Supporting Information

Fe_2O_3-supported nano-gold catalyzed one-pot synthesis of N-alkylated anilines from nitroarenes and alcohols

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1. Materials and Methods

All solvent and chemicals were obtained commercially and were used as received. NMR spectra were measured using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). All spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Mass spectra were in general recorded on an HP 6890/5973 GC-MS. High-resolution TEM analysis was carried out on a JEM 2010 operating at 200 KeV. The catalyst samples after pretreatment were dispersed in methanol, and the solution was mixed ultrasonically at room temperature. A part of solution was dropped on the grid for the measurement of TEM images. Scanning electron microscopy (SEM) was performed with a Hitachi S4800 with a cold FEG (Field Emission Gun). The setup was equipped with an Energy Dispersive X-ray system EDAX Genesis 4.52. Samples were mounted on Al-holder with conducting carbon tape. XRD measurements are conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation and a 6° position sensitive detector (PSD). The XRD patterns are scanned in the 2θ range of 10-50°. For the data interpretation the software WinXpow (STOE) and the database of Powder Diffraction File (PDF) of the International Centre of Diffraction Data (ICDD) were used. The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Mg anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar^+ ion-gun. All spectra were recorded using non-monochromatic Mg Ka (1253.6 eV) radiation. Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Ag and Mo contents of the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

2. Chlorine concentration measurement

The Cl^- ion concentration was tested at 25 ^oC through potentialstatic scanning on a CHI660D or electrochemical workstation. A Cl^- ion electrode was used as a working electrode and a platinum wire and an Ag/AgCl electrode were used as counter and reference electrodes respectively. Before analysis, a series of Cl^- ion standard solutions including 2.0 ppm, 4.0 ppm, 8.0 ppm, 40.0 ppm, 200.0 ppm and 400.0 ppm were prepared using NaCl as the Cl^- ion source. The potentialstatic scanning was carried out at interval of 0.1s for 1 min in the standard solutions, and the corresponding average potential value (mV) was obtained, which were repeated three times. The calibrated results were shown in Table S1 and Fig. S1. The electrode system was calibrated with a 5.0 ppm standard solution and the chlorine determination could be carried out through potentialstatic scanning when the error bar is less than 0.5%.

Table S1. The results for Cl^- ion standard solutions and corresponding potentials

Concentration	Average Potential (standard deviation)/mV
2.0 ppm	253.0 (8.0) mV
4.0 ppm	237.0 (9.8)mV
8.0 ppm	222.7 (7.6)mV
40.0 ppm	187.7 (2.3)mV
200.0 ppm	150.0 (2.0)mV
400.0 ppm	131.7 mV (1.2mV)

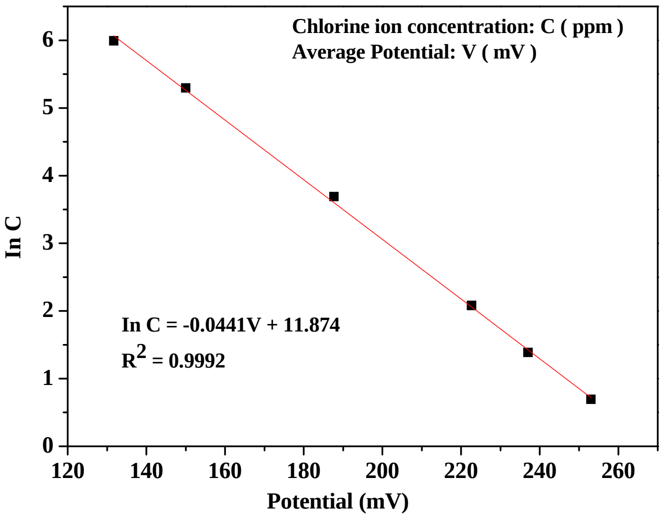


Fig. S1. The linearity of Cl^- ion standard solutions and corresponding potentials

3. Catalyst preparation

General procedure for the preparation of Fe_2O_3

An aqueous solution (16 mL) of $Fe(NO_3)_3 \cdot 9H_2O$ (13.00 mmol, 5.24 g) was drop wise added into 75 mL Na_2CO_3 solution (0.47 M) under vigorous stirring in 0.5 h, then ultrasonic washed for 1 h and centrifuged (10000 rpm for 10 min). The recovered precipitate was redispersed in 1000 mL distilled water and further ultrasonic washed for 1 h. Then the resulting slurry was calcined at 350 ^{o}C in static air. The temperature was ramped from room temperature at a rate of 8.75 ^{o}C/min to the final temperature, which was maintained for 5 h. In the end, ～1.00 g brown Fe_2O_3 catalyst was obtained.

General procedure for the preparation of Au/Fe_2O_3

Au/Fe_2O_3 catalysts were prepared by co-precipitation method. Aqueous solution (16 mL) of $Fe(NO_3)_3 \cdot 9H_2O$ (13.00 mmol, 5.24 g) and 0.63 mL, 1.02 mL, 1.47 mL, or 2.10 mL $HAuCl_4 \cdot 4H_2O$ (1g/10mL) were mixed and added into 75 mL Na_2CO_3 solution (0.47 M) under vigorous stirring in 0.5 h, then ultrasonic washed for 1 h and centrifuged (10000 rpm for 10 min). The recovered precipitates were redispersed in 330 mL, 500 mL, 700 mL and 1000 mL distilled water respectively and further ultrasonic washed for 1 h to remove residual chlorine. The operation was repeated till the remaining Cl^- ion concentration was less than 6 ppm. Then the resulting slurries were calcined at 350 ^{o}C in static air. The temperature was ramped from room temperature at a rate of 8.75 ^{o}C/min to the final temperature, which was maintained for 5 h. In the end, four different Au loading of ～1.00 g black Au/Fe_2O_3 catalysts were obtained and denoted as 1.8wt% Au/Fe_2O_3, 4.3wt% Au/Fe_2O_3, 6.3wt% Au/Fe_2O_3 and 9.1wt% Au/Fe_2O_3 respectively.

The catalysts Au/CeO_2, Au/Co_3O_4, Au/NiO, Pd/Fe_2O and Ru/Fe_2O_3 were prepared with the same procedure.

4. Table S2. ICP-AES and BET data of various catalysts

Sample	Loading (wt %)	Surface area (m^2/g)	Pore volume (cm^3/g)	BET average pore diameter (Å)
Fe_2O_3	0	135.2	0.354	110.2
Au/Fe_2O_3	1.8	85.6	0.291	136.0
Au/Fe_2O_3	4.3	73.6	0.278	151.4
Au/Fe_2O_3	6.3	97.8	0.375	153.2
Au/Fe_2O_3	9.1	129.8	0.304	93.5
Au/CeO_2	4.6	77.4	0.055	28.6
Au/CoO	2.8	95.4	0.495	207.4
Au/NiO	2.5	128.1	0.210	65.4
Pd/Fe_2O_3	3.6	162.0	0.423	104.4
Ru/Fe_2O_3	2.9	101.0	0.335	132.7

5. General procedure for the reaction of nitrobenzene with d_7-benzyl alcohol

I. 0.1 mmol (12.3 mg) nitrobenzene, 1.0 mmol (115.0 mg) d_7-benzyl alcohol and 20 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube. Then, it was reacted at 160 °C under argon atmosphere for 1 h. After it was cooled to room temperature, the reaction mixture was dissolved in acetone and analyzed by GC-MS.

II. 0.1 mmol (12.3 mg) nitrobenzene, 1.0 mmol (115.0 mg) d_7-benzyl alcohol and 20 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube. Then, it was reacted at 160 °C under argon atmosphere for 2h. After it was cooled to room temperature, the reaction mixture was dissolved in acetone and analyzed by GC-MS.

6. General procedure for the H-D exchange reaction between aniline and D_2O

25.0 mmol (500.0 mg) D_2O, 12.5 mmol (1164.0 mg) aniline and 50 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 160 °C under argon atmosphere for 2.5 h. Then, the reaction mixture was dissolved in acetone after it was cooled to room temperature and analyzed by GC-MS.

7. Fig. S2. XRD patterns of the catalysts in the experiments.

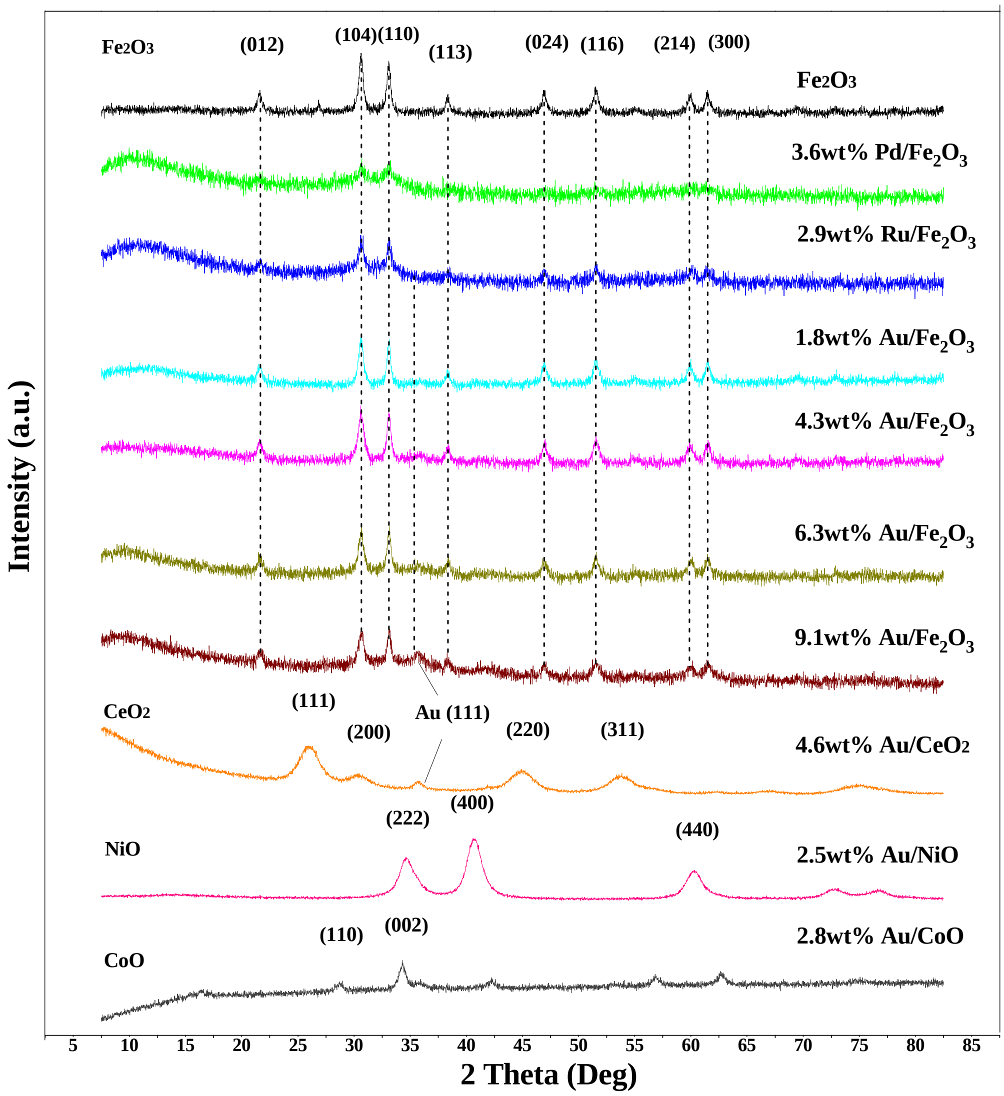


Fig. S2a. XRD patterns of the catalyst samples

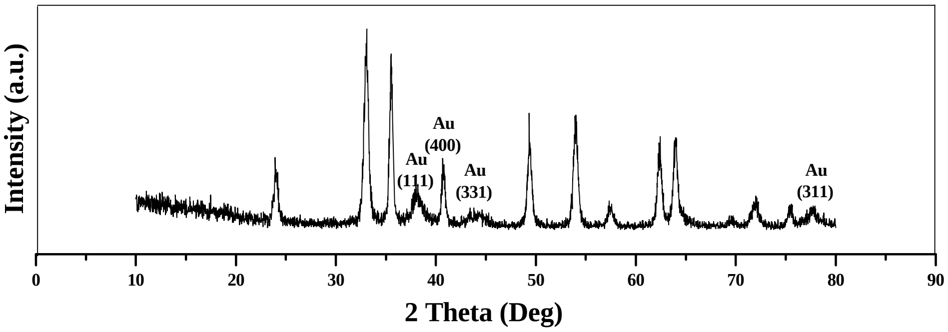


Fig. S2b. XRD patterns of 9.1wt% Au/Fe$_2$O$_3$ after being used for 2 times

8. XPS spectra of catalyst samples

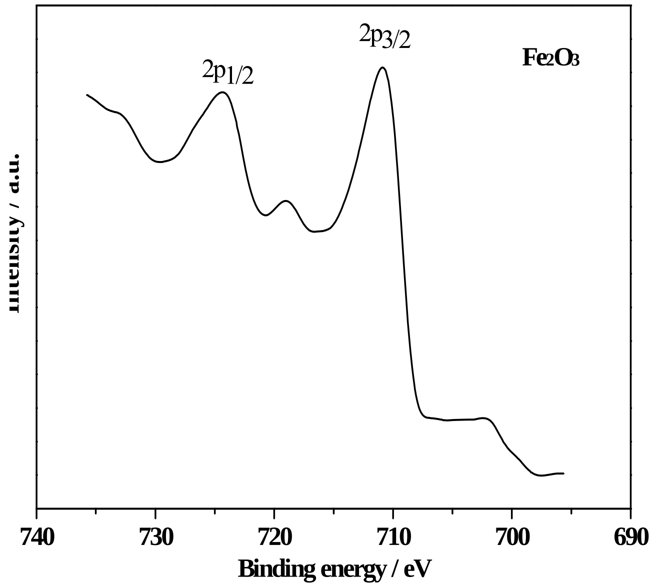


Fig. S3a. XPS spectra of the Fe_2O_3

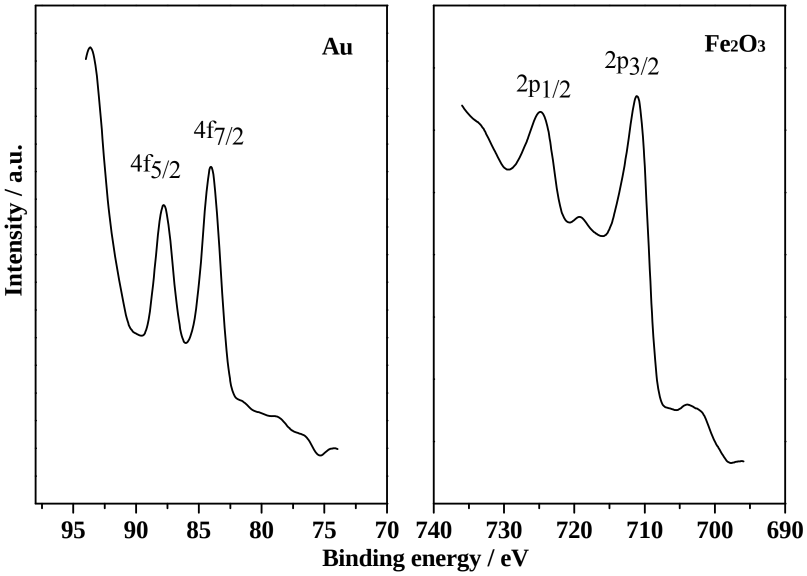


Fig. S3b. XPS spectra of the 1.8 wt % Au/Fe_2O_3

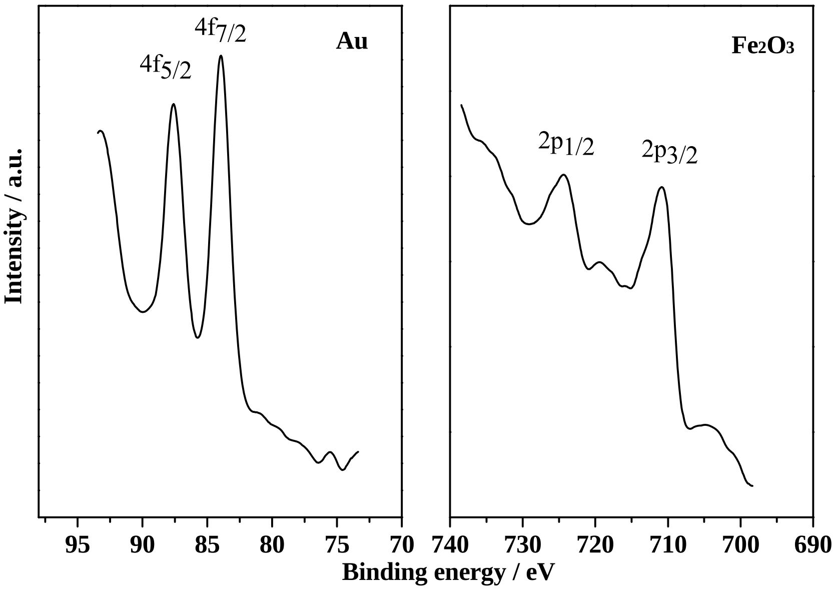


Fig. S3c. XPS spectra of the 4.3 wt % Au/Fe_2O_3

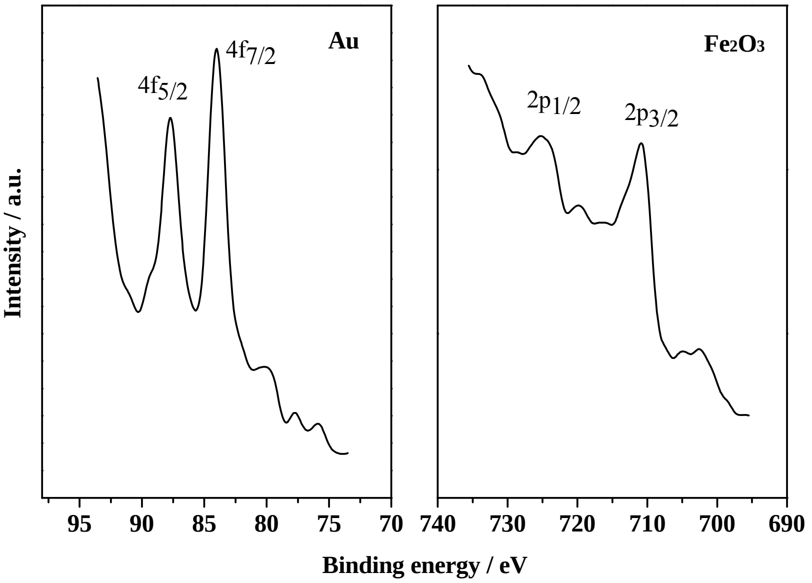


Fig. S3d. XPS spectra of the 6.3 wt % Au/Fe_2O_3

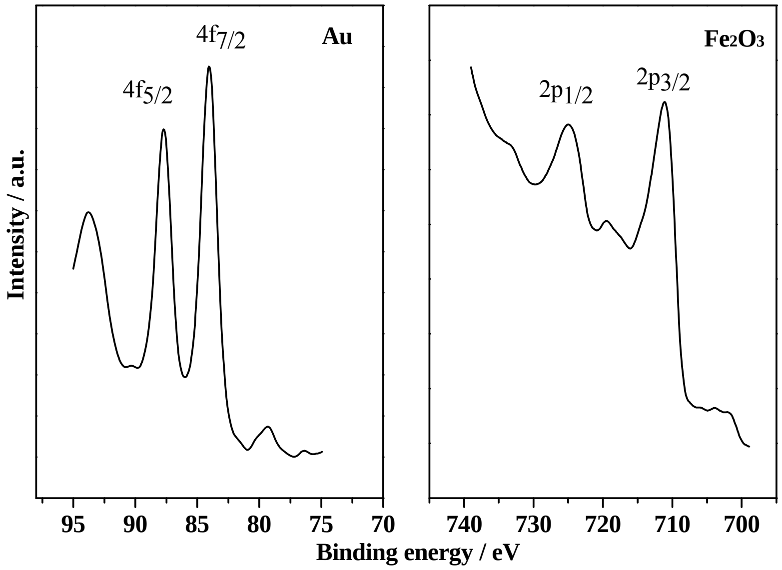


Fig. S3e. XPS spectra of the 9.1wt % Au/Fe_2O_3

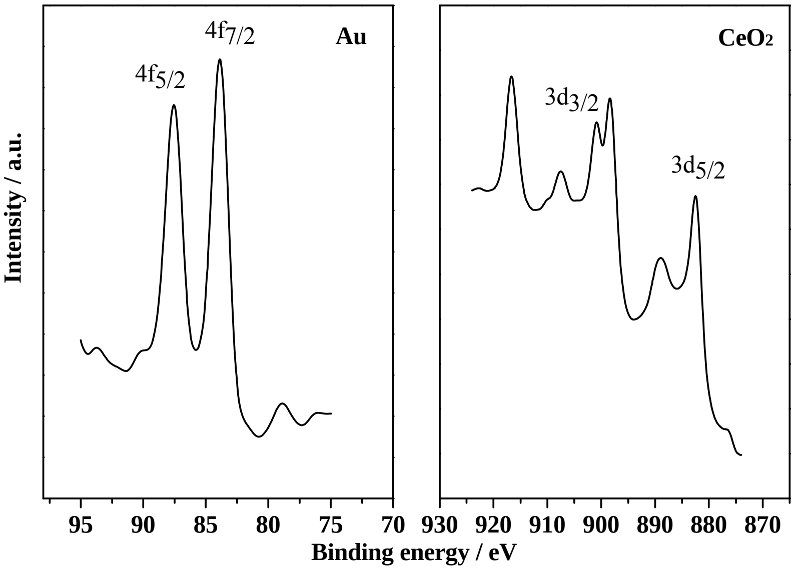


Fig. S3f. XPS spectra of the 4.6wt % Au/CeO_2

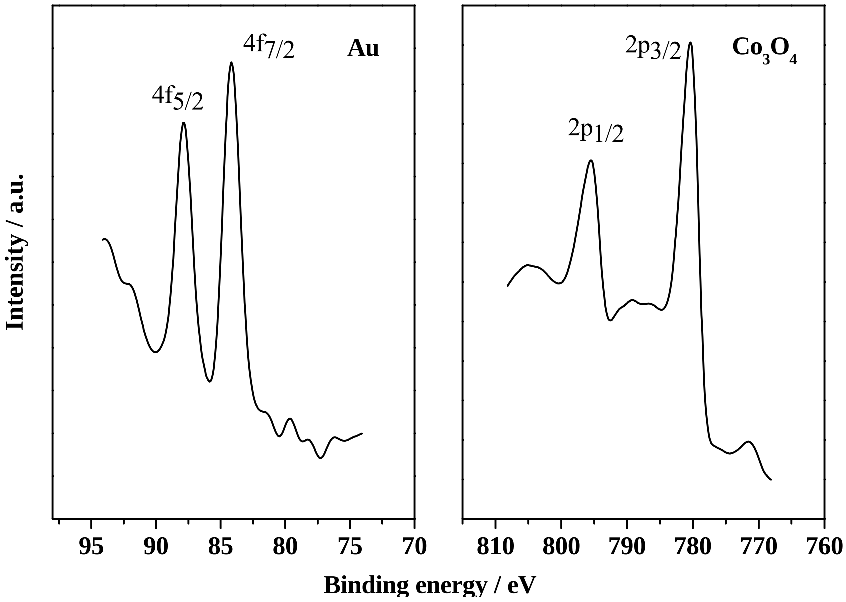


Fig. S3g. XPS spectra of the 2.8 wt % Au/Co_3O_4

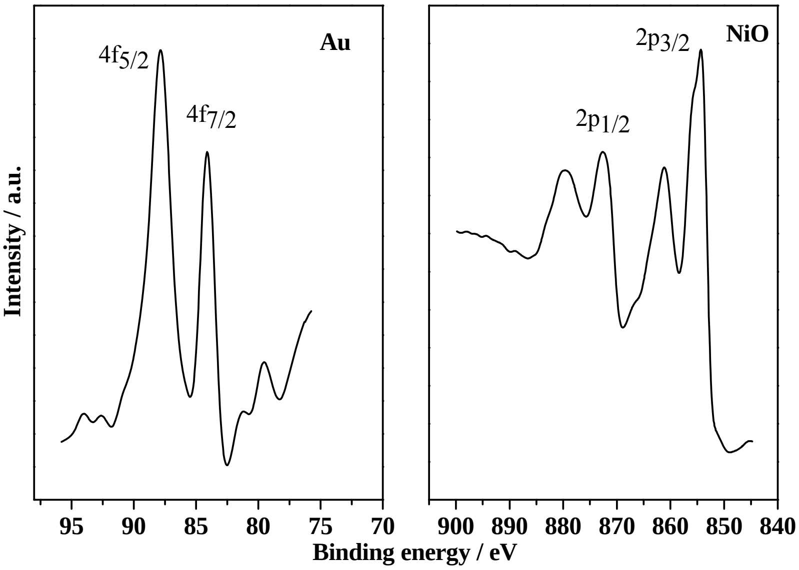


Fig. S3h. XPS spectra of the 2.5wt % Au/NiO

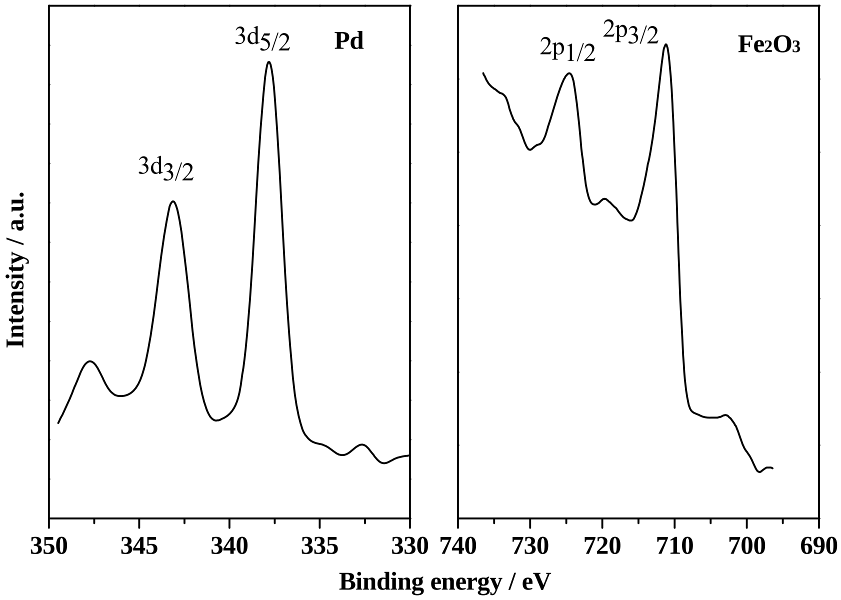


Fig. S3i. XPS spectra of the 3.6wt % Pd/Fe_2O_3

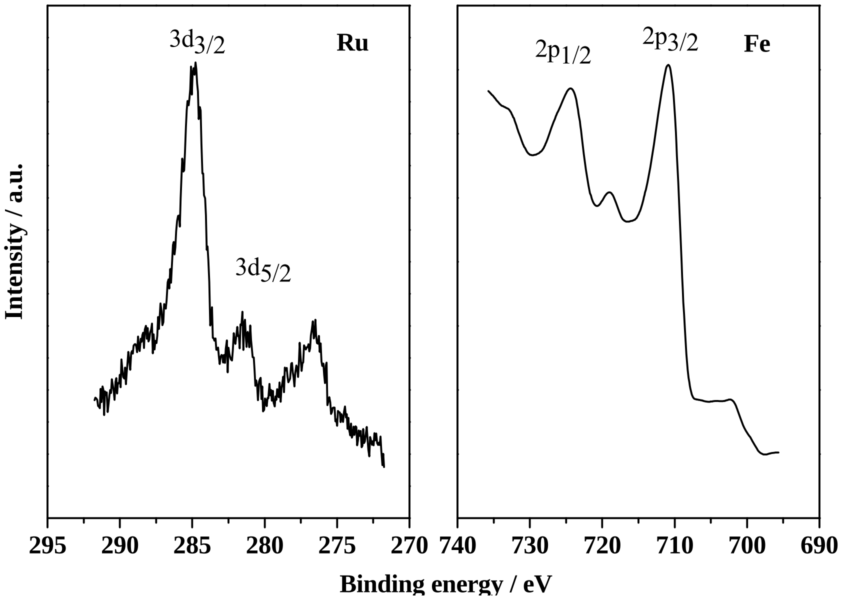
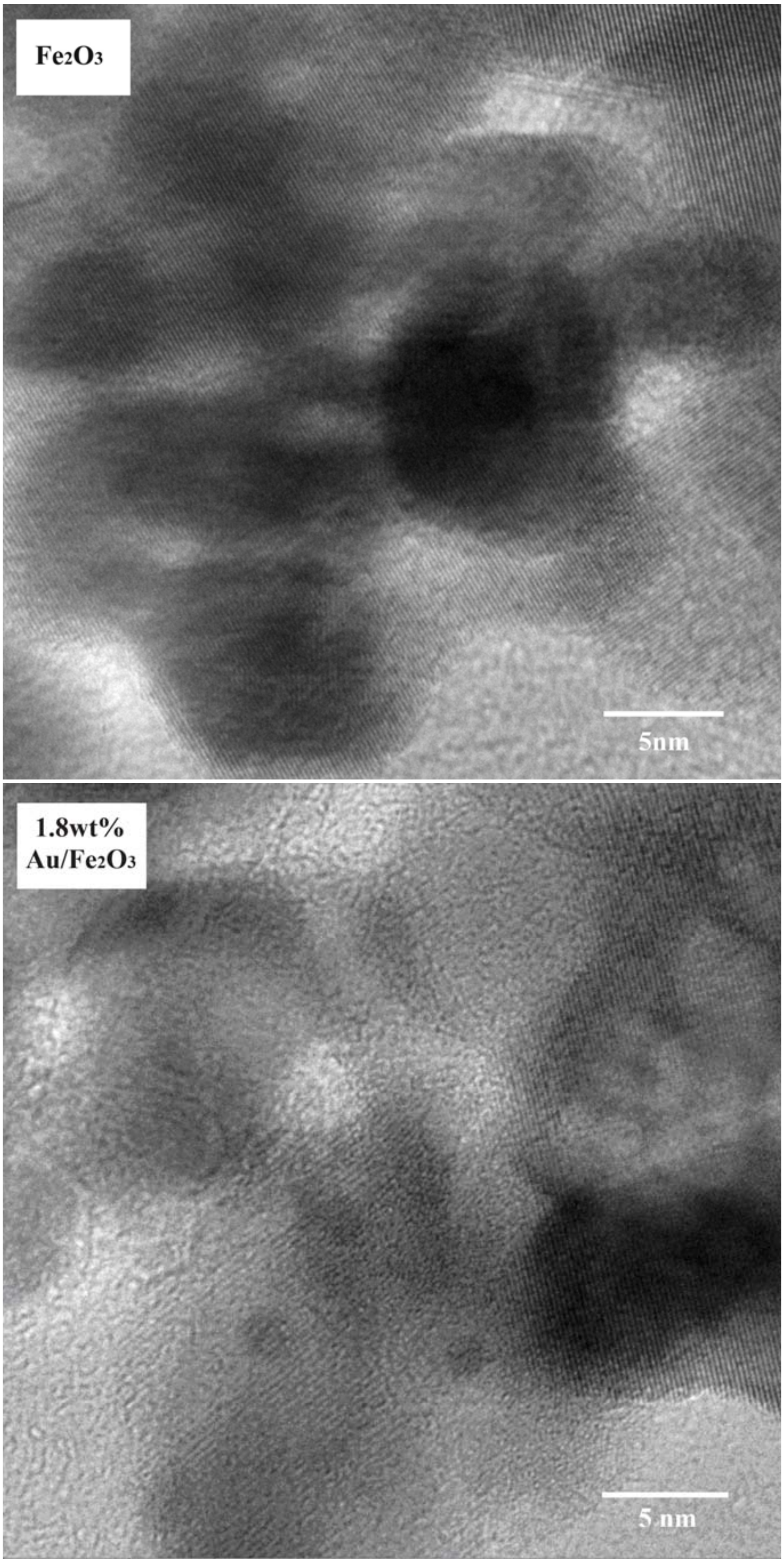
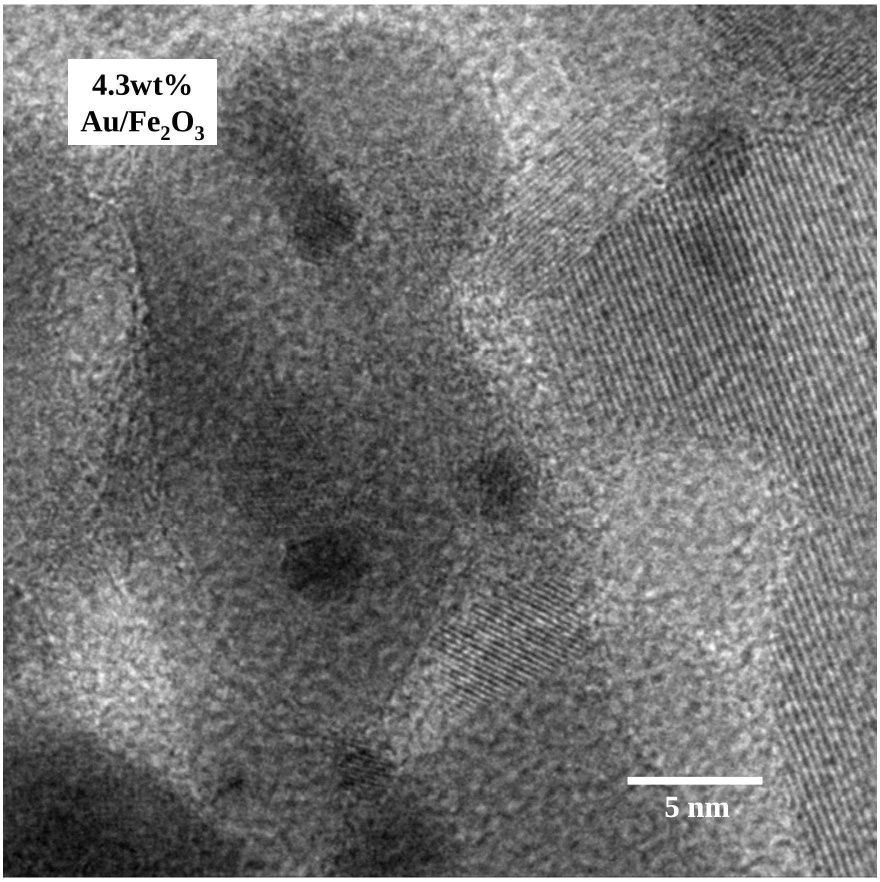
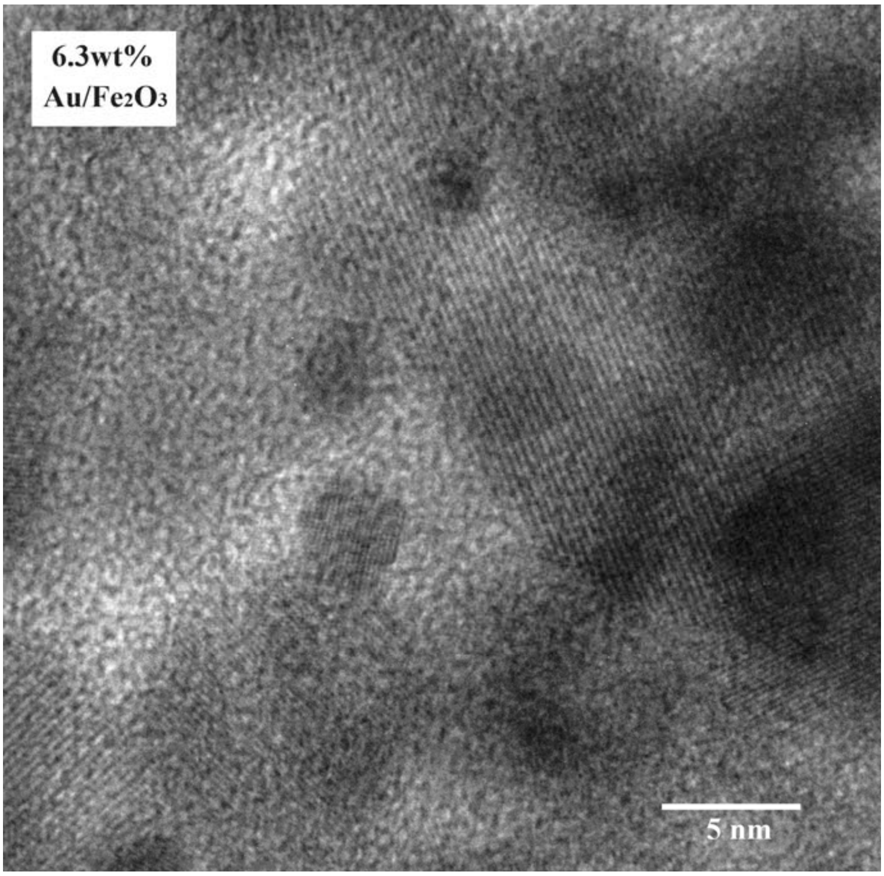


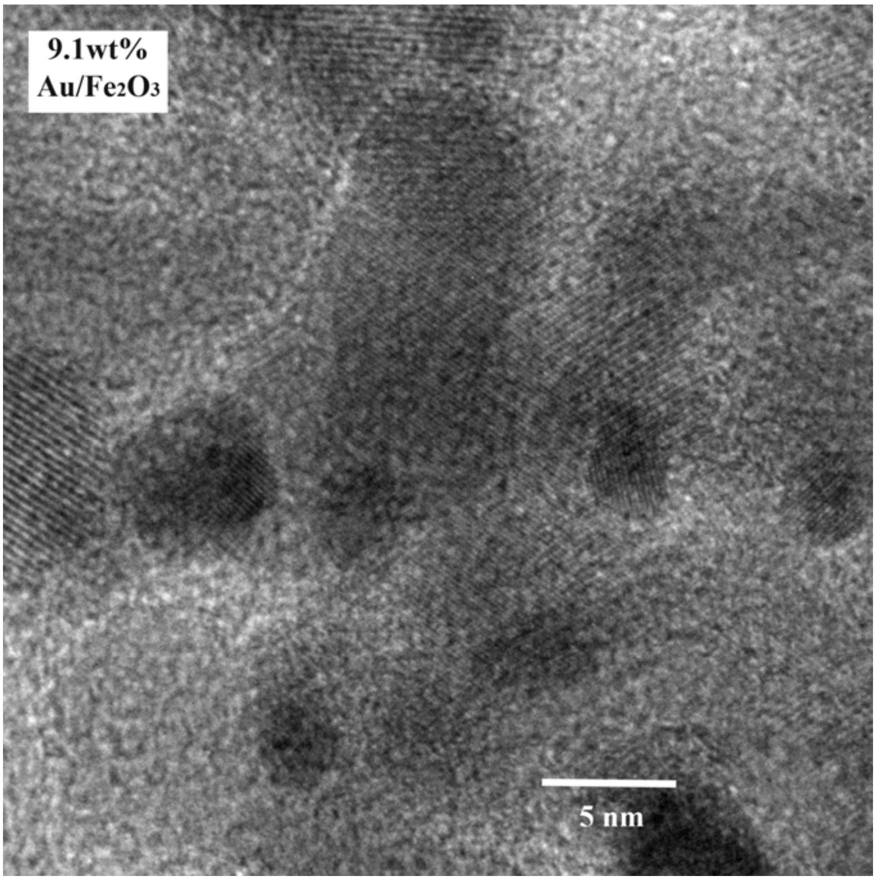
Fig. S3j. XPS spectra of the 2.9wt % Ru/Fe_2O_3

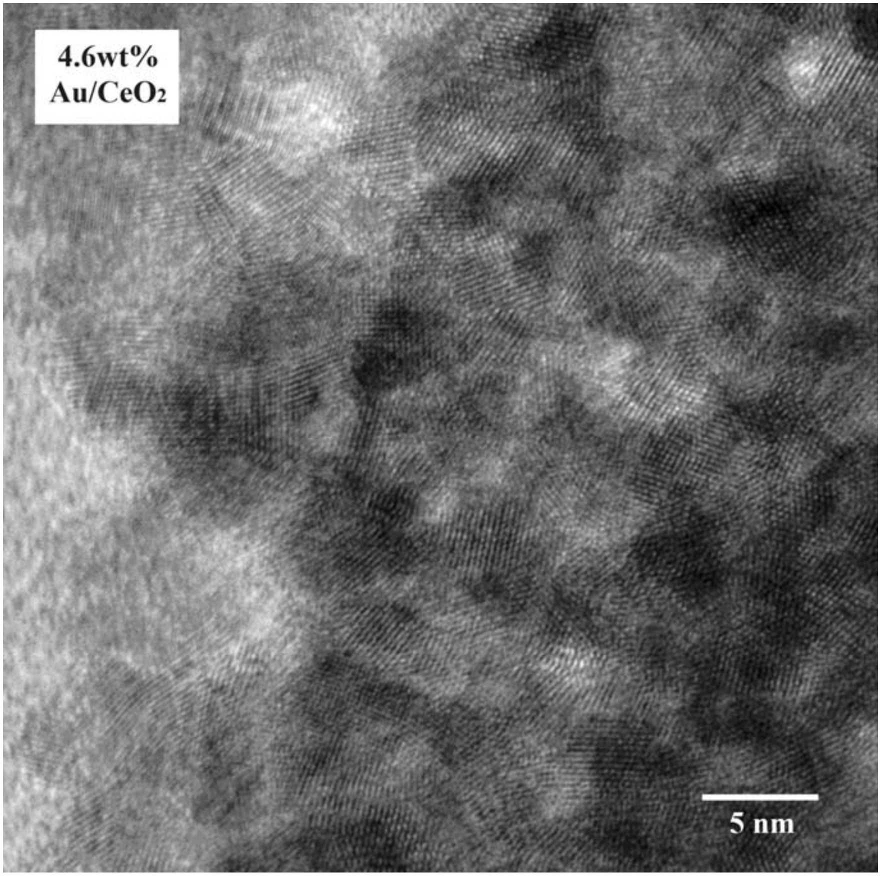
9. HRTEM images of the catalyst samples

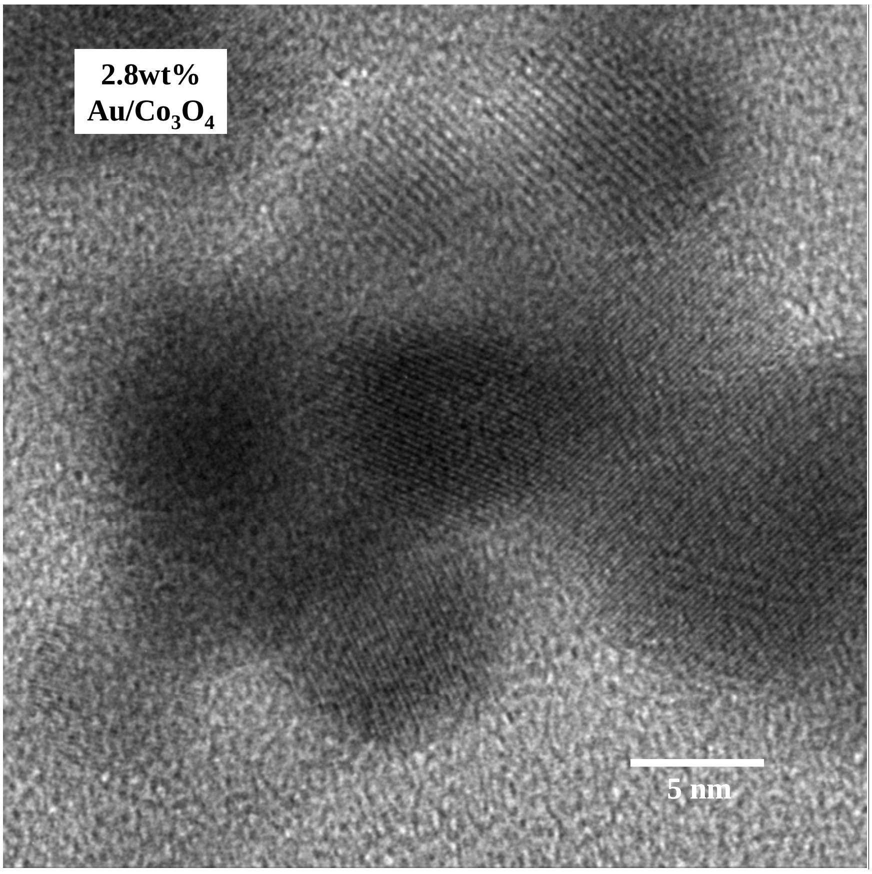


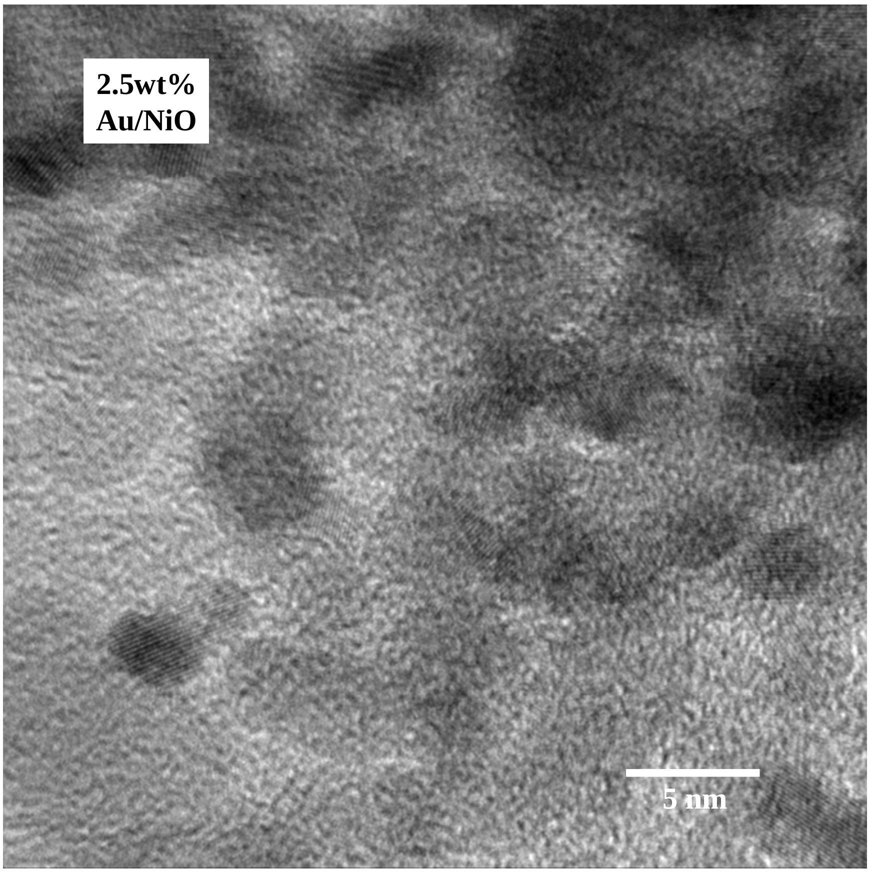

4.3wt%
Au/Fe_2O_3
5 nm


6.3wt%
Au/Fe_2O_3
5 nm


9.1wt%
Au/Fe2O3
5 nm


4.6wt%
Au/CeO2
5 nm


2.8wt%
Au/Co_3O_4
5 nm


2.5wt%
Au/NiO
5 nm

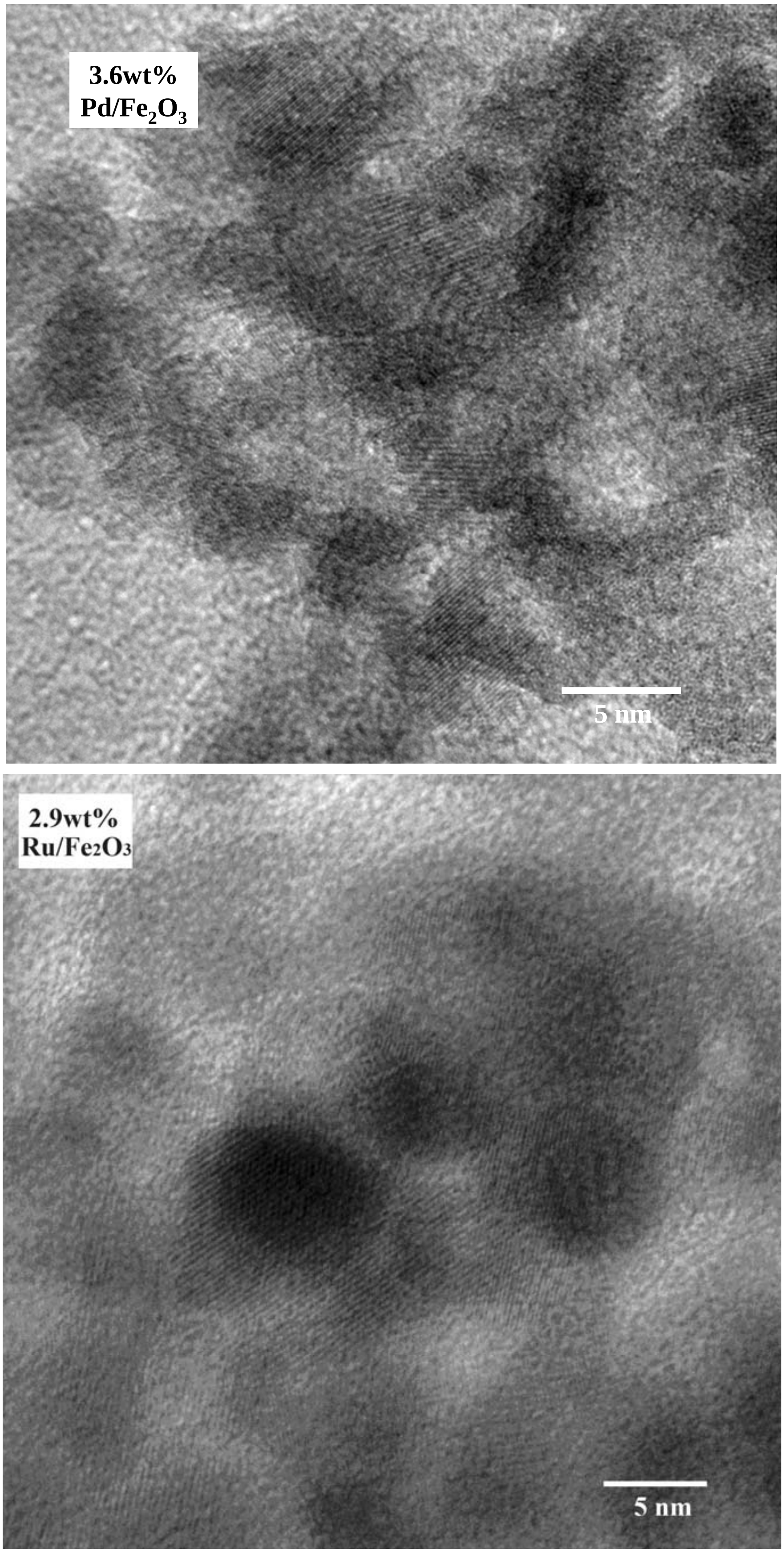


Fig. S4. TEM images of the catalysts

10. GC-MS spectra of compounds observed by GC-MS

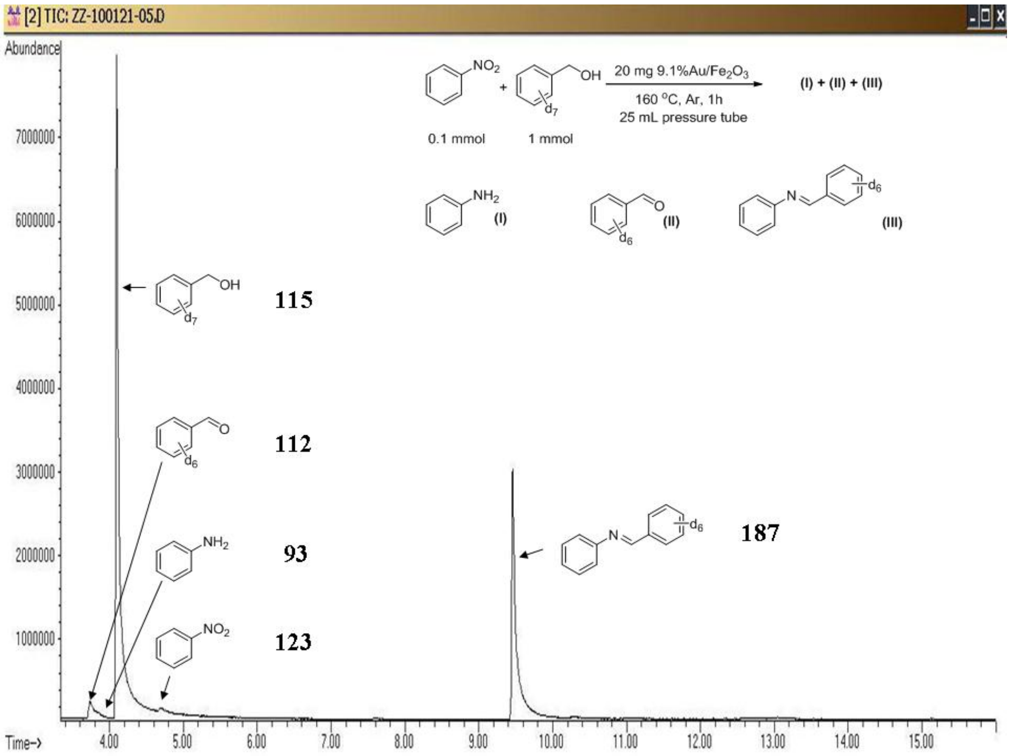


Fig. S5a. GC-MS spectra of substances produced from the reaction of d_7-benzyl alcohol (115.0 mg,1.0 mmol), nitrobenzene (12.3 mg, 0.1 mmol) and 20 mg 9.1wt % Au/Fe_2O_3 at 160 °C for 1h

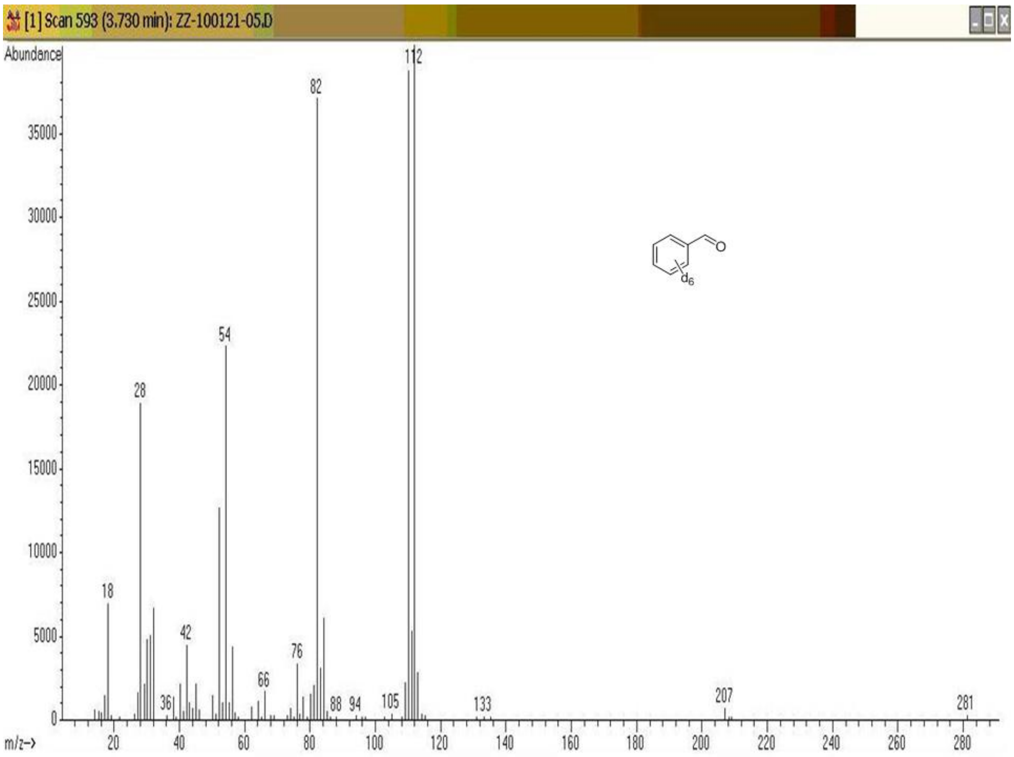


Fig. S5b. MS spectra of d_6- benzaldehyde

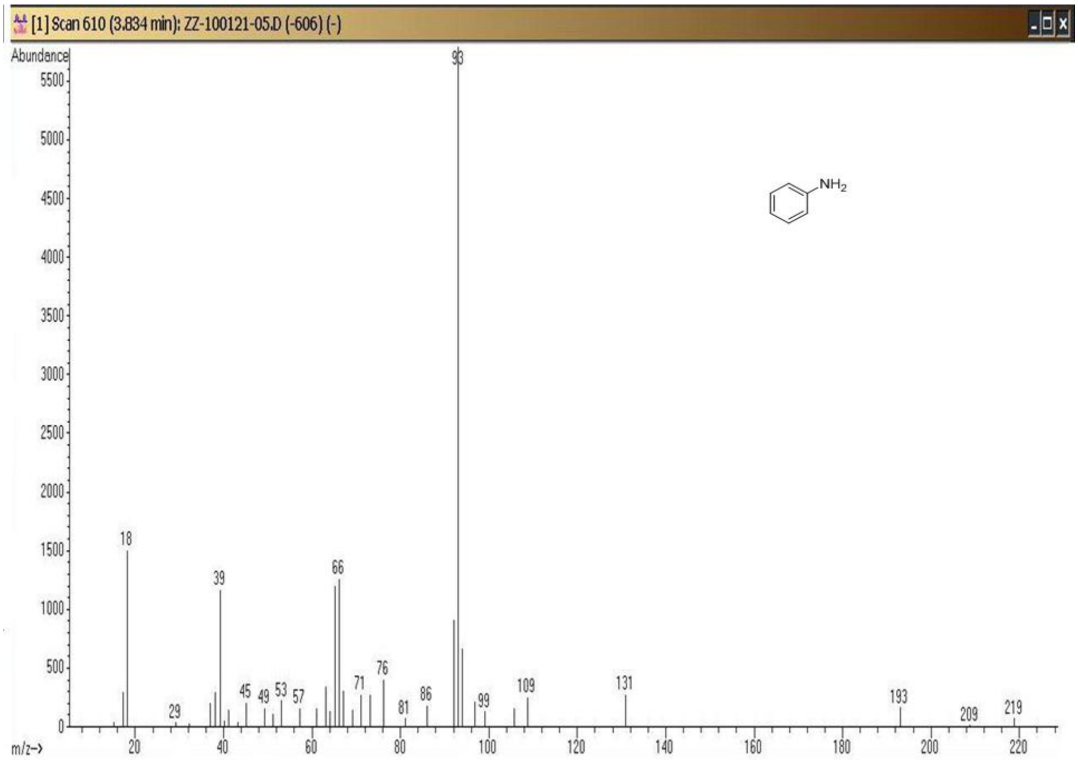


Fig. S5c. MS spectra of aniline

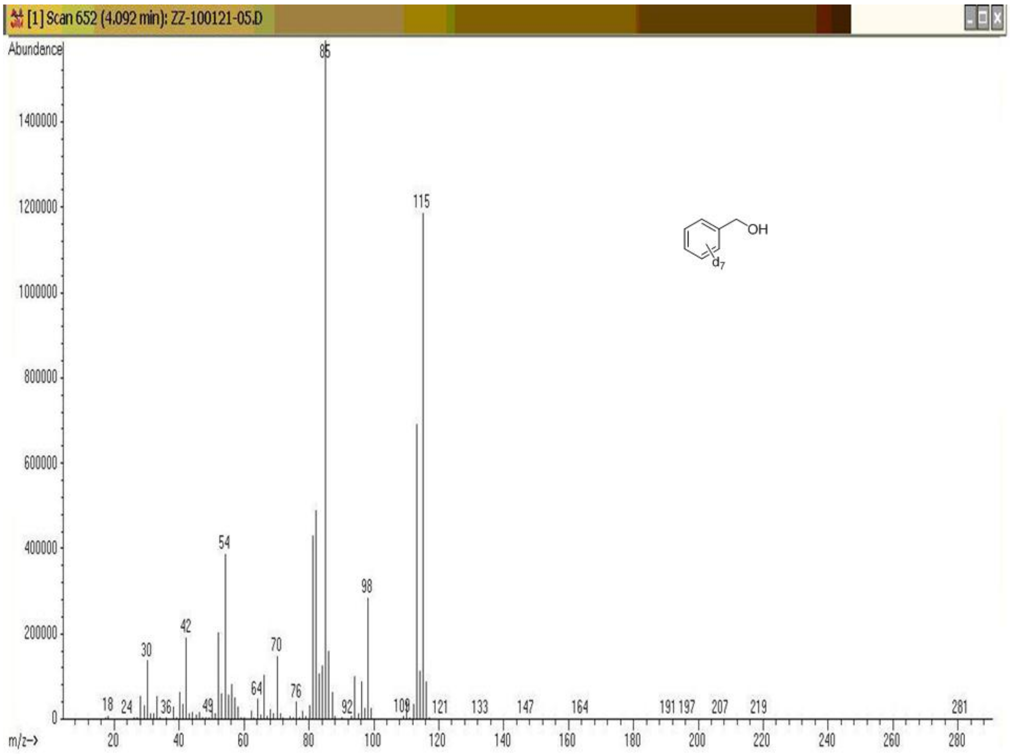


Fig. S5d. MS spectra of d_7- benzyl alcohol

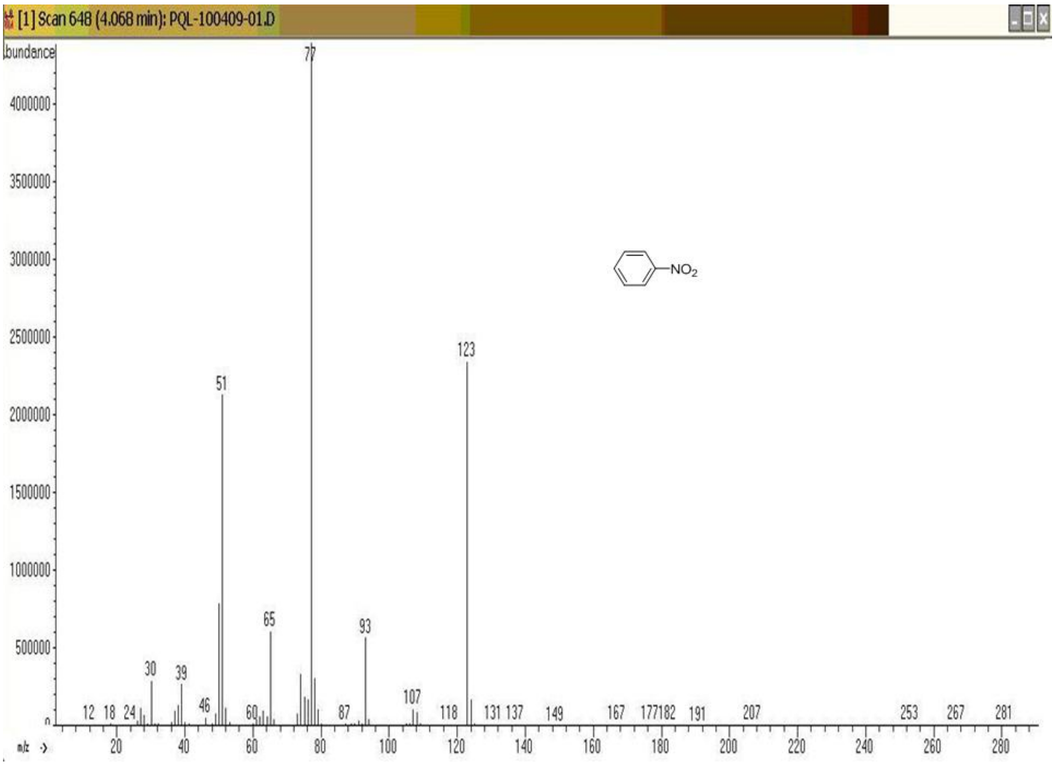


Fig. S5e. MS spectra of nitrobenzene

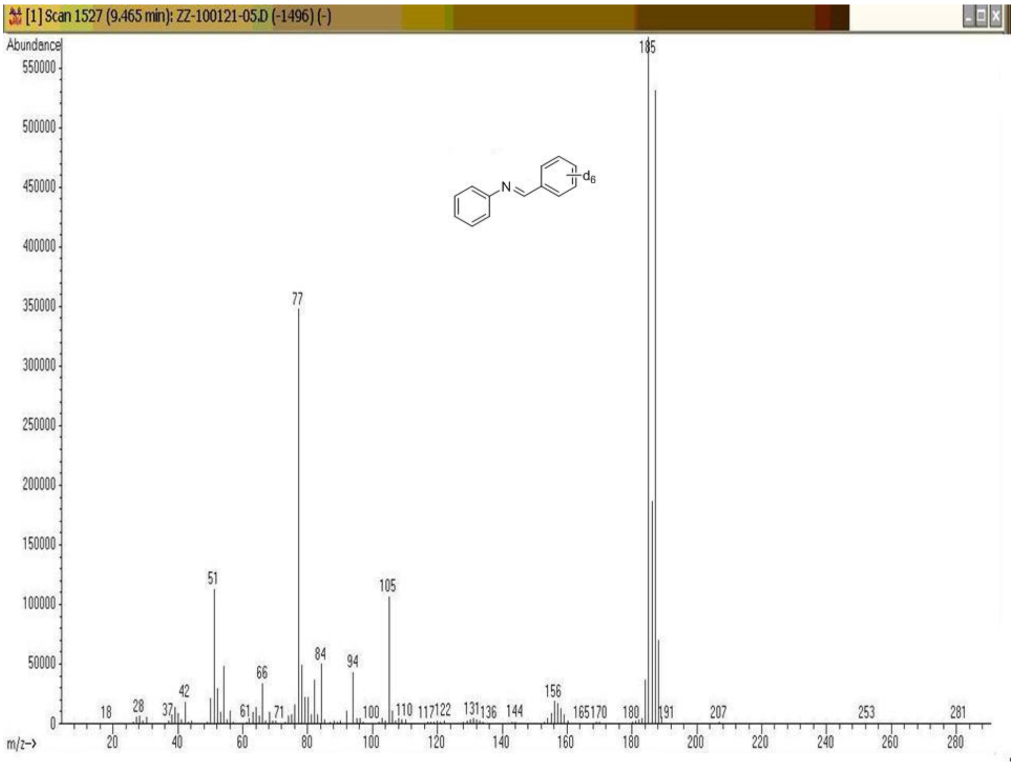


Fig. S5f. MS spectra of d_6-N-(2-phenylethylidene) aniline

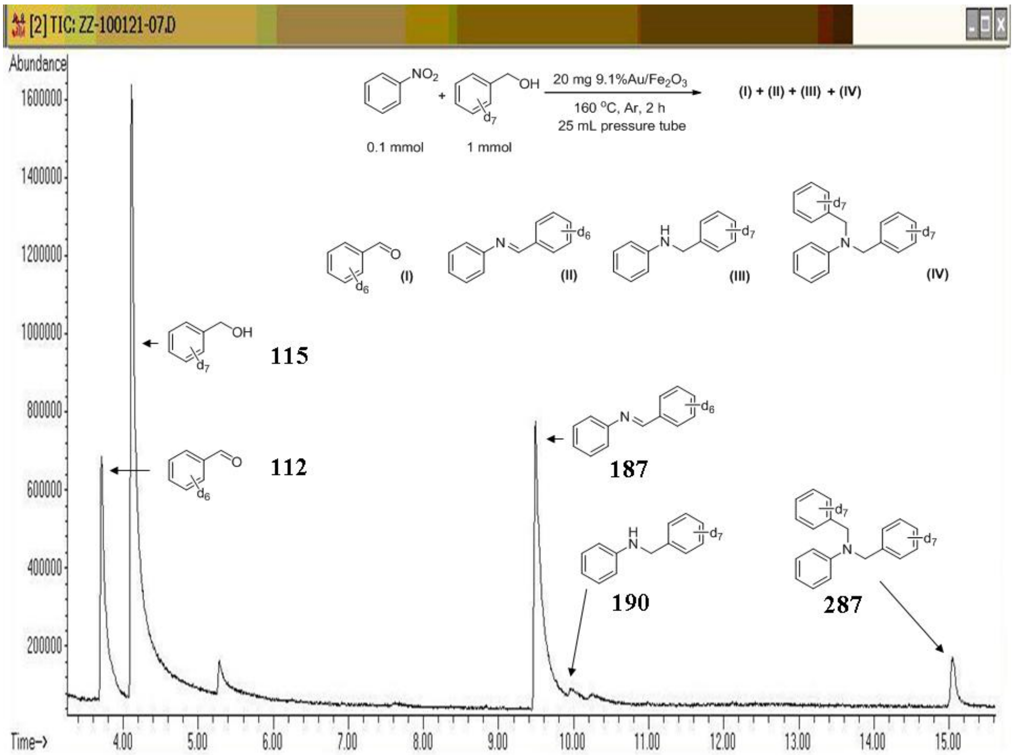


Fig. S6a. GC-MS spectra of all substances produced from the reaction of d$_7$-benzyl alcohol (115.0 mg, 1.0 mmol), nitrobenzene (12.3 mg, 0.1 mmol) and 20 mg 9.1wt % Au/Fe$_2$O$_3$ at 160 °C for 2h

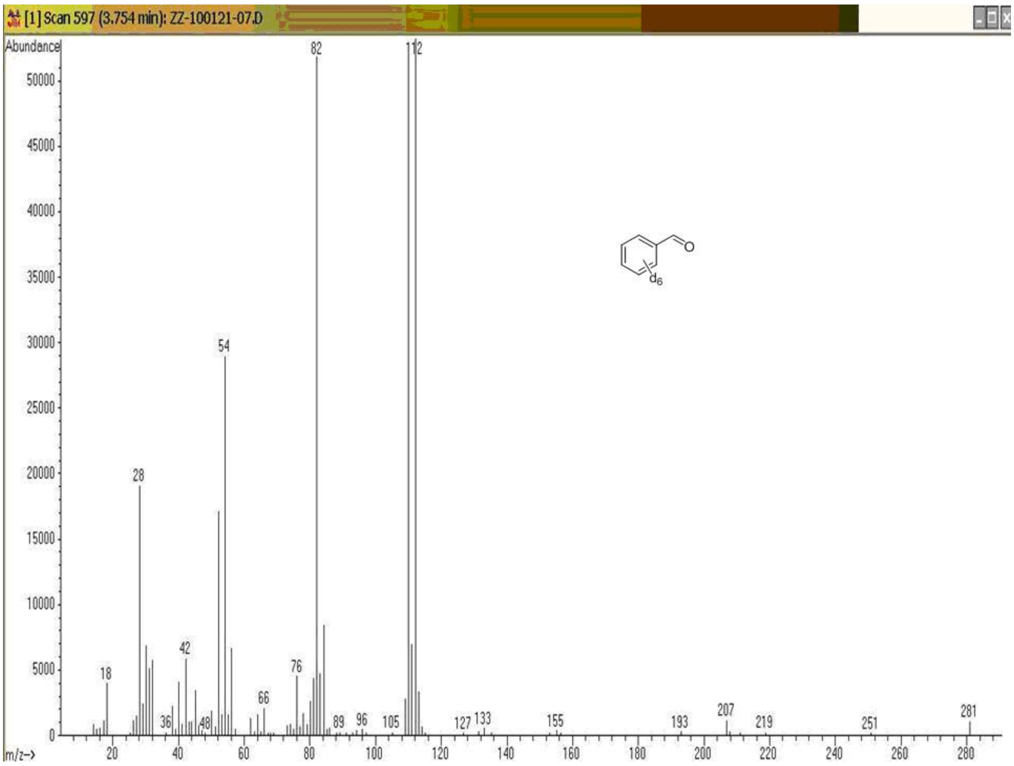


Fig. S6b. MS spectra of d$_6$- benzaldehyde

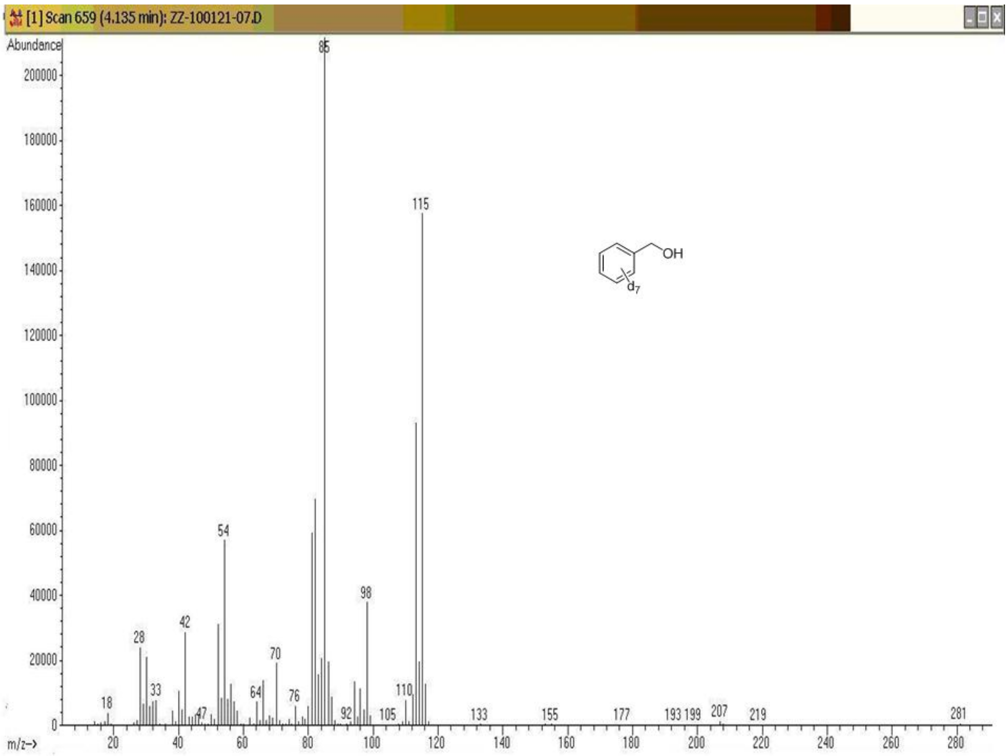


Fig. S 6c. MS spectra of d_7- benzyl alcohol

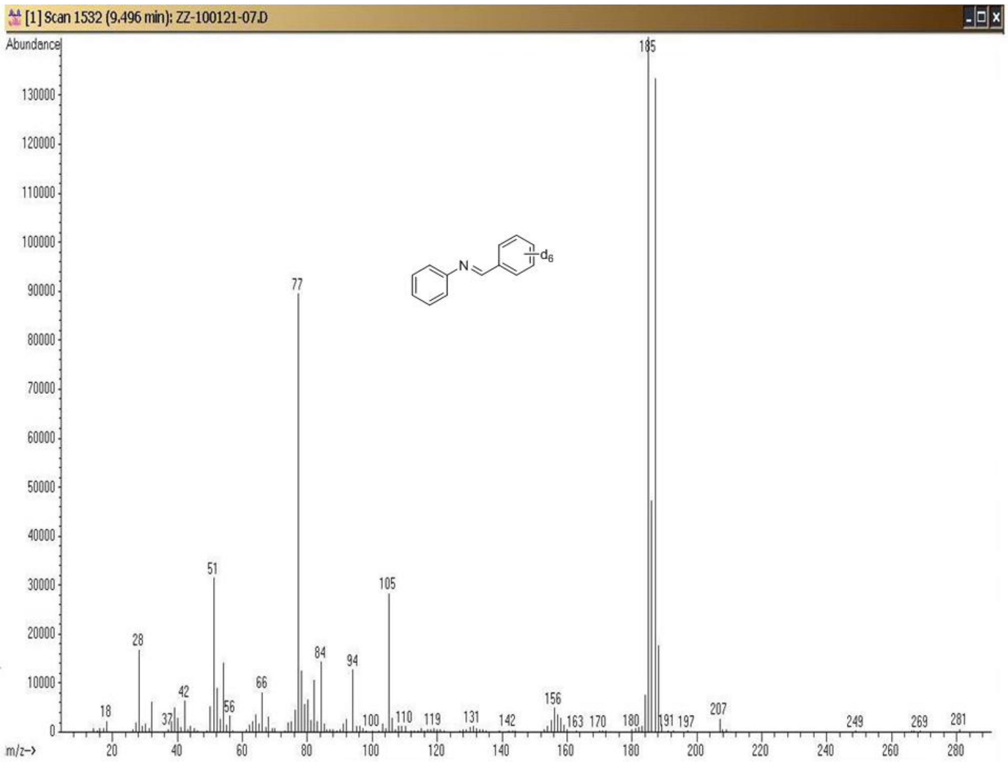


Fig. S6d. MS spectra of d_6-N-(2-phenylethylidene) aniline

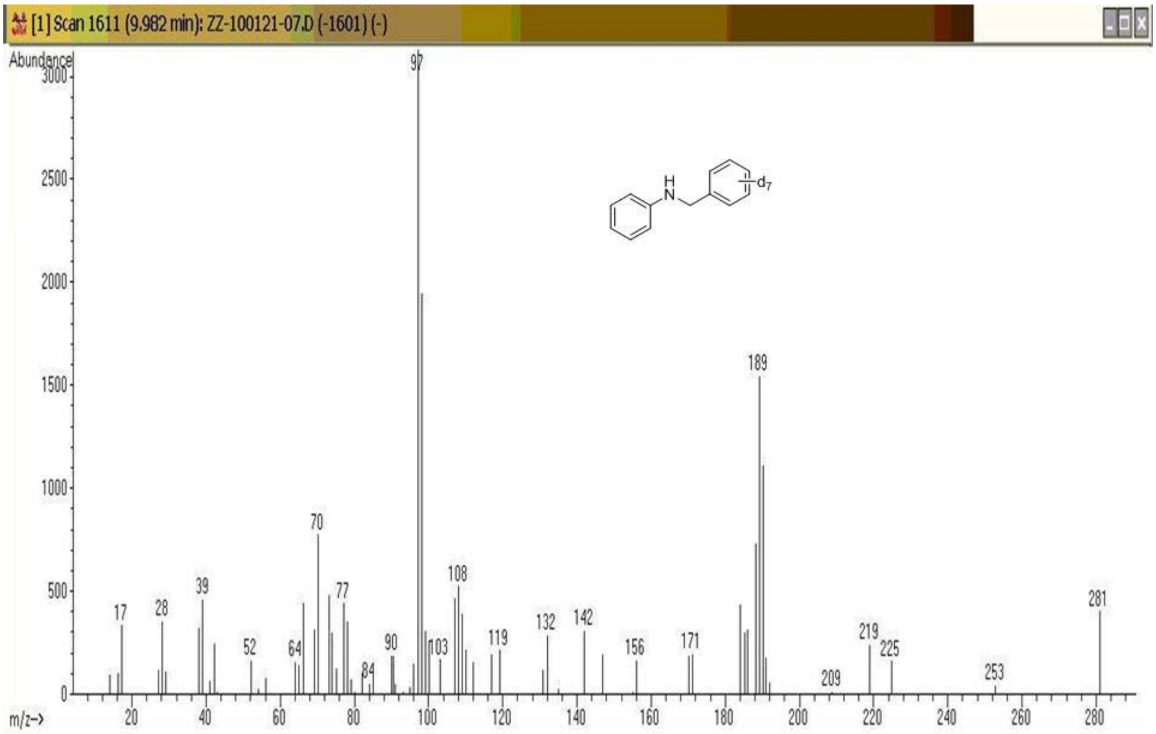


Fig. S6e. MS spectra of d$_7$-N-benzylaniline

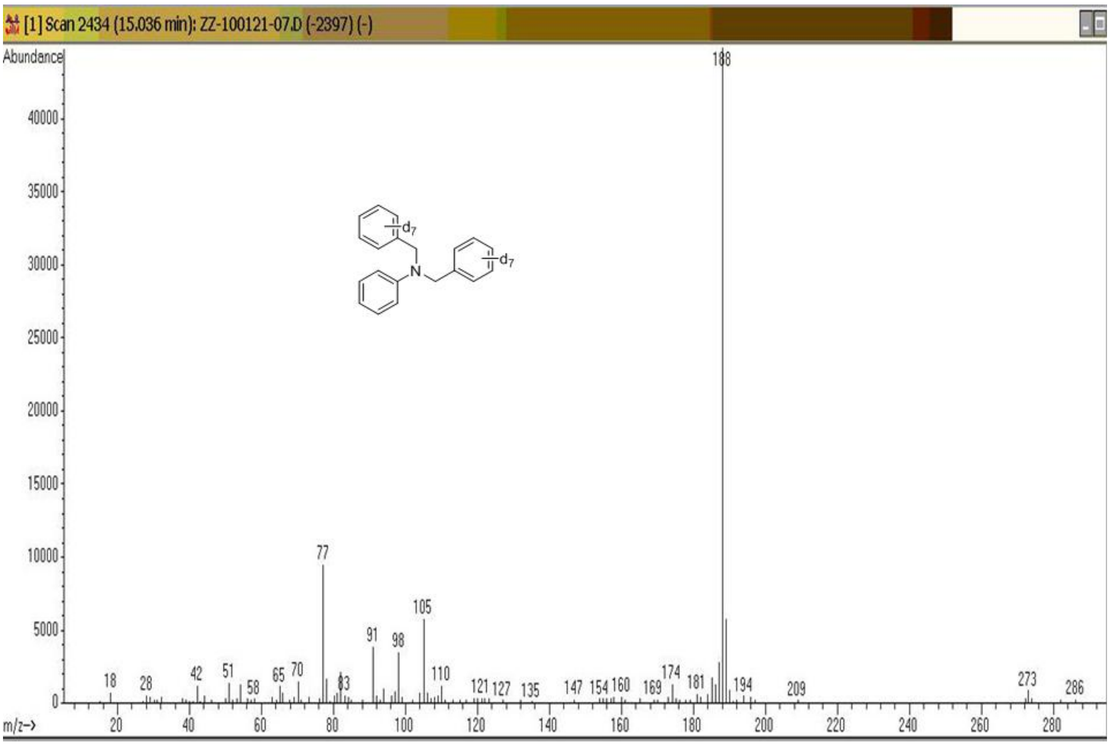


Fig. S6f. MS spectra of d$_{14}$- N, N-dibenzylaniline

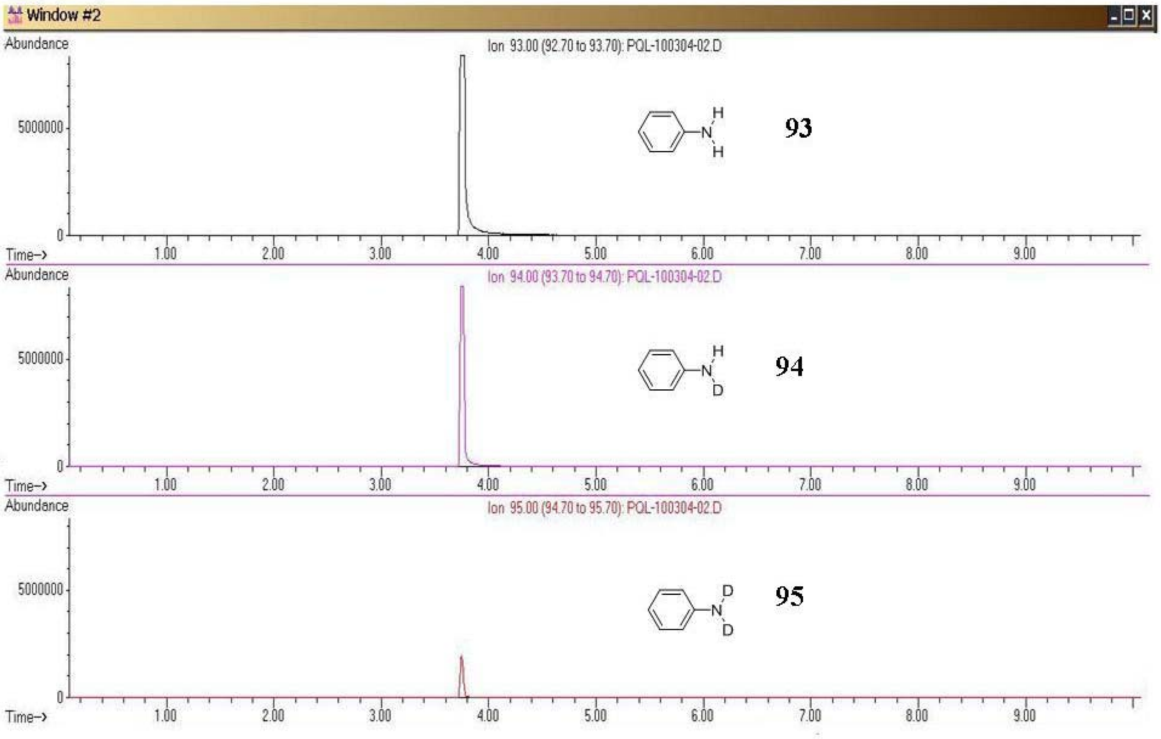
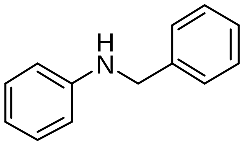


Fig. S7. Ion selective MS spectra of H-D exchange reaction between aniline and D_2O

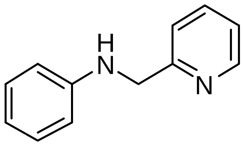
11. Compounds characterization and NMR spectra

Synthesis of *N*-Benzyl aniline



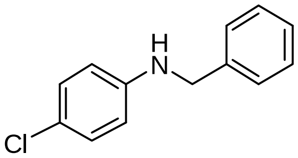
Nitrobenzene (246.2 mg, 2 mmol), benzyl alcohol (1081.4 mg, 10 mmol) and 100 mg 9.1wt % Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 160 °C under Argon atmosphere for 17 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine/petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.207). Following the procedure above, *N*-benzyl aniline was obtained as a yellow solid (346 mg, Isolated yield = 94%, mp = 34 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.15-7.45 (m, 7H), δ 6.55-6.80 (m, 3H), δ 4.32 (s, 2H), δ 4.02 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 148.12, 139.40, 129.25, 128.62, 127.49, 127.21, 117.53, 112.80, 48.29. *m/z* (rel. int.) 183(56), 182(21), 106(17), 91(100), 77(20), 65(20), 51(11).

Synthesis of *N*-(pyridin-2-ylmethyl) aniline



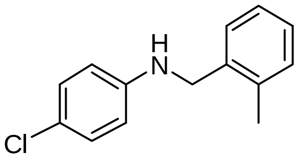
Nitrobenzene (246.2 mg, 2 mmol), pyridin-2-ylmethanol (2182.6 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted under Argon atmosphere at 160 °C for 9 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 25/1/50, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.387). Following the procedure above, *N*-(pyridin-2-ylmethyl) aniline was obtained as a white solid (340 mg, Isolated yield = 92%, mp = 52 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 8.50-8.70 (d, 1H), δ 7.60-7.70 (t, 1H), δ 7.25-7.40 (d, 1H), δ 7.05-7.25 (m, 3H), δ 6.60-6.80 (m, 3H), δ 4.48 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 158.49, 149.20, 147.87, 136.64, 129.24, 122.09, 121.58, 117.58, 113.03, 49.28. *m/z* (rel. int.) 185(10), 184(74), 183(50), 107(23), 106(100), 105(13), 80(23), 79(19), 78(14), 77(37), 65(15), 51(18), 39(12).

Synthesis of *N*-benzyl-4-chloroaniline



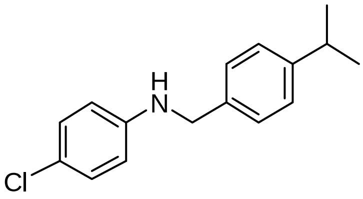
1-Chloro-4-nitro-benzene (315.1 mg, 2 mmol), benzyl alcohol (1189.5 mg, 11 mmol) and 100 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 150 °C under Argon atmosphere for 24 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.162). Following the procedure above, *N*-benzyl-4-chloroaniline was obtained as a yellow solid (370 mg, Isolated yield = 85%, mp = 43 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.20-7.40 (m, 5H), δ 7.05-7.15 (m, 2H), δ 6.50-6.60 (m, 2H), δ 4.30 (s, 2H), δ 4.21 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 146.52, 138.84, 129.05, 128.68, 127.42, 127.37, 122.20, 113.97, 48.37. *m/z* (rel. int.) 217(34), 91(100), 65(12).

Synthesisof 4-chloro-*N*-(2-methylbenzyl) aniline



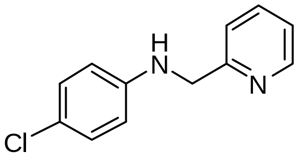
1-Chloro-4-nitro-benzene (315.1 mg, 2 mmol), 2-methyl benzyl alcohol (1342.9 mg, 11 mmol) and 100 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 150 °C under Argon atmosphere for 24 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.207). Following the procedure above, 4-chloro-*N*-(2-methylbenzyl) aniline was obtained as a yellow solid (375 mg, Isolated yield = 81%, mp = 40 °C). ^1H NMR (400MHz, $CDCl_3$, ppm): δ 7.00-7.40 (m, 6H), δ 6.50-6.60 (m, 2H), δ 4.24 (s, 2H), δ 4.35 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 146.20, 136.31, 136.13, 130.46, 129.06, 128.19, 127.60, 126.17, 122.87, 114.13, 46.61, 18.88. *m/z* (rel. int.) 231(28), 105(100), 104(33), 79(11), 77(15).

Synthesis of 4-chloro-*N*-(4-isopropylbenzyl) aniline



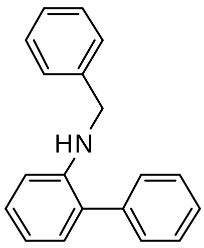
1-Chloro-4-nitro-benzene (315.1 mg, 2 mmol), (4-Isopropyl-phenyl)-methanol (1652.4 mg, 11 mmol) and 100 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 150 °C under Argon atmosphere for 26 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.216). Following the procedure above, 4-chloro-*N*-(4-isopropylbenzyl) aniline was obtained as a yellow solid (472 mg, Isolated yield = 91%, mp = 41 °C). ^1H NMR (400MHz, $CDCl_3$, ppm): δ 7.00-7.30 (m, 6H), δ 6.50-6.60 (m, 2H), δ 4.25 (s, 2H), 4.10 (s, 1H), δ 2.80-3.00 (m, 1H), δ 1.20-1.30 (d, 6H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 148.11, 146.62, 136.13, 129.02, 127.52, 126.72, 122.01, 113.89, 48.12, 33,77, 23.99. *m/z* (rel. int.) 260(25), 259(100), 134(34), 133(99), 118(22), 117(45), 115(17), 105(50), 91(33).

Synthesis of 4-chloro-*N*-(pyridin-2-ylmethyl) aniline



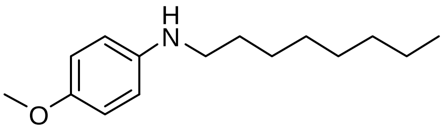
1-Chloro-4-nitro-benzene (315.1 mg, 2 mmol), pyridin-2-ylmethanol (2182.6 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 160 °C under Argon atmosphere for 9 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 25/1/50, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.315). Following the procedure above, 4-chloro-*N*-(pyridin-2-ylmethyl) aniline was obtained as a white solid (394 mg, Isolated yield = 90%, mp = 85 °C). ^1H NMR (400MHz, $CDCl_3$, ppm): δ 8.50-8.60 (d, 1H), δ 7.60-7.70 (t, 1H), δ 7.10-7.40 (m, 4H), δ 6.50-6.65 (m, 2H), δ 4.85 (s, 1H), δ 4.42 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 157.79, 149.16, 146.34, 136.66, 129.01, 122.19, 121.54, 114.05, 49.12. *m/z* (rel. int.) 218(79), 217(44), 142(31), 141(12), 140(100), 139(14), 111(14), 107(18), 93(13), 92(13), 91(11), 80(28), 79(25), 78(14), 77(11), 75(16), 65(17), 52(11), 51(13), 39(12).

Synthesis of *N*-benzylbiphenyl-2-amine



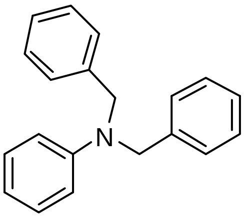
2-Nitro-biphenyl (398.4 mg, 2 mmol), benzyl alcohol (1081.4 mg, 10 mmol) and 100 mg 9.1wt% Au/Fe$_2$O$_3$ were added into a 25 mL pressure tube and reacted at 160 °C under Argon atmosphere for 19 h. The crude mixture was purified by column chromatograph (Et$_2$O / triethylamine / petroleum ether = 1/1/80, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.928). Following the procedure above, *N*-benzylbiphenyl-2-amine was obtained as a white solid (514 mg, Isolated yield = 99%, mp = 86 °C). ^{1}H NMR (400MHz, CDCl$_3$, ppm): δ 7.10-7.50 (m, 12H), δ 6.70-6.85 (m, 2H), δ 4.33(s, 2H); ^{13}C NMR (100MHz, CDCl$_3$, ppm): δ 139.12, 130.27, 129.33, 128.94, 128.70, 128.56, 127.33, 127.23, 127.17, 118.03, 111.89, 48.52. *m/z* (rel. int.) 259(100), 258(36), 182(14), 180(40), 166(11), 167(40), 166(11), 152(13), 106(13), 91(65), 65(10).

Synthesis of 4-methoxy-*N*-octylaniline



1-Methoxy-4-nitro-benzene (306.3 mg, 2 mmol), octan-1-ol (2604.6 mg, 20 mmol) and 250 mg 9.1wt% Au/Fe$_2$O$_3$ were added into a 25 mL pressure tube and reacted at 180 °C under Argon atmosphere for 24 h. The crude mixture was purified by column chromatograph (Et$_2$O / triethylamine / petroleum ether = 1/1/200, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.474). Following the procedure above, 4-methoxy-*N*-octylaniline was obtained as a yellow liquid (418 mg, Isolated yield = 89%). ^{1}H NMR (400MHz, CDCl$_3$, ppm): δ 6.75-6.80 (m, 2H), 6.55-6.65 (m, 2H), δ 3.74 (s, 3H), δ 3.43 (s, 1H), δ 3.00-3.10 (m, 2H), δ 1.55-1.65 (m, 2H) , δ 1.25-1.40 (m, 10H) , δ 0.85-0.90 (m, 3H); ^{13}C NMR (100MHz, CDCl$_3$, ppm): δ 151.99, 142.68, 114.83, 114.09, 55.78, 45.06, 31.80, 29.61, 29.41, 29.23, 27.17, 22.63, 14.06. *m/z* (rel. int.) 235(23), 136(100).

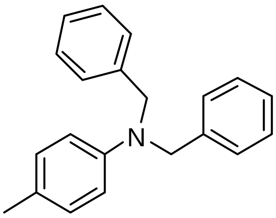
Synthesis of *N*, *N*-dibenzylaniline



Nitrobenzene (246.2 mg, 2 mmol), benzyl alcohol (2162.8 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe$_2$O$_3$ were added into a 25 mL pressure tube and reacted at 160 °C under

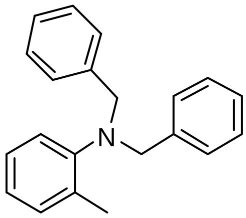
Argon atmosphere for 15 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.513). Following the procedure above, *N*, *N*-dibenzylaniline was obtained as a yellow solid (526 mg, Isolated yield = 96%, mp = 68 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.00-7.40 (m, 12H), δ 6.60-6.80 (m, 3H), δ 4.66 (s, 4H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 149.08, 138.53, 129.20, 128.62, 126.87, 126.65, 116.70, 112.42, 54.18. *m/z* (rel. int.) 273(44), 196(18), 182(18), 181(12), 104(10), 92(10), 91(100), 77(22), 65(14).

Synthesis of *N*, *N*-dibenzyl-4-methylaniline



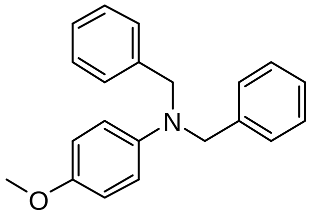
1-Methyl-4-nitro-benzene (275 mg, 2 mmol), benzyl alcohol (2162.8 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 170 °C under Argon atmosphere for 17 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.504). Following the procedure above, *N*, *N*-dibenzyl-4-methylaniline was obtained as a white solid (544 mg, Isolated yield = 95%, mp = 52 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.20-7.40 (m, 10H), δ 6.95-7.00 (m, 2H), δ 6.60-6.70 (m, 2H), δ 4.61 (s, 4H), δ 2.22 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 146.99, 138.83, 129.70, 128.55, 126.67, 125.82, 112.63, 54.39, 20.19. *m/z* (rel. int.) 287(56), 210(19), 196(17), 195(20), 194(12), 118(10), 91(100), 65(17).

Synthesis of *N*, *N*-dibenzyl-2-methylaniline



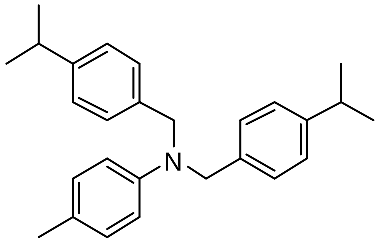
1-Methyl-2-nitro-benzene (275 mg, 2 mmol), benzyl alcohol (2162.8 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 160 °C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.273). Following the procedure above, *N*, *N*-dibenzyl-2-methylaniline was obtained as a white solid (486 mg, Isolated yield = 85%, mp = 42 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.10-7.40 (m, 11H), δ 7.00-7.10 (t, 1H), δ 6.90-7.00 (m, 2H), δ 4.07 (s, 4H), δ 2.45 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 149.85, 138.54, 134.01, 131.06, 128.66, 128.11, 126.85, 126.04, 123.44, 122.42, 56.84, 18.53. *m/z* (rel. int.) 287(31), 210(12), 196(34), 195(11), 194(11), 118(18), 91(100), 65(19).

Synthesis of *N, N*-dibenzyl-4-methoxyaniline



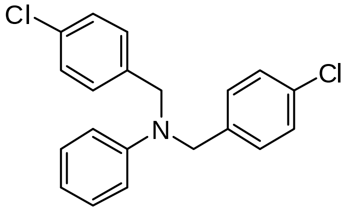
1-Methoxy-4-nitro-benzene (306.3 mg, 2 mmol), benzyl alcohol (2162.8 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 160 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.255). Following the procedure above, *N, N*-dibenzyl-4-methoxyaniline was obtained as a white solid (547 mg, Isolated yield = 90%, mp = 85 ^{o}C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.00-7.50 (m, 10H), δ 6.50-7.00 (m, 4H), δ 4.57 (s, 4H), δ 3.72 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 151.63, 143.78, 138.97, 128.54, 126.87, 126.80, 114.69, 114.42, 55.70, 55.09. *m/z* (rel. int.) 303(90), 226(11), 213(13), 212(81), 211(13), 196(12), 168(17), 134(19), 104(10), 92(16), 91(100), 77(16), 65(22).

Synthesis of *N, N*-bis(4-isopropylbenzyl)-4-methylaniline



1-Methyl-4-nitro-benzene (275 mg, 2 mmol), (4-Isopropyl-phenyl)-methanol (3004.4 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 170 ^{o}C under Argon atmosphere for 24 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.446). Following the procedure above, *N, N*-bis (4-isopropylbenzyl)-4-methylaniline was obtained as a white solid (627 mg, Isolated yield = 84%, mp = 51 ^{o}C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 6.95-7.30 (m, 10H), δ 6.60-6.80 (m, 2H), δ 4.55-4.65 (m, 4H), δ 2.85-2.95 (m, 2H), δ 2.20-2.30 (m, 3H), δ 1.20-1.30 (d, 12H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 147.41, 136.31, 129.73, 126.65, 125.61, 112.60, 54.08, 33.79, 24.08, 20.25. *m/z* (rel. int.) 371(50), 237(21), 134(11), 133(100), 118(28), 117(22), 105(30), 91(32).

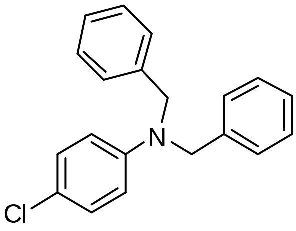
Synthesis of *N, N*-bis (4-chlorobenzyl) aniline



Nitrobenzene (246.2 mg, 2 mmol), (4-Chloro-phenyl)-methanol (2851.6 mg, 20 mmol) and 250 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 170 ^{o}C under Argon atmosphere for 15 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh;

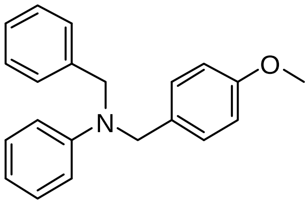
Rf = 0.336). Following the procedure above, *N*, *N*-bis (4-chlorobenzyl) aniline was obtained as a white solid (646 mg, Isolated yield = 94%, mp = 123 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.10-7.35 (m, 10H), δ 6.60-6.80 (m, 3H), δ 4.58 (s, 4H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 136.75, 132.70, 129.34, 128.81, 128.77, 128.09, 117.48, 112.79, 53.81. *m/z* (rel. int.) 341(23), 127(33), 125(100), 89(14), 77(19).

Synthesis of *N*, *N*-dibenzyl-4-chloroaniline



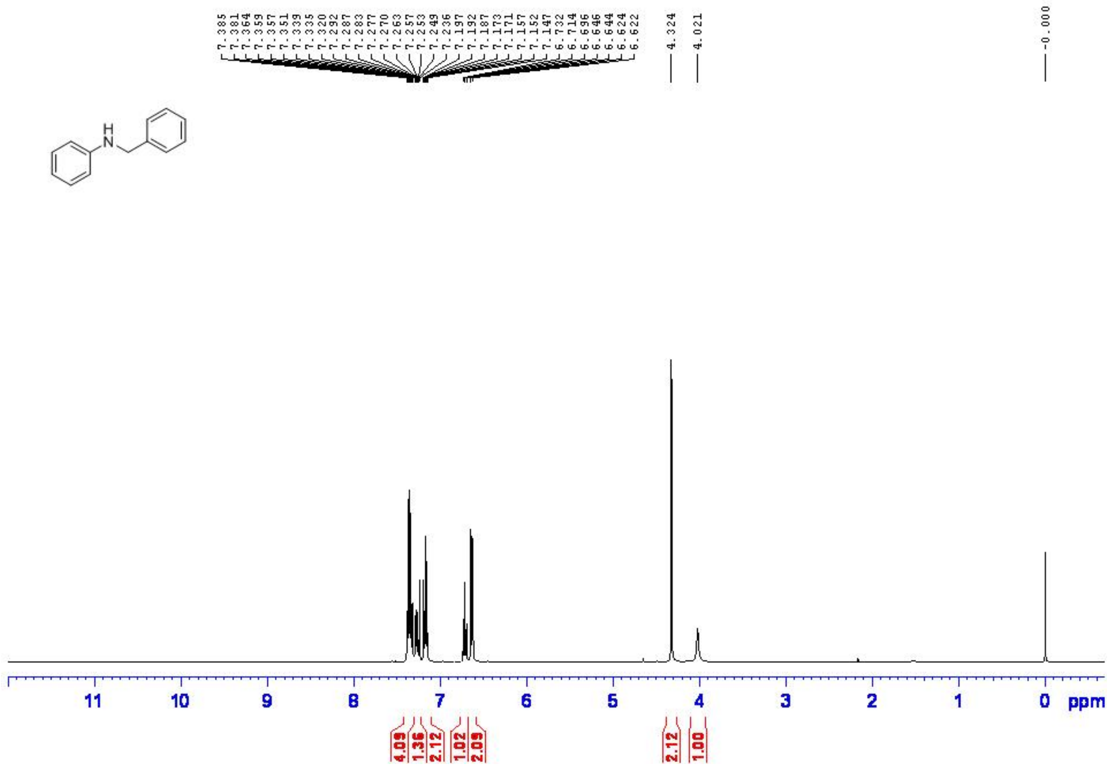
1-Chloro-4-nitro-benzene (315.1 mg, 2 mmol), benzyl alcohol (2162.8 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 160 °C under Argon atmosphere for 15 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.356). Following the procedure above, *N*, *N*-dibenzyl-4-chloroaniline was obtained as a yellow solid (497 mg, Isolated yield = 81%, mp = 98 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.00-7.40 (m, 12H), δ 6.60-6.80 (m, 2H), δ 4.64 (s, 4H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 137.92, 128.99, 128.72, 127.09, 126.62, 113.83, 54.61. *m/z* (rel. int.) 307(30), 216(11), 91(100), 65(12).

Synthesis of *N*-benzyl-*N*-(4-methoxybenzyl) aniline

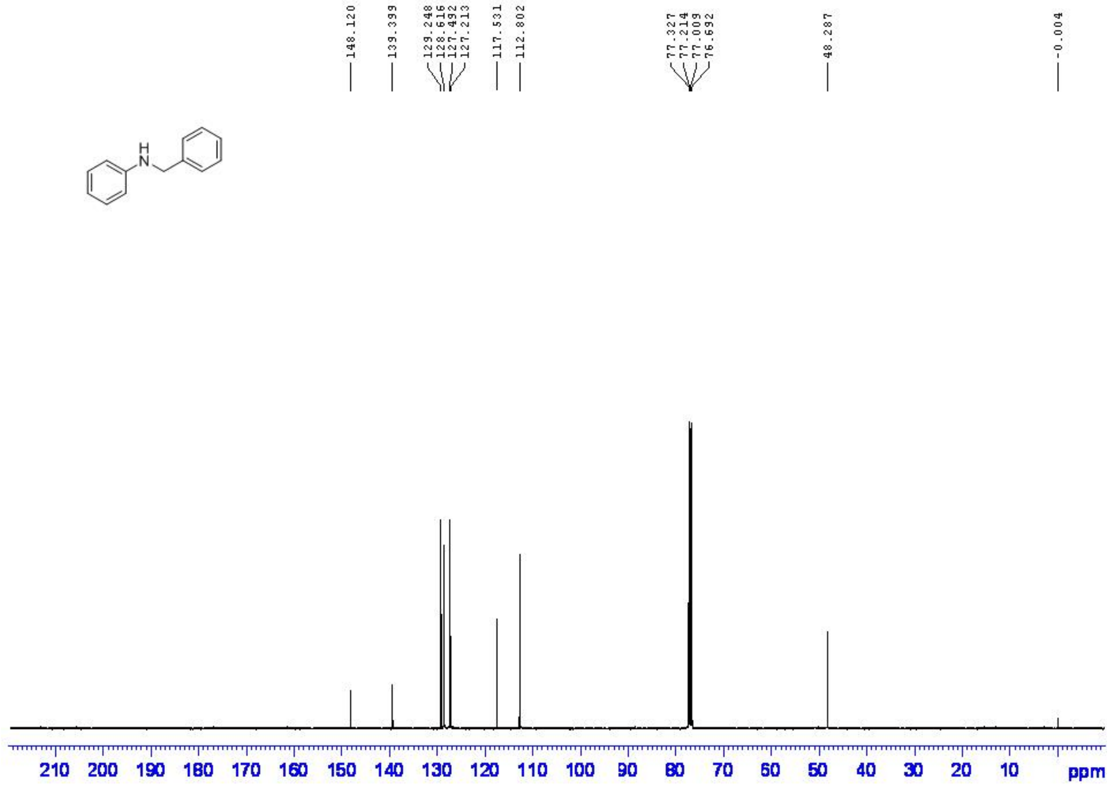


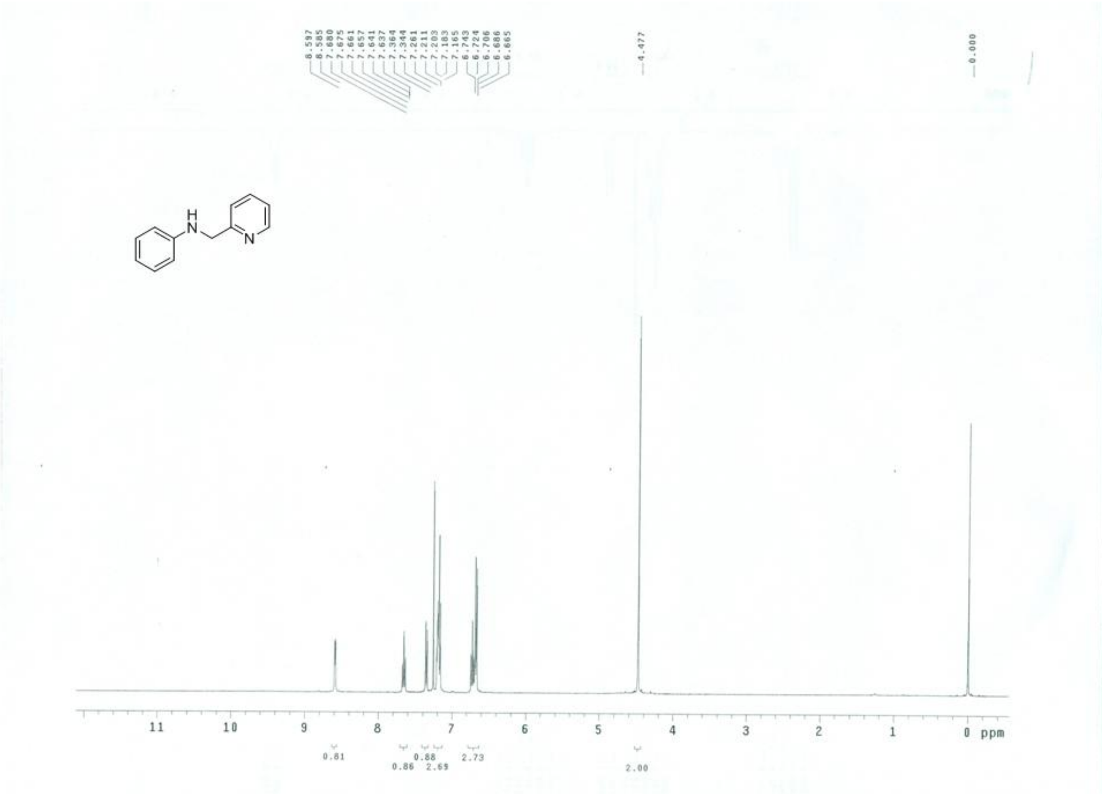
Benzyl-phenyl-amine (366.5 mg, 2 mmol), (4-Methoxy-phenyl)-methanol (2763.2 mg, 20 mmol) and 200 mg 9.1wt% Au/Fe_2O_3 were added into a 25 mL pressure tube and reacted at 170 °C under Argon atmosphere for 20 h. The crude mixture was purified by column chromatograph (Et_2O / triethylamine / petroleum ether = 1/1/100, v/v/v; Silica Gel: 200-300 mesh; Rf = 0.194). Following the procedure above, *N*-benzyl-*N*-(4-methoxybenzyl) aniline was obtained as a white solid (590 mg, Isolated yield = 97%, mp = 54 °C). ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.10-7.40 (m, 9H), δ 6.60-6.90 (m, 5H), δ 4.62 (s, 2 H), 4.59 (s, 2H), δ 3.78-3.80 (d, 3H); ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 158.60, 149.21, 138.69, 130.42, 129.17, 128.57, 127.85, 126.81, 126.65, 116.66, 114.01, 112.53, 55.24, 53.99, 53.58. *m/z* (rel. int.) 303(19), 121(100), 91(16), 77(12).

100204-3-PenJL-HNMR(6)



100204-3-PenJL-CNMR(7)





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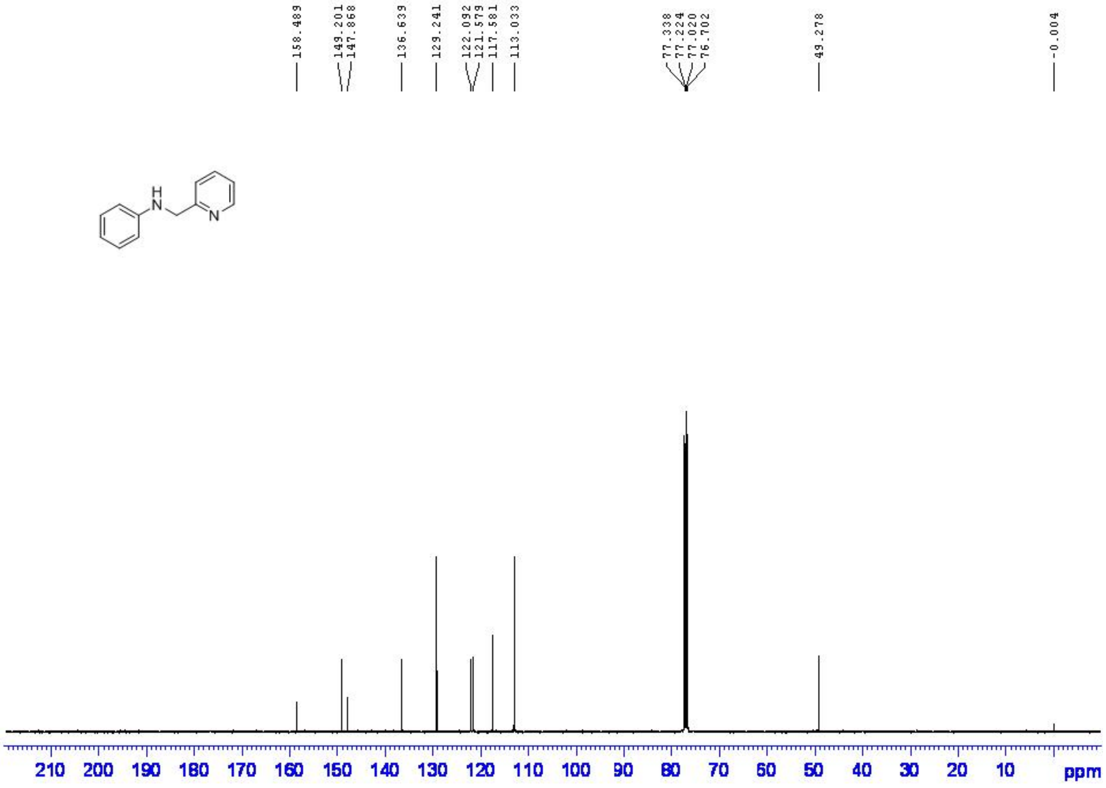

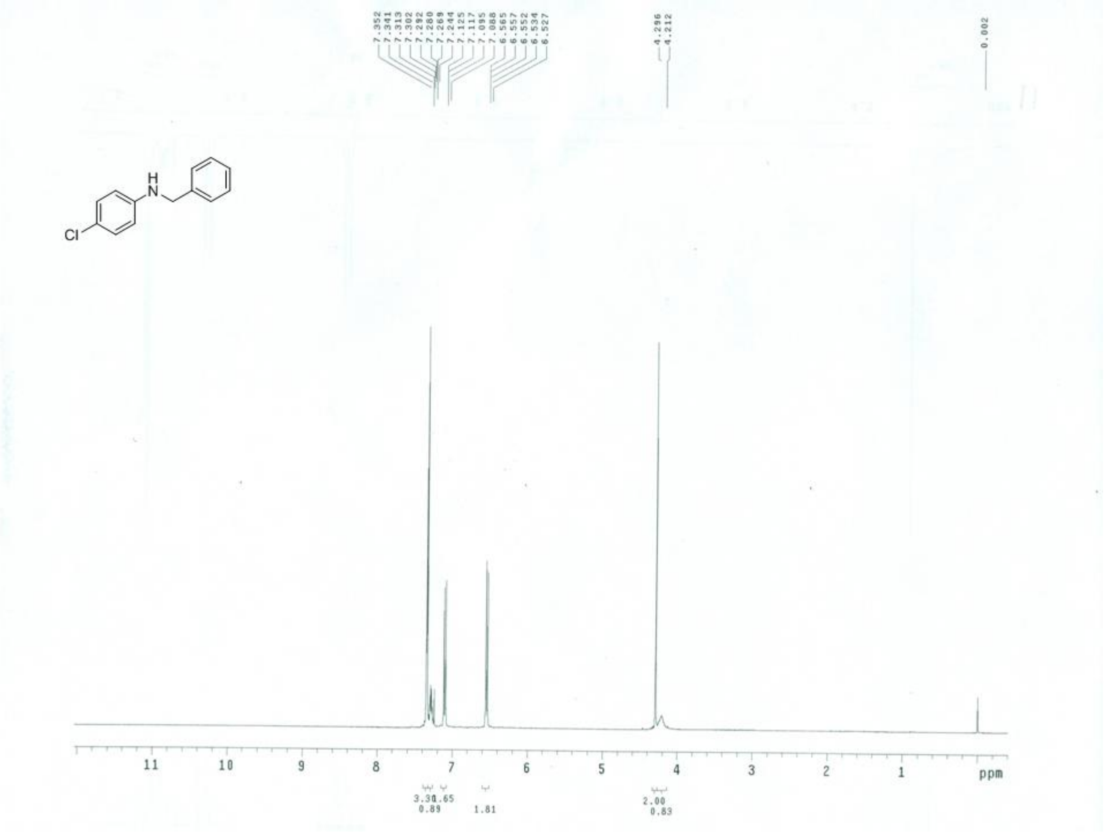
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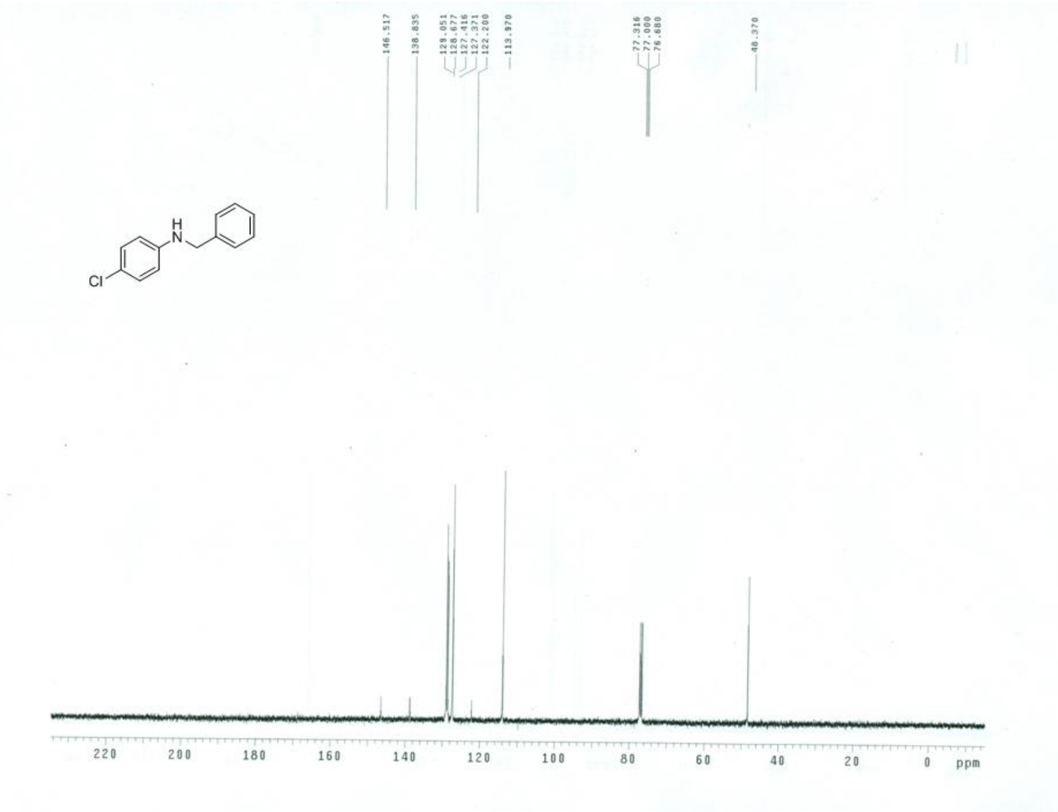
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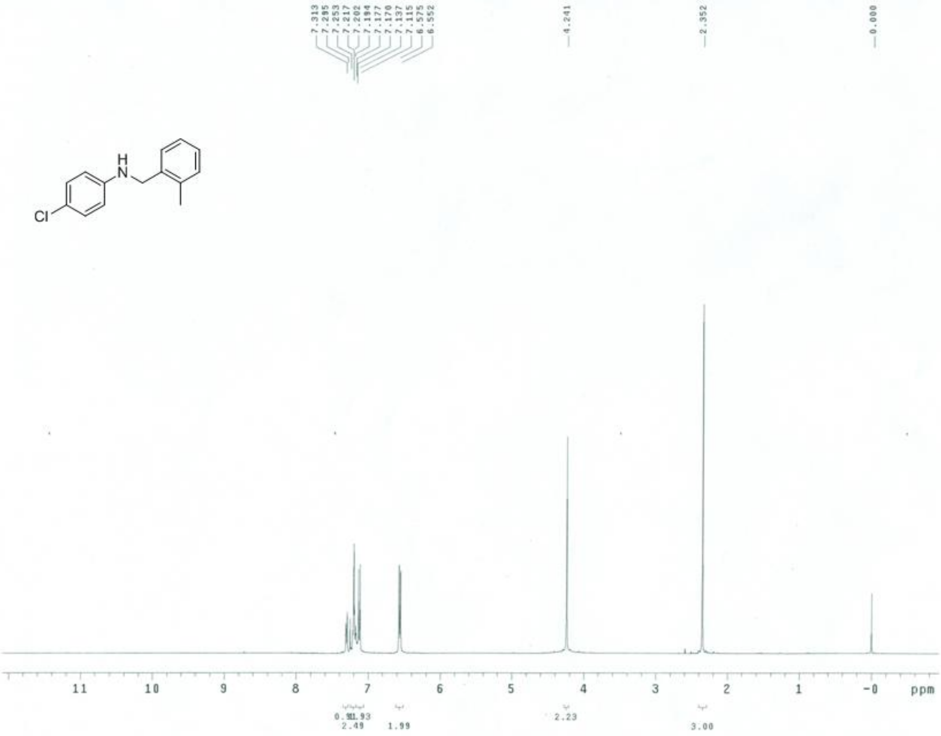
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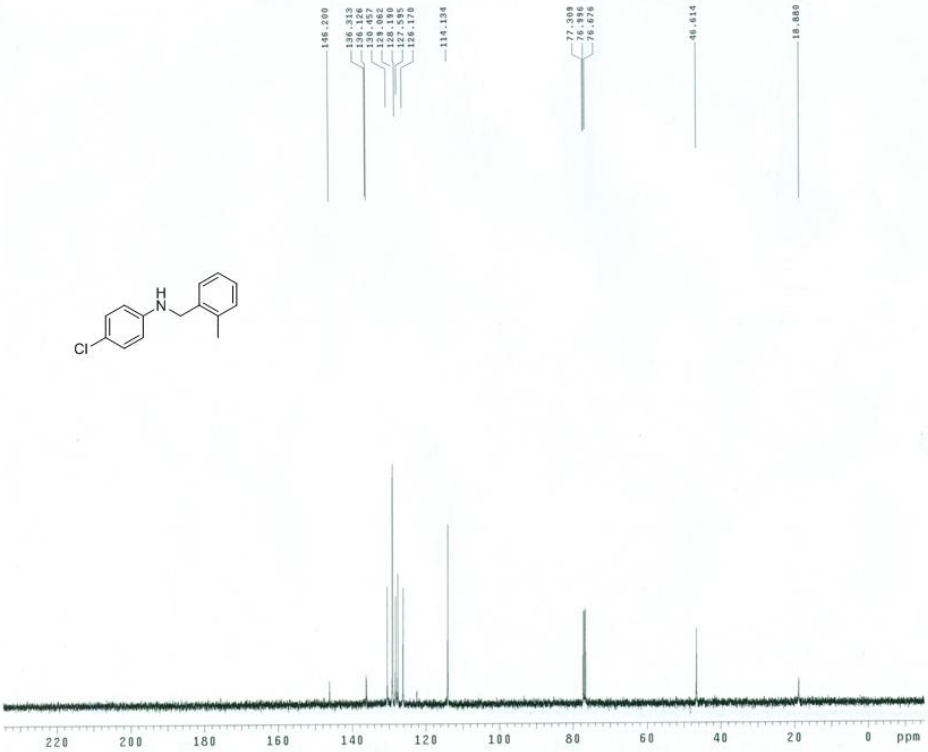
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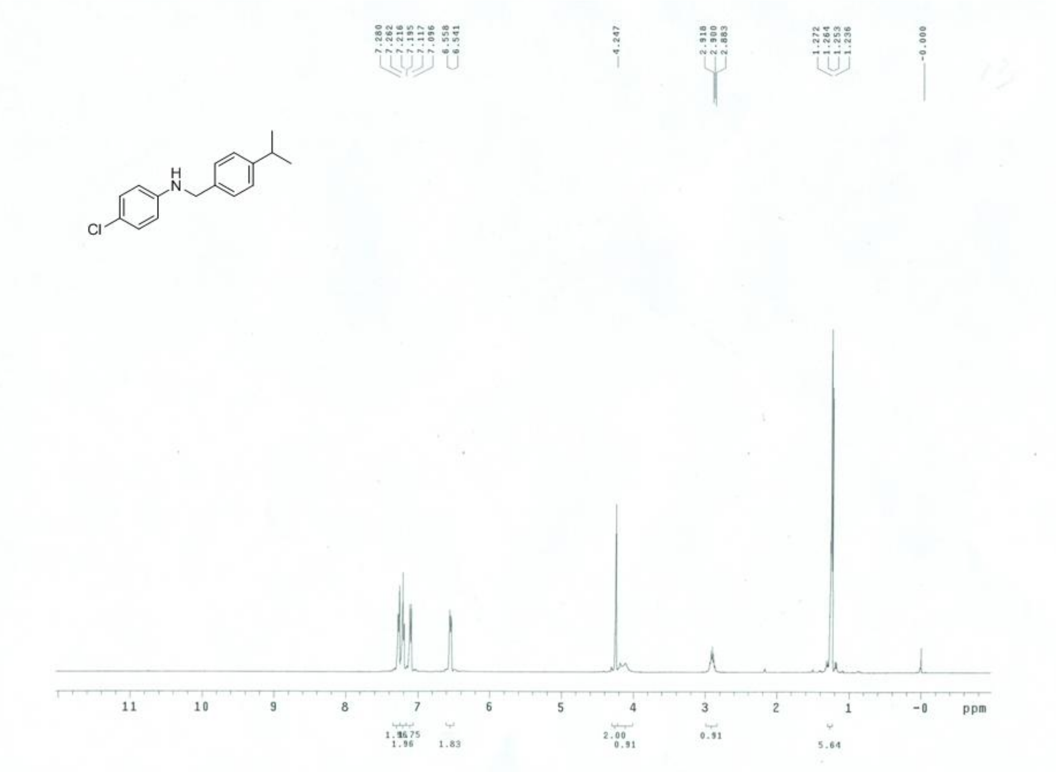
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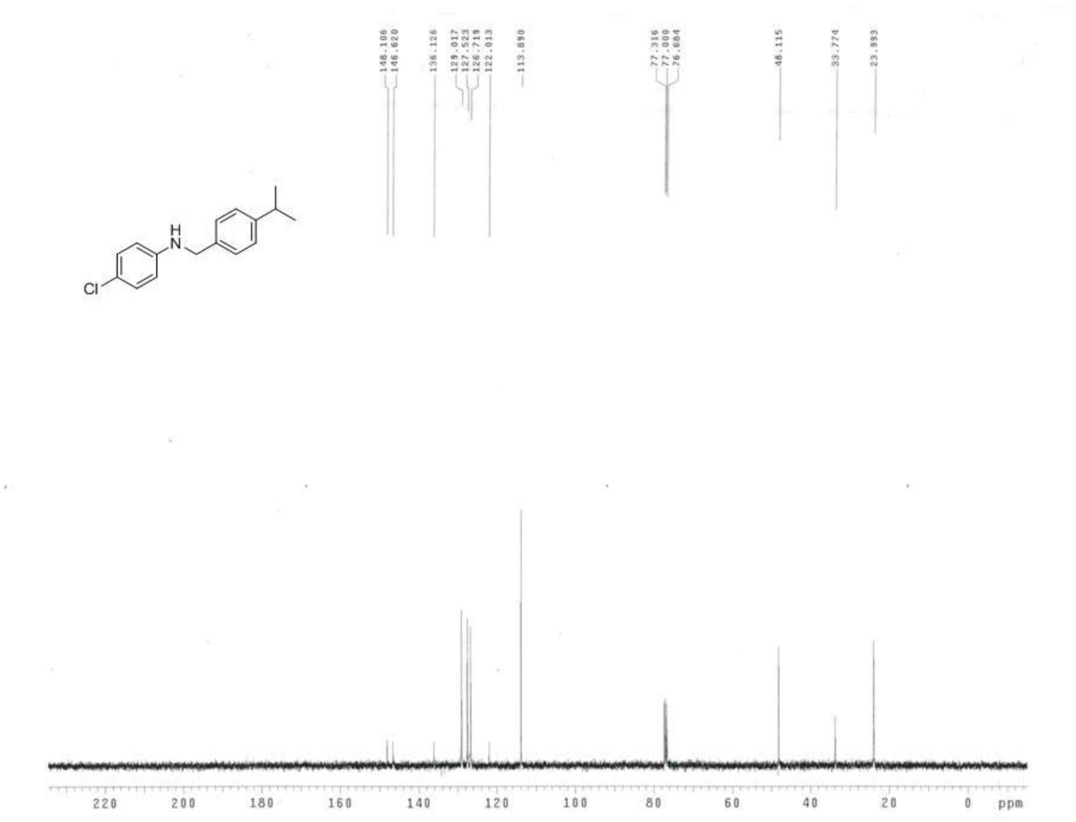
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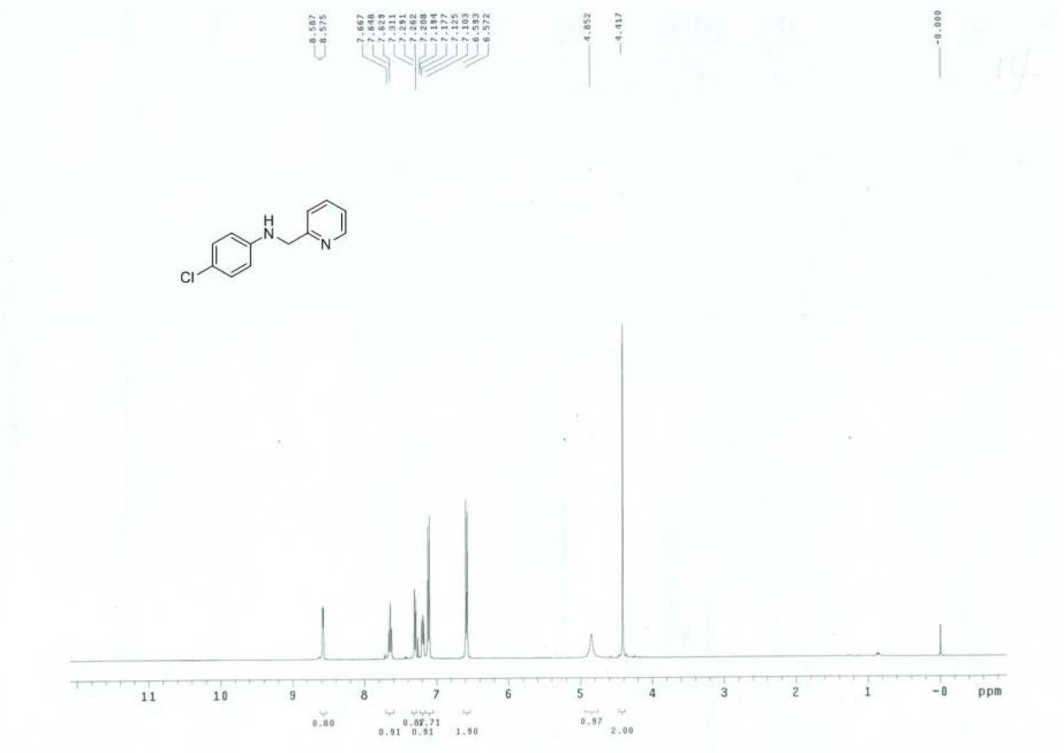
ppm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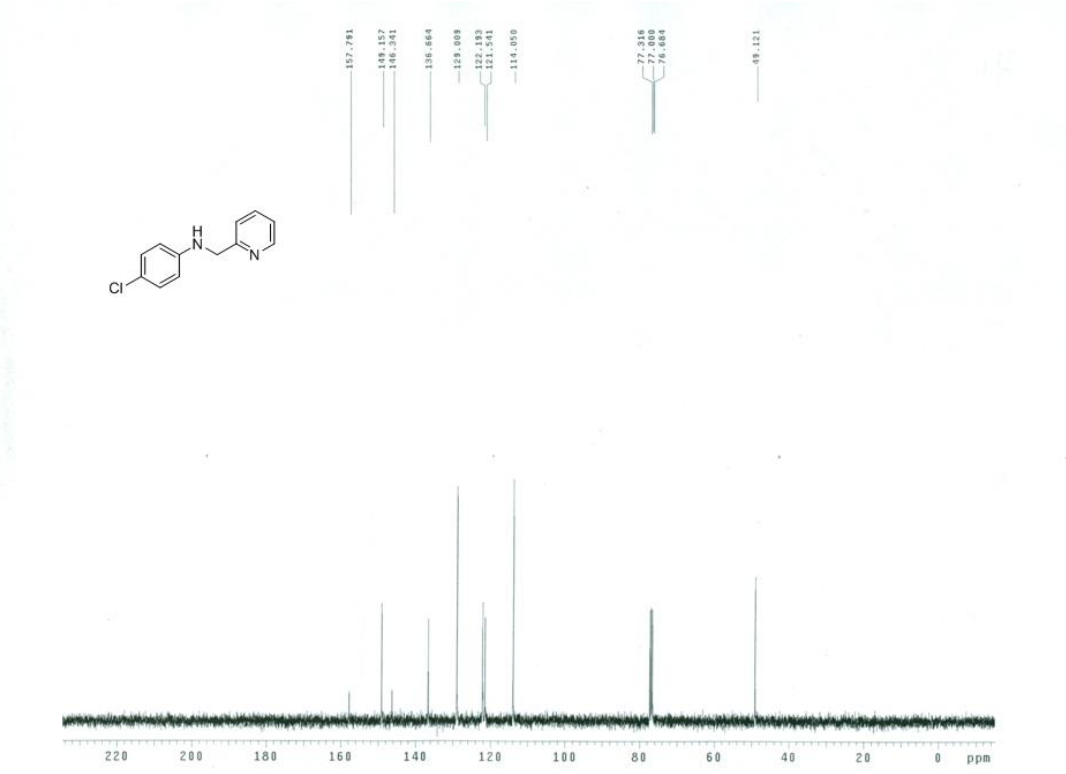
8.575
7.667
7.648
7.629
7.311
7.291
7.262
7.208
7.194
7.177
7.125
7.103
6.593
6.572
4.852
4.417
-0.000
H
N
N
Cl
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.80
0.91
0.87
1.71
0.91
1.90
0.97
2.00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149.157
146.341
136.664
129.009
122.193
121.541
114.050
77.316
77.000
76.684
49.121
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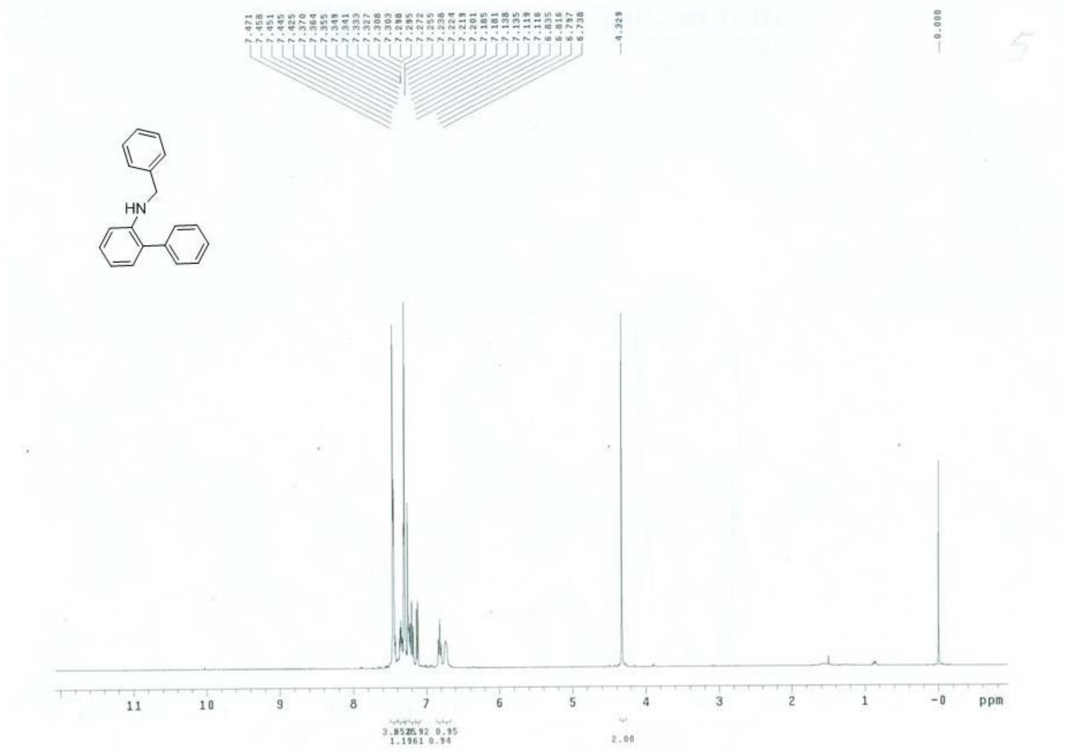
N
N
Cl
220
200
180
160
140
120
100
80
60
40
20
0
ppm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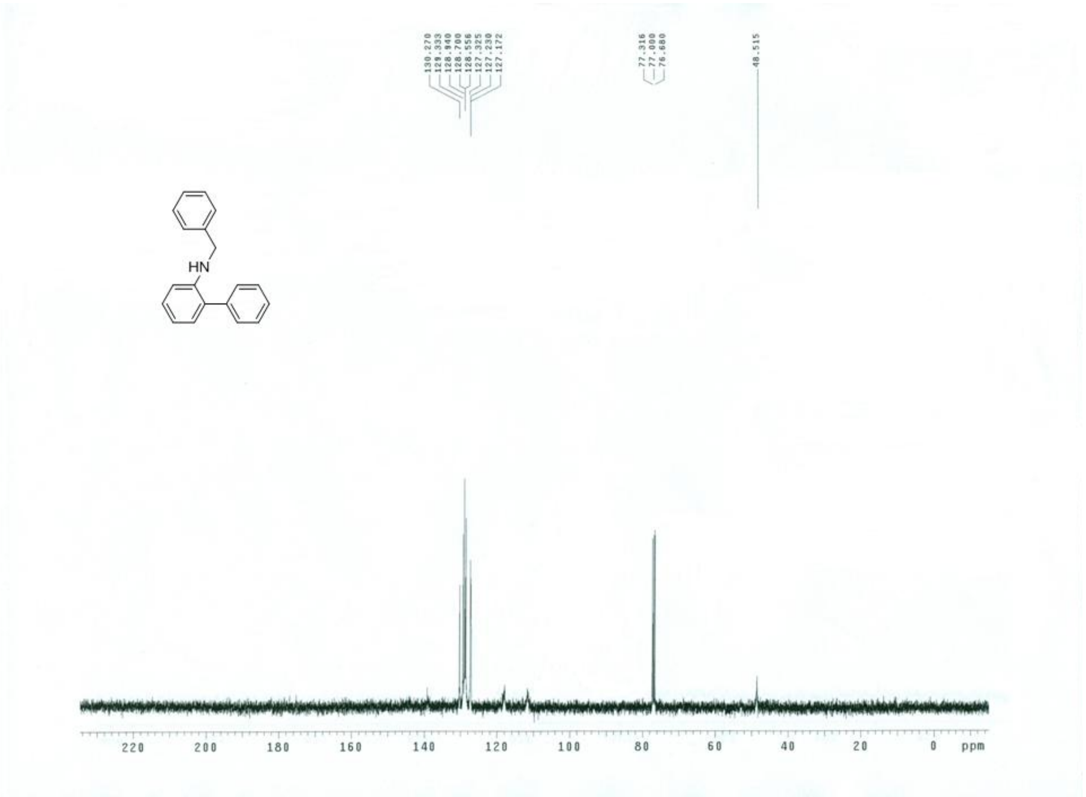
7.445
7.425
7.370
7.364
7.355
7.349
7.341
7.333
7.327
7.308
7.303
7.298
7.295
7.272
7.255
7.238
7.224
7.219
7.201
7.185
7.181
7.138
7.135
7.119
7.116
6.835
6.816
6.797
6.738
4.329
0.000
5
HN
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.8525.92
1.1961
0.95
0.94
2.00


130.270
129.333
128.940
128.700
128.556
127.325
127.230
127.172
77.316
77.000
76.680
48.515
HN
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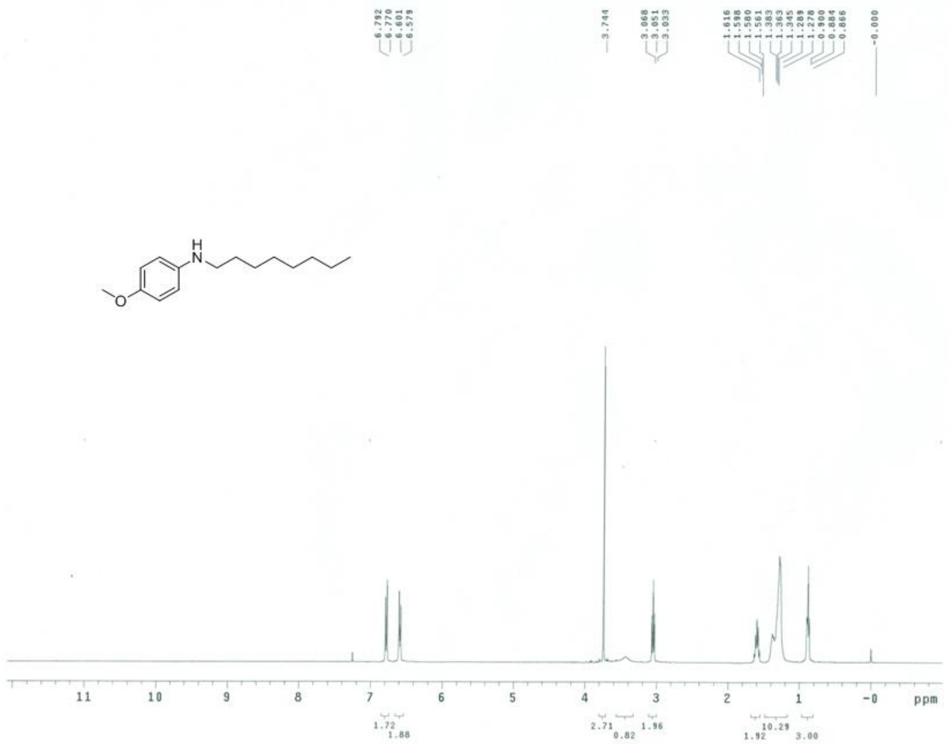
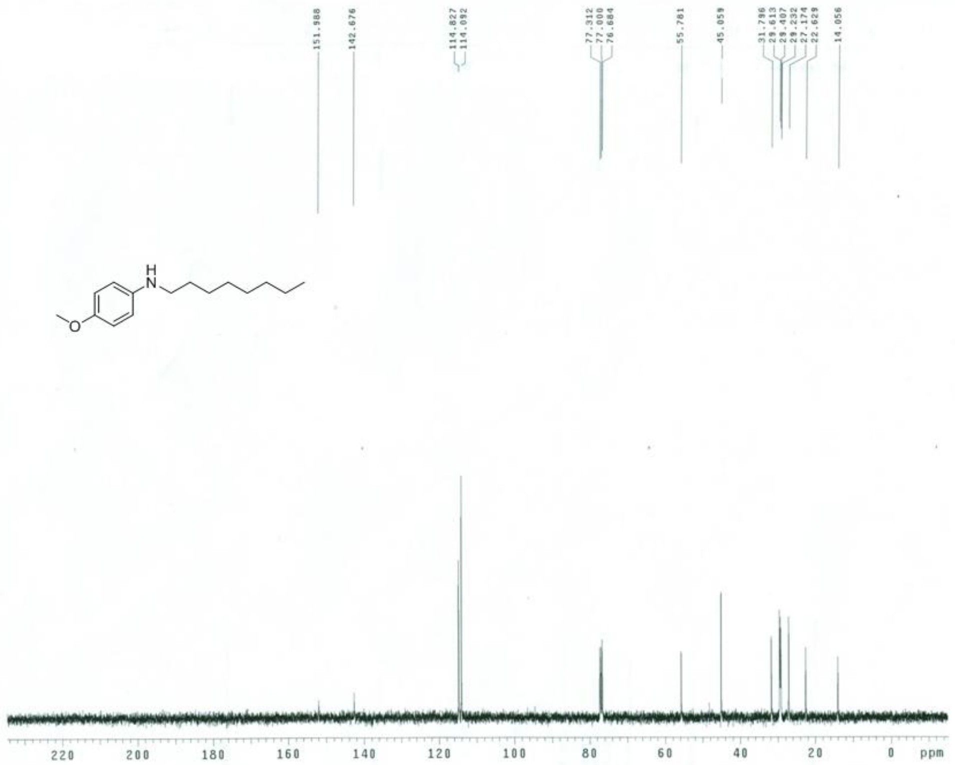
200
180
160
140
120
100
80
60
40
20
0
ppm


6.792
6.770
6.601
6.579
3.744
3.068
3.051
3.033
1.616
1.598
1.580
1.561
1.383
1.363
1.345
1.289
1.278
0.900
0.884
0.866
-0.000
H
N
O
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.72
1.88
2.71
0.82
1.96
1.92
10.29
3.00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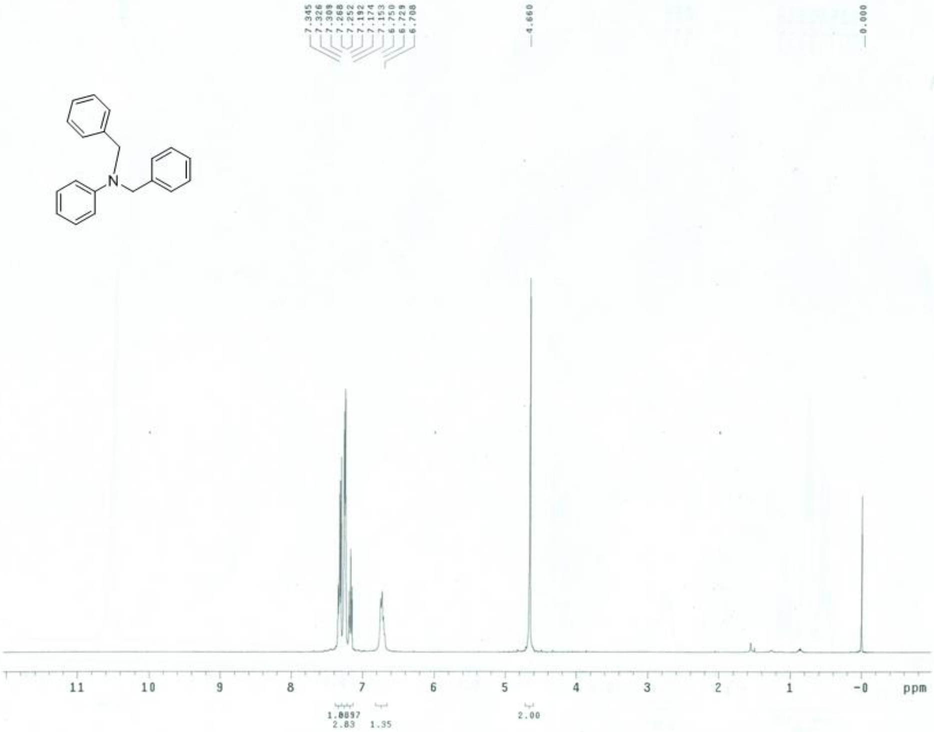
142.676
114.827
114.092
77.312
77.000
76.684
55.781
45.059
31.796
29.613
29.407
29.232
27.174
22.629
14.056
H
N
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.345
7.326
7.309
7.268
7.252
7.192
7.174
7.153
6.750
6.729
6.708
4.660
0.000
N
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
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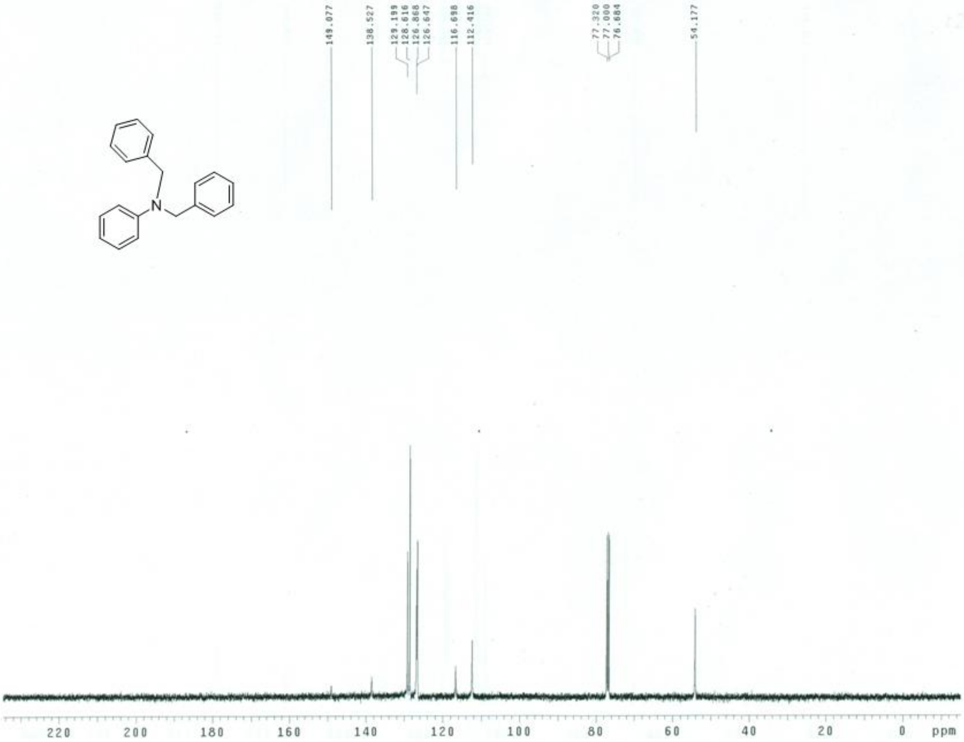
2.83
1.35
2.00


149.077
138.527
129.199
128.616
126.868
126.647
116.698
112.416
77.320
77.000
76.684
54.177
N
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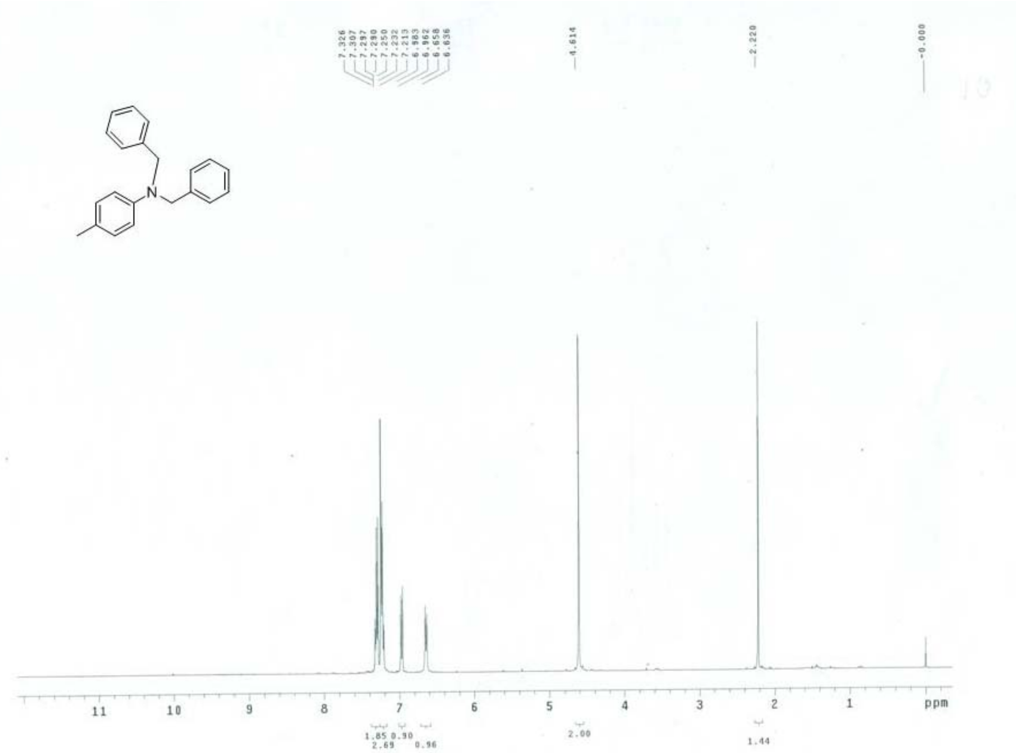
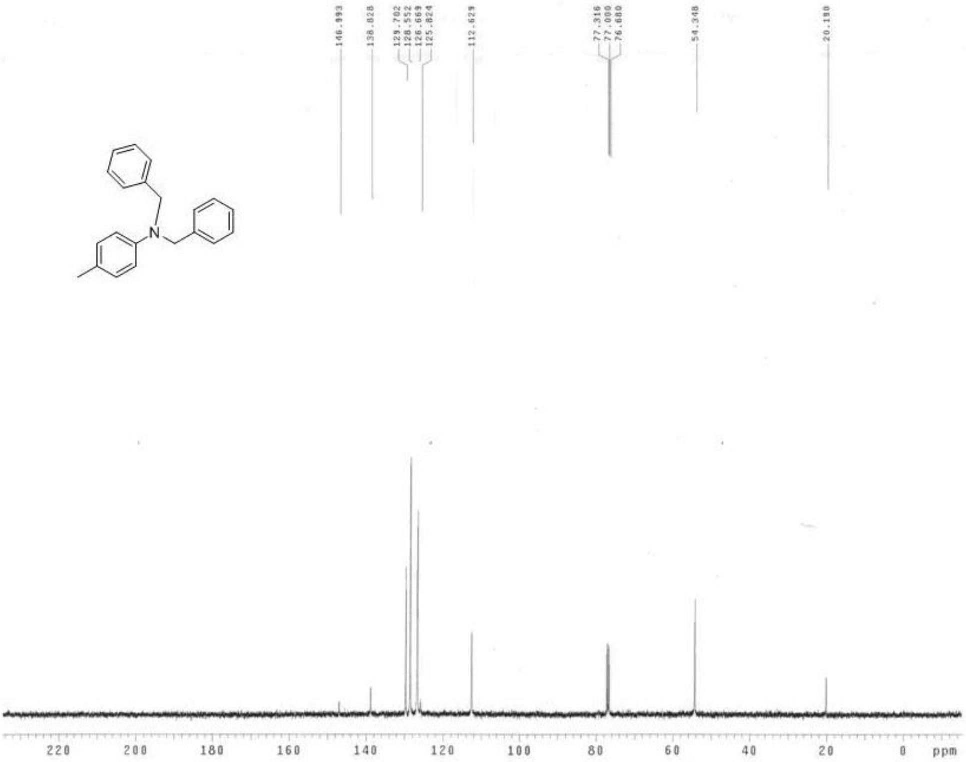
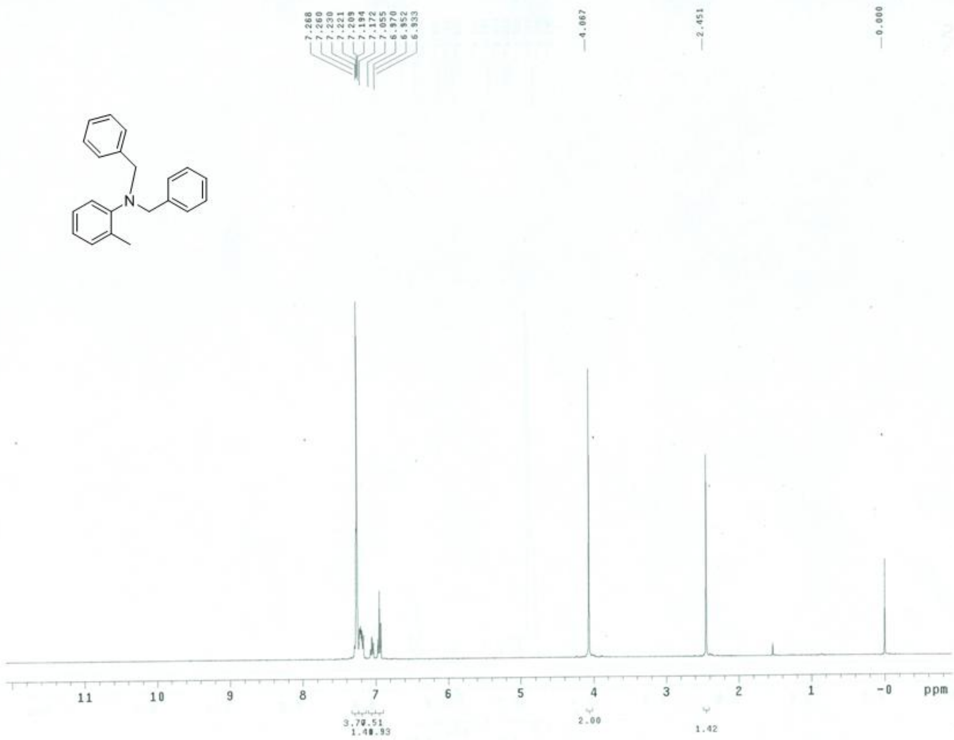
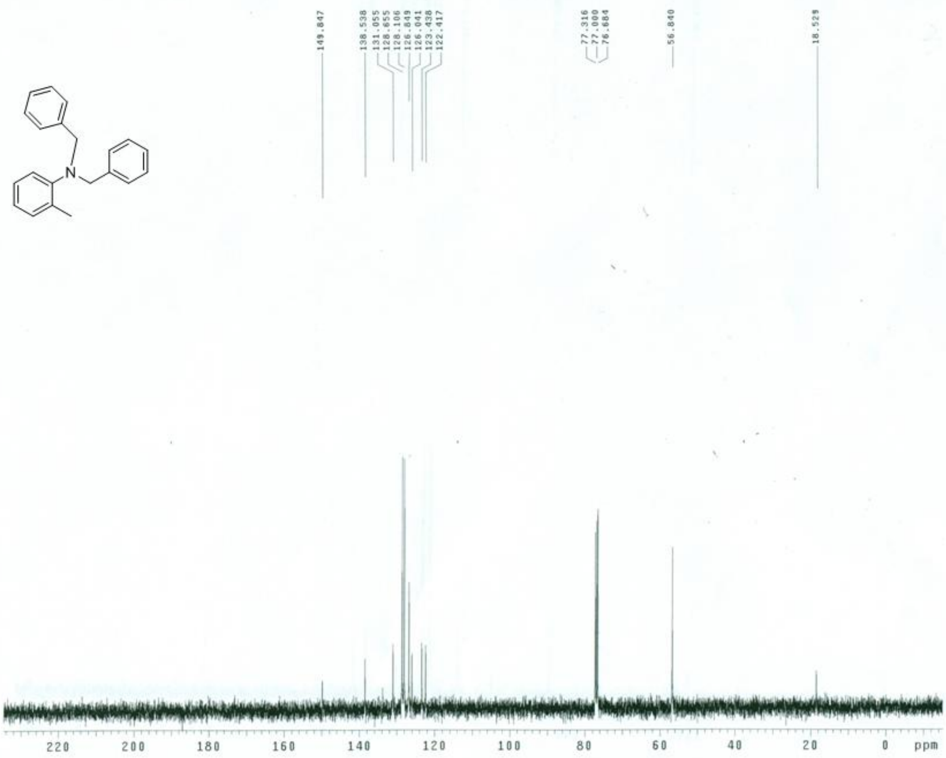
200
180
160
140
120
100
80
60
40
20
0
ppm

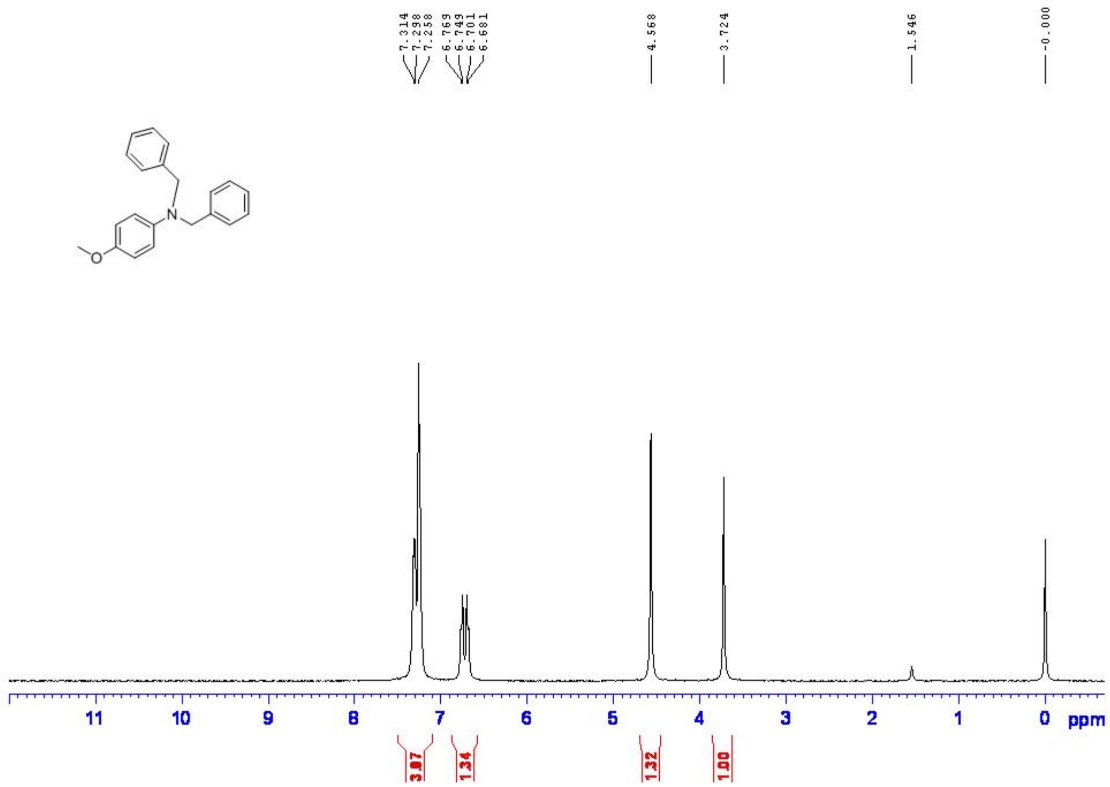

7.326
7.307
7.297
7.290
7.250
7.232
7.213
6.983
6.962
6.658
6.636
4.614
2.220
-0.000
N
11
10
9
8
7
6
5
4
3
2
1
ppm
1.85
2.69
0.90
0.96
2.00
1.44


146.993
138.828
129.702
128.552
126.669
125.824
112.629
77.316
77.000
76.680
54.348
20.190
N
220
200
180
160
140
120
100
80
60
40
20
0
ppm

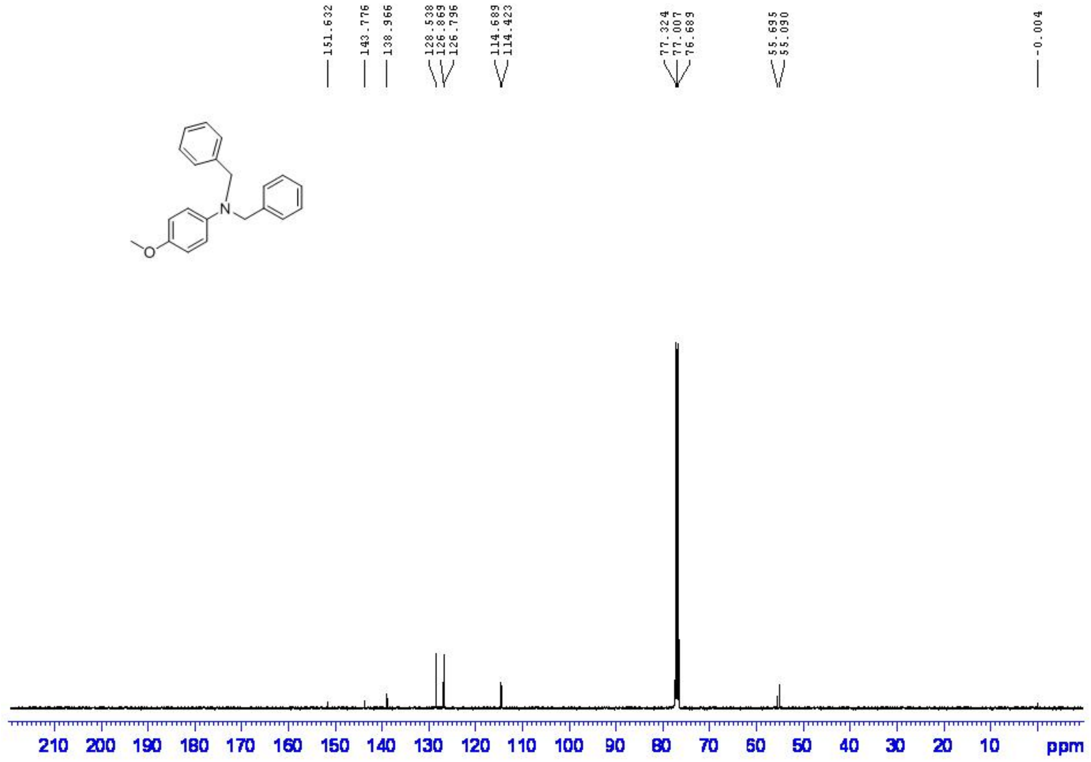

7.268
7.260
7.230
7.221
7.209
7.194
7.172
7.055
6.970
6.952
6.933
4.067
2.451
0.000
N
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.70.51
1.40.93
2.00
1.42

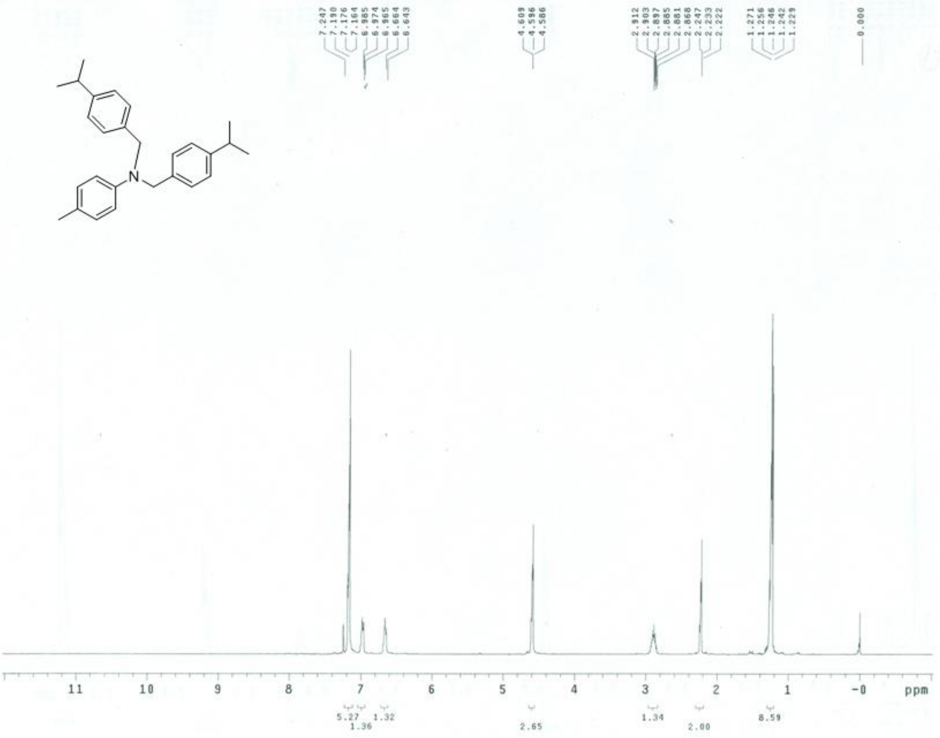

149.847
138.538
131.055
128.655
128.106
126.849
126.041
123.438
122.417
77.316
77.000
76.684
56.840
18.529
N
220
200
180
160
140
120
100
80
60
40
20
0
ppm

100205-1-PenJL-HNMR(1)



100205-1-PenJL-CNMR(2)




N
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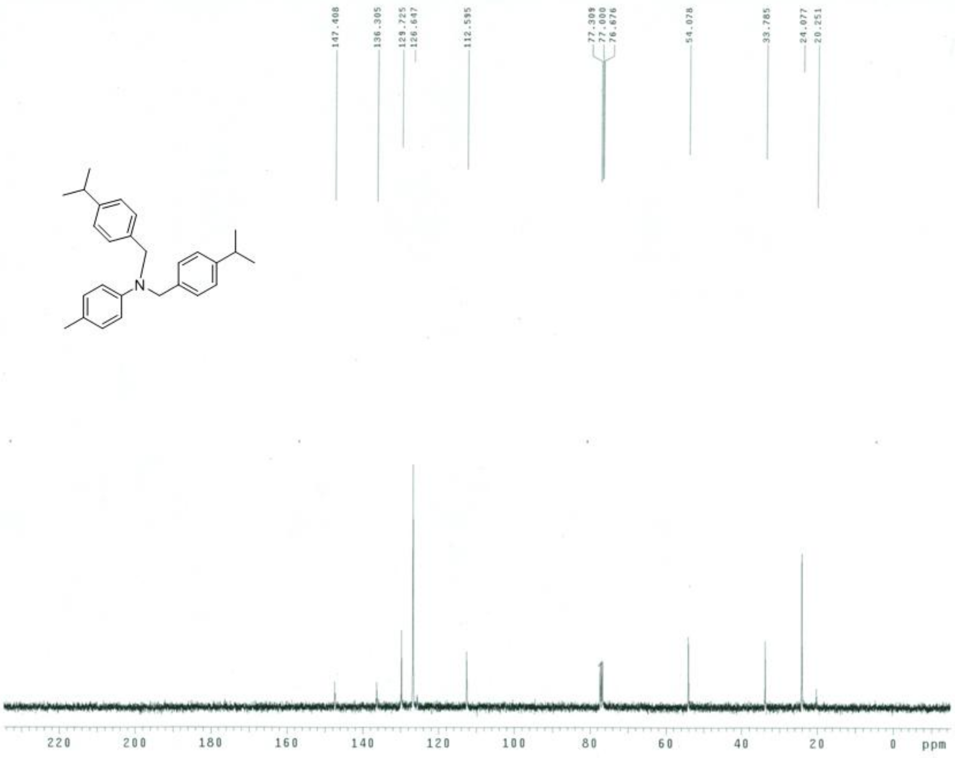
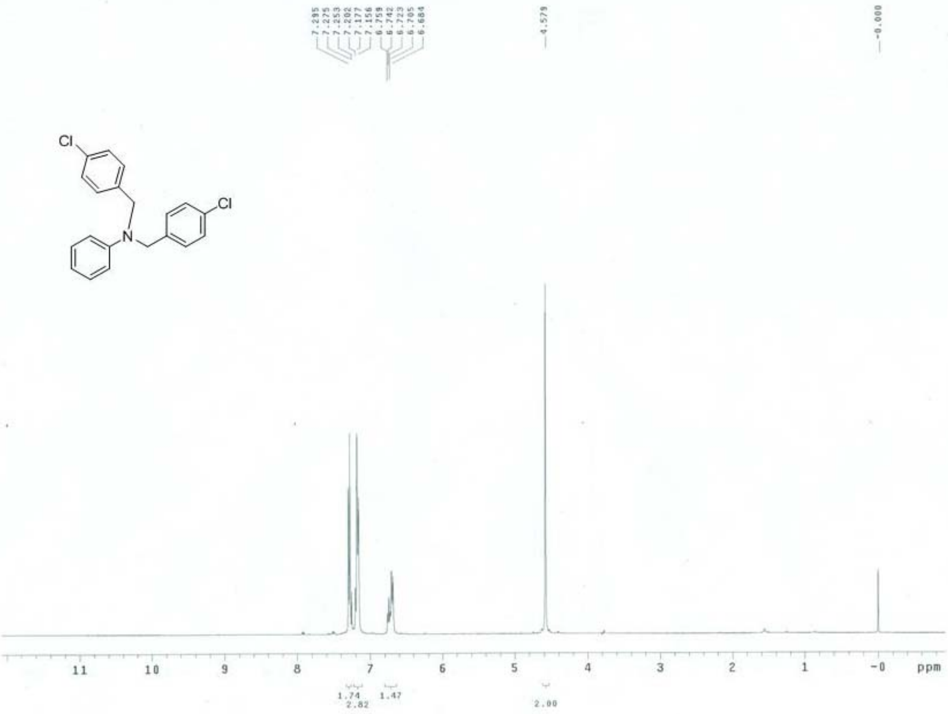
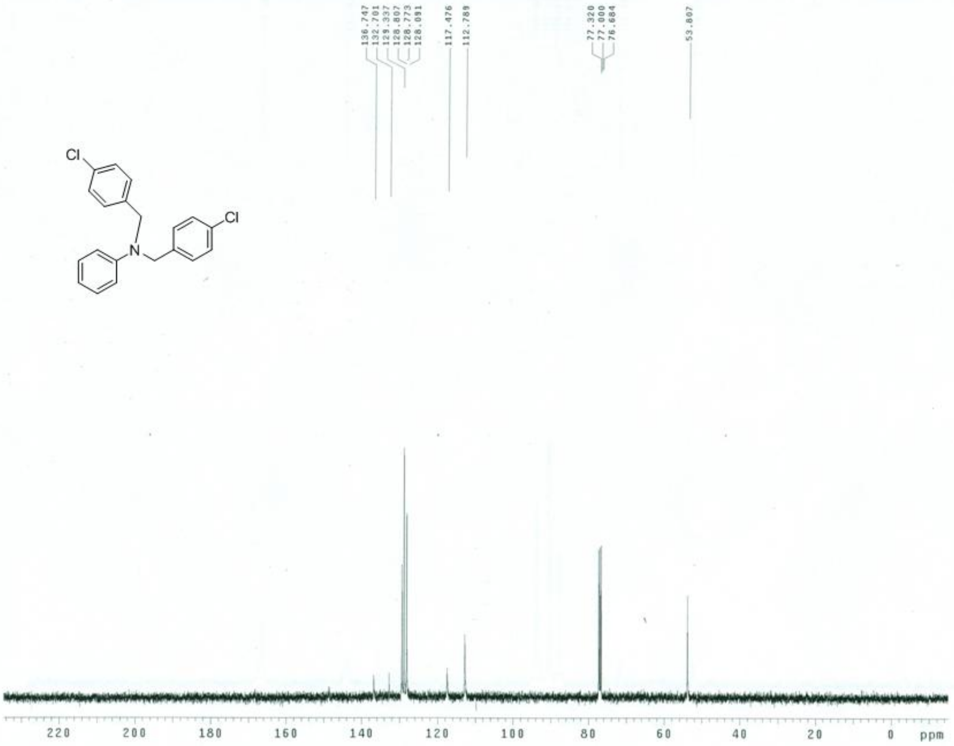
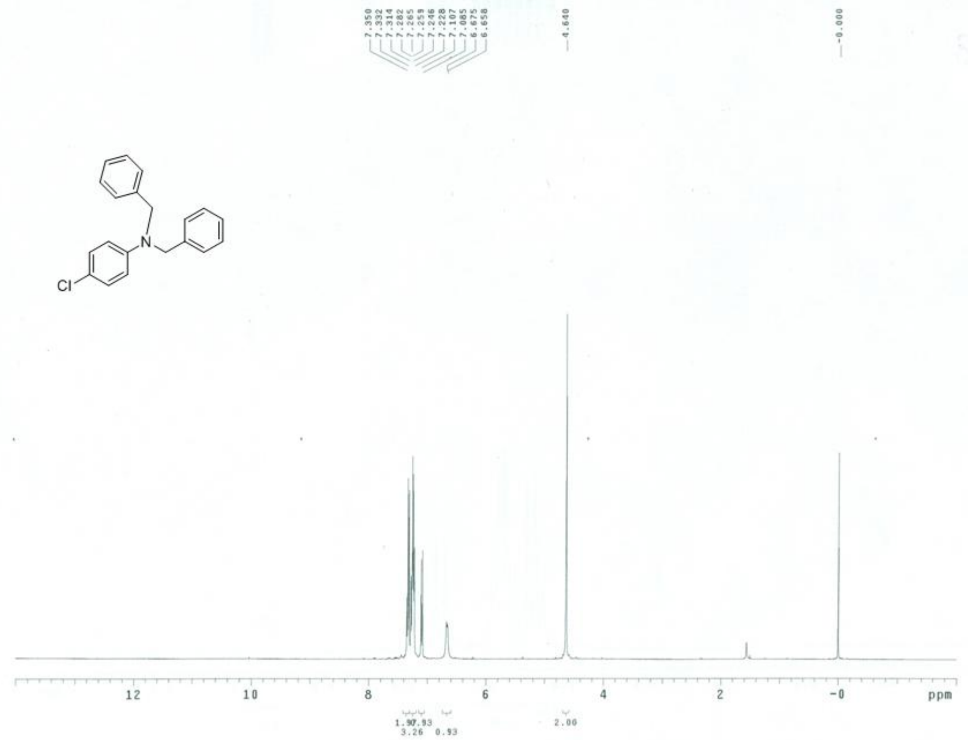
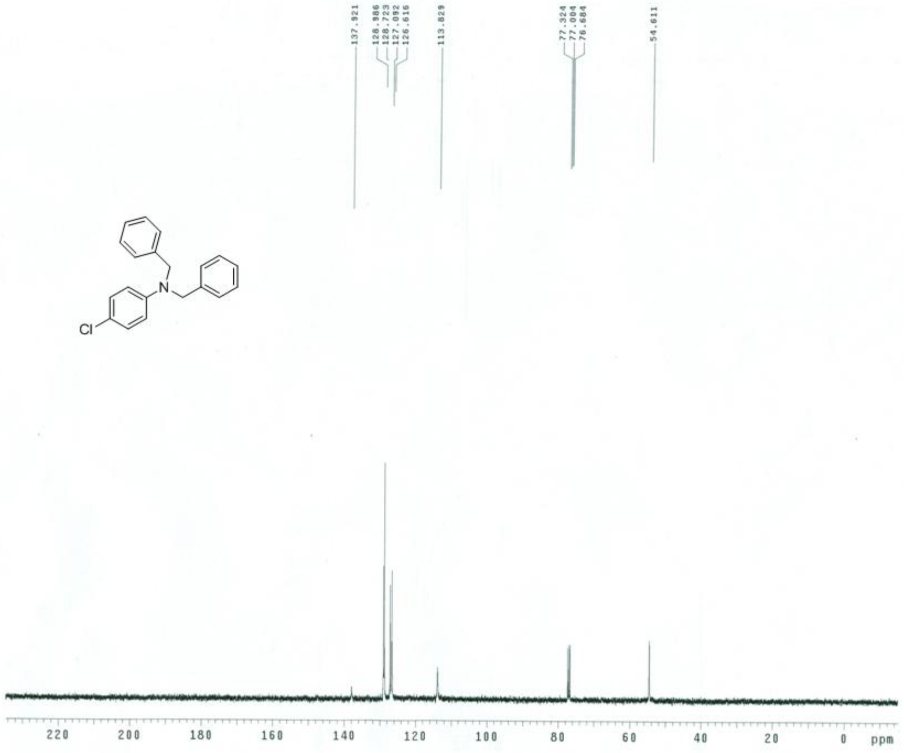
7.190
7.176
7.164
6.985
6.974
6.965
6.664
6.643
4.609
4.596
4.586
2.912
2.903
2.897
2.885
2.881
2.868
2.247
2.233
2.222
1.271
1.256
1.246
1.242
1.229
0.000
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
5.27
1.36
1.32
2.65
1.34
2.00
8.59

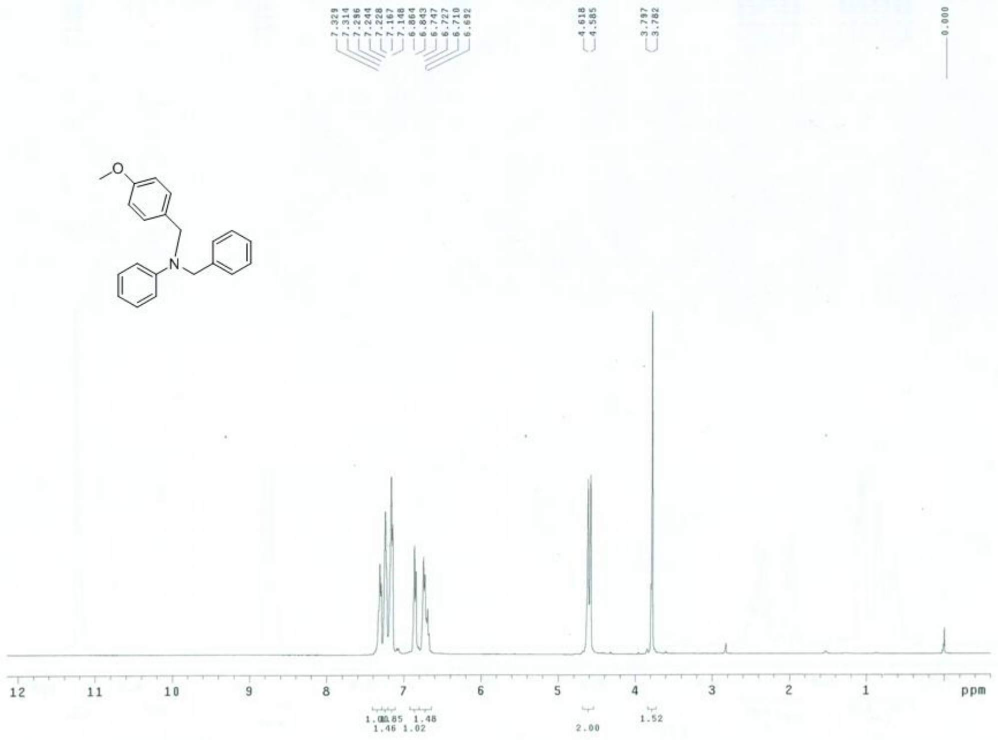

147.408
136.305
129.725
126.647
112.595
77.309
77.000
76.676
54.078
33.785
24.077
20.251
N
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.295
7.275
7.253
7.202
7.177
7.156
6.759
6.742
6.723
6.705
6.684
4.579
-0.000
Cl
Cl
N
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.74
2.82
1.47
2.00


136.747
132.701
129.337
128.807
128.773
128.091
117.476
112.789
77.320
77.000
76.684
53.807
Cl
Cl
N
220
200
180
160
140
120
100
80
60
40
20
0
ppm


7.350
7.332
7.314
7.282
7.265
7.259
7.246
7.228
7.107
7.085
6.675
6.658
4.640
-0.000
N
Cl
12
10
8
6
4
2
-0
ppm
1.97
2.93
3.26
0.93
2.00


137.921
128.986
128.723
127.092
126.616
113.829
77.324
77.004
76.684
54.611
N
Cl
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.314
7.296
7.244
7.228
7.167
7.148
6.864
6.843
6.747
6.727
6.710
6.692
4.618
4.585
3.797
3.782
0.000
O
N
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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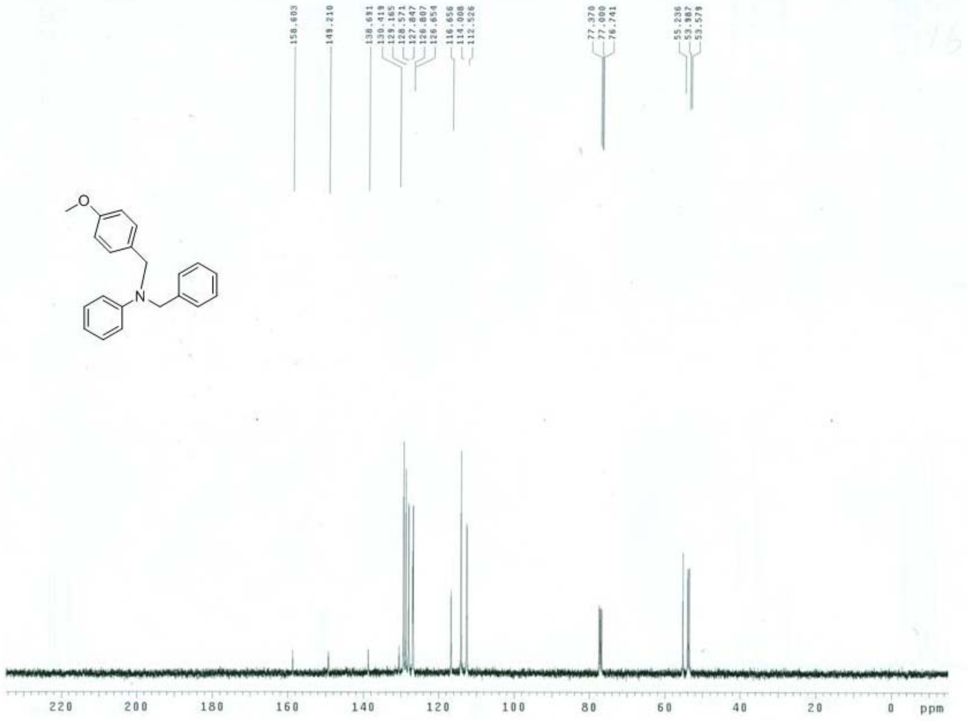
1.48
1.46
1.02
2.00
1.52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127.847
126.807
126.654
116.656
114.008
112.526
77.370
77.000
76.741
55.236
53.987
53.579
O
N
220
200
180
160
140
120
100
80
60
40
20
0
ppm