

## Electronic Supplementary Information

### A DNA-Templated Catalyst: The Preparation of Metal-DNA

### Nanohybrids and Their Application in Organic Reactions

Ye Wang, Guanghui Ouyang, Jintang Zhang and Zhiyong Wang\*

*Hefei National Laboratory for Physical Science at the Microscale, CAS Key Laboratory of Soft  
Matter Chemistry and Department of Chemistry,*

*University of Science and Technology of China, Hefei, 230026, P. R. China*

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## General Remarks

UV-Vis tests were taken on a Persee TU1901 UV-Vis spectromter. All the solutions were diluted to similar concentration and gained the desirable normalized curves. The morphology and size of the Pd, Au, Ag, and Pt NPs were characterized on transmission electron microscopy (TEM) (JEOL-2010 and Hitachi H7650). The diluted solutions of the as-synthesized M-DNA nanohybrid were used as samples directly and dried on the carbon-coated Cu grids. X-ray powder diffraction (XRD) experiments were carried out with a Philips X'Pert Pro Super diffractometer with Cu KR radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The accurate concentrations of M-DNA nanohybrid were directly determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) using Perkin Elmer Optima 7300 DV.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR were recorded on a Bruker AC-300 FT ( $^1\text{H}$  NMR 300 MHz,  $^{13}\text{C}$  NMR 75 MHz) using TMS as internal reference. Infrared samples of DNA and Pd-DNA were recorded on a Thermo Scientific Nicolet 8700 spectrometer. HRMS were recorded on a MicroMass GCT TOF-MS. GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. And the yield was determined by internal standard.

## **General procedures for synthesis of M-DNA and organic reactions catalyzed by M-DNA**

### **General procedures for synthesis and purification of M-DNA nanohybrids**

0.1 mmol of the corresponding metal salt ( $K_2PdCl_4$ ,  $KAuCl_4$ ,  $AgNO_3$ ,  $K_2PtCl_6$ ) and 10 mg of fish sperm DNA were dissolved in 10 ml Tris buffer (10mM, pH = 7.4). The combined solution was stirred for 24 h to ensure the corresponding metal ion ( $Pd^{2+}$ ,  $Ag^+$ ,  $Au^{3+}$ ,  $Pt^{4+}$ ) thoroughly bind to DNA. After this aging process, 0.5 mmol of freshly dissolved  $NaBH_4$  in 10 ml Tris buffer was added dropwise under  $N_2$  atmosphere at 0 °C. After reduction, the solution was stirred for another 24 h in  $N_2$  from 0 °C to room temperature to obtain the resulting M-DNA nanohybrids (*c.a.* 5 mM in Tris). Then M-DNA nanohybrid was purified by adding 2-3 volume of EtOH to the reaction solutions and placing still for precipitation in 1-2 h. Then by direct decantation or with the aid of centrifugation at 5000 r/min for 5 minutes, the clear solution was poured out and the residue was redispersed and preserved in different buffers or aqueous solutions (Tris, MES,  $NaHCO_3$ - $Na_2CO_3$ , or many other inorganic salts) of the same volume before purification. This synthesis method can be scaled up to hundreds of millilitres easily at a time.

### **General procedure of hydrogenation reactions**

To 1 mmol of nitrophenyl compound 4 ml of M-DNA in Tris buffer solution was added (M = Pd, Au, Ag, Pt). When the solubility of nitrophenyl compound was poor in this M-DNA solution, 2 ml of ethanol was added to promote the dissolution of nitrophenyl compound. Then the reaction mixture was stirred under  $H_2$  balloon at 25 °C after degasification. The reaction process was monitored by TLC in 4-8 h. When the reaction was completed according to the TLC tracking, the reaction was stopped and the mixture was worked up. After addition 2-3 volume of EtOH to the reaction solutions, the reaction mixture was placed still for precipitation in 1-2 h and then

centrifuged at 5000 r/min for 5 minutes. After phase separation, the catalyst can be used for the next round. The reaction solution was evaporated with a rotovapor and the obtained residue was purified with column chromatography over silica gel. The resulting products were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS.

### **General procedure of the oxidation reaction**

2 ml M-DNA (M = Pd, Au, Ag, Pt) in Tris was precipitated and redispersed in 2 ml solutions containing 1 mmol of different bases. Then 0.5 mmol of secondary alcohol was added to the homogeneous solution and the oxidation reactions were stirred at 25 °C in air or O<sub>2</sub> balloon for 10-12 hours. After the reaction was finished, the reaction yield was determined by GC-MS with an internal standard. The catalyst M-DNA can be recovered by a simple phase separation after adding 2-3 volume of EtOH to the reaction solution. The recovered M-DNA could be directly reused in the next round.

## Optimization in synthesis of M-DNA and detailed characterizations

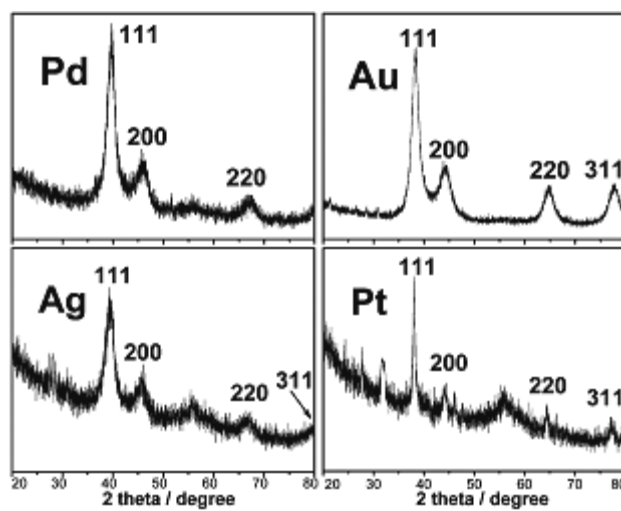
### Optimization of reduction agents for the synthesis of M-DNA

In the beginning, we attempted to extend the previous work<sup>1</sup> to prepare Pd-DNA nanohybrid in larger scale, but only Pd black was obtained. The reason of this failure was perhaps due to the lack of the DNA amount as template to stabilize all the produced Pd atoms. Therefore the dosage of the DNA was increased and the mixture of black precipitation and black suspension was obtained. This implied that the selection of suitable reductants had a great influence on the fabrication of nanohybrids.<sup>2</sup> Initially, urotropine was employed as a reducing agent to reduce Pd<sup>2+</sup> under nitrogen. However, no palladium nanoparticles were observed. Then vitamin C was used to replace urotropine and to reduce palladium ions. In this case some small black particles suspended in the solution rather than the formation of DNA-nanohybrid. When hydrated hydrazine was used as a reducing agent, a filar precipitate was observed instead of uniform solution. Finally, sodium borohydride was employed to reduce palladium and the desired uniform black solution was obtained.

### Reference

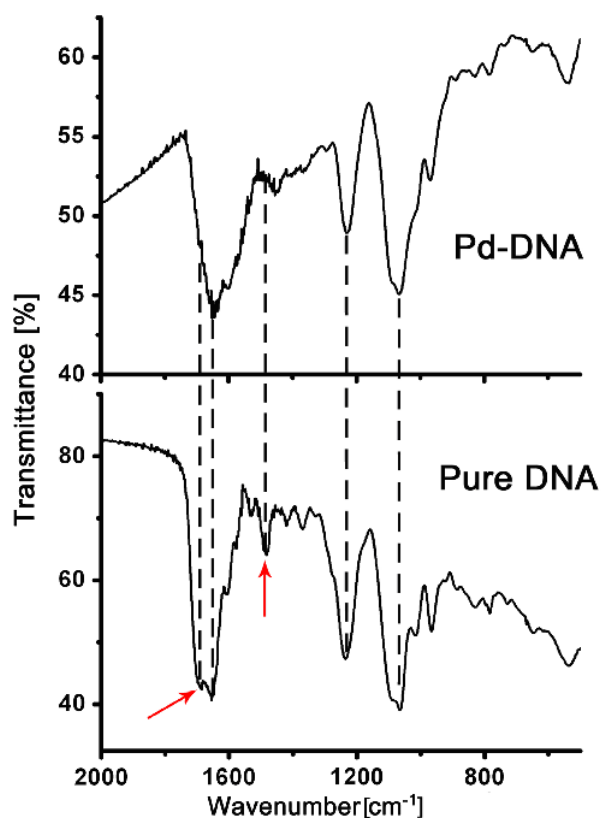
- 1 J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke and H. K. Schackert, *Adv. Mater.*, 2000, **12**, 507.
- 2 Y. Hatakeyama, M. Umetsu, S. Ohara, F. Kawadai, S. Takami, T. Naka and T. Adschiri, *Adv. Mater.*, 2008, **20**, 1122.

### XRD patterns for M-DNA nanohybrids



**Fig. ESI-1** XRD patterns of different kinds of M-DNA nanohybrids

### IR spectra and $^{31}\text{P}$ NMR spectra of pure DNA and Pd-DNA.



**Fig. ESI-2** IR spectra of Pd-DNA and pure DNA

No obvious variation was found before and after reduction at 1060 and 1230  $\text{cm}^{-1}$ , which were the symmetric and antisymmetric stretching modes of  $\text{PO}_2^-$ , showing that Pd NPs didn't bind to this area. The variation at 1650-1685  $\text{cm}^{-1}$ , which was contributed from C=C, C-N, C=O stretching modes, indicated that the base pairs of the DNA may interacted with Pd NPs. Especially, the weakening of 1480  $\text{cm}^{-1}$  (C=N) implied that Pd NPs may had interaction with the nitrogen atom of the base pairs. All of these indicated that Pd-DNA nano hybrid was formed.

### $^{31}\text{P}$ NMR spectra of pure DNA and Pd-DNA.

The  $^{31}\text{P}$  NMR spectra of pure fish sperm DNA in Tris and the Pd-DNA solution which was gained through precipitating and re-dissolving procedure by adding excess EtOH indicated that after pouring out the fair solution, DNA remained in the black precipitation. Secondly, the chemical shift of  $^{31}\text{P}$  in Pd-DNA system was almost the same as the pure DNA showed that Pd did not bind with the P atoms in the DNA.

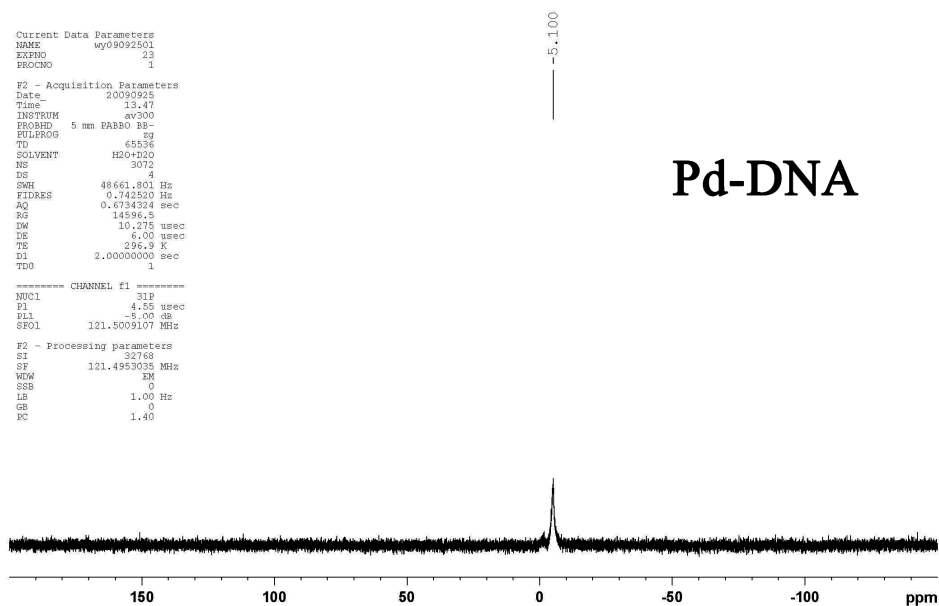
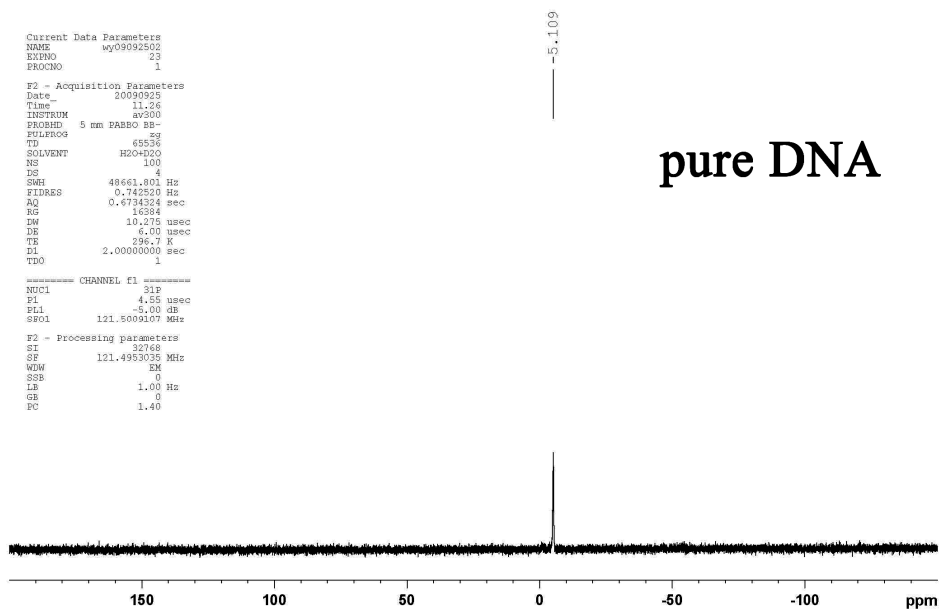
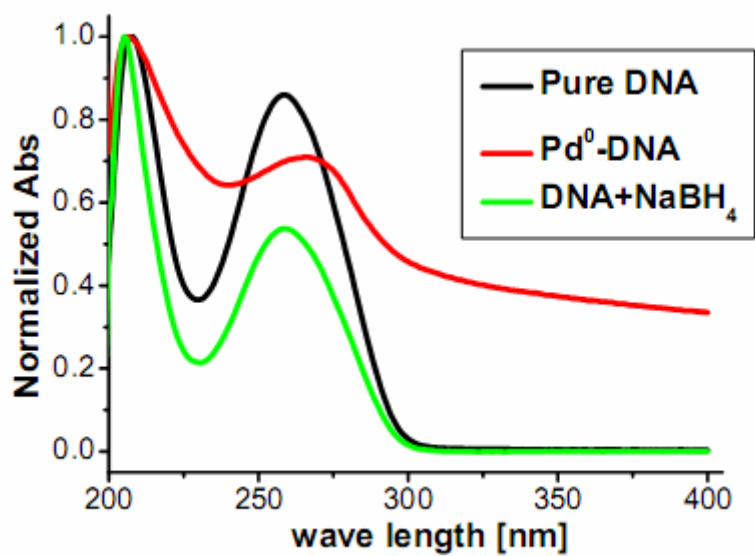


Fig. ESI-3  $^{31}\text{P}$  NMR spectra of pure DNA and Pd-DNA

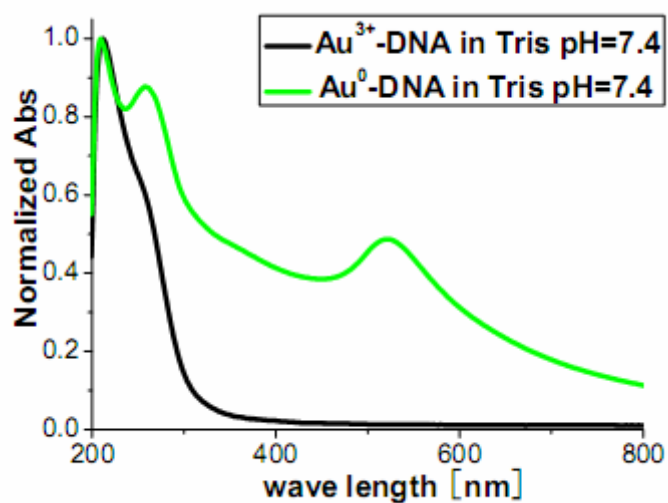


### Uv-Vis Spectra of control experiment with only DNA and NaBH<sub>4</sub>

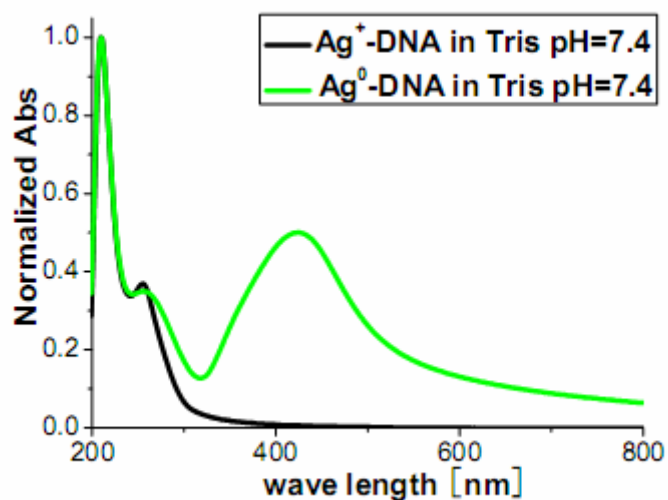


**Fig. ESI-4** Uv-Vis spectra of pure DNA (black line), Pd-DNA nanohybrid (red line) and pure DNA after only adding NaBH<sub>4</sub> (green line).

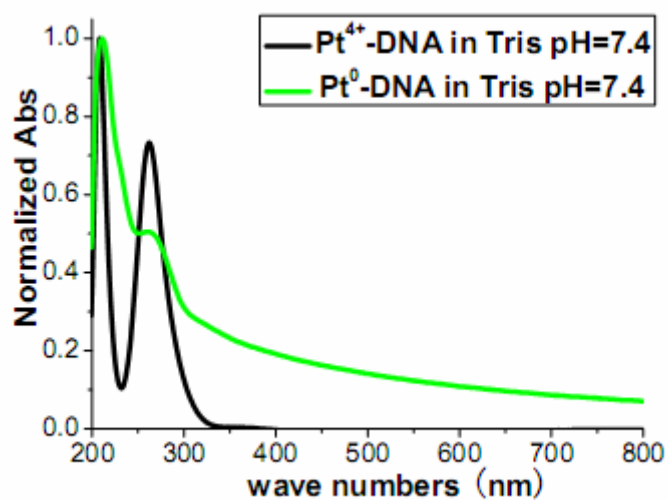
### Uv-Vis Spectra of other M-DNA



Peak at 520 nm showed the visible purple color of the Au-DNA



Peak at 425 nm showed the visible brown color of the Ag-DNA



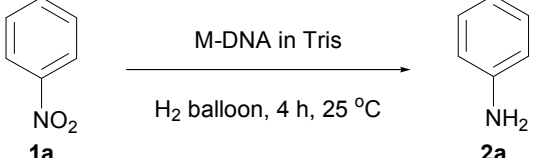
No peak at 400-800 nm showed the black color of the Pt-DNA

Fig. ESI-5 Uv-Vis data of other M<sup>n+</sup>-DNA and M-DNA (M = Au, Ag, Pt)

## Further detailed experiments for hydrogenation and oxidation

### Optimization for hydrogenation of nitrobenzene

**Table ESI-1** Different M-DNA in hydrogenation of nitrobenzene<sup>a</sup>

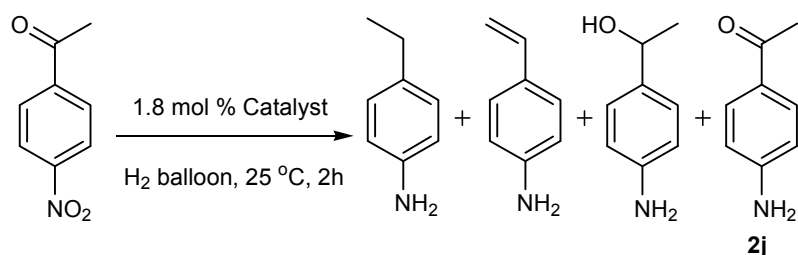


| Entry | M  | Yield (%) <sup>b</sup> |
|-------|----|------------------------|
| 1     | Pd | 95                     |
| 2     | Pt | 50                     |
| 3     | Au | trace                  |
| 4     | Ag | trace                  |

<sup>a</sup> Reaction conditions: nitrobenzene (1 mmol), M-DNA in Tris (4 ml). <sup>b</sup> Isolated yield.

### Comparison of Pd-DNA and other hydrogenation catalyst

**Table ESI-2** Comparison of Pd-DNA and other catalyst in hydrogenation<sup>a</sup>

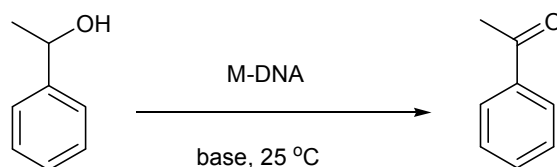


| Entry | Catalyst                   | Conversion (%) <sup>b</sup> | Yields (%) <sup>b</sup> |      |      |                       |
|-------|----------------------------|-----------------------------|-------------------------|------|------|-----------------------|
| 1     | Pd-DNA                     | >99                         | n.d.                    | n.d. | n.d. | >99(93 <sup>c</sup> ) |
| 2     | Pd/C (10%)                 | >99                         | 17                      | 30   | 26   | 27                    |
| 3     | Pt/C (5%)                  | >99                         | trace                   | 12   | n.d. | 88                    |
| 4     | Pd@diatomite <sup>d</sup>  | 52                          | n.d.                    | n.d. | n.d. | >99                   |
| 5     | Pd@MMT <sup>e</sup>        | 62                          | n.d.                    | n.d. | n.d. | >99                   |
| 6     | Pd-PVP <sup>f</sup>        | 40                          | n.d.                    | n.d. | n.d. | >99                   |
| 7     | Pd-Starch <sup>f,g</sup>   | 45                          | n.d.                    | n.d. | n.d. | >99                   |
| 8     | Pd-Gum Arabic <sup>f</sup> | 63                          | n.d.                    | n.d. | n.d. | >99                   |

<sup>a</sup> Reaction conditions: 4-nitroacetophenone (1 mmol), Pd-DNA in Tris (4 ml) and 2 ml EtOH in entry 1; 1.8 mol % different catalysts in 4 ml Tris buffer and 2 ml EtOH in entry 2-8. <sup>b</sup> Conversions and yields were determined by the area ratio of substrates and products in GC-MS spectra. n.d. : not detected. <sup>c</sup> Isolated yield. <sup>d</sup> The Pd@diatomite NPs were synthesized according to ref. 3. <sup>e</sup> The Pd@Na-MMT NPs were synthesized according to ref. 3 by the similar method using Na-MMT instead of diatomite. Na-MMT = sodium montmorillonite. <sup>f</sup> The water-soluble Pd nano-catalysts were synthesized by the similar method as Pd-DNA using other water-soluble templates such as PVP, starch and gum Arabic instead of DNA. PVP = Poly vinylpyrrolidone. <sup>g</sup> Pd NPs were aggregated and homogeneous water solution was destroyed after the reaction.

## Optimization of oxidation of alcohol to ketone

**Table ESI-3.** Optimization of oxidation reaction catalyzed by M-DNA<sup>a</sup>



| Entry | M         | base   | gas                  | time (h)  | Yield (%) <sup>b</sup> |
|-------|-----------|--|----------------------|-----------|------------------------|
| 1     | Pd        | NaOH   | air                  | 10        | 6                      |
| 2     | Au        | NaOH   | air                  | 10        | 20                     |
| 3     | Ag        | NaOH   | air                  | 10        | n.d.                   |
| 4     | Pt        | NaOH   | air                  | 10        | trace                  |
| 5     | Au        | KOH  | air                  | 10        | 25                     |
| 6     | Au        | LiOH·H <sub>2</sub> O                              | air                  | 10        | 45                     |
| 7     | Au        | Na <sub>2</sub> CHO <sub>3</sub>                   | air                  | 10        | 19                     |
| 8     | Au        | K <sub>2</sub> CO <sub>3</sub>                     | air                  | 10        | 15                     |
| 9     | Au        | Cs <sub>2</sub> CO <sub>3</sub>                    | air                  | 10        | 12                     |
| 10    | Au        | KOAc   | air                  | 10        | trace                  |
| 11    | Au        | CH <sub>3</sub> CH <sub>2</sub> ONa                | air                  | 10        | 21                     |
| 12    | Au        | <sup>t</sup> BuOK                                  | air                  | 10        | 44                     |
| 13    | Au        | K <sub>3</sub> PO <sub>4</sub> ·3H <sub>2</sub> O  | air                  | 10        | 29                     |
| 14    | Au        | K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O | air                  | 10        | trace                  |
| 15    | Au        | LiOH·H <sub>2</sub> O                              | O <sub>2</sub>       | 10        | 88                     |
| 16    | Au        | <sup>t</sup> BuOK                                  | O <sub>2</sub>       | 10        | 80                     |
| 17    | <b>Au</b> | <b>LiOH·H<sub>2</sub>O</b>                         | <b>O<sub>2</sub></b> | <b>12</b> | <b>&gt;99</b>          |

<sup>a</sup> Reaction conditions: 1-phenylethanol (0.5 mmol), 2 ml of initial M-DNA (~2 mol %) redissolved in 2 ml solution of 1 mmol bases, O<sub>2</sub> balloon or air, 25 °C. <sup>b</sup> Determined by GC-MS analysis with internal standard.

## Comparison of Au-DNA and other hydrogenation catalyst

**Table ESI-4** Comparison of Au-DNA and other Au catalyst in oxidation<sup>a</sup>

1.9 mol % Au Catalyst  
LiOH·H<sub>2</sub>O  
O<sub>2</sub> balloon, 25 °C, 12h

| Entry          | Au Catalyst                       | Yield (%) <sup>b</sup> | Entry             | Au Catalyst   | Yield (%) <sup>b</sup> |
|----------------|-----------------------------------|------------------------|-------------------|---------------|------------------------|
| 1              | Au-DNA                            | >99                    | 8 <sup>c</sup>    | Au@diatomite  | 14                     |
| 2 <sup>c</sup> | Au@TiO <sub>2</sub>               | 32                     | 9 <sup>c</sup>    | Au@kaolin     | 23                     |
| 3 <sup>c</sup> | Au@SiO <sub>2</sub>               | 10                     | 10 <sup>c</sup>   | Au@Na-MMT     | 34                     |
| 4 <sup>c</sup> | Au@Al <sub>2</sub> O <sub>3</sub> | 44                     | 11 <sup>d</sup>   | Au-PVP        | 55                     |
| 5 <sup>c</sup> | Au@ZnO                            | 25                     | 12 <sup>d,e</sup> | Au-Starch     | 83                     |
| 6 <sup>c</sup> | Au@Fe <sub>2</sub> O <sub>3</sub> | 10                     | 13 <sup>d,e</sup> | Au-Gum Arabic | 97                     |
| 7 <sup>c</sup> | Au@ZrO <sub>2</sub>               | 26                     |                   |               |                        |

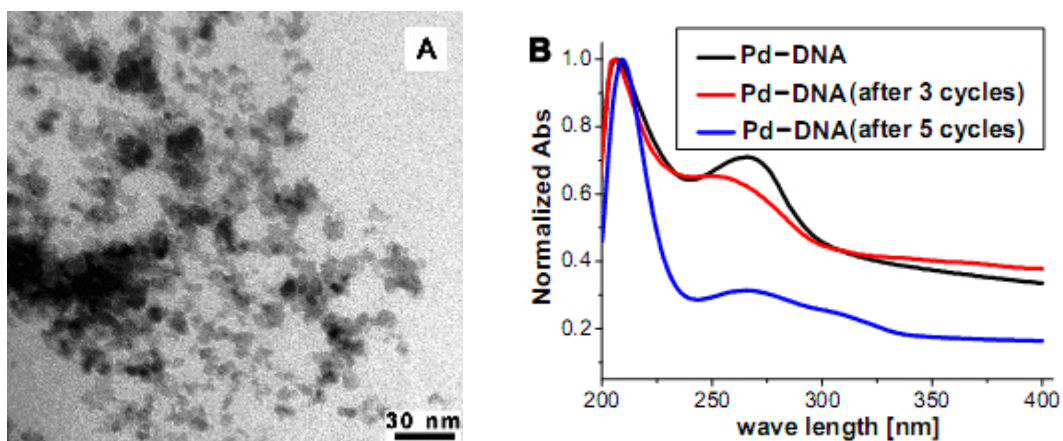
<sup>a</sup> Reaction conditions: 1-phenylethynol (0.5 mmol), 2 ml of initial Au-DNA redissolved in 2 ml solution of 1 mmol LiOH·H<sub>2</sub>O for entry 1; Au catalysts (1.9 mol %), LiOH·H<sub>2</sub>O (1 mmol), deionized water (2 ml) in entries 2 to 13; O<sub>2</sub> balloon, 25 °C, 12 h. <sup>b</sup> Determined by GC-MS analysis with internal standard. <sup>c</sup> The water-insoluble Au nano-catalysts were synthesized using the homogeneous deposition–precipitation technique according to ref. 4. The loading of Au is 4 wt%. Na-MMT = sodium montmorillonite. <sup>d</sup> The water-soluble Pd nano-catalysts were synthesized by the similar method as Au-DNA using other water-soluble templates such as PVP, starch and gum Arabic instead of DNA. PVP = Poly vinylpyrrolidone. <sup>e</sup> Au NPs were aggregated and homogeneous water solution was destroyed after the reaction.

## Reference

- 3 Z. H. Zhang, Z. Y. Wang, *J. Org. Chem.* 2006, **71**, 7485.  
4 (a) R. Zanella, S. Giorgio, C. R. Henry, C. Louis, *J. Phys. Chem. B.* 2002, **106**, 7634. (b) F. Moreau and G. C. Bond, *Catal. Today*, 2007, **122**, 260.

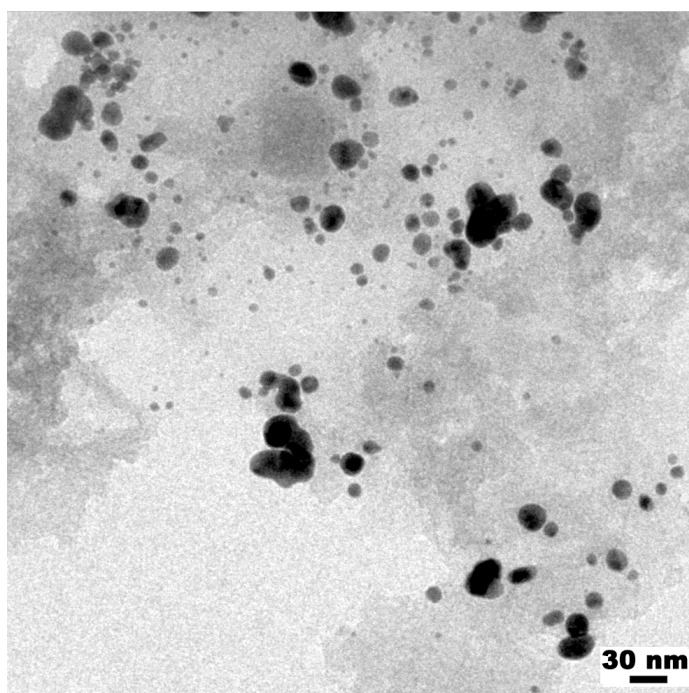
## Characterization of Pd-DNA and Au-DNA after recycles

### Characterization of Pd-DNA after recycles



**Fig. ESI-6** (A) TEM image of the Pd-DNA nanohybrid after fifth round; (B) UV-Vis of the Pd-DNA nanohybrid before reaction, after third and fifth round.

### Characterization of Au-DNA after recycles



**Fig. ESI-7** TEM image of Au-DNA nanohybrid after seventh round.

## Characterization data of hydrogenation products

### Aniline (2a).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.12 (ddd,  $J$ = 7.4, 6.6, 0.8 Hz, 2H), 6.73 (t,  $J$ = 7.4 Hz, 1H), 6.61 (dd,  $J$ = 7.4, 0.8 Hz, 2H), 3.54 (s, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 146.5, 129.3, 116.5, 115.1.

HRMS: calcd for  $\text{C}_6\text{H}_7\text{N}$ : 93.0578, found 93.0576.

### o-Toluidine (2b).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.00 (t,  $J$ = 7.4 Hz, 2H), 6.67 (t,  $J$ = 7.4 Hz, 1H), 6.60 (d,  $J$ = 7.7 Hz, 1H), 3.48 (s, 2H), 2.11 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 144.6, 130.4, 126.9, 122.3, 118.6, 114.9, 17.3.

HRMS: calcd for  $\text{C}_7\text{H}_9\text{N}$ : 107.0735, found 107.0731.

### p-Toluidine (2c).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 6.94 (d,  $J$ = 8.0 Hz, 2H), 6.57 (d,  $J$ =8.0 Hz, 2H), 3.46 (s, 2H), 2.22 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 143.9, 129.8, 127.6, 115.3, 20.5.

HRMS: calcd for  $\text{C}_7\text{H}_9\text{N}$ : 107.0735, found 107.0733.

### 4-methoxybenzenamine (2d).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 6.72 (d,  $J$ = 8.8 Hz, 2H), 6.59 (d,  $J$ =8.8 Hz, 2H), 3.70 (s, 2H), 3.40 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 152.7, 140.1, 116.3, 114.8, 55.7.

HRMS: calcd for  $\text{C}_7\text{H}_7\text{N}$ : 123.0684, found 123.0681.

**4-aminobenzoic acid (2e).**

$^1\text{H}$  NMR (300 MHz,  $d^6$ -DMSO):  $\delta$  [ppm] = 11.94 (br, 1H), 7.64 (d,  $J=8.3$  Hz, 2H), 6.56 (d,  $J=8.3$  Hz, 2H), 5.83 (br, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $d^6$ -DMSO):  $\delta$  [ppm] = 167.6, 157.1, 131.3, 117.0, 112.7.

HRMS: calcd for  $\text{C}_7\text{H}_7\text{NO}_2$ : 137.0477, found 137.0472.

**ethyl 4-aminobenzoate (2f).**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.87 (dd,  $J=6.8, 2.0$  Hz, 2H), 6.65 (dd,  $J=6.8, 2.0$  Hz, 2H), 4.33 (q,  $J=7.1$  Hz, 2H), 4.05 (br, 2H), 1.38 (t,  $J=7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 166.9, 151.0, 131.5, 119.8, 113.8, 60.3, 14.4.

HRMS: calcd for  $\text{C}_9\text{H}_{11}\text{NO}_2$ : 165.0790, found 165.0792.

**4-aminophenyl 4-methylbenzenesulfonate (2g).**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.68 (d,  $J=8.0$  Hz, 2H), 7.28 (d,  $J=8.0$  Hz, 2H), 6.73 (d,  $J=8.7$  Hz, 2H), 6.51 (d,  $J=8.7$  Hz, 2H), 3.65 (br, 2H), 2.44 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 145.5, 145.2, 141.6, 132.5, 129.7, 128.6, 123.2, 115.4, 21.7.

HRMS: calcd for  $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{S}$ : 263.0616, found 263.0617.

**Benzene-1,3-diamine (2h).**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 6.93 (t,  $J=7.9$  Hz, 1H), 6.10 (dd,



$J=7.9, 2.1$  Hz, 2H), 6.00 (t,  $J=2.1$  Hz, 1H), 3.51 (s, 4H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 147.6, 130.2, 106.0, 102.0.

HRMS: calcd for  $\text{C}_6\text{H}_8\text{N}_2$ : 108.0687, found 108.0685.

### **2-aminobenzaldehyde (2i).**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 9.87 (s, 1H), 7.47 (d,  $J=7.7$  Hz, 1H), 7.31 (t,  $J=7.1$  Hz, 1H), 6.74 (t,  $J=7.4$  Hz, 1H), 6.65 (d,  $J=8.3$  Hz, 1H), 6.13 (br, 2H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 194.2, 150.0, 135.8, 135.3, 118.9, 116.5, 116.1.

HRMS: calcd for  $\text{C}_7\text{H}_7\text{NO}$ : 121.0528, found 121.0526.

### **1-(4-aminophenyl)ethanone (2j).**

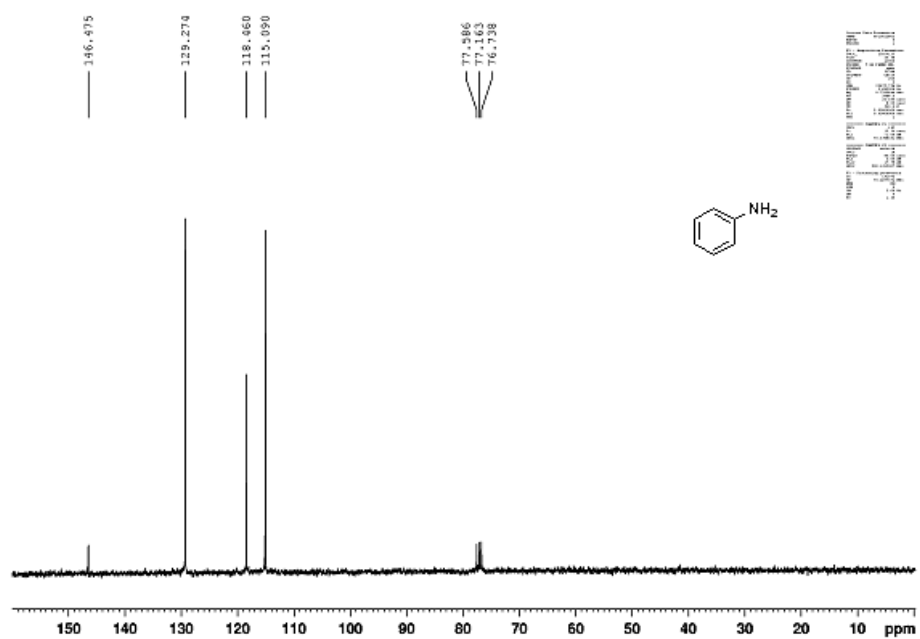
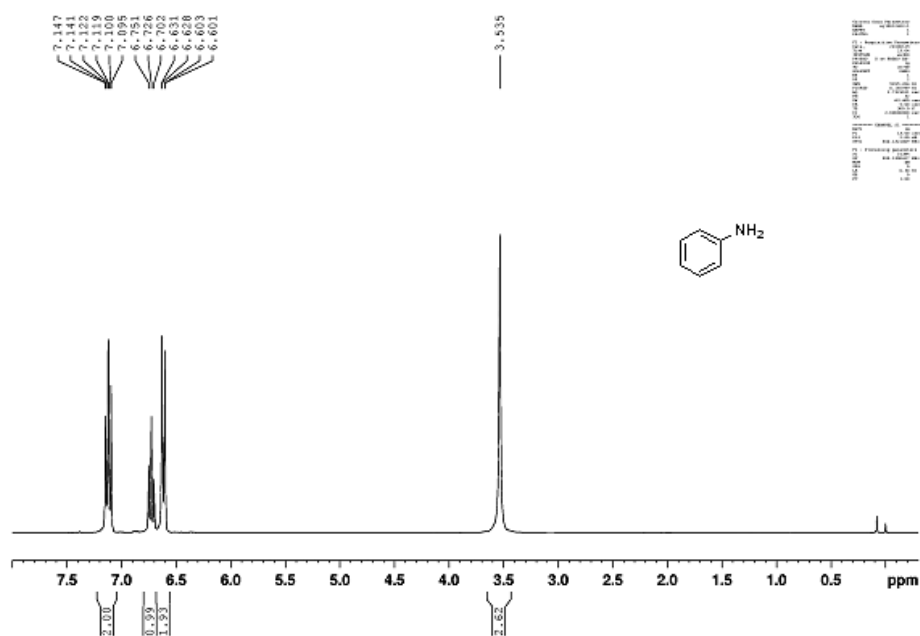
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 7.80 (d,  $J=8.7$  Hz, 2H), 6.64 (d,  $J=8.7$  Hz, 2H), 4.14 (br, 2H), 2.50 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = 196.7, 151.6, 130.8, 127.4, 113.6, 26.0.

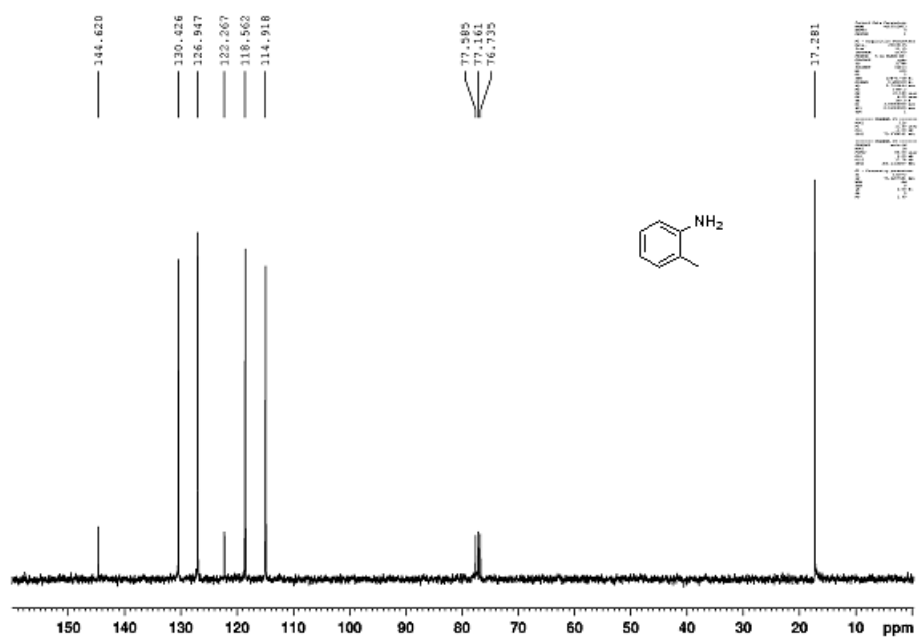
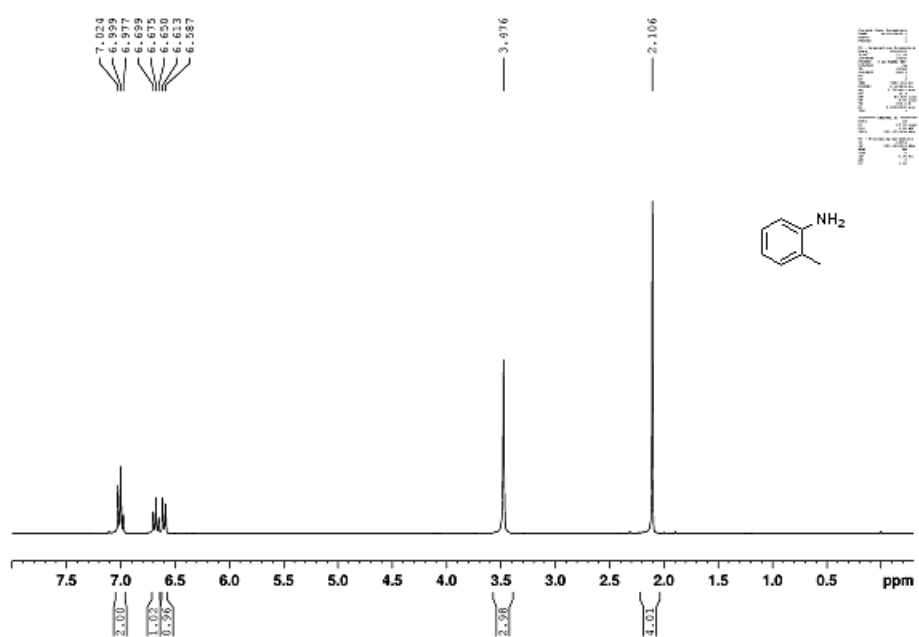
HRMS: calcd for  $\text{C}_8\text{H}_9\text{NO}$ : 135.0684, found 135.0688.

## NMR Spectra of hydrogenation products.

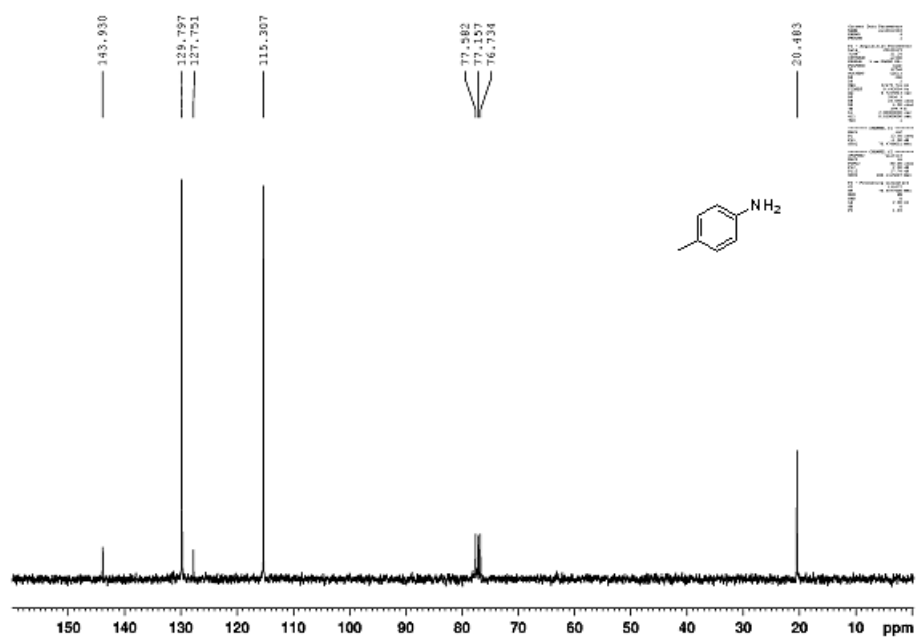
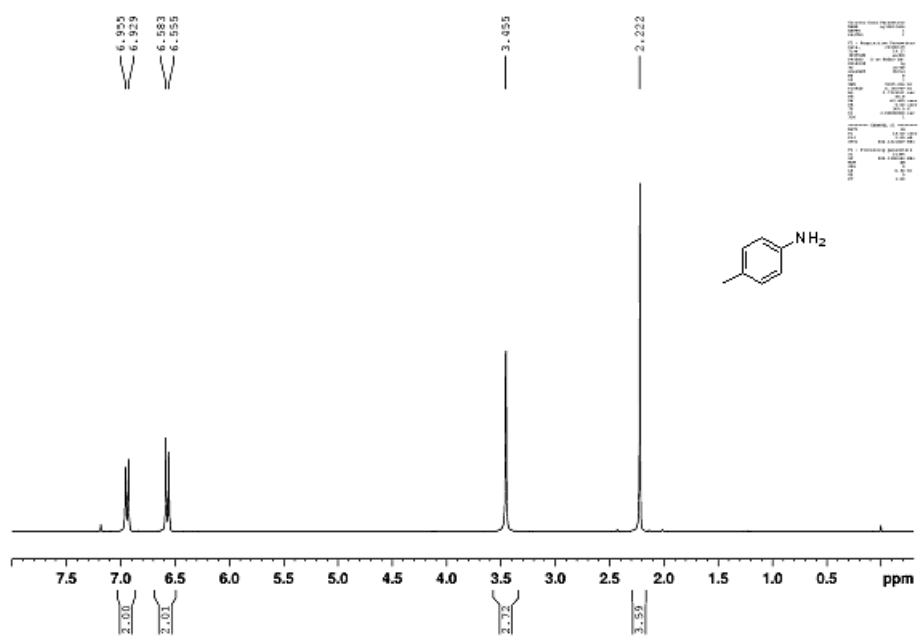
2a:



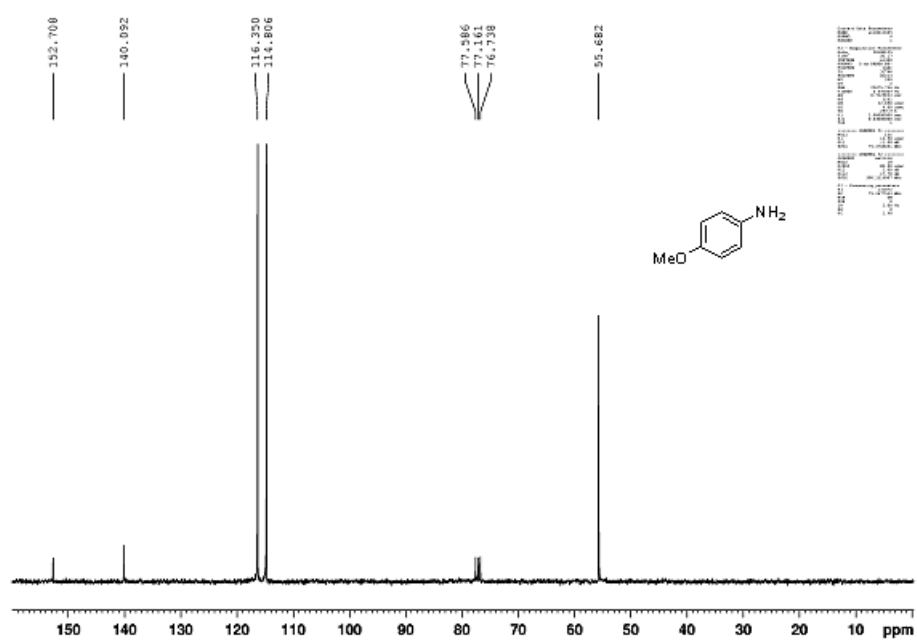
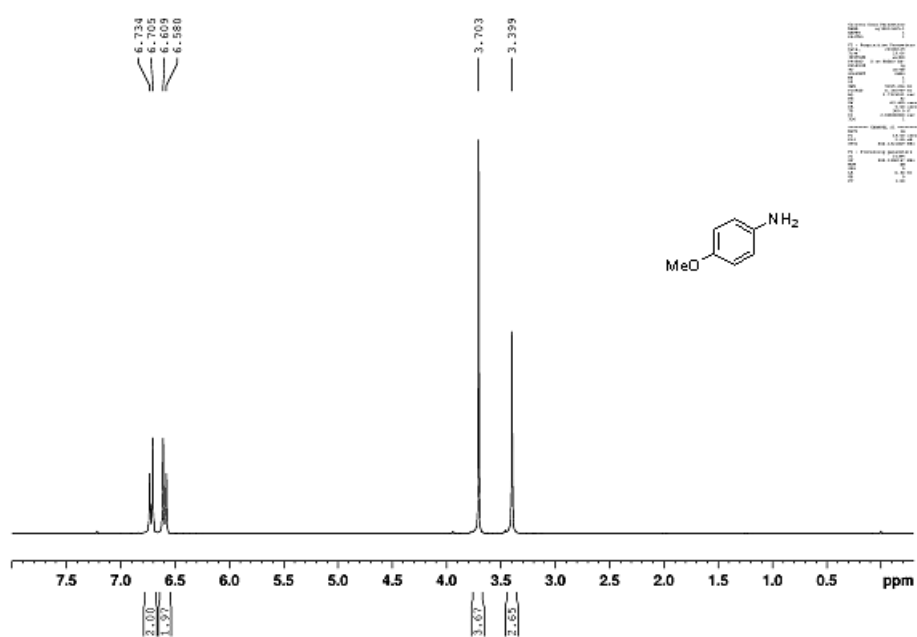
2b:



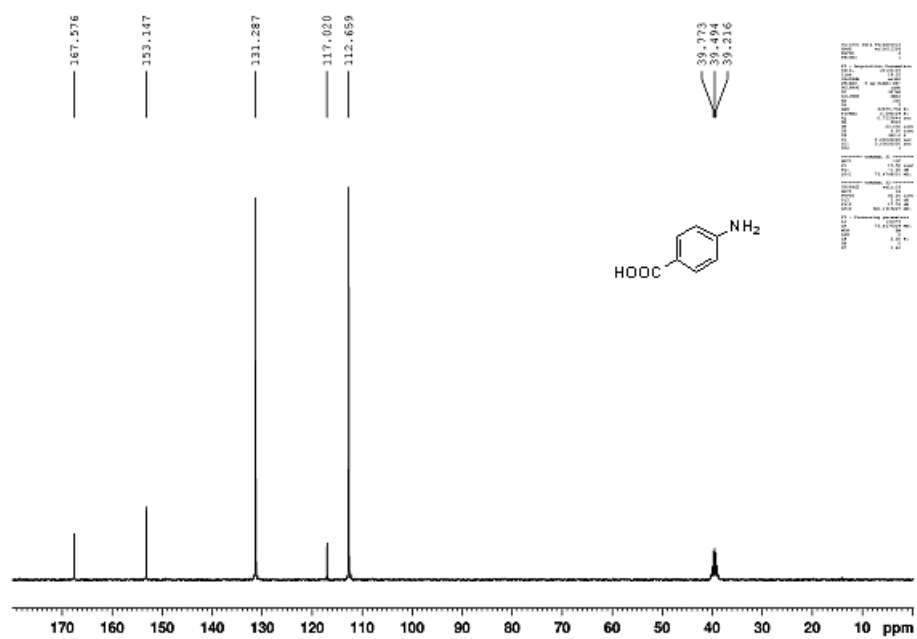
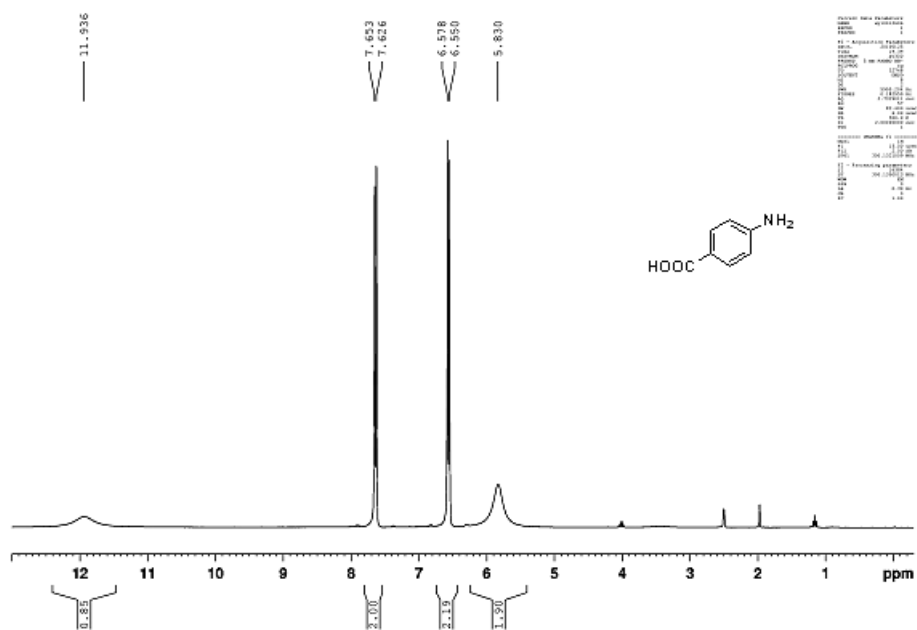
2c:



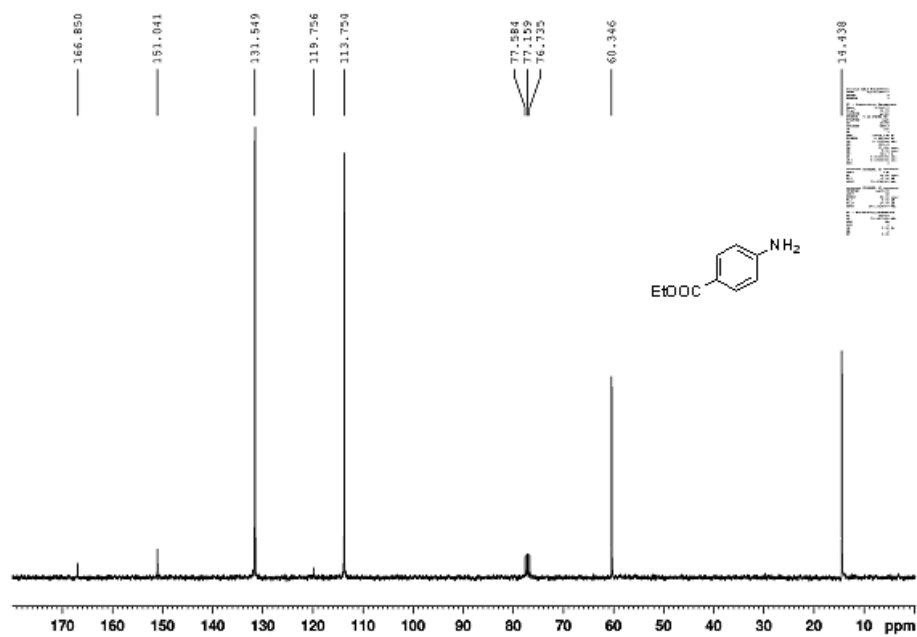
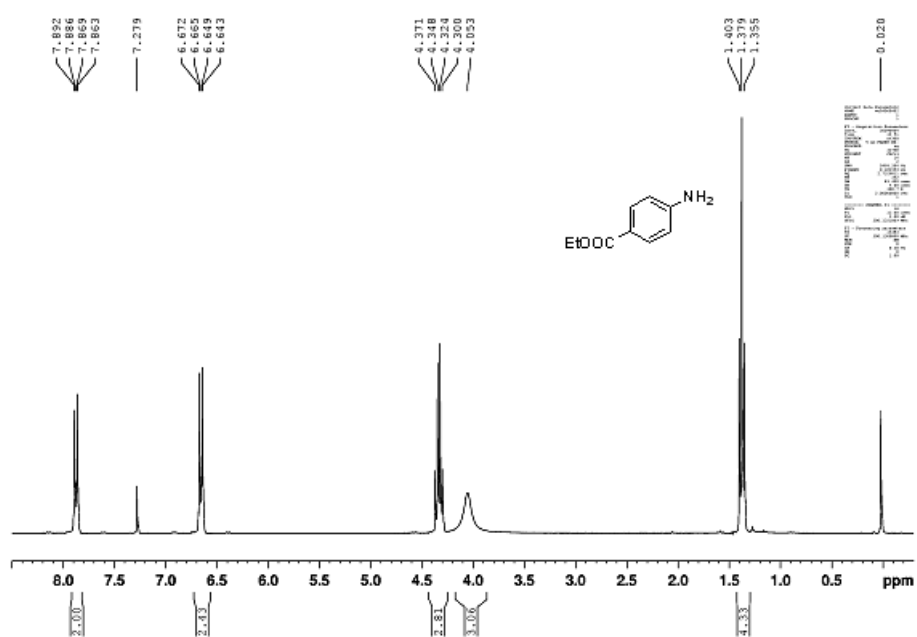
2d:



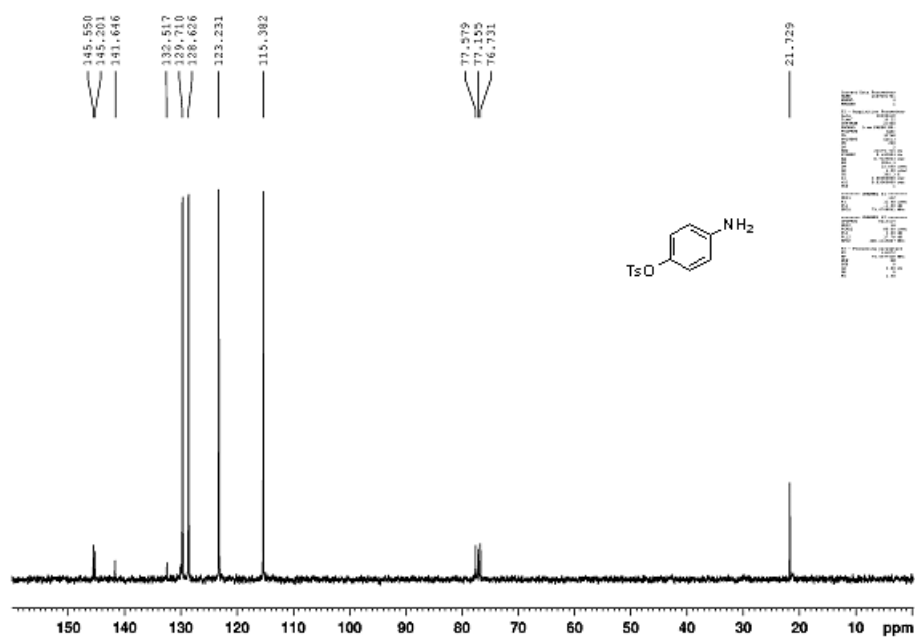
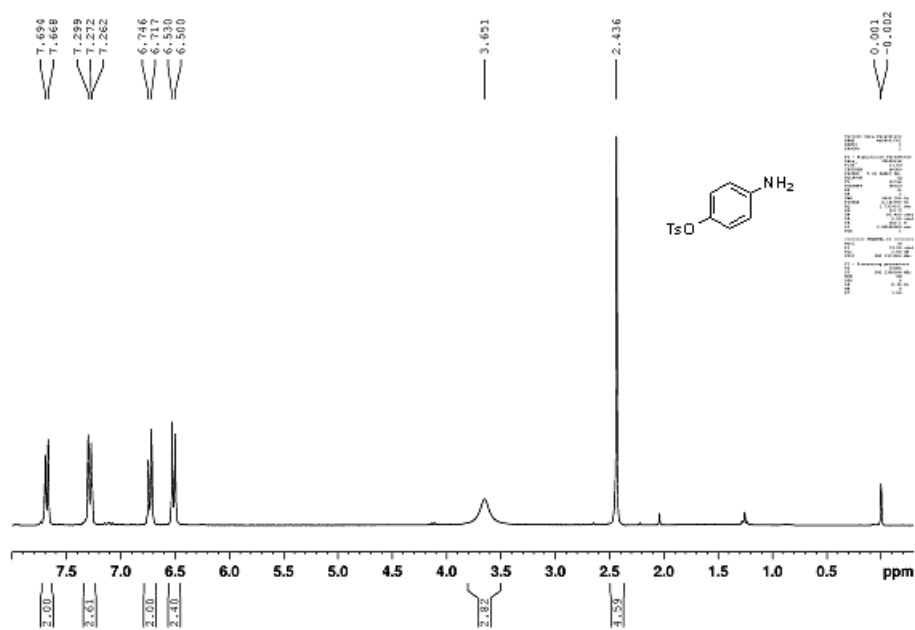
2e:



2f:

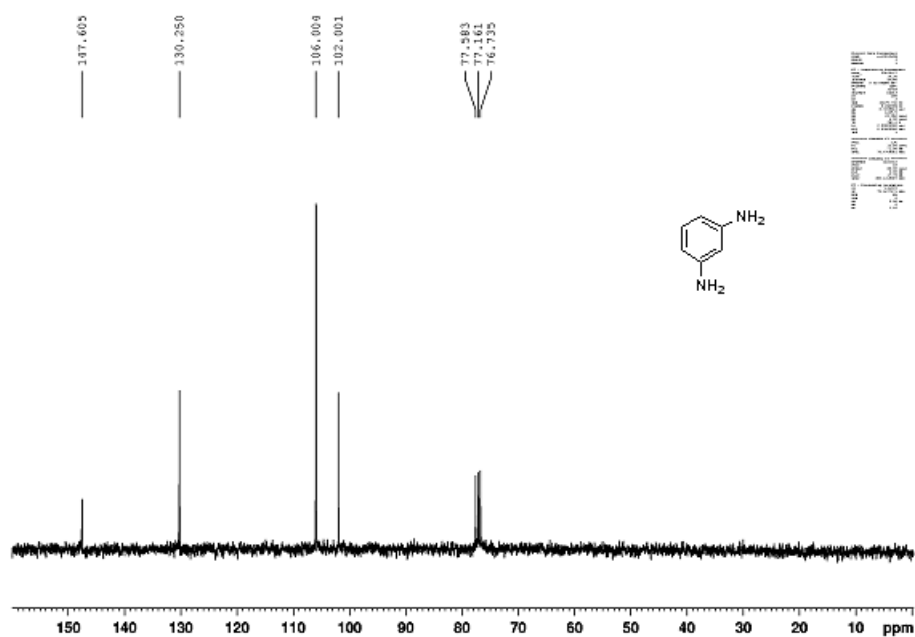
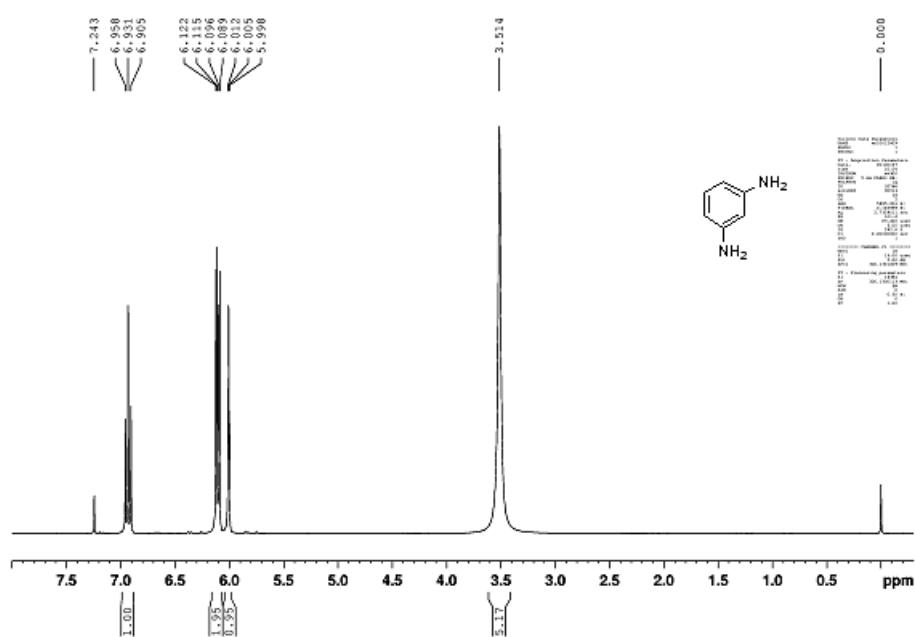


2g:

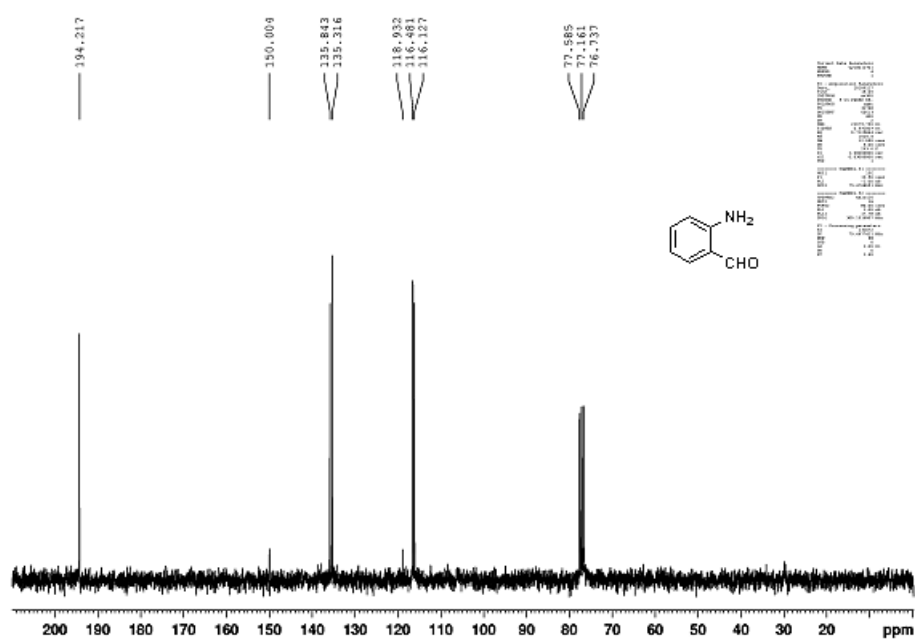
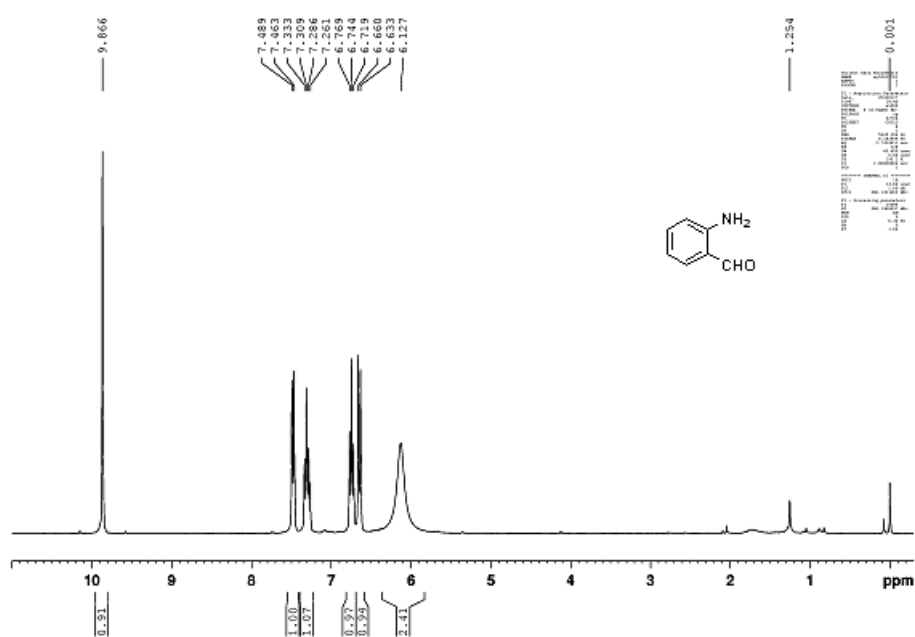




2h:



2i:



2j:

