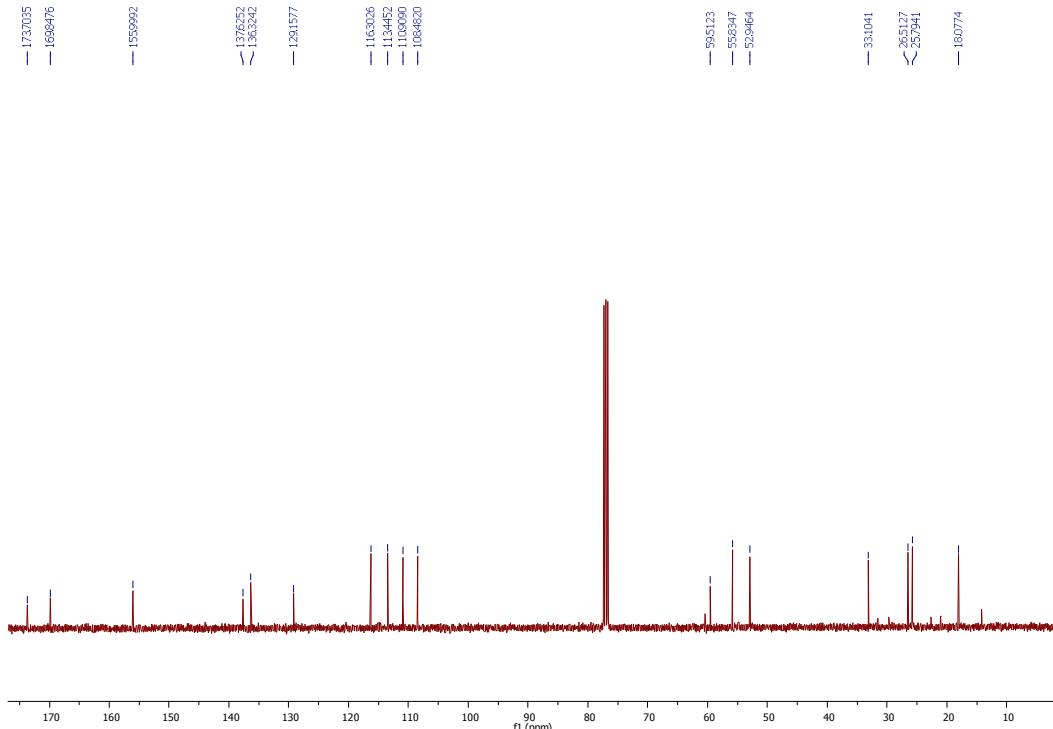
Scanned copy of mass spectrum of compound (±)-4p



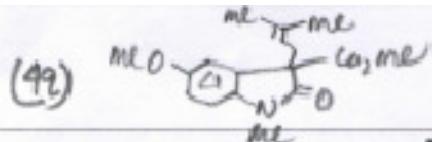
(4q)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**4q**)



Display Report

Analysis Info

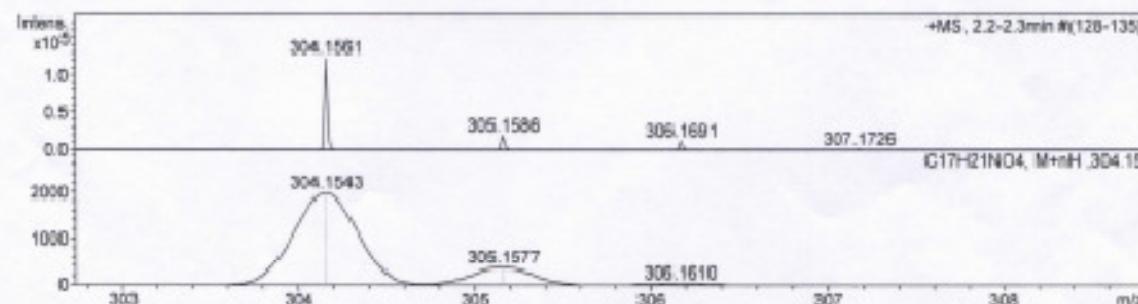
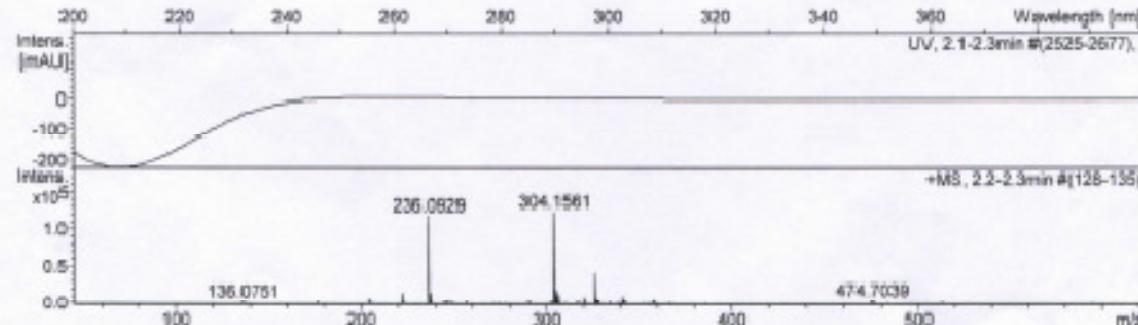
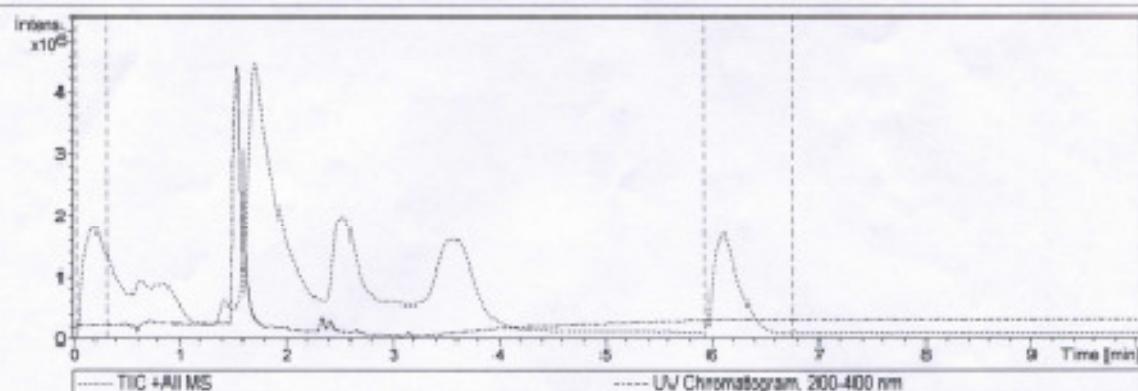
Analysis Name: D:\Data\user data\DEC 08\Dr. A. Bisai- SG3-287_1-A,2_O1_465.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG3-287
 Comment:

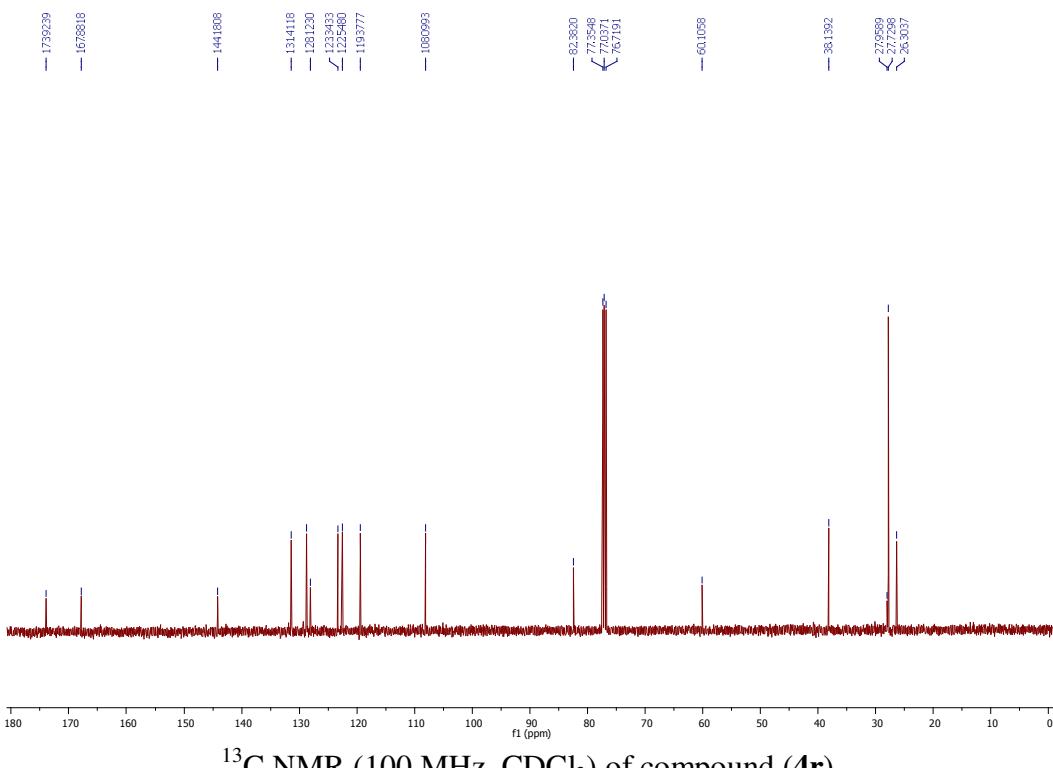
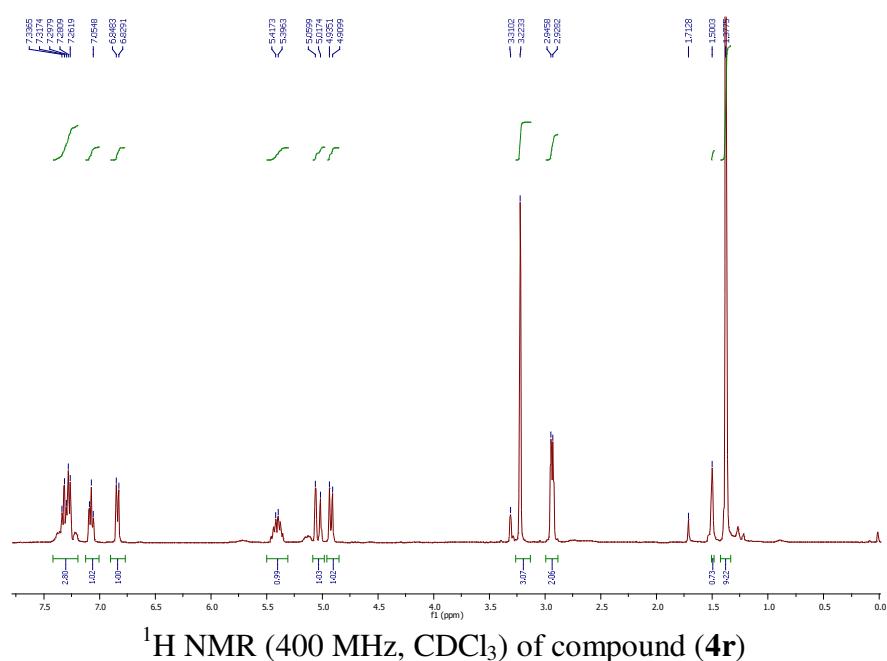
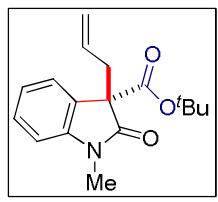
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

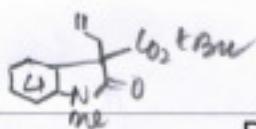
Acquisition Parameter

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Scan End:	3600 m/z	Set Collision Cell RF:	150.0 Vpp	Set Divert Valve:	Waste





(4r)



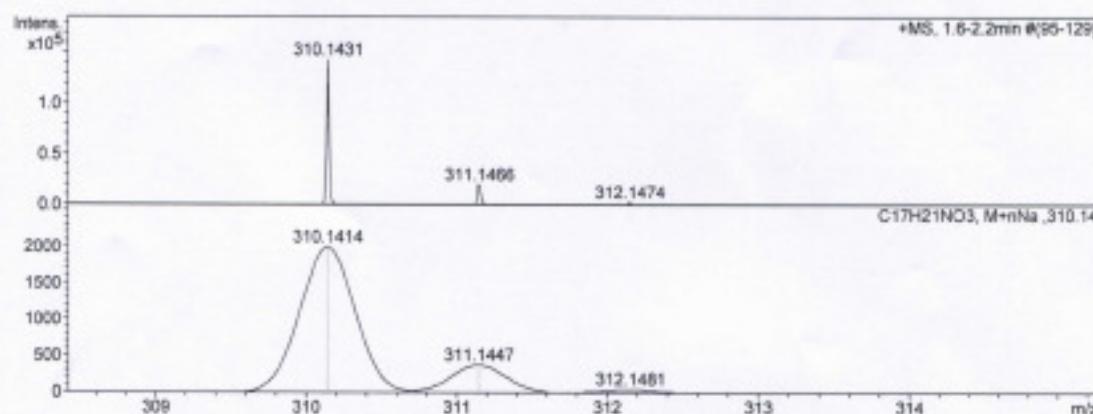
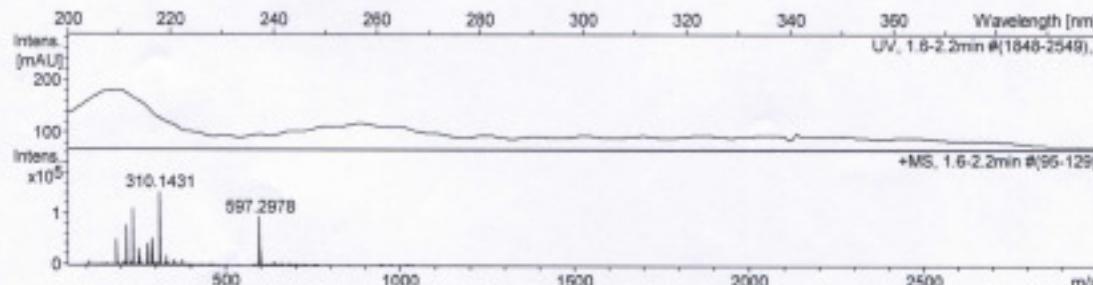
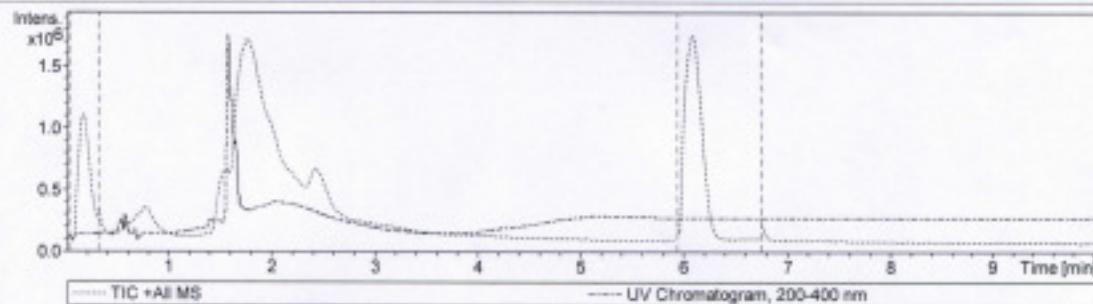
Display Report

Analysis Info

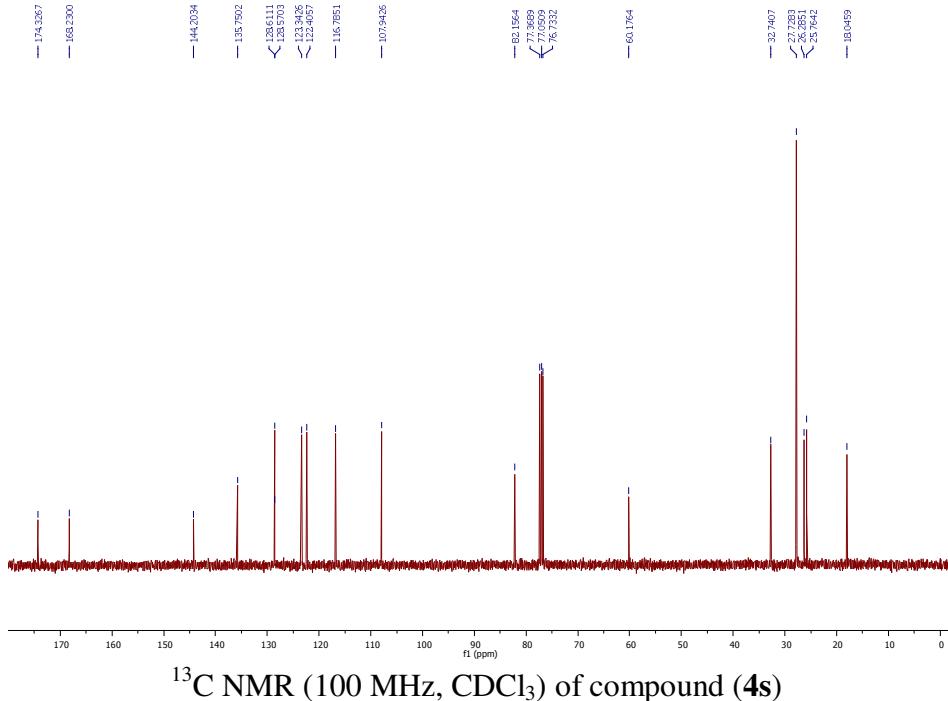
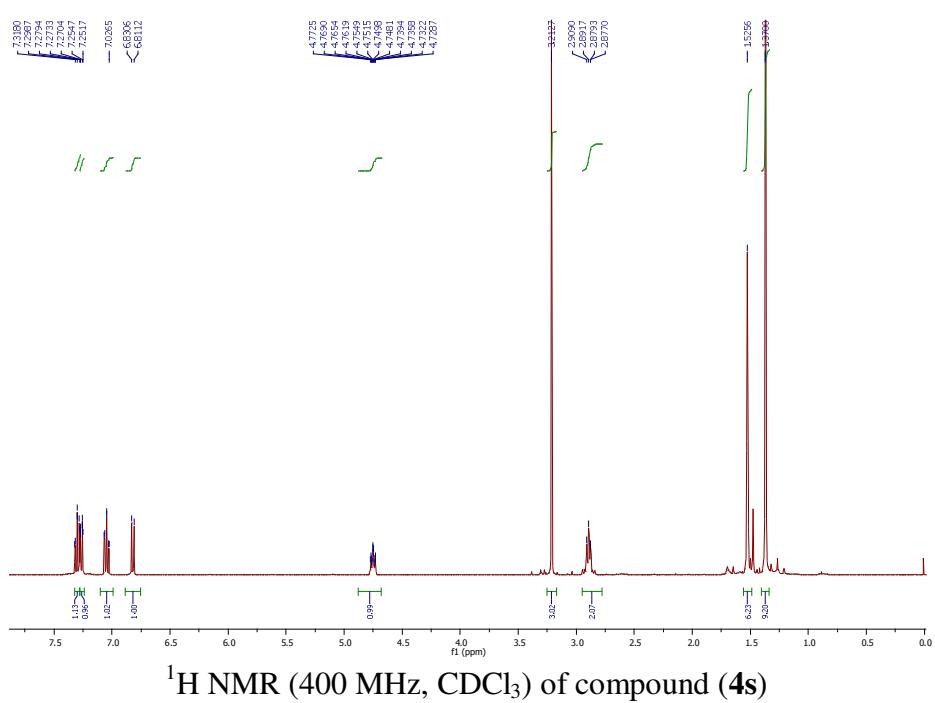
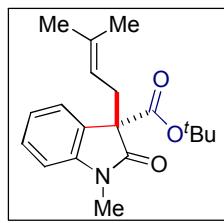
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Method	HRLCMS-20 Sept.m	Operator	Meena Sharma
Sample Name	Dr. A. Bisai- SG4-346	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

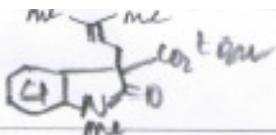
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
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Scanned copy of mass spectrum of compound (\pm)-4r



(4s)



Display Report

Analysis Info

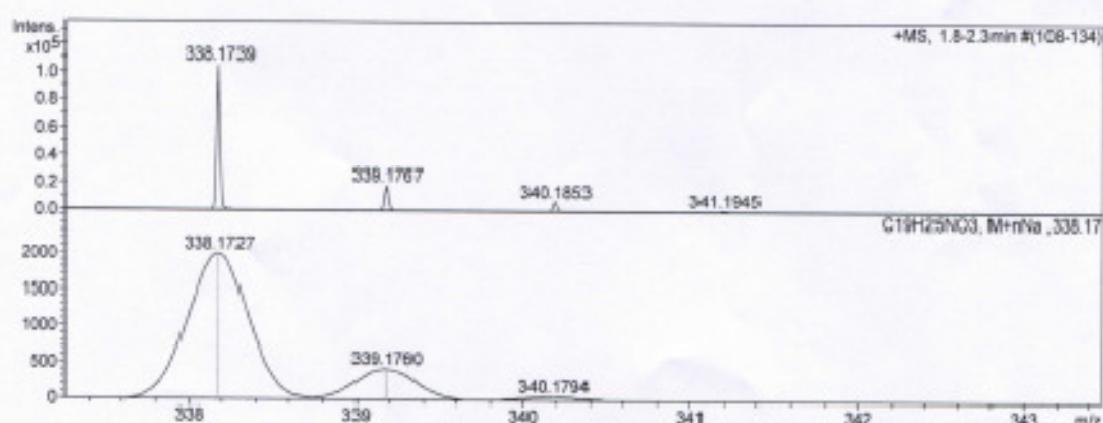
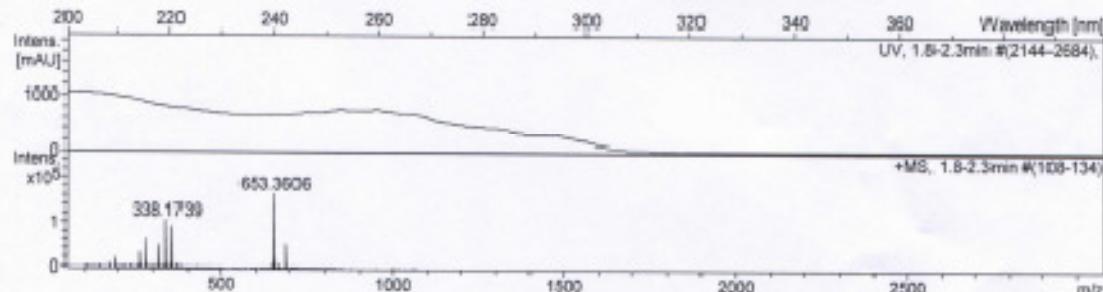
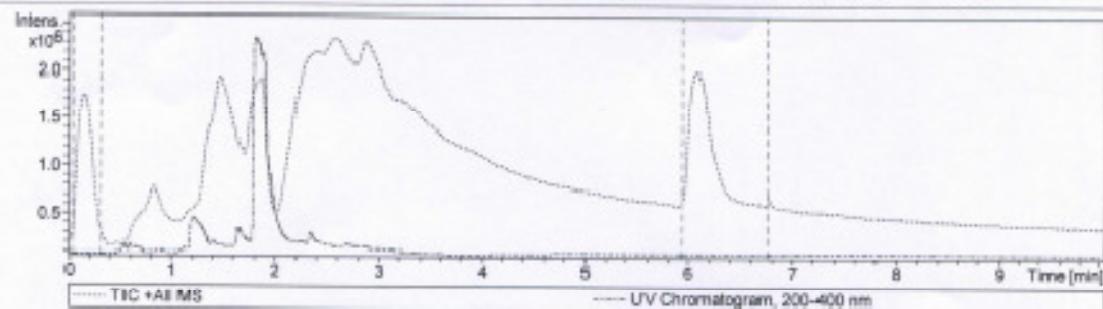
Analysis Name: D:\Data\user\data\April 2012\14 APR\Dr. A. Bisal- SG4-352_1-A,B_01_1782.d
Method: HRLCMS-20 Sept.m
Sample Name: Dr. A. Bisal- SG4-352
Comment:

Acquisition Date: 4/14/2012 4:07:41 PM

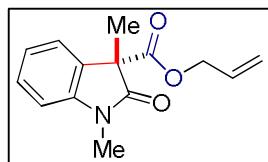
Operator: Meena Sharma
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

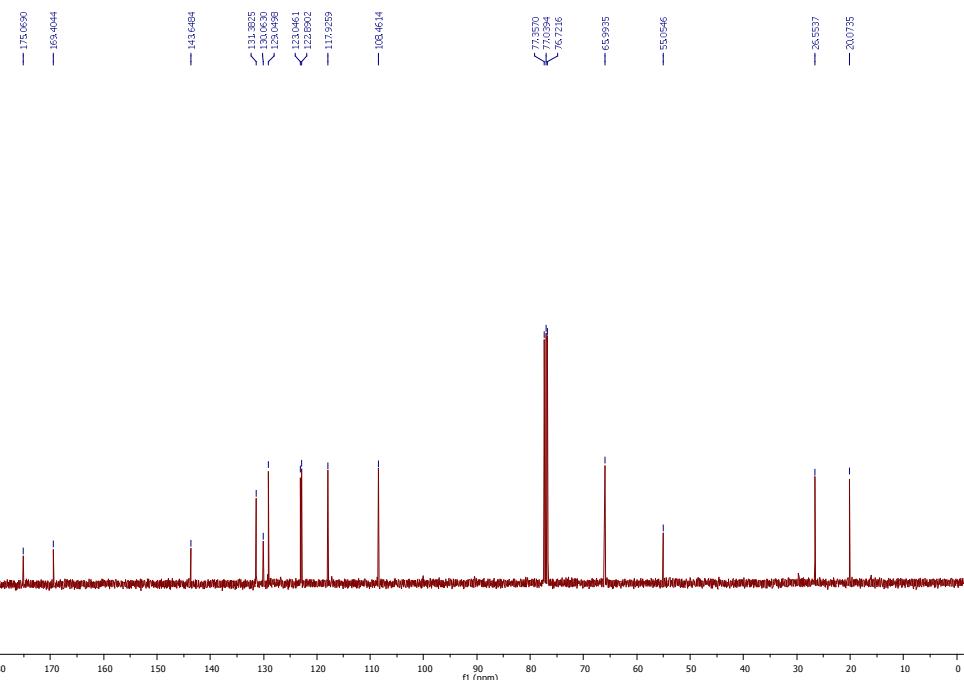
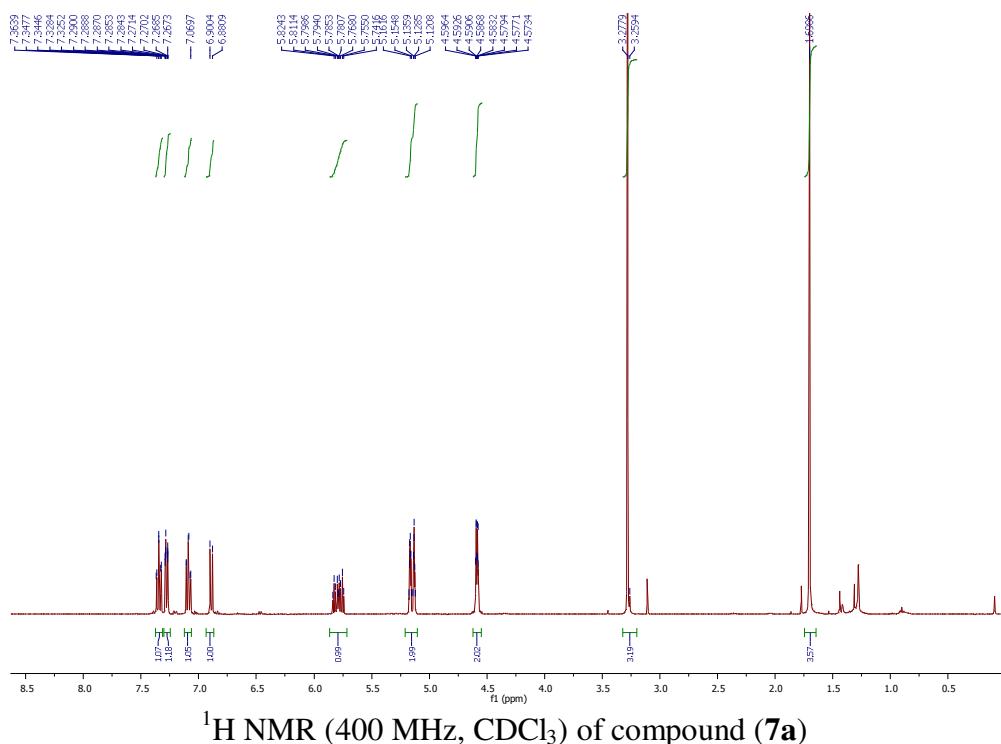
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

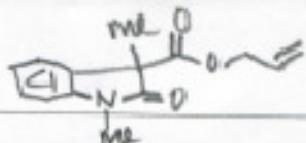


Scanned copy of mass spectrum of compound (\pm)-4s



(7a)





Display Report

Analysis Info

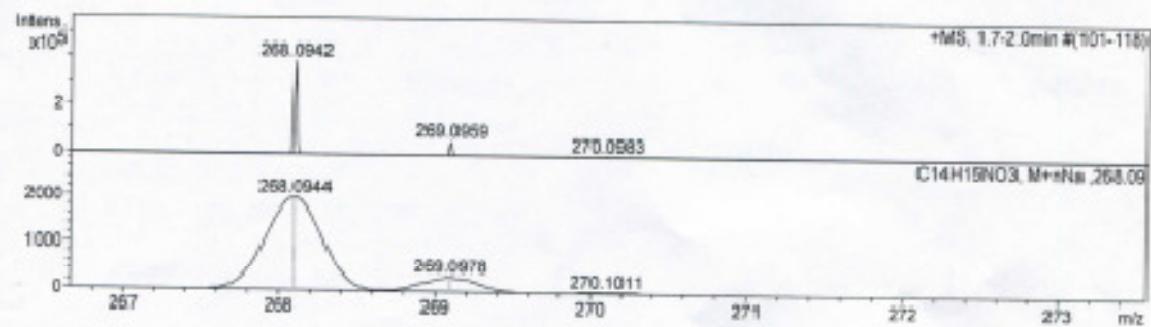
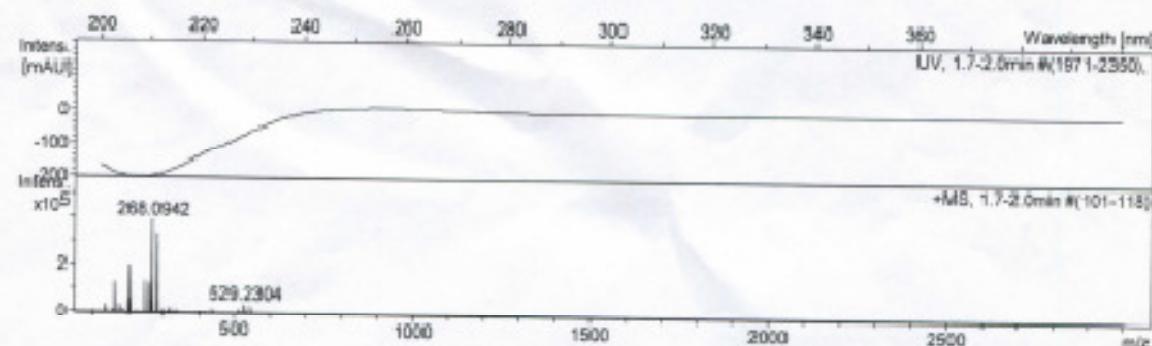
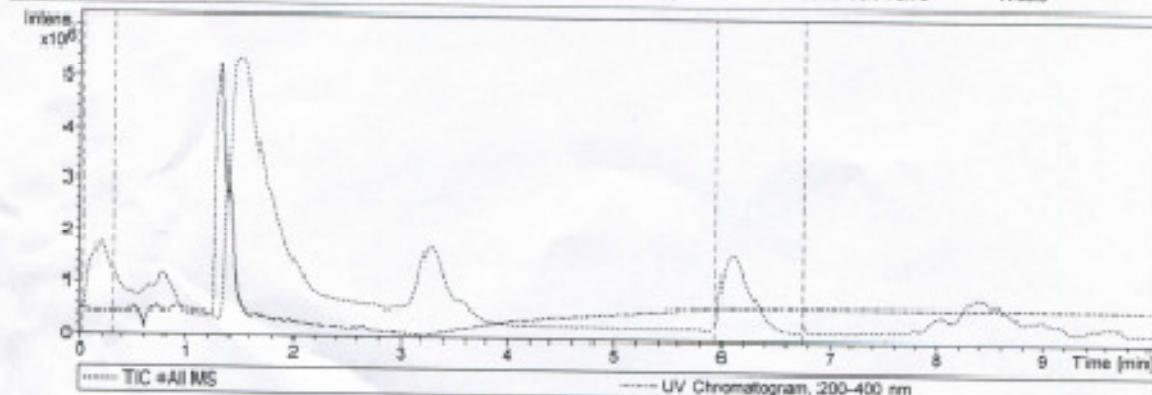
Analysis Name: D:\Data\user_data\DEC 01\Dr. A. Bisai-SG3-277_1-A_2_01_408.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-SG3-277
 Comment:

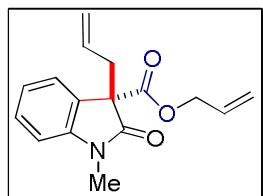
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

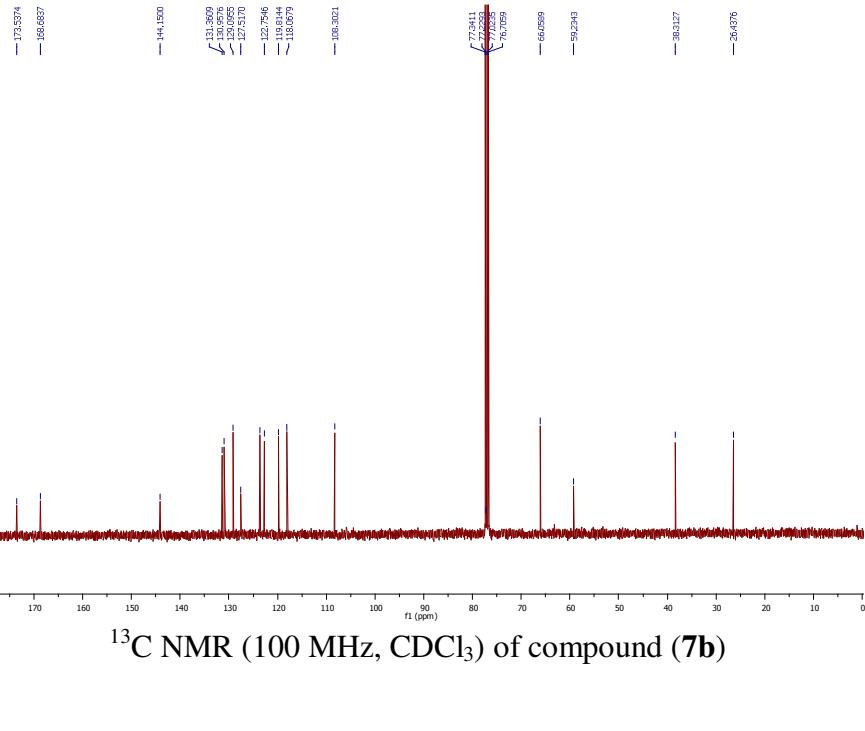
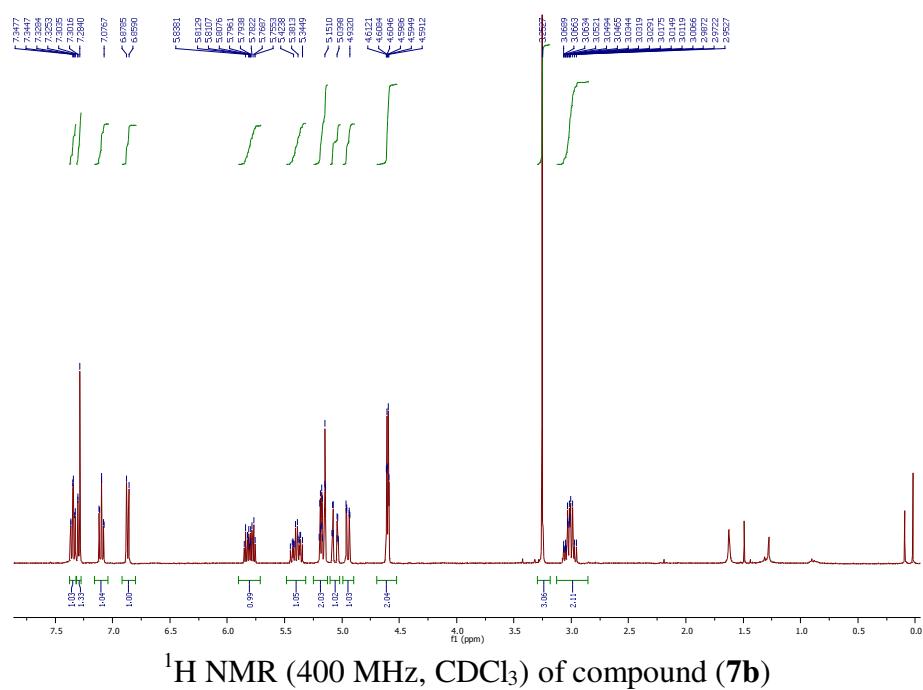
Acquisition Parameter

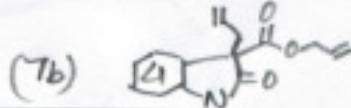
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell R/F	130.0 Vpp	Set Divert Valve	Waste





(7b)





me

Display Report

Analysis Info

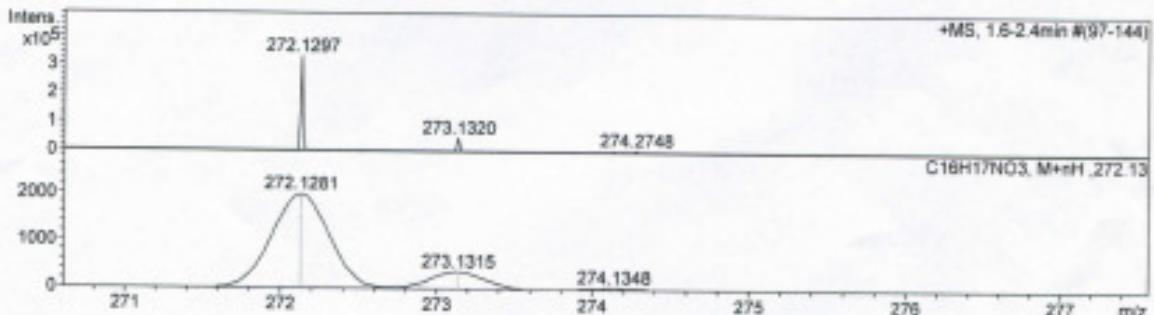
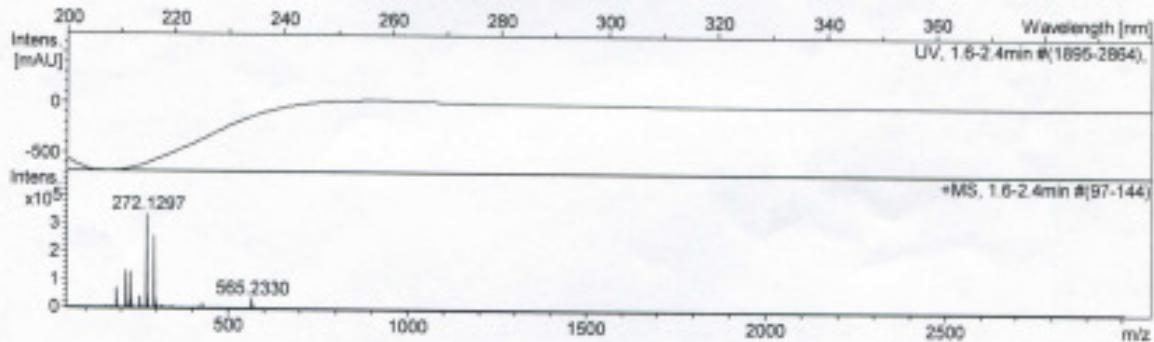
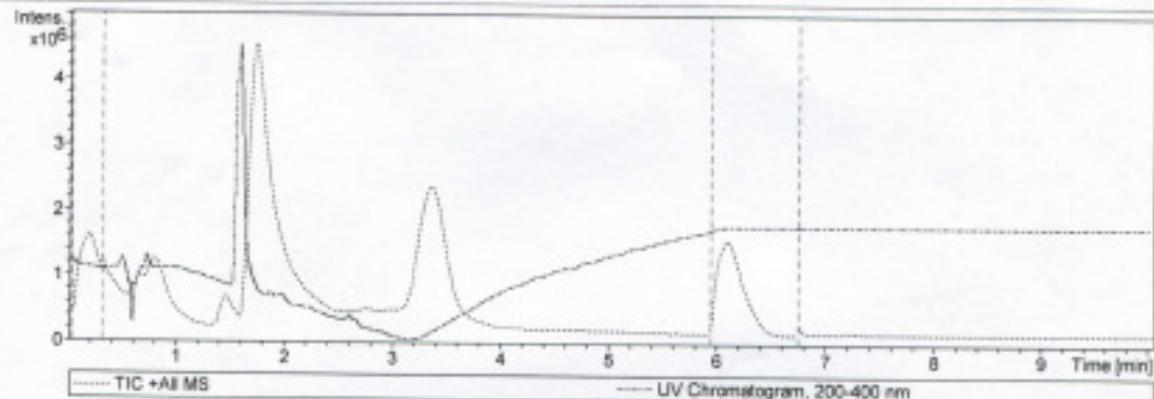
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-SG3-275
 Comment:

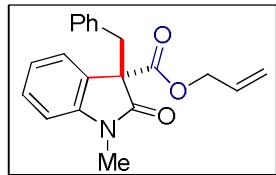
Acquisition Date: 11/30/2011 3:04:41 PM

Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

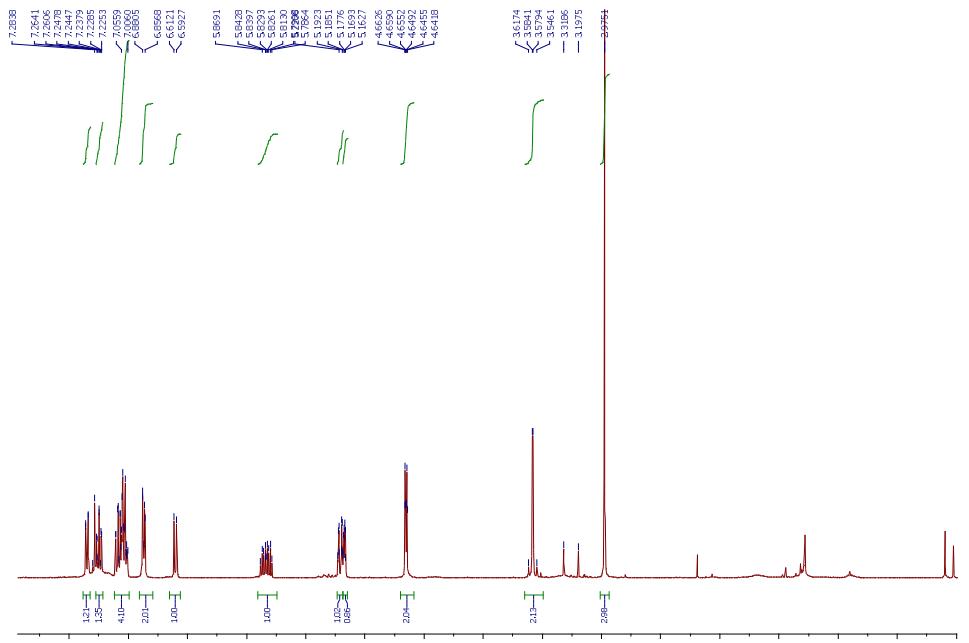
Acquisition Parameter

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Scan Begin	80 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





(7c)



¹H NMR (400 MHz, CDCl₃) of compound (7c)

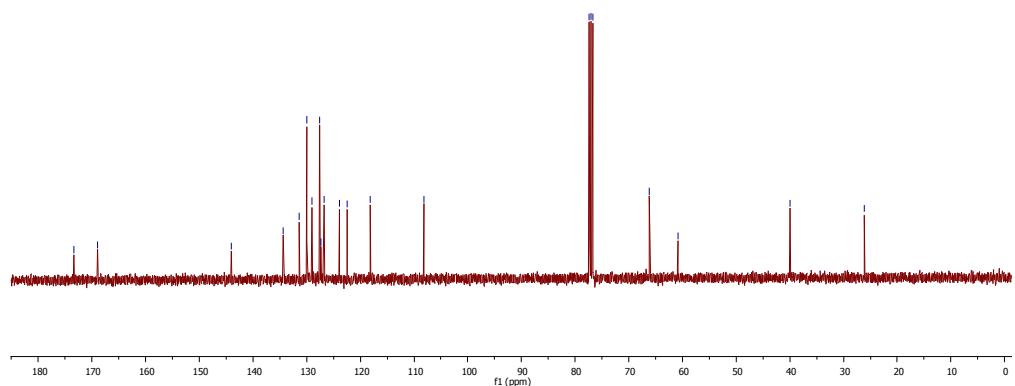
— 173,3605
— 168,9252

- 144 0796

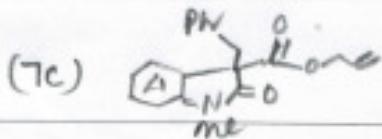
- 108.1770

76.7209
77.0385
77.3559

— 39739 —



¹³C NMR (100 MHz, CDCl₃) of compound (**7c**)



Display Report

Analysis Info

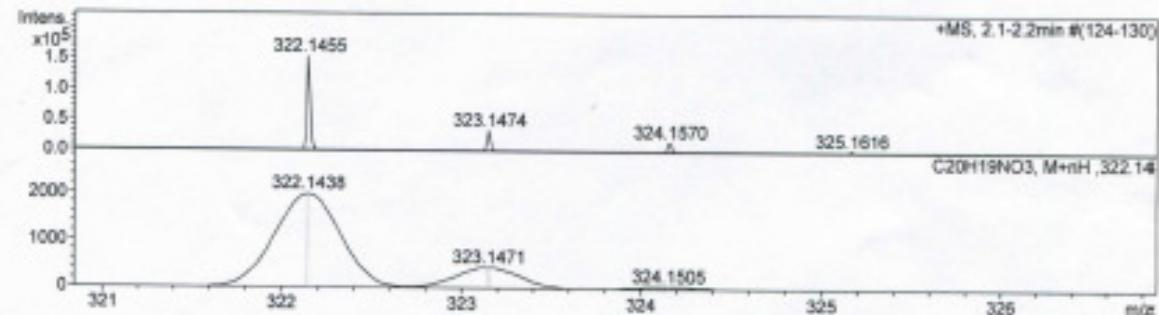
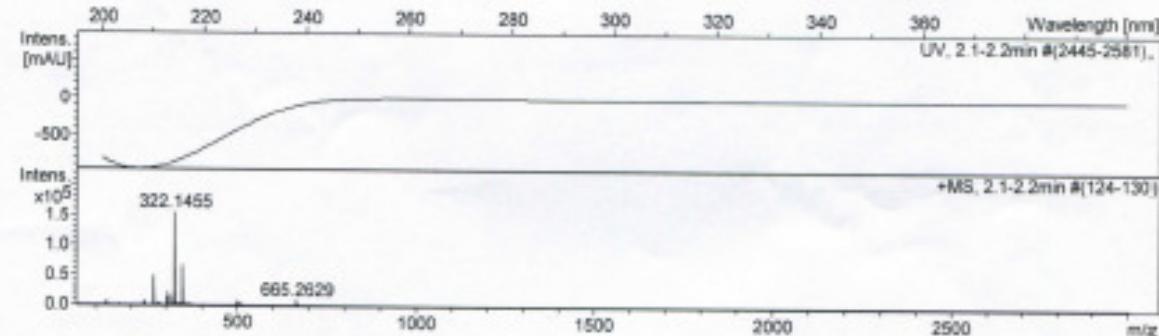
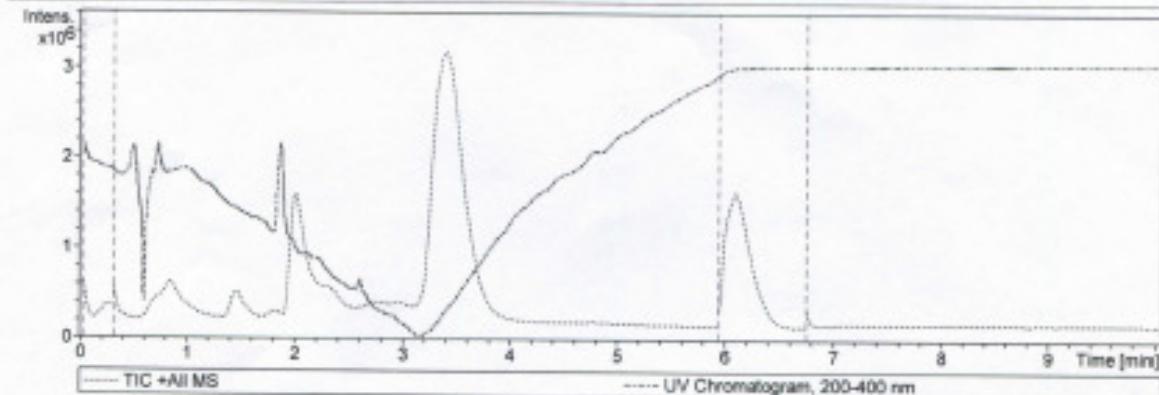
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-SG3-276
 Comment:

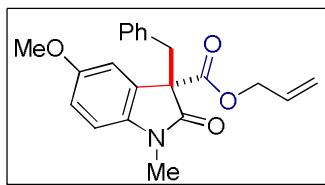
Acquisition Date: 11/30/2011 2:39:34 PM

 Operator: Meena Sharma
 Instrument: microOTOF-Q II 10330

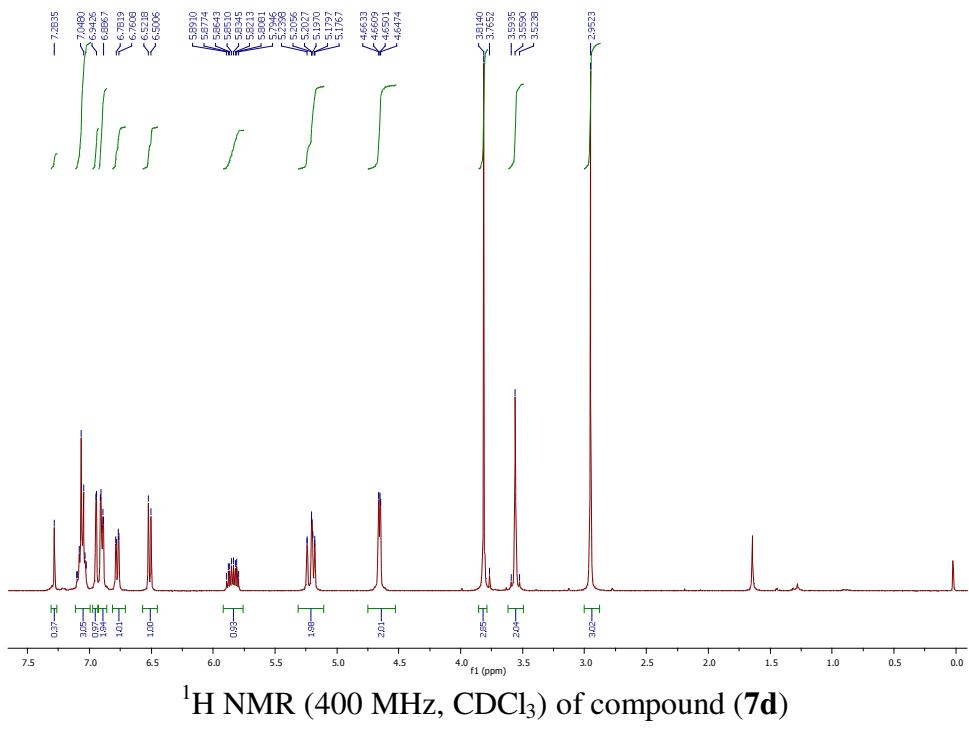
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



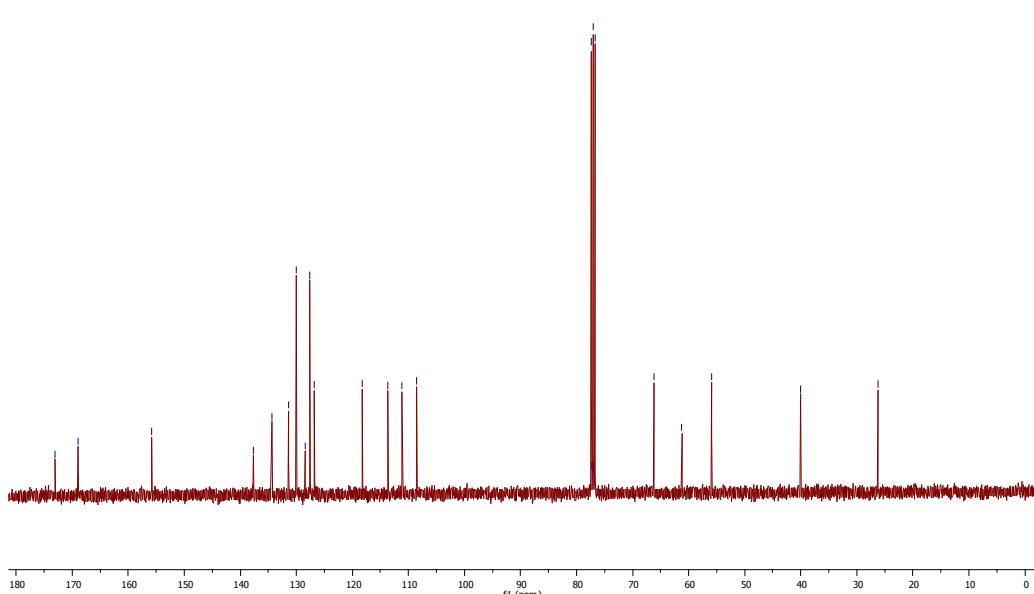


(7d)

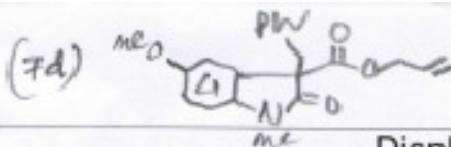


^1H NMR (400 MHz, CDCl_3) of compound (7d)

Peak labels (ppm):
 — 173.0119
 — 168.8922
 — 158.8995
 — 157.4945
 — 154.7853
 — 151.9563
 — 150.8886
 — 128.4456
 — 127.050
 — 126.1675
 — 118.2337
 — 113.0552
 — 111.1348
 — 108.2588
 — 77.3470
 — 77.2259
 — 77.0394
 — 76.7117
 — 66.1995
 — 61.2110
 — 55.9117
 — 40.0345
 — 26.2264



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



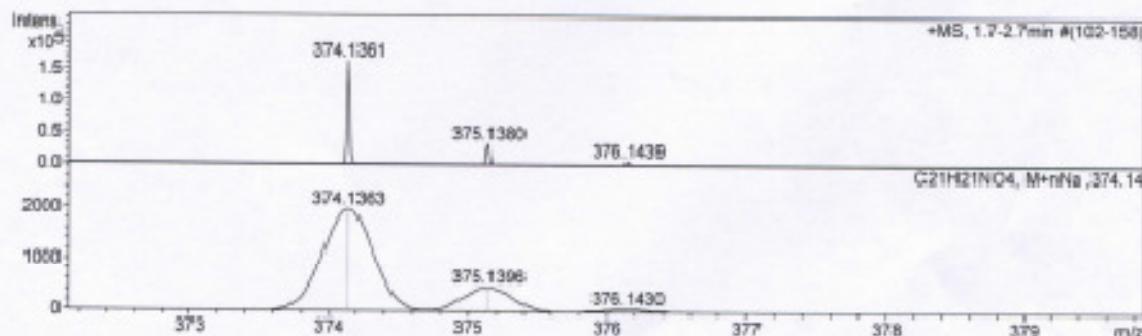
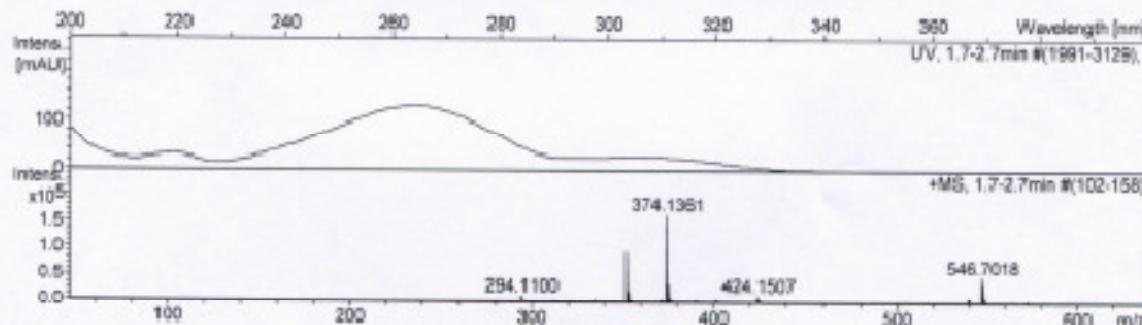
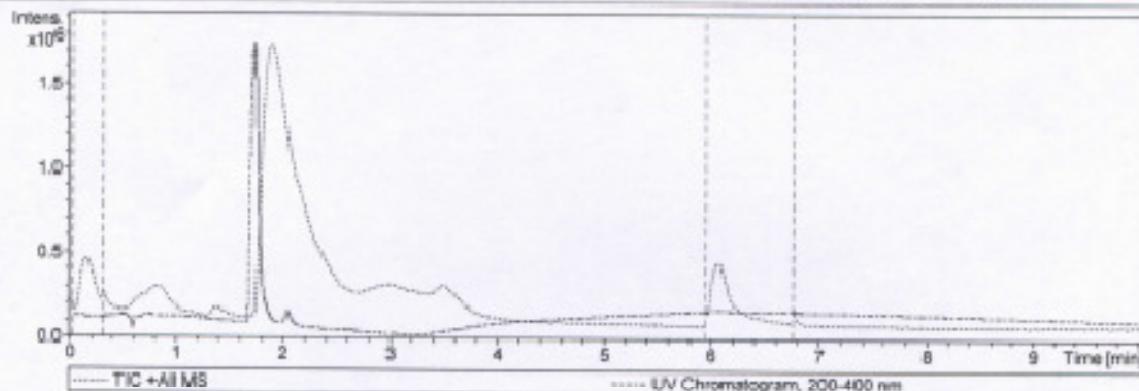
Display Report

Analysis Info

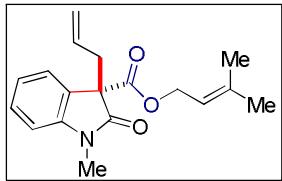
Analysis Name: D:\Data\user\data\DEC 23\Dr. A. Bisai-SG3-351_1-A,8_01_667.d Acquisition Date: 12/23/2011 3:33:37 PM
 Method: HRLCMS-20 Sept.m Operator: Meena Sharma
 Sample Name: Dr. A. Bisai-SG3-351 Instrument: micrOTOF-Q II 10330
 Comment:

Acquisition Parameter

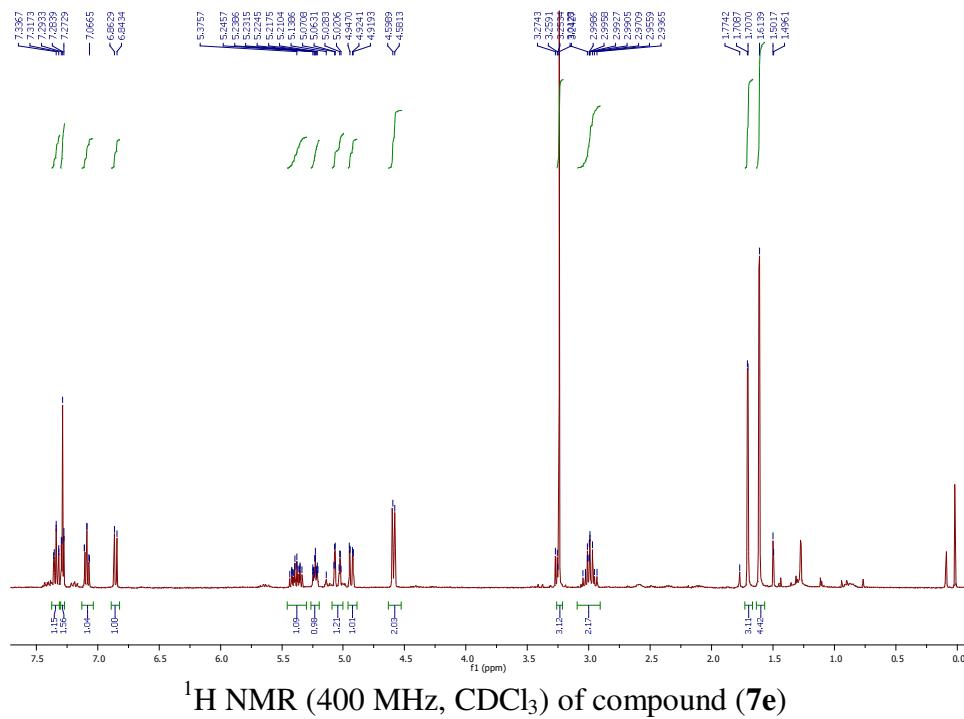
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FOCUS	Active	Set Capillary	-4500 V	Set Dry Heater	266 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



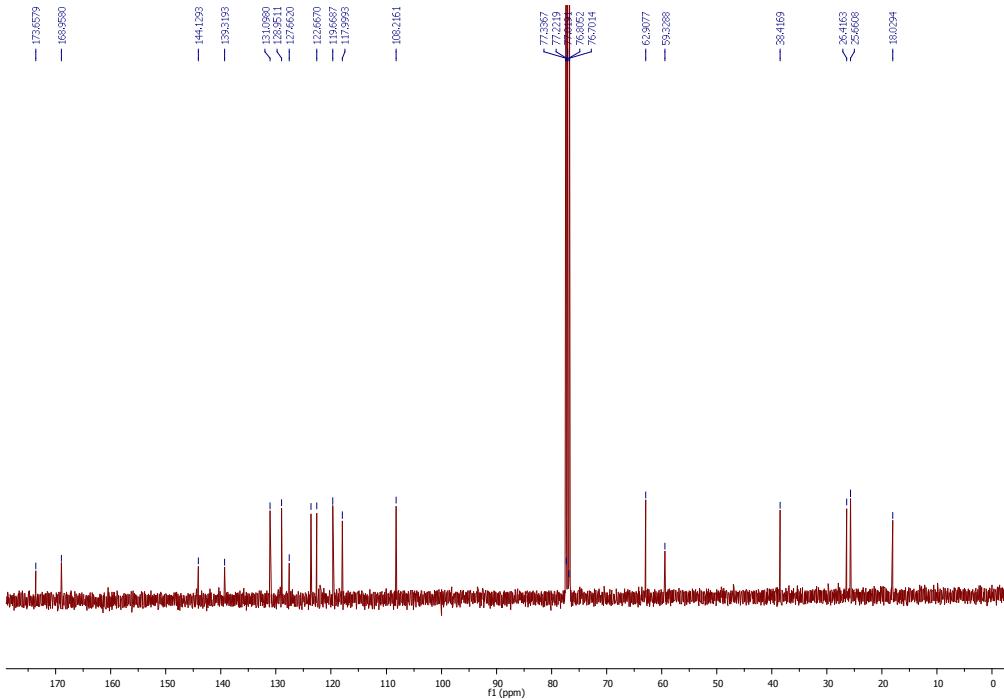
Scanned copy of mass spectrum of compound (\pm)-7d



(7e)

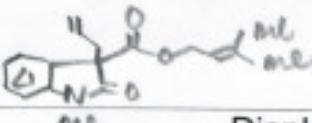


¹H NMR (400 MHz, CDCl₃) of compound (**7e**)



¹³C NMR (100 MHz, CDCl₃) of compound (**7e**)

(7e)



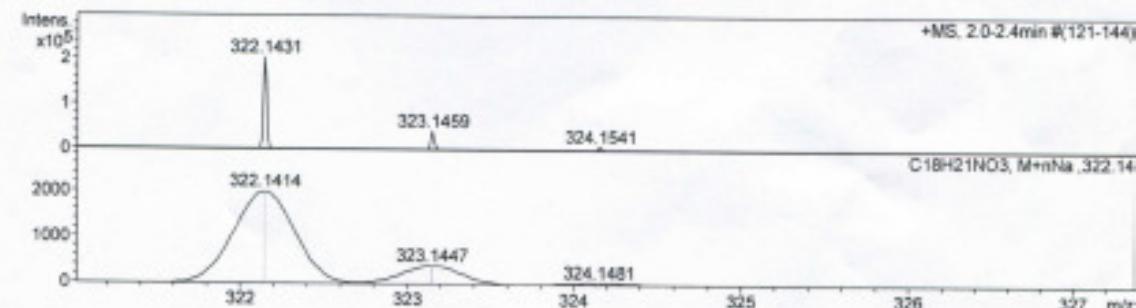
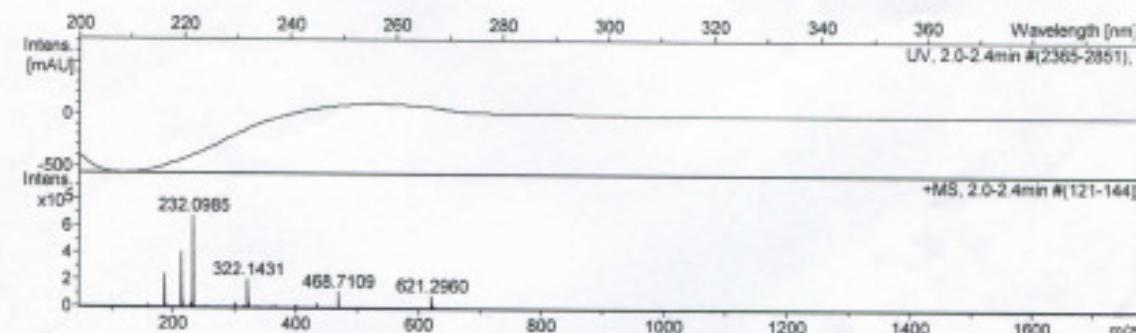
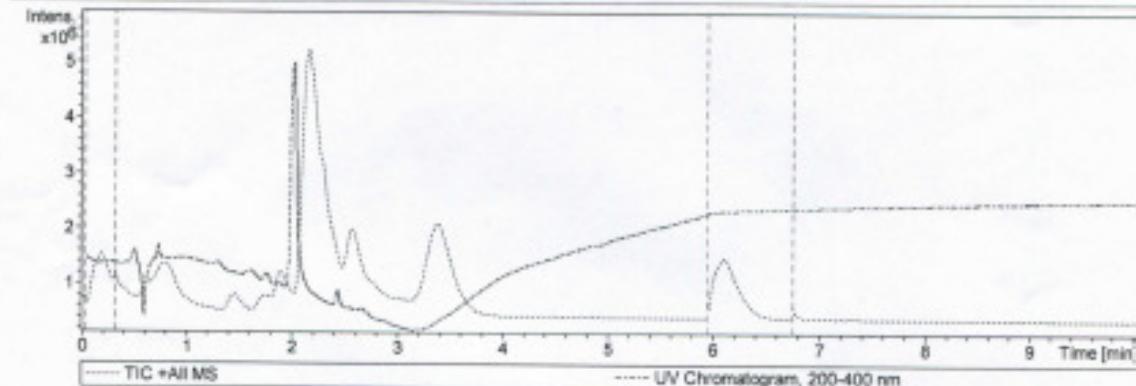
Display Report

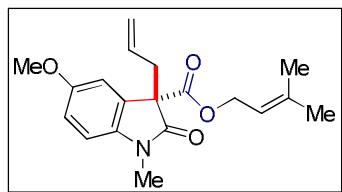
Analysis Info

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Method	HRLCMS-20 Sept.m	Operator	Meena Sharma
Sample Name	Dr. A. Bisai-AB-SG3-271	Instrument	micrOTOF-Q II 10330
Comment			

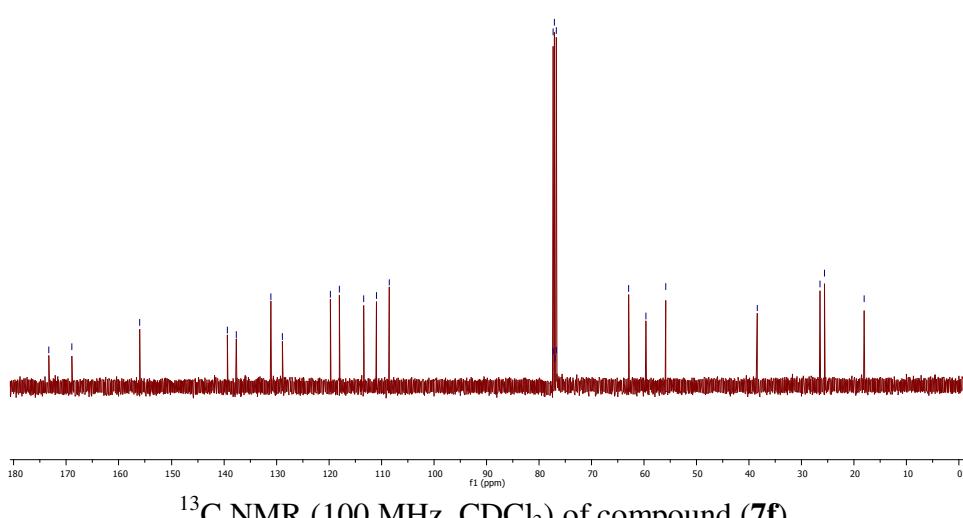
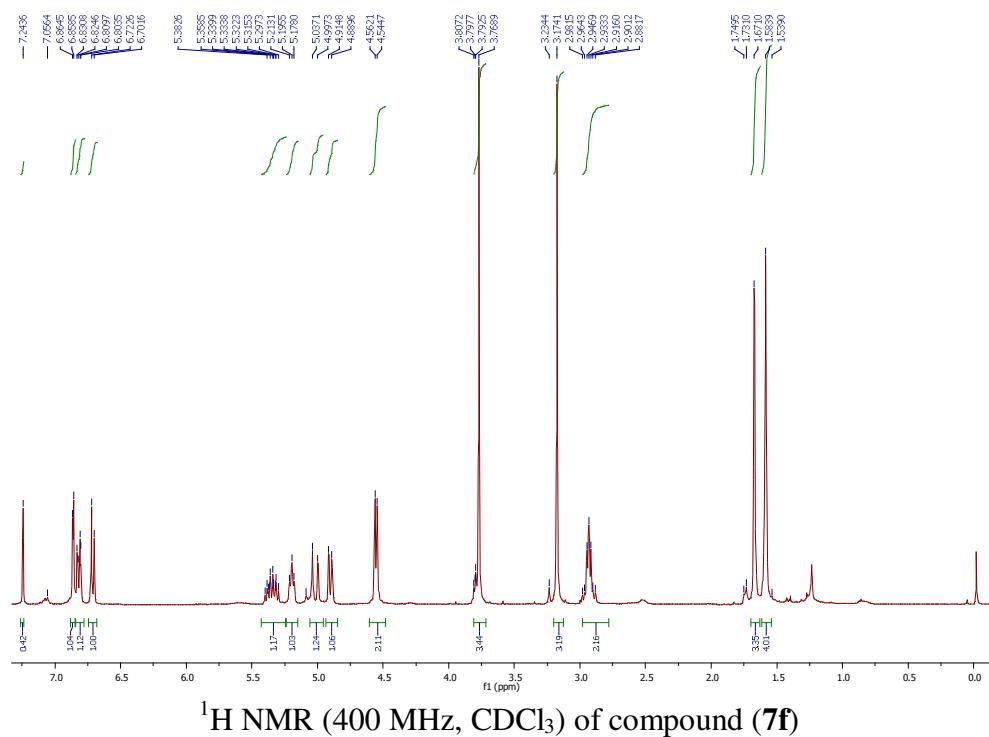
Acquisition Parameter

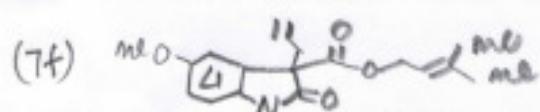
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





(7f)





Display Report

Analysis Info

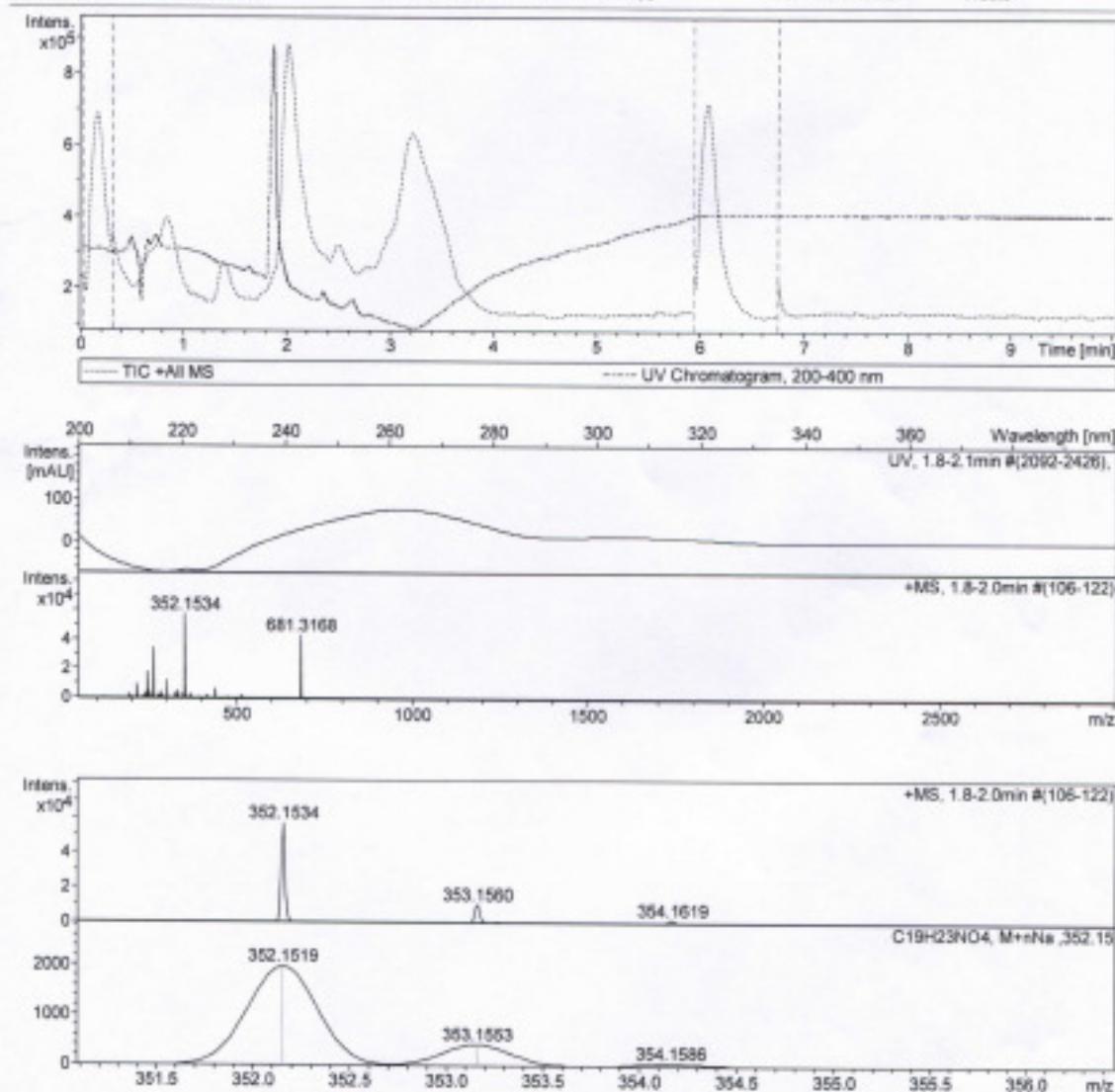
Analysis Name: D:\Data\user data\DEC 17\Dr. A. Bisai- SG3-332_1-A,5_01_586.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG3-332
 Comment:

Acquisition Date: 12/17/2011 2:54:11 PM

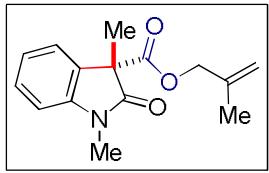
Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

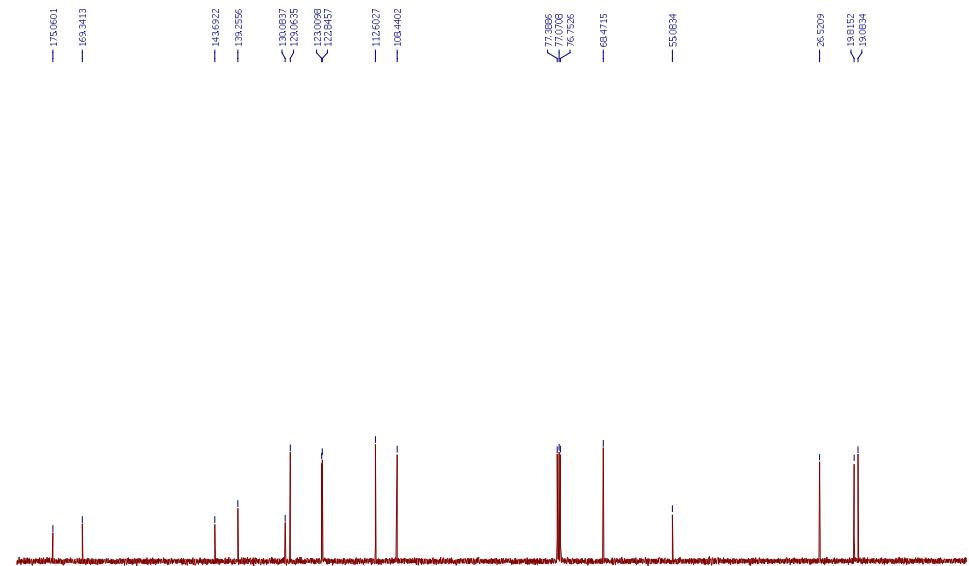
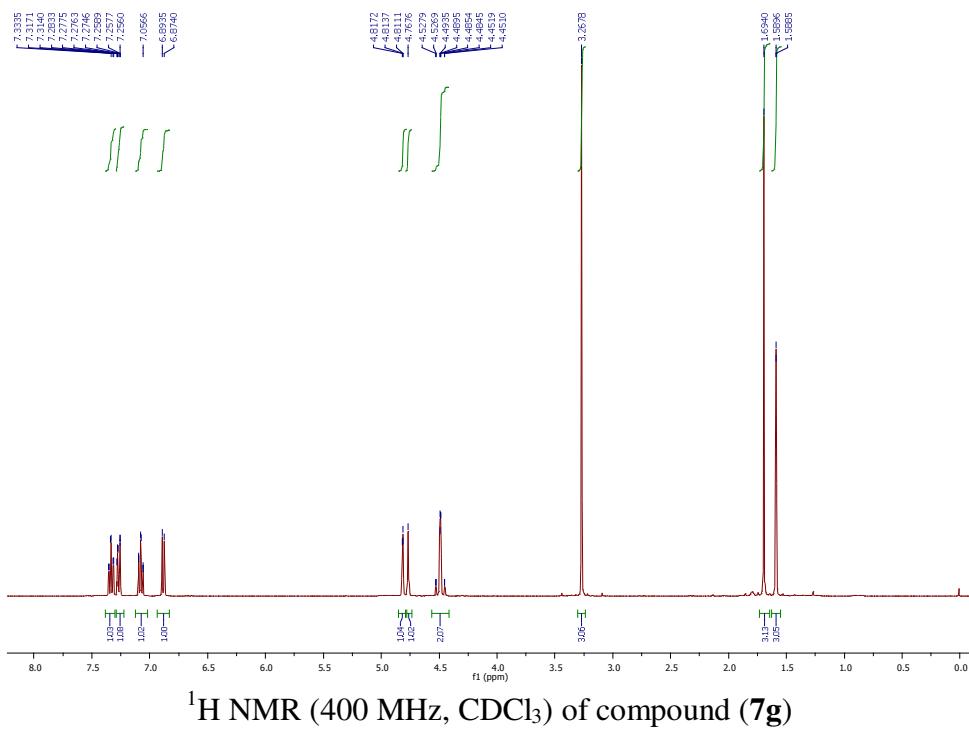
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



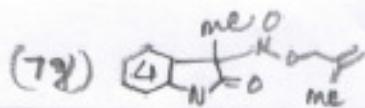
Scanned copy of mass spectrum of compound (\pm)-7f



(7g)



¹³C NMR (100 MHz, CDCl₃) of compound (7g)



Display Report

Analysis Info

Analysis Name: D:\Data\user data\JAN 2012\6 janvDr. A. bisai-SG4-16_1-A_5_01_802.d
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 Sample Name: Dr. A. bisai-SG4-16
 Comment:

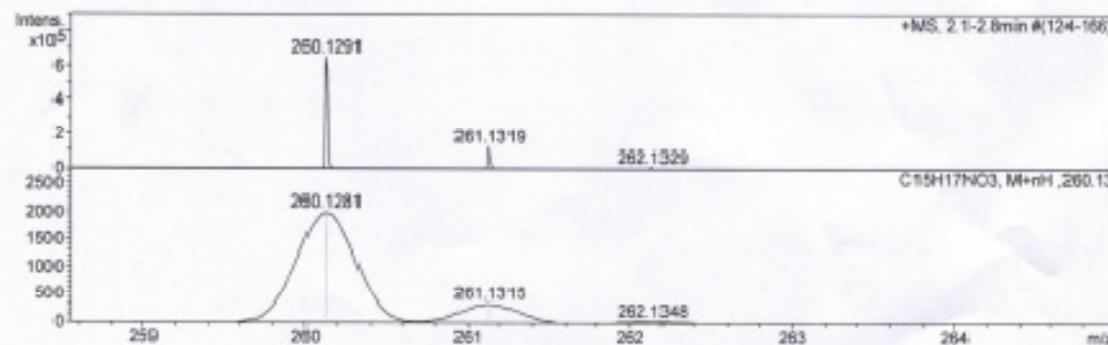
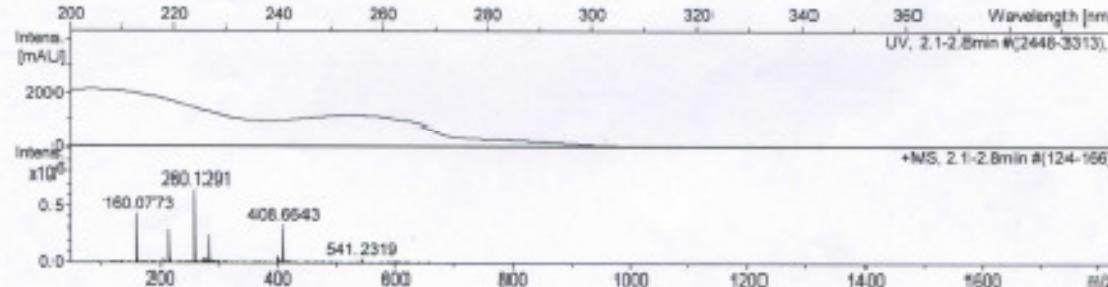
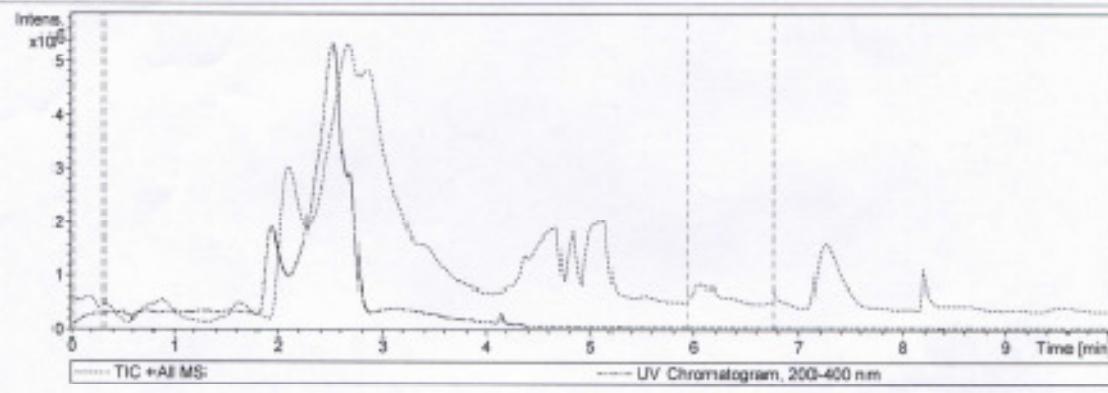
Acquisition Date: 1/6/2012 2:49:41 PM

Operator: Meena Sharma

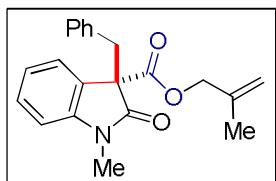
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

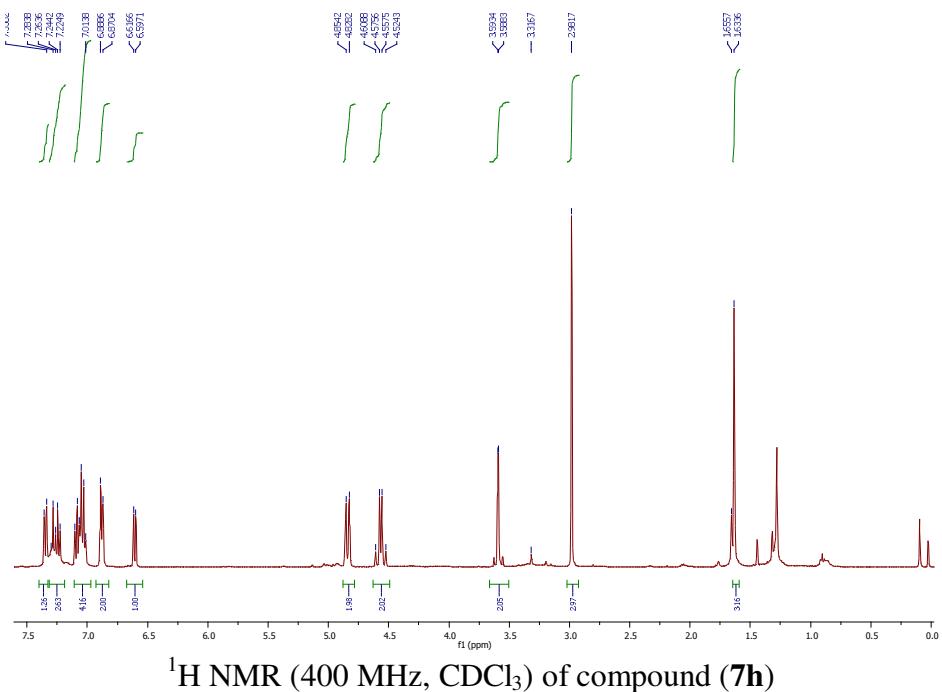
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



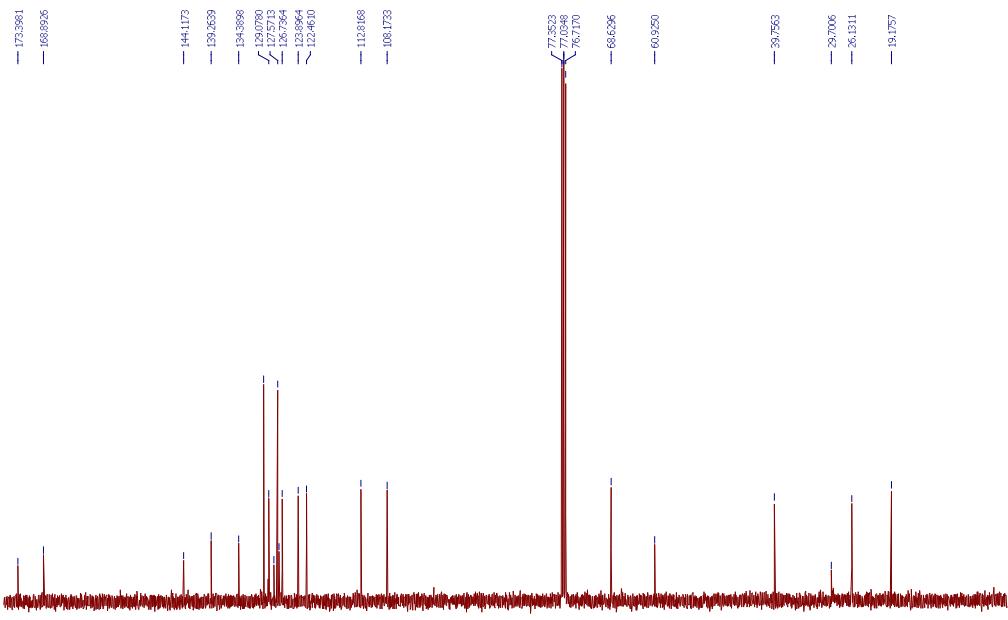
Scanned copy of mass spectrum of compound (\pm)-7g



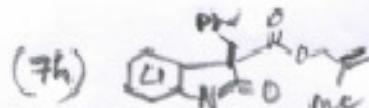
(7h)



^1H NMR (400 MHz, CDCl_3) of compound (7h)



^{13}C NMR (100 MHz, CDCl_3) of compound (7h)



Display Report

Analysis Info

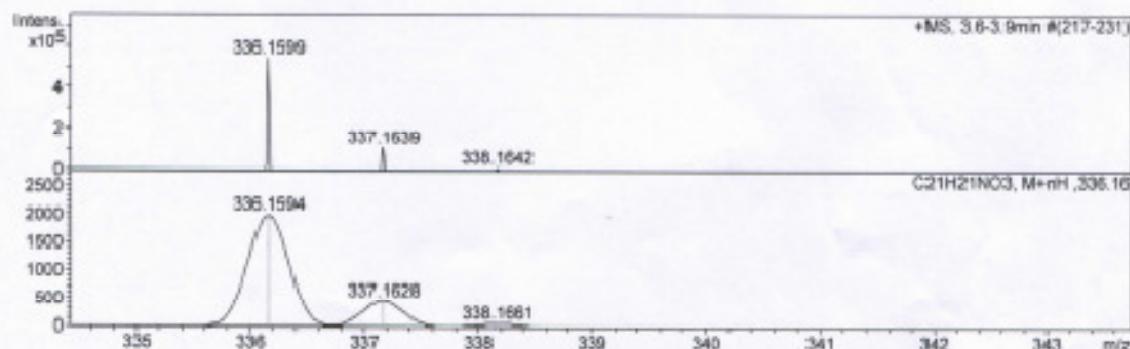
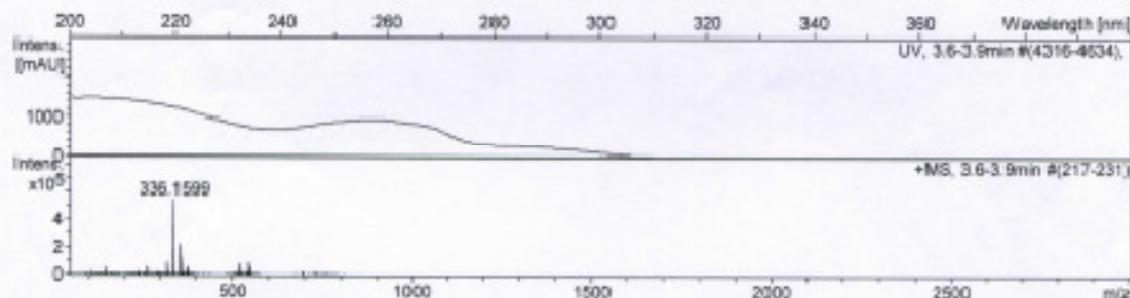
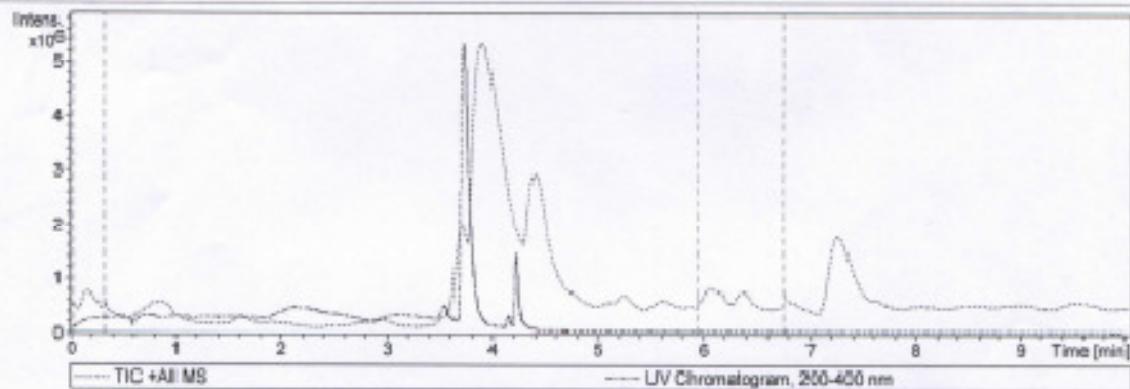
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 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. bisai-SG4-17
 Comment

Acquisition Date 1/6/2012 3:00:56 PM

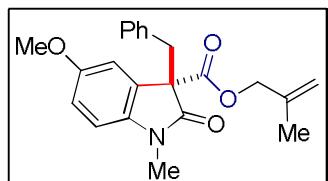
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

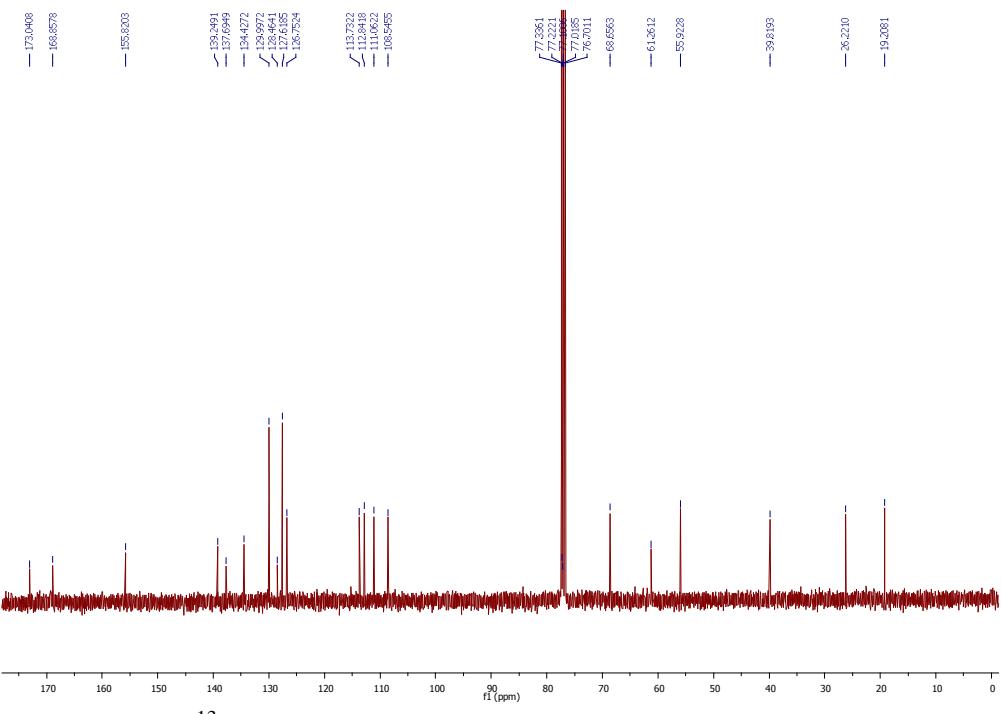
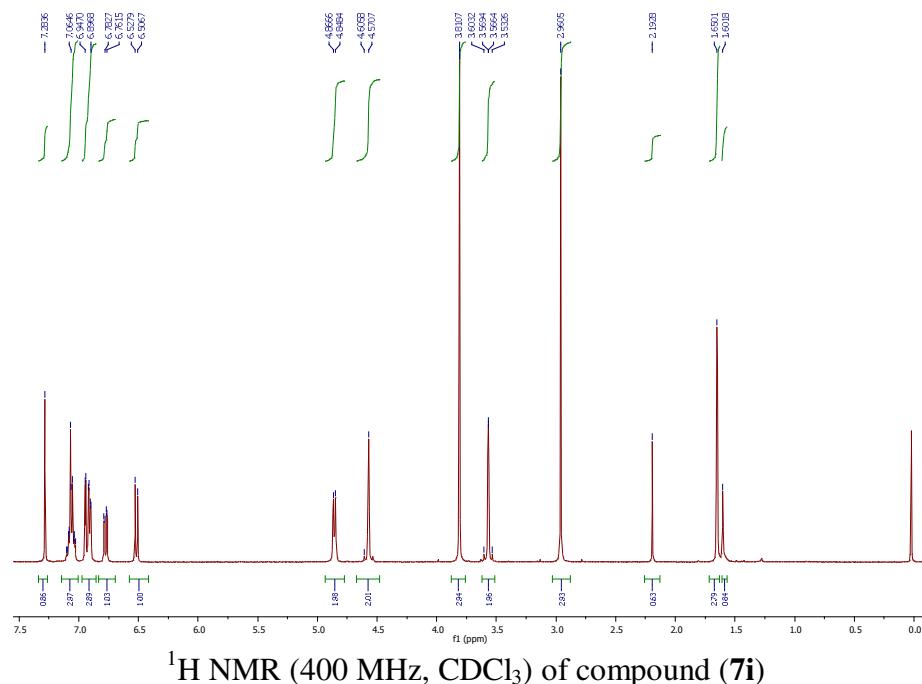
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Scan End	3050 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

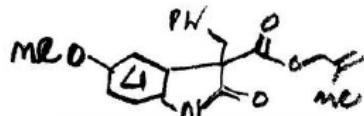


Scanned copy of mass spectrum of compound (\pm)-7h



(7i)





Display Report

Analysis Info

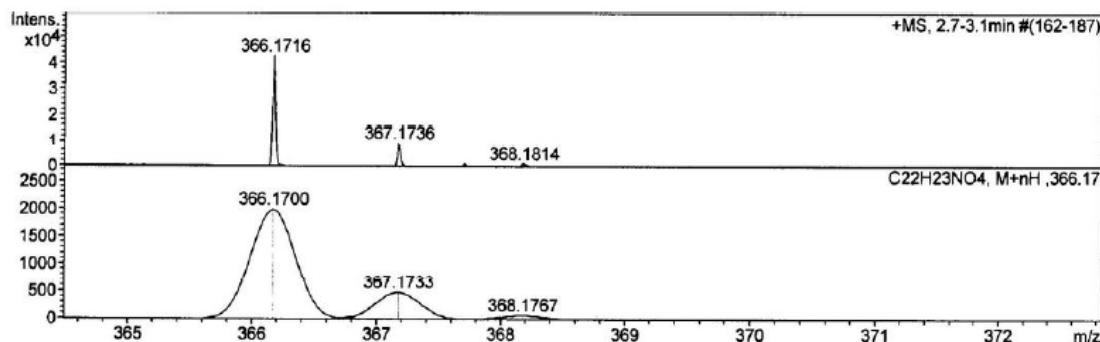
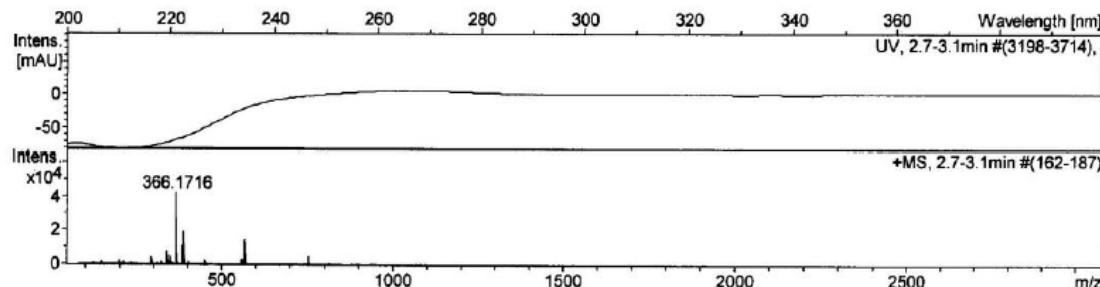
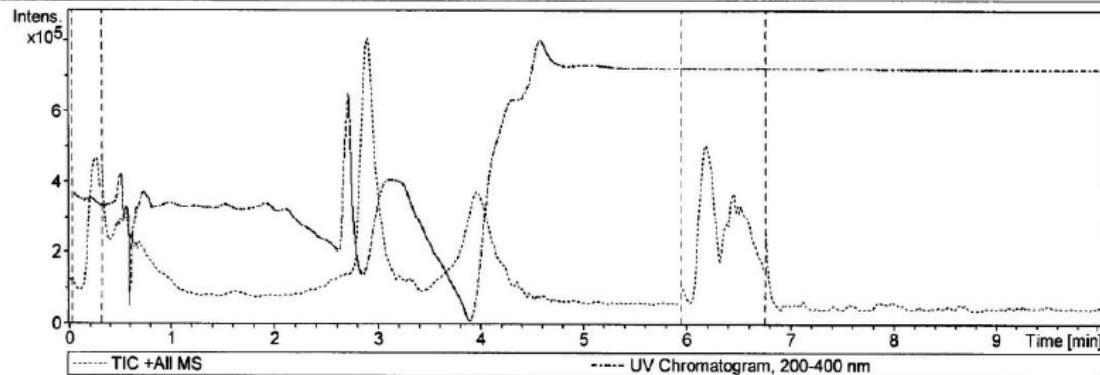
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 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai-SG4-22
 Comment

Acquisition Date 1/9/2012 2:54:29 PM

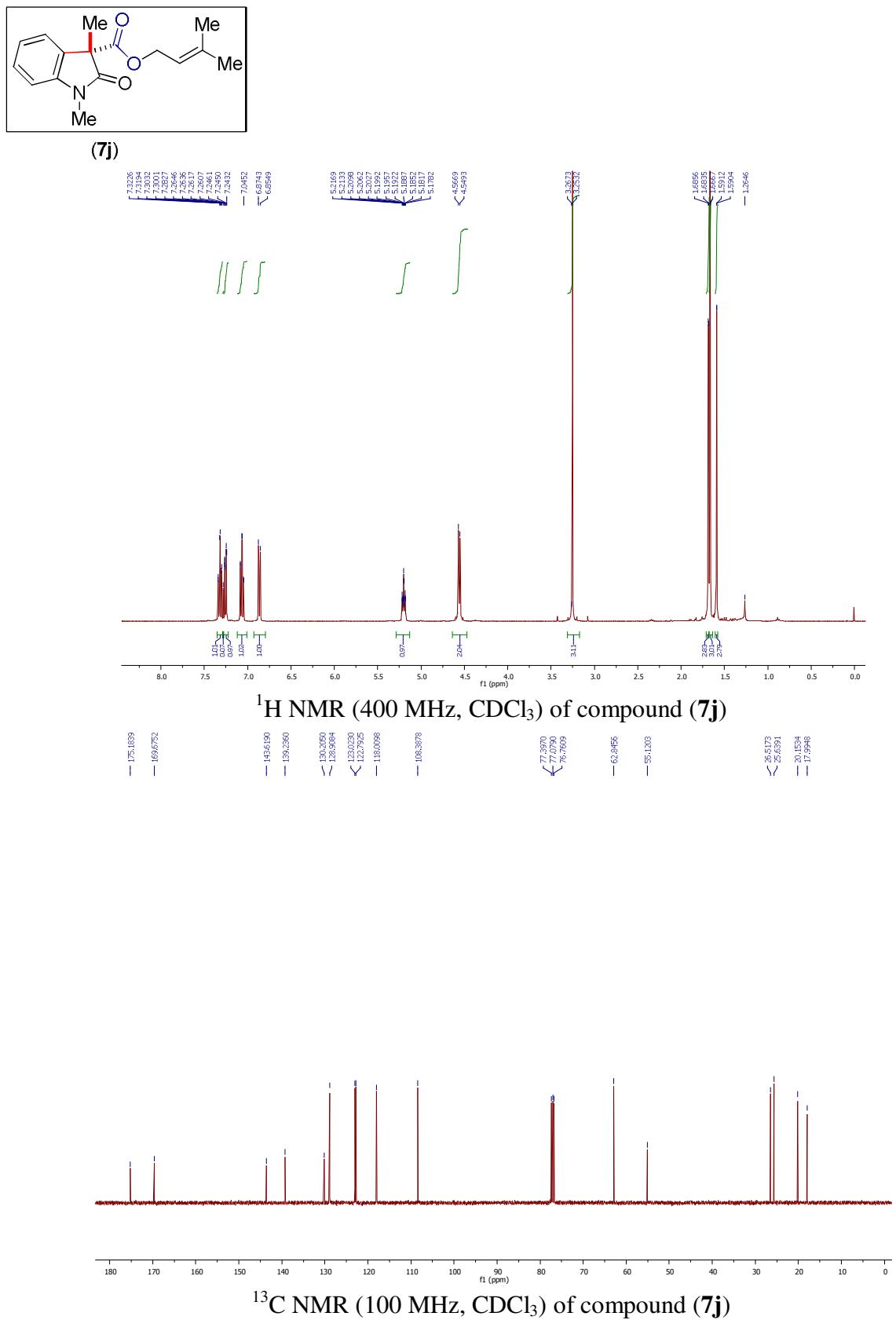
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

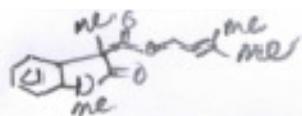
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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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 compound (\pm)-7i





Display Report

Analysis Info

Analysis Name: D:\Data\user data\April 2012\16 april\Dr. A. Bisal- SG4- 340_1-A_5_01_1796.d
 Method: HRICMS-20 Sept.m
 Sample Name: Dr. A. Bisal- SG4- 340
 Comment:

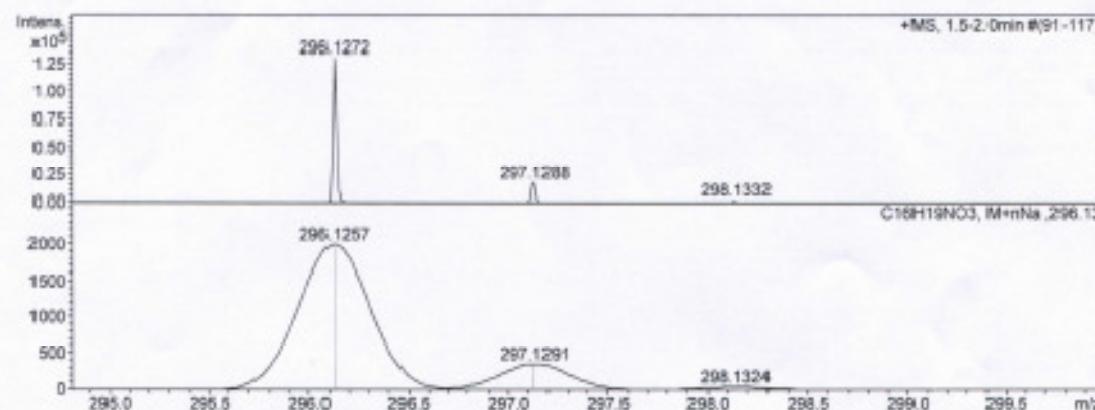
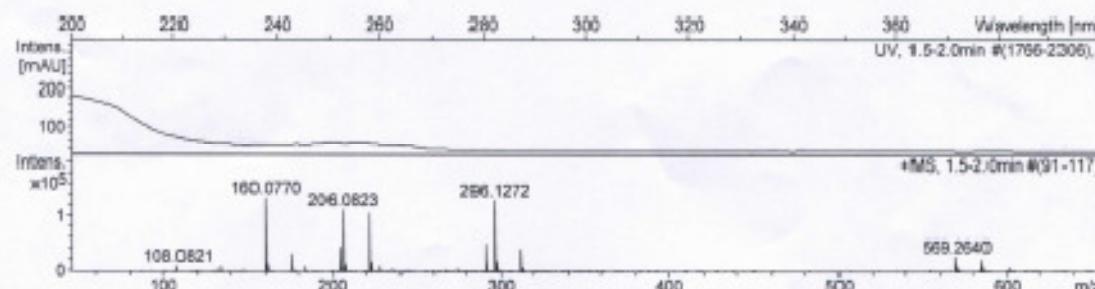
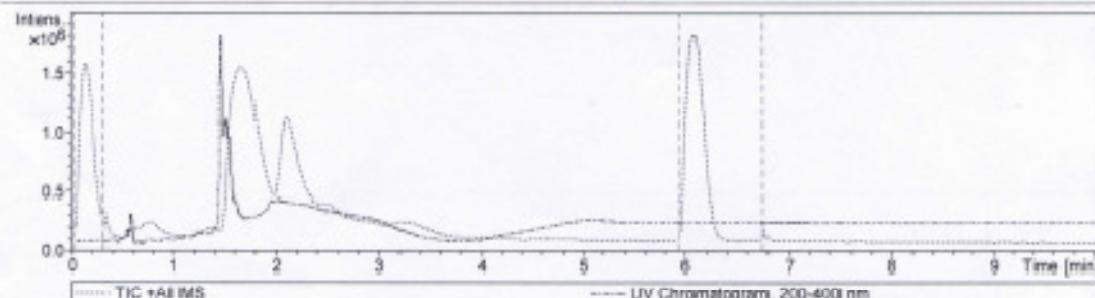
Acquisition Date: 4/16/2012 4:09:26 PM

Operator: Meena Sharma

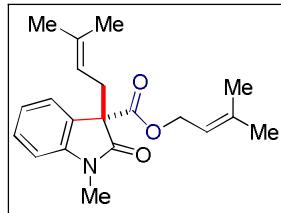
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

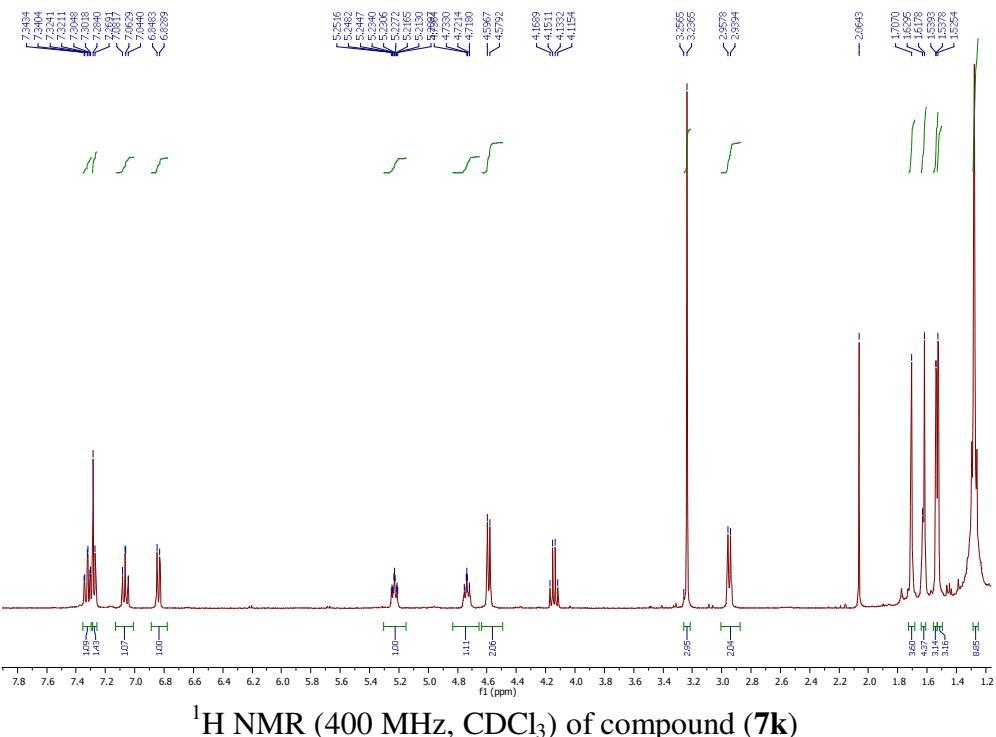
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

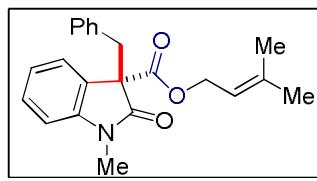


Scanned copy of mass spectrum of compound (\pm)-7j

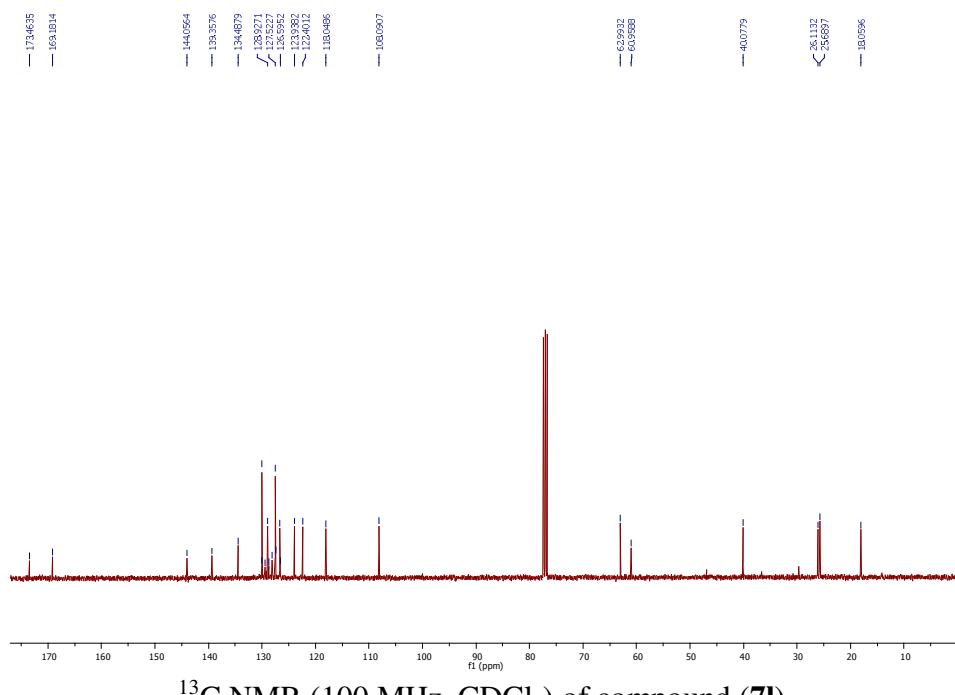
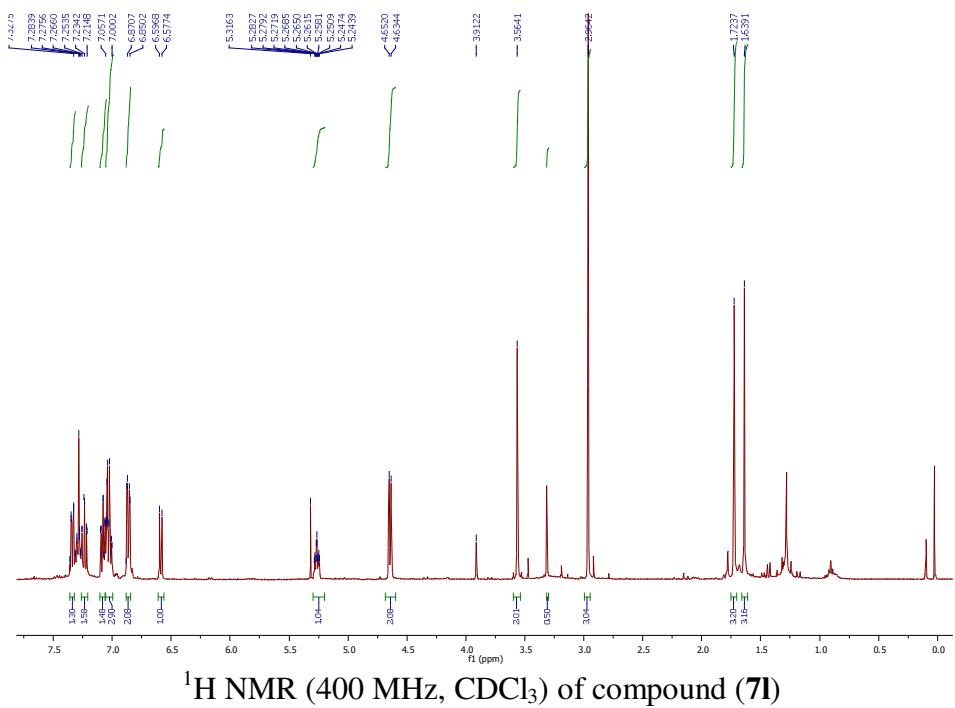


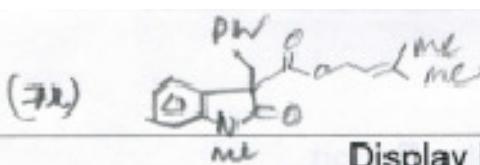
(7k)





(7l)





Display Report

Analysis Info

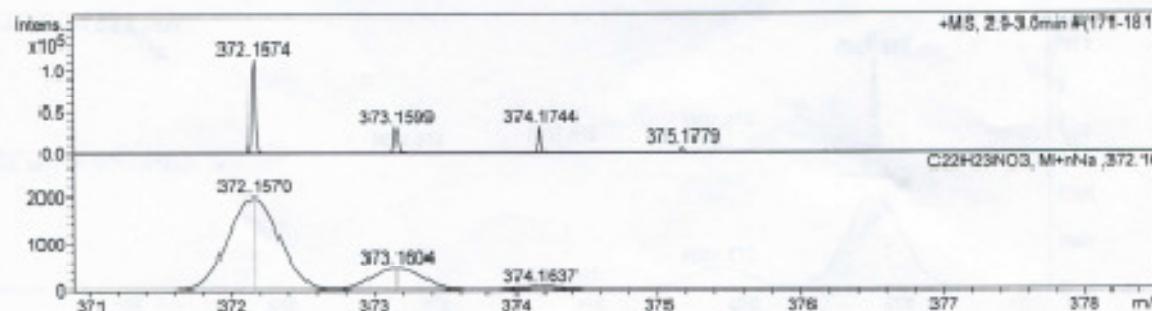
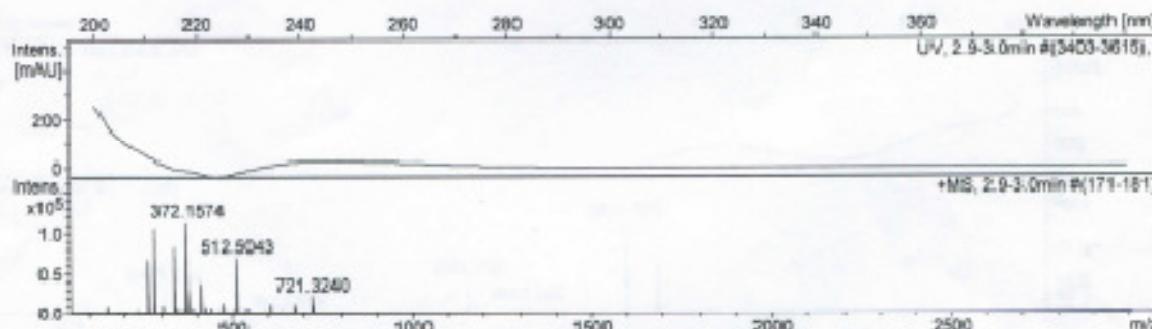
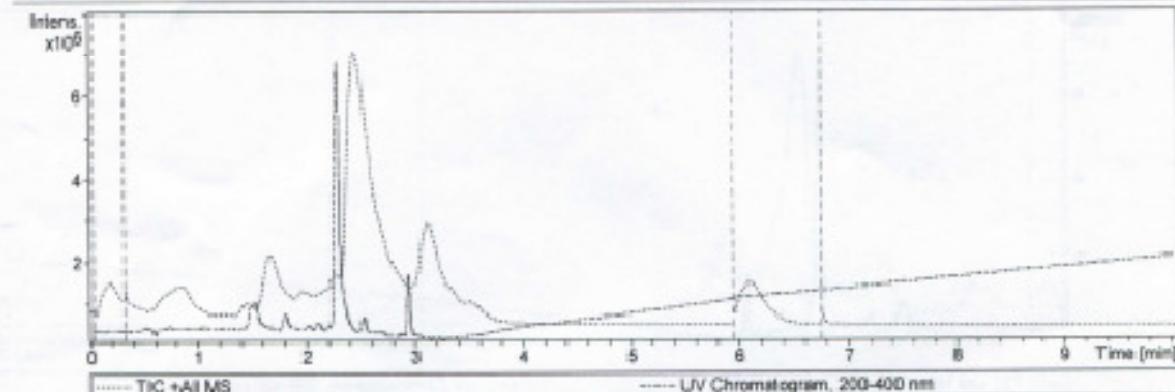
Analysis Name: D:\Data\user\data\NIOW 29\Dr. A. Bisai-AB-SG3-272_1-A,A_01_385.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-AB-SG3-272
 Comment:

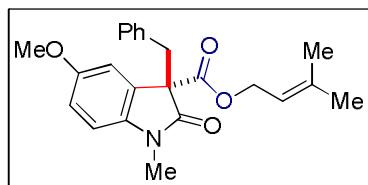
Acquisition Date: 11/28/2011 1:47:23 PM

Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

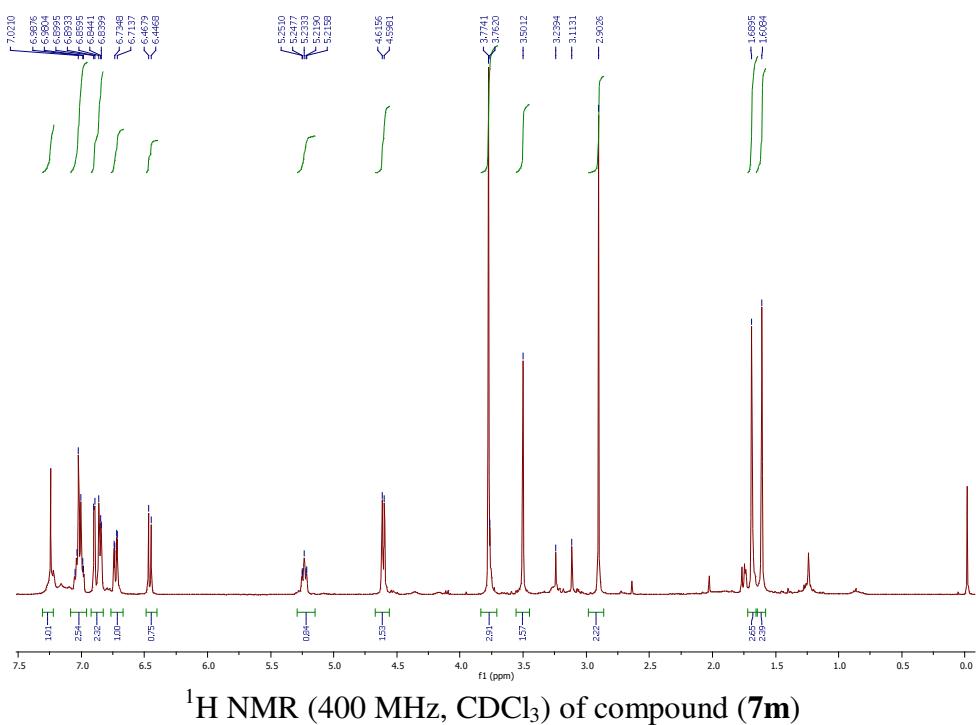
Acquisition Parameter

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

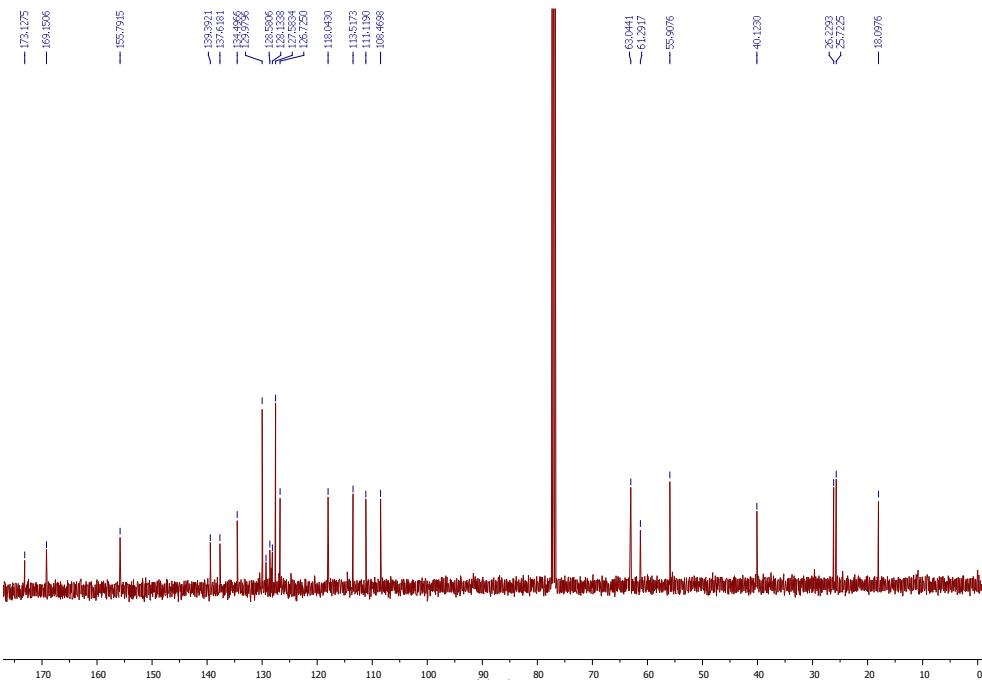




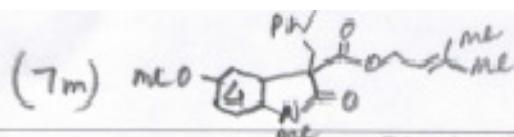
(7m)



^1H NMR (400 MHz, CDCl_3) of compound (7m)



^{13}C NMR (100 MHz, CDCl_3) of compound (7m)



Display Report

Analysis Info

Analysis Name: D:\Data\user data\DEC 17\Dr. A. Bisal- SG3-334_1-A_2_01_589.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisal- SG3-334
 Comment:

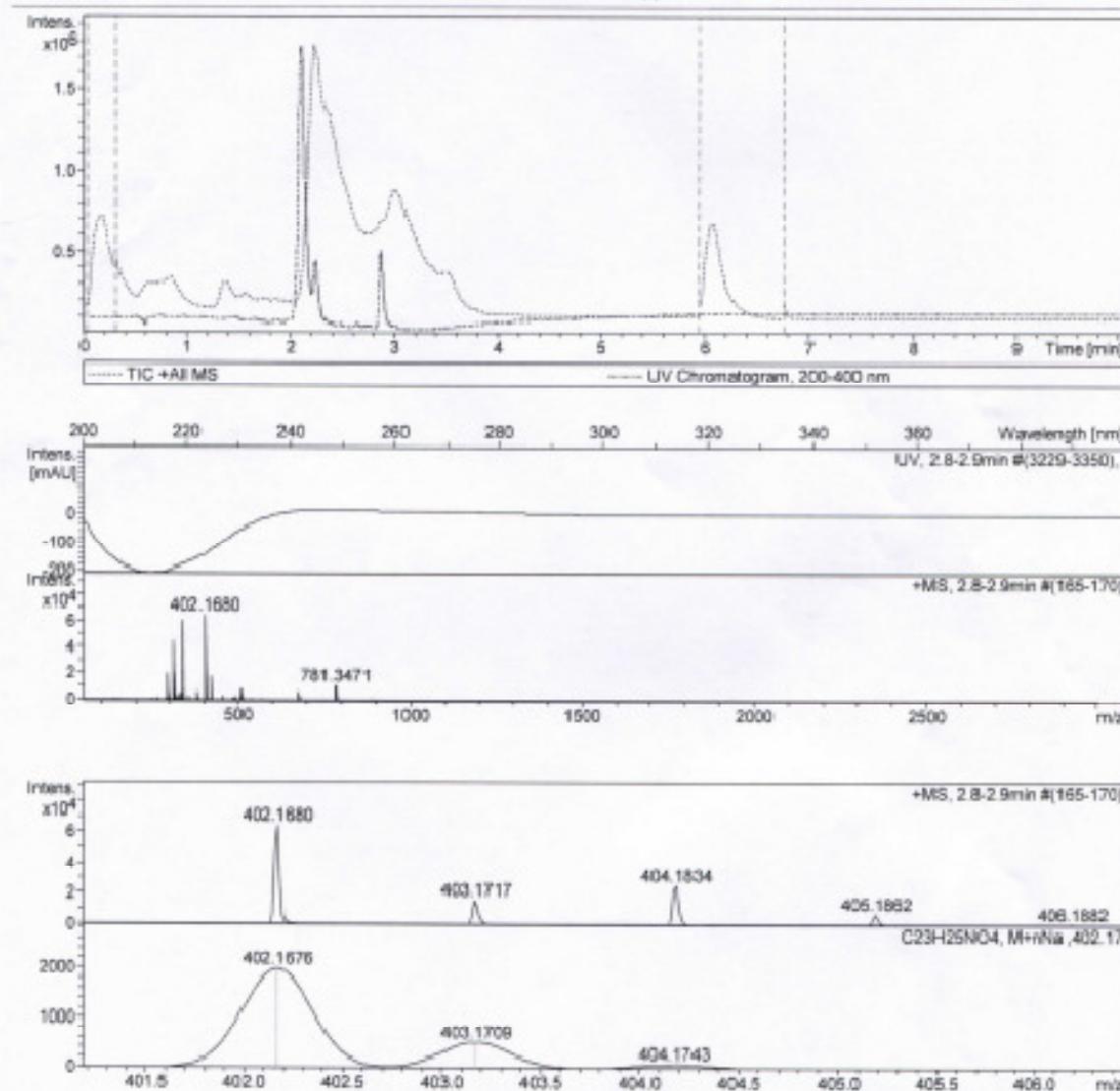
Acquisition Date: 12/17/2011 2:20:30 PM

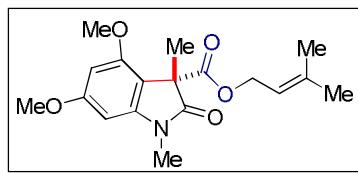
Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

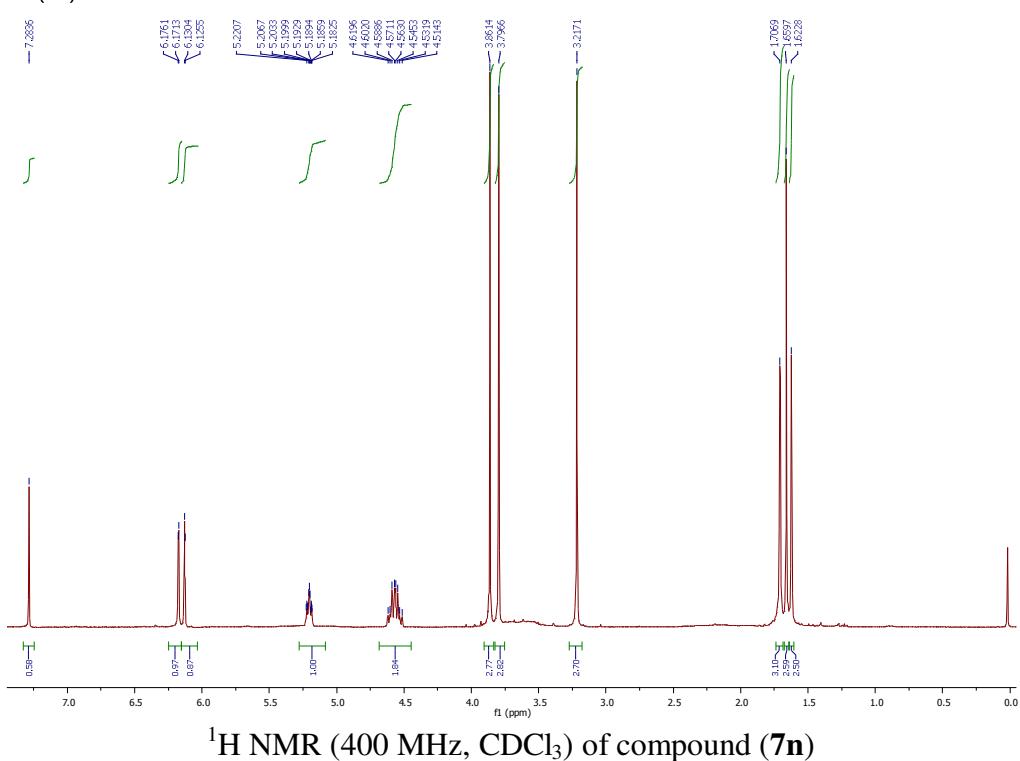
Acquisition Parameter

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Scan End	3000 mHz	Set Collision Cell RF	150.0 Vpp	Set Qvalve Valve	Waste

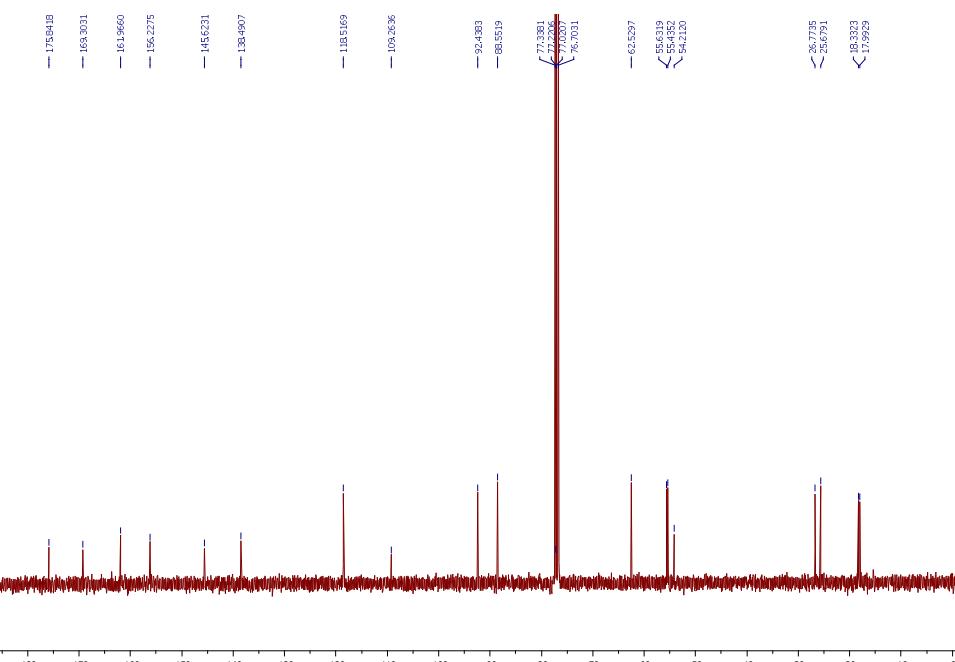




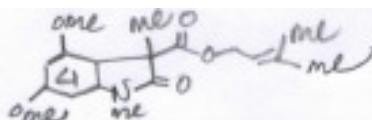
(7n)



^1H NMR (400 MHz, CDCl_3) of compound (7n)



^{13}C NMR (100 MHz, CDCl_3) of compound (7n)



Display Report

Analysis Info

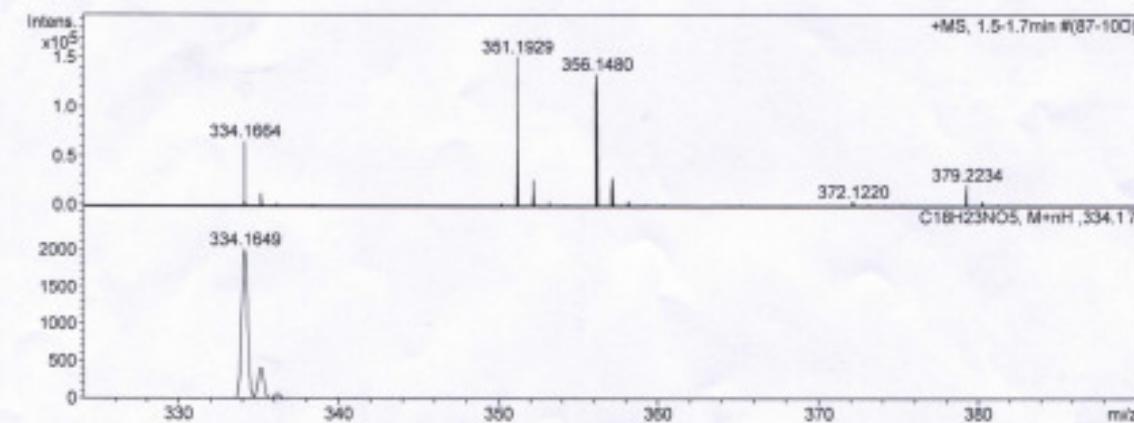
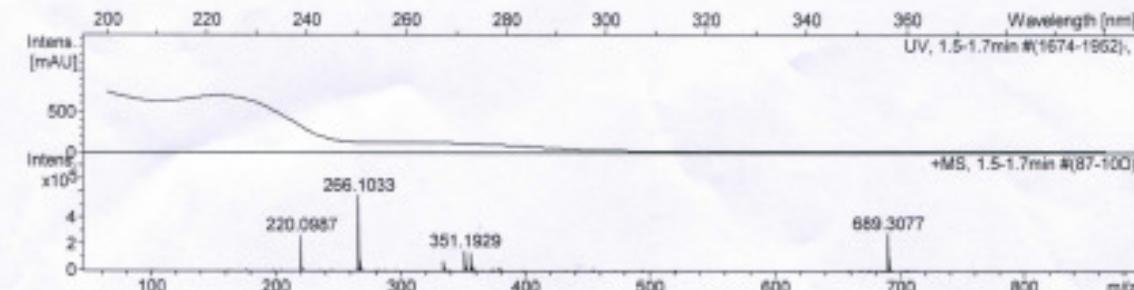
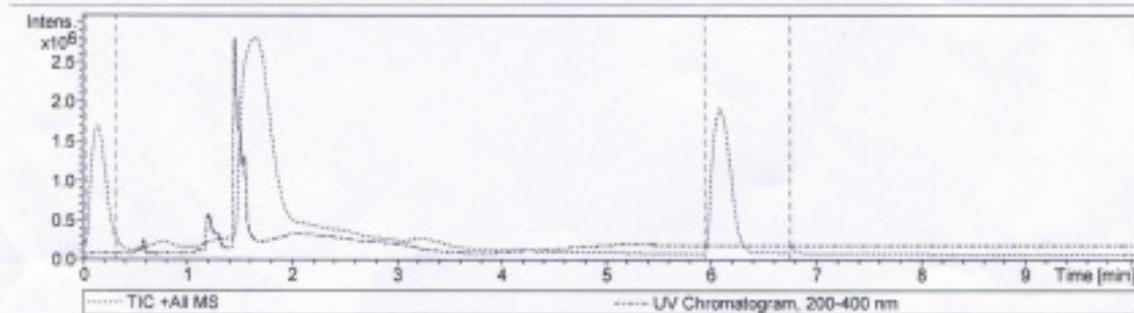
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 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG4-341-R
 Comment

Acquisition Date 4/16/2012 2:41:25 PM

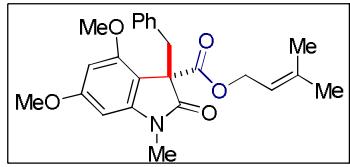
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

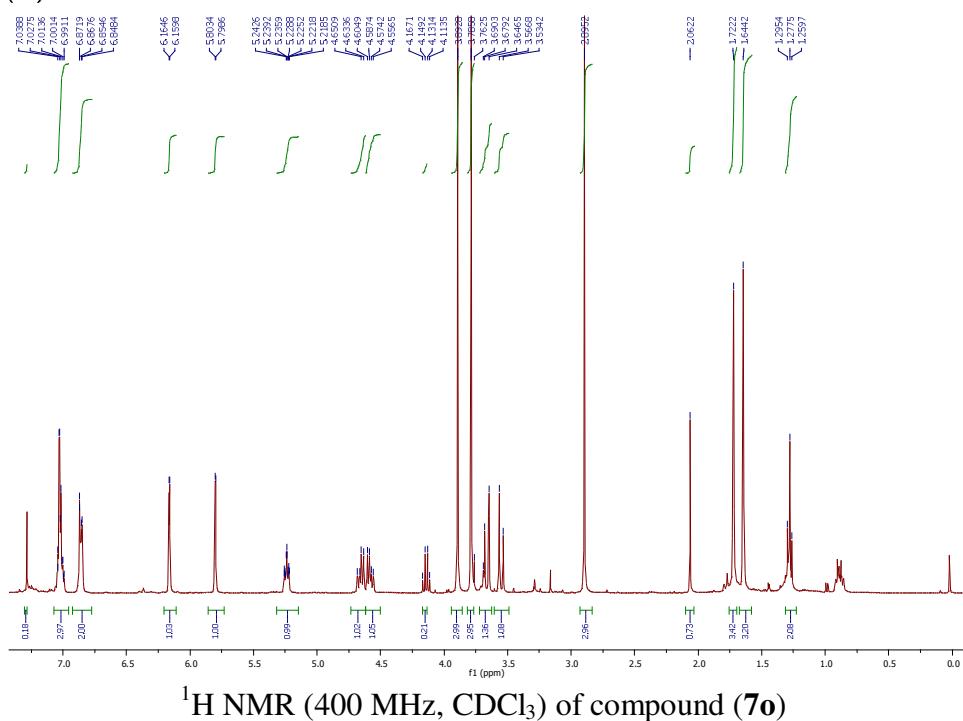
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



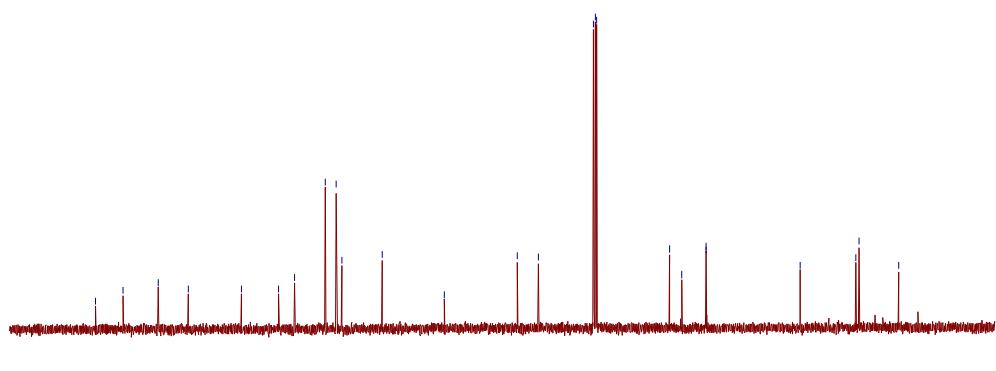
Scanned copy of mass spectrum of compound (\pm)-7n



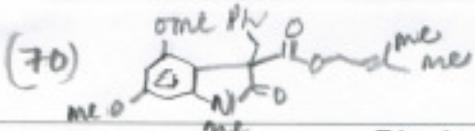
(70)



174,255	168,891.3	168,202.75	156,253.6	145,945.5	138,603.2	135,605.1	127,458.9	126,364.3	118,518.5	106,379.0	92,196.4	88,145.8	77,355.6	77,003.9	76,718.4	62,632.0	60,160.7	55,555.0	55,454.7	37,372.657
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¹³C NMR (100 MHz, CDCl₃) of compound (7o)



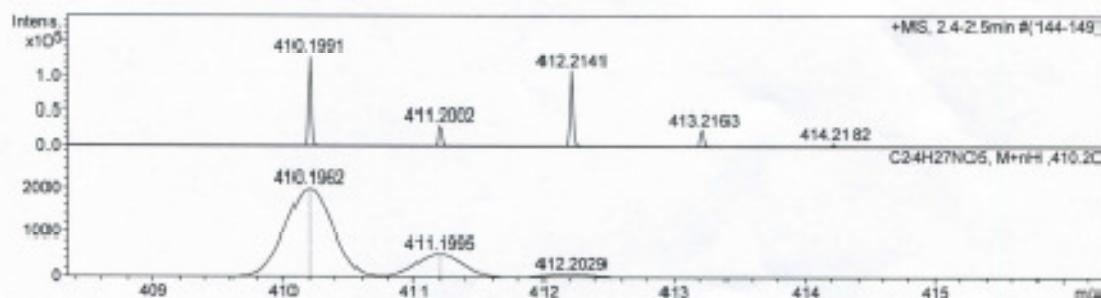
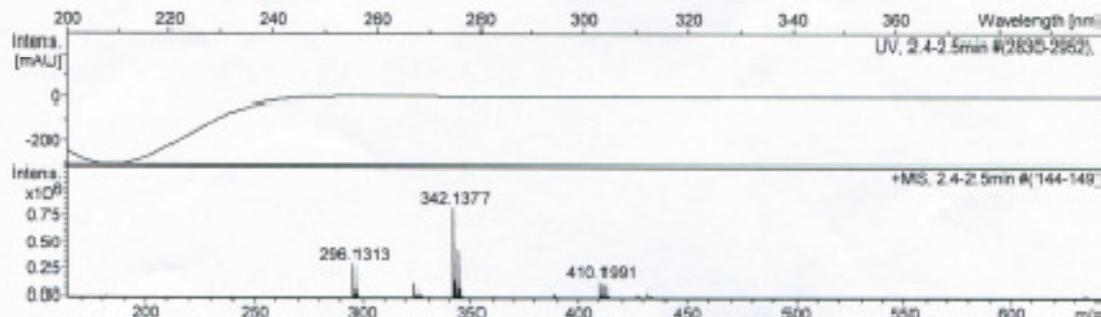
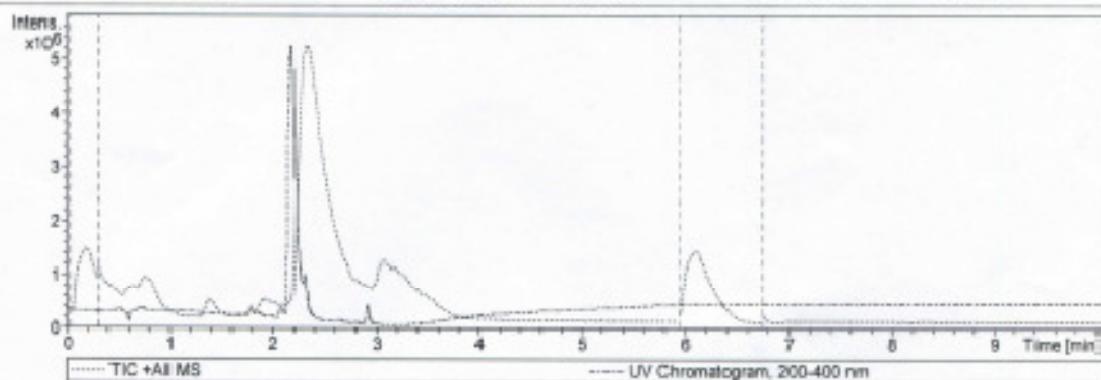
Display Report

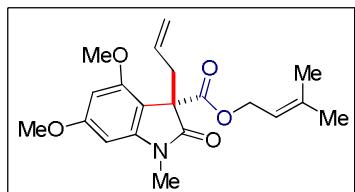
Analysis Info

Analysis Name: D:\Data\user data\DEC_07\Dr. A. Bisai-AB-SG3-284_1-A,3_01_446.d Acquisition Date: 12/7/2011 4:08:29 PM
 Method: HRLCMS-20 Sept.m Operator: Meena Sharma
 Sample Name: Dr. A. Bisai-AB-SG3-284 Instrument: micrOTOF-Q II 10330
 Comment:

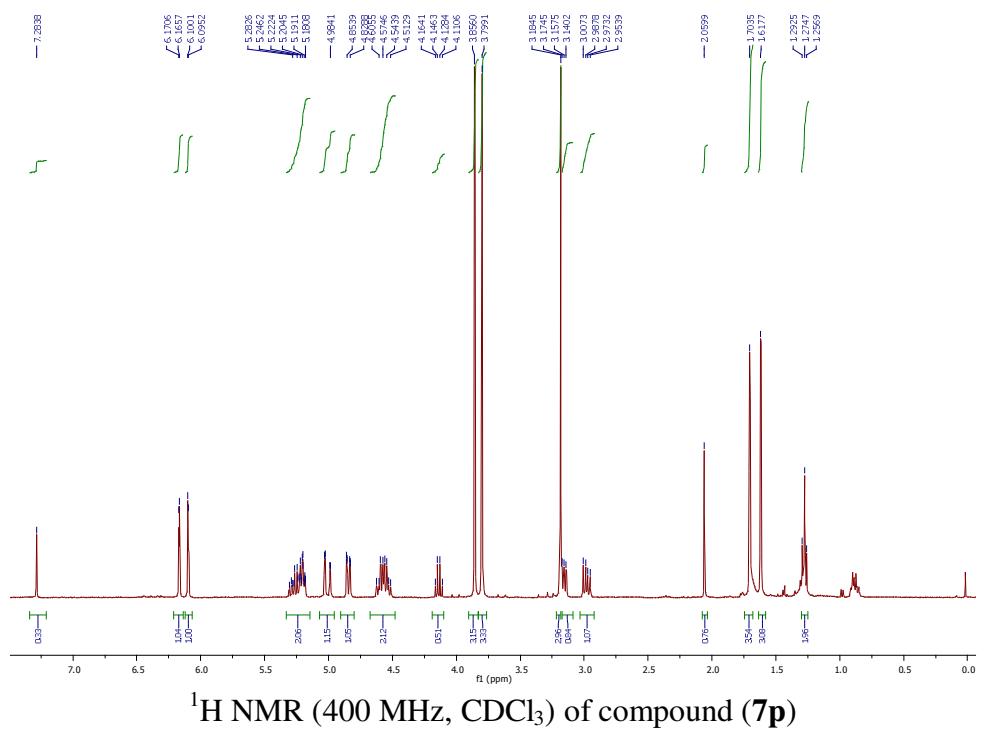
Acquisition Parameter

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

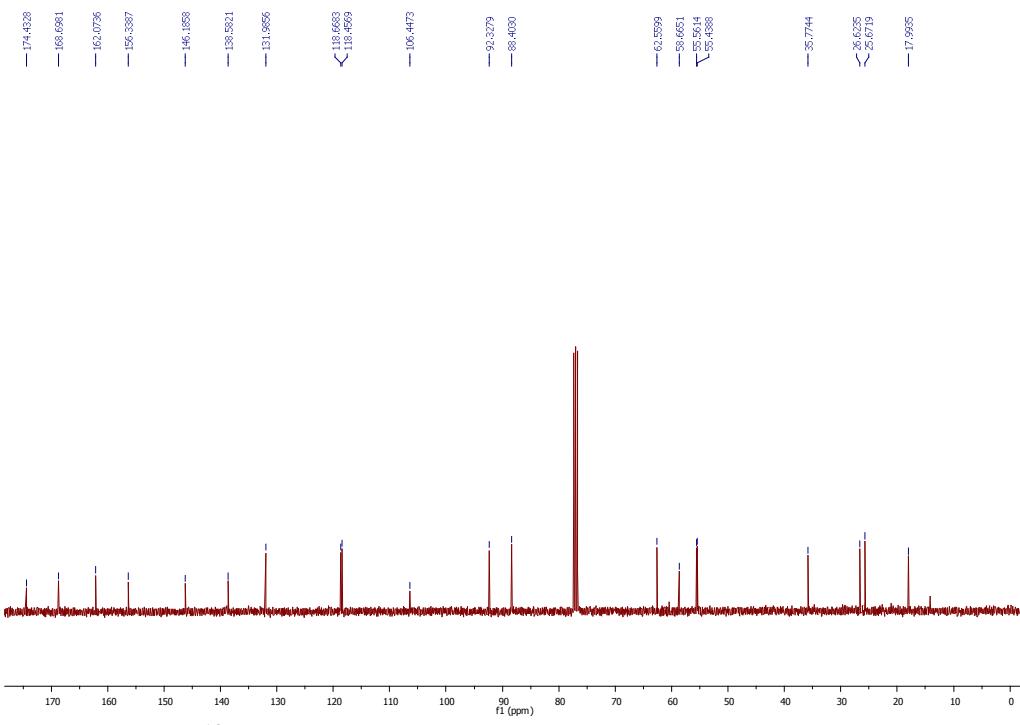




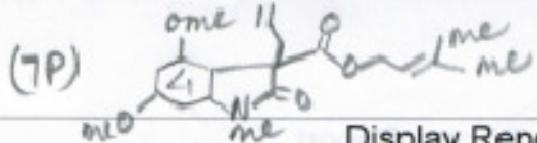
(7p)



^1H NMR (400 MHz, CDCl_3) of compound (7p)



^{13}C NMR (100 MHz, CDCl_3) of compound (7p)



Display Report

Analysis Info

Analysis Name: D:\Data\user data\DEC_07\Dr. A. Bisai-AB-SG3-283_1-A,2_01_449.d
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 Sample Name: Dr. A. Bisai-AB-SG3-283
 Comment:

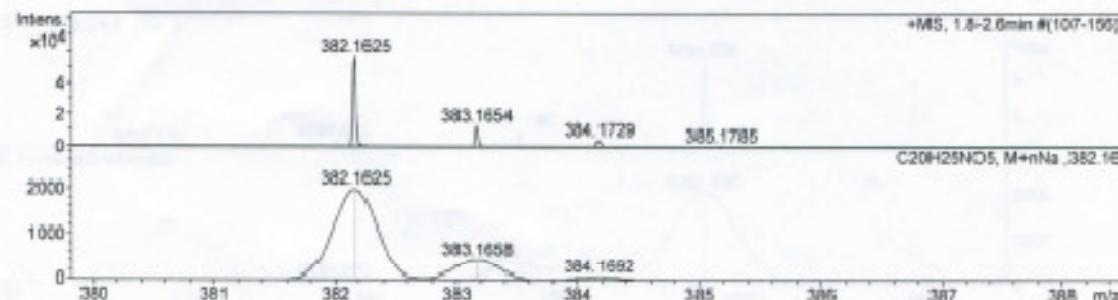
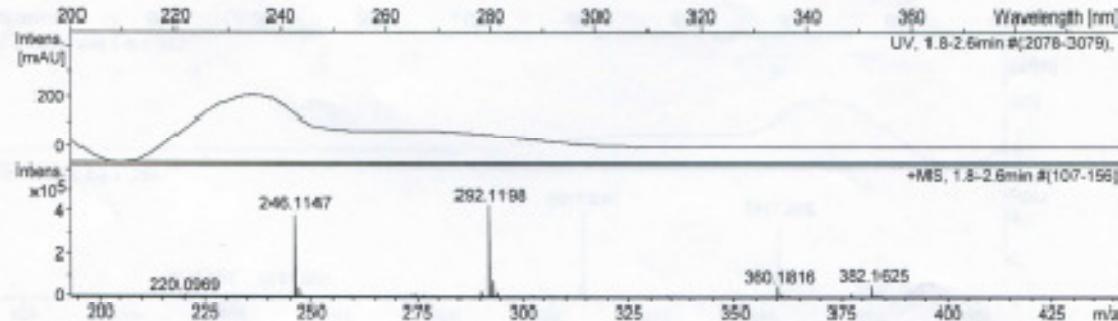
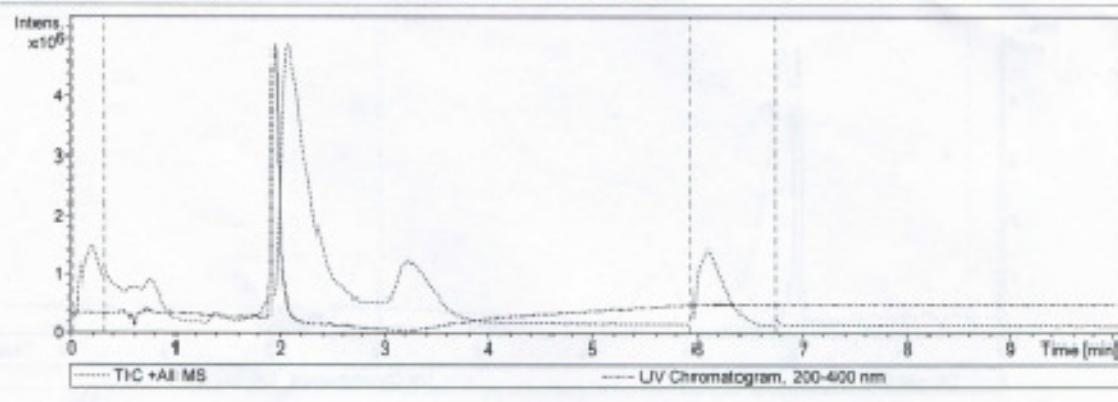
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Operator: Meena Sharma

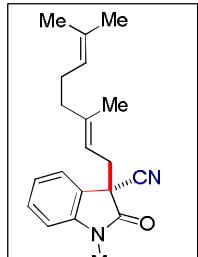
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

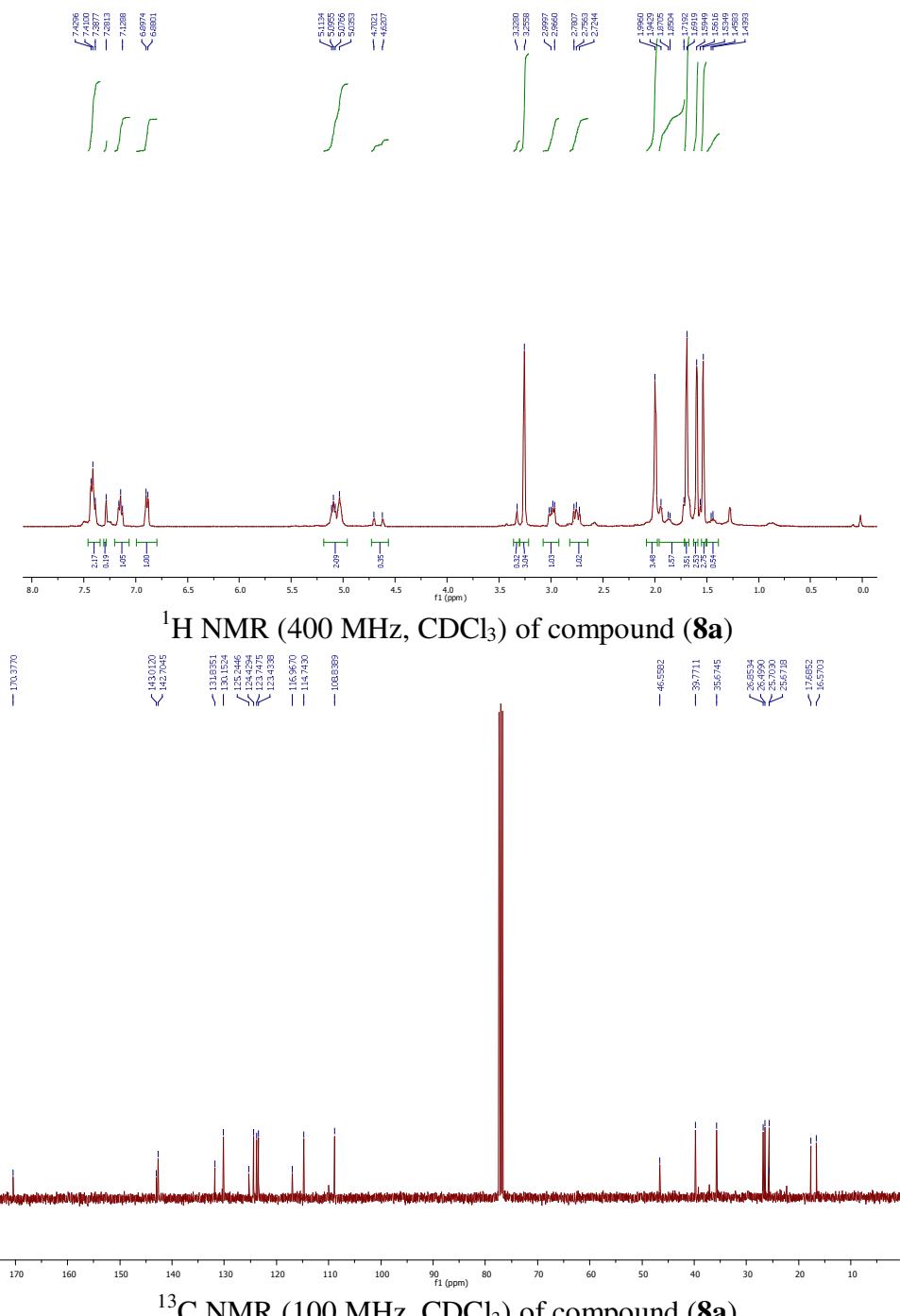
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



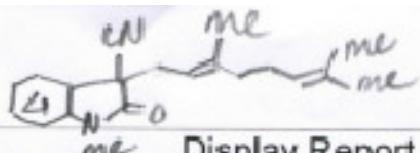
Scanned copy of mass spectrum of compound (\pm)-7p



(8a)



(8b)



Display Report

Analysis Info

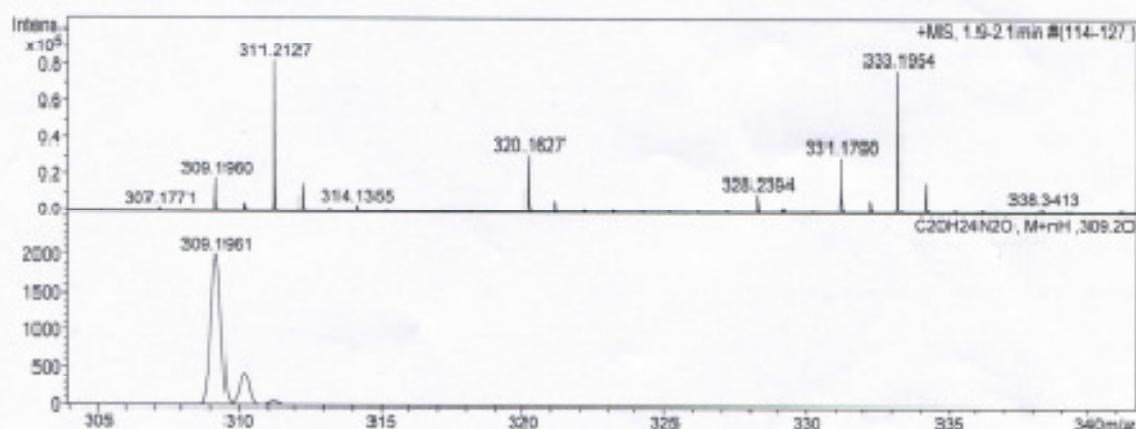
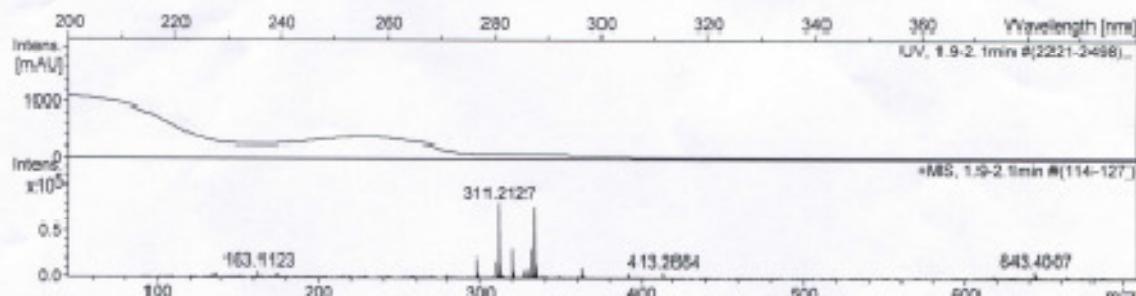
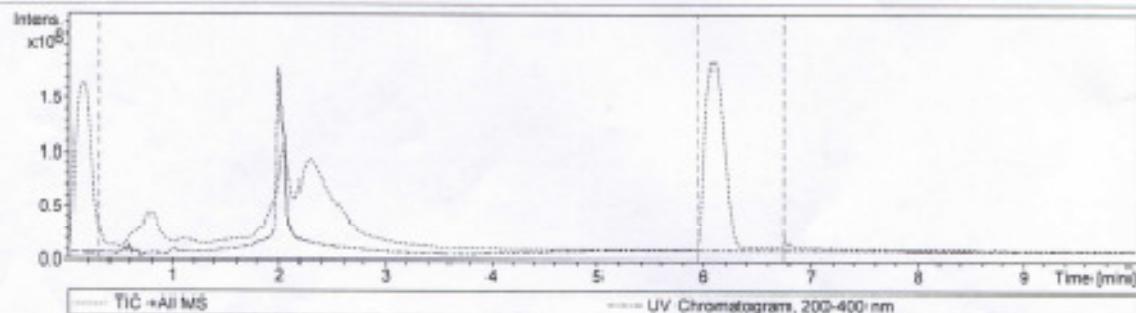
Analysis Name D:\Data\user data\April 2012\12 APR\Dr. A. Bisai- SG4-338_1-A.3_01_1748.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG4-338
 Comment

Acquisition Date 4/12/2012 1:51:05 PM

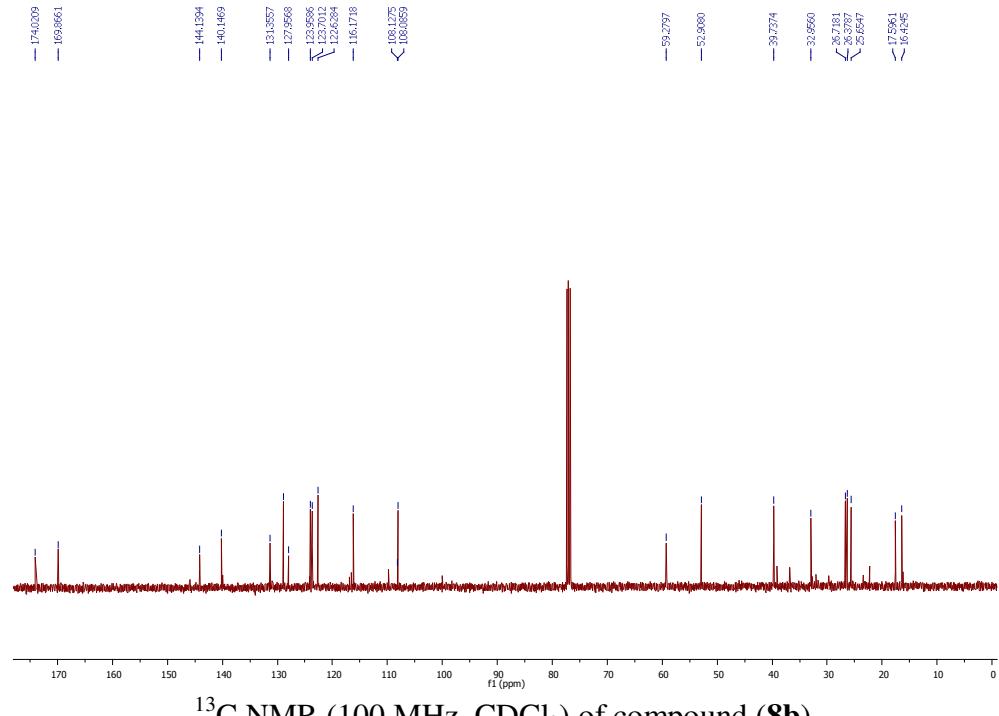
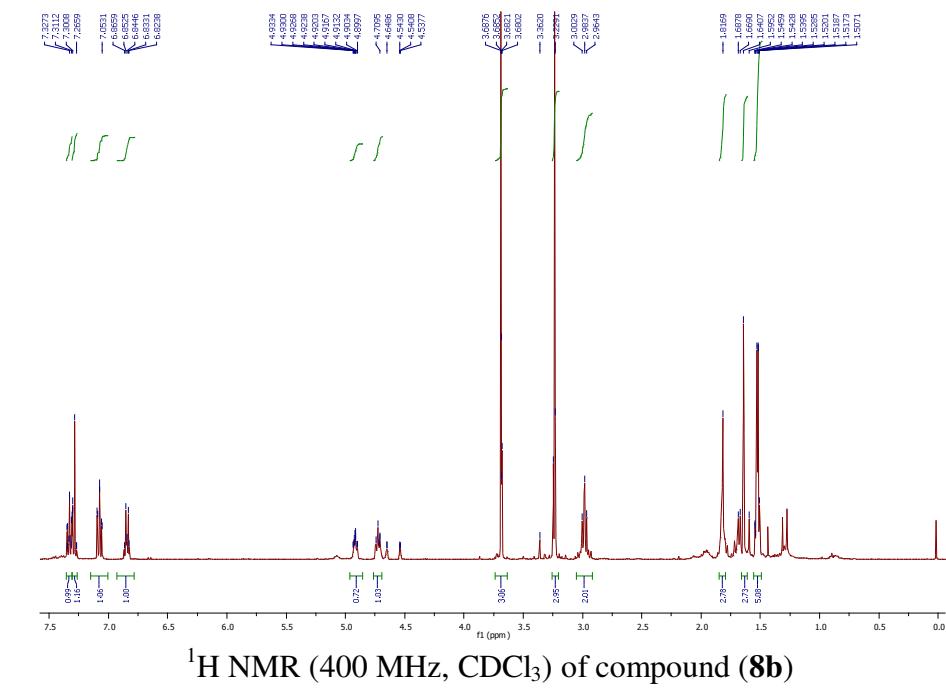
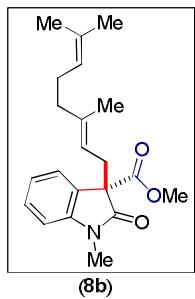
Operator Meena Shamma
 Instrument micrOTOF-Q II 10330

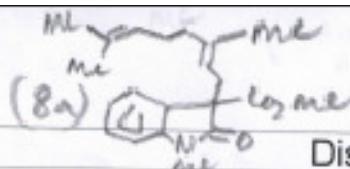
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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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 compound 8a





Display Report

Analysis Info

Analysis Name: D:\Data\user\data\MAR\CH 2012\26.maz
Method: HRLCMS-2D Sept.mn
Sample Name: Dr. A. Bisai- SG4-261
Comment:

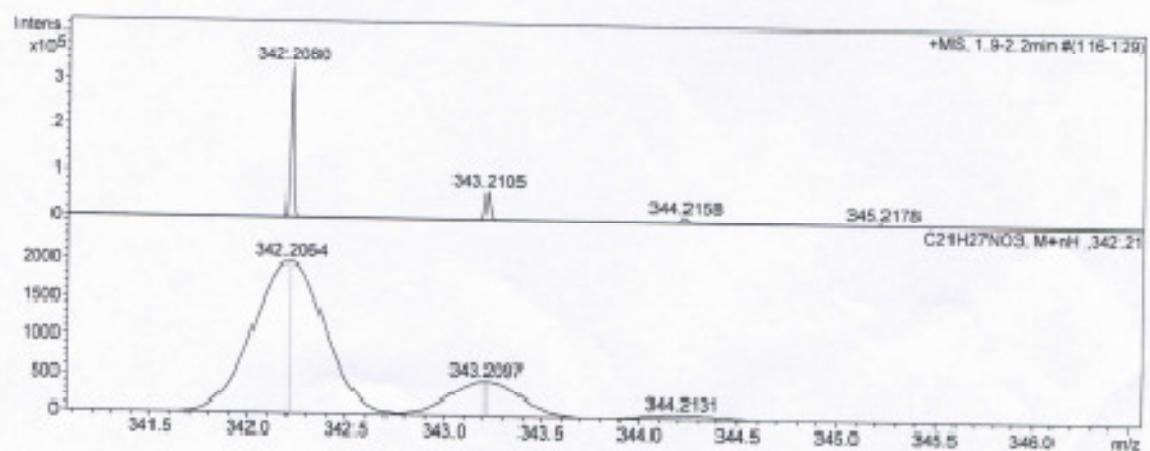
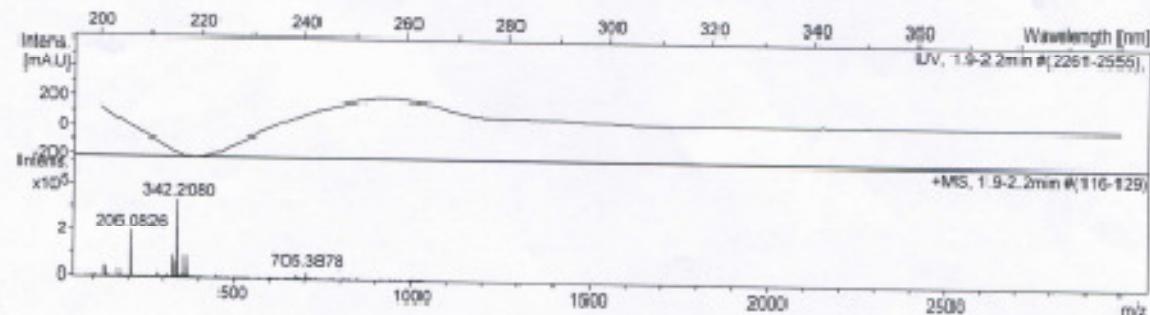
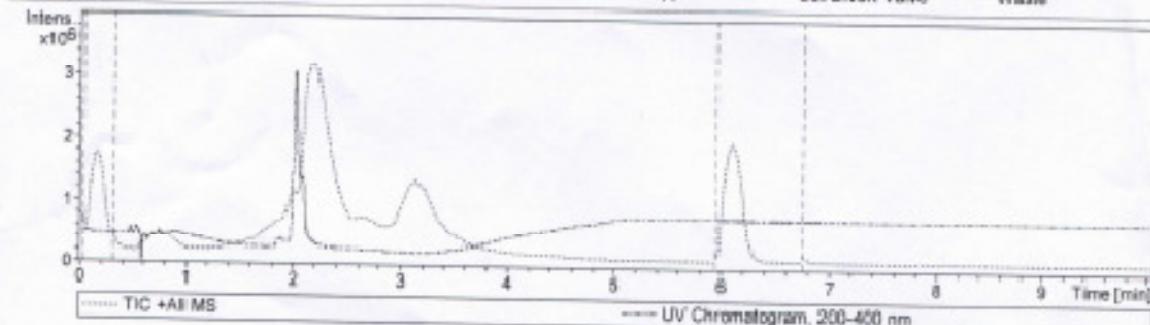
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Operator:

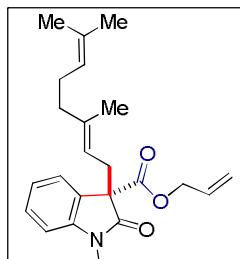
Instrument: Meena Sharma
micrOTOF-Q II 10330

Acquisition Parameter

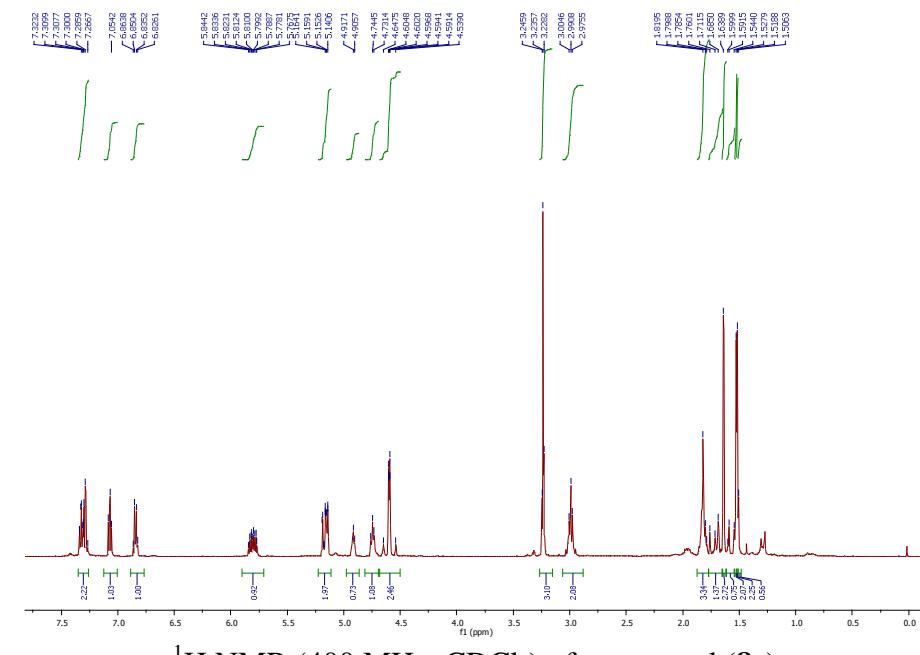
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Scan Begin:	50 m/z	Set End Plate Offset:	-600 V	Set Dry Gas:	7.0 l/min
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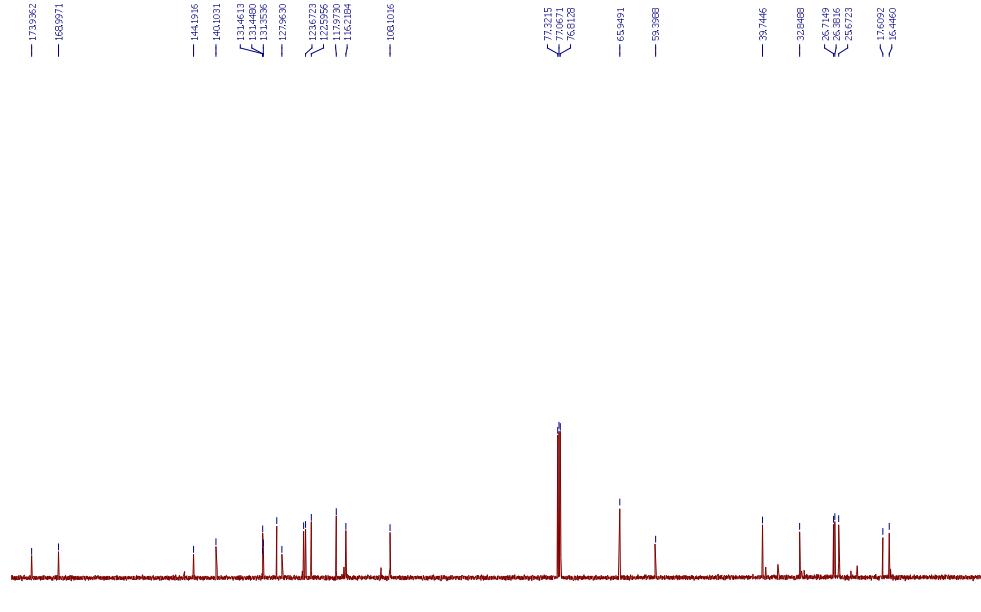
Scanned copy of mass spectrum of compound **8b**.



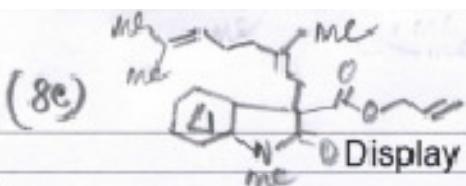
(8c)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**8c**)



Display Report

Analysis Info

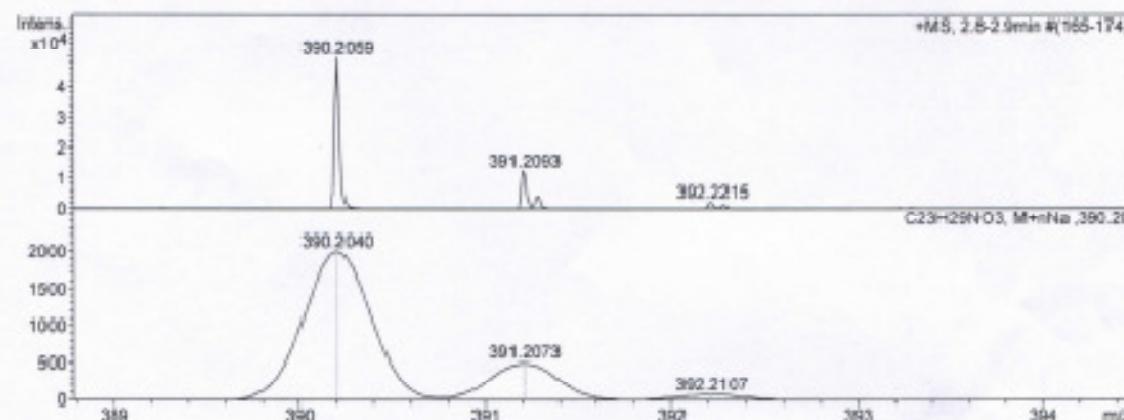
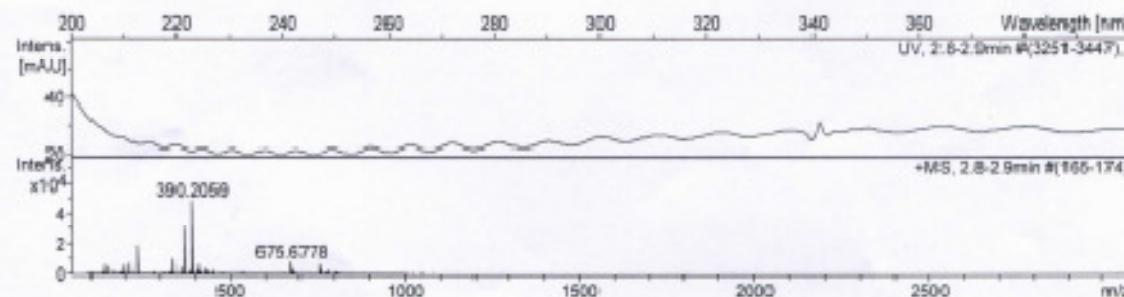
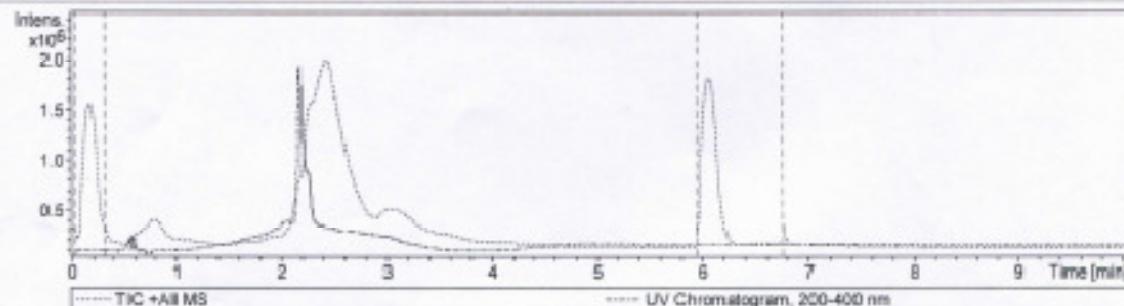
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG4-285
 Comment:

Acquisition Date: 3/27/2012 3:56:16 PM

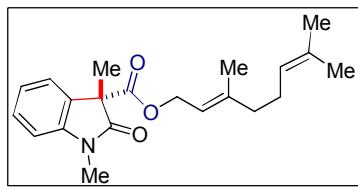
Operator: Meena Sharma
 Instrument: microQTOF-Q II 10330

Acquisition Parameter

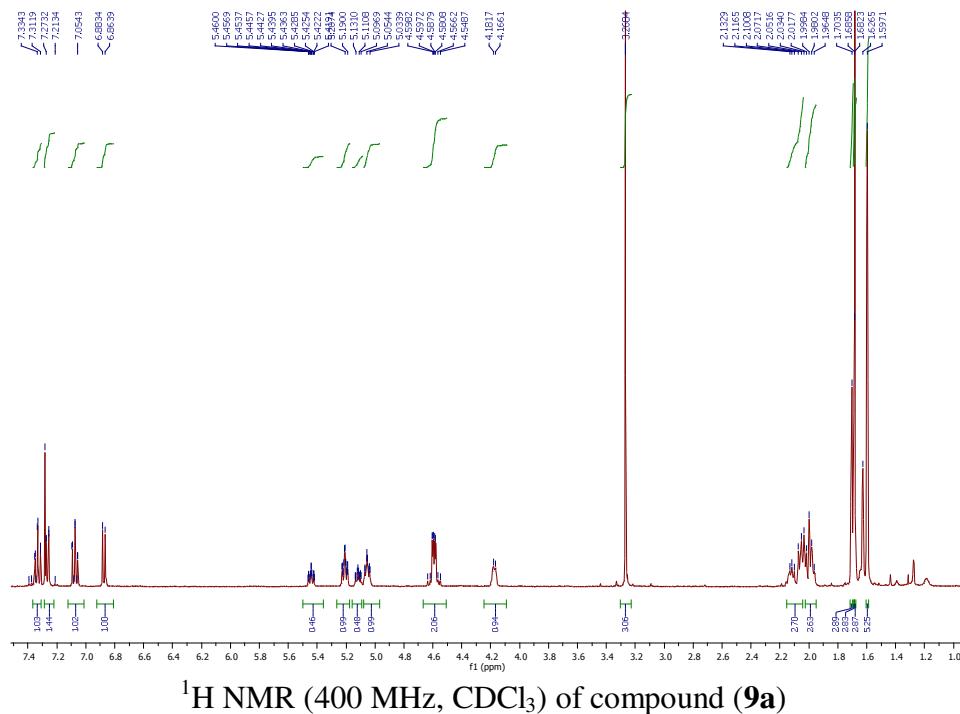
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



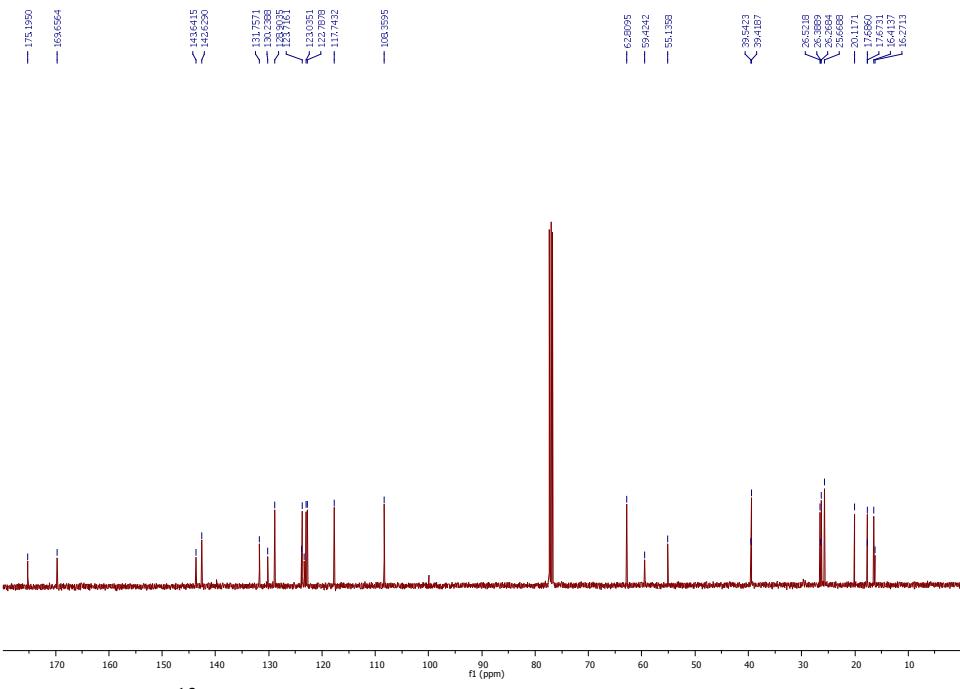
Scanned copy of mass spectrum of compound 8c



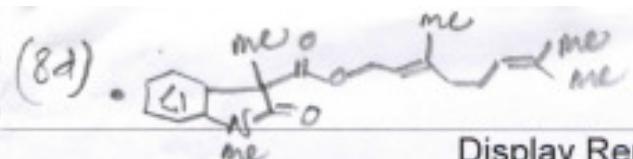
(9a)



^1H NMR (400 MHz, CDCl_3) of compound (9a)



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



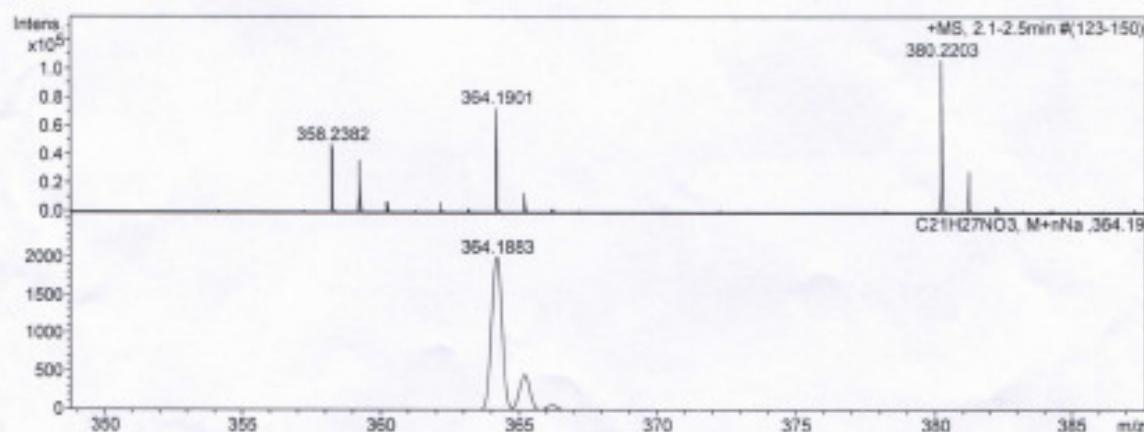
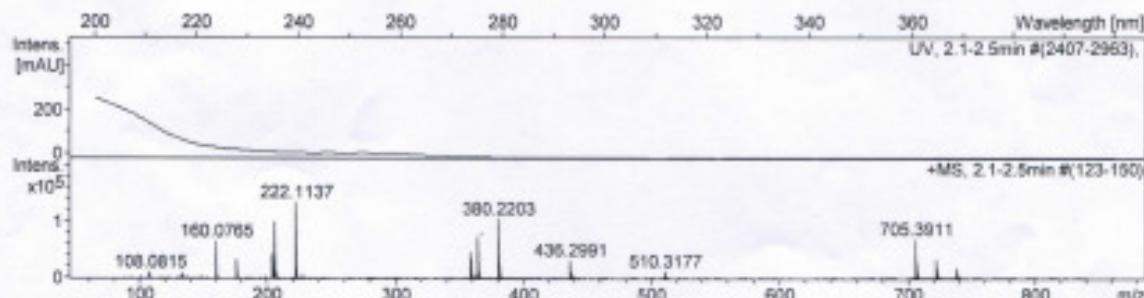
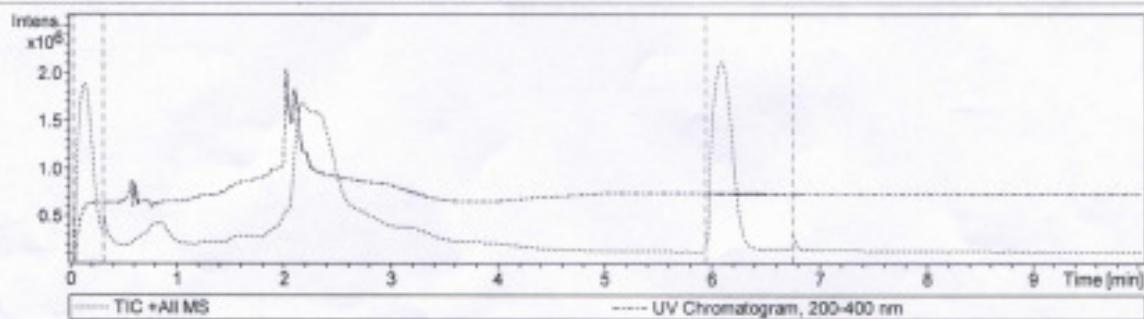
Display Report

Analysis info

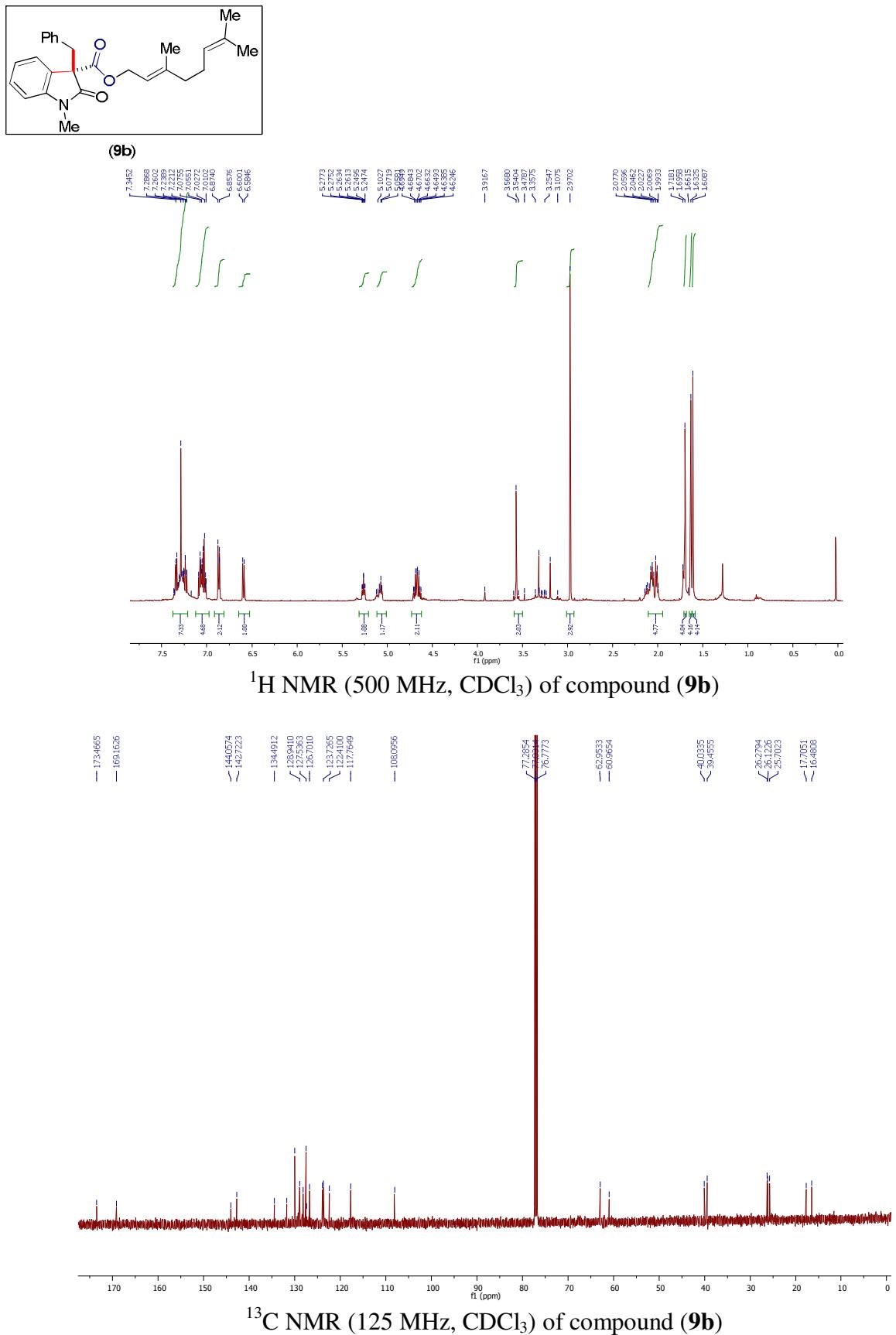
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Analysis Name D:\Data\user data\MARCH 2012\29 mar\Dr. A. Bisai- SG4-271_1-A_6_01_1571.d
Method HRLCMS-20 Sept.m Operator Meena Sharma
Sample Name Dr. A. Bisai- SG4-271 Instrument micrOTOF-Q II 10330
Comment

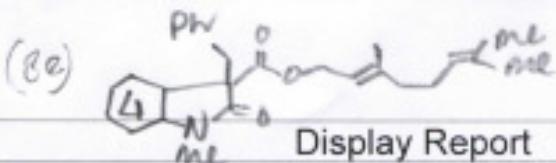
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-600 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 compound **9a**





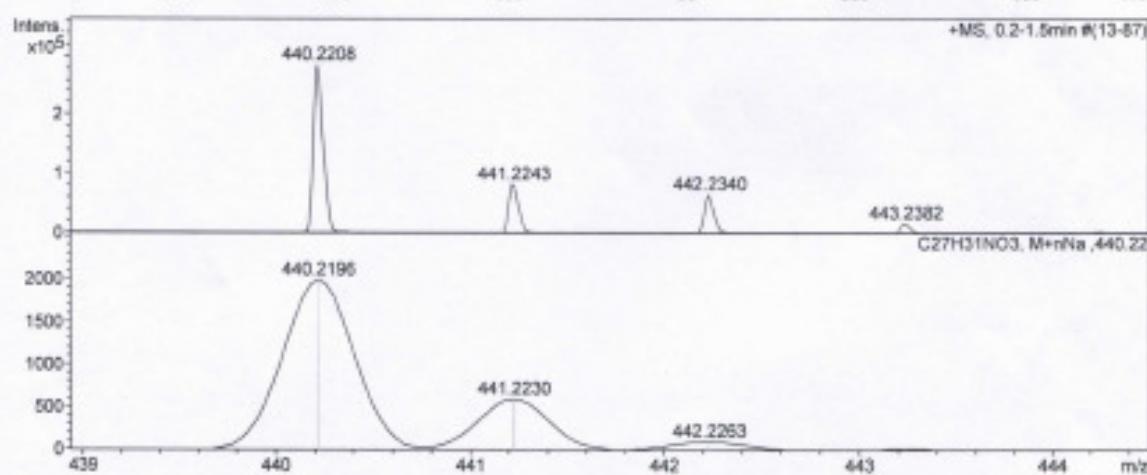
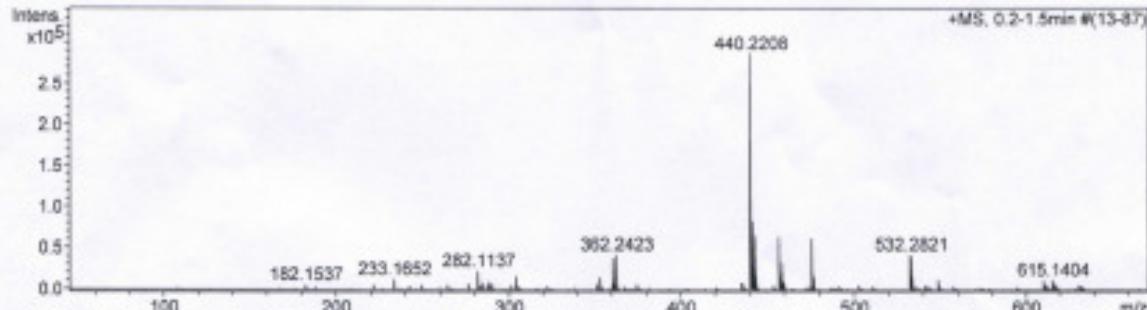
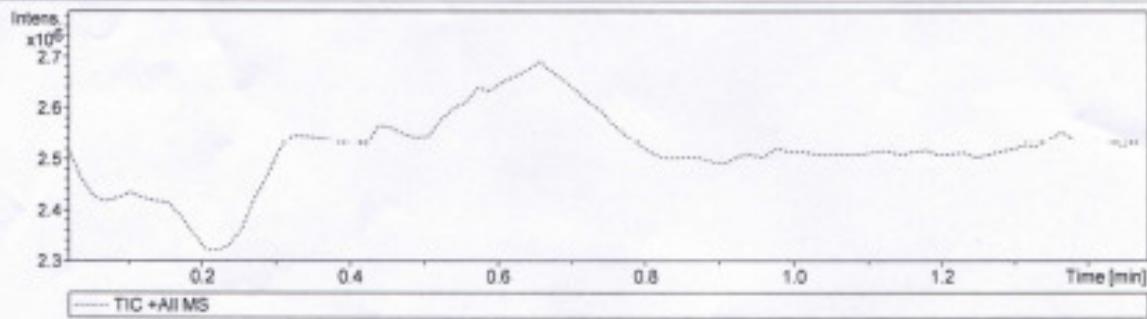
Display Report

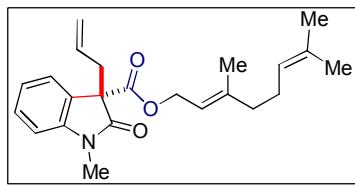
Analysis Info

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Method	tune_low.m	Operator	Meena Sharma
Sample Name	AB-SG4-273	Instrument	micrOTOF-Q II 10330
Comment			

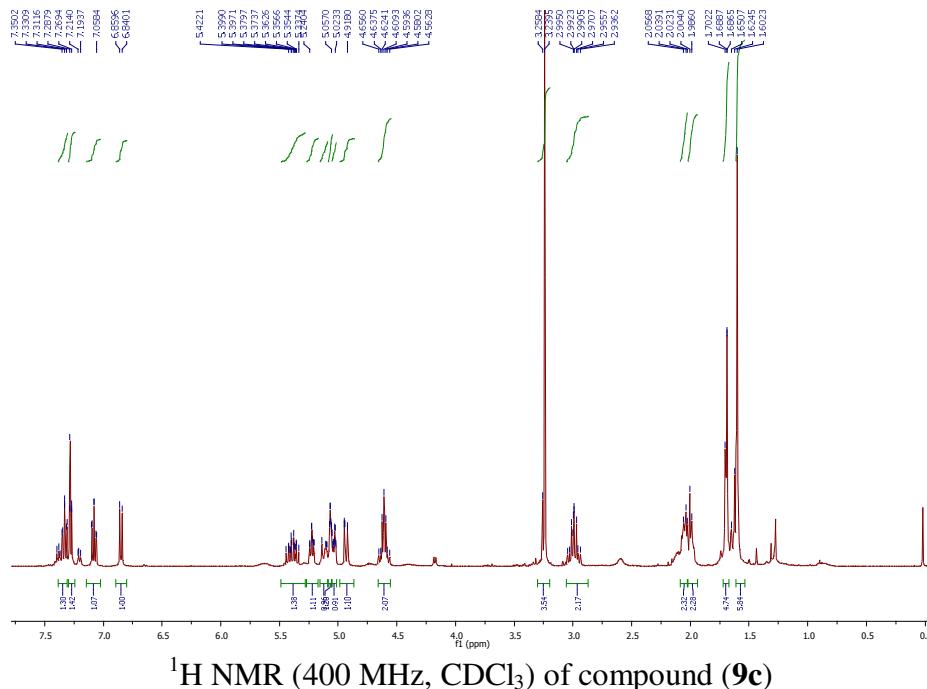
Acquisition Parameter

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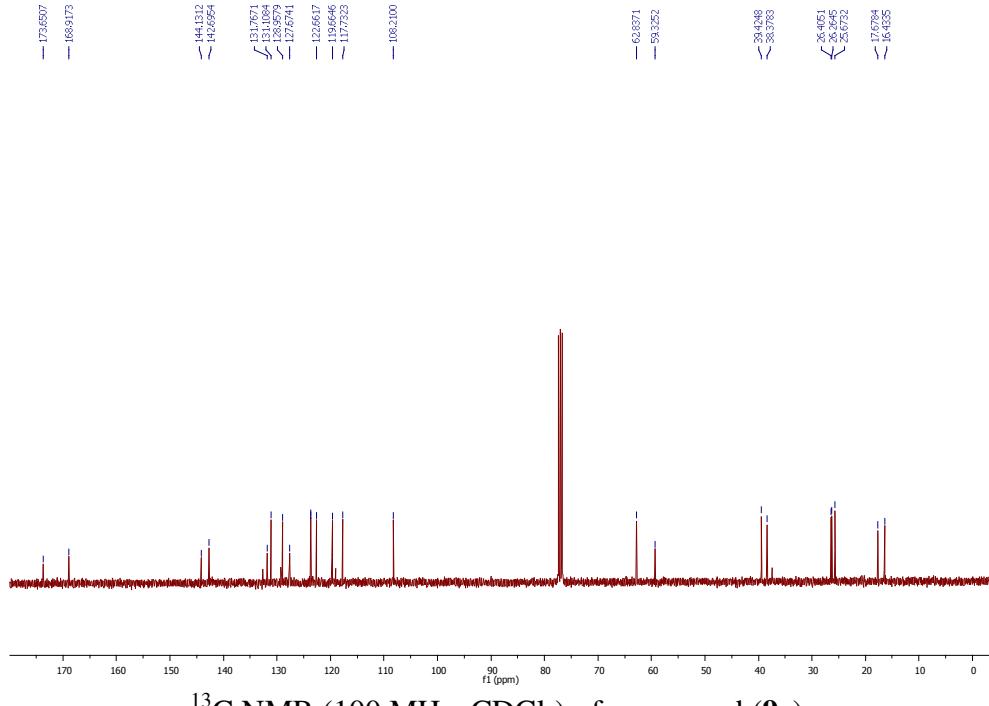




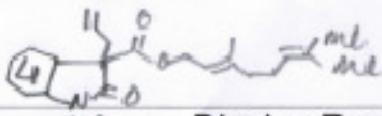
(9c)



— 144.1312
— 142.5564
— 131.0761
— 131.0884
— 128.9579
— 127.5741
— 126.6517
— 125.6617
— 119.6464
— 117.9573
— 108.2000



(84)



m/e Display Report

Analysis Info

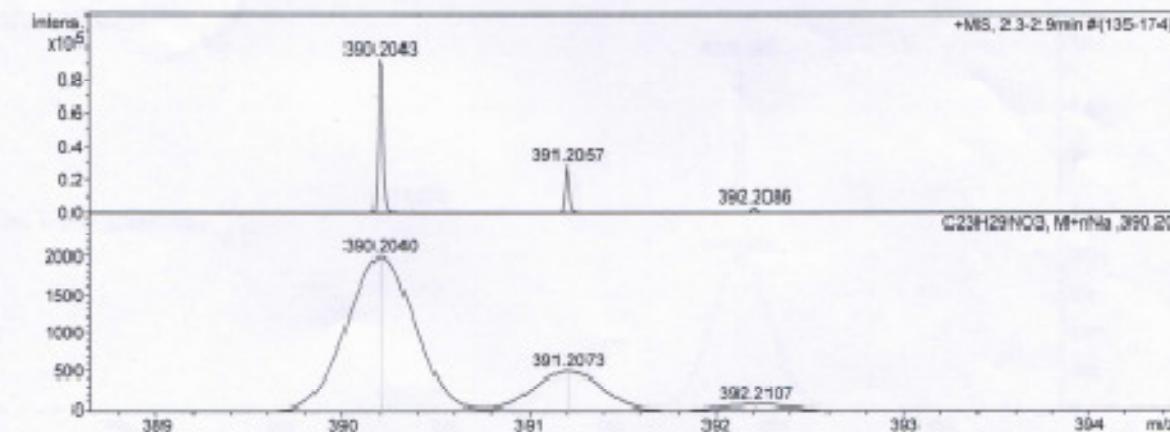
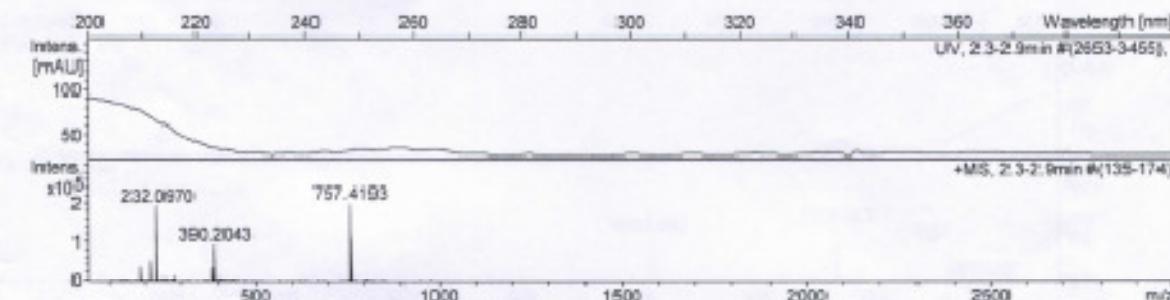
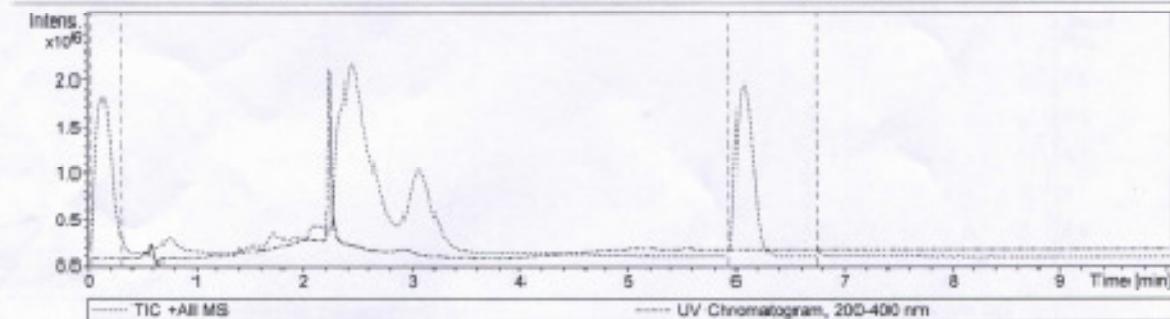
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 Sample Name: Dr. A. Bisai-SG4-275
 Comment:

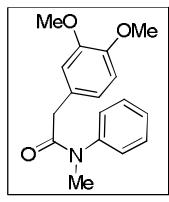
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Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

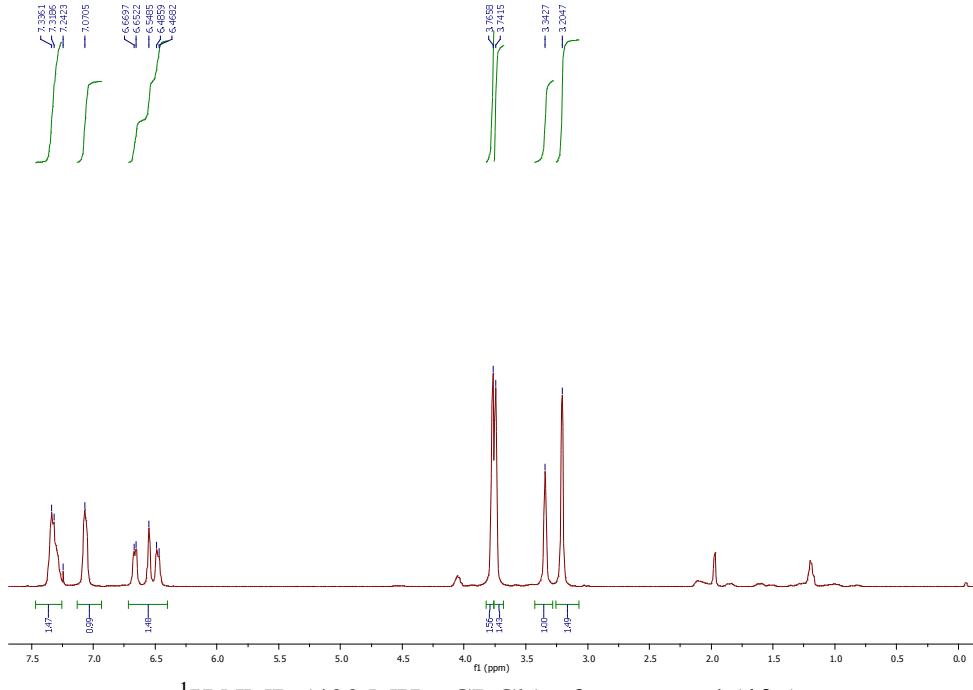
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 lBar
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

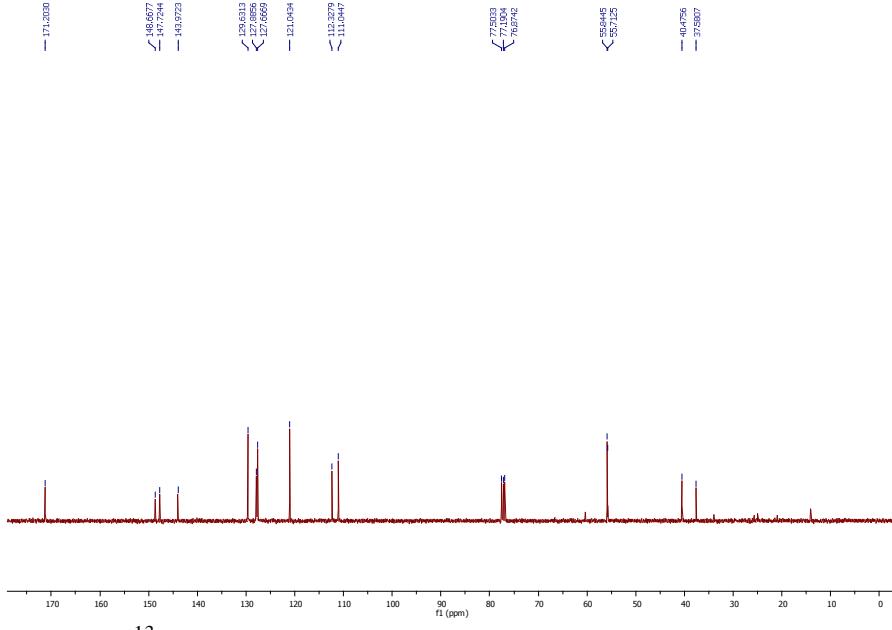




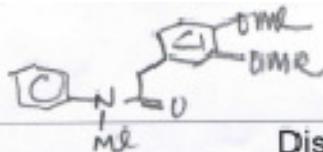
(10a)



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



¹³C NMR (100 MHz, CDCl₃) of compound (**10a**)



Display Report

Analysis Info

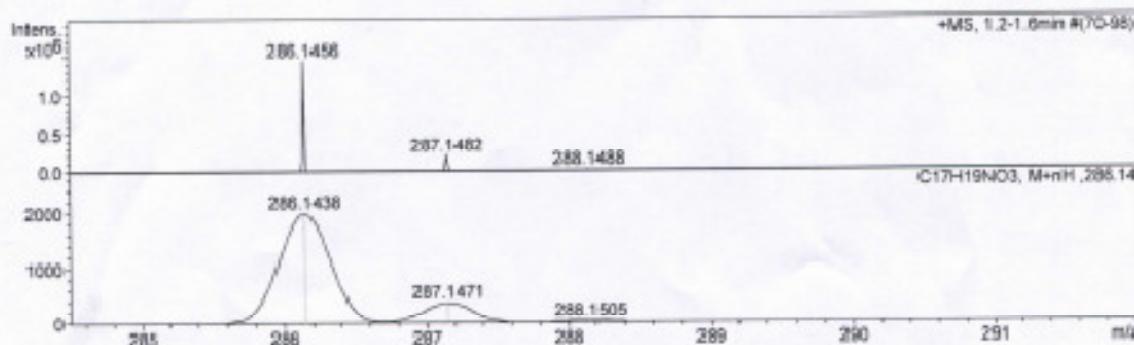
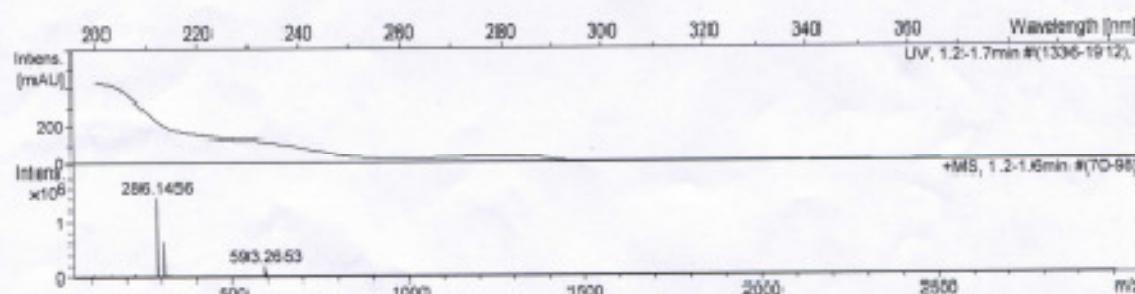
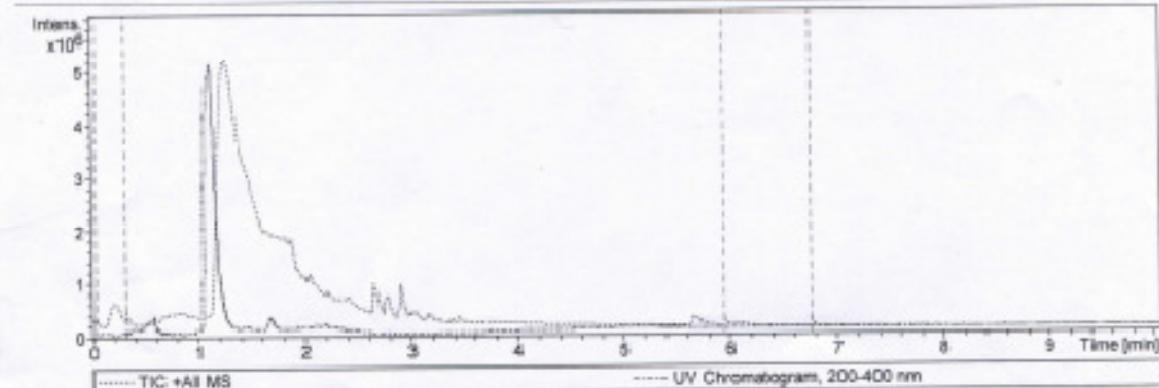
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 Sample Name: Dr. A. Bisal-SG4-063 PS
 Comment:

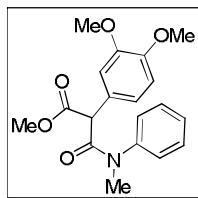
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 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

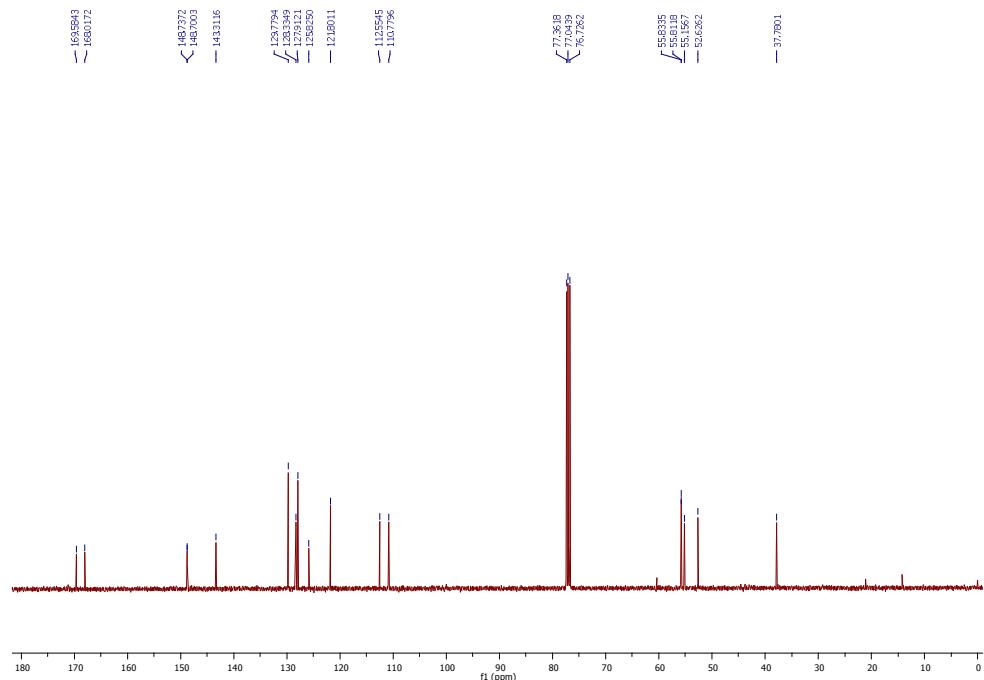
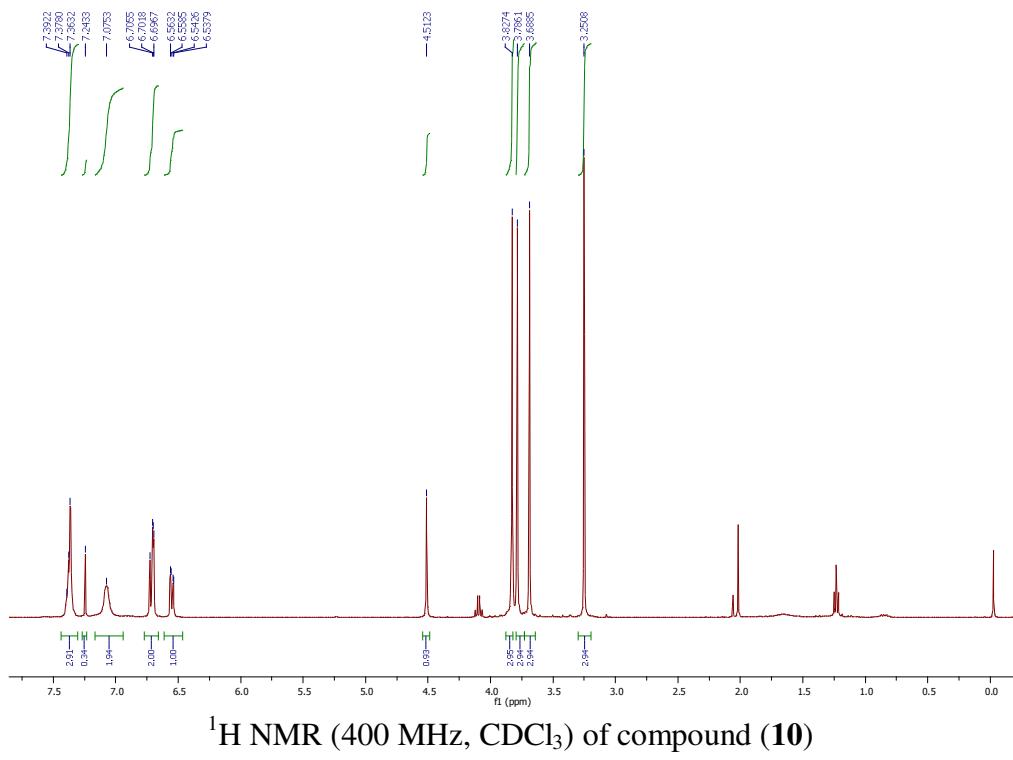
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

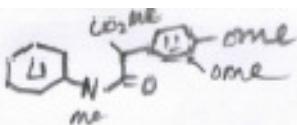




±(10)



¹³C NMR (100 MHz, CDCl₃) of compound (**10**)



Display Report

Analysis Info

Analysis Name: D:\Data\user data\JAN 2012\30 Jan\Dr. A. Bisai-SG4-078_9-A,3_01_1003.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-SG4-078
 Comment:

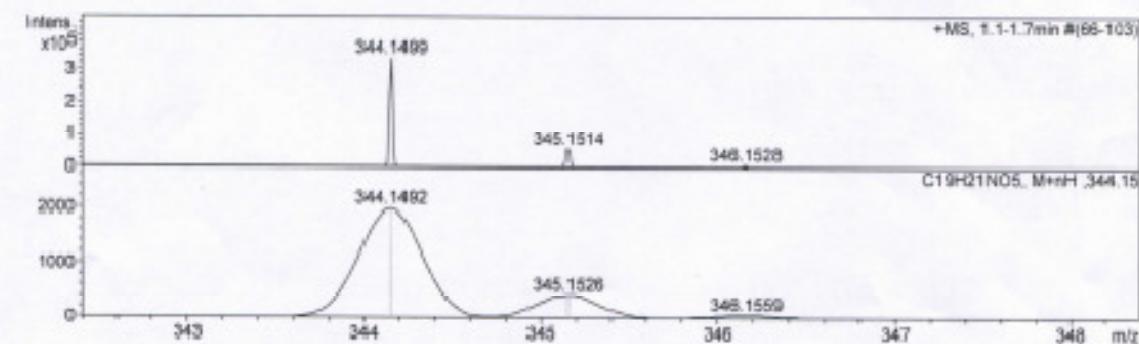
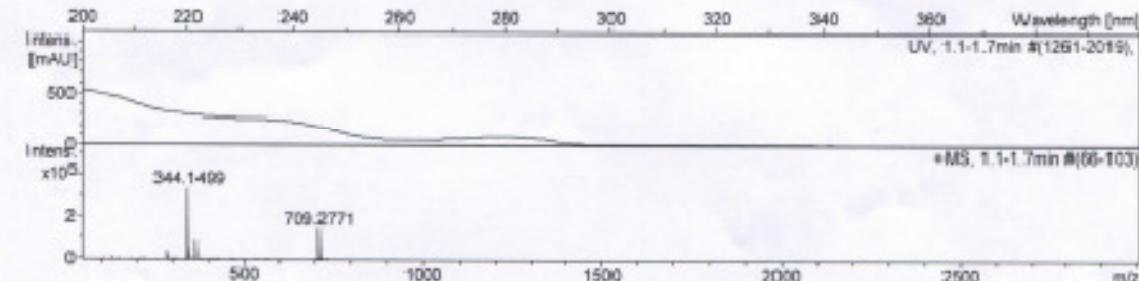
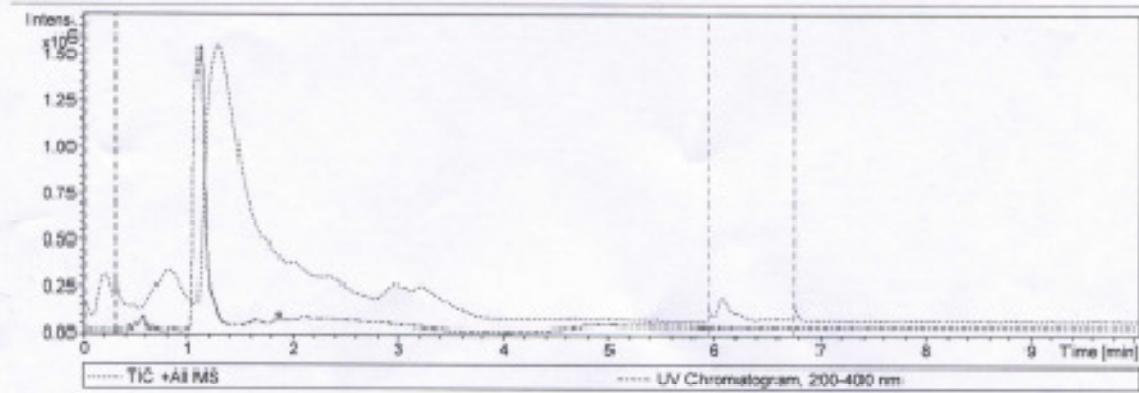
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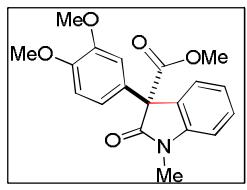
Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

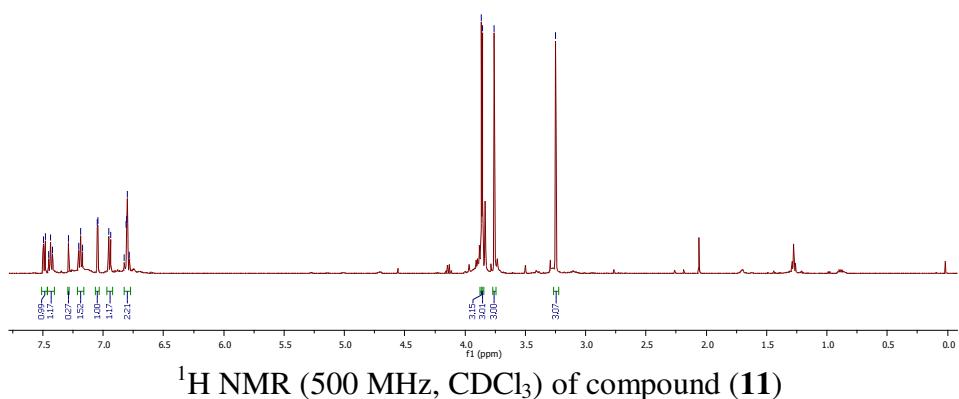
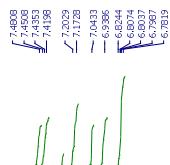
Acquisition Parameter

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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



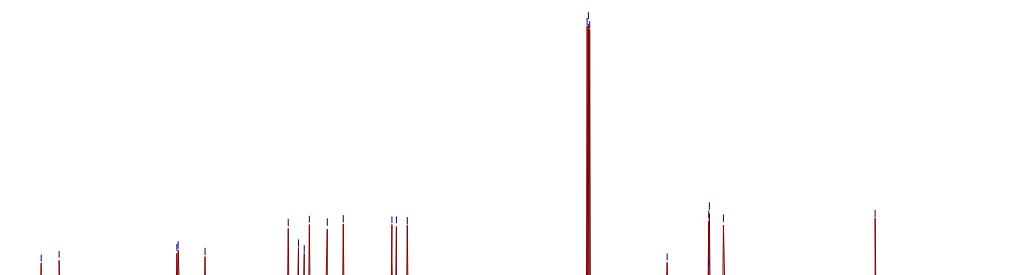


\pm (11)



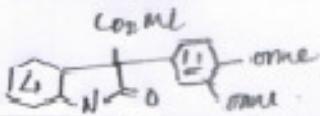
^1H NMR (500 MHz, CDCl_3) of compound (11)

— 173.0191
— 169.8579
— 169.1794
< 168.9513
— 152.9277
— 152.1527
— 151.1177
— 144.2947
— 140.0794
— 122.8759
— 120.0794
< 111.5313
< 110.7095
< 108.7755
— 34.8639
— 34.5553
— 34.5552
— 34.4966
— 34.0747



^{13}C NMR (125 MHz, CDCl_3) of compound (11)

(11)



Display Report

Analysis Info

Analysis Name: D:\Data\user\data\April 2012\10 apr\Dr. A. Bisai- SG4-251_1-A_6_01_1716.d
 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai- SG4-251
 Comment:

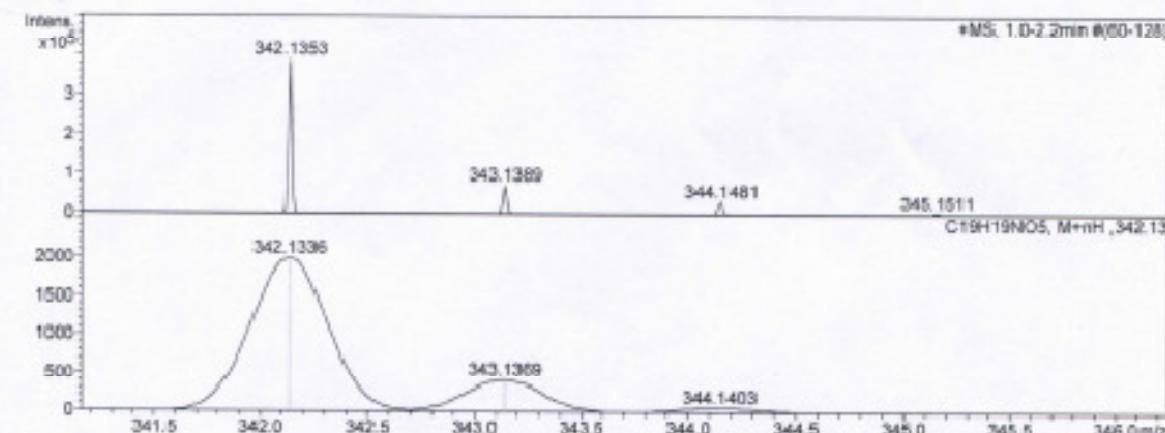
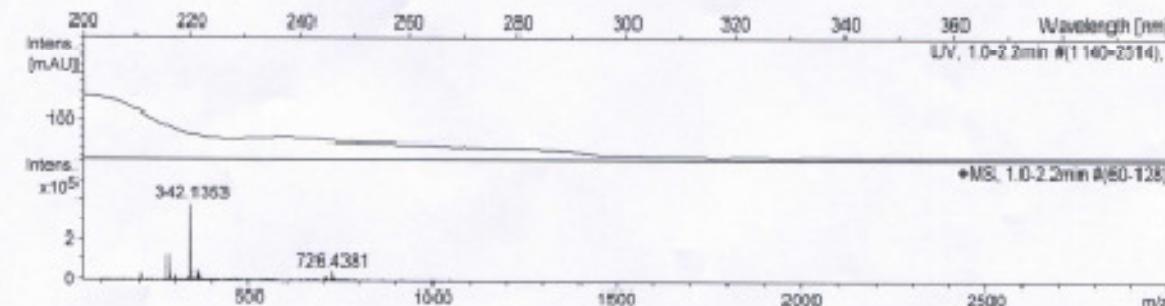
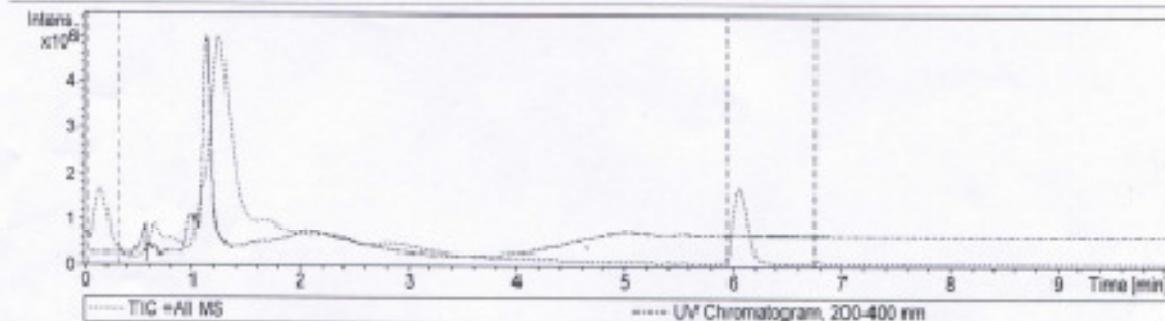
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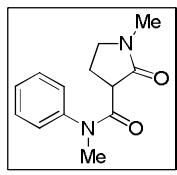
Operator: Meena Sharma

Instrument: microTOF-Q II 10330

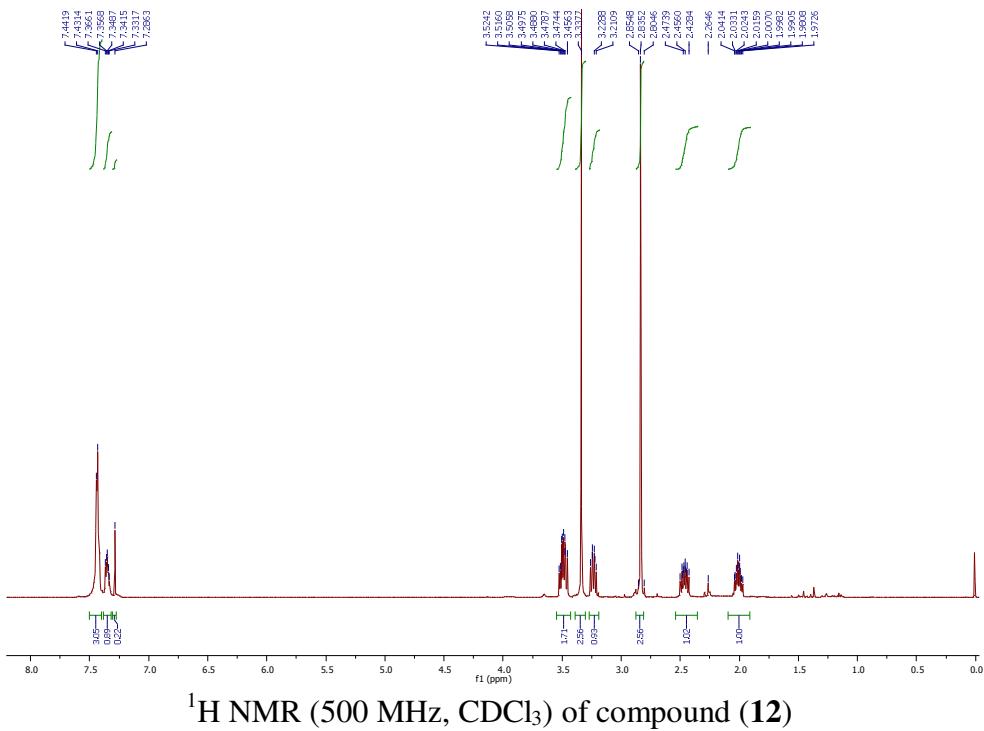
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

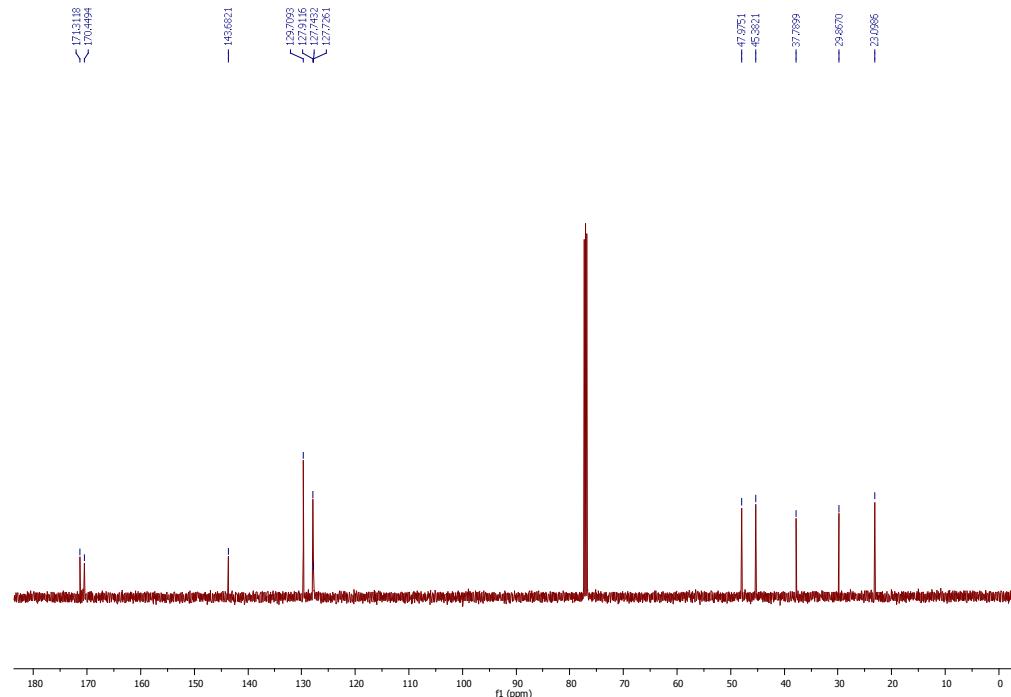




±(12)

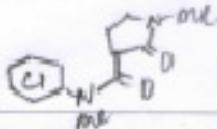


¹H NMR (500 MHz, CDCl₃) of compound (**12**)



¹³C NMR (125 MHz, CDCl₃) of compound (12)

$\pm (n)$



Display Report

Analysis Info

Analysis Name: D:\Data\user data\April 2012\13.apr\Dr. A. Bisal- SG4-90_1-A_6_01_1780.d
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 Sample Name: Dr. A. Bisal- SG4-90
 Comment:

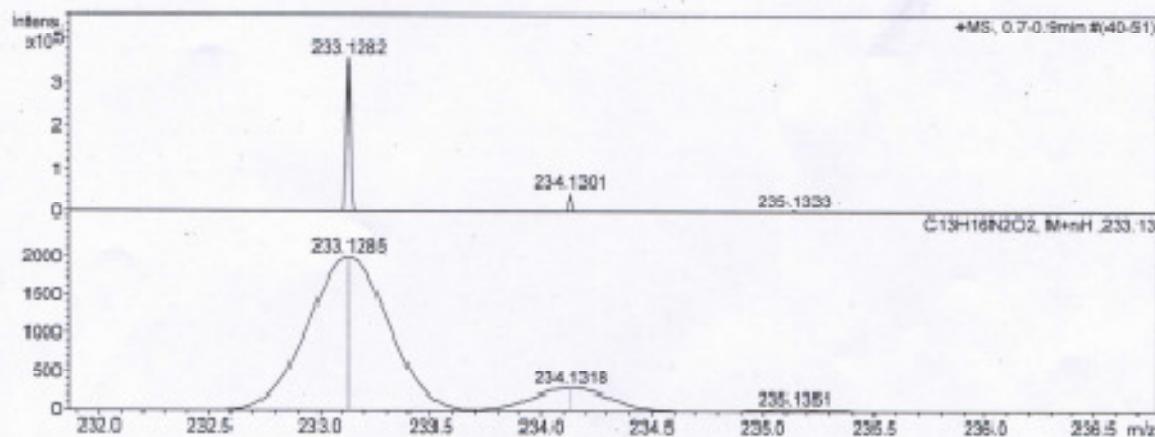
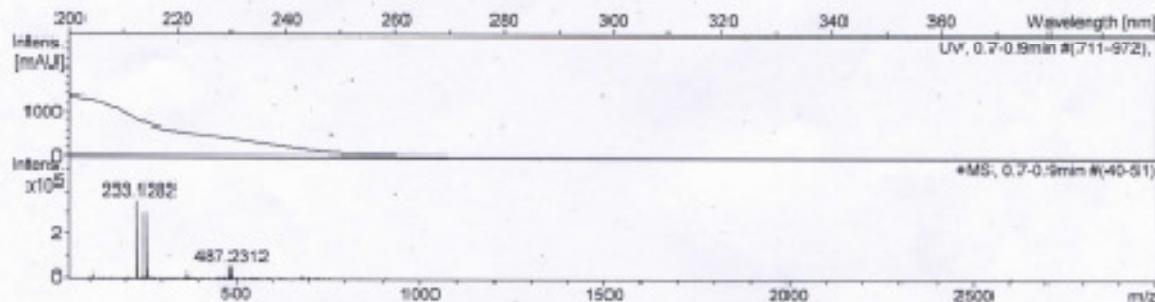
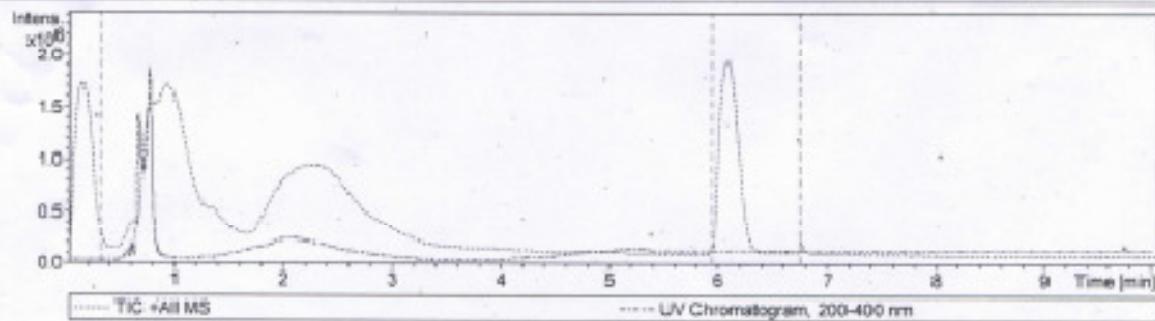
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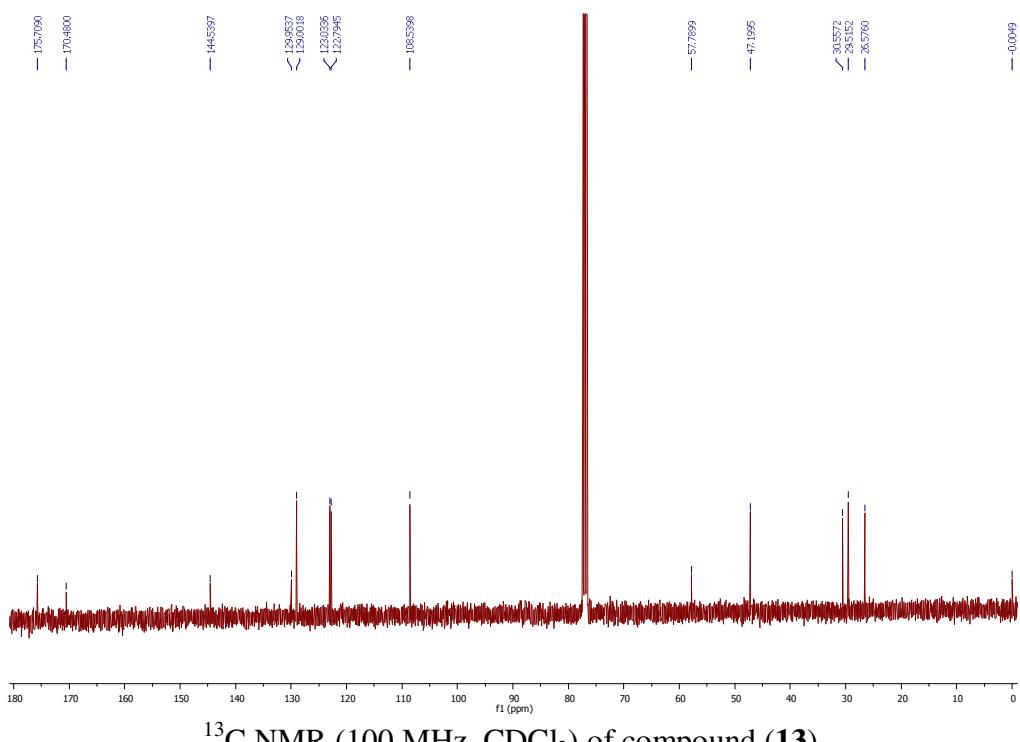
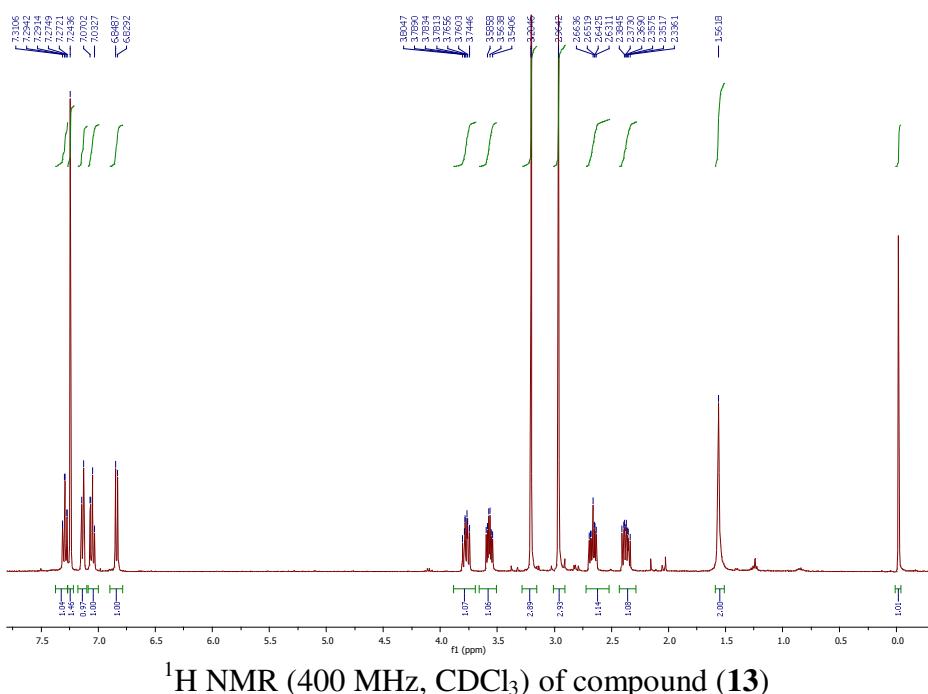
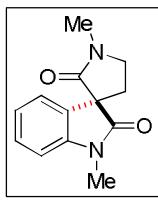
Operator: Meena Sharma

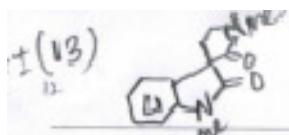
Instrument: micrOTOF-Q II 10330

Acquisition Parameter

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







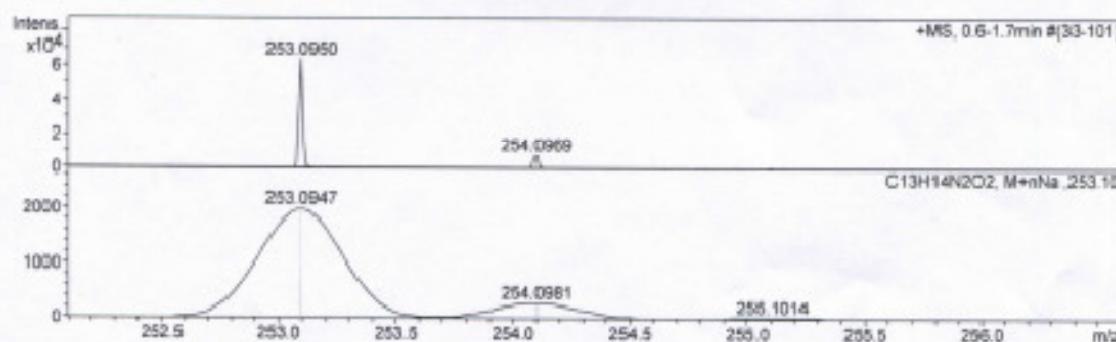
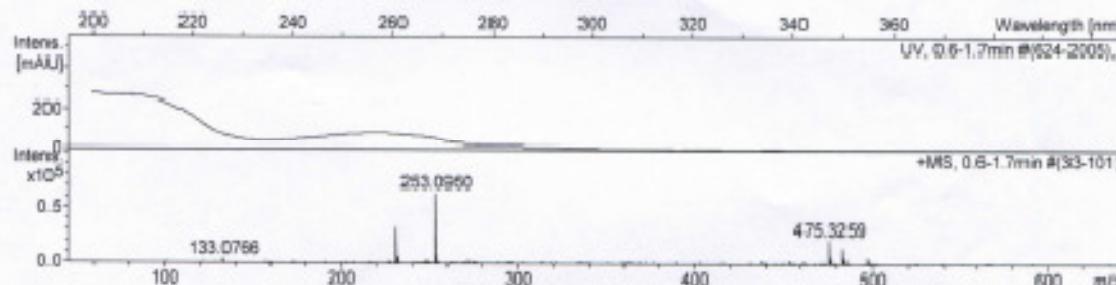
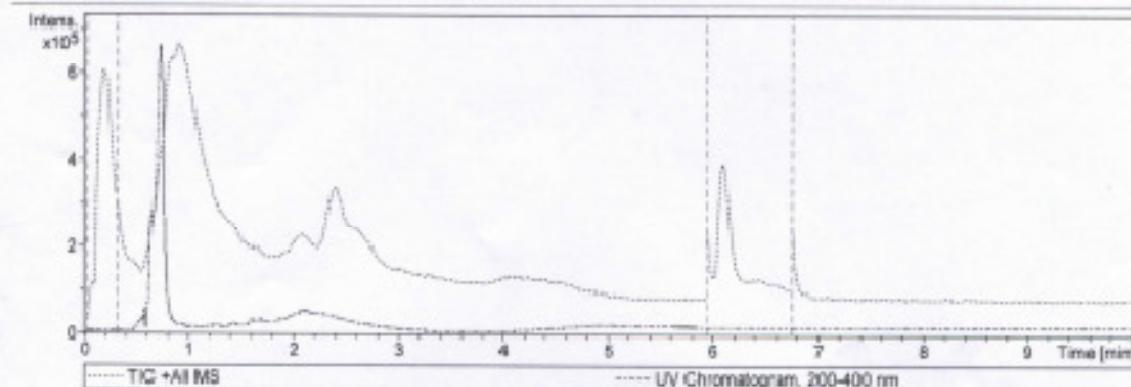
Display Report

Analysis Info

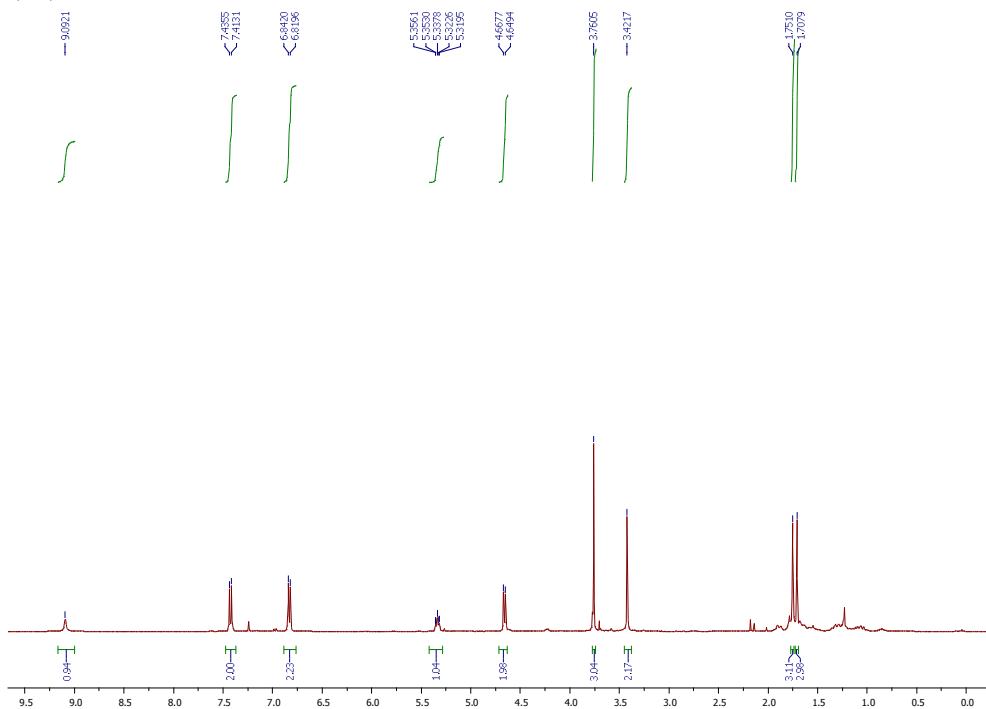
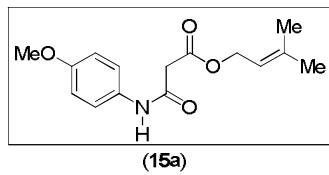
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Method	HRLCMS-20 Sept.m	Operator	Meena Sharma
Sample Name	Dr.A. Bisai-SG4-96	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

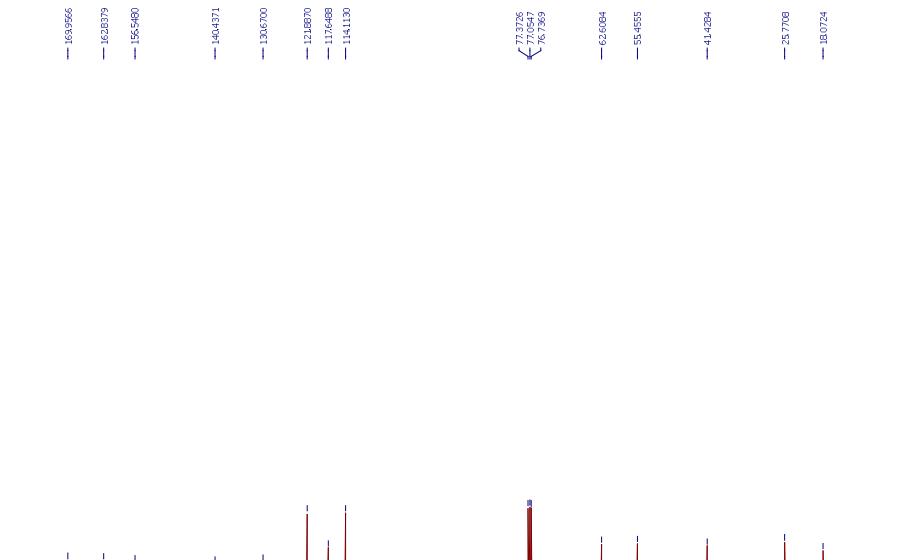
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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of compound 13



^1H NMR(400 MHz, CDCl_3) of compound (\pm) -15a



^{13}C NMR(100 MHz, CDCl_3) of compound (\pm) -15a

Display Report

Analysis Info

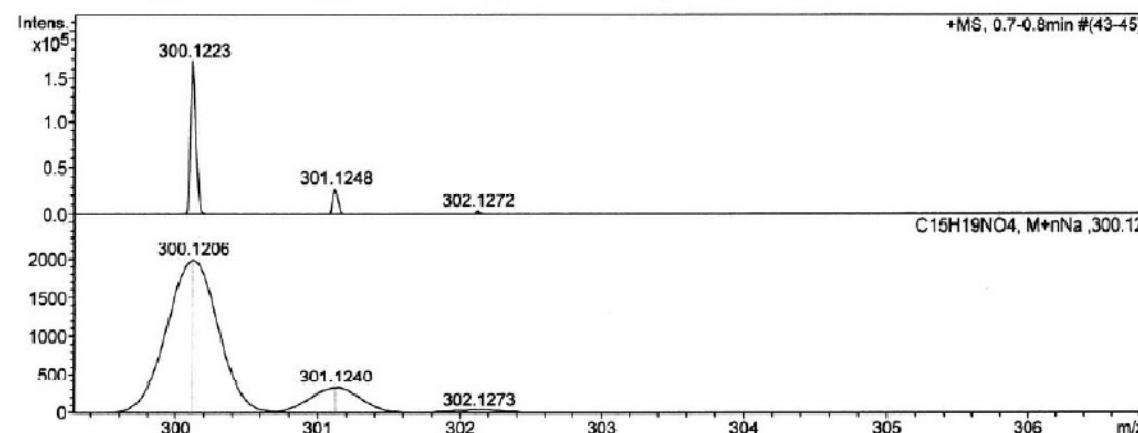
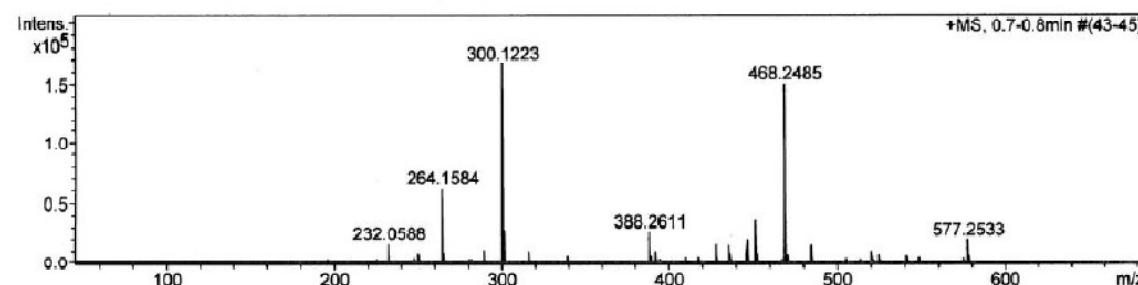
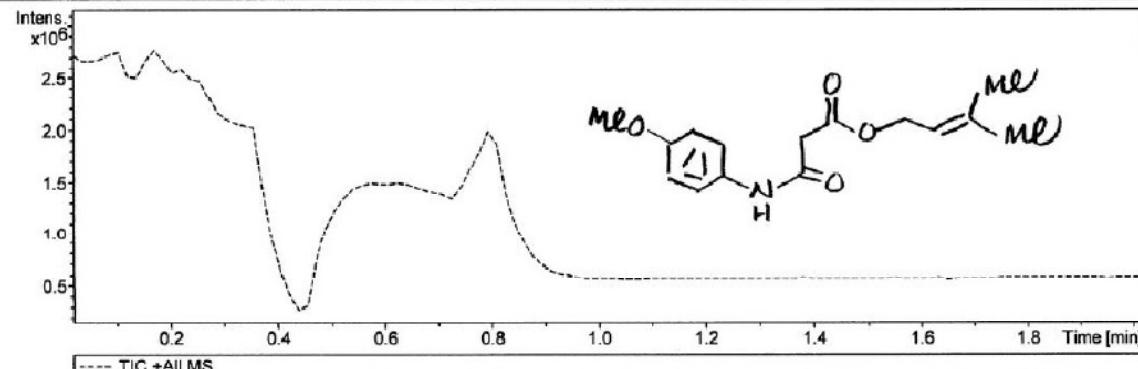
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 Sample Name SG-5-278
 Comment

Acquisition Date 10/30/2012 2:28:35 PM

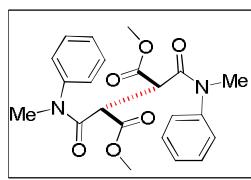
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

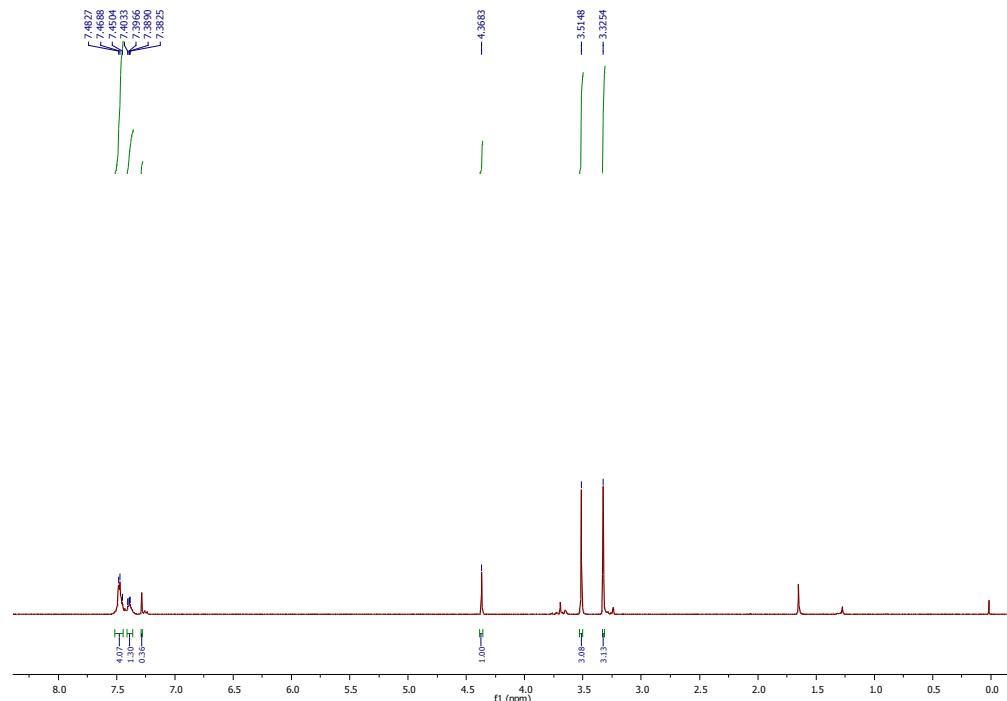
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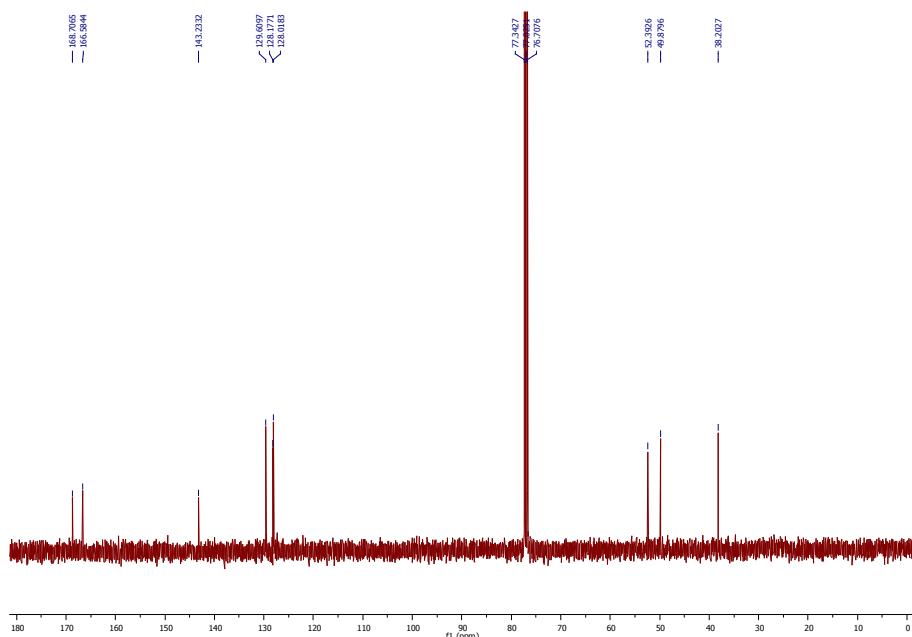
Scanned copy of mass spectrum of compound (±)-15a



\pm (16a)



^1H NMR(400 MHz, CDCl_3) of compound \pm (16a)



^{13}C NMR(100 MHz, CDCl_3) of compound \pm (16a)

Display Report

Analysis Info

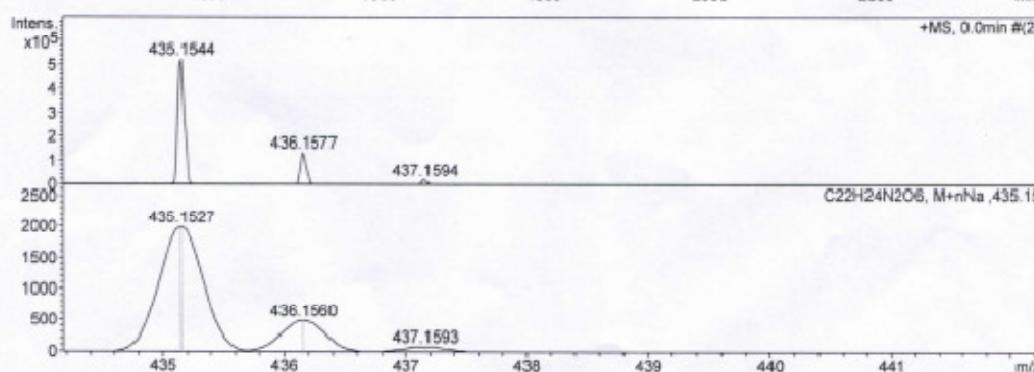
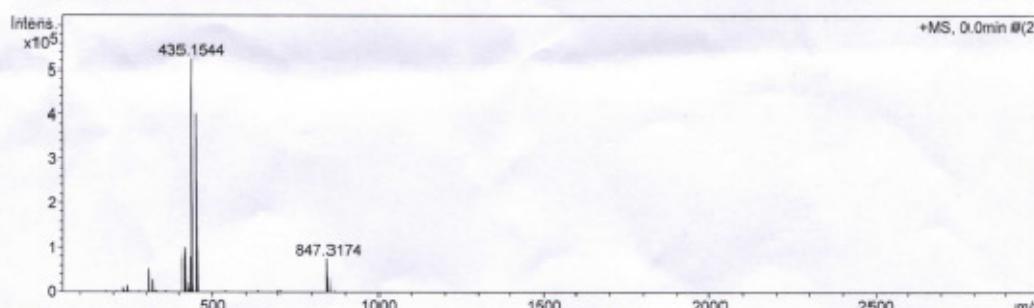
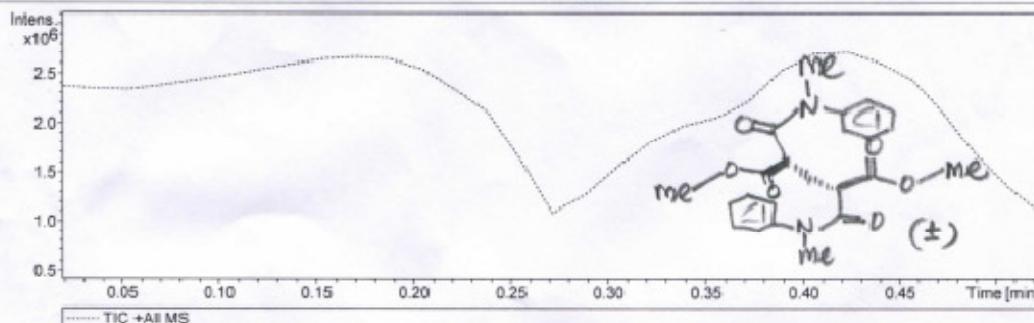
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 Method: tune_low.m
 Sample Name: AB-SG5-91
 Comment:

Acquisition Date: 7/19/2012 1:04:27 PM

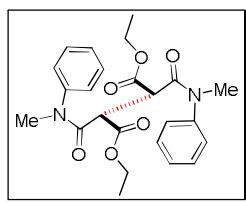
 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

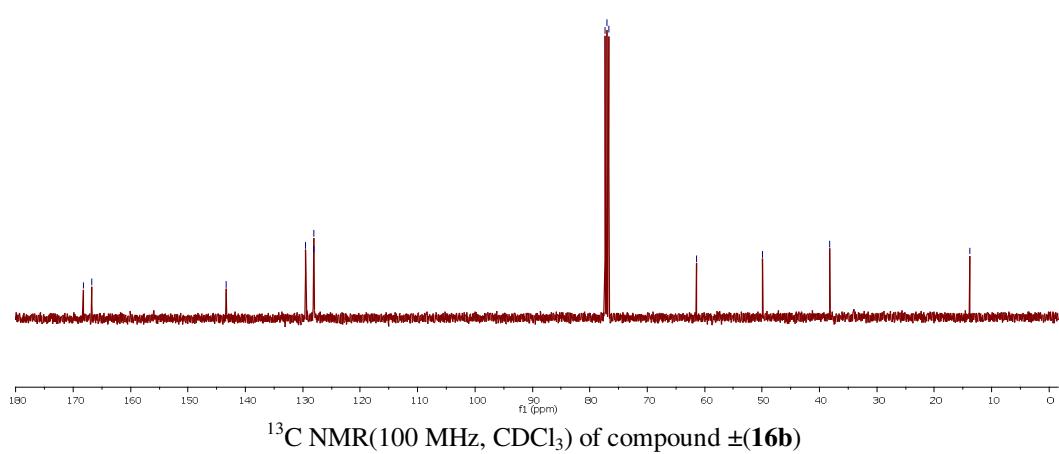
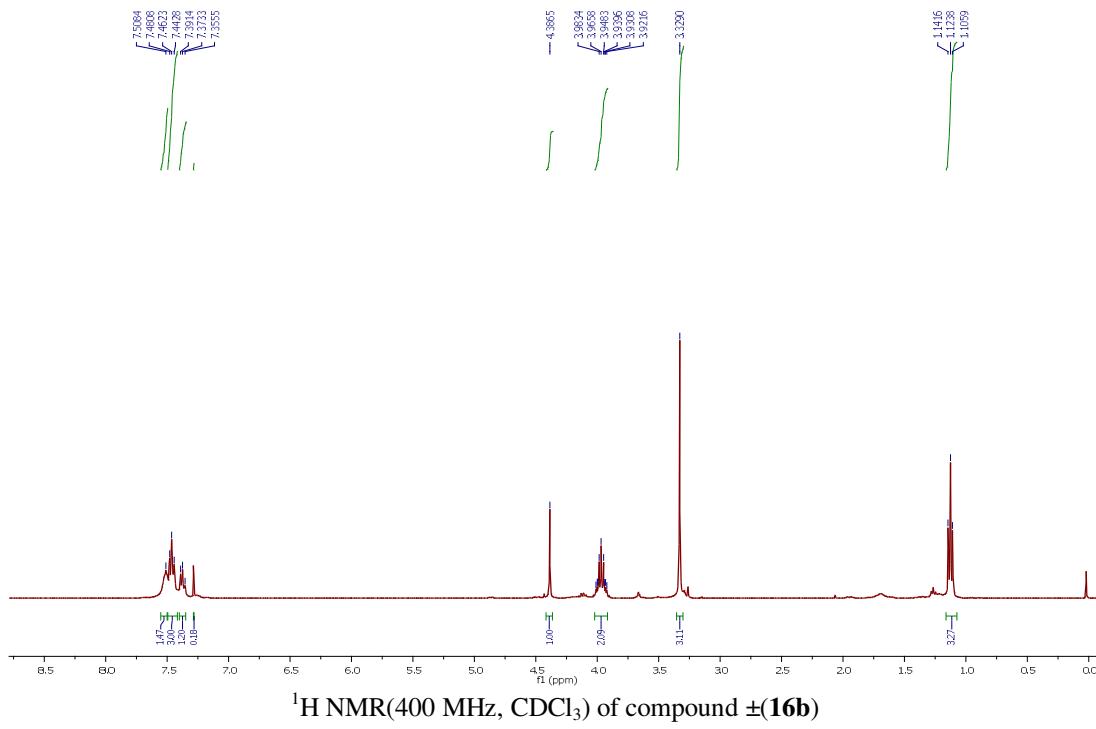
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Scanned copy of mass spectrum of compound $\pm(16a)$



±(16b)



Display Report

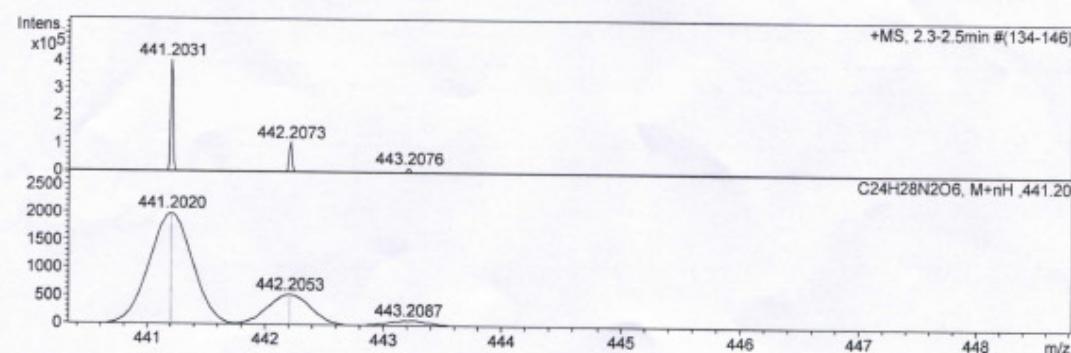
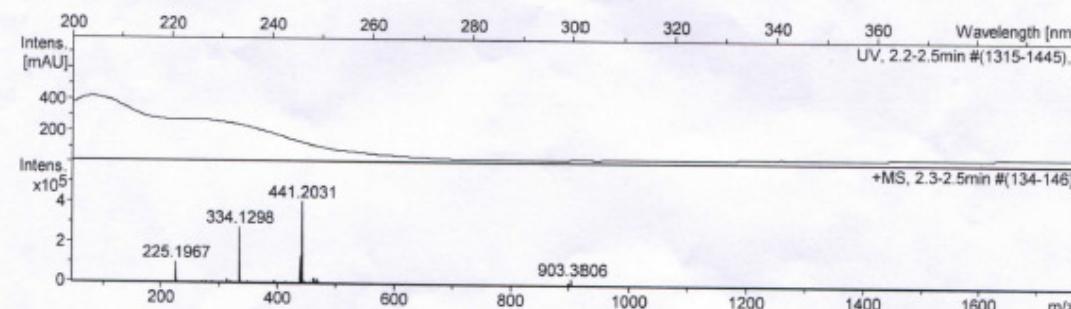
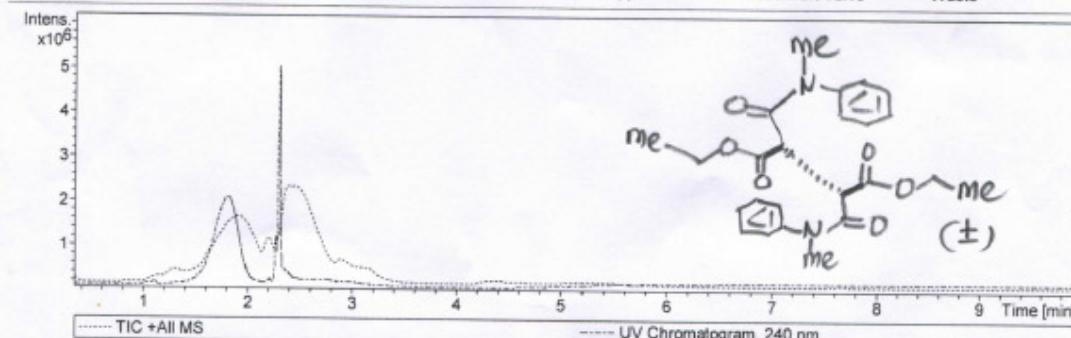
Analysis Info

Analysis Name D:\Data\user data\JULY-2012\JULY 18\Dr. A. Bisai- SG-5-88_1-A_5_01_2777.d
 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG-5-88
 Comment

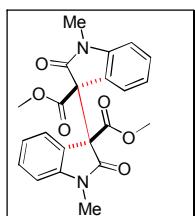
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 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

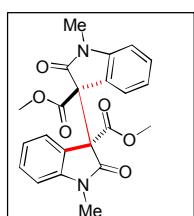
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of compound ±(16b)



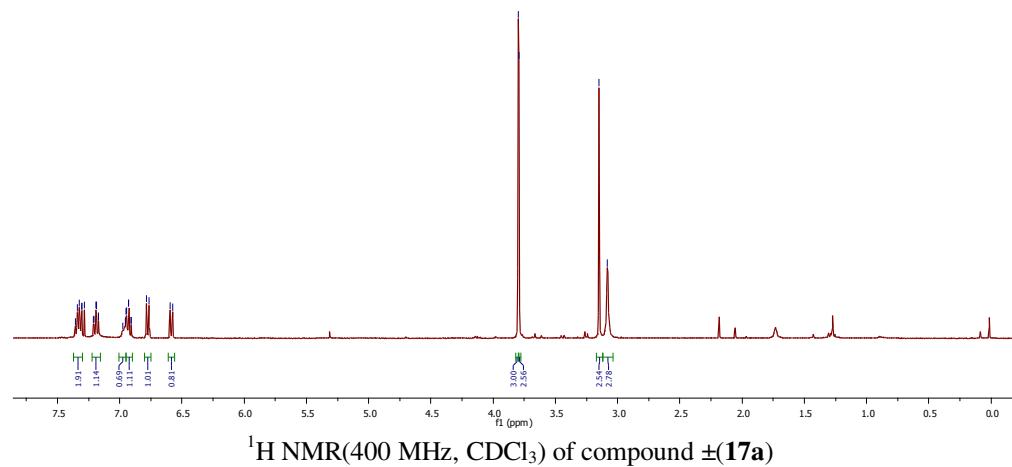
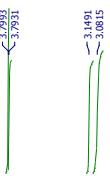
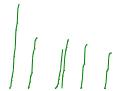
trans \pm (17a)
Major diastereomer



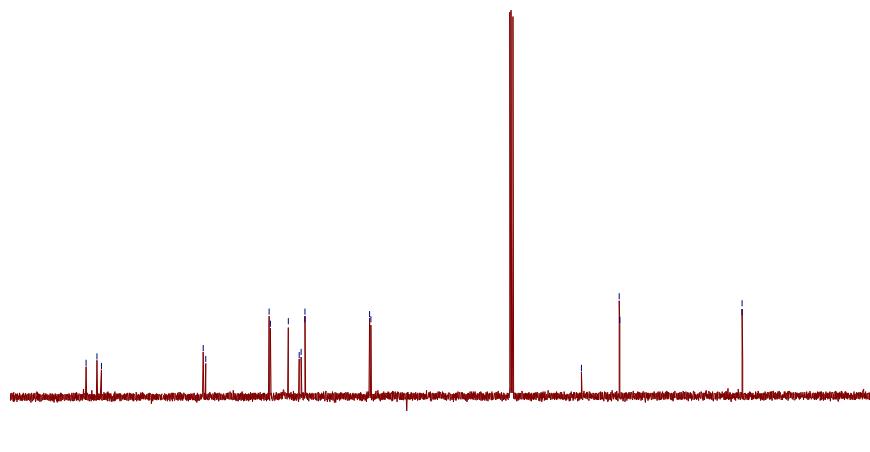
meso-(17a)
Minor diastereomer

t, *d*, *dt*, *dd*

7.833
7.8097
7.8068
7.8063
7.1875
7.1770
7.1681
6.9455
6.9073
6.7660
6.5956
6.5762



194.0252
167.7933
166.8026
143.9023
138.1211
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125.8715
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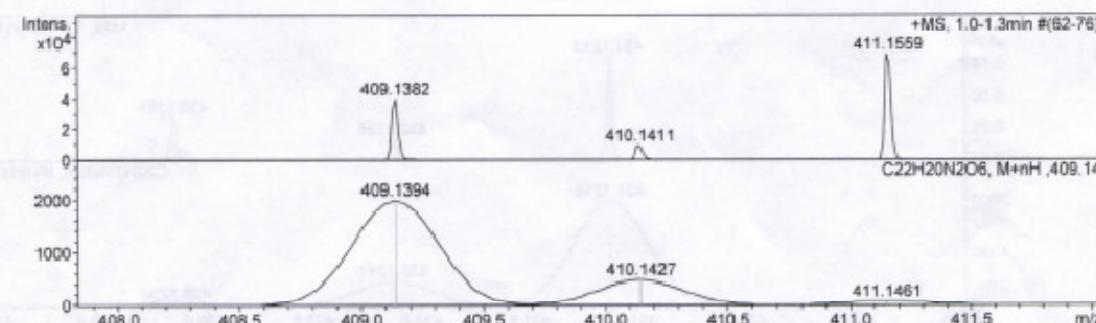
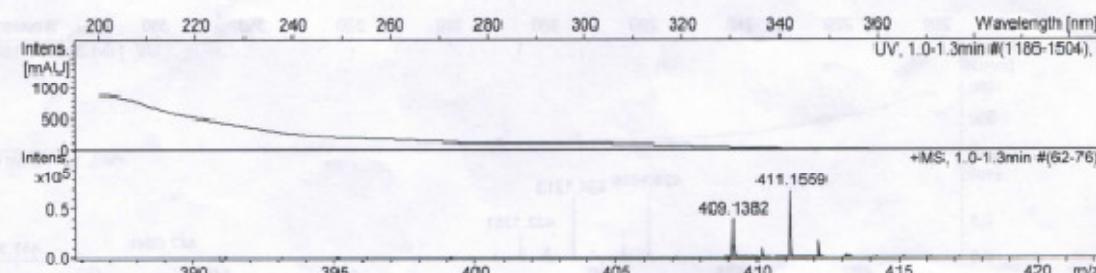
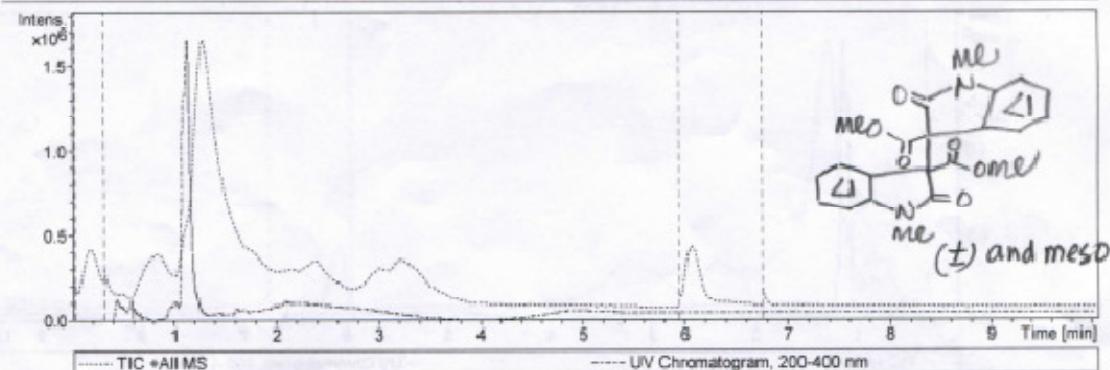
Display Report

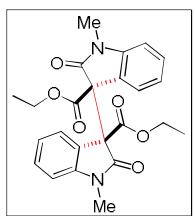
Analysis Info

Analysis Name	D:\Data\user data\FEB 2012\01 FEB\Dr. A. Bisai-SG4-88PS_1-A_8_01_991.d	Acquisition Date	2/1/2012 12:22:42 PM
Method	HRLCMS-20 Sept.m	Operator	Meena Sharma
Sample Name	Dr. A. Bisai-SG4-88PS	Instrument	microTOF-Q II 10330
Comment			

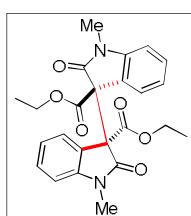
Acquisition Parameter

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

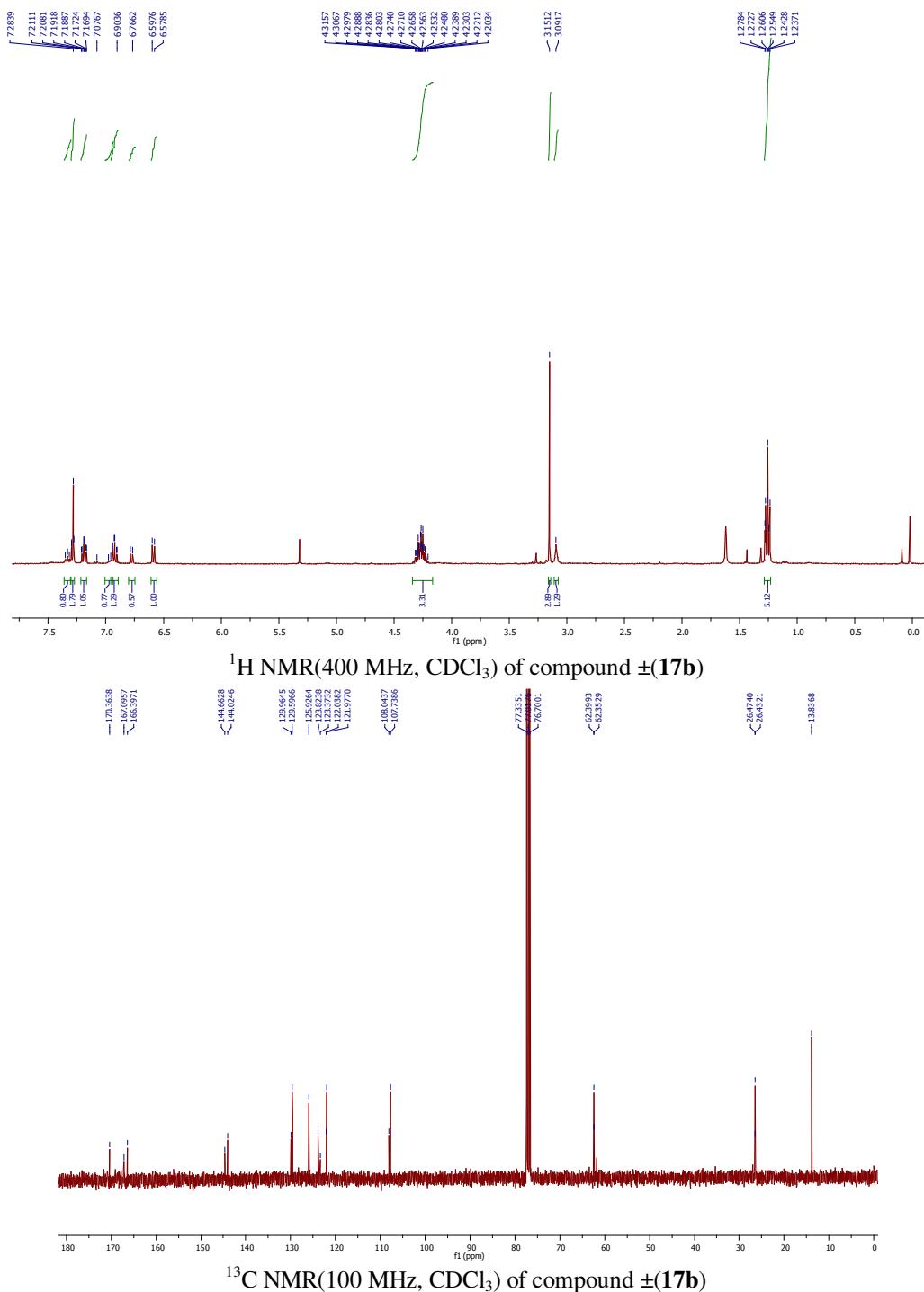




trans- \pm (17b)
Major diastereomer



meso-(17b)
Minor diastereomer



Display Report

Analysis Info

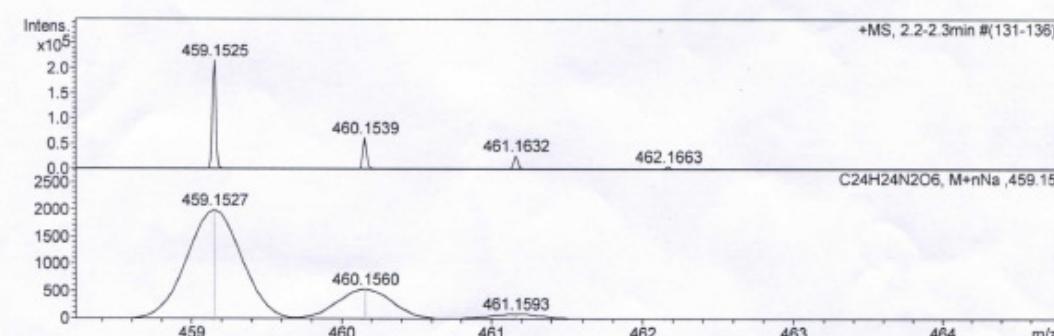
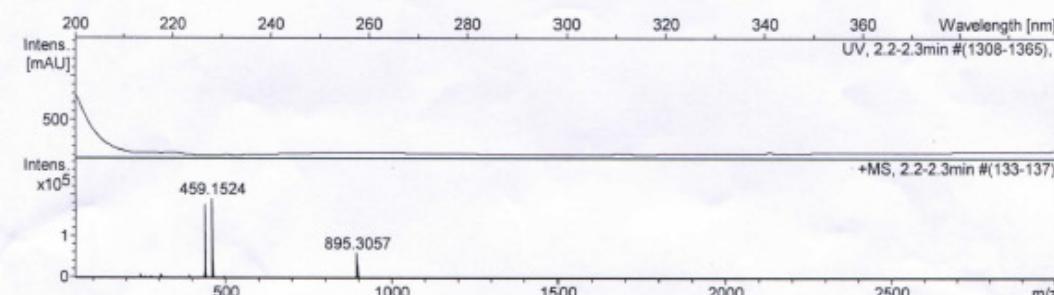
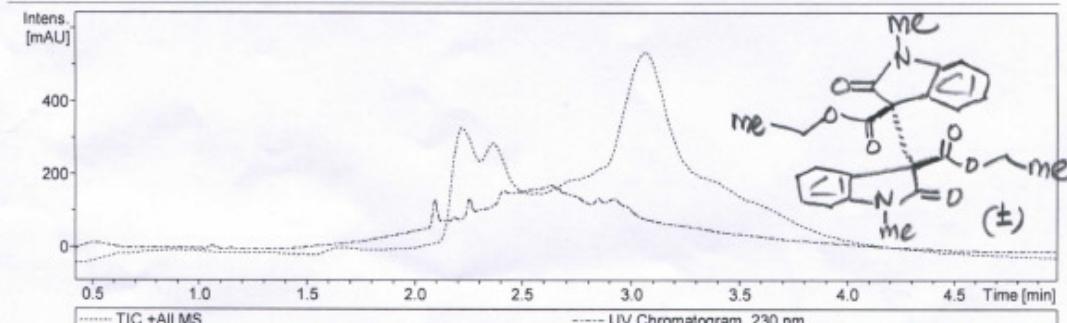
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 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG5-62
 Comment

Acquisition Date 7/18/2012 2:08:25 PM

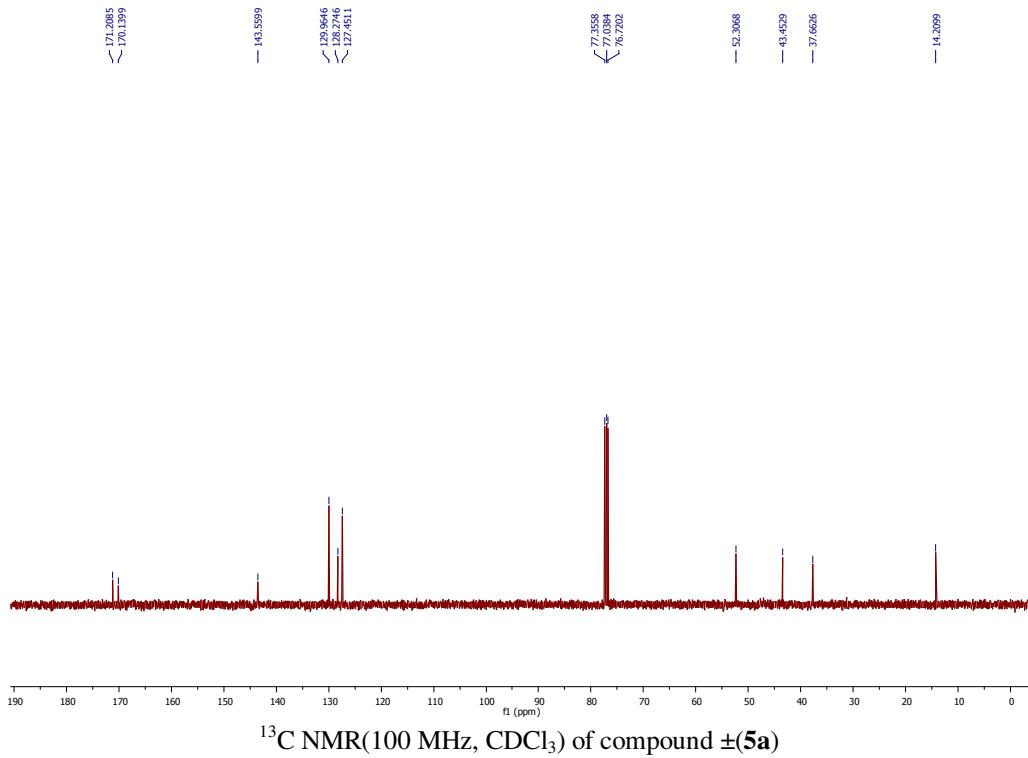
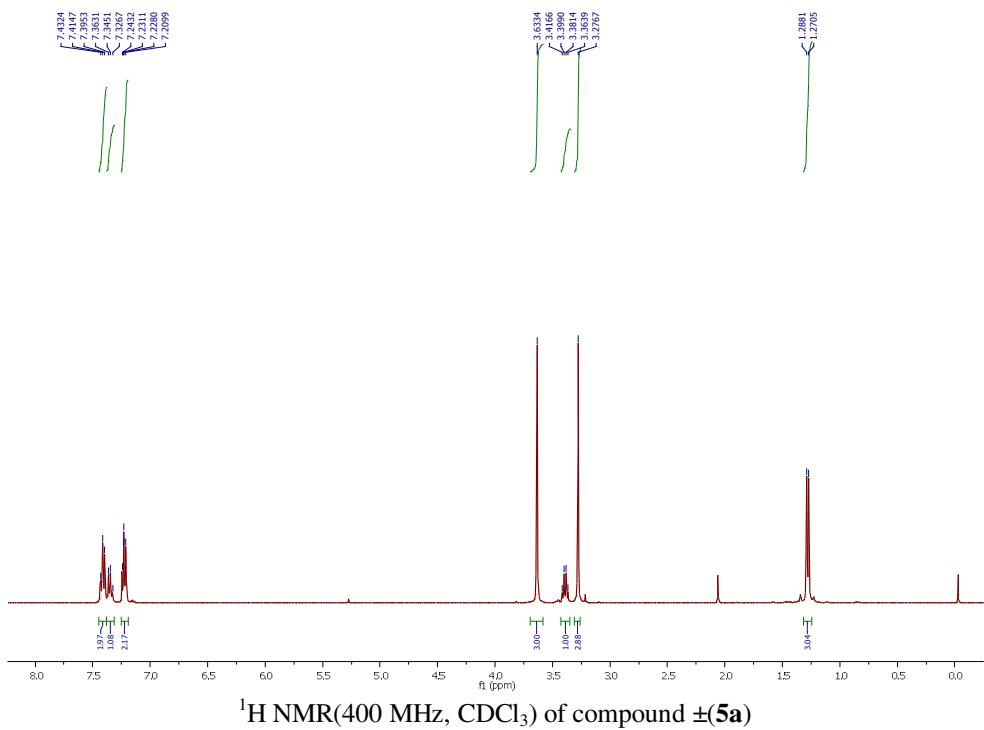
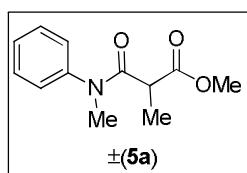
 Operator Meena Sharma
 Instrument micrOTOF-Q II 10330

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



Scanned copy of mass spectrum of compound \pm (17b)



Display Report

Analysis Info

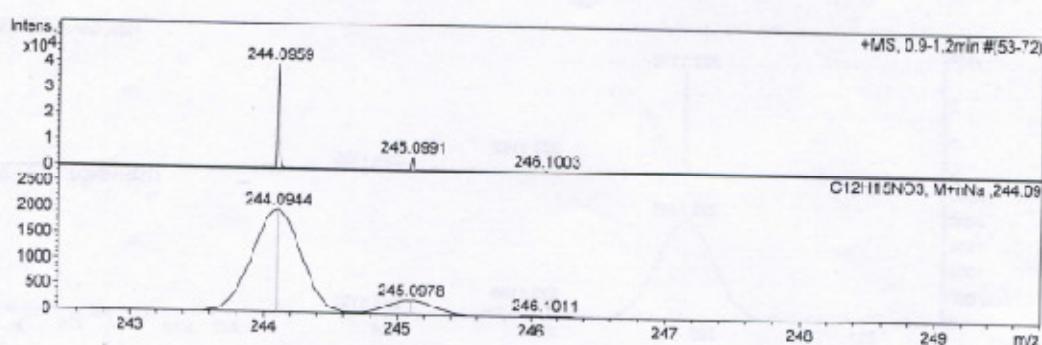
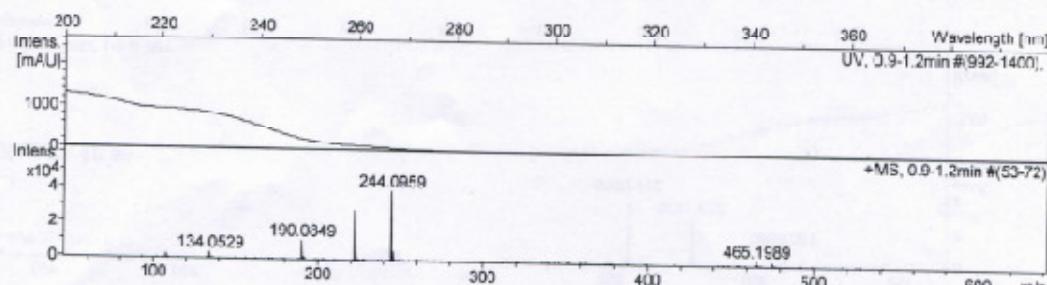
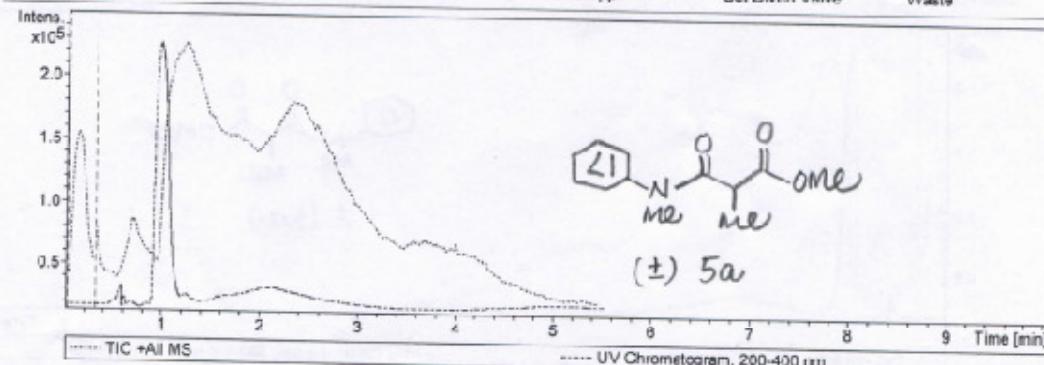
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 Method HRLCMS-20 Sept.m
 Sample Name Dr. A. Bisai- SG4-181
 Comment

Acquisition Date 3/6/2012 4:42:49 PM

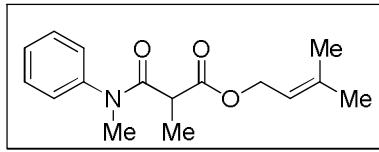
 Operator Meenu Sharma
 Instrument micrOTOF-Q II 10330

Acquisition Parameter

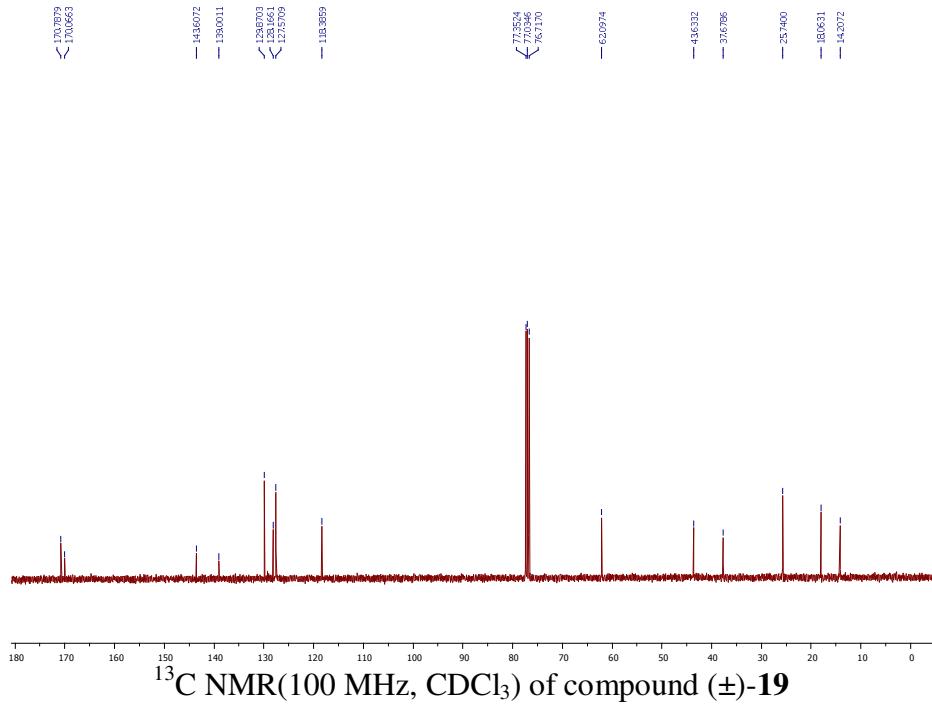
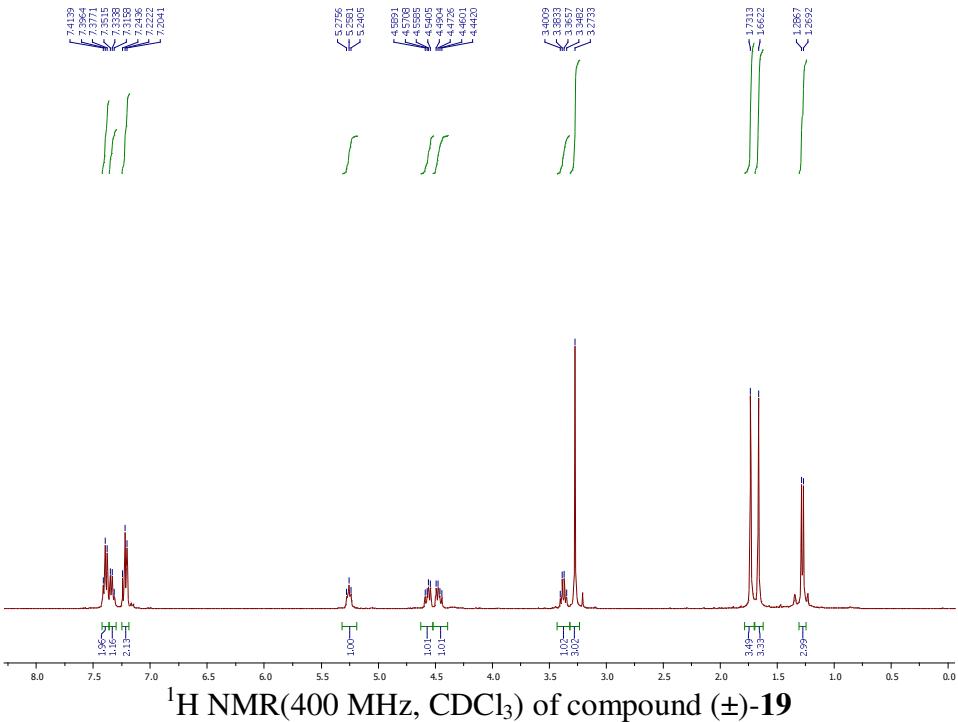
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



Scanned copy of mass spectrum of compound \pm (5a)



±(19)

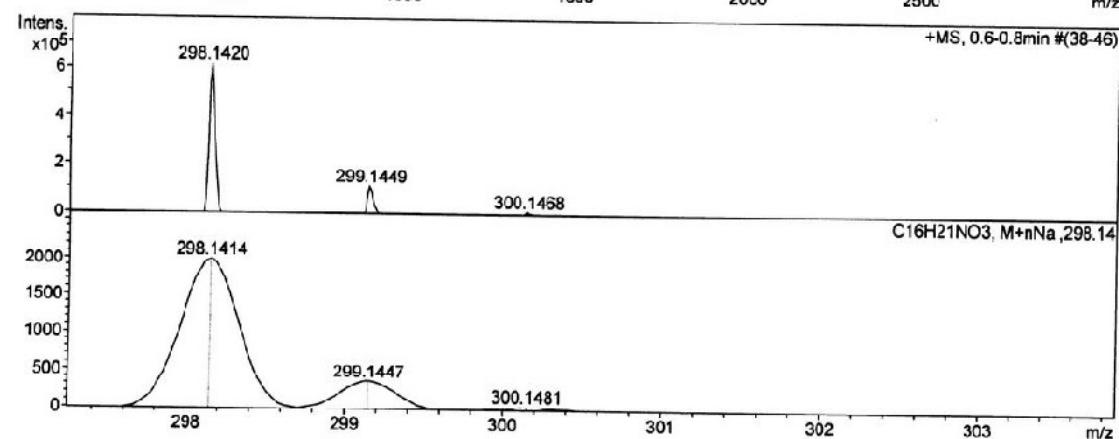
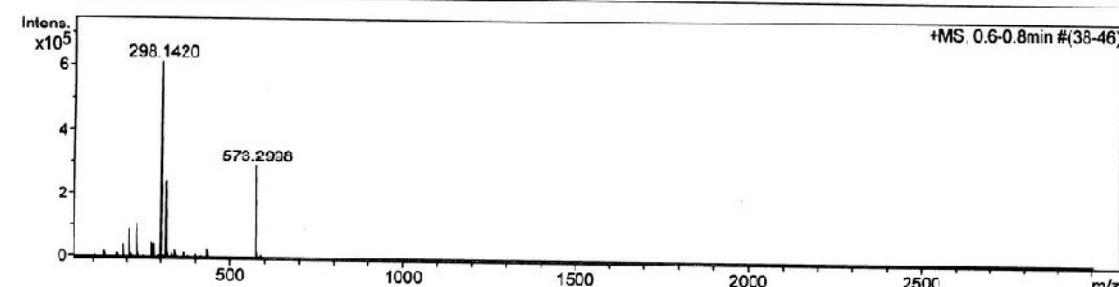
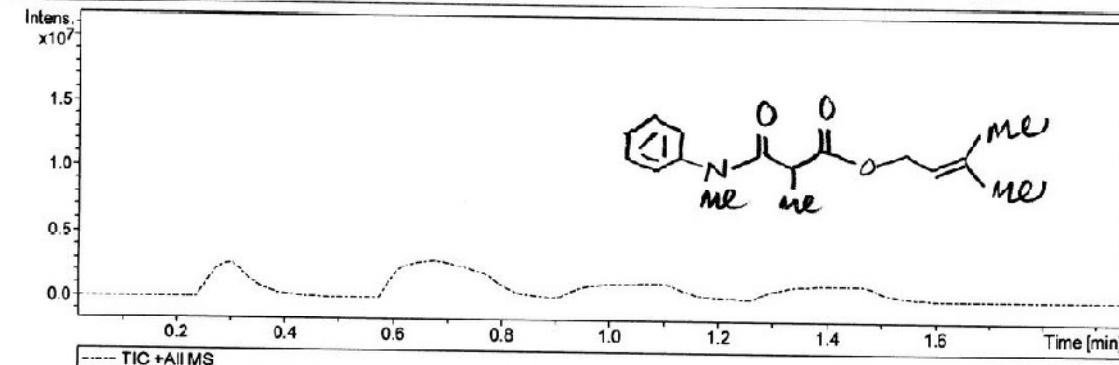


Display Report

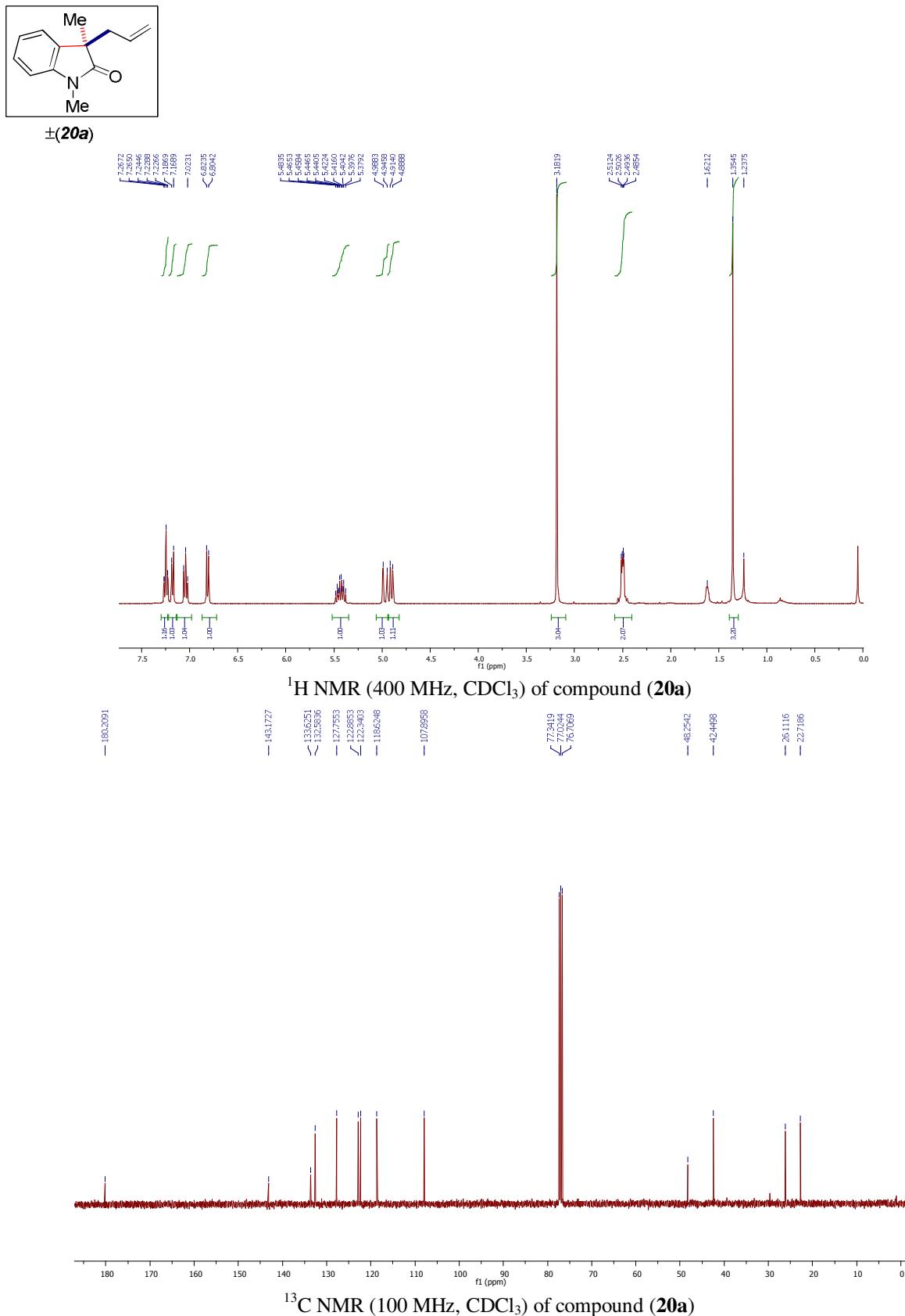
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Method	tune_low.m	Operator	Meena Sharma
Sample Name	AB-SG5-279	Instrument	micrOTOF-Q II 10330
Comment			

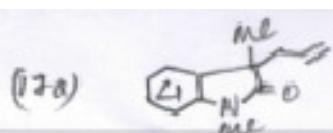
Acquisition Parameter

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
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Scanned copy of mass spectrum of compound (\pm)-19





Display Report

Analysis Info

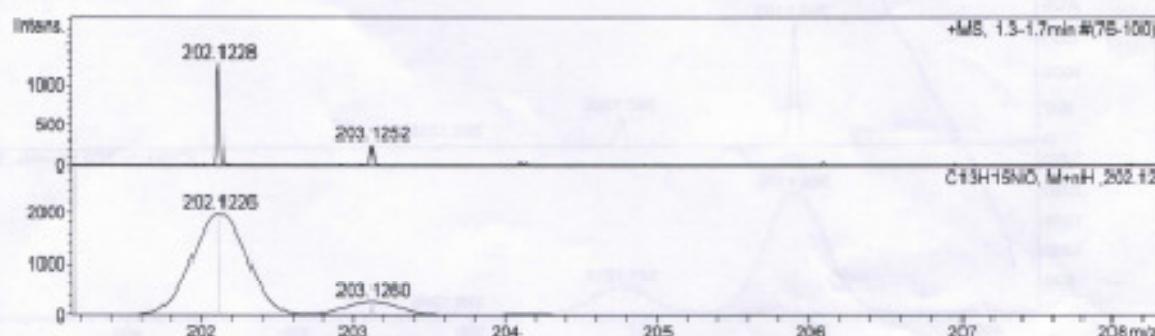
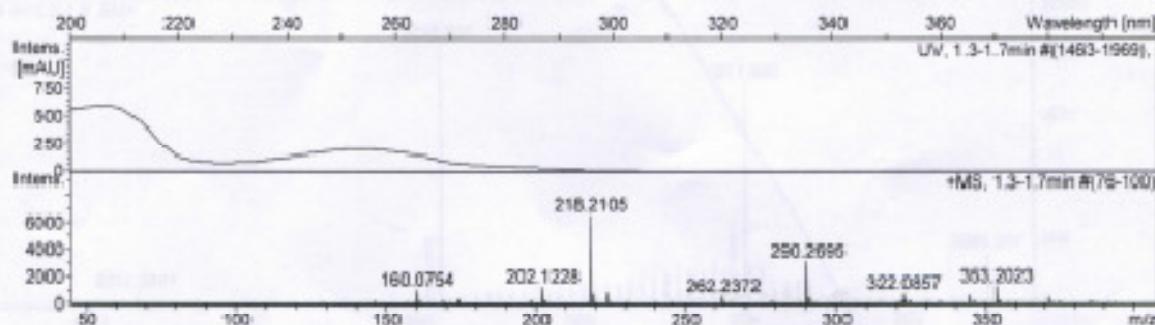
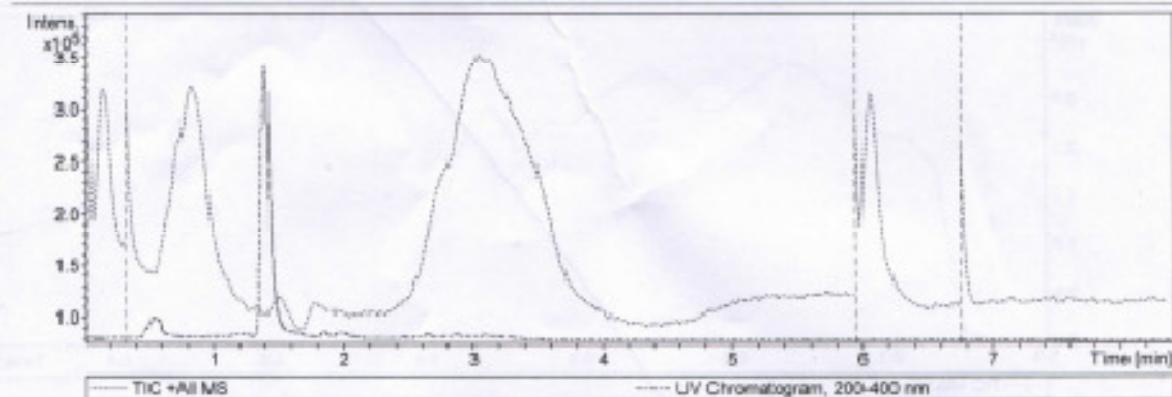
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 Method: HRLCMS-20 Sept.m
 Sample Name: Dr. A. Bisai-SG4-001
 Comment:

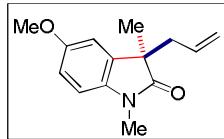
Acquisition Date: 12/26/2011 12:53:08 PM

 Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

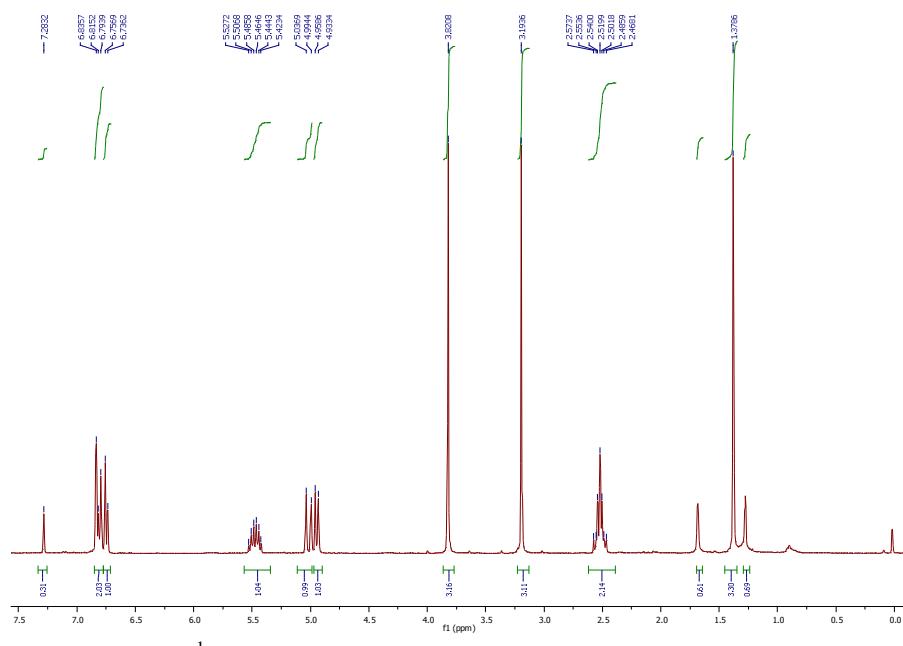
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

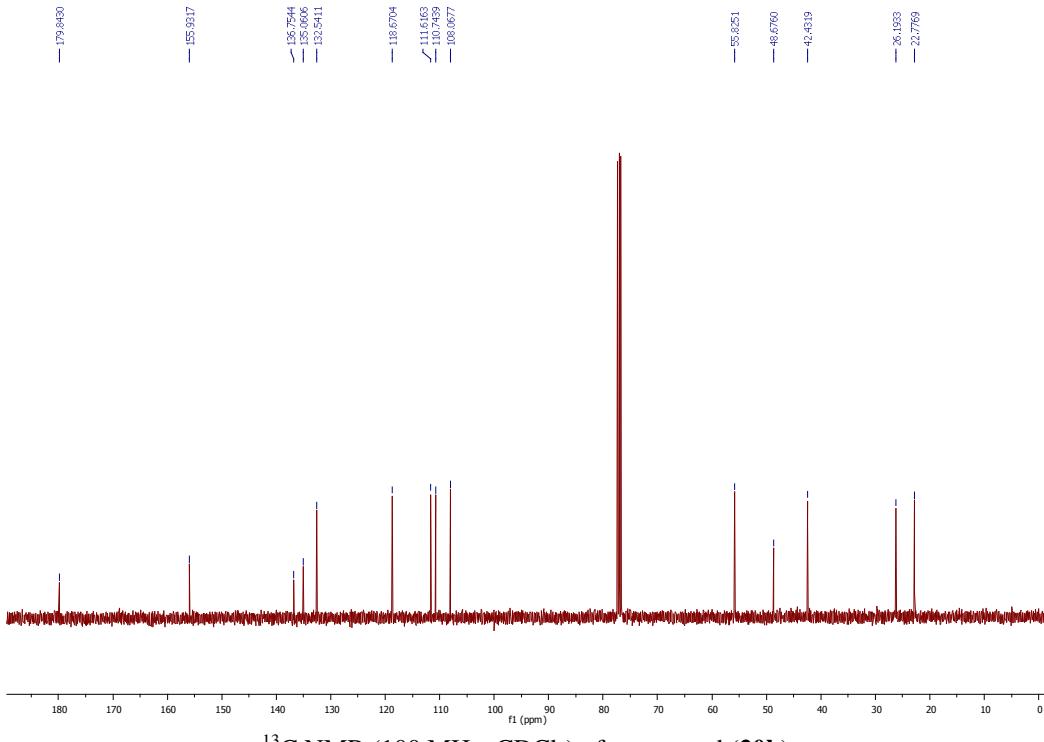




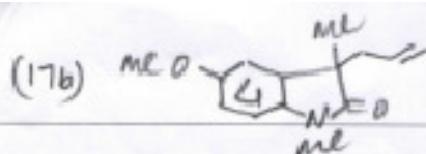
$\pm(20b)$



¹H NMR (400 MHz, CDCl₃) of compound (**20b**)



¹³C NMR (100 MHz, CDCl₃) of compound (**20b**)



Display Report

Analysis Info

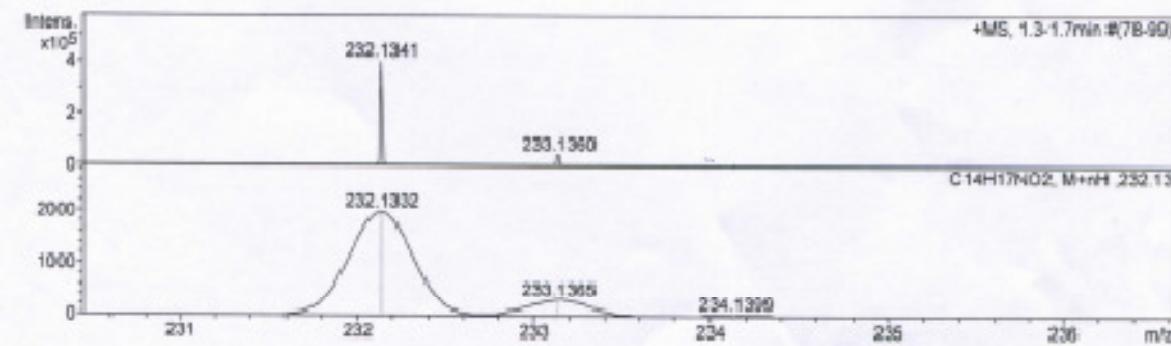
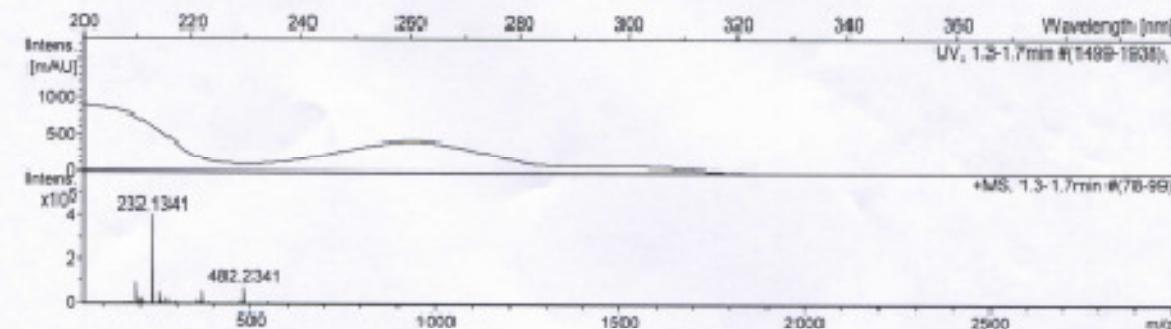
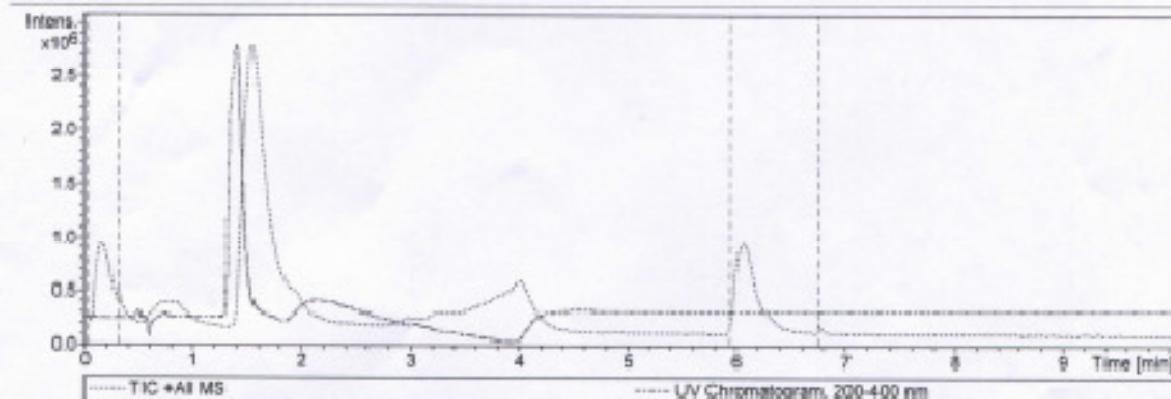
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 Sample Name: Dr. A. Bisal-SG4-08
 Comment:

Acquisition Date: 12/29/2011 4:06:08 PM

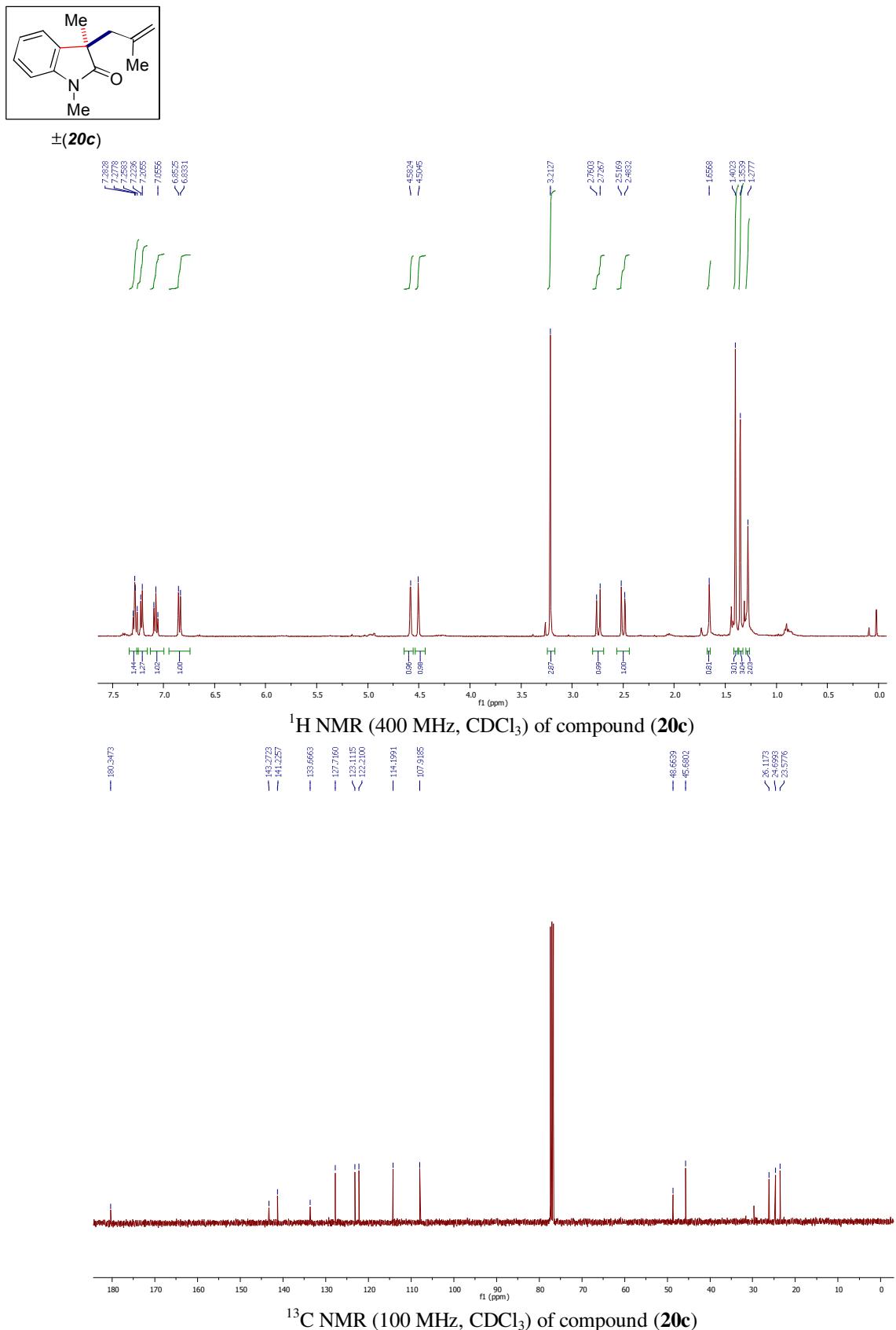
Operator: Meena Sharma
 Instrument: microTOF-Q II 10330

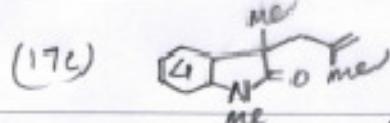
Acquisition Parameter

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



Scanned copy of mass spectrum of compound ±(20b)





Display Report

Analysis Info

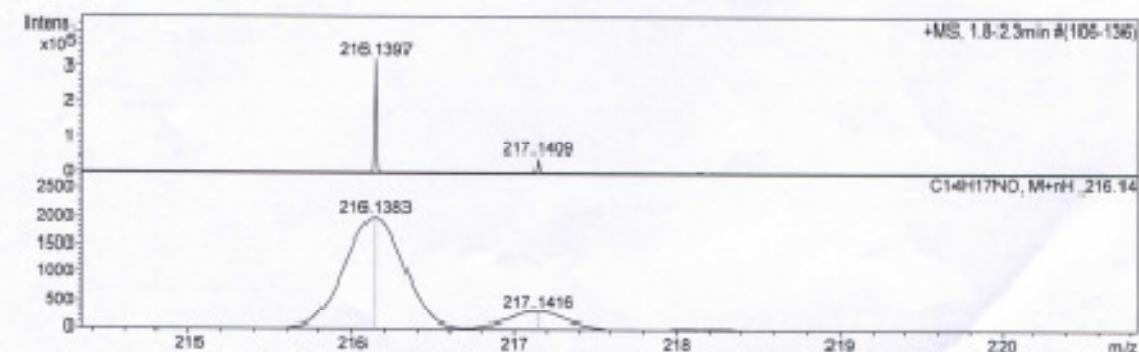
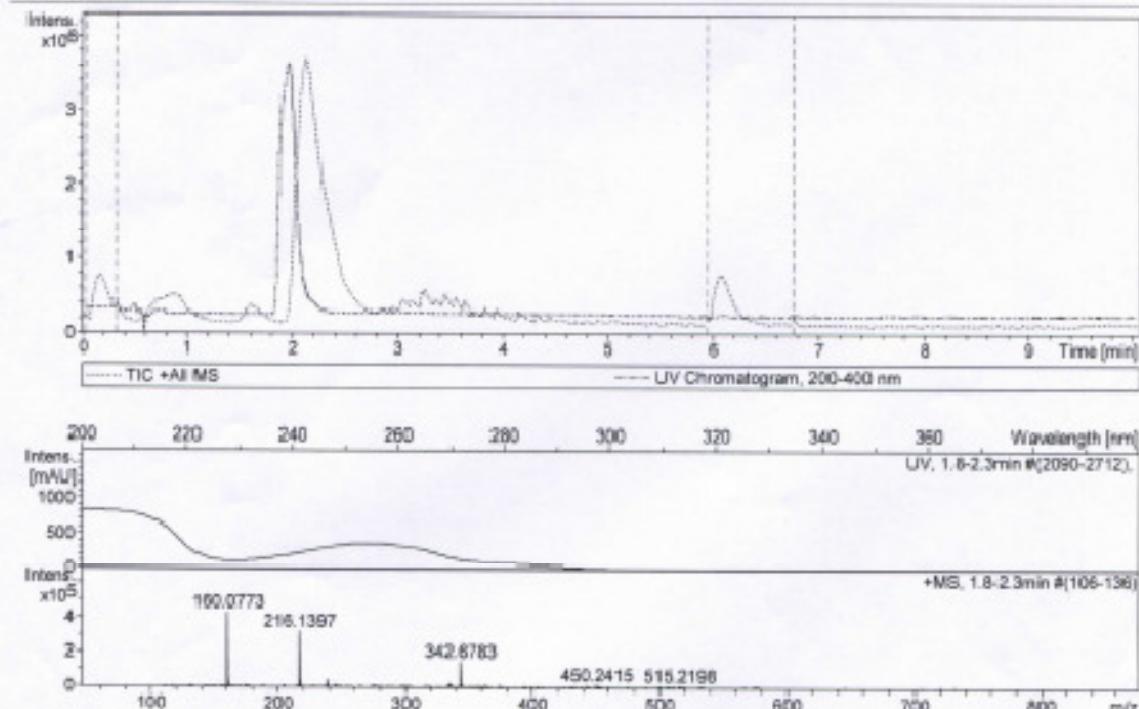
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 Sample Name: Dr. A. Bisai-SG4-19
 Comment:

Acquisition Date: 1/6/2012 3:56:53 PM

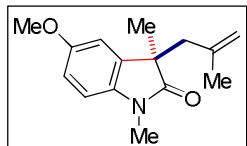
Operator: Meena Sharma
 Instrument: micrOTOF-Q II 10330

Acquisition Parameter

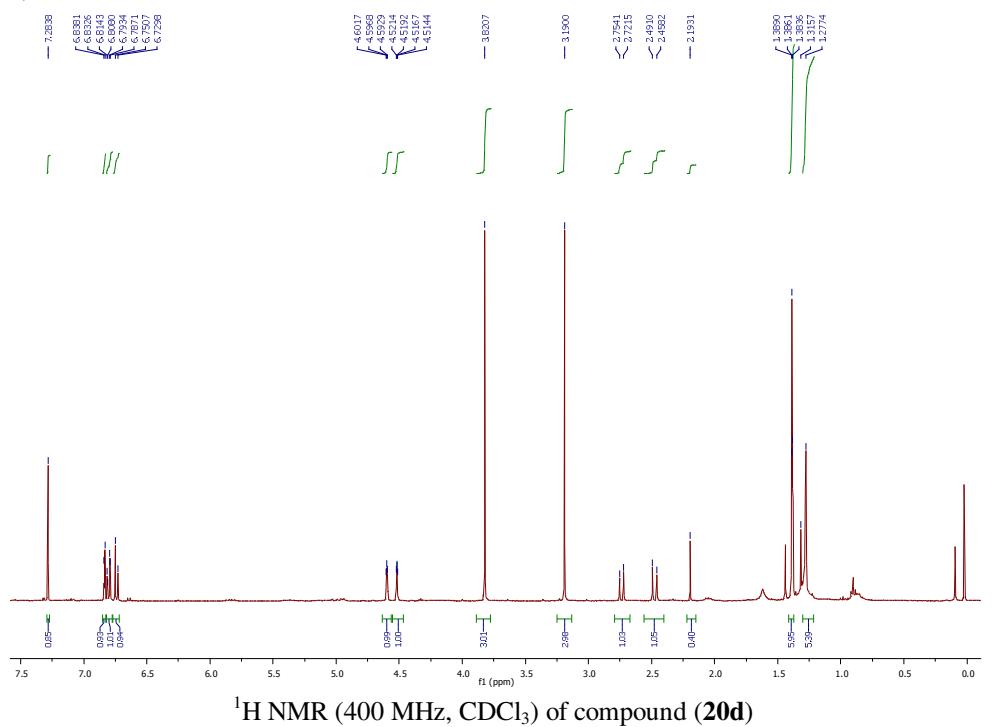
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



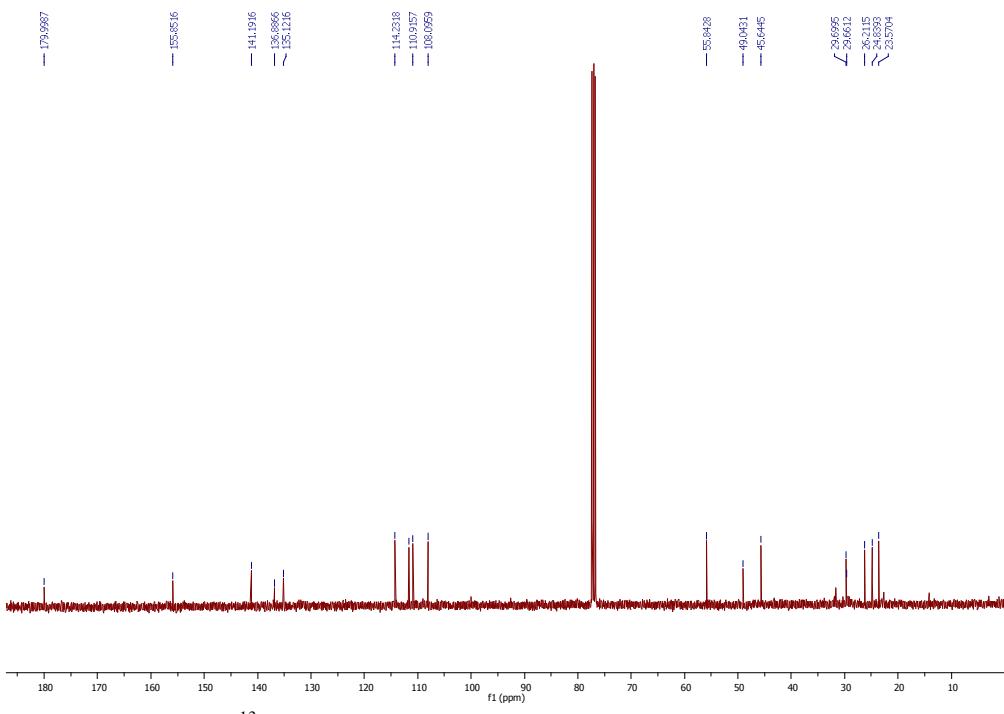
Scanned copy of mass spectrum of compound ±(20c)



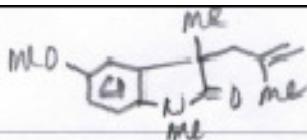
±(20d)



¹H NMR (400 MHz, CDCl₃) of compound (**20d**)



¹³C NMR (100 MHz, CDCl₃) of compound (**20d**)



Display Report

Analysis Info

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 Sample Name: Dr. A. Bisai- SB4-023
 Comment:

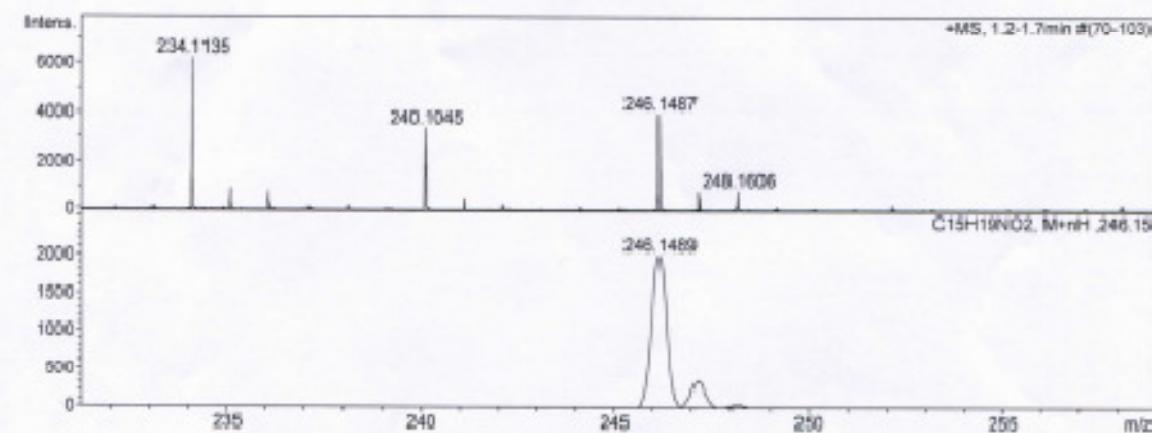
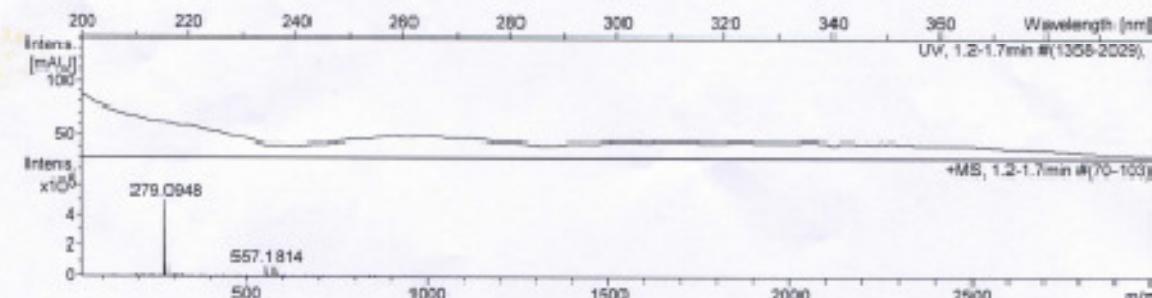
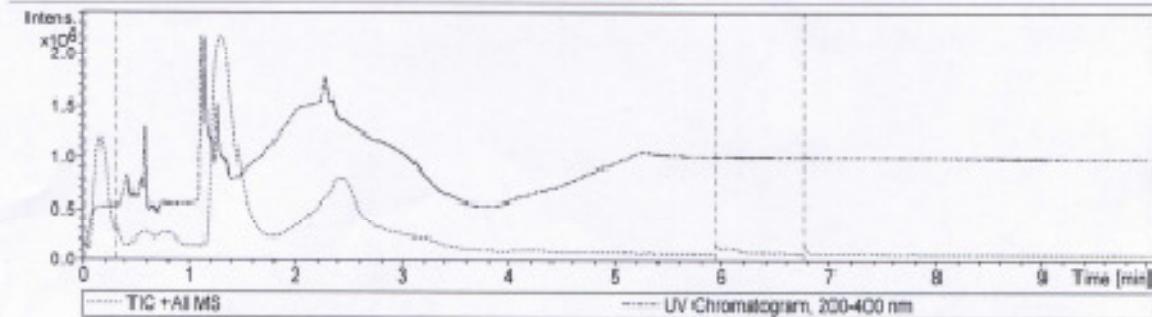
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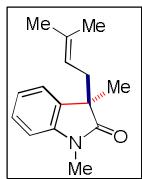
Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

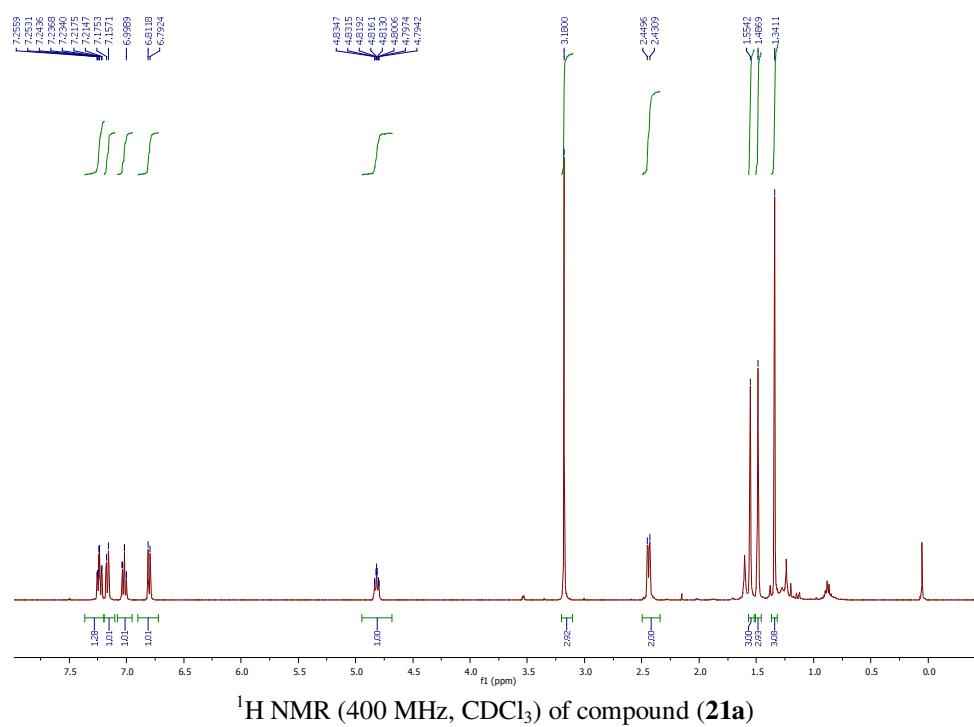
Acquisition Parameter

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Focus:	Active	Set Capillary:	4500 V	Set Dry Heater:	200 °C
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Scan End:	3000 m/z	Set Collision Cell RF:	130.0 Vpp	Set Divert Valve:	Waste

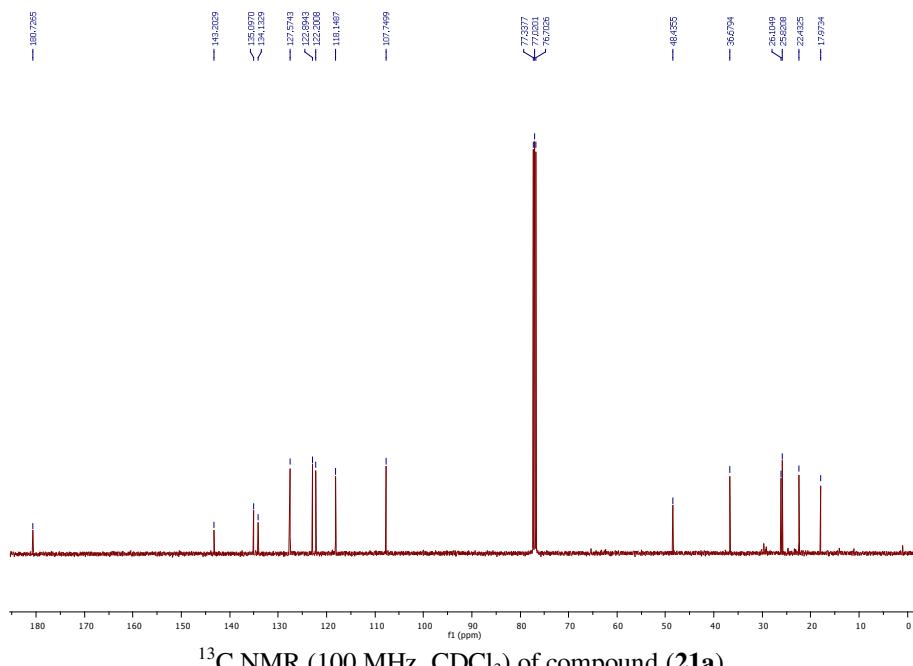




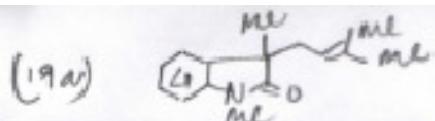
±(21a)



¹H NMR (400 MHz, CDCl₃) of compound (**21a**)



¹³C NMR (100 MHz, CDCl₃) of compound (**21a**)



AB-SG4-13-NPS2

Display Report

Analysis Info

Analysis Name: D:\Data\user\data\DEC 30\Dr. A. Bisai-SG4-NPS2_1-A.7_01_743.d
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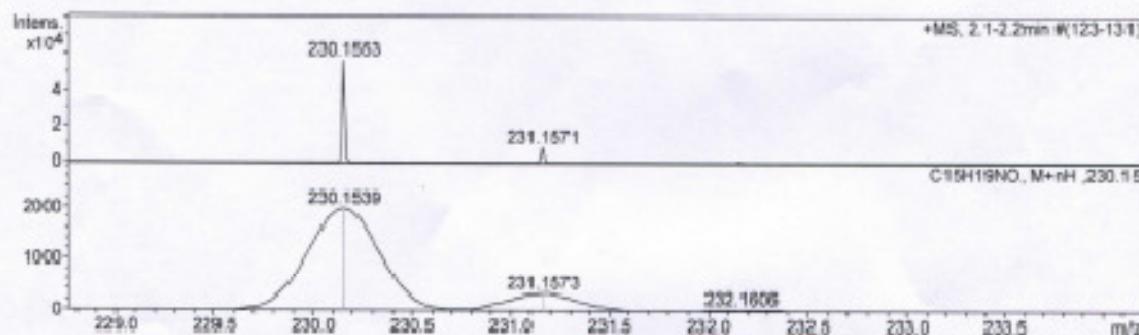
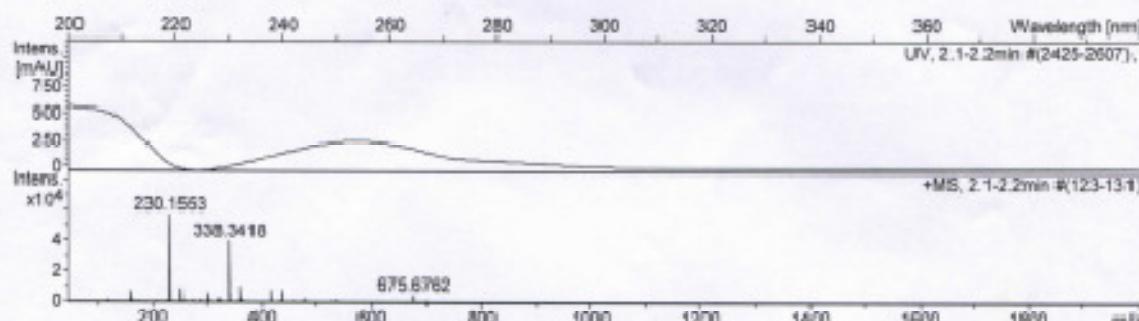
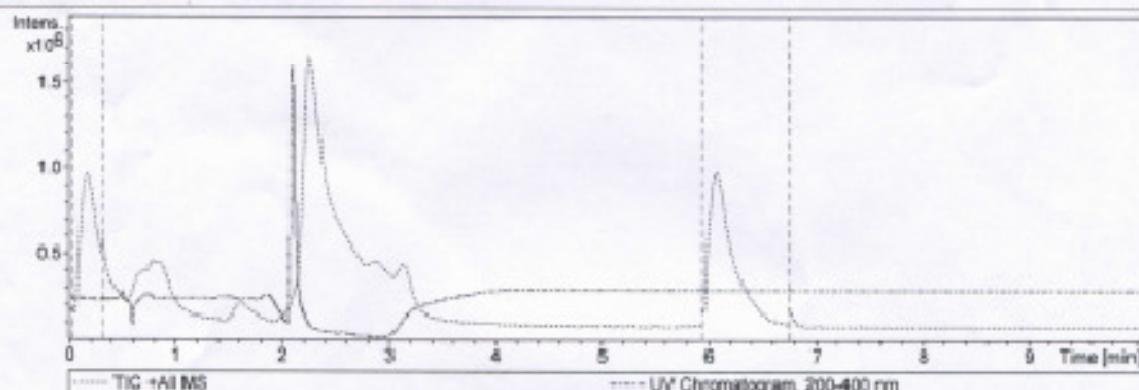
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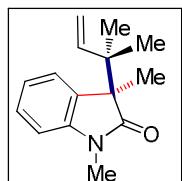
Operator: Meena Sharma

Instrument: micrOTOF-Q II 10330

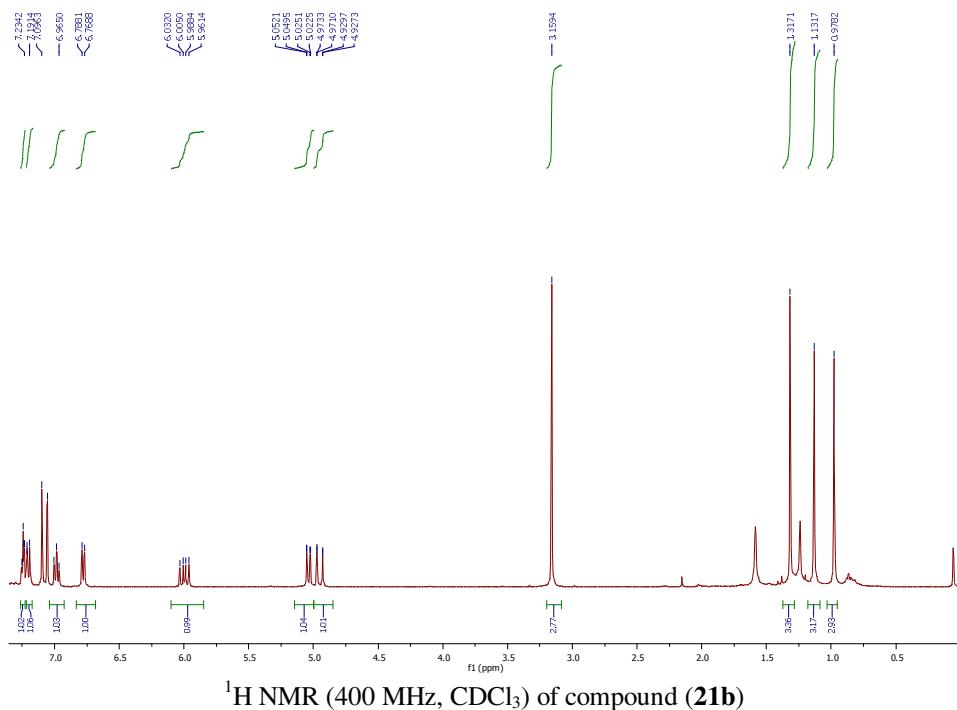
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.2 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



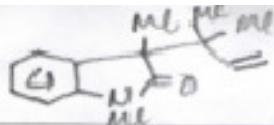


\pm (**21b**)



^1H NMR (400 MHz, CDCl_3) of compound (**21b**)

(20a)



Display Report

Analysis Info

Analysis Name: D:\Data\user data\DEC_30\Dr. A. Bisal-SG4-013 NPS1_1-A_4_01_745.d
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 Sample Name: Dr. A. Bisal-SG4-013 NPS1
 Comment:

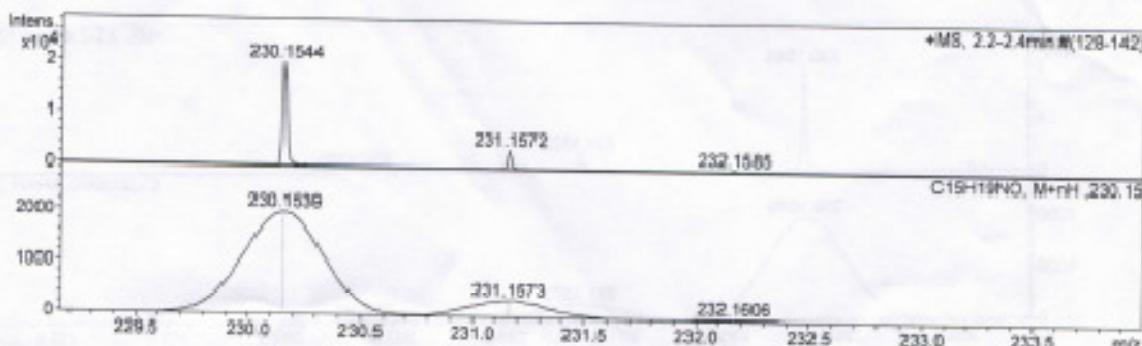
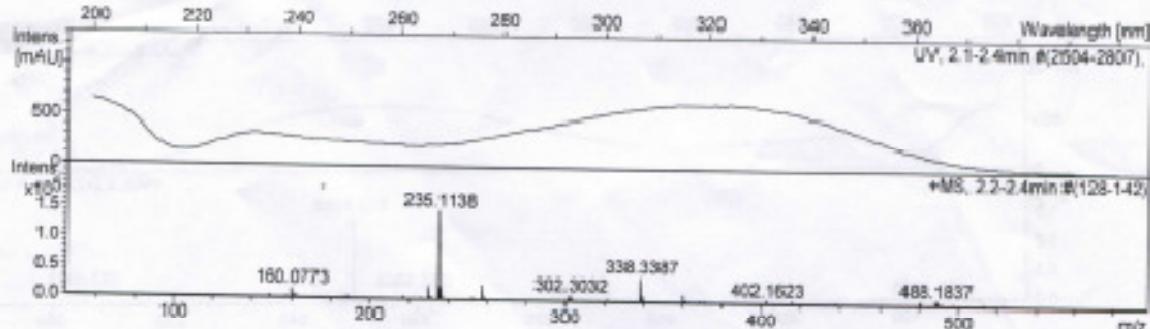
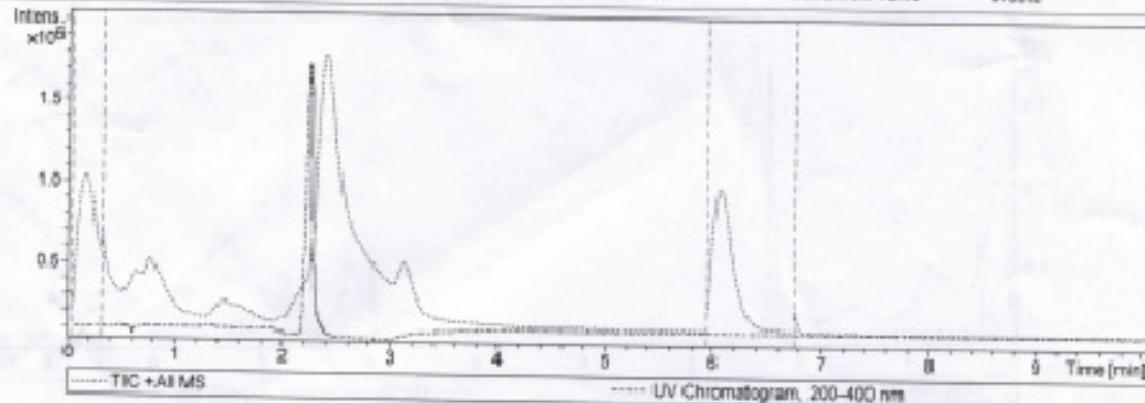
Acquisition Date: 12/31/2011 1:19:30 PM

Operator: Meena Sharma

Instrument: microTOF-Q II 10330

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.2 Bar
Focus	Active	Set Capillary	-4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-600 V	Set Dry Gas	7.0 l/min
Scan End	4000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert: Valve	Waste

Scanned copy of mass spectrum of compound \pm (21b)