Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Formal Total Synthesis of Calothrixin B and Its *N*-Benzyl Analogues

Nagarajan Ramkumar and Rajagopal Nagarajan*

School of Chemistry, University of Hyderabad, Hyderabad-500046, India.

E-mail: rnsc@uohyd.ernet.in

Table of Contents

General Information and Methods:

The NMR experiments were performed with 400 MHz or 500 MHz spectrometer, and chemical shifts are expressed in ppm (δ) with TMS as an internal reference. Coupling constant *J* values are given in Hz. IR spectra were recorded by using KBr pellets or neat. ESI-TOF mass analyzer type used for the HRMS measurements. Reactions were carried out under an inert atmosphere refer to the use of nitrogen and monitored by TLC. Column chromatography was performed on silica gel (100–200 mesh) in glass columns to purify the compounds. Solvents tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) and anisole were dried by using standard distillation methods. Commercially available reagents and solvents were used without further purification and were purchased. Melting points were determined using open capillary tubes and are uncorrected.

Procedure for the synthesis of 8-bromophenanthridine-7,10-dione (5):

To a soultion of 8-bromo-7,10-dimethoxy-5-(methoxymethyl)phenanthridin-6(5*H*)-one **3** (1 g, 2.6 mmol) in dry THF (30 mL), $LiAlH_4$ (500 mg, 13.2 mmol) was added a portionwise at 0 ^oC. The resulting mixture was allowed to stir at the same temperature for 2 h. After completion (TLC), the mixture was poured into 150 g of crushed ice. The precipitate formed was filtered through a celite pad and repeatedly washed with ethyl acetate (50 mL). The combined filtrate was further extracted with ethyl acetate (50 mL) and separated. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to give a crude oil.

The crude oil obtained (800 mg) was redissolved in acetonitrile (40 mL) and distilled water (20 mL). To this solution, CAN (700 mg, 1.26 mmol) was added and stirred for 2 h at room temperature. After completion of the reaction (TLC), the reaction mixture was poured into water (100 mL), extracted with ethyl acetate (3 × 50 mL) and dried over anhydrous Na_2SO_4.

The solvent was evaporated to afford crude oil which was purified by silica gel column chromatography using petroleum ether/ethyl acetate.

R_f = 0.41 (petroleum ether: EtOAc, 4:1); yellow solid (584 mg, 78%): mp 124-126 ^oC; IR (neat): 2968, 1738, 1588, 1365, 1212, 1013, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.65 (s, 1H), 9.44 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.92 (t, J = 6.8 Hz, 1H), 7.83 (t, J = 8.4 Hz, 1H), 7.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.1, 185.3, 152.0, 147.5, 139.9, 136.2, 132.1, 131.6, 130.6, 130.3, 127.6, 122.8, 122.0; HRMS (ESI): $[M+Na]^+$ calcd for $C_{13}H_6BrNO_2$ 309.9480, found 309.9483.

Procedure for the synthesis of 8-(2-chlorophenyl)phenanthridine-7,10-dione (7):

To a solution of 8-bromophenanthridine-7,10-dione **5** (500 mg, 1.7 mmol) and (2-chlorophenyl)boronic acid **6** (540 mg, 3.4 mmol) in DMF (5 mL), $Pd(PPh_3)_4$ (196 mg, 0.17 mmol) and K_2CO_3 (470 mg, 3.4 mmol) were added. The resulting mixture was stirred at 140 ^oC for 8 h. After completion (TLC), the mixture was poured into water (100 mL) and extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated to give crude residue which was purified by silica gel column chromatography using petroleum ether/ethyl acetate.

R_f = 0.36 (petroleum ether: EtOAc, 7:3); yellow solid (469 mg, 84%): mp 206-208 ^oC; IR (neat): 2978, 1658, 1588, 1335, 1212, 1043, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.77 (s, 1H), 9.52 (d, J = 8.8 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.16 (t, J = 8.4 Hz, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.30-7.20 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.9, 185.2, 152.1, 147.9, 140.1, 136.2, 135.1, 133.2, 131.3, 130.3, 130.1, 128.0, 127.8, 127.7, 125.1, 124.4, 123.9, 123.3, 123.1; HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{10}ClNO_2$ 320.0478, found 320.0475.

General procedure for copper-catalyzed domino synthesis of *N*-benzylcalothrixins (9a-i):

A Schlenk tube was equipped with a magnetic pellet, evacuated and back-filled with nitrogen. 8-(2-Chlorophenyl)phenanthridine-7,10-dione **7** (60 mg, 0.18 mmol), appropriate benzylamine **8a-i** (1.1 equiv), Cu powder (1 mg, 0.015 mmol), CuO (3 mg, 0.036 mmol), *t*-BuOK (42 mg, 0.37 mmol) and NMP (1 mL) were added. The resulting mixture was heated at 140 ^{o}C for appropriate time under nitrogen atmosphere. After completion of the reaction, the mixture was poured into water (25 mL) and filtered through a celite pad and washed with chloroform (60 mL). The organic layer was separated and washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated to give crude residue which was purified by silica gel column chromatography using petroleum ether/ethyl acetate.

12-Benzyl-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9a):

R_f = 0.30 (petroleum ether: EtOAc, 4:1); red solid (57 mg, 78%): mp 260-262 ^{o}C; IR (neat): 3040, 1653, 1538, 1430, 1258 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.79 (s, 1H), 9.54 (d, J = 8.8 Hz, 1H), 8.46-8.44 (dd, J = 1.2, 6.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.85-7.81 (m, 1H), 7.75-7.71 (m, 1H), 7.46-7.40 (m, 3H), 7.34-7.28 (m, 3H), 7.23 (d, J = 7.2 Hz, 2H), 6.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.9, 181.0, 152.1, 147.8, 140.1, 136.2, 135.1, 133.2, 131.1, 130.3, 130.1, 128.9 (2C), 128.0, 127.8, 127.6, 126.6 (2C), 125.1, 124.4, 123.9, 123.2, 123.1, 117.6, 111.5, 48.5; HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{16}N_2O_2$ 389.1290, found 389.1289.

12-(4-Methylbenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9b):

R_f = 0.65 (petroleum ether: EtOAc, 7:3); red solid (57 mg, 76%): mp 246-248 ^{o}C; IR (neat): 3030, 2922, 1736, 1649, 1522, 1459, 1239, 1075, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.77 (s, 1H), 9.54 (d, J = 8.8 Hz, 1H), 8.43 (d, J = 7.2 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.82

(t, J = 7.2 Hz, 1H), 7.73 (t, J = 7.2 Hz, 1H), 7.47-7.38 (m, 3H), 7.14-7.10 (m, 4H), 5.94 (s, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.9, 180.9, 152.0, 147.8, 140.0, 137.6, 135.0, 133.26, 133.22, 131.3, 130.2, 130.0, 129.5 (2C), 127.9, 127.7, 126.6 (2C), 125.1, 124.4, 123.8, 123.2, 123.1, 117.6, 111.6, 48.3, 21.0; HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{18}N_2O_2$ 403.1446, found 403.1439.

12-(4-Methoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9c):

R_f = 0.61 (petroleum ether: EtOAc, 7:3); red solid (63 mg, 81%): mp 230-232 ^{o}C; IR (neat): 3008, 2248, 1740, 1369, 1222, 1050, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.74 (s, 1H), 9.52 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 7.6 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.71 (t, J = 8.0 Hz, 1H), 7.46-7.35 (m, 3H), 7.19 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 5.88 (s, 2H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.8, 180.8, 159.2, 152.1, 147.8, 139.9, 134.9, 133.1, 131.3, 130.3, 130.0, 128.3, 128.1 (2C), 127.8, 127.6, 125.0, 124.4, 123.8, 123.2, 123.0, 117.5, 114.2 (2C), 111.5, 55.2, 47.9; HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{18}N_2O_3$ 419.1395, found 419.1382.

12-(4-Chlorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9d):

R_f = 0.65 (petroleum ether: EtOAc, 7:3); red solid (49 mg, 63%): mp 242-244 ^{o}C; IR (neat): 2920, 1739, 1646, 1456, 1365, 1229, 1075, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.80 (s, 1H), 9.54 (dd, J = 1.0, 9.0 Hz, 1H), 8.48-8.46 (m, 1H), 8.20 (dd, J = 1.0, 8.5 Hz, 1H), 7.85 (td, J = 1.5, 8.5 Hz, 1H), 7.75 (td, J = 1.5, 8.5 Hz, 1H), 7.51-7.43 (m, 3H), 7.29 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 9.0 Hz, 2H), 5.97 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 182.0, 181.0, 152.2, 147.8, 140.0, 135.0, 134.7, 133.8, 133.2, 131.4, 130.4, 130.2, 129.1 (2C), 128.2, 128.0 (2C), 127.6, 125.3, 124.4, 124.0, 123.3, 123.1, 117.8, 111.3, 47.9; HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{15}ClN_2O_2$ 423.0900, found 423.0896.

12-(4-Fluorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9e):

R_f = 0.72 (petroleum ether: EtOAc, 7:3); red solid (44 mg, 58%): mp 228-230 ^oC; IR (neat): 2920, 2851, 1649, 1506, 1463, 1339, 1232, 1074, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.79 (s, 1H), 9.54 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 7.85-7.82 (td, J = 1.0, 7.0 Hz, 1H), 7.76-7.73 (td, J = 1.0, 6.5 Hz, 1H), 7.48-7.41 (m, 3H), 7.25-7.22 (m, 2H), 7.01 (t, J = 8.5 Hz, 2H), 5.96 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 182.0, 180.9, 152.1, 147.8, 139.9, 134.9, 133.2, 132.0, 131.9, 131.4, 130.3, 130.2, 128.5, 128.4, 128.1, 127.6, 125.2, 124.4, 124.0, 123.3, 123.1, 117.7, 111.3, 47.9; HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{15}FN_2O_2$ 407.1196, found 407.1189.

12-(3,4-Dimethoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9f):

R_f = 0.64 (petroleum ether: EtOAc, 1:1); red solid (72 mg, 86%): mp 186-188 ^oC; IR (neat): 2922, 1733, 1645, 1512, 1239, 1139, 1019, 739 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.70 (s, 1H), 9.48 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 7.2 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.78 (t, J = 7.2 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.43-7.31 (m, 3H), 6.86 (s, 1H), 6.76-6.68 (m, 2H), 5.85 (s, 2H), 3.809 (s, 3H), 3.804 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.8, 180.7, 152.0, 149.2, 148.7, 147.7, 139.9, 134.9, 133.0, 131.3, 130.2, 130.0, 128.7, 127.8, 127.6, 125.0, 124.3, 123.7, 123.1, 123.0, 119.0, 117.5, 111.5, 111.3, 110.3, 55.9, 55.8, 48.2; HRMS (ESI): $[M]^+$ calcd for $C_{28}H_{20}N_2O_4$ 448.1423, found 448.1433.

12-(2,4-Dichlorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9g):

R_f = 0.57 (petroleum ether: EtOAc, 4:1); red solid (37 mg, 46%): mp 256-258 ^oC; IR (neat): 3004, 2127, 1710, 1424, 1359, 1219, 783 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.84 (s, 1H), 9.53 (d, J = 8.8 Hz, 1H), 8.53-8.51 (m, 1H), 8.22 (d, J = 8.4 Hz, 1H), 7.86 (t, J = 6.8 Hz, 1H), 7.75 (t, J = 7.2 Hz, 1H), 7.55 (s, 1H), 7.51-7.49 (m, 2H), 7.36-7.35 (m, 1H), 7.05 (d, J = 8.4

Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.07 (s, 2H); **Note**: ^{13}C NMR was unable to record due to its poor solubility in common NMR solvents. HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{14}Cl_2N_2O_2$ 457.0510, found 457.0512.

12-(3-Methoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9h):

R_f = 0.56 (petroleum ether: EtOAc, 7:3); red solid (62 mg, 80%): mp 192-194 ^oC; IR (neat): 2945, 2837, 1649, 1457, 1239, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.81 (s, 1H), 9.56 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 7.84 (t, *J* = 6.8 Hz, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.48-7.42 (m, 3H), 7.24 (t, *J* = 8.0 Hz, 1H), 6.83-6.77 (m, 3H), 6.00 (s, 2H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 182.0, 181.0, 160.0, 152.2, 147.9, 140.1, 137.8, 135.1, 133.3, 131.3, 130.3, 130.1, 130.0, 128.0, 127.7, 125.1, 124.5, 123.9, 123.3, 123.1, 118.8, 117.7, 112.8, 112.6, 111.5, 55.2, 48.4; HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{18}N_2O_3$ 419.1395, found 419.1387.

12-(2-Bromobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9i):

R_f = 0.50 (petroleum ether: EtOAc, 4:1); red solid (59 mg, 68%): mp 234-236 ^oC; IR (neat): 2968, 1738, 1588, 1446, 1365, 1212, 1013, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.75 (s, 1H), 9.47 (d, *J* = 9.0 Hz, 1H), 8.46-8.43 (m, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.81-7.78 (td, *J* = 1.0, 7.0 Hz, 1H), 7.70-7.67 (m, 2H), 7.43-7.41 (m, 2H), 7.30-7.28 (m, 1H), 7.14-7.11 (td, *J* = 1.5, 7.5 Hz, 1H), 7.08-7.04 (td, *J* = 1.5, 8.0 Hz, 1H), 6.40-6.38 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.00 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 181.8, 180.9, 152.1, 147.8, 139.9, 135.3, 135.2, 133.1, 133.0, 131.5, 130.27, 130.21, 129.1, 128.2, 127.9, 127.6, 126.3, 125.4, 124.4, 123.9, 123.2, 123.0, 122.0, 117.8, 111.3, 49.0; HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{15}BrN_2O_2$ 467.0395, found 467.0398.

Procedure for the synthesis of 7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (Calothrixin B) (2):

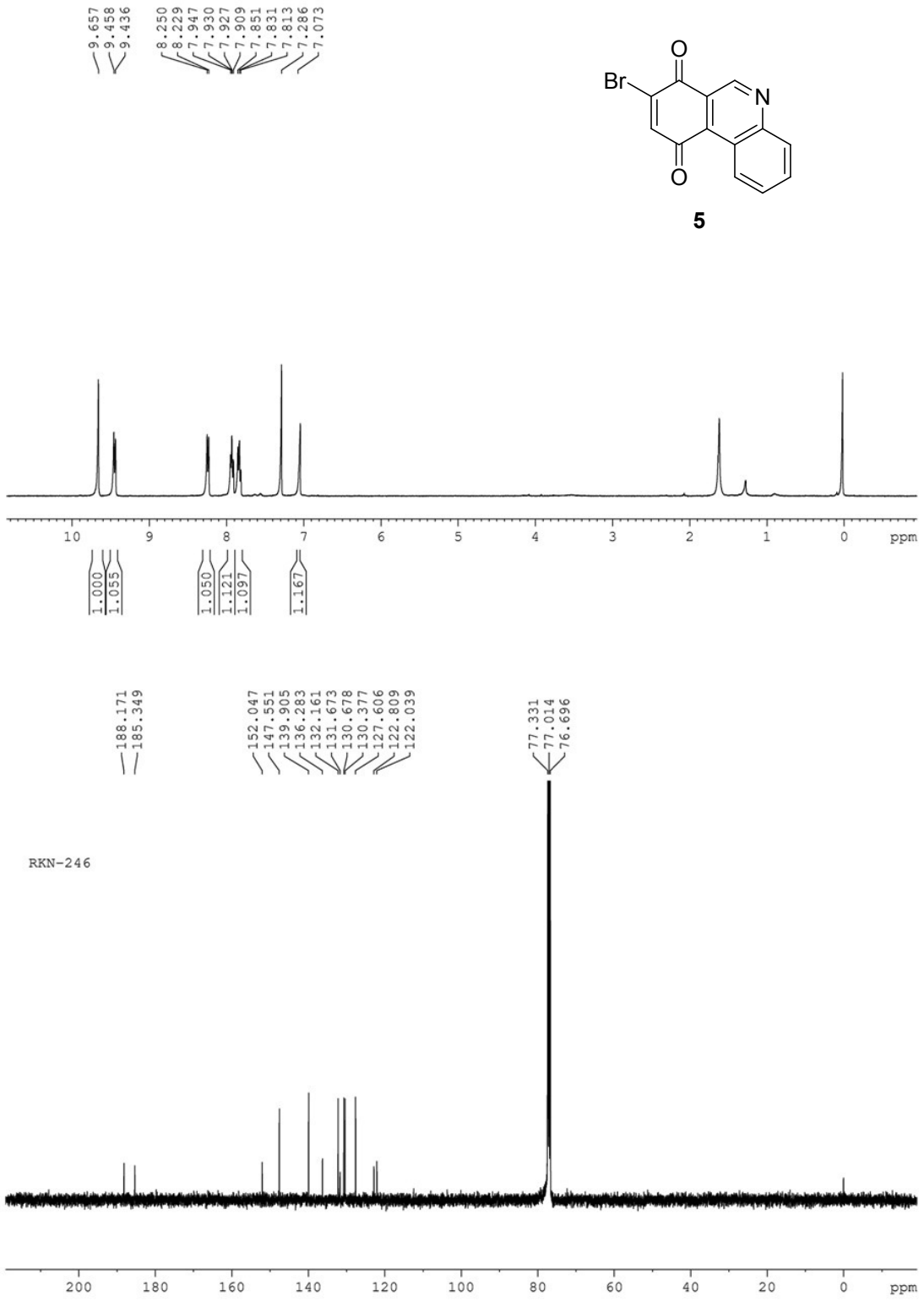
To a solution of 12-(3,4-dimethoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione **9f** (25 mg, 0.055 mmol) in dry anisole (3 mL), anhydrous $AlCl_3$ (37 mg, 0.277 mmol) was added and heated at 100 ^oC for 8 h. After completion of the reaction, the reaction mixture was quenched with water and extracted with ethyl acetate (3 × 30 mL). The organic layer was washed with saturated aqueous Na_2CO_3 solution (30 mL) and separated, and dried over anhydrous Na_2SO_4. The solvent was evaporated to give crude residue which was purified by silica gel column chromatography using petroleum ether/ethyl acetate.

R_f = 0.30 (petroleum ether: EtOAc, 5:1); red solid (11 mg, 68%): mp > 300 ^oC (lit.[1] mp ≥ 300 ^oC); IR (neat): 3430, 2968, 1653, 1425, 1089 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 9.60 (s, 1H), 9.56 (d, J = 8.8 Hz, 1H), 8.17-8.14 (dd, J = 3.2, 6.4 Hz, 2H), 7.94 (t, J = 6.8 Hz, 1H), 7.87 (t, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H) (**Note**: *N*-**H** not observed); ^{13}C NMR (DMSO-d_6, 400 MHz): δ 181.3, 180.8, 151.7, 147.9, 138.8, 138.5, 133.1, 132.0, 130.7, 130.3, 129.7, 127.6, 125.3, 124.8, 123.8, 123.0, 122.7, 116.0, 114.4; HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{10}N_2O_2$ 299.0820, found 299.0818.

References:

1 R. W. Rickards, J. M. Rothschild, A. C. Willis, N. M. de Chazal, J. Kirk, K. Kirk, K. J. Saliba and G. D. Smith, *Tetrahedron* 1999, **55**, 13513.

^{1}H and ^{13}C NMR of 8-bromophenanthridine-7,10-dione (5)



HRMS of 8-bromophenanthridine-7,10-dione (5)

BRUKER MAXIS HRMS REPORT

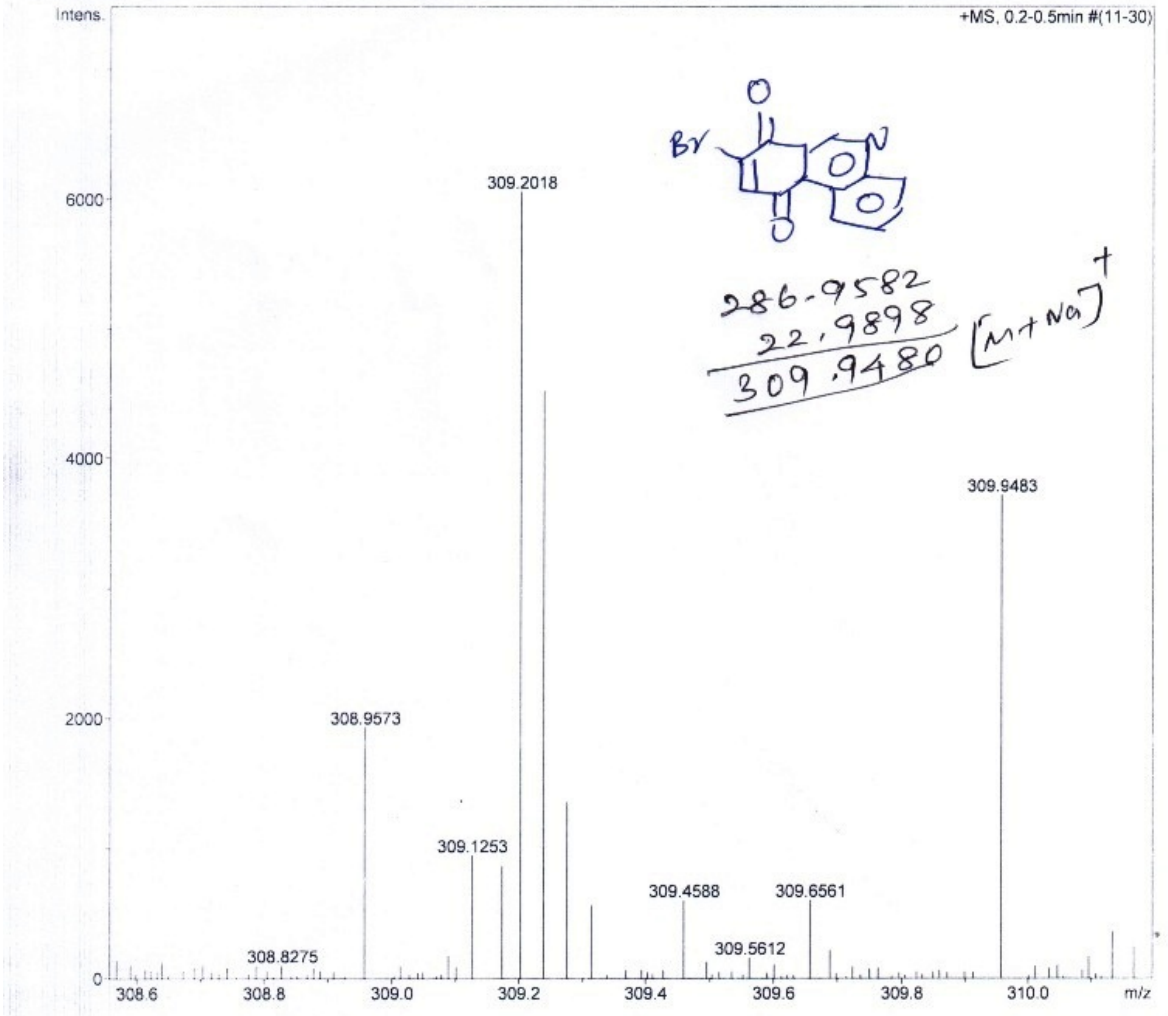
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JULY\RKN-286.d	Acquisition Date	7/14/2015 11:15:12 AM
Method	tune_low.m	Operator	Ramu Sridhar
Sample Name	RKN-286-DCM-MEOH	Instrument	maXis 10138
Comment			

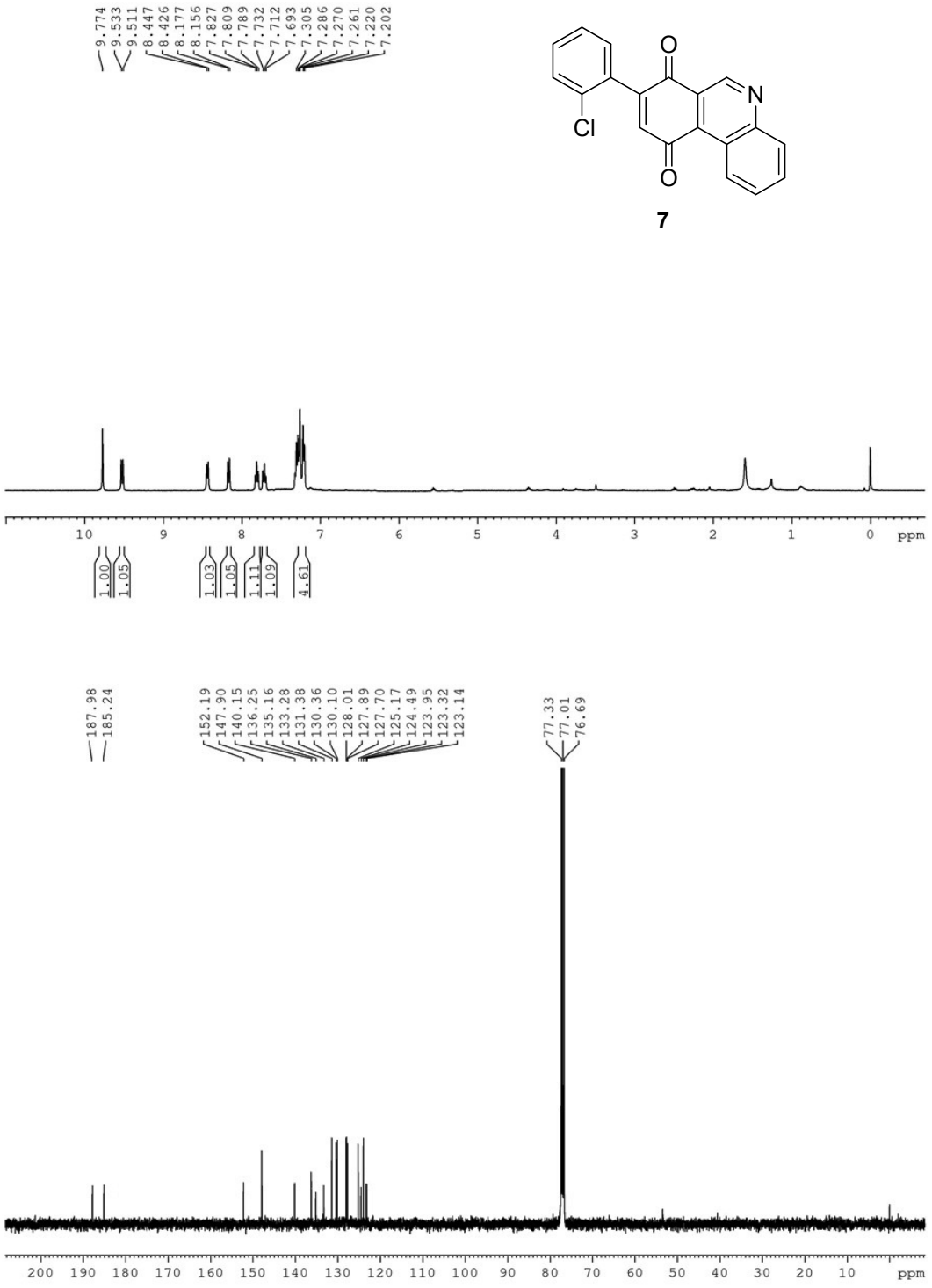
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.4 psi
Focus	Not active	Set Capillary	3200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

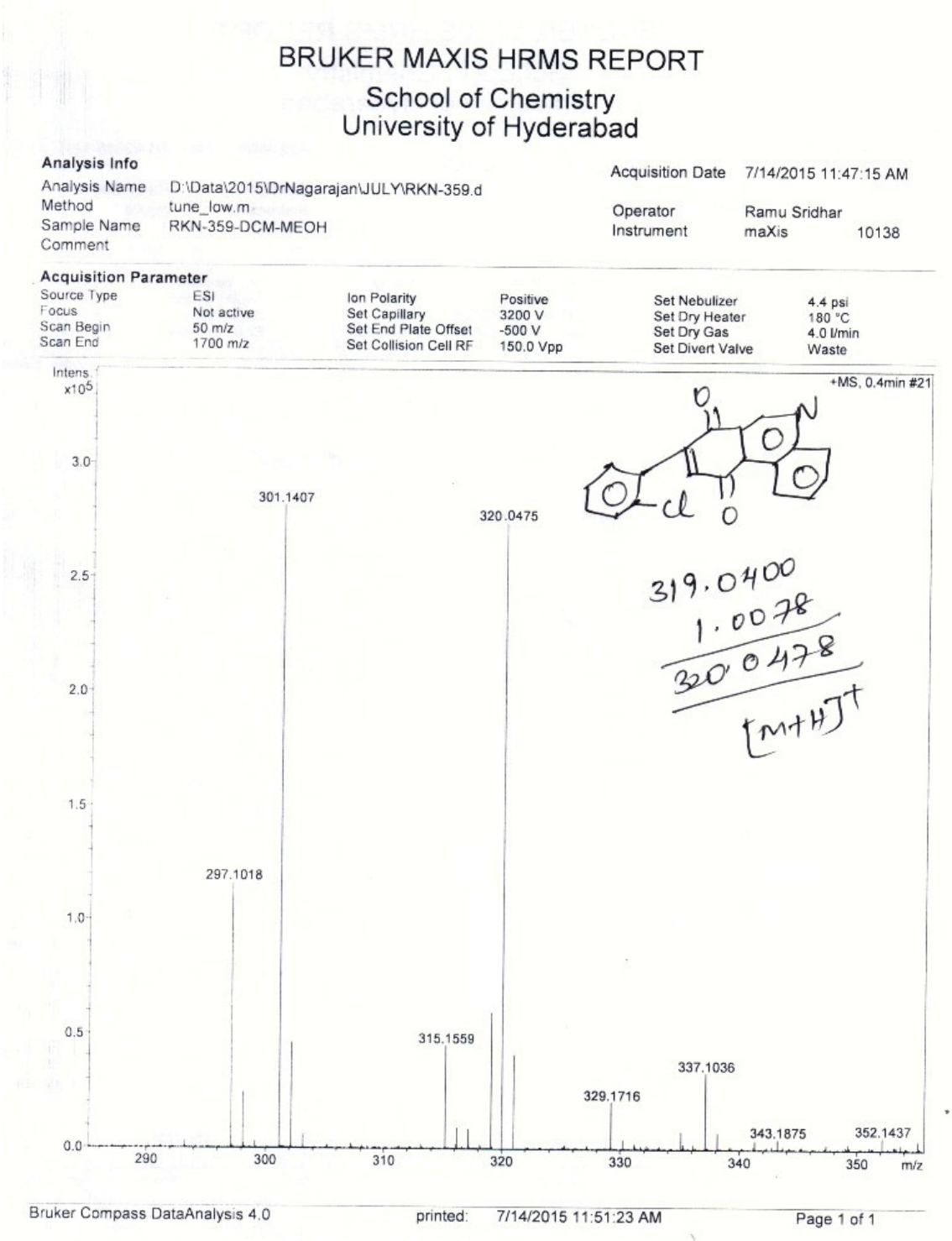


Bruker Compass DataAnalysis 4.0 printed: 7/14/2015 11:24:12 AM Page 1 of 1

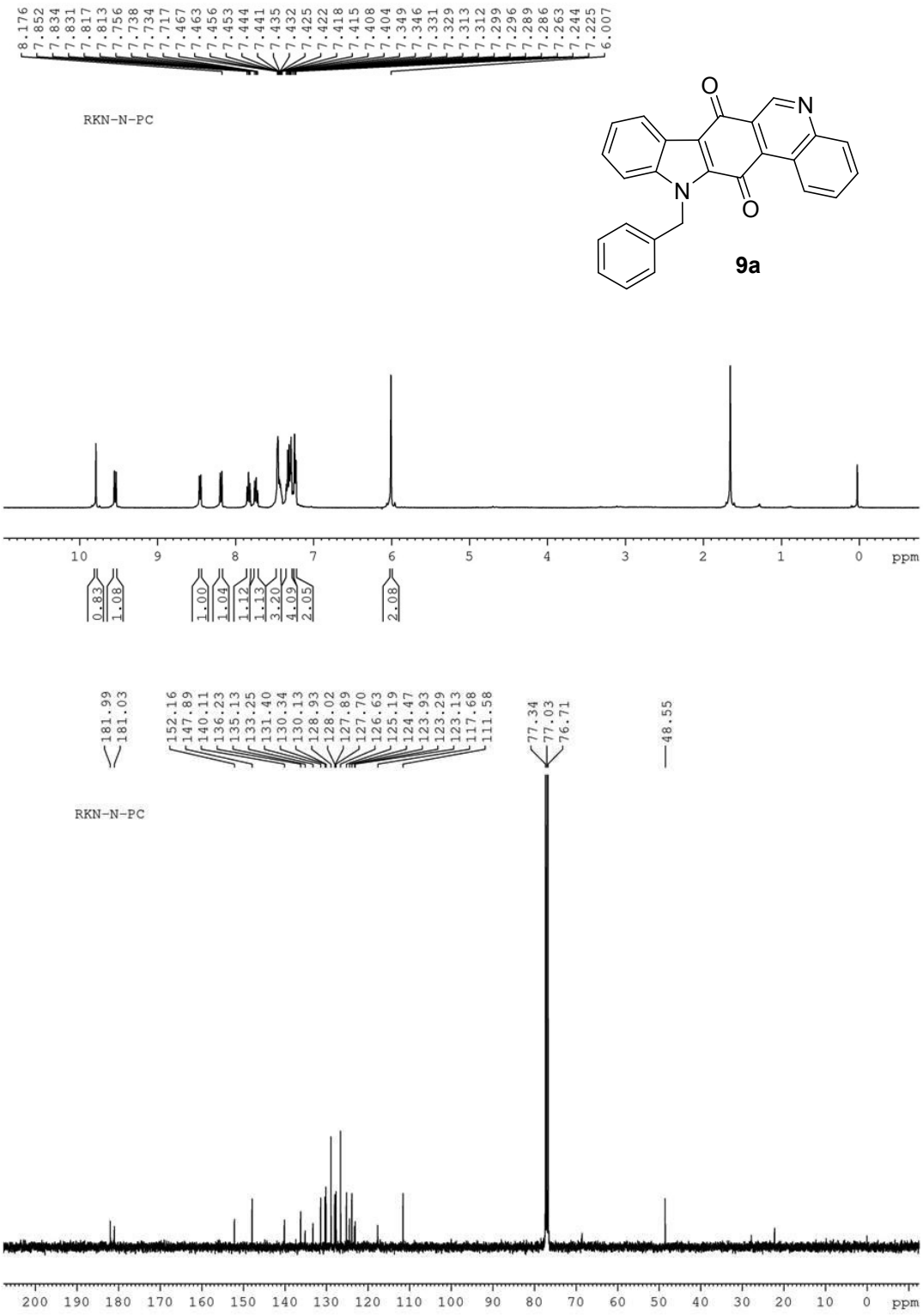
^{1}H and ^{13}C NMR of 8-(2-chlorophenyl)phenanthridine-7,10-dione (7)



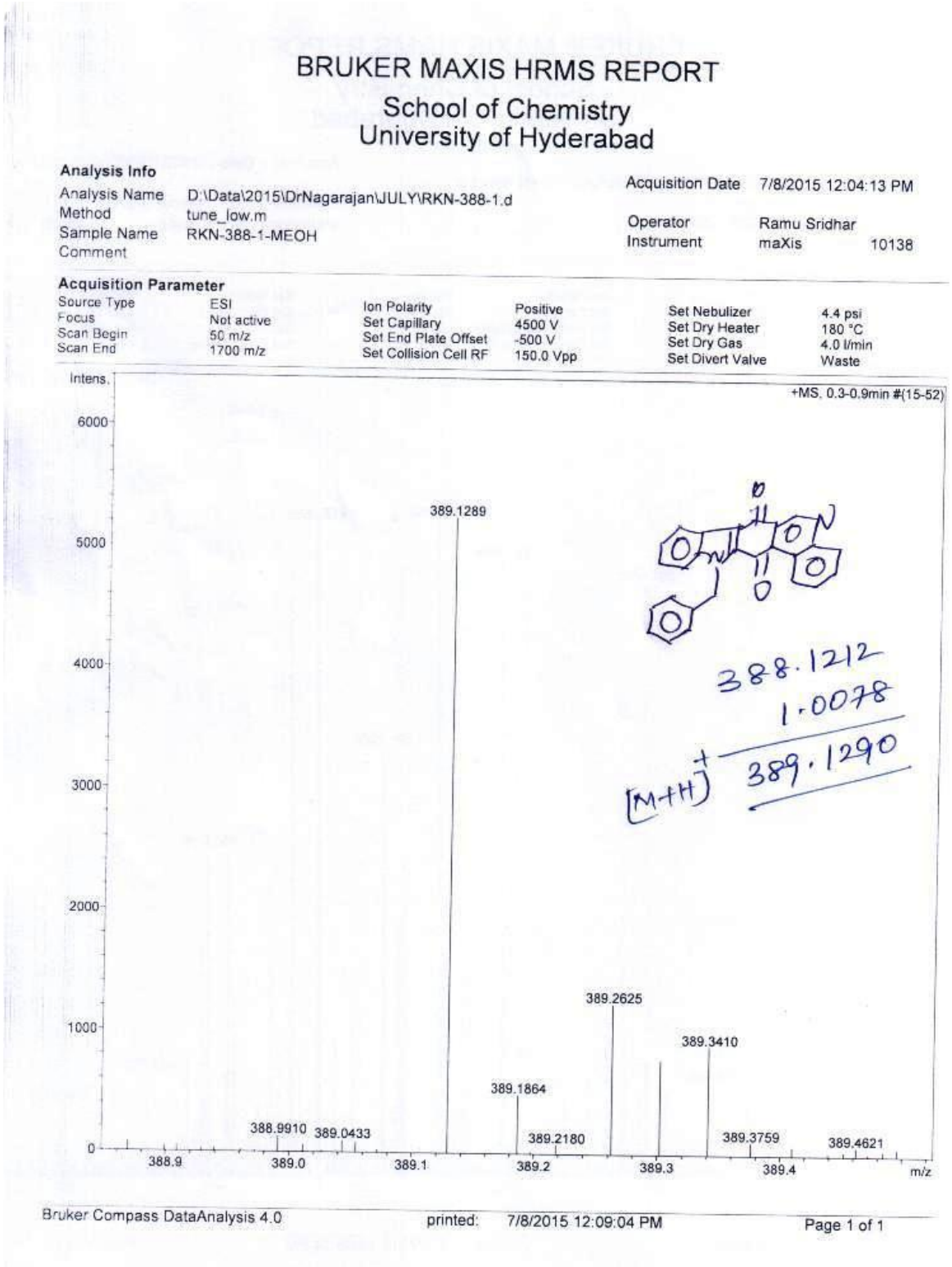
HRMS of 8-(2-chlorophenyl)phenanthridine-7,10-dione (7)



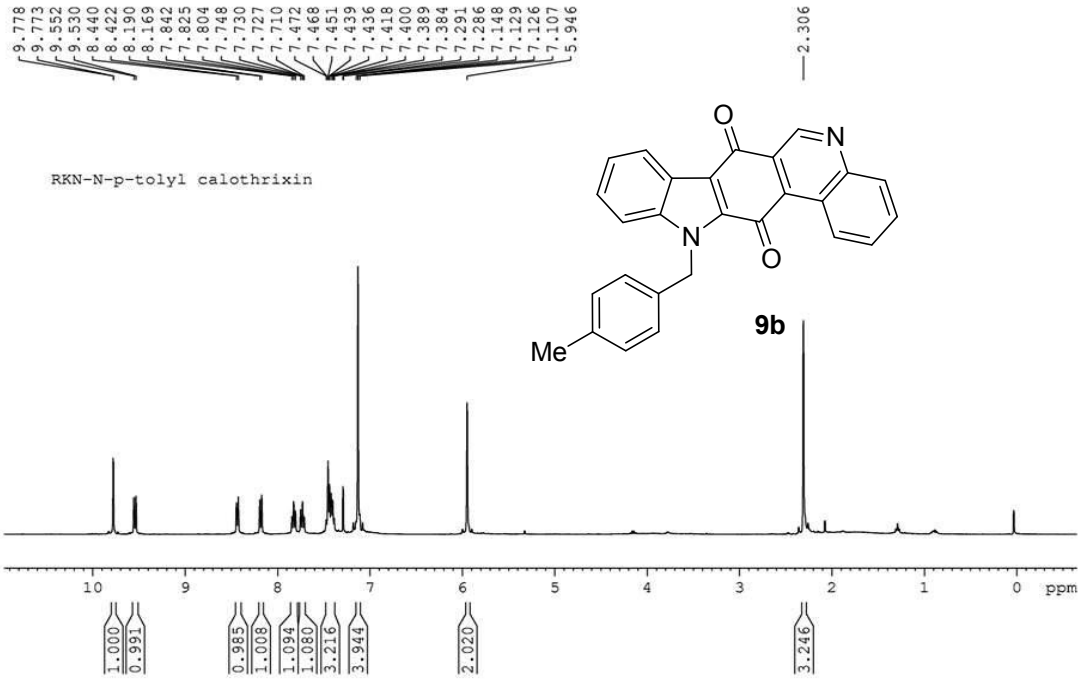
^{1}H and ^{13}C NMR of 12-benzyl-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9a)

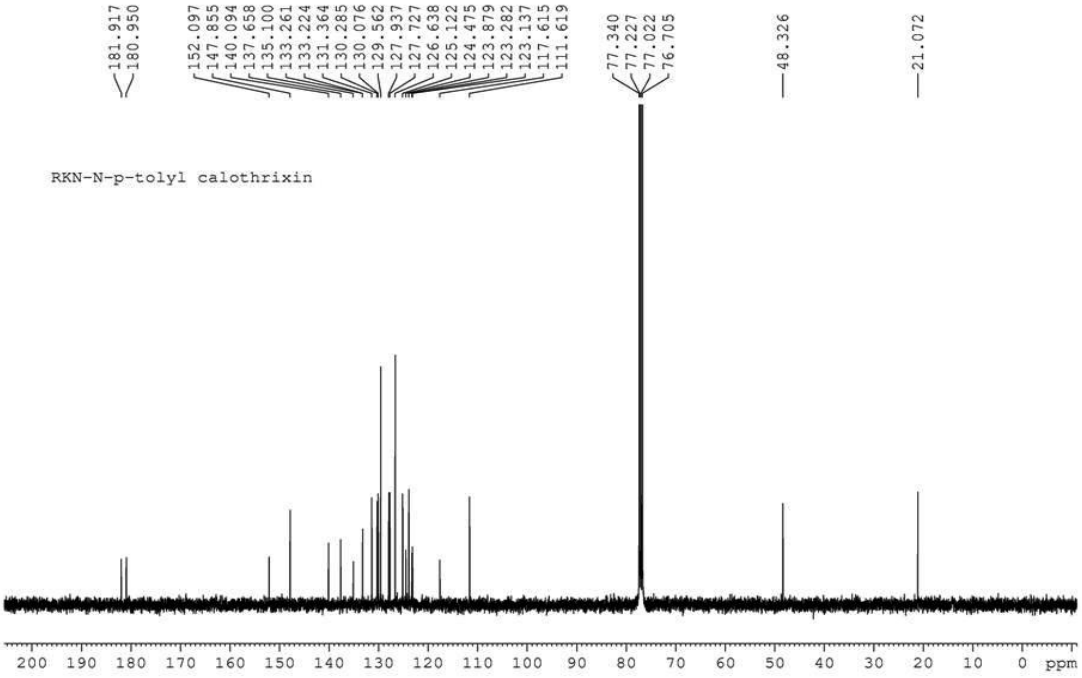


HRMS of 12-benzyl-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9a)



^{1}H and ^{13}C NMR of 12-(4-methylbenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9b)





HRMS of 12-(4-methylbenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9b)

BRUKER MAXIS HRMS REPORT

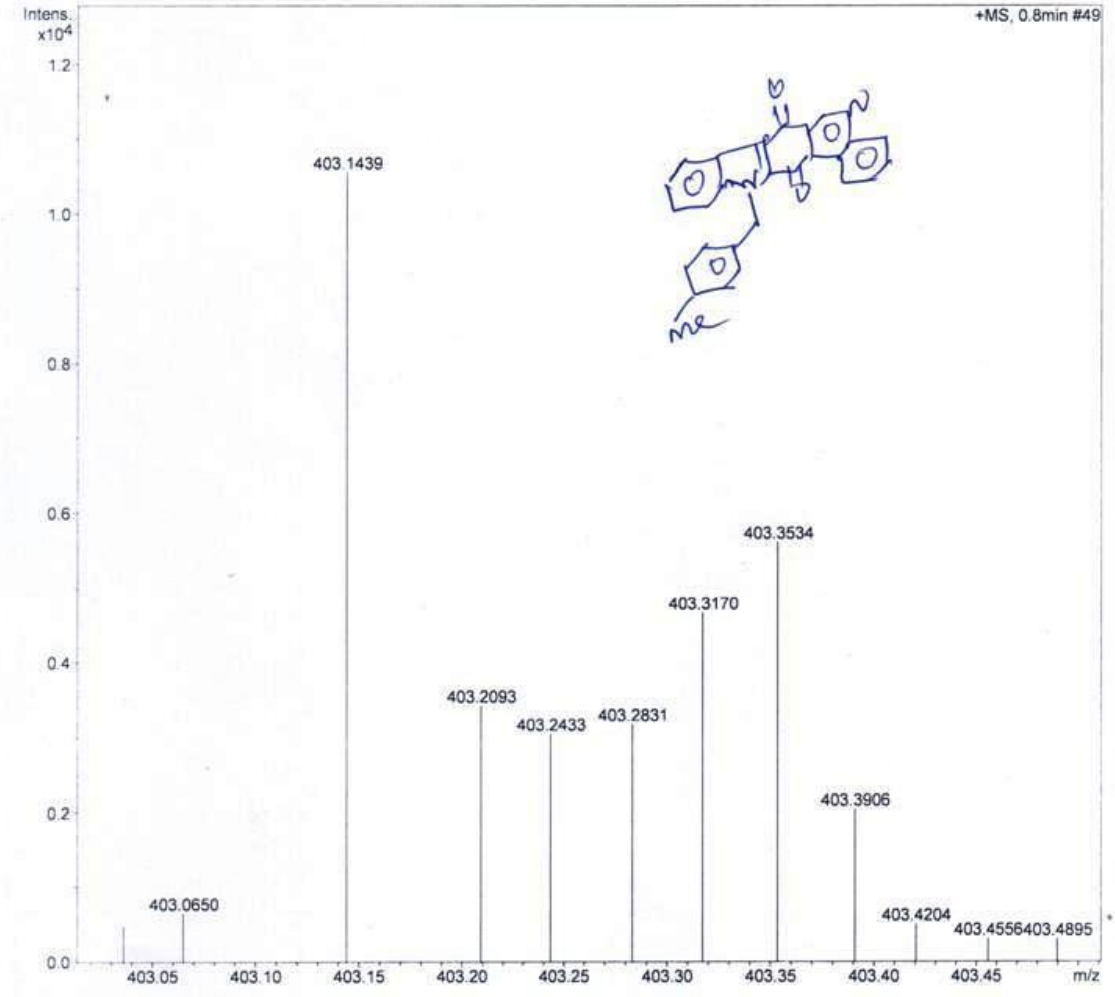
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-402R2.d	Acquisition Date	6/5/2015 11:34:44 AM
Method	tune_low_Pos.m	Operator	Ramu Sridhar
Sample Name	RKN-402-MEOH	Instrument	maXis 10138
Comment			

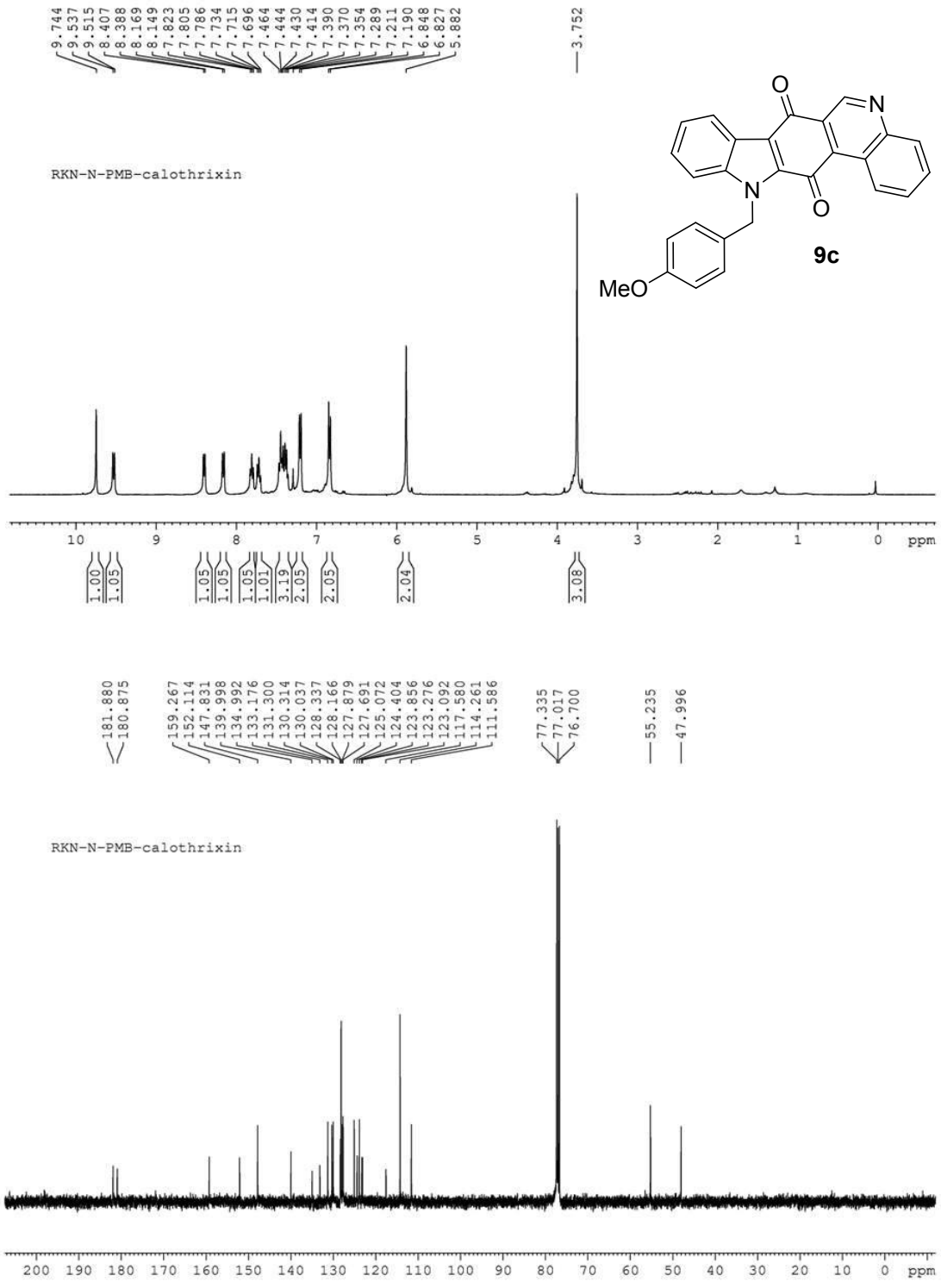
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.4 psi
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 6/5/2015 3:19:04 PM Page 1 of 1

^{1}H and ^{13}C NMR of 12-(4-methoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9c)



HRMS of 12-(4-methoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9c)

BRUKER MAXIS HRMS REPORT

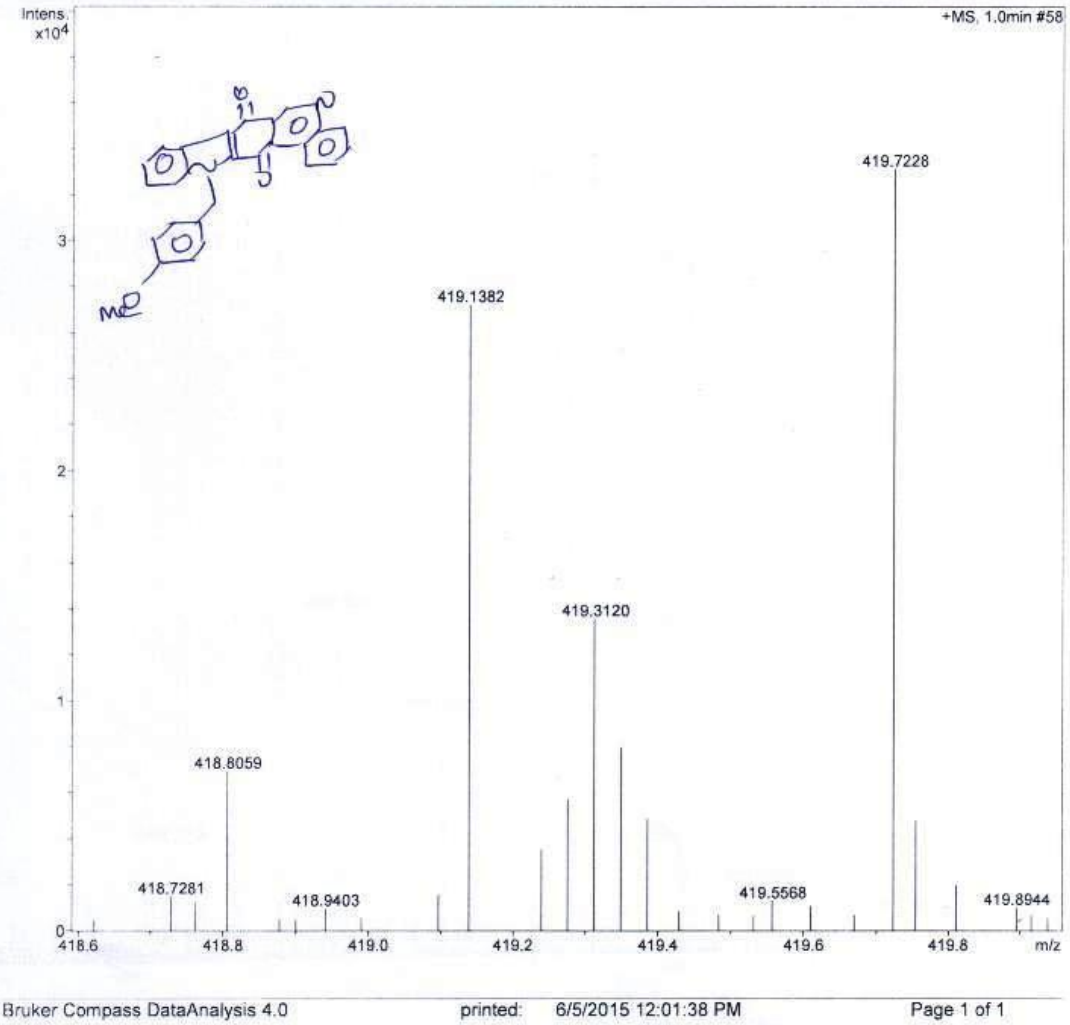
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-418R1.d	Acquisition Date	6/5/2015 11:54:34 AM
Method	tune_low_Pos.m	Operator	Ramu Sridhar
Sample Name	RKN-418-MEOH	Instrument	maXis 10138
Comment			

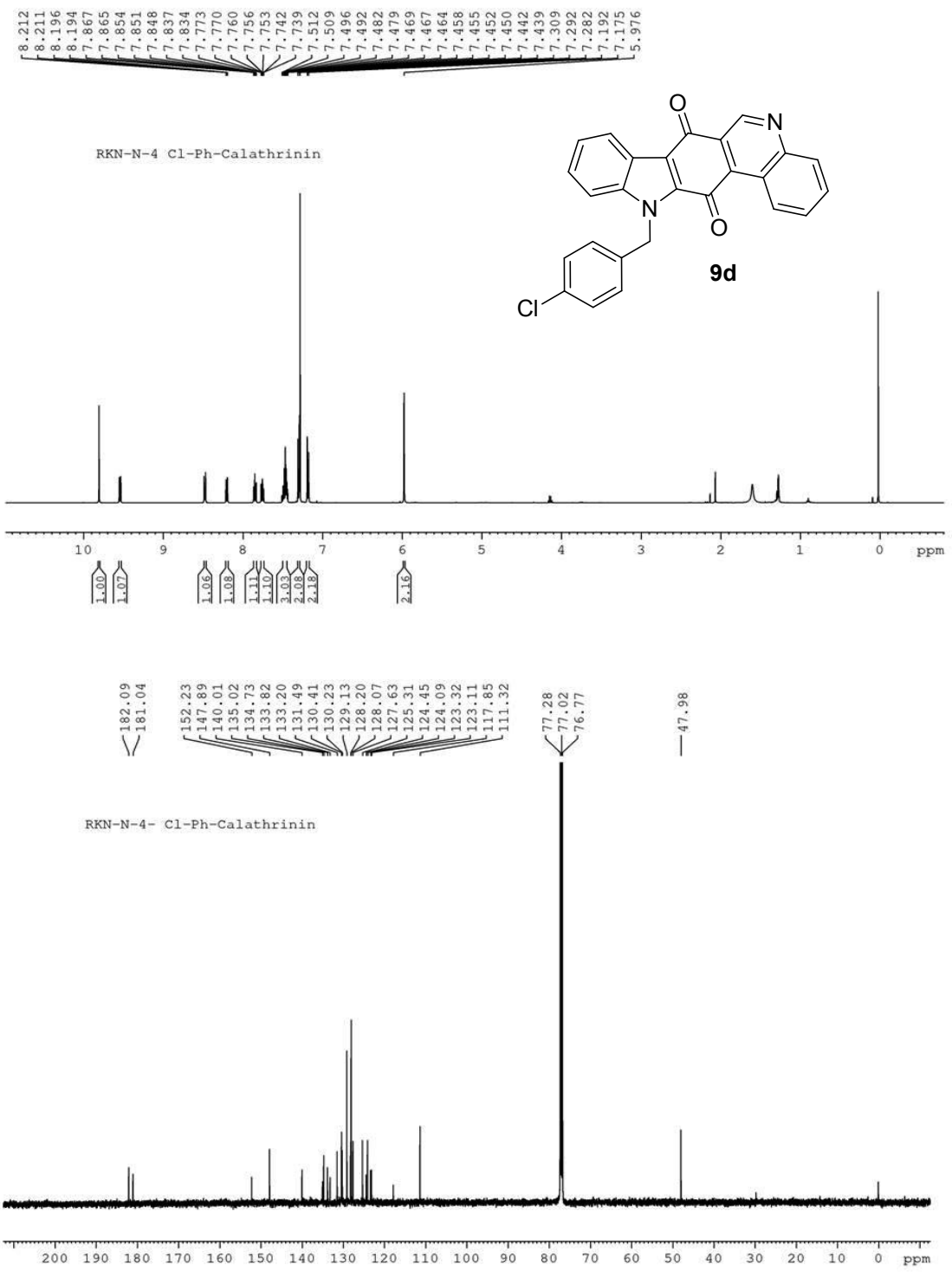
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.4 psi
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 6/5/2015 12:01:38 PM Page 1 of 1

^{1}H and ^{13}C NMR of 12-(4-chlorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9d)



HRMS of 12-(4-chlorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9d)

BRUKER MAXIS HRMS REPORT

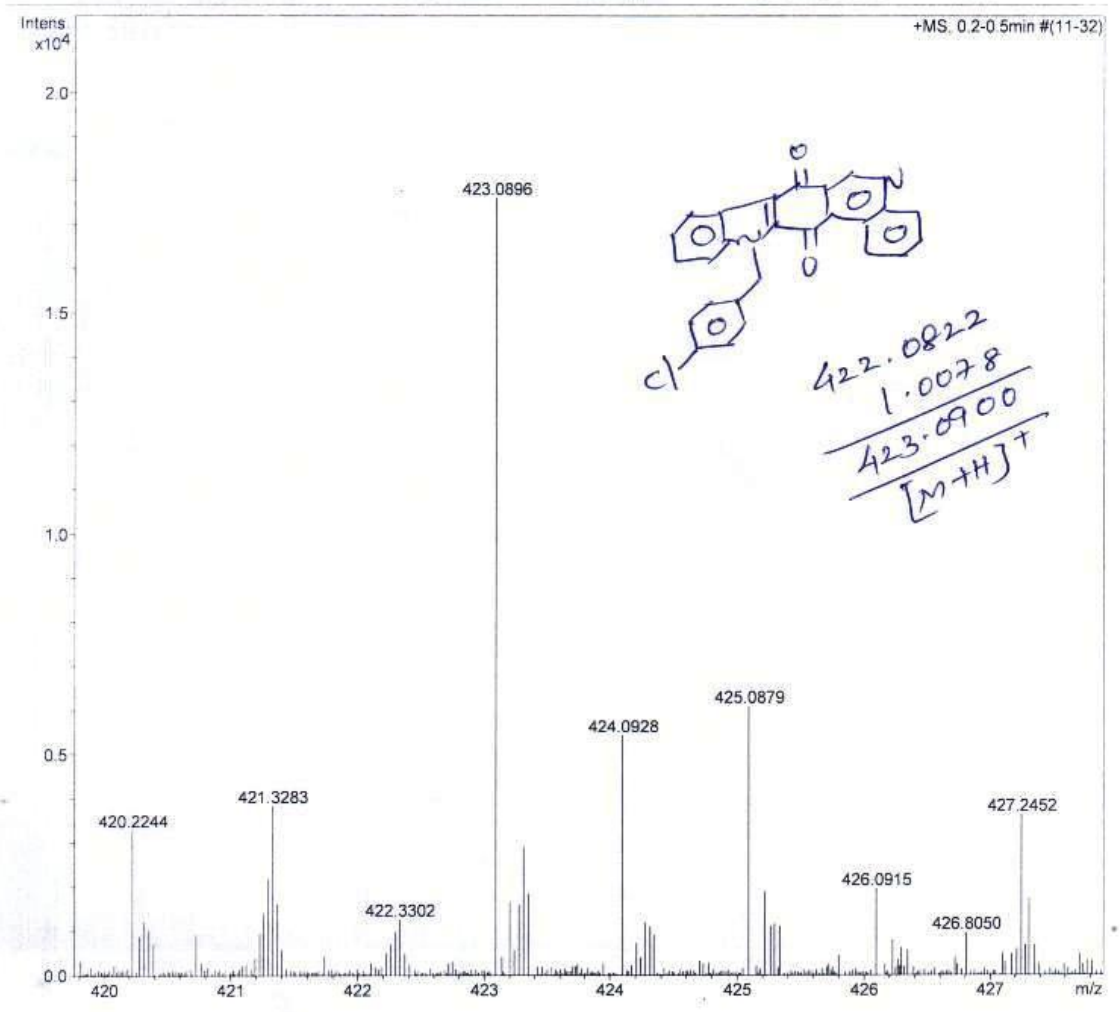
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-422.d	Acquisition Date	6/30/2015 12:49:14 PM
Method	tune_low.m	Operator	Ramu Sridhar
Sample Name	RKN-422-MEOH	Instrument	maXis 10138
Comment			

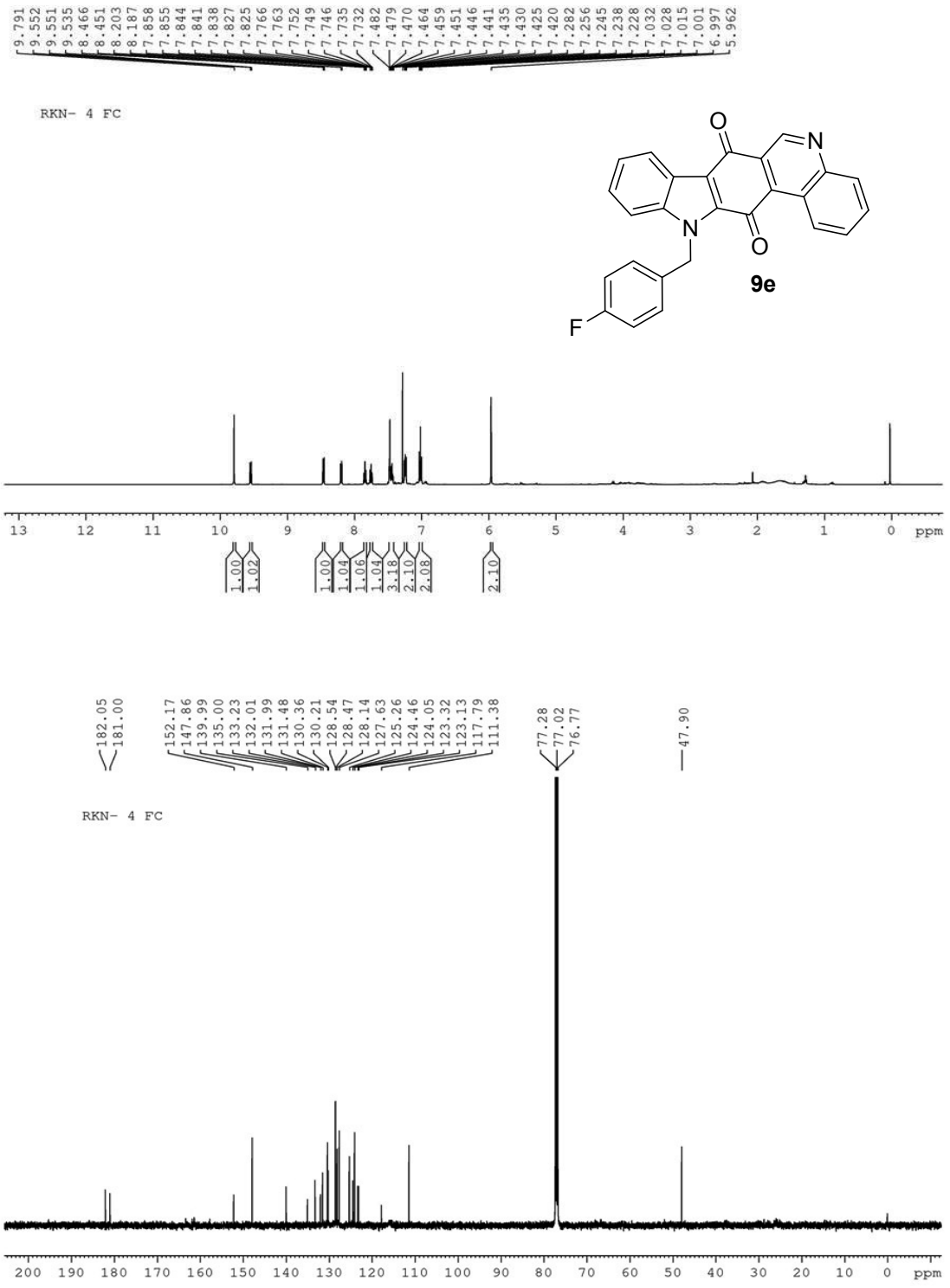
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	6.0 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 6/30/2015 12:53:23 PM Page 1 of 1

^{1}H and ^{13}C NMR of 12-(4-fluorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9e)



HRMS of 12-(4-fluorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9e)

BRUKER MAXIS HRMS REPORT

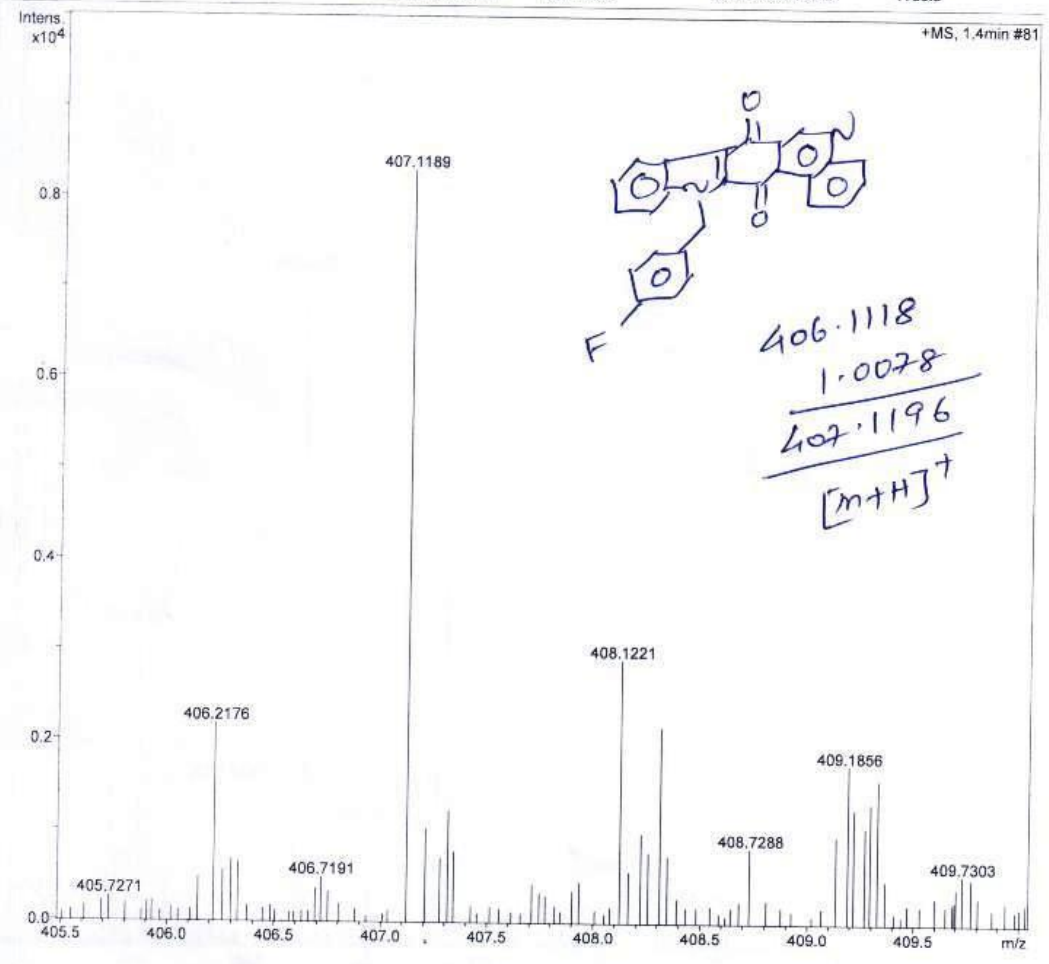
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-406R2.d	Acquisition Date	6/30/2015 12:27:30 PM
Method	tune_low.m	Operator	Ramu Sridhar
Sample Name	RKN-406-MEOH	Instrument	maXis 10138
Comment			

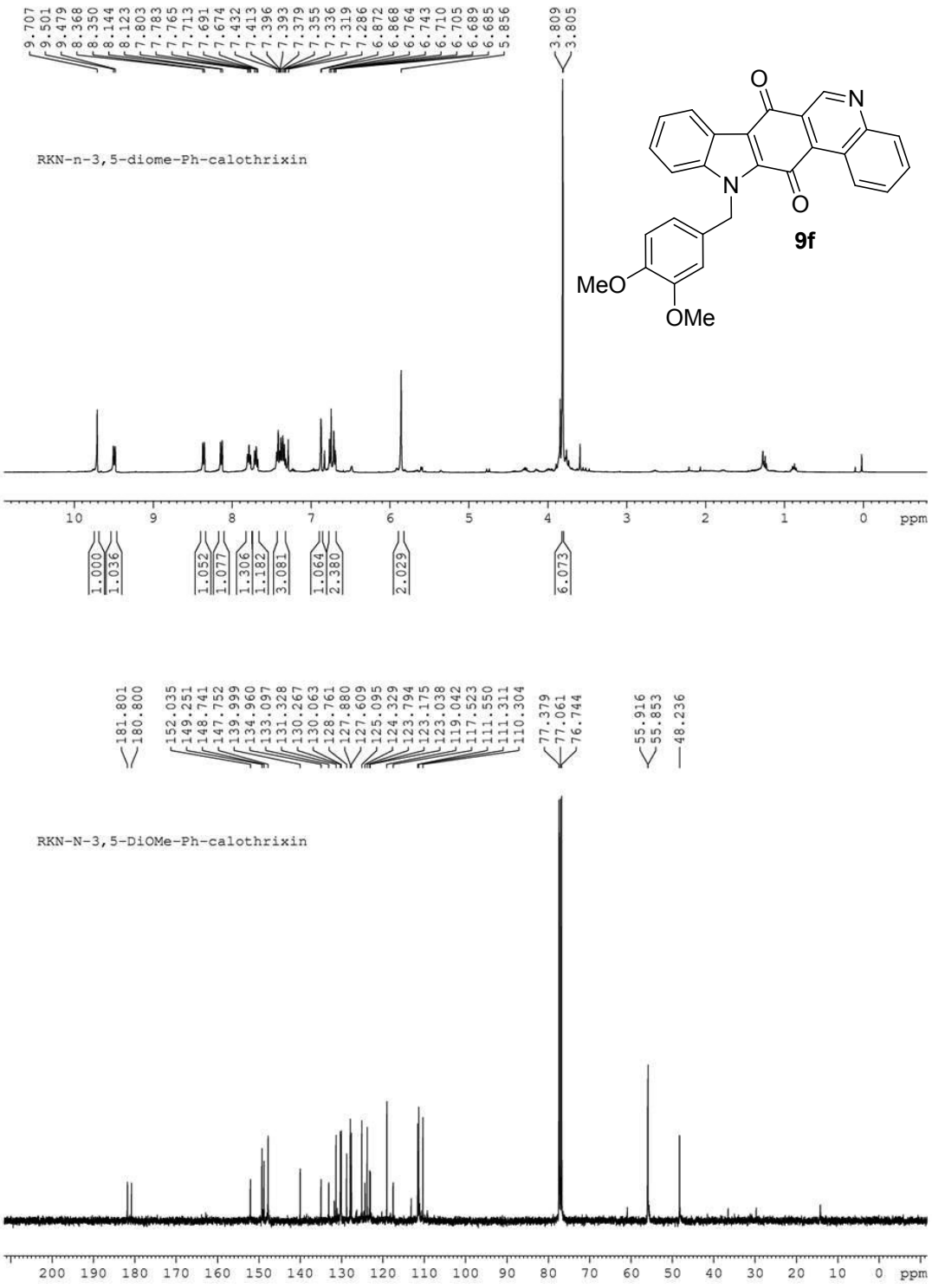
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	5.0 psi
Focus	Not active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

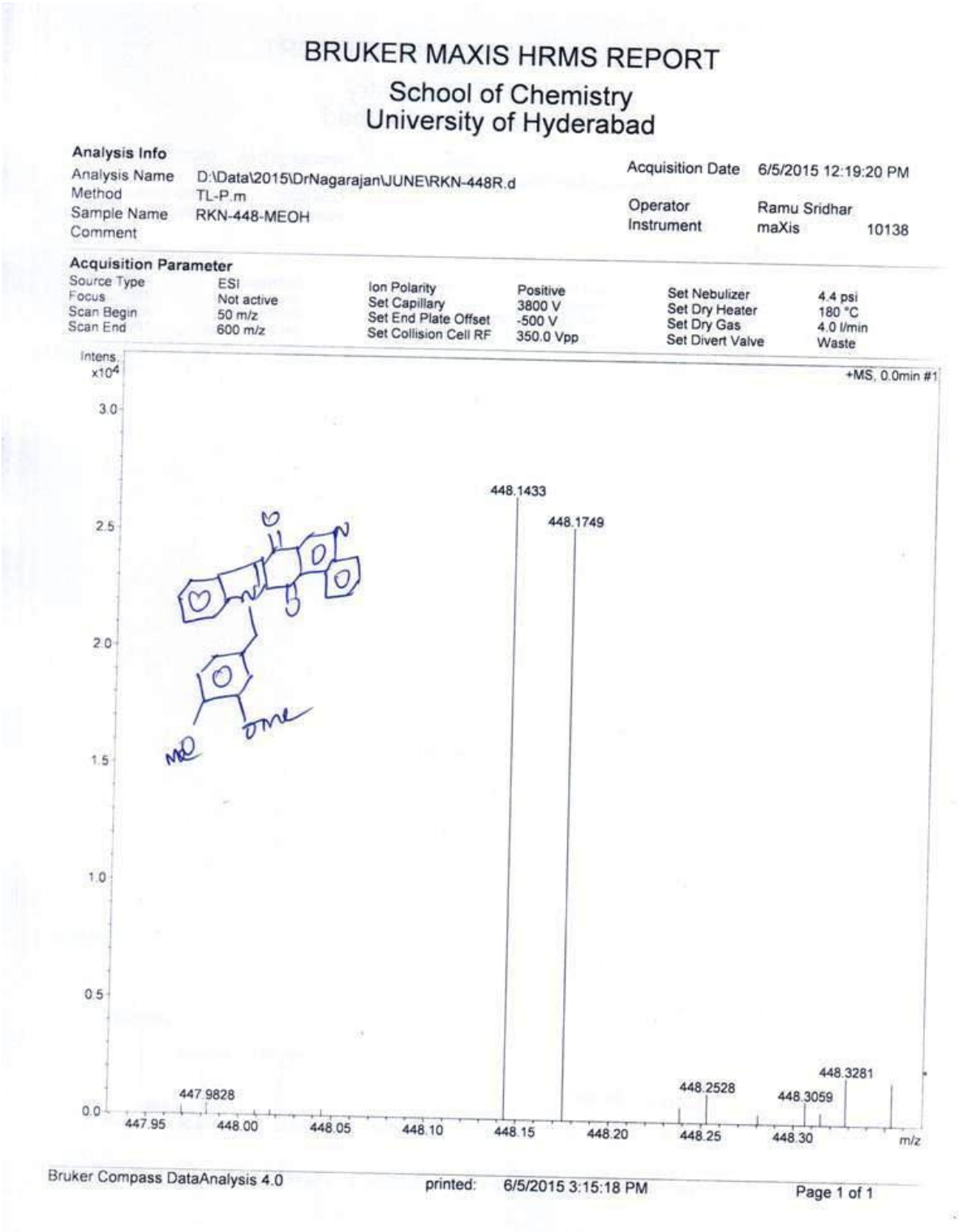


Bruker Compass DataAnalysis 4.0 printed: 6/30/2015 12:33:08 PM Page 1 of 1

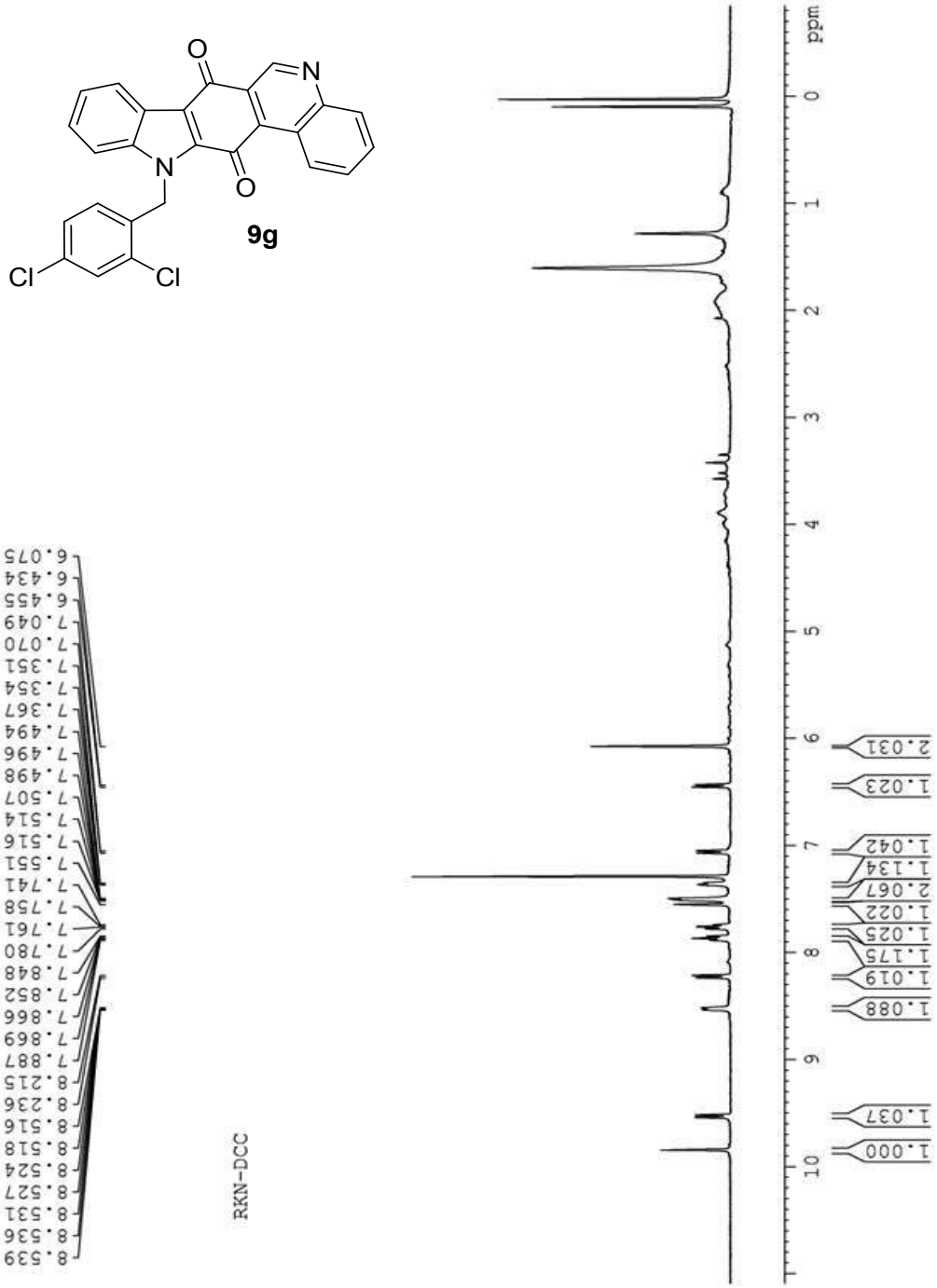
^{1}H and ^{13}C NMR of 12-(3,4-dimethoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9f)



HRMS of 12-(3,4-dimethoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9f)



^{1}H and ^{13}C NMR of 12-(2,4-dichlorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9g)



HRMS of 12-(2,4-dichlorobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9g)

BRUKER MAXIS HRMS REPORT

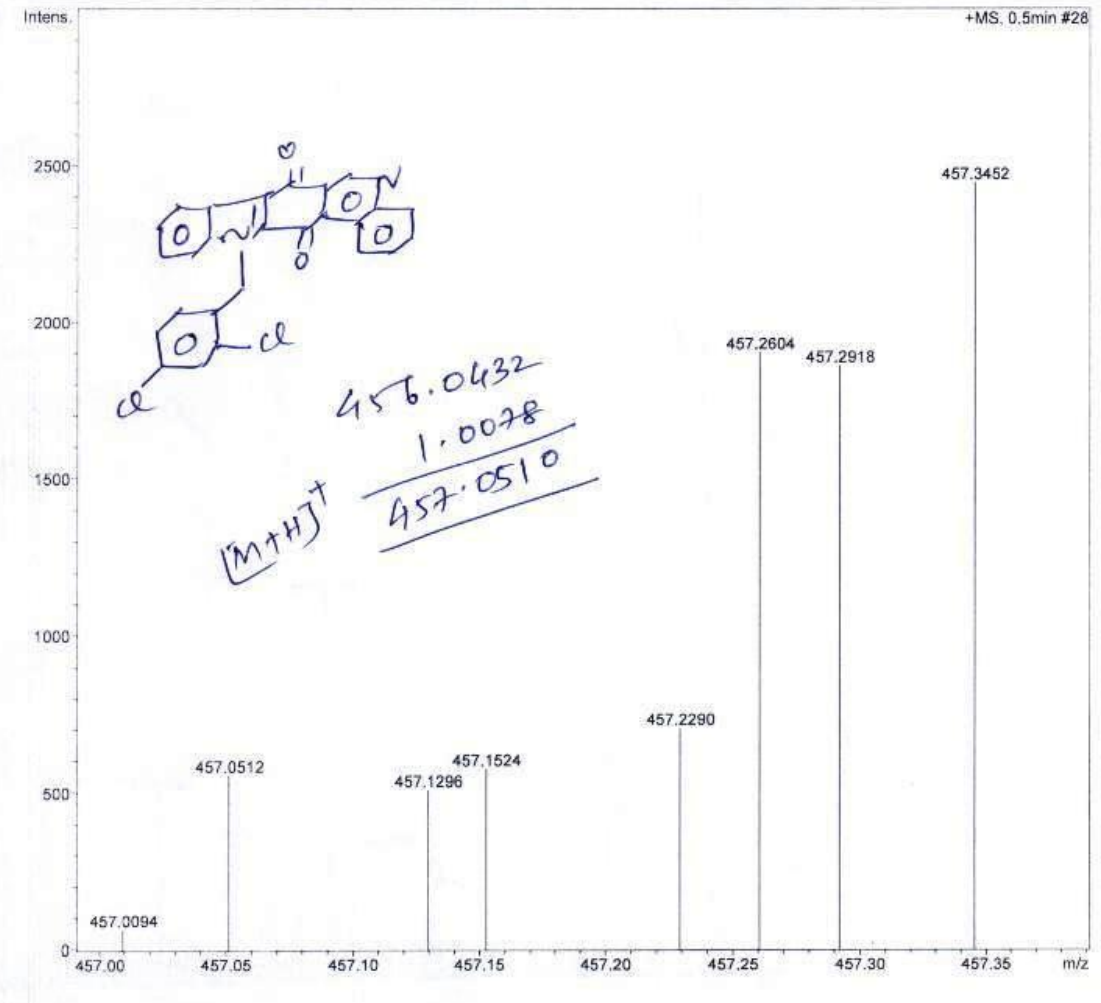
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-456I.d	Acquisition Date	6/30/2015 1:07:58 PM
Method	tune_low.m	Operator	Ramu Sridhar
Sample Name	RKN-456-MEOH	Instrument	maXis 10138
Comment			

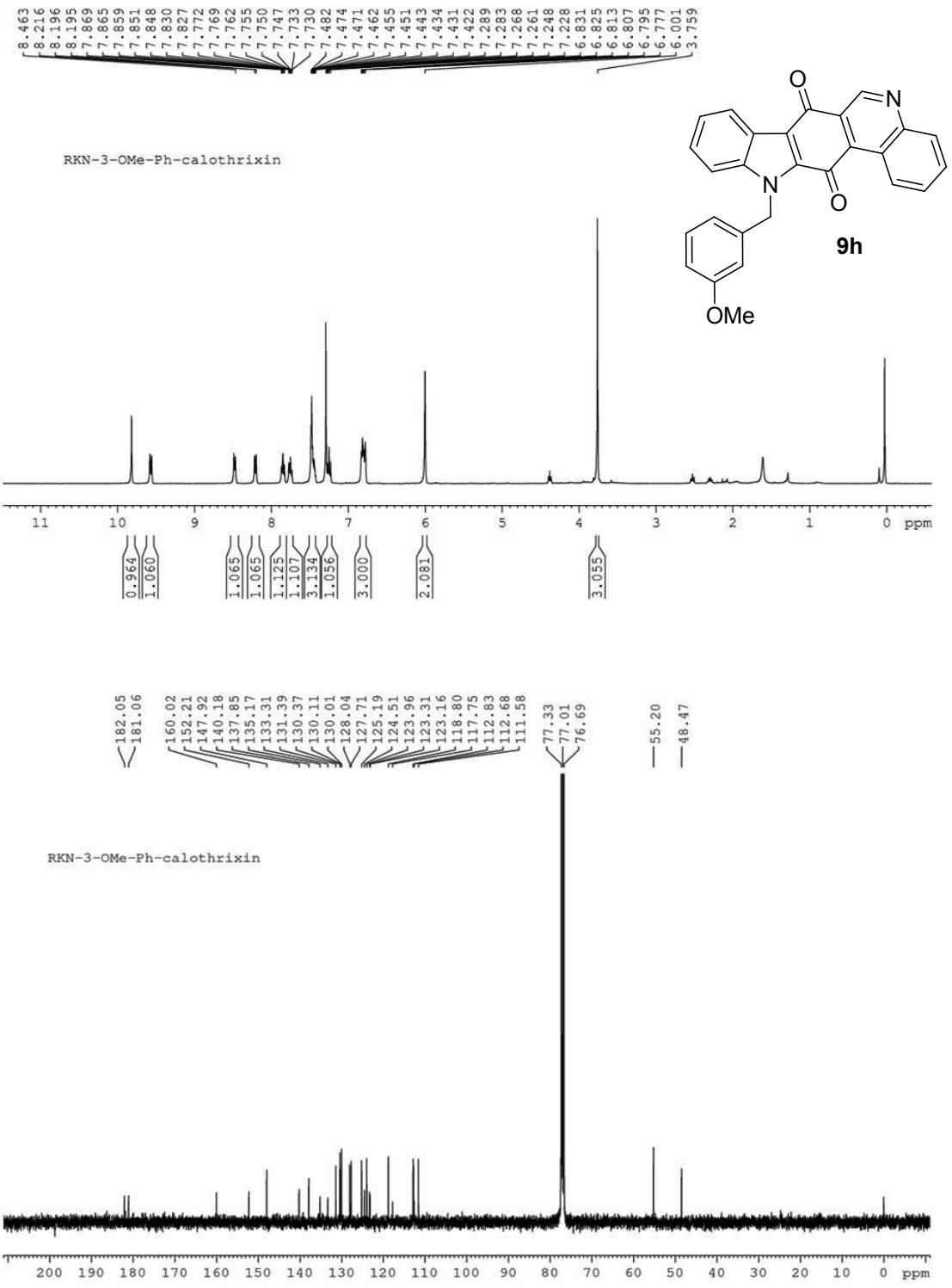
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.0 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 6/30/2015 1:12:00 PM Page 1 of 1

^{1}H and ^{13}C NMR of 12-(3-methoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9h)



HRMS of 12-(3-methoxybenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9h)

BRUKER MAXIS HRMS REPORT

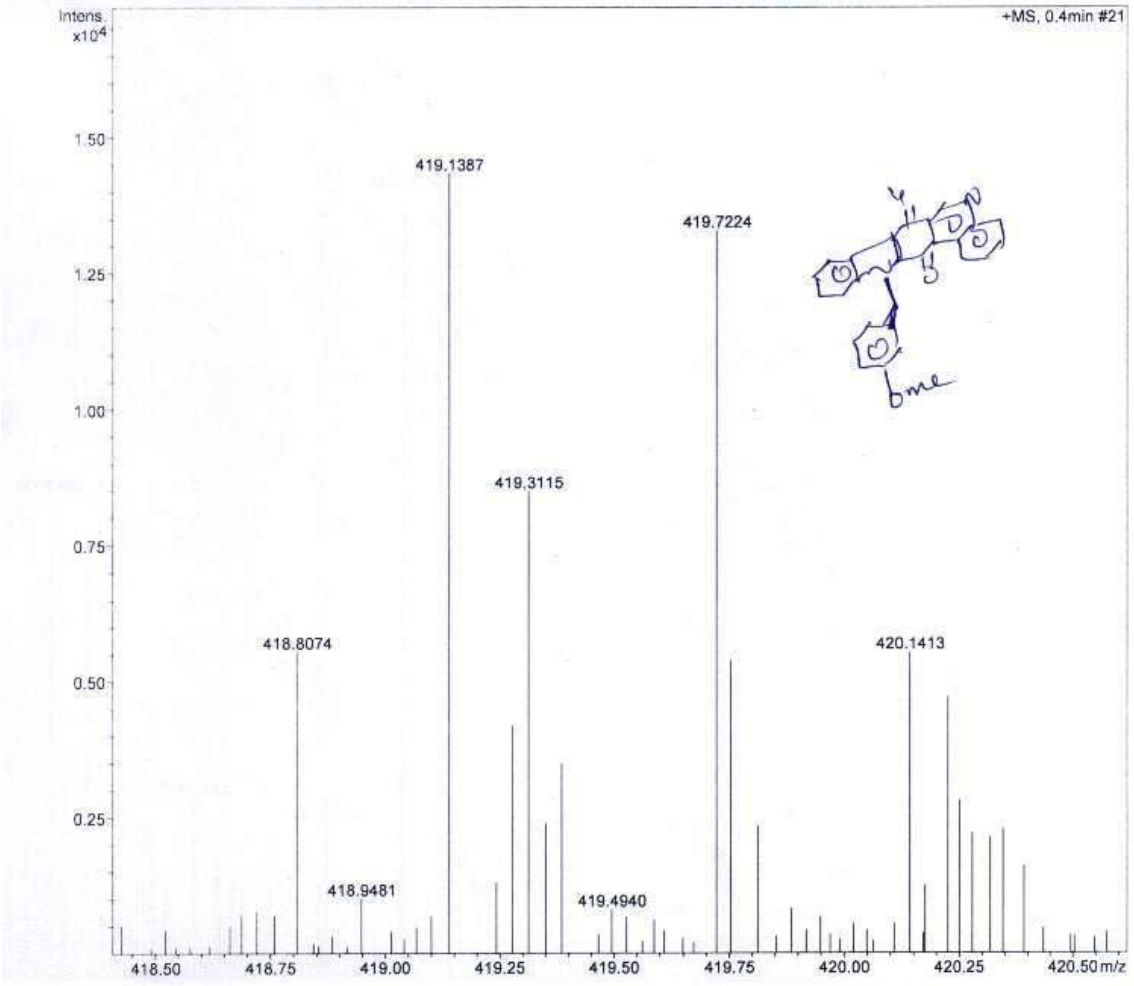
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-418-3.d	Acquisition Date	6/5/2015 11:59:43 AM
Method	tune_low_Pos.m	Operator	Ramu Sridhar
Sample Name	RKN-418-3-MEOH	Instrument	maXis 10138
Comment			

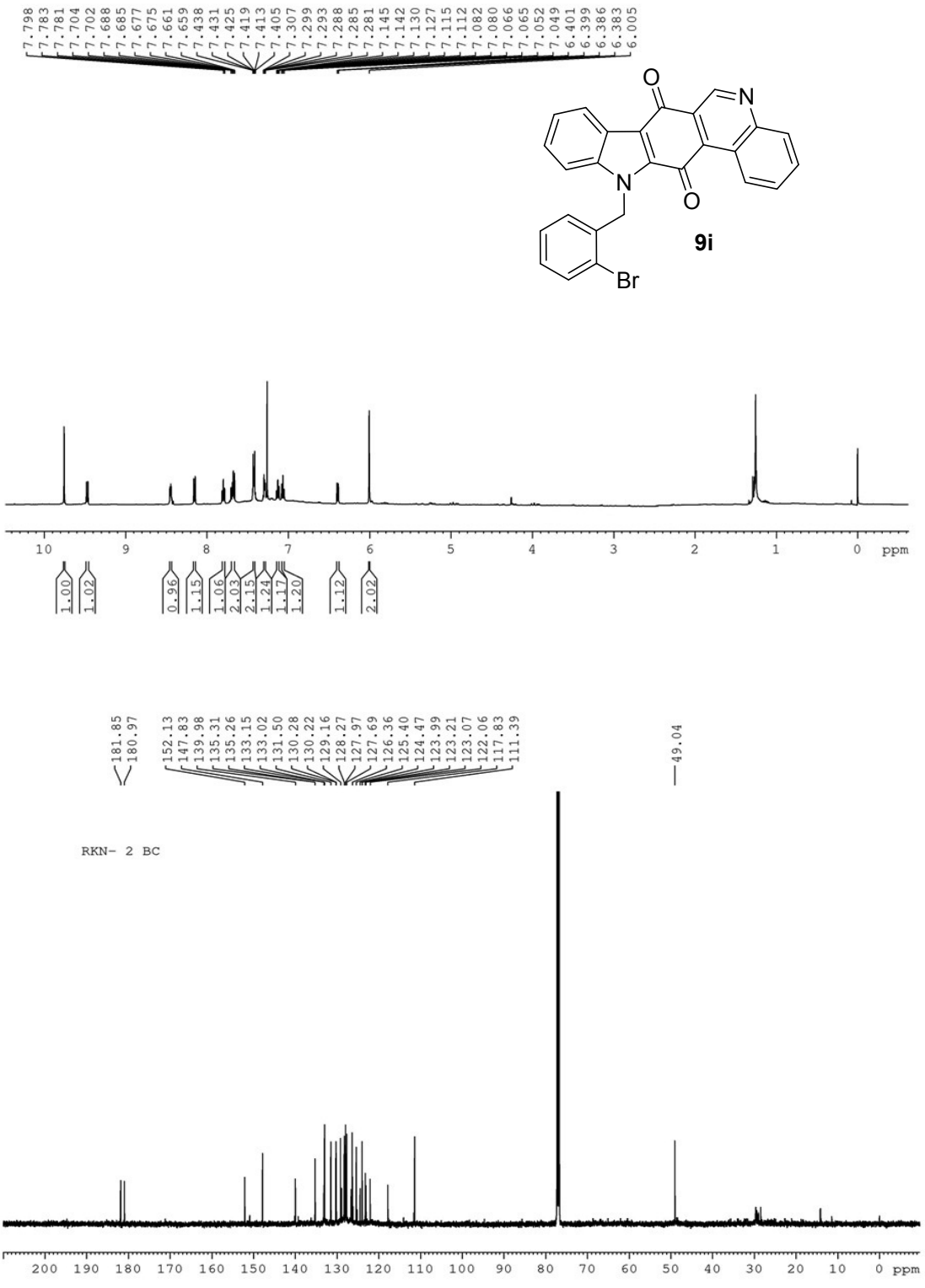
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.4 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	350.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 6/5/2015 12:03:57 PM Page 1 of 1

^{1}H and ^{13}C NMR of 12-(2-bromobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9i)



HRMS of 12-(2-bromobenzyl)-7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (9i)

BRUKER MAXIS HRMS REPORT

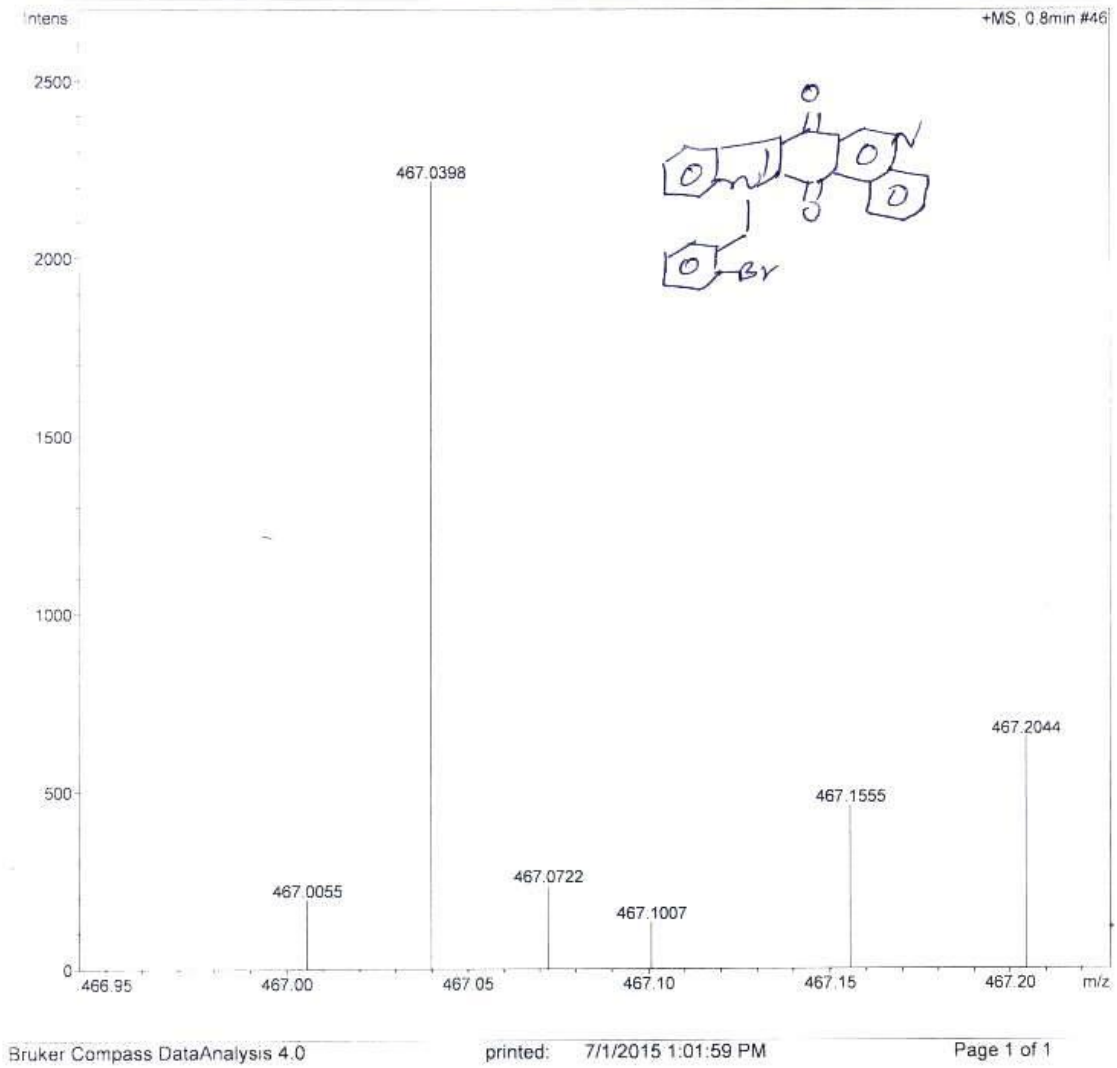
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JUNE\RKN-466.d	Acquisition Date	6/30/2015 1:21:30 PM
Method	tune_low.m	Operator	Ramu Sridhar
Sample Name	RKN-466-MEOH	Instrument	maXis 10138
Comment			

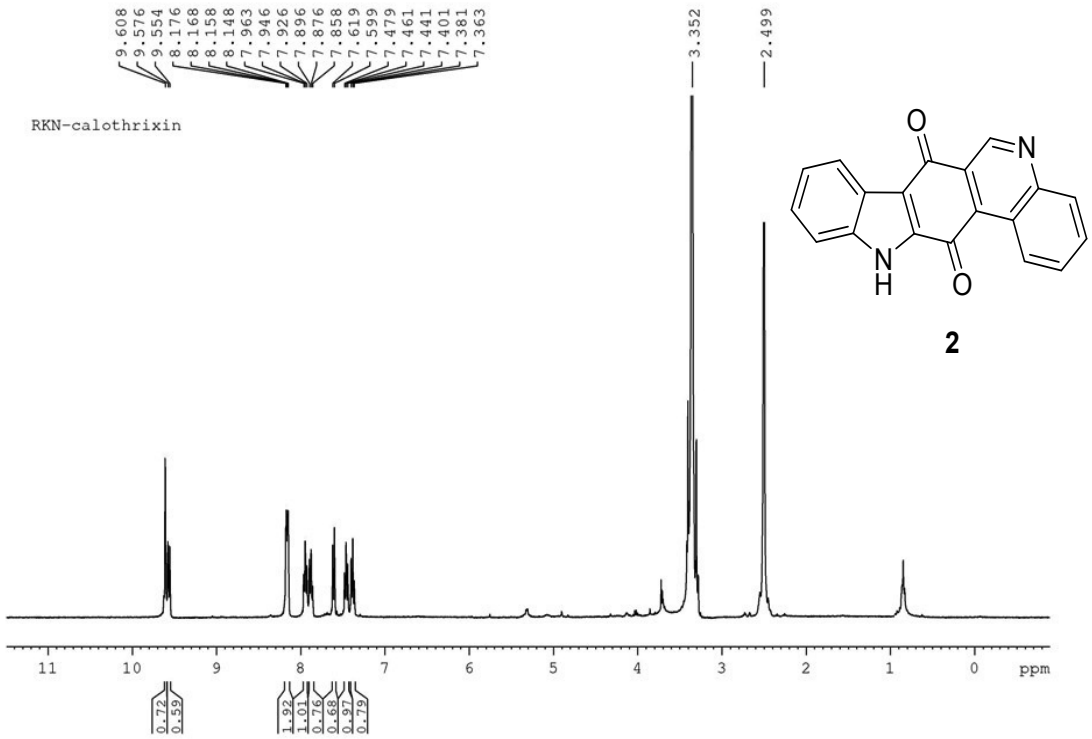
Acquisition Parameter

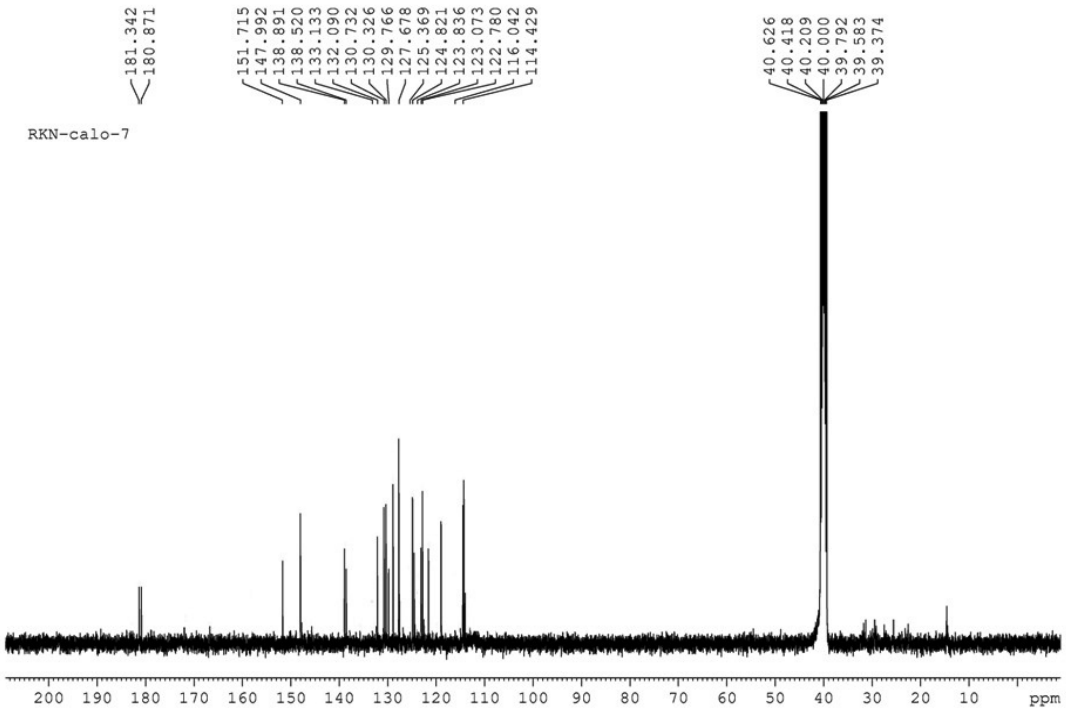
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	4.0 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 7/1/2015 1:01:59 PM Page 1 of 1

^{1}H and ^{13}C NMR of 7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (2)


9.608
9.576
9.554
8.176
8.168
8.158
8.148
7.963
7.946
7.926
7.896
7.876
7.858
7.619
7.599
7.479
7.461
7.441
7.401
7.381
7.363
3.352
2.499
RKN-calothrixin
O
N
N
H
O
2
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.72
0.59
1.92
1.01
0.76
0.68
0.97
0.79


181.342
180.871
151.715
147.992
138.891
138.520
133.133
132.090
130.732
130.326
129.766
127.678
125.369
124.821
123.836
123.073
122.780
116.042
114.429
40.626
40.418
40.209
40.000
39.792
39.583
39.374
RKN-calo-7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

HRMS of 7*H*-indolo[3,2-*j*]phenanthridine-7,13(12*H*)-dione (2)

BRUKER MAXIS HRMS REPORT

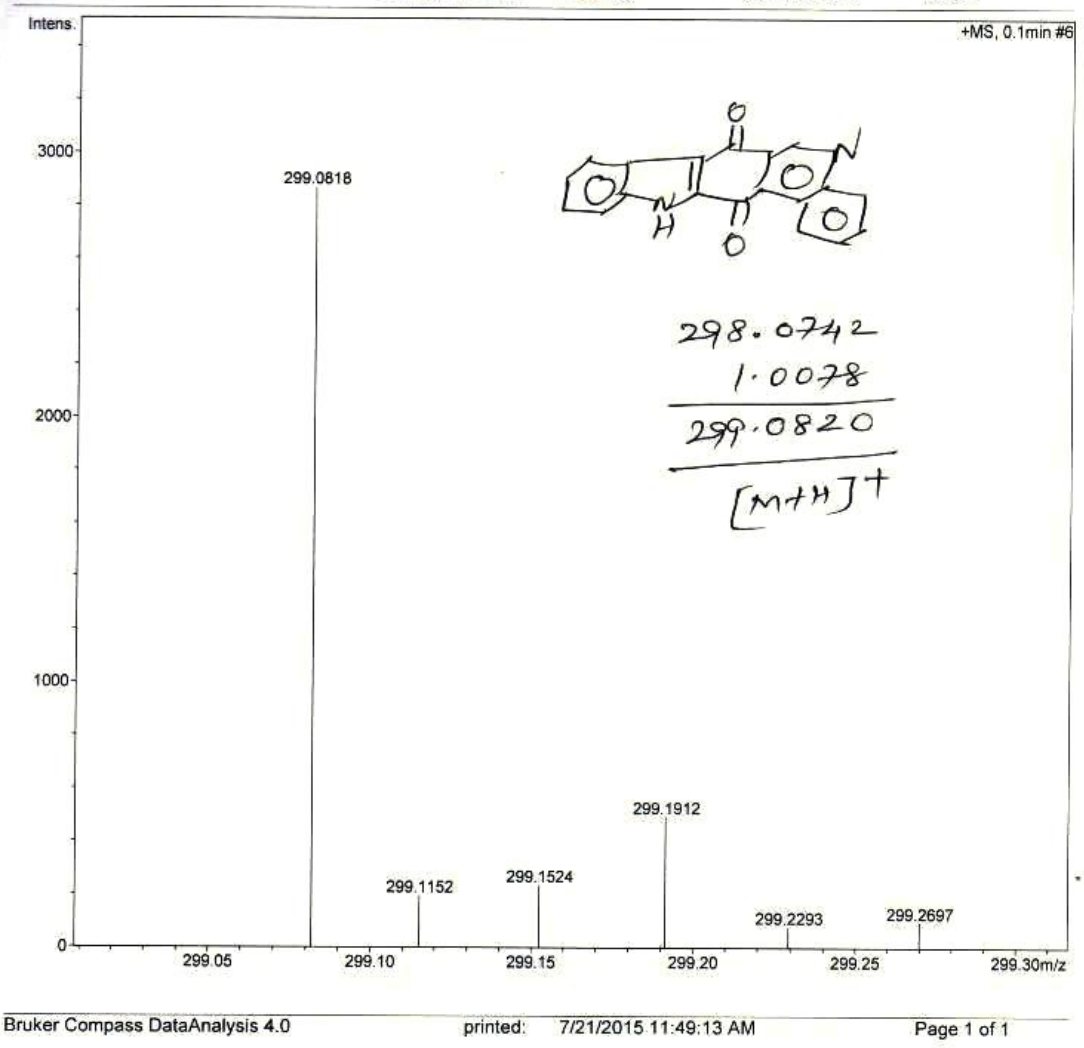
School of Chemistry
University of Hyderabad

Analysis Info

Analysis Name	D:\Data\2015\DrNagarajan\JULY\RKN-298-1R2.d	Acquisition Date	7/21/2015 11:44:23 AM
Method	tune_low.m	Operator	Ramu Sridhar
Sample Name	RKN-298-1-MEOH	Instrument	maXis 10138
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	6.0 psi
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	250.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 7/21/2015 11:49:13 AM Page 1 of 1