A Novel Nano-Catalyst Praseodymium Oxide (Pr_6O_{11}) for Efficient and Sustainable Synthesis of Chromene Derivatives by Ultrasound Irradiation in Aqueous Hydrotopic medium

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13. XRD of Pr_6O_{11}

General

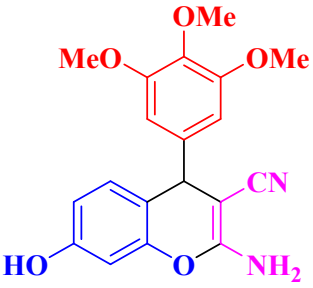
All chemicals were garnered from Loba and Sigma-Aldrich chemical companies and used without any else purification. Double distilled water was employed as an aqueous medium. The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively.

Experimental Procedure: -

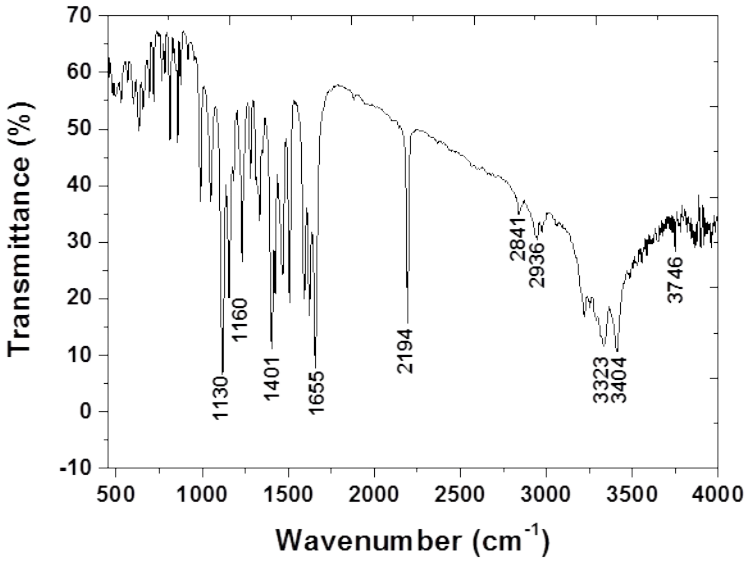
. In order to develop a green protocol and check the viability of the reaction in the aqueous and partially alcoholic media, a long screening test involving various parameters like catalyst, NaPTS, application of ultrasound frequencies, and the solvents being fully or partially aqueous; a method development has been carried out. The developed method is nomenclatured as 'model reaction 2'. Aqueous solutions of 0.101 mL of 1 mM Benzaldehyde, 0.063 mL of 1 mM malononitrile, 0.11 g of 1 mM resorcinol, and 20 % NaPTS were added in a container. To these reactants, 0.01 g of 10 mol% Pr_6O_{11} NPs were added as a catalyst. These reactants were then subjected to ultrasound irradiations at room temperature for five minutes, and the progress of the reaction was monitored on TLC (ethyl acetate: hexane 8:2). The product was filtered with the Whatman filter paper no. 41 to separate the catalyst (Pr_6O_{11}) NPs. The catalyst NPs were preserved for the recyclability test. The product devoid of catalyst obtained after filtration was re-crystallized by Ethanol and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy.

Spectroscopic data:

Compound-1[Entry-4g] -: 2-Amino-3-cyano-7-hydroxy-4-(3,4,5-trimethoxy)-4H-chromene.

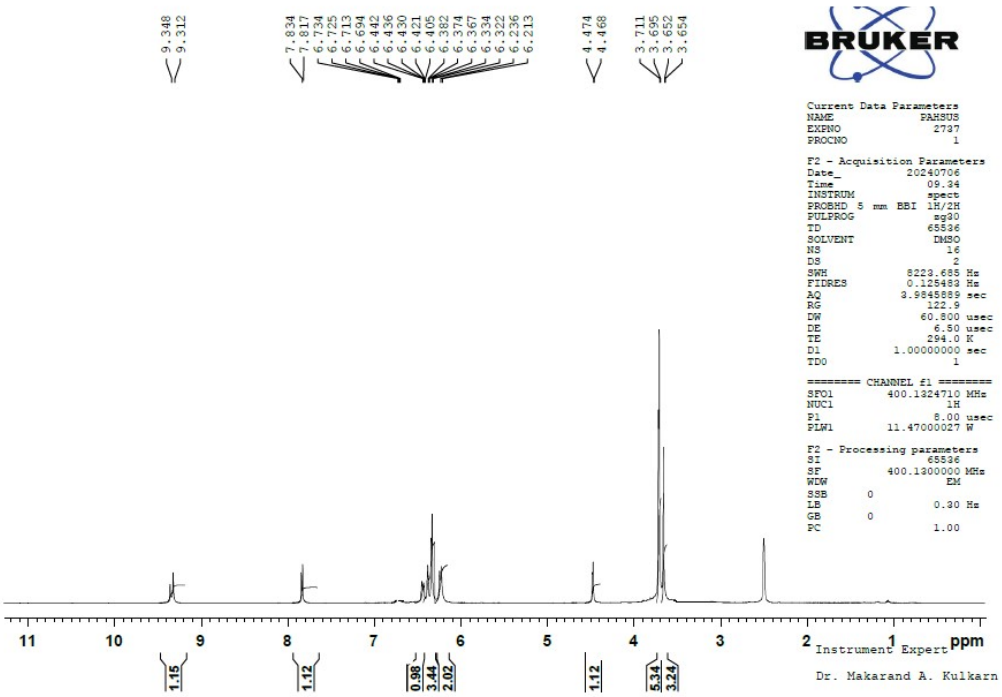


IR (KBr)cm^{-1}: 3600 (-OH), 3450 (-NH_2), 2963 (Ar-CH), 2225(-CN), 1660,(aromatic), 1130, 1150, 1260 (C-O)



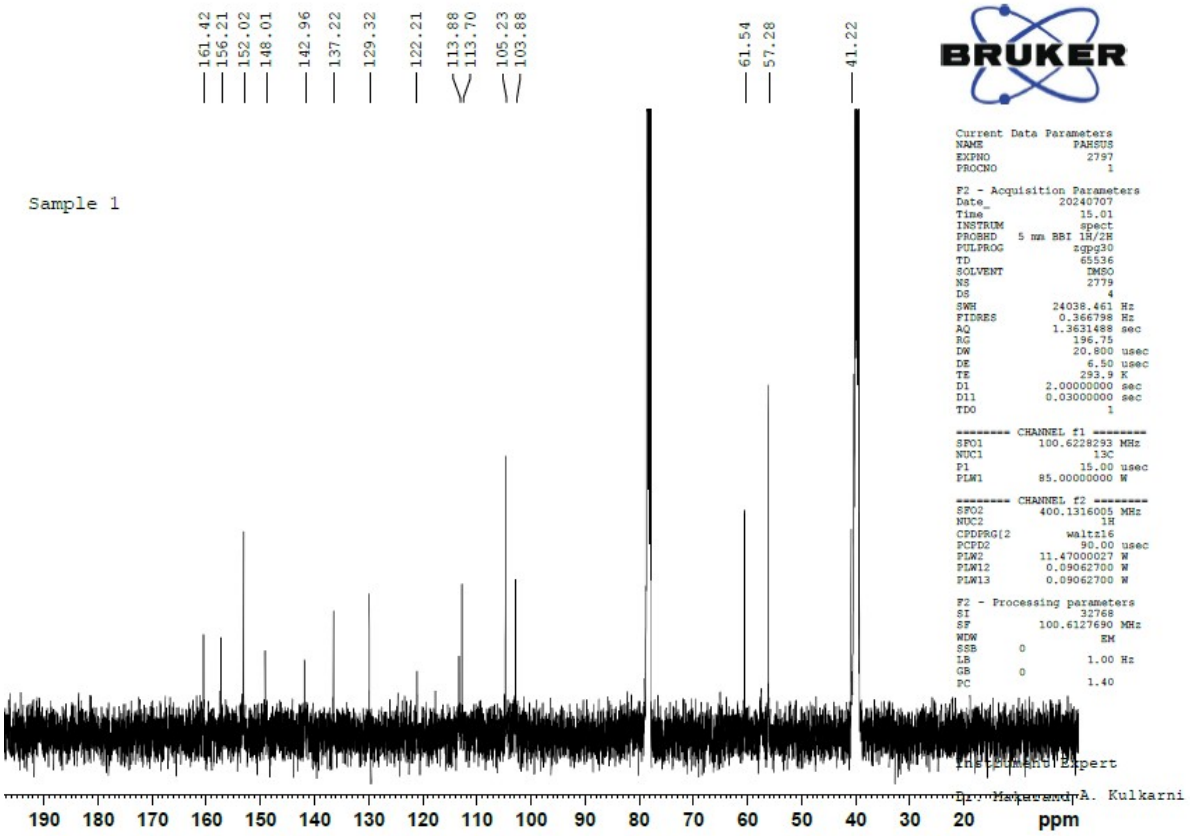
^{1}H-NMR: -

^{1}H NMR (400 MHz DMSO-d6): 3.67 (s, 9H, OMe), 4.47 (s, 1H, CH), 6.40 (s, 2H, NH_2),6.69-6.73 (m, 4H), 7.83(dd,1H), 9.34(s, 1H, OH)



^{13}C-NMR: -

^{13}C NMR (400 MHz DMSO-d6) d(ppm): 161.42, 156.21, 152.02, 148.01, 142.96, 137.22, 129.32, 122.21, 113.88, 113.70, 112.6, 113.70, 105.23, 103.88, 61.54, 57.28.


161.42
156.21
152.02
148.01
142.96
137.22
129.32
122.21
113.88
113.70
105.23
103.88
61.54
57.28
41.22
Sample 1
Current Data Parameters
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EXPNO 2797
PROCNO 1
F2 - Acquisition Parameters
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Time 15.01
INSTRUM spect
PROBHD 5 mm BBI 1H/2H
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TD 65536
SOLVENT DMSO
NS 2779
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
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RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 293.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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SFO1 100.6228293 MHz
NUC1 13C
P1 15.00 usec
PLW1 85.00000000 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 11.47000027 W
PLW12 0.09062700 W
PLW13 0.09062700 W
F2 - Processing parameters
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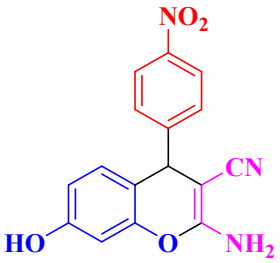
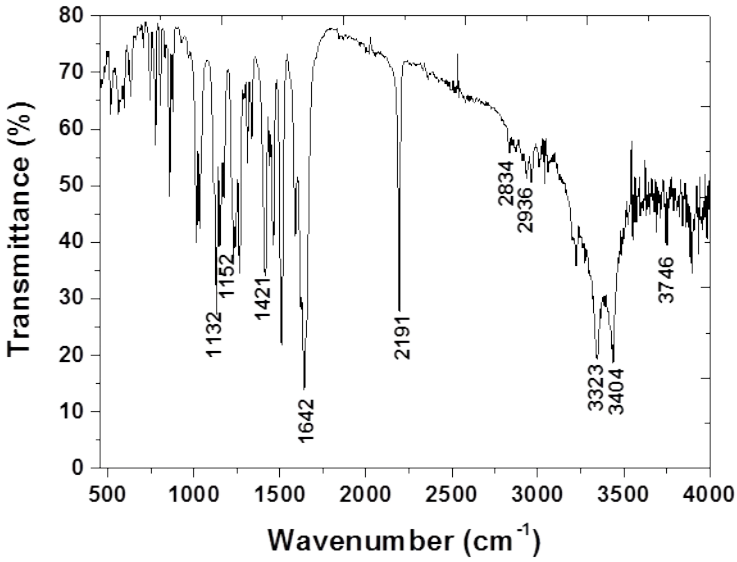
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

Compound-2[Entry-4b]: - 2-Amino-3-cyano-7-hydroxy-4-(4-nitrophenyl)-4H-chromene.

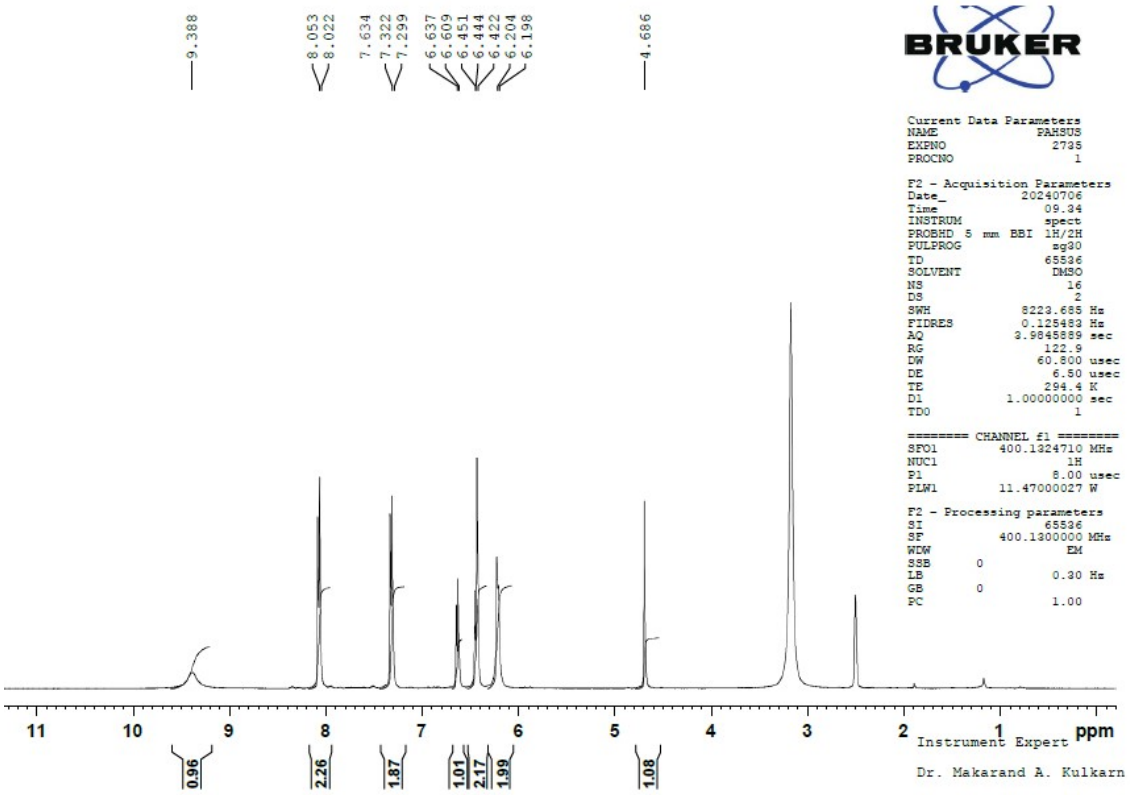


IR (KBr)cm^{-1}: 3500 (-OH), 3450 (-NH_2), 2950 (Ar-CH), 2225 (CN), 1660, 1580 (aromatic), 1490 (NO_2), 1250,1120 (C-O



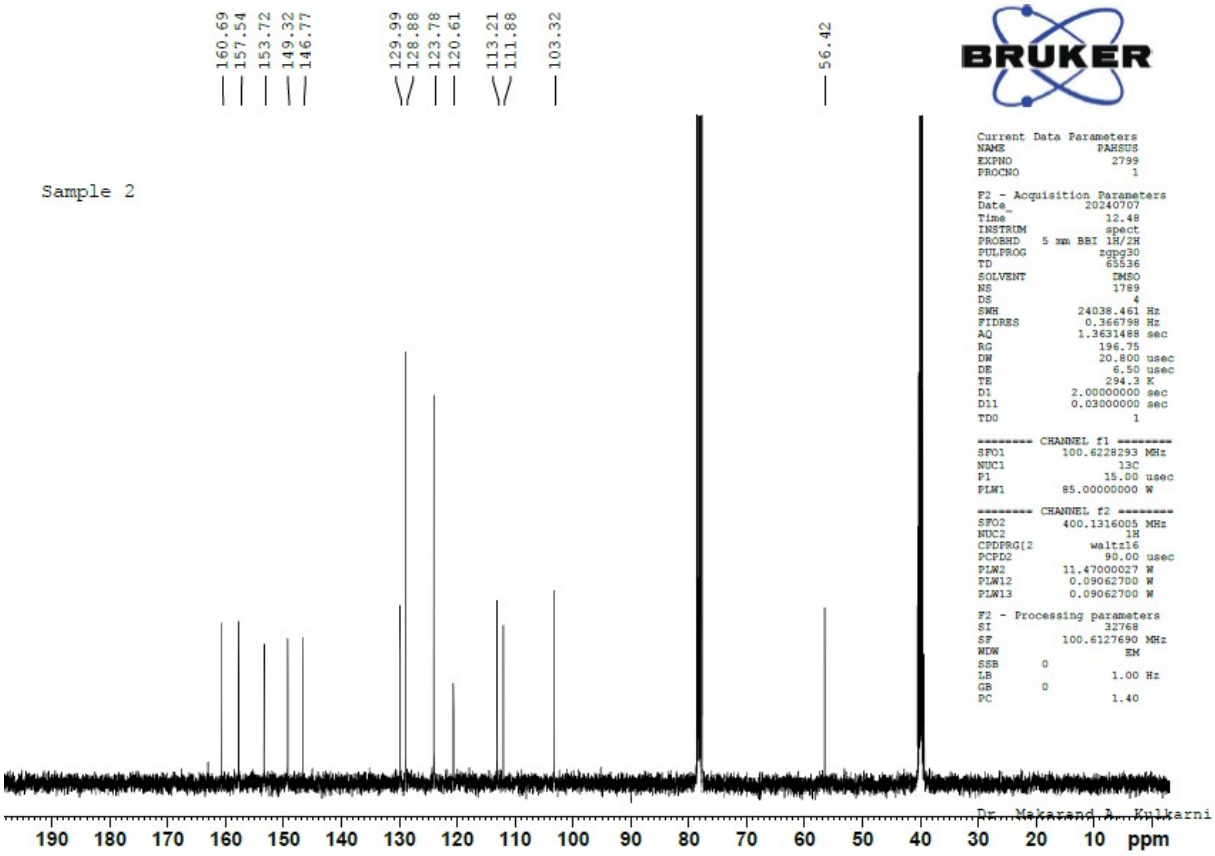
[1]H-NMR: -

[1]H NMR (400 MHz DMSO-d6) δ ppm: 4.68 (s, 1H, CH), 6.19(s, 2H, NH_2), 6.42-6.45 (m, 2H, ortho to Ar-OH), 6.60-6.63 (d,1H, J = 8.00 meta to Ar-OH), 7.2-7.3(m, 2H, meta to Ar-NO_2), 8.02-8.05 (m, 2H, ortho to Ar-NO_2), 9.38 (s, 1H, OH);

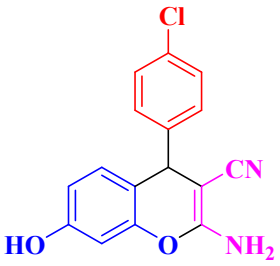


^{13}C-NMR: -

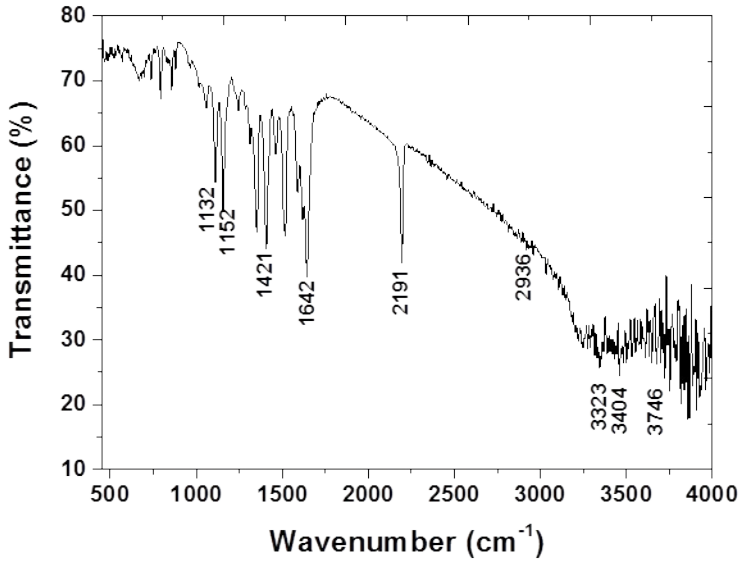
^{13}C NMR (400 MHz DMSO- d6) δ (ppm): 160.69, 157.54, 153.72, 149.32, 146.77, 129.99, 128.88, 123.78, 120.61, 113.21, 111.88, 103.32, 56.42.



Compound-3[Entry-4f]: - 2-Amino-4-(4-chlorophenyl)-3-cyano-7-hydroxy-4H-chromene.

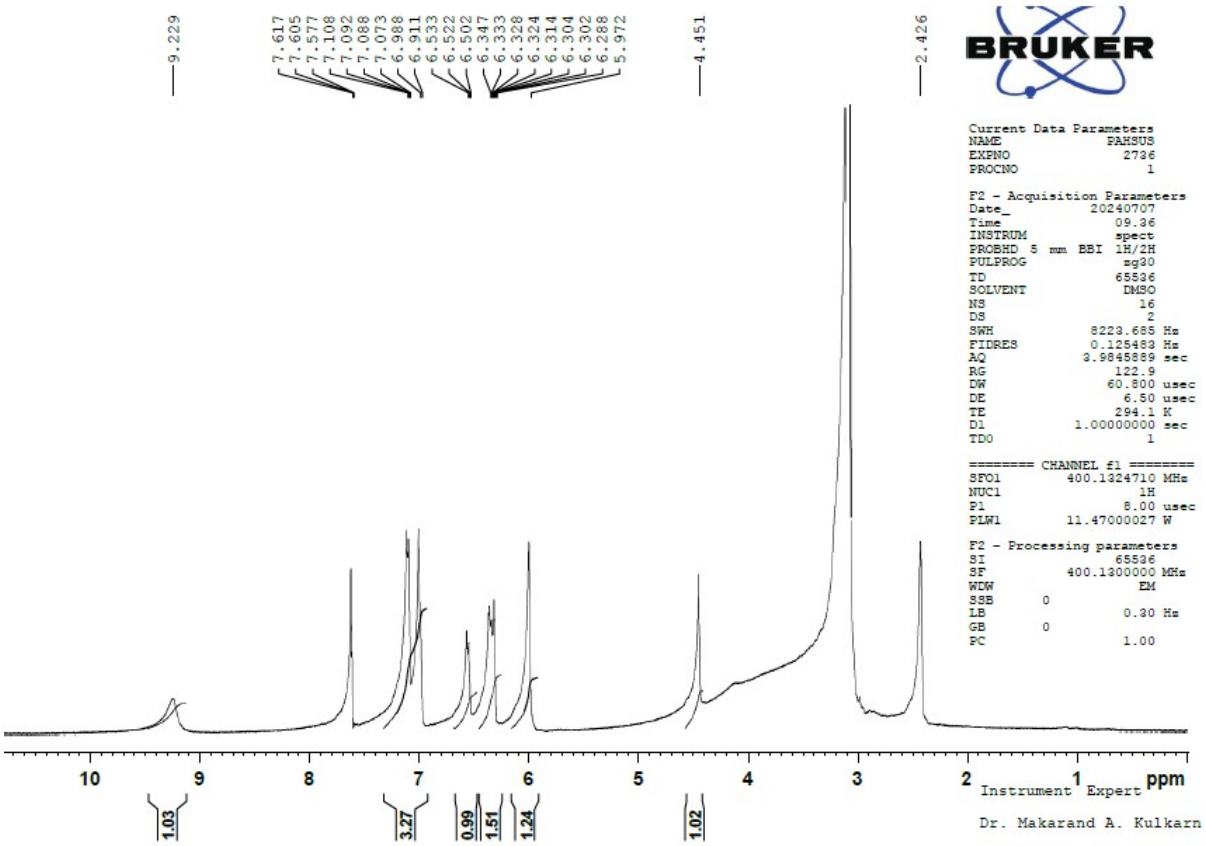


IR ((KBr)cm−1: 3500(-OH), 3350(-NH_2),2225(-CN), 1640 (aromatic),1120,1242 (C-O).



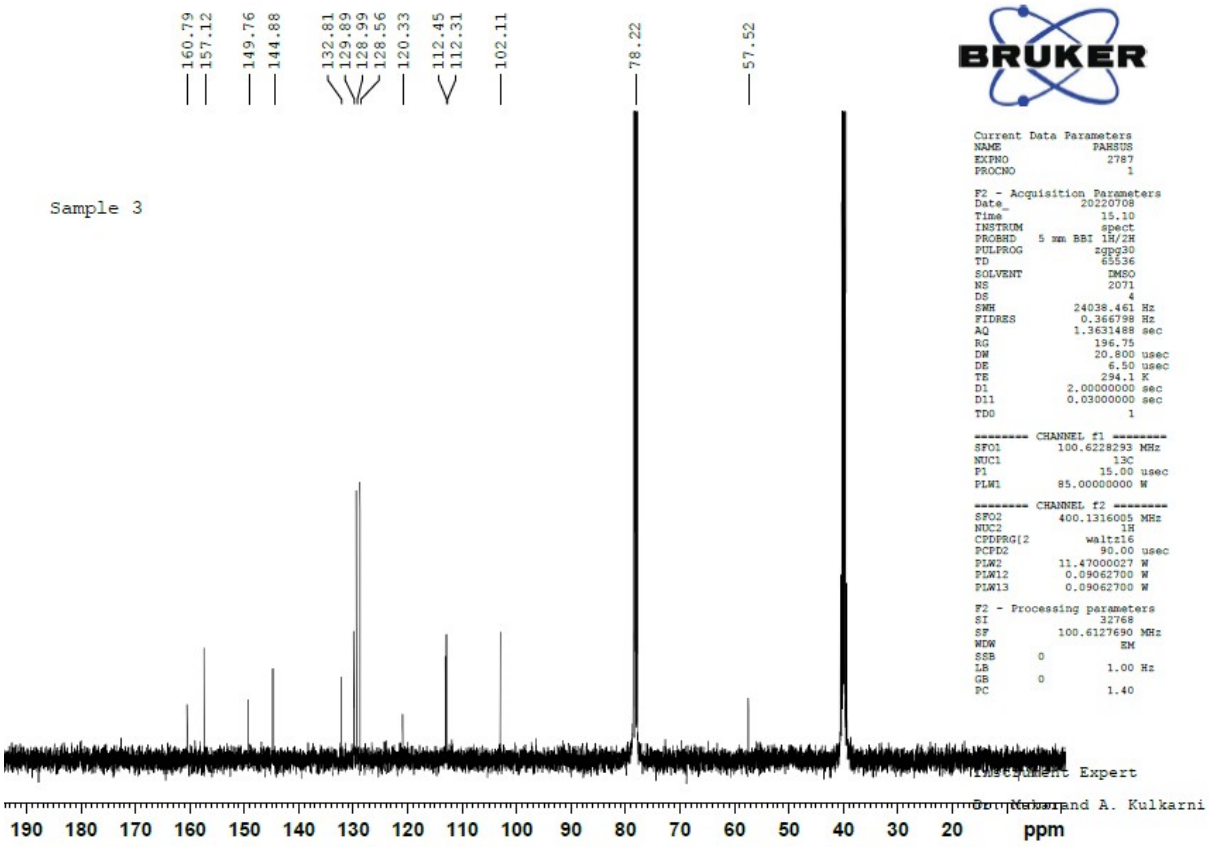
[1]H-NMR: -

[1]H-NMR (ppm1H NMR (400MHz DMSO-d6) δ ppm: 4.45 (s, 1H, CH), 5.9-6.3 (d, 2H, ortho to Ar-OH), 6.53 (d, 1H, meta to Ar-OH), 6.32-6.34 (s, 2H, NH_2), 7.07-7.10(d, 2H, J¼8.04Hz, meta to Ar-NO2), 7.57-7.61 (d,2H, J¼ 8.40Hz, ortho to $ArNO_2$), 9.22(s,1H, OH).

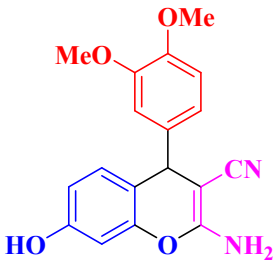


^{13}C-NMR: -

^{13}CNMR (400MHz DMSO-d6) δ(ppm): 160.79, 157.12, 149.76, 144.88, 132.81, 128.56, 120.33, 112.31, 102.11, 78.22, 57.52.

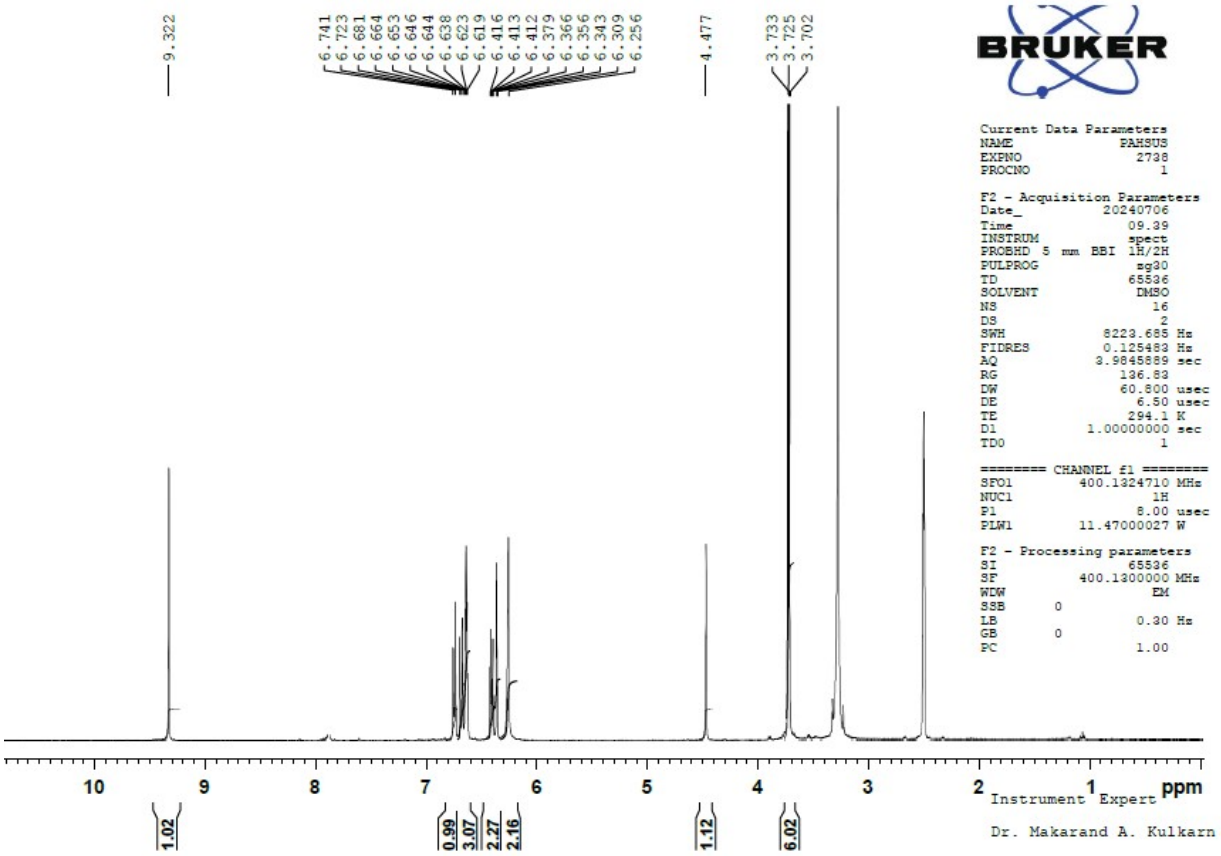


Compound-4 [Entry-4e]: - 2-Amino-3-cyano-7-hydroxy-4-(3,4-dimethoxy)-4H-chromene.



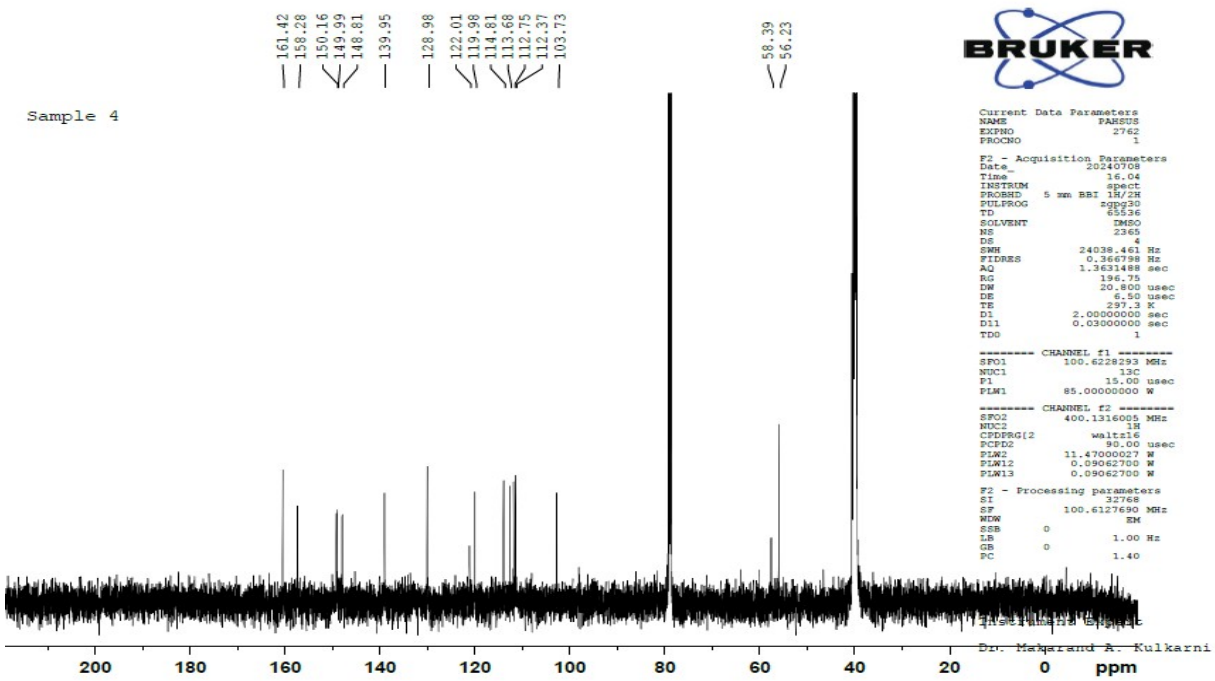
^{1}H-NMR: -

^{1}H NMR (400MHz DMSO-d6) δ(ppm): 3.72 (s, 6H, OMe), 4.47 (s, 1H, CH), 6.40 (s, 2H, NH_2), 6.37-6.41 (d, 2H, ortho to Ar-OH), 6.61-6.64 (dd,1H, meta to Ar-OH), 6.65-6.74(d,6H-Ar(OMe)2), 9.32(s, 1H, OH);



^{13}C-NMR: -

^{13}C NMR (400MHz DMSO-d6) δ(ppm): 161.42, 158.28, 150.16, 149.99, 148.81, 139.95, 128.98, 122.01, 119.98, 114.81, 113.68, 112.75, 112.37, 103.73, 58.39, 56.23.



13. XRD of Pr_6O_{11}

peak search

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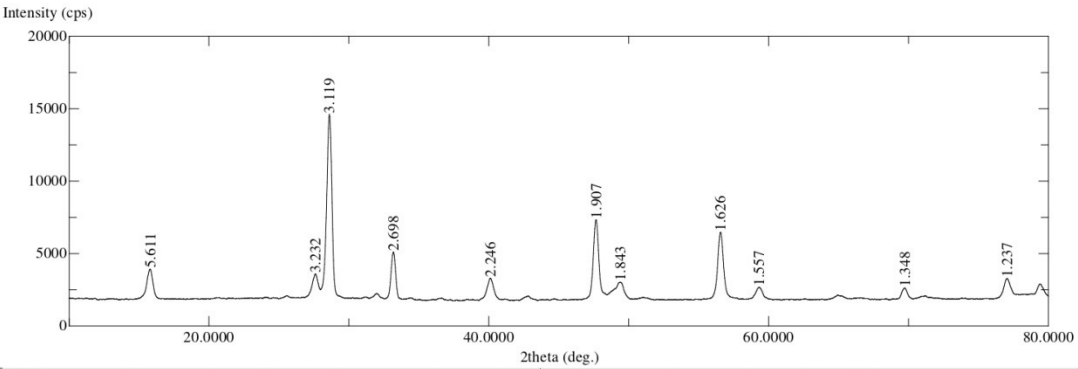
Method	: 2nd differential	Typical width	: 0.800 deg.	Min. height	: 500.00 cps			



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2	27.580		0.518	3.2315	3571	25							
3	28.600		0.518	3.1186	14603	100							
4	33.180		0.494	2.6978	5113	36							
5	40.120		0.588	2.2457	3310	23							
6	47.660		0.541	1.9065	7349	51							
7	49.400		0.612	1.8434	3023	21							
8	56.560		0.565	1.6258	6481	45							
9	59.320		0.612	1.5566	2680	19							
10	69.720		0.541	1.3477	2626	18							
11	77.060		0.612	1.2366	3271	23							