PdAg Bimetallic Nanocatalyst for Selective Reductive Amination of Nitroarenes

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Support Information

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1. Syntheses of the bimetallic $Pd_{1-x}Ag_x$ nanoparticles

Typical procedure: $Pd(acac)_2$ (amount see Table S1) and $AgOOCF_3$ (amount see table S1) were dissolved in oleylamine (5 mL) and heated to 60 ^{o}C. A solution of borane-tert-butylamine (100 mg, 1.15 mmol) in oleylamine (1 mL) was added quickly in one portion, upon when the reaction mixture immediately turned from colorless to brown. The reaction was heated to 90 ^{o}C and kept for 30 minutes before it was cooled down to room temperature. The products were isolated by adding ethanol and centrifugation. The as-obtained nanoparticles were dispersed in cyclohexane for future use.

Table S1.Preparation of PdAg nanoparticles and their ICP detection

Designed compositions		Pd_3Ag_1	Pd_2Ag_1	Pd_1Ag_1	Pd_1Ag_2	Pd_1Ag_3	Pd_3Ag_5
Amount of precursors (mg)	$Pd(acac)_2$	22.5	20.0	15.0	10.0	7.5	11.3
	$AgOOCCF_3$	6.8	9.0	13.5	18.0	20.3	16.9
Pd/Ag ratio found by ICP		2.25/1	1.40/1	1/1.14	1/2.15	1/4.17	1/1.70

2. Characterization of the as-obtained bimetallic nanoparticles.

TEM observation was performed on a Hitachi model H-800 transmission electron microscope (JEM 2010F, JEOL) operated at 200 kV. TEM specimens were prepared via the following procedure: the samples were dispersed in cyclohexane with the aid of 10 min ultrasonic vibration. Then a drop of the solution was transferred onto a standard holey carbon-covered-copper TEM micro grid. Powder X-ray diffraction

(XRD) patterns of all the products obtained in this work were recorded with a Bruker D8-advance X-ray powder diffractometer with monochromatized CuKα radiation (λ = 1.5406 Å). The exact contents of the each bimetallic nanoparticle were determined by ICP (Table S1). The ICP results were used to calculate the Pd and Ag in the nanocatalysts. For example, with bimetallic $Pd_1Ag_{1.70}$ nanoparticle in each 1mL stock solution there was 168.54 μg Pd and 290.14 μg Ag.

3. Screening of the bimetallic $Pd_{1-x}Ag_x$ (x =0-1) nanocatalysts

Preparation of nanocatalysts: With the known mass and the Pd/Ag ratio of each bimetallic $Pd_{1-x}Ag_x$ (x =0-1) nanoparticle, we dispersed each of the PdAg NP catalyts in certain volume of cyclohexane so that every 1000 μL stock solution contains 1.6 μmol Pd.

Typical reaction conditions: An aliquot of 1000 μL stock solution of Pd_xAg_{1-x} bimetallic nanoparticle in cyclohexane (0.1685g/L Pd, 0.2901g/L Ag), (1.60μmolPd, 0.0016eq. Pd) was added to a flask containing the benzaldehyde (106.0 mg, 1.0mmol, 1.0 eq.) and nitrobenzene (147.6 mg, 1.0mmol, 1.0eq.) in 4 mL of ethanol. The flask was purged with nitrogen for 10 minutes and then with hydrogen for 10 minutes. Then the reaction was stirred at room temperature under hydrogen atmosphere. The completion of the reaction was monitored by TLC. The reaction mixture was analysed by GC and n-Tridecane was used as the internal standard. The conversion and selectivity data in Table 1 was obtained from the average of two repeated experiments.

4. Recycling of the $Pd_1Ag_{1.70}$ nanocatalyst

Recovery of the catalyst: The reaction solution was centrifuged under 9900 r/min after the reaction was over. Then we removed the supernatant and washed the deposit (PdAg bimetallic nanoparticle) three times with 4 mL of ethanol.

Reuse of the catalyst: The recovered bimetallic PdAg nanocatalyst was used directly for the next run of the model reaction using the method described in section **3**.

Table S2. Recycling the $Pd_1Ag_{1.70}$nanocatalyst for 5 cycles[a]

Run	1	2	3	4	5	6	Average
Yield (%)	95	91	92	89	90	93	92

[a] Reaction conditions: substrate **1a** (1.0mmol), **2a** (1.0mmol), 0.16 mol % $Pd_1Ag_{1.70}$ bimetallic catalyst (based on Pd) in 4 mL ethanol under room temperature / H_2 balloon conditions.

[b] Conversion and selectivity were determined by GC using *n*-Tridecane as the internal standard. The yield of each run was calculated based on the conversion and selectivity.

Characterization of the spent catalyst: The catalyst recovered after the sixth run was dispersed in cyclohexane and subjected to TEM study. Figure S1 shows that the morphology and size of the catalyst did not undergo obvious change.

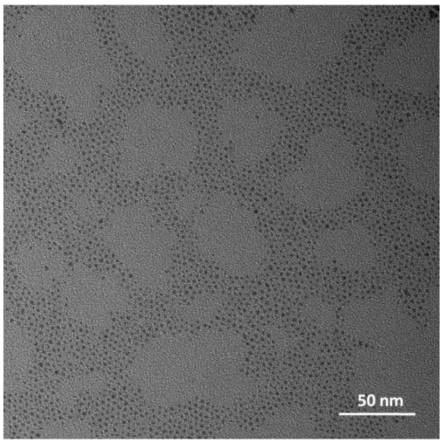
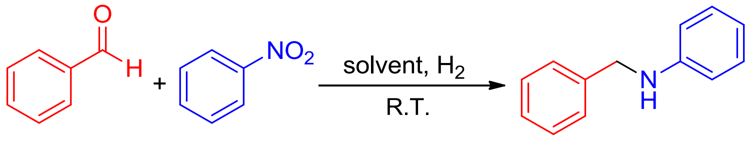


***Figure* S1.** TEM image of $Pd_1Ag_{1.70}$ nanocatalyst after the sixth run

5. Screening of the solvents

Reaction conditions described in section **3** was used to screen for the optimal solvents. The conversion and selectivity of each reaction was determined by GC using *n*-Tridecane as the internal standard (Table S3).

Table S3. Condition optimization of reductive amination between nitrobenzene and benzaldehyde catalyzed by $Pd_1Ag_{1.70}$ bimetallic nanocatalyst.[a]



1a **2a** **3a**

Entry	solvent	Time [h]	Conversion of **1a** [%]	selectivity of **3a**[b]
1	THF	24	0	-
2	DCM	24	9.3	43.0
3	1,4-dioxane	24	30.0	7.9
4	EA	24	44.3	32.7
5	Toluene	24	>99	83.5
6	Cyclohexane	12	>99	90.8
7	**EtOH**	**4**	**>99**	**93.4**

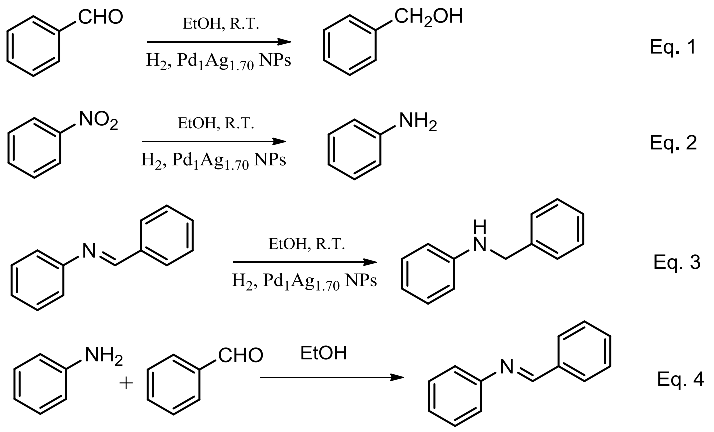
[a] Reaction conditions: substrate **1a** (1.0mmol), **2a**, 0.16 mol % catalyst (based on Pd) in 4 mL solvent under room temperature / H_2 balloon conditions.

[b] Conversion and selectivity were analyzed by GC and n-Tridecane was used as the internal standard.

6. Reaction rates of key model reactions

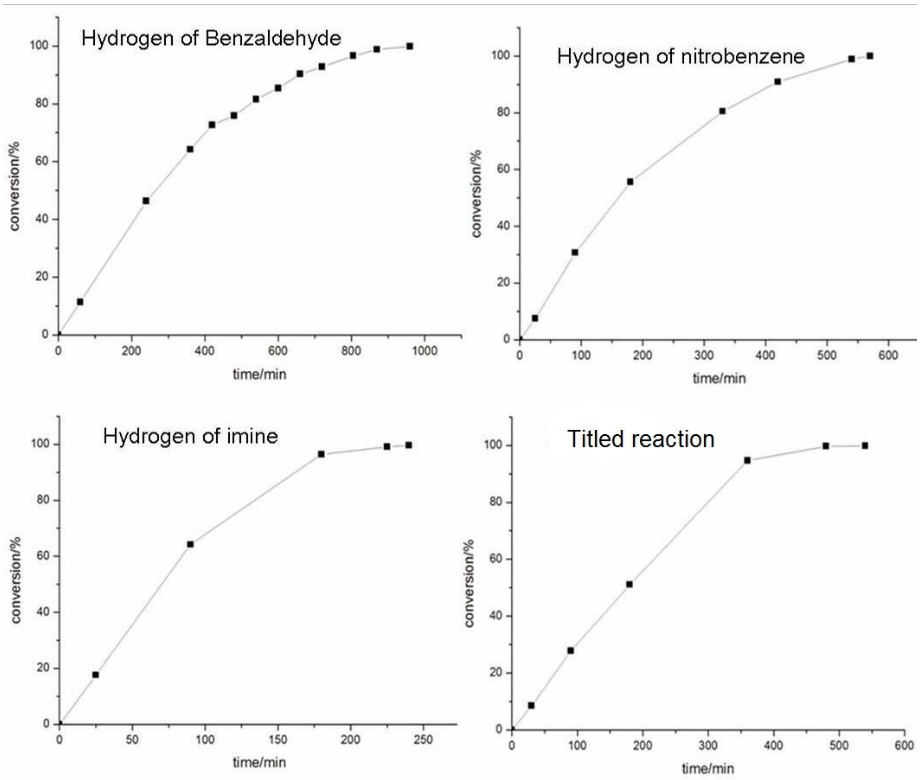
Using similar conditions described in section **3**, we conducted the hydrogenations of the benzaldehyde (in absence of the nitrobenzene) (Eq. 1, Scheme S1), the nitrobenzene (in absence of the benzaldehyde) (Eq. 2, Scheme S1) and the imine (Eq. 3, Scheme S1) with 0.16 mol% $Pd_1Ag_{1.70}$ nanocatalyst. We also conducted the imine formation using aniline and benzaldehyde in ethanol (in absence of the $Pd_1Ag_{1.70}$ nanocatalyst), which completed in 30 min (data not shown).

Reactions shown in eq. 1-3 as well as the titled reaction (section 3, entry 9 in Table 1 in the text) were monitored by GC using *n*-Tridecane as the internal standard.



Schem S1. Study of the rates of four key model reactions

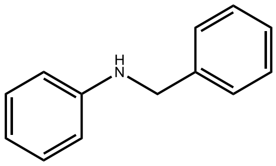
For each reaction the conversion of the specific starting material was plotted against reaction time (Scheme S2).



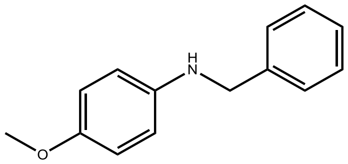
Scheme S2. Curves on the relationship between conversion and time

7. Reaction scope study

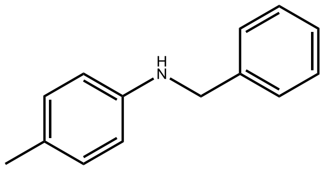
General procedure: An aliquot of 1000 µL stock solution of $Pd_1Ag_{1.70}$ bimetallic nanoparticle in cyclohexane (0.1685g/L Pd, 0.2901g/L Ag) (1.60 µmol Pd, 0.0016eq. Pd) was concentrated under reduced pressure to remove the solvent. The resulting solid was dispersed in 4 mL of ethanol, to which was added the benzaldehyde (106.0 mg, 1.0mmol, 1.0 eq.) and nitrobenzene (147.6 mg, 1.0mmol, 1.0eq.) The flask was purged with nitrogen for 10 minutes and then with hydrogen for 10 minutes. The resulting mixture was stirred at room temperature under hydrogen atmosphere until the nitroarene was found absent by TLC. The reaction was stopped and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography with PE: EA (v/v 20:1 – 5:1) as the eluent.



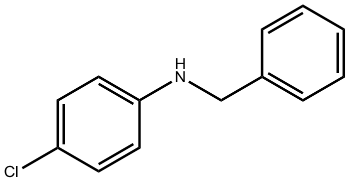
Compound **3a:** ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 4.01 (brs, 1H), 4.32 (brs, 2H), 6.63 (d, 2H, *J* = 7.8 Hz), 6.71 (t, 1H, *J* = 7.2Hz), 7.17 (d, 2H, *J* = 7.5 Hz), 7.23 – 7.37 (m, 5H).



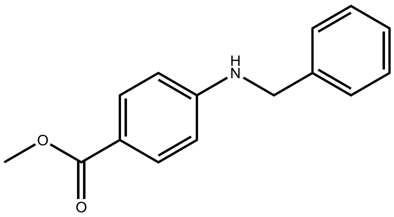
Compound **3b:** ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.70 (brs, 1H), 4.21 (s, 2H), 6.53 (d, 2H, *J* = 9.0 Hz), 6.69 (d, 2H, *J* = 9.0 Hz), 7.19-7.30 (m, 5H).



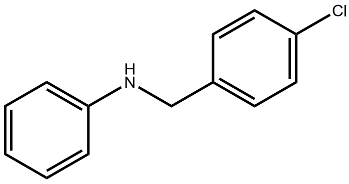
Compound **3c:** ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 2.25 (s, 3H), 4.32 (s, 2H), 4.85 (brs, 1H), 6.61 (d, 2H, *J* =8.5 Hz), 7.00 (d, 2H, *J* = 8.5 Hz), 7.27 – 7.39 (m, 5H).



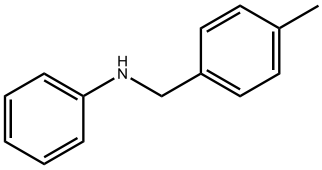
Compound **3d:** **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.31 (s, 2H), 6.56 (d, 2H, *J* =8.8 Hz), 7.11 (d, 2H, *J* = 8.8 Hz), 7.28 – 7.35 (m, 5H).



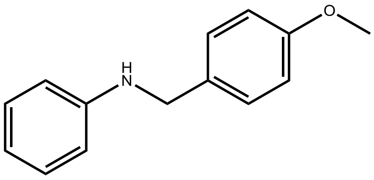
Compound **3e:** **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 7.29-7.36 (m, 5H), 4.39 (s, 2H), 4.51 (brs, 1H), 6.59 (d, 2H, *J* = 8.8 Hz), 7.86 (d, 2H, *J* = 8.8 Hz).



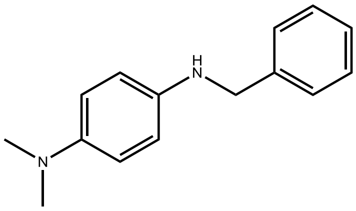
Compound **3f:** **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.13 (brs, 1H), 4.31 (s, 2H), 6.61 (d, 2H, *J* = 8.7 Hz), 6.73 (t, 1H, *J* = 7.3 Hz), 7.14-7.19 (m, 2H), 7.30 (s, 4H).



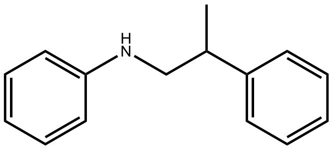
Compound **3g:** **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 4.29 (s, 2H), 4.70 (brs, 1H), 6.68 (d, 2H, *J* = 7.6 Hz), 6.75 (t, 1H, *J* = 7.4 Hz), 7.15 – 7.21 (m, 4H), 7.27 (d, 2H, *J* = 7.9 Hz).



Compound **3h:** **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 3.96 (brs, 1H), 4.27 (s, 2H), 6.65 (d, 2H, *J* = 7.6 Hz), 6.74 (t, 1H, *J* = 7.4 Hz), 6.90 (d, 2H, *J* = 8.5 Hz), 7.19 (t, 2H, *J* = 7.4 Hz), 7.31 (d, 2H, *J* = 8.7 Hz).

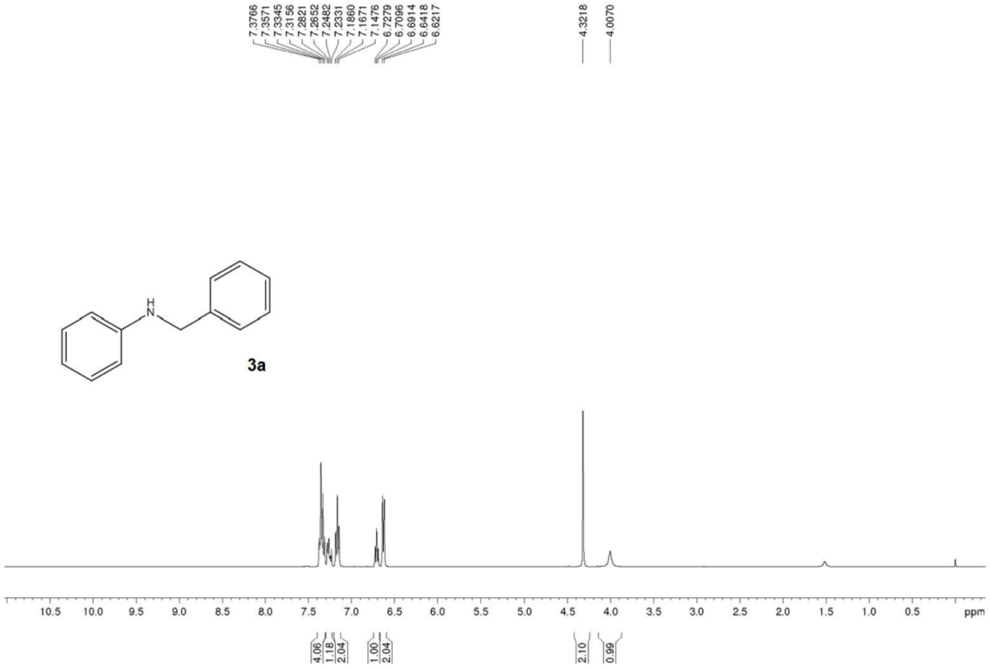


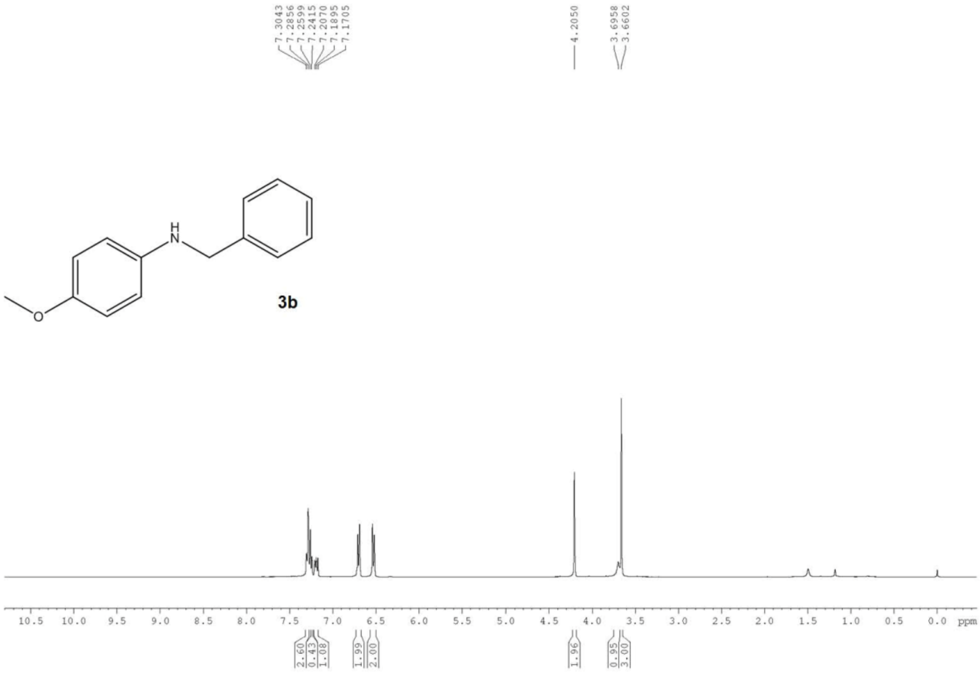
Compound **3i:** **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.83 (s, 6H), 3.70 (brs, 1H), 4.30 (s, 2H), 6.64 (d, 2H, *J* =8.4 Hz), 6.75 (d, 2H, *J* = 8.4 Hz), 7.28 – 7.40 (m, 5H).



Compound **3j:** **^{1}H NMR** (400 MHz, CDCl$_3$): δ 1.33 (d, 3H, *J* = 6.9 Hz), 3.01 – 3.10 (m, 1H), 3.20 – 3.26 (m, 1H), 3.31 – 3.36 (m, 1H), 3.57 (brs, 1H), 6.57 (d, 2H, *J* = 8.5 Hz), 6.68 (t, 1H, *J* = 7.3 Hz), 7.15 (t, 2H, *J* =8.4 Hz), 7.23 – 7.35 (m, 5H).

8. ^{1}H NMR spectrum of the N-alkylamine products

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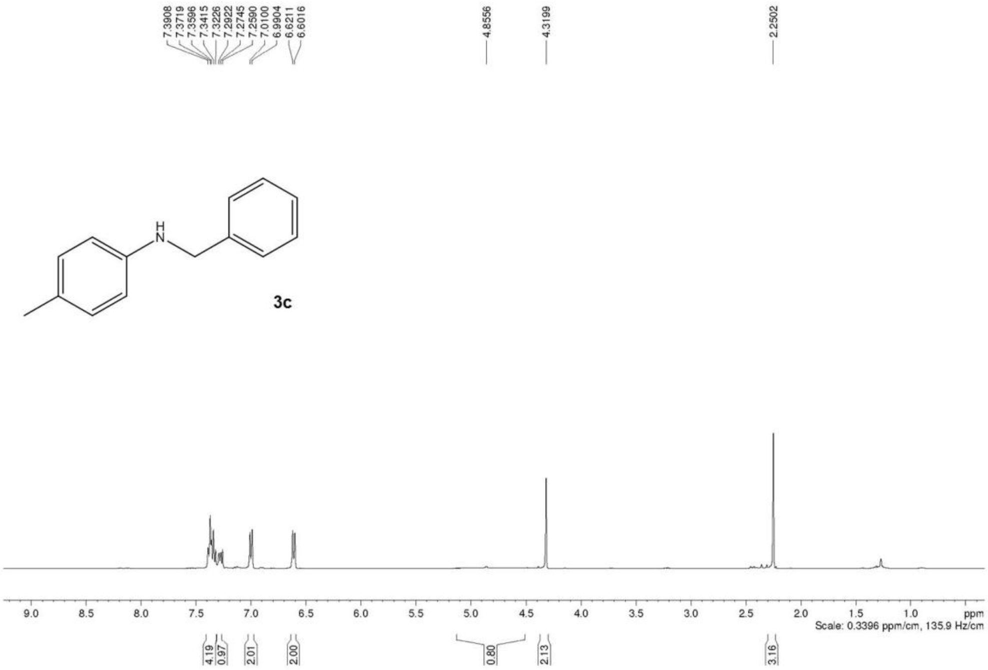
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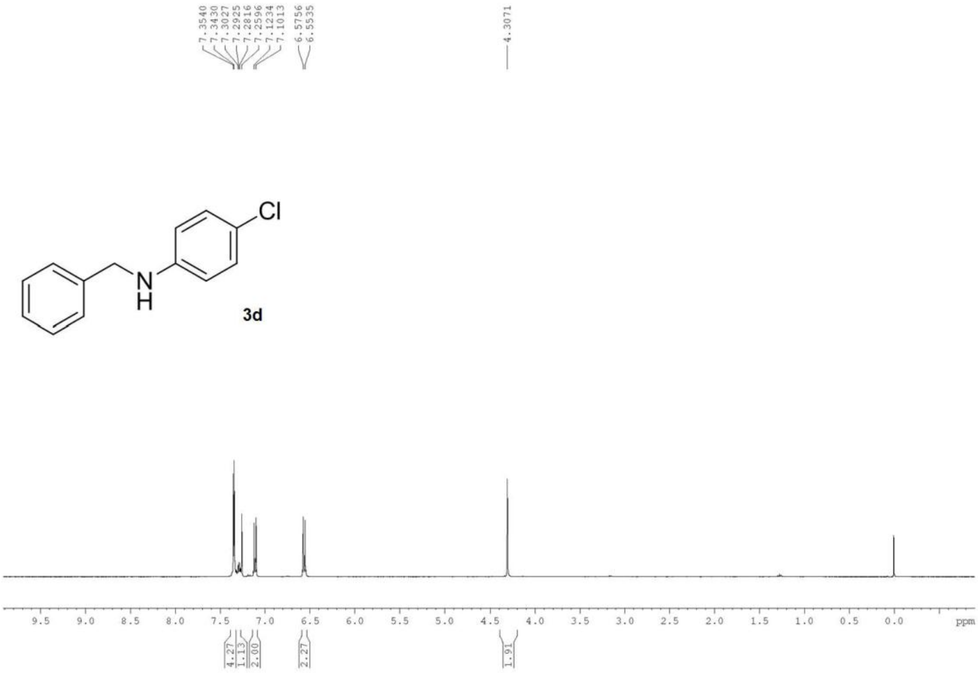
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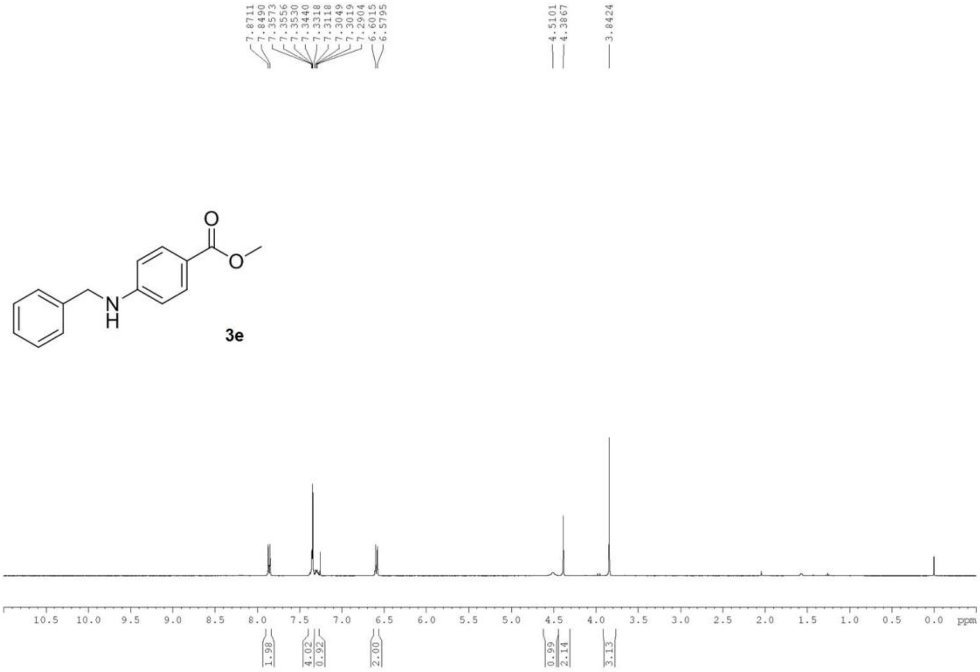
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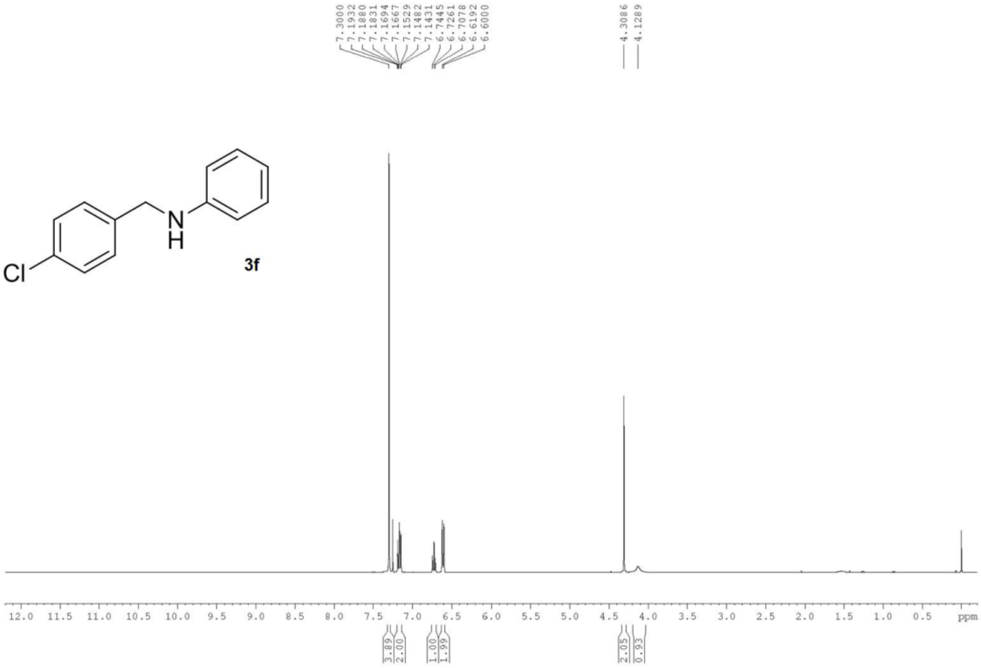
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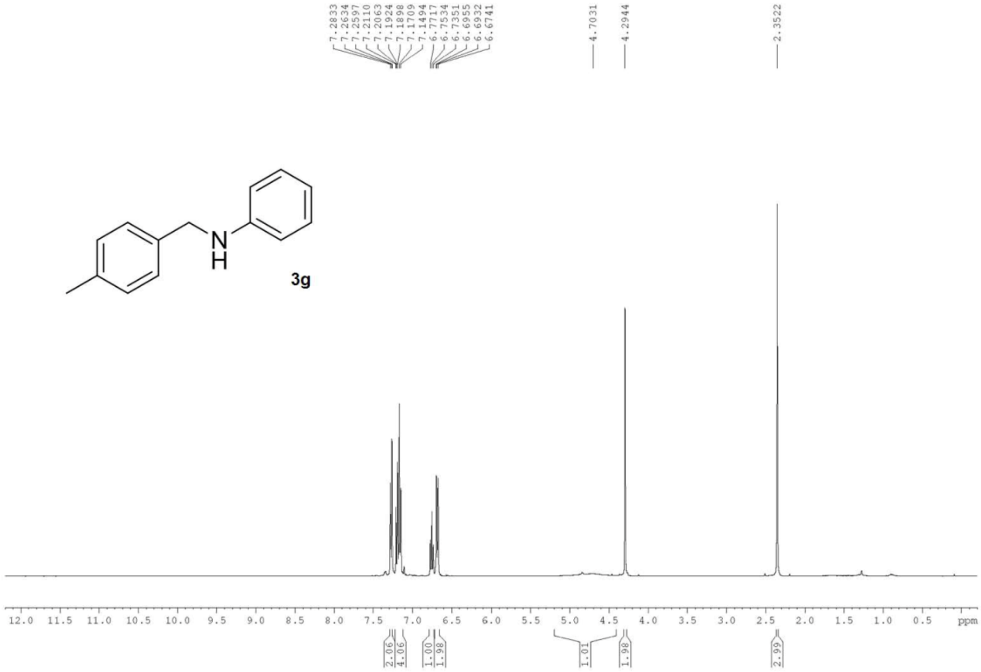
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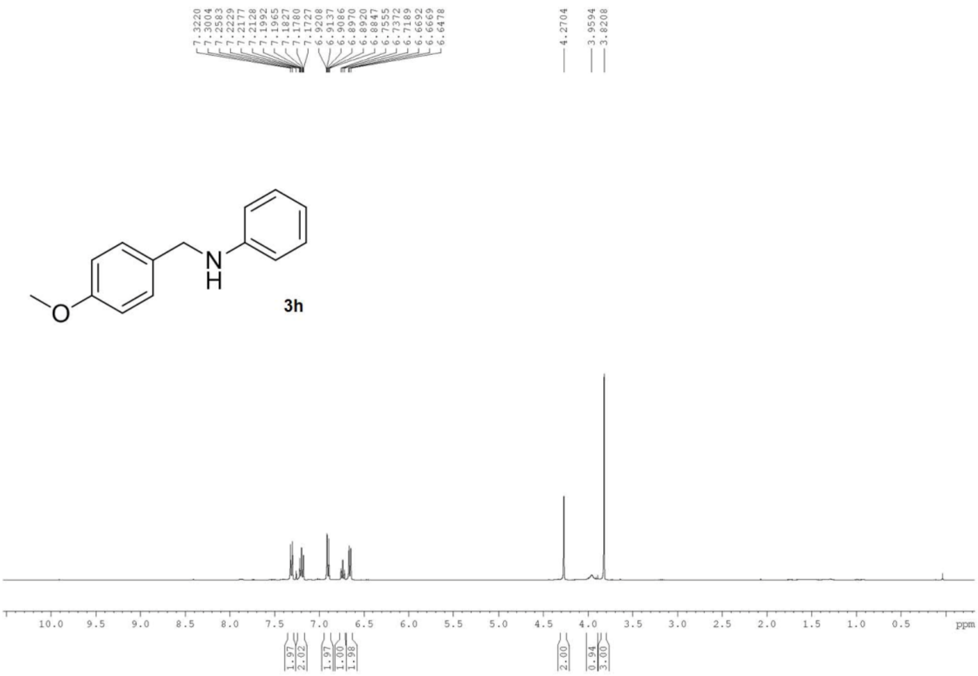
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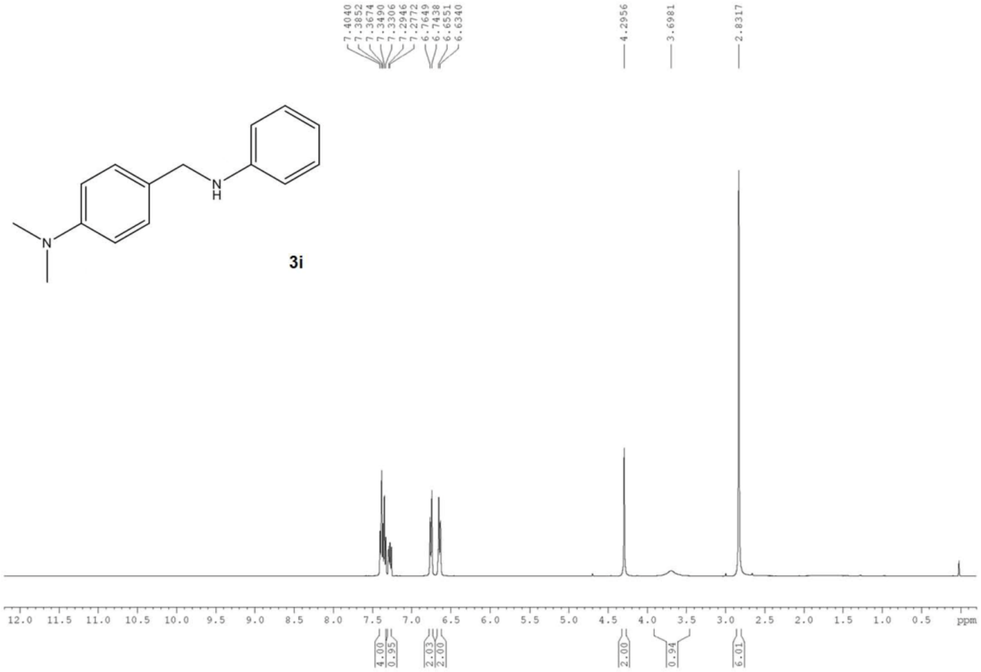
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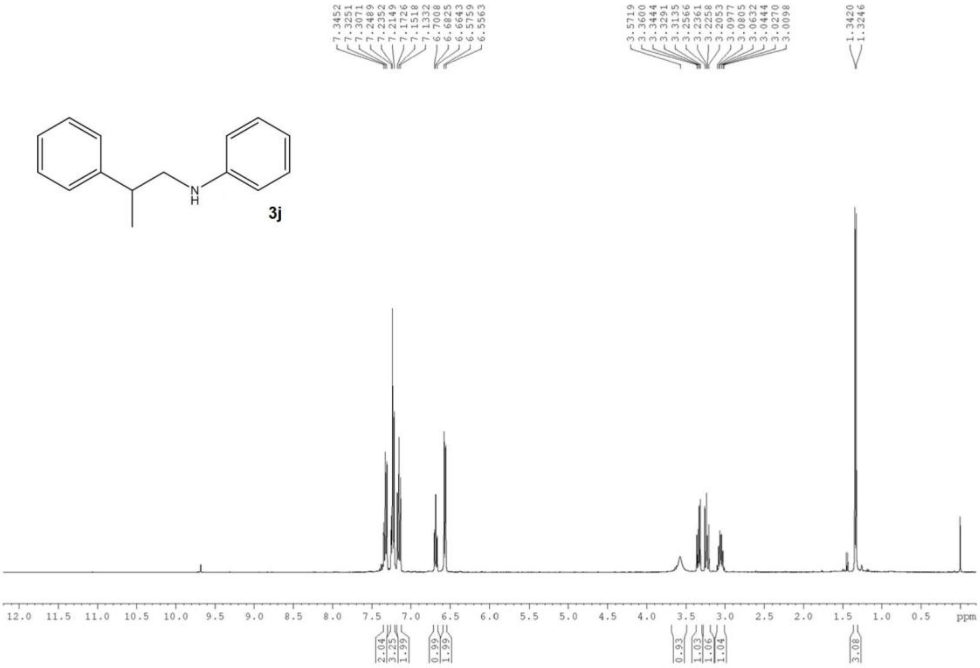

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1.99
0.93
1.03
1.06
1.04
3.08