Supporting Information

Recyclable Bi_2WO_6-nanoparticle mediated one-pot multicomponent reactions in aqueous medium at room temperature†#

BanothPaplal,[a] S. Nagaraju,[a] Palakollu Veerabhadraiah,[b] Kodam Sujatha,[a]
Sriram Kanvah,[b] B. Vijaya Kumar[c]* and Dhurke Kashinath[a]*
[a]Department of Chemistry, National Institute of Technology, Warangal-506 004, India
e-mail: kashinath@nitw.ac.in; kashinath.dhurke@gmail.com
Tel. +91-870-2462677; FAX No. +91-870-2459547
[b]Department of Chemistry, Indian Institute of Technology, Gandhinagar, Ahmedabad, India
[c]Department of Chemistry, Nizam College, Osmania University, Hyderabad, India

Preparation of $BiVO_4$, Bi_2O_3 and Bi_2WO_6:[1]

The chemicals ($Bi(NO_3)_3.5H_2O$, Na_2WO_6 and V_2O_5) were analytical grade reagents (purchased from Sigma-Aldrich). A Bismuth stock solution prepared with a concentration of 0.2 mol L^{-1} by dissolving $Bi(NO_3)_3.5H_2O$ in 1.5 mol L^{-1} nitric acid.

$BiVO_4$: 25 mL of bismuth stock solution was diluted with 25 mL of deionized water, and added Bi/V=1 molar ratio of V_2O_5 and the mixture was stirred for 3 days at RT. The solid was filtered and washed with water (4 X 10 mL) and dried.

Bi_2O_3: Conc.NaOH was added to 15 mL of Bismuth stock solution till the pH of 11.5. The solution was stirred at RT for 24h, filtered, washed with double distilled water for (4X 10 mL) and dried.

Bi_2WO_6: Tungstate solution was prepared by dissolving sodium tungstate in HNO_3 (1.5 $molL^{-1}$). Bismuth and tungstate stock solution was mixed with Bi/W = 2 (in the molar ratio of Bi/W = 2), this solution was transferred in to a Teflon lined autoclave and then heated at 200^oC for 24h under autogenous pressure. After 24h, autoclave was cooled to RT and the compound obtained was washed with deionized water (4x10 mL) and dried.

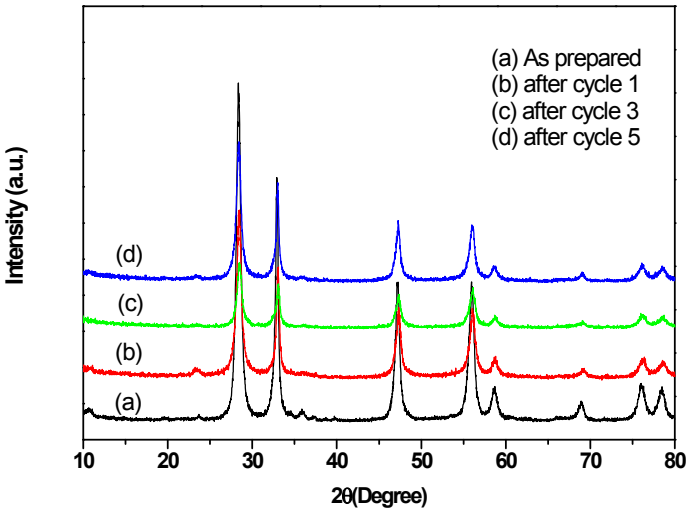
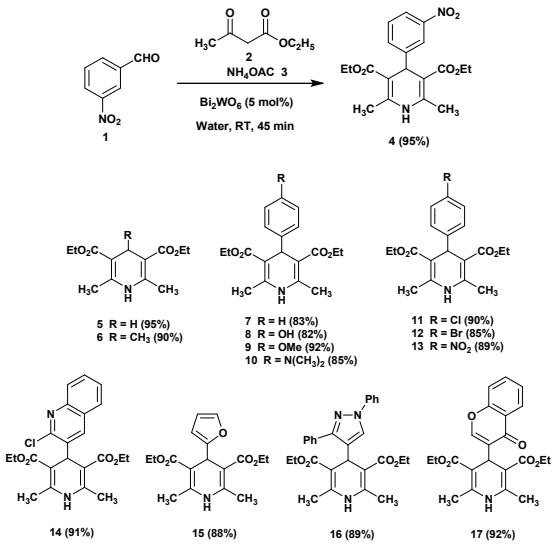


Figure-1. Powder XRD graph of Bi_2WO_6 (Before the reaction and after the reaction up to 5 cycles)

General procedure for the synthesis of Dihydropyridines (4-17):



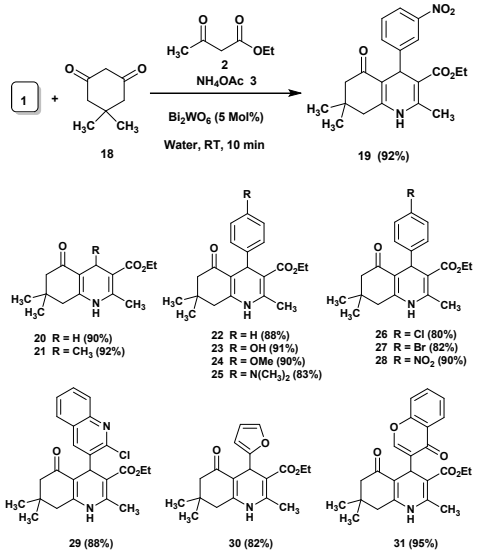
To a mixture of aldehyde (1 equiv), and Ethyl acetoacetate (2 equiv) in water (3-5 mL) was added NH_4OAc (2.5 equiv) followed by Bi_2WO_6 (5 mol%). The mixture was stirred at RT for 60 min. After completion of the reaction (monitored by TLC), the contents were transferred to separating funnel and extracted with EtOAc (3X 10 mL). The combined organic layers were washed with brine, water, dried over Na_2SO_4 and filtered. Evaporation of the solvent gave the crude product which was purified by recrystallization using EtOH as solvent (Some of the derivatives were purified using

silica gel column chromatography. Elution of the column with Petroleum ether:EtOAc mixture gave the desired dihydropyridines **4-17**).

Product No	Measured MP °C	Reported MP °C
6	125-128	130[2b]
7	158-160	156–158[2a]
8	238-240	240-242[2c]
9	159-161	158–160[2a]
10	228-230	227-230[2c]
11	148-150	145–147[2a]
12	162-164	162–164[2a]
13	132-133	130–132[2a]
15	160-162	160–162[2a]

Table-1. Comparison of physical data (MP) of the known compounds

General procedure for the synthesis of polyhydroquinolones (19-31):



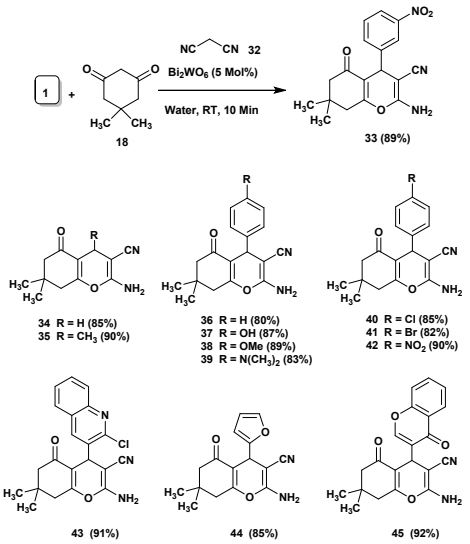
To a mixture of aldehyde (1 equiv), ethyl acetoacetate (1equiv) and dimedone (1 equiv) in water (3-5 mL) was added NH_4OAc (2.5 equiv) followed by Bi_2WO_6 (5 mol%). The mixture was stirred at RT for 10 min. After completion of the reaction (monitored by TLC), the contents were transferred to separating funnel and extracted with EtOAc (3X 10 mL). The combined organic layers were washed with brine, water, dried over Na_2SO_4 and filtered. Evaporation of the solvent gave the crude product

which was purified by recrystallization using EtOH as solvent(Some of the derivatives were purified using silica gel column chromatography. Elution of the column with Petroleum ether:EtOAc mixture gave the desired products).

Product No	Measured MP ^{o}C	Reported MP ^{o}C
19	178-180	174–176[3a]
22	205-206	202–204[3a]
23	234-235	231–233[3a]
24	250-254	255–257[3a]
25	233-235	230–232[3a]
26	240-245	245–247[3a]
27	251-253	252–253[3a]
28	242-246	244–246[3a]
30	246-248	246–248[3a]

Table-2. Comparison of physical data (MP) of the known compounds

General procedure for the synthesis of 4H-chromenederivatives (33-45):



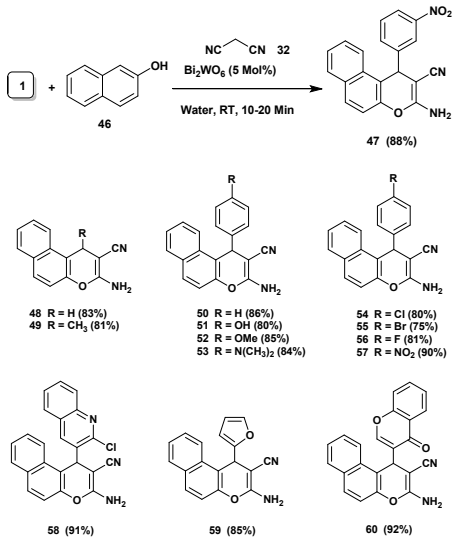
To a mixture of aldehyde (1 equiv), and dimedone (1 equiv) in water (3-5 mL) was added melanonitrile (1 equiv) followed by Bi_2WO_6 (5 mol%). The mixture was stirred at RT for 10 min. After completion of the reaction (monitored by TLC), the contents were transferred to separating funnel and extracted with EtOAc (3X 10 mL). The combined organic layers were washed with brine, water, dried over Na_2SO_4 and

filtered. Evaporation of the solvent gave the crude product which was purified by recrystallization using EtOH as solvent (Some of the derivatives were purified using silica gel column chromatography. Elution of the column with Petroleum ether:EtOAc mixture gave the desired products).

Product No.	Measured MP ^{o}C	Reported MP ^{o}C
33	214-216	210–212[4a]
34	190-192	--
36	228-230	224–226[4a]
37	210-212	212–215[4a]
38	193-195	190–192[4a]
39	208-210	206–208[4a]
40	207-210	210–212[4a]
41	215-218	216-218[4a]
42	183-184	186-189[4a]
44	210-213	200–204[4a]

Table-3. Comparison of physical data (MP) of the known compounds

General procedure for the synthesis of 2-amino-4H-benzo[b]pyran derivatives (47-60):



To a mixture of aldehyde (1 equiv), and β-naphthol (1 equiv) in water (3-5 mL) was added melanonitrile (1 equiv) followed by Bi_2WO_6 (5 mol%). The mixture was stirred at RT for 20 min. After completion of the reaction (monitored by TLC), the contents

were transferred to separating funnel and extracted with EtOAc (3X 10 mL). The combined organic layers were washed with brine, water, dried over Na_2SO_4 and filtered. Evaporation of the solvent gave the crude product which was purified by recrystallization using EtOH as solvent(Some of the derivatives were purified using silica gel column chromatography. Elution of the column with Petroleum ether:EtOAc mixture gave the desired products).

Product No	Measured MP ^oC	Reported MP ^oC
47	209-211	233–235[4a]
48	200-202	--
49	170-175	--
50	276-278	274–276[4a]
51	245-246	246–248[4a]
52	216-218	217–218[4a]
53	225-228	227-230[4a]
54	204-205	205–206[4a]
55	240-242	242–244[4a]
56	232-234	233–234[4a]
57	184-185	186–187[4a]
58	260-263	--
59	226-228	226–227[4b]

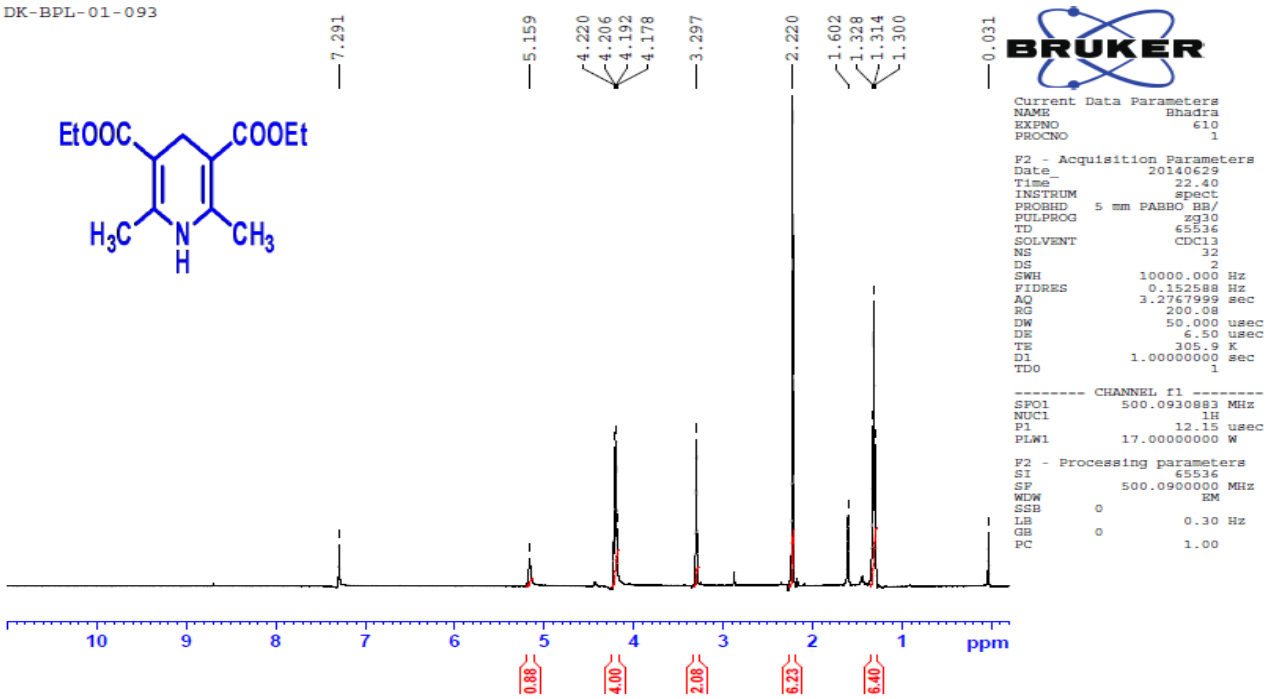
Table-4. Comparison of physical data (MP) of the known compounds

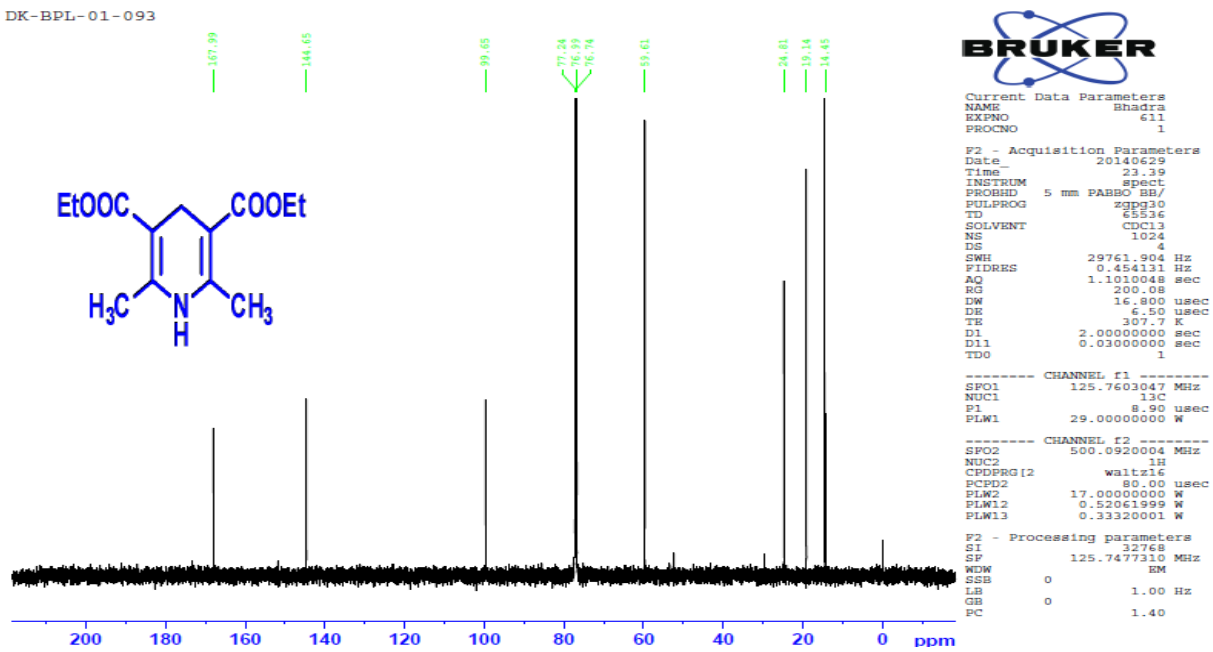
References:

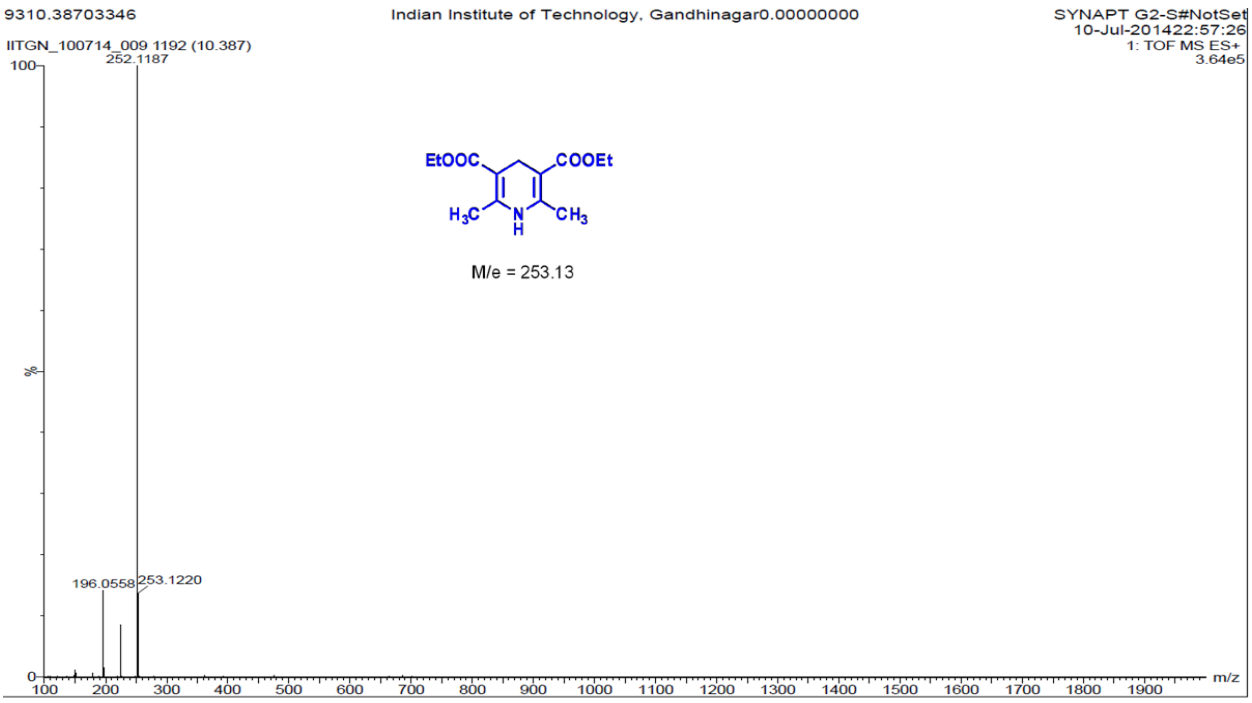
1. (a) T. Saison, P. Gras, N. Chemin, C. Chanéac, O. Durupthy, V. Brezová, C. Colbeau–Justin, J.–P. Jolivet, *J. Phys. Chem. C,* **2013**, *117*, 22656–22666; (b) B. V. Kumar, N. K. Veldurthi, J. R. Reddy, M. Vithal, *Micro &NanoLett.*, **2012**, *7*, 544–548.
2. (a) A. Debache, W. Ghalem , R. Boulcina, B.Ali, S. Rhouati, B. Carboni, *Tetrahedron Lett.*, **2009**, *50*, 5248–5250; (b) S. Ghosh, F. Saikh, J. Das, A. K. Pramanik, *Tetrahedron Lett.*, **2013**, *54*, 58–62; (c) P. Ghosh, P. Mukherjee, Asish, R. Das, *RSC Adv.*, **2013**, *3*, 8220–8226.
3. (a)S. B. Sapkal, K. F. Shelke, B. B. Shingate, M. S. Shingare, *Tetrahedron Lett.,* **2009**, *50,* 1754–1756.

4. J. K Rajput, G. Kaur, *Catal. Sci. Technol.,* 2014, *4*, 142–151.
5. (a) J. Albadi, A. Mansournezhad , M. Darvishi-Paduk, *Chin. Chem. Lett.,* **2013**, *24*, 208–210; (b) K. Gong, H.-L. Wang, D. Fang, Z.-L. Liu, *Catal. Commun.*, **2008**, *9*, 650–653.

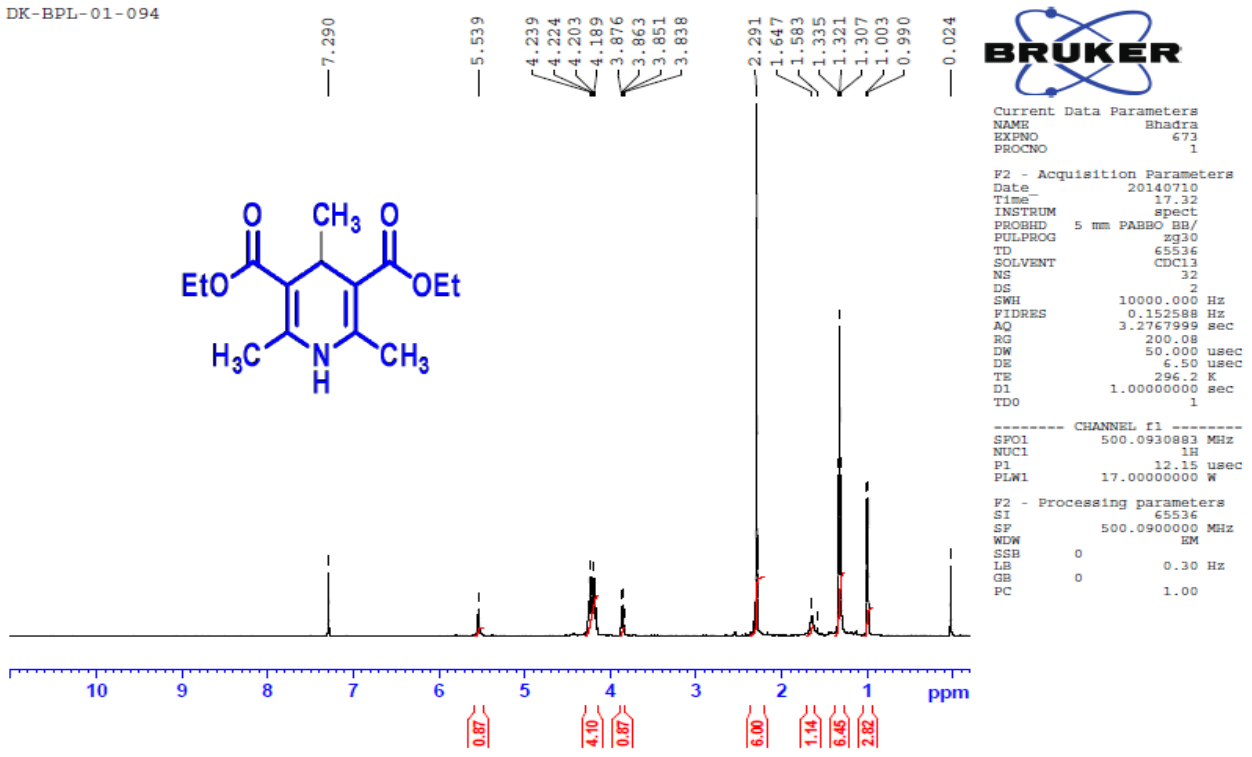
Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5):

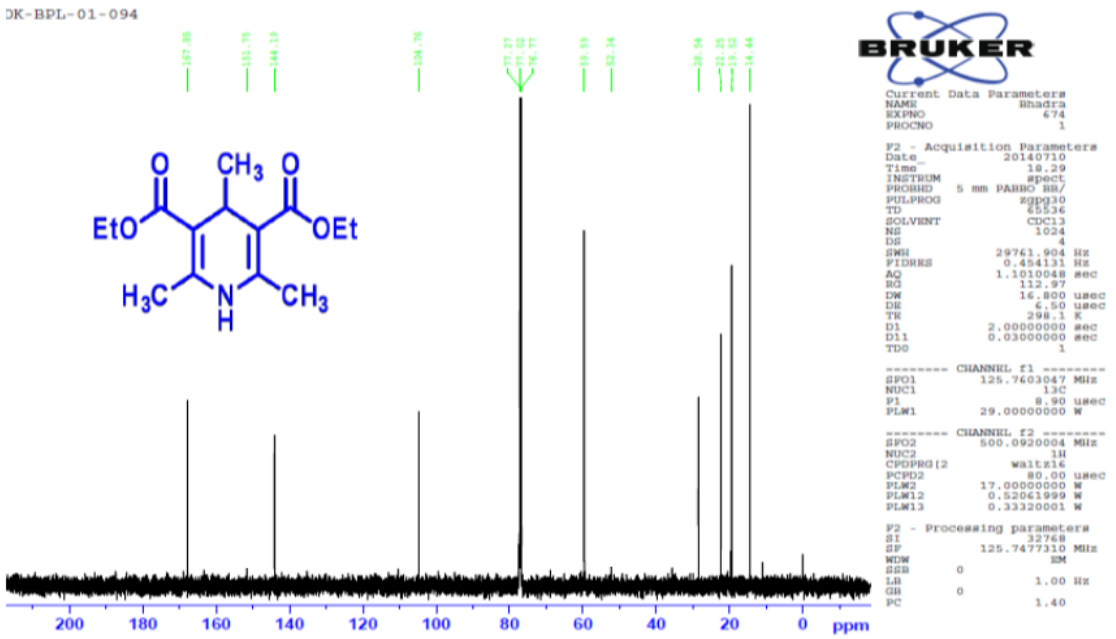




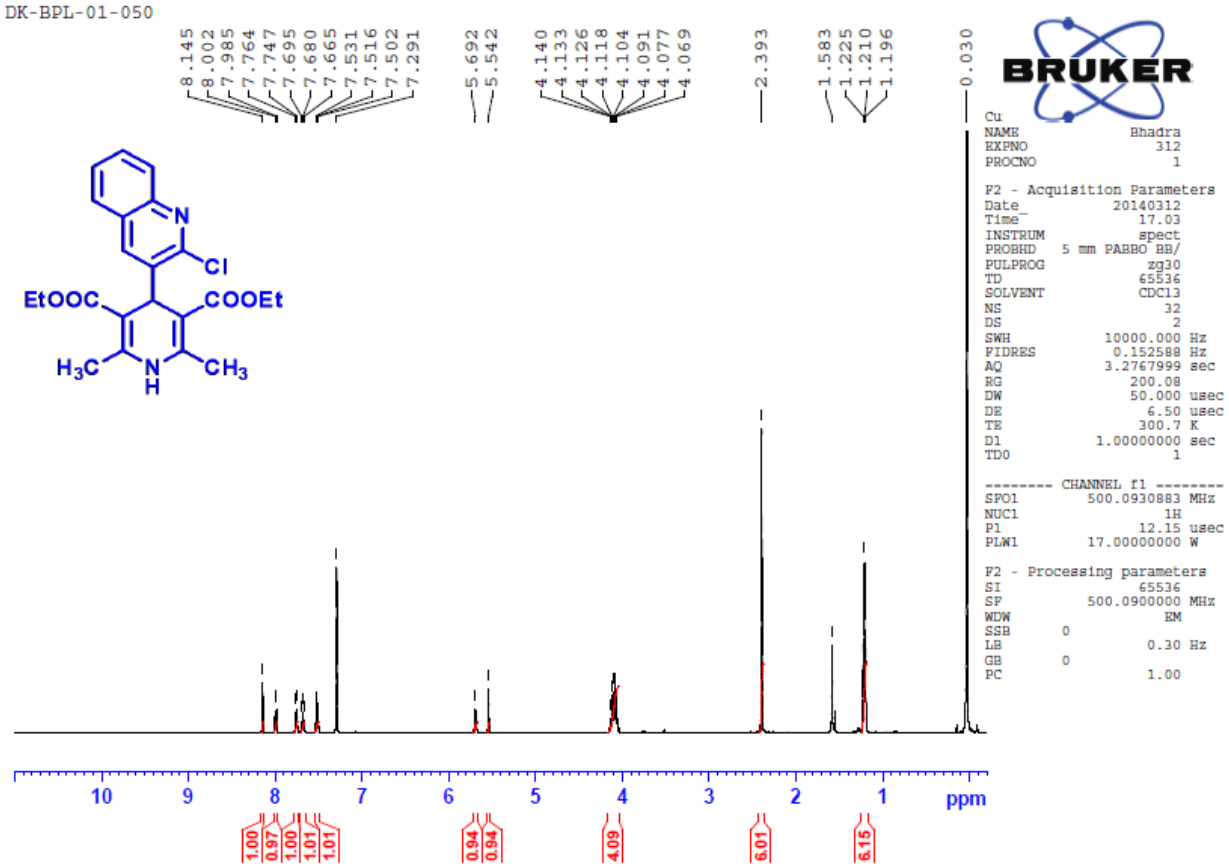


Diethyl 2,4,6-trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (6):

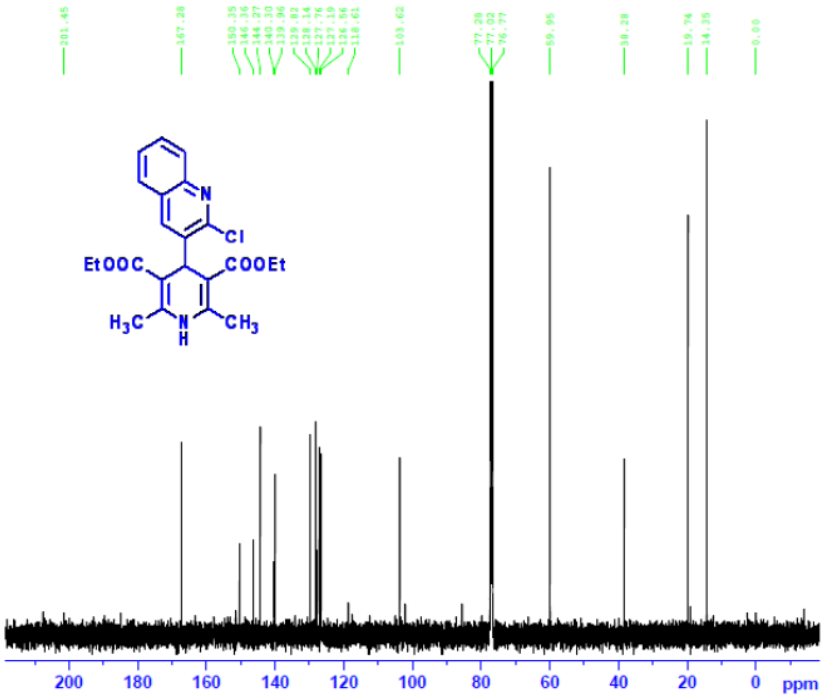




Diethyl 4-(2-chloroquinolin-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (14):



DK-BPL-01-50

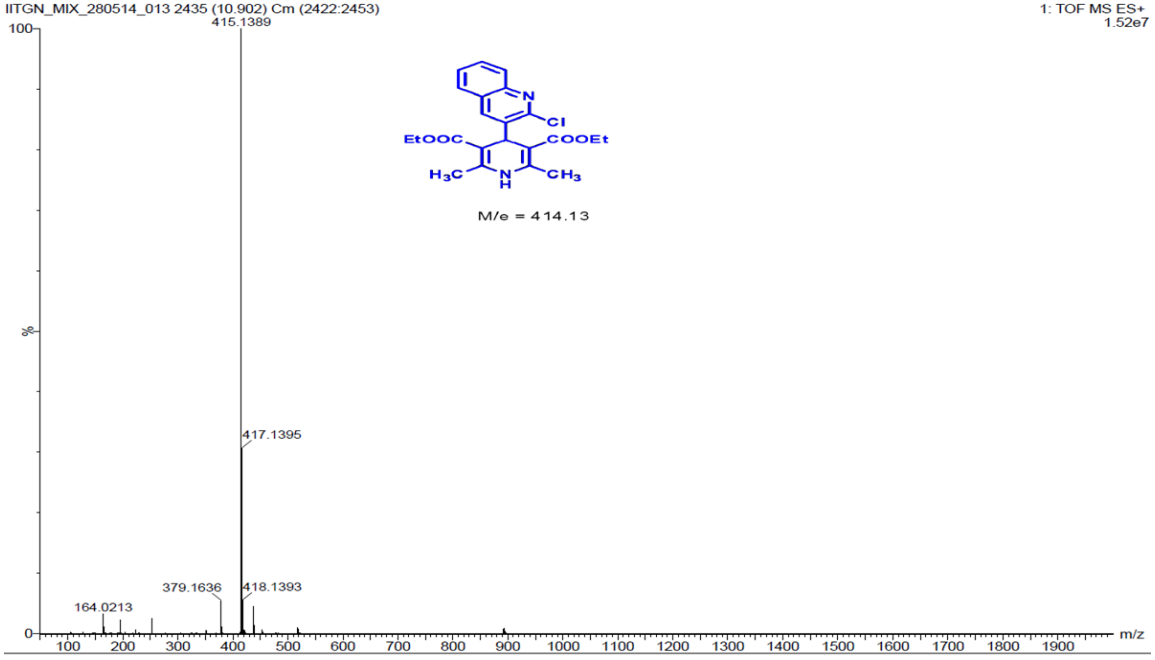



```
Current Data Parameters
NAME                  Bhadra
EXPNO                    549
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140708
Time_                 23.54
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1500
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                  297.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        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

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

NAG 5010.90168381 Indian Institute of Technology, Gandhinagar0.00000000

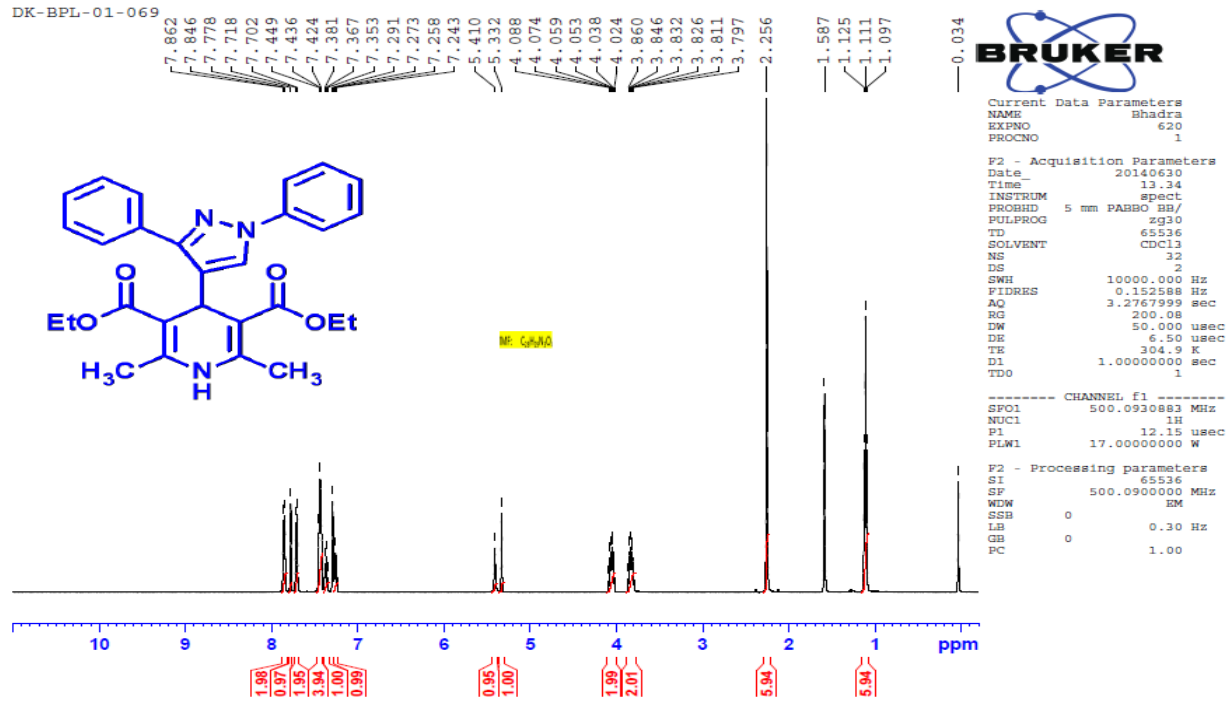
SYNAPT G2-S#NotSet
01-Jun-201422:32:26
1: TOF MS ES+
1.52e7

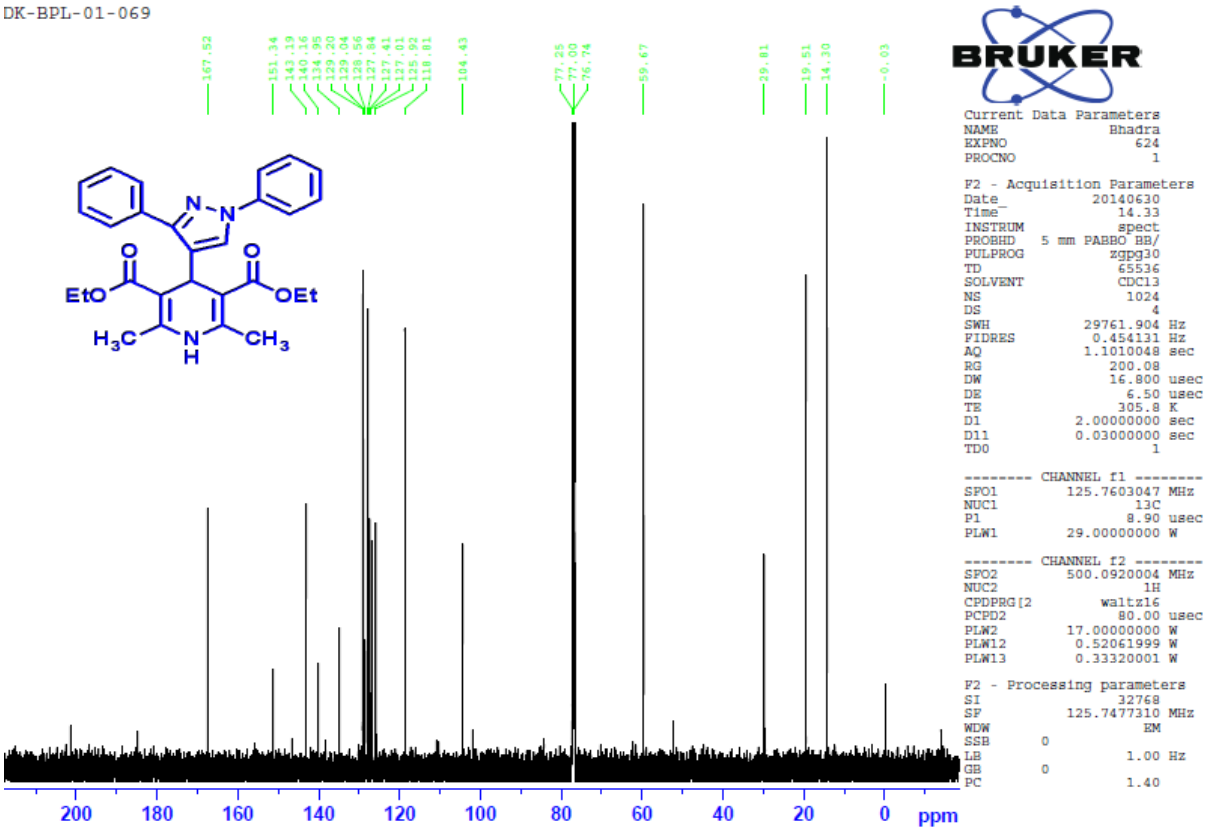
IITGN_MIX_280514_013 2435 (10.902) Cm (2422:2453)

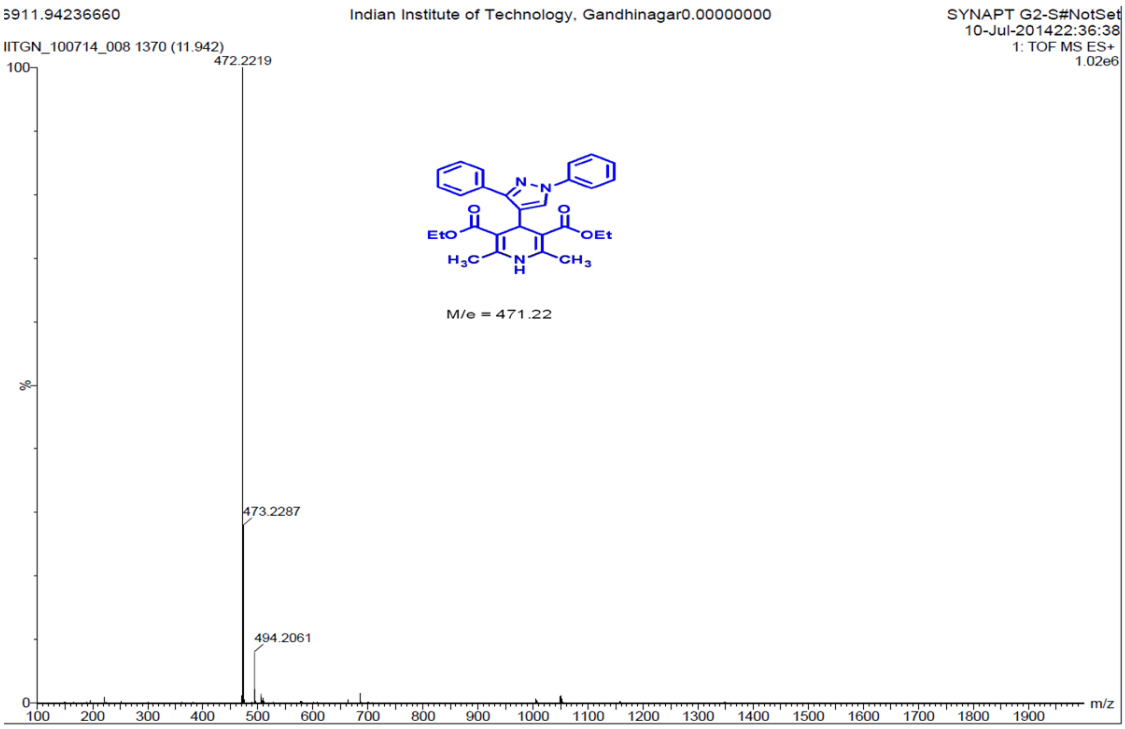


M/e = 414.13

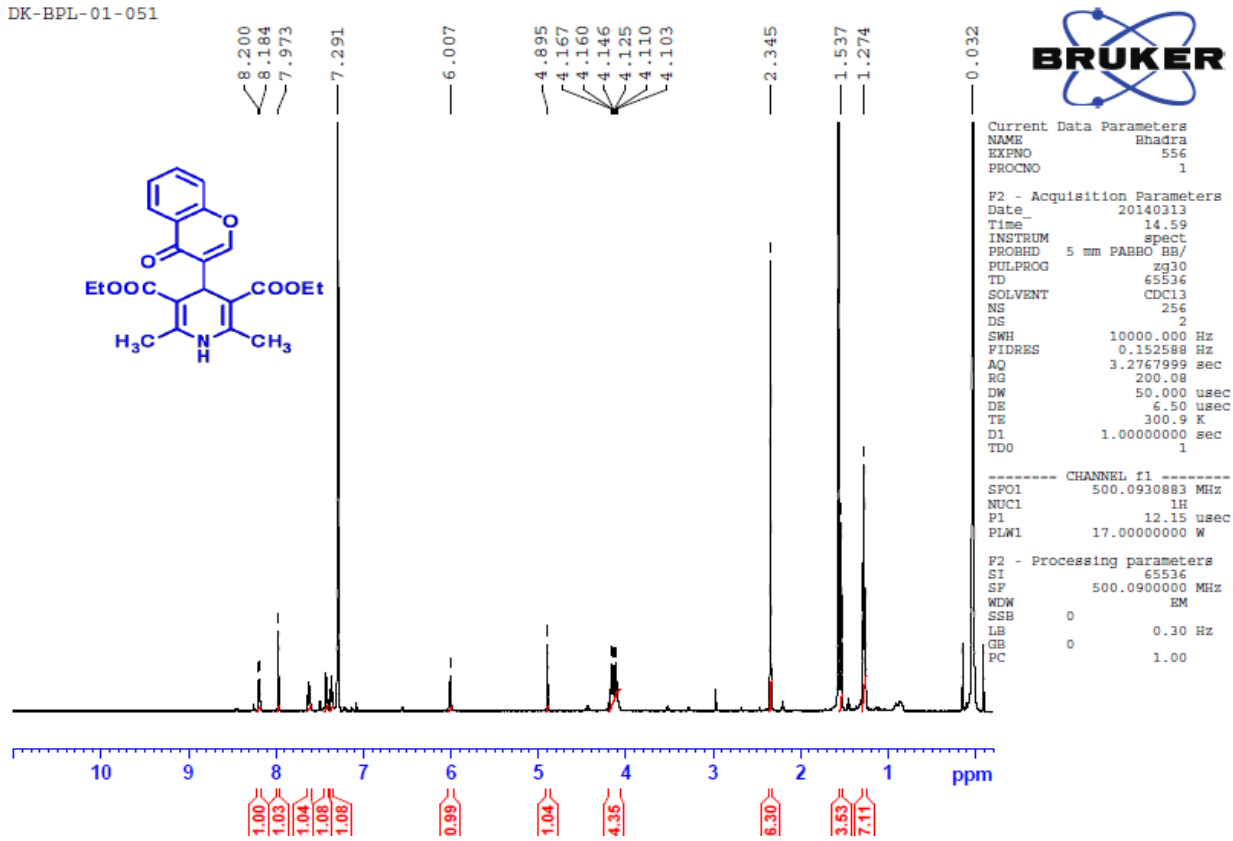
Diethyl 4-(1, 3 diphenyl-1*H*-pyrazole-4-yl)-2,6-dimethyl-1,4dihydropyridine-3,5-dicarboxylate(16):

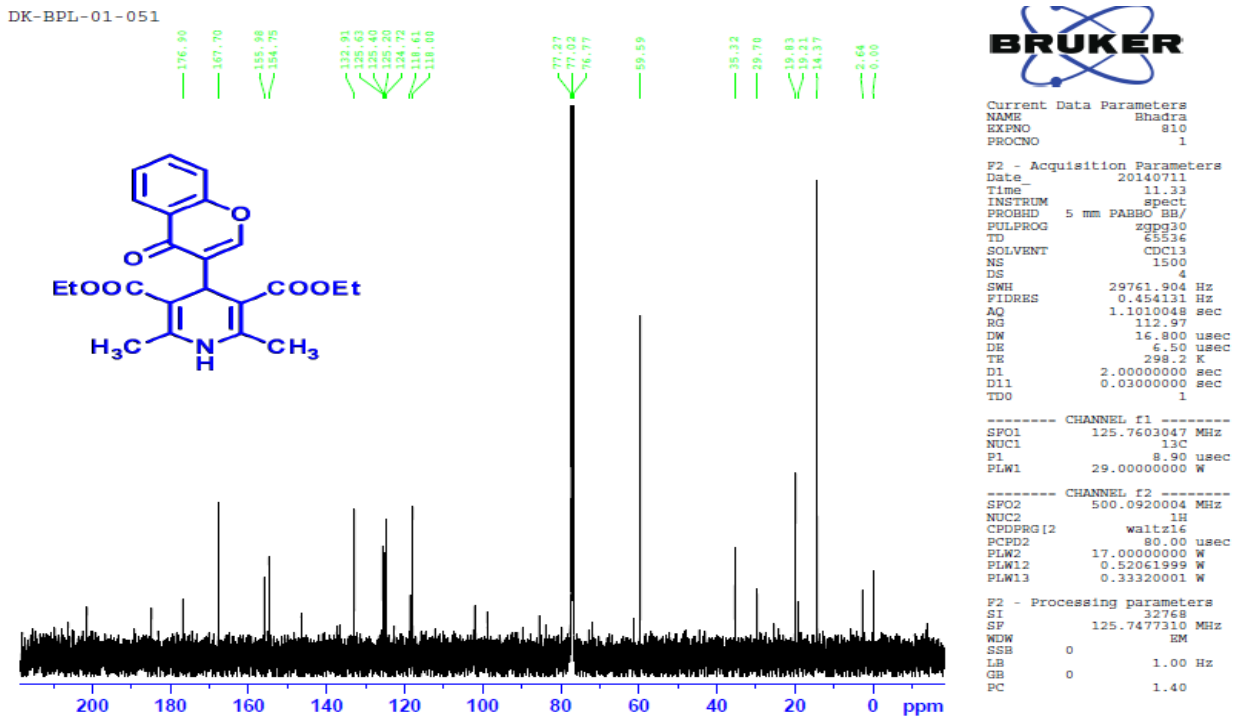




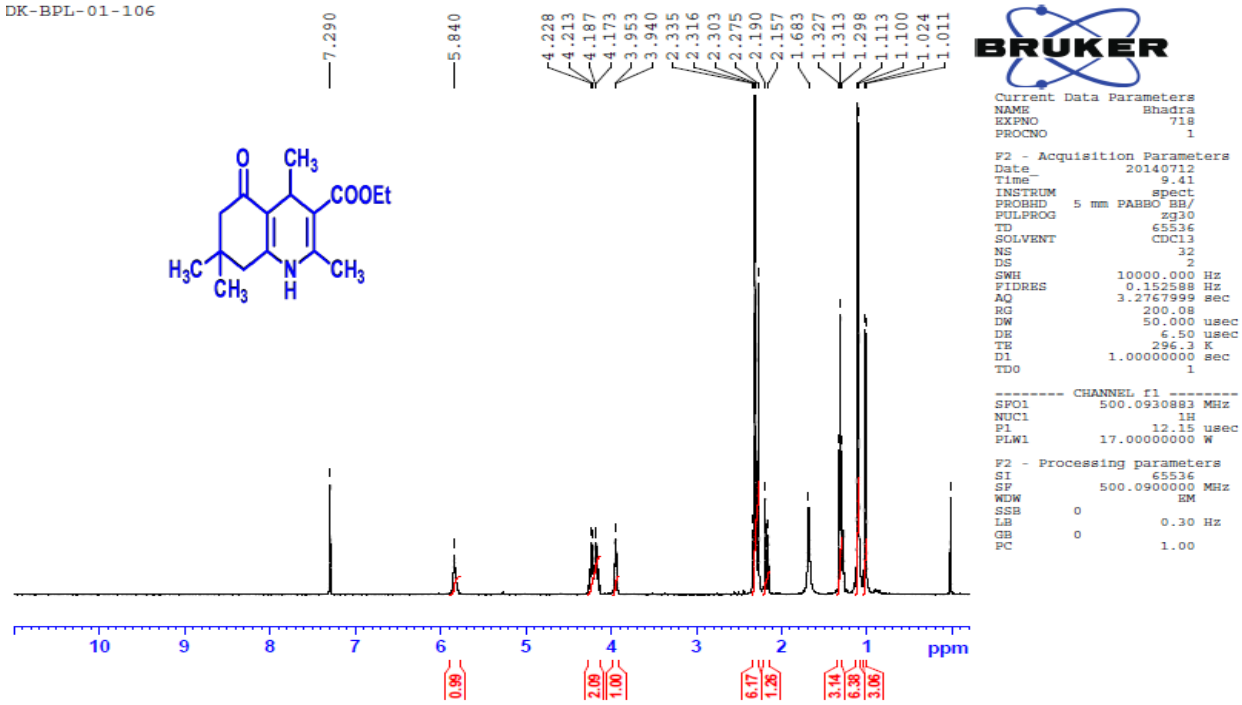


Diethyl 2, 6-dimethyl-,4-(4-oxo-4*H*-chromene-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate(17):

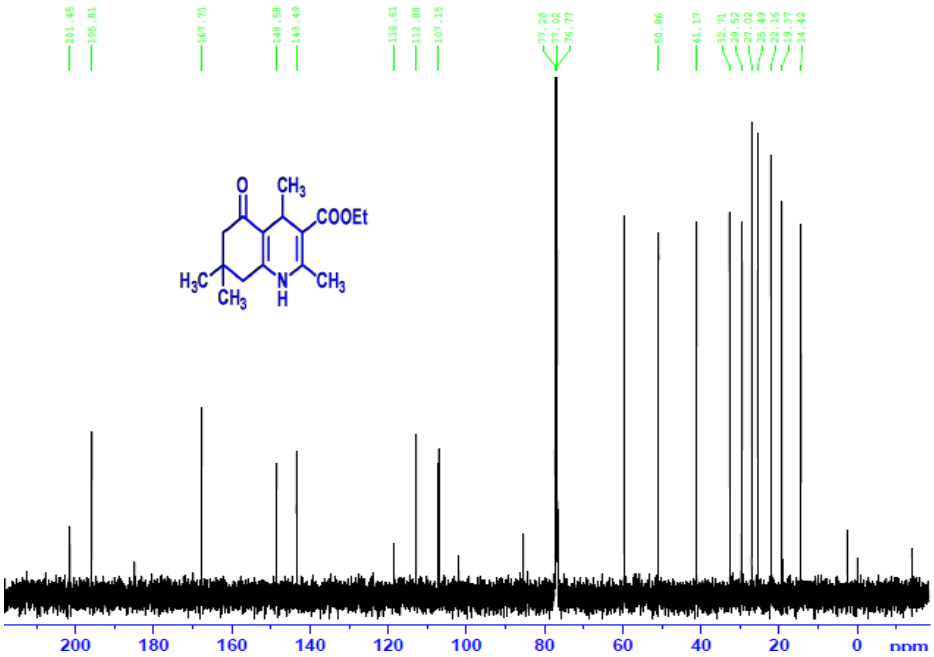




Ethyl 2,4,7,7-tetramethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3carboxylate(21):

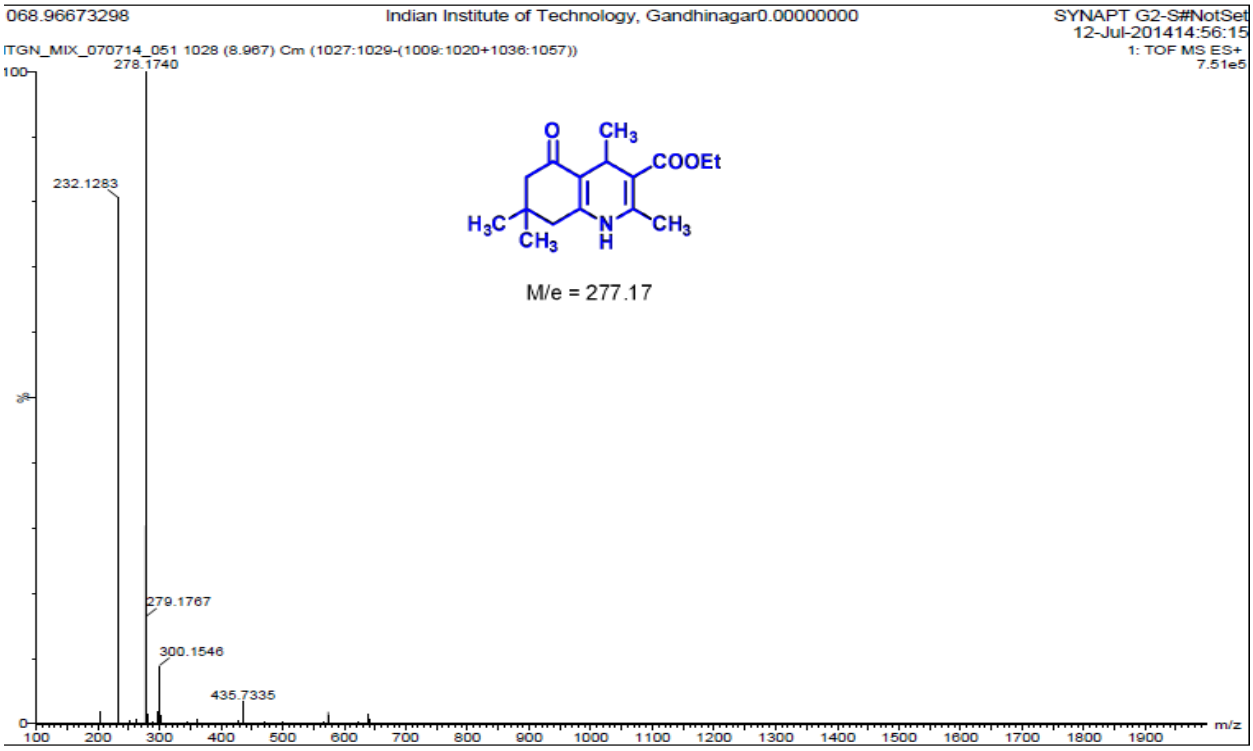


DK-BPL-01-106



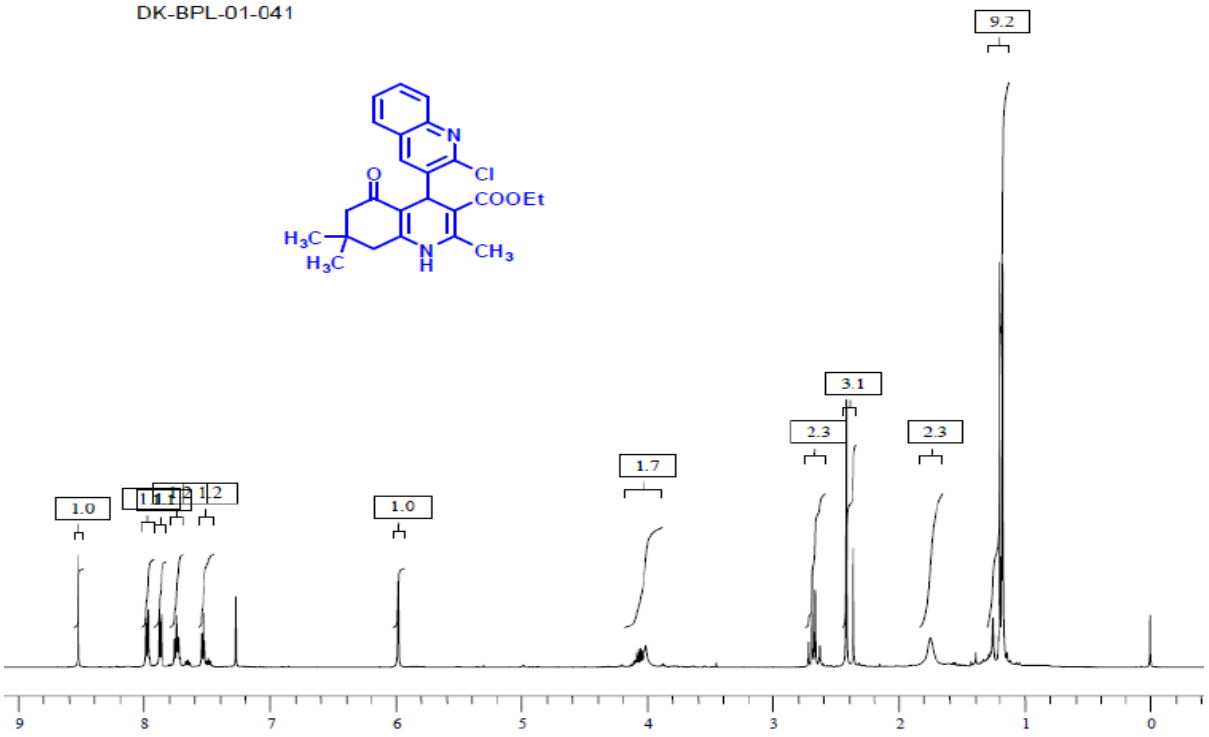
BRUKER

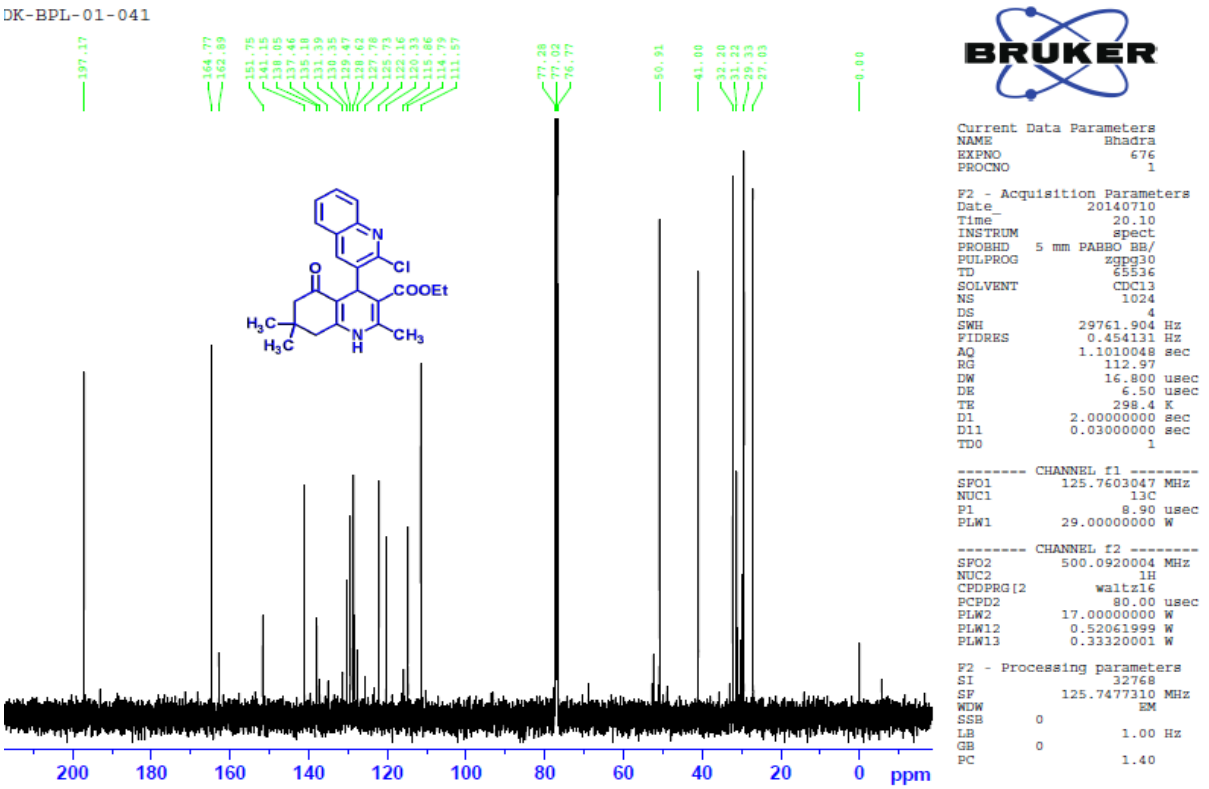
```
Current Data Parameters
NAME                  Bhadra
EXPNO                    719
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140712
Time                  10.41
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                  298.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                        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

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

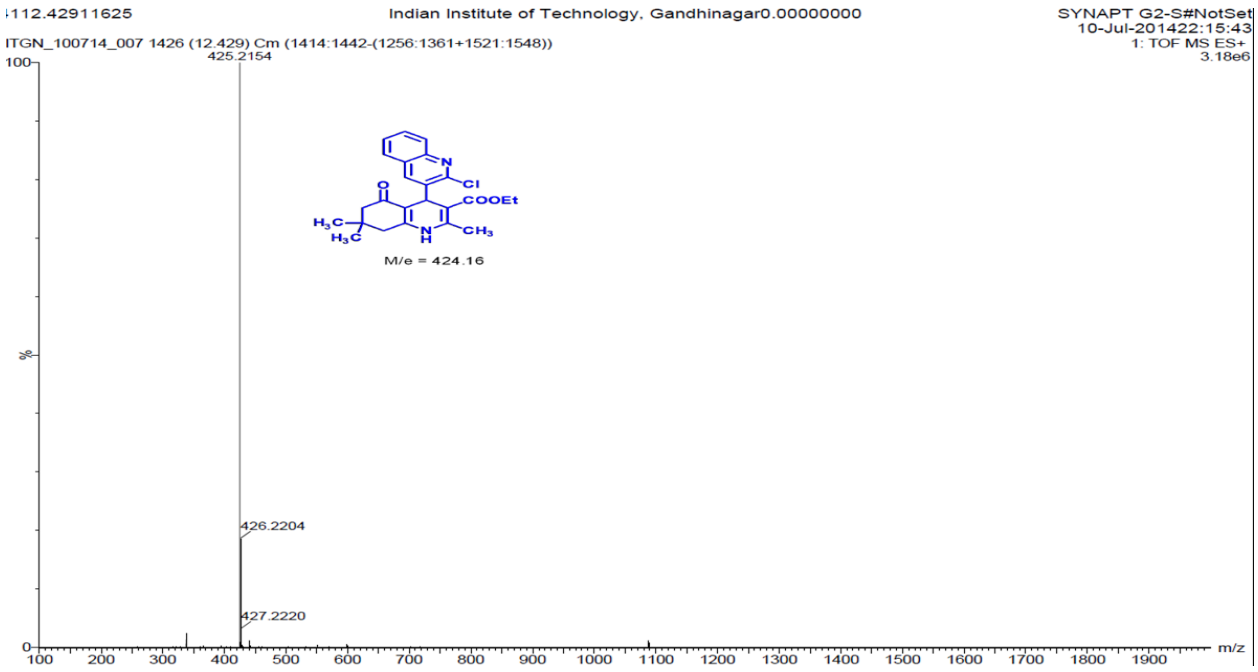


M/e = 277.17

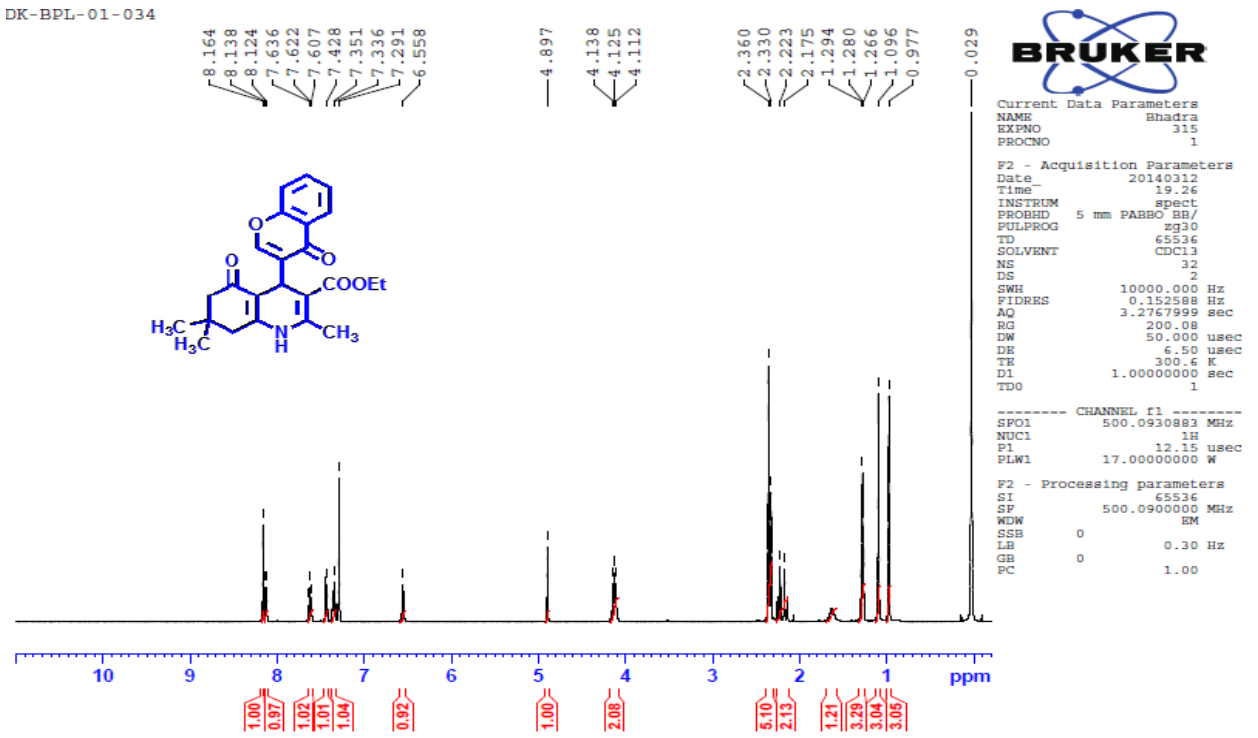
Ethyl 2-chloro-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydro-(3,4-biquinoline)-3-carboxylate (29):



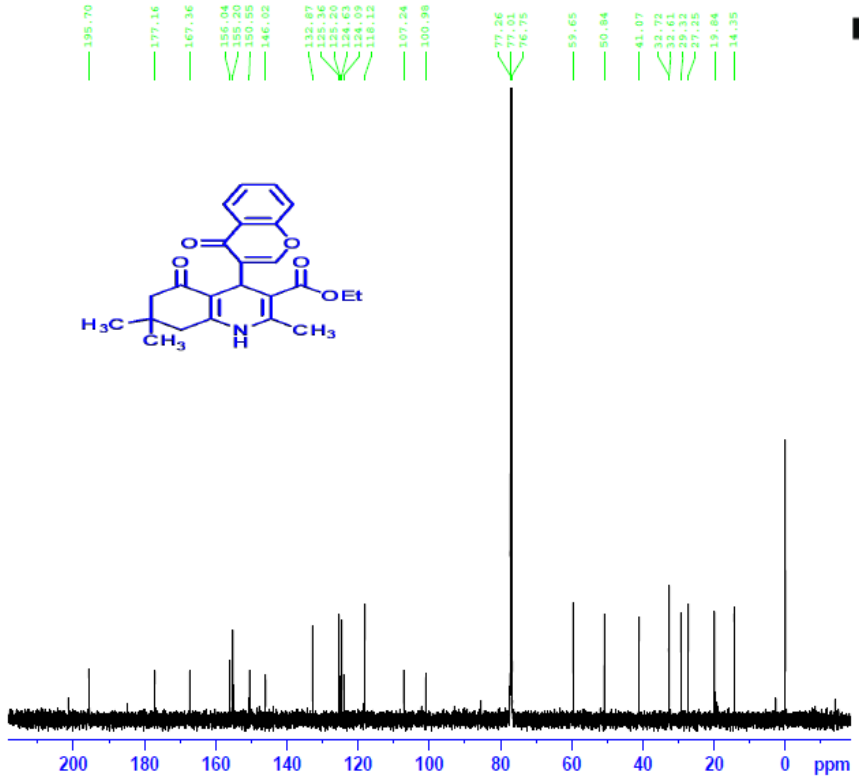




Ethyl 2,7,7-trimethyl-5-oxo-4-(4-oxo-4*H*-chromene-3-yl)-1,4,5,6,7,8-hexahydroquinoline -3-carboxylate (31):



DK-BPL-01-034



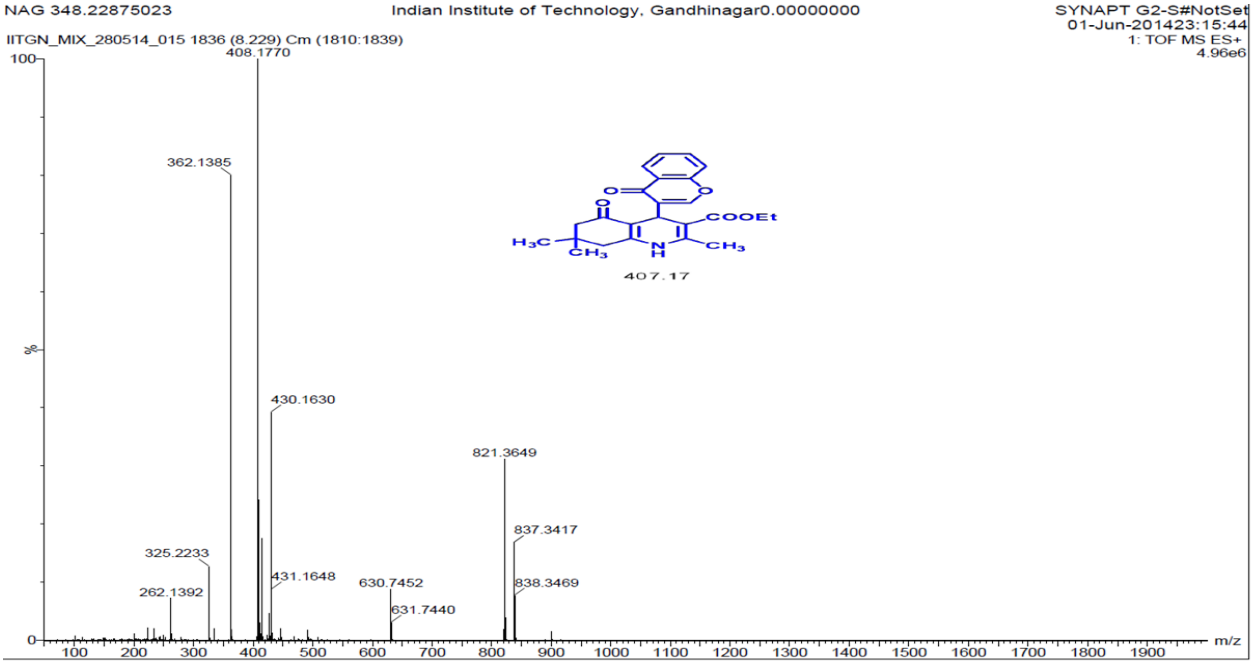
BRUKER

```
Current Data Parameters
NAME                  Bhadra
EXPNO                    956
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140712
Time               20.38
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                 302.6 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                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

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

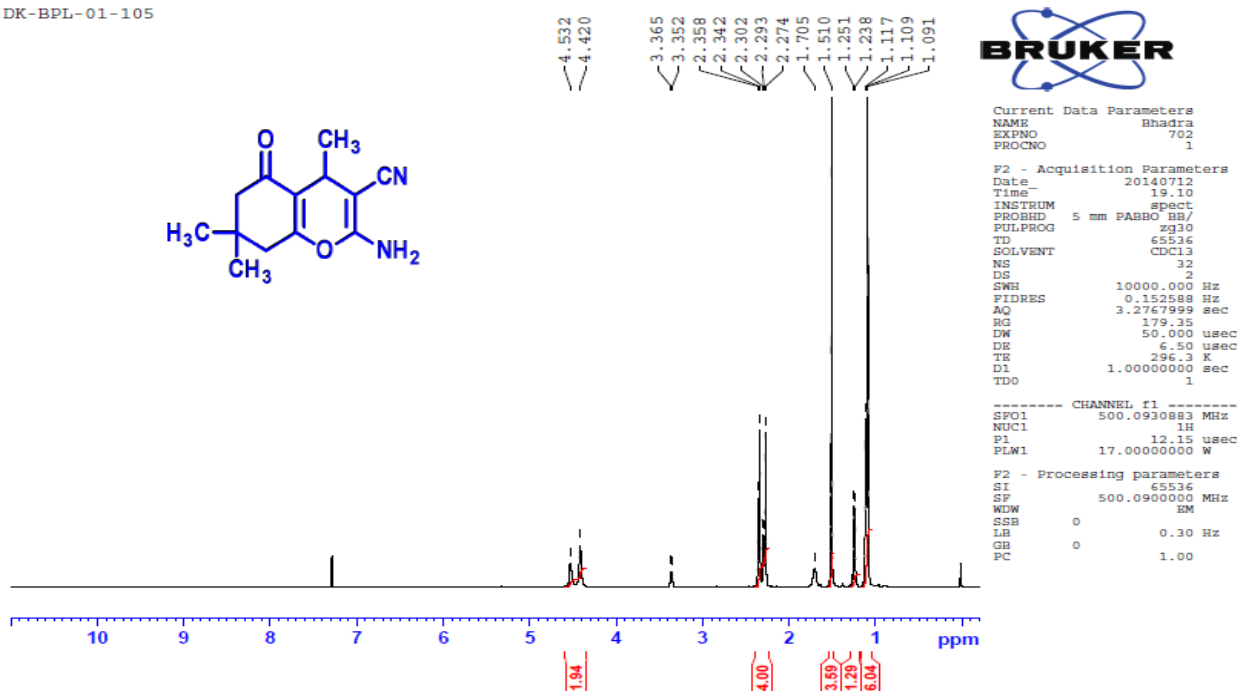
NAG 348.22875023 Indian Institute of Technology, Gandhinagar0.00000000

SYNAPT G2-S#NotSet
01-Jun-201423:15:44
1: TOF MS ES+
4.96e6

IITGN_MIX_280514_015 1836 (8.229) Cm (1810:1839)



2-amino-4,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (35):



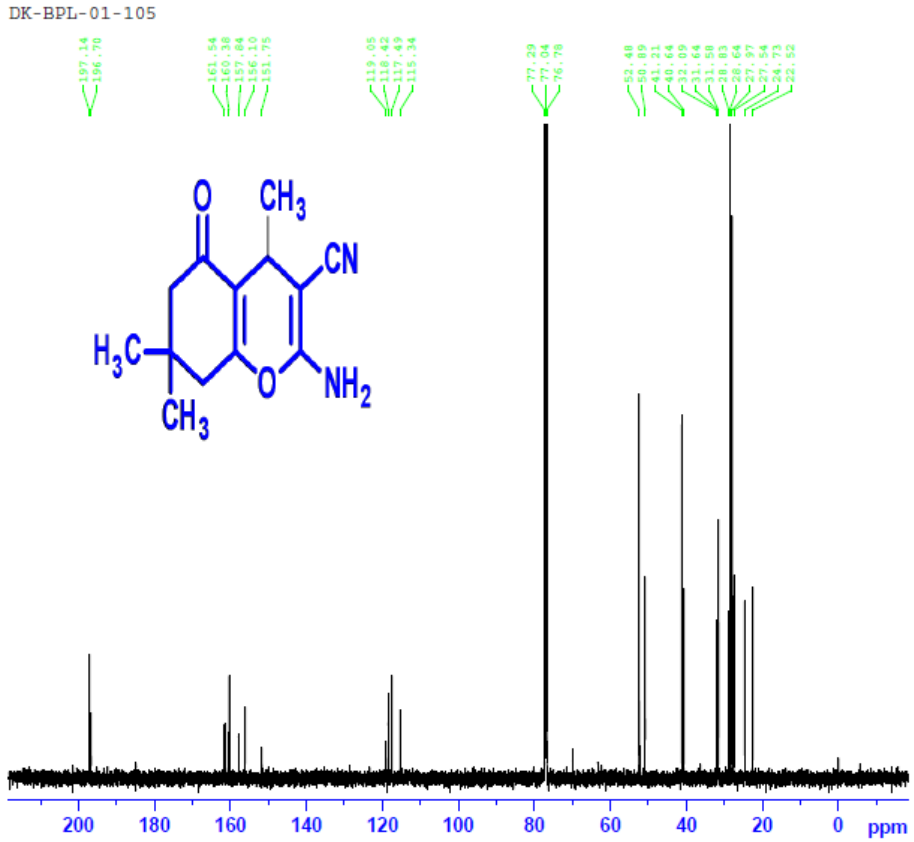
BRUKER

Current Data Parameters
NAME Bhadra
EXPNO 702
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140712
Time 19.10
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 179.35
DW 50.000 usec
DE 6.50 usec
TE 296.3 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
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

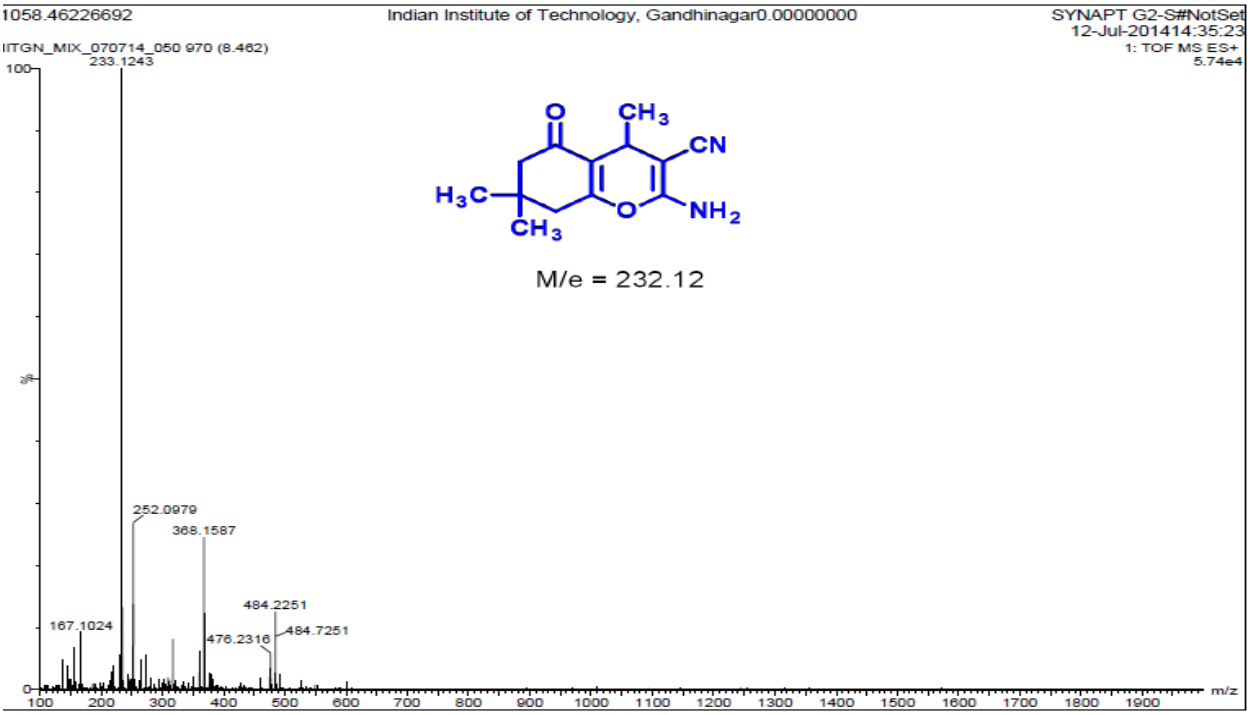
Current Data Parameters
NAME Bhadra
EXPNO 703
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140712
Time 20.07
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 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

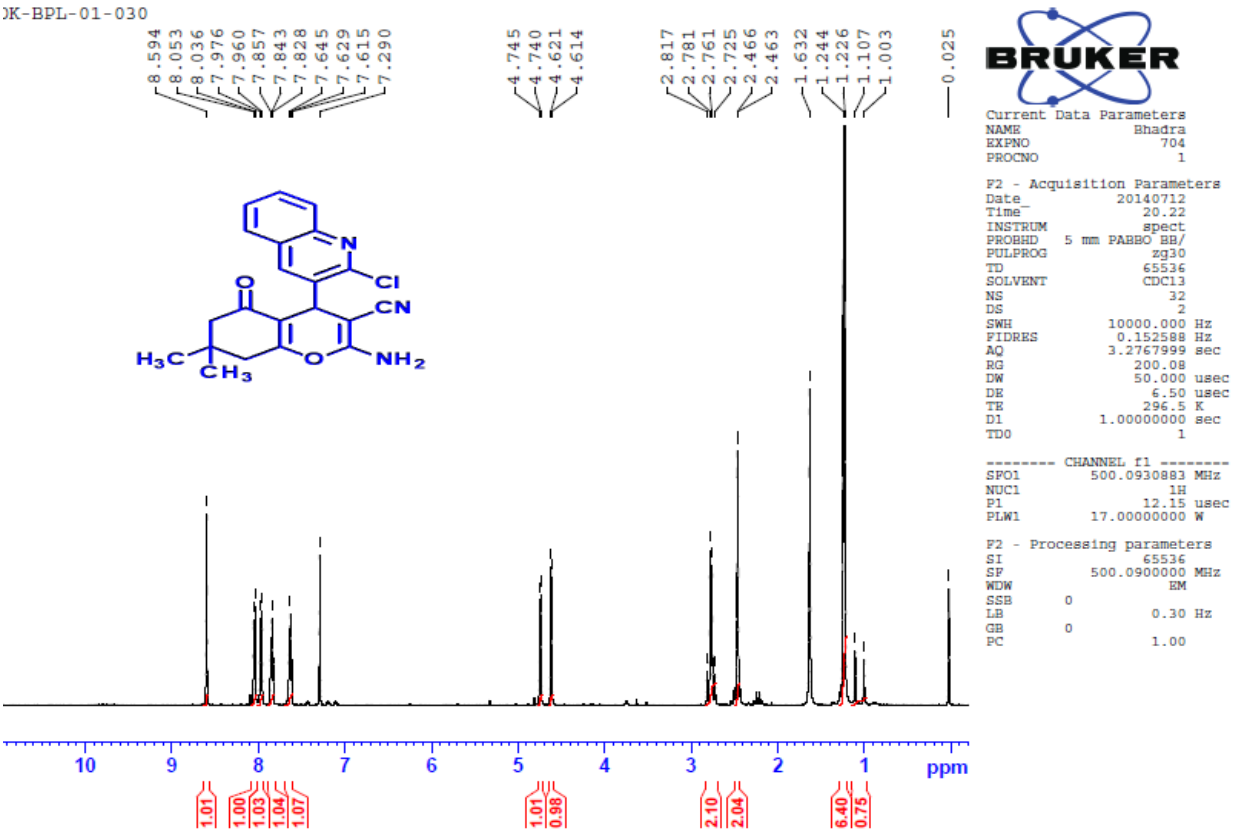
-------- CHANNEL f1 --------
SFO1 125.7603047 MHz
NUC1 13C
P1 8.90 usec
PLW1 29.00000000 W

-------- 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

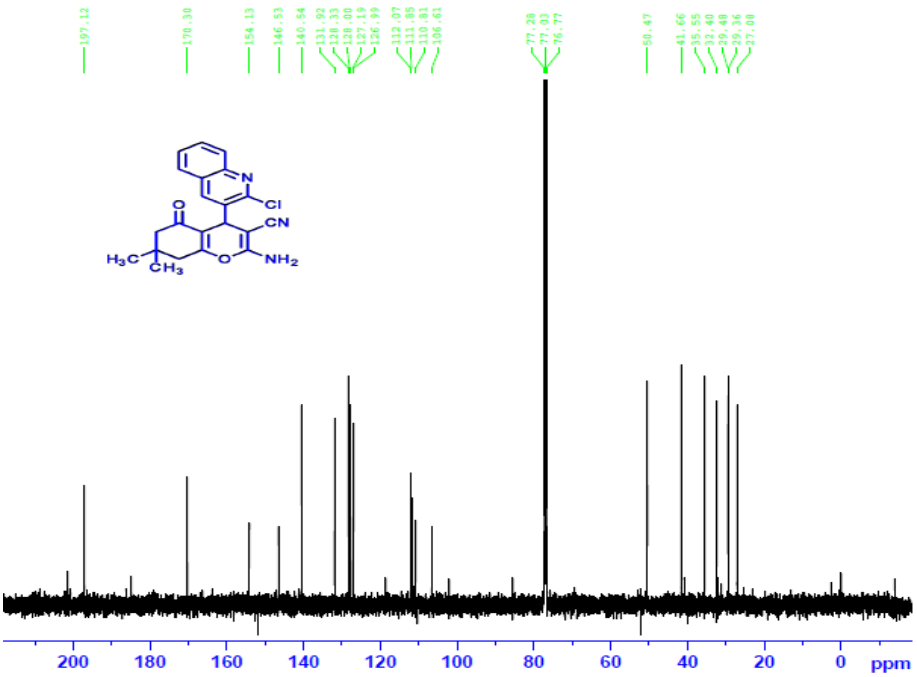
F2 - Processing parameters
SI 32768
SF 125.7477310 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



2-amino-4-(2-chloroquinolene-3-yl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-3-carbonitrile (43):



DK-BPL-01-030



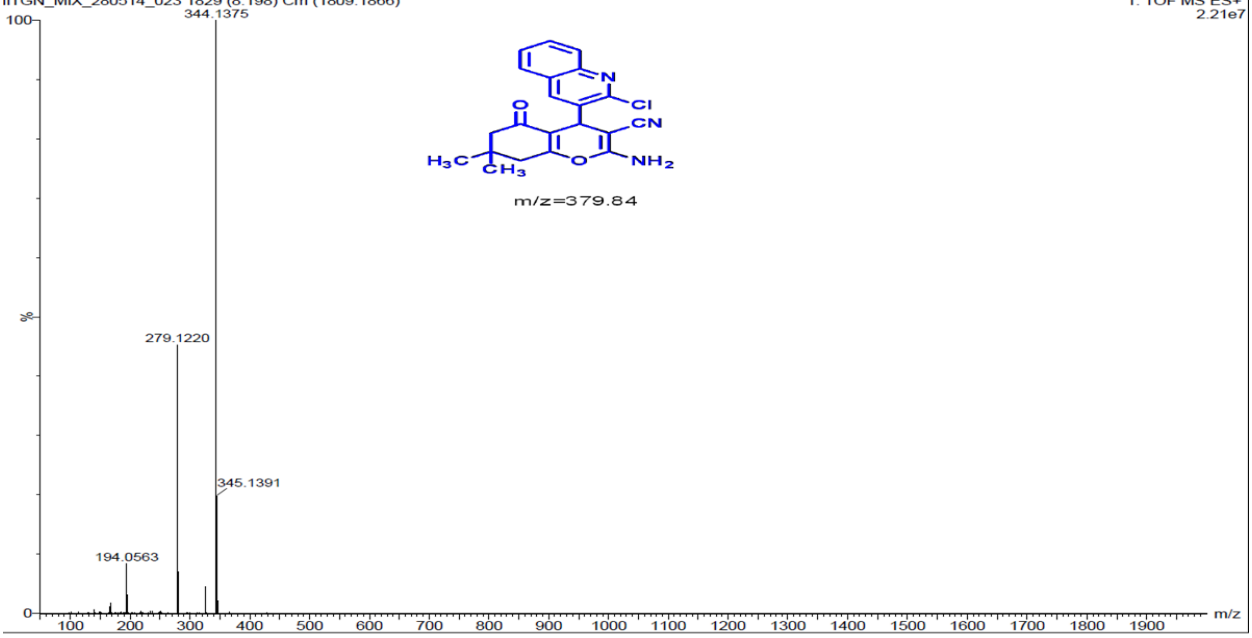
BRUKER

```
Current Data Parameters
NAME                  Bhadra
EXPNO                    705
PROCNO                     1

F2 - Acquisition Parameters
Date_              20140712
Time                  20.27
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                 297.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      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

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

NAG 308.19801712 Indian Institute of Technology, Gandhinagar0.00000000

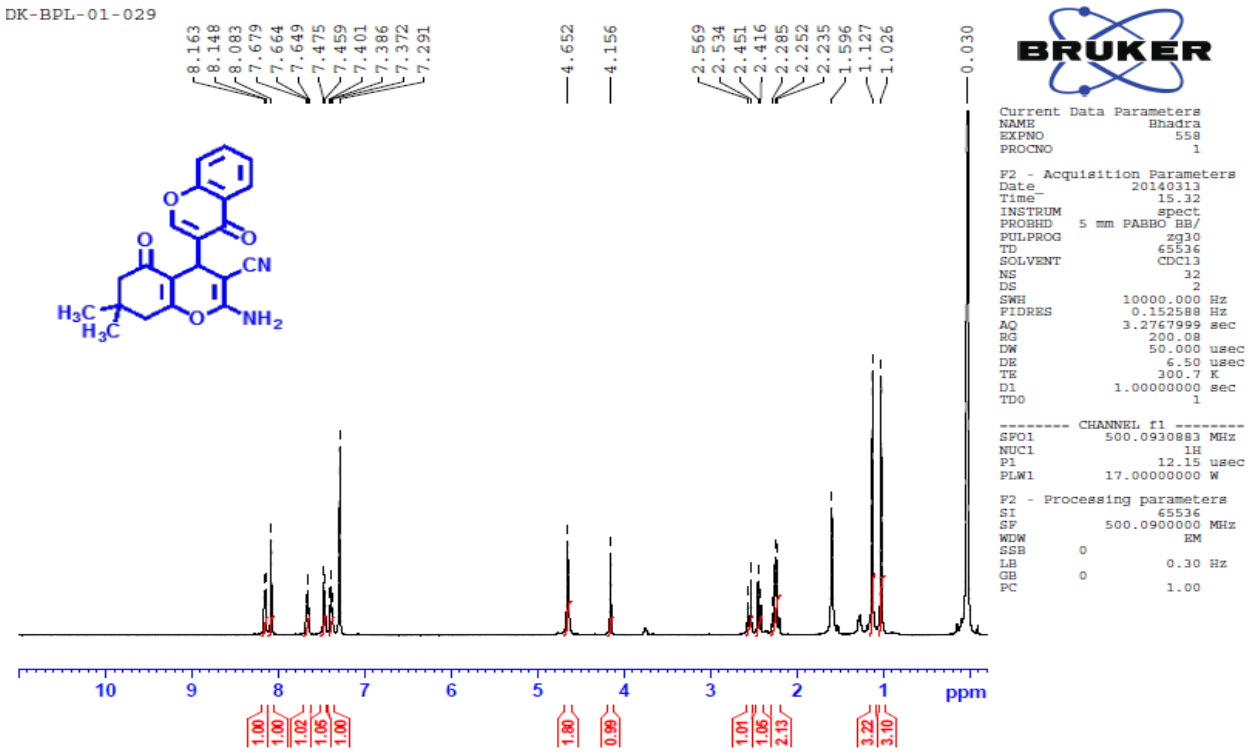
SYNAPT G2-S#NotSet
02-Jun-201417:44:51
1: TOF MS ES+
2.21e7

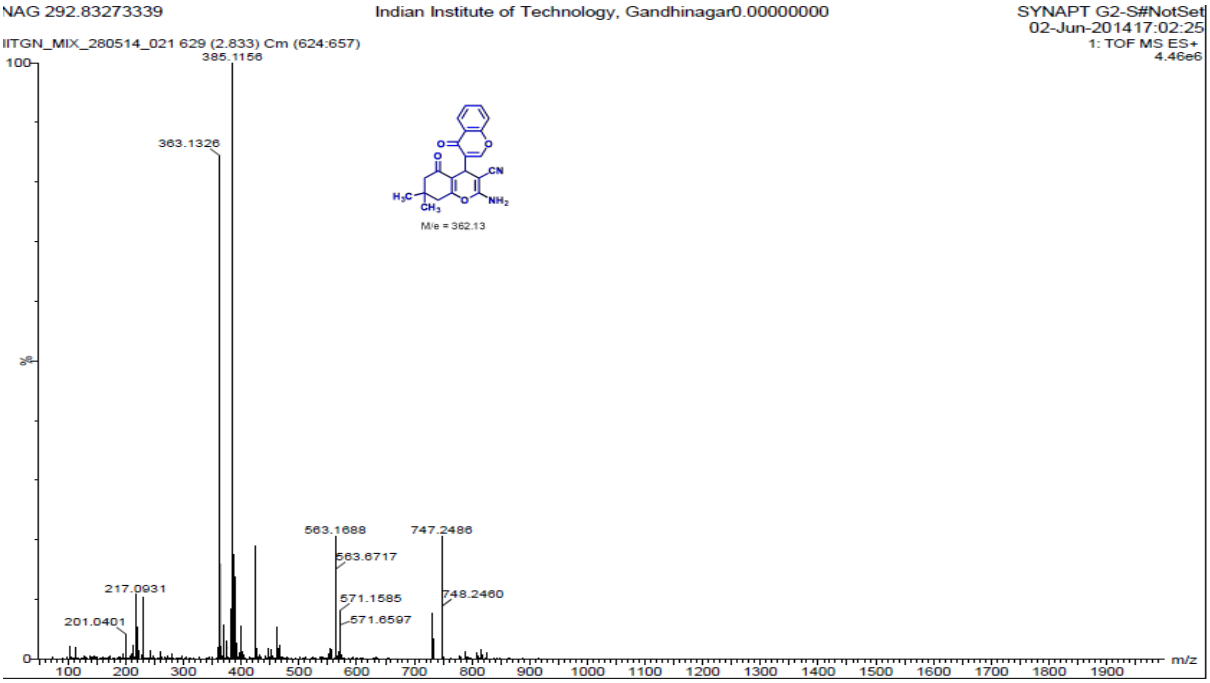
IITGN_MIX_280514_023 1829 (8.198) Cm (1809:1866)



m/z=379.84

2-amino-7,7-dimethyl-4,5-dioxo-5,6,7,8-tetrahydro-4*H*,4'*H*-(3,4'-bichromene)-3-carbonitrile (45):





3-amino-1-(4-oxo-4*H*-chromene-3-yl)-1*H*-benzo(*f*)chromene-2-carbonitrile(60):