Supporting Information

GO-Cu_7S_4 catalyzed *ortho*-aminomethylation of phenol derivatives with *N,N*-dimethylbenzylamines : site selective oxidative CDC†

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EXPERIMENTAL SECTION

General Remarks

All reactions were carried out in oven-dried round bottom flasks. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on a 0.25 mm silica gel plates (60F−254) and visualized under UV illumination at 254 nm and iodine chamber. Further visualization was achieved by iodine vapour adsorbed on silica gel depending on the product type. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Column chromatography was performed on silica gel 100–200 mesh using a mixture of hexane and ethyl acetate as eluent, and isolated compounds were characterized by ^{1}H NMR, ^{13}C{1H} NMR, and HRMS data. NMR spectra for all the samples were taken in deuterochloroform ($CDCl_3$) as the solvent. ^{1}H and ^{13}C-NMR spectra were recorded at ambient temperature on 400MHz, 300 MHz and 75 MHz spectrometer using tetramethylsilane (TMS) as internal reference. The chemical shifts are quoted in δ units, parts per million (ppm) up field from the signal of internal TMS. ^{1}H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, td = triplet of doublets), integration and coupling constant(s) *J* in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflectron experiments.

For EDX studies, instrument was used Model QuanTax 200, based on the SDD technology and giving an energy resolution of 127 eV at Mn*K*α to estimate elemental compositions. Sample was mounted on a circular metallic sample holder with a sticky carbon tape. Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer using Ni-filtered Cu*Kα* radiation, scan speed of 1 s and scan step of 0.05^{o}. Transmission electron microscopic (TEM) studies were carried out using a JEOL JEM200CX TEM instrument operated at 200 kV. The

specimens for these studies were prepared by dispersing the powdered sample in ethanol by ultrasonic treatment. Few drops of resulting solution were put on a porous carbon film supported on a copper grid and dried in air. ICP-AES was done using ARCOS system from M/s. Spectro, Germany. Raman spectra were recorded with a Renishaw (INVIA) confocal microdispersive Raman spectrometer using a 532 nm solid state laser in a regular mode. IR (KBr) spectra (4000–400 cm^{-1}) were recorded on a Nicolet Protege 460 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an EA 125 electron spectrometer manufactured by OMICRON Nanotechnology GmbH (Germany), with Al-Kα radiation (1486.7 eV).

Reagent Information

Trioctylphosphine (TOP), $CuSO_4.5H_2O$, Thiophenol, 6-bromo naphthol, and 7-methoxy naphthol were procured from Sigma-Aldrich (USA). *N*,*N*-dimethylbenzylamine (Acros organics) were used as received. All solvents of AR grade *i.e.* acetone, diethylether, ethanol were dried and distilled before use by known standard procedures.[1]

Synthesis of graphene oxide (GO)[2]

GO was synthesized by the modified Hummers' procedure. Graphite powder (500 mg) and sodium nitrate (2.0 g) were put into cold (temp. <5 ^oC) concentrated H_2SO_4 (18 mL, 98%). The mixture was stirred continuously for 1 h at temperature ~5 ^oC in an ice bath. Potassium permanganate (3 g) was added gradually and the reaction continued for another 2 h at temperature below 5 ^oC. The mixture was heated for 30 min at 35 ^oC during which 40 mL of deionised (DI) water was added slowly. The temperature of the mixture was increased to 100 ^oC and kept at that temperature for 15 min. The mixture was cooled to room temperature and diluted with 70 mL of DI water. Thereafter 10 mL of H_2O_2 (35%) was added. The colour of the suspension changed to bright yellow. The suspension was filtered and washed successively with 400 mL of 5% HCl twice and 70 mL of DI water thrice. Finally, the precipitate was dried in a vacuum desiccator for at least 5 days before further use.

Procedure for the synthesis of Cu_2S Nanoparticles

A slurry containing 0.5 mmol CuSPh in 2 mL trioctylphosphine (TOP) in a three neck 50 mL round bottom flask was heated under N_2 atmosphere to 100 ºC to remove water and oxygen. The resulting homogeneous solution was heated to 320 ºC for 1.5 h with continuous stirring affording

brownish black colloidal solution. The mixture was cooled to room temperature and 20 mL of acetone was added into the flask to obtain a brown precipitate which was separated by centrifugation. The precipitate was washed three times with acetone (20 mL) and dried in vacuum.

Procedure for the synthesis of GO-Cu_7S_4 Nanoparticles

In a typical synthesis, 100 mg of GO synthesized as above was completely dissolved in 20 mL of DI water. 40 mg of Cu_2S prepared as above was dispersed in 20 mL of toluene and was added to GO solution. The mixture was stirred for 24 h at room temperature. The precipitate was separated and washed with acetone. The composite so obtained were labelled as GO–Cu_7S_4 NPs.

HRTEM Images

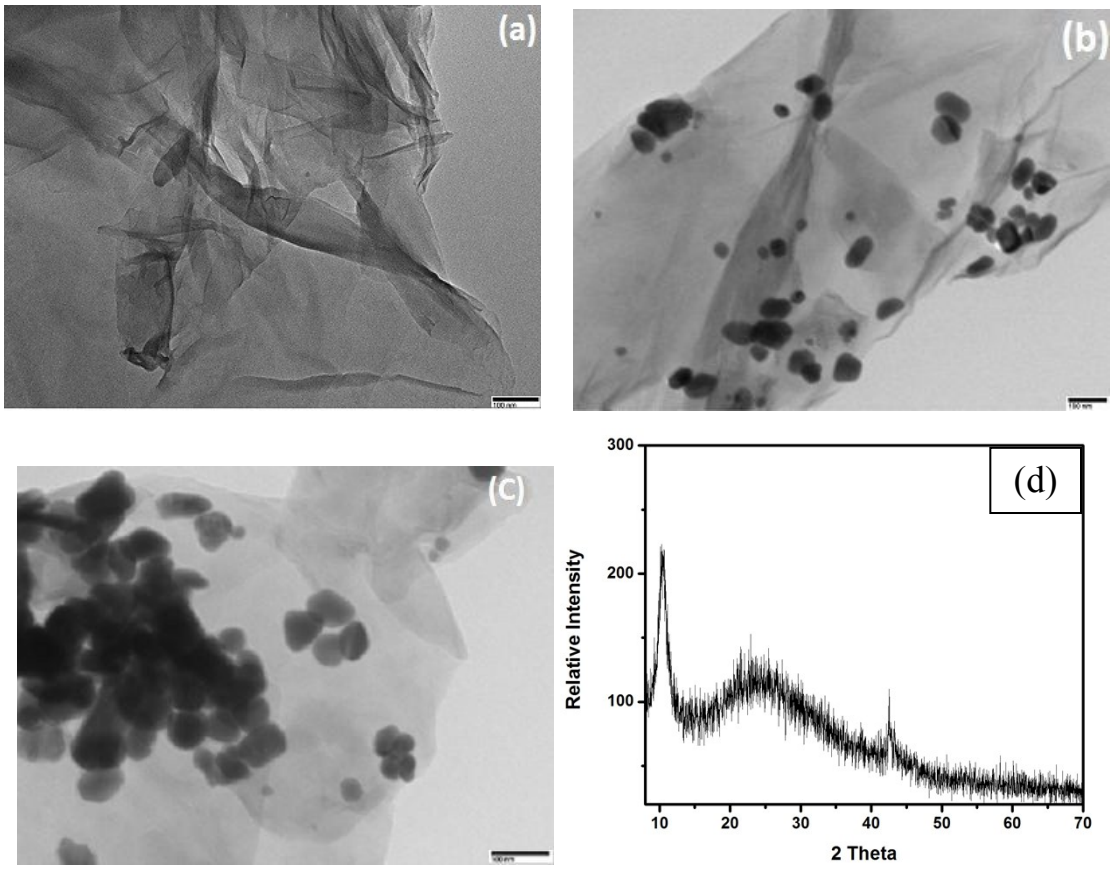


Fig. S1 HRTEM images (100 nm) of (a) GO and (b) GO-Cu_7S_4 NPs (c) GO-Cu_7S_4 NPs after 6th cycle and (d) PXRD pattern of GO

SEM-EDX Data

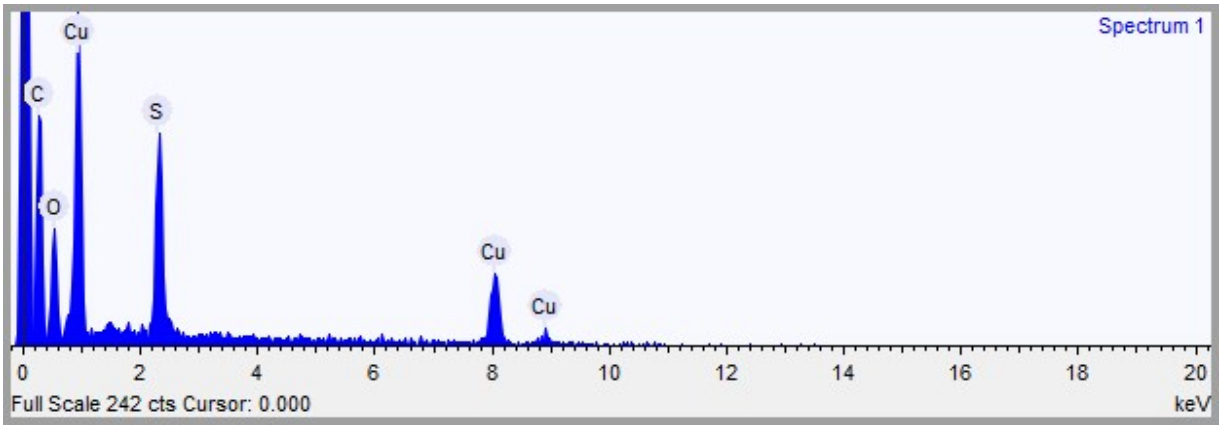


Fig. S2 SEM-EDX of GO-Cu_7S_4 NPs

Elemental mapping:

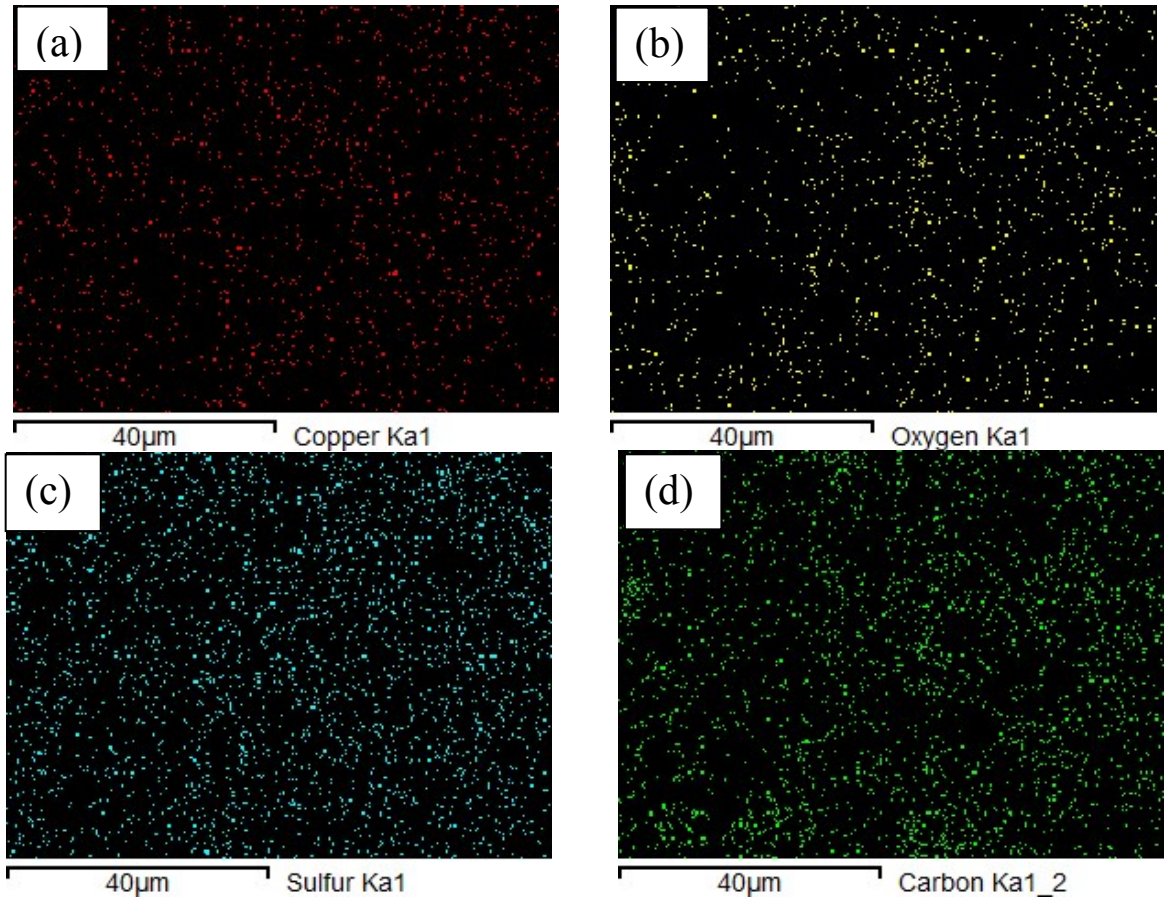


Fig. S3 Elemental mapping of GO-Cu_7S_4 NPs (a) Cu, (b) O, (c) S and (d) C

To investigate the elemental composition of the prepared catalyst, energy-dispersive X-ray spectroscopy (EDX) elemental mappings of the GO-Cu_7S_4 catalyst were carried out (Fig. S3), and peaks corresponding to the elements carbon, oxygen, copper and sulphur were detected. The elemental mapping images indicated a homogeneous distribution of the elements (C, O, Cu and S) in GO-Cu_7S_4. Coexistence of C and O with Cu and S confirmed the loading of Cu_7S_4 on the surface of graphene oxide. The percentages of Cu, S, C and O elements in the catalysts were also determined from the EDX spectrum (Fig. S2), and the Cu/S ratio (7/4) matched with the PXRD data.

Powder–XRD Data

The powder X-ray diffraction pattern of Cu_7S_4 NPs (Fig. S4) was indexed on the basis of a monoclinic unit cell (JCPDS # 23-0958) with d values (Å) (hkl): 3.60 (372), 3.35 (1600), 3.00 (804), 2.86 (1821), 2.63 (2001), 2.53 (2040), 2.45 (155), 2.37, 2.12 (6141), 1.93 (0160), 1.86 (886).

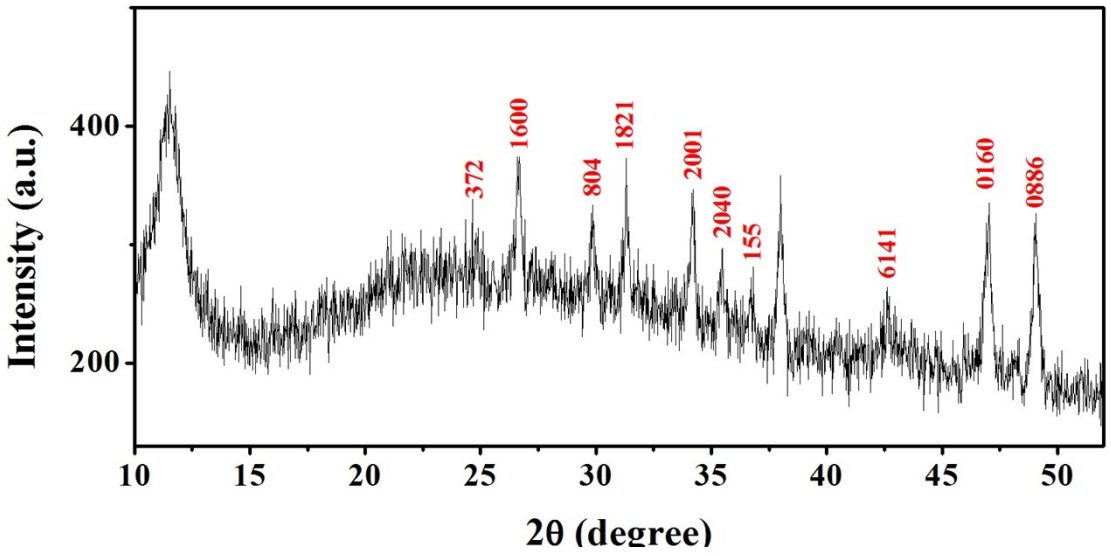


Fig. S4 PXRD of GO-Cu_7S_4 NPs

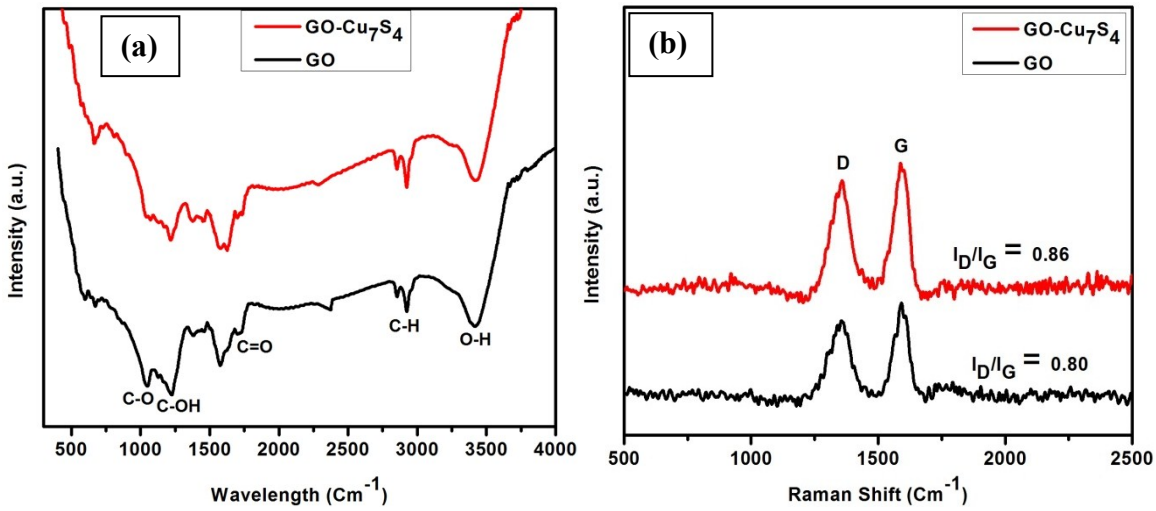


Fig. S5 (a) IR and (b) Raman spectra of GO, and GO–Cu_7S_4

Fig. S5(a) represents the FTIR spectra of GO, and GO-Cu_7S_4 samples. The FTIR spectrum of GO clearly shows the abundance of oxygen containing groups. For GO, broad absorption at 3425 cm^{-1} can be assigned to O–H stretching vibration. Other peaks at 1725, 1245 and 1041 cm^{-1} appear due to C-O stretching, O–H bending and C–O (epoxy) stretching modes. The peaks centered at 2856 and 2925 cm^{-1} in the GO spectrum also remain prominent in GO-Cu_7S_4, and can be assigned to -CH_2 stretching vibrations of graphene sheets. The FTIR spectrum of GO-Cu_7S_4 sample showed appearance of a new absorption peak at 660 cm^{-1} due to metal-oxygen bond.

As depicted by Raman {Fig. S5(b)}, D band at 1357 cm^{-1} and G band at 1588 cm^{-1} corresponding to typical features of GO was observed. The intensity ratio calculated for D and G band shows increase in I_D/I_G ratio. The increase in intensity ratio in case of GO–Cu_7S_4 indicates the abundance of surface defects and disorder in graphene sheets caused by the presence of copper sulphide nanoparticles. The structural defects are believed to enhance the catalytic activity.[3]

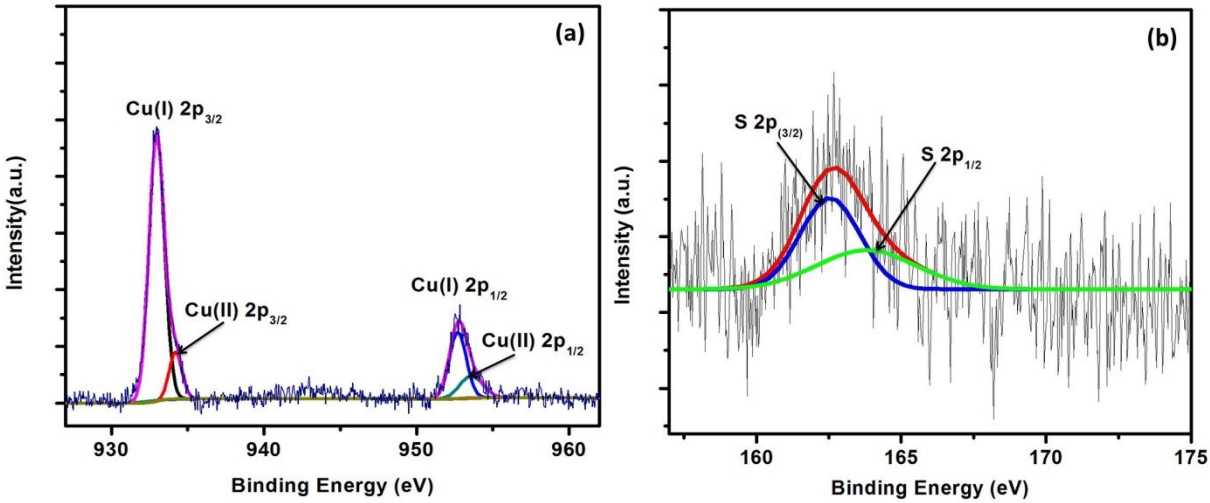


Fig. S6 High-resolution XPS of Cu_7S_4 NPs (a) Cu 2p and (b) S 2p

Size Distribution Curve:

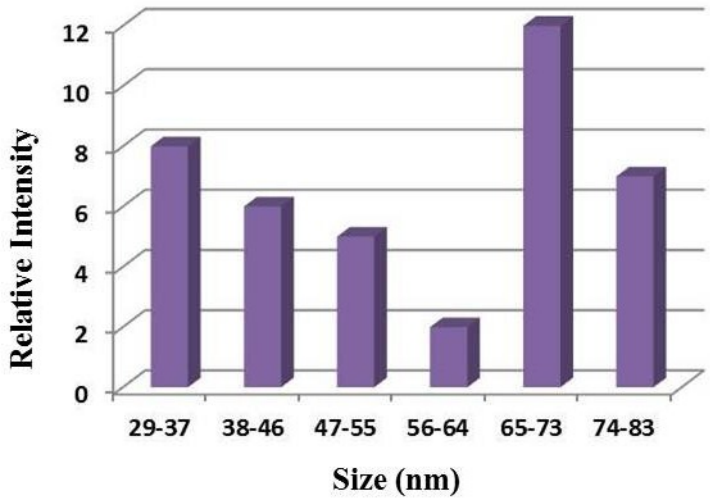


Fig. S7 Size distribution curve of GO-Cu_7S_4 NPs

Reusability of GO-Cu_7S_4 NPs

To check the reusability of the catalyst for the next catalytic cycle, it was recovered from the reaction mixture by centrifugation, washed with ethanol and dried in vacuum. It was reused for a fresh batch of reaction between *N,N*-dimethylbenzylamine and phenol. The activity of the recovered GO-Cu_7S_4 catalyst was examined up to seven cycles, and was found to decrease slightly after every reaction (Fig. S8 of SI). After the sixth cycle, the reaction mixture containing catalyst was centrifuged, and its surface morphology was compared to fresh catalyst using TEM (Fig. S1(c)) which showed agglomeration of the catalyst. The copper content GO-Cu_7S_4 was

studied using ICP-AES before and after the sixth reaction cycle. It was 1 mol % in fresh sample and 0.88 mol % after sixth run. The change in amount of copper present in catalyst was insignificant and ruled out leaching of metal.

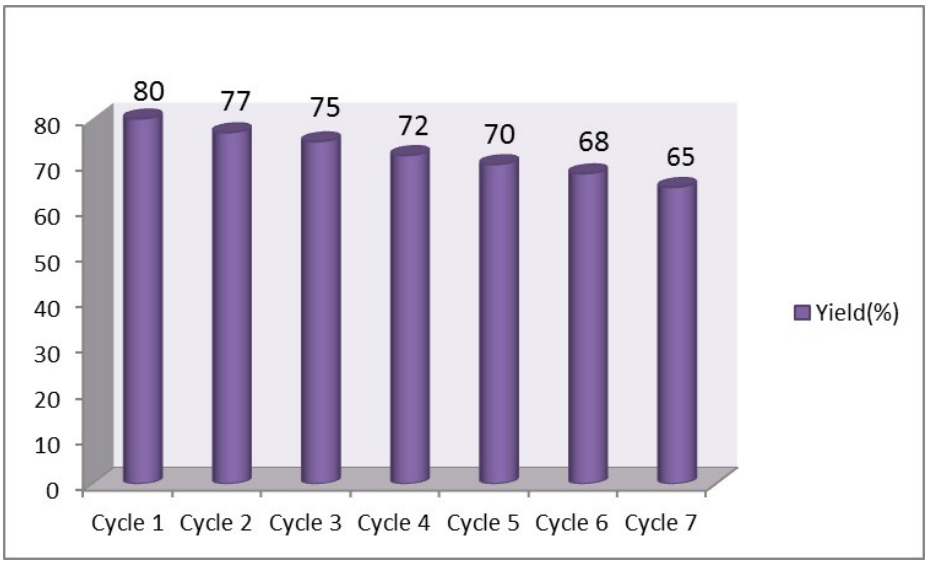


Fig. S8 Reusability graph of GO-Cu_7S_4 NPs till 7th cycle

Solubility and Stability of GO-Cu_7S_4 NPs

GO-Cu_7S_4 NPs were found to be sparingly soluble in toluene, EtOH, DMF and DMSO; and insoluble in $CHCl_3$, CH_2Cl_2, diethyl ether, ethyl acetate, hexane, CH_3CN and CH_3OH. The NP could be stored for up to two months in vacuum under desiccator. The stability was checked by taking its PXRD taken after 6 months. (Fig. S9)

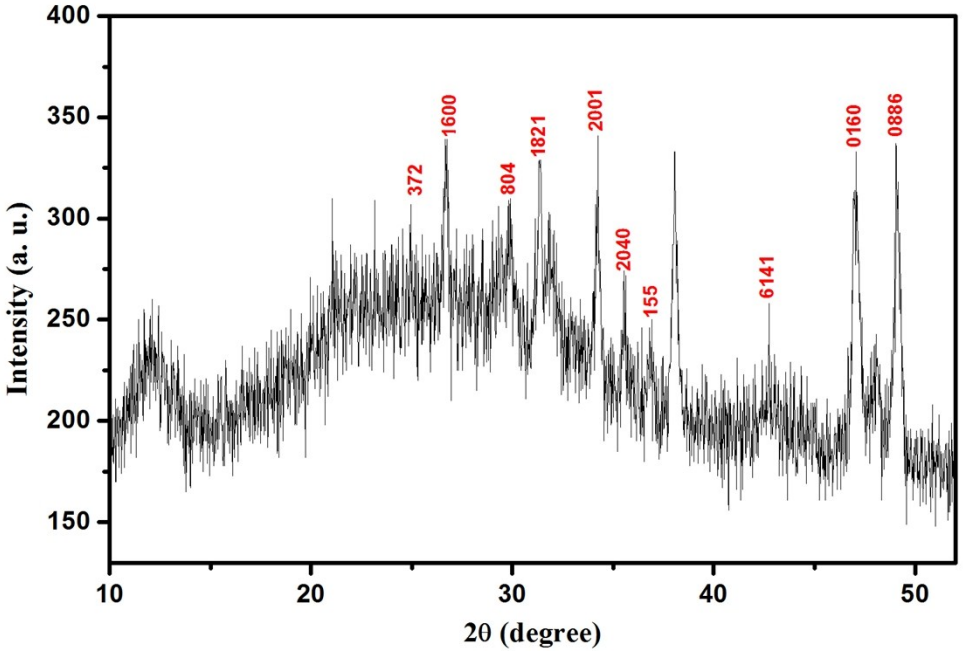


Fig. S9 PXRD of GO-Cu_7S_4 NPs after 6 months

General procedure for the preparation of *N, N*-dimethyl benzylamines:

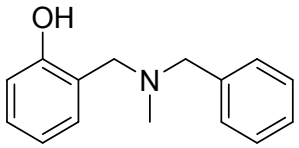
In a beaker containing 30 mL aq. solution of KOH (73.1 mmol), dimethylamine hydrochloride (38.5 mmol) was added, and the contents were stirred for 5 min. This solution was then added to a 100 mL round bottom flask containing benzyl bromide or chloride (5.0 mmol) in 30 mL DCM. The reaction mixture was stirred for 5h at room temperature. After completion of the reaction, the mixture was washed with brine (1 x 10 mL), subsequently with distilled water (2 x 10 mL) and then dried over anhydrous Na_2SO_4. Solvent was evaporated.

General procedure for the synthesis of compounds (3a-3p, 5a-5k and 7a-7e):

To the mixture of phenol (**1**)/naphthol (**4**) (0.5 mmol), *N*,*N*-dimethylbenzylamine (**2**) (1.0 mmol), and GO-Cu_7S_4 NP catalyst (4 mg, 1 mol%), *tert*-butyl hydroperoxide (0.2 mL, 1.2 mmol decane solution) was added under nitrogen at room temperature. The reaction temperature was raised to 50 °C and the contents were stirred at the same temperature for 2 h. The reaction mixture was then cooled to room temperature. The resulting suspension was diluted with ethylacetate and the organic layer was washed off with brine solution (3 × 10 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 95:5).

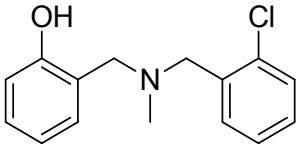
Spectral Data:

2-((benzyl(methyl)amino)methyl)phenol (3a):



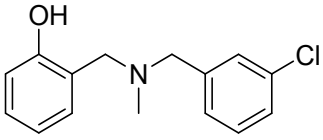
Colourless liquid (0.182 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.40-7.31 (m, 5H), 7.21 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.88 (dd, J_1 = 8.1 Hz, J_1 = 0.9 Hz, 1H), 6.82 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 3.78 (s, 2H), 3.63 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.8, 136.8, 129.3, 128.8, 128.6, 128.5, 127.6, 121.9, 119.1, 116.1, 61.4, 60.9, 41.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}NO$ 228.1383; Found 228.1393.

2-(((2-chlorobenzyl)(methyl)amino)methyl)phenol (3b):



Colourless liquid (0.191 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.47-7.42 (m, 2H), 7.32-7.26 (m, 2H), 7.20 (t, J = 6.0 Hz, 1H), 7.05 (d, J = 5.7 Hz, 1H), 6.89 (d, J = 6.3 Hz, 1H), 6.82 (t, J = 5.7 Hz, 1H), 3.86 (s, 2H), 3.85 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.5, 134.9, 133.8, 131.8, 129.9, 129.4, 129.2, 129.0, 127.1, 121.2, 119.3, 116.4, 60.2, 58.6, 40.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}ClNO$ 262.0993; Found 262.0990.

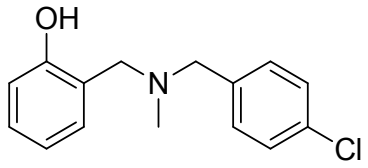
2-(((3-chlorobenzyl)(methyl)amino)methyl)phenol (3c):



Colourless liquid (0.193 g, 74%).^{1}H NMR (300 MHz, $CDCl_3$): 7.31-7.19 (m, 5H), 7.03 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.83 (t, J = 7.2 Hz, 1H), 3.79 (s, 2H), 3.61 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.6, 138.7, 134.4, 129.9, 129.4, 129.0, 128.7, 127.9, 127.4, 121.4, 119.3, 116.2, 60.8, 60.7, 41.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for

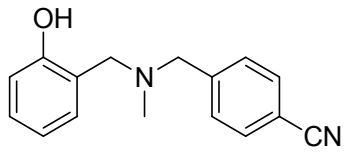
$C_{15}H_{17}ClNO$ 262.0993; Found 262.0994.

2-(((4-chlorobenzyl)(methyl)amino)methyl)phenol (3d):



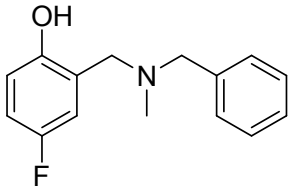
Colourless liquid (0.196 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.36-7.33 (m, 2H), 7.28-7.18 (m, 3H), 7.02 (d, J = 7.2 Hz, 1H), 6.89-6.80 (m, 2H), 3.77 (s, 2H), 3.58 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.7, 135.3, 133.5, 130.6, 128.9, 128.8, 128.6, 121.64, 119.2, 116.1, 60.9, 60.5, 41.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}ClNO$ 262.0993; Found 262.0993.

4-(((2-hydroxybenzyl)(methyl)amino)methyl)benzonitrile (3e):



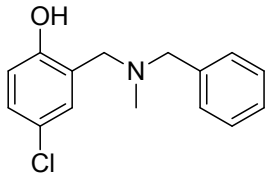
Colourless liquid (0.214 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.68 (d, J = 7.8 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.91-6.82 (m, 2H), 3.80 (s, 2H), 3.66 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.5, 142.5, 132.4, 129.9, 129.1, 128.7, 121.4, 119.4, 118.6, 116.2, 111.7, 61.3, 60.9, 41.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}N_2O$ 253.1335; Found 253.1333.

2-((benzyl(methyl)amino)methyl)-4-fluorophenol (3f):



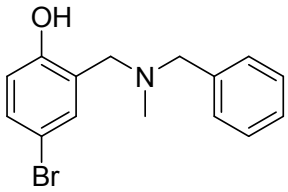
Colourless liquid (0.179 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.38-7.28 (m, 5H), 6.87 (td, J_1 = 8.4 Hz, J_2 = 3.0 Hz, 1H), 6.79-6.76 (m, 1H), 6.75-6.70 (m, 1H), 3.71 (s, 2H), 3.60 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 136.7, 129.4, 128.7, 127.9, 122.8 (2C), 116.8, 116.7, 115.1, 114.8, 61.5, 60.6, 41.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}FNO$ 246.1289; Found 246.1299.

2-((benzyl(methyl)amino)methyl)-4-chlorophenol (3g):



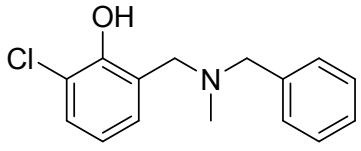
Colourless liquid (0.198 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.41-7.28 (m, 5H), 7.14 (dd, J_1 =8.4 Hz, J_2 = 2.4 Hz, 1H), 6.99 (d, J = 2.4 Hz, 1H), 6.80 (d, J = 8.7 Hz, 1H), 3.73 (s, 2H), 3.62 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.5, 136.5, 129.3, 128.6, 128.5, 128.2, 127.8, 123.6, 123.3, 117.4, 61.4, 60.4, 41.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}ClNO$ 262.0993; Found 262.0992.

2-((benzyl(methyl)amino)methyl)-4-bromophenol (3h):



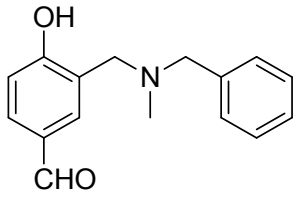
Colourless liquid (0.241 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.42-7.28 (m, 6H), 7.14 (d, J = 2.7 Hz, 1H), 6.76 (d, J = 8.7 Hz, 1H), 3.74 (s, 2H), 3.63 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.1, 136.5, 131.5, 131.1, 129.3, 128.7, 127.8, 123.9, 117.9, 110.8, 61.5, 60.3, 41.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}BrNO$ 306.0488; Found 306.0487.

2-((benzyl(methyl)amino)methyl)-6-chlorophenol (3i):



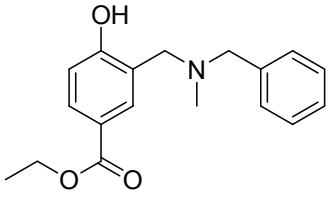
Colourless liquid (0.188 g, 72%), ^{1}H NMR (300 MHz, $CDCl_3$): 7.39-7.32 (m, 5H), 7.29-7.27 (m, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 3.79 (s, 2H), 3.66 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.7, 136.2, 129.4, 129.1, 128.7, 127.9, 126.8, 123.0, 120.8, 119.3, 61.6, 60.5, 41.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}ClNO$ 262.0993; Found 262.0993.

3-((benzyl(methyl)amino)methyl)-4-hydroxybenzaldehyde (3j):



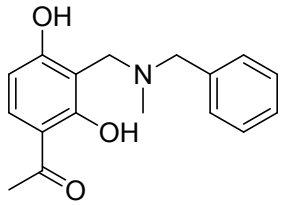
Colourless liquid (0.173 g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): 9.83 (s, 1H), 7.73 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 1H), 7.61 (d, J = 1.8 Hz, 1H), 7.42-7.31 (m, 5H), 6.96 (d, J = 8.4 Hz, 1H), 3.85 (s, 2H), 3.66 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 164.4, 136.1, 132.4, 129.9, 129.4, 128.7, 128.7, 128.0, 122.3, 116.7, 61.4, 60.3, 41.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2$ 256.1332; Found 256.1332.

ethyl 3-((benzyl(methyl)amino)methyl)-4-hydroxybenzoate (3k):



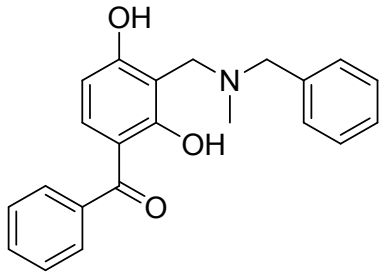
Colourless liquid (0.242 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.91 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1H), 7.60 (d, J = 1.2 Hz, 1H), 7.41-7.31 (m, 5H), 6.88 (d, J = 8.4 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 3.82 (s, 2H), 3.64 (s, 2H), 2.27 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 162.4, 136.4, 130.9, 130.4, 129.3, 128.7, 127.8, 121.4, 121.3, 116.0, 61.4, 60.5, 60.5, 41.2, 14.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}NO_3$ 300.1594; Found 300.1597.

1-(3-((benzyl(methyl)amino)methyl)-2,4-dihydroxyphenyl)ethanone (3l):



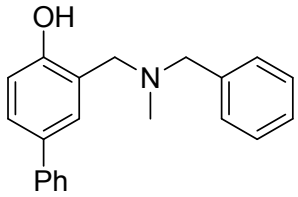
Colourless liquid (0.234 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): 13.2 (s, 1H, OH), 7.59 (d, J = 8.7 Hz, 1H), 7.41-7.32 (m, 5H), 6.40 (d, J = 9.0 Hz, 1H), 3.93 (s, 2H), 3.68 (s, 2H), 2.56 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 202.5, 166.6, 162.4, 136.2, 131.7, 129.4, 128.7, 127.9, 112.5, 108.5, 107.7, 61.4, 52.9, 41.2, 26.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_3$ 286.1438; Found 286.1438.

(3-((benzyl(methyl)amino)methyl)-2,4-dihydroxyphenyl)(phenyl)methanone (3m):



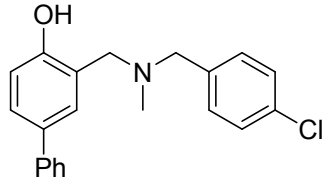
Colourless liquid (0.309 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): 13.2 (s, 1H, OH), 7.66-7.63 (m, 2H), 7.59-7.46 (m, 4H), 7.43-7.31 (m, 5H), 6.37 (d, J = 8.7 Hz, 1H), 4.0 (s, 2H), 3.72 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 200.0, 166.9, 163.5, 138.5, 136.2, 134.8, 131.2, 129.4, 128.8, 128.7, 128.2, 127.9, 111.7, 108.5, 107.8, 61.4, 53.0, 41.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}NO_3$ 348.1594; Found 348.1583.

3-((benzyl(methyl)amino)methyl)-[1,1'-biphenyl]-4-ol (3n):



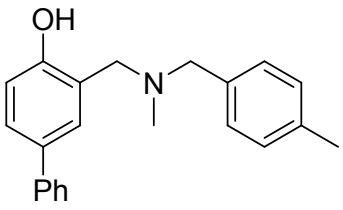
Colourless liquid (0.261 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.51 (d, J = 7.5 Hz, 2H), 7.43-7.22 (m, 10H), 6.91 (d, J = 8.4 Hz, 1H), 3.80 (s, 2H), 3.62 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 141.0, 136.8, 132.3, 129.4, 128.7, 128.6, 127.7, 127.5, 127.3, 126.6, 126.5, 122.1, 116.5, 61.5, 61.1, 41.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}NO$ 304.1696; Found 304.1697.

3-(((4-chlorobenzyl)(methyl)amino)methyl)-[1,1'-biphenyl]-4-ol (3o):



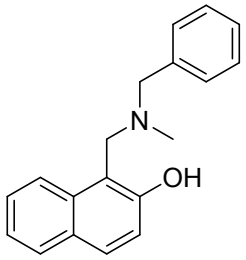
Colourless liquid (0.283 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.56-7.53 (m, 2H), 7.47-7.39 (m, 3H), 7.36-7.32 (m, 3H),7.31-7.25 (m, 3H), 6.94 (d, J = 8.4 Hz, 1H), 3.83 (s, 2H), 3.61 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4, 140.9, 135.3, 133.6, 132.5, 130.7, 128.8, 128.7, 127.6, 127.3, 126.6, 126.5, 121.9, 116.5, 61.1, 60.7, 41.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}ClNO$ 338.1306; Found 338.1306.

3-((methyl(4-methylbenzyl)amino)methyl)-[1,1'-biphenyl]-4-ol (3p):



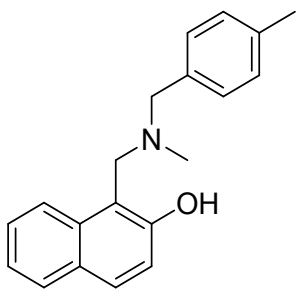
Colourless liquid (0.276 g, 87%), ^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (d, J = 8.1 Hz, 2H), 7.47-7.42 (m, 3H), 7.35-7.19 (m, 6H), 6.97 (d, J = 8.4 Hz, 1H), 3.84 (s, 2H), 3.64 (s, 2H), 2.39 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 157.6, 141.1, 137.4, 133.7, 132.3, 129.4, 129.3, 128.7, 127.4, 127.2, 126.6, 126.5, 122.2, 116.5, 61.2, 60.9, 41.3, 21.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{24}NO$ 318.1852; Found 318.1861.

1-((benzyl(methyl)amino)methyl)naphthalen-2-ol (5a):



Yellow solid (0.20 g, 72%). m.p. 118-120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.86 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.49-7.43 (m, 1H), 7.41-7.29 (m, 6H), 7.15 (d, J = 9.0 Hz, 1H), 4.22 (s, 2H), 3.72 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.6, 136.7, 132.6, 129.4, 129.3, 128.9, 128.7, 128.6, 127.8, 126.3, 122.4, 121.0, 119.2, 111.5, 61.6, 55.8, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}NO$ 278.1539; Found 278.1533.

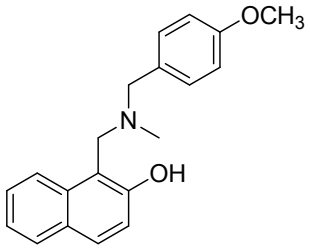
1-((methyl(4-methylbenzyl)amino)methyl)naphthalen-2-ol (5b):



Yellow solid (0.218 g, 75%). m.p. 114-116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.75 (d, J = 8.7 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H) 7.61 (d, J = 9.6 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.22-7.13 (m, 3H), 7.09-7.03 (m, 3H), 4.11 (s, 2H), 3.59 (s, 2H), 2.26 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.6, 137.4, 133.6, 132.7, 129.4, 129.3, 129.2, 128.9, 128.5, 126.3,

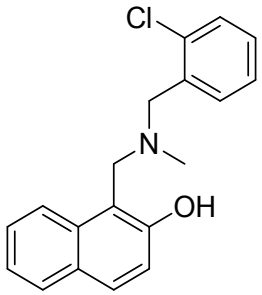
122.4, 121.0, 119.2, 111.5, 61.3, 55.6, 41.4, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}NO$ 292.1696; Found 292.1710.

1-(((4-methoxybenzyl)(methyl)amino)methyl)naphthalen-2-ol (5c):



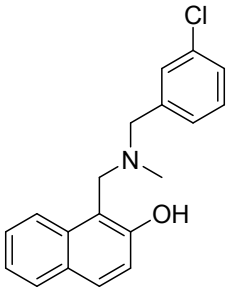
Yellow solid (0.240 g, 78%). m.p. 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.89 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.37-7.31 (m, 3H), 7.20 (d, J = 8.8 Hz, 1H), 6.95 (d, J = 8.4 Hz, 2H), 4.24 (s, 2H), 3.86 (s, 3H), 3.70 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 159.1, 156.5, 132.6, 130.6, 129.1, 128.9, 128.6, 128.4, 126.2, 122.4, 120.9, 119.1, 113.9, 111.4, 60.8, 55.4, 55.2, 41.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}NO_2$ 308.1645; Found 308.1645.

1-(((2-chlorobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5d):



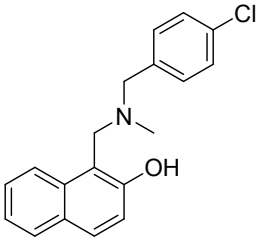
Yellow solid (0.218 g, 70%). m.p. 113-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.87 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.48-7.41 (m, 3H), 7.32-7.25 (m, 3H), 7.10 (d, J = 9.0 Hz), 4.23 (s, 2H), 3.86 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.3, 134.9, 134.4, 132.9, 132.6, 131.6, 129.9, 129.2, 128.9, 128.5, 127.0, 126.3, 122.4, 120.9, 119.1, 111.4, 59.1, 55.5, 41.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}ClNO$ 312.1150; Found 312.1156.

1-(((3-chlorobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5e):



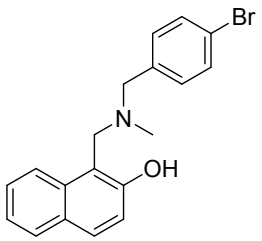
Yellow viscous liquid (0.224 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.86 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.48 (t, J = 8.1 Hz, 1H), 7.35-7.30 (m, 4H), 7.26 (d, J = 4.2 Hz, 1H), 7.18 (d, J = 8.7 Hz, 1H), 4.21 (s, 2H), 3.66 (s, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.5, 138.8, 134.5, 132.7, 130.1, 129.6, 129.5, 129.0, 128.7, 128.0, 127.6, 126.5, 122.6, 121.0, 119.2, 111.4, 60.9, 55.8, 41.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}ClNO$ 312.1150; Found 312.1153.

1-(((4-chlorobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5f):



Yellow solid (0.233 g, 75%). m.p. 100-102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.84 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.47 (td, J_1 = 8.7 Hz, J_2 = 1.5 Hz, 1H), 7.36-7.26 (m, 5H), 7.15 (d, J = 8.7 Hz, 1H), 4.20 (s, 2H), 3.66 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.4, 135.1, 133.6, 132.6, 130.7, 129.4, 128.9, 128.8, 128.6, 126.4, 122.5, 120.9, 119.1, 111.3, 60.7, 55.7, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}ClNO$ 312.1150; Found 312.1165.

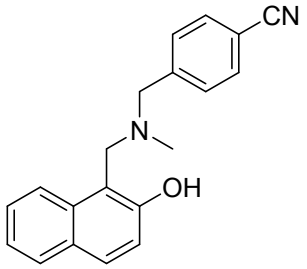
1-(((4-bromobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5g):



Yellow solid (0.27 g, 76%). m.p. 108-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.83 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 8.7 Hz, 1H), 7.50-7.42 (m, 3H), 7.31 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 9.0 Hz, 1H), 4.19 (s, 2H), 3.64 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.4, 135.6 132.5, 131.8, 131.1, 129.4, 128.9, 128.5, 126.4, 122.5, 121.7, 120.9, 119.1, 111.3,

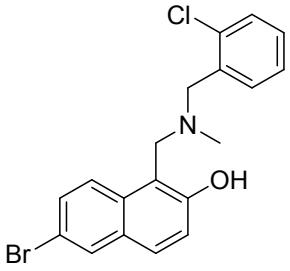
60.7, 55.7, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}BrNO$ 356.0645; Found 356.0648.

4-((((2-hydroxynaphthalen-1-yl)methyl)(methyl)amino)methyl)benzonitrile (5h):



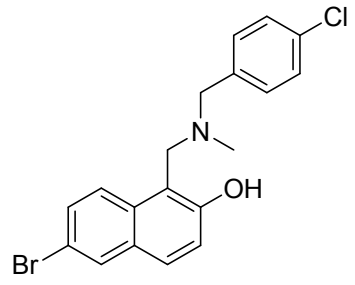
Yellow solid (0.242 g, 80%). m.p. 104-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.81 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.47-7.40 (m, 3H), 7.29 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 8.7 Hz, 1H), 4.19 (s, 2H), 3.68 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.2, 142.3, 132.4, 129.9, 129.6, 129.0, 128.6, 126.5, 122.6, 120.9, 119.0, 118.6, 111.7, 111.2, 60.9, 55.9, 41.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}N_2O$ 303.1492; Found 303.1478.

6-bromo-1-(((2-chlorobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5i):



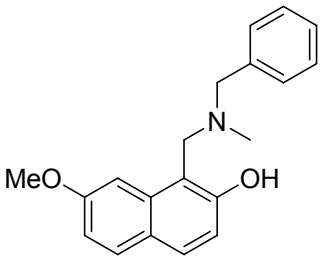
Yellow viscous liquid (0.307 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.89 (d, J = 2.1 Hz, 1H), 7.731 (d, J = 9.6 Hz, 1H), 7.57 (d, J = 9.3 Hz, 1H), 7.49 (dd, J_1 = 9.45 Hz, J_2 = 1.5 Hz, 1H), 7.44-7.37 (m, 2H), 7.29-7.24 (m, 2H), 7.11 (d, J = 9.0 Hz, 1H) 4.18 (s, 2H), 3.84 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.6, 134.9, 134.2, 131.6, 131.1, 130.6, 130.0, 129.7, 129.4, 129.3, 128.3, 127.0, 122.8, 120.2, 115.9, 111.7, 59.1, 55.4, 41.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}BrClNO$ 390.0255; Found 390.269.

6-bromo-1-(((4-chlorobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5j):



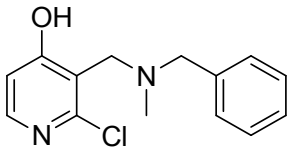
Yellow solid (0.276 g, 71%). m.p. 108-110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 7.89 (d, J = 2.1 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H) 7.59 (d, J = 9.0 Hz, 1H), 7.49 (dd, J_1 = 9.15, J_2 = 2.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 9.0 Hz, 1H), 4.14 (s, 2H), 3.64 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 156.8, 134.8, 133.7, 131.1, 130.7, 130.1, 129.8, 129.5, 128.9 128.5, 122.7, 120.2, 116.0, 111.6, 60.7, 55.6, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}BrClNO$ 390.0255; Found 390.0268.

1-((benzyl(methyl)amino)methyl)-7-methoxynaphthalen-2-ol (5k):



Yellow viscous liquid (0.246 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.69 (d, J = 9.3 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.41-7.32 (m, 5H), 7.13 (d, J = 2.1 Hz, 1H), 7.02-6.98 (m, 2H), 4.16 (s, 2H), 3.95 (s, 3H), 3.73 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz $CDCl_3$), δ 158.3, 157.2, 136.6, 133.8, 130.4, 129.4, 129.0, 128.6, 127.7, 123.9, 116.7, 114.1, 110.5, 100.8, 61.4, 55.9, 55.3, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}NO_2$ 308.1645; Found 308.1645.

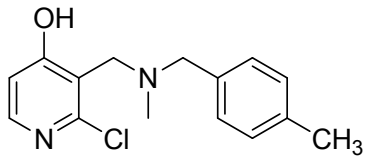
3-((benzyl(methyl)amino)methyl)-2-chloropyridin-4-ol (7a):



Colourless liquid (0.218 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.05 (d, J = 5.7 Hz, 1H), 7.41-7.30 (m, 5H), 6.68 (d, J = 5.7 Hz, 1H), 3.97 (s, 2H), 3.68 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 167.6, 150.0, 149.1, 135.5, 129.5, 128.9, 128.2, 115.2, 112.1,

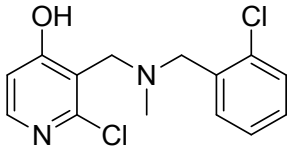
61.5, 57.0, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}ClN_2O$ 263.0946; Found 263.0950.

2-chloro-3-((methyl(4-methylbenzyl)amino)methyl)pyridin-4-ol (7b):



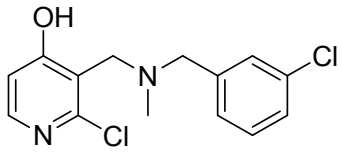
Colourless liquid (0.235 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.06 (d, J = 5.4 Hz, 1H), 7.21 (m, 4H), 6.68 (d, J = 5.4 Hz, 1H), 3.97 (s, 2H), 3.66 (s, 2H), 2.37 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 167.7, 150.0, 149.0, 138.0, 132.4, 129.5, 129.4, 115.2, 112.1, 61.1, 56.8, 41.4, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{18}ClN_2O$ 277.1102; Found 277.1102.

2-chloro-3-(((2-chlorobenzyl)(methyl)amino)methyl)pyridin-4-ol (7c):



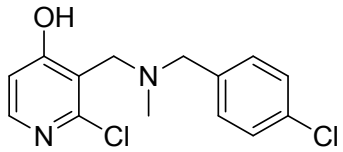
Colourless liquid (0.214 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.05 (d, J = 5.7 Hz, 1H), 7.47-7.44 (m, 1H), 7.38-7.29 (m, 3H), 6.66 (d, J = 5.4 Hz, 1H), 4.01 (s, 2H), 3.83 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 167.1, 150.1, 149.0, 135.0, 133.5, 131.8, 130.2, 129.8, 127.1, 115.2, 112.0, 59.2, 56.7, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}Cl_2N_2O$ 297.0556; Found 297.0545.

2-chloro-3-(((3-chlorobenzyl)(methyl)amino)methyl)pyridin-4-ol (7d):



Colourless liquid (0.208 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (d, J = 5.6 Hz, 1H), 7.29-7.23 (m, 3H), 7.17 (s, 1H), 6.67 (d, J = 5.6 Hz, 1H), 3.94 (s, 2H), 3.61 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 167.3, 150.1, 149.2, 137.6, 134.7, 130.2, 129.5, 128.4, 127.5, 115.1, 112.1, 60.9, 57.1, 41.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}Cl_2N_2O$ 297.0556; Found 297.0556.

2-chloro-3-(((4-chlorobenzyl)(methyl)amino)methyl)pyridin-4-ol (7e):



Colourless liquid (0.220 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.06 (d, J = 5.4 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 6.68 (d, J = 5.7 Hz, 1H), 3.96 (s, 2H), 3.64 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 167.3, 150.1, 149.2, 134.2, 134.0, 130.8, 129.1, 115.1, 112.1, 60.7, 57.0, 41.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}Cl_2N_2O$ 297.0556; Found 297.0553.

Crystallographic Description:

Data Collection and Refinement Single-crystal X-ray data of compounds was collected on Bruker SMART CCD Diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). Frames were collected at T = 298 K by ω, φ, and 2θ-rotations with full quadrant data collection strategy (four domains each with 600 frames) at 10s per frame with SMART. The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[4] Structure solution, refinement, and data output were carried out with the SHELXTL package by direct methods.[5] Non-hydrogen atoms were refined anisotropically using the WinGX (version 1.80.05) program package.[6] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software shown in figure S10. Further information on the crystal structure determination (excluding structure factors) has been given as table S1 and also deposited in the Cambridge Crystallographic Data Centre as supplementary publications numbers, 1832248. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

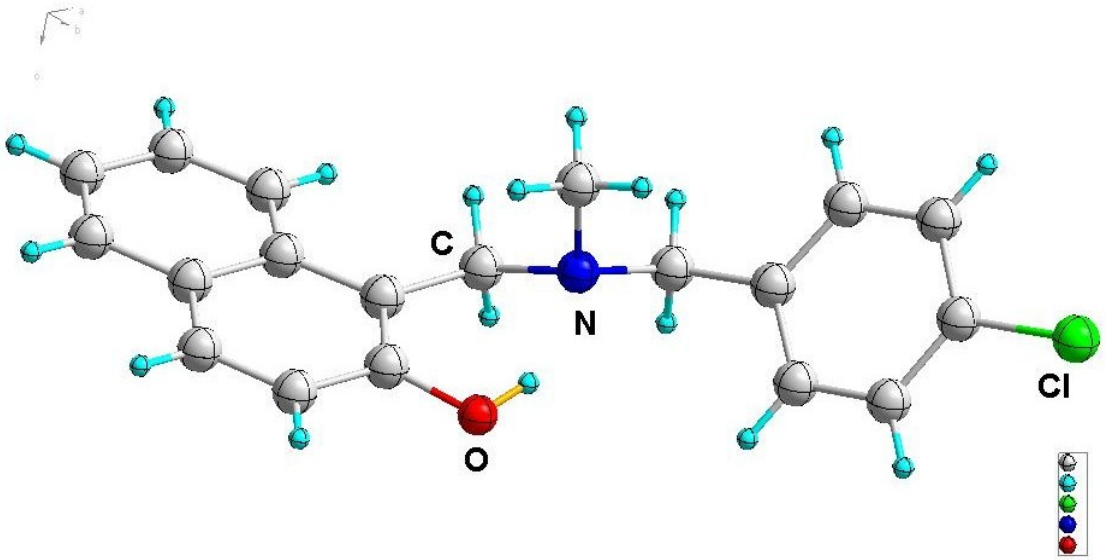


Fig. S10 ORTEP diagram of **5f** (ellipsoid of 50% probability)

Crystallographic description of 1-(((4-chlorobenzyl)(methyl)amino)methyl)naphthalen-2-ol (5f) (Table S1):

Identification code	**5f**
Empirical formula	$C_{19}H_{18}ClNO$
Formula weight	311.79
Temperature	302(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 20.1159(13) Å, a= 90°.
	b = 8.9951(5) Å, b= 93.382(2)°.
	c = 17.9253(11) Å, g= 90°.
Volume	3237.8(3) $Å^3$
Z	8
Density (calculated)	1.279 Mg/m^3
Absorption coefficient	0.237 mm^{-1}
F(000)	1312.0
Crystal size	0.33 x 0.32 x 0.29mm^3
Theta range for data collection	2.03 to 25.00°.
Index ranges	-22<=h<=22, -10<=k<=10, -20<=l<=20
Reflections collected	16532
Independent reflections	2496 [R(int) = 0.1548]
Completeness to theta = 25.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2493 / 0 / 201
Goodness-of-fit on F^2	1.134
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1633
R indices (all data)	R1 = 0.0726, wR2 = 0.1692
Largest diff. peak and hole	0.293 and -0.457 $e.A^{-3}$
CCDC	1832248

References

1. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry,* 5th Eds. ELBS, Longman Group U K Ltd., 1989.

2. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339. b) J. Liu, H. Jeong, K. Lee, J. Y. Park, Y. H. Ahn, S. Lee, *Carbon*, 2010, **48**, 2282.

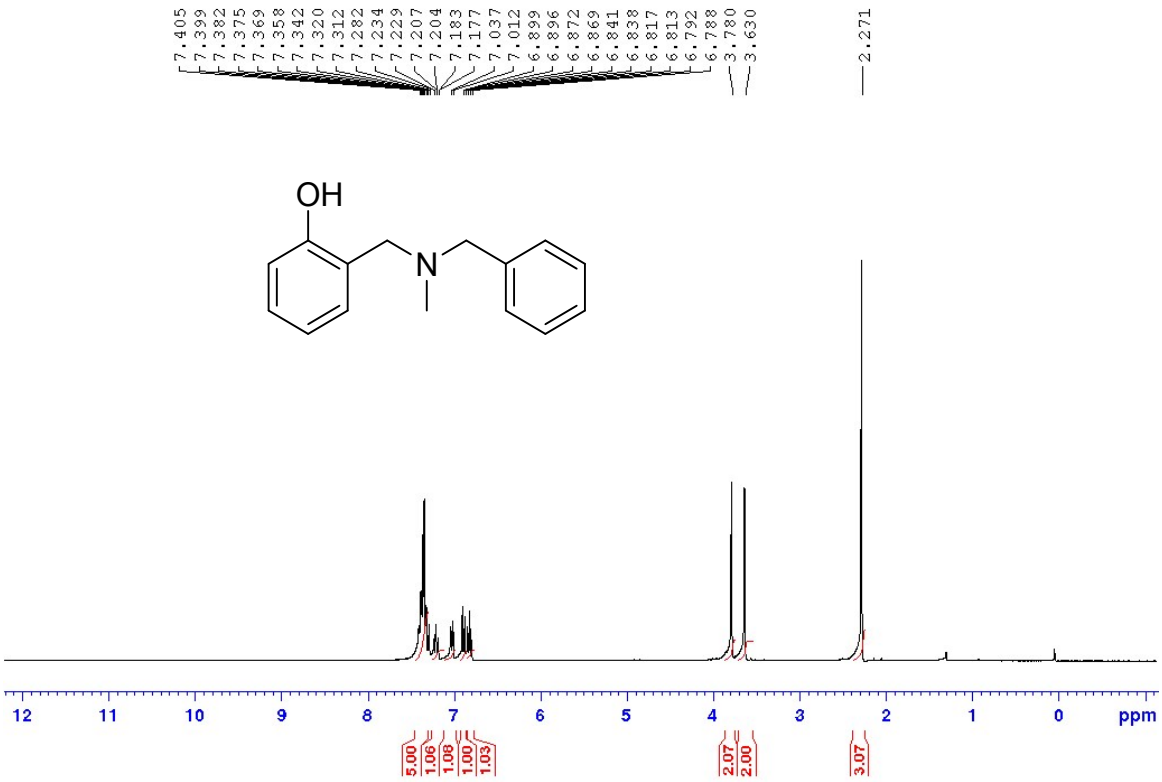
3. A. Kamal, V. Srinivasulu, J. N. S. R. C Murty, N. Shankaraiah, N. Nagesh, T. Srinivasa Reddy and A. V. S. Rao *Adv. Synth. Catal.* 2013, **355**, 2297-2307.

4. SADABS V2.10 (Sheldrick, G. M. 2003).

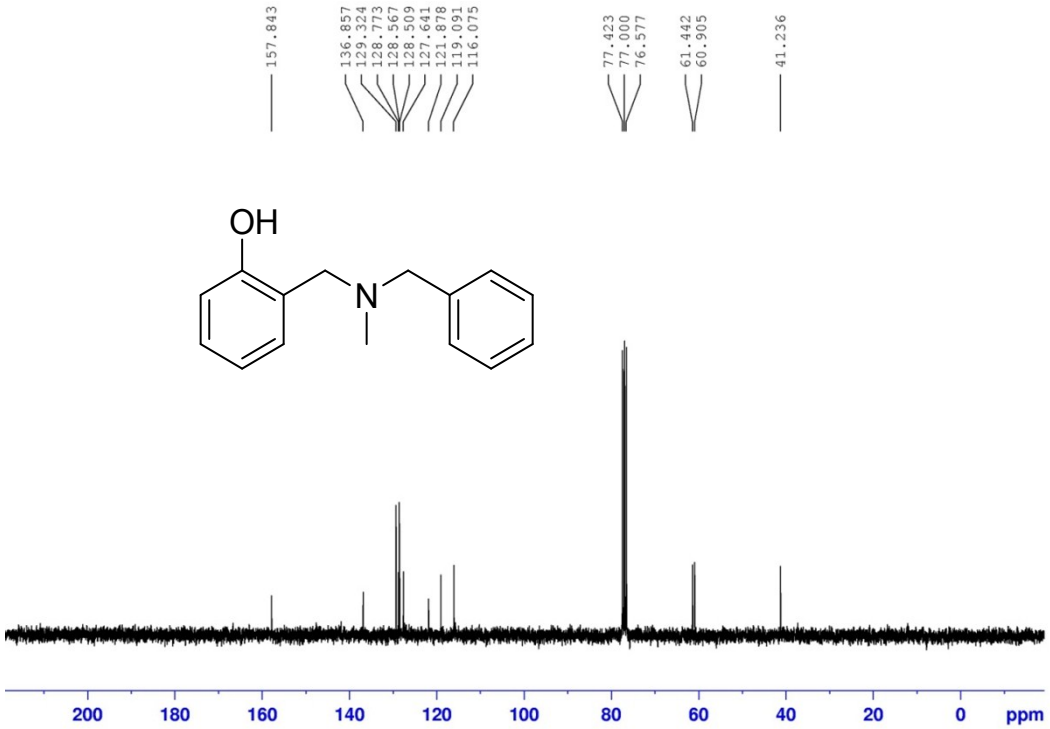
5. Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. *Crystallogr.*, 1990, **46**, 467.

6. Sheldrick, G. M. SHELXL-NT Version 6.12, University of Gottingen, Germany, 2000.

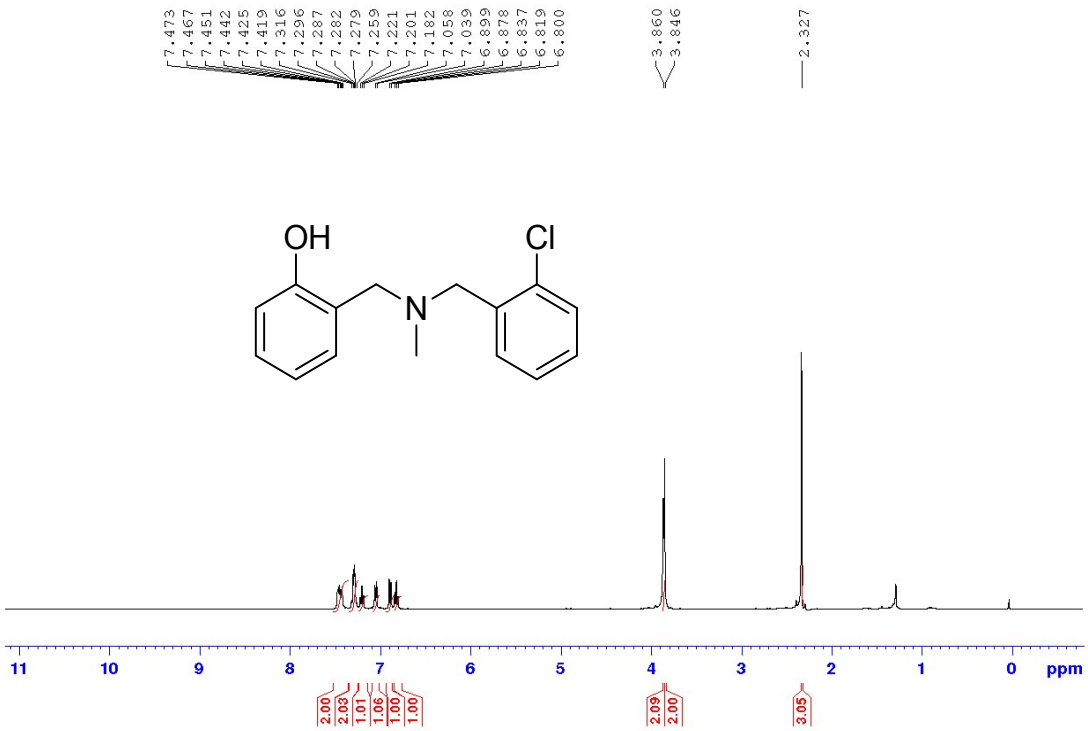
Spectra: ^{1}HNMR and ^{13}CNMR



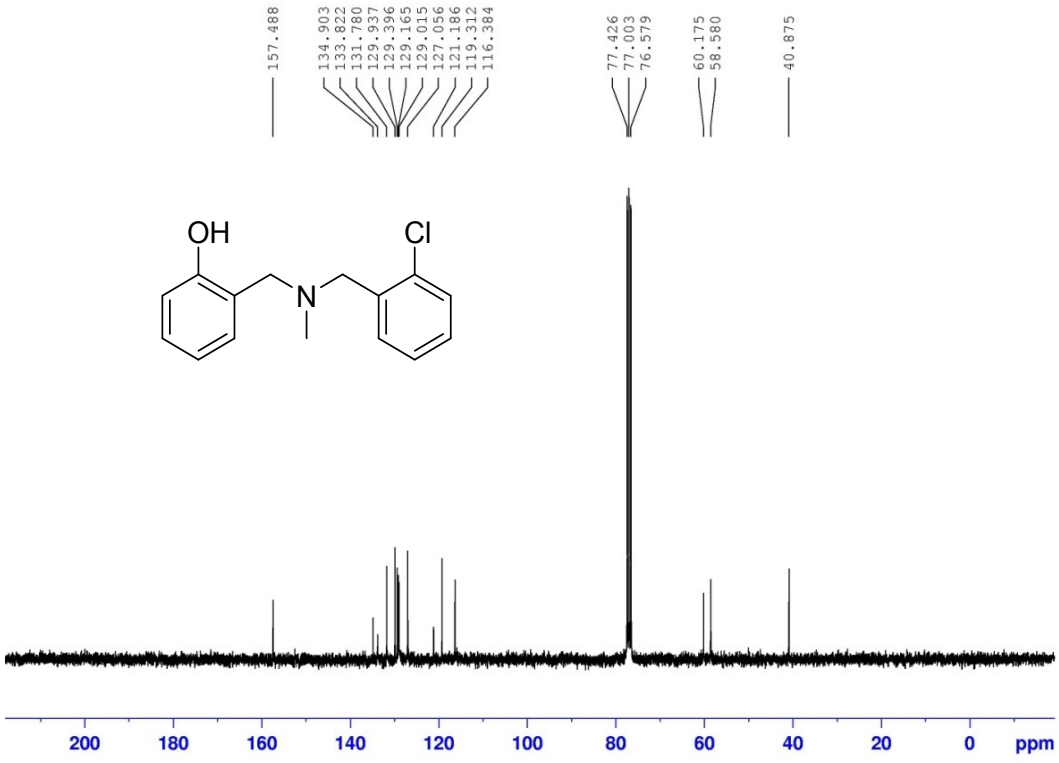
Spectrum1: ^{1}H NMR of 3a



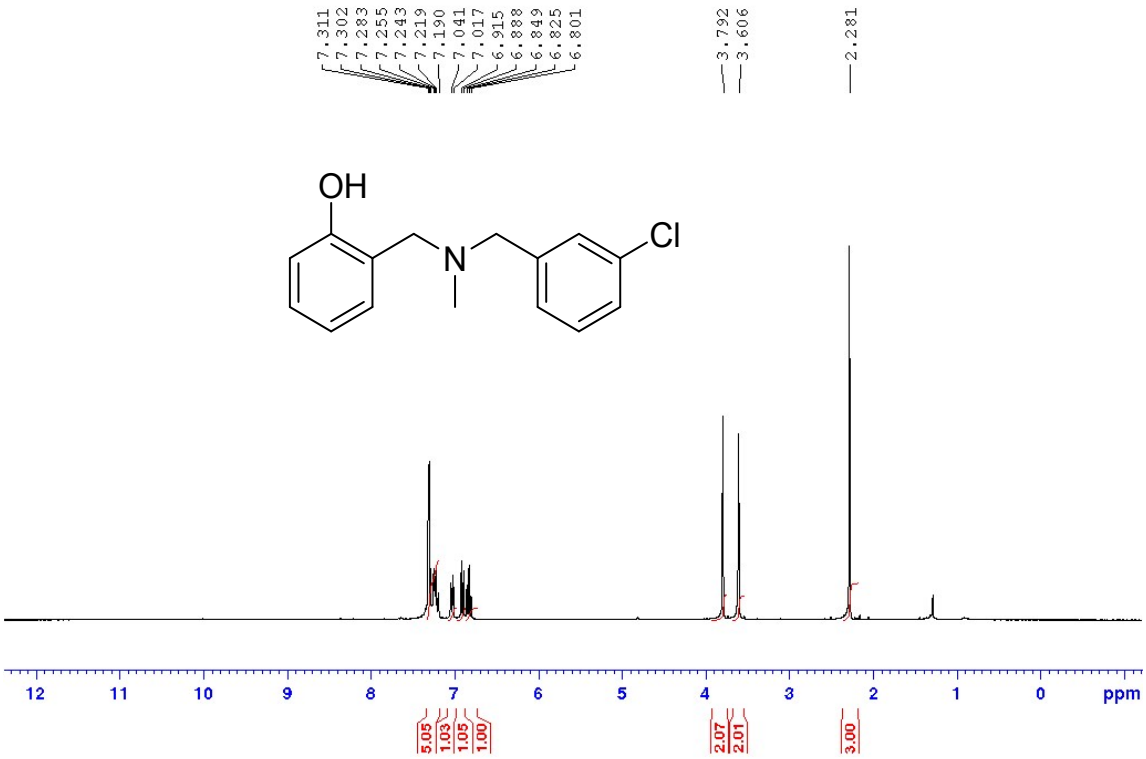
Spectrum2: ^{13}C{^{1}H} NMR of 3a



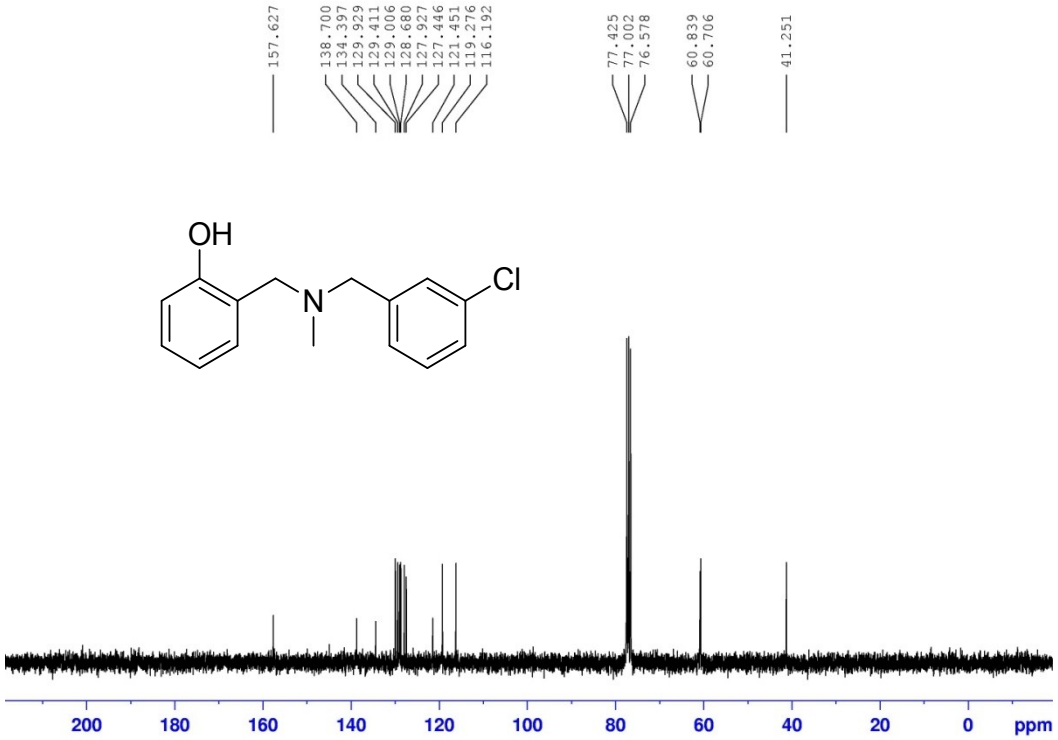
Spectrum3: ^{1}H **NMR of 3b**



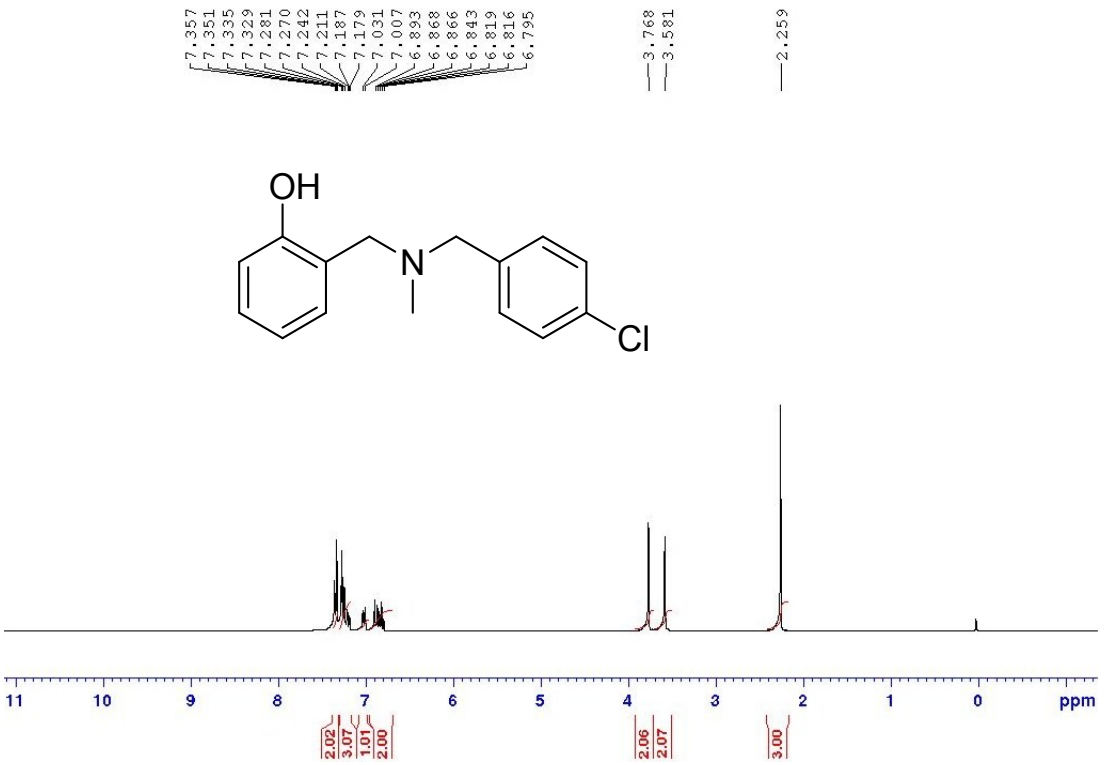
Spectrum4: ^{13}**C{**^{1}**H} NMR of 3b**



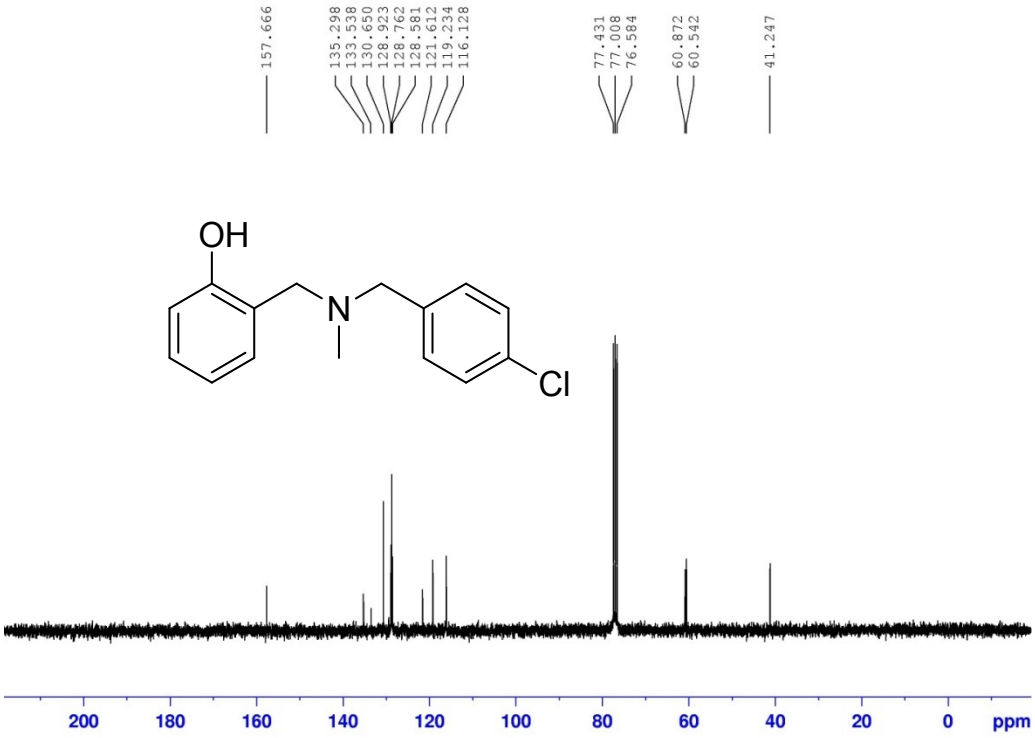
Spectrum5: ^{1}H **NMR of 3c**



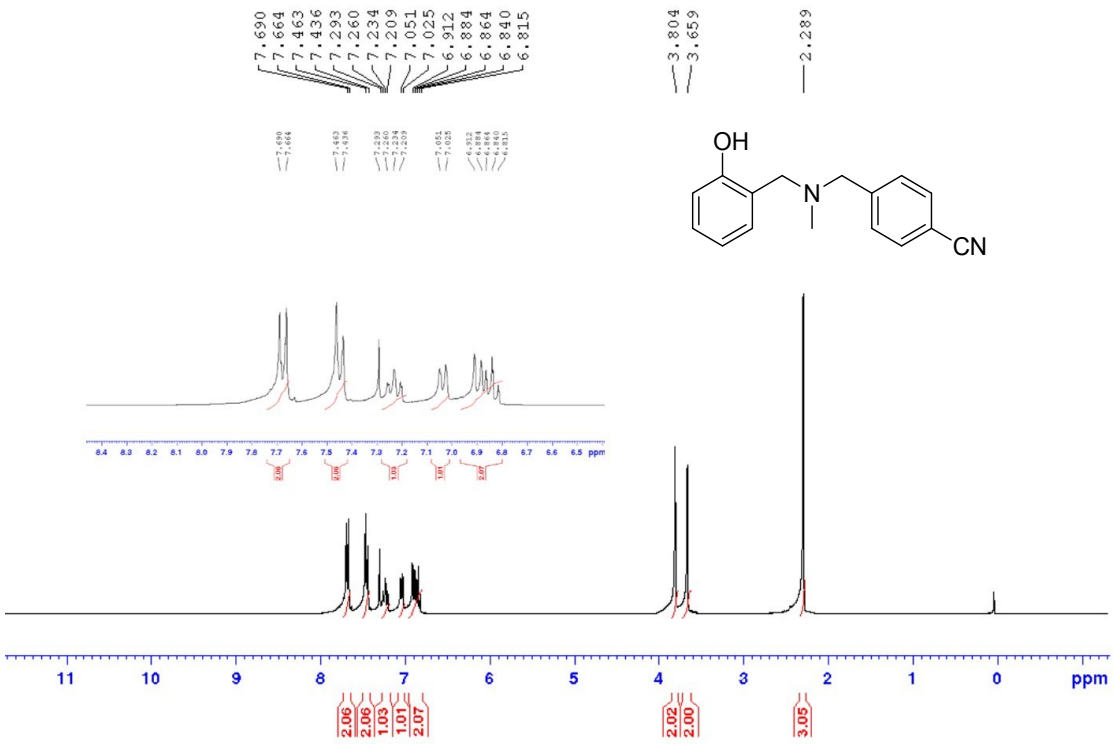
Spectrum6: ^{13}**C{**^{1}**H} NMR of 3c**



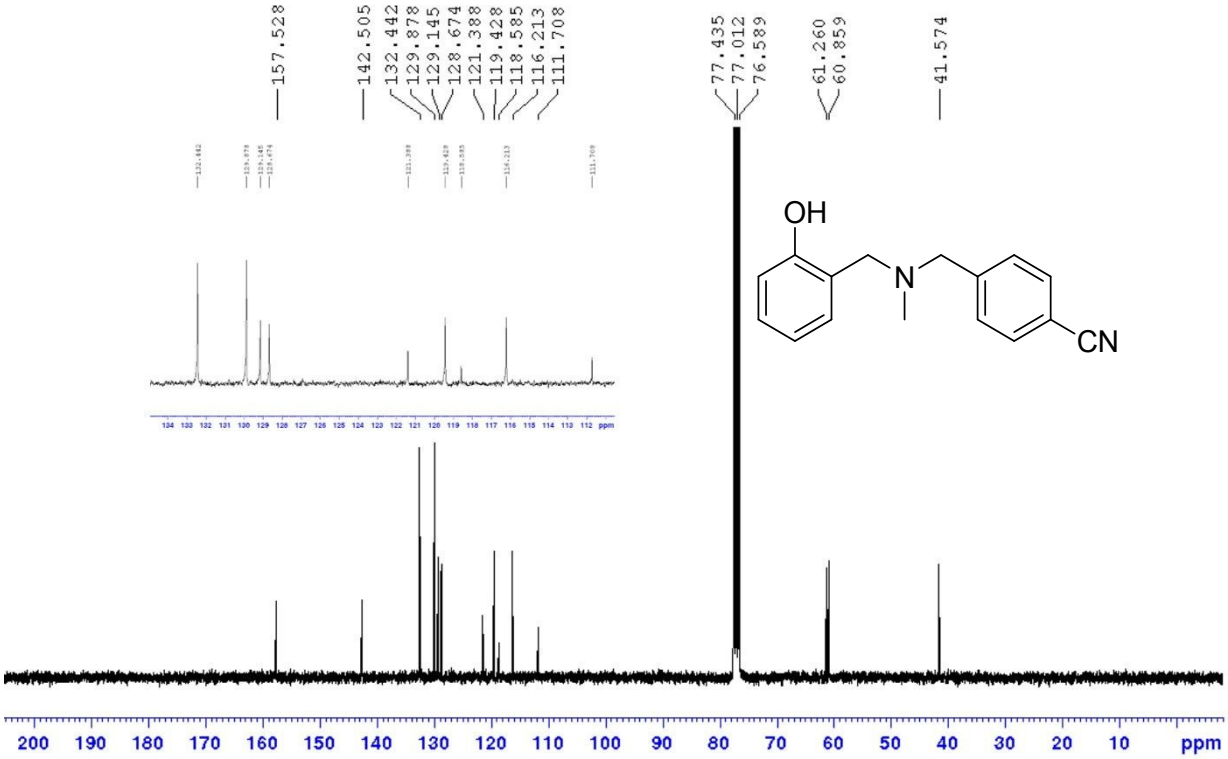
Spectrum7: ^{1}H **NMR of 3d**



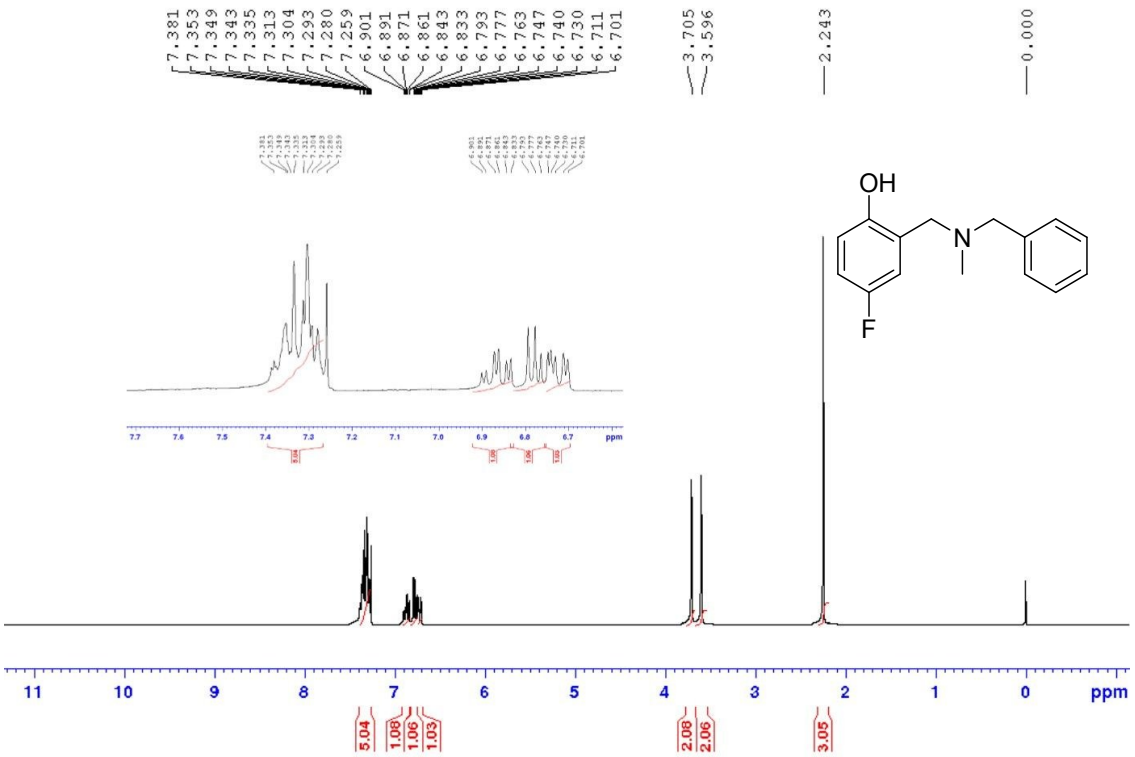
Spectrum8: ^{13}**C{**^{1}**H} NMR of 3d**



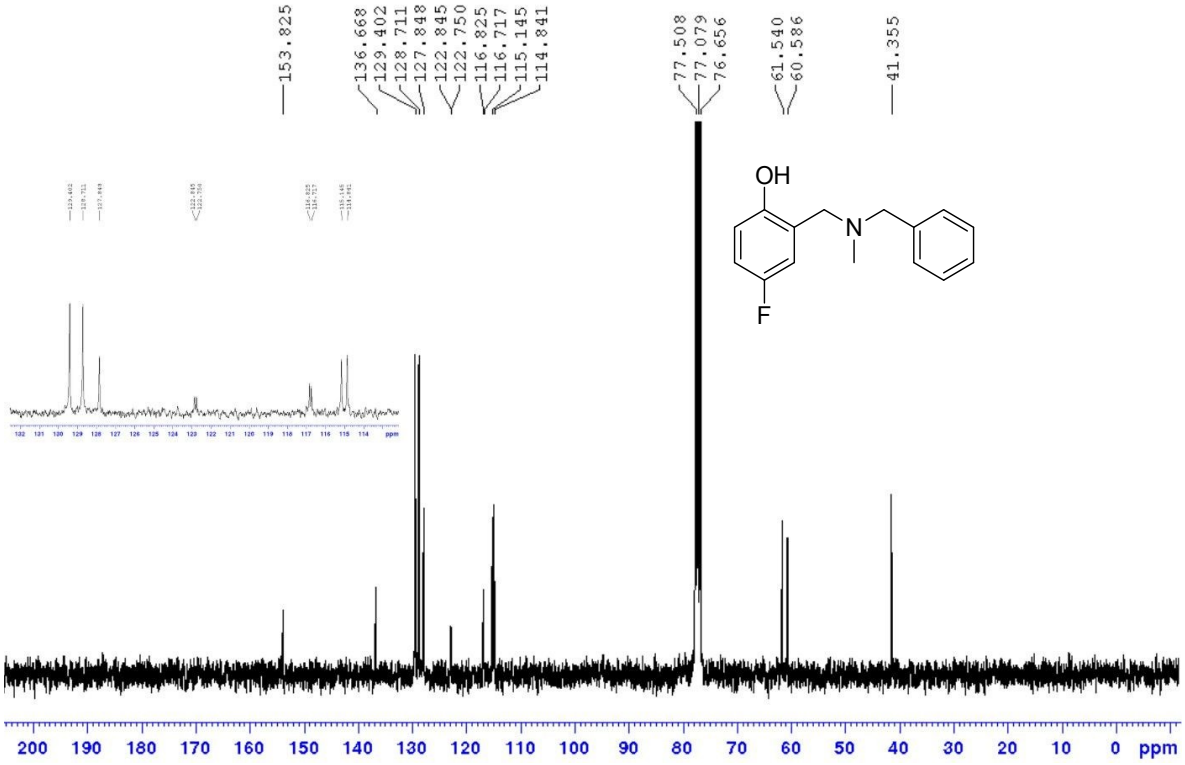
Spectrum9: ^{1}H **NMR of 3e**



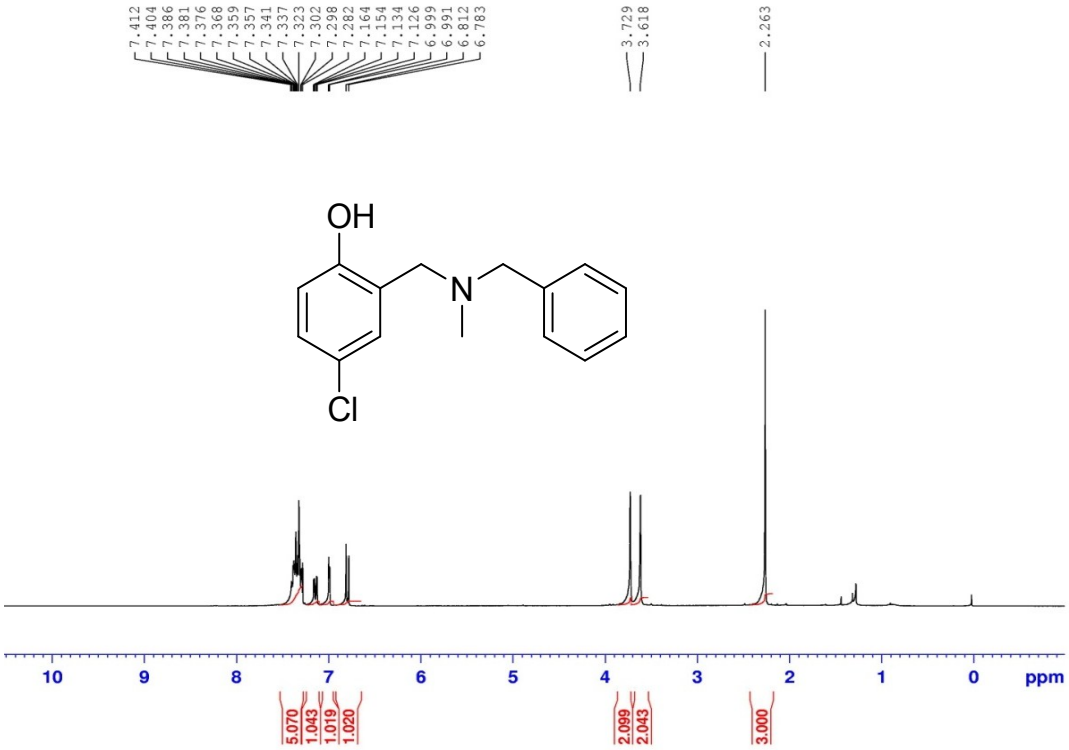
Spectrum10: ^{13}C{^{1}H} **NMR of 3e**



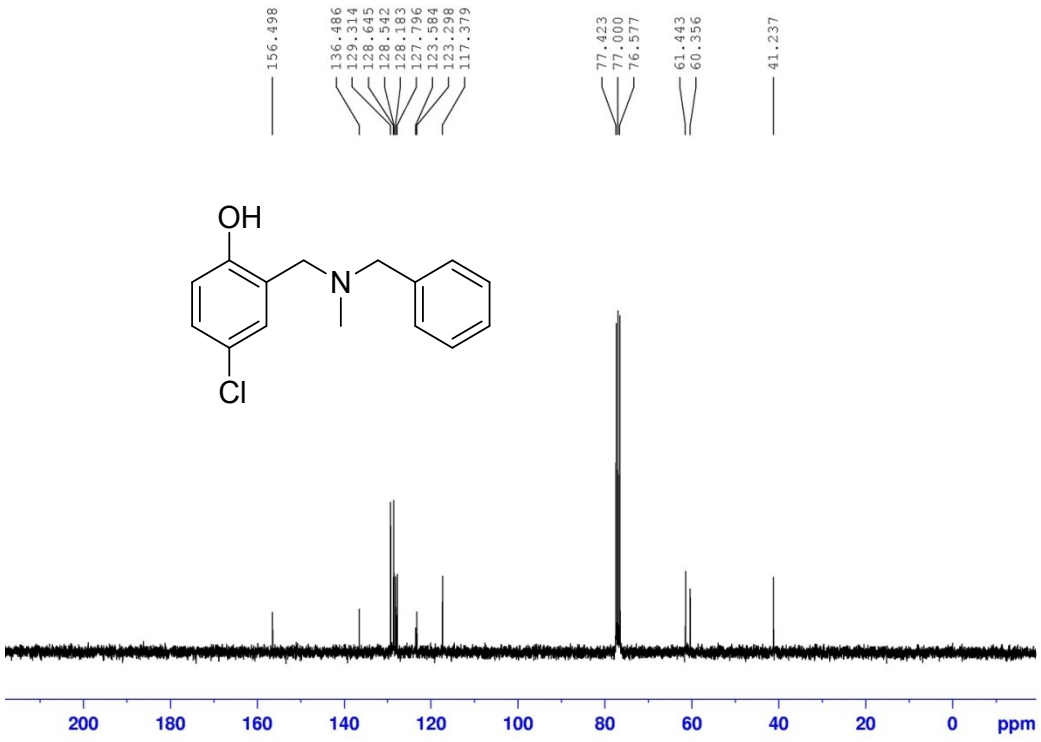
Spectrum11: ^{1}H **NMR of 3f**



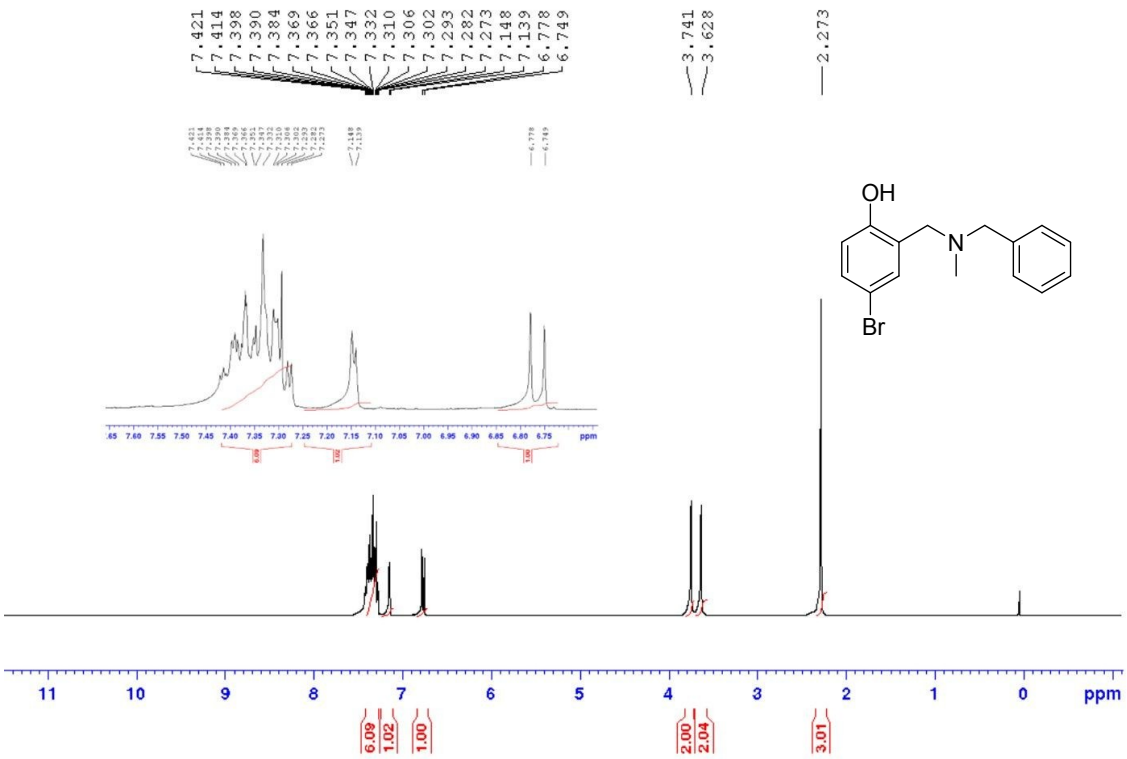
Spectrum12: ^{13}C{^{1}H} **NMR of 3f**



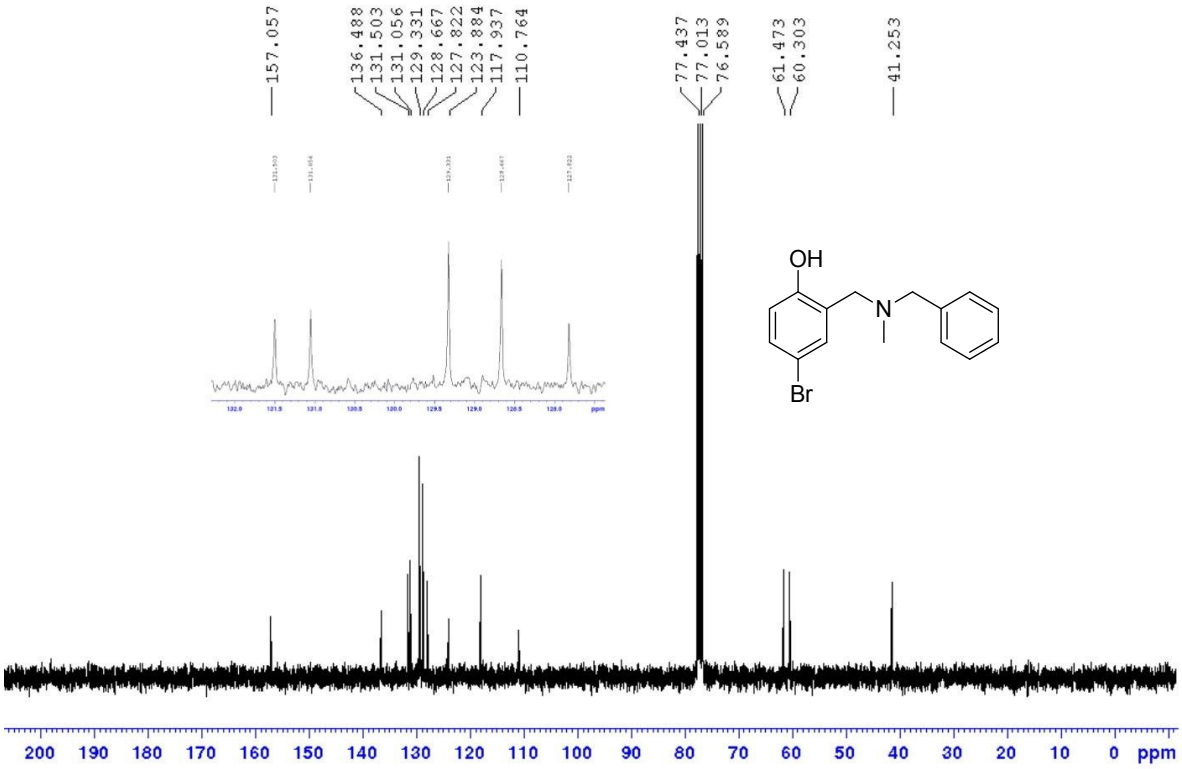
Spectrum13: ^{1}H **NMR of 3g**



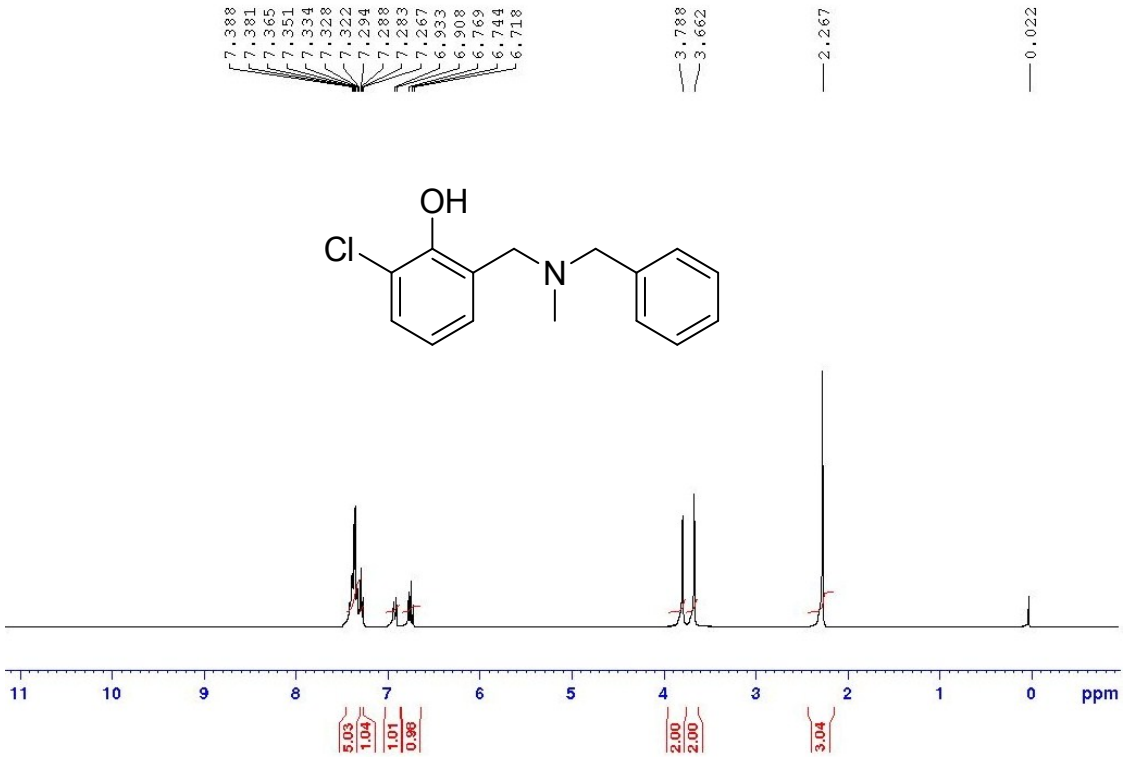
Spectrum14: ^{13}C{^{1}H} **NMR of 3g**



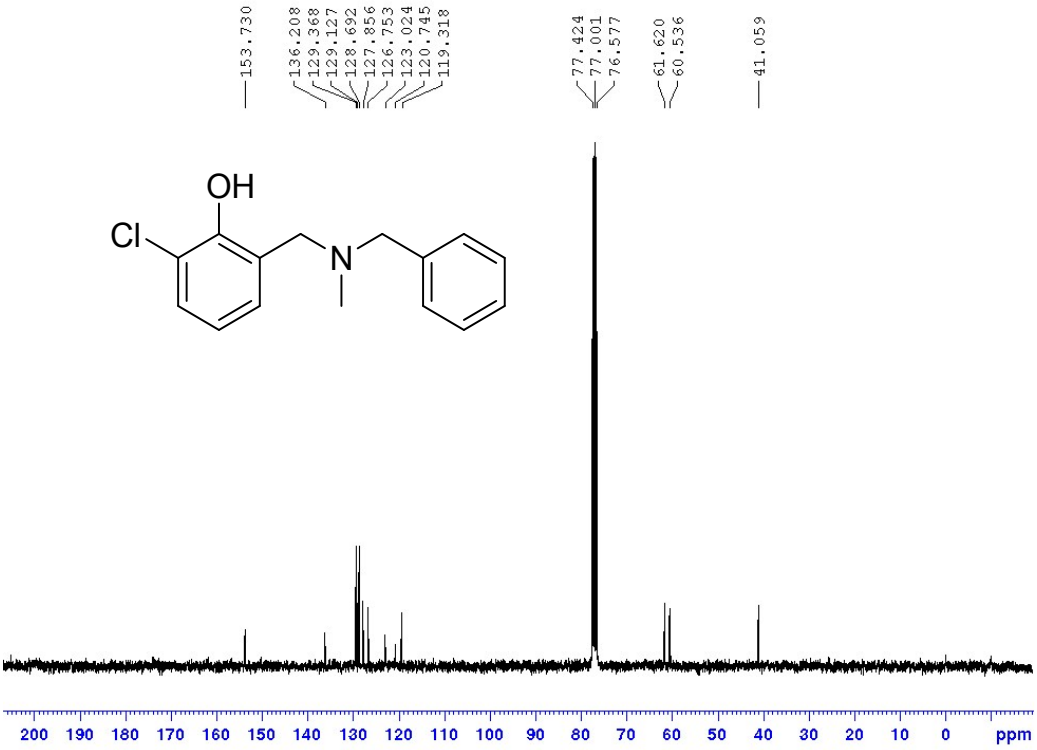
Spectrum15: ^{1}H NMR of 3h



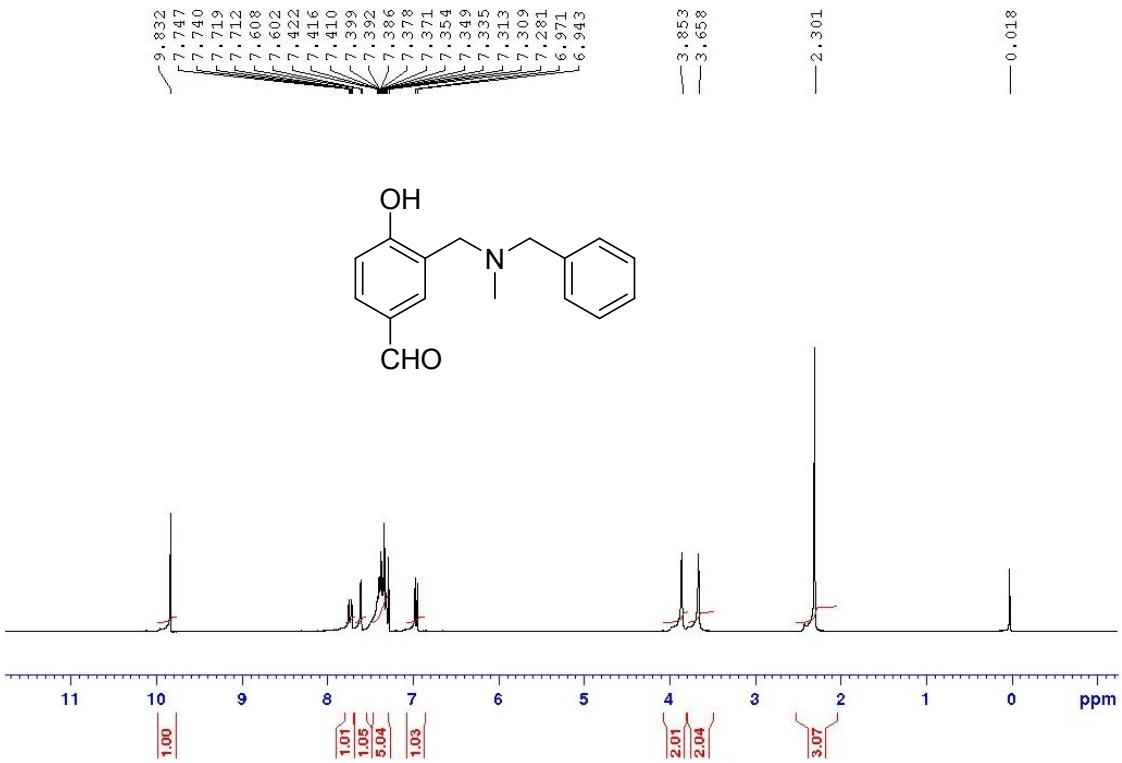
Spectrum16: ^{13}C{^{1}H} NMR of 3h



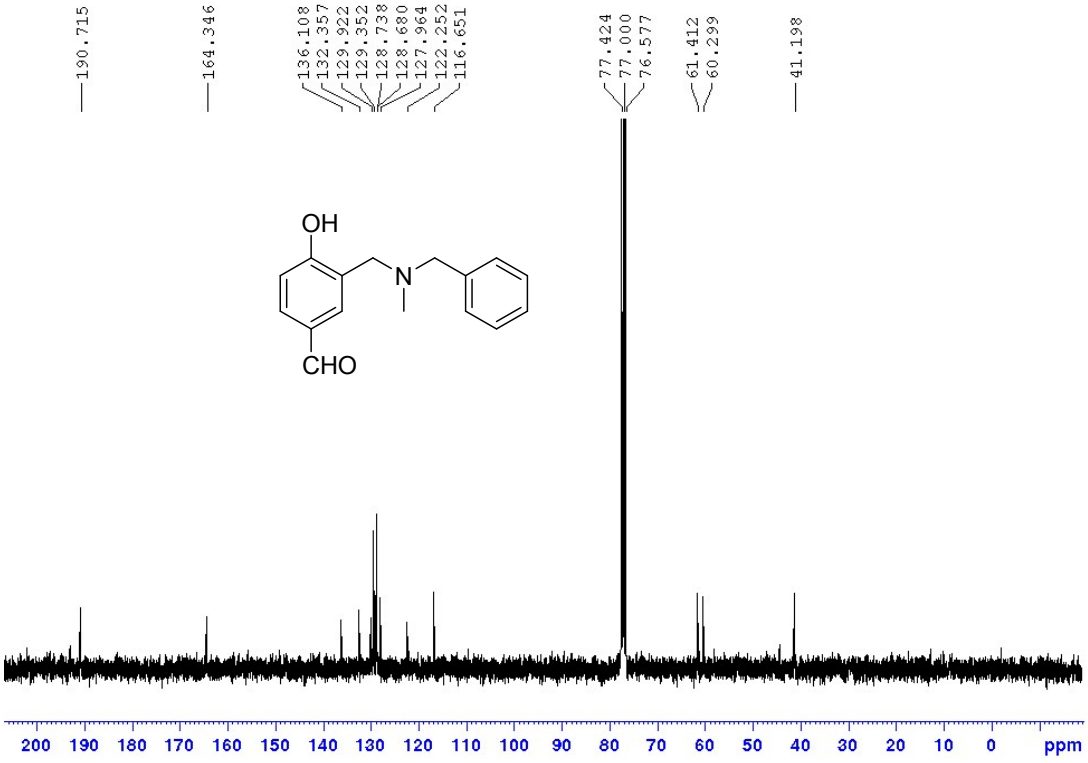
Spectrum17: ^{1}H **NMR of 3i**



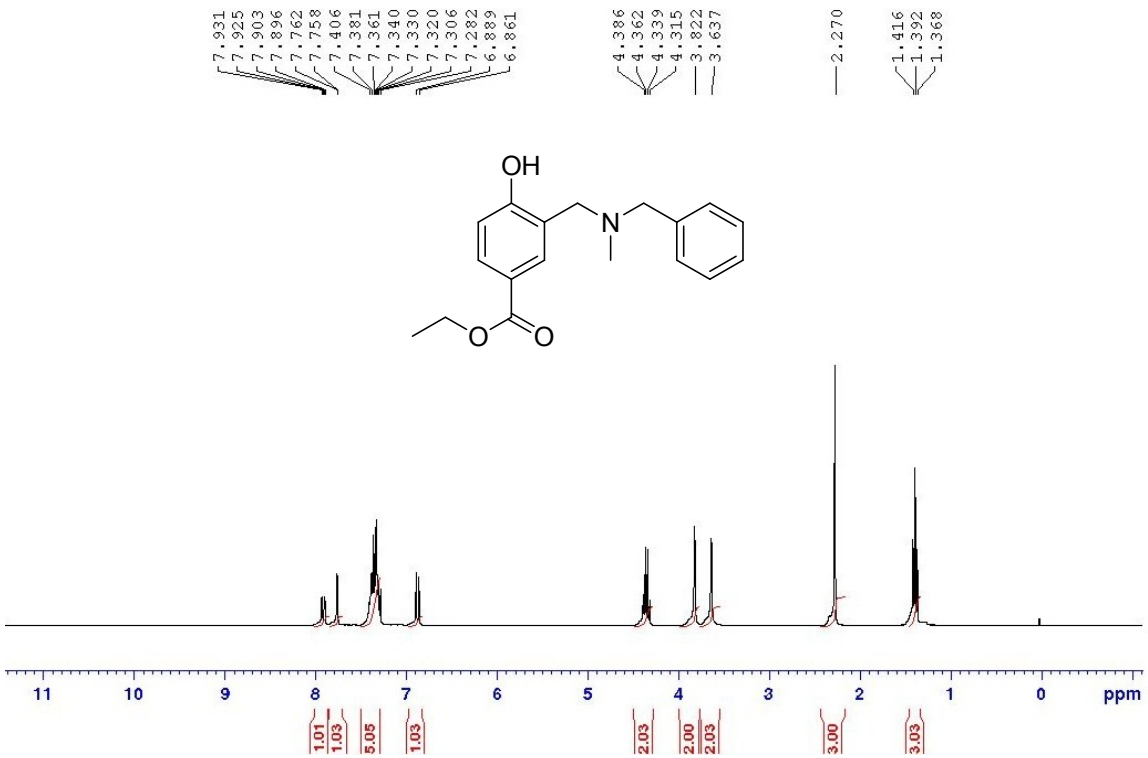
Spectrum18: ^{13}C{^{1}H} **NMR of 3i**



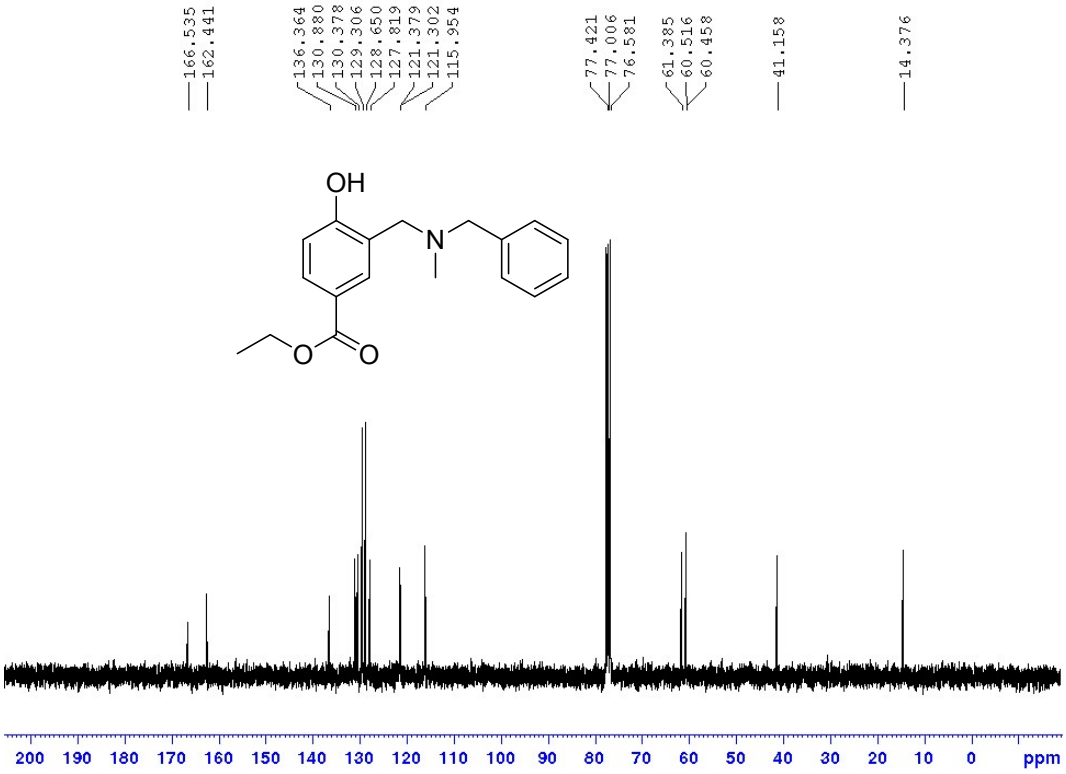
Spectrum19: ^{1}H **NMR of 3j**



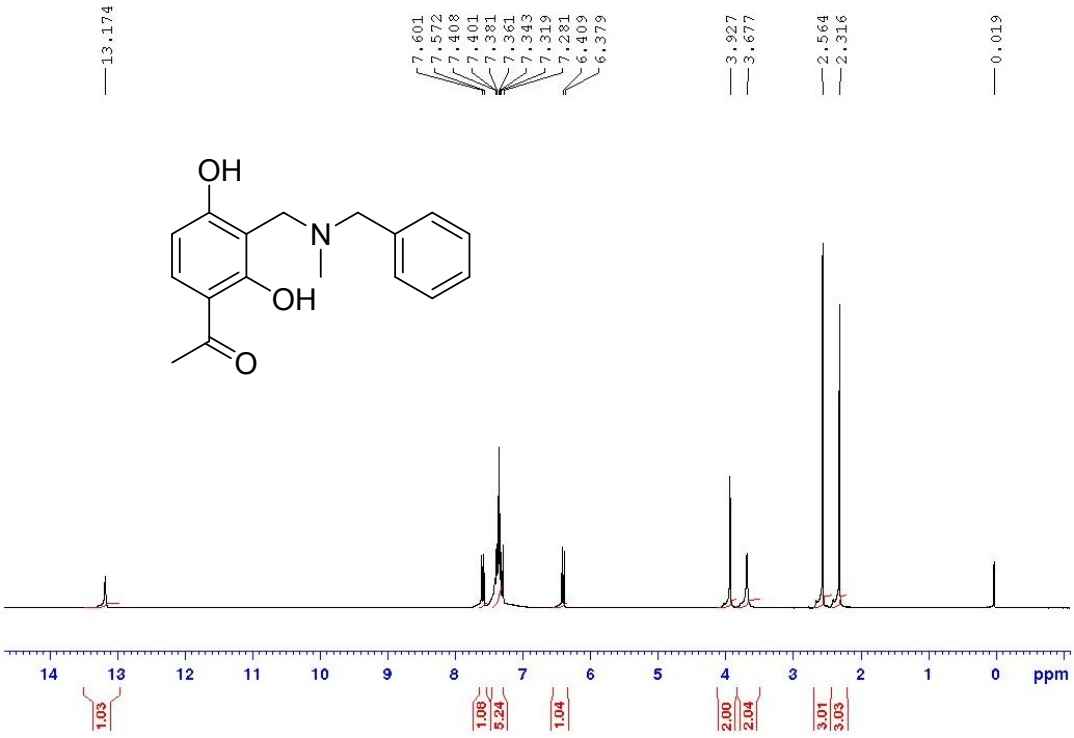
Spectrum20: ^{13}C{^{1}H} **NMR of 3j**



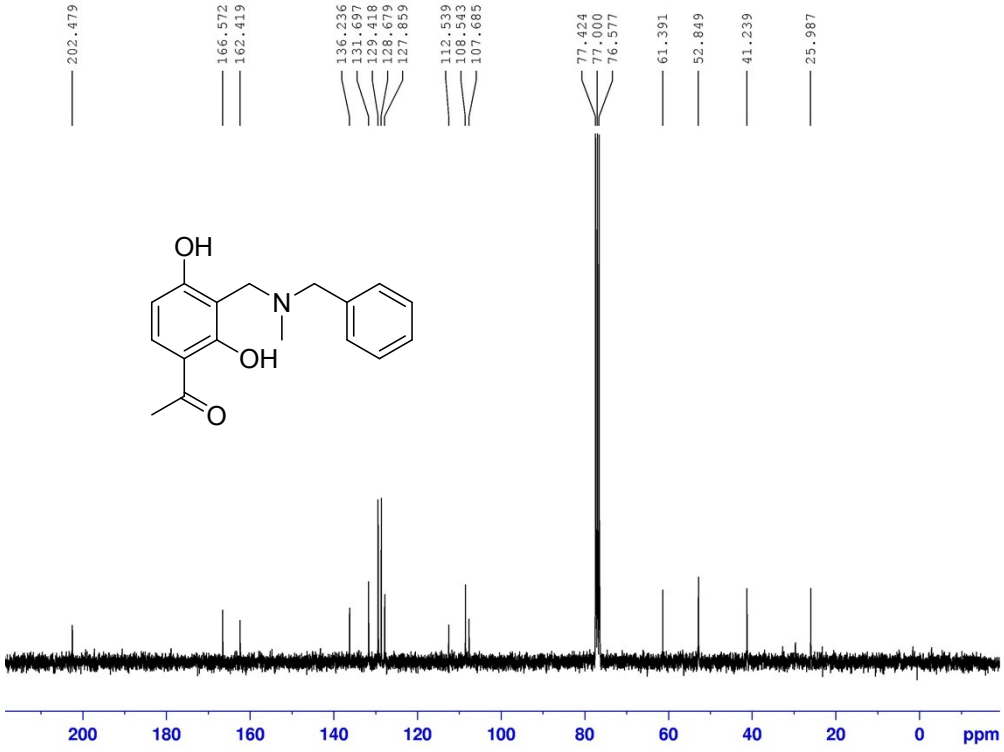
Spectrum21: ^{1}H **NMR of 3k**



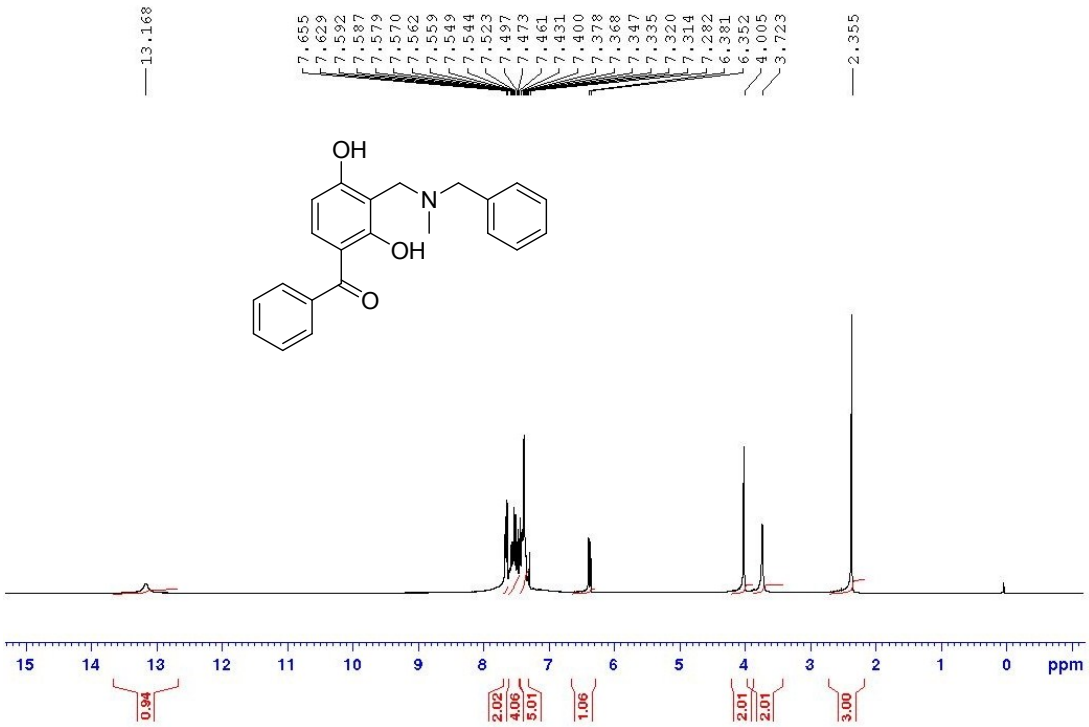
Spectrum22: ^{13}C{^{1}H} **NMR of 3k**



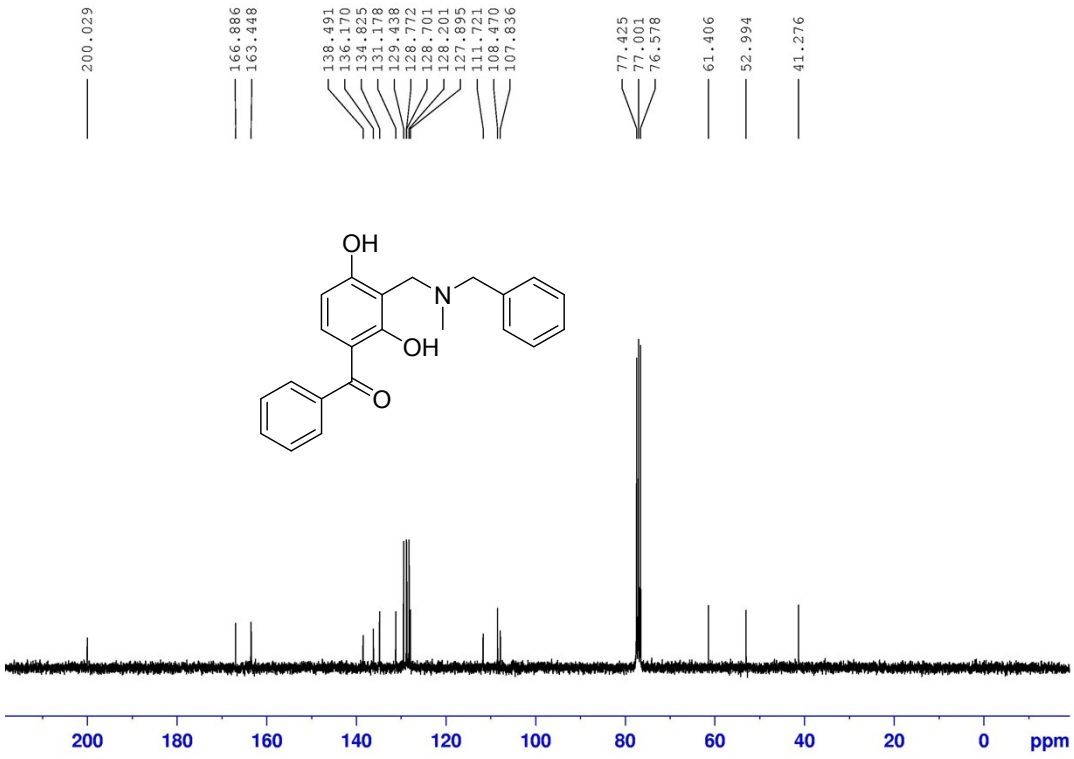
Spectrum23: ^{1}H **NMR of 3l**



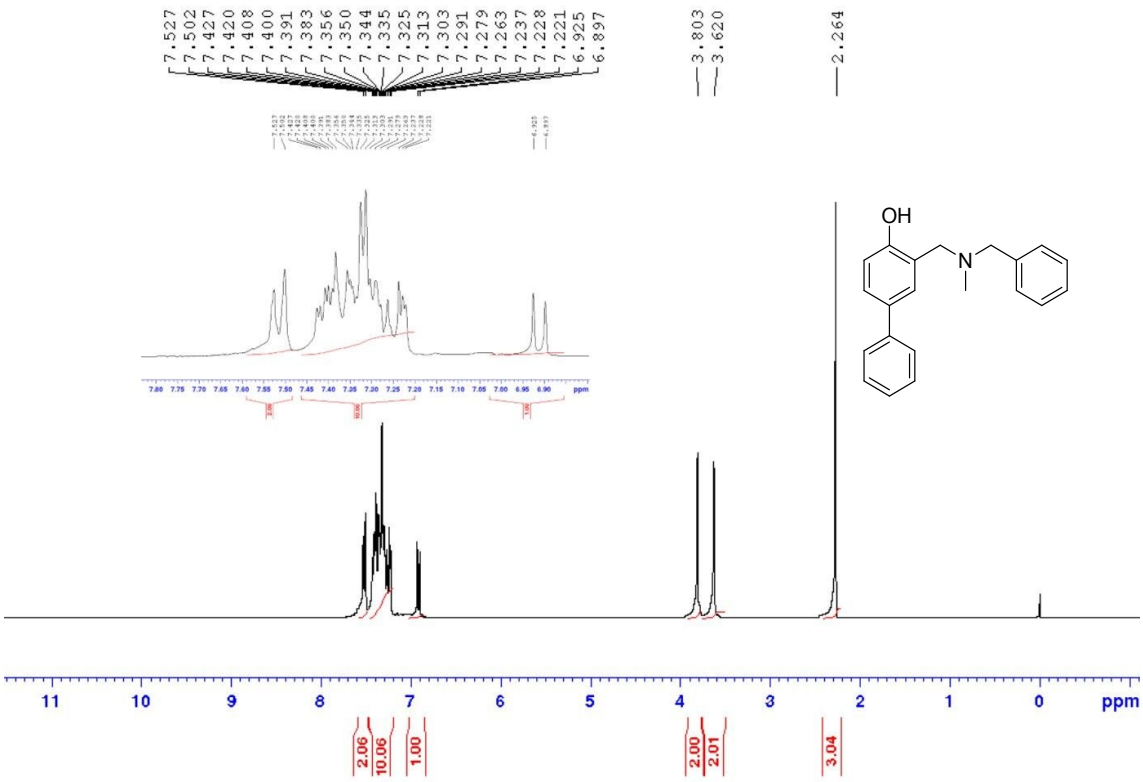
Spectrum24: ^{13}C{^{1}H} **NMR of 3l**



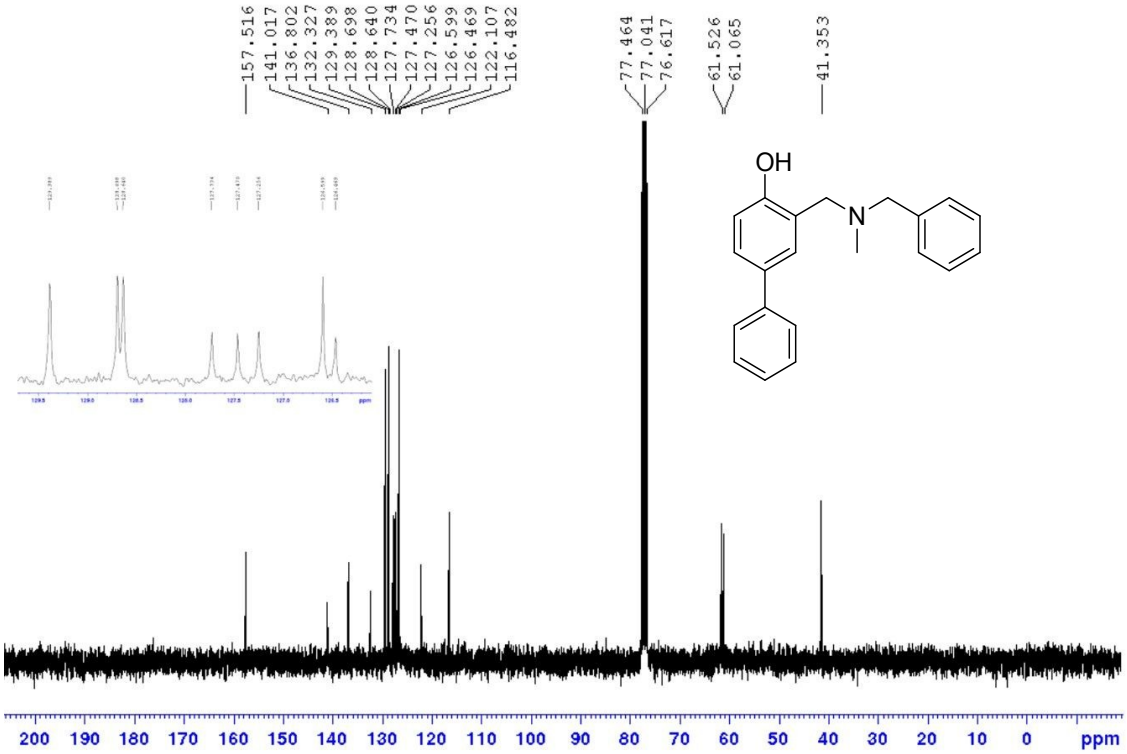
Spectrum25: ^{1}H **NMR of 3m**



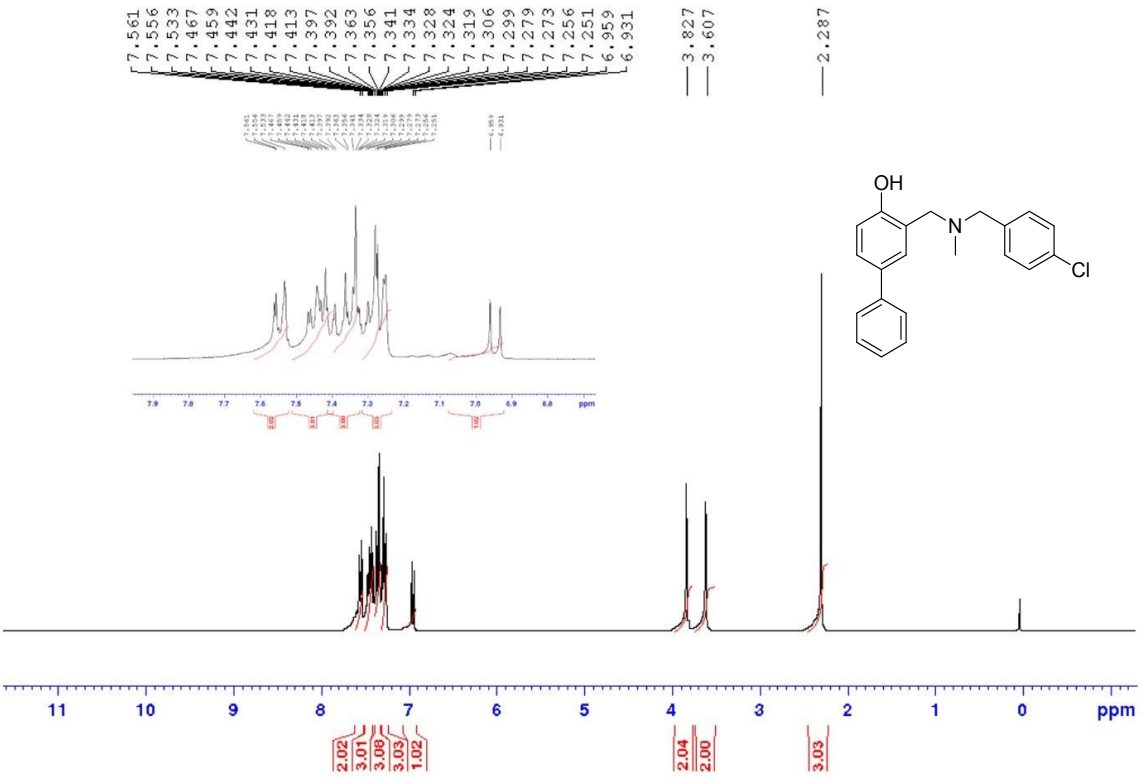
Spectrum26: ^{13}**C{**^{1}H**} NMR of 3m**



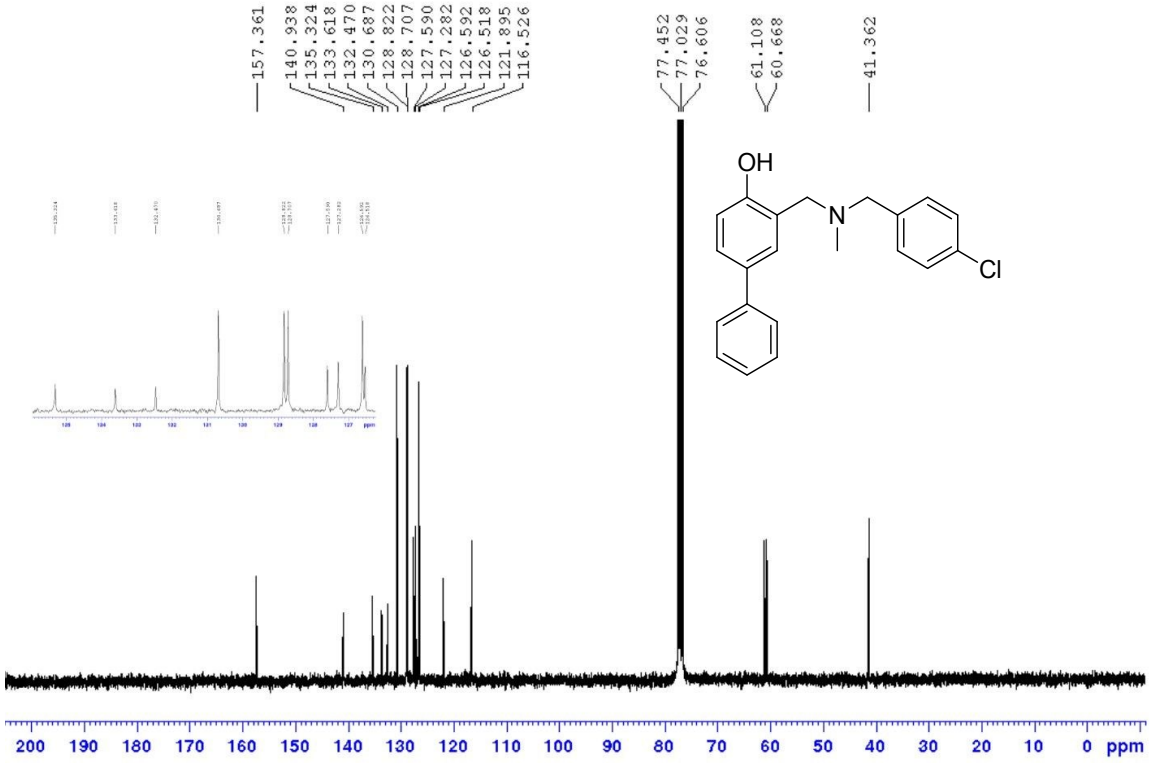
Spectrum27: ^{1}H **NMR of 3n**



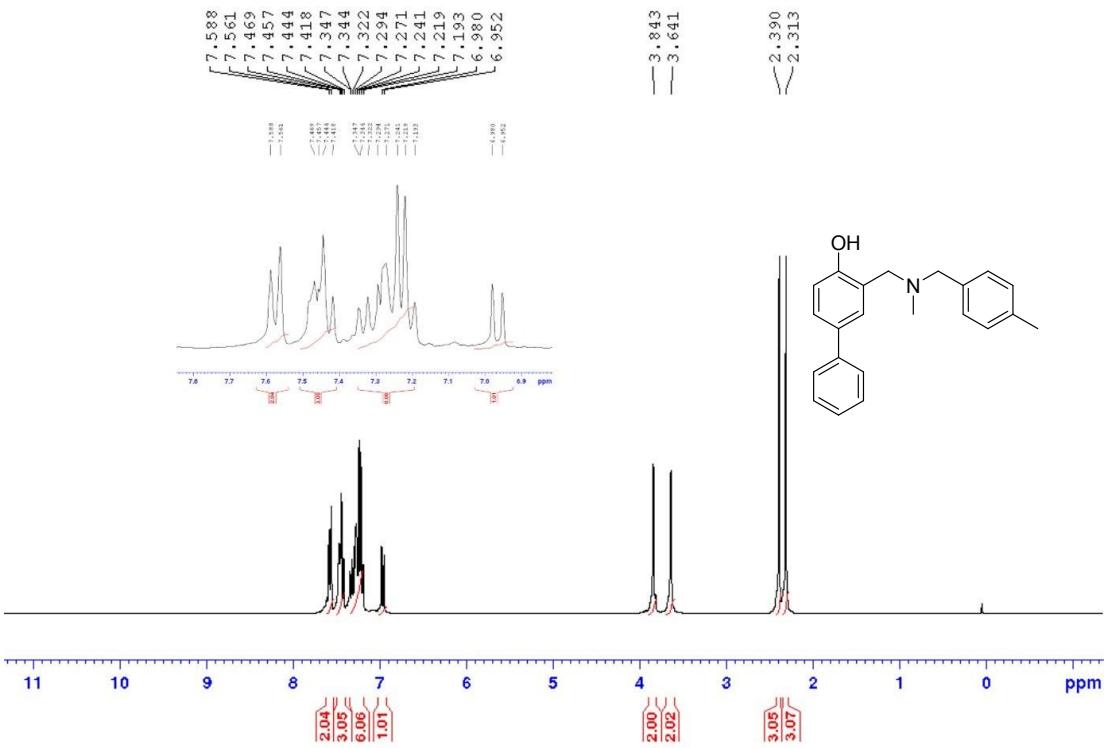
Spectrum28: ^{13}C{^{1}H} **NMR of 3n**



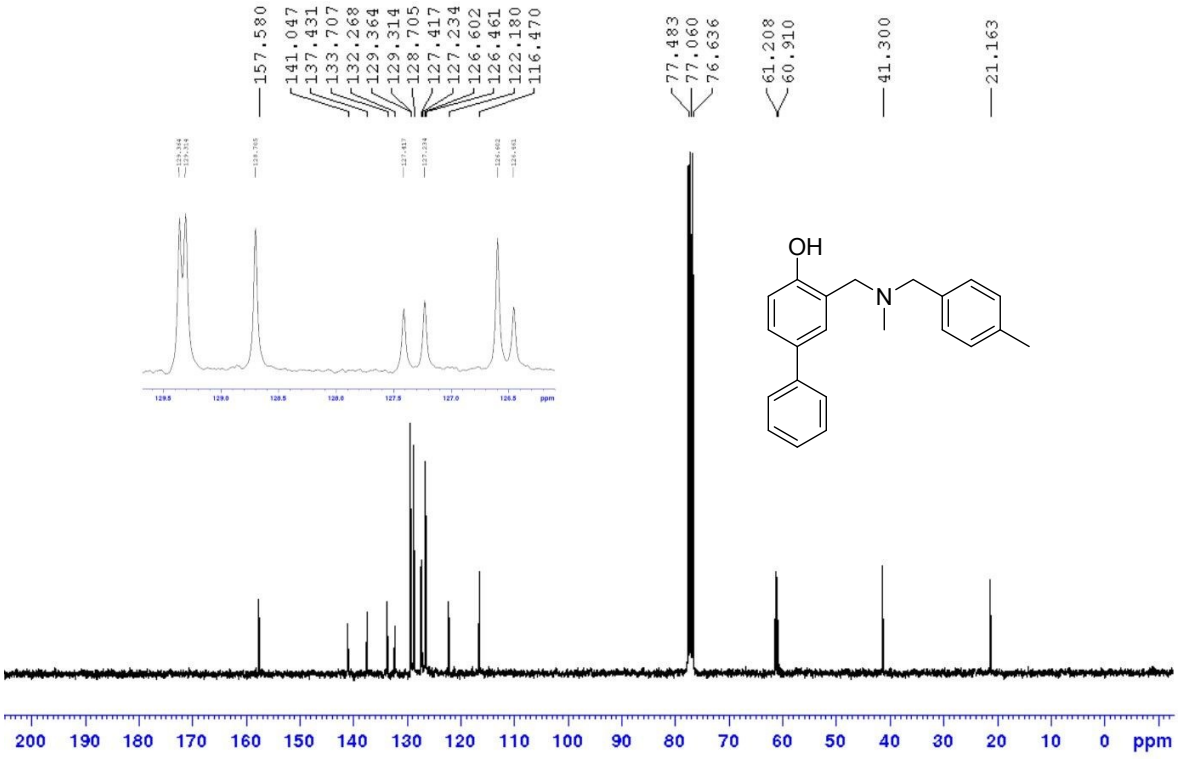
Spectrum29: ^{1}H **NMR of 3o**



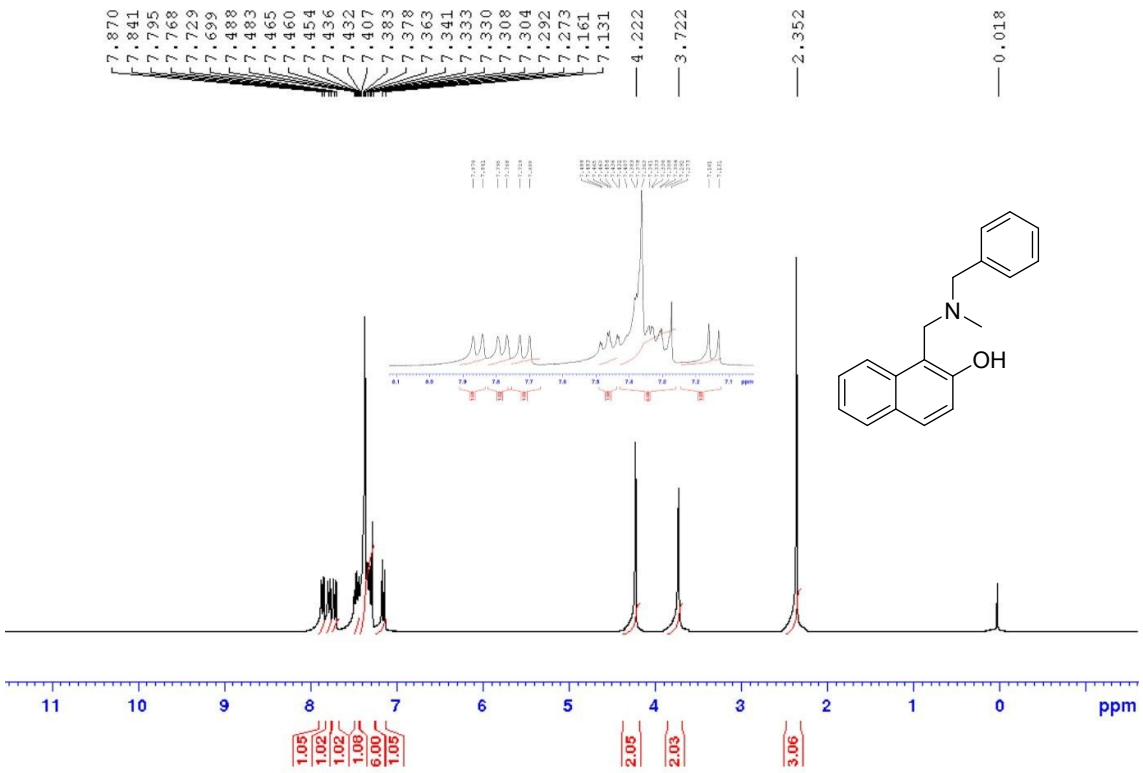
Spectrum30: ^{13}C{^{1}H} **NMR of 3o**



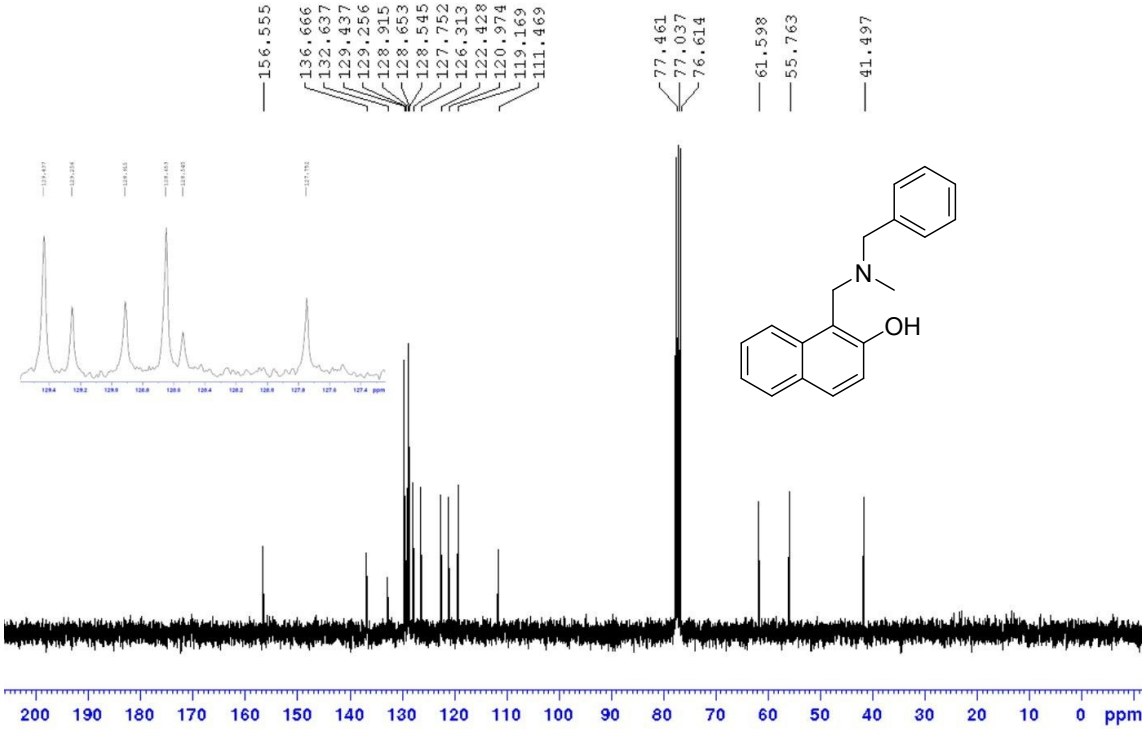
Spectrum31: ^{1}H **NMR of 3p**



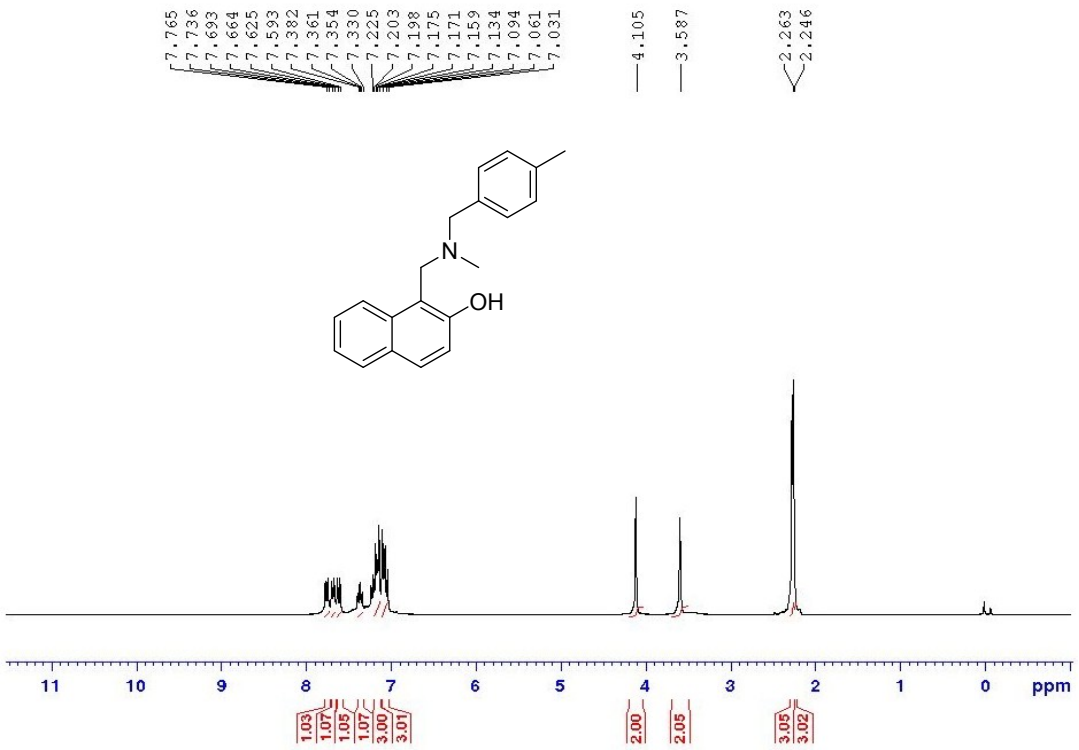
Spectrum32: ^{13}C{^{1}H} **NMR of 3p**



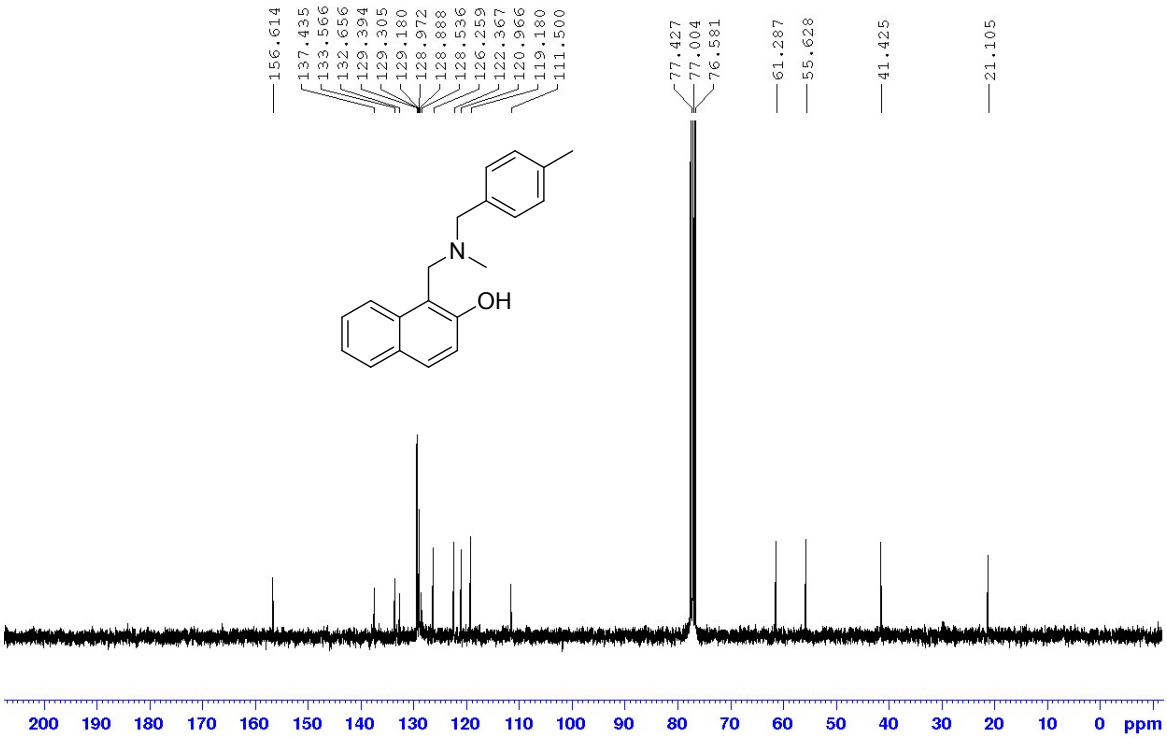
Spectrum33: ^{1}H **NMR of 5a**



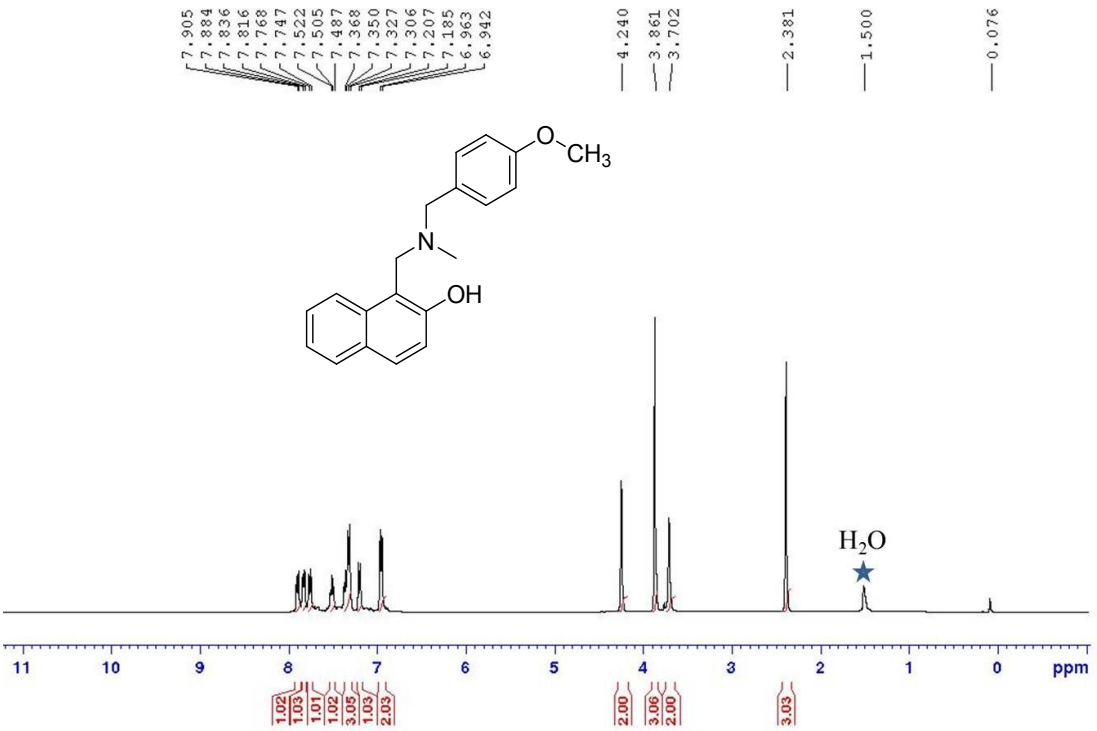
Spectrum34: ^{13}C{^{1}H} **NMR of 5a**



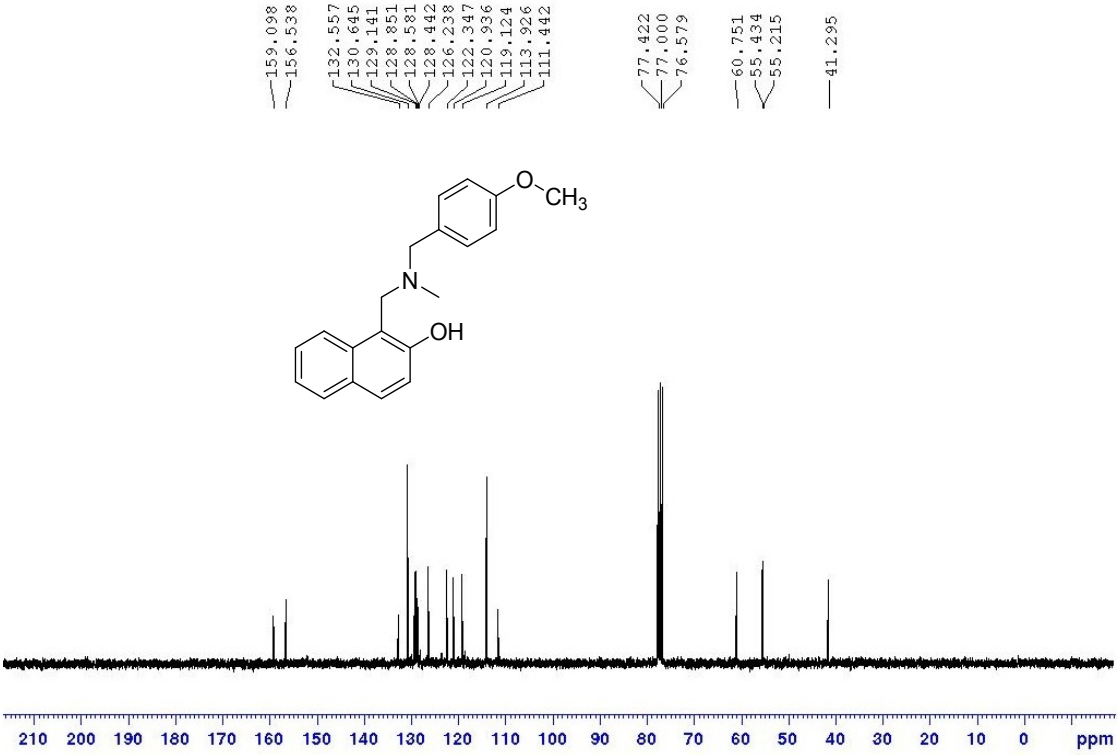
Spectrum35: ^{1}H **NMR of 5b**



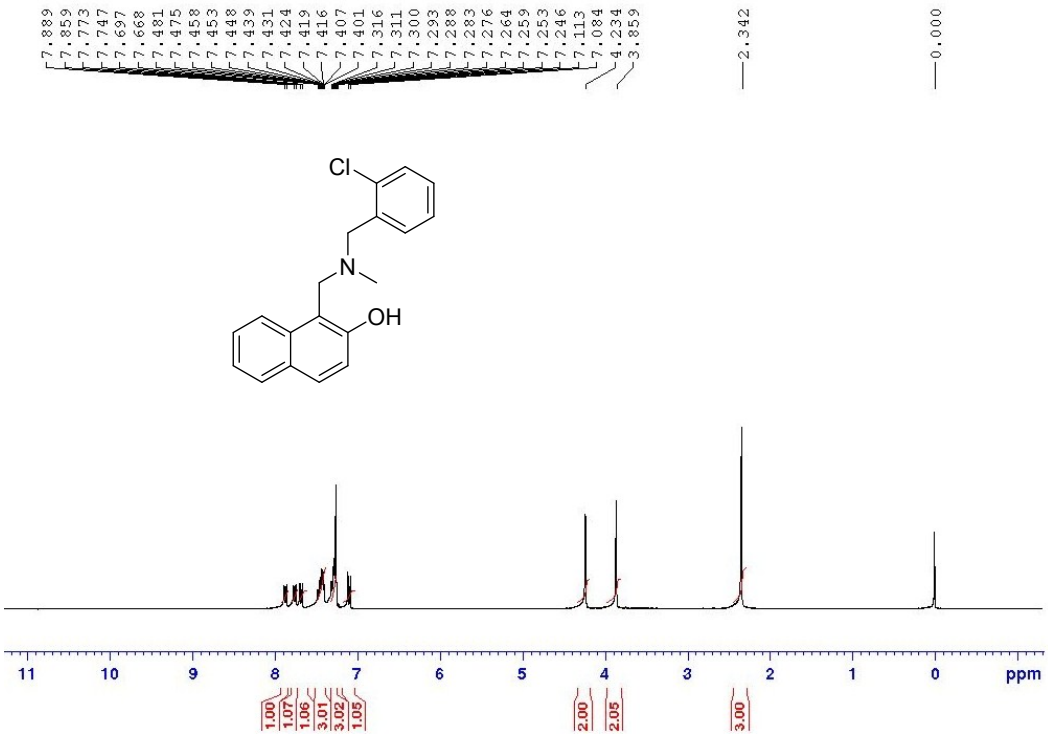
Spectrum36: ^{13}**C{**^{1}H**} NMR of 5b**



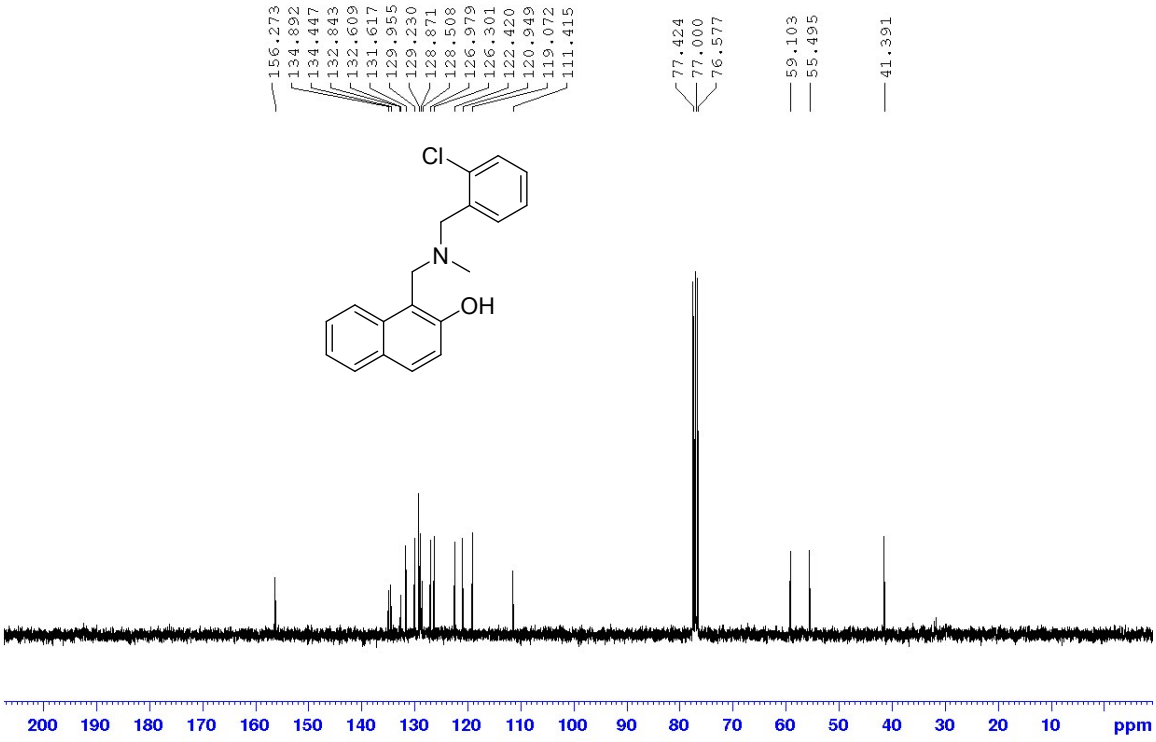
Spectrum37: ^{1}H **NMR of 5c**



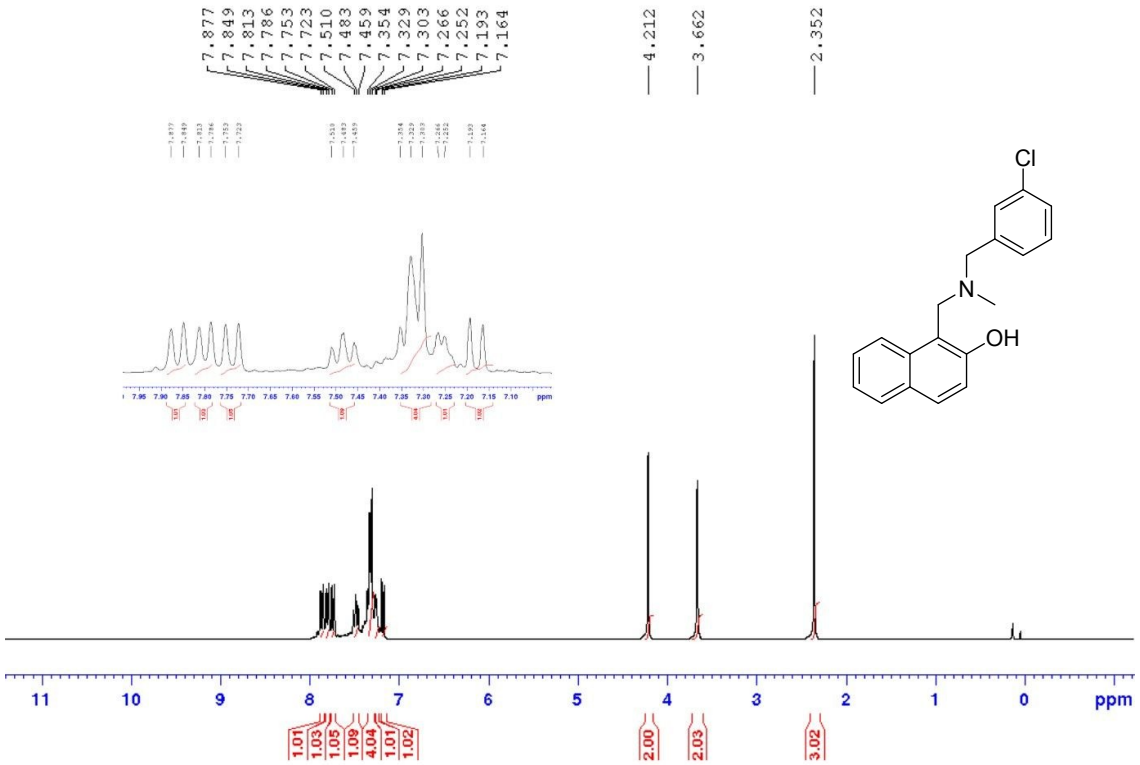
Spectrum38: ^{13}C{^{1}H} **NMR of 5c**



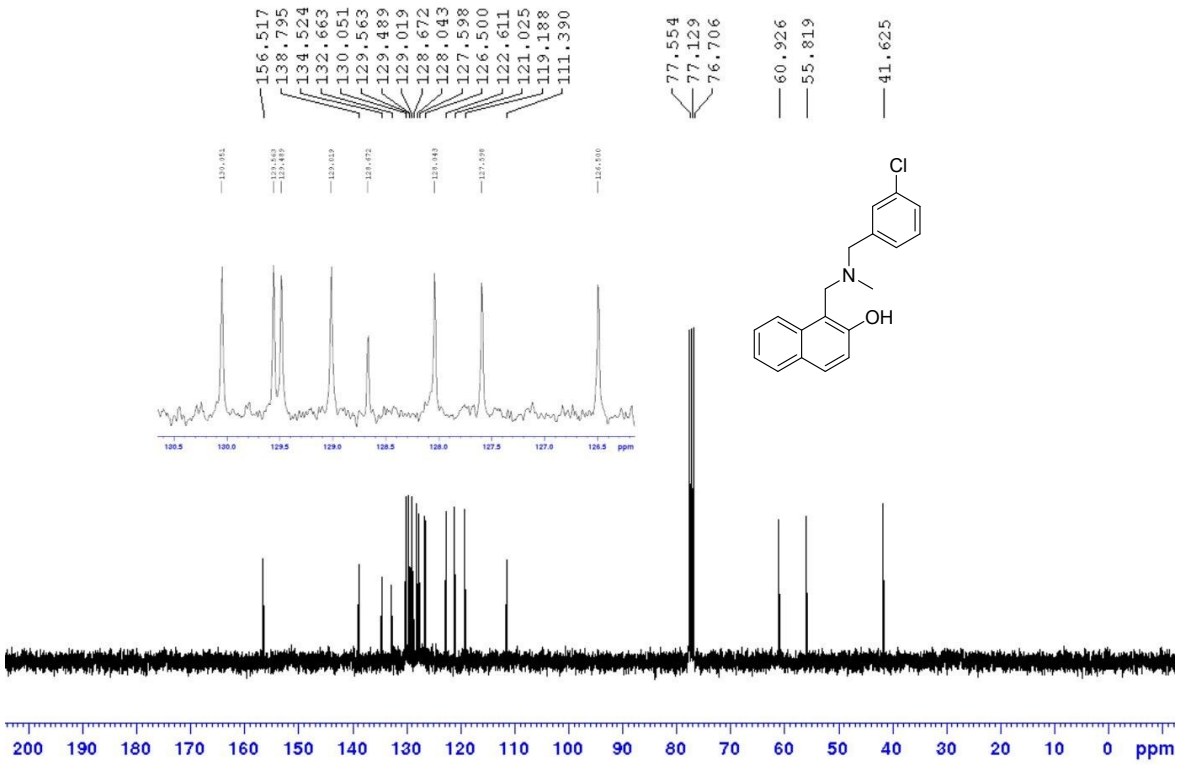
Spectrum39: ^{1}H **NMR of 5d**



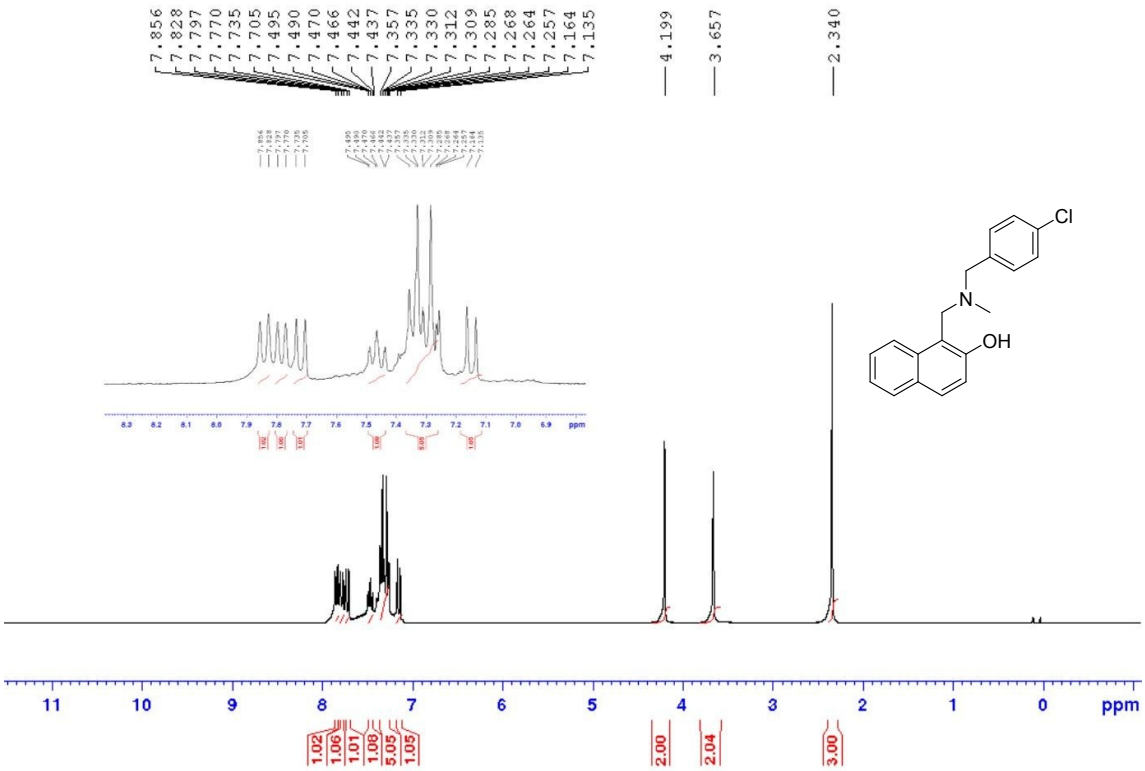
Spectrum40: ^{13}C{^{1}H} **NMR of 5d**



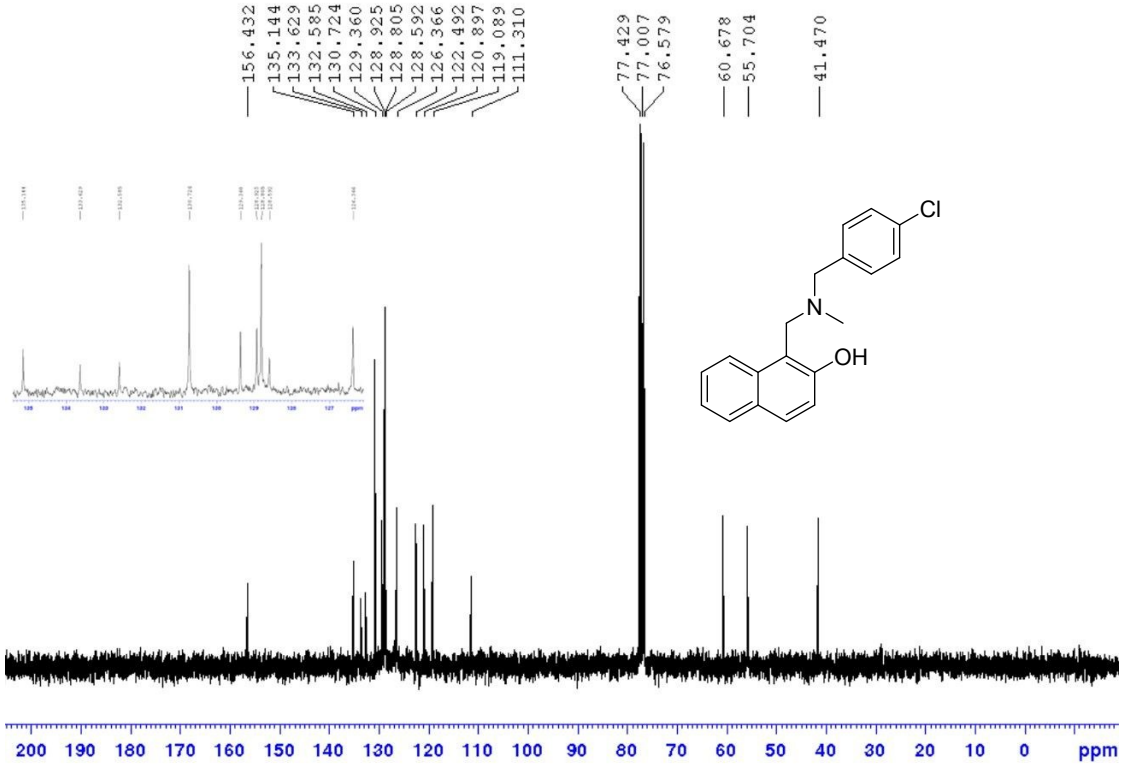
Spectrum41: ^{1}H **NMR of 5e**



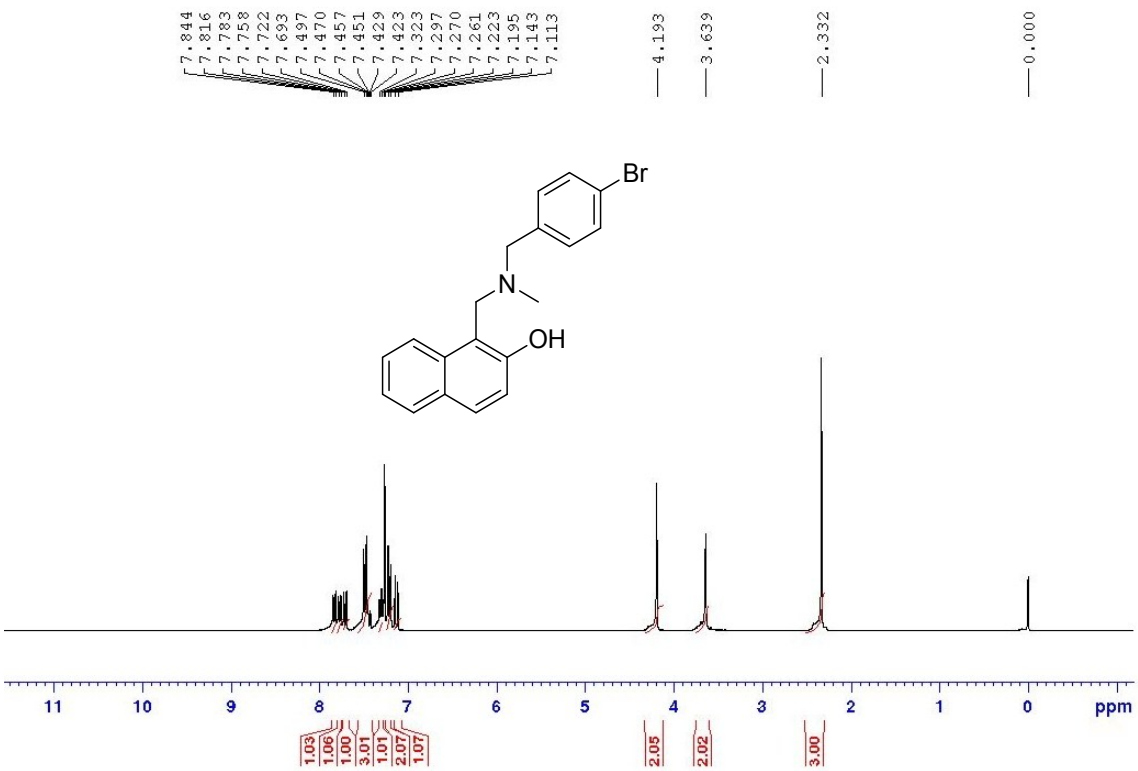
Spectrum42: ^{13}C{^{1}H} **NMR of 5e**



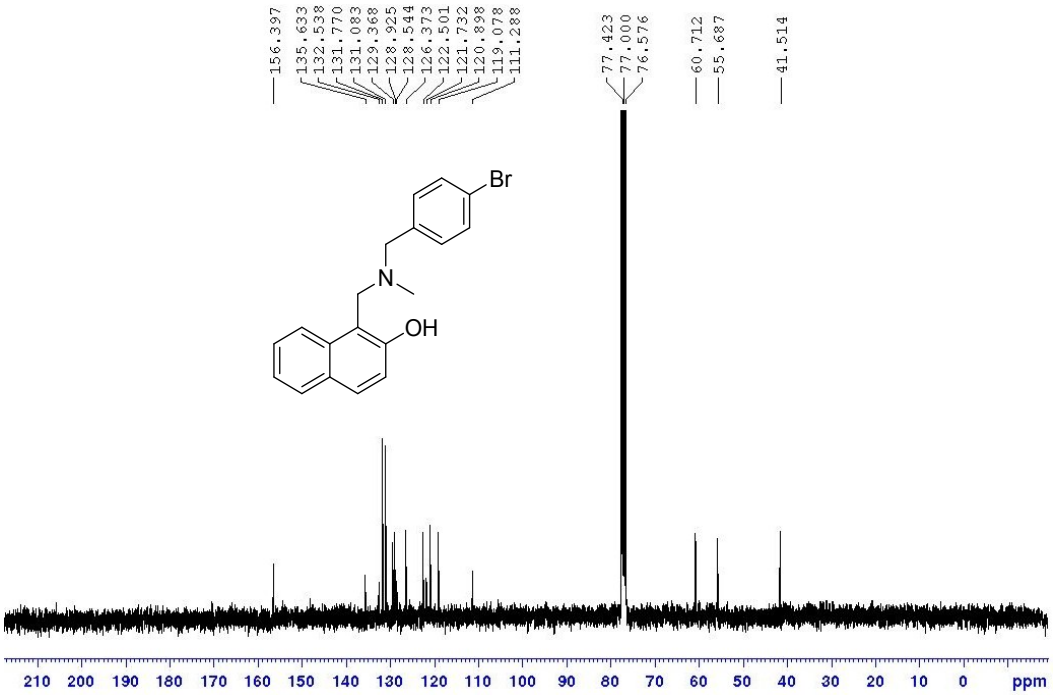
Spectrum43: ^{1}H **NMR of 5f**



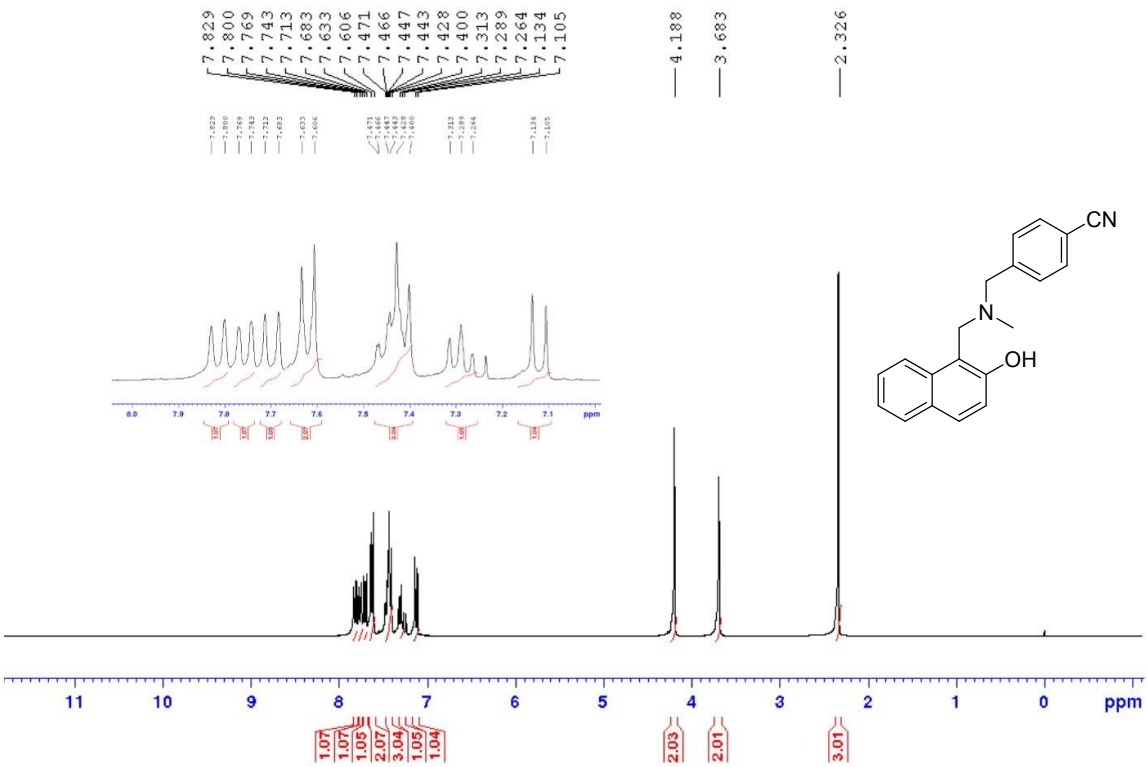
Spectrum44: ^{13}C{^{1}H} **NMR of 5f**



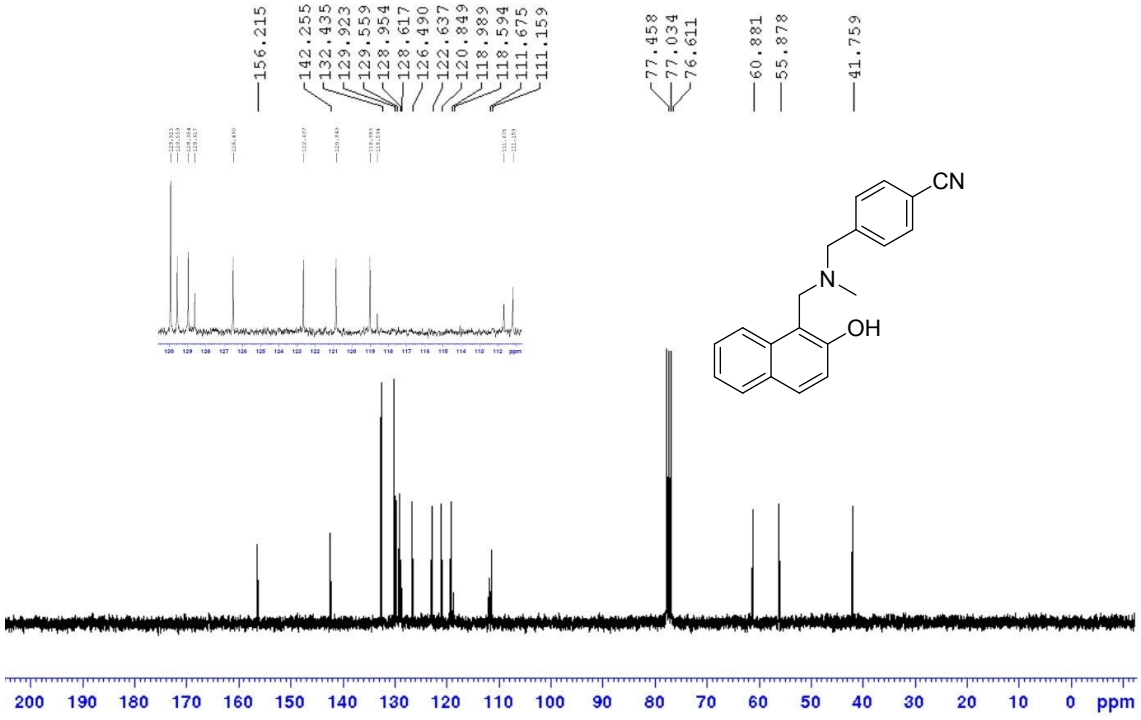
Spectrum45: ^{1}H **NMR of 5g**



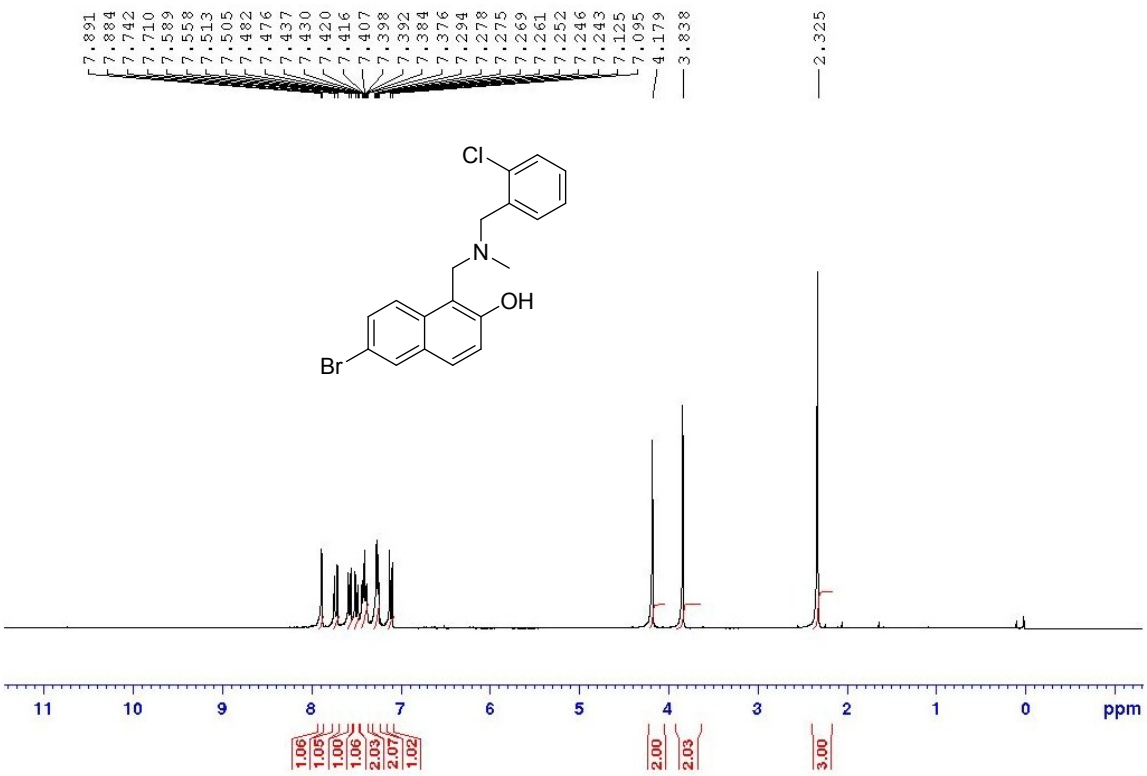
Spectrum46: ^{13}C{^{1}H} **NMR of 5g**



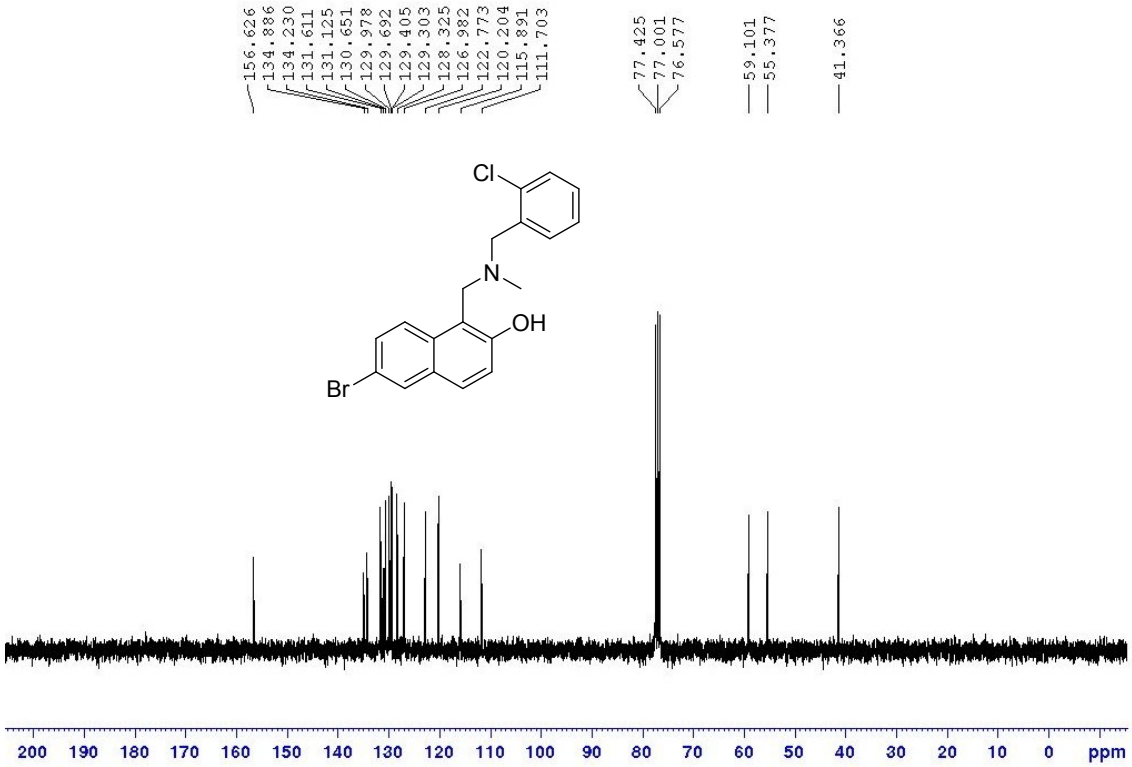
Spectrum47: ^{1}H **NMR of 5h**



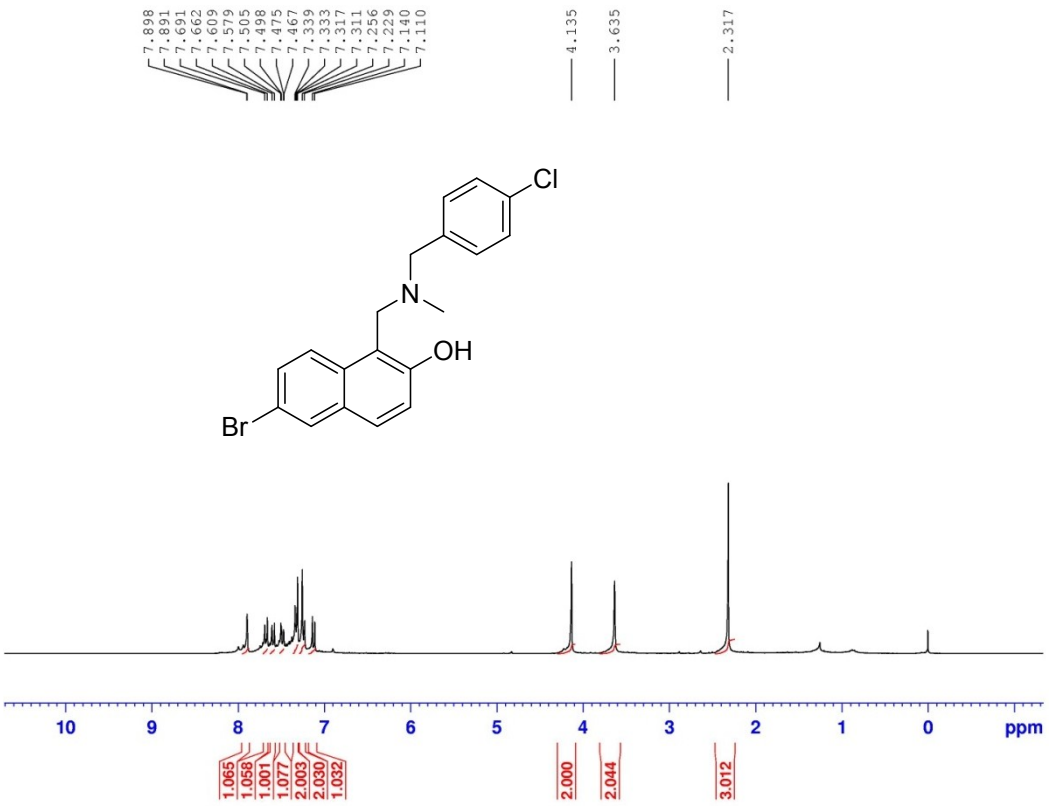
Spectrum48: ^{13}C{^{1}H} **NMR of 5h**



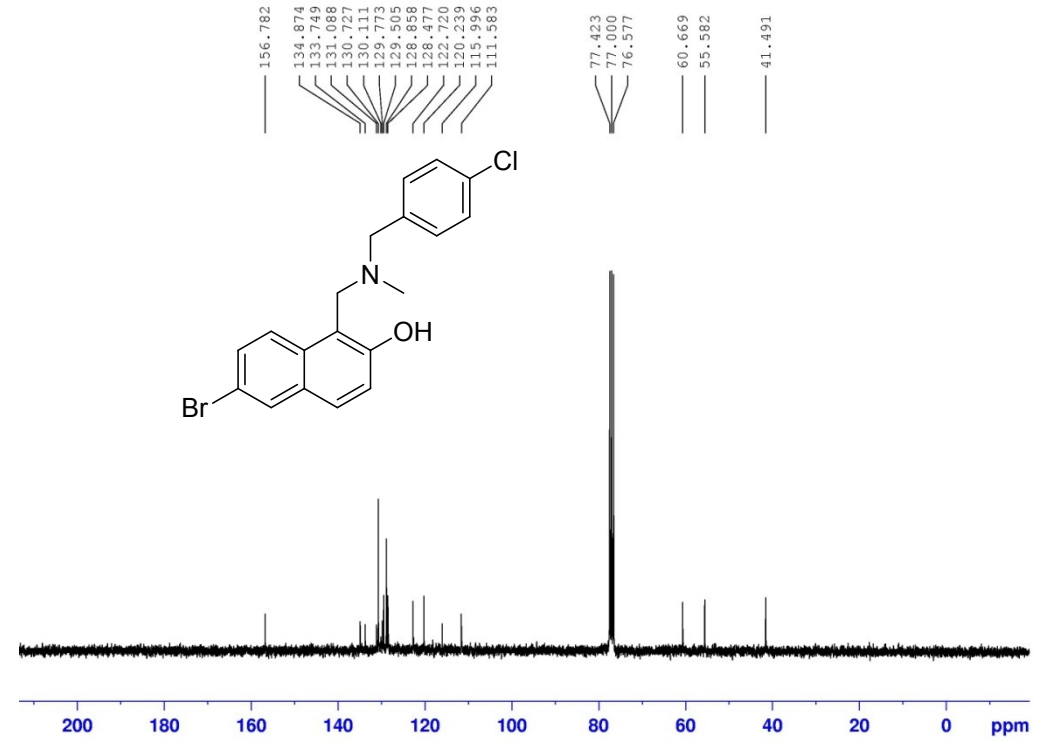
Spectrum49: ^{1}H **NMR of 5i**



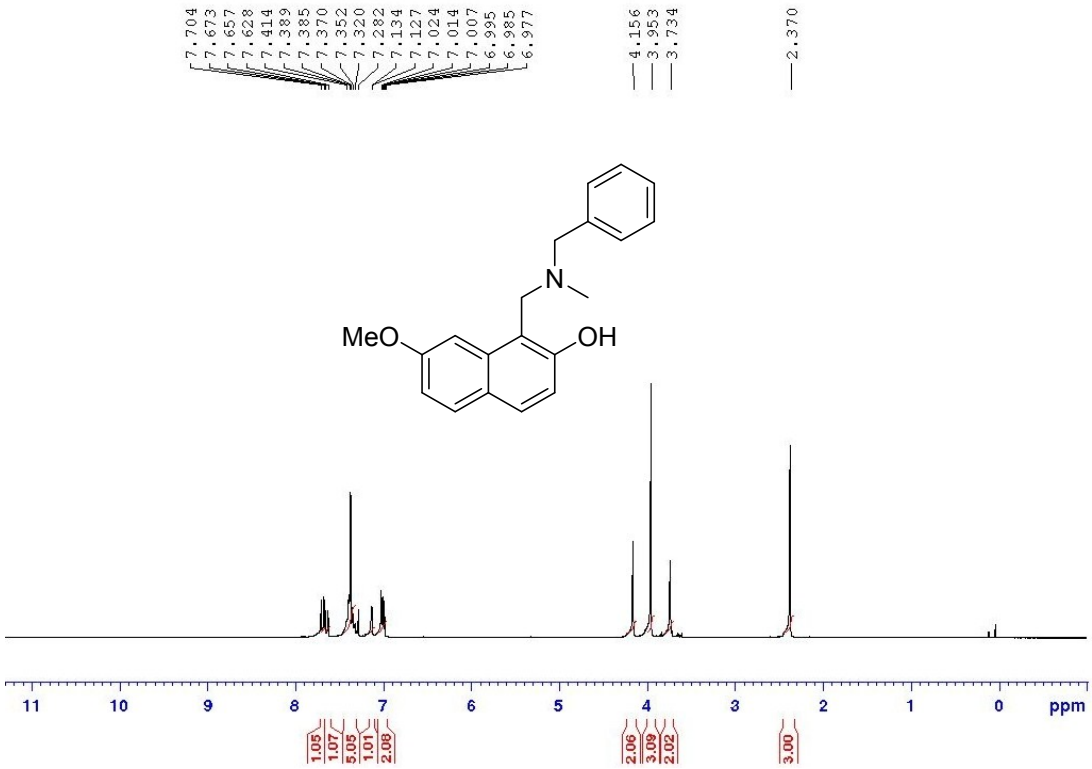
Spectrum50: ^{13}**C{**^{1}**H} NMR of 5i**



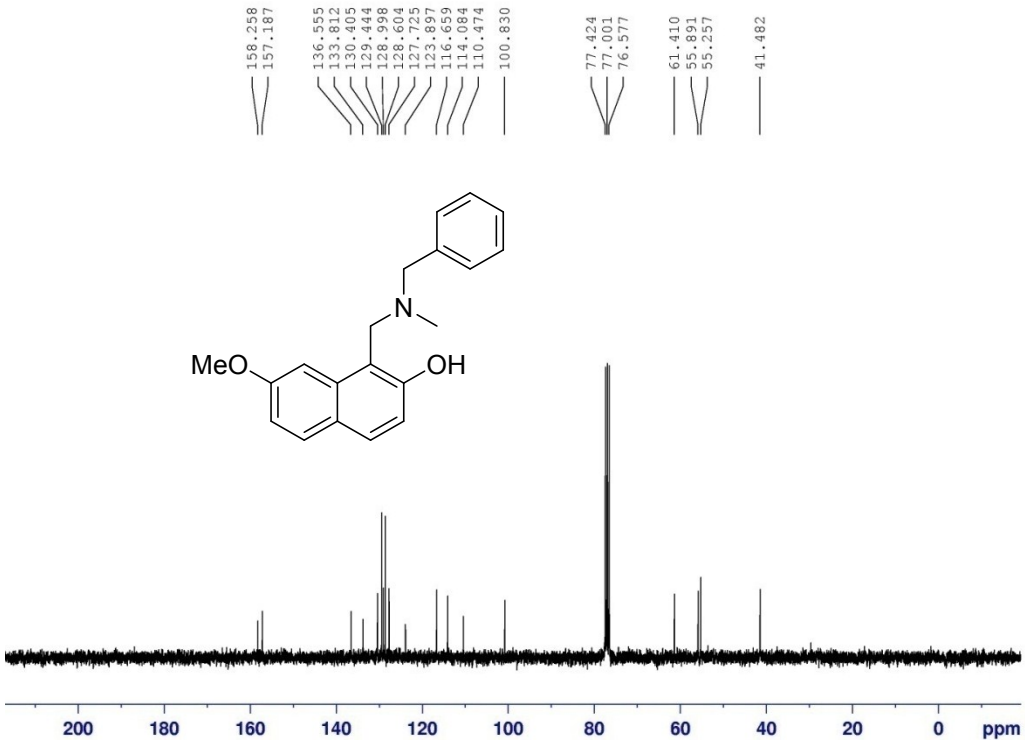
Spectrum51: ^{1}H **NMR of 5j**



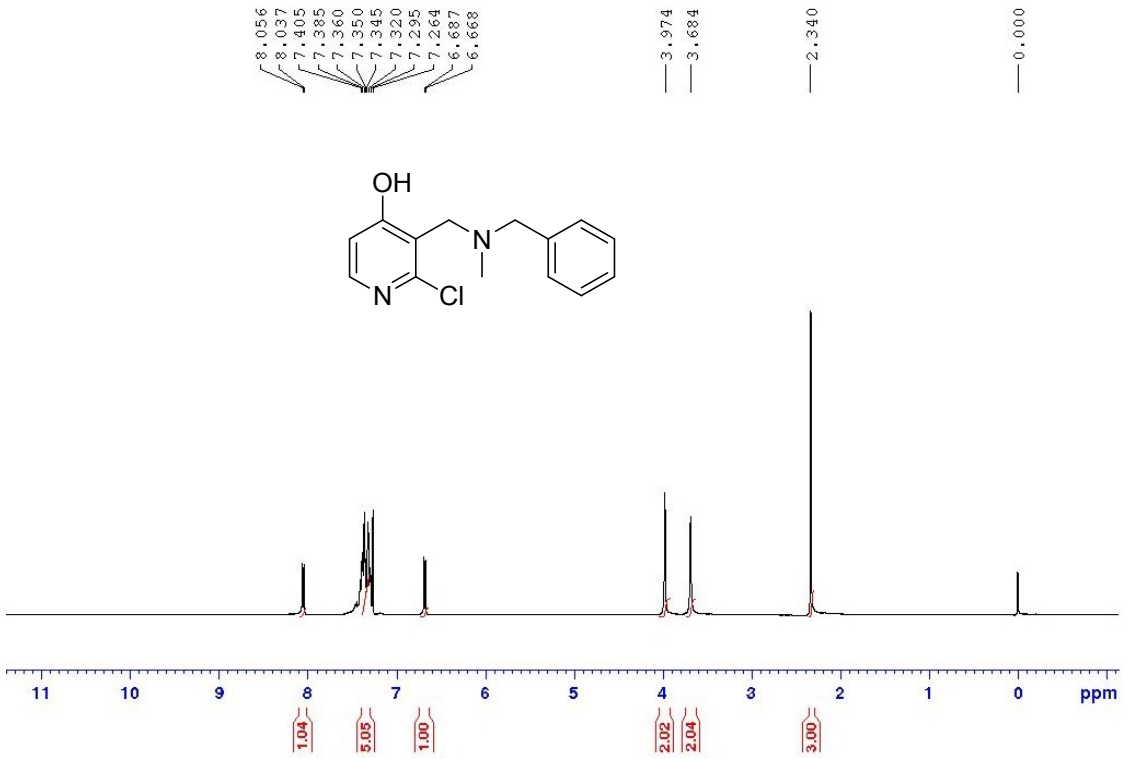
Spectrum52: ^{13}C{^{1}H} **NMR of 5j**



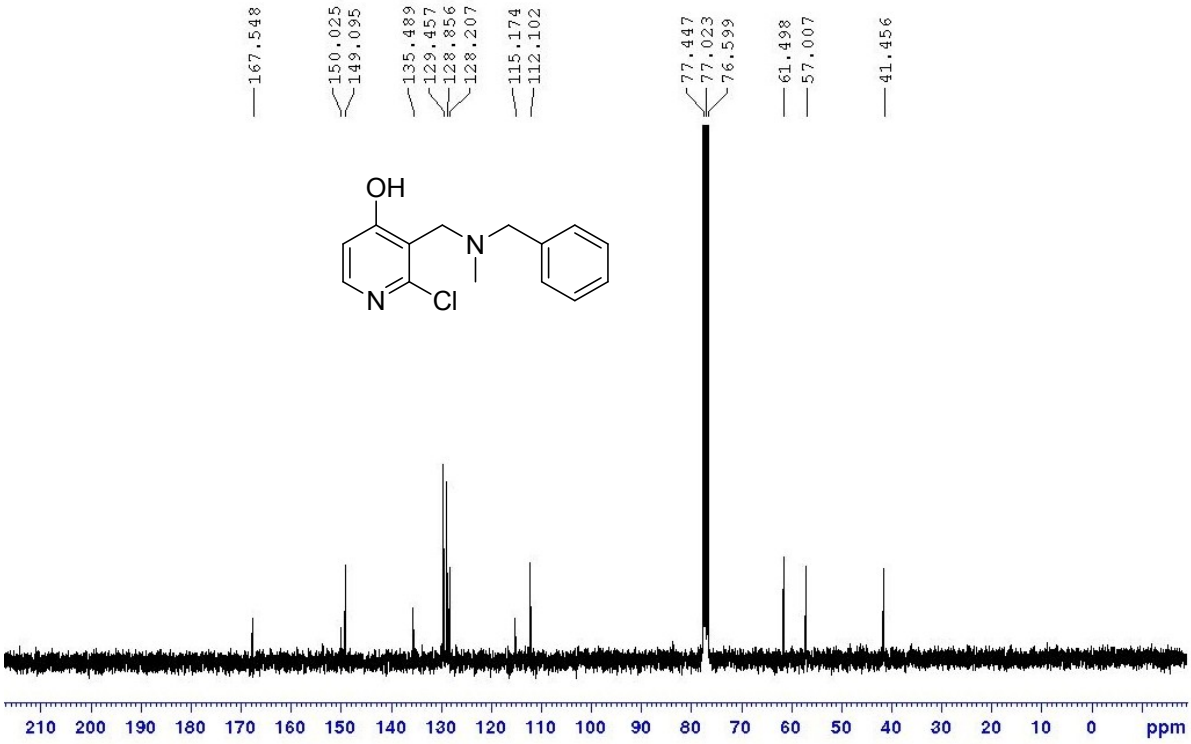
Spectrum53: ^{1}H **NMR of 5k**



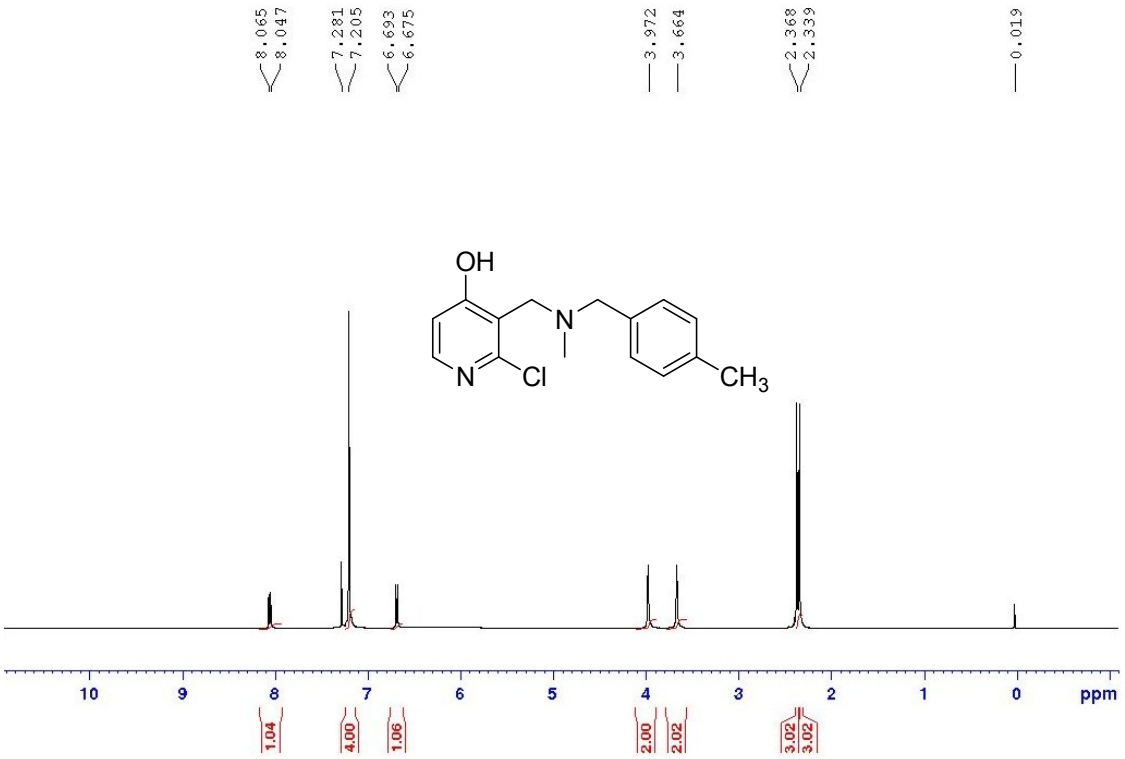
Spectrum54: ^{13}C{^{1}H} **NMR of 5k**



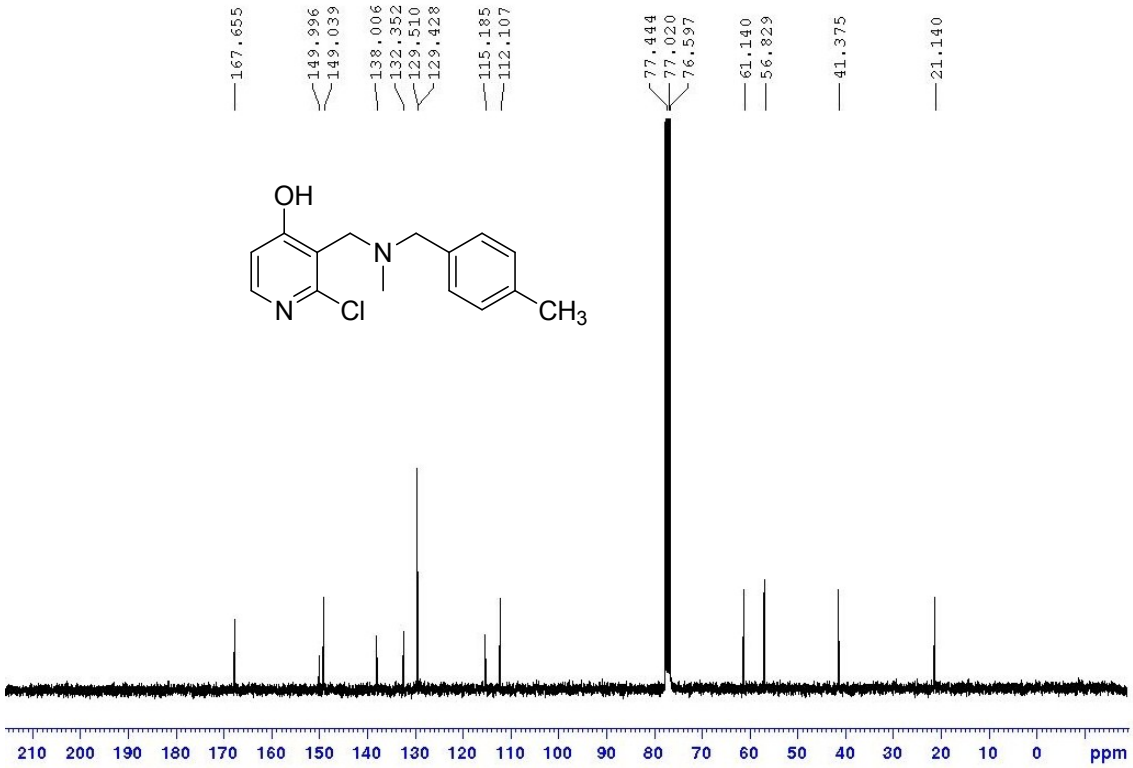
Spectrum55: ^{1}H **NMR of 7a**



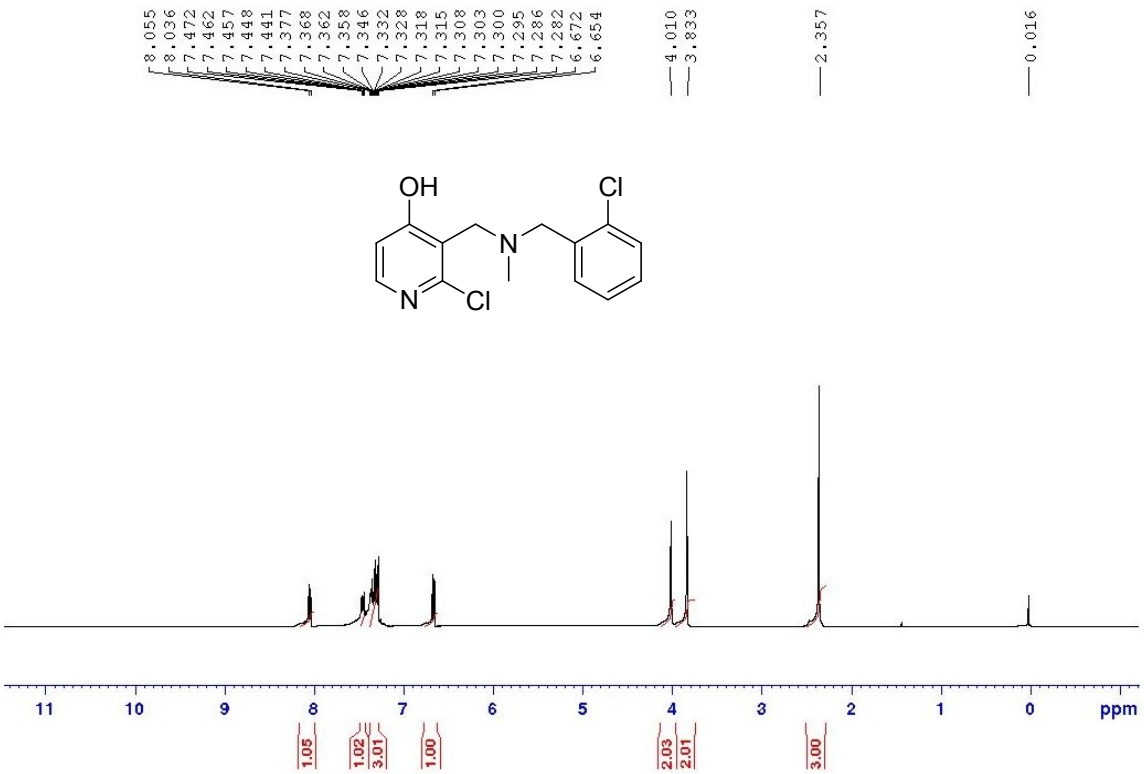
Spectrum56: ^{13}C{^{1}H} **NMR of 7a**



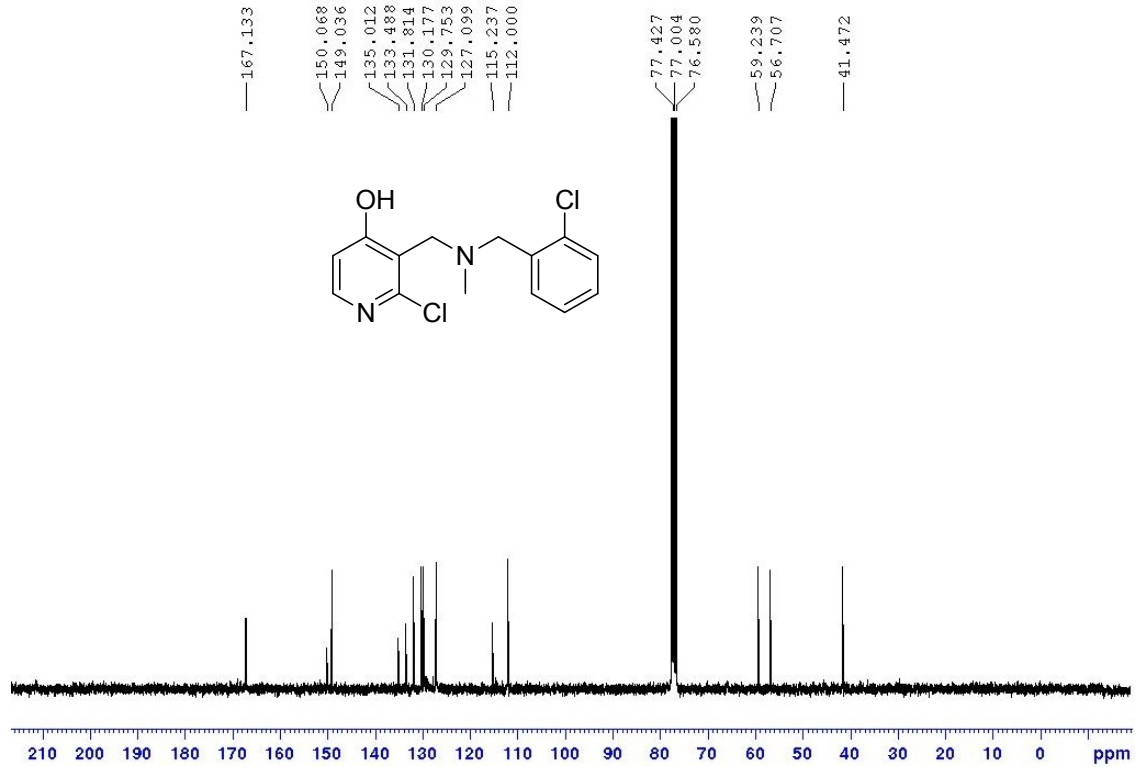
Spectrum57: ^{1}H **NMR of 7b**



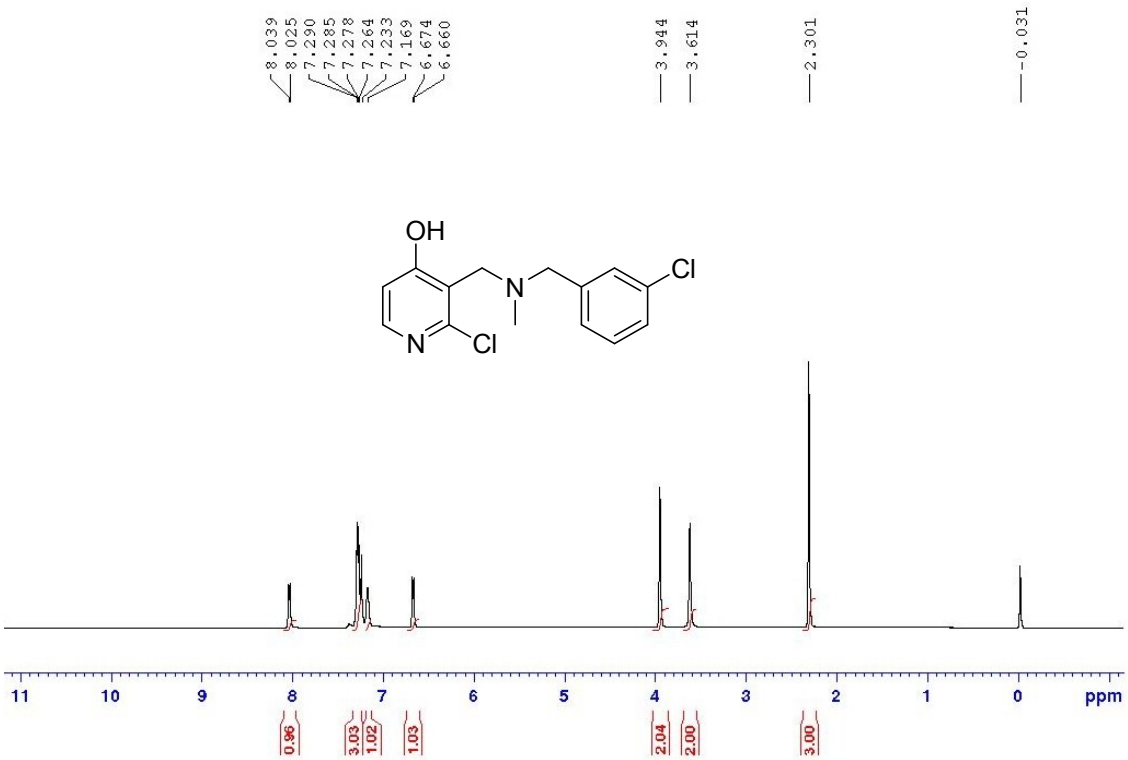
Spectrum58: ^{13}C{^{1}H} **NMR of 7b**



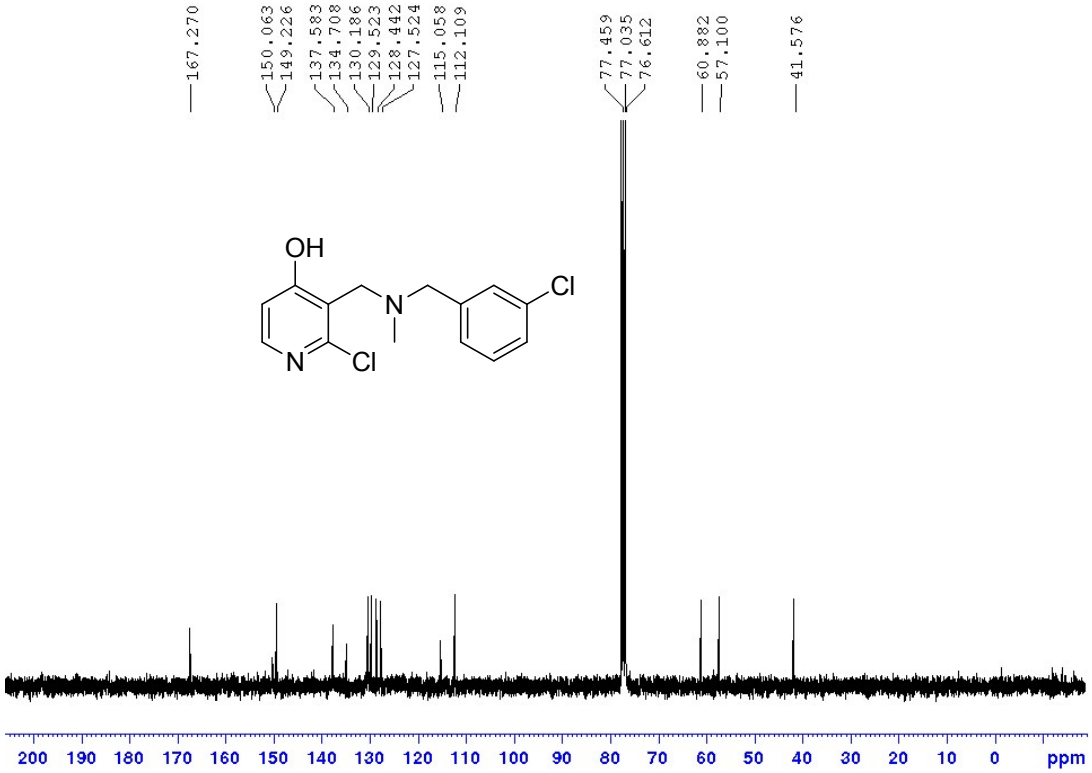
Spectrum59: ^{1}H **NMR of 7c**



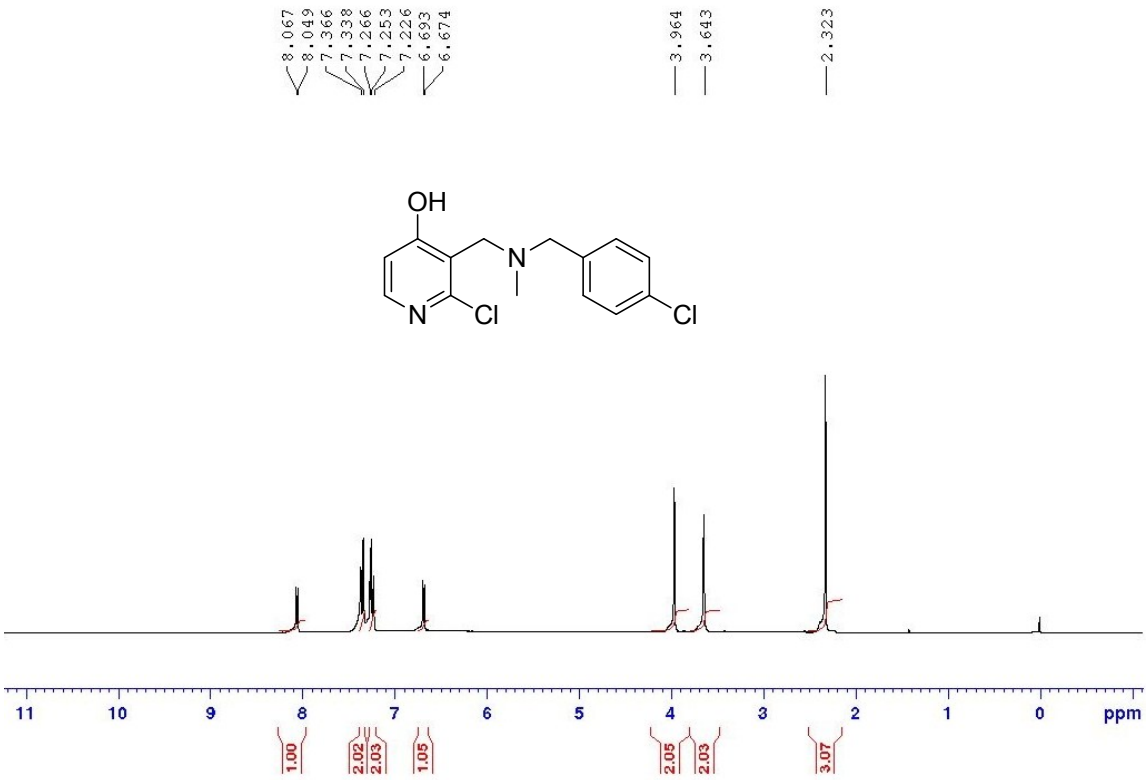
Spectrum60: ^{13}**C{**^{1}**H} NMR of 7c**



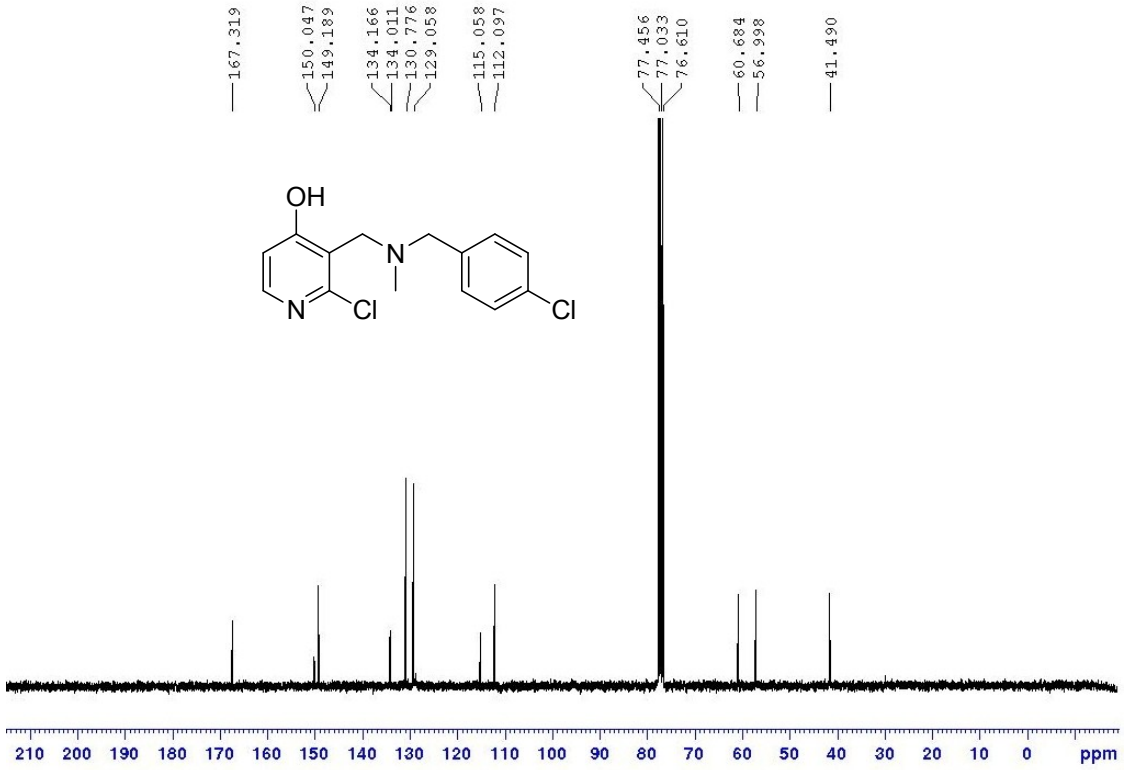
Spectrum61: ^{1}H **NMR of 7d**



Spectrum62: ^{13}C{^{1}H} **NMR of 7d**



Spectrum63: ^{1}H **NMR of 7e**



Spectrum64: ^{13}**C{**^{1}H**} NMR of 7e**

Procedure for free radical reaction: Inhibition by TEMPO

To the mixture of *N*,*N*-dimethylbenzylamine (**1a**, 0.1352 g, 1.0 mmol, 2 equiv.), phenol/naphthol (**2a**/**4a**, 0.5 mmol, 1 equiv.), *tert*-butyl hydroperoxide (0.2 mL, 1.2 mmol decane solution) and GO-Cu_7S_4 NP catalyst (4 mg, 1 mol%), TEMPO (1, 2, 3, 4 equiv.) was added under nitrogen at room temperature. The reaction temperature was raised to 50 °C and the contents were stirred at the same temperature for 2 h. The reaction mixture was cooled to room temperature. The resulting suspension was diluted with ethylacetate and the organic layer was washed with brine solution (3 × 10 mL) and dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 95:5). The corresponding product **3a** or **5a** was obtained in lower yield; and the yields were found to decrease in a dose dependent manner as shown below.

Concentration of TEMPO	Yield of **3a**	Yield of **5a**
1 equiv.	32%	25%
2 equiv.	12%	9%
3 equiv.	6%	4%
4 equiv.	0%	0%

Procedure for HRMS of reaction mixture: formation of Iminium ion

To the mixture of *N*,*N*-dimethylbenzylamine (**1a**, 1.0 mmol), phenol (**2a**, 0.5 mmol) and *tert*-butyl hydroperoxide (0.1 mL, 0.6 mmol decane solution), GO-Cu_7S_4 NPs catalyst (4 mg, 1 mol %) was added under nitrogen at room temperature. The reaction temperature was raised to 50 °C and the contents were stirred for 1 h. The reaction mixture was then cooled to room temperature. The resulting suspension was diluted with acetonitrile, filtered and injected for mass studies.

Procedure for Time dependent NMR Study

Five parallel reactions between *N,N*-dimethylbenzylamine and phenol were set up under the standard conditions on a 0.5 mmol scale. The reactions were consecutively stopped at 0, 20, 40, 60 and 120 minutes. 30μL of the sample was withdrawn from each reaction flask, and subjected

to ^{1}HNMR analysis after diluting it with $CDCl_3$ (0.5 mL). The NMR data was collected, and stacked together on same graph for analysis.

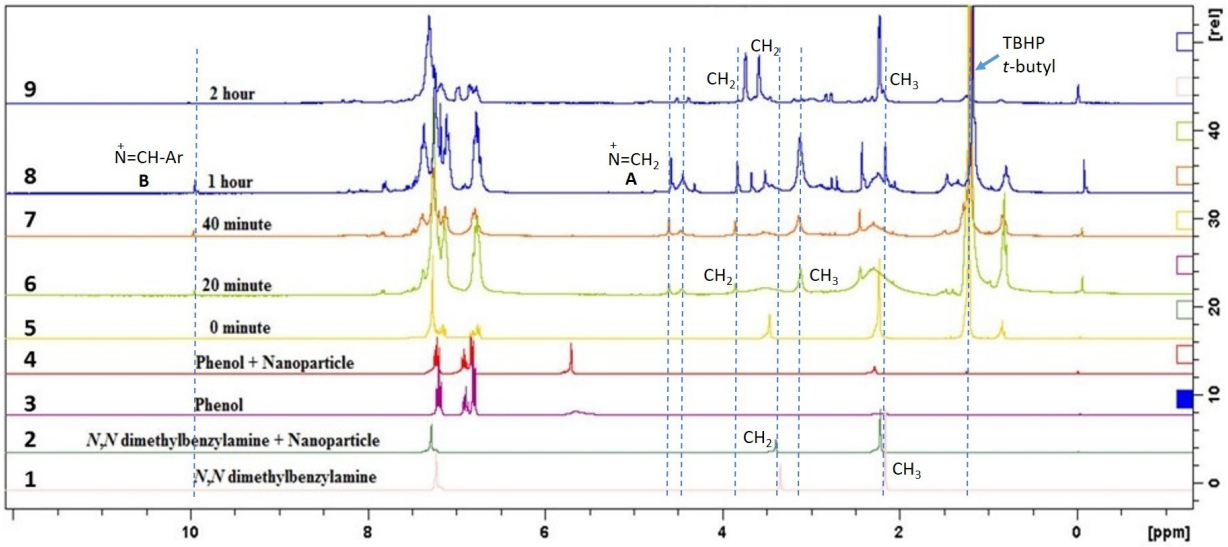


Fig. S11 Time dependent ^{1}HNMR spectra of reaction mixture

The downfield shifting of methyl and methylene protons of **1a**, and appearance of new peaks at around 4.5 and 10 ppm between 20-60 minutes indicated formation of iminium ion intermediates (**A** and **B**).

Proposed Mechanism

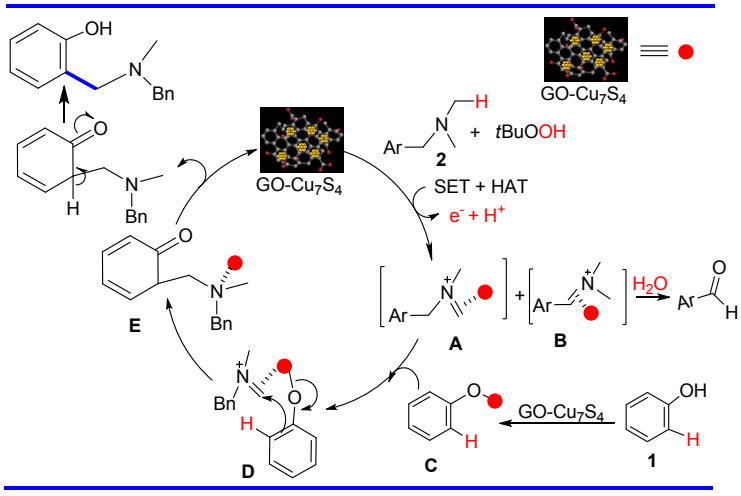


Fig. S12 Proposed Mechanism

A tert-butoxyl radical is believed to be generated by copper catalyzed decomposition of TBHP, which assists a single electron transfer (SET) from amine to generate a radical cation. This is followed by abstraction of sp^3 hydrogen of the radical cation to generate an iminium ion intermediate **A** or **B**. Iminium ion **B** upon hydrolysis results in the formation of benzaldehyde, which is seen in trace amounts. Coordination of phenol with GO–Cu_7S_4 provides the copper phenolate intermediate **C**. **C** upon coordination with **A** results in the formation of complex **D**. Nucleophilic attack by *ortho*-phenol carbon on the iminium ion generates the Cu-coordinated ketone **E**. The final C–C coupled aminomethylated product is formed after tautomerization, and concurrent regeneration of the GO–Cu_7S_4 catalyst for the next catalytic cycle.

General procedure for the synthesis of 3a on 20 g scale:

To the mixture of phenol (**1a**) (0.212 mol, 20g), *N*,*N*-dimethylbenzylamine (**2a**) (0.425 mol, 57.5g), and GO-Cu_7S_4 NP catalyst (1.7g, 1 mol%), *tert*-butyl hydroperoxide (85 mL, 5-6 M decane solution) was added under nitrogen at room temperature dropwise in 1 h. The reaction temperature was raised to 50 °C and the contents were stirred at the same temperature for 4 h. The reaction was monitored by TLC after 2 h, the conversion was 60%. The conversion completed in 6 h, after which the reaction mixture was cooled to room temperature. The resulting suspension was diluted with ethylacetate and the organic layer was washed off with brine solution and dried over anhydrous Na_2SO_4. Solvent was evaporated and the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 95:5) Colourless liquid Yield; 75% (36.2g,)