

Combustion synthesized La_2O_3 and $\text{La}(\text{OH})_3$:Recyclable catalytic activity towards

Knoevenagel and Hantzsch reactions

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Sharma*

Supporting Information

Table S1: Knoevenagel – condensation reaction

Entry	Reaction with La ₂ O ₃		Reaction with La(OH) ₃	
	Time	Yield (%)	Time	Yield (%)
1a	120	81	125	81
1b	190	76	220	79
1c	140	79	160	80
1d	110	89	130	82
1e	110	80	160	78
1f	150	82	160	75
1g	160	78	170	80
1h	140	80	180	82
1i	160	76	190	81

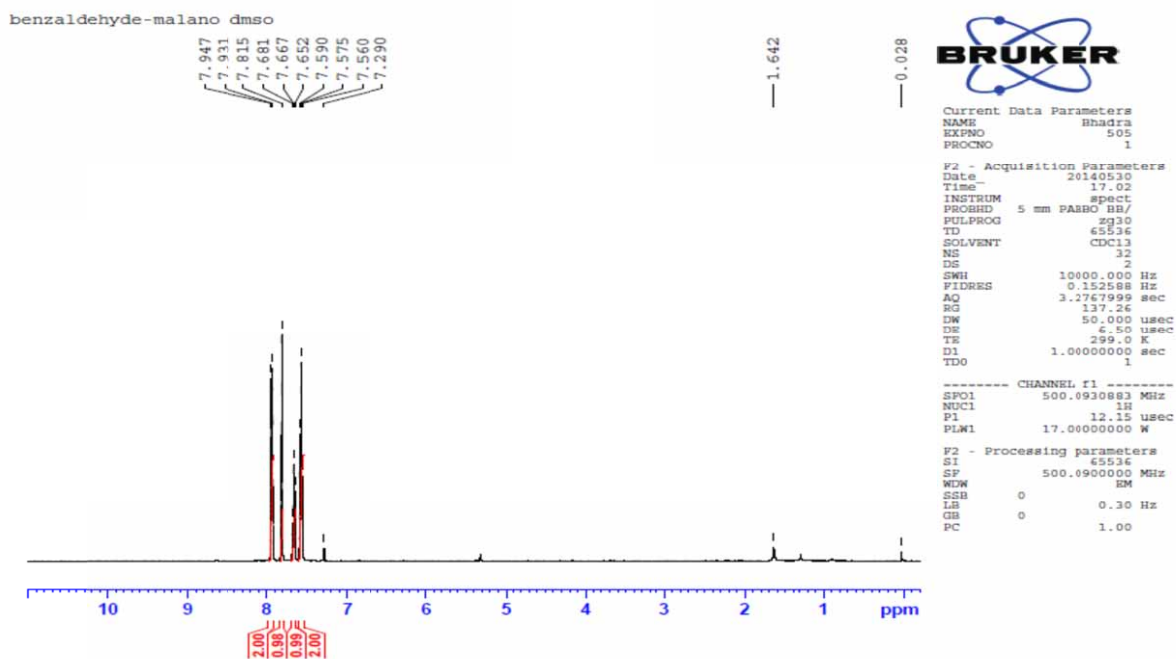
Table S2:Hantzsch Reaction

Entry	Reaction with La ₂ O ₃		Reaction with La(OH) ₃	
	Time	Yield (%)	Time	Yield (%)
2a	120	81	130	84
2b	140	76	160	79
2c	110	79	130	80
2d	150	89	160	82
2e	160	80	180	83
2f	160	82	190	85

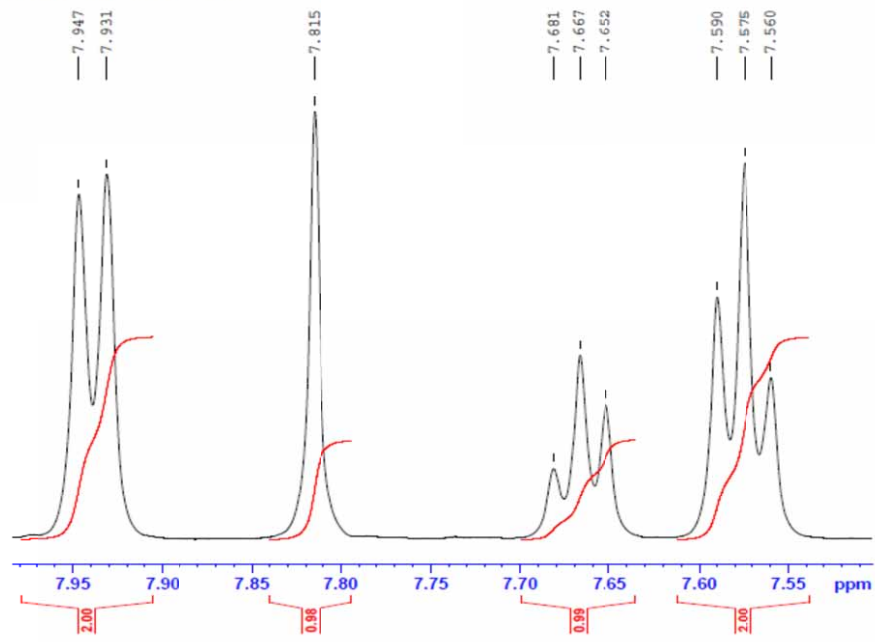
Table S3: Effect of catalyst loading on the reactivity of substrates in Knoevenagel (1a-Table 1) and Hantzsch (2d, Table-2) reactions in DMSO.

Loading (equiv)	Knoevenagel		Hantzsch	
	Time (min)	Yield (%)	Time (min)	Yield (%)
1	30	85	50	79
0.6	80	85	90	81
0.3	120	81	150	82
0.1	160	83	170	81
0.05	360	81	390	80

¹H NMR Spectrum of 2-benzylidenemalononitrile(1a)



benzaldehyde-malano dmsd



BRUKER

Current Data Parameters
NAME Bhadra
EXPNO 505
PROCNO 1

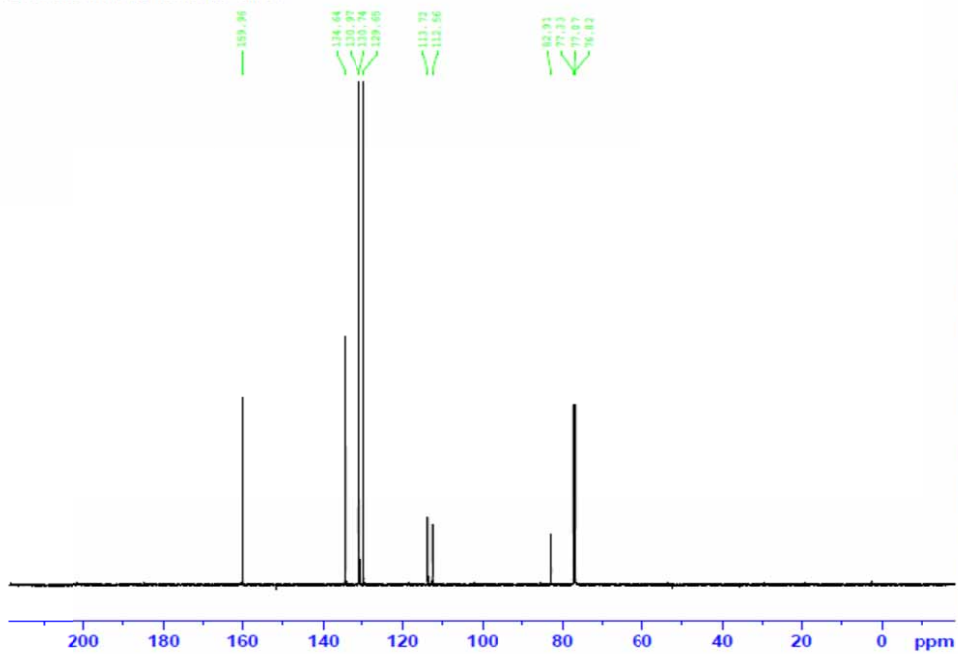
F2 - Acquisition Parameters
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Time 17.02
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 137.26
DW 50.000 usec
DE 6.50 usec
TE 299.0 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 500.0900000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C NMR Spectrum of 2-benzylidenemalononitrile

benzaldehyde-malano dmsd



BRUKER

Current Data Parameters
NAME Bhadra
EXPNO 506
PROCNO 1

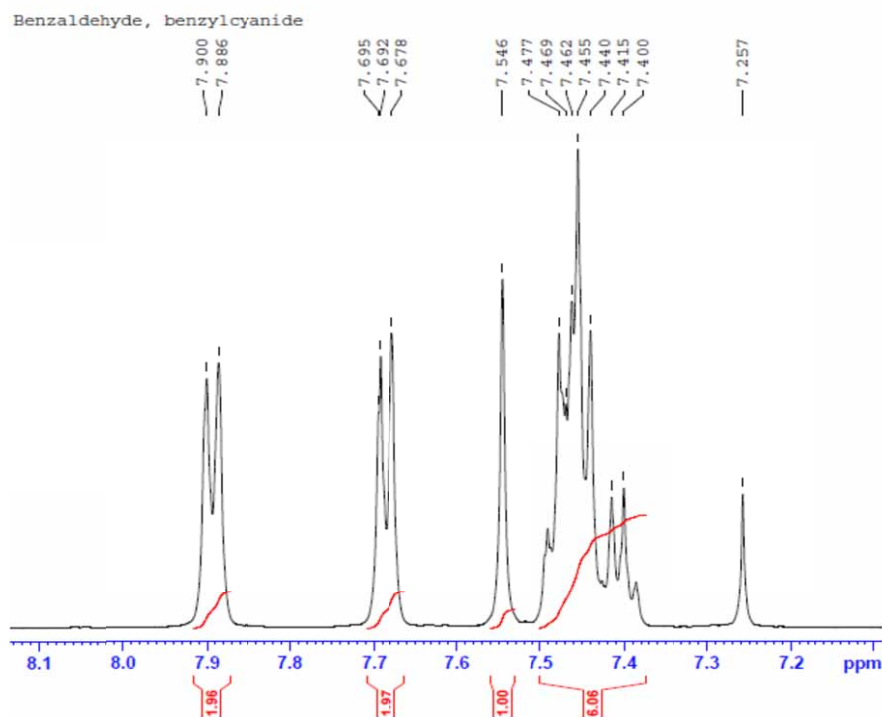
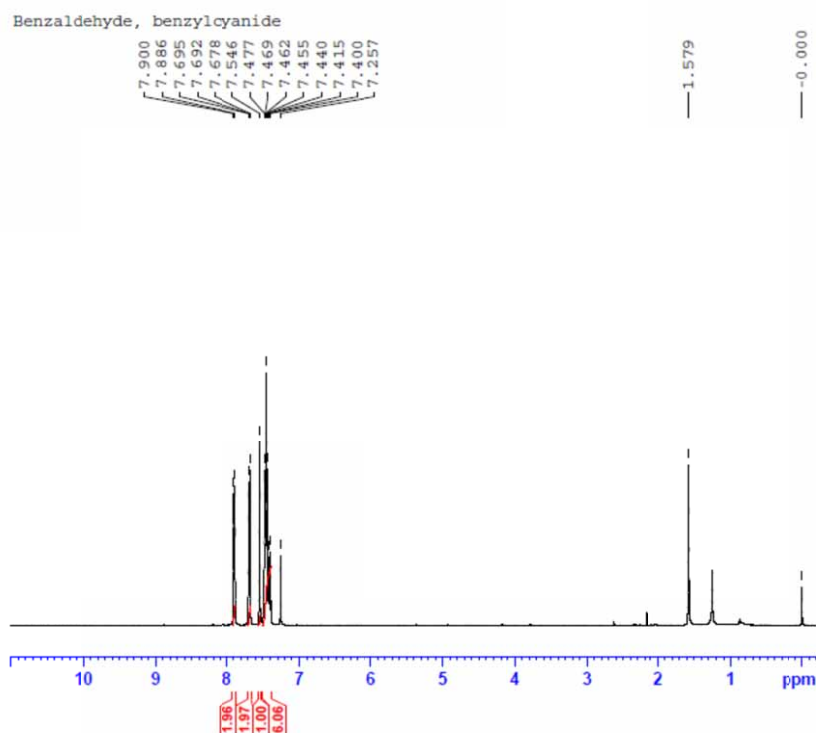
F2 - Acquisition Parameters
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Time 18.02
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TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 112.97
DW 16.800 usec
DE 6.50 usec
TE 301.2 K
D1 2.00000000 sec
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
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 17.00000000 W
PLW12 0.52061999 W
PLW13 0.33320001 W

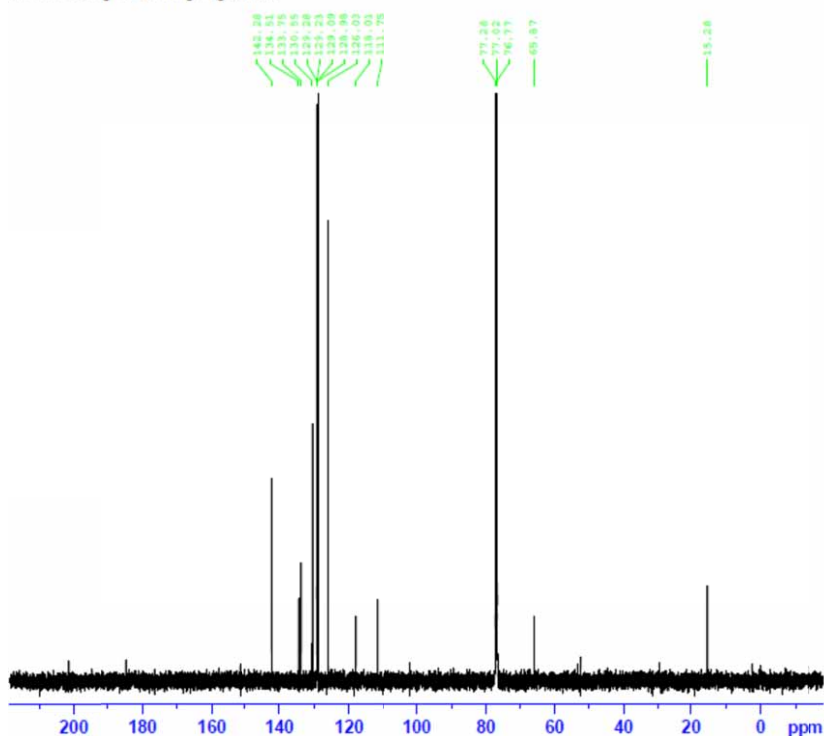
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

¹H NMR Spectrum of (Z)-2,3-diphenylacrylonitrile (1b)



¹³C NMR Spectrum of (Z)-2,3-diphenylacrylonitrile (1b)

benzaldehyde-benzylcyanide



Current Data Parameters
NAME Bhadra
EXPNO 641
PROCNO 1

F2 - Acquisition Parameters
Date 20140709
Time 20.30
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PULPROG zgpg30
TD 65536
SOLVRHT CDC13
NS 1024
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 298.3 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

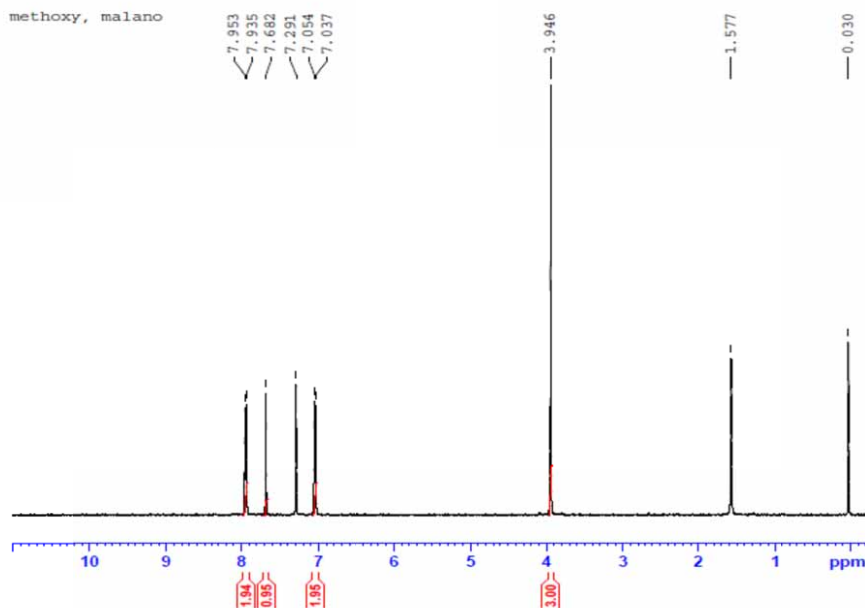
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NUC1 13C
P1 8.90 usec
PLW1 29.00000000 W

----- CHANNEL f2 -----
SFO2 500.0920004 MHz
NUC2 1H
CPDPRG12 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 2-(4-methoxybenzylidene) malononitrile . Reaction was performed with lanthanum oxide prepared by urea as fuel.

methoxy, malano

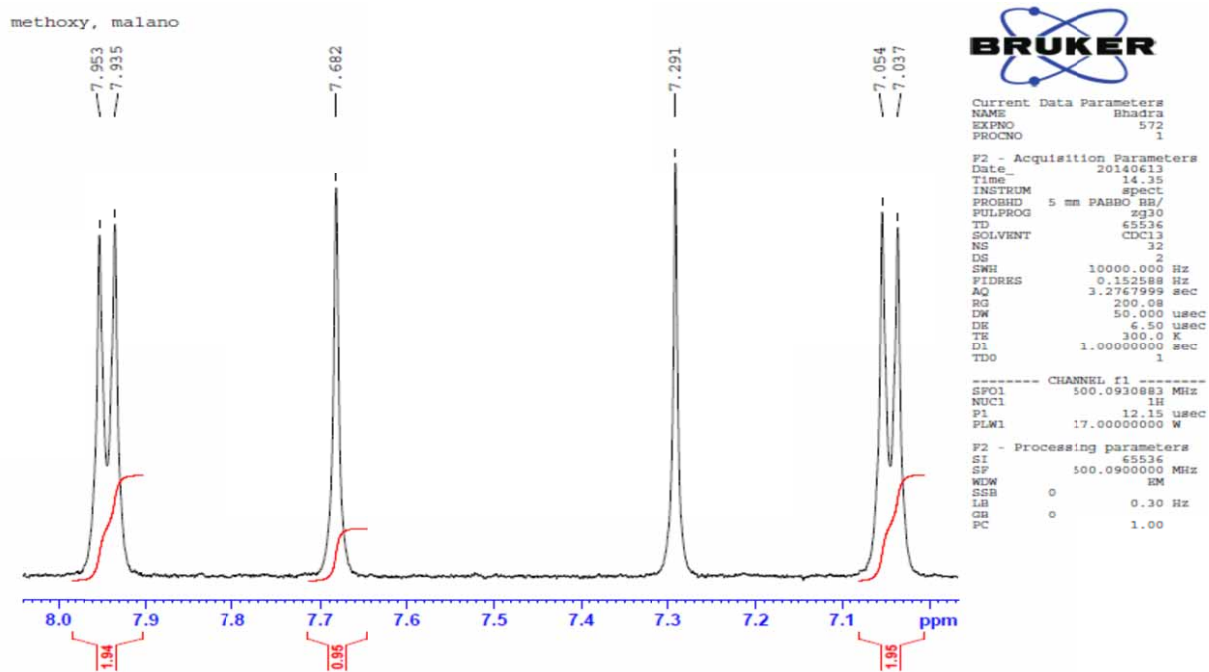


Current Data Parameters
NAME Bhadra
EXPNO 572
PROCNO 1

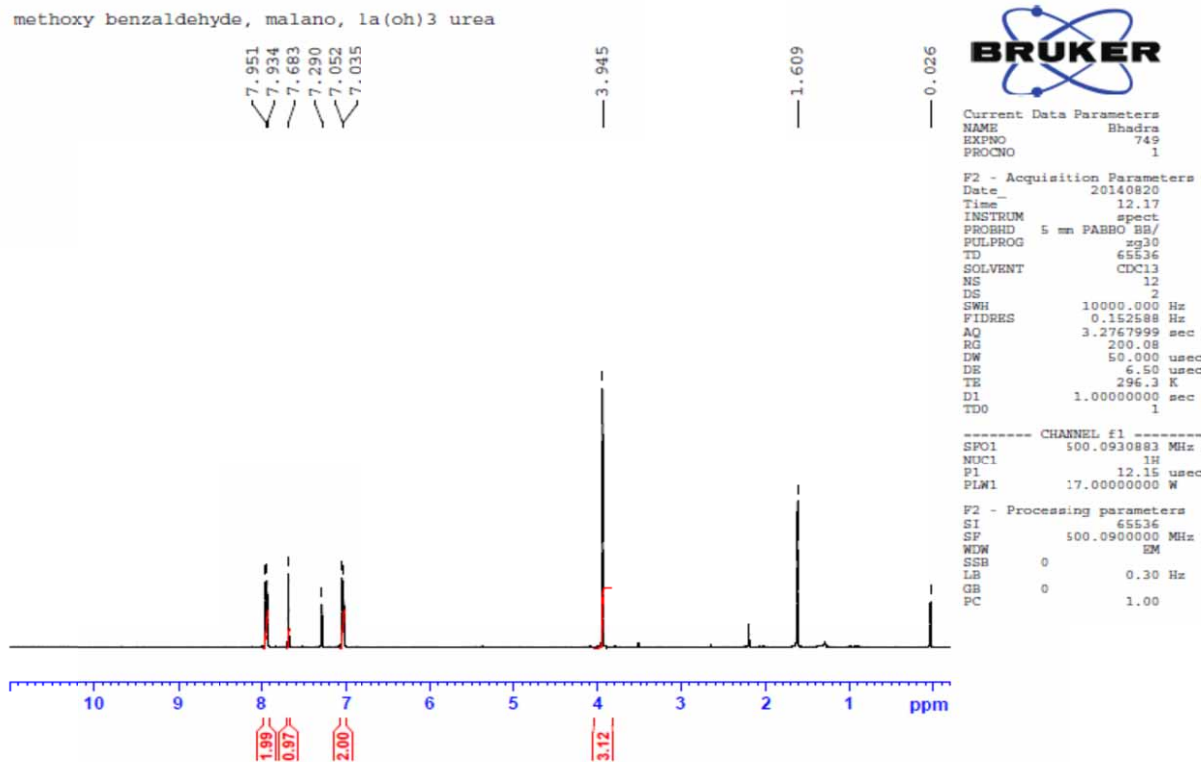
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TD 65536
SOLVENT CDC13
NS 32
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 200.08
DW 50.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.0000000 sec
TDO 1

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

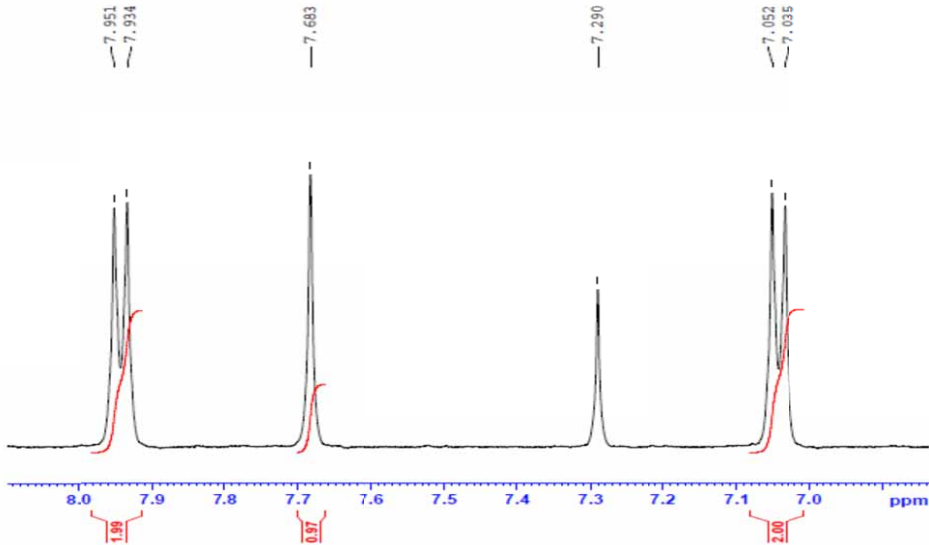
F2 - Processing parameters
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SF 500.0900000 MHz
WDW RM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



^1H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile . Reaction was performed with lanthanum hydroxide prepared by urea as fuel.



methoxy benzaldehyde, malano, 1a(oh)3 urea



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Current Data Parameters
NAME      Bhadra
EXPNO    749
PROCNO   1

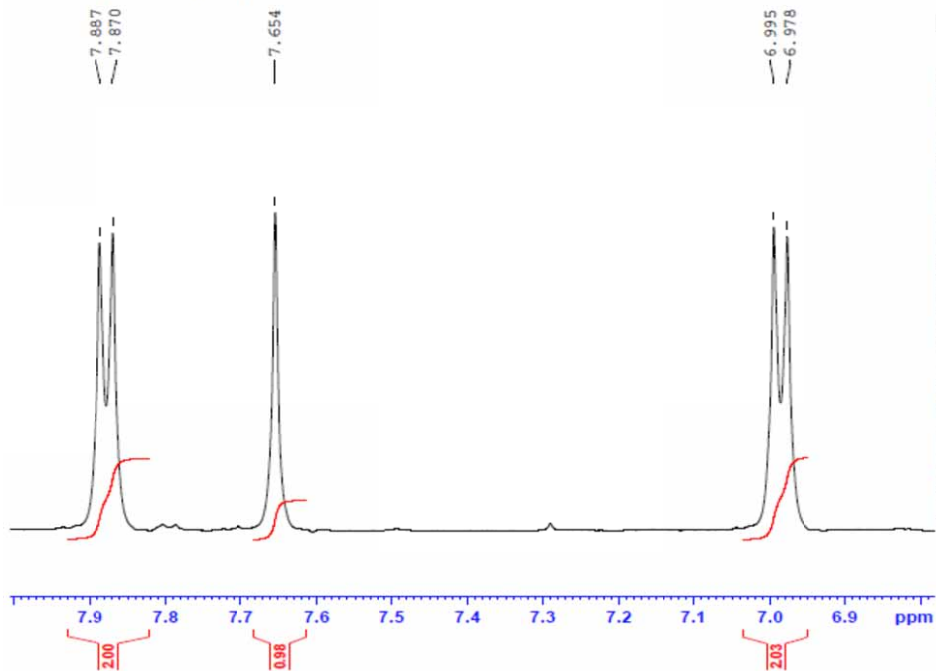
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Time     12.17
INSTRUM spect
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PULPROG zg30
TD       65536
SOLVENT  CDCl3
NS       2
DS       2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ       3.2767999 sec
RG       200.08
DW       50.000 usec
DE       6.50 usec
TE       296.2 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
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¹H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile. Reaction was done using glycine as fuel.

methoxy, malano, glycine as fuel



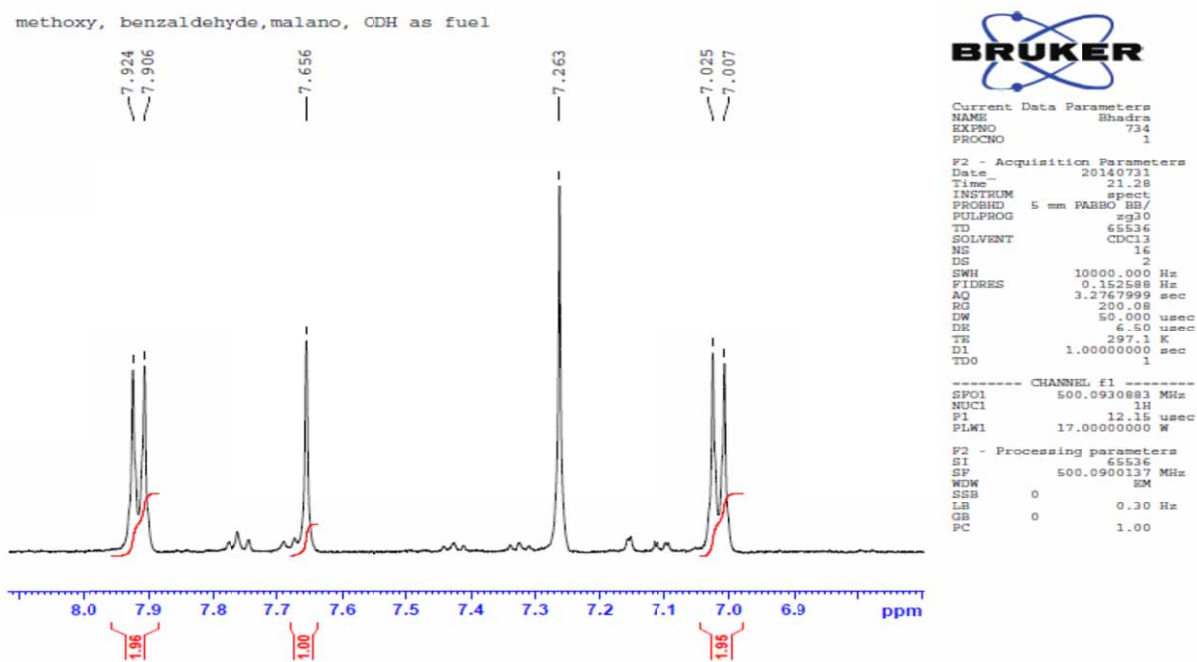
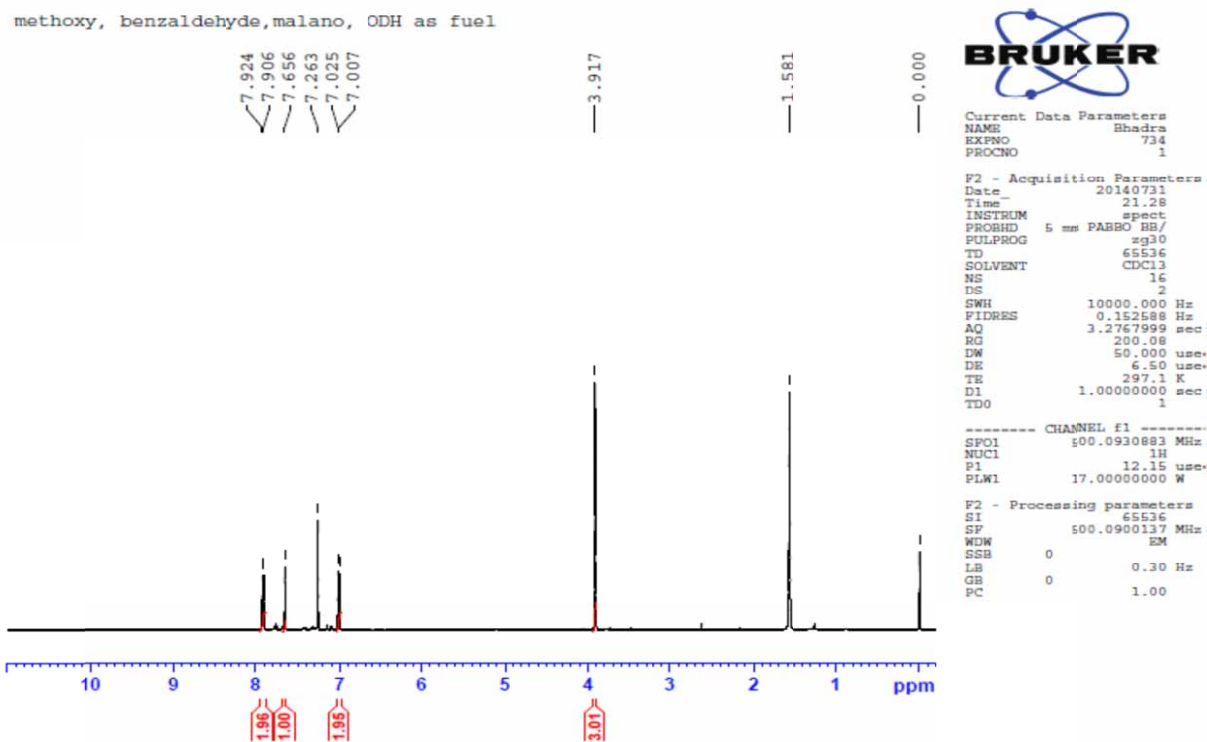
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NAME      Bhadra
EXPNO    542
PROCNO   1

F2 - Acquisition Parameters
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Time     19.19
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PULPROG zg30
TD       65536
SOLVENT  CDCl3
NS       2
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       299.1 K
D1       1.00000000 sec
TDO      1

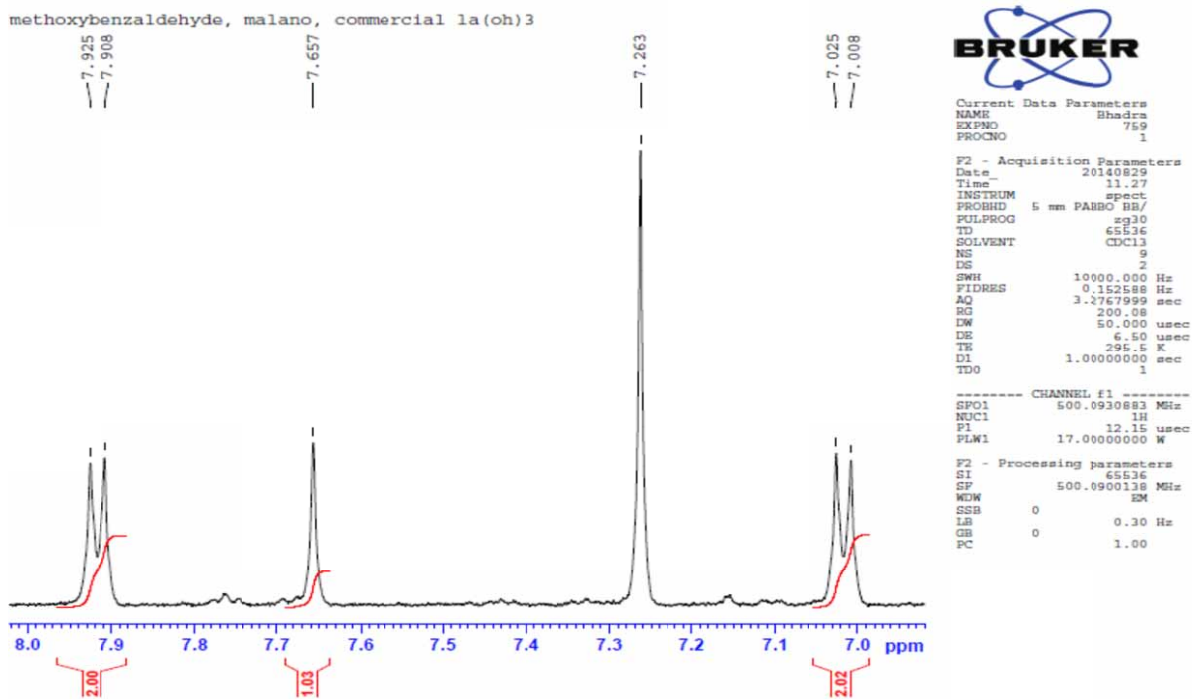
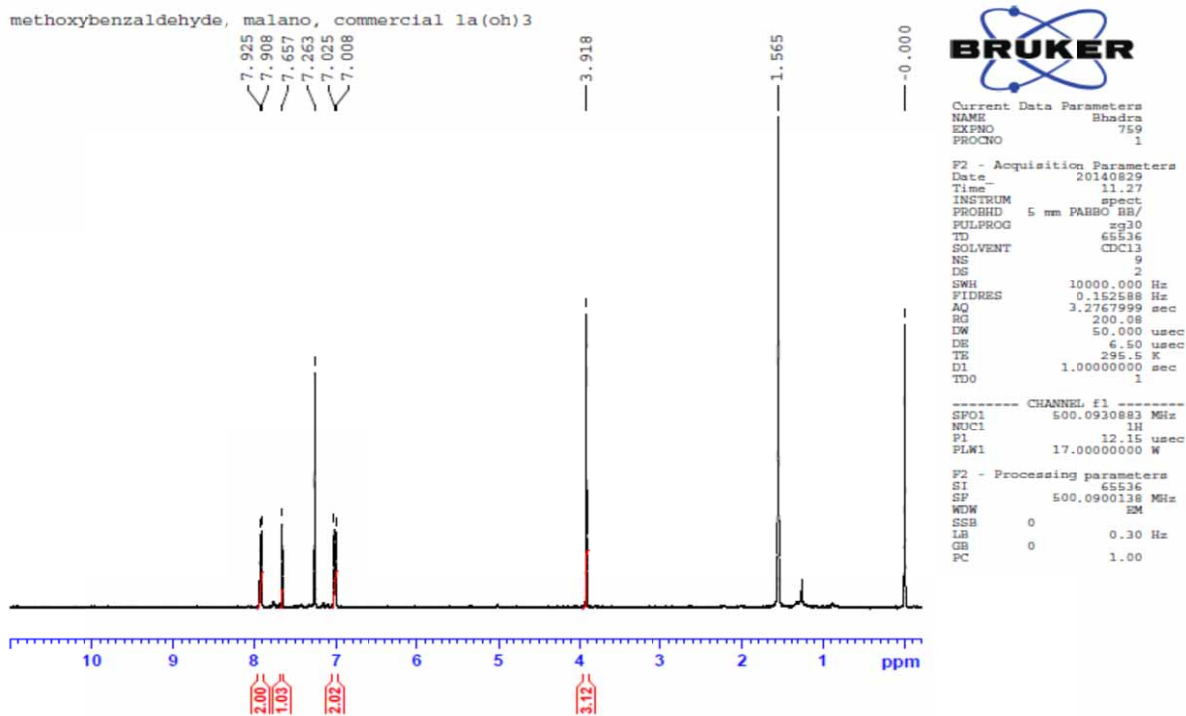
----- CHANNEL f1 -----
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NUC1     1H
P1       12.15 usec
PLW1    17.00000000 W

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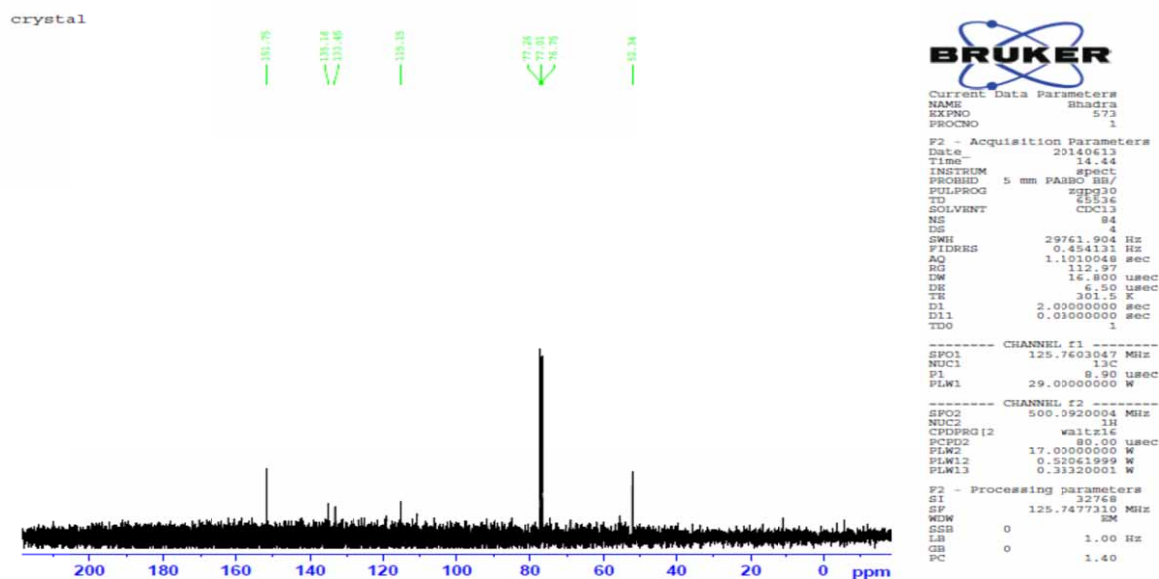

^1H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile. Reaction was carried out using ODH as fuel



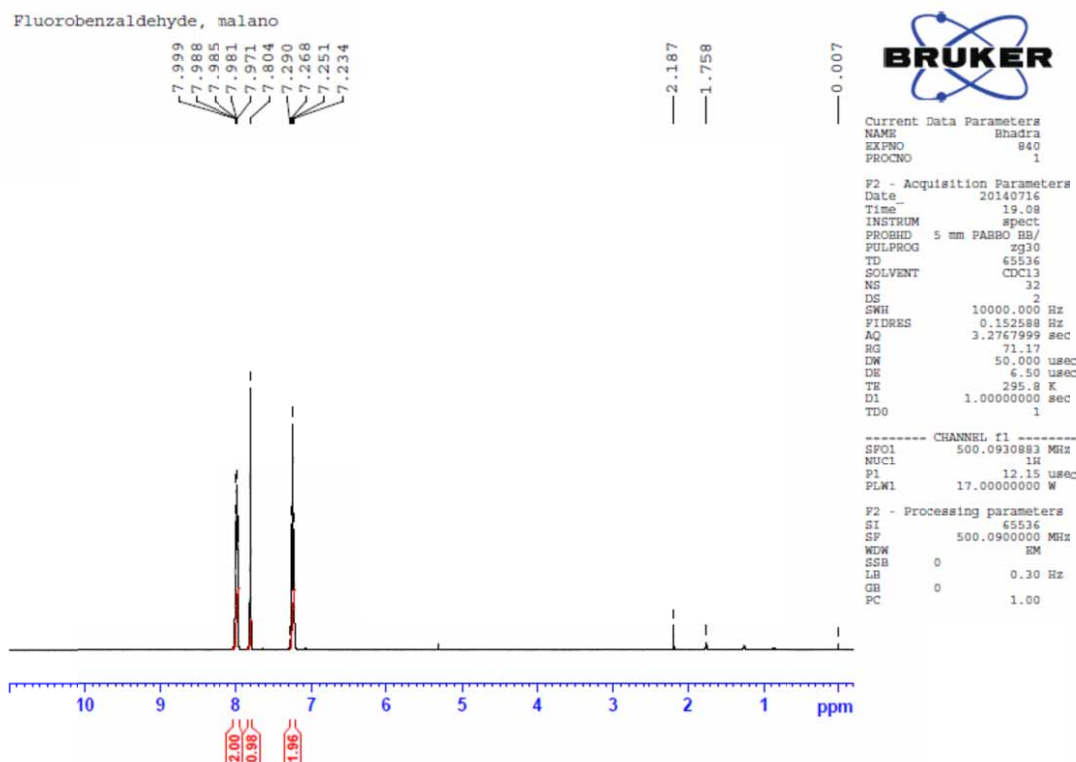
^1H NMR Spectrum of 2-(4-methoxybenzylidene) malononitrile. Reaction was performed by using lanthanum Hydroxide (commercial).



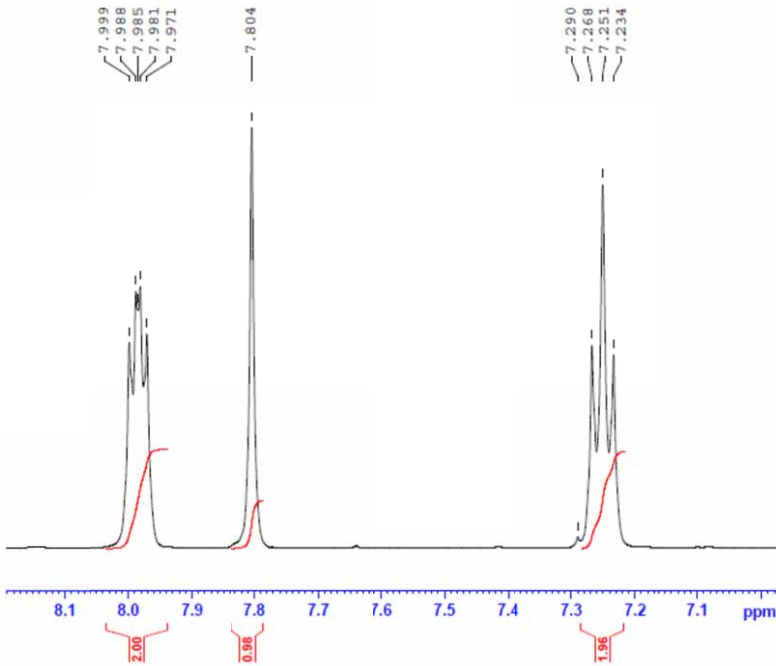
¹³C NMR Spectrum of 2-(4-methoxybenzylidene)malononitrile



¹H NMR Spectrum of 2-(4-Fluorophenylmethylidene) malononitrile (1d)



Fluorobenzaldehyde, malano



```
Current Data Parameters
NAME          Bhadra
EXPNO        840
PROCNO       1

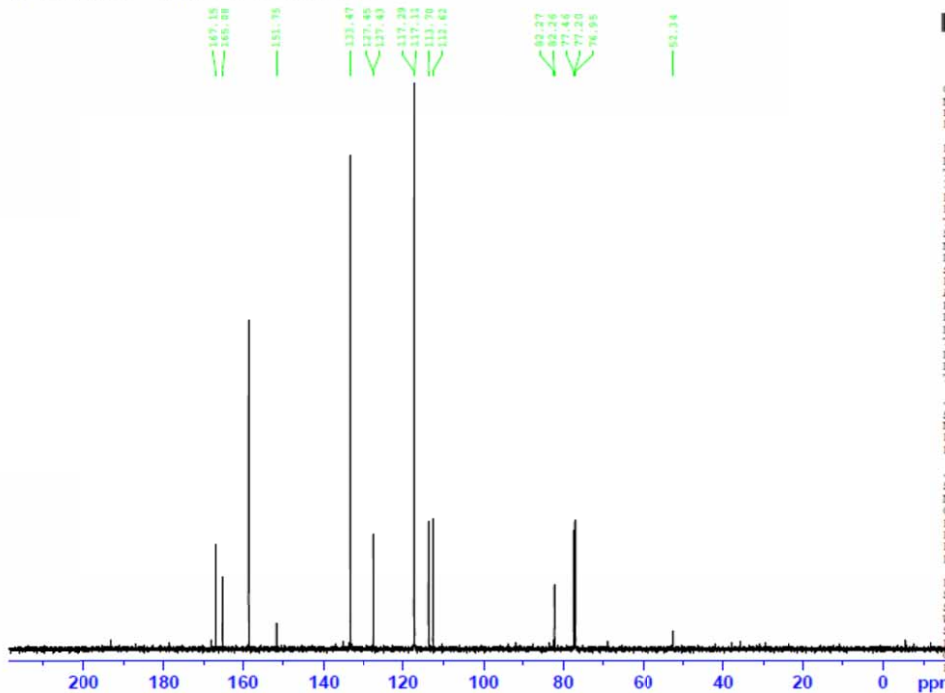
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Time_        19.08
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PULPROG      zg30
TD           65536
SOLVENT      CDCl3
NS           32
DS           2
SWH          10000.000 Hz
FIDRES       0.152588 Hz
AQ           3.2767999 sec
RG           71.17
DW           50.000 usec
DE           6.50 usec
TE           295.8 K
D1           1.00000000 sec
TD0          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
GB           0
PC           1.00
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¹³C Spectra of 2-(4-Fluorophenylmethylidene) malononitrile(1d)

Fluorobenzaldehyde, malanonitrile



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Current Data Parameters
NAME          Bhadra
EXPNO        841
PROCNO       1

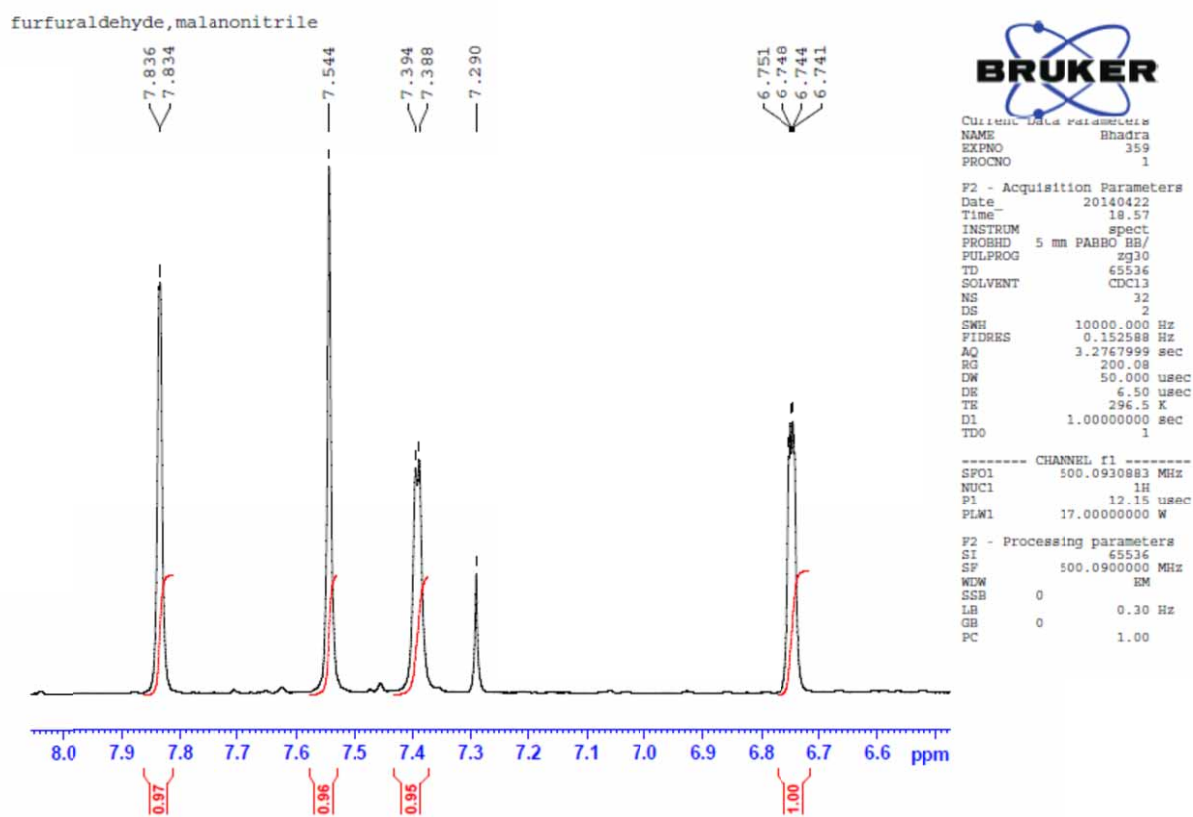
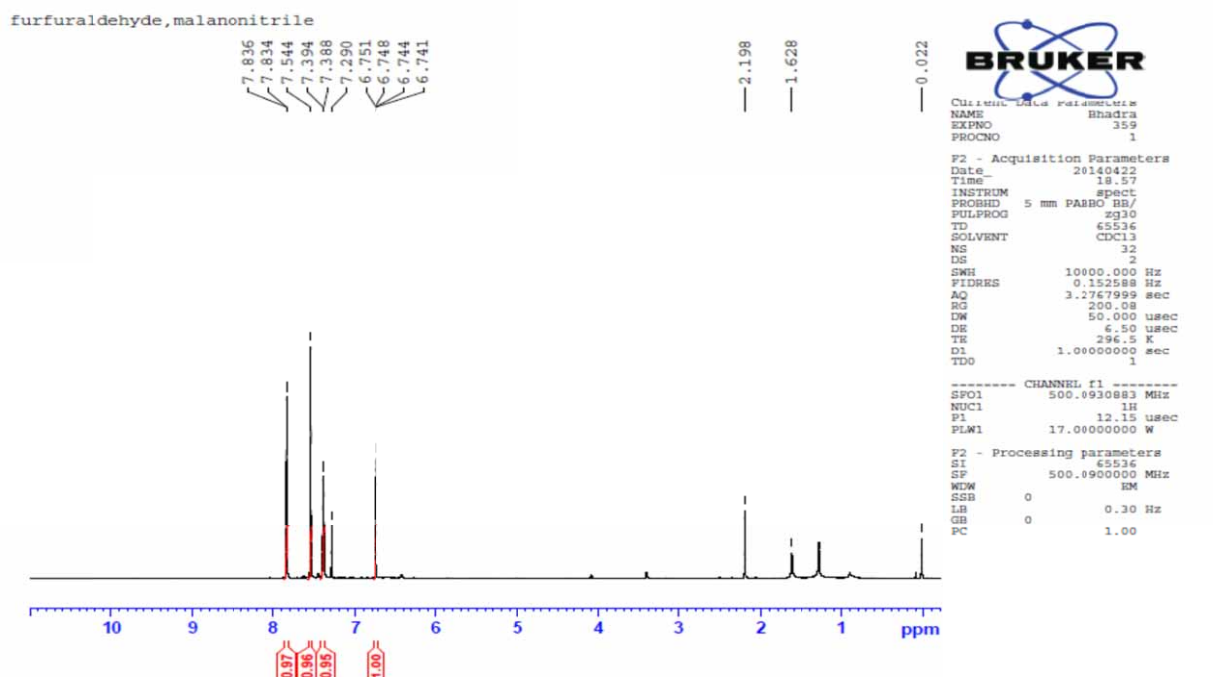
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Time_        19.18
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PULPROG      zgpg30
TD           65536
SOLVENT      CDCl3
NS           186
DS           4
SWH          29761.904 Hz
FIDRES       0.454131 Hz
AQ           1.1010048 sec
RG           112.97
DW           16.800 usec
DE           6.50 usec
TE           297.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0          1

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

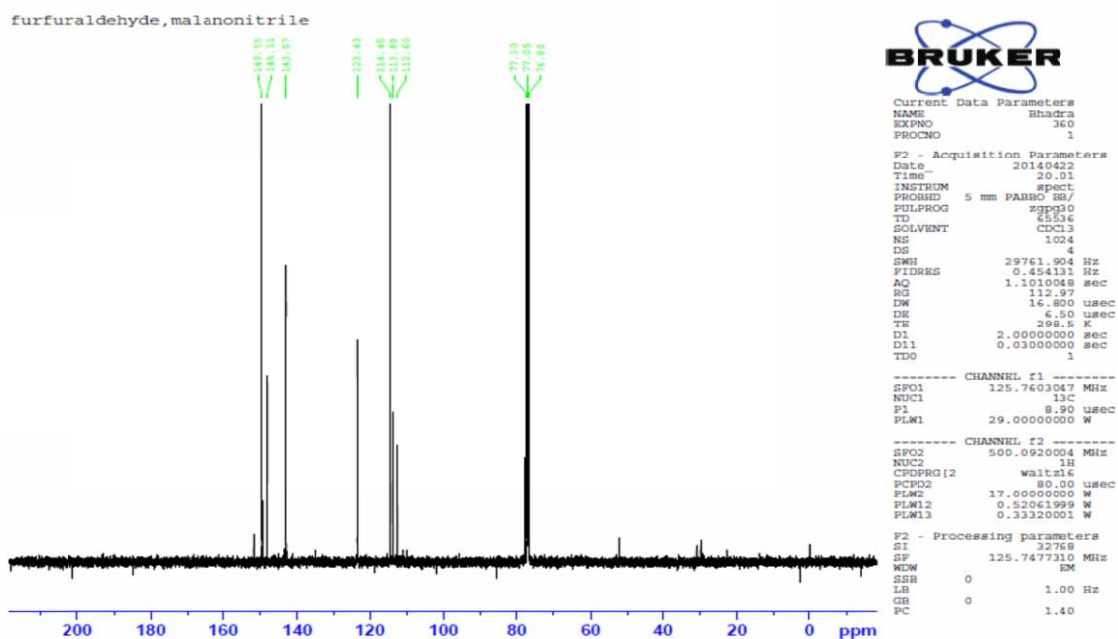
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NUC2         1H
CPDPRG[2]    waltz16
PCPD2        80.00 usec
PLW2         17.00000000 W
PLW12        0.52061999 W
PLW13        0.33320001 W

F2 - Processing parameters
SI           32768
SF           125.7477310 MHz
WDW          EM
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PC           1.40
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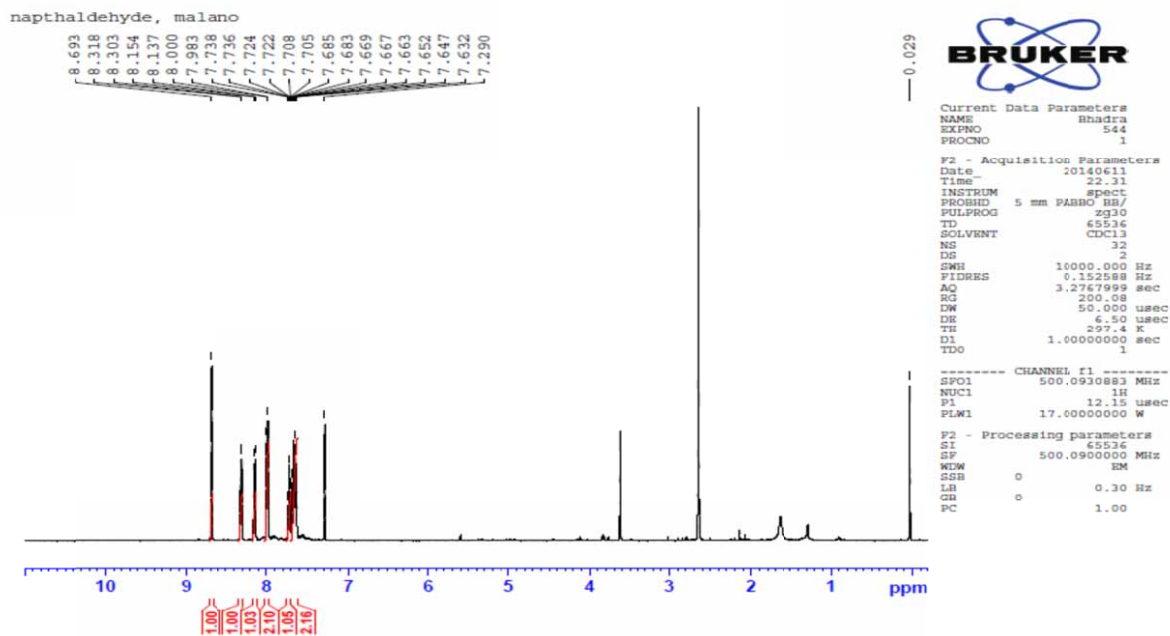
¹H NMR Spectrum of 2-(furan-2-ylmethylene) malononitrile (1e)

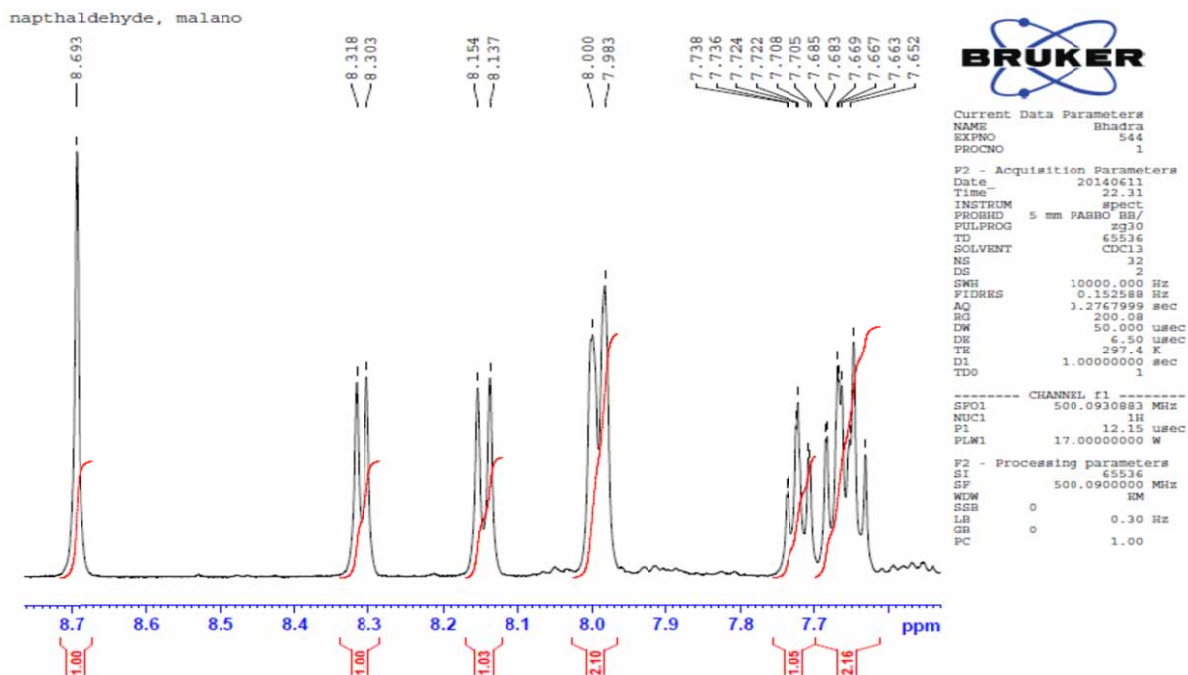


¹³C NMR Spectrum of 2-(furan-2-ylmethylene)malononitrile

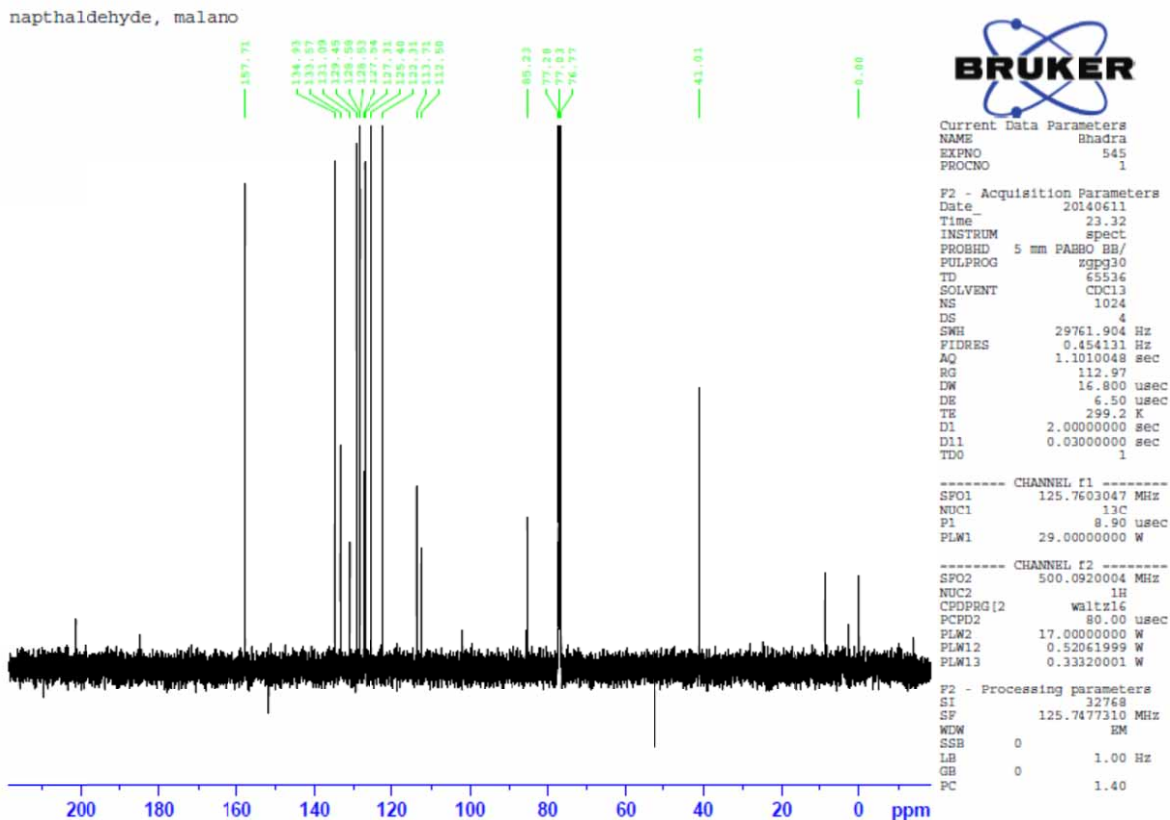


¹H NMR Spectrum of 2-(naphthalene-1-ylmethylene) malononitrile (1f)

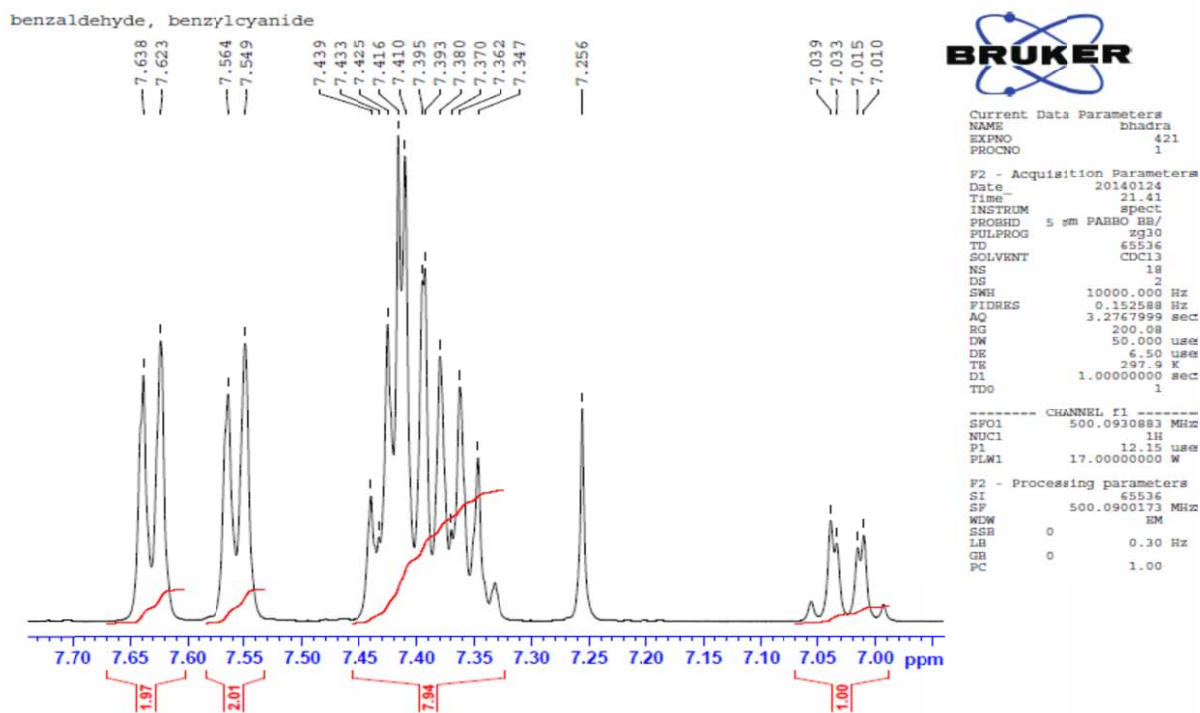
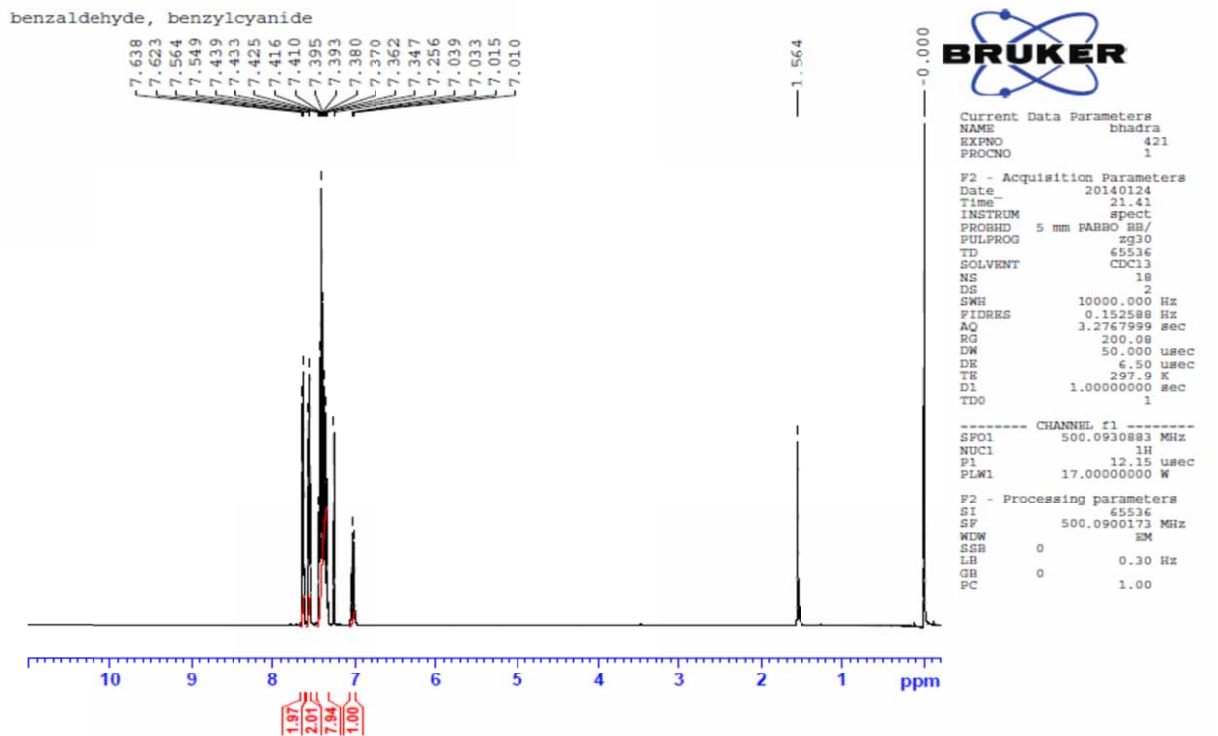




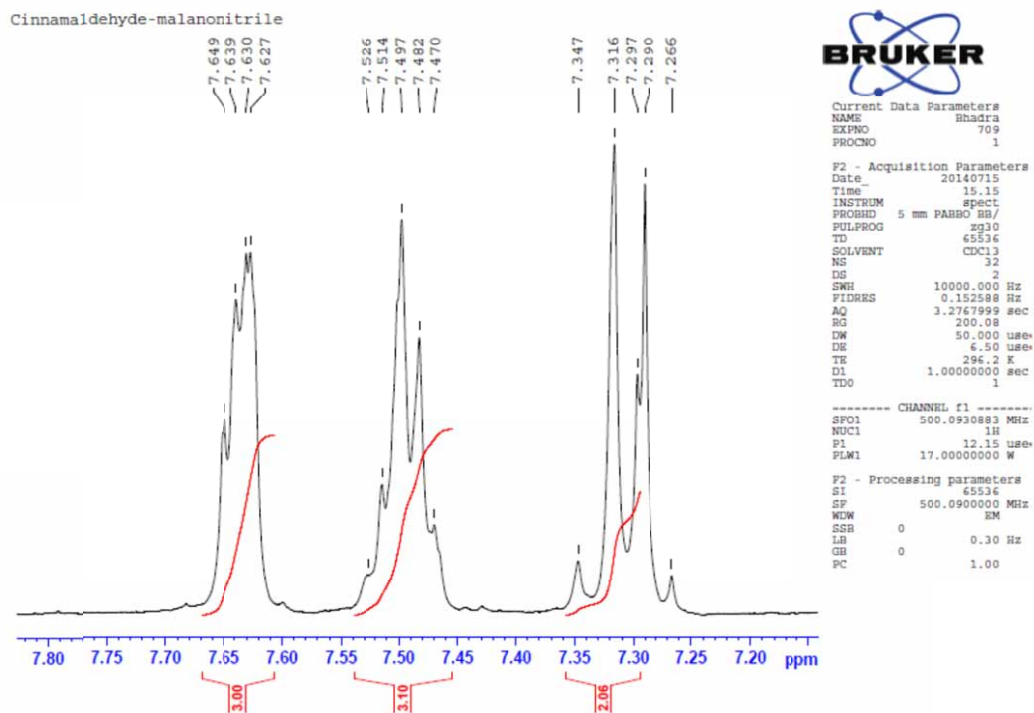
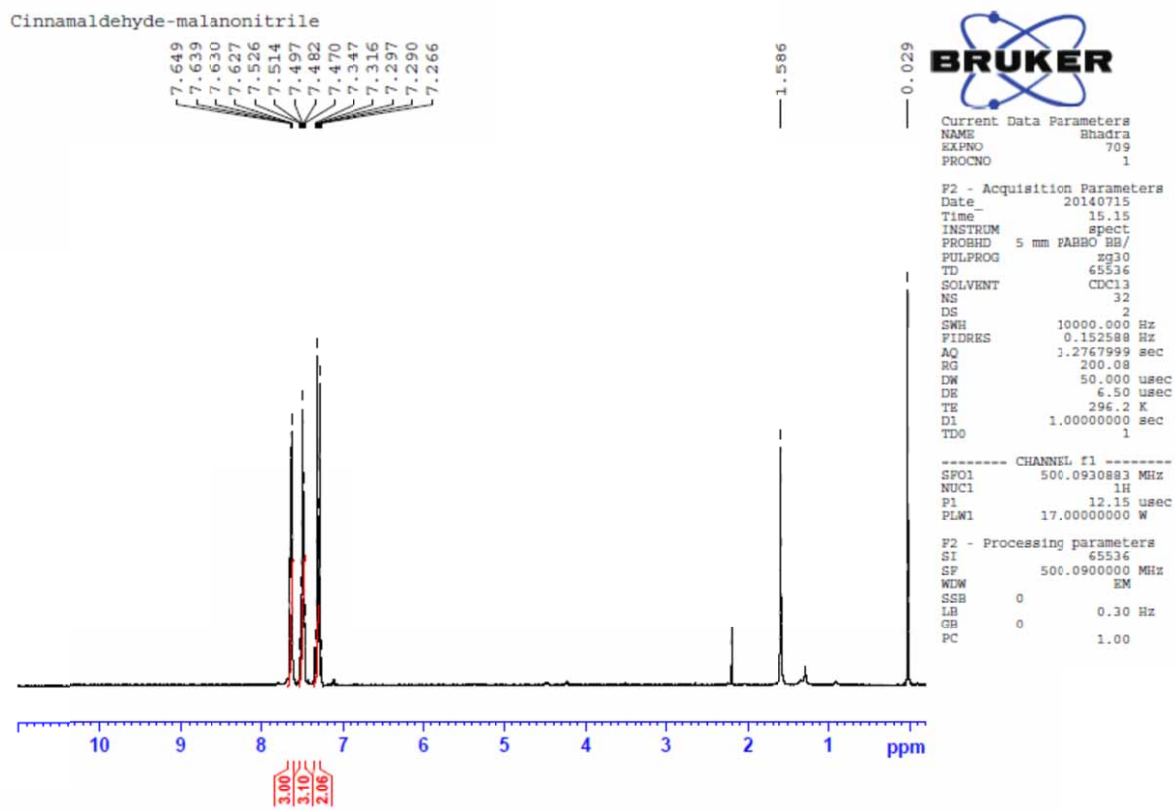
¹³C NMR Spectrum of 2-(naphthalene-1-ylmethylene)malononitrile



¹H NMR Spectrum of (2Z,4E)-2,5-diphenylpenta-2,4-dienitrile(1g)

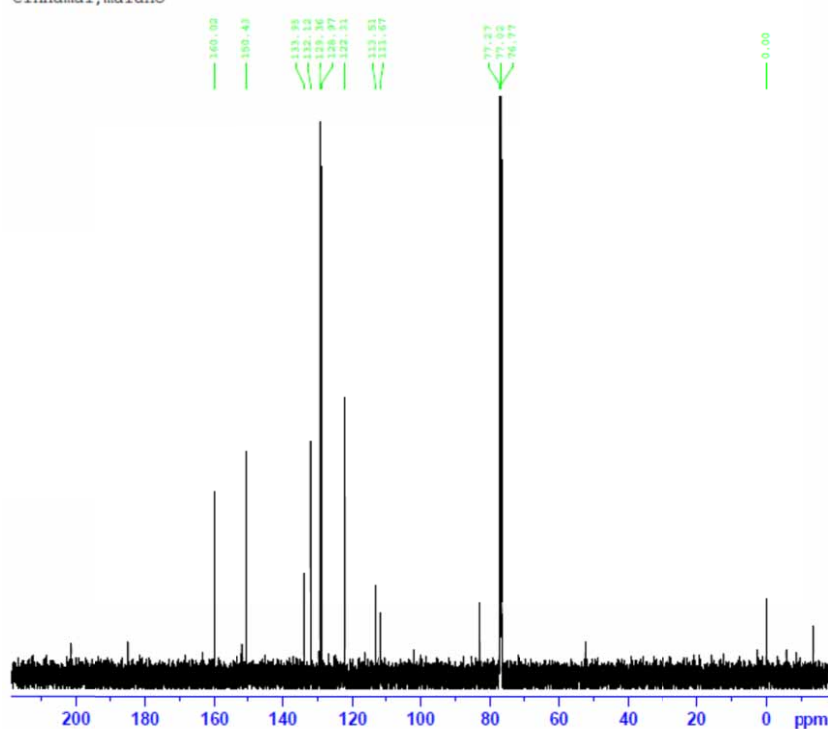


¹H NMR Spectrum of (Z)-2,3-diphenylacrylonitrile (1h)



¹³C Spectra of (Z)-2,3-diphenylacrylonitrile (1h)

cinnamal, malano



Current Data Parameters
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 EXPNO 785
 PROCNO 1

F2 - Acquisition Parameters
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 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 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 298.2 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
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 17.0000000 W
 PLW12 0.52061999 W
 PLW13 0.33320001 W

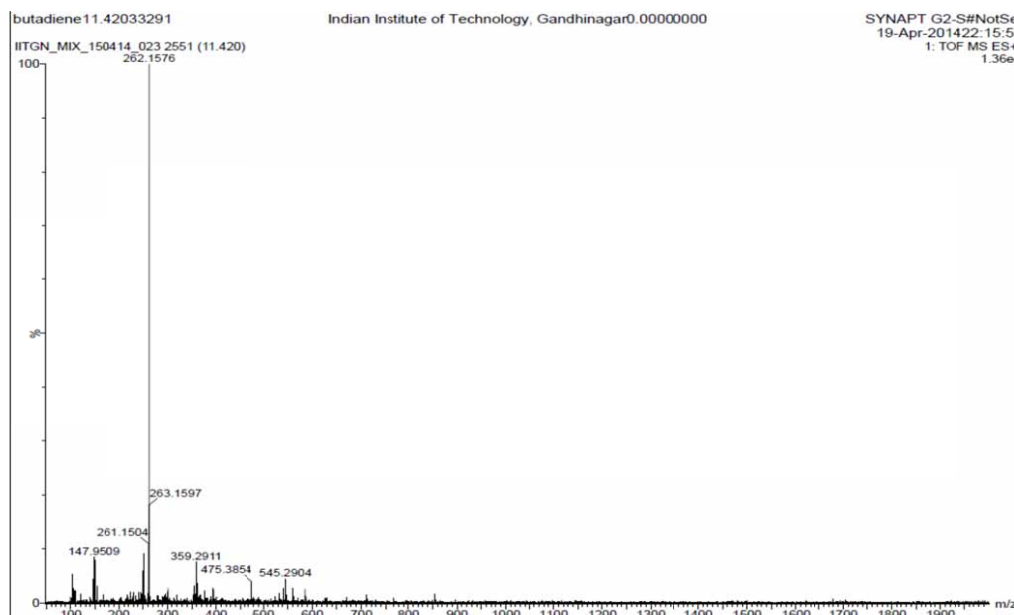
F2 - Processing parameters
 SI 32768
 SF 125.7477310 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Mass spectrum of (2Z,4E)-5-(4-methoxyphenyl)-2-phenylpenta-2,4-dienenitrile (1i)

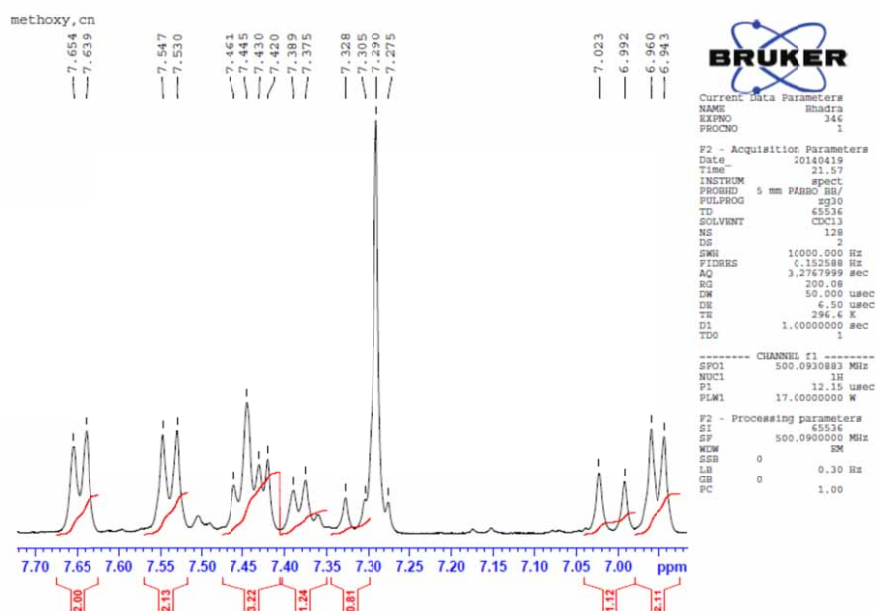
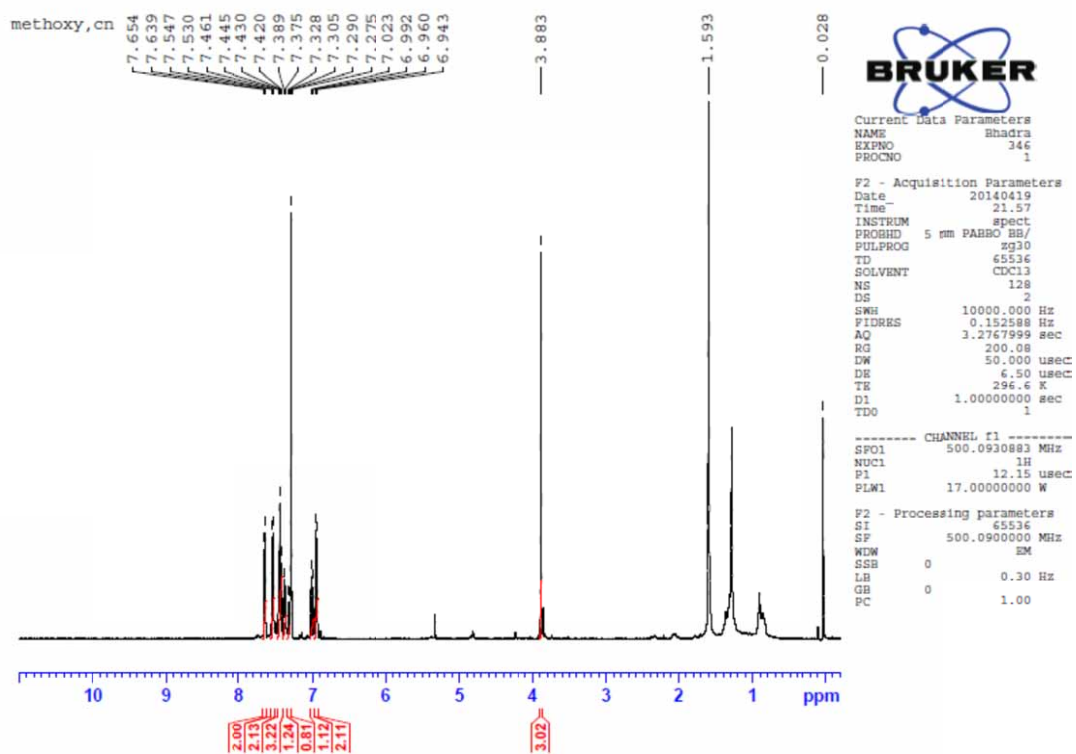
Exact mass: 261.12

Mass obtained in the positive mode: 262.1576

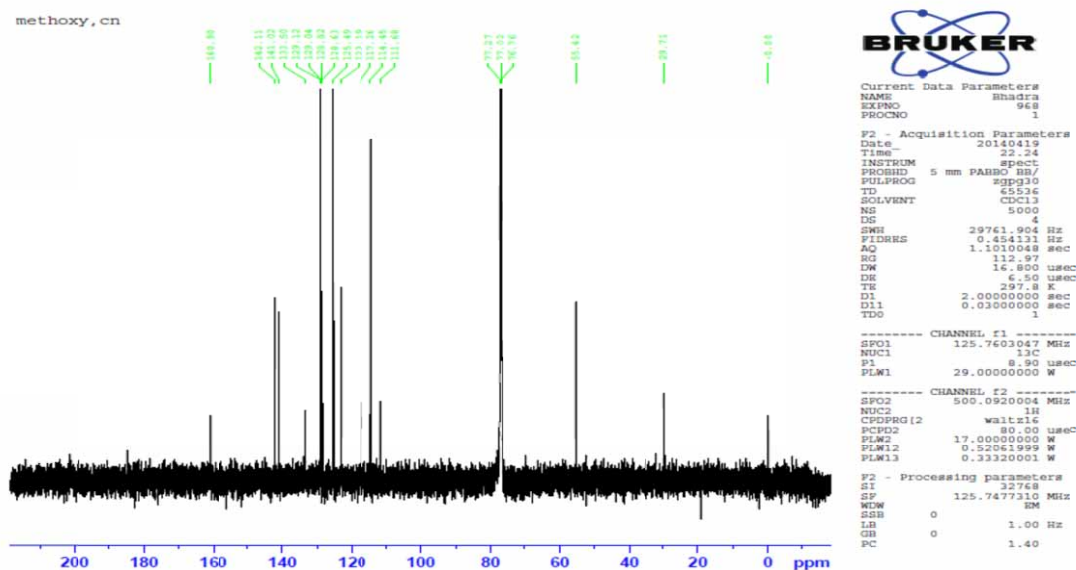
Elemental composition: C₁₈H₁₅NO



¹H NMR Spectrum of (2Z,4E)-5-(4-methoxyphenyl)-2-phenylpenta-2,4-dienitrile



¹³C NMR Spectrum of (2Z,4E)-5-(4-methoxyphenyl)-2-phenylpenta-2,4-dienitrile



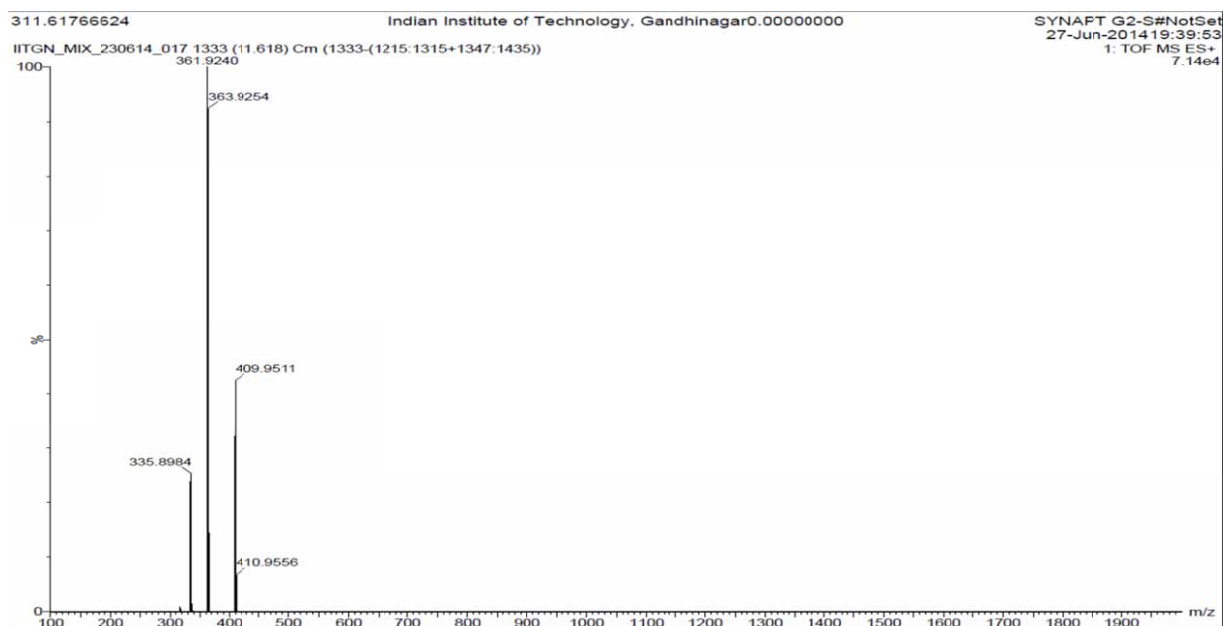
Hantzsch Reaction

Mass spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl,4-dihydropyridine-3,5-dicarboxylate (2a)

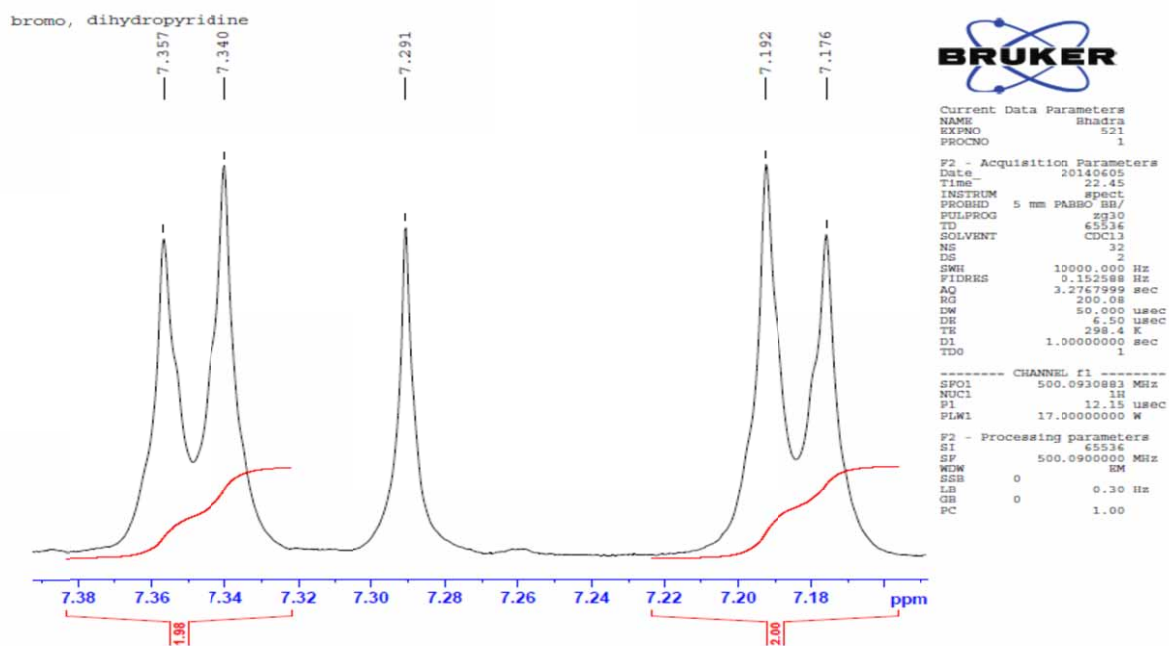
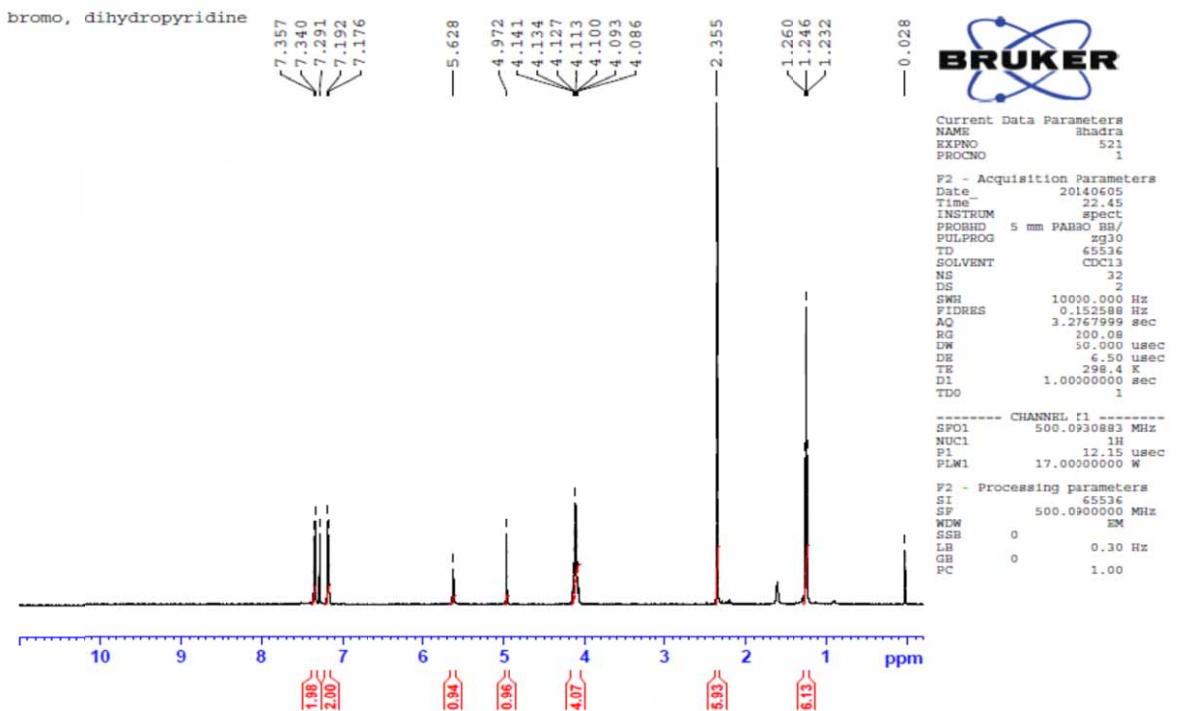
Exact mass: 407.07

Mass obtained in the positive mode: 409.9511

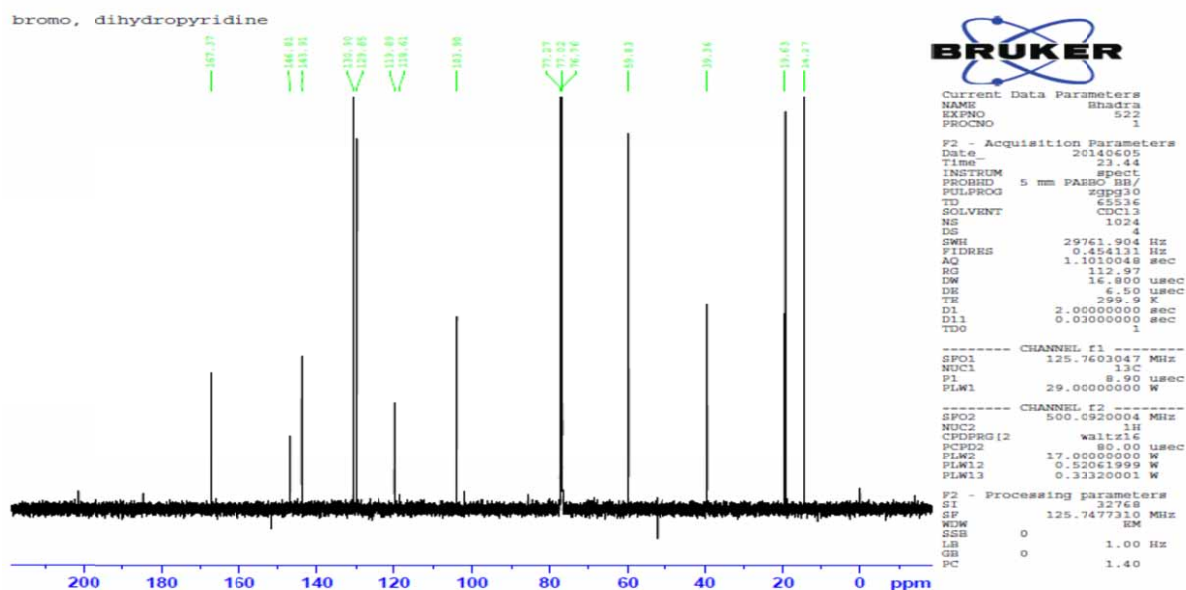
Elemental composition: C₁₉H₂₂BrNO₄



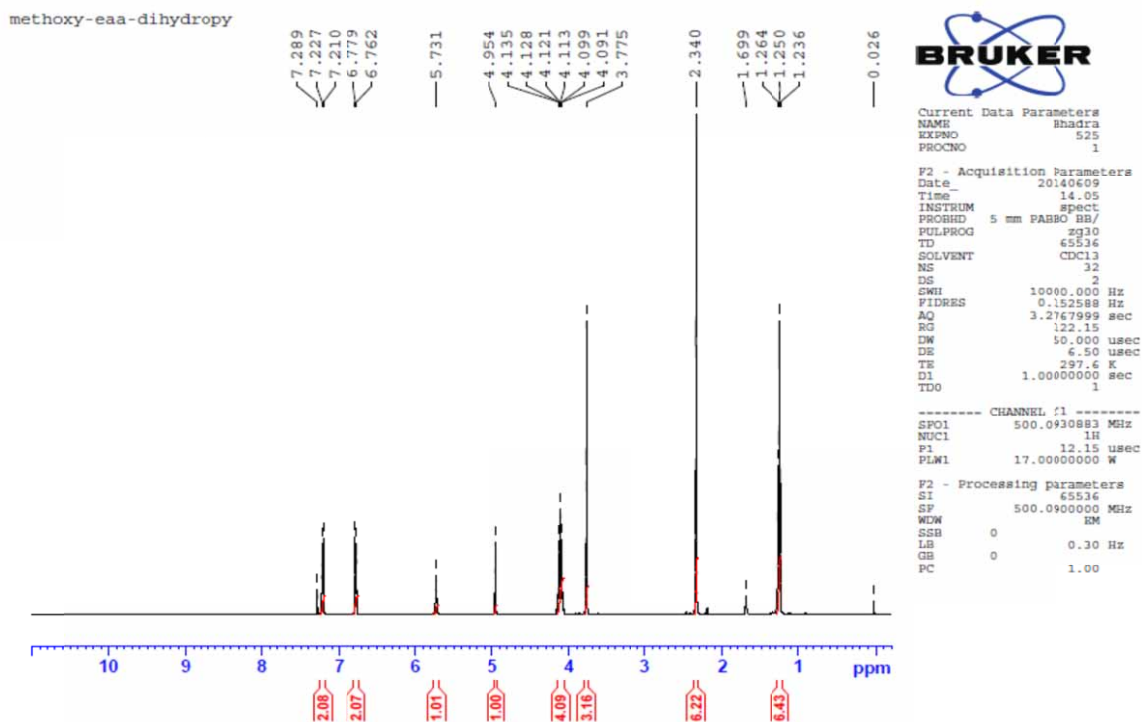
¹H NMR Spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl,4-dihydropyridine-3,5-dicarboxylate



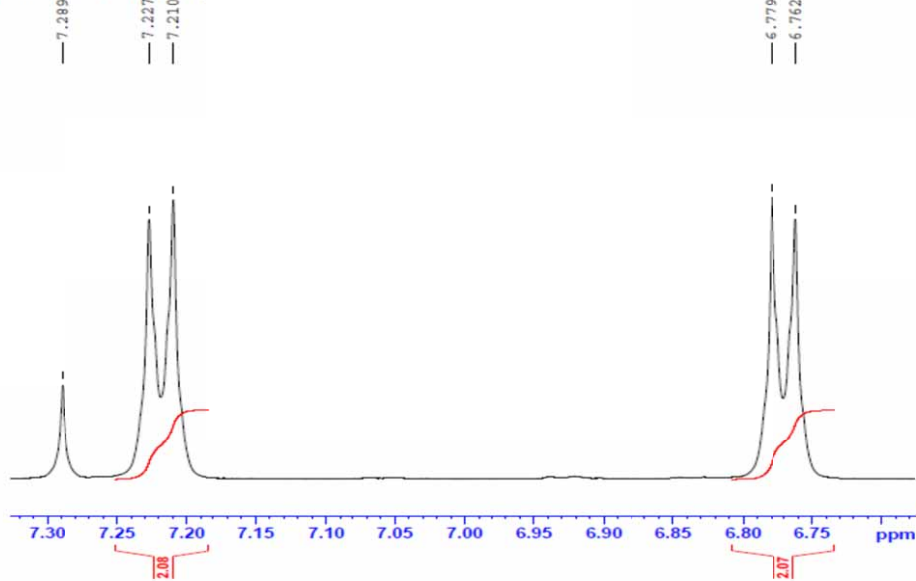
¹³C NMR Spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl,4-dihydropyridine-3,5-dicarboxylate



¹H NMR Spectrum of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate(2b)



methoxy-eaa-dihydropy



```
Current Data Parameters
NAME      Rhadra
EXPNO    525
PROCNO   1

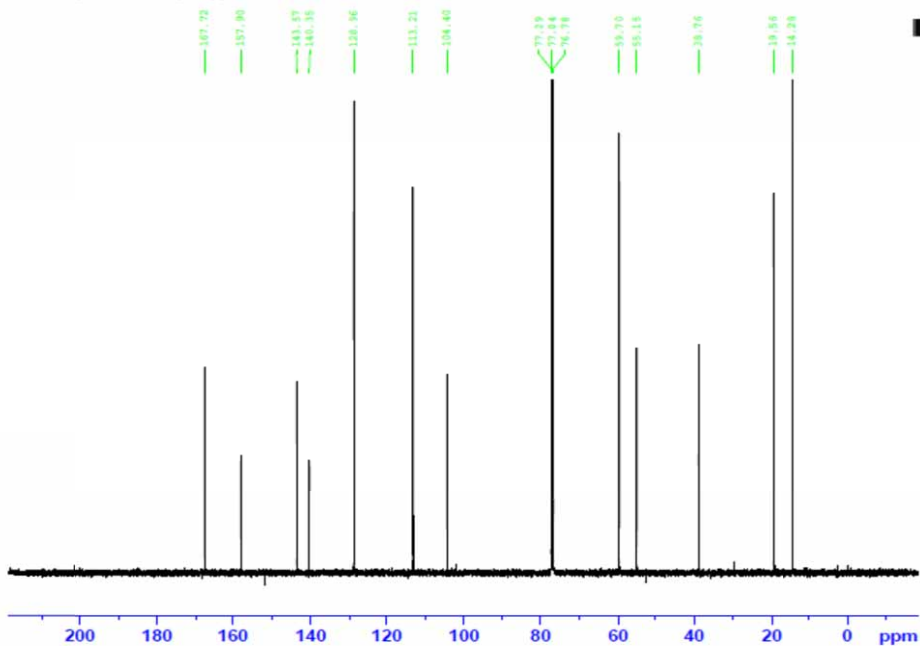
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PULPROG zg30
TD       65536
SOLVENT  CDCl3
NS       32
DS       4
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ       3.2767999 sec
RG       122.15
DW       50.000 usec
DE       6.50 usec
TE       297.6 K
D1       1.00000000 sec
TDO      1

----- 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     RM
SSB     0
LB      0.30 Hz
GB      0
PC      1.00
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¹³C NMR Spectrum of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate

methoxy-eaa-dihydropyridine



```
Current Data Parameters
NAME      Rhadra
EXPNO    528
PROCNO   1

F2 - Acquisition Parameters
Date_    20140609
Time     15.24
INSTRUM spect
PROBHD   5 mm PARBO BB/
PULPROG zgpg30
TD       65536
SOLVENT  CDCl3
NS       1024
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       300.5 K
D1       2.00000000 sec
D11      0.030000000 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
CPDPRG12 waltz16
PCPD2   80.00 usec
PLW2    17.00000000 W
PLW12   0.52061999 W
PLW13   0.33320001 W

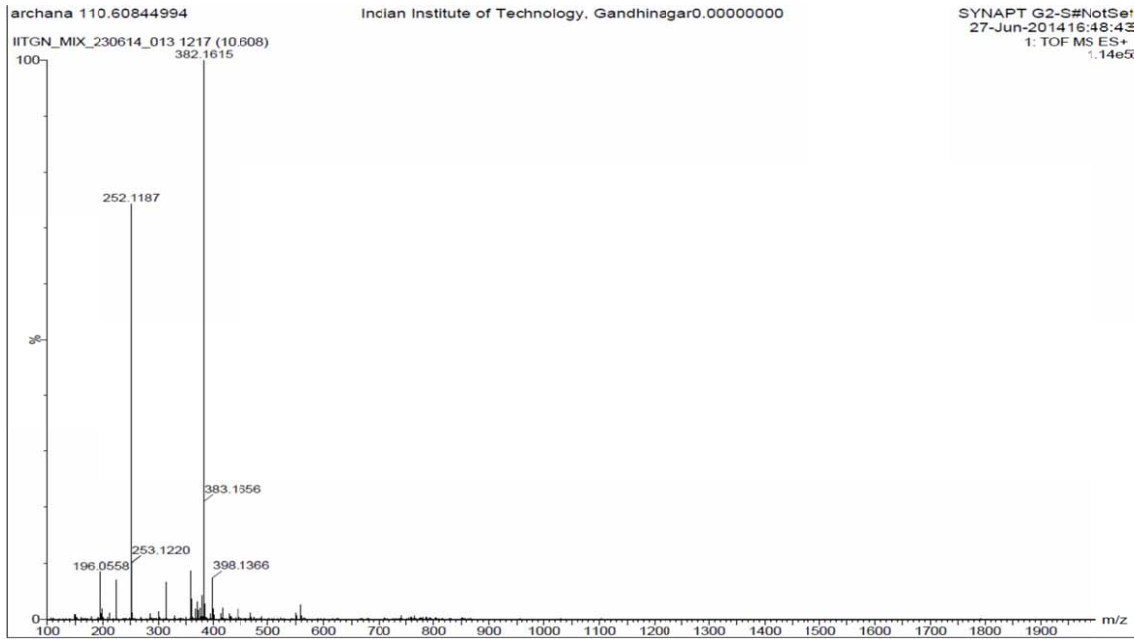
F2 - Processing parameters
SI      32768
SF      125.7477310 MHz
WDW     RM
SSB     0
LB      1.00 Hz
GB      0
PC      1.40
```

Mass spectrum of diethyl 2, 6-dimethyl-4-(naphthalene-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2c)

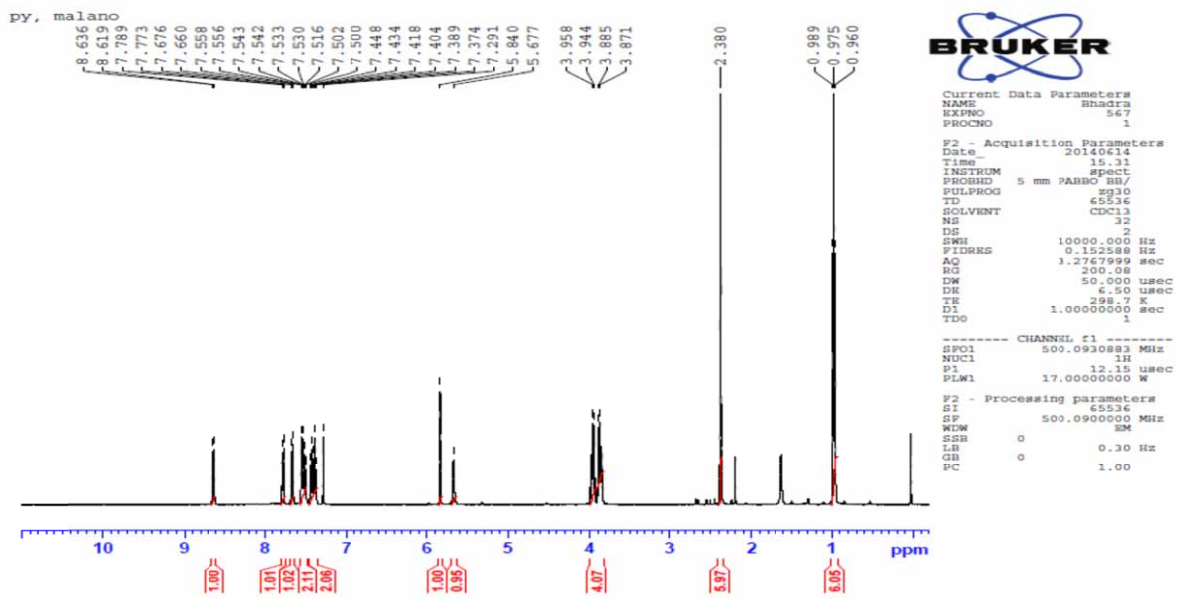
Exact mass: 379.18

Mass obtained in the positive mode: 382.165

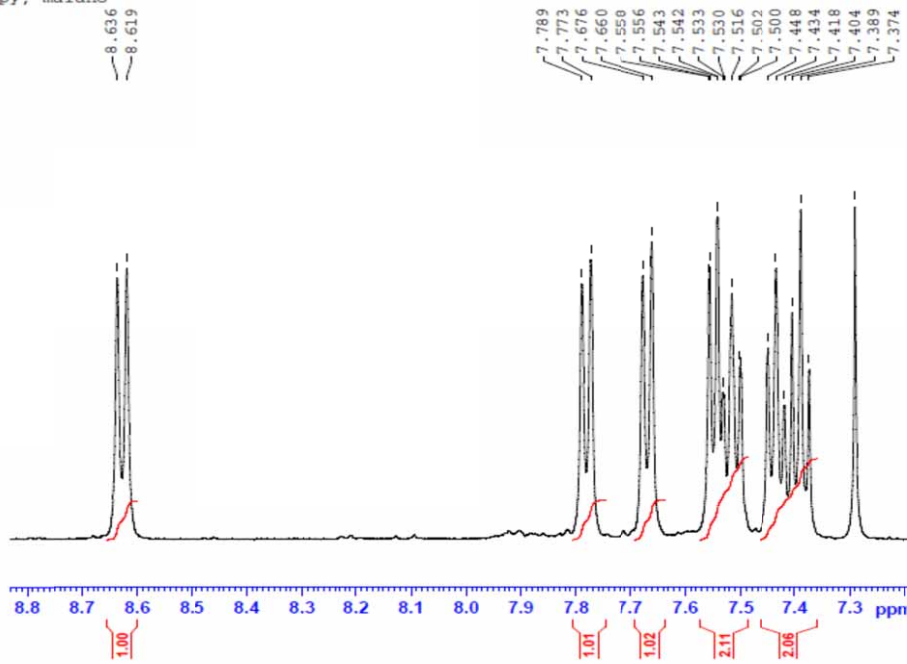
Elemental composition: C₂₃H₂₅NO₄



¹H NMR Spectrum of diethyl 2,6-dimethyl-4-(naphthalene-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate



py, malano



7.789
7.773
7.676
7.660
7.558
7.556
7.543
7.542
7.533
7.530
7.516
7.502
7.500
7.448
7.434
7.418
7.404
7.389
7.374



Current Data Parameters
 NAME Bhadra
 EXPNO 567
 PROCNO 1

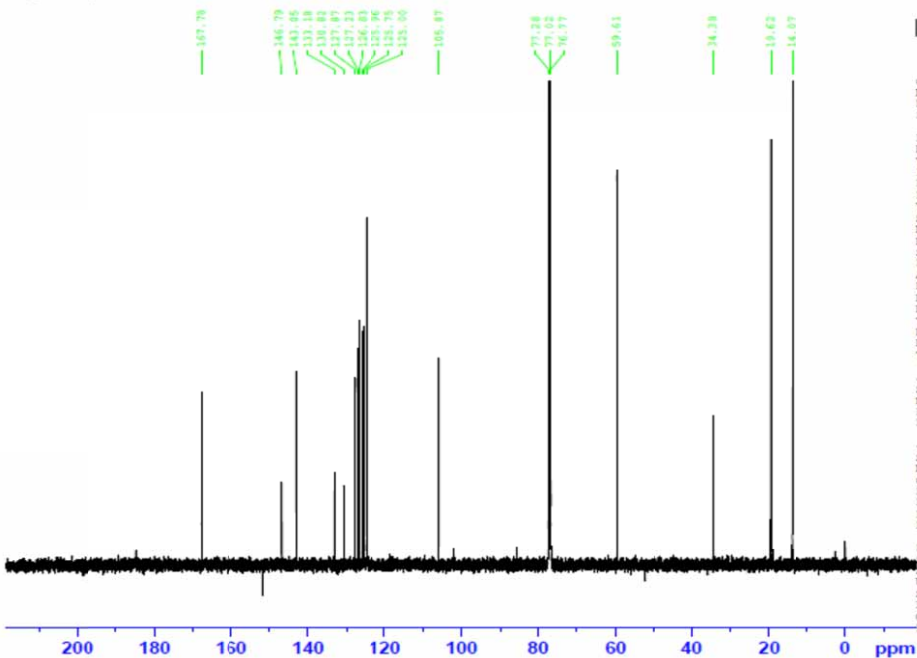
F2 - Acquisition Parameters
 Date_ 20140614
 Time 15.31
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 1.2767999 sec
 RG 200.08
 DW 50.000 usec
 DE 6.50 usec
 TE 298.7 K
 D1 1.00000000 sec
 TDO 1

----- 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 diethyl 2, 6-dimethyl-4-(naphthalene-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate

naphthal, hantzsch



Current Data Parameters
 NAME Bhadra
 EXPNO 568
 PROCNO 1

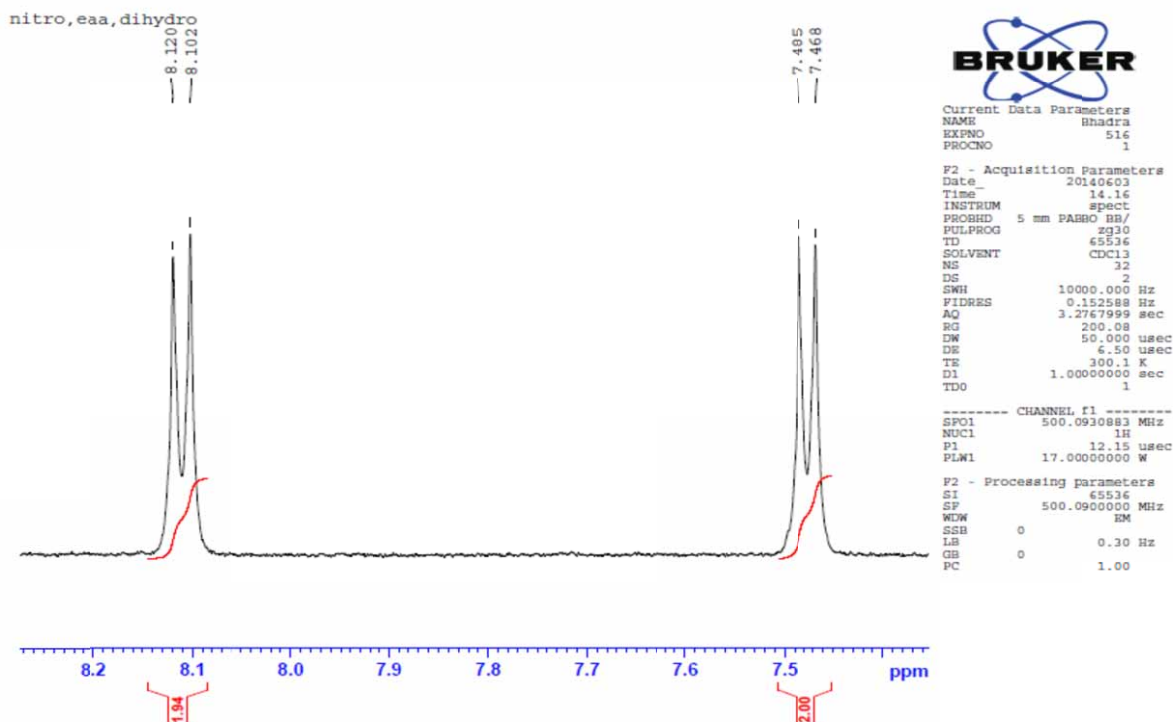
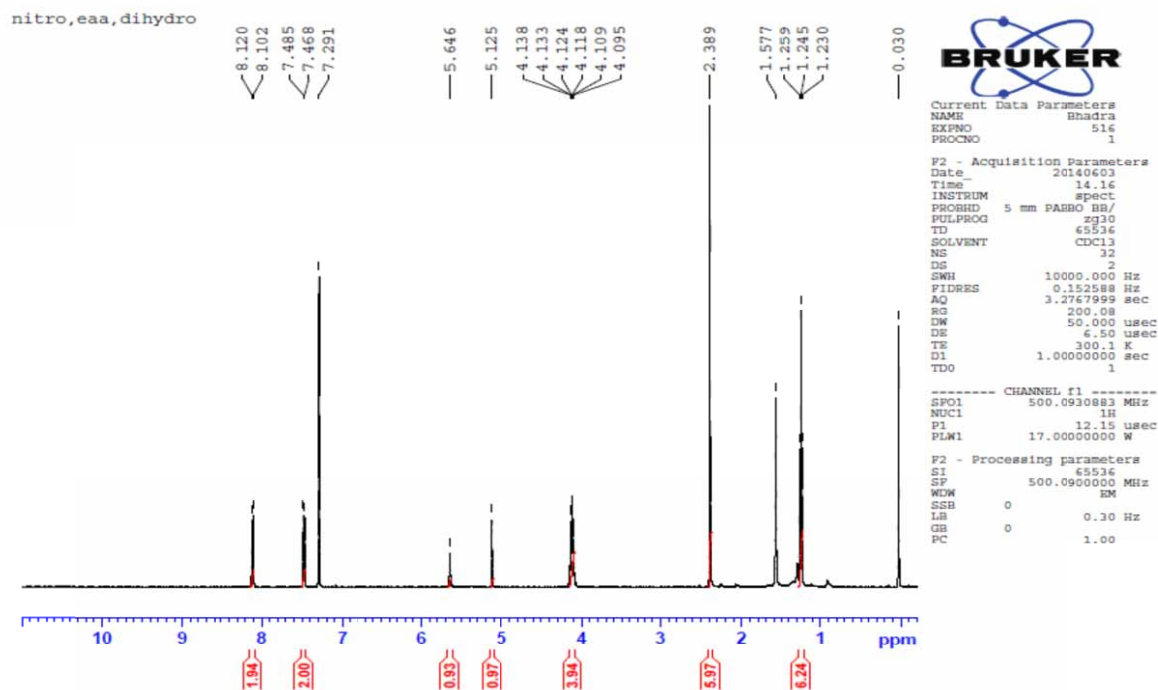
F2 - Acquisition Parameters
 Date_ 20140614
 Time 15.29
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 112.97
 DW 16.800 usec
 DE 6.50 usec
 TE 301.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

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

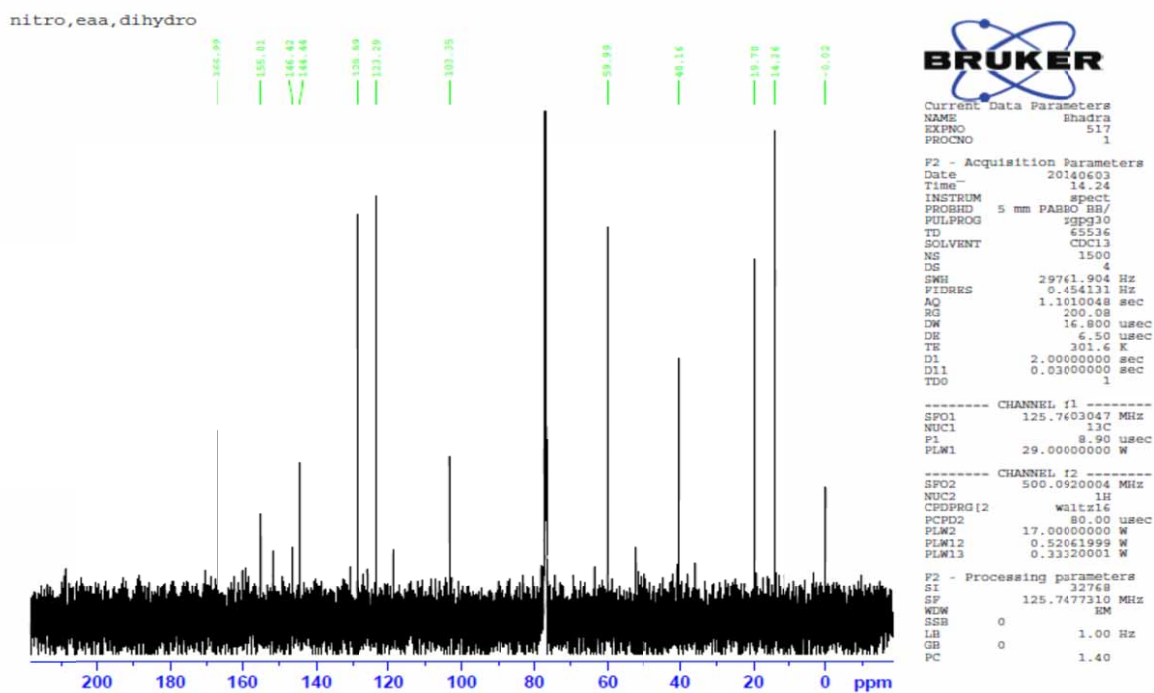
----- CHANNEL f2 -----
 SFO2 500.0920004 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 17.00000000 W
 PLW12 0.52061999 W
 PLW13 0.33320001 W

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

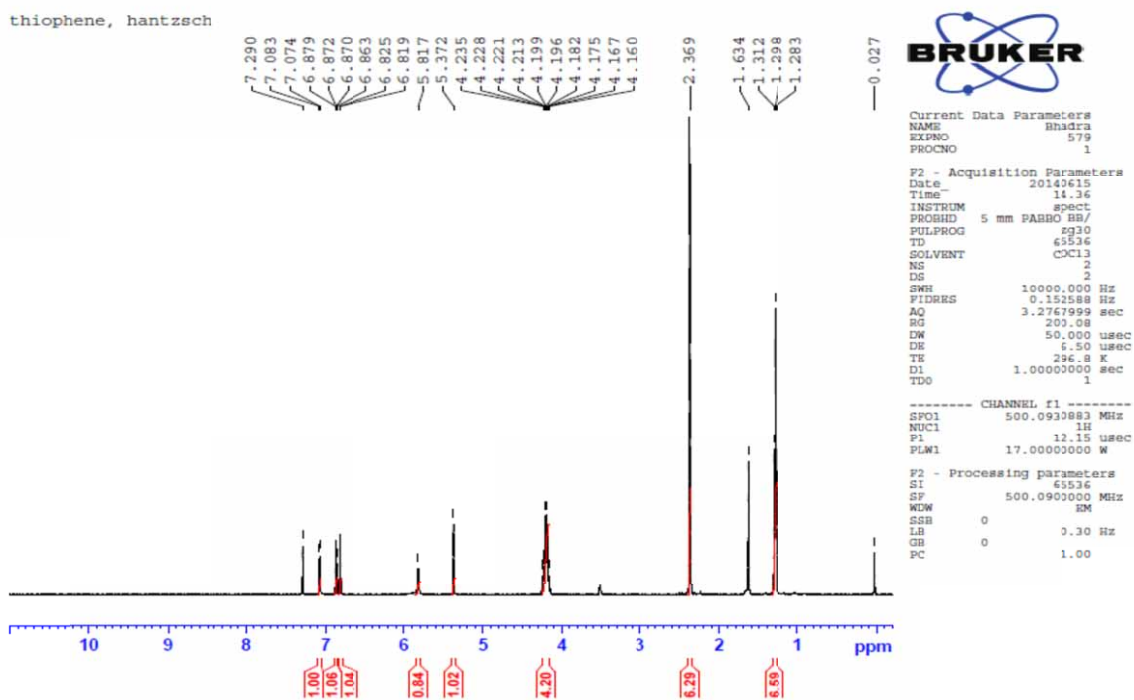
¹H NMR Spectrum of diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (2d)



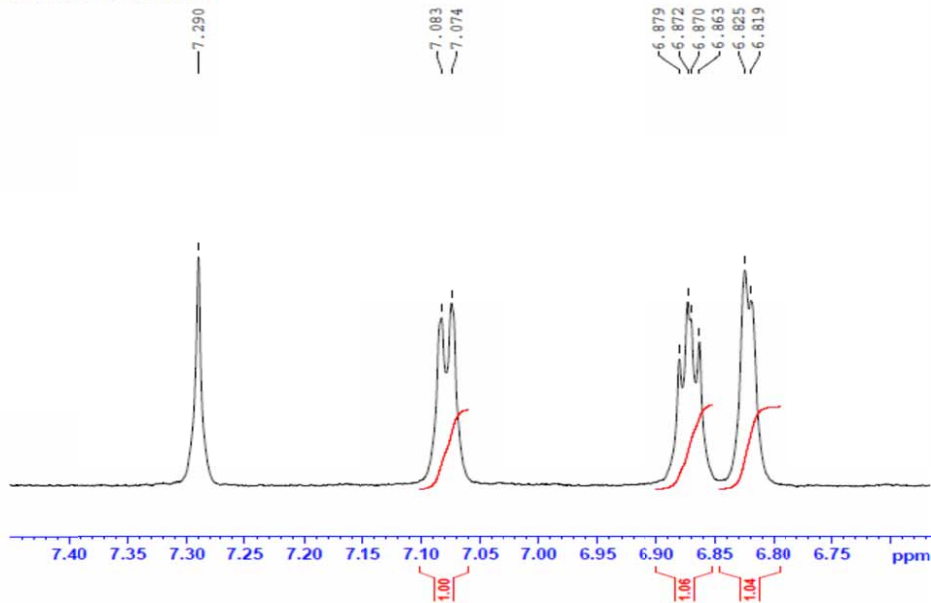
¹³C NMR Spectrum of diethyl 2, 6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate



¹H NMR Spectrum of diethyl 2,6-dimethyl-4-(thiophen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2e)



thiophene, hantzsch



```
Current Data Parameters
NAME      Bhadra
EXPNO    579
PROCNO   1

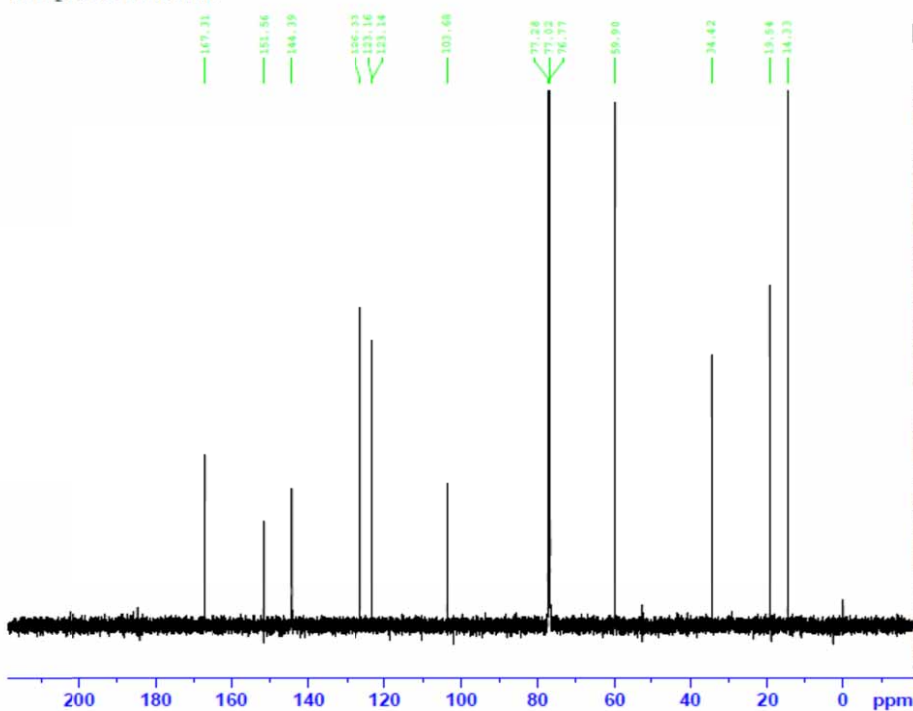
F2 - Acquisition Parameters
Date_    20140615
Time     14.36
INSTRUM spect
PROBHD   5 mm PABBO BB/
PULPROG zg30
TD       65536
SOLVENT  CDCl3
NS       2
DS       2
SWH      10000.000 Hz
FIDRES   0.152588 Hz
AQ       3.2767999 sec
RG       200.58
DW       50.000 usec
DE       6.50 usec
TE       296.8 K
D1       1.00000000 sec
TDO      1

----- CHANNEL f1 -----
SFO1    500.093083 MHz
NUC1     1H
P1       12.15 usec
PLW1     17.00000000 W

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

¹³C NMR Spectrum of diethyl 2,6-dimethyl-4-(thiophen-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate

thiophene hantzsch



```
Current Data Parameters
NAME      Bhadra
EXPNO    582
PROCNO   1

F2 - Acquisition Parameters
Date_    20140615
Time     15.11
INSTRUM spect
PROBHD   5 mm PABBO BB/
PULPROG zgpg30
TD       65536
SOLVENT  CDCl3
NS       1024
DS       4
SWH      29741.904 Hz
FIDRES   0.454131 Hz
AQ       1.1010048 sec
RG       112.97
DW       16.800 usec
DE       6.50 usec
TE       300.2 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
CPDPRG[2] waltz16
PCPD2    80.00 usec
PLW2     17.00000000 W
PLW12    0.52061999 W
PLW13    0.33200001 W

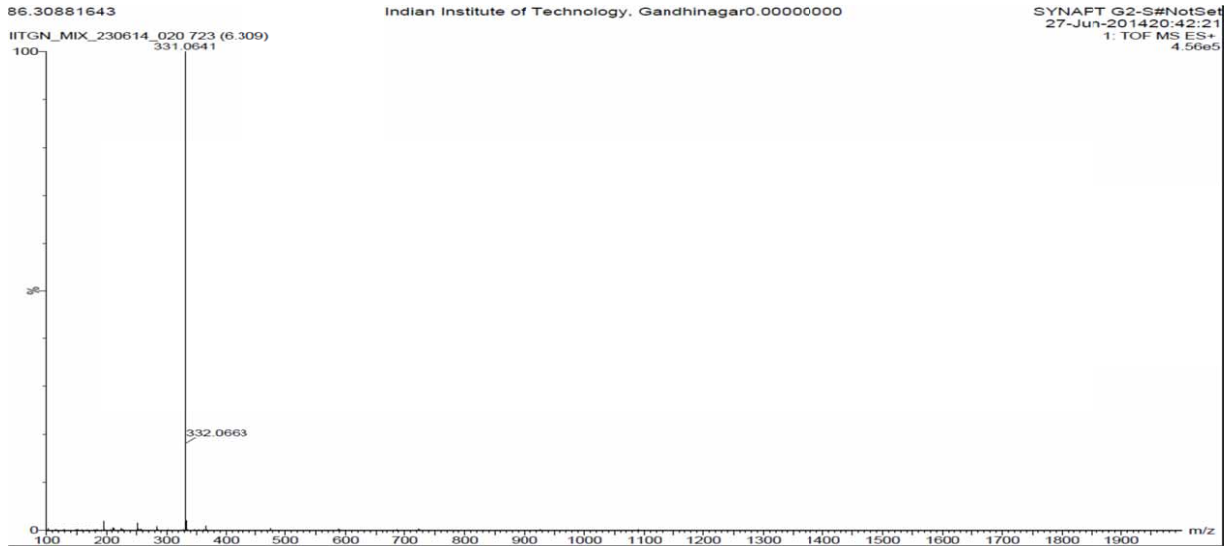
F2 - Processing parameters
SI       32768
SF       125.7477310 MHz
WDW      RM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
```

Mass spectrum of diethyl 2, 6-dimethyl-4-(pyridine-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate (2f)

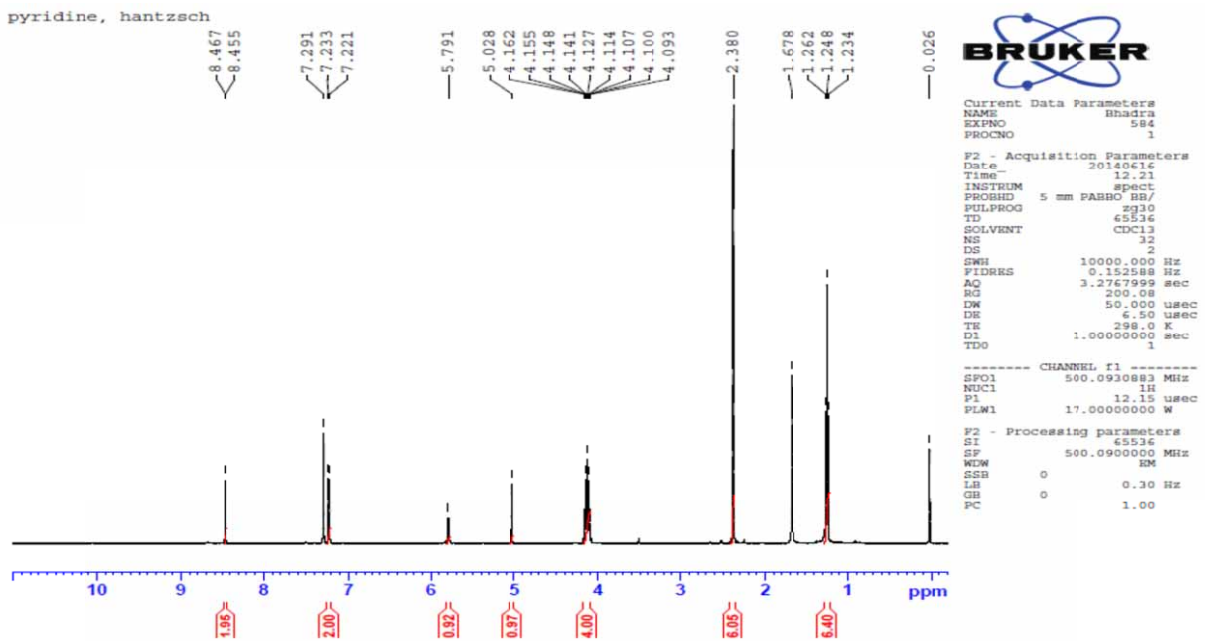
Exact mass: 330.16

Mass obtained in the positive mode: 331.0641

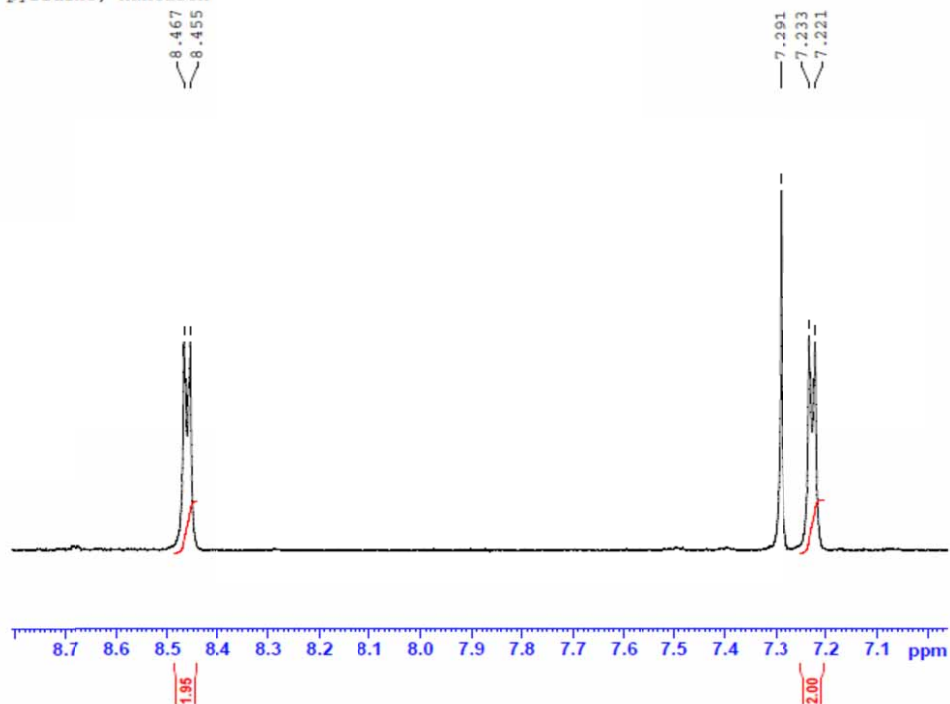
Elemental composition: C₁₈H₂₂N₂O₄



¹H NMR Spectrum of diethyl 2, 6-dimethyl-4-(pyridine-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate



pyridine, hantzsch



¹³C NMR Spectrum of diethyl 2, 6-dimethyl-4-(pyridine-4-yl)-1,4-dihydropyridine-3,5-dicarboxylate

pyridine, hantzsch

