Ceria-Molybdenum Mix Metal Oxide: A Mild and Efficient Recyclable Catalyst for One-Pot Synthesis of Polyhydroquinoline Via Hantzsch Reaction

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SUPPORTING INFORMATION

Experimental

All chemical purchased from spectrochem, Aldrich, alpha assar. Melting points were determined in open capillaries (using instrument Tempo) and are uncorrected. IR spectra were recorded on a FT-IR Bruker, spectrometer, ^{1}H NMR spectra were measured on brukeravance II 400 MHz in $CDCl_3$, d_6 DMSO as a solvent and TMS as an internal standard, Mass Spectra were determined mass spectrometers (GCMS).

General procedure for the synthesis of Catalyst:

The Ceria-Molybdenum (CM) metal oxide catalyst where prepared by simple grinding method, 0.33 gm of ammonium Ceric nitrate salt (as a source of Ce) and 0.49 gm of ammonium heptamolybdate salt (as a source of Mo) are well mix with mortal and piston for 20 mini. to change a colure of mixture to form a catalyst, then mixture was calcined at 500°C for 02 hr. Prepared Ceria-Molybdenum (CM) mix metal oxide used as a catalyst in organic transformation such as, in synthesis of polyhydroquinoline.

Typical procedure for the synthesis of polyhydroquinoline derivatives 5e:

A mixture of aldehyde 0.122 mg(1 mmol), dimedone0.140 mg(1mmol), ethyl acetoacetate 0.130 mg(1 mmol), ammonium acetate 0.170 mg (1.5 mmol) and 50 mg Ceria-Molybdenum as a catalyst (CM) were the mixture with ethanol solvent was refluxed up to completion of reaction. Reaction was monitored by using TLC (pet ether: ethyl acetate 6: 4, as an eluent). After completions of reaction then add 5ml excess ethanol to reactant disappeared, and filtered to separate a catalyst. Then few mL of child water was added drop wise with continuous stirring in the filtrate to obtained crud product of polyhydroquinoline, solid crud product which separated was filtered and recrystallized from ethanol to get a pure product.

The authenticity of synthesized derivatives was established by comparing their **M.P.** and the spectral data of **FT-IR, NMR, and GC-MS** for selected compounds are presented in the subsequent section under results.

*Ethyl-4-phenyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8- hexahydroquinoline-3-carboxylate (Table 1, **5a**)*: **^{1}H NMR (400MHz, DMSO, δ ppm):**0.91-1.04(S,6H,CH_3) 1.20(t,3H, CH_3) 2.10-2.20 (m,4H,CH_2), 2.24 (S,3H, CH_3), 4.03-4.08 (m, 2H, CH_2), 5.04(S,1H, CH), 7.06-7.31(m, 6H,Ar H); **^{13}C NMR(400 MHz, DMSO):**14.25, 19.15, 27.10, 29.49, 32.64, 36.65, 40.70, 50.82, 59.81, **76.77,** 105.86, 111.73, 128.01,

144.04, 147.23, 149.46, 167.61, 195.94; **FT-IR (cm^{-1})**: 686, 757, 1061, 1104, 1150, 1202, 1370 , 1475, 1593 , 2956, 3281; **M^+ (m/z)**= 338.14

*Ethyl-4-(4-chlorophenyl)-3-quinolinecarboxyl acid ethyl ester (Table 1,**5b**):*

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.91-1.05 (S, 6H, $2CH_3$), 1.17-1.21 (t, 3H,CH_3), 2.11-2.21 (m, 4H, $2CH_2$), 2.30-2.34 (S, 3H, CH_3), 4.03-4.08(m, 2H,CH_2), 5.02 (S,1H, CH), 6.81-7.27(m, 5H Ar H); **^{13}C NMR(400 MHz, DMSO):** 14.23, 19.27, 27.06, 29.46, 31.43, 32.65, 36.28, 40.82, 50.71, 69.92, 105.62, 111.56, 115.32, 127.99, 129.43, 131.60, 143.99, 145.70, 149.06, 167.32, 195.80, **FT-IR (cm^{-1})**: 827, 1076, 1205, 1372, 1482, 1593, 1641, 1696, 2950, 3195**; M^+ (m/z)**= 373.14

*Ethyl-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 1, **5e**)*: **^{1}H NMR (400 MHz, $CDCl_3$)** = *δ* 0.94 -1.04 (s, 6H, 2 CH_3), 1.18 (t, 3H, CH_3), 1.99-2.54 (m, 4H, 2 CH_2), 3.97-4.02(m, 2H, CH_2), 4.78 (s, 1H, CH), 6.54-6.99 (dd, 4H, Ar-H), 8.73 (s,1H, OH), 8.79 (broad, 1H, NH); **^{13}C NMR (400 MHz, $CDCl_3$):** δ 14.12, 18.22, 26.60, 29.17, 32.02, 34.86, 50.43, 58.75, 104.46, 110.56, 114.23, 128.30, 138.42, 144.01, 148.93, 155.02, 166.99, 194.30.; **FT-IR (cm^{-1}):** 3451, 3190, 2948, 2313, 1677, 1598, 1478,1373, 1211, 1153,1107, 1016, 839, 760; **Mass (GC-MS):** (m/z) M^+ = 355.14

Characterization of the catalyst:

The XRD pattern of the Cerium-Molybdenum (CM) catalyst calcined at 500°C for 02 hr are shown in **Fig. S1.** (supplementary data). The results are in accordance with crystal arrangement with unit cell parameter a= 18.42, b= 19.65, c= 7.42 **Å** and α = β= γ = 90º and 2dθ observed at 2θ = 12.9, 22.7, 23.5, 25.8, 27.5, with corresponding to the planes (hkl) 101, 401, 403, 202, 222. In xrd pattern shows highest peak at 2θ = 25.8 and (202) plane shows to the orthorhombic phase. Molecular formula of catalyst is calculated form EDX data, the formula is $Ce_1Mo_3O_9$ **Fig. S3**. SEM image of catalyst are shown in **Fig. S2**., Similarly, in FT-IR spectra bands at 442 cm^{-1} shows Ce-O tetrahedral bending vibrtion, 500 cm^{-1} ring vibration, 1080- 754 cm^{-1} internal assymetric stretch, externl symmetric stretch due to Ce-O-Ce or Mo-O-Mo bending vib. mode, 1153 cm^{-1} Ce-O-Mo streching vib., 3661-3427 cm^{-1} presence of Bridge OH stretching frequency (Ce-OH-Mo) shown in **Fig. S4**.

Sample Name grinding Ceria-Molybdenum XRD

Crystal system: Orthorombic Lattice Type: P
Radiation: Cu WaveLength: 1.540598
Lattice Parameter: a= 18.42 b= 19.65 c= 7.42 Lattice Parameter: Alpha= 90 Beta= 90 Gama=90
2Theta Start= 3 2Theta End= 69.9986
Total 46 Experimental Peaks! Total 38 matching Lines are found

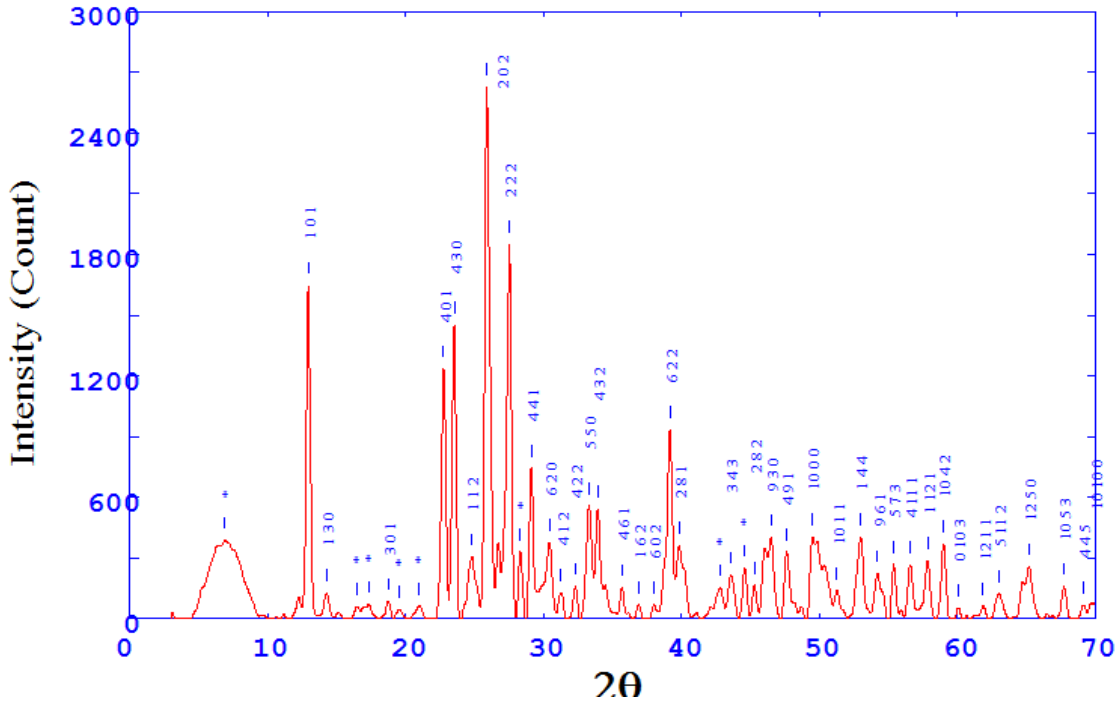


Fig. S1. XRD of Ceria-Molybdenum calcinend 500°C

Table. 1. (h k l) Peak file of XRD of Ceria-Molybdenum calcinend 500°C

H	K	L	2θ (Exp.)	2θ (Calc.)	2θ (Diff.)	d (Exp.)	d (Calc.)	Intensity (Exp.)
1	0	1	12.944	12.852	0.092	6.83398	6.88257	1646.87
1	3	0	14.288	14.340	-0.052	6.19392	6.17143	127.37
3	0	1	18.739	18.743	-0.004	4.73145	4.73044	85.13
4	0	1	22.755	22.708	0.046	3.90483	3.91271	1234.87
4	3	0	23.524	23.598	-0.074	3.77889	3.76715	1451.06
1	1	2	24.813	24.877	-0.064	3.58531	3.57622	305.14
2	**0**	**2**	**25.883**	**25.869**	**0.014**	**3.43947**	**3.44129**	**2627.03**
2	2	2	27.523	27.440	0.084	3.23812	3.24783	1852.08
4	4	1	29.110	29.155	-0.045	3.06519	3.06056	742.91
6	2	0	30.433	30.482	-0.049	2.93487	2.93028	376.89
4	1	2	31.266	31.268	-0.002	2.85853	2.85832	127.67
4	2	2	32.314	32.272	0.043	2.76814	2.77170	159.74
5	5	0	33.304	33.309	-0.004	2.68809	2.68774	557.39
4	3	2	33.932	33.885	0.047	2.63976	2.64334	542.32
4	6	1	35.690	35.724	-0.034	2.51365	2.51137	154.31
1	6	2	36.900	36.904	-0.004	2.43399	2.43371	68.17
6	0	2	38.013	38.013	0.000	2.36522	2.36522	68.38
6	2	2	39.152	39.143	0.009	2.29902	2.29952	934.39
2	8	1	39.831	39.847	-0.017	2.26139	2.26048	363.61
3	4	3	43.571	43.502	0.070	2.07552	2.07868	215.27
2	8	2	45.287	45.324	-0.038	2.00080	1.99923	165.84
9	3	0	46.487	46.446	0.041	1.95190	1.95352	400.39
4	9	1	47.621	47.659	-0.038	1.90804	1.90659	330.24
10	0	0	49.496	49.440	0.055	1.84007	1.84200	405.28
10	1	1	51.264	51.273	-0.009	1.78068	1.78038	138.62
1	4	4	52.984	52.954	0.030	1.72684	1.72775	405.48
9	6	1	54.208	54.233	-0.024	1.69070	1.69000	223.44
5	7	3	55.380	55.391	-0.012	1.65768	1.65736	268.69
4	11	1	56.576	56.592	-0.016	1.62543	1.62501	266.18
1	12	1	57.838	57.834	0.004	1.59293	1.59303	288.38

10	4	2	58.994	59.013	-0.019	1.56445	1.56399	369.48
0	10	3	60.075	60.088	-0.014	1.53886	1.53854	54.27
12	1	1	61.851	61.854	-0.003	1.49887	1.49879	62.51
5	11	2	62.988	62.970	0.017	1.47452	1.47489	123.22
12	5	0	65.181	65.196	-0.016	1.43011	1.42981	256.88
10	5	3	67.711	67.703	0.008	1.38269	1.38284	159.79
4	4	5	69.137	69.145	-0.008	1.35761	1.35747	65.87
10	10	0	69.989	69.947	0.042	1.34316	1.34387	90.76

SEM image

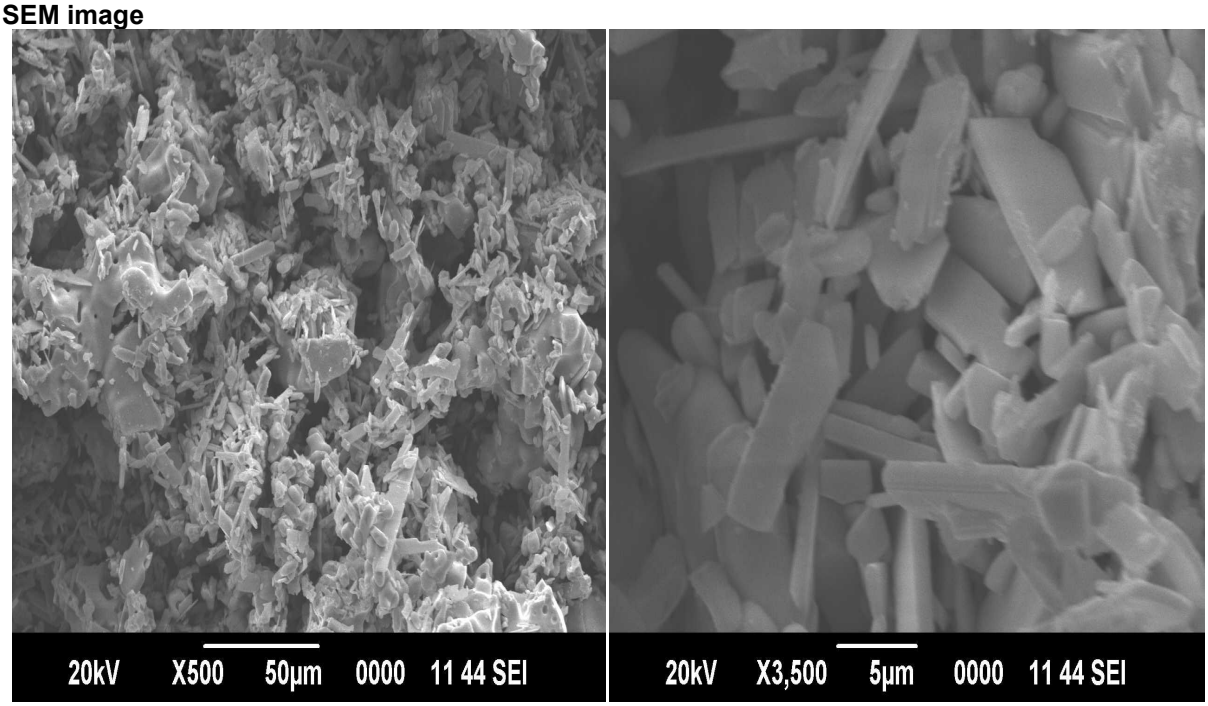


Fig. S2. SEM of Ceria-Molybdenum calcinend 500°C

EDX image:

Table 2. Elemental composition of Ceria-Molybdenum catalyst.

Sr. No.	Element	Wt. %	Atomic %
1	B	15.12	41.39
2	O	22.37	41.40
3	Mo	41.11	12.69
4	Ce	21.41	4.52
Total		100	100

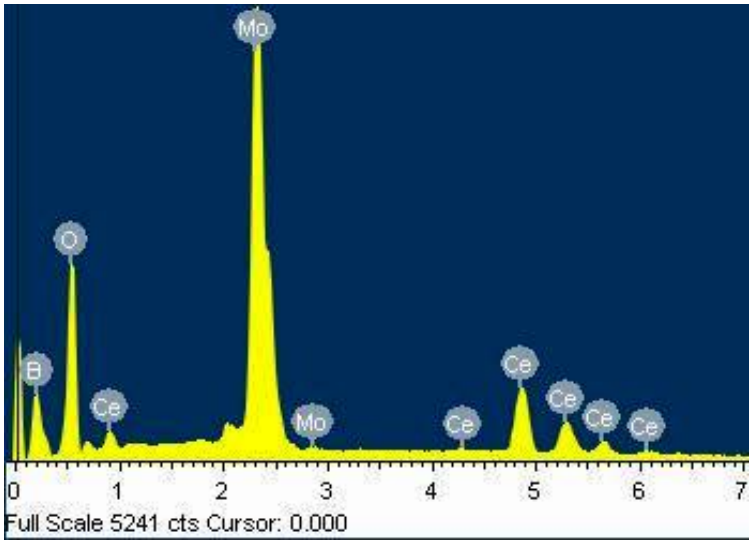


Fig. S3. EDX of Ceria-Molybdenum calcinend 500°C

FT-IR spectrum of Ceria-Molybdenum catalyst.

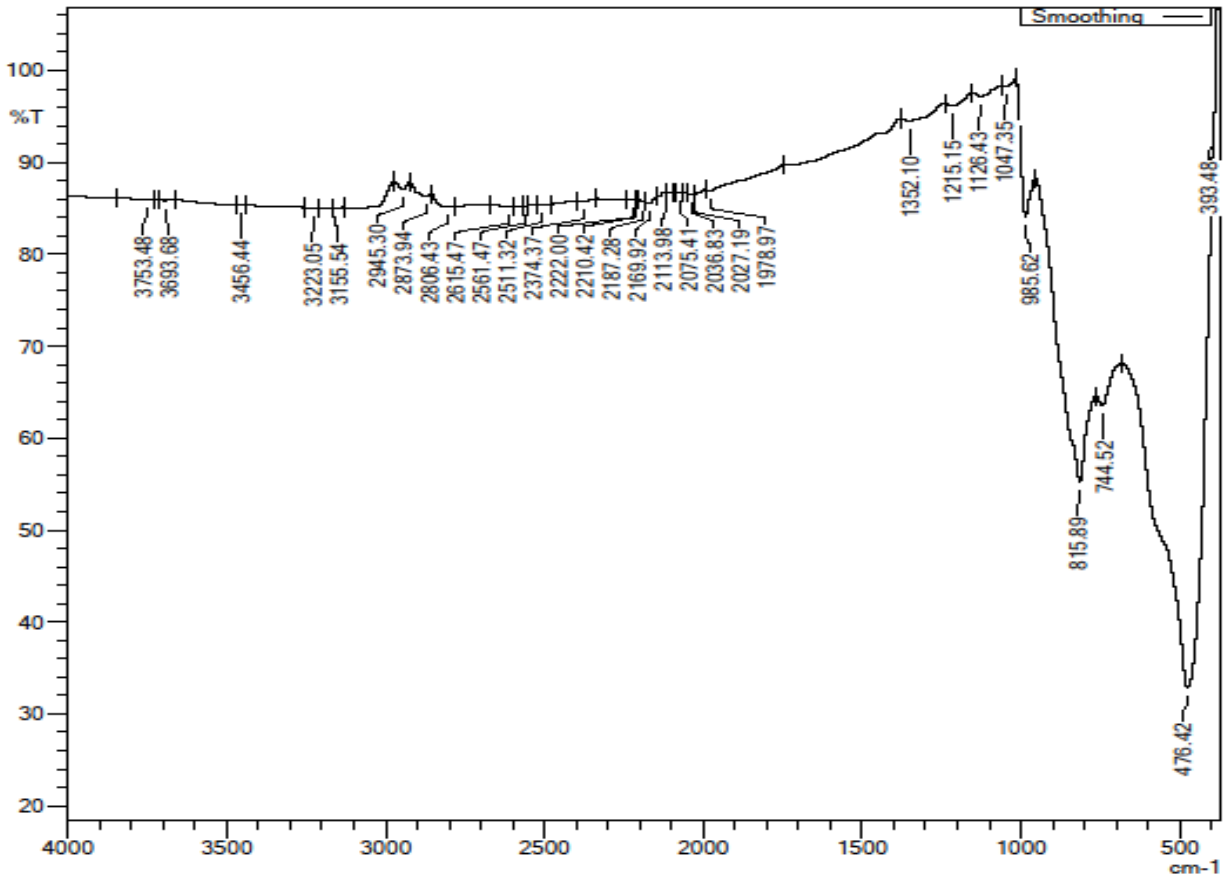
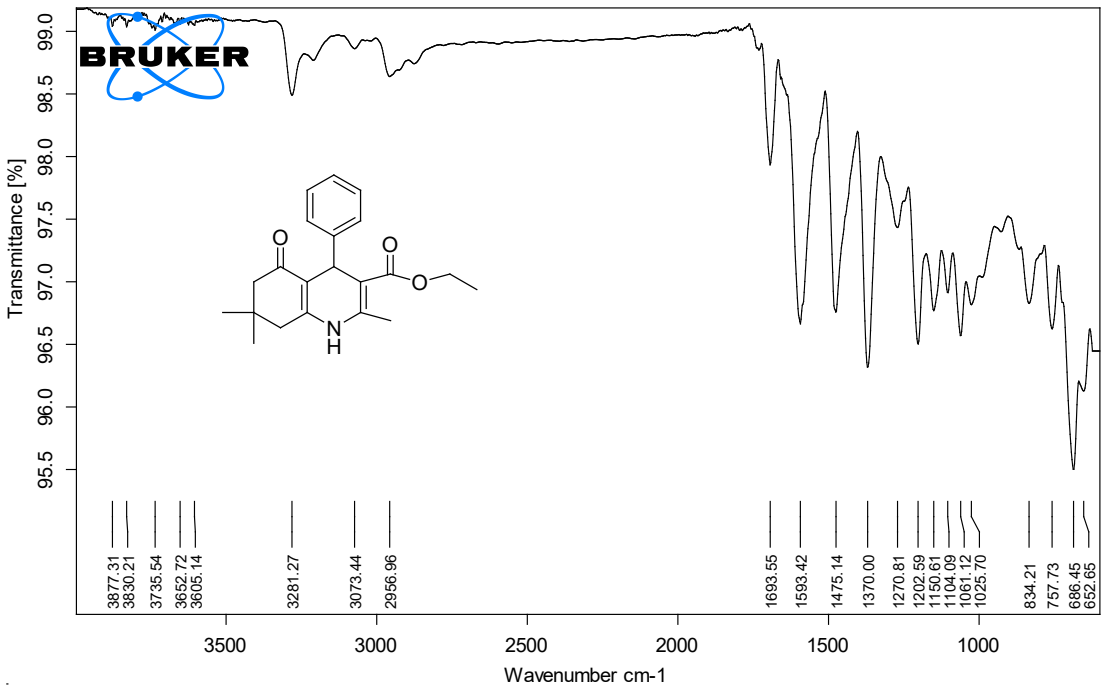
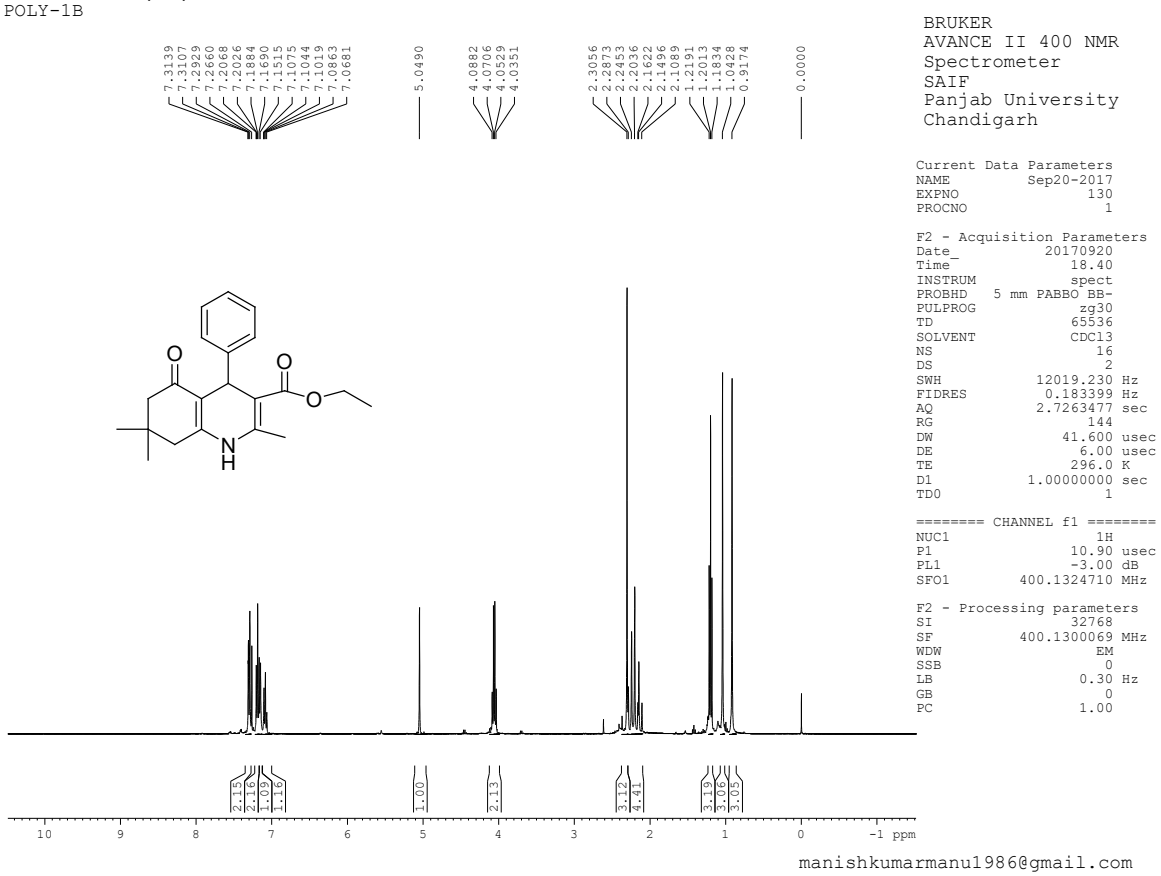


Fig. S4. FT-IR of Ceria-Molybdenum calcinend 500°C

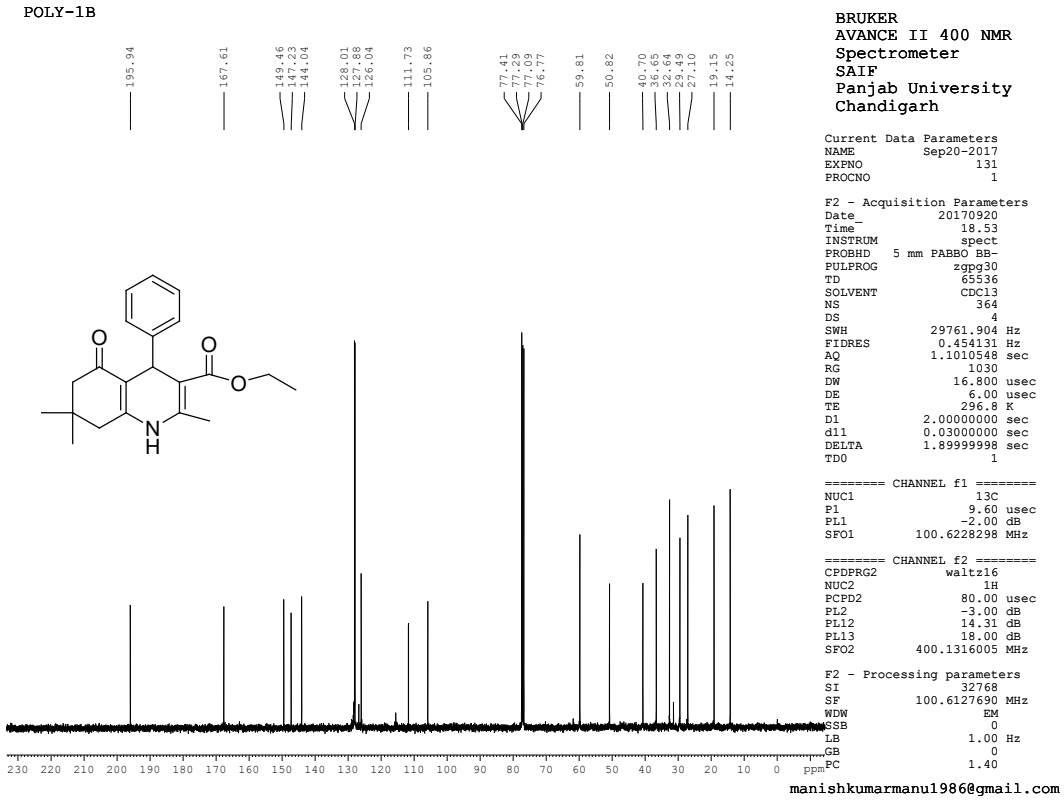
FT-IR of (**5a**)



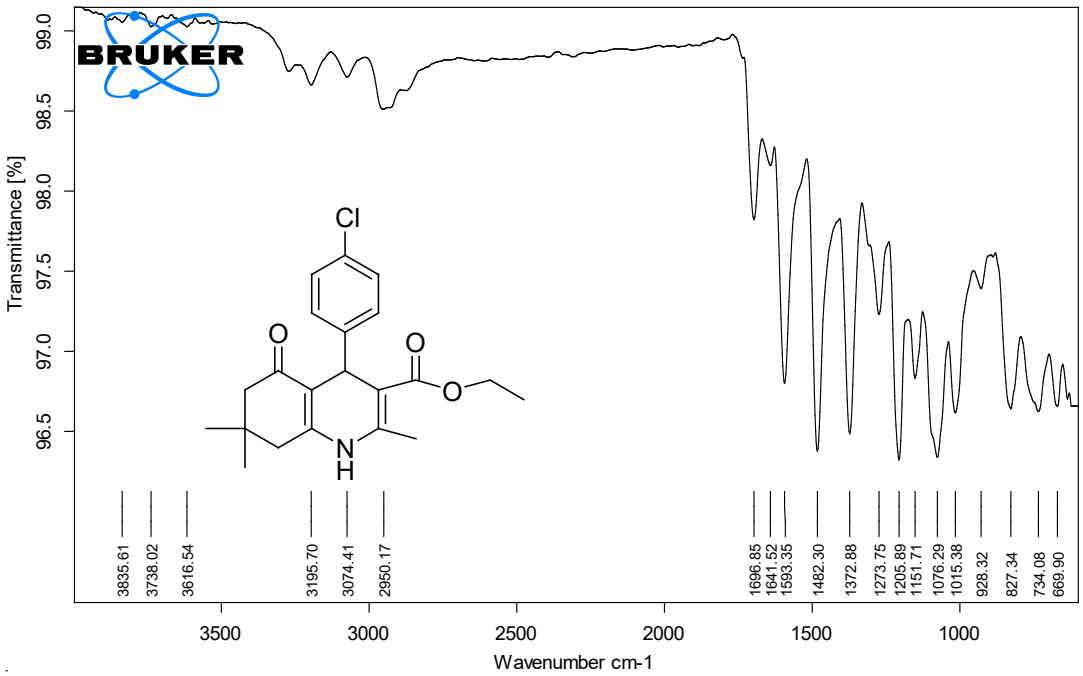
^{1}H-NMR of (**5a**)



^{13}CNMRof (**5a**)

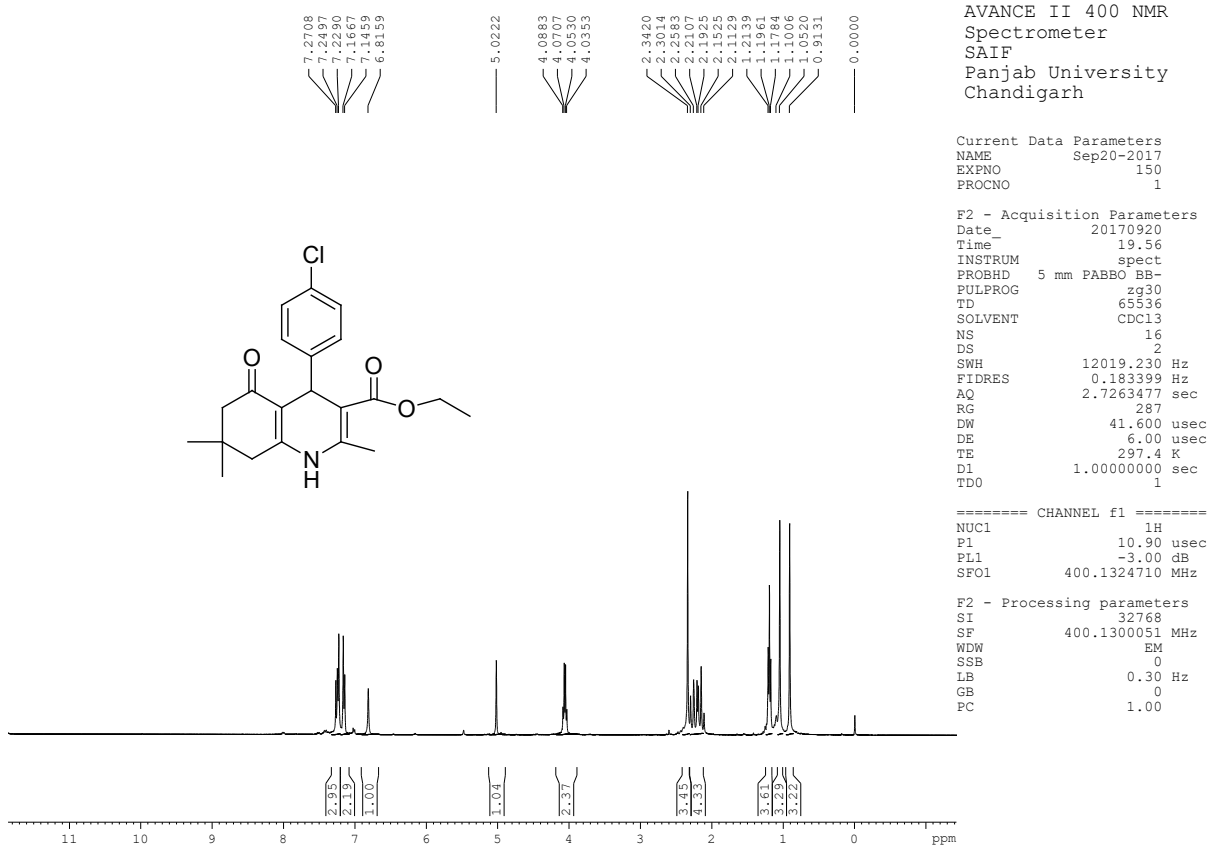


FT-IR of (5b)



^{1}H-NMR of (**5b**)

POLY-4CL



BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

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D1            1.00000000 sec
TD0                    1

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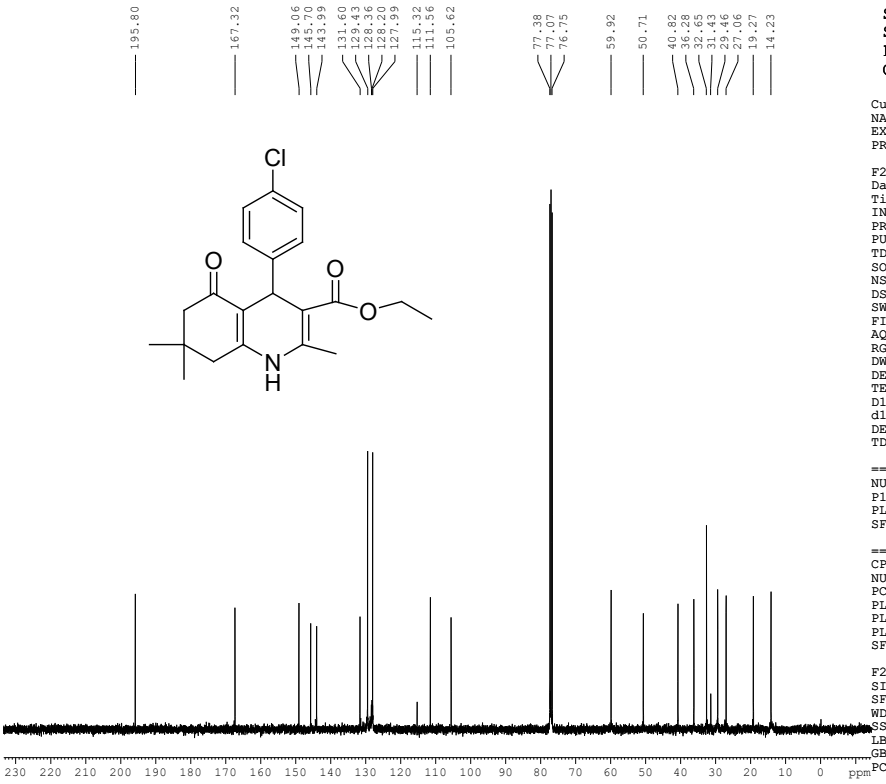
^{13}C-NMR of (**5b)**

POLY-4CL



BRUKER
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Spectrometer
SAIF
Panjab University
Chandigarh

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PL2                -3.00 dB
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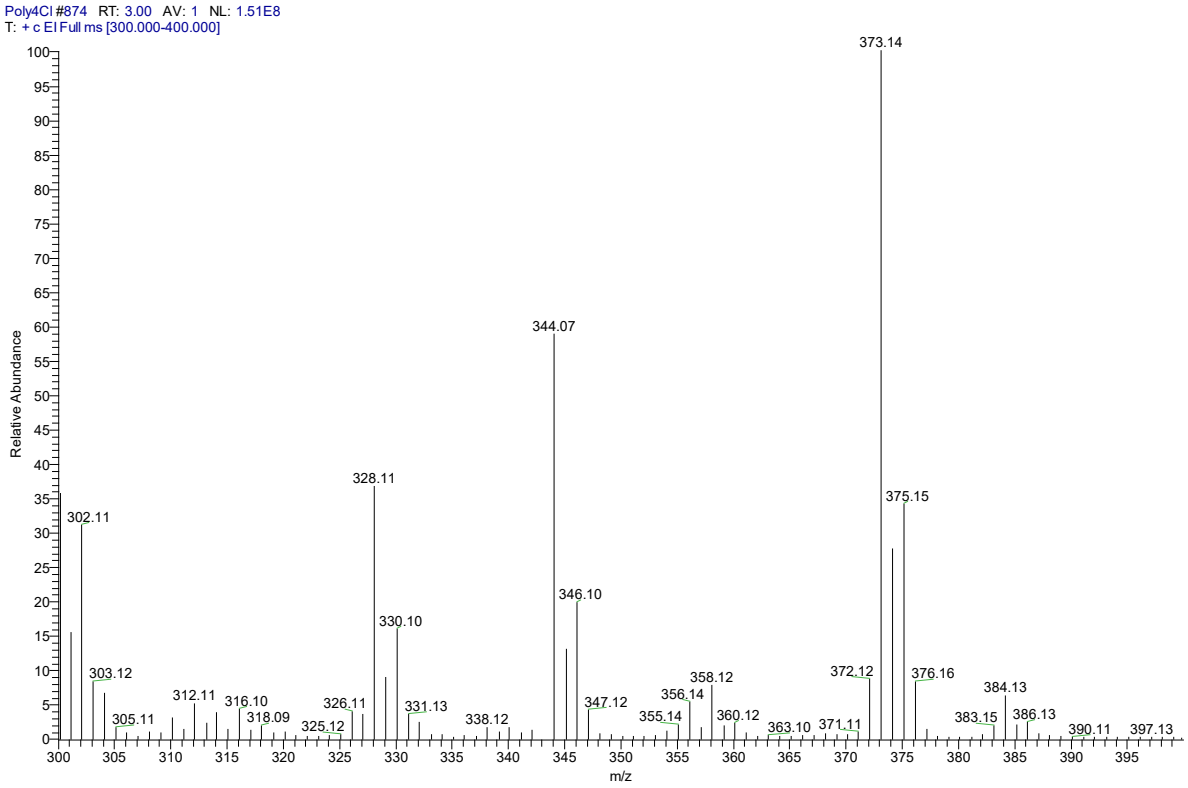
GC-MS of (5B)



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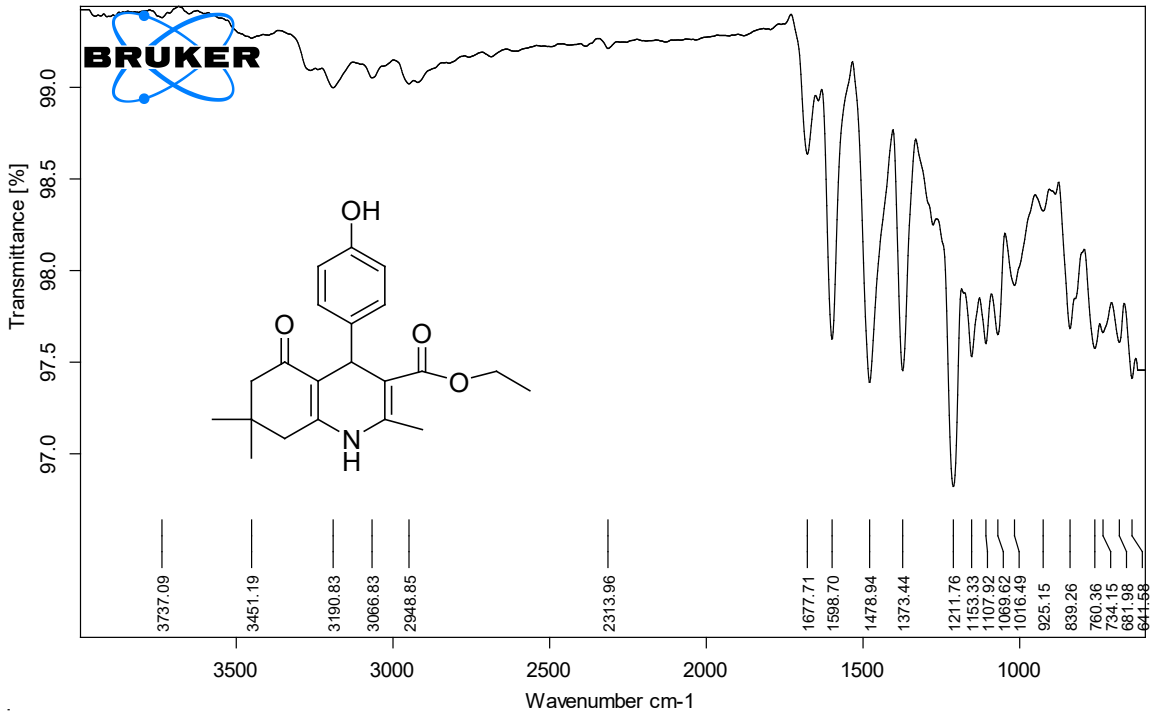

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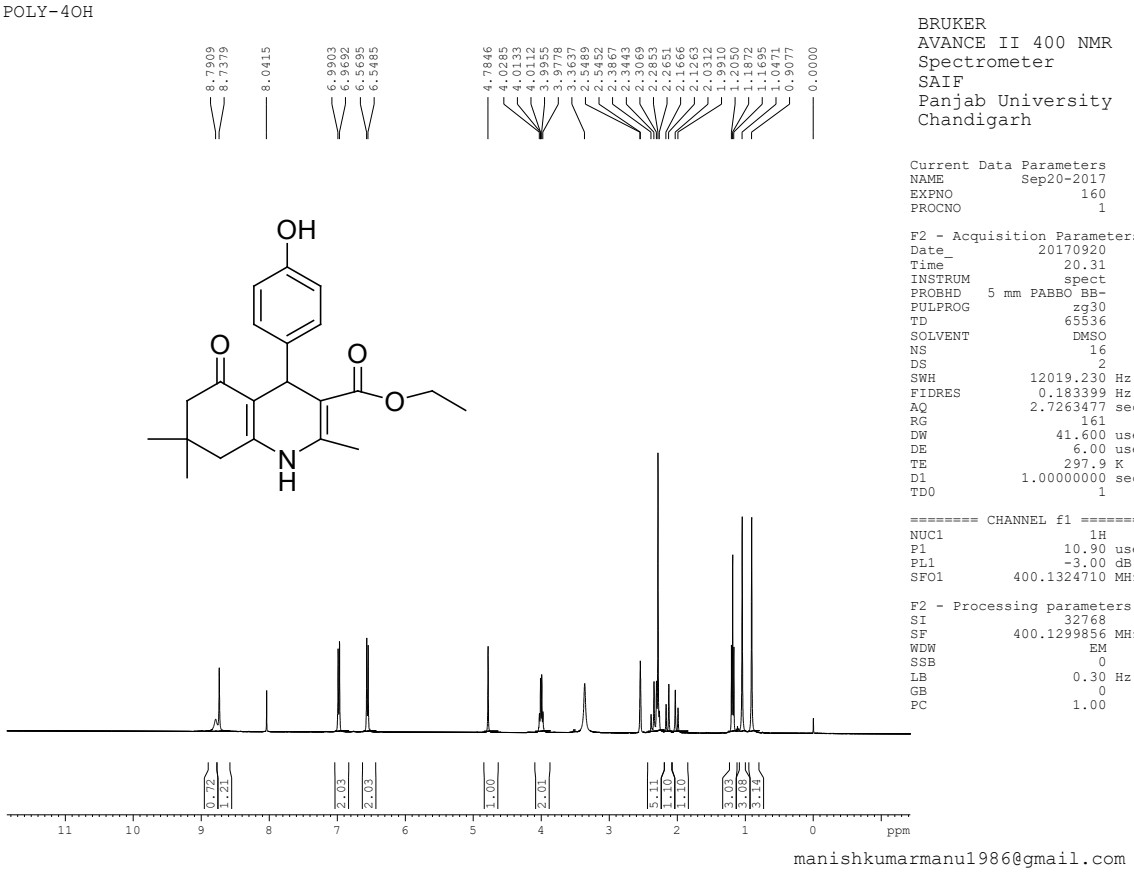

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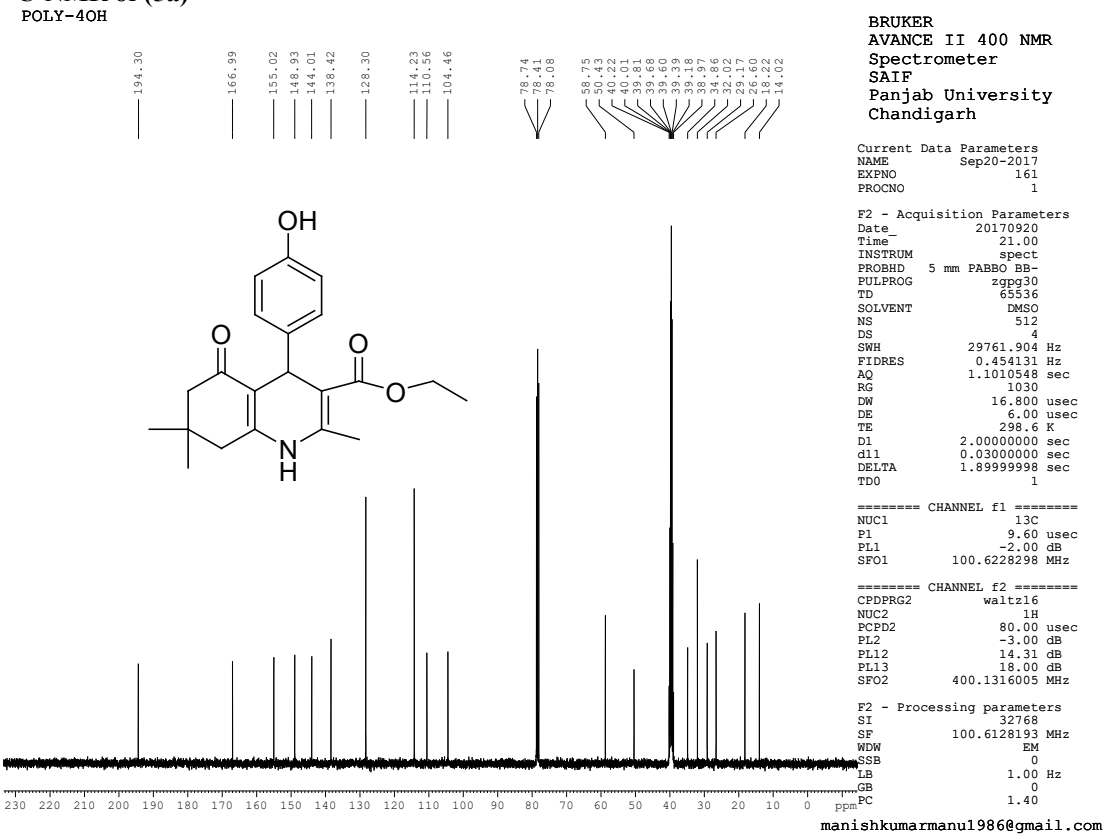

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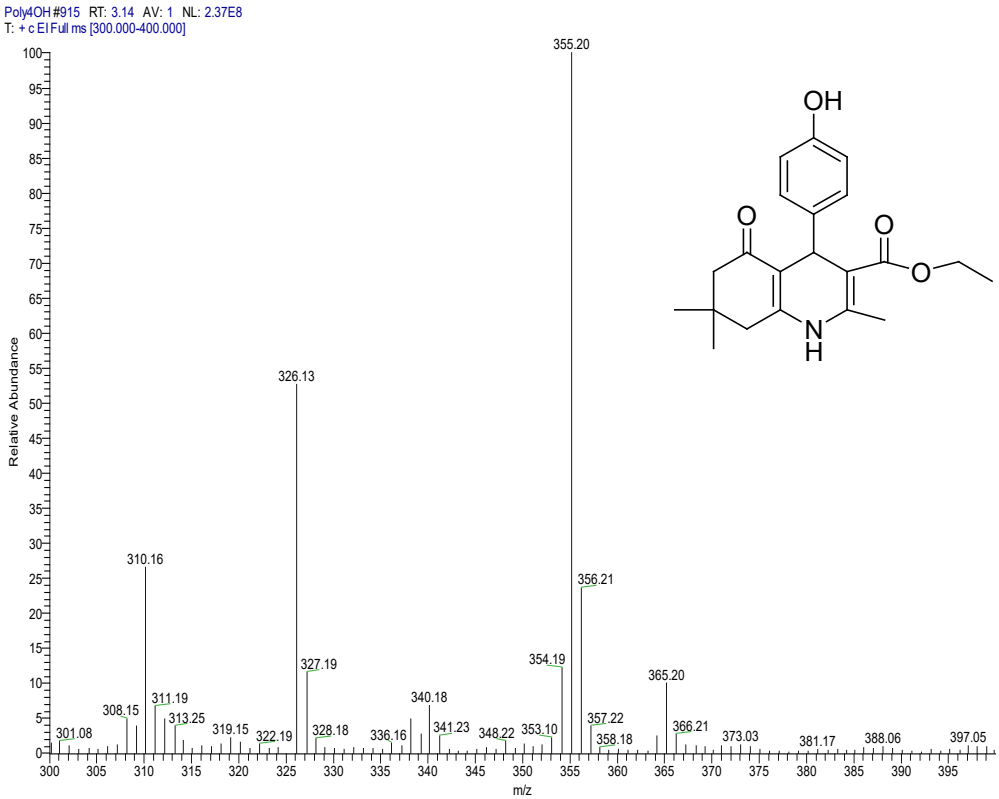
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N
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