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Oleic acid: A benign Brønsted acidic catalyst for densely substituted indole derivatives synthesis

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Experimental Section

General

All the chemicals were purchased from Sigma Aldrich, Loba chemicals, Merck, Avra synthesis, and SD Fine chemicals. Oleic acid (Pdt No: 61821625001730) was purchased from Merck and was used as such without further purification. All the substrates and reagents were used without further purification. IR spectra were recorded in the FT-IR PerkinElmer instrument. Melting points were recorded in the microscopic melting point meter and were uncorrected. NMR analysis (H^1 & C^{13}) were determined by Bruker Av-300MHz spectrometer.

Representative procedure of bis(indolyl)methane synthesis: A mixture of benzaldehyde (1 mmol, 0.1019 mL), indole (2 mmol, 0.2343 g) and oleic acid (12.5 mol%, 40 µL) were taken in the 3 ml of distilled water and was stirred at 100 °C for 2 h. After completion of reaction, the reaction mixture was cooled to room temperature and the formed solid were washed with distilled water (3×5 mL) followed by hexane (2×5 mL) for removing oleic acid. The solid mass was further stirred in hexane (10 mL) for 10 minutes and filtered through Whatman filter paper. The product thus obtained was essentially pure.

3-((1*H*-Indol-3-yl)(phenyl)methyl)-1*H*-indole (3a)

Yield: 98%; Appearance: Red solid; mp = 149-151 °C (Ref; 148-152°C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (s, 1H), 6.63 (s, 2H), 7.00 (t, *J* = 7.5 Hz, 2H), 7.14-7.40 (m, 11H), 7.89 (s, 2H);

3–[1*H*-indole-3-yl(4-nitrophenyl)methyl]-1*H*-indole (3b)

Yield: 99%; Appearance: Yellow Solid; mp = 218-220 °C (Ref; 218-220 °C)[2]; ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.03 (s, 1H), 6.85-6.90 (m, 4H), 7.03-7.08 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 8.7 Hz, *J* = 1.2 Hz 2H), 8.15 (dd, *J* = 8.7 Hz, *J* = 2.7 Hz, 2H), 10.94 (s, 2H);

3–[1*H*-indole-3-yl(3-nitrophenyl)methyl]-1*H*-indole (3c)

Yield: 85%; Appearance: Pale Yellow Solid; mp = 263-264 °C (Ref; 264-265 °C)[2]; ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.99 (s, 1H), 6.66 (s, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 7.17-7.25 (m, 3H), 7.34-7.45 (m, 4H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.98 (s, 2H), 8.08 (d, *J*= 8.1 Hz, 1H), 8.21 (s, 1H).

3-[(4-fluorophenyl)(1*H*-indole-3-yl)]-1*H*-indole (3d)

Yield: 92%; Appearance: Reddish brown Solid; mp = 77-79 °C (Ref; 76-78 °C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (s, 1H), 6.65 (d, 2H, *J* = 2.1 Hz), 6.65-7.04 (m, 4H), 7.18 (t, *J* = 9 Hz, 2H), 7.26-7.32 (m, 2H), 7.37 (d, 4H, *J* = 8.7 Hz), 7.95 (s, 2H);

3-[(4-chlorophenyl)(1*H*-indole-3-yl)]-1*H*-indole (3e)

Yield: 96%; Appearance: Reddish brown Solid; mp = 78-80 °C (Ref; 78-80 °C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (s, 1H), 6.65 (s, 2H), 7.00 (t, *J* = 7.5 Hz, 2H), 7.14-7.40 (m, 10H), 7.90 (s, 2H);

Representative procedure for the synthesis of 4*H*-chromene derivatives: A mixture of salicylaldehyde (1 mmol, 0.106 mL), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol, 0.140 g), indole (1 mmol, 0.117 g) and oleic acid (12.5 mol%, 40 µL) were taken in 3 ml of water and was stirred at 100 °C for 2 h. After completion, the reaction mixture was cooled to room temperature and the formed solid were washed with distilled water (3×5 mL) followed by hexane (2×5 mL) for removing oleic acid. The solid was further stirred with hexane (1×10 mL) for 10 minutes and filtered through Whatman filter paper. The white solid thus obtained was essentially pure. Suitable crystals for the single crystal XRD studies were obtained by crystallizing the product in chloroform and ethyl acetate mixture (2:2 v/v).

9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5a)

Yield:98%; Appearance: white Solid; mp = 189-191 °C (Ref; 189-191 °C)[3]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95 (s, 3H), 1.10 (s, 3H), 2.15-2.28 (m, 2H), 2.50-2.64 (m, 2H), 5.31 (s, 1H), 6.94-7.25 (m, 8H), 7.39 (d, *J* = 8.1 Hz, 1H), 8.11 (br s, 1H)

9-(5-methoxy-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5b)

Yield:86%; Appearance: white Solid; mp = 106-109 °C (Ref; 100-102 °C)[4]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (s, 3H), 1.11 (s, 3H), 2.16-2.30 (m, 2H), 2.56 (s, 2H), 3.75 (s, 3H), 5.29 (s, 1H),

6.73 (dd, *J* = 8.7 Hz, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 2.4 Hz, 1H), 7.00 (td, *J* = 7.2 Hz, *J* = 1.5 Hz 1H), 7.10-7.19 (m, 5H), 7.89 (s, 1H);

9-(2-hydroxynaphthalen-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5c)

Yield:73%; Appearance: white Solid; mp = 235-239 °C (Ref; 234−236°C)[5]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (s, 3H), 1.08 (s, 3H), 2.10 (d, *J* = 16.2Hz, 1H), 2.34 (d, *J* = 16.2 Hz, 1H), 2.54-2.74 (m, 2H), 5.75 (s, 1H), 6.61 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.85-6.90 (m,1H), 7.0 (d, *J* = 7.5Hz, 1H), 7.38-7.51 (m, 3H), 7.87 (t, *J* = 7.5Hz, 2H), 8.32 (d, *J* = 8.4Hz, 1H), 9.67 (s, 1H).

9-(1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5d)

Yield:84%; Appearance: white Solid; mp = 217-220°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88-1.99 (m, 2H), 2.26-2.33 (m, 2H), 2.70-2.77 (m, 2H), 5.21 (s, 1H), 6.88-6.93 (m, 1H), 6.97-7.05 (m, 2H), 7.13-7.18 (m,3H), 7.29(t, *J* = 7.8 Hz,2H), 7.47 (d, *J* = 8.1 Hz, 1H), 10.83 (s, 1H). ^{13}C NMR (75 MHz, CDCl3, δ ppm); 20.5, 27.6, 29.0, 37.0, 112.1, 113.6, 116.6, 118.7, 119.1, 120.1, 121.4, 123.1, 125.2, 125.7, 126.2, 128.0, 130.1, 136.9, 149.4, 167.0, 197.4. IR (cm^{-1}): 3430, 3334, 3061, 2947, 2915, 2843, 1636, 1580, 1484, 1378, 1234, 1178, 993, 623. MS (LC): m/z = 316 (M+1).

9-(1-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5e)

Yield:90%; Appearance: white Solid; mp =116-119 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88-2.02 (m, 2H), 2.26-2.50 (m, 2H), 2.71-2.77 (m, 2H), 3.67 (s, 3H), 5.20 (s, 1H), 6.93-7.28 (m, 6H), 7.29-7.32 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm); 20.1, 27.1, 28.2, 32.2, 36.6, 109.7, 113.2, 116.1, 118.5, 118.6, 118.9, 120.9, 124.7, 125.6, 125.8, 127.0, 127.4, 129.6, 136.7, 148.9, 166.2, 196.2.IR (cm^{-1}): 3446, 3117, 3061, 2955, 2915, 2883, 1644, 1580, 1484 , 1370, 1330, 1242, 1178, 1130, 993, 751, 574, 534. MS (LC): m/z = 330 (M+1).

12-(1*H*-indol-3-yl)-2,3,4,12-tetrahydro-1*H*-5-oxatetraphen-1-one(5f)

Yield:98%; Appearance: white Solid; mp = 235-238 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74-1.81 (m, 1H), 1.94-2.0 (m, 1H), 2.23-2.36 (m, 2H), 2.73-2.77 (m, 2H), 5.88 (s, 1H), 6.83 (t, *J*= 6.9Hz, 1H), 6.93 (t, *J*= 7.2 Hz, 1H), 7.21-7.48 (m, 6H), 7.87(d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* =

8.4Hz, 1H), 10.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm); 20.0, 25.8, 26.8, 27.1, 36.5, 38.6, 111.5, 113.8, 116.9, 117.3, 117.9, 118.2, 118.5, 120.5, 122.7, 123.3, 124.1, 124.7, 125.3, 126.8, 128.4, 128.6, 131.0, 136.1, 147.0, 165.1, 196.3; IR (cm^{-1}): 3462, 3342, 3061, 2915, 1644, 1370, 1226, 1186, 993, 945, 807, 751; MS (LC): m/z = 366 (M+1).

12-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,12-tetrahydro-1*H*-5-oxatetraphen-1-one (5g)

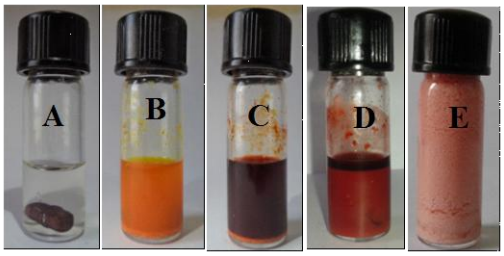
Yield:88; Appearance: white Solid; mp = 234-237°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (s, 3H), 1.05 (s, 3H), 2.05-2.33 (m, 2H), 2.57-2.73 (m, 2H), 5.86 (s, 1H), 6.83 (t,, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.5 Hz,1H), 7.21(d, *J* = 7.8 Hz, 1H), 7.33-7.47 (m, 5H), 7.85 (d, *J* = 7.1 Hz, 2H), 8.22 (d, *J* = 7.8 Hz, 1H), 10.85 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm); 25.9, 26.4, 28.8, 31.7, 50.2, 111.5, 112.5, 117.0, 117.2, 117.7, 118.2, 118.4, 120.5, 123.4, 124.1, 124.7, 125.3, 126.7, 128.4, 128.6, 131.0, 136.1, 146.9, 163.2, 196.1; IR (cm^{-1}): 3440, 3241, 2958, 2914, 1639, 1595, 1373, 1223, 1099, 815, 745, 622; MS (LC): m/z = 394 (M+1).

Procedure for the recyclability of oleic acid catalyst on 4*H*-chromene (5d) synthesis: A mixture of salicylaldehyde (1 mmol, 0.106 mL), 1,3-cyclohexanedione (1 mmol, 0.112 g), indole (1 mmol, 0.117 g) and oleic acid (12.5 mol%, 40 µL) were taken in 3 ml of water and was stirred at 100 °C for 2 h. After completion, the reaction mixture was decanted to remove aqueous layer and the residue was extracted twice with hexane:ethyl acetate mixture (4.5:0.5 v/v) to remove trace oleic acid catalyst embedded with product **5d**. The organic solvents were evaporated and the residue was mixed with the previously isolated aqueous layer. The reaction was repeated by freshly adding substrates to the mixture of recovered oleic acid on water.

Number of cycles	5d Yield (%)
1	**84**
2	**84**
3	**83**
4	**81**

Representative procedure of spirooxindoles synthesis :. A mixture of isatin (1 mmol, 0.147 g) , 5,5-dimethyl-1,3-cyclohexanedione (1mmol, 0.140 g), malononitrile (1 mmol, 63 µL) and oleic acid (12.5 mol%, 40 µL) were taken in the 3 ml of ethanol and was stirred at room temperature

for appropriate time. After completion, the reaction mixture was quenched with water and the formed solids were filtered through Whatman filter paper and were washed with distilled water (3×5 mL) followed hexane (2×5mL) for removing oleic acid. The white solid thus obtained was essentially pure.



Sequence (A) Oleic acid in ethanol (B) After addition of isatin and barbituric acid (C) After addition of malononitrile (D) After completion the reaction (E) After quenching with water

7'-amino-2,2',4'-trioxo-1,1',2,2',3',4'-hexahydrospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6a)

Yield: 91% Appearance: white Solid; mp = 273-275 °C (Ref; 277-278 °C)[6]; ^{1}H NMR (300 MHz, DMSO-d6); δ 6.79 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 7.12-7.19 (m, 2H), 7.38 (s, 2H), 10.49 (s, 1H), 11.13 (s, 1H), 12.32 (br s,1H);

2-amino-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carbonitrile (6b)

Yield: 90% Appearance: white Solid; mp = 277-279 °C (Ref; 278-280 °C)[7]; ^{1}H NMR (300 MHz, DMSO-d6); δ 1.92 (t, *J* =6.3Hz, 2H), 2.22-2.23 (m, 2H), 2.66 (t, *J* = 6.0 Hz, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.23 (s, 2H), 10.40 (s, 1H);

2-amino-7,7-dimethyl-2',5-dioxo-1',2',5,6,7,8-hexahydrospiro[chromene-4,3'-indole]-3-carbonitrile (6c)

Yield: 97% Appearance: white Solid; mp = 267-270 °C (Ref; 268-270 °C)[8]; ^{1}H NMR (300 MHz, DMSO-d6); δ 0.99 (s, 3H), 1.03 (s, 3H), 2.09 (d, *J* = 15.9 Hz, 1H), 2.18 (d, *J* = 15.9 Hz, 1H), 2.53 (s, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.24 (s, 2H), 10.41 (s, 1H).

7'-amino-2,4'-dioxo-2'-sulfanylidene-1,1',2,2',3',4'-hexahydrospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6d)

Yield: 91% Appearance: white Solid; mp = 239-241 °C (Ref; 238-242 °C)[9]; ^{1}H NMR (300 MHz, DMSO-d6); δ 6.80 (d, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.43 (s, 2H), 10.55 (s, 1H), 12.53 (s, 1H);

ethyl 7'-amino-2,2',4'-trioxo-1,1',2,2',3',4'-hexahydrospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carboxylate (6e)

Yield: 73% Appearance: white Solid; mp = 189-190 °C (Ref; 189-190 °C)[6]; ^{1}H NMR (300 MHz, DMSO-d6); δ 0.78 (t, *J* = 7.2 Hz, 3H), 3.71 (q, *J* = 3.3 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H) 6.78 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.95 (s, 2H), 10.24 (s, 1H), 10.97 (s, 1H), 12.16 (br s, 1H);

7'-amino-1',3'-dimethyl-2,2',4'-trioxo-1,1',2,2',3',4'-hexahydrospiro[indole-3,5'-pyrano[2,3-d]pyrimidine]-6'-carbonitrile (6f)

Yield: 89%; Appearance: white Solid; mp = 226-227 °C (Ref; 228-229 °C)[6]; ^{1}H NMR (300 MHz, DMSO-d6) δ 3.02 (s, 3H), 3.38 (s, 3H merged with DMSO-water peak), 6.80 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.2 Hz, 1H), 7.11-7.19 (m, 2H), 7.57 (s, 2H), 10.51 (s, 1H);

Procedure of spiro[indoline-3,4′-pyrano[2,3-c]pyrazole] synthesis: A mixture of hydrazine (1.5 mmol, 47 µL) , ethylacetoacetate, (1mmol, 128 µL), malononitrile (1 mmol, 63 µL), isatin (1 mmol, 0.147 g), oleic acid (12.5 mol%, 40 µL) were taken in the 3 ml of ethanol and it was stirred at 80 ^{o}C for 1 h. After completion, the reaction was quenched with water and the formed solids were filtered through Whatman filter paper and were washed with distilled water (3×5 mL) and hexane (2×5mL) for removing oleic acid. The Light red powder thus obtained was essentially pure.

6'-amino-3'-methyl-2-oxo-1,2,5',6'-tetrahydro-1'H-spiro[indole-3,4'-pyrano[2,3-c]pyrazole]-5'-carbonitrile (7)

Yield: 94%; Appearance: Light red powder; mp = 286-289 °C (Ref; 285-286 °C)[10]; 1H NMR (300 MHz, DMSO-d6) δ 1.53 (s, 3H), 6.80 (d, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.97-7.05 (m, 2H), 7.26 (s, 3H), 10.61 (s, 1H); 12.30 (s, 1H).

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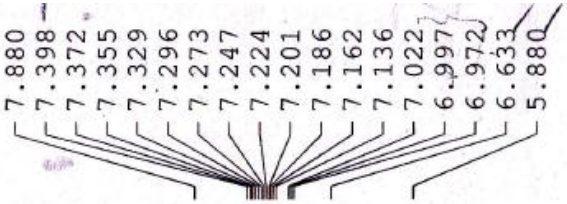

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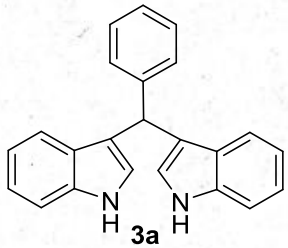

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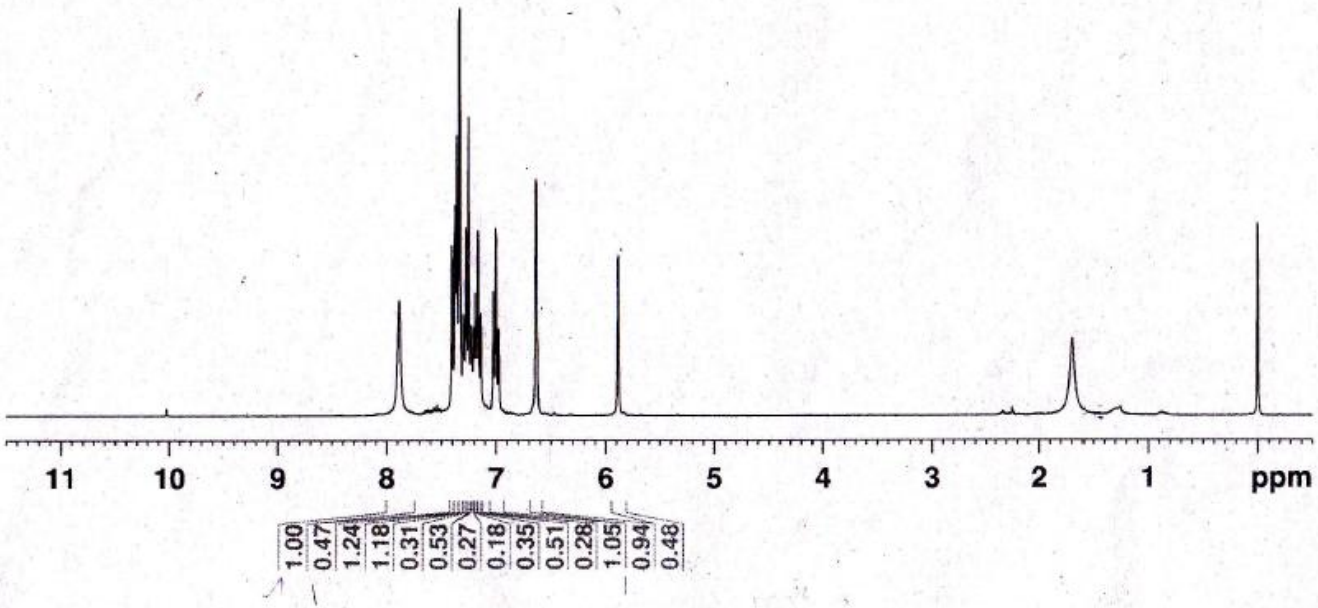


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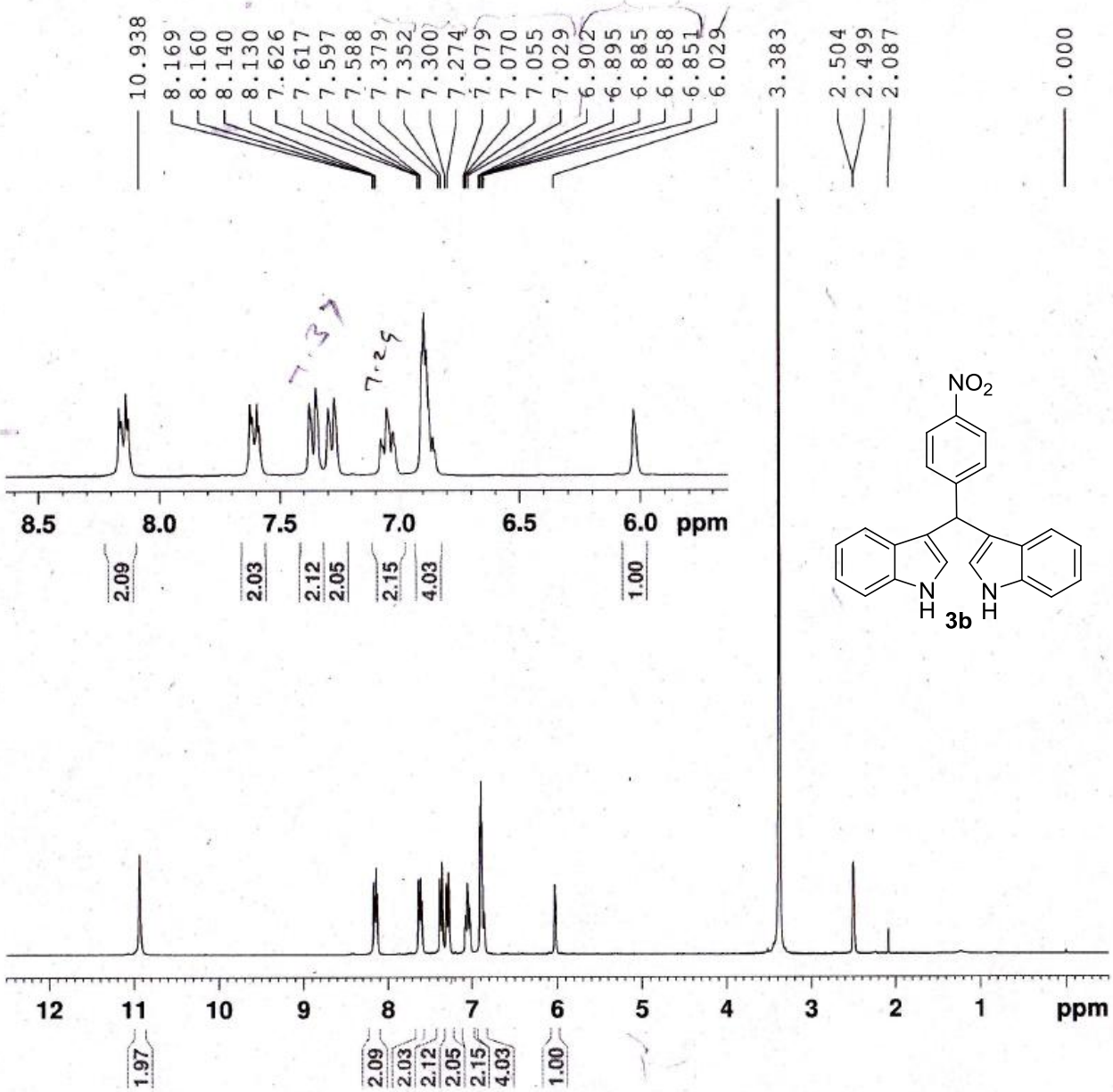

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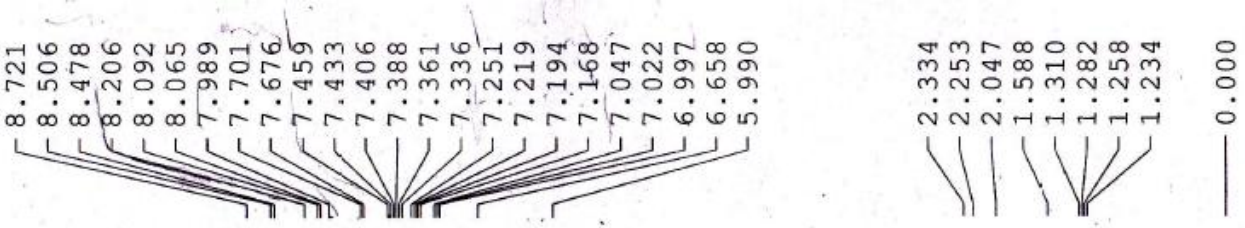

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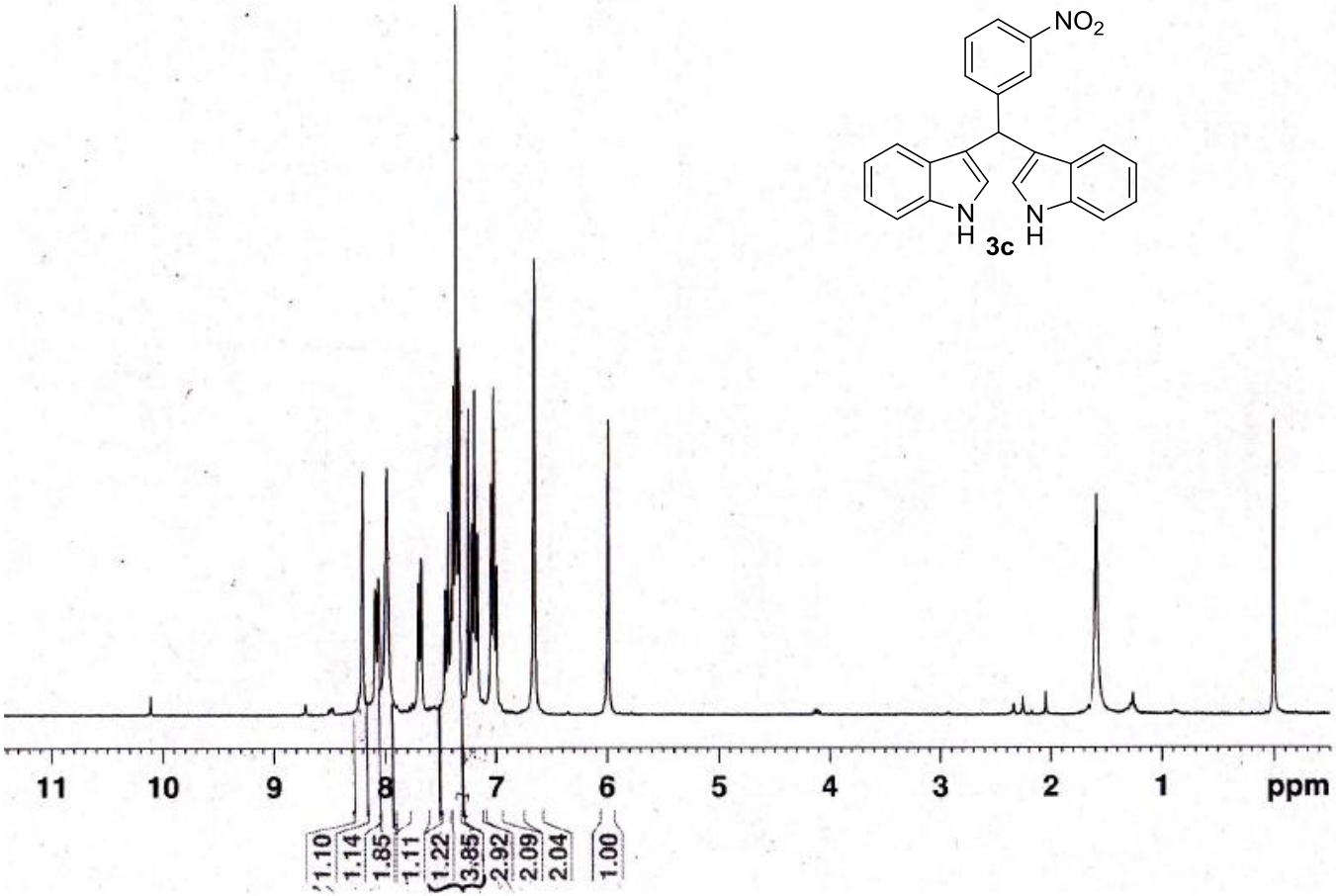


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PC                     1.00
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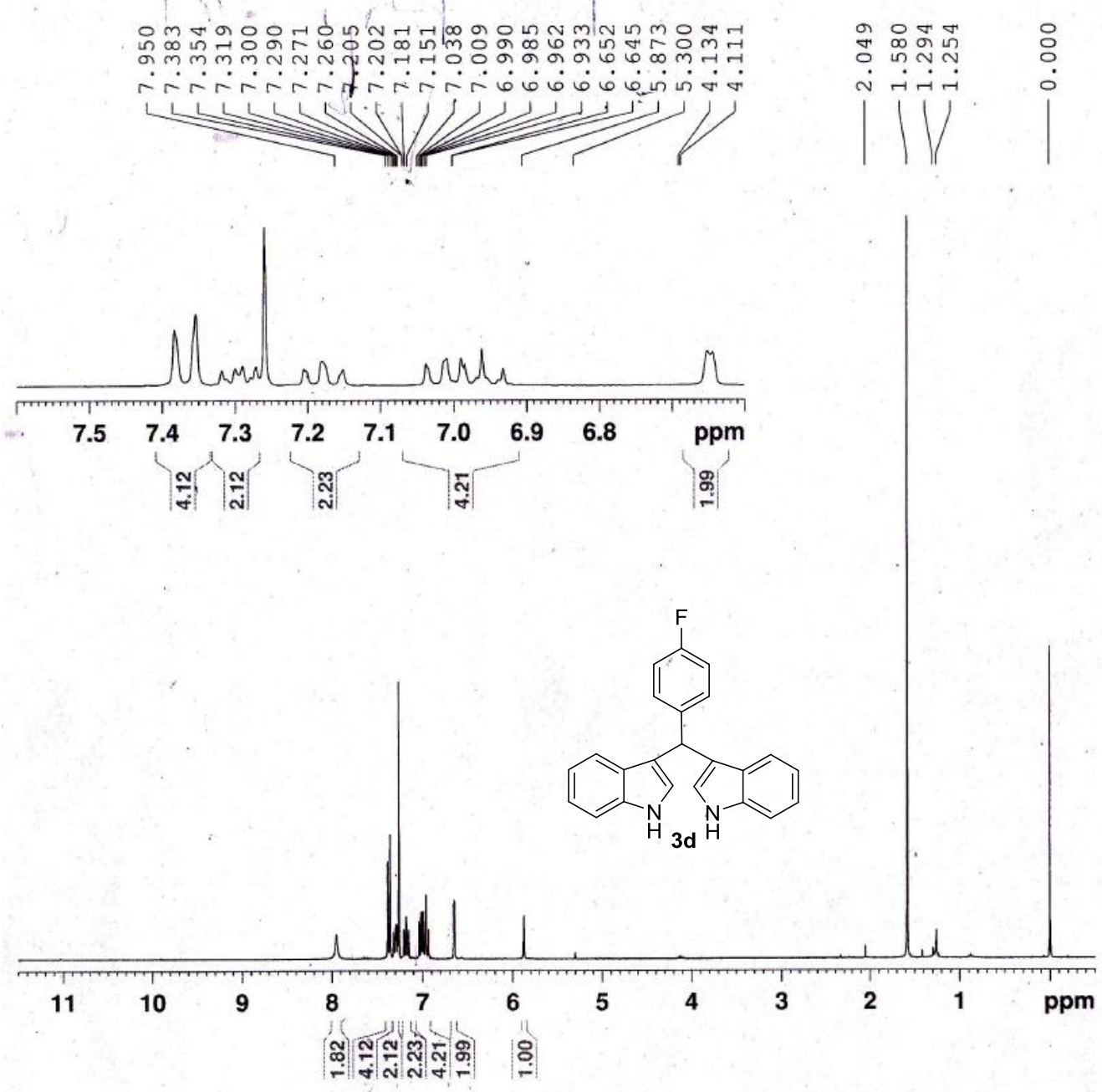
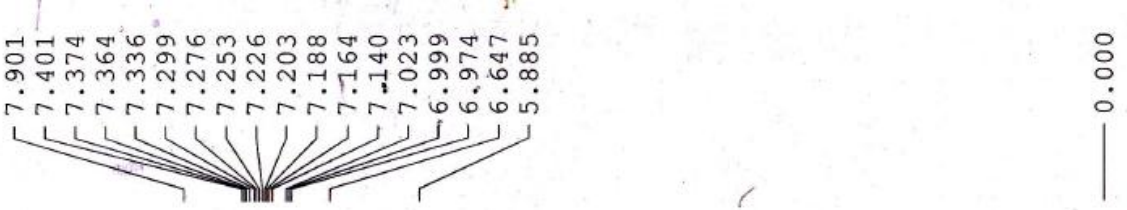
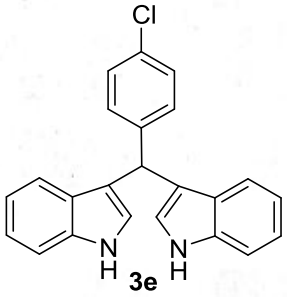
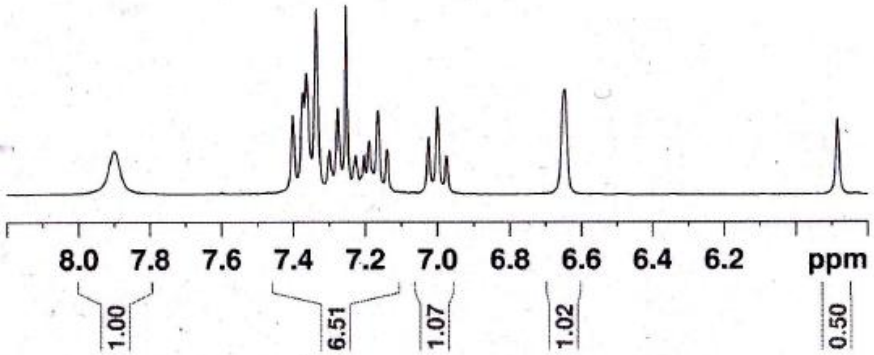
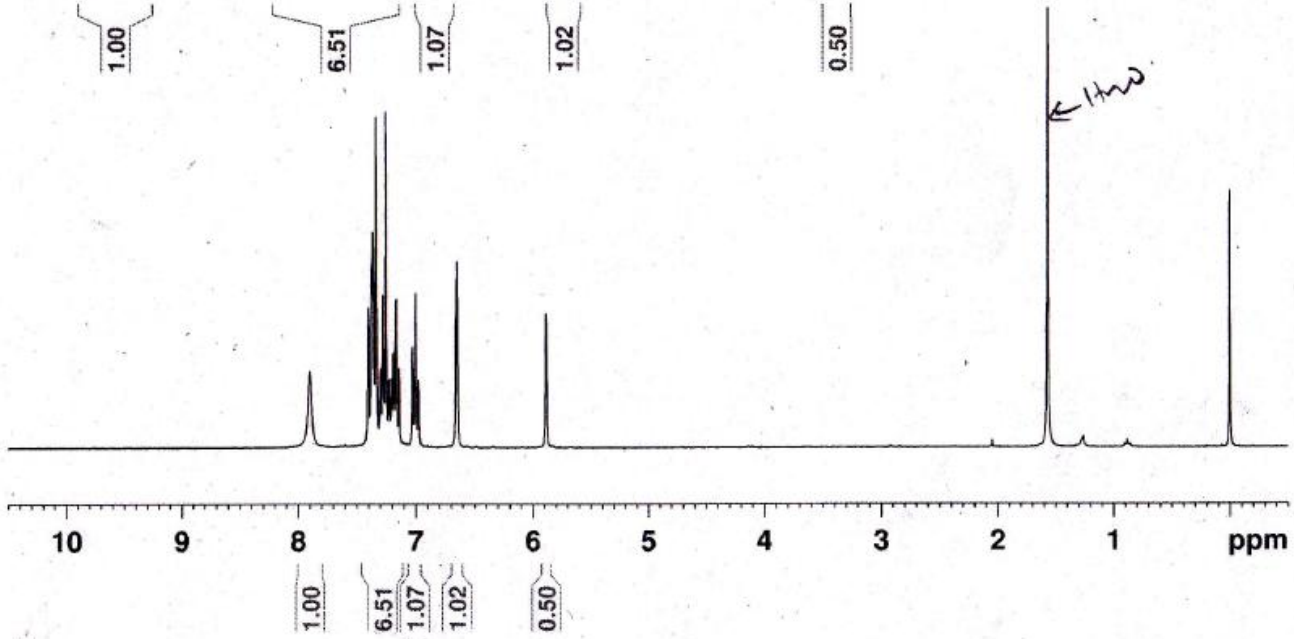



```
Current Data Parameters
NAME                  1066E
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141025
Time                 12.43
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      322
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                  8.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300064 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```

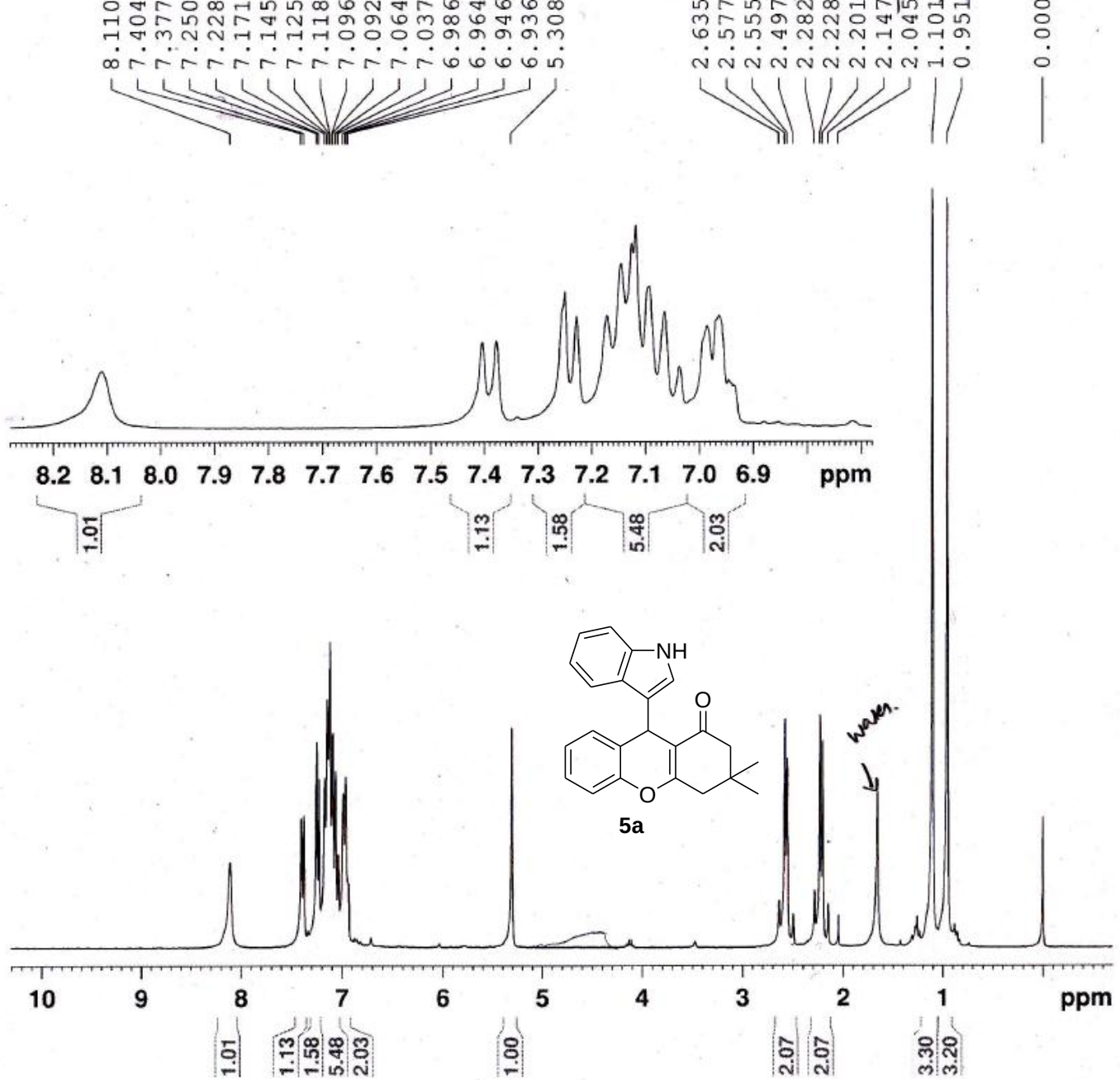




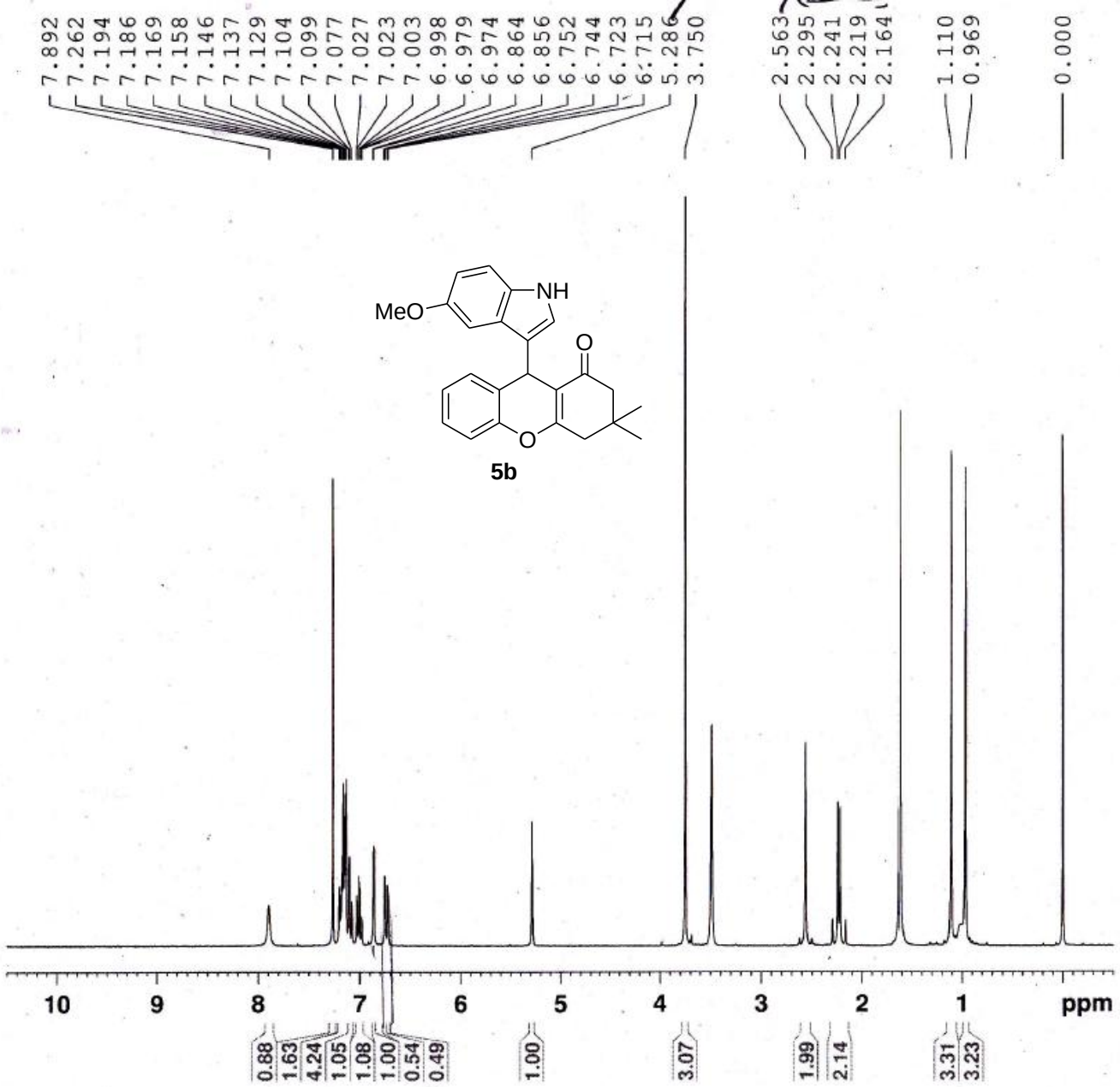




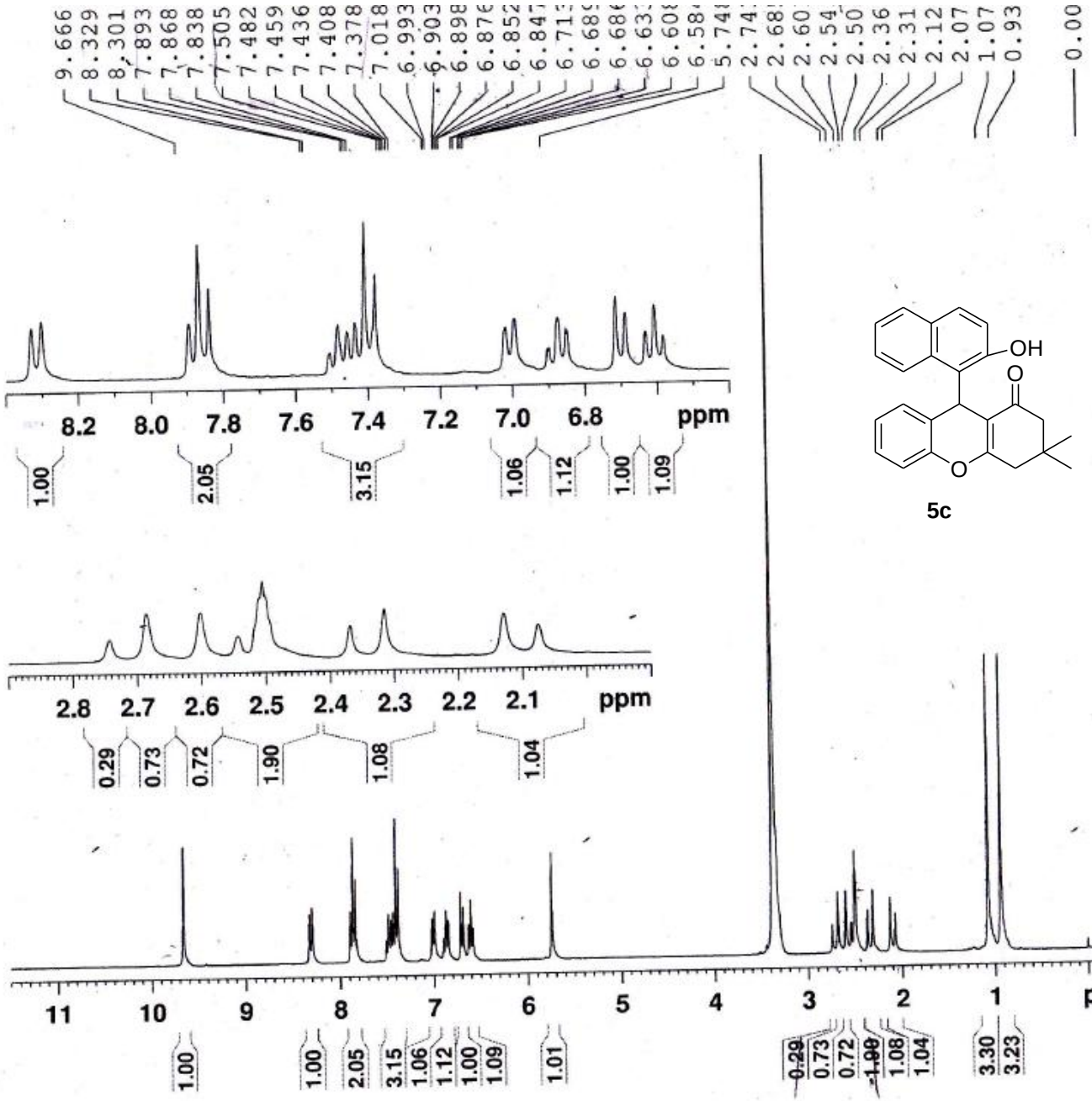

```
Current Data Parameters
NAME                  1065E
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141016
Time                 17.50
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       16
DS                        2
SWH               6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      322
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.60 usec
PL1                 -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF           300.1300083 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```




```
Current Data Parameters
NAME                  1049D
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141014
Time                 14.36
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                     161
DW                  80.800 usec
DE                   6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300091 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

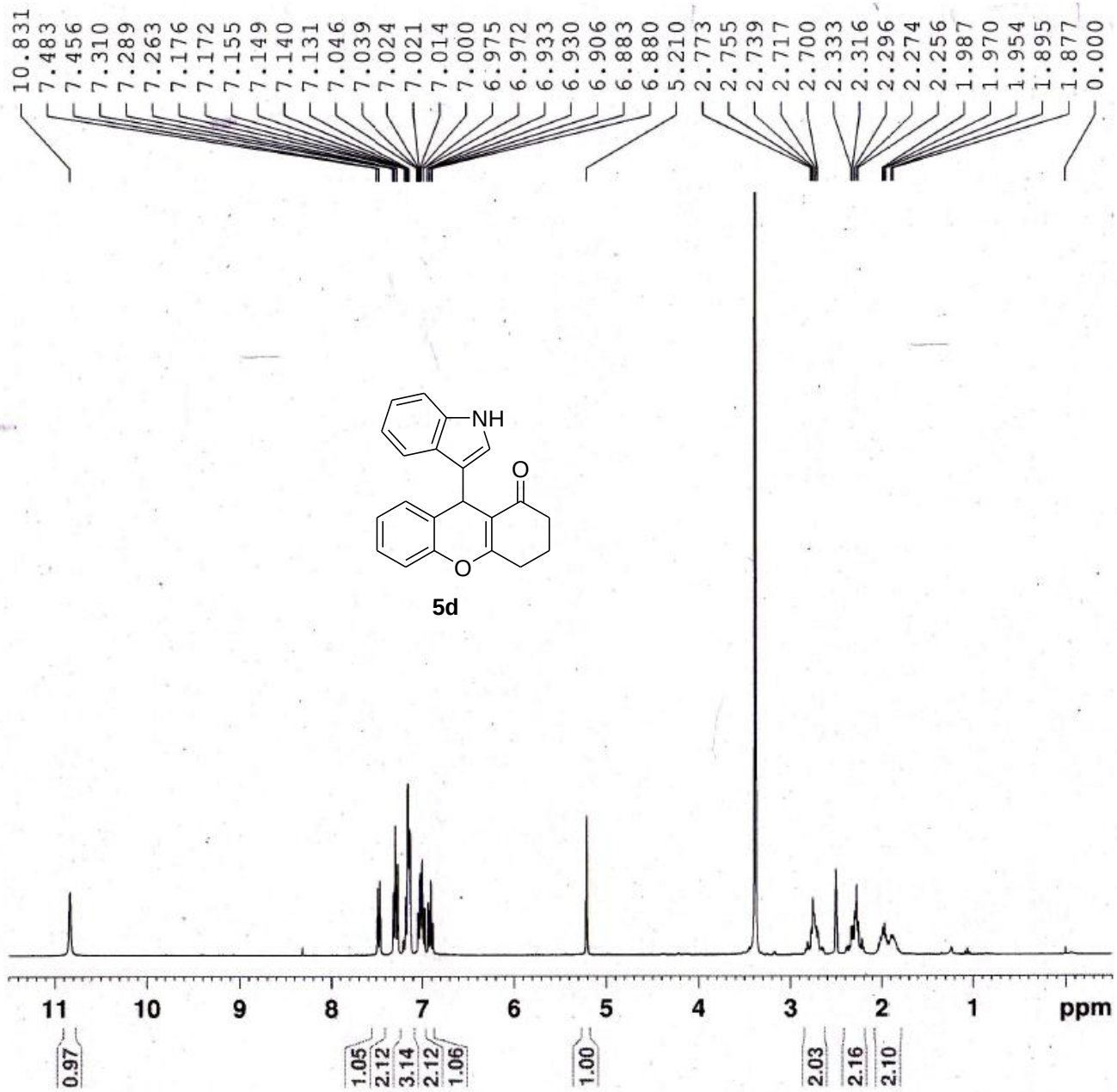



```
Current Data Parameters
NAME                  1049F
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141014
Time                  14.43
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      287
DW                   80.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    8.60 usec
PL1                  -2.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF             300.1300056 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.00
```



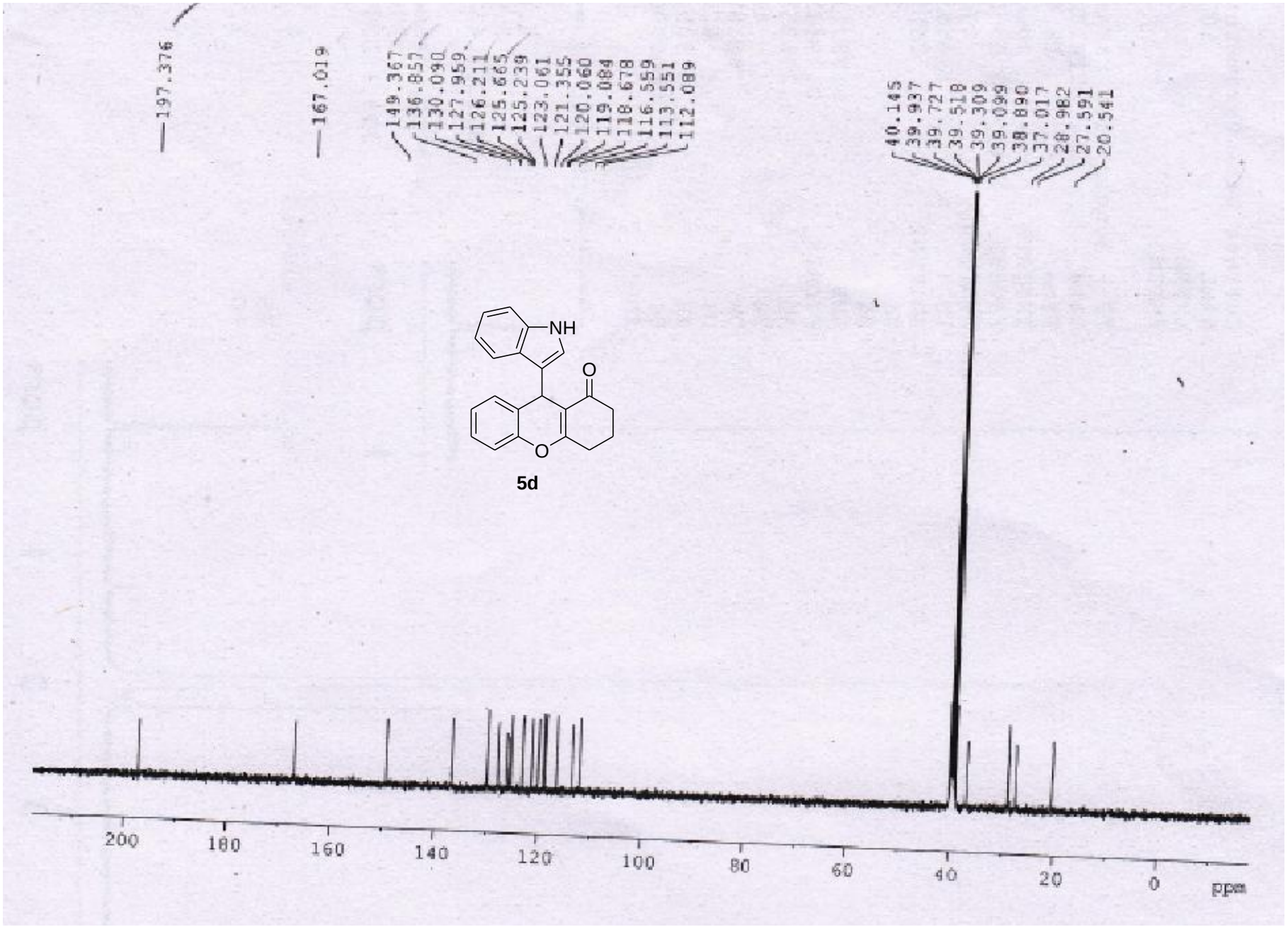
5c

```
Current Data Parameters
NAME                  1059A
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141015
Time                 15.16
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                       16
DS                        2
SWH               6188.119 Hz
FIDRES               0.094423 Hz
AQ                5.2953587 sec
RG                      181
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1299998 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



5d

```
Current Data Parameters
NAME                  1065C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141016
Time                  17.05
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      161
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                  8.60 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300009 MHz
WDW                      EM
SSB                       0
LB                 0.30 Hz
GB                        0
PC                     1.00
```

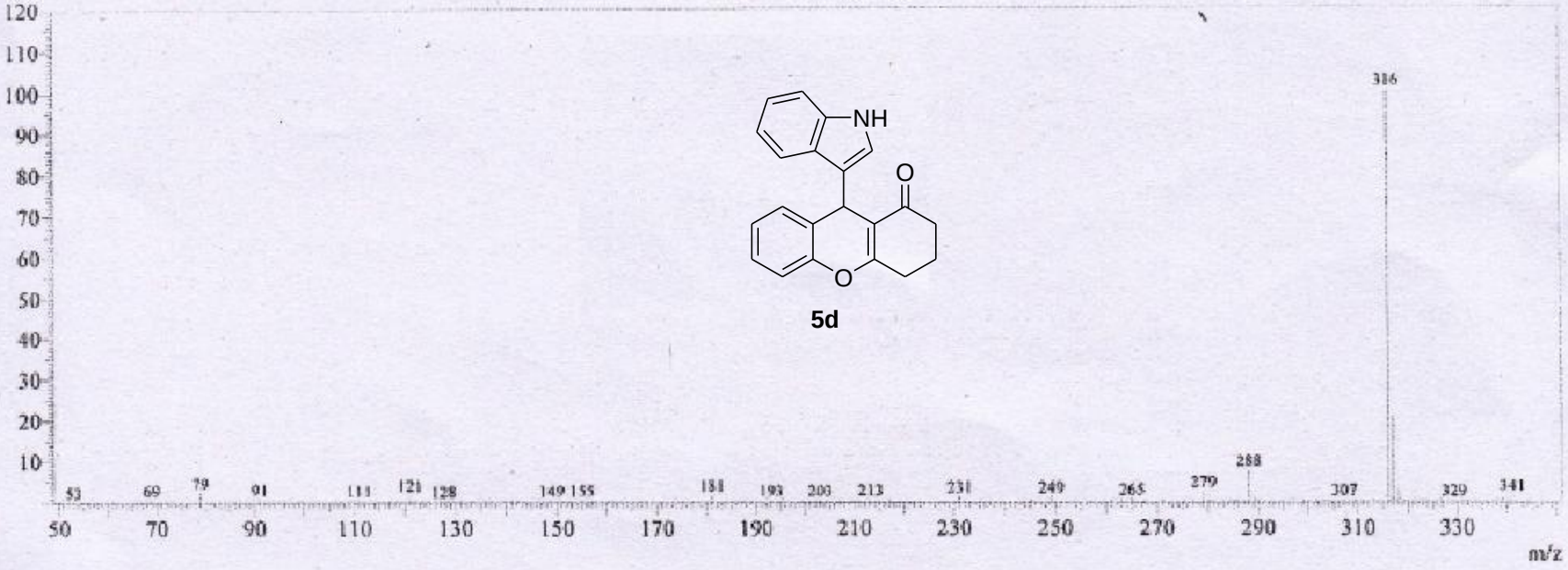

197.376
167.019
149.367
136.857
130.090
127.959
126.211
125.665
125.239
123.061
121.355
120.060
119.084
118.678
116.559
113.551
112.089
40.145
39.937
39.727
39.518
39.309
39.099
38.890
37.017
28.982
27.591
20.541
NH
O
O
200
180
160
140
120
100
80
60
40
20
0
ppm

5d

User : Admin
Sample : SEL-A
Inj. Volume : 5.000
Data Name : C:\LCMSsolution\User\Data\SEL-A-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

MS Spectrum

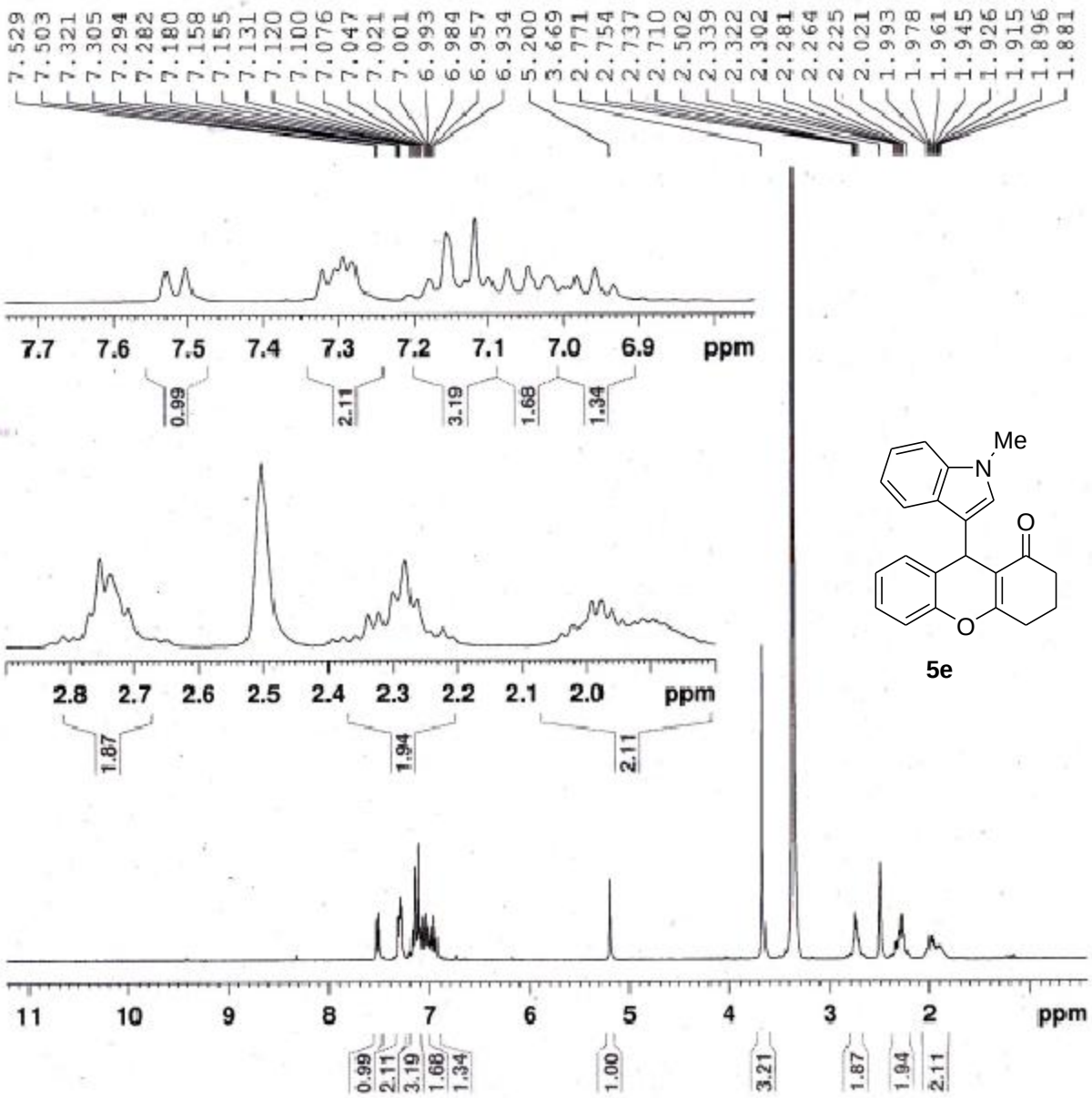
Line#:1 R.Time:0.772(Scan#:47) Positive
MassPeaks:246 BasePeak:316.10(4308381)
RawMode:Single 0.772(47)
BG Mode:Peak Start 0.560(34)



5d

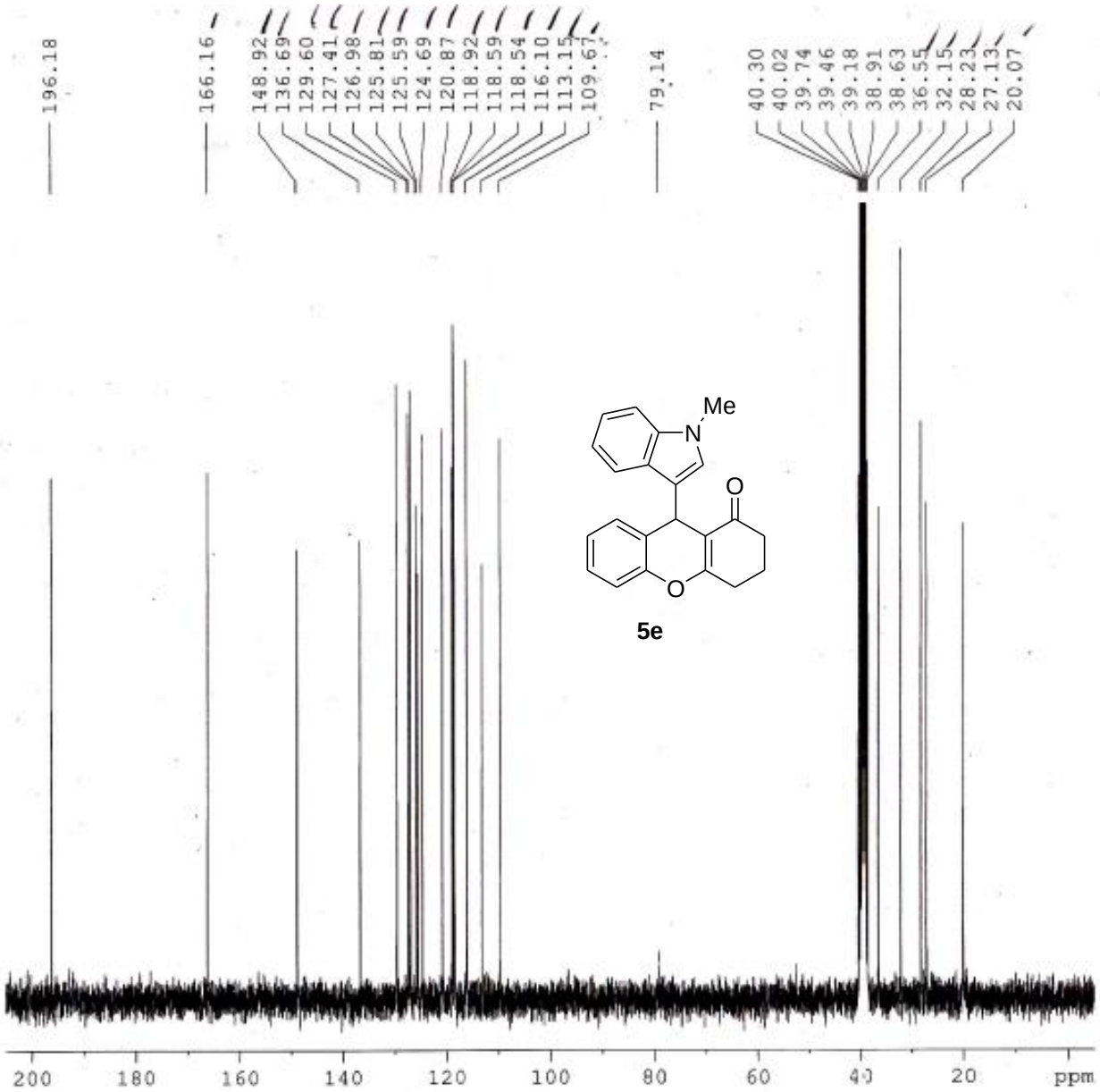
MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.772	0.560	1.110	135371879	12071155	11.21		100.00		316.10	4308381
				135371879	12071155			100.00			



5e

```
Current Data Parameters
NAME                  1059D
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141015
Time                  15.49
INSTRUM                spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      203
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                  8.60 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300004 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```



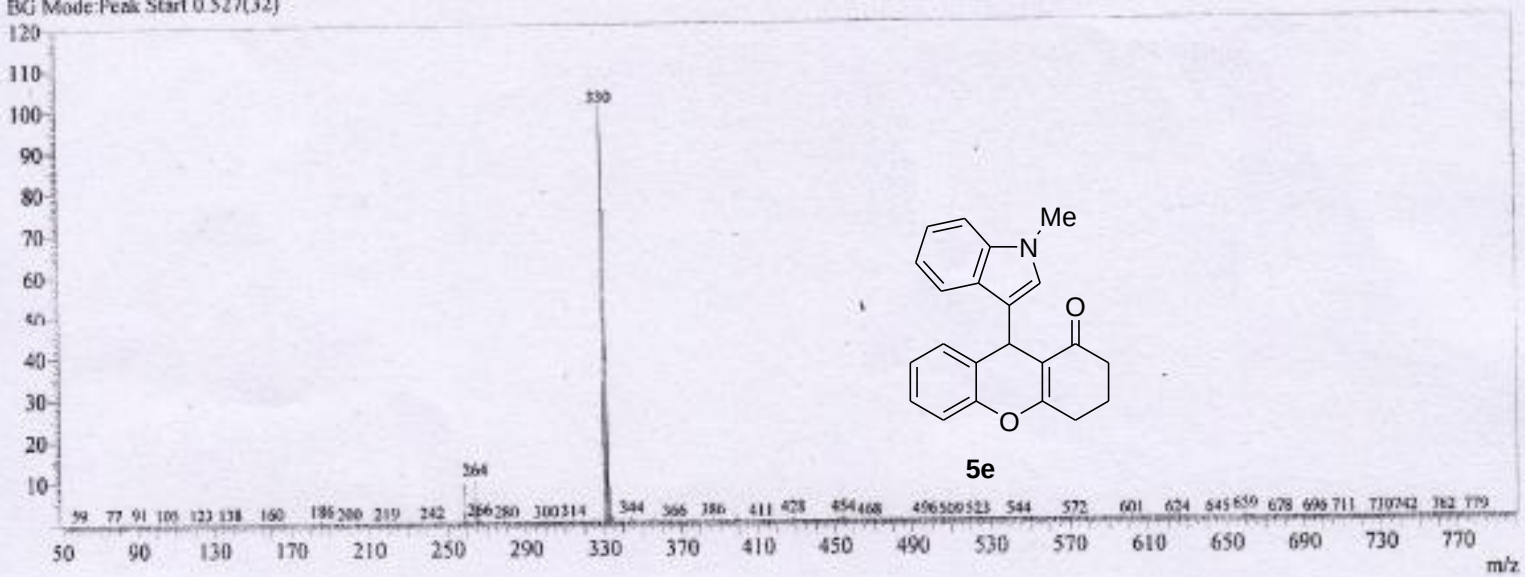
5e

```
Current Data Parameters
NAME                  1073A
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141024
Time                 11.31
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                     603
DS                       4
SWH              18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175818 sec
RG                     362
DW                27.733 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                  9.50 usec
PL1                 0.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               17.37 dB
PL13               20.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF            75.4677867 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```

User : Admin
Sample : SEL-B
Inj. Volume : 5.000
Data Name : C:\LCMSsolution\User\Data\SEL-B-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

MS Spectrum

Line#:1 R.Time:0.809(Scan#:49) Positive
MassPeaks:629 BasePeak:330.15(15762060)
RawMode:Single 0.809(49)
BG Mode:Peak Start 0.527(32)

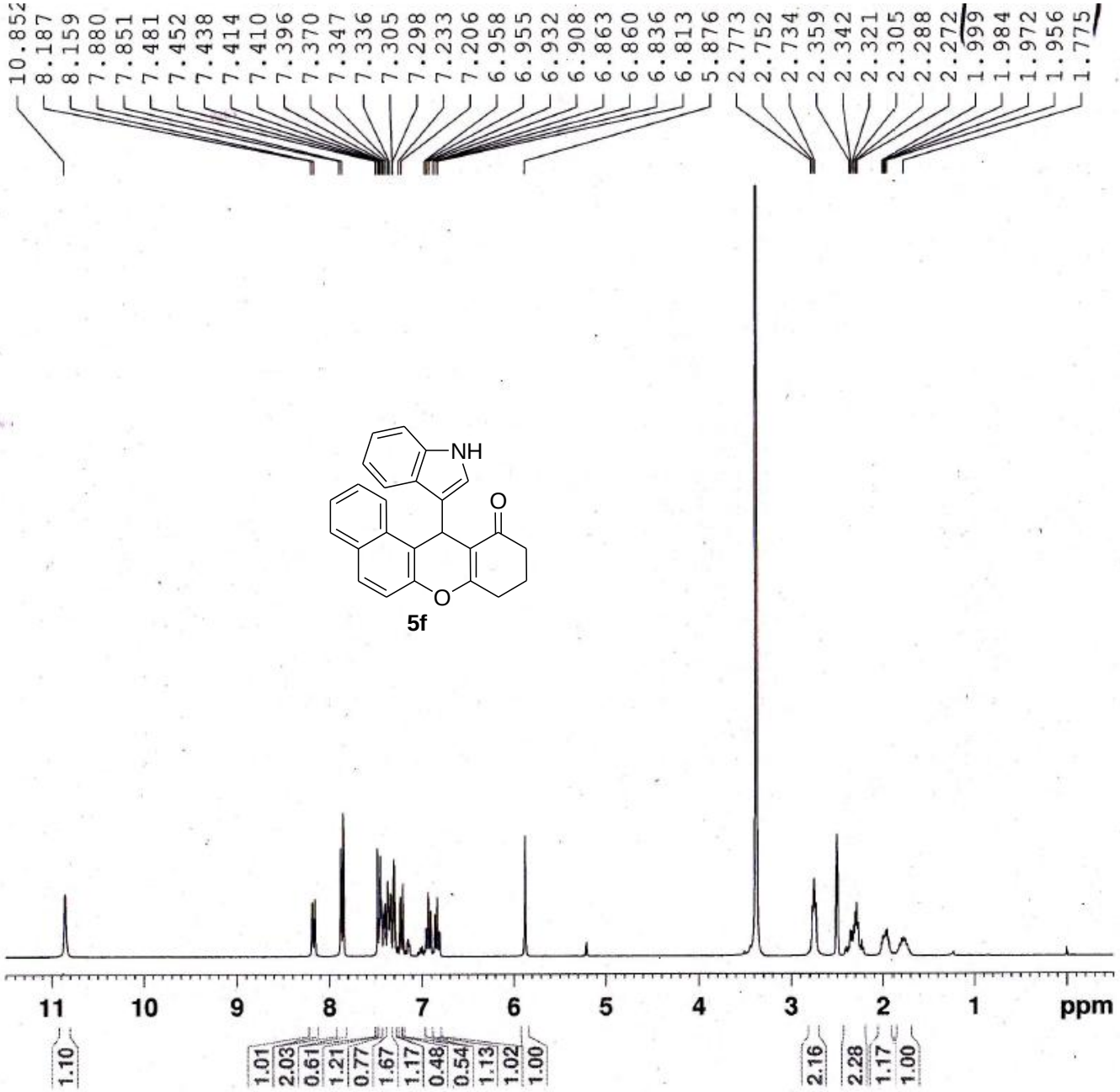


5e

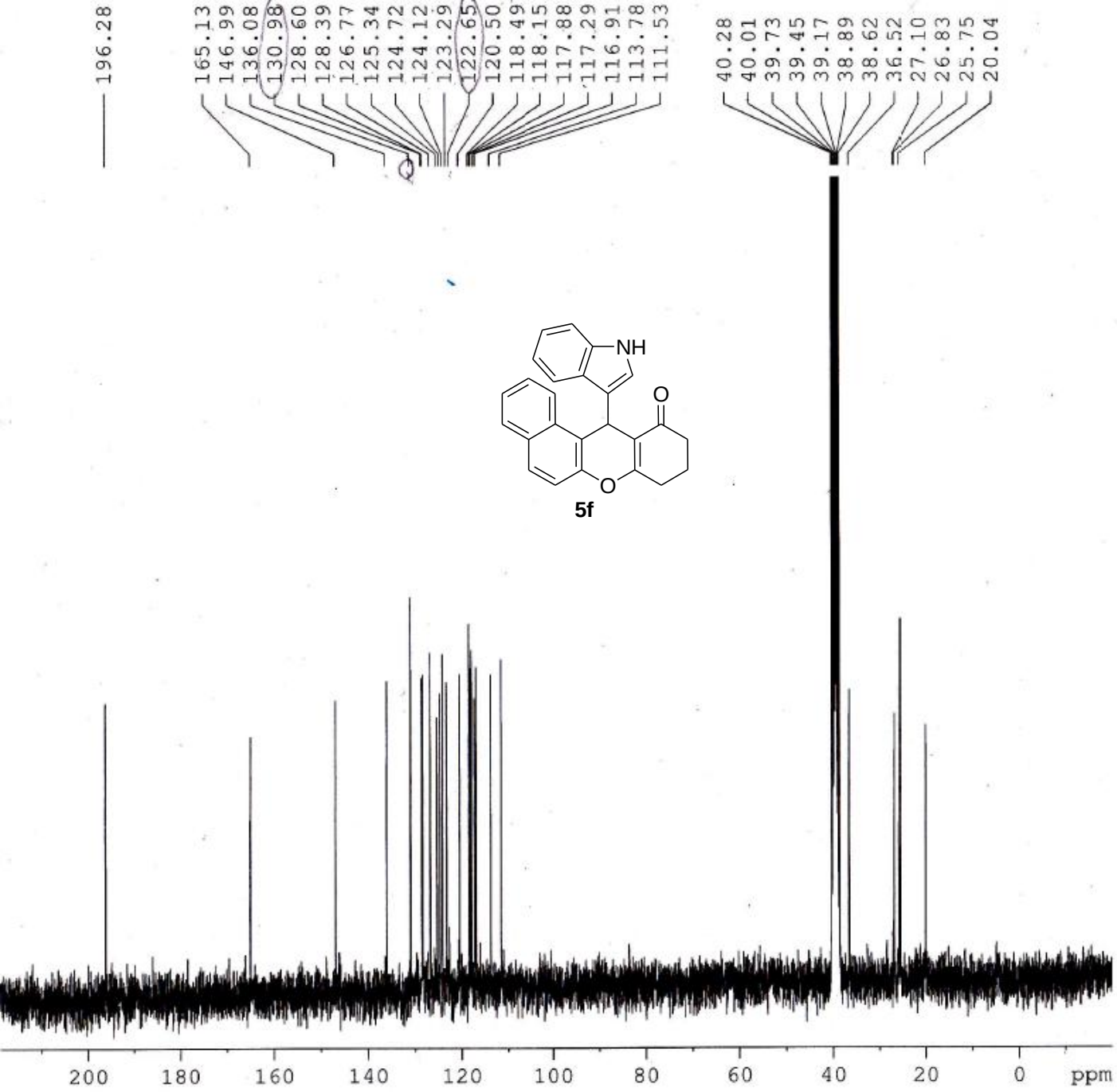
MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
1	0.809	0.527	1.243	909626621	42484149	21.41		100.00	
				909626621	42484149			100.00	

Base m/z	Base Int.
330.15	15762060




```
Current Data Parameters
NAME                  1065B
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141016
Time                 16.52
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                       16
DS                        2
SWH               6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953587 sec
RG                      181
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300003 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



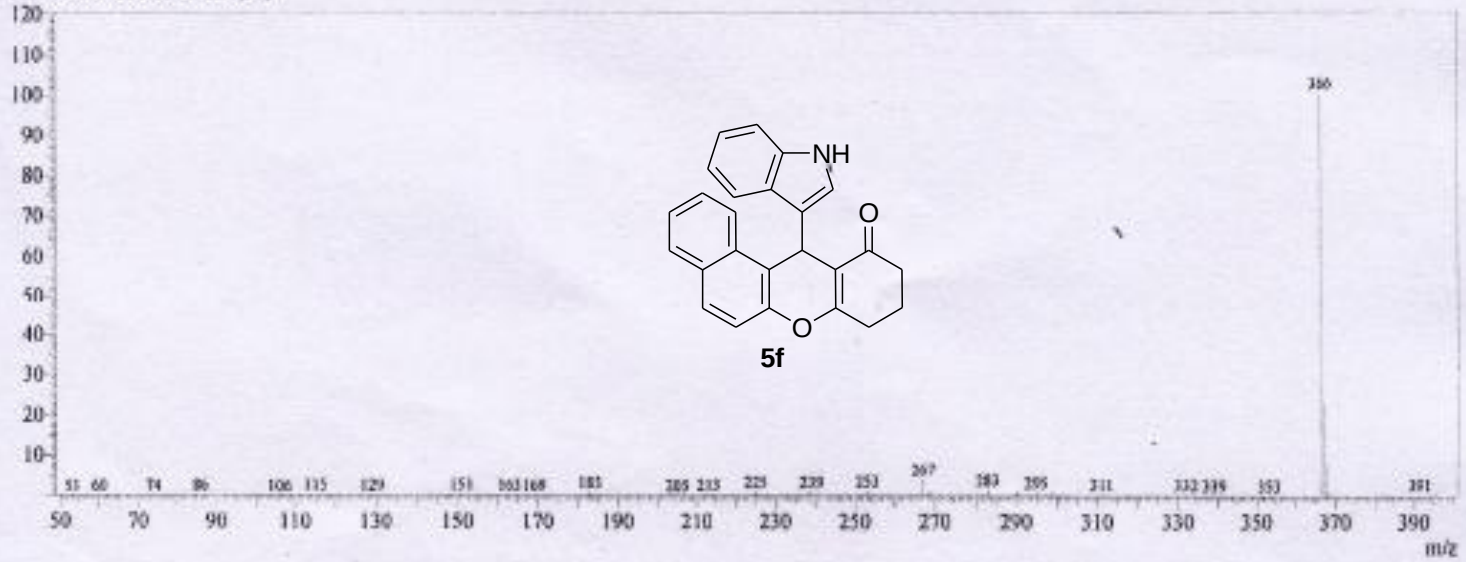
5f

```
Current Data Parameters
NAME                  1074B
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141025
Time                 16.57
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT                DMSO
NS                     1462
DS                        4
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175818 sec
RG                      322
DW                 27.733 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                   9.50 usec
PL1                  0.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                17.37 dB
PL13                20.00 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                    32768
SF             75.4677867 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                     1.40
```

User	: Admin
Sample	: SEL-E
Inj. Volume	: 5.000
Data Name	: C:\LCMSsolution\User\Data\SEL-E-APCI-POS1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

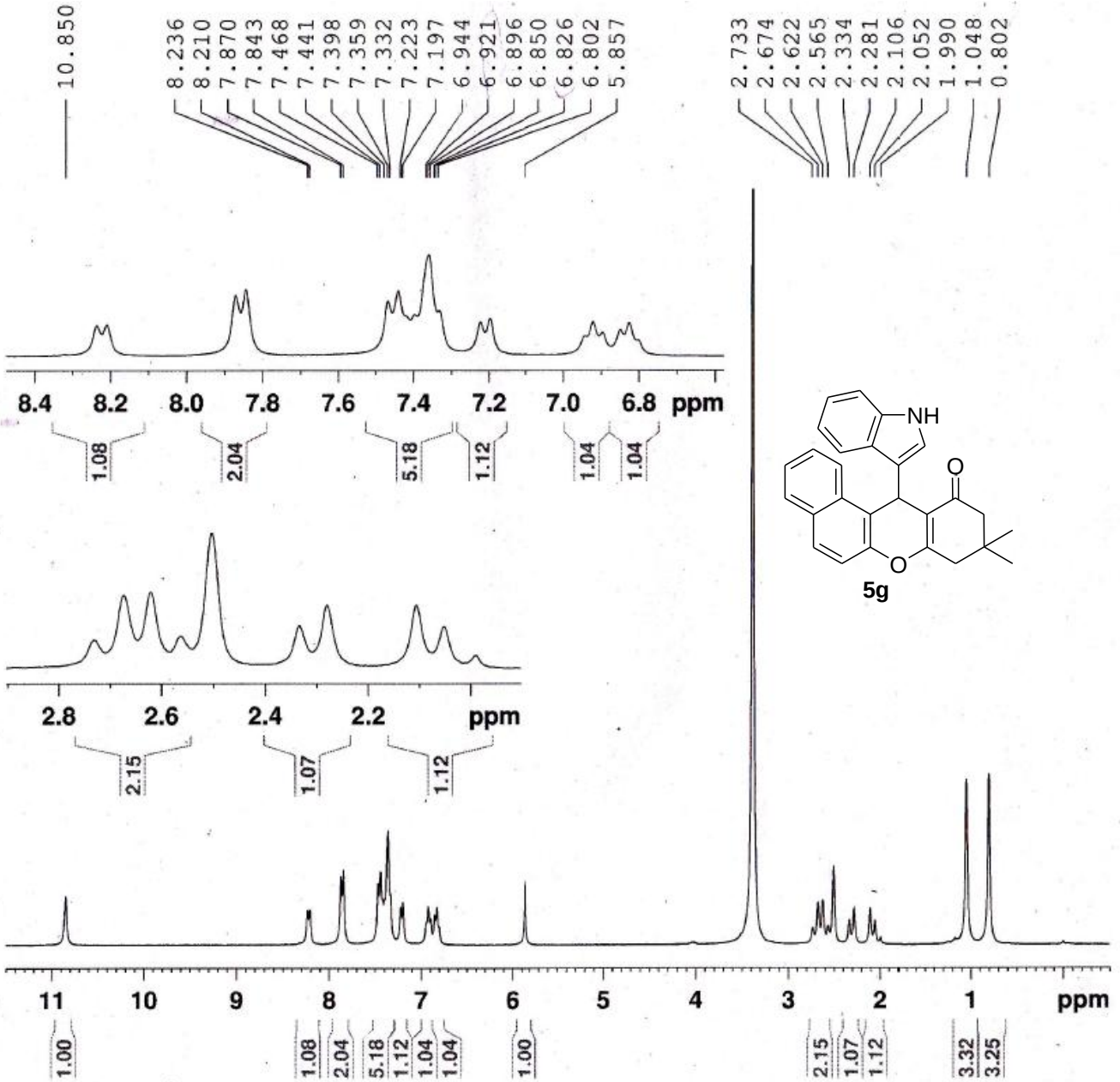
MS Spectrum

Line#:1 R.Time:0.754(Scan#:46) Positive
MassPeaks:268 BasePeak:366.15(9469886)
RawMode:Single 0.754(46)
BG Mode:Peak Start 0.610(37)



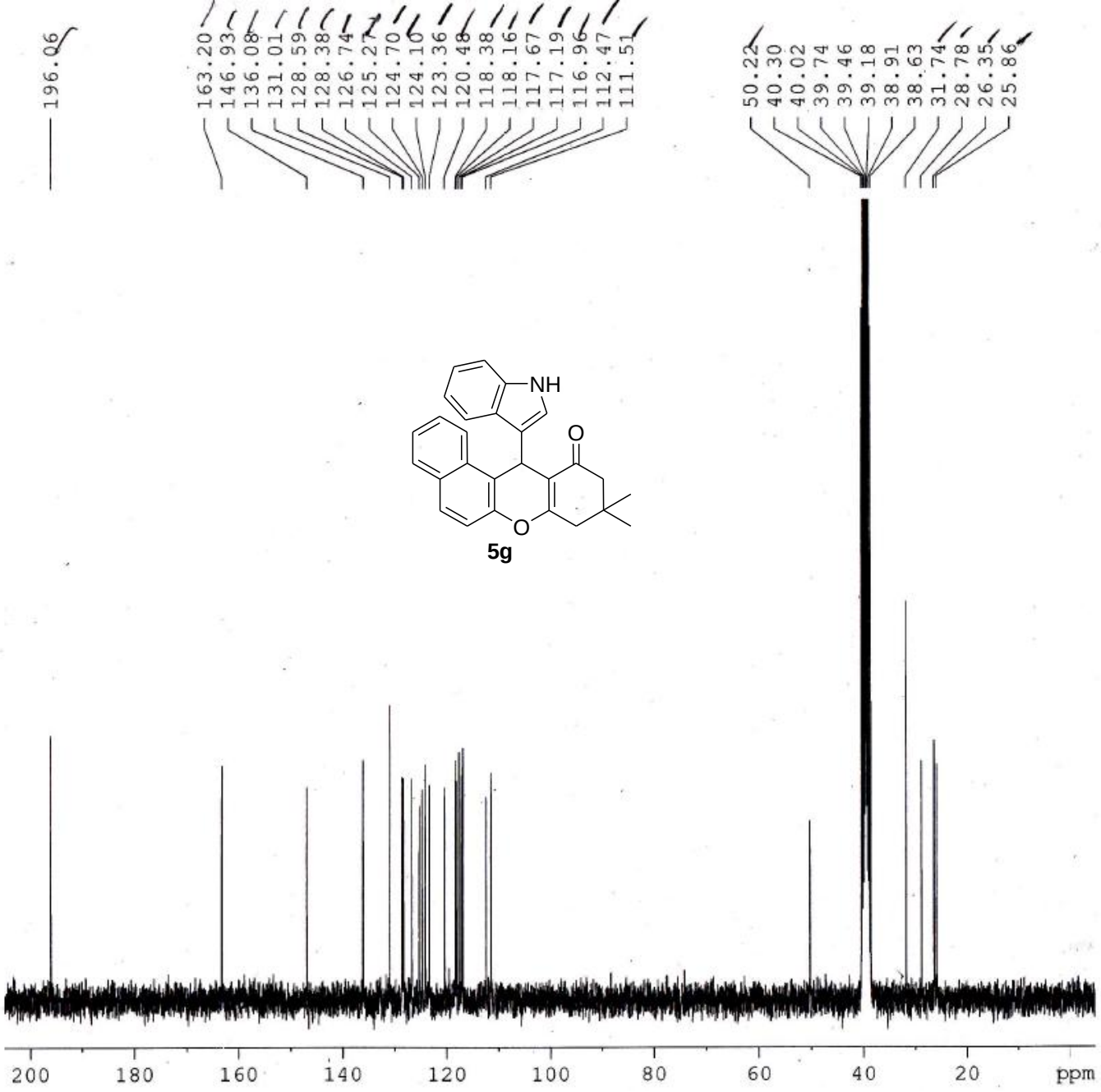
MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int
1	0.754	0.610	0.993	195390900	17335826	11.27		100.00		366.15	9469886
				195390900	17335826			100.00			



5g

```
Current Data Parameters
NAME                  1065A
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141016
Time                 16.46
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               6188.119 Hz
FIDRES               0.094423 Hz
AQ                5.2953587 sec
RG                     181
DW                  80.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   8.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1299997 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



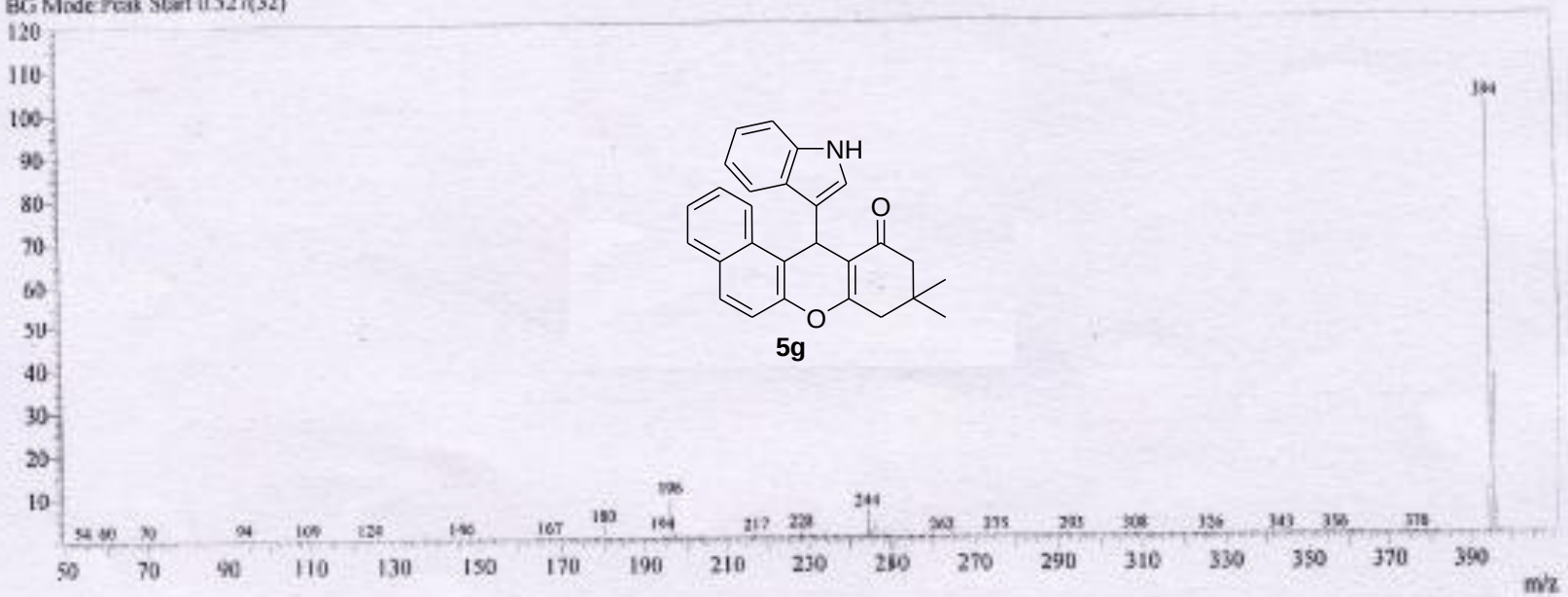
5g

```
Current Data Parameters
NAME                  1074C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141027
Time                 12.10
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT               DMSO
NS                    1185
DS                       4
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ               1.8175818 sec
RG                     287
DW                27.733 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                 9.50 usec
PL1                0.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              17.37 dB
PL13              20.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                   32768
SF            75.4677867 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```

User : Admin
Sample : SEL-D
Inj. Volume : 5.000
Data Name : C:\LCMSsolution\User\Data\SEL-D-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

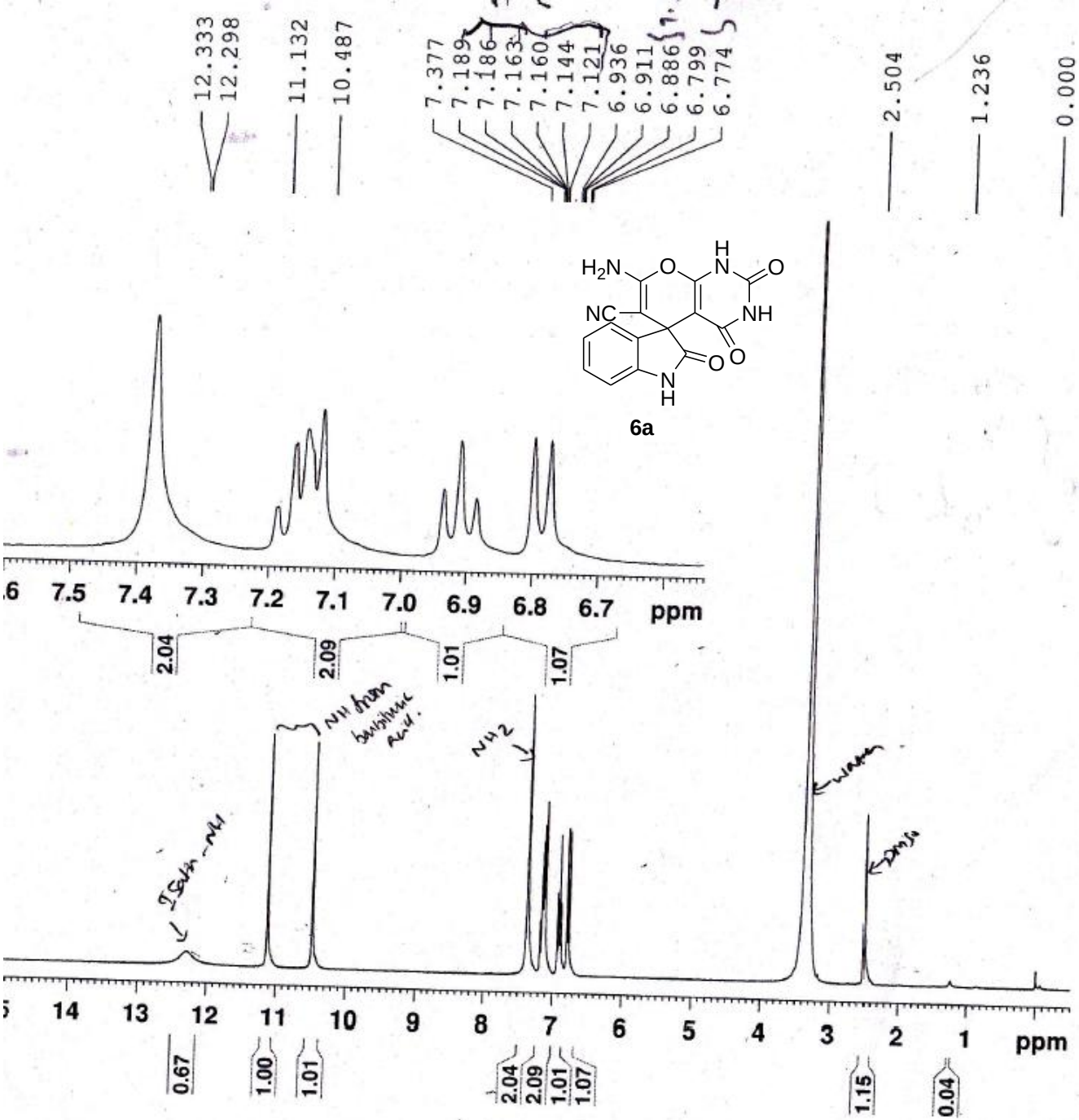
MS Spectrum

Line#:1 R.Time:0.765(Scan#:46) Positive
MassPeaks:238 BasePeak:394.40(9529569)
RawMode:Single 0.765(46)
BG Mode:Peak Start 0.527(32)



MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name	Base m/z	Base Int.
1	0.765	0.527	1.043	130690240	10465791	12.48		100.00		394.40	9529569
				130690240	10465791			100.00			



Current Data Parameters

NAME	1049C
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

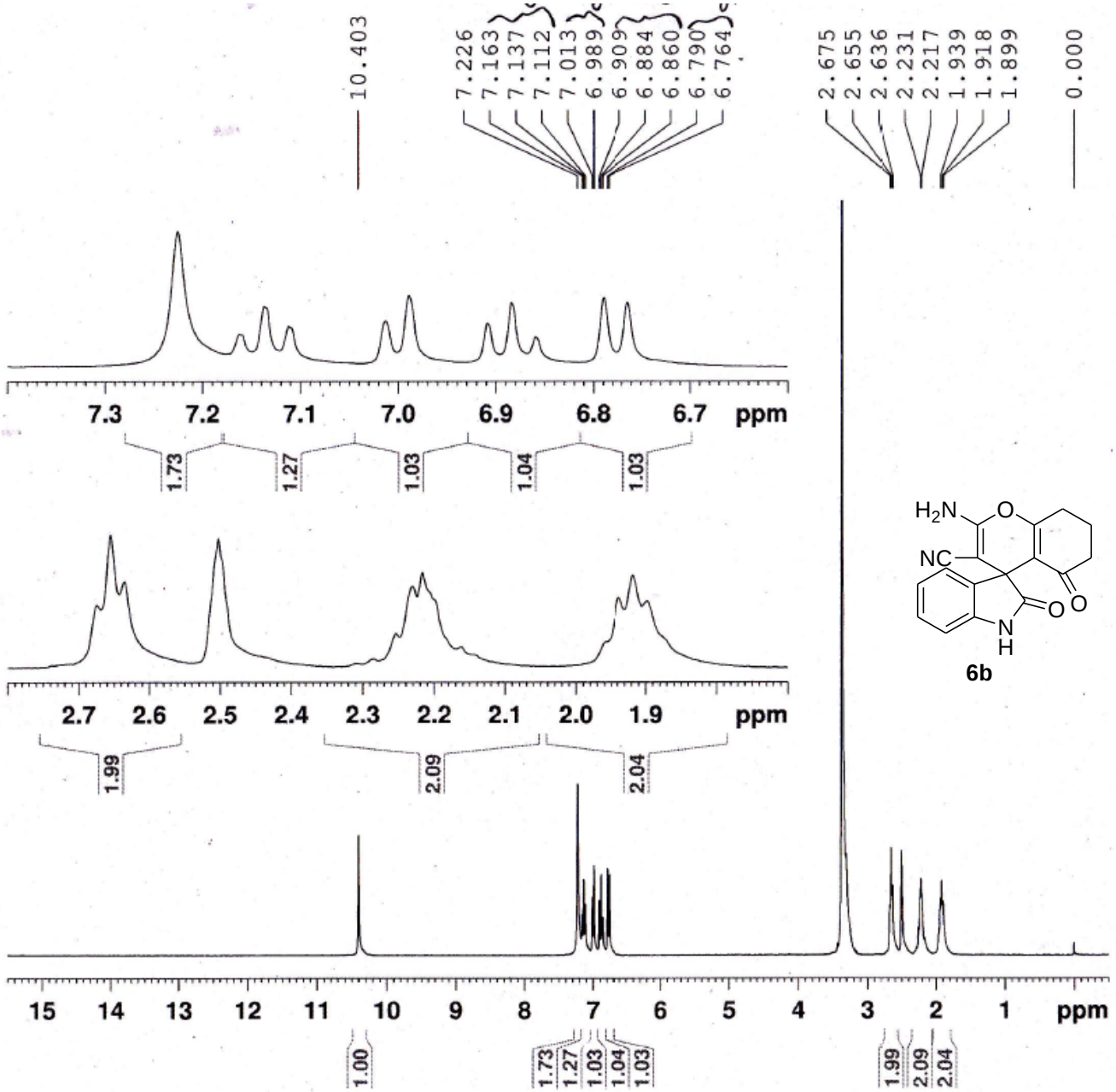
Date_	20141015
Time	12.34
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 sec
RG	228
DW	80.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	8.60 usec
PL1	-2.00 dB
SFO1	300.1318534 MHz

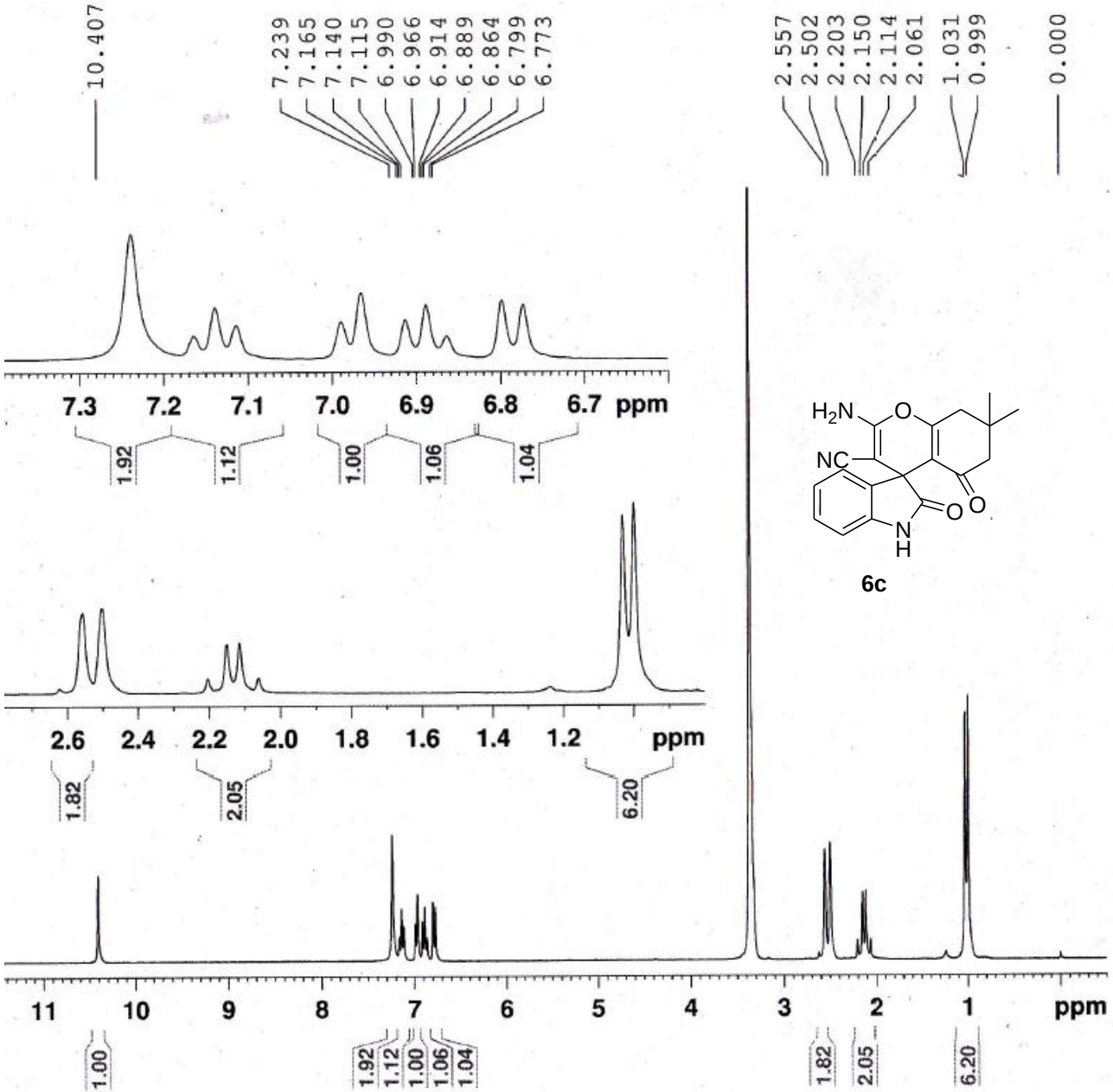
F2 - Processing parameters

SI	32768
SF	300.1300001 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



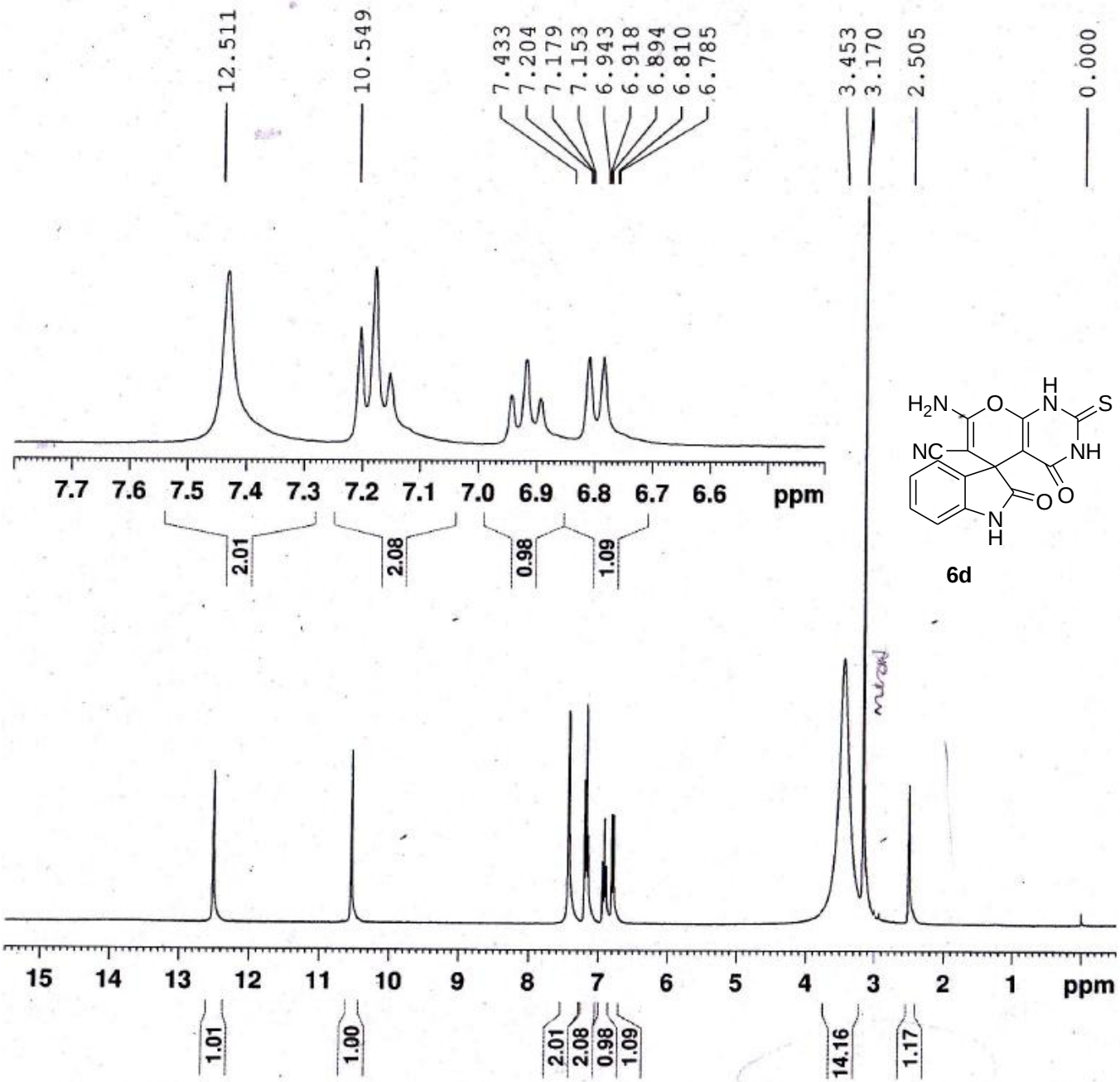
6b

```
Current Data Parameters
NAME                  1049B
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141015
Time                 12.26
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH               6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                     228
DW                  80.800 usec
DE                   6.00 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.60 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300004 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



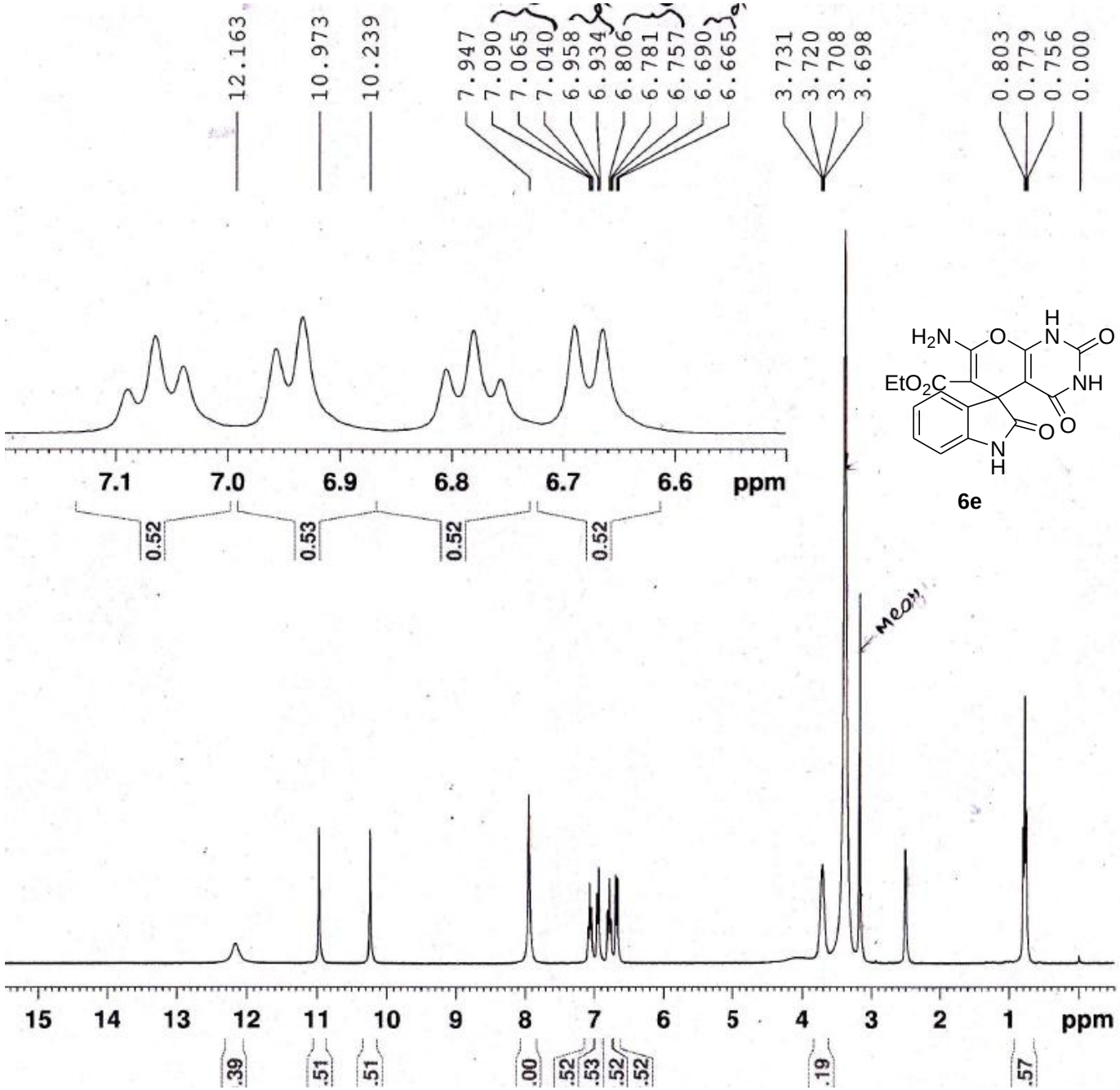
6c

```
Current Data Parameters
NAME                  1059C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141015
Time                  15.26
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      203
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                  8.60 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300006 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```



6d

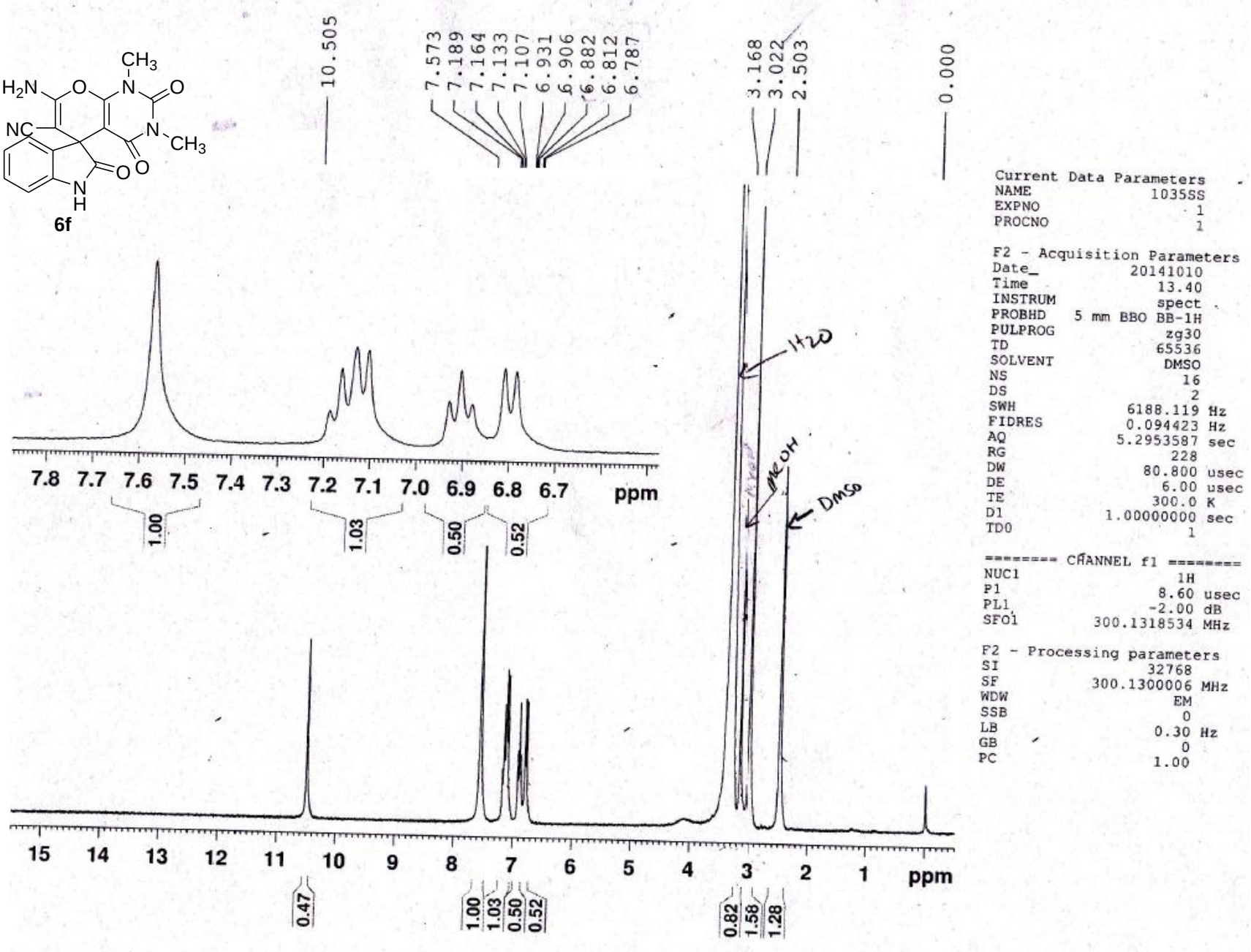
```
Current Data Parameters
NAME                  1049A
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141015
Time                  12.20
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      181
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                  8.60 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1299996 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```



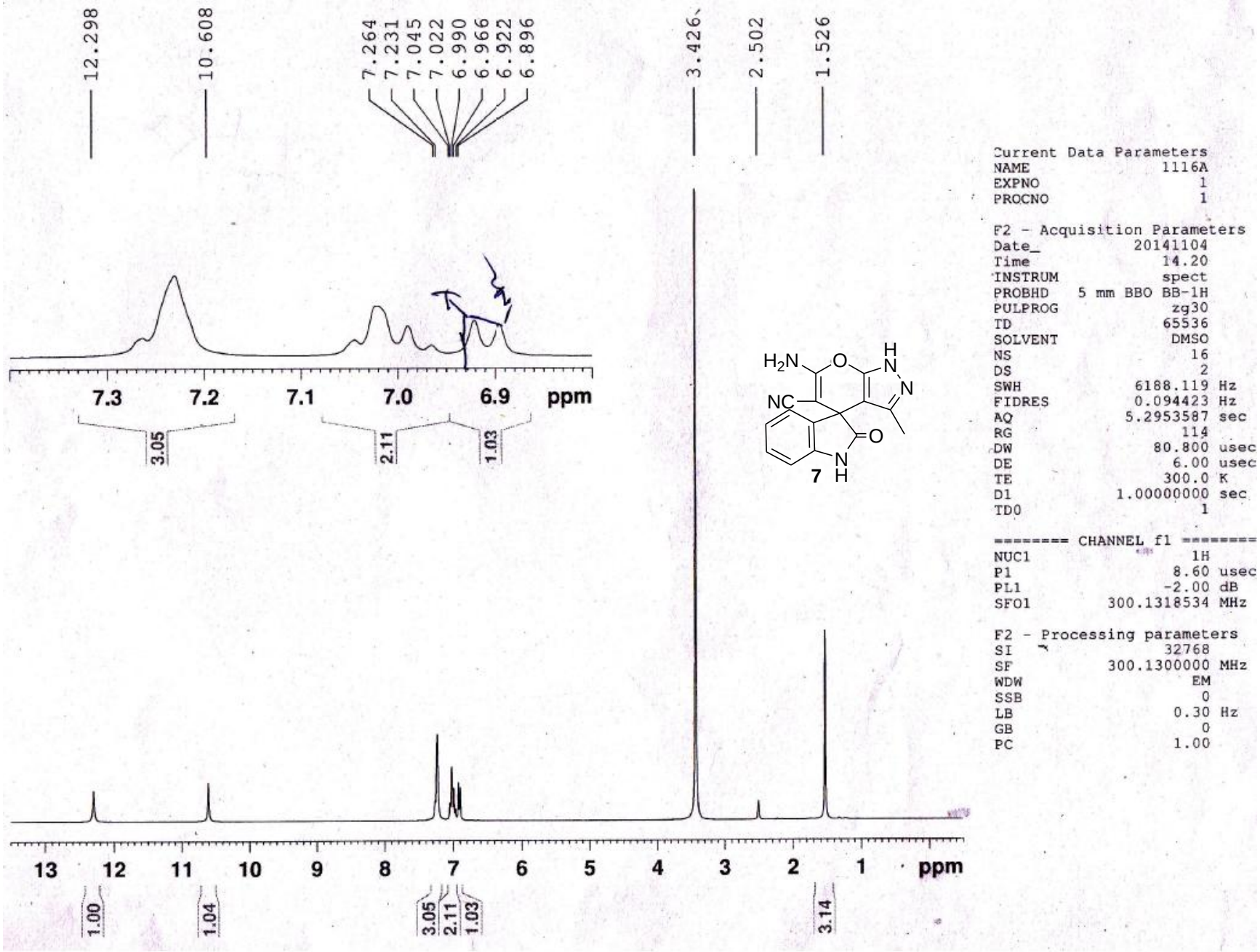
6e

```
Current Data Parameters
NAME                  1059E
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20141015
Time                 15.32
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                       16
DS                        2
SWH               6188.119 Hz
FIDRES           0.094423 Hz
AQ               5.2953587 sec
RG                      181
DW                 80.800 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                  8.60 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1299997 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

6f




```
Current Data Parameters
NAME                  1035SS
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20141010
Time                  13.40
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                       16
DS                        2
SWH                6188.119 Hz
FIDRES            0.094423 Hz
AQ                5.2953587 sec
RG                      228
DW                 80.800 usec
DE                  6.00 usec
TE                  300.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                  8.60 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                    32768
SF            300.1300006 MHz
WDW                      EM
SSB                       0
LB                 0.30 Hz
GB                        0
PC                     1.00
```



Current Data Parameters

NAME	1116A
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20141104
Time	14.20
INSTRUM	spect
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.094423 Hz
AQ	5.2953587 sec
RG	114
DW	80.800 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	8.60 usec
PL1	-2.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	32768
SF	300.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00