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Functionalized Imidazolium Salt: An Efficient Catalyst for Buchwald-Hartwig type C–N Cross-Coupling of (Hetero)aryl Chlorides/Bromides with Amines Under Solvent-, Inert gas-, and Base-free Ambience

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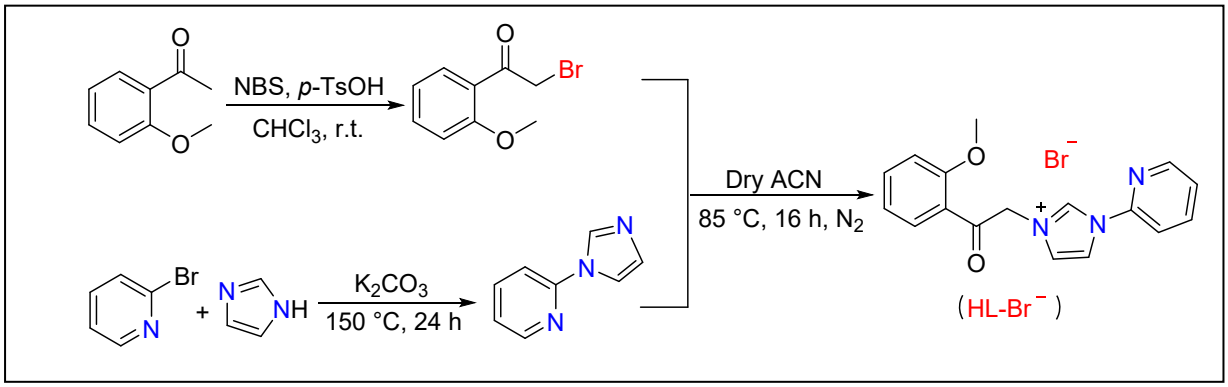
1. General experimental conditions:

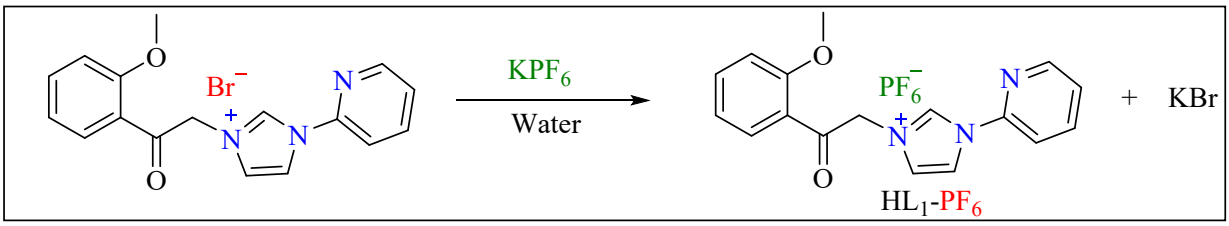
Each component of laboratory glassware's were oven dried and then used for carrying out the general experimental procedures. ^{1}H-NMR and ^{13}C - NMR spectra were measured on FT-NMR Bruker 400 MHz machine. Whereas some spectra were also analyzed on a JEOL ECS-400 spectrometer which was functioning at 400 MHz for ^{1}H proton NMR and 100 MHz for 13C{^{1}H} NMR and utilization of $CDCl_3$ and DMSO-d_6 was done as solvent for preparing the samples. Both Tetramethylsilane (TMS) (0.00 ppm) and $CDCl_3$ were applied as the internal standards while recording the ^{1}H proton NMR (δ 7.246 ppm) and ^{13}C (δ 77.0 ppm)]proton NMR. Pattern of the chemical shifts in proton NMR were described in parts per million(ppm). While peak splitting patterns were defined as singlet (s), broad singlet (brs), doublet (d), double doublet (dd), triplet (t), and multiplet (m). All Coupling constant (J) values were stated in Hertz (Hz). High-Resolution Electron Impact Mass Spectra (HR-EIMS) were analyzed on Xevo G2-SQ-Tof (Waters, USA) which are compatible with ACQUITY UPLC® and nano ACQUITY UPLC® systems. Column chromatography was done using a normal (particle size: 100-200 Mesh) and flash (particle size: 230-400 Mesh) silica gel, which were obtained from QualigensTM (India), Spectrochem (India), and Rankem (India). TLC plates coated with silica gel (Kiesel 60-F254, Merck (India)) were used to track the progress of chemical reactions. The visualizing agents which were utilized for TLC were UV light. For drying and concentrating all the solvents, BUCHI's Rotavapor R-210 was used. All the supplied solvents were of analytical grade such as MeOH, EtOH and they were used without any prior purification. The chemicals and reagents used for the chemical reactions were purchased from Sigma Aldrich chemicals company (USA), TCI (India) Pvt. Ltd., Merck (India), and/or Spectrochem (India) etc. were used without any purification prior to use.

2. Synthesis of Imidazolium salts ($\mathbf{HL_1}$**-Br** and $\mathbf{HL_1PF_6}$**):** The novel imidazolium salt (**$\mathbf{HL_1}$-Br**) was formed using the methodology depicted in Scheme 2. Previously reported methods were used to prepare 2-(1H-imidazol-1-yl)pyridine and 2-bromo-1-(2-methoxyphenyl)ethan-1-one.[9] **$\mathbf{HL_1}$-Br** was synthesized using the known reaction of 2-(1H-imidazol-1-yl)pyridine (280 mg, 1.05 mmol) and 2-bromo-1-(2-methoxyphenyl)ethan-1-one (420mg, 1.0 mmol) in ACN under N_2 atmosphere at 85 °C for 16 h.[10] The result was a colourless solid precipitate. After cooling to room temperature, the reaction mixture was filtered using filter paper.With 2 0 mL of dry acetonitrile, the leftover solid was washed. To get the ligand in an analytically pu re form, the colourless product was dried and then stored in a calcium chloride vacuum desiccator. The bromide anions of the ligand were exchanged to hexafluorophosphate in

water using potassium hexafluorophosphate (1.16 g, 6.3 mmol) in excess. The solid residue that was formed was filtered and rinsed with excess water. To acquire the li gand in an analytically pure form, the colourless compound was first air dried and then stored in a calcium chloride vacuum desiccator for 12 hours. ^{1}H NMR, ^{13}C NMR, and HRMS-mass data were recorded to characterise the ligand.



Scheme1. Synthesis of 3-(2-(2-methoxyphenyl)-2-oxoethyl)-1-(pyridin-2-yl)-1H-imidazo-3-ium bromide (**HL$_1$-Br**)



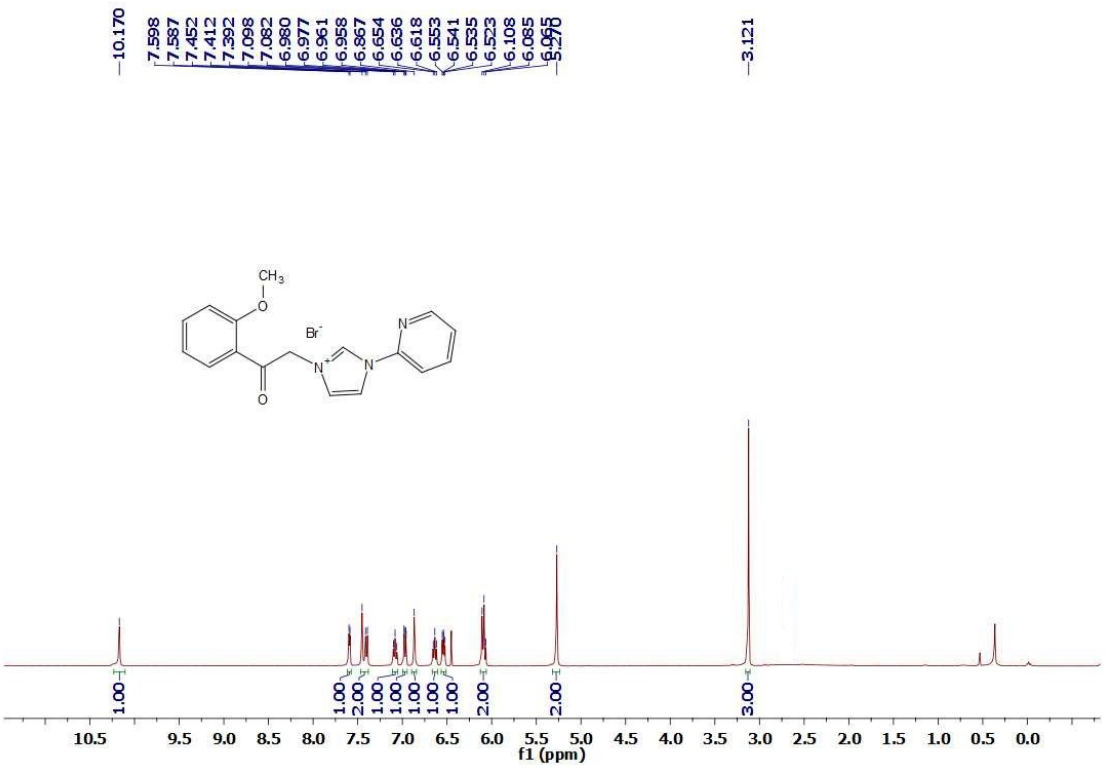
Scheme2. Exchange of bromide ion to hexafluorophosphate for synthesis of (**HL$_1$-PF$_6$**)

3-(2-(2-methoxyphenyl)-2-oxoethyl)-1-(pyridin-2-yl)-1H-imidazol-3-ium bromide (HL$_1$-Br):

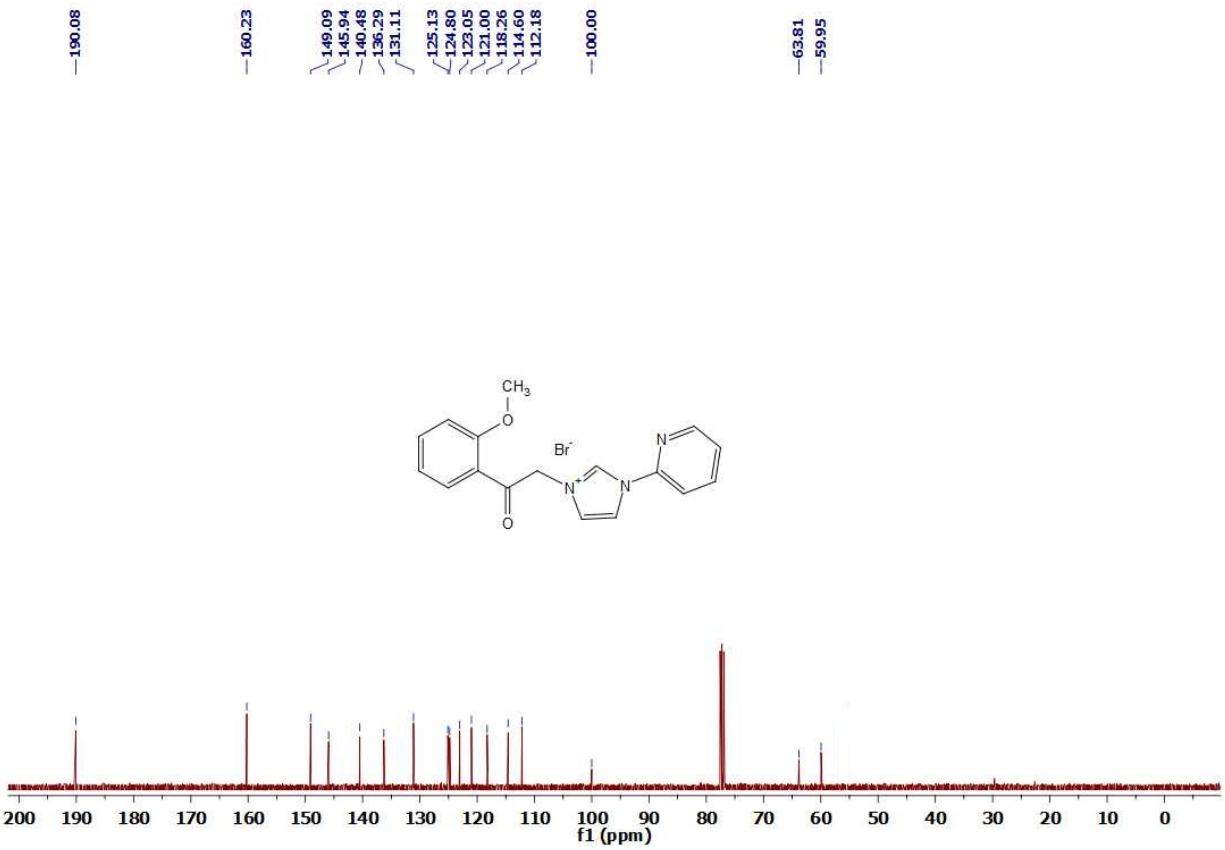
^{1}H NMR (400 MHz): δ = 10.17 (s, 1H), 7.59 (d, *J* = 4.4 Hz, 1H), 7.45 – 7.39. (m, 2H), 7.10-7.06 (m, 1H), 6.97 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.87 (s, 1H), 6.64 (t, 7.2 Hz, 1H), 6.54 (dd, *J* = 7.2, 4.8 Hz, 1H), 6.11-6.06 (m, 2H), 5.27 (s, 2H), 3.12 (s, 3H), ^{13}C{^{1}H} NMR (100 MHz): δ = 190.08, 160.23, 149.09, 145.94, 140.48, 136.29, 131.11, 125.13, 124.80, 123.05, 121.00, 118.26, 114.60, 112.18, 100.00, 63.81, 59.95; HRMS (ESI/QTOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}BrN_3O_2$ 374.0499; found 374.0495.

(**HL$_1$- PF$_6$**): ^{1}H NMR (400 MHz): δ = 9.21 (t, *J* = 1.6 Hz, 1H), 8.53 (ddd, *J* = 4.8, 1.8, 0.8 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.88-7.86 (m, 1H), 7.70 (d, *J*= 8.4 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.54 – 7.49 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.08 – 7.04 (m, 1H), 5.72 (s, 2H), 3.98 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, Acetonitrile-d_3) δ = 190.15, 160.40, 149.57, 140.55, 136.46,

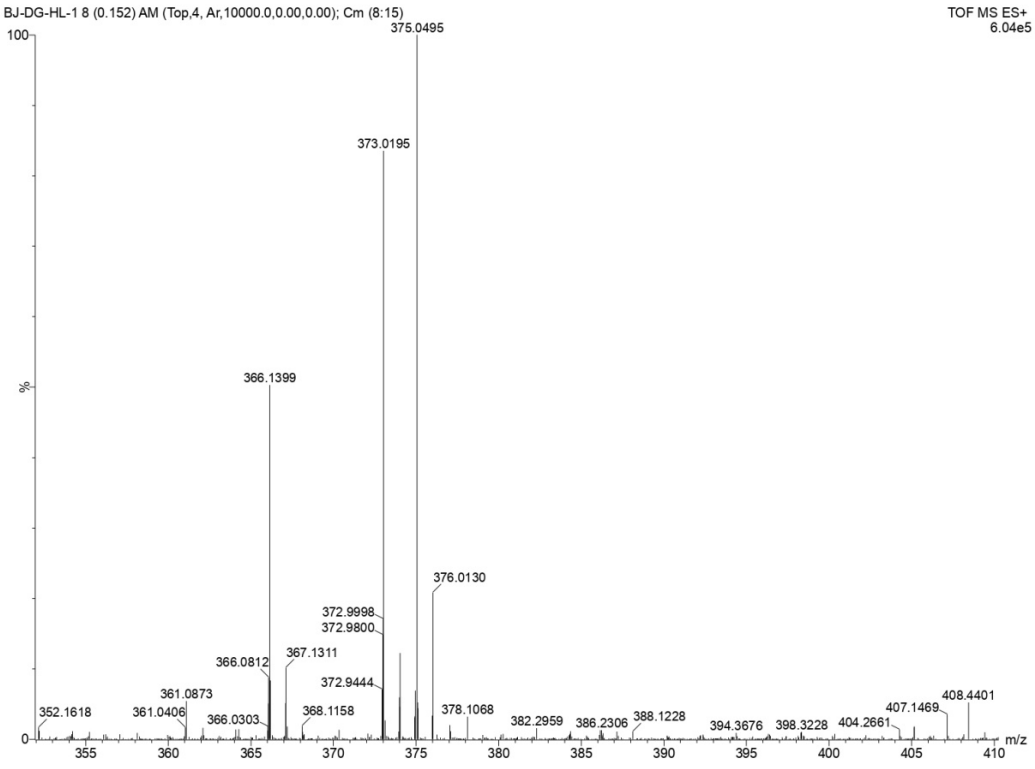
135.24, 130.81, 125.57, 125.20, 123.24, 121.16, 118.97, 114.24, 112.81, 59.78, 55.92. $^{31}P\{^{1}H\}$ NMR (162 MHz, Acetonitrile-d_3) δ = -130.93, -135.29, -139.66, -144.02, -148.39, -152.76, -157.13; HRMS (ESI/QTOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}F_6N_3O_2P$ 440.0957; found 440.0958.



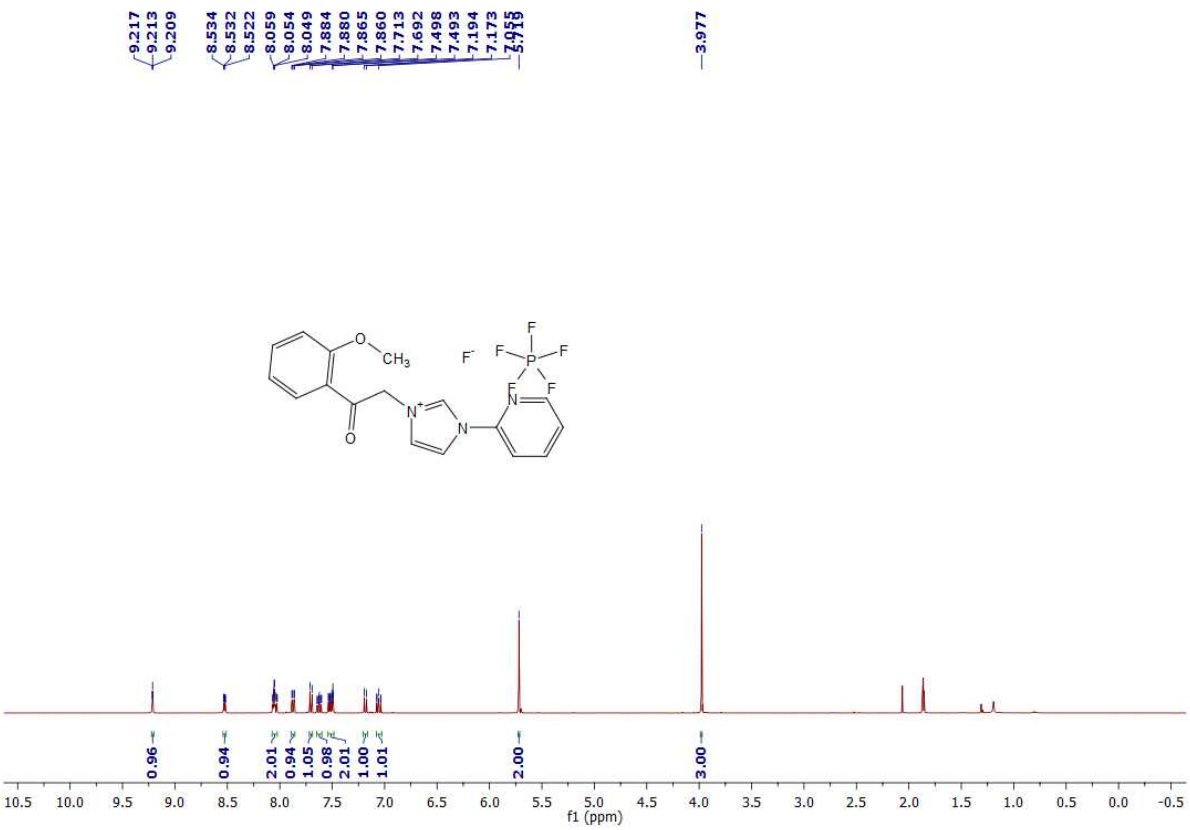
^{1}H NMR of (400 MHz, Chloroform-*d*) spectra of imidazolium salt (HL_1-Br)



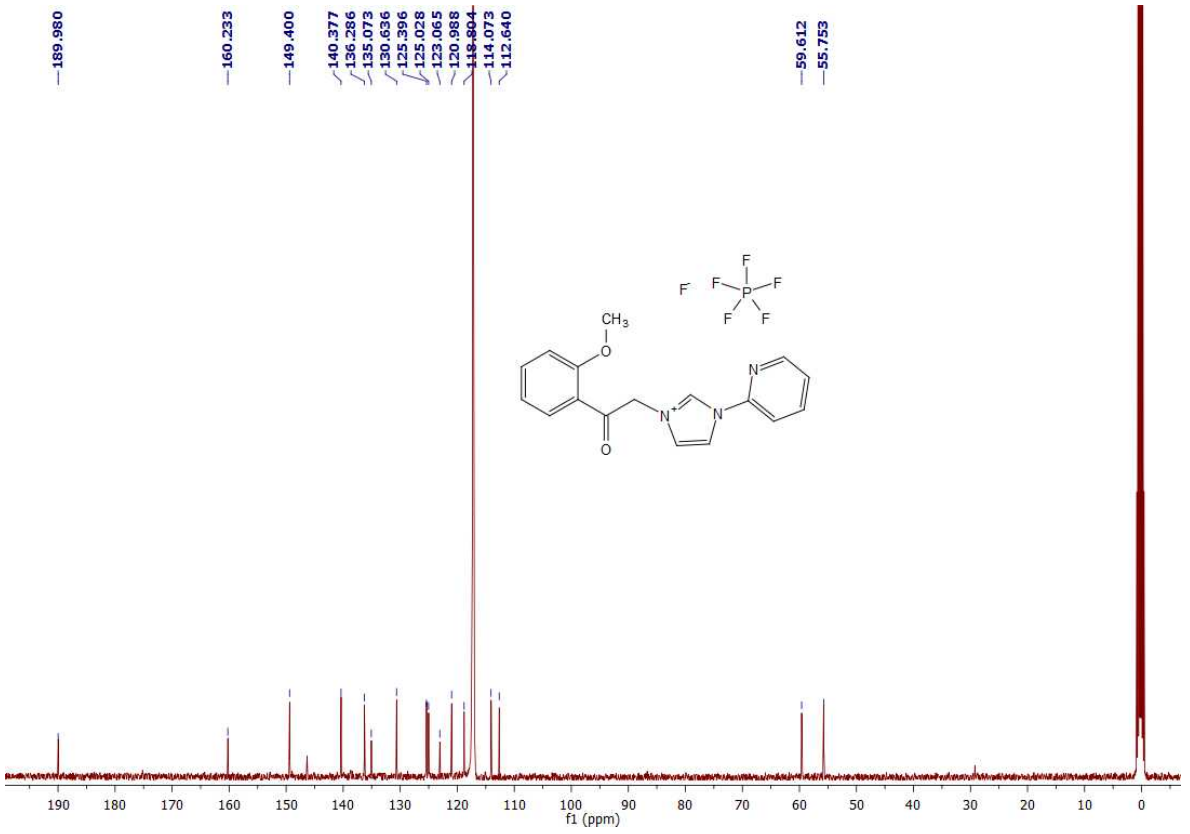
$^{13}C\{^{1}H\}$ NMR of (100 MHz, Chloroform-*d*) spectra of imidazolium salt (**HL_1-Br**)



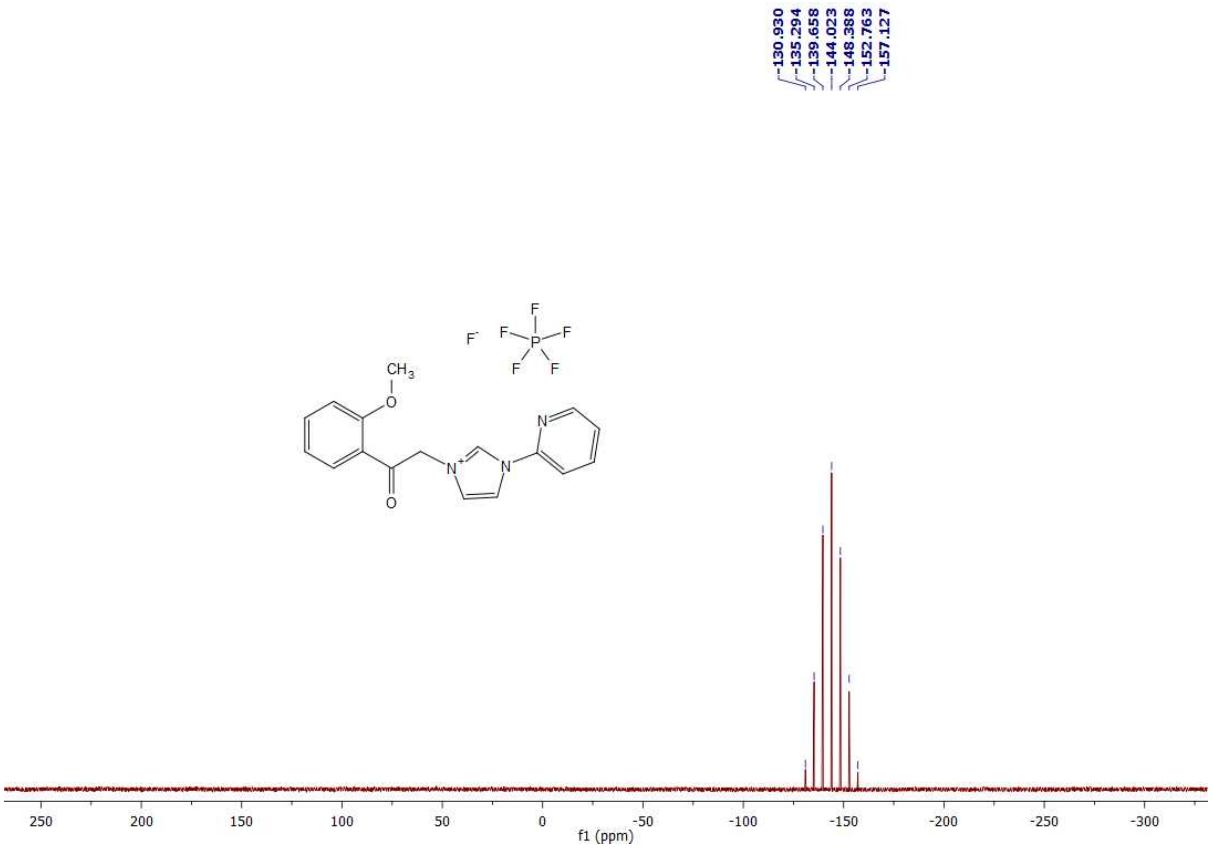
Mass Spectra of imidazolium salt (**HL_1-Br**)

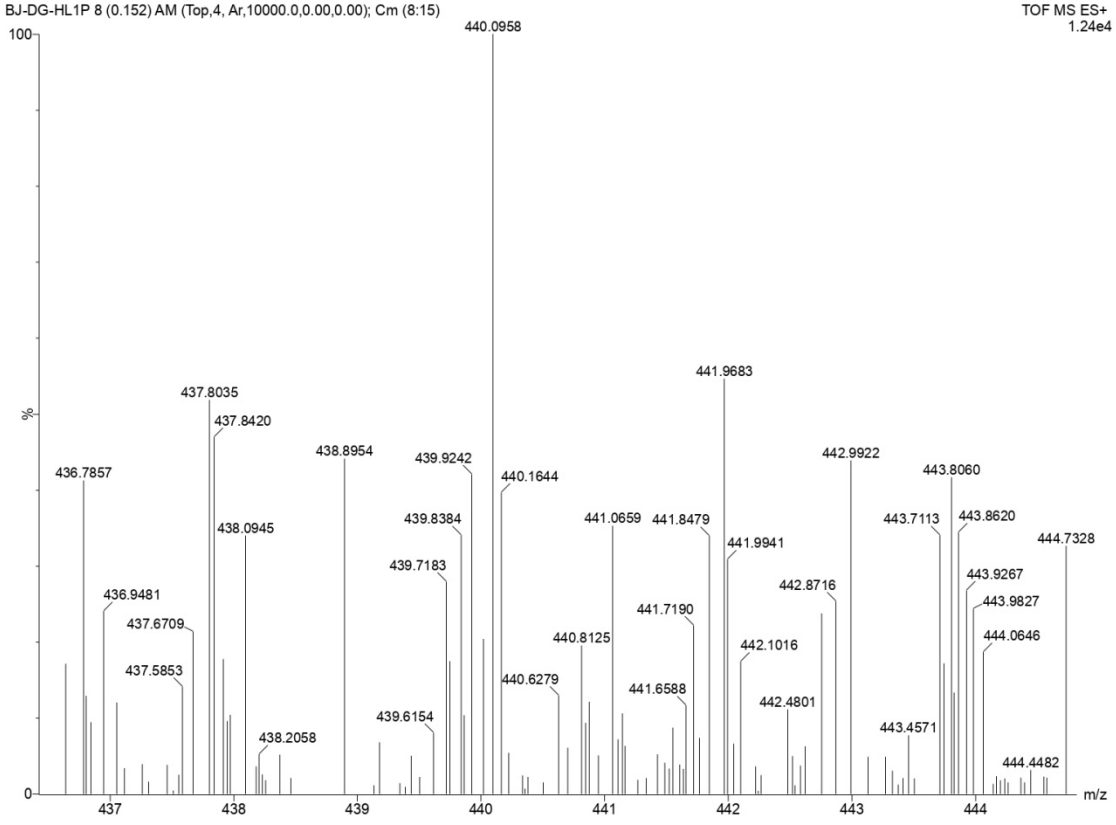


^{1}H NMR of (400 MHz, Chloroform-d) spectra of imidazolium salt (**HL_1-PF_6**)



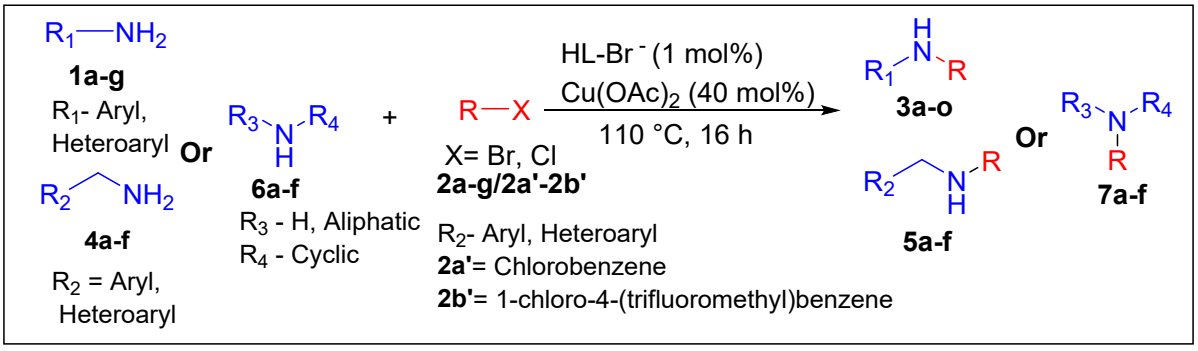
^{13}C{^{1}H} NMR of (100 MHz, Chloroform-*d*) spectra of imidazolium salt (**HL_1-PF_6**)





Mass Spectra of imidazolium salt ($\mathbf{HL_1\text{-}PF_6}$)

3. General procedure for the synthesis of C-N coupling of variety of Amines (1a-g, 4a-f, 6a-f) with different type of Aryl/Hetero-aryl halides (2a-g/2a'-2b') : A mixture of different type of amines **(1a-g, 4a-f, 6a-f)** (0.5 mmol) with various aryl/hetero-aryl halides **(2a-g/2a'-2b')** (0.6 mmol) in the presence of HL-Br^- (1 mol%) and $Cu(OAc)_2$ (40 mol%) was charged in a reaction tube at a temperature of 110°C for 16 h. After the completion of the reaction, the reaction mixture was cooled and the work-up was done with H_2O (15 mL) and ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as eluting solvent to afford the C-N coupling product **3a-o, 5a-f** and **7a-f** in 35-93 % yield.



Scheme 2. Synthesis of C-N coupling product using different type of amines **(1a-g, 4a-f, 6a-f)** with various aryl/hetero-aryl halides **(2a-g/2a'-2b')**

4. Characterization data of C-N coupling product 3a-o, 5a-f and 7a-f:

Diphenylamine (3a)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20-7.17 (m, 4H), 6.99 (d, *J* = 7.5 Hz, 4H), 6.86-6.83 (m, 2H), 5.61 (br, 1H); $^{13}C\{^1H\}$ was found in good agreement with the ref [1a].

4-methyl-N-phenylaniline (3b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 – 7.21 (m, 2H), 7.08 (d, *J*= 8.0 Hz, 2H), 7.01 – 6.98 (m, 4H), 6.89 – 6.85 (m, 1H), 5.60 (br, 1H), 2.30 (s, 3H); $^{13}C\{^1H\}$ was found in good agreement with the ref [1a].

4-methoxy-N-phenylaniline (3c)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J*=8.8 Hz, 1H), 7.17-7.11 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.79-6.73 (m, 3H), 5.40 (br, 1H), 3.72 (s, 3H); $^{13}C\{^1H\}$ was found in good agreement with the ref [1b].

4-chloro-N-phenylaniline (3d)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.90 – 6.84 (m, 3H), 5.55 (br, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.79 (s), 142.01 (s), 129.42 (d, *J* = 13.7 Hz), 125.62 (s), 121.66 (s), 118.95 (s), 118.25 (s).

4-nitro-N-phenylaniline (3e)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 9.2 Hz, 4H), 7.27 (br, 1H), 7.13 (d, *J* = 9.2 Hz, 5H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.35 (s), 139.66 (s), 129.90 (s), 126.38 (s), 124.84 (s), 122.10 (s), 113.85 (s).

2-(phenylamino)benzonitrile (3f)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.22 (m, 5H), 6.68 – 6.63 (m, 4H), 4.33 (br, 1H); ^{13}C{^{1}H} was found in good agreement with the ref [1a].

N-phenylnaphthalen-1-amine (3g)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.29-7.24 (m, 2H), 7.16-7.13 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.82-6.79 (m, 1H), 5.80 (s, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 144.85 (s), 138.84 (s), 134.86 (s), 129.48 (s), 128.67 (s), 127.91 (s),126.25 (s), 126.14 (s), 125.83 (s), 123.21 (s), 121.96 (s), 120.73 (s), 117.60 (s), 116.15 (s).

N-phenyl-4-(trifluoromethyl)aniline (3h)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.09 – 7.07 (m, 2H), 7.00 – 6.96 (m, 3H), 5.77 (s, 1H); ^{13}C{^{1}H} was found in good agreement with the ref [1a].

1-(3-(phenylamino)phenyl)ethan-1-one (3i)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (t,J= 2.0 Hz, 1H), 7.40 (ddd, *J* = 7.6, 1.6, 1.2 Hz, 1H), 7.28 – 7.18 (m, 4H), 7.03-7.01 (m, 2H), 6.93-6.90 (m, 1H), 5.78 (br, 1H), 2.50 (s, 3H); ^{13}C was found in good agreement with the ref [1b].

2,4,6-trimethyl-N-phenylaniline (3j)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16-7.12 (m, 2H), 6.94 (s, 2H), 6.74-6.70 (m, 1H), 6.49-6.47 (m, 2H), 5.08 (s, 1H), 2.30 (s, 3H), 2.17 (s, 6H); ^{13}C{^{1}H} was found in good agreement with the ref [1a].

4-methyl-N-phenylaniline (3k)

Since the structure of compound **3k** is same as **3b,** so ^{1}H NMR of **3k** is matched with **3b** and it found in good agreement with ref [1a]

4-methoxy-N-phenylaniline (3l)

Since the structure of compound **3l** is same as **3c,** so ^{1}H NMR of **3l** is matched with **3c** and it found in good agreement with ref [1b]

N-phenyl-4-(trifluoromethyl)aniline (3m)

Since the structure of compound **3m** is same as **3h,** so ^{1}H NMR of **3m** is matched with **3h** and it found in good agreement with ref [1a]

N-phenylnaphthalen-1-amine (3n)

Since the structure of compound **3n** is same as **3g,** so ^{1}H NMR of **3n** is matched with **3g** and it found in good agreement with ref [1b]

N-phenylisoquinolin-4-amine (3o)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.5 Hz, 4H), 7.38 (br, 1H), 7.25-7.22 (m, 5H), 7.04-7.01 (m, 2H); $^{13}C\{^{1}H\}$ was found in good agreement with the reference [1h]

N-benzylaniline (5a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.14 (m, 6H), 7.12-7.08 (m, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H), 3.98 (br, 1H); $^{13}C\{^{1}H\}$ was found in good agreement with the ref [1c].

N-benzyl-4-methylaniline (5b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.0 Hz, 2H), 7.10-7.05 (m, 4H), 6.64-6.60 (m, 1H), 6.53 (d, *J* = 7.6 Hz, 2H), 4.18 (s, 2H), 3.87 (br, 1H), 2.25 (s, 3H); $^{13}C\{^{1}H\}$ was found in good agreement with the ref [1c].

N-(4-bromobenzyl)aniline (5c)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15-7.12 (m, 2H), 6.71-6.67 (m, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.26 (s, 2H), 4.02 (br, 1H); $^{13}C\{^{1}H\}$ was found in good agreement with the ref [1d].

N-(4-methoxybenzyl)aniline (5d)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, *J* = 8.8 Hz, 2H), 7.16 (t, J=8.0 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.72-6.68 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.23 (s, 2H), 3.93 (br, 1H), 3.78 (s, 3H); $^{13}C\{^{1}H\}$ was found in good agreement with the ref [1c].

N-phenethylaniline (5e)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 – 7.20 (m, 2H), 7.16-7.05 (m, 5H), 6.64-6.59 (m, 1H), 6.53-6.50 (m, 2H), 3.53 (br, 1H), 3.30 (t, *J* = 6.9 Hz, 2H), 2.84-2.79 (m, 2H); $^{13}C\{^{1}H\}$ was found in good agreement with the ref [1e].

N-(2-(1H-indol-3-yl)ethyl)aniline (5f)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (br, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.02 (m, 4H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.64-6.60 (m, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 3.40-3.36 (m, 2H), 3.02-2.97 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 148.38 (s),

136.53 (s), 129.42 (s), 127.58 (s), 122.33 (s), 122.19 (s), 119.60 (s), 118.96 (s), 117.50 (s), 113.54 (s), 113.19 (s), 111.38 (s), 44.11 (s), 25.26 (s).

1-phenylpyrrolidine (7a)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26-7.21 (m, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.58 (dd, *J* = 8.7, 0.9 Hz, 2H), 3.29 (t, *J* = 6.6 Hz, 4H), 2.03 – 1.98 (m, 4H); ^{13}C{^{1}H} was found in good agreement with the ref [1f].

N-cyclohexylaniline (7b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 – 7.14 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 3.07 – 3.05 (m, 4H), 1.65-1.60 (m, 4H), 1.51-1.46 (m, 5.8 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ =152.37 (s), 129.09 (s), 119.27 (s), 116.63 (s), 50.78 (s), 25.98 (s), 24.44 (s).

1,4-diphenylpiperazine (7c)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.36 (m, 4H), 7.05 (d, *J* = 8.5 Hz, 4H), 6.98-6.96 (m, 2H), 3.40 (s, 8H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.36 (s), 129.27 (s), 120.11 (s), 116.42 (s), 49.48 (s).

4-phenylmorpholine (7d)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22-7.19 (m, 2H), 6.85 – 6.79 (m, 3H), 3.79 – 3.77 (m, 4H), 3.09 – 3.07 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.45 (s), 129.32 (s), 120.19 (s), 115.87 (s), 67.08 (s), 49.54 (s)

N-cyclohexylaniline (7e)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 – 7.06 (m, 2H), 6.60 – 6.51 (m, 3H), 3.18 (br, 1H), 1.98 (d, *J* = 12.8 Hz, 2H), 1.70-1.55 (m, 3H), 1.31 – 1.05 (m, 6H); ^{13}C{^{1}H} was found in good agreement with the ref [1a].

4-(propylamino)benzonitrile (7f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.12 (br, 1H), 3.29-3.24 (m, 2H), 1.50 (dd, *J* = 14.4, 7.2 Hz, 2H), 0.84 (m, 3H); ^{13}C{^{1}H} was found in good agreement with the ref [1g].

General procedure for the competition reaction

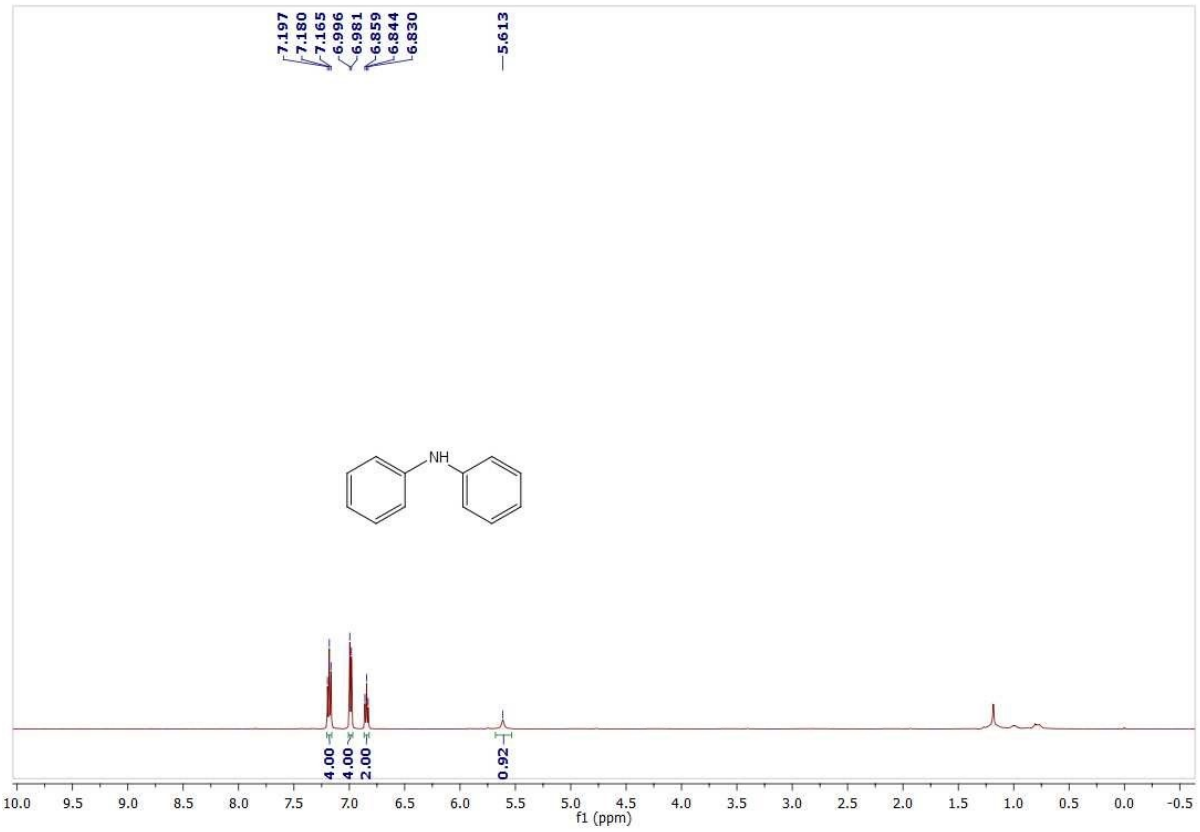
A mixture of 4-methoxyaniline **1c** (0.5 mmol), 4-nitroaniline **1f** (0.5 mmol), bromobenzene **2a** (0.5 mmol) in the presence of HL_1-Br^- (1 mol%) and $Cu(OAc)_2$ (40 mol%) were charged at a temperature of 110 °C for 16 h in a sealed reaction tube. After completion of the reaction, the reaction mixture was cooled and the work-up was done with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column

chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as an eluting solvent afforded the corresponding product **3c** in 55 % and **3f** in 30 % yields, respectively. A mixture of aniline **1a** (0.5 mmol), 2-phenylethan-1-amine **4e** (0.5 mmol), bromobenzene **2a** (0.5 mmol) in the presence of HL_1-Br^- (1 mol%) and $Cu(OAc)_2$ (40 mol%) were charged at a temperature of 110 °C for 16 h in a sealed reaction tube. After the completion of the reaction, the reaction mixture was cooled and the work-up was done ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to get the crude residue which was further purified through column chromatography on silica gel (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as an eluting solvent which afforded the corresponding product **3a** in 65 % and **5e** in 20 % yields, respectively. The above reaction is repeated by taking a mixture of aniline **1a** (0.5 mmol), phenylmethanamine **4a** (0.5 mmol), bromobenzene **2a** (0.5 mmol) underneath the standard reaction conditions. After usual work-up, the crude residue was purified through silica gel column chromatography (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as an eluting solvent which afforded the corresponding product **3a** in 58 % and **5a** in 17 % yields, respectively. Furthermore, a mixture of 2-phenylethan-1-amine **4e** (0.5 mmol), pyrrolidine **6a,** bromobenzene **2a** (0.5 mmol) was charged at standard conditions. After customary work-up, the crude residue was purified through silica gel column chromatography (230-400 mesh) using hexane: ethyl acetate (99:1 ratio) as an eluting solvent which afforded the corresponding product **5e** in 50 % and **7a** in 38 % yields, respectively.

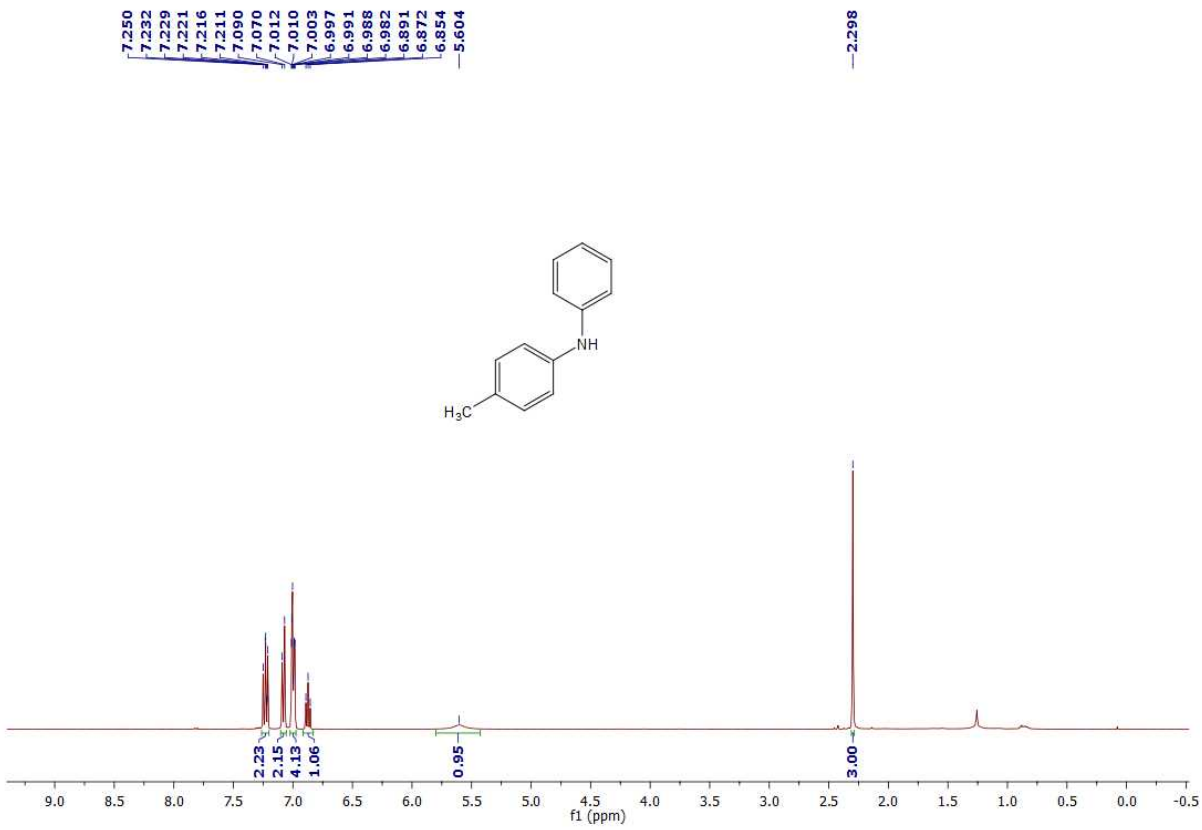
References

1. (a) Benjamin R. Walker, Shuhei Manabe, Andrew T. Brusoe, and Christo S. Sevov, *J. Am. Chem. Soc*, **2021** 143, 6257-6265; (b) Sawant, S.D., Srinivas, M.; Aravinda Kumar, K.A.; Lakshma Reddy, G.; Singh, P.P.; Singh, B.; Sharma, A.K.; Sharma, P.R.; Vishwakarma, R.A. *Tetrahedron Letters* **2013**, *54*, 5351-5354; (c) Emine Ozge Karaca, Zieneb Imene Dehimat, Sedat Yasar, Nevin Gürbüz, Dahmane Tebbani, Bekir Çetinkaya, Ismail Ozdemir, *Inorganica Chimica Acta*, 2021, 520, 120294; (d) Di Wu, Qingqing Bu, Cheng Guo, Bin Dai, Ning Liu, Molecular Catalysis **2021**, 503, 111415; (e) Dirk Hollmann, Sebastian Bahn, Annegret Tillack, and Matthias Beller, *Angew. Chem. Int. Ed.* **2007**, *46*, 8291 –8294; (f) Jayita Dutta, Michael G. Richmond and Samaresh Bhattacharya, *Dalton Trans.,* **2015**, *44*, 13615-13632; (g) Charu Sharma, Avinash Kumar Srivastava, Kamal Nayan Sharma, Raj Kumar Joshi, ***Org. Biomol. Chem.***, 2020,**18**, 3599-3606; (h) Parham, Amir Hossain; Eberle, Thomas; Jatsch, Anja; Grossmann, Tobias; Kroeber, Jonas Valentin; Anemian, Remi ManoukWorl Intellectual Property Organization, WO2016023608 A1 2016-02-18

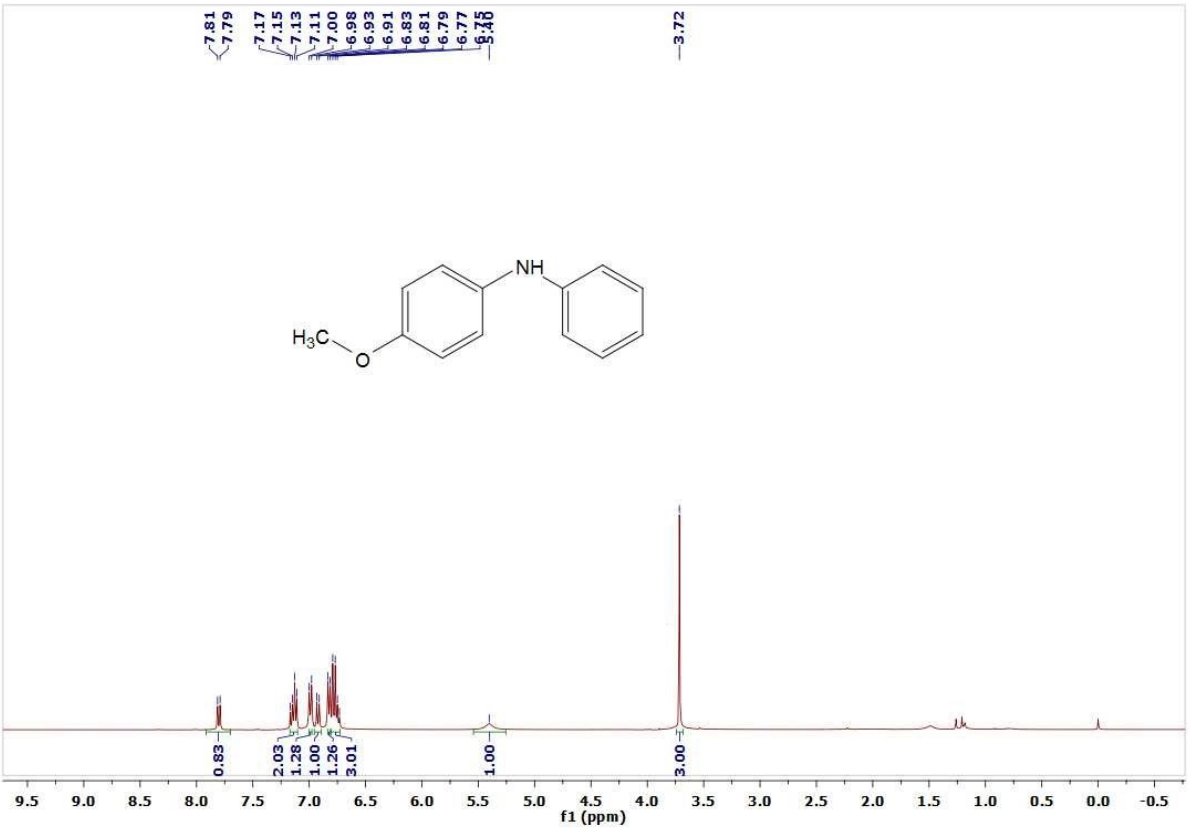
5. Spectral Data: ^{1}H and ^{13}C spectral data of of C-N coupling product **3a-o**, **5a-f** and **7a-f**:



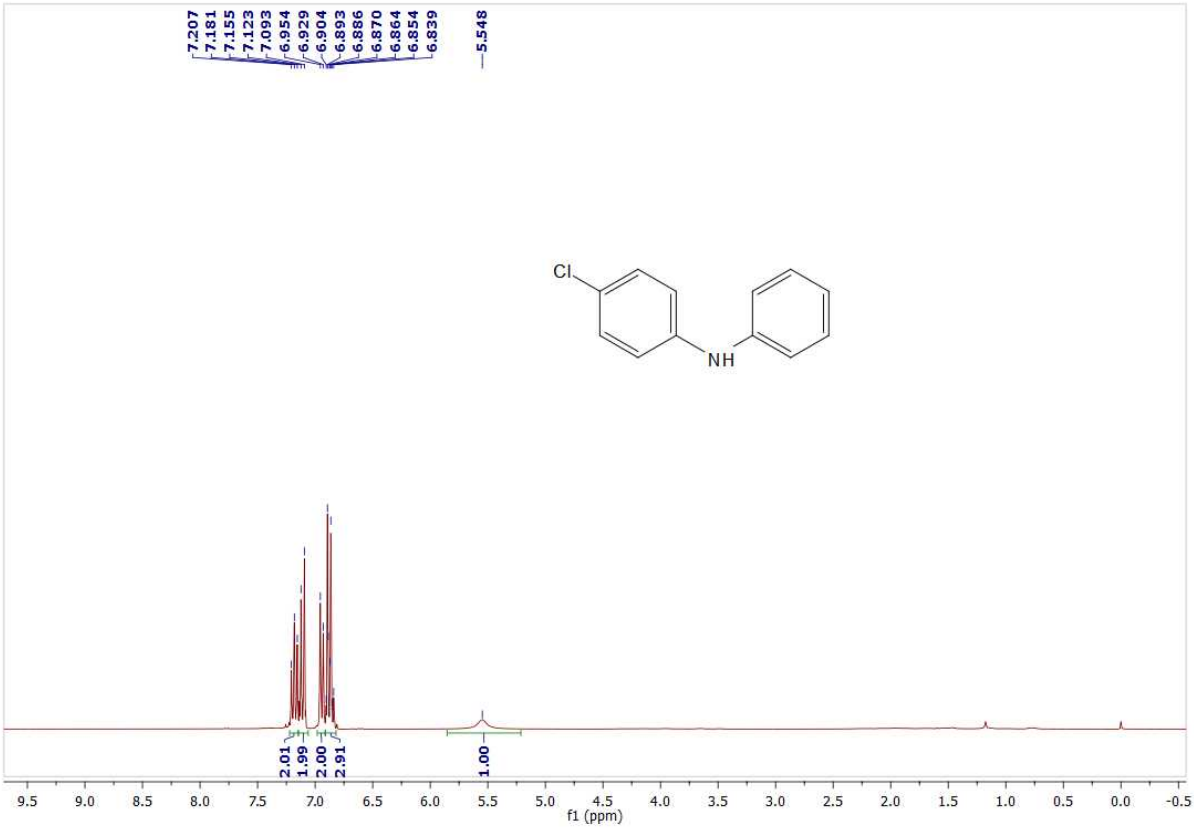
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of **3a**



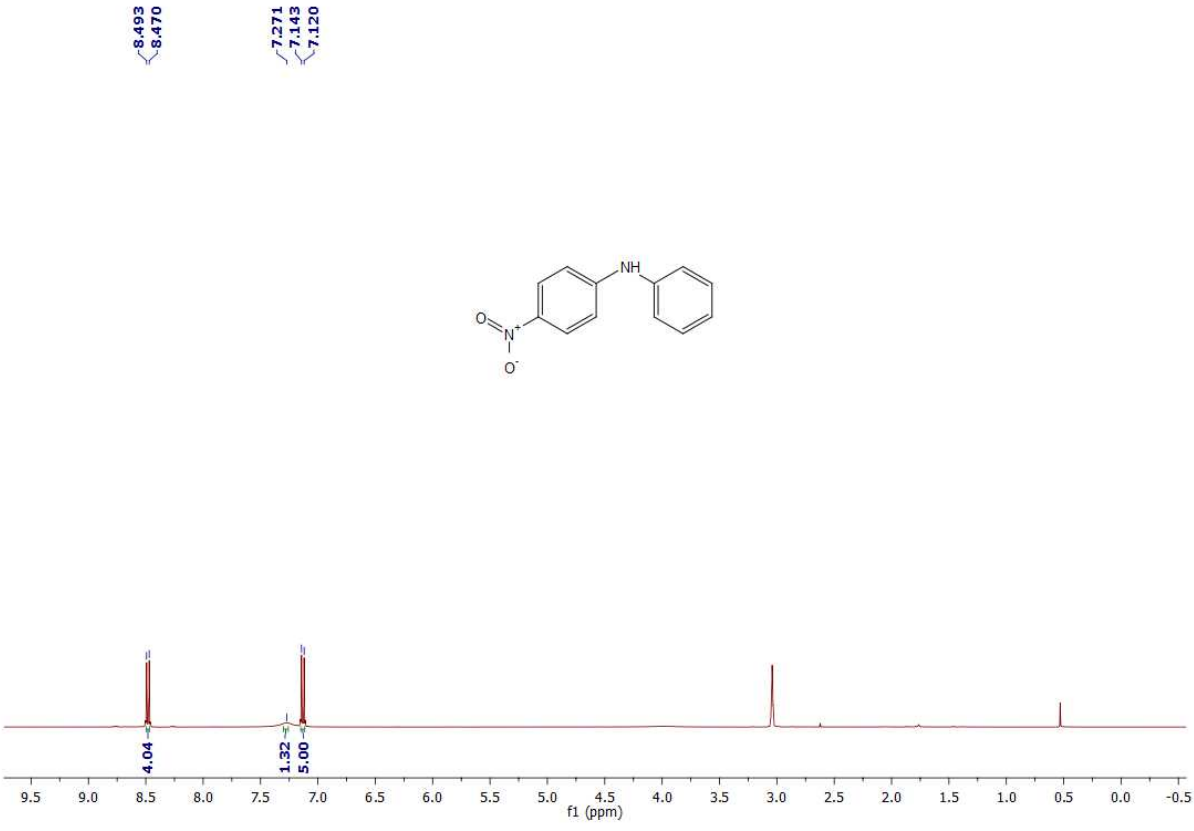
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **3b**



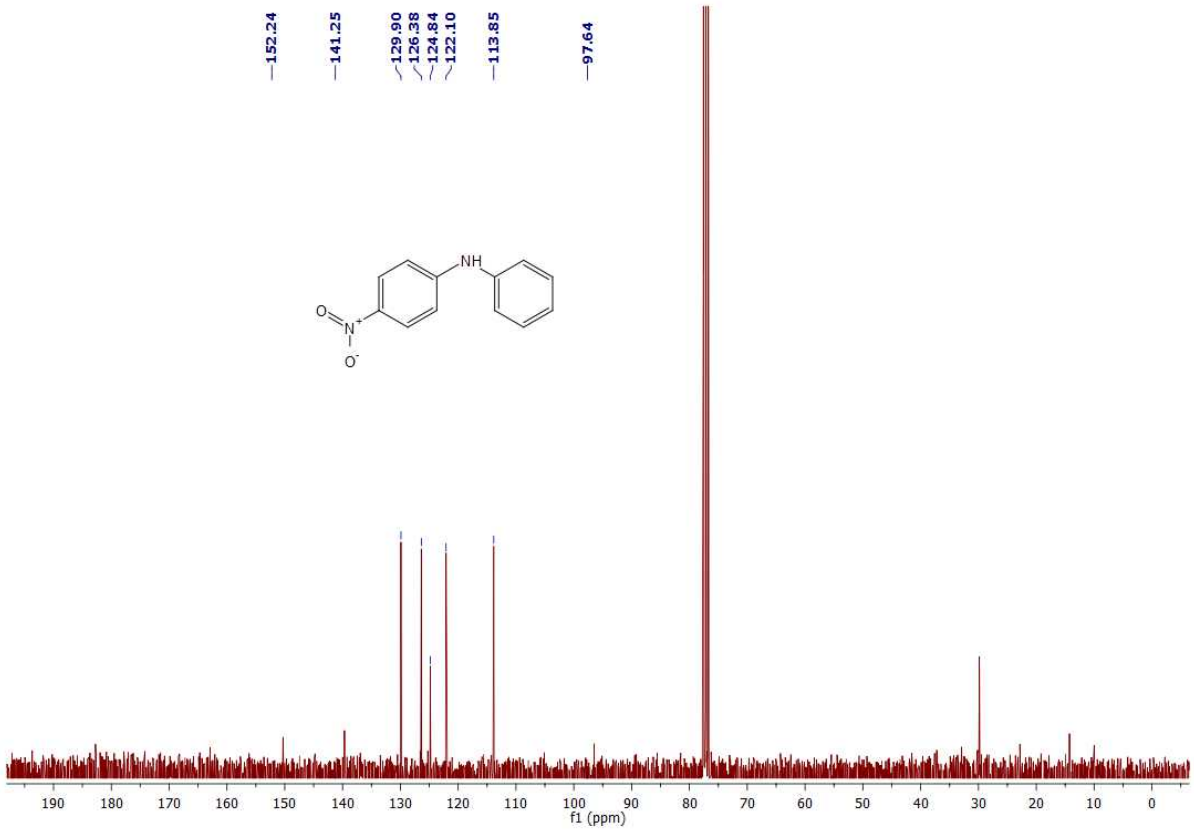
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **3c**



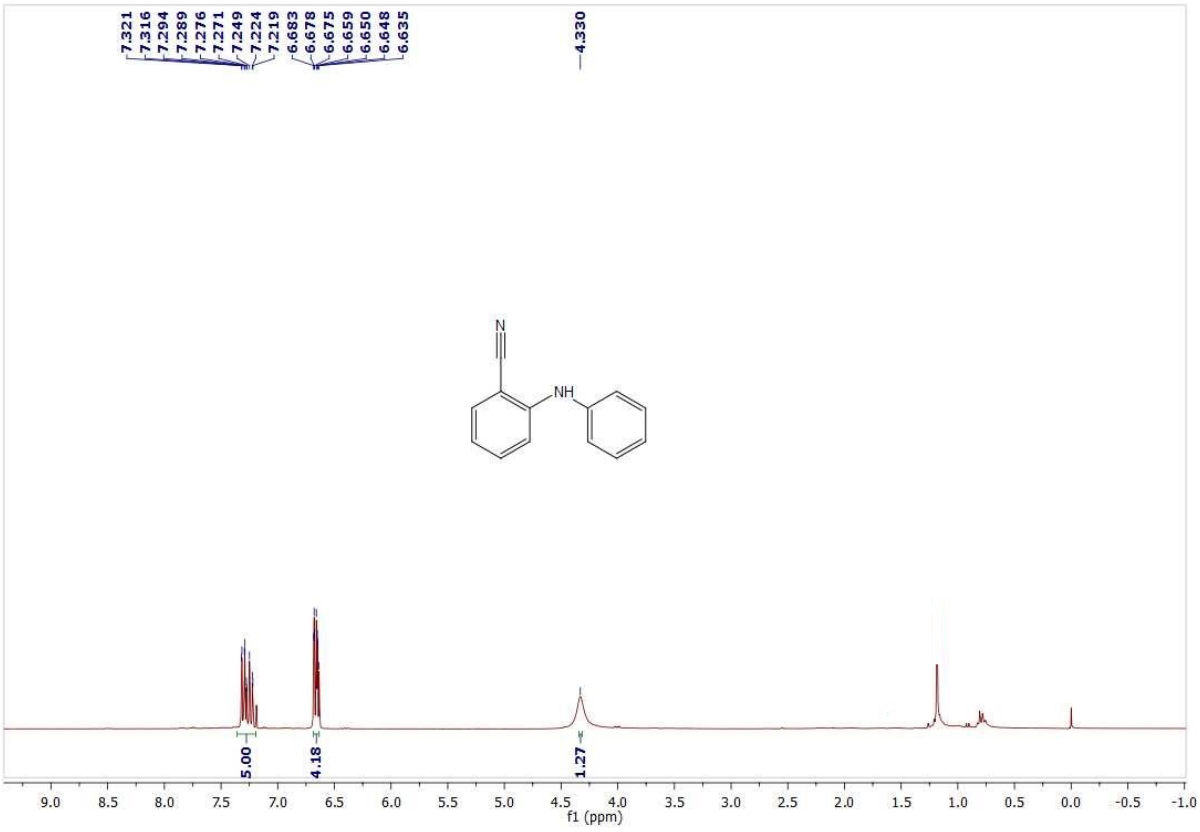
^{1}H NMR (300 MHz, Chloroform-*d*) Spectra of **3d**



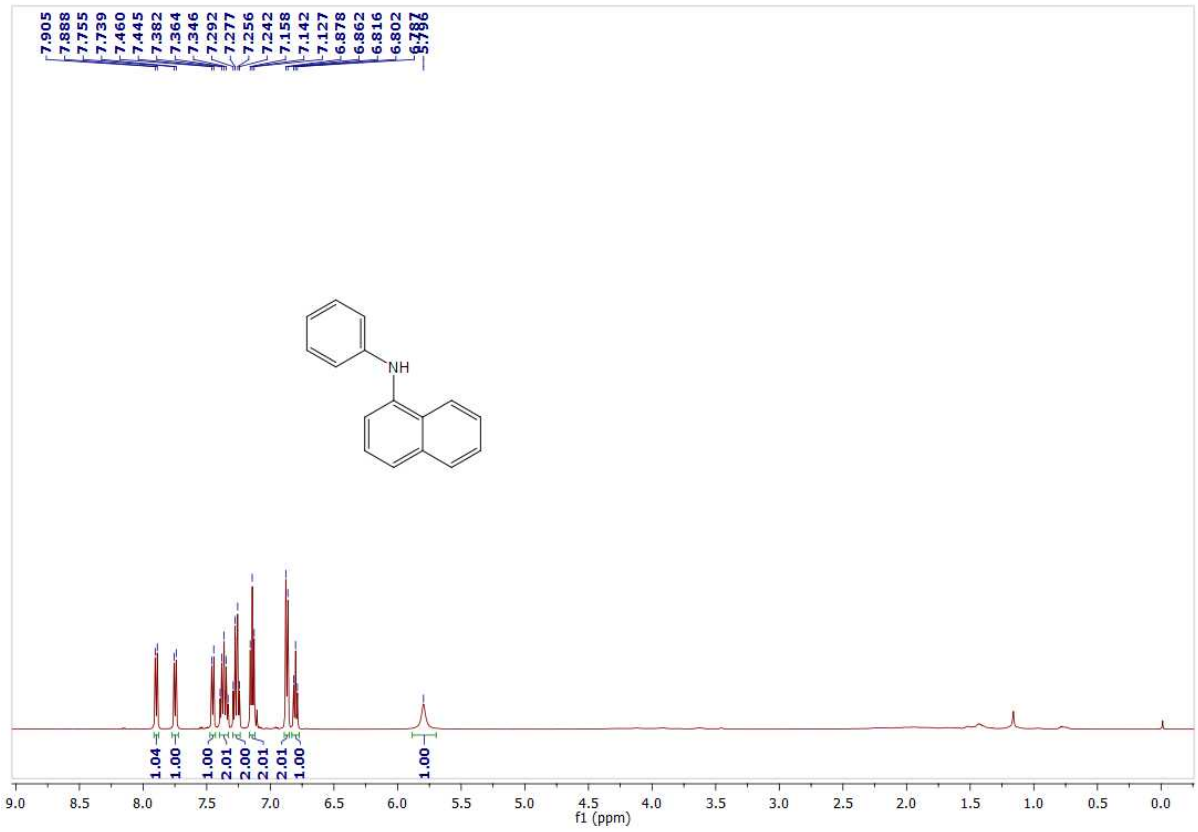
^{1}H NMR (400 MHz, DMSO-d_6) Spectra of **3e**



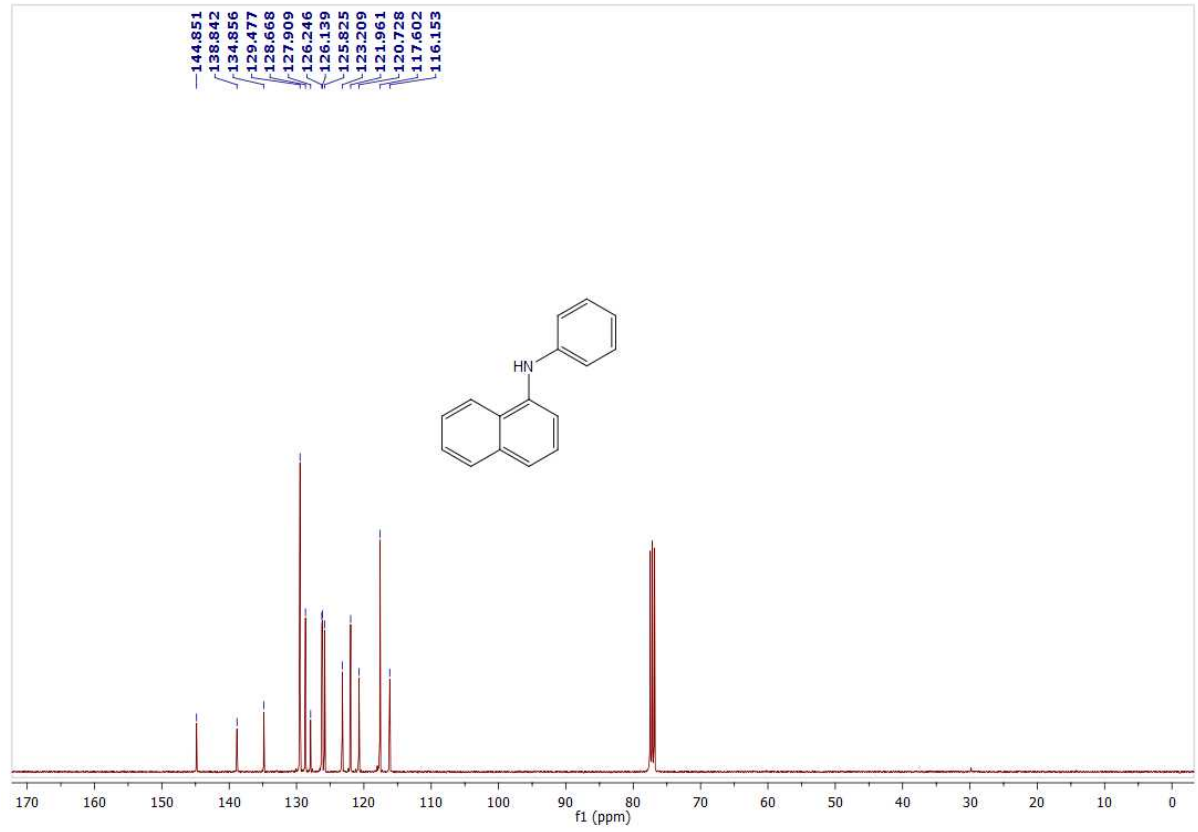
^{13}C NMR (75 MHz, DMSO-d_6) Spectra of **3e**



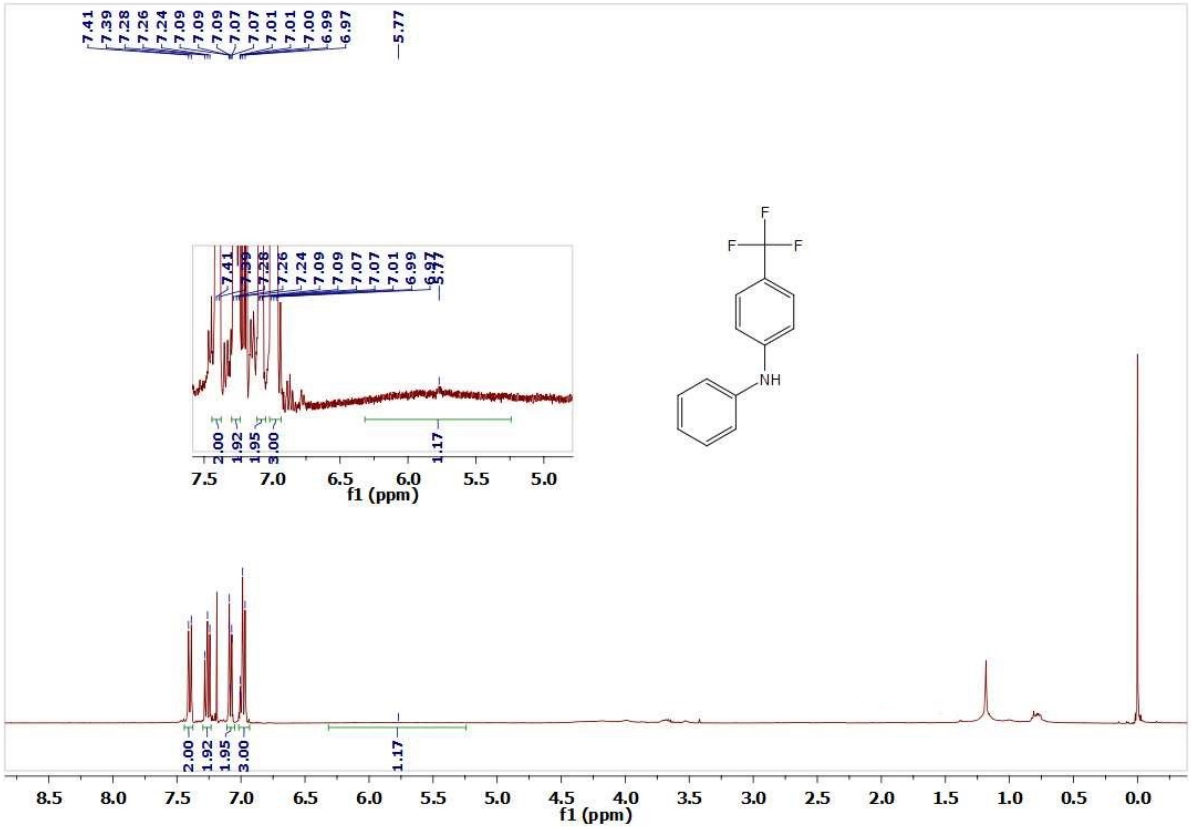
^{1}H NMR (300 MHz, Chloroform-*d*) Spectra of **3f**



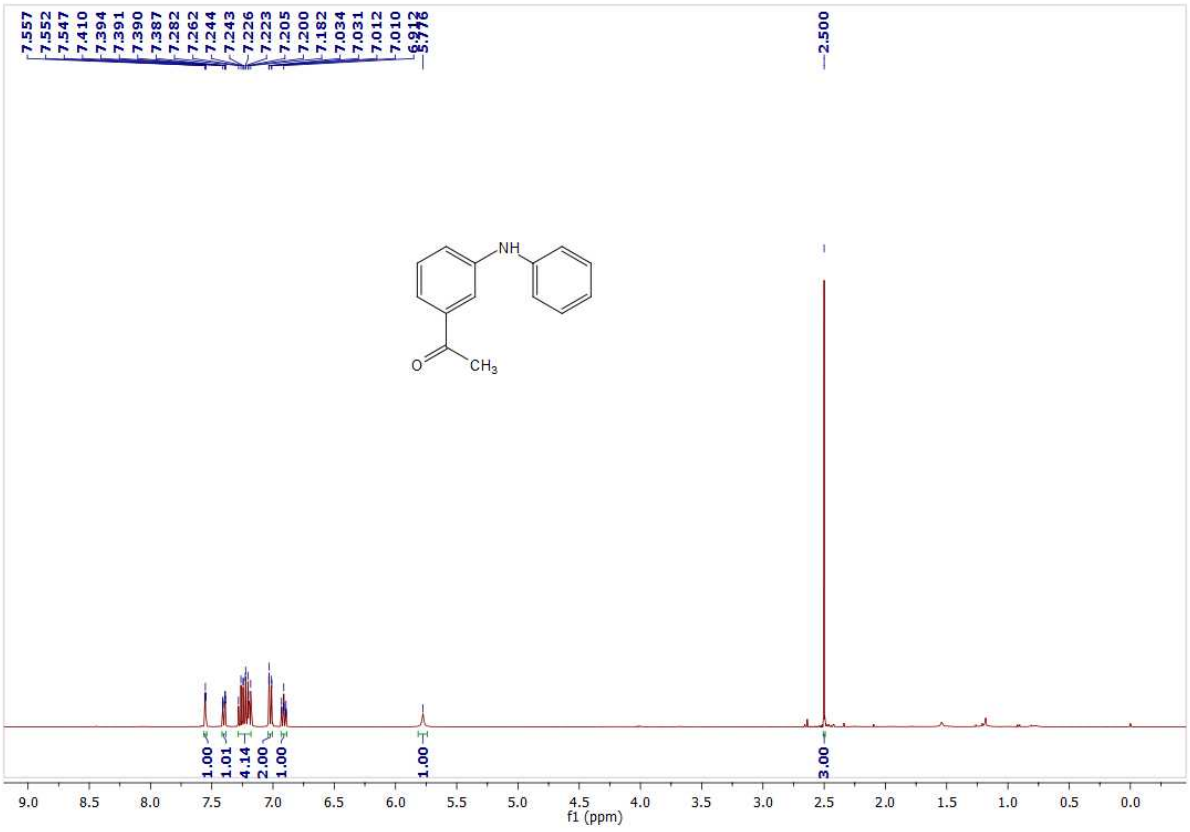
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of **3g**



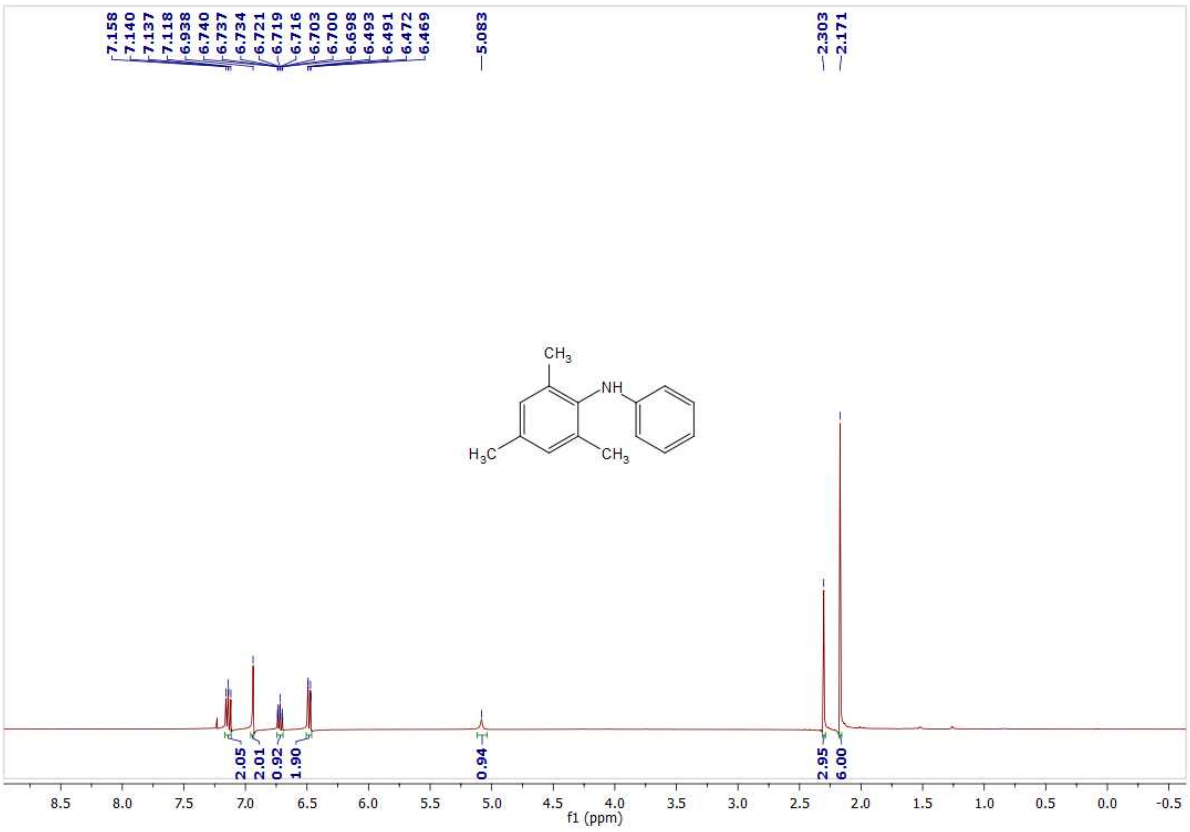
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of **3g**



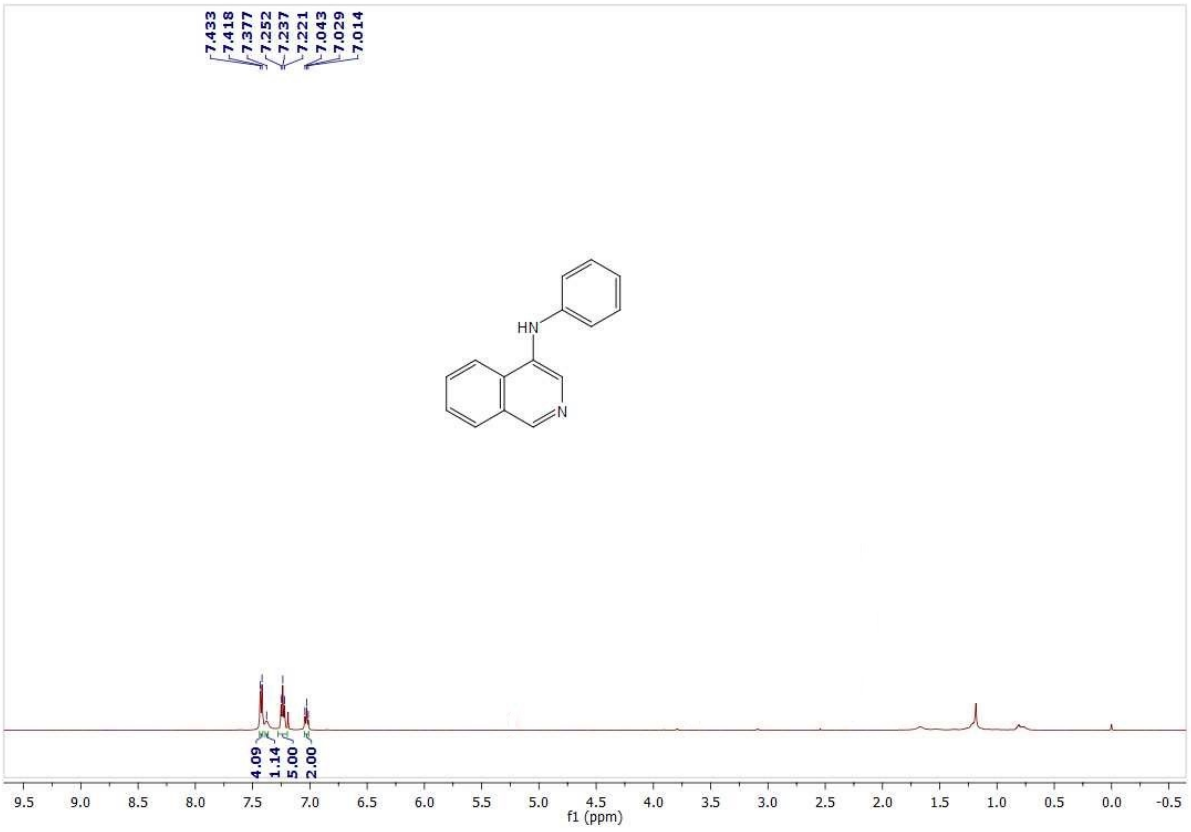
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **3h**



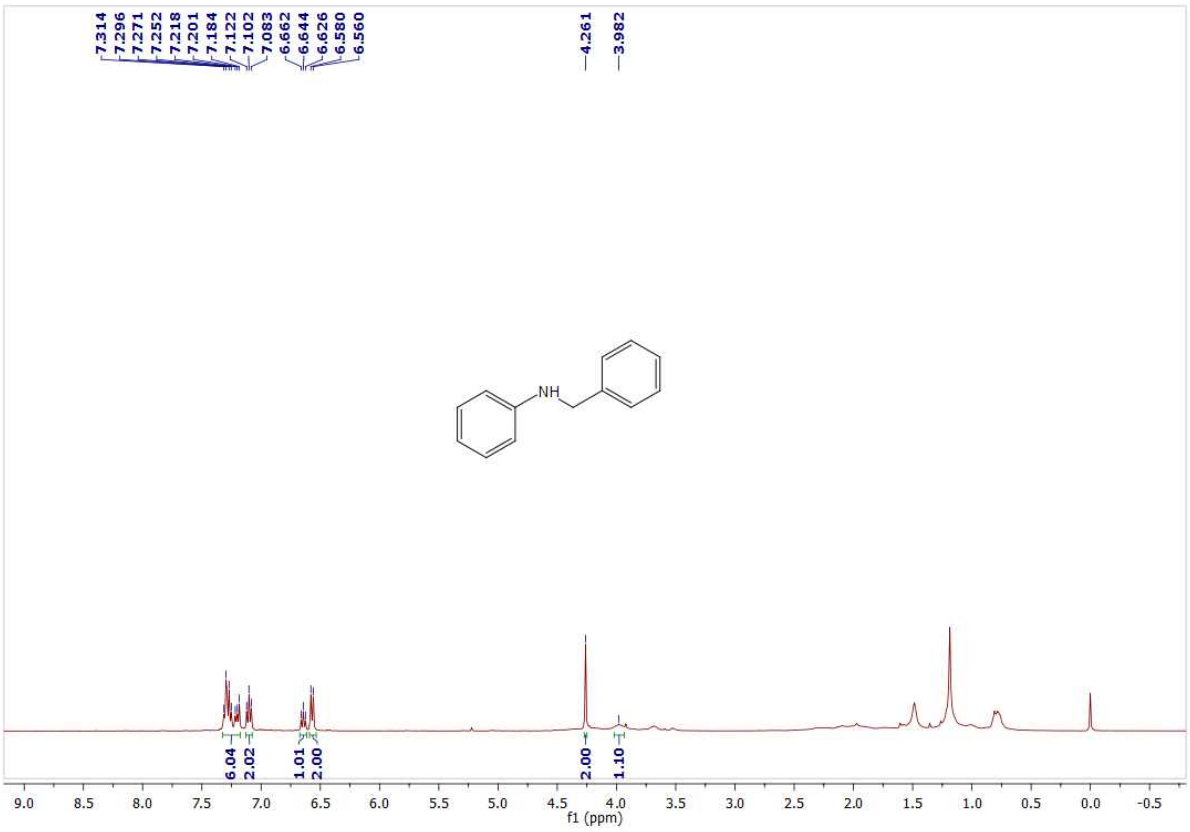
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **3i**



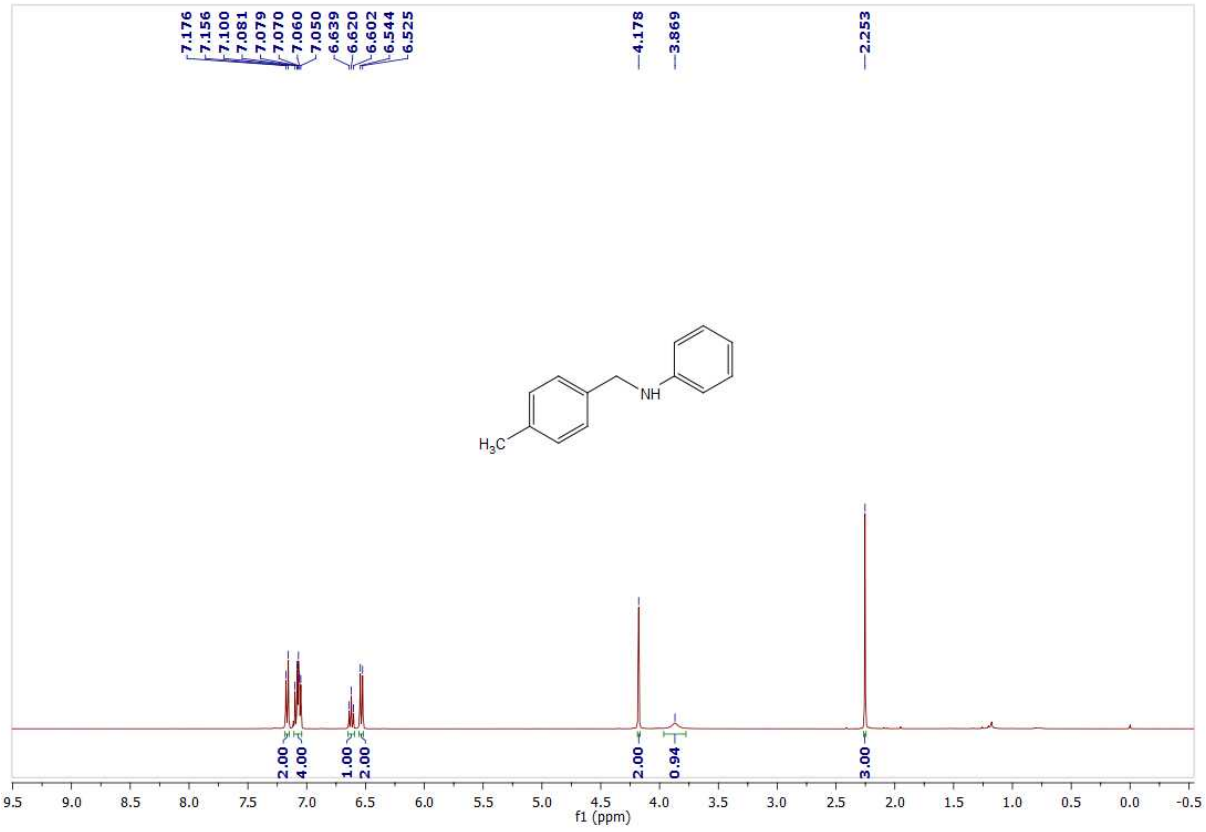
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **3j**



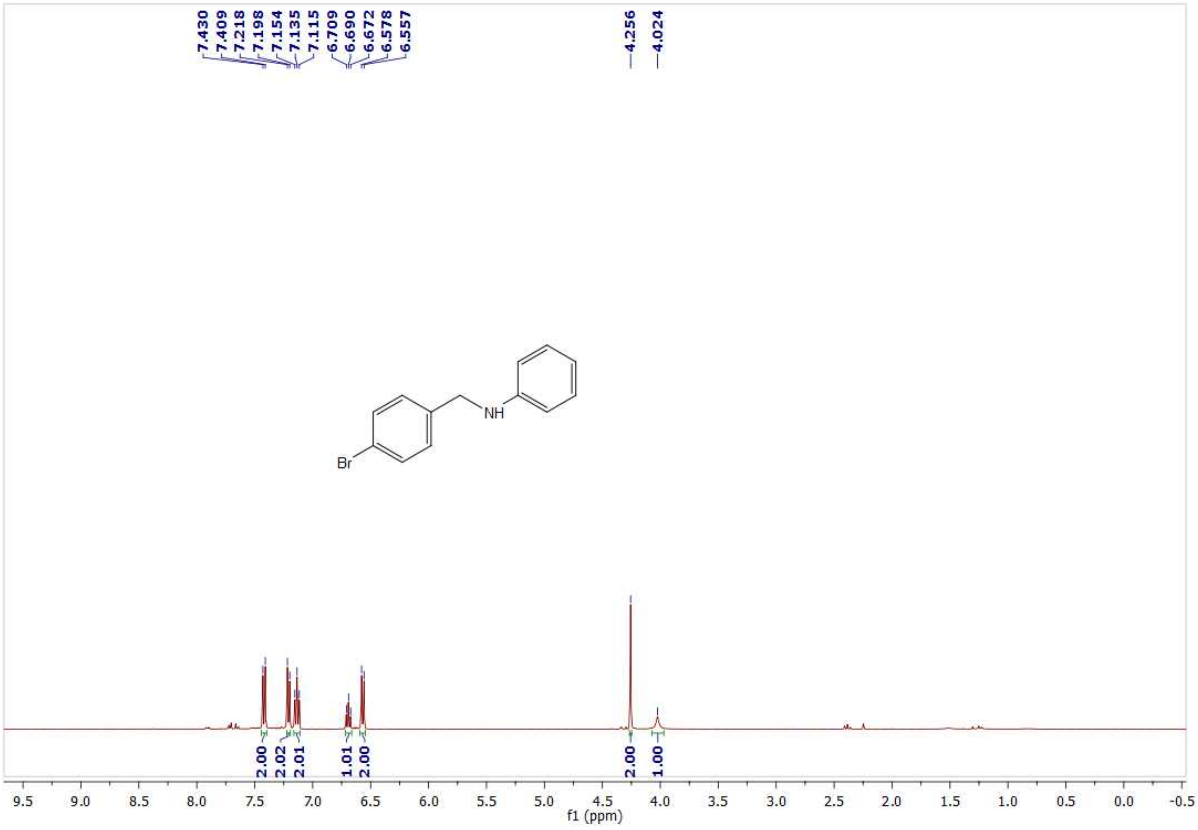
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of **3o**



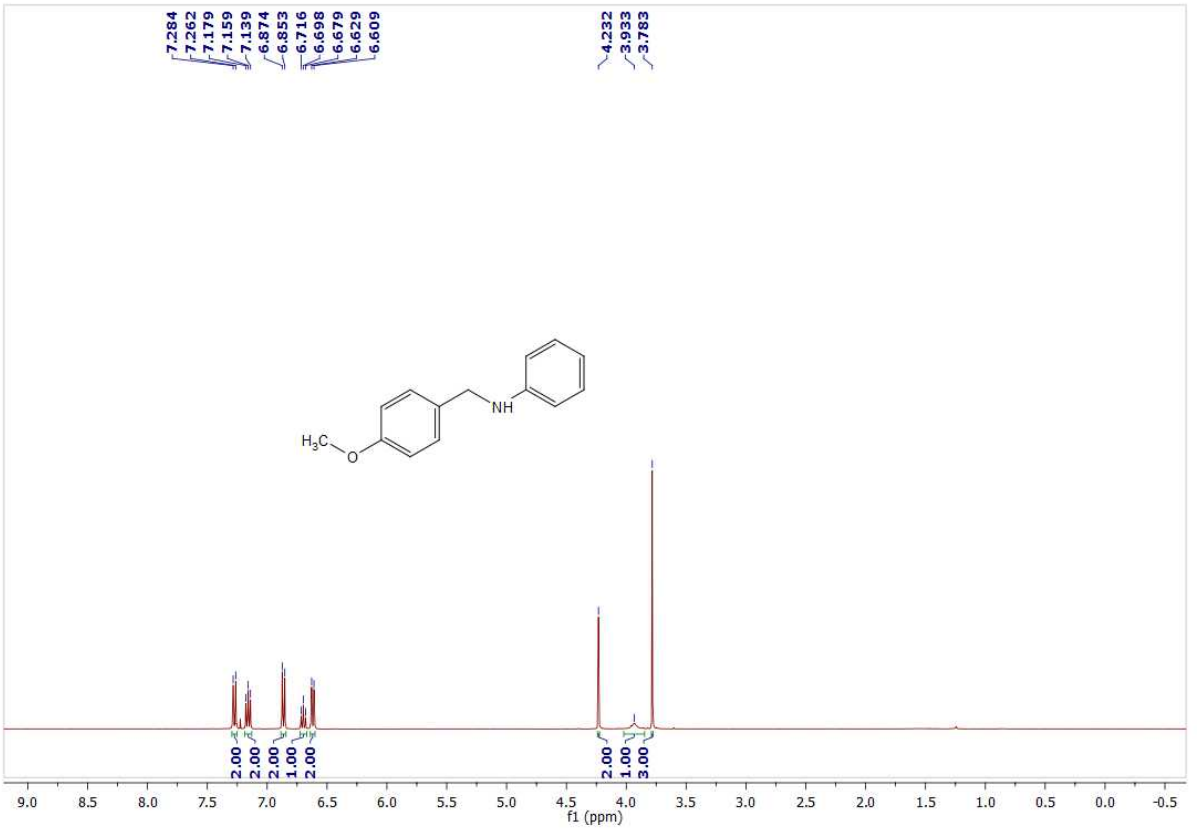
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **5a**



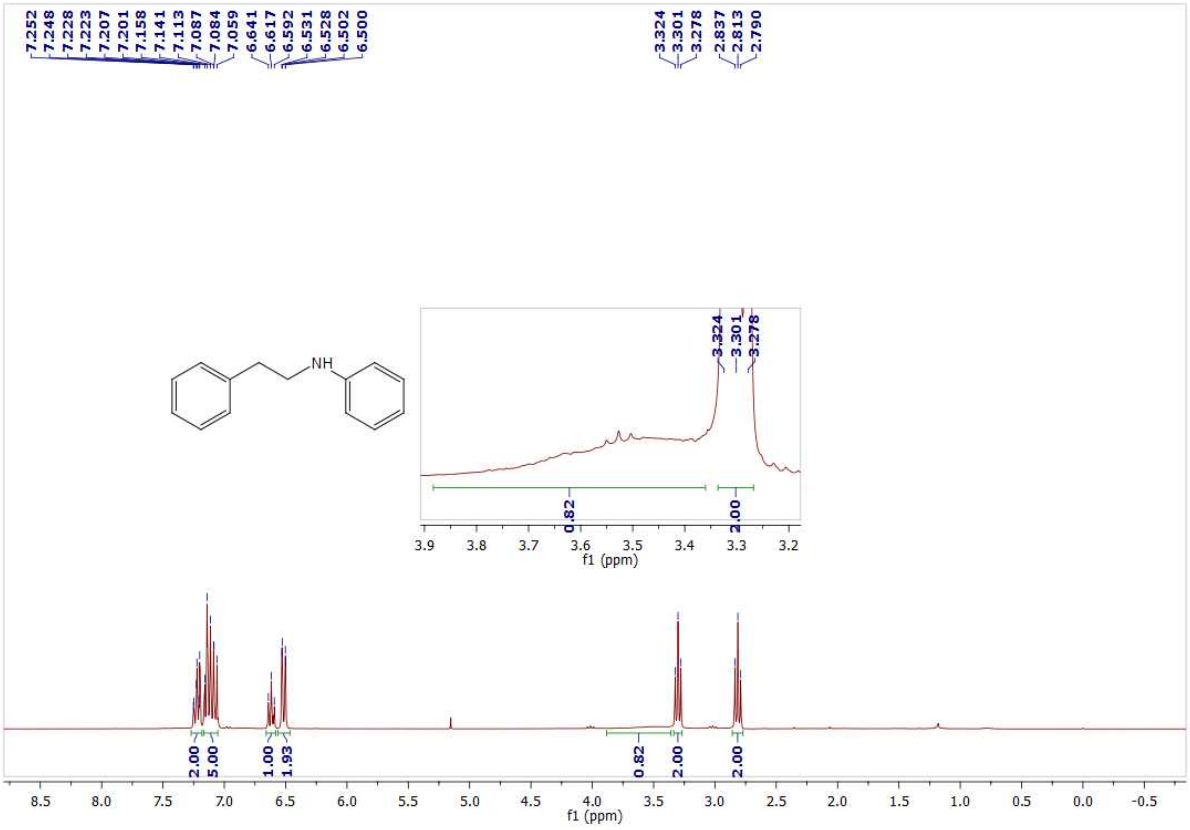
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **5b**



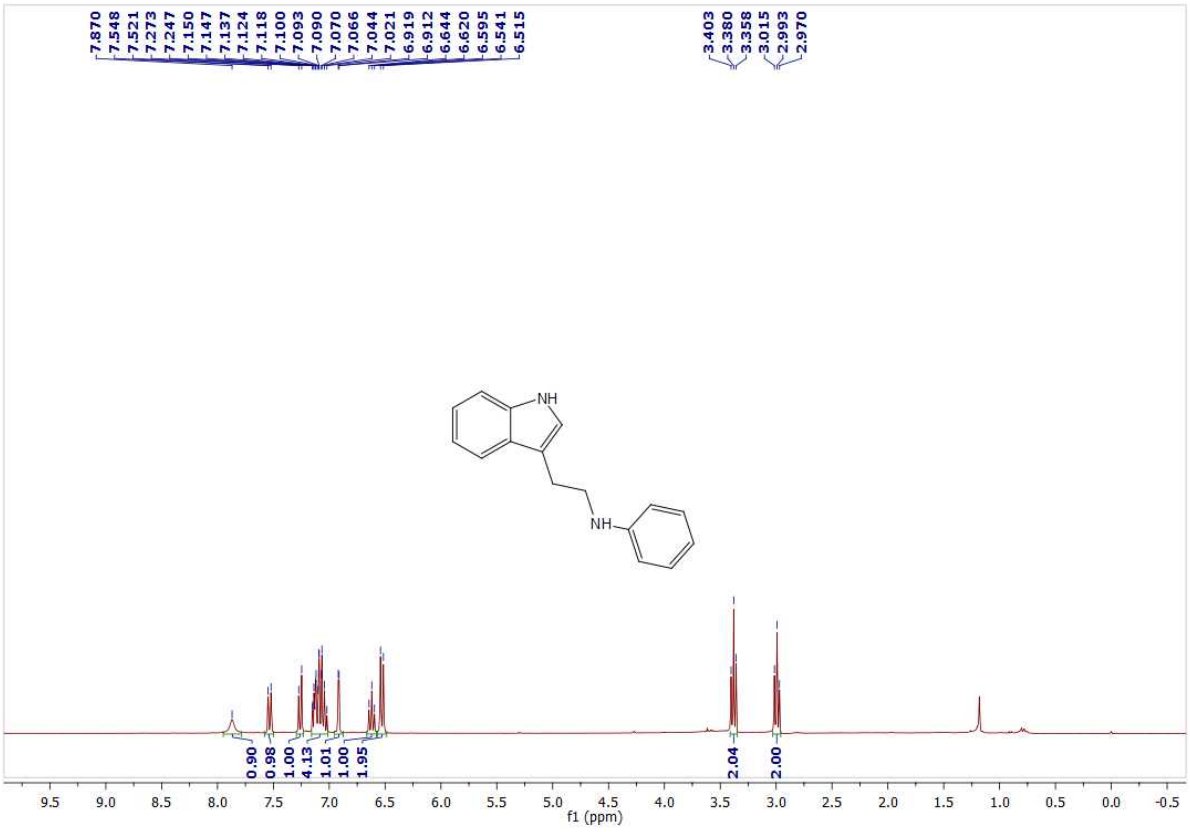
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **5c**



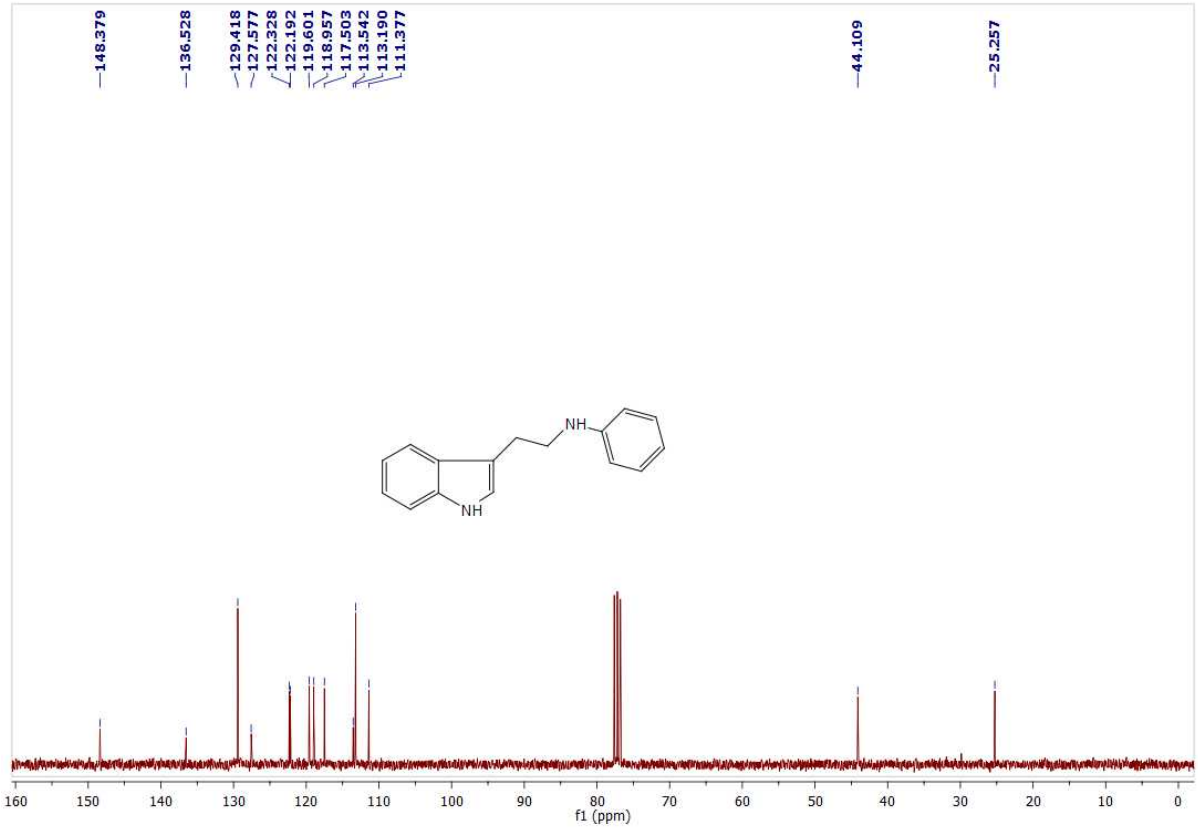
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **5d**



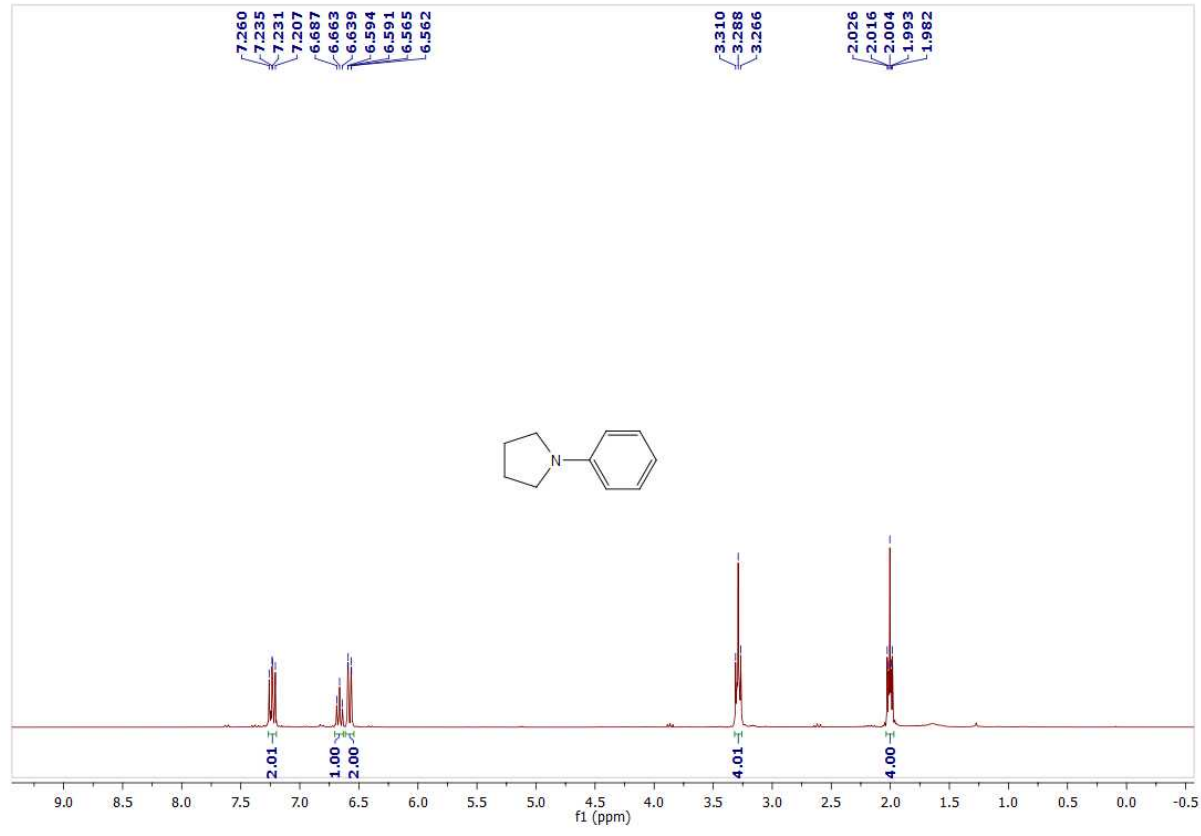
^{1}H NMR (300 MHz, Chloroform-*d*) Spectra of **5e**



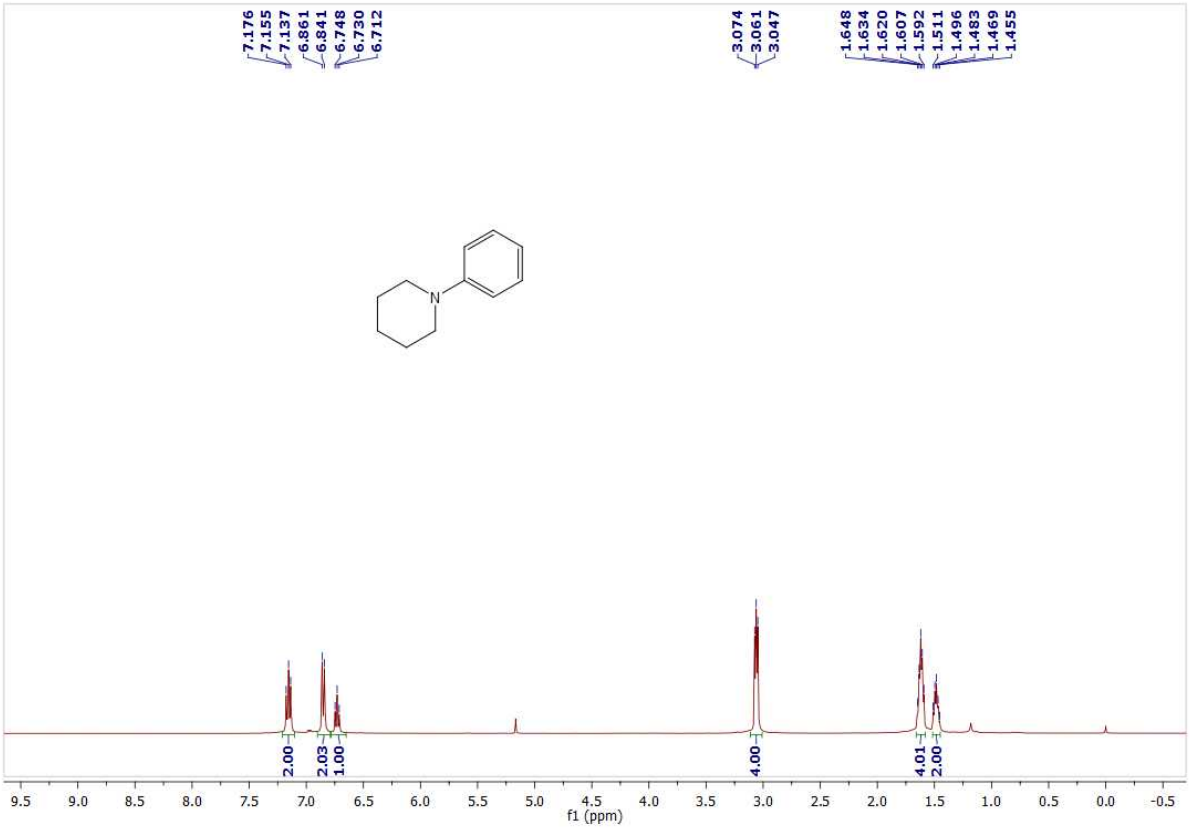
^{1}H NMR (300 MHz, Chloroform-*d*) Spectra of **5f**



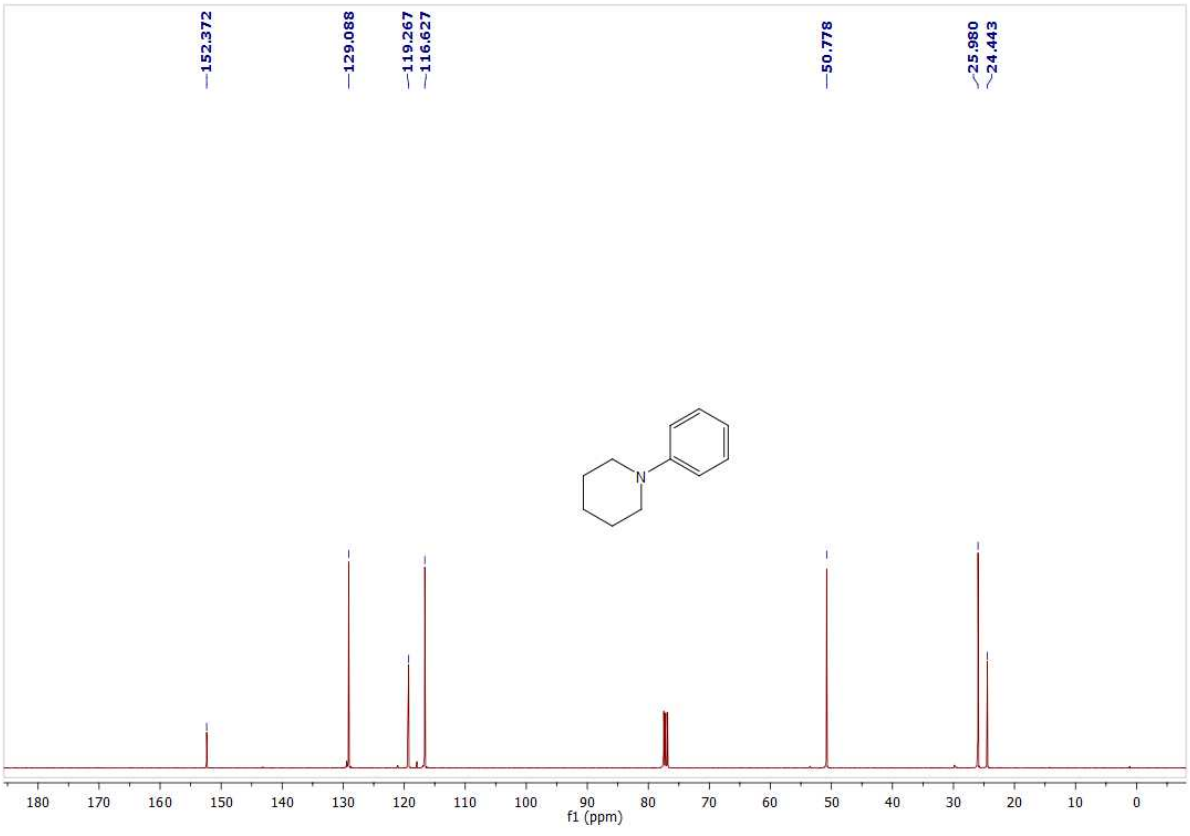
^{1}H NMR (300 MHz, Chloroform-*d*) Spectra of **5f**



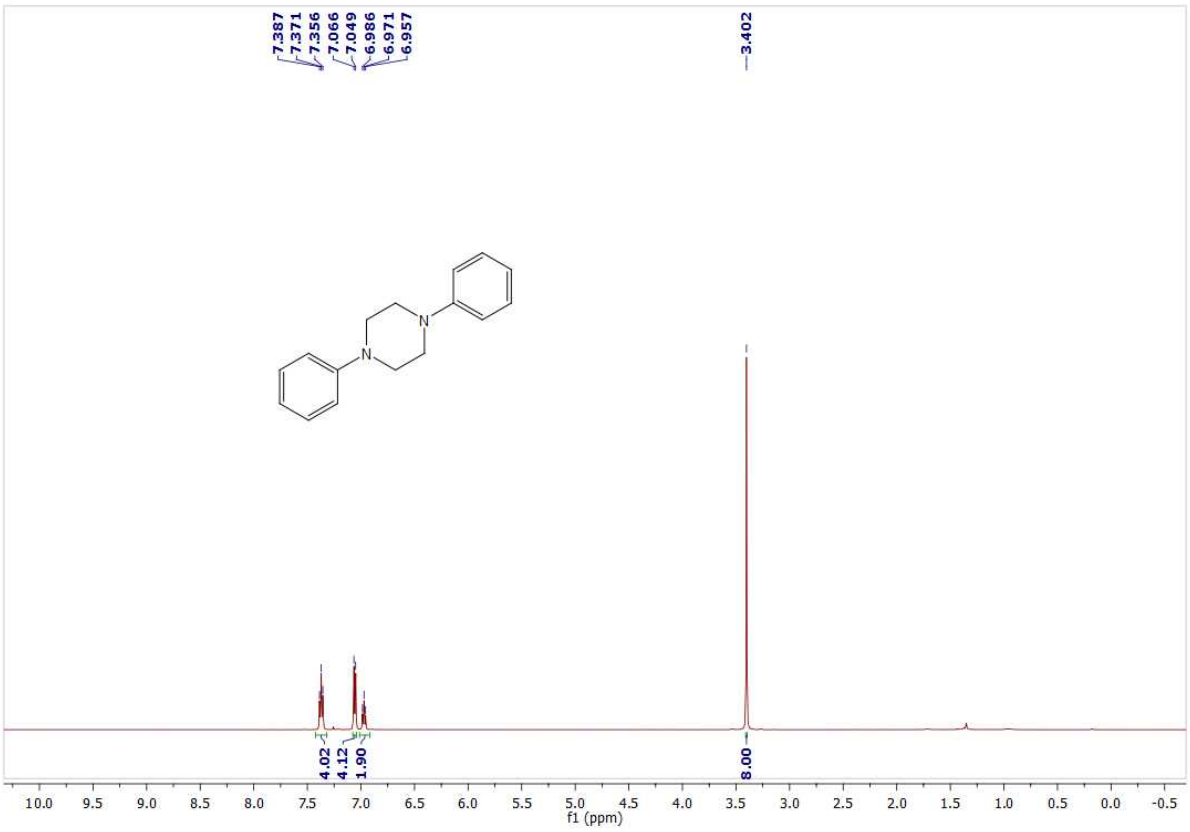
^{1}H NMR (300 MHz, Chloroform-*d*) Spectra of **7a**



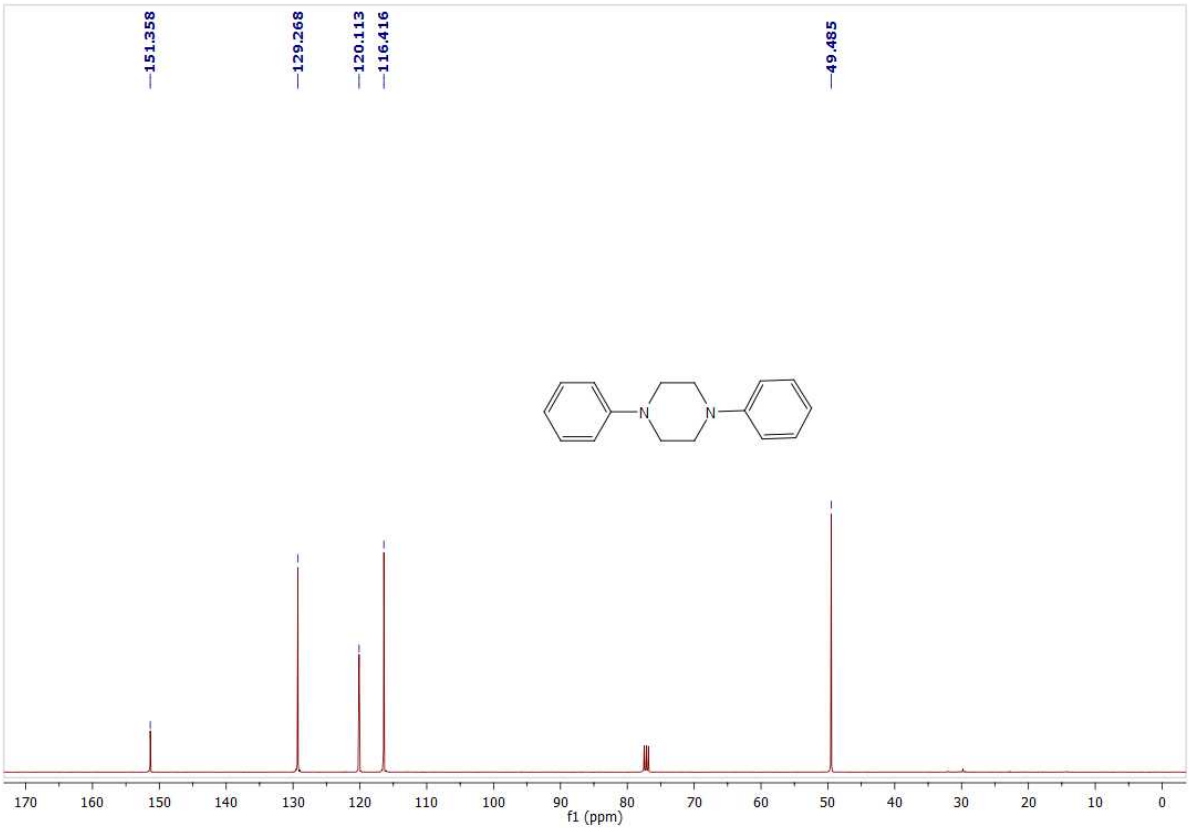
^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **7b**



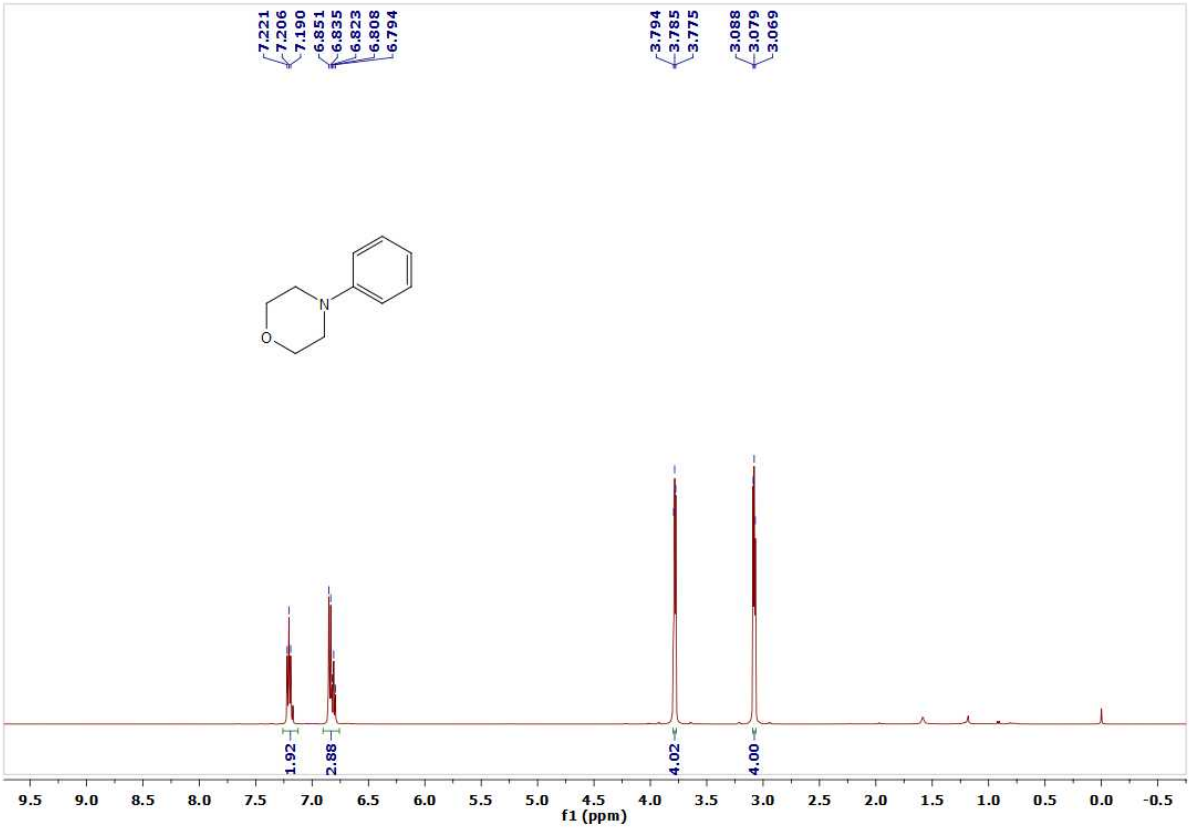
^{13}C NMR (101 MHz, Chloroform-*d*) Spectra of **7b**



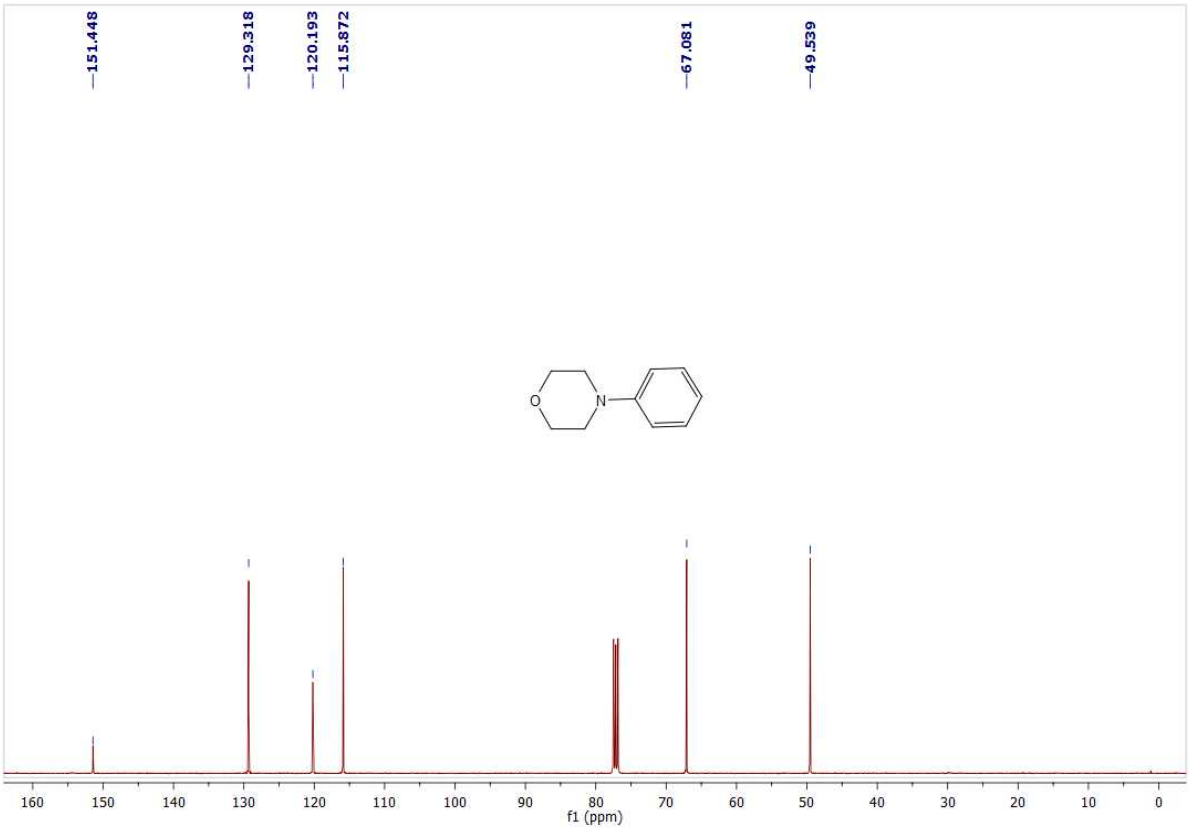
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of **7c**



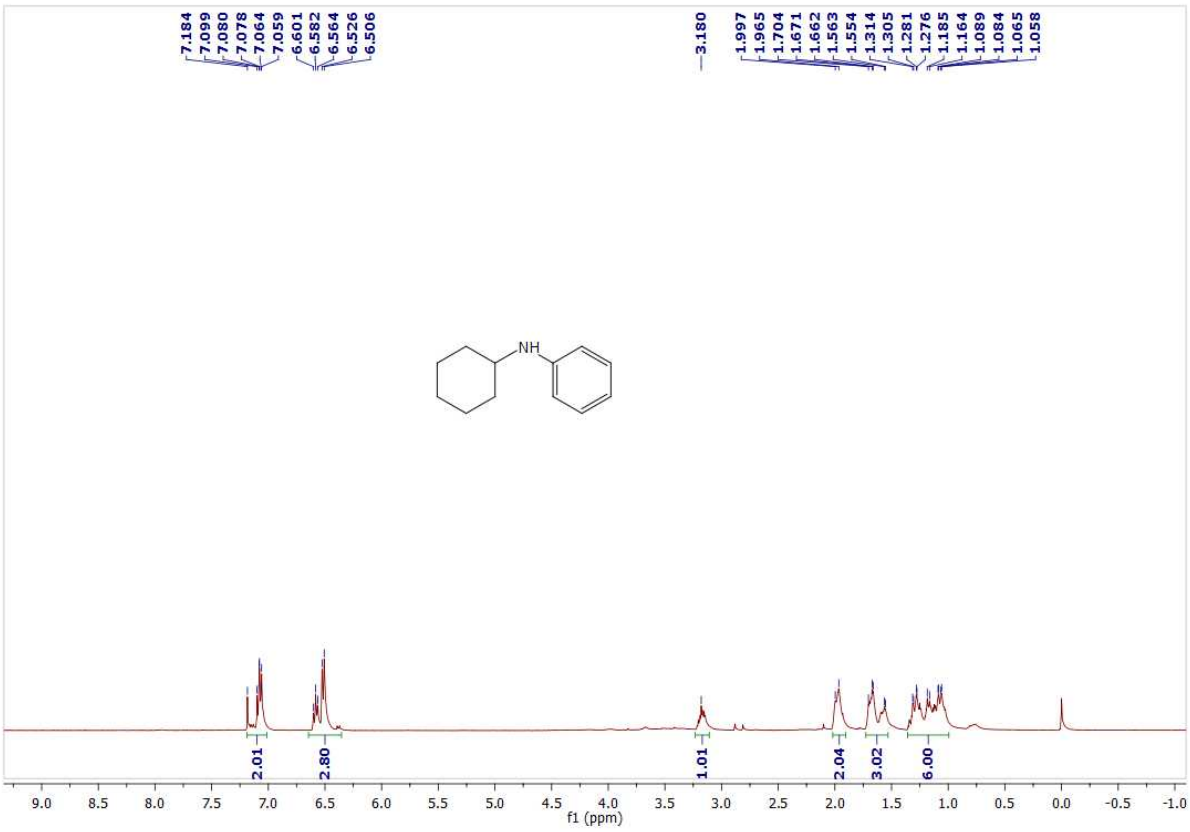
^{13}C NMR (100 MHz, Chloroform-*d*) Spectra of **7c**



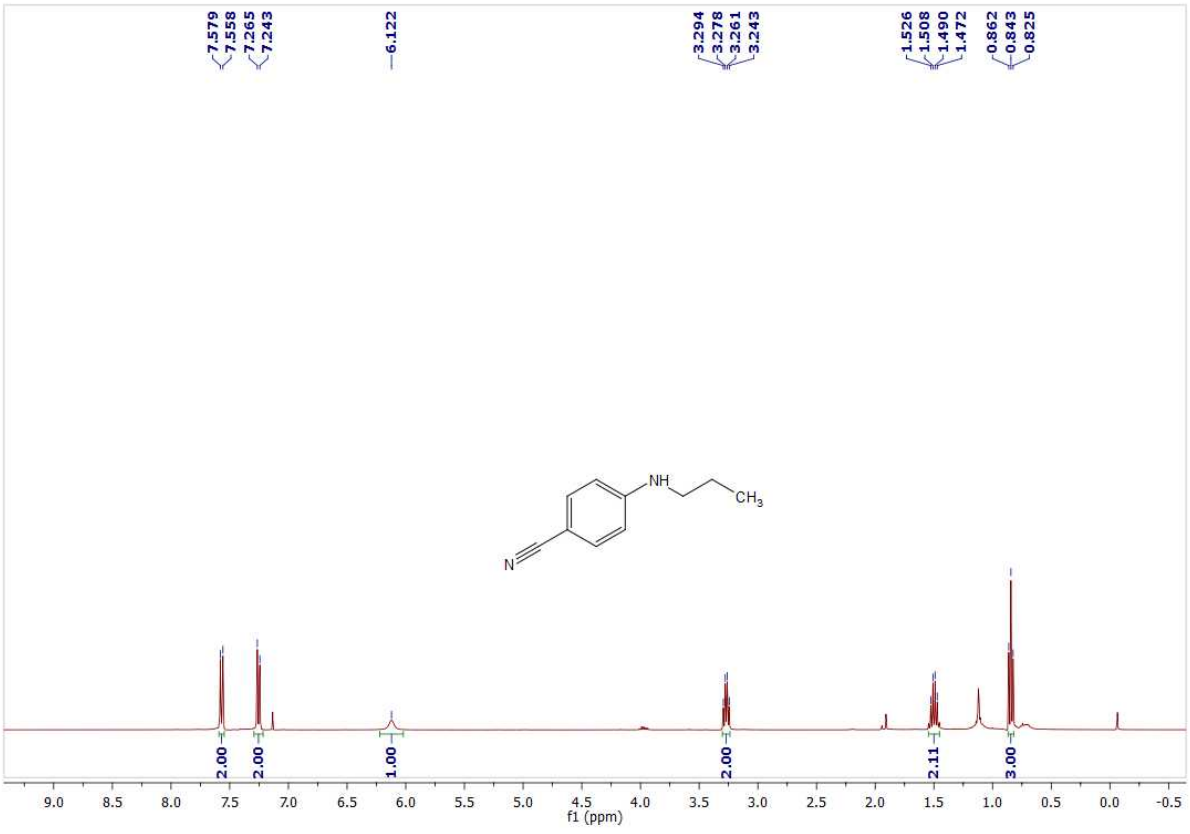
^{1}H NMR (500 MHz, Chloroform-*d*) Spectra of **7d**



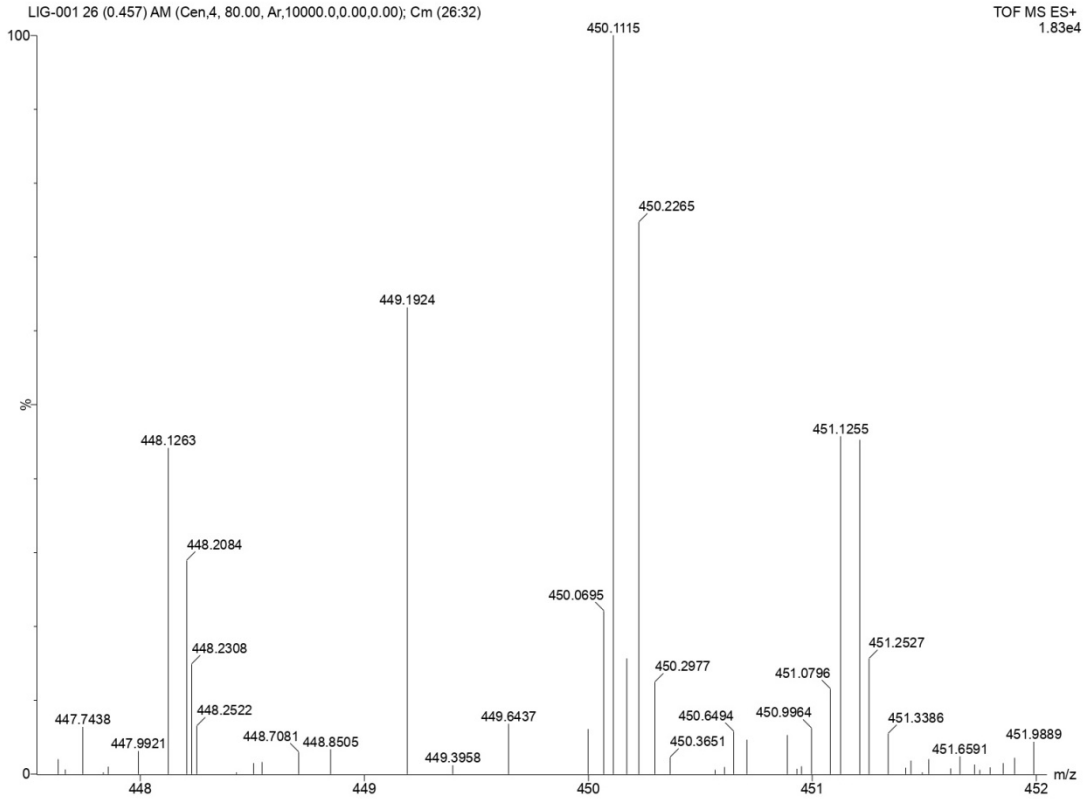
^{13}C NMR (100 MHz, Chloroform-*d*) Spectra of **7d**



^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **7e**



^{1}H NMR (400 MHz, Chloroform-*d*) Spectra of **7f**



Mass Spectra of intermediate 3