Supporting Information

Zinc Triflate Catalyzed 1,3-Indolylation of Cyclohexanones: Tandem Condensation, Dehydrogenation and Aromatization Sequence

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2. Hydrogen gas Evolution Experiment:

In control experiment, hydrogen gas evolution experiment was performed using GCMS technique. To a stirred mixture of *N*-methyl indole (**1a**) (200 mg, 1.52 mmol) in 1,4-Dioxane, cyclohexanone (**2a**) (90 mg, 0.92 mmol) and Zn(OTf)$_2$ (111 mg, 20 mol%) were added in ace pressure tube and covered by rubber septum attached with a tedlar bag. The mixture was stirred at 120 ^{0}C temperature. After 24 h, the tedlar bag was removed and reattached into the inlet of GCMS instrument for detecting the gases formed in the reaction mixture. The peak for hydrogen gas was observed from the reaction mixture, which exactly matched with the standard for identifying hydrogen gas (at 0.088 minutes' retention time) (**Figure S1-S2**).

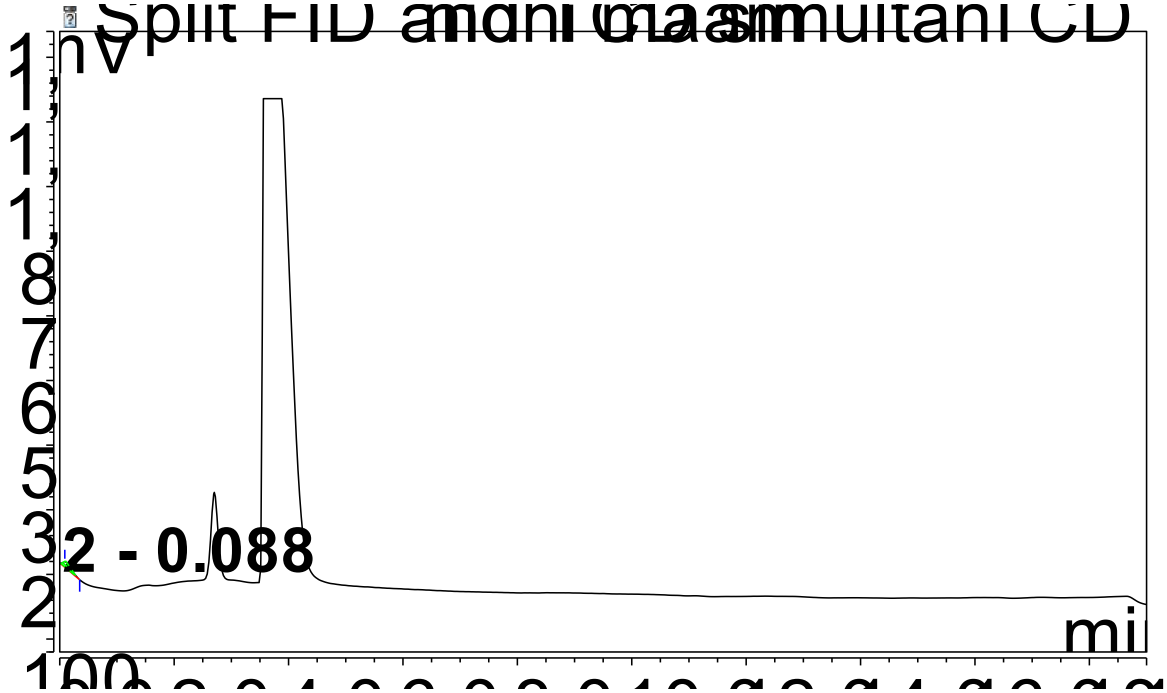


Figure S1. Hydrogen gas peak from reaction mixture.

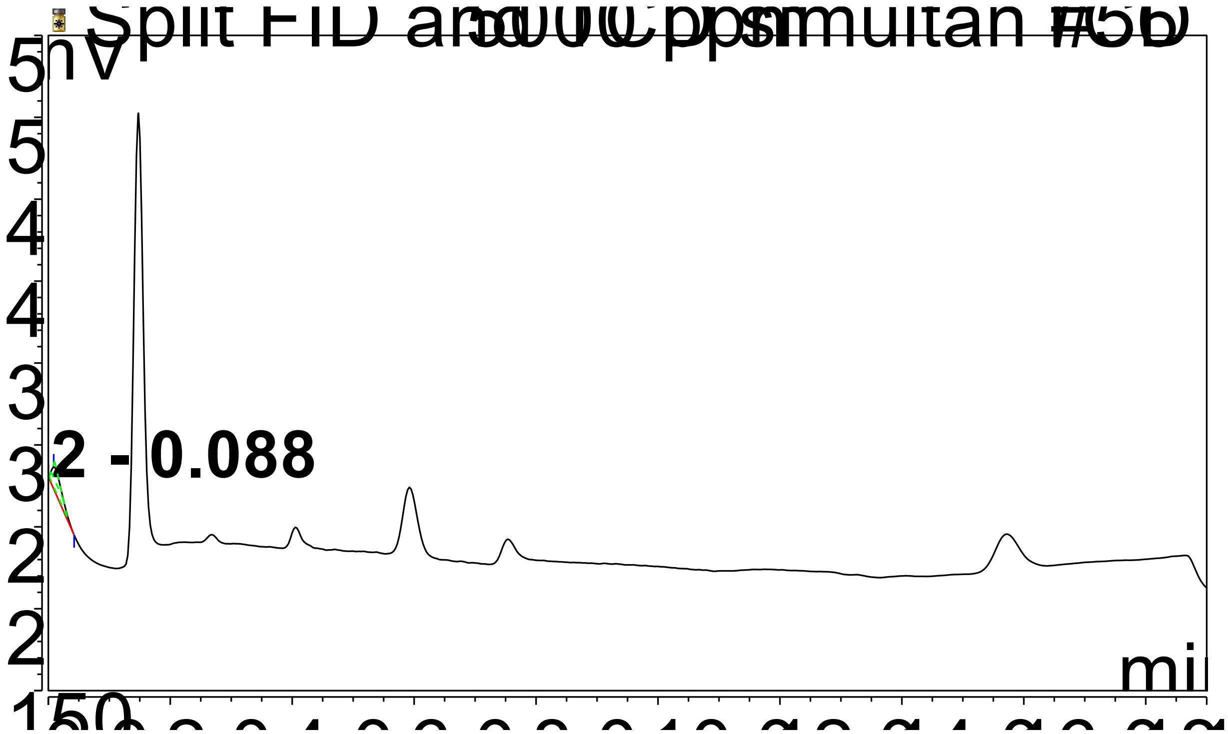


Figure S2. Standard for identifying Hydrogen gas.

3. Time dependent ^{1}H NMR of reaction mixture:

The mechanism was probed by time dependent NMR studies of the reaction mixture (**Figure S3**). The reaction of *N*-methyl indole (**1a**) (200 mg, 1.52 mmol) was performed with cyclohexanone (**2a**) (90 mg, 0.92 mmol) under the standard reaction conditions. At different time intervals, 20 µL aliquot was drawn out from reaction mixture and ^{1}H NMR of the sample was carried out. The time dependent ^{1}H NMR of reaction mixture showed appearance of new olefinic proton peaks at 4.1 and 6.2 ppm at 6 h and 12 h of reaction time respectively.

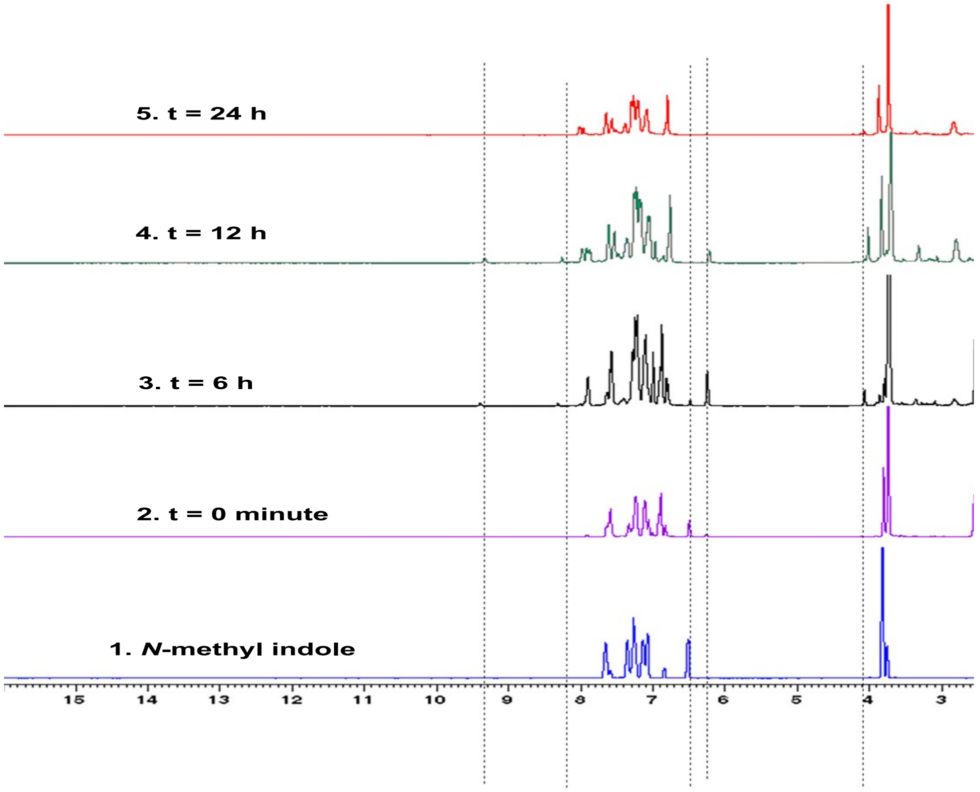
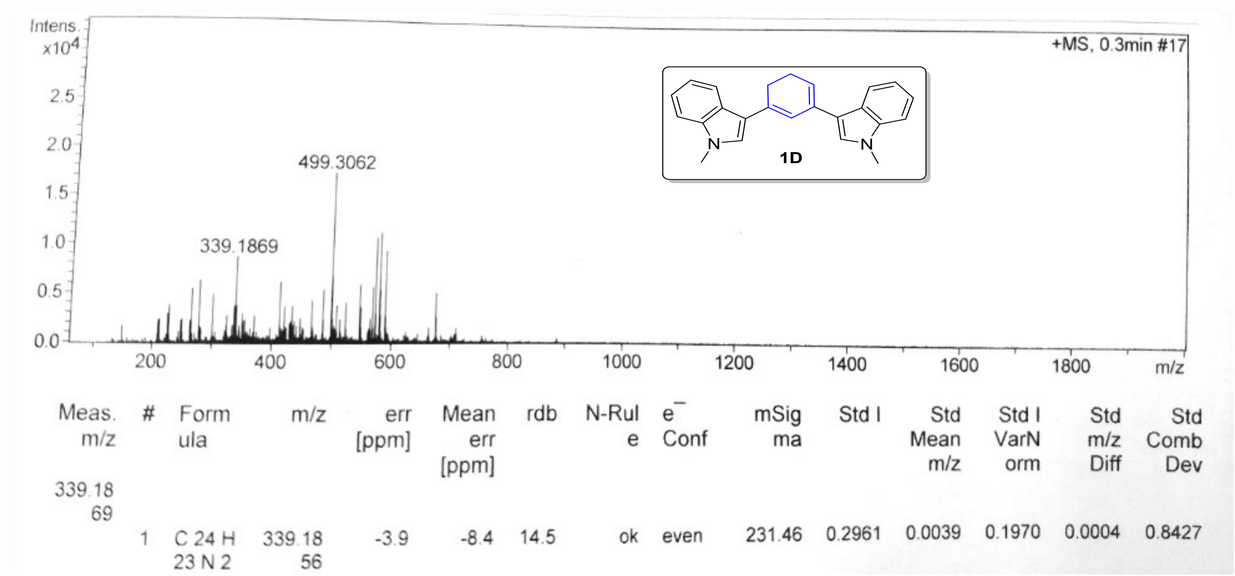


Figure S3. Time dependent ^{1}H NMR spectra of reaction mixture.

4. HRMS (ESI-MS) of intermediate 1D:

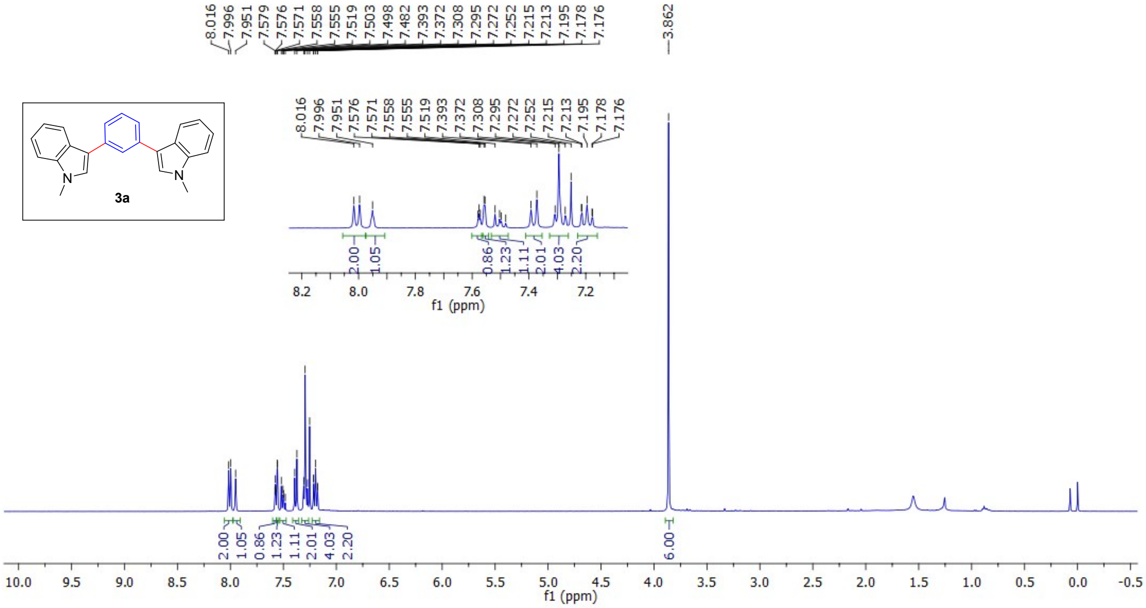
The formation of intermediate **1D** is detected by HRMS of reaction mixture. For this, a reaction of *N*-methyl indole (**1a**) (200 mg, 1.52 mmol) was performed with cyclohexanone (**2a**) (90 mg, 0.92 mmol) under the standard reaction conditions. After 12 h, an aliquot was drawn out, extracted extracted with ethyl acetate and concentrated. The resulting suspension was diluted with acetonitrile, filtered and injected for HRMS study. HRMS of the reaction mixture showed mass/charge $[M+H]^+$ at 339.1869 for the intermediate **1D (Figure S4**).



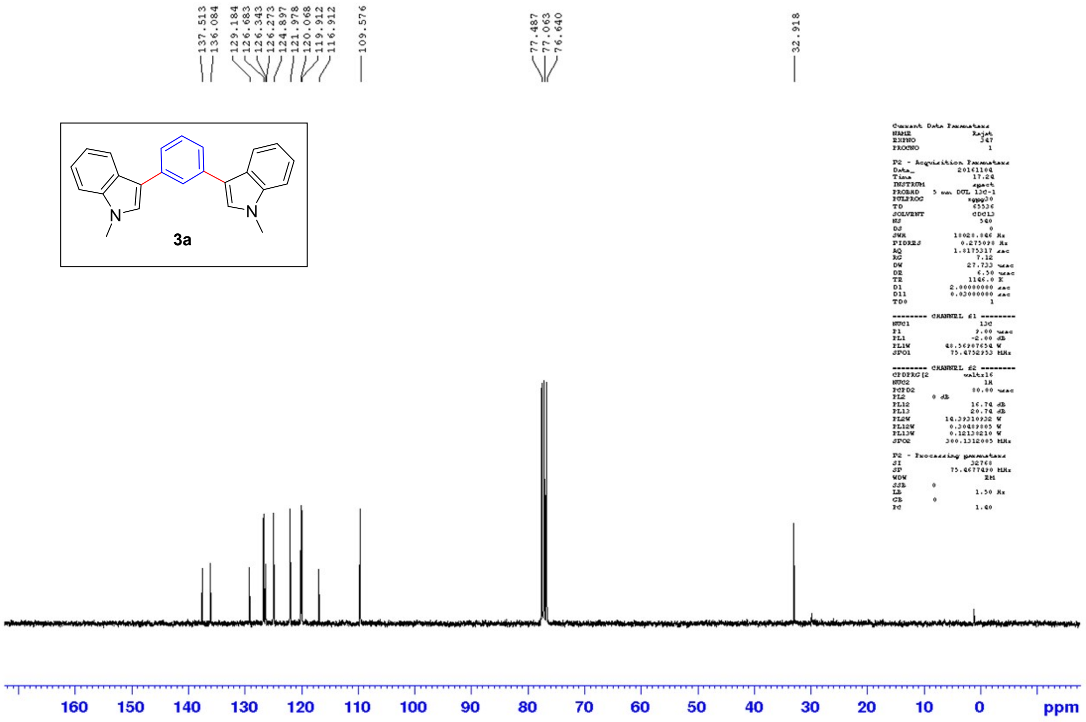
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e$^-$ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
339.1869														
	1	C 24 H 23 N 2	339.1856	-3.9	-8.4	14.5	ok	even	231.46	0.2961	0.0039	0.1970	0.0004	0.8427

Figure S4. HRMS of intermediate **1D**.

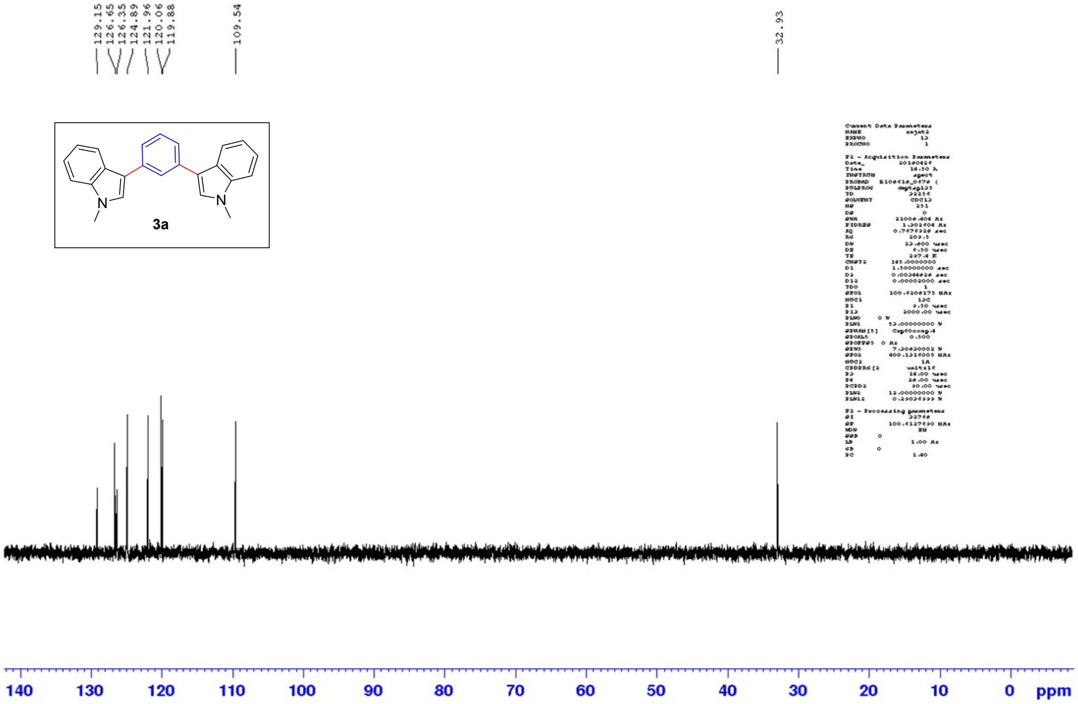
8. Copies of ^{1}H NMR, ^{13}C NMR and DEPT-135 spectra:



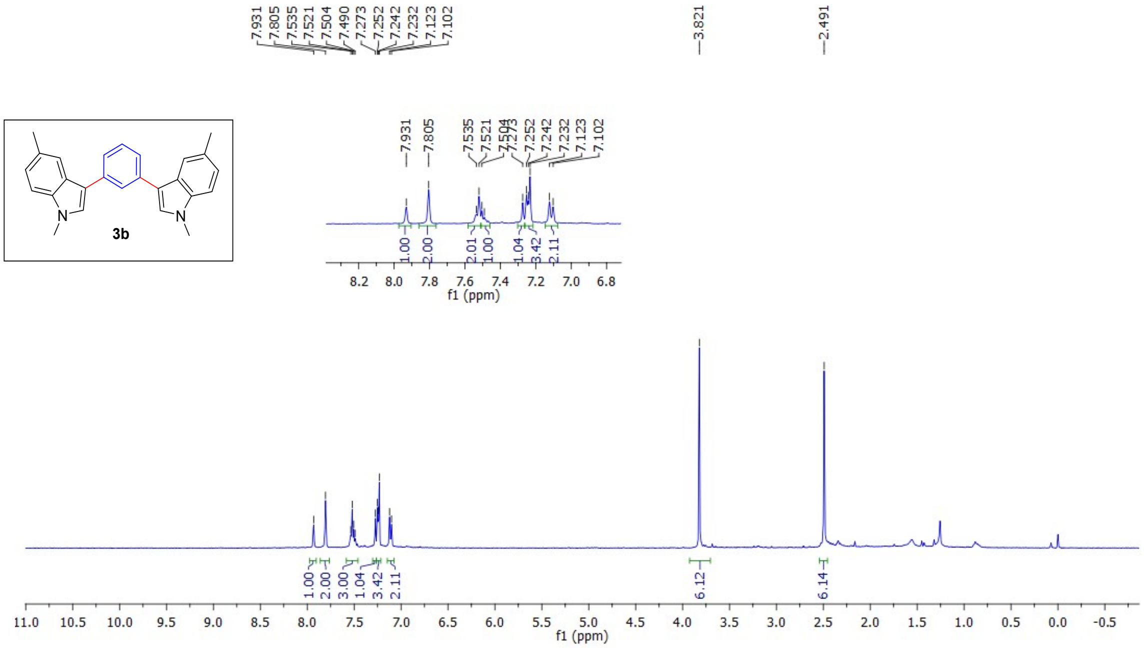
Spectrum 1. 400 MHz ^{1}H NMR of compound 3a



Spectrum 2. 75 MHz ^{13}C NMR of compound 3a



Spectrum 3. 100 MHz DEPT-135 NMR of compound 3a



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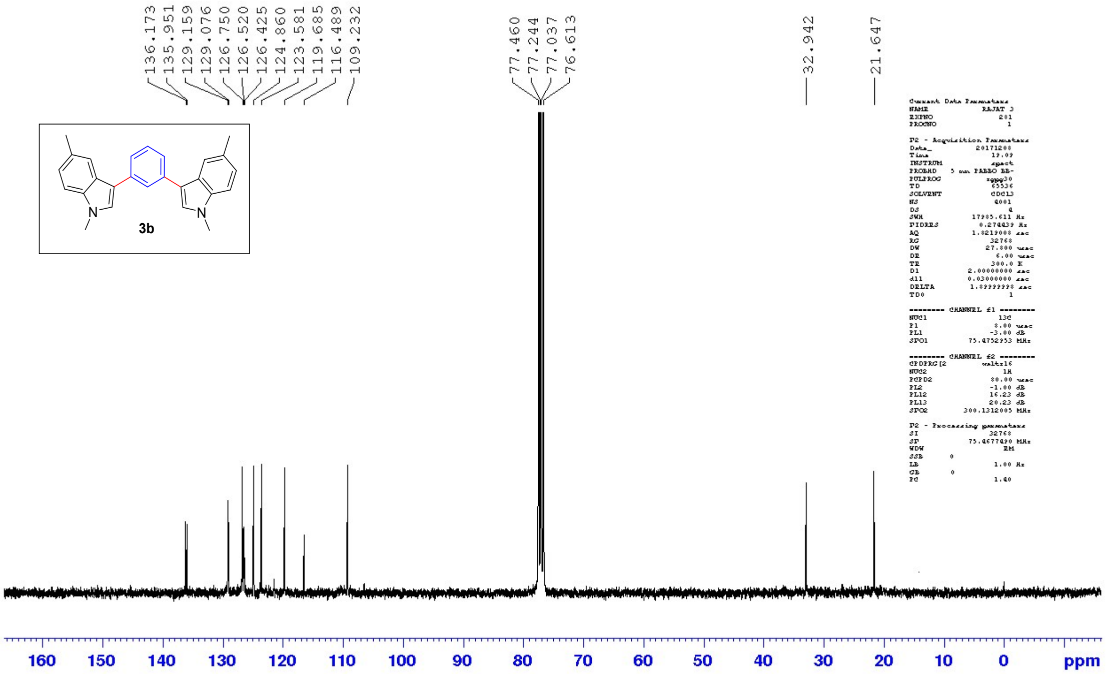
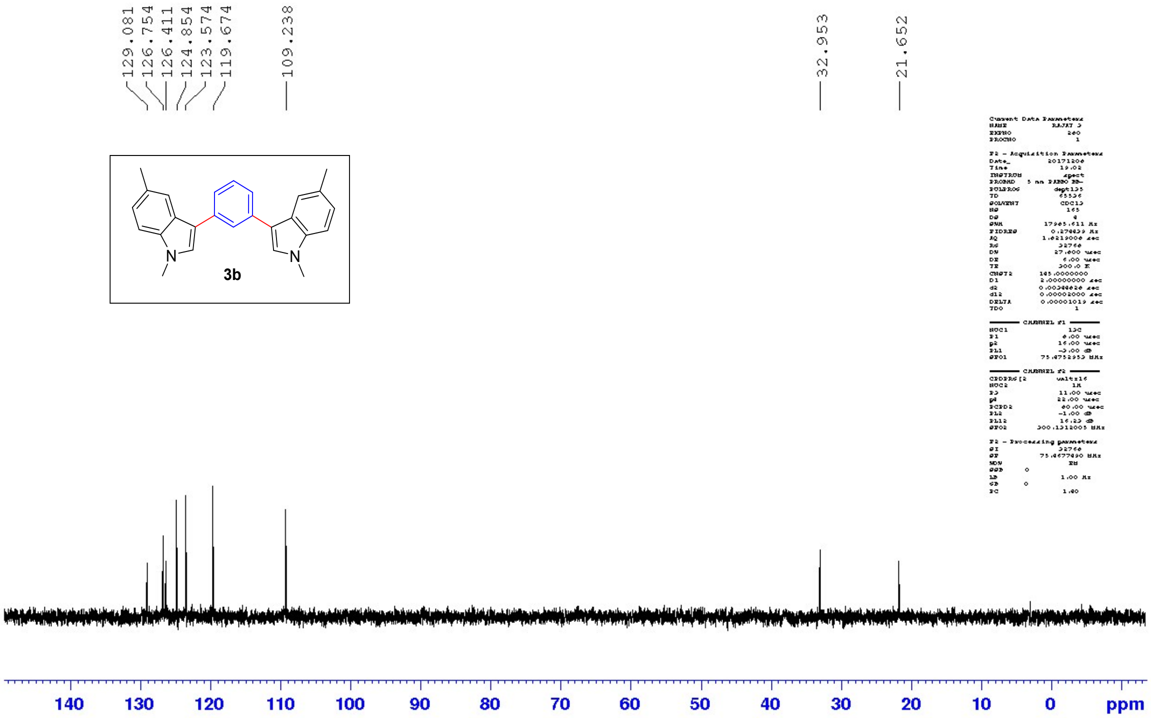
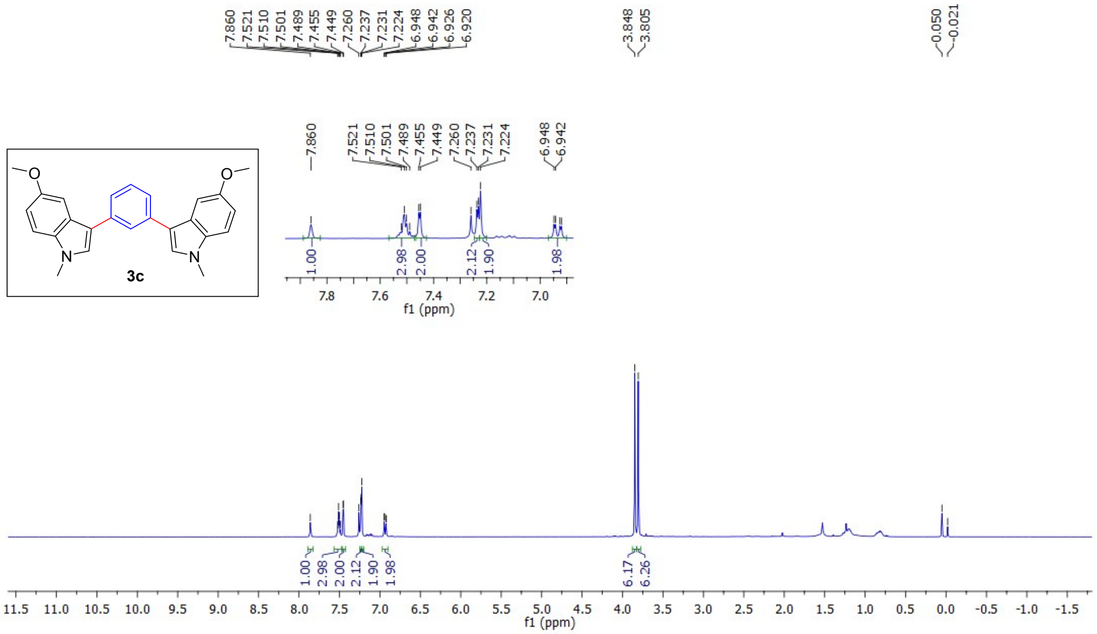


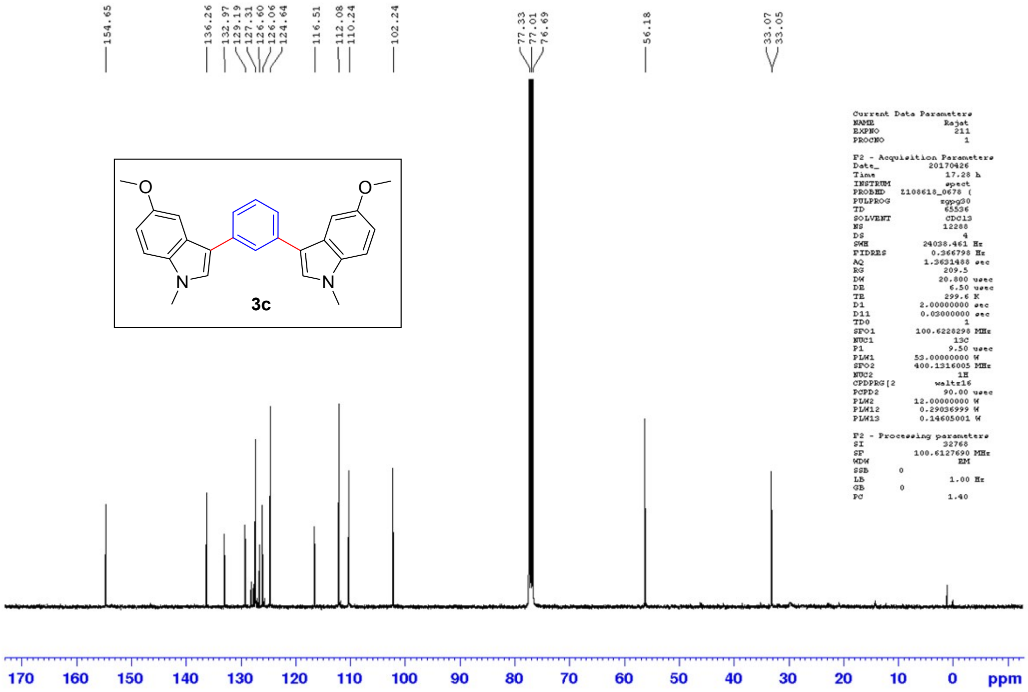
Spectrum 5. 75 MHz ^{13}C NMR of compound 3b



Spectrum 6. 75 MHz DEPT-135 NMR of compound 3b



Spectrum 7. 400 MHz ^{1}H NMR of compound 3c



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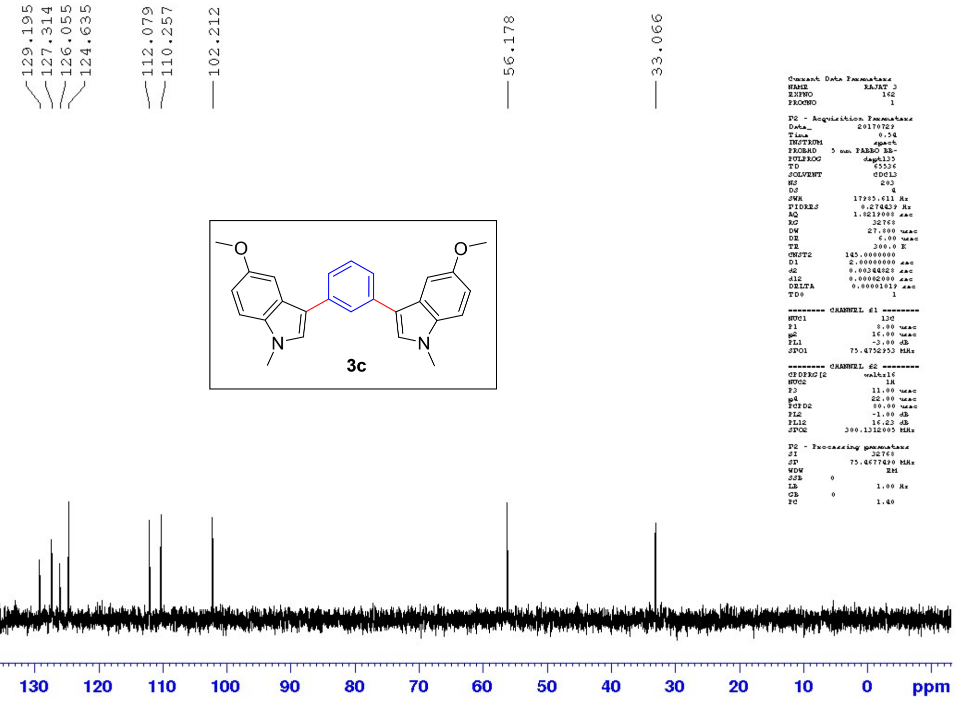
Spectrum 8. 100 MHz ^{13}C NMR of compound 3c



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NUC2                   1H
P3                  11.00 usec
p4                  22.00 usec
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SFO2          300.1312005 MHz

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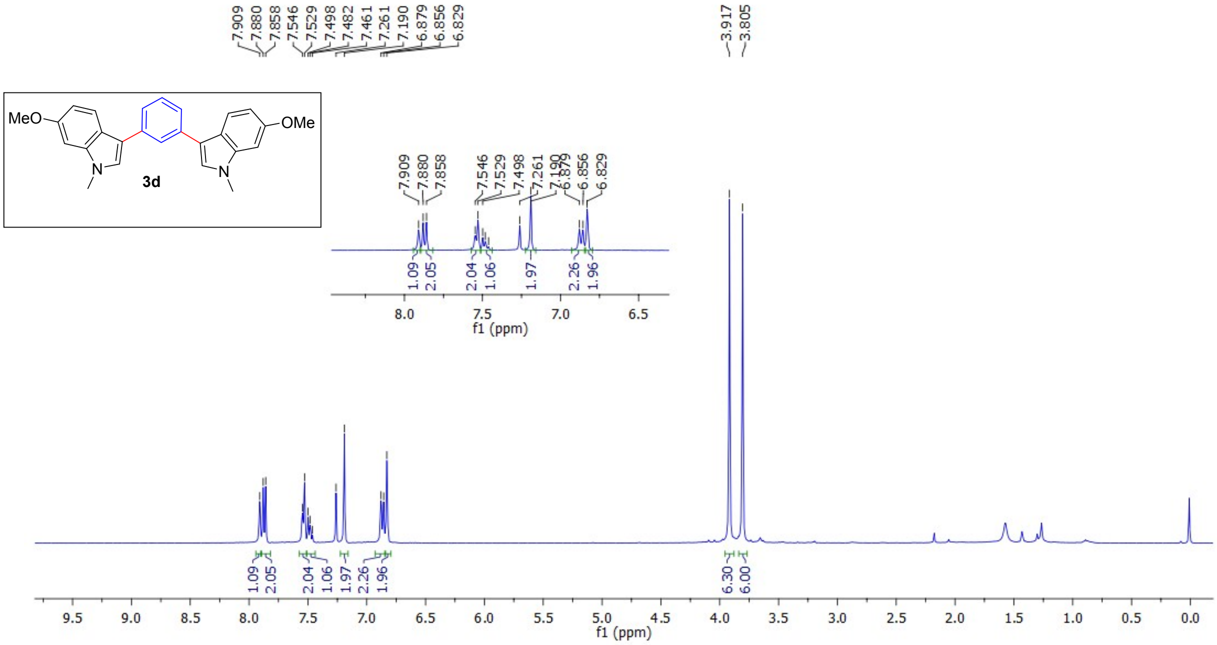
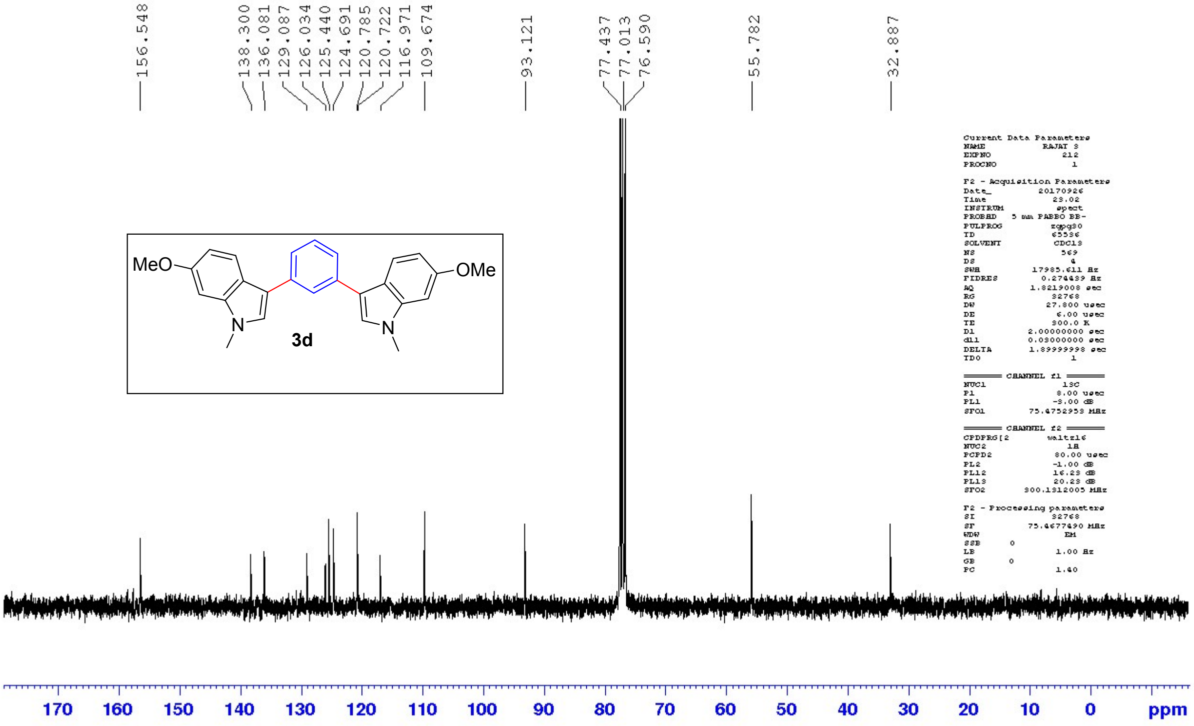
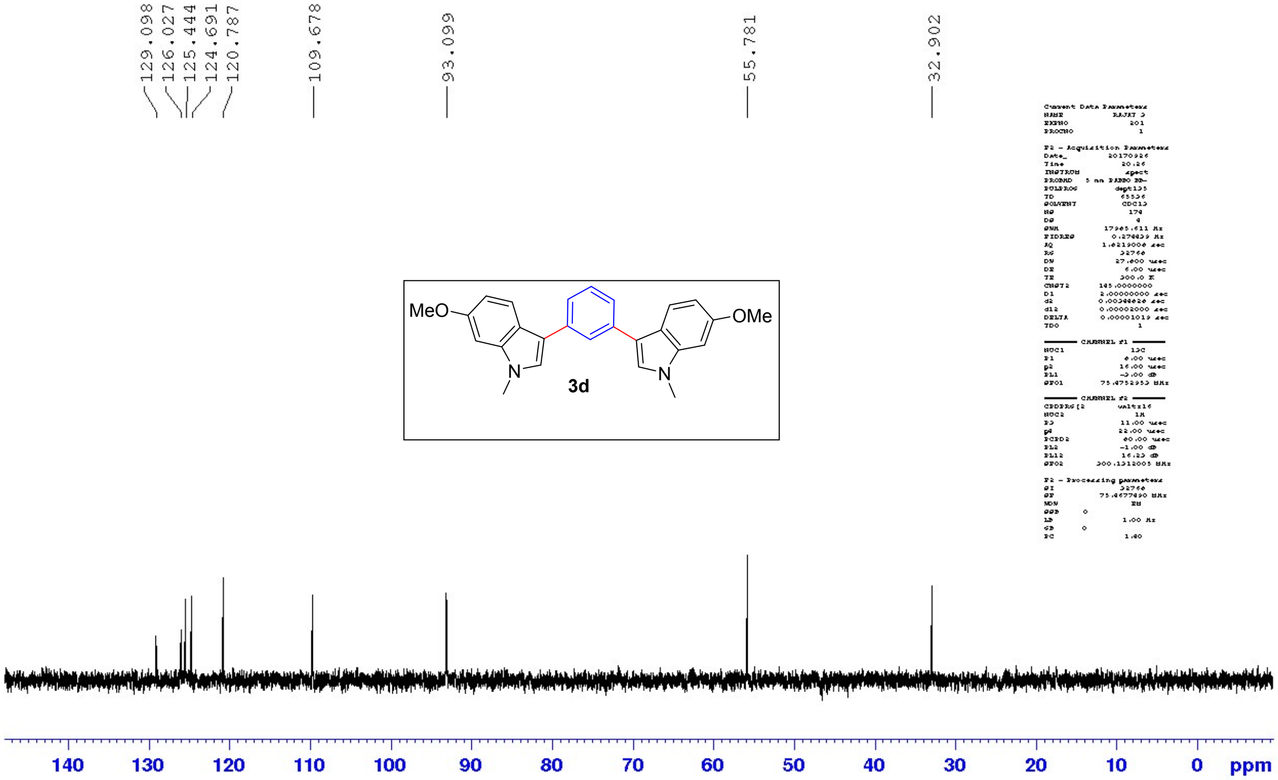
Spectrum 9. 75 MHz DEPT-135 NMR of compound 3c



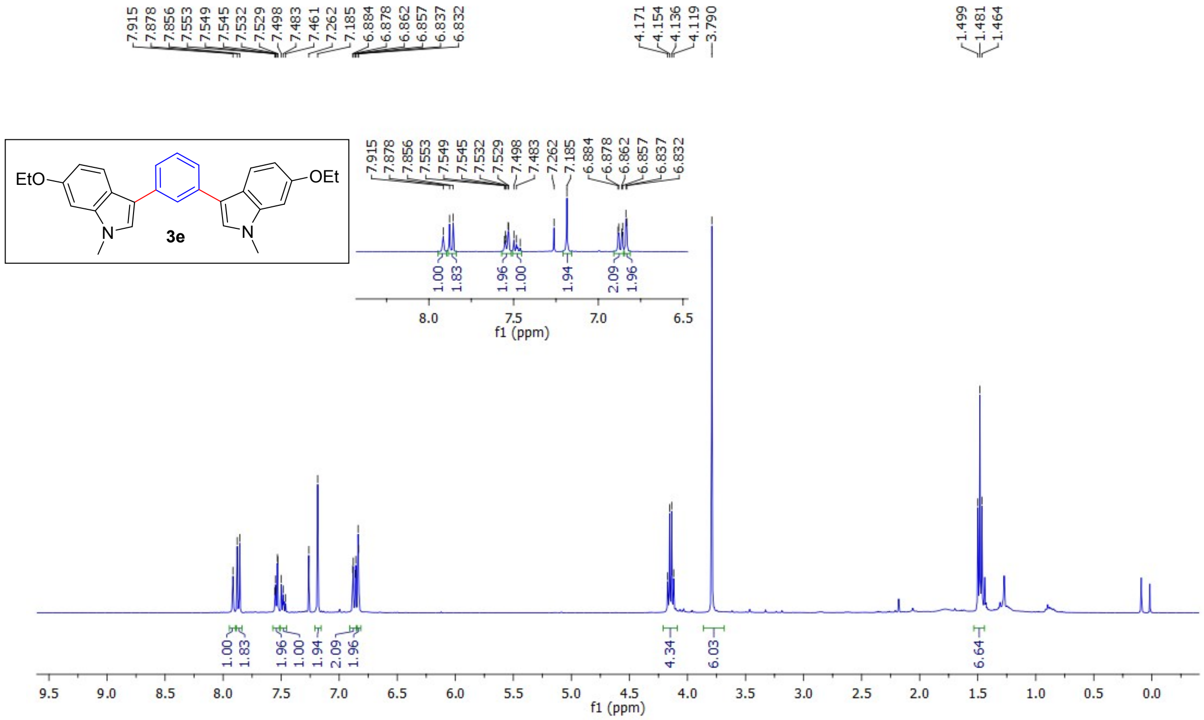
Spectrum 10. 400 MHz ^{1}H NMR of compound 3d



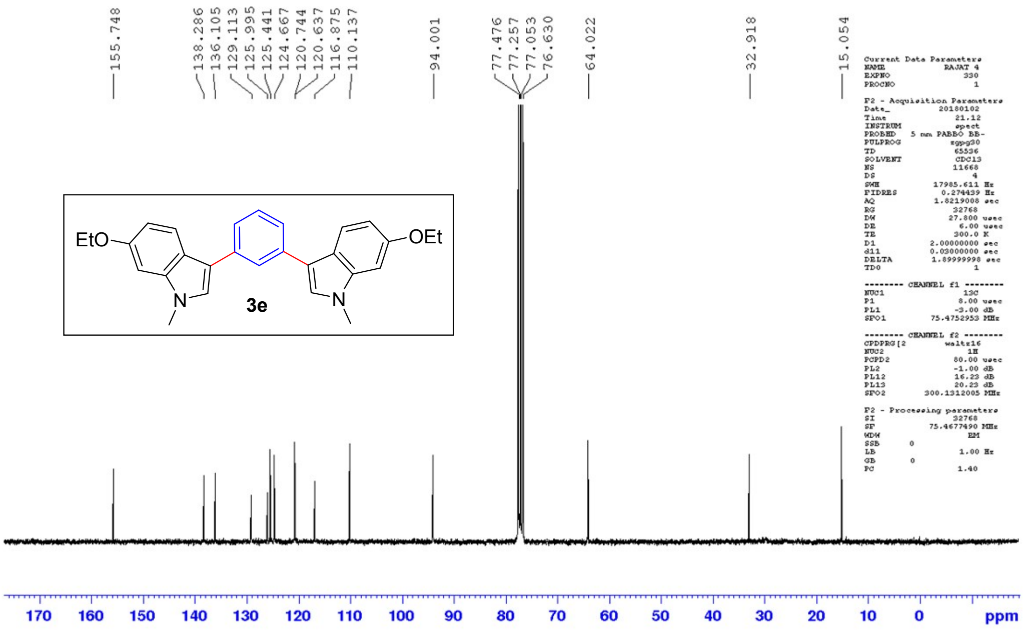
Spectrum 11. 75 MHz ^{13}C NMR of compound 3d



Spectrum 12. 75 MHz DEPT-135 NMR of compound 3d



Spectrum 13. 400 MHz ^{1}H NMR of compound 3e



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DELTA          1.89999998 sec
TD0                     1

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P1                   8.00 usec
PL1                 -3.00 dB
SFO1           75.4752953 MHz

-------- CHANNEL f2 --------
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NUC2                   1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                16.23 dB
PL13                20.23 dB
SFO2          300.1312005 MHz

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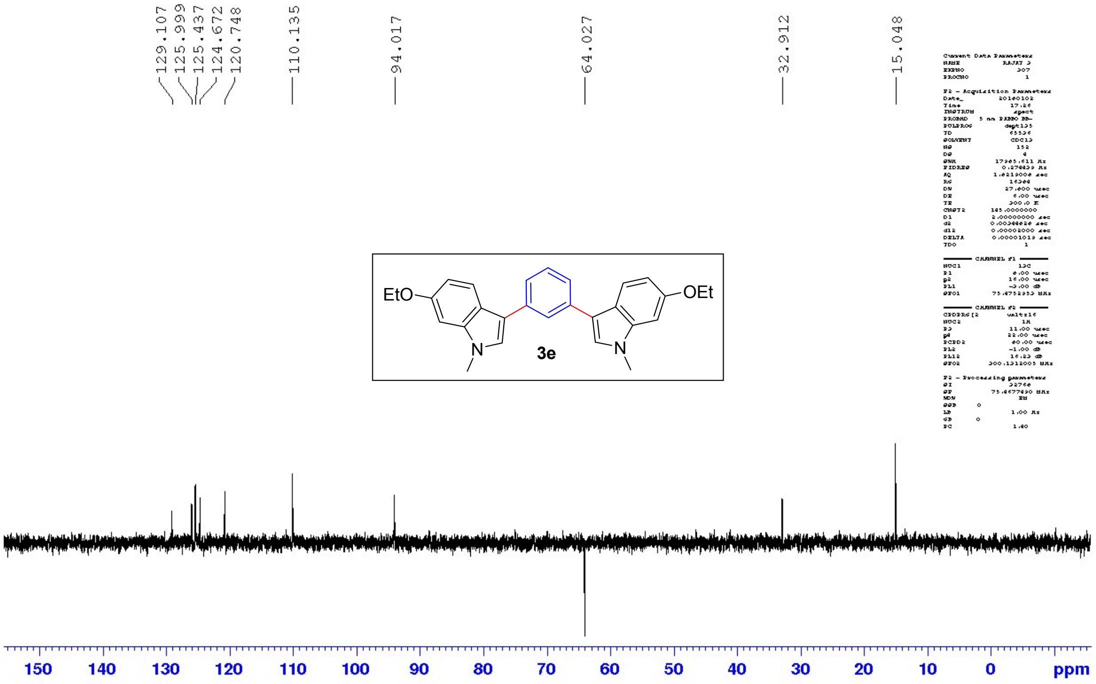

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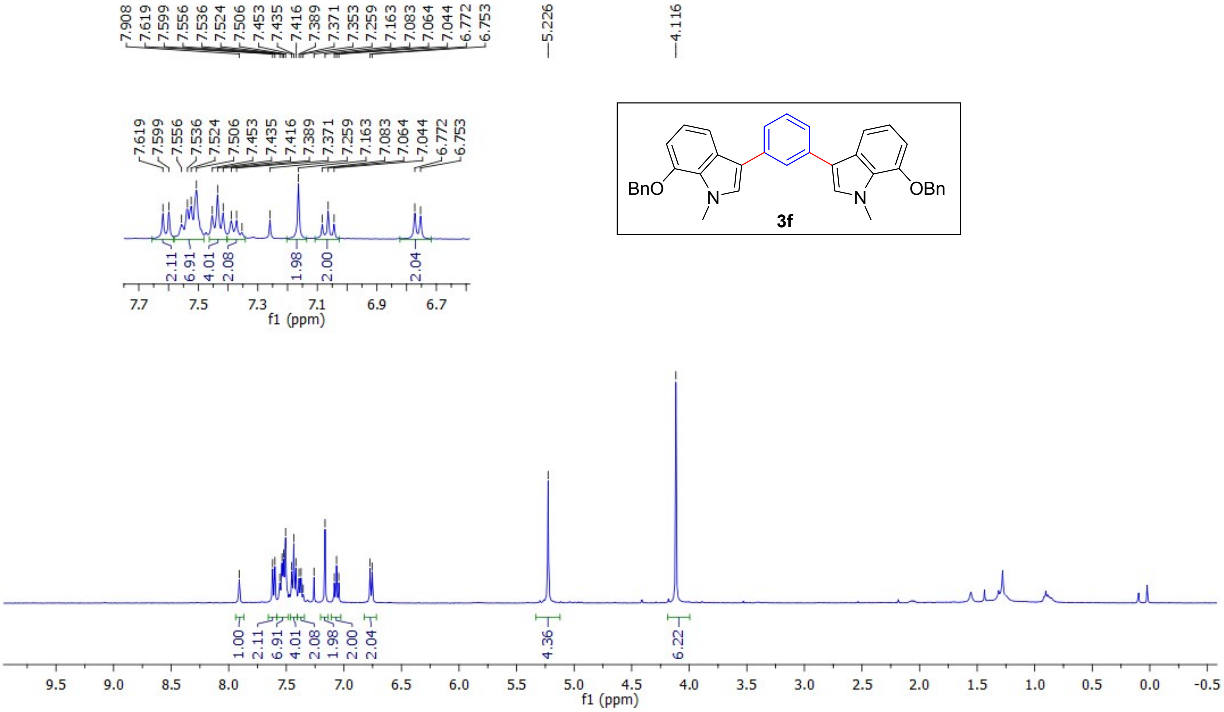
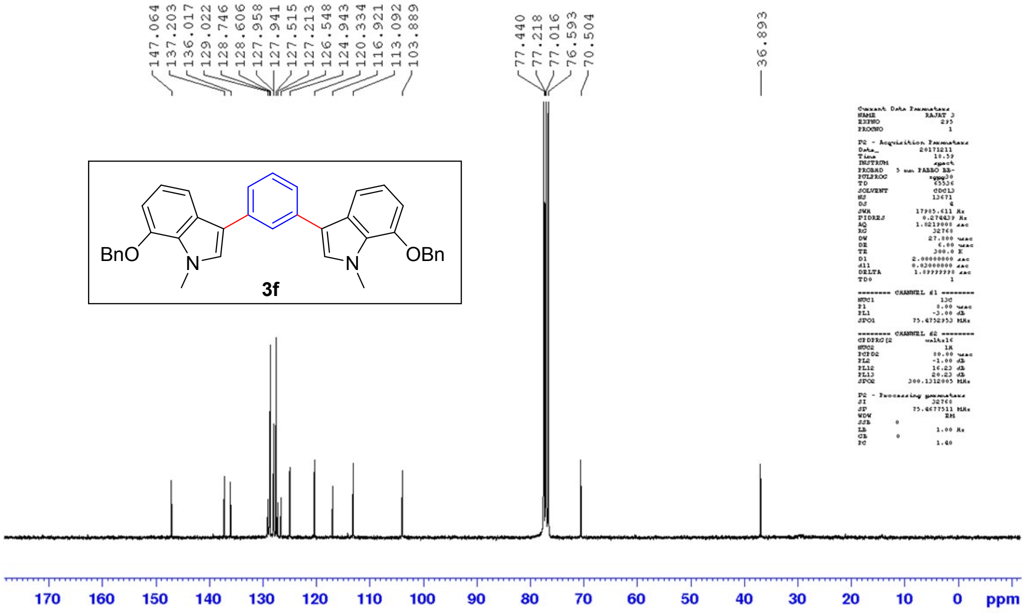
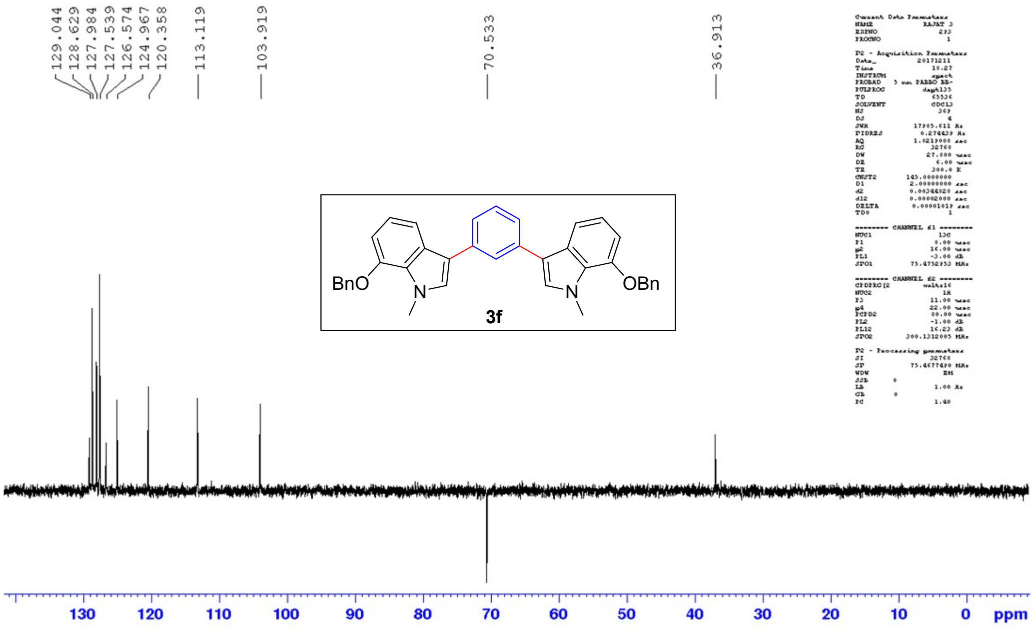


Spectrum 16. 400 MHz ^{1}H NMR of compound 3f



Spectrum 17. 75 MHz ^{13}C NMR of compound 3f



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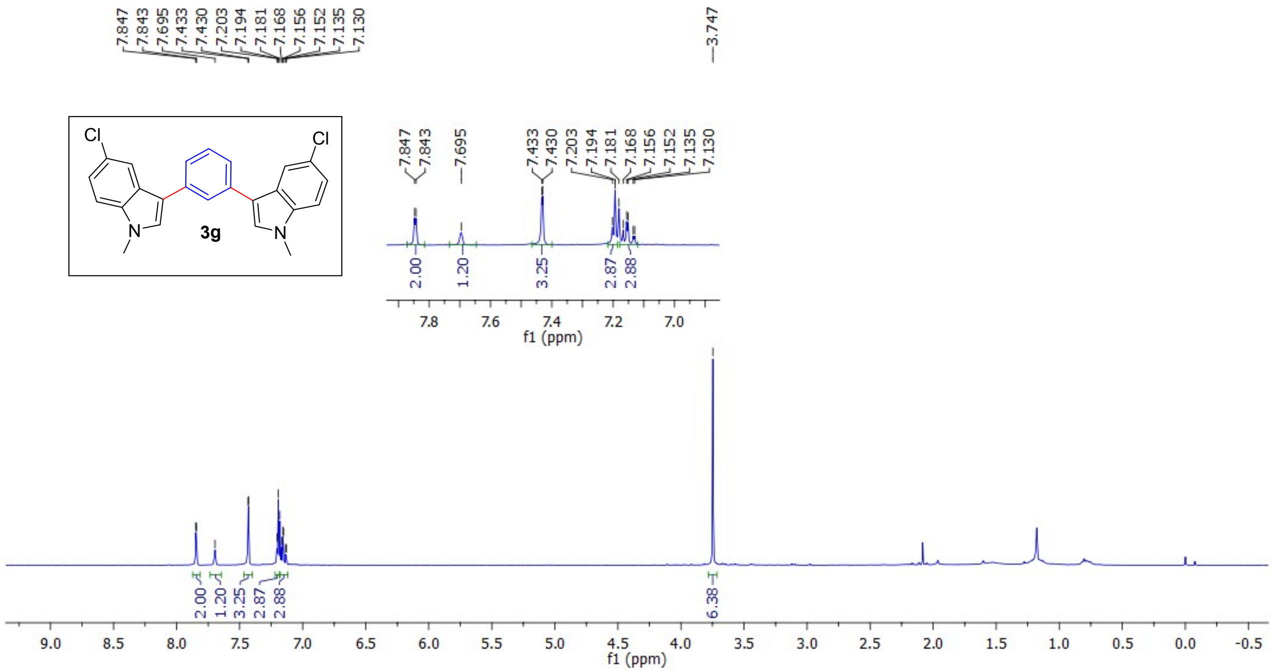
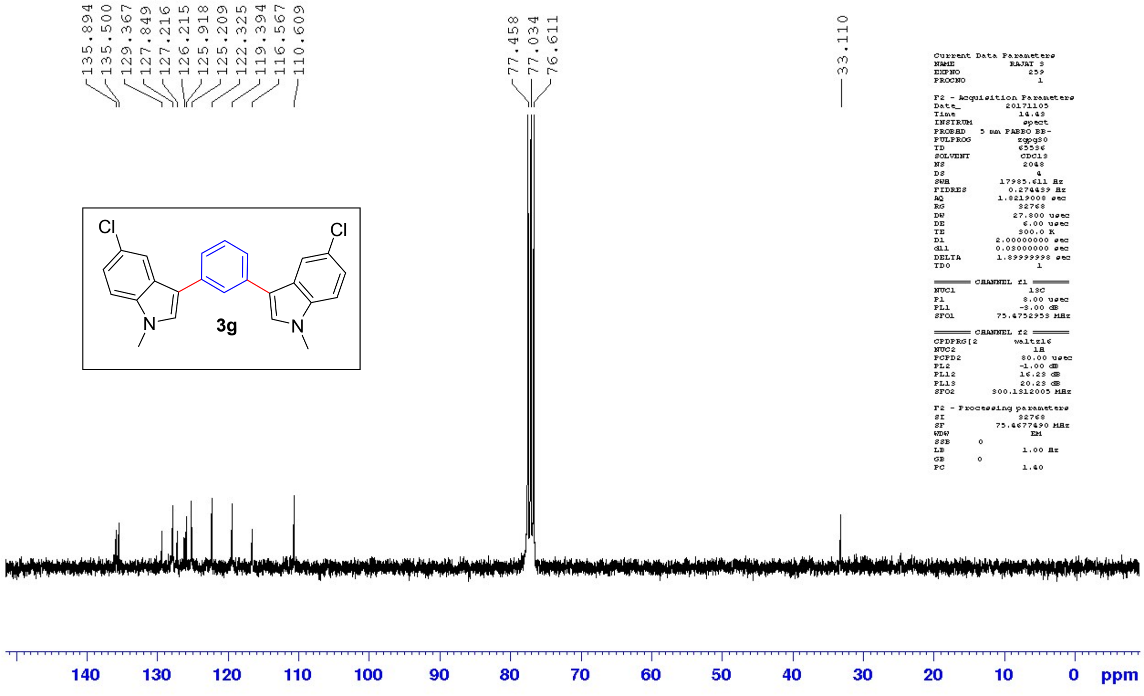


Spectrum 19. 400 MHz ^{1}H NMR of compound 3g



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PL12              16.23 dB
PL13              20.23 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
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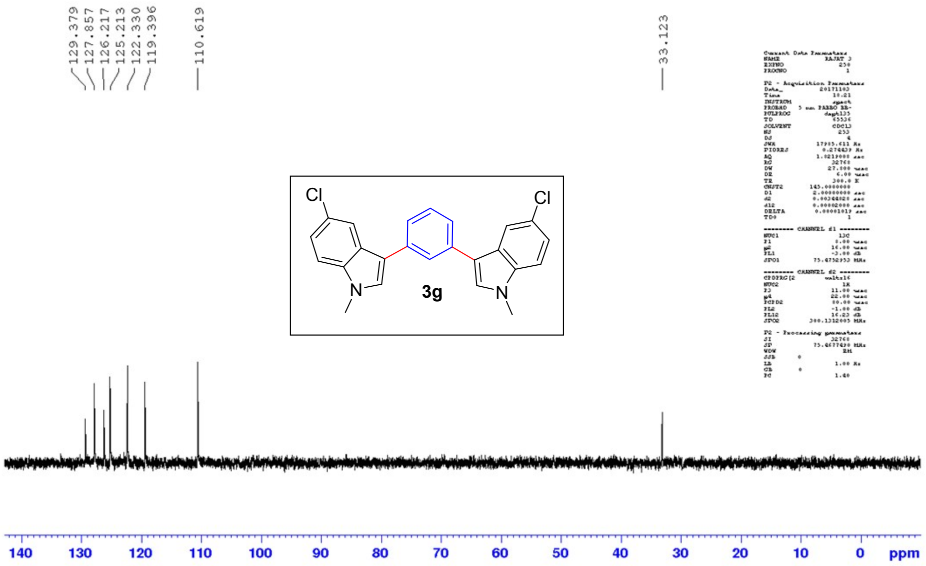

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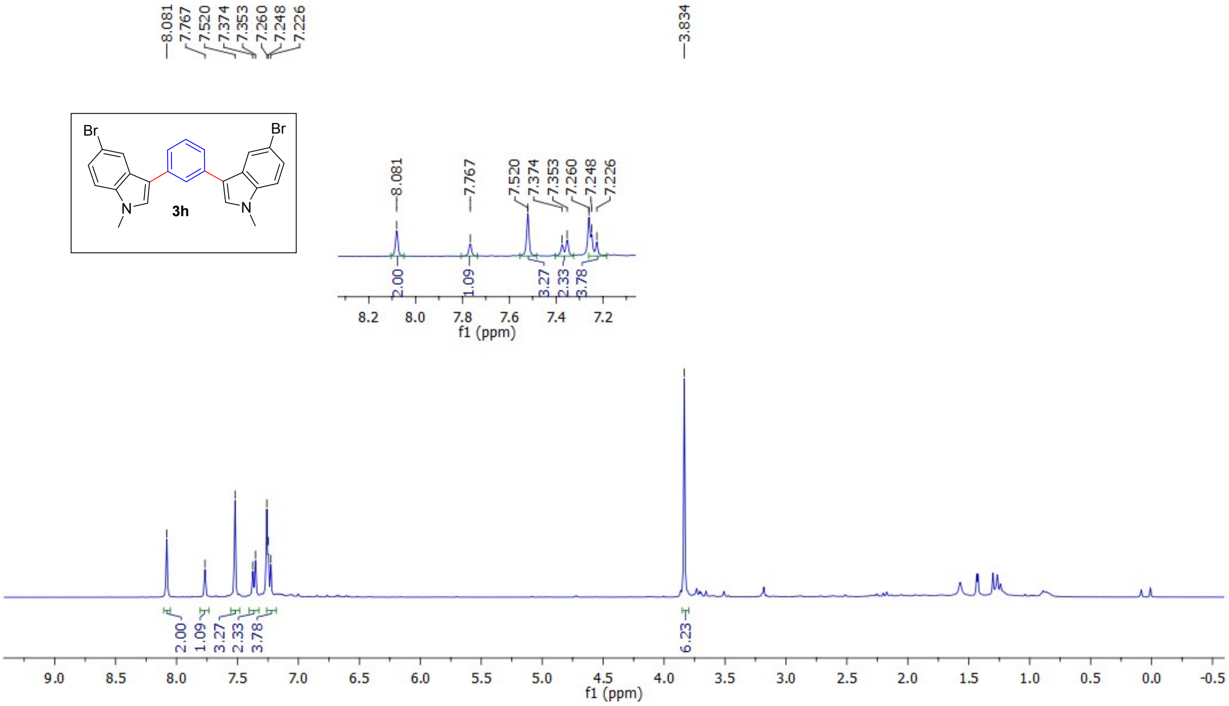
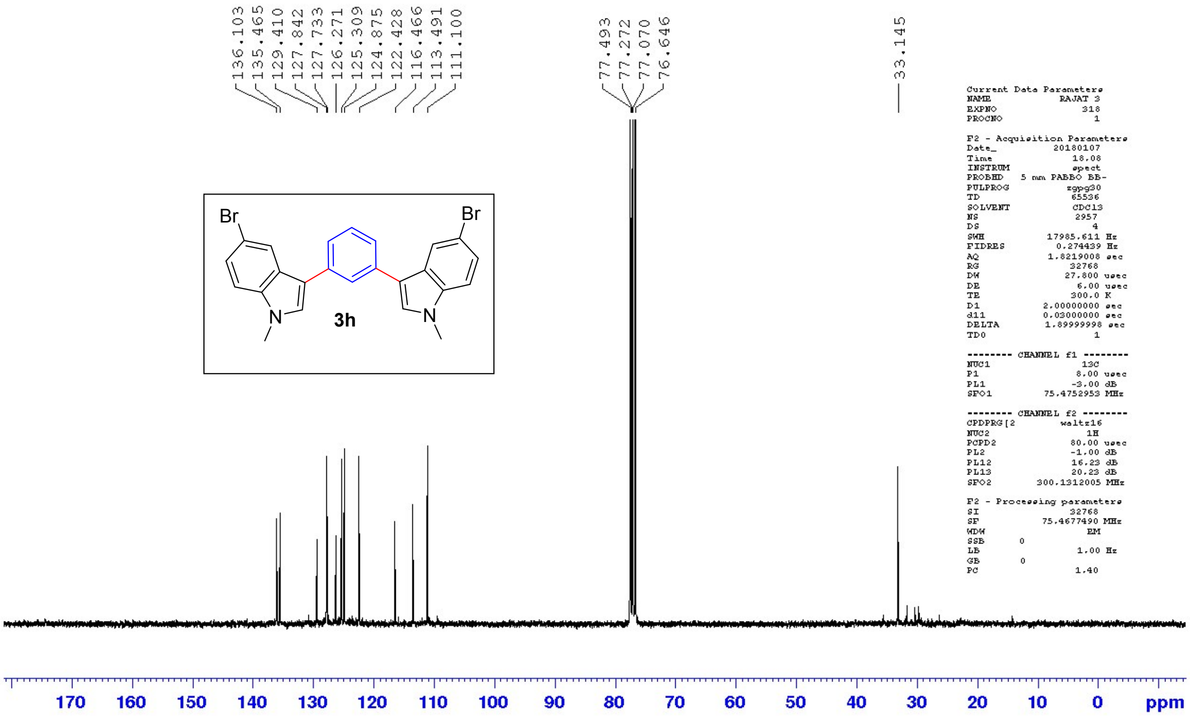


Spectrum 22. 400 MHz ^{1}H NMR of compound 3h



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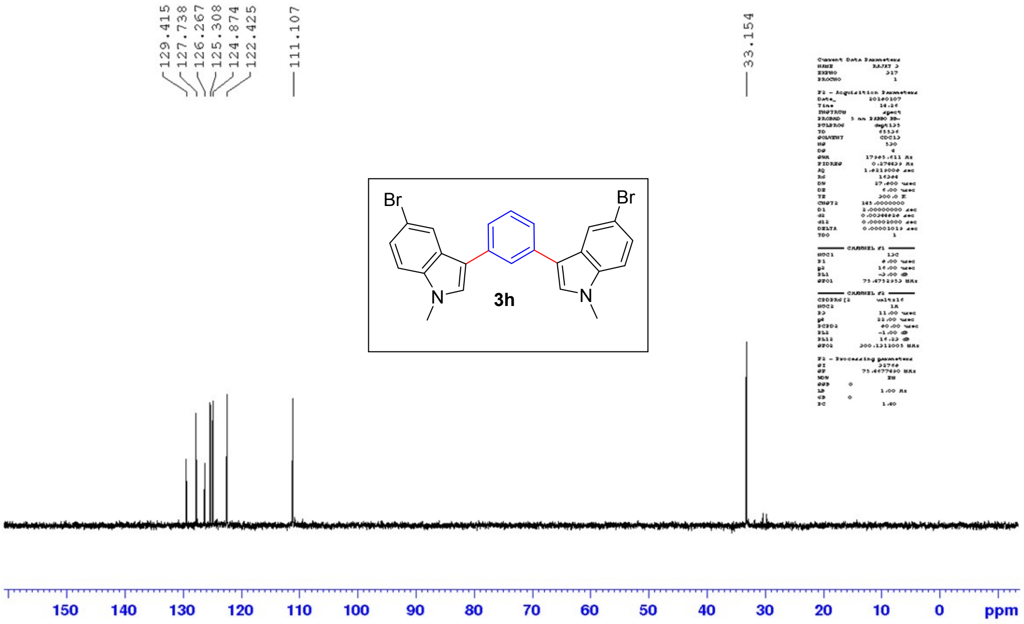

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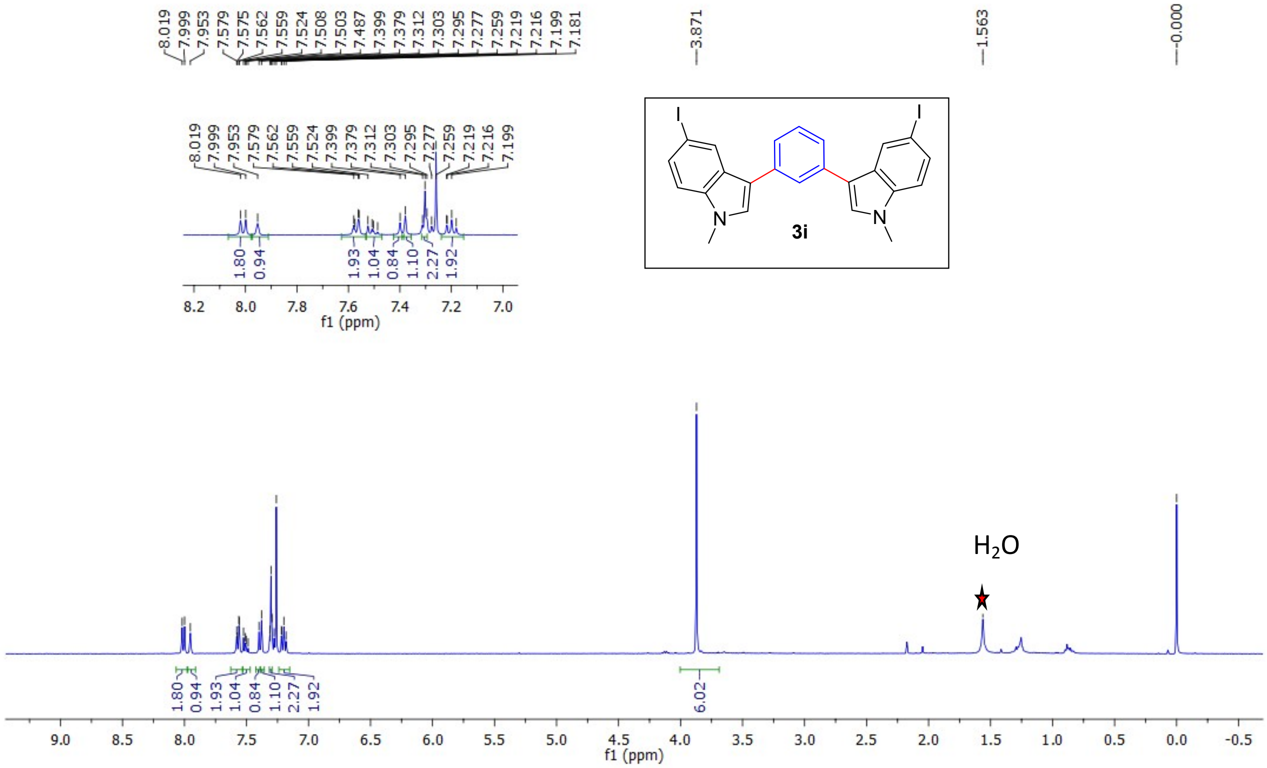

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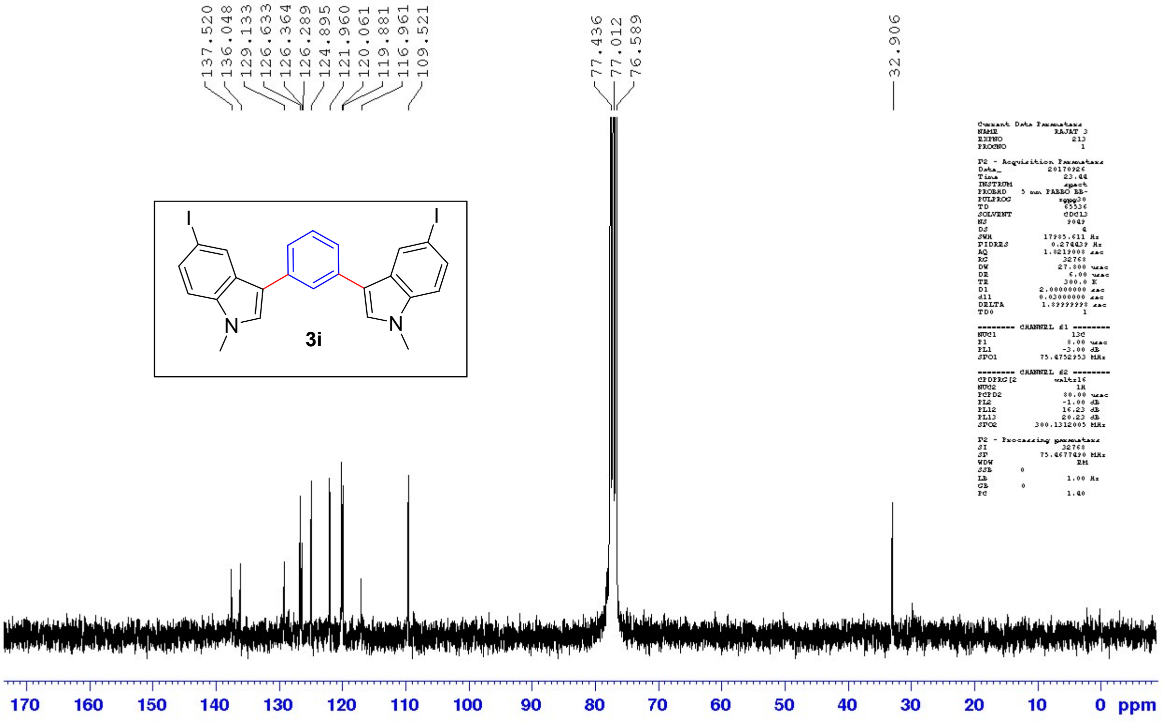

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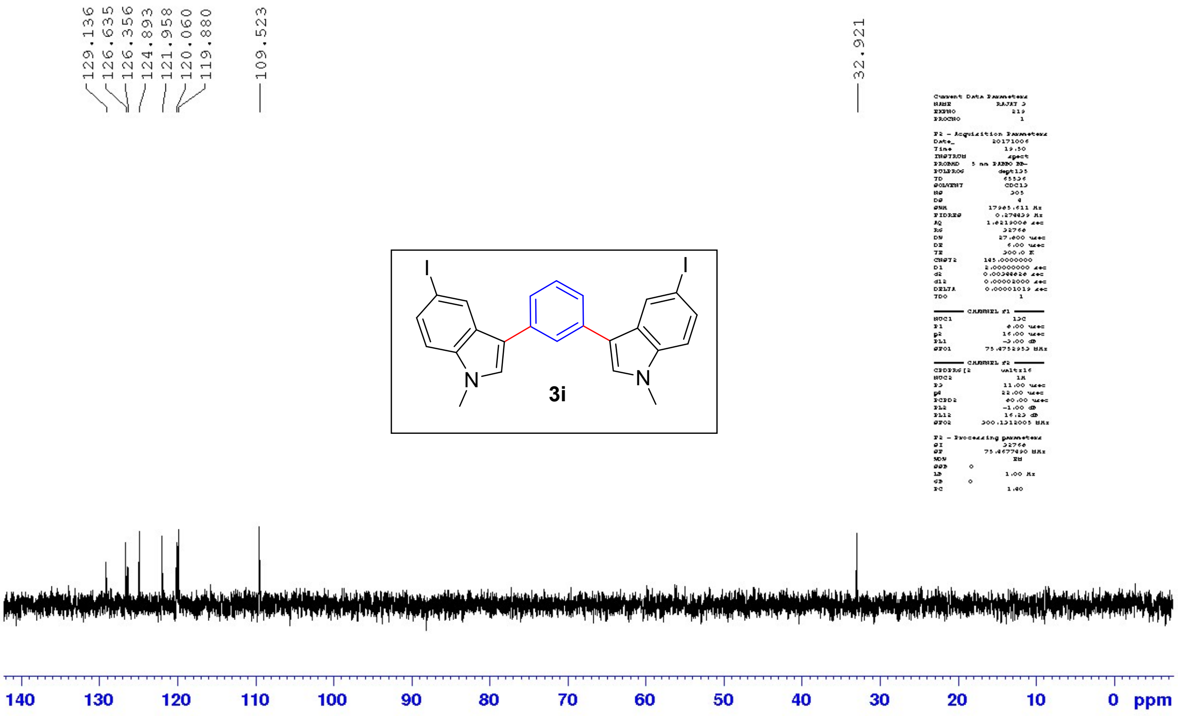
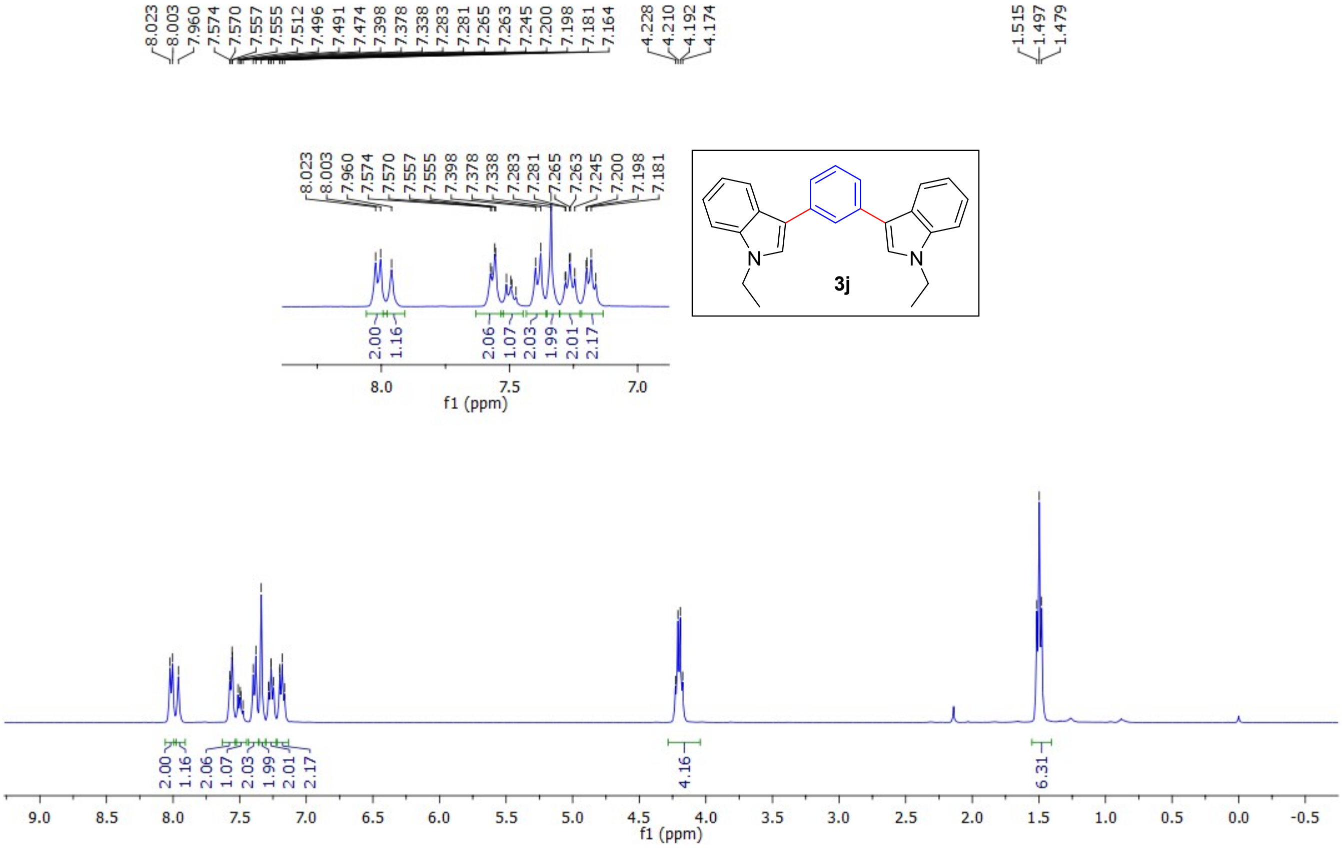


Spectrum 27. 75 MHz DEPT-135 NMR of compound 3i



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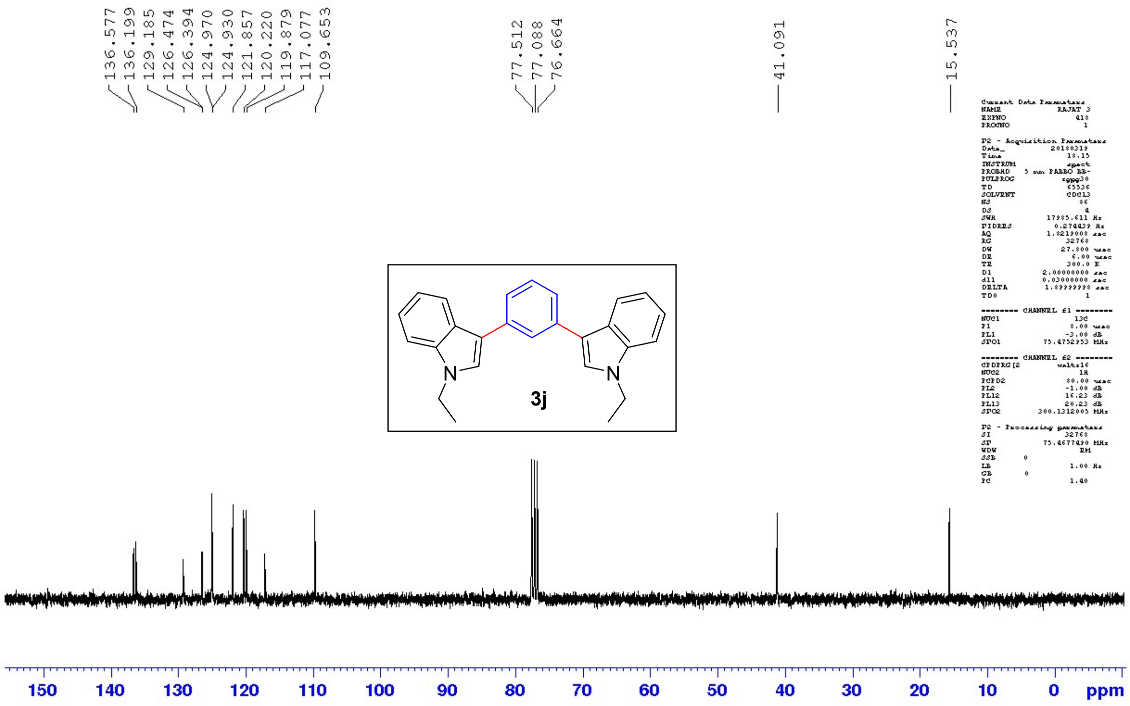

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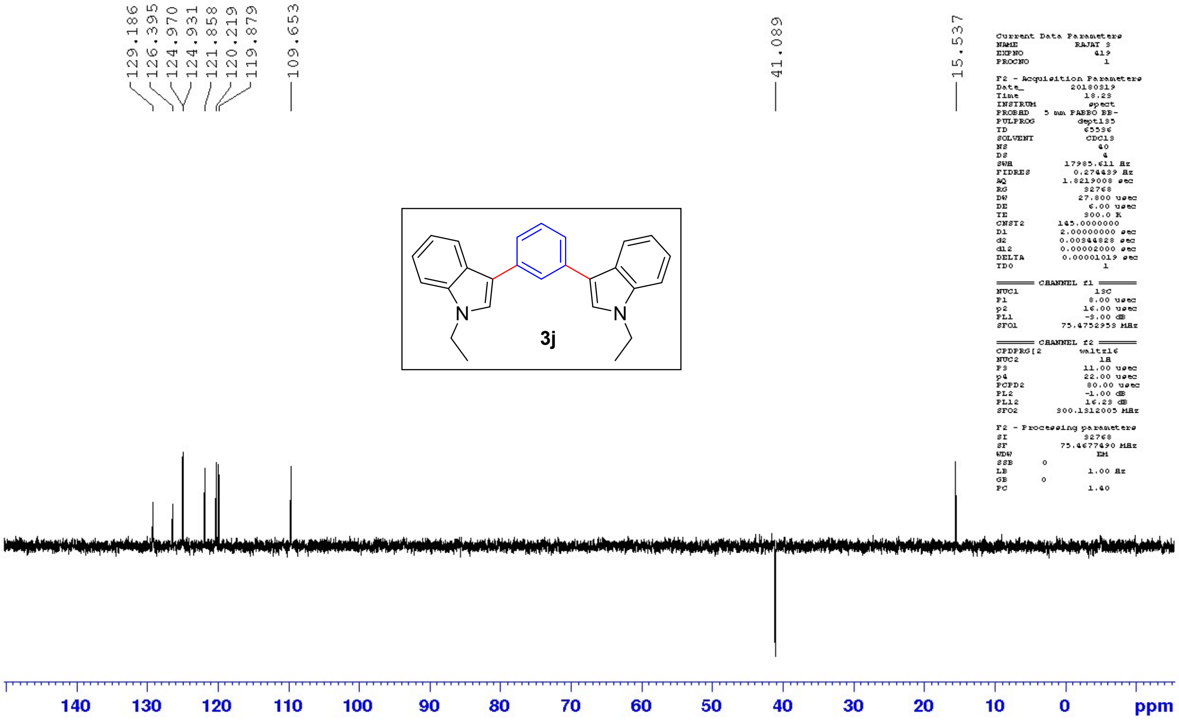

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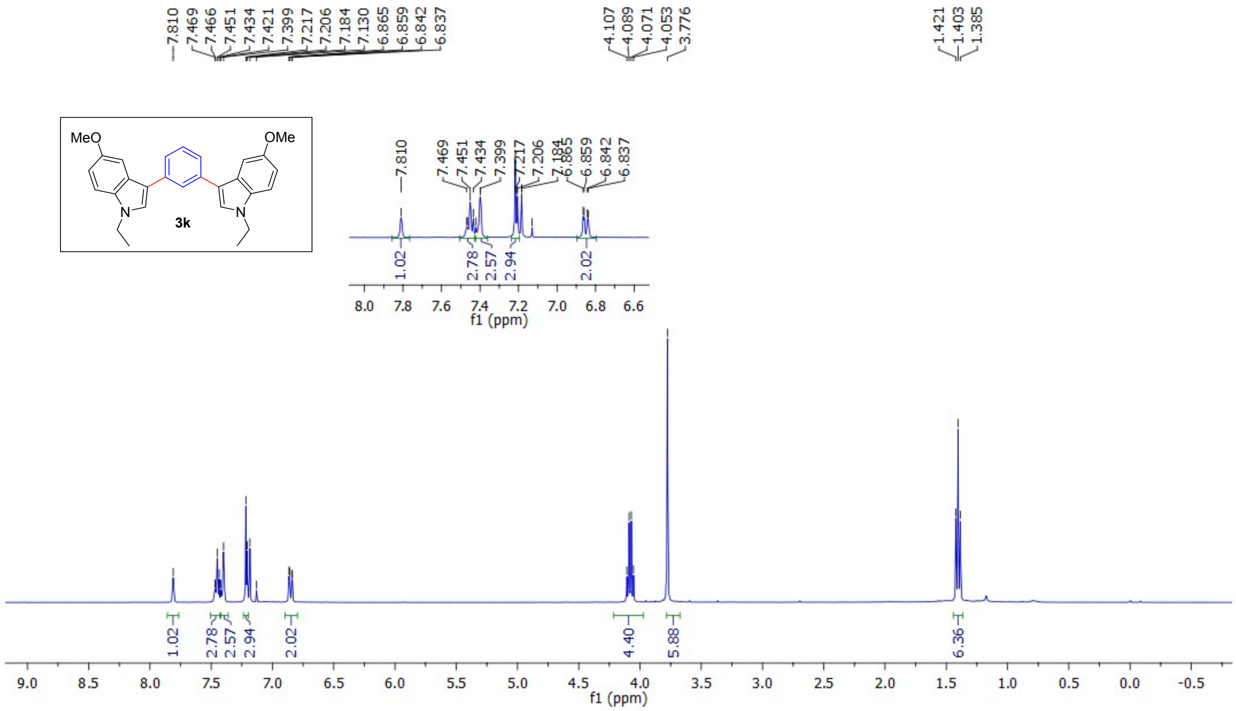

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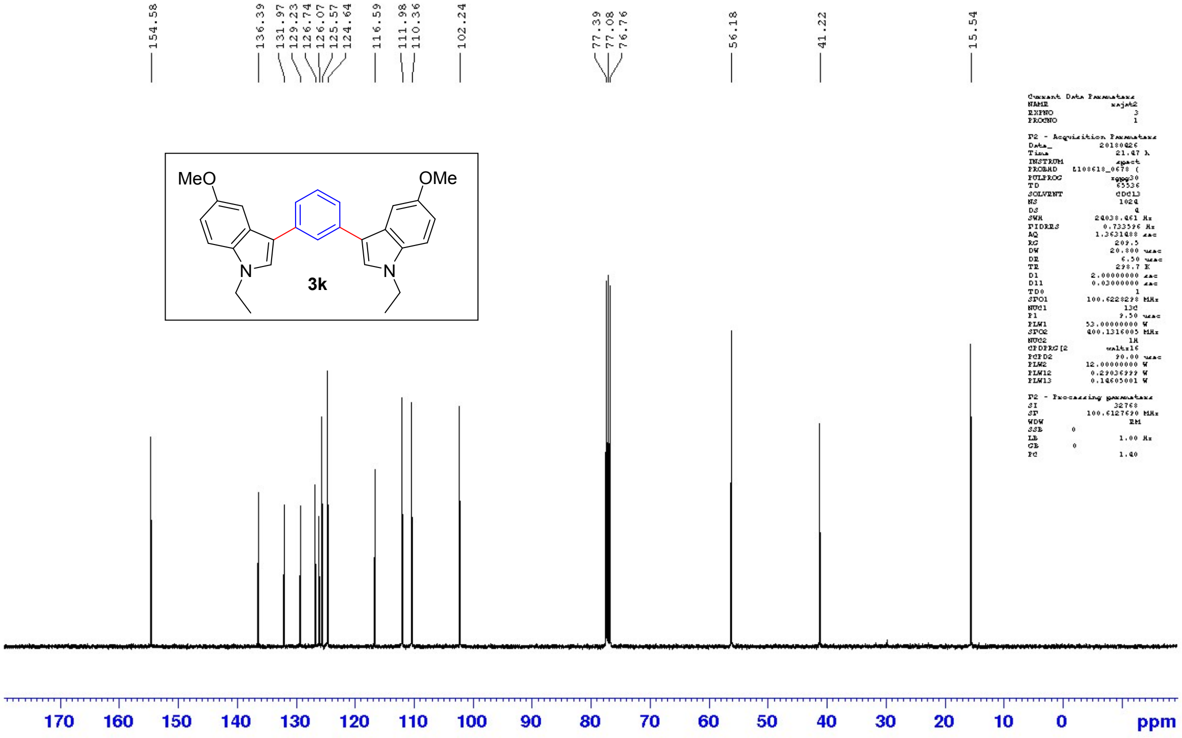

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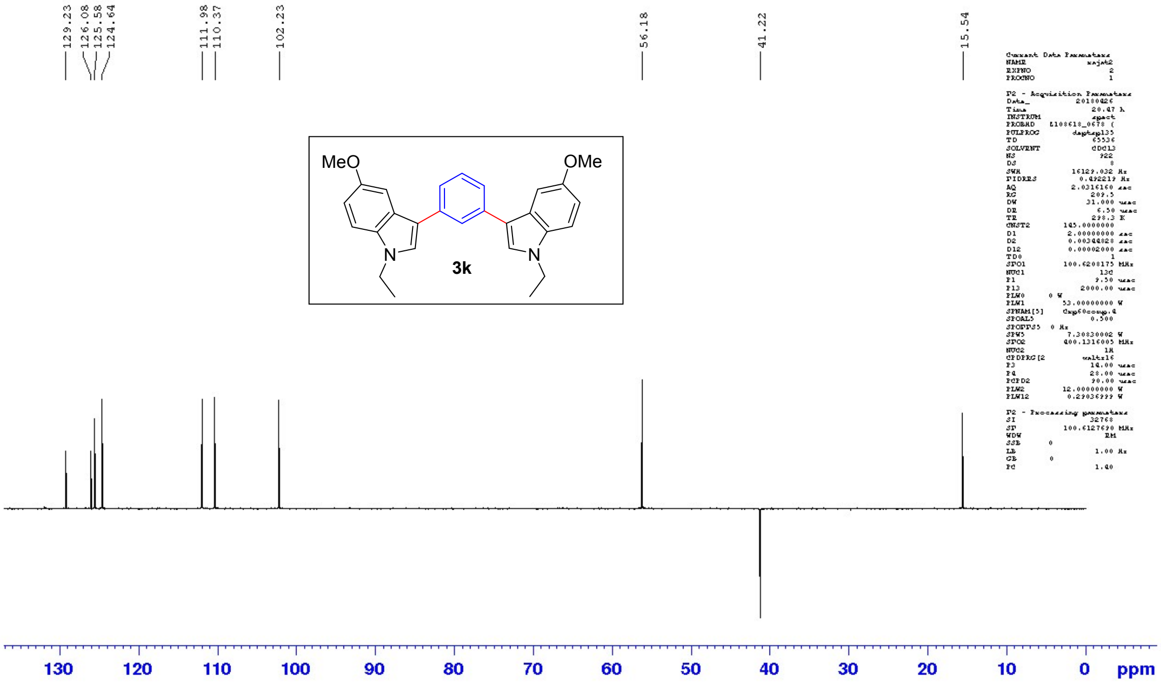
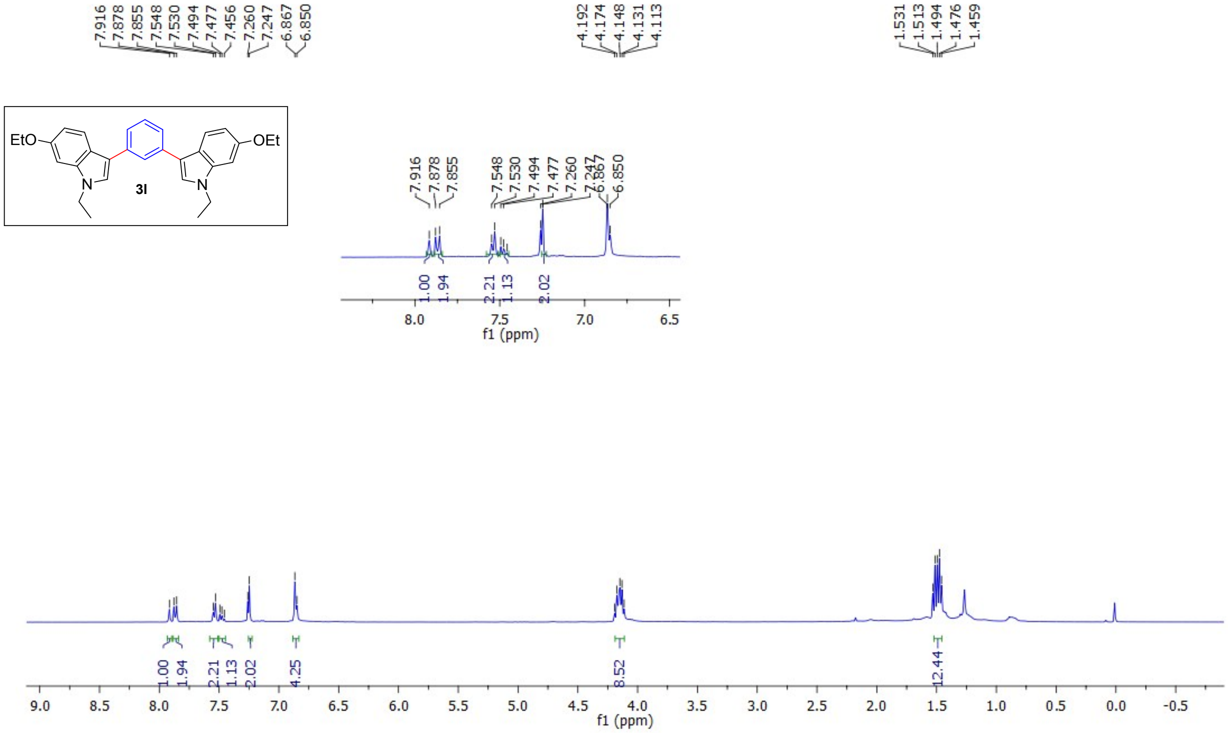
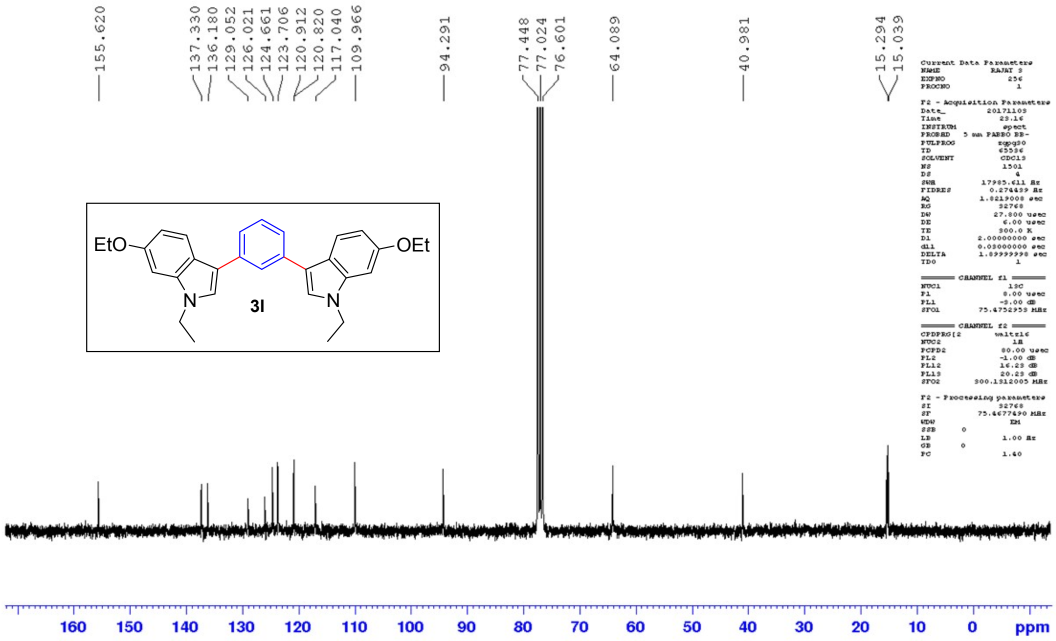


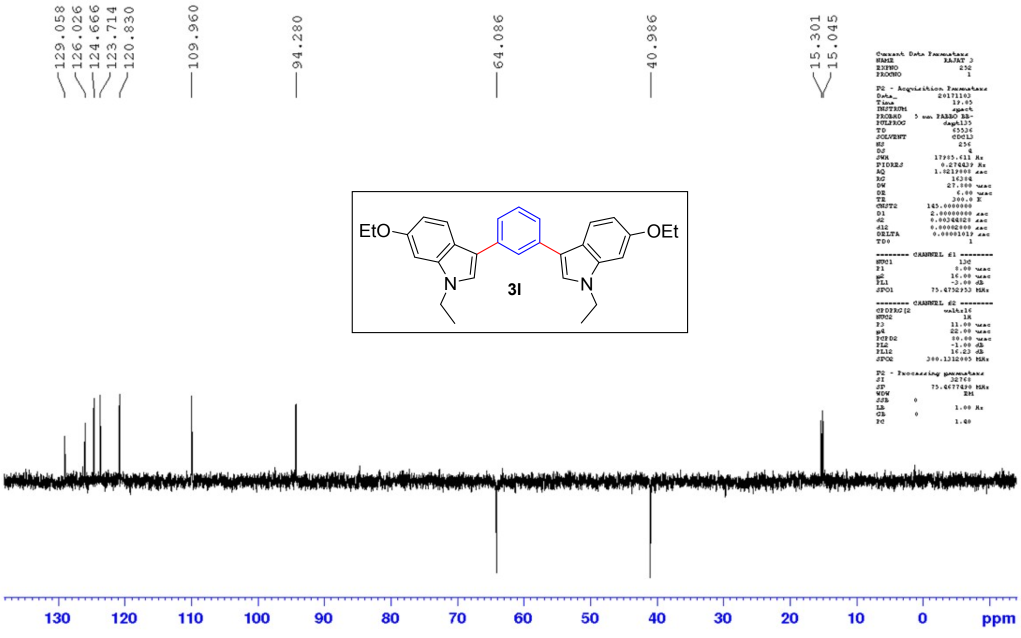
Spectrum 33. 100 MHz DEPT-135 NMR of compound 3k



Spectrum 34. 400 MHz ^{1}H NMR of compound 3l



Spectrum 35. 75 MHz ^{13}C NMR of compound 3l



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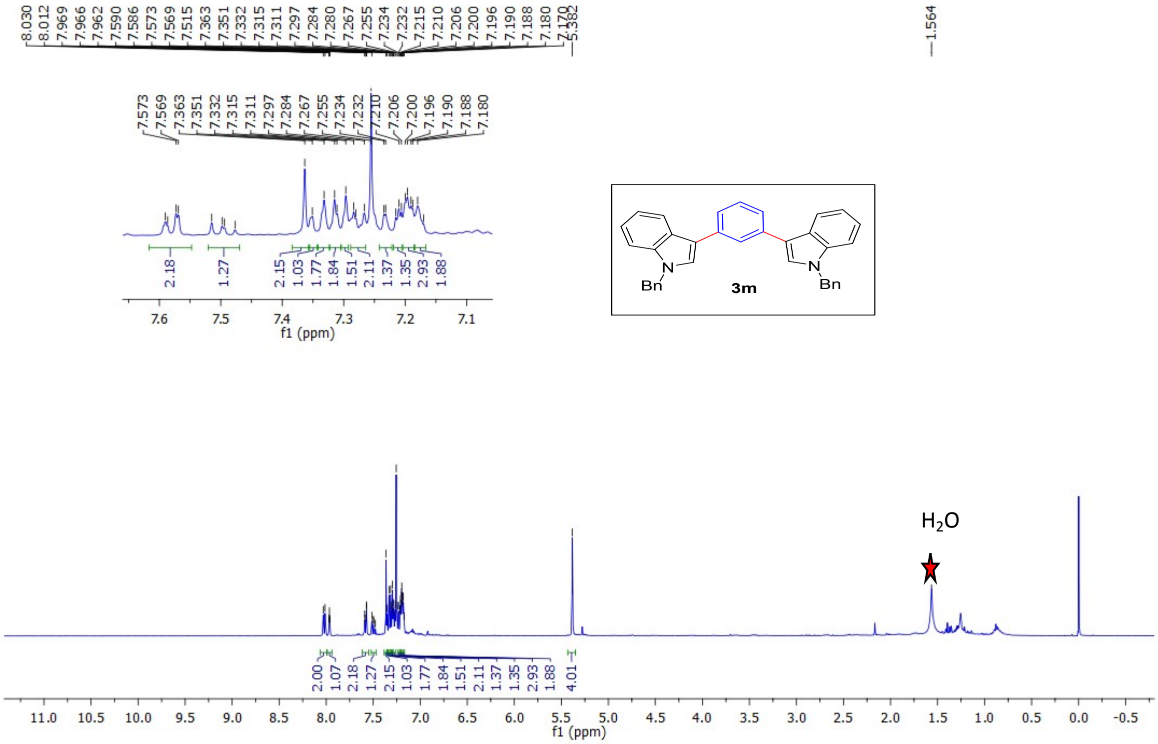

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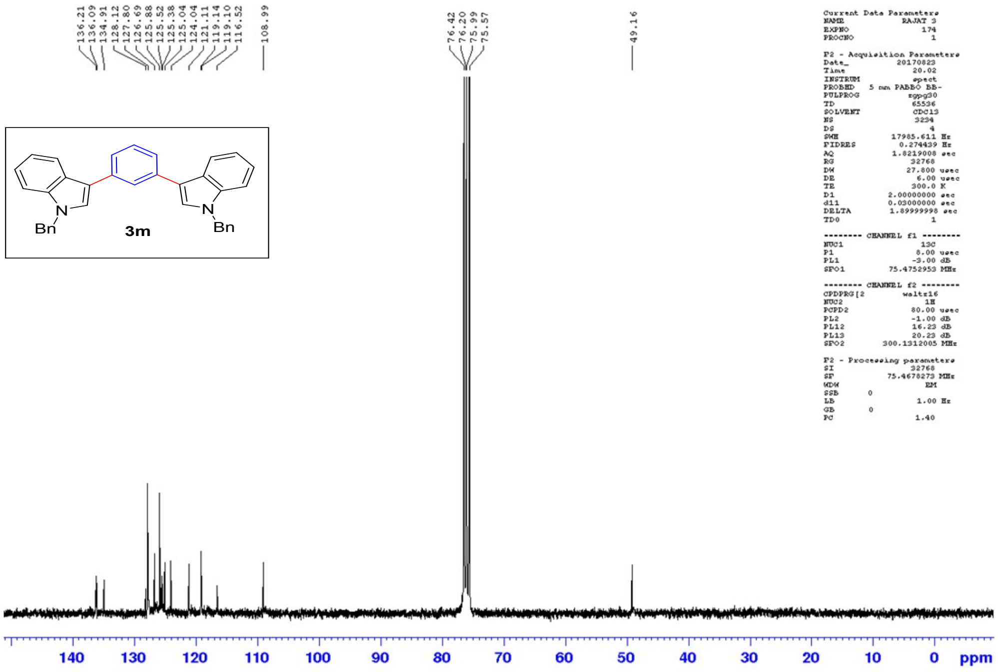

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RG                  32768
DW                 27.800 usec
DE                   6.00 usec
TE                  300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                     1

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PL1                 -3.00 dB
SFO1          75.4752953 MHz

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NUC2                   1H
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PL12                16.23 dB
PL13                20.23 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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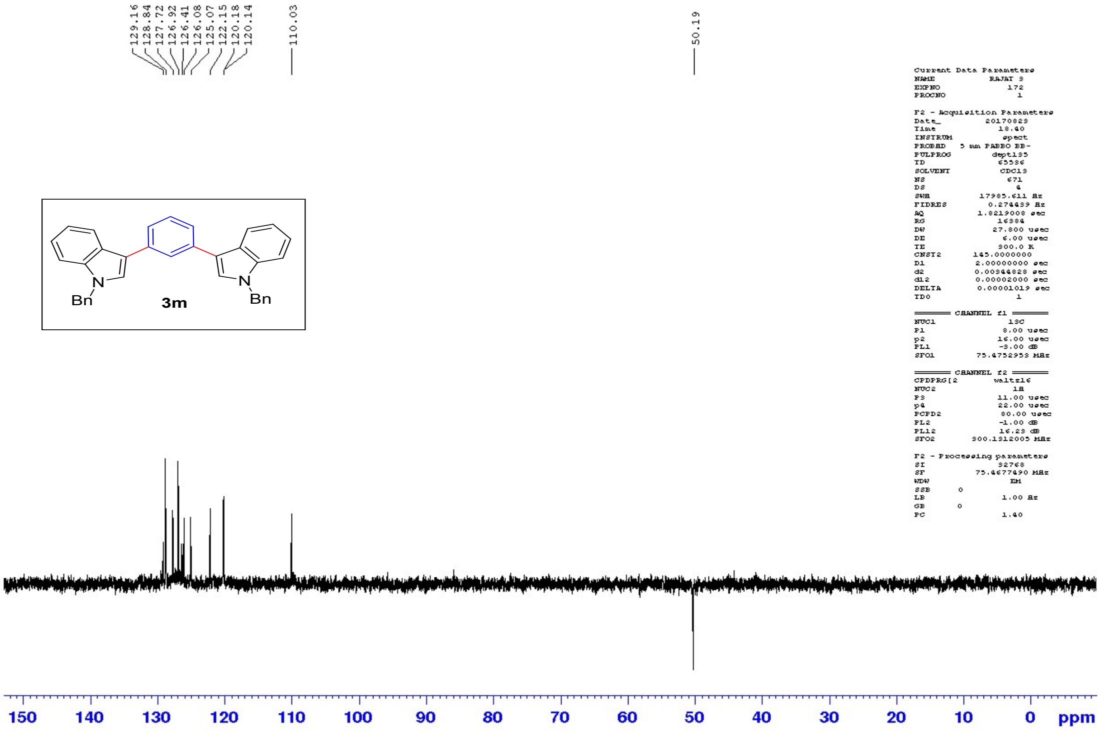
Spectrum 38. 75 MHz ^{13}C NMR of compound 3m



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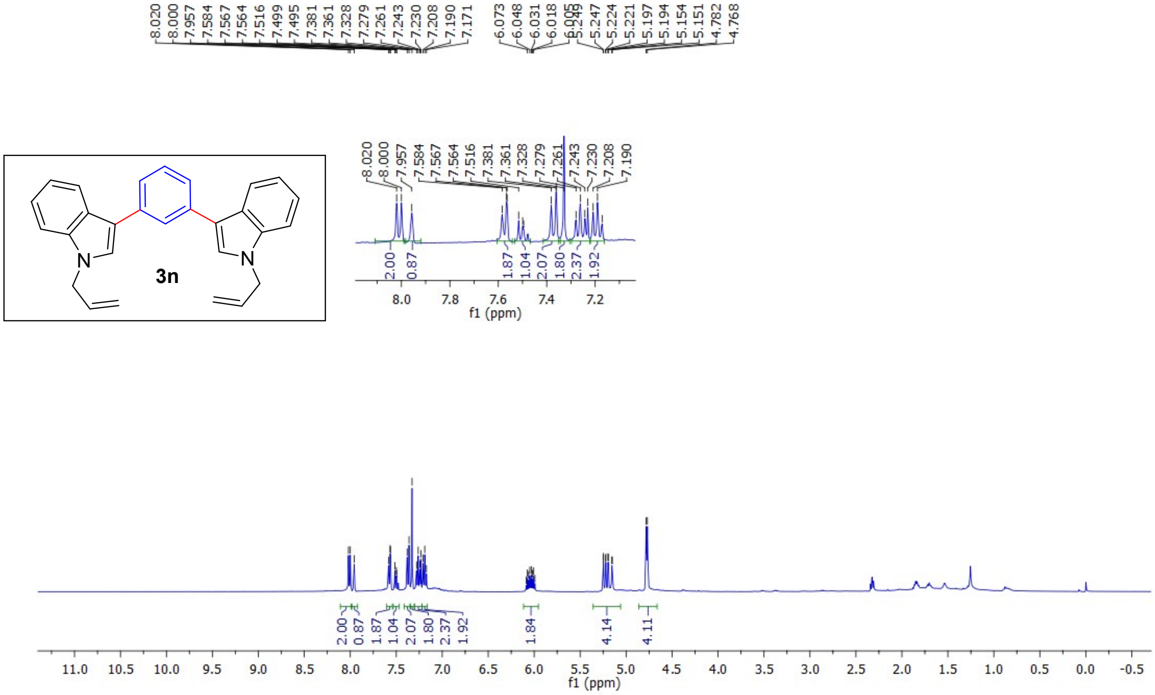
FIDRES        0.274439 Hz
AQ           1.8219008 sec
RG                16384
DW              27.800 usec
DE                6.00 usec
TE               300.0 K
CNST2       145.0000000
D1          2.00000000 sec
d2          0.00344828 sec
d12         0.00002000 sec
DELTA       0.00001019 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
p2                16.00 usec
PL1               -3.00 dB
SFO1         75.4752953 MHz

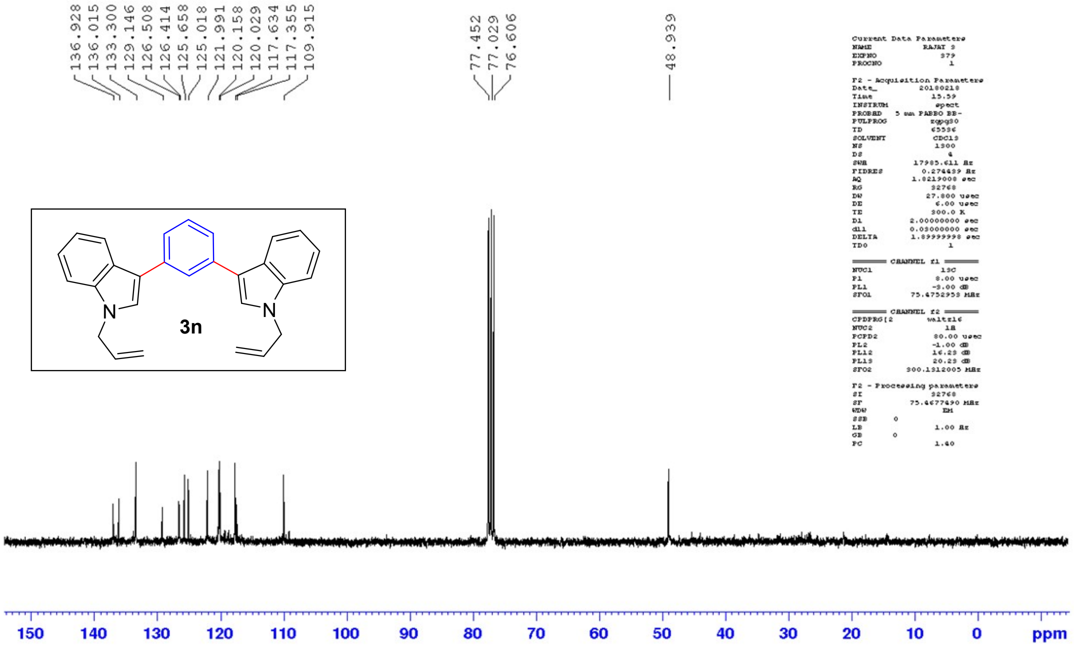
======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
P3                11.00 usec
p4                22.00 usec
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              16.23 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

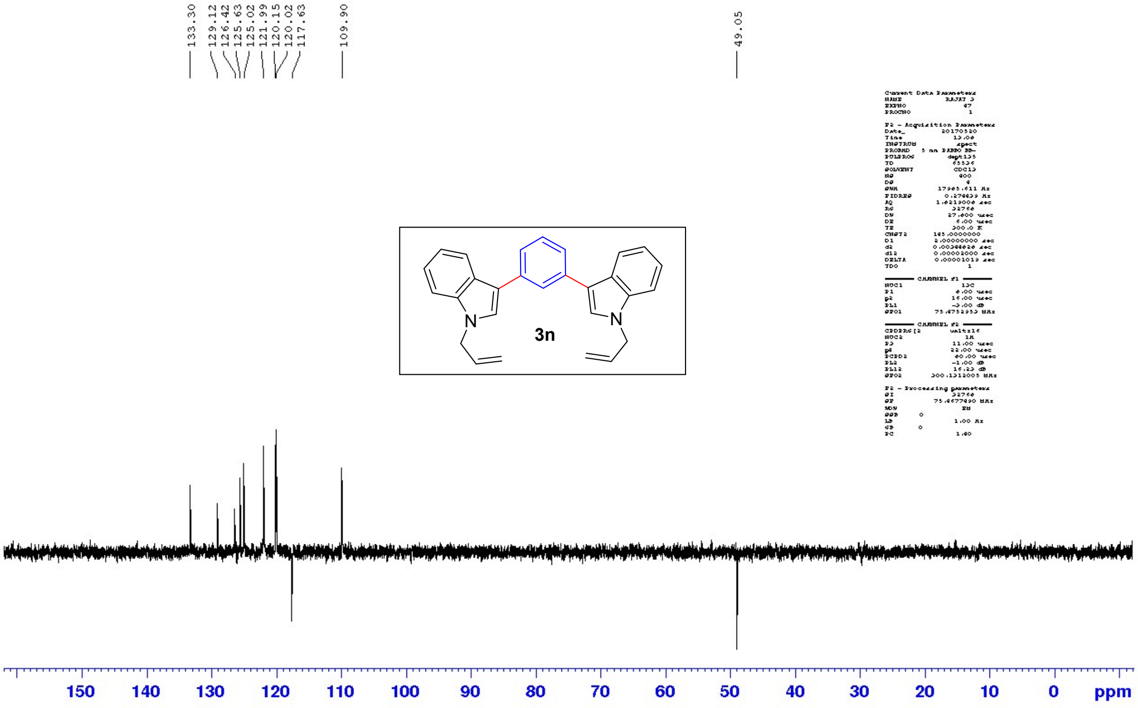
Spectrum 39. 75 MHz DEPT-135 NMR of compound 3m



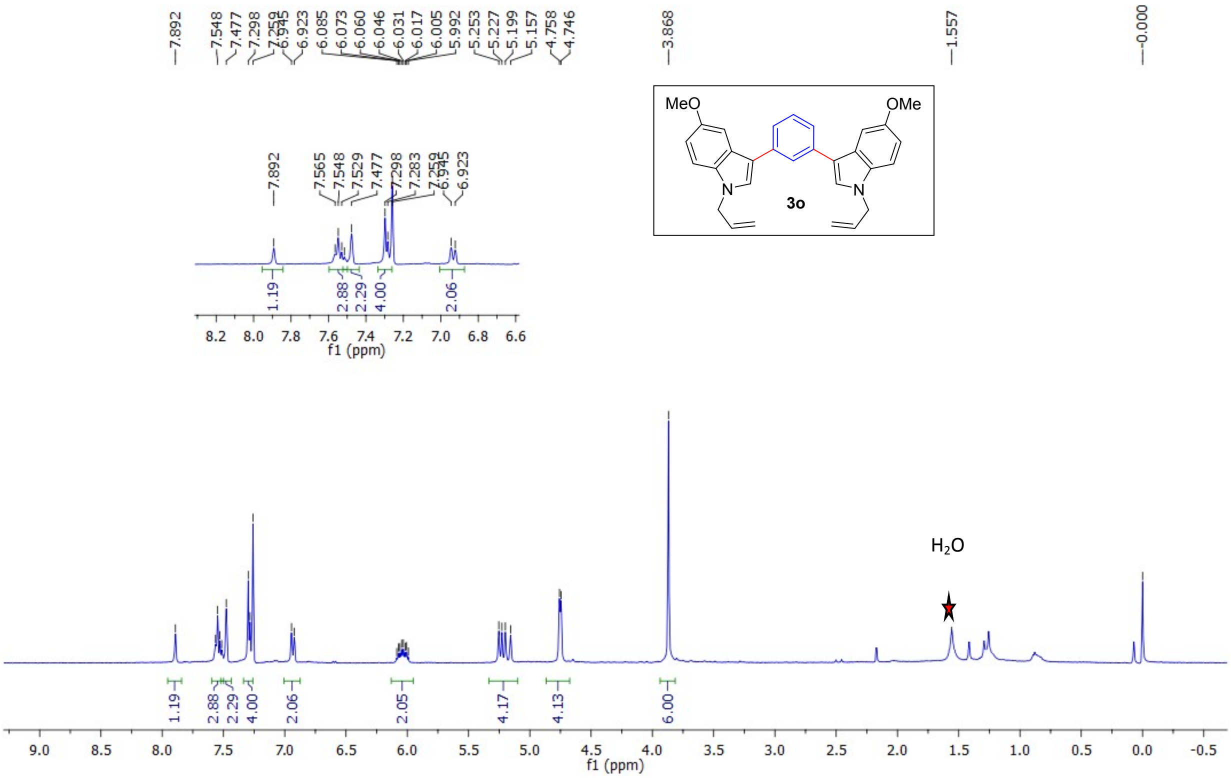
Spectrum 40. 400 MHz ^{1}H NMR of compound 3n



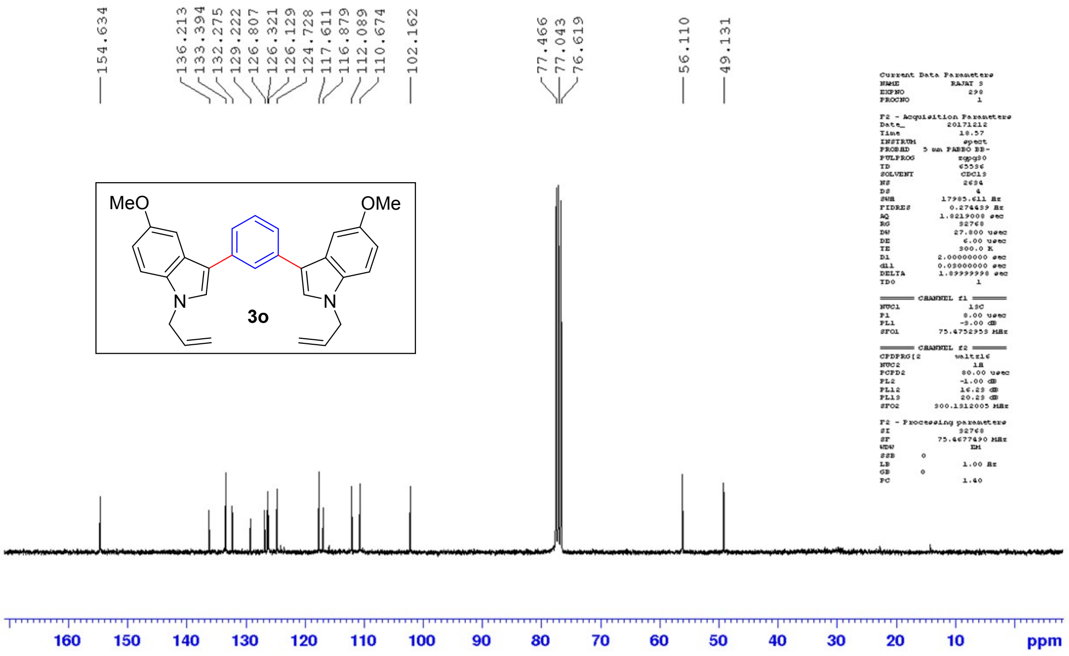
Spectrum 41. 75 MHz ^{13}C NMR of compound 3n



Spectrum 42. 75 MHz DEPT-135 NMR of compound 3n



Spectrum 43. 400 MHz ^{1}H NMR of compound 3o



```
Current Data Parameters
NAME              RAJAT 3
EXPNO                 298
PROCNO                  1

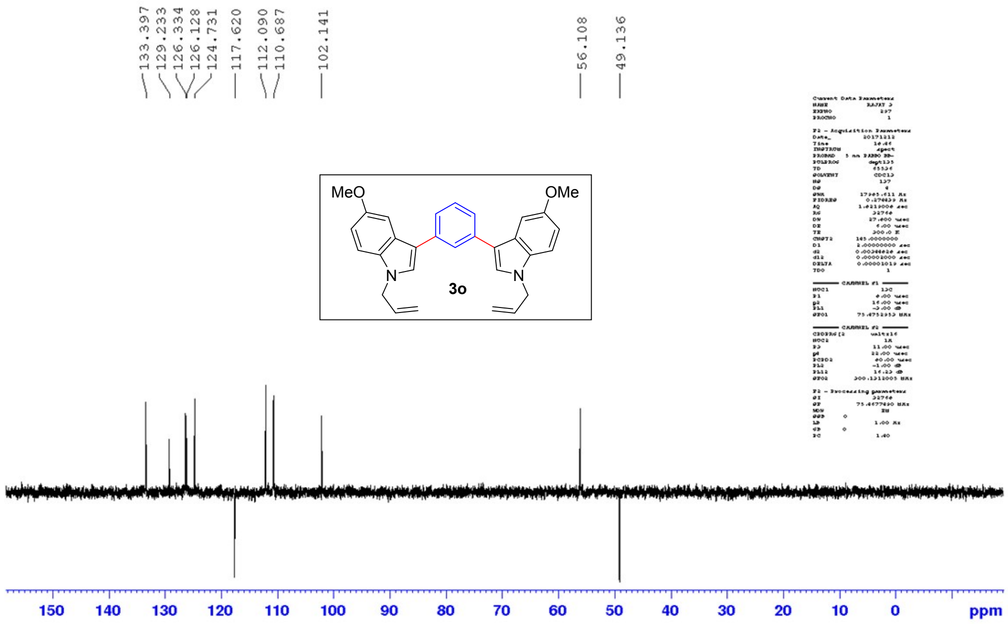
F2 - Acquisition Parameters
Date_            20171212
Time                18.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   2694
DS                      4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ            1.8219008 sec
RG                  32768
DW               27.800 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -3.00 dB
SFO1        75.4752953 MHz

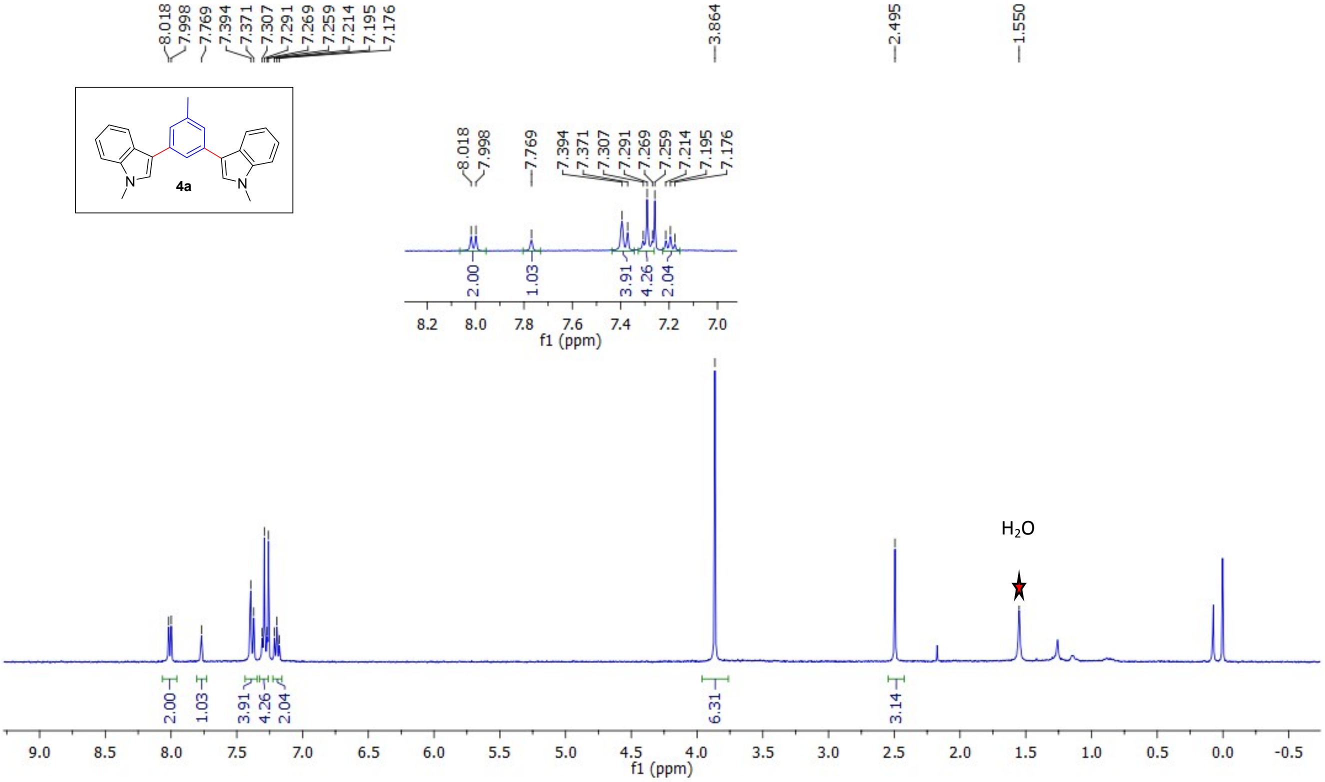
======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              16.23 dB
PL13              20.23 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF          75.4677490 MHz
WDW                    EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

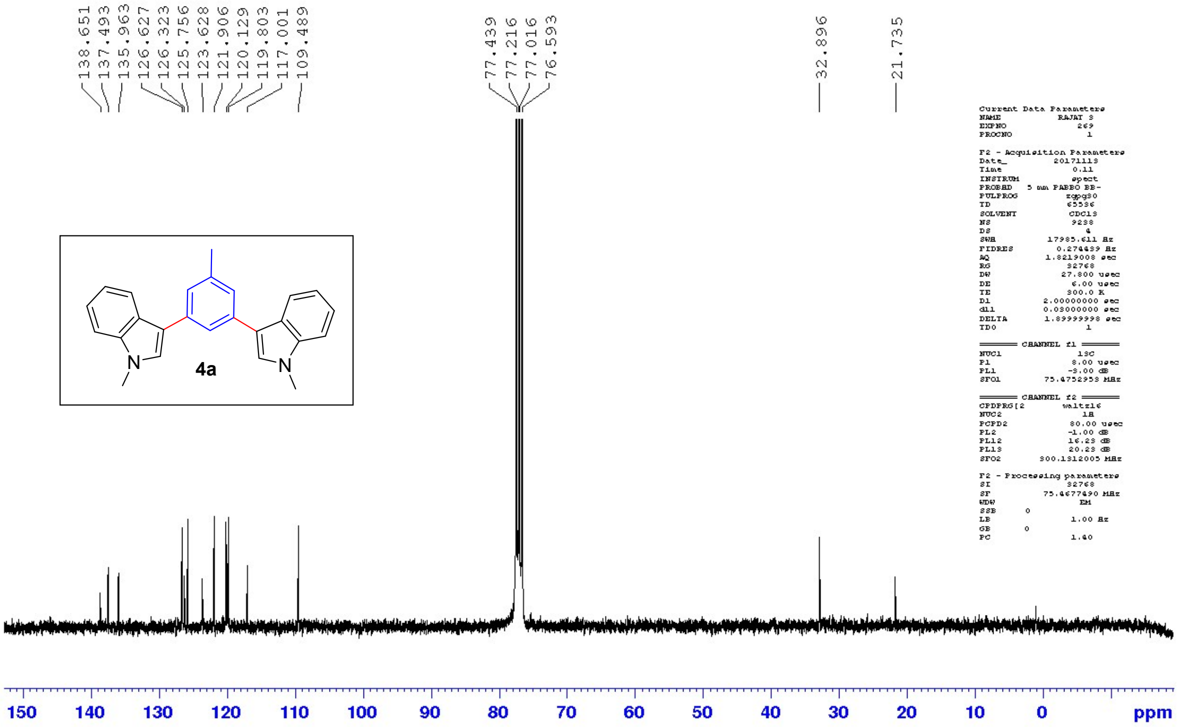
Spectrum 44. 75 MHz ^{13}C NMR of compound 3o



Spectrum 45. 75 MHz DEPT-135 NMR of compound 3o



Spectrum 46. 400 MHz ^{1}H NMR of compound 4a



```
Current Data Parameters
NAME          RAJAT 3
EXPNO             269
PROCNO              1

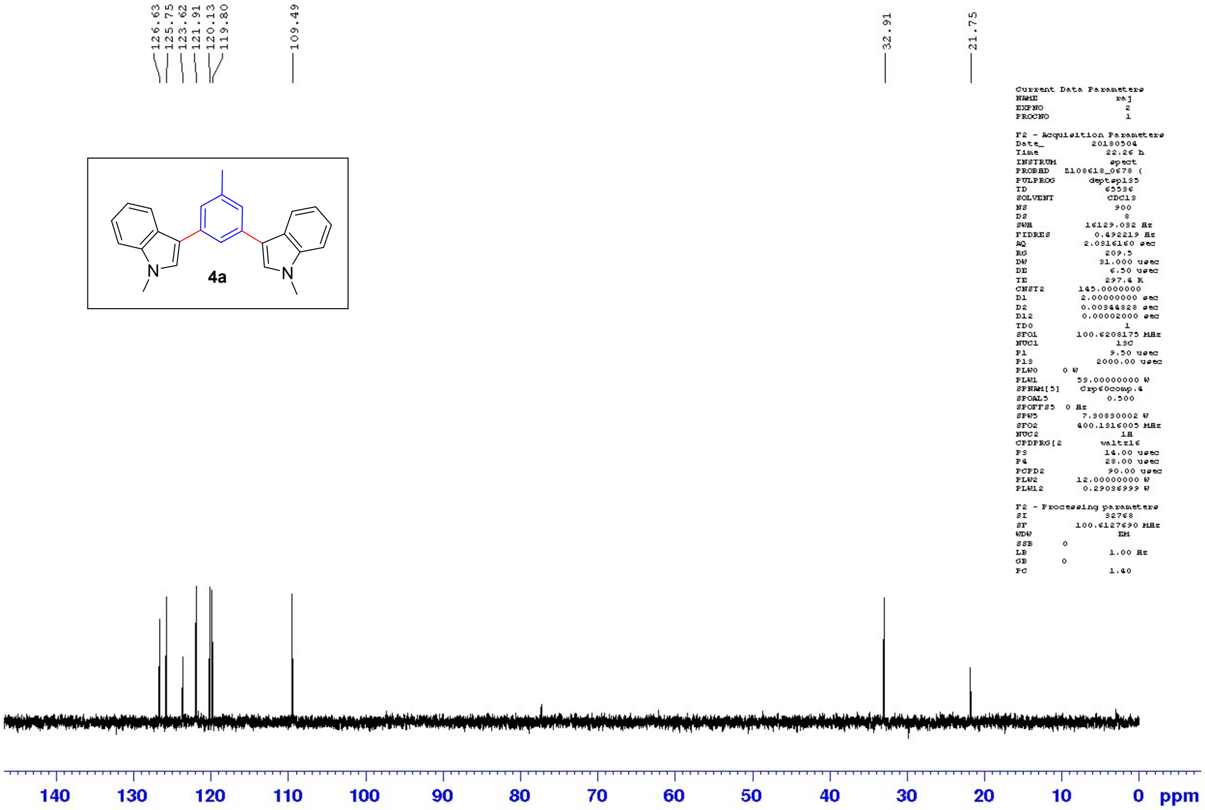
F2 - Acquisition Parameters
Date_        20171113
Time             0.11
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS               9238
DS                  4
SWH       17985.611 Hz
FIDRES     0.274439 Hz
AQ        1.8219008 sec
RG              32768
DW           27.800 usec
DE             6.00 usec
TE            300.0 K
D1       2.00000000 sec
d11      0.03000000 sec
DELTA    1.89999998 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1            8.00 usec
PL1          -3.00 dB
SFO1      75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2      waltz16
NUC2               1H
PCPD2         80.00 usec
PL2           -1.00 dB
PL12          16.23 dB
PL13          20.23 dB
SFO2     300.1312005 MHz

F2 - Processing parameters
SI              32768
SF        75.4677490 MHz
WDW                EM
SSB      0
LB              1.00 Hz
GB       0
PC               1.40
```

Spectrum 47. 75 MHz ^{13}C NMR of compound 4a

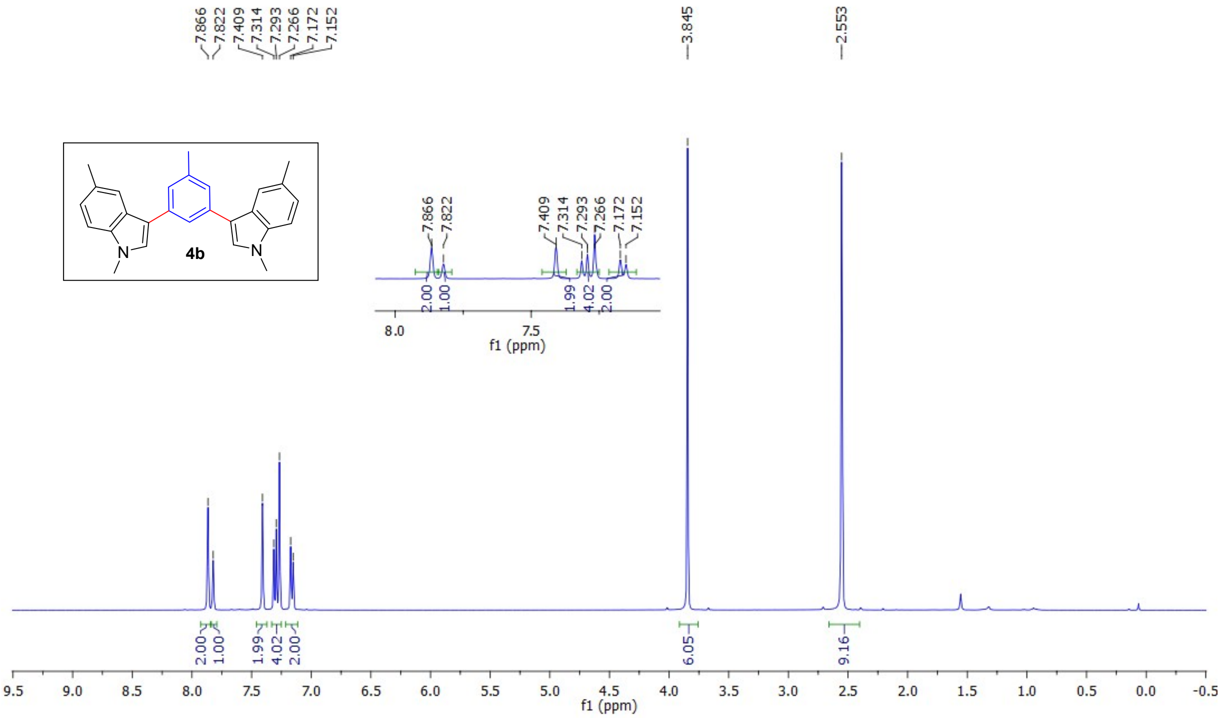


```
Current Data Parameters
NAME              raj
EXPNO               2
PROCNO              1

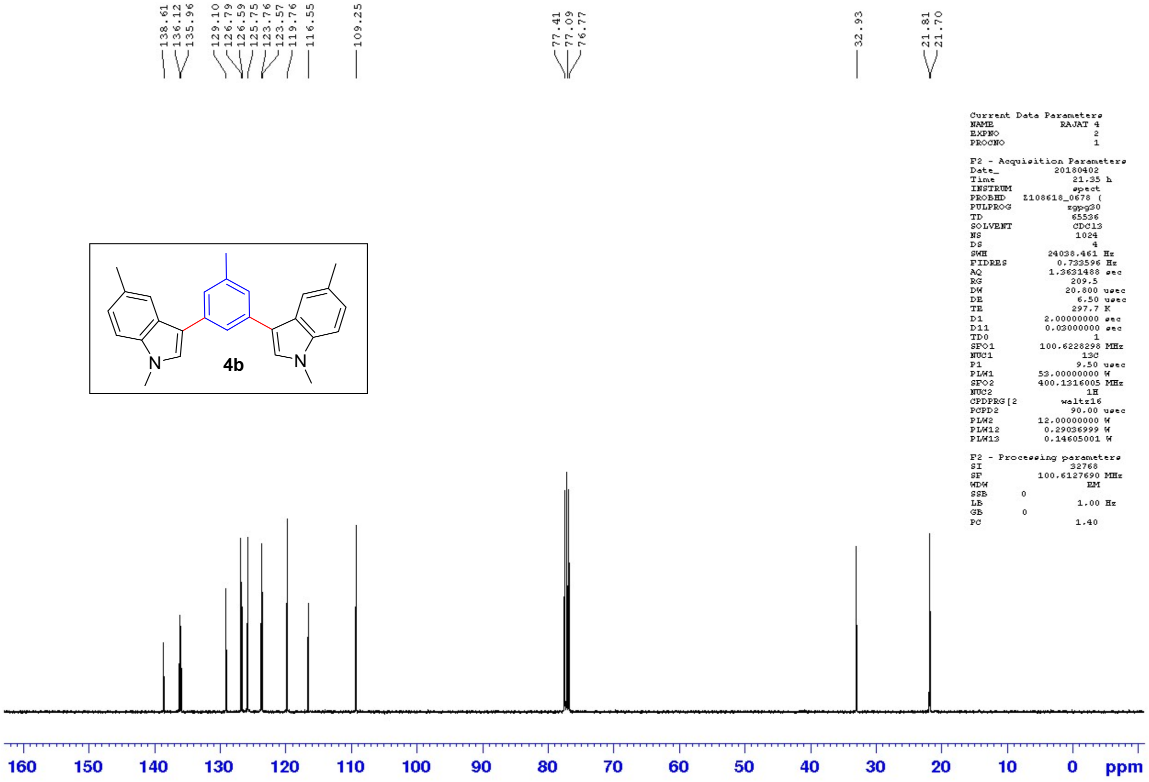
F2 - Acquisition Parameters
Date_        20180504
Time            22.26 h
INSTRUM         spect
PROBHD   Z108618_0678 (
PULPROG      deptsp135
TD              65536
SOLVENT         CDCl3
NS                900
DS                  8
SWH       16129.032 Hz
FIDRES     0.492219 Hz
AQ        2.0316160 sec
RG              209.5
DW           31.000 usec
DE             6.50 usec
TE            297.4 K
CNST2     145.0000000
D1       2.00000000 sec
D2       0.00344828 sec
D12      0.00002000 sec
TD0                 1
SFO1     100.6208175 MHz
NUC1              13C
P1             9.50 usec
P13         2000.00 usec
PLW0     0 W
PLW1     53.00000000 W
SPNAM[5]   Crp60comp.4
SPOAL5          0.500
SPOFFS5  0 Hz
SPW5      7.30830002 W
SFO2     400.1316005 MHz
NUC2               1H
CPDPRG[2      waltz16
P3            14.00 usec
P4            28.00 usec
PCPD2         90.00 usec
PLW2     12.00000000 W
PLW12     0.29036999 W

F2 - Processing parameters
SI              32768
SF       100.6127690 MHz
WDW                EM
SSB      0
LB              1.00 Hz
GB       0
PC               1.40
```

Spectrum 48. 100 MHz DEPT-135 NMR of compound 4a



Spectrum 49. 400 MHz ^{1}H NMR of compound 4b

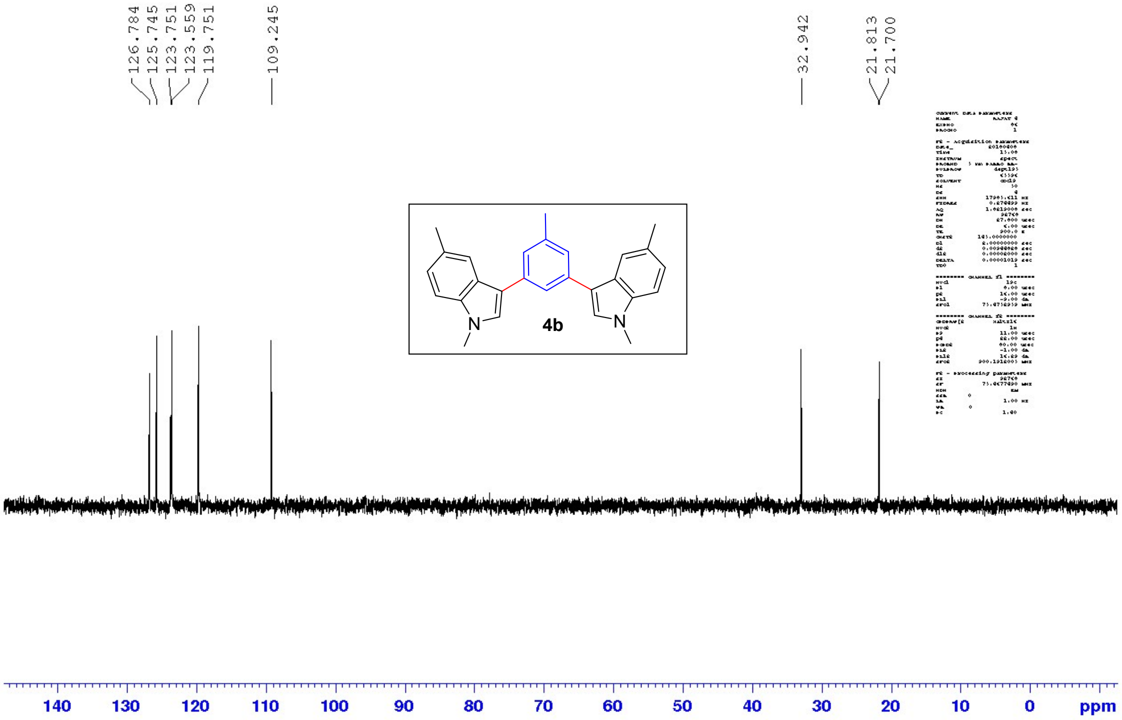


```
Current Data Parameters
NAME              RAJAT 4
EXPNO                   2
PROCNO                  1

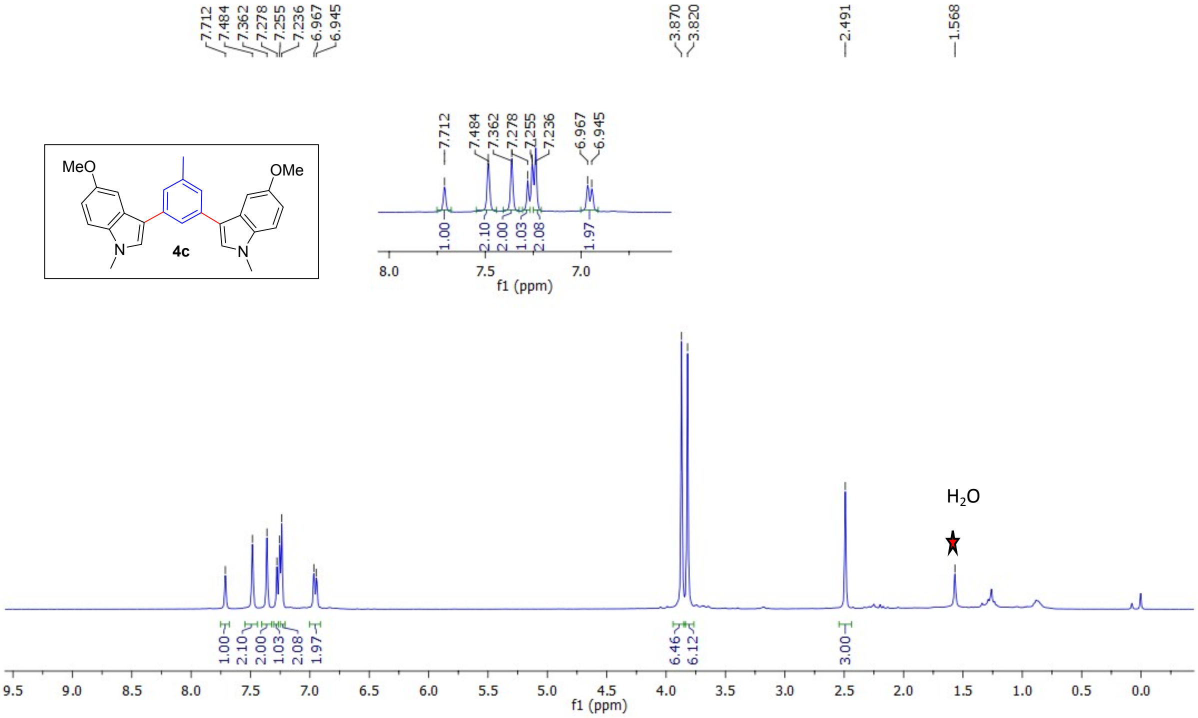
F2 - Acquisition Parameters
Date_            20180402
Time              21.35 h
INSTRUM             spect
PROBHD   Z108618_0678 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG                 209.5
DW                20.800 usec
DE                  6.50 usec
TE                 297.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        100.6228298 MHz
NUC1                 13C
P1                  9.50 usec
PLW1        53.00000000 W
SFO2        400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2        12.00000000 W
PLW12        0.29036999 W
PLW13        0.14605001 W

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

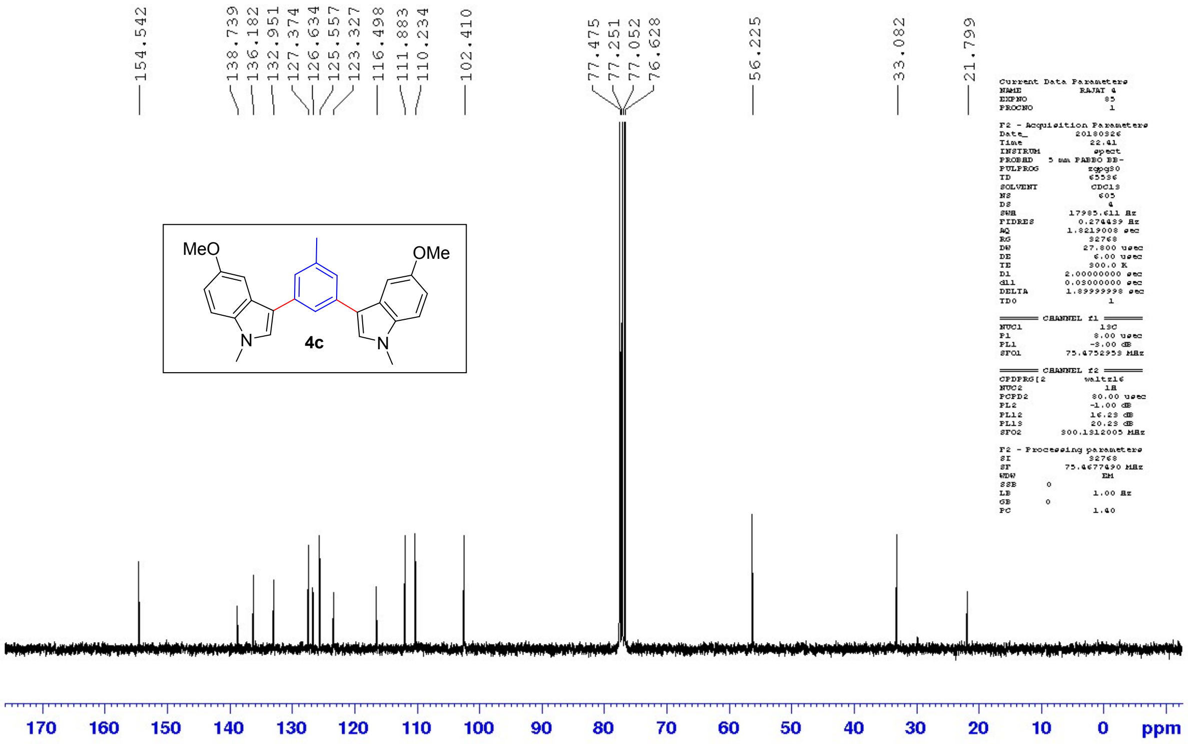
Spectrum 50. 100 MHz ^{13}C NMR of compound 4b



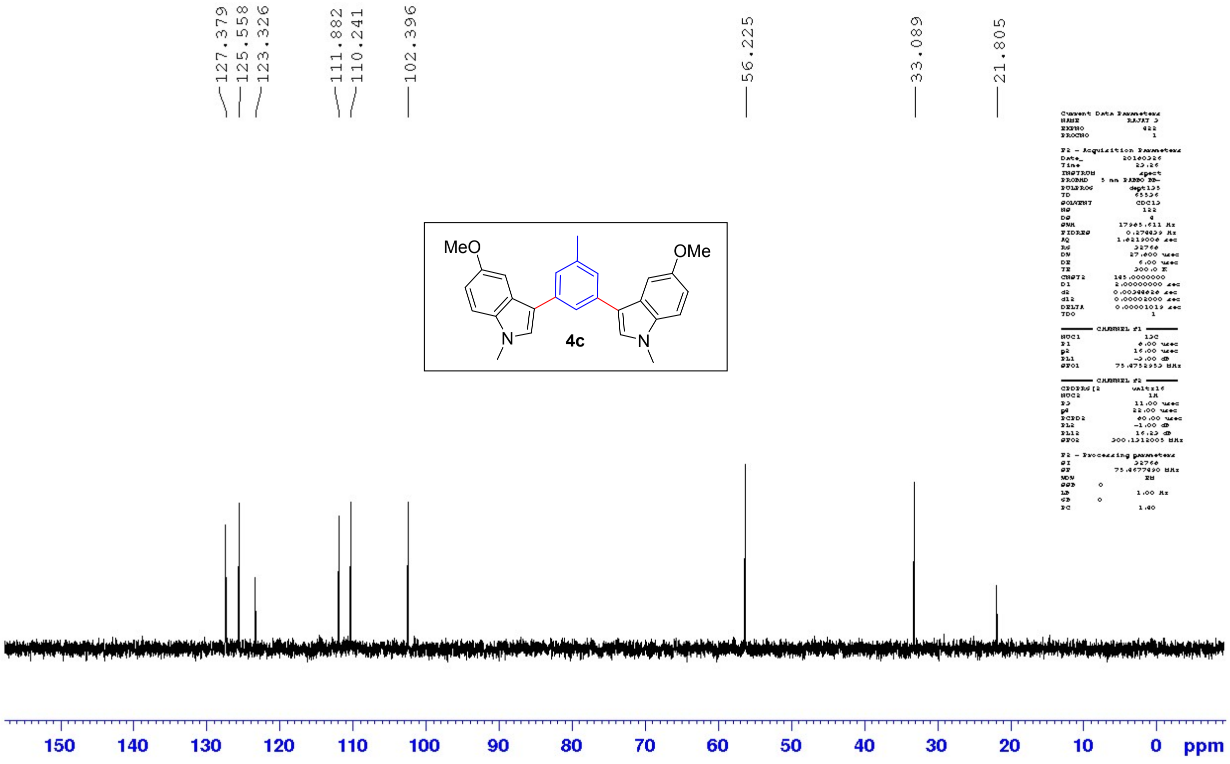
Spectrum 51. MHz DEPT-135 NMR of compound 4b



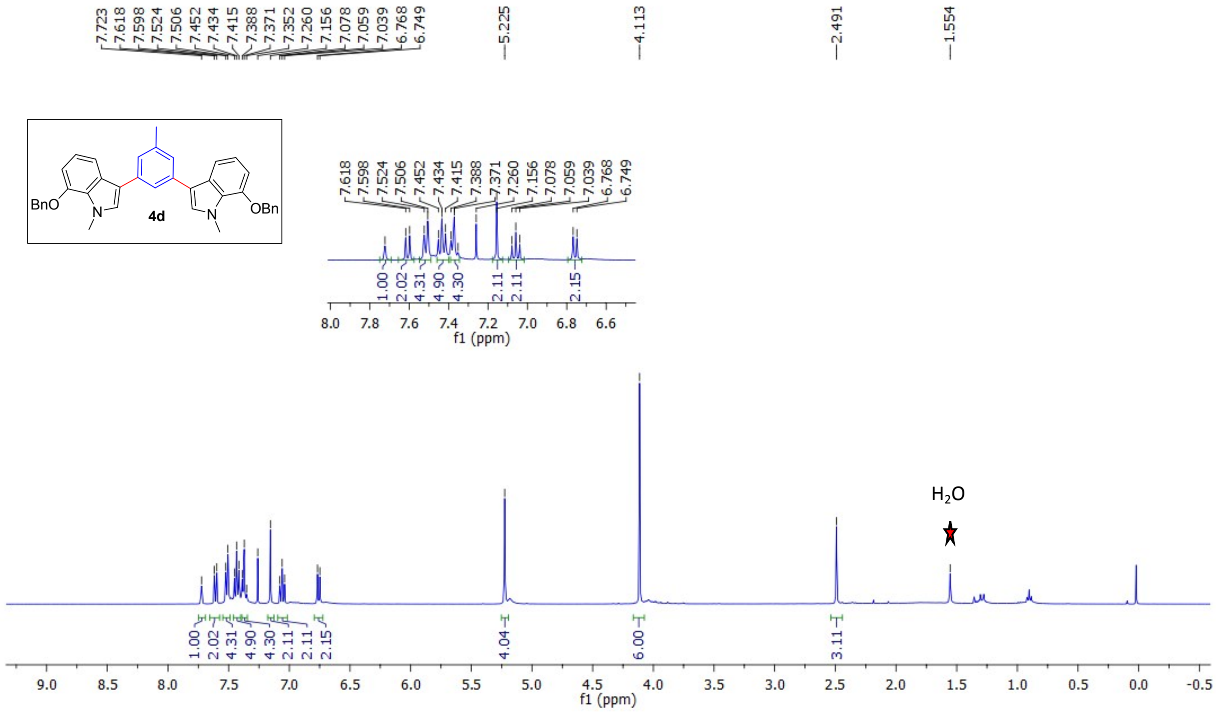
Spectrum 52. 400 MHz ^{1}H NMR of compound 4c



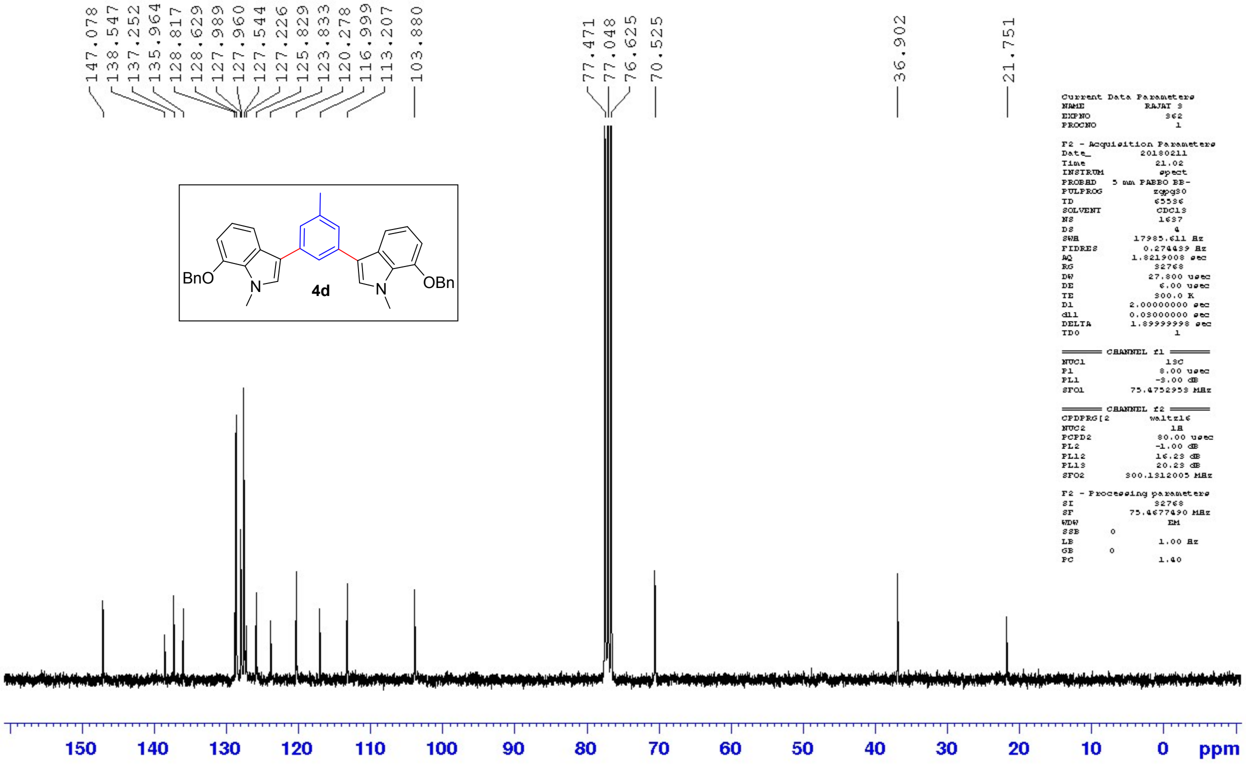
Spectrum 53. 75 MHz ^{13}C NMR of compound 4c



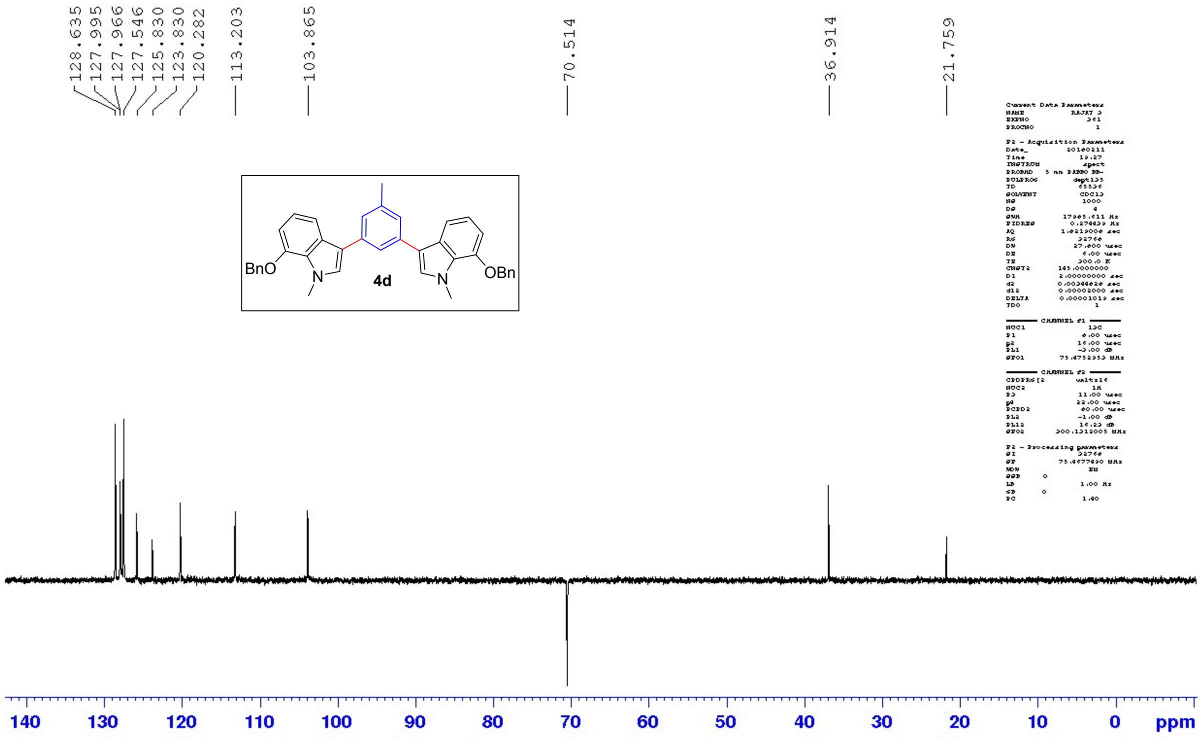
Spectrum 54. 75 MHz DEPT-135 NMR of compound 4c



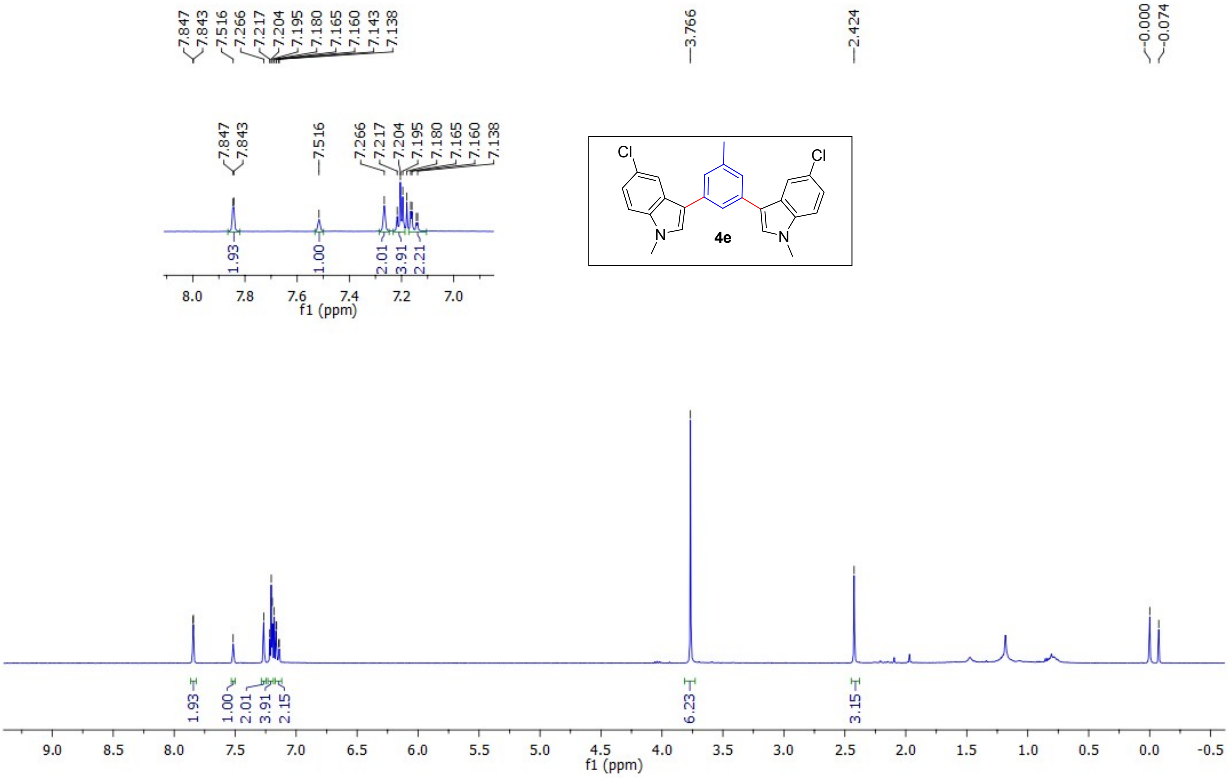
Spectrum 55. 400 MHz ^{1}H NMR of compound 4d



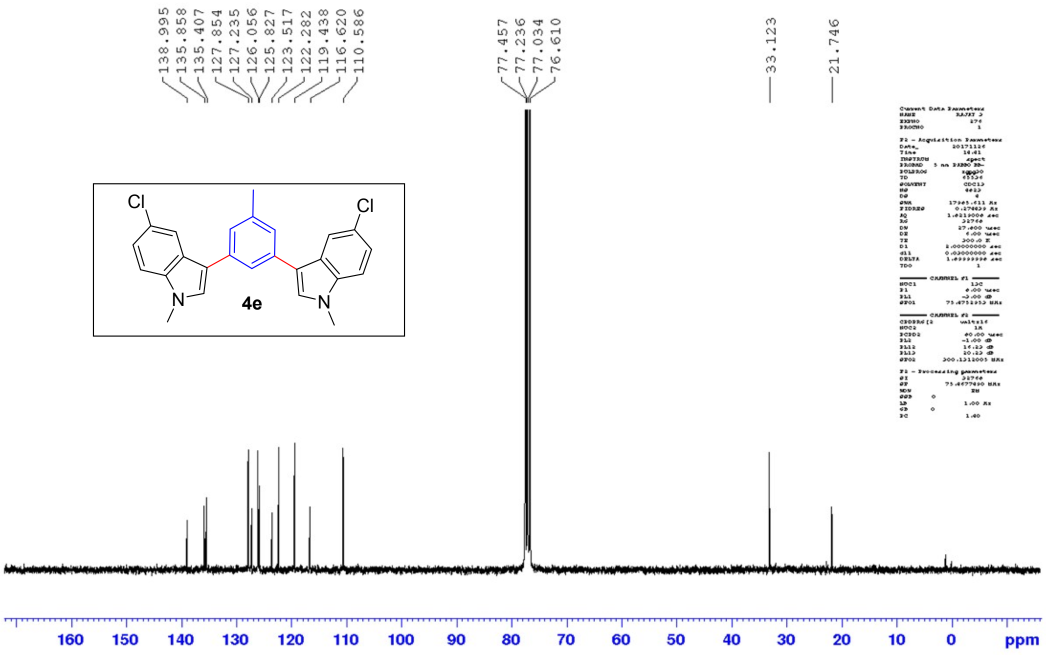
Spectrum 56. 75 MHz ^{13}C NMR of compound 4d



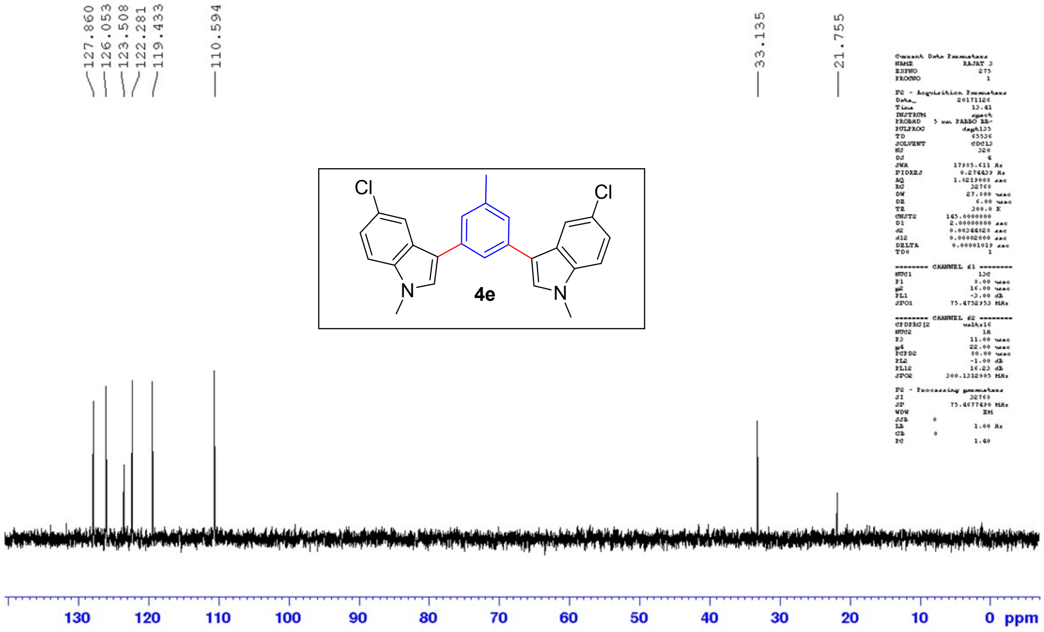
Spectrum 57. 75 MHz DEPT-135 NMR of compound 4d



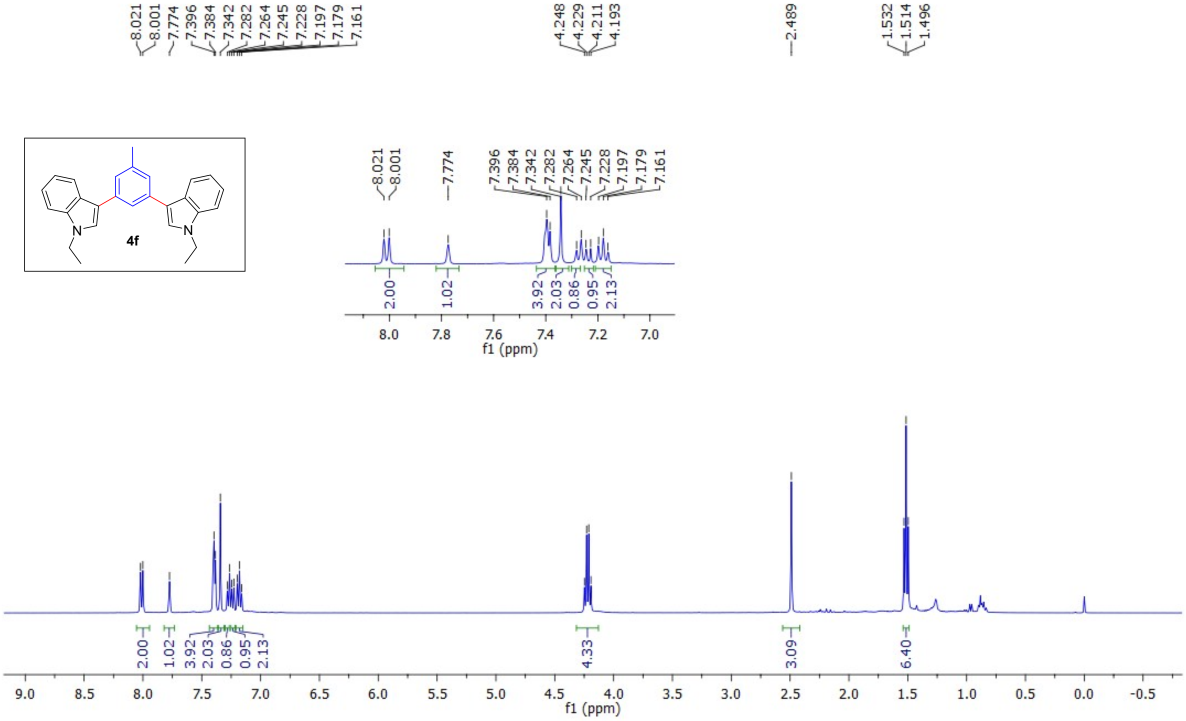
Spectrum 58. 400 MHz ^{1}H NMR of compound 4e



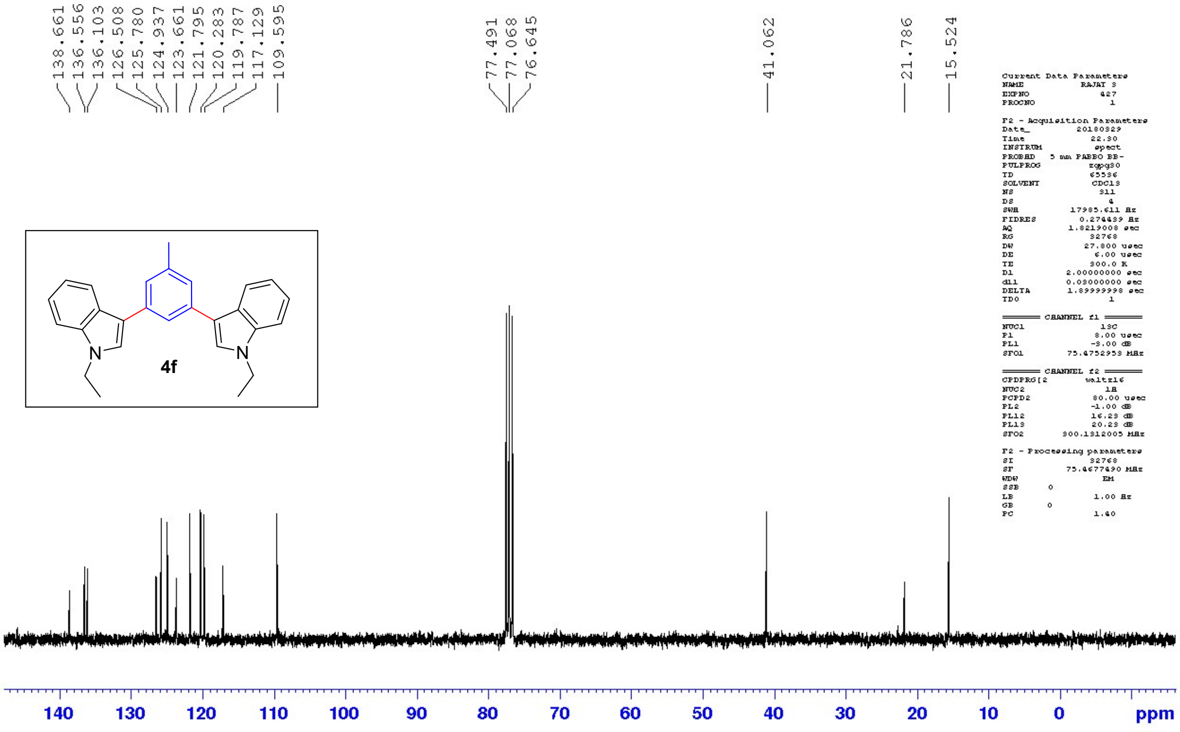
Spectrum 59. 75 MHz ^{13}C NMR of compound 4e



Spectrum 60. 75 MHz DEPT-135 NMR of compound 4e



Spectrum 61. 400 MHz ^{1}H NMR of compound 4f



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Current Data Parameters
NAME             RAJAT S
EXPNO                427
PROCNO                 1

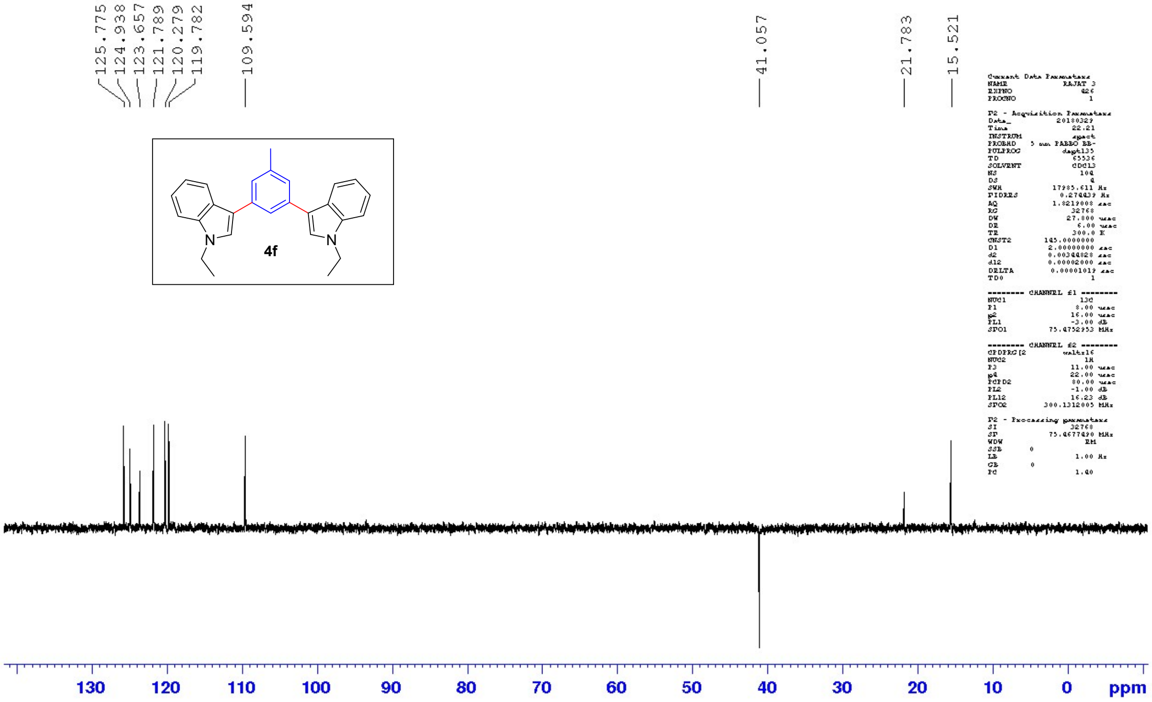
F2 - Acquisition Parameters
Date_           20180329
Time               22.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  311
DS                    4
SWH         17985.611 Hz
FIDRES       0.274439 Hz
AQ          1.8219008 sec
RG                32768
DW             27.800 usec
DE               6.00 usec
TE              300.0 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1               8.00 usec
PL1             -3.00 dB
SFO1        75.4752953 MHz

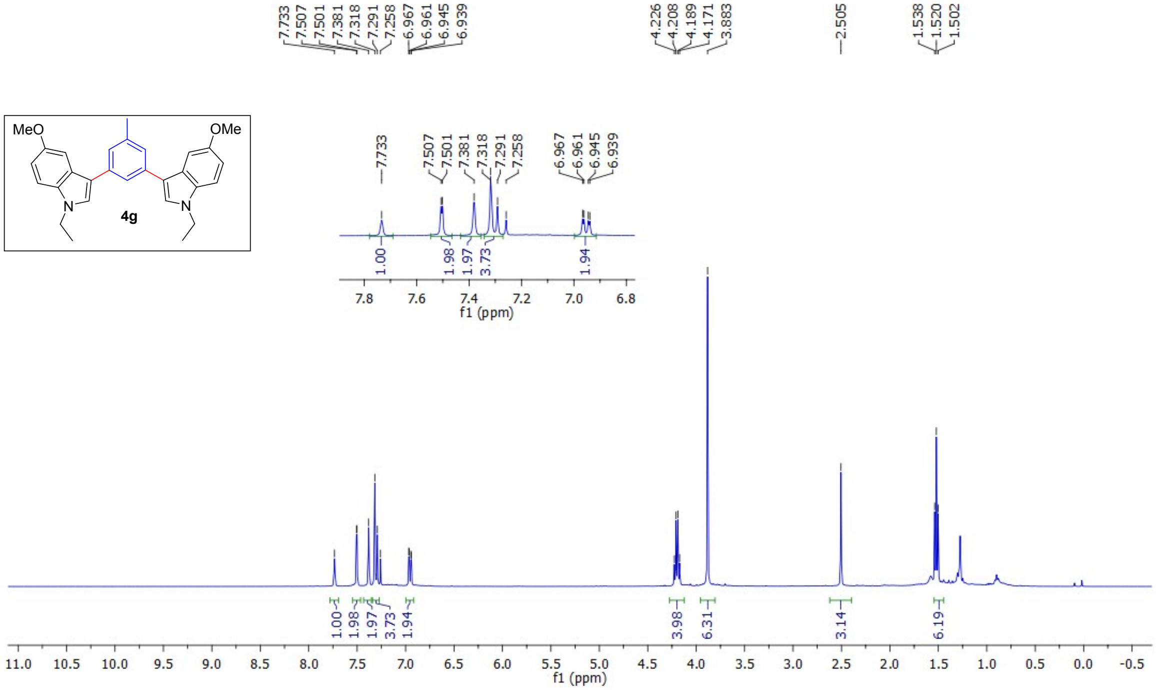
======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2           80.00 usec
PL2             -1.00 dB
PL12            16.23 dB
PL13            20.23 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677490 MHz
WDW                  EM
SSB      0
LB               1.00 Hz
GB       0
PC                 1.40
```

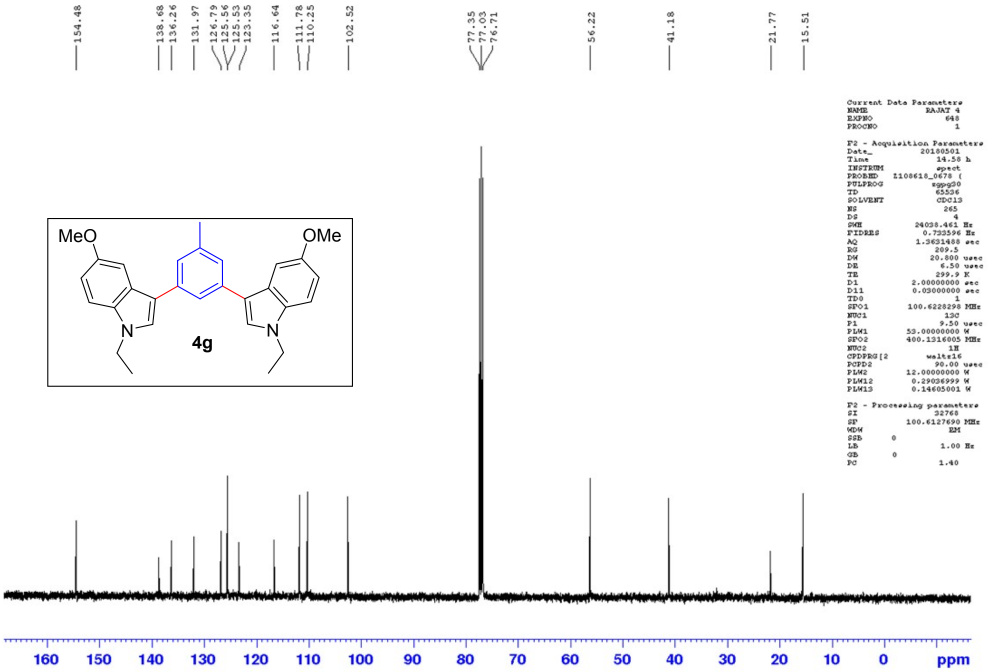
Spectrum 62. 75 MHz ^{13}C NMR of compound 4f



Spectrum 63. 75 DEPT-135 NMR of compound 4f



Spectrum 64. 400 MHz ^{1}H NMR of compound 4g

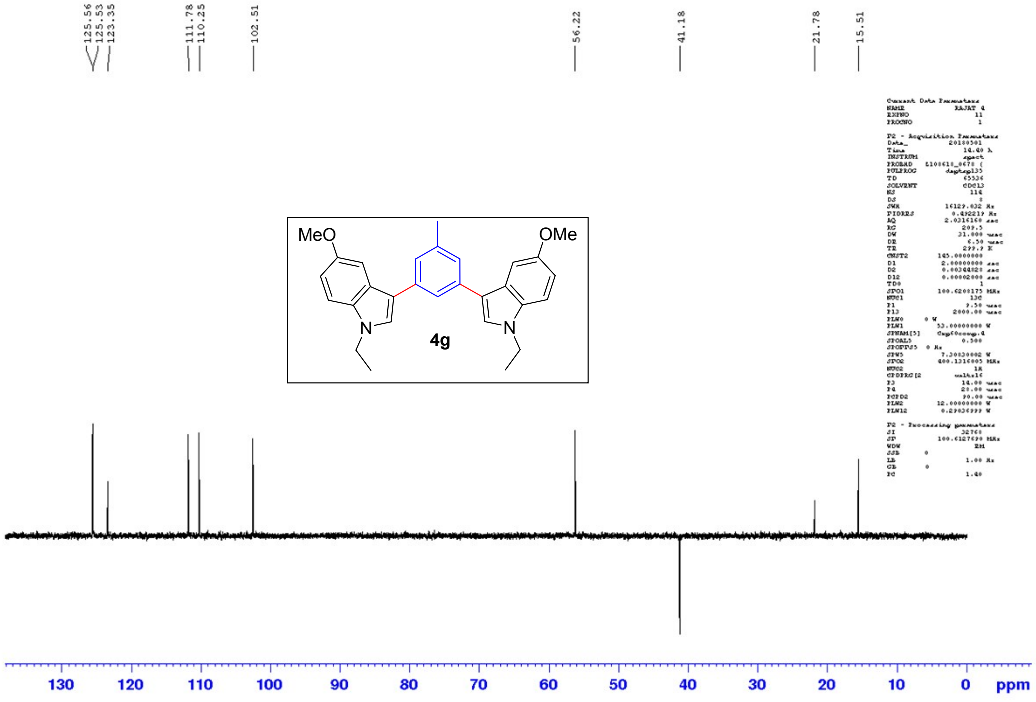


```
Current Data Parameters
NAME             RAJAT 4
EXPNO                648
PROCNO                 1

F2 - Acquisition Parameters
Date_          20180501
Time              14.58 h
INSTRUM           spect
PROBHD   Z108618_0678 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  265
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG                209.5
DW               20.800 usec
DE                 6.50 usec
TE                299.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1                13C
P1                 9.50 usec
PLW1        53.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.29036999 W
PLW13        0.14605001 W

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Spectrum 65. 100 MHz ^{13}C NMR of compound 4g

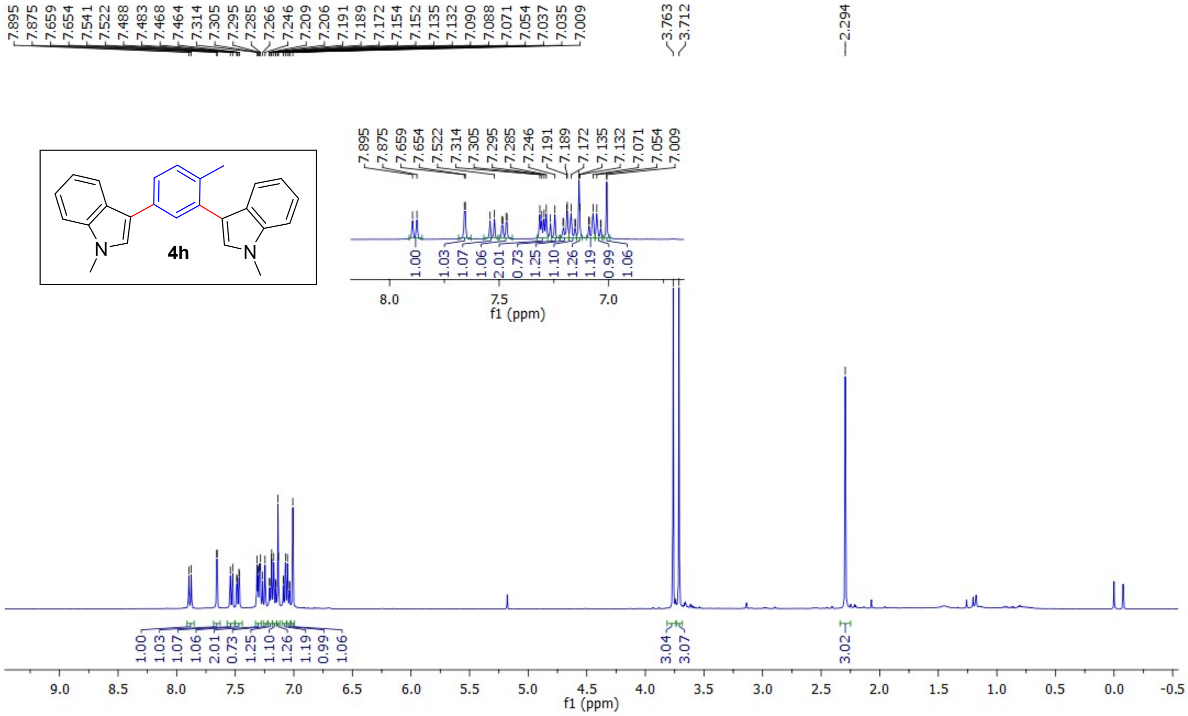


```
Current Data Parameters
NAME             RAJAT 4
EXPNO                 11
PROCNO                 1

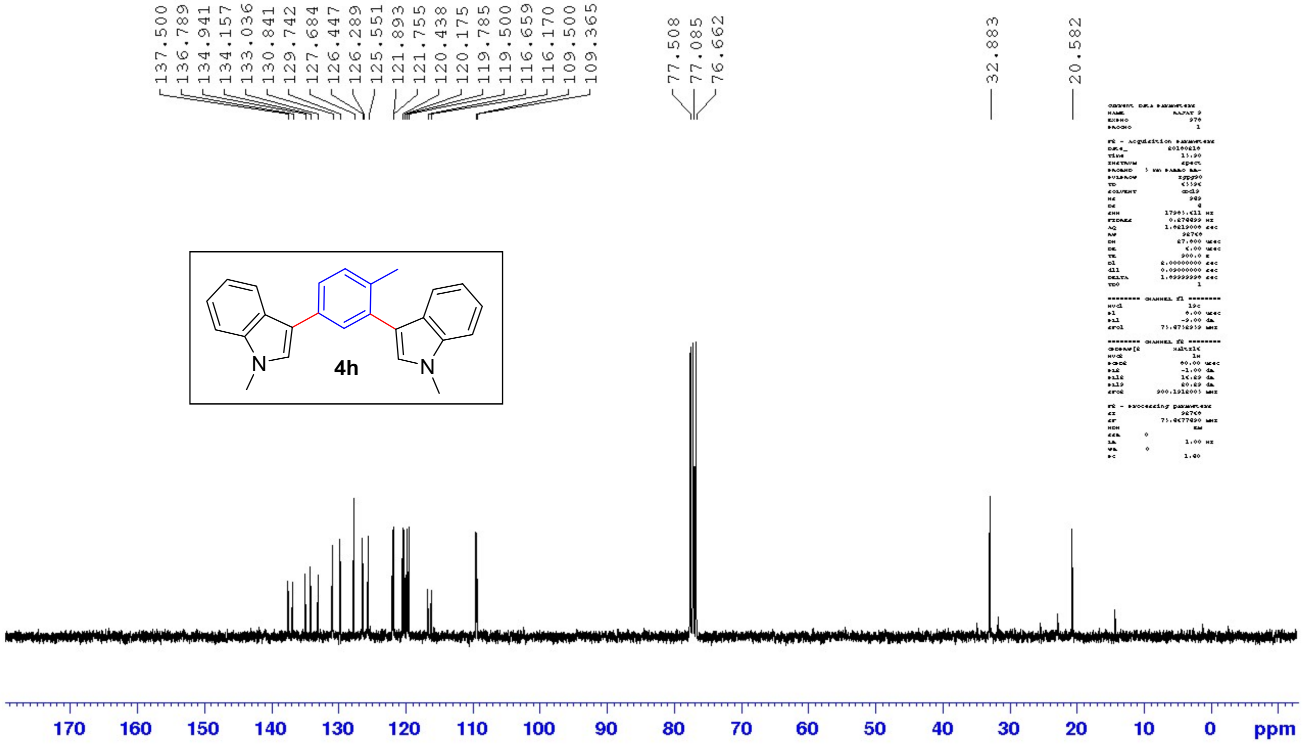
F2 - Acquisition Parameters
Date_          20180501
Time              14.40 h
INSTRUM           spect
PROBHD   Z108618_0678 (
PULPROG       deptsp135
TD                65536
SOLVENT           CDCl3
NS                  114
DS                    8
SWH           16129.032 Hz
FIDRES         0.492219 Hz
AQ            2.0316160 sec
RG                209.5
DW               31.000 usec
DE                 6.50 usec
TE                299.9 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                   1
SFO1        100.6208175 MHz
NUC1                13C
P1                 9.50 usec
P13             2000.00 usec
PLW0      0 W
PLW1        53.00000000 W
SPNAM[5]    Crp60comp.4
SPOAL5            0.500
SPOFFS5   0 Hz
SPW5         7.30830002 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
P3                14.00 usec
P4                28.00 usec
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.29036999 W

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

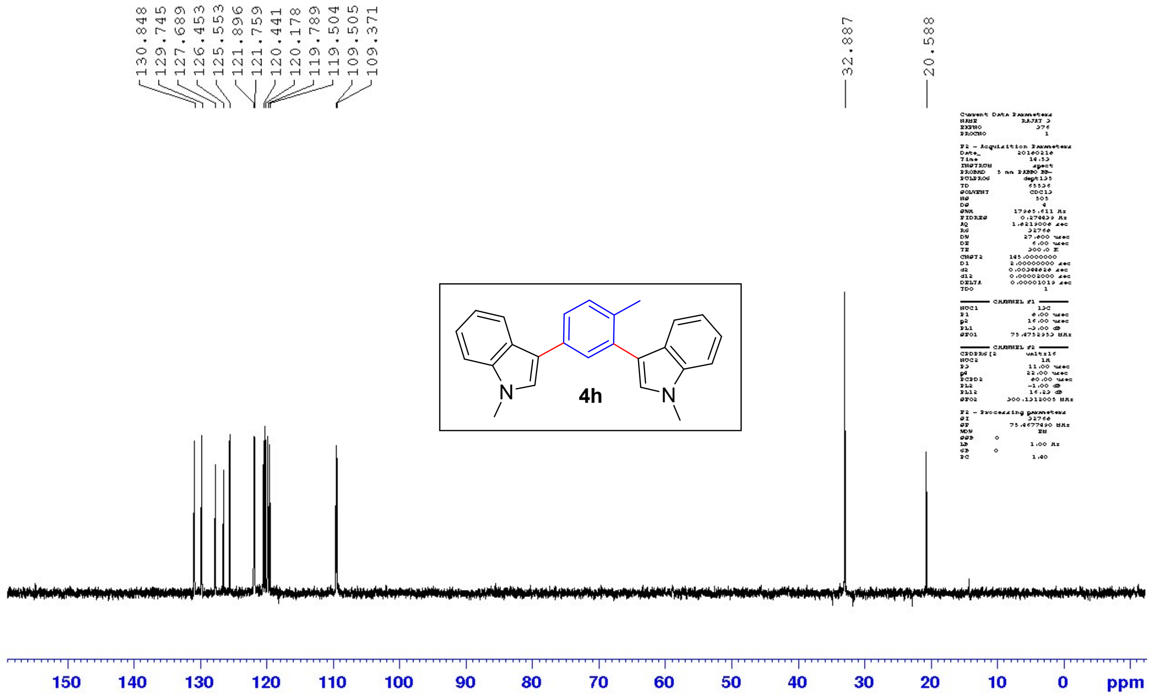
Spectrum 66. 100 MHz DEPT-135 NMR of compound 4g



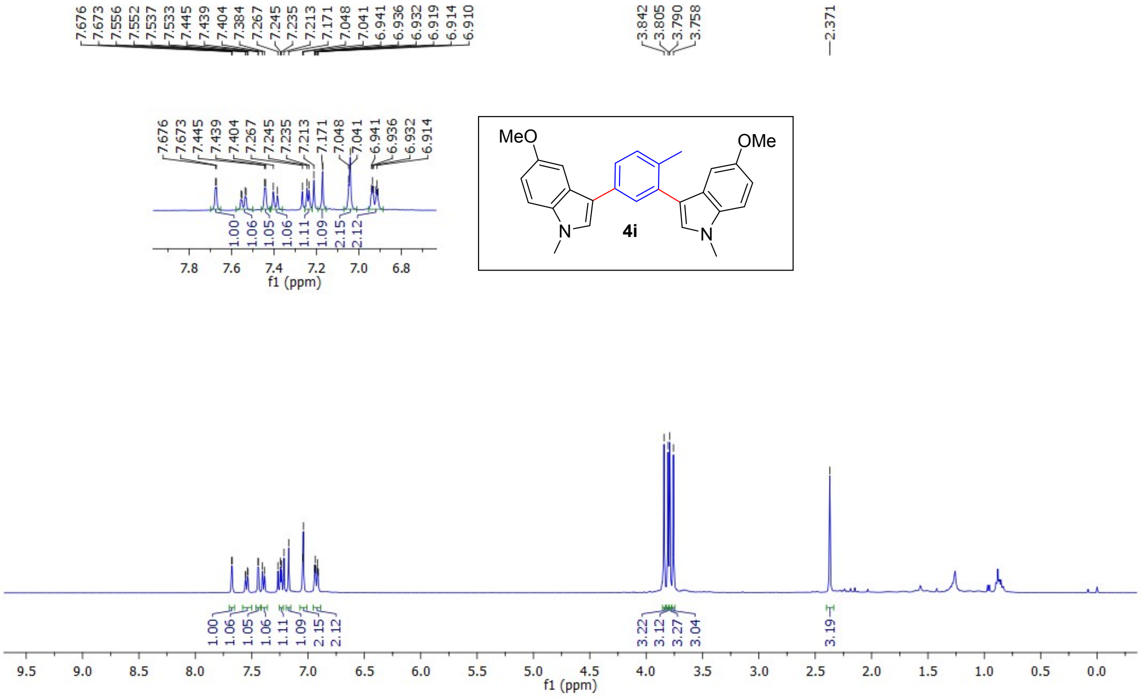
Spectrum 67. 400 MHz ^{1}H NMR of compound 4h



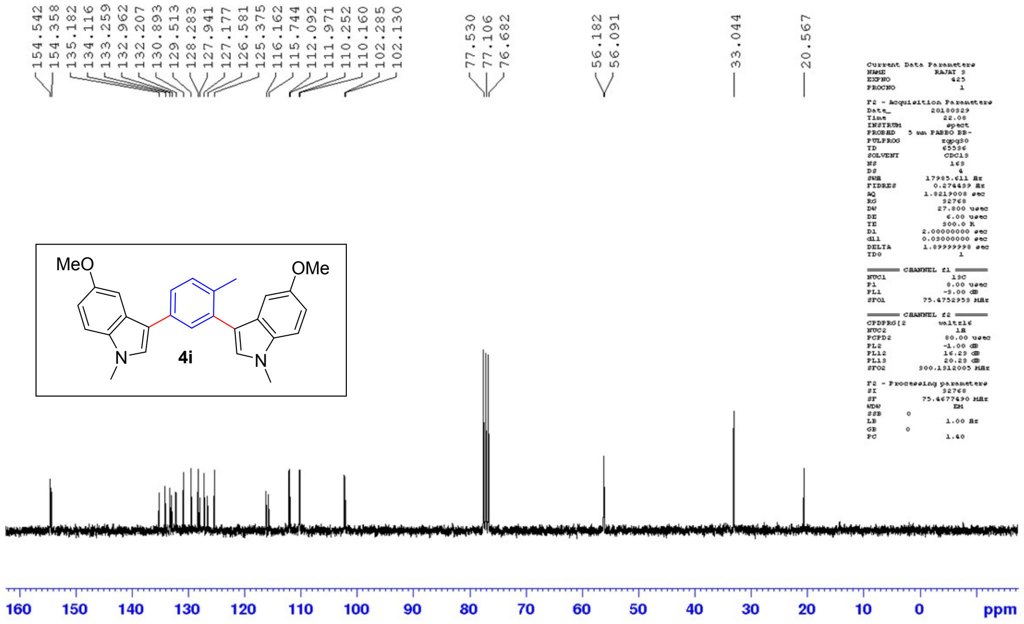
Spectrum 68. 75 MHz ^{13}C NMR of compound 4h



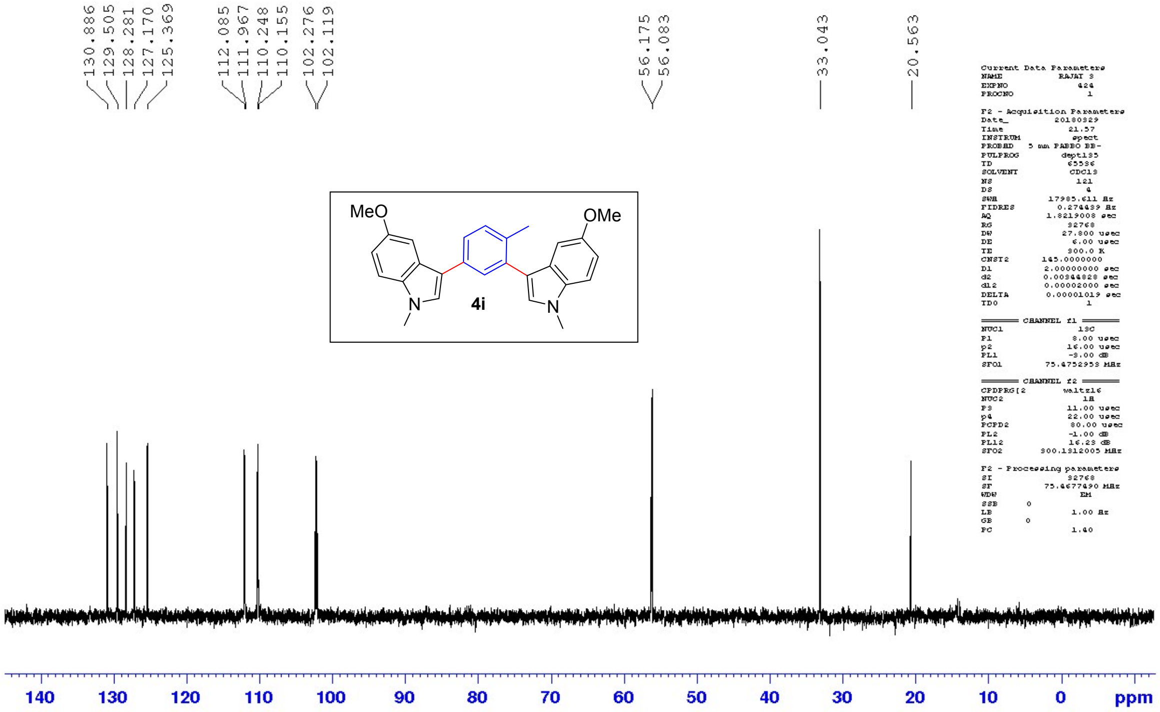
Spectrum 69. 75 MHz DEPT-135 NMR of compound 4h



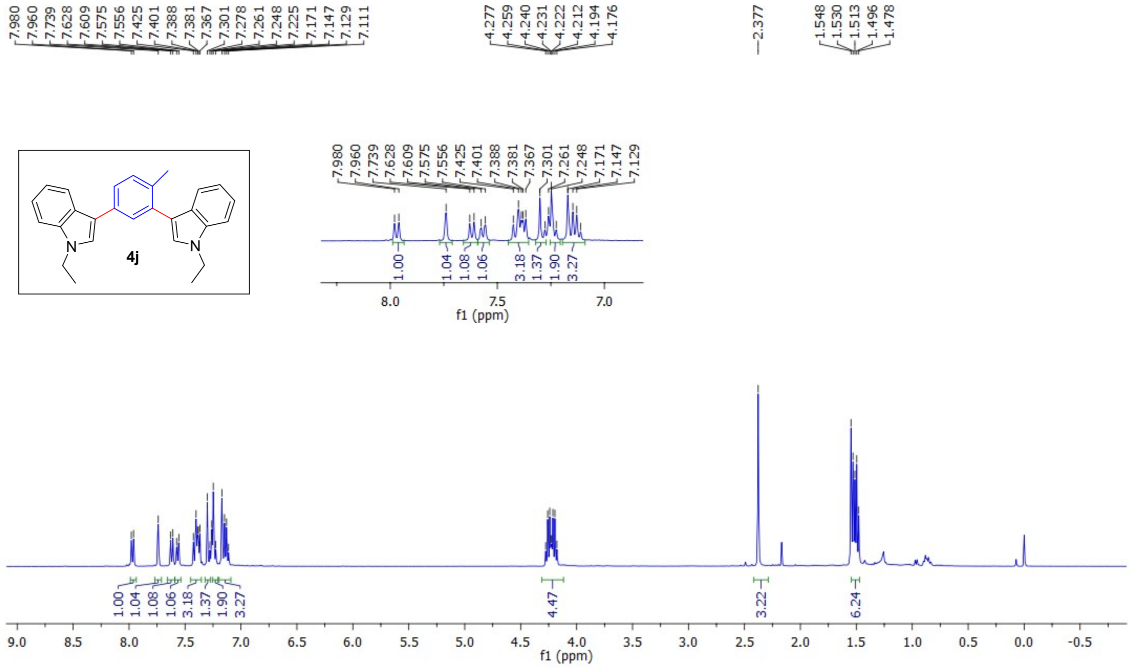
Spectrum 70. 400 MHz ^{1}H NMR of compound 4i



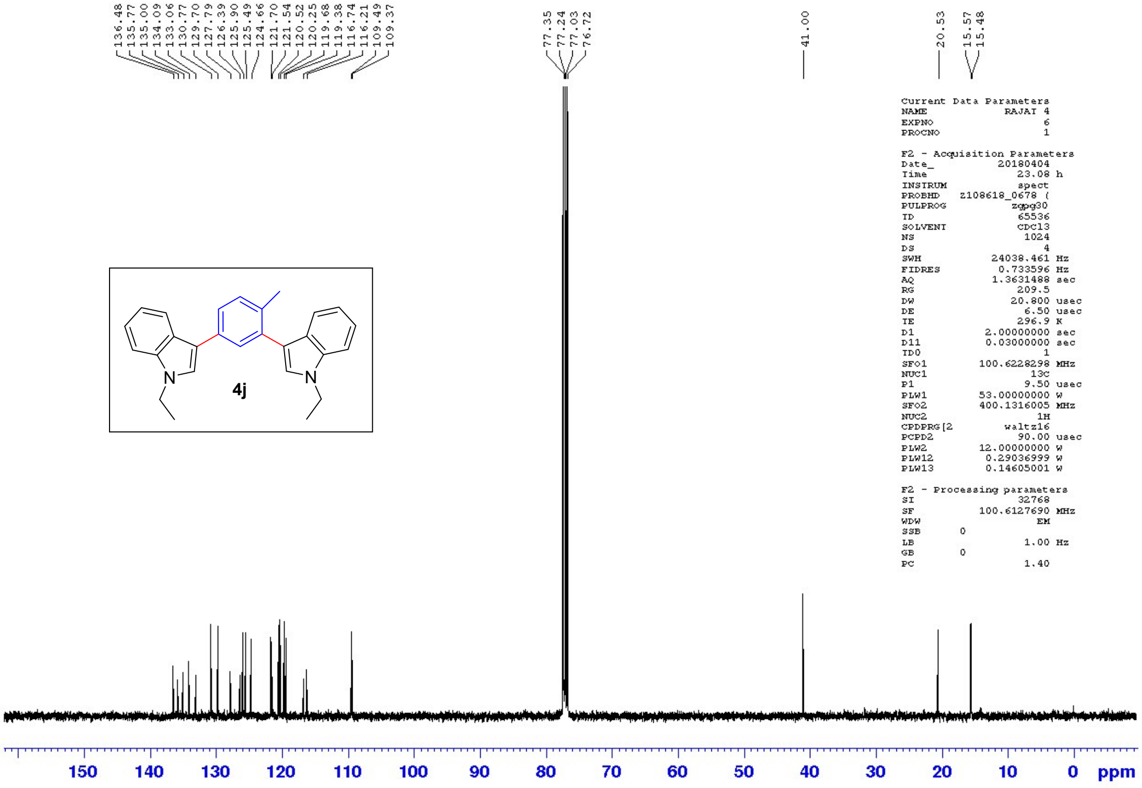
Spectrum 71. 75 MHz ^{13}C NMR of compound 4i



Spectrum 72. 75 MHz DEPT-135 NMR of compound 4i



Spectrum 73. 400 MHz ^{1}H NMR of compound 4j

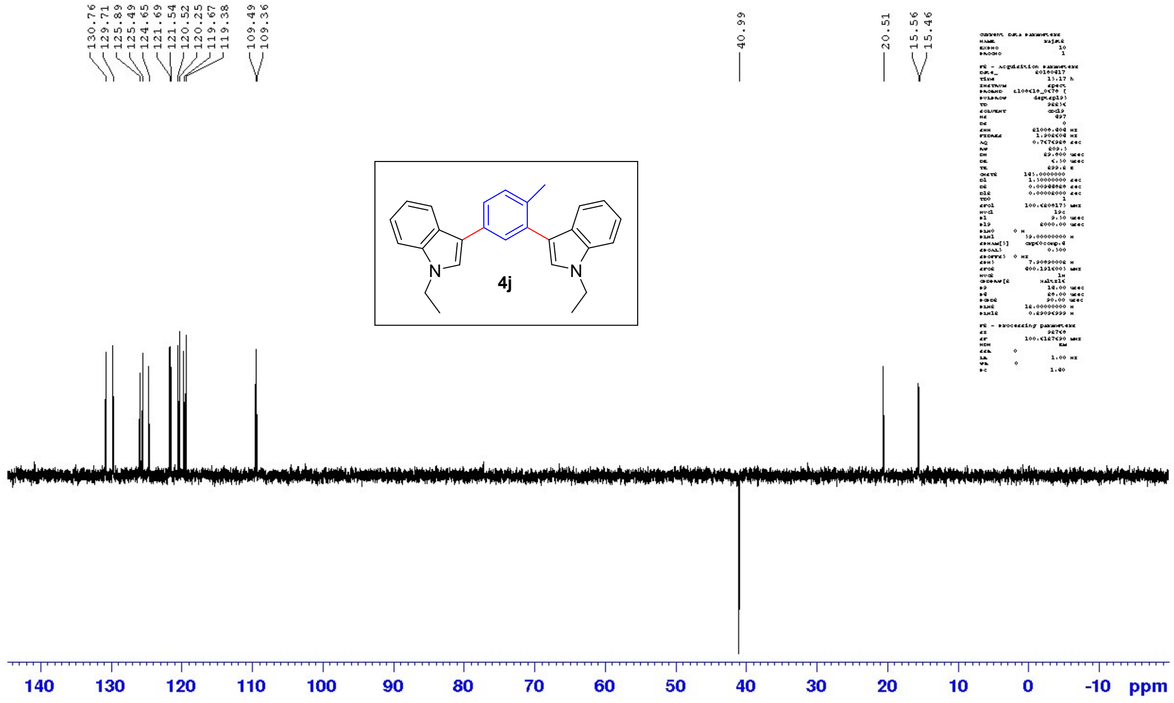


```
Current Data Parameters
NAME             RAJAT 4
EXPNO                  6
PROCNO                 1

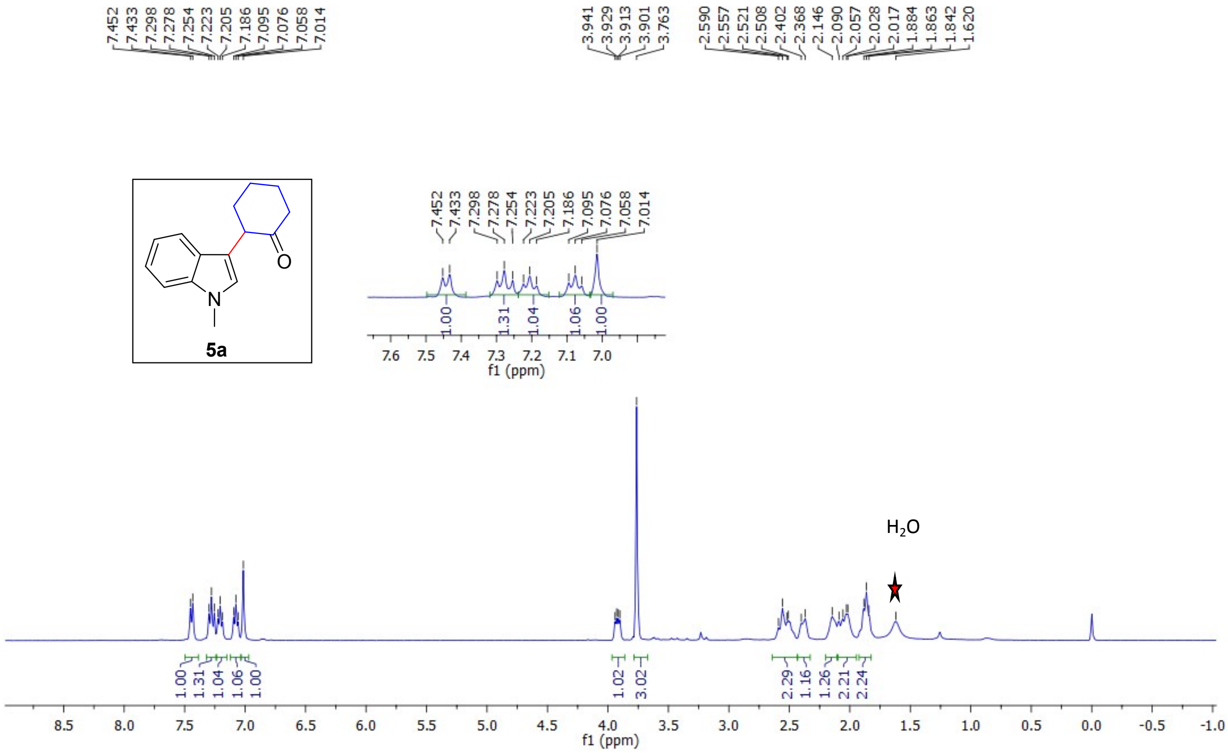
F2 - Acquisition Parameters
Date_           20180404
Time               23.08 h
INSTRUM            spect
PROBHD   Z108618_0678 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             1.3631488 sec
RG                 209.5
DW                20.800 usec
DE                  6.50 usec
TE                 296.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         100.6228298 MHz
NUC1                 13C
P1                  9.50 usec
PLW1         53.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.29036999 W
PLW13         0.14605001 W

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

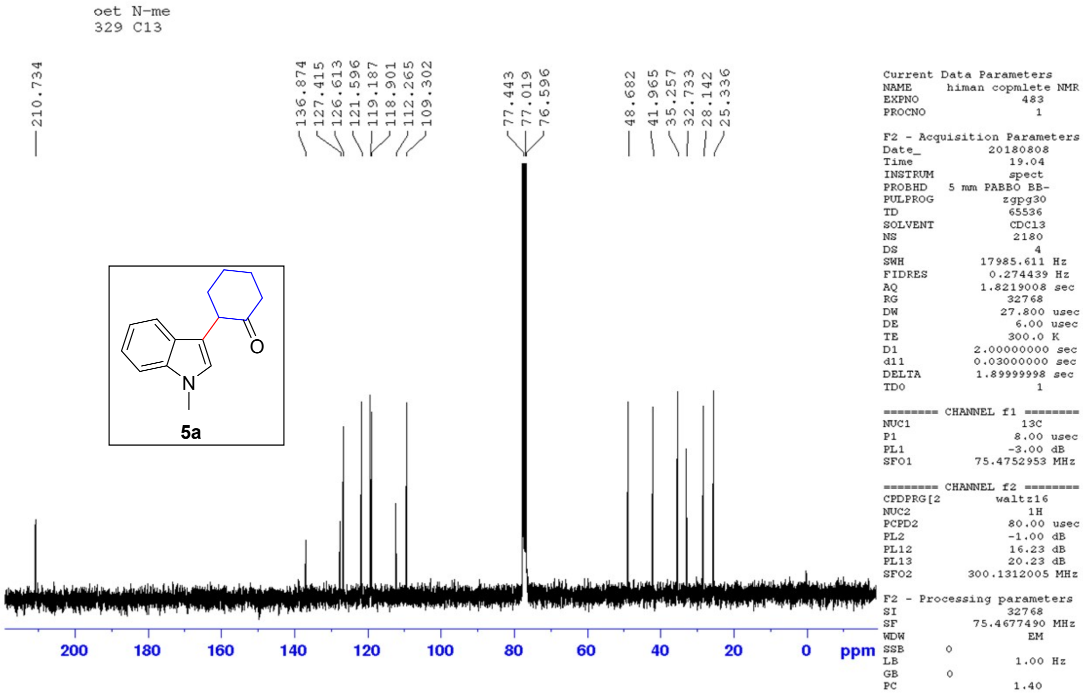
Spectrum 74. 100 MHz ^{13}C NMR of compound 4j



Spectrum 75. 100 DEPT-135 NMR of compound 4j



Spectrum 76. 400 MHz ^{1}H NMR of compound 5a



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Current Data Parameters
NAME      himan copmlete NMR
EXPNO                  483
PROCNO                   1

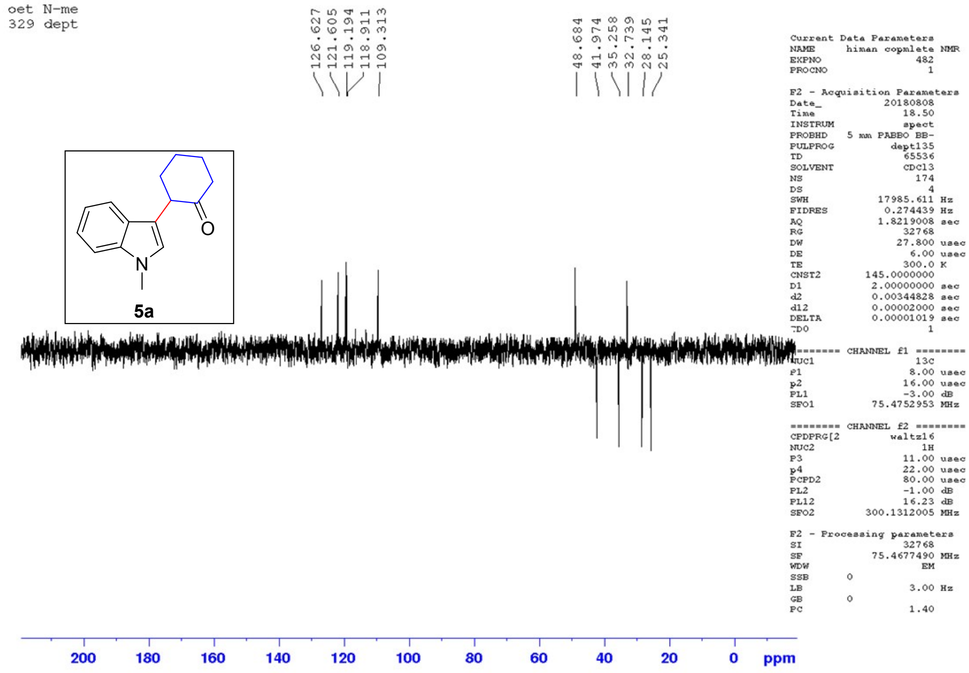
F2 - Acquisition Parameters
Date_             20180808
Time                 19.04
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2180
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219008 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                  -3.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.23 dB
PL13                 20.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Spectrum 77. 75 MHz ^{13}C NMR of compound 5a



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Current Data Parameters
NAME      himan copmlete NMR
EXPNO                  482
PROCNO                   1

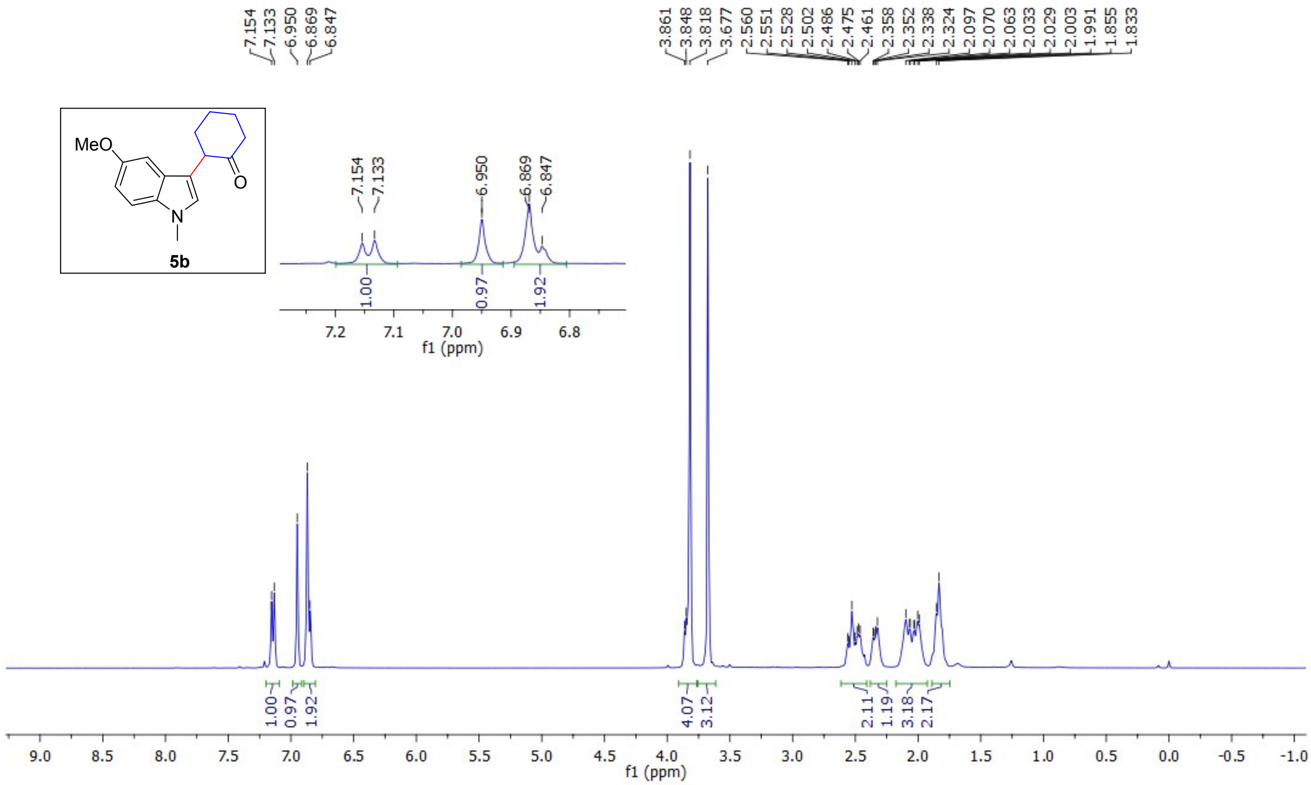
F2 - Acquisition Parameters
Date_             20180808
Time                 18.50
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG           dept135
TD                   65536
SOLVENT              CDCl3
NS                     174
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219008 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001019 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
p2                   16.00 usec
PL1                  -3.00 dB
SFO1            75.4752953 MHz

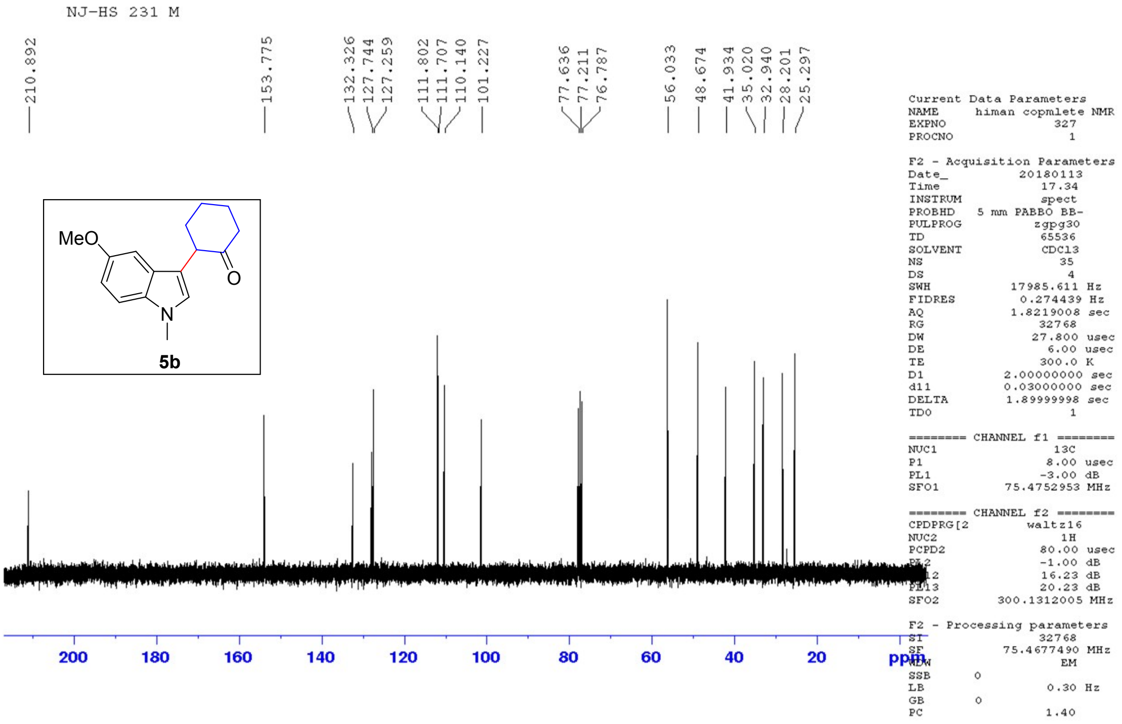
======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
P3                   11.00 usec
p4                   22.00 usec
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB       0
LB                    3.00 Hz
GB        0
PC                    1.40
```

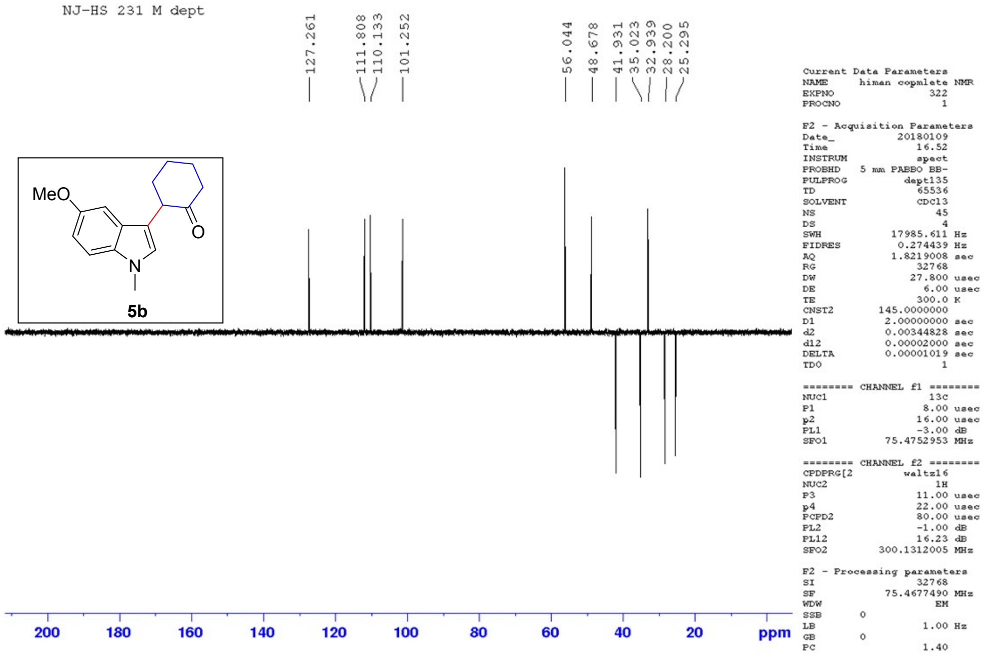
Spectrum 78. 75 MHz DEPT-135 NMR of compound 5a



Spectrum 79. 400 MHz ^{1}H NMR of compound 5b



Spectrum 80. 75 MHz ^{13}C NMR of compound 5b



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Current Data Parameters
NAME      himan copmlete NMR
EXPNO                  322
PROCNO                   1

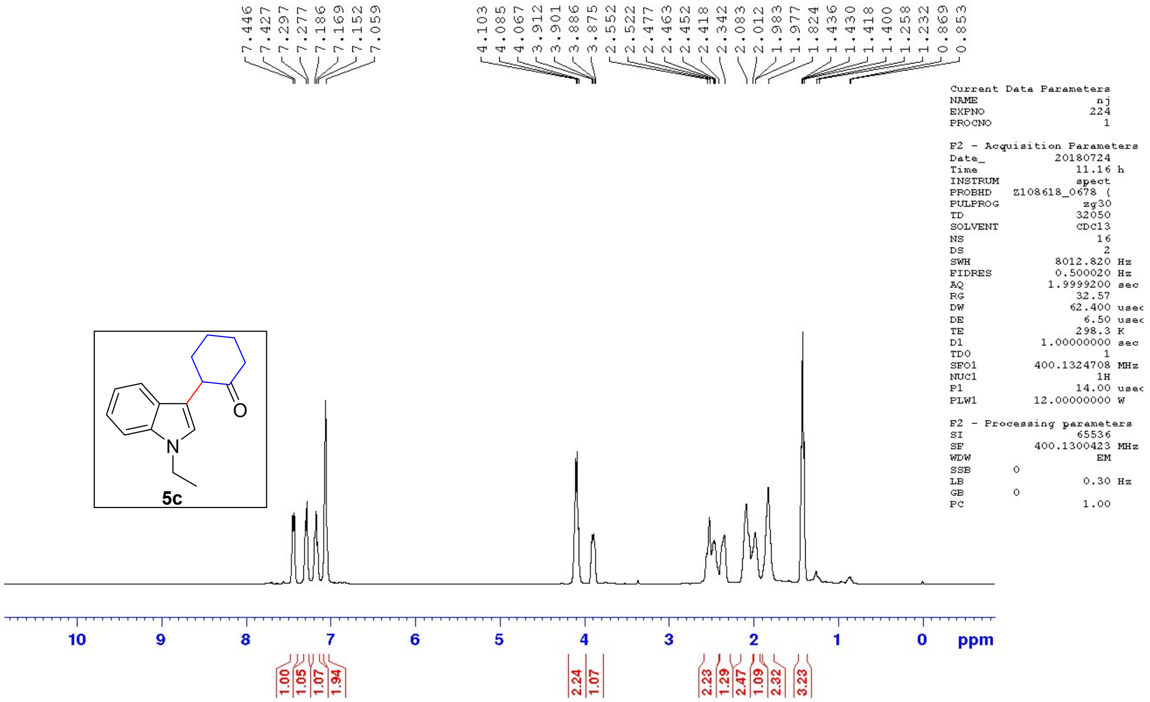
F2 - Acquisition Parameters
Date_             20180109
Time                 16.52
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            dept135
TD                   65536
SOLVENT              CDCl3
NS                      45
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219008 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00001019 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
p2                   16.00 usec
PL1                  -3.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
P3                   11.00 usec
p4                   22.00 usec
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Spectrum 81. 75 MHz DEPT-135 NMR of compound 5b

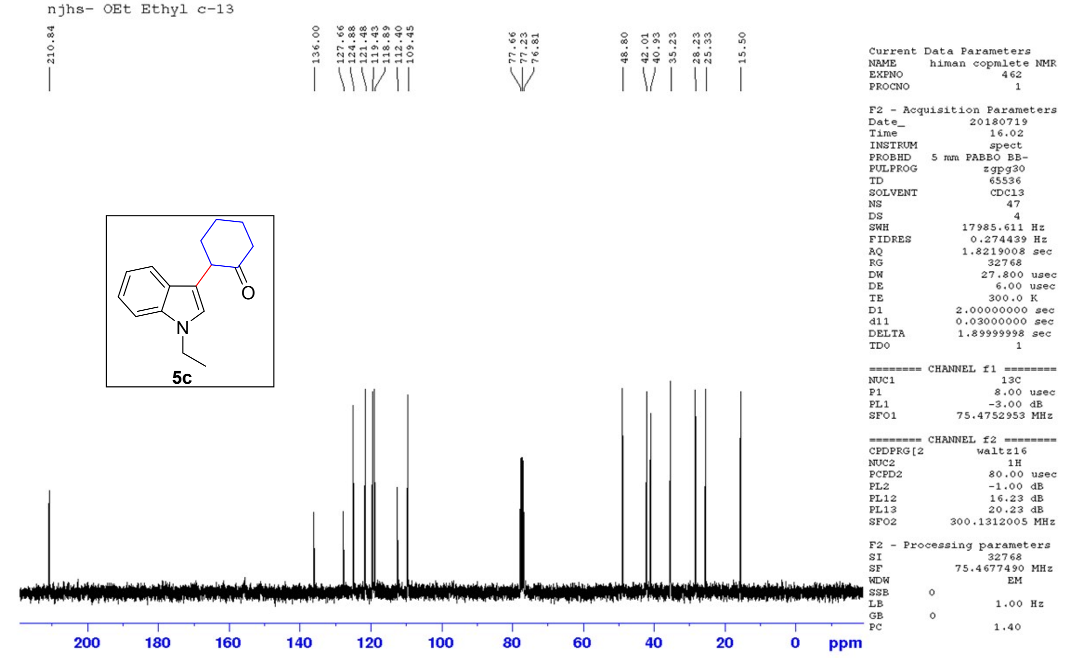


```
Current Data Parameters
NAME                    nj
EXPNO                  224
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180724
Time                 11.16 h
INSTRUM              spect
PROBHD   Z108618_0678 (
PULPROG               zg30
TD                   32050
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.500020 Hz
AQ               1.9999200 sec
RG                   32.57
DW                  62.400 usec
DE                    6.50 usec
TE                   298.3 K
D1              1.00000000 sec
TD0                      1
SFO1           400.1324708 MHz
NUC1                    1H
P1                   14.00 usec
PLW1           12.00000000 W

F2 - Processing parameters
SI                   65536
SF             400.1300423 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

Spectrum 82. 400 MHz ^{1}H NMR of compound 5c



```
Current Data Parameters
NAME      himan copmlete NMR
EXPNO                  462
PROCNO                   1

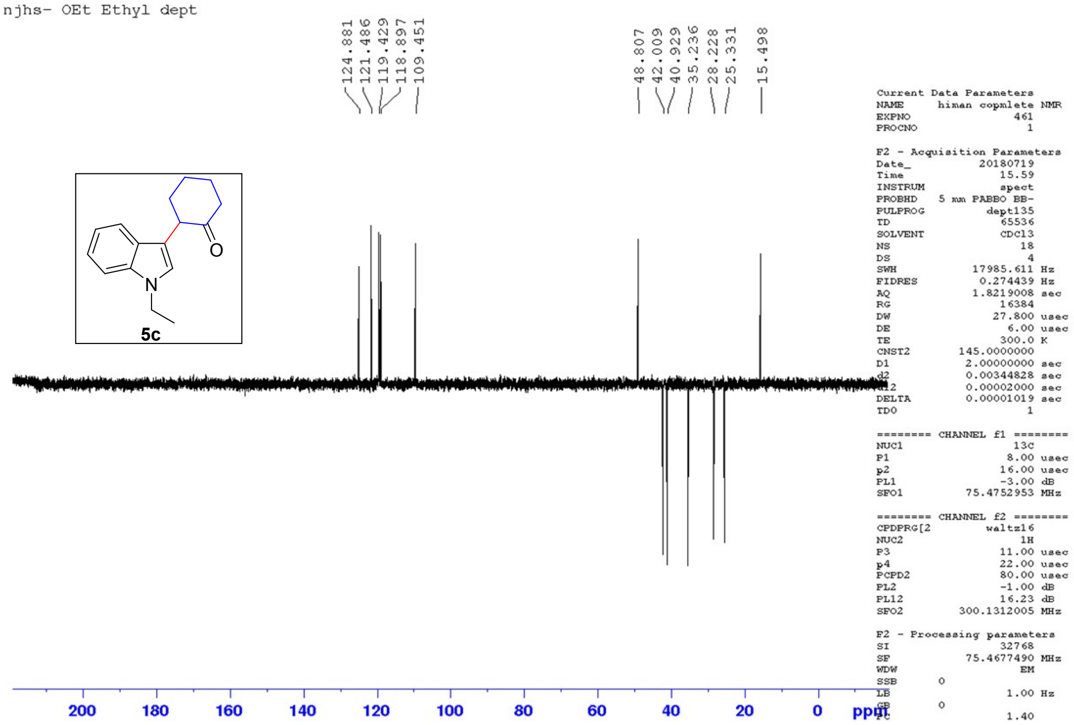
F2 - Acquisition Parameters
Date_             20180719
Time                 16.02
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      47
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219008 sec
RG                   32768
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                  -3.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.23 dB
PL13                 20.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Spectrum 83. 75 MHz ^{13}C NMR of compound 5c



```
Current Data Parameters
NAME      himan copmlete NMR
EXPNO                  461
PROCNO                   1

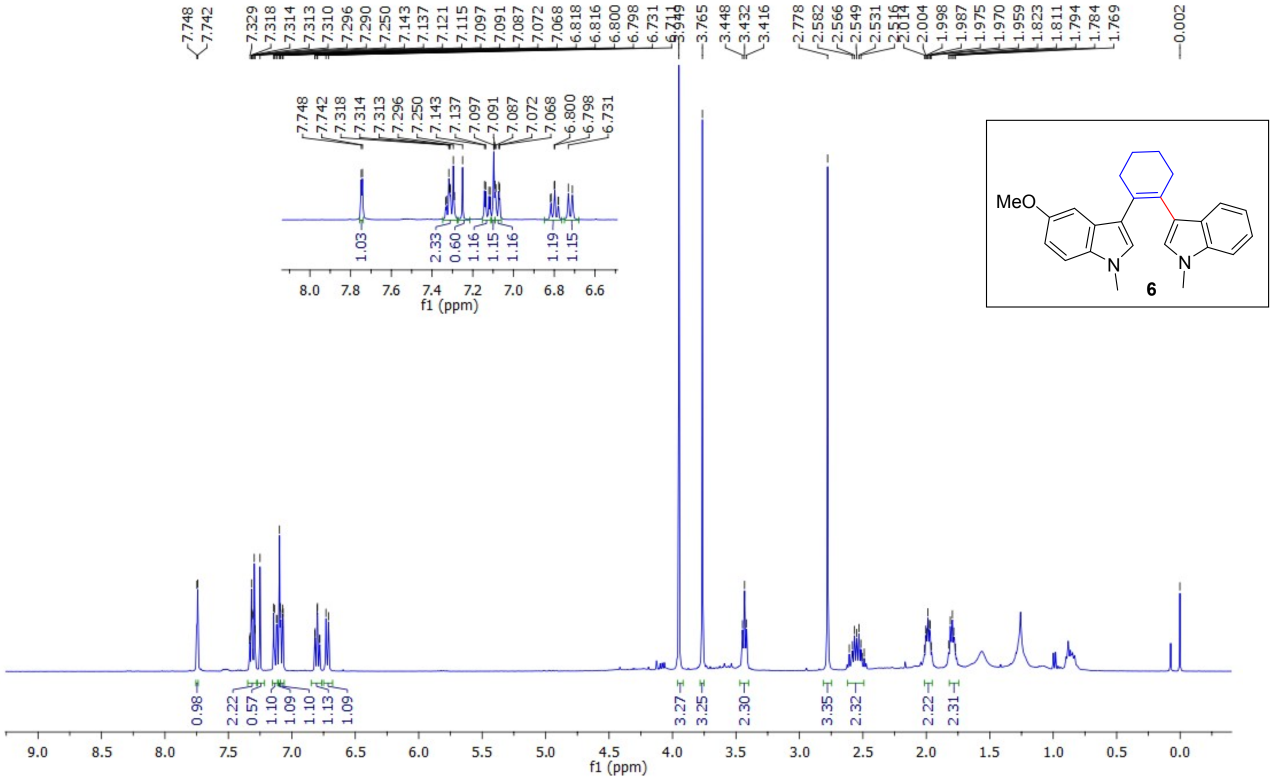
F2 - Acquisition Parameters
Date_             20180719
Time                 15.59
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            dept135
TD                   65536
SOLVENT              CDCl3
NS                      18
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219008 sec
RG                   16384
DW                  27.800 usec
DE                    6.00 usec
TE                   300.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001019 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
p2                   16.00 usec
PL1                  -3.00 dB
SFO1            75.4752953 MHz

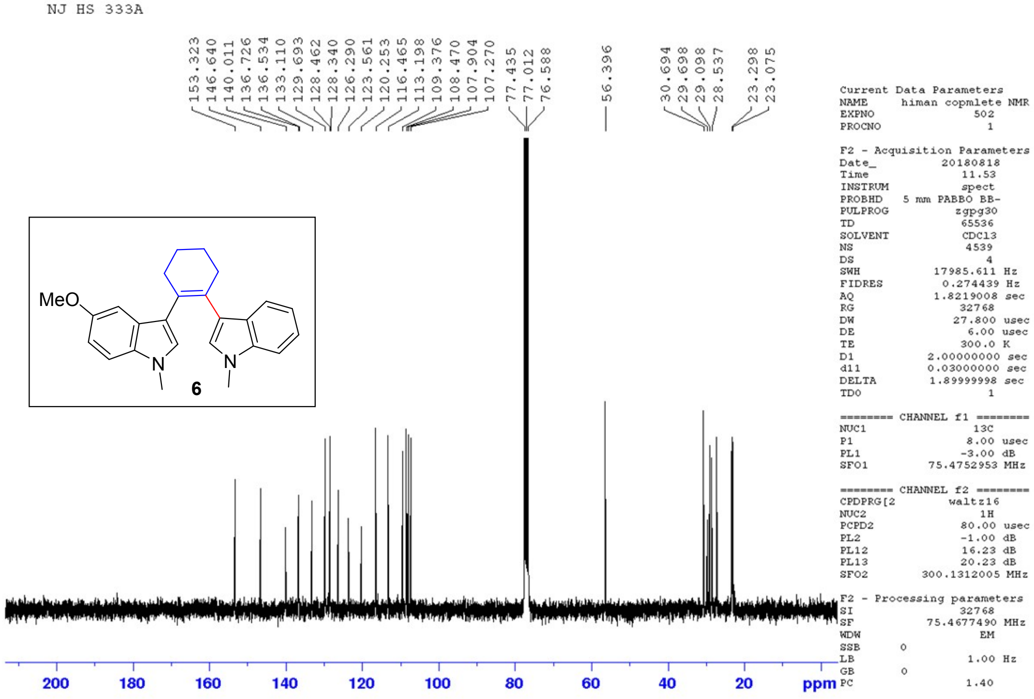
======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
P3                   11.00 usec
p4                   22.00 usec
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 16.23 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF              75.4677490 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Spectrum 84. 75 MHz DEPT-135 NMR of compound 5c



Spectrum 85. 400 MHz ^{1}H NMR of compound 6



```
Current Data Parameters
NAME     himan copmlete NMR
EXPNO                 502
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180818
Time               11.53
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                 4539
DS                    4
SWH         17985.611 Hz
FIDRES       0.274439 Hz
AQ          1.8219008 sec
RG                32768
DW             27.800 usec
DE              6.00 usec
TE             300.0 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -3.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               16.23 dB
PL13               20.23 dB
SFO2        300.1312005 MHz
F2 - Processing parameters
SI                32768
SF          75.4677490 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Spectrum 86. 75 MHz ^{13}C NMR of compound 6

9. Crystallographic Description:

Data collection and refinement single-crystal X-ray data of compounds was collected on Bruker SMART CCD Diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). Frames were collected at T = 297 K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[1] Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods.[2] Non-hydrogen atoms were refined anisotropicallyusing the WinGX (version 1.80.05) program package.[3] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software shown in **figure S5**. Further information on the crystal structure determination (excluding structure factors) has been given as **table S1** and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications number 1918563. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

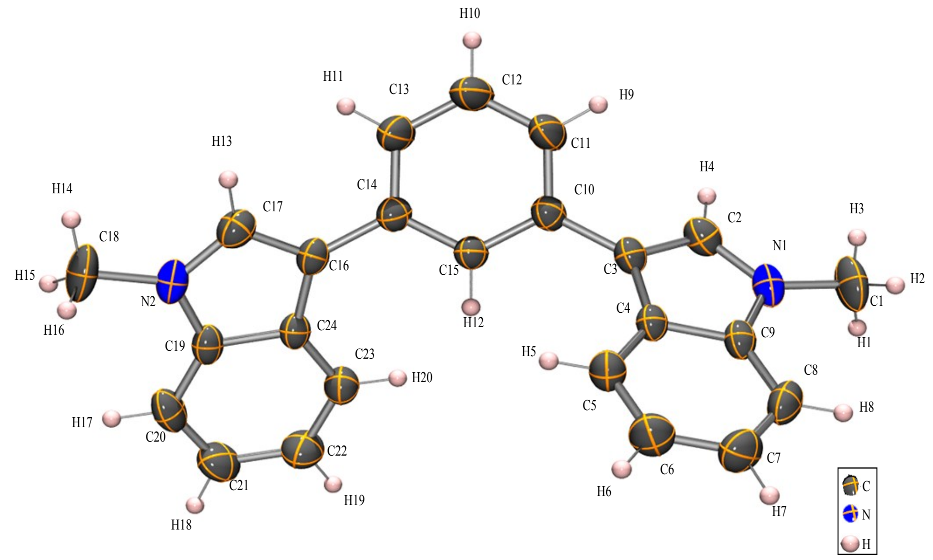


Figure S5. ORTEP diagram of **3a.**

Crystallographic description of 1,3-bis(1-methyl-1H-indol-3-yl)benzene (3a) (Table S1):

Identification code	DD_NA_0m_a
Empirical formula	$C_{24}H_{20}N_2$
Formula weight	336.42
Temperature	297 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 15.931(2) Å α = 90°.
	b = 14.7572(15) Å β = 106.219(4)°.
	c = 8.0025(9) Å γ = 90°.
Volume	1806.5(4) $Å^3$
Z	4
Density (calculated)	1.237 g/cm^3
Absorption coefficient	0.073
F(000)	712.0
Crystal size	0.22 x 0.12 x 0.10 mm^3
Theta range for data collection	2.66 to 24.68°.
Index ranges	-16<=h<=18, -15<=k<=17, -9<=l<=7
Reflections collected	1572
Independent reflections	4820 [R(int) = 0.0397]
Completeness to theta = 24.68°	97.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4820 / 0 / 120
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1448
R indices (all data)	R1 = 0.0900, wR2 = 0.1312
CCDC	1918563

10. References:

(1) SADABS V2.10 (Sheldrick, G. M. **2003**).

(2) (a) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr., **1990**, *46*, 467; (b) Sheldrick, G. M. SHELXL-NT Version 6.12, University of Gottingen, Germany, **2000**.

(3) Farrugia, L. J. J. Appl. Cryst. **1999**, *32*, 837.