

**α -cyanostilbene based Fluorophores: Aggregation Induced Enhanced
Emission, Solvatochromism and pH effect**

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Supporting Information

Part 1. Absorption and emission spectra of stilbenes (1), (4), (5) and (6) in homogeneous solvents

Part 2. Emission studies in dioxane-water system for stilbenes (2), (3), (4), (5), (6); Intensity plot for stilbenes (4)-(6)

Part 3. pH dependent optical properties of stilbene (4) and its NMR interpretation

Part 4. NMR, Mass characterization of the synthesized molecules

Part 1. Absorption and emission spectra of stilbenes (1), (4), (5) and (6) in homogeneous solvents

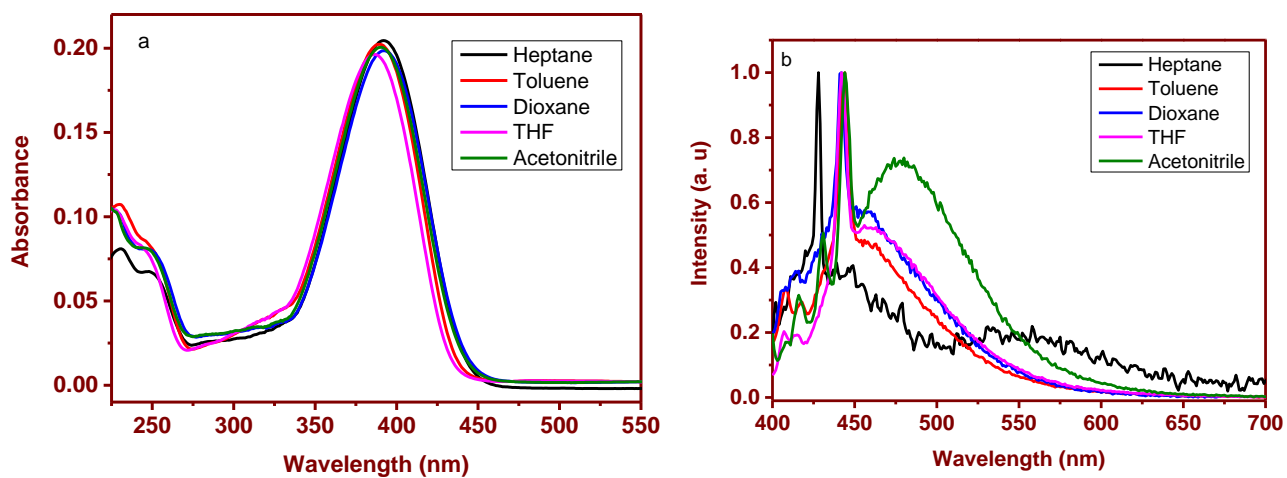


Figure S1: Absorption and emission spectra of stilbene (1) in homogeneous solvents (excitation wavelength is 390 nm)

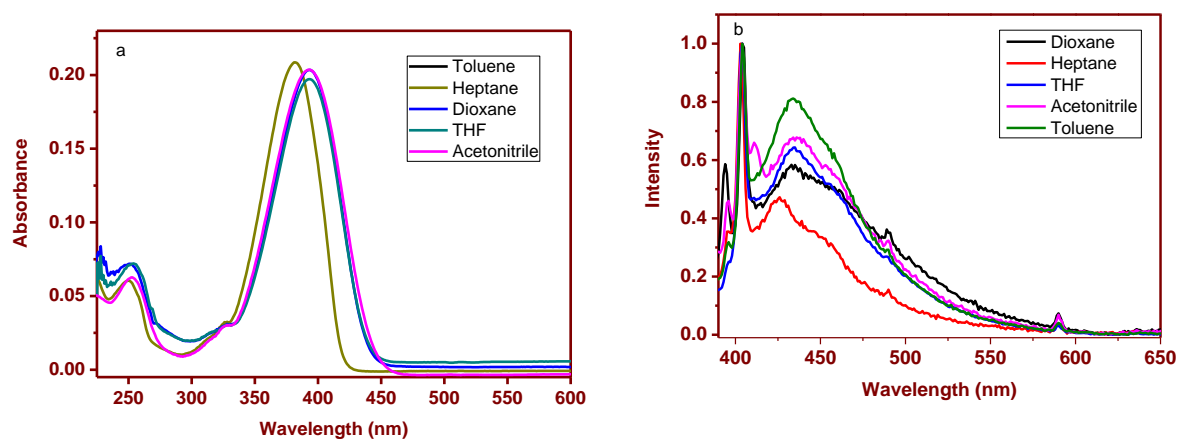


Figure S2: Absorption and emission spectra of stilbene (4) in homogeneous solvents (excitation wavelength is 380 nm)

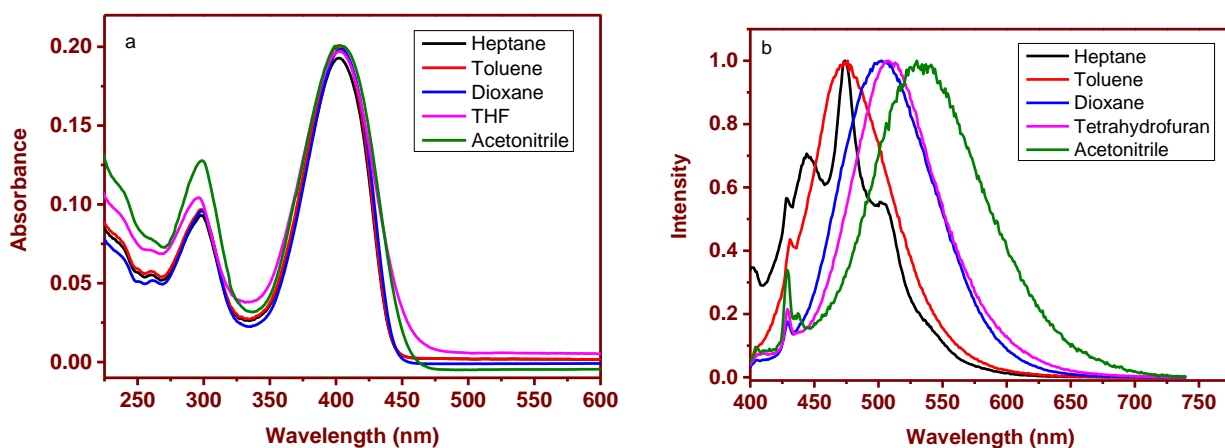


Figure S3: Absorption and emission spectra of stilbene (**5**) in homogeneous solvents (excitation wavelength is 395 nm)

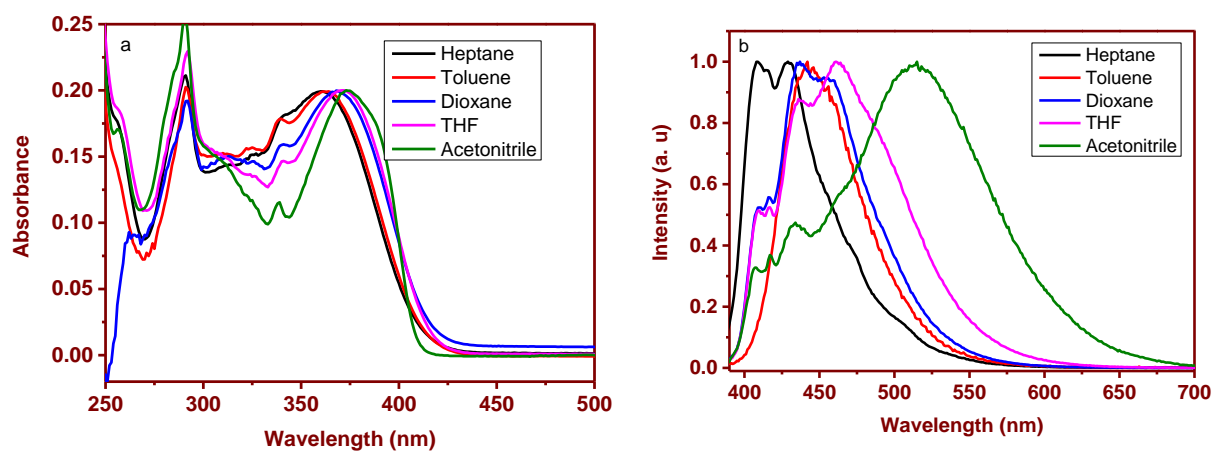


Figure S4: Absorption and emission spectra of stilbene (**6**) in homogeneous solvents (excitation wavelength is 365 nm)

Part 2. Emission studies in dioxane-water system for stilbenes (2), (3), (4), (5), (6);

Intensity plot for stilbenes (4)-(6)

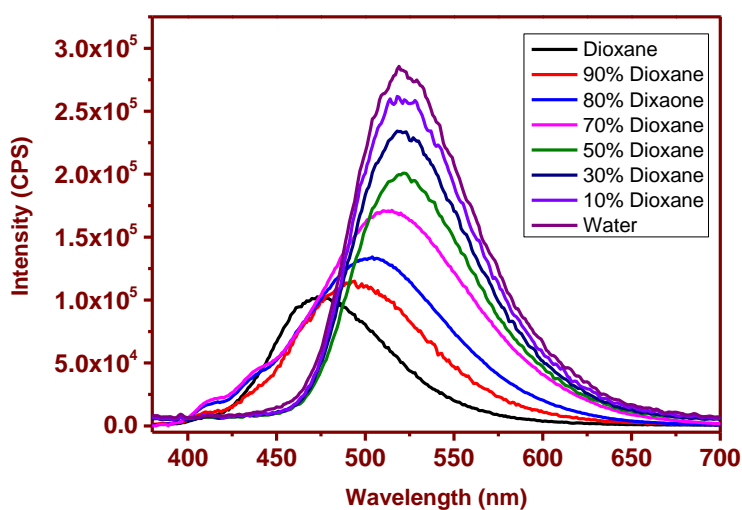


Figure S5: Fluorescence spectral changes of stilbene(2) with various proportions of dioxane and water (excitation wavelength is 395 nm)

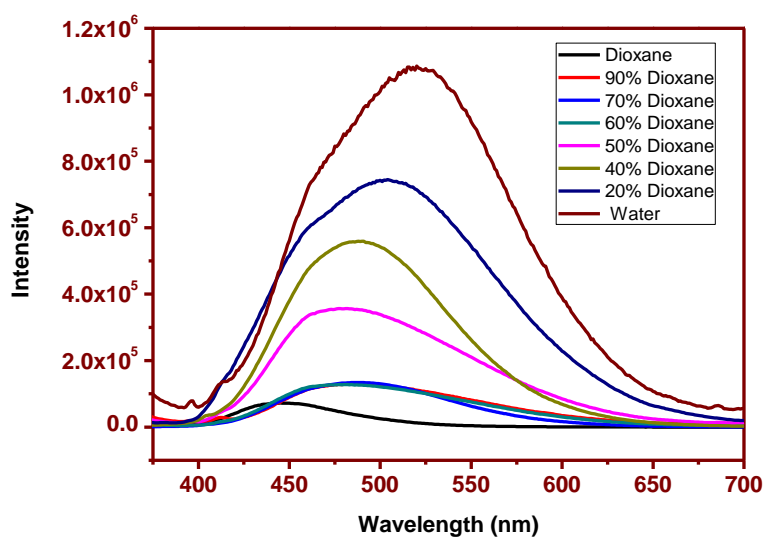


Figure S6: Fluorescence spectral changes of stilbene (3) with various proportions of dioxane and water (excitation wavelength is 370 nm)

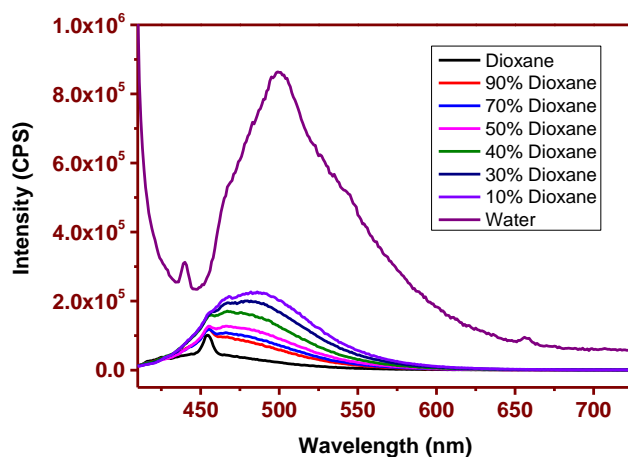


Figure S7: Fluorescence spectral changes of stilbene (**4**) with various proportions of dioxane and water (excitation wavelength is 390 nm)

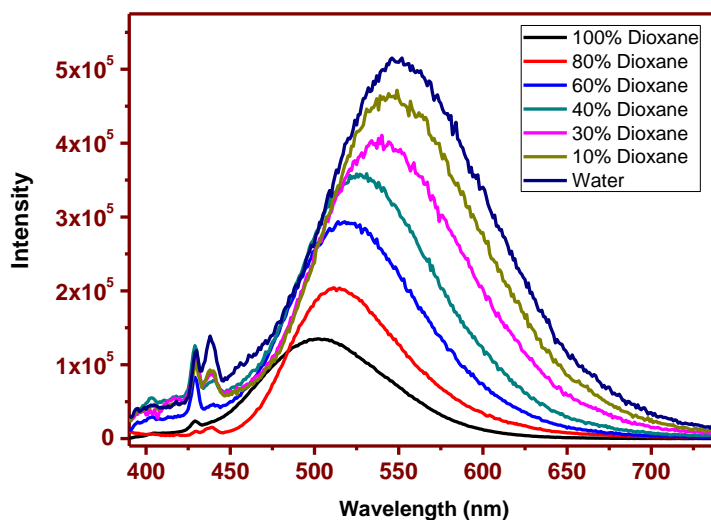


Figure S8: Fluorescence spectral changes of stilbene (**5**) with various proportions of dioxane and water (excitation wavelength is 400 nm)

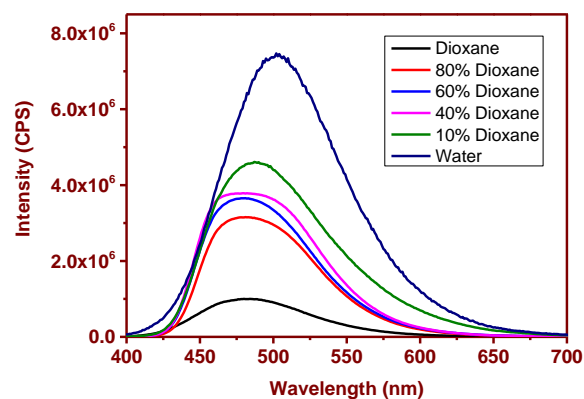


Figure S9: Fluorescence spectral changes of stilbene (6) with various proportions of dioxane and water (excitation wavelength is 365 nm)

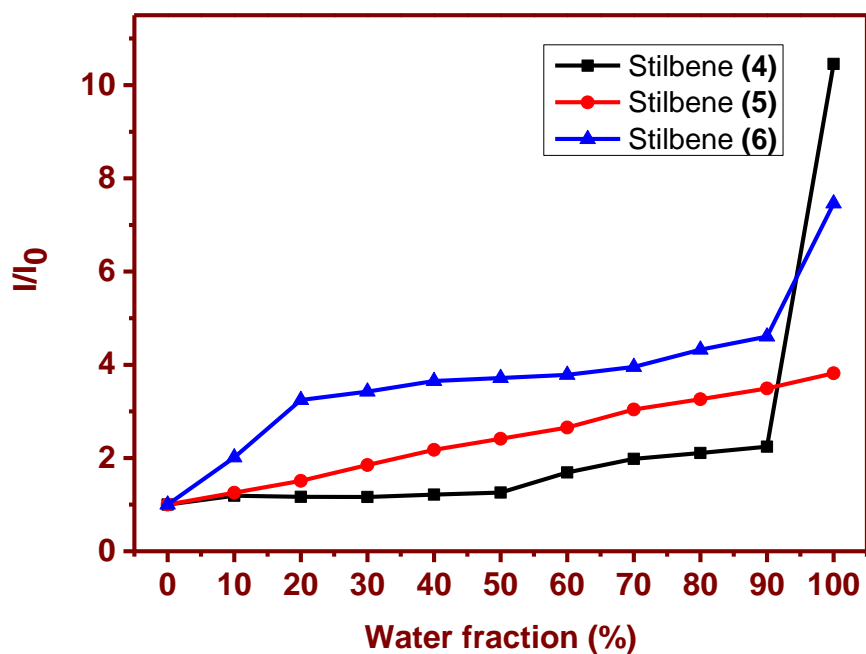


Figure S10: A plot of I/I_0 vs water fraction of stilbenes (4)-(6)

Table S1: Fluorescence quantum yields of stilbenes in dioxane and water

Molecule	Dioxane	Water	Molecule	Dioxane	Water
(1)	0.056	0.181	(4)	0.0089	0.124
(2)	0.125	0.154	(5)	0.0524	0.110
(3)	0.127	0.160	(6)	0.086	0.121

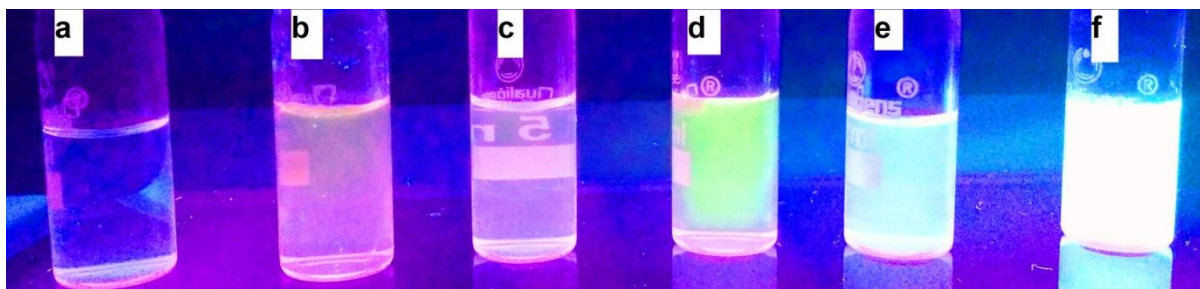


Figure S11: Colors of stilbenes (black background) in water and dioxane using hand-held UV lamp. (a), (b), (c) are in dioxane and (d), (e), (f) are in water for stilbenes (1), (2), (3) respectively. (The sample concentration is of the order 10^{-4} M).

Part 3. pH dependent optical properties of stilbene (4) and its NMR interpretation

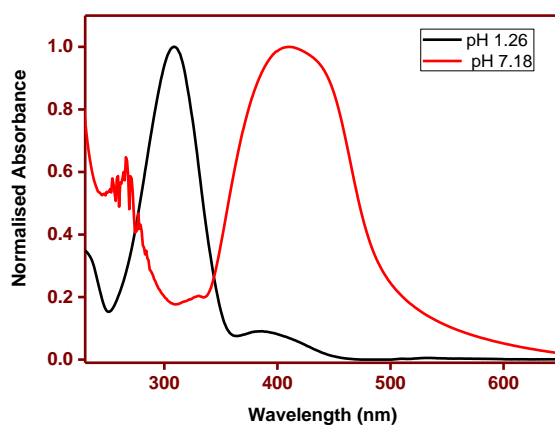


Figure S12: Absorption spectra stilbene (4) recorded at various pH 1.26 and 7.18

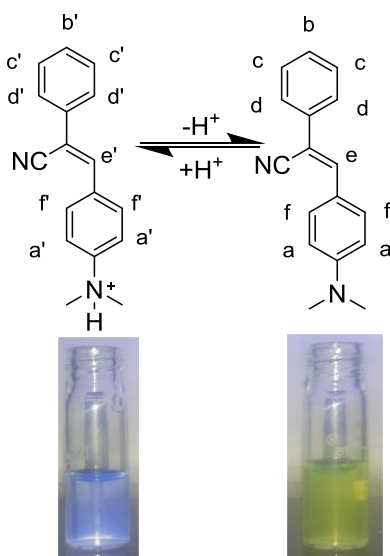


Figure S13: Switching mechanism of stilbene (4) under various pH conditions and corresponding colors under UV lighting conditions. 1A- acidic species, 1-neutral species

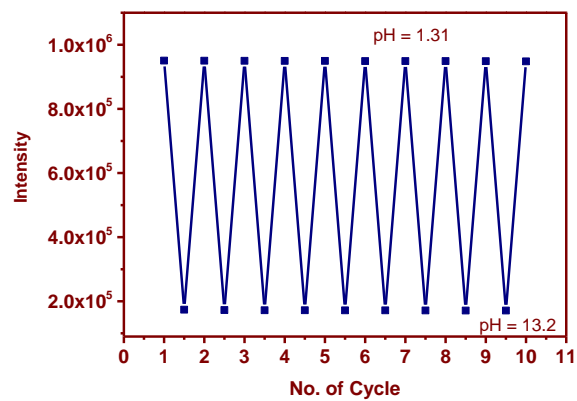


Figure S14: Acid-base reversibility cycle by fluorescence intensity for stilbene (3)



Figure S15: Dye coated filter paper in acidic, neutral, basic and acidic (reversibility from basic medium) (from left to right)

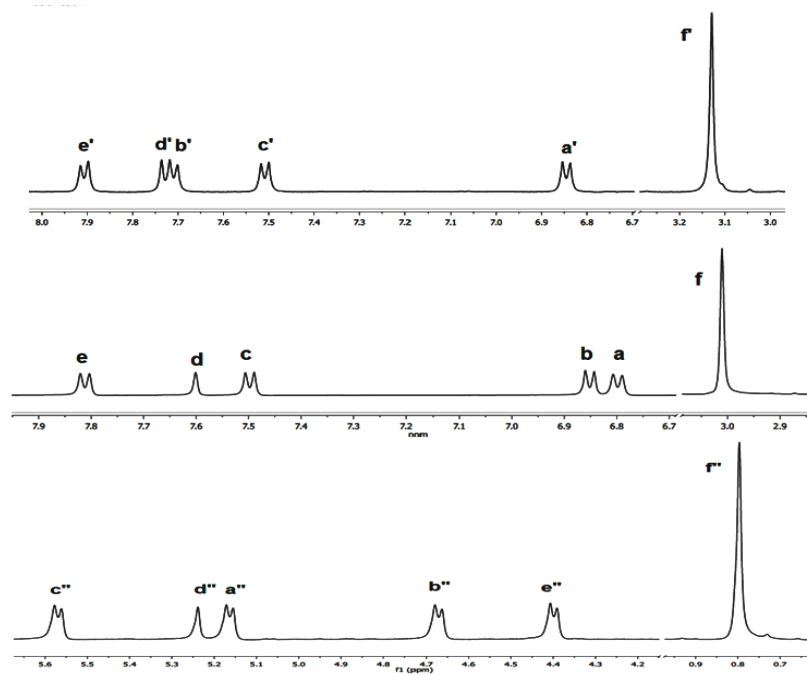


Figure S16: ^1H NMR spectra under various pH conditions in $\text{DMSO}(D_6)\text{-D}_2\text{O}$. **1A:** acidic medium, **1:** neutral medium, **1B:** basic medium (solvent peaks were discarded for clarity).

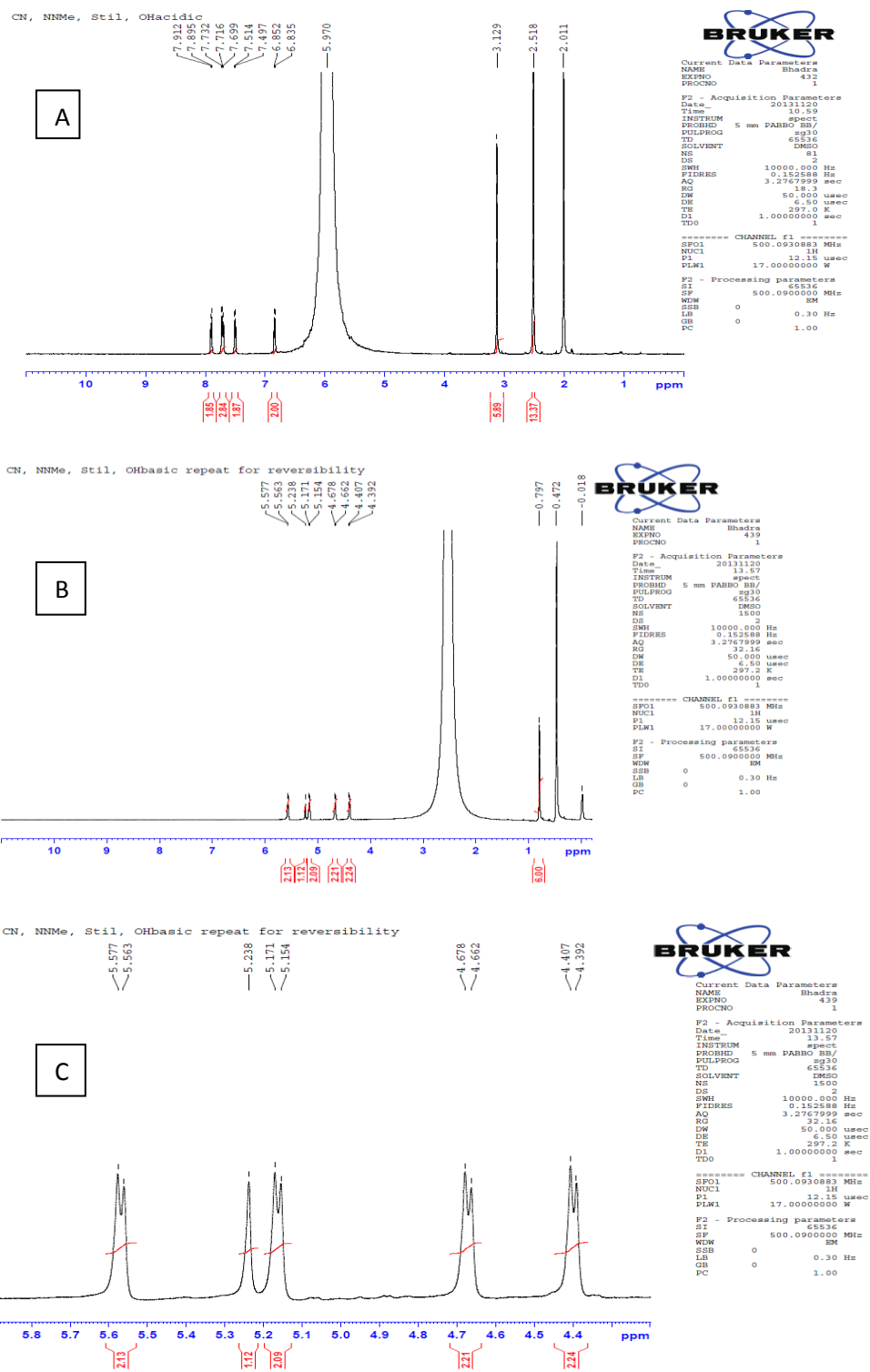


Figure S17: Examination of acid-base reversibility for stilbene (**1**) by NMR spectroscopy. **A**): **1** in Acidic medium. **B**. To the NMR tube of **1** in acidic medium, a solution 1M NaOH is added and the resulting spectrum is shown. **C**: Expanded spectra of **1** in basic medium. **B** (&C) is identical to that obtained in the basic medium.

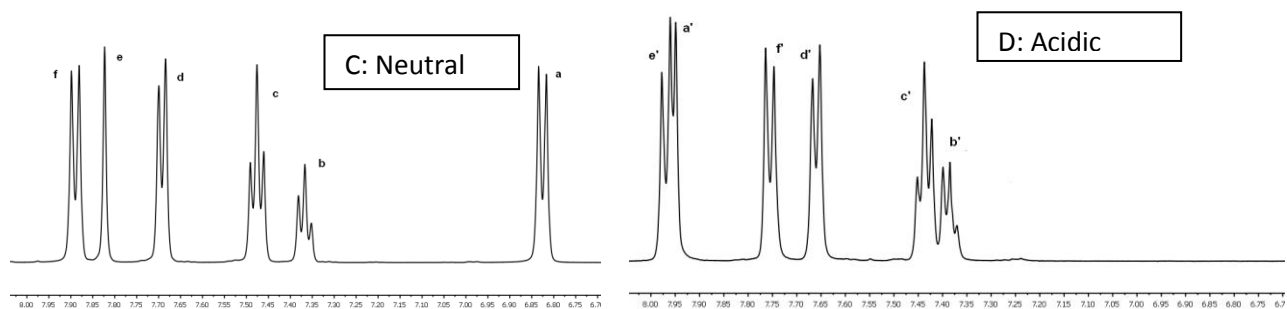
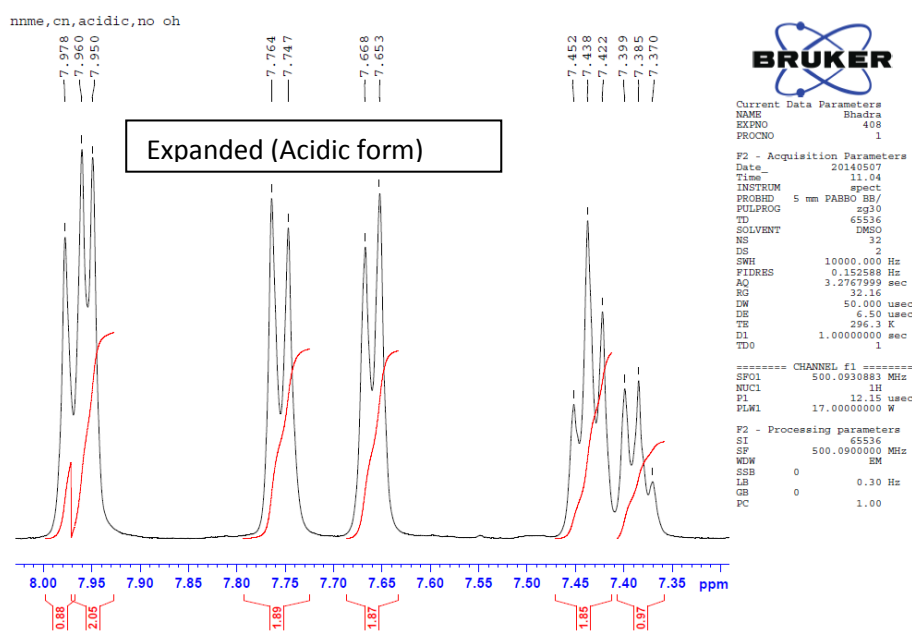
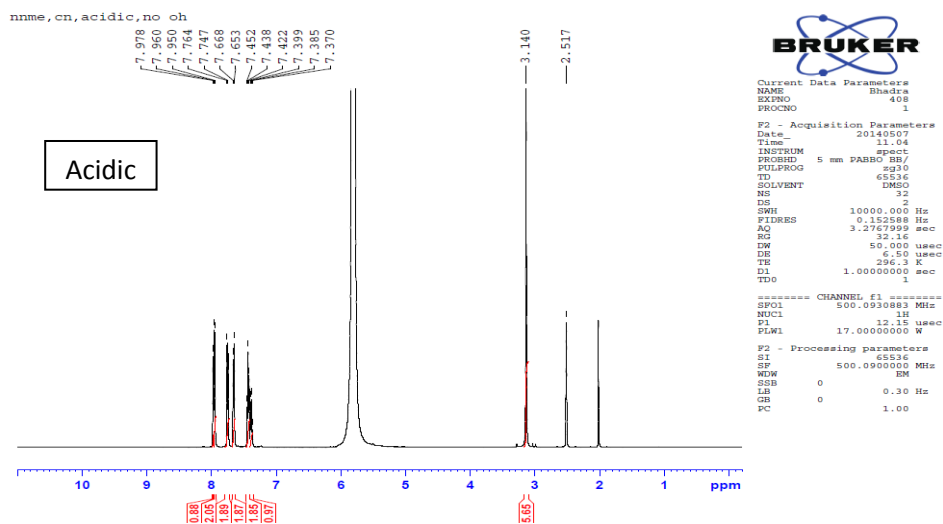


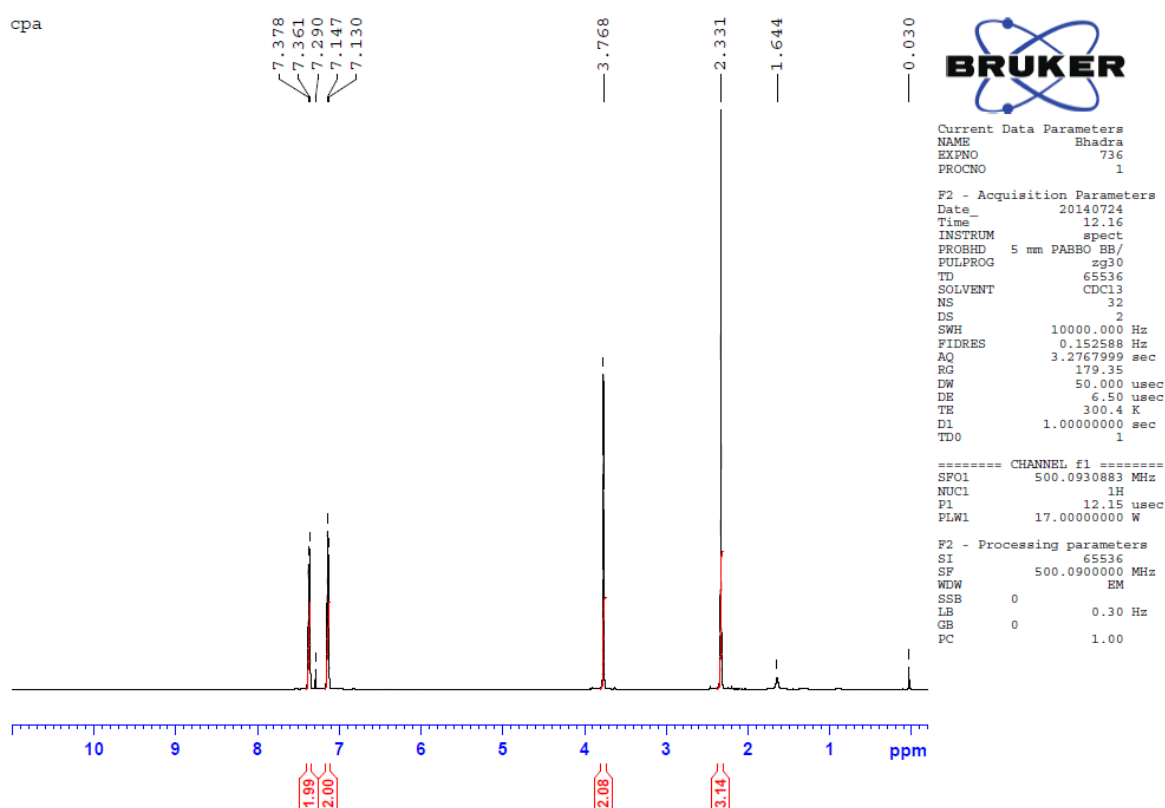
Figure S18: ^1H NMR spectra of stilbene (**4**) under acidic pH conditions in DMSO(d_6). Comparison is provided with NMR obtained neutral (C) and in acidic (D) medium. (Solvent peaks were discarded for clarity)

Table S2: pH dependent optical properties of stilbenes (4)-(6)

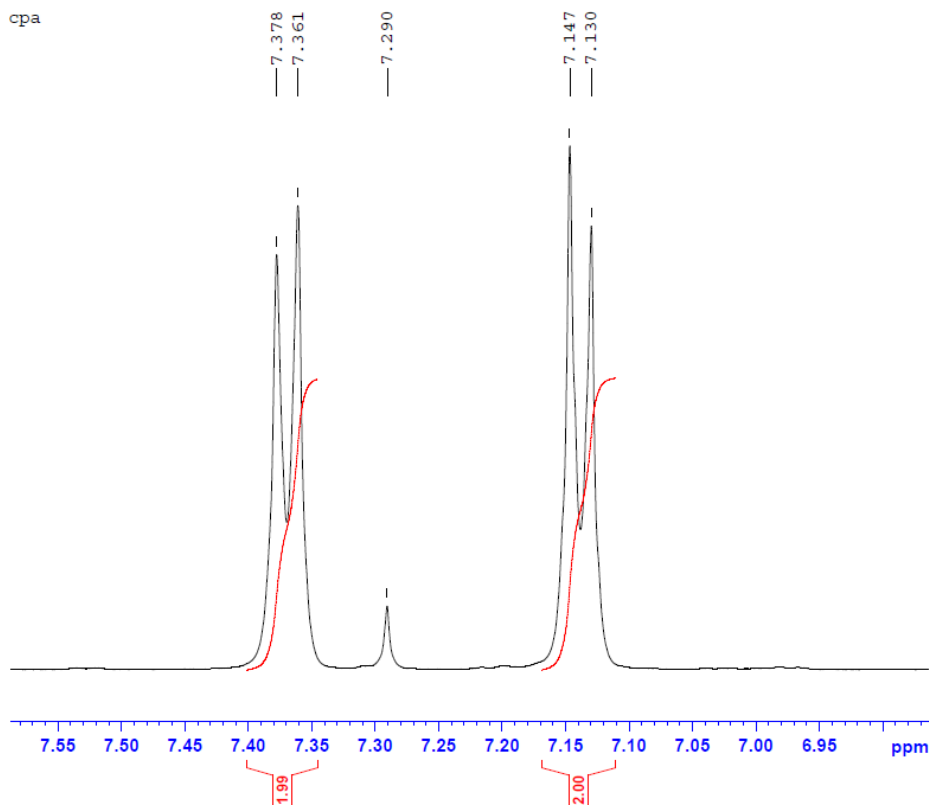
Sample	pH	λ_a (nm)	λ_f (nm)	ϕ_f
(4)	1.26	328	391	0.061
	7.18	410	499	0.124
	13.02	409	498	0.121
(5)	1.26	403	548	0.109
	7.18	405	550	0.110
	13.02	405	551	0.110
(6)	1.26	376	500	0.122
	7.18	378	502	0.121
	13.02	377	502	0.121

Part 4. NMR, Mass characterization of the synthesized molecules

¹H NMR Spectrum of 4-(cyanomethyl)phenyl acetate (8)



cpa



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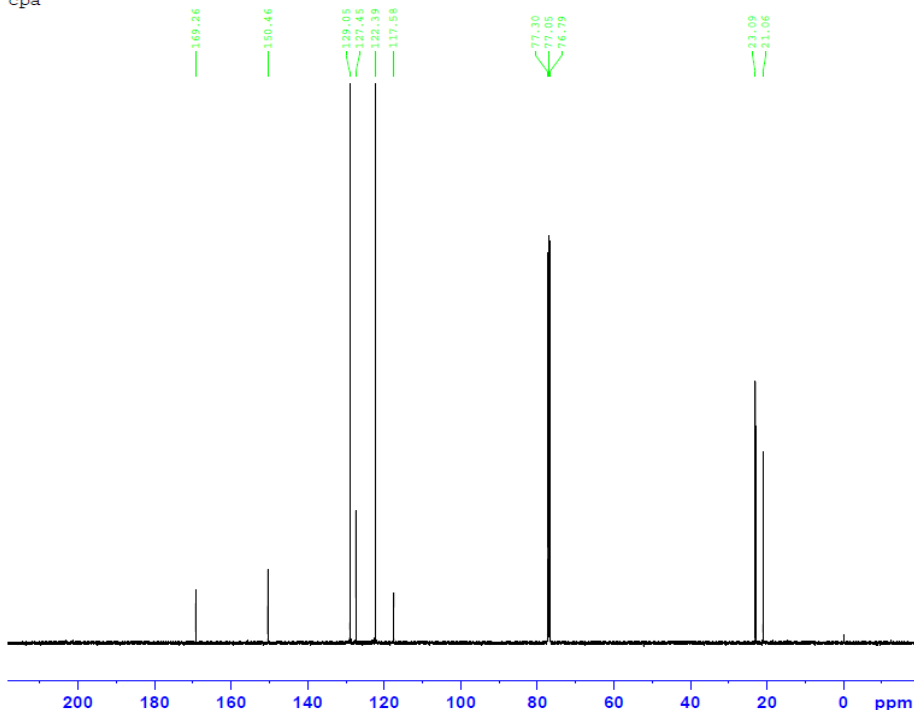
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¹³C NMR Spectrum of 4-(cyanomethyl)phenyl acetate (8)

cpa



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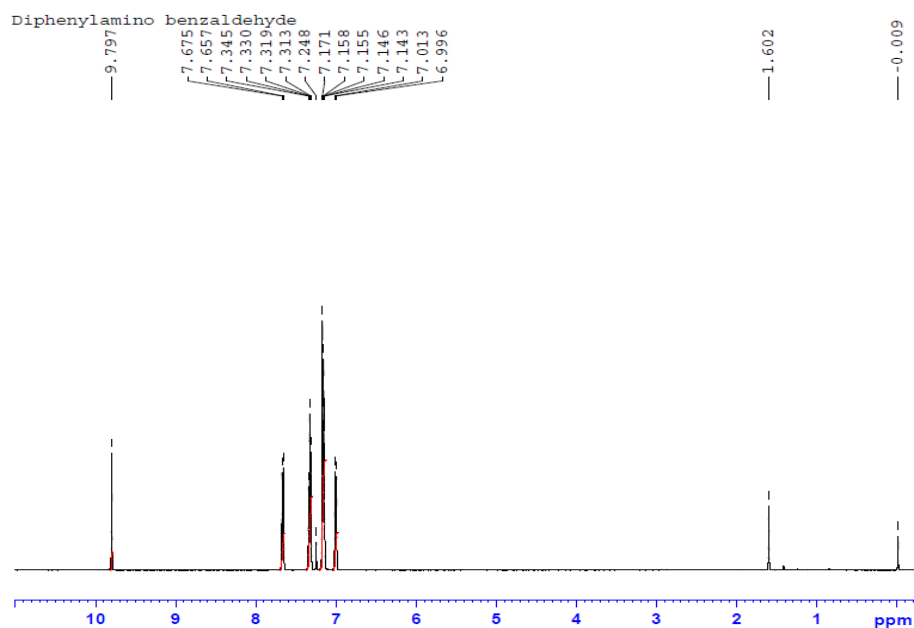
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 PLW12 0.52061999 W
 PLW13 0.33320001 W

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¹H NMR Spectrum of 4-(diphenylamino)benzaldehyde(10)

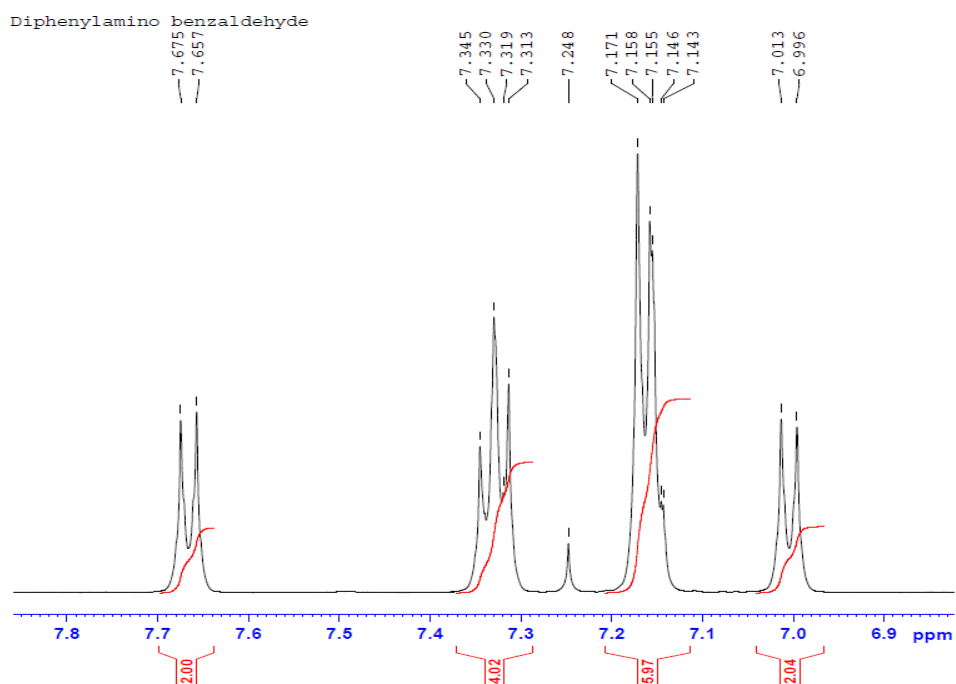


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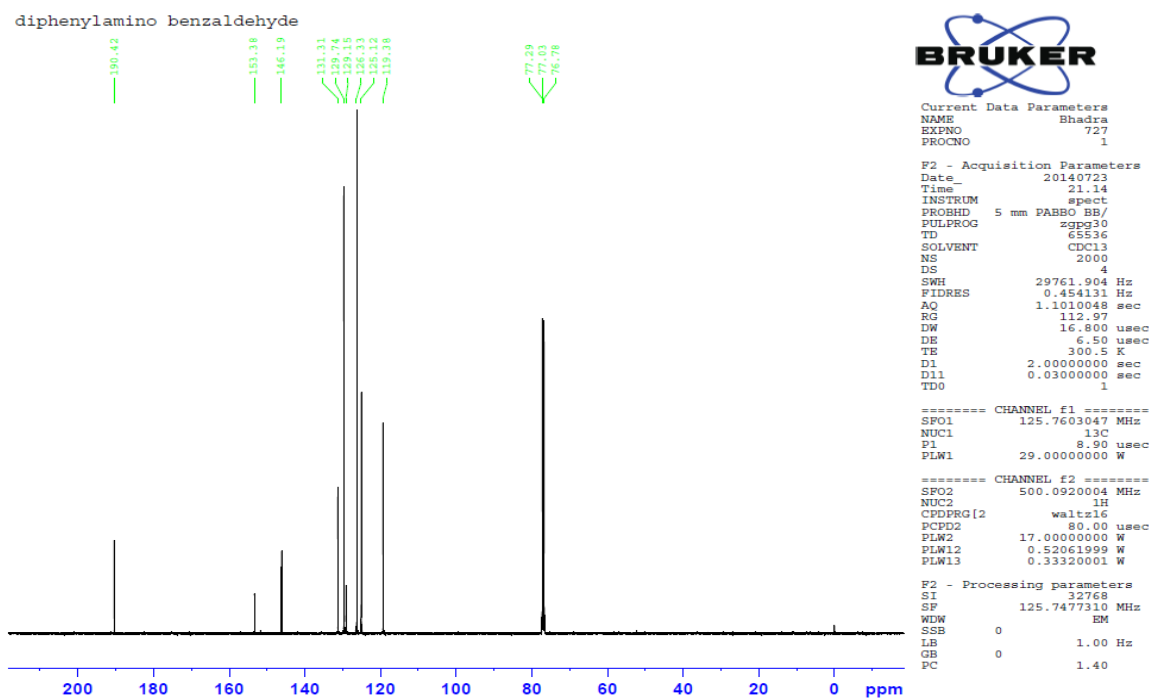
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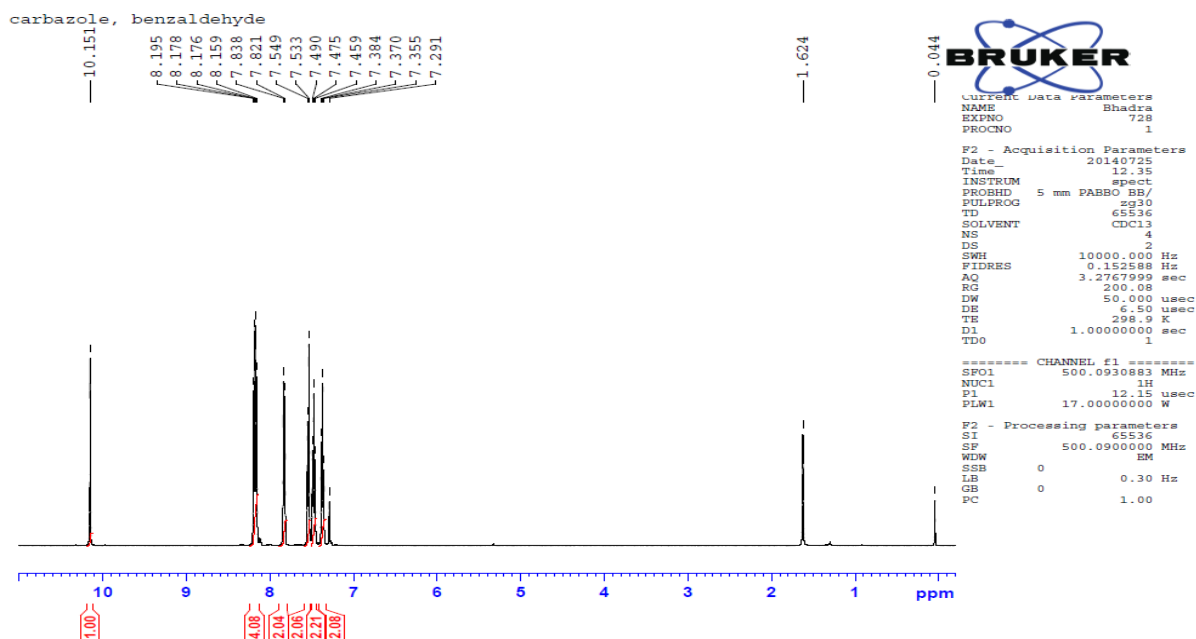
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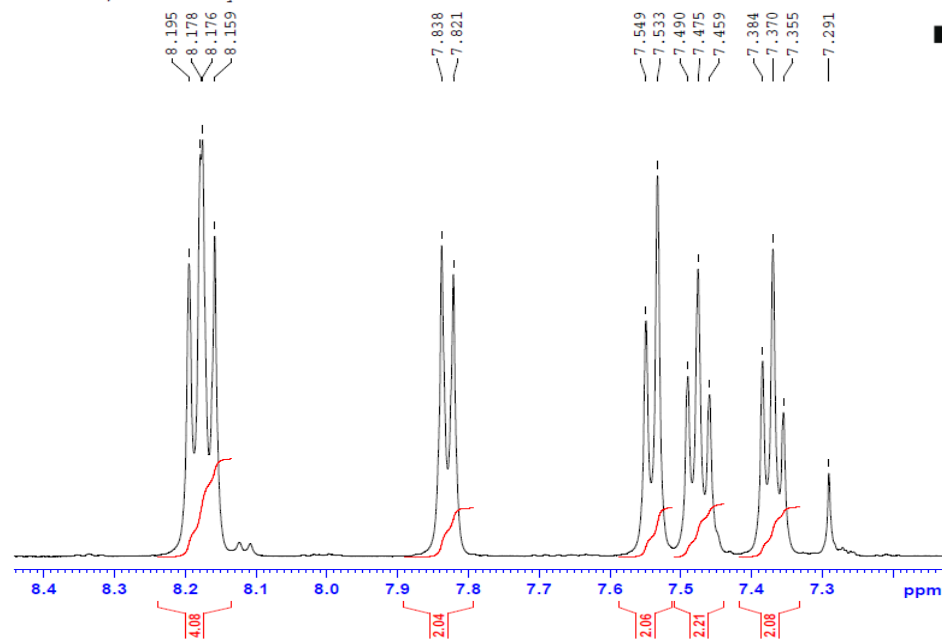
¹³C NMR Spectrum of 4-(diphenylamino)benzaldehyde(10)



¹H NMR Spectrum of 4-(9H-carbazol-9-yl)benzaldehyde (11)



carbazole, benzaldehyde



BRUKER

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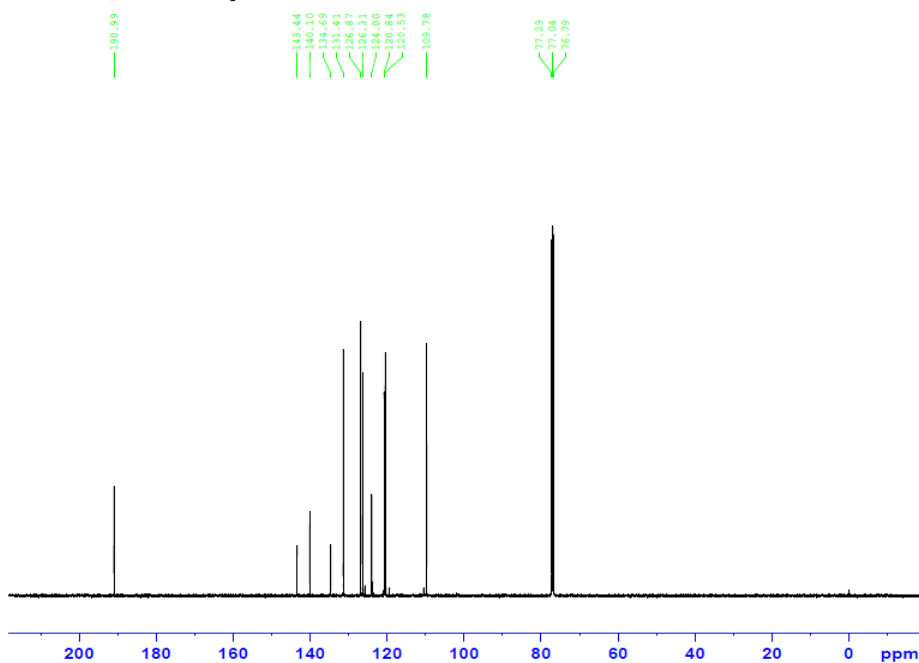
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¹³C NMR Spectrum of 4-(9H-carbazol-9-yl)benzaldehyde (11)

carbazole, benzaldehyde



BRUKER

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EXPNO 729
PROCNO 1

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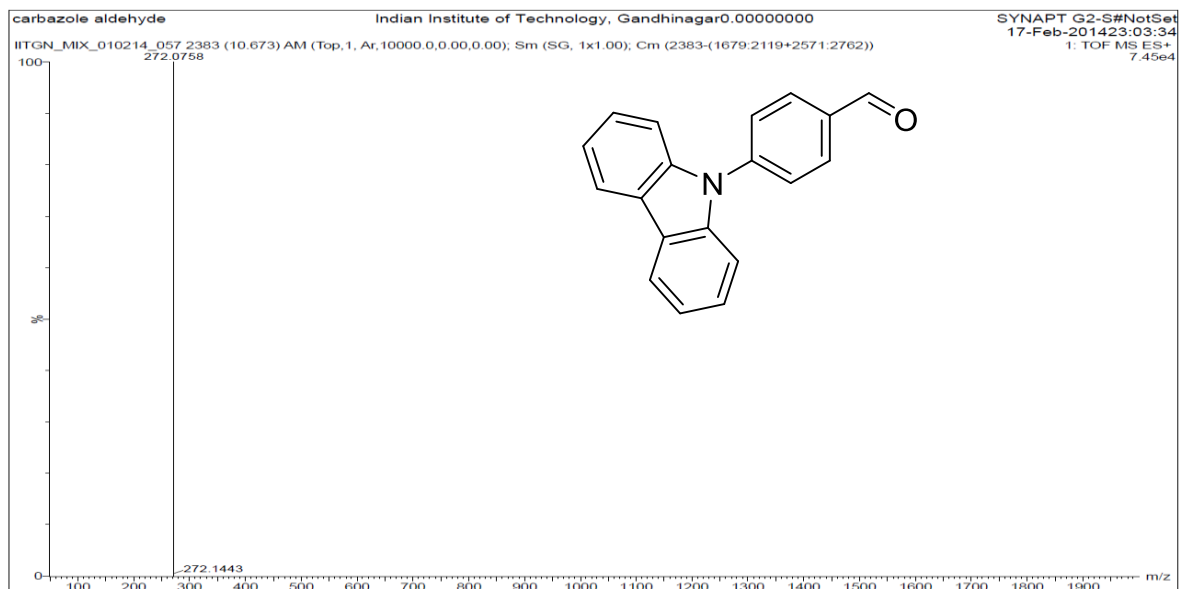
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Mass spectrum of 4-(9H-carbazol-9-yl)benzaldehyde (11)

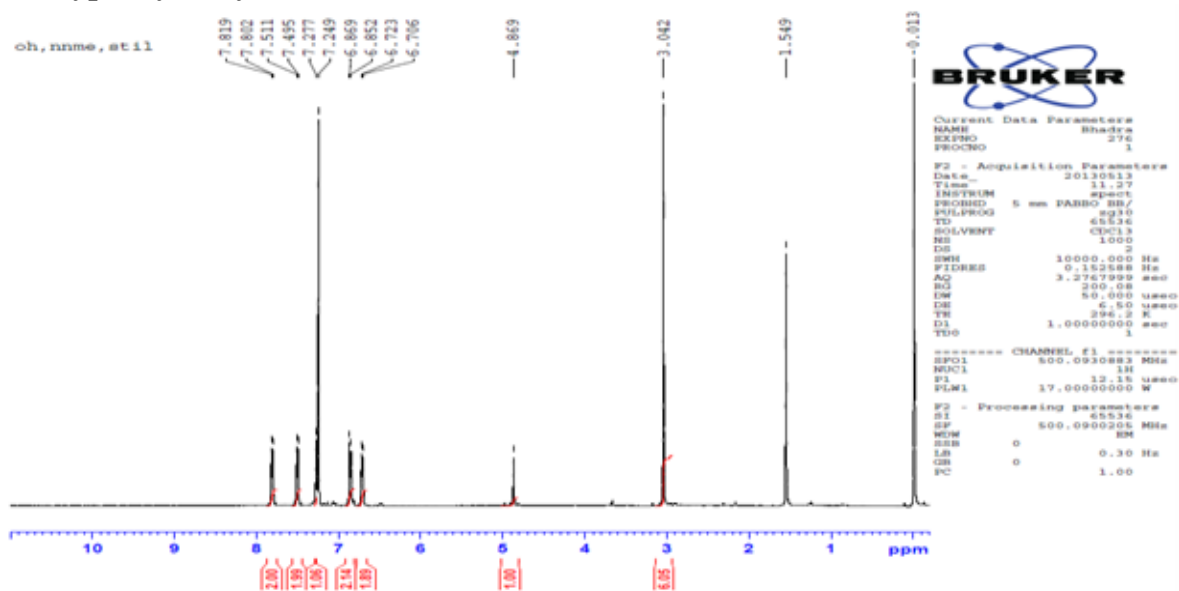
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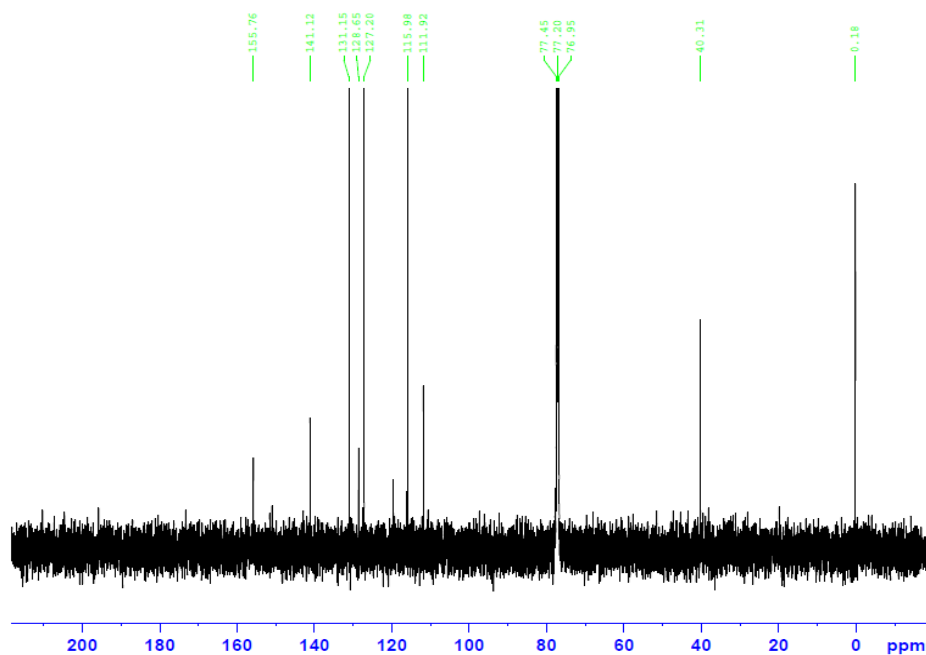


¹H NMR Spectrum of (Z)-3-(4-(dimethylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (1)



¹³C NMR Spectrum of (Z)-3-(4-(dimethylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (1)

oh, nmme, stil



```

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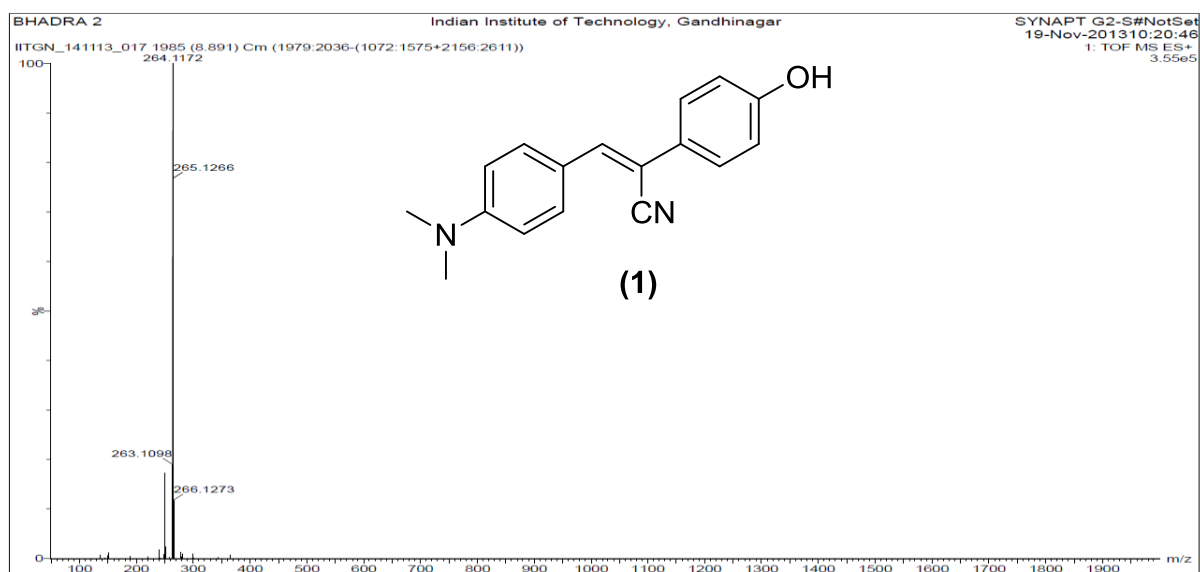
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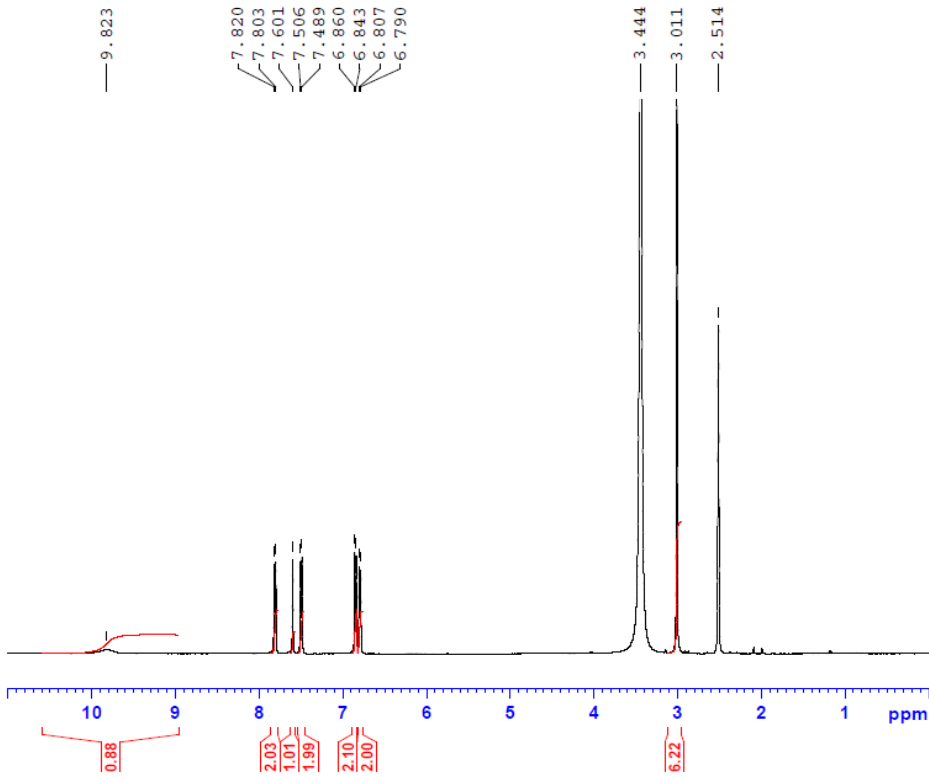
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CN, NNMe, Stil, OHneutral



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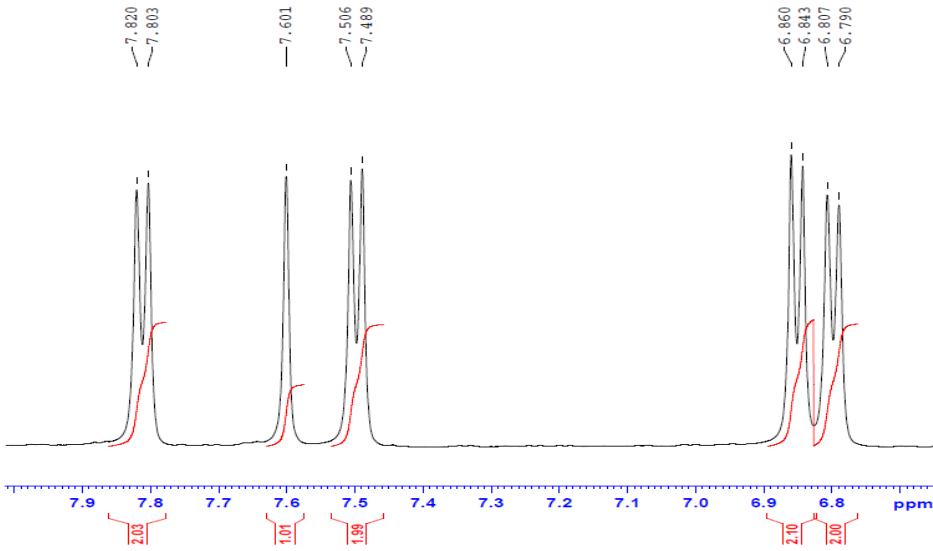
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CN, NNMe, Stil, OHneutral



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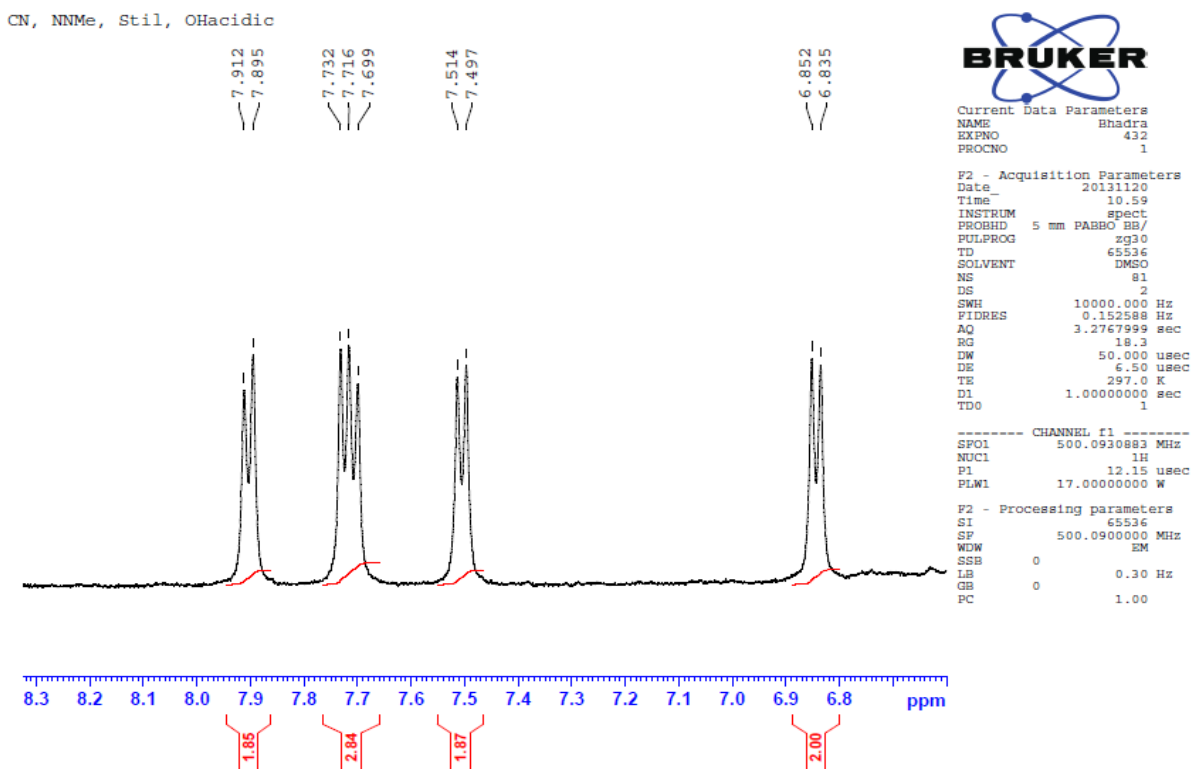
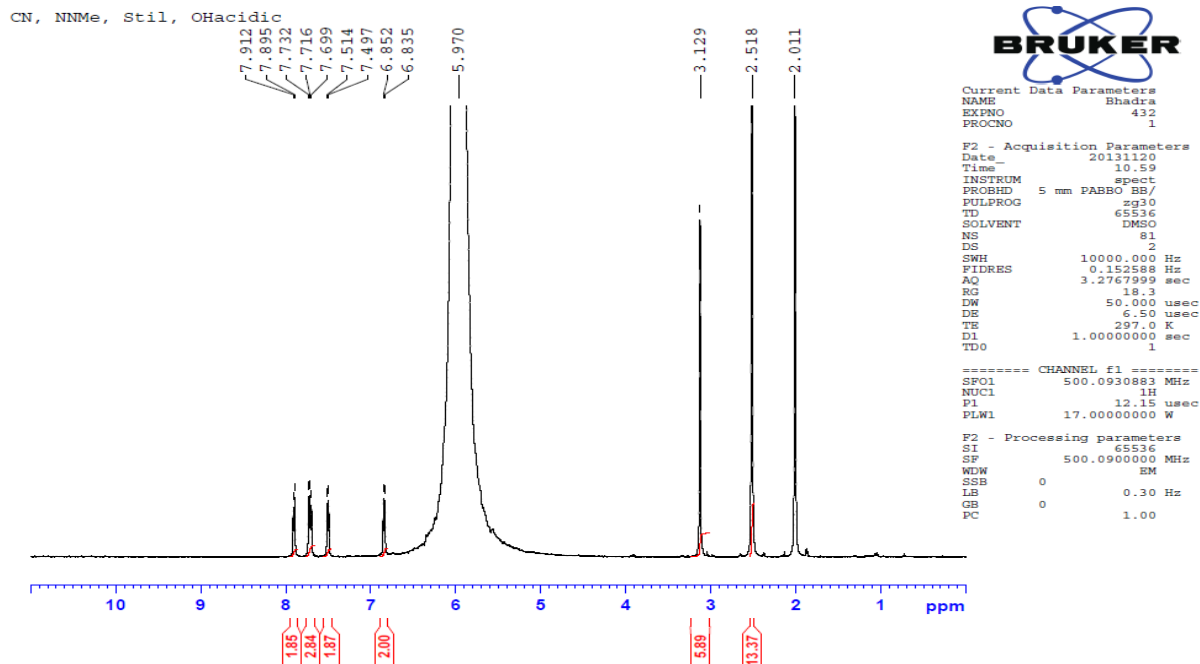
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FIDRES       0.152588 Hz
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RG           87.12
DW           50.000 usec
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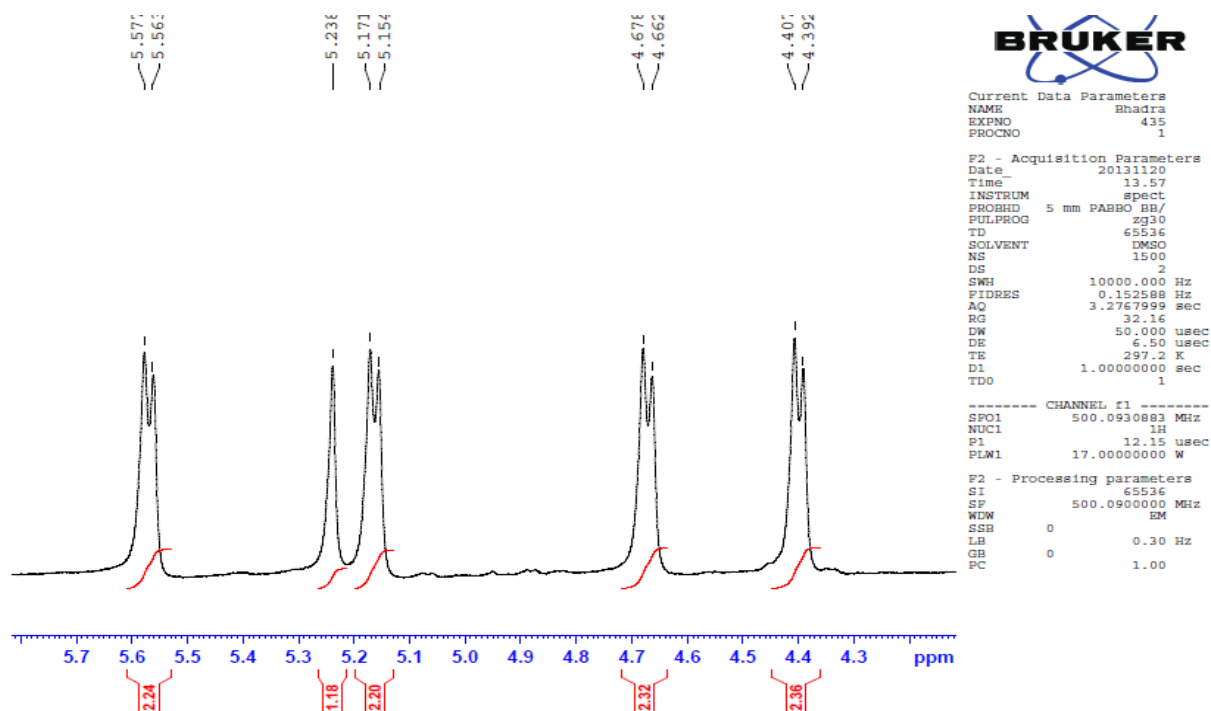
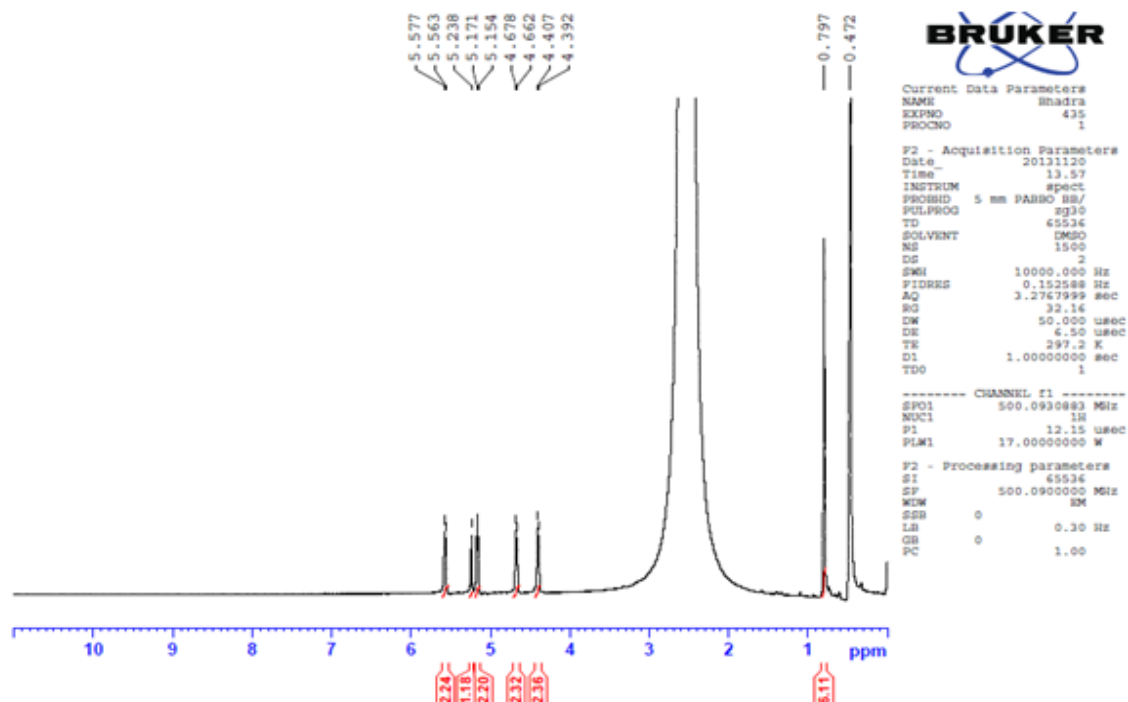
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¹H NMR Spectrum of (Z)-3-(4-(dimethylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (1) in acidic medium

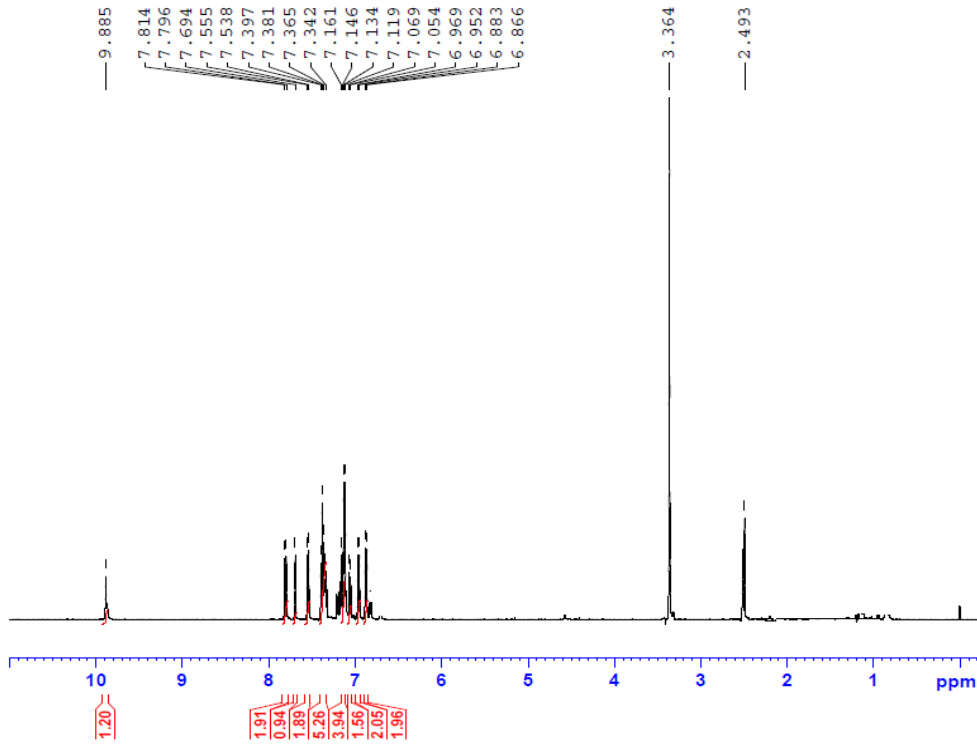


¹H NMR Spectrum of (Z)-3-(4-(dimethylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (1) in basic medium



¹H NMR Spectrum of stilbene (Z)-3-(4-(diphenylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (2)

nmmeqh, cn, stil, oh



```

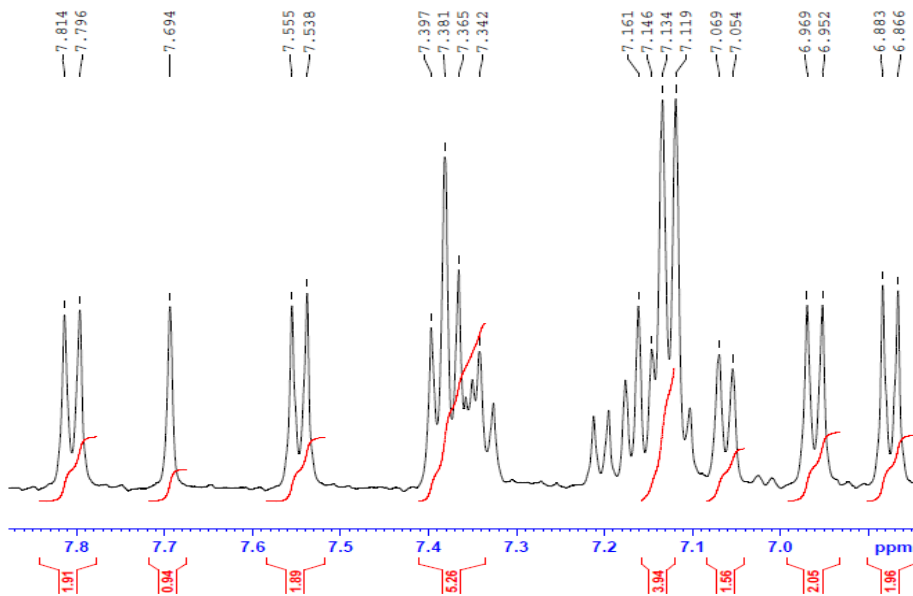
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nmmeqh, cn, stil, oh



```

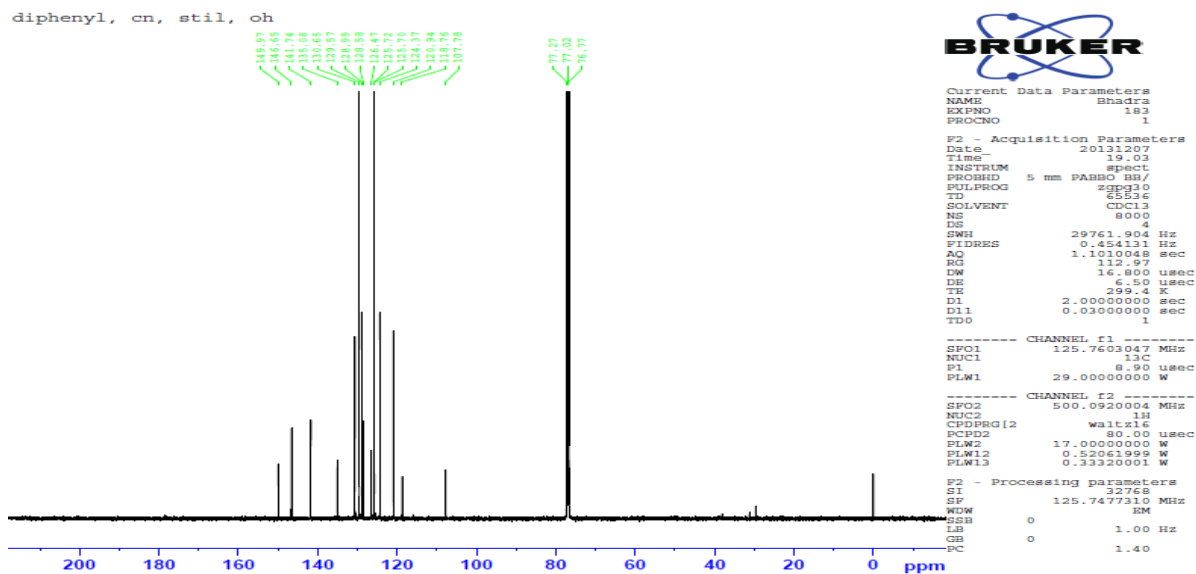
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PROCNO        1

F2 - Acquisition Parameters
Date_         20140109
Time          18.52
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zg30
TD            65536
SOLVENT       DMSO
NS            32
DS            2
SWH           10000.000 Hz
FIDRES        0.152588 Hz
AQ            3.2767999 sec
RG            137.26
DW            50.000 usec
DE            6.50 usec
TE            297.5 K
D1            1.00000000 sec
TDO           1

----- CHANNEL f1 -----
SPOL          500.0930883 MHz
NUC1          1H
P1            12.15 usec
PLW1          17.00000000 W

F2 - Processing parameters
SI            65536
SF            500.0900000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
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¹³C NMR Spectrum of stilbene (Z)-3-(4-(diphenylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (2)

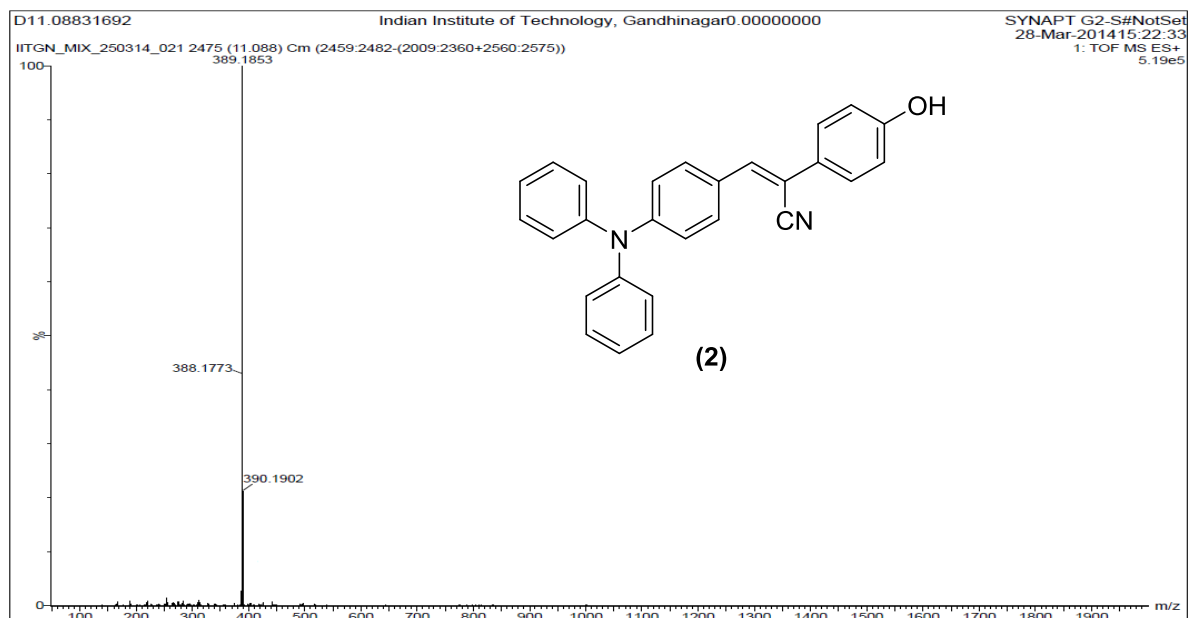


Mass spectrum of stilbene (Z)-3-(4-(diphenylamino)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (2)

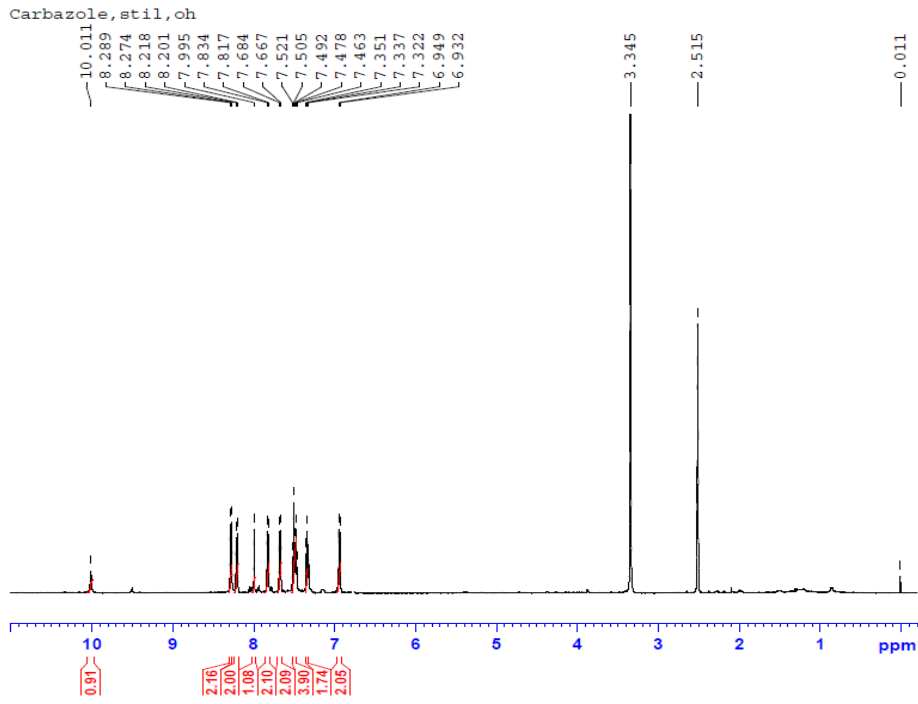
Exact mass 388.16

Mass obtained in positive mode 389.1853 (M+1)

Elemental Composition C₂₇H₂₁N₂O (Obtained in the positive mode)



¹H NMR Spectrum of stilbene (Z)-3-(4-(9H-carbazol-9-yl)phenyl)-2-(4-hydroxyphenyl)acrylonitrile (3)

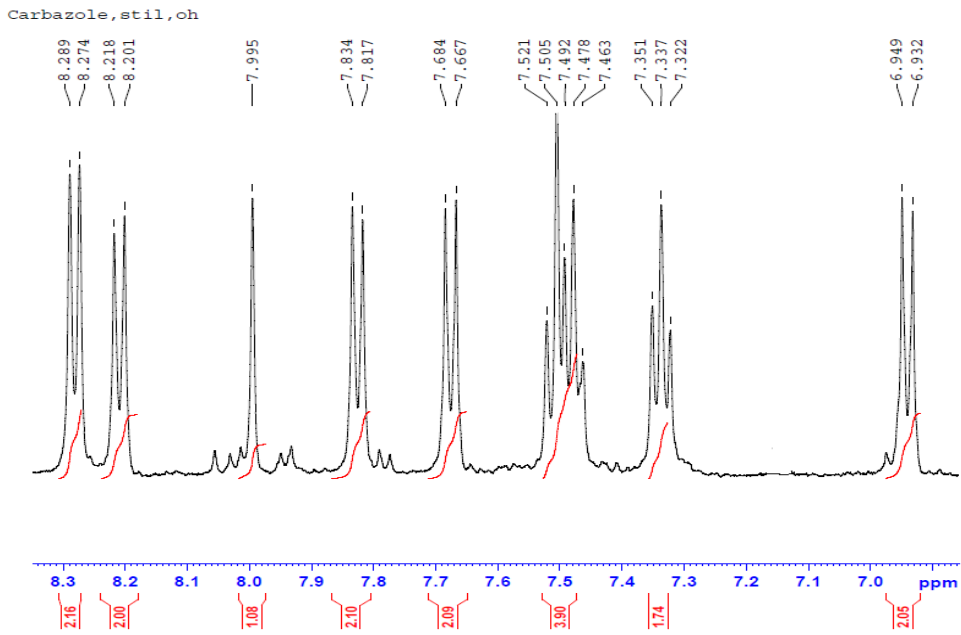


Current Data Parameters
 NAME Bhadra
 EXPNO 494
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140304
 Time_ 11.45
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 200.08
 DW 50.000 usec
 DE 6.50 usec
 TE 299.6 K
 D1 1.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 SFO1 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.00000000 W

F2 - Processing parameters
 SI 65536
 SF 500.0900000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME Bhadra
 EXPNO 494
 PROCNO 1

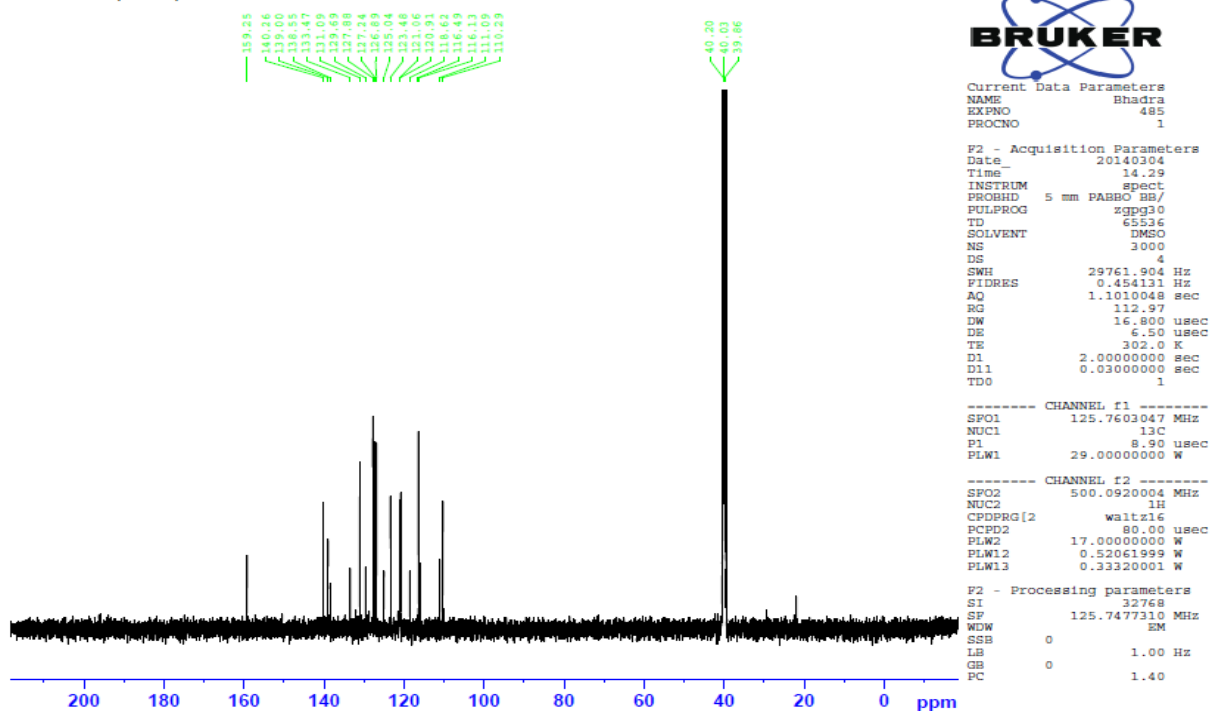
F2 - Acquisition Parameters
 Date_ 20140304
 Time_ 11.45
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 200.08
 DW 50.000 usec
 DE 6.50 usec
 TE 299.6 K
 D1 1.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 SFO1 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.00000000 W

F2 - Processing parameters
 SI 65536
 SF 500.0900000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

¹³C NMR Spectrum of stilbene (3)

Carbazole, stil, oh

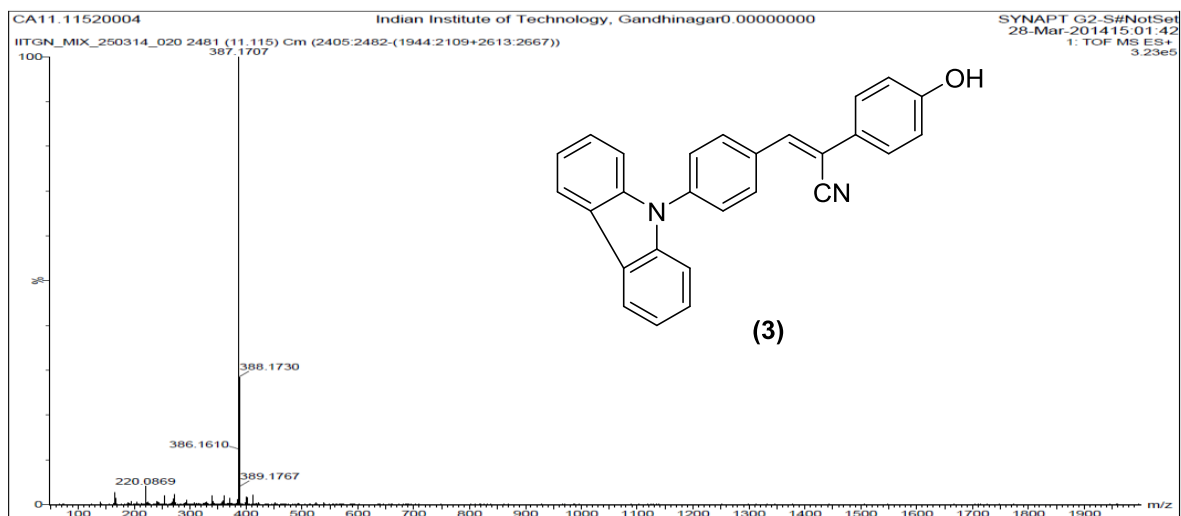


Mass spectrum of stilbene (3)

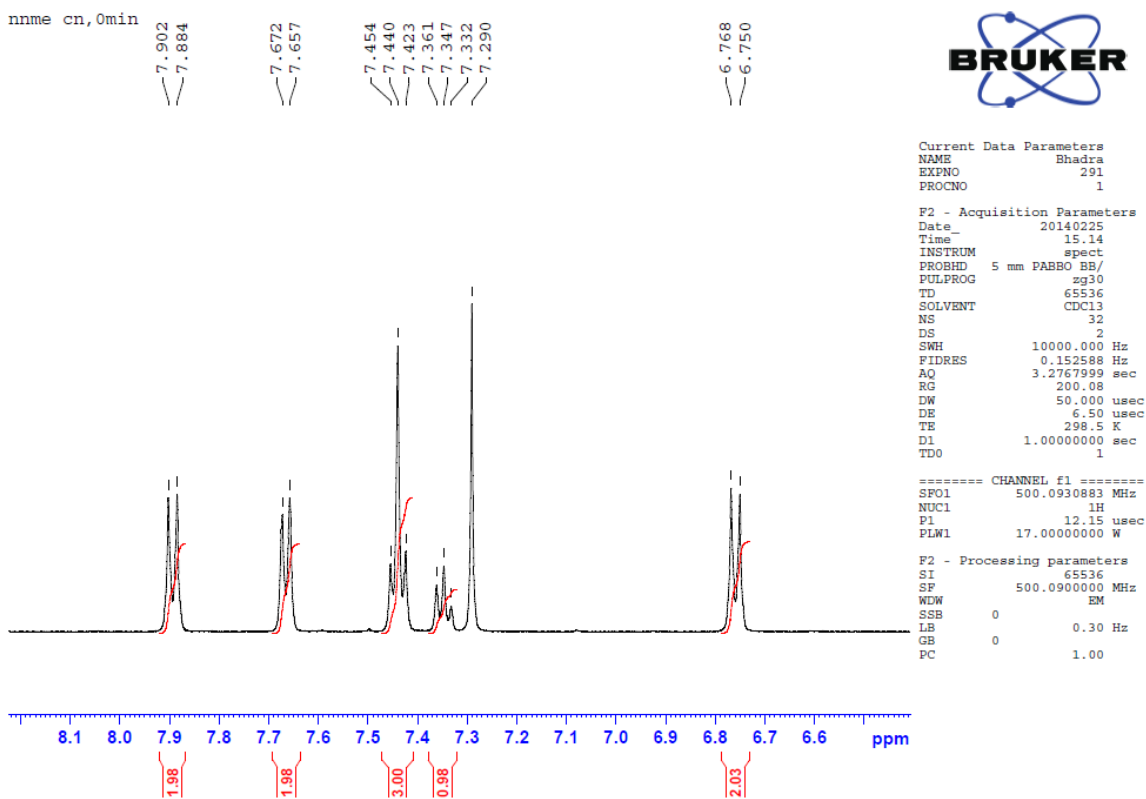
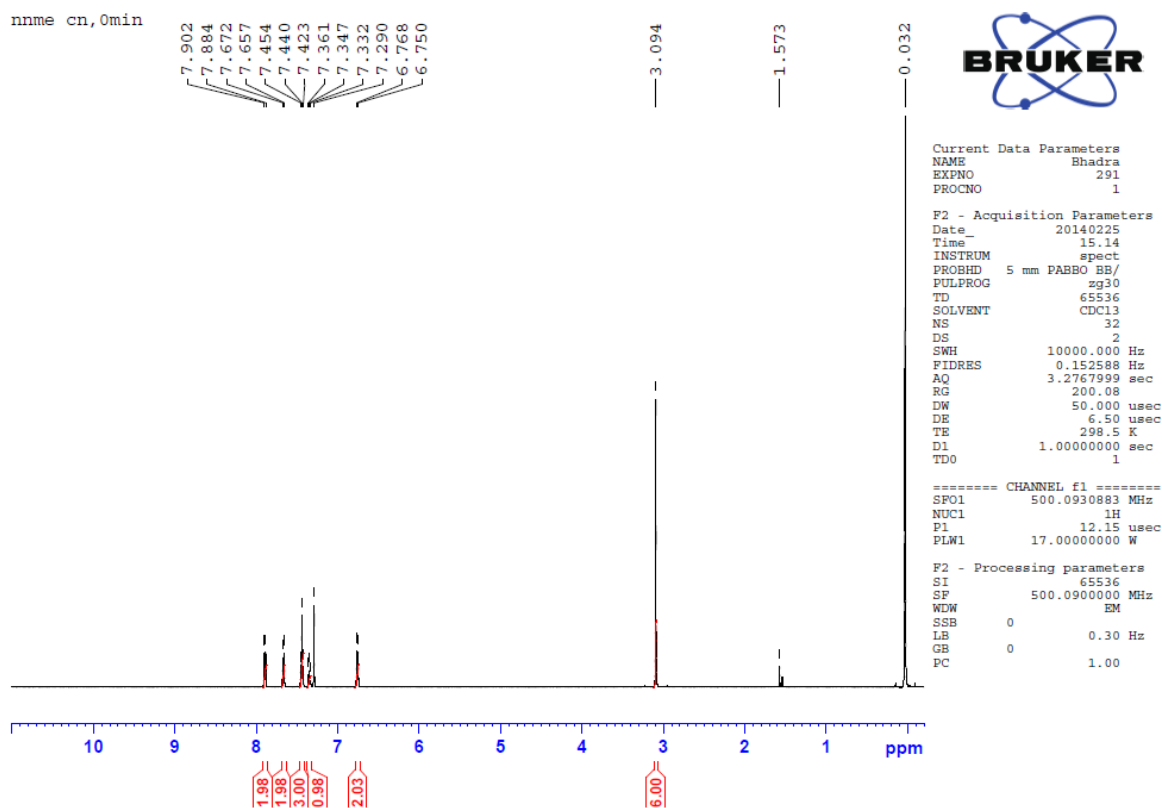
Exact mass 386.14

Mass obtained in positive mode 387.1707 (M+1)

Elemental Composition C₂₇H₁₉N₂O (Obtained in the positive mode)

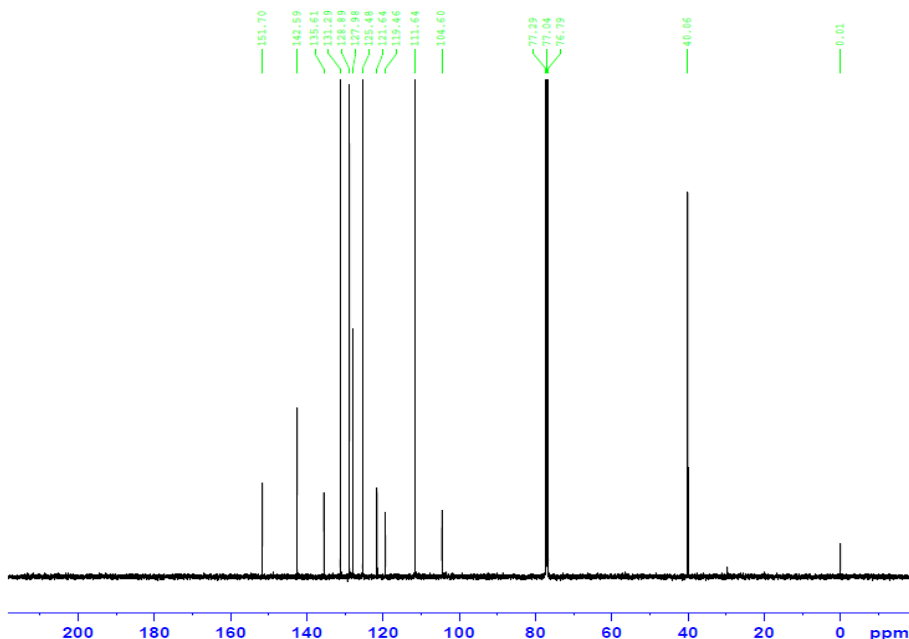


¹H NMR Spectrum of stilbene (4)



¹³C NMR Spectrum of stilbene (4)

CN, NNMe, Stil (no OH) c13



Current Data Parameters
 NAME Bhadra
 EXPNO 164
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20131119
 Time 12.00
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 2000
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 200.08
 DW 16.800 usec
 DE 6.50 usec
 TE 299.3 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

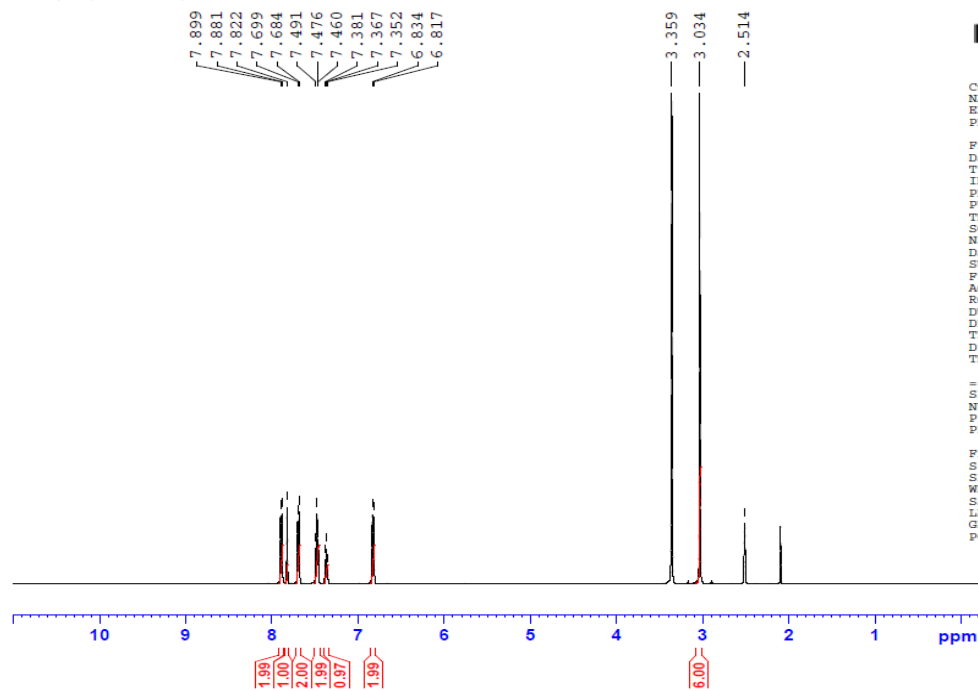
===== CHANNEL f1 =====
 SFO1 125.7603047 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 29.0000000 W

===== CHANNEL F2 =====
 SFO2 500.0920004 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 17.0000000 W
 PLW12 0.52061999 W
 PLW13 0.33320001 W

F2 - Processing parameters
 SI 32768
 SF 125.7477310 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

¹H NMR Spectrum of stilbene (4) in neutral medium

nnme, cn, neutral, no oh



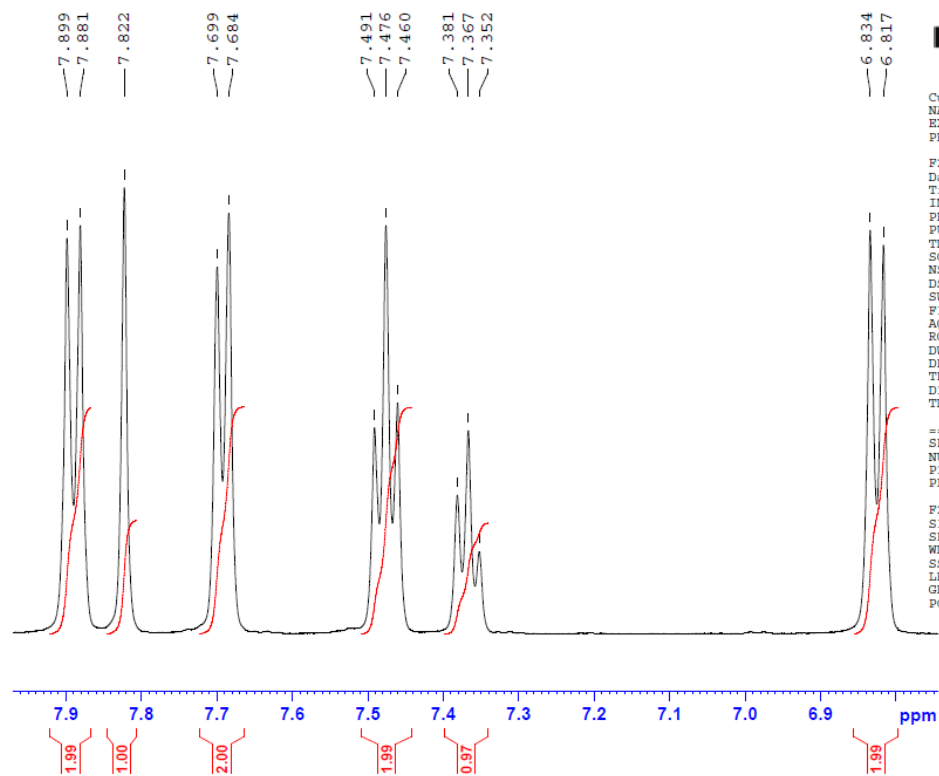
Current Data Parameters
 NAME Bhadra
 EXPNO 406
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140507
 Time 10.51
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 157.63
 DW 50.000 usec
 DE 6.50 usec
 TE 296.6 K
 D1 1.0000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.0000000 W

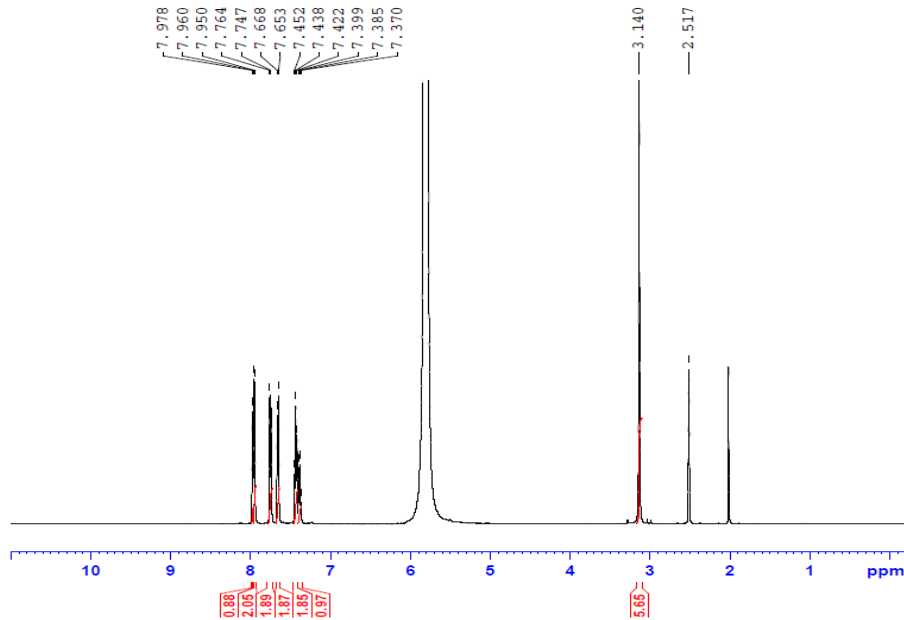
F2 - Processing parameters
 SI 65536
 SF 500.0900000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

nmme, cn, neutral, no oh

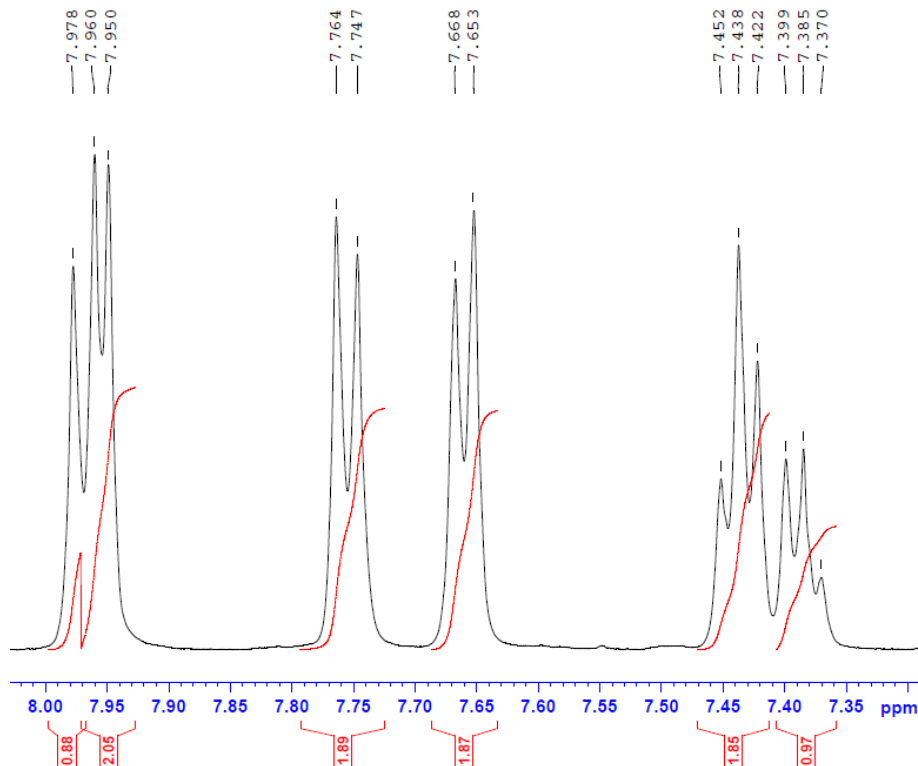


¹H NMR Spectrum of stilbene (4) in acidic medium

nmme, cn, acidic, no oh



nmme, cn, acidic, no oh



Current Data Parameters
 NAME Bhadra
 EXPNO 408
 PROCNO 1

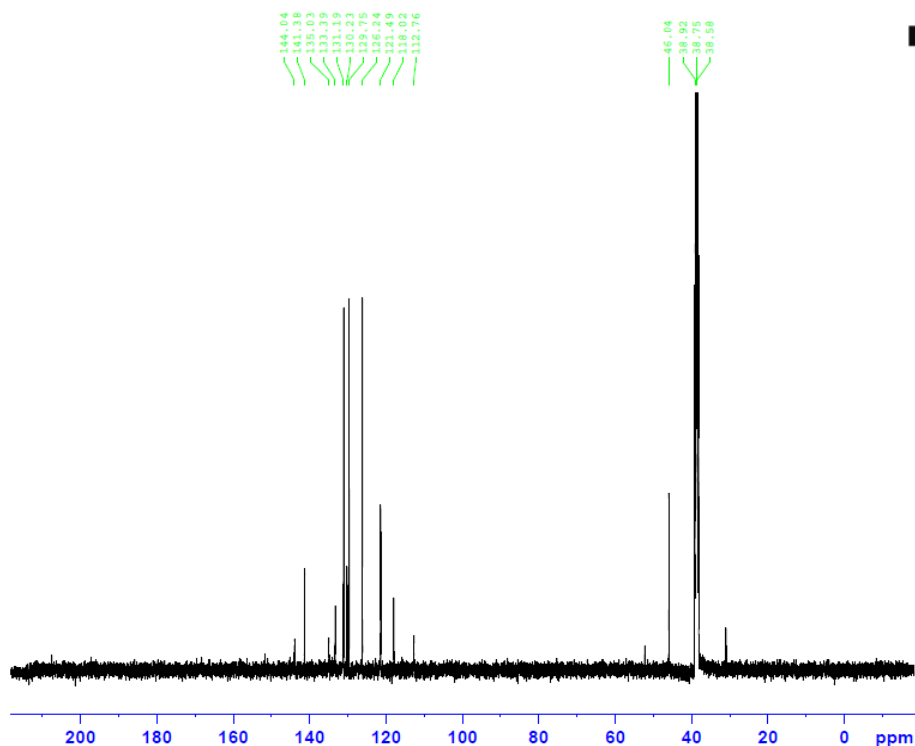
F2 - Acquisition Parameters
 Date_ 20140507
 Time 11.04
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT DMSO
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 32.16
 DW 50.000 usec
 DE 6.50 usec
 TE 296.3 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 SF01 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.00000000 W

F2 - Processing parameters
 SI 65536
 SF 500.0900000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

¹³C NMR Spectrum of stilbene (4) in acidic medium

nmme, cn, acidic, no oh



Current Data Parameters
 NAME Bhadra
 EXPNO 409
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140507
 Time 12.55
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 2000
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 112.97
 DW 16.800 usec
 DE 6.50 usec
 TE 299.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

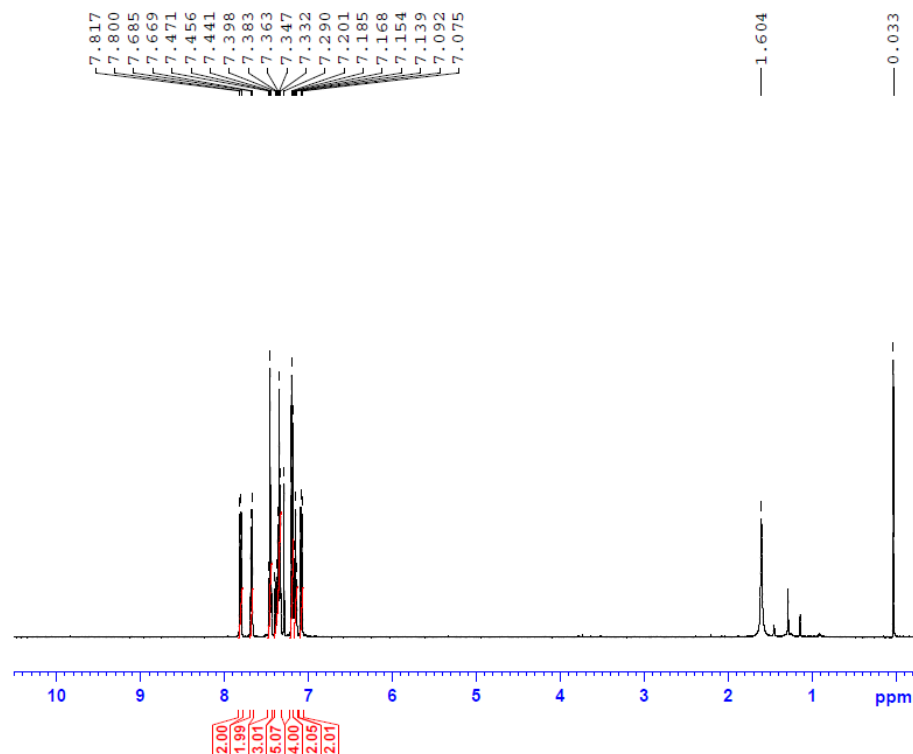
===== CHANNEL f1 =====
 SF01 125.7603047 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 29.00000000 W

===== CHANNEL f2 =====
 SF02 500.0920004 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 80.00 usec
 PLW2 17.00000000 W
 PLW12 0.52061999 W
 PLW13 0.33320001 W

F2 - Processing parameters
 SI 32768
 SF 125.7477310 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

¹H NMR Spectrum of stilbene (5)

diphenyl, cn, stil, no oh



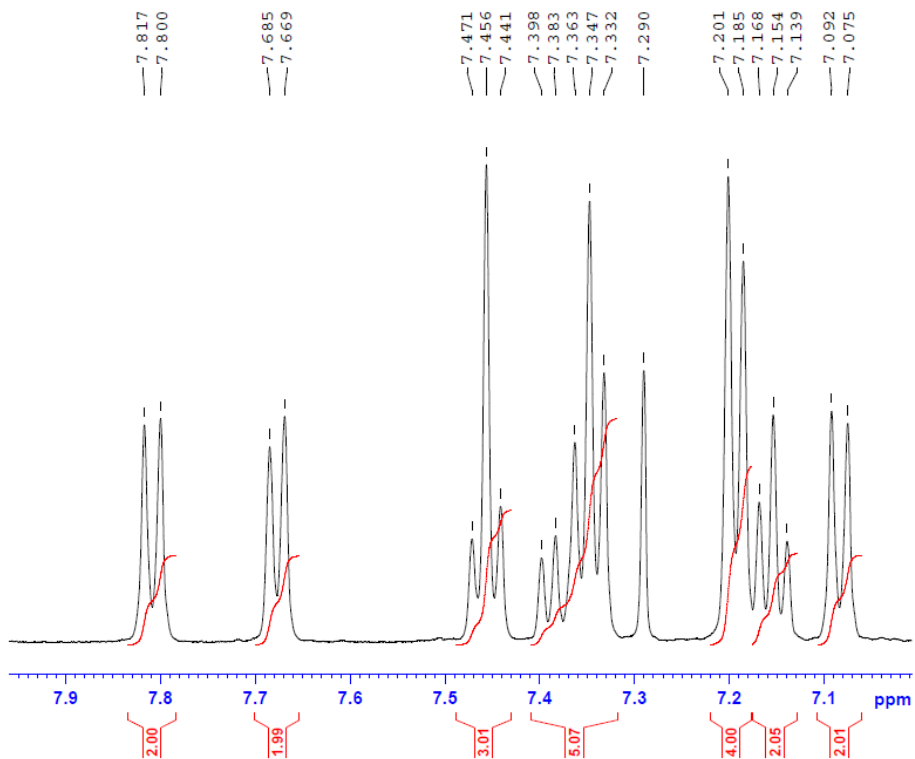
Current Data Parameters
 NAME Bhadra
 EXPNO 182
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20131207
 Time 11.56
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 200.08
 DW 50.000 usec
 DE 6.50 usec
 TE 297.5 K
 D1 1.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 SF01 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.00000000 W

F2 - Processing parameters
 SI 65536
 SF 500.0900000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

diphenyl, cn, stil, no oh



Current Data Parameters
 NAME Bhadra
 EXPNO 182
 PROCNO 1

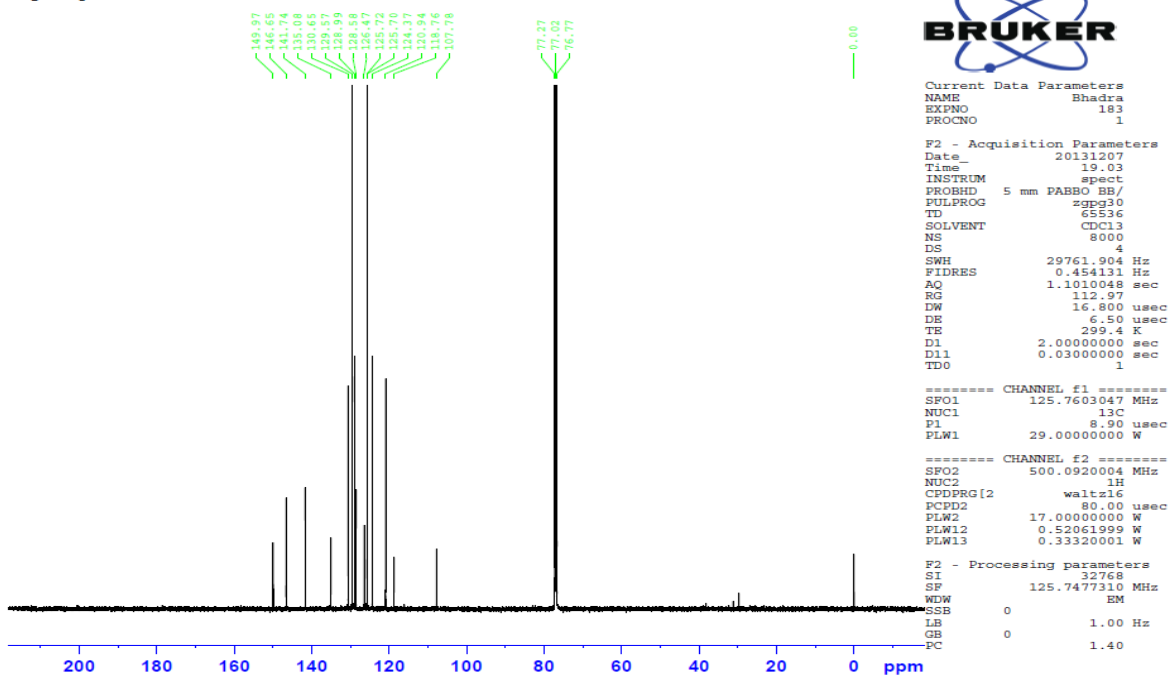
F2 - Acquisition Parameters
 Date_ 20131207
 Time 11.56
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 200.08
 DW 50.000 usec
 DE 6.50 usec
 TE 297.5 K
 D1 1.00000000 sec
 TDO 1

==== CHANNEL f1 =====
 SF01 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.00000000 W

F2 - Processing parameters
 SI 65536
 SF 500.0900000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

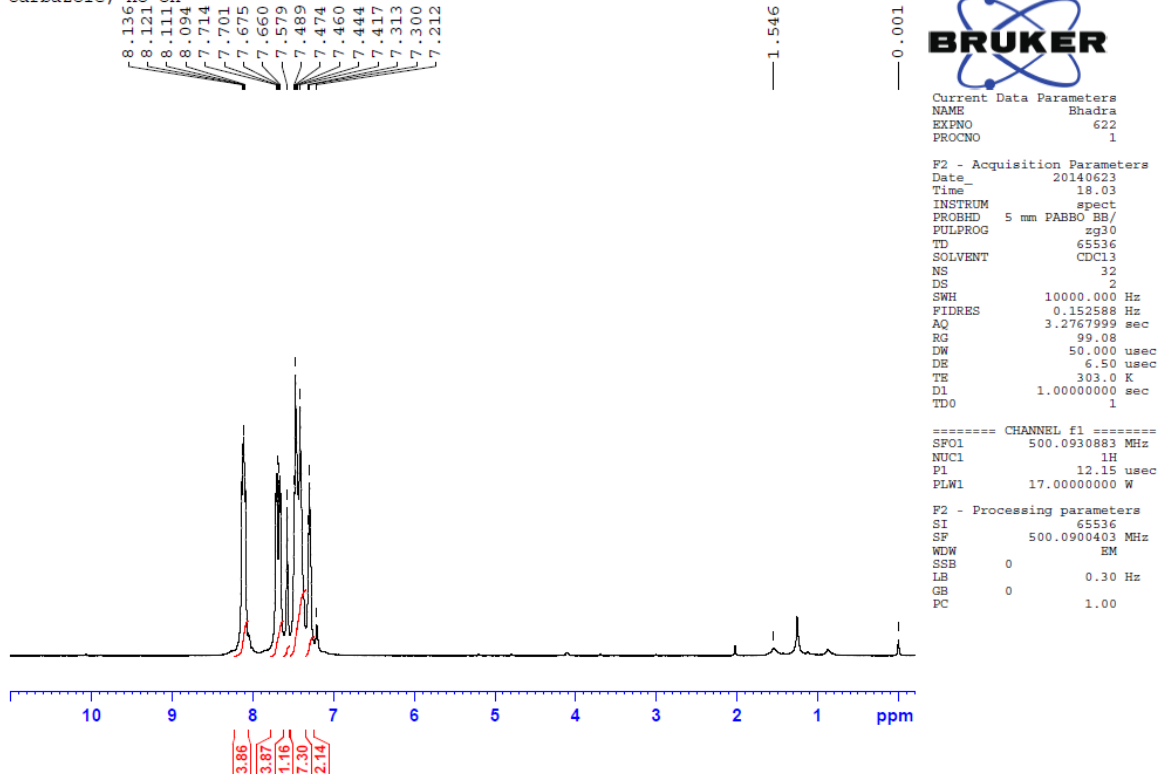
¹³C NMR Spectrum of stilbene (5)

diphenyl, cn, stil, no oh

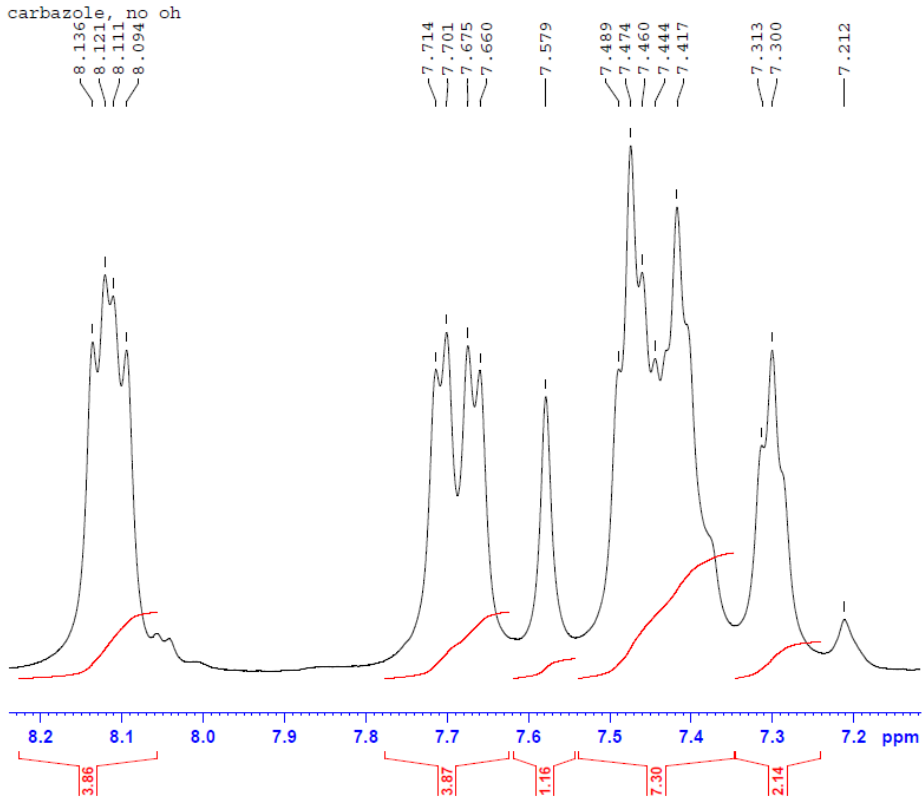


¹H NMR Spectrum of stilbene (6)

carbazole, no oh



carbazole, no oh



Current Data Parameters
 NAME Bhadra
 EXPNO 622
 PROCNO 1

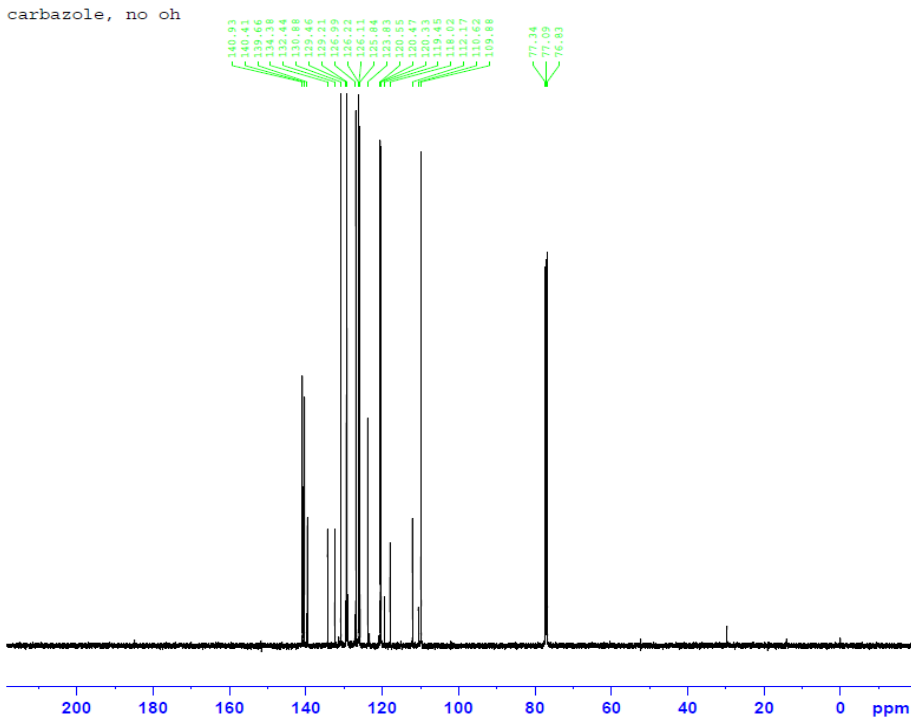
F2 - Acquisition Parameters
 Date_ 20140623
 Time 19.03
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 99.08
 DW 50.000 usec
 DE 6.50 usec
 TE 303.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 500.0930883 MHz
 NUC1 1H
 P1 12.15 usec
 PLW1 17.00000000 W

F2 - Processing parameters
 SI 65536
 SF 500.0900403 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

¹³CNMR Spectrum of stilbene (6)

carbazole, no oh



Current Data Parameters
 NAME Bhadra
 EXPNO 623
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140623
 Time 19.03
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 200.08
 DW 16.800 usec
 DE 6.50 usec
 TE 304.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 125.7603047 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 29.00000000 W

===== CHANNEL f2 =====
 SFO2 500.0920004 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 17.00000000 W
 PLW12 0.52061999 W
 PLW13 0.33320001 W

F2 - Processing parameters
 SI 32768
 SF 125.7477310 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40