

## Supporting Information

### **Synthesis and characterization of Glucosulfonic acid supported on Fe<sub>3</sub>O<sub>4</sub> nanoparticles as novel and magnetically recoverable nanocatalyst and its application in the synthesis of polyhydroquinoline and 2,3-dihydroquinazolin-4(1H)-one derivatives**

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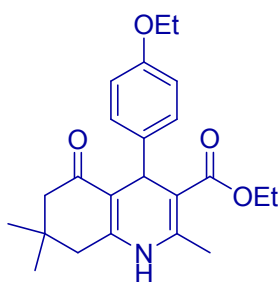
E-mail address: [mhajjami@yahoo.com](mailto:mhajjami@yahoo.com) or [m.hajjami@mail.ilam.ac.ir](mailto:m.hajjami@mail.ilam.ac.ir)

### **General procedure for the synthesis of polyhydroquinoline derivatives**

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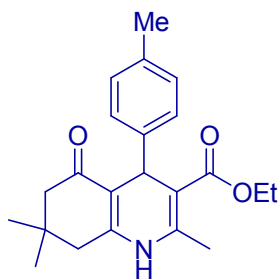
A mixture of aldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol), ammonium acetate (1.2 mmol) and GSA@MNPs (0.05 g) was stirred in ethanol under reflux conditions and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet and washed with ethylacetate. Then, the solvent was evaporated and all products were recrystallized in ethanol, which the pure polyhydroquinoline derivatives were obtained in good to excellent yields.

### Compounds Characterization Data



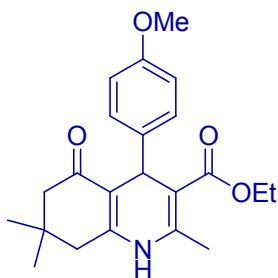
#### **Ethyl-4-(4-ethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, table 2):**

Mp: 176-179 °C. IR (KBr)  $\text{cm}^{-1}$ : 3446, 3276, 3198, 1684, 1607, 1494.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$  = 7.28-7.19 (m, 2H), 6.74-6.72 (d,  $J=8$ , 2H), 5.80 (s, 1H), 4.99 (s, 1H), 4.07-4.05 (t,  $J=4$ , 2H), 3.97-3.96 (t,  $J=3.6$ , 2H), 2.39-2.15 (m, 7H), 1.38-1.37 (m, 3H), 1.21-1.20 (m, 3H), 1.07 (s, 3H), 0.95 (s, 3H) ppm.



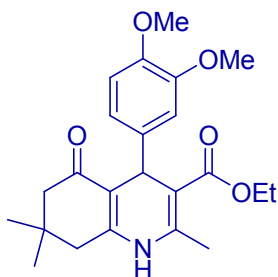
#### **Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 3, table 2):**

Mp: 252-254 °C. IR (KBr)  $\text{cm}^{-1}$ : 3276, 3246, 3208, 1702, 1648, 1423.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$ = 9.04 (s, 1H), 7.05-7.03 (d,  $J=8$ , 2H), 7.00-6.98 (d,  $J=8$ , 2H), 4.82 (s, 1H), 4.00-3.95 (q,  $J=7.2$ , 2H), 2.45-2.41 (d,  $J=16$ , 1H), 2.31-2.27 (m, 4H), 2.21-2.15 (m, 4H), 2.10-1.96 (d,  $J=16$ , 1H), 1.17-1.13 (t,  $J=6.8$ , 3H), 1.02 (s, 3H), 0.86 (s, 3H) ppm.



**Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, table 2):**

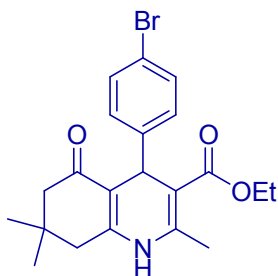
Mp: 249-250 °C. IR (KBr)  $\text{cm}^{-1}$ : 3278, 3246, 3208, 1701, 1649, 1423.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$ = 9.04 (s, 1H), 7.08-7.06 (d,  $J=8.4$ , 2H), 6.77-6.75 (d,  $J=8.4$ , 2H), 4.80 (s, 1H), 4.02-3.96 (q,  $J=7.2$ , 2H), 3.69 (s, 3H), 2.52-2.45 (d,  $J=29.2$ , 1H), 2.31-2.29 (m, 4H), 2.20-2.16 (d,  $J=16$ , 1H), 2.01-1.97 (d,  $J=16.4$ , 1H), 1.17-1.14 (t,  $J=7.2$ , 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.



**Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, table 2):**

Mp: 204-205 °C. IR (KBr)  $\text{cm}^{-1}$ : 3280, 3213, 1696, 1645, 1452.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$ = 9.05 (s, 1H), 6.79-6.76 (m, 2H), 6.65-6.63 (d,  $J=8$ , 1H), 4.80 (s, 1H), 4.04-3.99 (q,  $J=7.2$ ,

2H), 3.69-3.68 (d,  $J=4.4$ , 5H), 2.47-2.42 (d,  $J=17.2$ , 2H), 2.35-2.27 (m, 4H), 2.22-2.18 (d,  $J=16$ , 1H), 2.03-1.99 (d,  $J=16$ , 1H), 1.20-1.16 (t,  $J=6.8$ , 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.



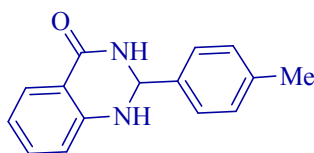
**Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 8, table 2):**

Mp: 251-252 °C. IR (KBr)  $\text{cm}^{-1}$ : 3276, 3243, 3207, 1703, 1649, 1421.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}=$  9.14 (s, 1H), 7.41-7.39 (d,  $J=8.4$ , 2H), 7.13-7.11 (d,  $J=8$ , 2H), 4.84 (s, 1H), 4.01-3.96 (q,  $J=6.8$ , 2H), 2.52-2.46 (d,  $J=26.4$ , 1H), 2.31-2.27 (m, 4H), 2.21-2.17 (d,  $J=16$ , 1H), 2.01-1.97 (d,  $J=16$ , 1H), 1.15-1.12 (t,  $J=7.2$ , 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.

**General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives**

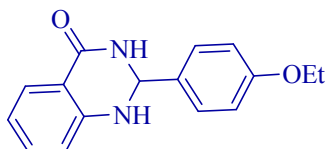
A mixture of GSA@MNPs (0.01 g), anthranilamide (1 mmol) and aldehyde (1 mmol) was stirred at 80 °C in ethanol (2 mL). The progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature.  $\text{CH}_2\text{Cl}_2$  (2  $\times$  5 mL) was added and the catalyst was separated using an external magnet.  $\text{CH}_2\text{Cl}_2$  was evaporated under reduced pressure to afford the essentially pure products and all products was recrystallized in ethanol for further purification.

**Compound Characterization Data**



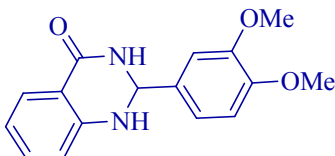
**2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 4, table 4):**

Mp: 228-230 °C. IR (KBr)  $\text{cm}^{-1}$ : 3313, 1658, 1611, 1439.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$  = 8.21 (s, 1H), 7.62-7.59 (d,  $J=7.5$ , 1H), 7.38-7.35 (d,  $J=7.5$ , 2H), 7.26-7.14 (m, 3H), 7.03 (s, 1H), 6.75-6.64 (m, 2H), 5.71 (s, 1H), 2.49-2.42 (s, 3H) ppm.



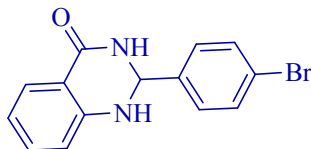
**2-(4-ethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 5, table 4):**

Mp: 167-169 °C. IR (KBr)  $\text{cm}^{-1}$ : 3301, 1650, 1613, 1443.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$  = 7.95-7.94 (b, 1H), 7.52-7.50 (m, 2H), 7.34 (s, 1H), 7.26 (s, 1H), 6.95-6.90 (m, 3H), 6.68-6.67 (m, 1H), 5.85 (s, 1H), 5.75 (s, 1H), 4.07-4.05 (q,  $J=4$ , 2H), 1.46-1.44 (s, 3H) ppm.



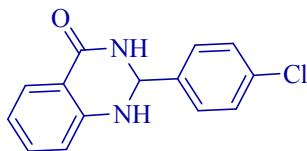
**2-(3,4-dimethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 6, table 4):**

Mp: 211-213 °C. IR (KBr)  $\text{cm}^{-1}$ : 3335, 1671, 1610, 1436.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}$  = 8.21 (s, 1H), 7.64-7.62 (d,  $J=7.6$ , 1H), 7.28-7.24 (t,  $J=0.8$ , 1H), 7.15 (d,  $J=1.6$ , 1H), 7.04-6.97 (m, 2H), 6.95 (s, 1H), 6.78-6.76 (d,  $J=8$ , 1H), 6.72-6.67 (t,  $J=1.2$ , 1H), 5.71 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H) ppm.



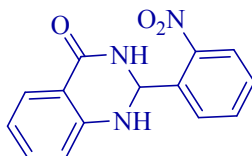
**2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 8, table 4):**

Mp: 197-199 °C. IR (KBr)  $\text{cm}^{-1}$ : 3310, 1656, 1608, 1433.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}=$  8.17-8.14 (m, 1H), 7.80-7.78 (m, 1H), 7.63-7.59 (m, 3H), 7.47-7.44 (m, 2H), 7.30-7.24 (m, 1H), 6.77-6.72 (d,  $J=19.2$ , 1H), 6.71-6.68 (m, 1H), 5.76 (s, 1H) ppm.



**2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 9, table 4):**

Mp: 202-204 °C. IR (KBr)  $\text{cm}^{-1}$ : 3309, 1655, 1611, 1435.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}=$  8.29 (s, 1H), 7.61-7.43 (m, 5H), 7.26-7.20 (t,  $J=7.5$ , 1H), 7.12 (s, 1H), 6.75-6.63 (m, 2H), 5.75 (s, 1H) ppm.

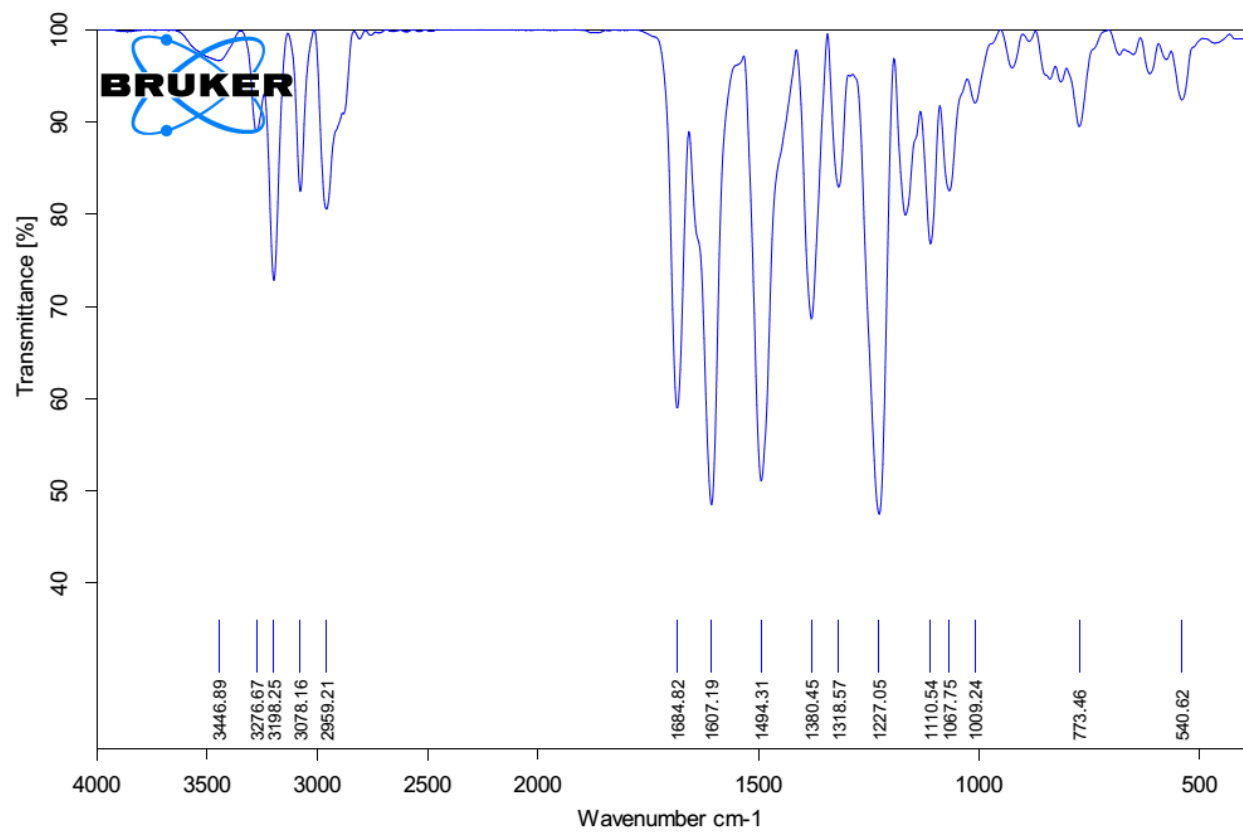


**2-(2-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 10, table 4):**

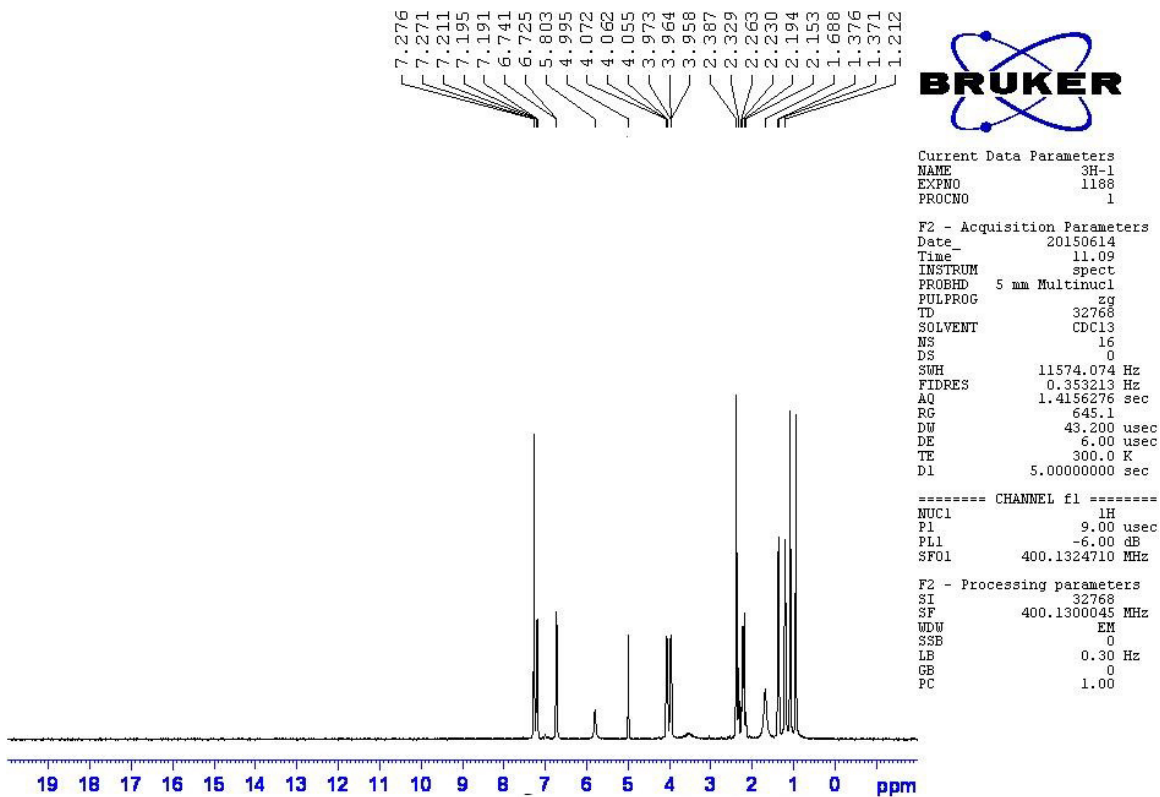
Mp: 190-192 °C. IR (KBr)  $\text{cm}^{-1}$ : 3372, 1667, 1613, 1517, 1453, 1342.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_{\text{H}}=$  8.26 (s, 1H), 8.10-8.08 (d,  $J=8$ , 1H), 7.89-7.87 (d,  $J=8$ , 1H), 7.83-7.80 (t,  $J=0.8$ , 1H), 7.70-7.63 (m, 2H), 7.30-7.26 (m, 1H), 7.04 (s, 1H), 6.81 (d,  $J=1.2$ , 1H), 6.77-6.72 (m, 1H), 6.36 (m, 1H) ppm.

**IR and  $^1\text{H}$ NMR Spectra**

**IR of Ethyl-4-(4-ethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, table 2)**

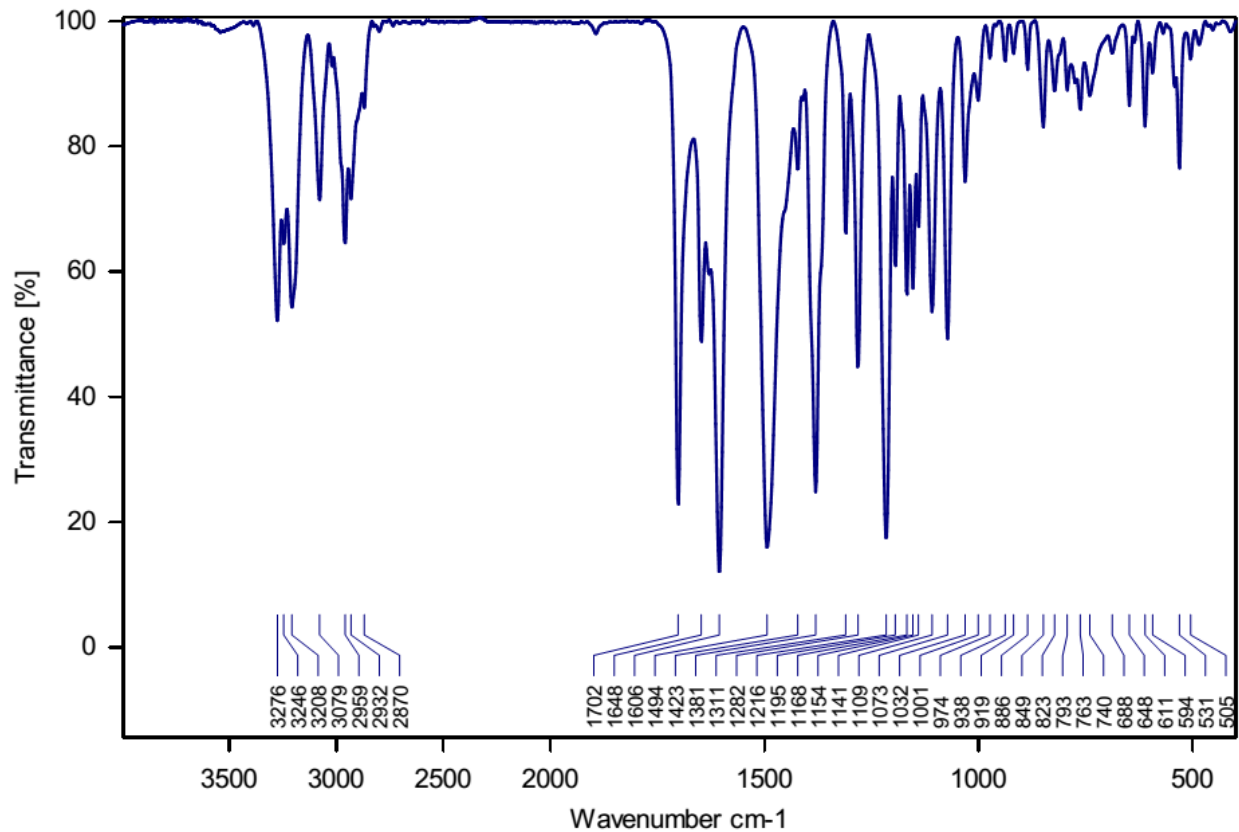


**<sup>1</sup>H NMR of Ethyl-4-(4-ethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, table 2)**

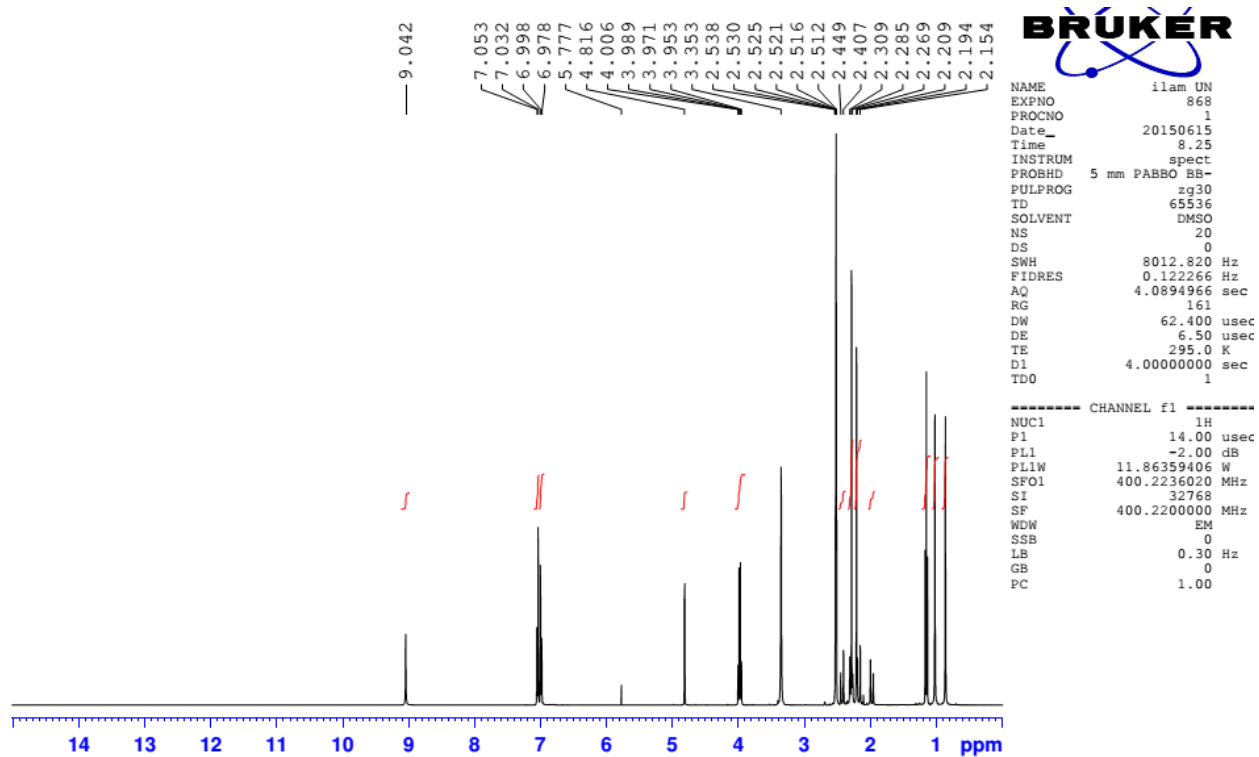


**IR of Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 3, table 2)**

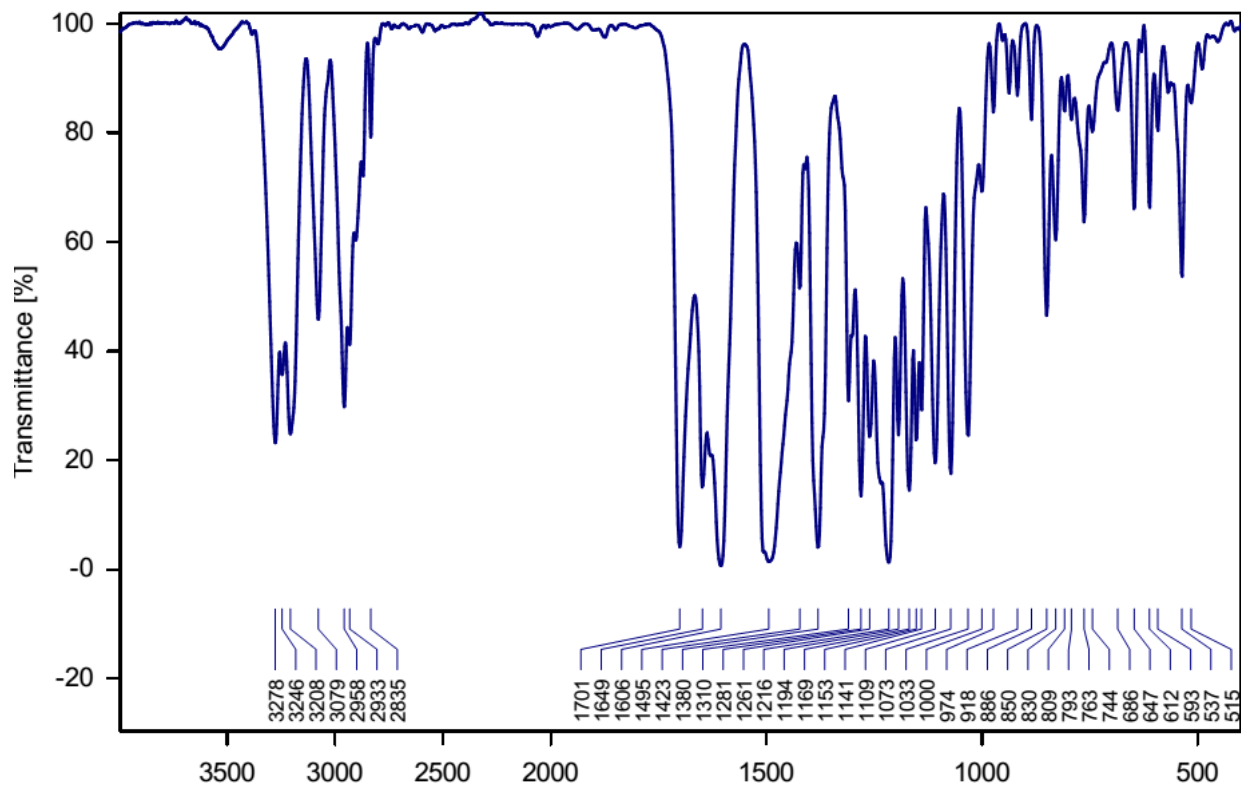




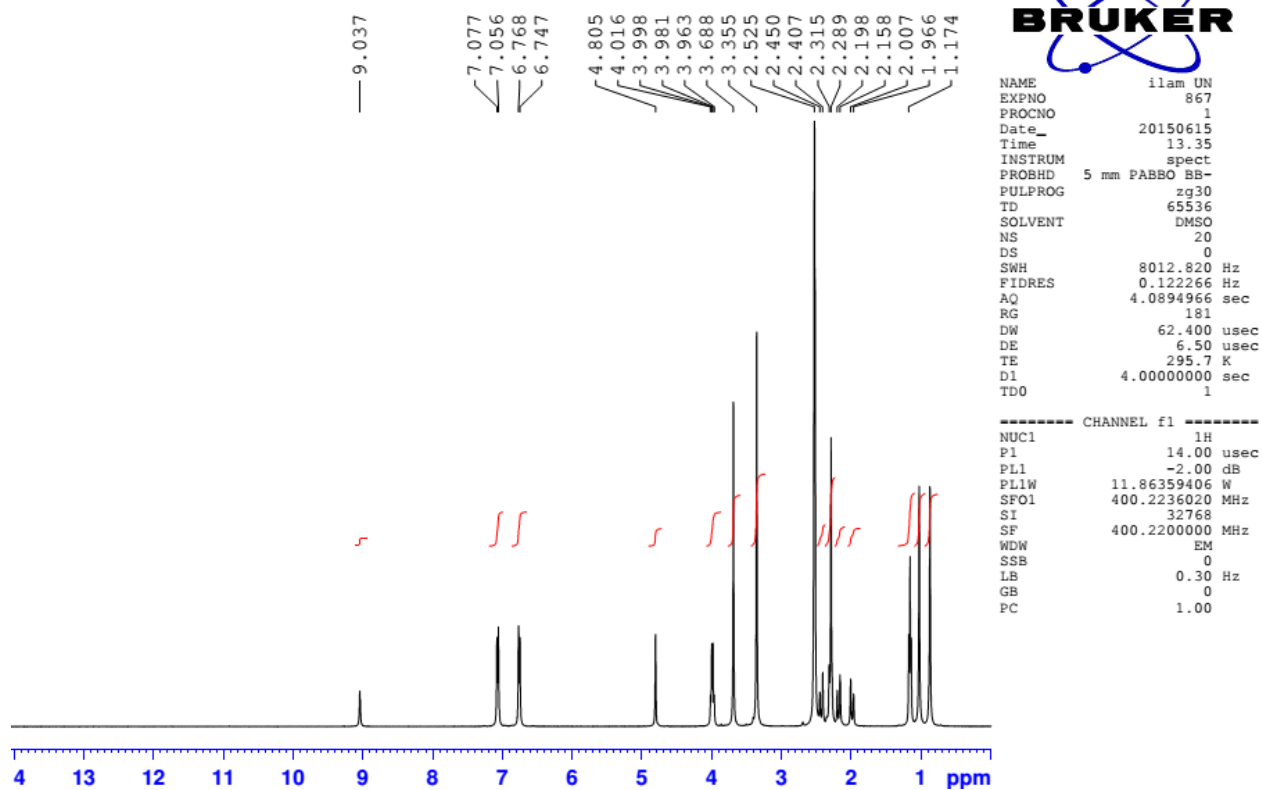
**<sup>1</sup>HNMR of Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 3, table 2)**



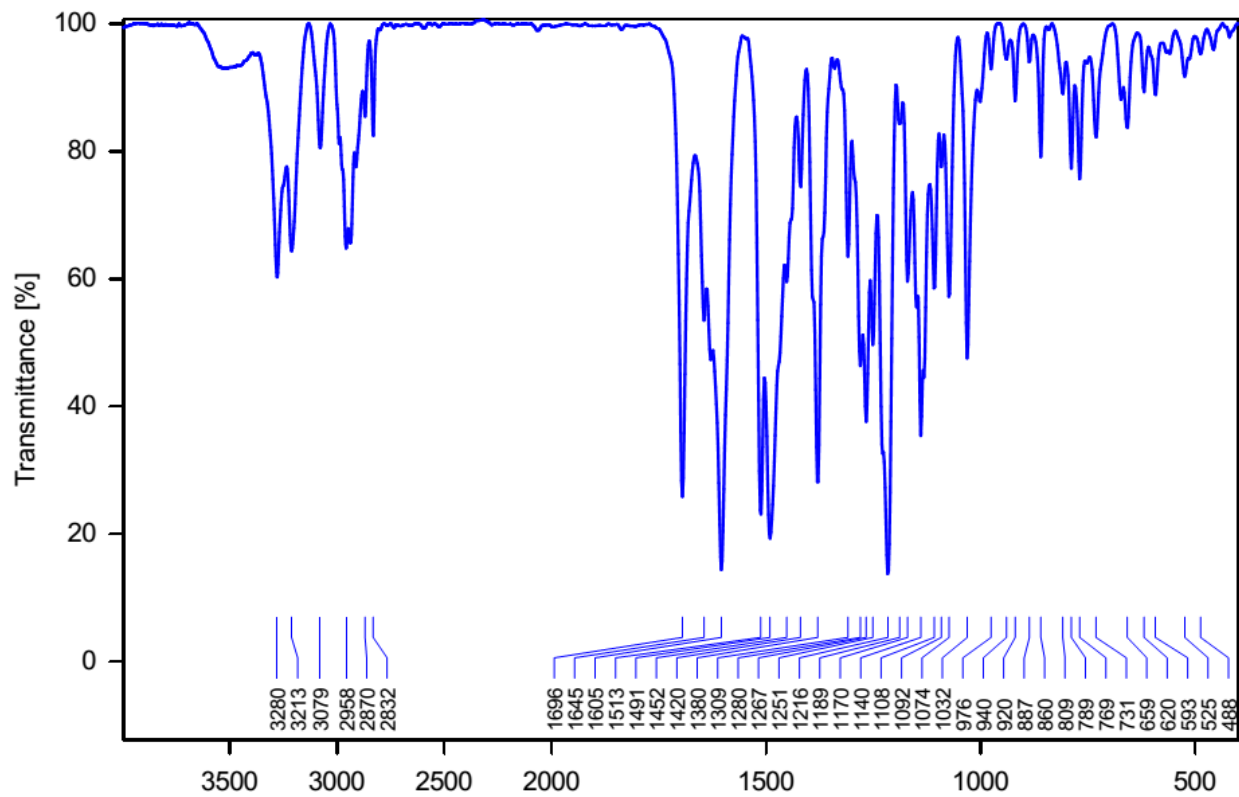
IR of Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, table 2)



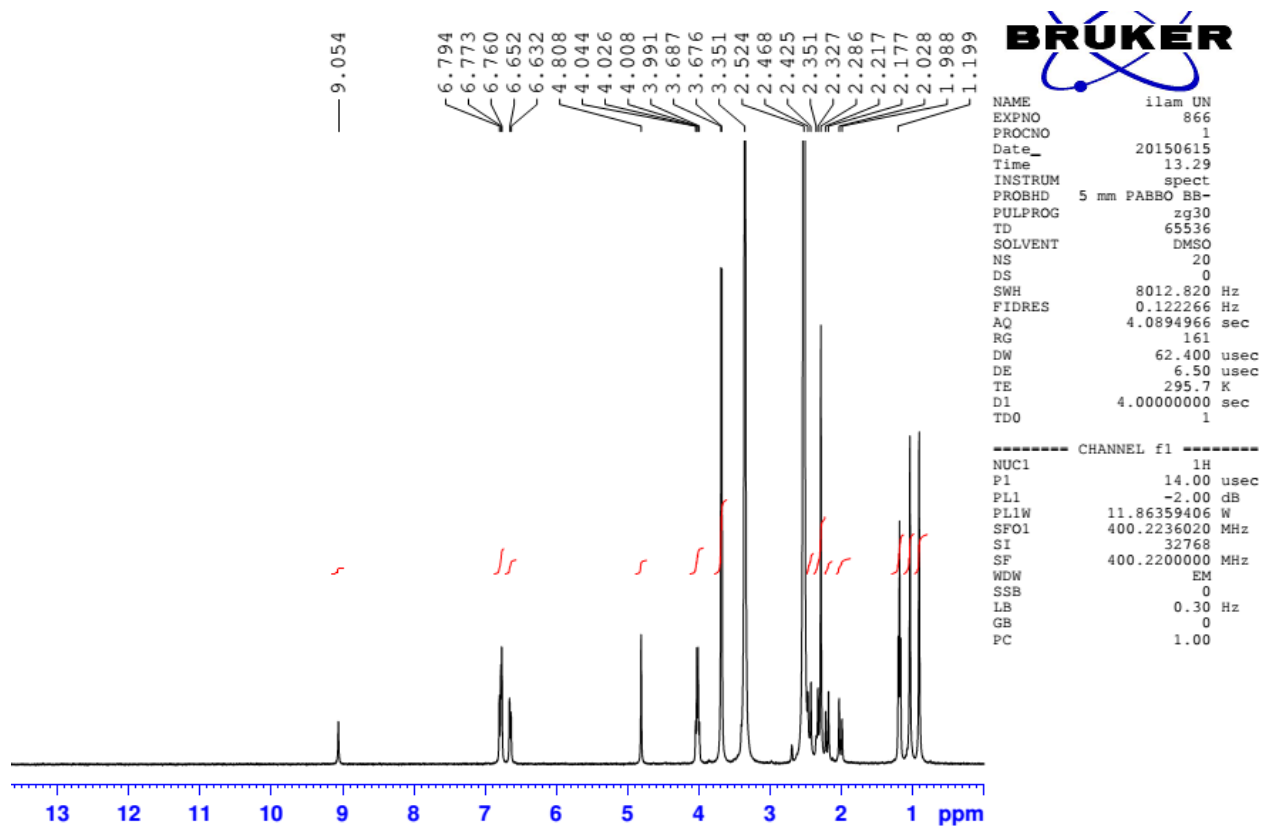
**<sup>1</sup>HNMR of Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, table 2)**



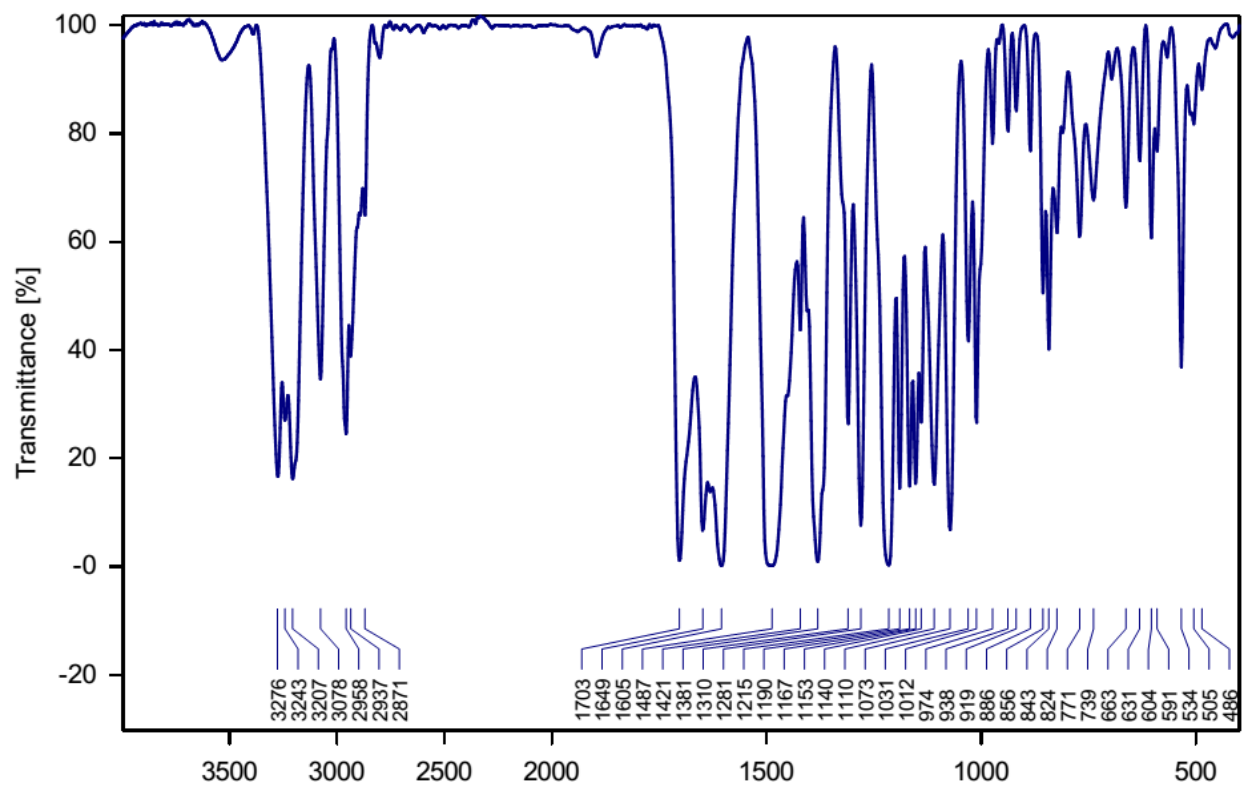
**IR of Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, table 2)**



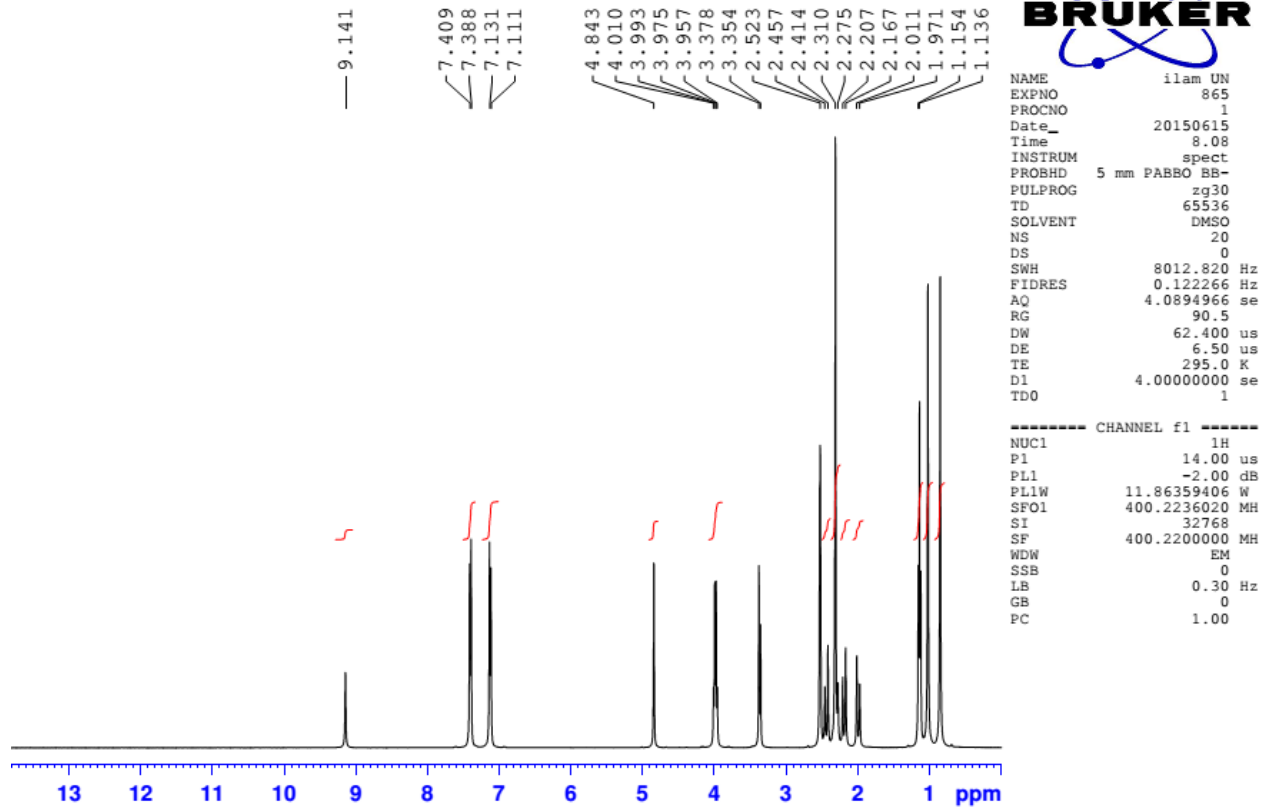
**<sup>1</sup>HNMR of Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, table 2)**



**IR of Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 8, table 2)**

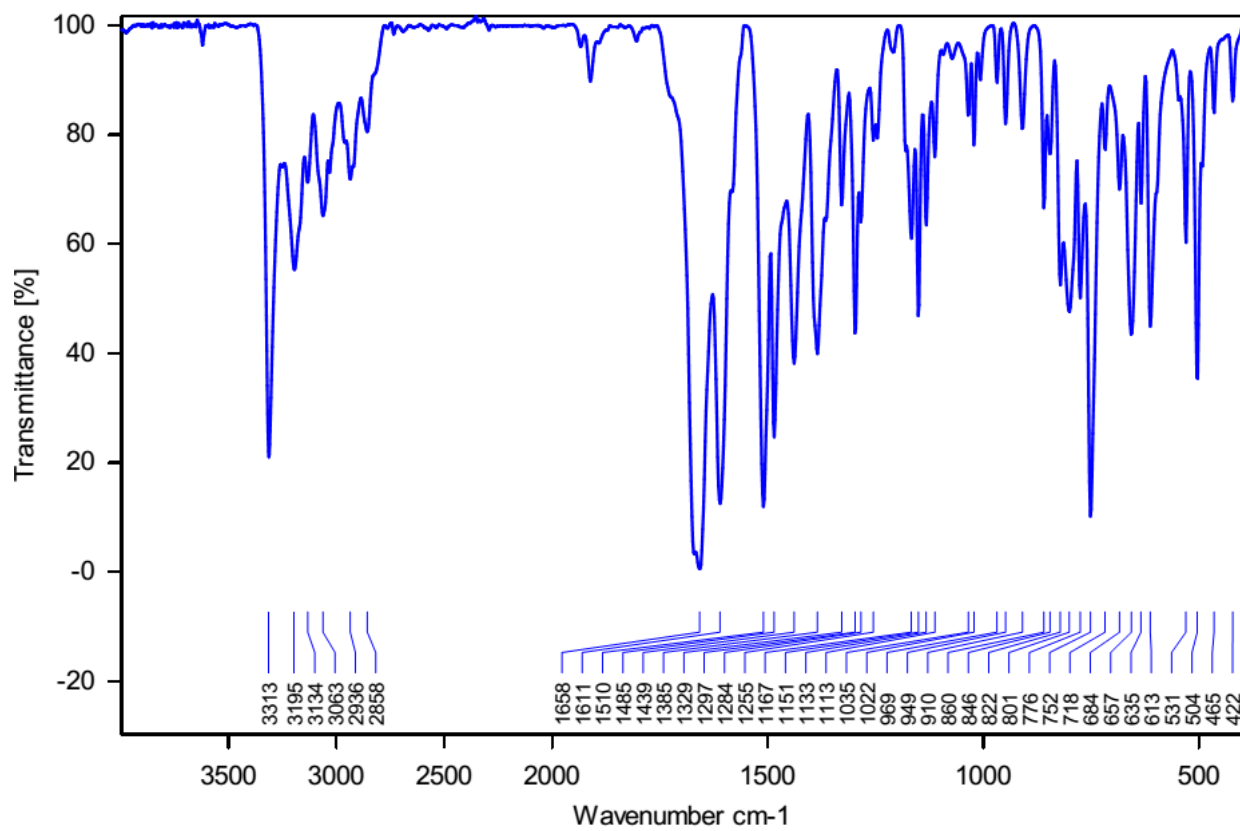


**<sup>1</sup>HNMR of Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 8, table 2)**



IR of 2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 4, table 4)





**<sup>1</sup>H NMR of 2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 4, table 4)**

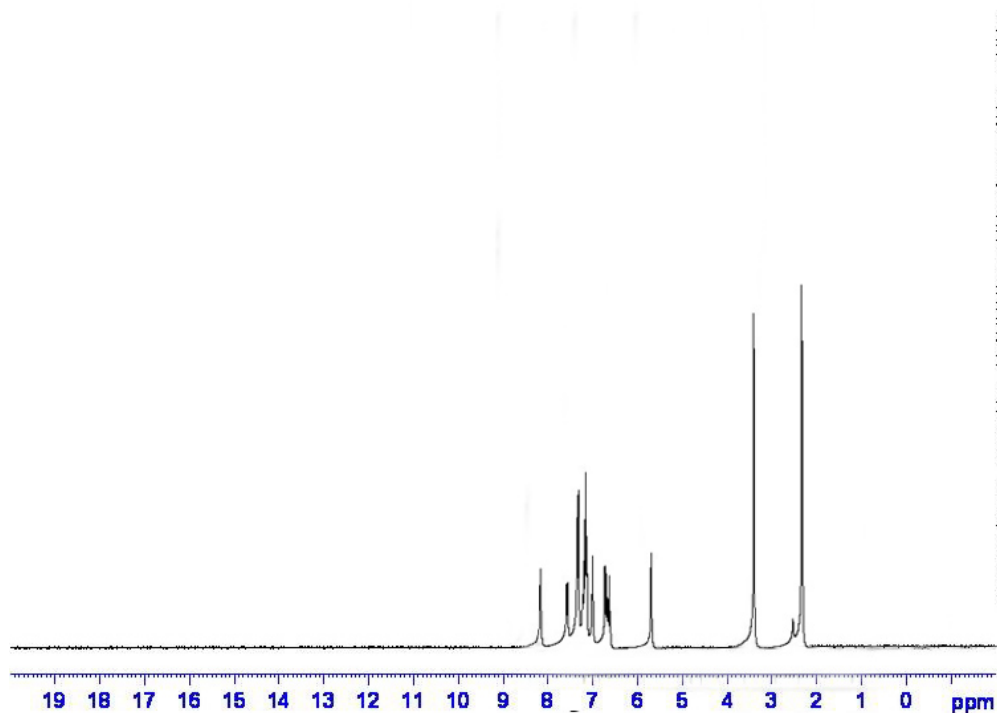


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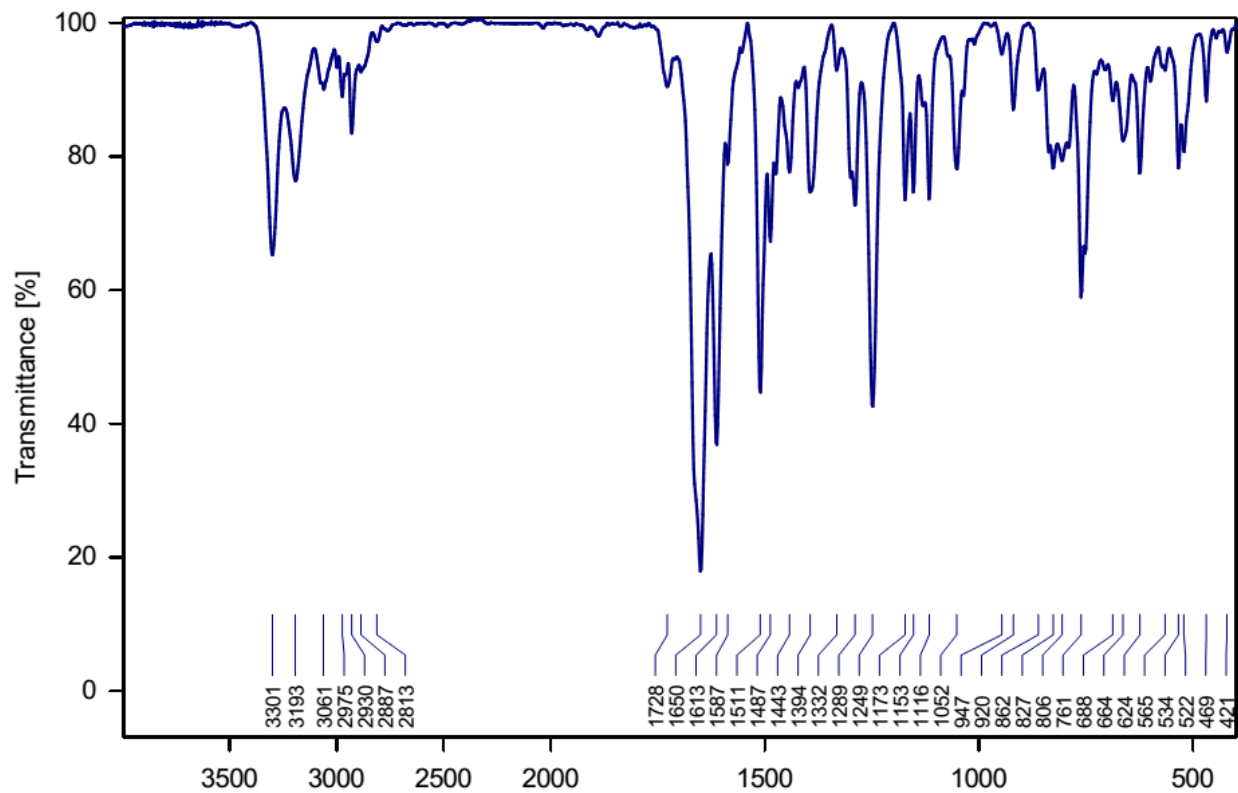
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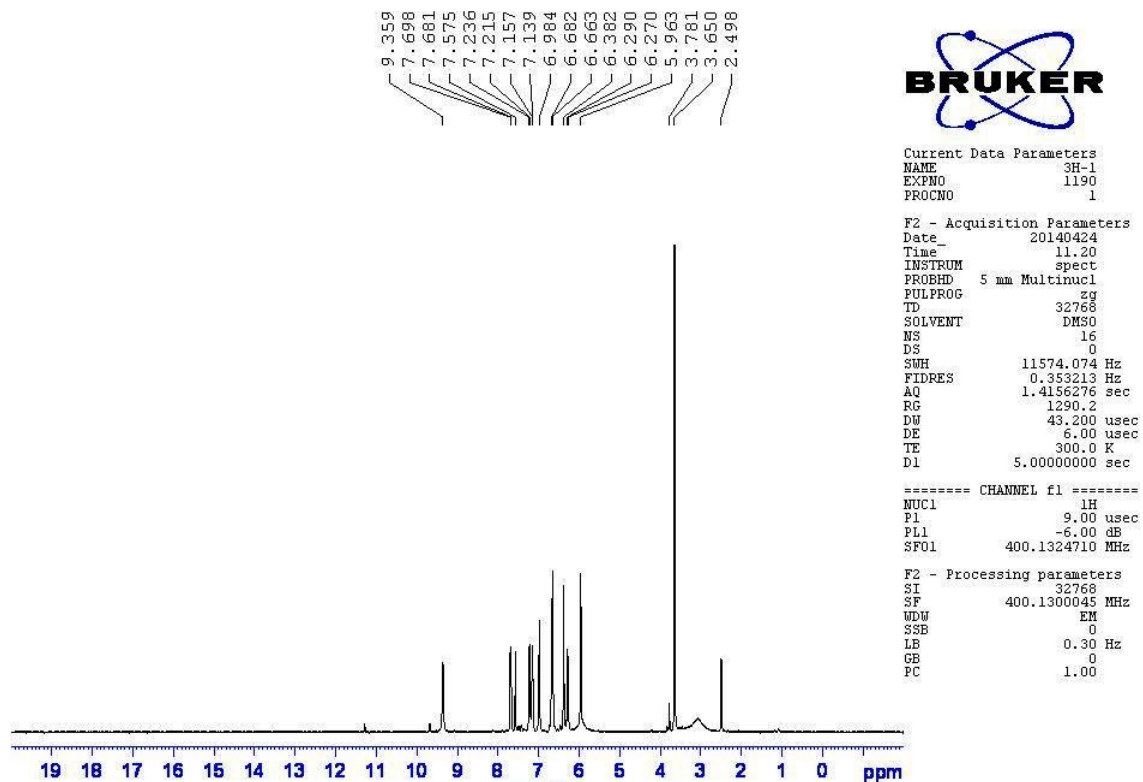
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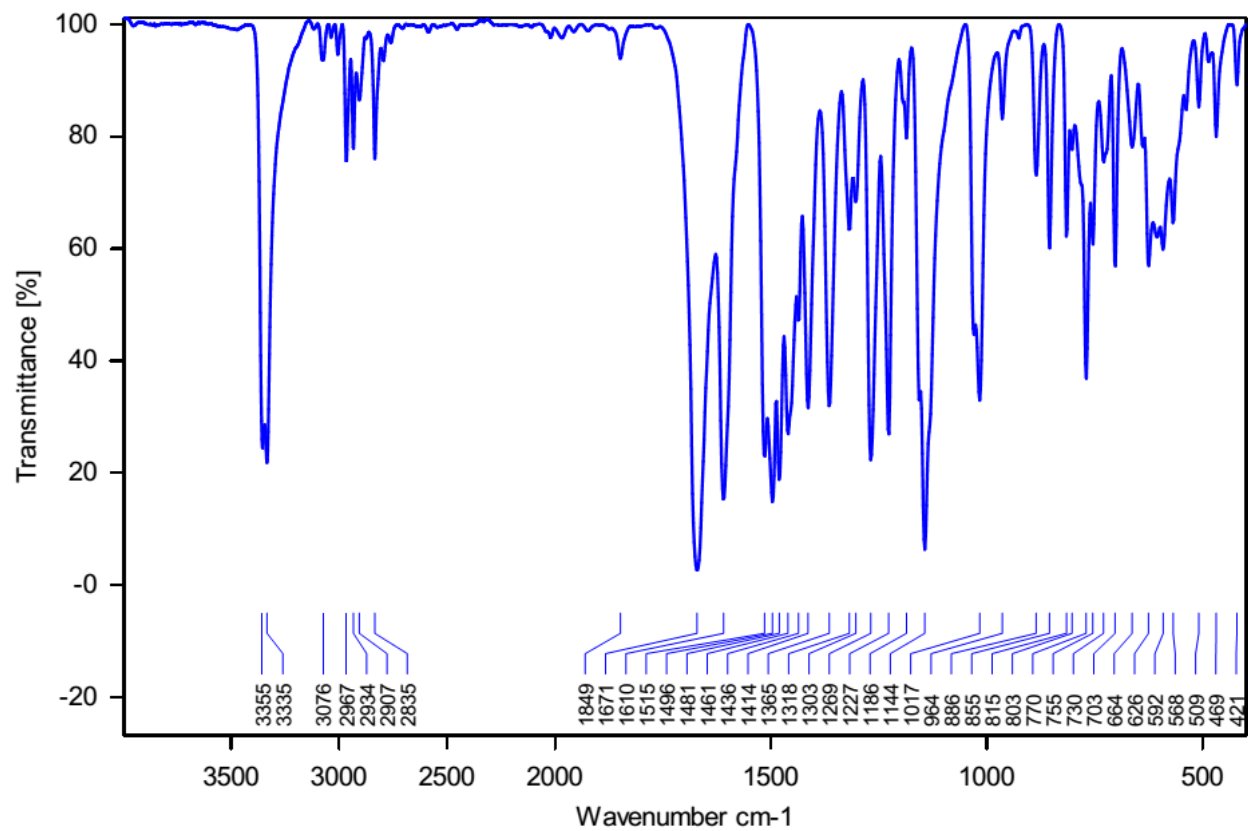
IR of 2-(4-ethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 5, table 4)



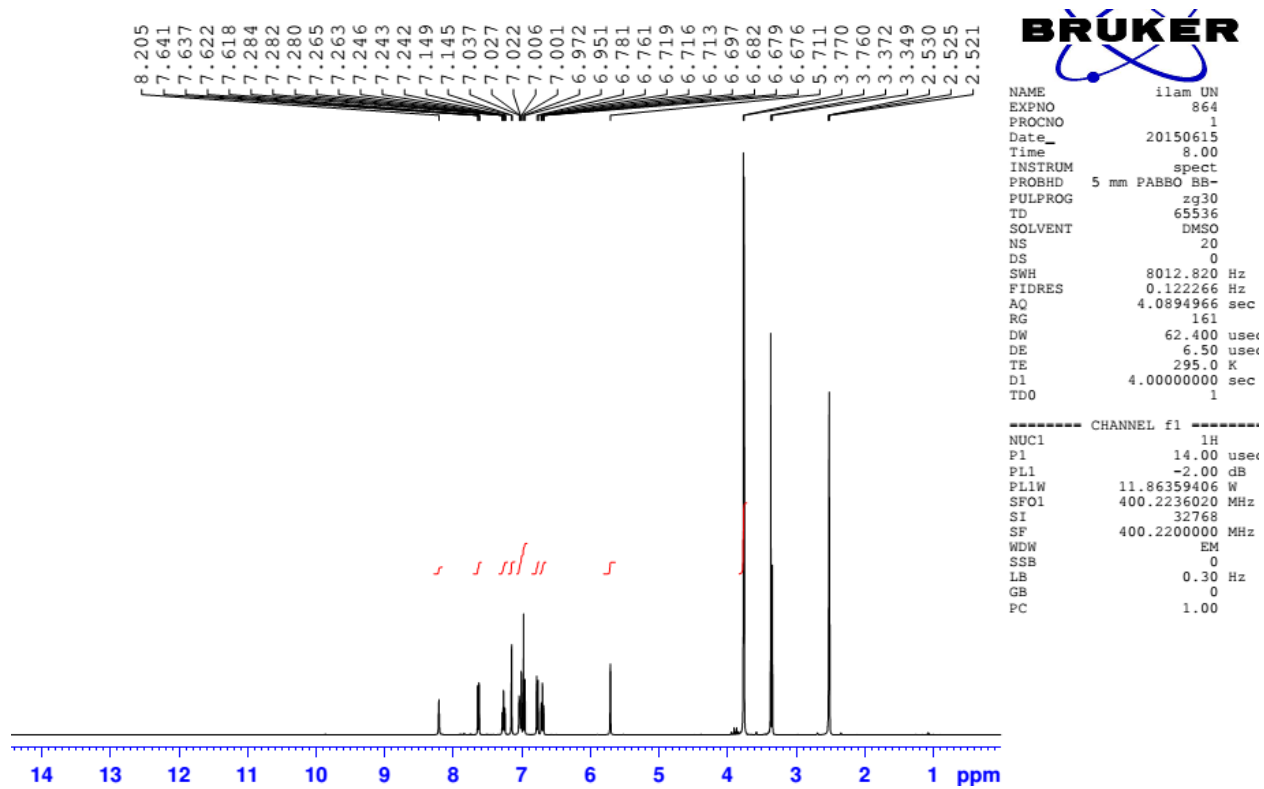
**<sup>1</sup>H NMR of 2-(4-ethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 5, table 4)**



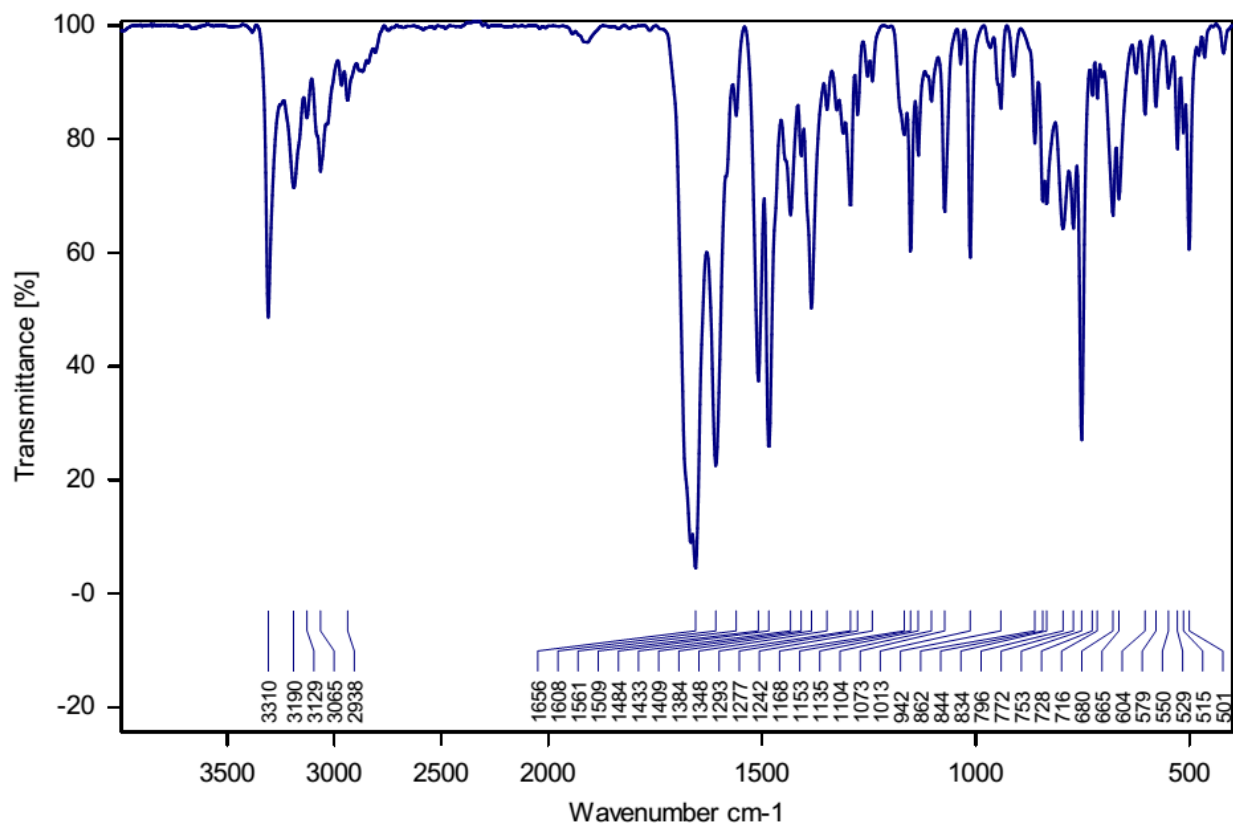
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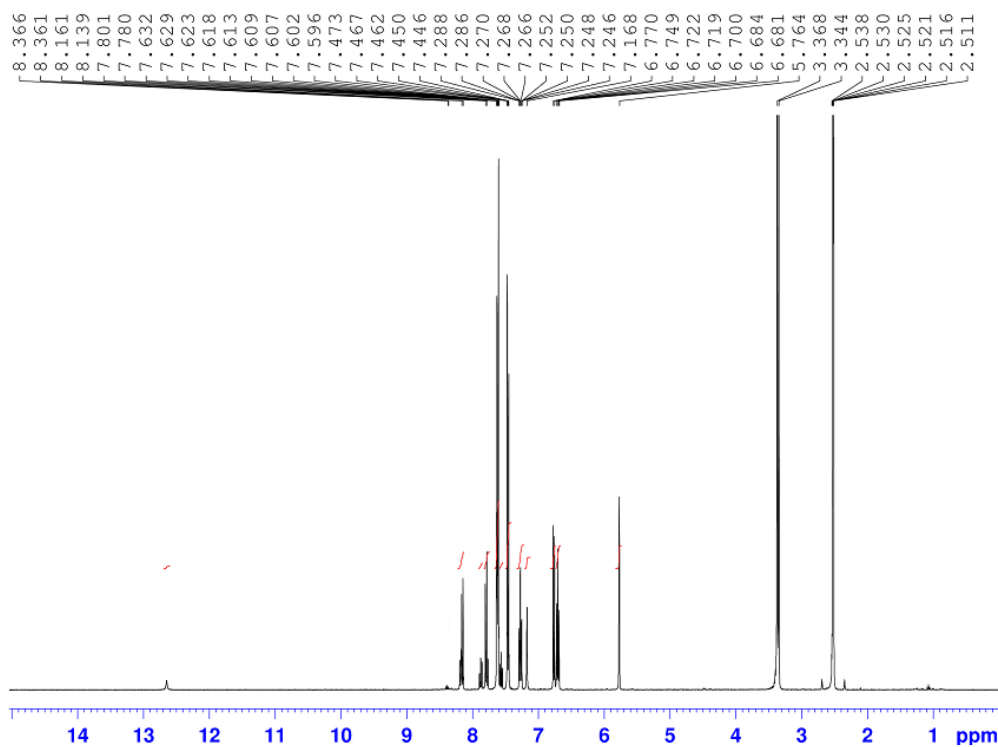
**<sup>1</sup>HNMR of 2-(3,4-dimethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 6, table 4)**



IR of 2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 8, table 4)



**1HNMR of 2-(4-bromophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 8, table 4)**



**BRUKER**

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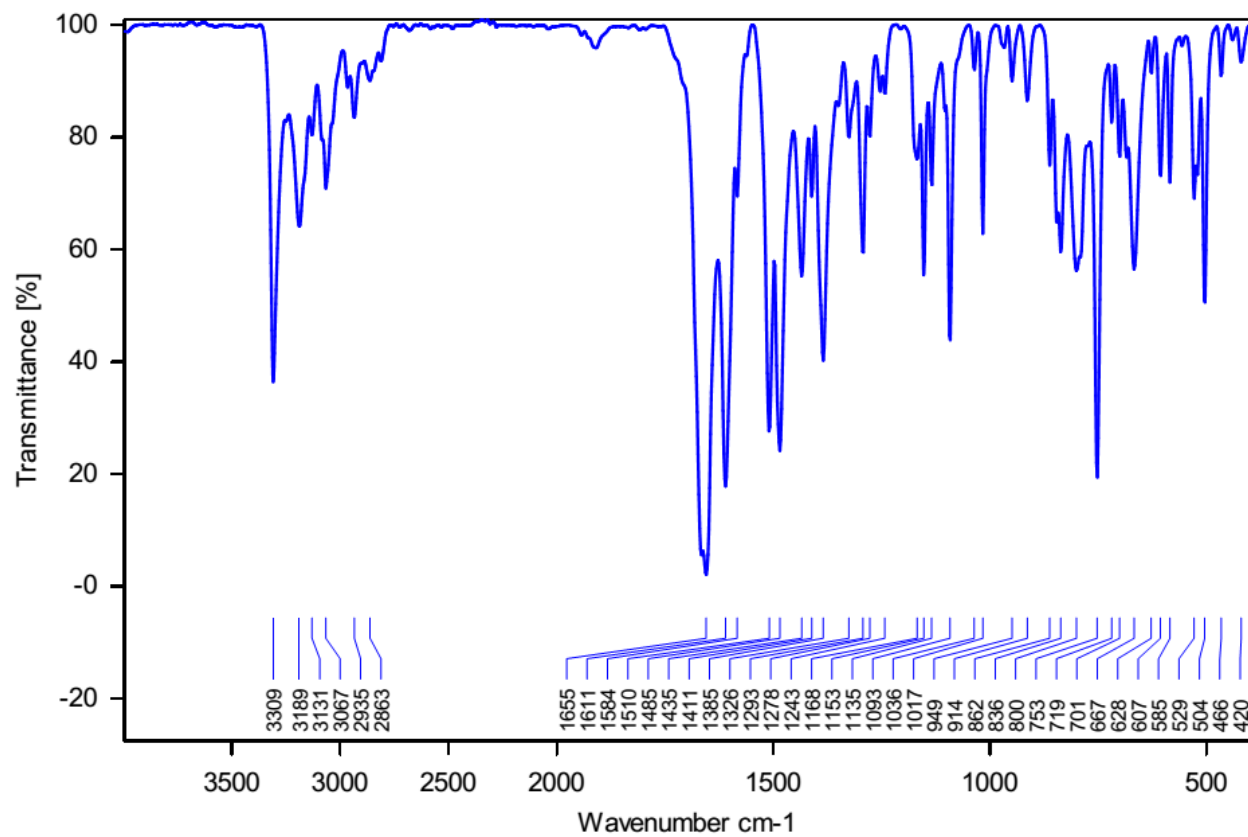
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**IR of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 9, table 4)**





**<sup>1</sup>HNMR of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 9, table 4)**

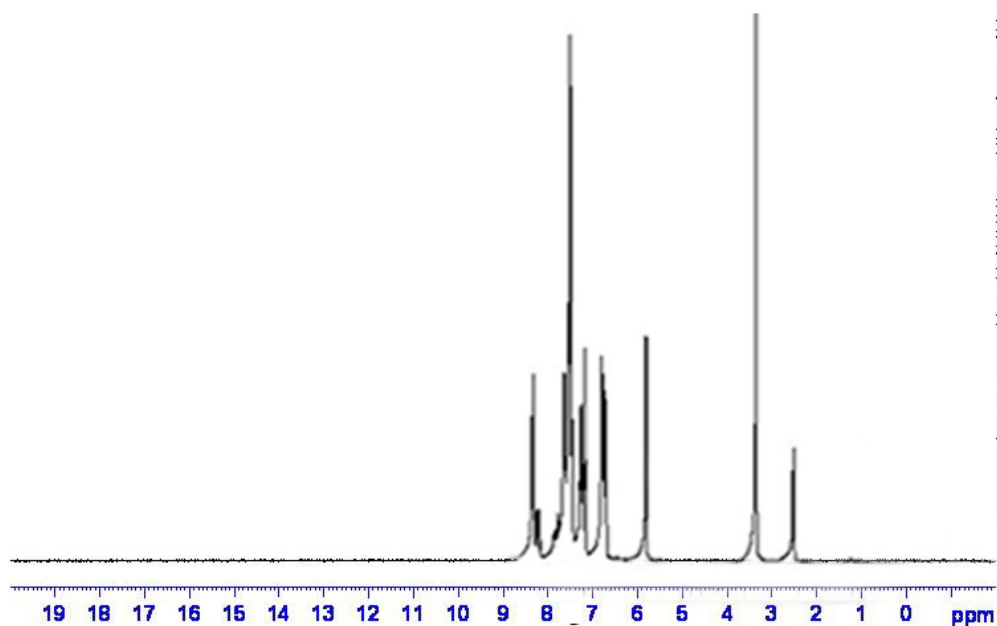


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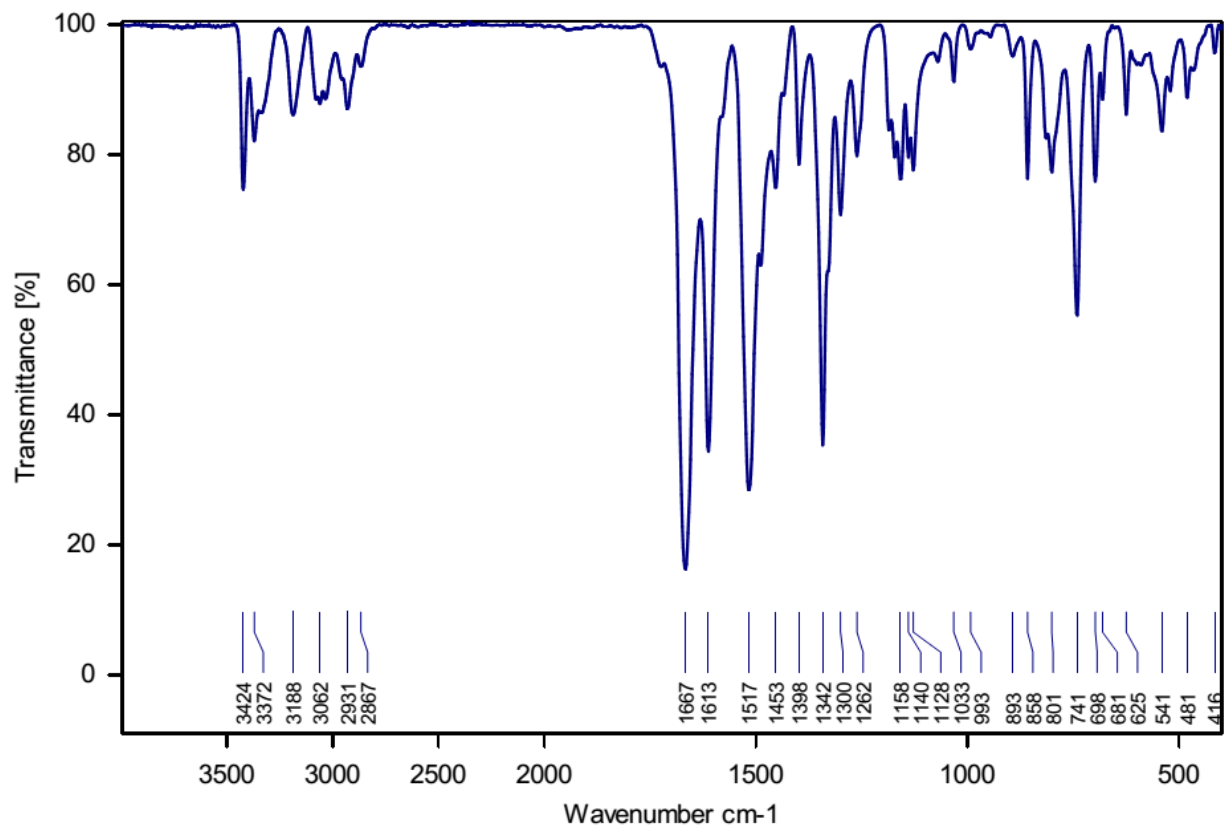
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NUC1 1H  
P1 9.00 usec  
PL1 -6.00 dB  
SF01 400.1324710 MHz

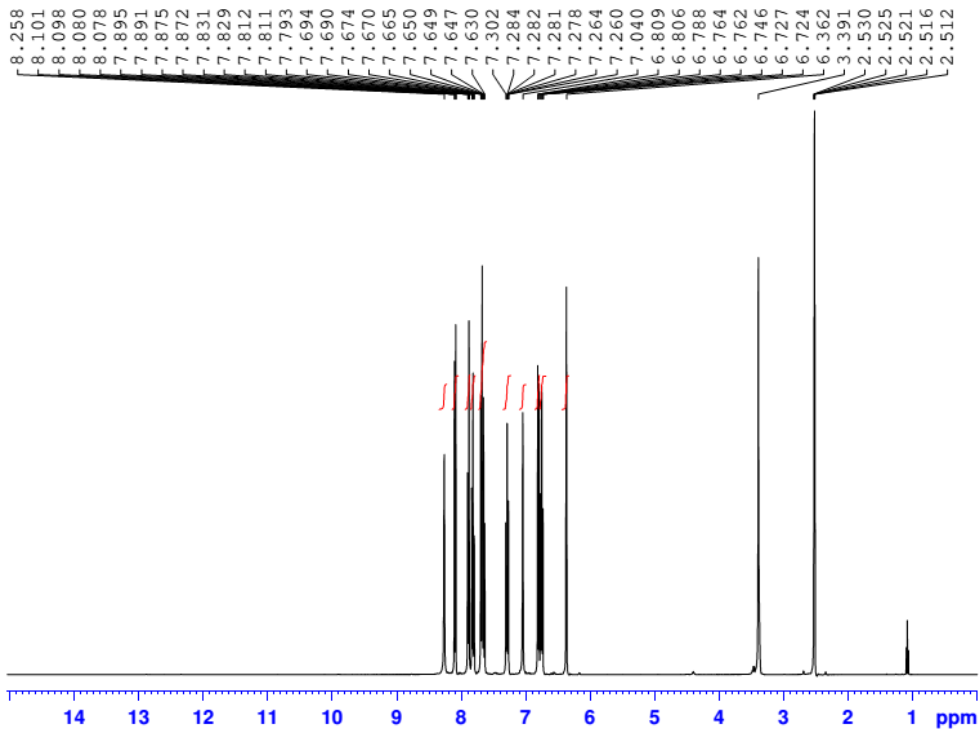
F2 - Processing parameters  
SI 32768  
SF 400.1300045 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00



**IR of 2-(2-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 10, table 4)**



**<sup>1</sup>HNMR of 2-(2-nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 10, table 4)**



```

NAME          ilam UN
EXPNO         862
PROCNO        1
Date_         20150615
Time          7.50
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT       DMSO
NS            20
DS            0
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894966 sec
RG            128
DW            62.400 usec
DE            6.50 usec
TE            295.0 K
D1            4.00000000 sec
TDO           1

```

```

----- CHANNEL f1 -----
NUC1          1H
P1            14.00 usec
PL1           -2.00 dB
PL1W         11.86359406 W
SFO1         400.2236020 MHz
SI            32768
SF           400.2200000 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00

```