Ce-ZSM-11 Zeolite:
An Efficient Heterogeneous Catalyst
for One Pot Synthesis of 4H-Pyran Derivatives

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ABSTRACT: *ZSM-11 zeolite was synthesized by hydrothermal treatment and cerium ion was incorporated by the ion exchange method. The catalytic activity of cerium modified ZSM-11 zeolite was tested for the one pot synthesis of 4H-pyran derivatives by cyclocondensation of aromatic aldehyde, malononitrile and ethyl acetoacetate. The synthesized catalyst was characterized by Powder-X Ray Diffraction, Scanning Electron Microscopy, Energy Dispersive Spectroscopy, Fourier Transform Infrared Spectroscopy, Brunauer-Emmer-Teller surface area analysis and Temperature programmed desorption (ammonia) analysis. The present method offers significant advantages over the reported methods like easy separation of catalyst, simple work-up procedure, excellent yield of desired products and reusability of catalyst without significant loose in activity.*

KEYWORDS: *Ce-ZSM-11 zeolite; 4H-pyran; Aromatic aldehyde; Malononitrile; Ethyl acetoacetate.*

INTRODUCTION

Polyfunctionalized pyrans are important class of heterocyclic compounds because of their wide range of biological and pharmacological activities [1, 2]. These heterocyclic compounds are used as anti-cancer, anti-coagulants, anti-anaphylactic and spasmolytic agents [3-5]. In addition, pyran derivatives have been utilized for the treatment of neurodegenerative diseases such as Alzheimer's, schizophrenia and myoclonus diseases [6]. Furthermore, numbers of 2-amino-4H-pyran derivatives are valuable photoactive materials [7]. In view of their wide range of application, 4H-pyran derivatives have attracted considerable attention towards their synthesis for synthetic chemist.

Several strategies have been reported for the synthesis of 4H-pyran derivatives which includes synthetic methods catalyzed by Mg/La mixed oxide [6], silica nanoparticles [8], ZnO/MgO containing ZnO nanoparticle [9], nano crystalline ZnO [10], nano $SnCl_2$/ SiO_2 [11], Cu(II) oxymetasilicate [12], silica bonded S-sulfonic acid (SBSSA) [13], CsF [14], Ca-MCM [15] and nano ZrP_2O_7 catalysts [16]. Although these reported methods have good efficiency, some of these protocols suffer from one or more drawbacks such as use of hazardous solvent, long reaction time, tedious work-up procedure and use of expensive catalyst which also lack reusability. Thus, the development of new route for efficient synthesis of 4H-pyran derivatives is highly desirable.
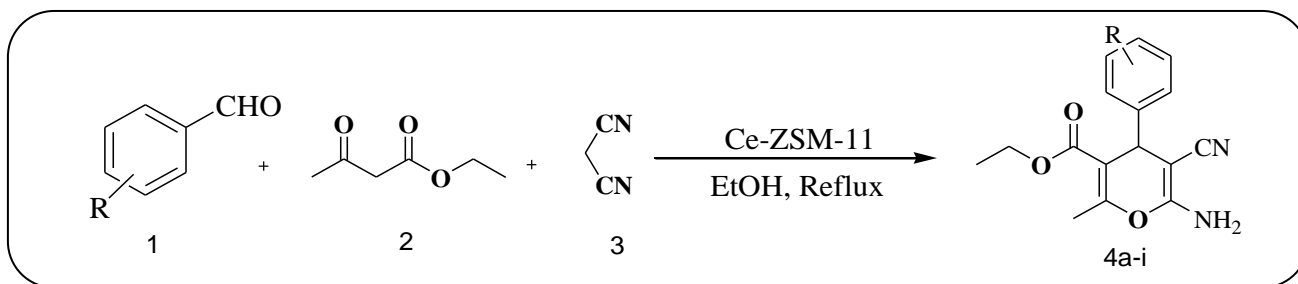
Zeolites are microporous, crystalline, aluminosilicate compounds composed of staggered framework of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ tetrahedra which generates a network of pores and cavities having molecular dimensions. Zeolites find extensive applications in heterogeneous catalysis

Scheme 1: Synthesis of 4H-pyran derivatives.

due to their tunable pore sizes, high surface area, framework acid/base properties and they provides greener alternatives to the homogeneous catalysts [17]. ZSM-11 belongs to pentasil family of zeolites which has straight micropore with MEL framework topology [18]. ZSM-11 zeolite possesses unique properties, such as high-surface area, acidity and shape selectivity characters [19]. Therefore, it has been utilized as heterogeneous catalyst for various transformations such as conversion of methanol to hydrocarbon, aromatization and isomerization of 1-hexene, cracking of pentene to C_2-C_4 olefins and conversion of methanol into light olefins [20-23]. The transition metal doped ZSM-11 possesses greater Lewis acidity compared to parent ZSM-11 and showed better catalytic performance in some reaction such as degradation of Dichlorvos, decomposition of N_2O, conversion of methane (C1) into higher hydrocarbons, dehydrogenation-aromatization of alkane and decomposition of low-density polyethylene [24-28].

Thus, in continuation to our research work [29, 30], herein we report the synthesis, characterization and catalytic application of Ce-ZSM-11 zeolite catalyst for one pot synthesis of 4H-Pyran derivatives *via* cyclocondensation of aromatic aldehyde, malononitrile and ethyl acetoacetate using catalytic amount of Ce-ZSM-11under reflux condition in ethanol as solvent (Scheme 1).

EXPERIMENTAL SECTION
Chemicals and Instruments

All the chemicals were purchased from Merck, Avra and Spectrochem and were used without purification. Thin layer chromatography was performed on Merck pre-coated silica gel 60F$_{254}$ aluminum sheets as adsorbent. Melting points were taken in an open capillary and are uncorrected. FT-IR spectra were recorded on Bruker and Thermo Nicolet; Avatar 370. ^{1}H NMR spectra were recorded on a 400 MHz, using DMSO-d_6 and Methanol-d$_4$ as solvent and tetramethylsilane (TMS) as an internal standard. The X-Ray Diffraction (XRD) patterns were recorded on Bruker AXS D8 Advance X-ray diffractometer using monochromatic Cu-Kα radiation having wavelength λ= 1.5406 Å. Scanning Electron Microscope (SEM) image was obtained on JSM - 6390LV operated at 30.0 kV. Surface area and porosity (BET) of catalyst was measured on micromeritics, ASAP 2010 instrument. Temperature Programmed Desorption (TPD) ammonia was measured on micromeritics instrument.

Preparation of Catalyst

The ZSM-11 zeolite was synthesized by hydrothermal method. Tetraethyl orthosilicate and sodium aluminate were used as silicon and aluminum source respectively and tetra propyl ammonium bromide was used as structure directing agent. In a Typical synthetic procedure, tetraethyl orthosilicate (20.8 g) was mixed with 50 ml deionized water and stirred at room temperature for 2 h to obtain silica sol. Sodium aluminate (0.246g) and 2g sodium hydroxide were dissolved in 50 ml deionized water and added drop-wise to stirred solution of silica sol. Tetra propyl ammonium bromide (2 g) was dissolved in 20 ml of deionized water and added drop wise to above solution. The resulting mixture was stirred at room temperature for 12 h. The viscous homogeneous gel was transferred in Teflon lined stainless steel autoclave and treated hydrothermally under static condition and autogenous pressure at 150 °C for 24 h. Thus obtained solid was collected, filtered and washed with deionized water. Finally, it was dried in an oven and calcined at 550 °C for 4 h in muffle furnace.

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For the enhancement of Lewis acidic sites in the catalyst, the cerium ion containing ZSM-11 was prepared by ion exchange method. In this procedure 2 g ZSM-11 zeolite and 20 ml 0.1 M ceric ammonium nitrate solution was stirred at 50 °C for 12 h. The resulting product (Ce-ZSM-11) was filtered, washed with deionized water and dried in oven at 100 °C for 5 h.

General procedure for the synthesis 4H-Pyran derivatives (4a-i)

A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol) and Ce-ZSM-11 catalyst in ethanol (10 mL) as solvent was refluxed for the time shown in (Table 4). The progress of the reaction was monitored by TLC (petroleum ether: ethyl acetate =7:3 as eluent). After completion of the reaction, the reaction mixture was filtered to separate the catalyst. The crude product obtained was recrystallized from ethanol to afford pure product (4a-i).

Selected Spectroscopic data
Ethyl-6-Amino-5-cyno-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylate (4d).

Light Yellow; FT-IR, 3338, 3322 (NH$_2$), 2194(CN), 1680(C=O) cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d6) δ ppm = 1.1(3H, t), 3.9(2H, q), 2.4(3H, S), 4.5(1H,S), 6.4(2H, s, –NH$_2$), 7.4 (2H, d, J = 8.0 Hz), 8.1 (2H, d, J = 8.0 Hz); ^{13}C NMR (400 MHz, DMSO-d6): δ ppm 13.45, 18.24, 38.55, 57.75, 60.23, 106.03, 118.78, 123.27, 127.96, 146.20, 151.55, 157.74, 158.15, 164.91

Ethyl-6-Amino-5-cyno-2-methyl-4-(4-bromo-phenyl)-4H-pyran-3-carboxylate(4e)

White solid; FT-IR 3423, 3330 (NH$_2$), 2187(CN), 1678(C=O) cm^{-1}, ^{1}H NMR (400 MHz, DMSO) δ ppm 0.9 (3H, t), 3.94(2H, q), 2.50(3H,S), 4.9(1H,S), 7.1(2H, s, –NH$_2$), 7.3 (2H, d, J = 7.6 Hz), 7.5 (2H, d, J = 8.0 Hz), ^{13}C NMR (400 MHz, DMSO-d6): δ ppm 14.11, 18.57, 39.80, 60.55, 106.73, 119.51, 123.14, 128.80, 129.09, 130.25, 132.96, 144.36, 158.20, 158.87,165.61

Ethyl-6-Amino-5-cyno-2-methyl-4-(4-chloro-phenyl)-4H-pyran-3-carboxylate (4g).

White solid; FT-IR 3330, 3312 (NH$_2$), 2194(CN), 1685(C=O) cm^{-1}, ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 1.9 (3H, t), 3.8(2H, q), 3.6(3H,S), 3.9(1H,S), 9.5(2H, s, –NH$_2$), 6.7 (2H, d, J = 8.0 Hz), 6.8 (2H, d, J = 8.0 Hz), ^{13}C NMR (400 MHz, CDCl$_3$): δ ppm 14.48, 17.10, 39.27, 57.25, 60.62, 106.26, 119.78, 123.27, 129.62, 146.93, 151.36,154.26, 158.10, 164.15.

RESULTS AND DISCUSSION
Catalyst Characterizations
Powder X-ray diffraction analysis

X-ray diffraction patters of parent ZSM-11 and Ce-ZSM-11 are shown in Fig. 1 which shows intense peaks at 2θ° = 8.17, 9.08, 14.15, 15.00, 23.30, 24.04, 26.05, 27.06, 29.45, 45.31 with corresponding planes (101), (111), (221), (301) (223), (303), (441), (413), (224), (814) respectively, the high intense peaks at 23.30 and 24.04 are the characteristic peak for the MEL type framework topology which indicate the presence of ordered tetragonal crystal structure of ZSM-11 material [31]. Fig.1 (b) shows decreased peak intensities as compared Fig. 1(a) this may be due to insertion of cerium ion inside the channels of parent ZSM-11. However, crystal structure of parent ZSM-11 is retained after ion exchange.

Scanning electron microscopy-Energy dispersive Spectroscopy analysis

Surface morphology and chemical composition of catalyst were analyzed by SEM-EDS spectroscopy. The Fig. 2 (a) and (b) shows SEM images of ZSM-11 zeolite and Ce-ZSM-11 respectively. The catalysts possess uniform sphere shaped crystals which is characteristic morphology of ZSM-11. It was observed that prepared catalyst has uniform particle size and ordered morphology. The Fig. 3 (a) shows EDS spectrum of ZSM-11 which confirms the presence of Si, Al, O and Na with atomic wt% 30.98, 1.25, 67.31 and 0.46 respectively. The Fig. 3(b) shows the EDS spectrum of Ce-ZSM-11 which confirm the presence of Si, Al, O and Ce with atomic wt% 29.82, 1.11, 67.82, 1.25 respectively.

Fourier transforms infrared spectroscopy analysis

The FT-IR spectrum of the ZSM-11 and Ce-ZSM-11 zeolite is shown in (Fig. 4). The FT-IR spectrum shows sharp peak at 451, 550, 798, 1104, 1229 cm^{-1} which are characteristic adsorption bands of ZSM-11. The band at 798, 1229 assigned for external symmetric and asymmetric stretching vibration and sharp band at 1104 cm^{-1} is assigned to internal asymmetric stretching of
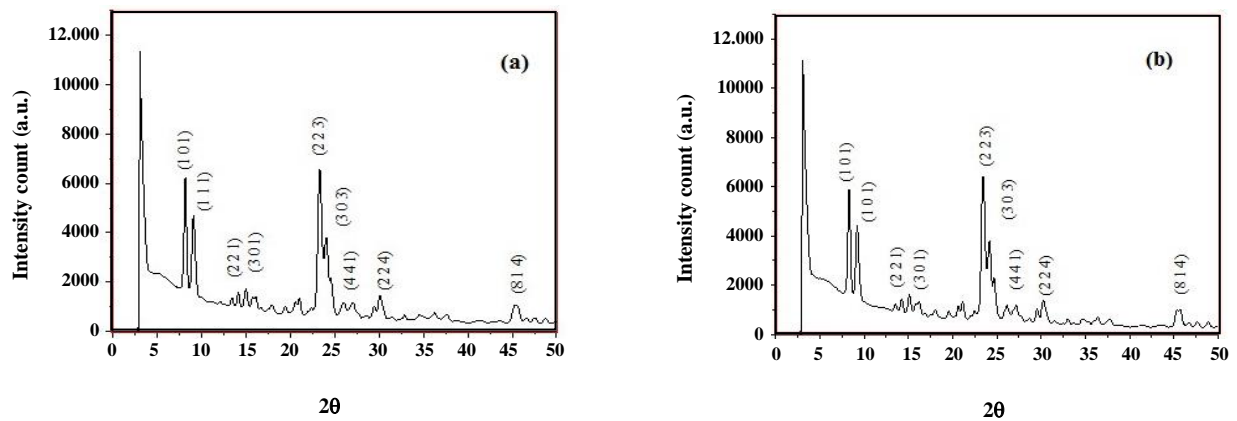
Fig. 1: Powder XRD pattern of (a) ZSM-11 zeolite (b) Ce-ZSM-11 zeolite.
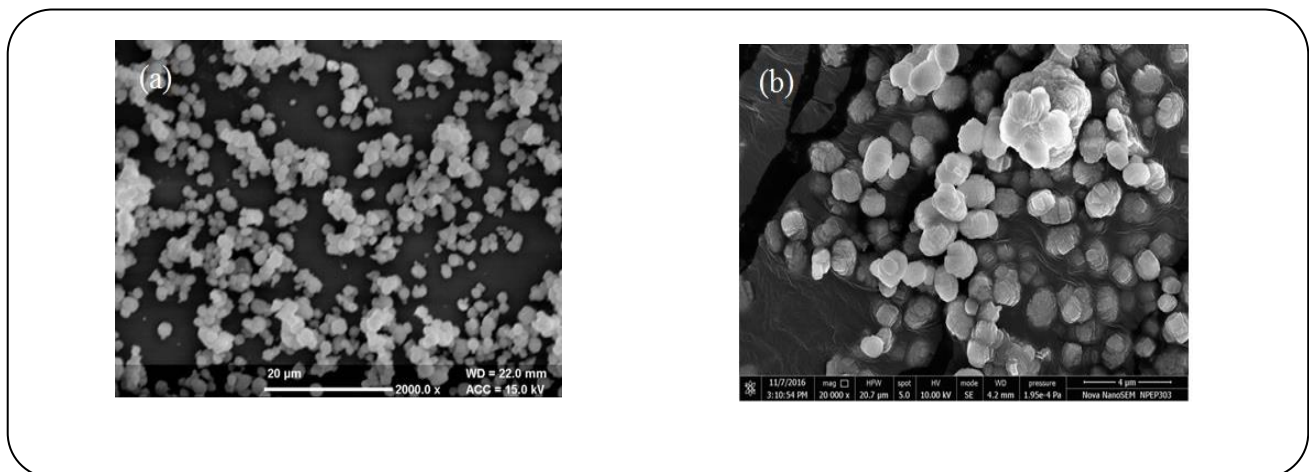

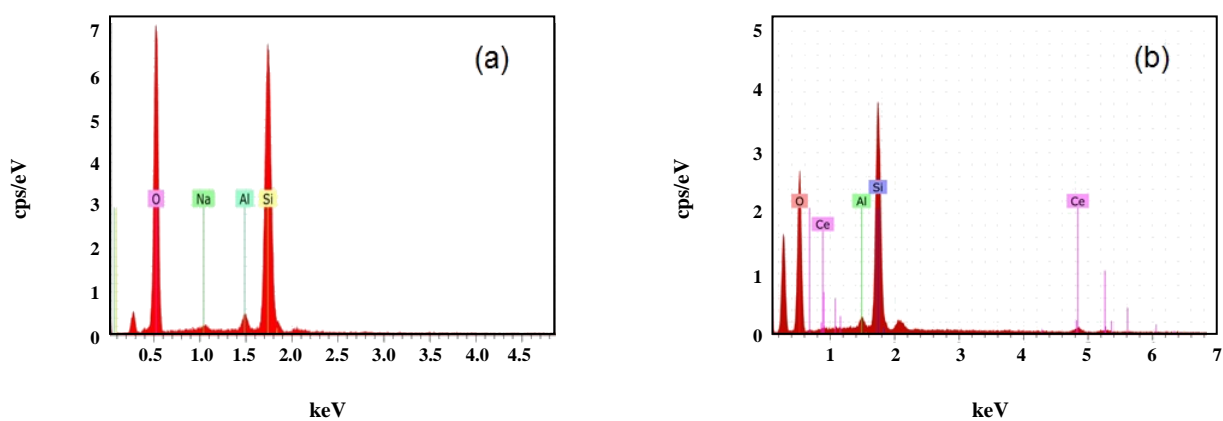*Fig. 2: (a) SEM images of ZSM-11 zeolite (b) SEM images of Ce-ZSM-11 zeolite.*

Fig. 3: (a) EDS-Spectrum of ZSM-11 zeolite and (b) EDS-Spectrum of Ce-ZSM-11 zeolite.

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Table 1: BET surface area, micropore volume and average pore diameter for ZSM-11 and Ce-ZSM-11

Sr. No.	Sample	Surface area (m²/g)	Micropore volume(cm³/g)	Average pore diameter (Å)
1	ZSM-11	641.37	0.52	16.37
2	Ce-ZSM-11	541.44	0.35	13.12
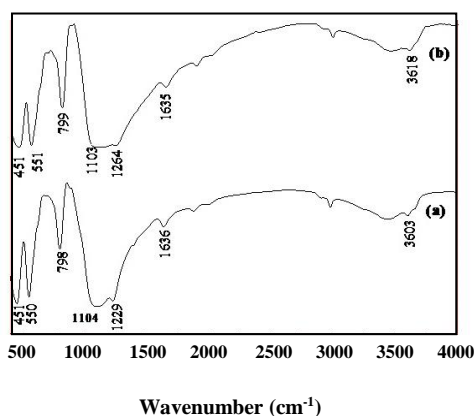
Fig. 4: FT-IR Spectrum of (a) ZSM-11 zeolite (b) Ce-ZSM-11 zeolite.

T-O-T(T= Si or Al) unit in ZSM-11 framework. The band at 550 cm^{-1} confirms the presence of double five member rings which is secondary building unit of pentasil family zeolites framework MEL [32] and MFI [33]. The peak at 1636 cm^{-1} is attributed to deformation mode of Si-OH bond. The band appear at 3603 cm^{-1} confirms presence of bridged hydroxyl group i.e. Bronsted acidic site [34].

Brunauer-Emmer-Teller surface area analysis

The presence of intercrystalline pore was studied by N$_2$ adsorption-desorption isotherm. It was observed that surface area, micropore volume and average pore diameter of Ce-ZSM-11 zeolites decreased compared to ZSM-11 zeolite which implies that cerium ions are well dispersed in the framework (Table 1).

Temperature Programmed Desorption (Ammonia) analysis

The NH$_3$-TPD profiles of ZSM-11 and Ce-ZSM-11 zeolites are shown in Fig. 5a and 5b. The peak at 662.5 °C for ZSM-11and 623.4 °C for Ce-ZSM-11 which indicates desorption of ammonia is takes place at high temperature. It confirms the presence of strong acidic sites in the zeolite framework. The total acidity was found 1.8195 mmol/g and 2.6178 mmol/g for ZSM-11 and

Ce-ZSM-11 respectively. It was observed that the acidity of ZSM-11 zeolite increases after ion exchange.

Optimization of reaction conditions
Optimization of Solvent and catalyst amount

In order to investigate suitable solvent for the synthesis of 4H-Pyran derivatives, 4-Nitro benzaldehyde (1 mmol) ethyl acetoacetate (1 mmol), malononitrile (1 mmol) and Ce-ZSM-11 (0.1g) were used as model substrates. Initially the model reaction was performed under solvent free condition low yield of desired product was obtained. The same reaction was performed using different solvents such as H$_2$O, THF, MeOH and EtOH under reflux condition. Amongst all these solvents maximum yield was obtained in EtOH, hence EtOH was selected as optimum solvent (Table 2). Therefore, further optimization of catalyst amount was carried out in ethanol on model reaction. It was observed that 0.1g of catalyst is sufficient for the reaction and use of excessive catalyst had no effect on either the rate of reaction or on the product yield (Table 3).

The scope and efficiency of the present method was studied. A series of 4H-Pyran derivative were prepared by using various substituted aromatic aldehyde reacting with ethyl acetoacetate and malononitrile in ethanol in the presence Ce-ZSM-11 zeolite catalyst and obtained results are summarized in (Table 4). In all cases, it was found that aromatic aldehydes having electron withdrawing or electron donating group reacted effectively and gave the product in good yields. It was observed that the substituents in aromatic ring of aldehydes have little effect on yield of the product.

Reusability of catalyst

The main advantage of present method is reusability of Ce-ZSM-11 zeolite catalyst and efficient recovery. The reusability of catalyst was investigated on model reaction. The catalyst was separated after completion of reaction by diluting reaction mixture in hot ethanol and filtration. The recovered catalyst was washed with acetone

Table 2: Effect of various solvents on the synthesis of synthesis of 4H-pyran derivatives[a].

Entry	Solvent	Time (min.)	Yield(%)[b]
1	Solvent free	90	20
2	H_2O	90	35
3	THF	90	25
4	MeOH	90	40
5	EtOH	90	92

[a]*Reaction conditions: 4-Nitro benzaldehyde (1 mmol) ethyl acetoacetate (1 mmol), malononitrile (1 mmol) and Ce-ZSM-11 catalyst (0.1g) with different solvents (10 ml) at reflux condition.* [b] *Isolated yields.*

Table 3: Optimization of catalyst amount for the synthesis of 4H-pyran derivatives[a].

Entry	Catalyst amount (g)	Time (min)	Yield(%)[b]
1	0	90	-
2	0.05	90	85
3	0.10	90	92
4	0.15	90	92
5	0.20	90	92

[a]*Reaction conditions: 4-Nitro benzaldehyde (1 mmol) ethyl acetoacetate (1 mmol), malononitrile (1 mmol), catalyst and ethanol (10 ml) at reflux condition.* [b] *Isolated yields.*
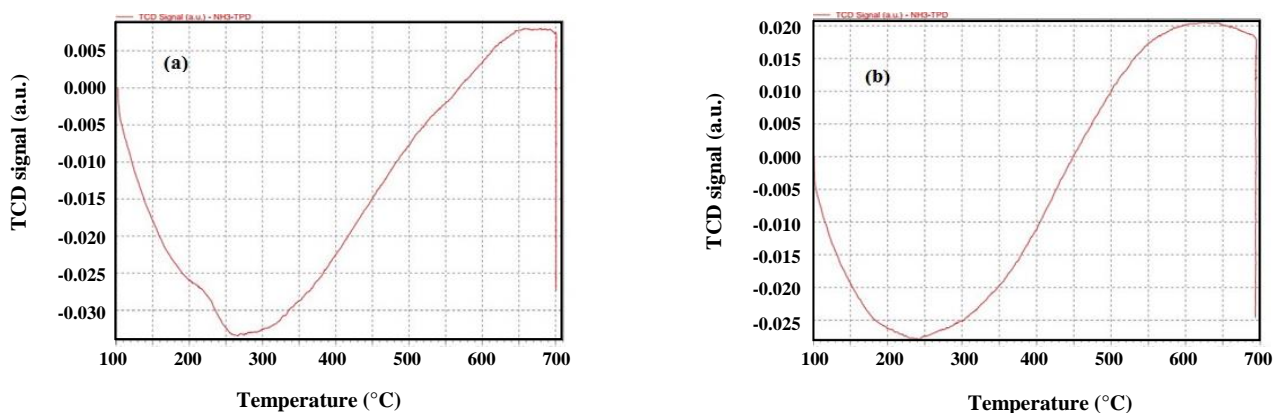
Fig. 4: NH3-TPD Spectrum of (a) ZSM-11 and (b) Ce-ZSM-11.

and dried at 100 °C for 3 h before the next catalytic run. It was observed that after three catalytic cycles, the catalyst retains its activity (Table 5).

To specify the advantages of present methods, results of different reported methods are compared with present work and summarized in (Table 6). It was observed that, Ce-ZSM-11 zeolite promote reaction more effectively than other reported catalyst.

CONCLUSIONS

In summary, we described the synthesis, characterization of ZSM-11 and Ce-ZSM-11 zeolite catalyst. The acidic strength of ZSM-11 zeolite is increased after Cerium metal ion exchange treatment. The Ce-ZSM-11 zeolite was found efficient catalyst for the synthesis of 4H-Pyran derivatives. The distinguished advantages of present method are use of inexpensive

Table 4: Ce-ZSM-11 catalyzed synthesis of 4H-Pyran derivatives[a]

Entry	Aldehyde (R)	Product	Time (min.)	Yield (%)[b]	M.P. (°C) Observed	M.P. (°C) Literature
1	H	4a	90	85	188-190	190-191 [11]
2	4-OCH$_3$	4b	90	82	142-144	141-144[11]
3	3-OH	4c	90	84	163-165	160-165[15]
4	4-NO$_2$	4d	90	92	180-182	180-182 [11]
5	4-Br	4e	90	88	174-176	175-177 [17]
6	2-Cl	4f	90	90	180-182	179-180 [15]
7	4-Cl	4g	90	88	174-176	172-174 [17]
8	4-CH$_3$	4h	90	80	176-178	175-178[11]
9	3-NO$_2$	4i	90	90	182-184	180-182 [16]

[a]*Reaction condition: 4-NO$_2$ benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), malononitrile(1 mmol) and catalyst 0.1g in ethanol 10 mL.* [b]*Isolated yields*

Table 5: Catalyst reusability and recovery.

No. of cycle	Catalyst recovery (%)	Yield(%)[b]
Fresh	94	92
I[st]	94	92
IInd	90	90
IIIrd	85	90

[b]*Isolated yield*

Table 6: Catalytic performance of different reported catalysts for the synthesis of 4H-Pyran derivatives.

Entry	Catalyst	Condition	Time (min.)	Yield (%)	Reference
1	Mg/La mixed oxide	Methanol, reflux	90	78	[6]
2	Silica nanoparticle	EtOH, R.T.	120	88	[8]
3	ZnO/MgO containing ZnO nanoparticle	[bmim]BF$_4$, R.T.	30	91	[9]
4	Nano crystalline ZnO	Ethanol: Water (1:1) R.T.	180	96	[10]
5	SnCl$_2$/nano SiO$_2$	Ethanol, reflux	30	91	[11]
6	Cu(II) Oxymetasilicate	CH$_3$CN, reflux	60	92	[12]
7	Silica bonded S-sulfonic acid (SBSSA)	Ethanol/water, reflux	45	94	[13]
8	CsF	EtOH, R. T.	05	91	[14]
9	Ca-MCM	Ethanol, R. T.	720	98	[15]
10	Nano ZrP$_2$O$_7$	Ethanol, reflux	45	92	[16]
11	Ce-ZSM-11	Ethanol, reflux	90	92	Present result

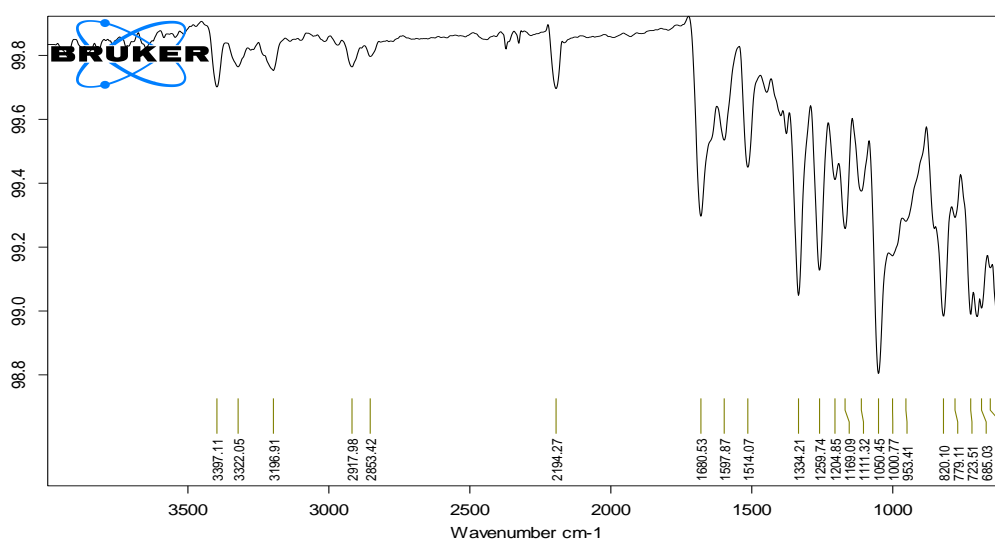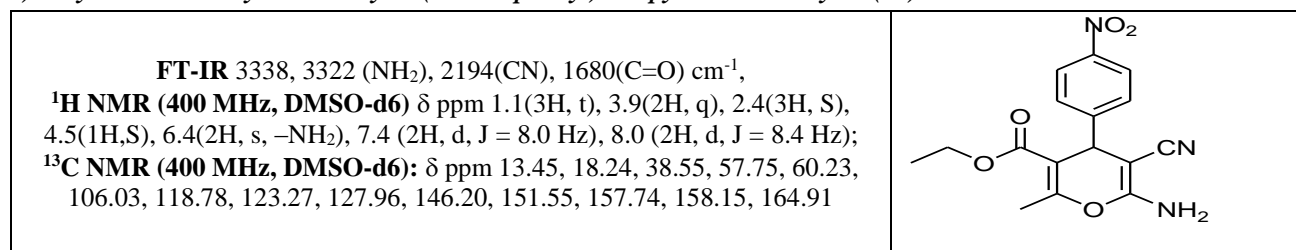catalyst, simple reaction workup, excellent yield and reusability of catalyst.

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Supplementary

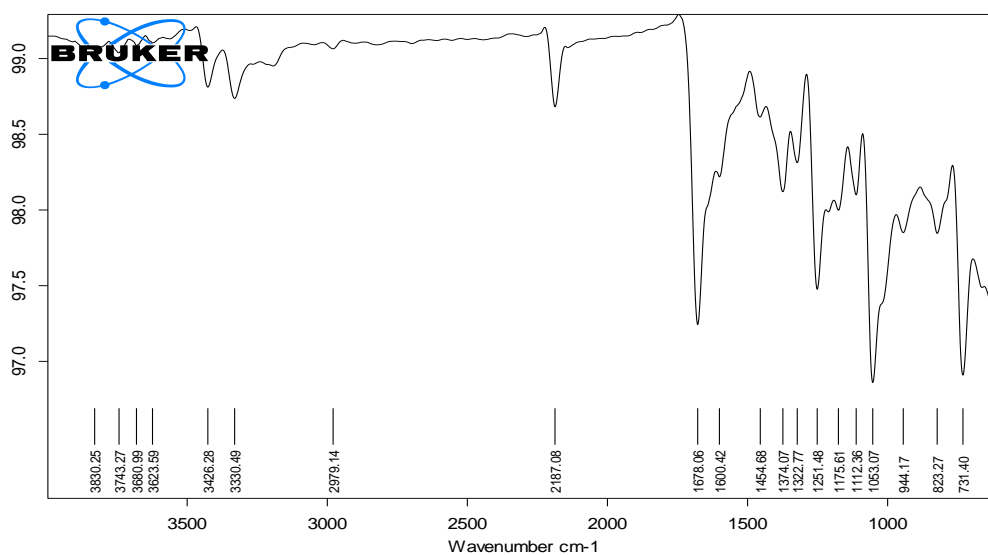### 1) Ethyl-6-Amino-5-cyno-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylate(4d)

FT-IR 3338, 3322 (NH$_2$), 2194(CN), 1680(C=O) cm^{-1},
^{1}H NMR (400 MHz, DMSO-d6) δ ppm 1.1(3H, t), 3.9(2H, q), 2.4(3H, S), 4.5(1H,S), 6.4(2H, s, –NH$_2$), 7.4 (2H, d, J = 8.0 Hz), 8.0 (2H, d, J = 8.4 Hz);
^{13}C NMR (400 MHz, DMSO-d6): δ ppm 13.45, 18.24, 38.55, 57.75, 60.23, 106.03, 118.78, 123.27, 127.96, 146.20, 151.55, 157.74, 158.15, 164.91

FT-IR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylate (4d)
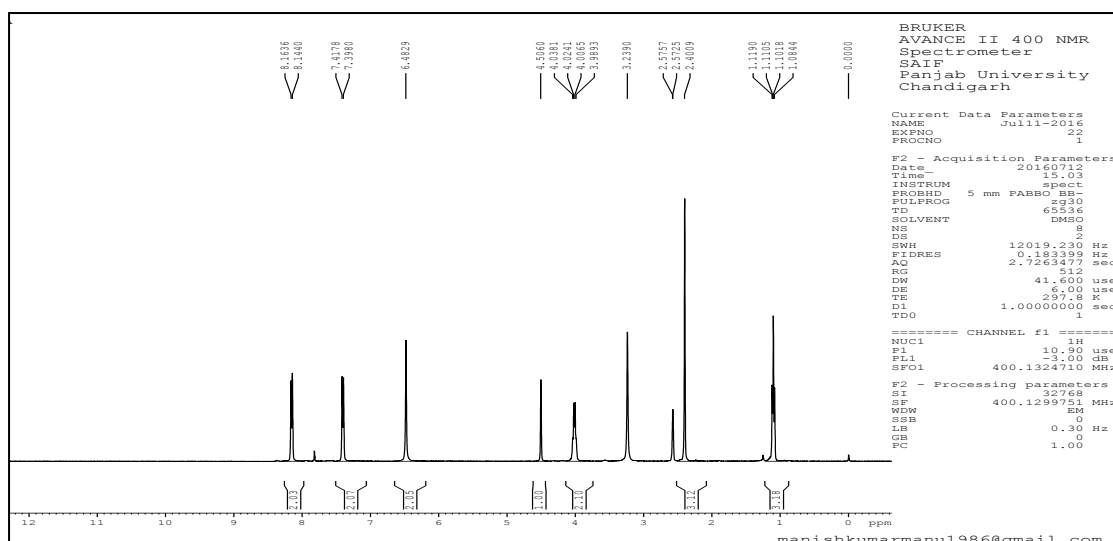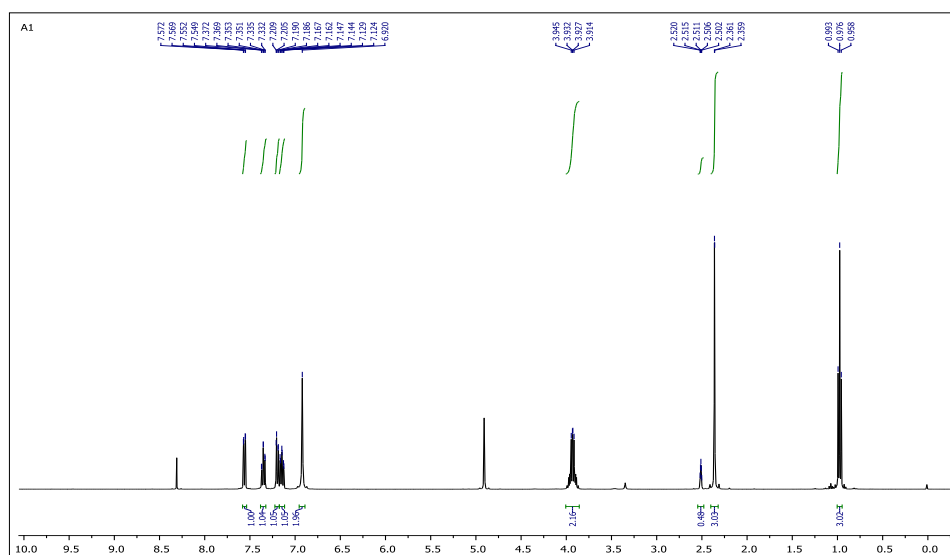

^{1}H-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylate (4d)
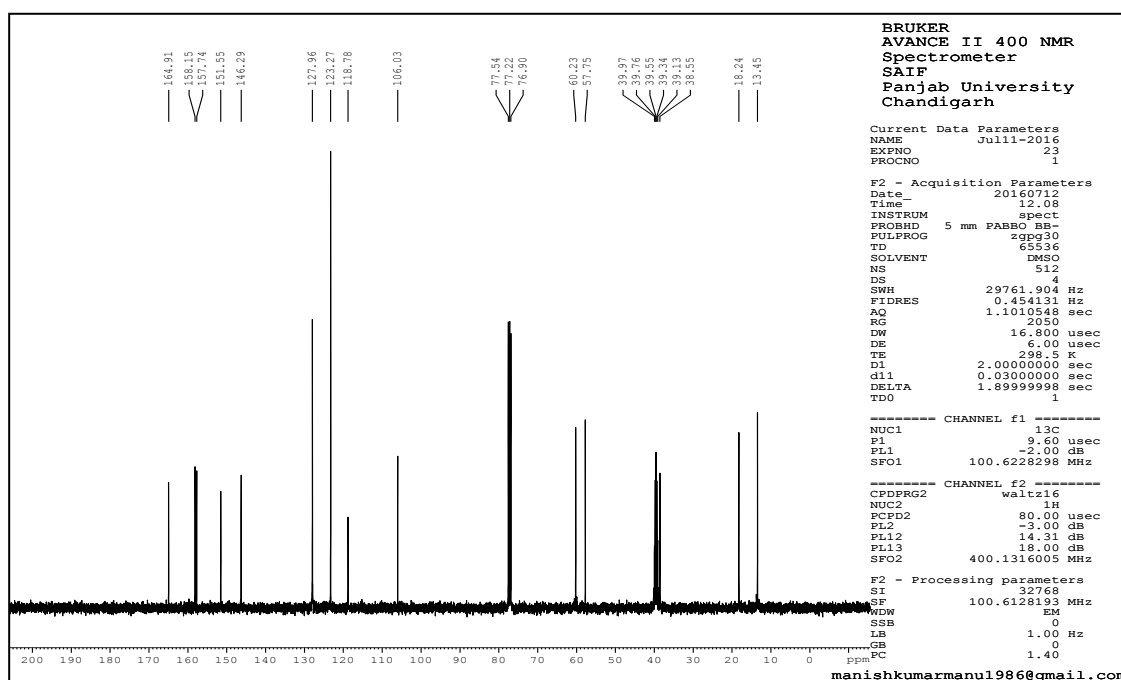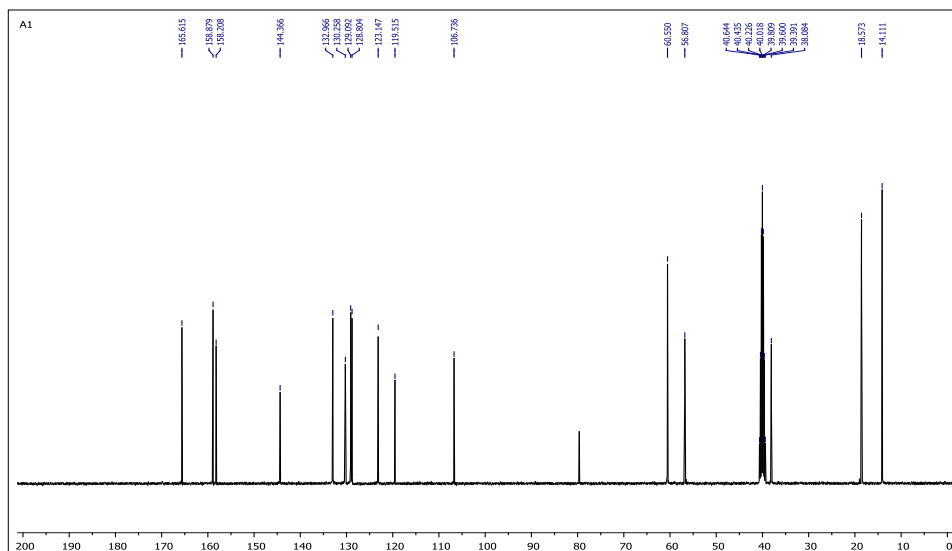
^{1}H-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylate (4d)
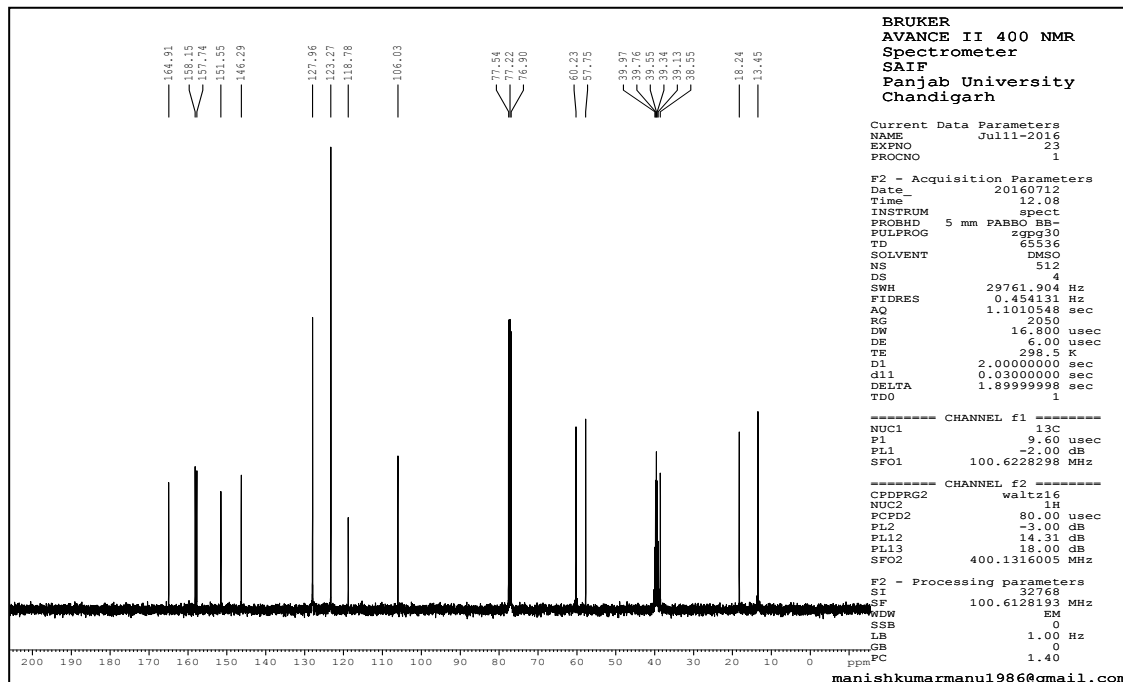
^{13}C-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylate (4d)

2) *Ethyl-6-Amino-5-cyno-2-methyl-4-(4-bromo-phenyl)-4H-pyran-3-carboxylate(4e)*

FT-IR 3423, 3330 (NH$_2$), 2187(CN), 1678(C=O) cm^{-1} **^{1}H NMR (400 MHz, DMSO)** δ ppm 0.9 (3H, t), 3.94(2H, q), 2.50(3H,S), 4.9(1H,S), 7.1(2H, s, –NH$_2$), 7.3 (2H, d, J = 7.6 Hz), 7.5 (2H, d, J = 8.0 Hz) **^{13}C NMR (400 MHz, DMSO-d6):** δ ppm 14.11, 18.57, 39.80, 60.55, 106.73, 119.51, 123.14, 128.80, 129.09, 130.25, 132.96, 144.36, 158.20, 158.87,165.61
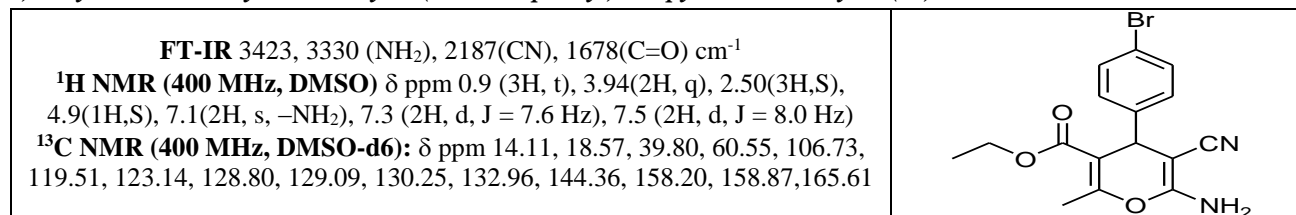
FT-IR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-bromo-phenyl)-4H-pyran-3-carboxylate (4e)

^{1}H-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-bromo-phenyl)-4H-pyran-3-carboxylate (4e)
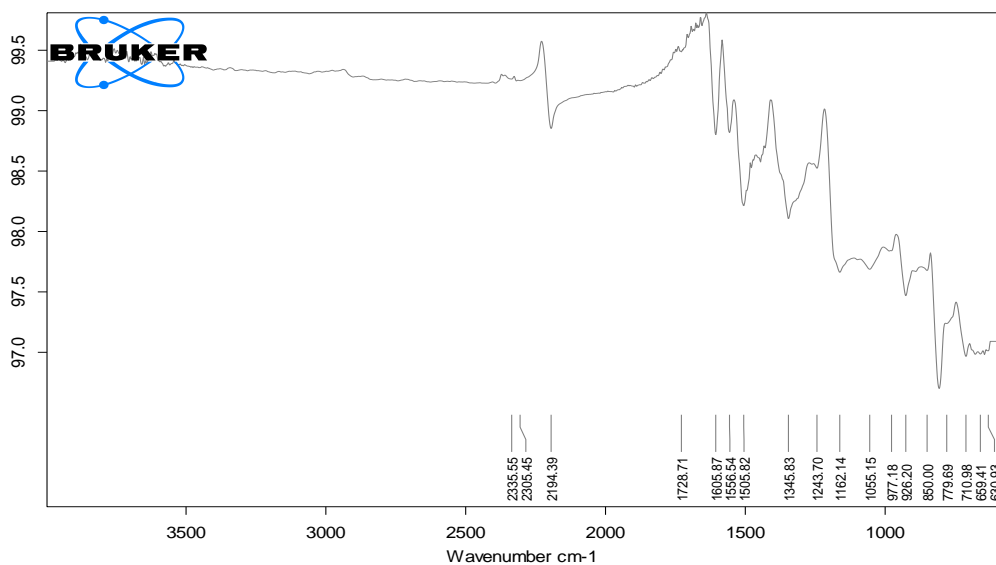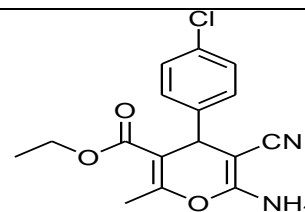
Research Article

^{13}C-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-bromo-phenyl)-4H-pyran-3-carboxylate (4e)

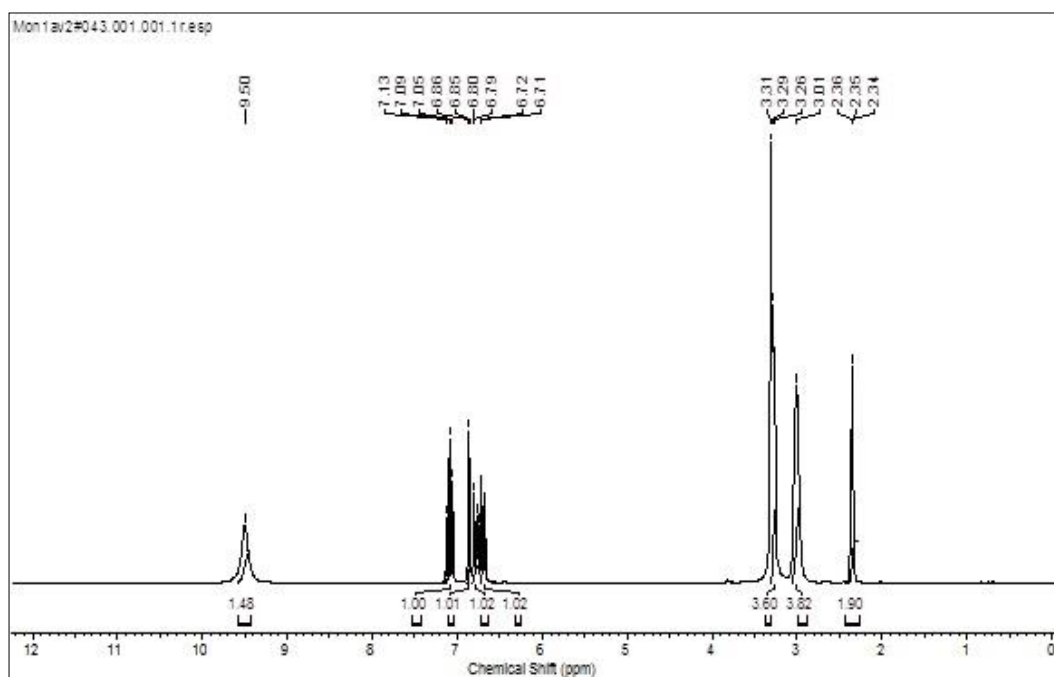### 3) Ethyl-6-Amino-5-cyno-2-methyl-4-(4-chloro-phenyl)-4H-pyran-3-carboxylate(4g)

FT-IR 3330, 3312 (NH$_2$), 2194(CN), 1685(C=O) cm^{-1}
^{1}H NMR (400 MHz, CDCl$_3$) δ ppm 1.9 (3H, t), 3.8(2H, q), 3.6(3H,S), 3.9(1H,S), 9.5(2H, s, –NH$_2$), 6.7 (2H, d, J = 8.0 Hz), 6.8 (2H, d, J = 8.0 Hz)
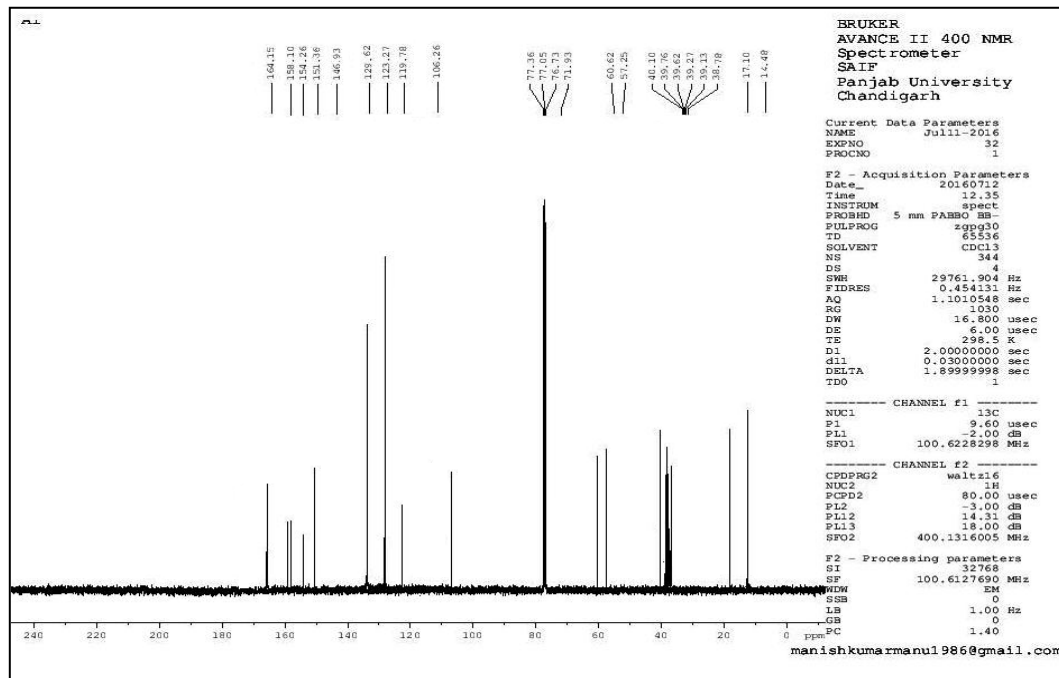**^{13}C NMR (400 MHz, CDCl$_3$):** δ ppm 14.48, 17.10, 39.27, 57.25, 60.62, 106.26, 119.78, 123.27, 129.62, 146.93, 151.36,154.26, 158.10, 164.15.

FT-IR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-chloro-phenyl)-4H-pyran-3-carboxylate (4g)

¹H-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-chloro-phenyl)-4H-pyran-3-carboxylate (4g)

¹³C-NMR spectrum of Ethyl-6-Amino-5-cyno-2-methyl-4-(4-chloro-phenyl)-4H-pyran-3-carboxylate (4g)