

Supporting Information

Organic–inorganic hybrid polyoxometalate and its graphene oxide-Fe₃O₄ nanocomposite, synthesis, characterization and their applications as nanocatalysts for the Knoevenagel condensation and the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones

Roushan Khoshnavazi, Liela Bahrami, Forugh Havasi*

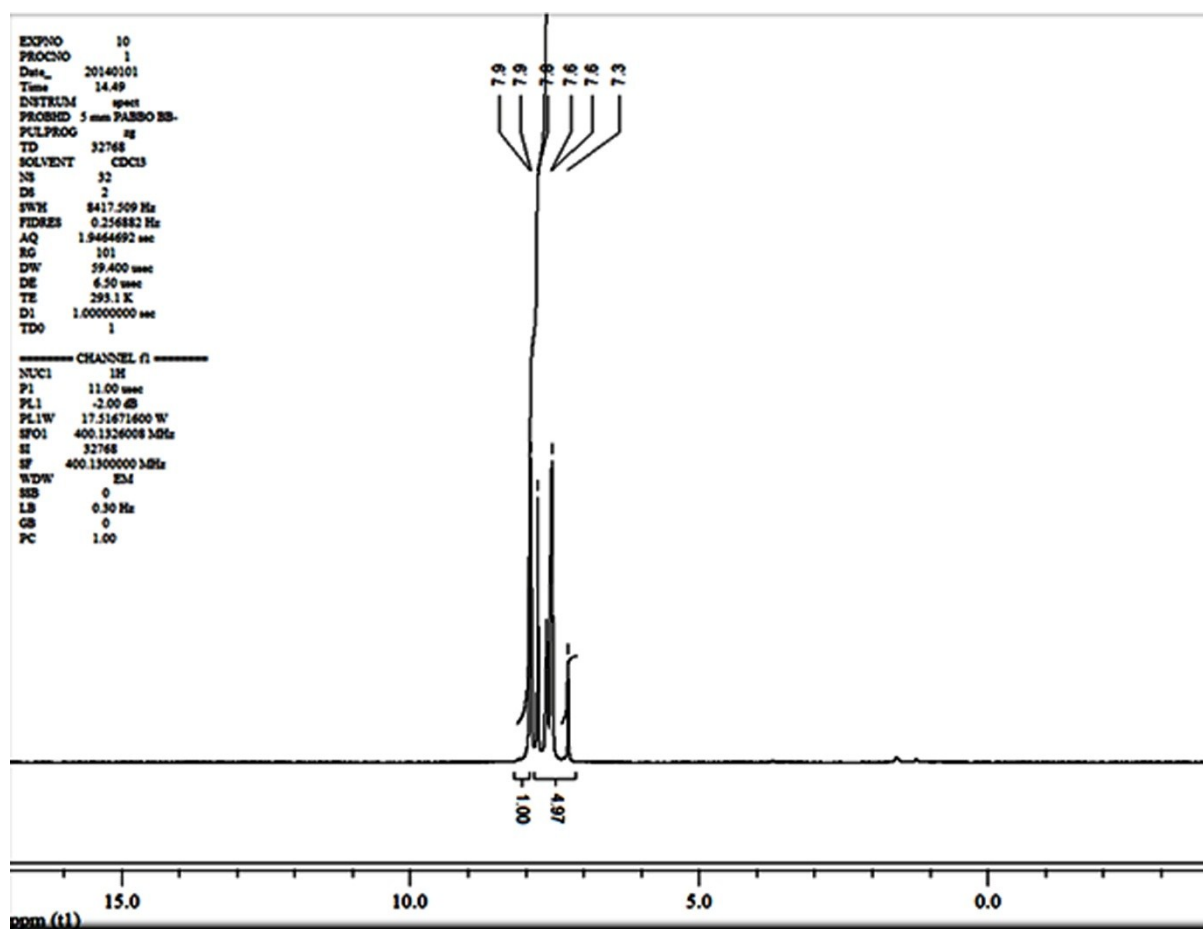
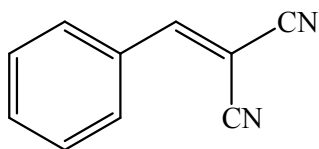
Department of chemistry, University of Kurdistan P.O. Box 66135-416, Sanandaj, Iran

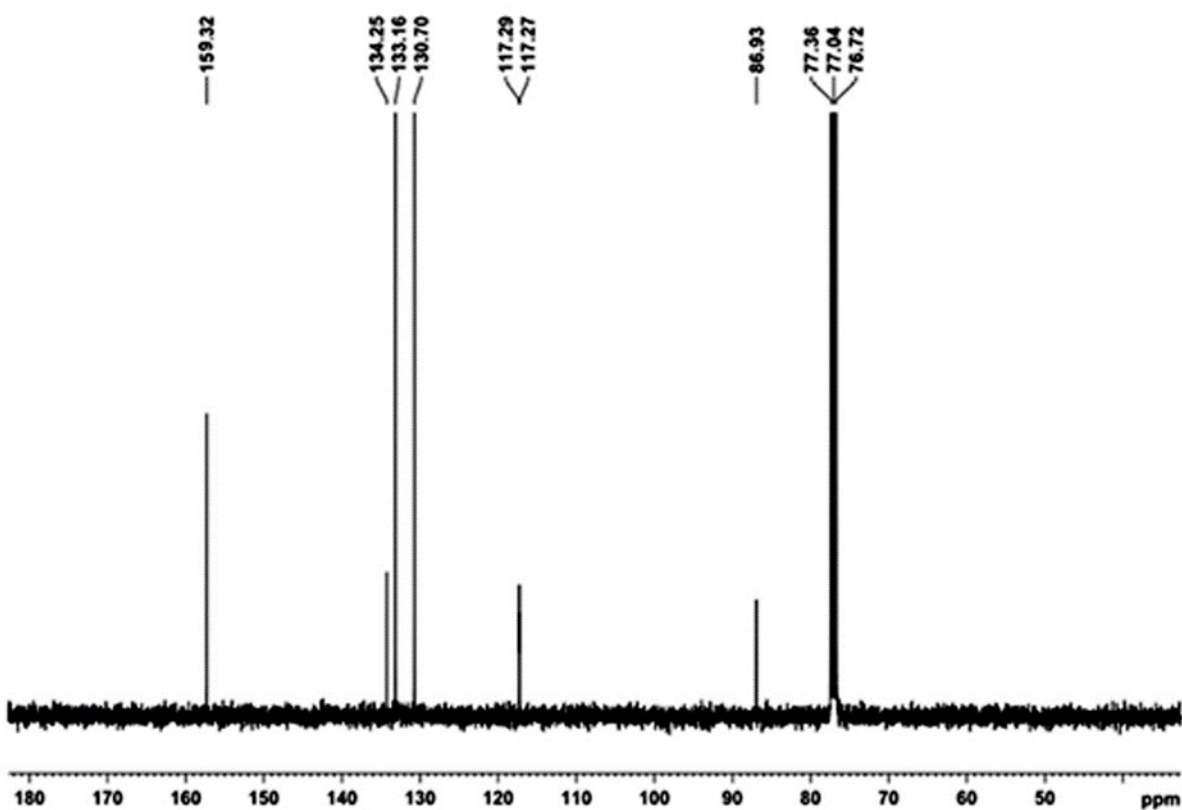
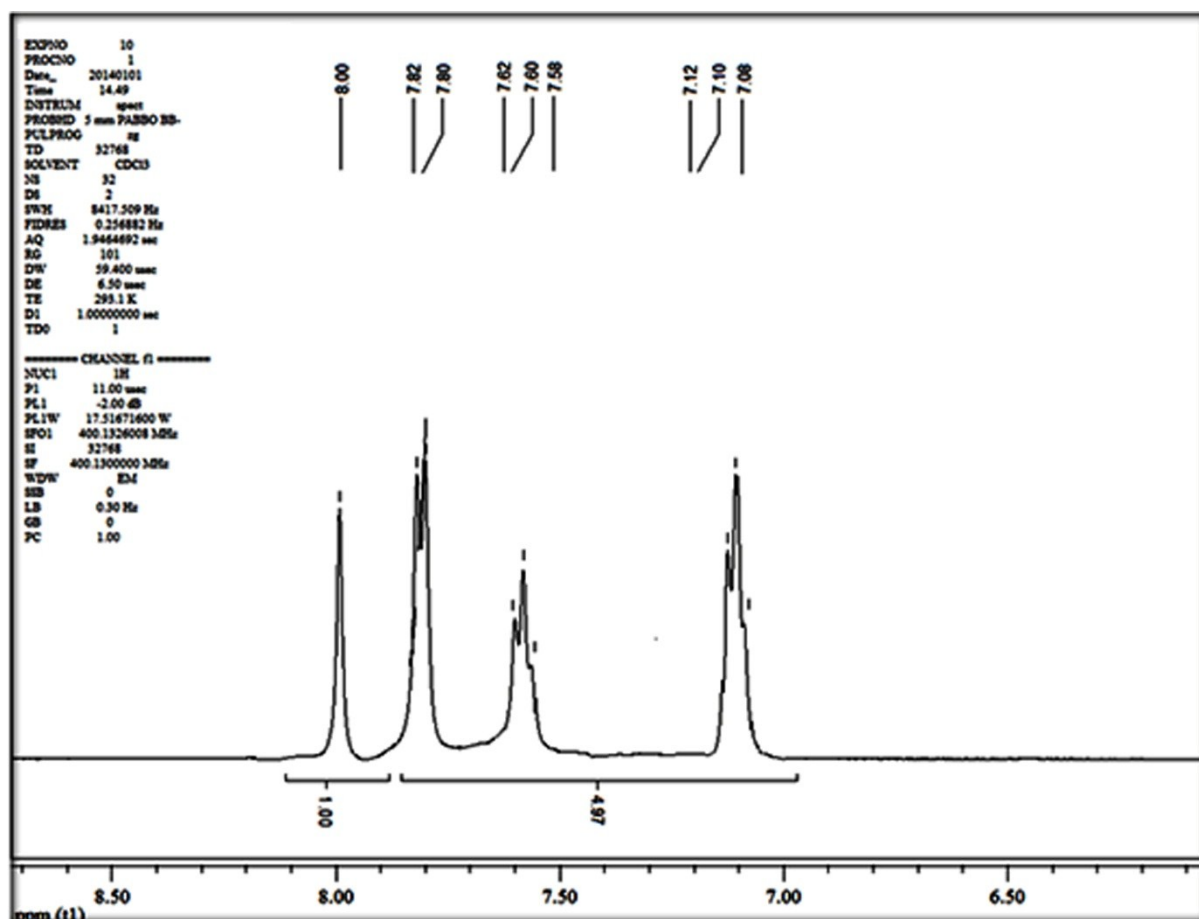
E-mail address : r.khoshnavazi@uok.ac.ir or khoshnavazi@yahoo.com

¹H NMR and ¹³C NMR spectra of the catalytic synthesized compounds

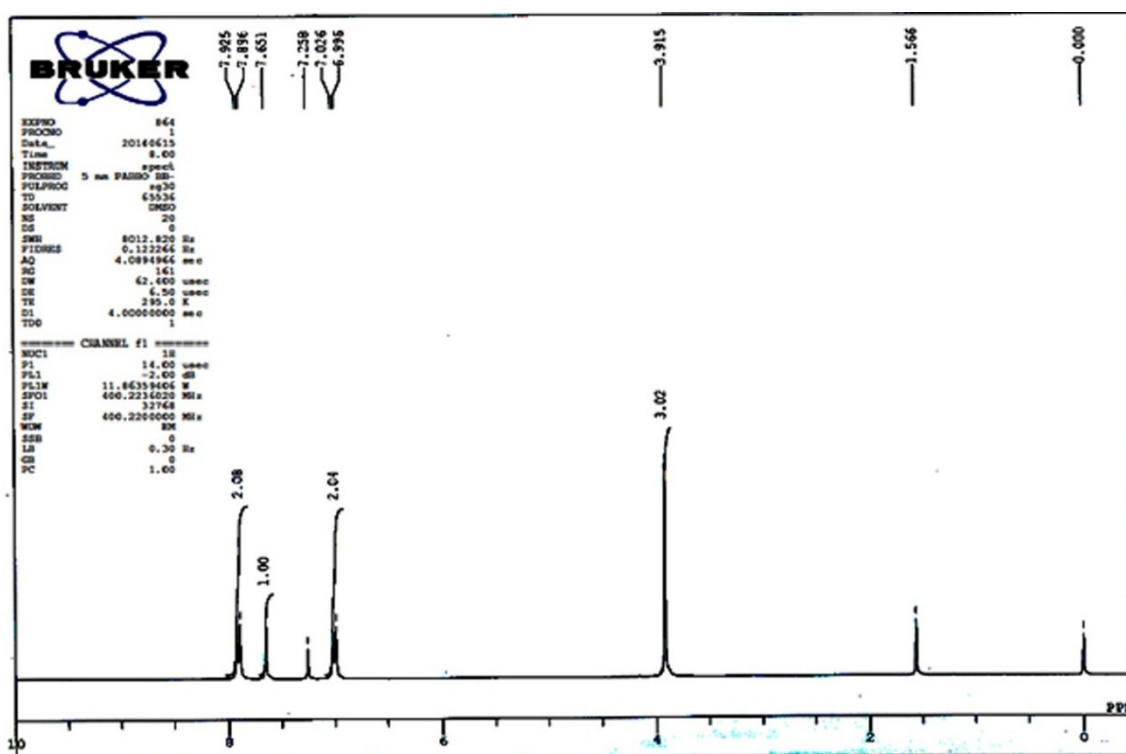
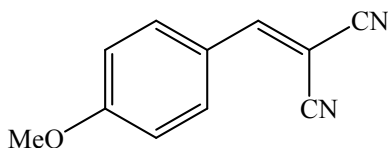
NMR Spectra of Knoevenagel Products

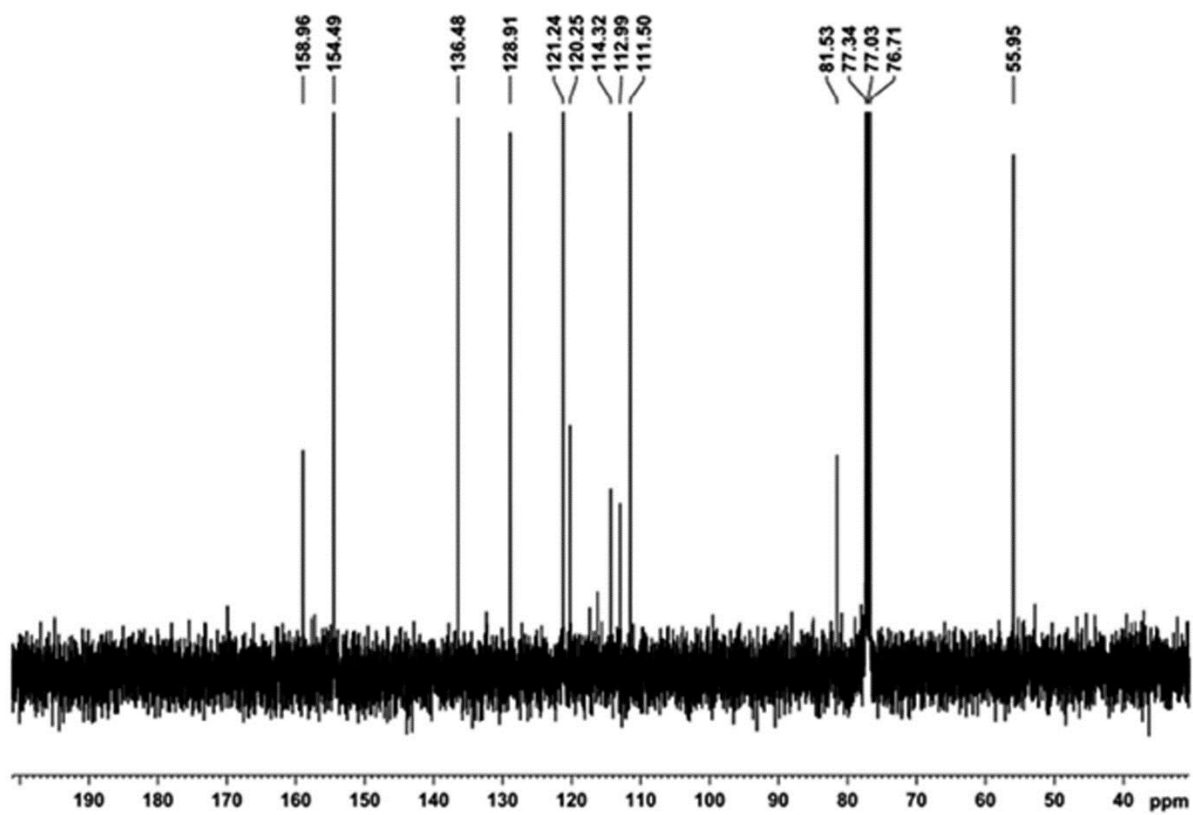
2-Benzylidene-malononitrile (table 2, entry 1): Mp: 82-83 °C [59]; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.1 (t, $J = 8.0$ Hz, 2H), 7.6 (t, $J = 8.0$ Hz, 1H), 7.8 (d, $J = 8.20$ Hz, 2H), 8 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3); $\delta = 159.3, 134.2, 133.1, 130.7, 117.2, 117.2, 86.9$.



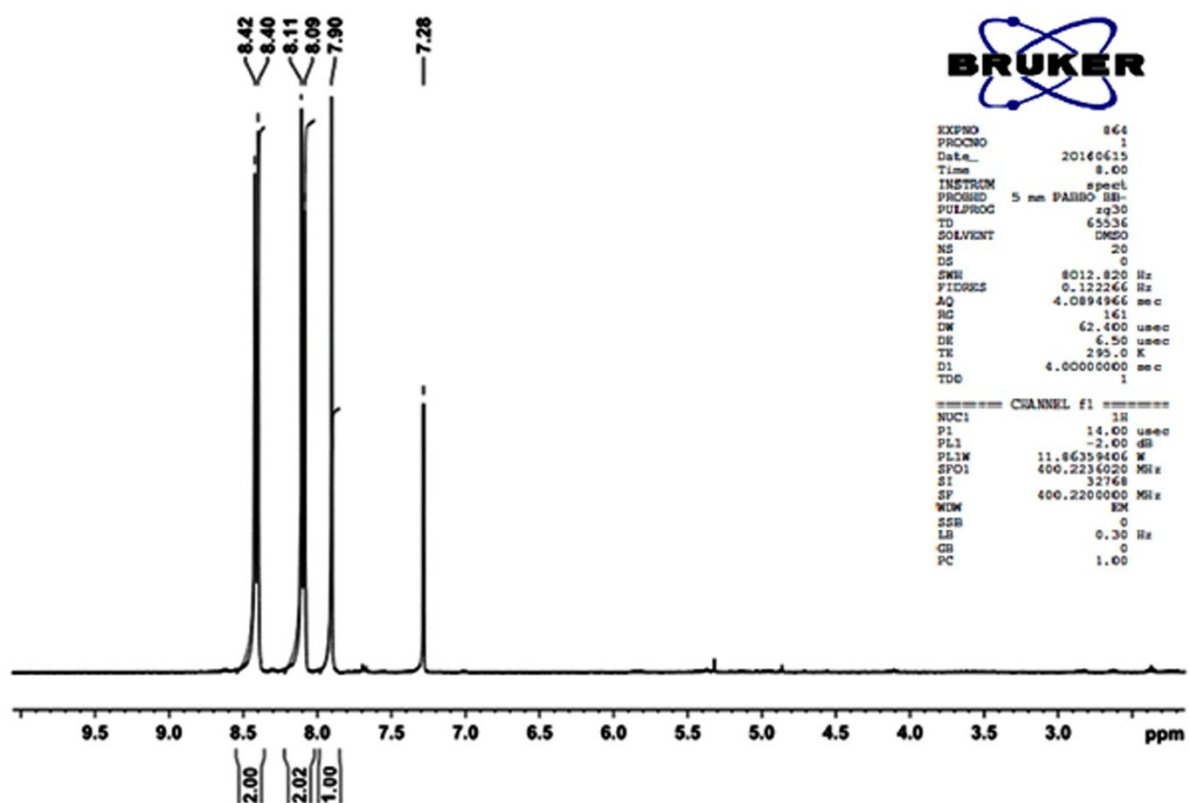
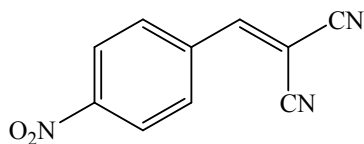


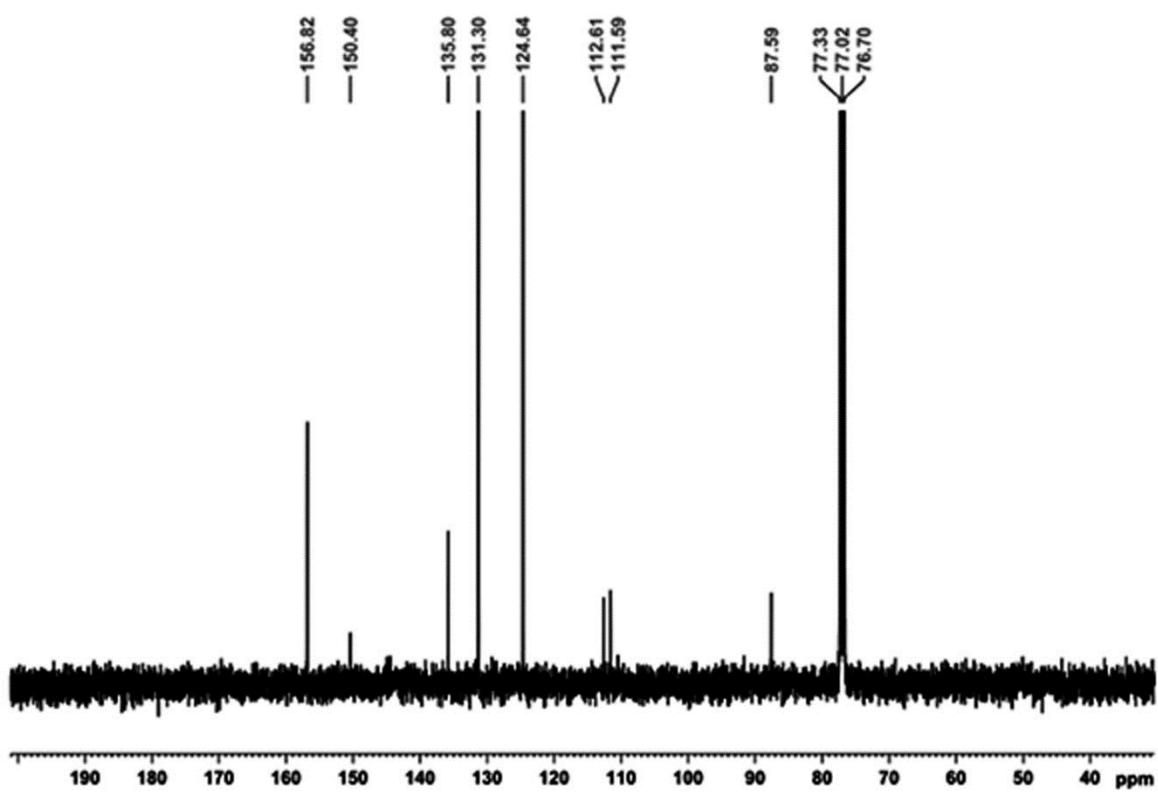
2-(4-methoxybenzylidene)malononitrile (table 2, entry 2): Mp: 112-114 °C [59]; ¹H-NMR (400MHz, CDCl₃): δ (ppm): 7.91 (d, *J* = 10.5 Hz, 2H), 7.65 (s, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 158.9, 154.4, 136.4, 128.9, 121.2, 120.2, 114.3, 112.9, 111.5, 81.5, 55.9.



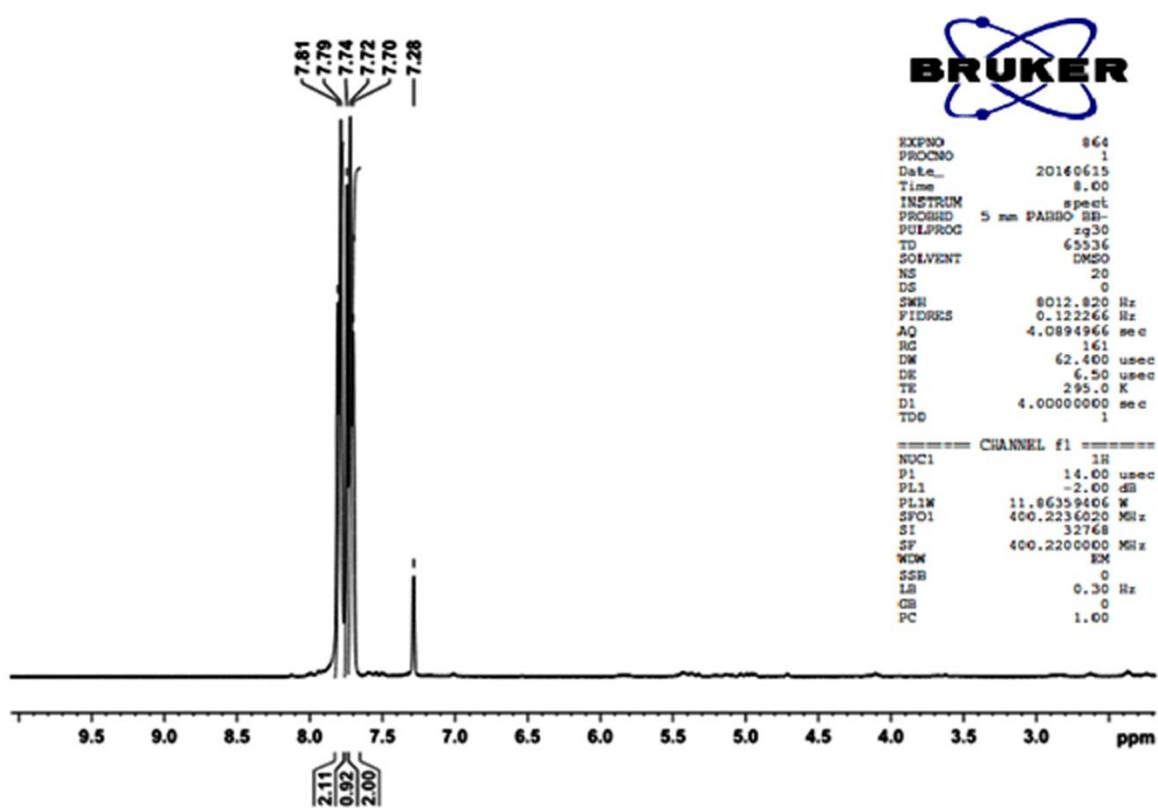
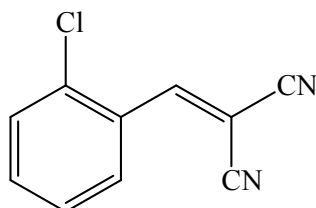


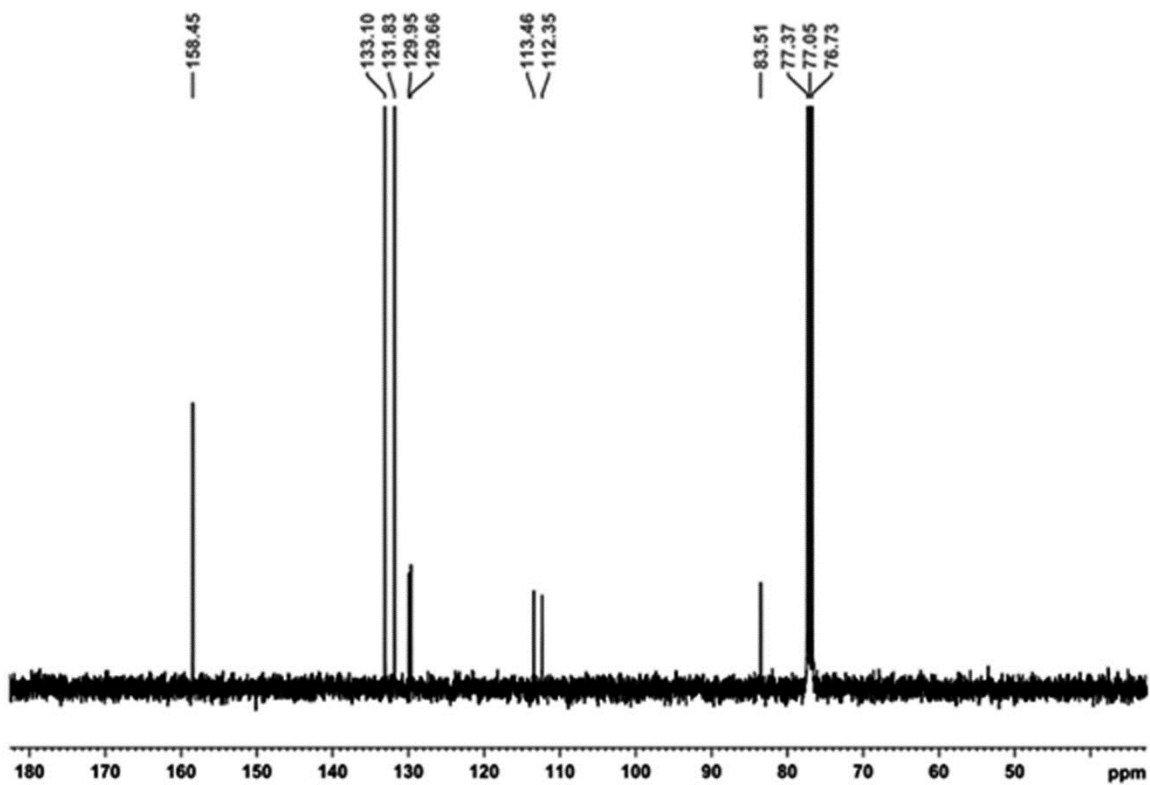
2-(4-nitrobenzylidene)malononitrile (table 2, entry 4): Mp:158-159 °C [59]; ¹H-NMR (400MHz, CDCl₃): δ (ppm): 8.41 (d, *J*=8.84, 2H), 8.10 (d, *J*=8.84, 2H), 7.90 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 156.8, 150.4, 135.8, 131.3, 124.6, 112.6, 111.5, 87.5.



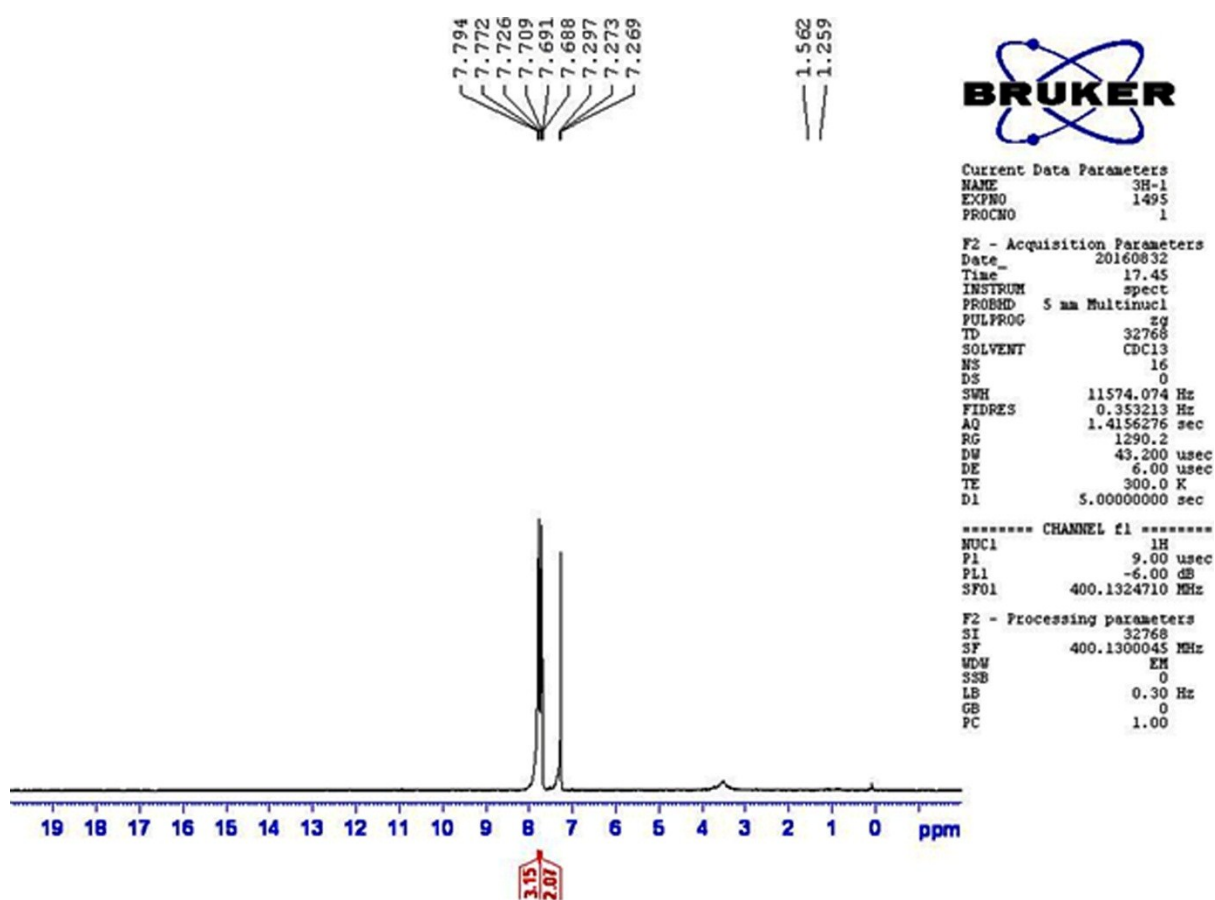
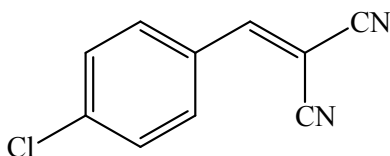


2-(2-chlorobenzylidene)malononitrile (table 2, entry 5): Mp:79-82 °C [61]; ¹H-NMR (400MHz, CDCl₃): δ (ppm): 7.80 (d, *J*=7.84, 2H), 7.74 (s, 1H), 7.71 (d, *J*=7.84, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm):158.4, 133.1, 131.8, 129.9, 129.6, 113.4, 112.3, 83.5.





2-(4-chlorobenzylidene)malononitrile (table 2, entry 6): Mp:162-164 °C [61]; ¹H-NMR (400MHz, CDCl₃): δ (ppm):7.78(m, 3H), 7.69(d, *J*=6.8 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm):159.6, 134.2, 132.9, 131.1, 130.8, 114.6, 113.5, 84.6.





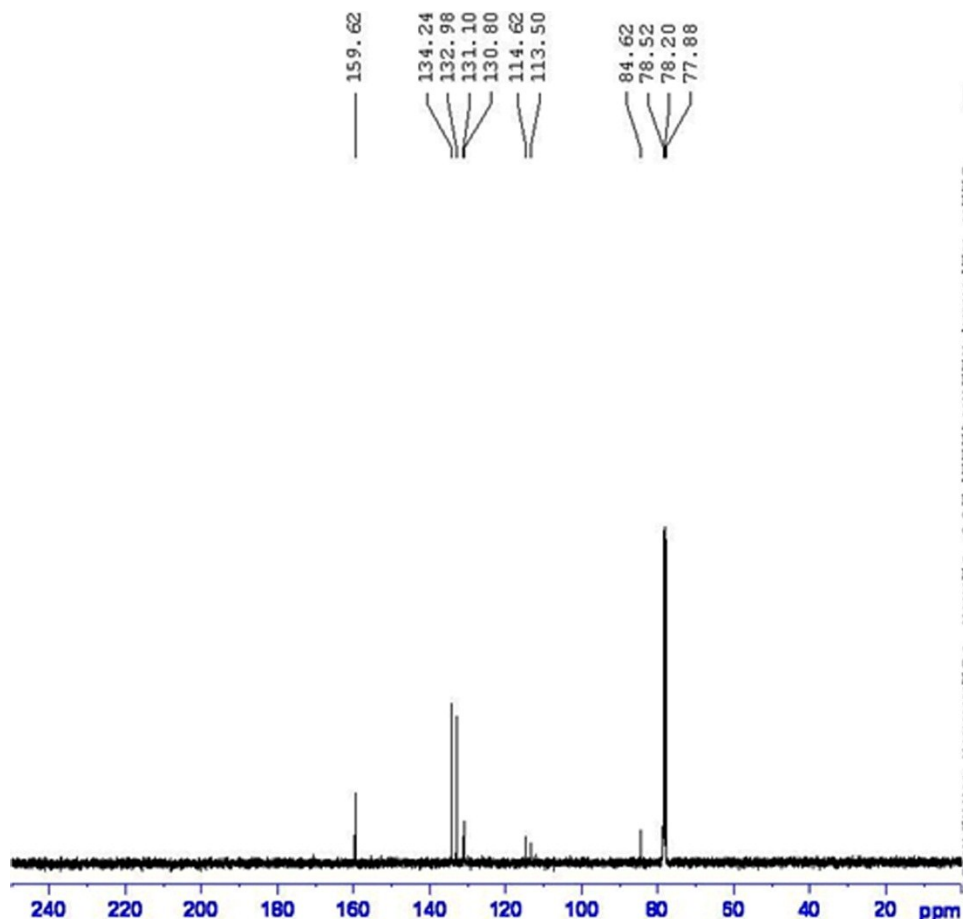
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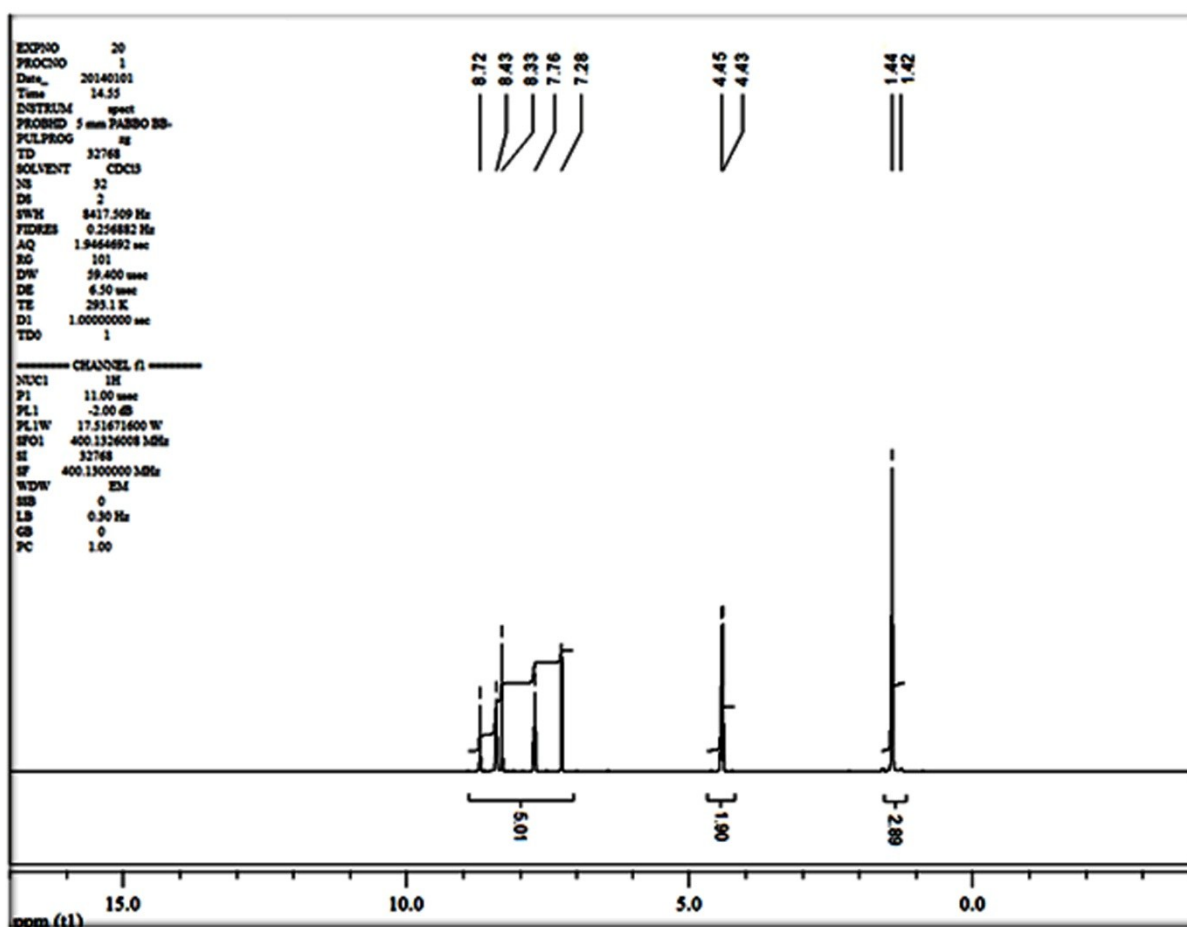
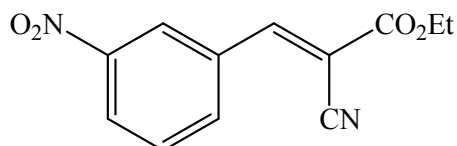
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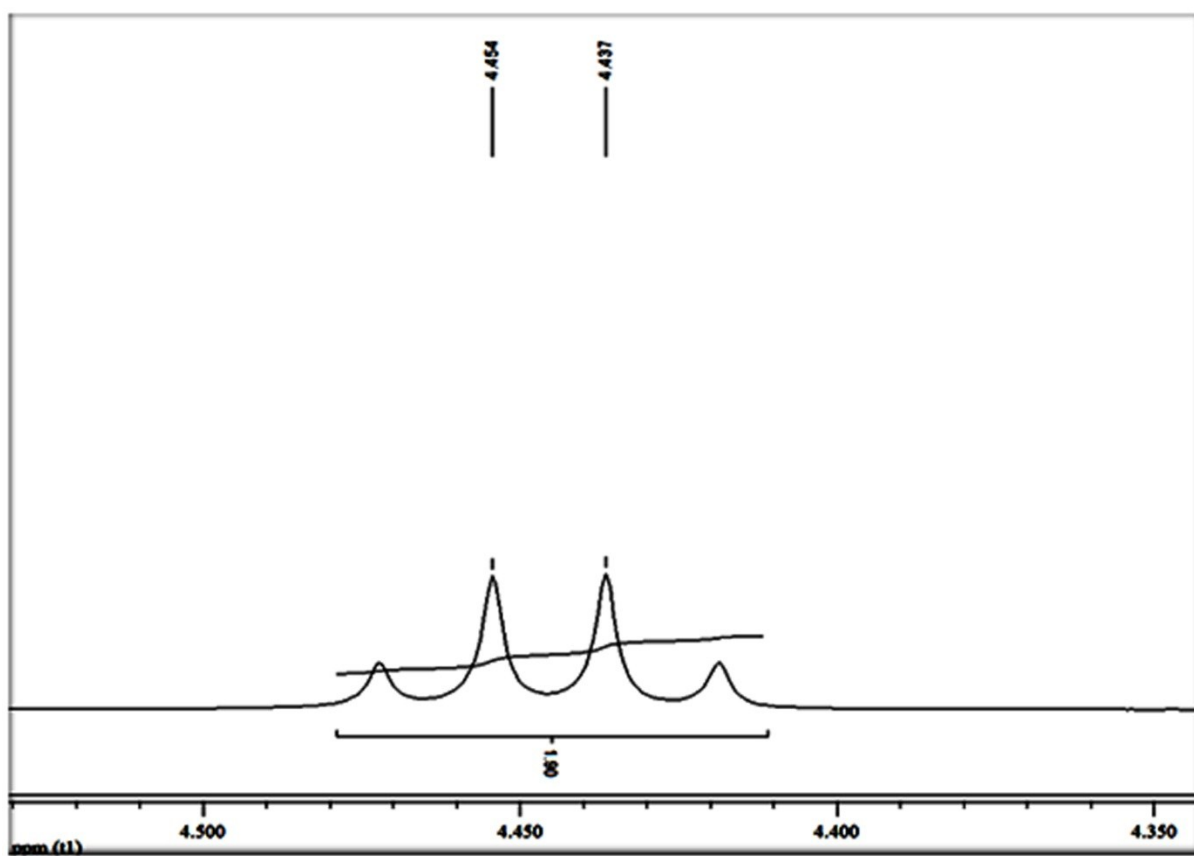
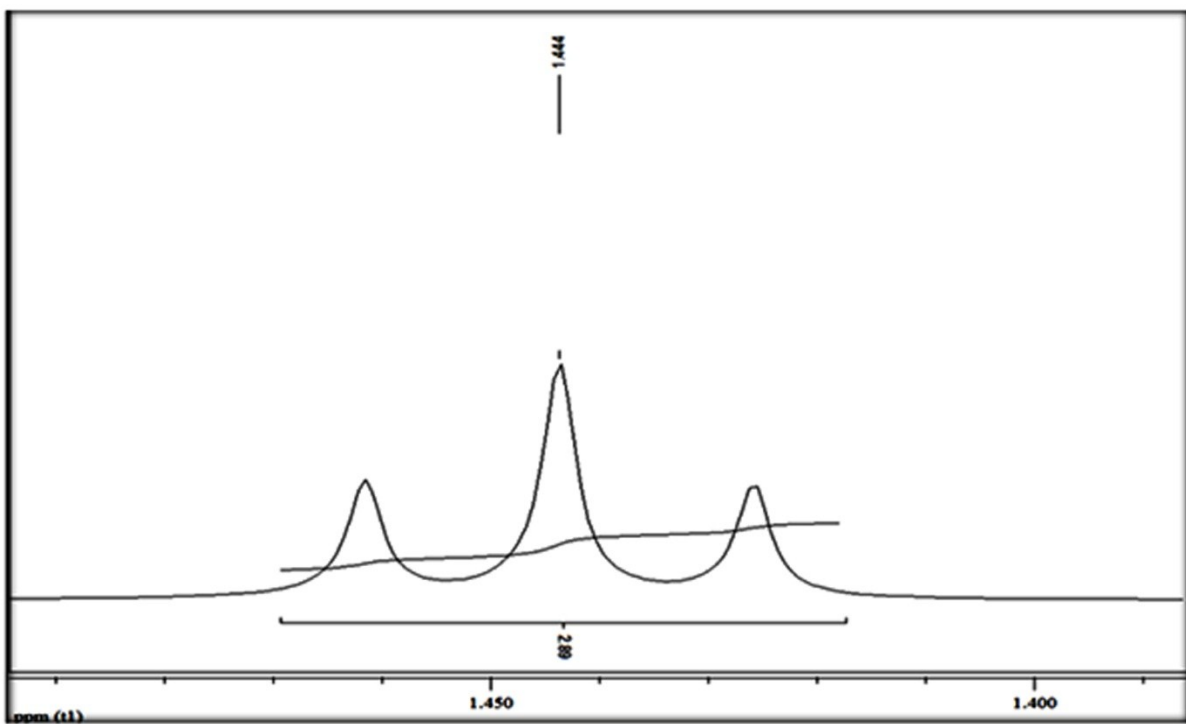
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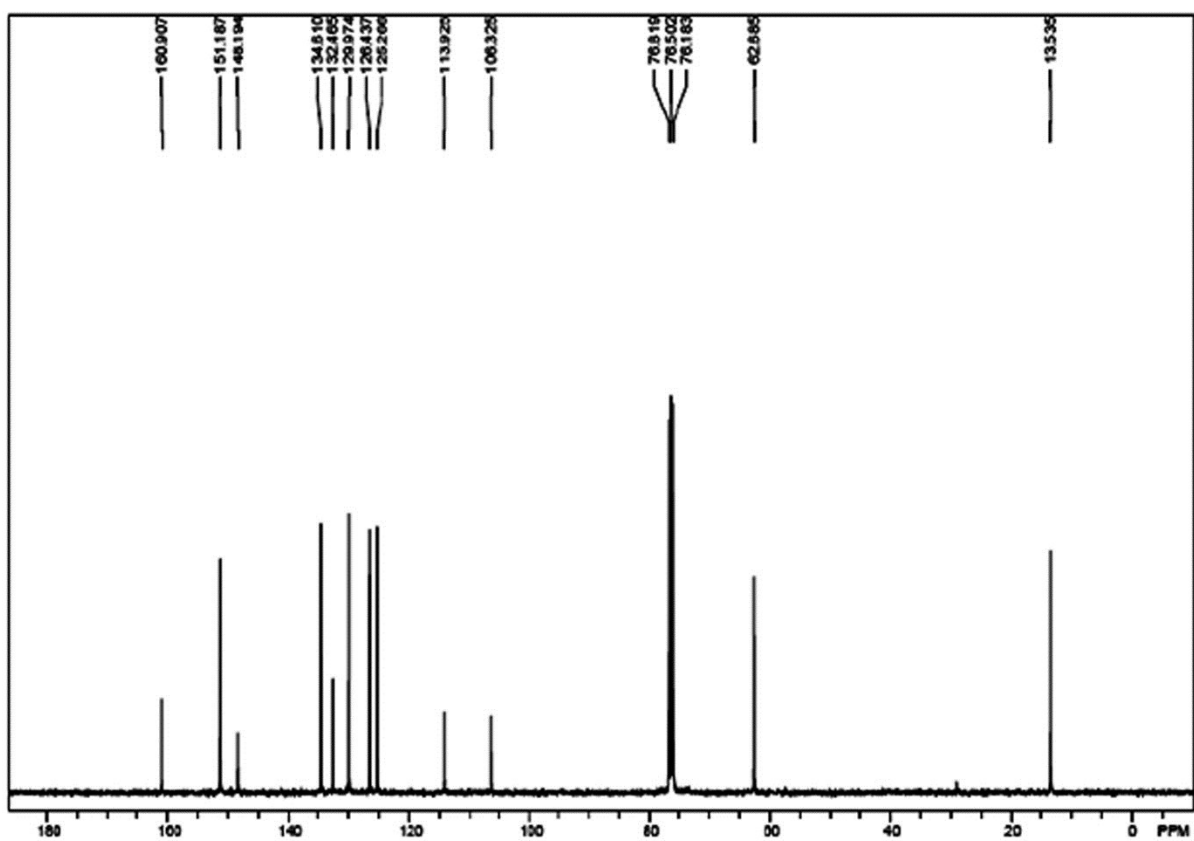
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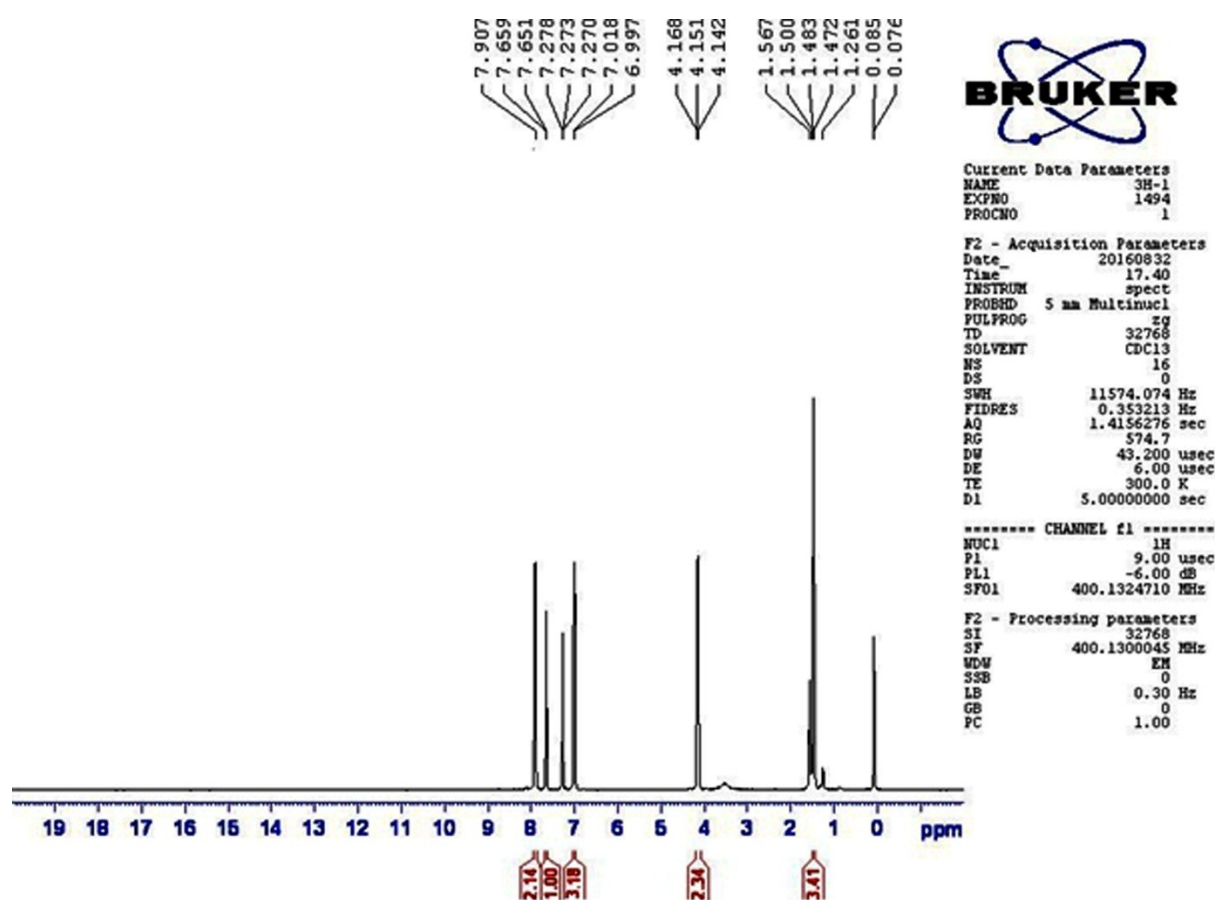
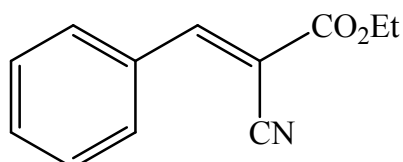
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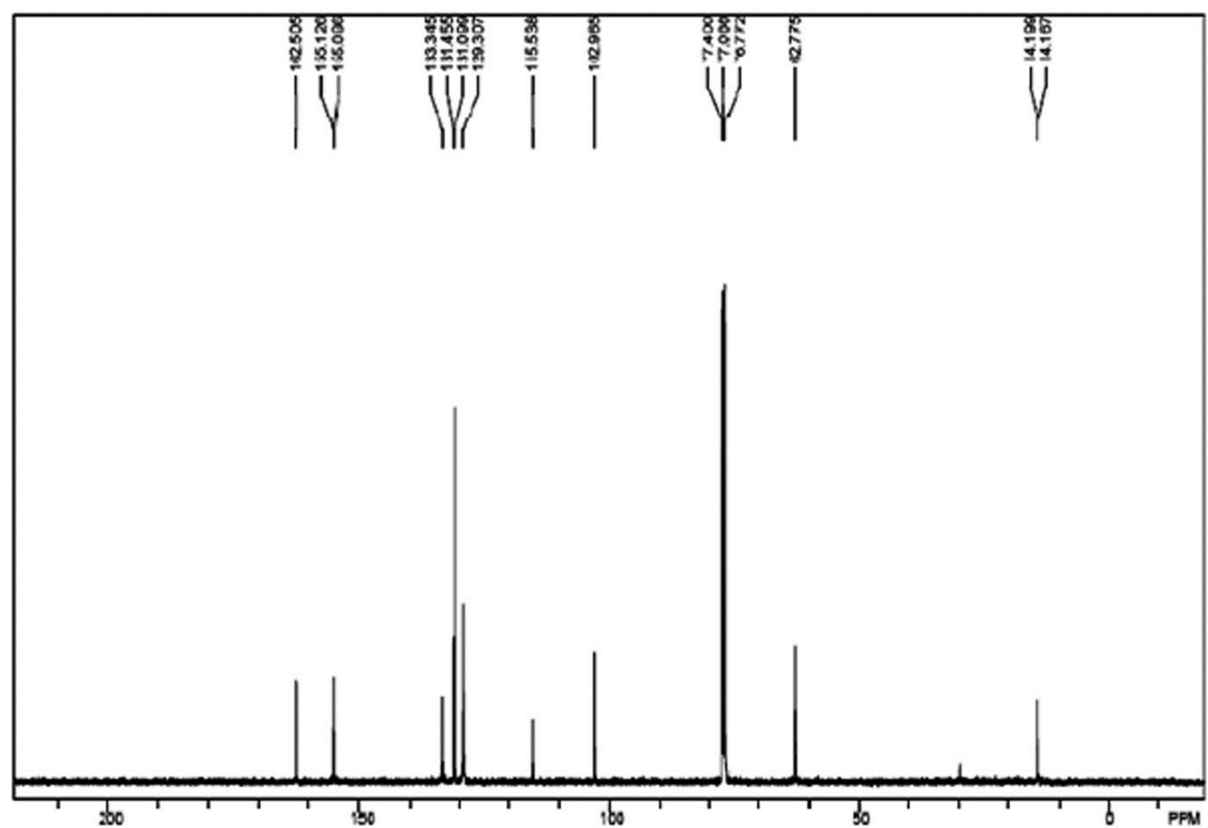




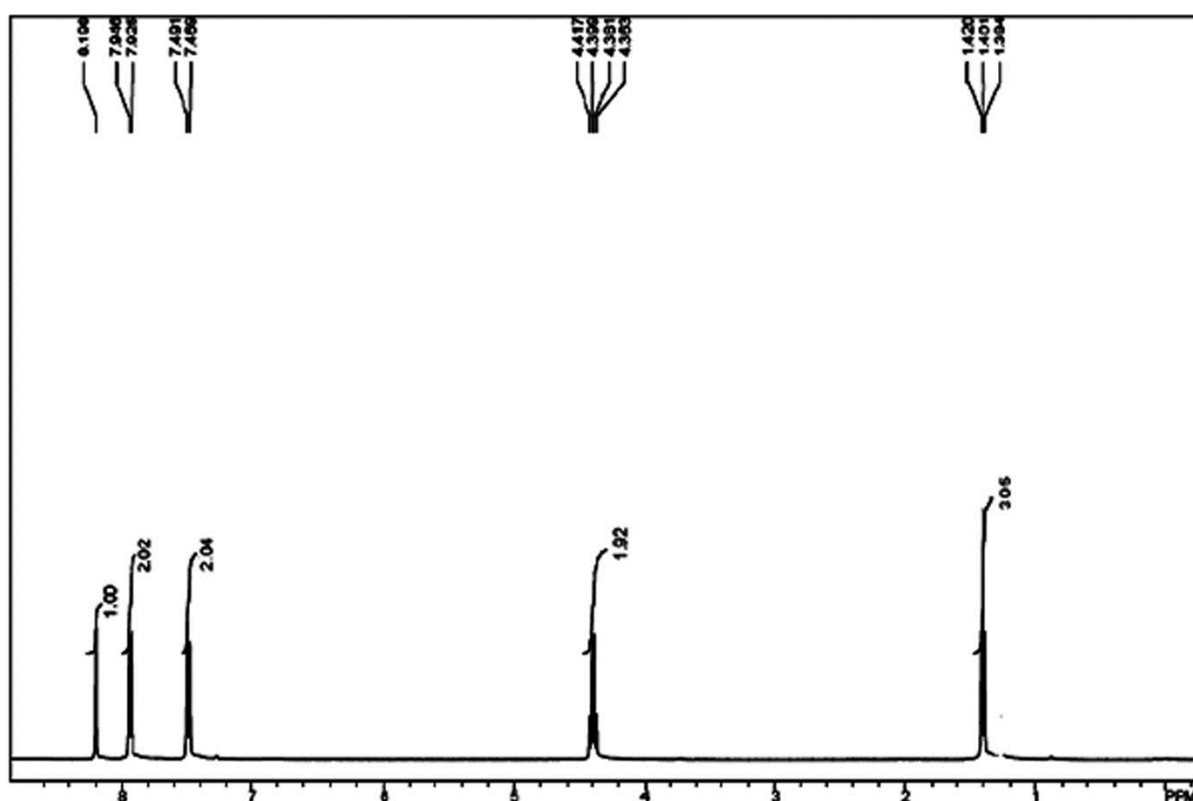
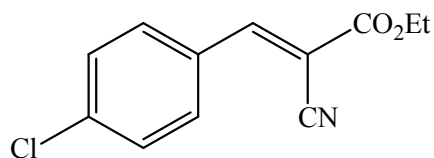


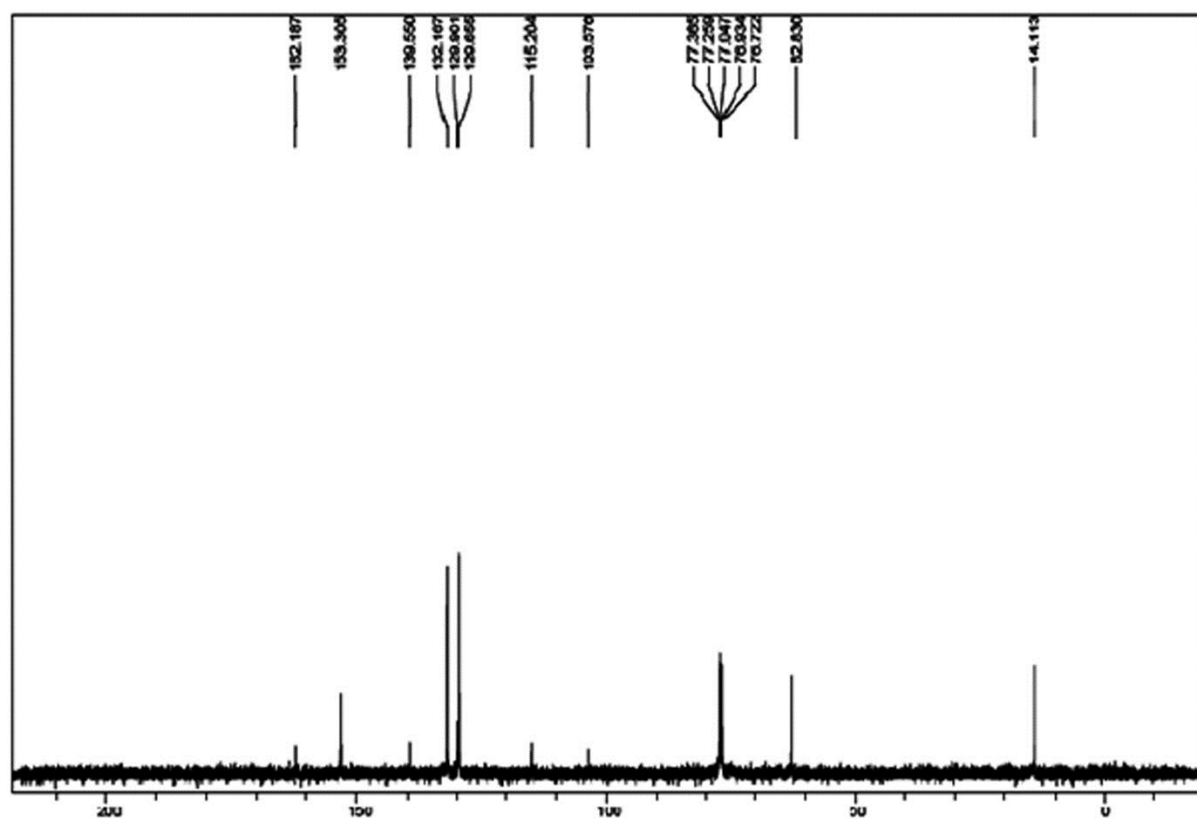
Ethyl 2-cyano-3-phenylacrylate (table 2, entry 9): Mp: 50-52 °C [59]; ¹H-NMR (400MHz, CDCl₃): δ (ppm): 1.49 (t, *J*= 6.8 Hz, 3H) 4.16 (q, *J*= 6.8 Hz, 2H) 6.99-7.01 (m, 3H) 7.65 (d, *J*=8.4Hz, 1H) 7.66-7.90 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 162.5, 155.1, 155.0, 133.3, 131.4, 131.1, 129.3, 115.5, 103.0, 62.7, 14.2.





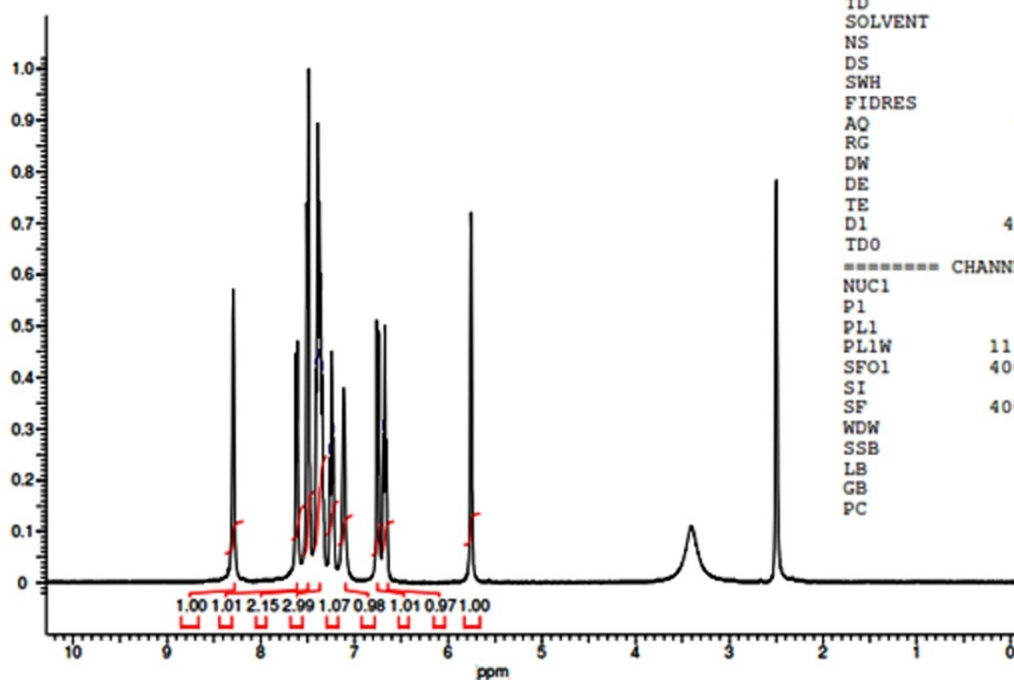
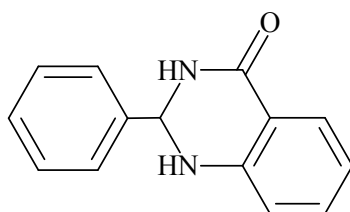
Ethyl 3-(4-chlorophenyl)-2-cyanoacrylate (table 2, entry 12): Mp: 87-89 °C [64]; ¹H-NMR (400 MHz, CDCl₃): δ (ppm): 8.20 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ (ppm): 162.2, 153.3, 139.5, 132.1, 129.9, 129.6, 115.2, 103.6, 62.8, 14.1.



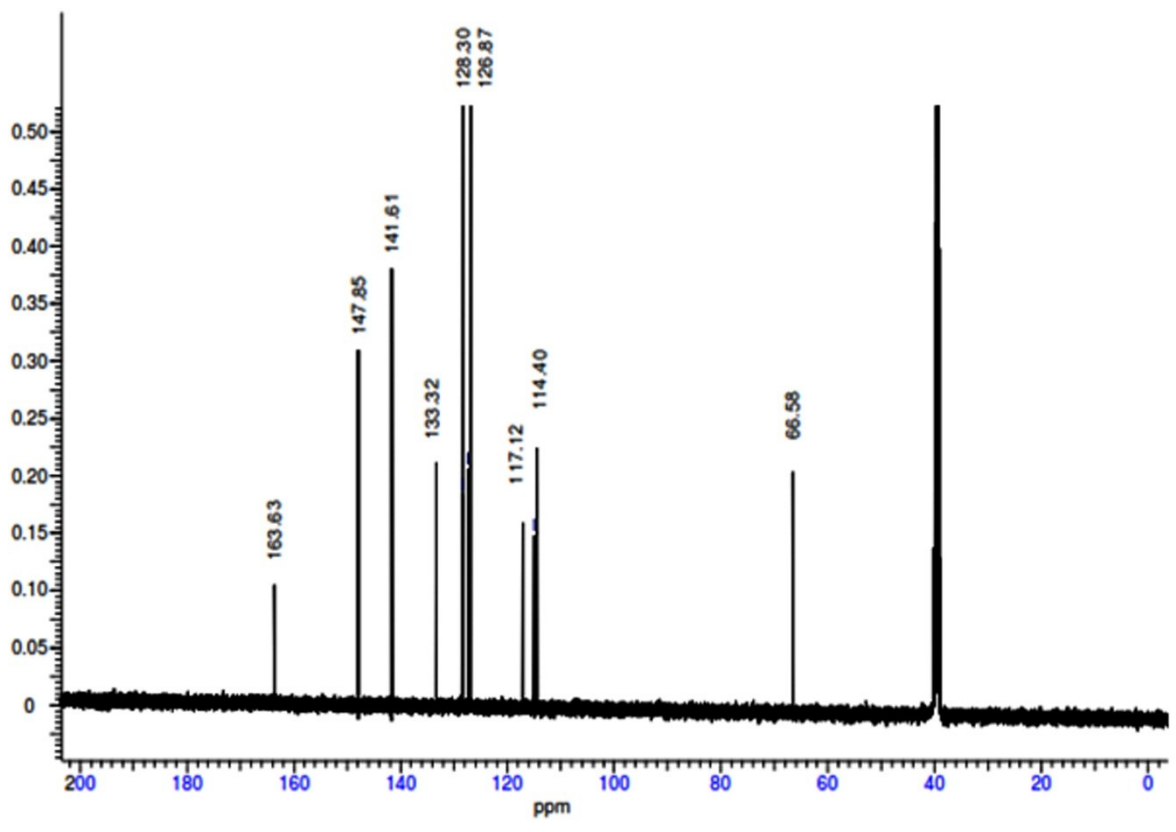


NMR Spectra of 2,3-dihydroquinazolin-4(1H)-one Products

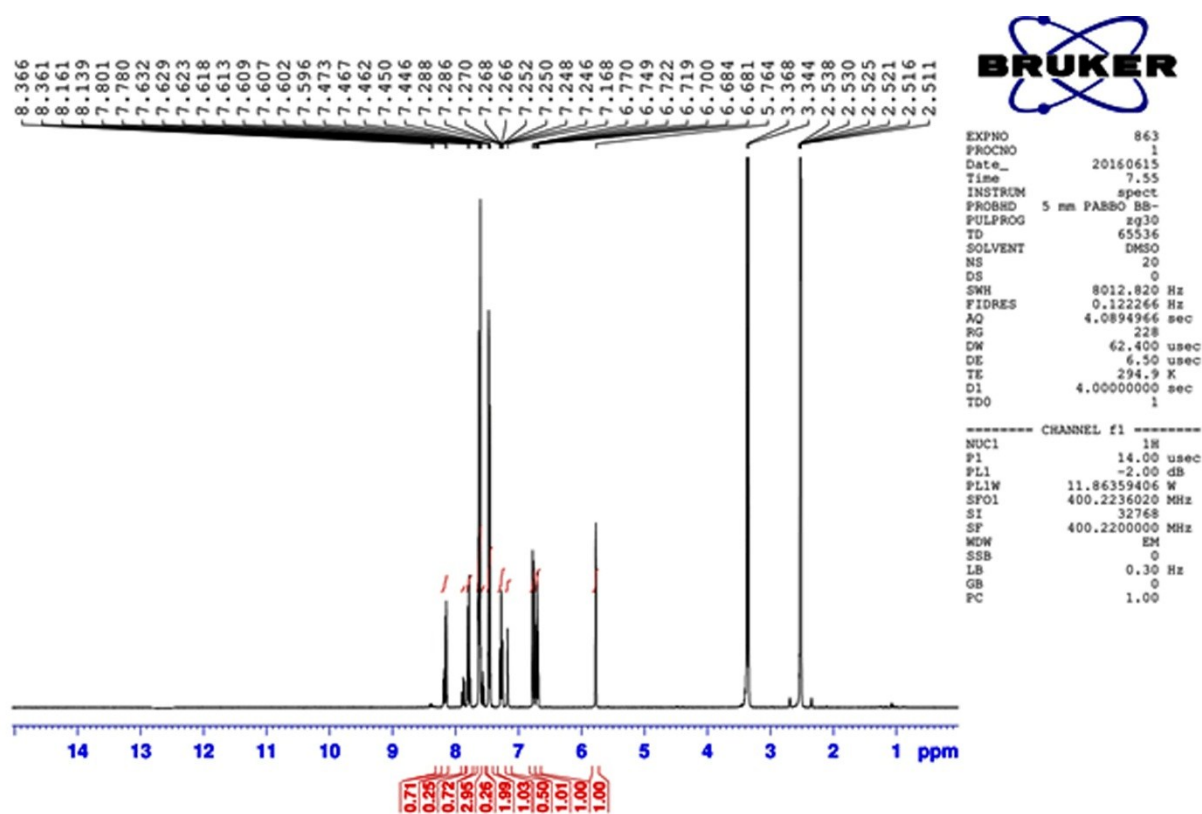
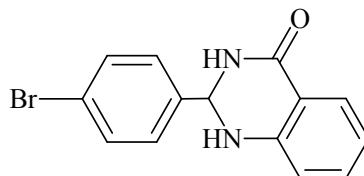
2-Phenyl-2,3-dihydroquinazolin-4(1H)-one(table 4, entry 1):Mp:223-224 °C [66]; ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm):8.29 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.41-7.35 (m, 3H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.69 (t, *J* = 7.8 Hz, 1H), 5.76 (s, 1H); ¹³C-NMR (100 MHz, DMSO-d₆) δ (ppm):163.6, 147.8, 141.6, 133.3, 128.4, 128.3, 127.3, 126.8, 117.1, 114.9, 114.4, 66.5.

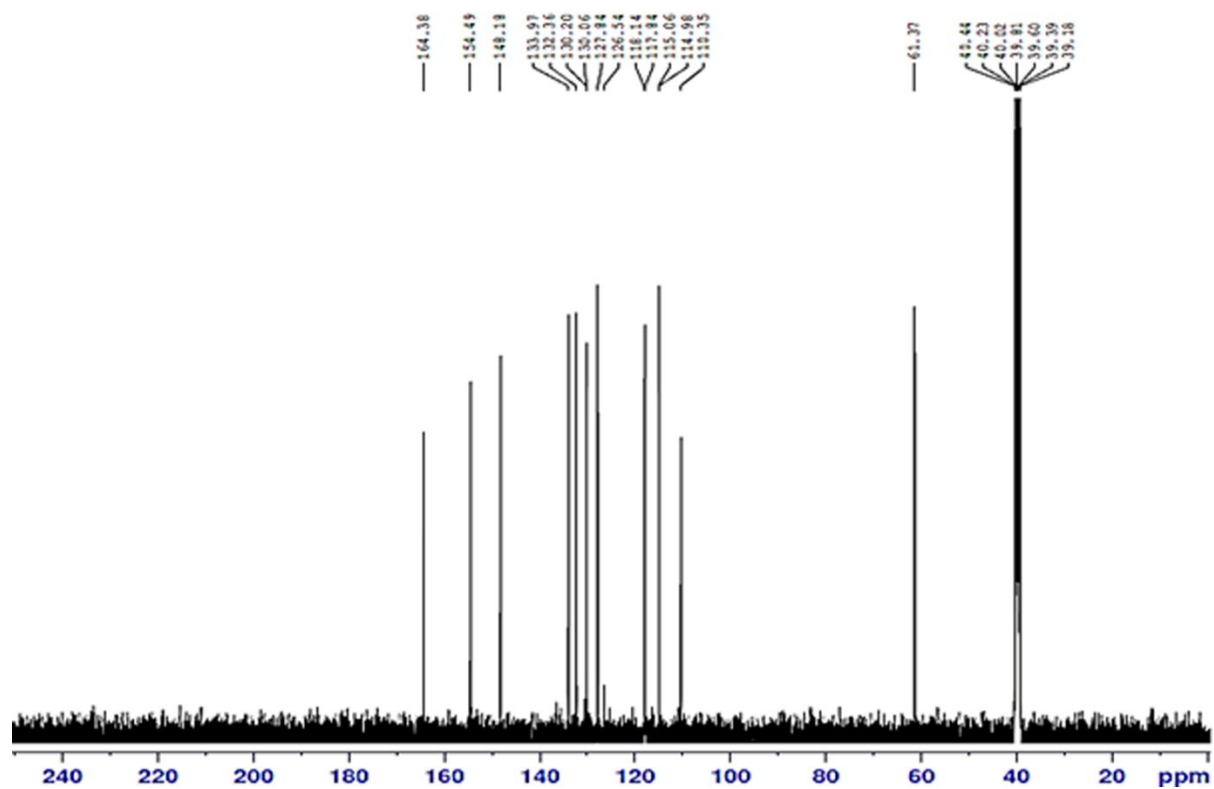


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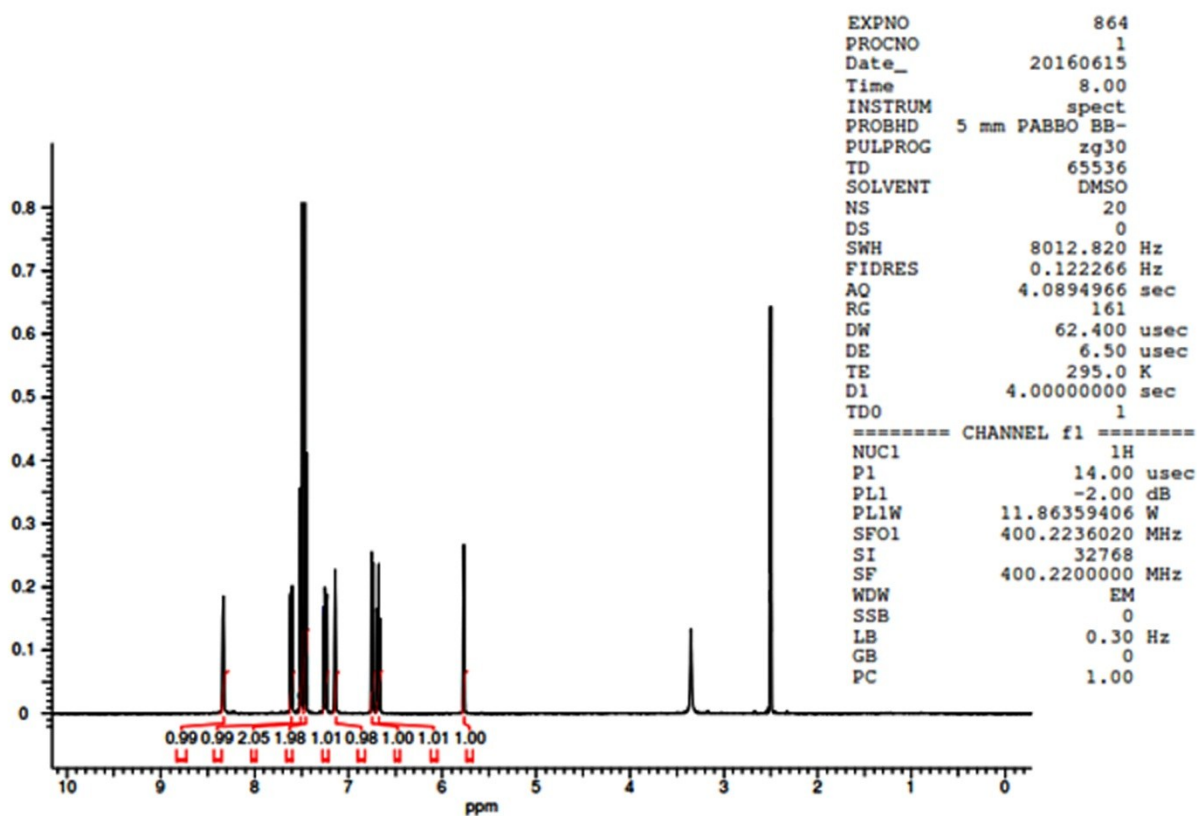
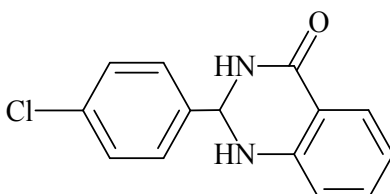


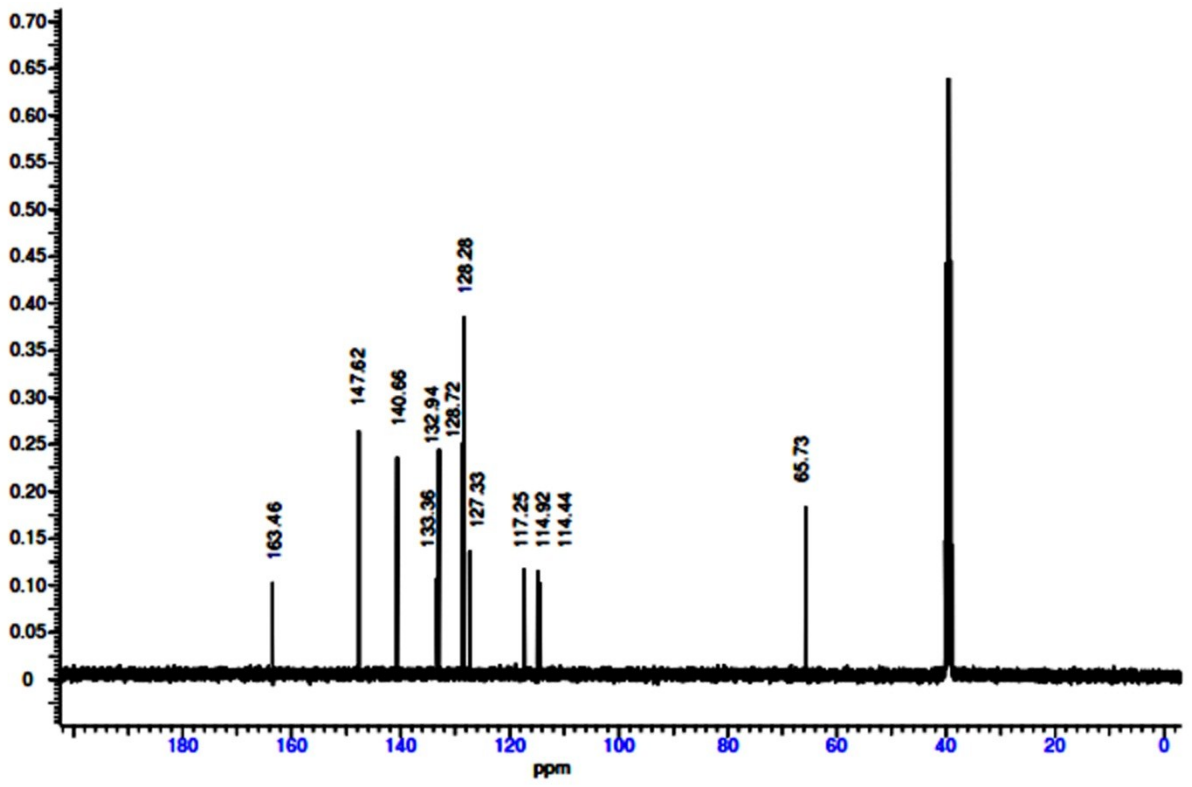
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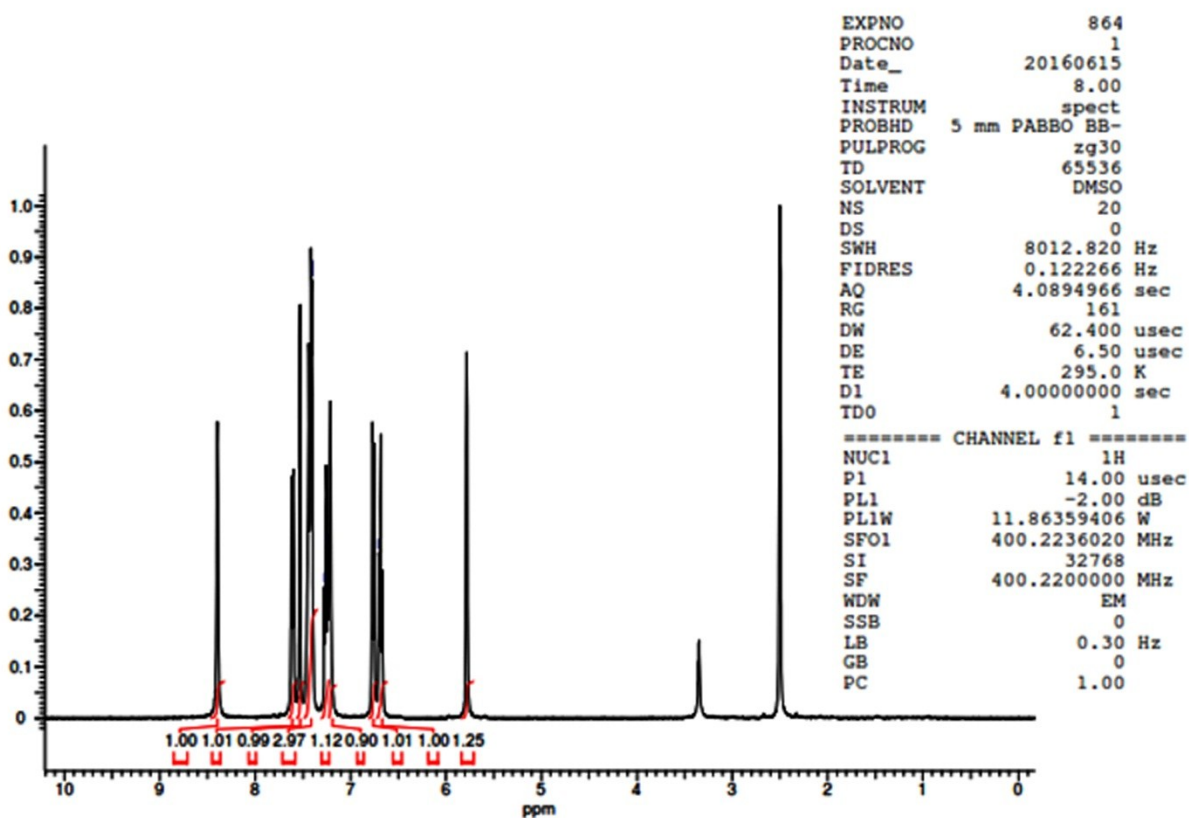
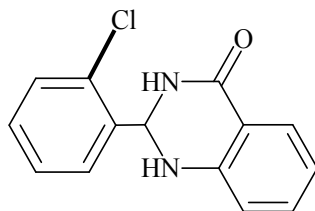


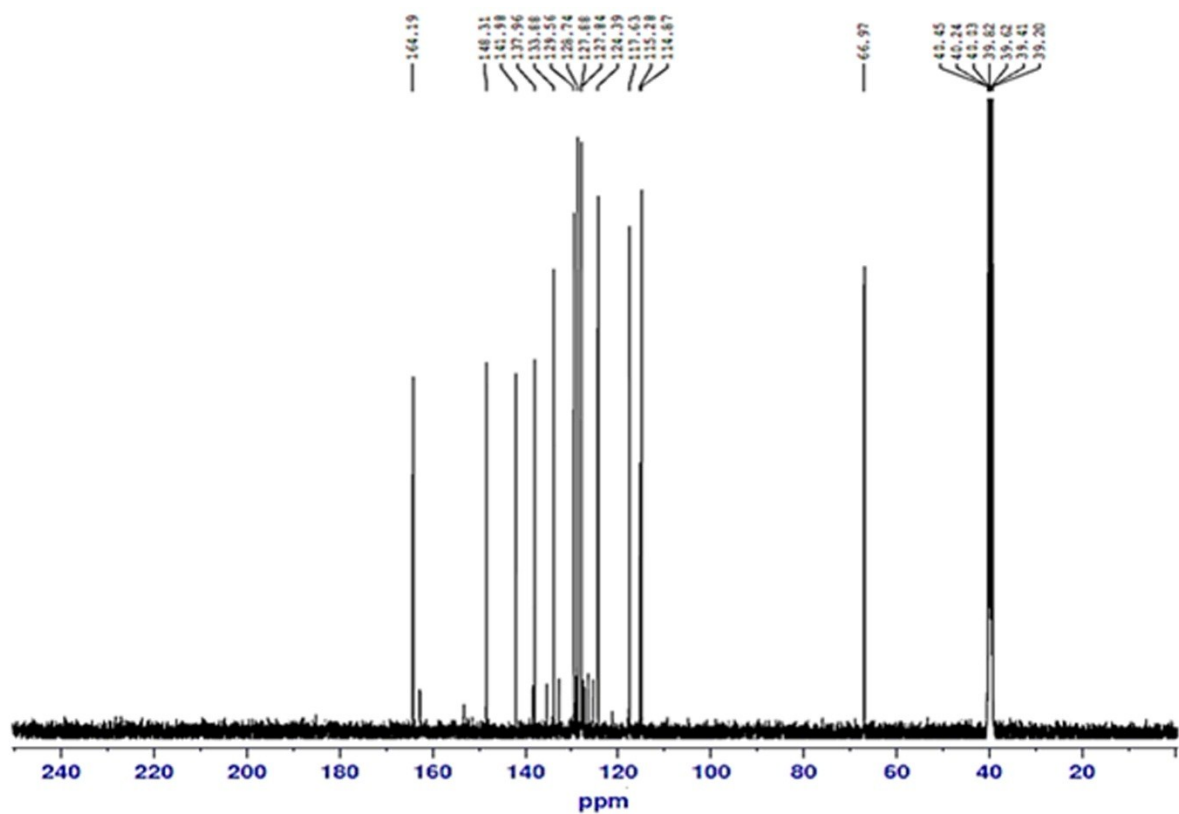
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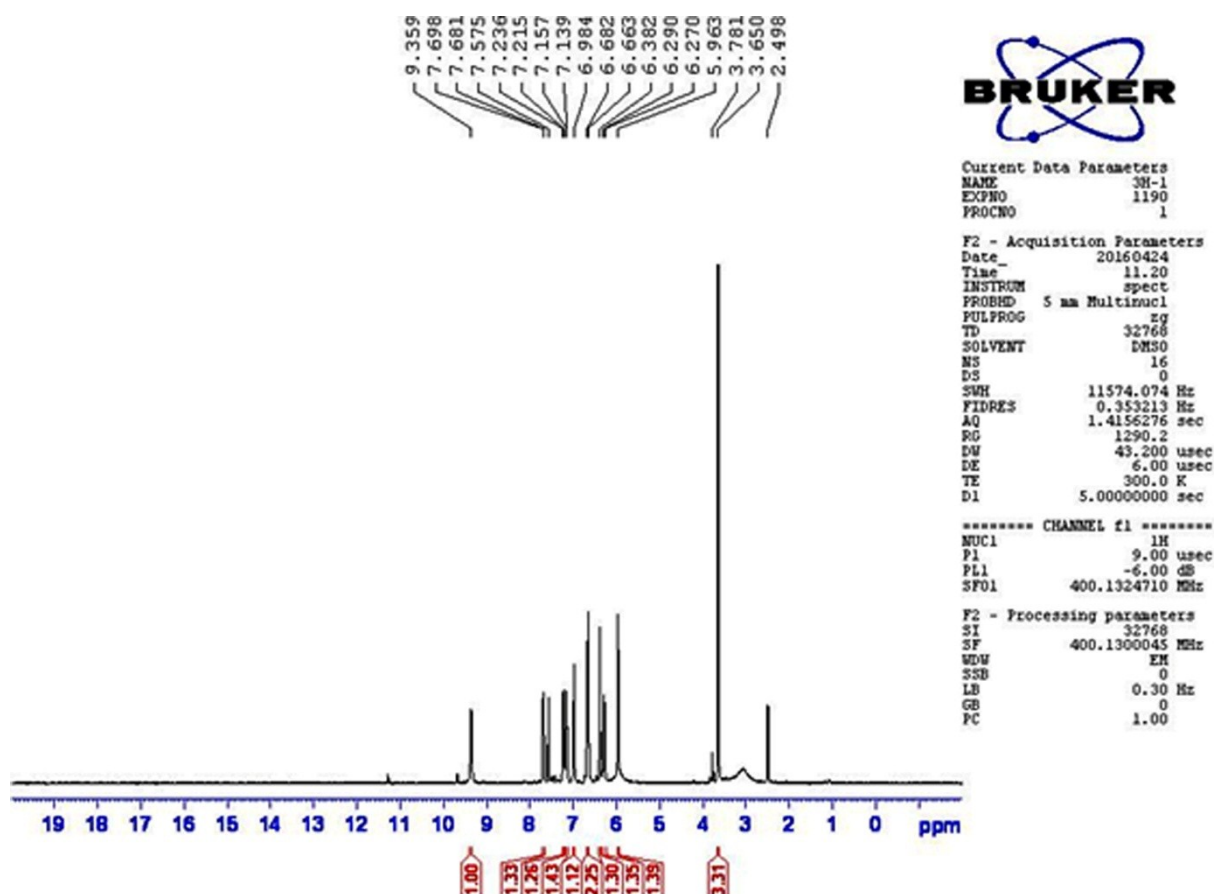
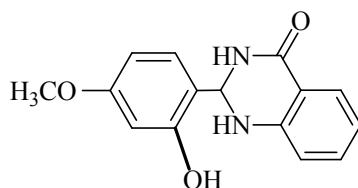


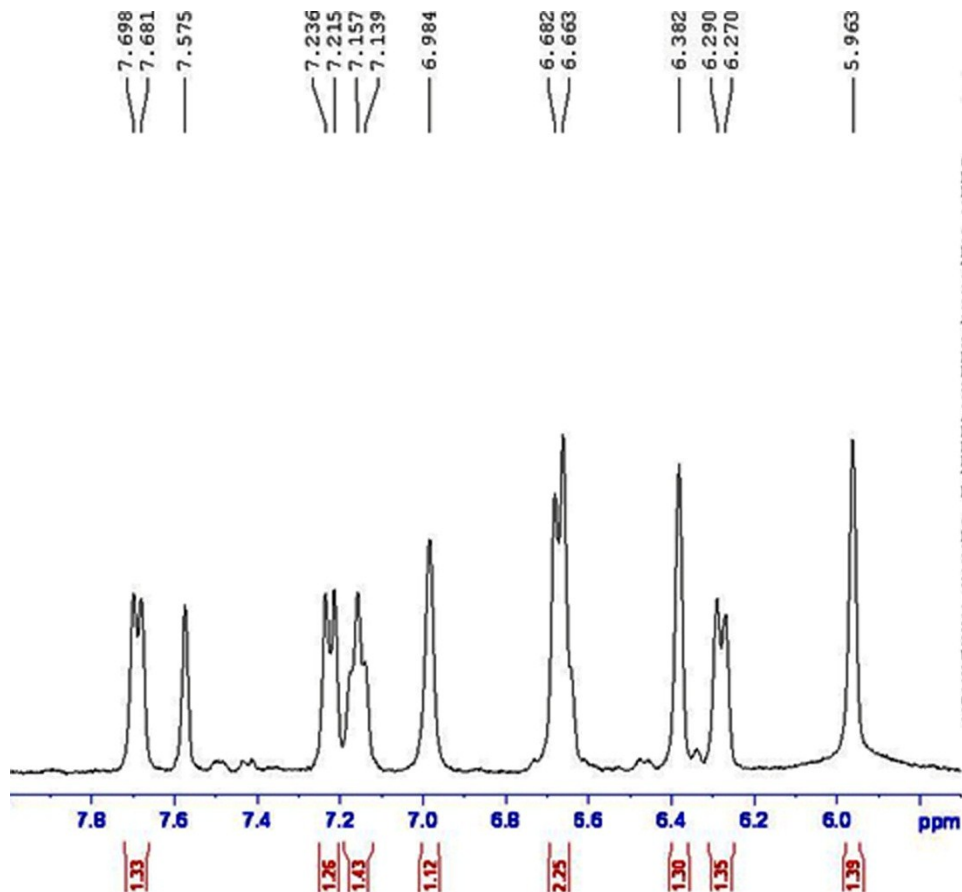
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2-(2-Hydroxy-4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one (table 4, entry 6):
 Mp: 262-263 °C [68]; ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm): 9.35 (s, 1H), 7.68 (d, J = 6.8 Hz, 1H), 7.57 (s, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.15-7.13 (m, 1H), 6.98 (s, 1H), 6.68-6.66 (m, 2H), 6.38 (s, 1H), 6.29-6.27 (m, 1H), 5.96 (s, 1H), 3.65 (s, 3H); ¹³C-NMR (100 MHz, DMSO-d₆) δ (ppm): 163.5, 159.2, 147.7, 143.3, 133.3, 129.4, 127.3, 118.9, 117.0, 114.9, 114.3, 113.6, 112.5, 66.2, 55.0.



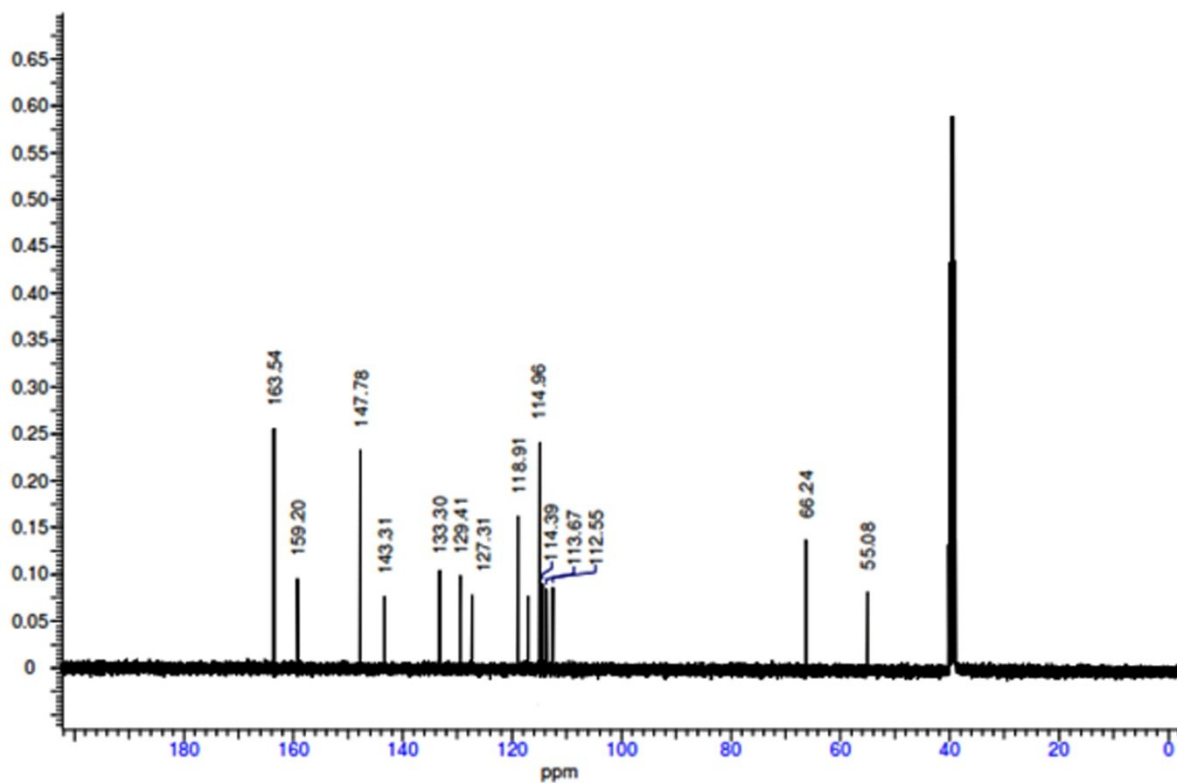


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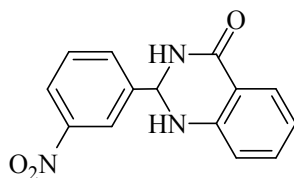
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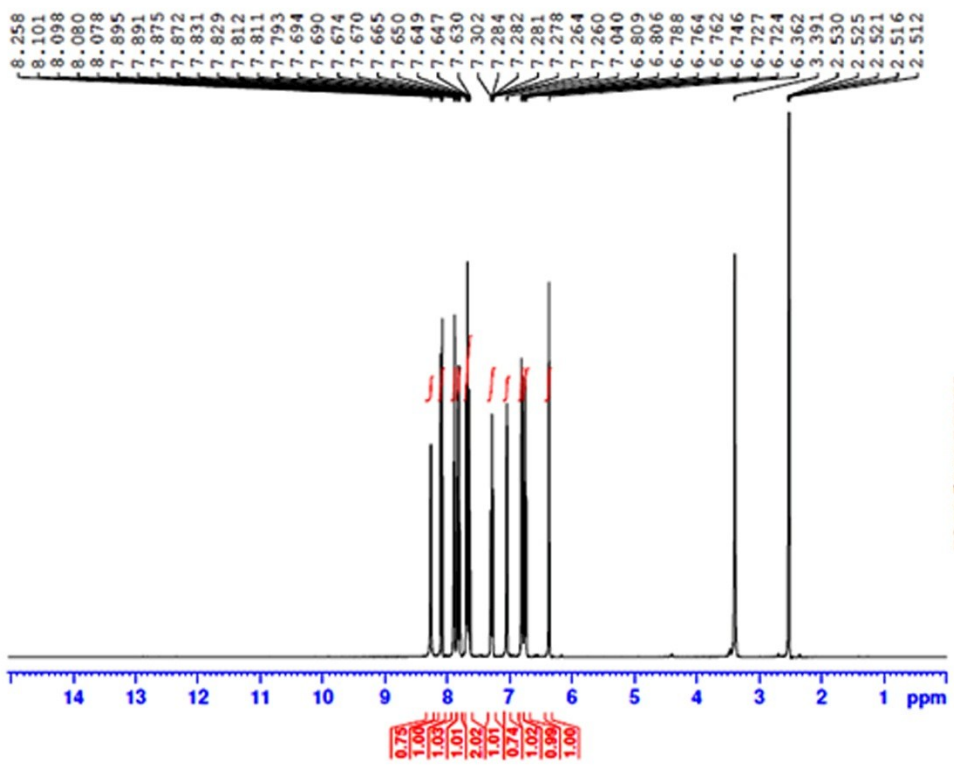
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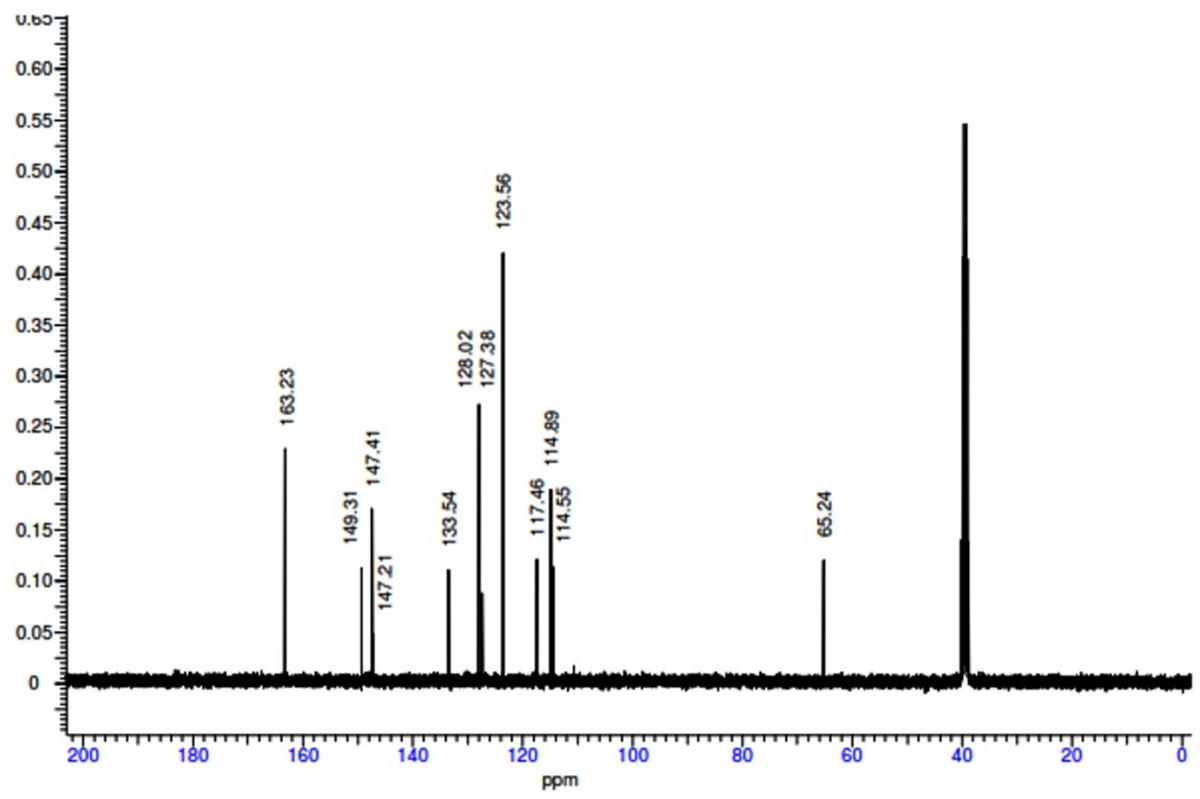


2-(3-Nitrophenyl)-2,3-dihydroquinazolin-4(1H)-one (table 4, entry 7): Mp: 180-182 °C [67]; $^1\text{H-NMR}$ (400 MHz, DMSO- d_6): δ (ppm): 8.25 (s, 1H), 8.09 (d, $J = 7.2$, 1H), 7.89 (d, $J = 6.4$, 1H), 7.83-7.80 (m, 1H), 7.70-7.63 (m, 2H), 7.30 (t, $J = 7.2$, 1H), 7.04 (s, 1H), 6.80-6.72 (m, 2H), 6.36 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ (ppm): 163.2, 149.3, 147.4, 147.2, 133.5, 128.0, 127.3, 123.5, 117.4, 114.8, 114.5, 65.2.

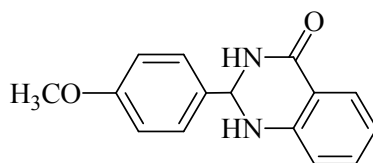




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 GB 0
 PC 1.00



2-(4-Methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one(table 4, entry 9): Mp:182-183 °C [68]; ¹H-NMR (400 MHz, DMSO-d6): δ (ppm):8.20 (s, 1H), 7.64-7.62 (d, *J*= 6, 1H), 7.28-7.24 (t, *J*= 6, 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, 2H), 5.71 (s, 1H), 3.77 (s, 3H); ¹³C-NMR (100 MHz, DMSO-d6) δ (ppm):163.6, 159.4, 147.9, 133.4, 133.2, 128.1, 127.3, 117.0, 114.9, 114.3, 113.6, 66.2, 55.1.



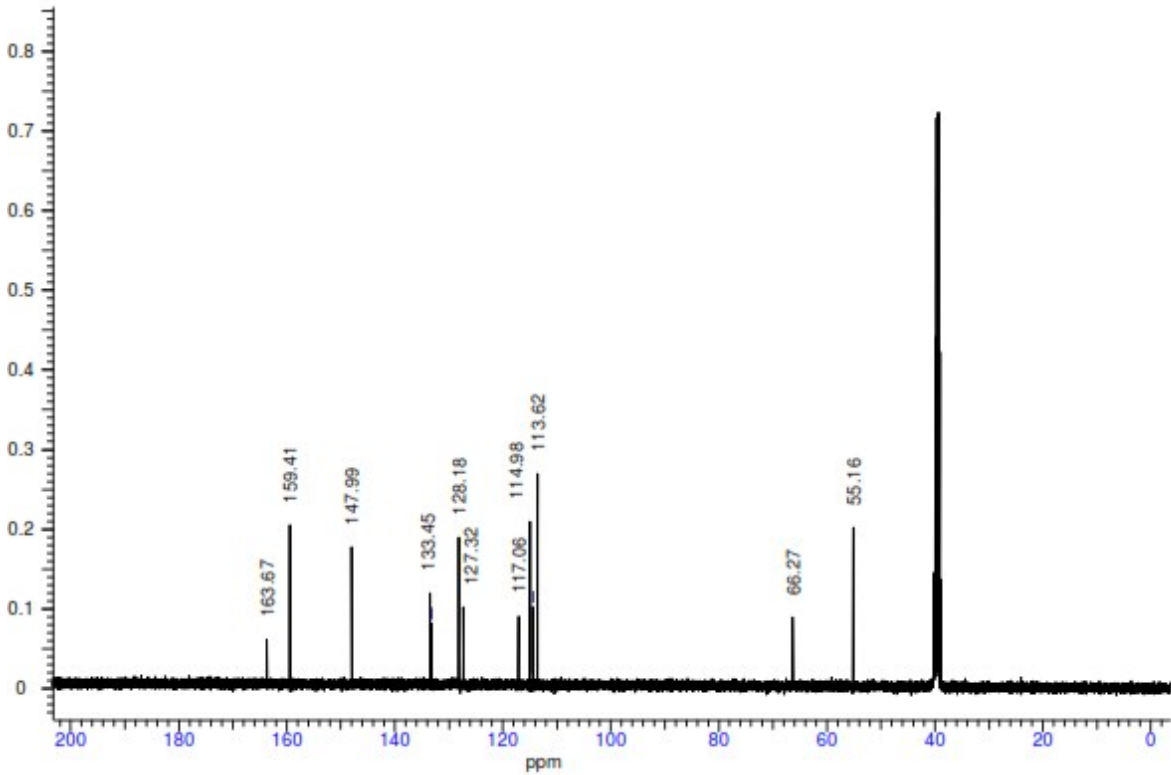
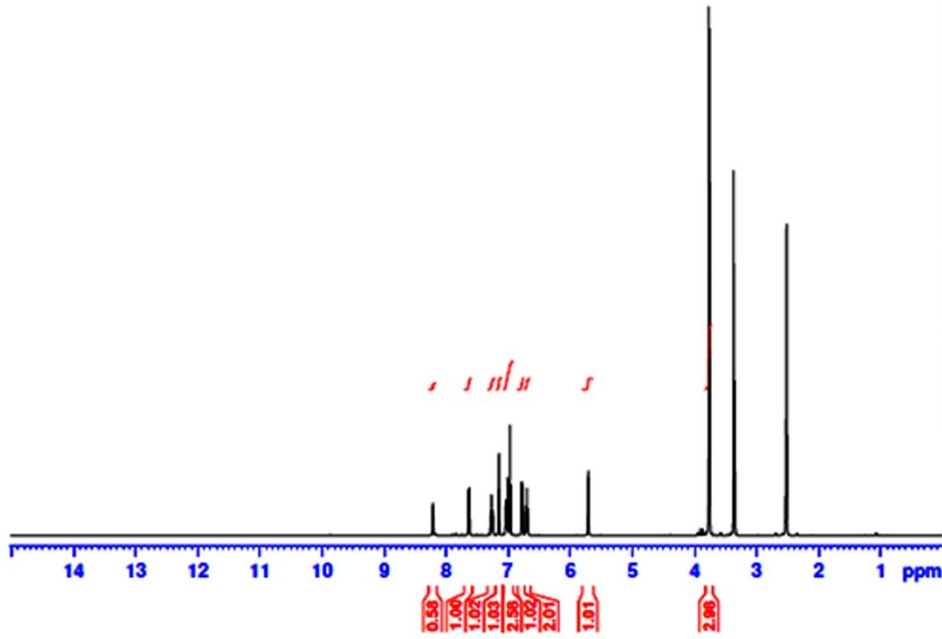
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7.149
7.145
7.037
7.027
7.022
7.006
7.001
6.972
6.951
6.781
6.761
6.719
6.716
6.713
6.697
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3.760
3.372
3.349
2.530
2.525
2.521



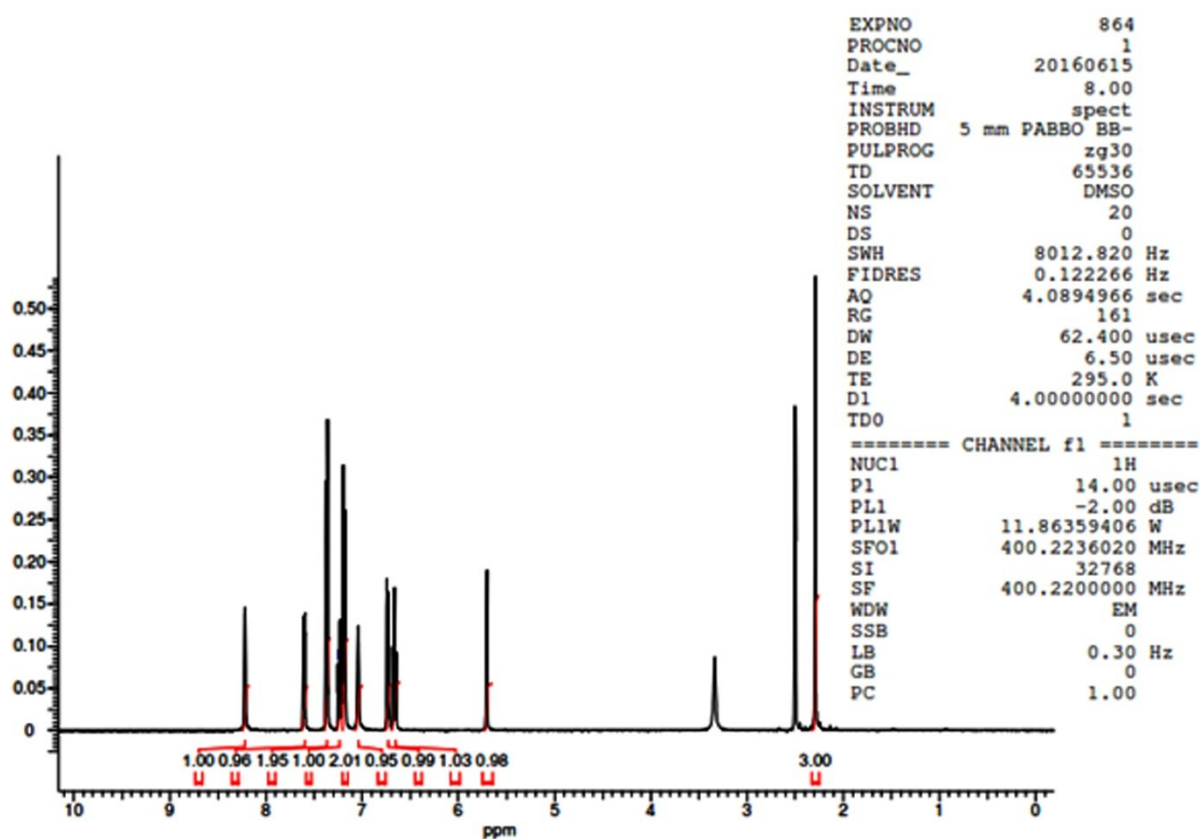
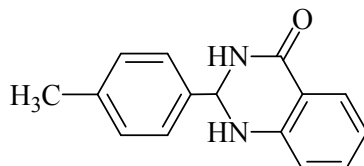
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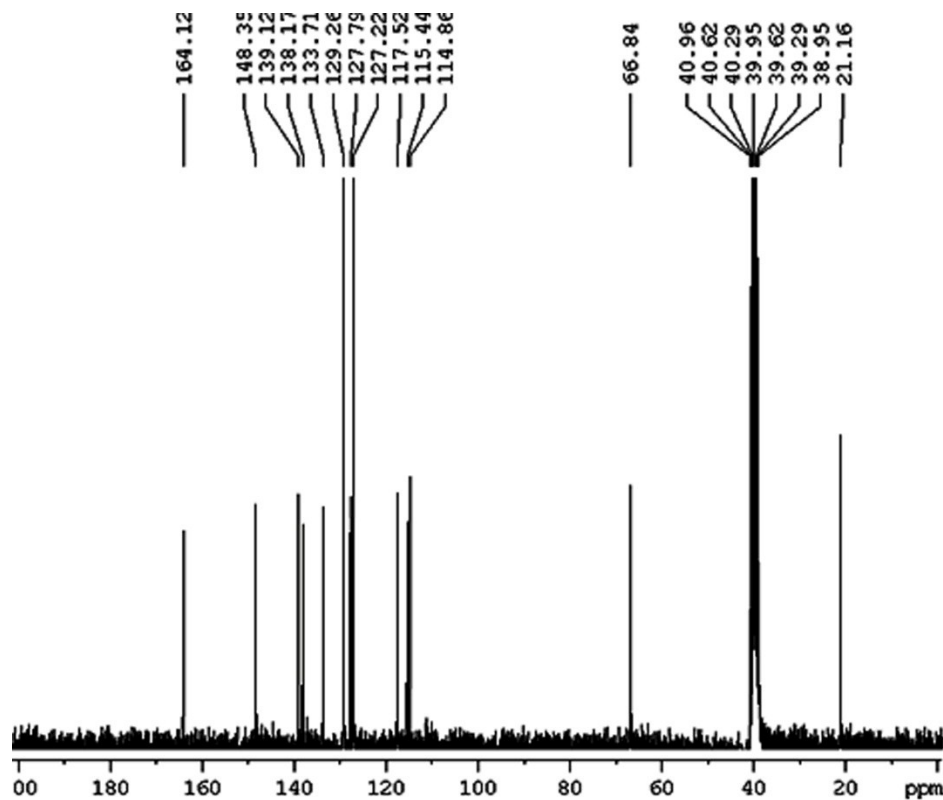
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DS          0
SWH         8012.820 Hz
FIDRES     0.122266 Hz
AQ          4.0894966 sec
RG          161
DW          62.400 usec
DE          6.50 usec
TE          295.0 K
D1          4.00000000 sec
TDO         1

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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
  
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2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (table 4, entry 10): Mp: 225-226 °C [35]; ¹H-NMR (400 MHz, DMSO-d₆): δ (ppm): 8.22 (s, 1H), 7.62 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.25-7.21 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.04 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.68-6.64 (m, 1H), 5.71 (s, 1H), 2.29 (s, 3H); ¹³C-NMR (100 MHz, DMSO-d₆) δ (ppm): 164.1, 148.4, 139.1, 138.2, 133.7, 129.3, 127.8, 127.2, 117.5, 115.4, 114.9, 66.8, 21.2.





Current Data Parameters

EXFNO 79
PROCNO 1

F2 - Acquisition Parameters

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FIDRES 0.229801 Hz
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DW 33.200 usec
DE 6.00 usec
TE 300.0 K
D1 5.0000000 sec
d11 0.0300000 sec
d12 0.0000200 sec

----- CHANNEL f1 -----

NUC1 13C
P1 8.00 usec
PL1 0.00 dB
SFO1 62.9015280 MHz

----- CHANNEL f2 -----

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PCPD2 80.00 usec
PL2 3.00 dB
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PL13 20.00 dB
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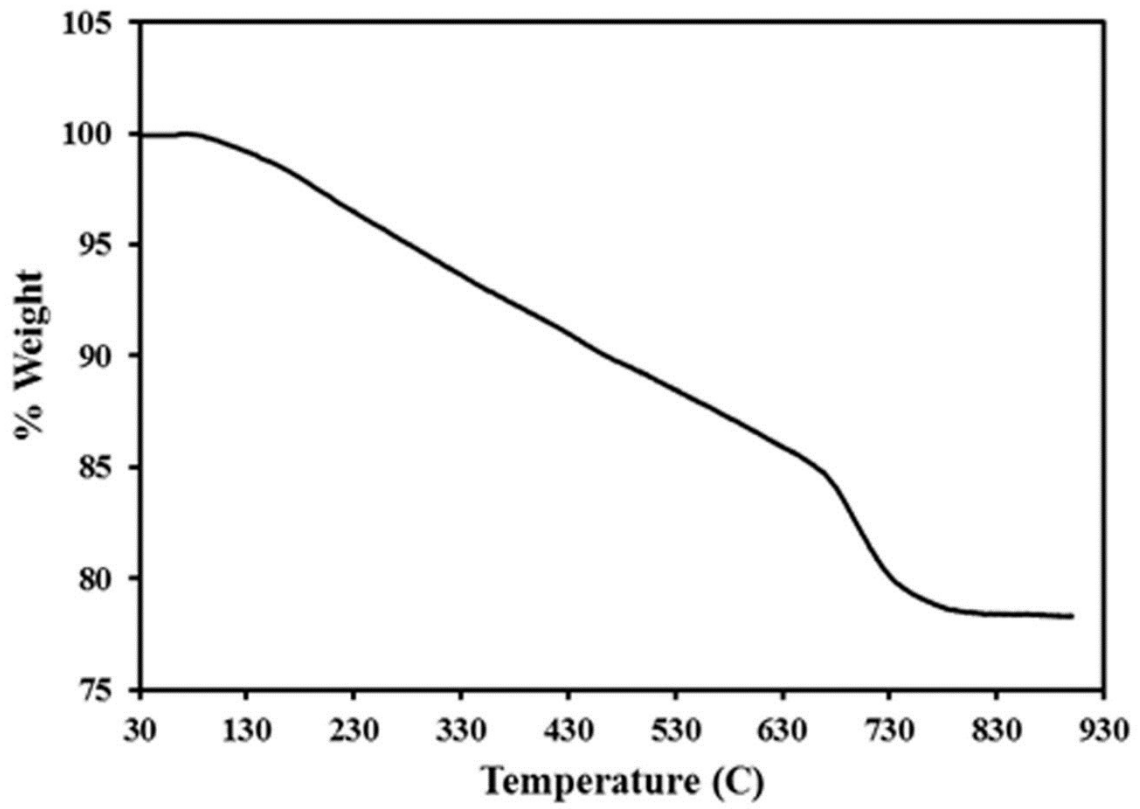


Fig. S1 TG analysis of Graphene Oxide.

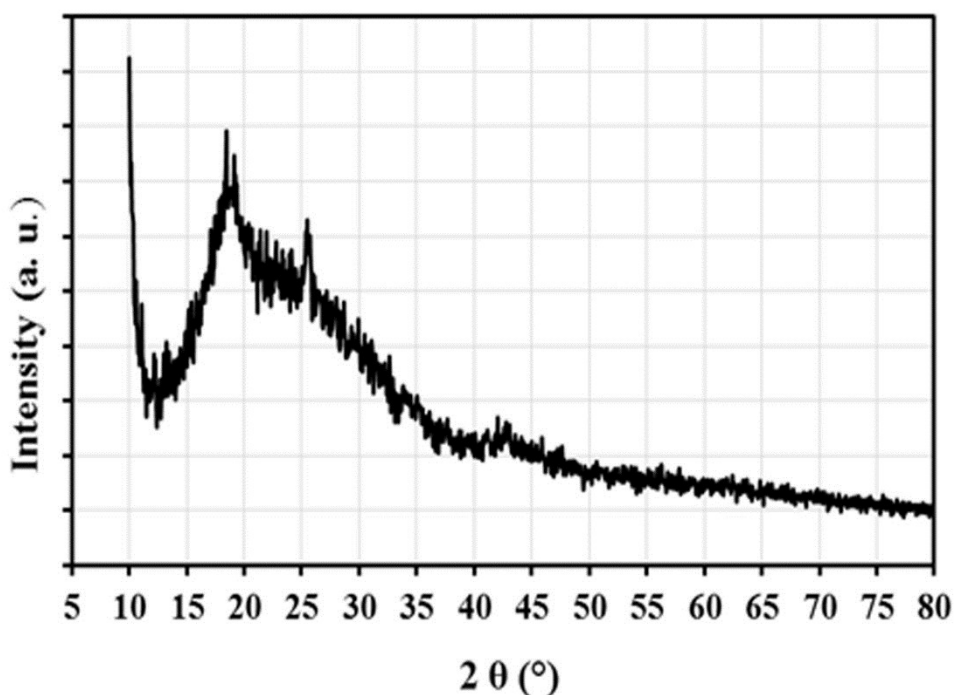


Fig. S2 XRD analysis of Graphene Oxide.

The common methods such as titration with Hammett indicators, temperature programmed desorption of adsorbed molecules such as ammonia or pyridine, adsorption microcalorimetry, NMR spectroscopy have been employed to describe the acidity of POMs in the solid state both qualitatively and quantitatively [43]. Potentiometric titration with n-butylamine let us to estimate the number of acid sites and their distribution [22]. The titration curves show that HybPOM and Go/Fe₃O₄/HybPOM with the initial electrode potential -165.9 and -73.8 mV are classified as very weak and weak acid, respectively. Difference in the acid strength of HybPOM and Go/Fe₃O₄/HybPOM is attributed to the total number of free NH₂ groups on them. For Go/Fe₃O₄/ HybPOM some of NH₂ groups are involved in the bonding with Go/Fe₃O₄ nanoparticle."

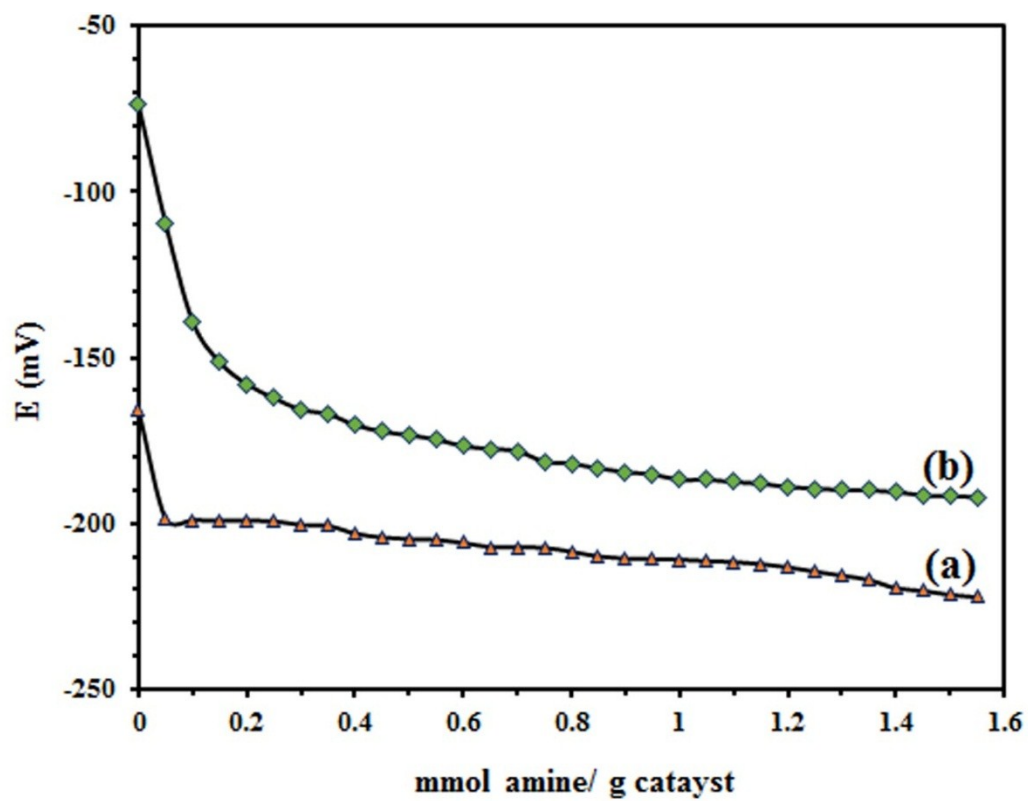


Fig. S3 The acid-base titration curves of HybPOM (a) and Go/Fe₃O₄/HybPOM (b)