

# 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

Vikas D. Kadu<sup>a\*</sup>, Sankala Naga Chandrudu<sup>b</sup>, Mahesh G. Hublikar<sup>a</sup>, Dattatraya G. Raut<sup>a</sup>,  
Raghunath B. Bhosale<sup>a</sup>

<sup>a</sup>School of Chemical Sciences, Punyashlok Ahilyadevi Holkar Solapur University  
Solapur- 413255, Maharashtra (India)

<sup>b</sup>Department of Chemistry, College of Engineering, Rayalseema University, Kurnool-518002,  
Andhrapradesh (India)

### \*Corresponding Author:

Vikas Dadabhau Kadu  
Organic Research Laboratory, School of Chemical Sciences  
Punyashlok Ahilyadevi Holkar Solapur University,  
Solapur- 413255, Maharashtra (India)  
Email: [vikaskadul@gmail.com](mailto:vikaskadul@gmail.com)

## Table of Contents

|            |  |          |
|------------|--|----------|
| <b>1.1</b> | <b>GENERAL INFORMATION.....</b>  | <b>2</b> |
| <b>1.2</b> | <b>GENERAL PROCEDURE FOR THE SYNTHESIS OF BIS(INDOLYL)METHANES (3) .....</b> | <b>3</b> |
| <b>1.3</b> | <b>CHARACTERIZATION DATA OF PURE BIS(INDOLYL)METHANES PRODUCTS .....</b>     | <b>3</b> |
| 1.3.1      | <i>Synthesis of 4-methyl-N-(4-methylbenzylidene)benzylamine (4) .....</i>    | <i>3</i> |
| <b>1.4</b> | <b>SPECTRAL DATA.....</b>  | <b>4</b> |
| 1.4.1      | <i><sup>1</sup>H NMR of compound: 4 .....</i>                                | <i>4</i> |
| 1.4.2      | <i><sup>13</sup>C NMR of compound: 4 .....</i>                               | <i>4</i> |
| 1.4.3      | <i>DEPT of compound: 4 .....</i>   | <i>5</i> |
| 1.4.4      | <i>IR of compound: 3ca .....</i>   | <i>5</i> |
| 1.4.5      | <i><sup>1</sup>H NMR of compound: 3ca .....</i>                              | <i>6</i> |
| 1.4.6      | <i><sup>13</sup>C NMR of compound: 3ca .....</i>                             | <i>6</i> |
| 1.4.7      | <i>IR of compound: 3la.....</i>  | <i>7</i> |

|        |  |    |
|--------|--|----|
| 1.4.8  | <sup>1</sup> H NMR of compound: 3la .....  | 7  |
| 1.4.9  | <sup>13</sup> C NMR of compound: 3la ..... | 8  |
| 1.4.10 | HRMS of compound: 3la .....                | 8  |
| 1.4.11 | IR of compound: 3ma .....                  | 9  |
| 1.4.12 | <sup>1</sup> H NMR of compound: 3ma .....  | 9  |
| 1.4.13 | <sup>13</sup> C NMR of compound: 3ma ..... | 10 |
| 1.4.14 | HRMS of compound: 3ma .....                | 10 |
| 1.4.15 | IR of compound: 3ta .....                  | 11 |
| 1.4.16 | <sup>1</sup> H NMR of compound: 3ta .....  | 11 |
| 1.4.17 | <sup>13</sup> C NMR of compound: 3ta ..... | 12 |
| 1.4.18 | IR of compound: 3ua .....                  | 12 |
| 1.4.19 | <sup>1</sup> H NMR of compound: 3ua .....  | 13 |
| 1.4.20 | <sup>13</sup> C NMR of compound: 3ua ..... | 13 |
| 1.4.21 | HRMS of compound: 3ua .....                | 14 |
| 1.4.22 | IR of compound: 3va .....                  | 14 |
| 1.4.23 | <sup>1</sup> H NMR of compound: 3va .....  | 15 |
| 1.4.24 | <sup>13</sup> C NMR of compound: 3va ..... | 15 |
| 1.4.25 | HRMS of compound: 3va .....                | 16 |
| 1.4.26 | IR of compound: 3wa .....                  | 16 |
| 1.4.27 | <sup>1</sup> H NMR of compound: 3wa .....  | 17 |
| 1.4.28 | <sup>13</sup> C NMR of compound: 3wa ..... | 17 |
| 1.4.29 | HRMS of compound: 3wa .....                | 18 |

## 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<sub>254</sub>) 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 Bruker 400 MHz (<sup>1</sup>H at 400 MHz, <sup>13</sup>C at 100 MHz), using DMSO-*d*<sub>6</sub> or

CDCl<sub>3</sub> 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<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub> (10 mL), and washed with water (2 x 10 mL). The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> 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

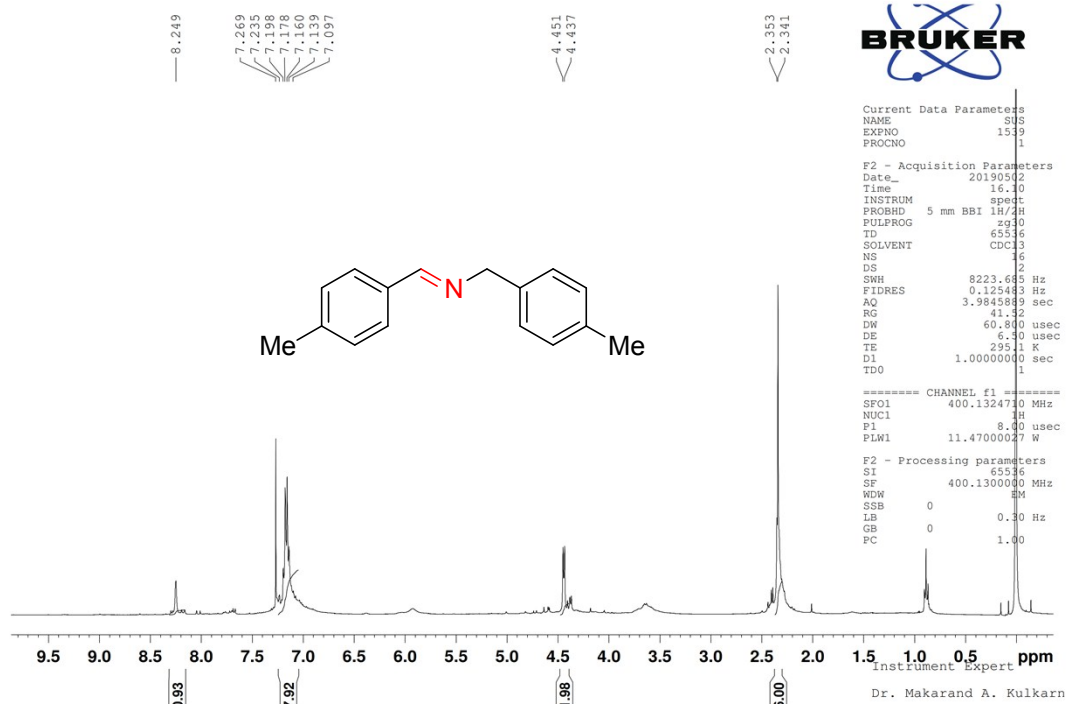
### 1.3.1 Synthesis of 4-methyl-*N*-(4-methylbenzylidene)benzylamine (**4**)

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<sub>2</sub> 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.

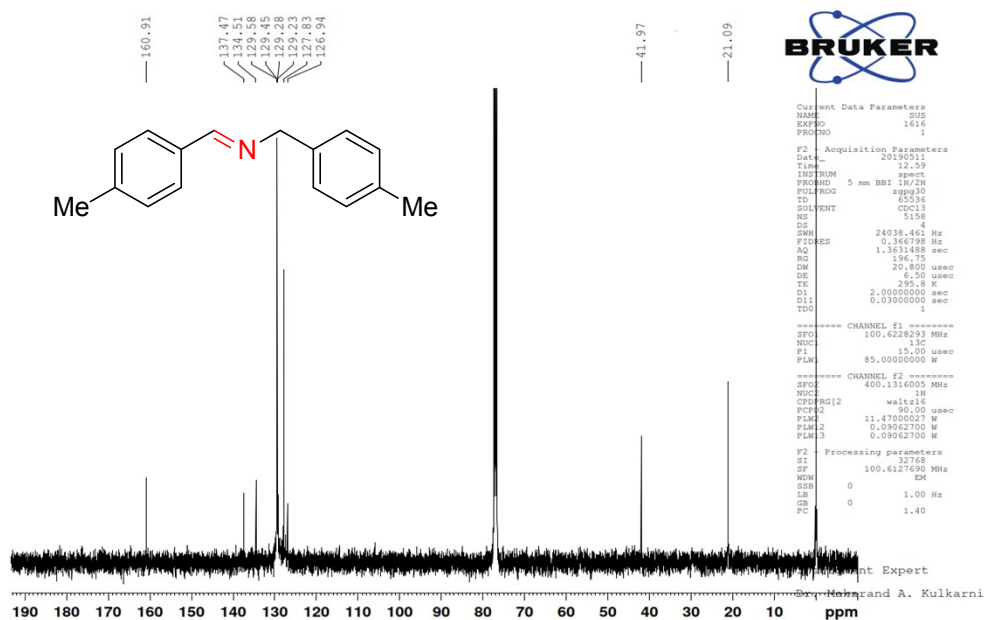
IR (cm<sup>-1</sup>): 3022, 2923, 2853, 1646, 1514, 1174, 1021, 811, 711; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.24 (s, 1H), 7.07–7.26 (m, 8H, ArH), 4.5 (d, *J* = 5.6 Hz, 2H), 2.35 (s, 3H), 2.34 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.91, 137.47, 134.51, 129.58, 129.45, 129.28, 129.23, 127.83, 126.94, 41.97, 21.09 ppm; <sup>13</sup>C NMR DEPT-135 (100 MHz, CDCl<sub>3</sub>): 160.93 (=CH, up), 129.58, 129.45, 127.83, 126.94, 41.97 (CH<sub>2</sub>, down), 21.09 (2xCH<sub>3</sub>, up) ppm.

## 1.4 Spectral data

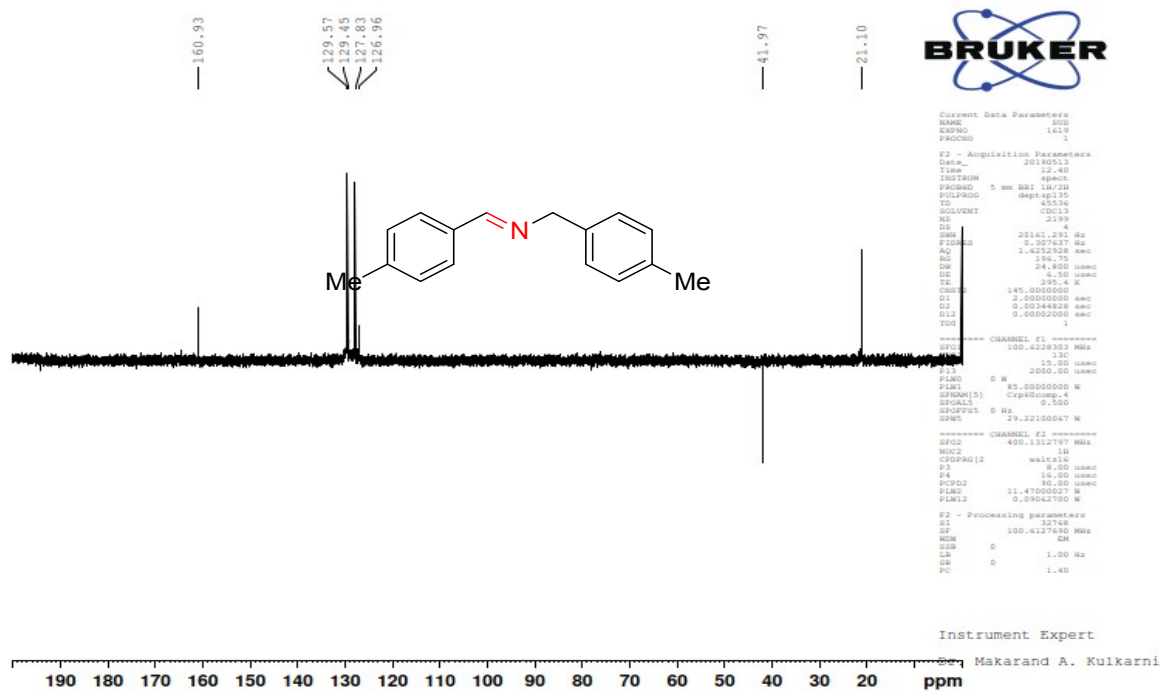
### 1.4.1 <sup>1</sup>H NMR of compound: 4



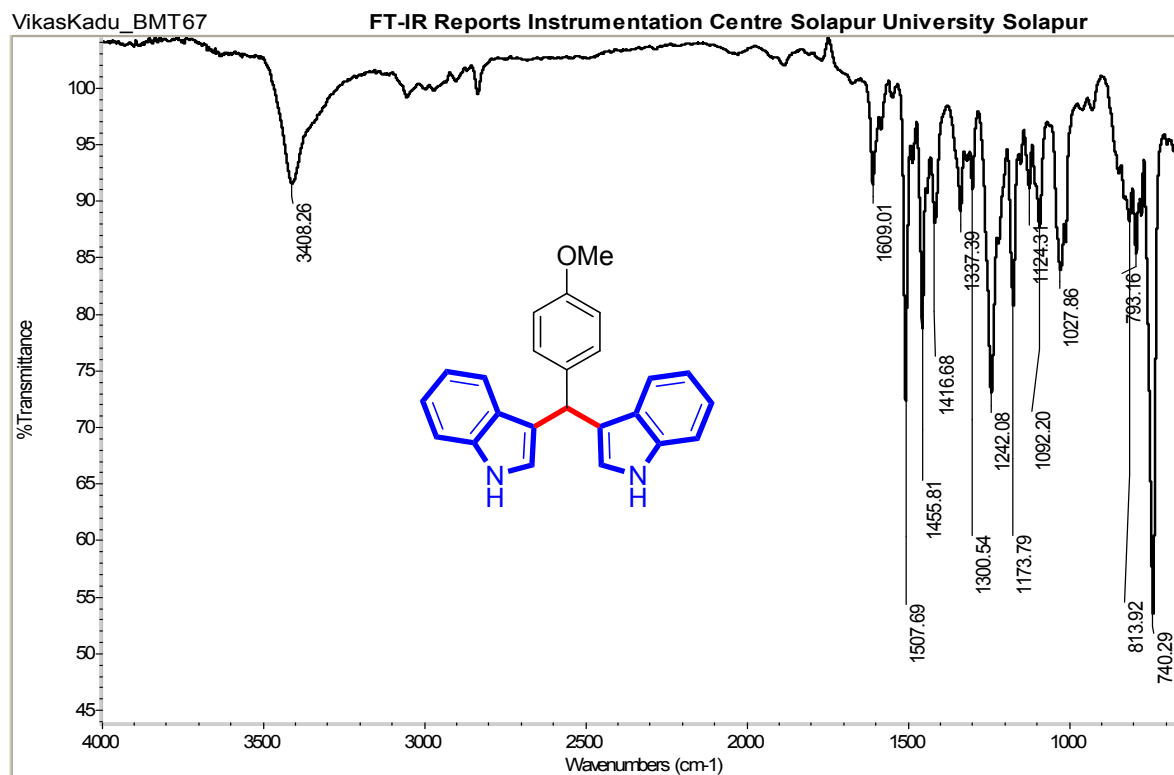
### 1.4.2 <sup>13</sup>C NMR of compound: 4



### 1.4.3 DEPT of compound: 4



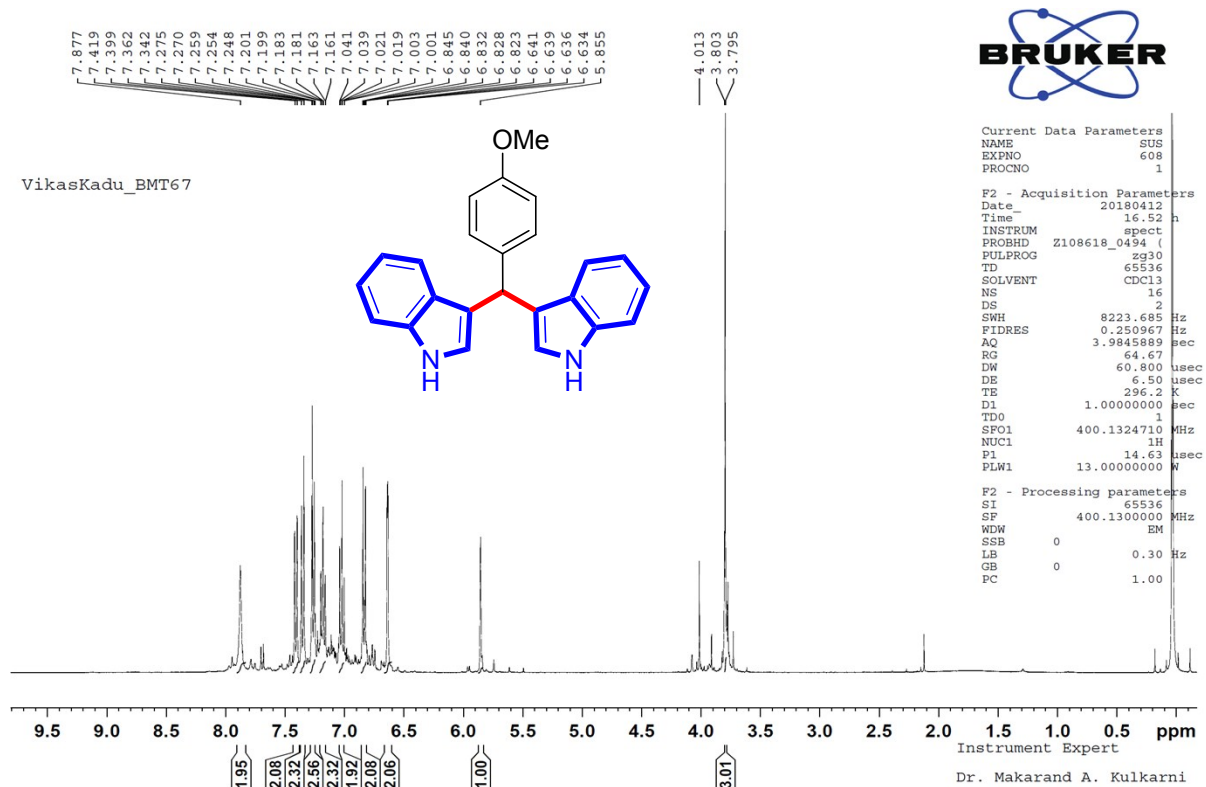
### 1.4.4 IR of compound: 3ca



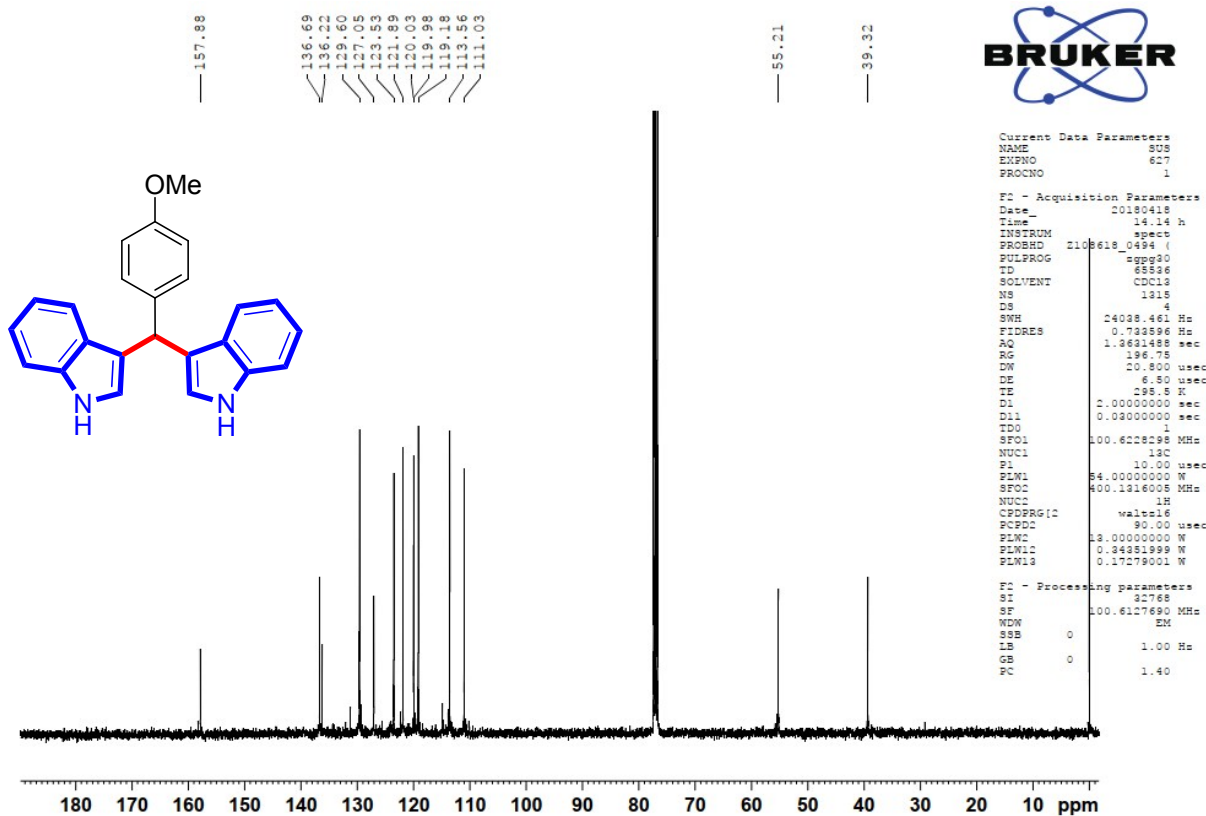
Fri Aug 10 15:39:14 2018 (GMT+05:30)

Dr.Makarand Kulkarni

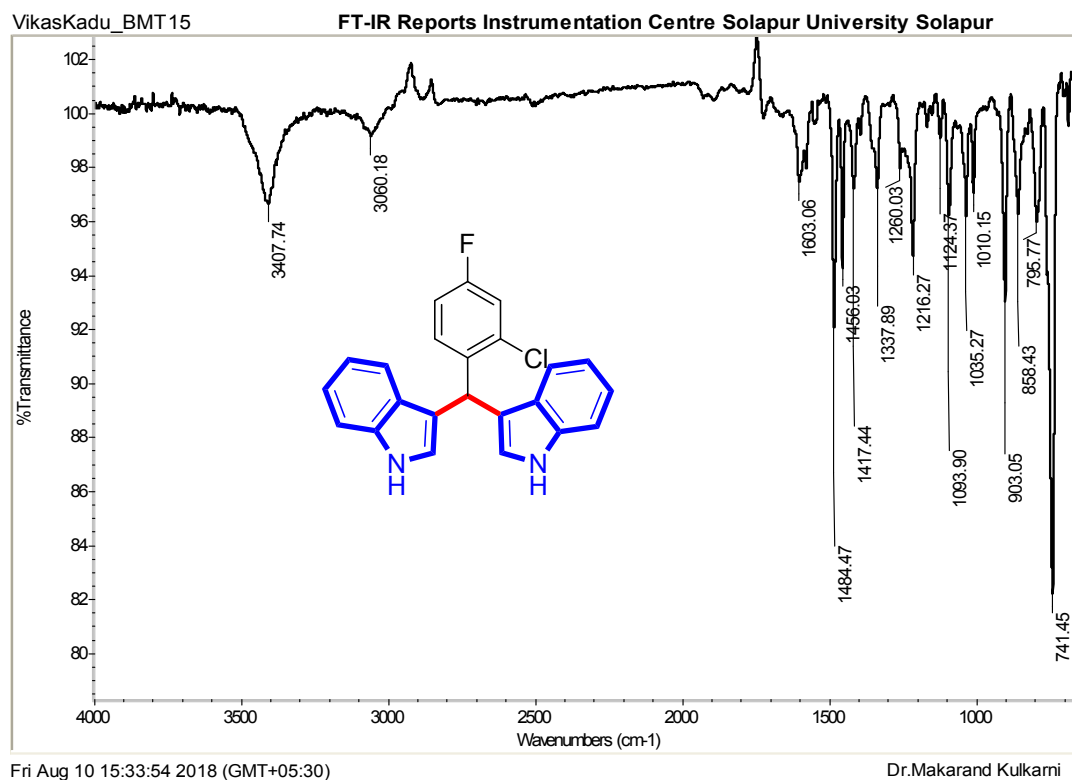
### 1.4.5 <sup>1</sup>H NMR of compound: 3ca



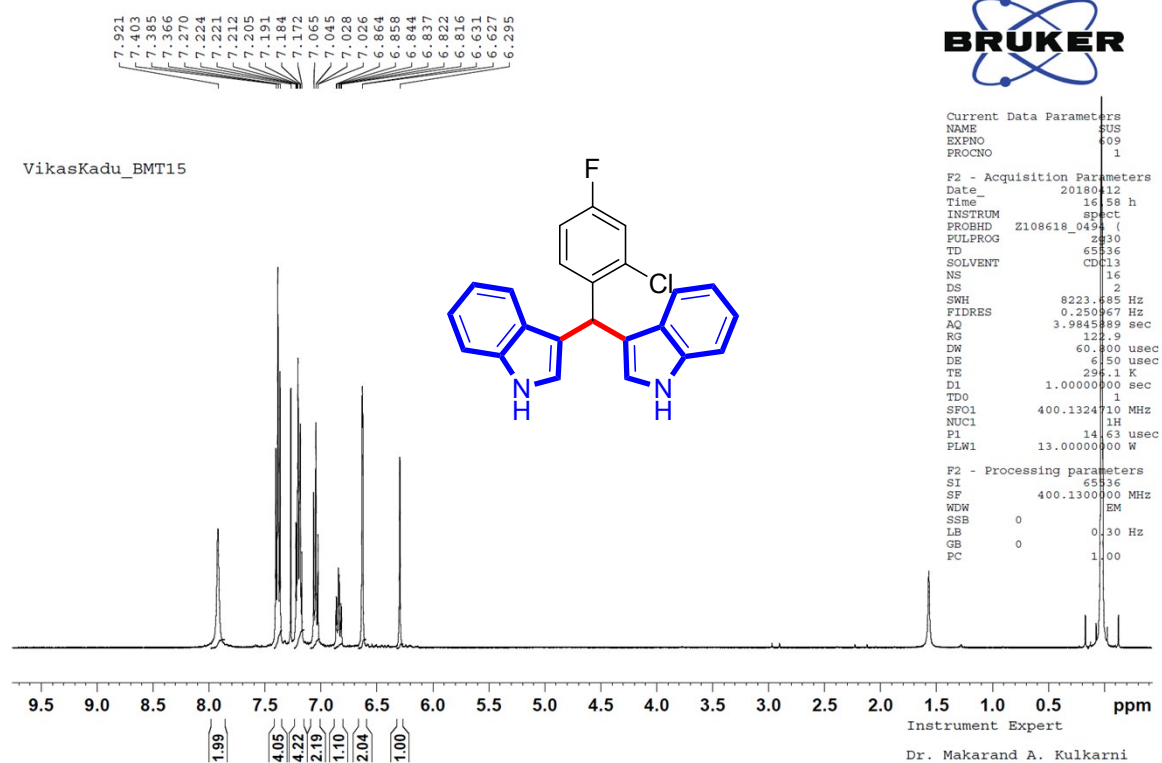
### 1.4.6 <sup>13</sup>C NMR of compound: 3ca



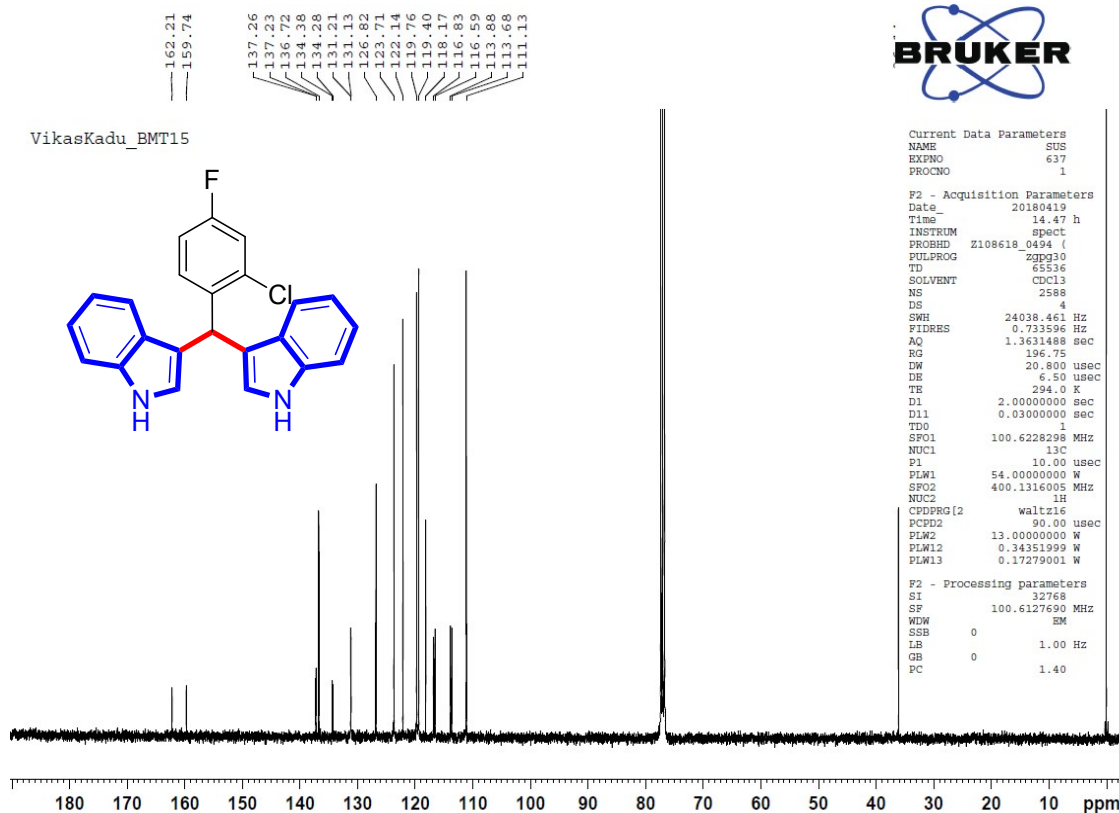
### 1.4.7 IR of compound: 3la



### 1.4.8 <sup>1</sup>H NMR of compound: 3la

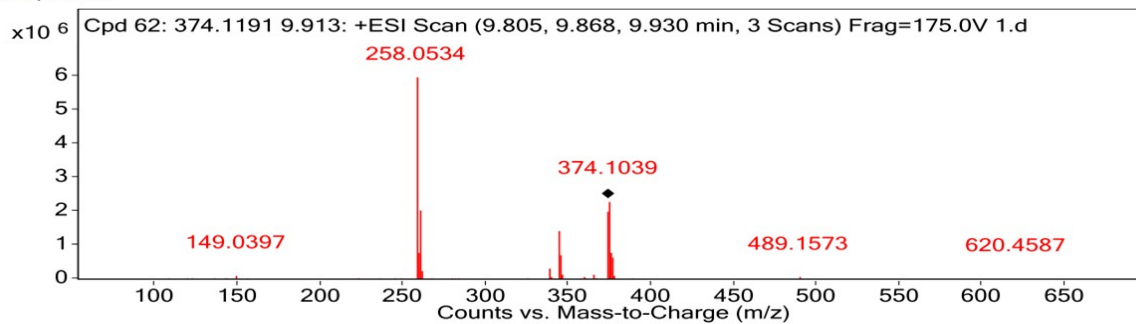


### 1.4.9 <sup>13</sup>C NMR of compound: 3la



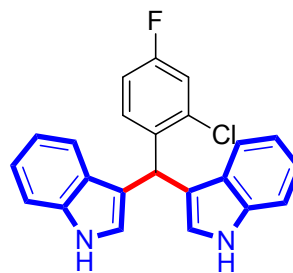
### 1.4.10 HRMS of compound: 3la

MS Spectrum



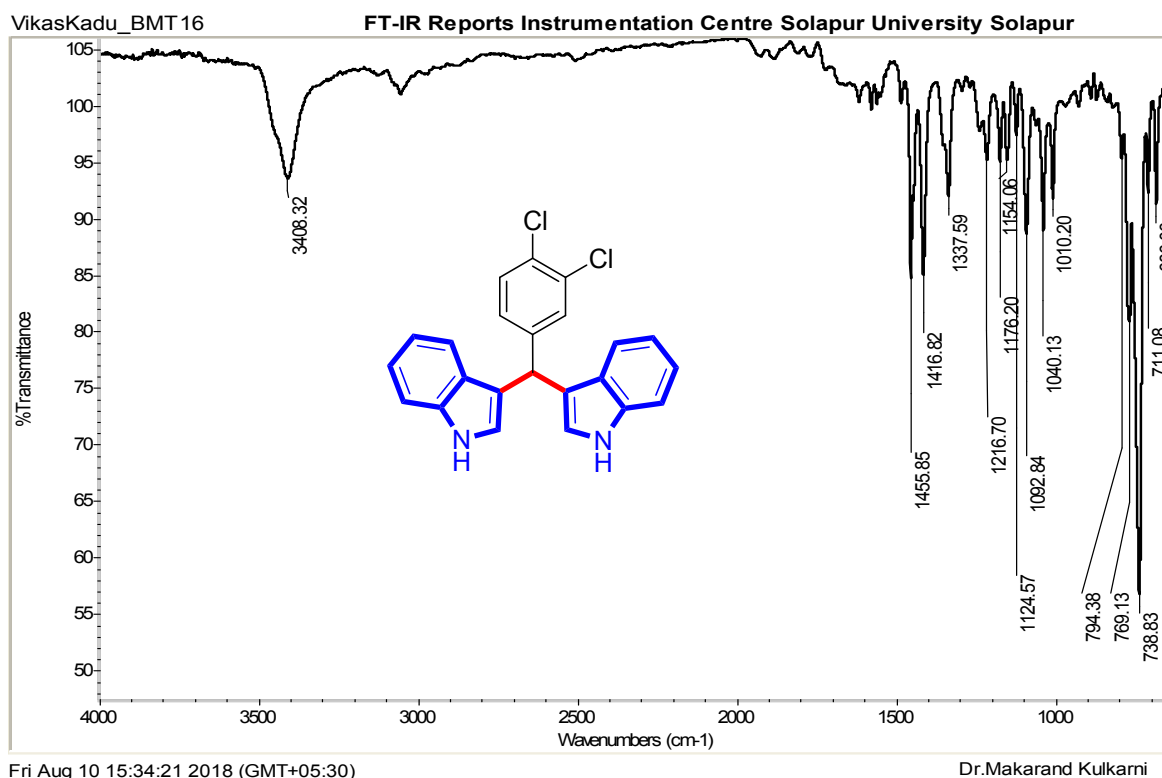
MS Spectrum Peak List

| 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  |

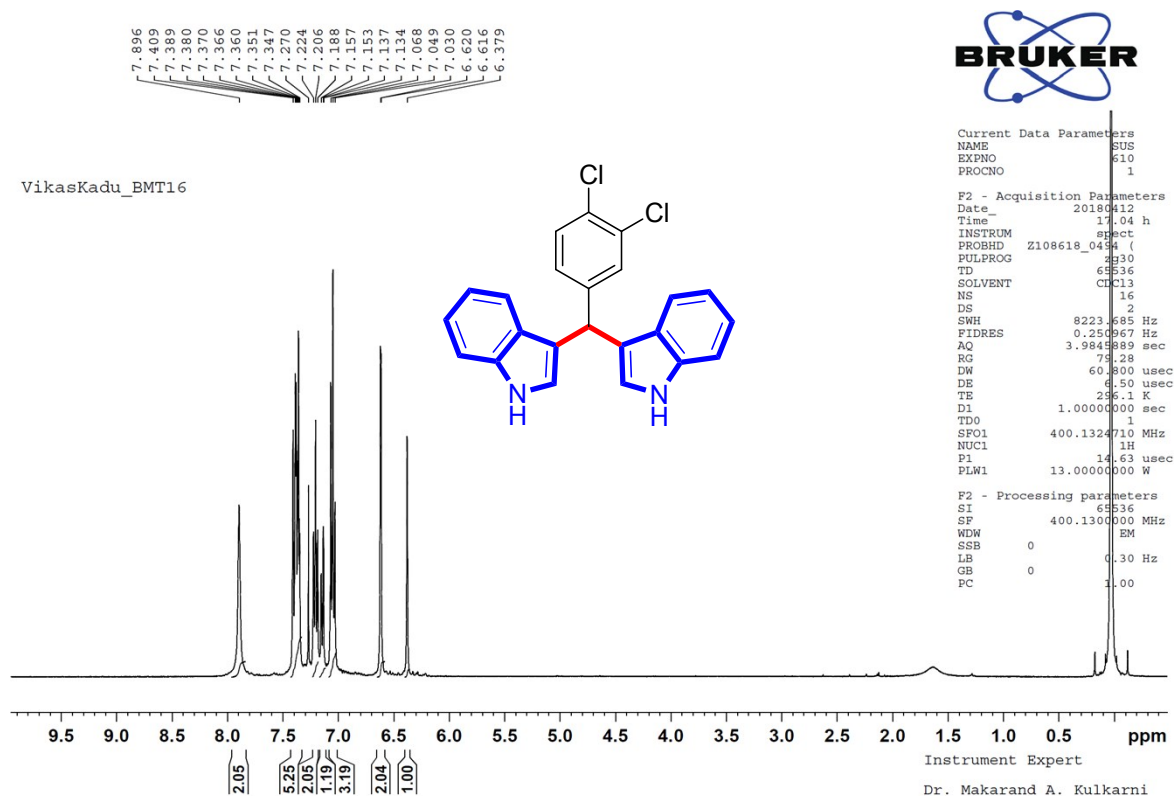




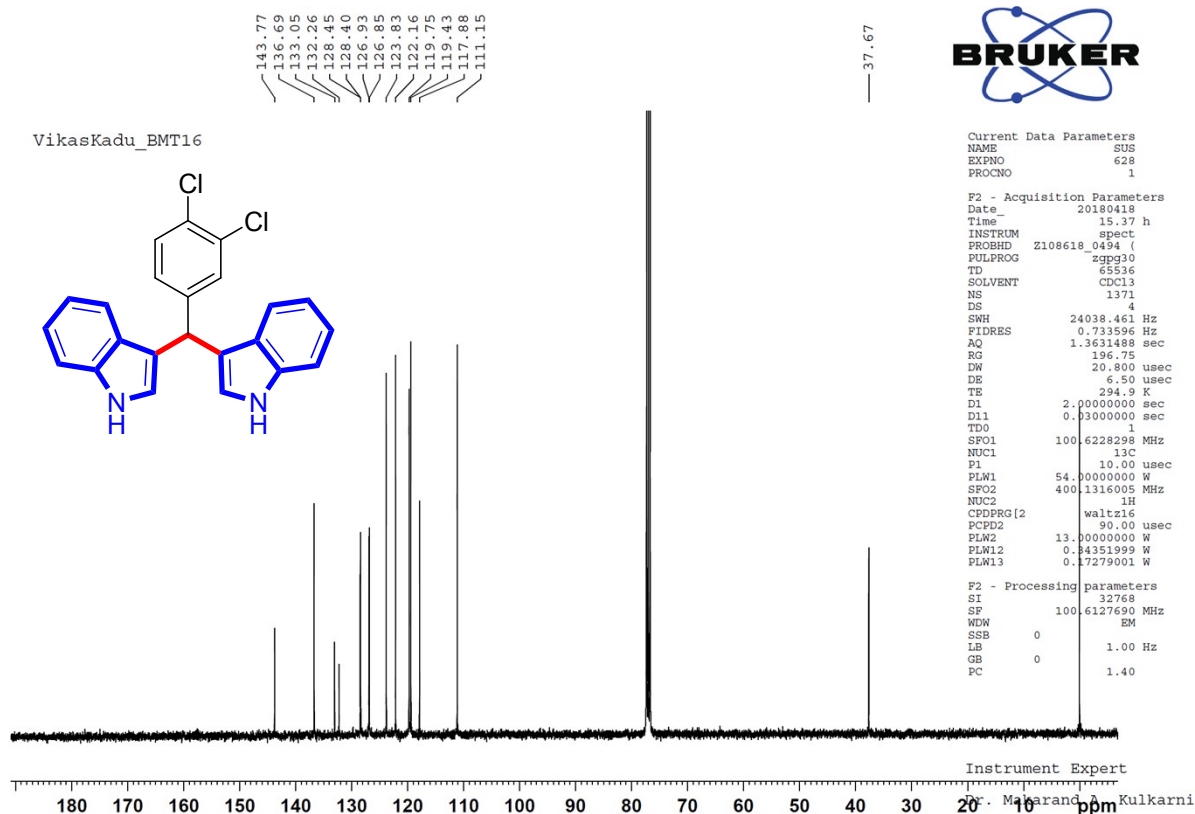
### 1.4.11 IR of compound: 3ma



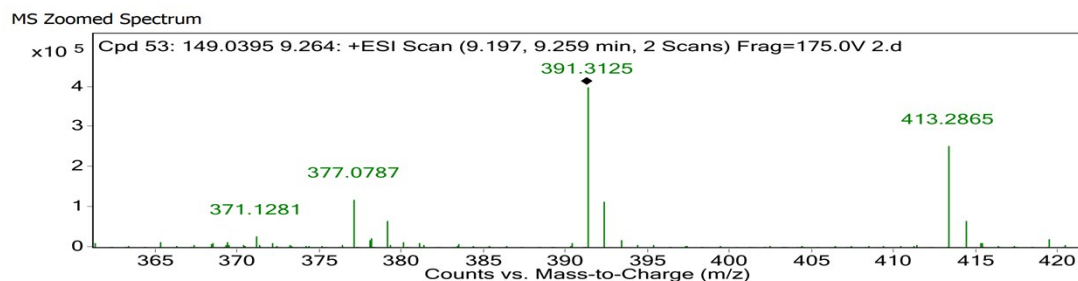
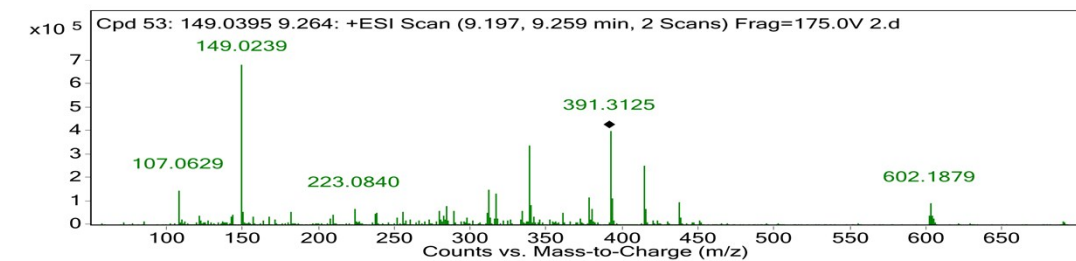
### 1.4.12 <sup>1</sup>H NMR of compound: 3ma



### 1.4.13 <sup>13</sup>C NMR of compound: 3ma

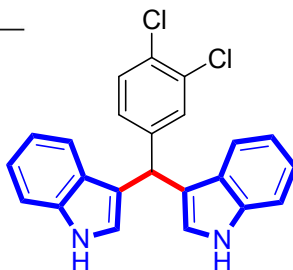


### 1.4.14 HRMS of compound: 3ma

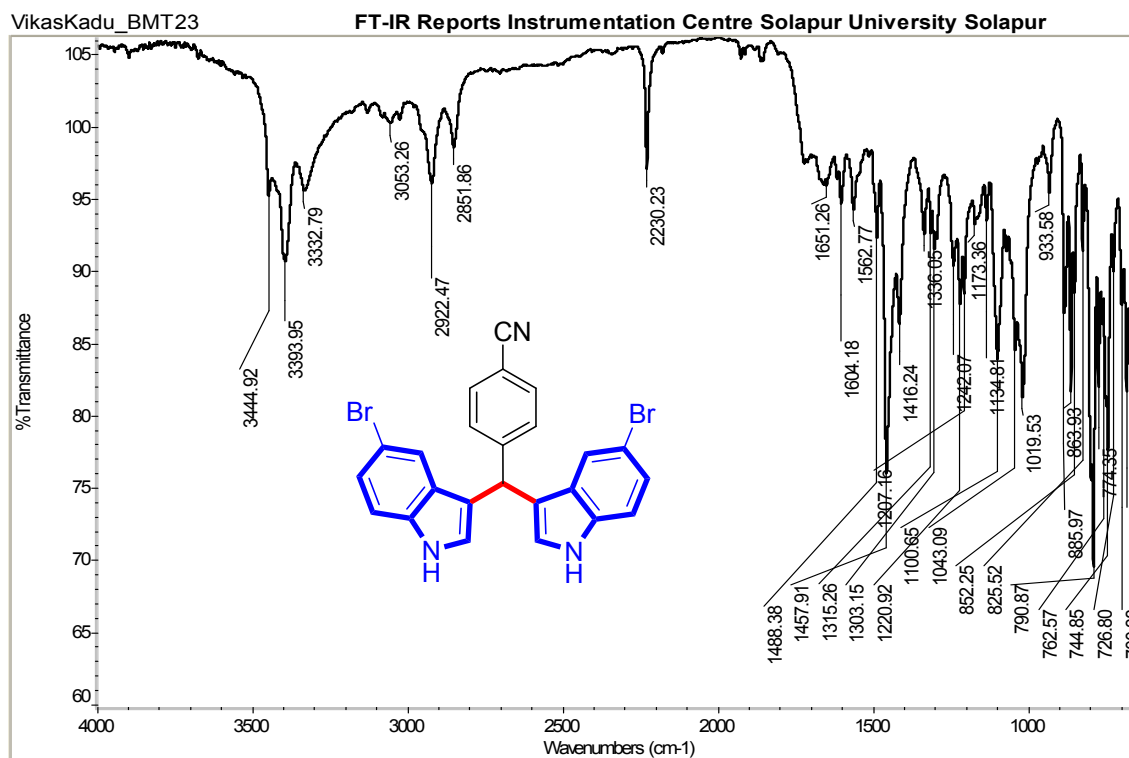


MS Spectrum Peak List

| m/z      | z | Abund     |
|----------|---|-----------|
| 107.0629 | 1 | 147934.83 |
| 149.0239 | 1 | 684467.06 |
| 149.0403 | 1 | 491771.19 |
| 311.1877 | 1 | 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 |



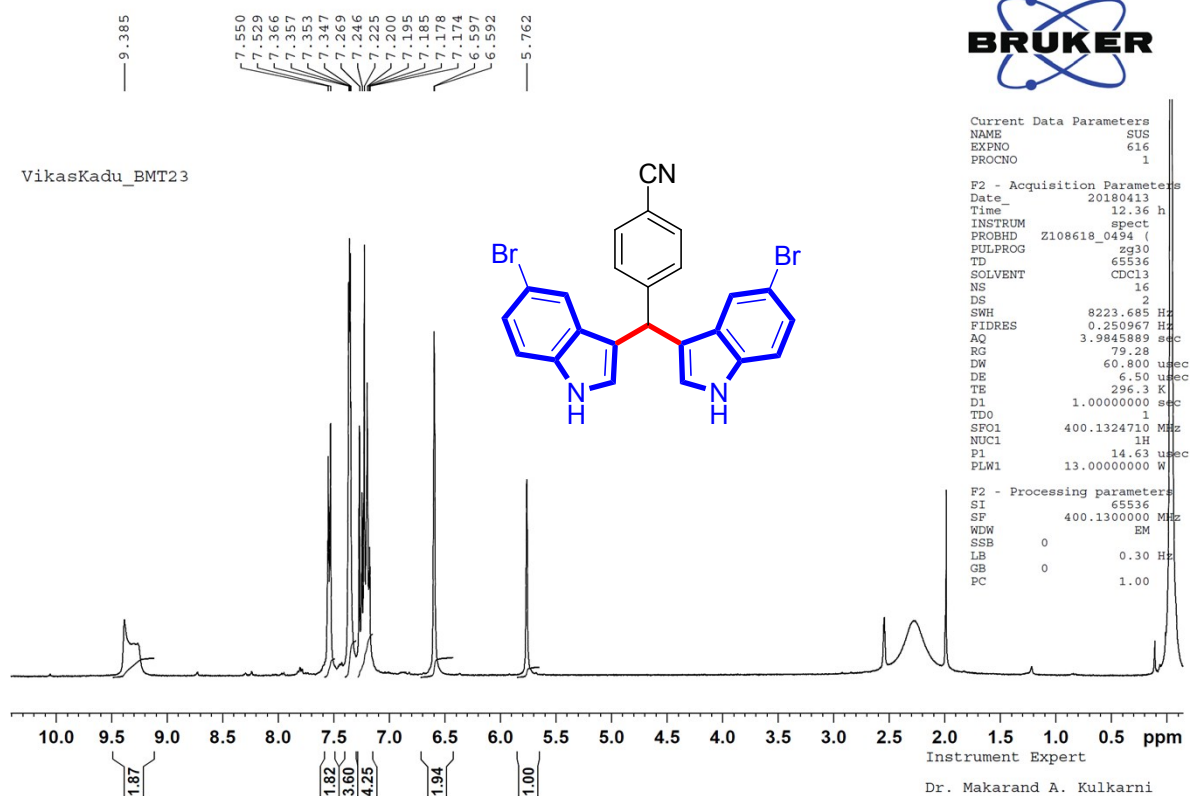
### 1.4.15 IR of compound: 3ta



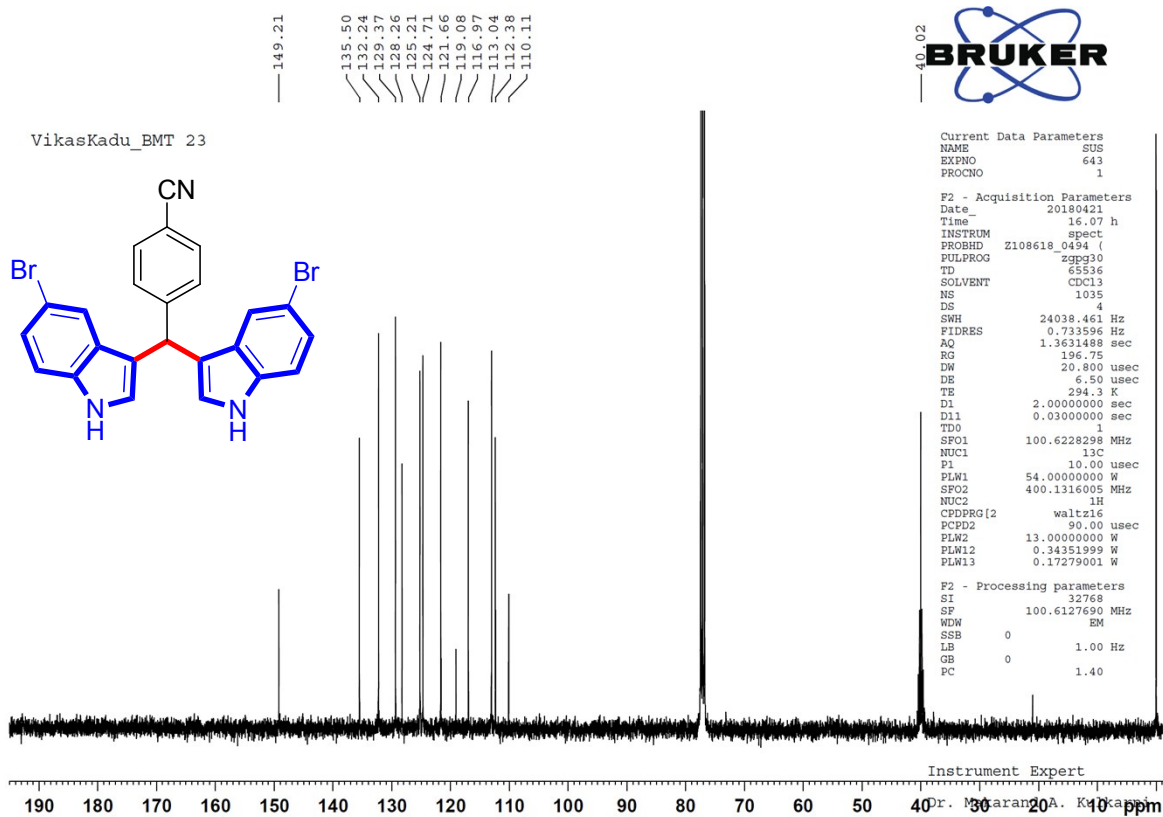
Fri Aug 10 15:35:15 2018 (GMT+05:30)

Dr.Makarand Kulkarni

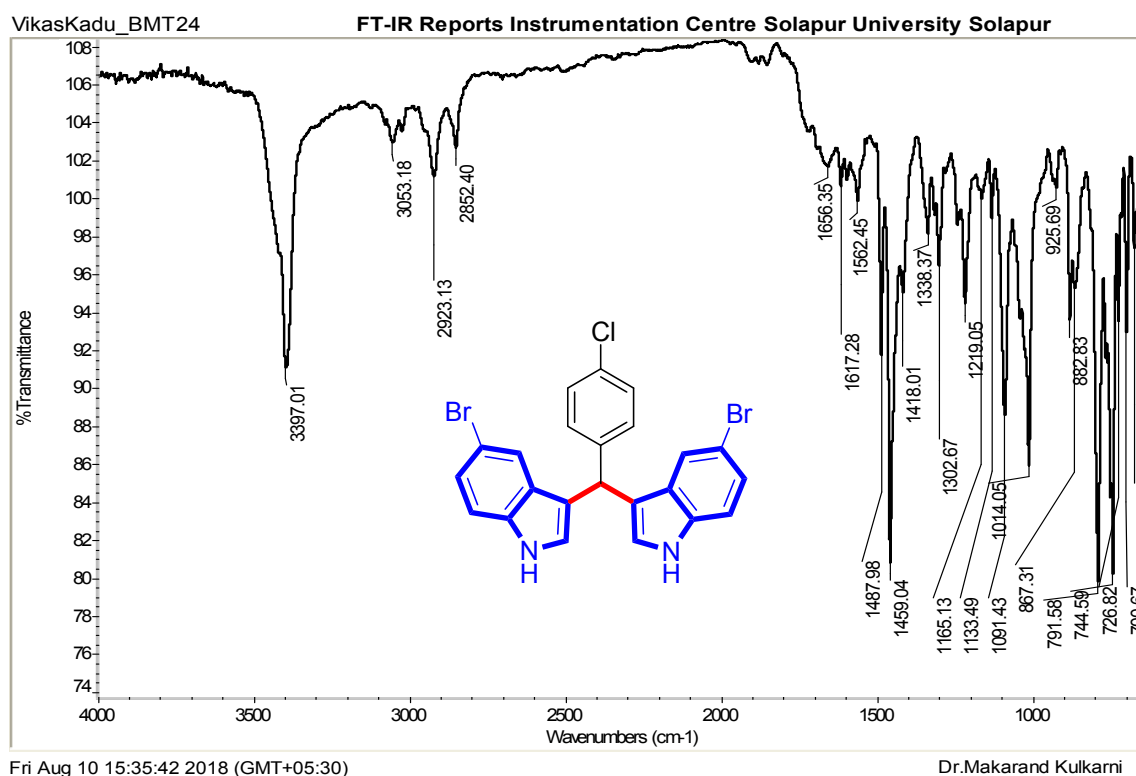
### 1.4.16 <sup>1</sup>H NMR of compound: 3ta



### 1.4.17 <sup>13</sup>C NMR of compound: 3ta

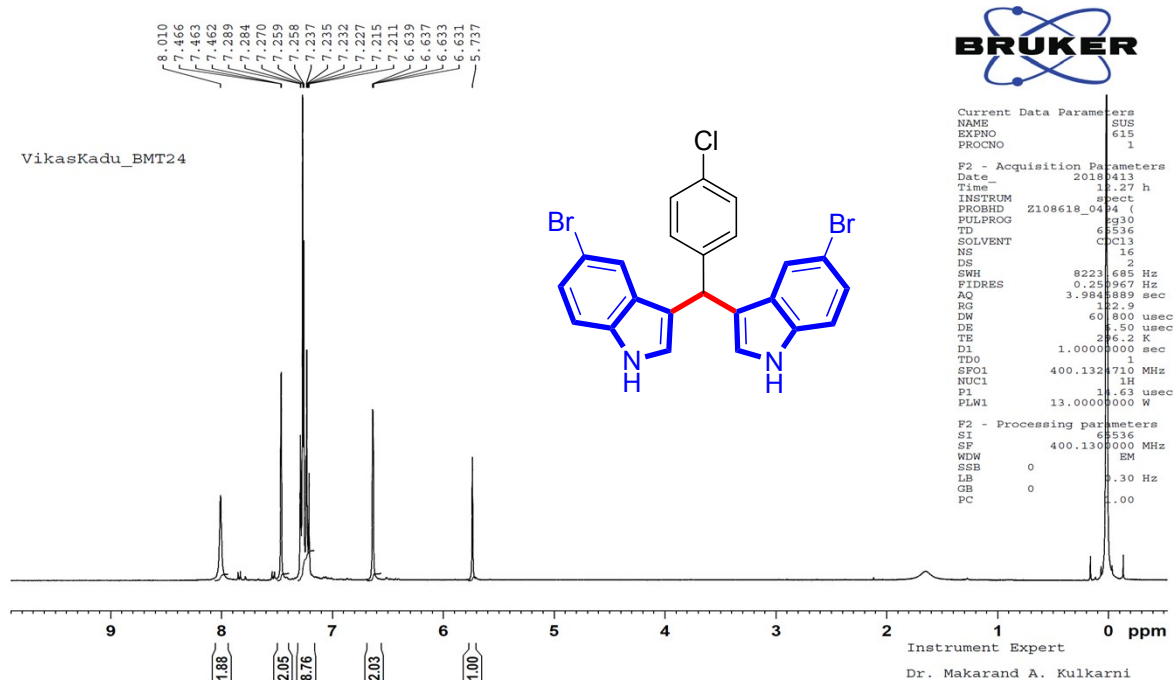


### 1.4.18 IR of compound: 3ua

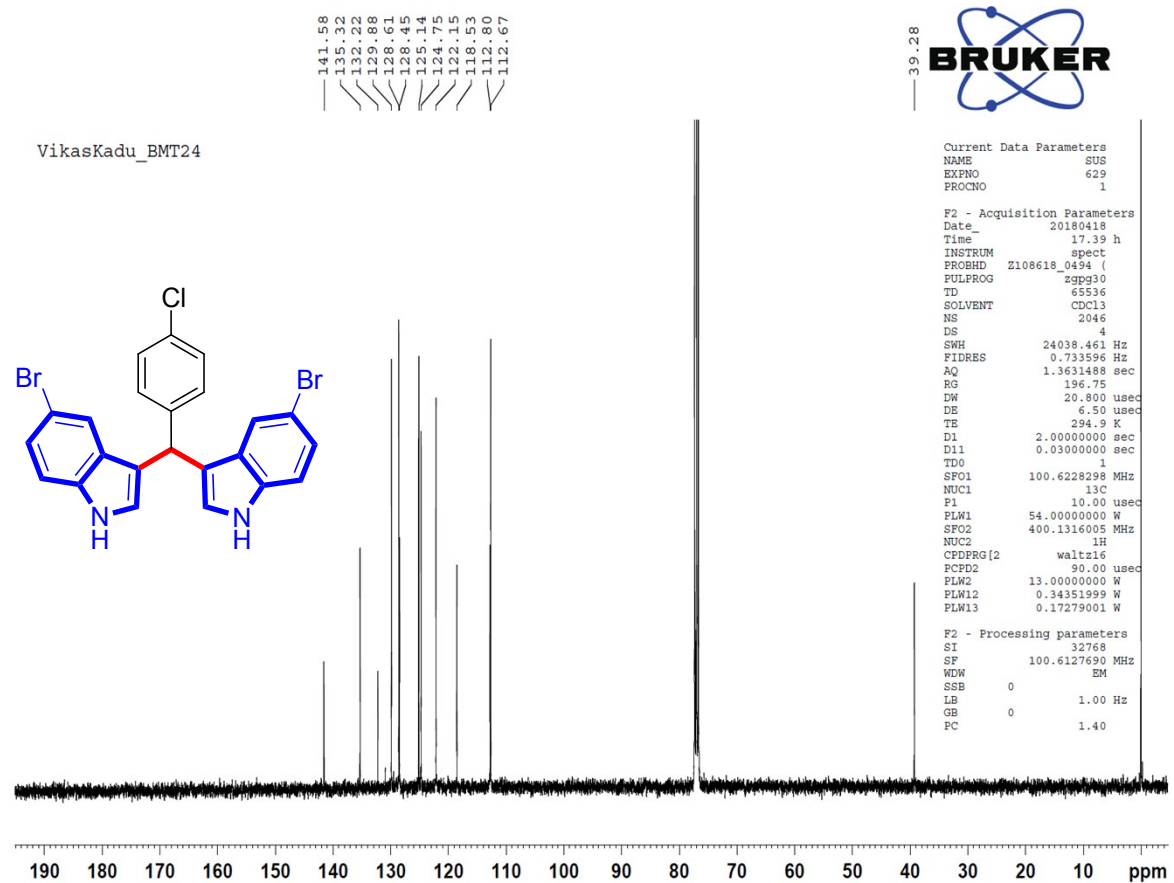


Fri Aug 10 15:35:42 2018 (GMT+05:30)

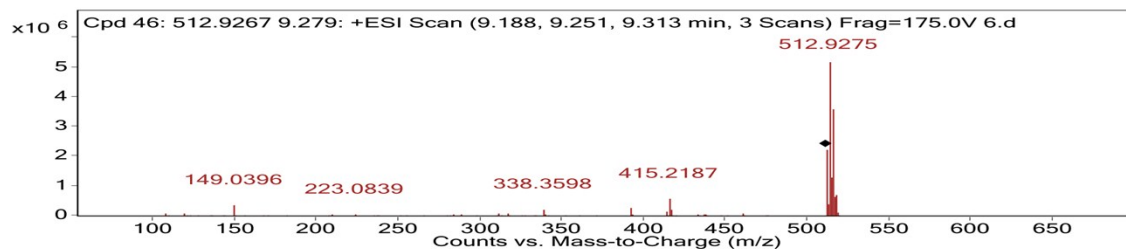
### 1.4.19 <sup>1</sup>H NMR of compound: 3ua



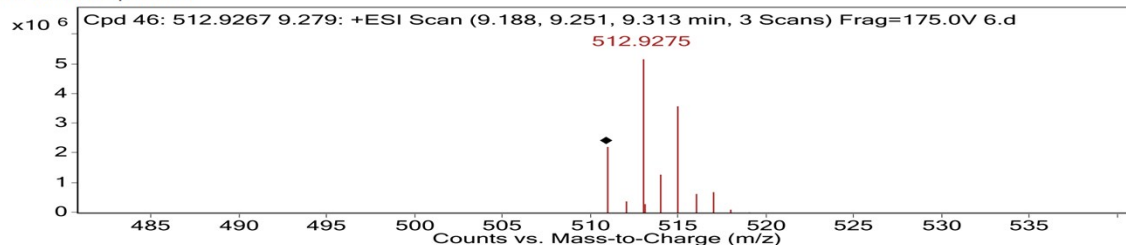
### 1.4.20 <sup>13</sup>C NMR of compound: 3ua



### 1.4.21 HRMS of compound: 3ua

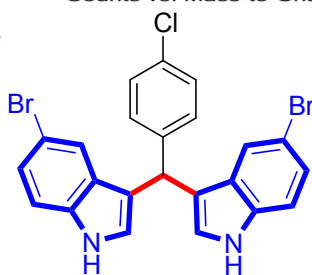


MS Zoomed Spectrum

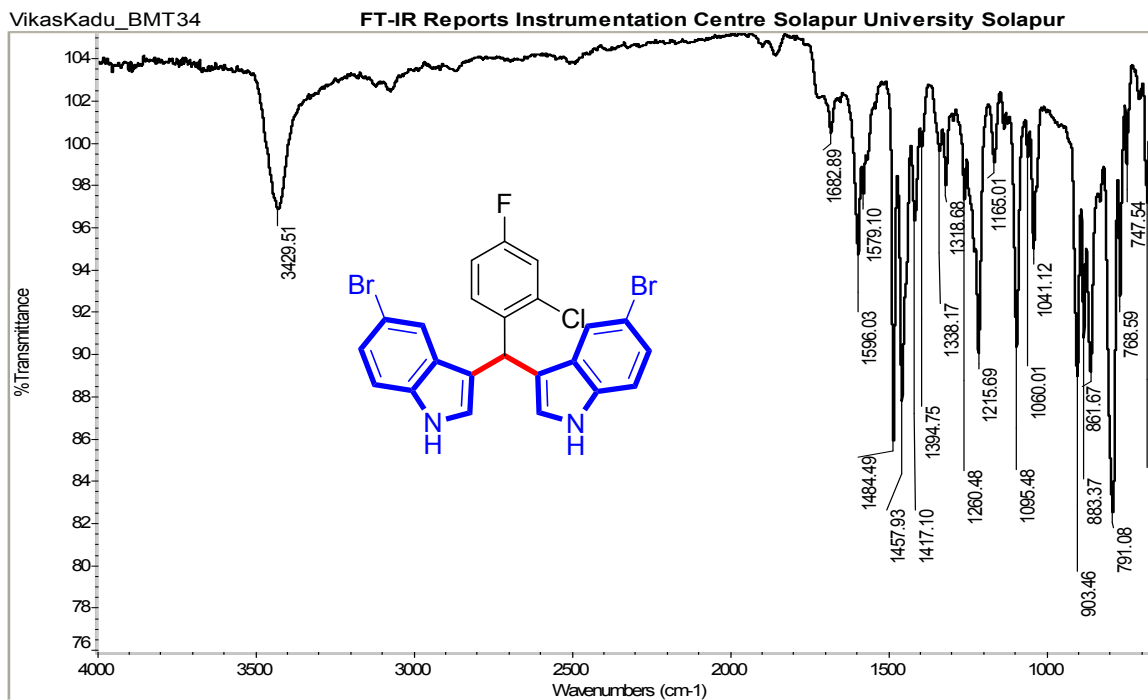


MS Spectrum Peak List

| 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    |



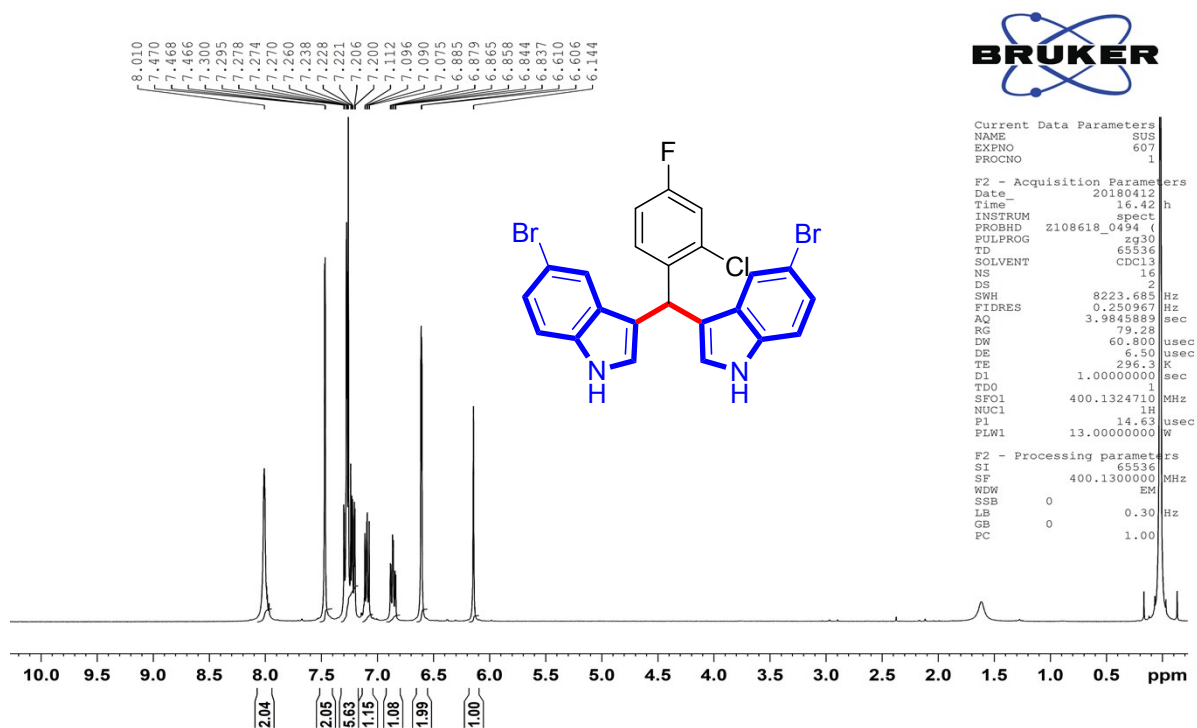
### 1.4.22 IR of compound: 3va



Fri Aug 10 15:38:48 2018 (GMT+05:30)

Dr.Makarand Kulkarni

### 1.4.23 <sup>1</sup>H NMR of compound: 3va



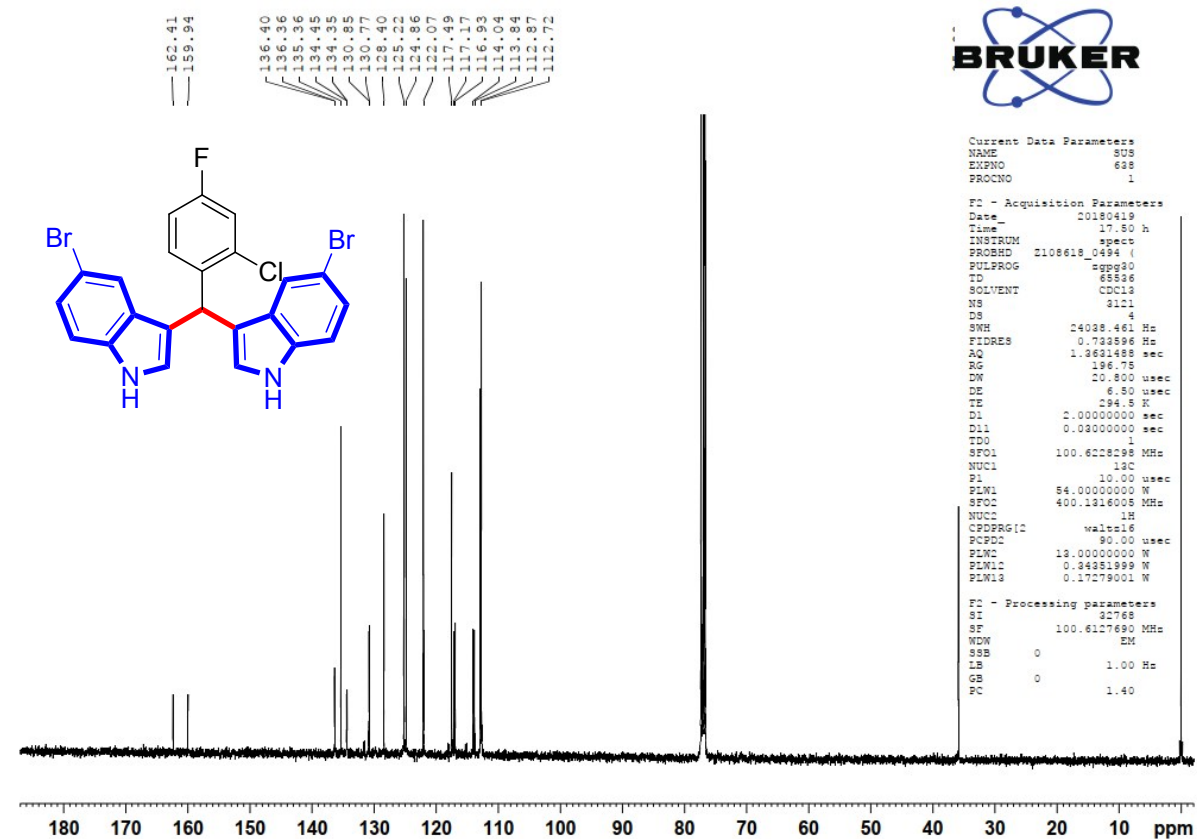
```

Current Data Parameters
NAME      SUS
EXPNO    607
PROCNO   1

F2 - Acquisition Parameters
Date_    20180413
Time_    16.42 h
INSTRUM  spect
PROBHD   Z108618_0494 (
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       8223.685 Hz
FIDRES    0.250967 Hz
AQ         3.9845889 sec
RG         79.28
DW         60.800 usec
DE         6.50 usec
TE         296.3 K
D1         1.00000000 sec
TDO        1
SFO1      400.1324710 MHz
NUC1       1H
F1         14.63 usec
PLW1      13.00000000 W

F2 - Processing parameters
SI         65536
SF         400.1300000 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```

### 1.4.24 <sup>13</sup>C NMR of compound: 3va



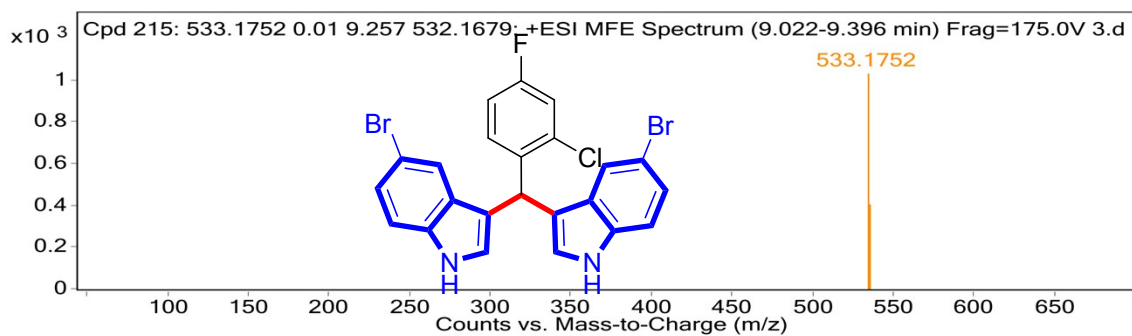
```

Current Data Parameters
NAME      SUS
EXPNO    68
PROCNO   1

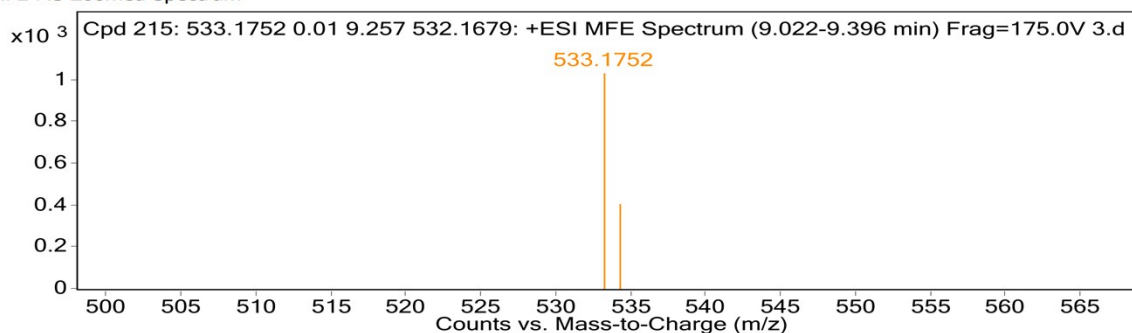
F2 - Acquisition Parameters
Date_    20180419
Time_    17.50 h
INSTRUM  spect
PROBHD   Z108618_0494 (
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        3121
DS        4
SWH       24028.461 Hz
FIDRES    0.722596 Hz
AQ         1.3621488 sec
RG         196.75
DW         20.800 usec
DE         6.50 usec
TE         294.5 K
D1         2.00000000 sec
D11        0.03000000 sec
TDO        1
SFO1      100.6228298 MHz
NUC1       13C
F1         10.00 usec
PLW1      84.00000000 W
SFO2      400.1316005 MHz
NUC2       1H
CPDPRG2   waltz16
PCPD2     90.00 usec
PLWC      13.00000000 W
PLW2     0.34451999 W
PLW3     0.17279001 W

F2 - Processing parameters
SI         22768
SF         100.6127690 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

### 1.4.25 HRMS of compound: 3va



MFE MS Zoomed Spectrum

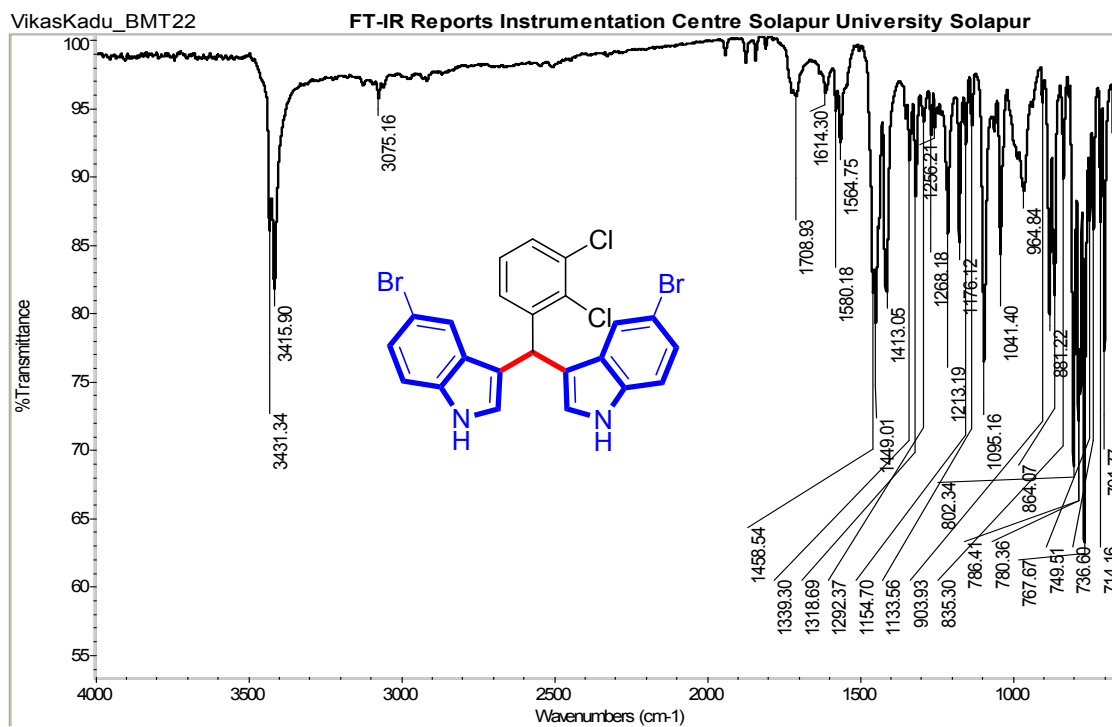


MS Spectrum Peak List

| m/z      | z | Abund  | Ion                |
|----------|---|--------|--------------------|
| 533.1752 | 1 | 1035.1 | (M+H) <sup>+</sup> |
| 534.1848 | 1 | 408.16 | (M+H) <sup>+</sup> |

MS Spectrum

### 1.4.26 IR of compound: 3wa

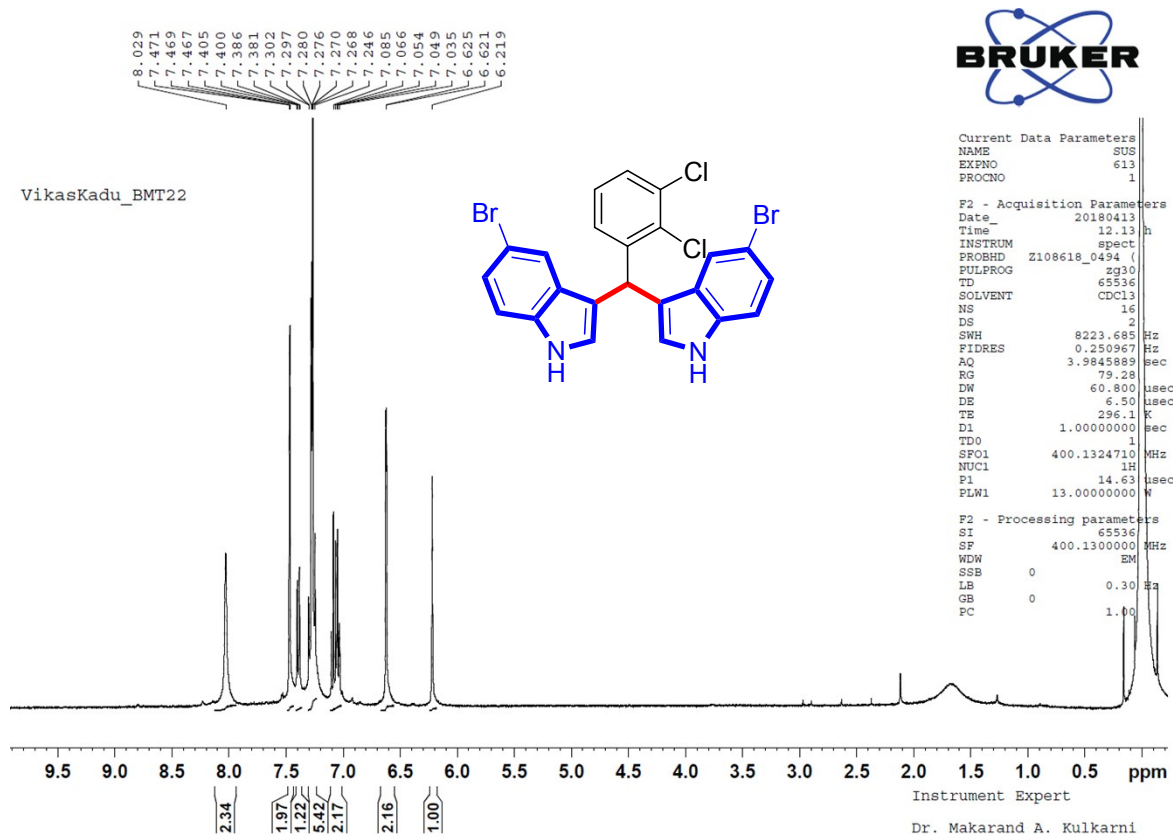


Fri Aug 10 15:34:49 2018 (GMT+05:30)

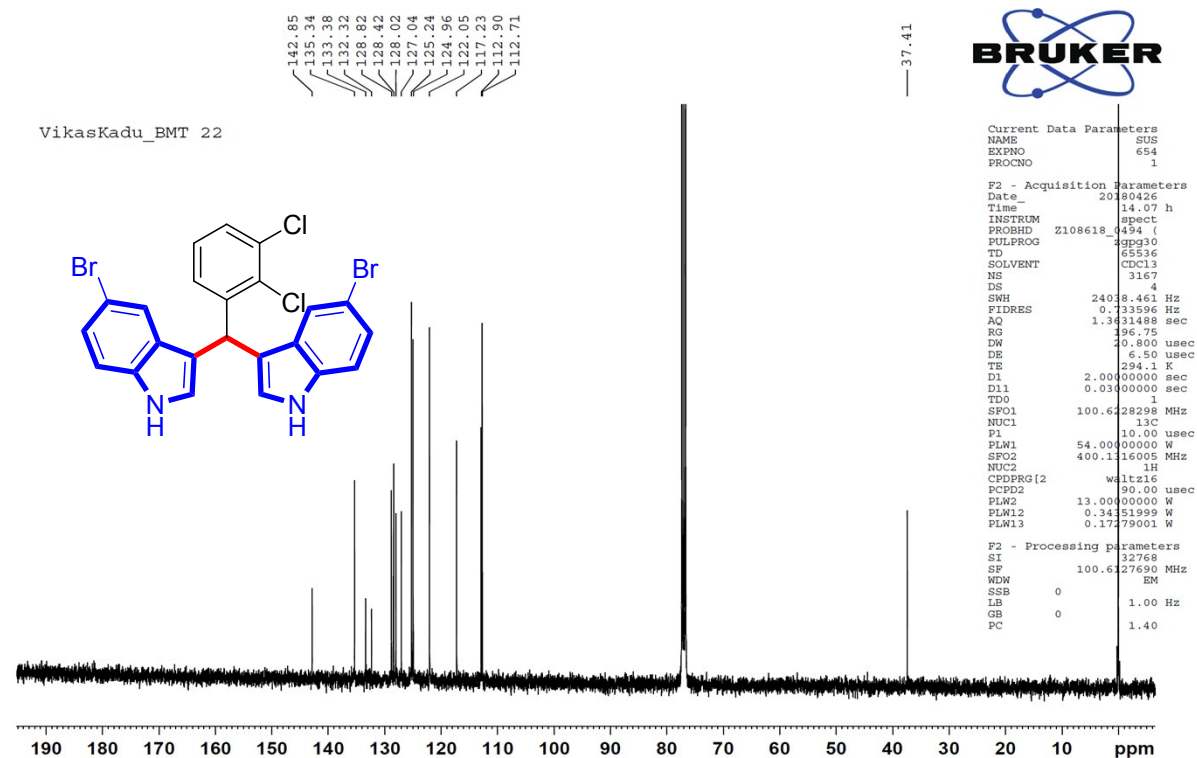
Dr.Makarand Kulkarni



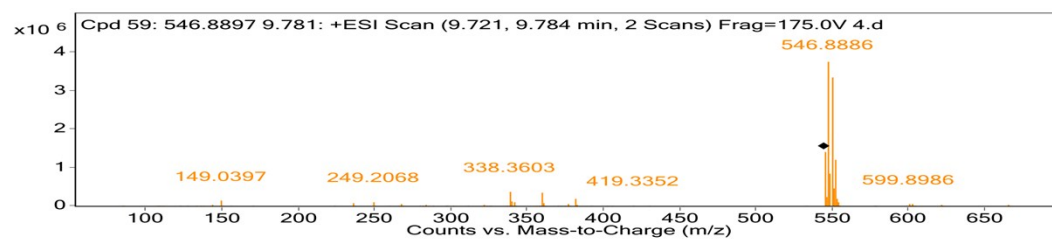
### 1.4.27 <sup>1</sup>H NMR of compound: 3wa



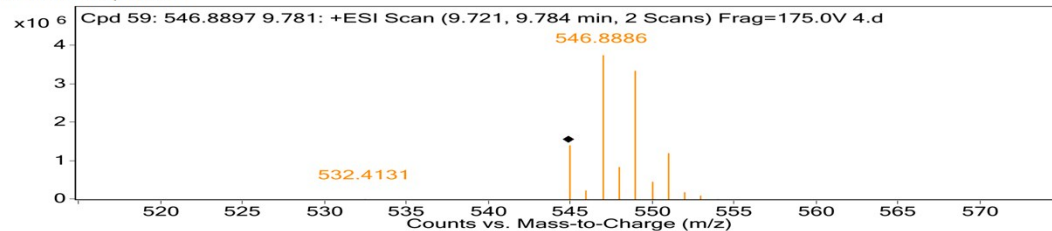
### 1.4.28 <sup>13</sup>C NMR of compound: 3wa



### 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 | 1 | 517668.06  |
| 548.8866 | 1 | 3358197.75 |
| 549.9018 | 1 | 467957.56  |
| 550.8863 | 1 | 1208713.38 |

