# Supporting Information

## Novel Synthesis of N-alkyl amines from tandem Coupling of either Methylamine or Nitroalkane with Aldehyde

Shuanglong Lu, Jie Peng, Junjie Wu, Chao Li, Xueqin Cao and Hongwei Gu*

## Experimental Section

### Preparation of Pt nanowires catalyst:

Ultrathin Pt NWs were achieved through etching of FePt NWs. The mixed 0.2 g $Pt(acac)_2$ and 20 mL oleylamine were heated to 60 $^oC$ under $N_2$ atmosphere to make it dissolved thoroughly. This solution was heated to 120$^oC$ under stirring and then kept for 15 minutes. 0.15 mL $Fe(CO)_5$ was injected into the hot solution and then the temperature was gradually raised up to 160$^oC$. The reaction was kept at this temperature for half an hour without stirring. The black solution was then cooled to room temperature and centrifuged in excess ethanol. The precipitate was redispersed in methanol. The mixture was firstly treated by oxygen bubbling at 100$^oC$, and 10 mL HCl/methanol (1:1) solution was added into the above suspension. The solution was heated and stirred at 70$^oC$ for 1 hour, the resultant precipitates were obtained following 10 minutes of centrifugation (4000 rpm). The dark solid was washed with methanol for at least two times and stored in methanol. Based on the XPS and ICP analysis, no Fe element could be detected at the surface of the catalyst, which indicates the surface is composed by Pt atoms.

### General procedure for the synthesis of N-alkylamine from coupling of methylamine with aldehyde using Pt NWs as the catalyst:

Pt NW catalyst in methanol (0.5% mmol) was added in a Schlenk tube and the methanol was evacuated by pressure reducing. Then 2 ml solvent is added, after which, ultrasonic stirring was used to make the catalyst to disperse uniformly. Aldehyde and methylamine solution were injected into the mixture. The reaction tube was thrice evaluated and flushed with hydrogen. The reaction took place at a certain temperature under a hydrogen atmosphere. After reaction, the resultant product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. All the reactions were performed for at least 5 times till their differences were within an acceptable error range. The products were purified by flash chromatography and characterized by $^1H$ NMR and $^{13}C$ NMR.

**General procedure for the synthesis of N-alkylamine from coupling of nitromethane with aldehyde using Pt NWs as the catalyst:**

Pt NW catalyst in methanol (0.5% mmol) was added in a Schlenk tube and the methanol was evacuated by pressure reducing. Then 2 ml solvent is added, after which, ultrasonic stirring was used to make the catalyst to disperse uniformly. Aldehyde and nitromethane were injected into the mixture and then addictive was added. The reaction tube was thrice evaluated and flushed with hydrogen. The reaction took place at a certain temperature under a hydrogen atmosphere. After reaction, the resultant product mixtures were analyzed by GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector) and GC-MS (VARIAN 450-GC & VARIAN 240-GC) equipped with a CP8944 capillary column (30 m × 0.25 mm) and an FID detector. All the reactions were performed for at least 5 times till their differences were within an acceptable error range. The products were purified by flash chromatography and characterized by $^{1}H$ NMR and $^{13}C$ NMR.

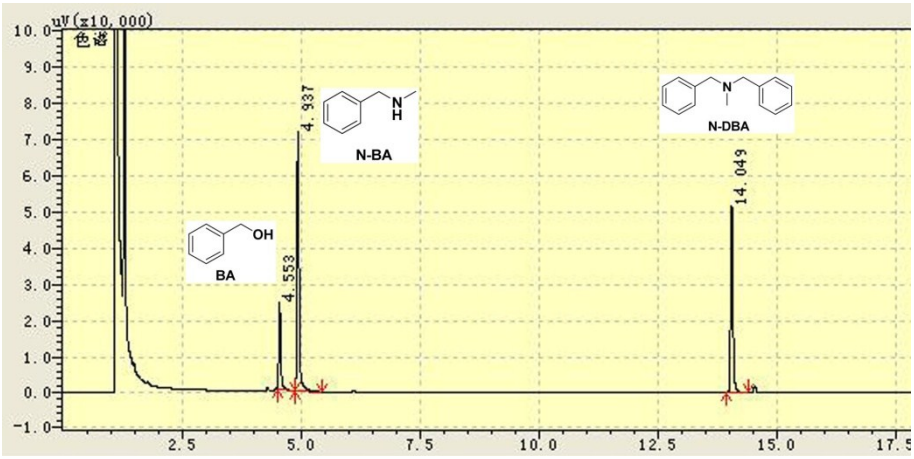



**Figure S1** Gas chromatograph spectrum of the testing experiment: 2 mmol benzaldehyde, 1 mmol $CH_3NH_2$, 0.5 mol% Pt NW, 1 bar $H_2$ balloon, 2 ml ethanol at 80°C for 24 h (corresponding to entry 4 in table 1).

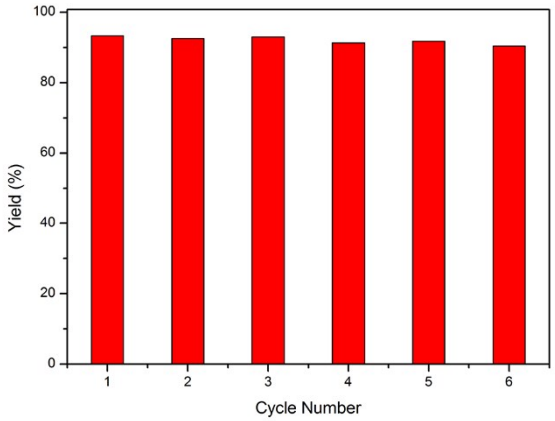



**Figure S2** catalytic stability of Pt nanowires: 2 mmol benzaldehyde, 1 mmol $CH_3NH_2$, 0.5 mol% Pt NW (recycled), 1 bar $H_2$ balloon, 2 ml DMF at 100°C for 24 h. Yields of the product were determined by GC.

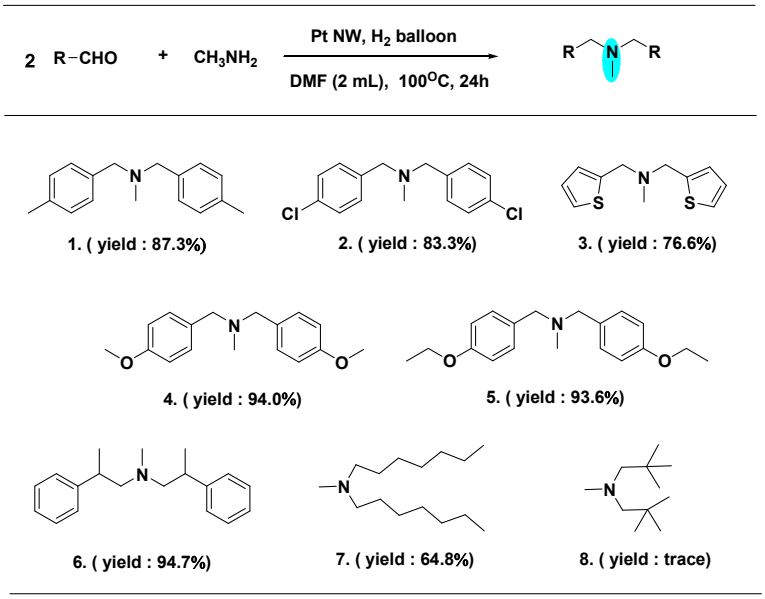
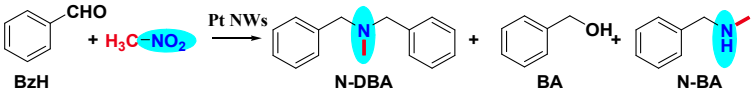



**Figure S3** N-methyl-dibenzylamine formation from different aldehydes. Reaction conditions: 2 mmol aldehyde, 1 mmol $CH_3NH_2$, 0.5 mol% Pt NW, 1 bar $H_2$ balloon, 2 ml DMF as solvent at 100°C for 24 h, GC yield.

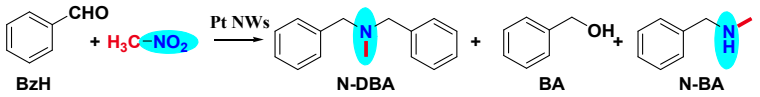
**Table S1** optimization of the reaction conditions where benzaldehyde is coupling with nitromethane.[a]




| Entry | BzH /mmol | $CH_3NO_2$ /mmol | Solvent | T/°C | Conv./% [b] | Sel./ % [b] |
|---|---|---|---|---|---|---|
| 1 | 1 | 2.5 | methanol | 40 | 100 | --- |
| 2 | 1 | 2.5 | ethanol | 80 | 100 | 8.2 |
| 3 | 1 | 2.5 | heptane | 100 | 100 | -- |
| 4 | 1 | 2.5 | 1,4-dioxane | 100 | 100 | 24.8 |
| 5 | 1 | 2.5 | xylene | 80 | 100 | 36.2 |
| 6 | 1 | 2.5 | xylene | 100 | 100 | 44.9 |
| 7 | 1 | 2.5 | DMF | 100 | 100 | 67.4 |
| 8 | 1 | 36 | $CH_3NO_2$ | 100 | 100 | --- |
| 9 | 2 | 1 | toluene | 100 | 100 | 6.8 |
| 10 | 1 | 2 | toluene | 100 | 100 | 68.7 |
| **11** | **1** | **2.5** | **toluene** | **100** | **100** | **84.3** |
| 12 | 1 | 3 | toluene | 100 | 100 | 61.3 |
| 13 | 1 | 4 | toluene | 100 | 100 | 35.3 |

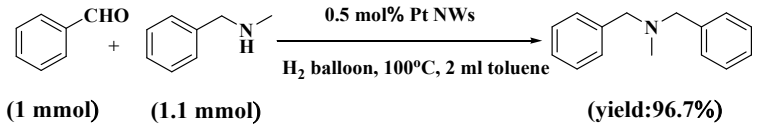
[a] Reaction conditions: 0.5 mol% Pt NW, 1 bar $H_2$ balloon, 2 ml solvent at corresponding temperature; [b] GC yield.

**Table S2** optimization of the reaction conditions where benzaldehyde is coupling with nitromethane.[a]



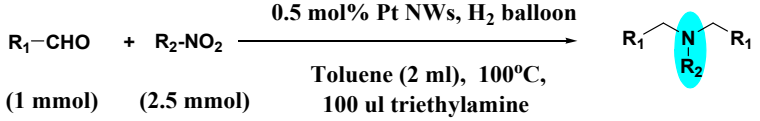

| Entry | Catalyst | $H_2$ (bar) | Addictive | T/°C | Yield / % [e] |
|---|---|---|---|---|---|
| 1 | Pt NW | 1 | *t*-$C_4H_9OK$ | 100 | --- |
| **2** | **Pt NW** | **1** | **triethylamine** | **100** | **91.3** |
| 3 | Pt NW | 1 | Acetic acid | 100 | 71.0 |
| 4[b] | --- | 1 | triethylamine | 100 | N.D.[d] |
| 5[c] | Pt NW | --- | triethylamine | 100 | N.D.[d] |

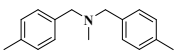
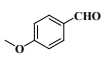
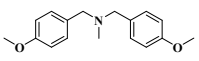
[a] Reaction conditions: 1 mmol aldehyde, 2.5 mmol nitroalkane, 0.5 mol% Pt NW, 100 ul additive, 1 bar $H_2$ balloon, 2 ml toluene at 100°C for 24 h; [b] no Pt NW; [c] no $H_2$ balloon; [d] not detected; [e] GC yield.

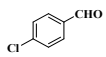
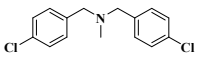
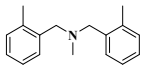
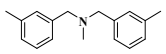
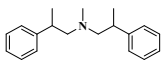
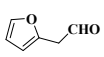
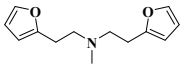
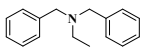
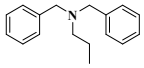
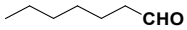
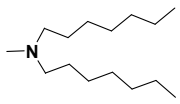



**Scheme S1** Control experiment: coupling of benzaldehyde (1 mmol) with N-methylamine (1.1 mmol). Yield was determined by GC.

**Table S3** N-alkyl amines prepared using different aldehydes and nitroalkane over Pt NWs.[a]




| Entry | Aldehydes | Nitroalkane | N-alkyl amines | Yield/ %[b] |
|---|---|---|---|---|
| 1 |  | $CH_3NO_2$ |  | 86.0 |
| 2 |  | $CH_3NO_2$ |  | 77.1 |

| | | | | |
|---|---|---|---|---|
| 3 |  | $CH_3NO_2$ |  | 31.4 |
| 4 |  | $CH_3NO_2$ |  | 36.9 |
| 5 |  | $CH_3NO_2$ |  | 38.8 |
| 6 |  | $CH_3NO_2$ |  | 60.7 |
| 7 |  | $CH_3NO_2$ |  | 62.7 |
| 8 |  | $CH_3CH_2NO_2$ |  | 66.8 |
| 9 |  | $CH_3CH_2CH_2NO_2$ |  | 74.7 |
| 10 |  | $CH_3NO_2$ |  | 60.6 |
| 11 |  | $CH_3NO_2$ |  | Trace |

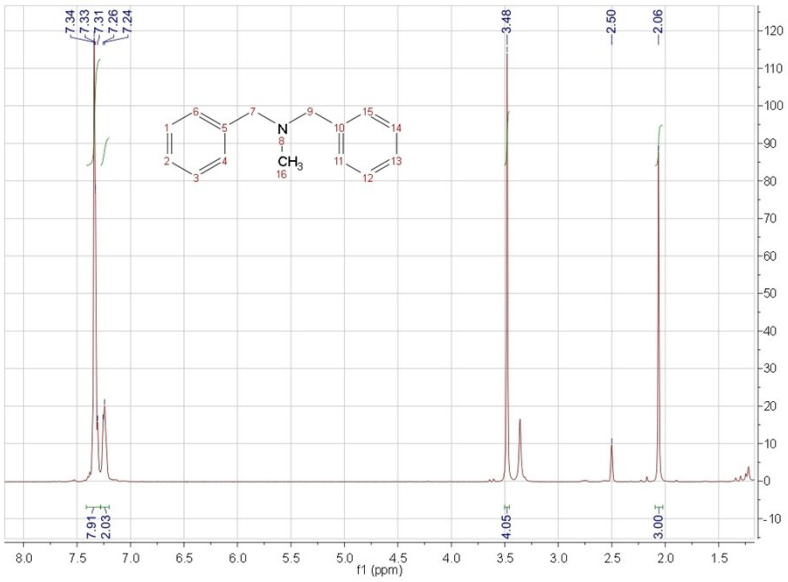
Reaction conditions: 1 mmol aldehyde, 2.5 mmol nitroalkane, 0.5 mol% Pt NW, 100 ul triethylamine as additive, 1 bar $H_2$ balloon, 2 ml toluene at 100$^{o}$C; [b] GC yield.

## Analysis.

$^{1}$H NMR and $^{13}$C NMR data were recorded at 400.0 and 100 MHz on a Varian Inova 400 spectrometer. The $^{1}$H NMR and $^{13}$C NMR chemical shifts are reported relative to tetramethylsilane. All measurements were carried out at 298 K

N-methyl-dibenzylamine (N-DBA):

$^{1}$H NMR (400 MHz, DMSO-$d_6$): δ =2.06 (s, 3H), 3.48 (s, 4H), 7.24-7.26 (m, 2H), 7.31-7.34 (m, 8H).




$^{13}$C NMR (100 MHz, DMSO-$d_6$): δ =61.00, 126.88, 128.20, 128.56, 139.08.