Synthesis, Characterization and Mechanistic Studies of Activated Carbon Supported Nickel (Ni/C) Catalyst for the Effective Amidation of Aldehyde

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Supporting Information

Table of Contents: **Page No**

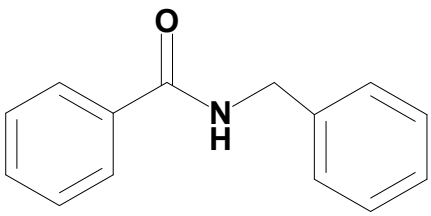
1. Experimental Process

For catalyst preparation, the supported precursor was prepared by pouring the support (activated carbon) over nickel chloride solution with appropriate concentration. After 15 min of rotation, the mixture was heated and dried at 383 K for 1h. The reduction of the supported precursors was performed in a 2 necked reaction flask fitted with a reflux condenser in a sand bath for heating. The reaction mixture was heated at 353 K under continuous stirring in an excess hydrazine solution to maintain desired pH. After reduction the solid obtained was filtrated off, washed with distilled water and dried to get expected Ni/AC catalyst. Then it was characterized by several spectroscopic techniques such as SEM, XRD etc. The morphology and particle size of catalyst was imaged by scanning electron microscope. Then the catalytic activity was checked by model reaction. For the model reaction, two reactants (benzaldehyde and benzyl amine) were added to a round bottom flask in 1:2 ratios to the catalyst. Then solvent was added to the reaction mixtures. This reaction mixture was heated around at 140 °C for 36 h with continuous stirring by magnetic bar. The progress of the reaction was monitored by thin layer chromatography with proper solvents. Finally, completion of the reaction was confirmed by TLC. After the completion of the reaction, catalyst was separated from the mixture by centrifugation, followed by washing with acetone and drying at 90 °C for 3 h. The recovered catalyst was reused over several cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. The products were purified by column chromatography & recrystallization separation technique. The synthesized pure amide products were identified by FT-IR, ^{1}H NMR, ^{13}C NMR. Same reaction procedure was followed for catalyst screening, solvent screening and optimization of other reaction parameters.

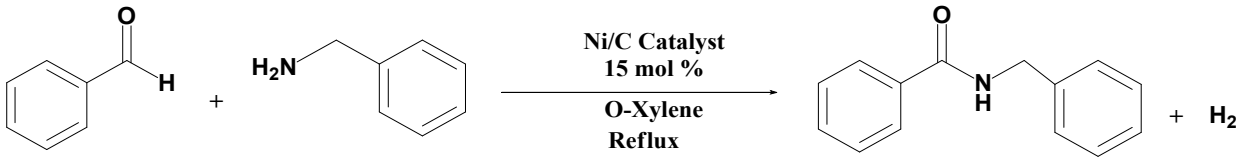
Computational Method

Gaussian 16 program and RB3LYP were performed with the basis set of 3-21G and the density functional theory (DFT) method was used and the values were determined in Hartree–Fock (HF) unit.

Synthesis of N-Bezylbenzamide



For synthesis of *N*-Benzyl benzamide, benzaldehyde (1 mmol) and benzylamine (1 mmol) were taken in a RB flask containing 15 mol% Ni/C and then added 5 mL *o*-xylene in the mixture. This reaction mixture was heated on hot plate around at 150 °C for 36 hrs in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction and reaction completion was confirmed by TLC. After the completion of the reaction, 5 ml 2-propanol was added to dissolve amides mixture. Then, Ni/C was separated from the mixture by centrifugation followed by washing with acetone and dried at 110°C for 3 hrs. The recovered Ni/C was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique in ethanol/water system.



Scheme S1 : Synthesis of N-Bezylbenzamide

Molecular weight: 212 g/mol

Molecular formula: $C_{14}NOH_{13}$

Solubility: Soluble in Chloroform.

Melting Point: 104-107 ºC

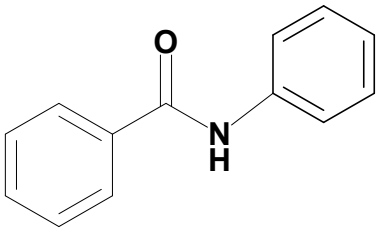
FT-IR (υ KBr): 3457.52, 3063.06, 2850.88, 1644.37, 1601.93, 1550.82, 1454.38 cm-1

1H-NMR (400 MHz, $CDCl_3$): δ 8.074-8.076 (m, 2H, C-3), 7.390-7.458 (m, 3H, C-2), 7.227-7.287 (m, 5H, C-1), 5.279 (s, 1H, -NH, N-5), 4.038 (S, 2H, C-4)

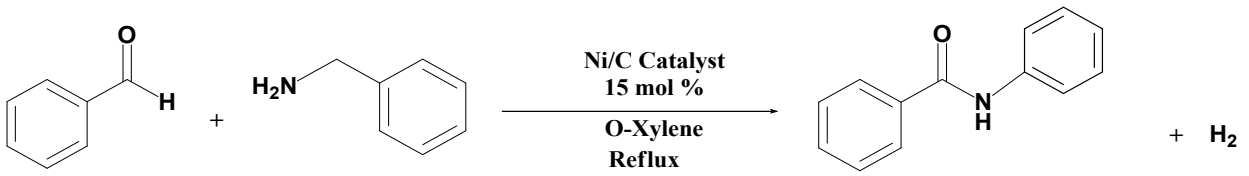
13C-NMR (100 MHz, $CDCl_3$) : δ 170.62 (C=O,1C, C-9), 134.31 (1C,C-8), 131.46 (1C, C-7), 128.81 (2C,C-1,C-6),128.75(4C, C-4,C-5), 127.04 (4C, C-2,C-3), 50.70(1C, C-9)

GC-MS ($CDCl_3$): The GC-MS spectrum exhibited retention time (in min) 7.091 min. mass spectrum (in m/e): Molecular ion peak (m/e): 211 , Base peak (m/e) : 105 and others m/e at 91, 77.

Synthesis of N-Phenyl Benzamide



For synthesis of *N*-Phenylbenzamide, benzaldehyde (1 mmol) and aniline (1 mmol) were taken in a RB flask containing 15 mol% Ni/C and then added 5 mL *o*-xylene in the mixture. The mixture was heated on hot plate around at 150 °C for 36 h in a sand bath with continuous stirring of magnetic bar at 300 rpm. The progress of the reaction was monitored by TLC in n-hexane and chloroform. Completion of the reaction was confirmed by TLC. After the completion of the reaction, 5 ml 2-propanol was added to dissolve amides mixture. Then, Ni/C was separated from the mixture by centrifugation followed by washing with acetone and dried at 110°C for 3 h. The recovered Ni/C was reused for three cycles without a marked decrease in the yield of the product. The solvent was removed from mixture by rotatory evaporator. Finally, the amide was purified by column chromatography with chloroform and n-hexane and recrystallization separation technique with ethanol and water



Scheme S2: Synthesis of N-Phenyl Benzamide

Molecular weight: 197 g/mol

Molecular formula: $C_{13}NOH_{11}$

Solubility: Soluble in Chloroform.

Melting Point: 162-164 ºC

FT-IR (υ KBr): 3450, 3063,1650, 1529.29, 1550.82, 1628.94,1183.70 cm^{-1}

^{1}H-NMR (400 MHz, $CDCl_3$) : δ 8.598 (s,1H, -NH, N-7), 8.119- 8.126 (m, 2H, C-4), 7.875-7.885 (m, 2H, C-3), 7.440-7.611 (m, 3H,C-5, C-6), 7.250-7.421 (m, 2H, C-2), 6.709-6.720 (3, 1H, C-1)

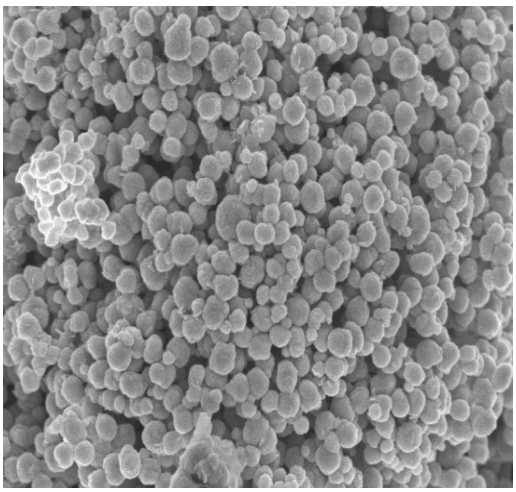
^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.193 (1C,C=O, C-5), 138.909 (1C,C-4), 136.012 (1C,C-6),131.801 (1C,C-9), 127.383-129.438 (4C, C-2,C-8) 126.10 (2C, C-7), 124.80 (1C, C-1),121.30 (2C, C-3).

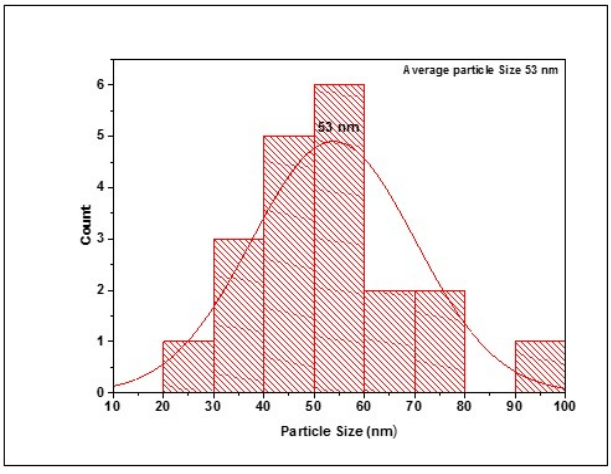
Surface morphology of Ni and Supported Ni catalyst

Table S1: Particle size of Ni and supported Ni Catalysts

Reduction Ratio	**Catalyst**	**Particle Size(nm) SEM**
1:12:12	Ni	53
1:12:12	Ni/C	53
1:4:4	Ni/C	121
1:12:12	Ni/Al_2O_3	67

(a)





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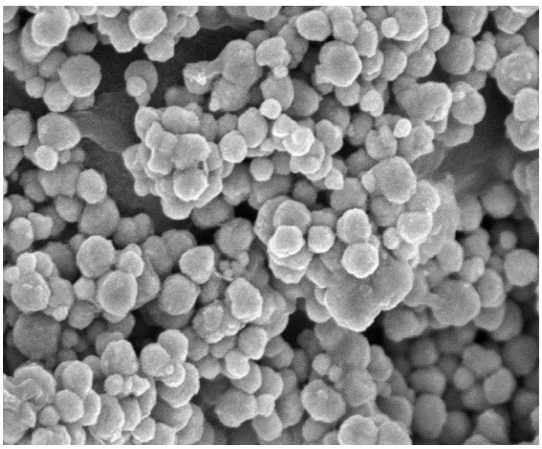
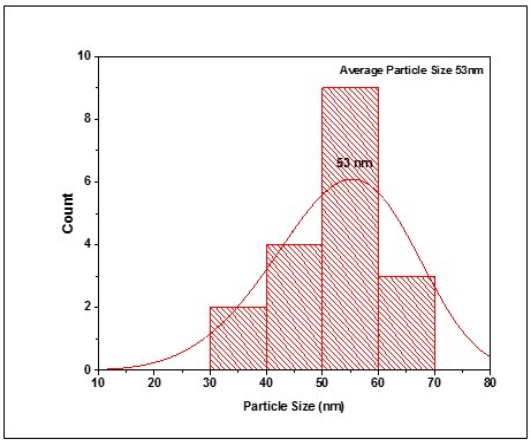
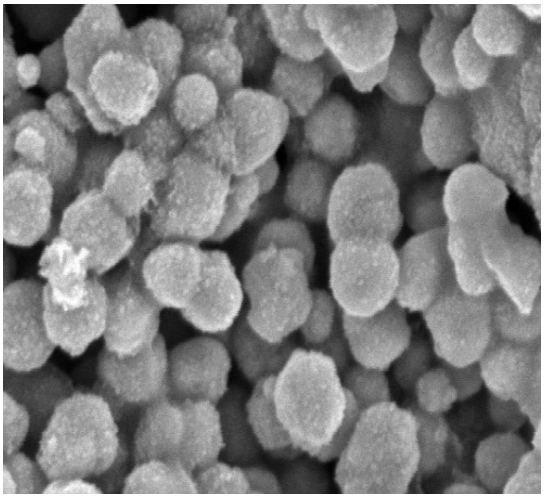
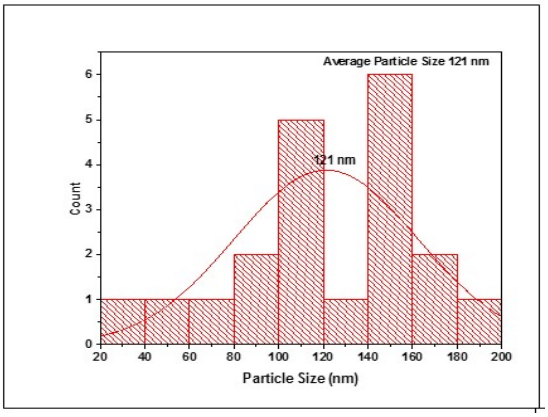


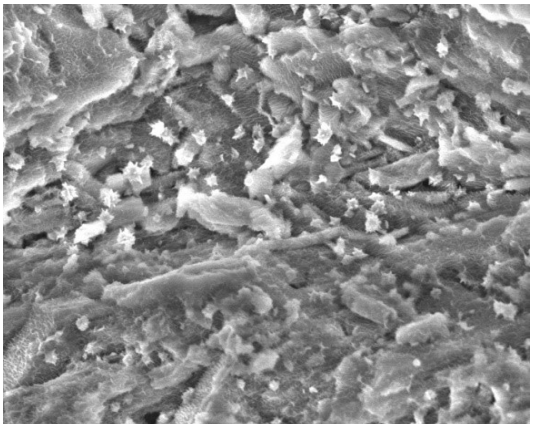

Average Particle Size 53nm
53 nm
Count
Particle Size (nm)

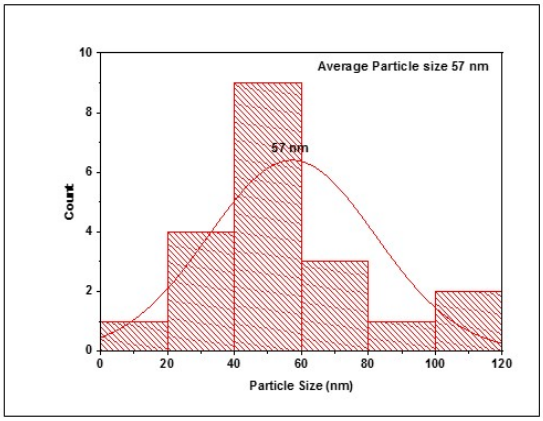
(c)




Average Particle Size 121 nm
121 nm
Count
Particle Size (nm)

(d)




Average Particle size 57 nm
57 nm
Count
Particle Size (nm)

Energy dispersive x-ray (EDX) spectral analysis

Table S2: Atom Percentage of the Nickel and supported Nickel catalysts

Reduction Ratio	**Catalyst**	**Relative atomic (%) (EDX)**	
1:12:12	Ni	Ni = 100	-
1:12:12	Ni/C	Ni = 10.04	C= 89.96
1:4:4	Ni/C	Ni =13.36	C = 86.64
1:12:12	Ni/Al2O3	Ni = 9.11	Al = 23.87 O = 67.02

Catalyst screening

Model reaction

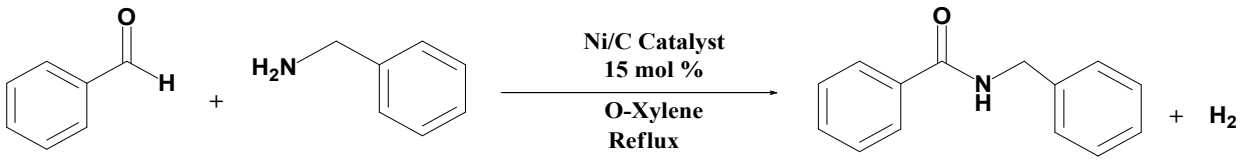


Table S3 : Catalyst screening for model reaction

Entry	**Catalyst**	**Reduction Ratio**	**% of Yields**
01	**No Catalyst/Reagent**	**-**	**0**
02	Ni	1:12:12	13
03	Ni/GO	1:12:12	34
04	Ni/C	1:4:4	28
05	Ni/C	1:12:12	71
06	Ni/C	1.35:4.5:3.6	14

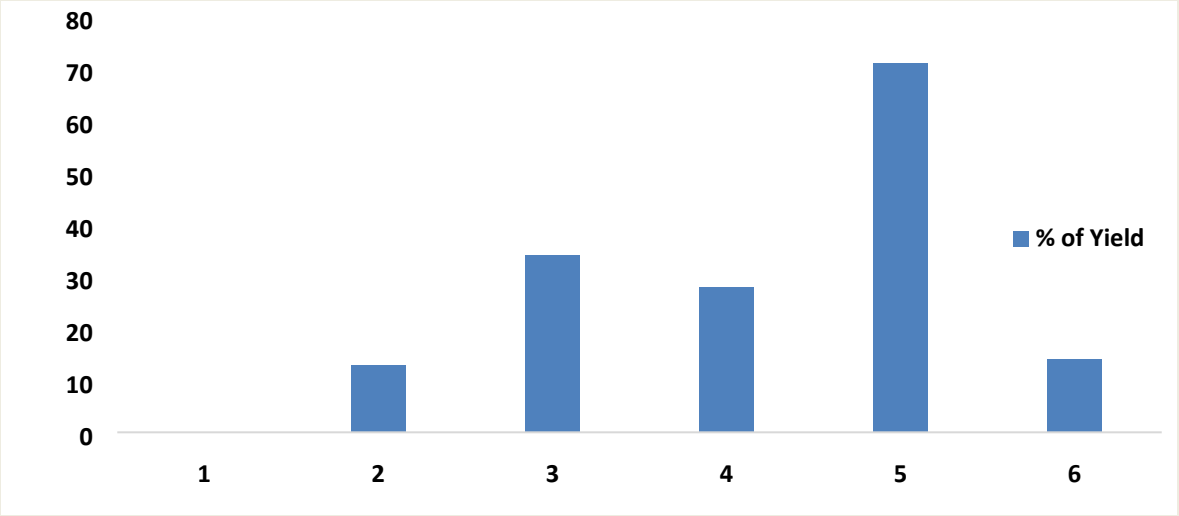


Figure S1: **Catalyst screening for model reaction**

Solvent Screening

Model reaction

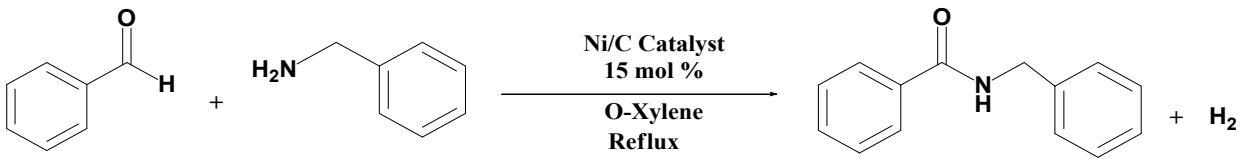


Table S4 : Solvent screening for model reaction

Entry	**Solvent**	**% of Yields**
01	No solvent	0
02	*o*-xylene	90
03	Benzene	20
04	Triethylamine	14
05	Toluene	29

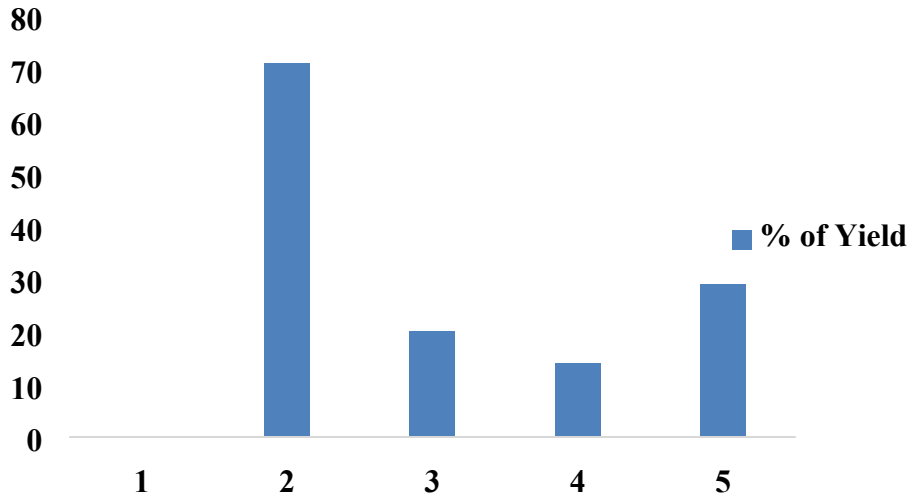


Figure S2: **Solvent screening for model reaction**

Reusability of Ni/C

Model reaction

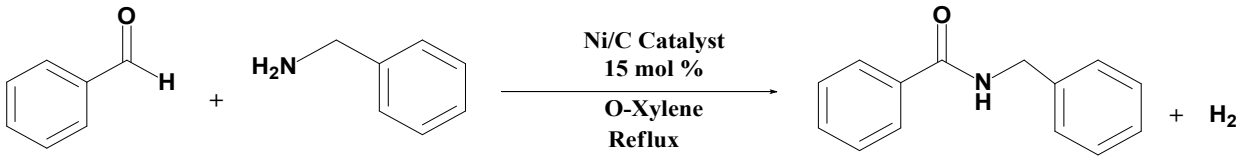


Table S5: Reusability of Ni/C for model reaction.

Cycle Number	**Catalyst**	**% of Yields**
01	Ni/C	71
02		68
03		65

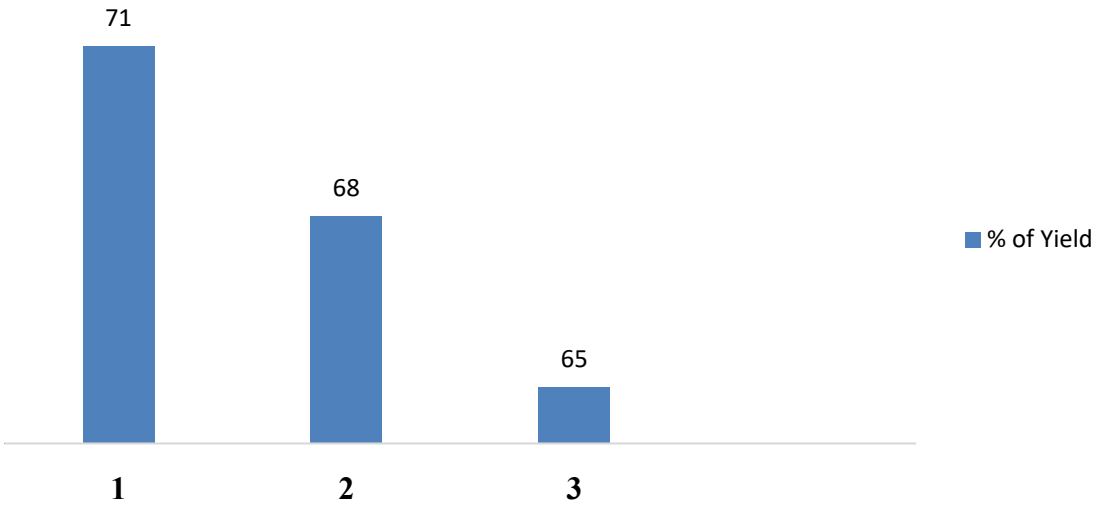
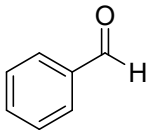
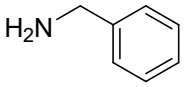
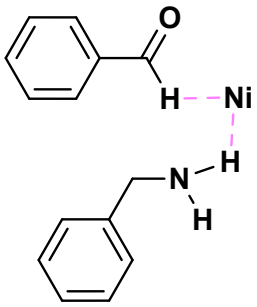
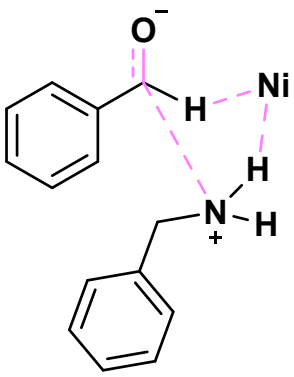
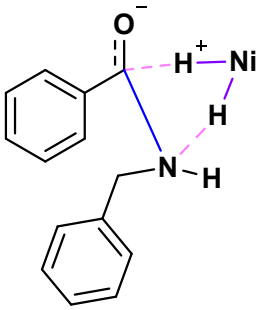


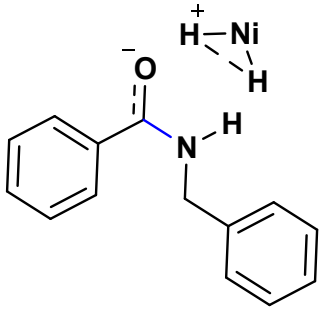
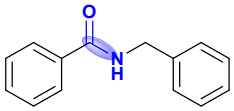
Figure S3 : **Reusability of Ni/C for model reaction**

DFT Calculation Data

Table S6: Energy Chart of Benzamide using Ni/C catalyst

Name	Structure	Energy (Hartree)
Starting Material 1	 Starting M1	-341.5111421

Starting Material 2	 Starting M2	-286.024067
Transition State 1		-2162.617066
Transition State 2		-2163.833700
Transition State 3		-2163.693821

Transition State 4		-667.795128
Final Product		-662.11

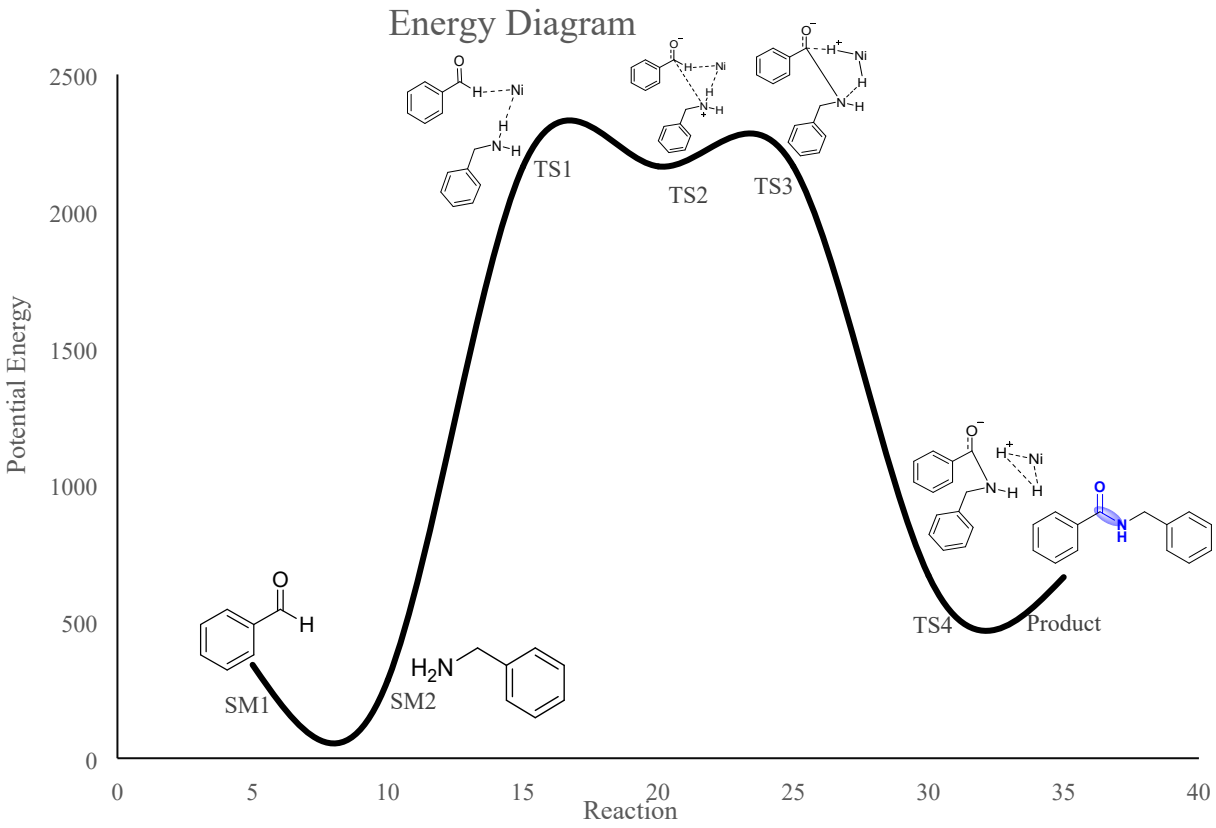


Figure S4: Calculated energy profile of Benzamide using Ni/C catalyst

2. Spectra of the compound 1:

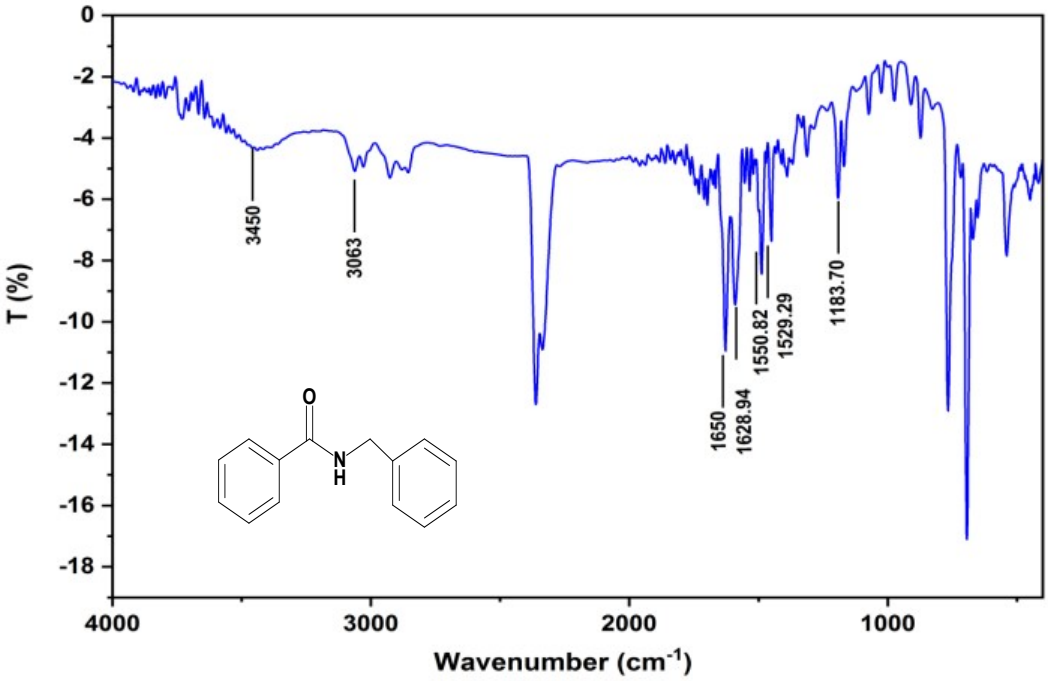


Figure S5 : FT -IR spectrum of compound 1

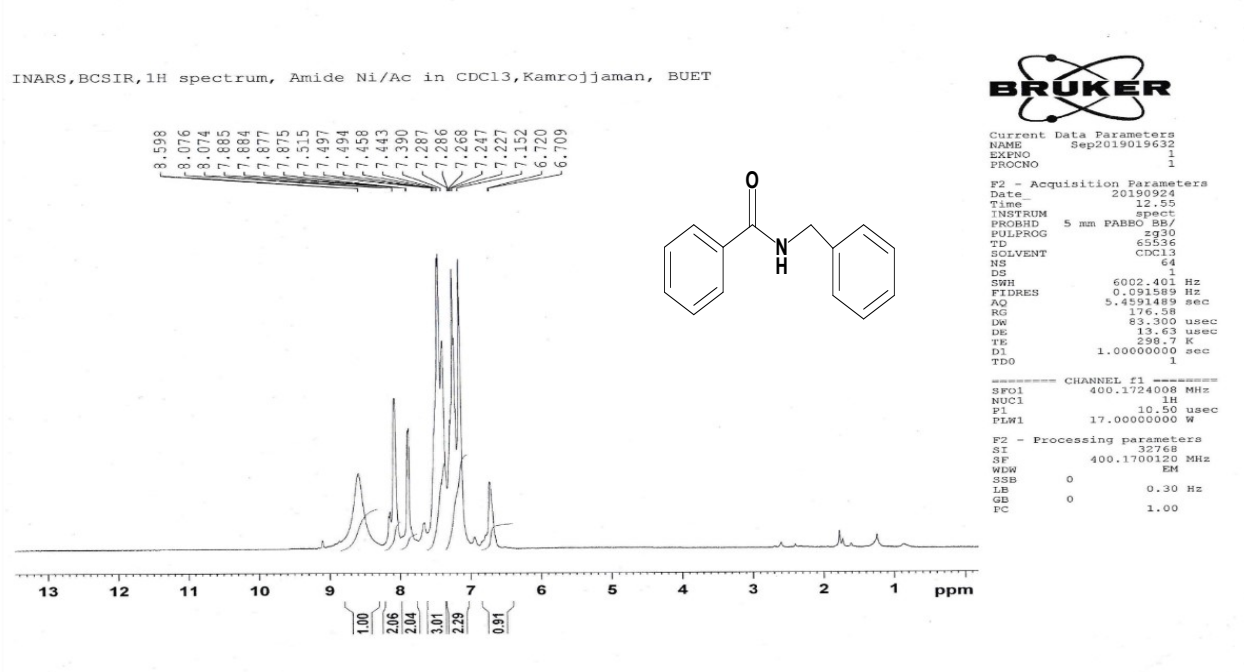


Figure S6: ^{1}H-NMR spectrum of compound 1

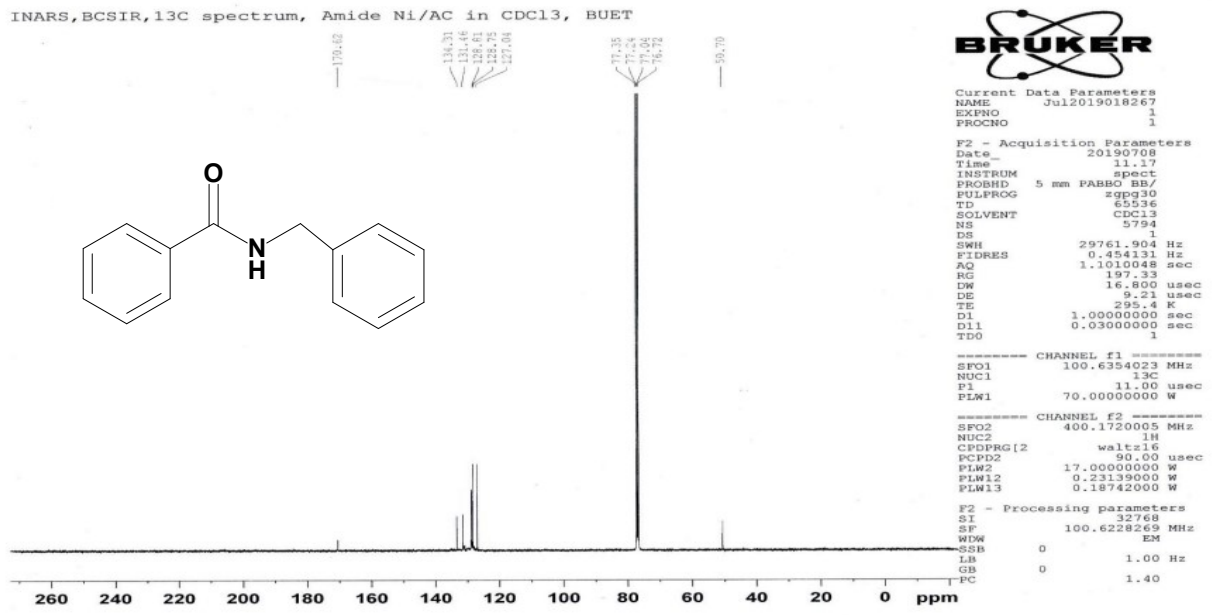


Figure S7: ^{13}C-NMR spectrum of compound 1

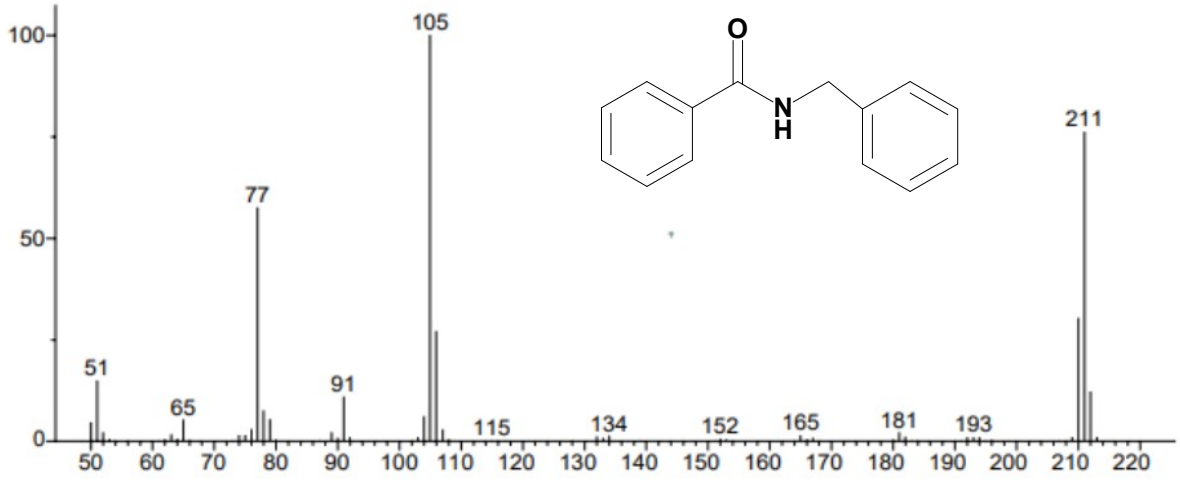


Figure S8: GC-MS spectrum of compound 1

3. Spectra of compound 2

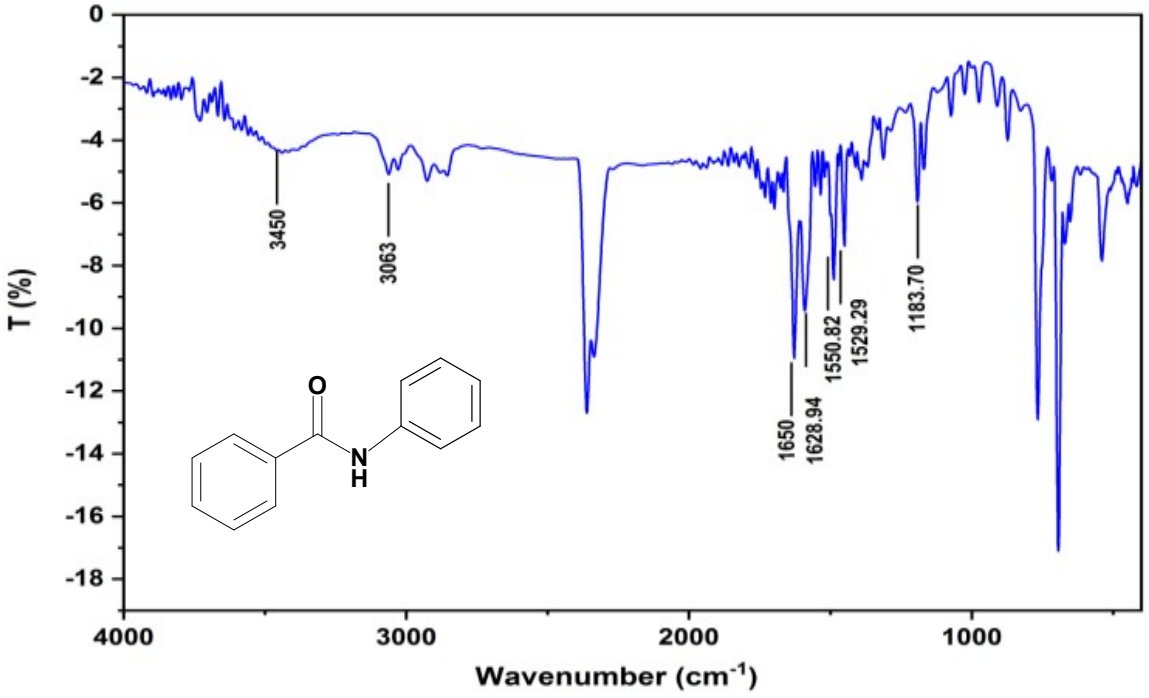


Figure S9: FT-IR spectrum of compound 2

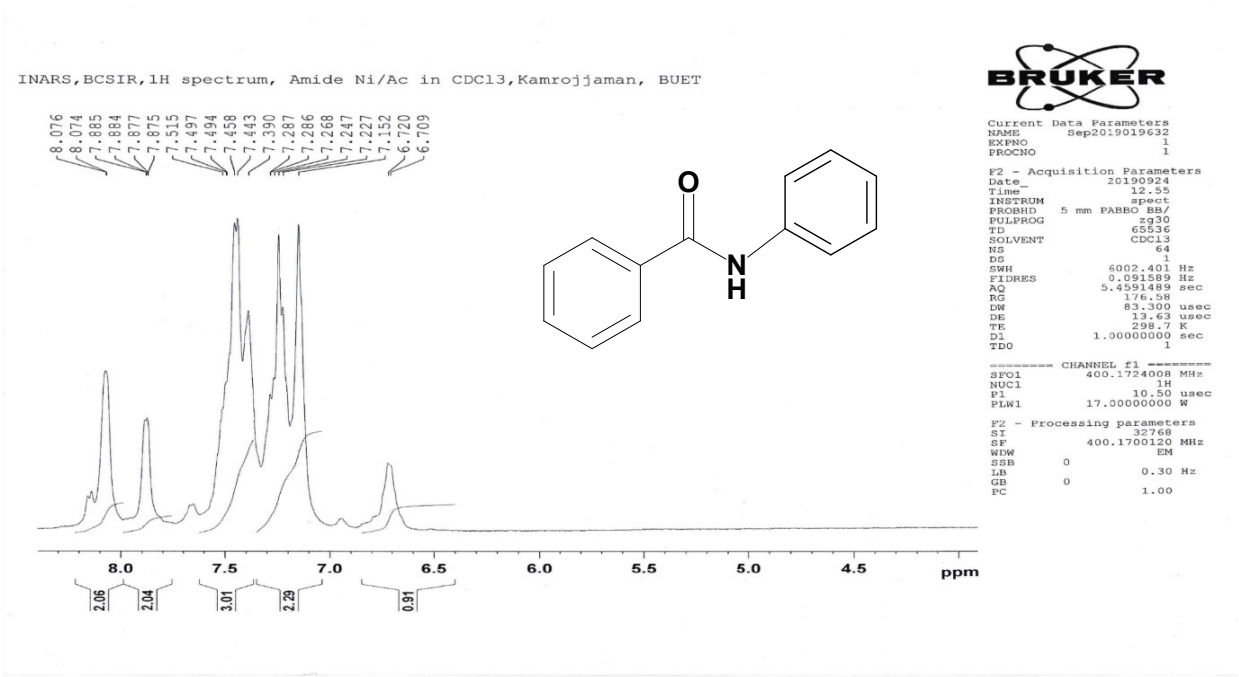


Figure S10: ^{1}H-NMR spectrum of compound 2

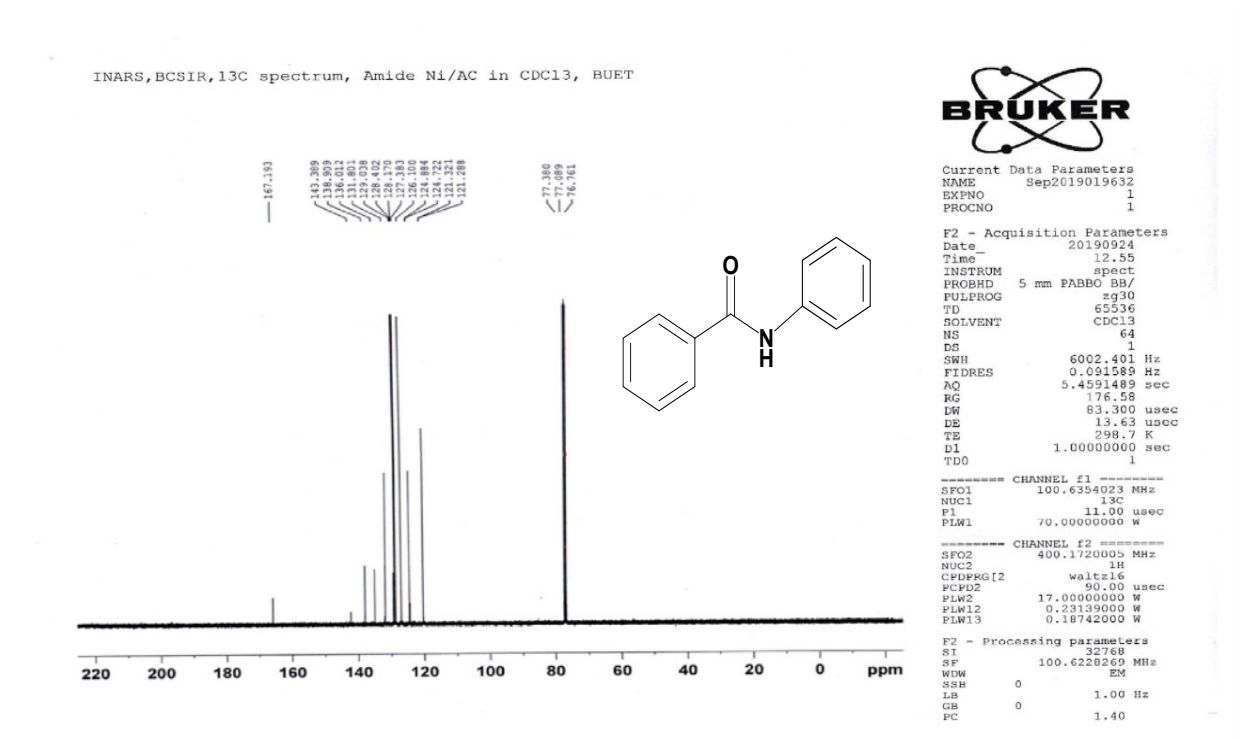


Figure S11: ^{13}C-NMR spectrum of compound 2