Supplemental material for:

Development of Catalytic Deacylative Alkylations (DaA) of 3-Acyl-2-Oxindoles: Total Synthesis of *meso*-Chimonanthine and Related Alkaloids

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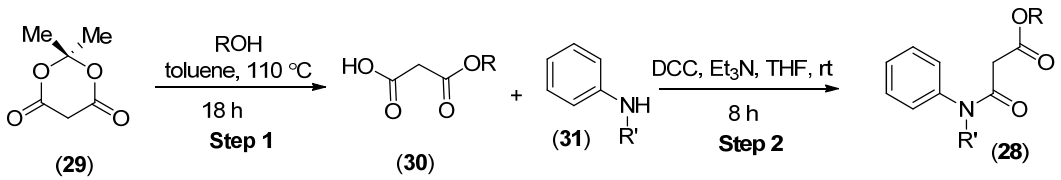
Materials and Methods

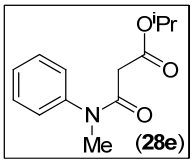
Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred *via* syringe using standard Schlenk techniques. Tetrahydrofuran (THF) 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 and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silica gel of particle size 100-200 mesh was used for flash chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded 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 ($CDCl_3$) signal (δ = 7.26 for ^1H NMR and δ = 77.0 for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) and Low-Resolution Mass Spectrometry (LRMS) data were recorded using methanol as solvent.

Procedure for the synthesis of compounds (±)-31:

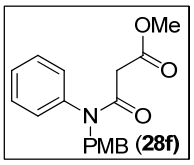


R' = R = Me; (**28a**)	R' = Me; R= ^{i}Pr; (**28e**)
R' = Me; R = Et; (**28b**)	R' = PMB; R= Me; (**28f**)
R' = Me; R= Bn; (**28c**)	R' = allyl; R= Me; (**28g**)
R' = Me; R= ^{t}Bu; (**28d**)	R' = prenyl; R= Me; (**28h**)

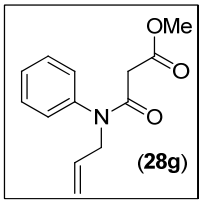
Experimental Procedure for the synthesis of compound **28** followed similar as described in **reference**[1]



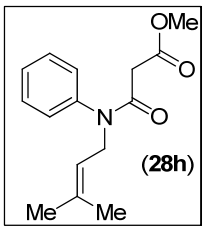
Isopropyl 3-(methyl(phenyl)amino)-3-oxopropanoate (**28e**): 87% yield (Reaction scale: 4.55 mmol) of (28**e**) as brown gel. R_f = 0.25 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.34-7.30 (m, 1H), 7.21-7.19 (m, 2H), 4.99-4.90 (m, 1H), 3.27 (s, 3H), 3.14 (s, 3H), 1.17 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (175 MHz, $CDCl_3$) δ 167.3, 166.1, 143.6, 129.9, 128.2, 127.3, 68.8, 41.8, 37.4, 21.7; **IR** (film) υ_{max} 2982, 2936, 1732, 1596, 1496, 1418, 1386, 1317, 1251, 1207, 1173, 1106, 972, 775, 702 cm^{-1}. **HRMS** (ESI) m/z 236.1299 $[M+H]^+$; calculated for $[C_{13}H_{17}NO_3 + H]^+$: 236.1281.



Methyl 3-((4-methoxybenzyl)(phenyl)amino)-3-oxopropanoate (**28f**): 54% yield (Reaction scale: 42.34 mmol) of (**28f**) as yellow gel. R_f = 0.22 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 3H), 7.15-7.12 (m, 2H), 7.02-6.97 (m, 2H), 6.81-6.75 (m, 2H), 4.85 (s, 2H), 3.78 (s, 3H), 3.67 (s, 3H), 3.21 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 165.8, 158.9, 141.6, 130.2, 129.7, 129.1, 128.5, 120.1, 113.8, 55.2, 52.5, 52.3, 41.7; **IR** (film) υ_{max} 2952, 1744, 1659, 1613, 1594, 1513, 1495, 1402, 1327, 1303, 1246, 1203, 1176, 1157, 1110, 1032, 847, 834, 702 cm^{-1}. **HRMS** (ESI) m/z 314.1412 $[M+H]^+$; calculated for $[C_{18}H_{19}NO_4 + H]^+$: 314.1387.



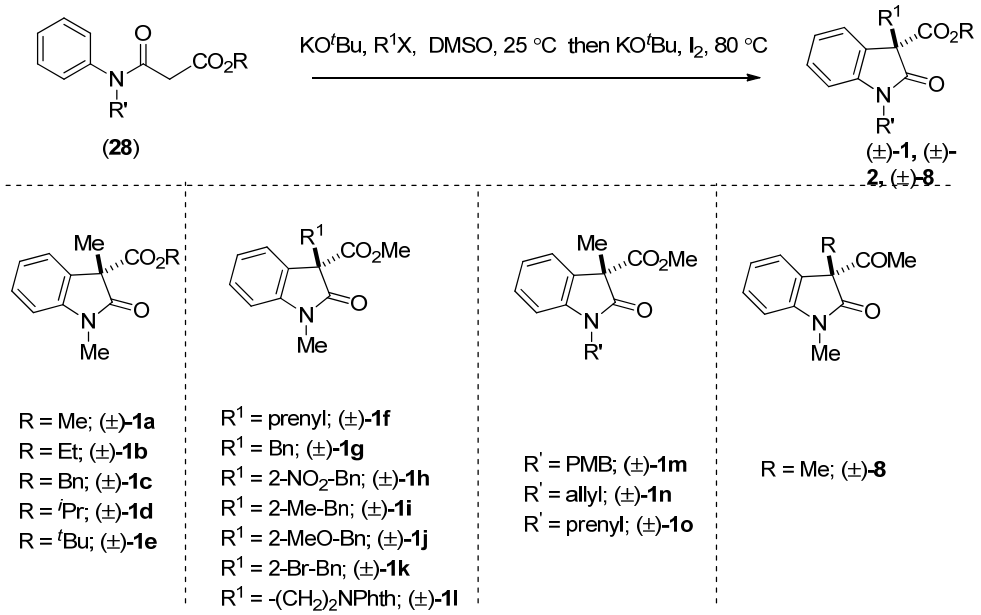
Methyl 3-(allyl(phenyl)amino)-3-oxopropanoate (**28g**): 52% yield (Reaction scale: 42.34 mmol) of (**28g**) as yellow gel. R_f = 0.25 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.37-7.34 (m, 1H), 7.20-7.18 (m, 2H), 5.90-5.82 (m, 1H), 5.14-5.09 (m, 2H), 4.32 (dd, *J* = 6.2, 1.1 Hz, 2H), 3.66 (s, 3H), 3.20 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.1, 165.6, 141.8, 132.5, 129.8, 128.5, 128.2, 118.3, 52.3, 52.3, 41.6; **IR** (film) υ_{max} 2952, 2853, 1754, 1595, 1495, 1434, 1402, 1326, 1228, 1225, 1159, 1075, 1050, 1002, 929 cm^{-1}. **HRMS** (ESI) m/z 234.1132 $[M+H]^+$; calculated for $[C_{13}H_{15}NO_3 + H]^+$: 234.1125.



Methyl 3-((3-methylbut-2-en-1-yl)(phenyl)amino)-3-oxopropanoate (**28h**): 73% yield (Reaction scale: 20.67 mmol) of (**28h**) as yellow gel. R_f = 0.26 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.36-7.33 (m, 1H), 7.17-7.16 (m, 2H), 5.24 (td, *J* = 7.3, 1.2 Hz, 1H), 4.31 (d, *J* = 7.3 Hz, 2H), 3.66 (s, 3H), 3.17 (s, 2H), 1.66 (s, 3H), 1.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.2, 165.4, 141.9, 136.8, 129.7, 128.4, 128.3, 118.8, 52.2, 47.2, 41.6, 25.7, 17.6; **IR** (film) υ_{max} 2933, 1748, 1652, 1596, 1496, 1417, 1317, 1290, 1236, 1156, 1047, 1025, 850 cm^{-1}. **HRMS** (ESI) m/z 262.1431 $[M+H]^+$; calculated for $[C_{15}H_{19}NO_3 + H]^+$: 262.1438.

For characterization of compounds (**28a-d**) see reference[1]

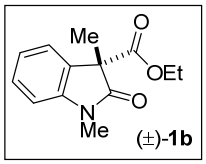
General procedure for intramolecular-dehydrogenative-coupling (IDC) promoted by Iodine:



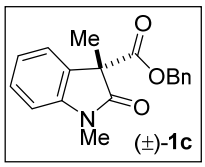
Experimental procedure for intramolecular-dehydrogenative-coupling promoted by Iodine: As described in reference[1], in a flame-dried round-bottom flask, was charged with compound **31** in DMSO at 25 °C. KO^{t}Bu (1.2 equiv) was added to the reaction mixture. After-wards alkyl halide (1.05 equiv) was added and stirring was continued for 15 minutes. Upon complete consumption of starting materials judged by TLC analysis, reaction mixture was further charged with KO^{t}Bu (1.2 equiv) followed by Iodine (1.2 equiv). Immediately, afterwards, the reaction vessel was placed over a pre heated oil bath maintaining temperature 80 ºC and stirring was continued for 1 h. After complete consumption of alkylated starting material, (judged by TLC analysis), reaction mixture was cooled to room temperature and diluted with 10 mL of EtOAc. Then the reaction mixture was quenched with 10 mL saturated sodium thiosulfate solution. The organic layer was separated and successively washed with water (10 mL), and brine (10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified through flash column chromatography using hexane and EtOAc mixture as eluents to afford the desired 2-oxindolesderivatives.

For characterization of compound (±)-**1a-c**, (±)-**1e-g**, see the reference[1a-c]

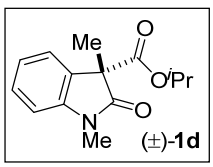
For experimental procedure as well as characterization of compounds (±)-**1p-q**, see **reference**[1a]



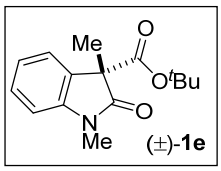
(±)-Ethyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (1b):[1c] The compound (**1b**) was isolated as colorless gel. R_f = 0.38 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.8, 1.2 Hz, 1H), 7.26 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.19-4.06 (m, 2H), 3.25 (s, 3H), 1.66 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 169.7, 143.6, 130.2, 128.95, 122.9, 122.9, 108.4, 61.9, 55.0, 26.5, 20.1, 13.9; **IR** (film) υ_{max} 3448(br), 2983, 1731, 1715, 1613, 1494, 1471, 1454, 1376, 1348, 1246, 1105, 1063, 1031, 1017, 925, 859, 752, 681 cm^{-1}.



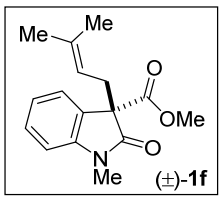
(±)-Benzyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (1c) :[1b] The compound (**1c**) was isolated as colorless solid. R_f = 0.26 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31-7.25 (m, 3H), 7.24-7.23 (m, 1H), 7.17-7.13 (m, 2H), 7.08 (td, *J* = 7.6, 0.9 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.16-5.10 (m, 2H), 3.27 (s, 3H), 1.71 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.0, 169.5, 143.7, 135.5, 129.9, 129.1, 128.4, 128.0, 127.3, 123.1, 122.9, 108.5, 67.1, 55.1, 26.5, 19.9; **IR** (film) υ_{max} 2935, 2889, 1731, 1608, 1494, 1470, 1454, 1373, 1348, 1223, 1158, 1106, 1063, 1030, 1018, 959, 909, 750 cm^{-1}.



(±)-Isopropyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (**1d**): 69% yield (Reaction scale: 1.00 mmol scale of reaction) of (**1d**) as yellow gel. R_f = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.7, 1.2 Hz, 1H), 7.26 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.03-4.95 (m, 1H), 3.26 (s, 3H), 1.66 (s, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.3, 169.2, 143.6, 130.3, 128.8, 122.8, 122.8, 108.3, 69.4, 55.2, 26.5, 21.4, 21.3, 19.9; **IR** (film) υ_{max} 2982, 2936, 1732, 1716, 1613, 1494, 1471, 1455, 1375, 1348, 1304, 1251, 1182, 1146, 1101, 1063 cm^{-1}; **HRMS** (ESI) m/z 248.1284 $[M+H]^+$; calculated for $[C_{14}H_{17}NO_3 + H]^+$: 248.1281.

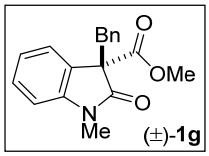


(±)-*tert*-butyl 1,3-dimethyl-2-oxoindoline-3-carboxylate (**1e**):[1c] The compound (**1e**) was isolated as yellow gel. R_f = 0.30 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (tt, *J* = 7.7, 1.0 Hz, 1H), 7.26-7.24 (m, 1H), 7.08-7.05 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.24 (s, 3H), 1.62 (s, 3H), 1.35 (s, 9H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 175.5, 168.7, 143.6, 130.6, 128.7, 122.72, 122.70, 108.3, 82.2, 55.9, 27.7, 26.4, 19.7; **IR** (film) υ_{max} 2979, 2933, 1732, 1715, 1613, 1494, 1471, 1455, 1371, 1347, 1256, 1162, 1119, 1063, 1029, 932, 842, 750 cm^{-1}.

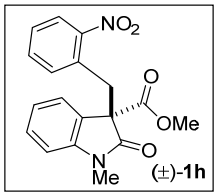


(±)-Methyl 1-methyl-3-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (**1f**):[1c] The compound (**1f**) was isolated as yellow solid. R_f = 0.32 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 7.7, 1.2 Hz, 1H), 7.28-7.26 (m, 1H), 7.07 (td, *J* = 7.6, 0.9 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 4.73-4.69 (m, 1H), 3.67 (s, 3H), 3.23 (s, 3H), 2.95 (d, *J* = 7.4 Hz, 2H), 1.52 (s, 3H), 1.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 169.8, 144.1, 136.3, 128.9, 127.9, 123.6, 122.6, 116.3, 108.1, 59.2, 52.9, 33.0,

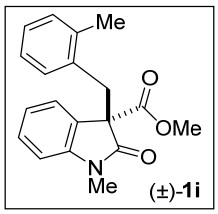
26.4, 25.8, 18.0; **IR** (film) υ_{max} 2919, 2858 1746, 1731, 1715, 1609, 1493, 1470, 1454, 1373, 1348, 1236, 1129, 1088, 1035, 1002 cm^{-1}; **HRMS** (ESI) m/z 274.1448 $[M+H]^+$; calculated for $[C_{16}H_{19}NO_3 + H]^+$: 274.1438; **MP** 58-63 ºC.



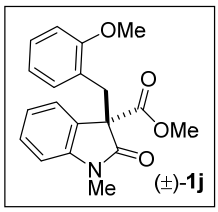
(±)-Methyl 3-benzyl-1-methyl-2-oxoindoline-3-carboxylate (1g):[1c] The compound (**1g**) was isolated as a yellow solid. R_f = 0.31 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.24 (td, *J* = 7.8, 1.2 Hz, 1H), 7.09 (td, *J* = 7.6, 0.9 Hz, 1H), 7.06-7.00 (m, 3H), 6.86-6.85 (m, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.57 (s, 2H), 2.96 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.4, 169.8, 144.0, 134.3, 129.9, 129.1, 127.6, 127.2, 126.8, 123.9, 122.5, 108.2, 60.7, 53.1, 40.0, 26.1; **IR** (film) υ_{max} 1742, 1714, 1609, 1560, 1491, 1471, 1353, 1239, 1089, 1063, 1020, 1002, 941, 881, 811, 750, 732, 588 cm^{-1}; **MP** 125-129 ºC.



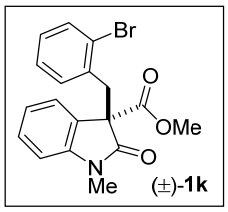
(±)-Methyl 1-methyl-3-(2-nitrobenzyl)-2-oxoindoline-3-carboxylate (1h): 70% yield (Reaction scale: 0.15 mmol) of (**1h**) as yellow solid. R_f = 0.27 (50% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.47-7.42 (m, 2H), 7.31-7.29 (m, 1H), 7.28-7.26 (m, 1H), 7.16-7.14 (m, 1H), 7.04 (td, *J* = 7.6, 0.9 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 4.41 (d, *J* = 13.9 Hz, 1H), 3.82 (d, *J* = 13.9 Hz, 1H), 3.71 (s, 3H), 3.06 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.2, 169.3, 149.9, 143.7, 133.34, 132.30, 129.9, 129.4, 128.0, 126.3, 124.6, 124.0, 123.3, 108.2, 60.1, 53.3, 35.1, 26.3; **IR** (film) υ_{max} 2925, 2853, 1744, 1722, 1609, 1526, 1494, 1470, 1453, 1372, 1352, 1245, 1159, 1128, 1090, 1065, 1022 cm^{-1}; **HRMS** (ESI) m/z 341.1093 $[M+H]^+$; calculated for $[C_{18}H_{16}N_2O_5 + H]^+$: 341.1132; **MP** 107-110 ºC.



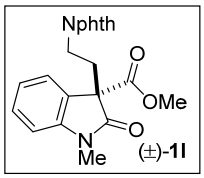
(±)-Methyl 1-methyl-3-(2-methylbenzyl)-2-oxoindoline-3-carboxylate (**1i**): 88% yield (Reaction scale: 3.21 mmol) of (**1i**) as colorless solid. R_f = 0.29 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.01-6.92 (m, 3H), 6.87-6.80 (m, 2H), 6.64 (d, *J* = 7.8 Hz, 1H), 3.70 (s, 3H), 3.67 (d, *J* = 14.3 Hz, 1H), 3.53 (d, *J* = 14.0 Hz, 1H), 3.02 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 169.9, 144.1, 137.3, 133.2, 130.2, 129.7, 129.2, 127.4, 126.8, 125.1, 124.3, 122.4, 108.1, 60.5, 53.1, 35.9, 26.3, 20.0; **IR** (film) υ_{max} 2953, 1738, 1722, 1610, 1494, 1470, 1373, 1353, 1232, 1130, 1116, 1098, 1084, 1063, 999, 941, 802, 752 cm^{-1}; **HRMS** (ESI) m/z 310.1464 $[M+H]^+$; calculated for $[C_{19}H_{19}NO_3 + H]^+$: 310.1438; **MP** 85-86 ºC.



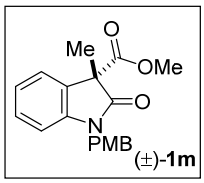
(±)-Methyl 3-(2-methoxybenzyl)-1-methyl-2-oxoindoline-3-carboxylate (**1j**): 69% yield of (**1j**) as colorless solid (Reaction scale: 2.13 mmol); R_f = 0.38 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 (dq, *J* = 7.5, 1.2 Hz, 1H), 7.18 (td, *J* = 7.8, 1.3 Hz, 1H), 7.07-7.02 (m, 2H), 6.97 (td, *J* = 7.6, 1.0 Hz, 1H), 6.71 (td, *J* = 7.5, 1.0 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.54 (dd, *J* = 8.2, 0.6 Hz, 1H), 4.02 (d, *J* = 13.4 Hz, 1H), 3.71 (s, 3H), 3.51 (s, 3H), 3.38 (d, *J* = 13.5 Hz, 1H), 3.08 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.2, 170.0, 157.4, 143.8, 130.9, 128.7, 128.1, 127.2, 125.0, 123.4, 121.7, 119.7, 109.8, 107.6, 60.5, 54.6, 53.0, 32.7, 26.3; **IR** (film) υ_{max} 2953, 2926, 1743, 1715, 1611, 1495, 1470, 1437, 1374, 1353, 1248, 1119, 1130, 1101, 1052, 1031, 1001, 941 cm^{-1}; **HRMS** (ESI) m/z 326.1401 $[M+H]^+$; calculated for $[C_{19}H_{19}NO_4 + H]^+$: 326.1387; **MP** 88-92 ºC.



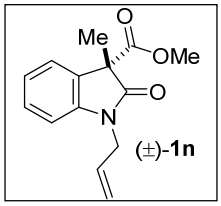
(±)-Methyl 3-(2-bromobenzyl)-1-methyl-2-oxoindoline-3-carboxylate (**1k**): 75% yield of (**1k**) as colorless solid (Reaction scale: 1.2 mmol); R_f = 0.34 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.29-7.24 (m, 2H), 7.23-7.20 (m, 1H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 6.99 (td, *J* = 7.6, 0.9 Hz, 1H), 6.96 (td, *J* = 7.6, 1.7 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.06 (d, *J* = 14.1 Hz, 1H), 3.72 (s, 3H), 3.65 (d, *J* = 14.1 Hz, 1H), 3.16 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.7, 169.6, 143.8, 134.9, 132.8, 130.8, 129.2, 128.5, 126.9, 126.5, 126.0, 125.1, 122.4, 108.0, 60.2, 53.2, 38.1, 26.5; **IR** (film) υ_{max} 2927, 1738, 1732, 1609, 1493, 1470, 1454, 1435, 1372, 1353, 1240, 1132, 1086, 1064, 1028, 1001, 751 cm^{-1}; **HRMS** (ESI) m/z 374.0383 $[M+H]^+$; calculated for $[C_{18}H_{16}BrNO_3 + H]^+$: 374.0386; **MP** 69-71 ºC.



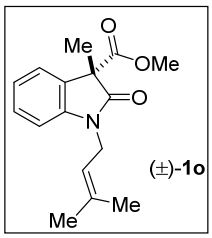
(±)-Methyl-3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1-methyl-2-oxoindoline-3-carboxylate (**1l**): 75% yield of (**1l**) was isolated as colorless solid (Reaction scale: 0.55 mmol scale); R_f = 0.21 (60% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 4H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.99 (td, *J* = 7.7, 0.8 1H), 6.72 (dd, *J* = 14.2, 7.5 Hz, 2H), 3.68-3.62 (m, 1H), 3.60 (s, 3H), 3.54-3.48 (m, 1H), 3.20 (s, 3H), 2.92-2.85 (m, 1H), 2.68-2.62 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.2, 169.3, 167.7, 144.1, 133.7, 131.8, 129.9, 126.8, 122.9, 122.9, 122.7, 108.7, 57.9, 53.1, 33.7, 30.6, 26.6; **IR** (film) υ_{max} 1770, 1714, 1610, 1493, 1469, 1444, 1398, 1374, 1355, 1274, 1239, 1124, 1086, 1029, 720 cm^{-1}; **HRMS** (ESI) m/z 379.1260 $[M+H]^+$; calculated for $[C_{21}H_{18}N_2O_5 + H]^+$: 379.1288; **MP** 101-104 ºC.



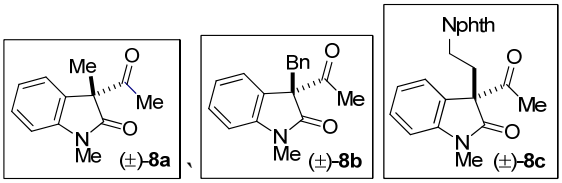
(±)-Methyl 1-(4-methoxybenzyl)-3-methyl-2-oxoindoline-3-carboxylate (**1m**): 35% yield of (**1m**) was isolated as brown solid (Reaction scale:1.44 mmol); R_f = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 3H), 7.22 (td, *J* = 7.8, 1.3 Hz, 1H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 6.88-6.85 (m, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.02 (d, *J* = 15.5 Hz, 1H), 4.80 (d, *J* = 15.5 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 1.74 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3, 170.3, 159.1, 142.7, 130.1, 129.0, 128.5, 127.6, 123.0, 122.9, 114.2, 109.6, 55.3, 55.0, 53.1, 43.3, 20.0; **IR** (film) υ_{max} 2934, 1746, 1715, 1610, 1514, 1488, 1467, 1454, 1376, 1357, 1293, 1248, 1179, 1110, 1033, 1004, 973, 895, 846, 815, 751 cm^{-1}; **HRMS** (ESI) m/z 326.1371 $[M+H]^+$; calculated for $[C_{19}H_{19}NO_4 + H]^+$: 326.1387; **MP** 79-82 ºC



(±)-Methyl 1-allyl-3-methyl-2-oxoindoline-3-carboxylate (**1n**): 65% yield of (**1n**) as brown gel (Reaction scale: 0.81 mmol); R_f = 0.22 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 5.90-5.82 (m, 1H), 5.26-5.21 (m, 2H), 4.47-4.42 (m, 1H), 4.35-4.30 (m, 1H), 3.66 (m, 3H), 1.70 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.9, 170.3, 142.7, 130.9, 130.0, 129.0, 123.1, 122.9, 117.3, 109.4, 54.9, 53.0, 42.3, 20.1; **IR** (film) υ_{max} 2955, 1645, 1615, 1488, 1470, 1374, 1361, 1241, 1184, 1157, 1109, 973, 928, 895, 839, 750, 702, 679, 553, cm^{-1}; **HRMS** (ESI) m/z 246.1137 $[M+H]^+$; calculated for $[C_{14}H_{15}NO_3 + H]^+$: 246.1125.

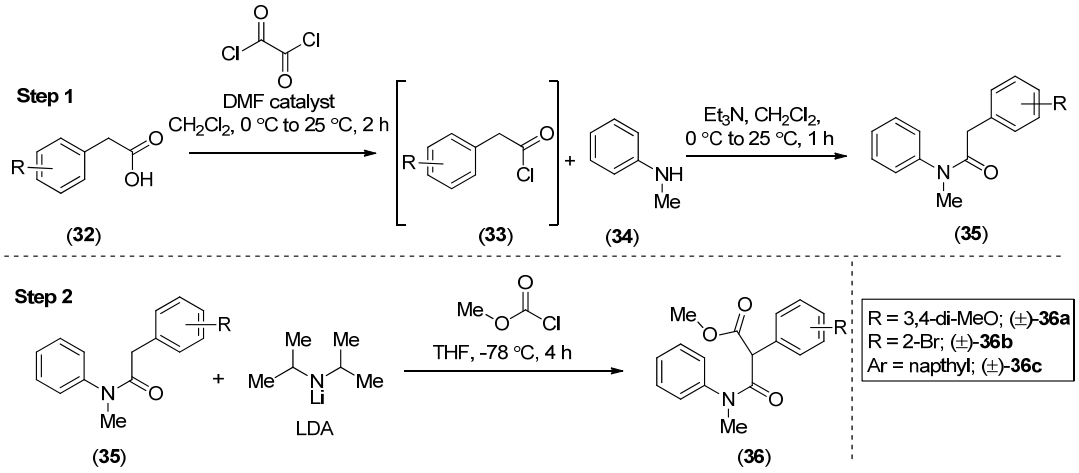


(±)-Methyl 3-methyl-1-(3-methylbut-2-en-1-yl)-2-oxoindoline-3-carboxylate (**1o**): 85% yield of (**1o**) obtained as colorless gel (Reaction scale: 0.72 mmol); R_f = 0.27 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (td, *J* = 7.7, 1.1 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.19 (tt, *J* = 6.6, 1.3 Hz, 1H), 4.40-4.32 (m, 2H), 3.65 (s, 3H), 1.84 (s, 3H), 1.74 (s, 3H), 1.67 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.7, 170.4, 142.9, 137.0, 130.1, 128.9, 123.1, 122.7, 118.1, 109.2, 54.9, 53.0, 38.3, 25.6, 20.2, 18.2; **IR** (film) υ_{max} 2933, 1747, 1732, 1714, 1609, 1488, 1468, 1453, 1376, 1354, 1241, 1176, 1149, 1110, 1041, 1078, 973 cm^{-1}; **HRMS** (ESI) m/z 274.1443 $[M+H]^+$; calculated for $[C_{16}H_{19}NO_3 + H]^+$: 274.1438.

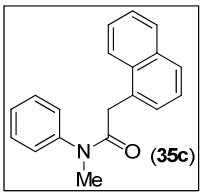


Experimental Procedure for the synthesis of compound **8a-c** followed similar as described in **reference**[1]

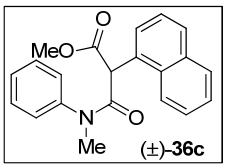
For characterization of compounds (**8a-c**) see reference[1]



Procedure for the synthesis of (**36**) followed similar as described in **reference**[1a]

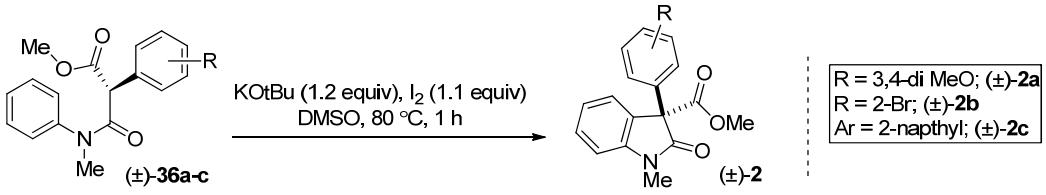


N-methyl-2-(naphthalen-1-yl)-N-phenylacetamide (**35c**): 80% yield (4.47 mmol scale of reaction) of (**35c**) as a colorless solid. R_f = 0.25 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.46-7.41 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.30 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 6.8 Hz, 1H), 3.91 (s, 2H), 3.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.0, 144.0, 133.8, 132.1, 131.9, 129.9, 128.6, 127.9, 127.5, 127.4, 127.4, 126.0, 125.5, 125.3, 123.9, 38.9, 37.8; **IR** (film) υ_{max} 2930, 1659, 1651, 1596, 1495, 1417, 1378, 1305, 1278, 1256, 1238, 1168, 1121, 1075, 1022, 1003, 785, 700 cm^{-1}; **HRMS** (ESI) m/z 276.1367 $[M+H]^+$; calculated for $[C_{19}H_{17}NO + H]^+$: 276.1383; **MP** 66-69 °C.

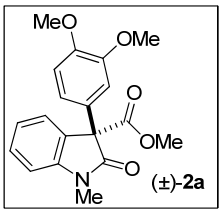


Methyl 3-(methyl(phenyl)amino)-2-(naphthalen-1-yl)-3-oxopropanoate (**36c**): **72**% yield (7.26 mmol scale of reaction) of (**36c**) as a yellow gel. **R_f** = 0.29 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 7.1 Hz,

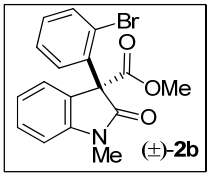
1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 6.8 Hz, 1H), 7.29-7.18 (m, 5H), 6.96 (br, s, 2H), 5.43 (s, 1H), 3.74 (s, 3H), 3.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 168.2, 142.9, 133.7, 131.2, 129.8, 129.7, 128.8, 128.6, 128.1, 127.6, 127.5, 126.2, 125.44, 125.41, 112.2, 52.8, 51.9, 37.9; **IR** (film) υ_{max} 3061, 2952, 1755, 1732, 1660, 1595, 1495, 1434, 1381, 1300, 1267, 1195, 1118, 1024, 997, 760, 735, 701 cm^{-1}; **HRMS** (ESI) m/z 334.1468 $[M+H]^+$; calculated for $[C_{21}H_{19}NO_3 + H]^+$: 334.1438.



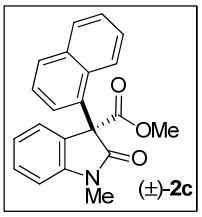
Procedure for the synthesis of (**2a-d**) followed similar as described in **reference**[1a,c]



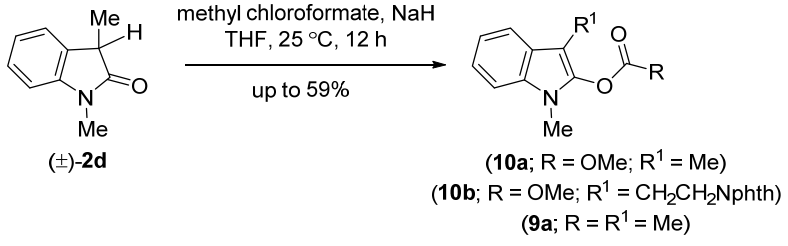
(±)-Methyl 3-(3,4-dimethoxyphenyl)-1-methyl-2-oxoindoline-3-carboxylate (2a):[1] 68% yield (2.91 mmol scale) of (**2a**) as colorless solid. R_f = 0.26 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.8, 1.0 Hz, 1H), 7.14 (td, *J* = 7.6, 0.6 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.78-6.73 (m, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.71 (s, 3H), 3.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 169.8, 149.2, 148.9, 144.3, 129.7, 127.9, 126.9, 125.9, 122.9, 120.1, 111.6, 110.7, 108.8, 63.2, 55.9, 55.8, 53.3, 26.7; **IR** (film) υ_{max} 2954, 2837, 1746, 1722, 1715, 1608, 1516, 1493, 1470, 1412, 1371, 1347, 1244, 1146, 1130, 1088, 1025, 752 cm^{-1}.



(±)-Methyl 3-(2-bromophenyl)-1-methyl-2-oxoindoline-3-carboxylate (2b):[1a] The compound (**2b**) was isolated as brown gel (Reaction scale: 2.21 mmol); R_f = 0.26 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.41-7.35 (m, 2H), 7.18-7.13 (m, 2H), 7.12-7.08 (m, 1H), 6.94 (dd, *J* = 7.3, 2.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 168.7, 144.2, 136.2, 135.2, 130.2, 129.9, 129.7, 127.7, 127.4, 126.0, 124.2, 123.2, 108.7, 65.3, 53.6, 26.8; **IR** (film) υ_{max} 2950, 1727, 1658, 1651, 1608, 1596, 1494, 1470, 1434, 1371, 1344, 1226, 1178, 1126, 1034, 1060, 1023, 971, 940, 796 cm^{-1}.

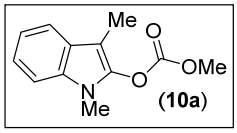


(±)-Methyl 1-methyl-3-(naphthalen-1-yl)-2-oxoindoline-3-carboxylate (2c): 57% yield of (**2c**) as colorless solid (Reaction scale: 1.64 mmol); R_f = 0.22 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.56 (td, *J* = 6.9, 1.2 Hz, 1H), 7.51-7.49 (m, 1H), 7.47-7.42 (m, 2H), 7.25-7.23 (m, 1H), 7.18 (td, *J* = 7.6, 0.6 Hz, 1H), 7.02 (d, *J* = 6.7 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 3.72 (s, 3H), 3.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 170.7, 144.2, 134.8, 132.9, 131.9, 129.9, 129.8, 128.8, 127.5, 126.6, 126.2, 126.1, 126.0, 125.9, 124.6, 123.1, 108.8, 64.1, 53.4, 26.7; **IR** (film) υ_{max} 2951, 1742, 1715, 1607, 1510, 1493, 1471, 1434, 1370, 1346, 1231, 1130, 1087, 1025, 1008, 975, 928 cm^{-1}; **HRMS** (ESI) m/z 332.1281 $[M+H]^+$; calculated for $[C_{21}H_{17}NO_3 + H]^+$: 332.1281; **MP** 163-167 ºC.



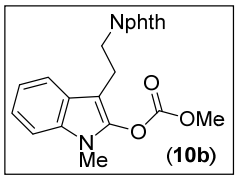
Experimental procedure for synthesis of methylcarbanate of 2-oxindole: In a flame-dried round-bottom flask, oxinole (1.0 equiv) was taken in THF (8 mL) at 25 °C. To this

reaction mixture NaH (60% suspension in mineral oil, 1.2 equiv) was added in one portion followed by methyl chloroformate (1.2 equiv)/ Acetyl chloride was added to the same at 25 °C and stirring was continued for 12 h. Upon completion of the reaction (judged by TLC analysis), diluted with 10 mL of EtOAc and quenched with 10 mL water. The organic layer was separated and successively washed with brine (10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford desired product (**10a-b/9a**).



(**10a**)

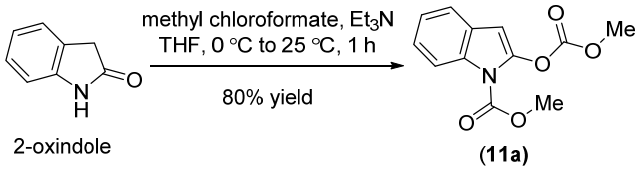
1,3-Dimethyl-1H-indol-2-yl methyl carbonate (**10a**): 22% yield of (**10a**) as yellow gel (Reaction scale: 6.20 mmol); R_f = 0.26 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.26-7.22 (m, 2H), 7.16-7.11 (m, 1H), 3.97 (s, 3H), 3.57 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 139.2, 132.6, 126.4, 121.6, 119.5, 118.9, 108.9, 96.4, 56.2, 28.2, 7.2; **IR** (film) υ_{max} 2992, 1776, 1734, 1633, 1472, 1436, 1386, 1368, 1247, 1207, 1155, 1118, 1019, 930, 780, 738, 715 cm^{-1}; **HRMS** (ESI) m/z 220.0953 $[M+H]^+$; calculated for $[C_{12}H_{13}NO_3 + H]^+$: 220.0968.



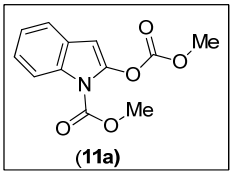
(**10b**)

3-(2-(1,3-Dioxoisoindolin-2-yl)ethyl)-1-methyl-1H-indol-2-yl methyl carbonate (**10b**): 22% yield of (**10b**) as yellow solid (Reaction scale: 0.46 mmol); R_f = 0.20 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.71-7.66 (m, 3H), 7.22-7.19 (m, 2H), 7.15-7.11 (m, 1H), 3.99 (s, 3H), 3.93-3.89 (m, 2H), 3.55 (s, 3H), 3.02-2.98 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 153.3, 139.9, 139.8, 132.6, 132.3, 125.5, 123.1, 121.8, 120.0, 118.9, 109.0, 97.2, 56.4, 37.5, 28.3, 22.3; **IR** (film) υ_{max} 3114, 1778, 1709, 1606, 1563, 1551, 1536, 1478, 1401, 1358, 1304, 1237, 1088, 1058, 1009, 932,

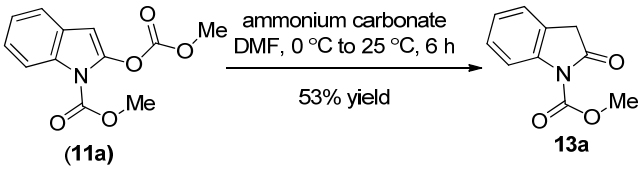
901, 882 cm^{-1}; **HRMS** (ESI) m/z 379.1265 $[M+H]^+$; calculated for $[C_{21}H_{18}N_2O_5 + H]^+$: 379.1288; **MP** 115-119 ºC.



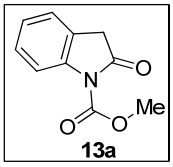
Experimental procedure for synthesis of *N*-methylcarbamate *O*-methylcarbanate of 2-oxindole (11a): In a flame-dried round-bottom flask, oxinole (1.0 equiv) was taken in THF (8 mL) at 0 °C. To this reaction mixture Et_3N (2.2 equiv) was added in one portion followed by methyl chloroformate (2.2 equiv) was added to the same at 0 °C and stirring was continued on 25 °C for 1 h. Upon completion of the reaction (judged by TLC analysis), diluted with 10 mL of EtOAc and quenched with 10 mL water. The organic layer was separated and successively washed with brine (10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford desired product (**11a**).



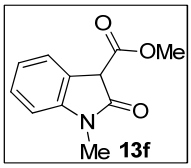
Methyl 2-((methoxycarbonyl)oxy)-1H-indole-1-carboxylate (**11a**): 80% yield of (**11a**) as yellow solid (Reaction scale: 15.01 mmol); R_f = 0.31 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.49 (dt, *J* =7.7, 1.1 Hz, 1H), 7.31 (td, *J* =7.4, 1.4 Hz, 1H), 7.24 (td, *J* = 6.2, 1.2 Hz,1H), 6.32 (s, 1H), 4.02 (s, 3H), 3.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 150.7, 141.5, 132.5, 126.5, 124.5, 123.6, 120.8, 115.4, 97.4, 56.2, 53.9; **IR** (film) υ_{max} 1732, 1614, 1580, 1436, 1383, 1371, 1329, 1305, 1242, 1211, 1124, 1101, 1055, 999 cm^{-1}; **HRMS** (ESI) m/z 272.0540 $[M + Na]^+$; calculated for $[C_{12}H_{11}NO_5 + Na]^+$: 272.0529; **MP** 57-60 ºC.



Experimental procedure for synthesis of N-methylcarbamate of 2-oxindole: In a flame-dried round-bottom flask, oxindole (1.0 equiv) was taken in DMF (5 mL) at 0 °C. To this reaction mixture ammonium carbonate (2.0 equiv) was added in one portion at 0 °C and stirring was continued on 25 °C for 6 h. Upon completion of the reaction (judged by TLC analysis), 10 mL water was added, stirred for 2 h. above mixture was diluted with 10 mL of EtOAc. The organic layer was separated, organic layer washed with brine (10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford desired product (**13a**).

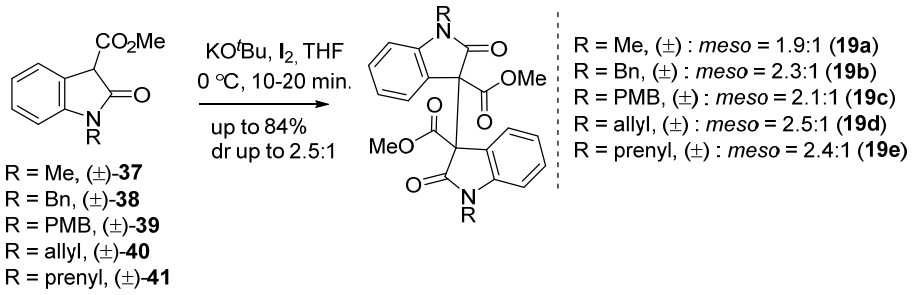


Methyl 2-oxoindoline-1-carboxylate (**13a**): Compound (**13a**) as yellow solid (Reaction scale: 4.01 mmol; 53% yield); R_f = 0.24 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* =7.9 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 3.99 (s, 3H), 2.66 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 151.5, 140.6, 128.2, 124.6, 124.2, 123.3, 115.2, 53.9, 36.5; **IR** (film) υ_{max} 2158, 1785, 1609, 1607, 1441, 1350, 1290, 1238, 1199, 1149, 1086, 1049, 1003, 908 cm^{-1}; **HRMS** (ESI) m/z 192.0656 $[M + H]^+$; calculated for $[C_{12}H_{11}NO_5 + H]^+$: 192.0655; **MP** 74-78 ºC.

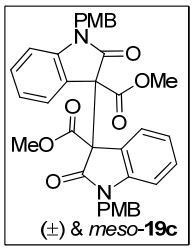


Experimental Procedure for the synthesis of compound **13f** followed similar as described in **reference**[2]

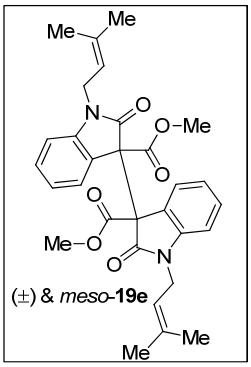
For characterization of compounds (**13f**) see reference[2]



For experimental procedure and characterization data of **19a, 19b, 19d** see the reference[2]

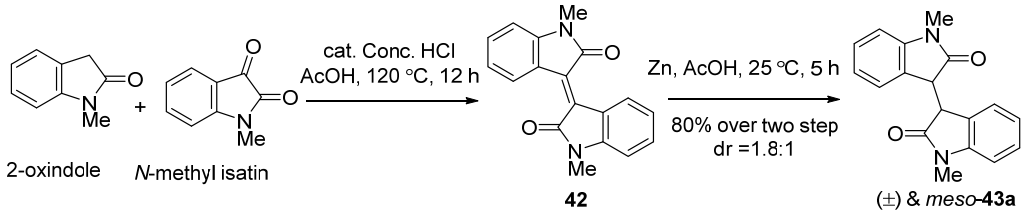


Dimethyl 1,1'-bis(4-methoxybenzyl)-2,2'-dioxo-[3,3'-biindoline]-3,3'-dicarboxylate (**19c**): Compound (**19c**) was isolated in 64% yield (Reaction scale: 4.17 mmol; dr = 2.1:1), as brown solid; R_f = 0.24 (75% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.7, 1.2 Hz, 1H for major), 7.18-7.16 (m, 2H for major + 2H for minor), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H for major), 6.82-6.77 (m, 2H for major + 4H for minor), 6.71-6.69 (m, 1H for major), 6.62 (d, *J* = 7.9 Hz, 1H for minor), 6.57 (d, *J* = 7.8 Hz, 1H for minor + 1H for major), 4.90 (d, *J* = 15.4 Hz, 1H for major + 1H for minor), 4.74 (d, *J* = 14.6 Hz, 1H for minor), 4.59 (d, *J* = 15.4 Hz, 1H for major), 3.80 (s, 3H for minor), 3.74-3.76 (m, 6H for major + 3H for minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.33, 170.32, 167.9, 167.2, 159.1, 158.9, 143.8, 143.4, 130.01, 130.02, 129.55, 129.54, 128.90, 128.89, 128.50, 128.49, 127.37, 127.36, 126.65, 126.64, 124.0, 123.1, 122.5, 122.3, 114.04, 114.03, 109.3, 108.9, 61.64, 61.63, 55.3, 55.2, 53.5, 53.4, 43.65, 43.64; **IR** (film) υ_{max} 2954, 2838, 1748, 1732, 1608, 1515, 1488, 1469, 1436, 1361, 1303, 1248, 1178, 1108, 1032, 984, 845, 813, 753, 736 cm^{-1}; **HRMS** (ESI) m/z 621.2256 $[M+H]^+$; calculated for $[C_{38}H_{32}N_2O_6 + H]^+$: 621.2231. MP 105-109 ºC

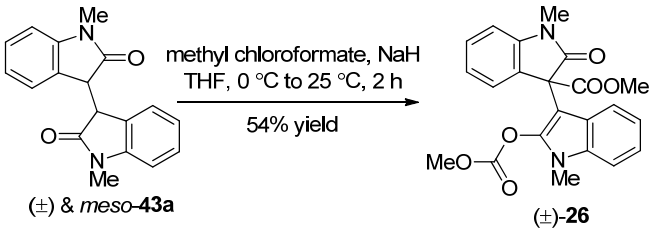


Dimethyl 1,1'-bis(3-methylbut-2-en-1-yl)-2,2'-dioxo-[3,3'-biindoline]-3,3'-dicarboxylate (**19e**): Compound (**19e**) was isolated in 65% yield (Reaction scale: 5.78 mmol; dr = 2.4:1) as red solid; R_f = 0.31 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6 Hz, 1H for minor), 7.40-7.36 (m, 1H minor), 7.31 (dd, *J* = 7.6, 1.2 Hz, 1H for major), 7.14-7.06 (m, 1H for major + 1H for minor), 6.85 (td, *J* = 7.7, 1.2 Hz, 1H for major + 1H for minor), 6.52 (d, *J* = 7.8 Hz, 1H for major), 5.15-5.12 (m, 1H for minor), 5.03-4.99 (m, 1H for major), 4.39-4.32 (m, 1H for major + 2H for minor), 4.16-4.10 (m, 1H for major), 3.76 (s, 3H for minor), 3.75 (s, 3H for major), 1.82-1.78 (m, 3H for major + 3H for minor), 1.70-169 (m, 3H for major + 3H minor); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 167.9, 166.9, 163.0, 144.0, 143.3, 136.7, 136.2, 129.9, 129.6, 126.4, 124.0, 123.6, 123.0, 122.5, 121.9, 117.8, 117.7, 110.1, 108.4, 61.4, 53.9, 53.3, 53.2, 38.5, 38.1, 25.6, 18.2, 18.1, 18.0; **IR** (film) υ_{max} 1738, 1614, 1490, 1350, 1240, 1165, 837, 750 cm^{-1}; **HRMS** (ESI) m/z 517.2354 $[M+H]^+$; calculated for $[C_{30}H_{32}N_2O_6 + H]^+$: 517.2333; MP 53-55 ºC.

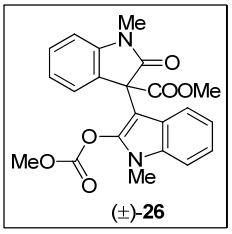
General Procedure for the synthesis of dihydroisoindigo (±)-43a:[3,4]



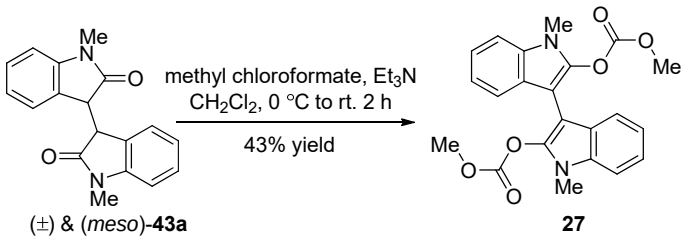
For experimental procedure and characterization data of (±)-**43a** see the reference[3,4]



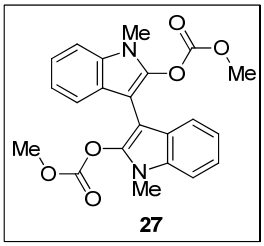
Experimental procedure for synthesis of ester-carbonate: In a flame-dried round-bottom flask, dihydroisoindigo (1.0 equiv) was taken in THF (8 mL) at 0 °C. To this reaction mixture NaH (60% suspension in mineral oil, 2.2 equiv) was added in one portion followed by methyl chloroformate (2.3 equiv) was added to the same at 0 °C and stirring was continued on 25 °C for 2 h. Upon completion of the reaction (judged by TLC analysis), diluted with 10 mL of EtOAc and quenched with 10 mL water. The organic layer was separated and successively washed with brine (10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford desired product (±)-**26**.



(±)-Methyl 3-(2-((methoxycarbonyl)oxy)-1-methyl-1H-indol-3-yl)-1-methyl-2-oxoindoline-3-carboxylate (±)-**26**: 54% yield (Reaction scale: 8.22 mmol) of (±)-**26** as pink solid; R_f = 0.24 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.38 (td, *J* =7.7, 1.3 Hz, 1H), 7.23-7.20 (m, 1H), 7.19-7.15 (m, 1H), 7.08 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03-6.98 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.52 (s, 3H), 3.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 169.4, 152.3, 144.3, 139.9, 132.5, 129.5, 126.5, 125.9, 124.1, 122.7, 122.0, 120.4, 119.9, 109.3, 108.2, 95.9, 58.2, 56.1, 53.4, 28.4, 26.6; **IR** (film) υ_{max} 1778, 1746, 1714, 1609, 1493, 1489, 1435, 1371, 1346, 1242, 1198, 1130, 1089, 1059, 929 cm^{-1}; **HRMS** (ESI) m/z 409.1366 $[M + H]^+$; calculated for $[C_{22}H_{20}N_2O_6 + H]^+$: 409.1394; **MP** 162-166 ºC.

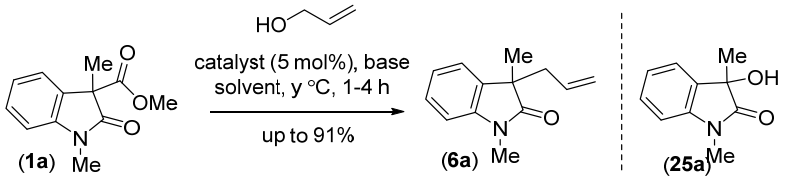


Experimental procedure for synthesis of dicarbonate: In a flame-dried round-bottom flask, dihydroisoindigo (1.0 equiv) was taken in CH_2Cl_2 (8 mL) at 0 °C. To this reaction mixture Et_3N (2.2 equiv) was added in one portion followed by methyl chloroformate (2.3 equiv) was added to the same at 0 °C and stirring was continued on 25 °C for 2 h. Upon completion of the reaction (judged by TLC analysis), diluted with 10 mL of CH_2Cl_2 and quenched with 10 mL water. The organic layer was separated and successively washed with brine (10 mL). The organic extracts were dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography (hexane and EtOAc as eluents) to afford desired product (**27**).

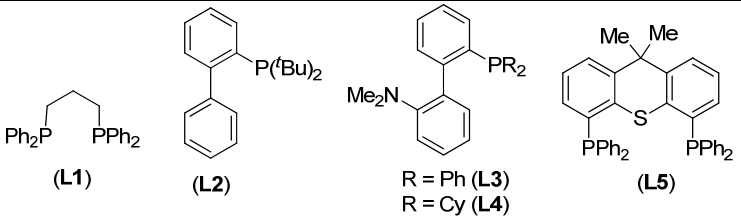


1,1'-dimethyl-1H,1'H-[3,3'-biindole]-2,2'-diyl dimethyl dicarbonate (**27**): 43% yield of (**26**) as light brown solid (Reaction scale: 7.88 mmol); R_f = 0.29 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26 (td, *J* = 7.0, 1.2 Hz, 1H), 7.13 (td, *J* = 7.0, 1.2 Hz, 1H), 3.84 (s, 3H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 139.3, 132.8, 125.7, 121.8, 120.7, 119.9, 109.0, 93.4, 56.0, 28.6; **IR** (film) υ_{max} 1646, 1614, 1556, 1436, 1242, 1123, 932, 779 cm^{-1}; **HRMS** (ESI) m/z 409.1369 $[M + H]^+$; calculated for $[C_{22}H_{20}N_2O_6 + H]^+$: 409.1394; **MP** 122-125 ºC.

Table 1: Optimization of deacylative allylation (DaA).



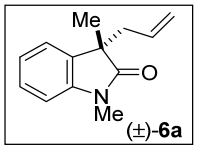
entry	catalyst	base	solvent	temp	time	**6a**[a,b]	**25a**[a,b]
1	$Pd_2(dba)_3$	NaH	THF	70 °C	2 h	44%	38%
2	$Pd_2(dba)_3$	KO^{t}Bu	THF	70 °C	2 h	25%	53%
3[c]	$Pd(OAc)_2$	NaH	THF	70 °C	3 h	46%	39%
4[c]	$Pd(OAc)_2$	KO^{t}Bu	PhMe	25 °C	2 h	42%	33%
5[c]	$Pd(OAc)_2$	NaH	PhMe	25 °C	3 h	59%	25%
6[d]	$Pd(OAc)_2$	NaH	PhMe	25 °C	2 h	65%	21%
7[e]	$Pd(OAc)_2$	NaH	PhMe	25 °C	2 h	62%	14%
8[f]	$Pd(OAc)_2$	NaH	PhMe	25 °C	3 h	79%	8%
9[g]	$Pd(OAc)_2$	NaH	PhMe	25 °C	3 h	87%	--
10[h]	$Pd(OAc)_2$	NaH	PhMe	25 °C	2 h	90%	--
11	$Pd(PPh_3)_4$	NaH	PhMe	25 °C	2 h	91%	--
12	$Pd(PPh_3)_4$	KO^{t}Bu	PhMe	25 °C	2 h	89%	--
13	$Pd(PPh_3)_4$	$NaNH_2$	PhMe	25 °C	3 h	54%	32%
14	$Pd(PPh_3)_4$	NaH	PhH	25 °C	2 h	84%	--
15	$Pd(PPh_3)_4$	NaH	xylene	25 °C	2 h	73%	18%
16	$Pd(PPh_3)_4$	NaH	mesitylene	25 °C	3 h	67%	26%
17	$Pd(PPh_3)_4$	NaH	Et_2O	25 °C	4 h	62%	15%
18	$Pd(PPh_3)_4$	NaH	CH_2Cl_2	25 °C	2 h	70%	20%
19	$Pd(PPh_3)_4$	NaH	DMSO	25 °C	4 h	67%	17%
20	$Pd(PPh_3)_4$	NaH	dioxane	25 °C	3 h	56%	21%
21	$Pd(PPh_3)_4$	NaH	MeCN	25 °C	3 h	83%	--
22	$Pd_2(dba)_3$	NaH	PhMe	25 °C	2 h	69%	13%
23	$Pd_2(dba)_3$	NaH	DMSO	25 °C	2 h	65%	10%
24	$Pd_2(dba)_3$	NaH	PhH	25 °C	2 h	65%	17%
25[i]	$Pd(PPh_3)_4$	NaH	PhMe	25 °C	5 h	86%	--
26[i]	$Pd(PPh_3)_4$	KO^{t}Bu	PhMe	25 °C	5 h	83%	--



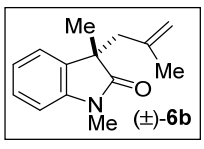
[a]reactions were carried out by using 0.25 mmol of **1a** with 0.375 mmol of allyl alcohol under argon atmosphere. [b]isolated yield after column purification. [c]10 mol% PPh_3 was used. [d]5 mol% **L1** was used. [e]10

mol% **L2** was used. [f]5 mol% **L3** was used. [g]5 mol% **L4** was used. [h]10 mol% **L5** was used. [i]2 mol% catalyst was used.

General experimental procedure for Palladium Catalyzed Deacyaltive Alkylation: In a flame-dried seal tube under argon atmosphere was charged with dry toluene or THF, to it allyl alcohol (1.5 equiv) was added and purged with argon for 30 minutes at 25 ºC. Afterwards NaH (60% suspension in mineral oil) [2.0 equiv] was added at once followed by 2-Oxindole derivative (1.0 equiv) and $Pd(PPh_3)_4$ (5 mol%), and stirring was continued for 2-3 h at 25 ºC. After complete consumption of 2-oxindole derivatives (judge by TLC analysis), reaction mixture was quenched by adding (4 mL) of water and extracted with EtOAc. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuo. The crude product was purified through flash column chromatography using hexane/EtOAc mixture as eluent to afford the desired product.

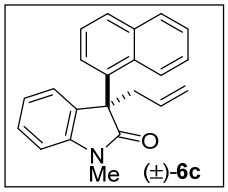


(±)-3-Allyl-1,3-dimethylindolin-2-one (6a)[1]: The product (**6a**) was isolated as yellow gel; R_f = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (td, *J* = 7.6, 1.1 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.04 (td, *J* = 7.6, 0.7 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.48-5.37 (m, 1H), 4.98-4.88 (m, 2H), 3.17 (s, 3H), 2.54-2.44 (m, 2H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.2, 143.2, 133.6, 132.6, 127.7, 122.9, 122.3, 118.6, 107.9, 48.2, 42.4, 26.1, 22.7; **IR** (film) υ_{max} 2966, 2926, 1711, 1613, 1493, 1489, 1452, 1377, 1350, 1317, 1306, 1250, 1123, 1099, 1084, 1027, 995, 919, 753 cm^{-1}.



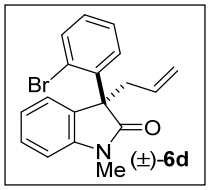
(±)-1,3-Dimethyl-3-(2-methylallyl)indolin-2-one (6b): Compound (**6b**) was isolated as colorless gel; R_f = 0.39 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 4.49 (d, *J* = 28.9 Hz, 2H), 3.15 (s, 3H), 2.69 (d, *J* = 13.5 Hz, 1H), 2.44 (d, *J* = 13.5 Hz,

1H) 1.34 (s, 3H), 1.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.3, 143.2, 141.2, 133.6, 127.7, 123.1, 122.2, 114.2, 107.9, 48.6, 45.7, 26.1, 24.7, 23.5; **IR** (film) υ_{max} 2927, 1715, 1614, 1494, 1471, 1455, 1377, 1349, 1329, 1256, 1157, 1123, 1099, 1064, 1026, 932, 898, 767, 753, 742, 589 cm^{-1}; **HRMS** (ESI) m/z 216.1388 $[M+H]^+$; calculated for $[C_{14}H_{17}NO + H]^+$: 216.1383.



(±)-**6c**

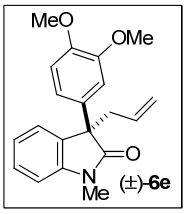
(±)-3-Allyl-1-methyl-3-(naphthalen-1-yl)indolin-2-one (**6c**): Compound (**6c**) was isolated as colorless solid; R_f = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 1H), 7.79 (t, *J* = 8.9 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.33-7.27 (m, 2H), 7.14 (t, *J* = 8.1 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.40-5.29 (m, 1H), 5.03 (d, *J* = 16.9 Hz, 1H), 4.94 (d, *J* = 10.2 Hz, 1H), 3.36 (s, 3H), 3.23-3.13 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 143.2, 135.0, 134.5, 134.2, 131.6 (2C), 129.1 (2C), 128.1, 126.2, 126.1, 125.3, 125.0, 123.5, 123.4, 123.0, 119.5, 108.1, 56.4, 43.2, 26.3; **IR** (film) υ_{max} 3081, 1711, 1609, 1563, 1551, 1536, 1342, 1304, 1246, 1138, 1082, 1059, 1018, 996, 979, 928, 880 cm^{-1}; **HRMS** (ESI) m/z 314.1545 $[M+H]^+$; calculated for $[C_{22}H_{19}NO + H]^+$: 314.1539; **MP** 78-81 ºC.



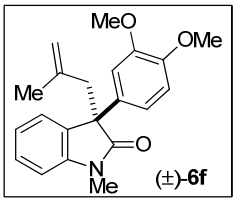
(±)-**6d**

(±)-3-Allyl-3-(2-bromophenyl)-1-methylindolin-2-one (**6d**): Product (**6d**) was isolated as colorless gel; R_f = 0.22 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 (td, *J* = 7.9, 1.3 Hz, 1H), 7.31 (td, *J* = 7.8, 1.1 Hz, 1H), 7.17 (td, *J* = 7.8, 1.6 Hz, 1H), 7.03-6.99 (m, 1H), 6.87-6.83 (m, 2H), 5.43-5.32 (m, 1H), 5.03 (dd, *J* = 16.9, 1.1 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H),

3.27 (s, 3H), 3.11-2.99 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.4, 144.9, 138.9, 137.7, 131.9, 131.3, 129.7, 129.1, 128.1, 127.3, 123.9, 122.9, 122.5, 119.5, 107.7, 57.2, 42.4, 26.4; **IR** (film) υ_{max} 2925, 1713, 1613, 1492, 1470, 1373, 1348, 1263, 1249, 1128, 1086, 1021, 998, 920, 817 cm^{-1}; **HRMS** (ESI) m/z 342.0505 $[M+H]^+$; calculated for $[C_{18}H_{16}BrNO + H]^+$: 342.0488.

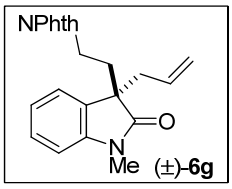


(±)-3-Allyl-3-(3,4-dimethoxyphenyl)-1-methylindolin-2-one (±)-**6e**: The compound (±)-**6e** as yellow gel; R_f = 0.25 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.7, 1.1 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.14 (td, *J* = 7.6, 0.7 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.46-5.36 (m, 1H), 5.04 (dd, *J* = 17.0, 1.4 Hz, 1H), 4.94 (dd, *J* = 10.2, 0.8 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.21 (s, 3H), 3.00 (d, *J* = 7.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.1, 148.9, 148.4, 143.8, 132.5, 131.9, 131.5, 128.2, 125.2, 122.3, 119.4, 119.0, 110.9, 110.7, 108.2, 55.9, 55.8, 42.4, 29.7, 26.3; **IR** (film) υ_{max} 2926, 1722, 1714, 1587, 1546, 1515, 1494, 1469, 1454, 1372, 1350, 1259, 1185, 1146, 1092, 1027, 924 cm^{-1}; **HRMS** (ESI) m/z 324.1588 $[M+H]^+$; calculated for $[C_{20}H_{21}NO_3 + H]^+$: 324.1594.

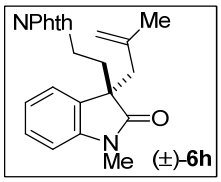


(±)-3-(3,4-Dimethoxyphenyl)-1-methyl-3-(2-methylallyl)indolin-2-one (±)-**6f**: Compound (±)-**6f** was isolated as yellow solid; R_f = 0.25 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.86-6.83 (m, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 4.56 (d, *J* = 28.8 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 3.18-3.15 (m, 4H), 2.86 (d, *J* = 13.5 Hz, 1H), 1.32 (s, 3H); **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 178.4, 148.8, 148.3, 143.9, 140.9, 132.8, 131.2, 128.2, 125.8, 122.1, 119.2, 115.1, 110.8, 110.6, 108.2, 56.0, 55.9, 55.8, 45.9, 26.3, 23.6; **IR** (film) υ_{max} 2933, 1714, 1643, 1612, 1515, 1494, 1470, 1373, 1349, 1259, 1145, 1129, 1090, 1027, 899, 861, 799, 756, 692 cm^{-1}; **HRMS** (ESI) m/z 338.1757 $[M+H]^+$; calculated for $[C_{21}H_{23}NO_3 + H]^+$: 338.1751; **MP** 60-63 ºC.

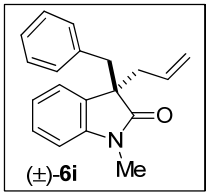


(±)-2-(2-(3-allyl-1-methyl-2-oxoindolin-3-yl)ethyl)isoindoline-1,3-dione (±)-**6g**: compound (±)-**6g** was isolated as colorless solid; R_f = 0.21 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 4H), 7.05 (d, *J* =7.3 Hz, 1H), 6.93 (td, *J* = 7.7, 0.8 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 5.41-5.31 (m, 1H), 4.93 (d, *J* = 17.0 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 3.59-3.52 (m, 1H), 3.45-3.38 (m, 1H), 3.14 (s, 3H), 2.49-2.42 (m, 3H), 2.32-2.25 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 167.8, 143.7, 133.5, 131.9, 131.6, 130.6, 127.6, 122.8, 122.6, 122.1, 119.1, 108.2, 51.2, 42.9, 34.3, 33.2, 26.1; **IR** (film) υ_{max} 3465, 2934, 1771, 1713, 1613, 1493, 1470, 1445, 1397, 1254, 1123, 1087, 1023, 925, 870, 753, 719, 700, 544, 530 cm^{-1}; **HRMS** (ESI) m/z 361.1545 $[M+H]^+$; calculated for $[C_{22}H_{20}N_2O_3 + H]^+$: 361.1547; **MP** 73-76 ºC.



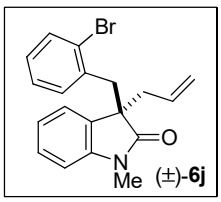
(±)-2-(2-(1-Methyl-3-(2-methylallyl)-*2*-oxoindolin-3-yl)ethyl)isoindoline-1,3-dione (±)-**6h**: The compound (±)-**6h** was isolated as colorless solid; R_f = 0.24 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 4H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.94 (td, *J* = 7.8, 0.9 Hz, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.51 (s, 1H), 4.43 (s, 1H), 3.58-3.35 (s, 1H), 3.45-3.38 (m, 1H), 3.13 (s, 3H), 2.65 (d, *J* = 13.2 Hz, 1H), 2.47-2.41 (m, 2H), 2.33-2.27 (m, 1H), 1.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 167.8, 143.9, 140.2, 133.6, 131.9, 130.6, 127.6, 122.9, 122.8, 122.0, 114.9, 108.2,

51.7, 46.2, 34.6, 34.2, 26.1, 23.7; **IR** (film) υ_{max} 2926, 1772, 1713, 1613, 1493, 1469, 1445, 1398, 1377, 1266, 1123, 1107 1088, 1022, 1011, 900, 792, 737, 719 cm^{-1}; **HRMS** (ESI) m/z 375.1715 $[M+H]^+$; calculated for $[C_{23}H_{22}N_2O_3 + H]^+$: 375.1703; **MP** 109-111 ºC.



(±)-**6i**

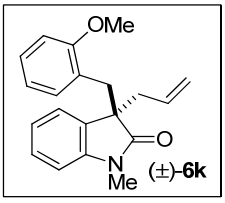
(±)-3-Allyl-3-benzyl-1-methylindolin-2-one (±)-**6i**: Compound (±)-**6i** as colorless solid; R_f = 0.25 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.13 (m, 2H), 7.03-6.98 (m, 4H), 6.83-6.81 (m, 2H), 6.56 (d, *J* = 7.7 Hz, 1H), 5.47-5.37 (m, 1H), 5.01 (dd, *J* = 17.0, 1.1 Hz, 1H), 4.89 (d, *J* = 10.1 Hz, 1H), 3.14 (d, *J* = 13.0 Hz, 1H), 3.03 (d, *J* = 13.0 Hz, 1H), 2.93 (s, 3H), 2.75-2.70 (m, 1H), 2.66-2.60 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.6, 143.7, 135.9, 132.4, 130.7, 129.9, 127.8, 127.5, 126.4, 123.8, 121.9, 118.7, 107.6, 54.4, 43.3, 41.2, 25.8; **IR** (film) υ_{max} 2923, 1686, 1694, 1682, 1642, 1531, 1504, 1436, 1403, 1361, 1306, 1307, 1270, 1000, 922, 784, 744, 726, 714, 677, 546 cm^{-1}; **HRMS** (ESI) m/z 278.1549 $[M+H]^+$; calculated for $[C_{19}H_{19}NO + H]^+$: 278.1539; **MP** 79-82 ºC.



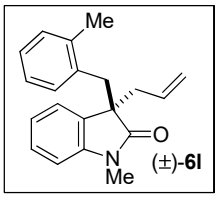
(±)-**6j**

(±)-3-Allyl-3-(2-bromobenzyl)-1-methylindolin-2-one (±)-**6j**: Compound (±)-**6j** as yellow gel; R_f = 0.30 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 1H), 7.21-7.16 (m, 2H), 7.11-7.05 (m, 2H), 6.99-6.92 (m, 2H), 6.66 (d, *J* = 7.7 Hz, 1H), 5.44-5.34 (m, 1H), 5.03 (d, *J* = 16.9 Hz, 1H), 4.93-4.90 (m, 1H), 3.50 (d, *J* = 13.8 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), 3.14 (s, 3H), 2.80-2.67 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9, 143.4, 136.2, 132.7, 132.1, 130.9, 129.9, 128.1, 127.9, 126.7, 125.7, 124.7, 121.9, 118.9, 107.4, 53.9, 41.4, 41.1, 26.0; **IR** (film) υ_{max} 2922, 1722, 1714,

1613, 1493, 1470, 1441, 1377, 1336, 1335, 1252, 1122, 1084, 1023, 996, 923, 752, 740 cm^{-1}; **HRMS** (ESI) m/z 356.0640 $[M+H]^+$; calculated for $[C_{19}H_{18}BrNO + H]^+$: 356.0645.

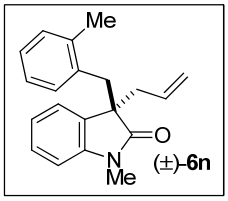


(±)-3-Allyl-3-(2-methoxybenzyl)-1-methylindolin-2-one (±)-**6k**: Compound (±)-**6k** as colorless gel; R_f = 0.21 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (td, *J* = 7.7, 1.0 Hz, 1H), 7.10-7.04 (m, 2H), 7.01 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.94 (td, *J* = 7.6, 0.6 Hz, 1H), 6.73 (td, *J* = 7.5, 0.7 Hz, 1H), 6.62 (d, *J* = 3.4 Hz, 1H), 6.60 (d, *J* = 3.8 Hz, 1H), 5.45-5.34 (m, 1H), 5.03-4.99 (m, 1H), 4.90-4.87 (m, 1H), 3.56 (s, 3H), 3.43 (d, *J* = 13.1 Hz, 1H), 3.08 (s, 3H),3.01 (d, *J* = 13.2 Hz, 1H), 2.78 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.65 (dd, *J* = 13.6, 6.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.3, 157.3, 143.5, 132.8, 131.2, 130.8, 127.7, 127.4, 124.9, 124.5, 121.2, 119.6, 118.4, 109.8, 107.1, 54.6, 54.1, 41.1, 35.7, 25.9; **IR** (film) υ_{max} 2924, 1715, 1614, 1495, 1470, 1440, 1377, 1357, 1336, 1292, 1248, 1119, 1083, 1052, 996, 922 cm^{-1}; **HRMS** (ESI) m/z 308.1650 $[M+H]^+$; calculated for $[C_{20}H_{21}NO_2 + H]^+$: 308.1645.

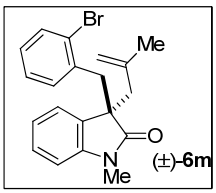


(±)-3-Allyl-1-methyl-3-(2-methylbenzyl)indolin-2-one (±)-**6l**: Compound (±)-**6l** as yellow solid; R_f = 0.32 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (td, *J* = 7.7, 1.9 Hz, 1H), 7.06-6.94 (m, 5H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.43-5.32 (m, 1H), 5.04 (dd, *J* = 16.9, 0.9 Hz, 1H), 4.90 (d, *J* = 10.2 Hz, 1H), 3.19-3.12 (m, 2H), 3.08 (s, 3H), 2.84-2.69 (m, 2H), 2.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 143.7, 137.1, 134.6, 132.4, 130.7, 130.4, 130.2, 127.9, 126.6, 125.0, 124.1, 121.8, 118.7, 107.6, 53.9, 41.0, 39.1, 25.9, 20.0; **IR** (film) υ_{max} 2924, 1713, 1612, 1493, 1470, 1376, 1356, 1334, 1251, 1157, 1121, 1084, 1021, 1010, 995, 921, 753 cm^{-1};

HRMS (ESI) m/z 292.1705 $[M+H]^+$; calculated for $[C_{20}H_{21}NO + H]^+$: 292.1696; **MP** 46-47 ºC.

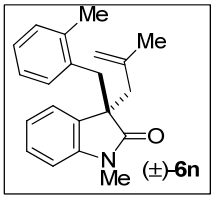


(±)-3-Allyl-1-methyl-3-(2-methylbenzyl)indolin-2-one (±)-**6n**: Compound (±)-**6n** as yellow solid; R_f = 0.32 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (td, *J* = 7.7, 1.9 Hz, 1H), 7.06-6.94 (m, 5H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.43-5.32 (m, 1H), 5.04 (dd, *J* = 16.9, 0.9 Hz, 1H), 4.90 (d, *J* = 10.2 Hz, 1H), 3.19-3.12 (m, 2H), 3.08 (s, 3H), 2.84-2.69 (m, 2H), 2.07 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 143.7, 137.1, 134.6, 132.4, 130.7, 130.4, 130.2, 127.9, 126.6, 125.0, 124.1, 121.8, 118.7, 107.6, 53.9, 41.0, 39.1, 25.9, 20.0; **IR** (film) υ_{max} 2924, 1713, 1612, 1493, 1470, 1376, 1356, 1334, 1251, 1157, 1121, 1084, 1021, 1010, 995, 921, 753 cm^{-1}; **HRMS** (ESI) m/z 292.1705 $[M+H]^+$; calculated for $[C_{20}H_{21}NO + H]^+$: 292.1696; **MP** 46-47 ºC.

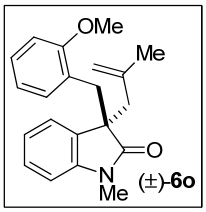


(±)-3-(2-Bromobenzyl)-1-methyl-3-(2-methylallyl)indolin-2-one (±)-**6m**: compound (±)-**6m** as yellow solid; R_f = 0.41 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.07-7.02 (m, 2H), 6.95-6.89 (m, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 4.53-4.48 (m, 2H), 3.43 (d, *J* = 13.6 Hz, 1H), 3.25 (d, *J* = 13.6 Hz, 1H), 3.08 (s, 3H), 2.89 (d, *J* = 13.5 Hz, 1H), 2.65 (d, *J* = 13.4 HZ, 1H), 1.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 143.5, 140.7, 136.0, 132.7, 131.1, 129.9, 128.1, 127.9, 126.6, 125.8, 125.2, 121.7, 114.6, 107.4, 54.2, 44.4, 42.5, 26.0, 23.7; **IR** (film) υ_{max} 2922, 1714, 1613, 1493, 1470, 1442, 1377, 1359, 1338, 1259, 1132, 1089, 1023,

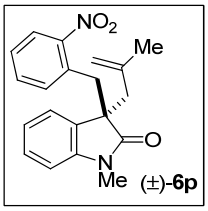
899, 752, 740 cm^{-1}; **HRMS** (ESI) m/z 370.0780 $[M+H]^+$; calculated for $[C_{20}H_{20}BrNO + H]^+$: 370.0801; **MP** 69-70 ºC.



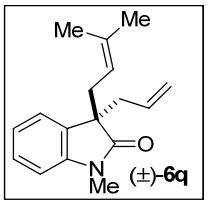
(±)-1-Methyl-3-(2-methylallyl)-3-(2-methylbenzyl)indolin-2-one (±)-**6n**: Compound (±)-**6n** as yellow gel; R_f = 0.37 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (td, *J* = 7.6, 1.6 Hz, 1H), 7.06-6.93 (m, 5H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 1H), 4.54 (d, *J* = 17.3 Hz, 2H), 3.13 (s, 2H), 3.07 (s, 3H), 2.96 (d, *J* = 13.5 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.05 (s, 3H), 1.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.4, 143.8, 141.0, 137.2, 134.4, 130.6, 130.5, 130.2, 127.9, 126.6, 124.9, 124.6, 121.6, 114.4, 107.6, 54.0, 44.0, 40.6, 25.9, 23.6, 20.0; **IR** (film) υ_{max} 2921, 1713, 1613, 1494, 1469, 1454, 1377, 1359, 1336, 1249, 1116, 1130, 1088, 1020, 898, 797, 753 cm^{-1}; **HRMS** (ESI) m/z 306.1844 $[M+H]^+$; calculated for $[C_{21}H_{23}NO + H]^+$: 306.1852.



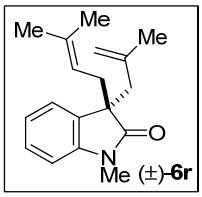
(±)-3-(2-methoxybenzyl)-1-Methyl-3-(2-methylallyl)indolin-2-one (±)-**6o**: compound (±)-**6o** as colorless gel; R_f = 0.25 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.04 (m, 3H), 6.99 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.95-6.91 (m, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.60-6.58 (m, 2H), 4.53 (d, *J* = 14.3 Hz, 2H), 3.55 (s, 3H), 3.41 (d, *J* = 13.1 Hz, 1H), 3.06 (s, 3H), 2.99 (d, *J* = 12.9 Hz, 1H), 2.93 (D, *J* = 13.3 Hz, 1H), 2.64 (d, *J* = 13.6 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.5, 157.4, 143.6, 141.3, 131.2, 130.8, 127.8, 127.3, 124.9, 124.7, 121.0, 119.6, 114.1, 109.8, 107.1, 54.6, 54.4, 44.1, 37.1, 25.9, 23.7; **IR** (film) υ_{max} 2921, 1712, 1643, 1613, 1494, 1469, 1440, 1377, 1359, 1337, 1292, 1247, 1131, 1118, 1031, 898, 752, 693 cm^{-1}; **HRMS** (ESI) m/z 322.1828 $[M+H]^+$; calculated for $[C_{21}H_{23}NO_2 + H]^+$: 322.1802.



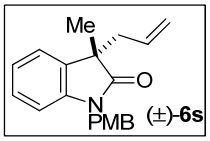
(±)-1-Methyl-3-(2-methylallyl)-3-(2-nitrobenzyl)indolin-2-one (±)-**6p**: compound (±)-**6p** as colorless solid; R_f = 0.23 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.6 Hz, 1H), 7.35-7.31 (m, 1H), 7.26-7.24 (m, 1H), 7.19-7.12 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 4.51 (d, *J* = 19.9 Hz, 2H), 4.00 (d, *J* = 13.4 Hz, 1H), 3.37 (d, *J* = 13.4 Hz, 1H), 2.87 (s, 3H), 2.86 (d, *J* = 13.5 Hz, 1H), 2.63 (d, *J* = 13.5 Hz, 1H), 1.28 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.4, 149.9, 143.3, 140.5, 132.9, 131.9, 130.8, 129.1, 128.1, 127.6, 124.4, 124.2, 122.7, 114.8, 107.6, 54.8, 44.5, 39.3, 25.8, 23.6; **IR** (film) υ_{max} 2924, 1714, 1529, 1493, 1470, 1452, 1377, 1353, 1261, 1158, 1128, 1092, 1020, 902 cm^{-1}; **HRMS** (ESI) m/z 337.1568 $[M+H]^+$; calculated for $[C_{20}H_{20}N_2O_3 + H]^+$: 337.1547; **MP** 79-82 ºC.



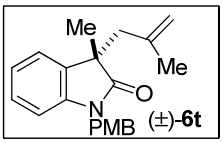
(±)-3-Allyl-1-methyl-3-(3-methylbut-2-en-1-yl)indolin-2-one (±)-**6q**: The compound (±)-**6q** as colorless gel; R_f = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 1H), 7.15 (d, *J* =7.3 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.39-5.29 (m, 1H), 4.94 (d, *J* = 16.8 Hz, 1H), 4.83 (d, *J* = 10.1 Hz, 1H), 4.77 (t, *J* = 7.4 Hz, 1H), 3.14 (s, 3H), 2.54 (d, *J* = 7.2 Hz, 2H), 2.47 (d, *J* = 7.3 Hz, 2H), 1.51 (s, 3H), 1.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.3, 143.8, 135.0, 132.6, 131.7, 127.6, 123.3, 122.1, 118.4, 117.8, 107.6, 52.8, 40.9, 35.6, 25.9, 25.8, 18.0; **IR** (film) υ_{max} 2913, 1722, 1714, 1613, 1494, 1470, 1453, 1378, 1349, 1252, 1122, 1085, 1020, 995, 920 cm^{-1}; **HRMS** (ESI) m/z 256.1709 $[M+H]^+$; calculated for $[C_{17}H_{21}NO + H]^+$: 256.1696.



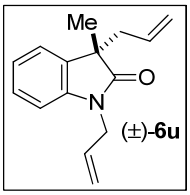
(±)-1-Methyl-3-(2-methylallyl)-3-(3-methylbut-2-en-1-yl)indolin-2-one (±)-**6r**: Compound (±)-**6r** was isolated as colorless gel; R_f = 0.26 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.15 (d, *J* = 6.8 Hz, 1H), 7.01 (td, *J* = 7.5, 0.6 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.80-4.76 (m, 1H), 4.51-4.46 (m, 2H), 3.14 (s, 3H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.52 (d, *J* = 13.6 Hz, 1H), 2.46 (d, *J* = 7.5 Hz, 2H), 1.54 (s, 3H), 1.48 (s, 3H), 1.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.6, 143.8, 141.2, 135.2, 131.7, 127.6, 123.7, 121.9, 117.7, 114.2, 107.6, 53.1, 44.0, 37.1, 26.0, 25.8, 23.6, 18.0; **IR** (film) υ_{max} 3416(br), 2925, 1714, 1613, 1493, 1470, 1453, 1377, 1349, 1251, 1128, 1090, 1020, 896, 798, 751, 693 cm^{-1}; **HRMS** (ESI) m/z 270.1860 $[M+H]^+$; calculated for $[C_{18}H_{23}NO + H]^+$: 270.1852.



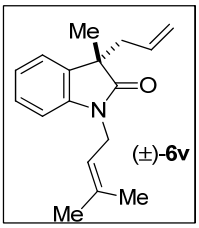
(±)-3-Allyl-1-(4-methoxybenzyl)-3-methylindolin-2-one (±)-**6s**: Product (±)-**6s** was isolated as yellow gel; R_f = 0.22 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.8 Hz, 3H), 7.12 (t, *J* =7.6 Hz, 1H), 7.0 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.48-5.38 (m, 1H), 5.01 (d, *J* = 17.7 Hz, 1H), 4.94-4.90 (m, 2H), 4.72 (d, *J* = 15.3 Hz, 1H), 3.74 (s, 3H), 2.62-2.51 (m, 2H), 1.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.2, 158.9, 142.3, 133.5, 132.7, 128.7, 128.1, 127.6, 122.9, 122.3, 118.8, 114.1, 109.0, 55.2, 48.3, 43.1, 42.5, 23.1; **IR** (film) υ_{max} 2927, 1722, 1714, 1613, 1587, 1514, 1488, 1469, 1454, 1374, 1357, 1303, 1248, 1179, 1109, 1034, 997, 922, 844 cm^{-1}; **HRMS** (ESI) m/z 308.1633 $[M+H]^+$; calculated for $[C_{20}H_{21}NO_2 + H]^+$: 308.1645.



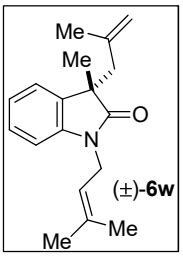
(±)-1-(4-Methoxybenzyl)-3-methyl-3-(2-methylallyl)indolin-2-one (±)-**6t**: Compound (±)-**6t** as yellow solid; R_f = 0.21 (10% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 3H), 7.16 (td, *J* = 7.7, 1.2 Hz, 1H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.86-6.83 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.94 (d, *J* = 15.4 Hz, 1H), 4.77 (d, *J* = 15.5 Hz, 1H), 4.61-4.56 (m, 2H), 3.79 (s, 3H), 2.80-2.78 (m, 1H), 2.54 (d, *J* = 13.4 Hz, 1H), 1.44 (s, 3H), 1.33 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.2, 158.9, 142.4, 141.2, 133.8, 128.7, 128.1, 127.6, 123.1, 122.1, 114.6, 113.9, 109.9, 55.2, 48.7, 45.5, 43.1, 25.1, 23.8; **IR** (film) υ_{max} 2923, 2850, 1715, 1613, 1558, 1540, 1514, 1488, 1467, 1456, 1436, 1374, 1353, 1303, 1248, 1175, 1109, 1033 cm^{-1}; **HRMS** (ESI) m/z 322.1800 $[M+H]^+$; calculated for $[C_{21}H_{23}NO_2 + H]^+$: 322.1802; **MP** 60-62 ºC.



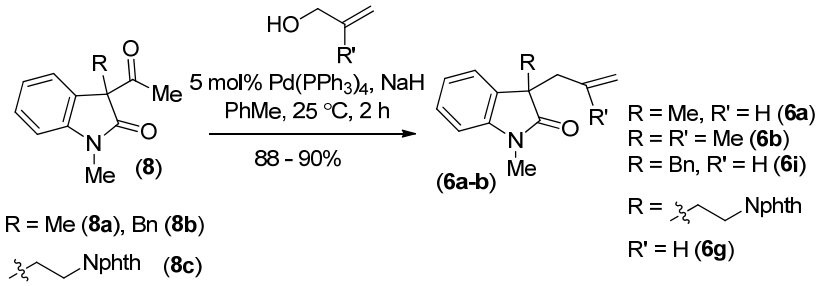
(±)-1,3-Diallyl-3-methylindolin-2-one (±)-**6u**: The compound (±)-**6u** was isolated as yellow gel; R_f = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.87-5.79 (m, 1H), 5.50-5.42 (m, 1H), 5.23-5.19 (m, 2H), 5.04-5.00 (m, 1H), 4.95-4.92 (m, 1H), 4.46-4.41 (m, 1H), 4.29-4.24 (m, 1H), 2.62-2.52 (m, 2H), 1.41 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.9, 142.3, 133.5, 132.6, 131.6, 127.6, 122.9, 122.3, 118.8, 117.2, 108.9, 48.3, 42.5, 42.1, 23.0; **IR** (film) υ_{max} 2924, 1721, 1613, 1488, 1467, 1436, 1374, 1355, 1184, 1133, 1103, 1031, 994, 919, 754, 741 cm^{-1}; **HRMS** (ESI) m/z 228.1407 $[M+H]^+$; calculated for $[C_{15}H_{17}NO + H]^+$: 228.1383.



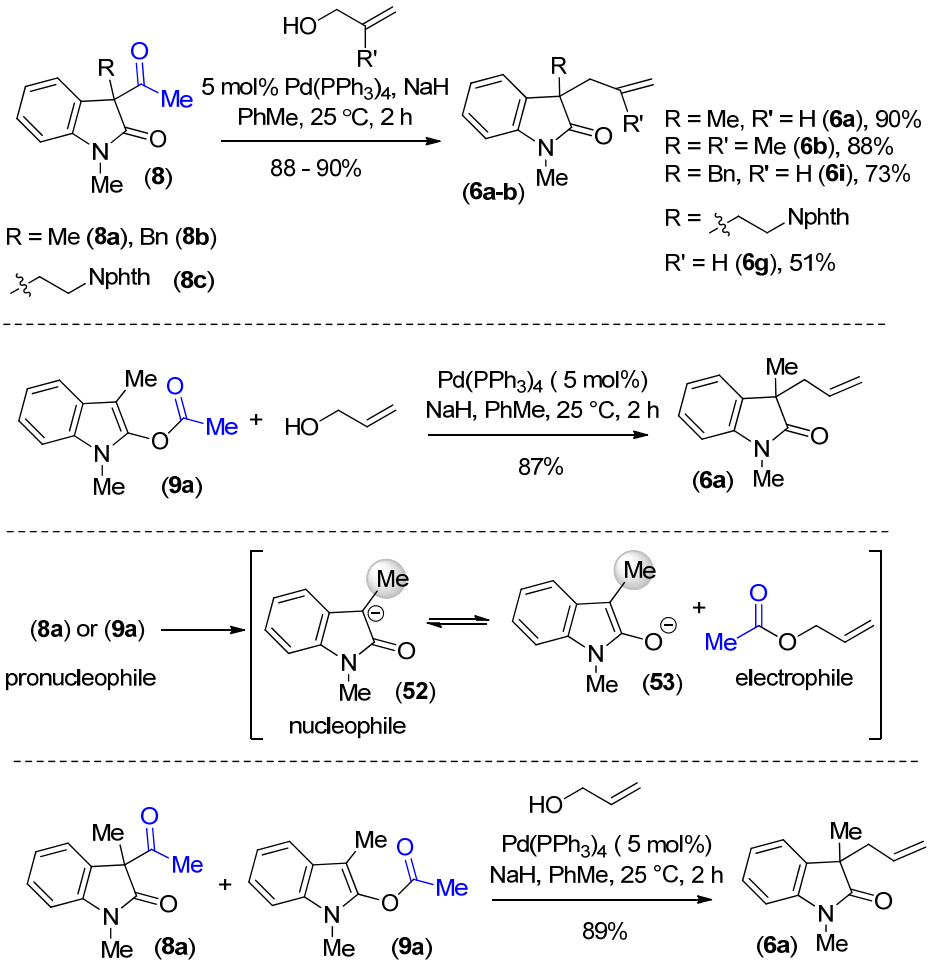
(±)-3-Allyl-3-methyl-1-(3-methylbut-2-en-1-yl)indolin-2-one (±)-**6v**: Product (±)-**6v** was isolated as colorless gel; R_f = 0.21 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.15 (m, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 5.47-5.37 (m, 1H), 5.12-5.09 (m, 1H), 4.97 (d, *J* = 16.8 Hz, 1H), 4.89 (d, *J* = 10.1 Hz, 1H), 4.34-4.22 (m, 2H), 2.55-2.45 (m, 2H), 1.78 (s, 3H), 1.69 (s, 3H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.7, 142.5, 136.3, 133.7, 132.6, 127.6, 122.9, 122.1, 118.7, 118.5, 108.6, 48.1, 42.5, 37.9, 25.6, 22.7, 18.1; **IR** (film) υ_{max} 2927, 1713, 1613, 1487, 1454, 1468, 1373, 1355, 1302, 1231, 1178, 1105, 1019, 934, 918, 842, 754 cm^{-1}; **HRMS** (ESI) m/z 256.1723 $[M+H]^+$; calculated for $[C_{17}H_{21}NO + H]^+$: 256.1696.



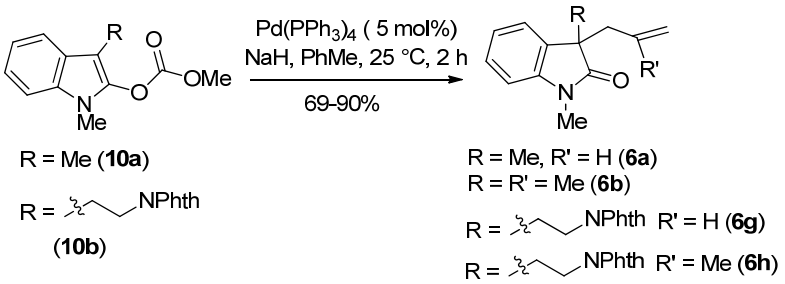
(±)-3-Methyl-3-(2-methylallyl)-1-(3-methylbut-2-en-1-yl)indolin-2-one (±)-**6w**: Product (±)-**6w** was isolated as colorless gel; R_f = 0.20 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.25 (m, 2H), 7.01 (td, *J* = 7.5, 0.6 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.11-5.08 (m, 1H), 4.54-4.47 (m, 2H), 4.37-4.20 (m, 2H), 2.71 (d, *J* = 13.5 Hz, 1H), 2.46 (d, *J* = 13.5 Hz, 1H), 1.80 (s, 3H), 1.69 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.8, 142.6, 141.2, 136.3, 133.8, 127.5, 123.1, 121.9, 118.7, 114.1, 108.6, 48.4, 45.9, 37.9, 25.6, 24.8, 23.6, 18.1; **IR** (film) υ_{max} 2925, 1714, 1613, 1488, 1468, 1454, 1374, 1354, 1302, 1226, 1168, 1104, 1020, 896, 753 cm^{-1}; **HRMS** (ESI) m/z 270.1865 $[M+H]^+$; calculated for $[C_{18}H_{23}NO + H]^+$: 270.1852.



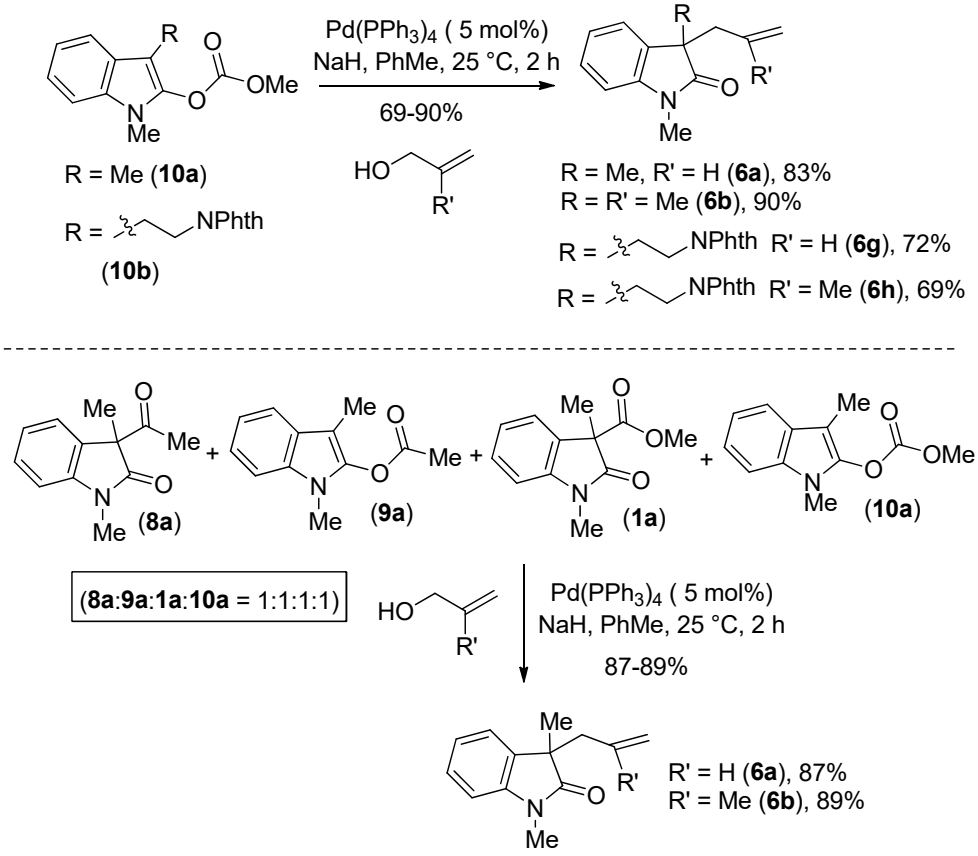
Similar procedure has been followed for the Pd(0) catalyzed deacylative allylation of compound **9a**.



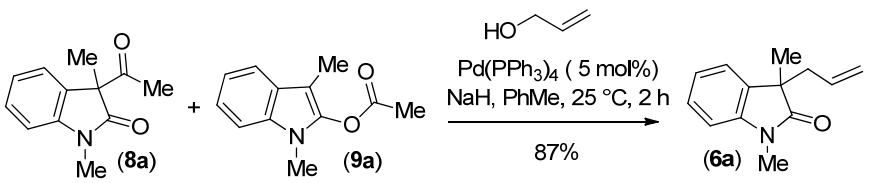
Scheme: Pd(0) catalyzed deacylative allylation of compound **8-9**



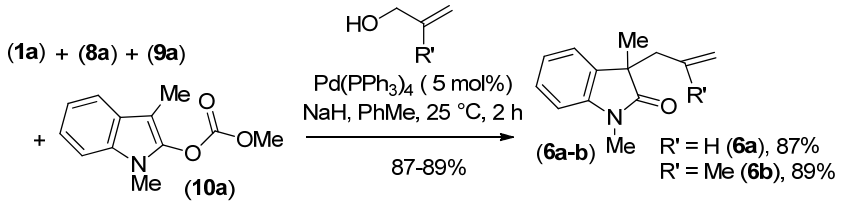
Similar procedure has been followed for the Pd(0) catalyzed deacylative allylation of compound **9a**.



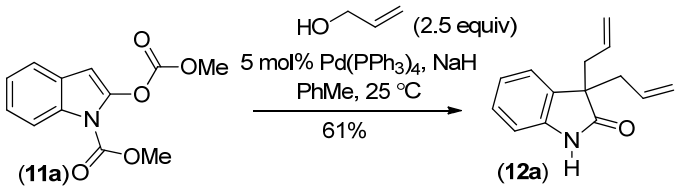
Scheme: Pd(0) catalyzed deacylative allylation of compounds **1**, **8**, **9** & **10**



Experimental procedure for Palladium Catalyzed Deacyaltive Alkylation of (1:1) mixture of (8a) and (9a): In a flame-dried seal tube under argon atmosphere was charged with dry toluene, in that solution allyl alcohol (1.5 equiv) was added and purged with argon for 30 minutes at 25 ºC. Afterwards NaH (60% suspension in mineral oil) [2.0 equiv] was added at once, followed by (1:1) mixture of 2-Oxindole derivatives (**8a** and **9a**) (1.0 equiv) and $Pd(PPh_3)_4$ (5 mol%) also added to the solution, and stirring was continued for 2-3 h. After complete consumption of 2-oxindole derivatives (judge by TLC analysis), reaction mixture was quenched by adding (4 mL) of water and extracted with EtOAc. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuo. The crude product was purified through flash column chromatography using hexane/EtOAc mixture as eluents to afford the desired product.

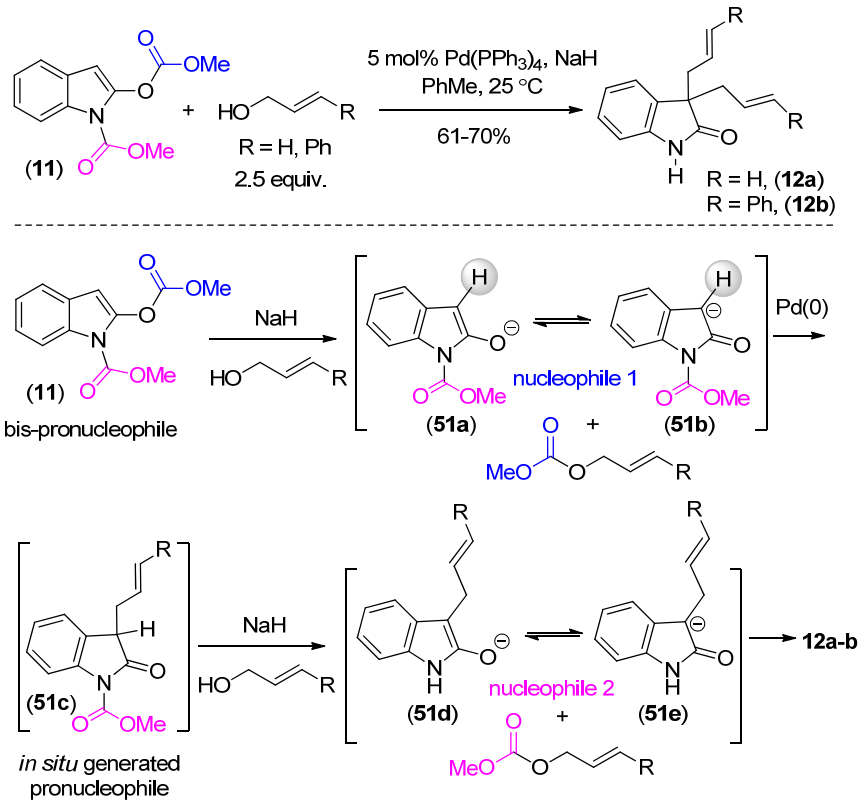


Similar procedure as described above for Pd(0) catalysed allylation has been followed in the case of (1:1:1:1) mixture of (**1a**), (**8a**),(**9a**),(**10a**)

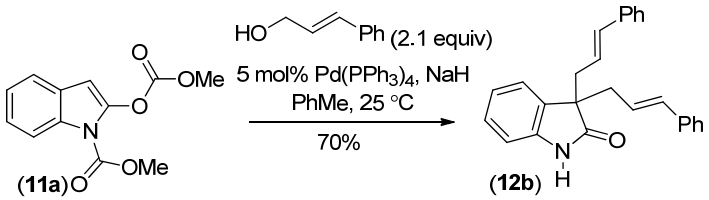


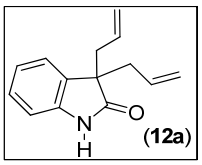
Procedure for the synthesis of (12a): In a flame-dried seal tube under argon atmosphere was charged with allyl alcohol (2.5 equiv) in dry toluene and purged with argon gas for 30 minutes at 25 ºC. Afterward, NaH (60% suspension in mineral oil) [3.0 equiv] was added at once. After stirring the reaction mixture for 5 minutes compound 7c (1.0 equiv), followed by $Pd(PPh_3)_4$ (5 mol%) were added to the solution and stirred for 2-3 h. After complete consumption of starting material (judge by TLC analysis), reaction mixture was quenched by adding (4 mL) of water and extracted with EtOAc. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude

product was purified through flash column chromatography using hexane/EtOAc mixture as eluent to afford the desired product.



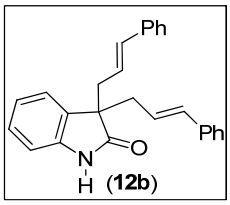
Scheme: Pd(0) catalyzed deacylative allylation of compounds **11**



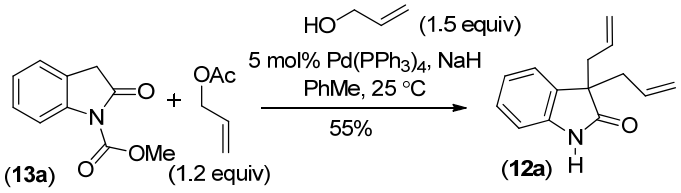


3,3-diallylindolin-2-one (**12a**): Compound (**12a**) as colorless solid (Reaction scale: 0.40 mmol; 61% yield); R_f = 0.26 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.19-7.15 (m, 2H), 7.01 (td, *J* = 7.5, 0.6 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H),

5.50-5.40 (m, 2H), 5.02-4.97 (m, 2H), 4.89 (td, *J* = 10.2, 1.9, 0.9 Hz, 2H), 2.62-2.52 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.9, 141.1, 132.2, 131.8, 127.9, 123.6, 122.8, 118.8, 109.9, 53.3, 41.2; **IR** (film) υ_{max} 2922, 2851, 1713, 1620, 995, 920, 789 cm^{-1}; **HRMS** (ESI) m/z 214.1246 $[M+H]^+$; calculated for $[C_{14}H_{15}NO + H]^+$: 214.1226; **MP** 74-75 ºC.

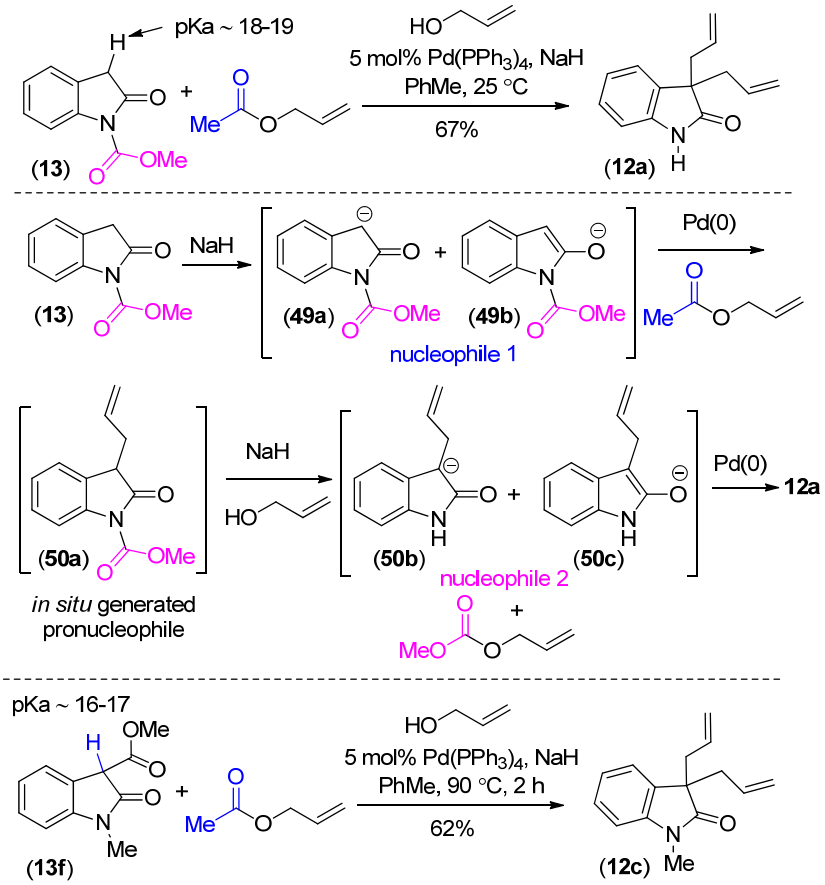


3,3-dicinnamylindolin-2-one (**12b**): compound (**12b**) as yellow gel (Reaction scale: 0.25 mmol; 70% yield); R_f = 0.22 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.26-7.22 (m, 2H), 7.20-7.14 (m, 10H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.37 (d, *J* = 15.8 Hz, 2H), 5.93-5.86 (m, 2H), 2.75 (s, 2H), 2.73 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.9, 140.7, 137.2, 133.9, 131.7, 128.4, 128.0, 127.2, 126.2, 123.8, 123.7, 122.4, 109.8, 53.7, 40.4; **IR** (film) υ_{max} 2922, 2851, 1703, 1620, 748, 692 cm^{-1}; **HRMS** (ESI) m/z 366.1868 $[M+H]^+$; calculated for $[C_{26}H_{23}NO + H]^+$: 366.1852.

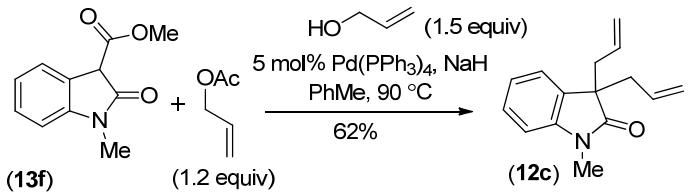


Procedure for the synthesis of (12a): In a flame-dried seal tube under argon atmosphere was charged with allyl alcohol (1.5 equiv) in dry toluene and purged with argon gas for 30 minutes at 25 ºC. Afterward, allyl acetate (1.2 equiv), NaH (60% suspension in mineral oil) [3.0 equiv] was added at once. After stirring the reaction mixture for 5 minutes compound **13a** (1.0 equiv), followed by Pd(PPh3)4 (5 mol%) were added to the solution and stirred for 2-3 h. After complete consumption of starting material (judge by TLC analysis), reaction mixture was quenched by adding (4 mL) of water and extracted with EtOAc. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under

reduced pressure. The crude product was purified through flash column chromatography using hexane/EtOAc mixture as eluent to afford the desired product.

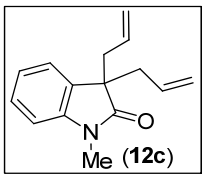


Scheme: Pd(0) catalyzed deacylative allylation of compounds **13**

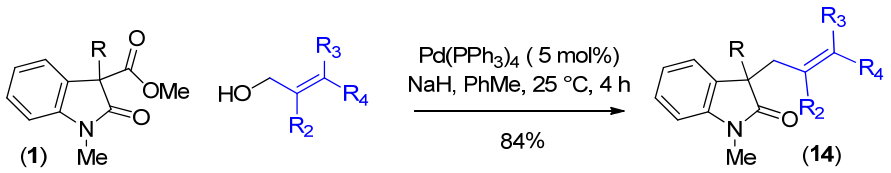


Procedure for the synthesis of (12c): In a flame-dried seal tube under argon atmosphere was charged with allyl alcohol (1.5 equiv) in dry toluene and purged with argon gas for 30 minutes at 25 ºC. Afterward, allyl acetate (1.2 equiv), NaH (60% suspension in mineral oil) [3.0 equiv] was added at once. After stirring the reaction mixture for 5

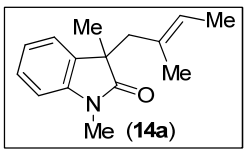
minutes compound **13f** (1.0 equiv), followed by Pd(PPh3)4 (5 mol%) were added to the solution and stirred for 2 h and heated on preheated oil bath. After complete consumption of starting material (judge by TLC analysis), reaction mixture was quenched by adding (4 mL) of water and extracted with EtOAc. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified through flash column chromatography using hexane/EtOAc mixture as eluent to afford the desired product.



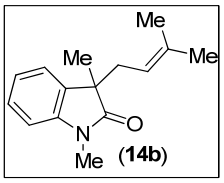
3,3-diallyl-1-methylindolin-2-one (**12c**): compound (**12c**) as light yellow gel (Reaction scale: 0.49 mmol; 62% yield); R_f = 0.48 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (td, *J* = 7.4, 1.3 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.04 (t, *J* = 7.1 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.43-5.33 (m, 2H), 4.98-4.84 (m, 4H), 3.15 (s, 3H), 2.55-2.49 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9, 143.7, 132.3, 131.3, 127.8, 123.3, 122.2, 118.7, 107.8, 52.6, 41.2, 26.0; **IR** (film) υ_{max} 2363, 1801, 1697, 1608, 1454, 1435, 1302, 1232, 1211, 1159, 1078, 1028, 1001, 984, 916, 897 cm^{-1}; **HRMS** (ESI) m/z 228.1371 $[M+H]^+$; calculated for $[C_{15}H_{17}NO + H]^+$: 228.1383.



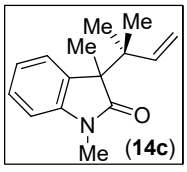
Experimental procedure for the synthesis of compound (**14**) is similar as general procedure for Palladium Catalyzed Deacyaltive Alkylation.



(±)-E-1,3-Dimethyl-3-(2-methylbut-2-en-1-yl)indolin-2-one (±)-**14a**: Compound (±)-**14a** was isolated as colorless gel; R_f = 0.21 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (td, *J* = 7.7, 1.1 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.05 (q, *J* = 6.5 Hz, 1H), 3.13 (s, 3H), 2.62 (d, *J* = 13.4 Hz, 1H), 2.40 (d, *J* = 13.3 Hz, 1H), 1.33-1.31 (m, 6H), 1.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.5, 143.2, 133.9, 131.1, 127.5, 123.3, 123.1, 122.0, 107.7, 49.0, 48.0, 26.0, 24.0, 16.8, 13.3; **IR** (film) υ_{max} 2926, 1714, 1614, 1493, 1470, 1454, 1377, 1349, 1321, 1248, 1122, 1062, 1020, 929, 833, 741, 753, 746, 698, 637 cm^{-1}; **HRMS** (ESI) m/z 230.1536 $[M+H]^+$; calculated for $[C_{15}H_{19}NO + H]^+$: 230.1539.

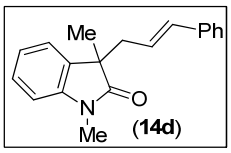


(±)-1,3-dimethyl-3-(3-methylbut-2-en-1-yl)indolin-2-one (±)-**14b**:[1b] Compound (±)-**14b** was isolated as yellow gel; R_f = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (td, *J* = 7.8, 1.2 Hz, 1H), 7.21-7.19 (m, 1H), 7.06 (td, *J* = 7.6, 0.8 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.87-4.82 (m, 1H), 3.21 (s, 3H), 2.53-2.43 (m, 2H), 1.58 (s, 3H), 1.52 (s, 3H), 1.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.9, 143.1, 135.1, 134.1, 127.6, 122.9, 122.3, 118.1, 107.8, 48.5, 36.7, 26.1, 25.8, 22.4, 17.9; **IR** (film) υ_{max} 2929, 1715, 1613, 1494, 1471, 1455, 1376, 1348, 1313, 1251, 1122, 1096, 1033, 1019, 929, 752 cm^{-1}.

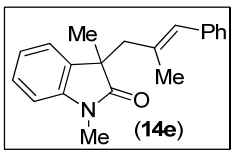


(±)-1,3-Dimethyl-3-(2-methylbut-3-en-2-yl)indolin-2-one (±)-**14c**:[1b] Compound (±)-**14c** was isolated as colorless gel; R_f = 0.21 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 5.99 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.03 (dd, *J* = 10.8, 0.8 Hz, 1H), 4.95 (d, *J* = 17.4 Hz, 1H), 3.15 (s, 3H), 1.31 (s, 3H), 1.13 (s, 3H), 0.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.9,

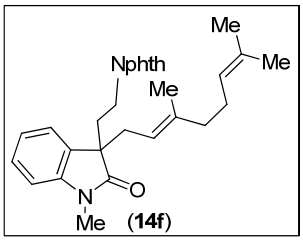
143.7, 143.6, 133.1, 127.6, 124.9, 121.5, 113.2, 107.4, 53.2, 41.5, 25.9, 22.2, 21.7, 18.2; **IR** (film) υ_{max} 3434(br), 2968, 1713, 1636, 1612, 1494, 1470, 1375, 1345, 1305, 1264, 1145, 1100, 1024, 916, 756, 743, 695 cm^{-1}.



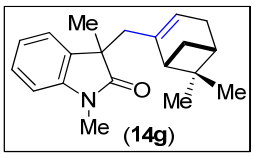
(±)-3-Cinnamyl-1,3-dimethylindolin-2-one (±)-**14d**: Compound (±)-**14d** was isolated as colorless gel; R_f = 0.25 (10% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.15 (m, 7H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 5.91-5.83 (m, 1H), 3.16 (s, 3H), 2.64 (d, *J* = 7.8 Hz, 2H), 1.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.2, 143.1, 137.3, 133.7, 133.6, 128.4, 127.8, 127.2, 126.2, 124.2, 122.9, 122.4, 108.0, 48.6, 41.6, 26.1, 22.5; **IR** (film) υ_{max} 2926, 1713, 1613, 1493, 1470, 1451, 1377, 1350, 1308, 1250, 1157, 1123, 1101, 1070, 1023, 968, 753, 744 cm^{-1}; **HRMS** (ESI) m/z 278.1542 $[M+H]^+$; calculated for $[C_{19}H_{19}NO + H]^+$: 278.1539.



(±)-E-1,3-Dimethyl-3-(2-methyl-3-phenylallyl)indolin-2-one (±)-**14e**: Compound (±)-**14e** was isolated as colorless gel; R_f = 0.25 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.21-7.18 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05 (td, *J* = 7.5, 0.7 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.08 (s, 1H), 3.15 (s, 3H), 2.84 (d, *J* = 13.0 Hz, 1H), 2.58 (d, *J* = 13.0 Hz, 1H), 1.43 (s, 3H), 1.41 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.3, 143.3, 138.1, 134.1, 133.5, 129.1, 129.0, 128.7, 128.2, 127.9, 127.8, 126.0, 123.4, 122.2, 107.9, 49.3, 48.2, 26.1, 23.9, 19.1; **IR** (film) υ_{max} 2834, 1709, 1610, 1579, 1563, 1514, 1486, 1467, 1355, 1303, 1248, 1178, 1086, 1035, 938, 825, 755 cm^{-1}; **HRMS** (ESI) m/z 292.1673 $[M+H]^+$; calculated for $[C_{20}H_{21}NO + H]^+$: 292.1696.



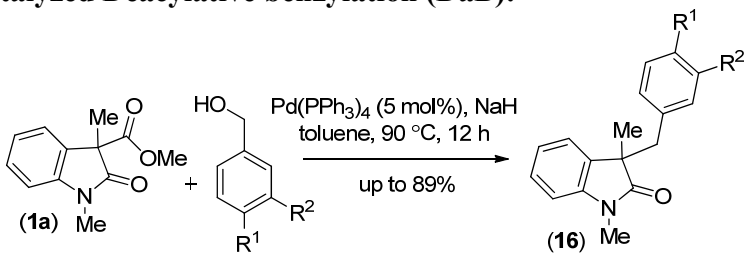
(±)-E-2-(2-(3-(3,7-Dimethylocta-2,6-dien-1-yl)-1-methyl-2-oxoindolin-3-yl)ethyl)isoindoline-1,3-dione (±)-**14f**: Compound (±)-**14f** was isolated as a yellow gel; R_f = 0.22 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.60 (m, 4H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.95 (td, *J* = 7.7, 1.0 Hz, 1H), 6.72-6.66 (m, 2H), 4.95-4.93 (m, 1H), 4.80 (t, *J* = 7.5 Hz, 1H), 3.62-3.55 (m, 1H), 3.48-3.41 (m, 1H), 3.16 (s, 3H), 2.53-2.45 (m, 3H), 2.36-2.29 (m, 1H), 1.89-1.80 (m, 4H), 1.64 (s, 3H), 1.53 (s, 3H), 1.45 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9, 167.8, 143.7, 139.3, 133.5, 131.9, 131.3, 131.0, 127.4, 124.1, 122.8, 122.7, 121.9, 117.1, 108.0, 51.5, 39.8, 37.3, 34.4, 32.9, 26.7, 26.1, 25.6, 17.6, 16.3; **IR** (film) υ_{max} 2923, 2855, 1772, 1723, 1714, 1613, 1493, 1469, 1445, 1397, 1377, 1294, 1253, 1189, 1122, 1108, 1088, 1021, 961 cm^{-1}; **HRMS** (ESI) m/z 457.2499 $[M+H]^+$; calculated for $[C_{29}H_{32}N_2O_3 + H]^+$: 457.2486.



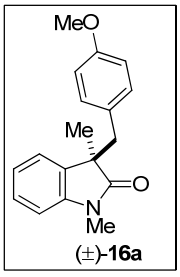
3-(((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl)-1,3-dimethylindolin-2-one 14g: Compound **14g** was isolated as colorless gel, dr = 2.6:1, R_f = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (td, *J* = 7.7, 1.0 Hz, 1H for major + 1H for minor), 7.18-7.14 (m, 1H for major + 1H for minor), 7.04-6.99 (m, 1H for major + 1H for minor), 6.75 (d, *J* = 7.8 Hz, 1H for major + 1H for minor), 5.12 (br, s, 1H for major), 4.97 (br, s, 1H for minor), 3.16 (s, 3H for major), 3.13 (s, 3H for minor), 2.67 (dd, *J* = 13.3, 0.6 Hz, 1H for major), 2.64-2.61 (m, 1H for minor), 2.46 (d, *J* = 13.2 Hz, 1H for minor), 2.34 (d, *J* = 13.2 Hz, 1H for minor), 2.08-2.03 (m, 1H for minor), 2.02-2.00 (br, m, 2H for major), 1.95 (br, s, 1H for minor), 1.90-1.86 (m, 1H for major), 1.81 (br, s, 2H for mjor), 1.75 (td, *J* = 5.6, 1.2 Hz, 1H for minor), 1.62 (br, s, 1H for major), 1.55 (td, *J* = 5.7, 1.3 Hz, 1H for major), 1.33 (s, 3H for minor), 1.32 (s, 3H for major), 1.14 (d, *J* = 9.9

Hz, 1H for minor), 1.05 (s, 3H for major), 1.01 (s, 3H for minor), 0.51 (s, 3H for major + 3H for minor), 0.45 (d, J = 8.5 Hz, 1H for major); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.6, 180.4, 143.75, 143.74, 143.4, 143.3, 133.9, 133.8, 127.6, 127.5, 123.26, 123.21, 122.04, 122.00, 121.4, 121.0, 107.85, 107.81, 49.2, 48.8, 47.1, 45.8, 45.7, 45.6, 40.1, 40.0, 37.5, 37.4, 31.53, 31.52, 31.3, 31.2, 26.2, 26.1, 26.08, 26.05, 24.5, 23.9, 20.8, 20.6; **IR** (film) υ_{max} 2831, 1712, 1611, 1564, 1551, 1536, 1491, 1470, 1349, 1137, 1094, 1062, 1028, 938, 903, 886, 809,752 cm^{-1}; **HRMS** (ESI) m/z 296.2027 $[M+H]^+$; calculated for $[C_{20}H_{25}NO + H]^+$: 296.2009.

Palladium-Catalyzed Deacylative benzylation (DaB):

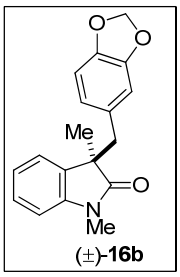


Experimental procedure has been followed similar as general procedure for Palladium Catalyzed Deacyaltive Benzylation(DcB) **16**.

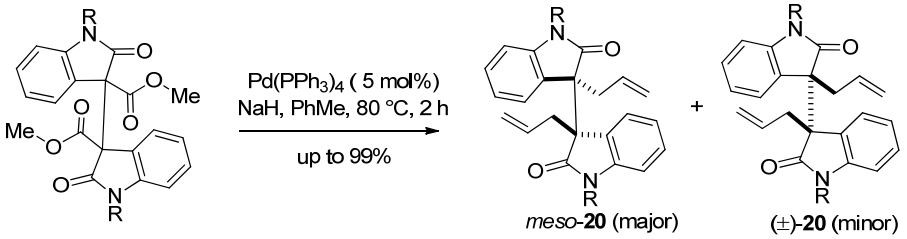


(±)-3-(4-methoxybenzyl)-1,3-dimethylindolin-2-one (±)-**16a**: Compound (±)-**16a** was isolated as colorless gel; R_f = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (td, J = 7.7, 1.4 Hz, 1H), 7.10 (dd, J = 7.4, 1.3Hz, 1H), 7.01 (td, J =7.4, 1.0 Hz, 1H), 6.75-6.72 (m, 2H), 6.60 (d, J = 7.8 Hz, 1H), 6.59-6.55 (m, 2H), 3.67 (s, 3H), 3.03 (d, J = 13.2 Hz, 1H), 2.97 (s, 3H), 2.93 (d, J = 13.2 Hz, 1H), 1.43 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.1, 158.1, 143.1, 130.8, 128.6, 127.7, 123.2, 122.0, 113.9, 112.9, 107.8, 55.1, 50.0, 43.7, 25.9, 22.6; **IR** (film) υ_{max} 2922, 2835, 1614, 1514, 1454, 1377,

1248, 1178, 1030, 929, 876 cm^{-1}; **HRMS** (ESI) m/z 282.1453 $[M+H]^+$; calculated for $[C_{18}H_{19}NO_2 + H]^+$: 282.1489.



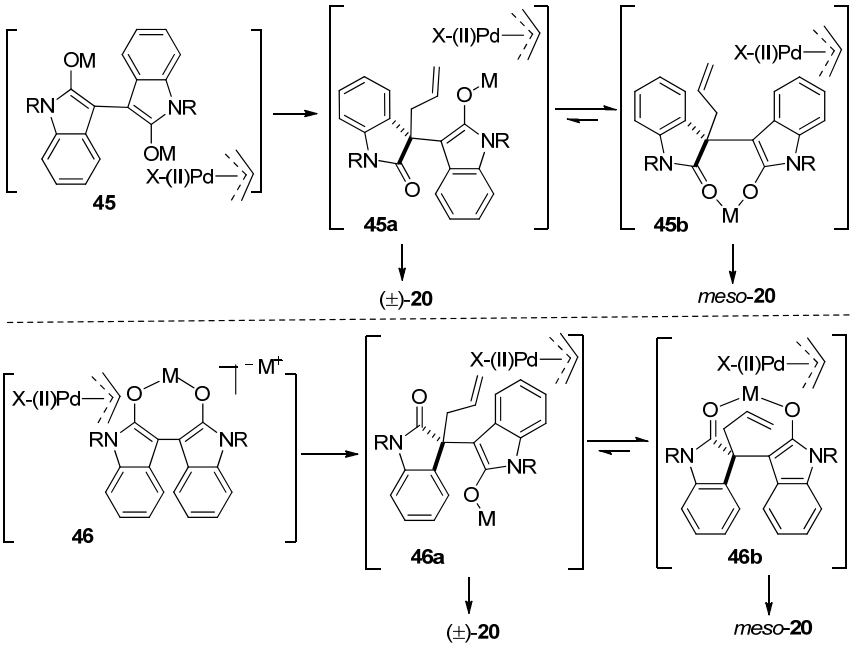
(±)-3-(benzo[d][1,3]dioxol-5-ylmethyl)-1,3-dimethylindolin-2-one (±)-**16b**: compound (±)-**16b** as yellow solid; R_f = 0.40 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.14 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.04-6.99 (m, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.48 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.32-6.30 (m, 2H), 5.78-5.77 (m, 2H), 3.03-3.00 (m, 4H), 2.90 (d, *J* = 13.3 Hz, 1H), 1.41 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.9, 146.8, 145.9, 143.2, 133.0, 129.9, 127.8, 123.2, 123.0, 122.1, 110.2, 107.9, 107.4, 100.6, 49.9, 44.1, 25.9, 22.9; **IR** (film) υ_{max} 2924, 1713, 1695, 1612, 1489, 1377, 1350, 1252, 1122, 1099, 1038, 933 cm^{-1}; **HRMS** (ESI) m/z 296.1299 $[M+H]^+$; calculated for $[C_{18}H_{17}NO_3 + H]^+$; 296.1281; MP 115-117 ºC.



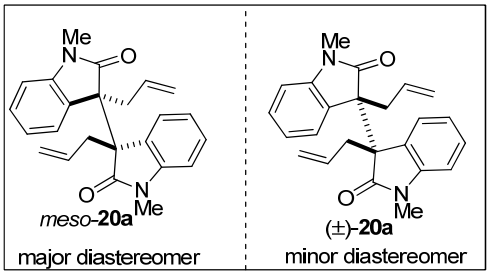
R = Me, (±) : *meso* = 1.9: 1 (**19a**)
R = Bn, (±) : *meso* = 2.3: 1 (**19b**)
R = PMB, (±) : *meso* = 2.1: 1 (**19c**)
R = allyl, (±) : *meso* = 3: 1 (**19d**)
R = prenyl, (±) : *meso* = 2.4: 1 (**19e**)

R = Me, 90%, *meso* : (±) = 2.3: 1 (**20a**)
R = Bn, 88%, *meso* : (±) = 2.1: 1 (**20b**)
R = PMB, 89%, *meso* : (±) = 3.1: 1 (**20c**)
R = allyl, 83%, *meso* : (±) = 2.7: 1 (**20d**)
R = prenyl, 72%, *meso* : (±) = 2.8: 1 (**20e**)

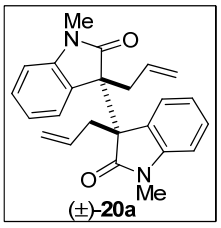
Experimental procedure has been followed similar as general procedure for Palladium Catalyzed Deacyaltive Dialkylation



Scheme: Mechanistic explanation for *meso* as a major product.

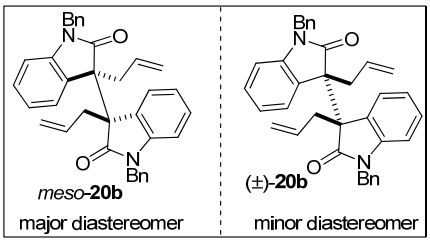


3,3'-Diallyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (*meso*-**20a**): Compound (*meso*-**20a**) (major product) was isolated as colorless solid (dr = 2.2:1); R_f = 0.21 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (td, *J* = 7.8, 0.8 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 6.1 Hz, 1H), 5.12-5.02 (m, 1H), 4.94-4.90 (m, 1H), 4.75 (dd, *J* = 9.9, 1.9 Hz, 1H), 3.45 (dd, *J* = 13.1, 7.4 Hz, 1H), 2.91 (s, 3H), 2.85 (dd, *J* = 13.1, 6.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.0, 144.6, 131.9, 128.5, 128.4, 124.1, 121.4, 119.2, 107.7, 56.5, 34.7, 25.8; **IR** (film) υ_{max} 2933, 1704, 1609, 1469, 1374, 1353, 1305, 1258, 1158, 1123, 1094, 1022, 993, 912, 778 cm^{-1}; **HRMS** (ESI) m/z 373.1921 $[M+H]^+$; calculated for $[C_{24}H_{24}N_2O_2 + H]^+$: 373.1911; MP 167-171 ºC.



(±)-**20a**

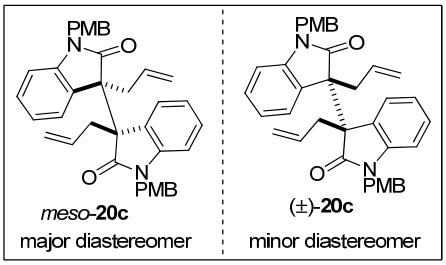
(±)-3,3'-diallyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (±)-**16a**: Compound (±)-**20a** (minor product) was isolated as colorless solid; R_f = 0.22 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.5 Hz, 1H), 6.98 (td, *J* =7.8, 1.0 Hz, 1H), 6.80 (td, *J* = 7.6, 0.7 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 1H), 5.07-4.93 (m, 2H), 4.74-4.71 (m, 1H), 3.62 (dd, *J* = 12.9, 5.8 Hz, 1H), 3.05-2.98 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.9, 143.3, 132.4, 128.2, 128.1, 123.4, 121.6, 118.9, 107.2, 55.9, 33.2, 25.6; **IR** (film) υ_{max} 2924, 1694, 1643, 1610, 1493, 1470, 1374, 1353, 1311, 1354, 1260, 1238, 1123, 1081, 1021, 991, 918, 758, 697, 627 cm^{-1}; MP 194-198 ºC.



3,3'-diallyl-1,1'-dibenzyl-[3,3'-biindoline]-2,2'-dione (*meso*-**20b**): Compound (*meso*-**20b**) (**major diastereomer**) was isolated as colorless solid (dr = 2.2:1); R_f = 0.41 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.10 (m, 4H), 6.97 (s, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 6.67 (br, s, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 5.18-4.98 (m, 2H), 4.82-4.69 (m, 3H), 3.61 (dd, *J* = 12.4, 7.7 Hz, 1H), 2.97 (dd, *J* = 12.9, 6.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 143.9, 135.8, 131.9, 128.6, 128.57, 128.50, 127.1 (2C), 124.3, 121.8, 119.7, 109.1, 56.3, 43.8, 35.5; **IR** (film) υ_{max} 1640, 1435, 1416, 1383, 1302, 1267, 1159, 1109, 1078, 970, 858, 800 cm^{-1}; **HRMS** (ESI) m/z 525.2531 $[M+H]^+$; calculated for $[C_{36}H_{32}N_2O_2 + H]^+$: 525.2537; MP 105-109 ºC.

(±)-3,3'-diallyl-1,1'-dibenzyl-[3,3'-biindoline]-2,2'-dione (±)-**20b**: Compound (±)-**20b** (**minor diastereomer**) was isolated as brown solid; R_f = 0.59 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 5H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.91 (td, *J* =

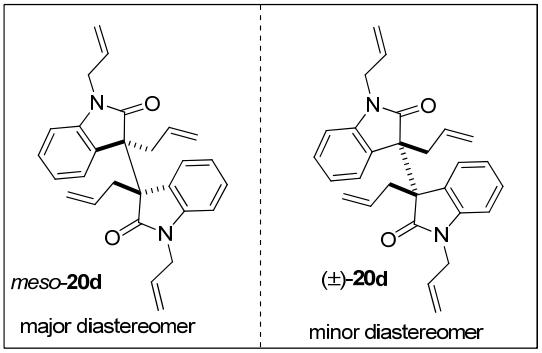
7.7, 0.8 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 15.5 Hz, 1H), 5.07-5.03 (m, 2H), 4.79 (t, *J* = 6.0 Hz, 1H), 4.47 (d, *J* = 15.6 Hz, 1H), 3.74 (dd, *J* = 14.1, 3.1 Hz, 1H), 3.12-3.07 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.1, 142.8, 135.5, 132.5, 128.6, 128.2, 128.1, 127.6, 127.5, 123.9, 121.9, 119.2, 108.4, 55.7, 43.7, 34.1; **IR** (film) υ_{max} 2957, 2362, 2195, 1844, 1419, 1300, 1198, 1159, 878 cm^{-1}; MP 192-198 ºC.



3,3'-Diallyl-1,1'-bis(4-methoxybenzyl)-[3,3'-biindoline]-2,2'-dione (***meso*-16c**): Compound (*meso*-**16c**) (**major diastereomer**) was isolated as colorless solid (dr = 3.1:1); R_f = 0.26 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (t, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.68-6.64 (m, 3H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.13-5.03 (m, 1H), 5.00-4.95 (m, 1H), 4.78 (dd, *J* = 9.9, 2.1 Hz, 1H), 4.70-4.60 (m, 2H), 3.72 (s, 3H), 3.60-3.54 (m, 1H), 2.94 (ABq, *J* = 6.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 158.7, 143.9, 131.9, 128.6, 128.5, 128.4, 127.8, 124.3, 121.7, 119.6, 113.9, 109.1, 56.2, 55.2, 43.2, 35.5; **IR** (film) υ_{max} 2853, 1710, 1608, 1579, 1572, 1514, 1487, 1467, 1356, 1303, 1247, 1178, 1105, 1089, 1035, 1015, 996, 925 cm^{-1}; **HRMS** (ESI) m/z 585.2777 $[M+H]^+$; calculated for $[C_{38}H_{36}N_2O_4 + H]^+$: 585.2748; MP 172-176 ºC.

(±)-3,3'-Diallyl-1,1'-bis(4-methoxybenzyl)-[3,3'-biindoline]-2,2'-dione (±)-**20c**: Compound (±)-**20c (minor diastereomer)** was isolated as light brown solid; R_f = 0.28 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.91-6.87 (m, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 5.05-4.99 (m, 3H), 4.78-4.74 (m, 1H), 4.39 (d, *J* = 15.4 Hz, 1H), 3.75 (s, 3H), 3.72-3.69 (m, 1H), 3.10-3.05 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0, 159.0, 142.7, 132.5, 129.0, 128.2, 128.0, 127.6, 123.9, 121.8, 119.1, 113.9, 108.4,

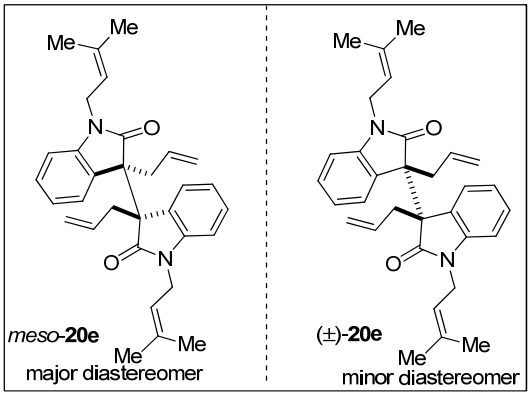
55.6, 55.2, 43.1, 34.0; **IR** (film) υ_{max} 2931, 1698, 1636, 1610, 1515, 1488, 1464, 1365, 1304, 1276, 1249, 1222, 1178, 1108, 1032, 999, 925, 876, 817 cm^{-1}; **HRMS** (ESI) m/z 585.2770 $[M+H]^+$; calculated for $[C_{38}H_{36}N_2O_4 + H]^+$: 585.2748; MP 163-167 ºC.



1,1',3,3'-tetraallyl-[3,3'-biindoline]-2,2'-dione (***meso*-20d**): Compound (***meso*-20d**) (**major diastereomer**) was isolated as colorless solid (dr = 2.63:1); R_f = 0.51 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.66-6.58 (m, 2H), 5.40-5.34 (m, 1H), 5.14-5.04 (m, 1H), 4.99-4.90 (m, 3H), 4.75 (d, *J* = 9.7 Hz, 1H), 4.15 (dd, *J* = 16.1, 4.6 Hz, 1H), 4.01 (dd, *J* = 16.1, 4.7 Hz, 1H), 3.48 (dd, *J* = 12.8, 7.4 Hz, 1H), 2.87 (dd, *J* = 12.9, 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 143.9, 131.9, 131.6, 128.5, 128.4, 124.3, 121.6, 119.4, 117.1, 108.8, 56.3, 42.1, 34.9; **IR** (film) υ_{max} 2089, 1844, 1666, 1335, 1315, 1302, 1275, 1159, 1130, 1067, 880 cm^{-1}; **HRMS** (ESI) m/z 425.2247 $[M+H]^+$; calculated for $[C_{28}H_{28}N_2O_2 + H]^+$: 425.2224; MP 82-84 ºC.

(±)-1,1',3,3'-tetraallyl-[3,3'-biindoline]-2,2'-dione (±)-**20d**: Compound (±)-**20c** (**minor diastereomer**) was isolated as colorless gel; R_f = 0.61 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.3 Hz, 1H), 6.96 (td, *J* = 7.7, 0.9 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 1H), 5.72-5.62 (m, 1H), 5.14-4.93 (m, 4H), 4.75-4.71 (m, 1H), 4.35-4.30 (m, 1H), 4.15-4.09 (m, 1H), 3.65 (dd, *J* = 12.5, 5.1 Hz, 1H), 3.01 (dd, *J* = 12.6, 6.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 142.7, 132.4, 131.3, 128.1, 128.0, 124.0, 121.8, 119.0, 117.8, 108.3, 55.5, 42.2, 33.9; **IR** (film) υ_{max} 2363, 2040, 1714, 1612, 1523, 1491, 1418, 1377, 1348, 1319, 1306, 1261, 1203, 1157, 1090,

970 cm^{-1}; **HRMS** (ESI) m/z 425.2215 $[M+H]^+$; calculated for $[C_{28}H_{28}N_2O_2 + H]^+$: 425.2224; MP 119-123 ºC.

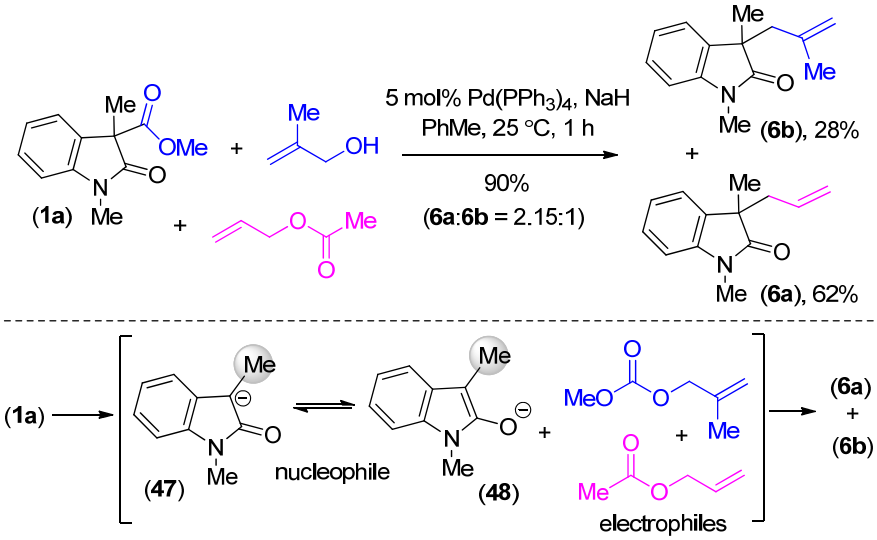


3,3'-diallyl-1,1'-bis(3-methylbut-2-en-1-yl)-[3,3'-biindoline]-2,2'-dione (***meso*-20e**): Major diastereomer (***meso*-20e**) was isolated as brown gel (dr = 2.8:1); R_f = 0.52 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.3 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.60-6.56 (m, 2H), 5.11-5.02 (m, 1H), 4.93 (dd, *J* = 16.9, 1.6 Hz, 1H), 4.74 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.57 (s, 1H), 4.16-4.00 (m, 2H), 3.47 (dd, *J* = 12.9, 7.3 Hz, 1H), 2.85 (dd, *J* = 12.9, 6.7 Hz, 1H), 1.69 (s, 3H), 1.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4, 144.0, 135.3, 132.0, 128.5, 128.3, 124.2, 121.3, 119.1, 118.8, 108.3, 56.1, 37.7, 34.8, 25.5, 18.0; **IR** (film) υ_{max} 1682, 1603, 1483, 1490, 1408, 1348, 1248, 1157, 1122, 1024, 742 cm^{-1}; **HRMS** (ESI) m/z 481.2851 $[M+H]^+$; calculated for $[C_{32}H_{36}N_2O_2 + H]^+$: 481.2850.

(±)-3,3'-diallyl-1,1'-bis(3-methylbut-2-en-1-yl)-[3,3'-biindoline]-2,2'-dione (±)-20e: The minor diastereomer (±)-**20e** was isolated as brown solid; R_f = 0.41 (5% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.3 Hz, 1H), 6.97 (td, *J* =7.7, 0.9 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 5.00-4.93 (m, 3H), 4.73-4.70 (m, 1H), 4.29-4.13 (m, 2H), 3.65 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.99 (dd, *J* = 12.0, 4.6 Hz, 1H), 1.79 (s, 3H), 1.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.5, 142.8, 136.0, 132.4, 128.3, 127.9, 124.2, 121.5, 118.7, 118.5, 107.8, 55.2, 37.8, 33.9, 25.6, 18.1; **IR** (film) υ_{max} 1778, 1681, 1639, 1440, 1415, 1319, 1274, 1147, 1089, 1042, 843 cm^{-1}; **HRMS**

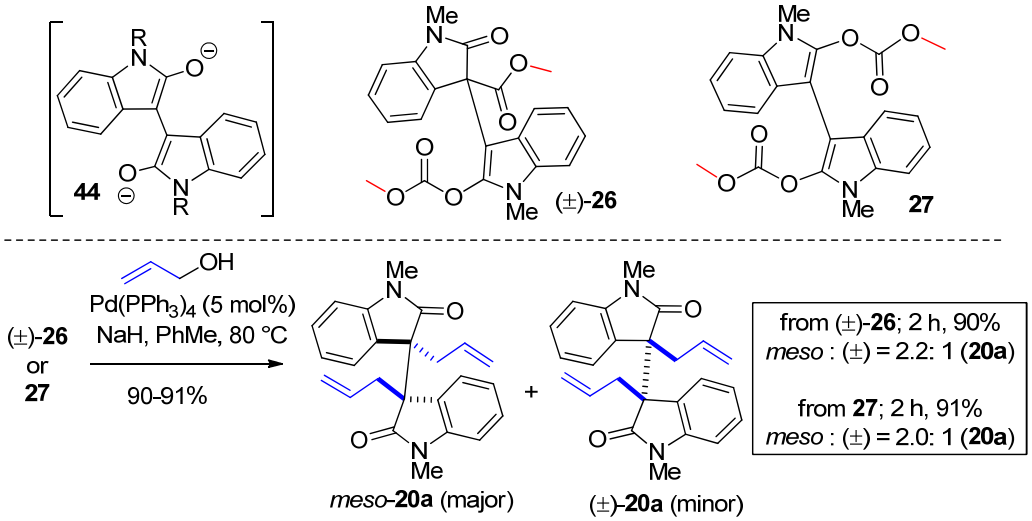
(ESI) m/z 481.2859 $[M+H]^+$; calculated for $[C_{32}H_{36}N_2O_2 + H]^+$: 481.2850; MP 99-103 °C.

Intermolecular nature of Pd(0)-catalyzed DaA:

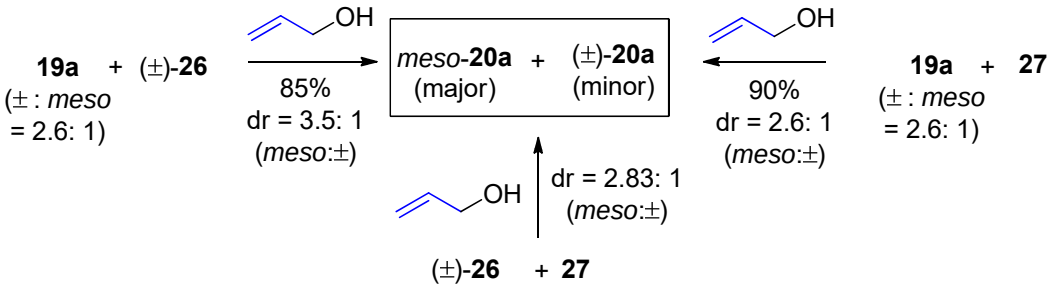


Scheme: Intermolecular nature of Pd(0)-catalyzed DaA.

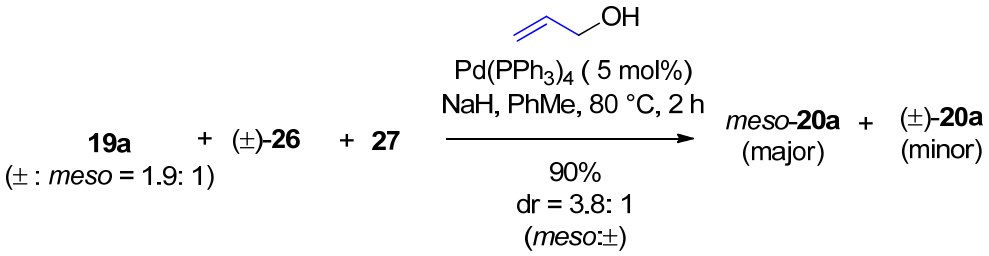
Experimental procedure for intermolecular nature experiment, has been similar as general procedure for Palladium-Catalyzed Deacyaltive Allylation(DaA) **1a**.



Scheme: Substrates scope of Pd(0)-catalyzed DaA.

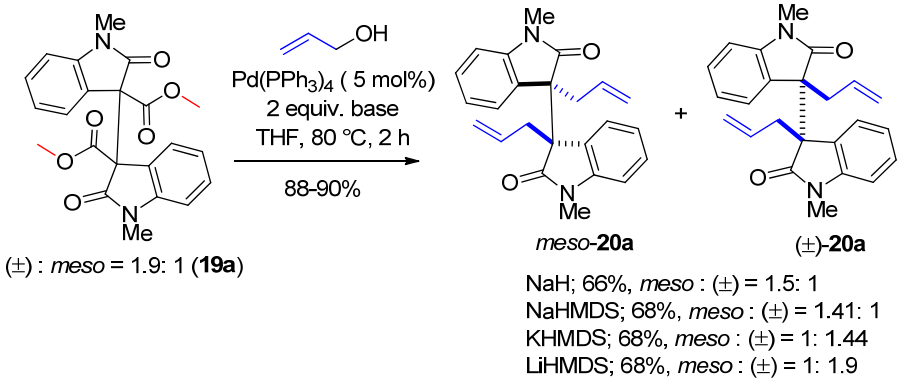


Scheme: Substrates scope of Pd(0)-catalyzed DaA.



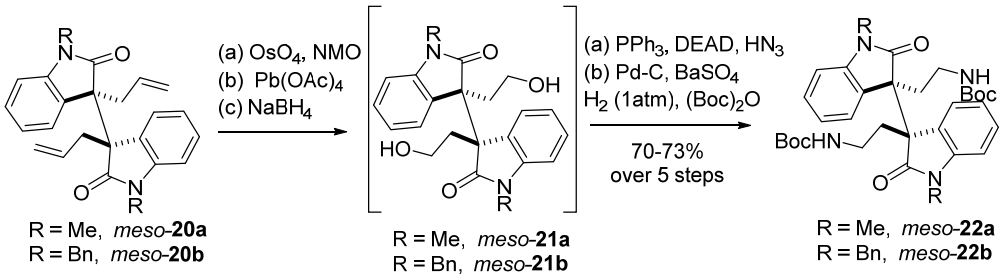
Scheme: Substrates scope of Pd(0)-catalyzed DaA.

Role of Cation over Pd(0)-catalyzed DaA:



Scheme: Cation control over Pd(0)-catalyzed DaA.

Experimental procedure has been similar as general procedure for Palladium-Catalyzed Deacyaltive Allylation(DaA)



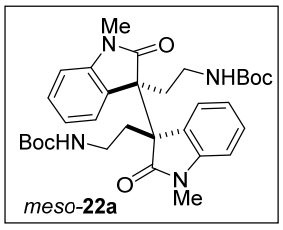
Procedure for the synthesis of compound (*meso*-**22**): To a stirred solution of compound (*meso*-**20a/20b)** (6.0 mmol; 1.0 equiv) in CH_2Cl_2 (80 mL) at 25 ºC were added *N*-methyl morpholine-*N*-oxide (2.1 g, 24.0 mmol, 4.0 equiv) and catalytic OsO_4 (300 µL) (4% solution in water). Then the reaction mixture was stirred for 12 h at 25 °C. Upon consumption of starting material (monitored by TLC) the reaction mixture was quenched with saturated aqueous solution of Na_2SO_3 (20 mL) and extracted with EtOAc (200 mL), organic layer was separated and dried over anhydrous Na_2SO_4. Then the organic layer was concentrated under reduced pressure.

The crude material was directly dissolved in 40 mL of benzene:MeOH (1:1) mixture. To that solution, $Pb(OAc)_4$ (6.9 g, 12.12 mmol, 2.2 equiv) was added at 0 ºC and stirred for 5 minutes and a black color solution was observed. To that reaction mixture $NaBH_4$ (2.3 g, 61.0 mmol, 10 equiv), and 20 mL of MeOH were added at 0 ºC. After 5 minutes of stirring a clear solution, black color precipitate crashed out, TLC analysis showed the complete consumption starting material. Then the above mixture was filtered by passing through silica gel bed, and washed with EtOAc (100 mL). Then the organic layer was washed with saturated aqueous $NaHCO_3$ solution (30 mL X 2). The collected organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure and dried by using high vacuum pump.

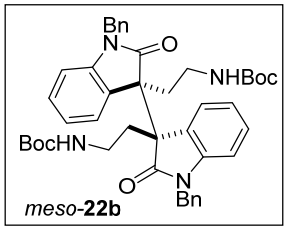
The crude material was dissolved in dry THF (50 mL) under argon atmosphere. To that solution was added PPh_3 (6.39 g, 24.4 mmol, 4.0 equiv) and hydrazoic acid (2.8 M in toluene) (8.7 mL, 24.4 mmol, 4.0 equiv) sequentially at 0 ºC. Afterward DEAD (4.50 mL, 24.4 mmol, 4.0 equiv) was added drop wise over a period 5 minutes at same temperature. Then the reaction mixture was warmed to 25 °C and stirred for 12 h. The crude reaction mixture was washed with saturated aqueous $NaHCO_3$ solution (40 mL),

and brine. The extracted organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure and dried by using high vacuum pump.

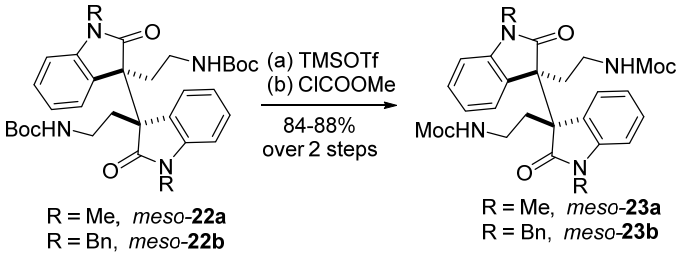
The crude compound was dissolved in MeOH (100 mL) and purge with nitrogen gas over 15 minutes, to that solution was added $(Boc)_2O$ (3.5 mL, 14.52 mmol; 2.2 equiv) and again purged with nitrogen gas for another 10 minutes. Afterward Lindlar catalyst (20% w/w) was added and purged with H_2 (g) balloon for 15 minutes. Then the mixture was stirred under H_2 (g) atmosphere at 25 °C for 12 h. Upon completation of the reaction (judged by TLC analysis), filtered through celite bed, and concentrated under reduced pressure. The crude product was purified by flash chromatography using (20% EtOAc in hexanes) mixture as eluents to afford the desired product *meso*-**22**.



Di-tert-butyl ((-1,1'-dimethyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))dicarbamate (*meso*-**22a**): Compound (*meso*-**22a**) as colorless gel (3.50 mmol scale; 63% yield over 4 step); R_f = 0.24 (30% EtOAc in hexane); **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.30-7.25 (m, 1H), 6.89 (br, s, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.59 (br, s, 1H), 4.41 (br, s, 1H), 2.94 (s, 3H), 2.82 (br, s, 1H), 2.73-2.70 (br, m, 1H), 2.59-2.55 (br, m, 1H), 2.43-2.40 (m, 1H), 1.37 (s, 9H); **^{13}C NMR** (175 MHz, $CDCl_3$) δ 176.1, 155.4, 144.2, 128.9, 127.4, 122.1, 108.1, 79.1, 36.8, 33.8, 29.7, 28.4, 25.9, 22.7; **IR** (film) υ_{max} 2920, 2849, 1869, 1635, 1273, 1171, 910 cm^{-1}; **HRMS** (ESI) m/z 579.3198 $[M+H]^+$; calculated for $[C_{32}H_{42}N_4O_6 + H]^+$: 579.3177.



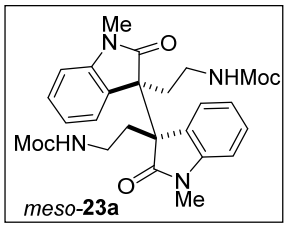
Di-tert-butyl ((-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))dicarbamate (*meso*-**22b**): Compound (*meso*-**22b**) as colorless foam (3.50 mmol scale; 57% yield over 4 step); R_f = 0.31 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.10 (m, 5H), 6.93 (br, s, 2H), 6.81 (br, s, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 4.86 (d, *J* = 15.7 Hz, 1H), 4.58 (br, s, 1H), 4.41 (br, s, 1H), 2.93 (br, s, 1H), 2.70 (br, s, 1H), 2.58 (br, s, 1H), 2.48 (br, s, 1H), 1.35 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 155.5, 143.6, 135.6, 128.9, 128.7, 127.8, 127.3, 127.1, 124.5, 122.5, 109.4, 79.1, 77.3, 44.2, 36.6, 29.7, 28.4; **IR** (film) υ_{max} 2098, 1793, 1715, 1693, 1682, 1468, 1454, 1382, 1298, 1221, 1117, 1109, 1078, 1029, 914, 864, 777 cm^{-1}; **HRMS** (ESI) m/z 731.3824 $[M+H]^+$; calculated for $[C_{44}H_{50}N_4O_6 + H]^+$: 731.30803.



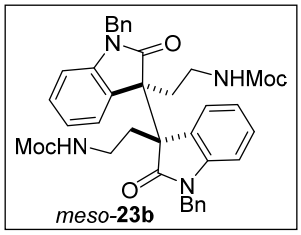
Procedure for the synthesis of compound (*meso*-**23a** and *meso*-**23b**): To a stirred solution of *meso*-**22** (2.15 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL), TMSOTf (1.05 g, 4.73 mmol; 2.2 equiv) was added at 0 °C. Then the reaction vessel was kept open and stirring was continued for 2 h. After complete consumption of starting material (judged by TLC analysis), the reaction mixture was quenched by careful addition of saturated $NaHCO_3$ (aq) solutution to metain the pH >7 (basic). Then reaction mixture was extracted with CH_2Cl_2. The organic layer was dried over anhydrous K_2CO_3 and concentrated under reduced pressure.

The crude product was taken in 14 mL (1:1) mixture of toluene and $NaHCO_3$ (saturated aqueous solution) at 25 ºC. To this reaction mixture methyl chloroformate (365 µL, 4.73 mmol, 2.2 equiv) was added drop wise and was stirred for 2 h at same temperature. Upon completion of the reaction (monitoring by TLC), it was diluted by 20 mL of EtOAc. The whole reaction mixture was taken in a separatory funnel and extracted with 10 mL of water. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was dried by using

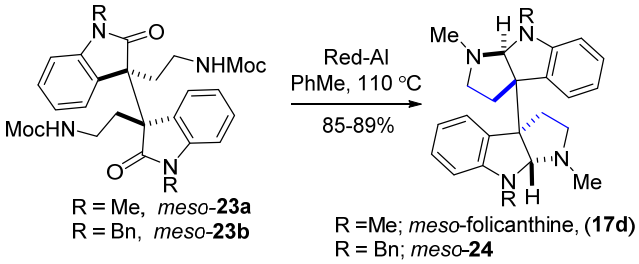
high vacuum pump. The crude product was purified by flash chromatography (in EtOAc/Hexane solvent system) as eluents to provide *meso*-**23a** and *meso*-**23b**.



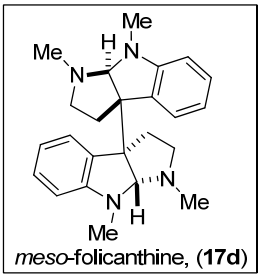
dimethyl ((-1,1'-dimethyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))dicarbamate (*meso*-**23a**): Compound (*meso*-**23a**) as yellow solid (2.15 mmol scale; 88% yield over 2 step); R_f = 0.39 (5% MeOH in CH_2Cl_2); **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.29-7.27 (m, 2H), 6.91 (br, s, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.59 (s, 1H), 3.57 (s, 3H), 2.94 (s, 3H), 2.86 (br,s, 1H), 2.78-2.73 (m, 1H), 2.66-2.63 (m, 1H), 2.45-2.41 (m, 1H); **^{13}C NMR** (175 MHz, $CDCl_3$) δ 176.1, 156.6, 144.2, 129.1, 127.3, 124.1, 122.1, 108.1, 55.6, 51.9, 37.2, 29.7, 25.9; **IR** (film) υ_{max} 2793, 1701, 1637, 1452, 1418, 1396, 1352, 1321, 1302, 1126, 1028, 962 cm^{-1}; **HRMS** (ESI) m/z 495.2229 $[M+H]^+$; calculated for $[C_{26}H_{30}N_4O_6 + H]^+$: 495.2238; **MP** 175-182 ºC.



dimethyl ((-1,1'-dibenzyl-2,2'-dioxo-[3,3'-biindoline]-3,3'-diyl)bis(ethane-2,1-diyl))dicarbamate (*meso*-**23b**): Compound (*meso*-**23b**) as colorless foam (2.15 mmol scale; 84% yield over 2 step); R_f = 0.34 (75% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.12 (m, 5H), 6.94 (br, s, 2H), 6.82 (br, s, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.85 (d, *J* = 15.7 Hz, 1H), 4.79-4.56 (m, 2H), 3.53 (s, 3H), 2.99-2.97 (m, 1H), 2.74-263 (m, 2H), 2.53-2.46 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 156.7, 143.6, 135.5, 129.1, 128.7, 127.7, 127.3, 127.1, 124.4, 122.6, 109.5, 55.2, 51.9, 44.1, 37.1, 29.7; **IR** (film) υ_{max} 2920, 1636, 1610, 1537, 1362, 1261, 754 cm^{-1}; **HRMS** (ESI) m/z 647.2877 $[M+H]^+$; calculated for $[C_{38}H_{38}N_4O_6 + H]^+$: 647.2864; **MP** 159-161 ºC.

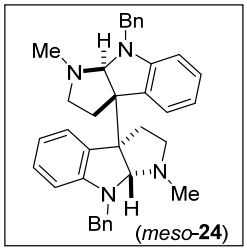


Procedure for the synthesis of compound (*meso*-**17d** and *meso*-**24**): To a stirred solution of *meso*-**23** (0.30 mmol, 1.0 equiv) in dry toluene under argon atmosphere at 25 ºC. To that solution Red-Al (2.4 mL, 6.0 mmol, 20.0 equiv) was added drop wise and stirred it for 15 minutes. Then the reaction mixture was placed over a preheated oil-bath maintaining temperature at 110 ˚C and continued for 24 h. Upon completion of the reaction (judged by TLC analysis) the reaction mixture was kept in ice-bath and quenched with MeOH (5 mL) and a saturated aqueous solution of Rochelle's salt (10 mL). The resulting mixture was extracted with EtOAc (2 X 50 mL) and the combined organic extracts were rinsed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography (in MeOH/CH_2Cl_2 solvent system) as eluents to provide *meso*-**17d** and *meso*-**24**.



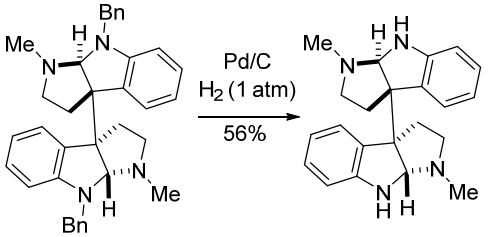
(3a,3'a,8a,8'a)-1,1',8,8'-tetramethyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole (*meso*-17d): The compound **(*meso*-17d)** was isolated as colorless solid (Reaction scale: 0.303 mmol; 89% yield); R_f = 0.58 (0.4 ml CH_3OH, 0.1 ml NH_4OH in 9.5 ml $CHCl_3$); **^{1}H NMR** (500 MHz, DMSO-d_6, 100 ˚C) δ 7.00 (t, J = 8.2 Hz, 2H), 6.45-6.43 (m, 3H), 6.37 (d, J = 7.9 Hz, 3H), 4.09 (s, 2H), 2.76-2.73 (m, 2H), 2.60 (s, 6H), 2.41-2.39 (m, 7H), 2.37 (d, J = 6.1 Hz, 1H), 2.35-2.31 (m, 2H), 1.93-1.90 (m, 2H); **^{13}C**

NMR (125 MHz, DMSO-d_6, 100 °C) δ 154.7, 133.6, 128.4, 124.0, 117.1, 107.2, 91.8, 63.3, 52.6, 36.6, 36.0, 36.5; **IR** (film) υ_{max} 2503, 2000, 1942, 1869, 1767, 1555, 1531, 1492, 1427, 1323, 1250, 1159, 1119, 929 cm^{-1}; **HRMS** (ESI) m/z 375.2570 $[M+H]^+$; calculated for $[C_{24}H_{30}N_4 + H]^+$: 375.2543; **MP** 293-296 ºC.



(*meso*-**24**)

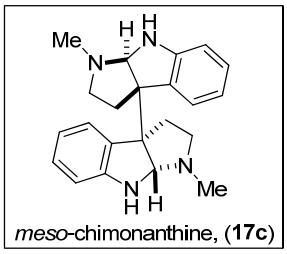
8,8'-dibenzyl-1,1'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole (*meso*-**24**): [4] The compound was obtained as brown gel (Reaction scale: 0.30 mmol; 85% yield); R_f = 0.60 (10% CH_3OH in CH_2Cl_2); **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.40-7.26 (br, s, 9H), 7.06 (br, s, 3H), 6.96 (br, s, 1H), 6.80 (br, s, 1H), 6.45 (br, s, 1H), 6.37 (br, s, 1H), 6.21 (br, s, 1H), 5.69 (br, s, 1H), 4.84 (br, s, 2H), 4.60 (br, s, 1H), 4.46 (br, s, 1H), 3.87 (br, s, 2H), 3.78 (br, s, 1H), 3.62 (br, s, 1H), 2.86 (br, s, 1H), 2.73 (br, s, 1H), 2.62 (br, s, 3H), 2.49 (br, s, 3H), 2.11 (br, s, 4H); **^{13}C NMR** (175 MHz, $CDCl_3$) δ 154.2, 152.8, 139.3, 133.7, 132.6, 128.4, 127.7, 127.2, 126.9, 126.5, 124.7, 123.7, 117.8, 117.4, 107.9, 106.8, 91.9, 90.4, 63.5, 63.1, 53.9, 53.1, 52.7, 37.9, 37.3, 35.5; **IR** (film) υ_{max} 2793, 1923, 1884, 1638, 1601, 1452, 1418, 1321, 1302, 1198, 1126, 1099, 1080, 962 cm^{-1}; **HRMS** (ESI) m/z 527.3193 $[M+H]^+$; calculated for $[C_{36}H_{38}N_4 + H]^+$: 527.3169



meso-**24** *meso*-chimonanthine, (**17c**)

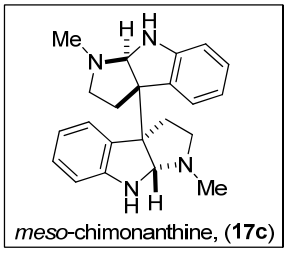
Procedure for the synthesis of compound (*meso*-**17c**): To a stirred solution of compound *meso*-(**24)** (20 mg, 0.038 mmol, 1.0 equiv) in EtOH (5 mL) was purged with nitrogen gas for 20 minutes at 25 ºC. To that solution, Pd/C (20 mg, 100% w/w) was added under

nitrogen atmosphere. The reaction mixture was then purged with H_2(g) balloon for 20 minutes and then stirring was continued under H_2 gas atmosphere for 36 h at 25 °C. Upon completation the reaction (judged by TLC analysis), reaction mixture was filtered through celite, concentrated under reduced pressure. The crude product was then purified by flash column chromatography using (9:1:1 to 9:1:2 $CHCl_3$-MeOH-NH_4OH) as eluent to afford the desired product (*meso*-**17c**).



meso-chimonanthine, (**17c**)

1,1'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole (*meso*-17c): The product **(*meso*-17c)** was isolated as colorless solid (reaction scale: 0.03 mmol; 56% yield); R_f = 0.29 (0.9 ml CH_3OH, 0.1 ml NH_4OH in 9 ml $CHCl_3$)[5]; **^{1}H NMR** (500 MHz, DMSO-d_6, 100 °C) δ 6.87 (t, *J* = 7.7 Hz, 2H), 6.55 (br, s, 2H), 6.39-6.35 (m, 4H), 5.49 (br, s, 2H), 4.58 (s, 2H), 2.71-2.68 (m, 2H), 2.48-2.43 (m, 2H), 2.36-2.33 (m, 2H), 2.31 (s, 6H), 1.91-1.88 (m, 2H); **^{13}C NMR** (125 MHz, DMSO-d_6, 100 °C) δ 153.0, 133.5, 127.8, 124.3, 116.7, 107.8, 83.6, 63.7, 52.2, 37.2, 35.9; **IR** (film) υ_{max} 1603, 1485, 1452, 1408, 1346, 1317, 1246, 1157, 1124, 744 cm^{-1}; **HRMS** (ESI) m/z 347.2210 $[M+H]^+$; calculated for $[C_{22}H_{26}N_4 + H]^+$: 347.2230; **MP** 210-215 ºC.



meso-chimonanthine, (**17c**)

Comparison of NMR Data of *meso*-Chimonanthine with literature of synthesis of *meso*-Chimonanthine by Willis:

Comparison of ^{1}H-NMR Data:

Willis's Report[5] *meso*-Chimonanthine (^{1}H-NMR, 500 MHz, DMSO-d_6,120 ºC)

δ (ppm)	**int.**	**mult.**	***J* (Hz)**
6.87	2H	dd	7.5, 7.6
6.55	2H	br-s	-
6.40-6.34	2H	m	-
6.40-6.33	2H	m	-
5.49	2H	br-s	-
4.58	2H	s	-
2.74-2.64	2H	m	-
2.52-2.43	2H	m	-
2.37-2.29	2H	m	-
2.28	6H	s	-
1.92-1.86	2H	m	-

This Work *meso*-Chimonanthine (^{1}H-NMR, 500 MHz, DMSO-d_6, 100 ºC)

δ (ppm)	**int.**	**mult.**	***J* (Hz)**
6.87	2H	t	7.7
6.55	2H	br-s	-
6.39-6.35	4H	m	-
5.49	2H	br-s	-
4.58	2H	s	-
2.71-2.68	2H	m	-
2.48-2.43	2H	m	-
2.36-2.33	2H	m	-
2.31	6H	s	-
1.91-1.88	2H	m	-

Comparison of ^{13}C-NMR Data:

Willis's Report[5] *meso*-Chimonanthine (^{13}C-NMR, 500 MHz, DMSO-d_6,120 ºC)

153.1
133.5
127.8
124.3
116.7
107.8

This Work *meso*-Chimonanthine (^{13}C-NMR, 500 MHz, DMSO-d_6, 100 ºC)

153.0
133.5
127.8
124.3
116.7
107.8

83.6
63.7
52.2
35.9
22.6

83.6
63.7
52.2
37.2
35.9

Comparison of NMR Data of *meso*-Chimonanthine with literature of synthesis of *meso*-Chimonanthine by Movassaghi:

Comparison of ^{1}H-NMR Data:

Movassaghi's Report[6]
meso-Chimonanthine (^{1}H-NMR, 500 MHz, DMSO-d_6,120 ºC)

δ (ppm)	**int.**	**mult.**	***J* (Hz)**
6.86	2H	App-t	7.7
6.54	2H	br-s	-
6.40-6.33	2H	m	-
6.40-6.33	2H	m	-
5.45	2H	br-s	-
4.58	2H	s	-
2.69	2H	ddd	1.8, 6.8, 8.8
2.48-2.43	2H	m	-
2.35-2.31	2H	m	-
2.30	6H	s	-

This Work
meso-Chimonanthine (^{1}H-NMR, 500 MHz, DMSO-d_6, 100 ºC)

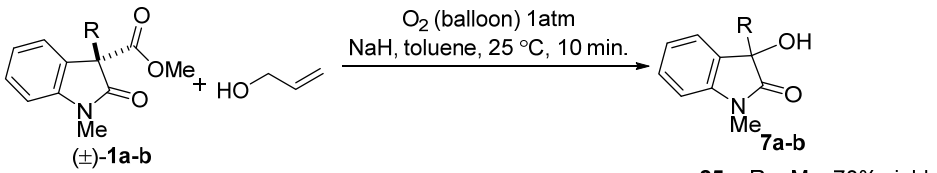
δ (ppm)	**int.**	**mult.**	***J* (Hz)**
6.87	2H	t	7.7
6.55	2H	br-s	-
6.39-6.35	4H	m	-
5.49	2H	br-s	-
4.58	2H	s	-
2.71-2.68	2H	m	-
2.48-2.43	2H	m	-
2.36-2.33	2H	m	-
2.31	6H	s	-

1.88	2H	ddd	1.8, 5.5, 11.6

1.91-1.88	2H	m	-

Comparison of ^{13}C-NMR Data:

Movassaghi's Report[6] *meso*-Chimonanthine (^{13}C-NMR, 500 MHz, DMSO-d_6,120 ºC)	**This Work** *meso*-Chimonanthine (^{13}C-NMR, 500 MHz, DMSO-d_6, 100 ºC)
151.9	153.0
132.3	133.5
126.7	127.8
123.1	124.3
115.4	116.7
106.7	107.8
82.5	83.6
62.6	63.7
51.1	52.2
36.1	37.2
34.8	35.9



25a; R = Me; 70% yield
25b; R = Bn; 68% yield

Procedure for the synthesis of compound ((±)-**25**): In a flame-dried seal tube dry toluene was taken, to it allyl alcohol (1.5 mmol) was added and purged with oxygen for 10 minutes on room temperature. To this NaH (60%, 3.0 mmol) was added at once, followed

by 2-Oxindole (1.0 mmol) under O_2(balloon) 1atm, stirred the above reaction mixture for 10 min., on completion (judge by TLC analysis), reaction mixture was quenched by adding few drops of water and extracted with EtOAc twice. Dried above organic extract over $MgSO_4$ and concentrated under vacuo. The crude product was purified by flash chromatography on silica gel using (30-40% EtOAc in Hexane) as eluent to afford the desired product (±)-**25a-b**.

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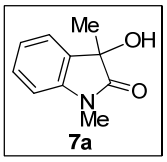
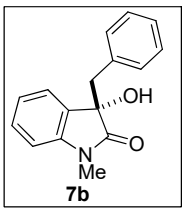


7a

(±)-3-hydroxy-1,3-dimethylindolin-2-one (25a): Compound **(25a)** was isolated as colorless solid R_f = 0.26 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 1H), 7.29 (td, *J* = 7.8, 1.2 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.32 (br, s, 1H), 3.17 (s, 3H), 1.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 142.7, 131.6, 129.5, 123.4, 123.3, 108.5, 73.7, 26.2, 24.8; **IR** (film) υ_{max} 2957, 1778, 1574, 1494, 1463, 1454, 1434, 1402, 1372, 1294, 1246, 1194, 1148, 1118, 1085, 1049 cm^{-1}; **HRMS** (ESI) m/z 200.0690 $[M+Na]^+$; calculated for $[C_{10}H_{11}NO_2 + Na]^+$: 200.0682; **MP** 120-122 ºC.



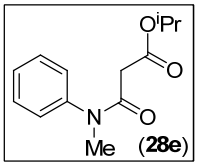
7b

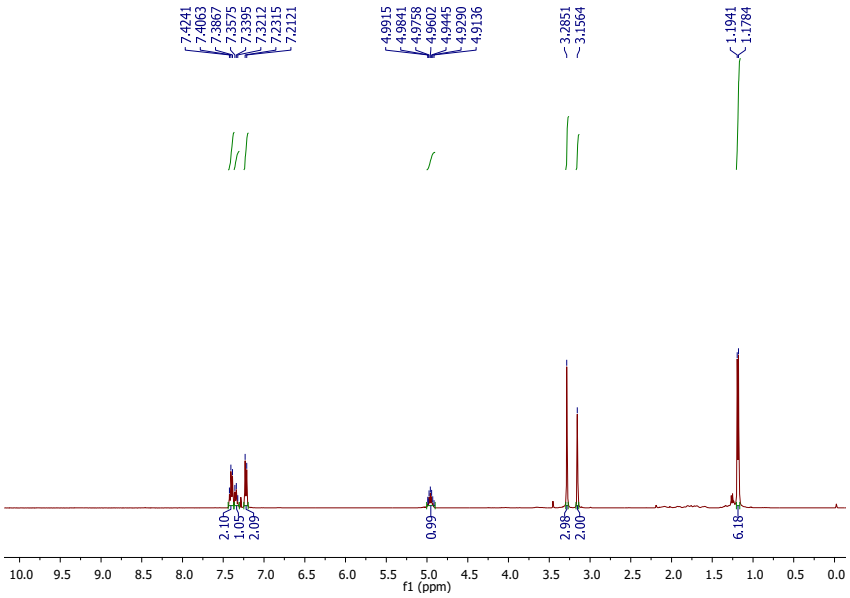
(±)-3,3'-dibenzyl-1,1'-dimethyl-[3,3'-biindoline]-2,2'-dione (25b): Compound **25b** was isolated as yellow solid; R_f = 0.31 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (td, *J* = 7.9, 1.4 Hz, 1H), 7.17 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.12-7.07 (m, 3H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.94-6.91 (m, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 3.66 (br, s, 1H), 3.30 (d, *J* = 12.7 Hz, 1H), 3.14 (d, *J* = 12.9 Hz, 1H), 2.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.0, 143.1, 134.0, 130.2, 129.6, 127.7, 126.8, 124.5, 122.9, 108.2, 44.9, 25.9; **IR** (film) υ_{max} 1697, 1636, 1614, 1299, 1217, 1092, 781 cm^{-1}; **HRMS** (ESI) m/z 276.1002 $[M+Na]^+$; calculated for $[C_{16}H_{15}NO_2 + Na]^+$: 276.0995; **MP** 200-202 ºC.

References:

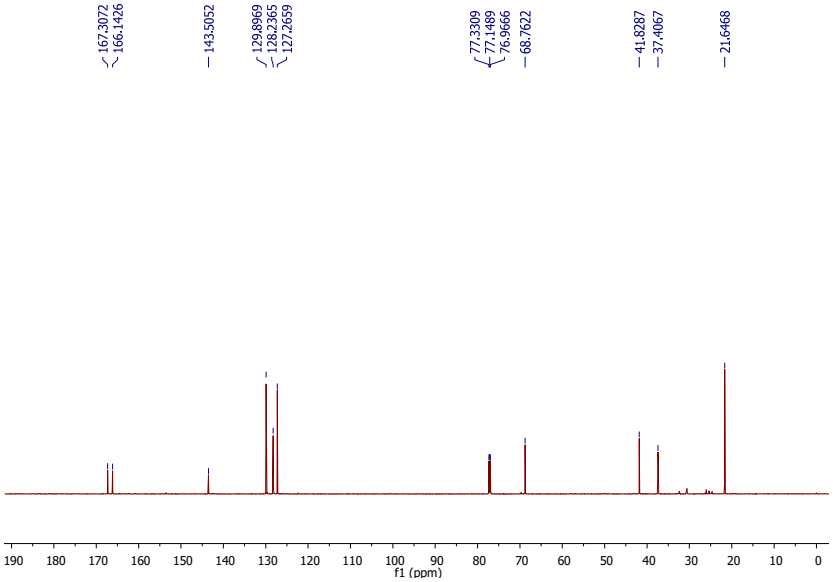
1. (a) N. Kumar, S. Ghosh, S. Bhunia, A. Bisai, *Beilstein J. Org. Chem.*, **2016**, *12*, 1153. (b) S. Ghosh, S. De, B. N. Kakde, S. Bhunia, A. Adhikary, A. Bisai, *Org. Lett.*, **2012**, *14*, 5864. (c) S. Bhunia, S. Ghosh, D. Dey, A. Bisai, *Org. Lett.*, **2013**, *15*, 2426.
2. S. Ghosh, S. Chaudhuri, A. Bisai, *Org. Lett.*, **2015**, *17*, 1373.
3. S. Ghosh, S. Bhunia, B. N. Kakde, S. De, A. Bisai, *Chem. Commun*., **2014**, *50*, 2434.
4. J. T. Link, L. E. Overman, *J. Am. Chem. Soc.*, **1996**, *118*, 8166.
5. R. H. Snell, R. L. Woodward, M. C. Willis, *Angew. Chem., Int. Ed.*, **2011**, *50*, 9116.
6. S. P. Lathrop, M. Movassaghi, *Chem. Sci*., **2014**, *5*, 333.

Spectral Graphics

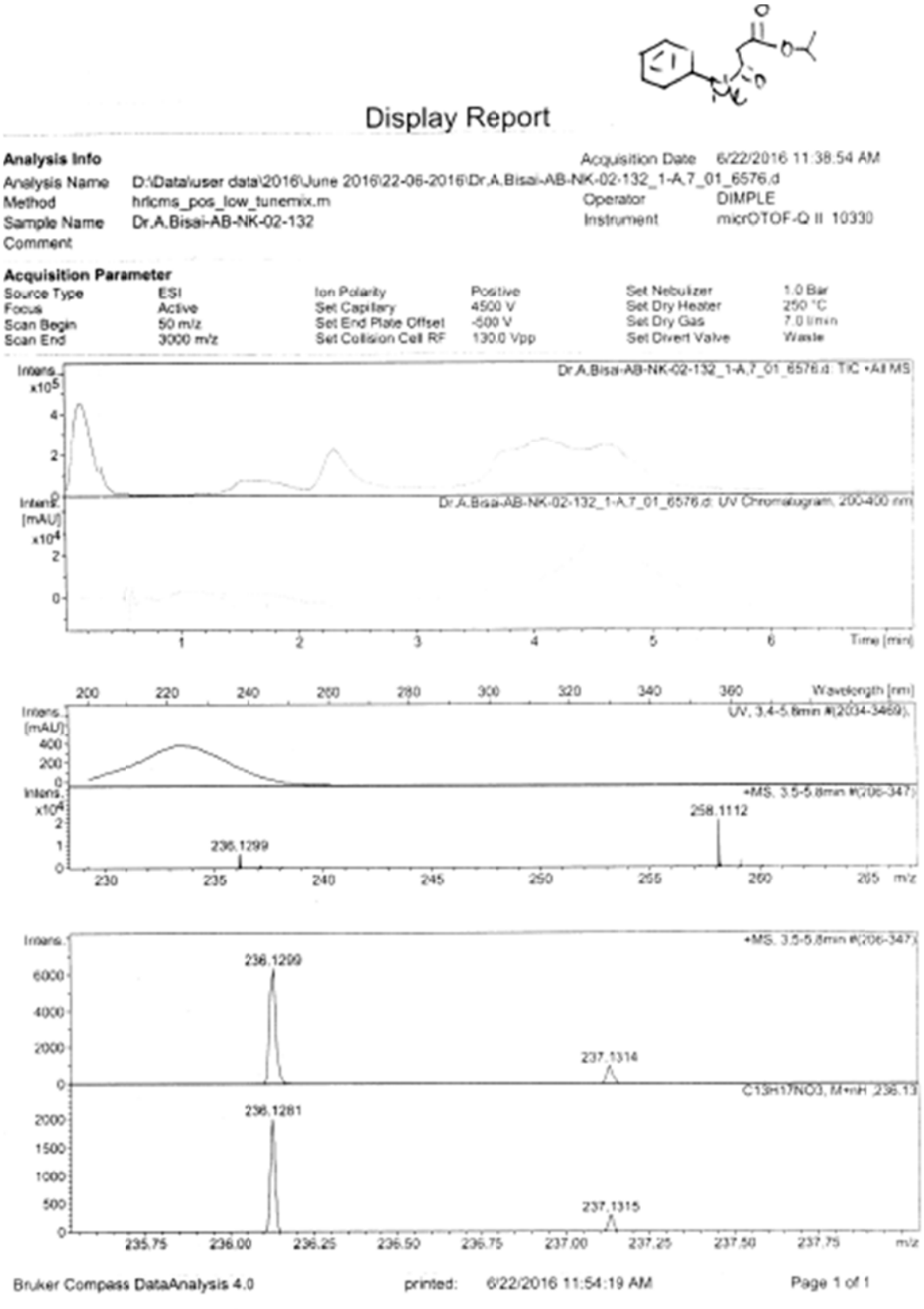




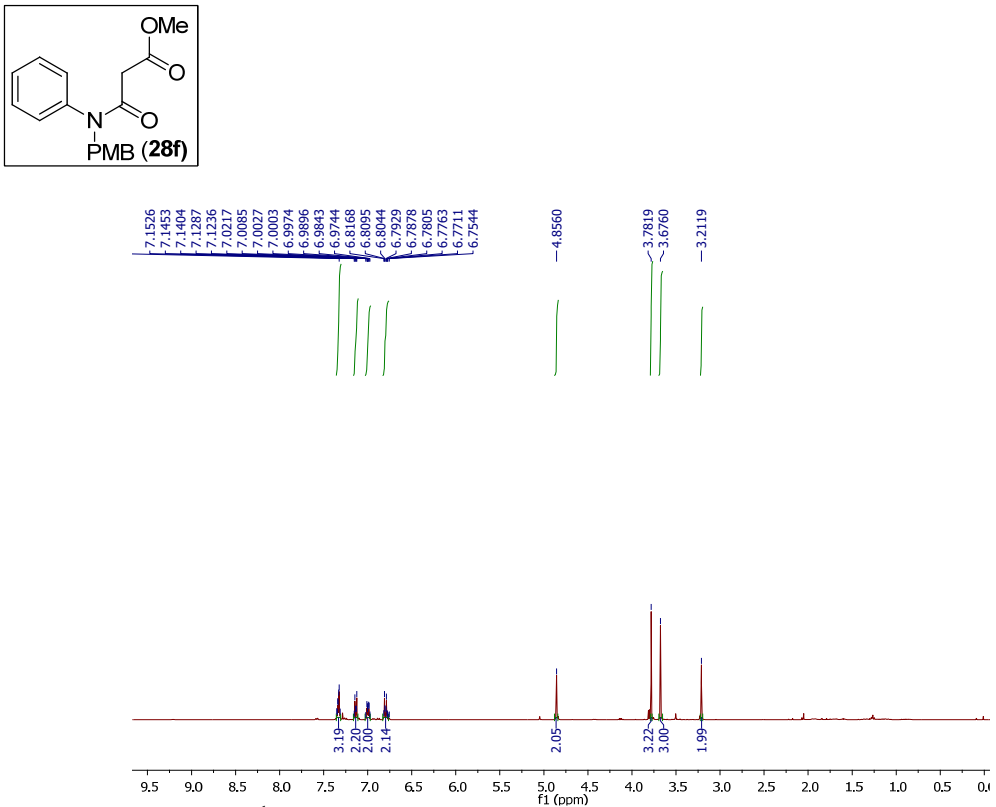
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**28e**)



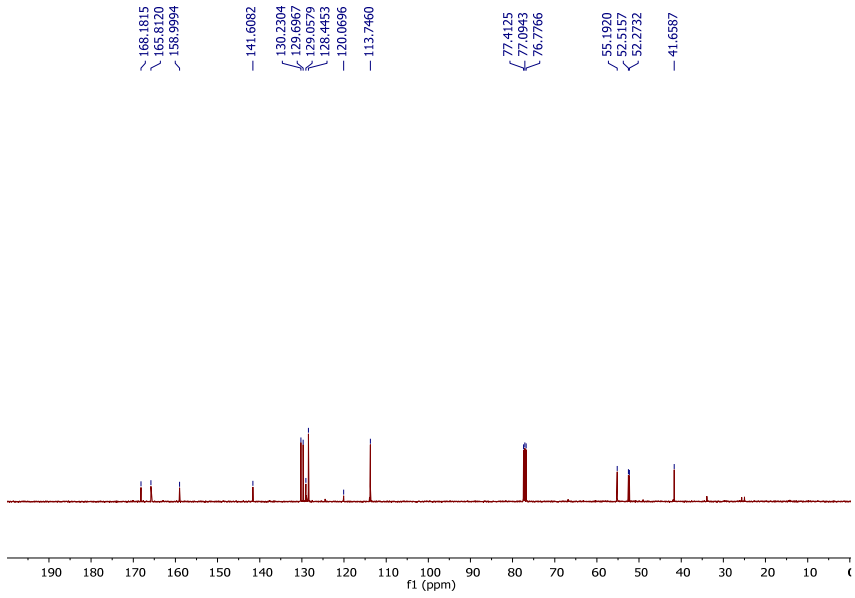
^{13}C NMR (175 MHz, $CDCl_3$) of compound (**28e**)



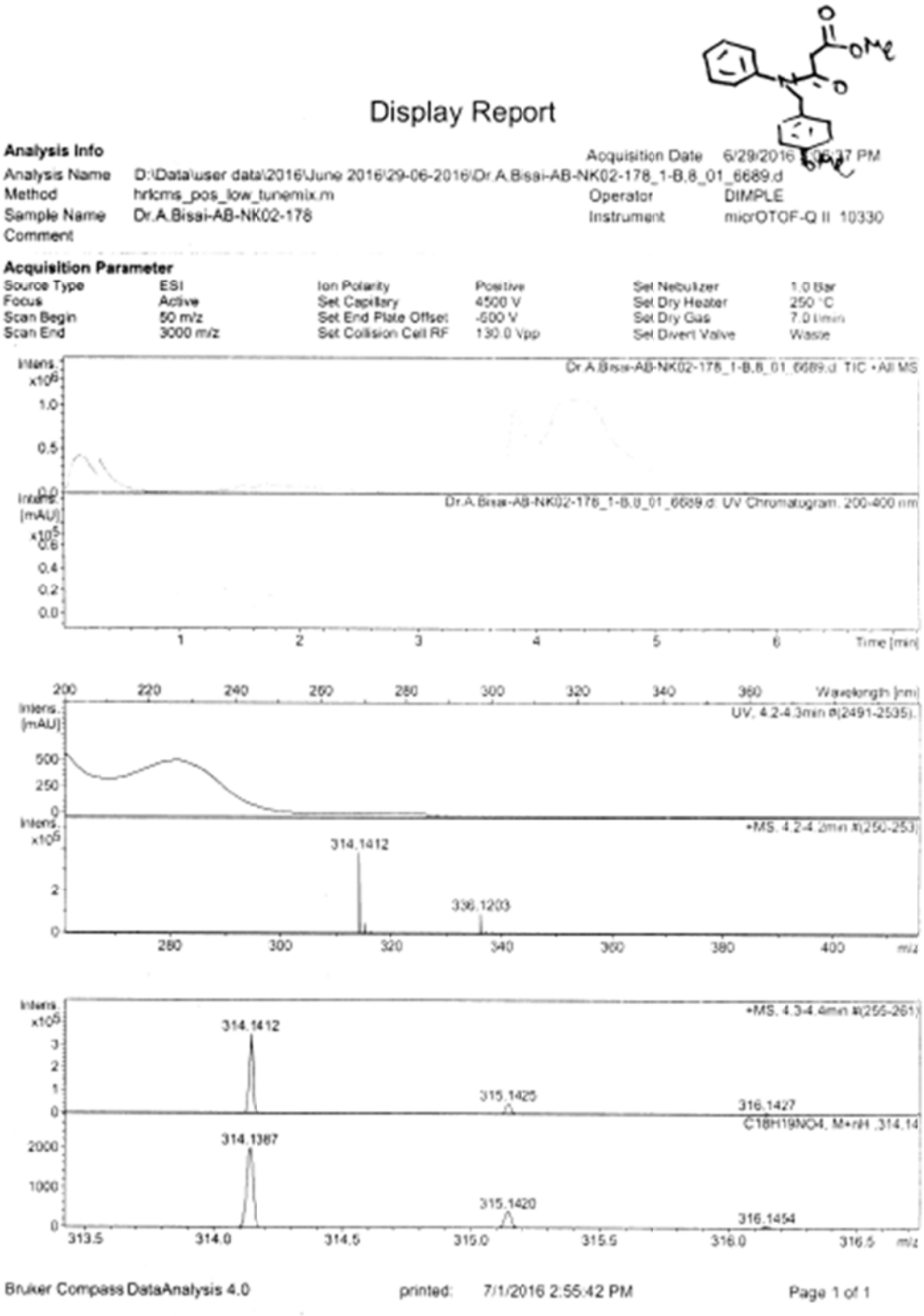
Scanned copy of mass spectrum (HRMS) of compound (**28e**)



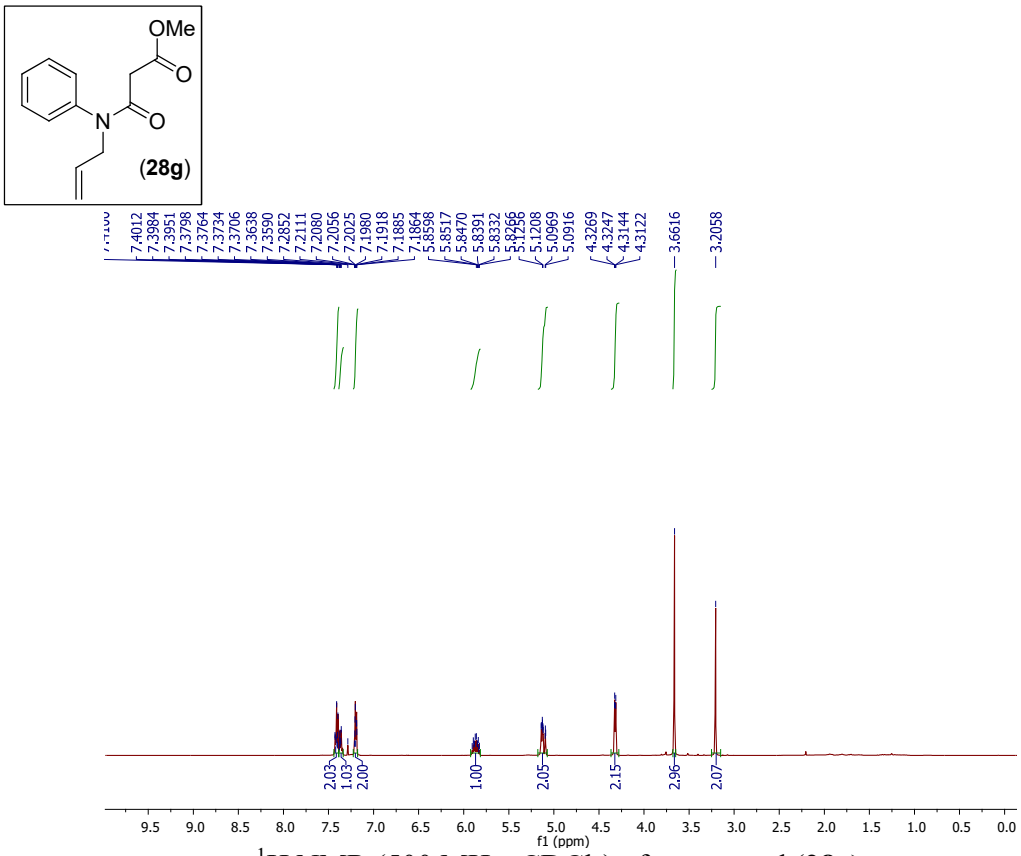
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**28f**)



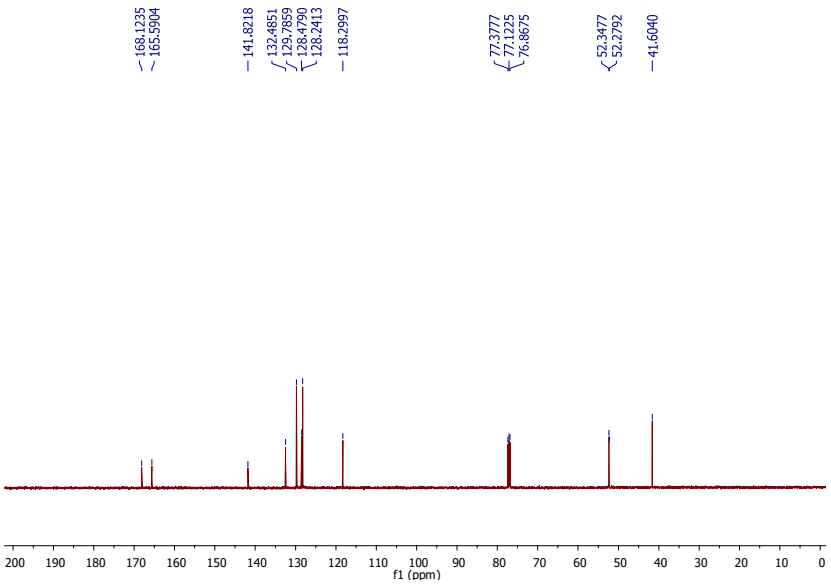
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**28f**)



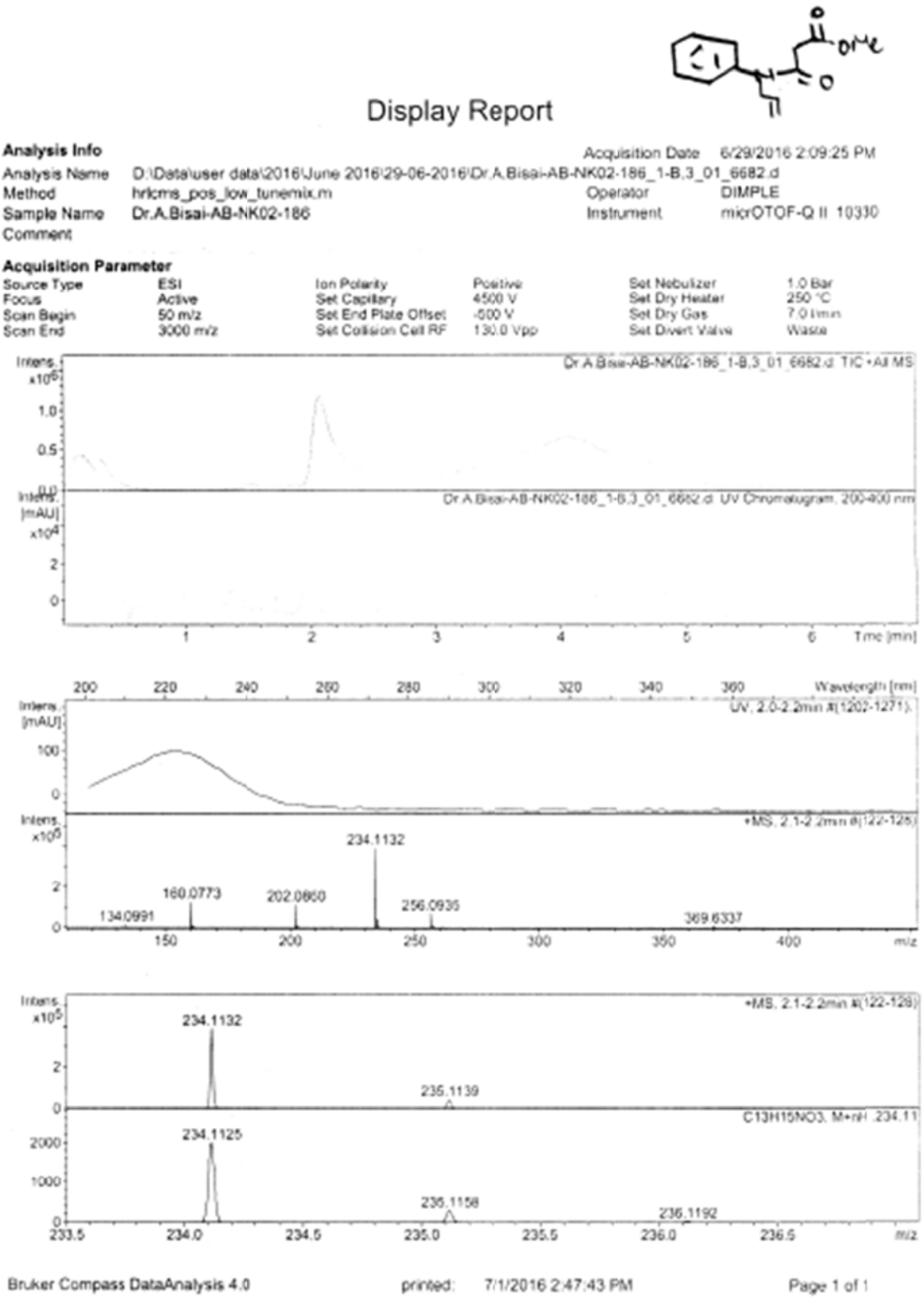
Scanned copy of mass spectrum (HRMS) of compound (**28f**)



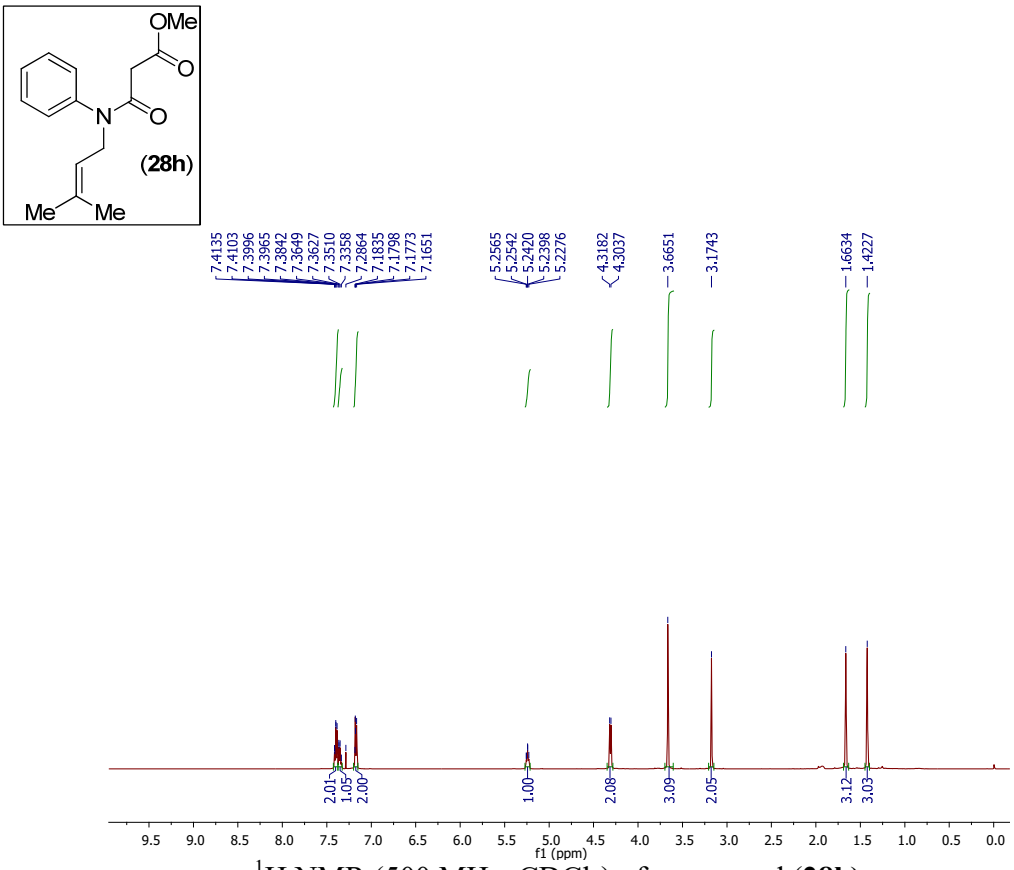
^{1}H NMR (500 MHz, $CDCl_3$) of compound (**28g**)



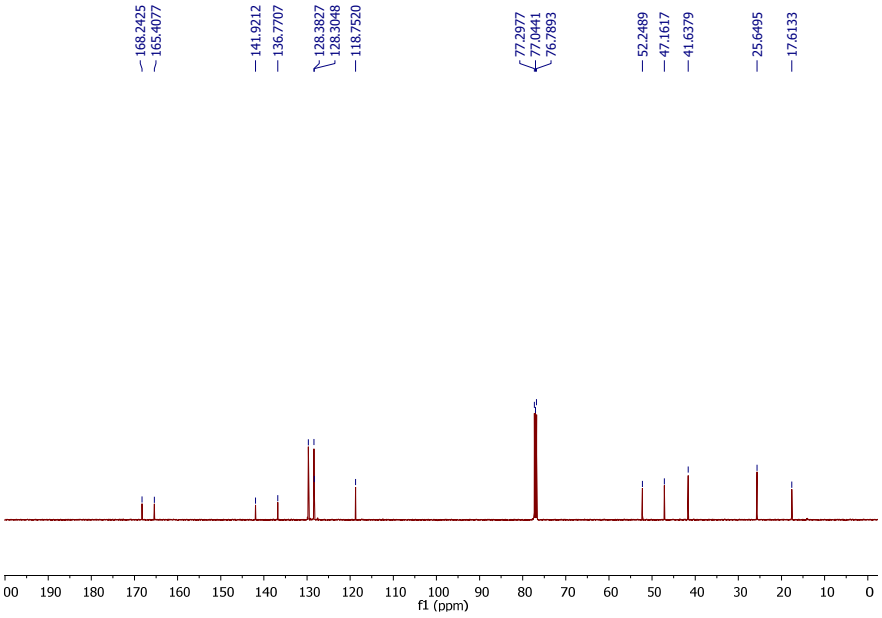
^{13}C NMR (125 MHz, $CDCl_3$) of compound (**28g**)



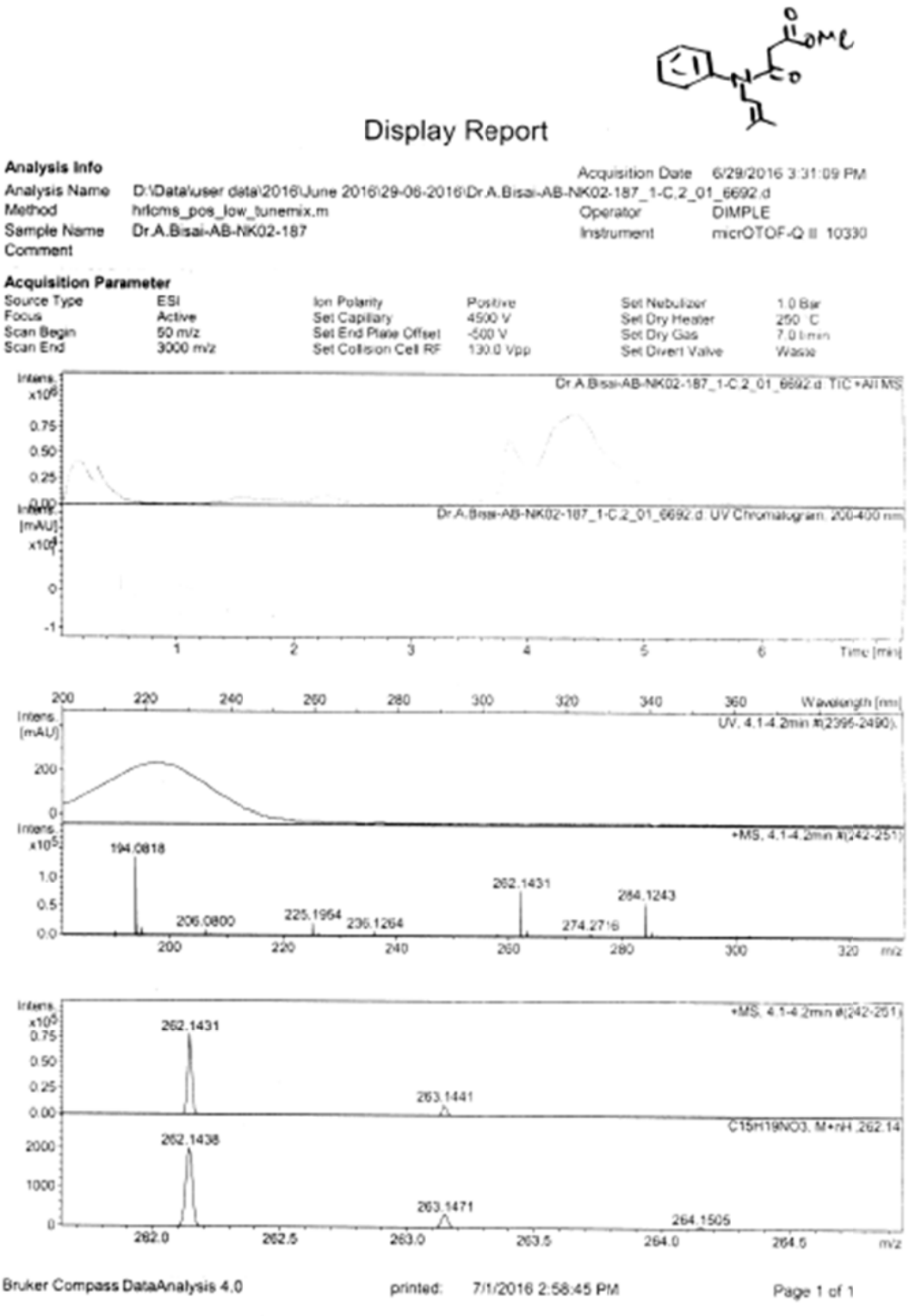
Scanned copy of mass spectrum (HRMS) of compound (**28g**)



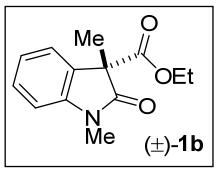
^{1}H NMR (500 MHz, $CDCl_3$) of compound (**28h)**

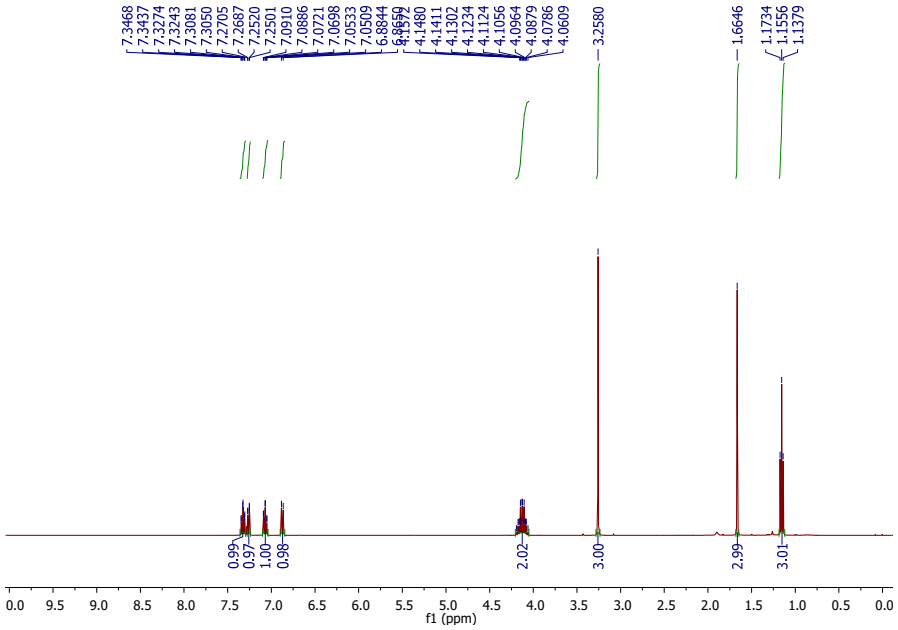


^{13}C NMR (125 MHz, $CDCl_3$) of compound (**28h)**

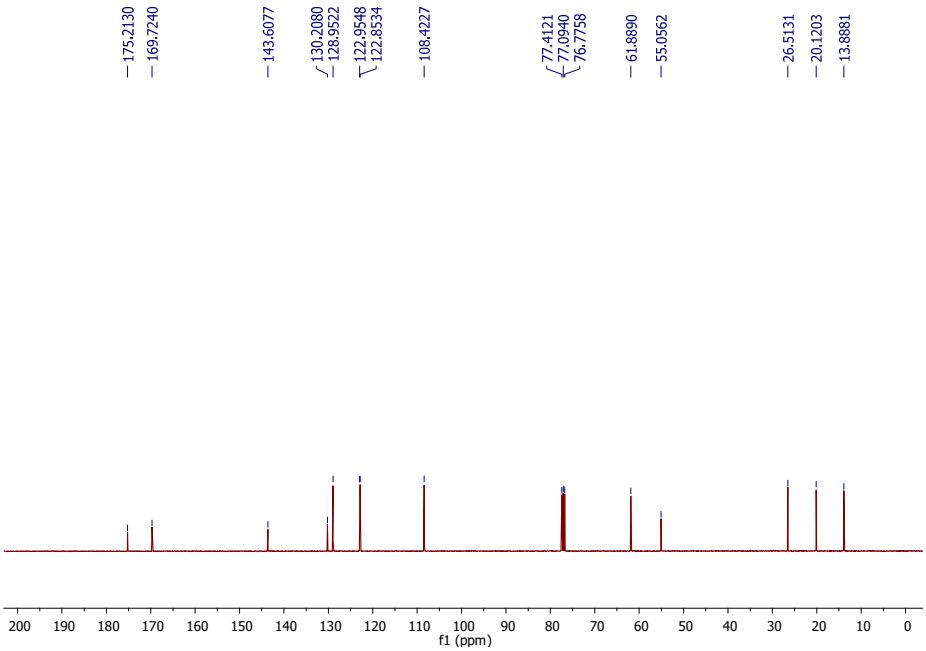


Scanned copy of mass spectrum (HRMS) of compound (**28h**)

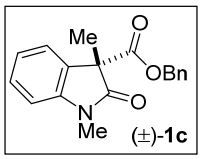


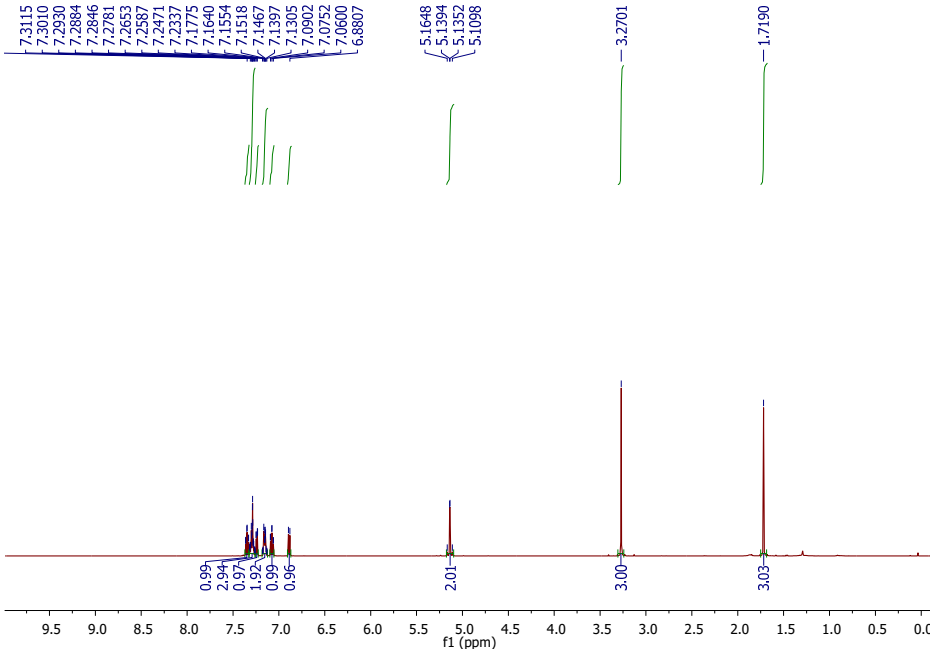


^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**1b**

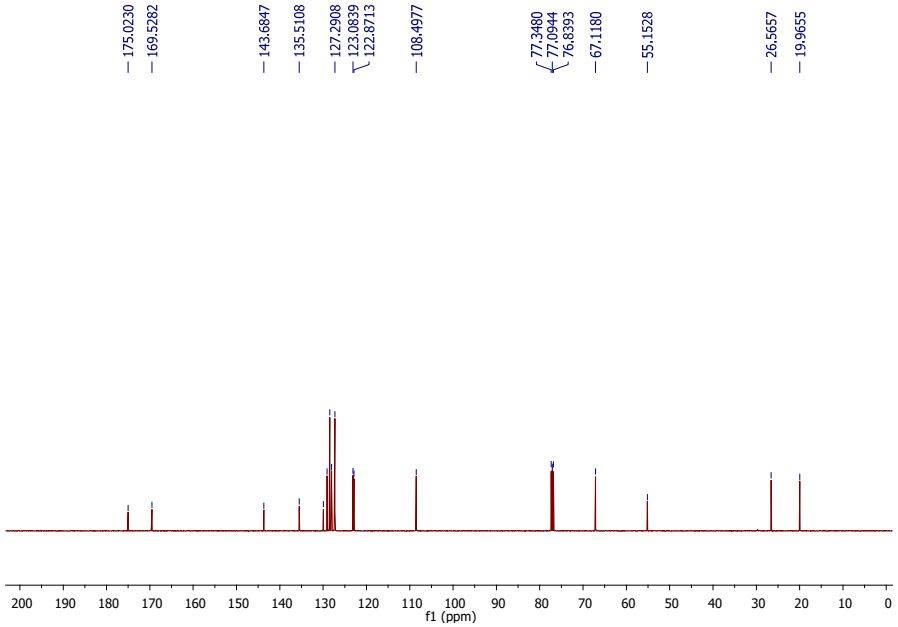


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**1b**

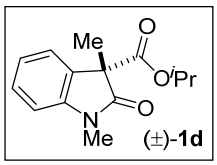


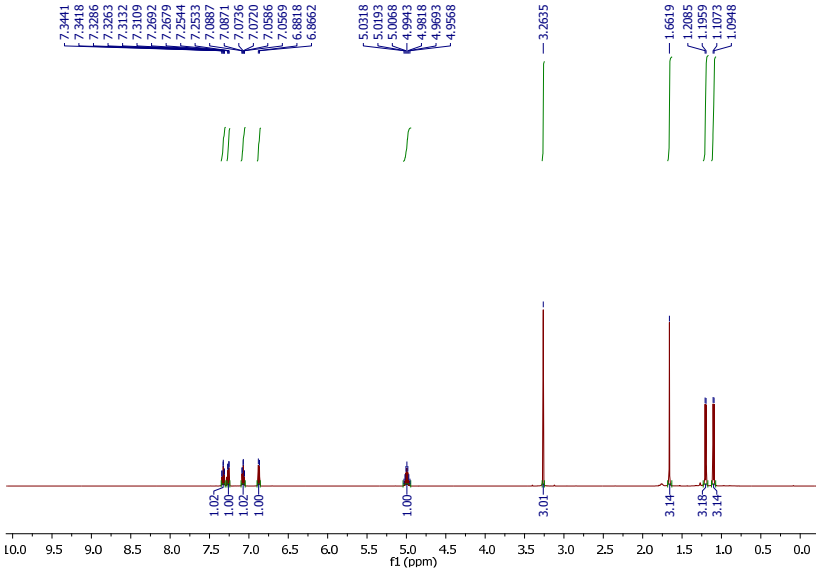


^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1c**

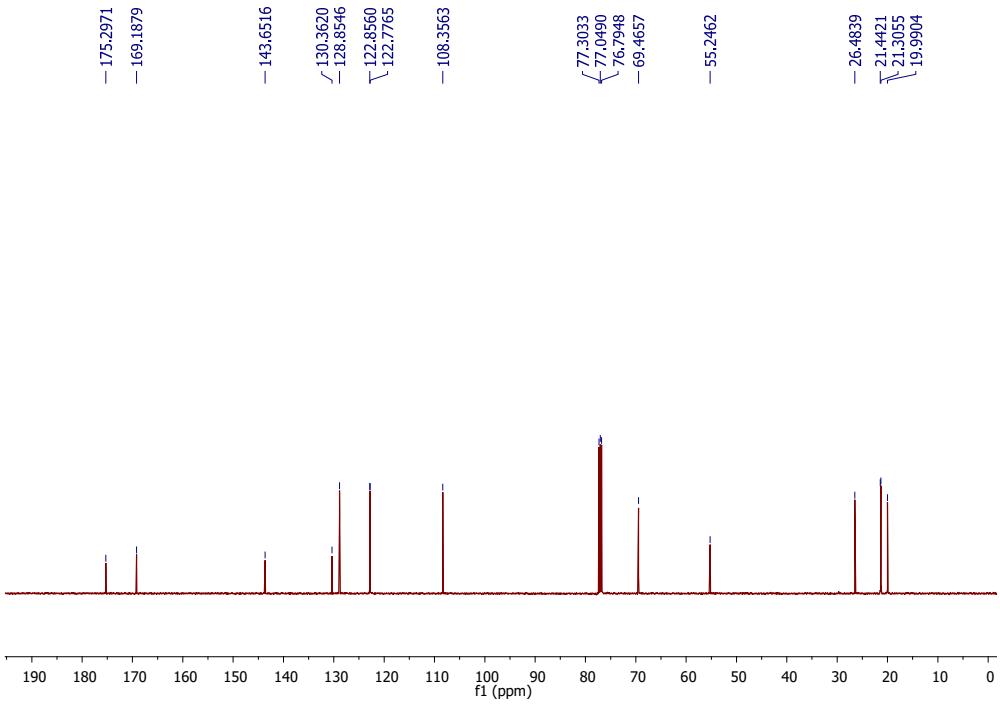


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1c**

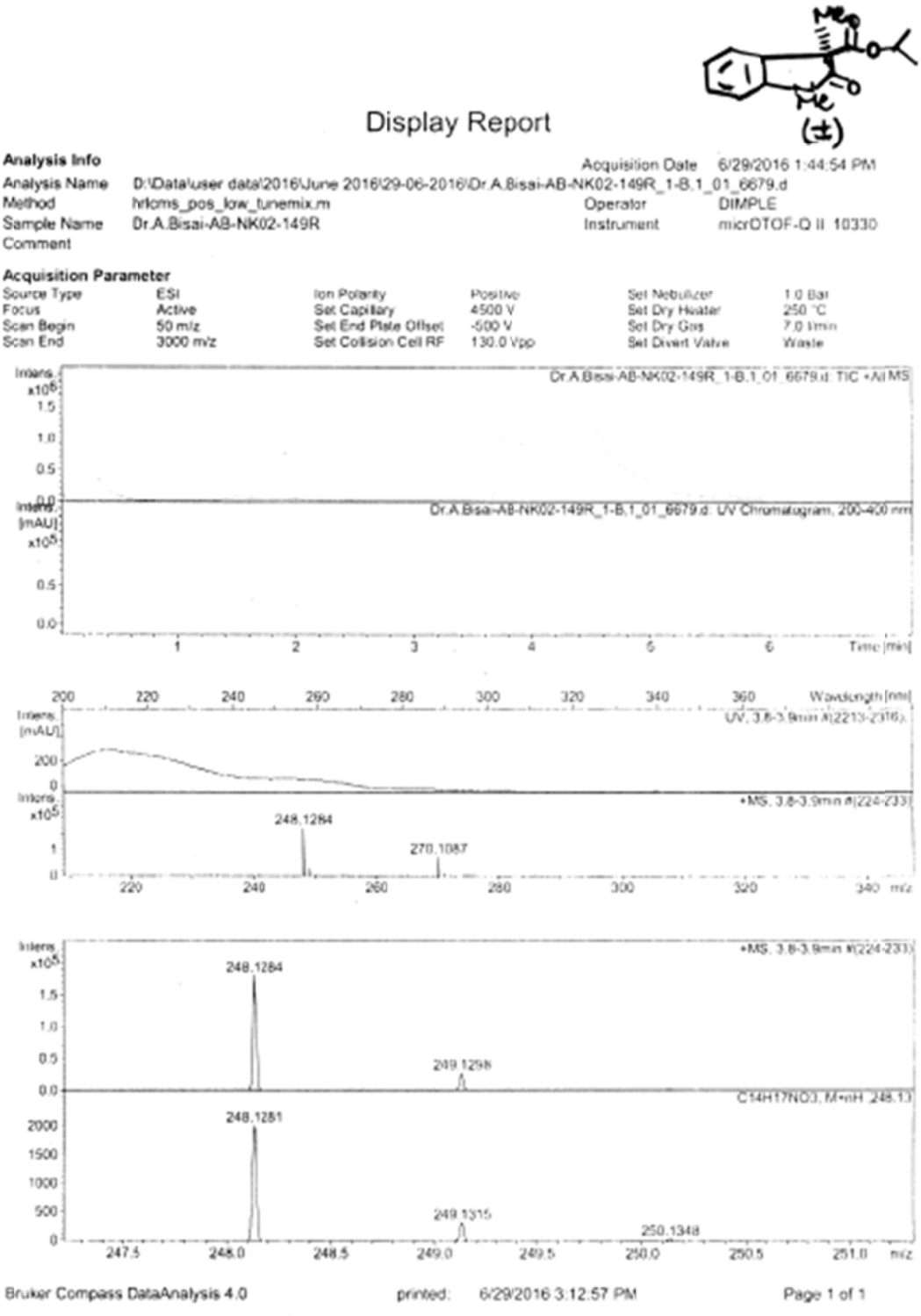




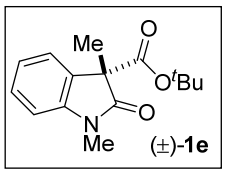
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1d**

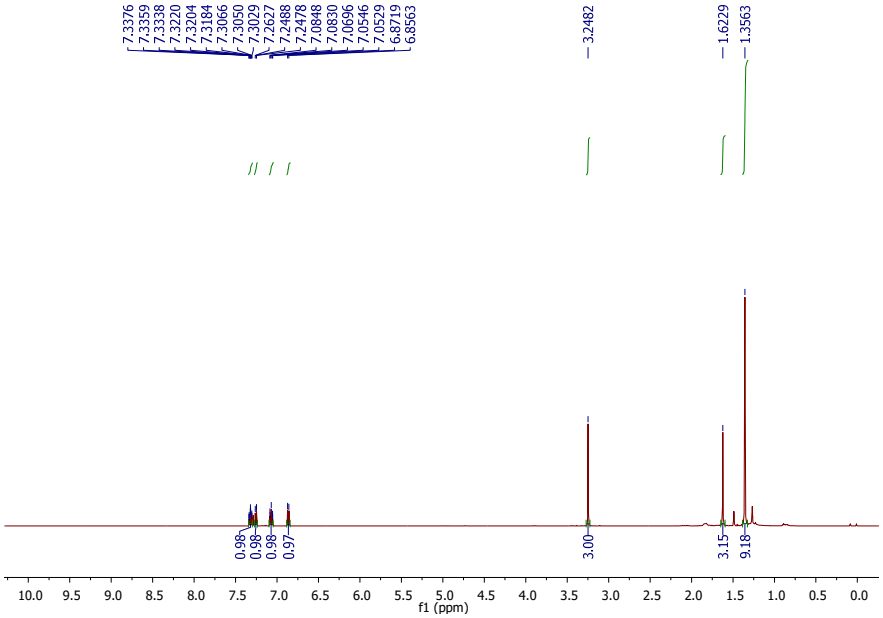


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1d**

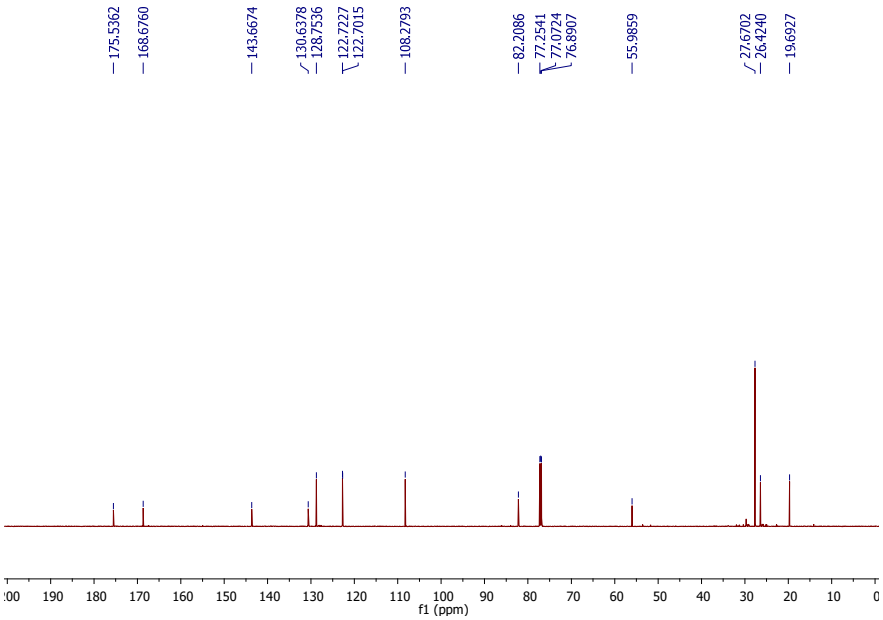


Scanned copy of mass spectrum (HRMS) of compound (±)-**1d**

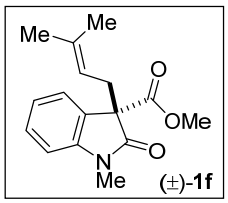


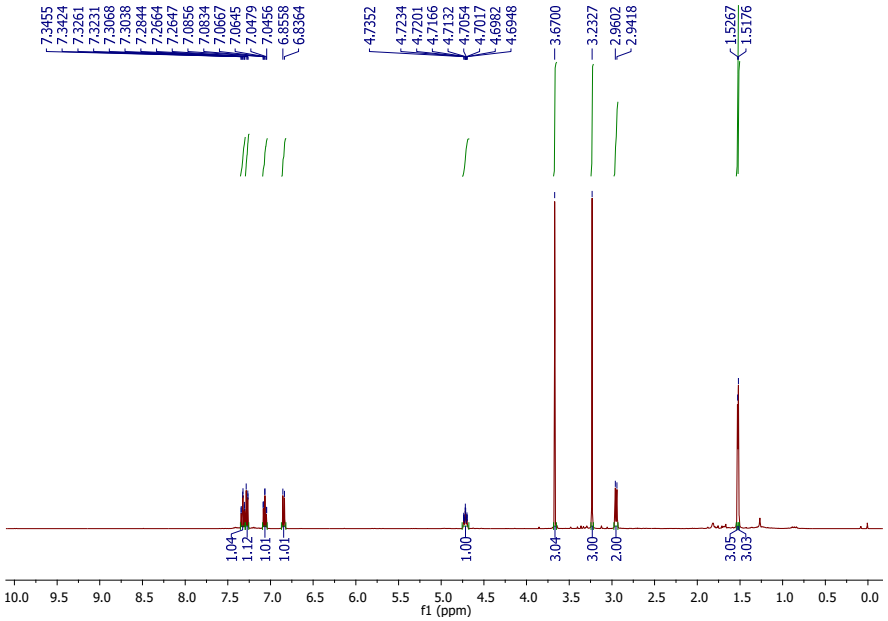


^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1e**

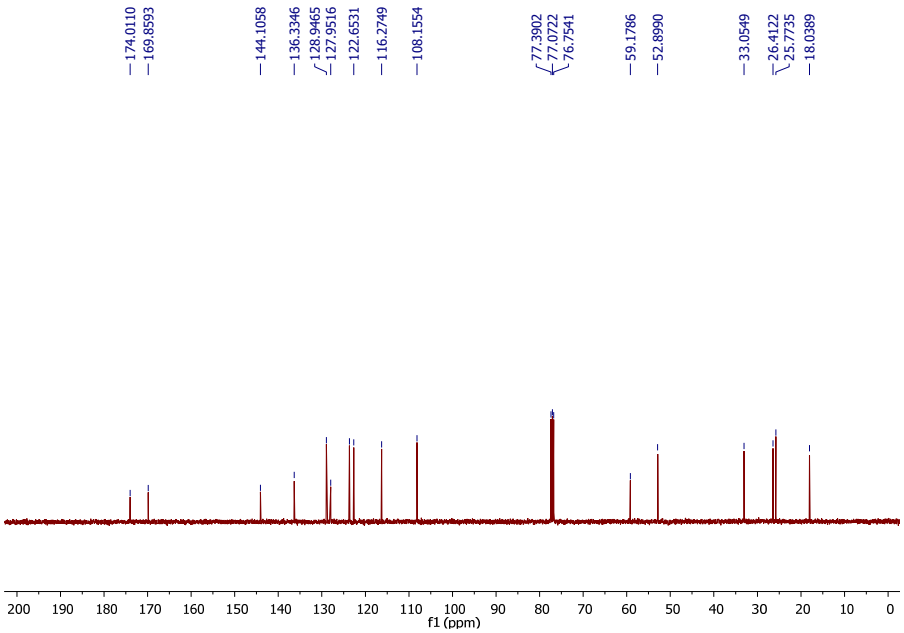


^{13}C NMR (175 MHz, $CDCl_3$) of compound (±)-**1e**

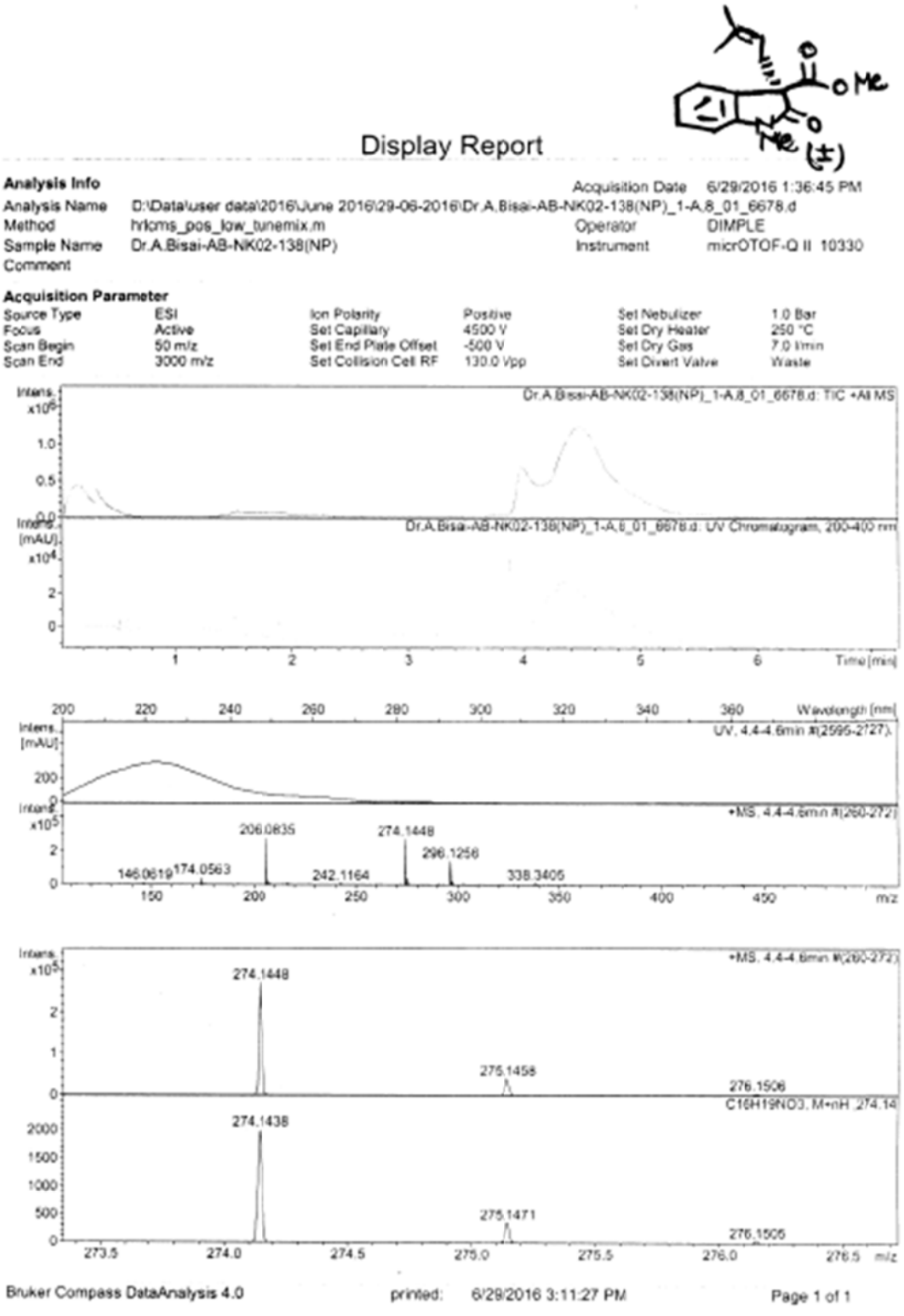




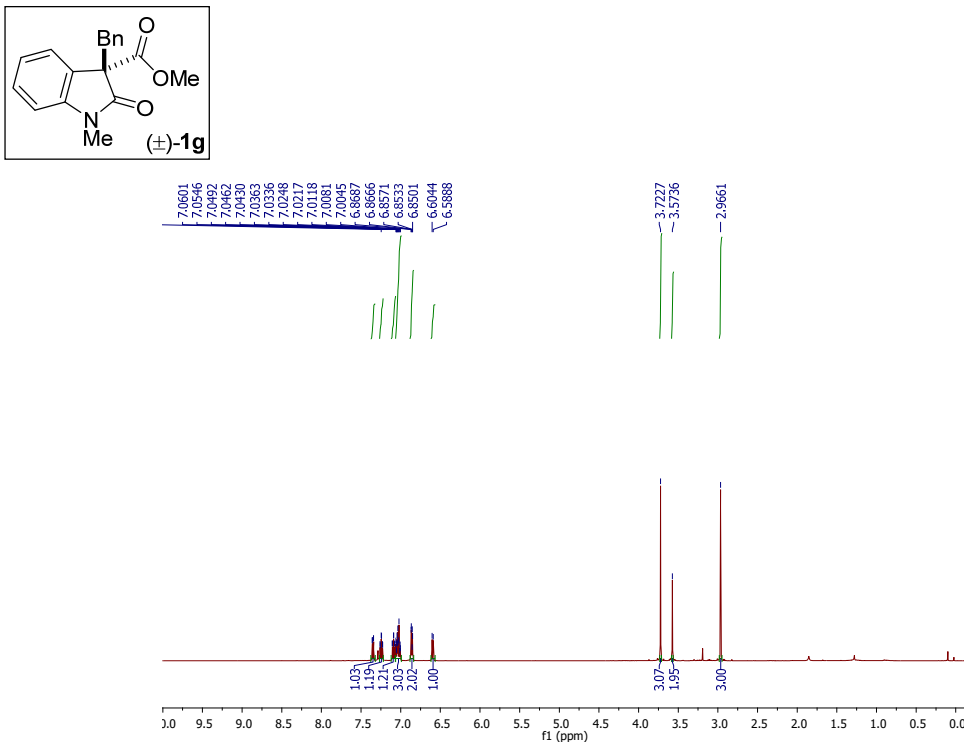
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**1f**



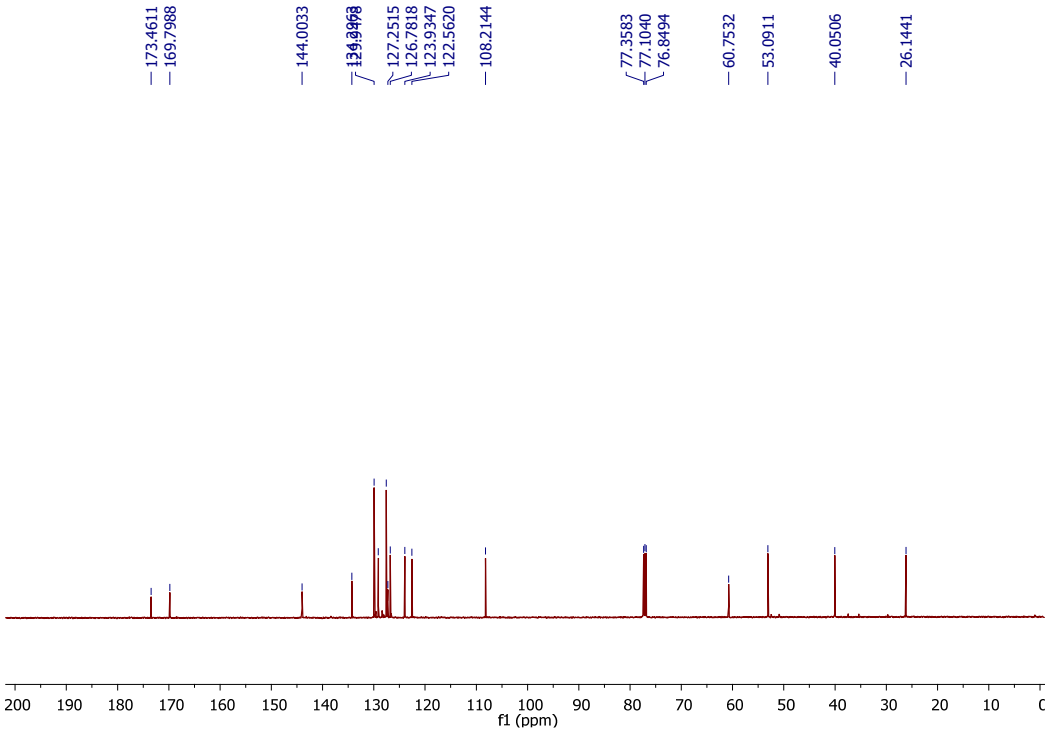
^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**1f**



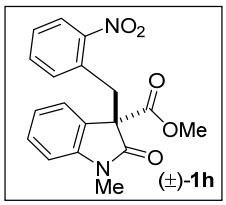
Scanned copy of mass spectrum (HRMS) of compound (±)-**1f**

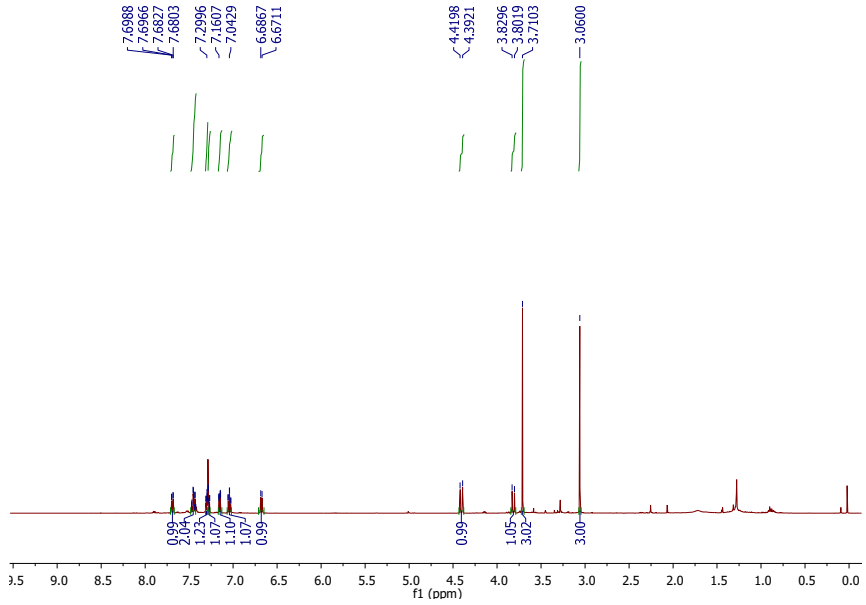


^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1g**

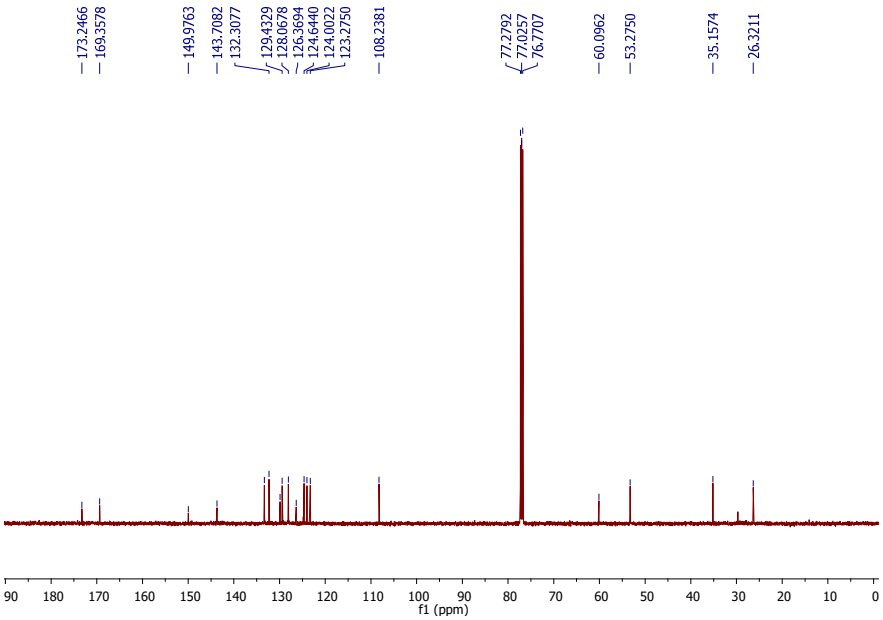


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1g**

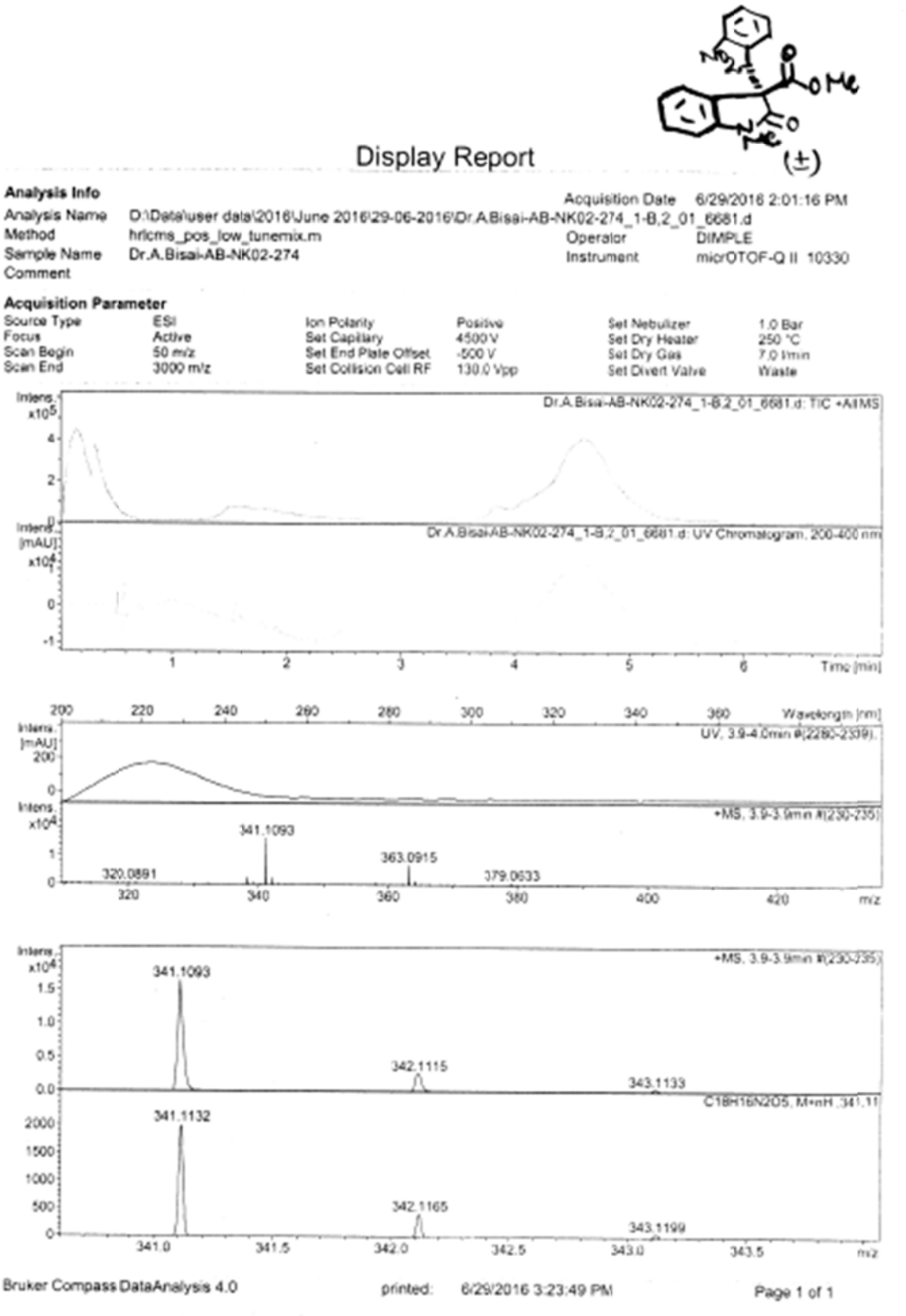




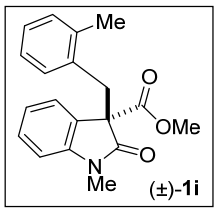
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1h**

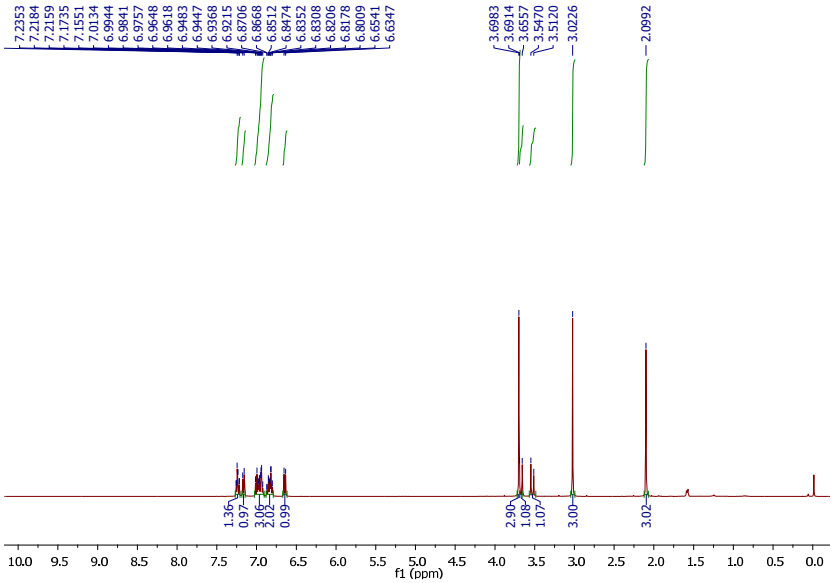


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1h**

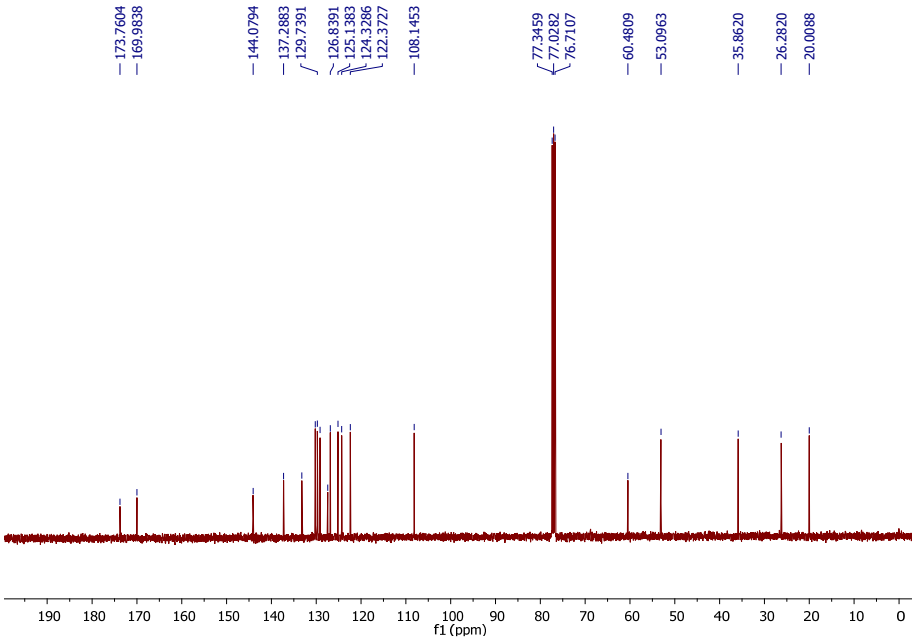


Scanned copy of mass spectrum (HRMS) of compound (±)-**1h**

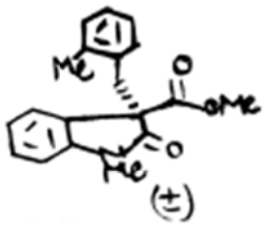




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**1i**



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



Display Report

Analysis Info

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Comment			

Acquisition Parameter

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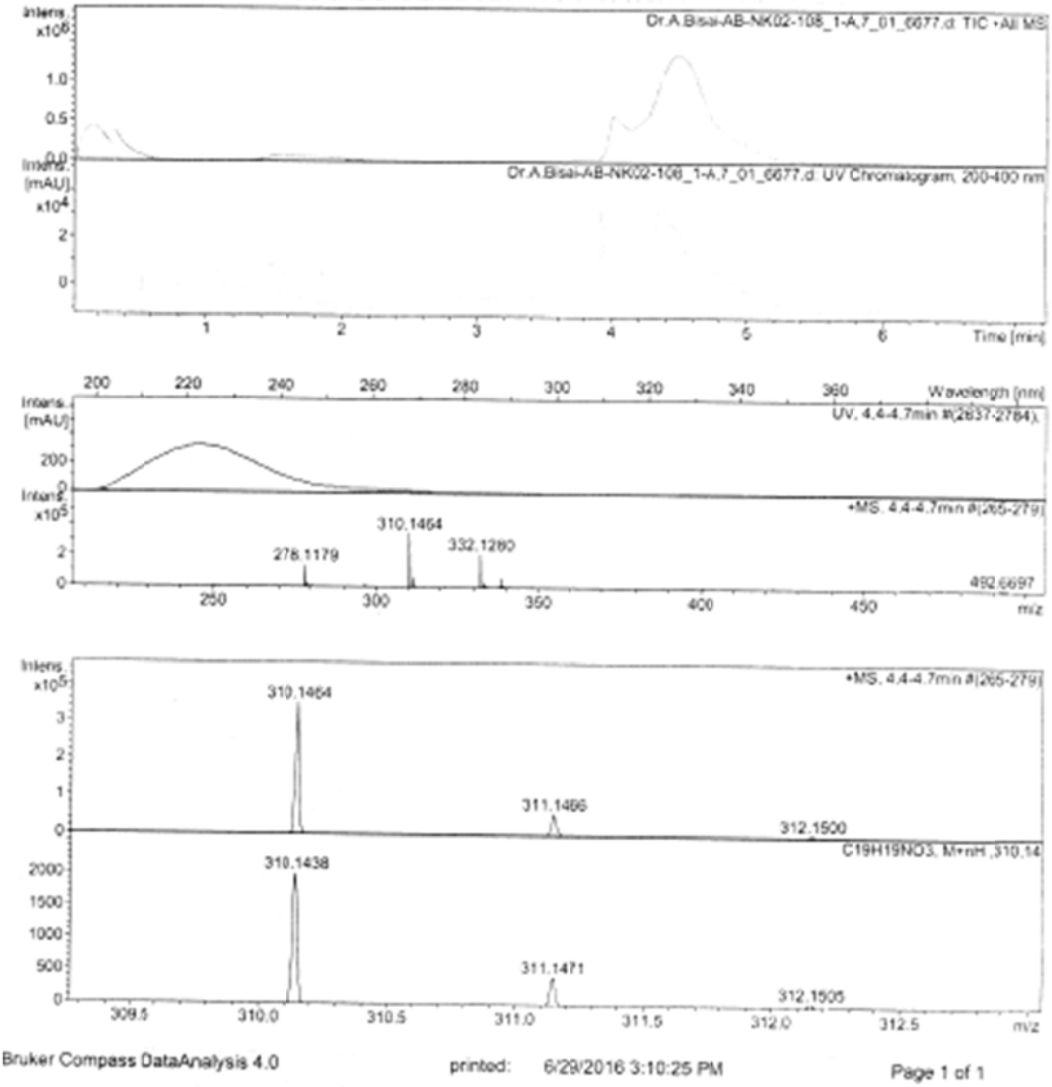
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



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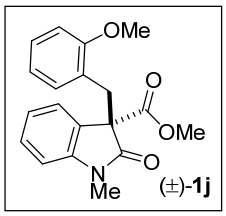
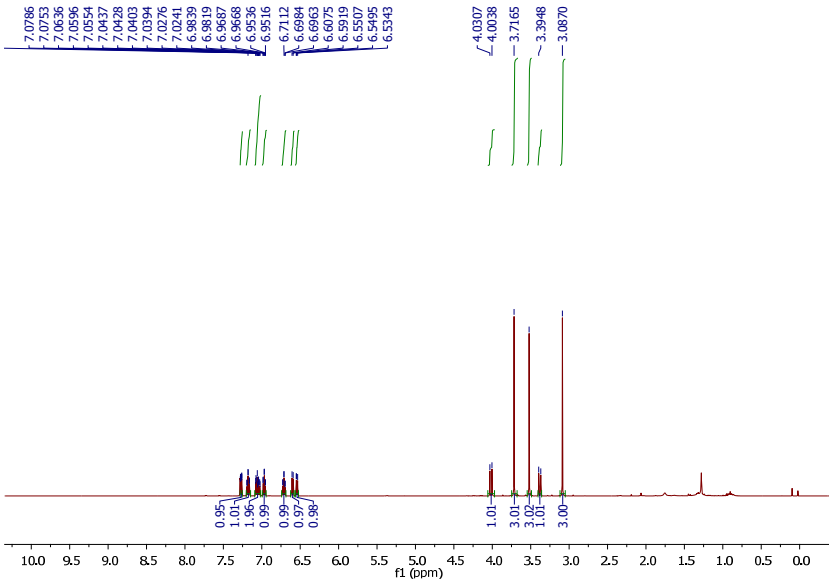
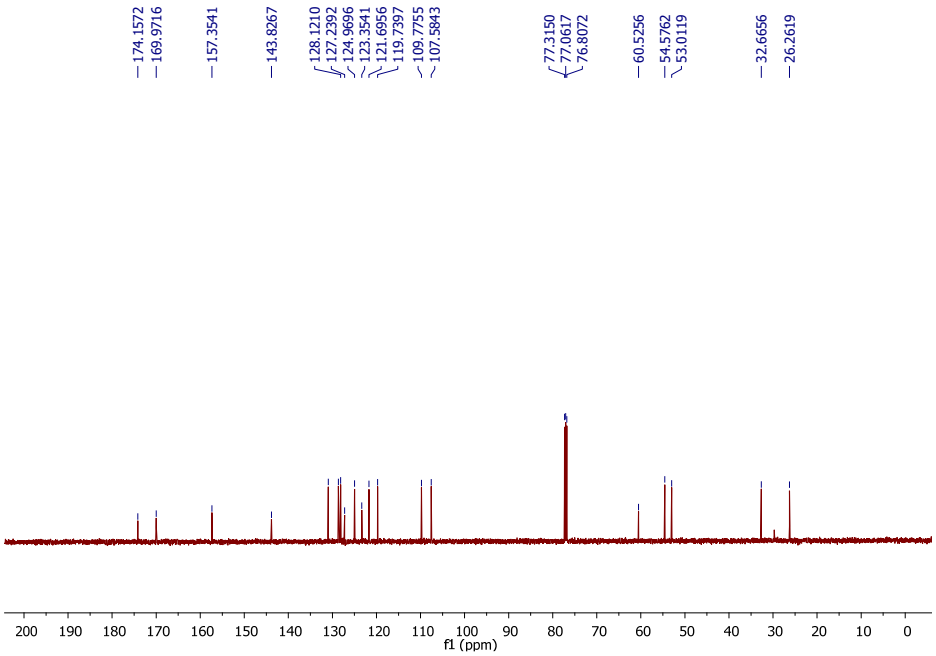
Scanned copy of mass spectrum (HRMS) of compound (±)-**1i**

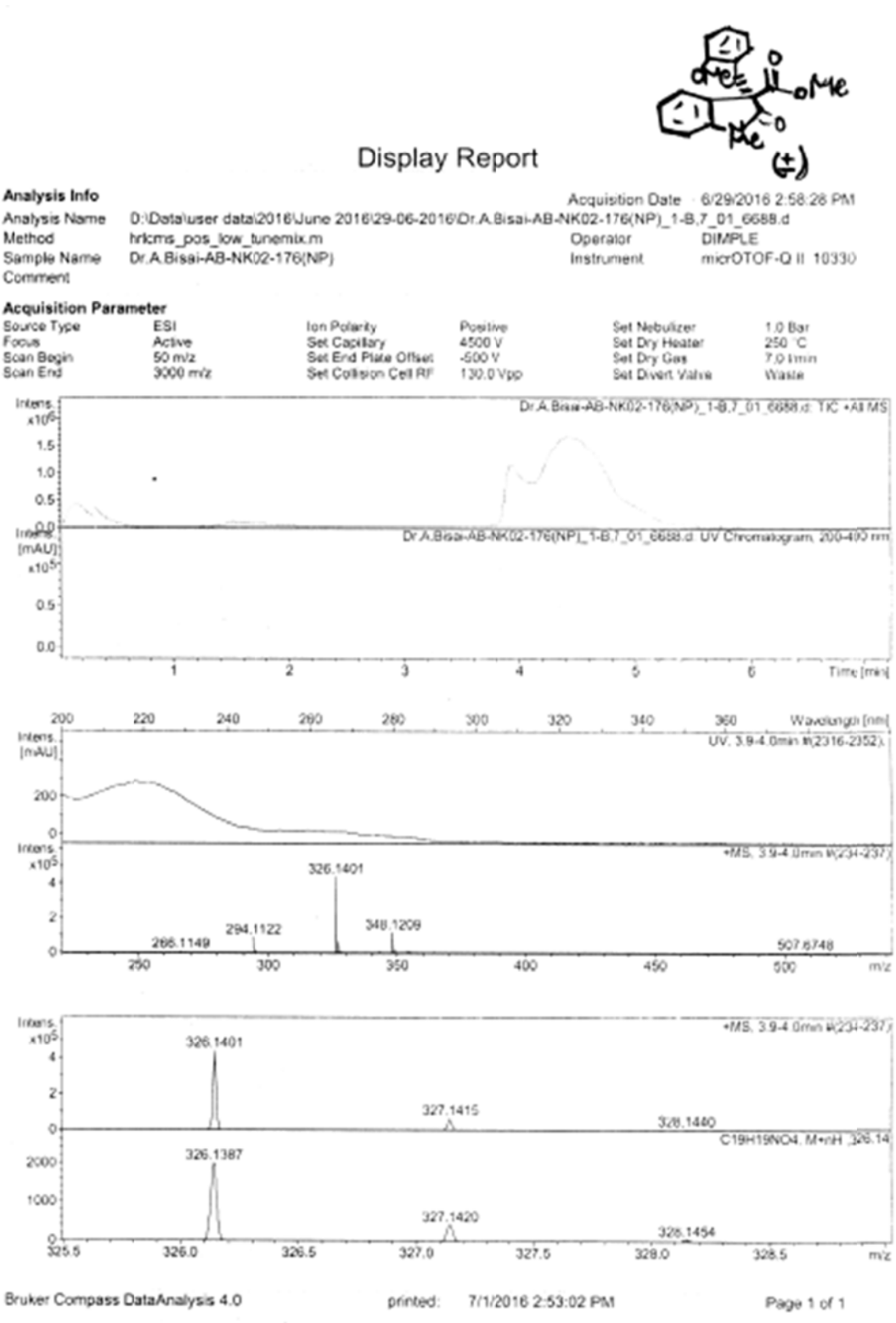




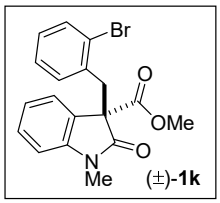
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1j**

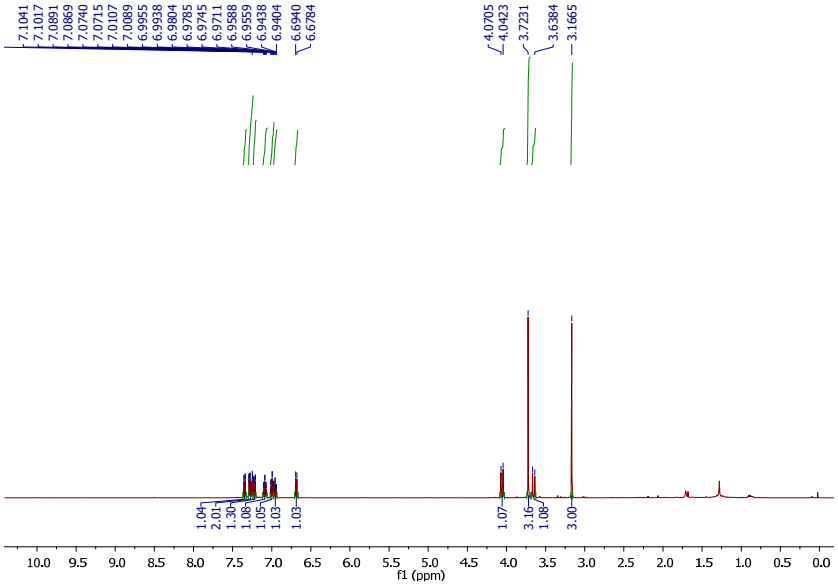


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1j**

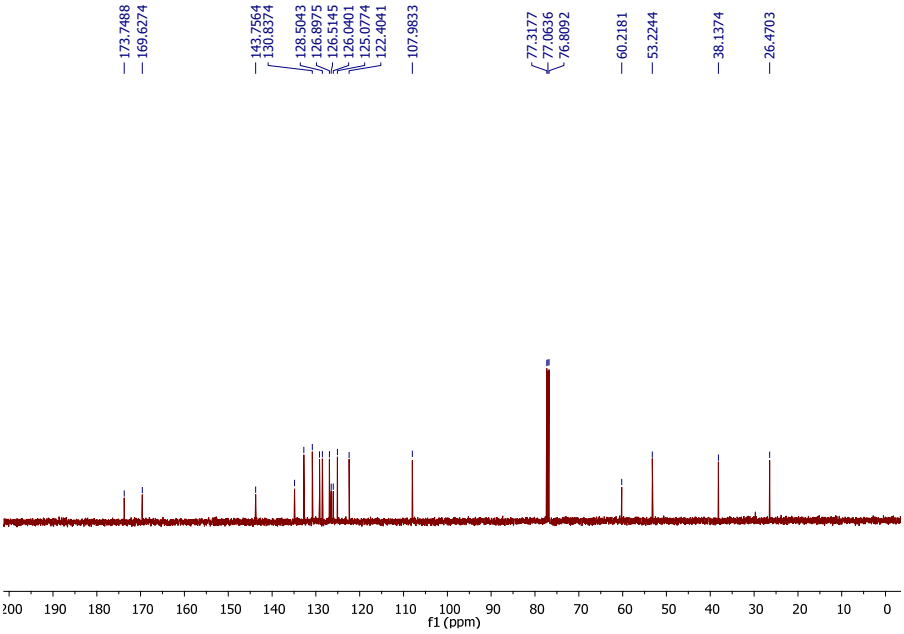


Scanned copy of mass spectrum (HRMS) of compound (±)-**1j**

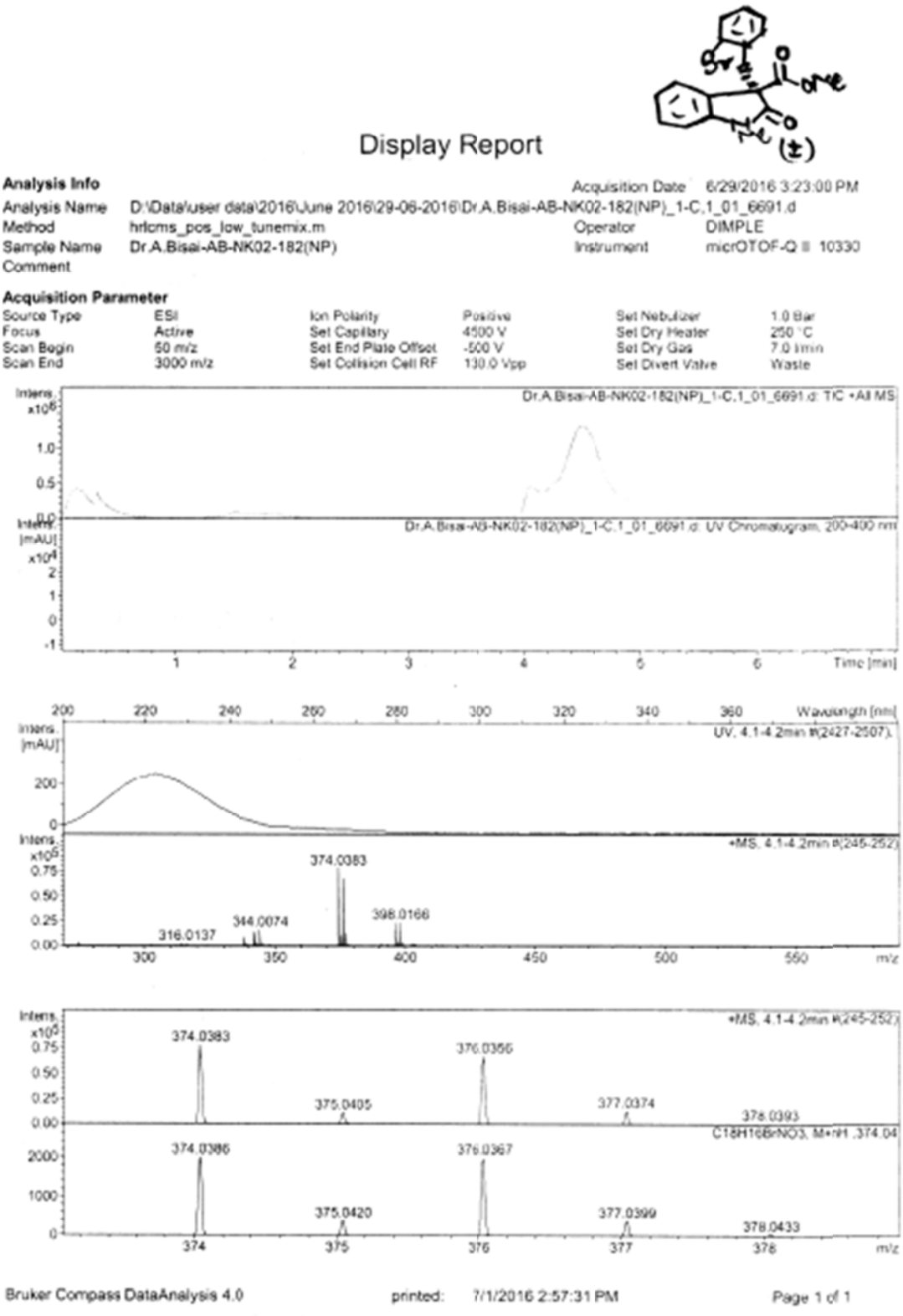




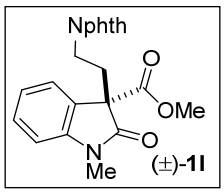
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1k**

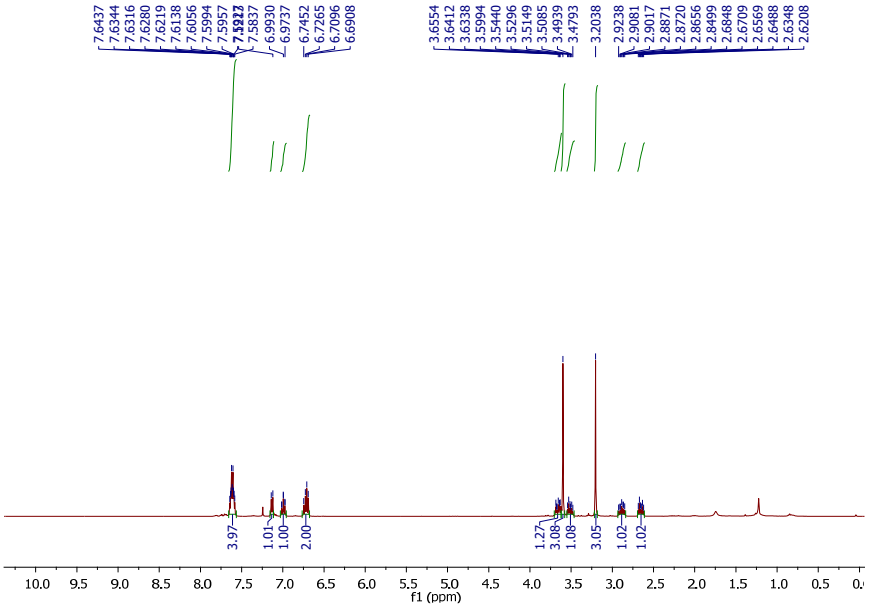


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1k**

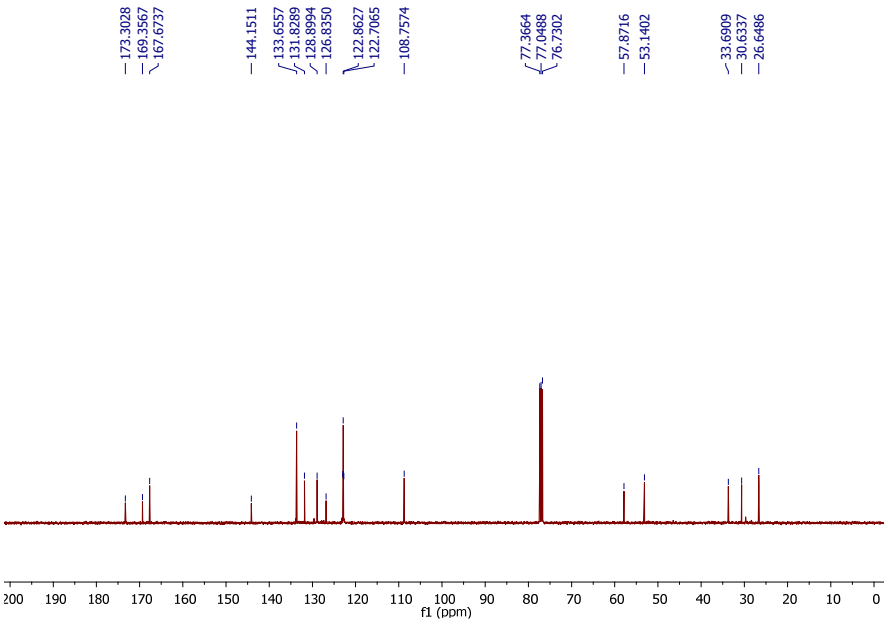


Scanned copy of mass spectrum (HRMS) of compound (±)-**1k**

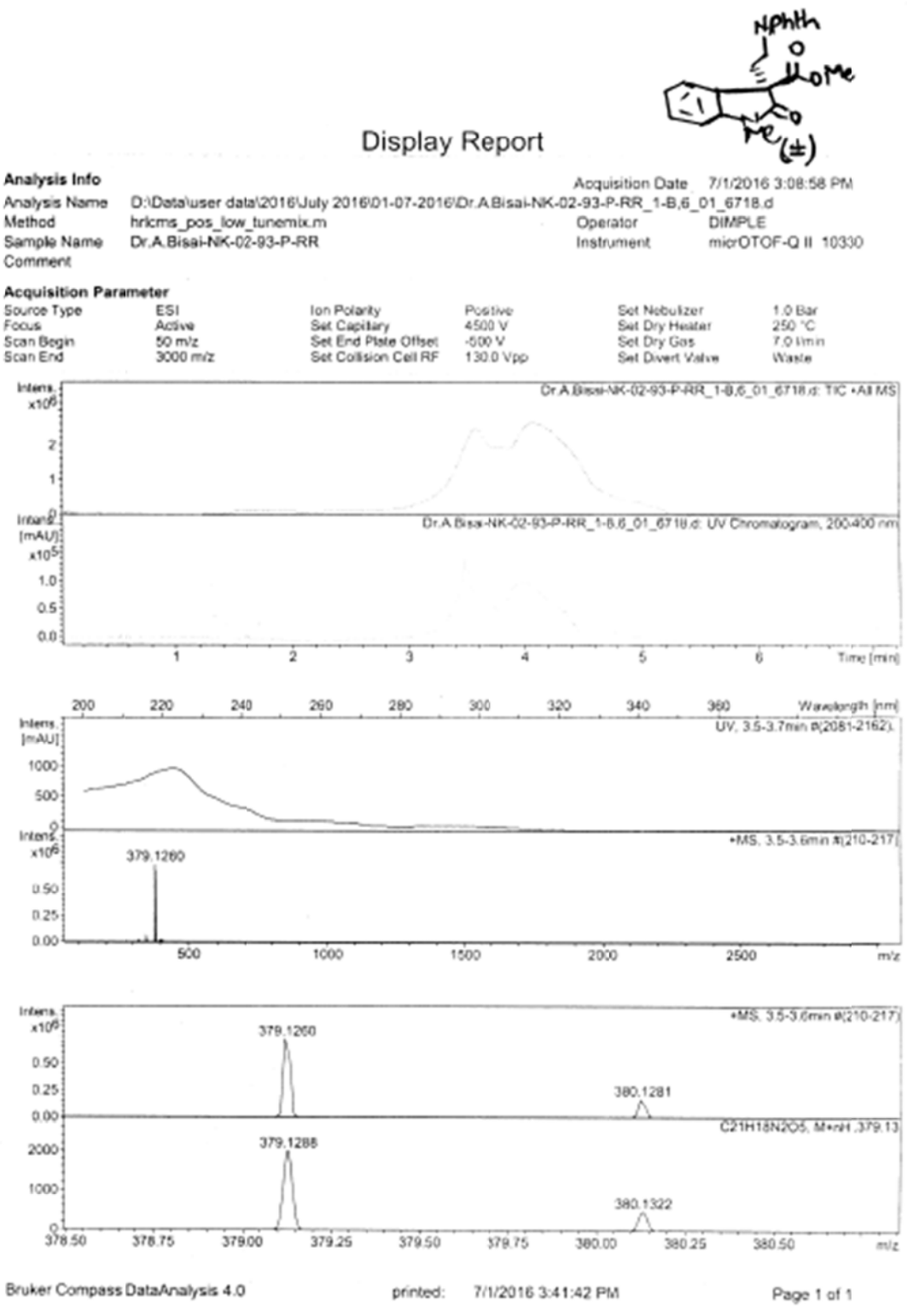




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**1l**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**1l**



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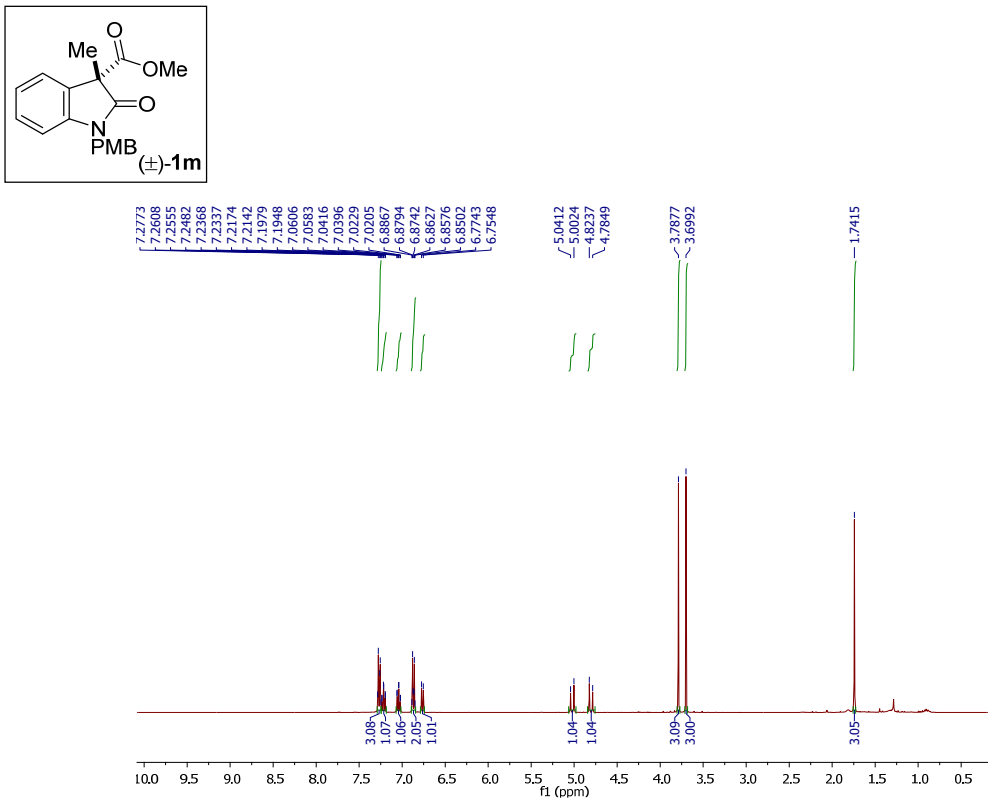
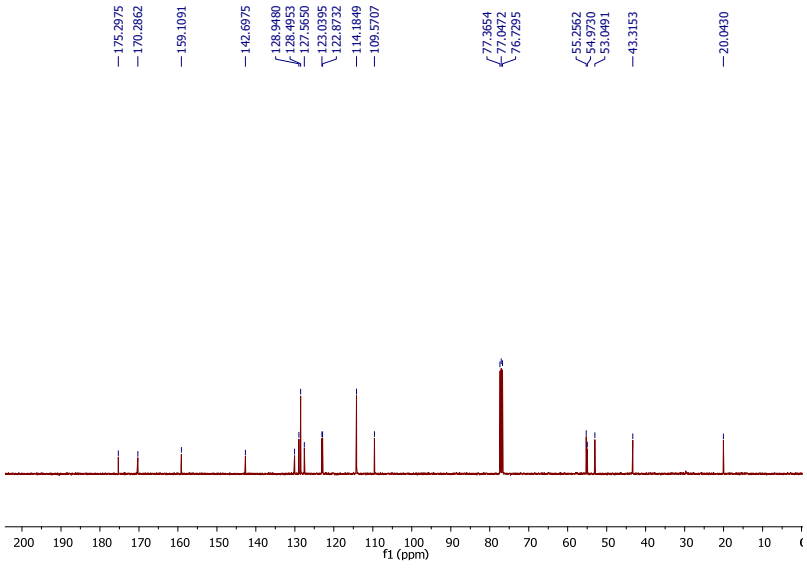
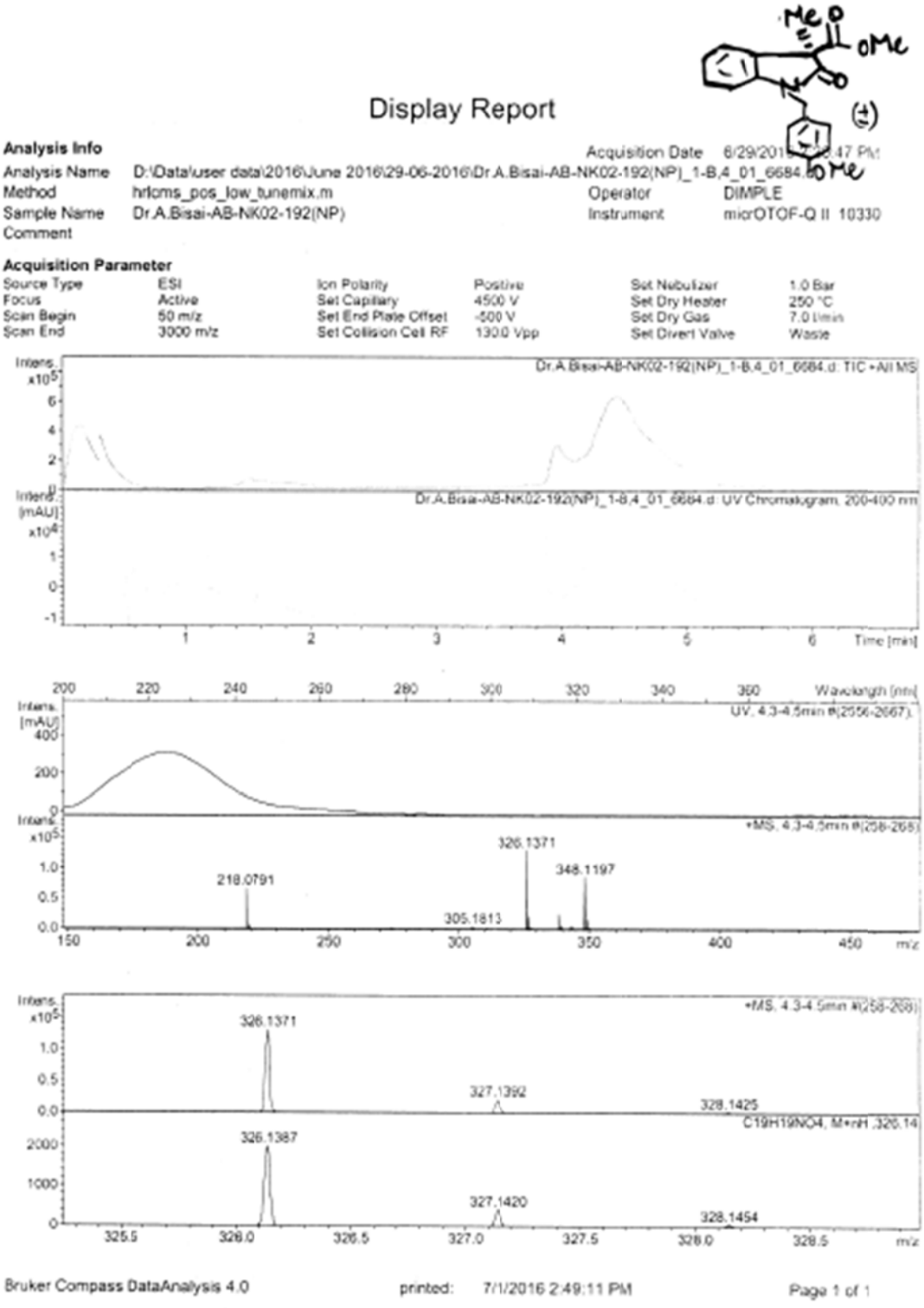
Scanned copy of mass spectrum (HRMS) of compound (±)-**1l**



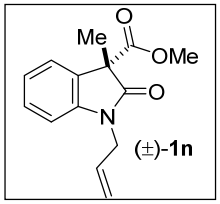
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**1m**

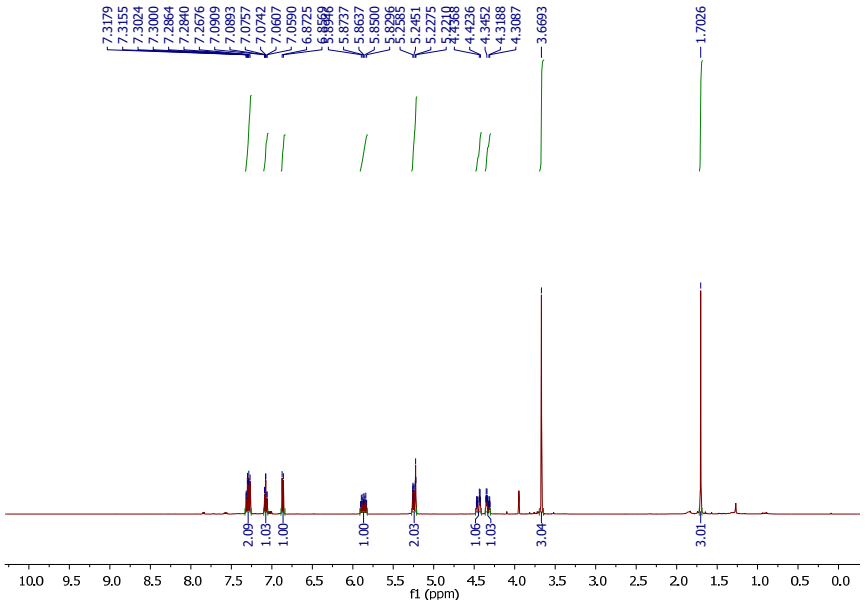


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**1m**

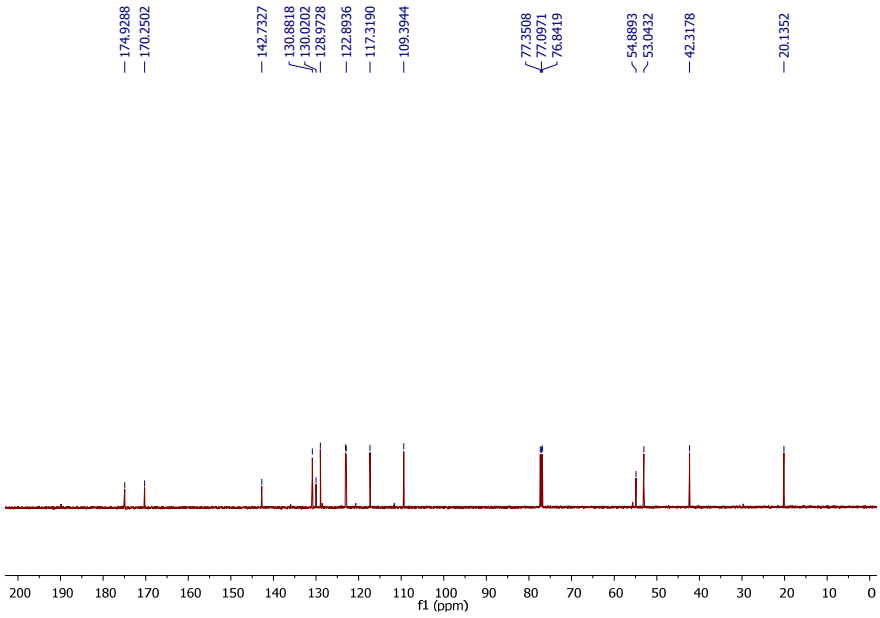


Scanned copy of mass spectrum (HRMS) of compound (±)-**1m**

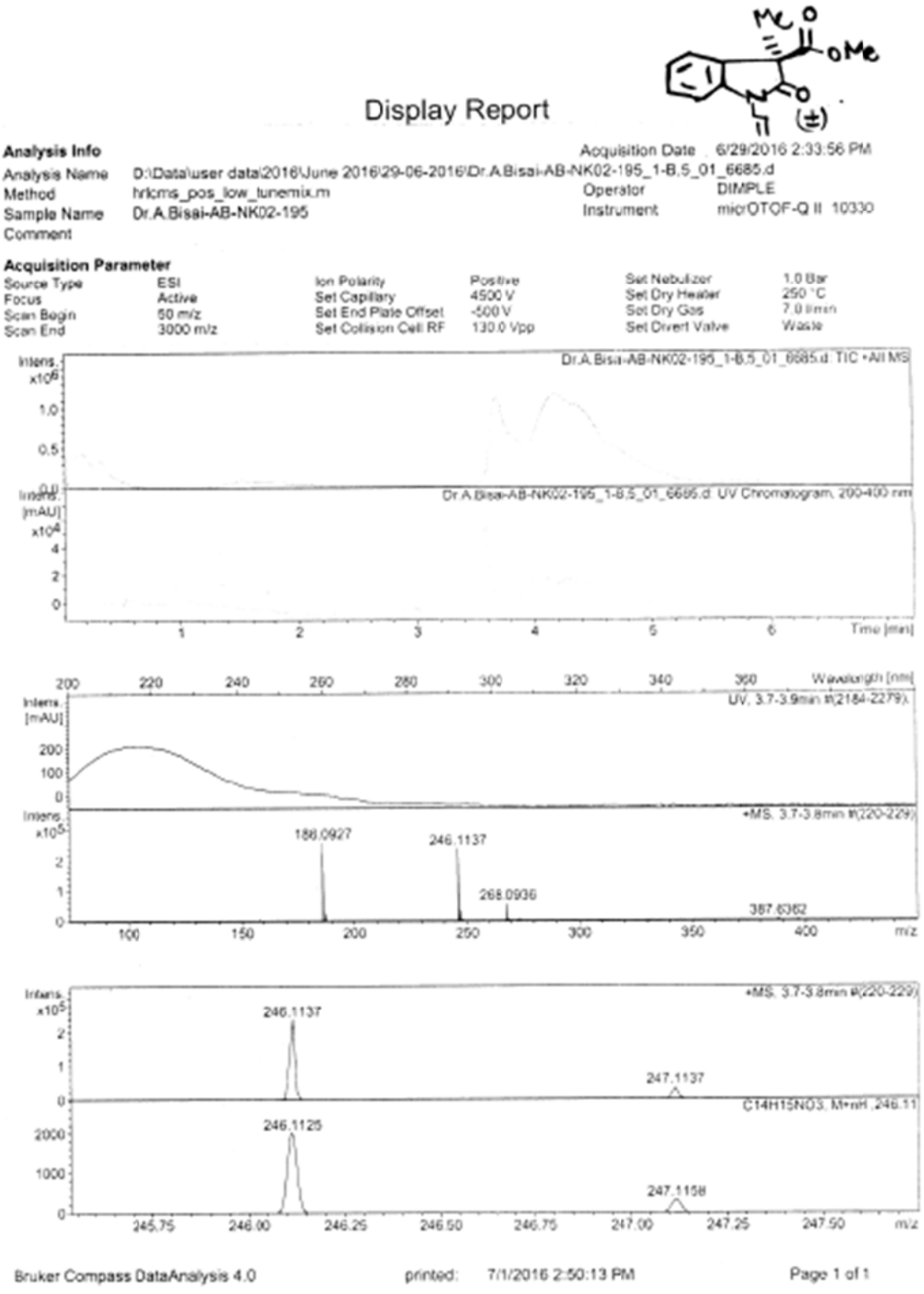




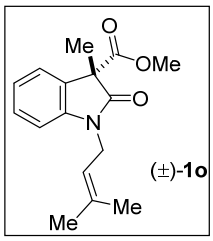
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1n**

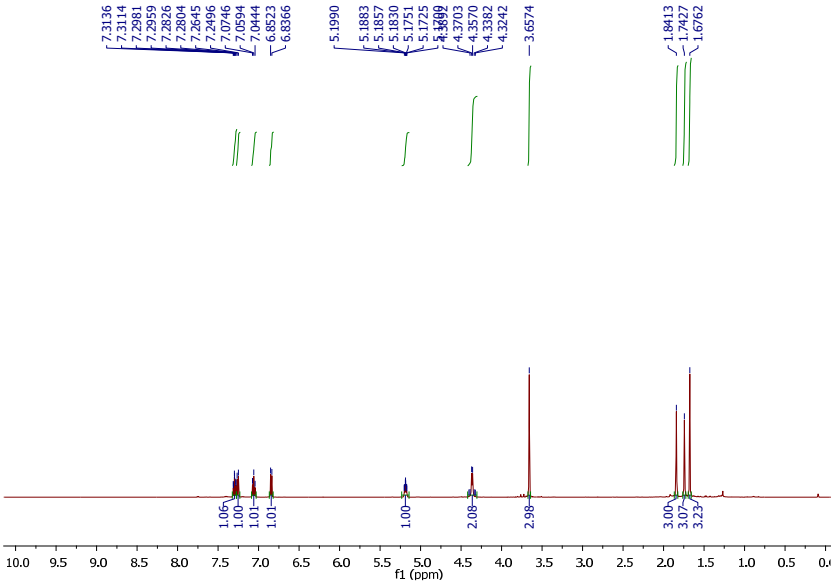


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1n**

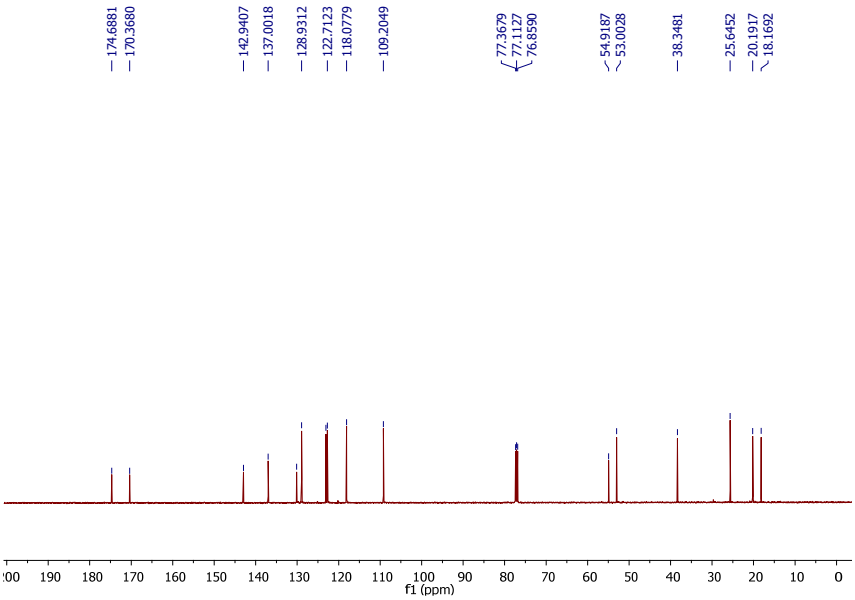


Scanned copy of mass spectrum (HRMS) of compound (±)-**1n**

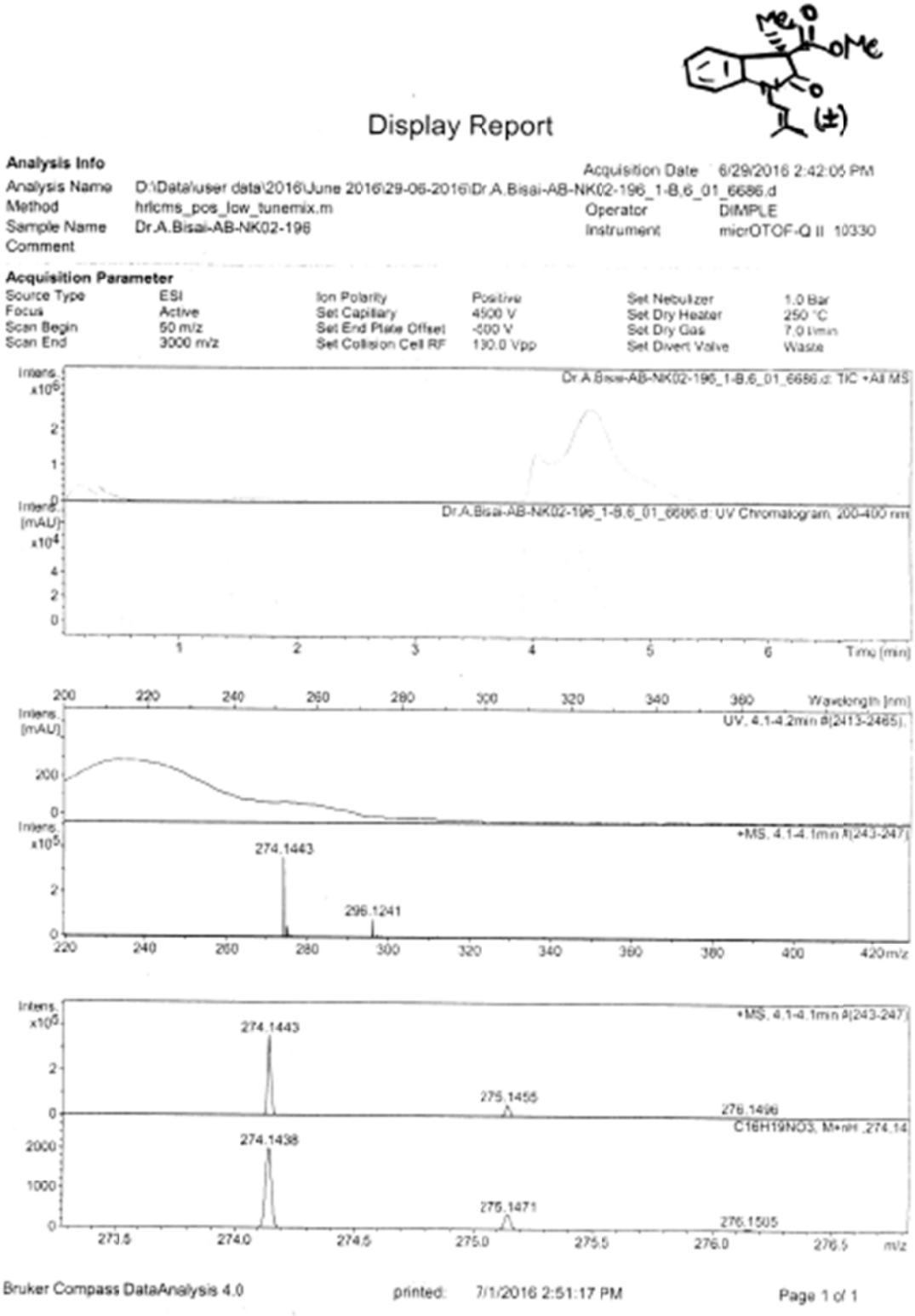




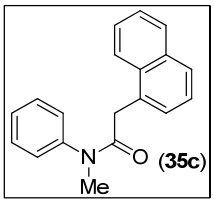
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**1o**

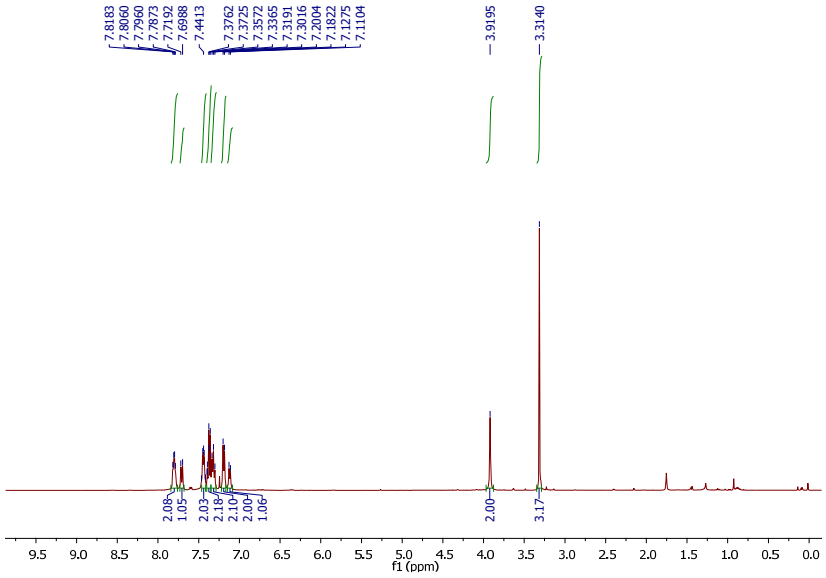


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**1o**

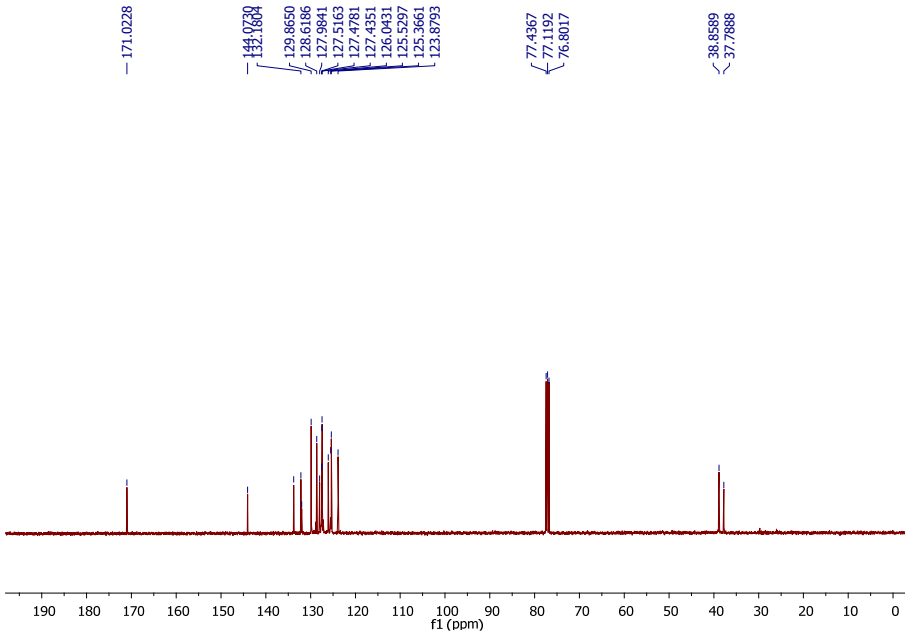


Scanned copy of mass spectrum (HRMS) of compound (±)-**1o**

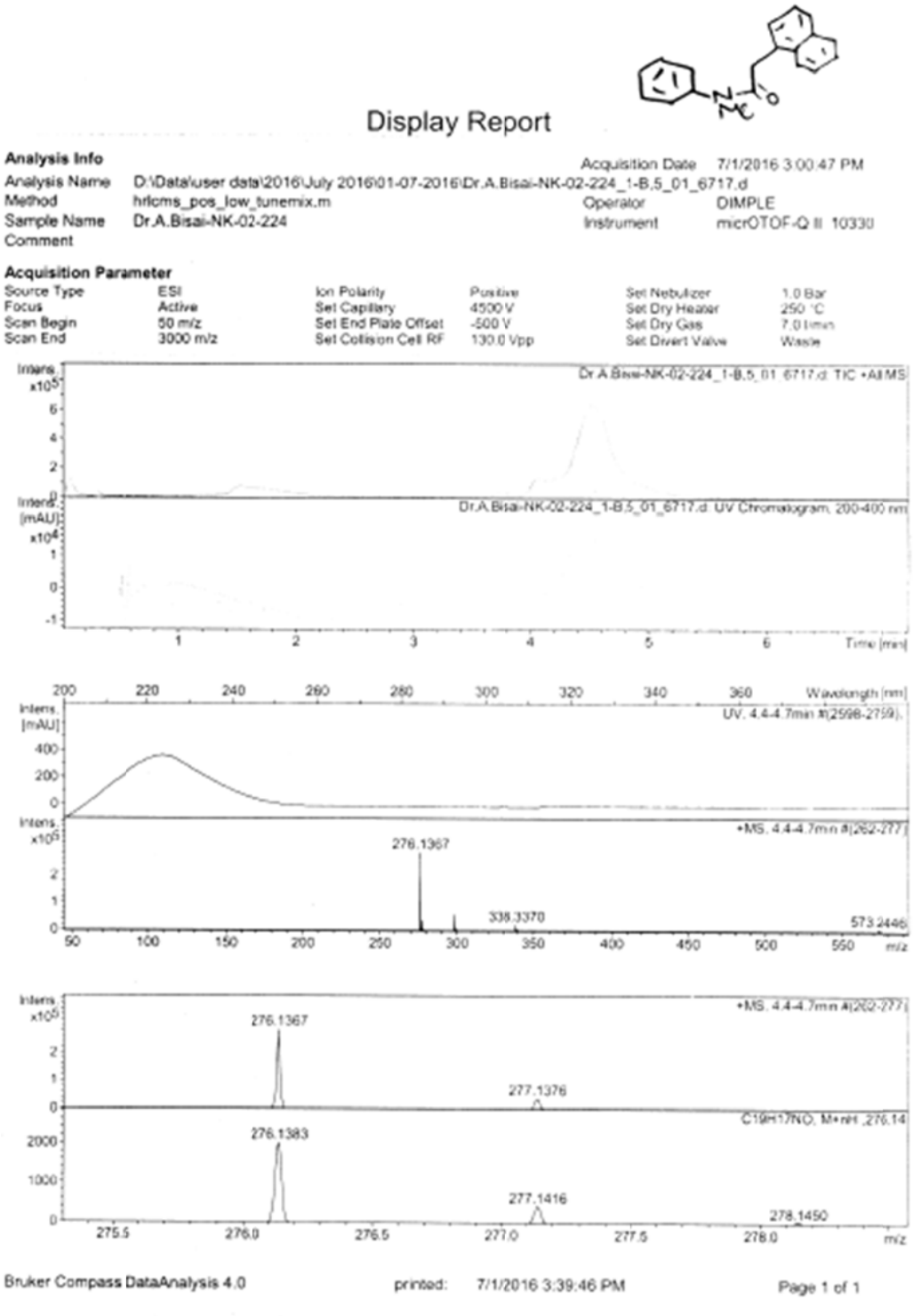




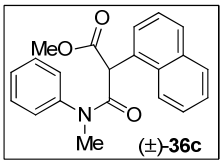
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**35c**)

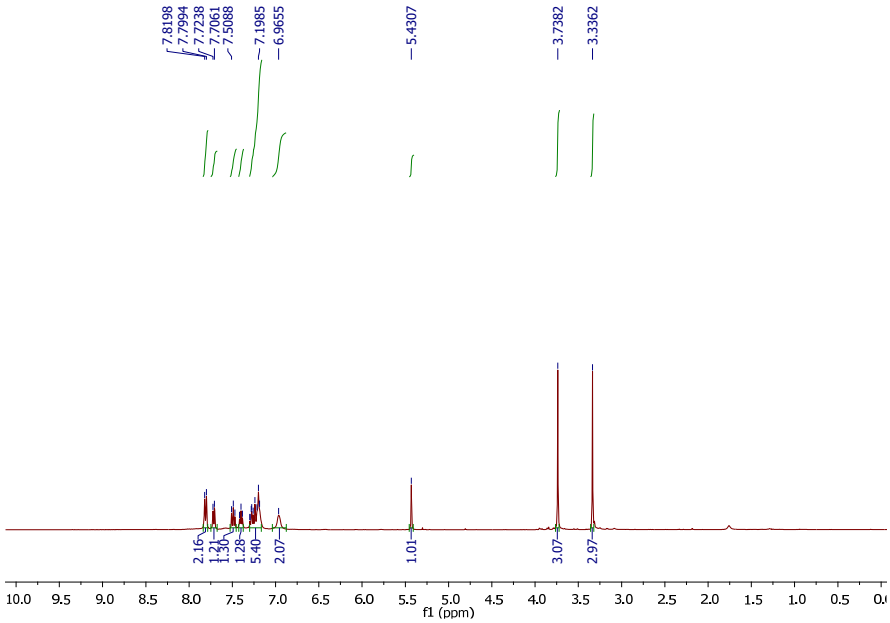


^{13}C NMR (100 MHz, $CDCl_3$) of compound (**35c**)

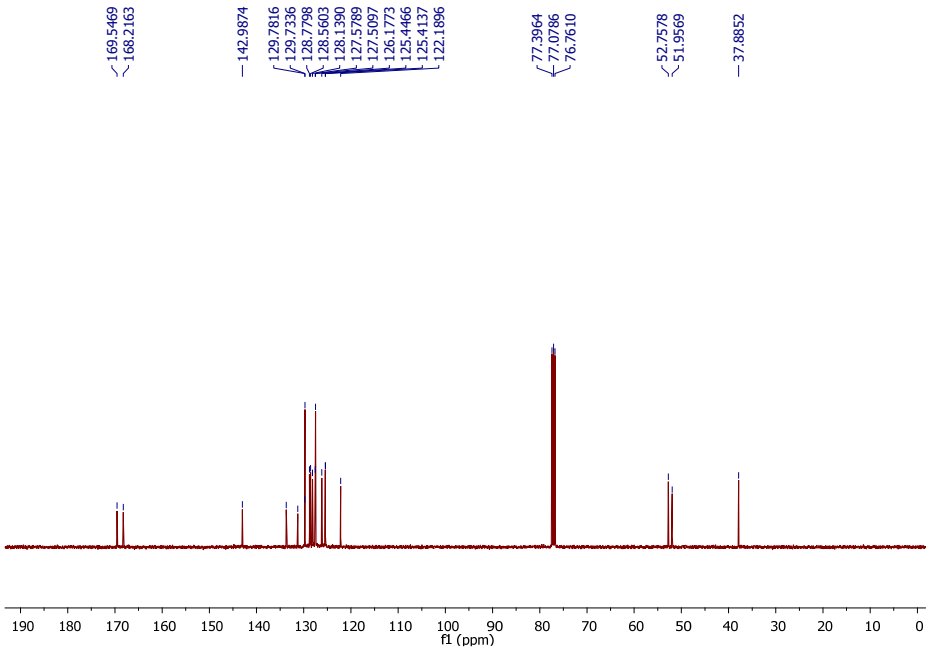


Scanned copy of mass spectrum (HRMS) of compound (**35c**)

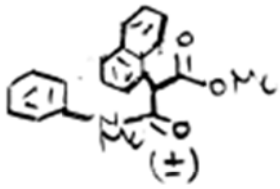




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**36c**



^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**36c**



Display Report

Analysis Info

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Sample Name	Dr.A.Bisai-AB-NK03-265R-1	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
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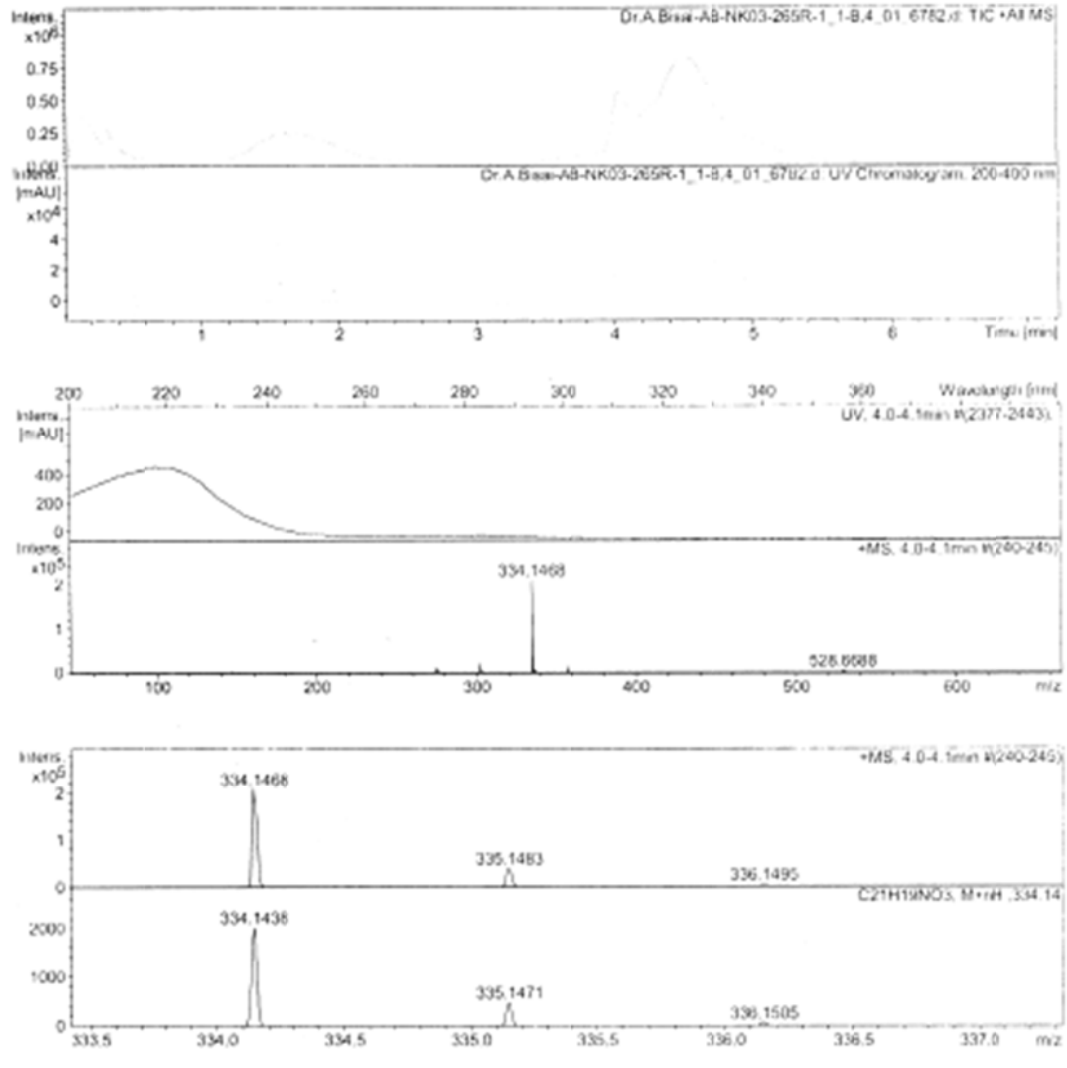
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



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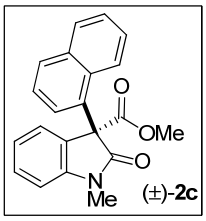
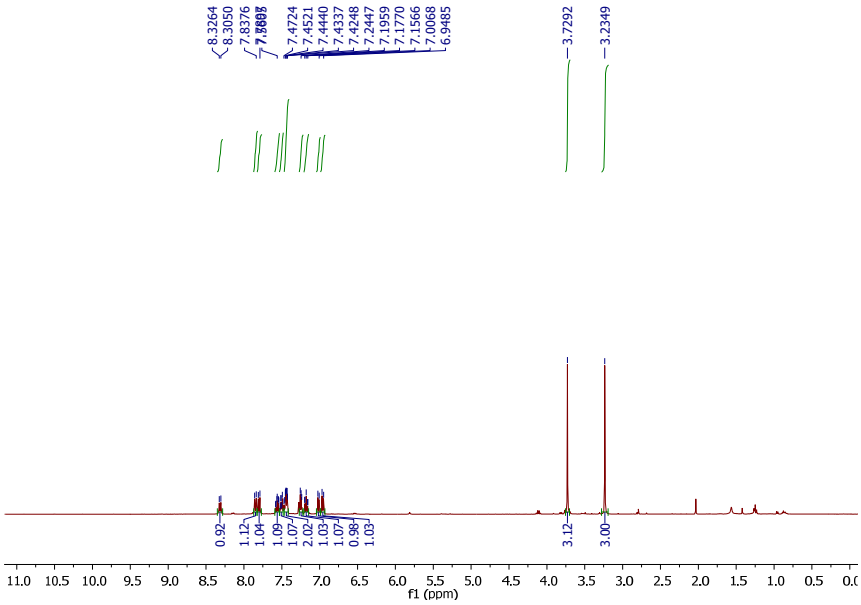
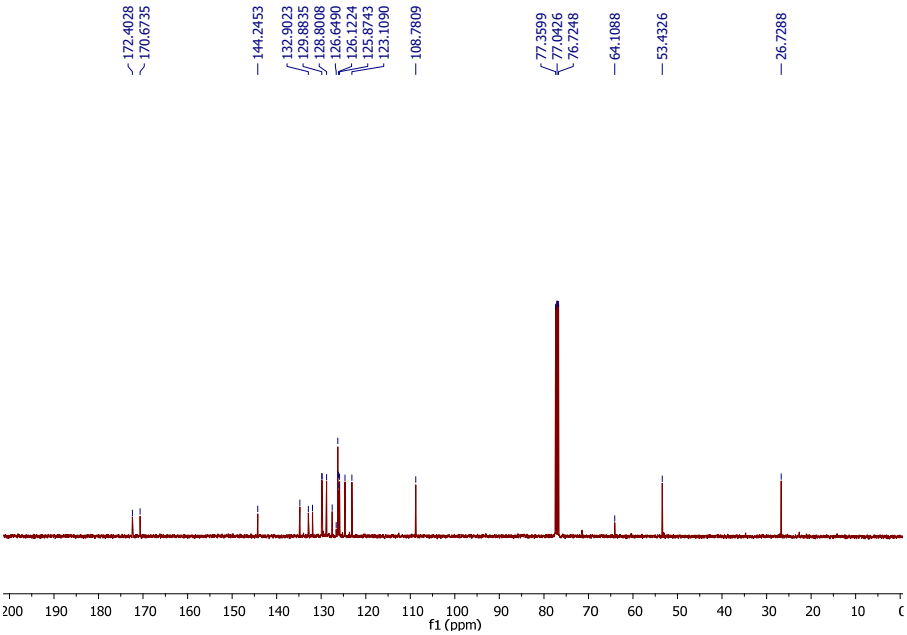
Scanned copy of mass spectrum (HRMS) of compound (±)-**36c**

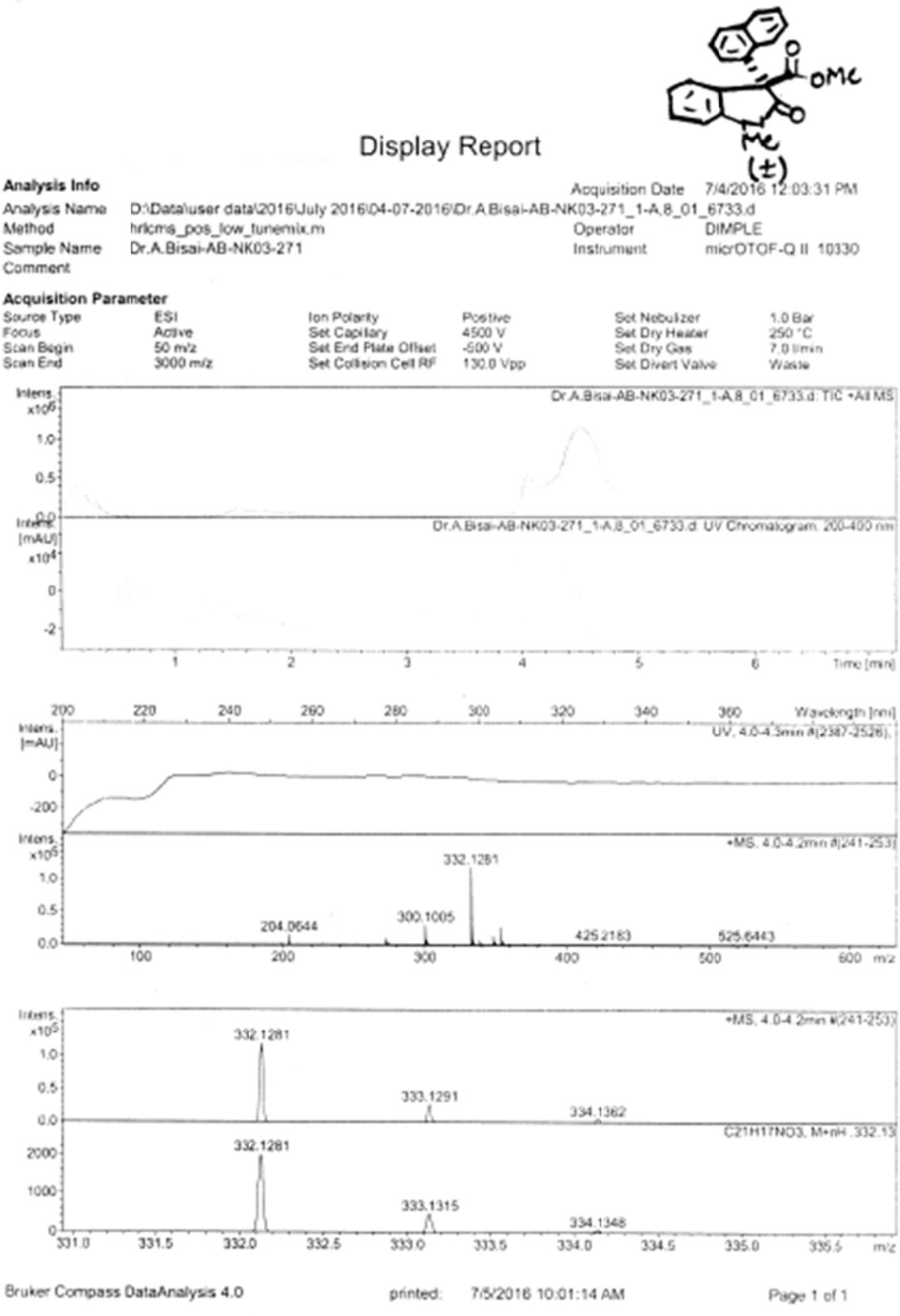




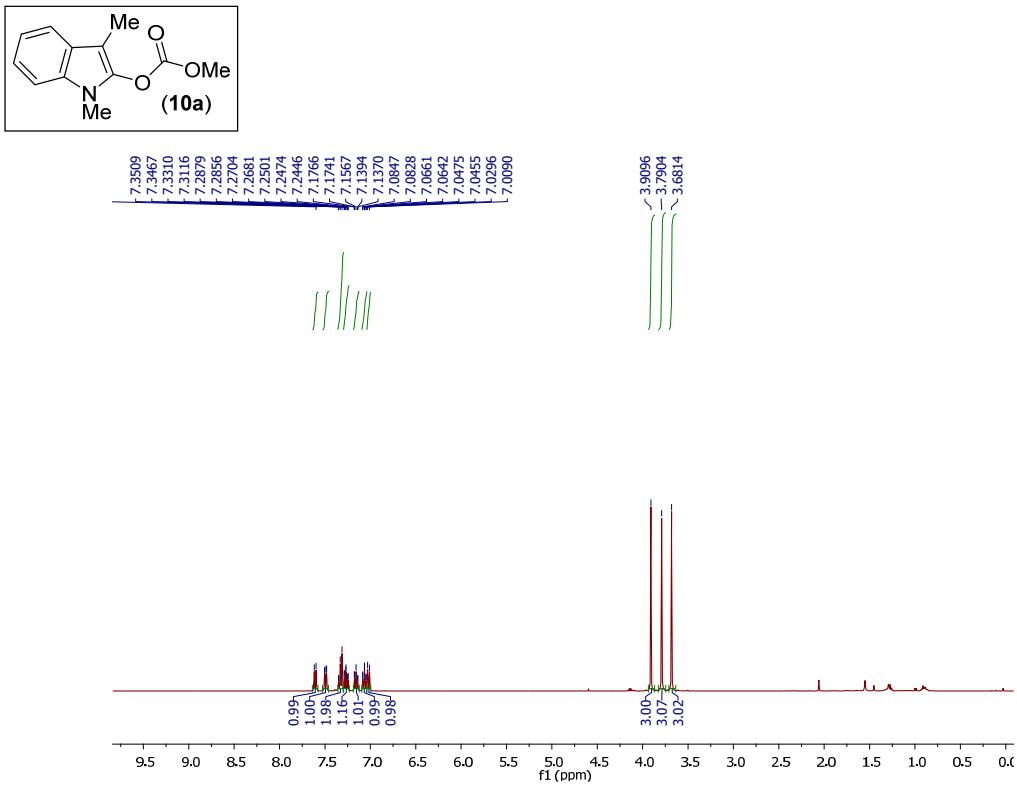
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**2c**



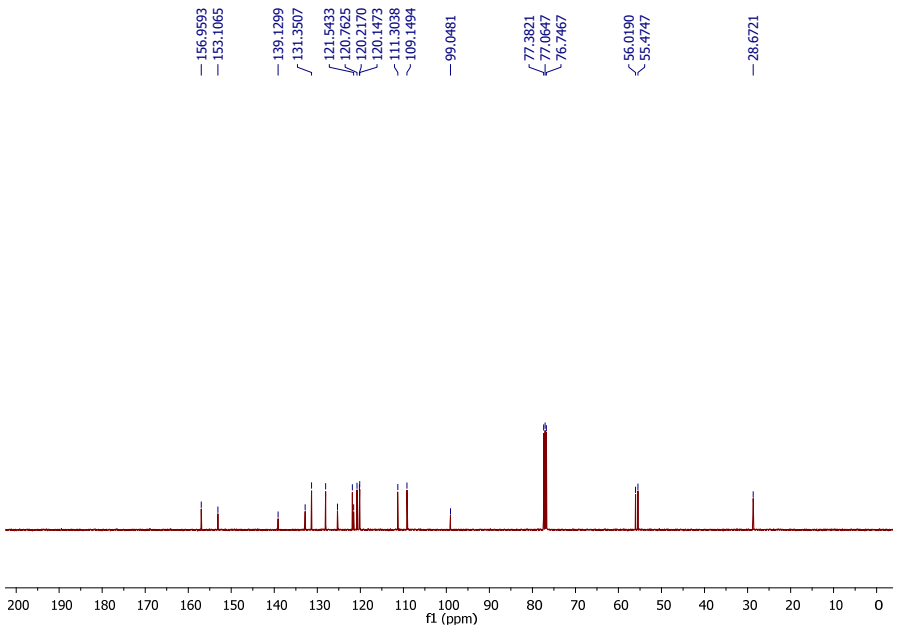
^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**2c**



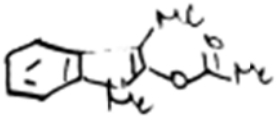
Scanned copy of mass spectrum (HRMS) of compound (±)-**2c**



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



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



Display Report

Analysis Info

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Sample Name	Dr.A.Bisai-AB-NK03-314-1	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

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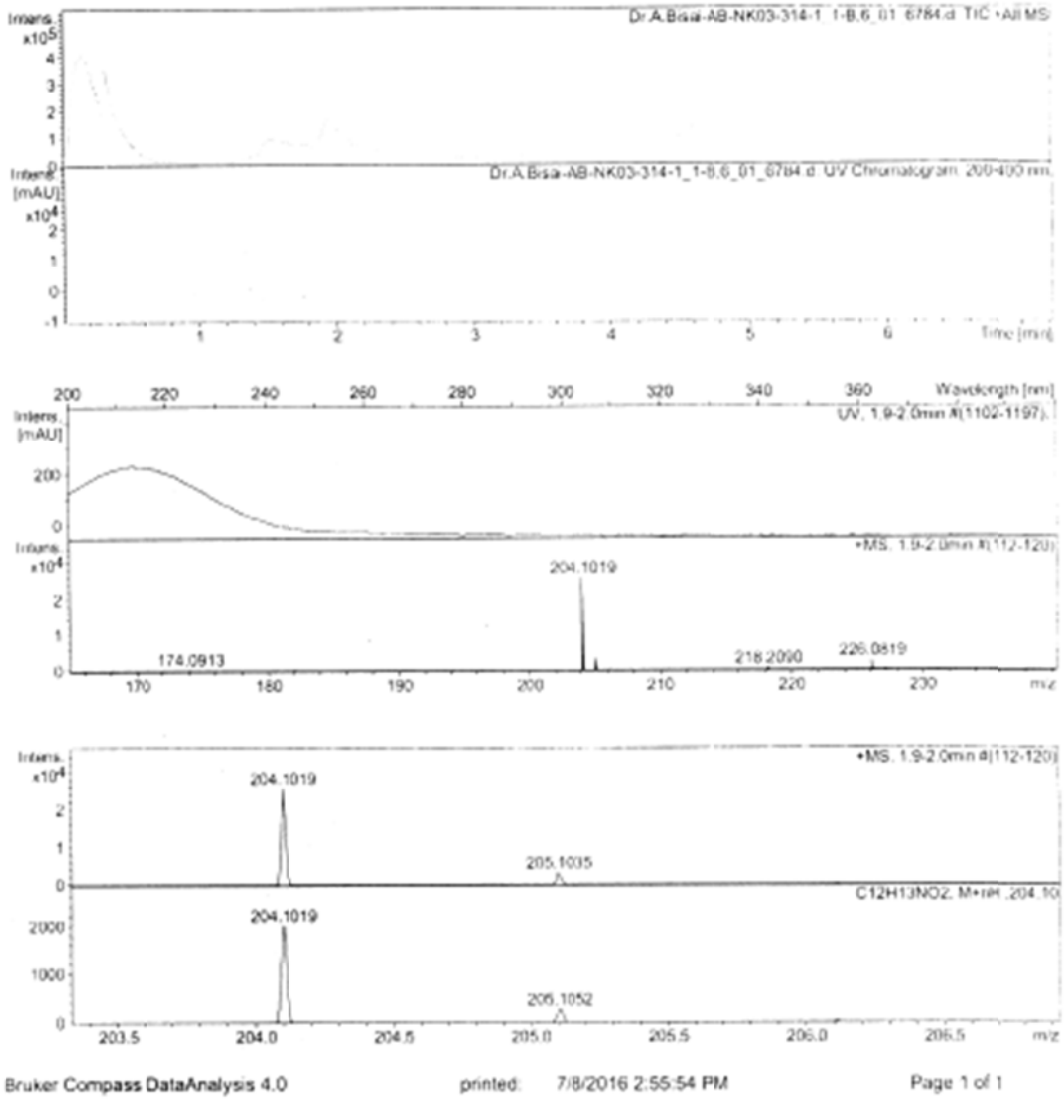
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



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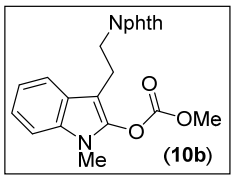
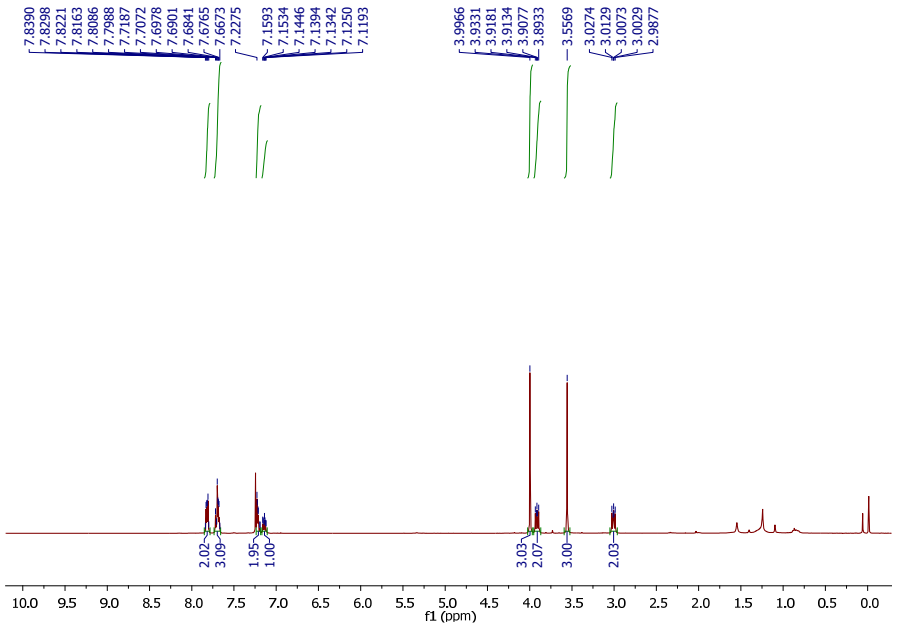
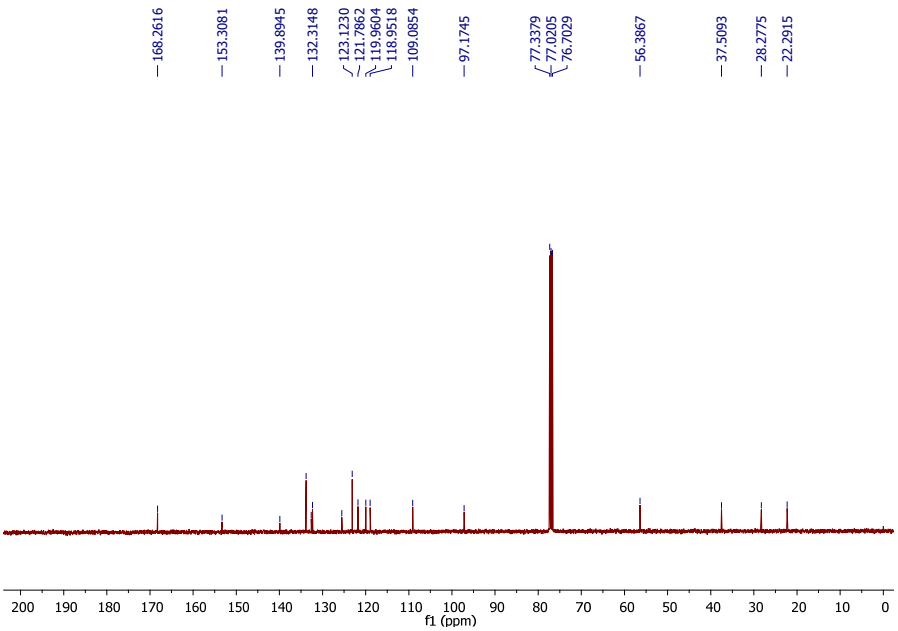
Scanned copy of mass spectrum (HRMS) of compound (**10a**)

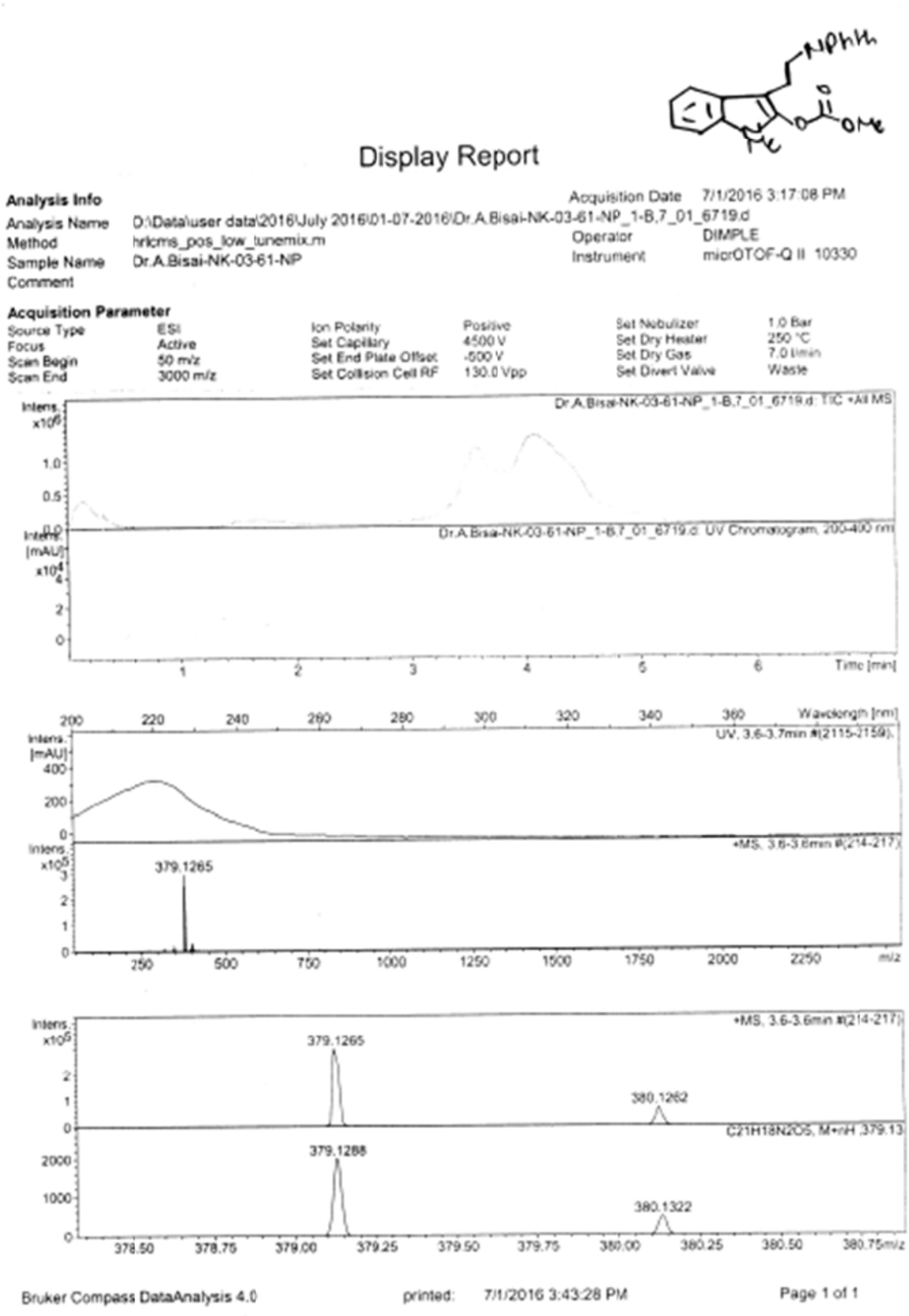




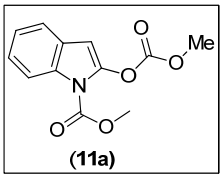
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**10b**)



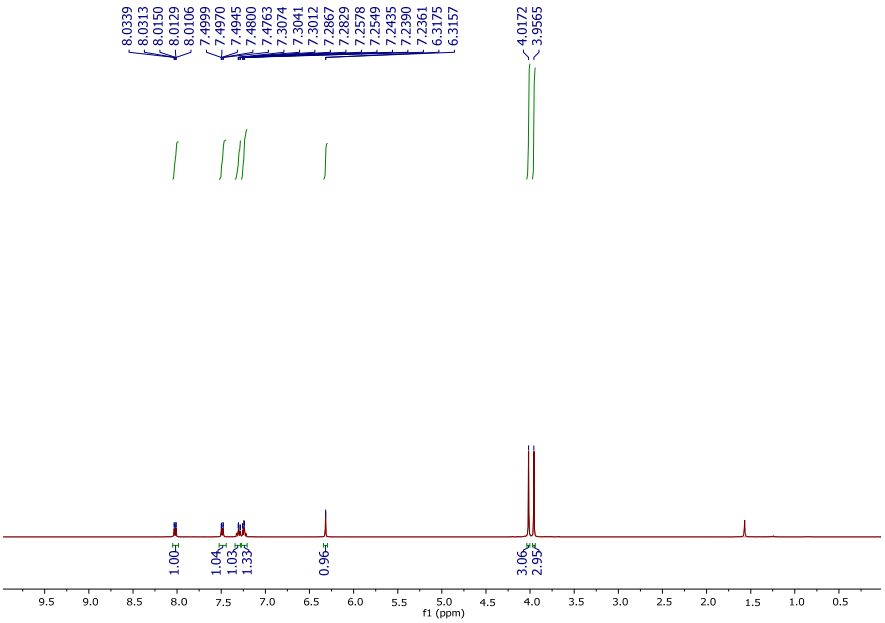
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**10b**)



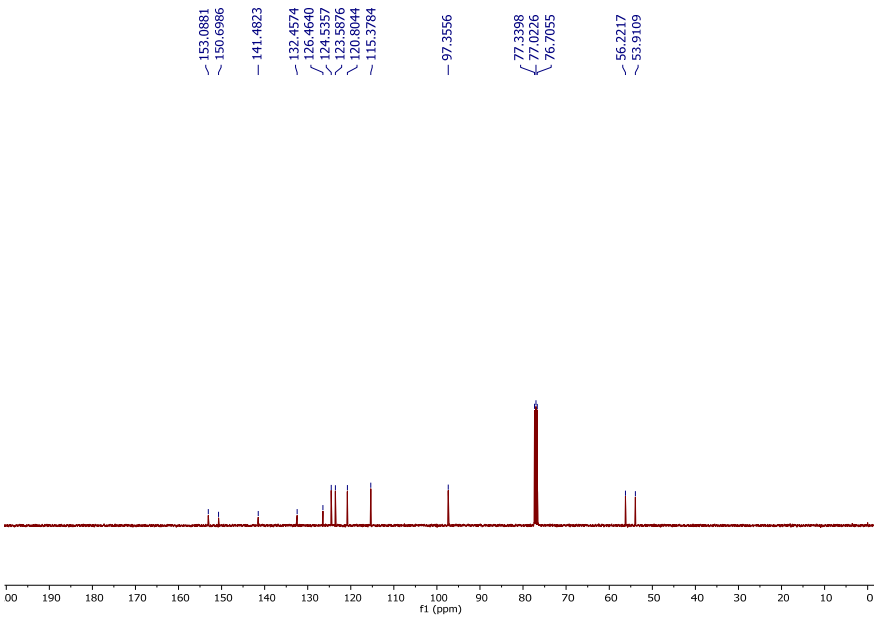
Scanned copy of mass spectrum (HRMS) of compound (**10b**)



(**11a**)



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



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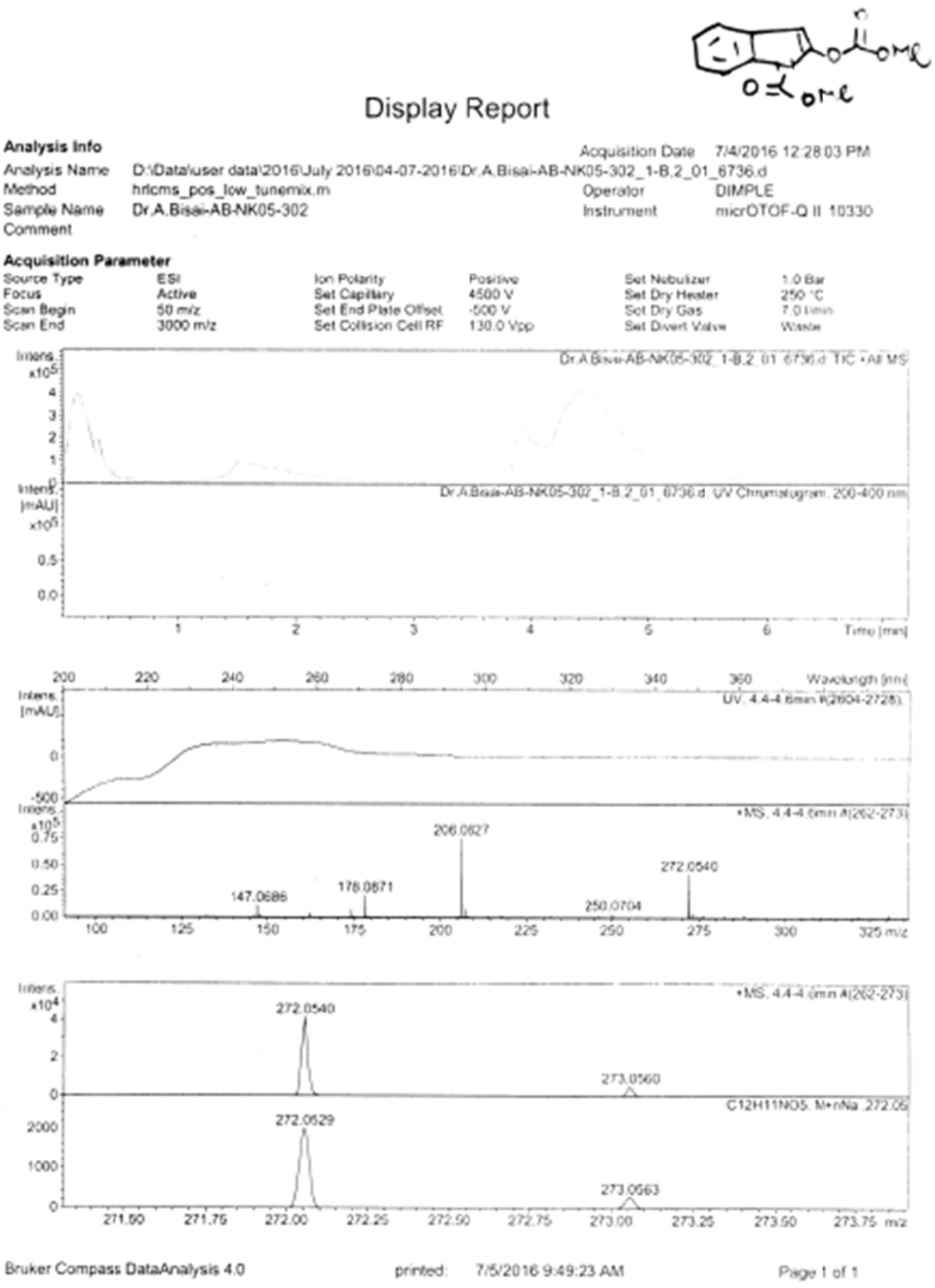
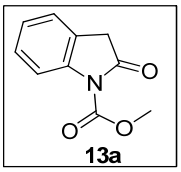
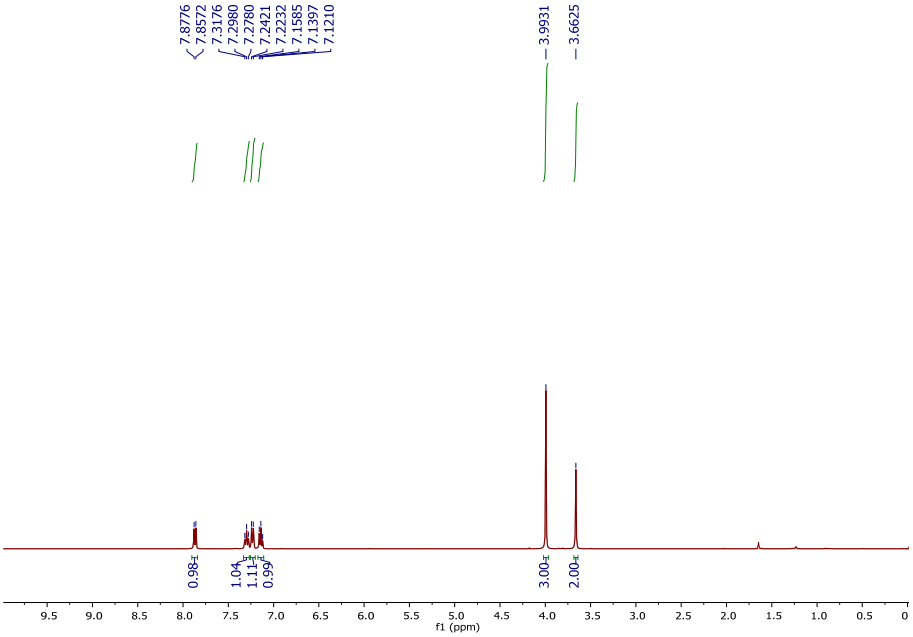
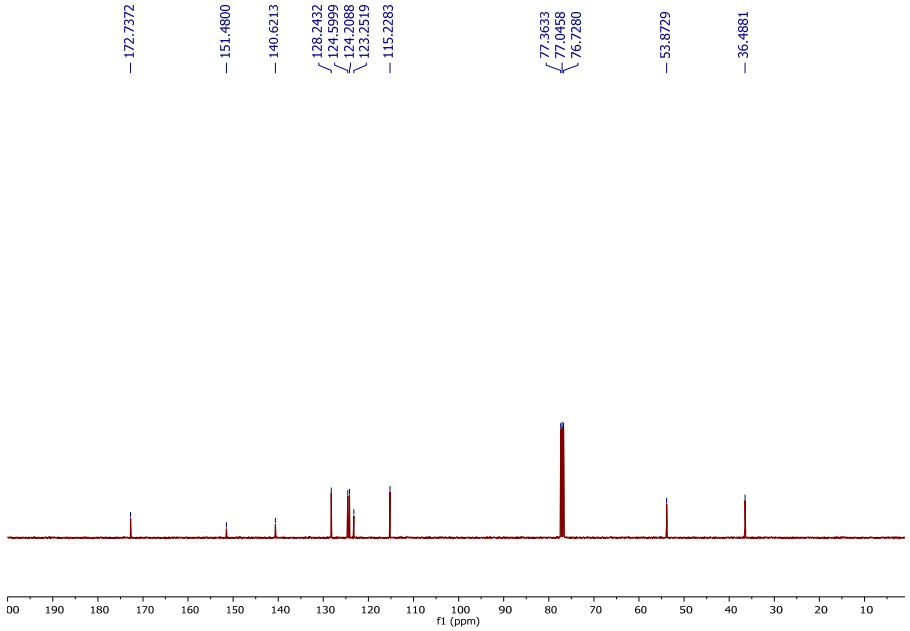


Scanned copy of mass spectrum (HRMS) of compound (**11a**)

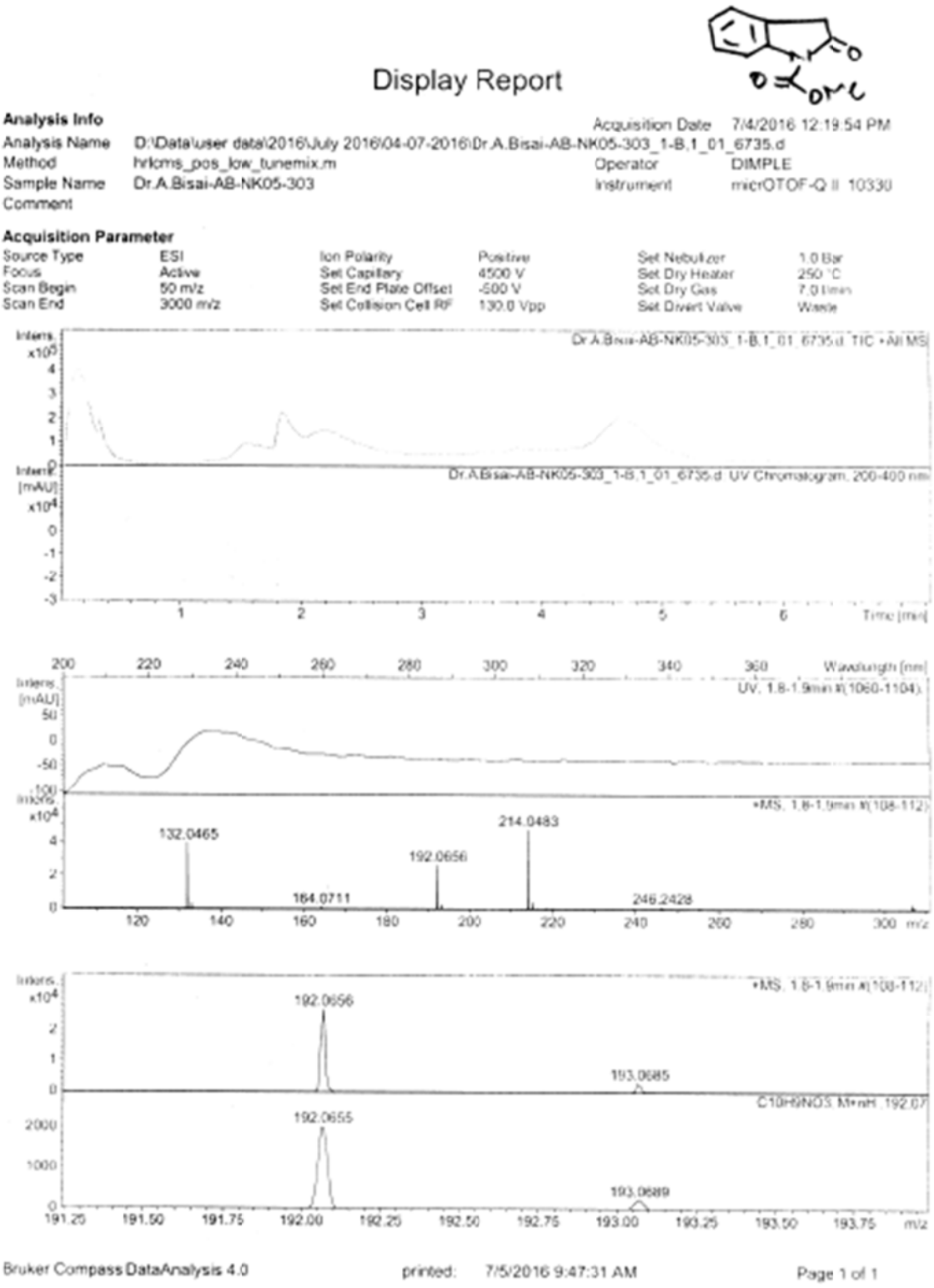




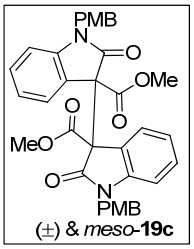
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**13a**)



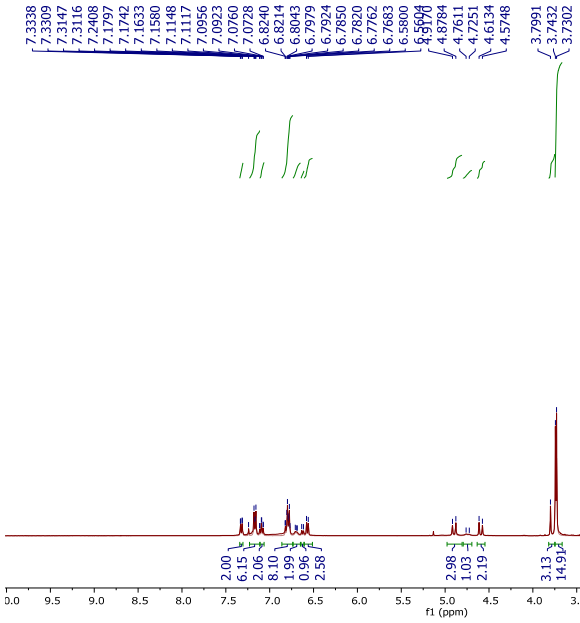
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**13a**)



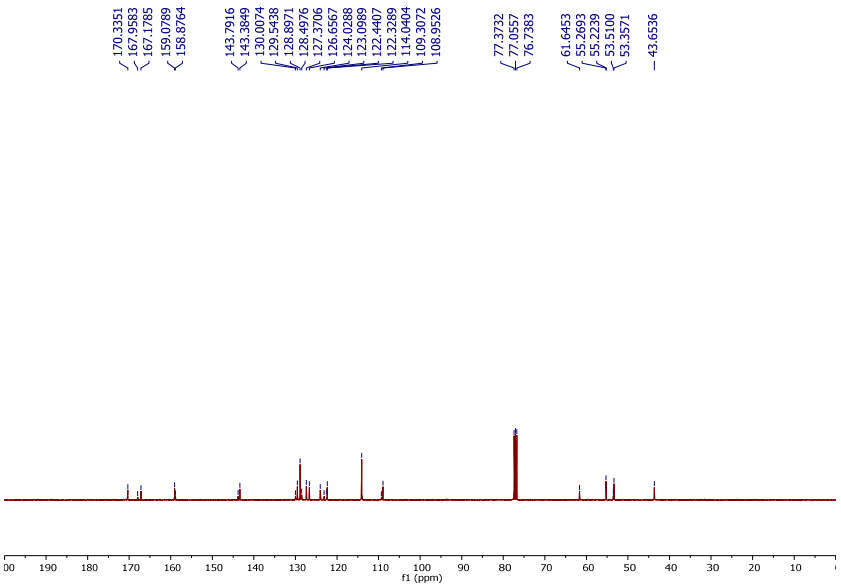
Scanned copy of mass spectrum (HRMS) of compound (**13a**)



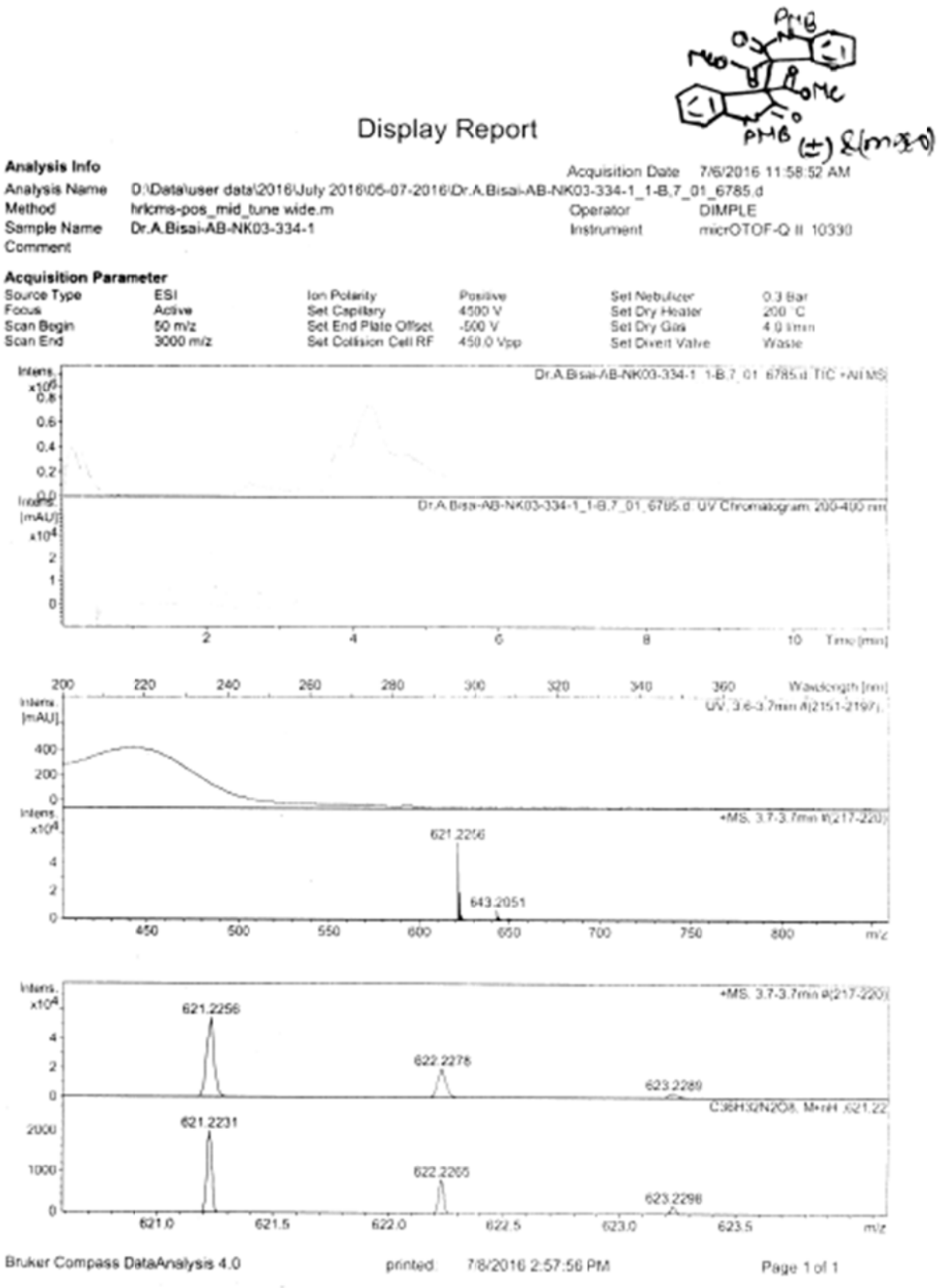
(±) & *meso*-**19c**



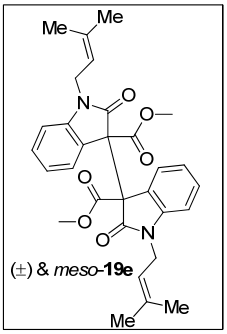
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±) & *meso*-**19c**

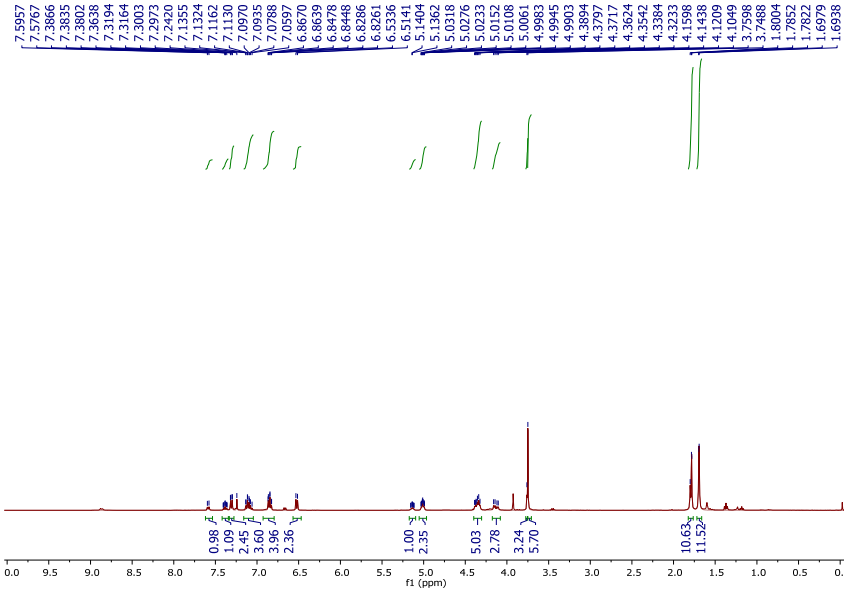


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±) & *meso*-**19c**

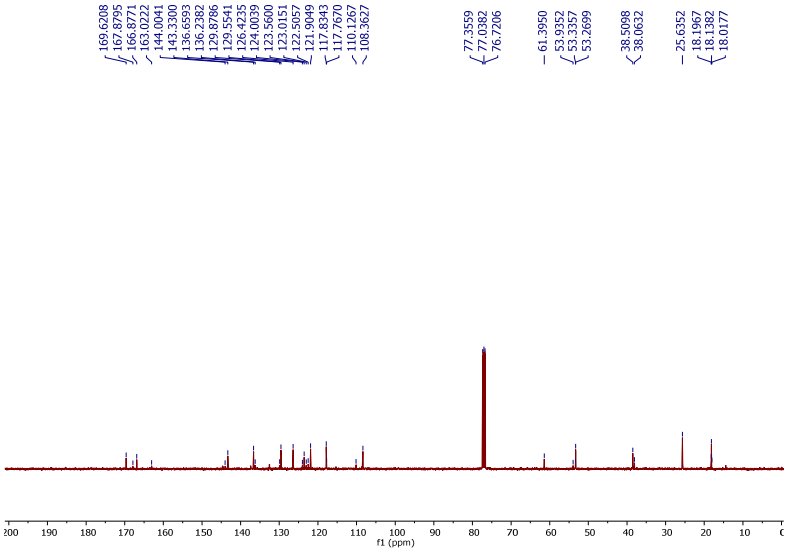


Scanned copy of mass spectrum (HRMS) of compound (±) & *meso*-**19c**

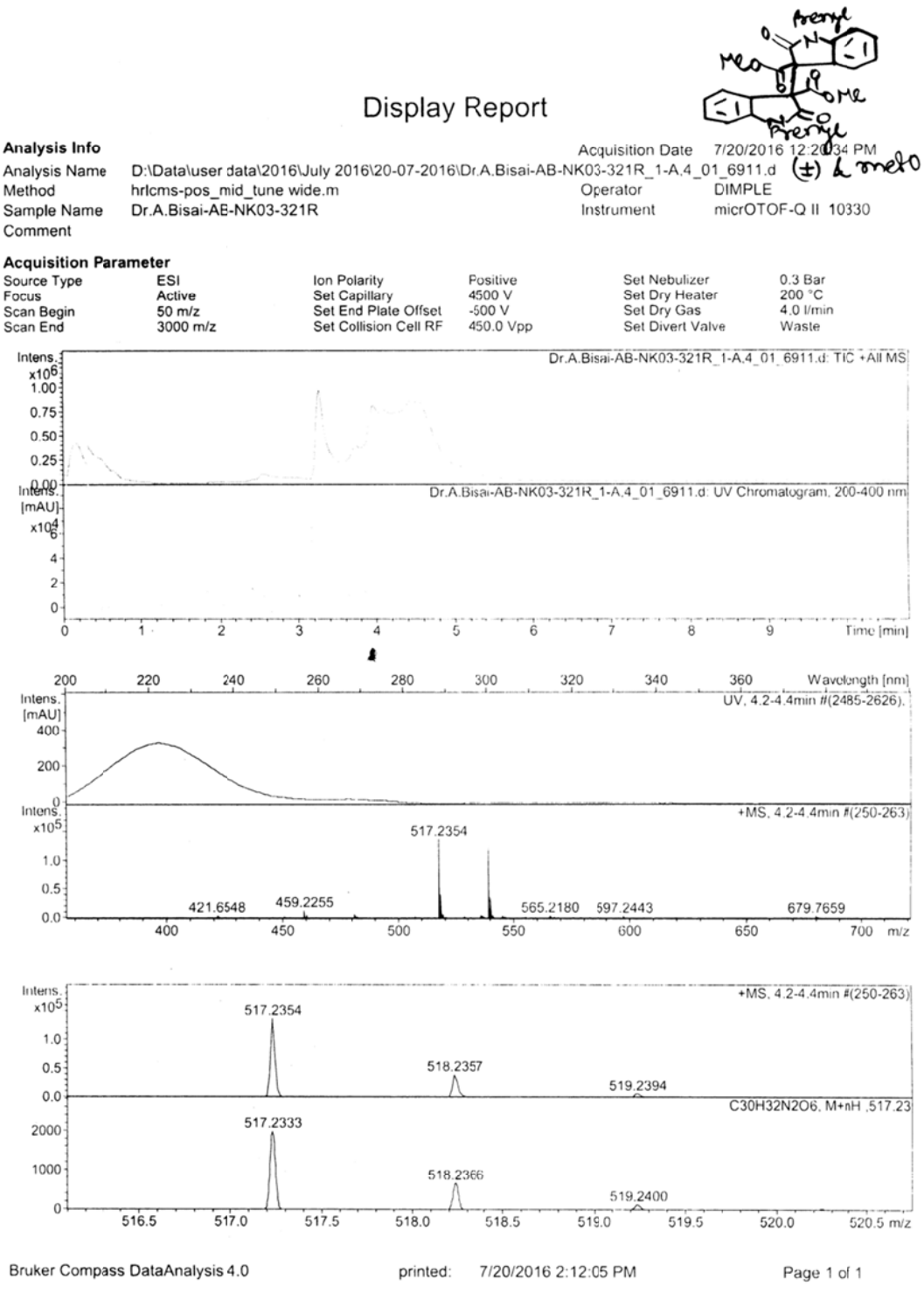




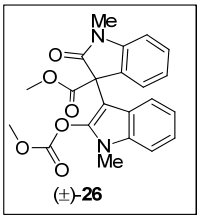
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±) & *meso*-**19e**

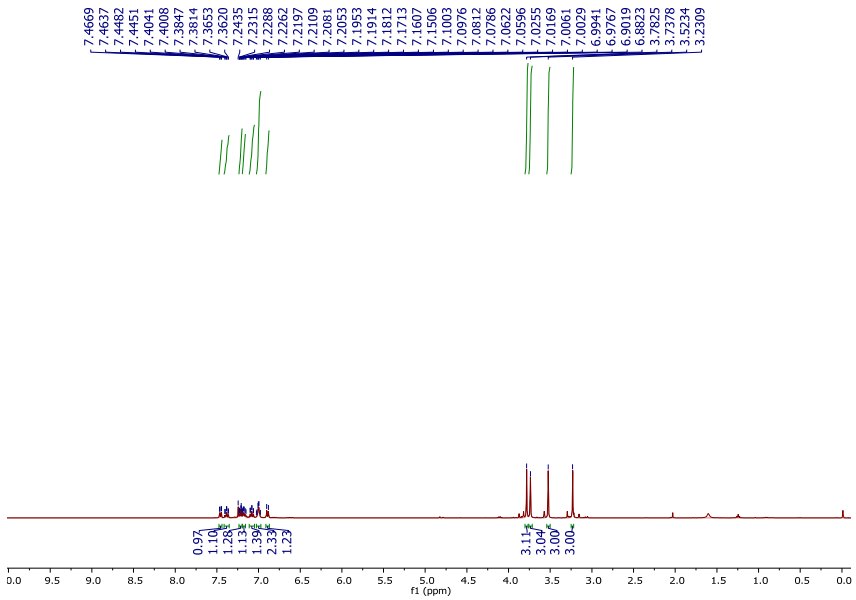


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±) & *meso*-**19e**

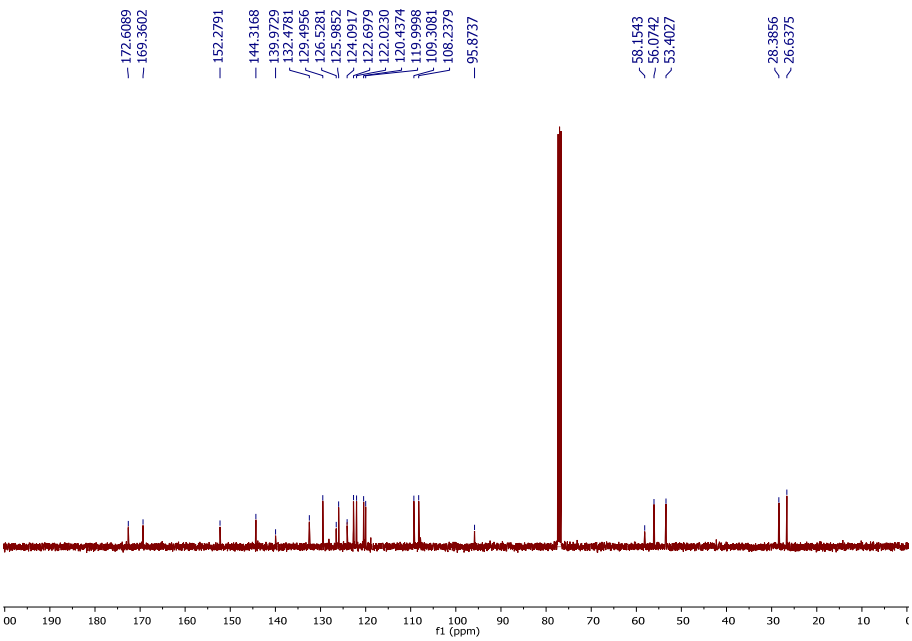


Scanned copy of mass spectrum (HRMS) of compound (±)-**19e**

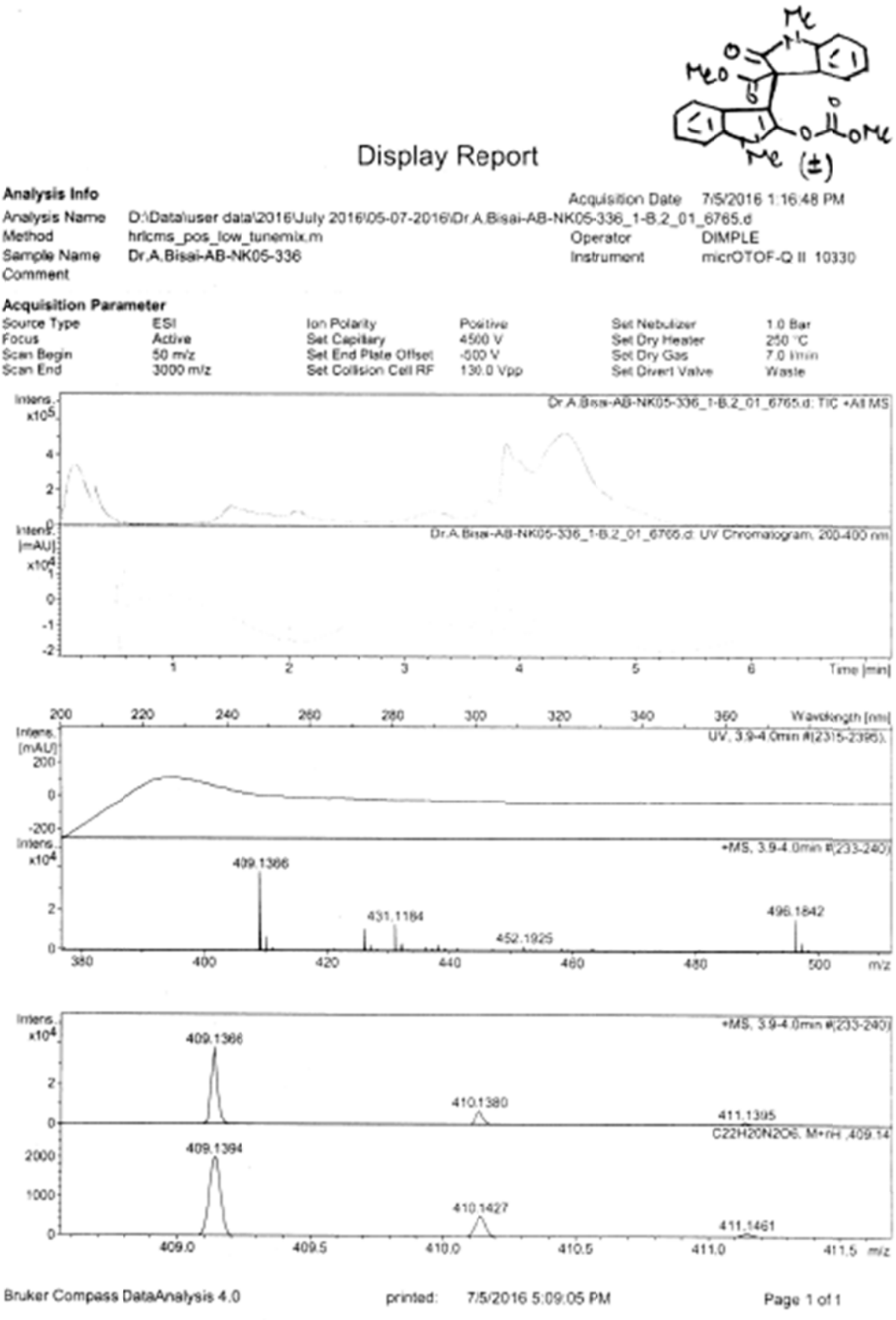




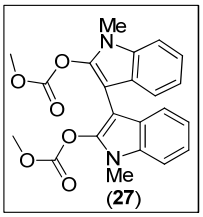
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**26**



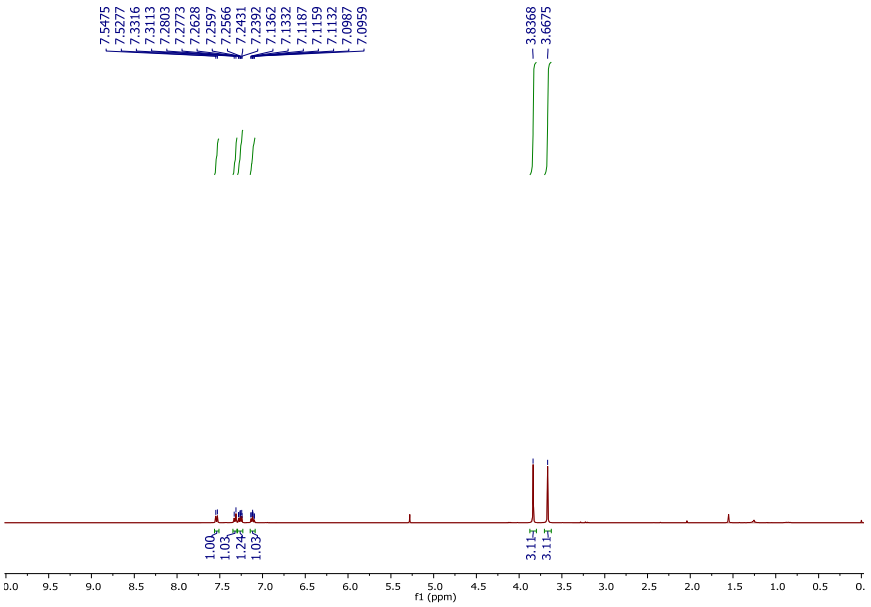
^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**26**



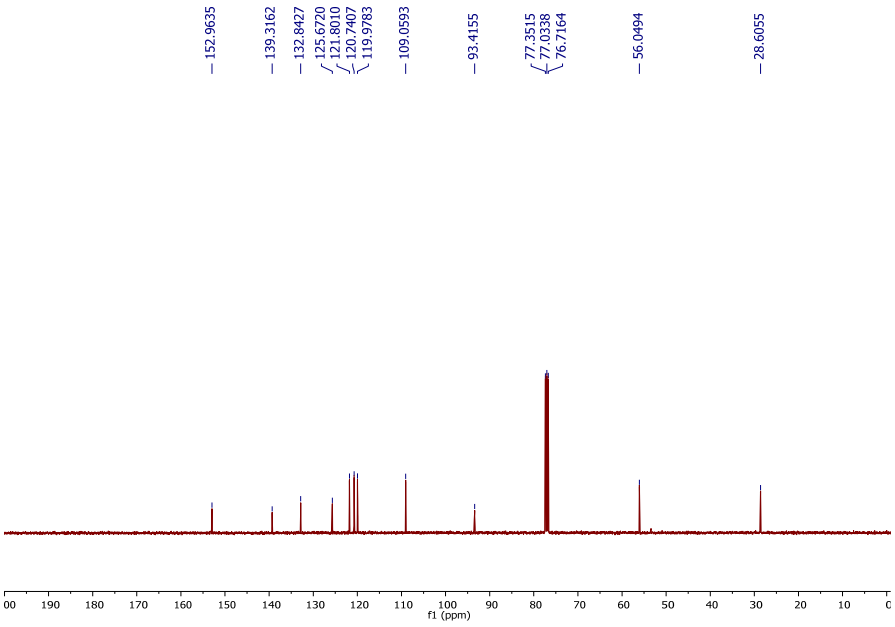
Scanned copy of mass spectrum (HRMS) of compound (±)-**26**



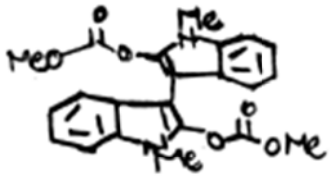
(**27**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound (**27**)



^{13}C NMR (100 MHz, $CDCl_3$) of compound (**27**)



Display Report

Analysis Info

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Method	hrlcms_pos_low_tunemix.m	Operator	DIMPLE
Sample Name	Dr.A.Bisai-AB-NK05-337	Instrument	microTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
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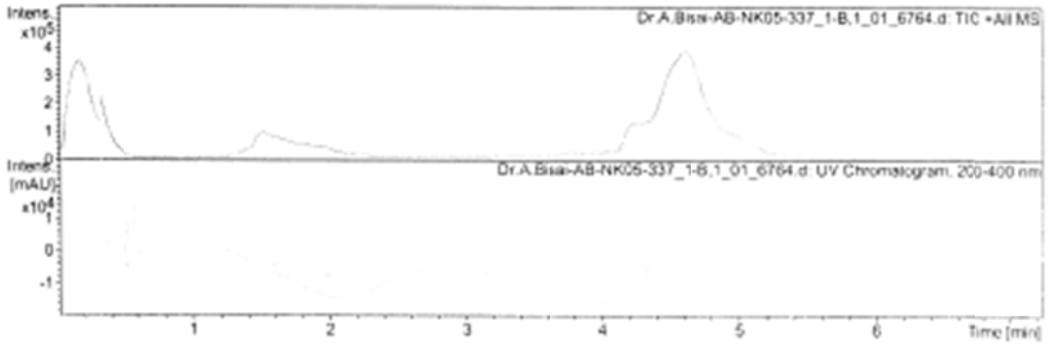
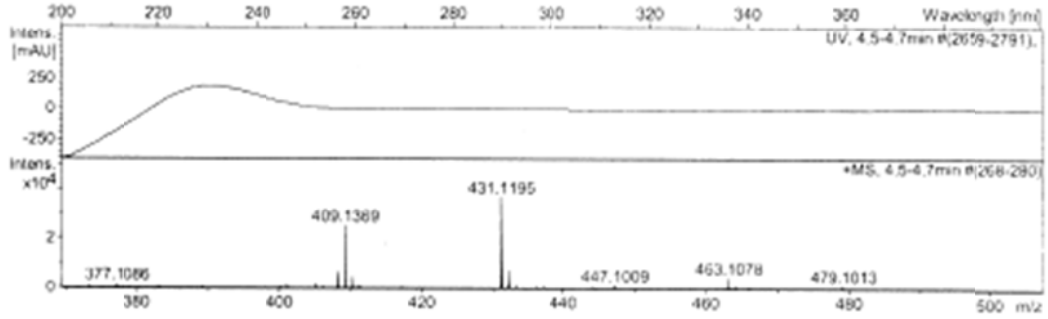
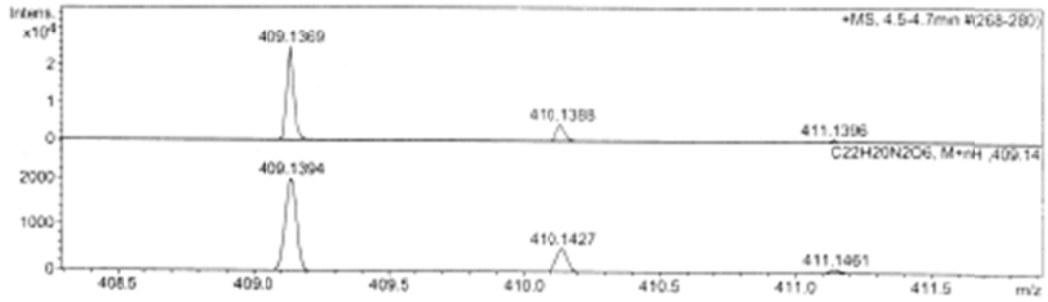
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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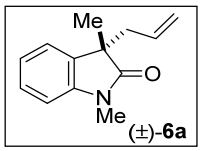
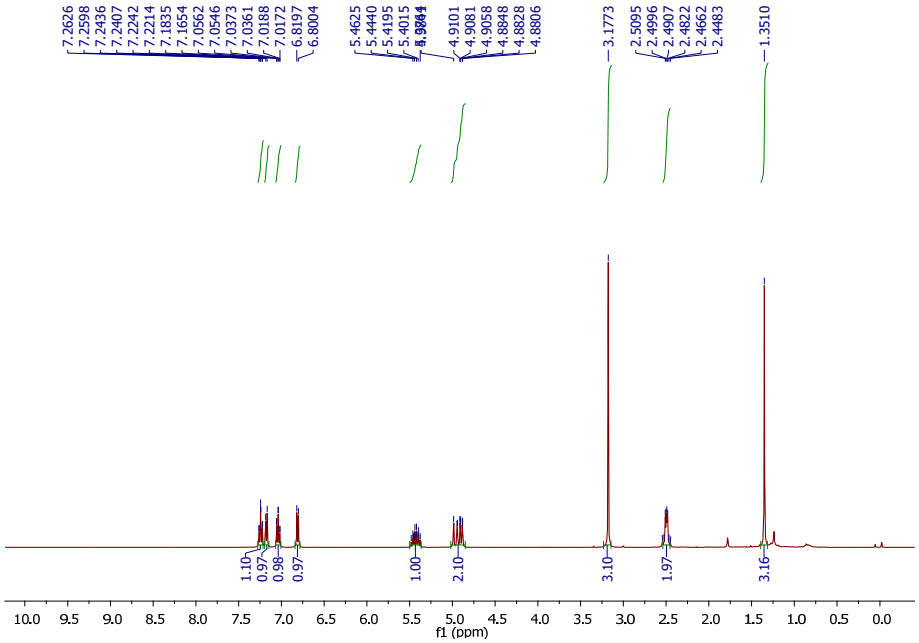
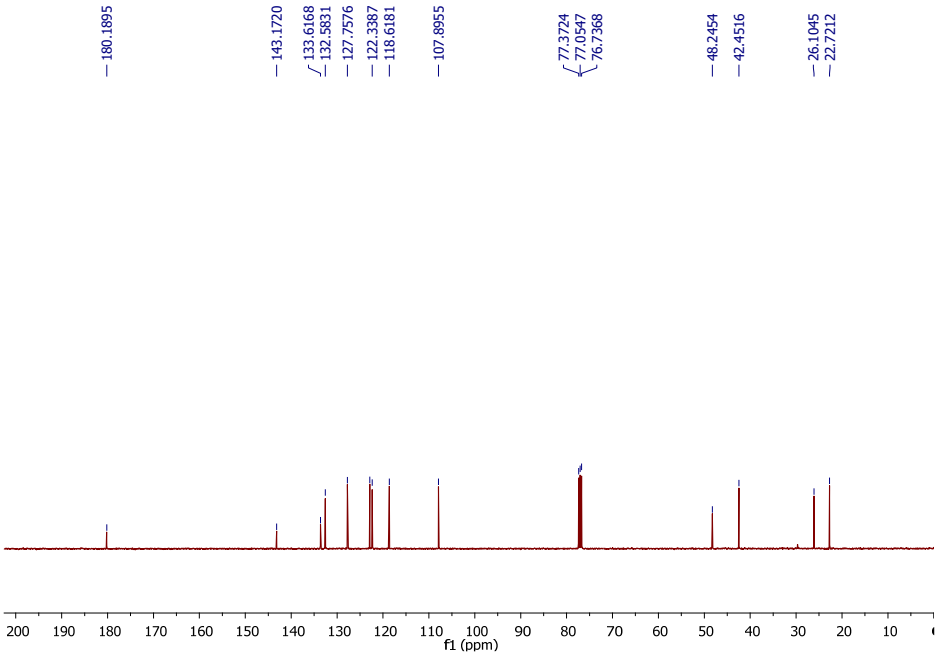
Scanned copy of mass spectrum (HRMS) of compound (**27**)

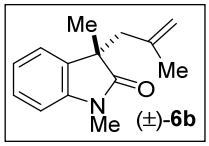


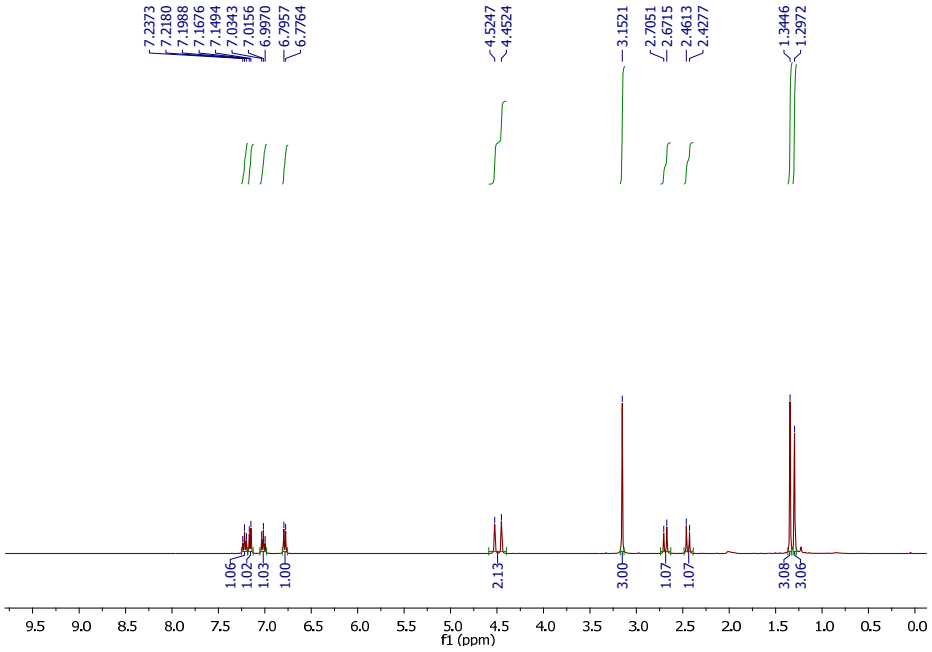


^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6a**

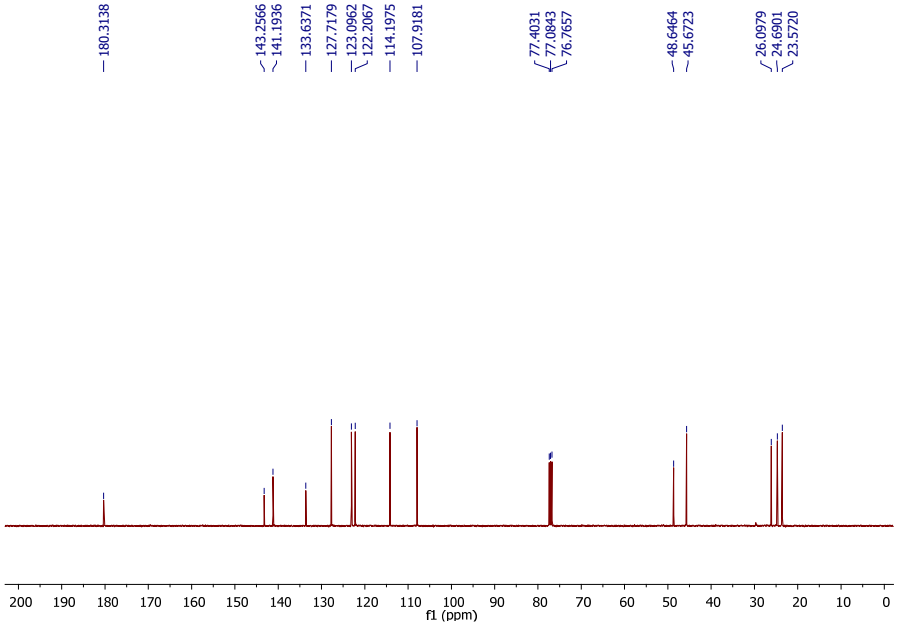


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6a**

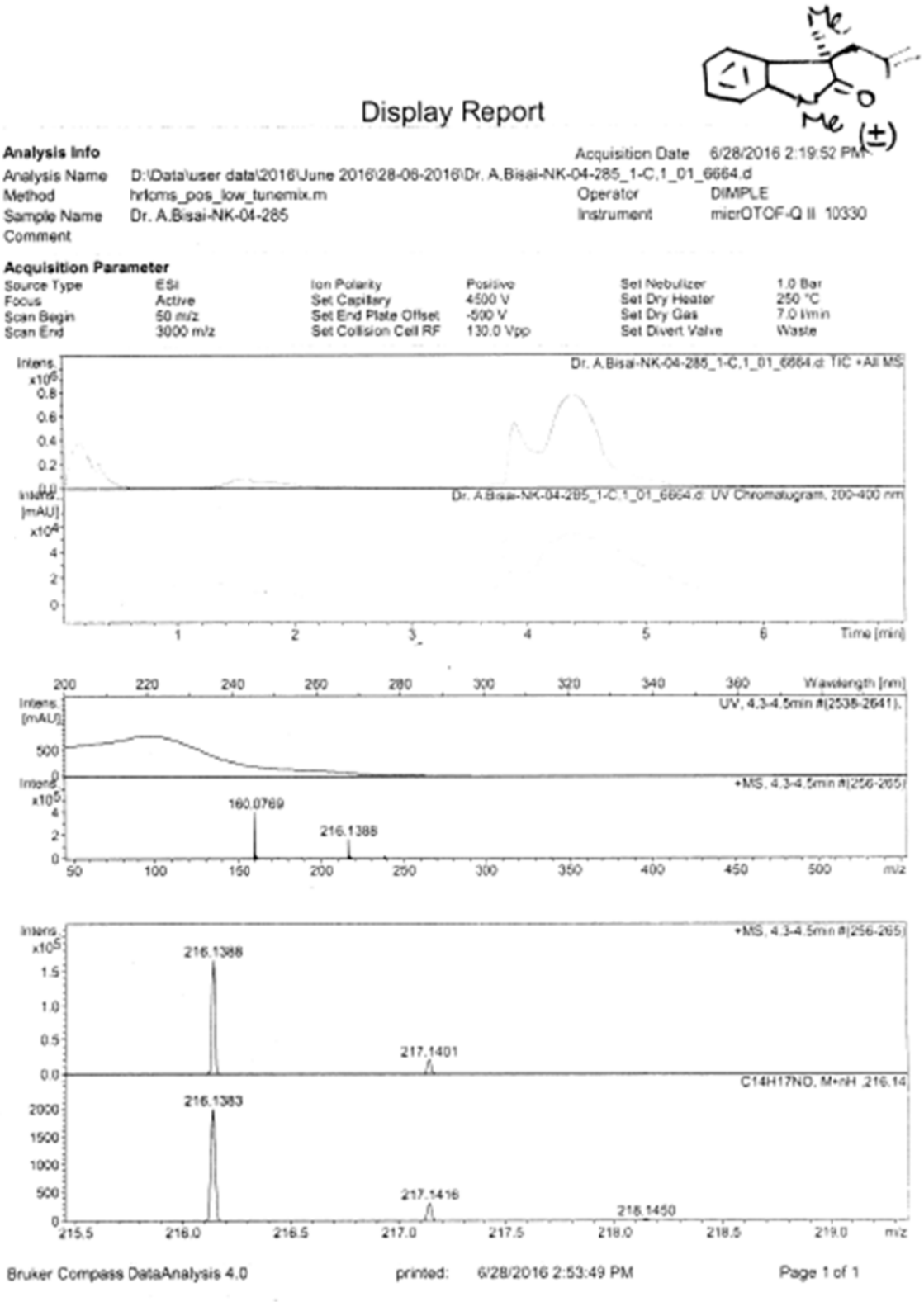




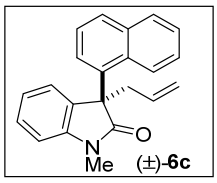
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6b**

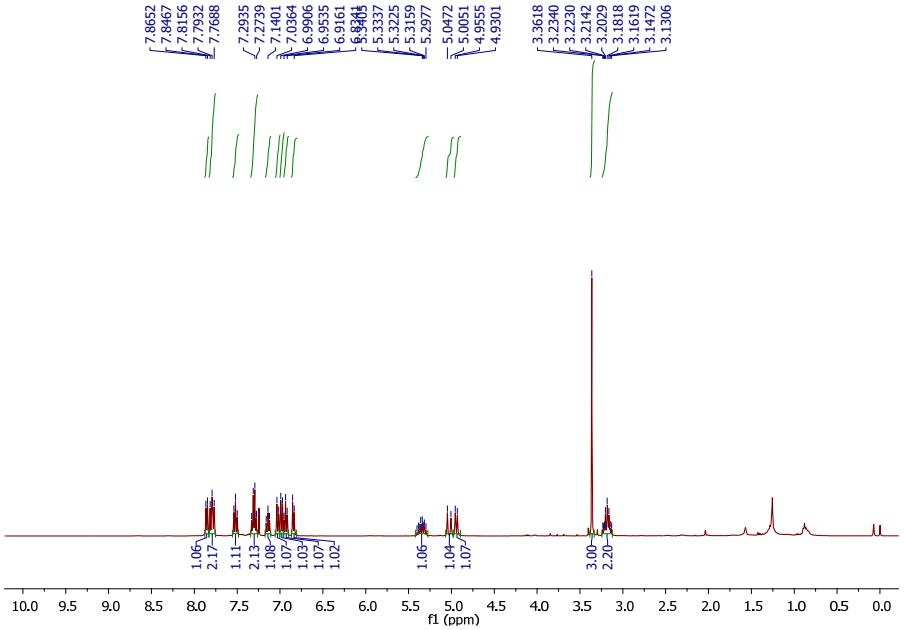


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6b**

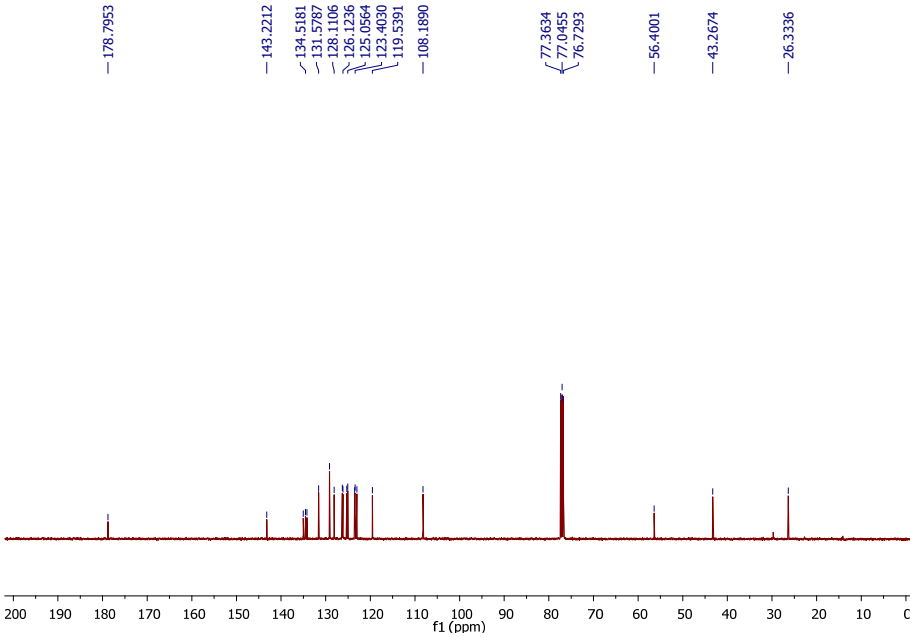


Scanned copy of mass spectrum (HRMS) of compound (±)-**6b**

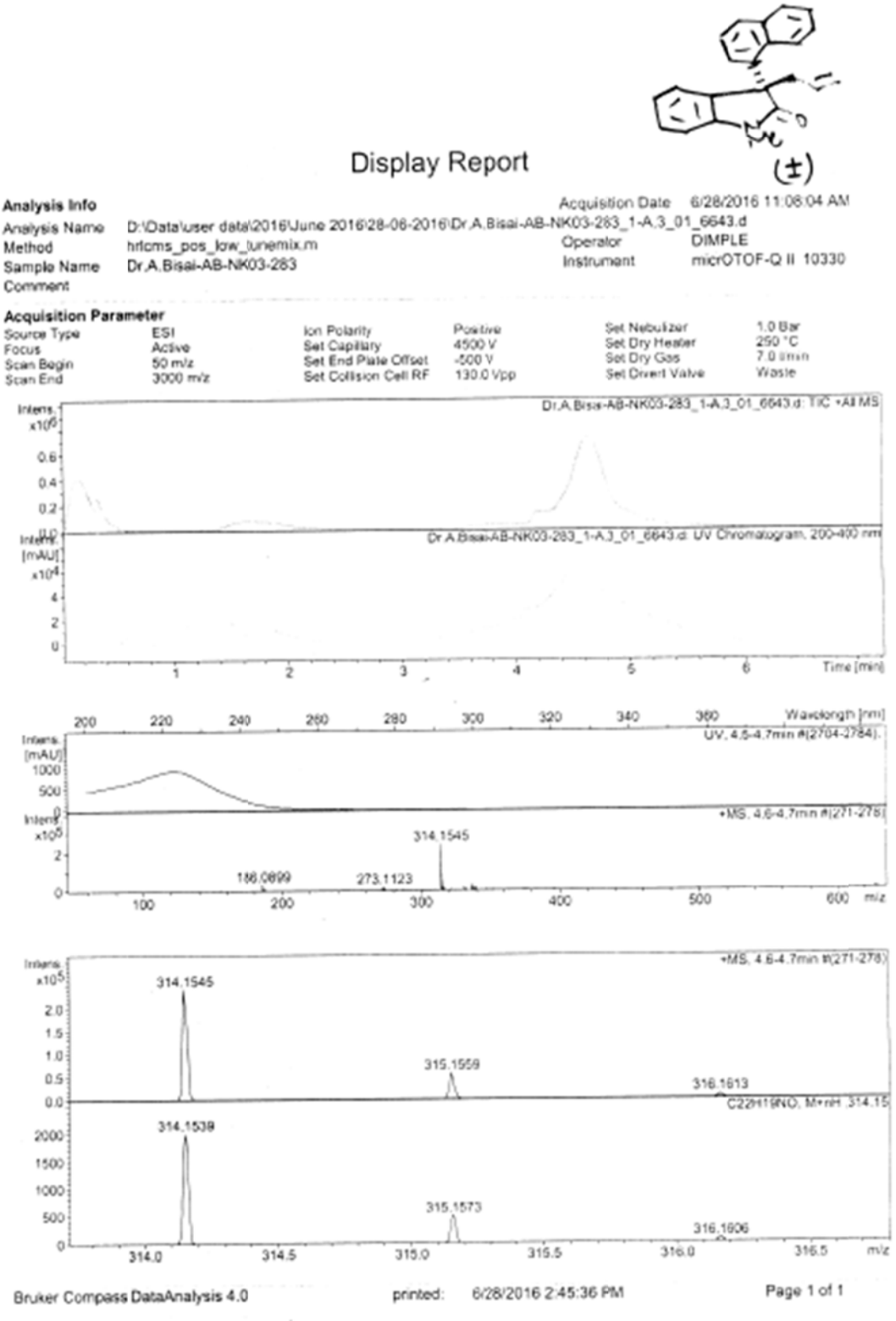




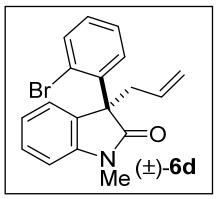
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6c**

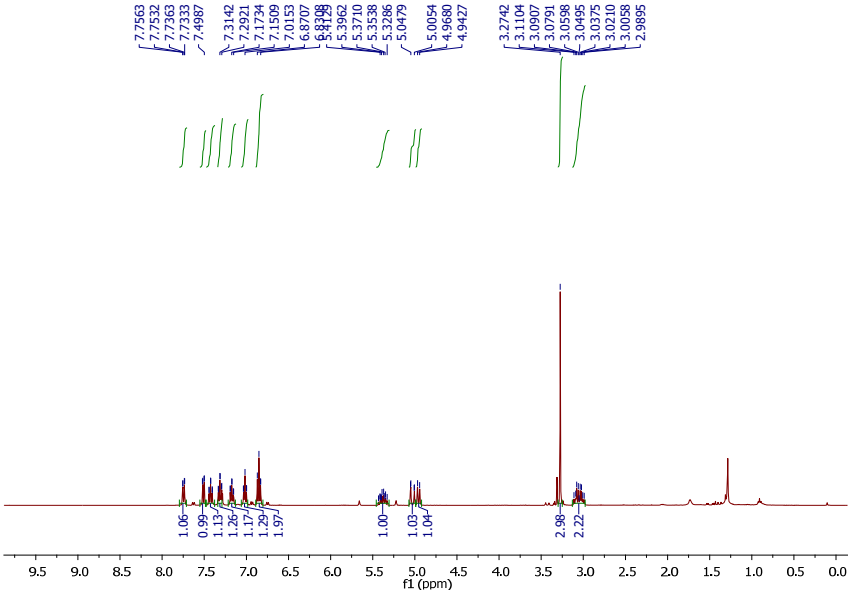


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6c**

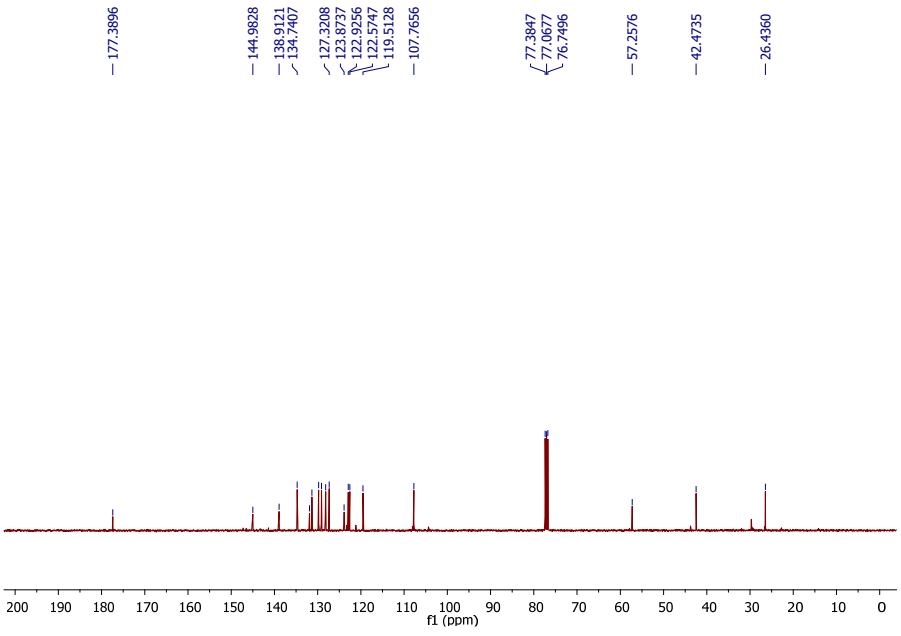


Scanned copy of mass spectrum (HRMS) of compound (±)-**6c**

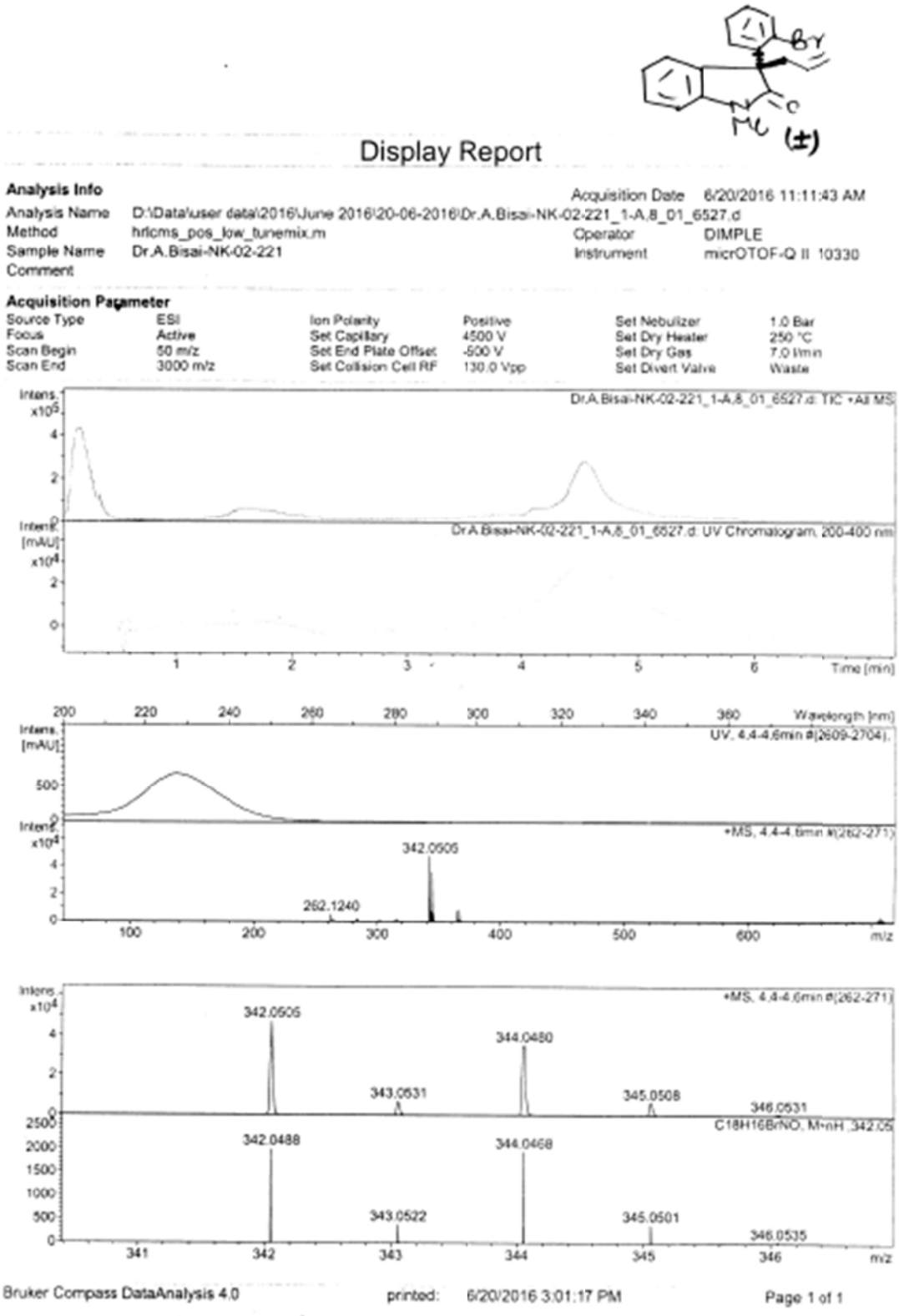




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6d**



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



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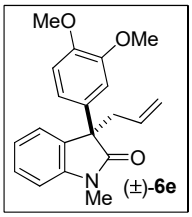
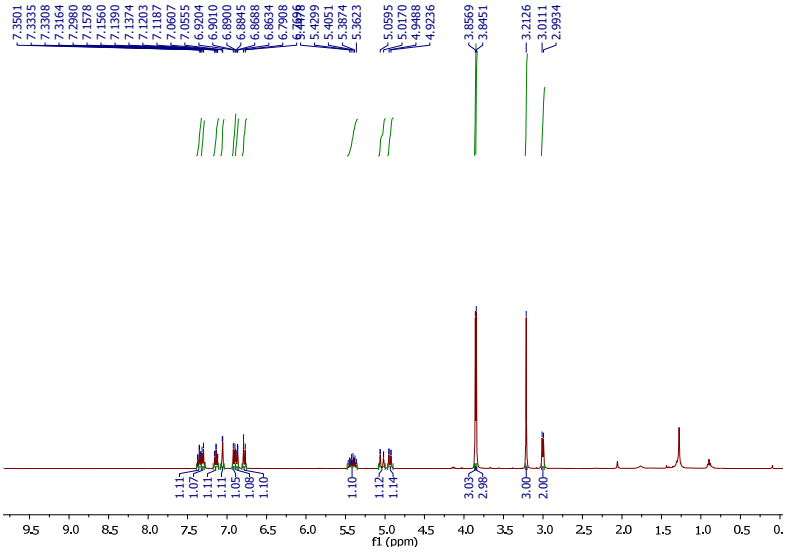
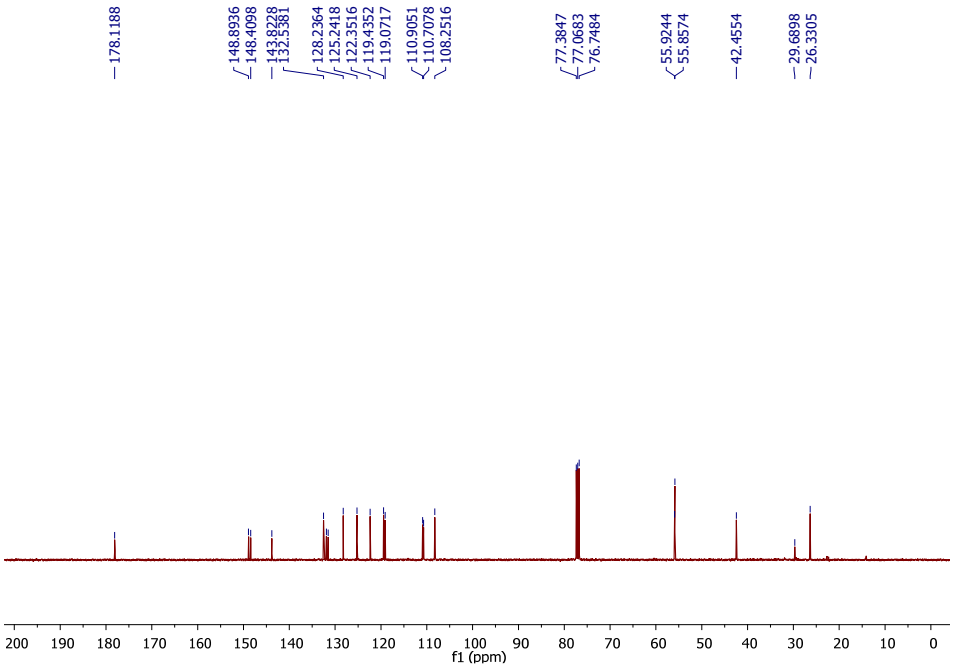
Scanned copy of mass spectrum (HRMS) of compound (±)-**6d**

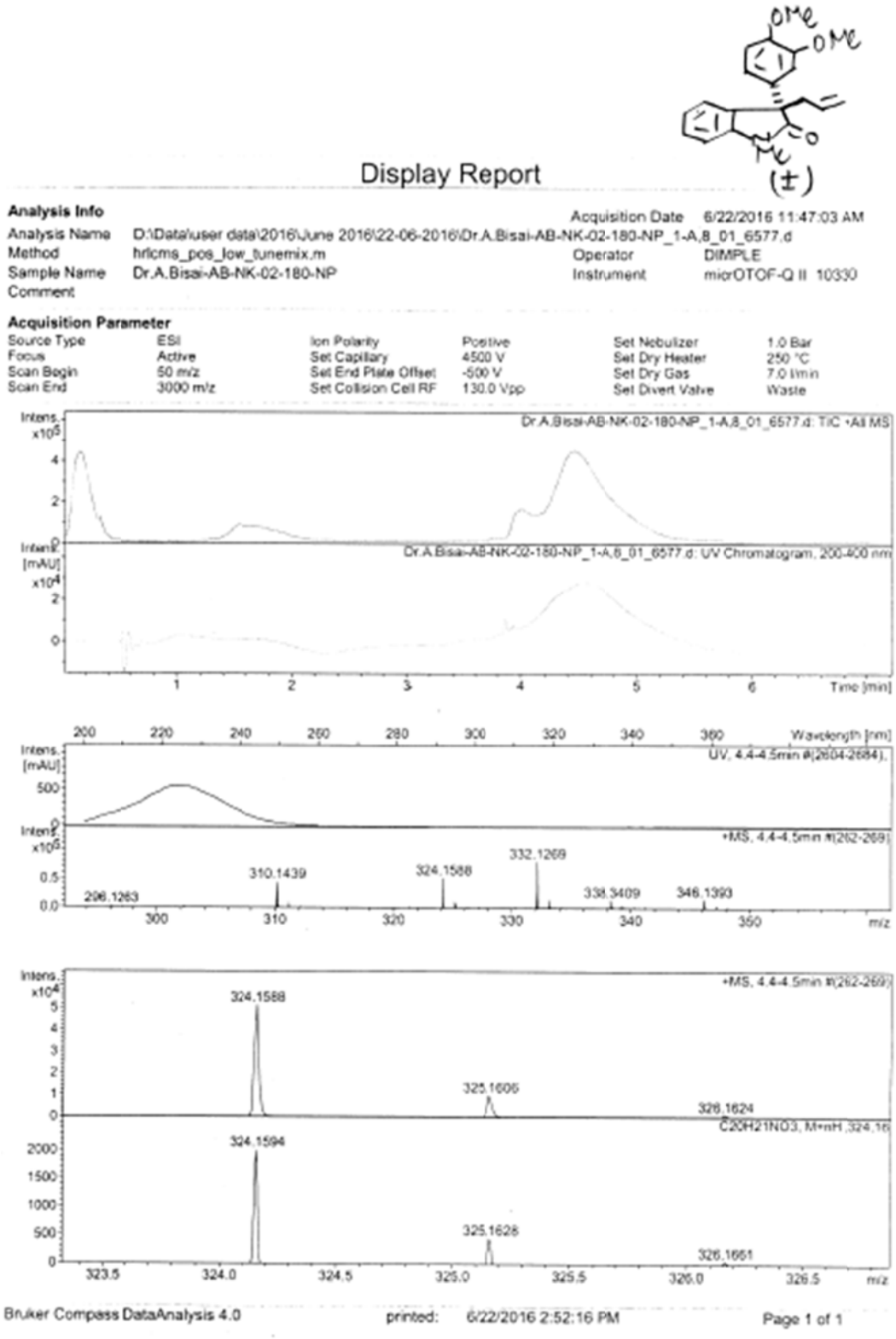




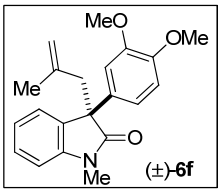
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6e**

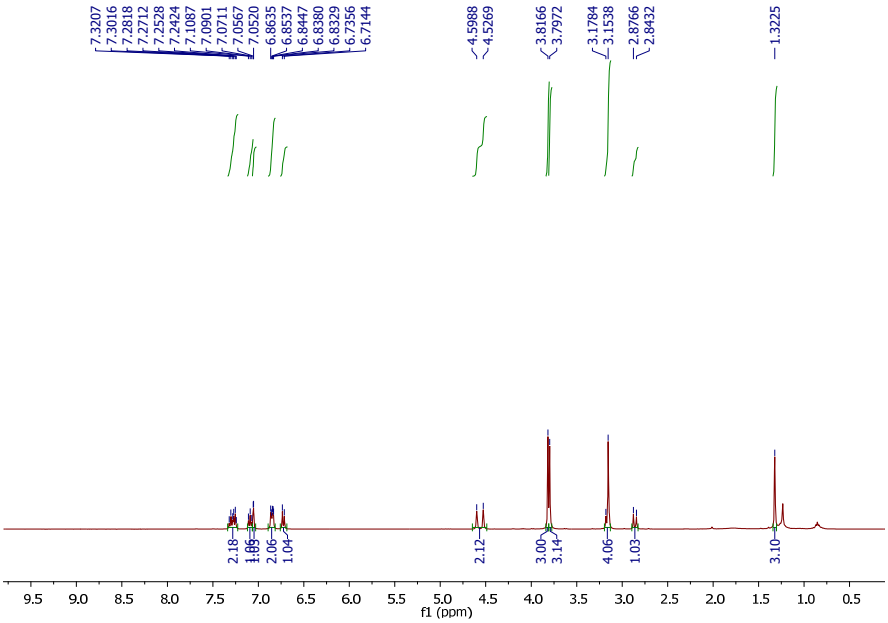


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6e**

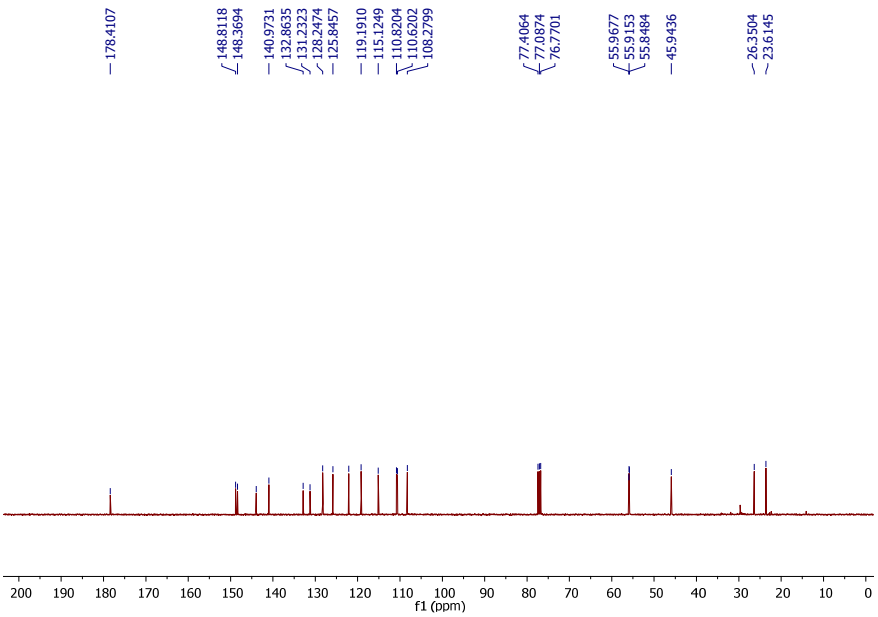


Scanned copy of mass spectrum (HRMS) of compound (±)-**6e**

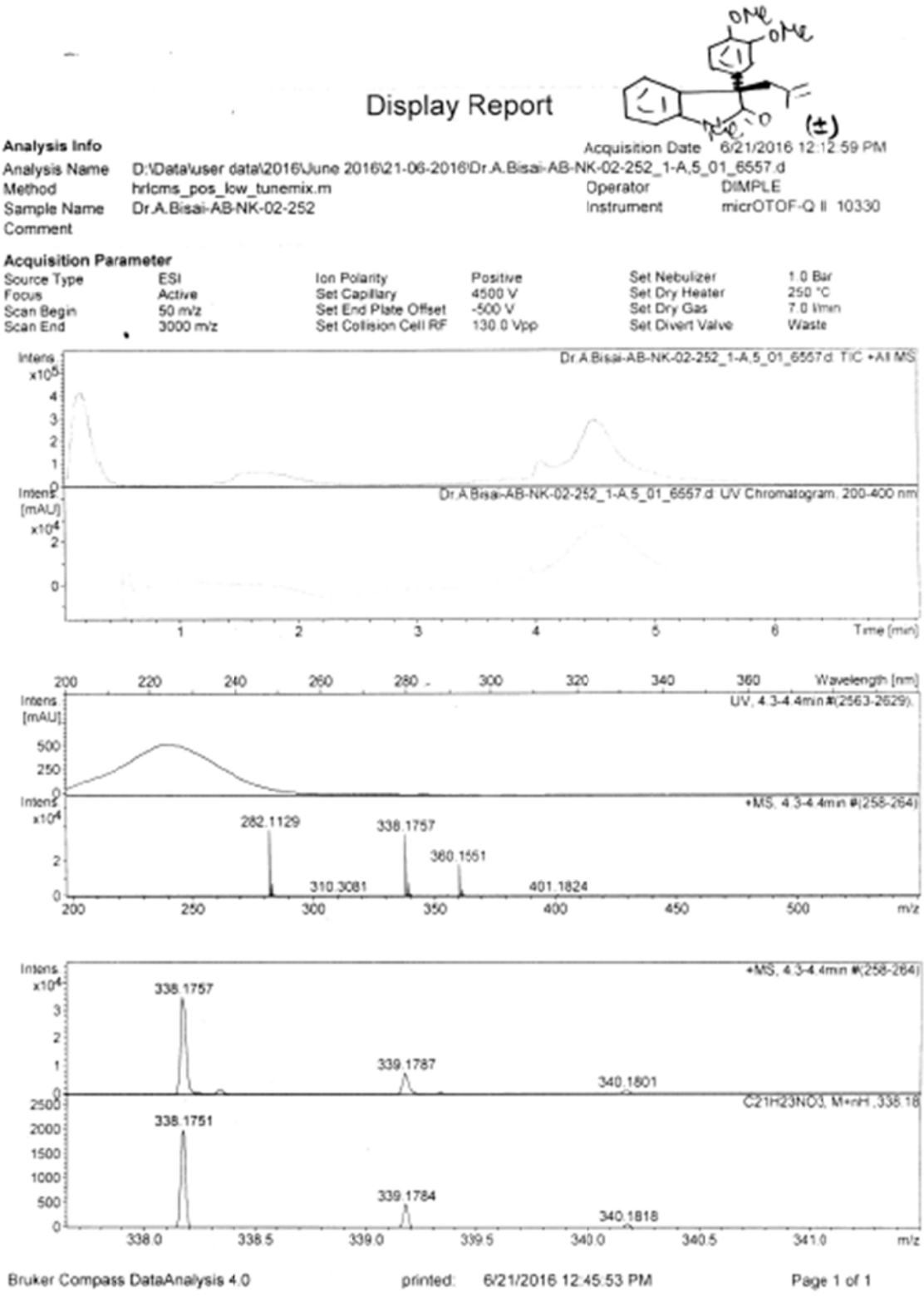




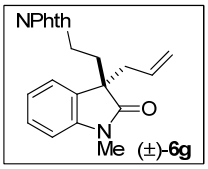
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6f**

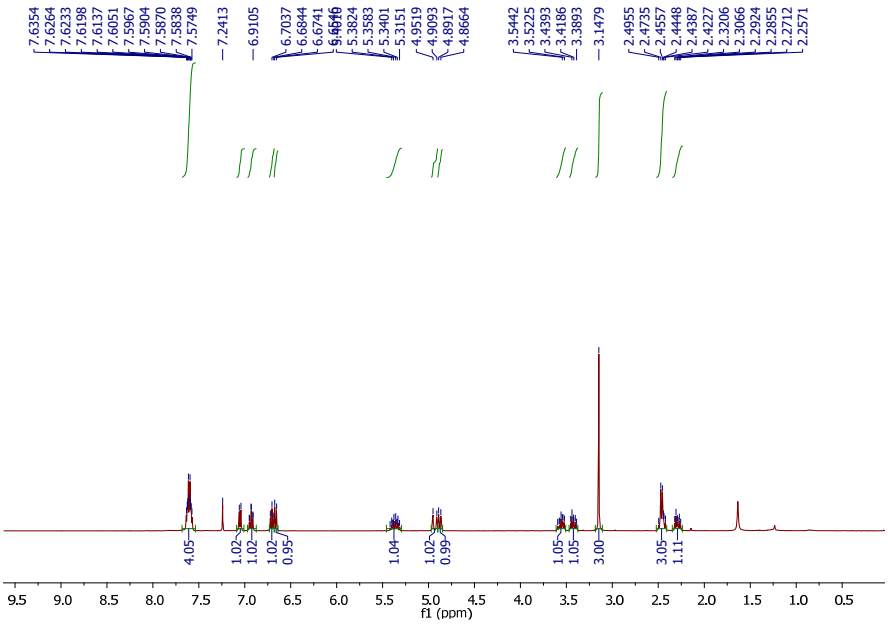


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6f**

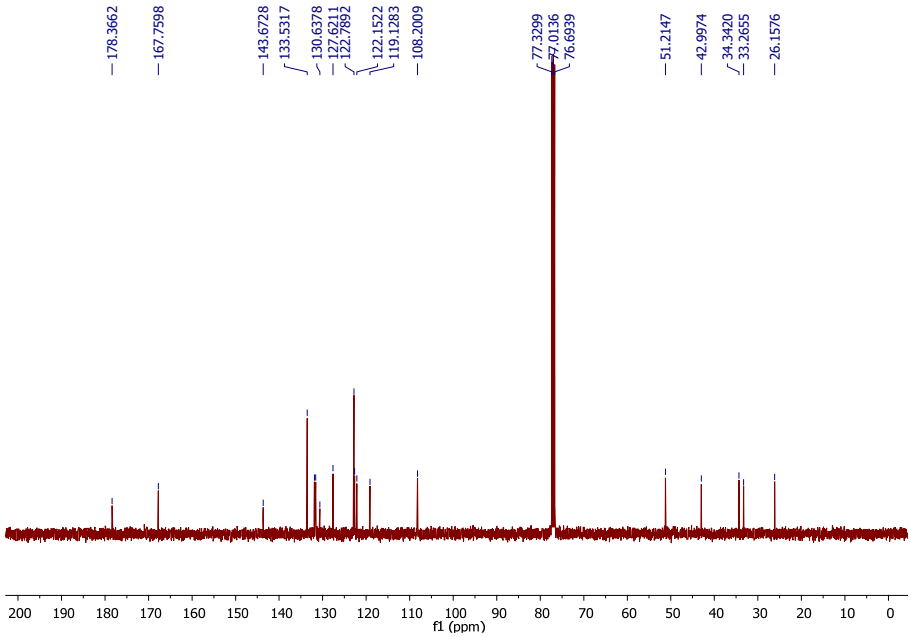


Scanned copy of mass spectrum (HRMS) of compound (±)-**6f**

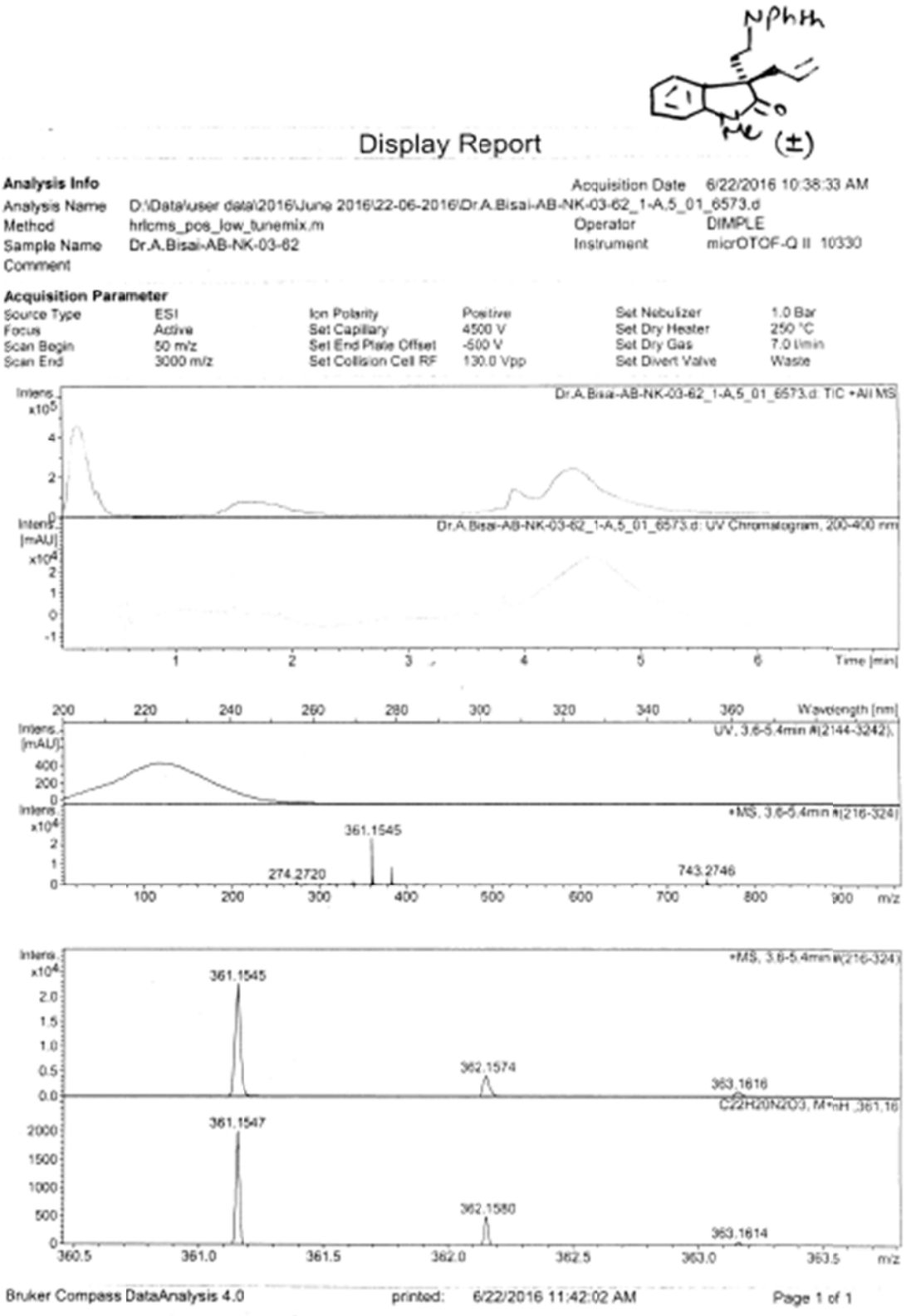




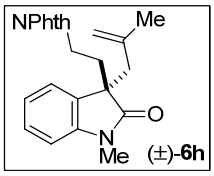
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6g**

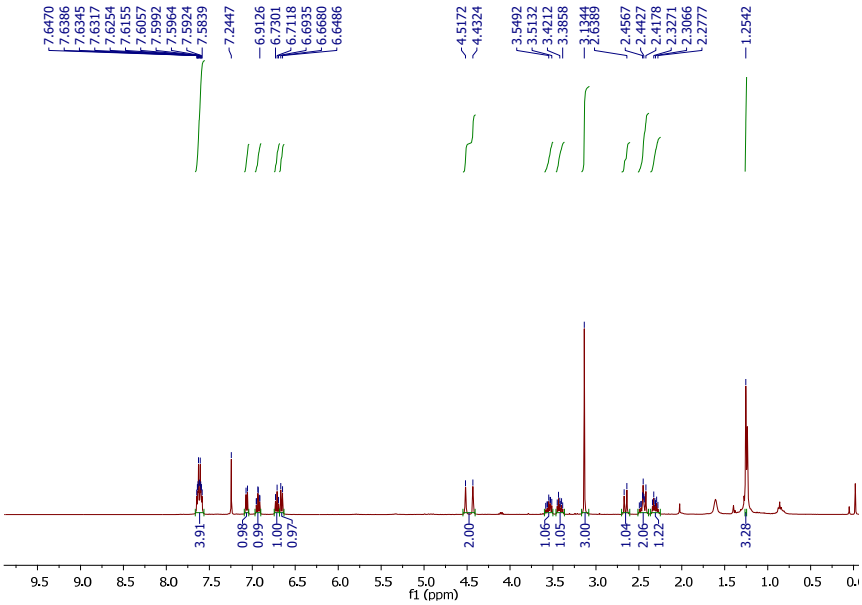


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6g**

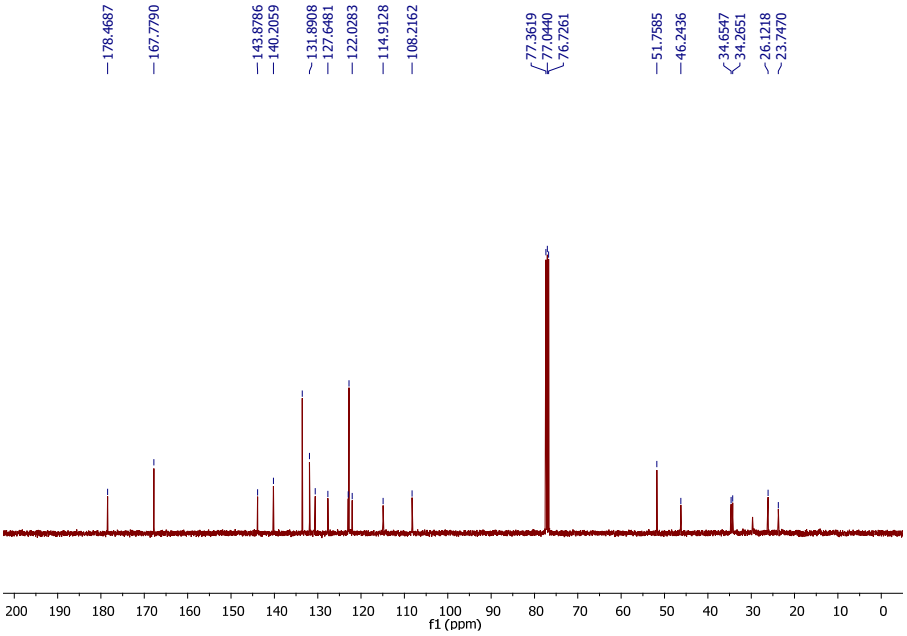


Scanned copy of mass spectrum (HRMS) of compound (±)-**6g**

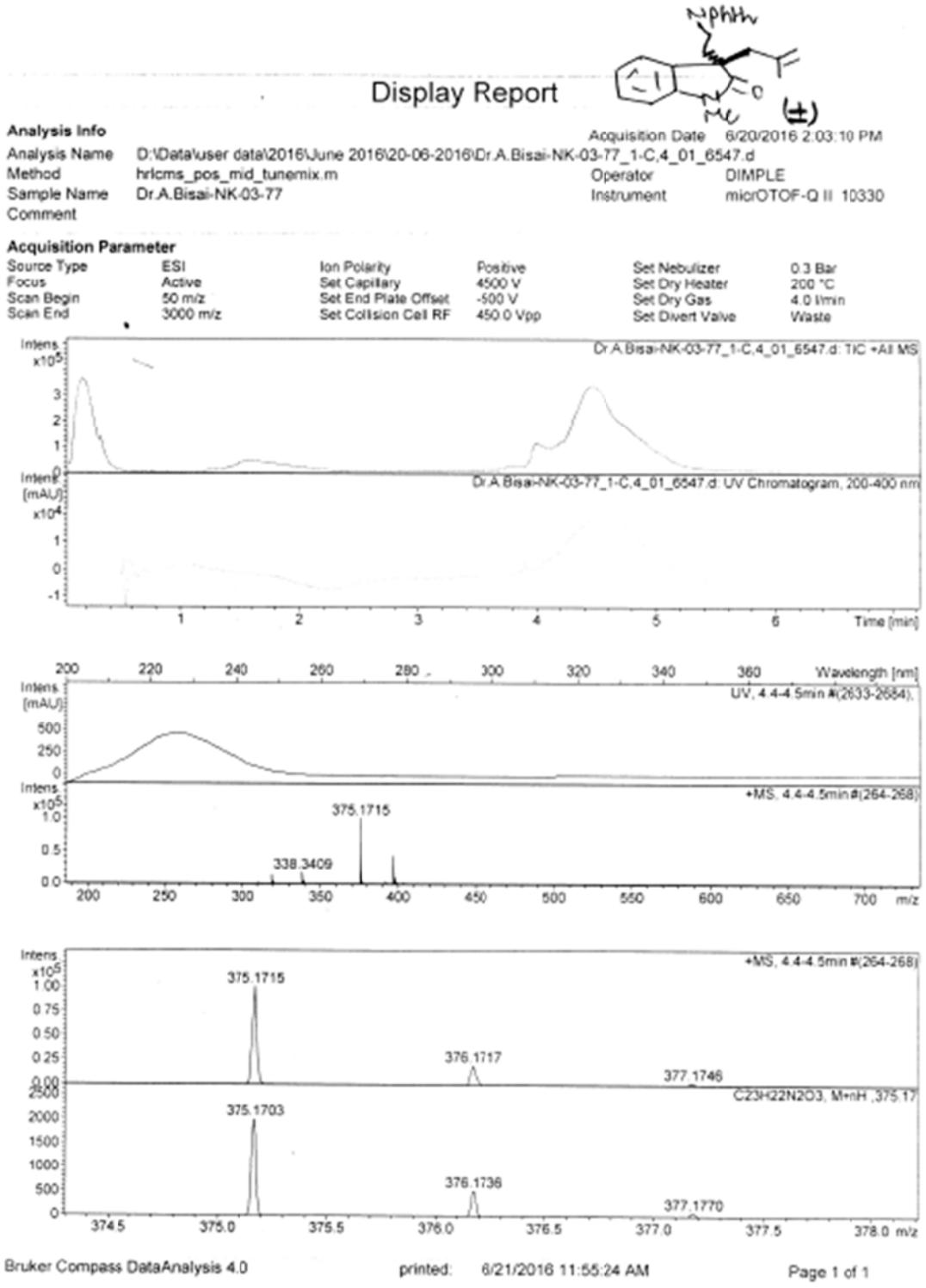




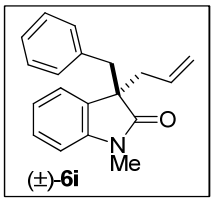
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6h**



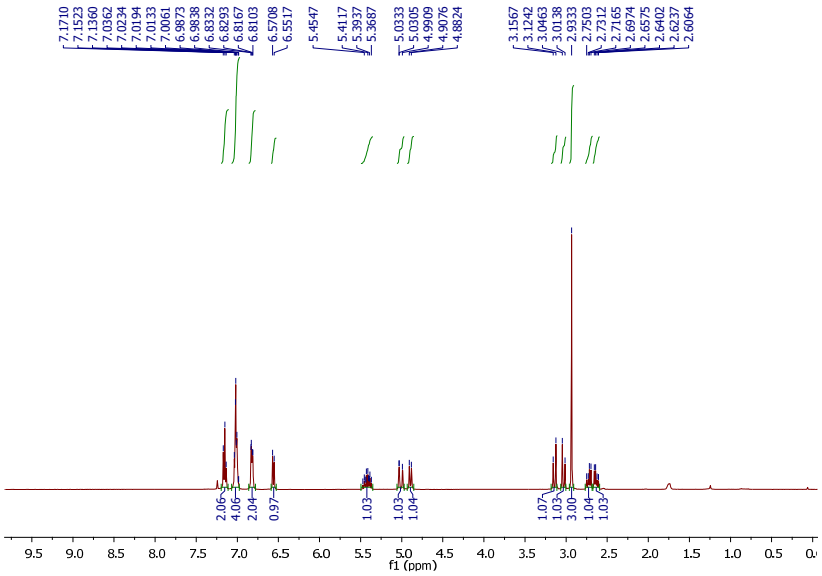
^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6h**



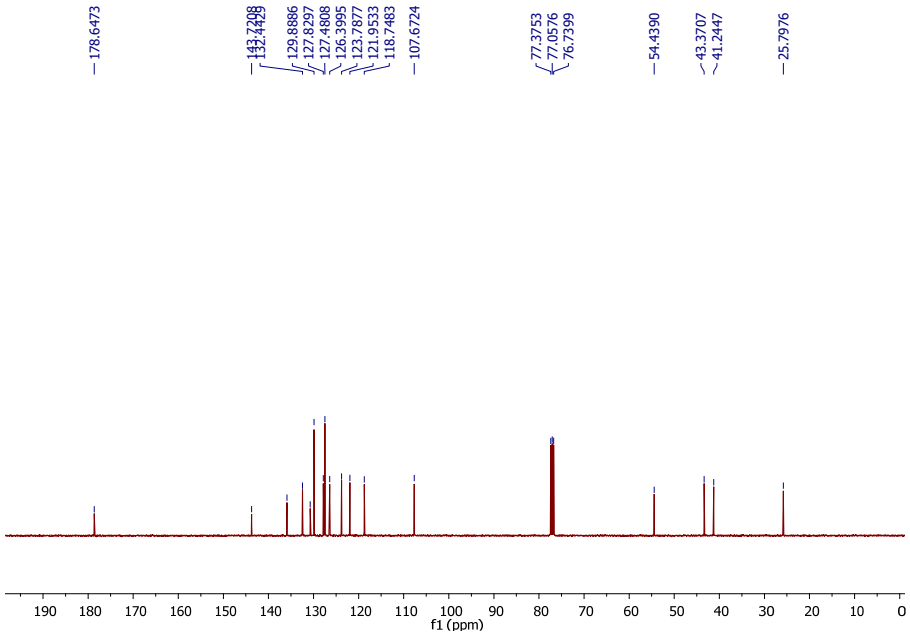
Scanned copy of mass spectrum (HRMS) of compound (±)-**6h**



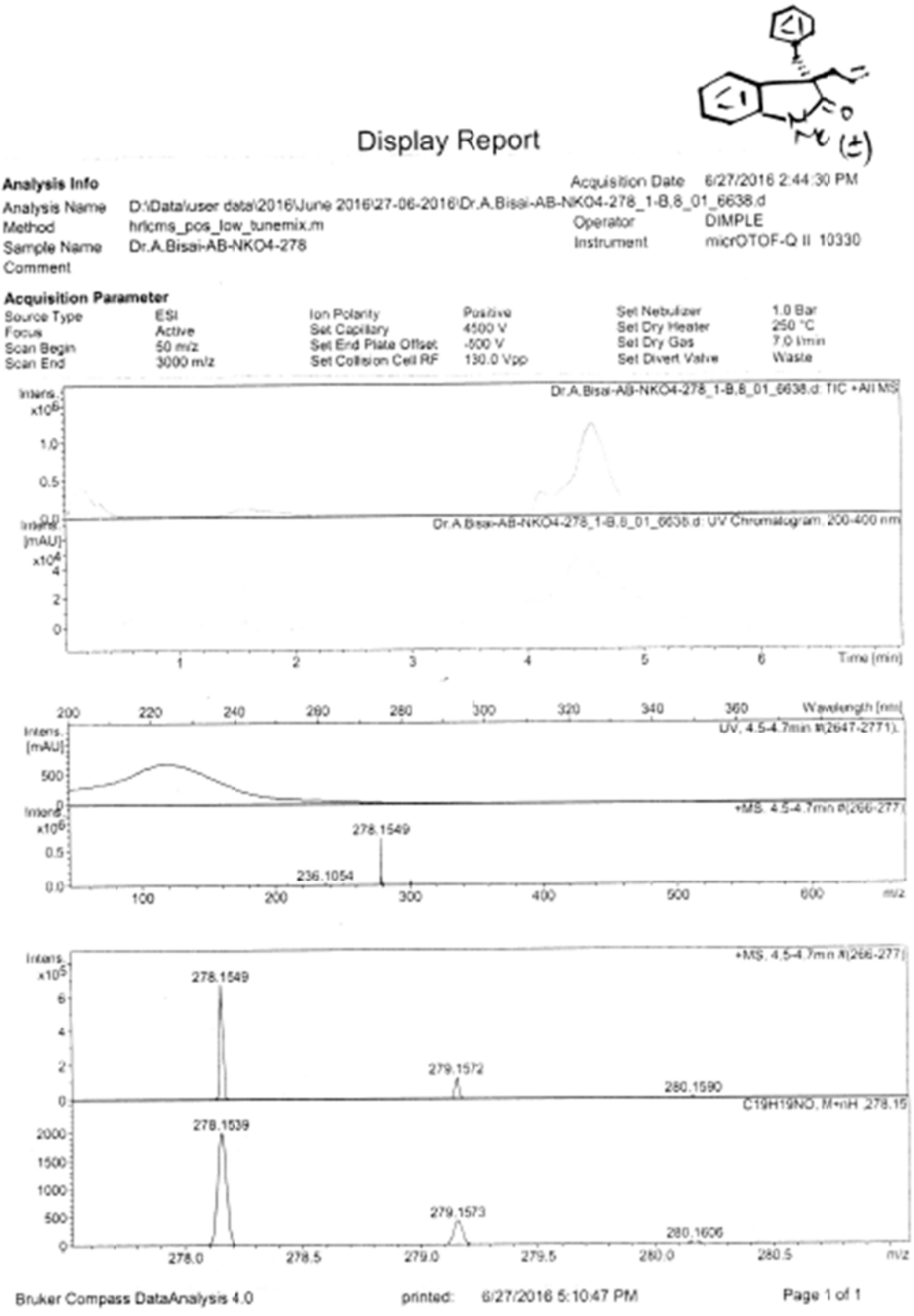
(±)-**6i**



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



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



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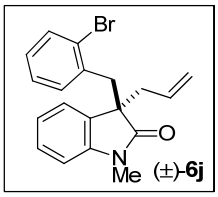
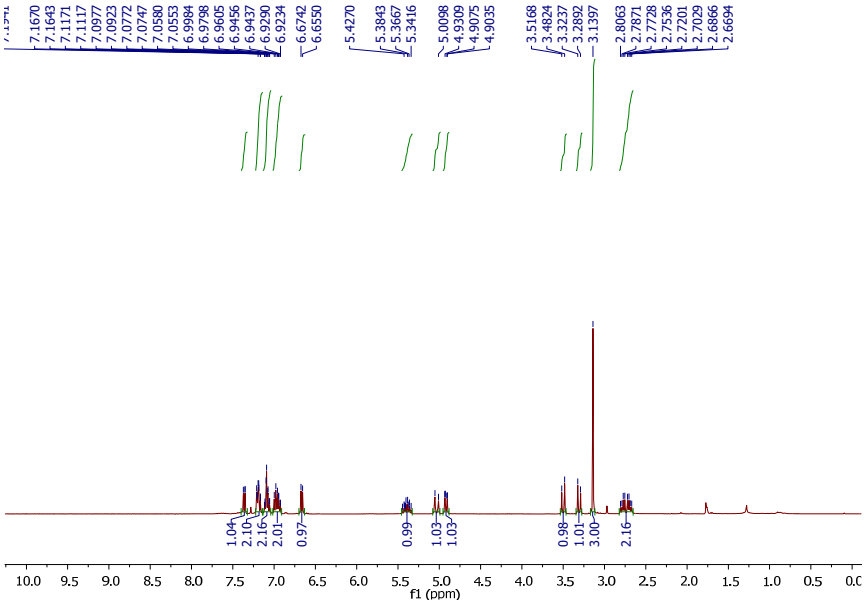
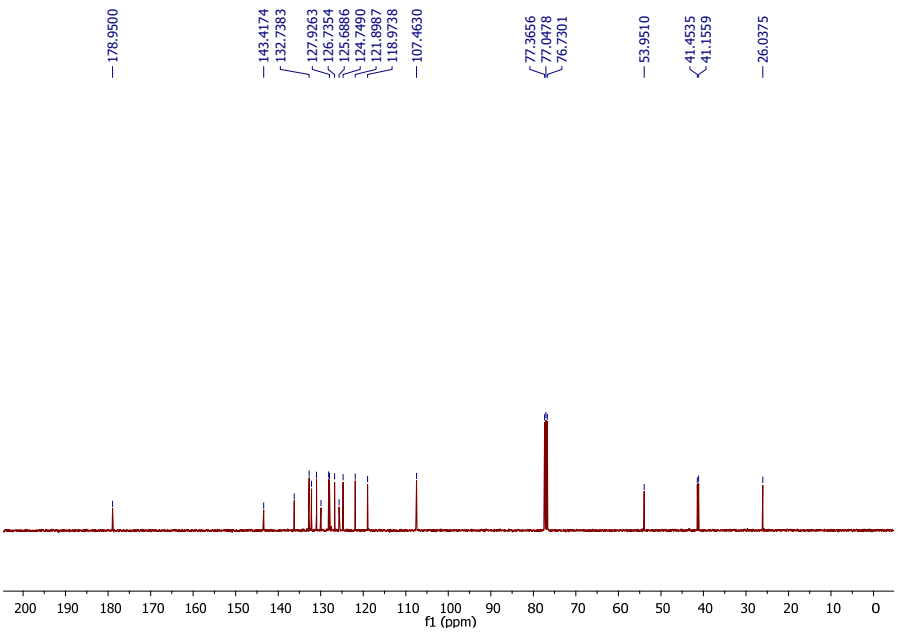
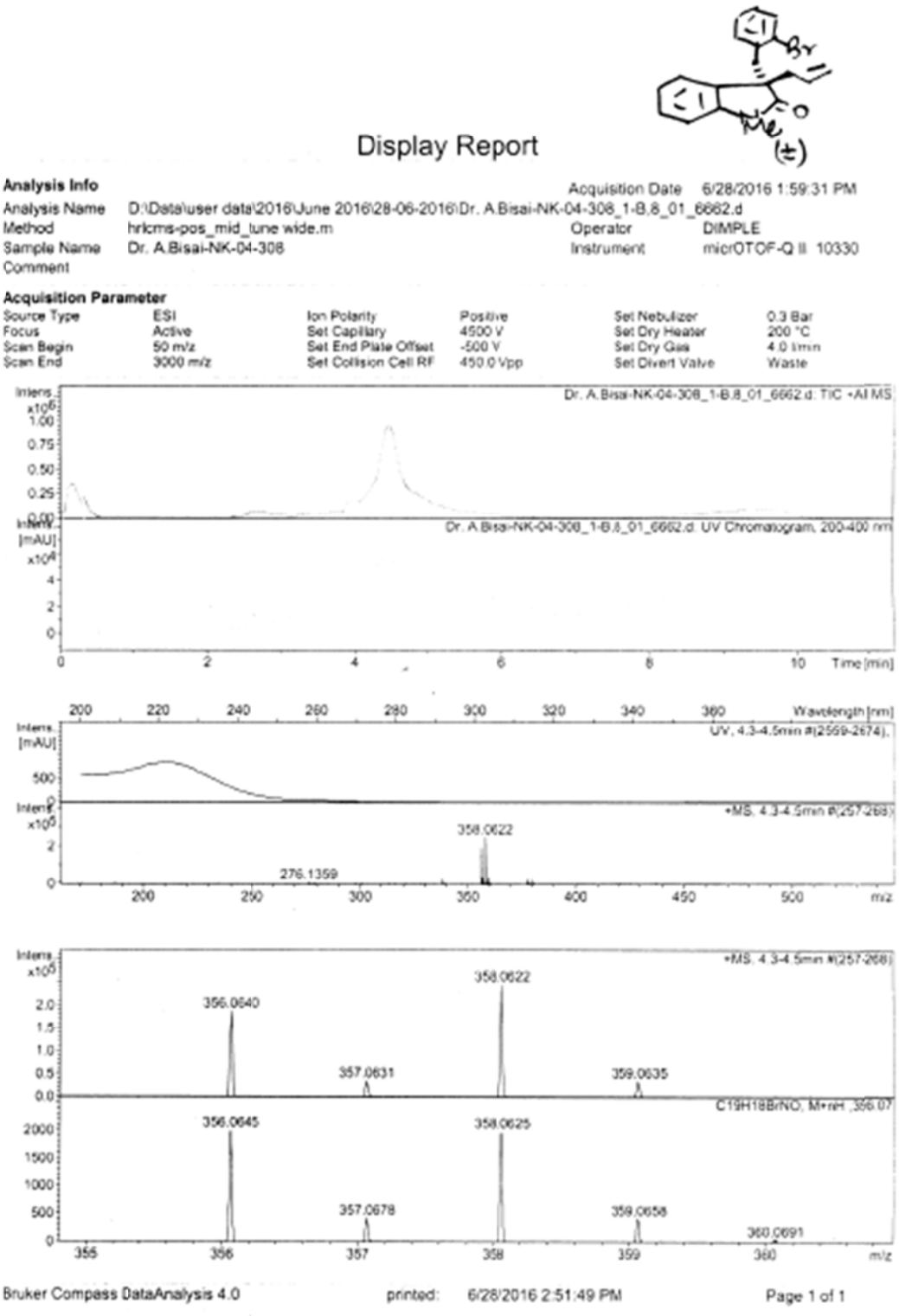




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6j**



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



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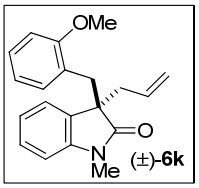
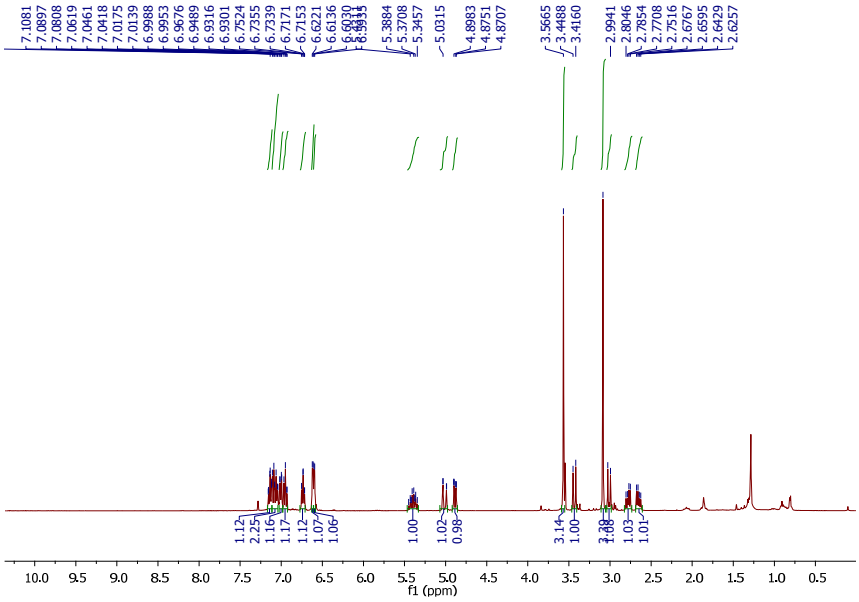
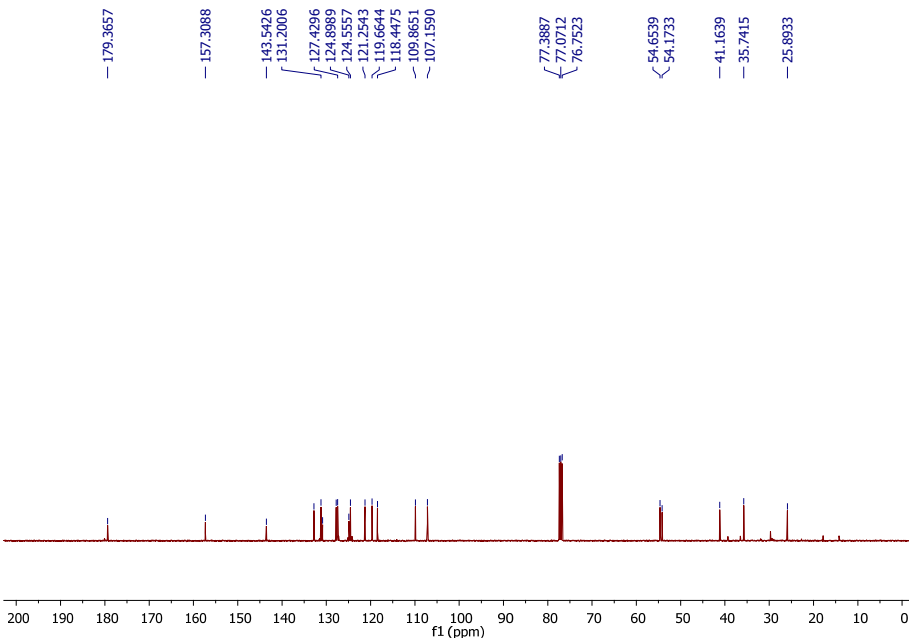
Scanned copy of mass spectrum (HRMS) of compound (±)-**6j**

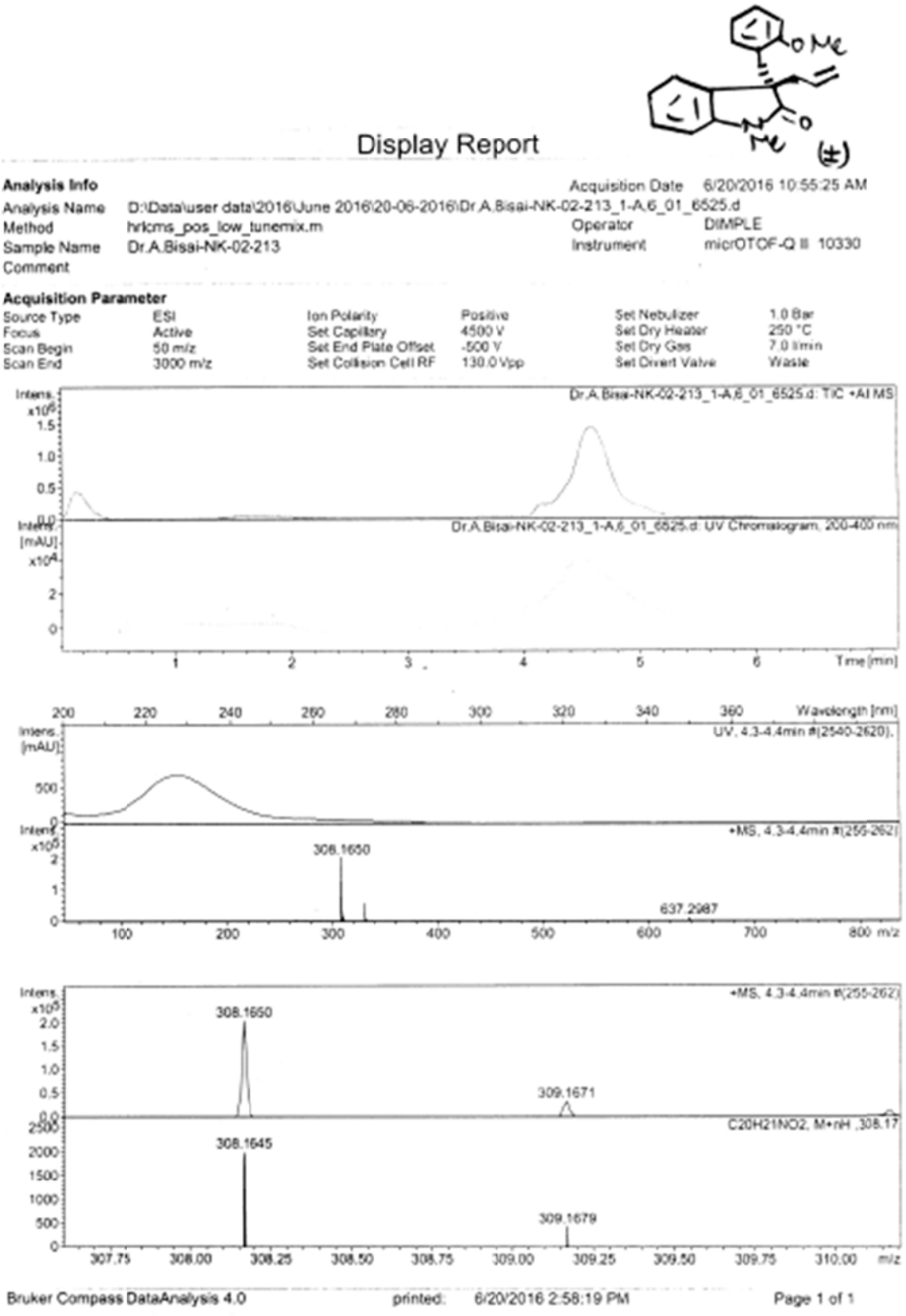




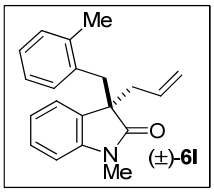
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6k**

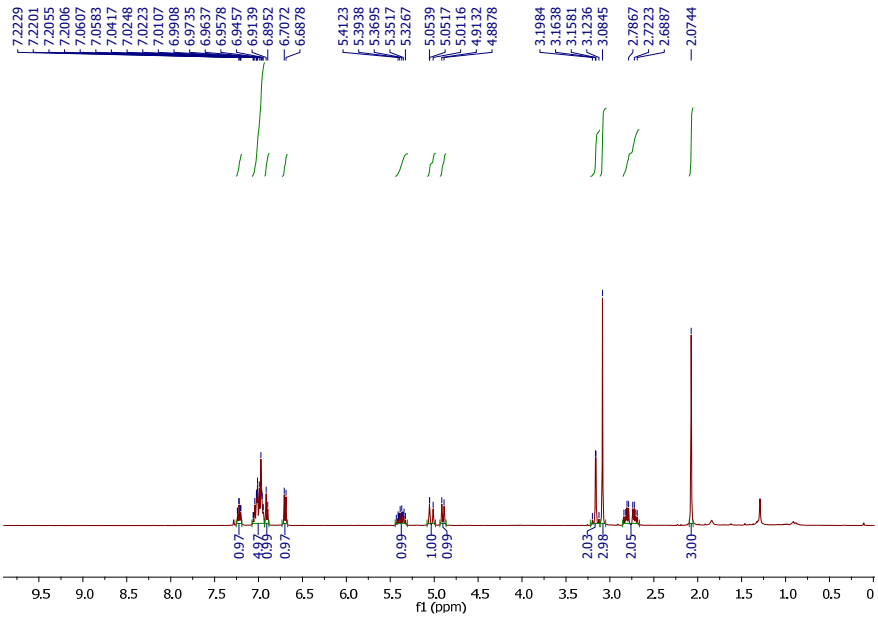


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6k**

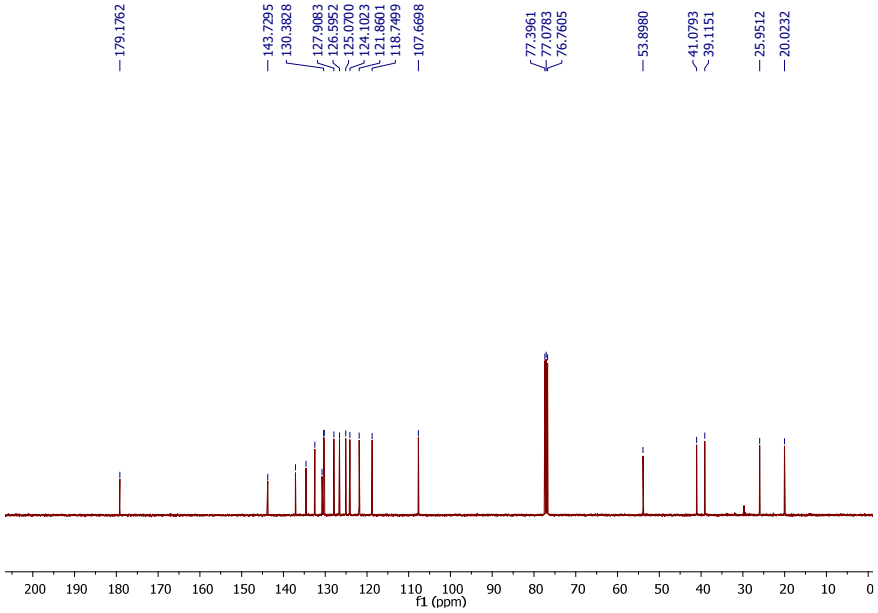


Scanned copy of mass spectrum (HRMS) of compound (±)-**6k**

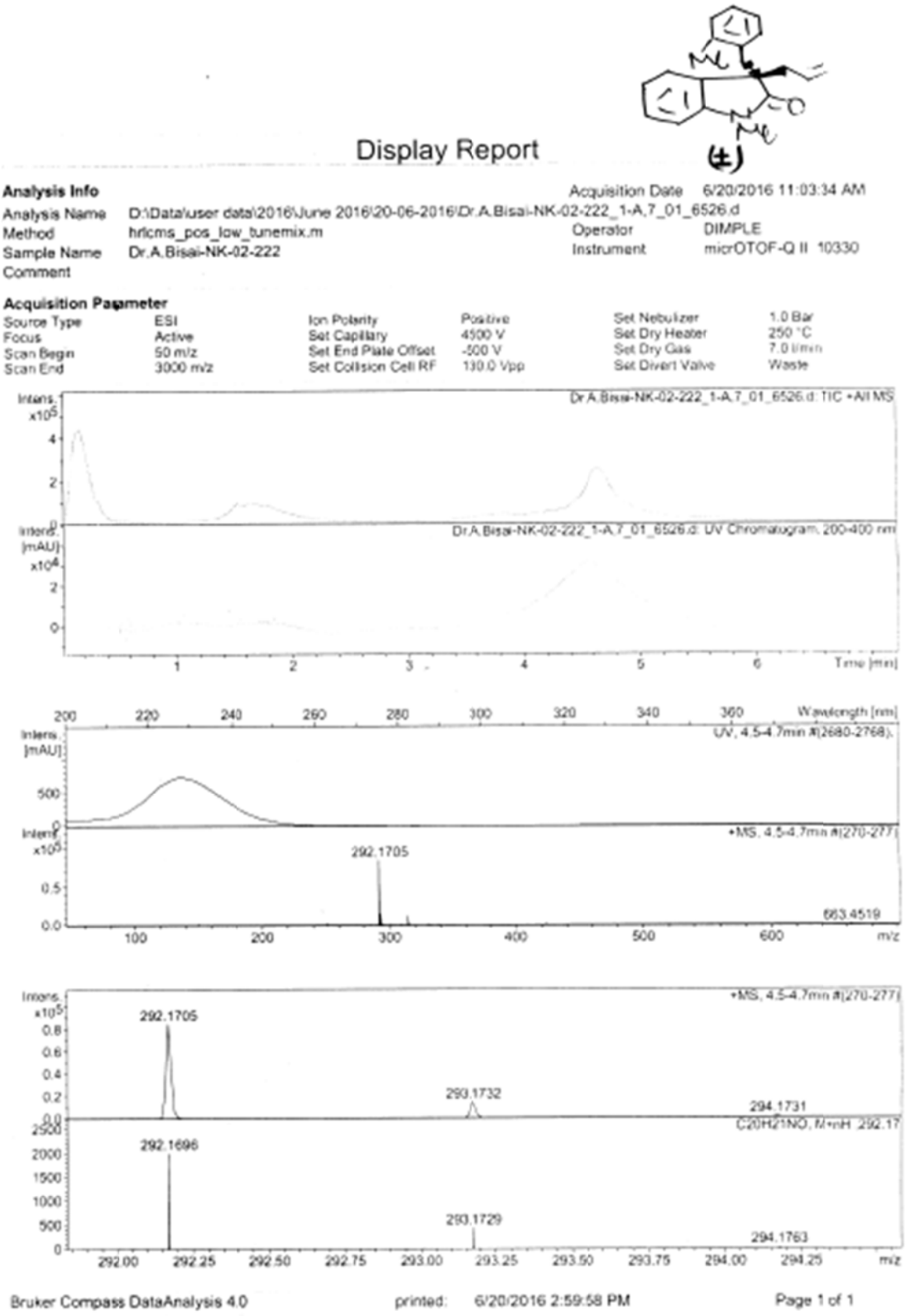




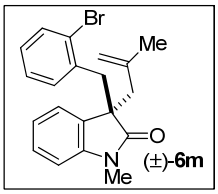
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6l**

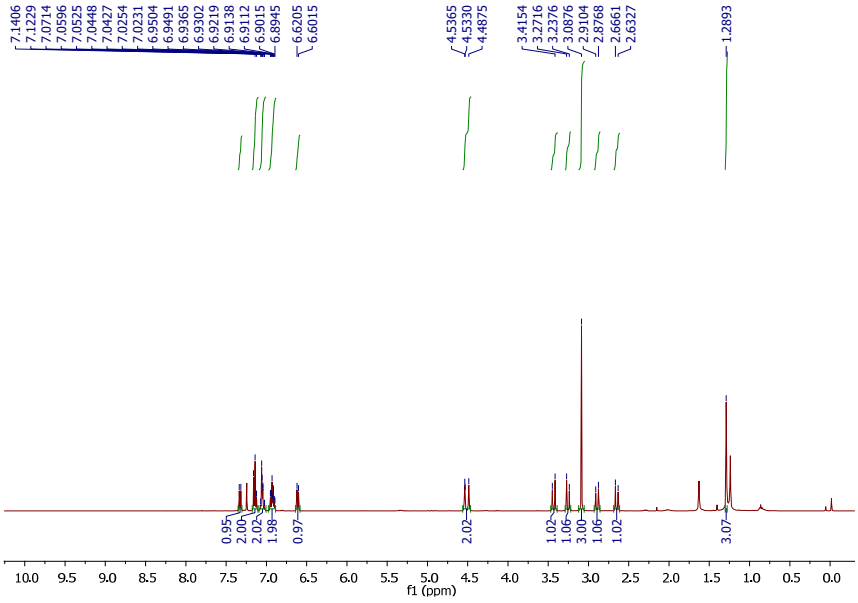


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6l**

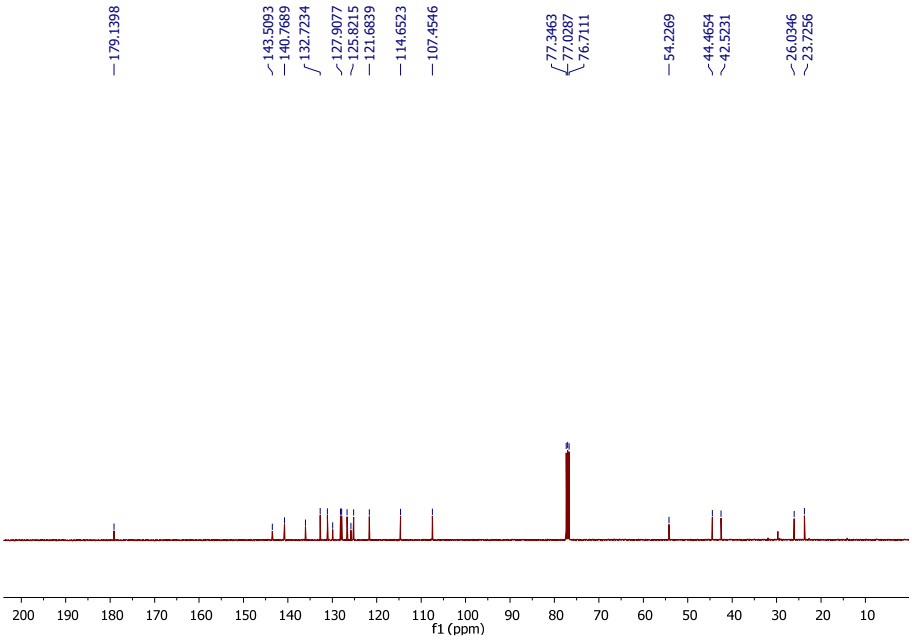


Scanned copy of mass spectrum (HRMS) of compound (±)-**6l**

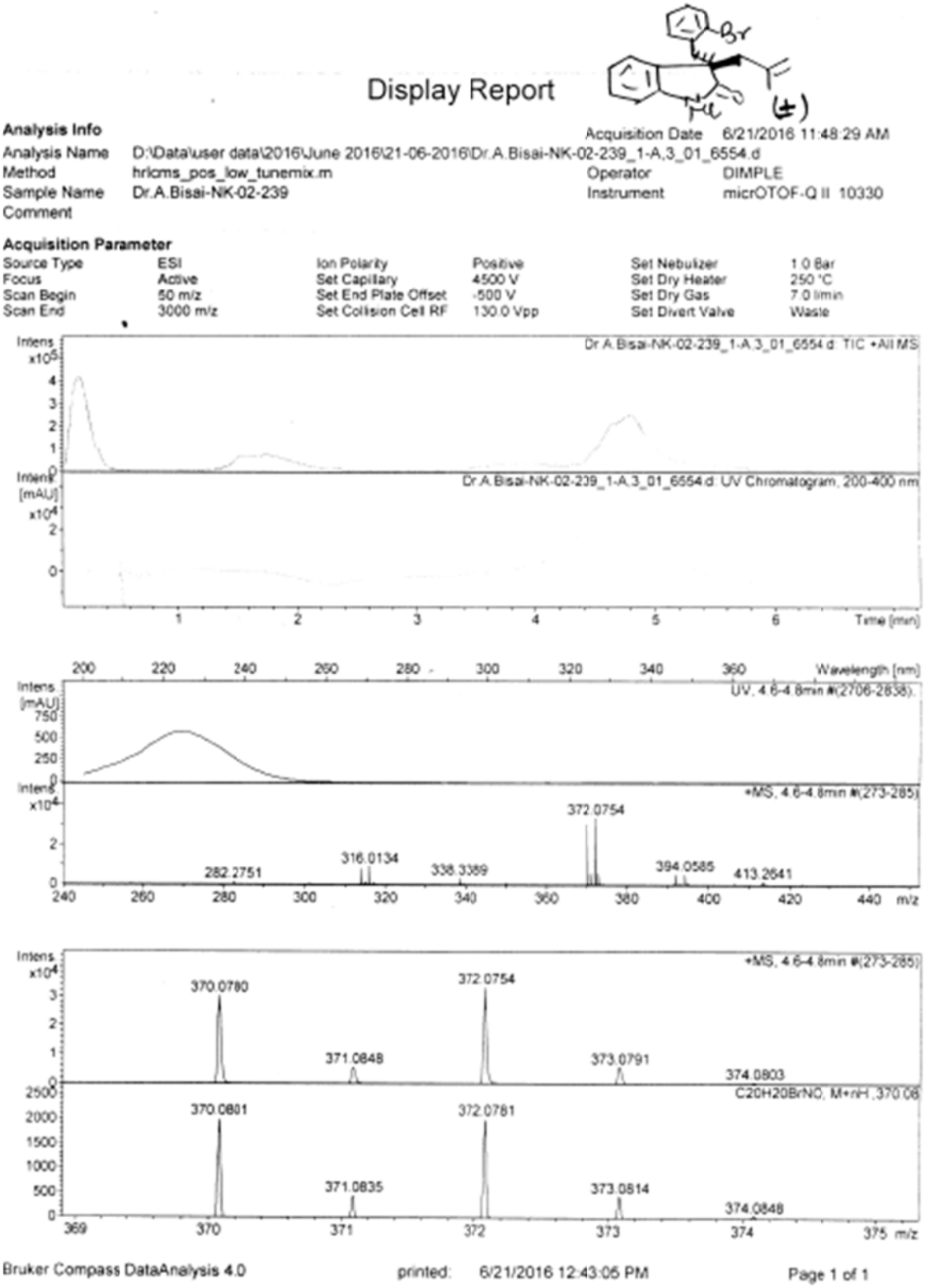




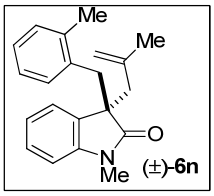
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6m**

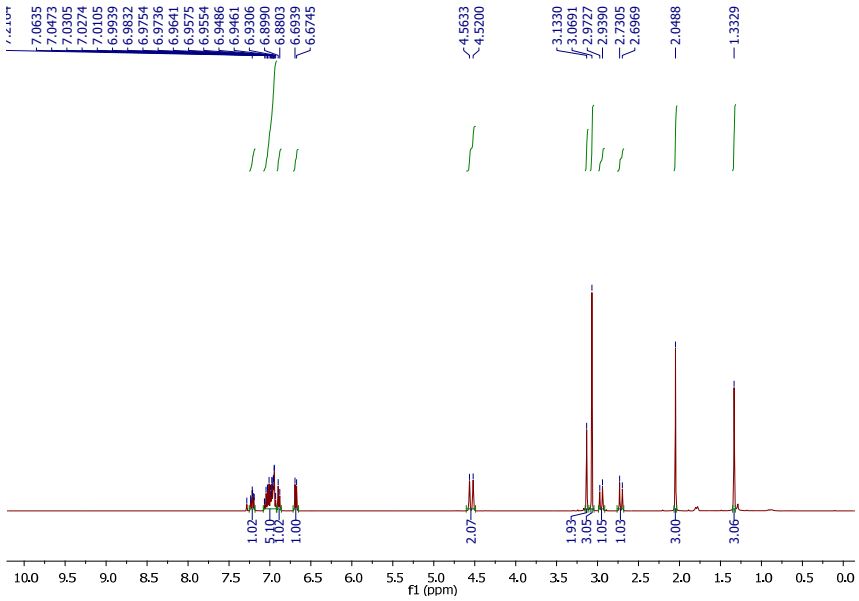


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6m**

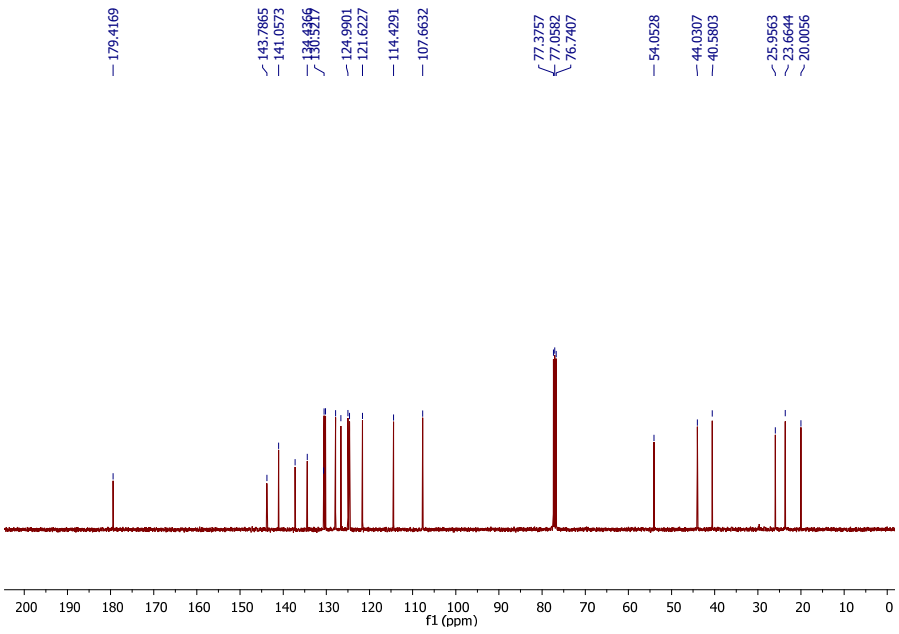


Scanned copy of mass spectrum (HRMS) of compound (±)-**6m**

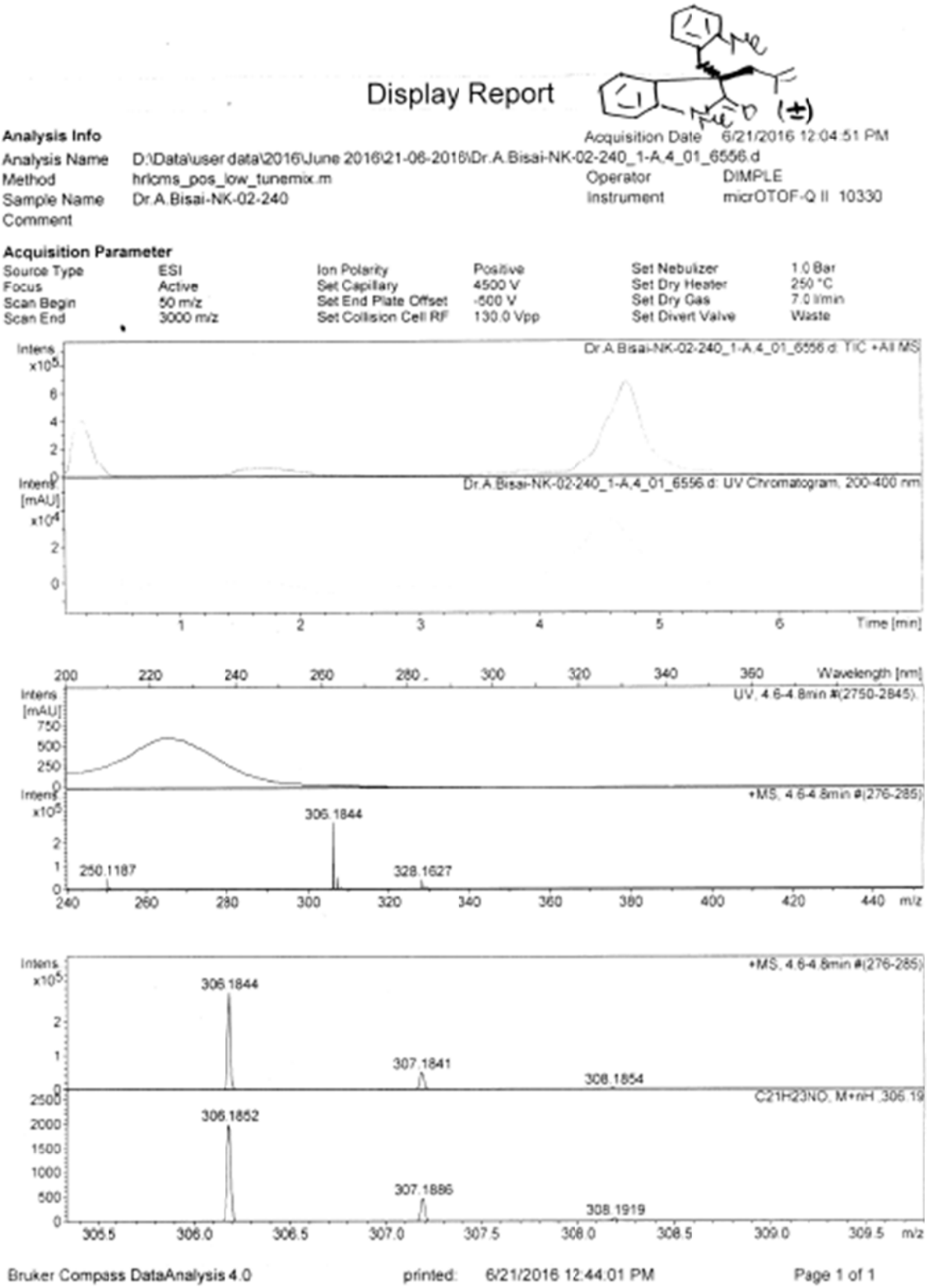




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6n**



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



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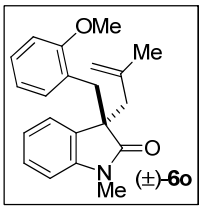
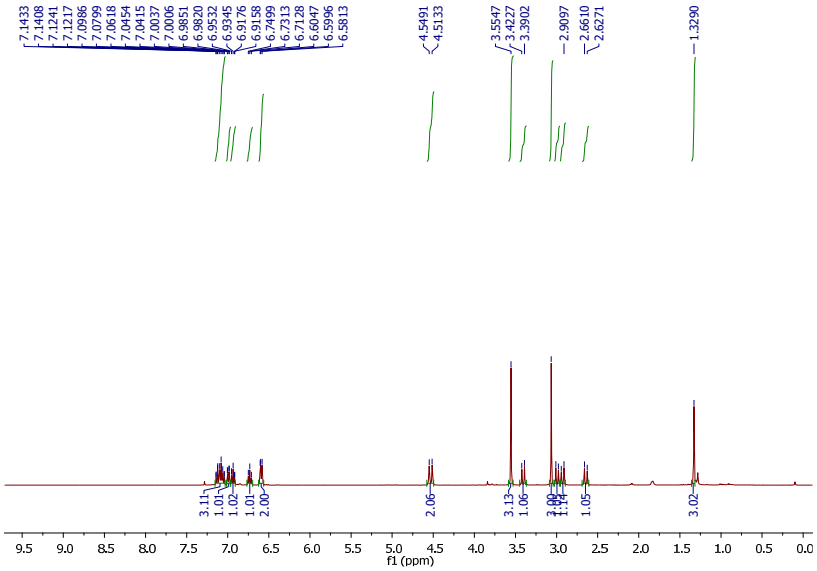
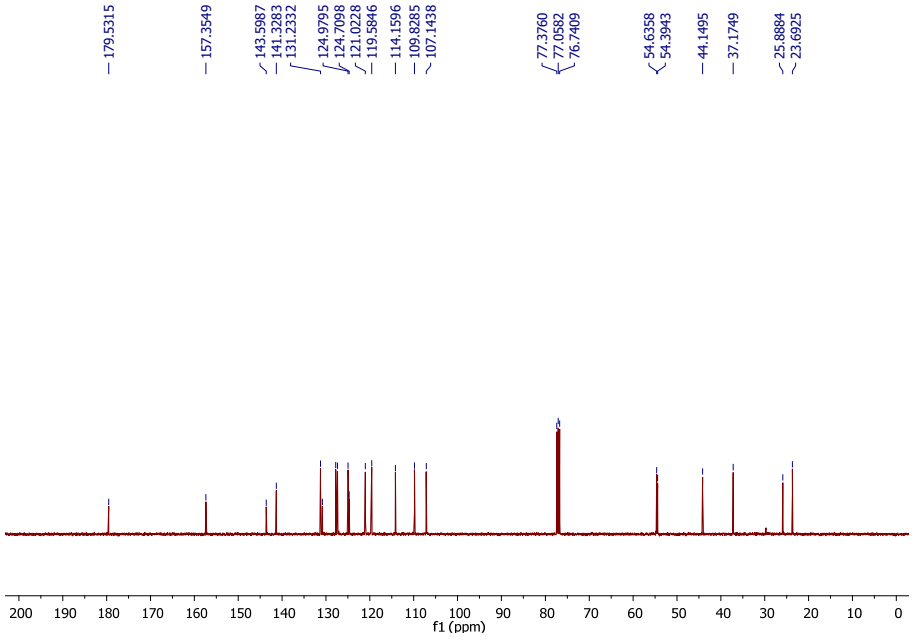
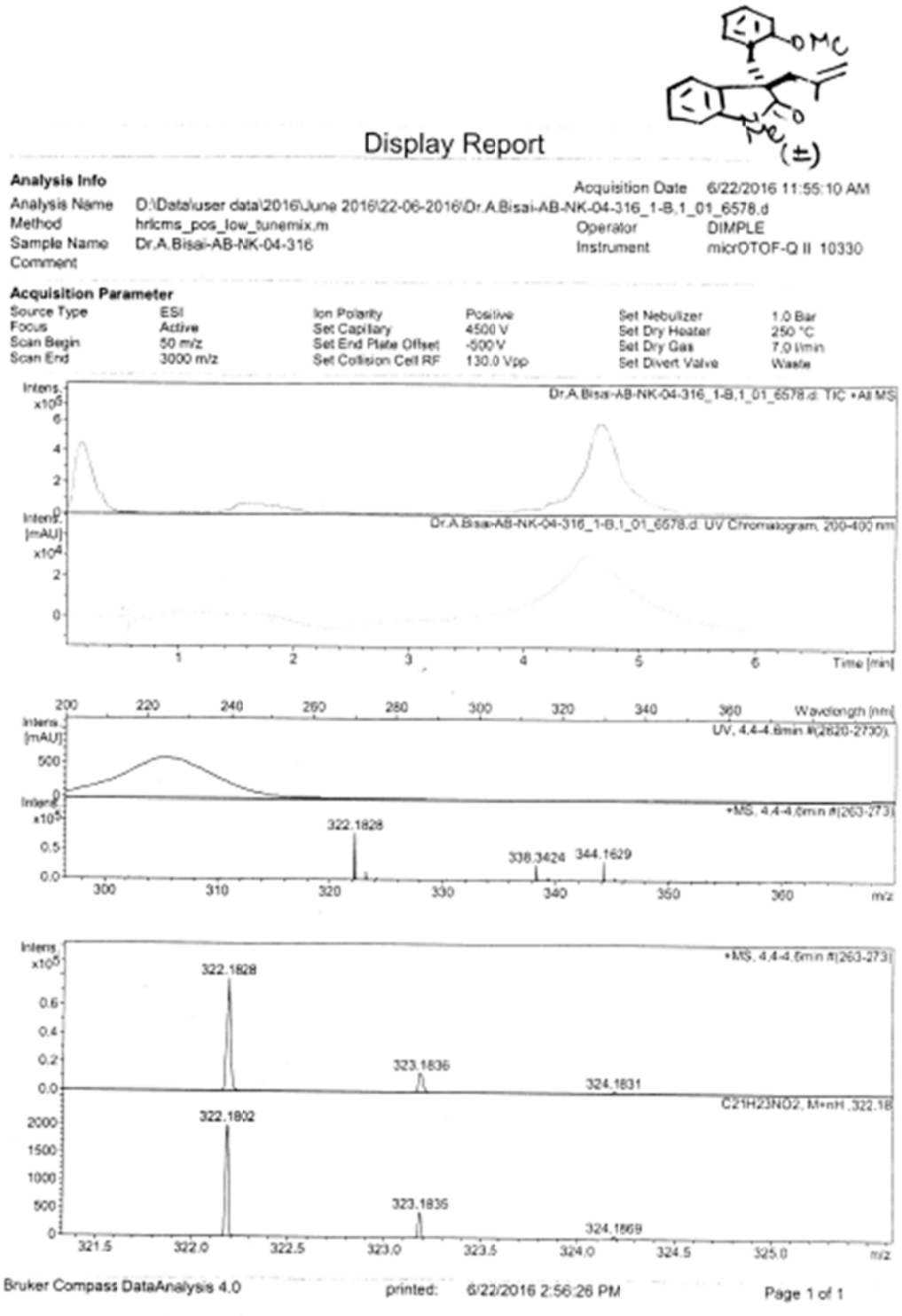




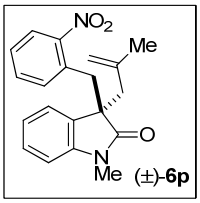
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6o**

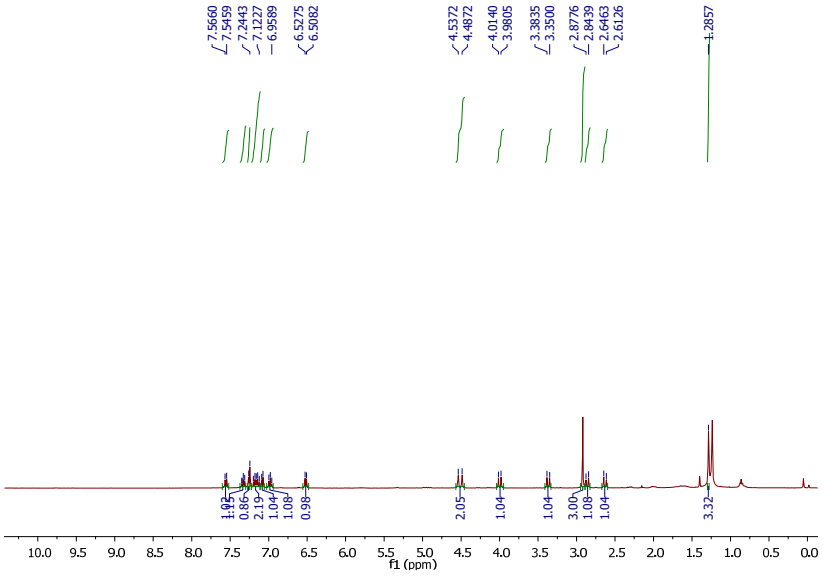


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6o**

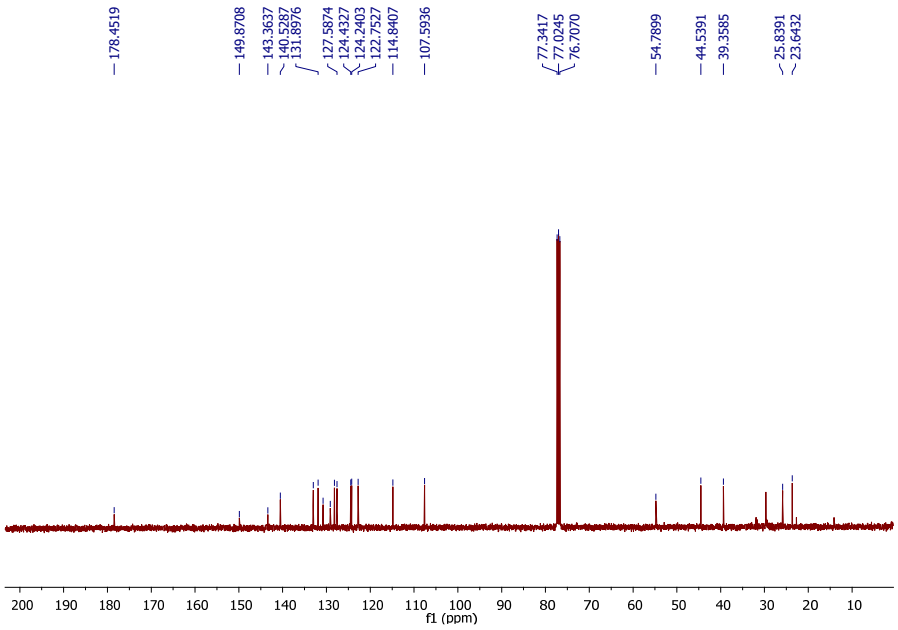


Scanned copy of mass spectrum (HRMS) of compound (±)-**6o**

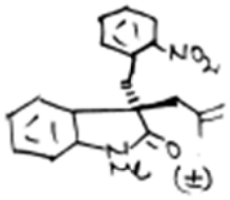




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6p**



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



Display Report

Analysis Info

Analysis Name	D:\Data\user data\2016\June 2016\24-06-2016\Dr.A.Bisai-AB-NK-03-283-1.d	Acquisition Date	6/24/2016 5:24:04 PM
Method	Pos_LOW_tunemix.m	Operator	DIMPLE
Sample Name	AB-NK-03-283-1	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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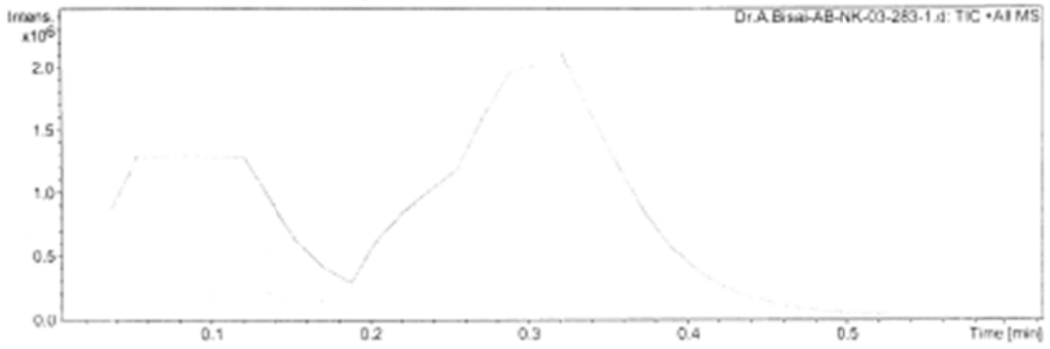
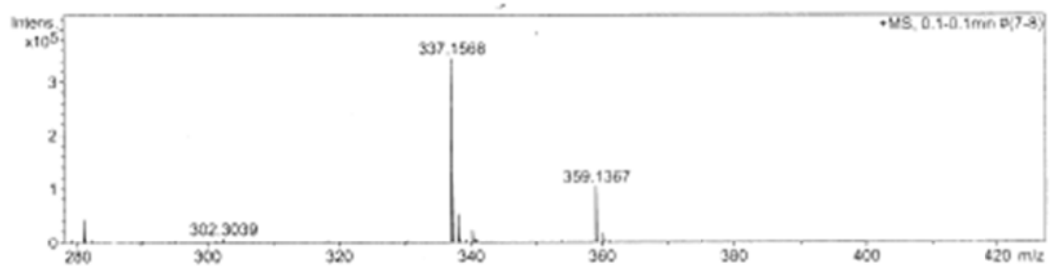
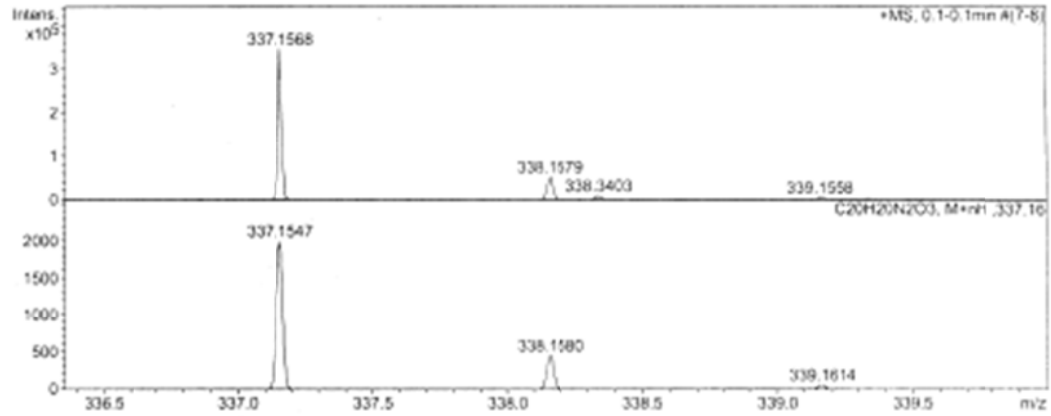
Scan End	3000 m/z	Set Collision Cell RF	1300 Vpp	Set Divert Valve	Waste







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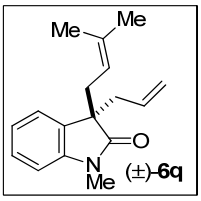
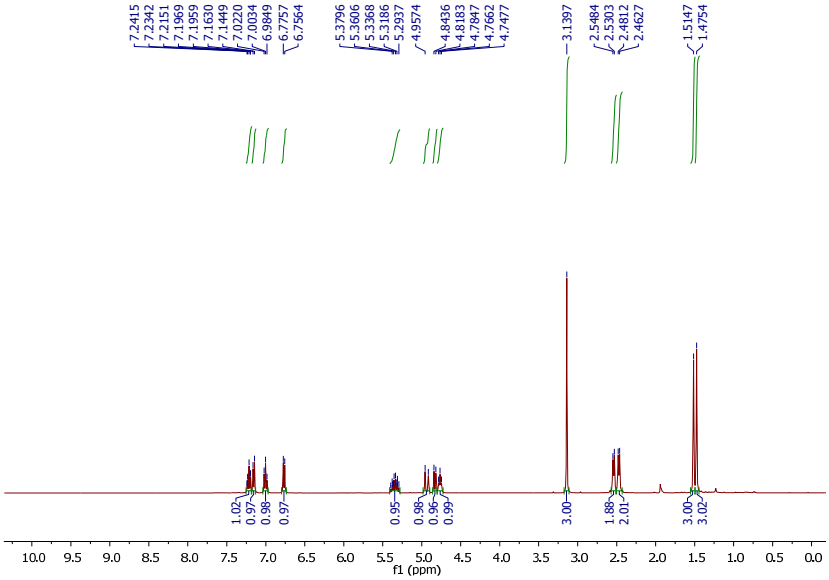
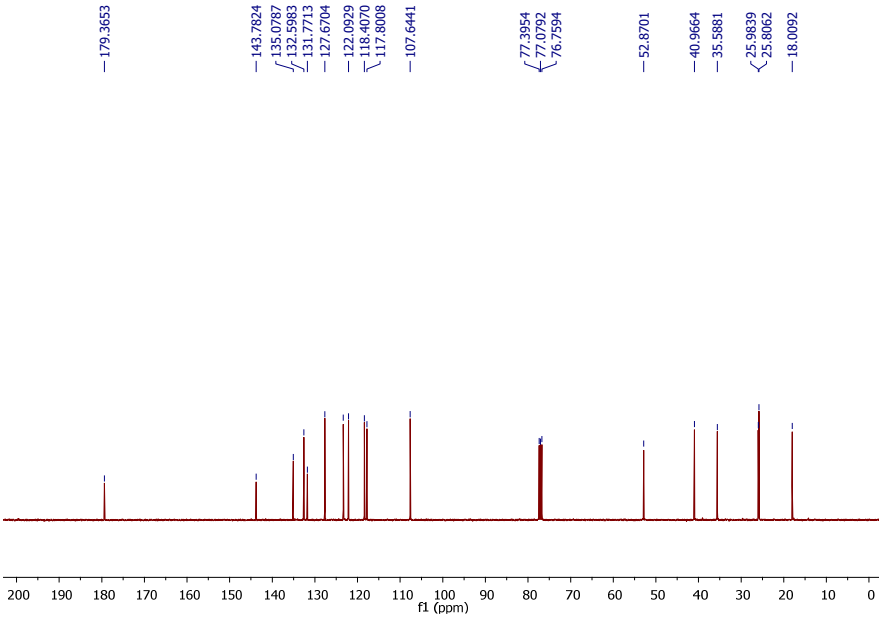
Scanned copy of mass spectrum (HRMS) of compound (±)-**6p**

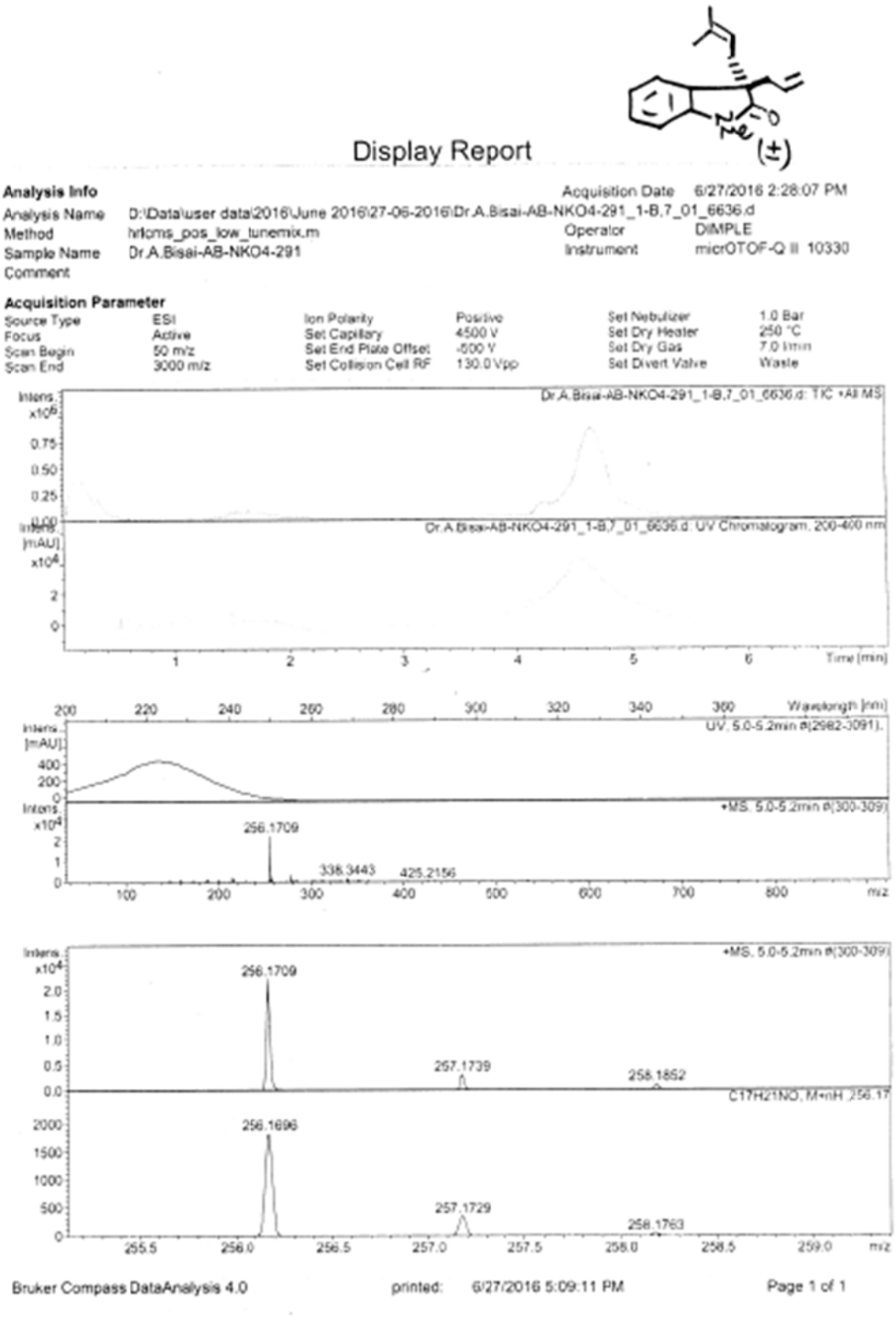




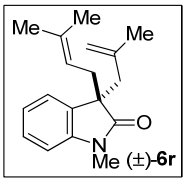
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6q**

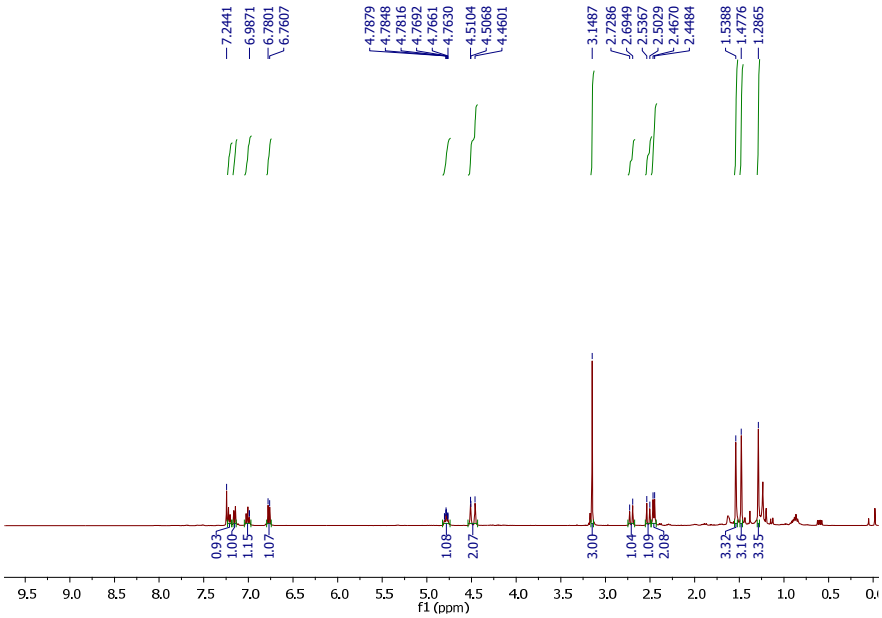


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6q**

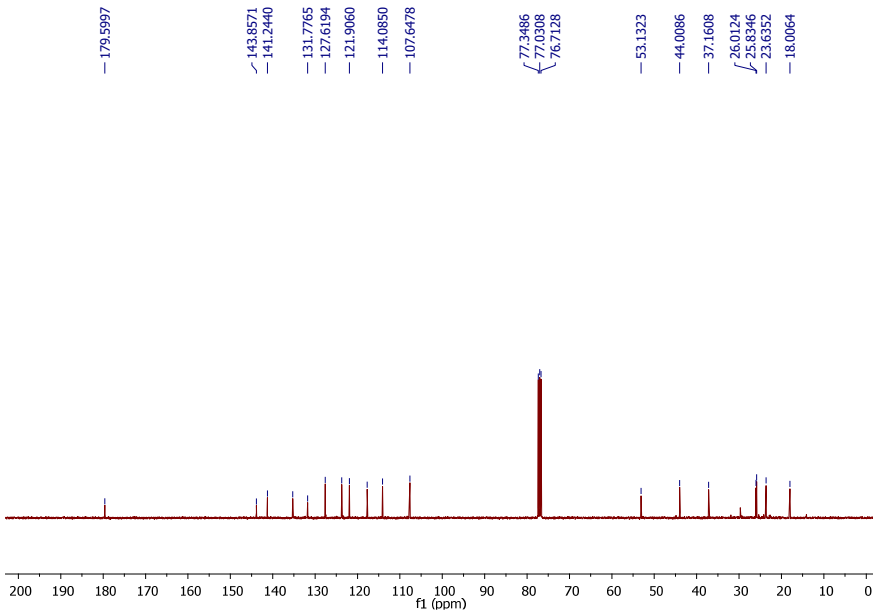


Scanned copy of mass spectrum (HRMS) of compound (±)-**6q**

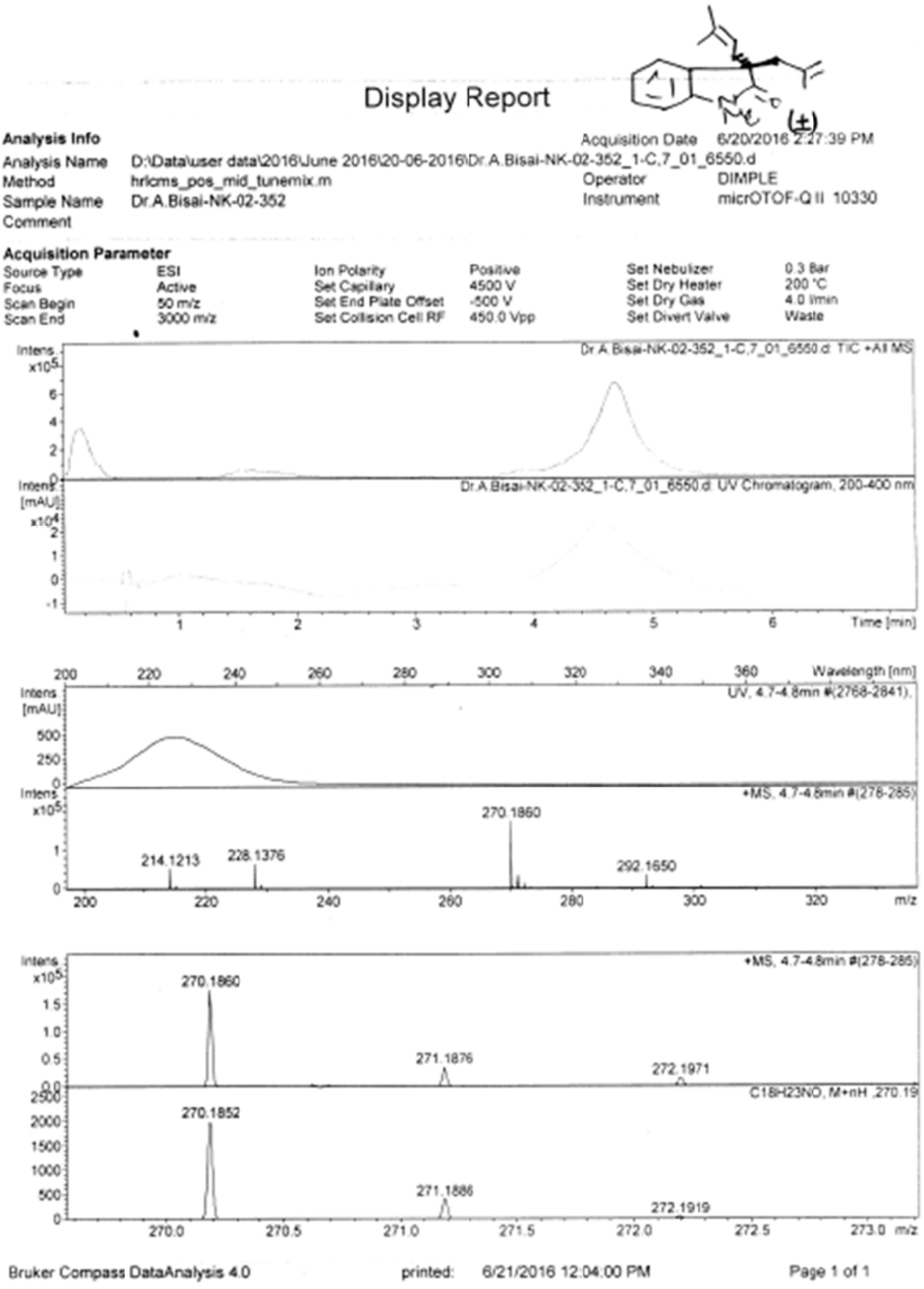




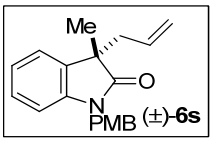
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6r**

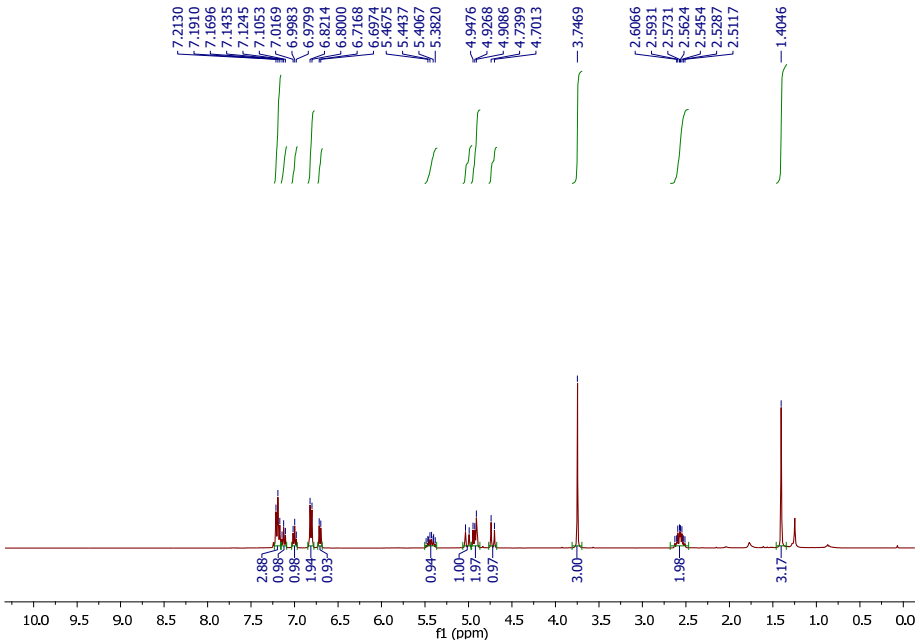


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6r**

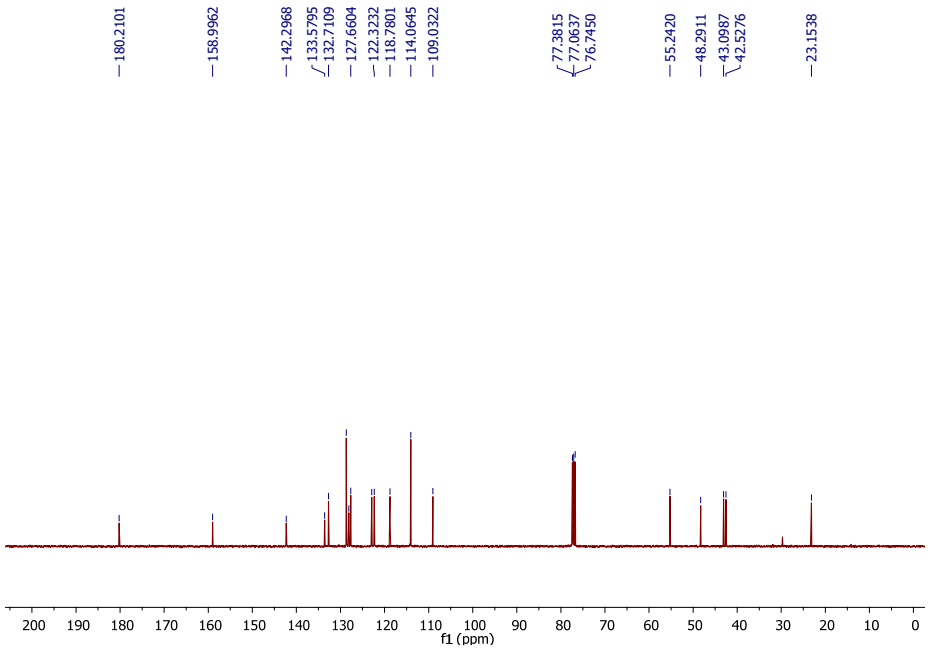


Scanned copy of mass spectrum (HRMS) of compound (±)-**6r**

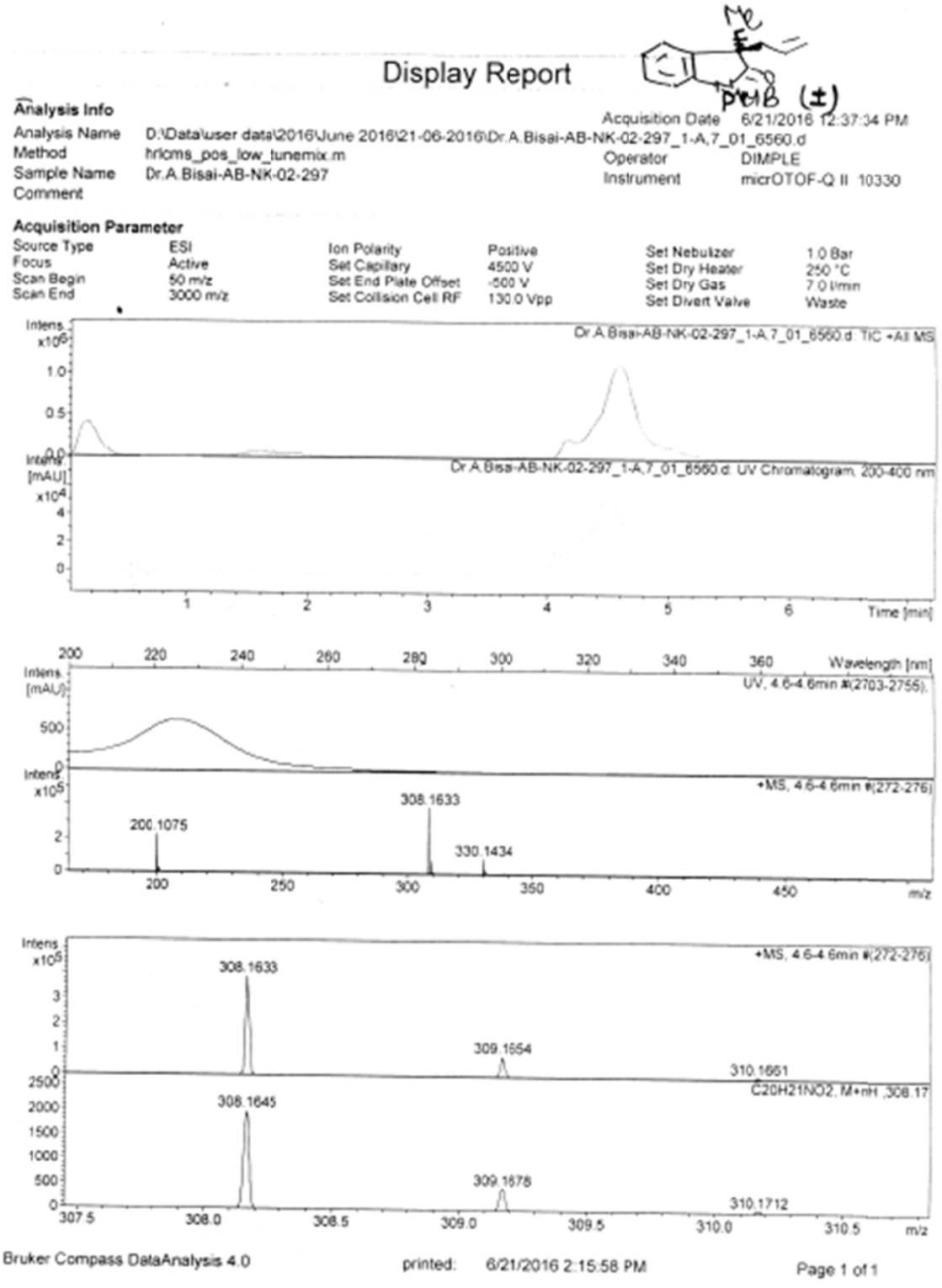




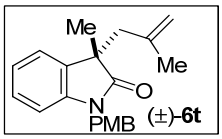
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6s**

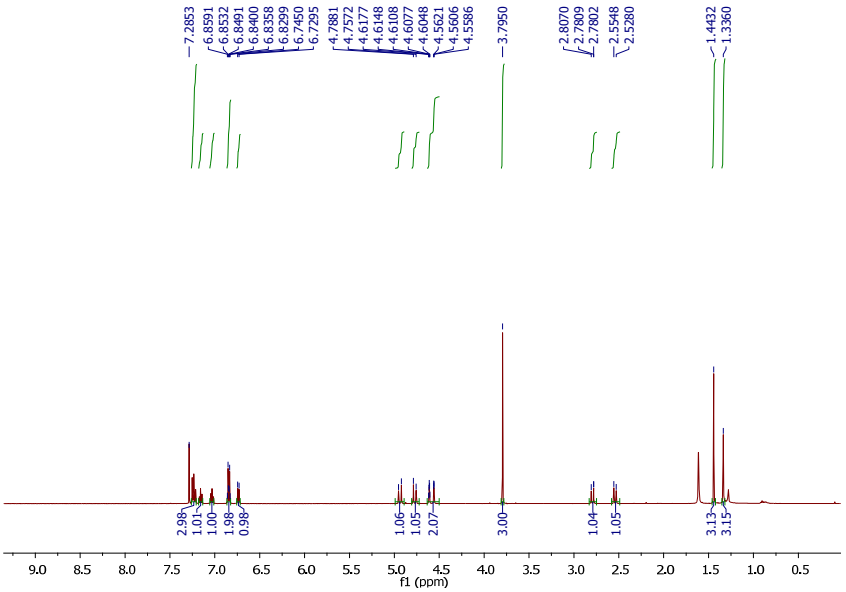


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6s**

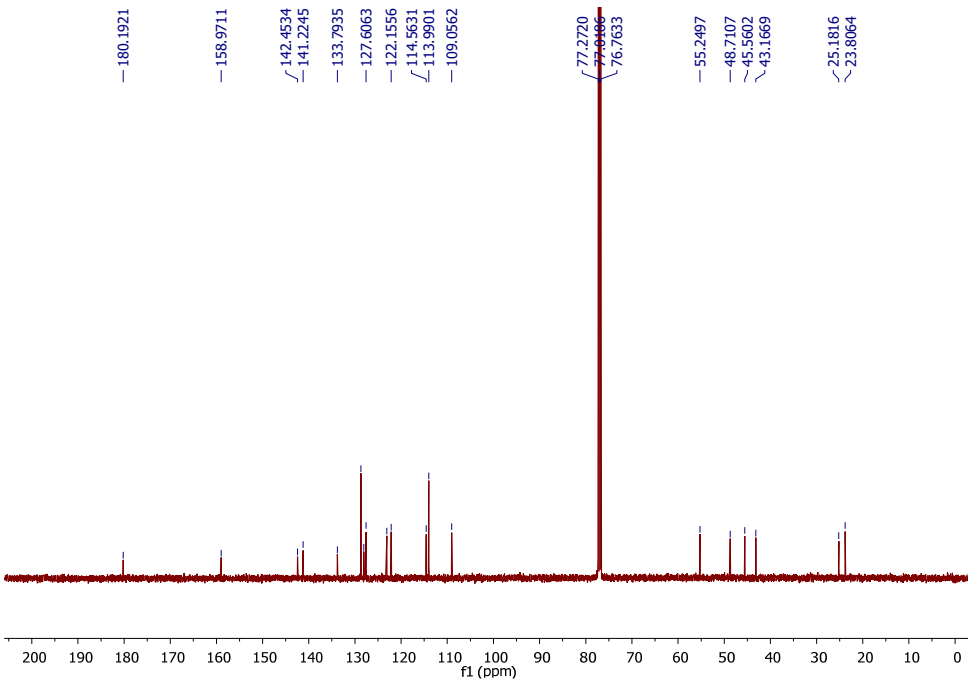


Scanned copy of mass spectrum (HRMS) of compound (±)-**6s**

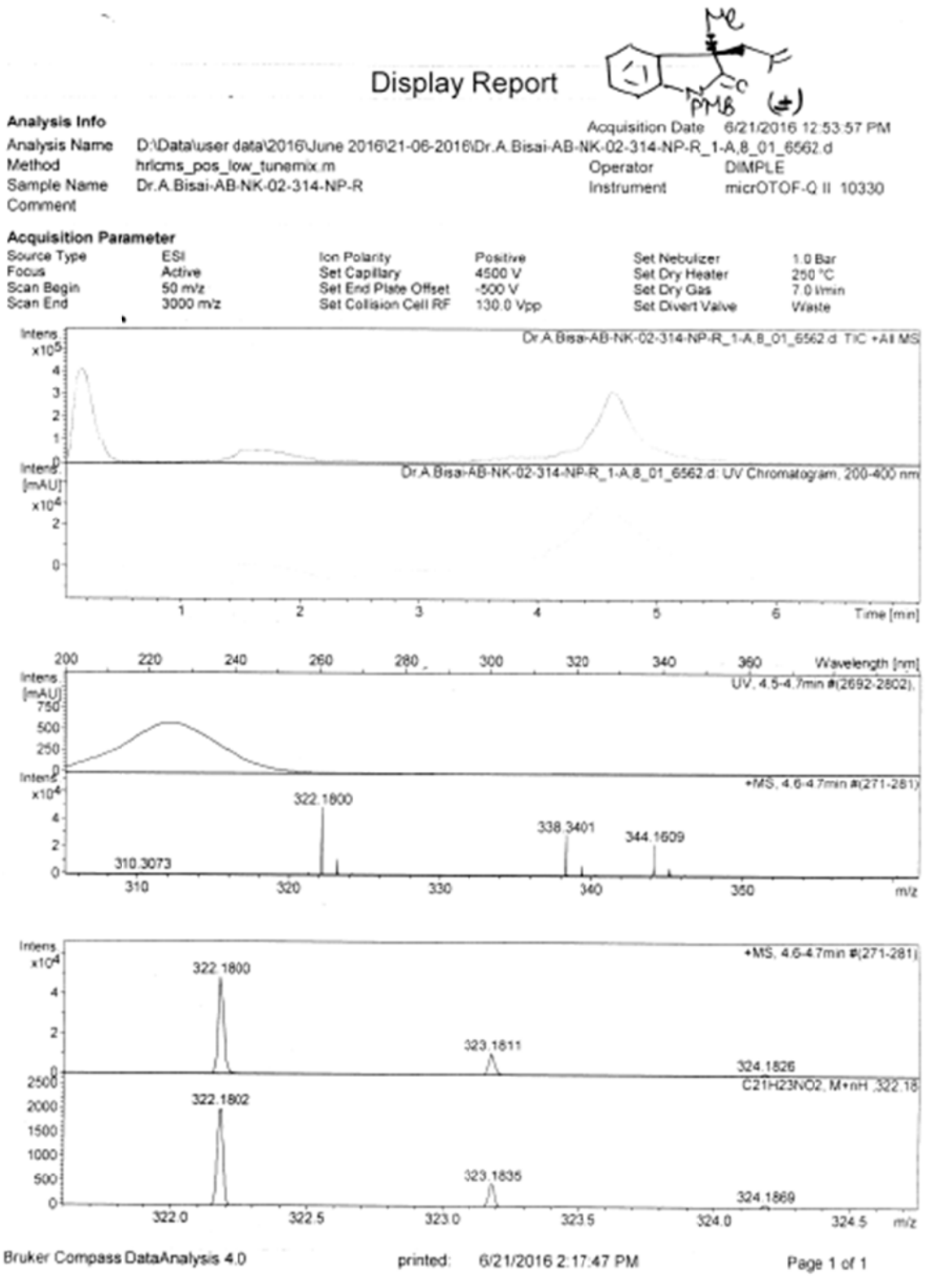




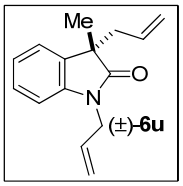
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**6t**

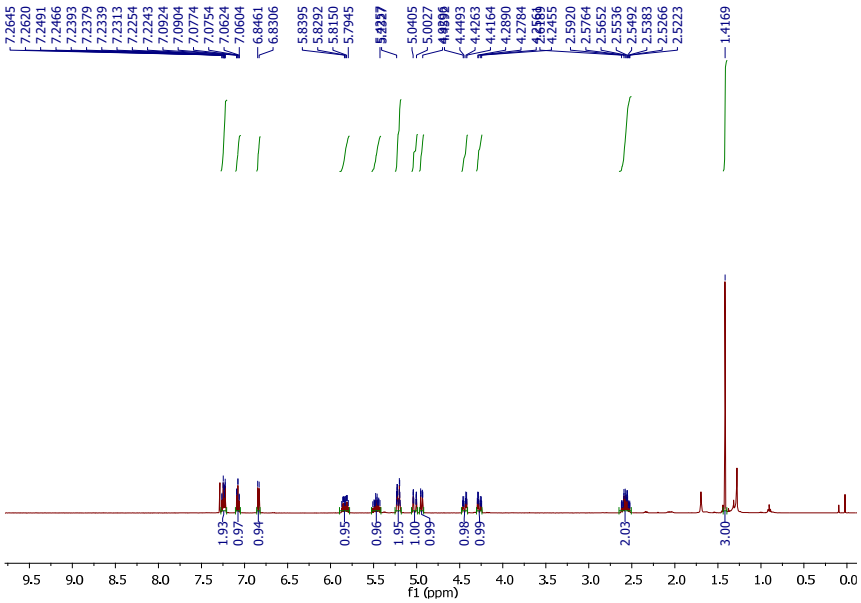


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**6t**

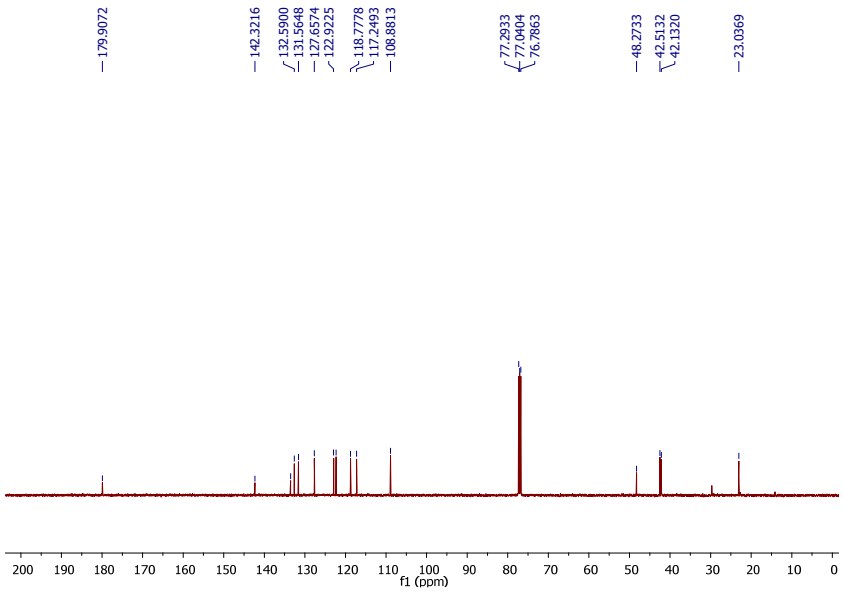


Scanned copy of mass spectrum (HRMS) of compound (±)-**6t**

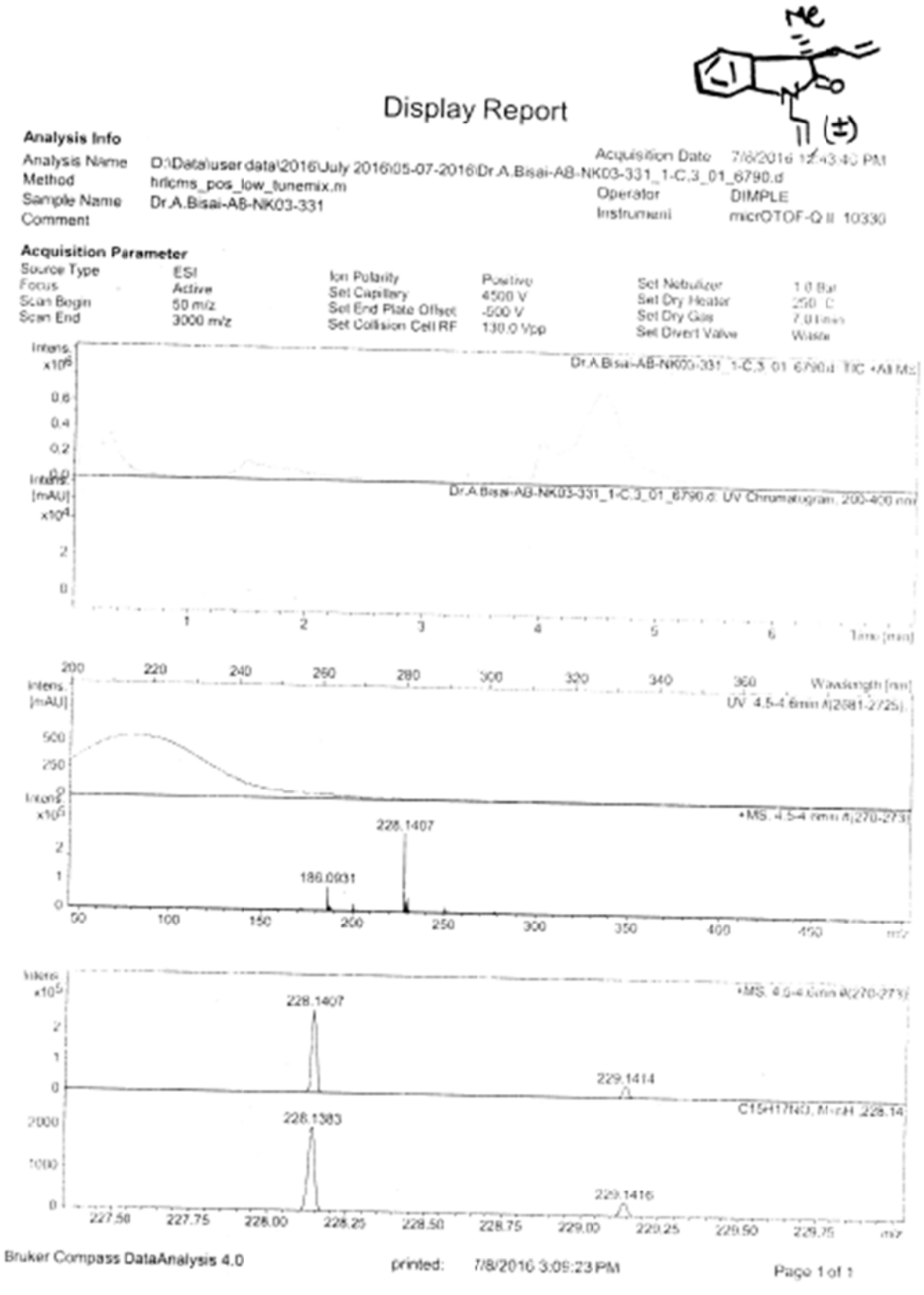




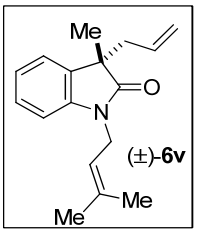
^{1}H NMR (500 MHz, $CDCl_3$) of compound (±)-**6u**

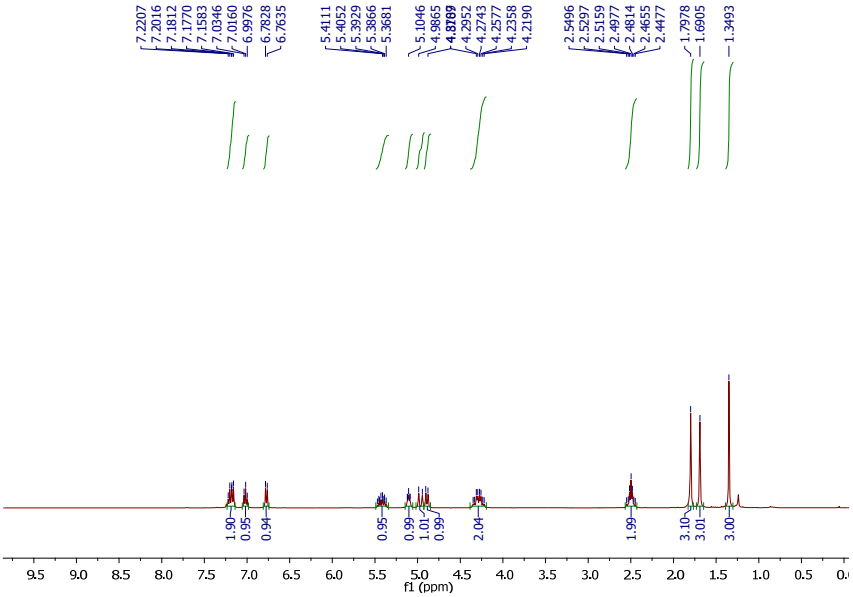


^{13}C NMR (125 MHz, $CDCl_3$) of compound (±)-**6u**

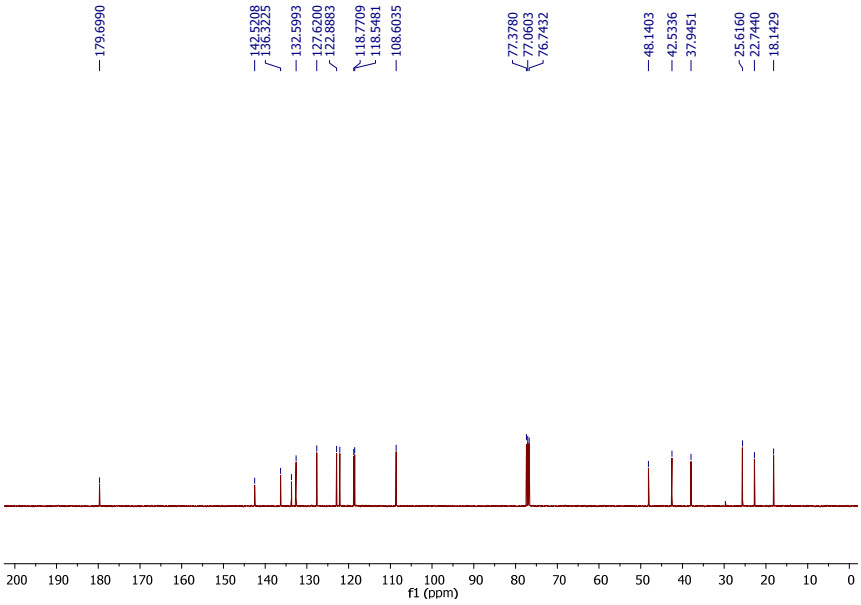


Scanned copy of mass spectrum (HRMS) of compound (±)-**6u**

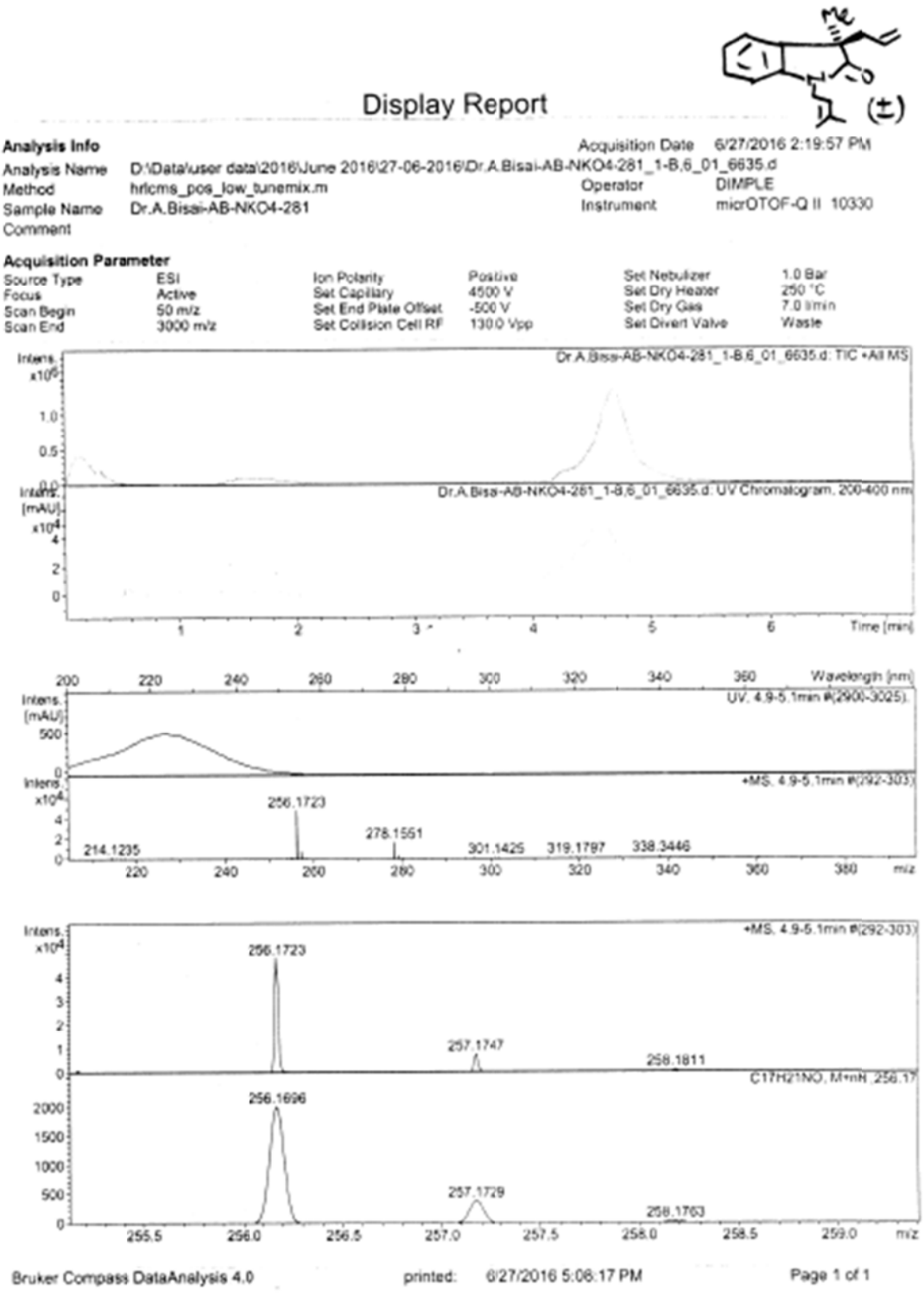




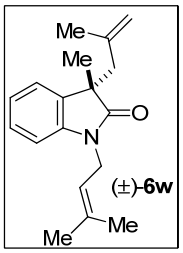
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6v**

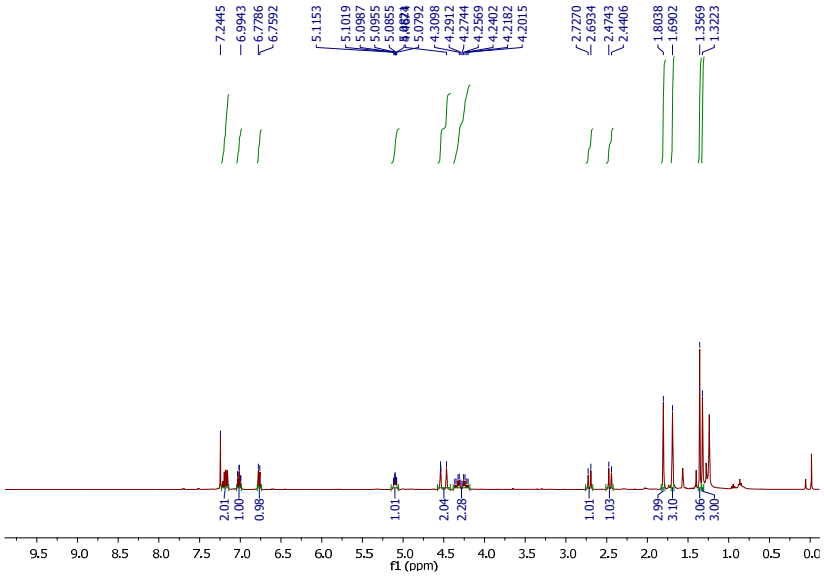


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6v**

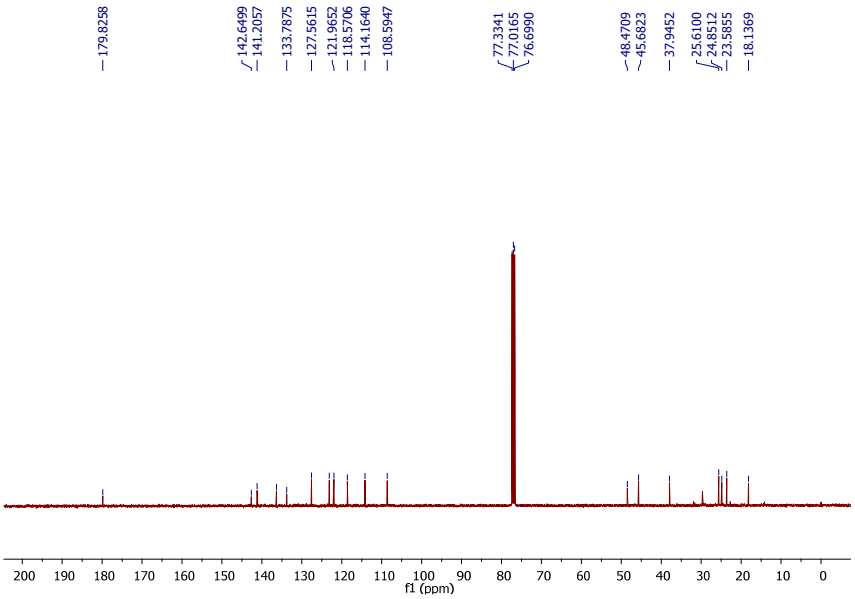


Scanned copy of mass spectrum (HRMS) of compound (±)-**6v**

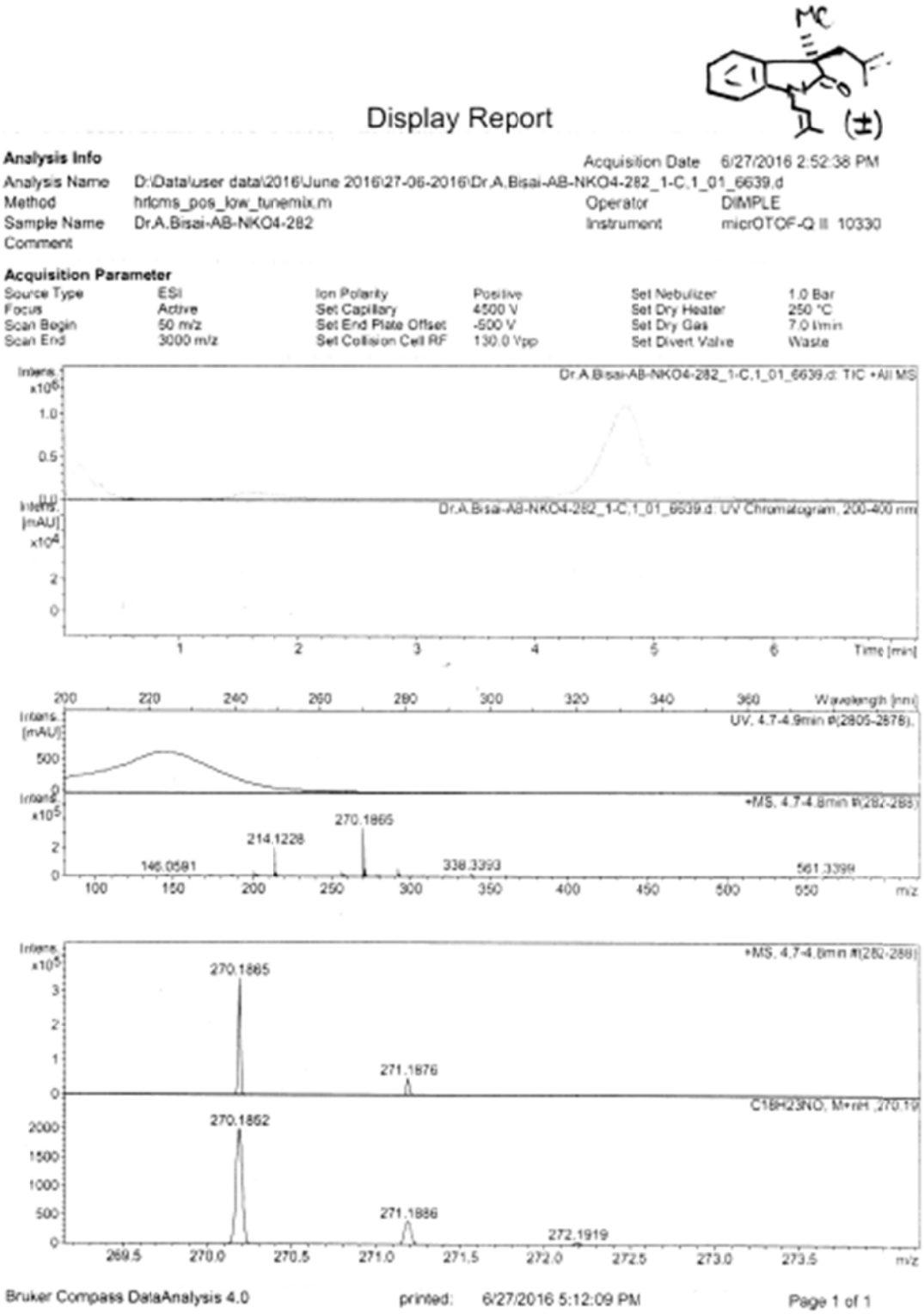




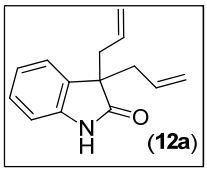
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**6w**

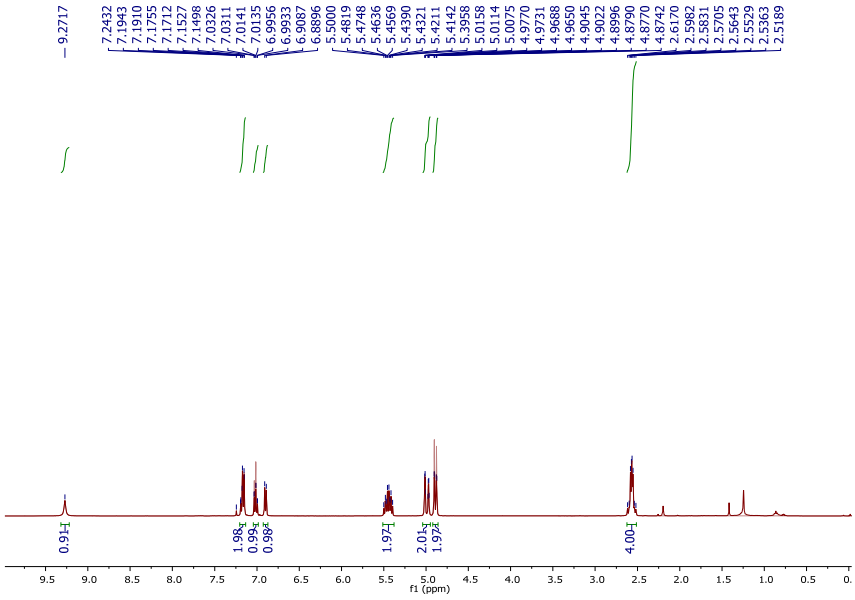


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**6w**

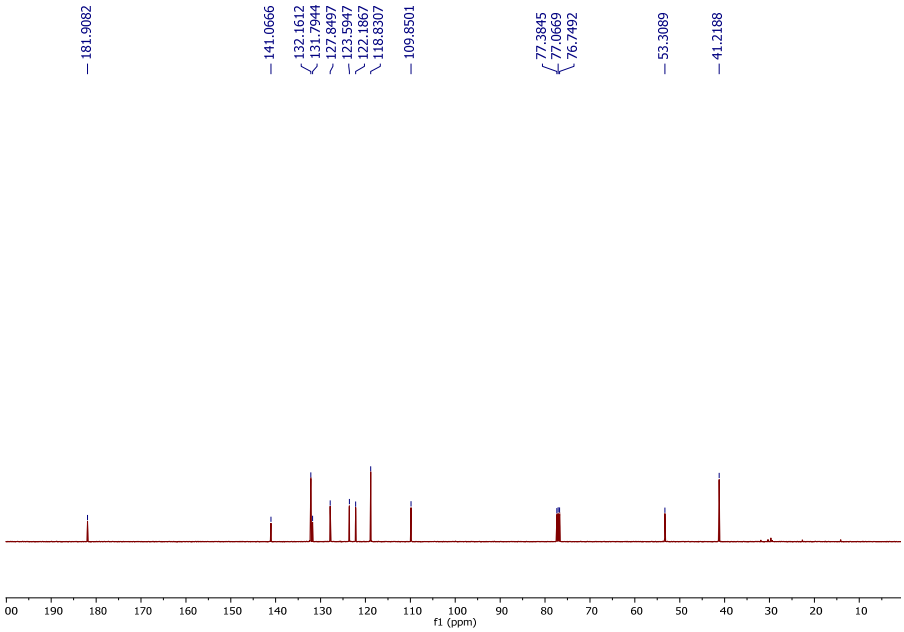


Scanned copy of mass spectrum (HRMS) of compound (±)-**6w**

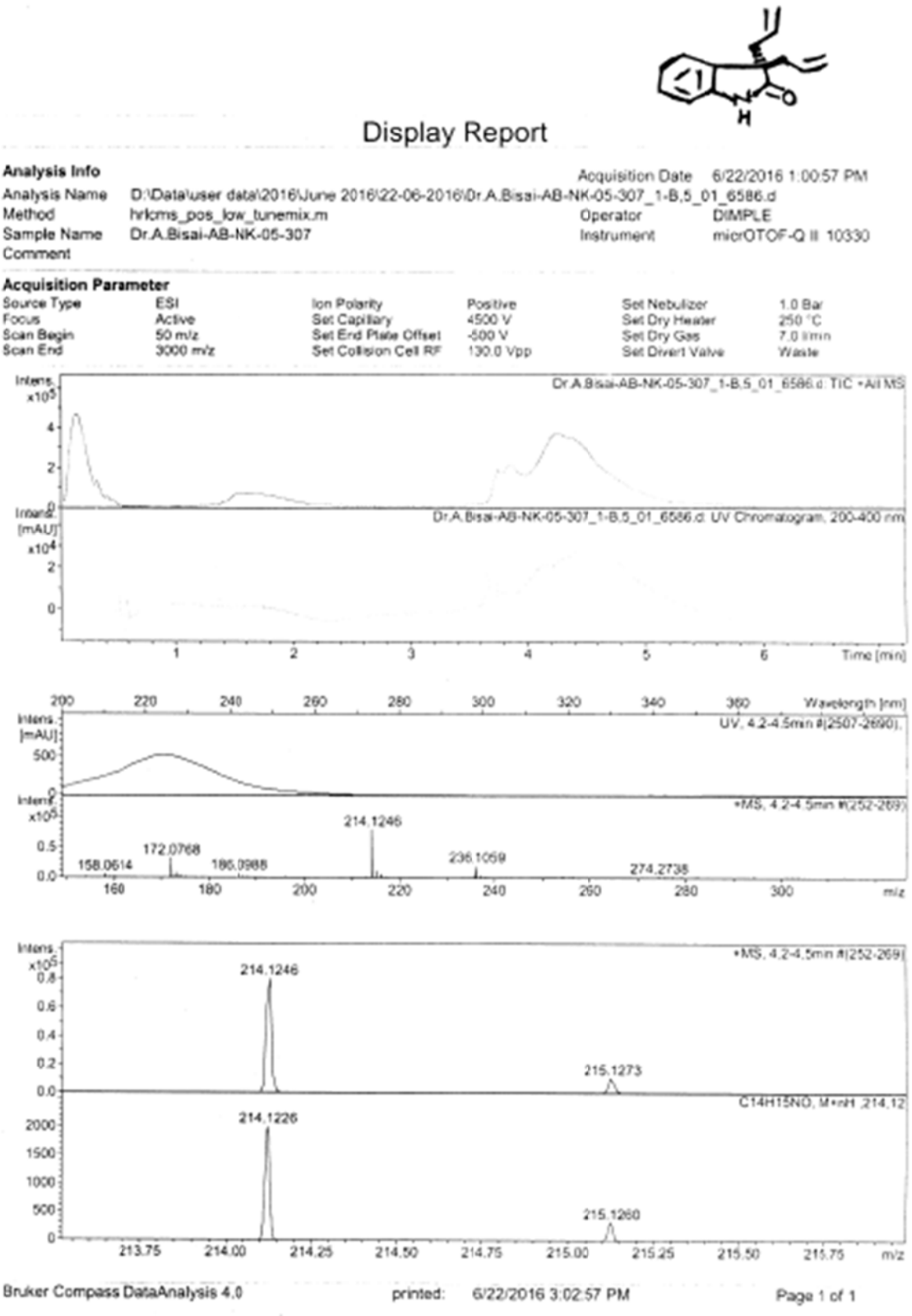




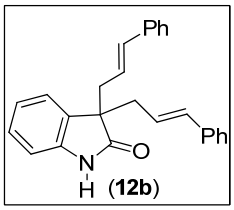
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**12a**)



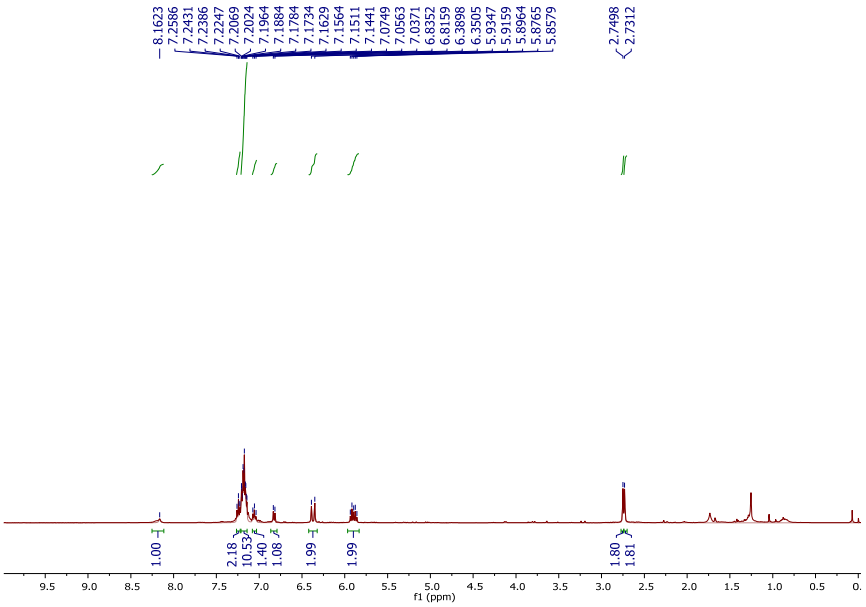
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**12a**)



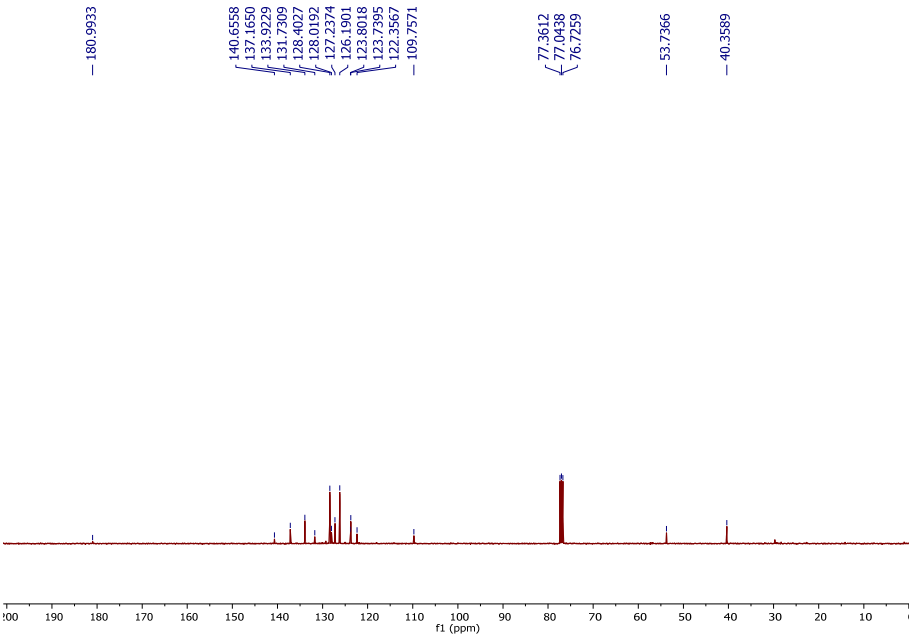
Scanned copy of mass spectrum (HRMS) of compound (**12a**)



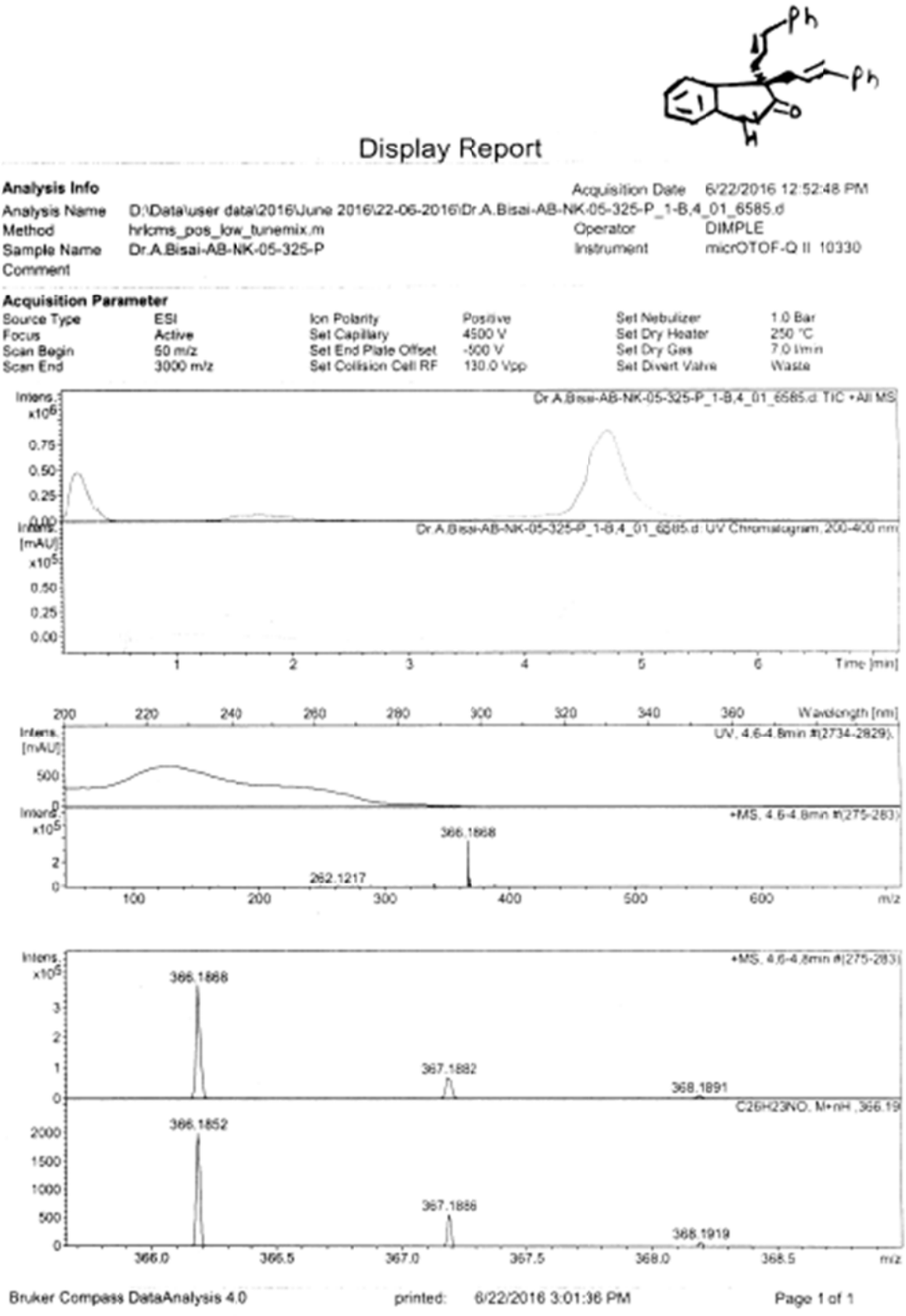
(**12b**)



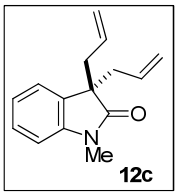
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**12b**)

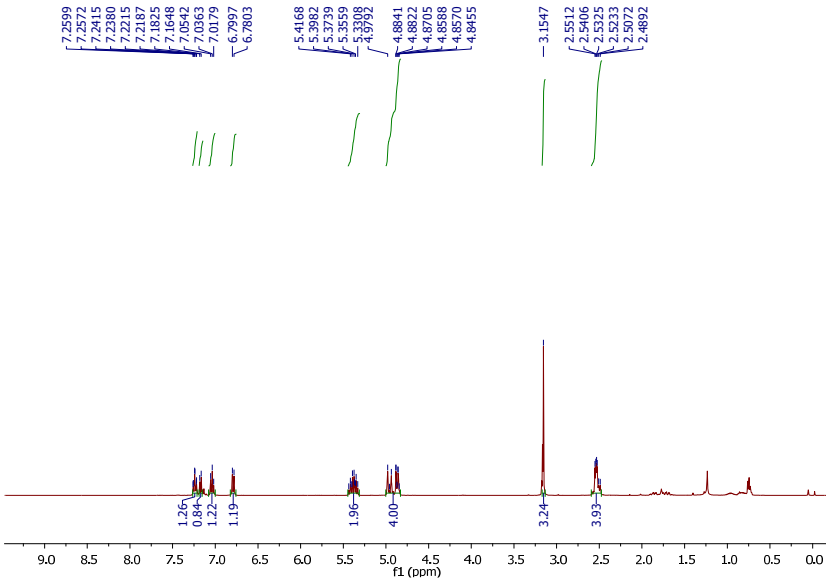


^{13}C NMR (100 MHz, $CDCl_3$) of compound (**12b**)

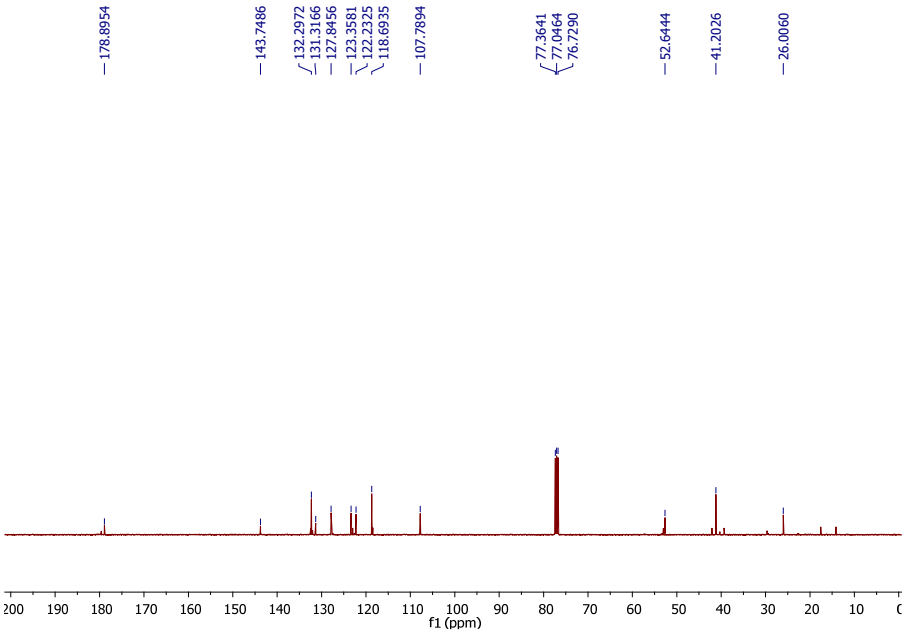


Scanned copy of mass spectrum (HRMS) of compound (**12b**)

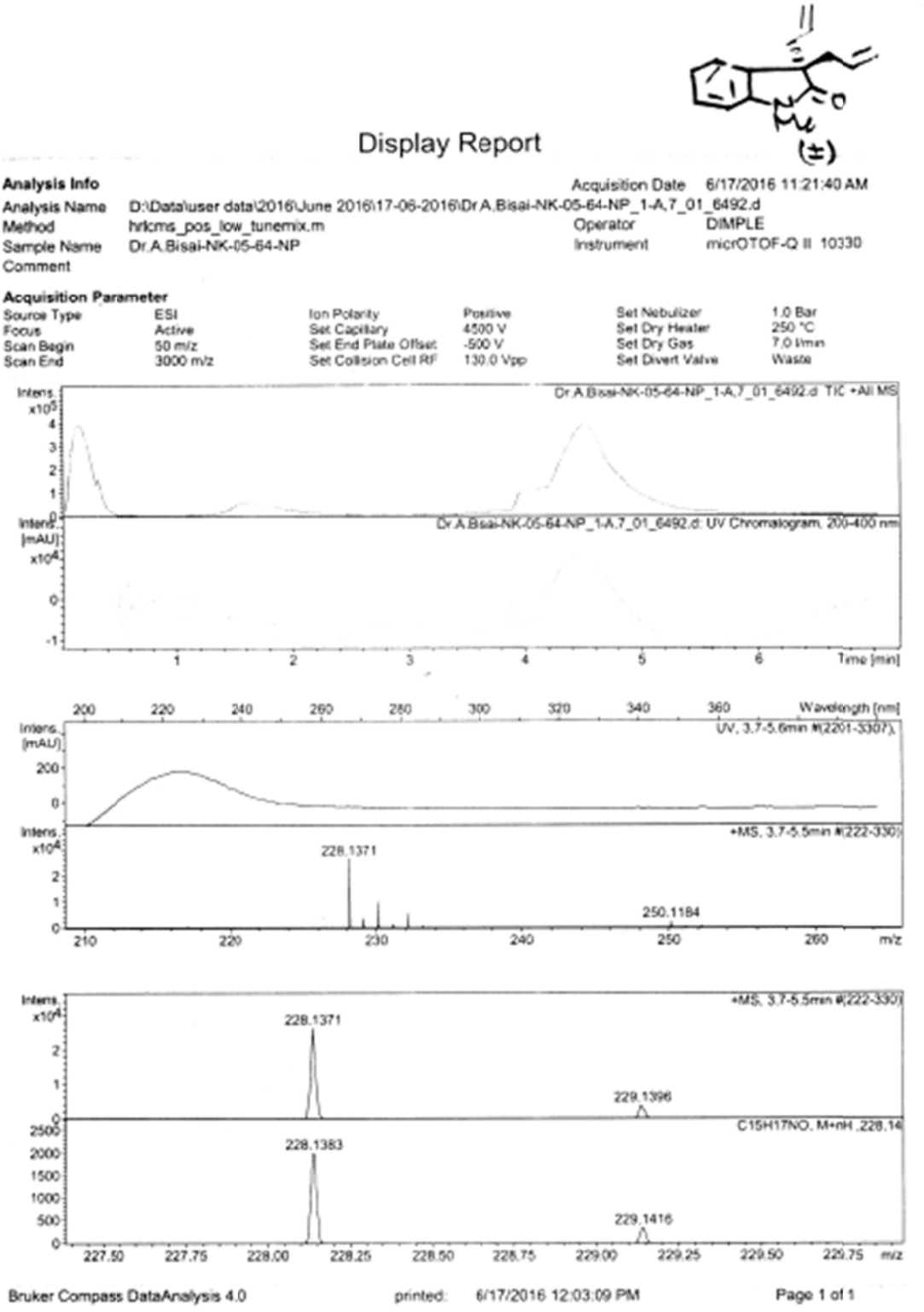




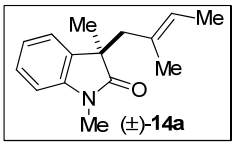
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**12c**)

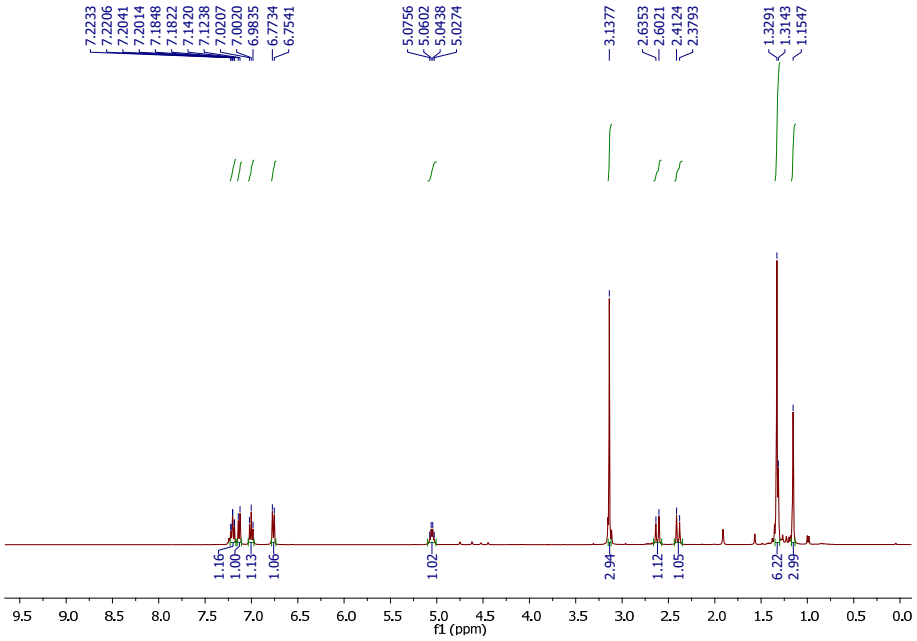


^{13}C NMR (100 MHz, $CDCl_3$) of compound (**12c**)

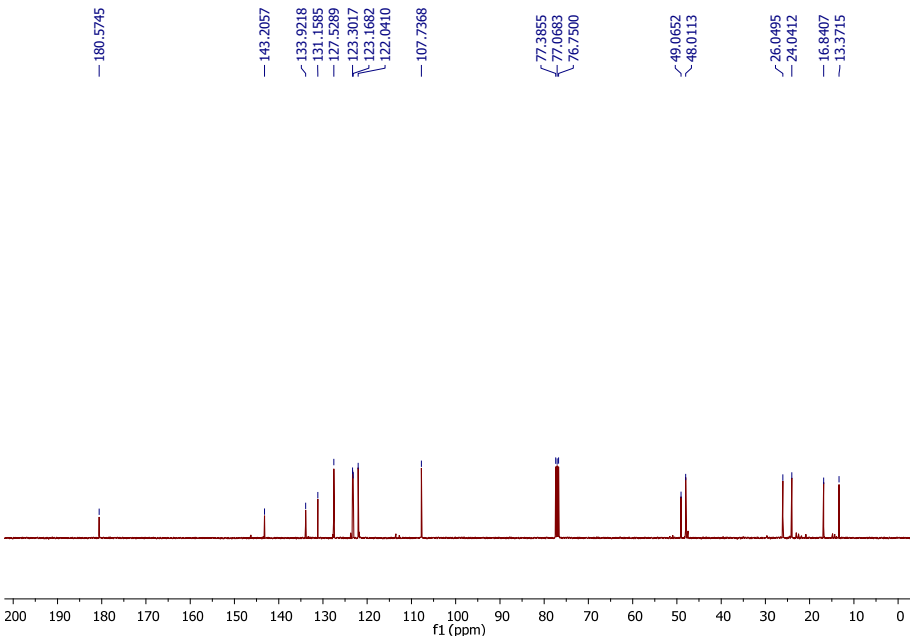


Scanned copy of mass spectrum (HRMS) of compound (**12c**)

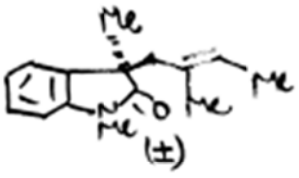




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**14a**



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



Display Report

Analysis Info

Analysis Name	D:\Data\user data\2016\June 2016\22-06-2016\Dr.A.Bisai-AB-NK-02-231_1-A,4_01_6572.d	Acquisition Date	6/22/2016 10:30:24 AM
Method	hrlcms_pos_low_tunemix.m	Operator	DIMPLE
Sample Name	Dr.A.Bisai-AB-NK-02-231	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
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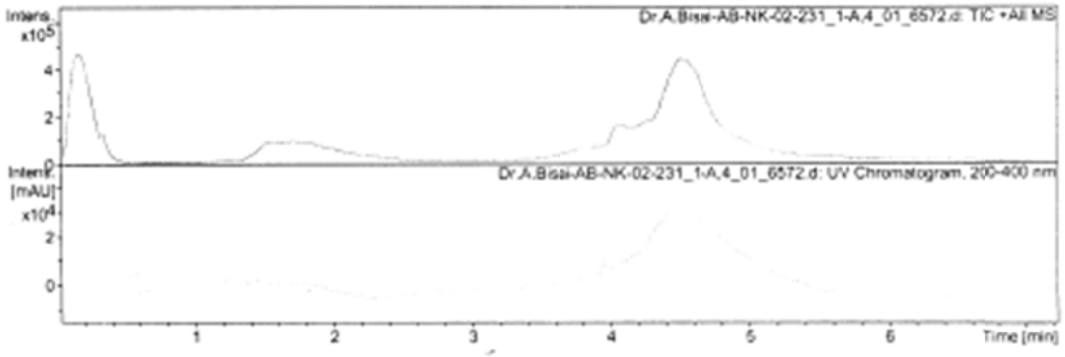
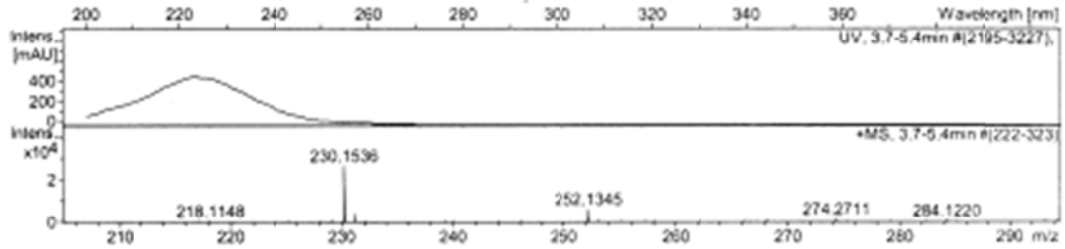
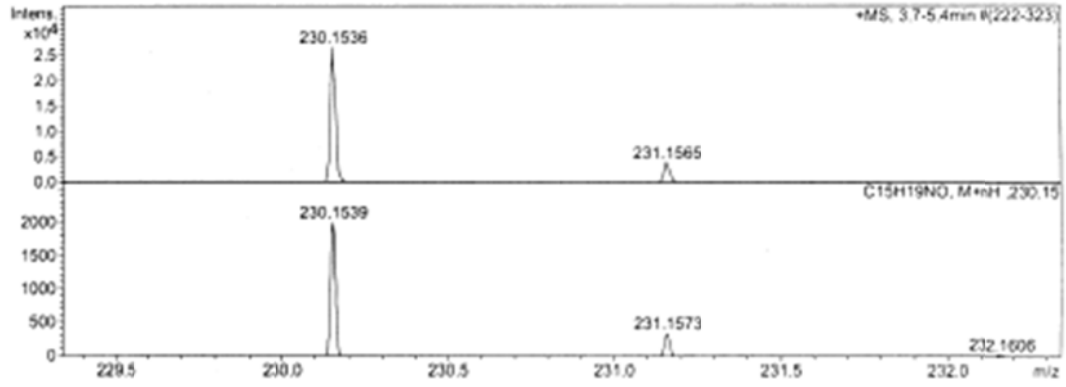
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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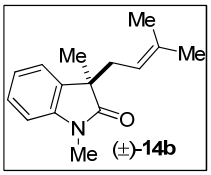
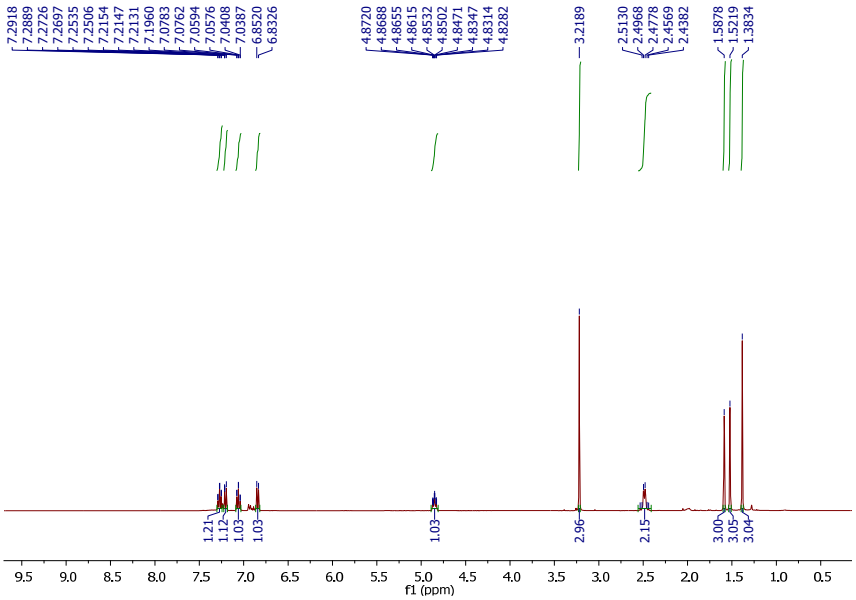
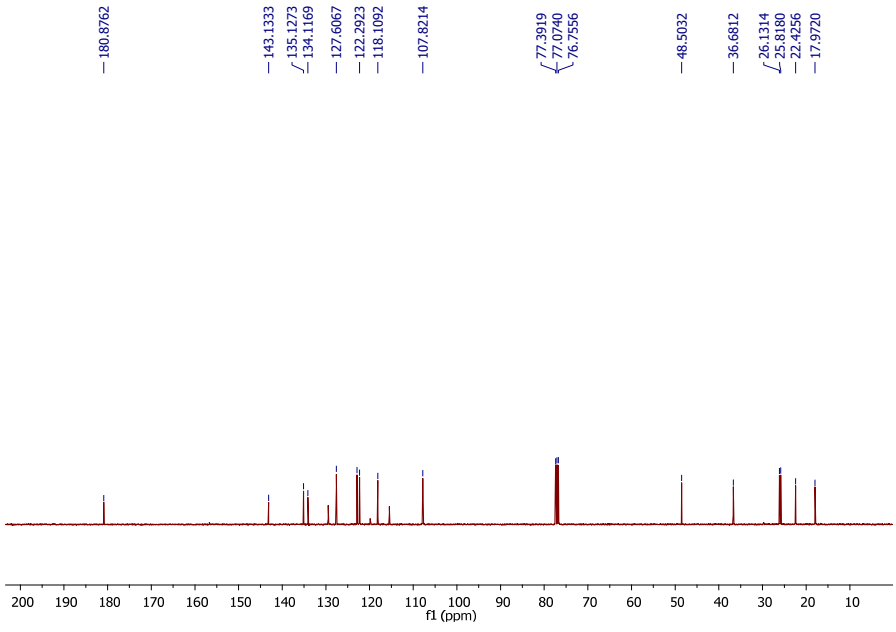
Scanned copy of mass spectrum (HRMS) of compound (±)-**14a**

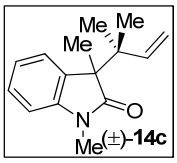


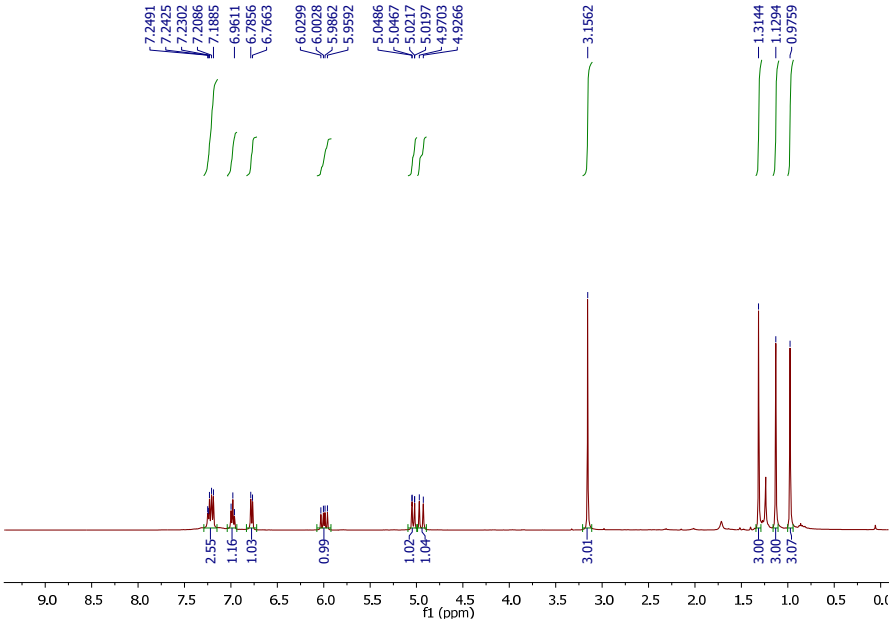


^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**14b**



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





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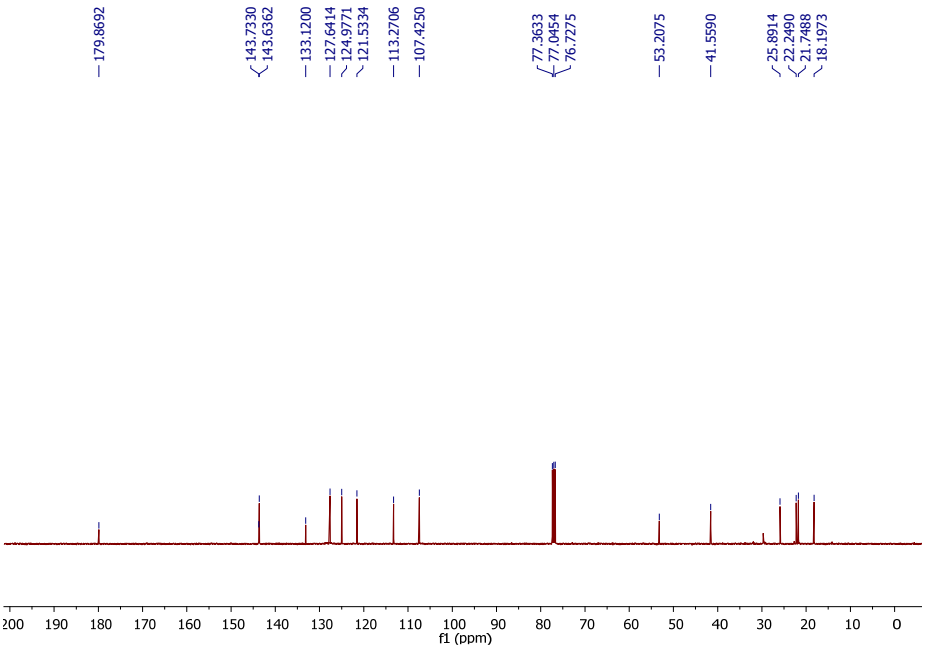
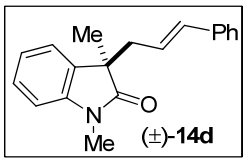
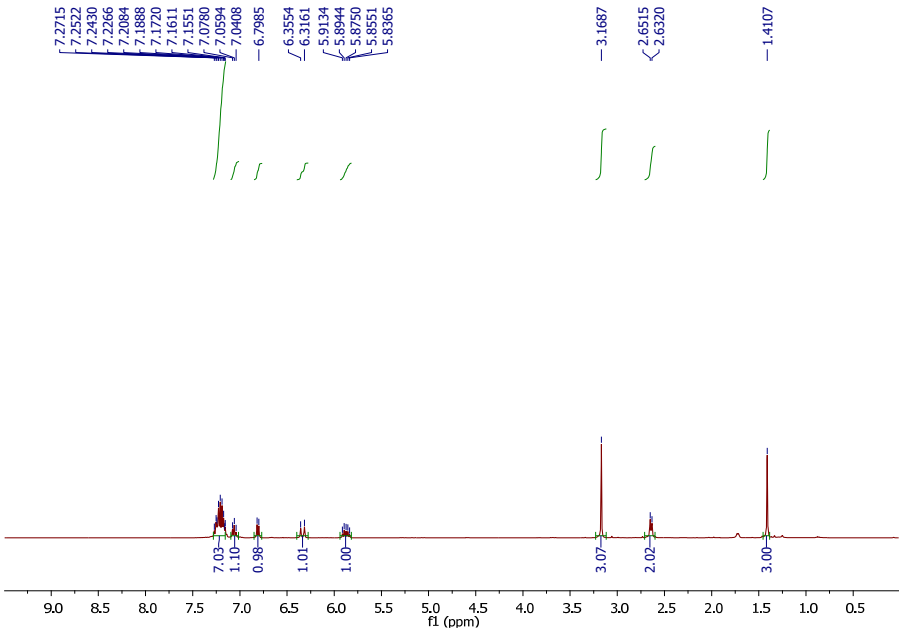
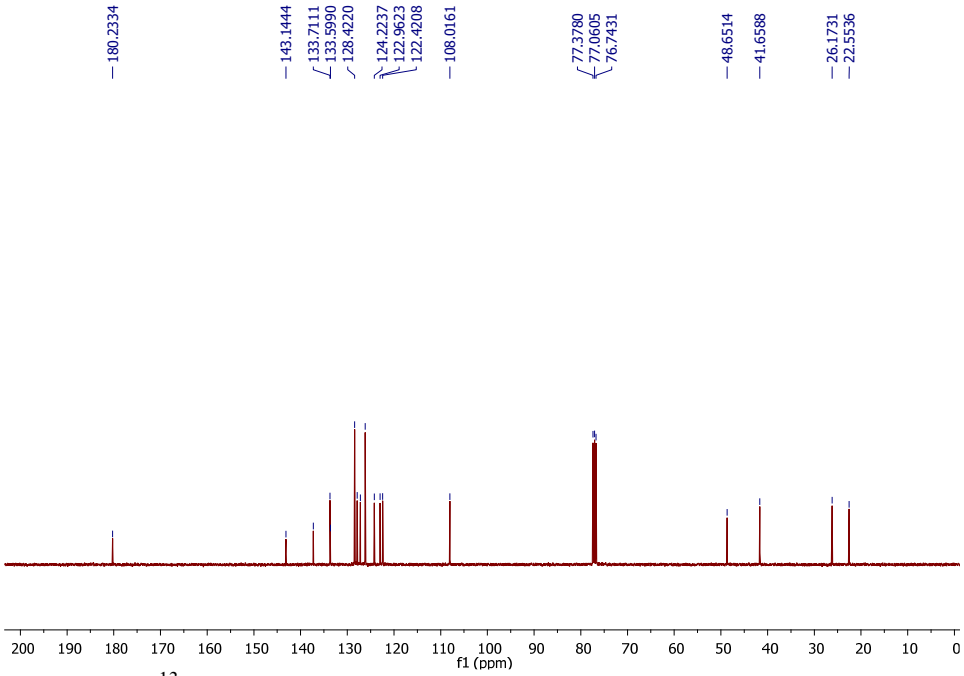


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**14c**

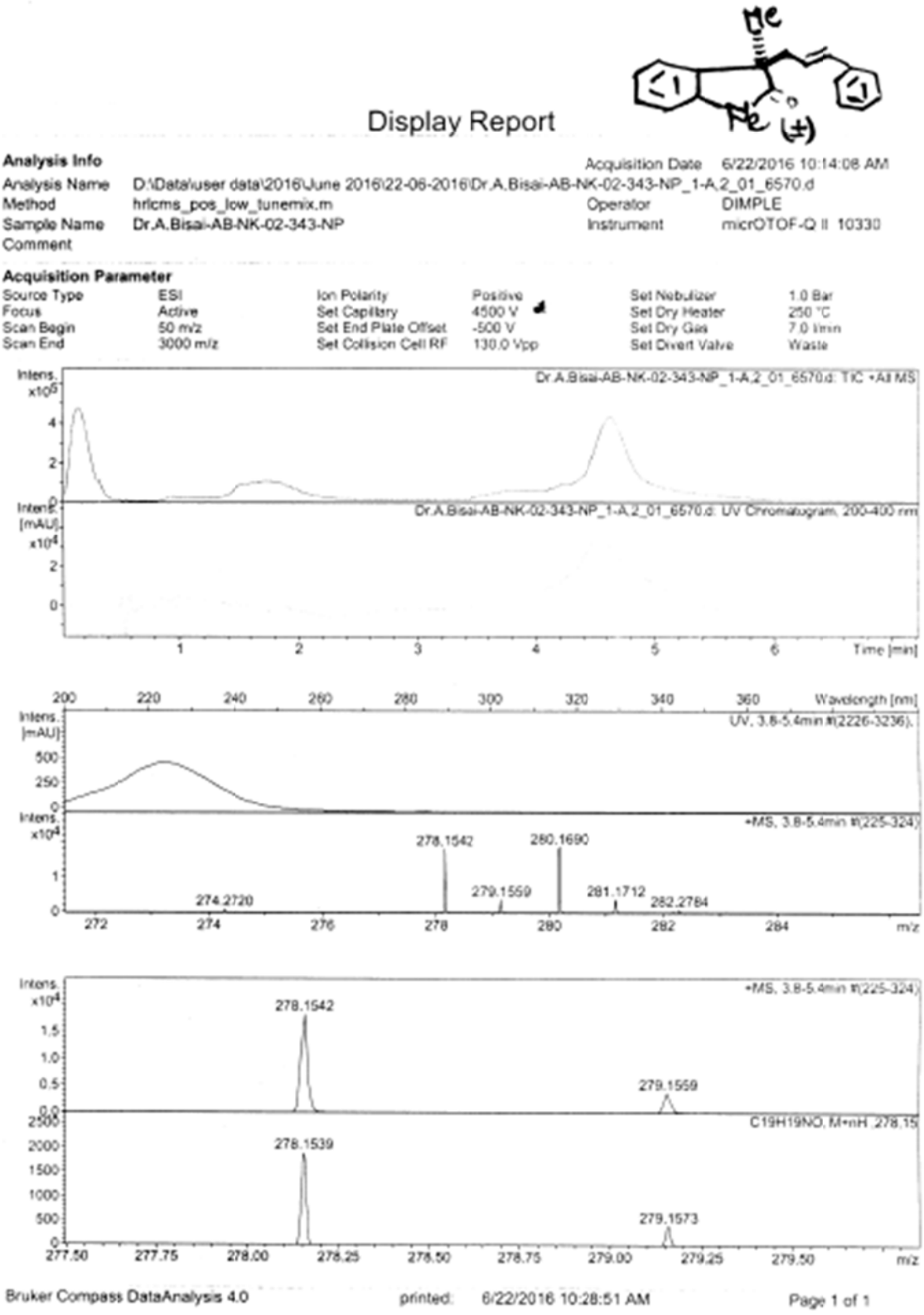




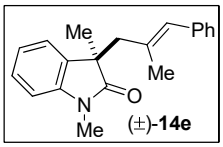
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**14d**

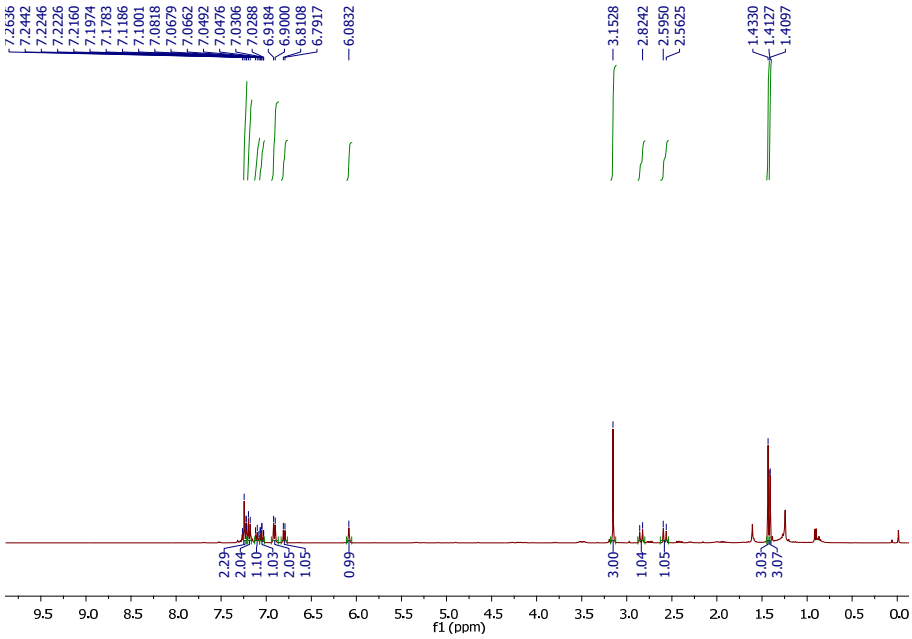


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**14d**

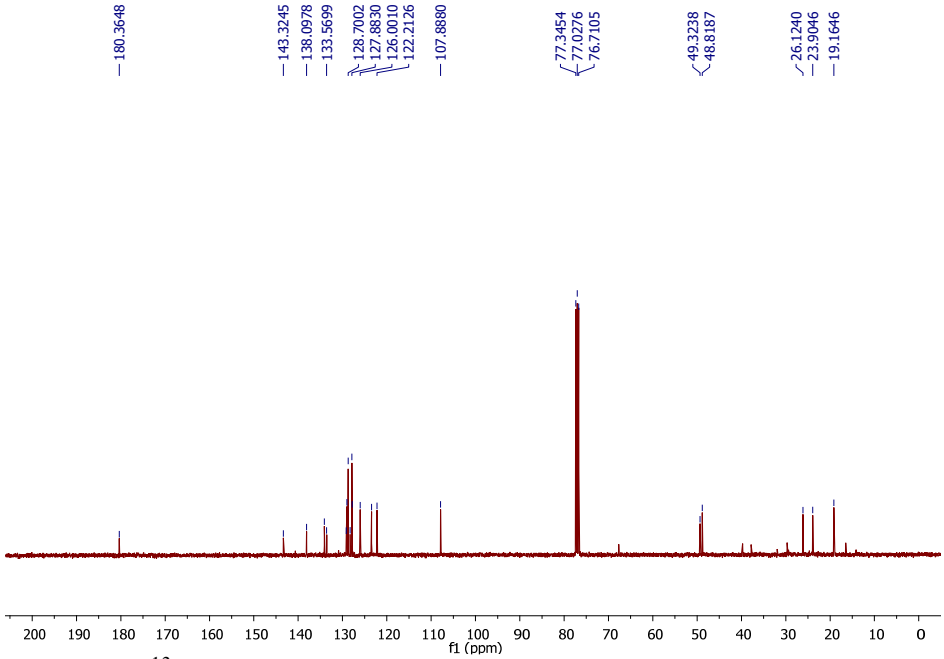


Scanned copy of mass spectrum (HRMS) of compound (±)-**14d**

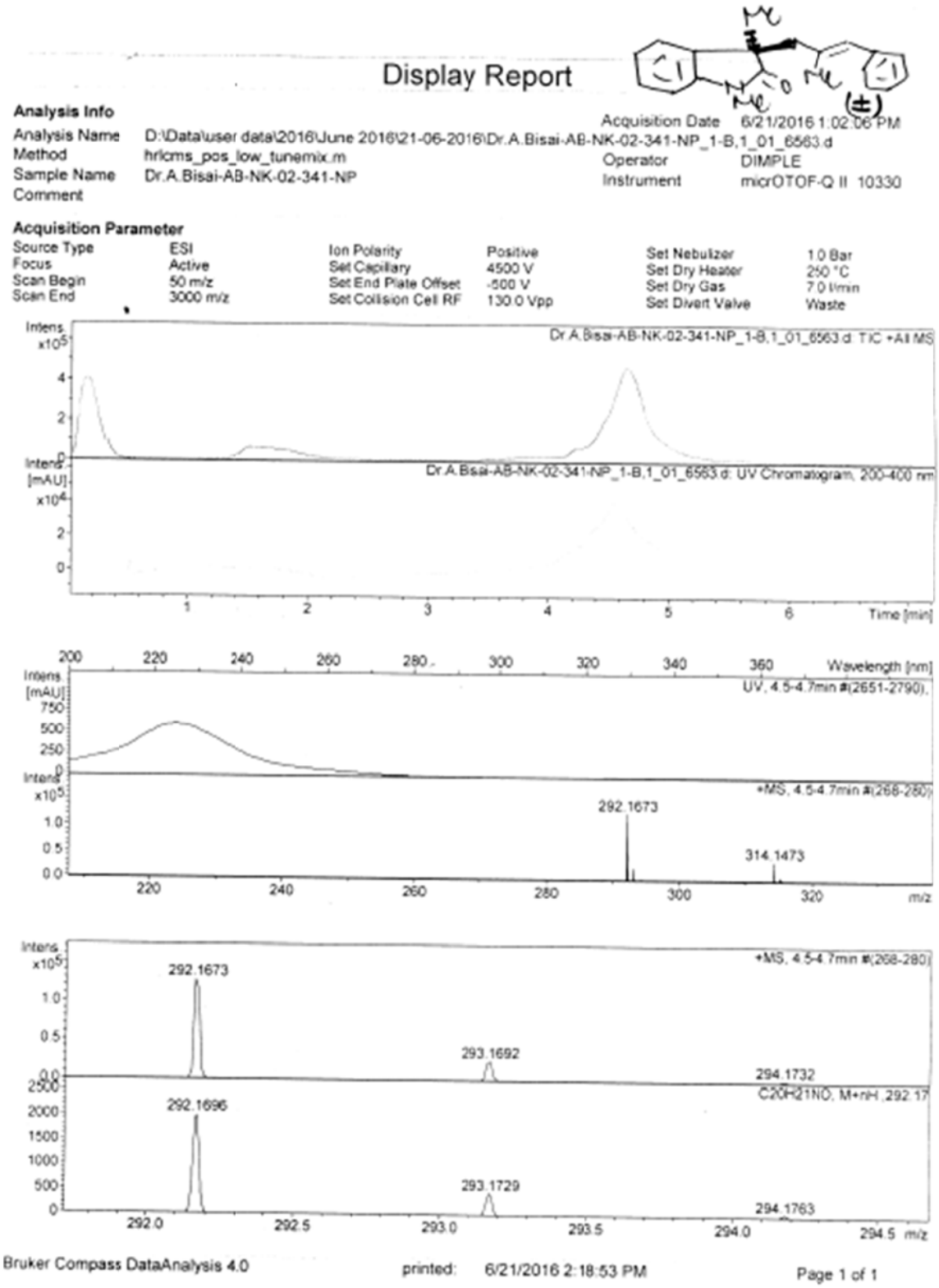




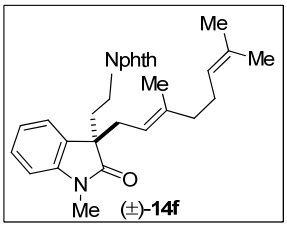
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**14e**

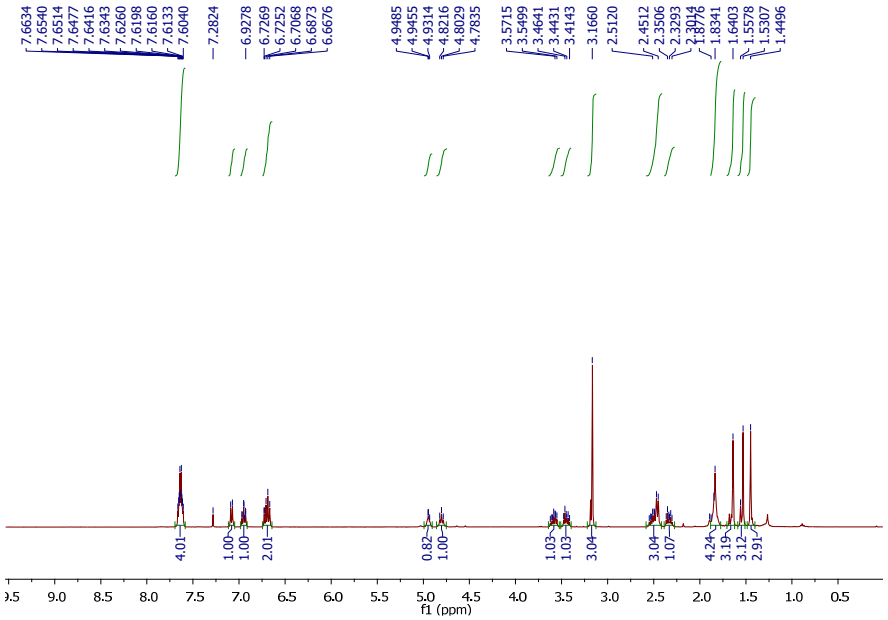


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**14e**

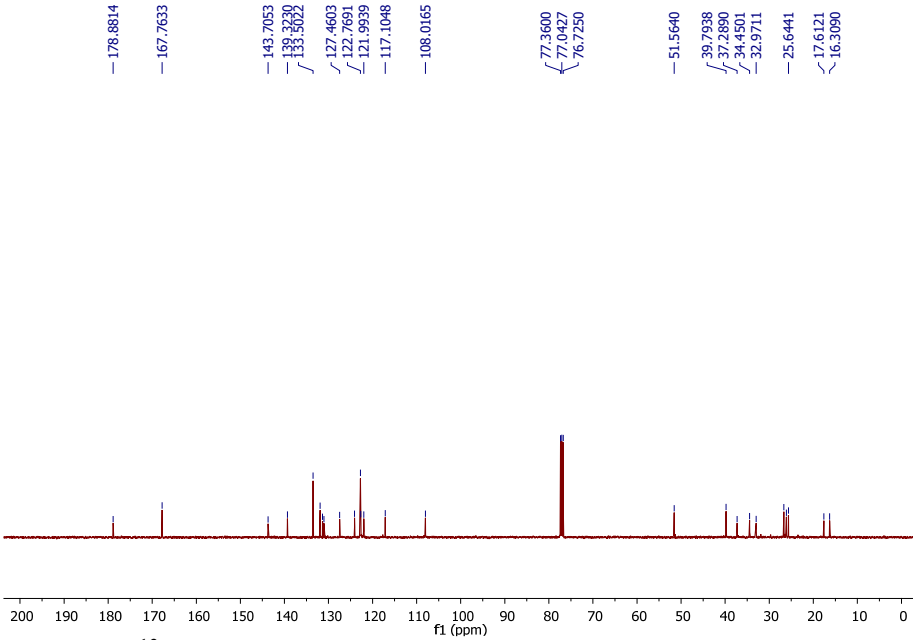


Scanned copy of mass spectrum (HRMS) of compound (±)-**14e**

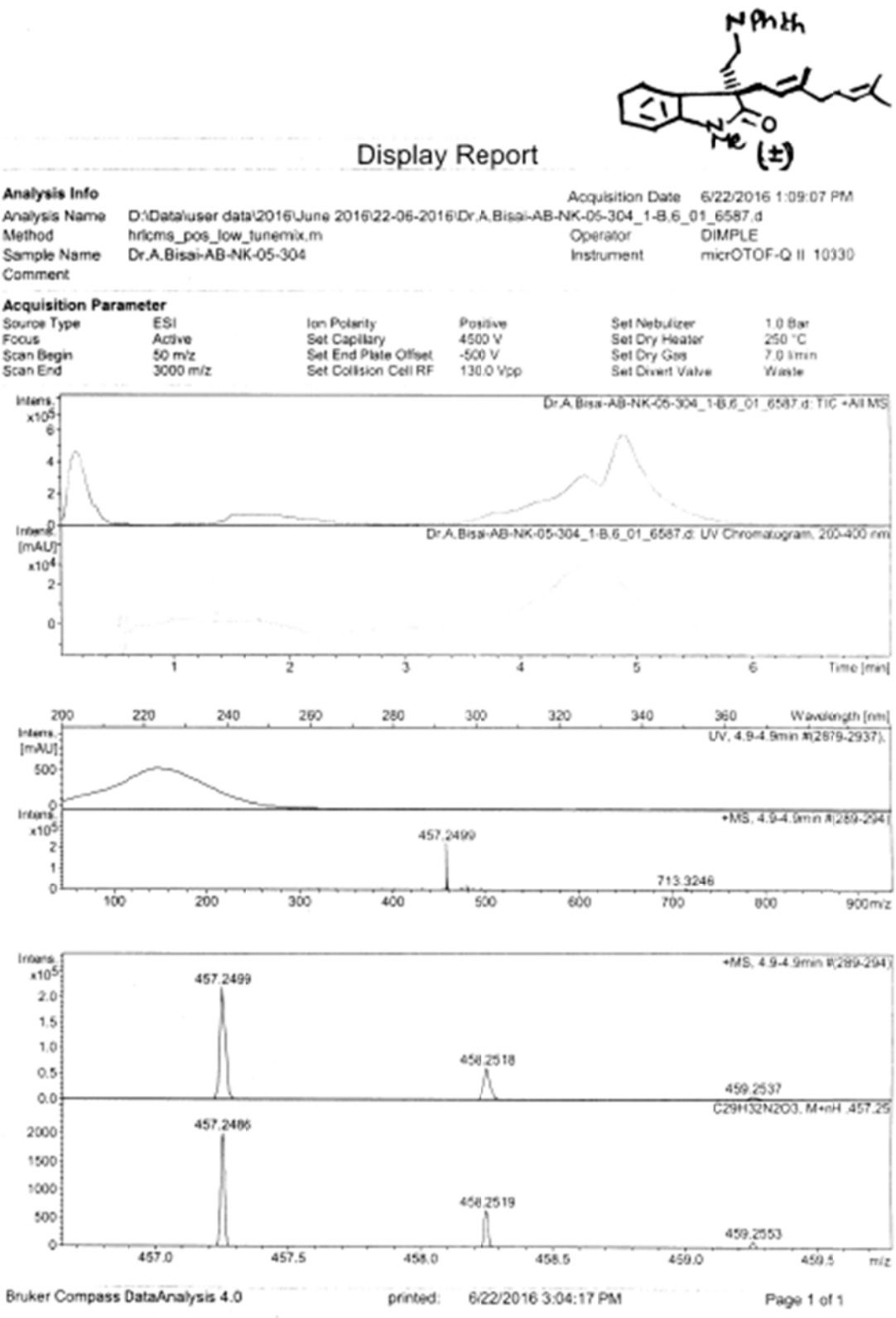




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**14f**



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



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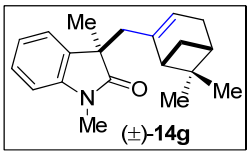
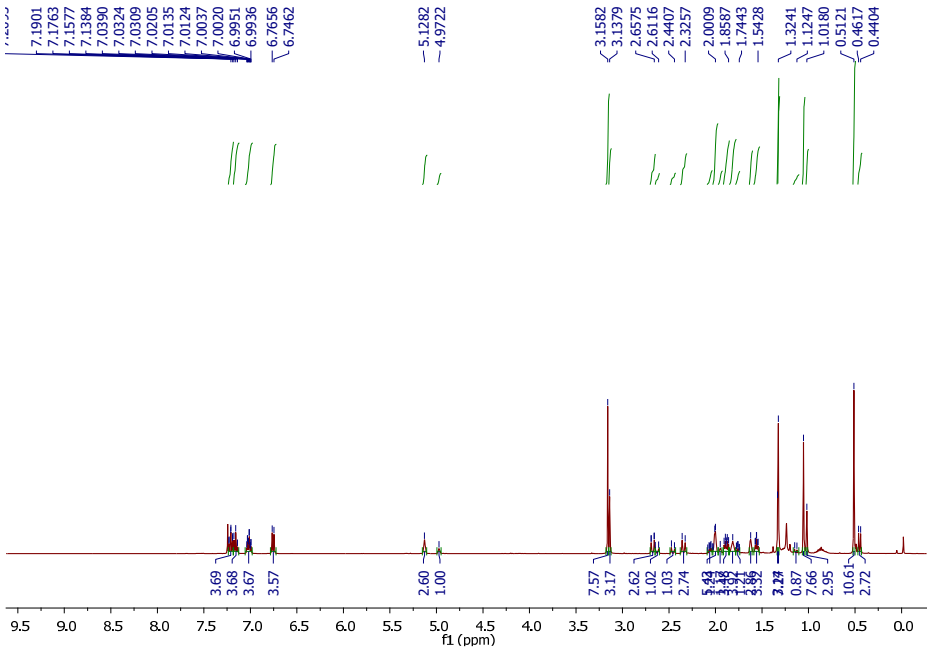
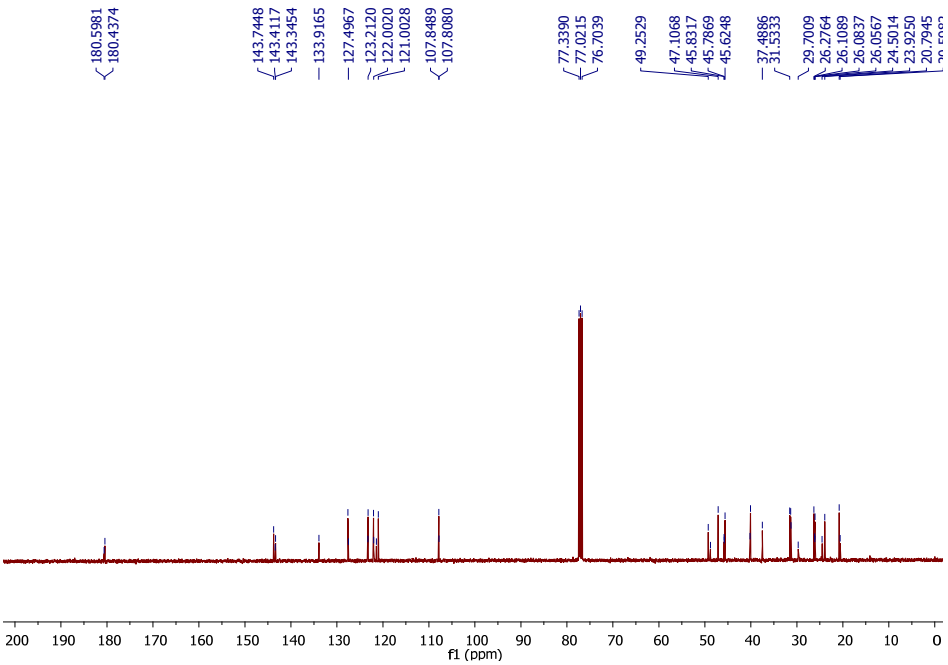
Scanned copy of mass spectrum (HRMS) of compound (±)-**14f**

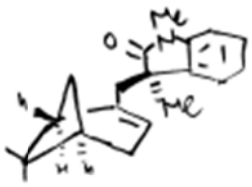




^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**14g**



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



Display Report

Analysis Info

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Method	hrlcms_pos_low_tunemix.m	Operator	DIMPLE
Sample Name	Dr.A.Bisai-AB-NK-02-342-NP	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
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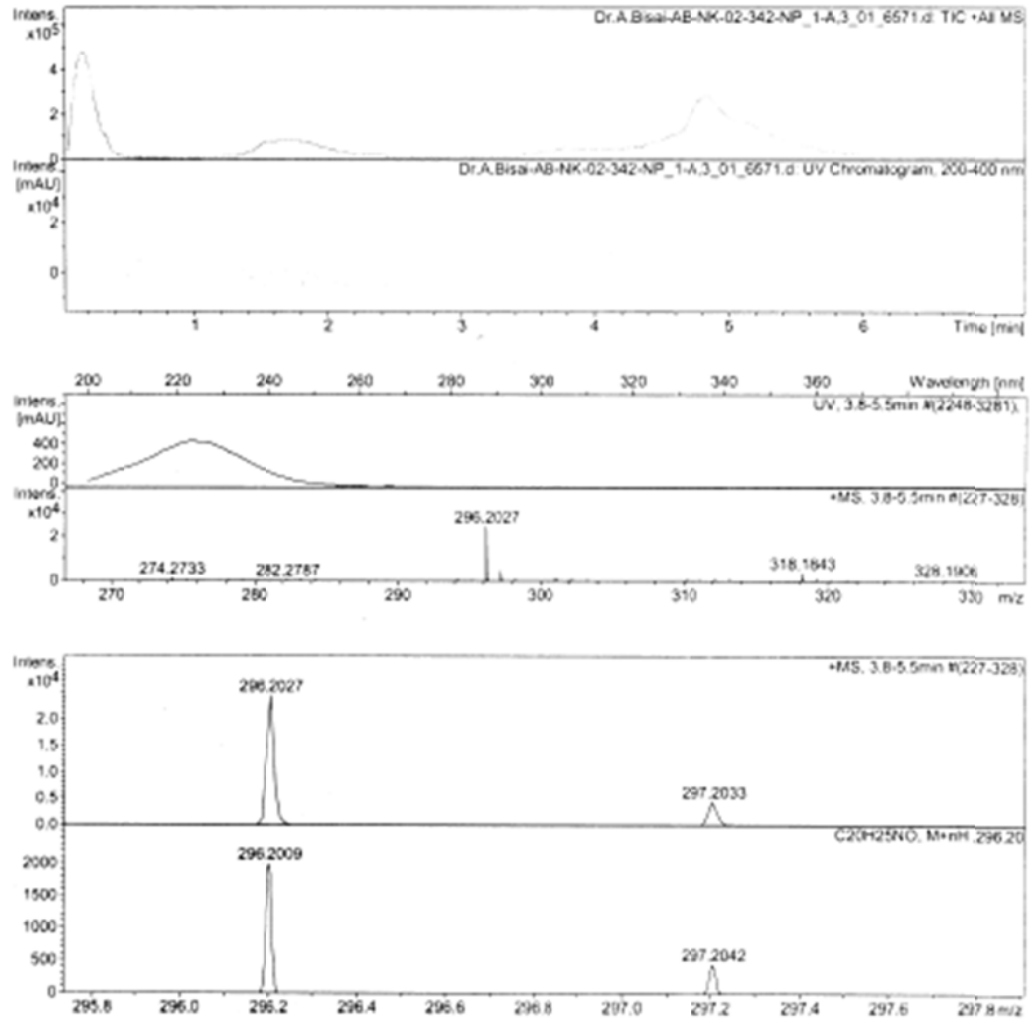
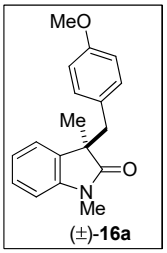
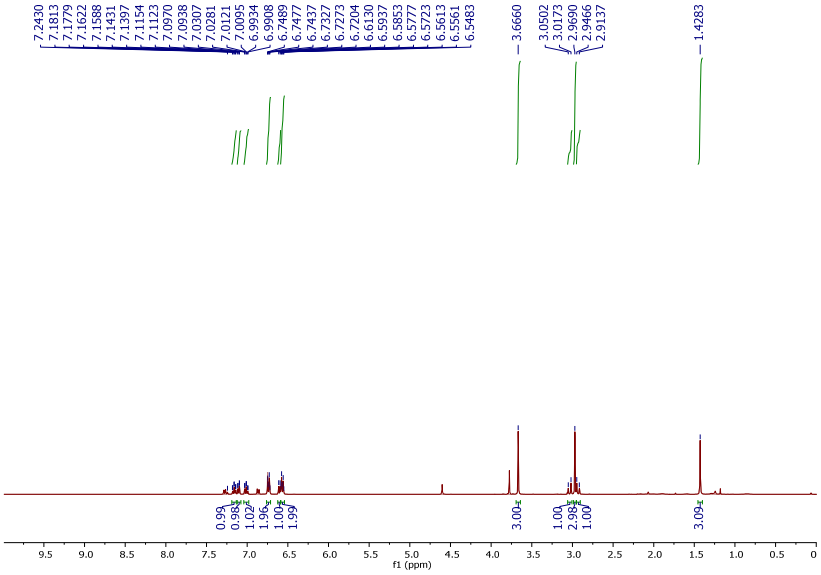
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



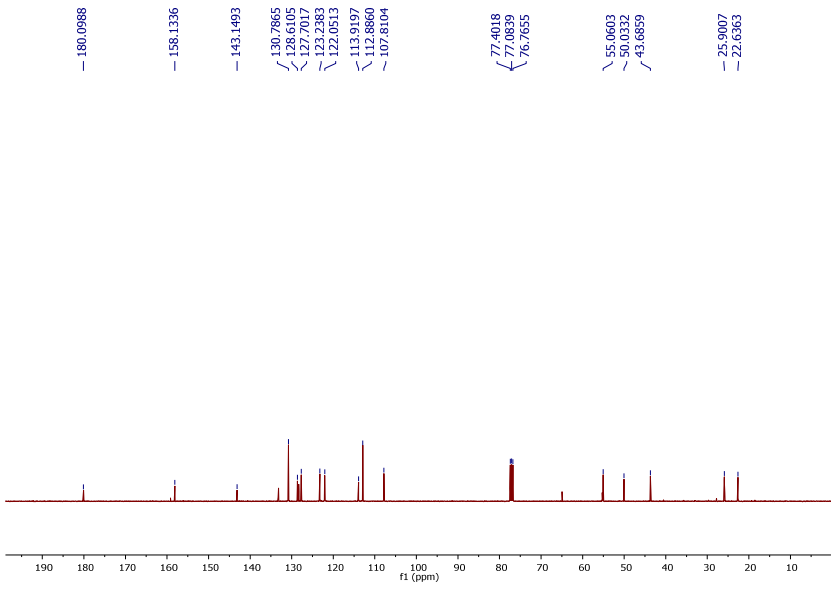
Bruker Compass DataAnalysis 4.0 printed: 6/22/2016 11:38:56 AM Page 1 of 1

Scanned copy of mass spectrum (HRMS) of compound (±)-**14g**

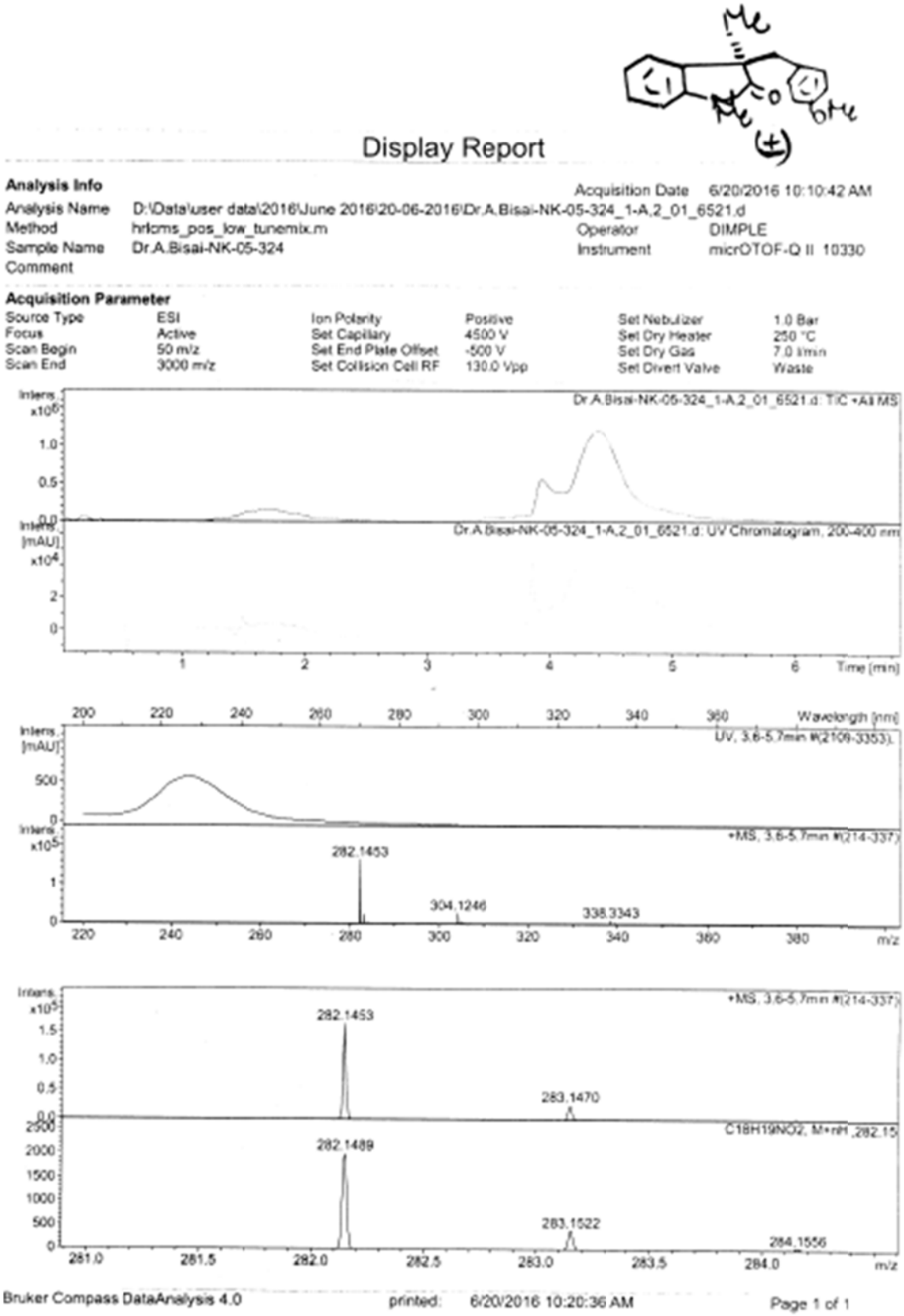




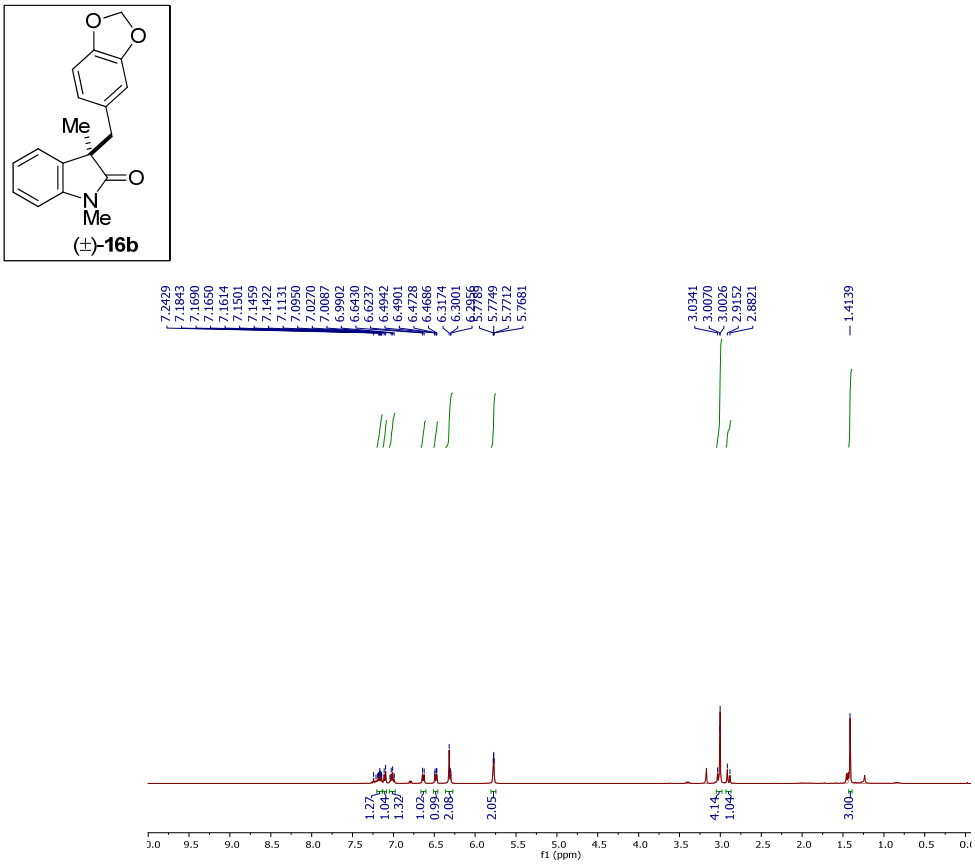
^{1}H NMR (400 MHz, $CDCl_3$) of compound (**16a**)



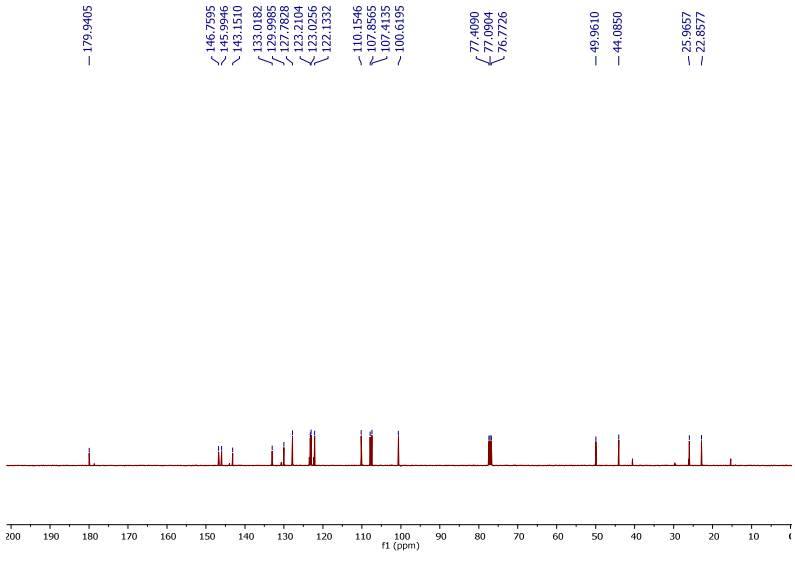
^{13}C NMR (100 MHz, $CDCl_3$) of compound (**16a**)



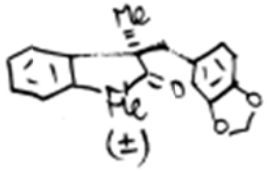
Scanned copy of mass spectrum (HRMS) of compound (**16a**)



^{1}H NMR (400 MHz, $CDCl_3$) of compound (**16b**)



^{13}C NMR (100 MHz, $CDCl_3$) of compound (**16b**)



Display Report

Analysis Info

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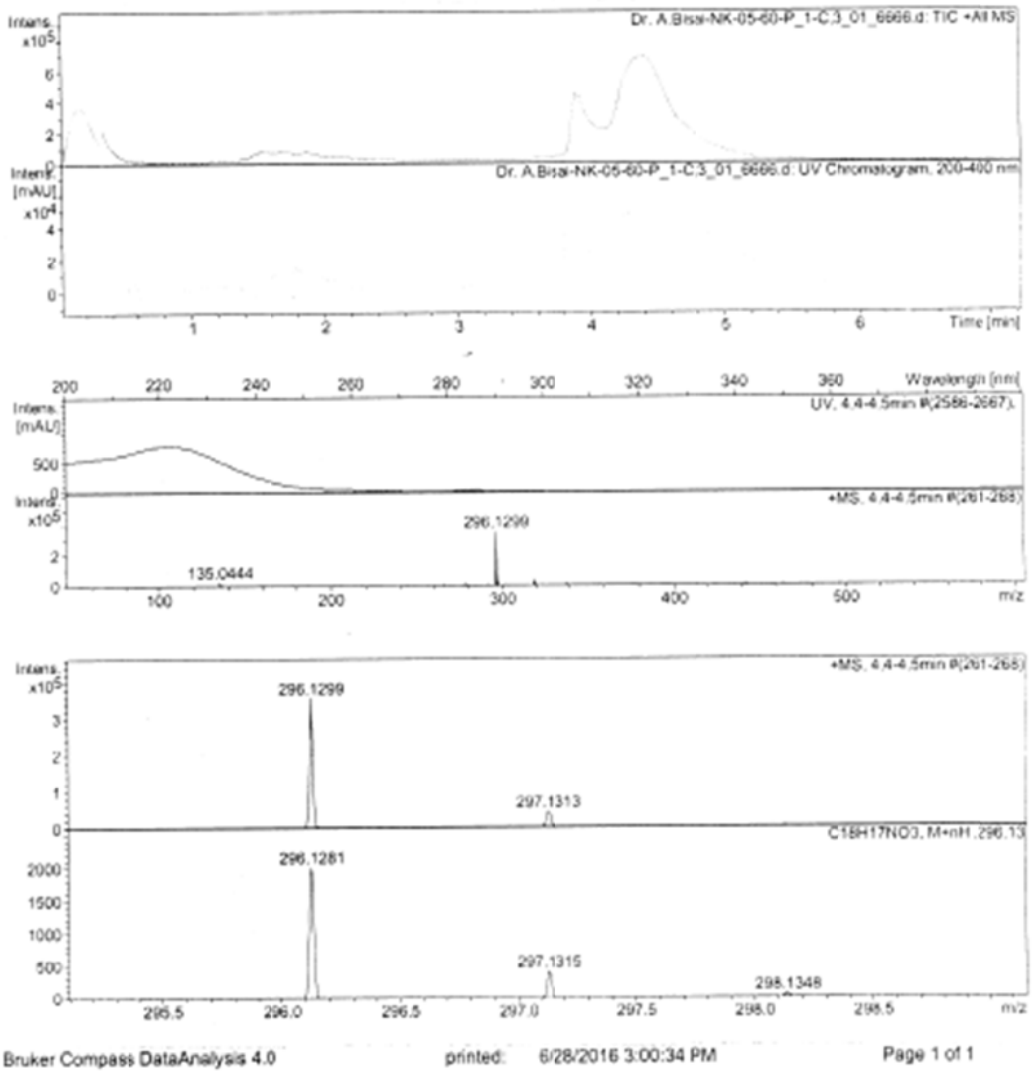
Method	hrlcms_pos_low_tunemix.m	Operator	DIMPLE
Sample Name	Dr. A.Bisai-NK-05-60-P	Instrument	micrOTOF-Q II 10330
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



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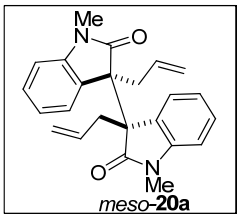
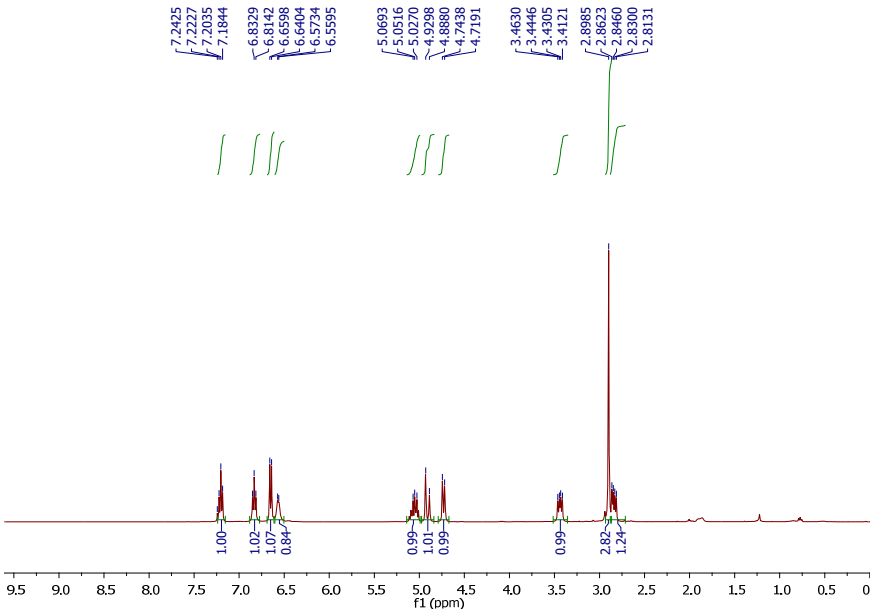
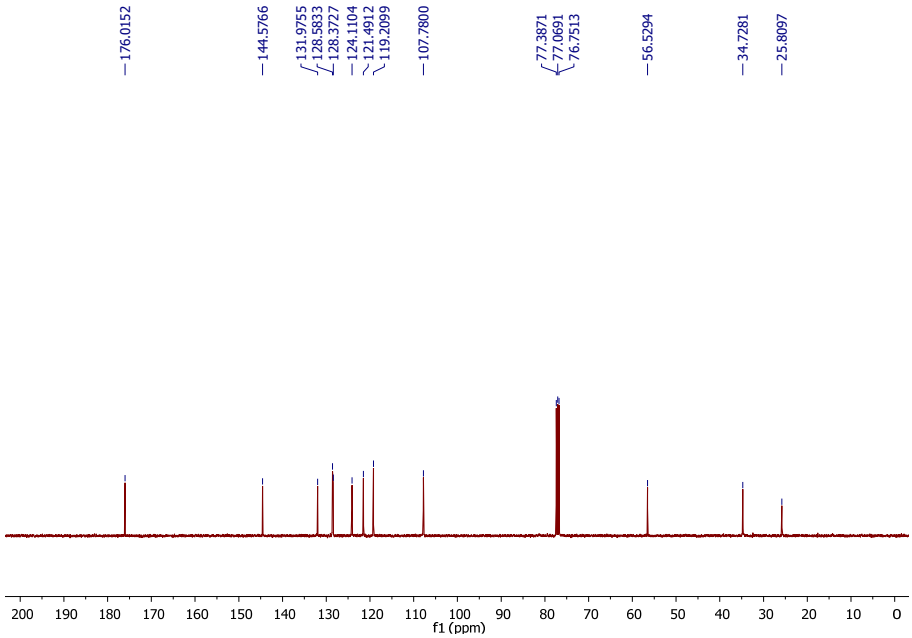
Scanned copy of mass spectrum (HRMS) of compound (**16b**)

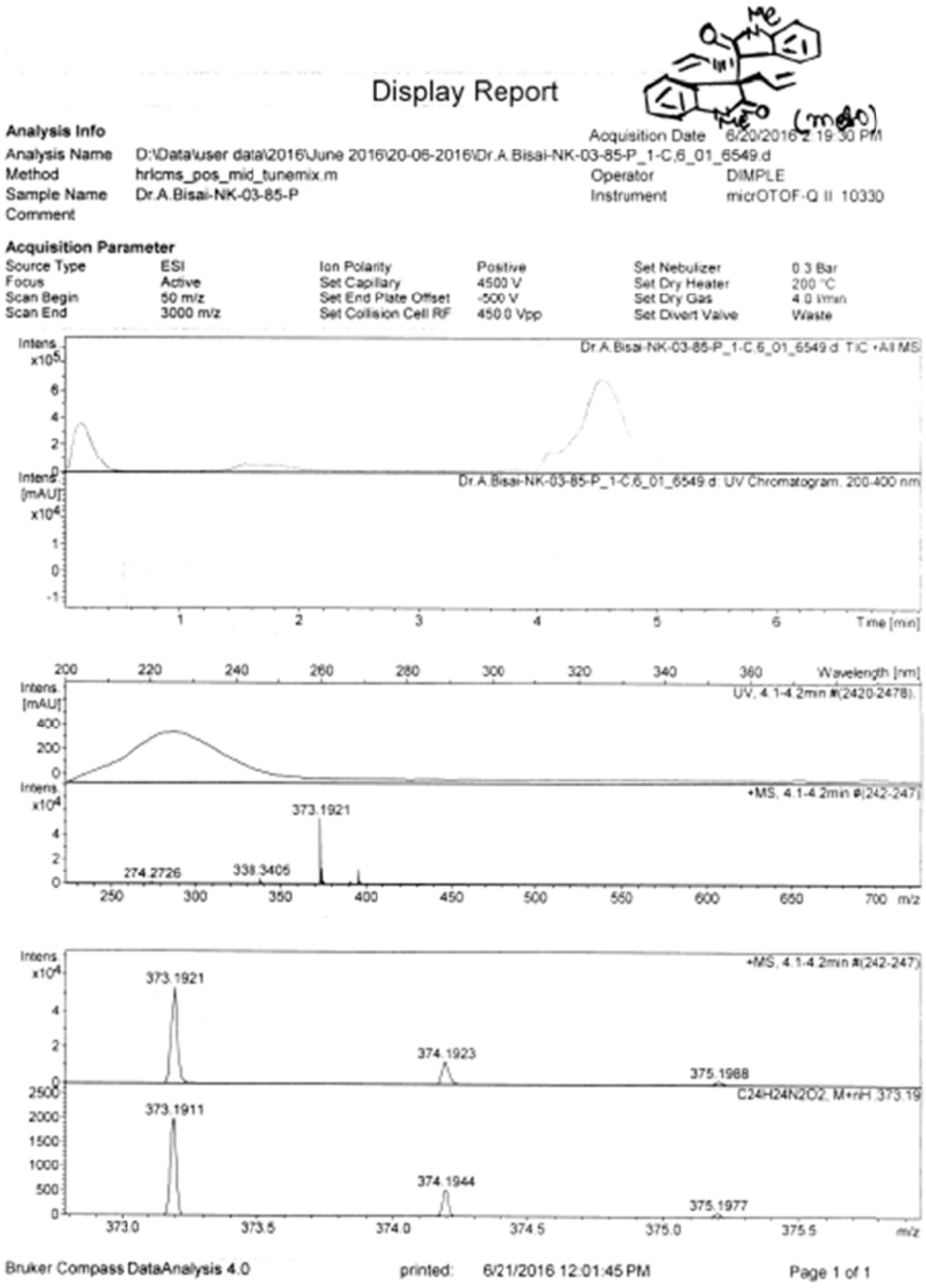




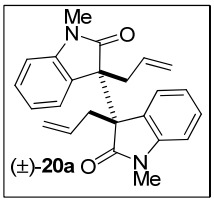
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**20a**)

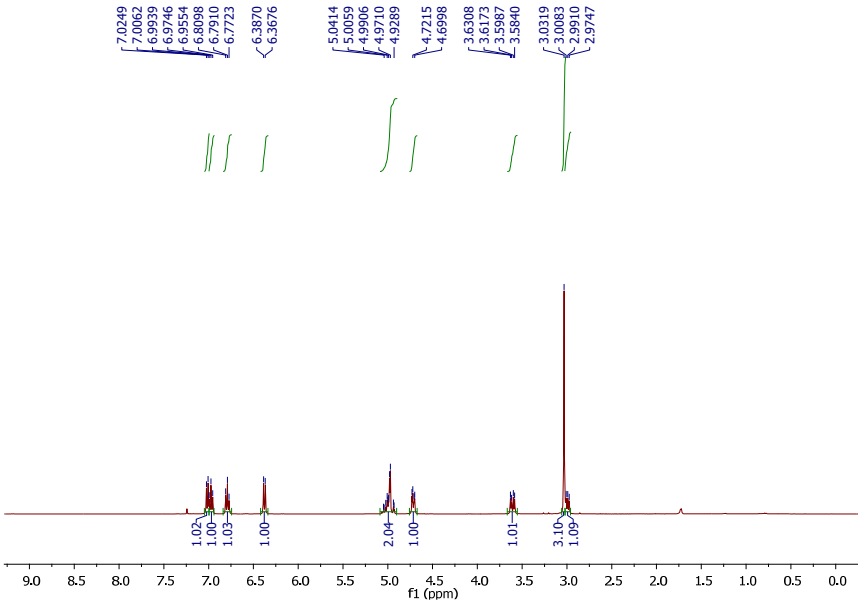


^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**20a**)

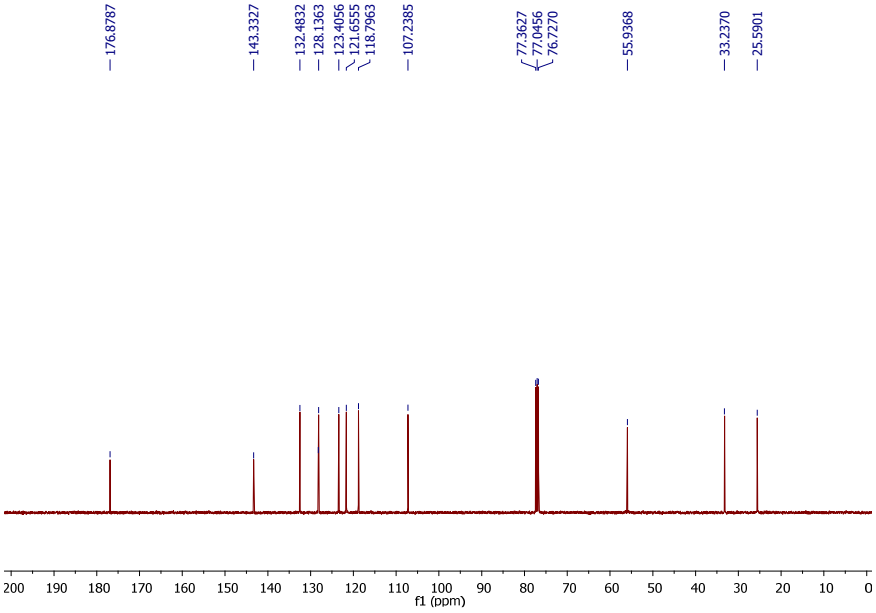


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**20a**)

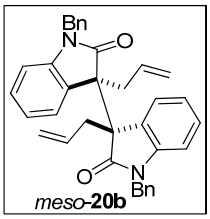


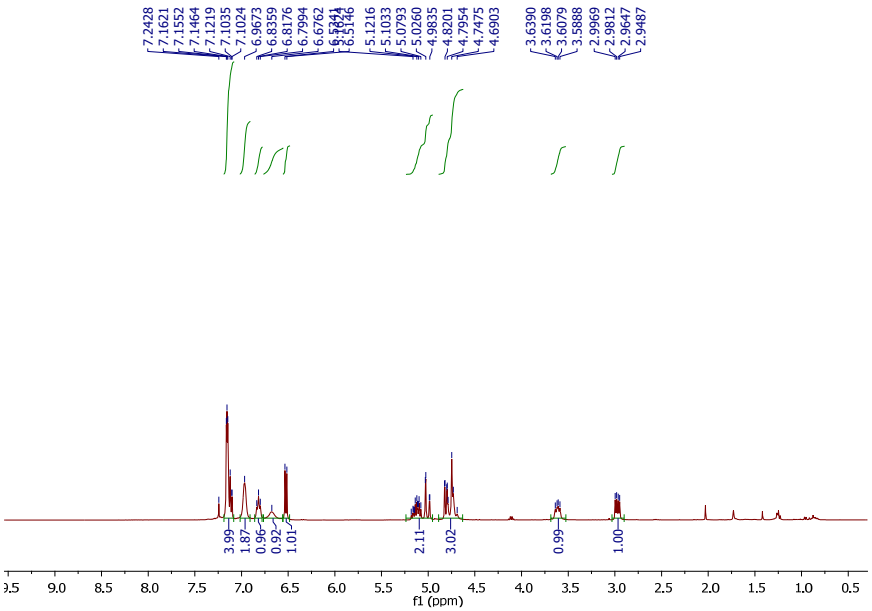


^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20a**

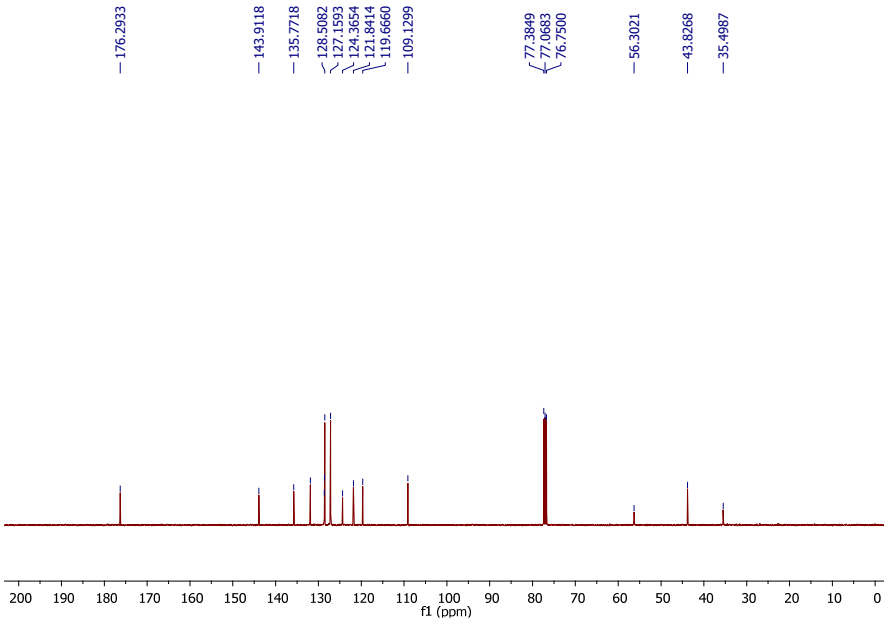


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20a**

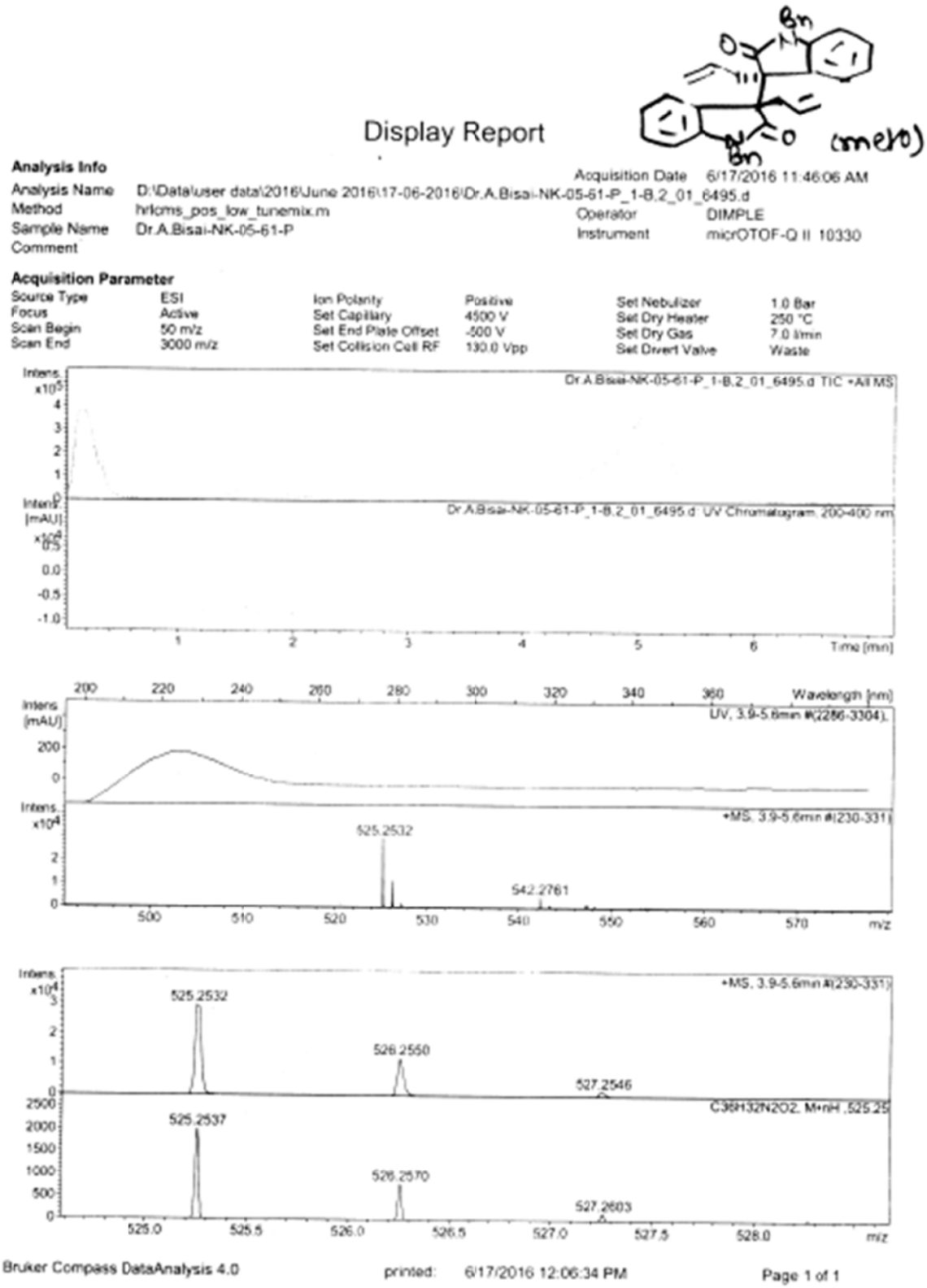




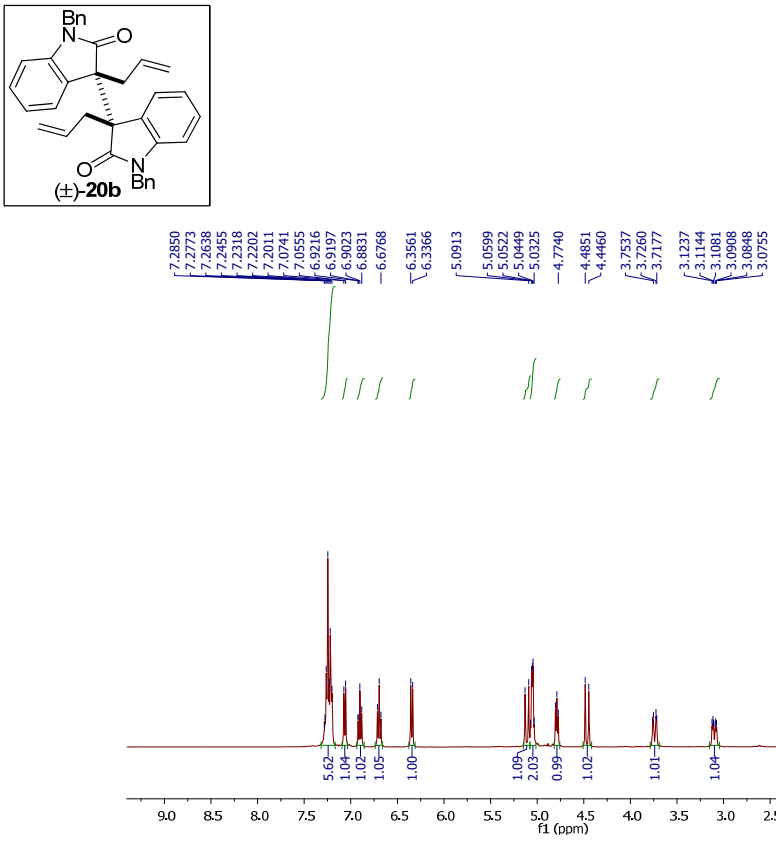
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**20b**)



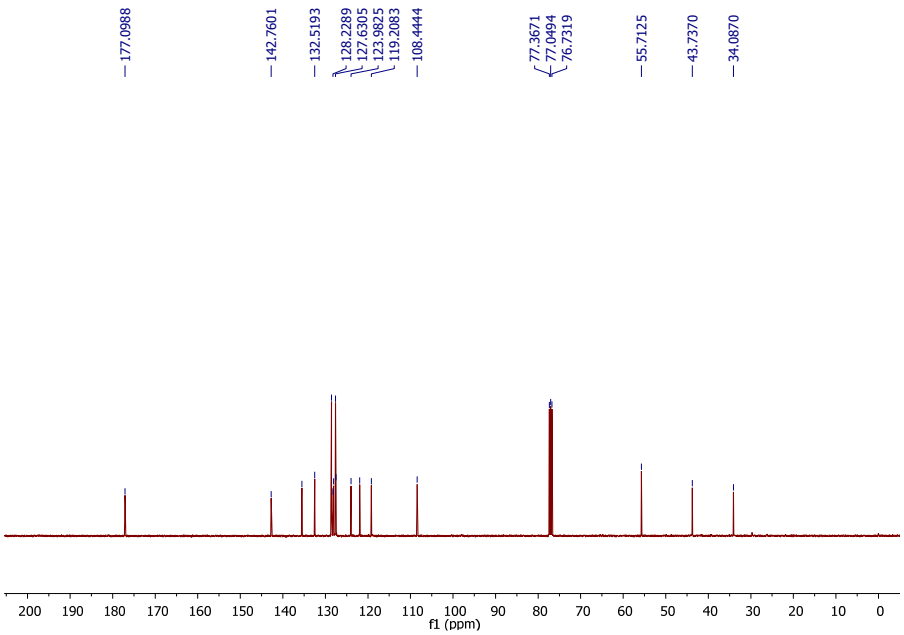
^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**20b**)



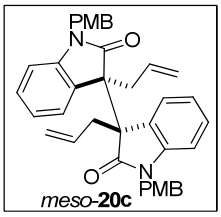
Scanned copy of mass spectrum (HRMS) of compound (*meso*-**20b**)

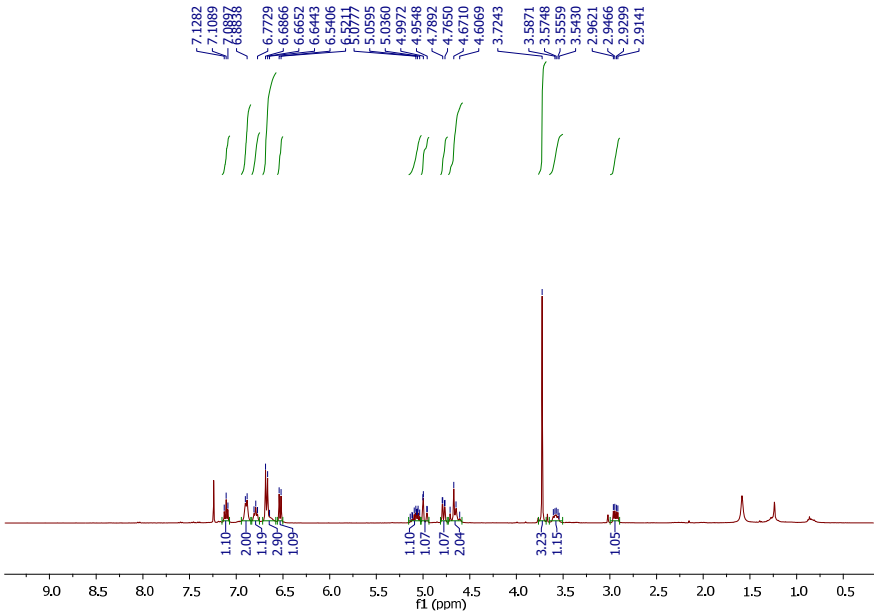


^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20b**

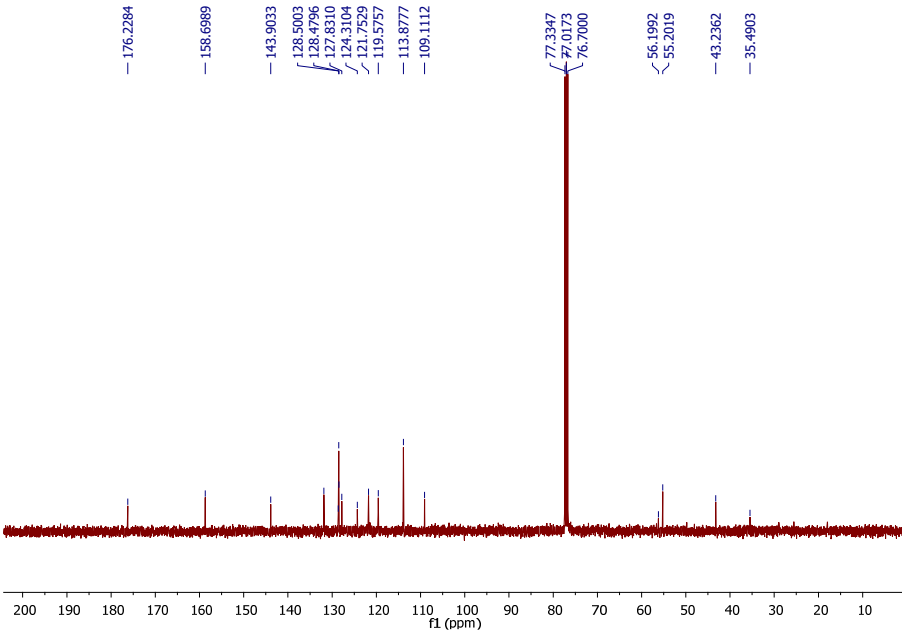


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20b**

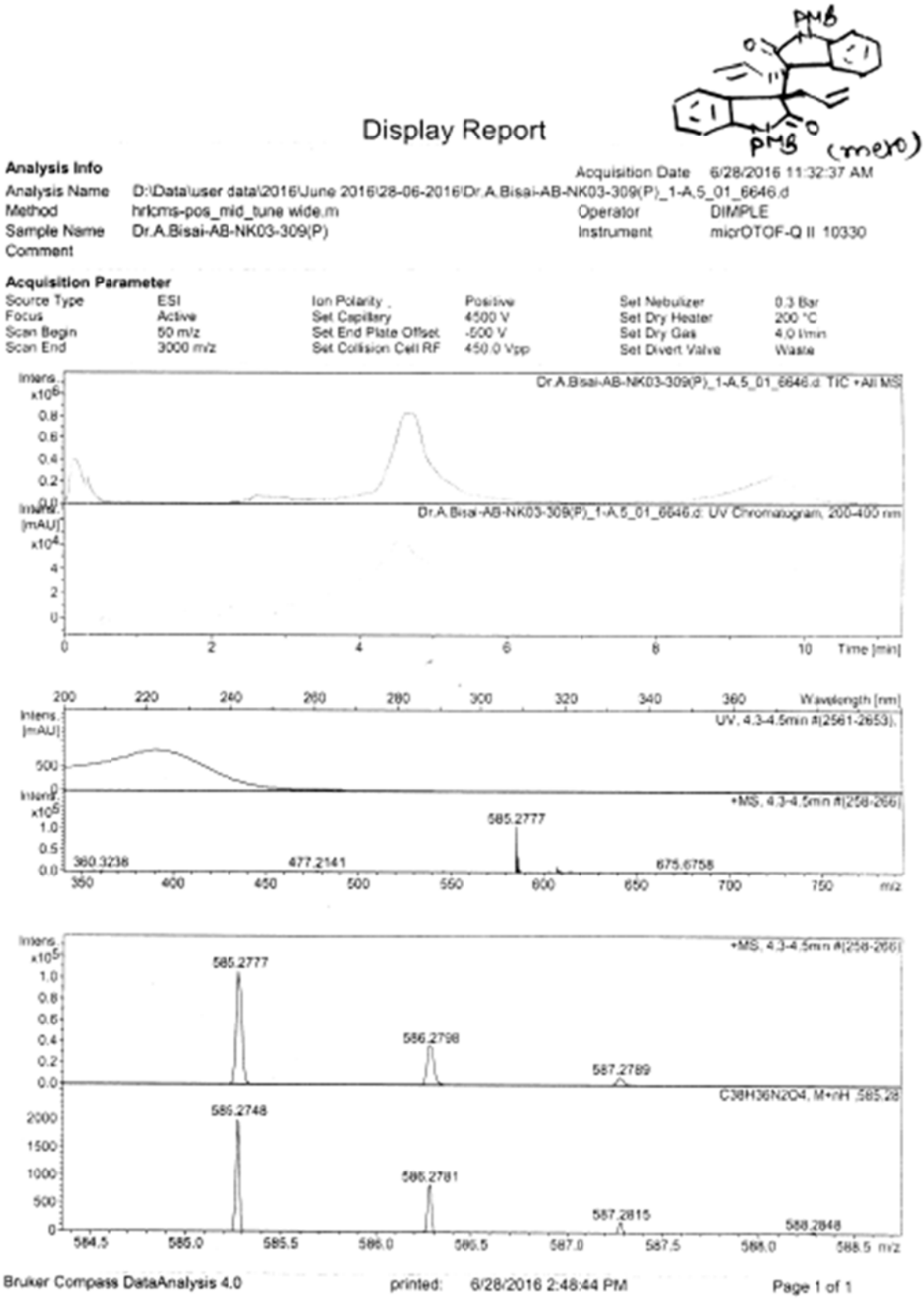




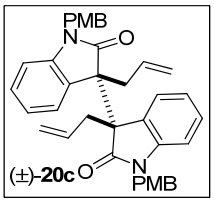
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**20c**)

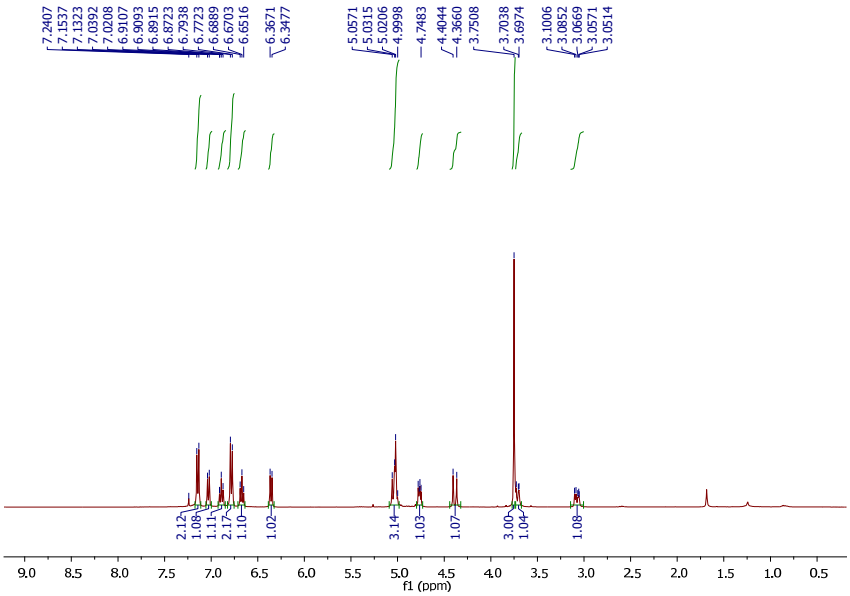


^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**20c**)

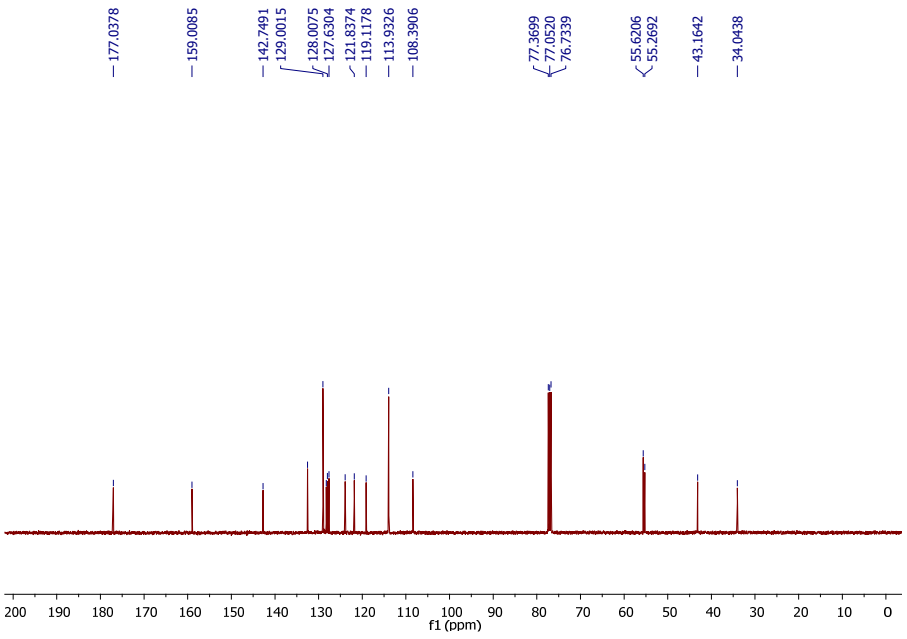


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**20c**)

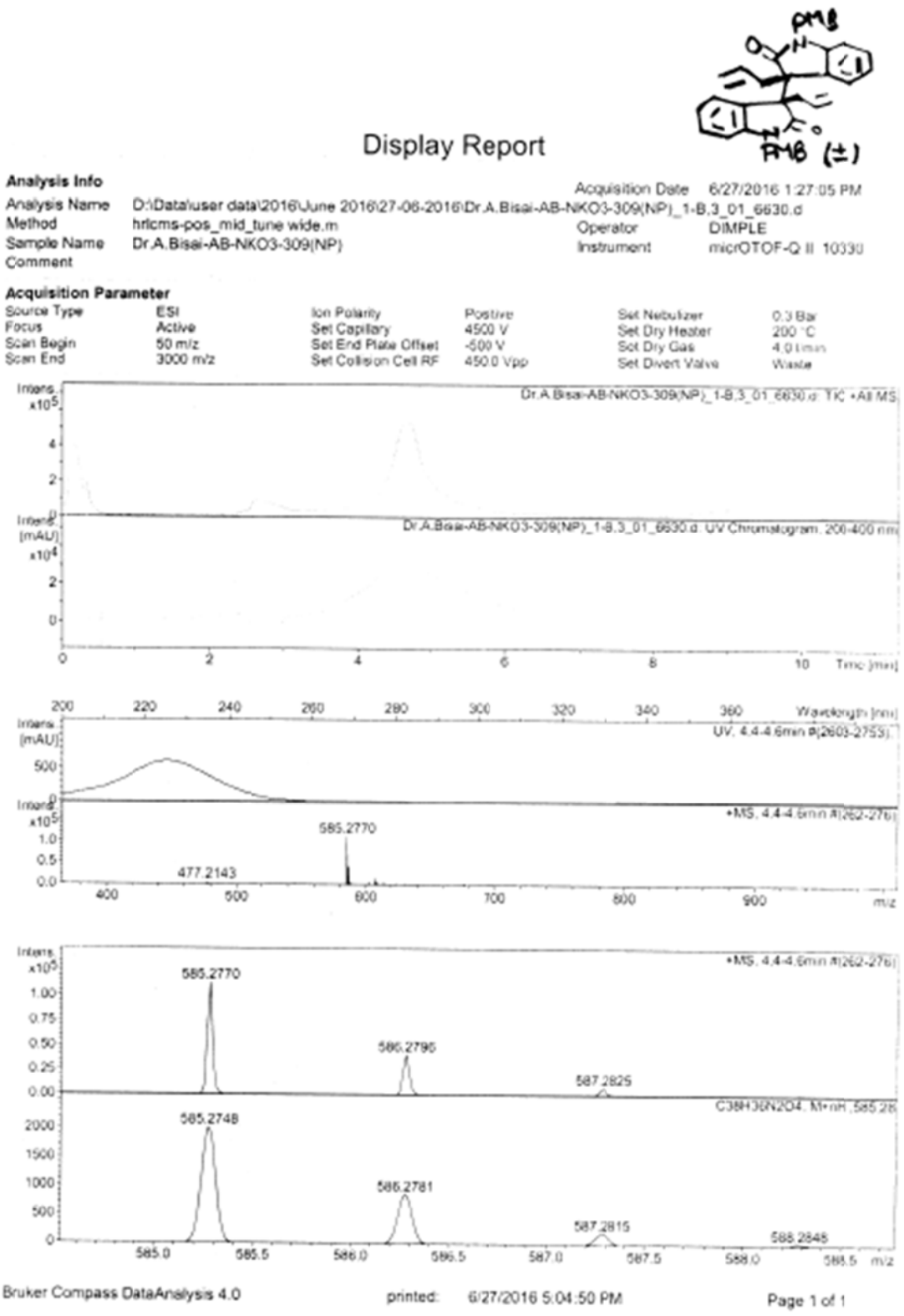




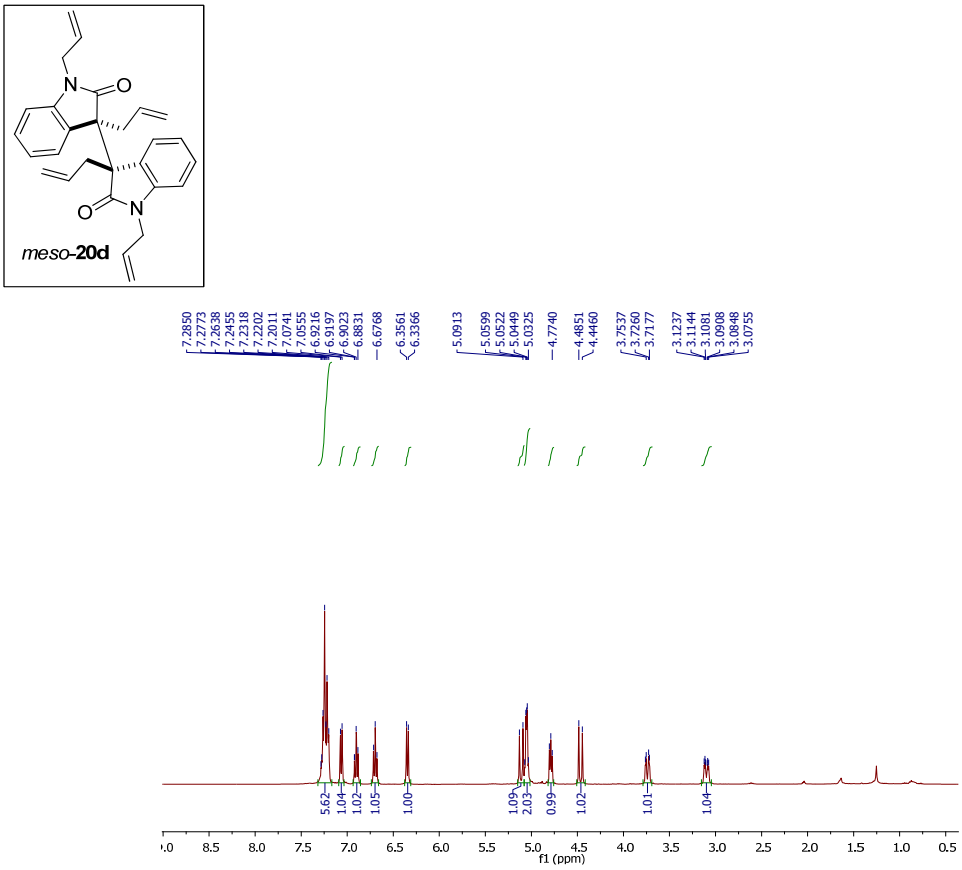
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20c**



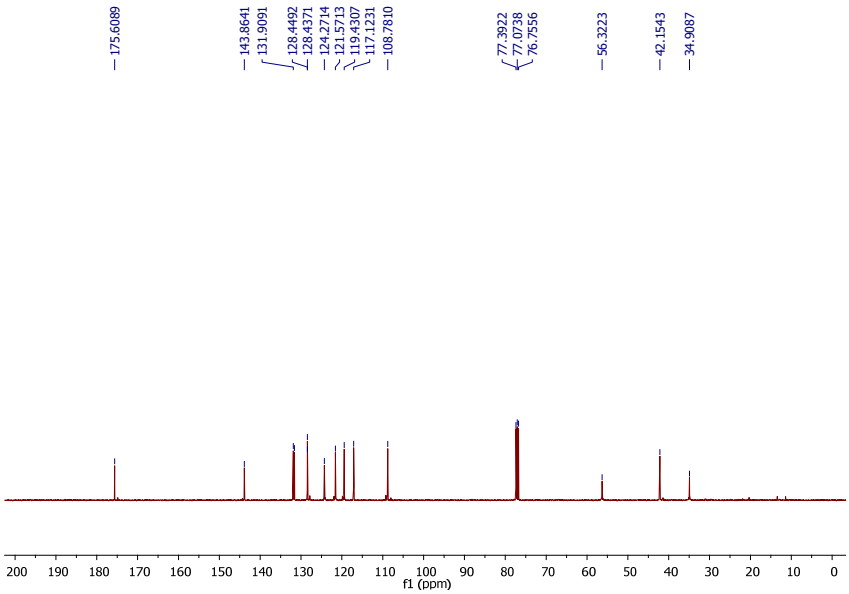
^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20c**



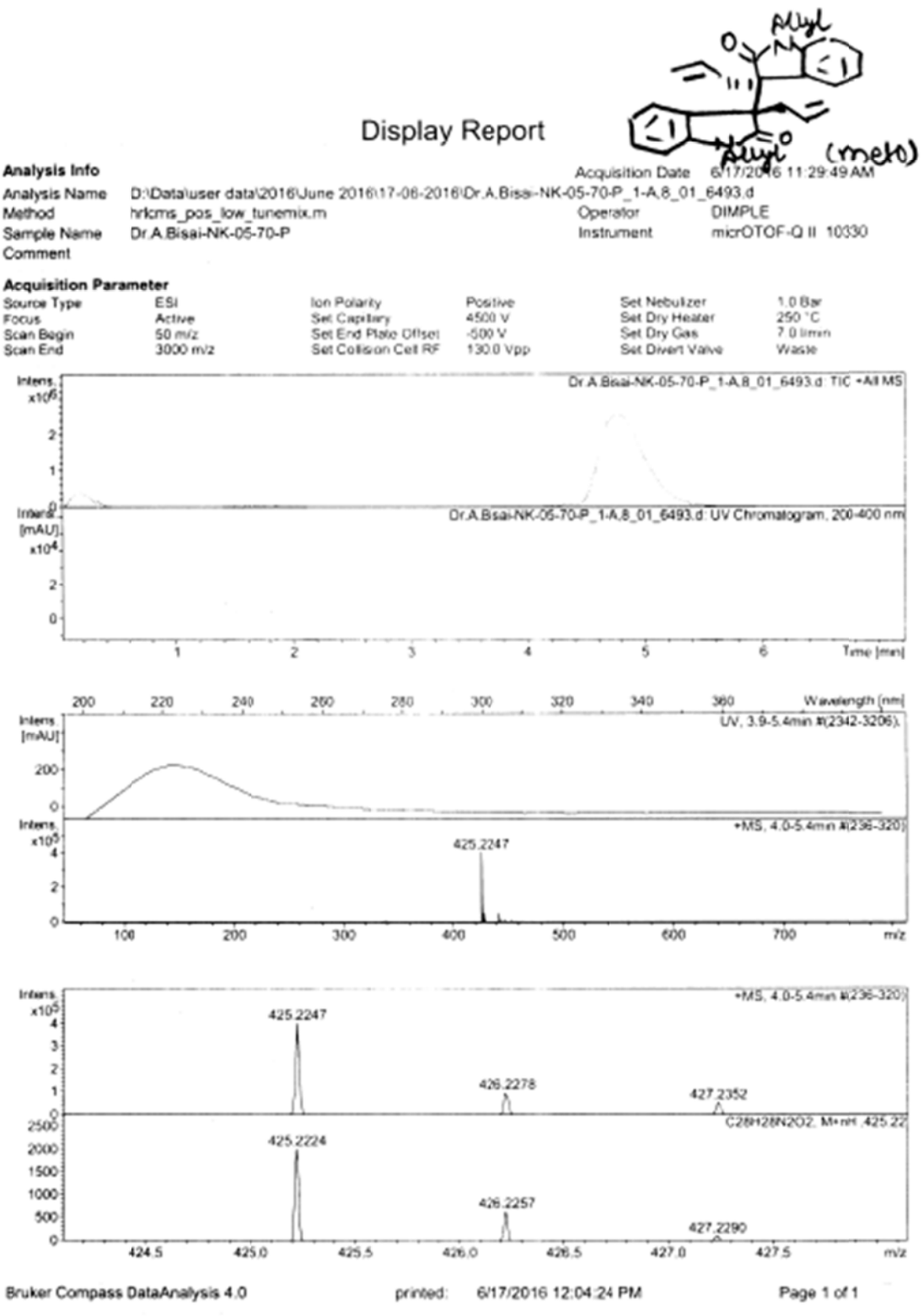
Scanned copy of mass spectrum (HRMS) of compound (±) -**20c**



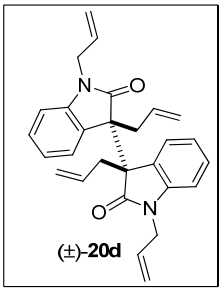
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**20d)**

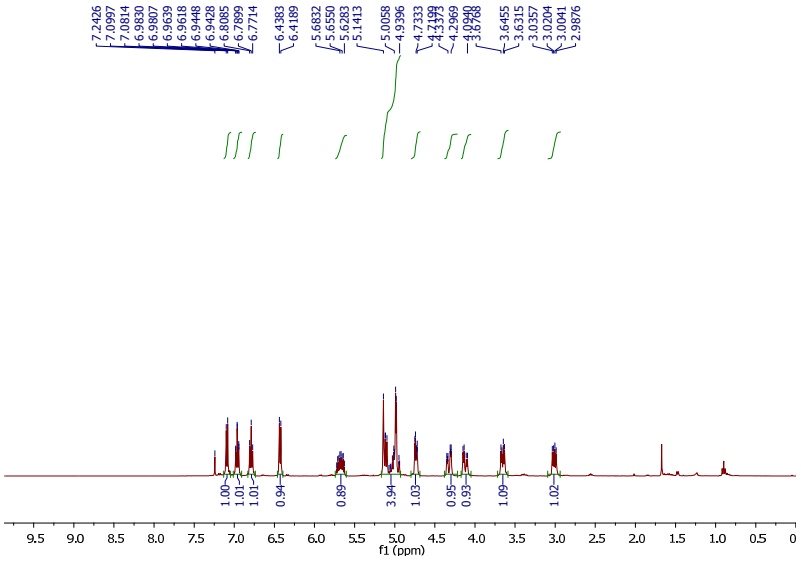


^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**20d**)

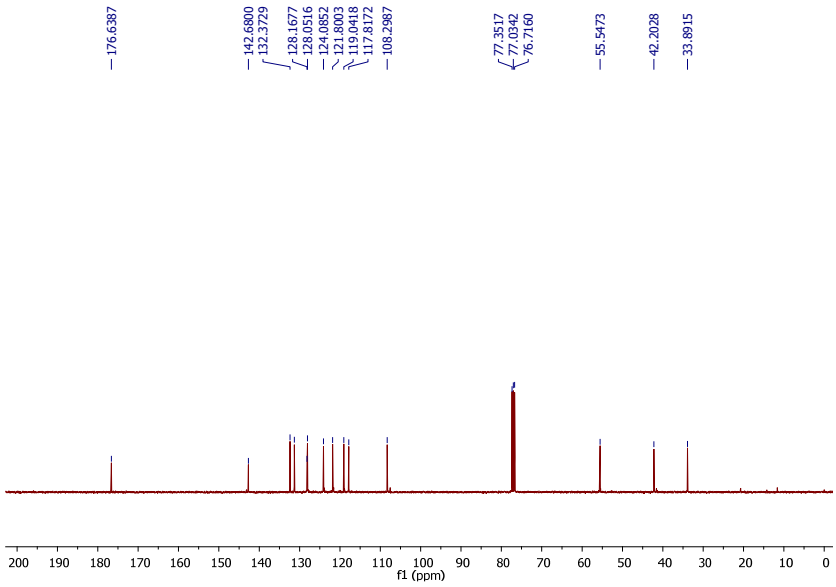


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**20d**)

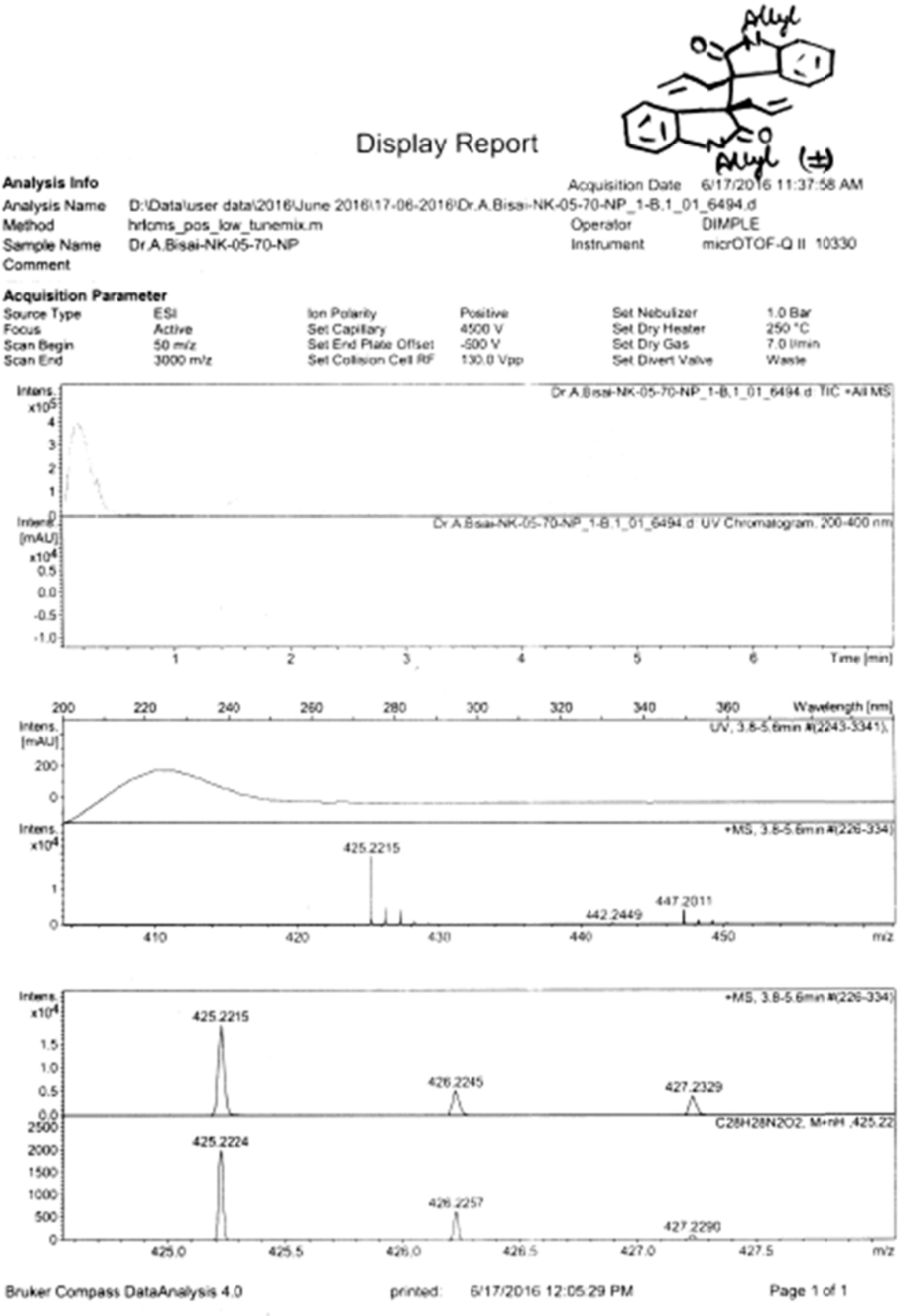




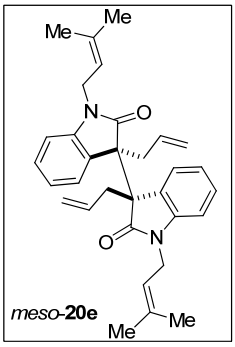
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20d**

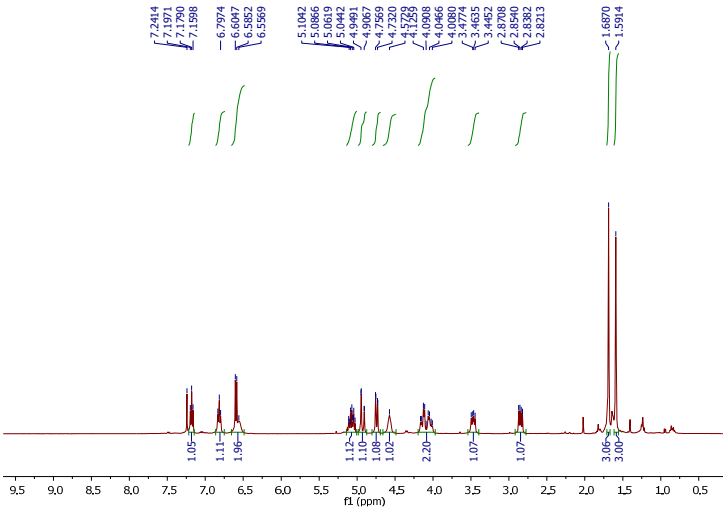


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20d**

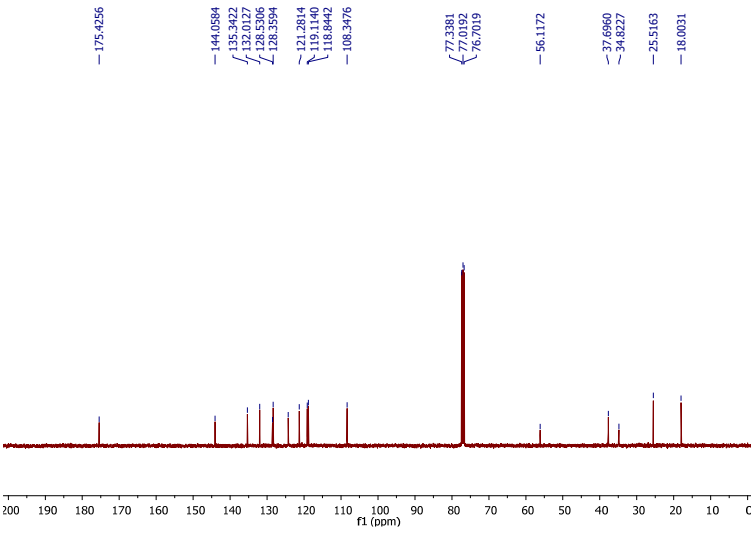


Scanned copy of mass spectrum (HRMS) of compound (±)-**20d**

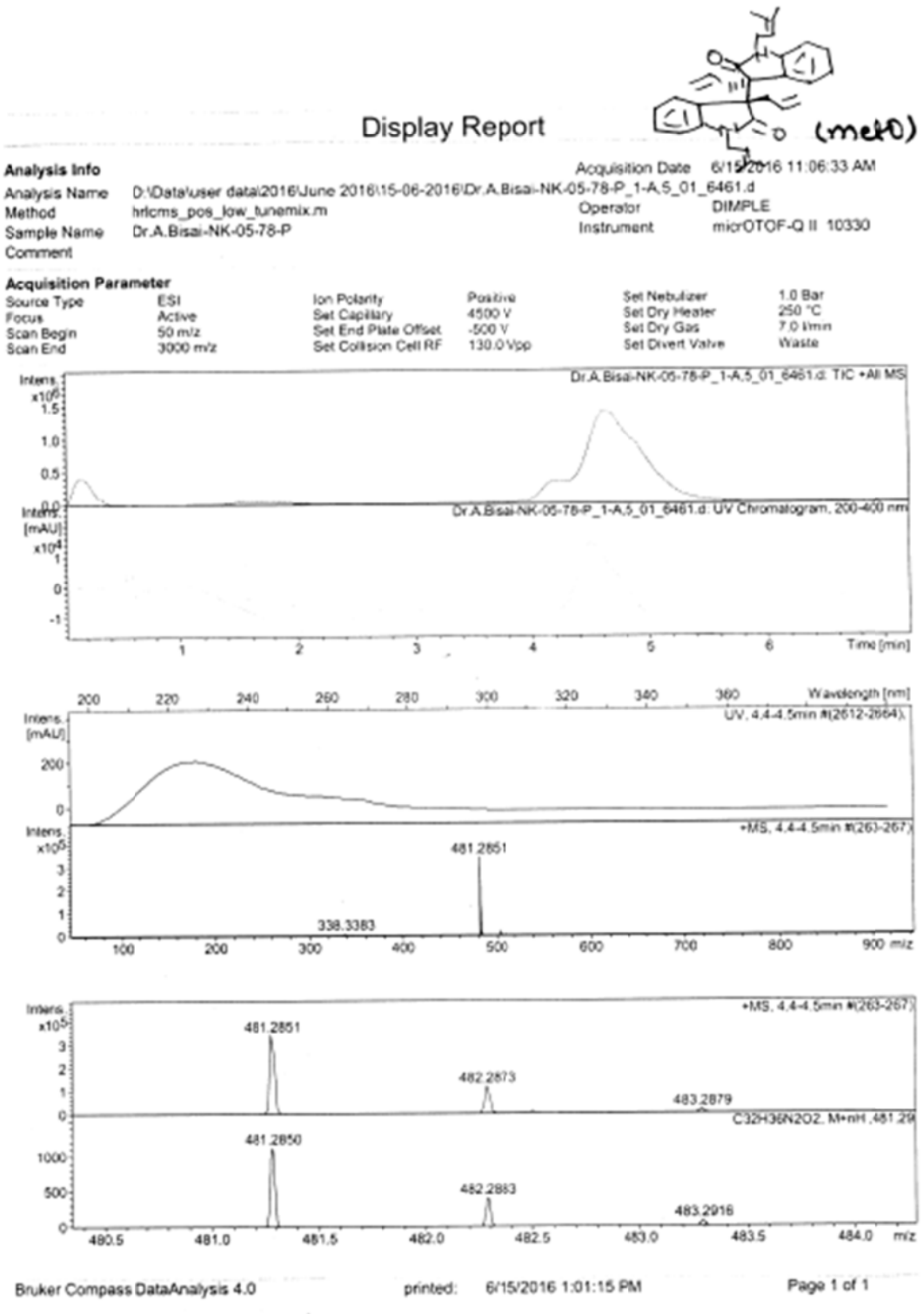




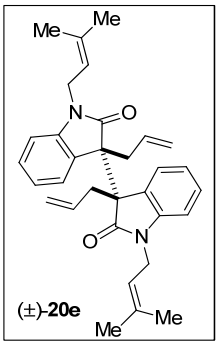
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**20e**)

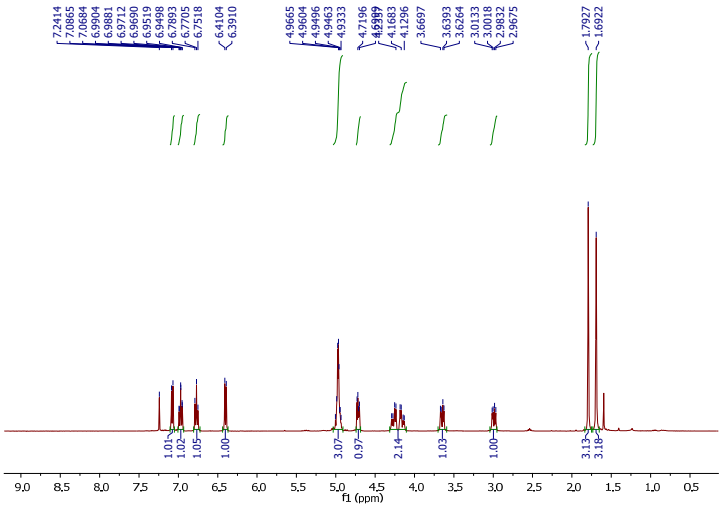


^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**20e**)

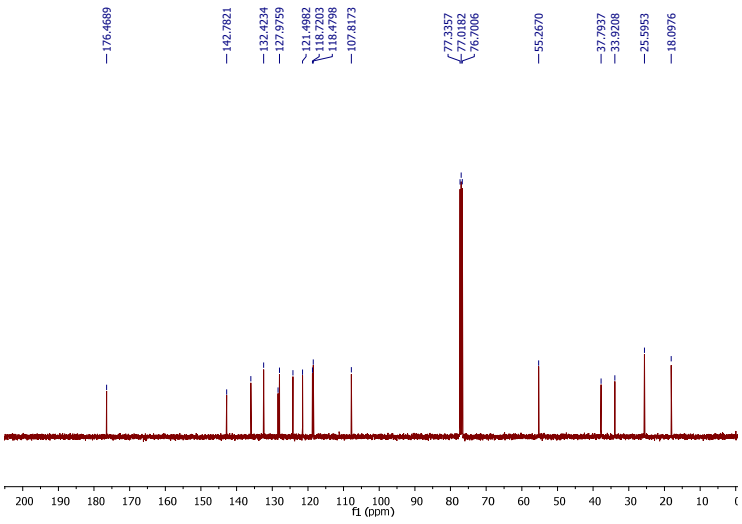


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**20e**)

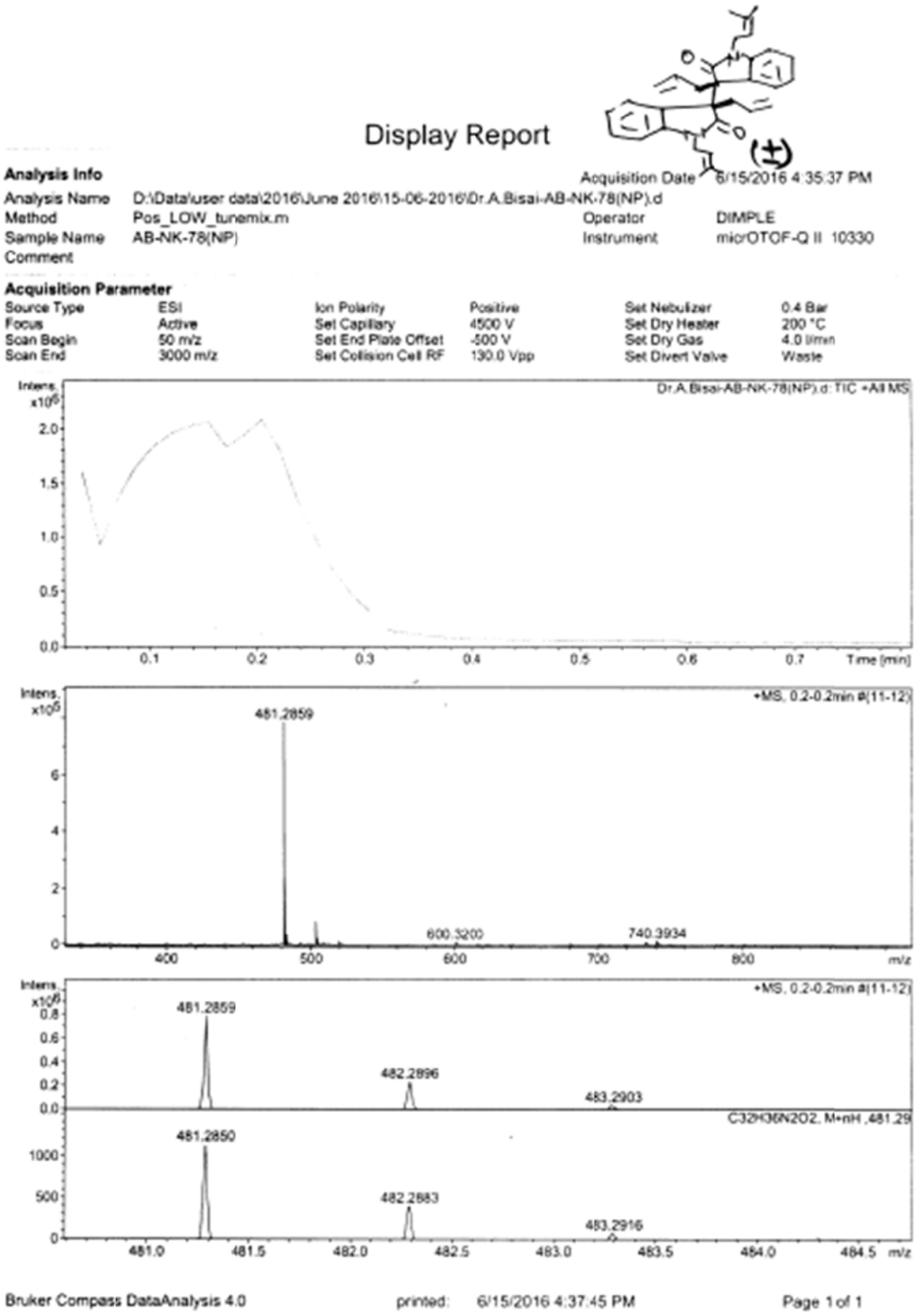




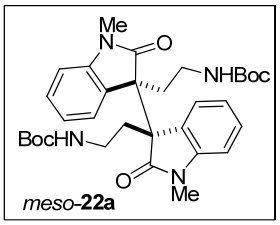
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**20e**

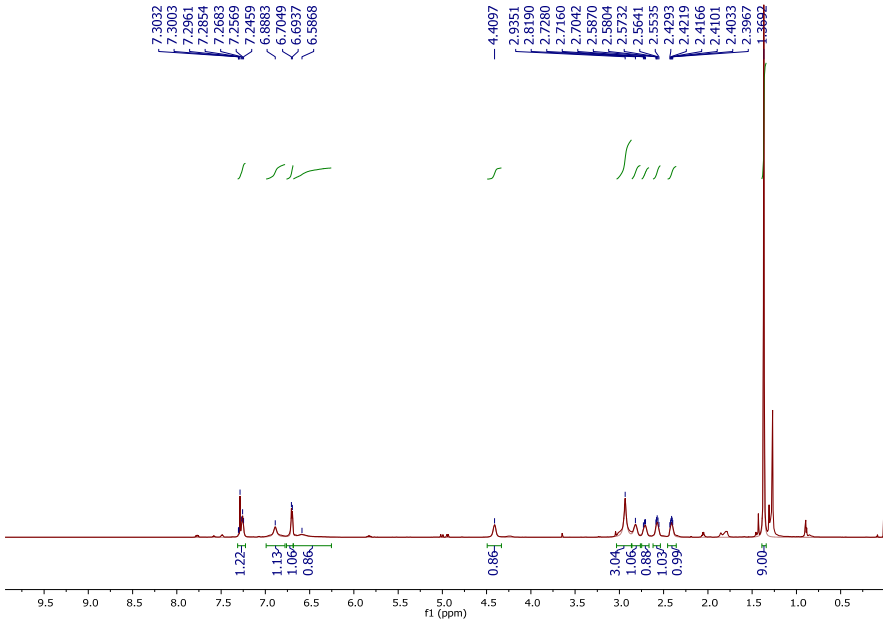


^{13}C NMR (100 MHz, $CDCl_3$) of compound (±)-**20e**

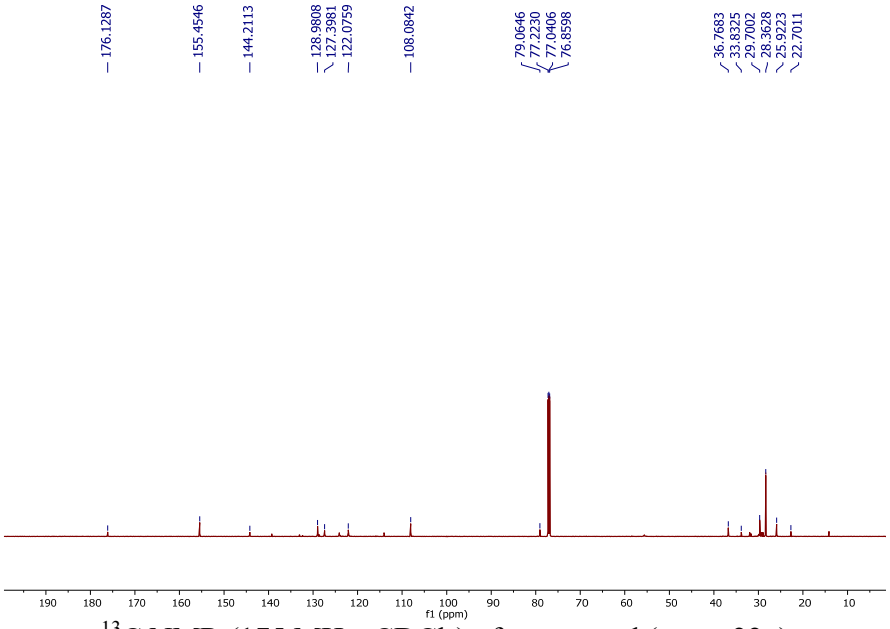


Scanned copy of mass spectrum (HRMS) of compound (±)-**20e**

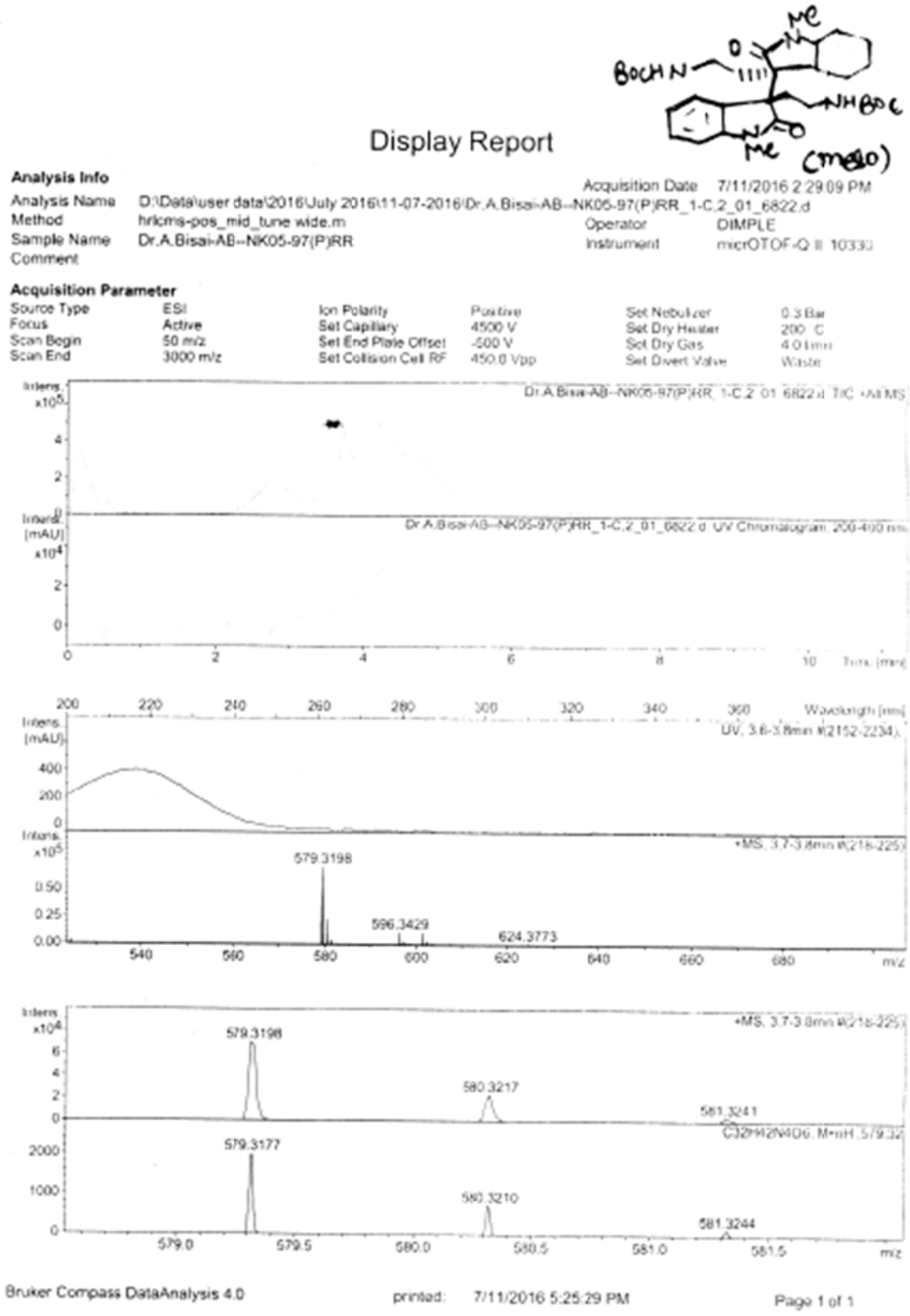




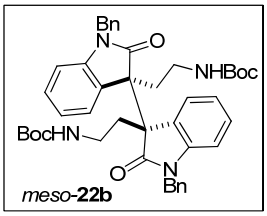
^{1}H NMR (700 MHz, $CDCl_3$) of compound (*meso*-**22a**)

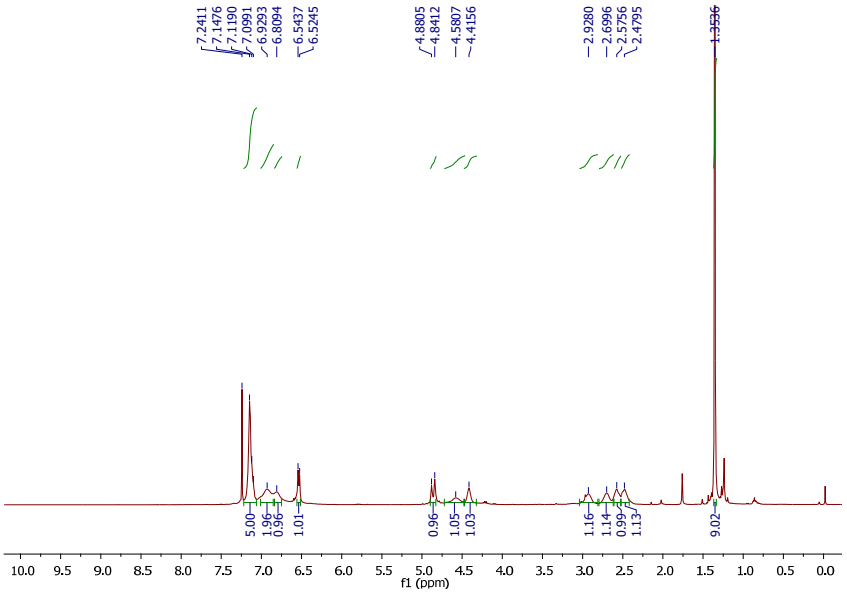


^{13}C NMR (175 MHz, $CDCl_3$) of compound (*meso*-**22a**)

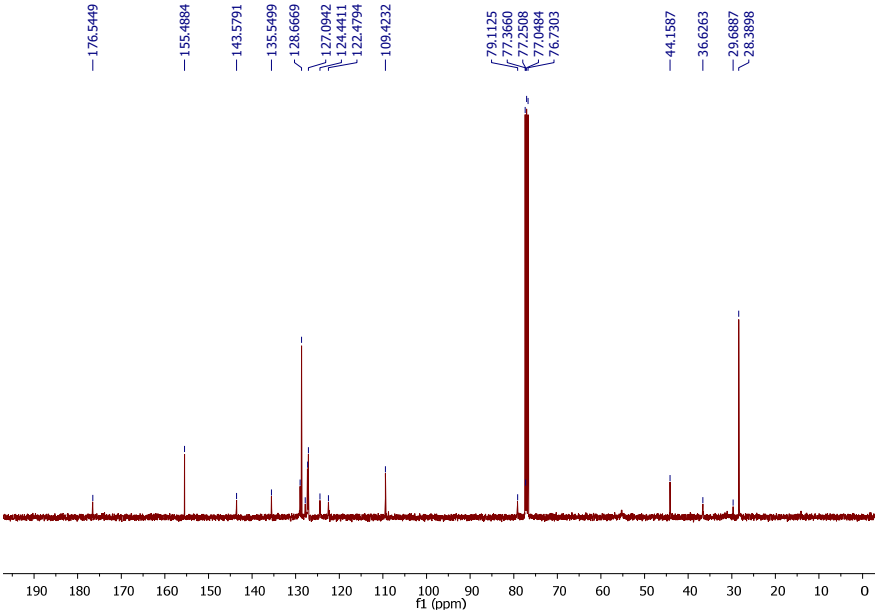


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**22a**)

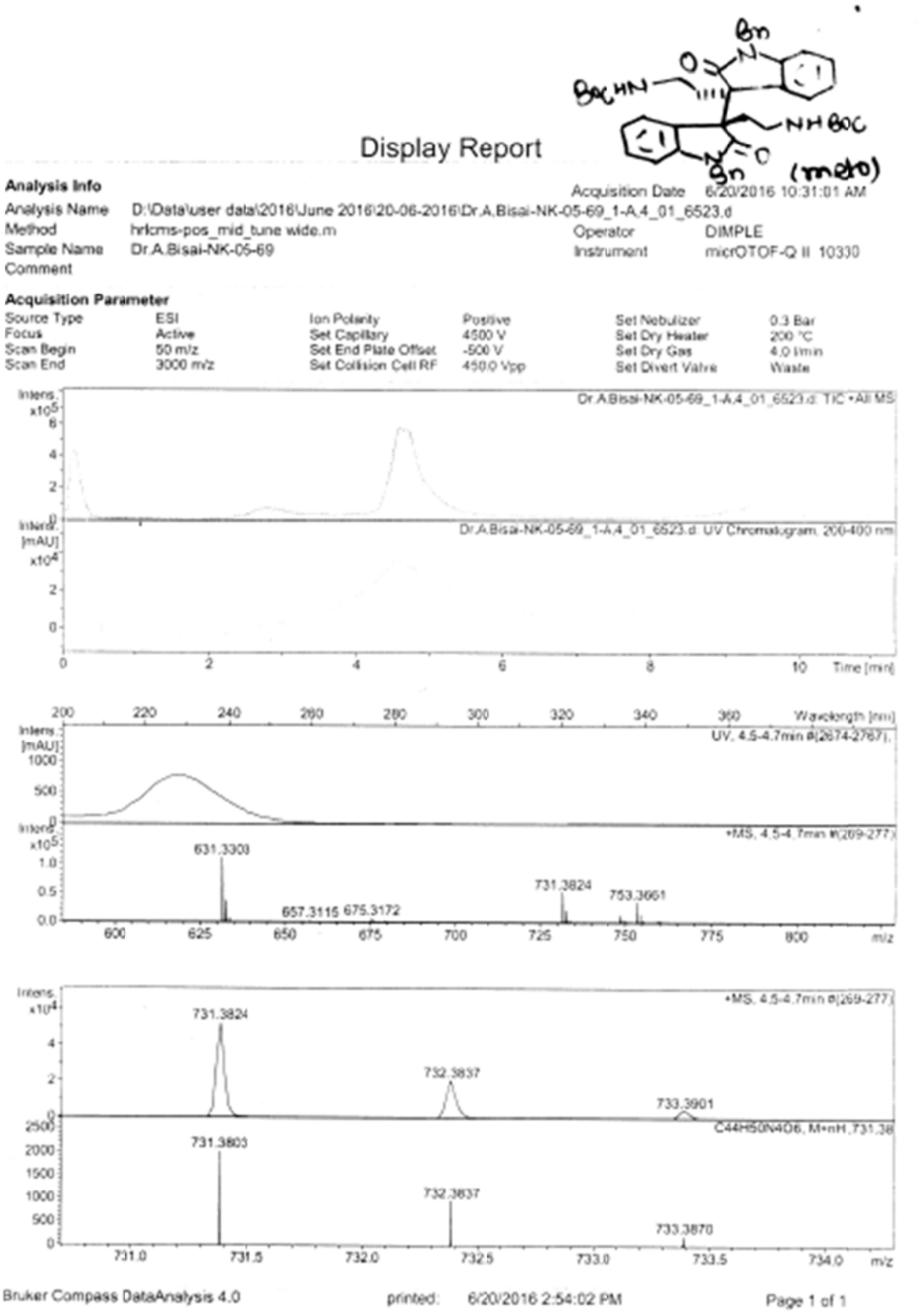




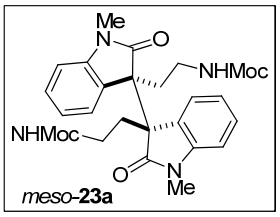
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**22b**)

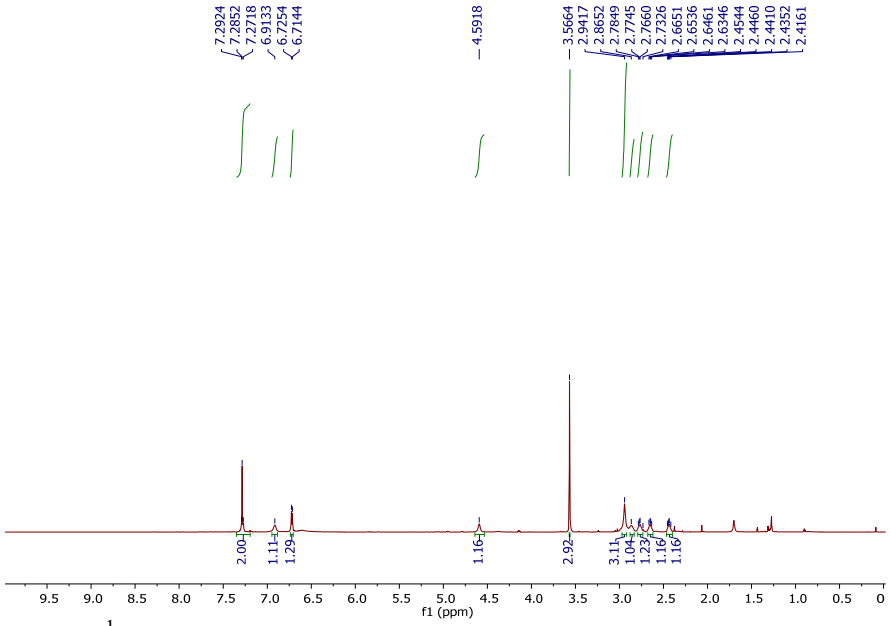


^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**22b**)

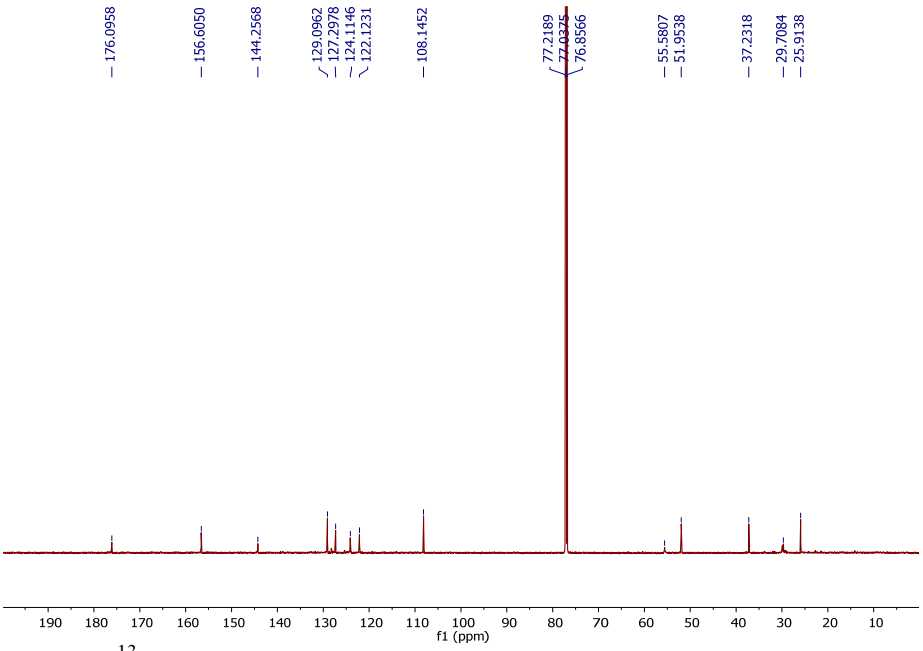


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**22b**)

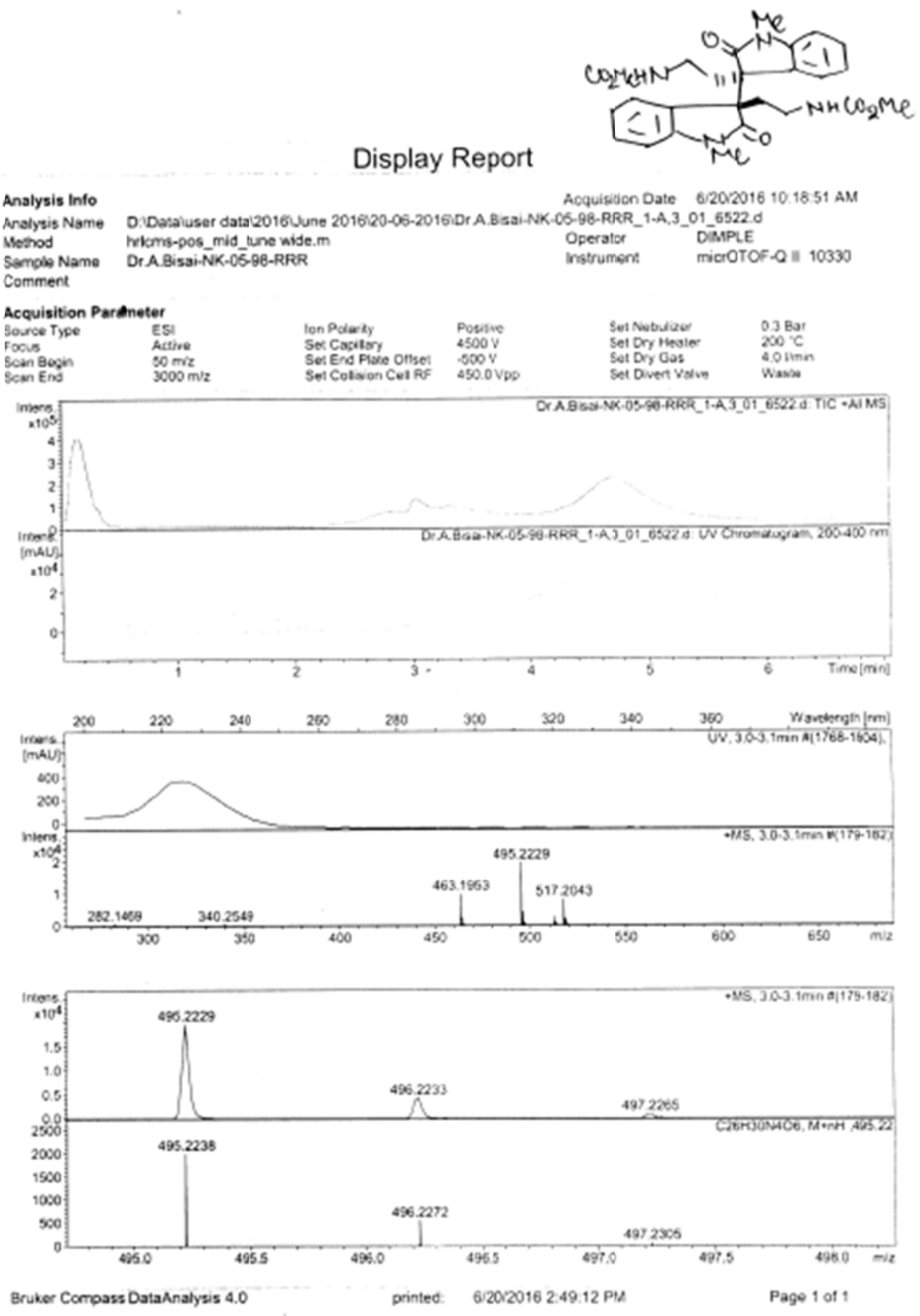




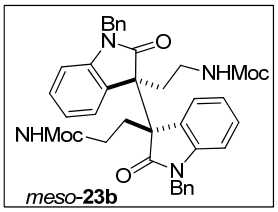
^{1}H NMR (700 MHz, $CDCl_3$) of compound (*meso*-**23a**)

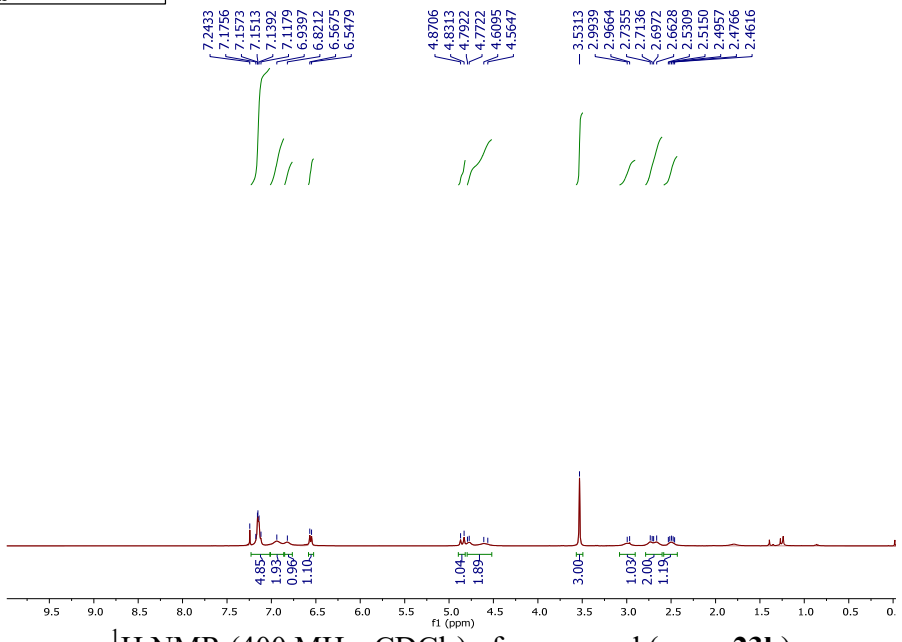


^{13}C NMR (175 MHz, $CDCl_3$) of compound (*meso*-**23a**)

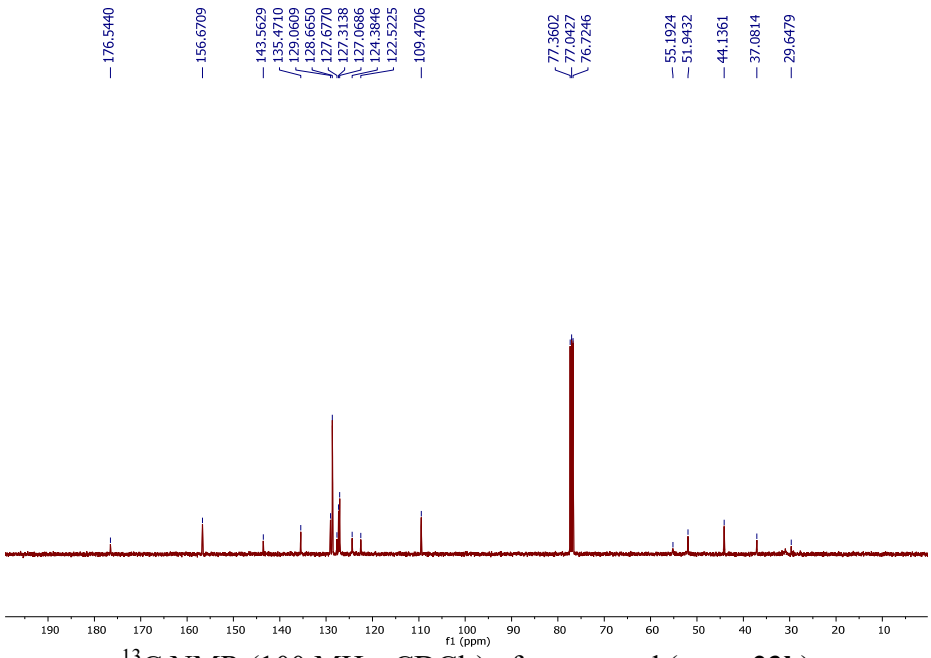


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**23a**)

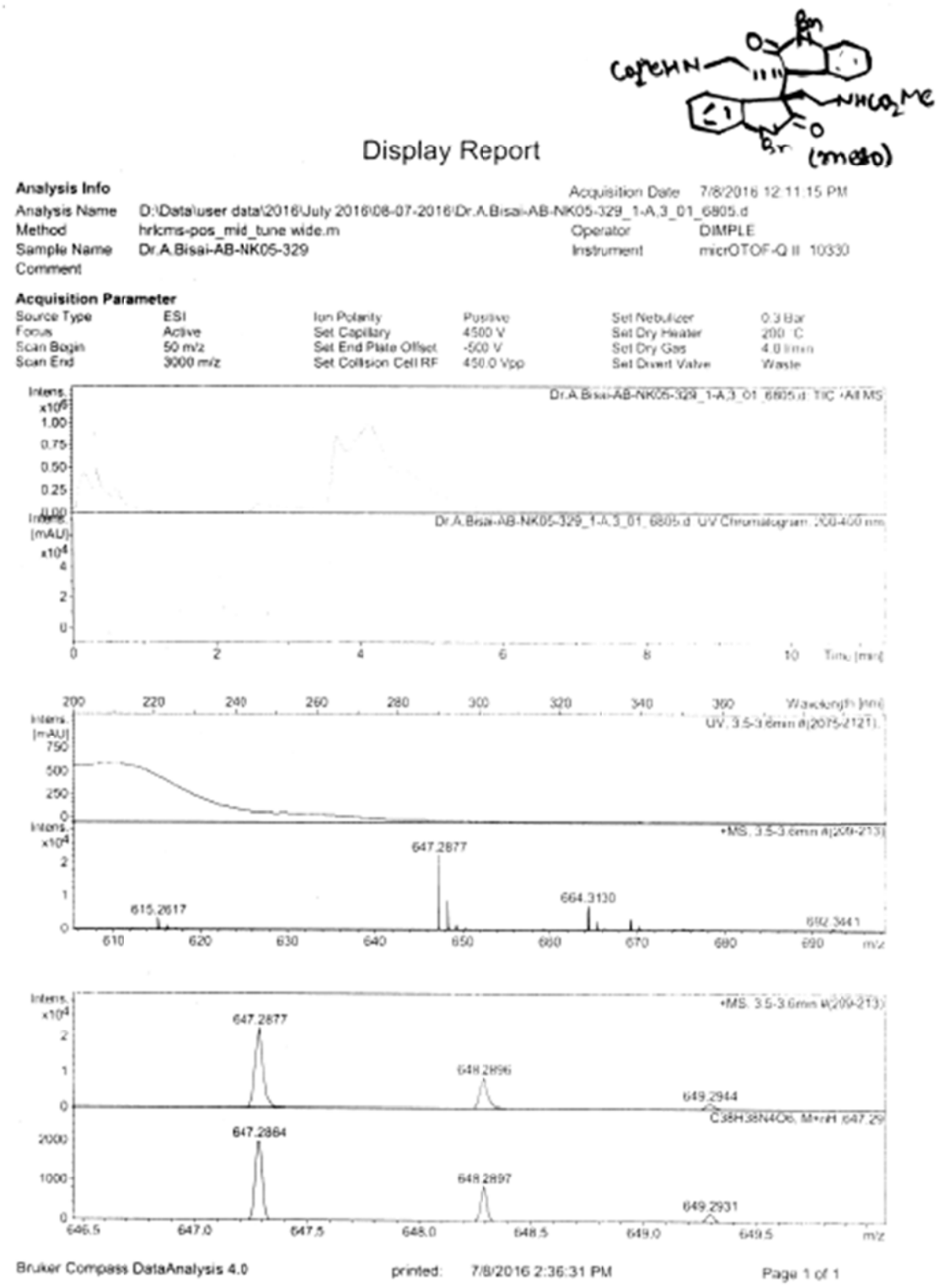




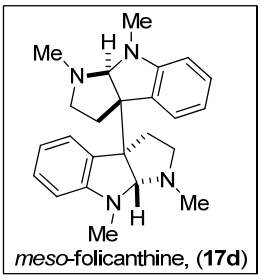
^{1}H NMR (400 MHz, $CDCl_3$) of compound (*meso*-**23b**)

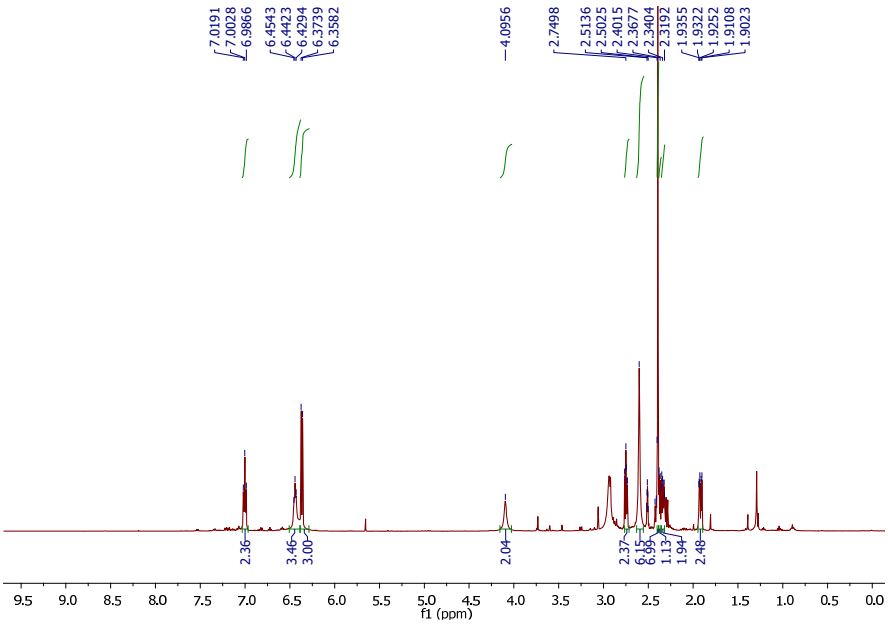


^{13}C NMR (100 MHz, $CDCl_3$) of compound (*meso*-**23b**)

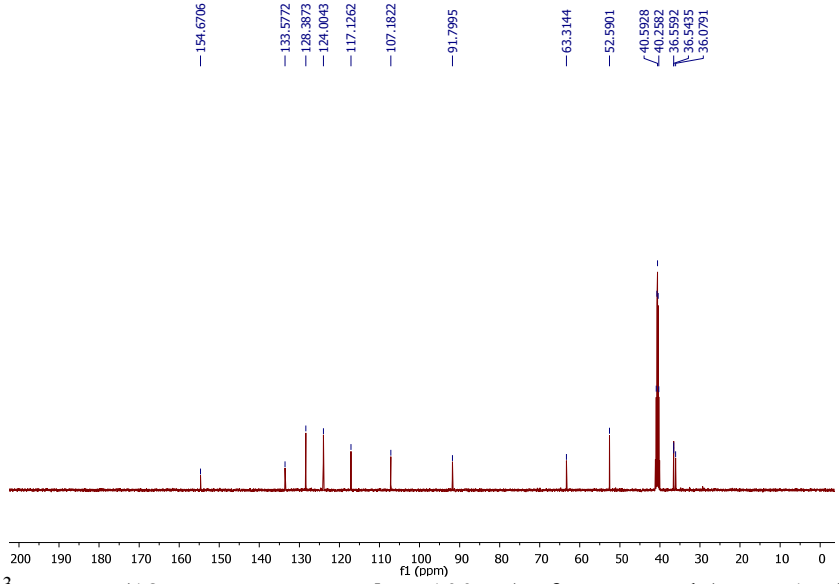


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**23b**)

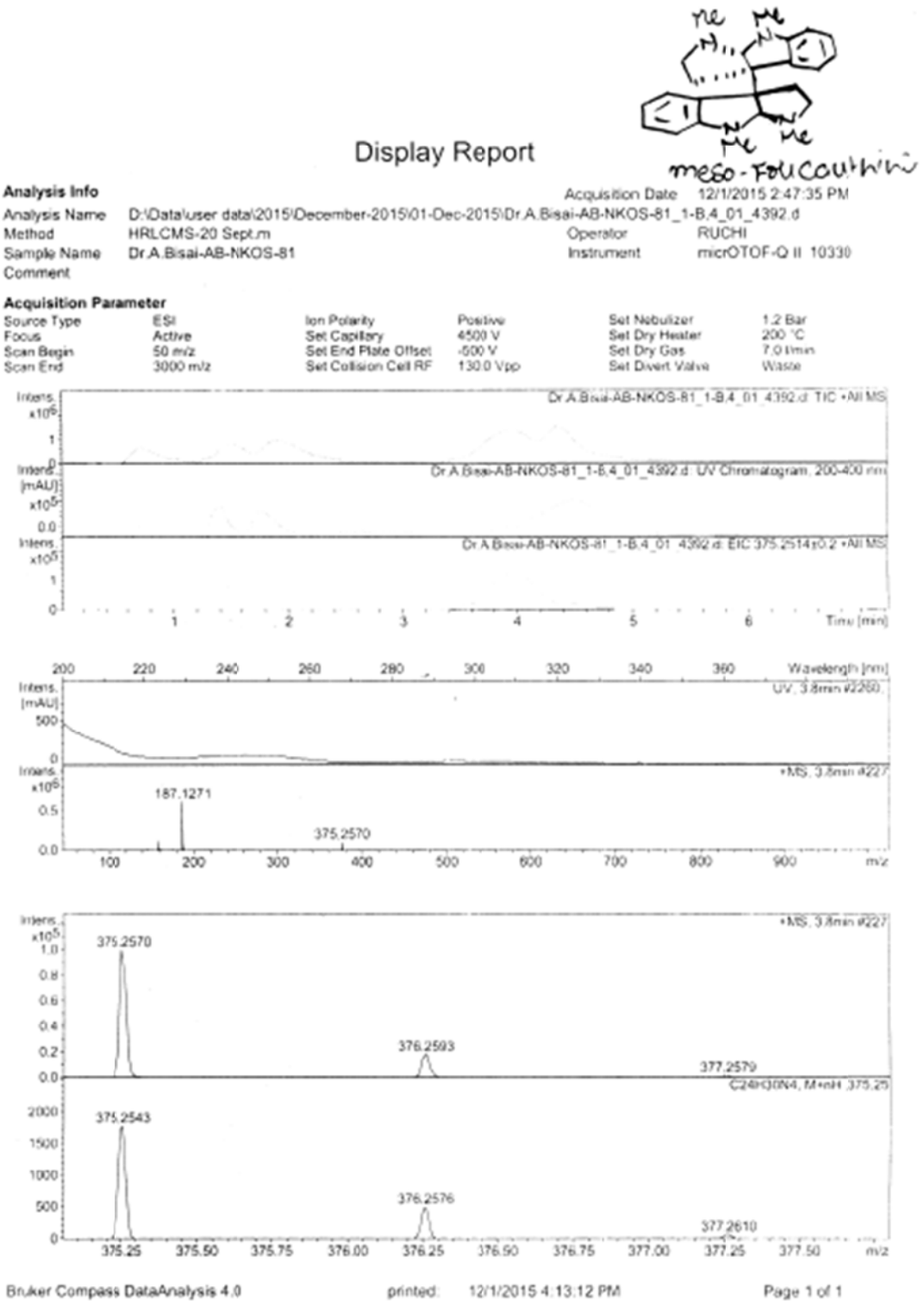




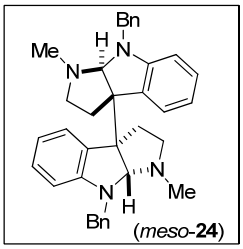
^{1}H NMR (500 MHz, DMSO-d_6 at 100 ºC) of compound (*meso*-**17d**)

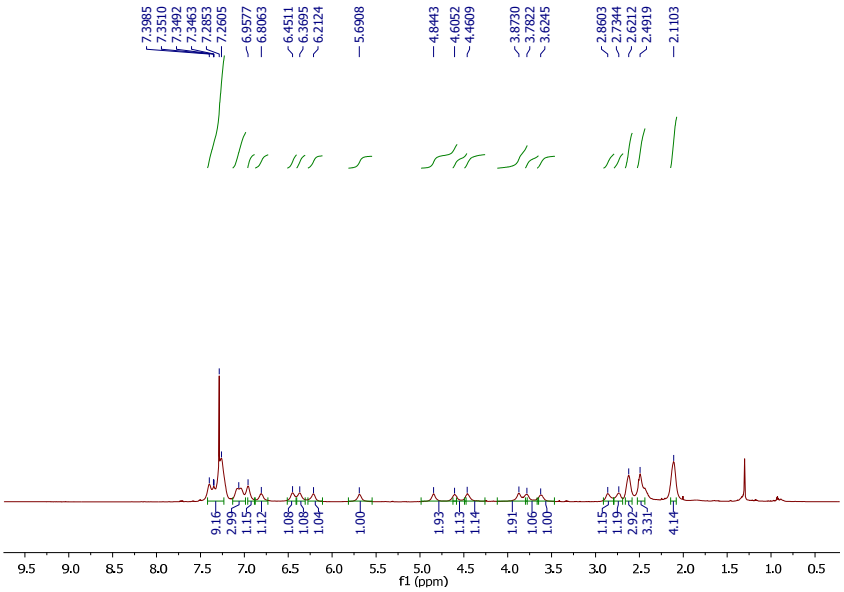


^{13}C NMR (125 MHz, DMSO-d_6 at 100 ºC) of compound (*meso*-**17d**)

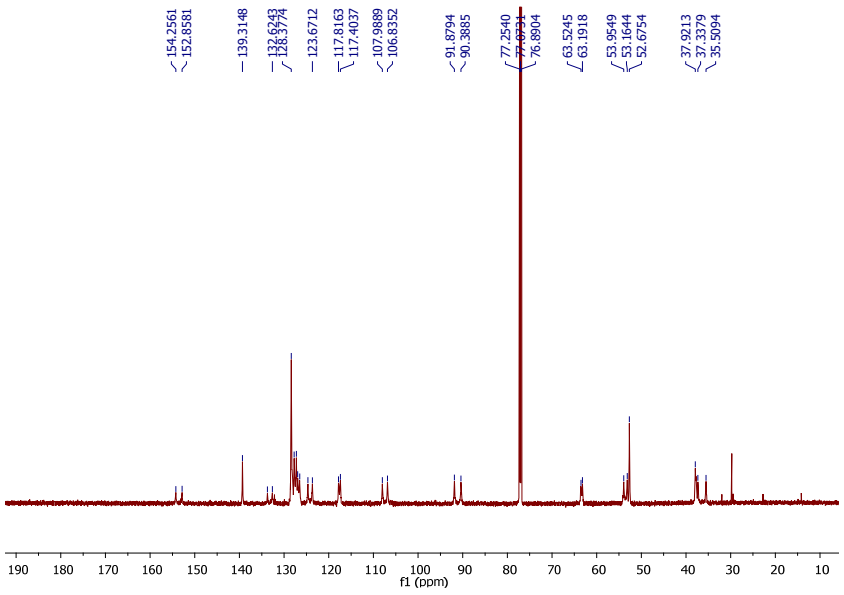


Scanned copy of mass spectrum (HRMS) of compound (*meso*-**17d**)

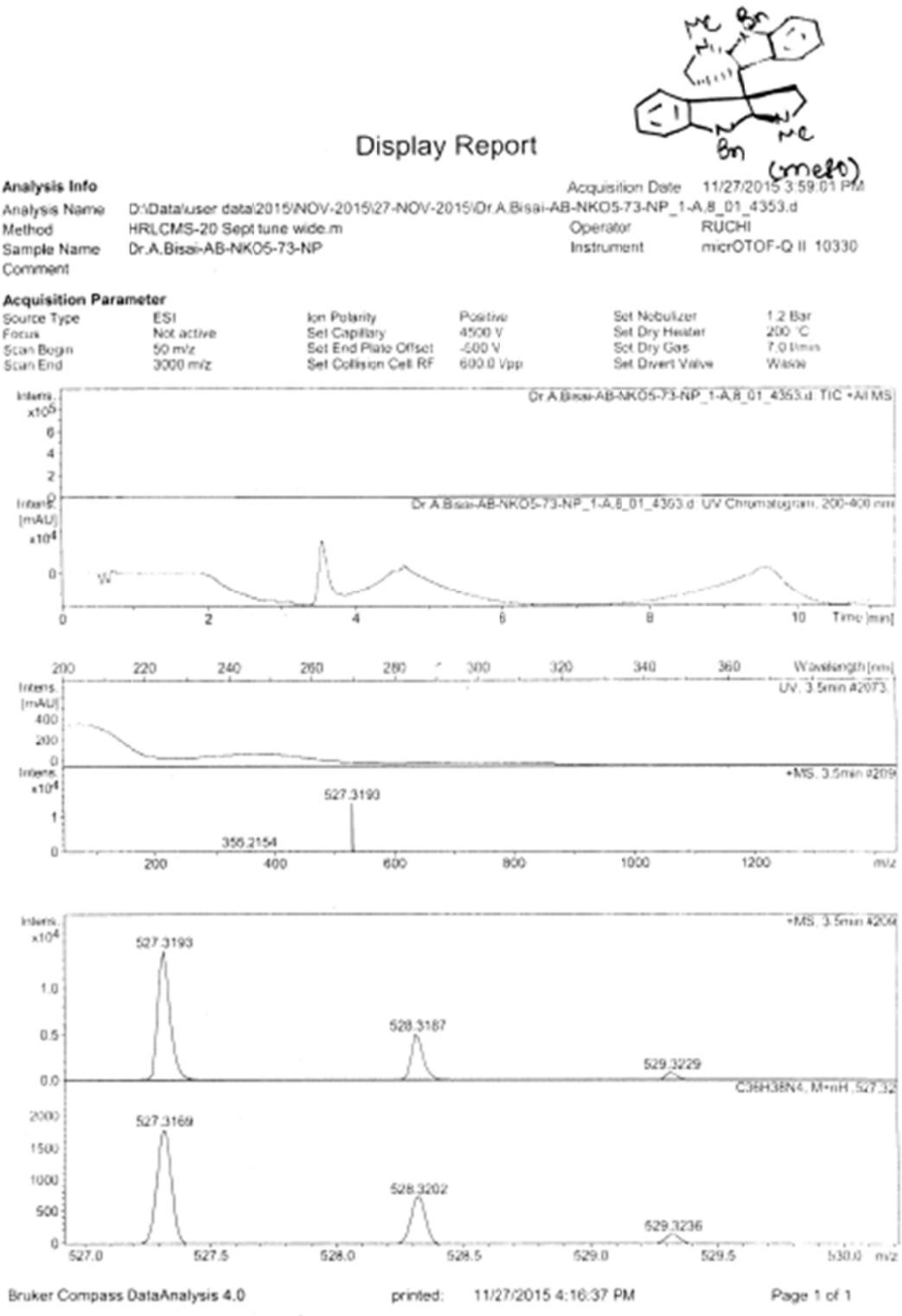




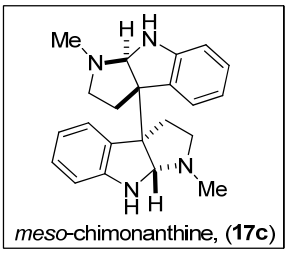
^{1}H NMR (700 MHz, $CDCl_3$) of compound (*meso*-**24**)



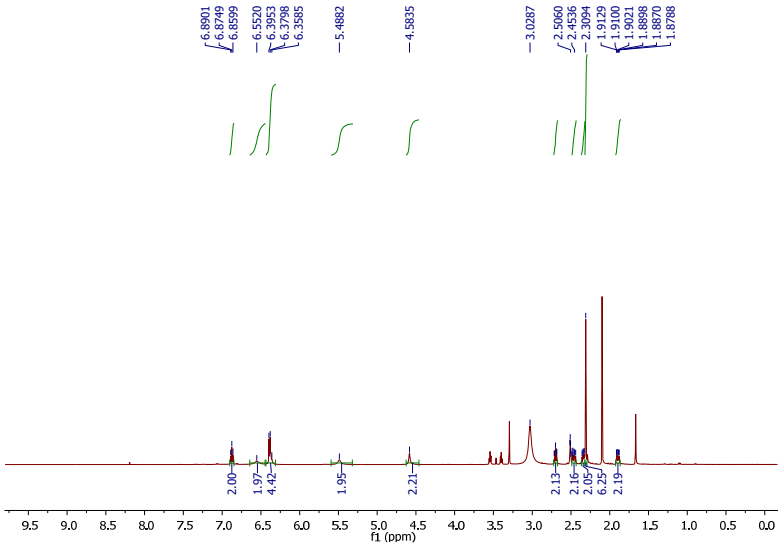
^{13}C NMR (175 MHz, $CDCl_3$) of compound (*meso*-**24**)



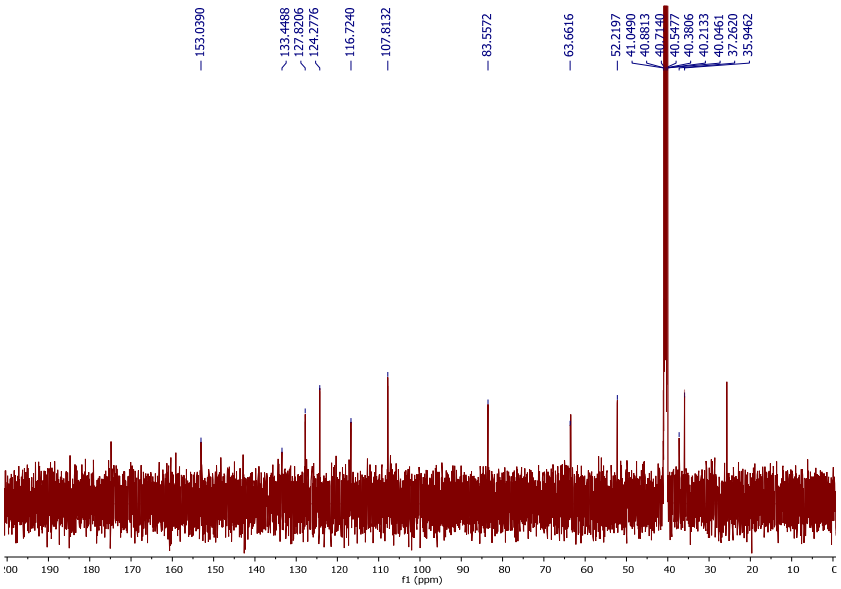
Scanned copy of mass spectrum (HRMS) of compound (*meso*-**24**)



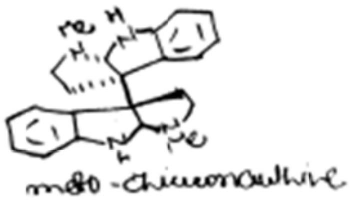
meso-chimonanthine, (**17c**)



^{1}H NMR (500 MHz, DMSO-d_6) of compound (*meso*-**17c**)



^{13}C NMR (125 MHz, DMSO-d_6) of compound (*meso*-**17c**)



Display Report

Analysis Info

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Method	HRLCMS-20 Sept.m	Operator	RUCHI
Sample Name	Dr.A.Bisai-AB-NKOS-90	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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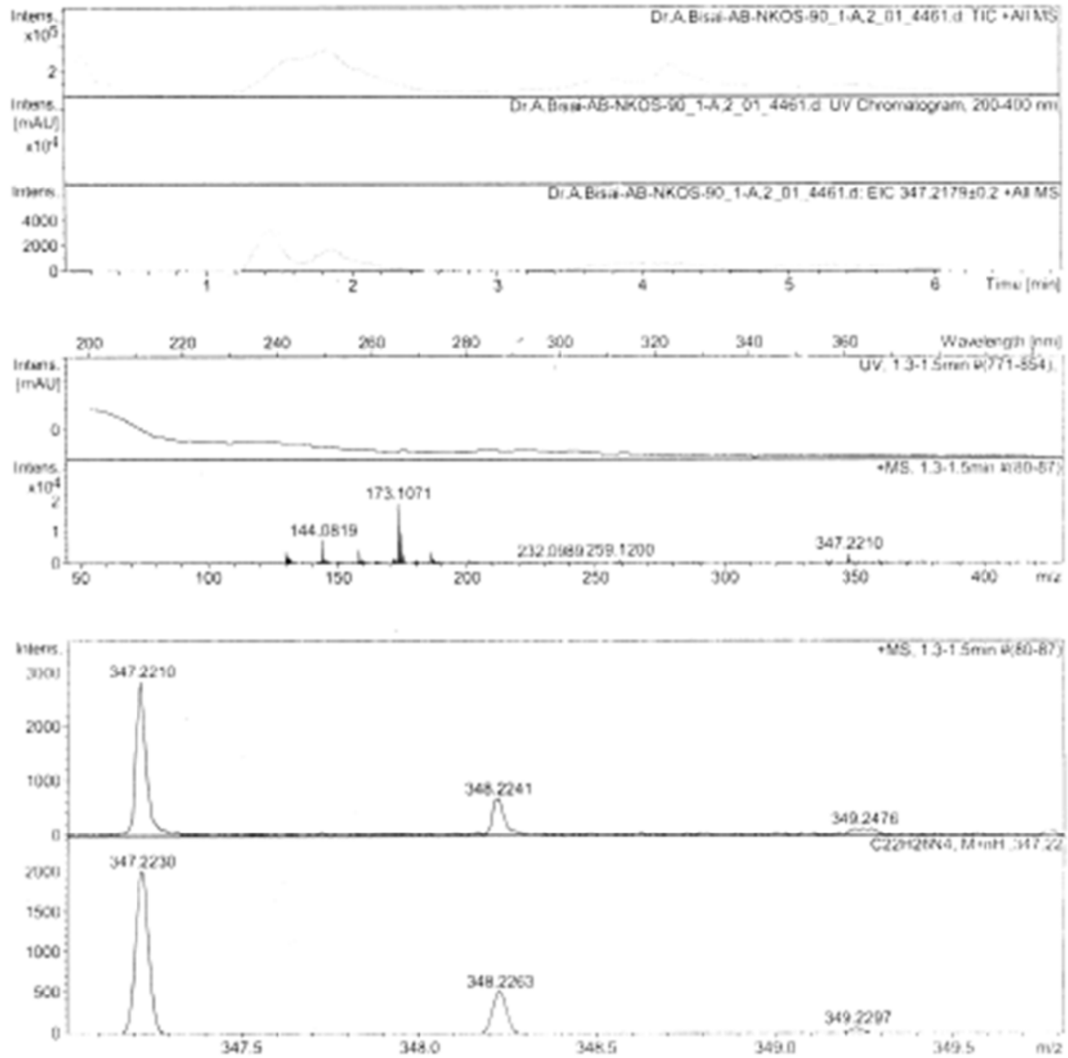
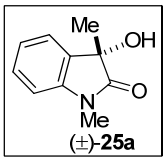
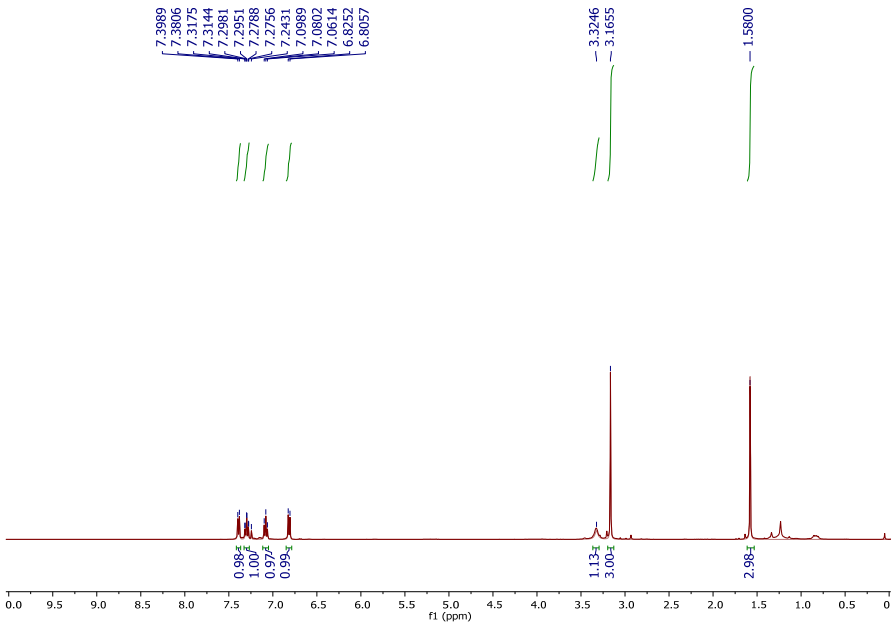
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste		



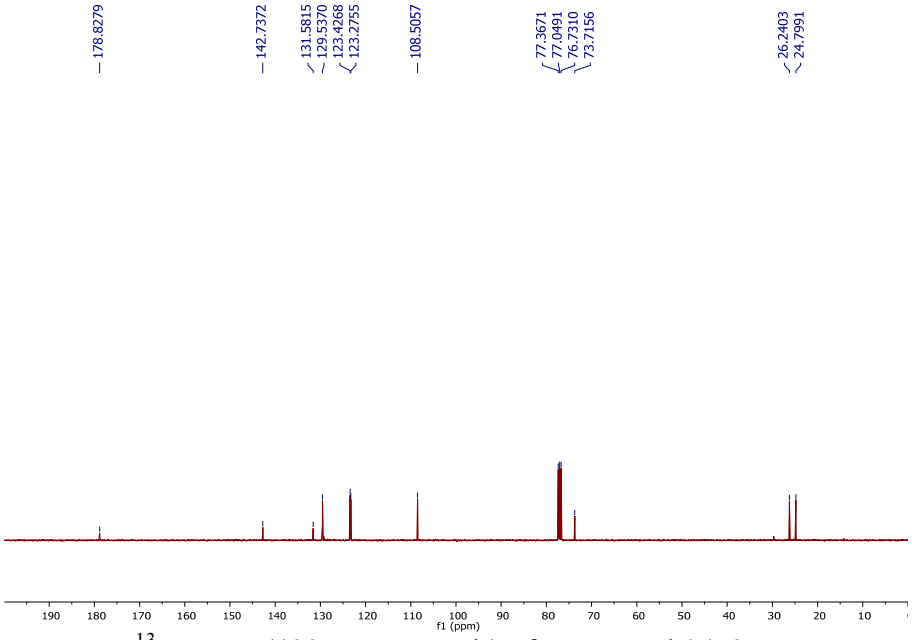
Bruker Compass DataAnalysis 4.0 printed: 12/8/2015 2:34:57 PM Page 1 of 1

Scanned copy of mass spectrum (HRMS) of compound (*meso*-**17c**)

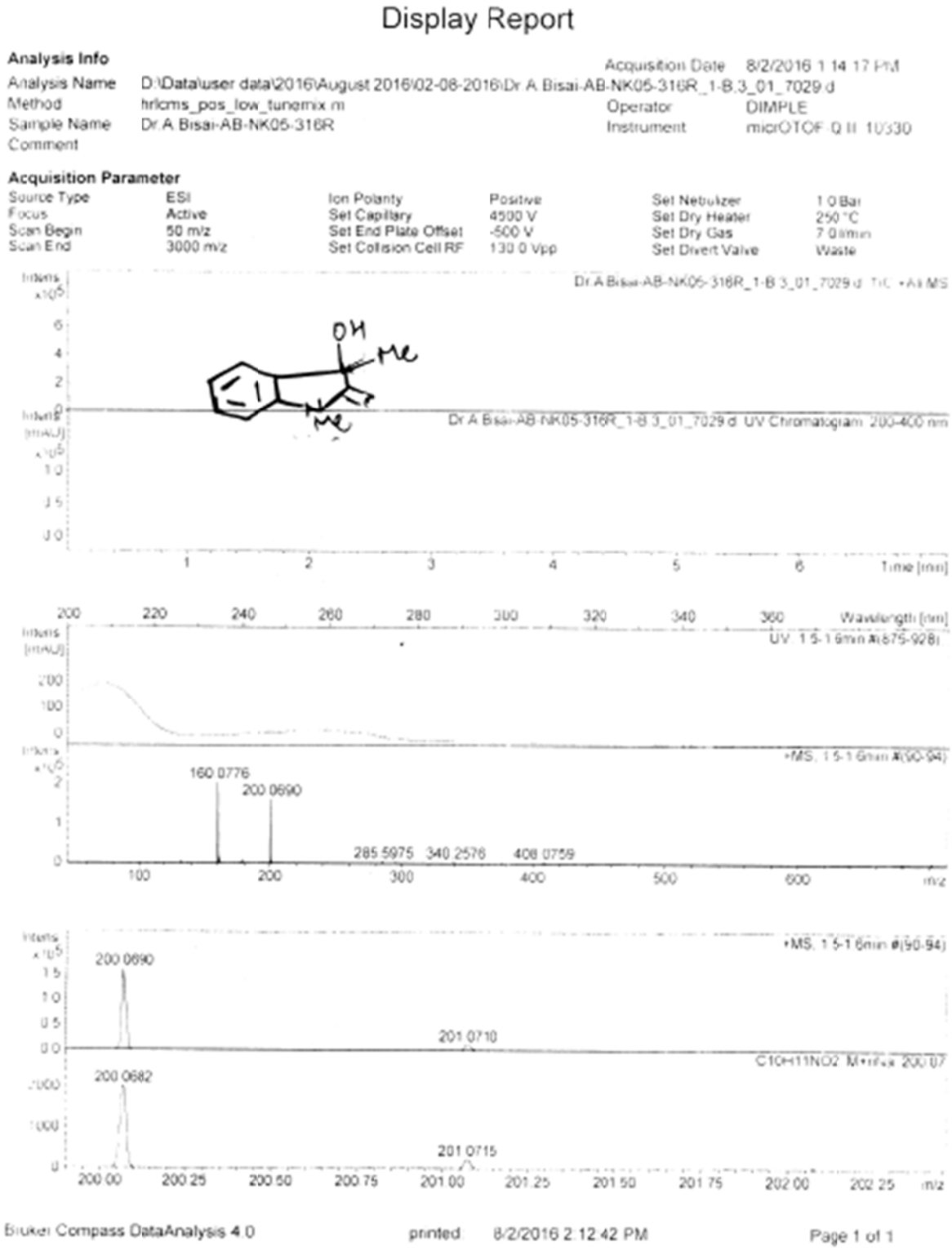




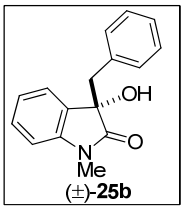
^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**25a**



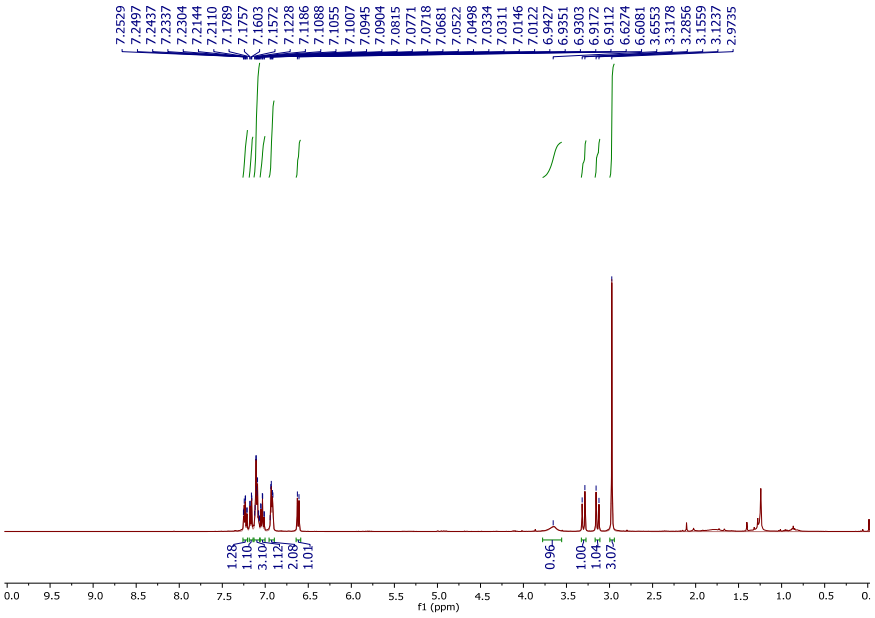
^{13}C NMR (400 MHz, $CDCl_3$) of compound (±)-**25a**



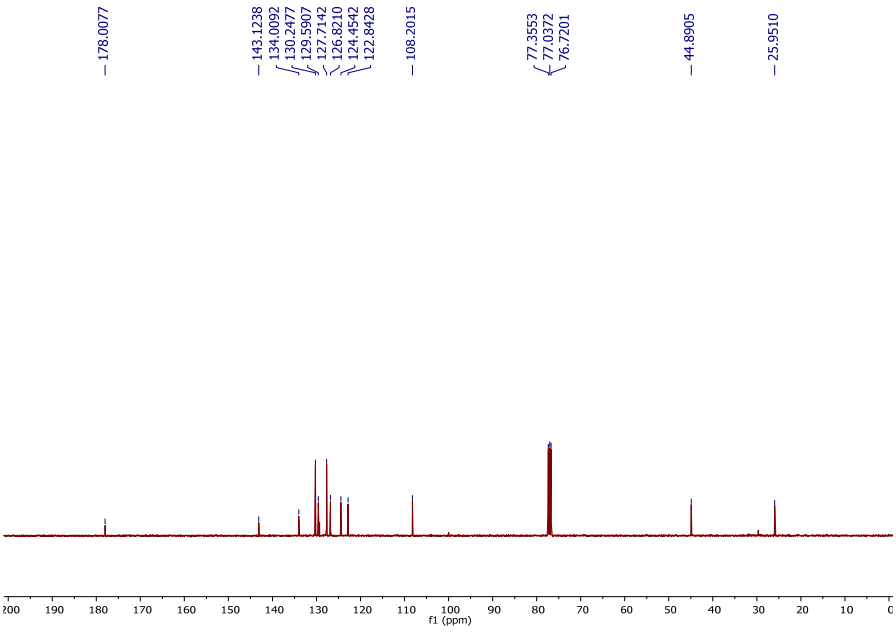
Scanned copy of mass spectrum (HRMS) of compound (±)-**25a**



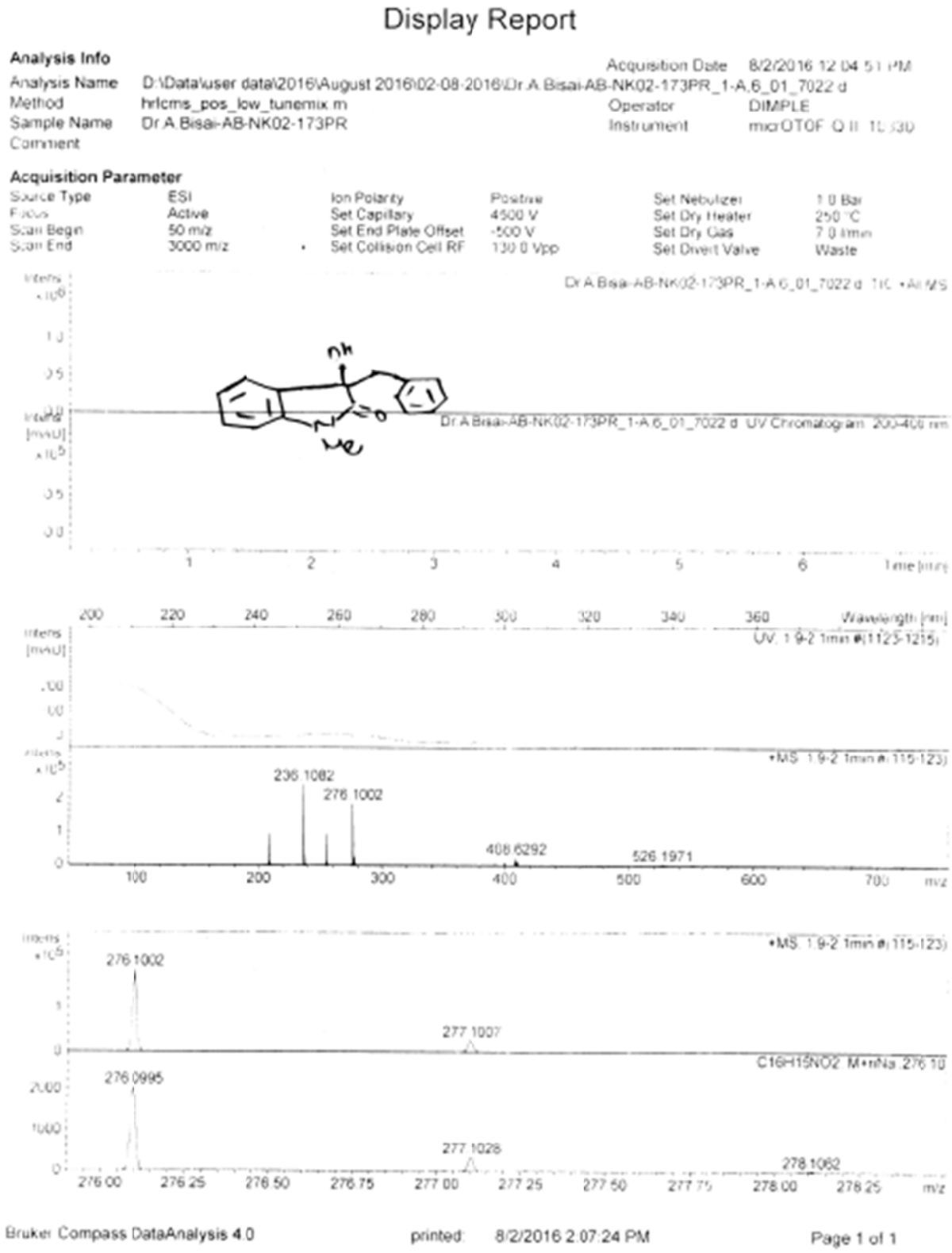
(±)-**25b**



^{1}H NMR (400 MHz, $CDCl_3$) of compound (±)-**25b**

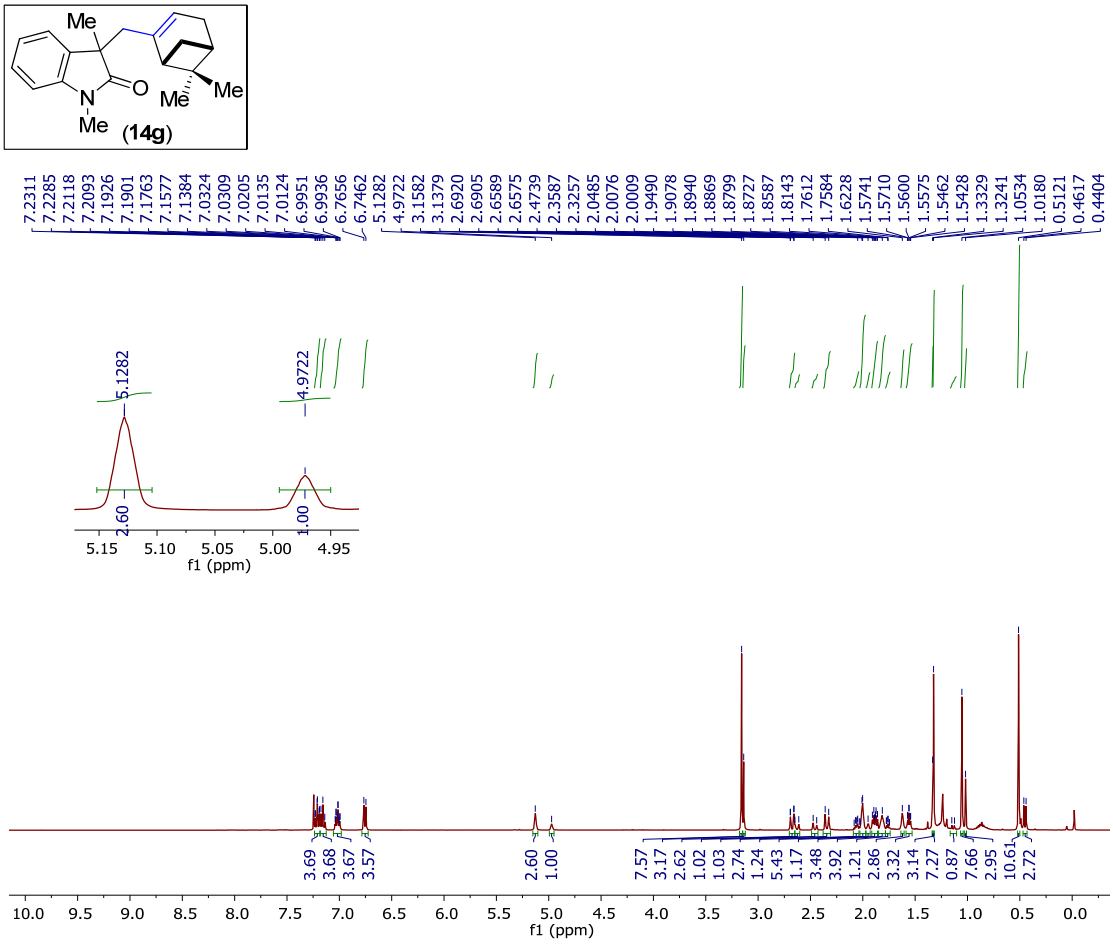


^{13}C NMR (400 MHz, $CDCl_3$) of compound (±)-**25b**



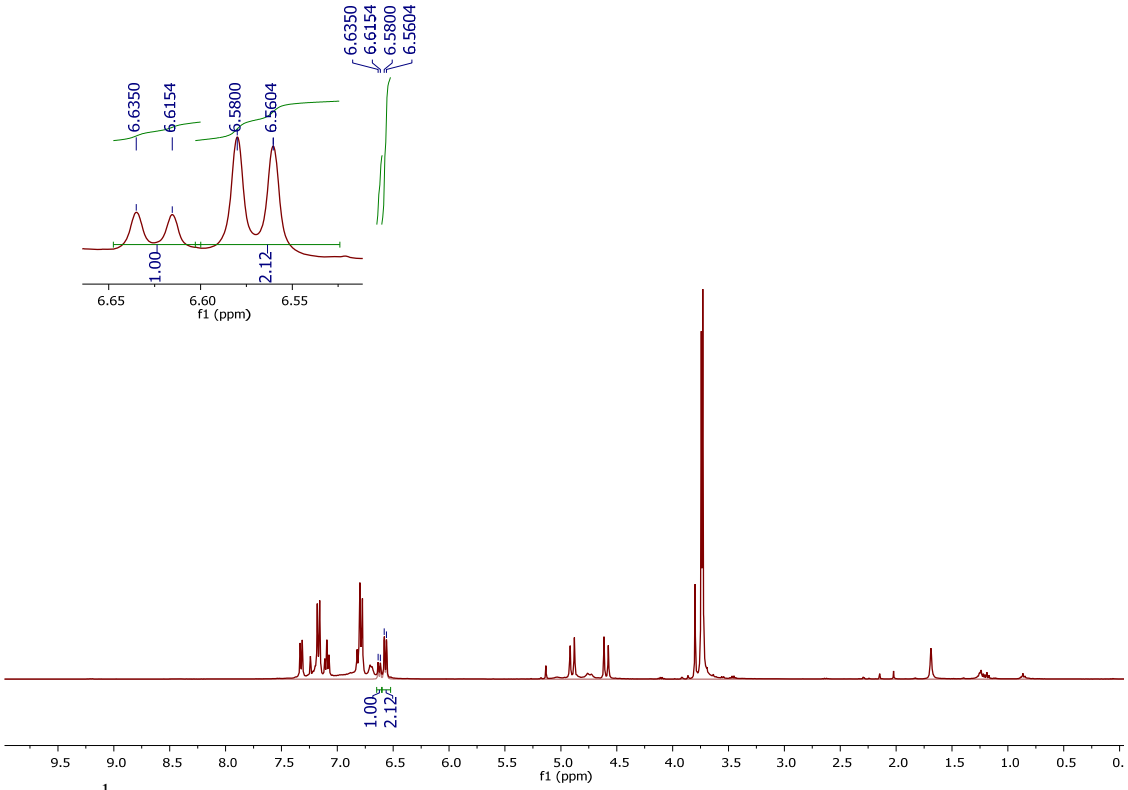
Scanned copy of mass spectrum (HRMS) of compound (±)-**25b**

Determination of diastereomeric ratio of compound (14g) from ^{1}H NMR of crude reaction mixture:



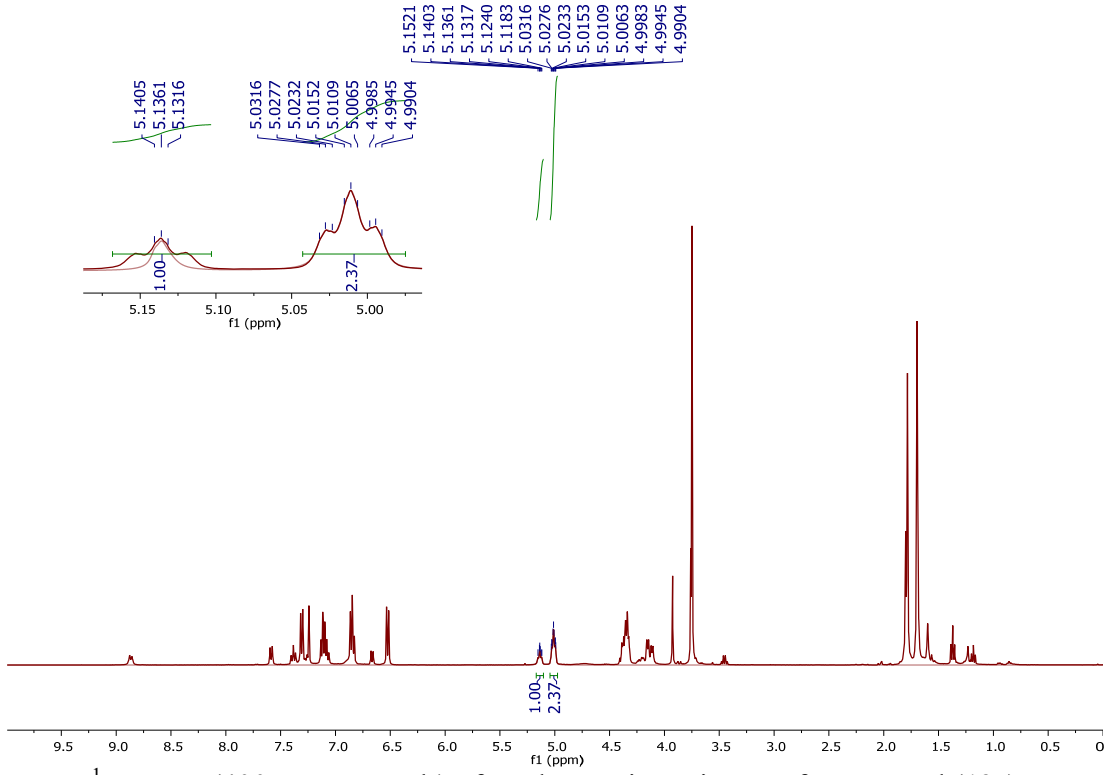
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**14g**)

Determination of diastereomeric ratio of compound (19c) from ^{1}H NMR of crude reaction mixture:



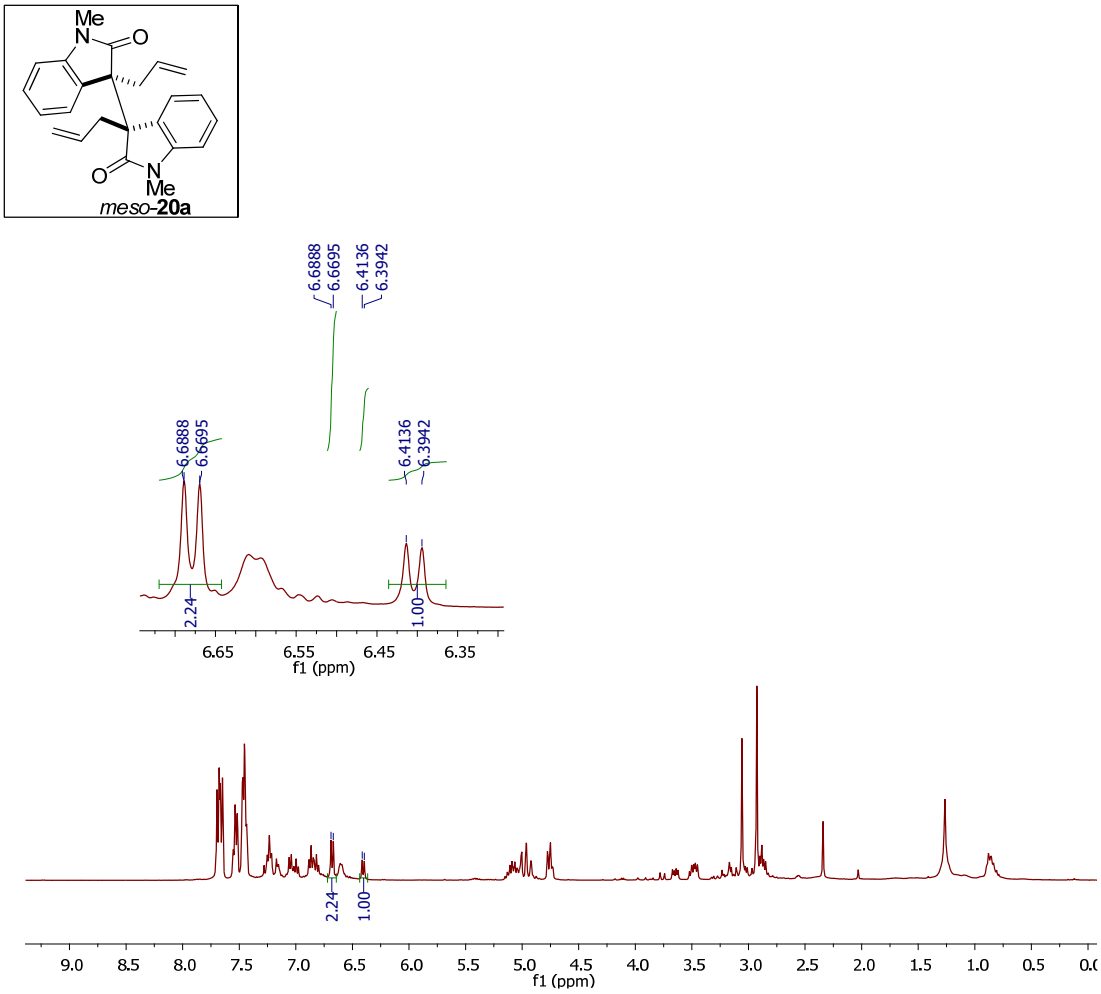
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**19c**)

Determination of diastereomeric ratio of compound (19e) from ^{1}H NMR of crude reaction mixture:



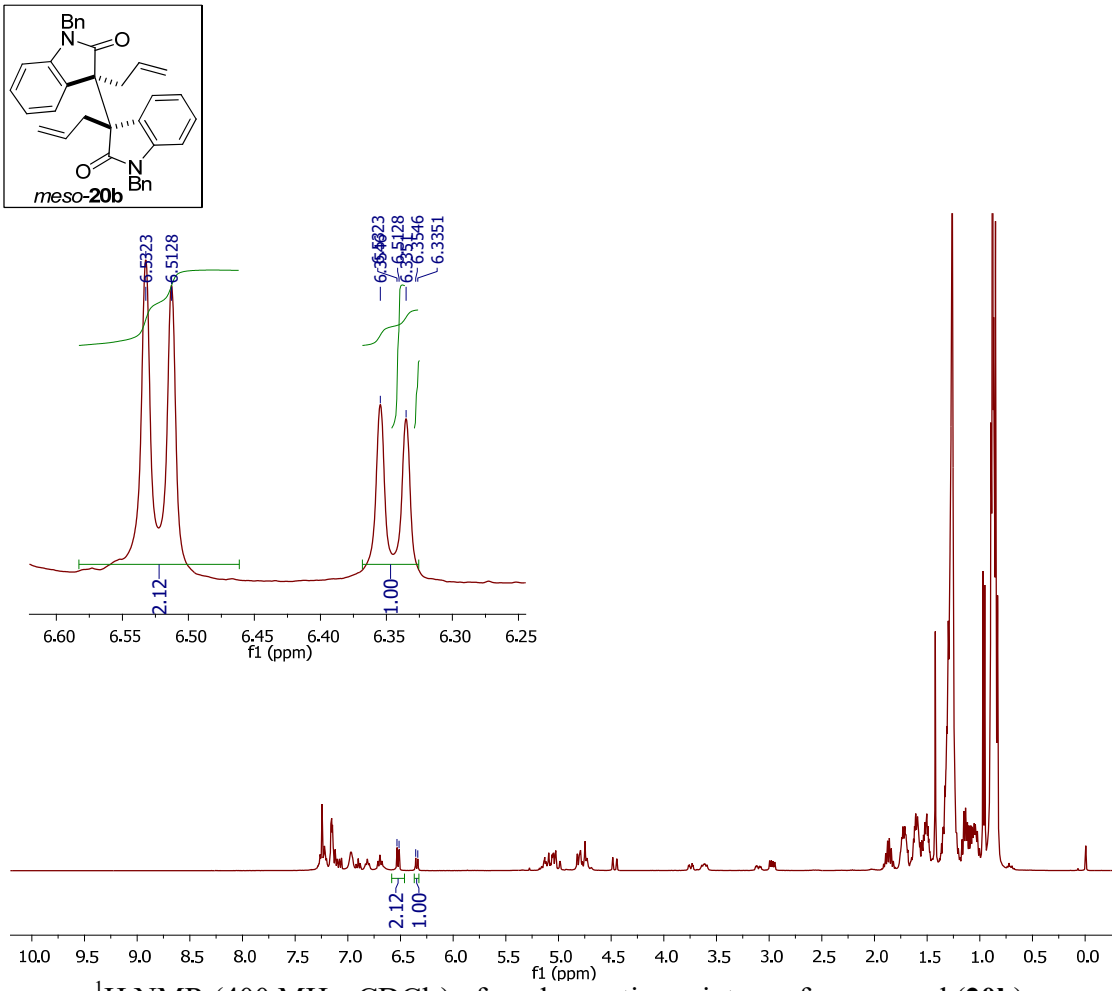
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**19e**)

Determination of diastereomeric ratio of compound (20a) from ^{1}H NMR of crude reaction mixture (19a):



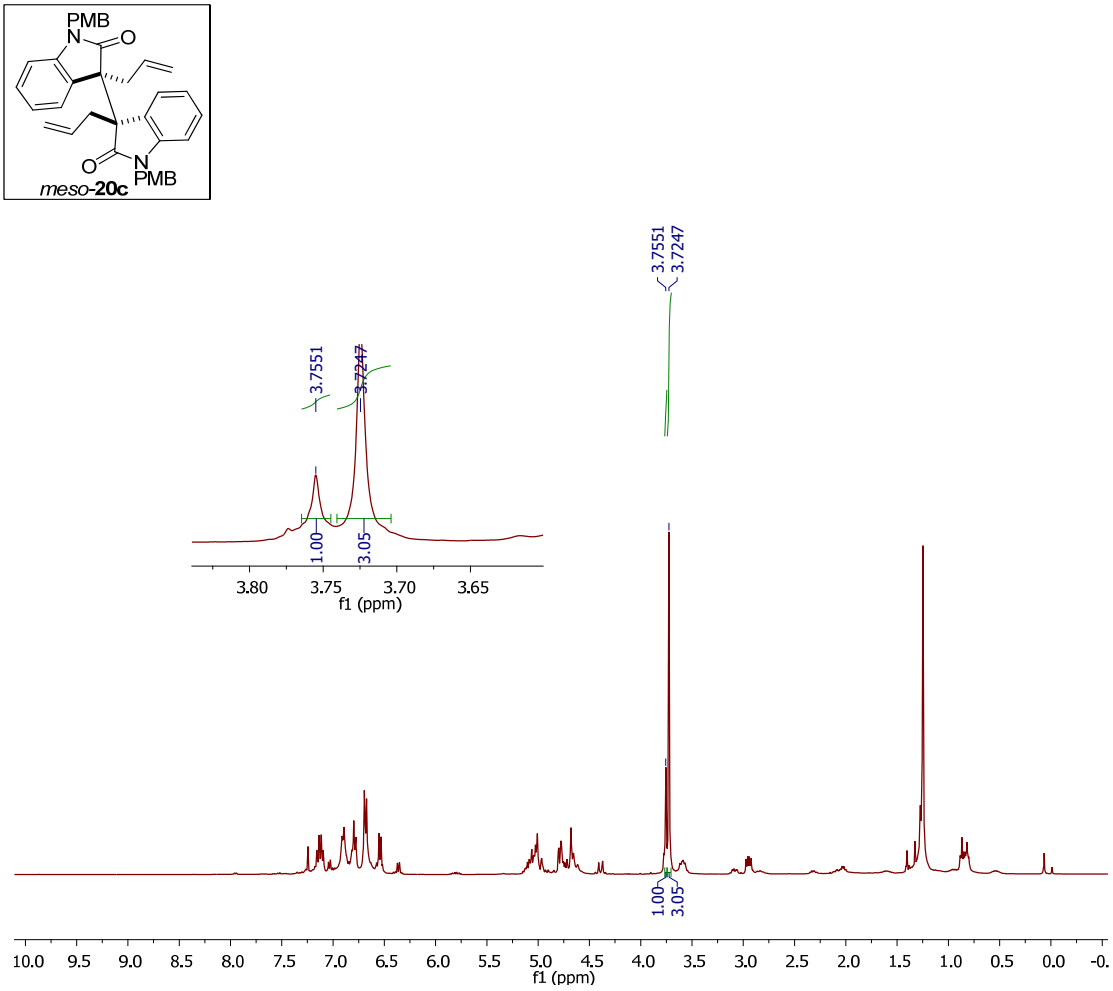
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**20a**)

Determination of diastereomeric ratio of compound (20b) from ^{1}H NMR of crude reaction mixture:



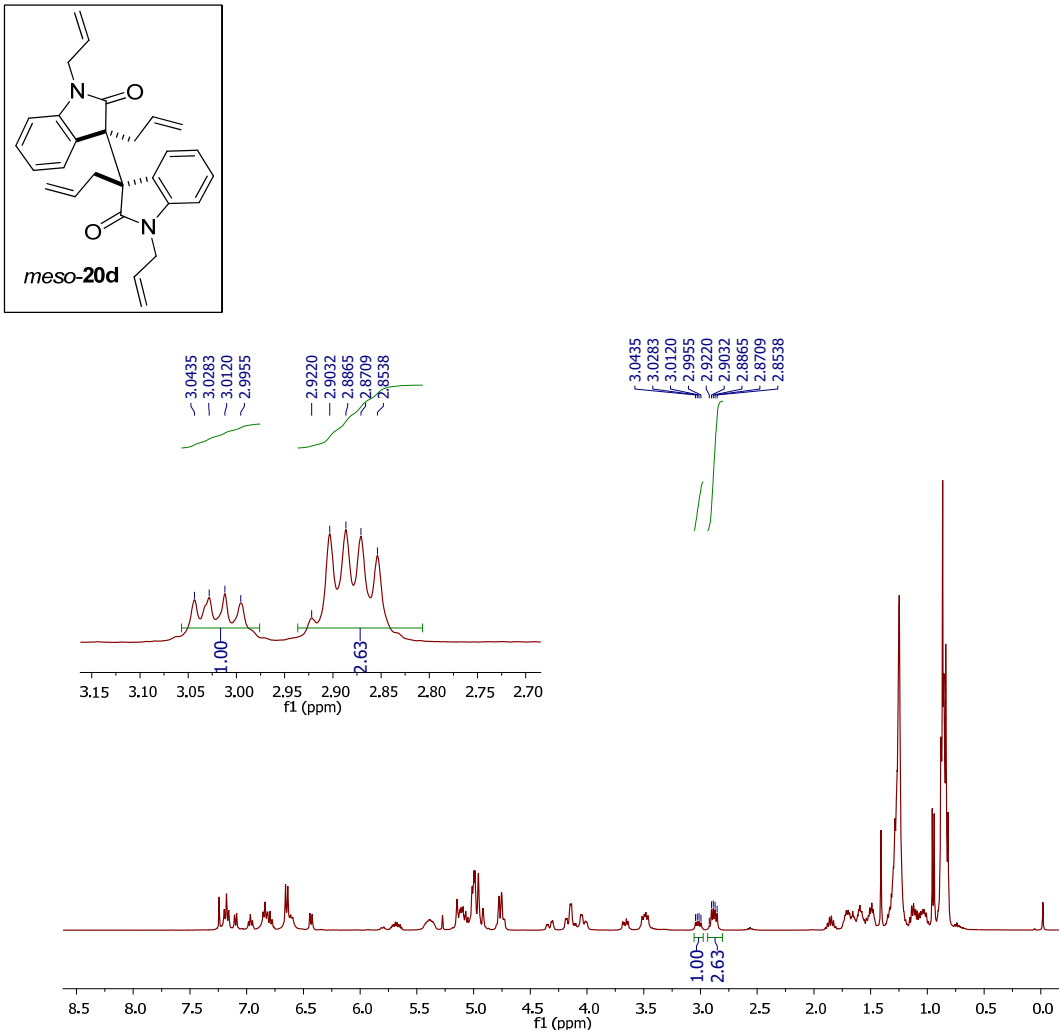
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**20b**)

Determination of diastereomeric ratio of compound (20c) from ^{1}H NMR of crude reaction mixture:



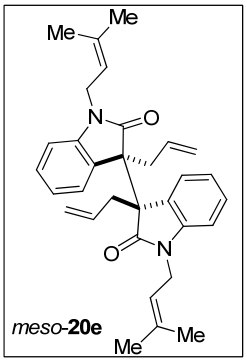
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**20c**)

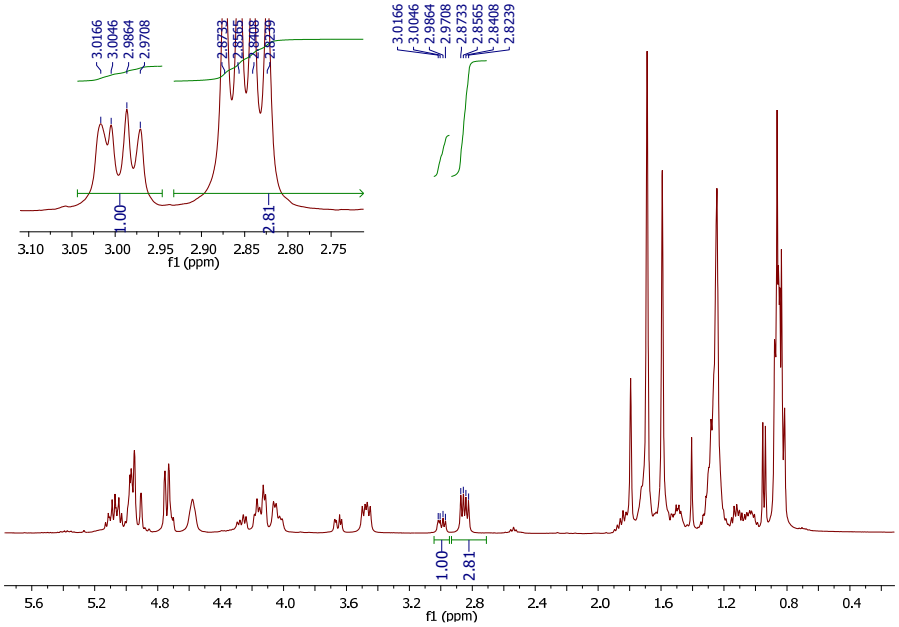
Determination of diastereomeric ratio of compound (20d) from ^{1}H NMR of crude reaction mixture:



^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**20d**)

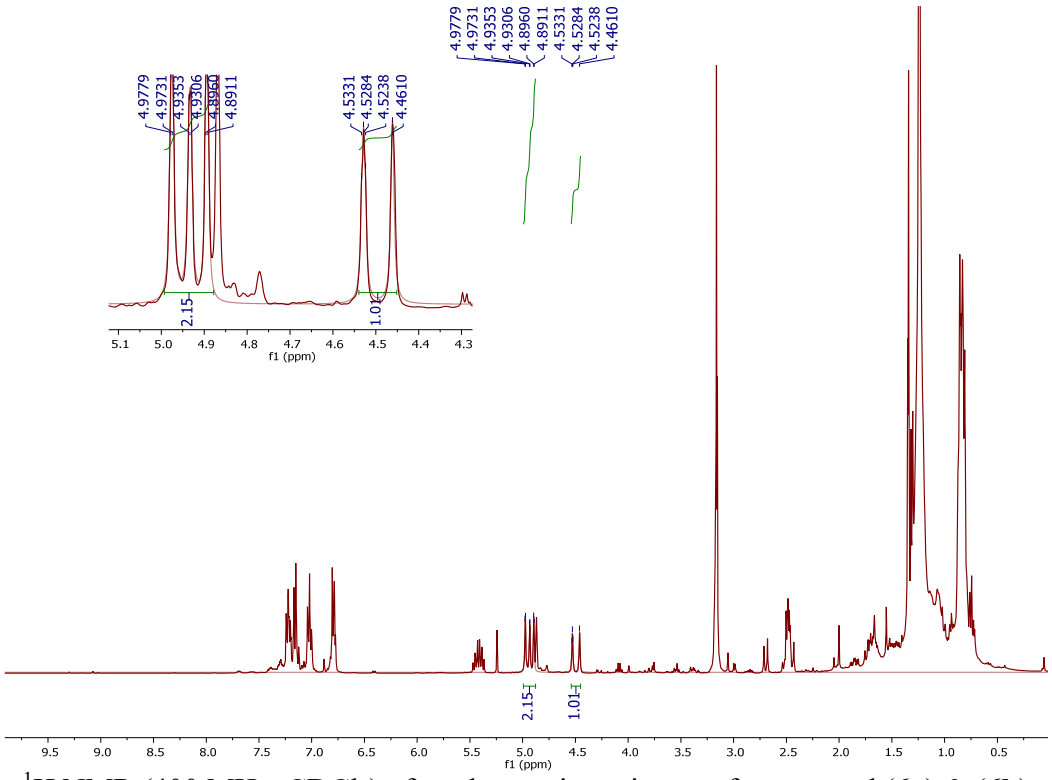
Determination of diastereomeric ratio of compound (20e) from ^{1}H NMR of crude reaction mixture:





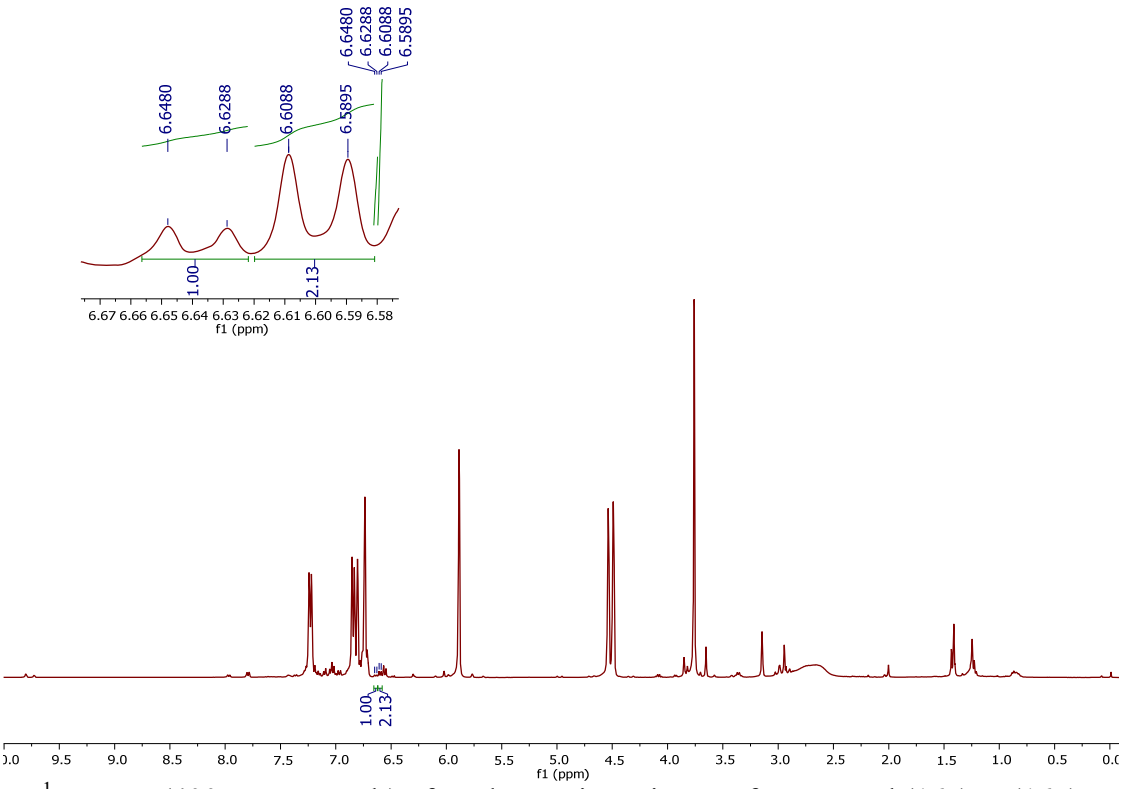
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**20e**)

Determination of product ratio of compound (6a) & (6b) from ^{1}H NMR of crude reaction mixture (allylacetate & methallyl alcohol, toluene, NaH (60% in mineral oil), 25 °C for 1 h) allylation was major product (Scheme 7):



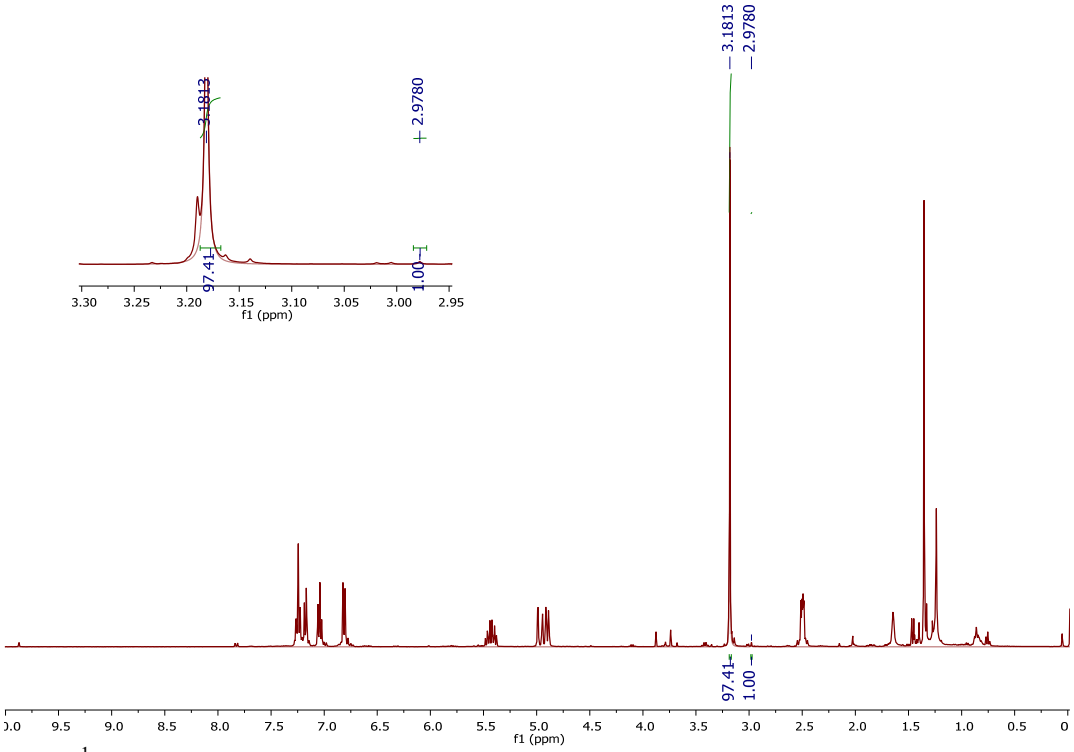
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**6a**) & (**6b**)

Determination of product ratio of compound (16a) & (16b) from ^{1}H NMR of crude reaction mixture (p-methoxybenzyl alcohol & pipernoyl alcohol, toluene, NaH (60% in mineral oil), 90 °C for 12 h) major product is (16a) (Scheme 8)



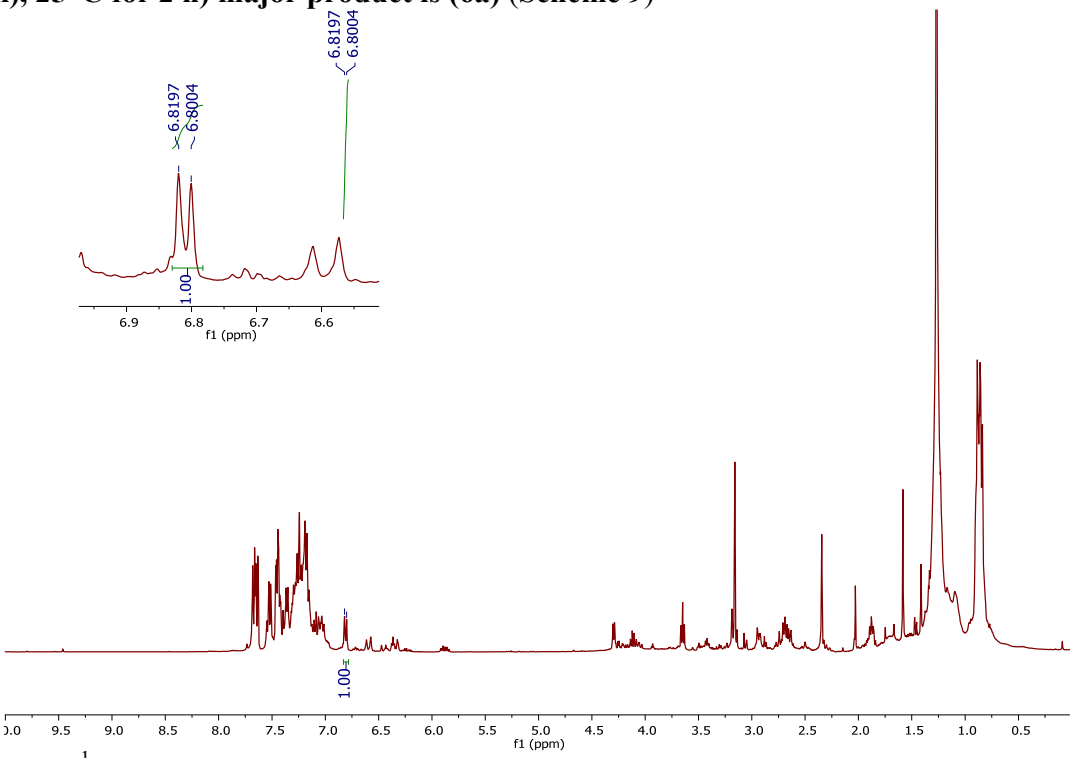
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**16a**) & (**16b**)

Determination of product ratio from ^{1}H NMR of crude reaction mixture (p-methoxybenzyl alcohol & allyl alcohol, toluene, NaH (60% in mineral oil), 25 °C for 3 h) only allylation was observed (scheme 9):



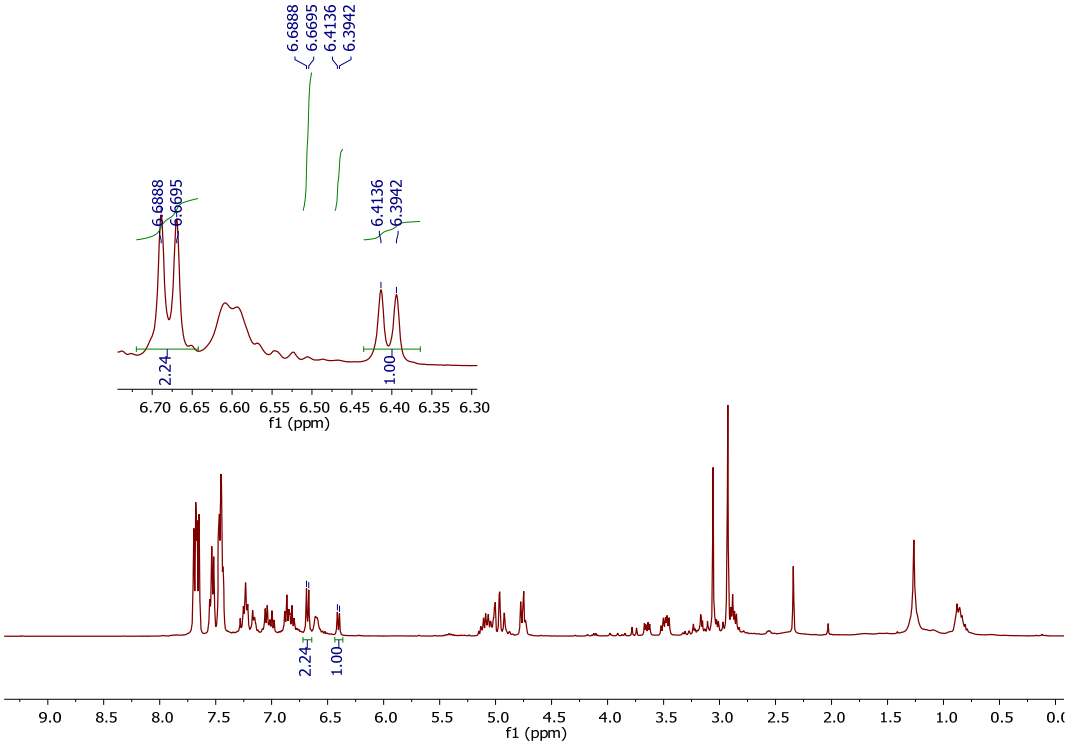
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**6a**)

Determination of product ratio of compound (16a) & (16b) from ^{1}H NMR of crude reaction mixture (cinnamyl alcohol & allyl alcohol, toluene, NaH (60% in mineral oil), 25 °C for 2 h) major product is (6a) (Scheme 9)



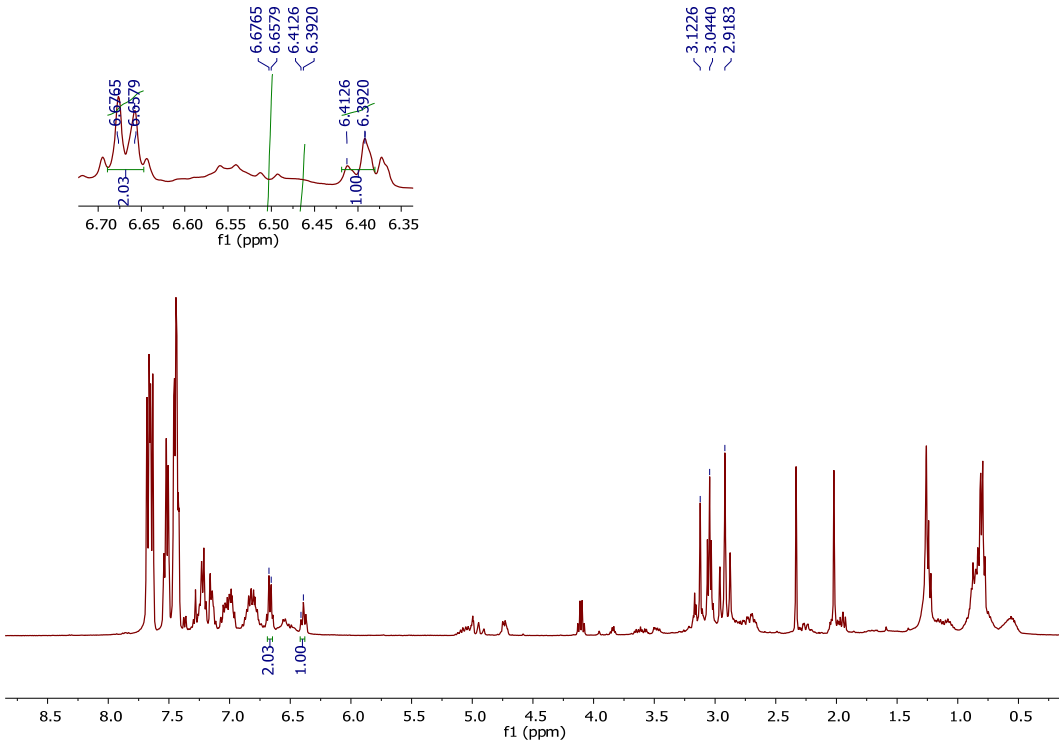
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound (**6a**)

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (26, toluene, NaH (60% in mineral oil), 80 °C for 2 h):



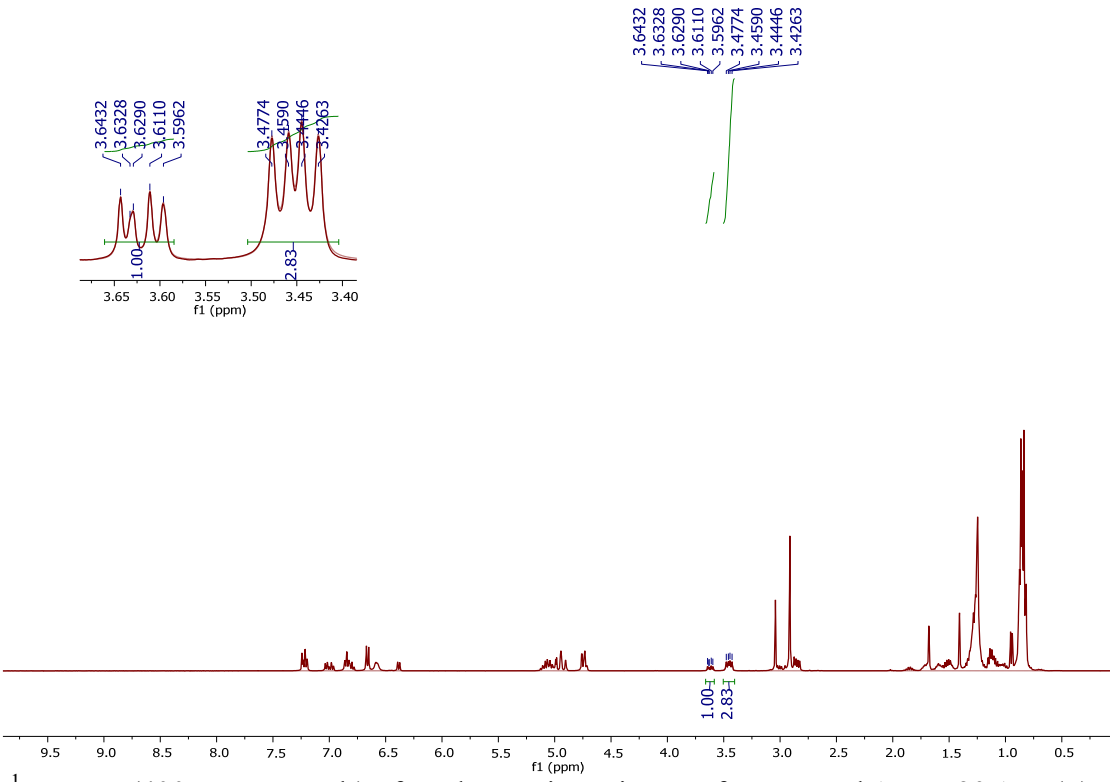
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (27, toluene, NaH (60% in mineral oil), 80 °C for 2 h):



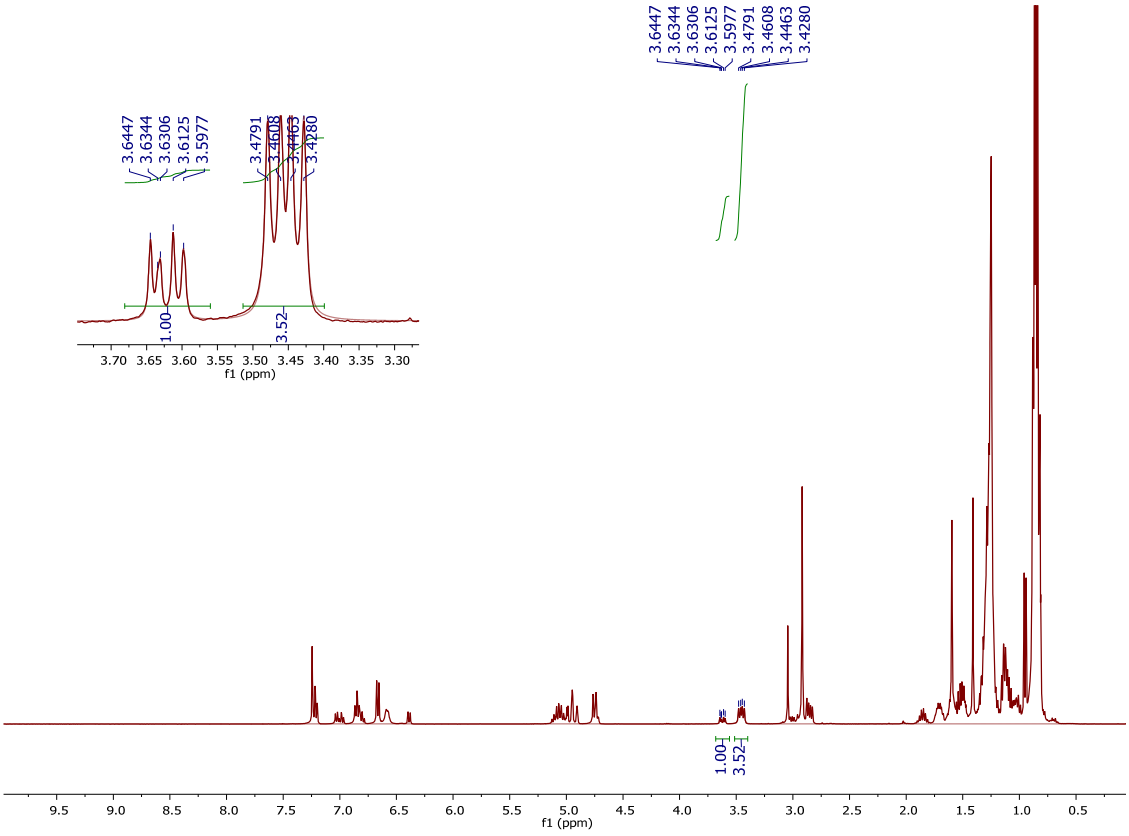
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (26 & 27, toluene, NaH (60% in mineral oil), 80 °C for 2 h):



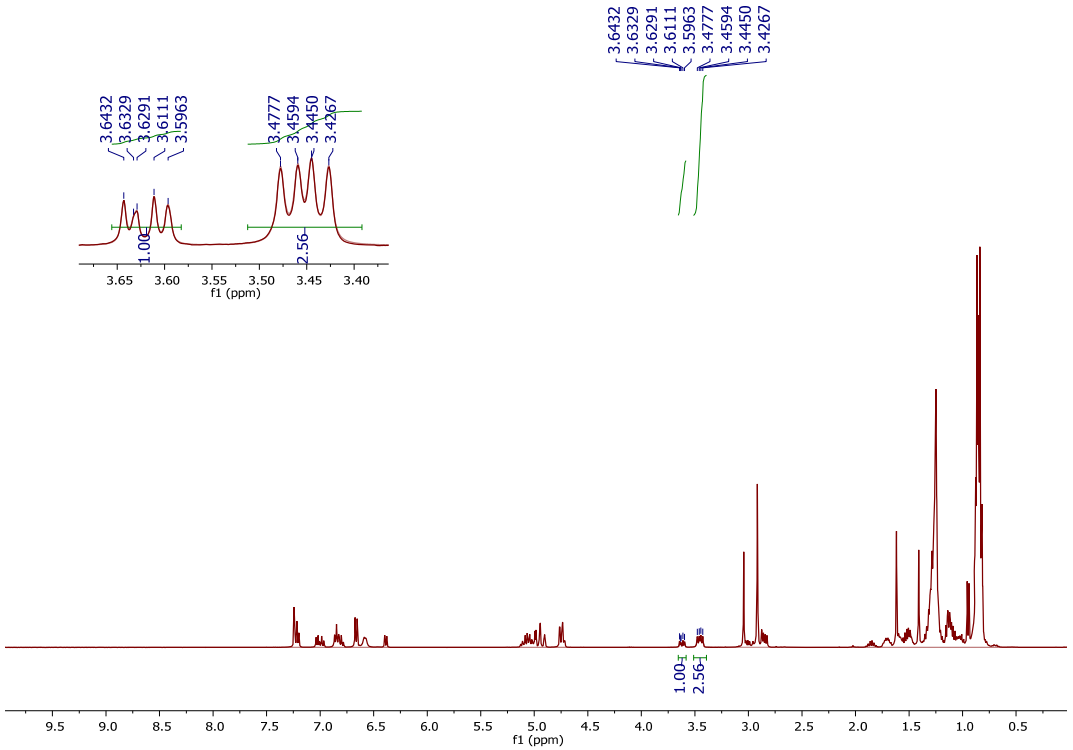
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (26 & 19a, toluene, NaH (60% in mineral oil), 80 °C for 2 h):



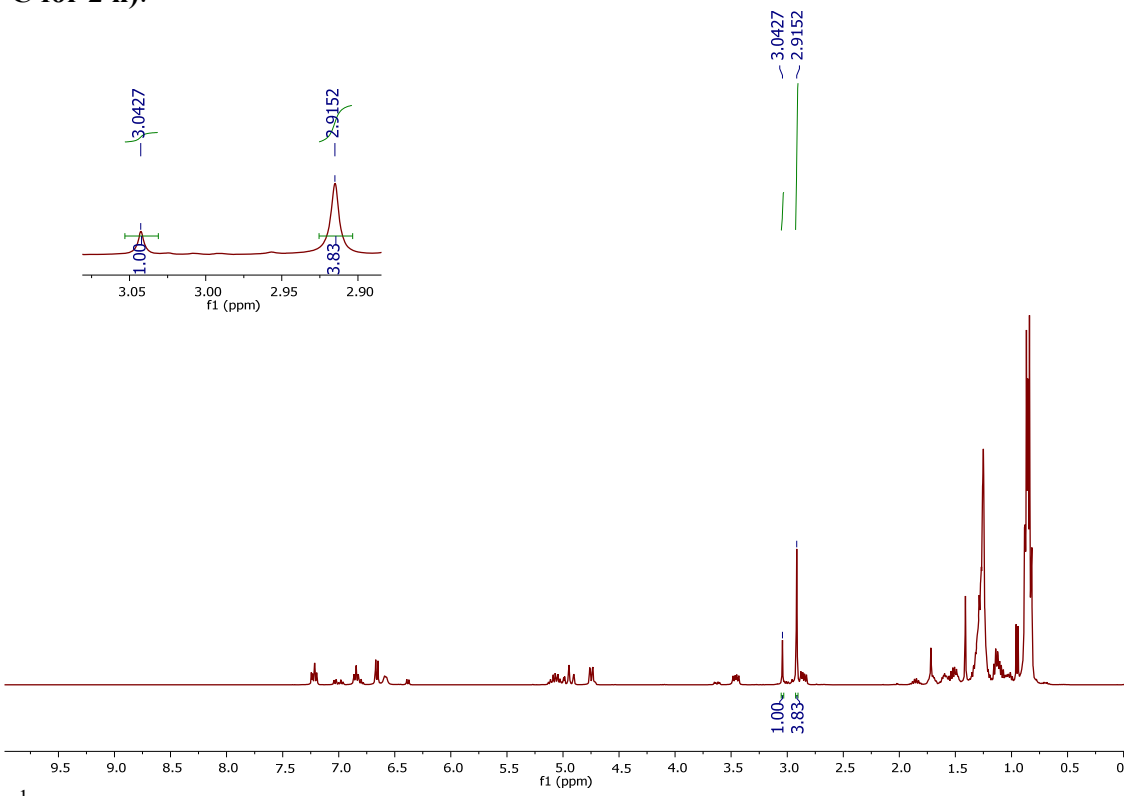
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (19a & 27, toluene, NaH (60% in mineral oil), 80 °C for 2 h):



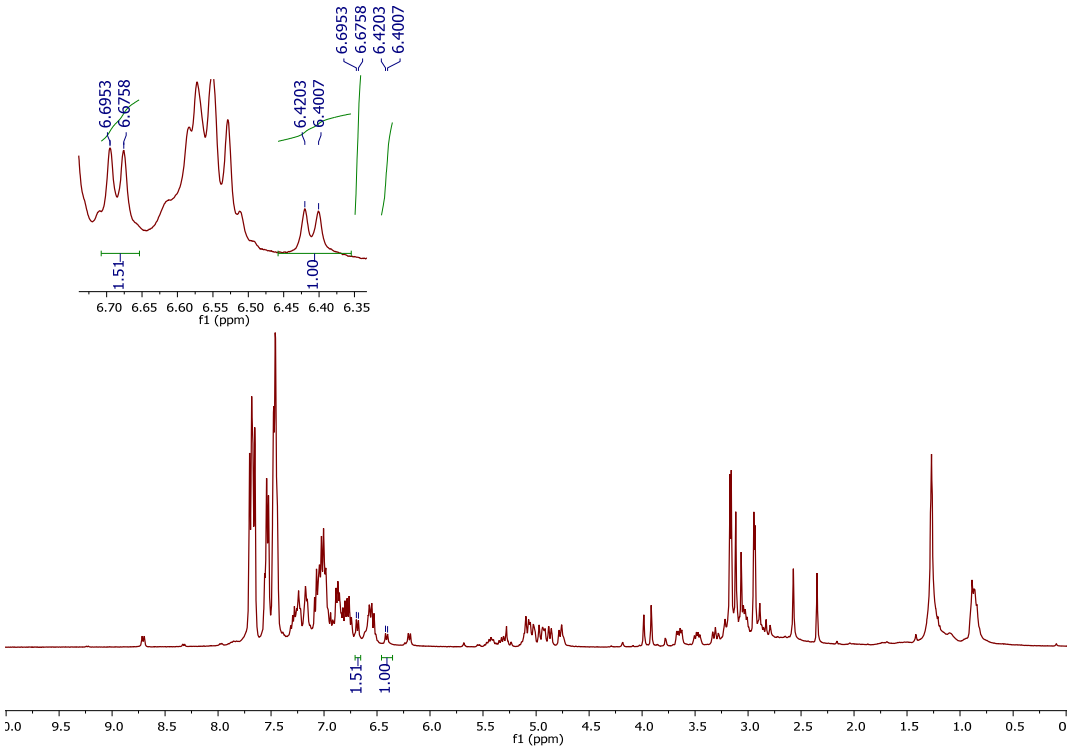
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (19a, 26 & 27, toluene, NaH (60% in mineral oil), 80 °C for 2 h):



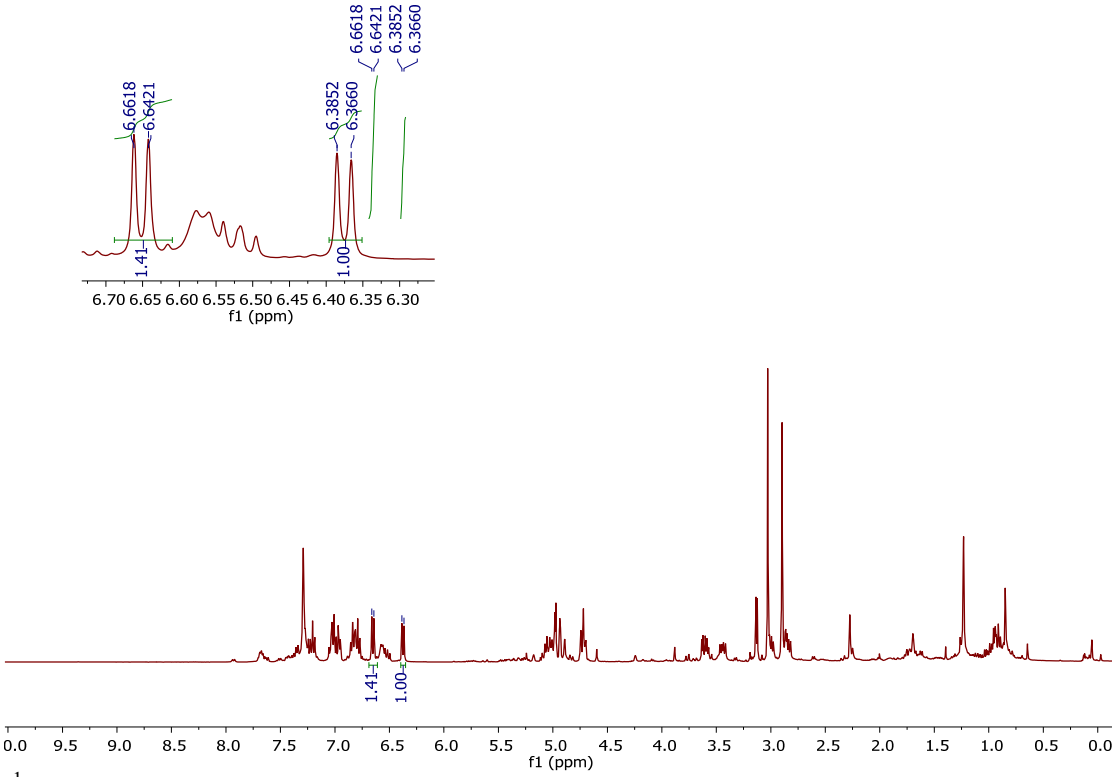
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (NaH (60%), THF, 80 °C for 2 h):



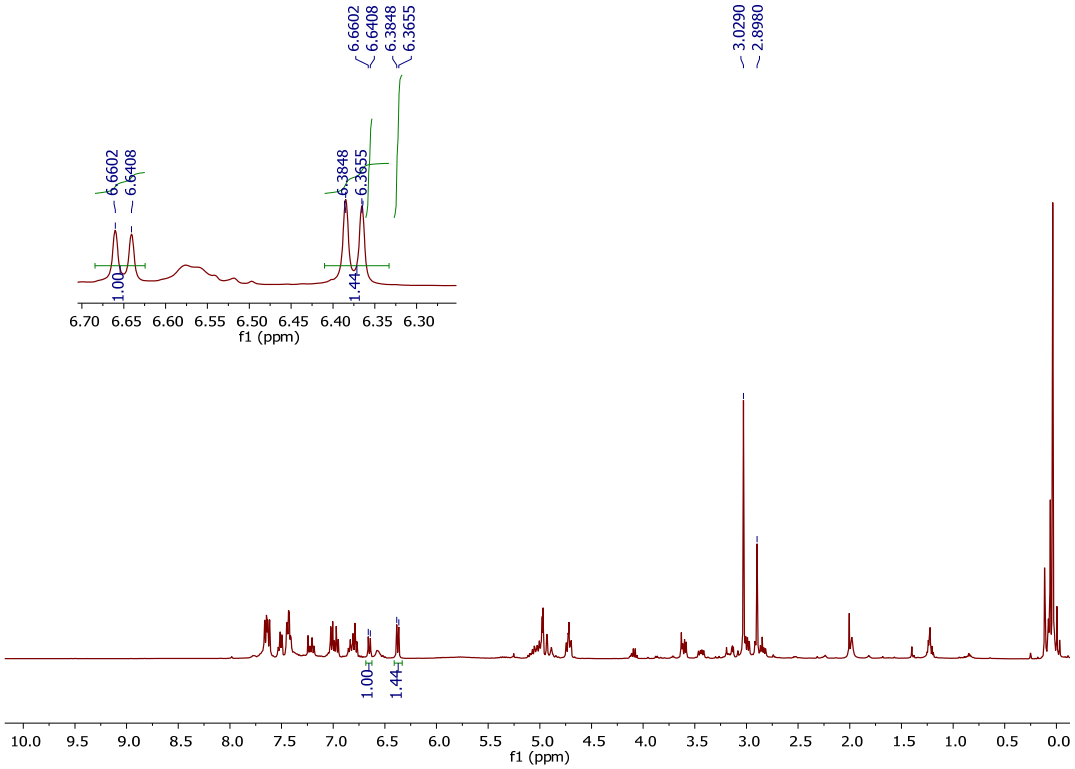
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (NaHMDS, THF, 80 °C for 2 h):



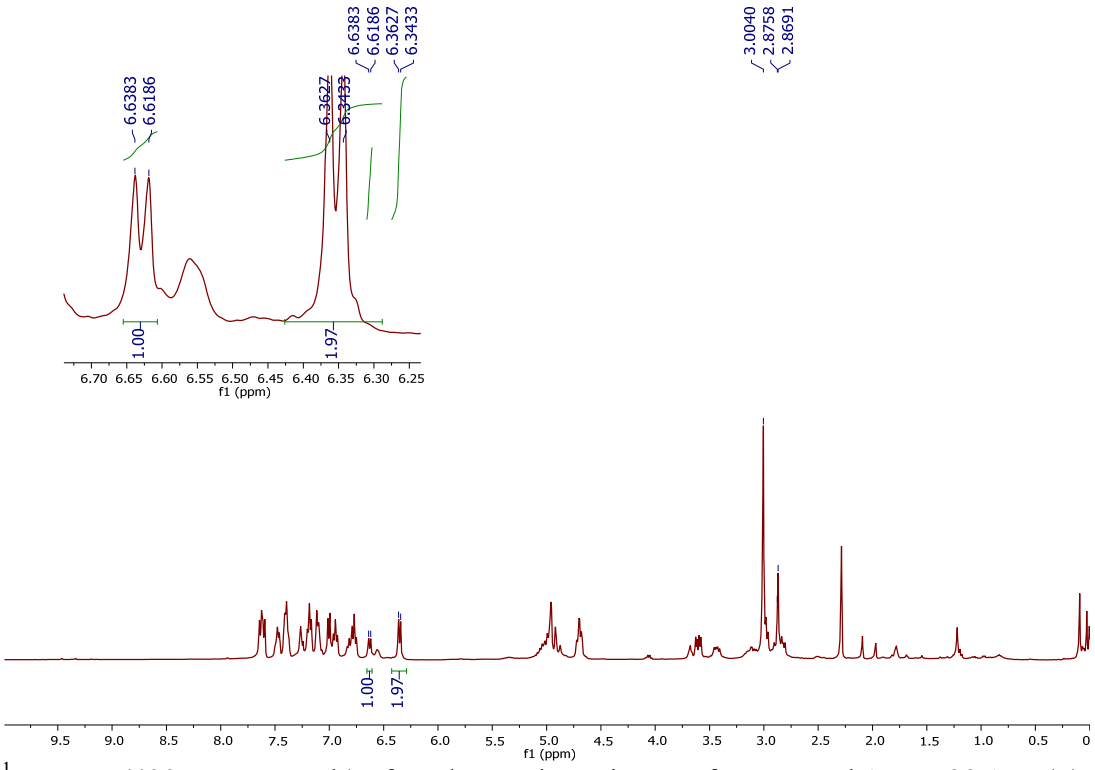
^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (KHMDS, THF, 80 °C for 2 h):



^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

Determination of diastereomeric ratio of compound (*meso*-20a) & (±)-20a from ^{1}H NMR of crude reaction mixture (LiHMDS, THF, 80 °C for 2 h):



^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture of compound **(*meso*-20a)** & (±)-**20a**

CheckCIF of *meso*-Folicanthine:

Datablock: shelx

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=9.0000(4) b=14.0771(7) c=15.5933(8)
alpha=90 beta=90.682(3) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1975.44(17)	1975.44(17)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C24 H30 N4	?
Sum formula	C24 H30 N4	C24 H30 N4 O0
Mr	374.52	374.52
Dx,g cm-3	1.259	1.259
Z	4	4
Mu (mm-1)	0.076	0.076
F000	808.0	808.0
F000'	808.25	
h,k,lmax	11,18,20	0,0,0
Nref	4670	4656
Tmin,Tmax		
Tmin'		

Correction method= Not given

Data completeness= 0.997 Theta(max)= 27.786

R(reflections)= 0.0595(2879) wR2(reflections)= 0.1832(4656)

S = 1.090 Npar= 254

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

Alert level C

PLAT030_ALERT_1_C _diffrn_reflns_number < _reflns_number_total Please Check
PLAT052_ALERT_1_C Info on Absorption Correction Method Not Given Please Do !
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ... Please Check
PLAT054_ALERT_1_C Medium Crystal Dimension Missing (or Error) ... Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ... Please Check
PLAT480_ALERT_4_C Long H...A H-Bond Reported H16C .. N3 .. 2.68 Ang.
PLAT480_ALERT_4_C Long H...A H-Bond Reported H16C .. N3 .. 2.68 Ang.

Alert level G

CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a

http://checkcif.iucr.org/cgi-bin/checkcif_hkl.pl 1/3

symmetry error - see SYMMG tests
From the CIF: _cell_formula_units_Z 4
From the CIF: _chemical_formula_sum C24 H30 N4 O0
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
C	96.00	96.00	0.00
H	120.00	120.00	0.00
N	16.00	16.00	0.00
O	4.00	0.00	4.00

PLAT194_ALERT_1_G Missing _cell_measurement_refIns_used Datum .... Please Add
PLAT195_ALERT_1_G Missing _cell_measurement_theta_max Datum .... Please Add
PLAT196_ALERT_1_G Missing _cell_measurement_theta_min Datum .... Please Add
PLAT793_ALERT_4_G The Model has Chirality at C3 (Centro SPGR) R Verify
And 3 other PLAT793 Alerts
More ...

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

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

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

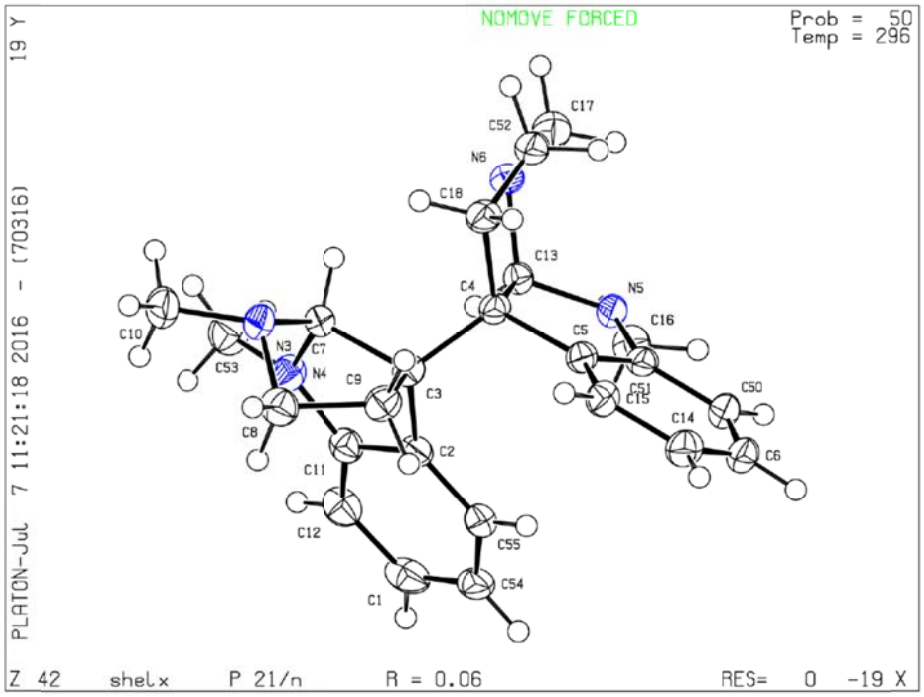
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section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

Publication of your CIF in other journals

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

PLATON version of 06/05/2016; check.def file version of 05/05/2016

Datablock shelx - ellipsoid plot



wnload CIF editor (publCIF) from the IUCr
wnload CIF editor (enCIFer) from the CCDC
st a new CIF entry

checkcif.iucr.org/cgi-bin/checkcif_hkl.pl 3/