

*Electronic supplementary information (ESI) for*

## **One-pot Reductive Amination of Carbonyl Compounds with Nitro Compounds over Ni/NiO composites**

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## 1. Materials

The following materials were used as received: NiO (Aldrich, 99.8% metal basis, <50 nm particle size), Raney alloy (Wako, ca. 50% as Ni), nitrobenzene (Kanto), toluene (Kanto), dichloromethane (Kanto), tetrahydrofuran (Kanto), methanol (Kanto), *N,N*-dimethylformamide (Kanto), acetonitrile (TCI), chloroform-*d* (Isotech), monochlorobenzene (Kanto), 4-nitroanisole (Kanto), *o*-methylnitrobenzene (TCI), methyl 4-nitrobenzoate (TCI), 5-chloronitrobenzene (TCI), *o*-tolaldehyde (TCI), *p*-anisaldehyde (TCI), and ethyl 4-formylbenzoate (Wako). Benzaldehyde (Wako) was distilled before use. TiO<sub>2</sub> (ST-01) and Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O were supplied from Ishihara Sangyo Kaisha, and Companhia Brasileira de Metalurgia e Mineração, respectively. SiO<sub>2</sub> (Q10) was provided by Fuji Silysia Chemical. ZrO<sub>2</sub> (JRC-ZRO-9) was obtained from the Catalysis Society of Japan as reference catalysts. Metal oxide supports were calcined at 500 °C for 2 h under air before preparation of the supported Ni catalysts.

## 2. Characterization

Brunauer–Emmett–Teller (BET) specific surface areas of the samples were measured by nitrogen adsorption–desorption at –196 °C (Quantachrome Nova-4200e). Prior to the adsorption measurements, the samples were degassed in situ under vacuum at 150 °C for 1 h. The BET surface area was determined using the multipoint BET algorithm in the  $P/P_0$  range from 0.05 to 0.3. X-ray diffraction (XRD; Ultima IV, Rigaku) patterns of all samples were obtained using Cu K $\alpha$  radiation (40 kV, 40 mA) in the  $2\theta$  range of 15–85°. X-ray photoelectron spectroscopy (XPS; ESCA-3200 Shimadzu) measurements were performed using Mg K $\alpha$  radiation (1486.6 eV). Samples were pressed into pellets and fixed on double-sided carbon tape. The binding energies were calibrated using sputtered C (1s peak at 284.6 eV). <sup>1</sup>H NMR (400 MHz), and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All <sup>1</sup>H NMR chemical shifts were recorded in ppm ( $\delta$ ) relative to tetramethylsilane or referenced to the chemical shifts of residual solvent resonances (CHCl<sub>3</sub> was used as internal standard,  $\delta$  7.26). All <sup>13</sup>C NMR chemical shifts were recorded in ppm ( $\delta$ ) relative to carbon resonances in CDCl<sub>3</sub> at  $\delta$  77.16. Scanning electron microscope (SEM) measurements were conducted using a multi-purpose transmission electron microscope (JEM-2100 plus) at an acceleration voltage of 200 kV with SEM detector (the samples were dispersed on a carbon sheet with ethanol, and dried). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were performed with a Shimadzu ICPS-8100 spectrometer. Flash column chromatography was conducted using an automated flash chromatography system (Smart Flash EPCLC AI-580s, Yamazen).

### 3. Preparation of Ni/NiO composite

The NiO was treated in 5% H<sub>2</sub>/Ar (flow rate = 30 mL/min) at designated temperature (200–500 °C) for 2 h to give Ni/NiO-X (X = reduction temperature).

### 4. Preparation of Supported Ni Catalysts

The 5 wt% Ni/support catalysts were prepared by wet impregnation method.<sup>S1</sup> Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (0.25 g, 0.86 mmol) was dissolved in water (20 mL). The support (1 g) was added into the aqueous Ni(NO<sub>3</sub>)<sub>2</sub> solution, and the mixture was evaporated at 60 °C until dryness. The obtained solid was further dried at 90 °C overnight. The dried sample was calcined at 300 °C for 1 h under air and reduced with 5% H<sub>2</sub>/Ar (30 mL/min) at 500 °C for 30 min.

### 5. Catalytic one-pot reductive amination

The catalytic reaction was conducted in an 18 mL stainless-steel autoclave equipped with a magnetic stirrer. 50 mg of catalyst was loaded into the reactor with 1.2 mmol of aldehyde, 1 mmol of nitro compound and 1 mL of toluene. The autoclave was purged with H<sub>2</sub> several times to remove air and then pressurized with H<sub>2</sub> at 1 MPa. After heating at 80 °C for 20 h, the catalyst was filtered off. The filtrate was analysed by GC and GC-MS using chlorobenzene as an internal standard.

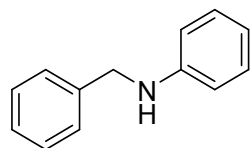
For substrate scope, the filtrate was evaporated to dryness after heating at 80 °C for 20 h. And the resulting crude mixture was purified by flash column chromatography.

### 6. Reuse experiments

The catalytic reaction was conducted according to the general procedure. For reuse experiments, the catalyst was recovered by filtration, washed with MeOH (25 mL), dried at 90 °C for 5 h. Reduction treatment: The recovered catalyst was reduced under H<sub>2</sub> flow (20 mL/min) at 150 °C for 1 h. XRD patterns of the recovered catalyst was not changed (Fig. S2).

### 7. Spectral Data

*N*-Benzylaniline (**3aa**)<sup>S2</sup>

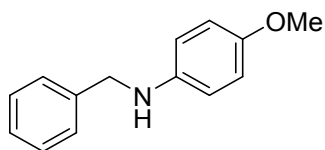


After the reaction was completed, the catalyst was separated by filtration. The crude product was purified by flash column chromatography (hexane : EtOAc = 9 : 1→7 : 3) to give the pure title compound (98%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38–7.32 (m, 4H), 7.29–7.24 (m, 1H), 7.17 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.71 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.33 (s, 2H), 4.02 (br s, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.5, 140.0, 129.6, 128.9, 127.8, 127.5, 117.8, 113.2, 48.5.

*N*-Benzyl-4-methoxyaniline (**3ba**)<sup>S3</sup>

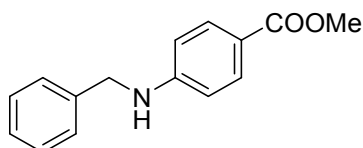


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2→5 : 5) to give the pure title compound (93 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.37–7.24 (m, 5H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.27 (s, 2H), 3.73 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.3, 142.5, 139.7, 128.6, 127.6, 127.2, 115.0, 114.1, 55.8, 49.3.

Methyl 4-(benzylamino)benzoate (**3ca**)<sup>S4</sup>

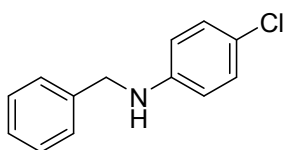


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2→6 : 4) to give the pure title compound (74 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83 (d, *J* = 8.8 Hz, 2H), 7.34–7.23 (m, 5H), 6.55 (d, *J* = 8.8 Hz, 2H), 4.61 (br s, 1H), 4.33 (s, 2H), 3.80 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 167.4, 151.9, 138.5, 131.6, 128.8, 127.5, 127.4, 118.6, 111.7, 51.5, 47.6.

*N*-benzyl-4-chloroaniline (**3da**)<sup>S3</sup>

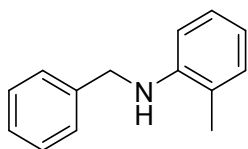


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2→6 : 4) to give the pure title compound (88 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35–7.25 (m, 5H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.9, 139.2, 129.3, 128.9, 127.6, 127.6, 122.1, 114.2, 48.4.

*N*-Benzyl-2-methylaniline (**3ea**)<sup>S5</sup>

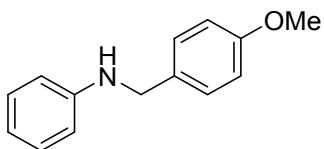


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2→5 : 5) to give the pure title compound (82 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.38–7.32 (m, 4H), 7.29–7.25 (m, 1H), 7.11–7.06 (m, 2H), 6.67 (dd,  $J$  = 7.2, 7.2 Hz, 1H), 6.61 (d,  $J$  = 7.6 Hz, 1H), 4.36 (s, 1H), 3.84 (br s, 1H), 2.15 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 146.2, 139.7, 130.2, 128.8, 127.7, 127.4, 127.3, 122.0, 117.3, 110.4, 48.5, 17.6.

#### *N*-(4-methoxybenzyl)aniline (**3ab**)<sup>S5</sup>

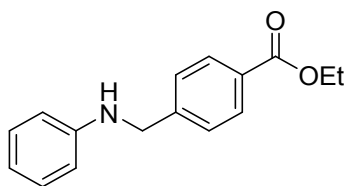


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2→6 : 4) to give the pure title compound (67 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.30 (d,  $J$  = 8.8 Hz, 2H), 7.17 (dd,  $J$  = 7.6, 8.4 Hz, 2H), 6.88 (d,  $J$  = 8.8 Hz, 2H), 6.71 (dd,  $J$  = 7.6, 7.2 Hz, 1H), 6.63 (d,  $J$  = 8.8 Hz, 2H), 4.25 (s, 2H), 3.93 (br s, 1H), 3.80 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.0, 148.4, 131.6, 129.4, 129.0, 117.6, 114.2, 113.0, 55.4, 47.9.

#### Ethyl 4-((phenylamino)methyl)benzoate (**3ac**)<sup>S6</sup>

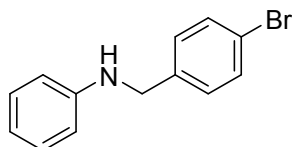


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2→6 : 4) to give the pure title compound (94 %).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01 (d,  $J$  = 8.0 Hz, 2H), 7.43 (d,  $J$  = 8.0 Hz, 2H), 7.16 (dd,  $J$  = 7.6, 8.4 Hz, 2H), 6.72 (dd,  $J$  = 7.2, 7.6 Hz, 1H), 6.61 (d,  $J$  = 8.0 Hz, 2H), 4.40–4.34 (m, 4H), 1.39 (t,  $J$  = 4.2 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.6, 148.1, 145.3, 130.0, 129.4, 127.2, 117.8, 113.0, 61.1, 47.9, 14.5.

*N*-(4-bromobenzyl)aniline (**3ad**)<sup>S7</sup>

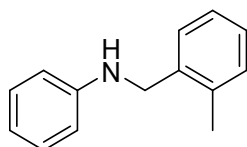


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 10 : 1 → 5 : 1) to give the pure title compound (95 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.16 (dd, *J* = 7.9, 7.3 Hz, 2H), 6.72 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 2H), 4.34 (s, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 147.9, 138.6, 131.8, 129.4, 129.1, 121.0, 117.9, 113.0, 47.7.

*N*-(2-methylbenzyl)aniline (**3ae**)<sup>S8</sup>

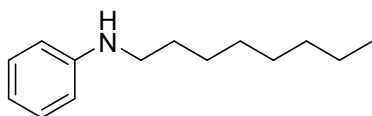


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The crude product was purified by flash column chromatography (hexane : EtOAc = 8 : 2 → 5 : 5) to give the pure title compound (74 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.34–7.32 (m, 1H), 7.20–7.15 (m, 5H), 6.72 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.27 (s, 2H), 3.84 (br s, 1H), 2.37 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.6, 137.3, 136.5, 130.7, 129.5, 128.5, 127.6, 126.4, 117.7, 112.9, 46.6, 19.2.

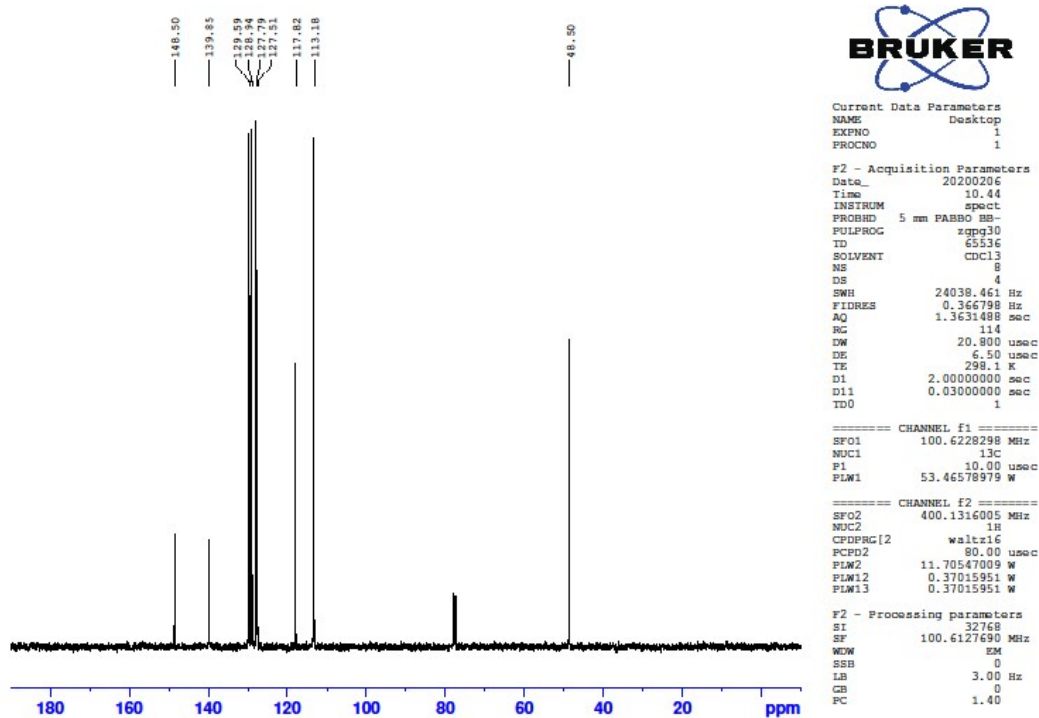
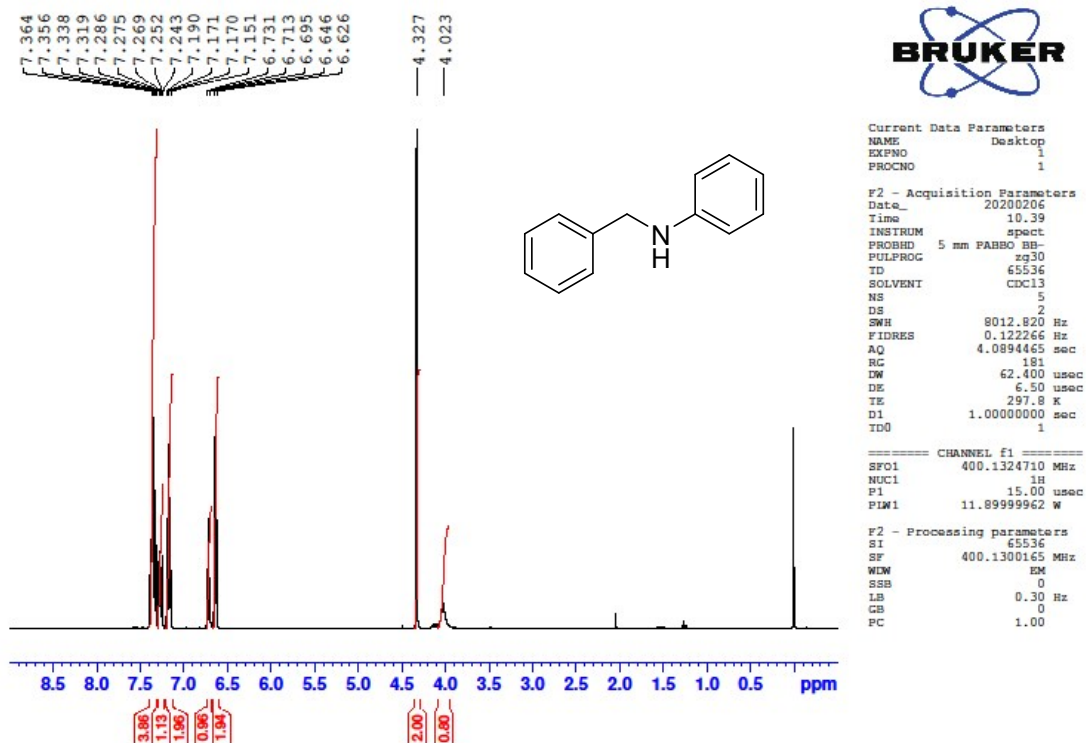
*N*-octylaniline (**3af**)<sup>S9</sup>

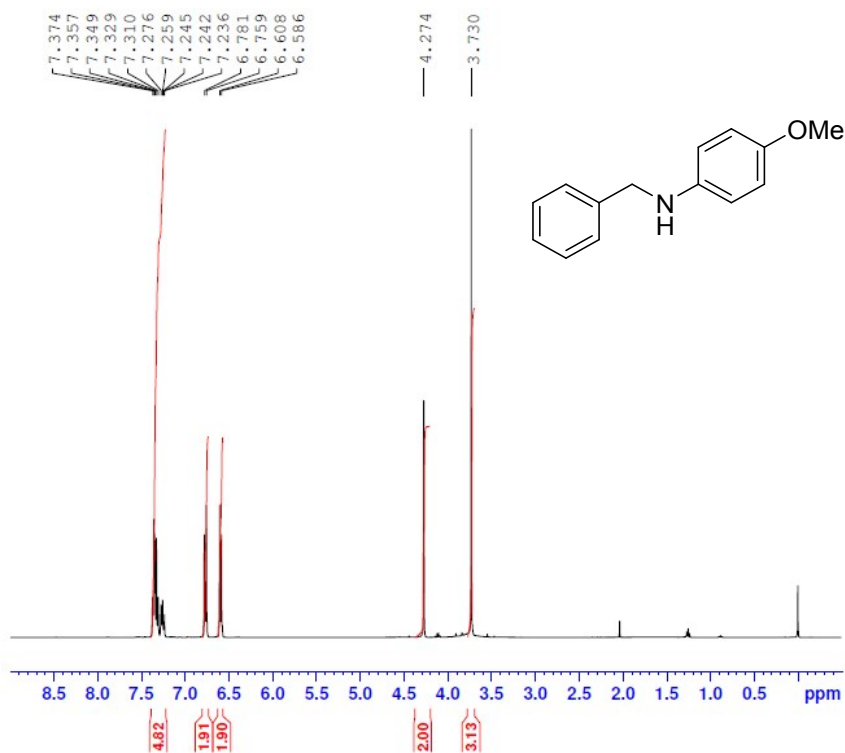


After the reaction was completed, catalyst was separated by filtration and the obtained solution was evaporated and dried *in vacuo*. The yield of was determined based on the phenanthrene as an internal standard.

*m/z* (rel. int.) 205(14), 107(8), 106(100), 77(8).

## 8. NMR spectra



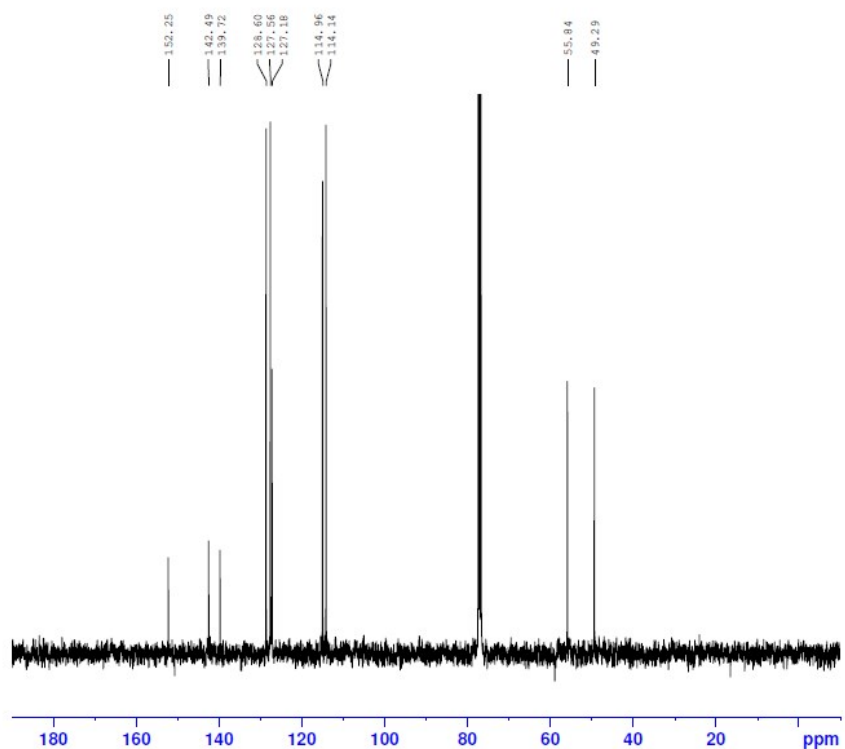


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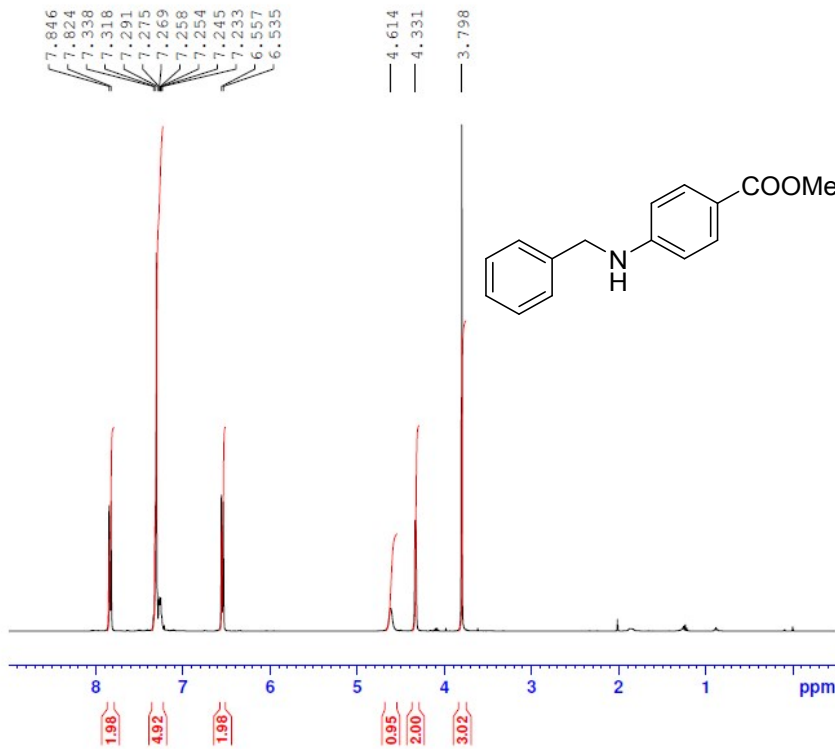
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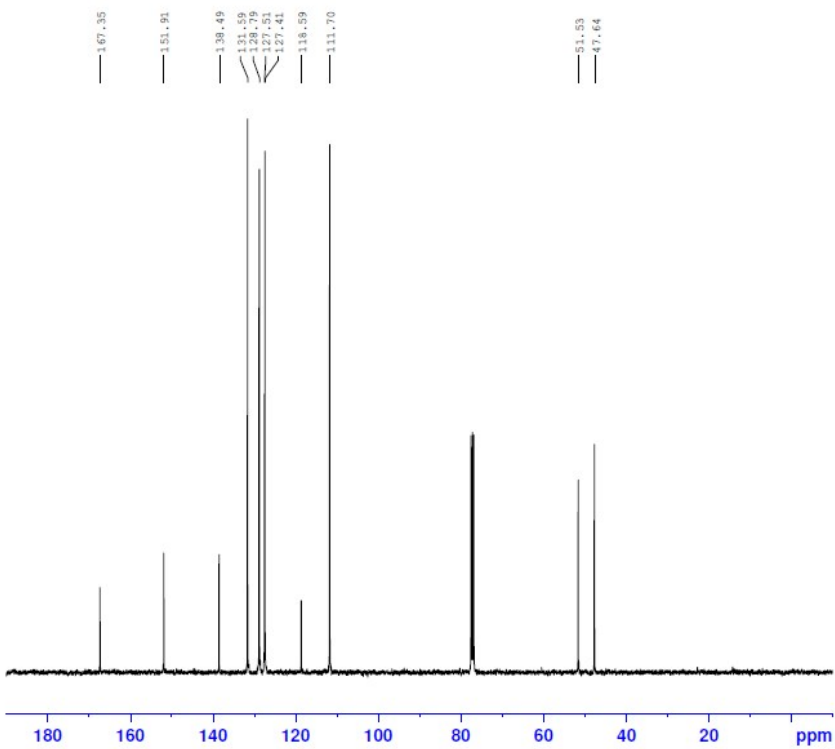
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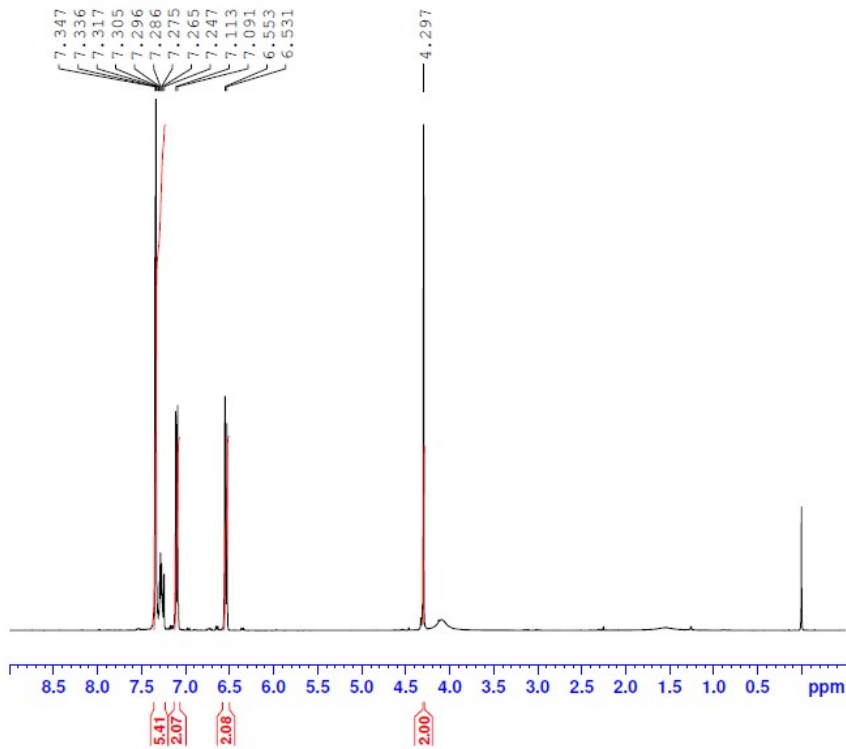
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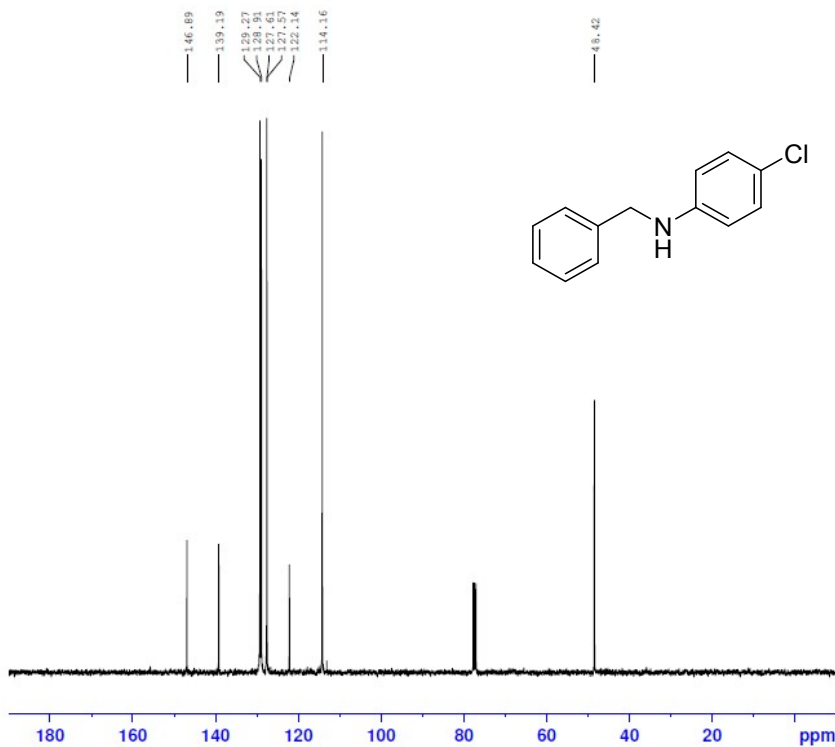


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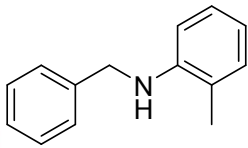
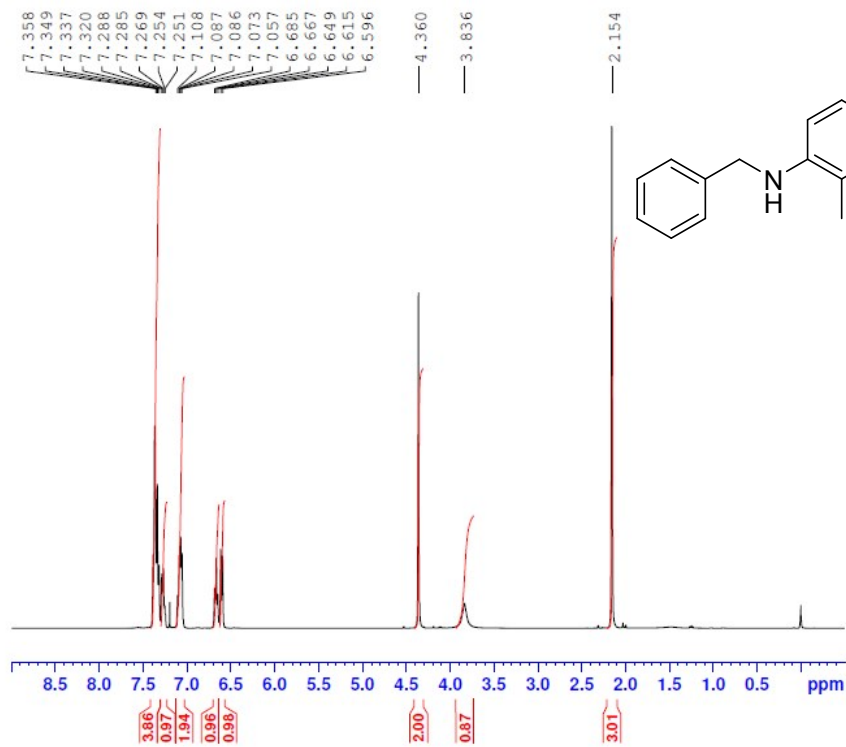
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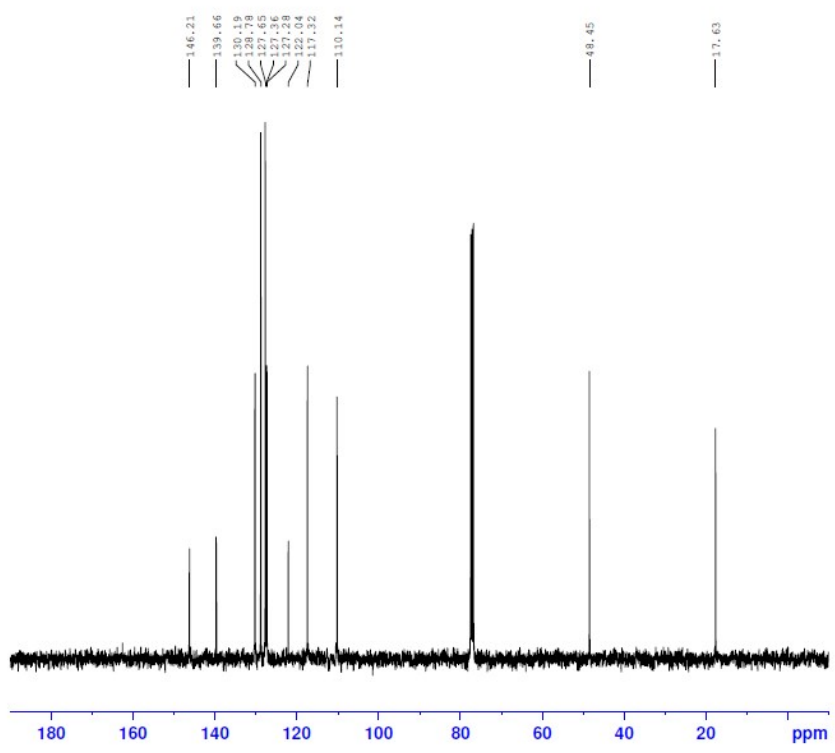
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**BRUKER**

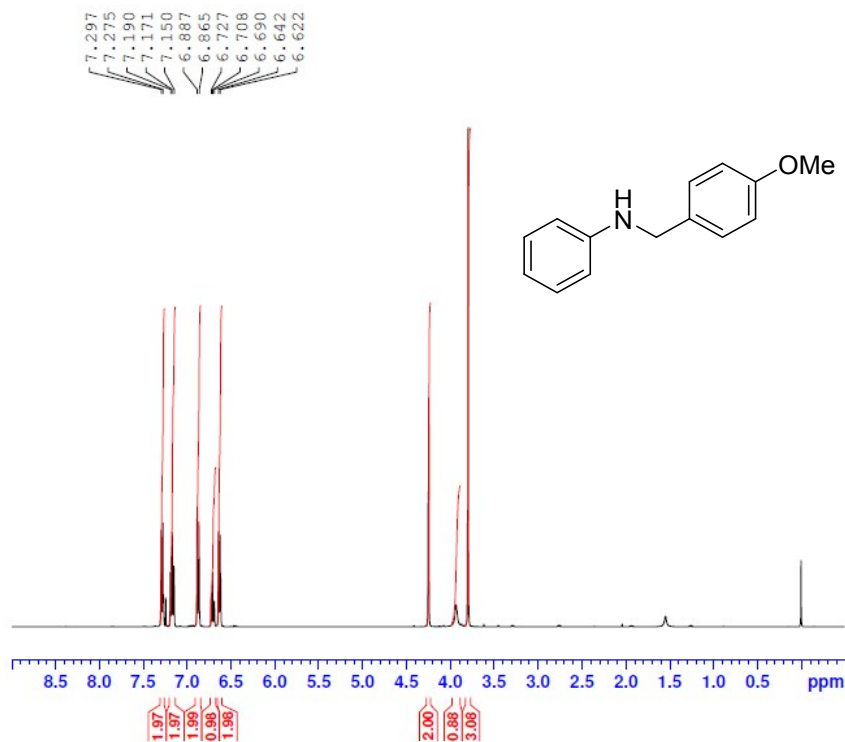
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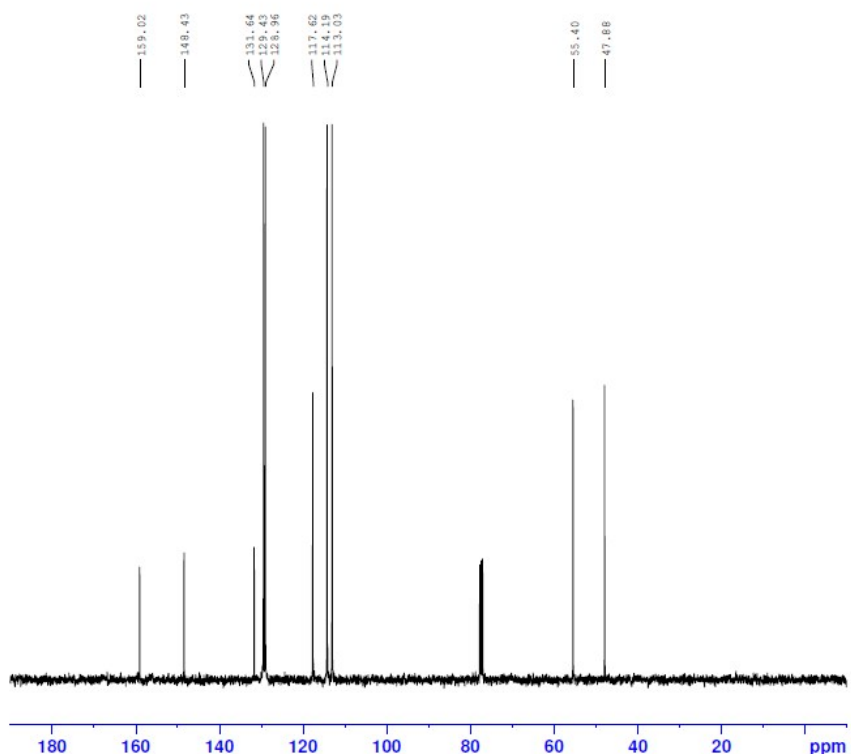


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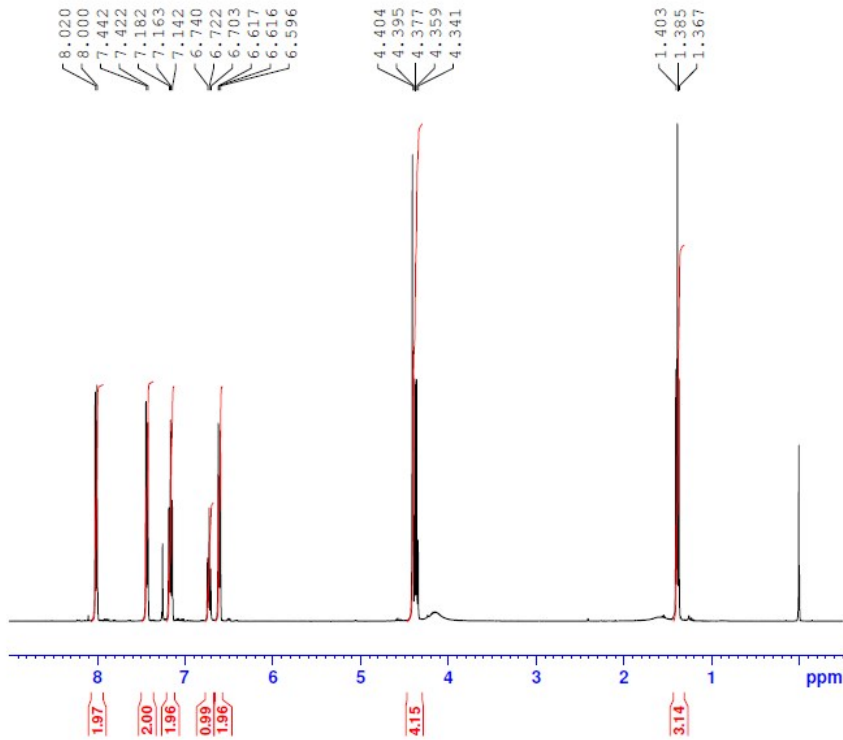
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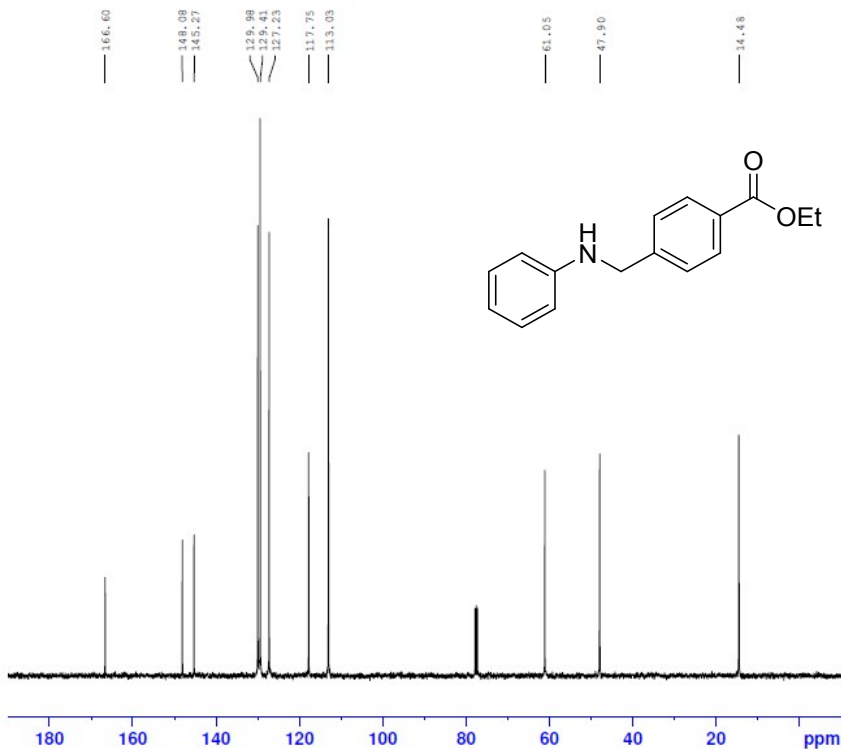


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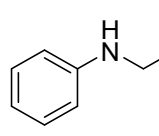
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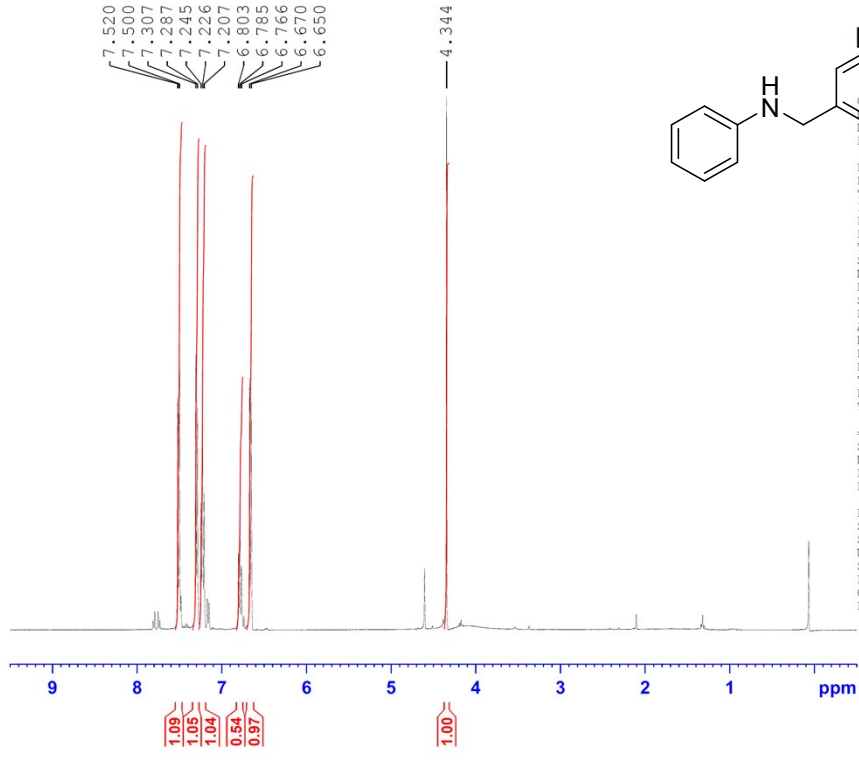


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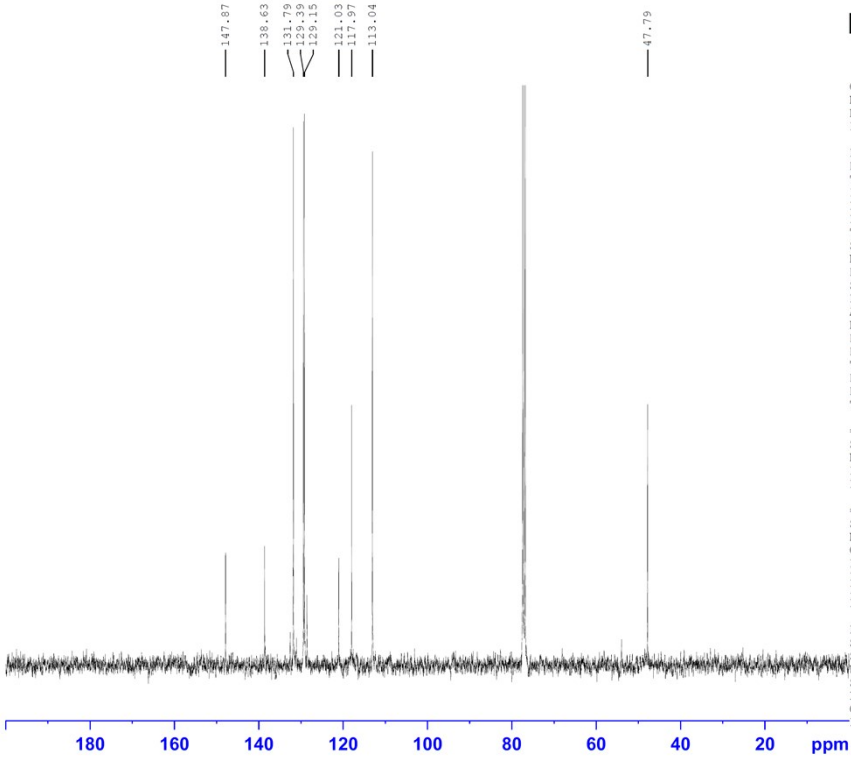
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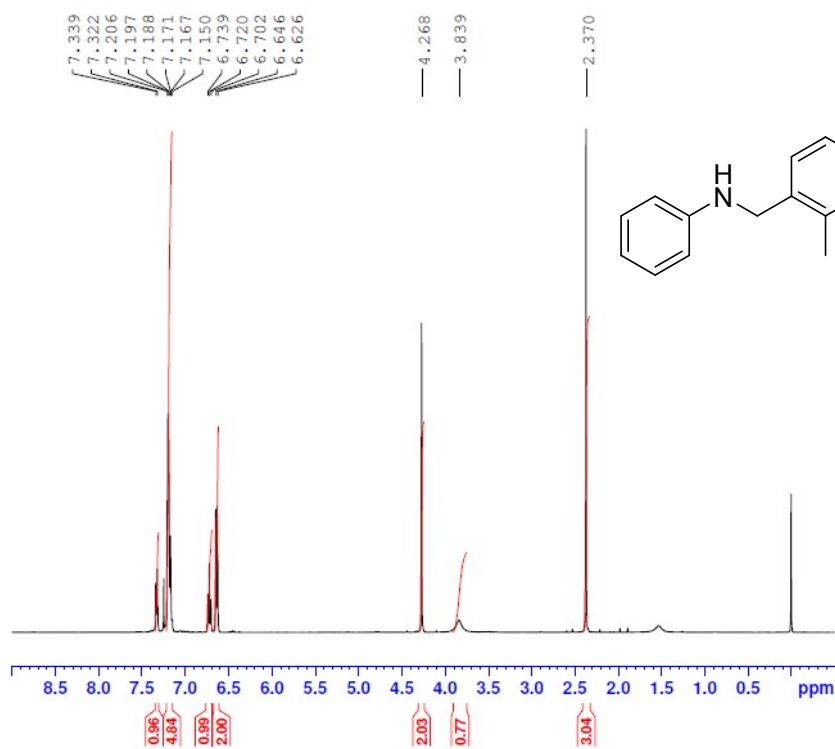
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PCPD2 80.00 usec  
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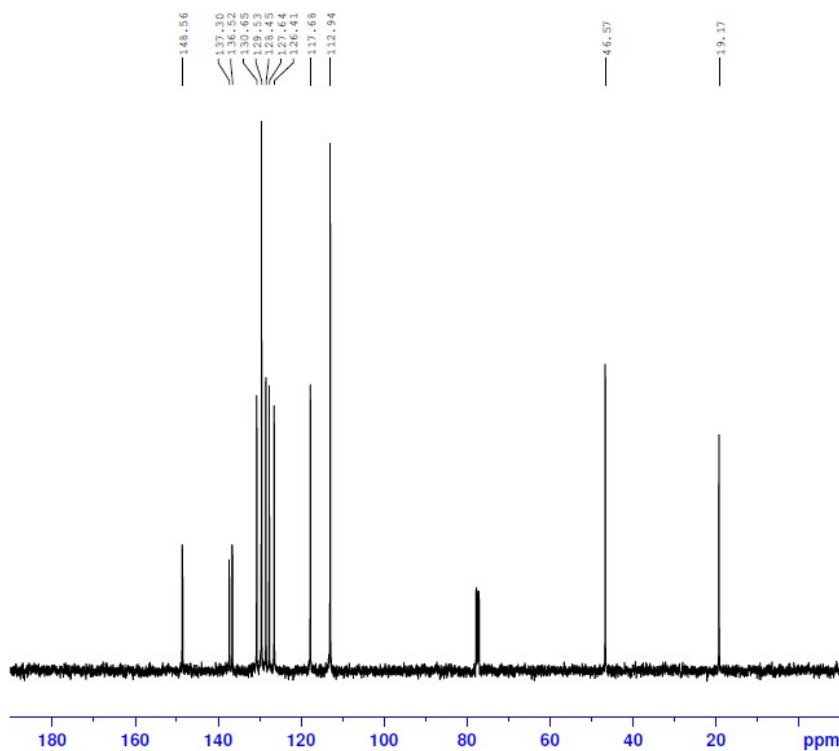


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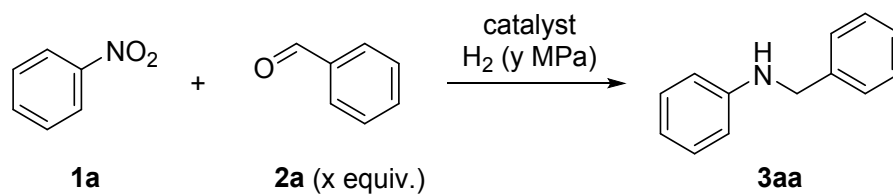
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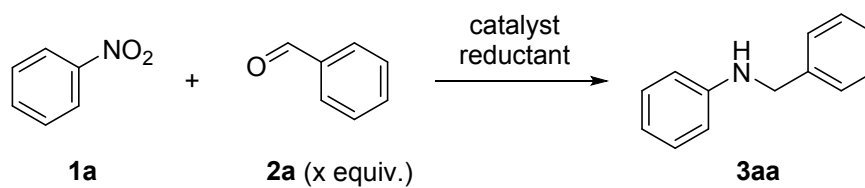


**Table S1** Reported Non-Precious Metal-Based Catalysts for One-pot Reductive Amination of Benzaldehyde with Nitrobenzene using H<sub>2</sub> as reductant.



entry	catalyst	x (equiv.)	y (MPa)	temp. (°C)	yield (%)	TON	ref.
1	Ni/NiO-300	1.2	0.5	80	89	4.1	This work
2	Fe <sub>2</sub> O <sub>3</sub> /NGr@C	2	7	170	85	17	S10
3	Cu/Al <sub>2</sub> O <sub>3</sub>	1.5	5	125	67	573	S11
4	Co <sub>2</sub> O <sub>3</sub> /NGr@C	2	5	110	95	47.5	S12
5	Co-DABCO-TPA@C	1.5	4	120	92	26.3	S13
6	Co-N <sub>x</sub> /C	2	1	110	98	5.8	S14
7	Co/mCN	1.5	1	150	99.8	49.2	S15
8	MoS <sub>2</sub>	1.4	2	120	85	13.7	S16
9	Ni@NC	2	2	100	98	44.9	S17

**Table S2** Reported Non-Precious Metal-Based Catalysts for One-pot Reductive Amination of Benzaldehyde with Nitrobenzene using other reductant.

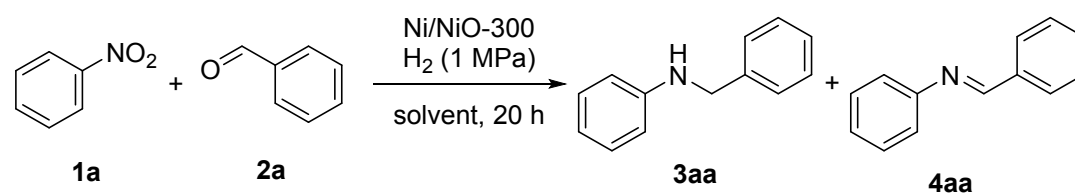


entry	catalyst	reductant	x (equiv.)	temp. (°C)	yield of <b>3aa</b> (%)	ref.
1	Co@CN-600AT	HCOOH	2	190	96	S18
2	Co@CN-800	HCOOH	2	170	89	S19
3	Co-Nx/C-800AT	HCOOH	2	150	96	S20
4	Co/N-C-600	CO/H <sub>2</sub> O	2	170	99	S21

**Table S3** Crystallite Diameter of Ni/NiO

Entry	Catalyst	Crystallite Diameter (nm) <sup>a</sup>	
		Ni	NiO
1	Ni/NiO-200	-	49
2	Ni/NiO-250	-	57
3	Ni/NiO-300	73	59
4	Ni/NiO-350	82	63
5	Ni/NiO-400	95	-
6	Ni/NiO-500	115	-

<sup>a</sup> Crystallite sizes were determined by XRD.

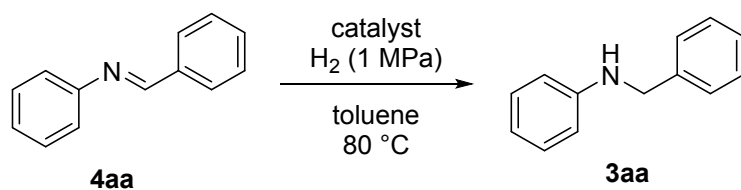
**Table S4** Optimization Study<sup>a</sup>

Entry	Solvent	Temp. (°C)	Conv. of <b>1a</b> (%)	Yield of <b>3aa</b> (%)	Yield of <b>4aa</b> (%)
1	toluene	80	>99	77	5
2	methanol	80	>99	trace	38
3	THF	80	23	–	3
4	DMF	80	>99	–	–
5	CH <sub>2</sub> Cl <sub>2</sub>	80	47	4	13
6	CH <sub>3</sub> CN	80	61	trace	20
7	toluene	100	>99	83	1
8	toluene	70	>99	76	4
9	toluene	60	>99	trace	70
10 <sup>b</sup>	toluene	80	>99	90	trace

<sup>a</sup> Reaction conditions: Ni/NiO-300 (0.05 g), **1a** (0.5 mmol), **2a** (0.5 mmol), solvent (5 mL), H<sub>2</sub> (1 MPa), 80 °C, 20 h. Conversion and yield were determined by GC analysis.

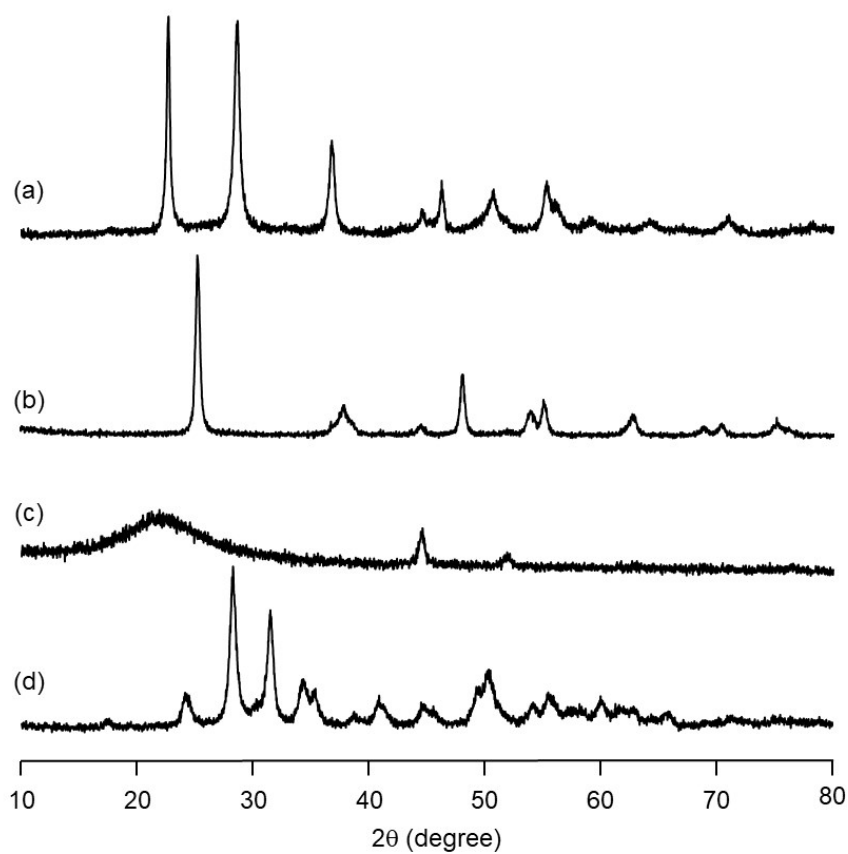
<sup>b</sup> 15 mg of Ni/NiO was used. Run for 40 h.



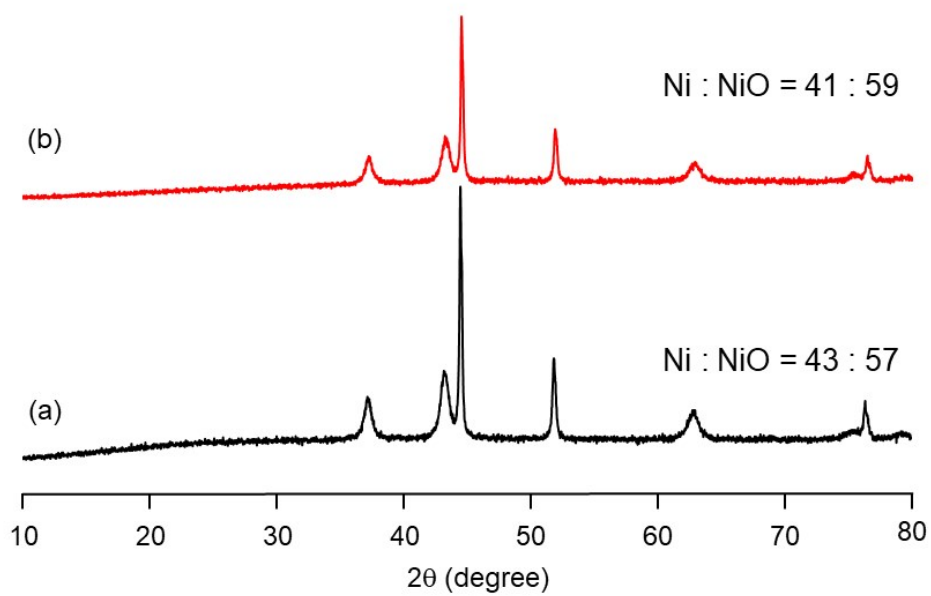


Entry	Catalyst	Time (h)	Conv. of <b>4aa</b> (%)	Yield of <b>3aa</b> (%)
1	Ni/NiO-300	5	92	89
2	Ni/NiO-300	10	99	92
3	Ni/NiO-300	15	>99	96
4	Ni/SiO <sub>2</sub>	5	20	5
5	Ni/SiO <sub>2</sub>	10	48	35
6	Ni/SiO <sub>2</sub>	15	83	70

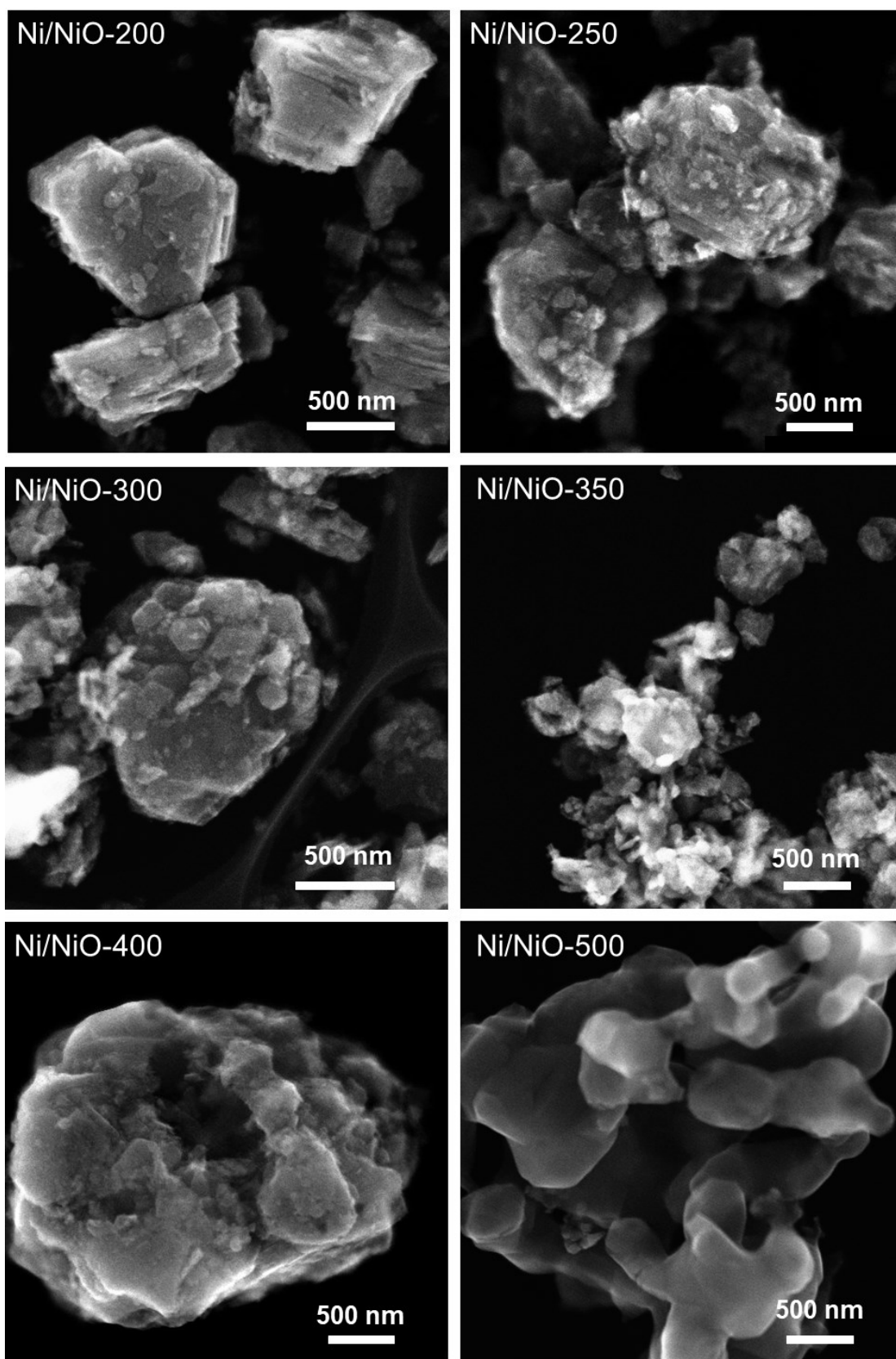
<sup>a</sup> Reaction conditions: catalyst (0.05 g), **4aa** (1 mmol), toluene (1 mL), H<sub>2</sub> (1 MPa), 80 °C. Conversion and yield were determined by GC analysis



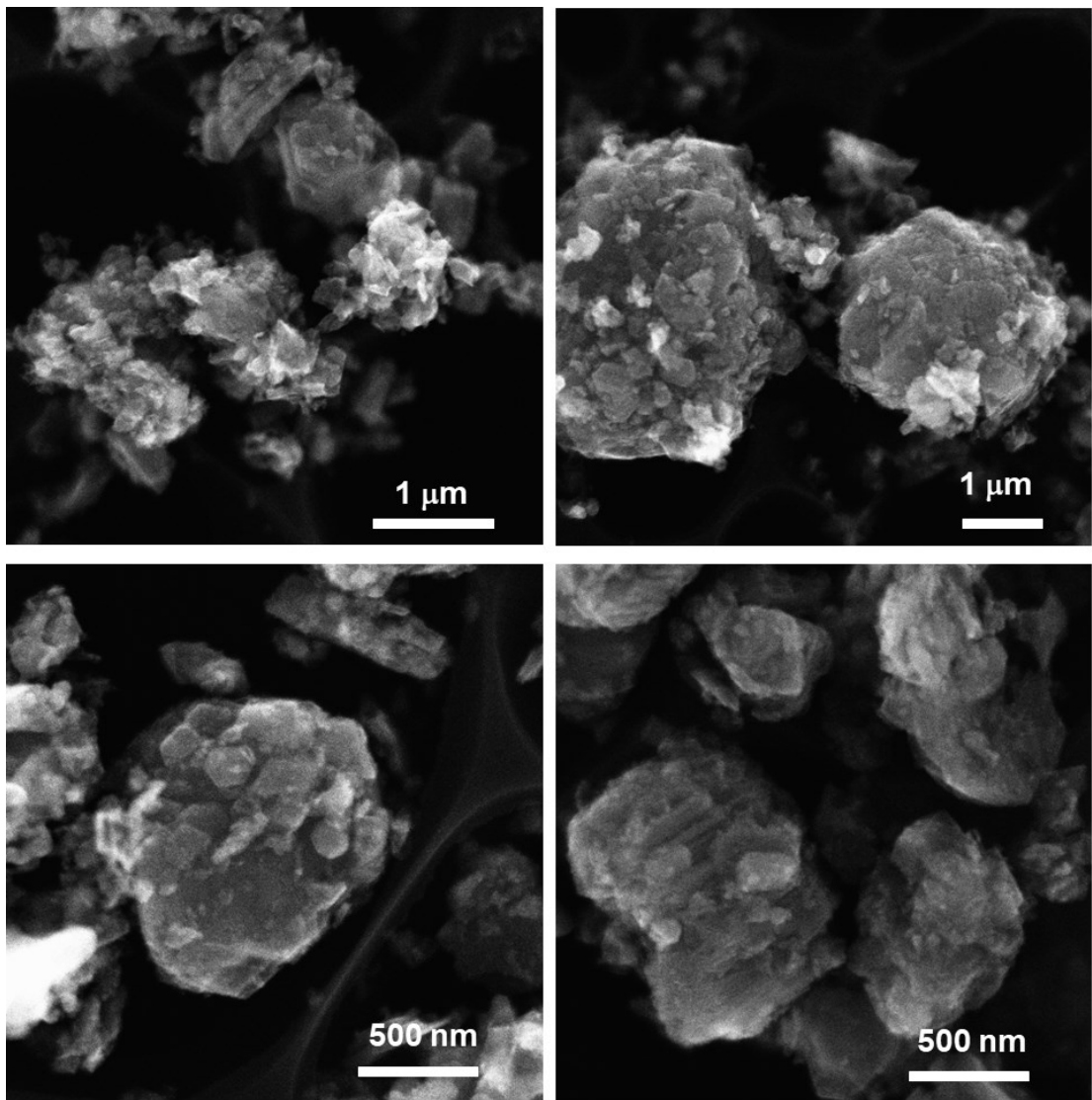
**Fig. S1** XRD patterns of supported Ni catalysts. (a) Ni/Nb<sub>2</sub>O<sub>5</sub>, (b) Ni/TiO<sub>2</sub>, (c) Ni/SiO<sub>2</sub>, (d) Ni/ZrO<sub>2</sub>.



**Fig. S2** XRD patterns for (a) fresh Ni/NiO-300 and (b) recovered Ni/NiO-300

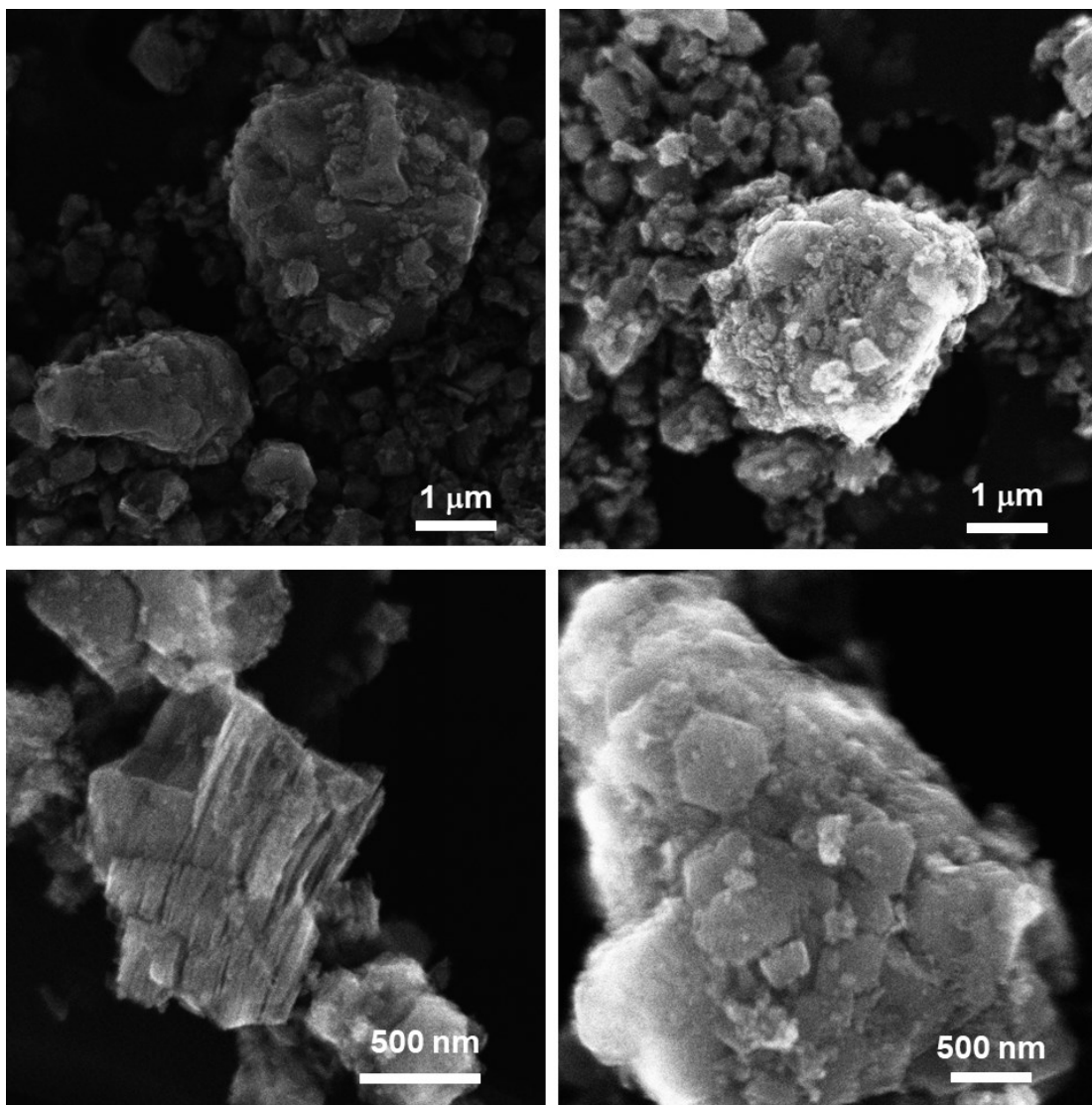


**Fig. S3** SEM images of Ni/NiO-x

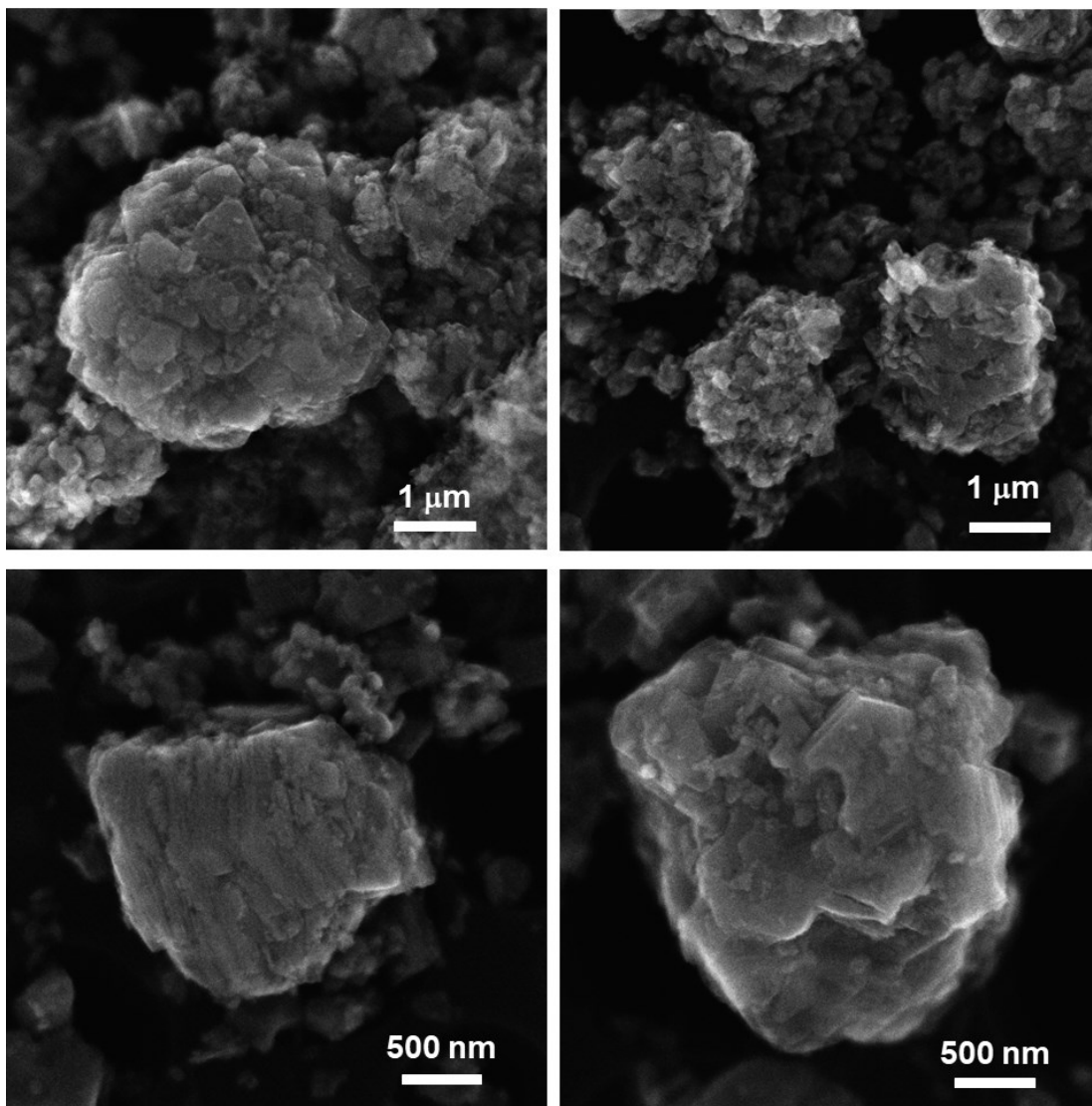


**Fig. S4** SEM images of Ni/NiO-300





**Fig. S5** SEM images of NiO



**Fig. S6** SEM images of recovered Ni/NiO-300

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