Supporting Information

A Transition-Metal-Free, Oxidative Coupling of Arylmethylamines with Indoles: A Simple, Environmentally Benign Approach to Synthesis of 3,3'-Bis(indolyl)methanes

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Experimental Section

1.1 General Information

All reactions were carried out in oven-dried glassware using dry solvents under molecular oxygen atmosphere unless stated otherwise. Iron salts were purchased from Sigma-Aldrich and used as received. All other chemicals were used as received from commercial sources. Reactions were monitored by TLC on 0.25-mm Merck silica gel plates (60 F_{254}) using UV light for visualization. Column chromatography purification was performed using silica gel 100-200 mesh. Melting points were measured on a Büchi melting point apparatus and were uncorrected. IR spectra were recorded on a Spectrum FT-IR spectrophotometer. NMR spectra were recorded on a spectrometer Brucker 400 MHz (^{1}H at 400 MHz, ^{13}C at 100 MHz), using DMSO-d_6 or

$CDCl_3$ as the solvent with TMS as the internal standard at room temperature. Mass spectra were recorded on a 6530 Accurate-Mass Q-TOF LC/MS using Agilent Technologies.

1.2 General procedure for the synthesis of bis(indolyl)methanes (3)

To the 25 mL round bottom flask were added benzylamine **1** (1.1 mmol), indole **2** (2.0 mmol), AcOH (10 mol %), and dry chlorobenzene (2 mL). The round bottom flask was equipped with an O_2 balloon, and the reaction mixture was stirred at 110 °C until complete consumption of indole **2**, as monitored by TLC. After the reaction was finished, the reaction mixture cooled to room temperature, diluted with CH_2Cl_2 (10 mL), and washed with water (2 x 10 mL). The organic extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography using hexane/ethyl acetate mixture to afford the corresponding bis(indolyl)methane products **3**.

1.3 Characterization data of pure bis(indolyl)methanes products

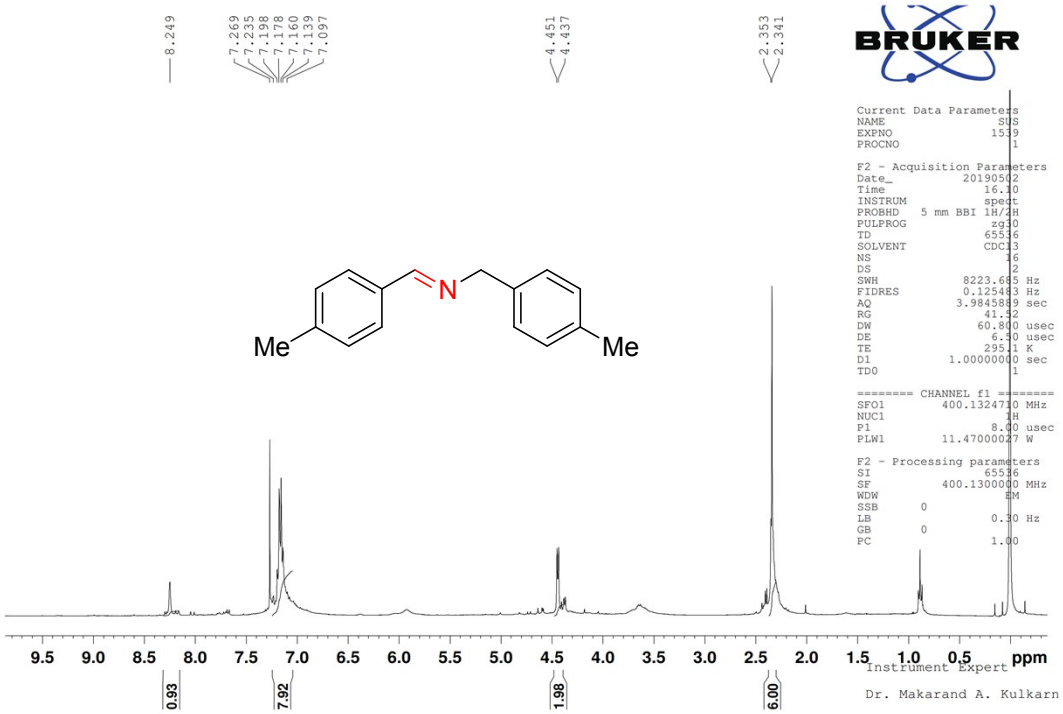
1.3.1 Synthesis of 4-methyl-*N*-(4-methylbenzylidene)benzylamine (4)

To the 25 mL round bottom flask were added 4-methylbenzylamine (**1a**) (350 mg, 2.89 mmol), AcOH (10 mol %), and dry chlorobenzene (2 mL). The round bottom flask was equipped with O_2 balloon, and the reaction mixture was stirred at 110 °C for 3.4 h. The reaction mixture was cooled to room temperature, and adsorbed on basic alumina. It was purified by column chromatography over basic alumina using hexane/ethyl acetate (9:1) mixture as eluent to afford 4-methyl-*N*-(4-methylbenzylidene)benzylamine (**4**) (232 mg, 72 % yield) as pale yellow solid.

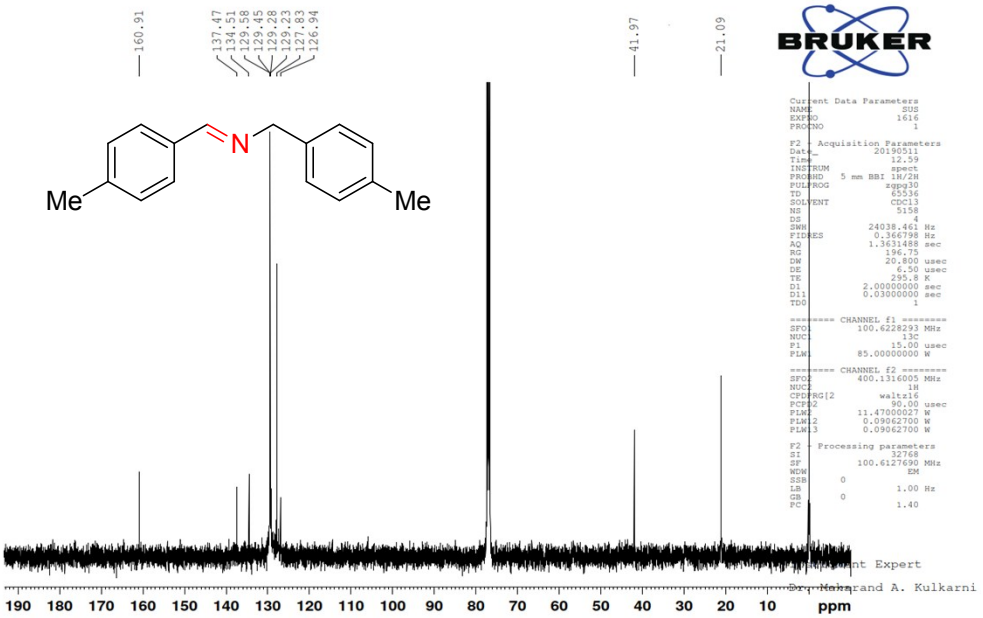
IR (cm^{-1}): 3022, 2923, 2853, 1646, 1514, 1174, 1021, 811, 711; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.07−7.26 (m, 8H, ArH), 4.5 (d, J = 5.6 Hz, 2H), 2.35 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.91, 137.47, 134.51, 129.58, 129.45, 129.28, 129.23, 127.83, 126.94, 41.97, 21.09 ppm; ^{13}C NMR DEPT-135 (100 MHz, $CDCl_3$): 160.93 (=CH, up), 129.58, 129.45, 127.83, 126.94, 41.97 (CH_2, down), 21.09 (2xCH_3, up) ppm.

1.4 Spectral data

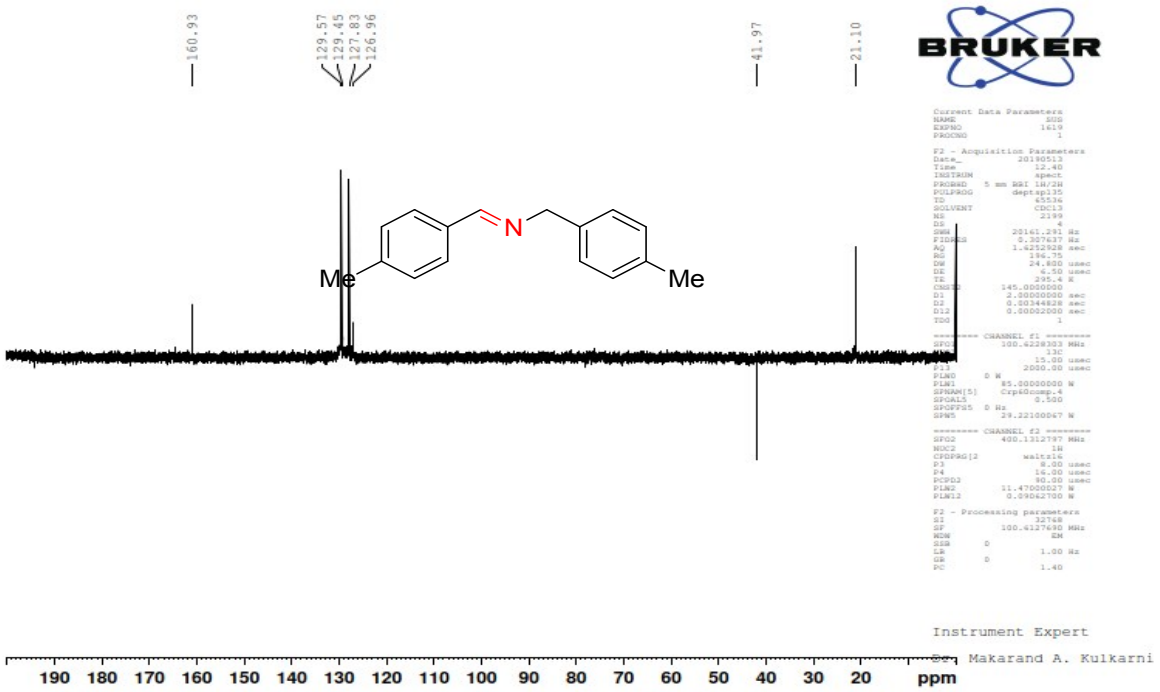
1.4.1 ^{1}H NMR of compound: 4



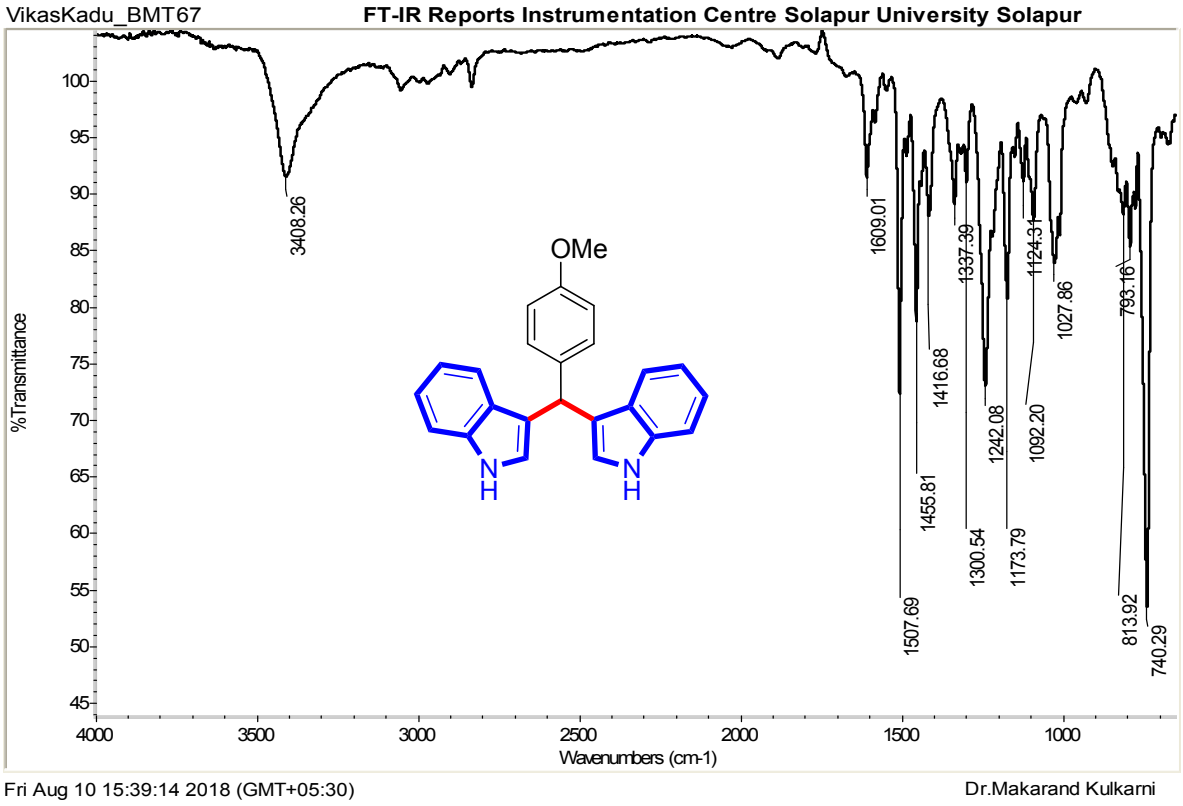
1.4.2 ^{13}C NMR of compound: 4



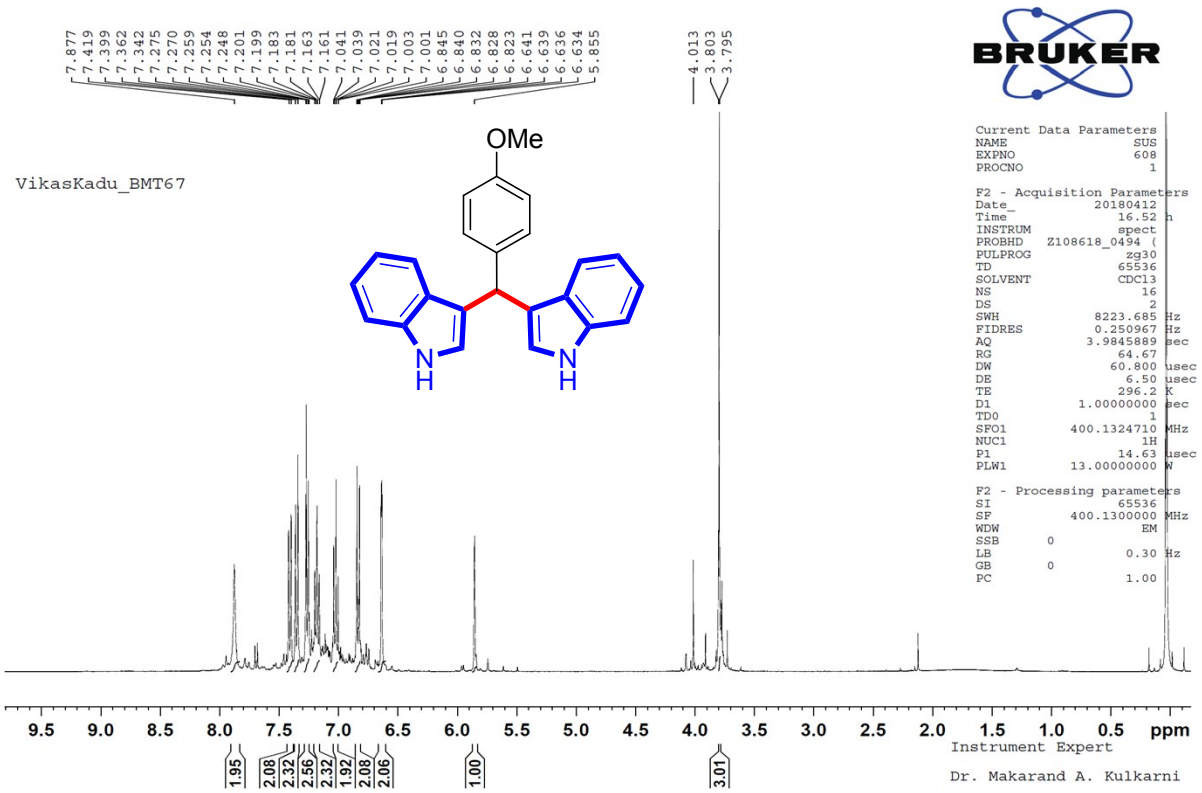
1.4.3 DEPT of compound: 4



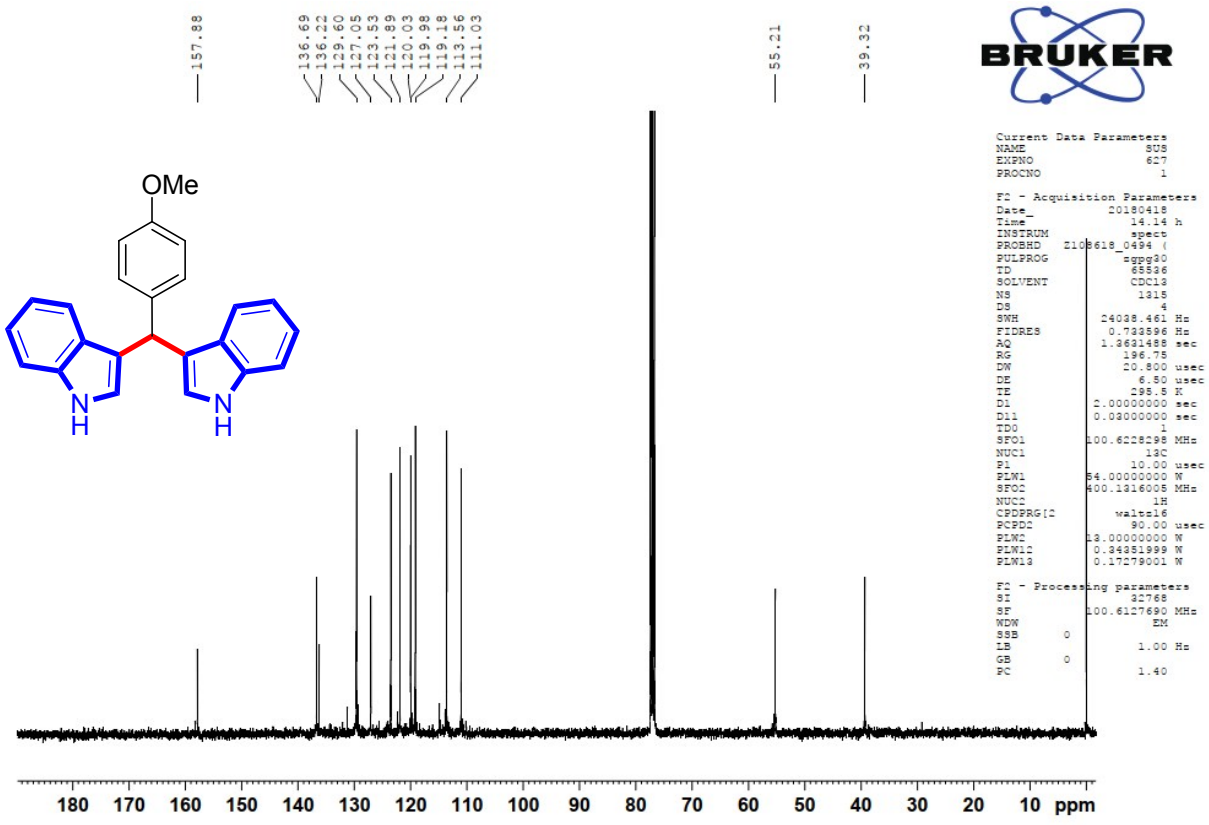
1.4.4 IR of compound: 3ca



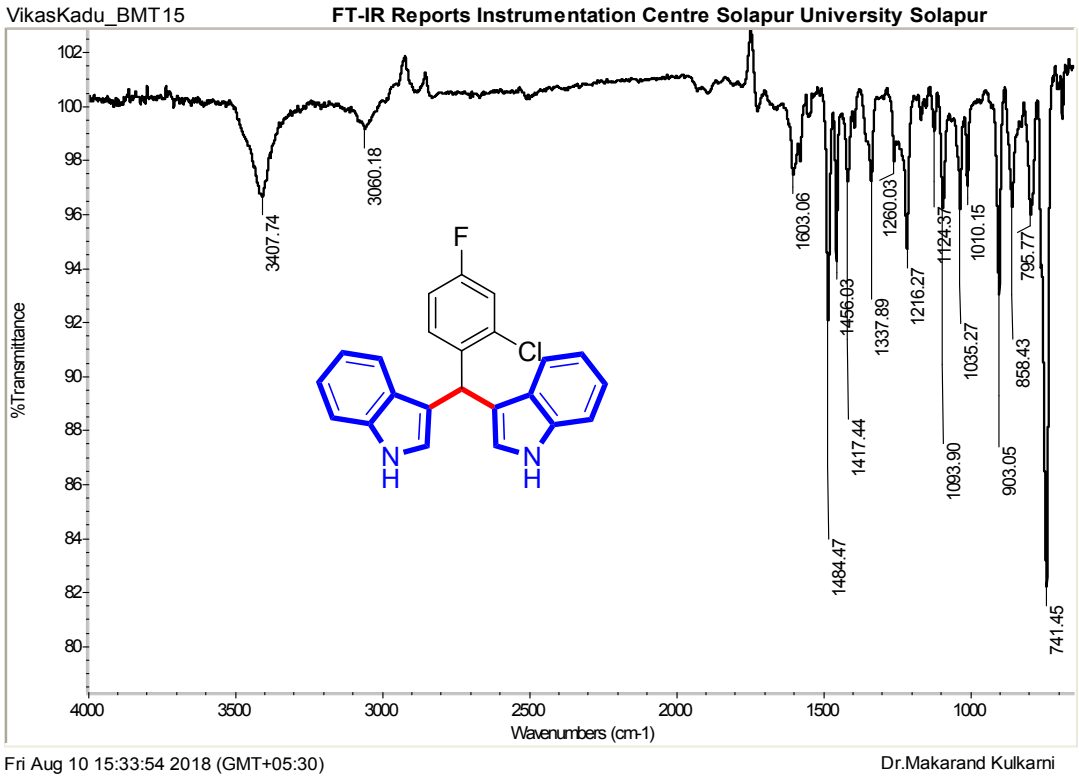
1.4.5 ^{1}H NMR of compound: 3ca



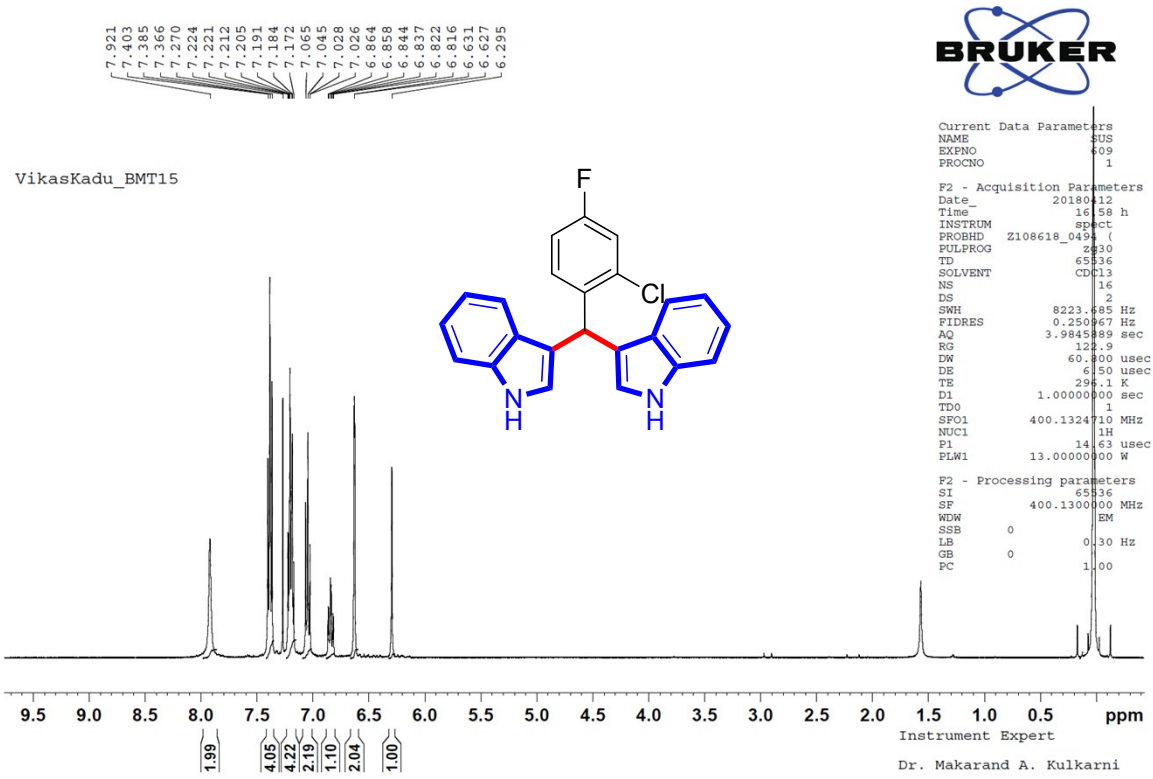
1.4.6 ^{13}C NMR of compound: 3ca



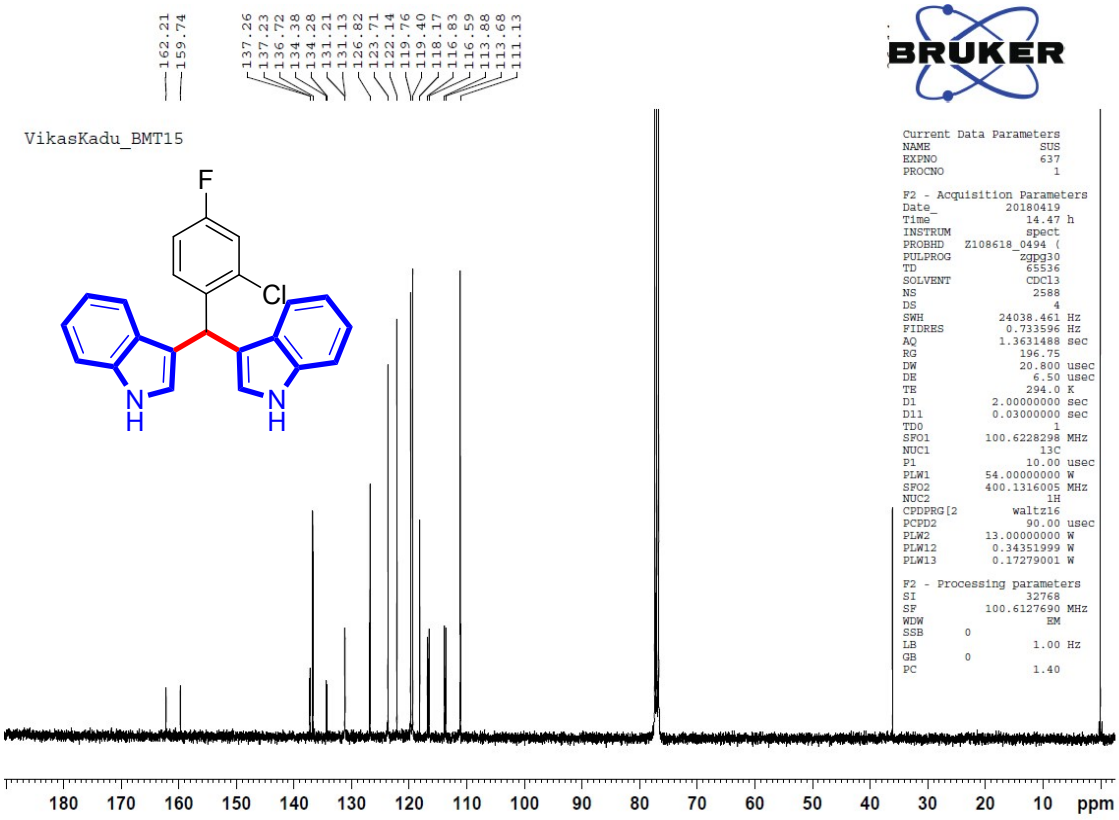
1.4.7 IR of compound: 3la



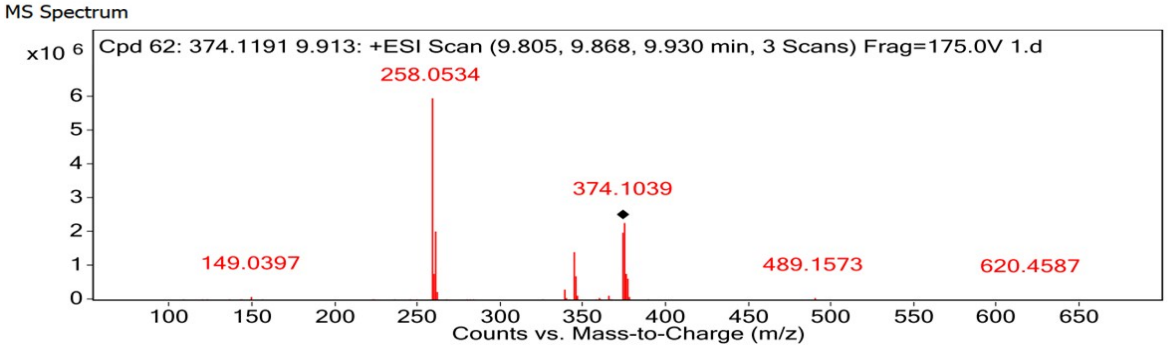
1.4.8 ^{1}H NMR of compound: 3la



1.4.9 ^{13}C NMR of compound: 3la

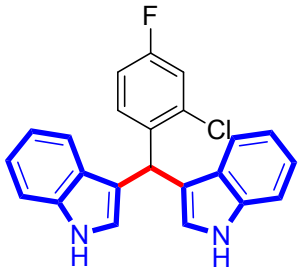


1.4.10 HRMS of compound: 3la

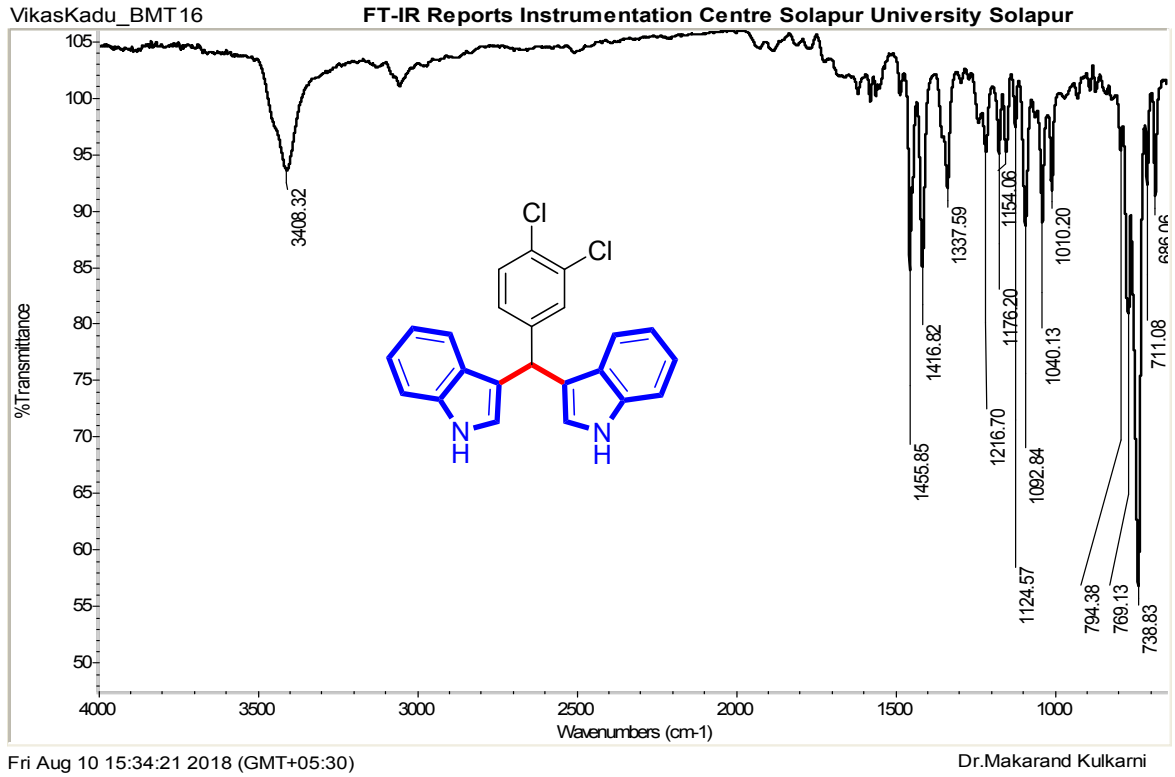


MS Spectrum Peak List

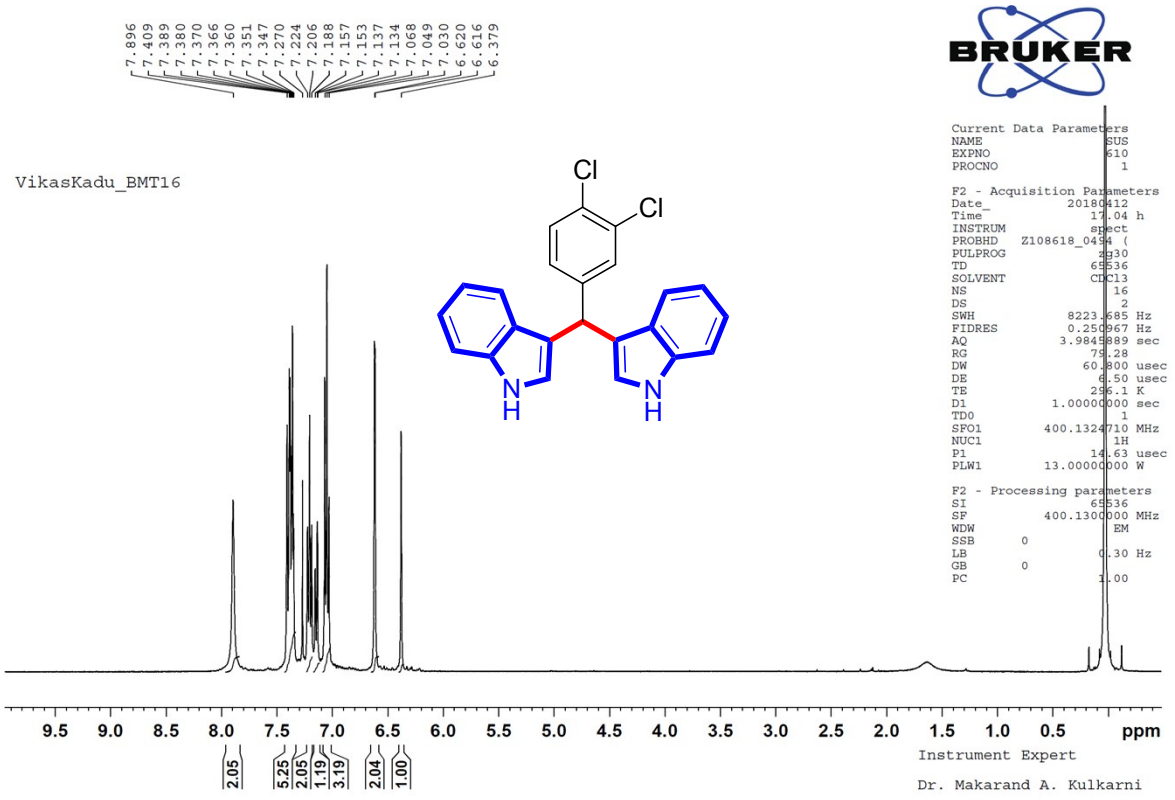
m/z	z	Abund
258.0534	1	5952729.5
259.0534	1	780950.06
259.0731		566914.69
260.0501	1	2037784.13
344.1242		1423508.13
345.1333	1	720158.81
373.0977		2011433.63
374.1039	1	2294657.25
375.1063	1	797636.19
376.1078	1	656586.44



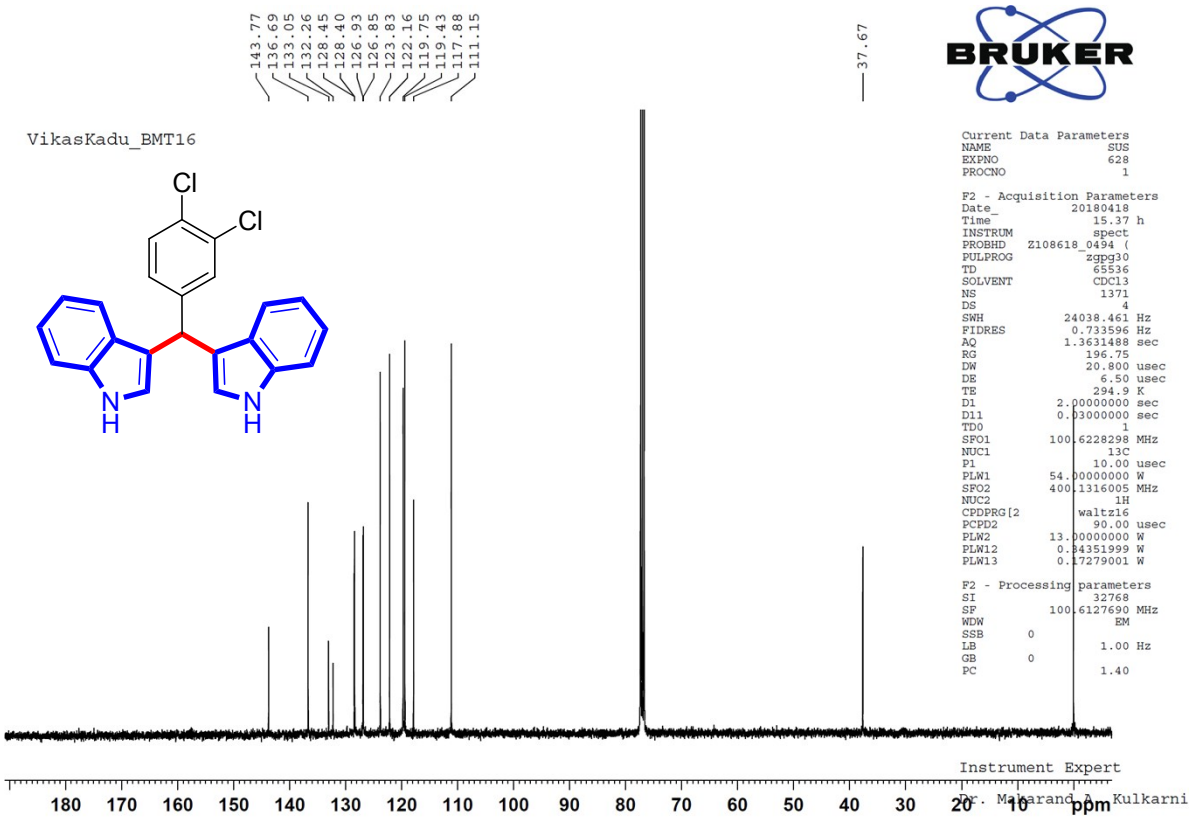
1.4.11 IR of compound: 3ma



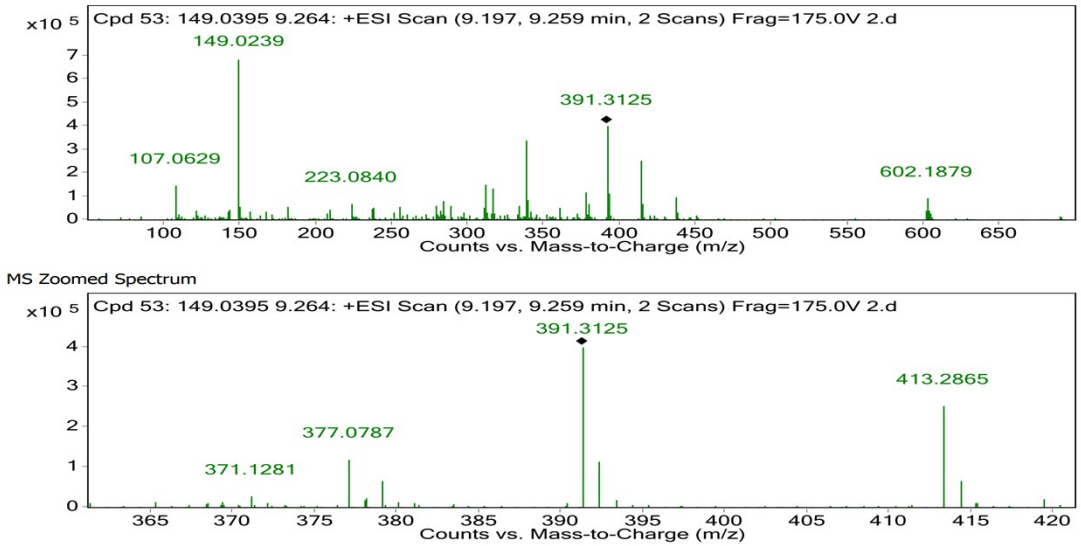
1.4.12 ^{1}H NMR of compound: 3ma



1.4.13 ^{13}C NMR of compound: 3ma



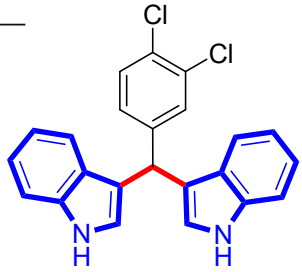
1.4.14 HRMS of compound: 3ma



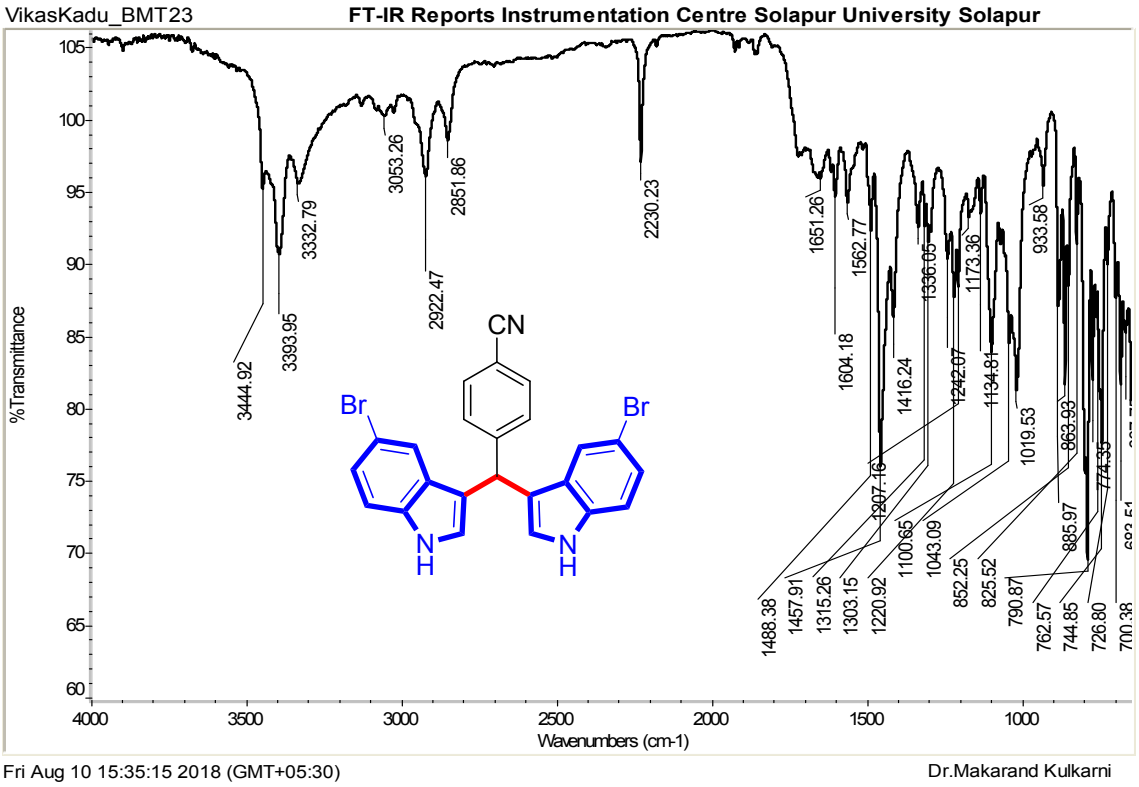
MS Zoomed Spectrum

MS Spectrum Peak List

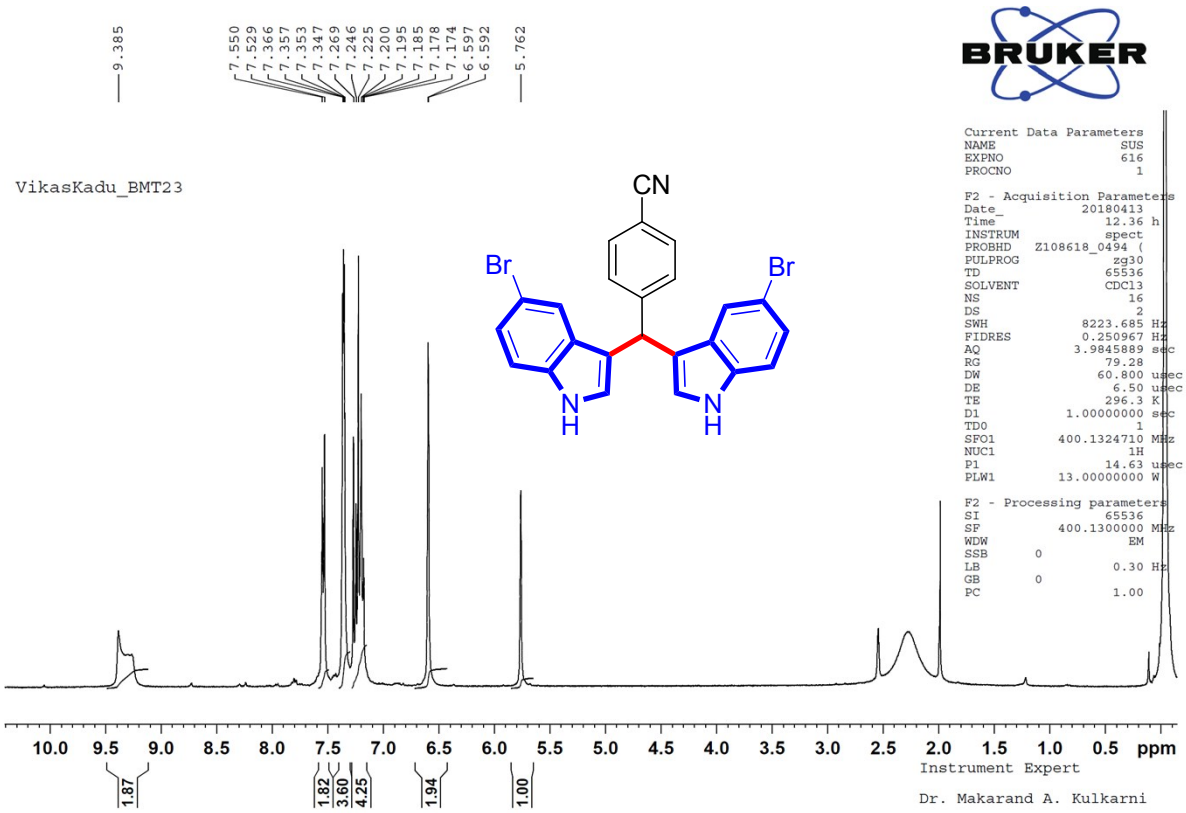
m/z	z	Abund
107.0629		147934.83
149.0239	1	684467.06
149.0403	1	491771.19
311.1877		126022.45
311.21	1	152575.44
316.3455	1	134170
338.3601	1	341769.63
391.2874	1	354411.69
391.3125	1	399574.06
413.2865	1	253896.81



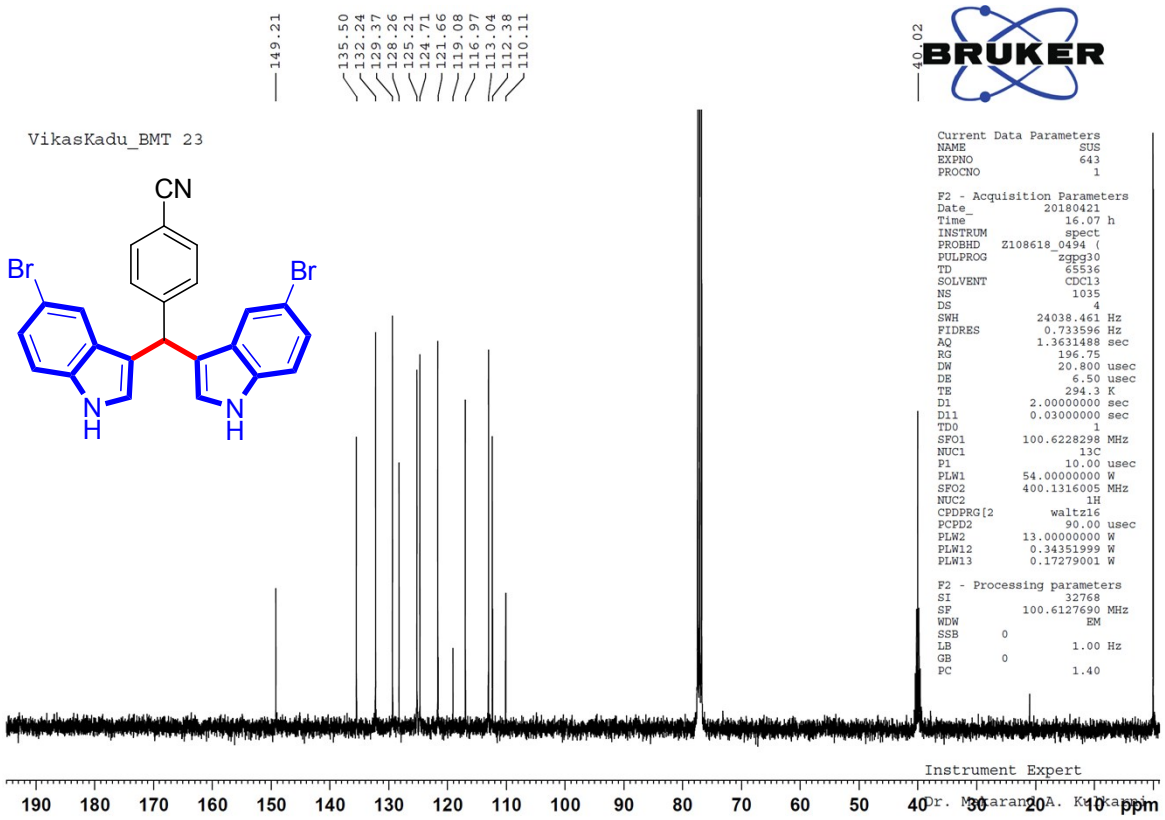
1.4.15 IR of compound: 3ta



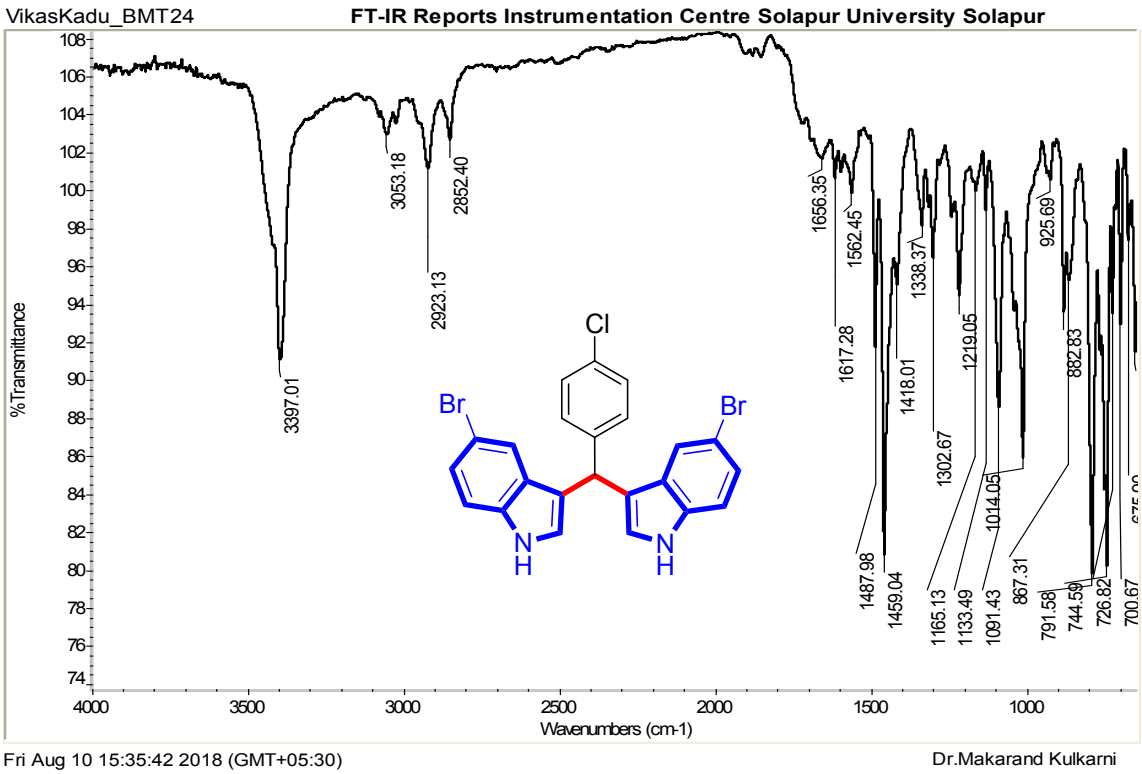
1.4.16 ^{1}H NMR of compound: 3ta



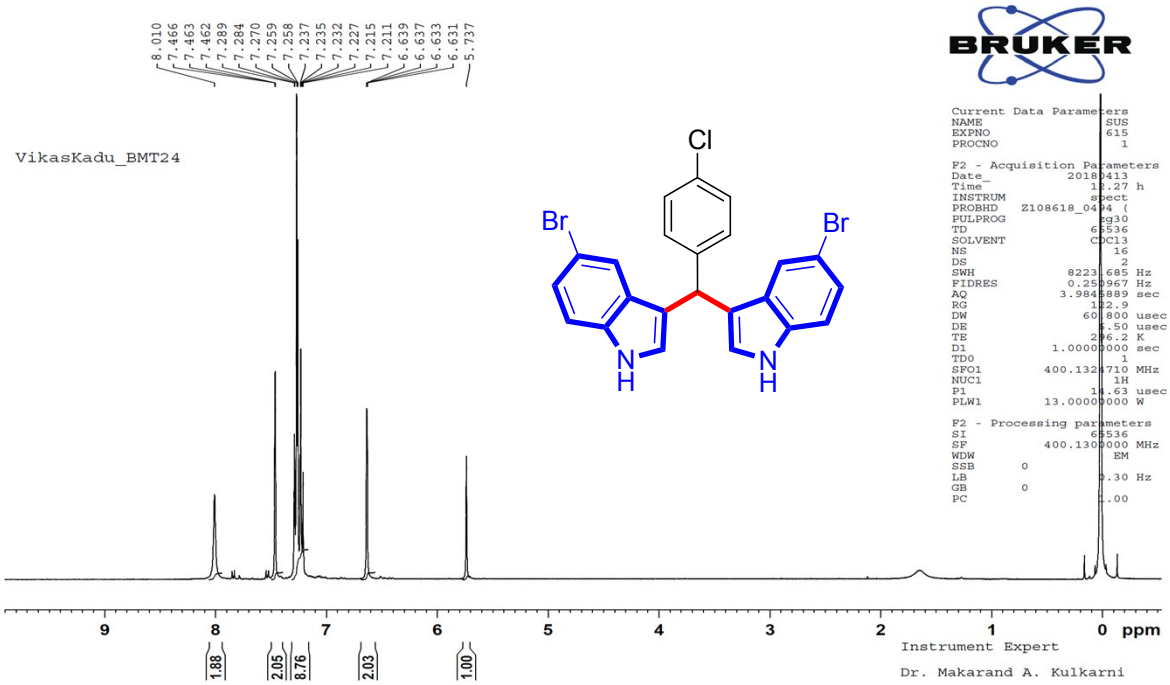
1.4.17 ^{13}C NMR of compound: 3ta



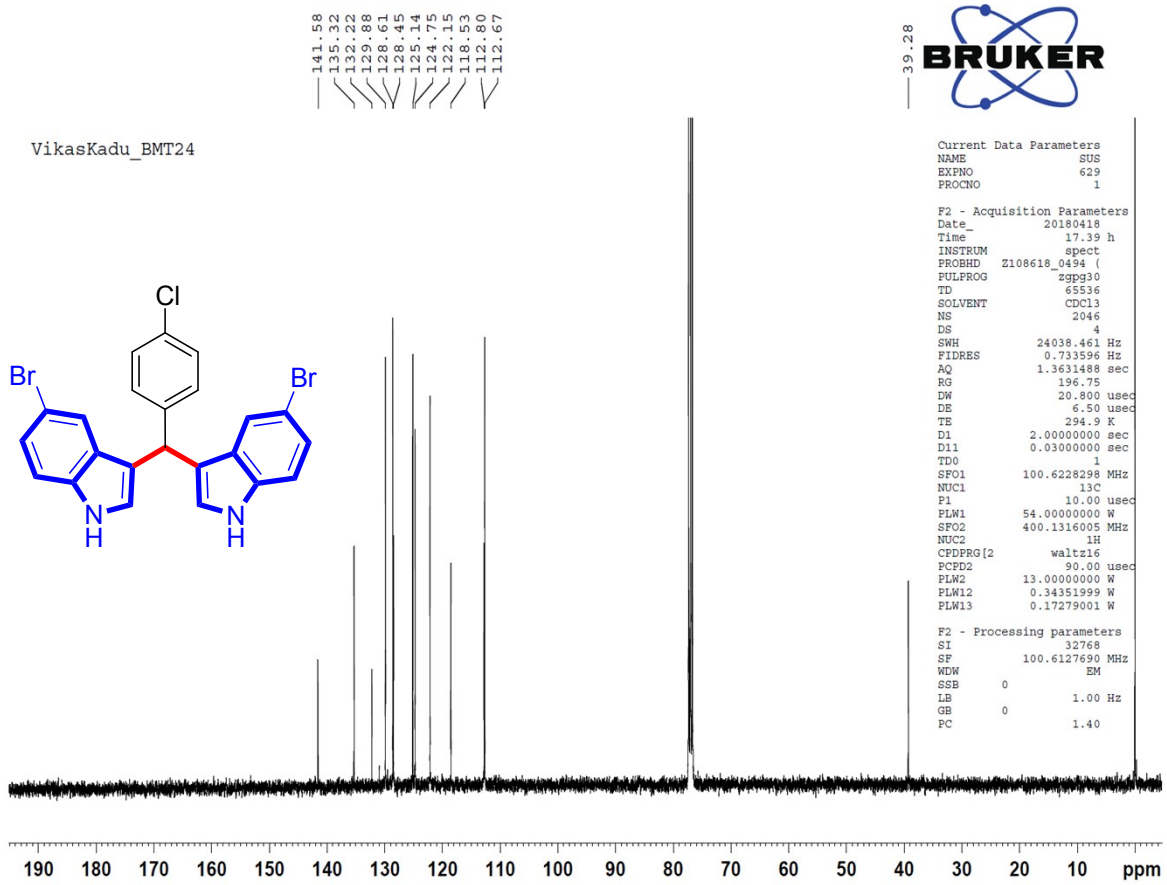
1.4.18 IR of compound: 3ua



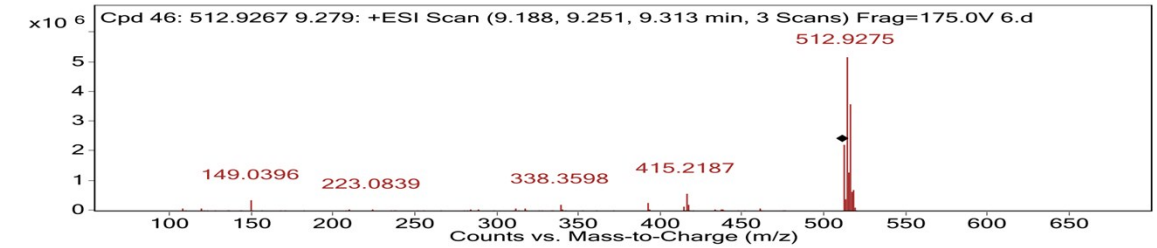
1.4.19 ^{1}H NMR of compound: 3ua



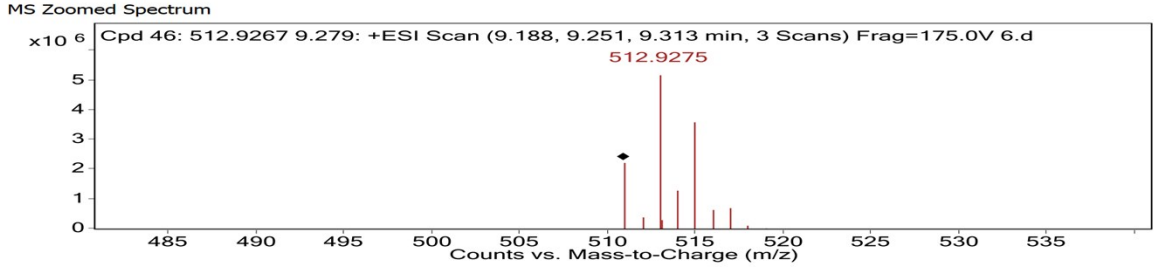
1.4.20 ^{13}C NMR of compound: 3ua



1.4.21 HRMS of compound: 3ua

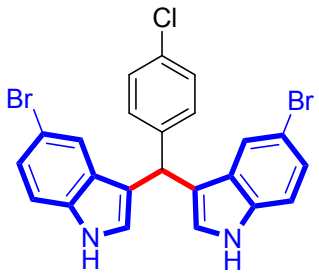


MS Zoomed Spectrum

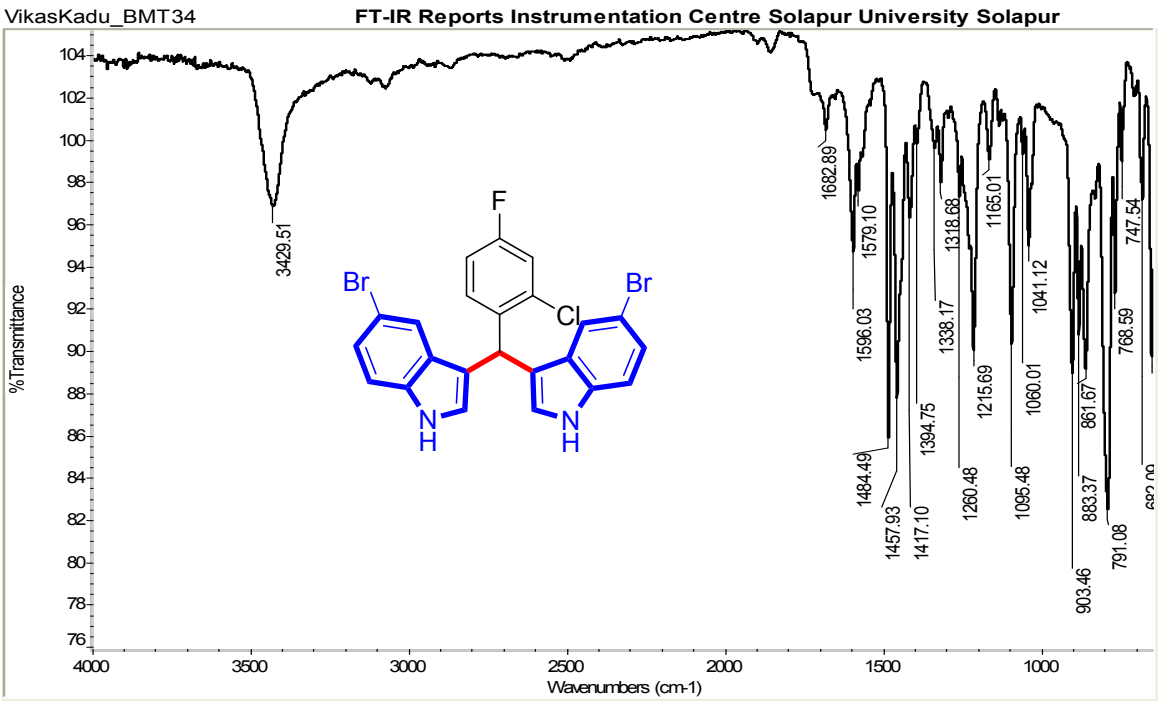


MS Spectrum Peak List

m/z	z	Abund
149.0239	1	301009.16
149.0396	1	361922.03
415.2187	1	580888.38
510.9286	1	2219903
511.9471	1	404925.84
512.9275	1	5177338.5
513.9312	1	1303297
514.925	1	3607994
515.9348	1	640195.69
516.9308	1	701115

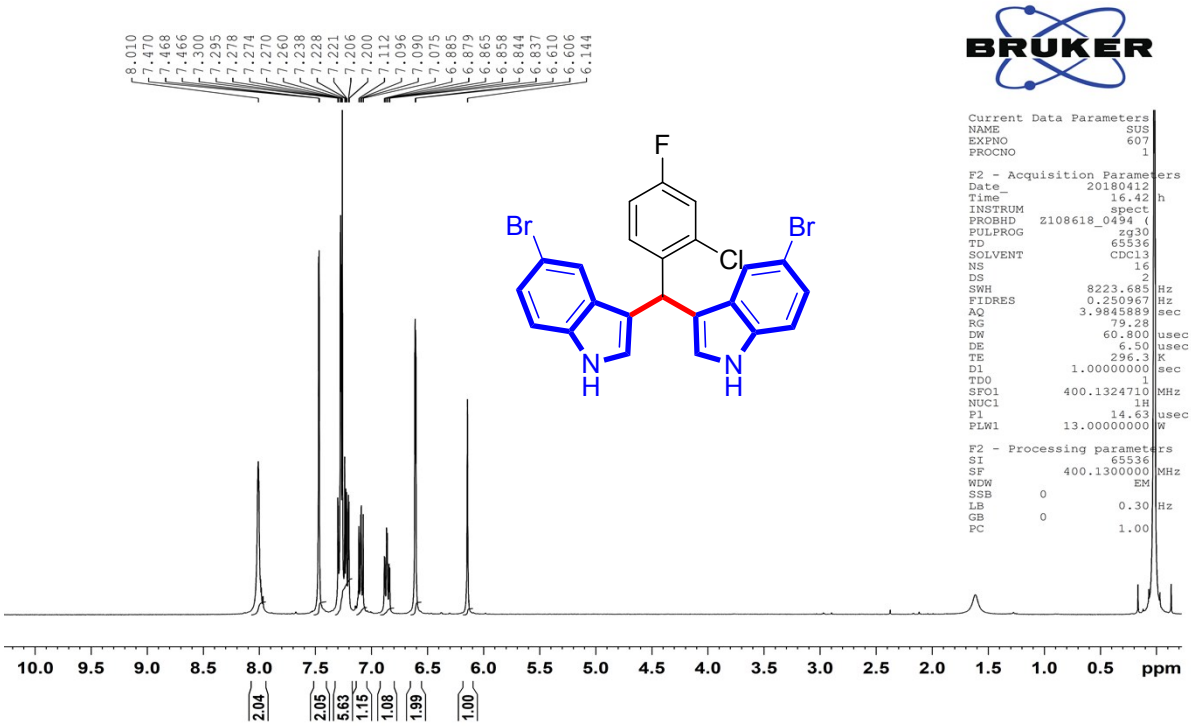


1.4.22 IR of compound: 3va

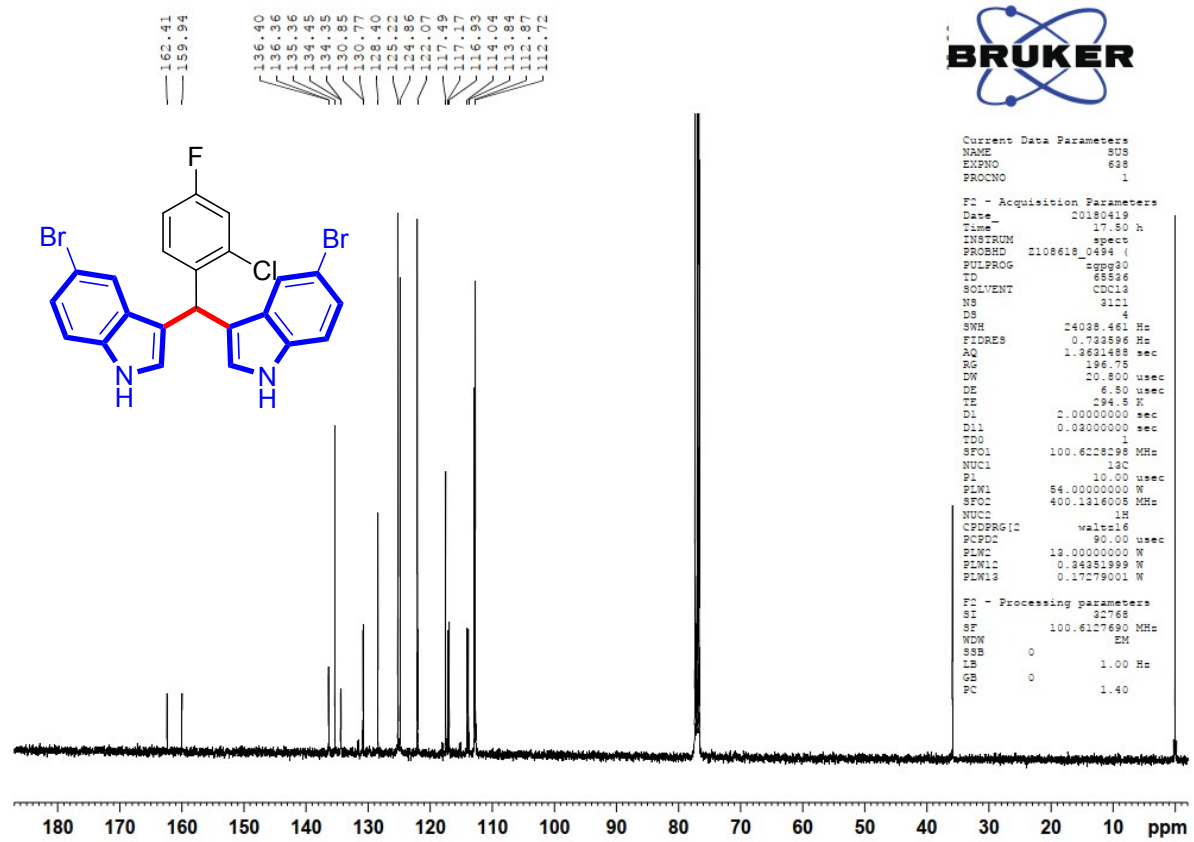


Fri Aug 10 15:38:48 2018 (GMT+05:30) Dr.Makarand Kulkarni

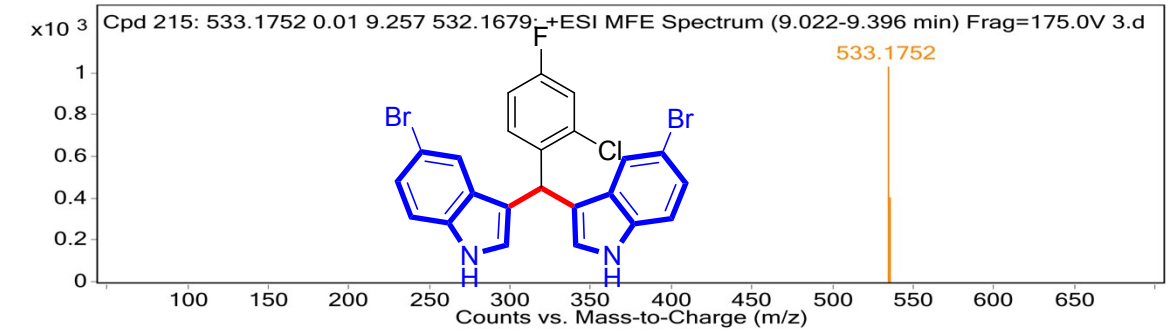
1.4.23 ^{1}H NMR of compound: 3va



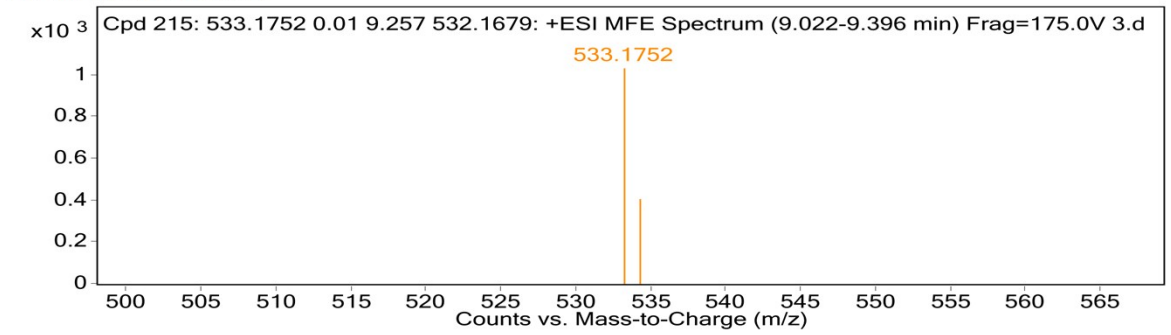
1.4.24 ^{13}C NMR of compound: 3va



1.4.25 HRMS of compound: 3va



MFE MS Zoomed Spectrum

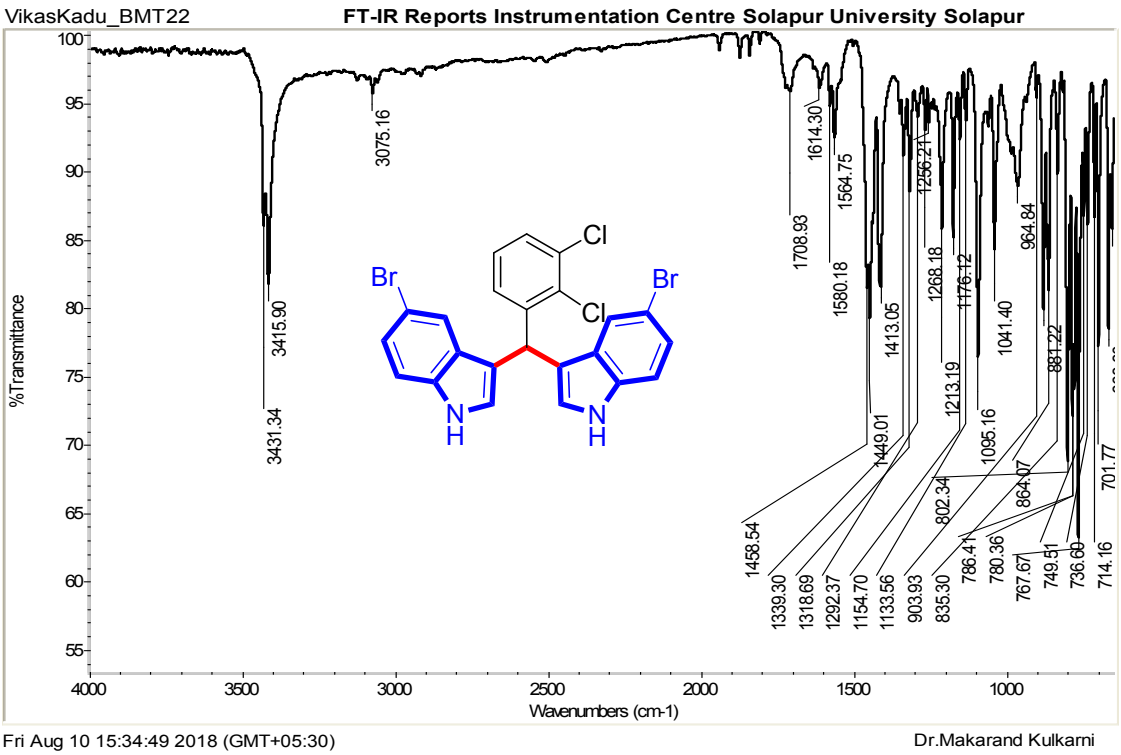


MS Spectrum Peak List

m/z	z	Abund	Ion
533.1752	1	1035.1	(M+H)+
534.1848	1	408.16	(M+H)+

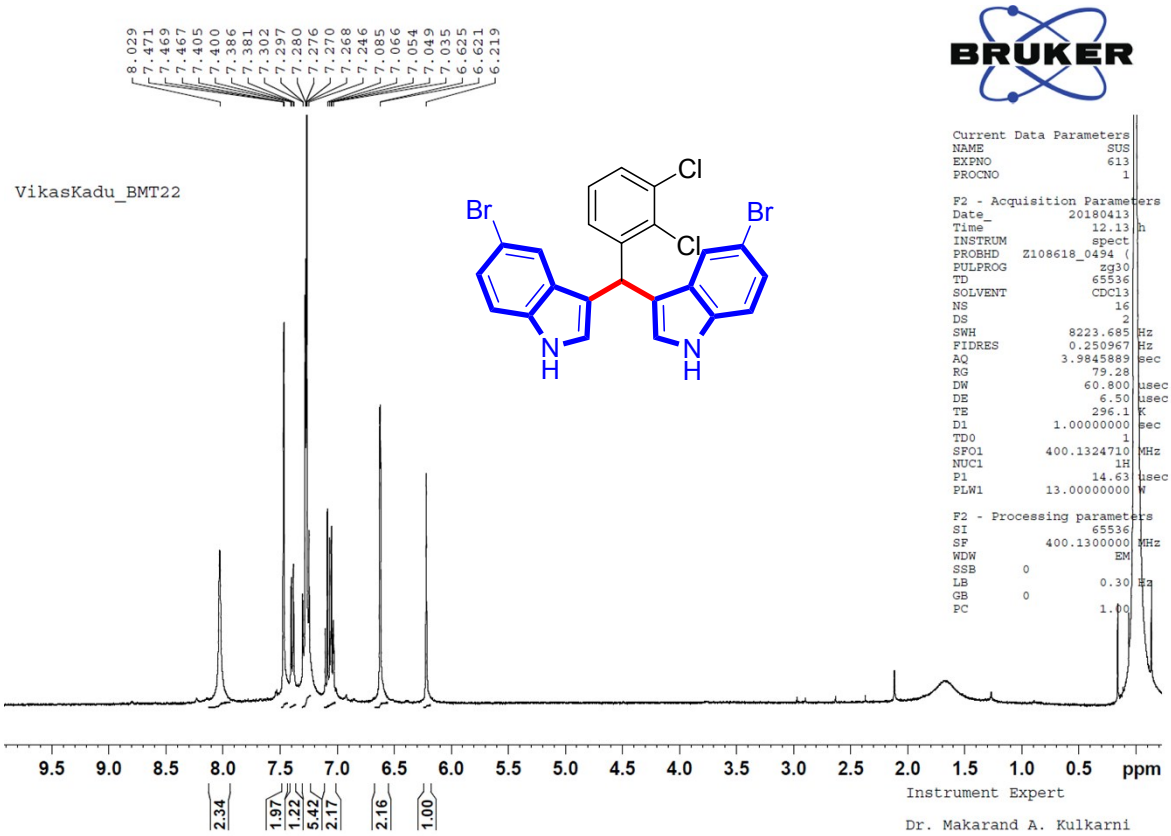
MS Spectrum

1.4.26 IR of compound: 3wa

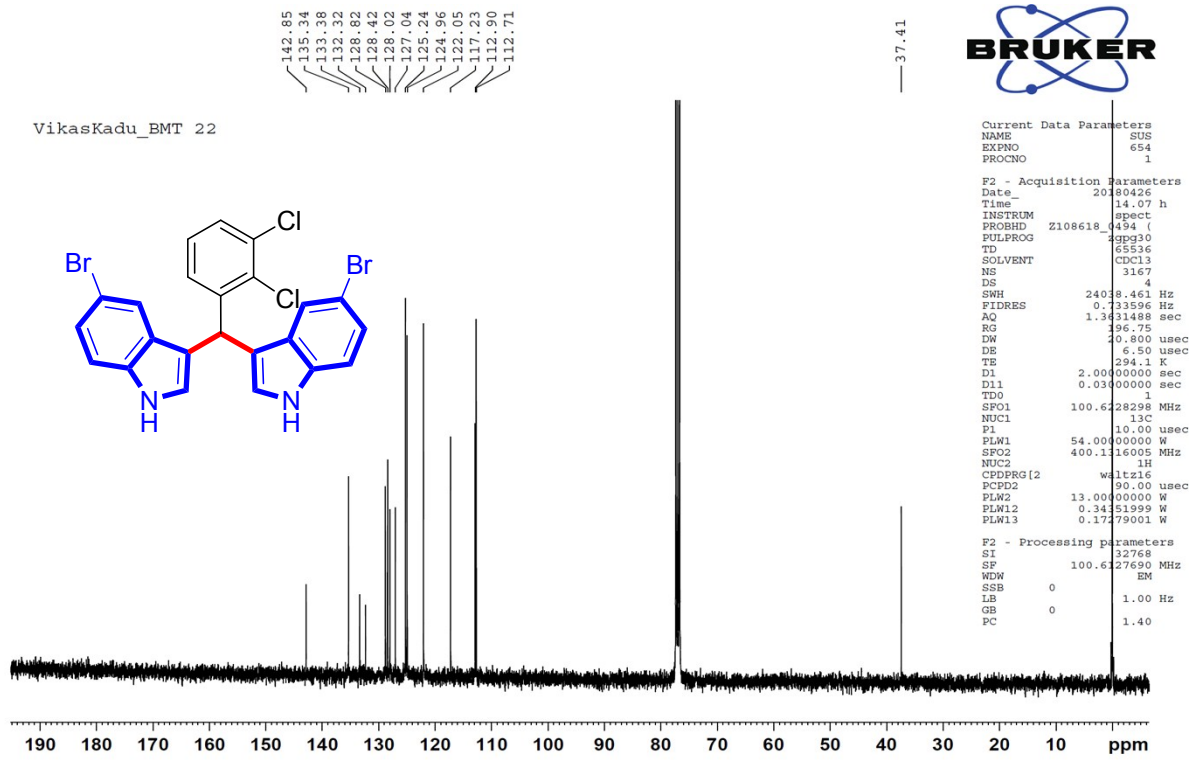


Fri Aug 10 15:34:49 2018 (GMT+05:30) Dr.Makarand Kulkarni

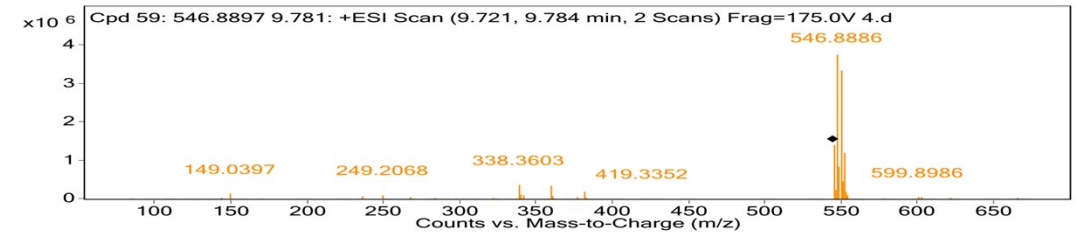
1.4.27 ^{1}H NMR of compound: 3wa



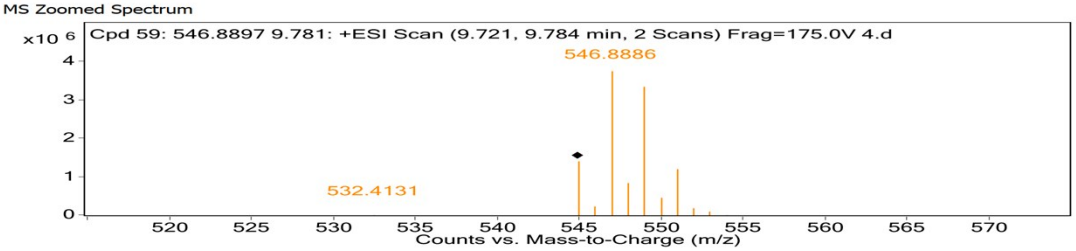
1.4.28 ^{13}C NMR of compound: 3wa



1.4.29 HRMS of compound: 3wa



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund
338.3603	1	382159.44
359.3338	1	357604.06
544.8921	1	1406796.88
545.909	1	258003.64
546.8886	1	3760183.25
547.8861	1	862920.25
547.9115		517668.06
548.8866	1	3358197.75
549.9018	1	467957.56
550.8863	1	1208713.38