Electronic Supporting Information

PS-Pd-NHC: An efficient and heterogeneous recyclable catalyst for direct reductive amination of carbonyl compounds with primary/secondary amines in aqueous medium

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1) General Information:

All chemicals and reagents were procured from M/s Sigma Aldrich, M/s Lancaster (Alfa-Aesar), M/s S. D. fine chemical and commercial suppliers. All reactions were carried out in 100 mL high pressure reactor (autoclave) under hydrogen atmosphere. The yields reported in table 3 are referred to isolated yields and pure as determined by ^{1}H NMR, ^{13}C NMR and GC-MS while yields reported in table 1 and table 2 are GC yields. All products are well known compounds and identified by appropriate technique such as ^{1}H NMR, ^{13}C NMR, GC-MS, FT-IR and were compared with previously reported data. The ^{1}H NMR spectra were recorded with Varian Mercury, 400 MHz NMR Spectrometer) in $CDCl_3$ and ^{13}C NMR spectra were recorded with Varian Mercury, 75 MHz NMR Spectrometer in $CDCl_3$ solvent. Chemical shifts are reported in parts per million (δ) relative to tetamethylsilane as internal standard. Mass spectra were obtained on Shimadzu GC-MS (QP 2010) (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min. rise) instrument. The IR spectra were recorded with FT-IR (Perkin Elmer). GC analysis was carried out on a Perkin Elmer (Clarus-400) gas chromatograph equipped with flame ionization detector with a capillary column (Elite-1, 30 m x 0.32 mm x 0.25 μm).

2) General procedure for the direct reductive amination of carbonyl compounds with primary/secondary amines:

To a 100 mL stainless steel high pressure reactor were added aldehyde (6 mmol) and amine (5 mmol) resulting in a white opaque solution indicating the formation of an imine intermediate. To this 20 mL solvent (deionised water) was added and finally 25 mg (0.15 mol%) polymer supported Pd-NHC complex was added. The reaction mixture was then pressurized to 35 bar of hydrogen gas; the reactor was heated to 80 °C and stirred for 8 h at 600 rpm. After completion of reaction, the reactor was cooled to room temperature and the remaining hydrogen gas was carefully vented and the reactor opened. The product was extracted in ethyl acetate. The extracts were dried over sodium sulphate and the solvent was evaporated in vacuum to get crude product and which was purified by column chromatography to afford the corresponding pure product.

3) Recyclability study of PS-Pd-NHC complex:

The reaction was carried out as mentioned above in typical experimental procedure. However after completion of reaction, the reactor was cooled to room temperature and the remaining hydrogen gas was carefully vented and the reactor opened, the product was extracted in ethyl acetate and the aqueous layer containing suspended catalyst was filtered, the filtered catalyst was washed vigorously with distilled water (5 × 10 mL) and methanol (5 × 10 mL) to remove all traces of product or reactant present. The filtered catalyst was then dried under reduced pressure and kept for activation at 80 °C for a period of 4 h prior to the next recycle. The dried catalyst was then used for catalyst recyclability experiment and it was observed that the recovered catalyst could be reused up to six consecutive cycles affording good to appreciable yield of the desired product.

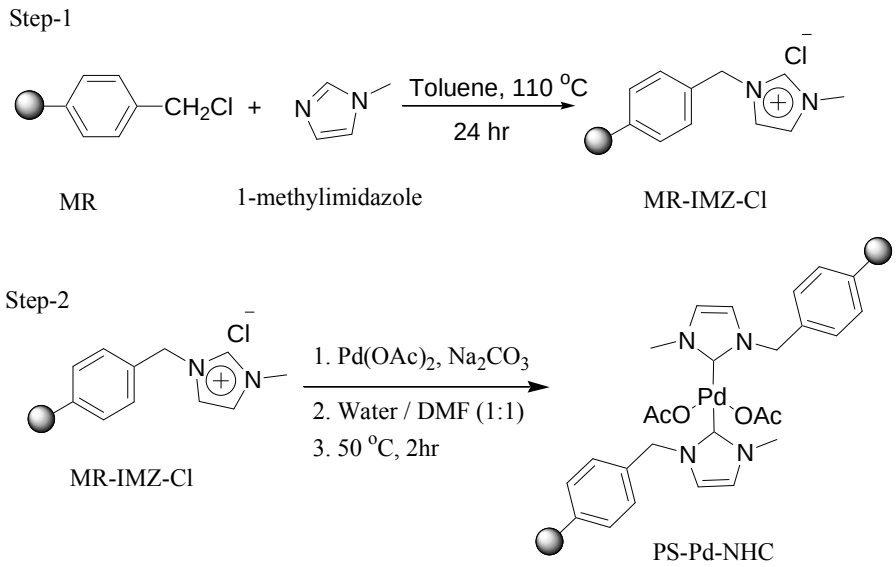
4) A typical procedure for the preparation of polymer supported palladium-*N*-heterocyclic carbene (PS-Pd-NHC) catalyst:

The polymer bound palladium complex was prepared according to reported method and characterized by different spectroscopic techniques such as solid state ^{13}C NMR (Bruker AvanceIII 700 MHz) and IR (Perkin-Elmer FTIR).

Step-1 Preparation of imidazolium-loaded polymeric support (MR-IMZ-Cl)

In 100 mL round bottom flask were added Merrifield peptide resin (2 % cross linked, 2.3 mmol Cl/g, Aldrich) 5 g, *N*-methyl imidazole (20 mmol) in toluene (50 mL) and refluxed for 24 h. On completion, the reaction mixture was cooled to room temperature. It was then filtered and the residue obtained was washed with toluene, 0.1 mol/L HCl, water and methanol sequentially followed by drying under reduced pressure to afford imidazolium-loaded polymeric support MR-IMZ-Cl (loading of ionic liquid : 1.67 mmol/g, determined by elemental analysis). The complex was further characterized by FT-IR to check the attachment of the ionic liquid. A strong band centred at 1569 cm^{-1} confirms the attachment of the imidazole on Merrifield resin.

Schematic representation of preparation of PS-Pd-NHC catalyst

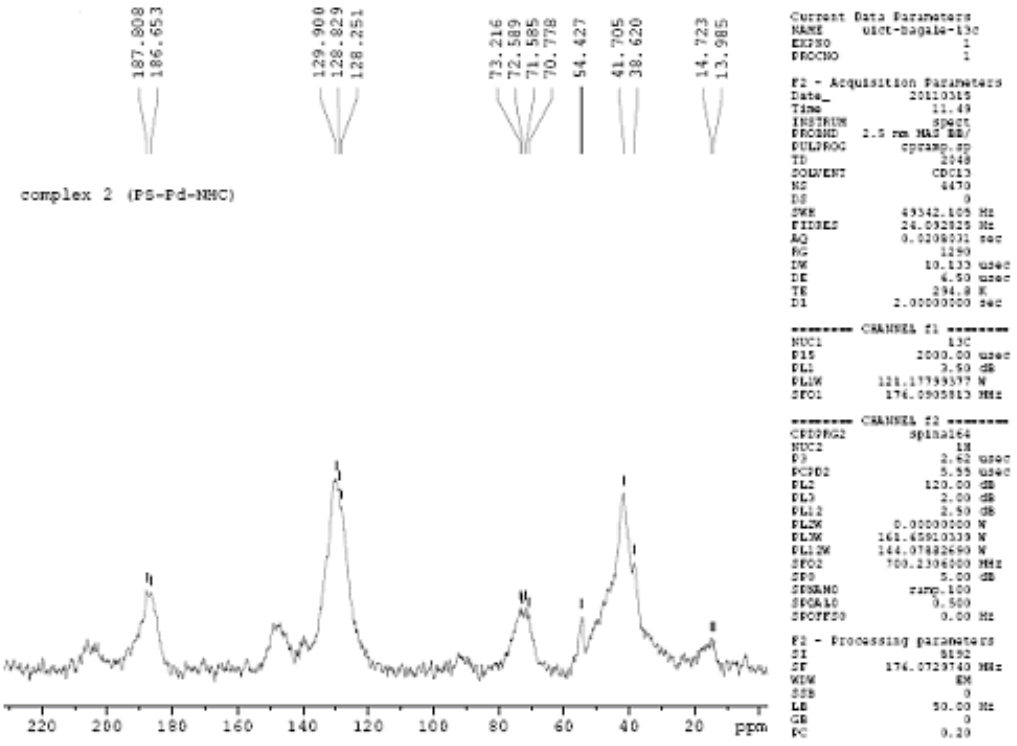


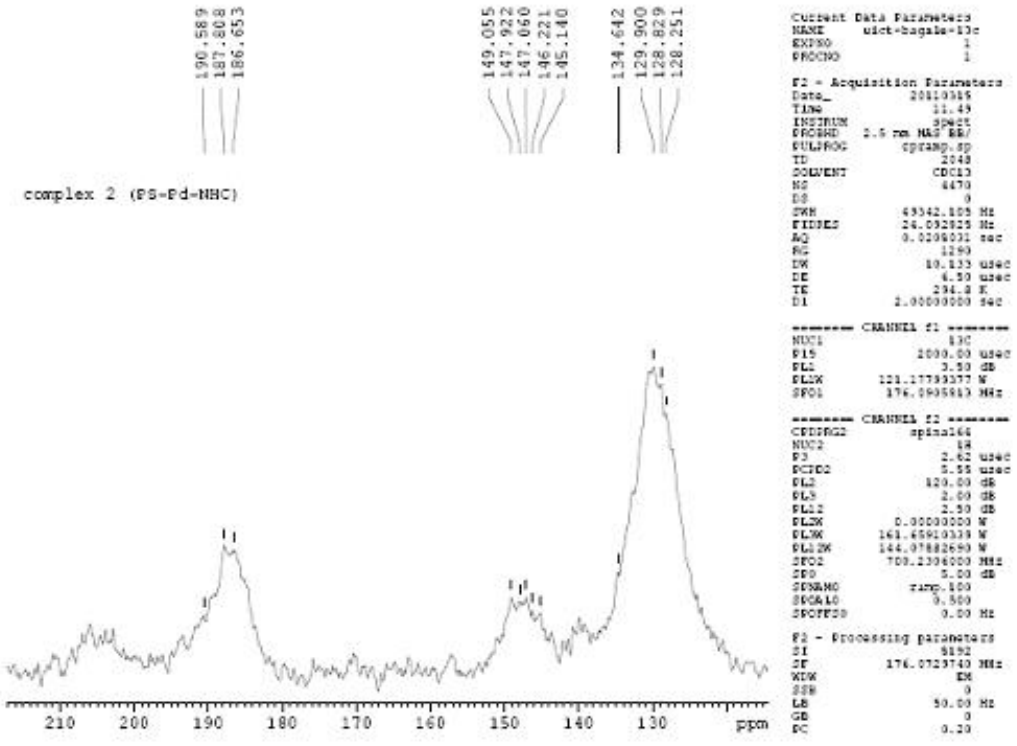
Step-2 Preparation of polymer supported palladium-*N*-heterocyclic carbene complex with the imidazolium loaded polymeric support (PS-Pd-NHC)

A mixture of the imidazolium loaded polymeric support (MR-IMZ-Cl) (1.0 g, 19.1 mmol/g) and $Pd(OAc)_2$ (0.225 g, 1 mmol) was suspended in DMF (20 mL). To this suspension an aqueous solution (20 mL) of Na_2CO_3 (1.06 g, 10.0 mmol) was added. The mixture was then sonicated at room temperature for 30 min and agitated in an orbital shaker at 50 °C for 2 h at 150 rpm. On completion, the reaction mixture was filtered and the polymeric support was washed vigorously with distilled water (5×10 mL), methanol (5×10mL), and dried under reduced pressure to provide PS-Pd-NHC. Prepared PS-Pd-NHC was then characterized by solid state ^{13}C NMR (Bruker AvanceIII 700 MHz); δ 14 (CH_3 aliphatic acetate skeleton), 42 (N-CH_3 skeleton), 54 (aliphatic polystyrene skeleton), 72 (NCN aliphatic), 128 (NCH, NCH, aromatic polystyrene skeleton), 147 (aromatic polystyrene skeleton), 187 (C=O acetate skeleton).

The amount of Pd loaded on the polymeric support was determined by using ICP-AES analysis. The polymer supported palladium-*N*-heterocyclic carbene complex (50 mg) was treated with a mixture (25 mL) of hydrochloric acid and nitric acid (1:1, v/v) at room temperature for 30 min. The orange-coloured solution formed was filtered, washed with distilled water. The filtrate and washing solution were combined to determine the amount of Pd by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and was found to about 0.29 mmol/g of support.

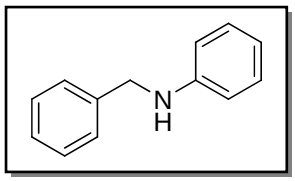
5) Solid state ^{13}C NMR spectra of PS-Pd-NHC complex





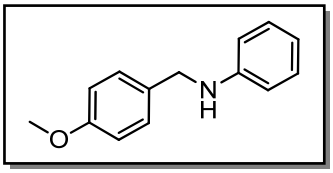
6) Characterization data of some selected compounds:

(1) ***N*-benzylaniline**



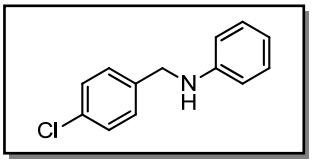
^{1}H NMR (CDCl3, 400 MHz) δ = 7.39-7.31 (m, 5H), 7.21 (t, 2H), 6.75 (t, 1H), 6.67 (d, 2H), 4.36 (s, 2H), 4.02 (br, 1H); ^{13}C NMR (CDCl3, 75 MHz) δ = 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 113.0, 48.3; IR (neat) νmax/cm^{-1} 3419, 3026, 2924, 2853, 1949, 1602, 1505, 1324, 11267, 989, 749. GC-MS (EI) *m/z* (%) =183(58), 182(21), 106(19), 91(100), 77(18), 65(17).

(2) *N*-(4-methoxybenzyl)aniline



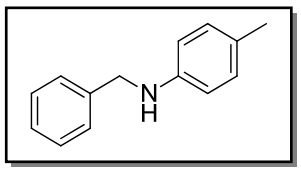
^{1}H NMR (CDCl3, 400 MHz) δ = 7.33 (d, 2 H), 7.22 (t, 2H), 7.01-6.98 (m, 2H), 6.92 (d, 2H), 6.76 (t, 1H), 6.67 (d, 2 H), 4.28 (s, 2H), 3.98 (br, 1H), 3.84 (s, 3H); ^{13}C NMR (CDCl3, 75 MHz) δ = 158.8, 148.2, 131.4, 129.3, 128.8, 117.5, 114.0, 112.8, 55.2, 47.7; IR (neat) νmax/cm^{-1} 3416, 3019, 2930, 2835, 1922, 1603, 1508, 1321, 1247, 1177, 1034, 824, 750, 692; GC-MS (EI) *m/z* (%) =213(25), 122(9), 121(100), 77(13), 65(17).

(3) *N*-(4-chlorobenzyl)aniline



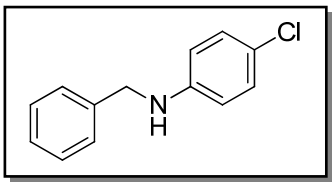
^{1}H NMR (CDCl3, 400 MHz) δ = 7.32 (s, 4H), 7.19 (t, 2H), 6.75 (t, 1H), 6.64 (d, 2H), 4.32 (s, 2H), 4.04 (br, 1H); ^{13}C NMR (CDCl3, 75 MHz) δ = 147.8, 138.0, 132.8, 129.3, 128.7, 117.8, 112.9, 47.6; IR (neat) νmax/cm^{-1} 3671, 3418, 2922, 2851, 1898, 1603, 1508, 1430, 1324, 1271, 1092, 1014, 814, 750, 692; GC-MS (EI) *m/z* (%) =219(15), 118(9), 117(46), 216(9), 127(32), 124(100), 106(12), 89(19), 77(19).

(4) *N*-benzyl-4-methylaniline



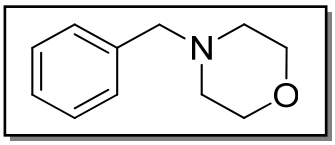
^{1}H NMR (CDCl3, 400 MHz) δ = 7.4-7.21 (m, 5H), 7.04 (d, 2H), 6.61 (d, 2H), 4.36 (s, 2H), 3.9 (br, 1H), 2.3 (s, 3H); ^{13}C NMR (CDCl3, 75 MHz) δ = 146.0, 139.6, 129.7, 128.6, 127.5, 127.1, 126.7, 113, 48.6, 20.4; IR (neat) νmax/cm^{-1} 3445, 3027, 2918, 2763, 1951, 1865, 1701, 1618, 1522, 1452, 1302, 1126, 807, 742, 697, 511; GC-MS (EI) *m/z* (%) =197(60), 196(20), 120(22), 91(100), 65(18).

(5) *N*-benzyl-4-chloroaniline



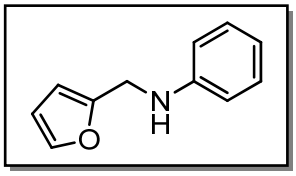
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.37-7.31 (m, 5H), 6.14 (d, 2H), 6.56 (d, 2H), 4.32 (s, 2H), 4.1 (br, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 146.7, 139.0, 129.0, 128.7, 127.4, 127.3, 122.0, 114.0, 48.3; IR (neat) νmax/cm^{-1} 3427, 3028, 2924, 2853, 1952, 1864, 1600, 1502, 1453, 1401, 1321, 1177, 1094, 915, 815, 733, 698, 505; GC-MS (EI) *m/z* (%) =219(10), 217(33), 91(100), 65(14), 45(13).

(6) 4-benzylmorpholine



^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.45-7.28 (m, 5H), 4.68 (s, 2H), 2.1-2.0 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 140.5, 129.4, 128.1, 126.9, 66.3, 64.9, 60.4; IR (neat) νmax/cm^{-1} 3034, 2986, 2631, 1717, 1377, 1245, 1045, 939, 750, 716, 699, 609; GC-MS (EI) *m/z* (%) =177(32), 146(27), 92(3), 91(100), 86(34), 65(15), 56(10).

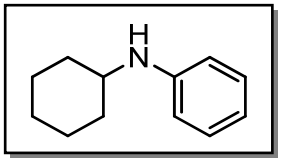
(7) *N*-(furan-2-ylmethyl)aniline



^{1}H NMR (CDCl3, 400 MHz) δ = 7.34 (s, 1H), 7.21 (t, 2H), 6.91 (m, 1H), 6.74 (m, 2H), 6.29 (s, 1H), 6.15 (s, 1H), 4.5 (s, 2H); ^{13}C NMR (CDCl3, 75 MHz) δ = 152.1, 148.4, 141.9, 129.1, 117.6, 113.4, 110.2, 107.5, 47.3; IR (neat) νmax/cm^{-1} 3672, 3116, 3040, 2925, 1921, 1598, 1507, 1437, 1375,

1347, 1183, 1157, 1075, 1007, 935, 808, 745, 691, 598; GC-MS (EI) *m/z* (%) =173(42), 172(26), 81(100), 77(11), 53(23).

(8) *N*-cyclohexylaniline



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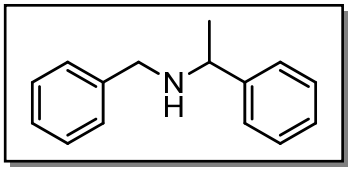
^{1}H NMR (CDCl3, 400 MHz) δ = 7.18-7.15 (m, 2H), 6.75-6.55 (m, 3H), 3.39 (s, 1H), 3.25 (m, 1H), 2.07-2.02 (m, 2H), 1.78-1.61 (m, 3H), 1.43-1.1 (m, 5H); ^{13}C NMR (CDCl3, 75 MHz) δ = 147.4, 129.2, 116.8, 113.1, 51.6, 33.5, 25.9, 25.0; IR (neat) νmax/cm^{-1} 3399, 3050, 2929, 2853, 1912, 1731, 1601, 1502, 1449, 1320, 1255, 1177, 1147, 1117, 887, 749, 692; GC-MS (EI) *m/z* (%) = 175(35), 132(100), 119(14), 77(11).

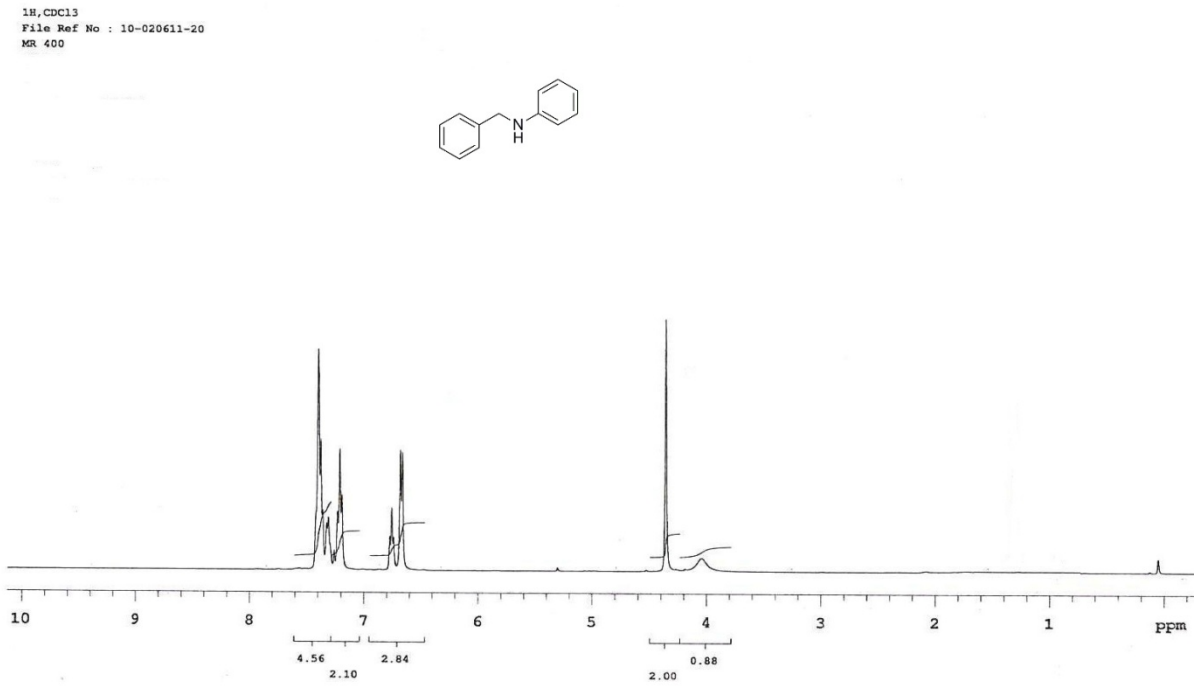
(9) *N*-benzyl-1-phenylethanamine

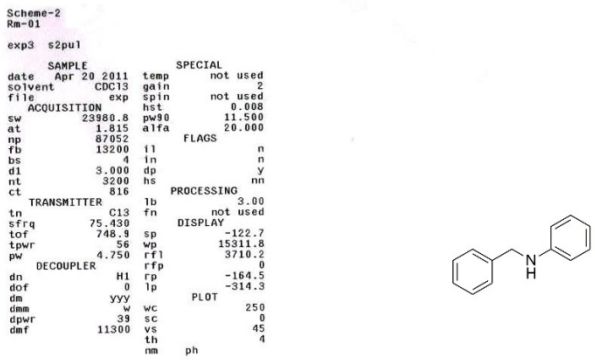


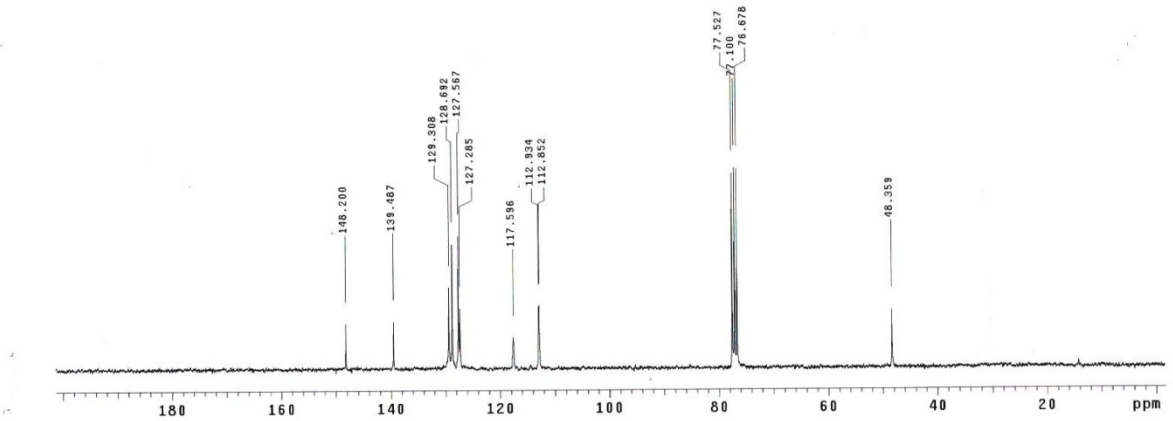
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.4-7.2 (m, 10H), 3.85 (s, 2H), 3.65 (q, 1H), 1.8 (s, 1H), 1.40 (d, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 145.6, 140.6, 128.5, 128.4, 128.1, 127.0, 126.9, 126.7, 57.5, 51.7, 24.5; IR (neat) νmax/cm^{-1} 3651, 3060, 3025, 2963, 2831, 1948, 1876, 1808, 1602, 1492, 1451, 1369, 1201, 1126, 1071, 911, 761, 699, 606; GC-MS (EI) *m/z* (%) =211(11), 196(60), 106(12), 105(16), 91(100), 77(12), 65(10).

7) ^{1}H and ^{13}C NMR Spectra of some compounds:

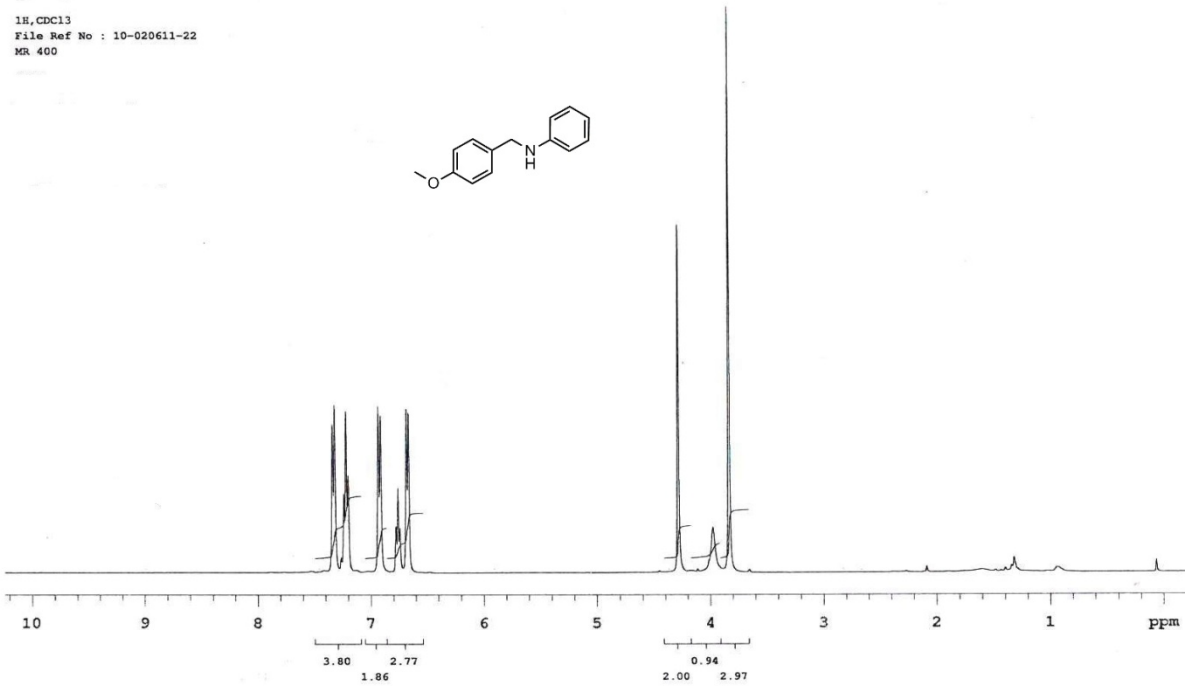
N-benzylaniline

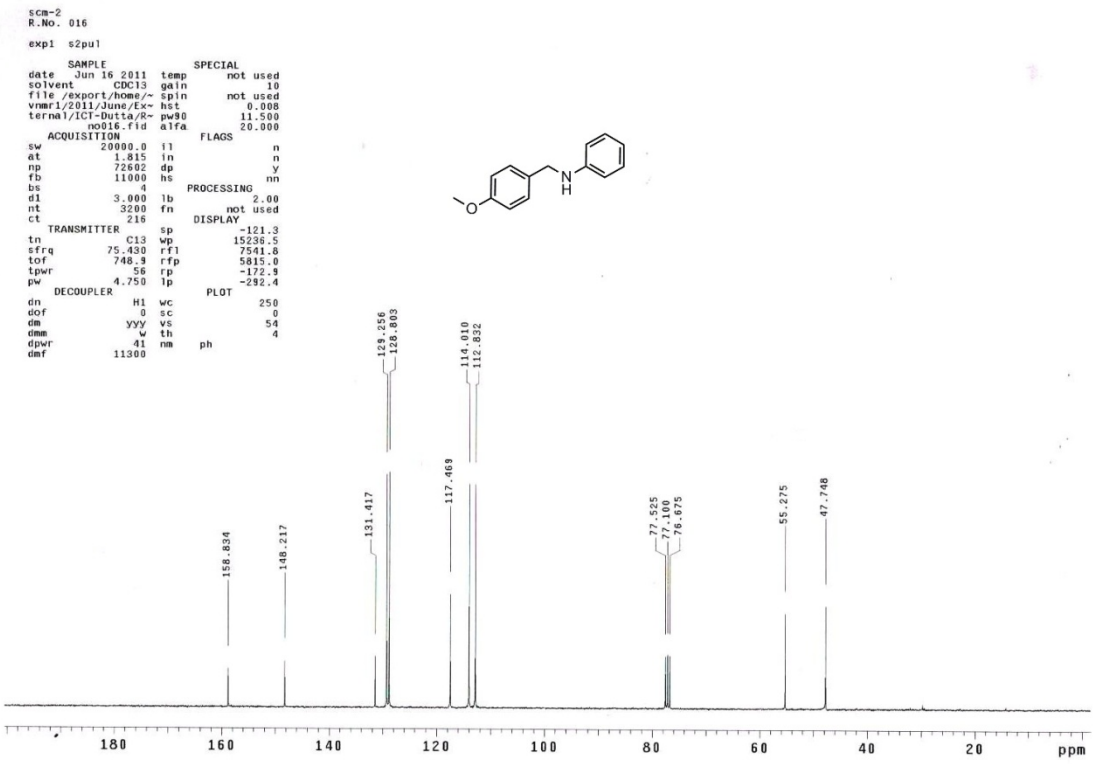




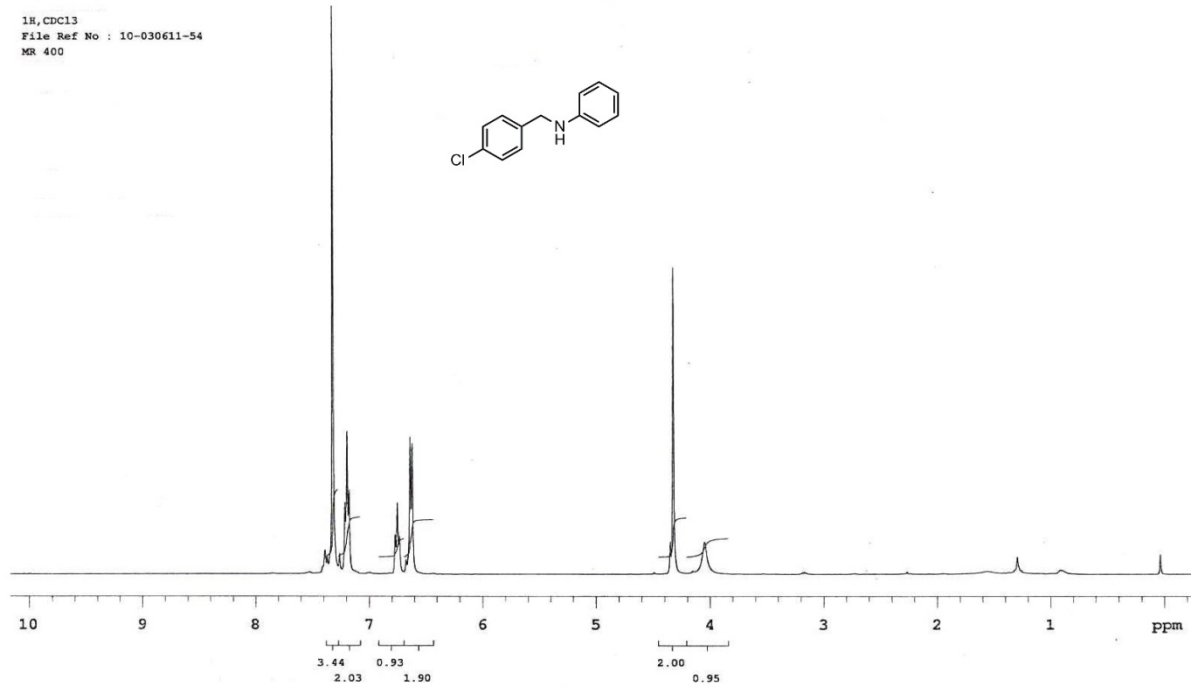


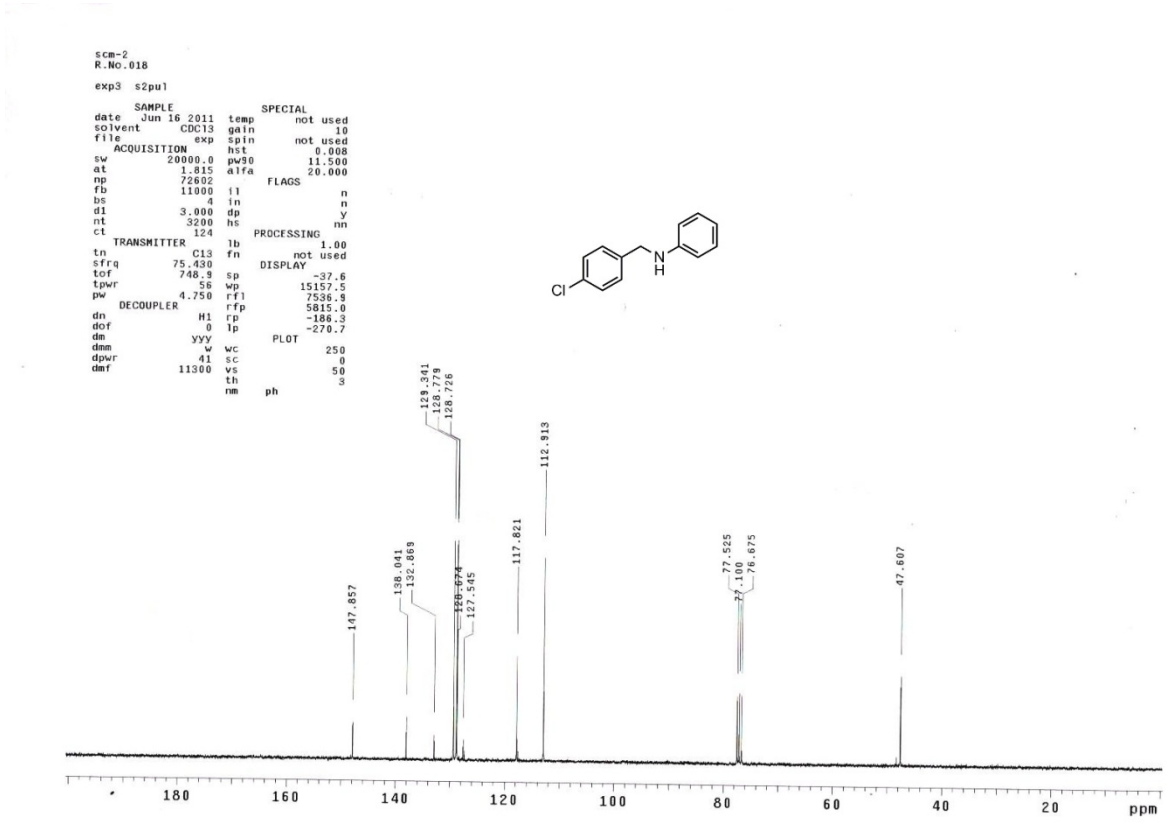
_N_-(4-methoxybenzyl)aniline



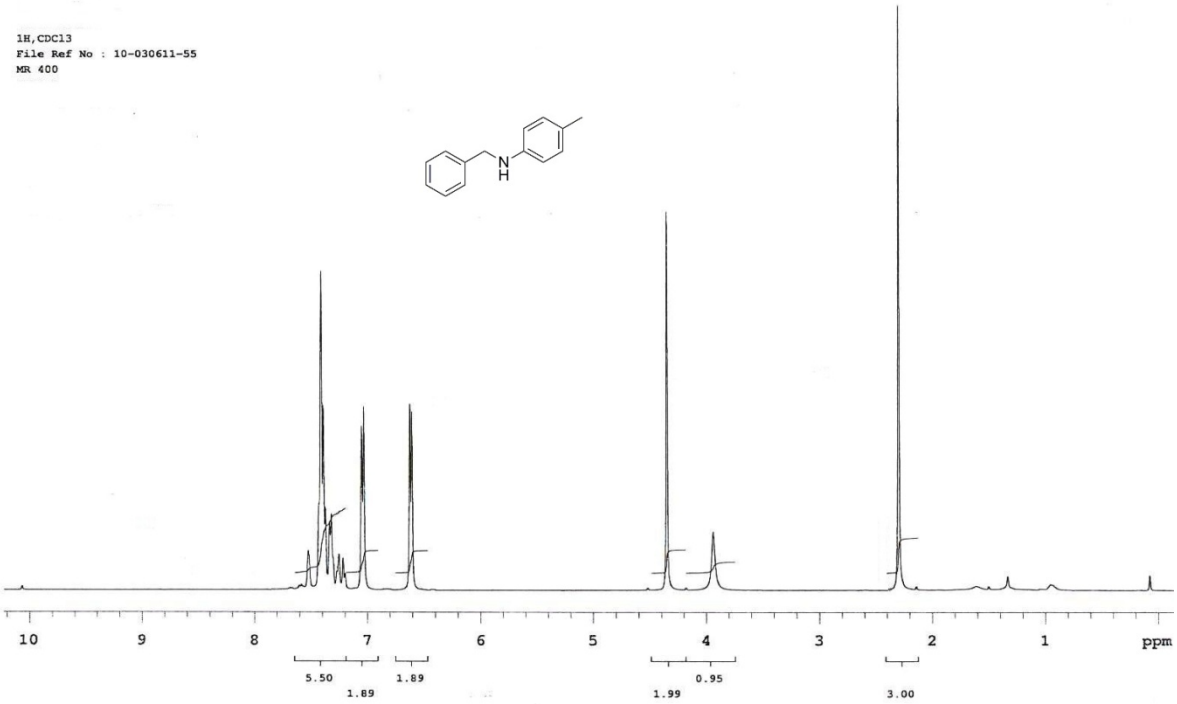


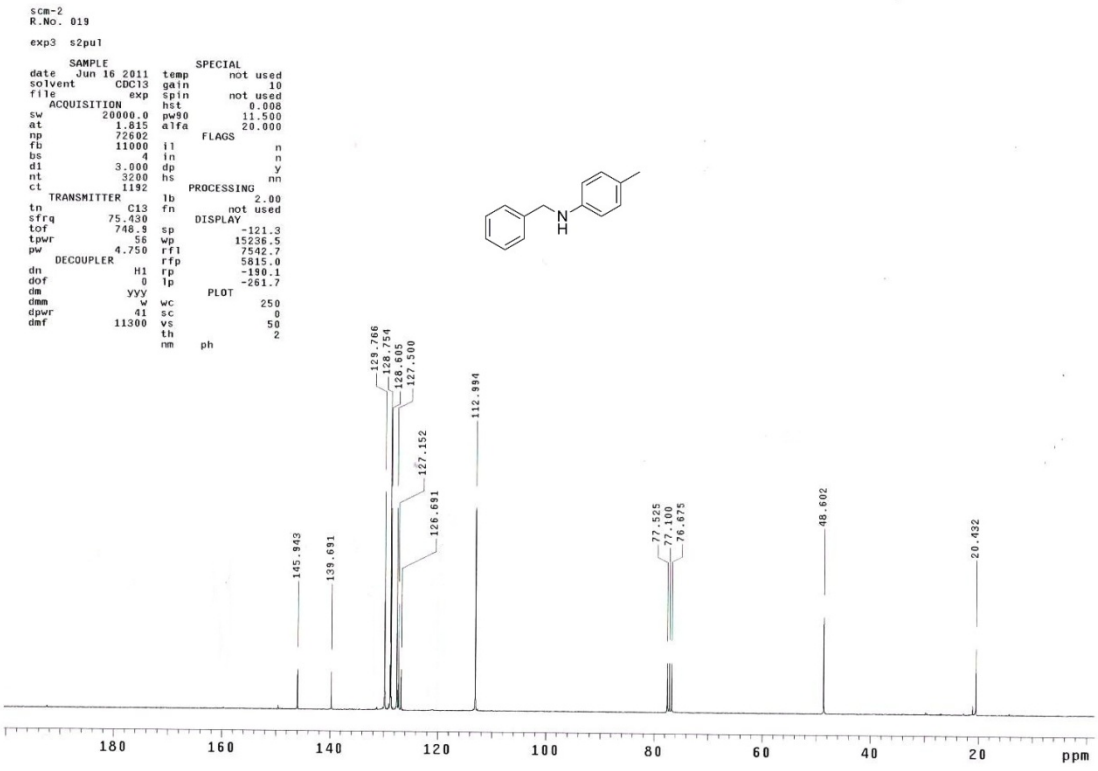
_N_-(4-chlorobenzyl)aniline



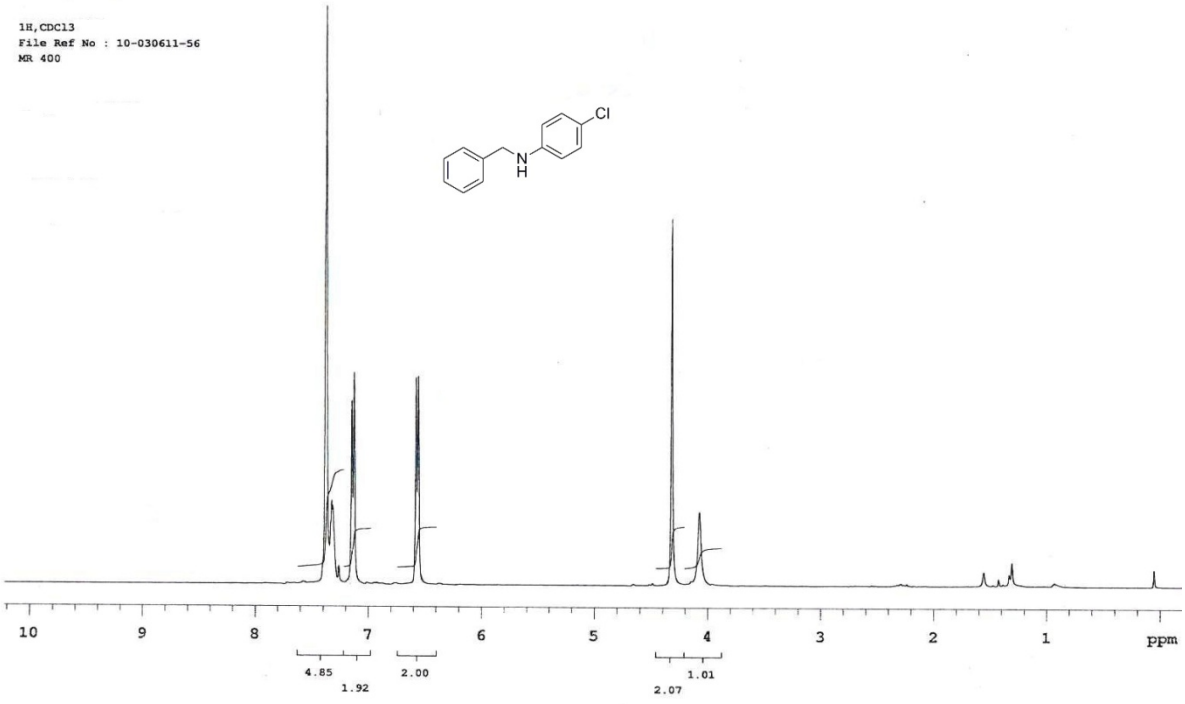


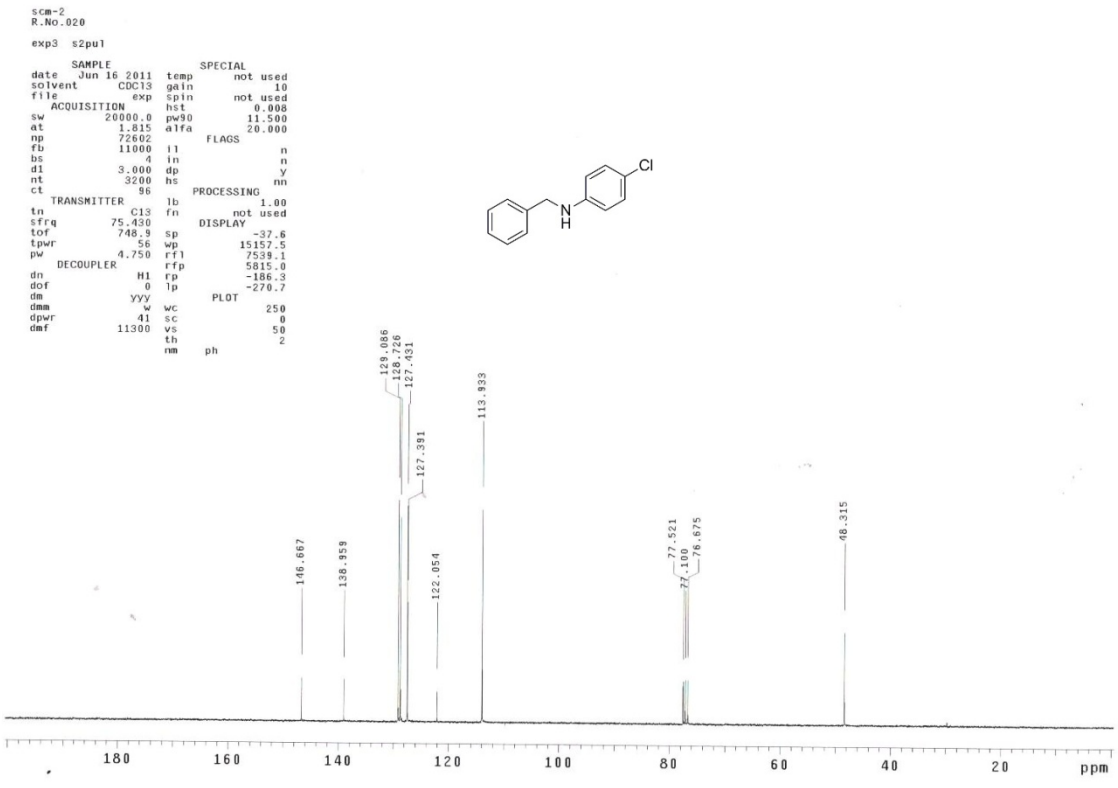
_N_-benzyl-4-methylaniline



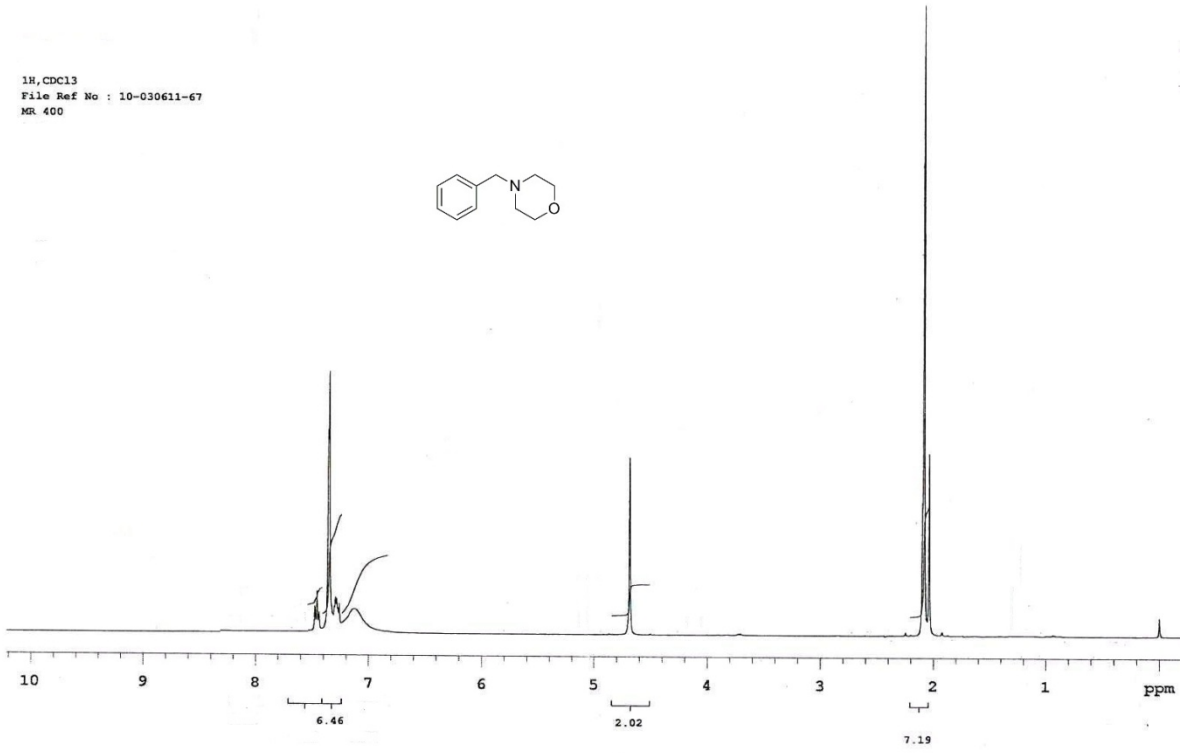


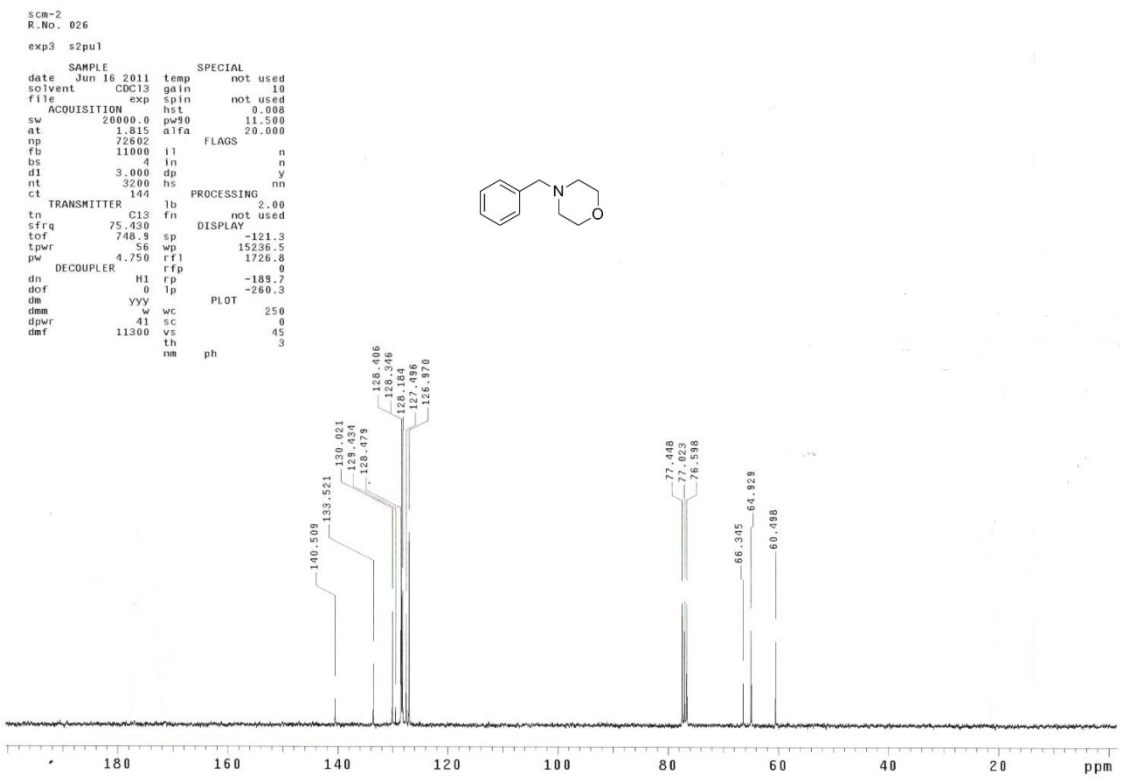
_N_-benzyl-4-chloroaniline



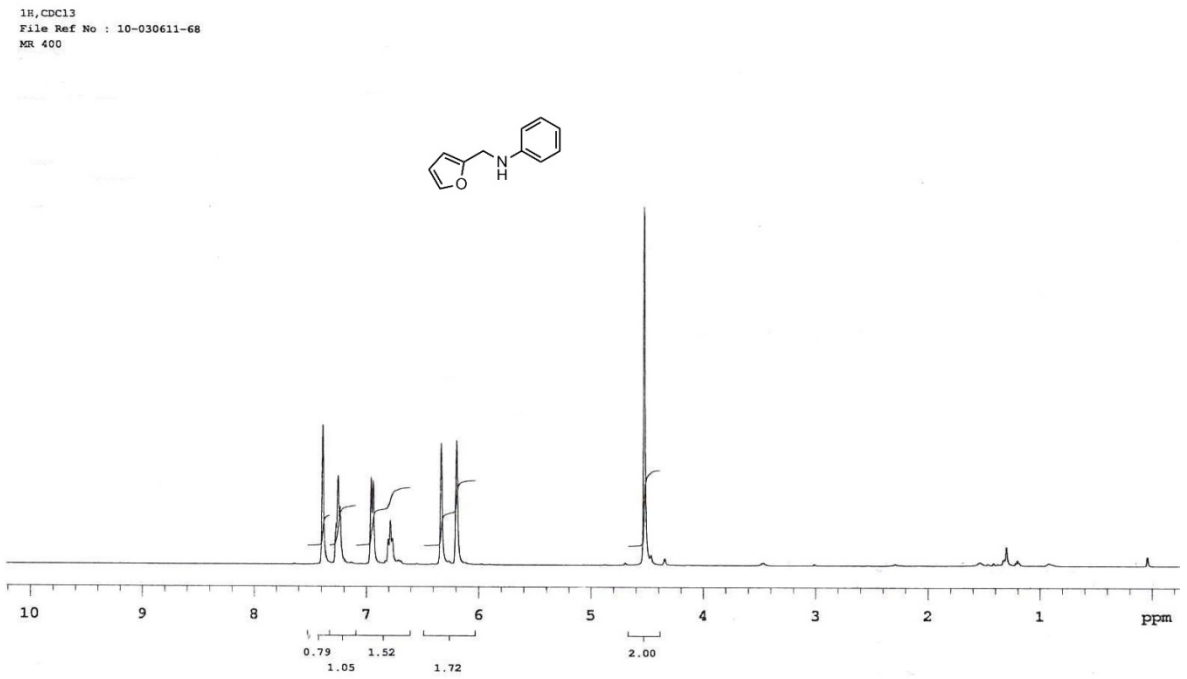


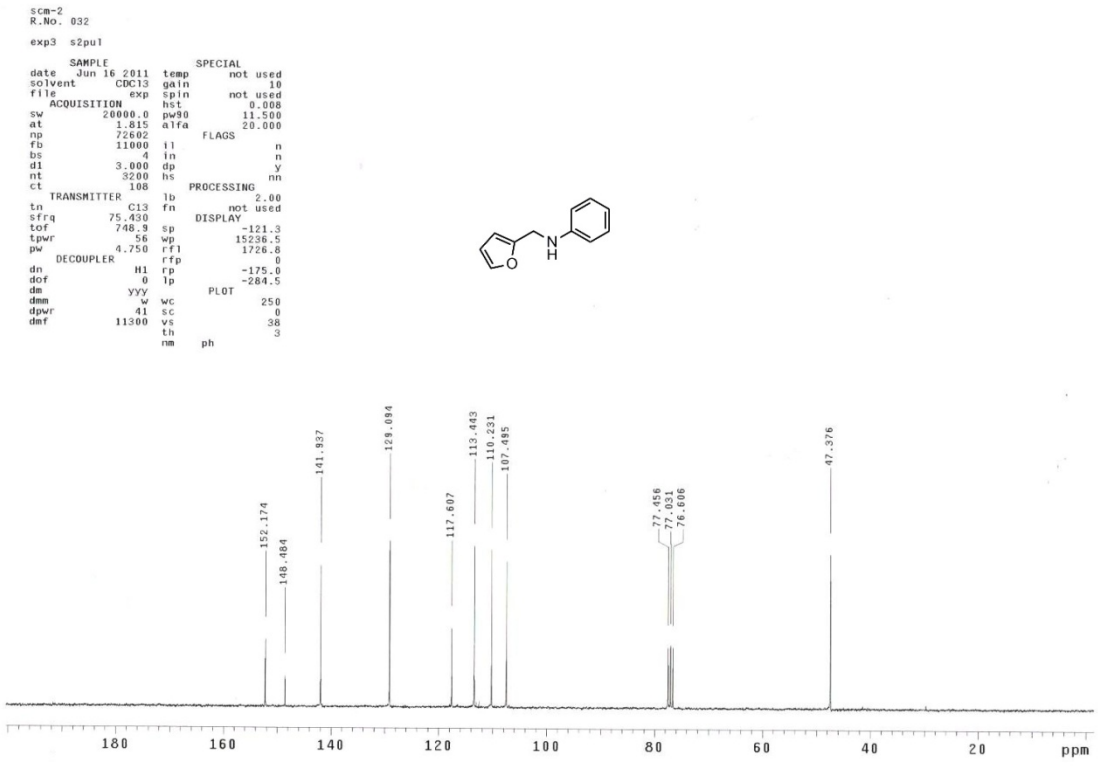
4-benzylmorpholine



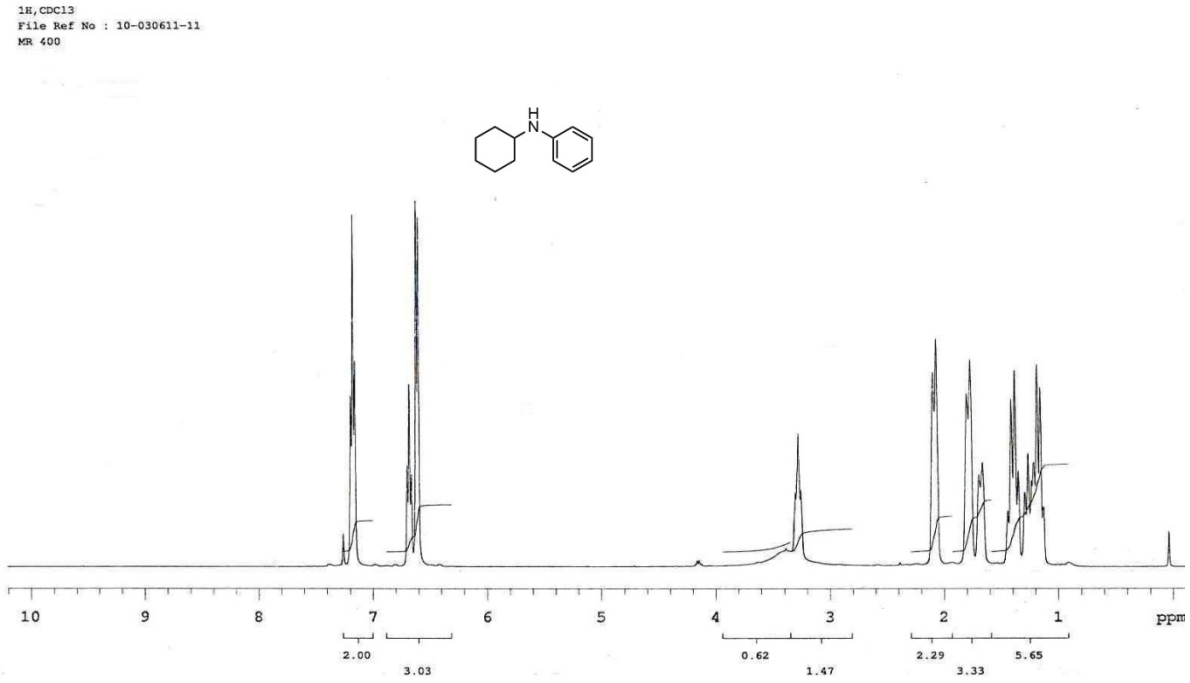


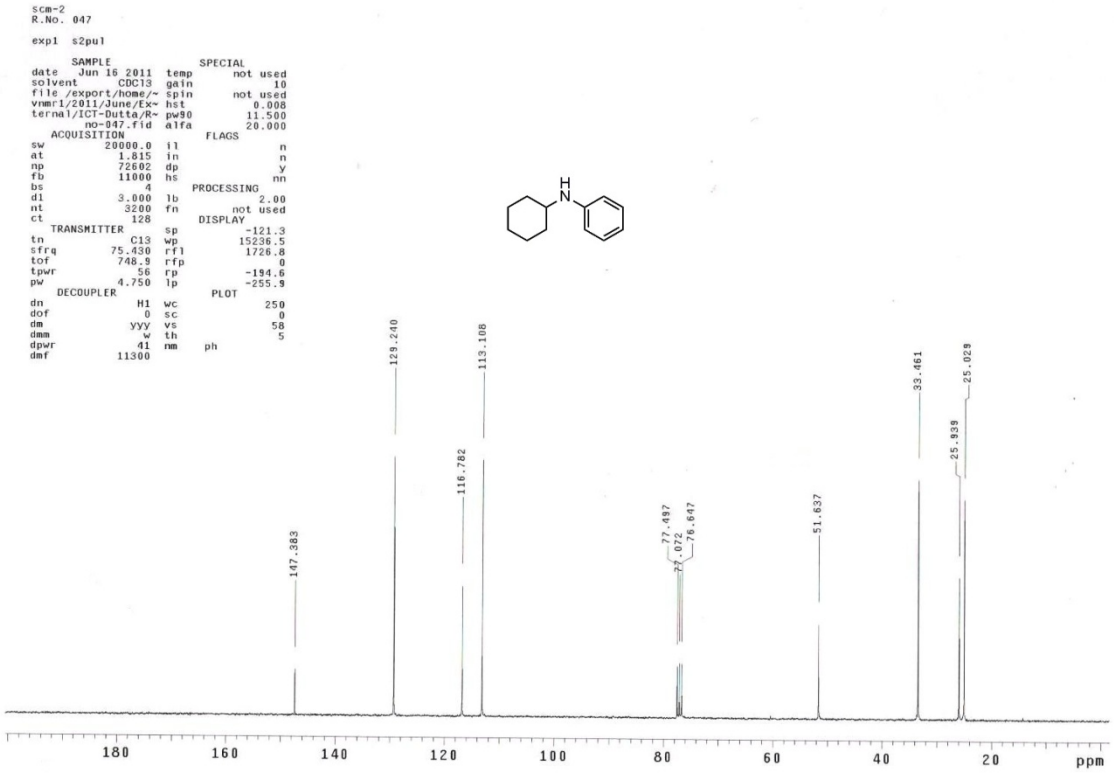
_N_-(furan-2-ylmethyl)aniline





N-cyclohexylaniline





_N_-benzyl-1-phenylethanamine