Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Sustainable Route for the Synthesis of Flowers-like Ni@N-doped Carbon Nanosheets from Bagasse and its Catalytic Activity towards Reductive Amination of Nitroarenes with Bio-derived Aldehydes

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Contents

S1. Physicochemical Methods

Powder X-ray diffraction (PXRD) data were collected using a PANalytical Empyrean (PIXcel 3D detector) system equipped with Cu Kα (λ=1.54 Å) radiation. The infrared spectra (IR) of the samples were recorded using the KBr pellet method on a Perkin–Elmer GX FTIR spectrometer in the region of 400−4000 cm^{-1}. Scanning electron microscopy (SEM) images were recorded on a microscope (JEOL JSM 7100F) with an accelerating voltage of 18 kV and with a probe current of 102 AMP. The transmission electron microscopy (TEM), high-resolution TEM observation was acquired on JEOL, JEM 2100 with an electron acceleration energy of 200 kV. The samples were ultrasonically dispersed in IPA for 30 min and deposited on the copper grid using capillary and dried overnight in air. The content of Ni in the catalysts was determined Inductive coupled plasma (ICP) analysis of the catalyst was carried out on Perkin Elmer, Optima 2000. The reaction mixture was analyzed by Gas Chromatography (GC-7890B and GC-MS (Shimadzu, QP-2010, Japan), with HP-5 column which consists of 5% diphenyl and 95% dimethyl polysiloxane capillary column and FID as a detector. The surface area of the catalyst was calculated using the Branauer-Emmette-Teller (BET) equation (micromeritics). X-ray photoelectron spectroscopy (XPS) was performed using an ESCA+ (Omicron Nanotechnology, Germany) with a monochromatized Al-Kα X-ray (hν = 1486.7 eV) as the excitation source (15 kV and 20 mA). The pass energy for the survey spectrum was 50 eV and 20 eV in the case of the short scan. The sample was placed on the copper tape and degassed in the XPS FEL chamber to minimize the air contamination. A charge neutralizer of 2 keV was used to overcome any charging problem, and the calibration was done using the adventitious C 1s feature at 284.6 eV as a reference. All the spectra were recorded at 90° of the X-ray source. ^{13}C solid-state nuclear resonance (NMR) spectroscopy was performed using a Bruker 11.7 T spectrometer equipped with a triple resonance 2.5 mm solid-state probe head and an avance III console. All experiments were performed at room temperature

S2. BET analysis of BC and Ni@NC-DC

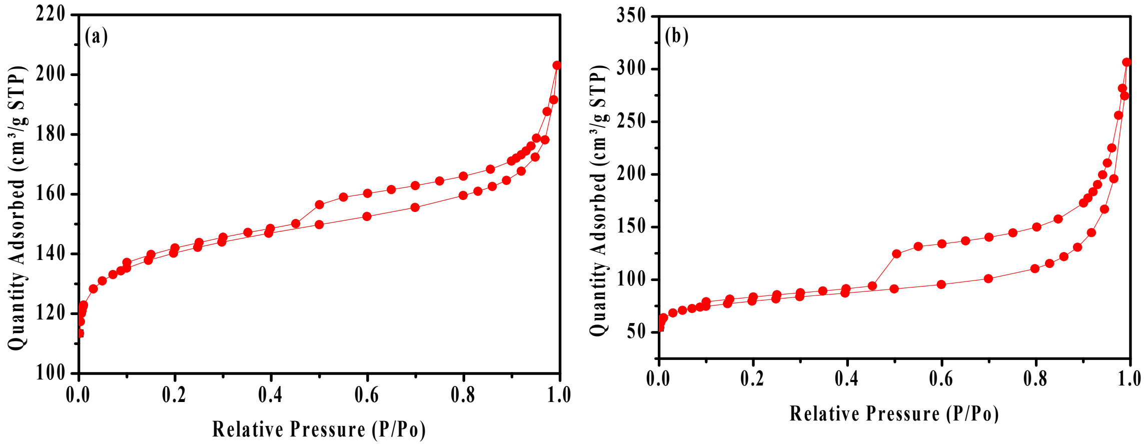

Figure S1. (a) BET spectrum of BC and (b) BET spectrum of Ni@NC-DC

S3. HRTEM images of before and after reduction of Ni@NC-DC

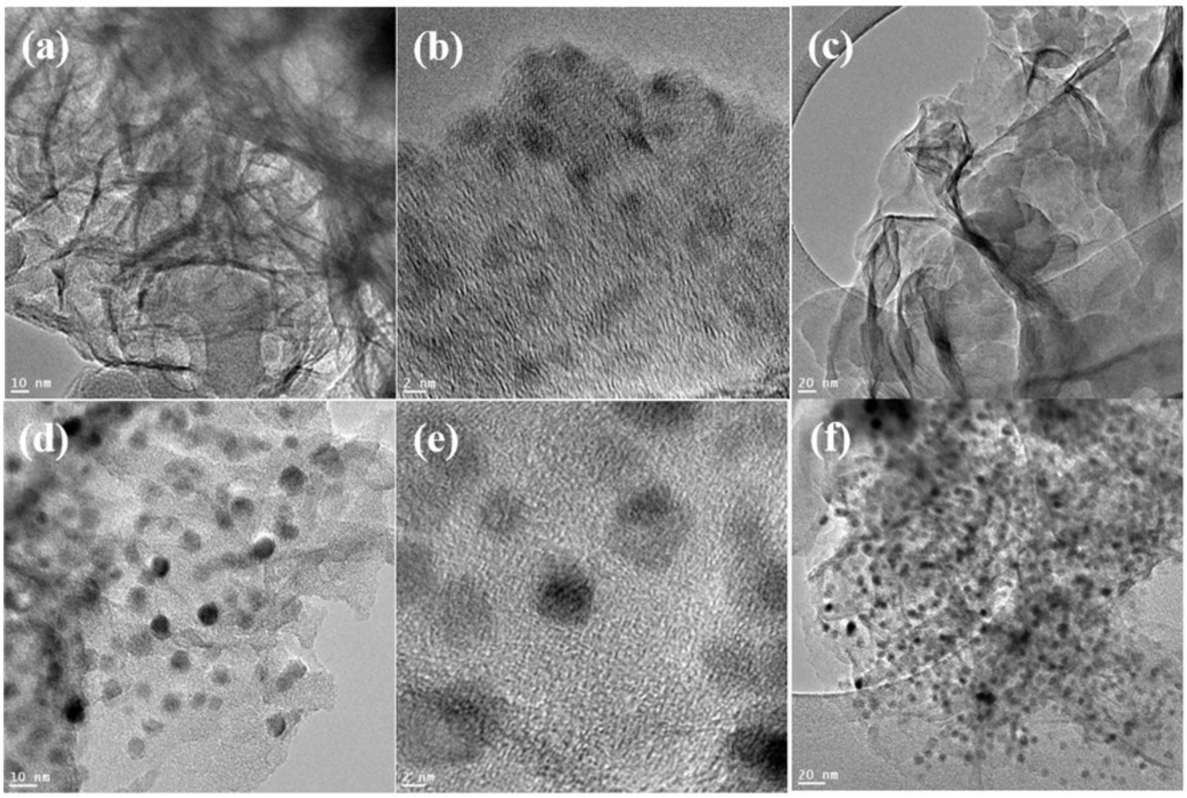

Figure S2. (a-c) HRTEM images before the reduction of Ni@NC-DC, (d-f) HRTEM images after the reduction of Ni@NC-DC.

S4. Particle size distribution of Ni@NC-DC catalyst

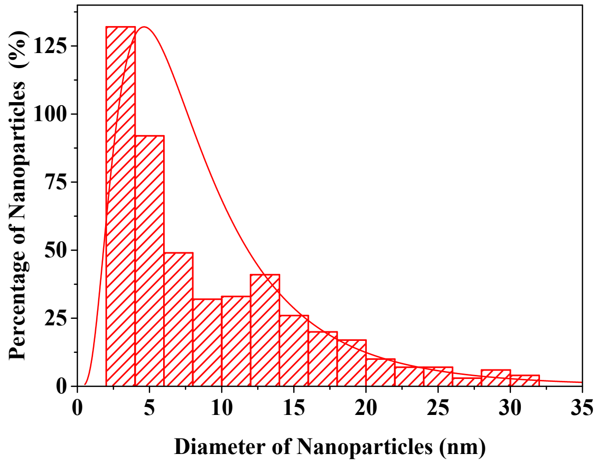

Figure S3. The particle size distribution of Ni@NC-DC catalyst.

S5. Activity of the catalyst

The activity of the catalyst was obtained by using the following formula

$$Catalytic\ activity = \frac{mmoles\ of\ the\ desired\ product\ formed}{gram\ of\ active\ catalyst\ \times reaction\ time\ in\ h}\ \mathrm{mmol{\cdot}g^{-1}h^{-1}}$$

S6. GC-Mass spectrum of products

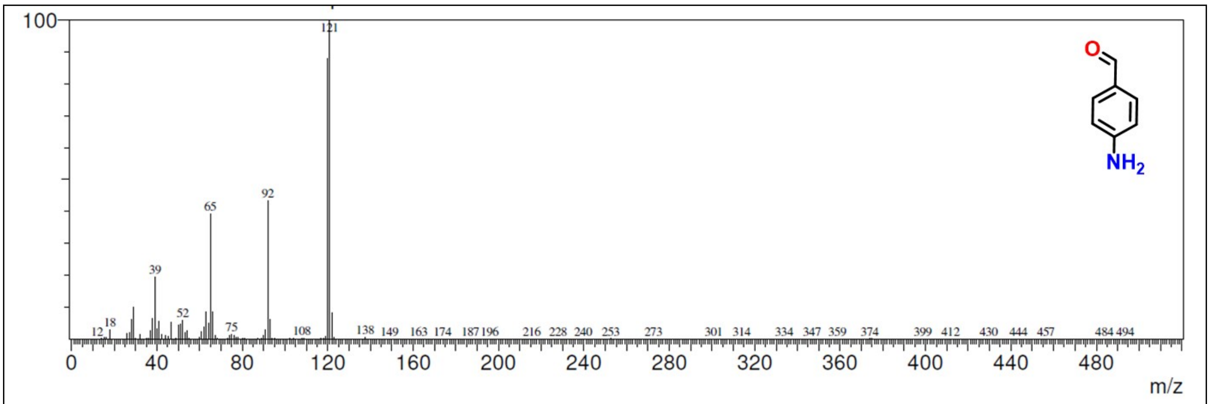

Figure S4.1. Mass spectrum of 4-aminobenzaldehyde

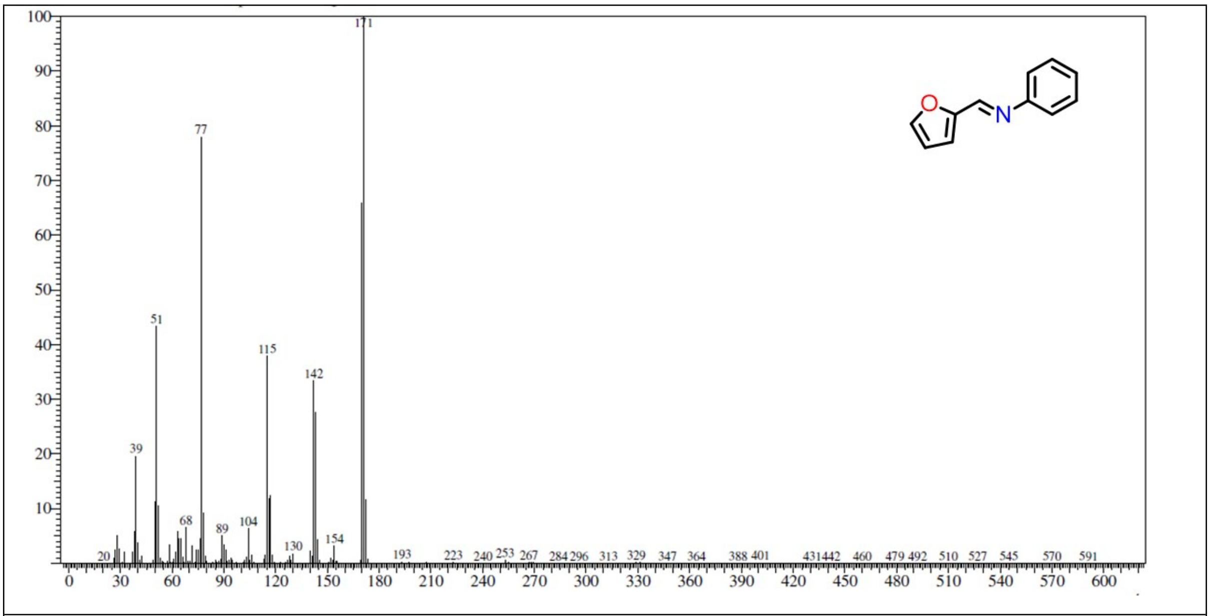

Figure S4.2. Mass spectrum of 1-(furan-2-yl)-*N*-phenylmethanimine

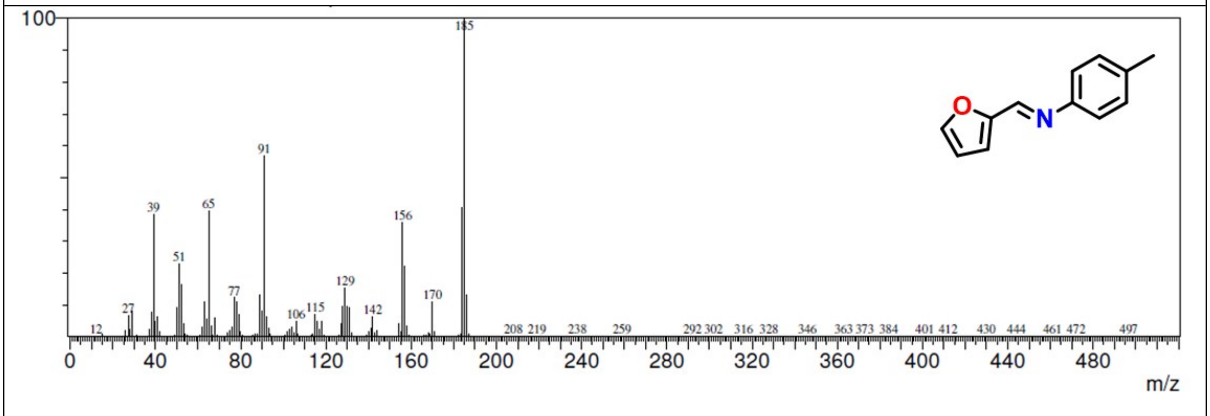

Figure S4.3. Mass spectrum of 1-(furan-2-yl)-*N*-(*p*-toly)methanimine

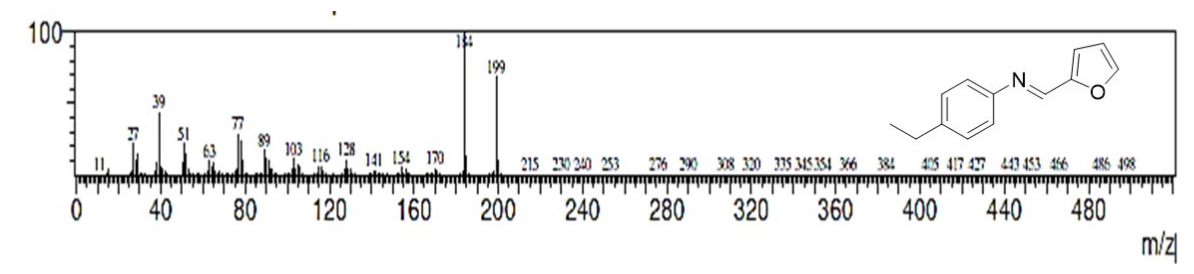

Figure S4.4. Mass spectrum of N-(4-ethylphenyl)-1-(furan-2-yl)methanimine

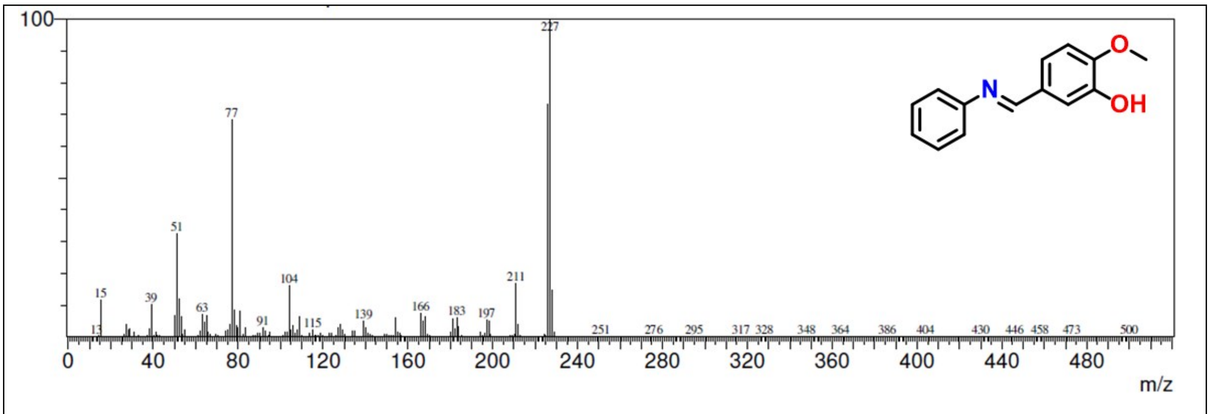

Figure S4.5. Mass spectrum of 2-methoxy-5-((phenylimino)methylphenol

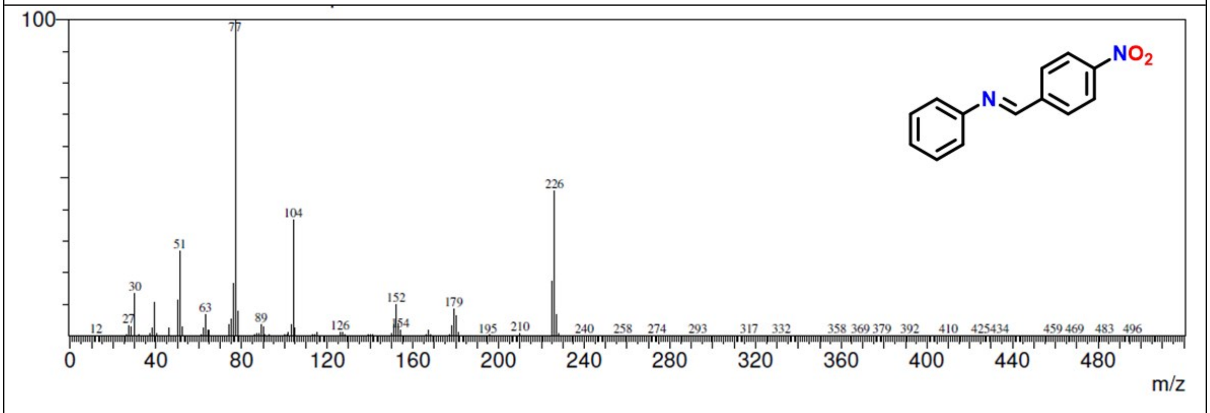

Figure S4.6. Mass spectrum of 1-(4-nitrophenyl)-*N*-pnenylmethanimine

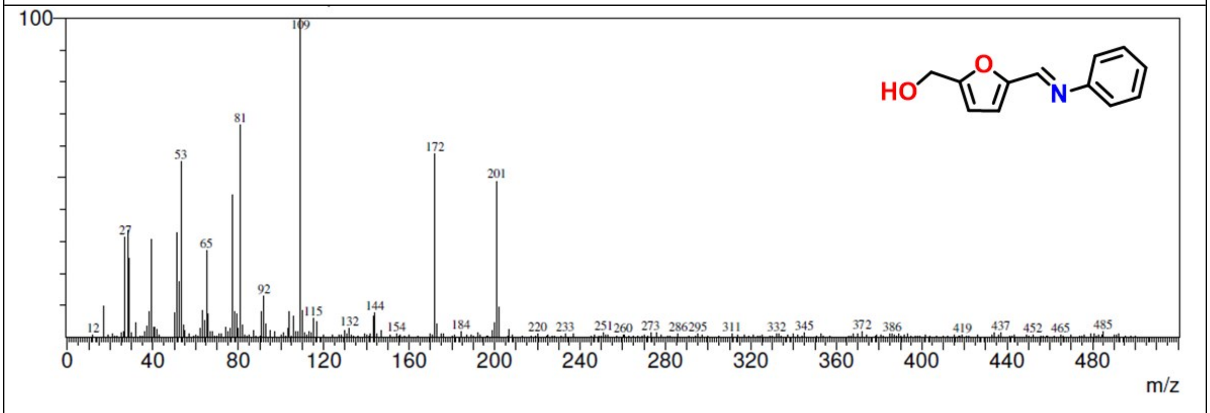

Figure S4.7. Mass spectrum of 5-(benzylideneamino)furan-2-yl)methanol

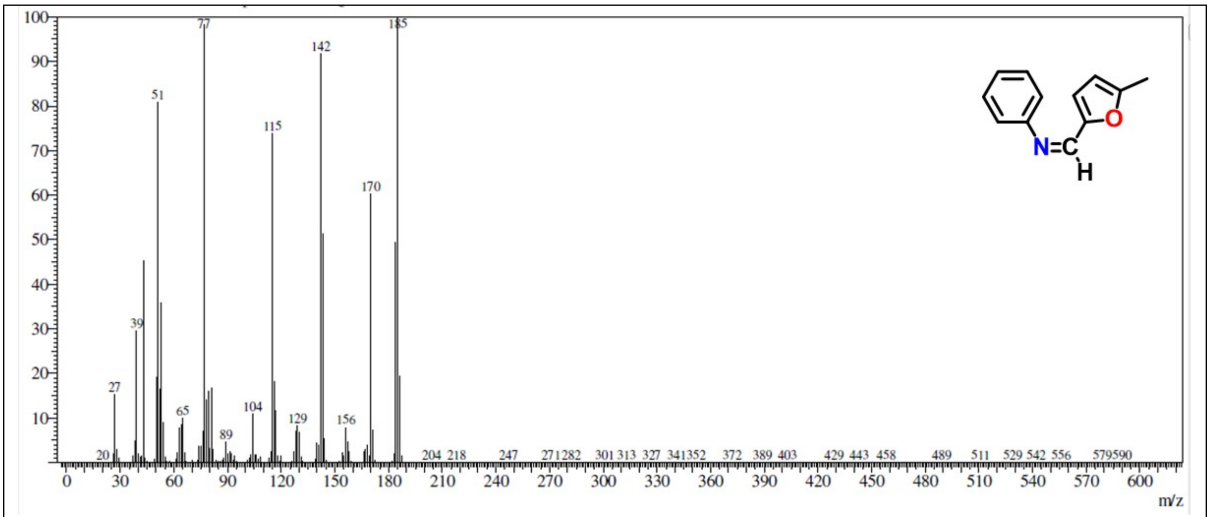

Figure S4.8. Mass spectrum of *N*-(5-methylfuran-2-yl)-1-phenylmethanimine

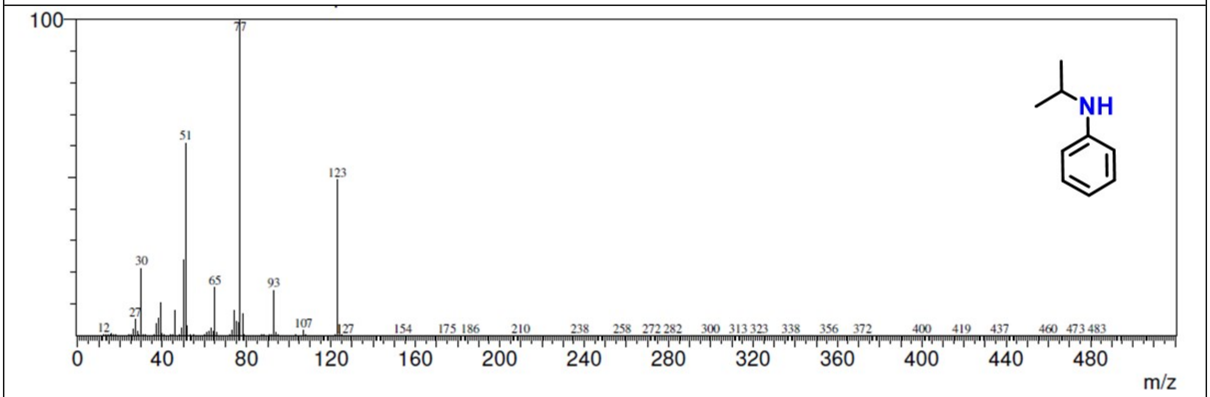

Figure S4.9. Mass spectrum of *N*-Isopropylaniline

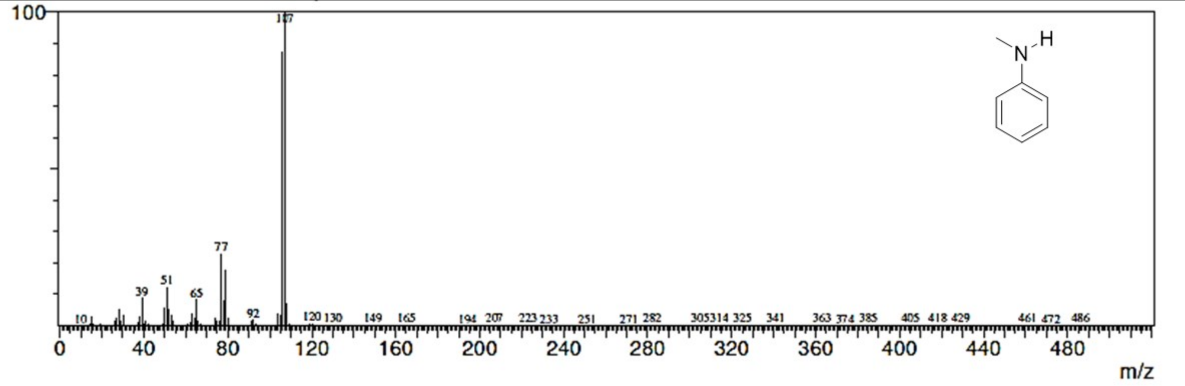

Figure S4.10. Mass spectrum of *N*-methylaniline

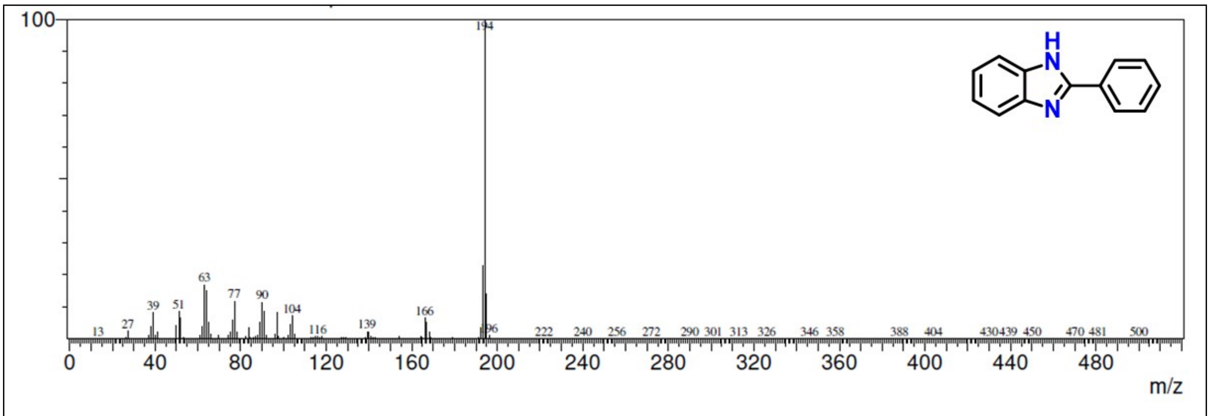

Figure S4.11. Mass spectrum of 2-phenyl benzimidazole

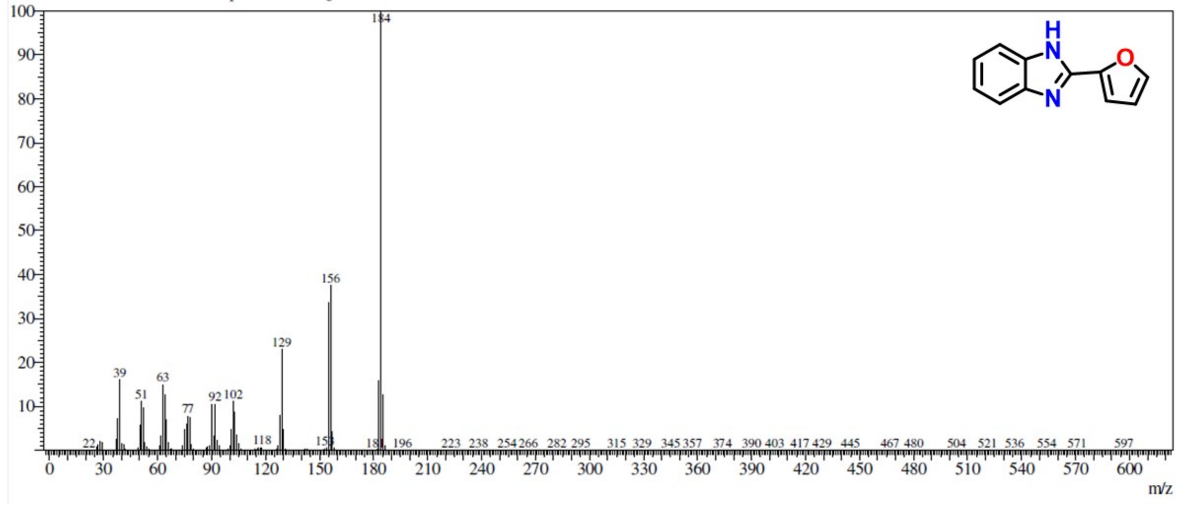

Figure S4.12. Mass spectrum of 2-furan benzimidazole

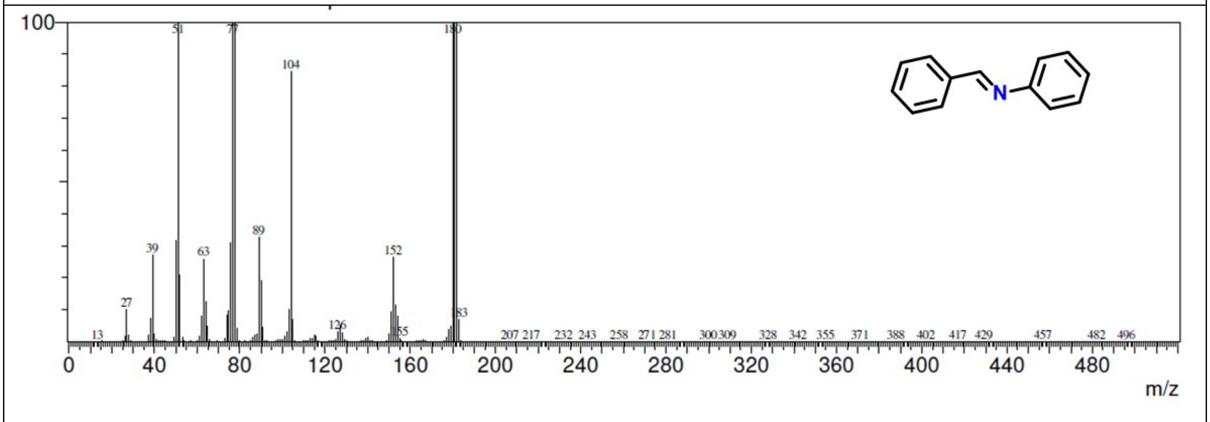

Figure S4.13. Mass spectrum of *N*-1-diphenylmethanimine

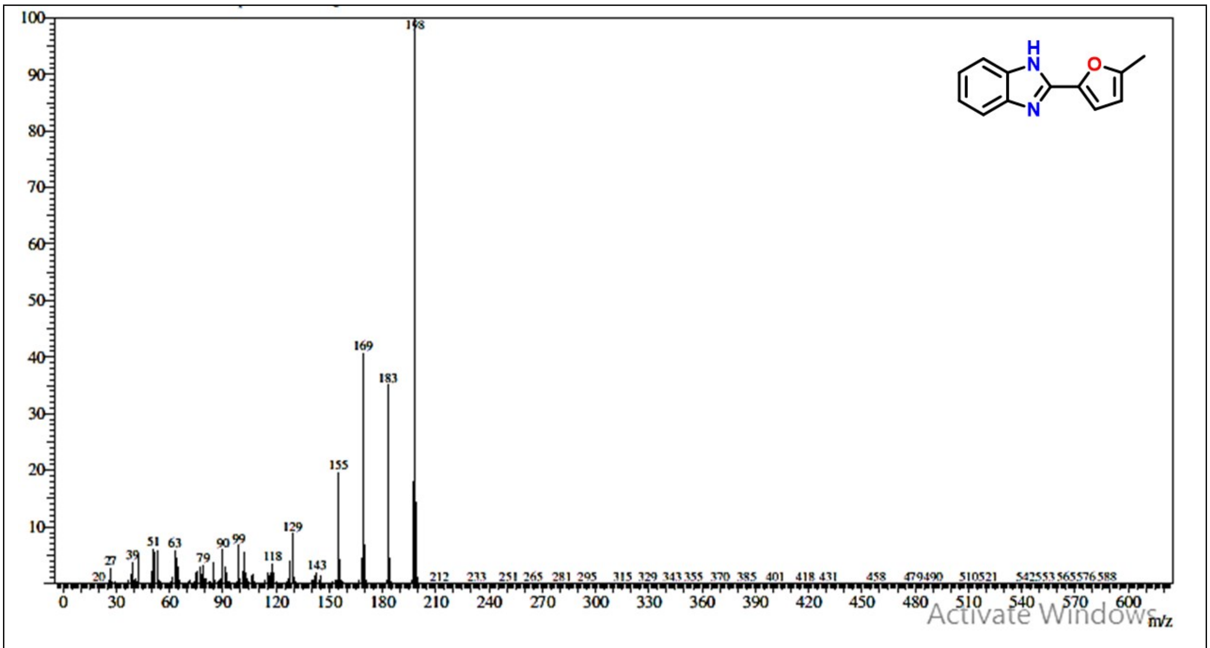

Figure S4.14. Mass spectrum of 2-(5-methylfuran-2-yl)-1H-benzo[d]imidazole

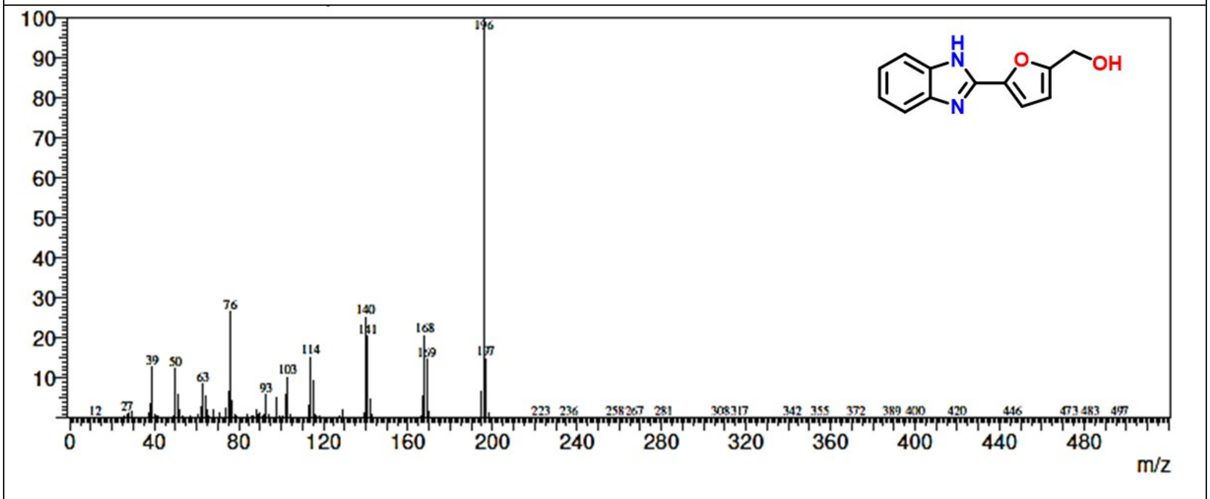

Figure S4.15. Mass spectrum of (5-(1H-benzo[d]imidazol-2-yl)furan-2-yl)methanol

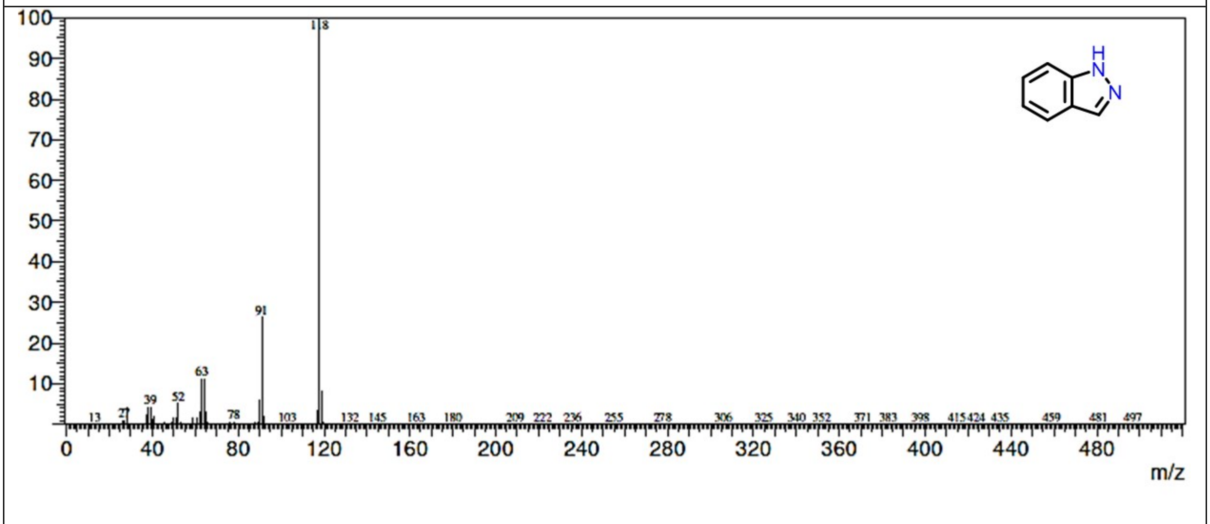

Figure S4.16. Mass spectrum of 1H-indazole

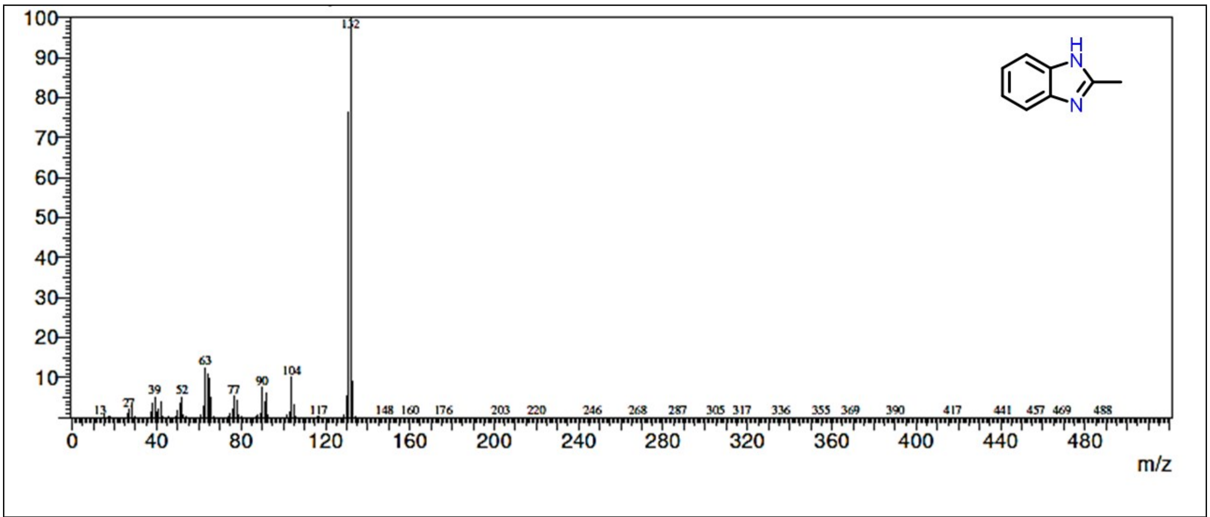

Figure S4.17. Mass spectrum of 2-methyl-1H-benzo[d]imidazole

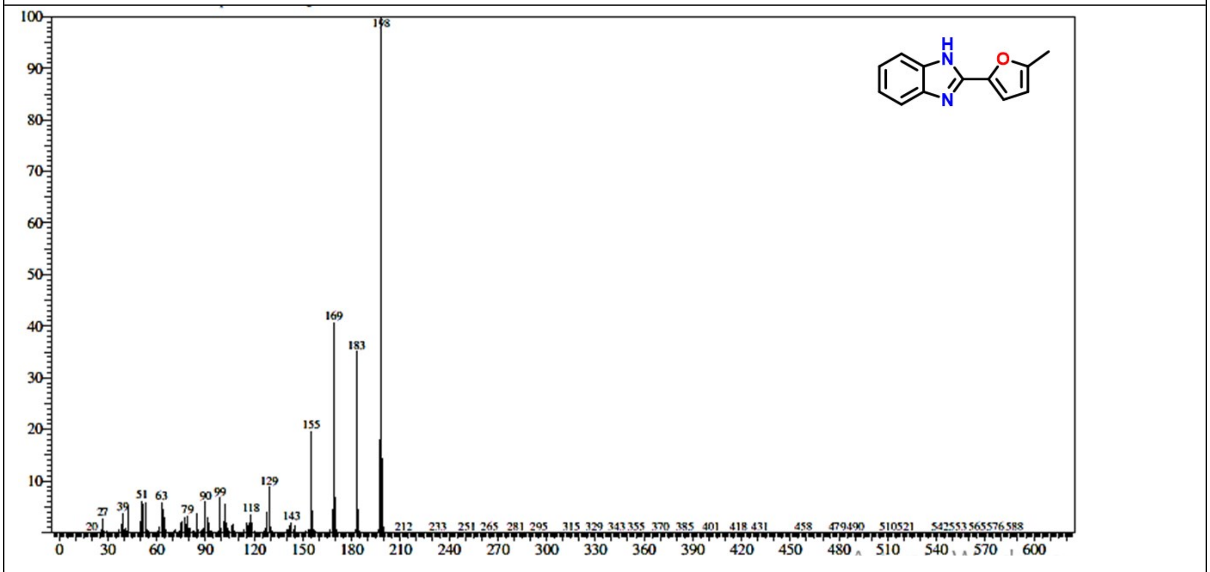

Figure S4.17. Mass spectrum of 2-methyl-1H-benzo[d]imidazole

S7. Recyclability studies of Ni@NC-DC catalyst

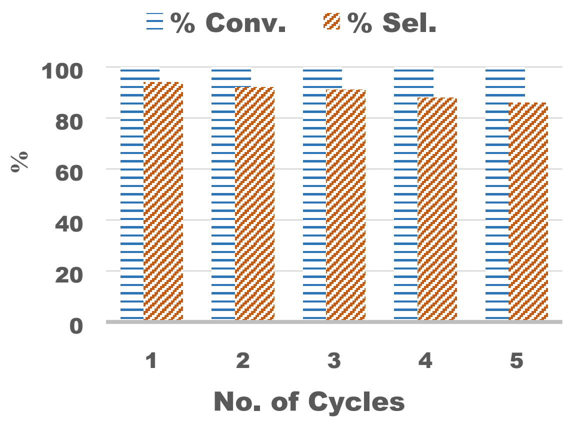

Figure S5. Recyclability studies of Ni@NC-DC catalyst.

S8. SEM analysis of catalyst before and after reaction

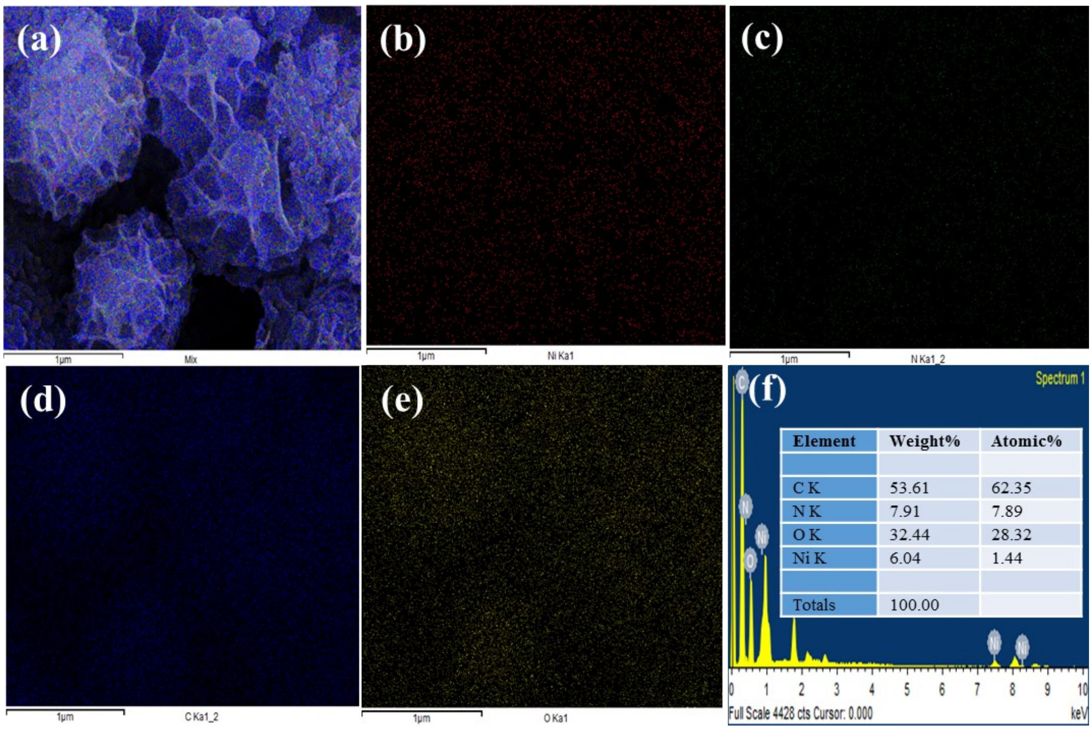

Figure S6. SEM elemental mapping of Fresh catalyst; Distribution of (a) Ni, N, C and O; (b) Nickel; (c) Nitrogen; (d) Carbon; (e) Oxygen and (f) SEM-EDAX.

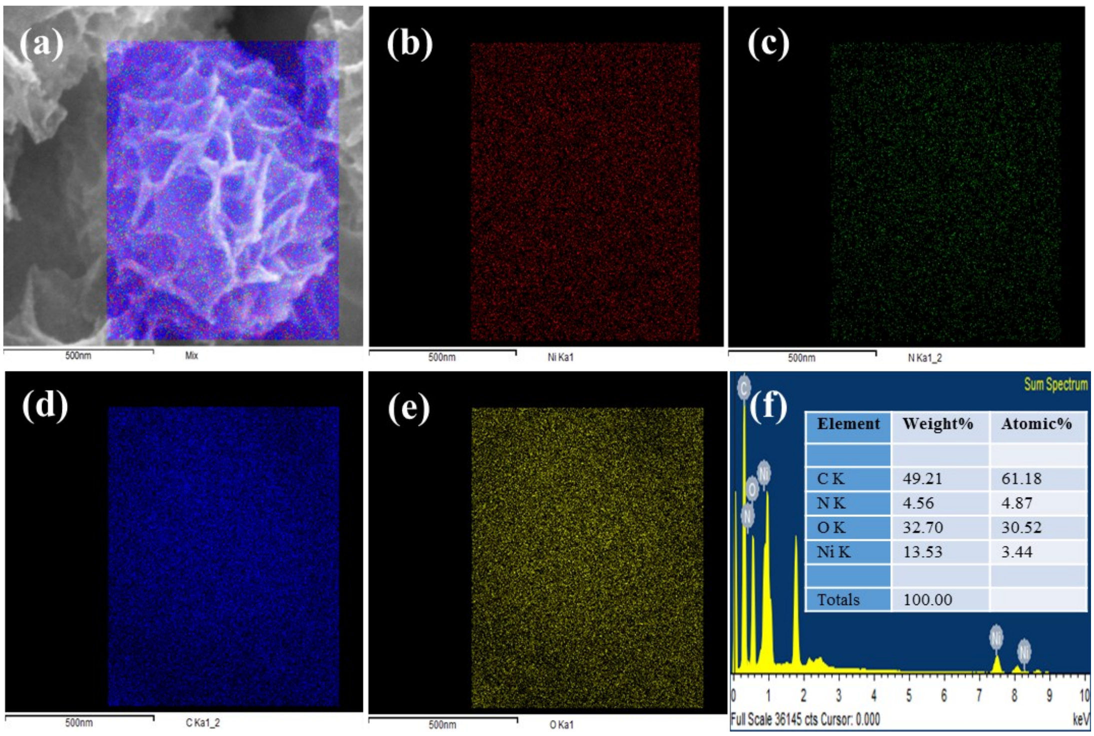

Figure S7. SEM elemental mapping of the catalyst after 5th cycle; Distribution of (a) Ni, N, C and O; (b) Nickel; (c) Nitrogen; (d) Carbon; (e) Oxygen and (f) SEM-EDAX.

S9. Comparison table for reductive amination using heterogeneous catalyst

Table S1. Comparison of different catalysts for reductive hydrogenation between nitrobenzene and benzaldehyde**.**

Catalyst	Solvent	Hydrogen source	Temp. (°C)	Press. (Mpa)	Time (h)	Conv. (%)	Selec. (%)		Ref.
							2° Amine	Imine	
Colloid Pd NPs	MeOH	H_2	25	NS	6	NS	88	NS	1
Mo_3S_4	THF [a]	H_2	70	2	18	>99	99	0	2
Mo_3S_4	THF[b]	H_2	70	2	18	50	0	30	3
Fe+PdC	H_2O	$H_2O:CO_2$	80	-	10	86	33	50	4
Fe+$FeCl_2$	H_2O	$H_2O:CO_2$	80	-	10	94	NS	93	4
Pd/Fe_3O_4@C	H_2O	H_2	60	NS	8	99	92	NS	5
Au@TiO_2	H_2O	HCOOH	80	-	3	>99	97	1	6
MoS_2	EtOH	H_2	120	2	5	100	85.2	0.7	7
MoS_2	H_2O	H_2	120	2	5	62.1	2.3	74.9	7
Pd@ZSM-5	H_2O	$NaBH_4$	25	-	20 min	100	98	NS	8
AgPd@C_3N_4	H_2O	HCOOH	20	-	20	>99	>99	NS	9
Co_2Rh_2/C	MeOH	H_2	25	0.1	24	100	93	-	10
Co-Nx/C-800-AT	EtAc	HCOOH	150	-	10	100	96	NS	11
Co@CN-600-AT	THF	HCOOH	190	-	15	100	96.1	NS	12
Co@CN-600-AT	THF	HCOOH	110	-	10	64.5	9.4	83.9	12
Co@NSC	THF:H_2O	HCOOH	170	-	6	100	94.9	NS	13
Co-SiCN[C]	EtOH:H_2O	H_2	110	5	24	NS	NS	82	14
CoOx@NC-800	THF: H_2O	H_2	110	5	24	NS	NS	88	15
Ni@NC-700-1.5	THF: H_2O	H_2		2	4	>99	46.26	34.4	16
Ni@NC-600-1.5	THF: H_2O	H_2		2	4	>99	97.96	2.04	16
Ni@NC-DC	THF:H_2O	H_2	100	20	4	100	95	95	**This work**

[a]water in ppm [b]Molecular Sieves [C] Triethylamine as additive. NS: Not specified

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