

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 ^1H 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 ^1H NMR, ^{13}C NMR, GC-MS, FT-IR and were compared with previously reported data. The ^1H 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 tetramethylsilane as internal standard. Mass spectra were obtained on Shimadzu GC-MS (QP 2010) (Rtx-17, 30 m \times 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80 $^\circ\text{C}$ to 240 $^\circ\text{C}$ at 10 $^\circ$ /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 \times 0.32 mm \times 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 $^\circ\text{C}$ 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.

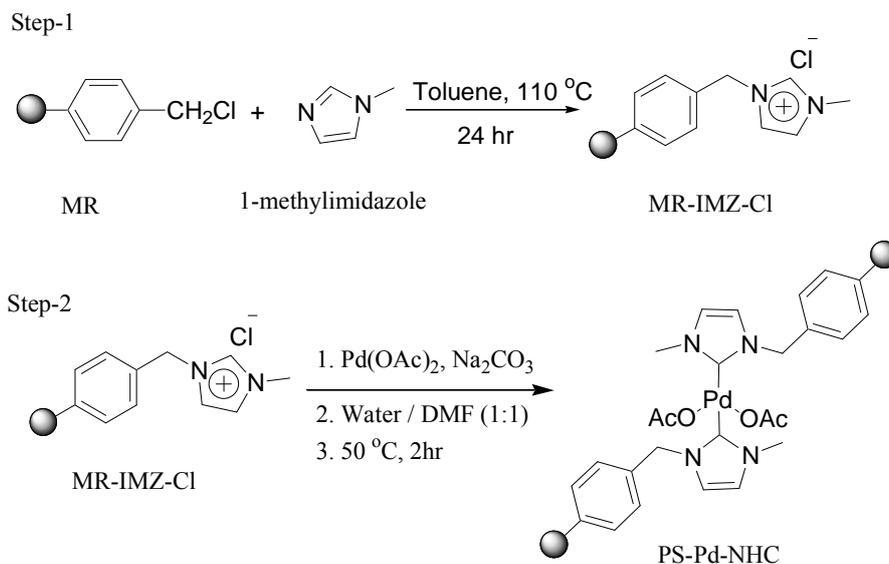
4) A typical procedure for the preparation of polymer supported palladium-*N*-heterocyclic carbene (PS-Pd-NHC) catalyst:

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

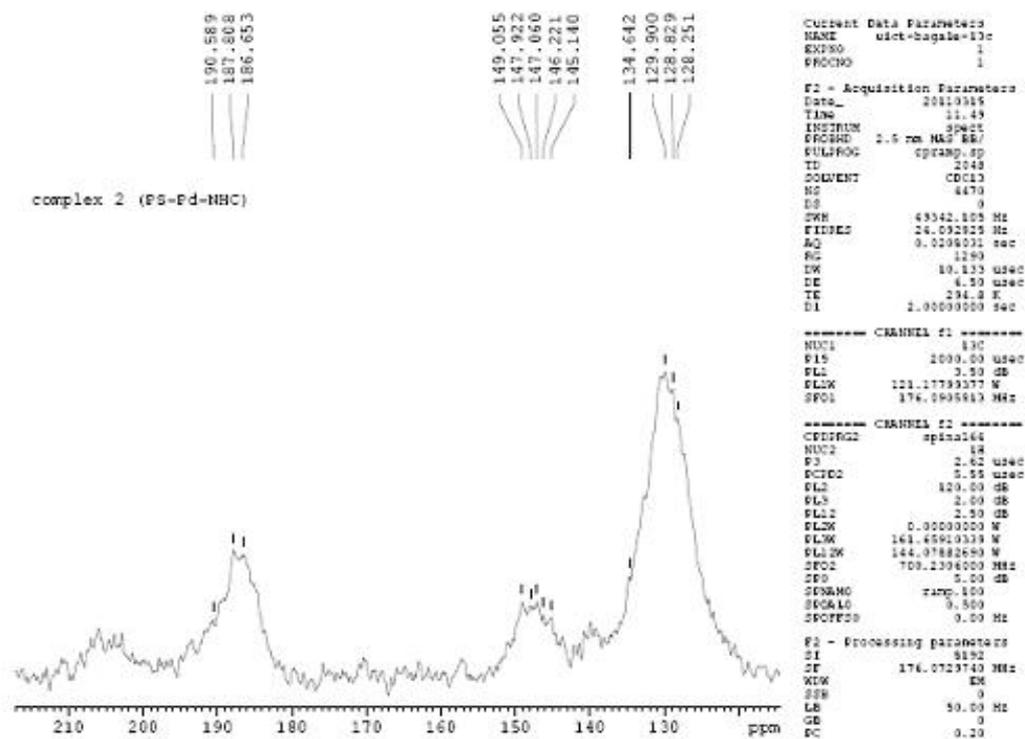
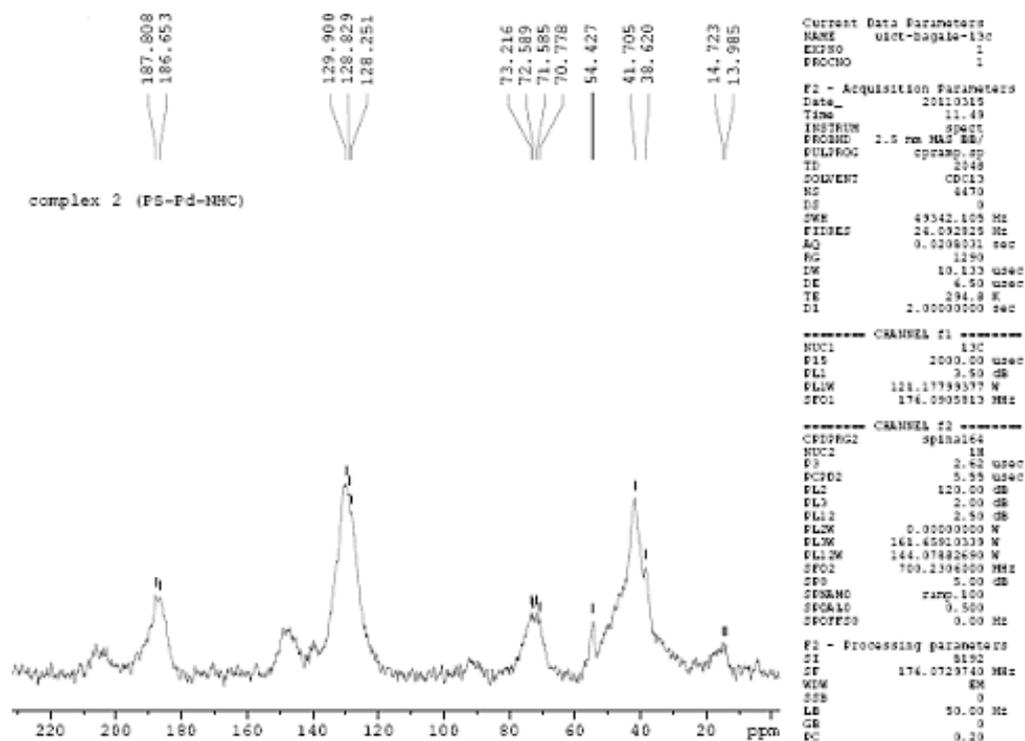


Step-2 Preparation of polymer supported palladium-*N*-heterocyclic carbene complex with the imidazolium loaded polymeric support (PS-Pd-NHC)

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 Na₂CO₃ (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 ¹³C NMR (Bruker AvanceIII 700 MHz); δ 14 (CH₃ aliphatic acetate skeleton), 42 (N-CH₃ skeleton), 54 (aliphatic polystyrene skeleton), 72 (NCN aliphatic), 128 (NCH, NCH, aromatic polystyrene skeleton), 147 (aromatic polystyrene skeleton), 187 (C=O acetate skeleton).

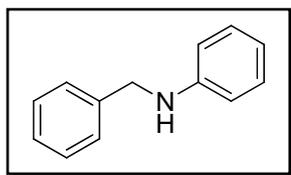
The amount of Pd loaded on the polymeric support was determined by using ICP-AES analysis. The polymer supported palladium-*N*-heterocyclic carbene complex (50 mg) was treated with a mixture (25 mL) of hydrochloric acid and nitric acid (1:1, v/v) at room temperature for 30 min. The orange-coloured solution 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



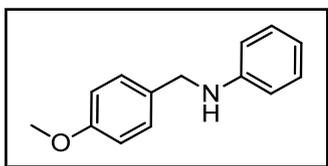
6) Characterization data of some selected compounds:

(1) *N*-benzylaniline



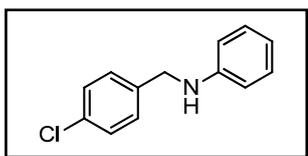
^1H NMR (CDCl_3 , 400 MHz) δ = 7.39-7.31 (m, 5H), 7.21 (t, 2H), 6.75 (t, 1H), 6.67 (d, 2H), 4.36 (s, 2H), 4.02 (br, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ = 148.2, 139.5, 129.3, 128.7, 127.6, 127.3, 117.6, 113.0, 48.3; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3419, 3026, 2924, 2853, 1949, 1602, 1505, 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



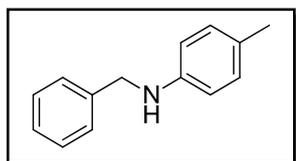
^1H NMR (CDCl_3 , 400 MHz) δ = 7.33 (d, 2 H), 7.22 (t, 2H), 7.01-6.98 (m, 2H), 6.92 (d, 2H), 6.76 (t, 1H), 6.67 (d, 2 H), 4.28 (s, 2H), 3.98 (br, 1H), 3.84 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ = 158.8, 148.2, 131.4, 129.3, 128.8, 117.5, 114.0, 112.8, 55.2, 47.7; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 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



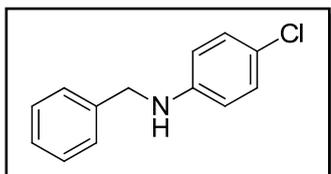
^1H NMR (CDCl_3 , 400 MHz) δ = 7.32 (s, 4H), 7.19 (t, 2H), 6.75 (t, 1H), 6.64 (d, 2H), 4.32 (s, 2H), 4.04 (br, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ = 147.8, 138.0, 132.8, 129.3, 128.7, 117.8, 112.9, 47.6; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3671, 3418, 2922, 2851, 1898, 1603, 1508, 1430, 1324, 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



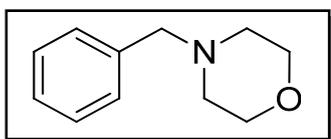
^1H NMR (CDCl_3 , 400 MHz) δ = 7.4-7.21 (m, 5H), 7.04 (d, 2H), 6.61 (d, 2H), 4.36 (s, 2H), 3.9 (br, 1H), 2.3 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ = 146.0, 139.6, 129.7, 128.6, 127.5, 127.1, 126.7, 113, 48.6, 20.4; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3445, 3027, 2918, 2763, 1951, 1865, 1701, 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



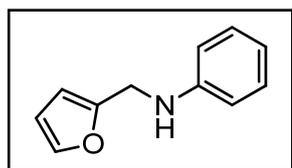
^1H NMR (CDCl_3 , 400 MHz) δ = 7.37-7.31 (m, 5H), 6.14 (d, 2H), 6.56 (d, 2H), 4.32 (s, 2H), 4.1 (br, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ = 146.7, 139.0, 129.0, 128.7, 127.4, 127.3, 122.0, 114.0, 48.3; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3427, 3028, 2924, 2853, 1952, 1864, 1600, 1502, 1453, 1401, 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



^1H 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) $\nu_{\text{max}}/\text{cm}^{-1}$ 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).

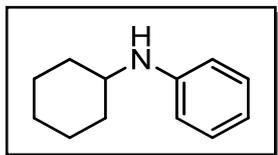
(7) *N*-(furan-2-ylmethyl)aniline



^1H NMR (CDCl_3 , 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 (CDCl_3 , 75 MHz) δ = 152.1, 148.4, 141.9, 129.1, 117.6, 113.4, 110.2, 107.5, 47.3; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3672, 3116, 3040, 2925, 1921, 1598, 1507, 1437, 1375,

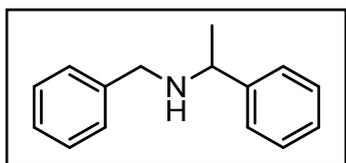
1347, 1183, 1157, 1075, 1007, 935, 808, 745, 691, 598; GC-MS (EI) m/z (%) = 173(42), 172(26), 81(100), 77(11), 53(23).

(8) *N*-cyclohexylaniline



^1H NMR (CDCl_3 , 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 (CDCl_3 , 75 MHz) δ = 147.4, 129.2, 116.8, 113.1, 51.6, 33.5, 25.9, 25.0; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 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

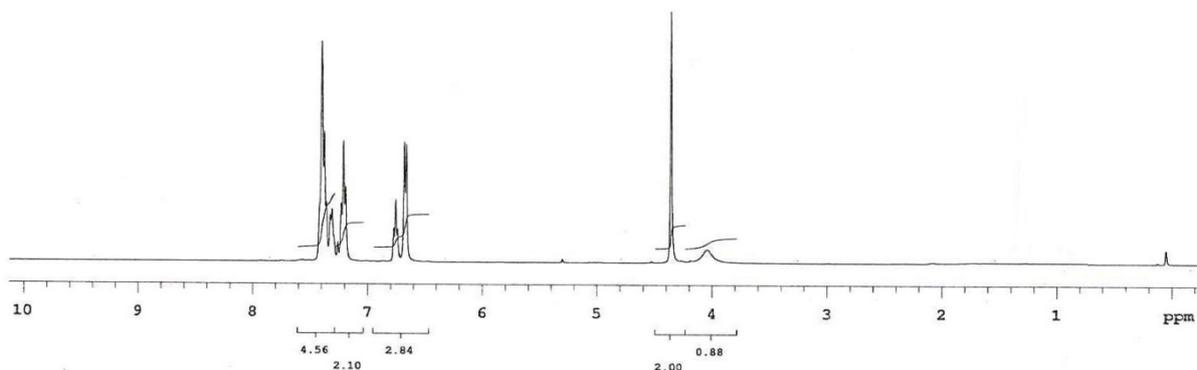
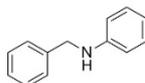


^1H NMR (CDCl_3 , 400 MHz) δ = 7.4-7.2 (m, 10H), 3.85 (s, 2H), 3.65 (q, 1H), 1.8 (s, 1H), 1.40 (d, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ = 145.6, 140.6, 128.5, 128.4, 128.1, 127.0, 126.9, 126.7, 57.5, 51.7, 24.5; IR (neat) $\nu_{\text{max}}/\text{cm}^{-1}$ 3651, 3060, 3025, 2963, 2831, 1948, 1876, 1808, 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) ^1H and ^{13}C NMR Spectra of some compounds:

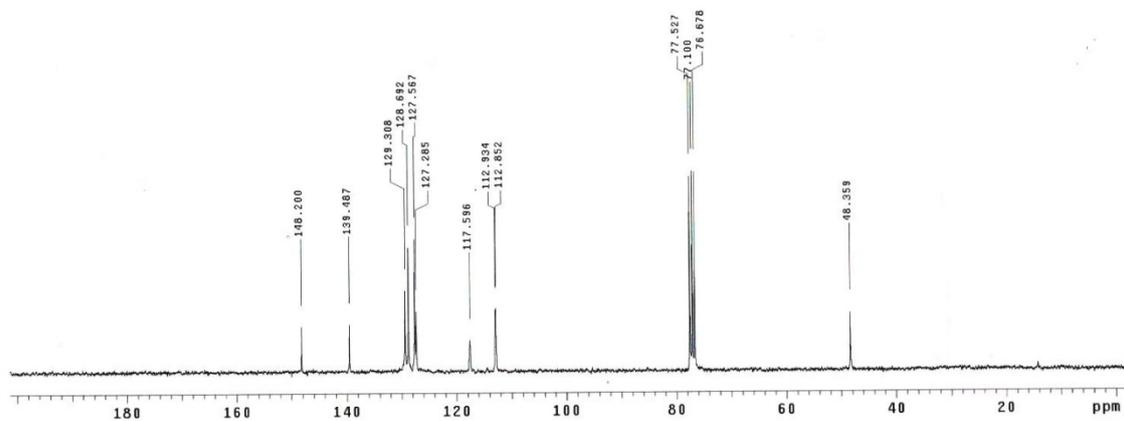
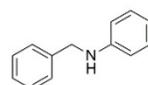
N-benzylaniline

^1H , CDC13
File Ref No : 10-020611-20
MR 400



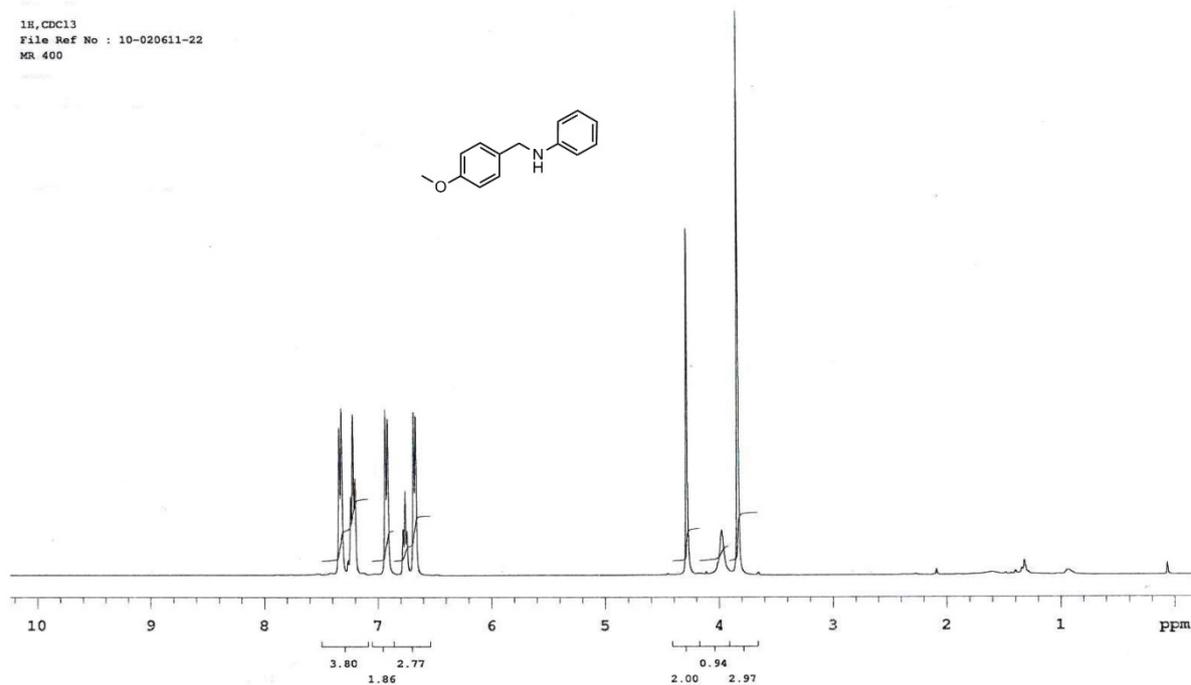
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		nm	ph



N-(4-methoxybenzyl)aniline

1H, CDC13
File Ref No : 10-020611-22
MR 400



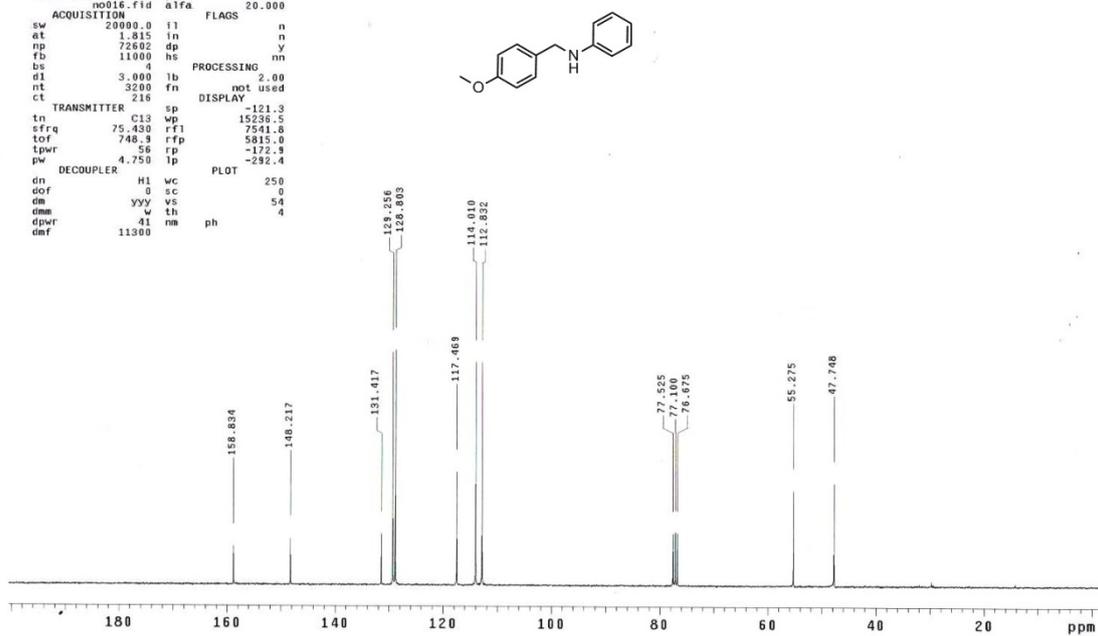
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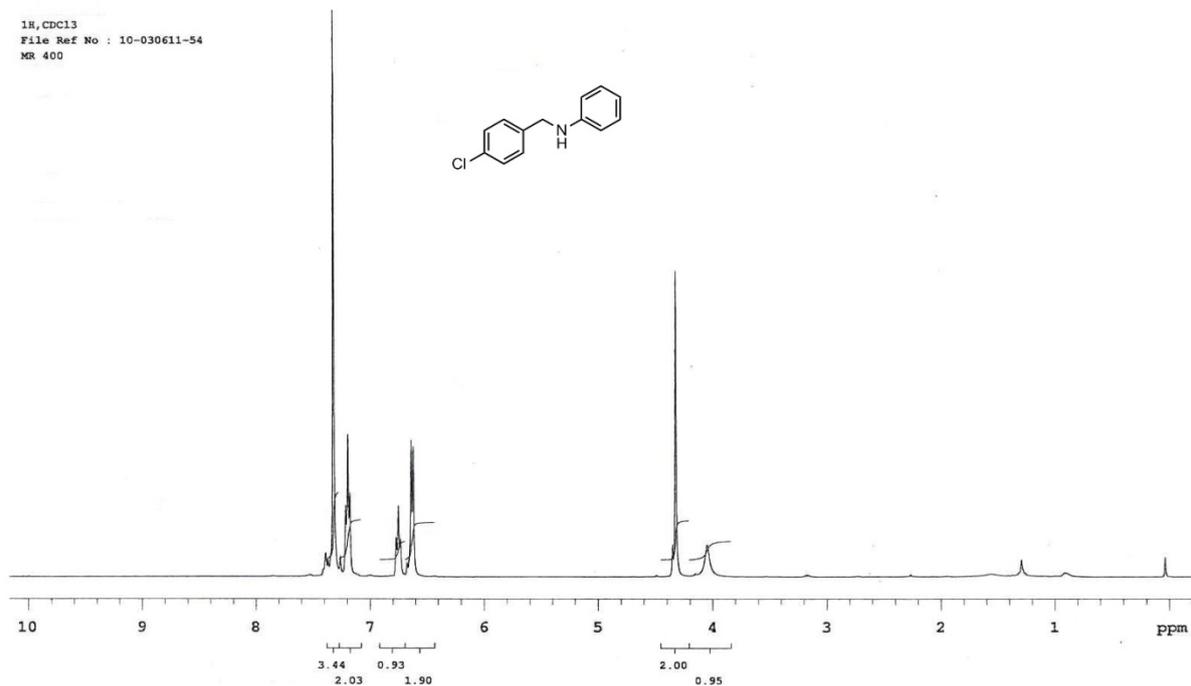
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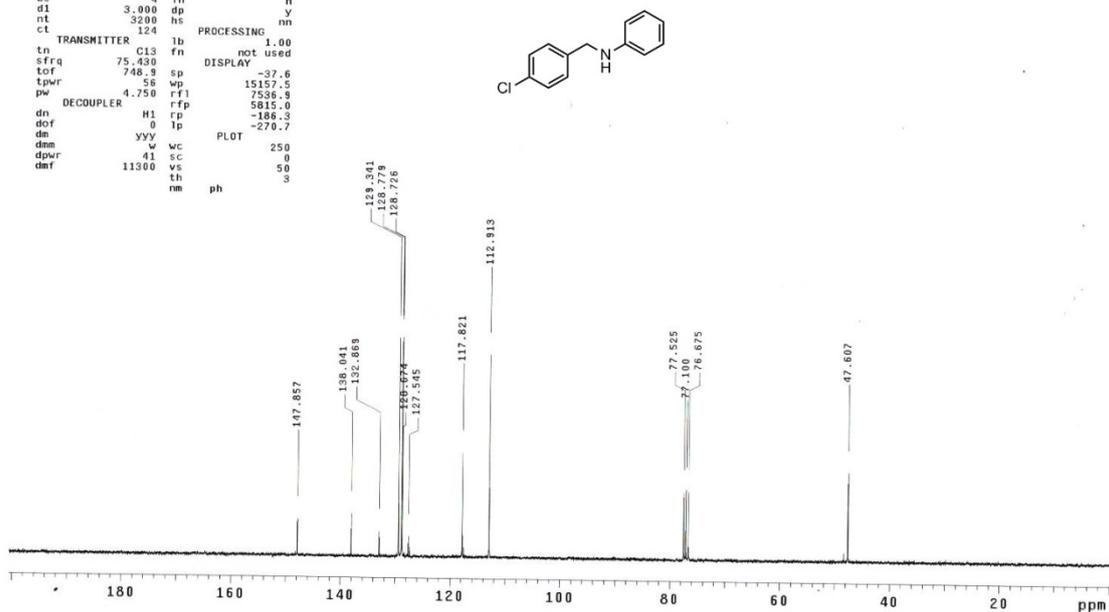
N-(4-chlorobenzyl)aniline

1H, CDCl3
File Ref No : 10-030611-54
MR 400



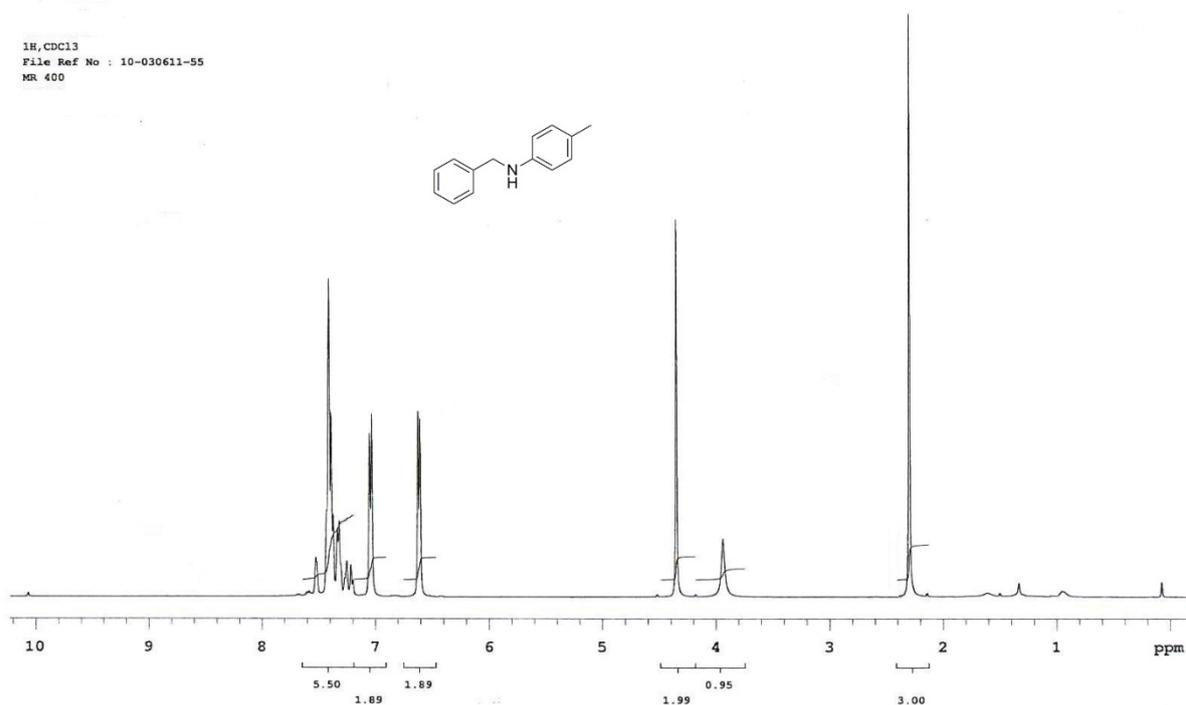
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bs	4	ln	n
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nt	3200	hs	nm
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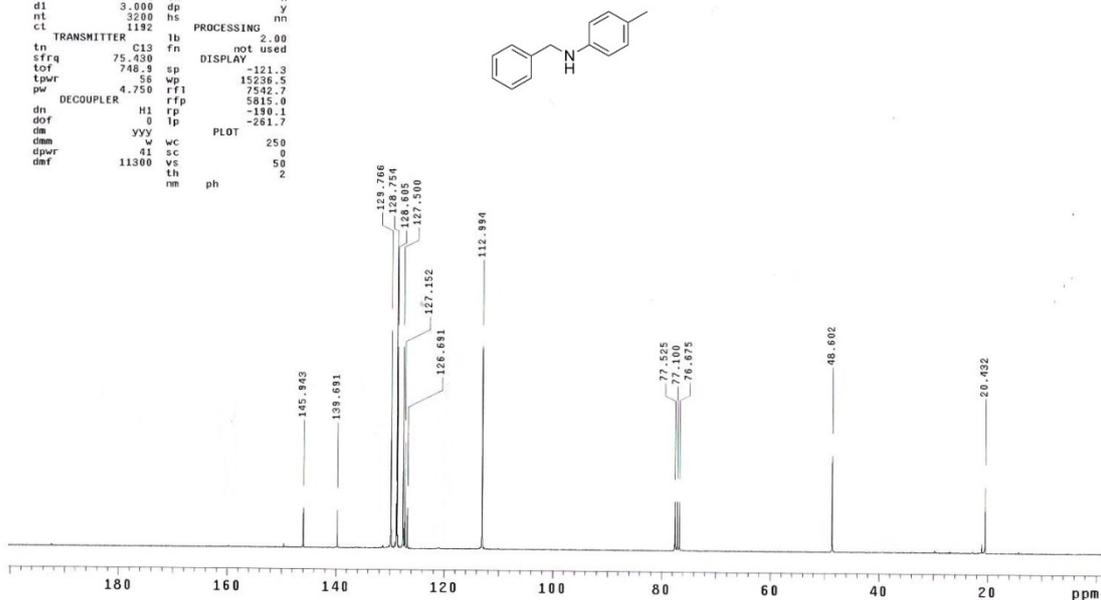
N-benzyl-4-methylaniline

1H, CDCl3
File Ref No : 10-030611-55
MR 400

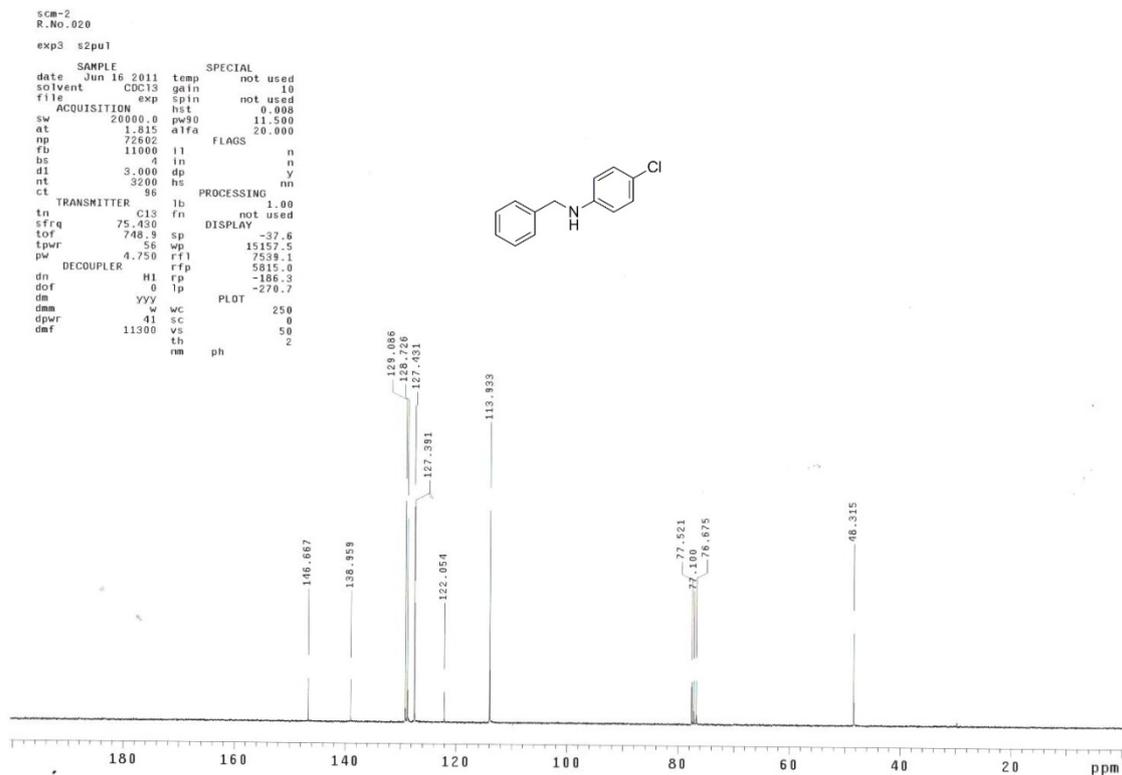
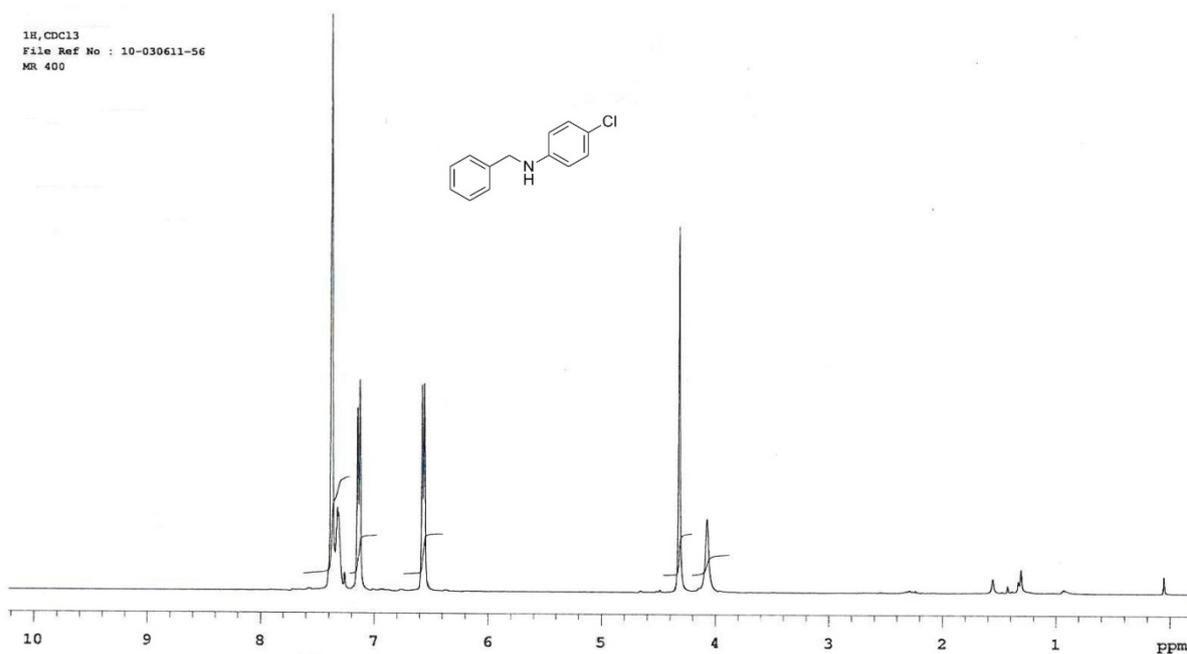


SCM-2
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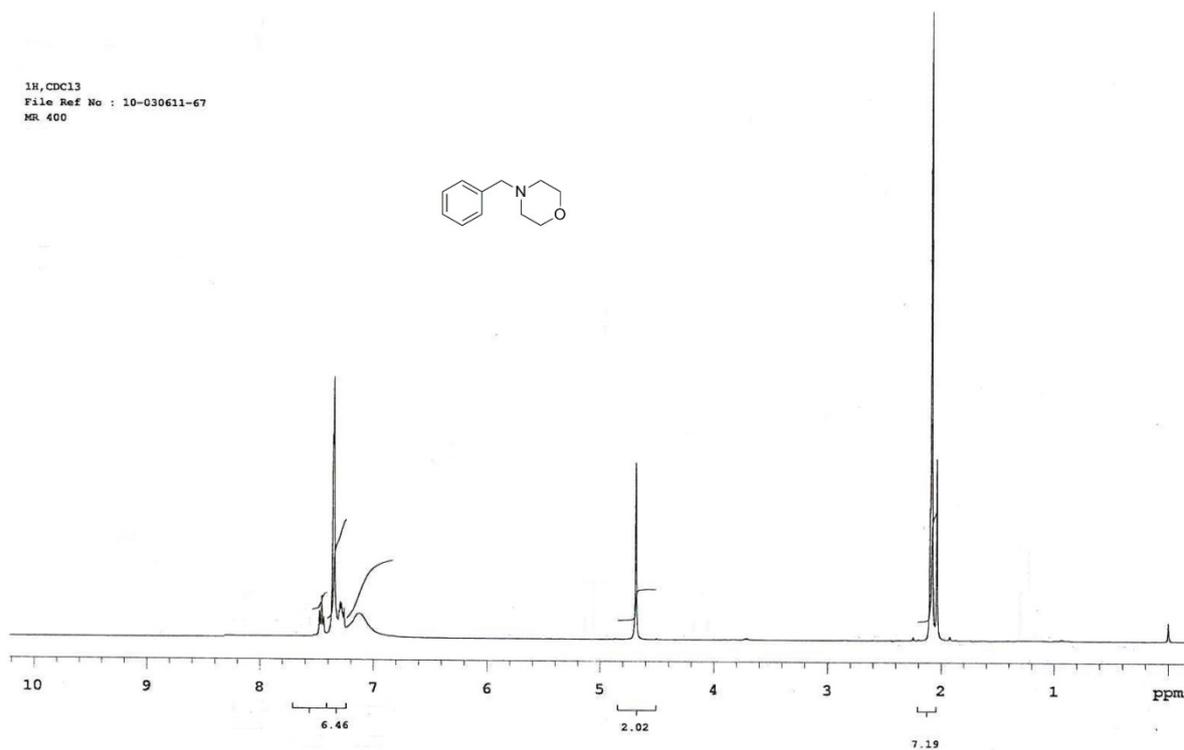
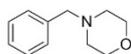


N-benzyl-4-chloroaniline



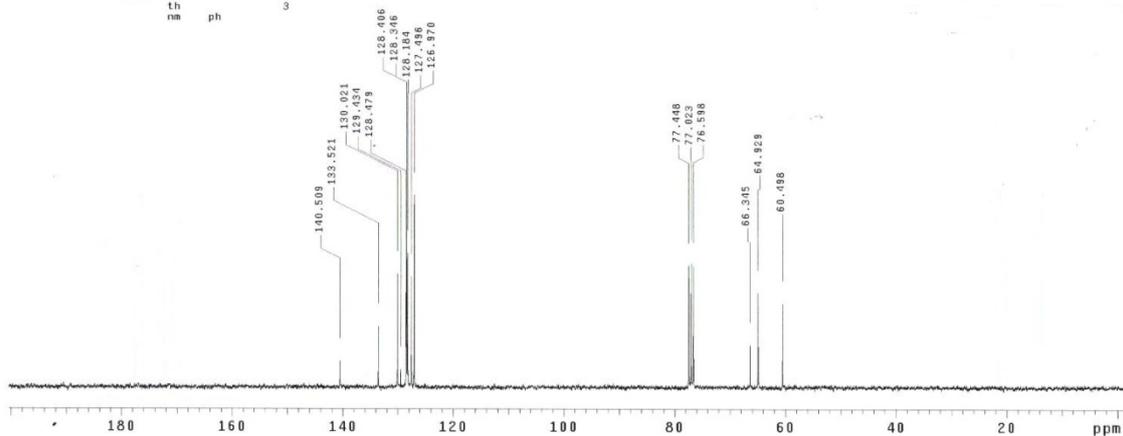
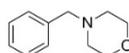
4-benzylmorpholine

1H, CDC13
File Ref No : 10-030611-67
MR 400



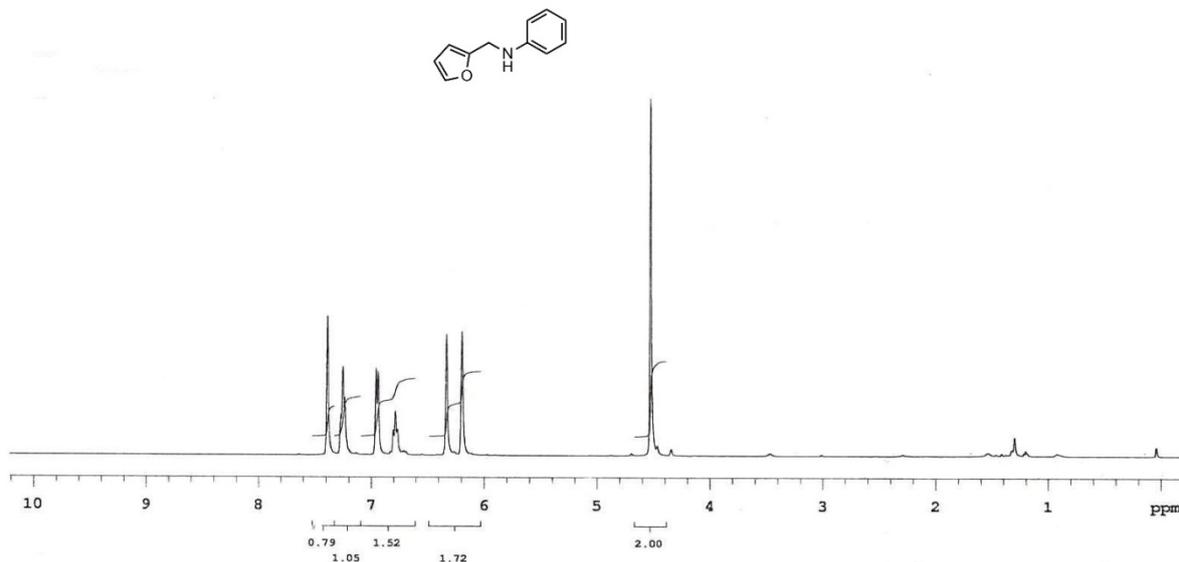
scw-2
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exp3 s2pu1

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ct	144		
TRANSMITTER	C13	fn	not used
sfrq	75.430	DISPLAY	-121.3
tof	748.9	sp	15238.5
tpwr	56	wp	1728.8
pw	4.750	rfl	0
DECOUPLER	H1	rfd	-189.7
dn	0	lp	-260.3
dof			
dm	yyy	wc	250
dmm	41	sc	0
dpwr	11300	vs	45
dmf		th	3
		nm	ph

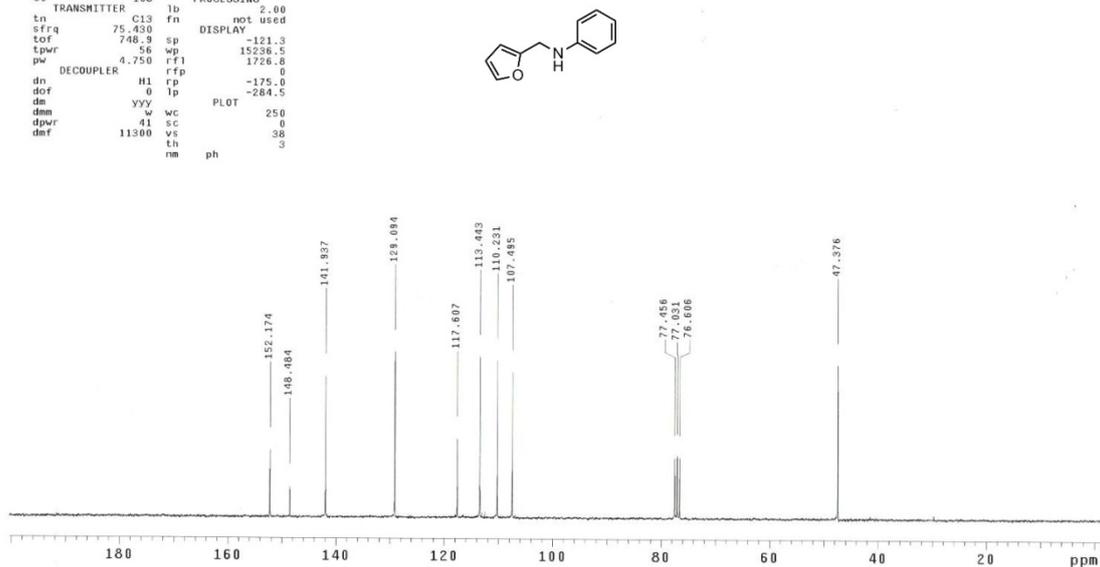


N-(furan-2-ylmethyl)aniline

1H, CDC13
File Ref No : 10-030611-68
MR 400

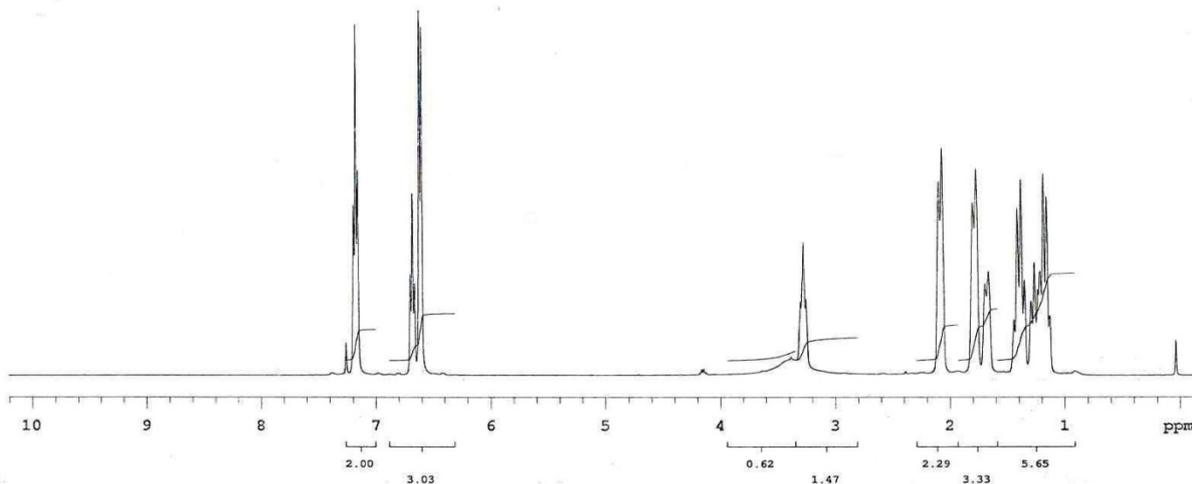
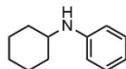


```
SCM-2  
R.No. 032  
exp3 s2pul  
SAMPLE  
date Jun 16 2011 temp SPECIAL  
solvent CDC13 gain not used  
file exp spin not used  
ACQUISITION hst 0.008  
sw 20000.0 pw90 11.500  
at 1.815 alfa 20.000  
np 72602 FLAGS  
fb 11000 il n  
bs 4 in n  
d1 3.000 dp y  
nt 3200 hs nn  
ct 108 PROCESSING 2.00  
TRANSMITTER lb fn not used  
tn C13 fn DISPLAY  
sfrq 75.430 sp -121.3  
tof 748.9 sp 15236.5  
tpwr 56 wf 1726.0  
pw 4.750 rfp 0  
DECOUPLER H1 rp -175.0  
dof 0 lp -284.5  
dm yyy PLOT  
dmm w wc 250  
dpar 41 sc 0  
dmf 11200 vs 38  
nm ph 3
```

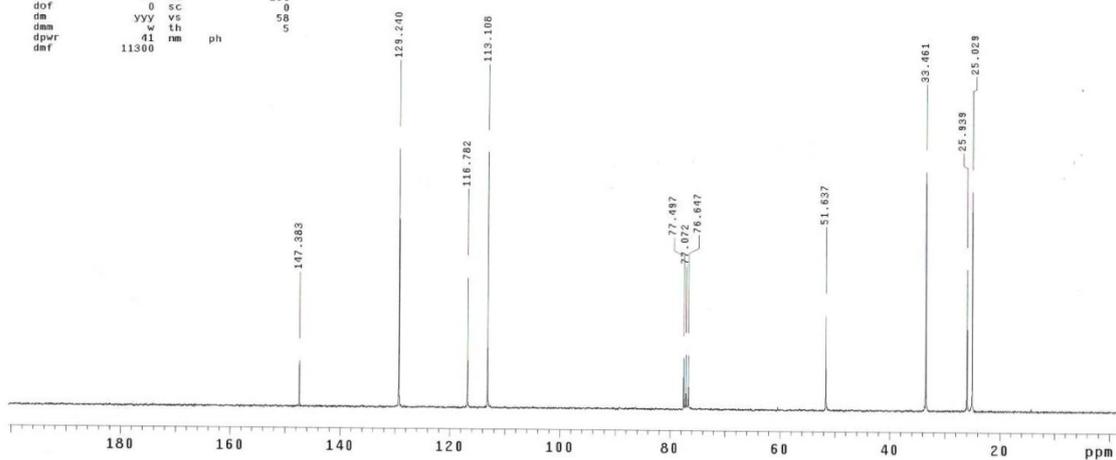
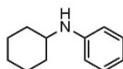


N-cyclohexylaniline

1H, CDC13
File Ref No : 10-030611-11
MR 400

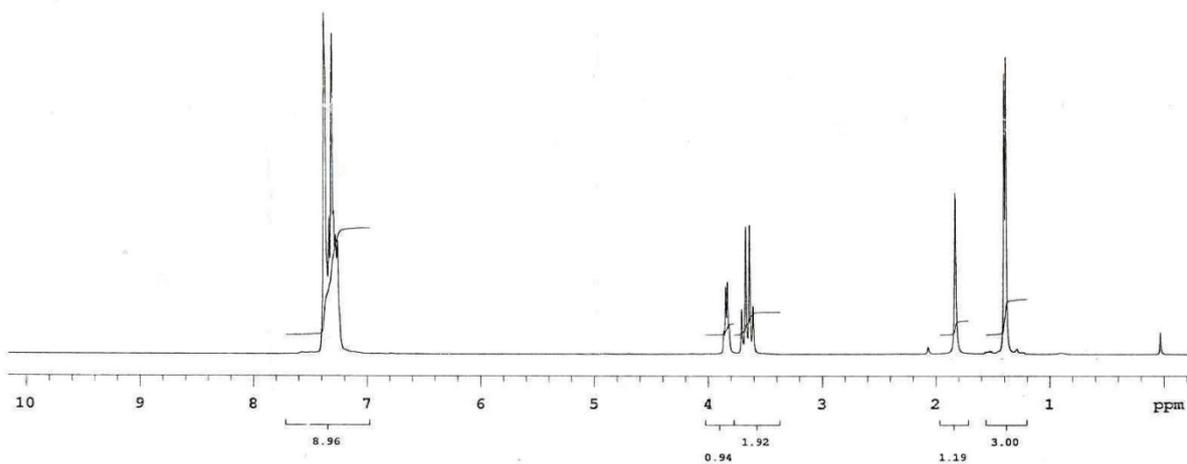
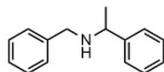


```
scm-2
R.No. 047
exp1 s2pu1
SAMPLE SPECIAL
date Jun 16 2011 temp not used
solvent CDCl3 gain 10
file /export/home/~ spin not used
vnmr1/2011/June/Ex~ hst 0.008
terna1/ICT-Dutta/R~ pw90 11.500
no-047.fid alfa 20.000
ACQUISITION FLAGS
sv 20000.0 f1 n
at 1.815 f2 n
np 72602 dp Y
fb 11000 hs
bs 4 PROCESSING mn
dl 3.000 lb not used 2.00
nt 3200 fn DISPLAY
ct 128
TRANSMITTER sp -121.3
tn C13 wp 15236.5
sfrq 75.430 rfl 1726.8
tof 748.9 rfp 0
tper 56 rp -194.6
pw 4.750 lp -255.9
DECOUPLER H1 wc PLOT 250
dof 0 sc 0
dm yy vs 58
dmm w lb
dpwr 41 nm ph 5
dmf 11300
```



N-benzyl-1-phenylethanamine

1H, CDC13
File Ref No : 10-030611-69
MR 400



scm-2
R.No. 049
exp3 s2pu1

SAMPLE		SPECIAL	
date	Jun 16 2011	temp	not used
solvent	CDC13	gain	10
file		spin	not used
ACQUISITION		hst	0.008
sw	20000.0	pw90	11.500
at	1.815	alfa	20.000
np	7282	FLAGS	
fb	11000	l1	n
bs	4	ln	n
d1	3.000	dp	y
nt	3200	hs	nn
ct	88	PROCESSING	
tn	C13	lb	2.00
sfreq	75.430	fn	not used
tof	748.9	sp	DISPLAY -121.3
tpwr	56	wp	15236.5
pw	4.750	rfl	7539.1
DECOUPLER		rfg	5815.0
dn	H1	rpf	-186.3
dof	0	lp	-270.7
ds	yyy	PLOT	
dsm	w	vc	250
dpwr	41	sc	0
def	11300	vs	50
		th	5
		nm	ph

