Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Synthesis of Tertiary arylamines: Lewis acid-catalyzed direct reductive *N*-alkylation of secondary amines with ketones through an alternative pathway**

Onkar S. Nayal, Maheshwar S. Thakur, Vinod Bhatt, Manoranjan Kumar, Neeraj Kumar,[$] Bikram Singh and Upendra Sharma**

[**] Department of Natural Product Chemistry and Process Development, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh 176 061, India.

Academy of Scientific and Innovative Research, New Delhi 110001, India.

E-mail: upendra@ihbt.res.in; bikramsingh@ihbt.res.in

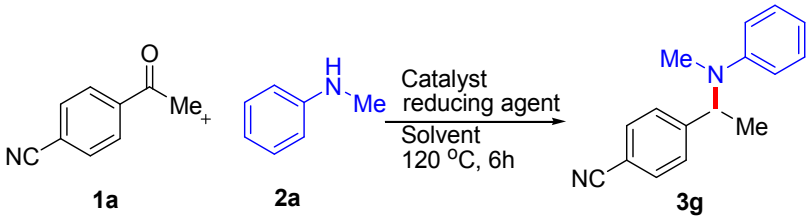
Supporting information

Table of Contents

General considerations: All reagents and solvents were obtained from commercial suppliers and were used without further purification for all reaction. Column chromatography was carried out with 60−120 and 230−400 mesh silica gel and monitored with TLC on silica gel 60 F254 plates using UV light as visualizing agent. ^{1}H and ^{13}C NMR spectra were obtained on 300 MHz and 600 MHz NMR instruments. Chemical shifts are reported in ppm relative to $CHCl_3$ downfield from an internal standard. Mass spectra were recorded on electrospray ionization quadrupole time of flight (ESI-QTOF-MS) mass spectrometer. The GC analysis was carried out on Gas Chromatograph, an AOC-20i autosampler coupled, and BP 20 capillary column (30 m × 0.25 mm i.d. 0.25 µm). The initial temperature of the column was held at 70 °C for 5 min and was programmed to 230 °C at 4 °C/min, then held for 15 min at 230 °C, the sample injection volume was 1 µL in GC grade dichloromethane. Nitrogen was used as the carrier gas at a flow rate of 1.1 mL/min.

Optimization detail

Table S1: Optimization of Reaction Conditions for Reductive *N*-Alkylation of *N*-methyl Aniline with 4-Acetylbenzonitrile.[a]



1a 2a 3g

entry	catalyst	reducing agent	solvent	additive	yield%[b]
1	$Fe(OTf)_2$	PMHS	toluene	-	NR
2	$Zn(OTf)_2$	PMHS	toluene	-	NR
3	$Cu(OTf)_2$	PMHS	toluene	-	NR
4	$Ni(OTf)_2$	PMHS	toluene	-	NR
5	$Ag(OTf)_2$	PMHS	toluene	-	NR
6	$Sc(OTf)_2$	PMHS	toluene	-	NR
7	$Bi(OTf)_3$	PMHS	toluene	-	NR
8	$In(OTf)_3$	PMHS	toluene	-	NR
9	**$Sn(OTf)_2$**	**PMHS**	**toluene**	**-**	**89**
10	$Sn(OTf)_2$	PMHS	toluene	-	50[c]
11	$Sn(OTf)_2$	PMHS	toluene	-	87[d]
12	-	PMHS	toluene	-	NR

13	$Sn(OTf)_2$	PMHS	benzene	-	63
14	$Sn(OTf)_2$	PMHS	MeCN	-	NR
15	$Sn(OTf)_2$	PMHS	DMF	-	NR
16	$Sn(OTf)_2$	PMHS	DMSO	-	NR
17	$Sn(OTf)_2$	PMHS	*n*-BuOH	-	NR
18	$Sn(OTf)_2$	PMHS	toluene	-	--[e]
19	$Sn(OTf)_2$	Ph_2SiH_2	toluene	-	34
20	$Sn(OTf)_2$	$PhsiH_3$	toluene	-	32
21	$Sn(OTf)_2$	Et_3SiH	toluene	-	27
22	$Sn(OTf)_2$	$HSiMe(OEt)_2$	toluene	-	62
23	$Sn(OTf)_2$	PMHS	toluene	-	64[f]
24	$Sn(OTf)_2$	PMHS	toluene	-	75[g]
25	$Sn(OTf)_2$	PMHS	toluene	-	89[h]
26	$Sn(OTf)_2$	-	toluene	-	trace
27	$Sn(OTf)_2$	PMHS	toluene	H_2O	89[i]
28	$Sn(OTf)_2$	PMHS	toluene	H_2O	75[j]
29	$Sn(OTf)_2$	PMHS	toluene	H_2O	13[k]
30	$Sn(OTf)_2$	PMHS	toluene	EtOH	61
31	$Sn(OTf)_2$	PMHS	toluene	MeOH	65
32	$Sn(OTf)_2$	PMHS	toluene	-	43[l]
33	$Sn(OTf)_2$	PMHS	toluene	-	76[m]
34	$Sn(OTf)_2$	PMHS	toluene	-	89[n]
35	$Sn(OTf)_2$	PMHS	toluene	-	56[o]
36	$Sn(OTf)_2$	PMHS	toluene	-	87[p]

[a]Reaction conditions: Catalyst (10 mol%), **1a** (2 mmol), **1b** (1 mmol), reducing agent (2 mmol), solvent (3 mL), 120 °C, 7 h. [b]GC yield using hexadecane as an internal standard. [c] 5 mol% of $Sn(OTf)_2$. [d] 15 mol% of $Sn(OTf)_2$. [e]Dry toluene and N_2 atm. [f] 1 equiv of PMHS. [g]1.5 equiv of PMHS. [h]3equiv of PMHS. [i]The reaction was carried out using 2 equiv. H_2O as an additive. [j]The reaction was carried out using 3 equiv. H_2O as an additive. [k]The reaction was carried out using 5 equiv. H_2O as an additive. [l]quantity of **1a** used was 1.0 mmol. [m]quantity of **1a** used was 1.5 mmol. [n]quantity of **1a** used was 2.0mmol. [o] At 100 °C.[p]At 130 °C. NR = no reaction

General experimental procedures

Experimental procedures for the synthesis of tertiary arylamines (Table 2): To an oven dried 15 mL test tube was added $Sn(OTf)_2$ (0.1 mmol), *N*-alkylaniline (1.0 mmol), ketone (2.0 mmol), toluene (3 mL) and PMHS (2.0 mmol). The test tube was capped and the reaction mixture was then heated to 120 °C under air in an oil bath. After completion of the reaction as observed by TLC, the reaction mixture was allowed to cool, add 20 mL ethyl acetate, filtered and passed through anhydrous sodium sulphate. The crude product was purified by column chromatography over silica gel (60-120 and 230-400 mesh) with an appropriate mixture of *n*-hexane and ethyl acetate.

***Experimental procedures for the synthesis of secondary anilines (Table 3)*:** To an oven dried 15 mL test tube was added $Sn(OTf)_2$ (0.1 mmol), aniline (1.0 mmol), ketone (2.0 mmol), toluene (3 mL) and PMHS (2.0 mmol). The test tube was capped and the reaction mixture

was then heated to 120 °C under air in an oil bath. After completion of the reaction as observed by TLC, the reaction mixture was allowed to cool, add 20 mL ethyl acetate, filtered and passed through anhydrous sodium sulphate. The crude product was purified by column chromatography over silica gel (60-120 and 230-400 mesh) with an appropriate mixture of *n*-hexane and ethyl acetate.

Experimental procedures for the synthesis of tertiary arylamines (Table 4): To an oven dried 15 mL test tube was added $Sn(OTf)_2$ (0.1 mmol), aniline (1.0 mmol), aldehydes (2.0 mmol), toluene (3 mL) and PMHS (2.0 mmol). The test tube was capped and the reaction mixture was then heated to 120 °C under air in an oil bath. After completion of the reaction as observed by TLC, the reaction mixture was allowed to cool, add 20 mL ethyl acetate, filtered and passed through anhydrous sodium sulphate. The crude product was purified by column chromatography over silica gel (60-120 and 230-400 mesh) with an appropriate mixture of *n*-hexane and ethyl acetate.

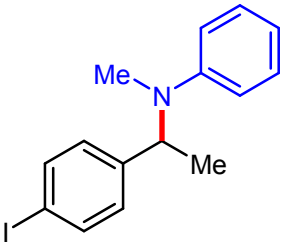
Experimental procedures for the synthesis of heterocyclic amines (Table 5): To an oven dried 15 mL test tube was added $Sn(OTf)_2$ (0.1 mmol), amine (1.0 mmol), carbonyl (2.0 mmol), toluene (3 mL) and PMHS (2.0 mmol). The test tube was capped and the reaction mixture was then heated to 120 °C under air in an oil bath. After completion of the reaction as observed by TLC, the reaction mixture was allowed to cool, add 20 mL ethyl acetate, filtered and passed through anhydrous sodium sulphate. The crude product was purified by column chromatography over silica gel (60-120 and 230-400 mesh) with an appropriate mixture of *n*-hexane and ethyl acetate.

Experimental Procedures for the Synthesis of isoindolinones and phthalazinones (Table 6): To an oven dried 15 mL test tube was added $Sn(OTf)_2$ (0.1 mmol), aniline or phenyl hydrazine derivates (1.0 mmol), 2-carboxybenzaldehyde (1.0 mmol), toluene (3 mL) and PMHS (2.0 mmol). The test tube was capped and the reaction mixture was then heated to 120 °C under air in an oil bath. After completion of the reaction as observed by TLC, the reaction mixture was allowed to cool, add 20 mL ethyl acetate, filtered and passed through anhydrous sodium sulphate. The crude product was purified by column chromatography

over silica gel (60-120 and 230-400 mesh) with an appropriate mixture of *n*-hexane and ethyl acetate.

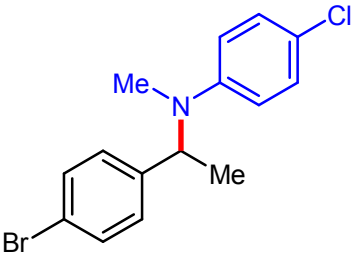
Characterization data of synthesized compounds

***N*-1-(4-Iodophenyl)ethyl-*N*-methylaniline (3a)**



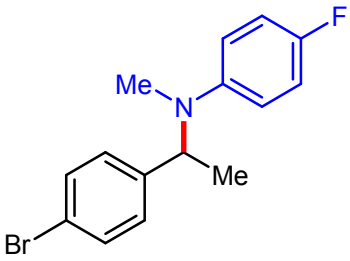
This compound was obtained as pale yellow oil with an isolated yield 83% (280 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.60 (d, 3H, J = 6.6 Hz), 2.76 (s, 3H), 5.13 (q, 1H, J = 7.0 Hz), 6.85 (t, 1H, J = 6.7 Hz), 6.92 (d, 2H, J = 7.7 Hz), 7.15 (d, 2H, J = 7.6 Hz), 7.35 (t, 2H, J = 7.2 Hz), 7.73 (d, 2H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.4, 32.1, 56.5, 92.4, 113.4, 117.2, 129.1, 129.4, 137.6, 142.8, 150.1; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{15}H_{17}IN$, 338.0406; found, 338.0389.

4-Chloro-*N*-1-(4-bromophenyl)ethyl-*N*-methylaniline (3b)



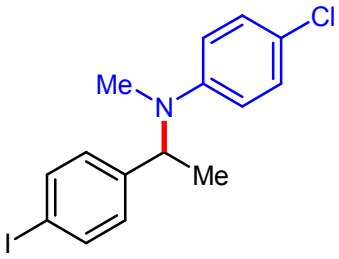
This compound was obtained as yellow oil with an isolated yield 73% (236 mg);mp 113-114 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.53 (d, 3H, J = 6.9 Hz), 2.66 (s, 3H), 4.99 (q, 1H, J = 6.8 Hz), 6.74 (d, 2H, J = 8.6 Hz), 7.16−7.19 (m, 4H), 7.46 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.4, 32.1, 56.7, 114.5, 120.9, 121.9, 128.6, 129.0, 131.6, 141.5, 148.6; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{15}H_{16}BrClN$, 324.0155; found, 324.0102.

4-Fluoro-*N*-1-(4-bromophenyl)ethyl-*N*-methylaniline (3c)



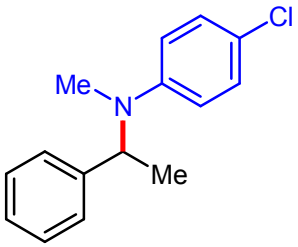
This compound was obtained as pale yellow oil with an isolated yield 71% (218 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.52 (d, 3H, J = 6.9 Hz), 2.65 (s, 3H), 4.92 (q, 1H, J = 6.8 Hz), 6.78–6.80 (m, 2H), 6.98 (t, 2H, J = 8.7 Hz), 7.20 (d, 2H, J = 8.5 Hz), 7.47(d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.4, 32.7, 57.9, 115.4 (d, J = 6.5 Hz), 115.6 (d, J = 21.9 Hz), 120.8, 128.8, 131.5, 141.8, 146.8, 155.9 (d, J = 236.3 Hz); HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{15}H_{16}BrFN$, 308.0450; found, 308.0431.

4-Chloro-*N*-1-(4-iodophenyl)ethyl-*N*-methylaniline (3d)



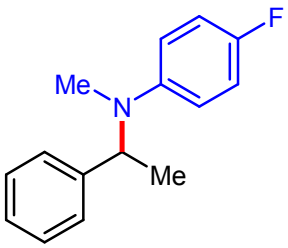
This compound was obtained as pale yellow solid with an isolated yield 75% (279 mg); mp 79-80 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.53 (d, 3H, J = 6.9 Hz), 2.67 (s, 3H), 4.99 (q, 1H, J = 6.8 Hz), 6.74 (d, 2H, J = 8.8 Hz), 7.05 (d, 2H, J = 8.2 Hz), 7.19 (d, 2H, J = 9.1 Hz), 7.66 (d, 2H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.5, 32.2, 56.8, 92.5, 114.5, 121.8, 128.9, 129.0, 137.6, 142.2, 148.6. HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{15}H_{16}ICIN$, 372.0016; found, 372.0001.

4-Chloro-*N*-1-phenylethyl-*N*-methylaniline (3e)[1]



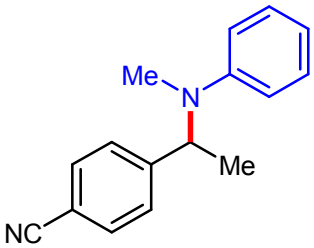
This compound was obtained as pale yellow oil with an isolated yield 73% (179 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.60 (d, 3H, J = 6.9 Hz), 2.72 (s, 3H), 5.11 (q, 1H, J = 6.9 Hz), 6.79 (d, 2H, J = 8.9 Hz), 7.23 (d, 2H, J = 9.0 Hz), 7.30−7.35 (m, 3H), 7.39 (t, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.5, 32.1, 56.9, 114.3, 121.4, 126.9, 127.1, 128.5, 129.0, 142.4, 148.9; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{17}ClN$, 246.1050; found, 246.1035.

4-Fluoro-*N*-1-phenylethyl-*N*-methylaniline (3f)[2]



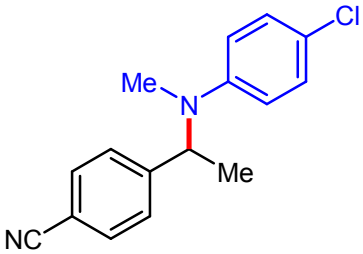
This compound was obtained as pale yellow oil with an isolated yield 73% (167 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.72 (d, 3H, J = 6.9 Hz), 2.84 (s, 3H), 5.17 (q, 1H, J = 6.9 Hz), 6.96−6.98 (m, 2H), 7.15 (t, 2H, J = 8.8 Hz), 7.46 (t, 1H, J = 6.9 Hz), 7.50−7.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.4, 32.6, 58.1, 115.1(d, J = 7.3 Hz), 115.5 (d, J = 21.9 Hz), 126.9, 128.4, 142.7, 147.1, 155.7 (d, J = 235.9 Hz); HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{15}H_{17}FN$, 230.1345; found, 230.133.

***N*-1-(4-Cyanophenyl)ethyl-*N*-methylaniline (3g)**



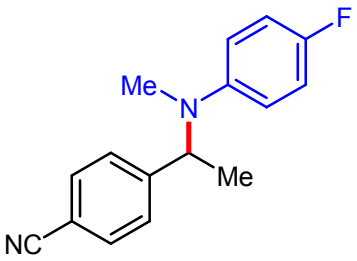
This compound was obtained as yellow oil with an isolated yield 79% (186 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.63 (d, 3H, *J* = 6.9 Hz) 2.76 (s, 3H), 5.17 (q, 1H, *J* = 6.9 Hz), 6.83 (t, 1H, *J* = 7.3 Hz), 6.88 (d, 2H, *J* = 8.3 Hz), 7.31 (t, 2H, *J* = 7.9 Hz), 7.5 (d, 2H, *J* = 8.2 Hz), 7.65 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.6, 32.3, 56.9, 110.8, 113.5, 117.6, 118.9, 127.7, 129.4, 132.4, 148.9, 149.9; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{16}H_{17}N_2$, 237.1392; found, 237.1374.

4-Chloro-*N*-1-(4-cyanophenyl)ethyl-*N*-methylaniline (3h)



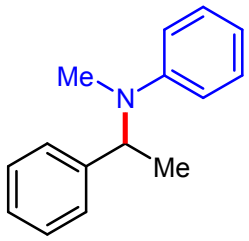
This compound was obtained as yellow oil with an isolated yield 61% (164 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.58 (d, 3H, *J* = 6.9 Hz), 2.69 (s, 3H), 5.04 (q, 1H, *J* = 6.8 Hz), 6.72 (d, 2H, *J* = 8.9 Hz), 7.17 (d, 2H, *J* = 8.9 Hz), 7.40 (d, 2H, *J* = 8.1 Hz), 7.61 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.6, 32.4, 57.1, 110.9, 114.6, 118.9, 122.2, 127.6, 129.1, 132.4, 148.3, 148.4; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{16}N_2Cl$, 271.1002; found, 271.0992.

4-Fluoro-*N*-1-(4-cyanophenyl)ethyl-*N*-methylaniline (3i)



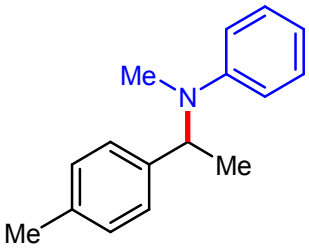
This compound was obtained as yellow oil with an isolated yield 69% (175 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.69 (d, 3H, J = 6.9 Hz), 2.81 (s, 3H), 5.11 (q, 1H, J = 6.8 Hz), 6.90−6.92 (m, 2H), 7.09 (t, 2H, J = 8.7 Hz), 7.51 (d, 2H, J = 8.1 Hz), 7.76 (d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.5, 33.1, 58.4, 110.8, 115.6 (d, J = 21.9 Hz), 115.6, 118.9, 127.7, 132.3, 146.6, 148.6, 156.0 (d, J = 236.8 Hz); HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{16}N_2F$, 255.1298; found, 255.1279.

_N_-1-Phenylethyl-_N_-methylaniline (3j)[2]



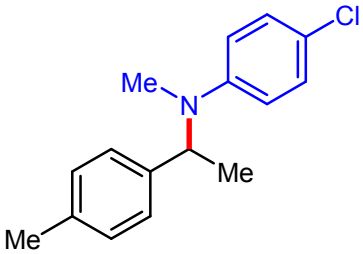
This compound was obtained as yellow oil with an isolated yield 92% (194 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.65 (d, 3H, J = 6.9 Hz), 2.78 (s, 3H), 5.24 (q, 1H, J = 6.9 Hz), 6.84 (t, 1H, J = 7.2 Hz), 6.95 (d, 2H, J = 8.2 Hz), 7.34−7.37 (m, 3H), 7.4 (d, 4H, J = 4.9 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.4, 31.9, 56.7, 113.2, 116.8, 126.9, 127.0, 128.5, 129.3, 142.9, 150.3; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{18}N$, 212.1439; found, 212.1417.

_N_-1-(4-methylphenyl)ethyl-_N_-methylaniline (3k)[3]



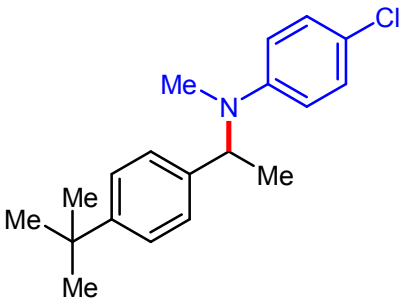
The title compound was obtained as colourless oil with an isolated 85% (191 mg); ^{1}H NMR (CDCl3, 600 MHz) δ 1.58 (d, 3H, J = 6.8 Hz), 2.39 (s, 3H), 2.72 (s, 3H), 5.16 (q, 1H, J = 6.4 Hz), 6.78 (t, 1H, J = 7.1 Hz), 6.89 (d, 2H, J = 7.9 Hz), 7.19 (d, 2H, J = 7.7 Hz), 7.26 (d, 2H, J = 7.3 Hz), 7.30 (d, 2H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.3, 20.9, 31.8, 56.4, 113.2, 116.7, 126.9, 129.1, 129.2, 136.4, 139.8, 150.3; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{20}N$, 226.1596; found, 226.1584.

4-Chloro-*N*-1-(4-methylphenyl)ethyl-*N*-methylaniline (3l)[3]



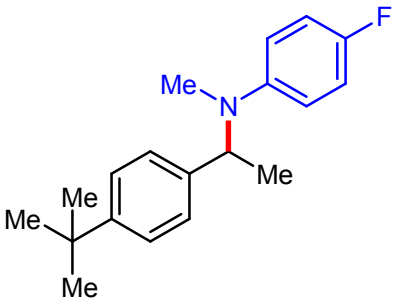
This compound was obtained as pale yellow oil with an isolated yield 73% (189 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.27 (d, 3H, J = 6.8 Hz), 3.08 (s, 3H), 3.39 (s, 3H), 5.77 (d, 1H, J = 6.5 Hz), 7.49 (d, 2H, J = 8.3 Hz), 7.87−7.91 (m, 6H), ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.5, 21.0, 32.0, 56.6, 114.2, 121.3, 126.8, 128.9, 129.2, 136.6, 139.3, 148.8; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{19}ClN$, 260.1206; found, 260.1188.

4-Chloro-*N*-1-(4-*tert*-butylphenyl)ethyl-*N*-methylaniline (3m)



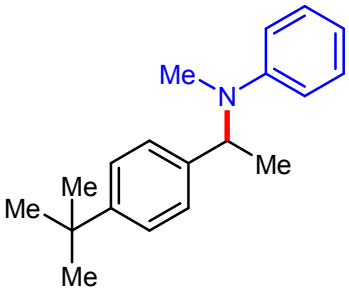
This compound was obtained as yellow oil with an isolated yield 69% (208 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.39 (s, 9H), 1.59 (d, 3H, *J* = 6.9 Hz), 2.72 (s, 3H), 5.10 (q, 1H, *J* = 6.8 Hz), 6.80 (d, 2H, *J* = 9.0 Hz), 7.23 (d, 2H, *J* = 9.0 Hz), 7.28 (d, 2H, *J* = 8.3 Hz), 7.42 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.5, 31.5, 32.1, 34.5, 56.6, 114.2, 121.3, 125.4, 126.6, 129.0, 139.3, 148.9, 149.9; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{19}H_{25}ClN$, 302.1676; found 302.1665,

4-Fluoro -*N*-1-(4-*tert*-butylphenyl)ethyl)-*N*-methylaniline (3n)[4]



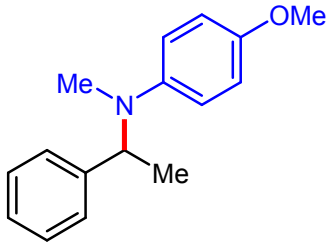
The title compound was obtained as pale yellow oil with an isolated yield 71% (202 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.39 (s, 9H), 1.57 (d, 3H, *J* = 6.8 Hz), 2.69 (s, 3H), 5.03 (q, 1H, *J* = 6.7 Hz), 6.83 (q, 2H, *J* = 4.2 Hz), 7.00 (t, 2H, *J* = 8.4 Hz), 7.30 (d, 2H, *J* = 7.9 Hz), 7.41 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.2, 31.5, 32.5, 34.5, 57.7, 114.9 (d, *J* = 7.3 Hz), 115.5 (d, *J* = 21.9 Hz), 125.3, 126.7, 139.6, 147.2, 149.8, 155.6 (d, *J* = 235.5 Hz); HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{19}H_{25}FN$, 286.1971; found, 286.1961.

***N*-1-(4-*tert*-Butylphenyl)ethyl-*N*-methylaniline (3o)**



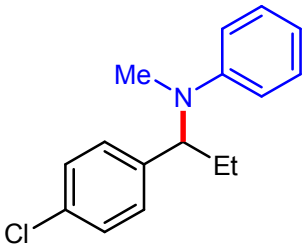
This compound was obtained as pale yellow oil with an isolated yield 85% (227 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.39 (s, 9H), 1.61 (d, 3H, J = 6.9 Hz), 2.75 (s, 3H), 5.19 (q, 1H, J = 6.6 Hz), 6.80 (t, 1H, J = 6.9 Hz), 6.93 (d, 2H, J = 7.7 Hz), 7.32 (t, 4H, J = 7.44 Hz), 7.42 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.3, 31.5, 34.5, 56.3, 113.1, 116.6, 125.3, 126.7, 129.3, 139.7, 149.7, 150.3; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{19}H_{26}N$, 268.2065; found, 268 2049.

_N_-1-phenylethyl-4-methoxy-_N_-methylaniline (3p)[5]



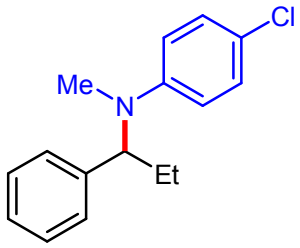
The title compound was obtained as white solid with an isolated yield 78% (187 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.59 (d, 3H, J = 6.7 Hz), 2.71 (s, 3H), 3.85 (s, 3H), 5.01 (t, 1H, J = 6.4 Hz), 6.95 (s, 4H), 7.43 (s, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz)δ 16.3, 33.1, 55.8, 58.9, 114.7, 116.5, 126.9, 127.2, 128.4, 143.1, 145.2, 152.4; HRMS (ESI-TOF) m/z:[M+H] calcd for $C_{16}H_{20}NO$, 242.1545; found, 242.1525.

_N_-1-(4-Chlorophenyl)propyl-_N_-methylaniline (3q)



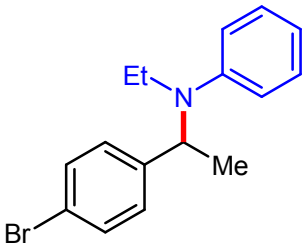
This compound was obtained as yellow oil with an isolated yield 90% (233 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.05 (t, 3H, J = 7.3 Hz), 1.99−2.15 (m, 2H), 2.74 (s, 3H), 4.88 (q, 1H, J = 5.0 Hz), 6.79 (t, 1H, J = 7.2 Hz), 6.89 (d, 2H, J = 8.2 Hz), 7.24 (d, 2H, J= 8.4 Hz), 7.29−7.33 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 11.7, 24.9, 31.6, 62.7, 113.1, 116.9, 128.5, 128.7, 129.3, 132.7, 140.3, 150.8; HRMS (ESI-TOF) m/z**:** [M+H] calcd for $C_{16}H_{19}ClN$, 260.1206; found, 260.1192.

4-Chloro-*N*-1-(phenyl)propyl-*N*-methylaniline (3r)



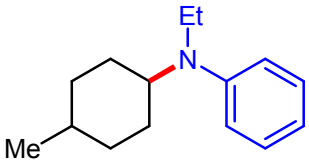
This compound was obtained as Colourless oil with an isolated yield 67% (173 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.00 (t, 3H, J = 7.3 Hz), 1.96−2.15 (m, 2H), 2.71 (s, 3H), 4.81 (q, 1H, J = 5.0 Hz), 6.76 (d, 2H, J = 9.0 Hz), 7.18 (d, 2H, J = 9.0 Hz), 7.26 (t, 3H, J = 8.7 Hz), 7.33 (t, 2H, J = 7.5 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz) δ 11.7, 24.9, 31.8, 63.4, 114.0, 121.1, 127.0, 127.1, 128.4, 128.9, 141.3,149.6; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{19}ClN$, 260.1206; found, 260.1193.

***N*-1-(4-Bromo phenyl)ethyl-*N*-ethylaniline (3s)**[3]



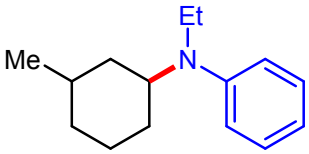
This compound was obtained as pale yellow oil with an isolated yield 71% (215 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.09 (t, 3H, *J* = 6.9 Hz), 1.57 (d, 3H, *J* = 6.9 Hz), 3.21 (q, 2H, *J* = 7.0 Hz), 4.99 (q, 1H, *J* = 6.9 Hz), 6.74 (t, 1H, *J* = 7.2 Hz), 6.81 (d, 2H, *J* = 8.3 Hz), 7.20 (d, 2H, *J* = 8.3 Hz), 7.24 (t, 2H, *J* = 7.9 Hz), 7.45 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ* 14.2, 17.7, 40.4, 56.6, 114.2, 117.0, 120, 128.8, 129.2, 131.4, 142.4, 148.3; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{19}BrN$, 304.0701; found, 304.0691.

***N*-1-(4-Methylcyclohexyl)-*N*-ethylaniline (3t)**



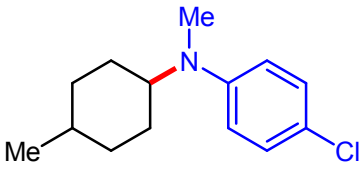
This compound was obtained as pale yellow oil with an isolated yield 76% (165 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.98 (d, 3H, *J* = 6.5 Hz), 1.07 (d, 3H, *J* = 7.2 Hz), 1.09−1.17 (m, 2H), 1.19-1.23 (m, 6H), 1.38−1.57 (m, 4H), 1.64−1.75 (m, 7H), 1.83−2.00 (m, 5H), 3.30−3.37 (m, 4H), 3.55−3.61 (m, 2H), 6.70 (q, 2H, *J* = 7.6 Hz), 6.79 (t, 4H, *J* = 9.2 Hz), 7.24−7.28 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ* 15.2, 15.3, 17.7, 22.4, 24.8, 26.8, 30.3, 31.5, 32.5, 34.9, 39.0, 39.5, 57.1, 57.4, 112.6, 113.1, 115.6, 115.9, 129.2, 148.6; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{24}N$, 218.1909; found, 218.1899

***N*-1-(4-Methylcyclohexyl)-*N*-ethylaniline (3u)**



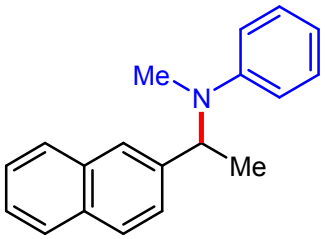
This compound was obtained as pale yellow oil with an isolated yield 76% (165 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.96 (d, 3H, *J* = 6.5 Hz), 1.12 (d, 3H, *J* = 7.3 Hz), 1.15−1.19 (m, 6H), 1.35−1.57 (m, 7H), 1.62−1.71 (m, 6H), 1.85 (d, 4H, J = 10.6 Hz), 2.19−2.20 (m, 1H), 3.26−3.31 (m, 4H), 3.61 (t, 1H, *J* = 11.2 Hz), 3.83−3.87 (m, 1H), 6.67 (q, 2H, *J* = 7.1 Hz), 6.74−6.77 (m, 4H), 7.23 (t, 4H, *J* = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ* 15.1, 15.2, 18.2, 20.8, 22.7, 25.6, 28.4, 30.1, 31.1, 31.4, 32.8, 34.7, 36.0, 38.9, 39.0, 39.4, 51.4, 56.9, 112.6, 112.9, 115.6, 115.8, 129.2, 148.5, 148.7; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{24}N$, 218.1909; found, 218.1899.

4-Chloro-*N*-4-methylcyclohexyl-*N*-methylaniline (3v)



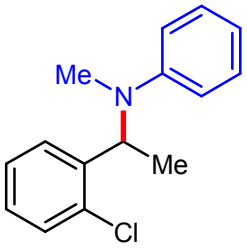
This compound was obtained as pale yellow oil with an isolated yield 83% (196 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) *δ* 0.94 (d, 3H, *J* = 6.5 Hz), 1.03 (d, 3H, *J* = 7.2 Hz), 1.08−1.12 (m, 2H), 1.34−1.39 (m, 1H), 1.50−155 (m, 4H), 1.63−1.67(m, 4H), 1.69−1.82 (m, 6H), 1.96−1.98 (m, 1H), 2.75 (s, 3H), 2.79 (s, 3H), 3.47-3.53 (m, 2H), 6.70 (t, 4H, *J* = 7.6 Hz), 7.17 (d, 4H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) *δ* 17.5, 22.3, 24.0, 26.5, 31.3, 31.4, 31.7, 32.3, 34.7, 58.3, 58.7, 114.3, 114.5, 120.9, 121.0, 128.8, 148.8; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{14}H_{21}ClN$, 238.1363; found, 238.1355.

***N*-1-naphathylethyl-*N*-methylaniline (3w)**[3]



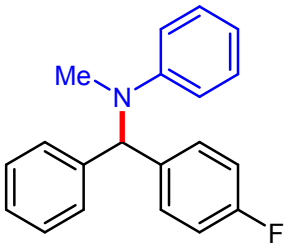
This compound was obtained as yellow solid with an isolated yield 83% (216 mg); mp 93-94 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.76 (d, 3H, J = 6.8 Hz), 2.80 (s, 3H), 5.39 (q, 1H, J = 6.8 Hz), 6.90 (t, 1H, J = 7.3 Hz), 7.02 (d, 2H, J = 8.2 Hz), 7.41 (t, 2H, J = 7.9 Hz), 7.56−7.61(m, 3H), 7.87−7.95 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.1, 32.0, 56.7, 113.3, 116.9, 125.1, 125.9, 126.2, 126.2, 127.7, 128.1, 128.2, 129.4, 132.7, 133.5, 140.6, 150.4; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{19}H_{20}N$, 262.1596; found, 262.1574.

***N*-1-(2-Chlorophenyl)ethyl-*N*-methylaniline (3x)**



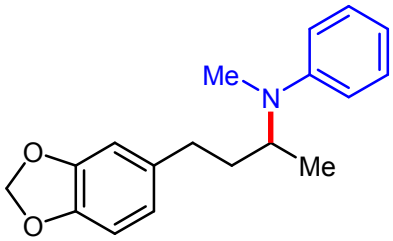
This compound was obtained as pale yellow solid with an isolated yield 83% (203 mg); mp 60-62 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.64 (d, 3H, J = 6.9 Hz), 2.96 (s, 3H), 5.36 (q, 1H, J = 6.9 Hz), 6.82 (t, 1H, J = 7.2 Hz), 6.88 (d, 2H, J = 8.4 Hz), 7.25−7.34 (m, 4H), 7.43 (d, 1H, J = 7.6 Hz), 7.47 (d, 1H, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 17.1, 32.4, 54.8, 112.9, 116.8, 127.0, 127.8, 128.3, 129.2, 130.0, 133.9, 141.3, 149.5. HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{17}ClN$, 246.1050; found, 246.1031.

***N*-[(4-Fluoro-phenyl)phenylmethyl]-*N*-methylaniline(3y)**



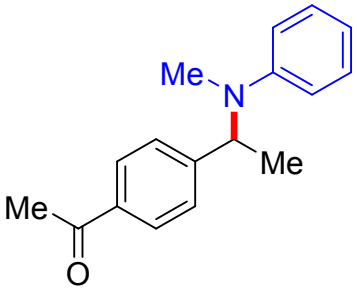
This compound was obtained as yellow oil with an isolated yield 45% (131 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.63 (s 3H), 6.07 (s, 1H), 6.66 (t, 1H, J = 7.3 Hz), 6.70 (d, 2H, J = 8.2 Hz), 6.92 (d, 2H, J = 8.6 Hz), 7.06−7.10 (m, 4H), 7.14 (t, 2H, J =7.9 Hz), 7.20 (t, 1H, J =7.2 Hz), 7.25 (t, 2H, J =7.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 34.4, 66.5, 113.1, 115.2 (d, J = 21.1 Hz), 117.1, 127.3, 128.5, 128.6, 129.2, 130.3 (d, J = 7.8 Hz), 136.4, 140.5, 150, 162.9 (d, J = 245.5 Hz); HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{20}H_{19}NF$, 292.1502; found, 292.1495.

***N*-Methyl-*N*-phenyl-*N*, *α*-methyl- 1, 3-Benzodioxole-5-propanamine, (3z)**



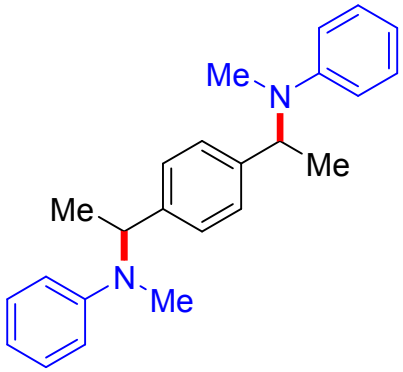
The title compound was obtained as white solid with an isolated yield 93% (263 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.21 (d, 3H, J = 6.6Hz), 178-1.84 (m, 1H), 1.96-2.02 (m, 1H), 2.57-2.67 (m, 2H), 2.83 (s, 3H), 3.97-4.02 (m, 1H), 5.97 (s, 2H), 6.67 (dd, 1H, J = 6.5 Hz), 6.73 (s, 1H), 6.78-6.81 (m, 2H), 6.84 (d, 2H, J= 8.1 Hz) 7.30-7.33(m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 17.0, 29.8, 32.9, 36.8, 52.7, 100.8, 108.2, 108.9, 113.2, 116.4, 121.2, 129.2, 136.0, 145.7, 147.6, 150.6; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{18}H_{22}NO_2$, 284.1651; found, 284.1532.

***N*-1-(4-Acetylphenyl)ethyl-*N*-methylaniline (3aa)**



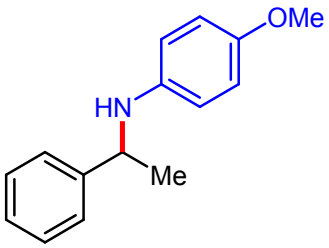
The title compound was obtained as yellow oil with an isolated yield 47% (119 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.61 (d, 3H, J = 6.9Hz), 2.61(s, 3H), 2.73 (s, 3H), 5.16 (q, 1H, J = 6.8Hz), 6.78 (t, 1H, J = 7.2Hz), 6.86 (d, 2H, J = 8.3Hz), 7.28 (t, 2H, J = 7.9Hz), 7.44 (d, 2H, J = 8.2Hz), 7.95 (d, 2H, J = 8.2Hz), ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.5, 26.6, 32.1, 56.8, 113.3, 117.2, 127.1, 128.6, 129.3, 148.7, 150.0, 197.7; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{17}H_{20}NO$, 254.1545; found, 254.1529.

1, 4- bis (1-N-Methylphenylamineethyl)benzene (3ab)



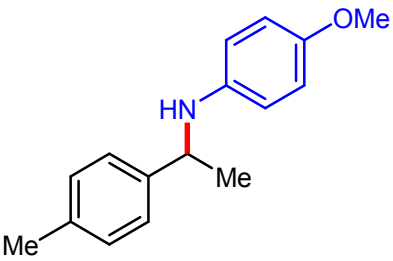
The title compound was obtained as pale yellow oil with an isolated yield 51% (175 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.60 (d, 6H, J = 6.9Hz), 2.73 (s, 6H), 5.18 (q, 2H, J = 6.8Hz), 6.79 (t, 2H, J = 7.2Hz), 6.90 (d, 4H, J = 8.2Hz), 7.31 (t, 4H, J = 7.8Hz), 7.33 (s, 4H), ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.3, 31.9, 56.3, 113.1, 116.7, 127.0, 129.2, 141.4, 150.3; HRMS (ESI-TOF) m/z:[M+H] calcd for $C_{14}H_{29}N_2$, 345.2331; found, 345.2319.

4-Methoxy-*N*-(1-phenylethyl)aniline (6a)[5]



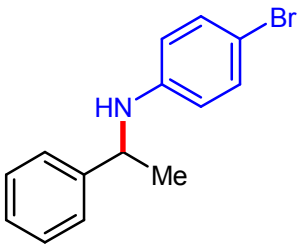
The title compound was obtained as yellow oil with an isolated yield 75% (170 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.59 (d, 3H, J = 6.7 Hz), 3.78 (s, 3H), 4.51 (q, 1H, J = 6.6 Hz), 6.58 (d, 2H, J = 8.7 Hz), 6.80 (d, 2H, J = 8.8 Hz), 7.32 (t, 1H, J = 6.9 Hz), 7.39–7.48 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 25.0, 54.3, 55.8, 114.7, 114.9, 125.9, 126.9, 128.7, 141.7, 145.6, 152.1; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{18}NO$, 228.1388; Found, 228.1369.

4-Methoxy-*N*-(1-*p*-tolylethyl)aniline (6b)[4]



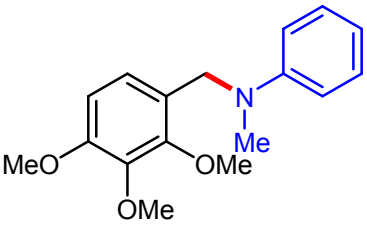
The title compound was obtained as yellow oil with an isolated yield 72% (174 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (d, 3H, J = 6.7 Hz), 2.42 (s, 3H), 3.74 (s, 3H), 4.41 (q, 1H, J = 6.7 Hz), 6.49 (d, 2H, J = 8.9 Hz), 6.75 (d, 2H, J = 8.9 Hz), 7.23 (d, 2H, J = 7.9 Hz), 7.36 (d, 2H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 25.1, 54.0, 55.8, 114.7, 114.9, 125.9, 129.3, 136.3, 141.8, 142.6, 152.0; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{20}NO$, 242.1545; found, 242.1536.

4-Bromo-*N*-(1-phenylethyl)aniline (6c)[4]



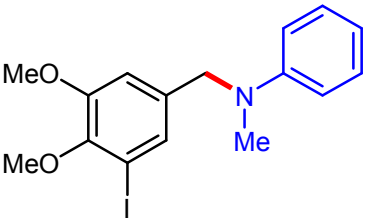
The title compound was obtained as yellow oil with an isolated yield 77 % (198 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.52 (d, 3H, J = 6.7 Hz), 4.44 (q, 1H, J = 6.7 Hz), 6.38 (d, 2H, J = 8.4 Hz), 7.16 (d, 2H, J = 8.4 Hz), 7.25-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 24.9, 53.5, 108.9, 114.9, 125.8, 127.1, 128.7, 131.8, 144.6, 146.2; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{14}H_{15}BrN$, 276.0388; found, 276.0365.

_N_-(2,3,4-Trimethoxybenzyl)-_N_-methylaniline (9a)[2]



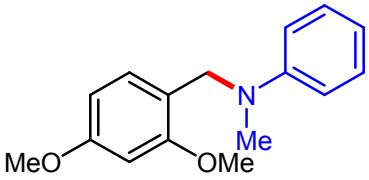
The title compound was obtained as pale yellow oil with an isolated yield 258 mg, (90%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.07 (s, 3H), 3.89 (s, 3H), 3.99-4.00 (overlapped, 6H), 4.58 (s, 2H), 6.65 (d, 1H, J= 8.5 Hz), 6.78 (t, 1H, J = 7.1 Hz), 6.85 (d, 2H, J = 8.1 Hz), 6.89 (d,1H, J = 8.5 Hz), 7.30 (t, 2H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.3, 51.7, 56.0, 60.7, 60.8, 107.2, 112.4, 116.4, 122.2, 124.4, 129.2,142.4, 149.4, 151.7, 152.9; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{17}H_{22}NO_3$, 288.1600; found, 288.1621.

_N_-(3-Iodo-4,5-dimethoxybenzyl)-_N_-methylaniline (9b)[2]



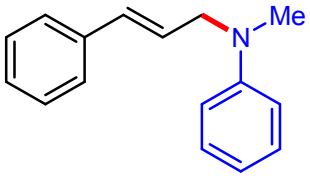
The title compound was obtained as greenish yellow solid with an isolated yield 357 mg, (93%), ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.02 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 4.44 (s, 2H), 6.77−6.80 (m, 4H), 7.27 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.6, 56.0, 56.3, 60.4, 92.6, 111.3, 112.8, 117.1, 128.4, 129.2, 137.3, 147.8, 149.8, 152.8; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{19}INO_2$, 384.0461; found, 384.0482.

_N_-(2,4-Dimethoxybenzyl)-_N_-methylaniline (9c)[1]



The title compound was obtained as yellow oil with an isolated yield 221 mg, (86%); ^{1}H NMR($CDCl_3$, 600 MHz) δ 3.08 (s, 3H), 3.83 (s, 3H), 3.88 (s, 3H), 4.52 (s,2H), 6.45 (d, 1H, *J* = 3.6 Hz), 6.55 (d, 1H, *J* = 2.3 Hz), 6.75 (t, 1H, *J* =7.2 Hz), 6.79 (d, 2H, *J* = 8.2 Hz), 7.04 (d, 1H, *J* = 8.3 Hz), 7.25-7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.4, 51.5, 55.2, 55.3, 98.5,103.8, 112.2, 116.1, 118.0, 128.0, 129.1, 149.8, 158.2, 159.9; HRMS(ESI-TOF) m/z: [M+H] calcd for $C_{16}H_{20}NO_2$, 258.1494; found, 258.1478.

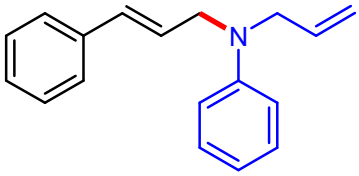
_N_-Cinnamyl-_N_-methylaniline (9d)[2]



The title compound was obtained as colourless oil with an isolated yield 212 mg, (95%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.01 (s, 3H), 4.11 (d, 2H, *J* =4.9 Hz), 6.27-6.30 (m, 1H), 6.56 (d, 1H, *J* = 15.8 Hz), 6.76 (t, 1H, *J* =6.9 Hz), 6.88 (d, 2H, *J* = 7.8 Hz), 7.23−7.34 (m, 5H), 7.38 (d, 2H, *J* =7.3 Hz); ^{13}C NMR (CDC_{l3}, 150 MHz) δ 38.0, 54.9, 112.7, 116.7,125.7, 126.3, 127.4, 128.5,

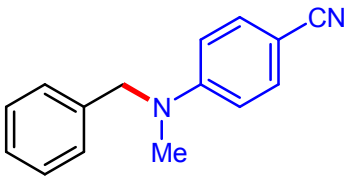
129.2, 131.3, 136.9, 149.6; HRMS (ESI-TOF)m/z: [M + H] calcd for $C_{16}H_{18}N$, 224.1439; found, 224.1429.

_N_- Cinnamyl-_N_-allylaniline (9e)



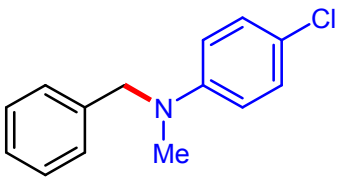
The title compound was obtained as pale yellow oil with an isolated yield 231 mg, (93%); ^{1}HNMR (600Mz) δ 4.04 (d, 1H, J = 4.0Hz), 4.15 (d, 1H J = 4.6Hz), 5.27 (d, 2H, J = 10.8Hz), 5.93-5.99 (m, 1H), 6.30, 6.34 (dt, 1H, J = 15.8 Hz, J = 5.1 Hz), 6.59 (d, 2H, J = 10.8Hz), 6.78 (t, 1H, J = 7.1Hz), 6.84 (d, 2H, J = 8.2 Hz), 7.29 (t, 3H, J = 7.3Hz), 7.37 (t, 2H, J = 7.5 Hz), 7.41 (d, 2H, J = 7.50Hz); ^{13}C NMR (600 Mz) δ 52.3, 52.7, 112.5, 116.2, 116.5, 126.0, 126.4, 127.4, 128.6, 129.2, 131.1, 134.1, 137.0, 148.8; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{18}H_{20}N$, 250.1596; found, 250.1581.

4-Cyano- _N_-methyl-_N_-benzylaniline (9f)



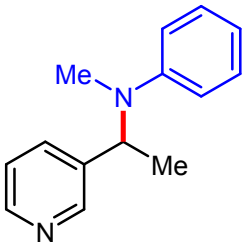
The title compound was obtained as yellow oil with an isolated yield 180 mg, (81%); ^{1}HNMR (600Mz) δ 3.13 (s, 3H), 4.62 (s, 2H), 6.69 (d, 2H, J = 8.1Hz), 7.18 (d, 2H, J = 6.6Hz), 7.28 (d, 1H, J = 6.6Hz), 7.34 (d, 2H, J = 6.8 Hz), 7.42 (d, 2H, J = 8.1Hz); ^{13}C NMR (600Mz) δ 38.8, 55.9, 97.7, 111.7, 120.6, 126.3, 127.4, 128.9, 133.5, 137.2, 152.0; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{15}H_{15}N_{2,}$ 223.1235; found, 223.1215.

4-Chloro-*N*-methyl-*N*-benzylaniline (9g)



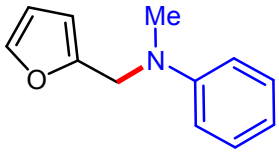
The title compound was obtained as pale yellow oil with an isolated yield 203 mg, (88%); ^{1}HNMR (600Mz) δ 3.08 (s, 3H), 4.58 (s, 2H), 6.72 (d, 2H, *J* = 9.0Hz), 7.23 (d, 2H, *J* = 9.0Hz), 7.29 (d, 2H, *J* = 7.5Hz), 7.34 (t, 1H, *J* = 9.0Hz), 7.40 (t, 2H, *J* = 7.5Hz); ^{13}C NMR (600Mz) δ 38.8, 56.7, 113.5, 121, 126.7, 127.1, 128.7, 129.0, 138.6, 148.3; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{14}H_{15}ClN$, 232.0893; found, 232.0875.

Methyl-phenyl-(1-pyridin-3-yl-ethyl)-amine (12a)



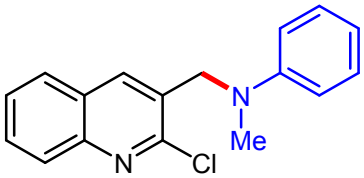
This compound was obtained as yellow oil with an isolated yield 77% (163 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.73 (d, 3H, *J* = 6.9 Hz), 2.83 (s, 3H), 5.29 (q, 1H, *J* = 6.8 Hz), 6.92 (t, 1H, *J* = 7.2 Hz), 7.01 (d, 2H, J = 8.3 Hz), 7.34−7.42 (m, 3H), 7.77 (d, 1H, *J* = 7.9 Hz), 8.67(d, 1H, *J* = 4.14 Hz), 8.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.1, 31.9, 55.2, 113.6, 117.5, 123.3, 129.3, 134.7, 138.1, 148.1, 148.7, 149.9; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{14}H_{17}N_2$, 213.1392; found, 213.1371.

Tetrahydro-*N*-methyl-*N*-phenyl-2-furanmethanamine (12b)[2]



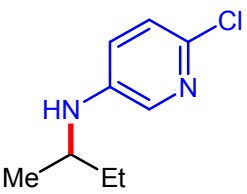
This compound was obtained as yellow oil with an isolated yield 63% (118 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.02 (s, 3H), 4.49 (s, 2H), 6.17 (d, 1H, J = 3.0 Hz), 6.32-6.33 (m, 1H), 6.79 (t, 1H, J = 7.2 Hz), 6.87 (d, 2H, J = 8.2 Hz), 7.28 (t, 2H, J = 7.9 Hz), 7.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.3, 49.9, 107.2, 110.2, 113.0, 117.1, 129.1, 141.8, 149.4, 152.4; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{12}H_{14}NO$, 188.1075; found, 188.1062.

***N*-(phenylmethyl)-2-chloro-3-Quinolinemethanamine (12c)**[6]



This compound was obtained as brown solid with an isolated yield 63% (178 mg); mp 140 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.18 (s, 3H), 4.71 (s, 2H), 6.73 (d, H, J = 8.1 Hz), 6.78 (t, H, J = 7.1 Hz), 7.25 (t, H, J = 7.7 Hz), 7.51 (t, H, J = 7.4 Hz), 7.69-7.72 (m, H), 7.92 (s, H), 8.04 (d, H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 38.9, 55.0, 112.1, 117.2, 127.0, 127.5, 127.5, 128.2, 129.4, 129.9, 130.0, 146.9, 149.0, 149.8; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_{17}H_{16}ClN_2$, 283.1002; found, 283.0975.

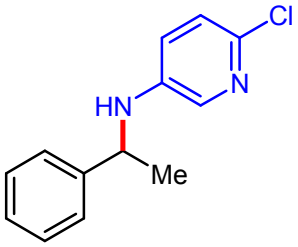
***Sec*-Butyl (6-chloro-3-pyridyl)amine (12d)**



The title compound was obtained as yellow oil with an isolated yield 89% (164 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3H, J = 7.4 Hz), 1.13 (d, 3H, J = 6.3 Hz), 1.39−1.58 (m, 2H), 3.30 (q,

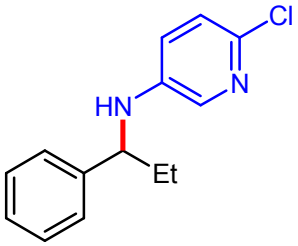
1H, *J* = 6.2 Hz), 6.80 (dd, 1H, *J* = 5.6 Hz), 7.02 (d, 1H, *J* = 8.6 Hz), 7.68 (d, 1H, *J* = 2.9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.2, 19.9, 29.3, 49.8, 122.2, 123.9, 134.6, 137.9, 142.9; HRMS (ESI-TOF) m/z: [M+H] calcd for $C_9H_{14}ClN_2$, 185.0845; found, 185.0831.

(6-Chloro-3-pyridinyl)-*N*-(1-phenyl-ethyl)amine (12e)



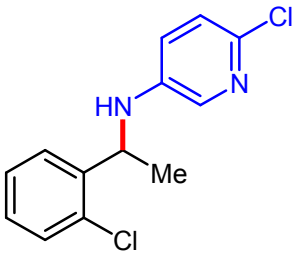
The title compound was obtained as yellow oil with an isolated yield 71% (164 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.53 (d, 3H, *J* = 6.5 Hz), 4.43 (q, 2H, *J* = 2 Hz), 6.72 (dd, 1H, *J* = 5.7 Hz), 6.97 (d, 1H, *J* = 8.5 Hz), 7.23-7.28 (m, 1H) 7.33 (brd s, 4H), 7.71 (d, 1H, *J* = 2.7 Hz); ^{13}C NMR ($CDCl_3$, 75 mHz) δ 24.8, 53.5, 122.6, 123.9, 125.7, 127.3, 128.9, 135.1, 138.7, 142.4, 143.7; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{13}H_{14}ClN_2$, 233.0845; found, 233.0831.

(6-Chloro-3-pyridinyl)-*N*-(1-phenyl-propyl)-amine (12f)



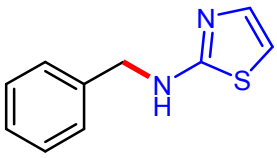
The title compound was obtained as yellow solid with an isolated yield 73% (180 mg);mp 115 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (t, 3H, *J* = 7.4 Hz), 1.74−1.95 (m, 2H), 4.18 (s, 1H), 4.30 (s, 1H), 6.73 (dd, 1H, *J* = 5.58 Hz), 6.97 (d, 1H, *J* = 8.6 Hz), 725-7.35 (m, 5H), 7.73(d, 1H, *J* = 2.9 Hz); ^{13}C NMR ($CDCl_3$, 75 mHz) δ 10.6, 31.5, 59.7, 122.5, 123.8, 126.4, 127.4, 128.7, 135.1, 138.7, 142.3, 142.6; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{14}H_{16}ClN_2$, 247.1002; found, 247.0989.

***N*-[1-(2-Chloro-phenyl)-ethyl]-(6-chloro-pyridin-3-yl)-amine (12g)**



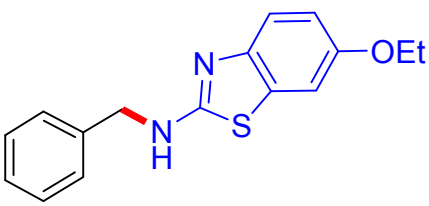
The title compound was obtained as white solid with an isolated yield 61% (162 mg); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50 (d, 3H, J = 6.6 Hz), 4.12 (q, 1H, J = 7.13 Hz), 6.65 (dd, 1H, J = 5.6 Hz), 6.96 (d, 1H, J = 8.6 Hz), 7.13−7.10 (m, 2H), 7.33−7.37(m, 2H), 7.66 (d, 1H, J = 2.9 Hz); ^{13}C NMR ($CDCl_3$, 75 mHz) δ 22.7, 50.3, 122.5, 123.9, 126.5, 127.5, 128.5, 129.9, 132.5, 135.0, 138.9, 140.5, 141.0; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{13}H_{13}ClN_2$, 267.0456; found, 267.0435.

2-Thiazolamine-4,5-dihydro-*N*-benzylamine (12 h)[7]



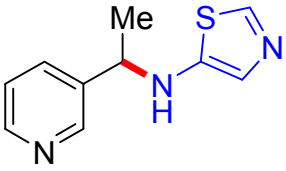
The title compound was obtained as white solid with an isolated yield 83% (158 mg); mp 124-125 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.46 (s, 2H), 6.45 (d, 1H, J = 3.6 Hz), 6.50 (s, 1H, NH), 6.98 (d, 1H, J = 3.5 Hz), 7.30 (t, 1H, J = 7.0 Hz), 7.34-7.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 50.0, 106.4, 127.7, 127.8, 128.7, 137.6, 138.9, 170.4; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{10}H_{11}N_2S$, 191.0643; found, 191.0633.

2-Benzothiazolamine-6-ethoxy-*N*-benzylamine (12i)[7]



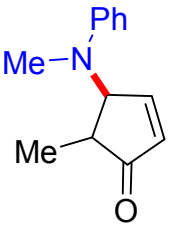
The title compound was obtained as white solid with an isolated yield 87% (247 mg); mp 123-124°C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.42 (t, 3H, J = 6.9 Hz), 4.00 (q, 2H, J = 6.9 Hz), 4.58 (s, 2H), 6.84 (dd, 1H, J = 6.2 Hz, J = 2.5 Hz), 7.10 (d, 1H, J = 2.5 Hz), 7.24 (d, 1H, J = 8.7 Hz), 7.30 (d, 1H, J = 7.2 Hz), 7.34 (t, 2H, J = 7.3 Hz), 7.40 (d, 2H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.9, 49.4, 64.2, 106.2, 114.2, 119.0, 127.6, 127.7, 128.7, 131.2, 137.8, 146.4, 154.4, 166.5; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{16}H_{17}N_2OS$, 285.1062; found, 285.1055.

(1-Pyridin-3-yl-ethyl)-thiazol-5-yl-amine (12j)



The title compound was obtained as reddish brown with an isolated yield 79% (163 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.62 (d, 3H, J = 6.8 Hz), 4.61 (q, 1H, J = 6.6 Hz), 6.41 (d, 1H, J = 3.5 Hz), 7.04 (d, 1H, J = 3.5 Hz), 7.32-7.26 (m, 1H), 7.53 (s, 1H, NH), 7.70 (d, 1H, J = 7.8 Hz), 8.50 (d, 1H, J = 4.3 Hz), 8.65 (s, 1H) ^{13}C NMR ($CDCl_3$, 150 MHz) δ 23.7, 53.7, 106.8, 123.6, 133.6, 138.4, 138.7, 148.3, 148.8, 169.6; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{10}H_{11}N_3S$, 206.0752; found, 206.0736.

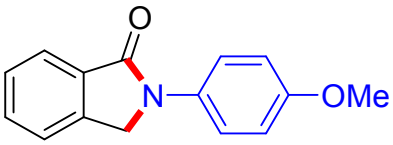
5-Methyl-4-(methyl-phenyl-amino)-cyclopent-2-enone (12k).



The title compound was obtained as reddish brown viscous oil with an isolated yield 65% (131 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.27 (d, 3H, J = 7.3Hz), 2.39 (dq, 1H, J = 3.5Hz), 2.74 (s, 3H), 4.79 (q, 1H, J = 2.2Hz), 6.33 (dd, 1H, J = 2.6Hz), 6.81(t, 1H, J = 7.2Hz), 6.90 (d, 2H, J =

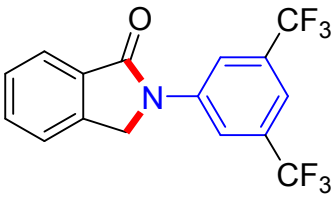
8.2Hz), 7.26-7.29(m, 2H), 7.55 (dd, 1H, *J* = 2.6Hz); ^{13}C NMR ($CDCl_3$, 600MHz) 14.3, 32.7, 44.5, 68.1, 114.1, 118.2, 129.3, 134.8, 149.6, 162.4, 208; ESI-MS m/z: [M + H] calcd for $C_{13}H_{16}NO$, 202.1232; found, 202.1449.

2-(4-Methoxy-phenyl) isoindol-1-one (15a)[9]



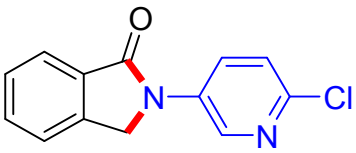
The title compound was obtained as reddish brown with an isolated yield 87% (207 mg); mp139-139.5 ^{o}C;^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.78 (s, 3H), 4.74 (s, 2H), 6.92 (d, 2H, *J* = 8.6 Hz), 7.46 (d, 2H, *J* = 6.48Hz), 7.54 (t, 1H, *J* = 7.1 Hz), 7.70 (d, 2H, *J* = 8.6 Hz), 7.87 (d, 1H, *J* = 7.5 Hz),^{13}C NMR ($CDCl_3$, 150 MHz) δ 51.1, 55.4, 114.3, 121.3, 122.5, 123.9, 128.2, 131.7, 132.6, 133.2, 140.1, 156.6, 167.1; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{15}H_{14}NO_2$, 240.1025; found, 240.1009.

2-(3,5-Bis-trifluoromethyl-phenyl) isoindol-1-one (15b).



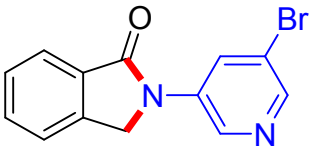
The title compound was obtained as white solid with an isolated yield 83% (203 mg); mp130-131^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.83(s, 2H), 7.42 (t, 1H, *J* = 7.4 Hz), 7.49 (d, 1H, *J* = 7.5 Hz), 7.56 (d, 1H, *J* = 7.3 Hz), 7.58 (s, 1H), 7.76 (d, 1H, *J*= 7.6 Hz), 8.33 (s, 2H), ^{13}C NMR ($CDCl_3$, 150 MHz) δ 50.2, 117.02-117.09 (m), 117.9 (d, *J* = 2.4 Hz), 122.8, 123.1 (d, *J* = 272.8 Hz), 124.2, 128.6, 131.9, 132.3 (q, *J* = 33.3 Hz), 133.0, 139.5, 140.8, 167.8; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{16}H_{10}F_6NO$, 346.0667; found, 346.0654.

2-(2-Chloropyridyl) isoindolinone (15c).



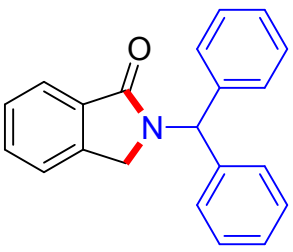
The title compound was obtained as white solid with an isolated yield 89% (217 mg); mp151-152^{o}C; ^{1}H NMR (DMSO-D_6, 600 MHz) δ 5.03 (s, 2H), 7.53 (t, 1H, J = 7.1Hz), 7.57 (d, 1H, J = 8.7 Hz), 7.65-7.70 (m, 2H), 7.78 (d, 1H, J = 7.5 Hz), 8.43 (d, 1H, J = 8.7 Hz), 8.89 (s, 1H); ^{13}C NMR (DMSO-D_6, 150 MHz) δ 50.4, 123.9, 123.9, 124.7, 128.8, 130.0, 131.9, 133.2, 136.1, 140.6, 141.6, 144.8, 167.6; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{13}H_{10}ClN_2O$, 245.0482; found, 245.0470.

2-(3-Bromopyridyl)isoindolinone (15d).



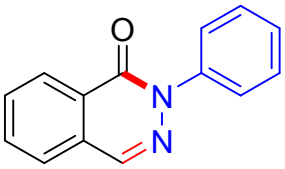
The title compound was obtained as white solid with an isolated yield 75% (215 mg); mp129-130^{o}C; ^{1}H NMR (DMSO-D_6, 600 MHz) δ 5.08 (s, 2H), 7.55 (t, 1H, J = 7.3Hz), 7.67 (d, 1H, J = 7.5 Hz), 7.71 (t, 1H, J = 7.3 Hz), 7.81 (d, 1H, J = 7.6 Hz), 8.49(s, 1H), 8.63 (t, 1H, J = 2.0 Hz), 9.09 (s, 1H); ^{13}C NMR (DMSO-D_6, 150 MHz) δ 50.4, 120.2, 123.9, 124.0, 128.4, 128.8, 131.8, 133.4, 137.6, 139.2, 141.8, 145.4, 167.7; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{13}H_{10}BrN_2O$, 288.9976; found, 288.9959.

2-(Biphenylmethyl) isoindolinone (15e)



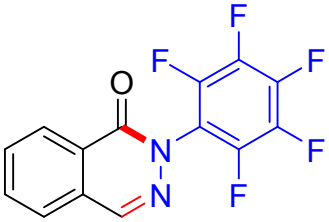
The title compound was obtained as colourless oil with an isolated yield 95% (284 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.23 (s, 2H), 6.94(s, 1H), 7.24(t, 4H, J = 8.3Hz), 7.30 (t, 2H, J = 7.2 Hz), 7.33-7.37 (m, 5H), 7.46 (t, 1H, J = 7.4 Hz), 7.51 (t, 1H, J = 7.1 Hz), 7.93 (d, 1H, J = 7.5 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz) δ 47.5, 58.7, 122.9, 124.0, 127.7, 128.1, 128.6, 128.6, 131.5, 132.3, 139.2, 141.5 168.5; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{21}H_{18}$ NO, 300.1388; found, 300.1365.

2-Phenylphthalazin-1(2H)-one (15f) [8]



The title compound was obtained as yellow solid with an isolated yield 90% (200 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.37 (t, 1H, J = 7.3 Hz), 7.48 (t, 2H, J = 7.8 Hz), 7.67 (d, 2H, J = 7.6 Hz), 7.71(d, 1H, J = 7.6 Hz), 7.76-7.82 (m, 2H), 8.26 (s, 1H), 8.49 (d, 1H, J = 7.7Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 125.7, 126.1, 127.2, 127.7, 128.5, 128.7, 129.5, 131.9, 133.4, 138.4, 141.9, 159.1; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{14}H_{11}N_2O$, 223.0871; found, 223.0859.

2-Pentafluorophenylphthalazin-1-(2H)-one (15g)



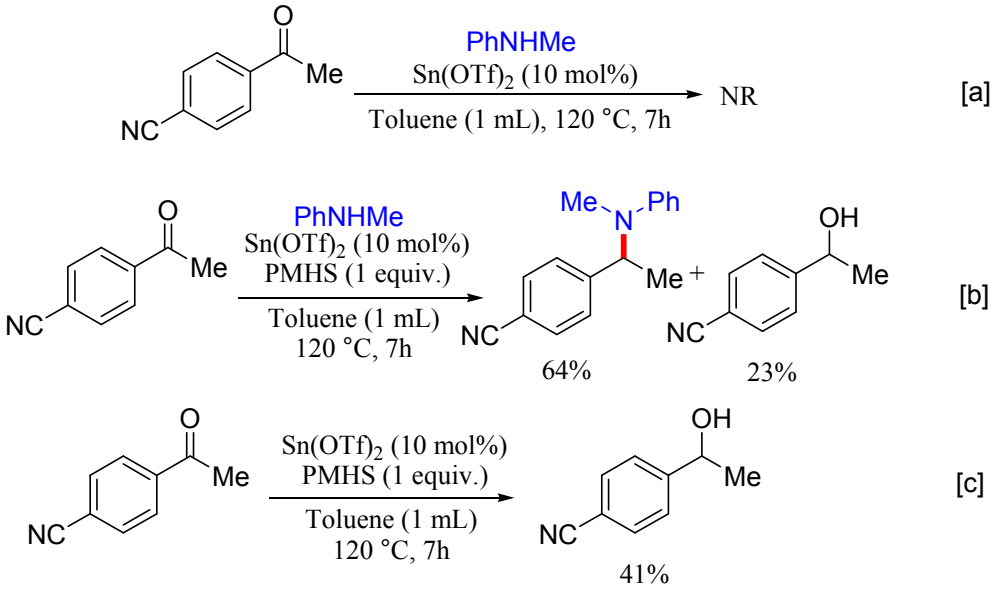
The title compound was obtained as white solid with an isolated yield 93% (290 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.78 (d, 1H, J = 7.7 Hz), 7.85 (t, 1H, J = 7.5 Hz), 7.91(t, 1H, J = 7.3 Hz), 8.28 (s, 1H), 8.46 (d, H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 116. 7 (d, J = 25.5 Hz), 126.7, 127.3, 127.6, 129.6, 132.6, 134.4, 137.9 (dd, J = 239.2 Hz), 140.2, 141.9 (d, J = 256.2

Hz), 144.0 (dd, *J* = 254.8 Hz), 158.7; HRMS (ESI-TOF) m/z: [M + H] calcd for $C_{14}H_6F_5N_2O$, 313.0400; found, 313.0392.

Mechanistic study

***Intermediate study**:*

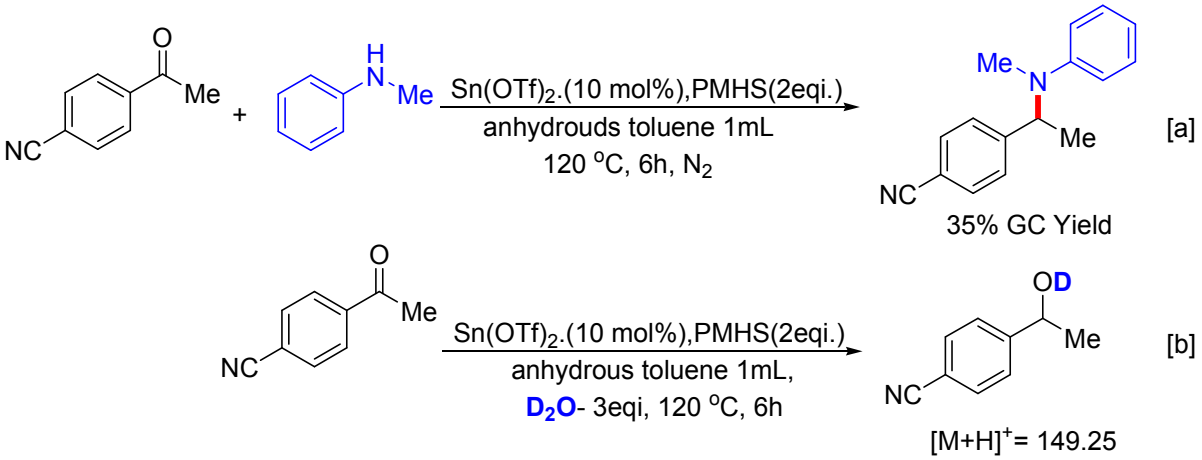
For preliminary understanding of reaction pathway, when the reaction was carried out under standard reaction in the absence of PMHS, no enamine or iminium ion intermediate was detected (scheme S1 equ. a). However, decreasing the amount of PMHS from 2.0 equivalent to 1.0 equivalent led to the formation of a mixture of desired amine and reduced product [1-(4-cyanophenyl) ethanol] of 4-acetylbenzonitrile (scheme S1 equ. b). Further, the reaction was carried out under standard conditions in the absence of *N*-methylaniline to gave reduced product of 4-acetylbenzonitrile (scheme S1 equ. c). These experiments completely ruled out the possibility of reductive amination pathway.



Scheme S1. Controlled experiments.

Role of water traces in the solvent: When the standard reaction was carried out in substantially anhydrous condition under N_2 atmosphere, comparatively low yield was

observed (scheme S2 equ. a). This observation suggested that traces of water are crucial for the success of the reaction. Further to confirm the role H_2O in the reaction, 4-cyanoacetophenone was reacted with PMHS (2 equiv.) in the presence of $Sn(OTf)_2$ (10 mol%) using anhydrous toluene with 3-equivalent D_2O as reaction medium for 1 h (scheme S2 equ. b). The crude reaction mixture was analysed with ESI-MS, which clearly showed mass of corresponding deuterated reduced product (m/z = 149) (Figure S1).



Scheme S2. Controlled experiments.

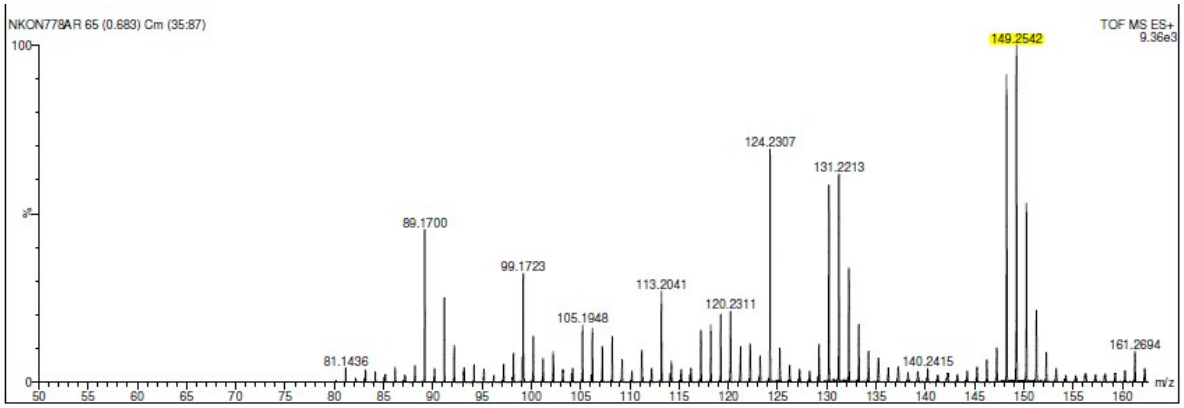
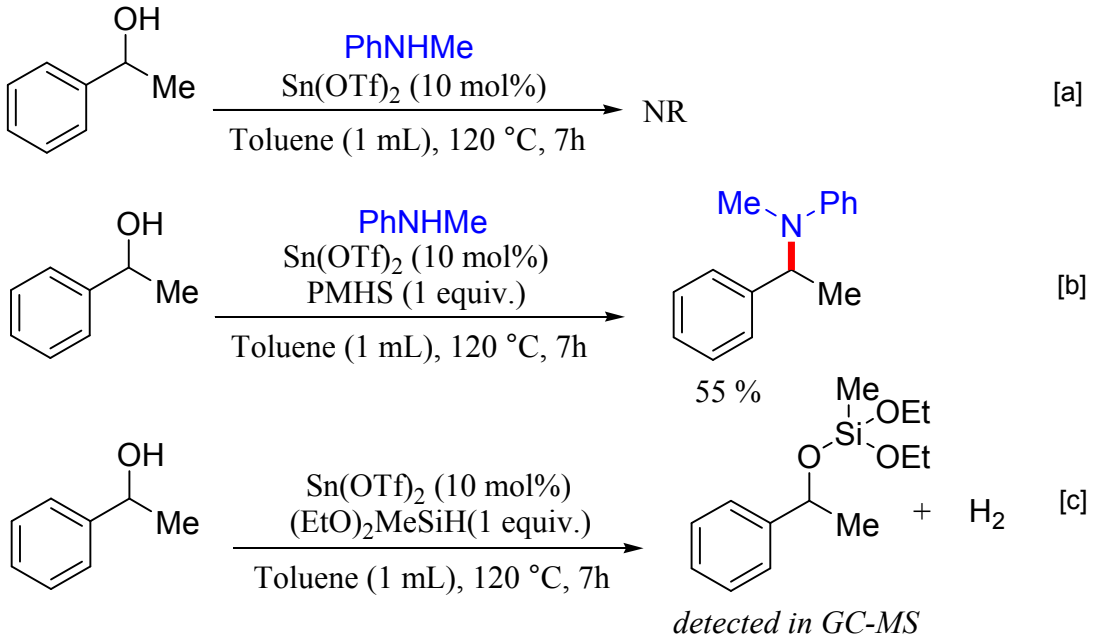


Figure S1. ESI-MS spectra of deuterated 1-(4-cyanophenyl)ethanol.

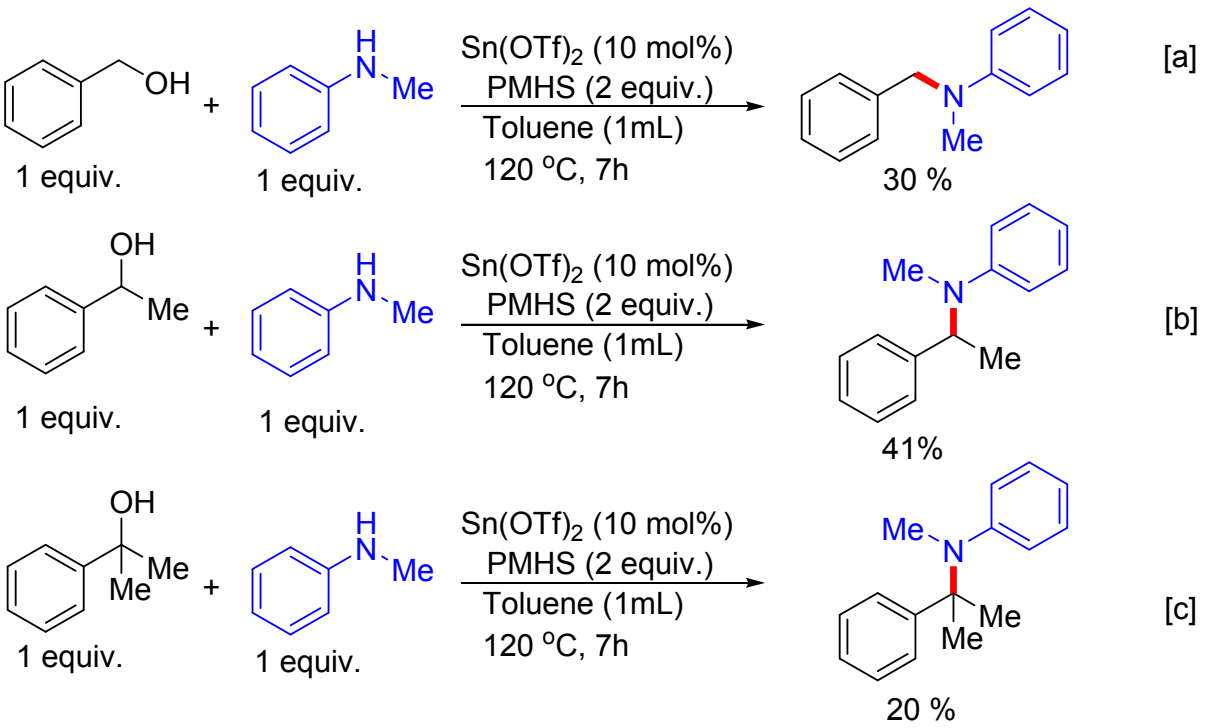
Further, the reaction was carried out with alcohol instead of ketone (See scheme S3). Unfortunately, the reaction of 1-phenylethanol with *N*-methylaniline did not proceed in the presence of tin(II) triflate (Scheme S3 equ.a), however, the addition of 1.0 equivalent of

PMHS in this reaction resulted in the formation of desired amine (Scheme S3 equ.b). These results reveled that PMHS plays critical role in the reduction of carbonyl[10] moiety as well as in the activation of *in situ* generated alcohol *via* silylation (Scheme S3, equ.c).[11]



Scheme S3. Controlled experiments with alcohols.

We found that 1° and 2 ° aromatic alcohols smoothly reacted with *N*-methylaniline to generate corresponding amines due to easily generation of carbocation *via* silylation of aromatic alcohols (scheme S4).



Scheme S4. *N*-alkylation of aniline with 1°, 2° and 3° alcohols.

However, tertiary alcohol also reacted with *N*-methylaniline and providing lower yield of desired amine. It is due to the silylation of 3° alcohol is more difficult as compare to 1° and 2° alcohols.[12]

Evidences for O-silylation of alcohol in the presence of tin(II) triflate/PMHS catalytic system:

To study the interaction of catalyst with reaction intermediate, tin(II) triflate (1 mmol) and 1-phenylethanol (2 mmol) were dissolved in deuterated toluene and stirred for 10 min at rt and the crude solution was analysed with ^{13}C NMR. We observed Downfield shift ($\Delta\delta$ =0.7) from δc = 69.7 to 70.4 ppm due to the formation of *O*-silylated product of 1-phenylethanol was observed which confirmed the silylation of alcohol (Figure S2).

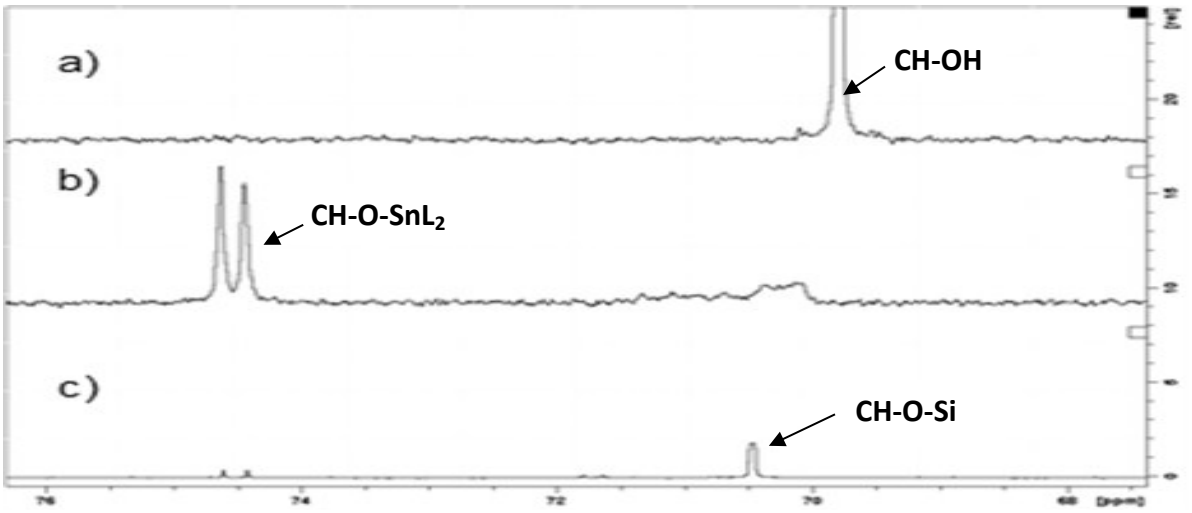


Figure S2. a) ^{13}C NMR spectra of 1-phenylethanol in $C_6D_5CD_3$. b) ^{13}C NMR spectra of mixture of tin (II) triflate and 1-phenylethanol in equivalent ratio in $C_6D_5CD_3$. c) ^{13}C NMR spectra of mixture of tin(II) triflate and 1-phenylethanol and PMHS in equivalent ratio in $C_6D_5CD_3$.

^{13}C NMR spectra of 1-phenylethanol

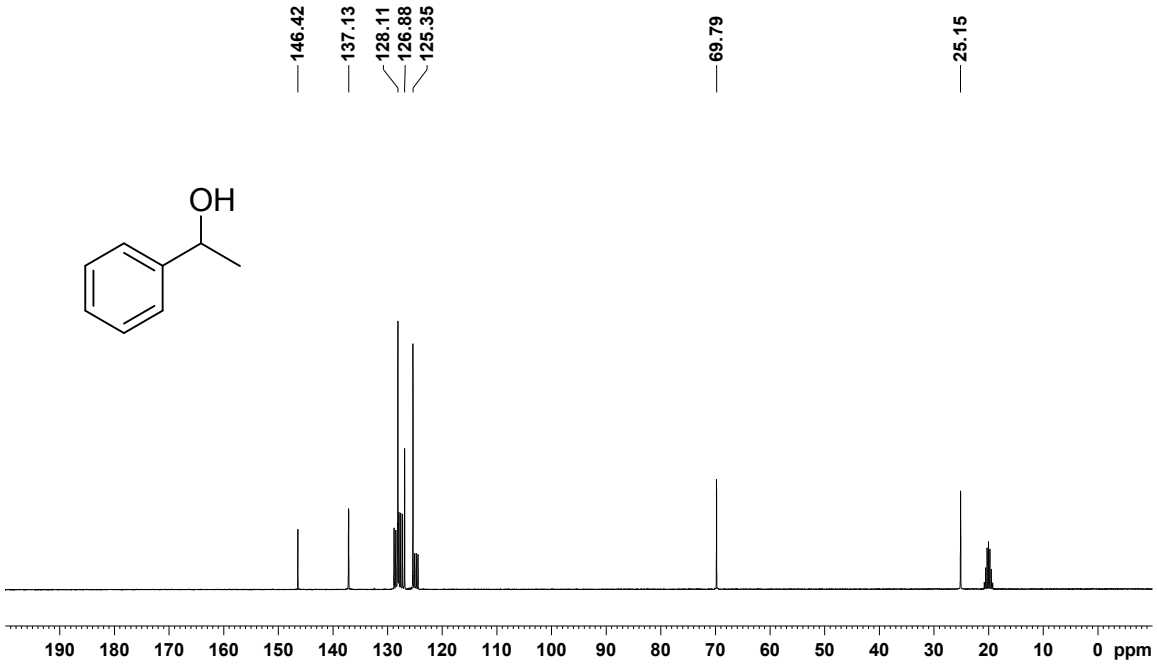


Figure S3a. ^{13}C NMR spectra of 1-phenylethanol in deuterated toluene.

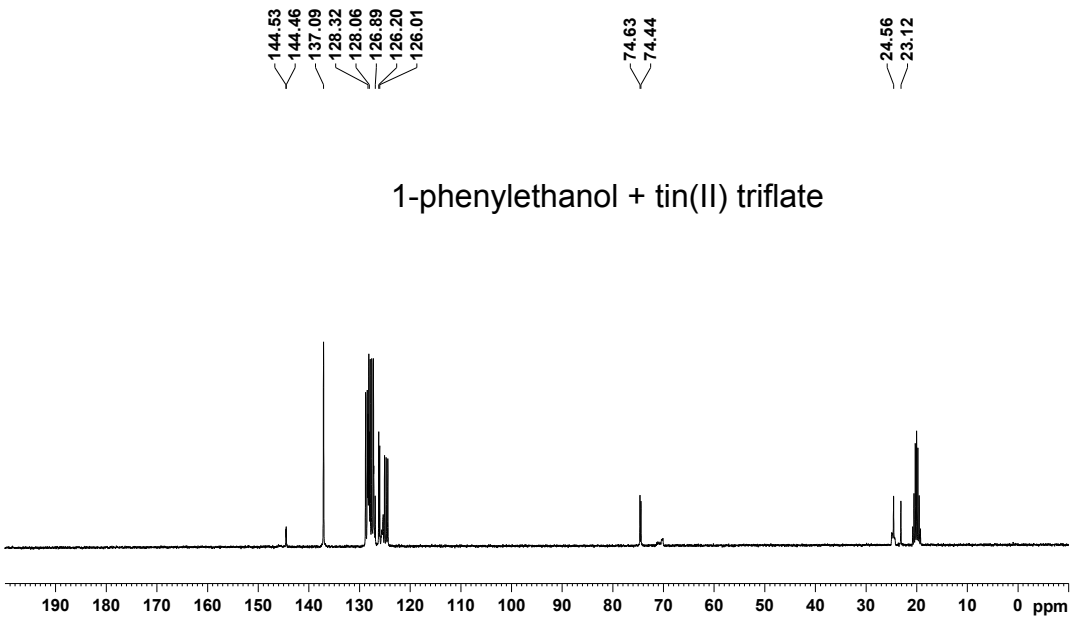


Figure S3b. ^{13}C NMR spectra of the mixture of 1-phenylethanol and tin(II) triflate in deuterated toluene**.**

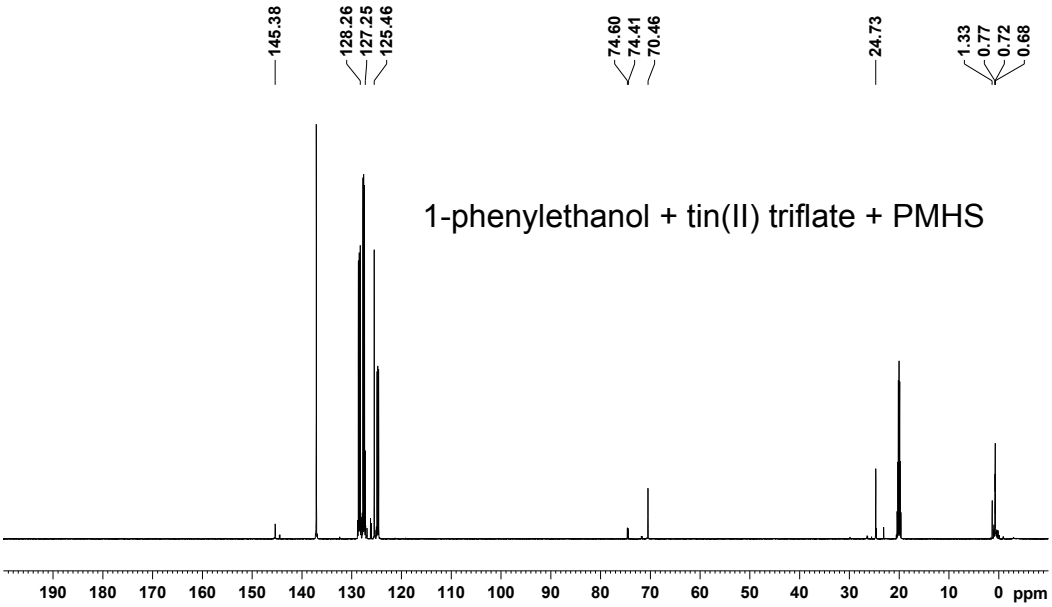
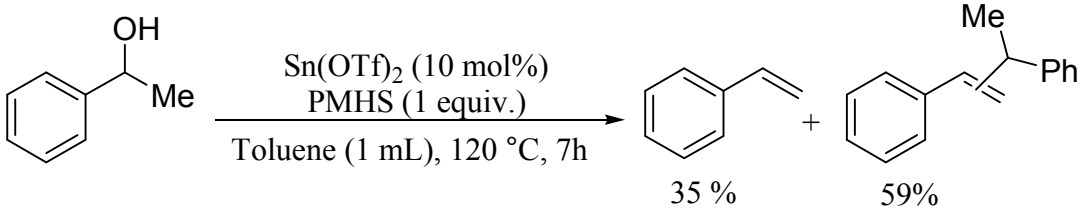


Figure S3c. ^{13}C NMR spectra of the mixture of 1-phenylethanol,tin(II) triflate and PMHS in deuterated toluene**.**

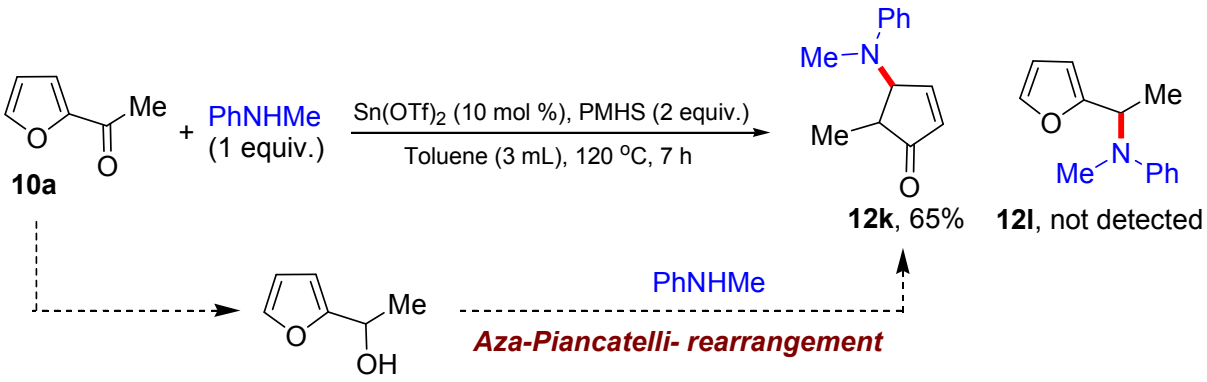
Evidence for carbocation as reaction intermediate:

When 1-phenylethanol was heated under the same reaction conditions in absence of *N*-methylaniline it converted into styrene and stilbene derivates, which indicates that reaction might be going through carbenium ion intermediate (Scheme S5). Earlier, Genaev group also described the generation of carbocation from *O*-silyltaed product *via* desilylation by protonic acid.[13]



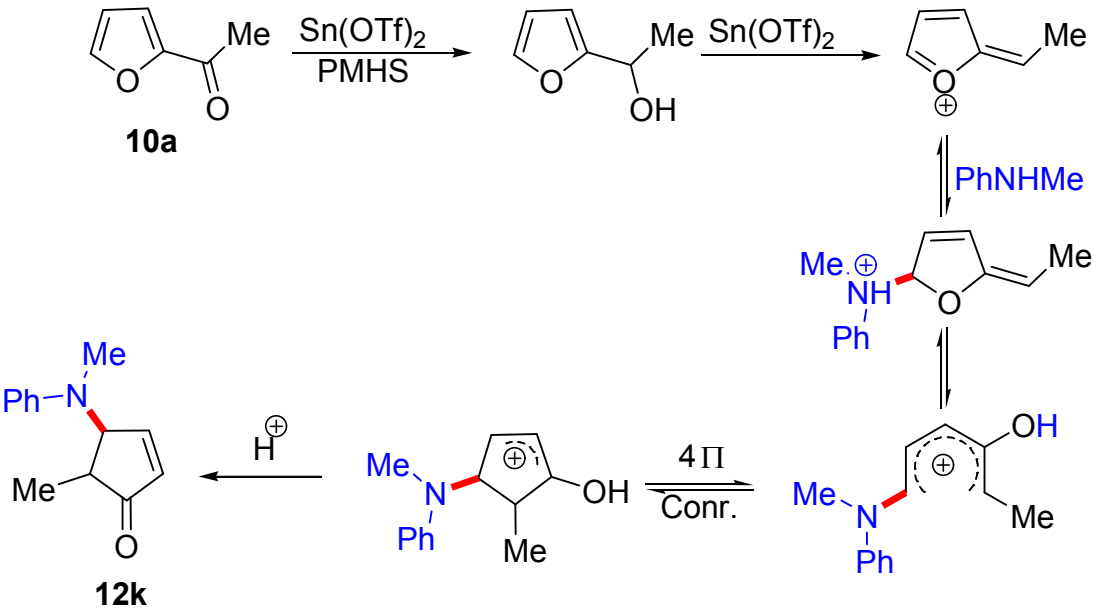
Scheme S5. Controlled experiments for the generation of carbocation.

When we were exploring the substrate scope of this developed method, we observed unexpected product **12K** instead of desired product **12l** from 2-furylmethylketone under standard reaction conditions (Scheme S6).



Scheme S6. Synthesis of 12k.

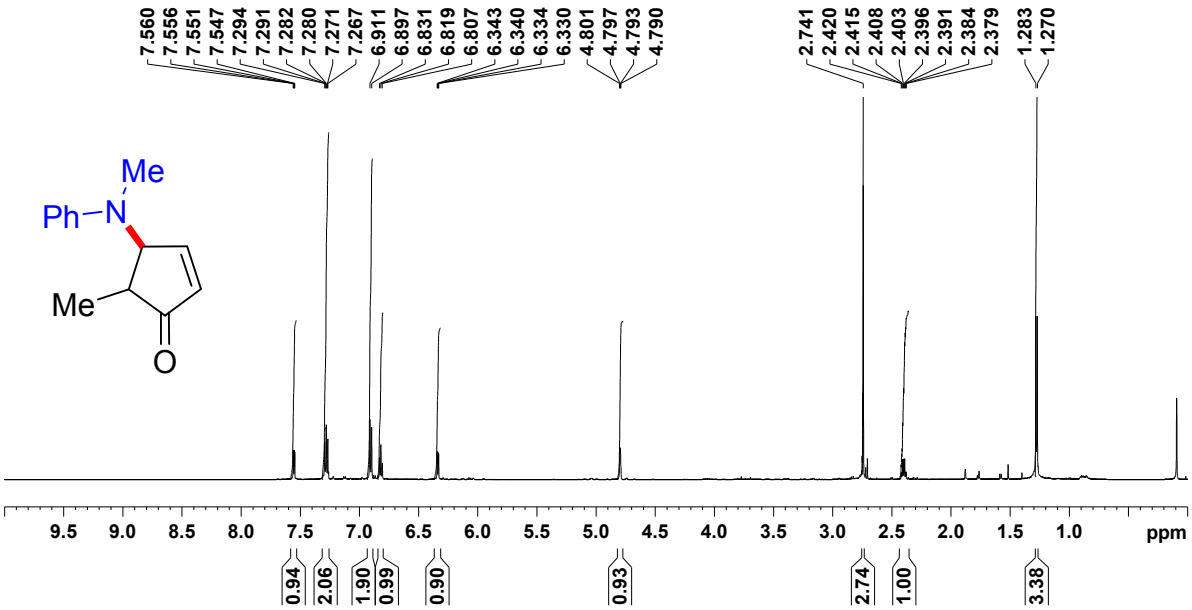
The reaction initially goes through ketone reduction to alcohol, which would further undergo rearrangement *via* carbenium ion pathways. This type of rearrangement is generally known as Aza-Piancatelli rearrangement (Scheme S7).[14]



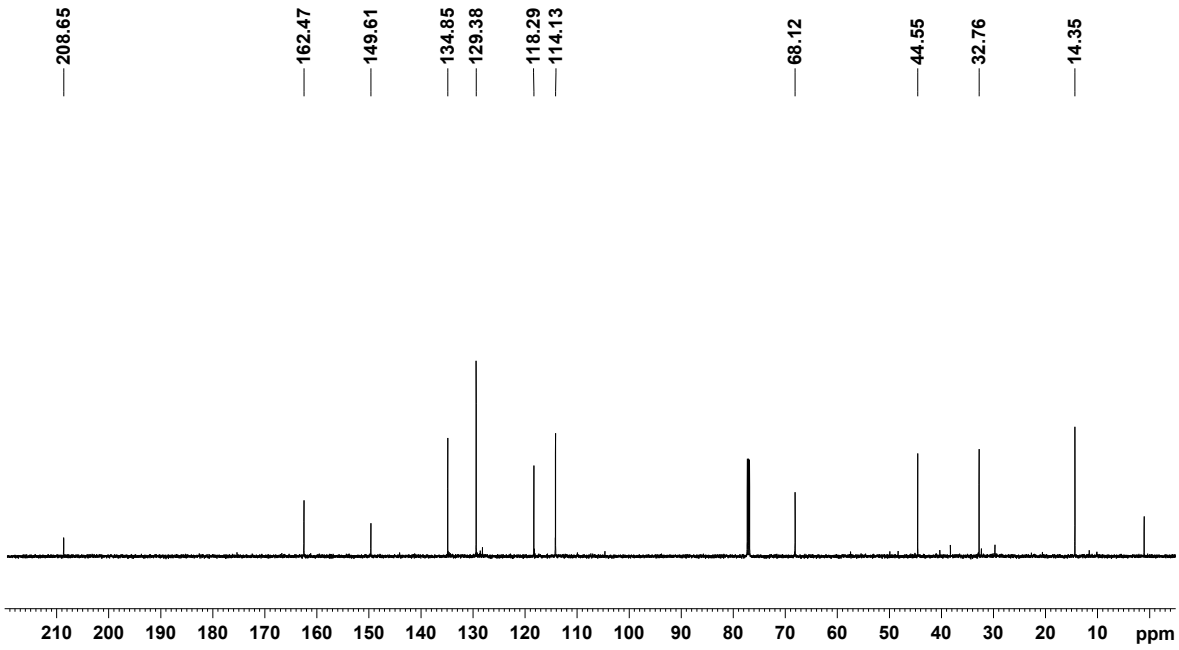
Scheme S7. Plausible mechanistic pathway for formation of **12k**.

Characterization data of 12 k. The **12k** was obtained as reddish brown viscous oil with an isolated yield 65% (131 mg); ^{1}H NMR ($CDCl_3$, 600MHz) 1.27 (d, 3H, *J* = 7.3Hz), 2.39 (dq, 1H, *J* = 3.5Hz), 2.74 (s, 3H), 4.79 (q, 1H, *J* = 2.2Hz), 6.33(dd, 1H, *J* = 2.6Hz), 6.81(t, 1H, *J* = 7.2Hz), 6.90(d, 2H, *J* = 8.2Hz), 7.26-7.29(m, 2H), 7.55(dd, 1H, *J* = 2.6Hz); ^{13}C NMR ($CDCl_3$, 600MHz) 14.3, 32.7, 44.5, 68.1, 114.1, 118.2, 129.3, 134.8, 149.6, 162.4, 208; ESI-MS m/z: $[M + H]^+$ calcd for $C_{13}H_{16}NO$, 202.1232; found, 202.1449.

^{1}H NMR of 12k

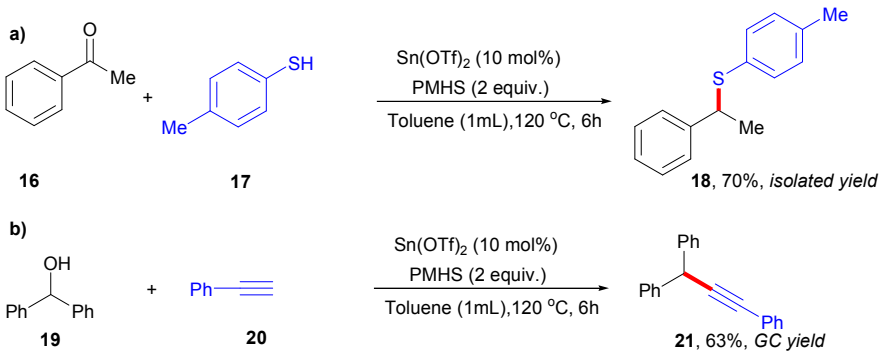


^{13}C NMR of 12k



Trapping of carbocation intermediates.

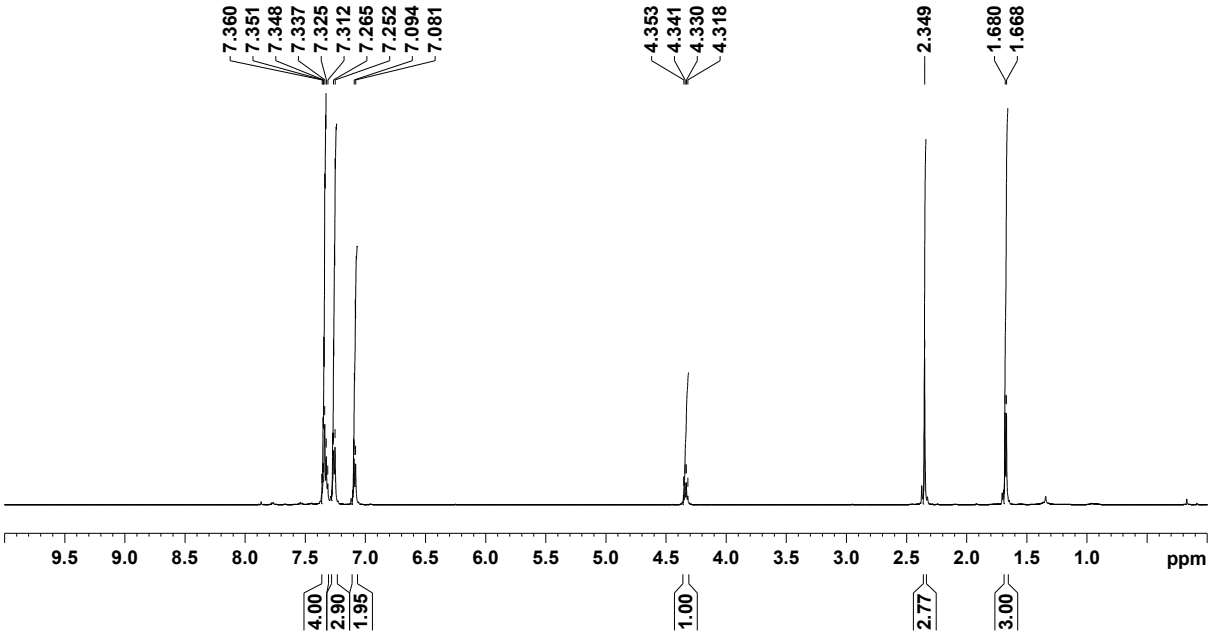
Further to confirm the carbocationic pathway, substrates **16** and **19** were reacted under the optimized reaction conditions with equimolar amounts of various nucleophiles (thiol, alkyne and alcohol), and corresponding product was observed.



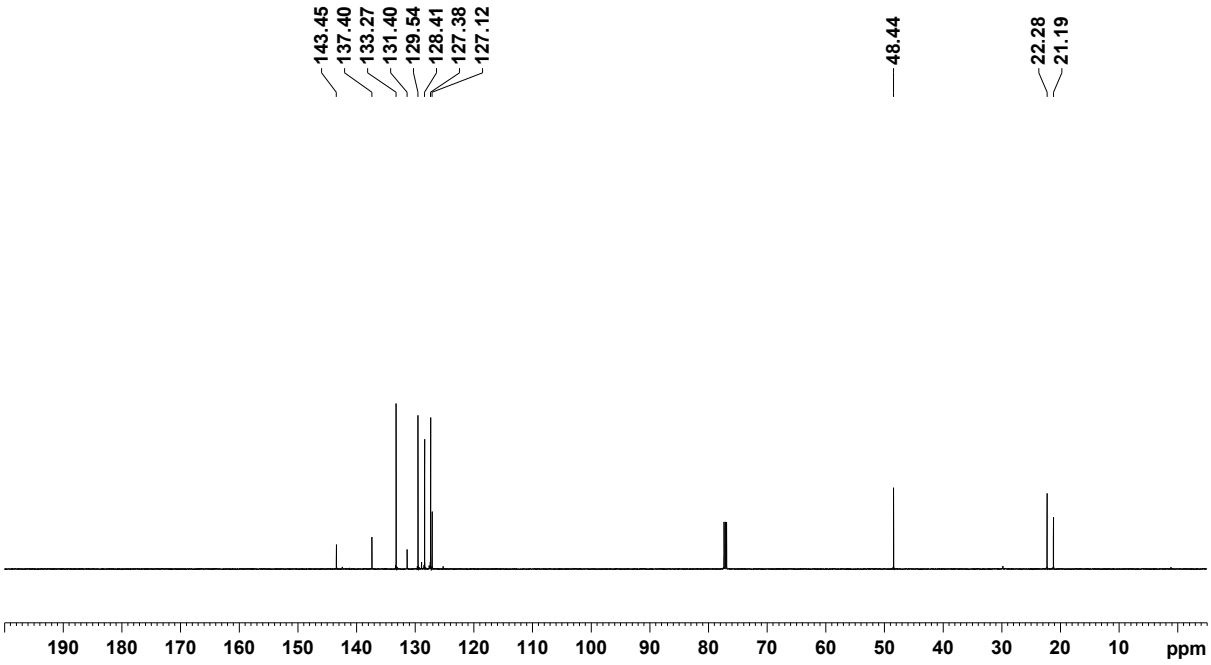
Scheme 8. Mechanistic probe for trapping of intermediate carbocations.

Characterization data of 18. The **18** was obtained as colourless oil with an isolated yield 70%; ^{1}H NMR ($CDCl_3$, 600MHz) 1.67(d, 3H, *J* =7.0 Hz), 2.34(s, 3H), 4.33 (q, 1H, *J* =7.0 Hz), 7.08(d, 2H, *J* =7.8 Hz), 7.25(d, 3H, *J* =7.8 Hz), 7.31-7.36(m, 4H); ^{13}C NMR ($CDCl_3$, 600MHz), 21.1, 22.2, 48.4, 127.1, 127.3, 128.4, 129.5, 131.4, 133.2, 137.4, 143.4.

^{1}H NMR of 18.



^{13}C NMR of 18



Reference

1. X. Jiang, C. Wang, Y. Wei, D. Xue, Z. Liu and J. Xiao, *Chem. Eur. J*., 2014, **20**, 58 -63.

2. O. S. Nayal, V. Bhatt, S. Sharma and N. Kumar *J. Org. Chem*., 2015, **80**, 5912-5918.

3. Z. Wang, D. Pei, Y. Zhang, C. Wang and J. Sun, *Molecules,* 2012, **17**, 5151-5163.

4. O. S. Nayal, M. S. Thakur, M. Kumar, S. Sharma and N. Kumar, *Adv. Synth. Catal.,* 2016, **358**, 1103 -1109.

5. Q. Sun, Y. Wang, D. Yuan, Y. Yao and Q. Shen, *Dalton Trans*., 2015, **44**, 20352-20360.

6. S. Kumar, S. Bawa, S. Drabu and B. P. Panda. *Med. Chem. Res.,* 2011, **20**, 1340-1348.

7. R. R.Donthiri, V.Pappula, D. C. Mohan, H. H. Gaywala and S. Adimurthy*, J. Org. Chem.,* 2013, **78**, 6775−6781.

8. S. Li, X. Li, Q. Li, Q. Yuan, X. Shi and Q. Xu, *Green Chem.,* 2015, **17**, 3260-3265.

9. L. Shi, L. Hu, J. Wang, X. Cao and H. Gu, *Org. Lett.,* 2012, **14**, 1876-1879.

10. H. Mimoun, *J. Org. Chem.,* 1999, **64***,* 2582-2589.

11. (a) J. T. Issenhuth, S. Dagorne and S. Bellemin-Laponnaz, *J. Mol. Catal. A: Chem.,* 2008, **286***,* 6 (b) J. Zhang, Y. Chen and M. A. Brook, *ACS Sustainable Chem. Eng*., 2014, **2**, 1983-1991.

12. B. Karimi, B.Golshani, *J. Org. Chem.,* 2000**, 65***,* 7228-7230.

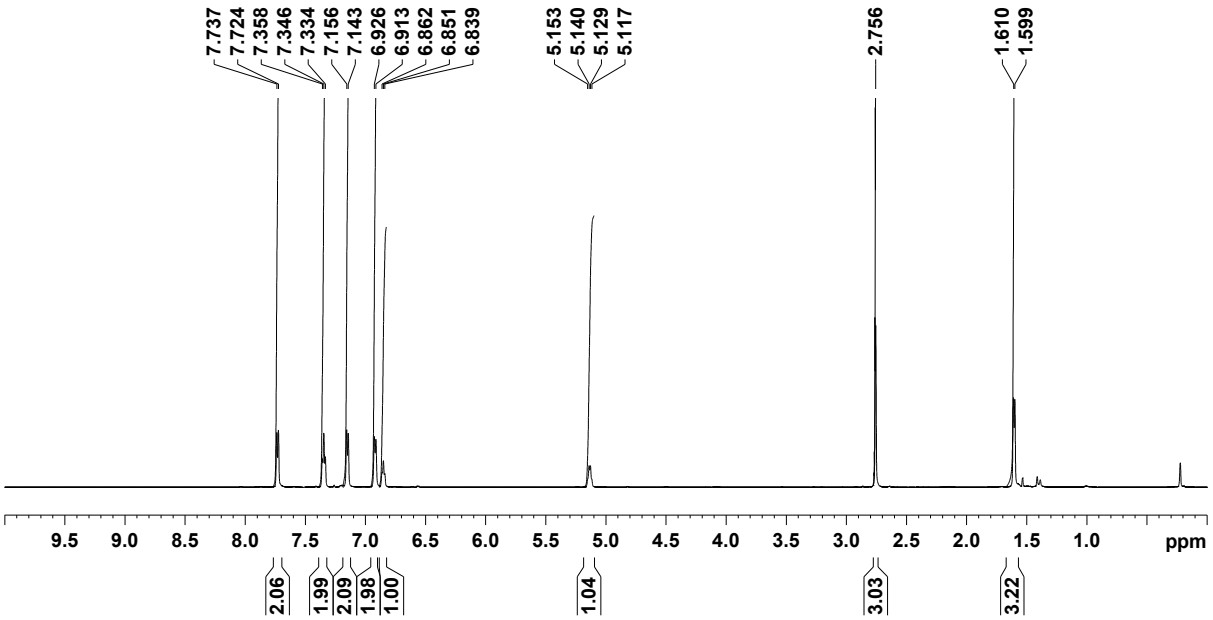
13. V. A. Bushmelev, A. M. Genaev, G. E. Salnikov and V. G. Shubin, *Russ. J. Org. Chem.,* 2011, **47,** 1057-1061.

14. G. K. Veits, D. R. Wenz and J. R. deAlaniz, *Angew. Chem. Int. Ed*., 2010, **49**, 9484-9487

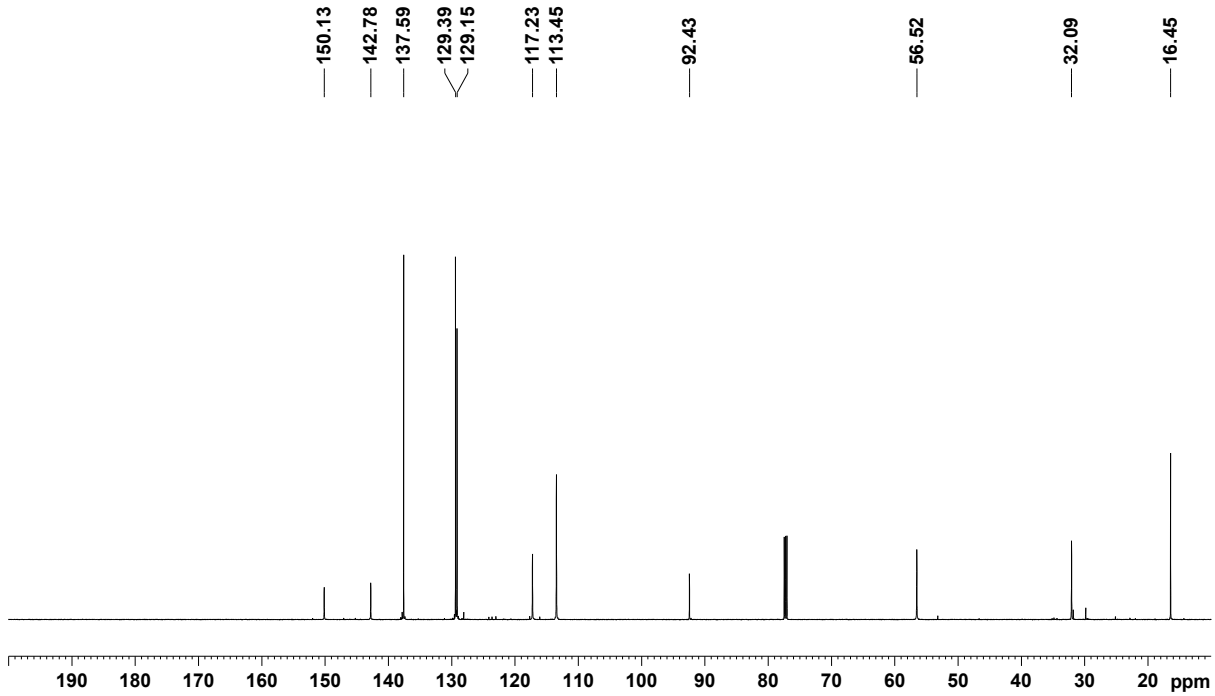
^{1}H and ^{13}C NMR Spectra of synthesized compounds

N-1-(4-Iodophenyl)ethyl-*N*-methylaniline (3a).

^{1}H NMR

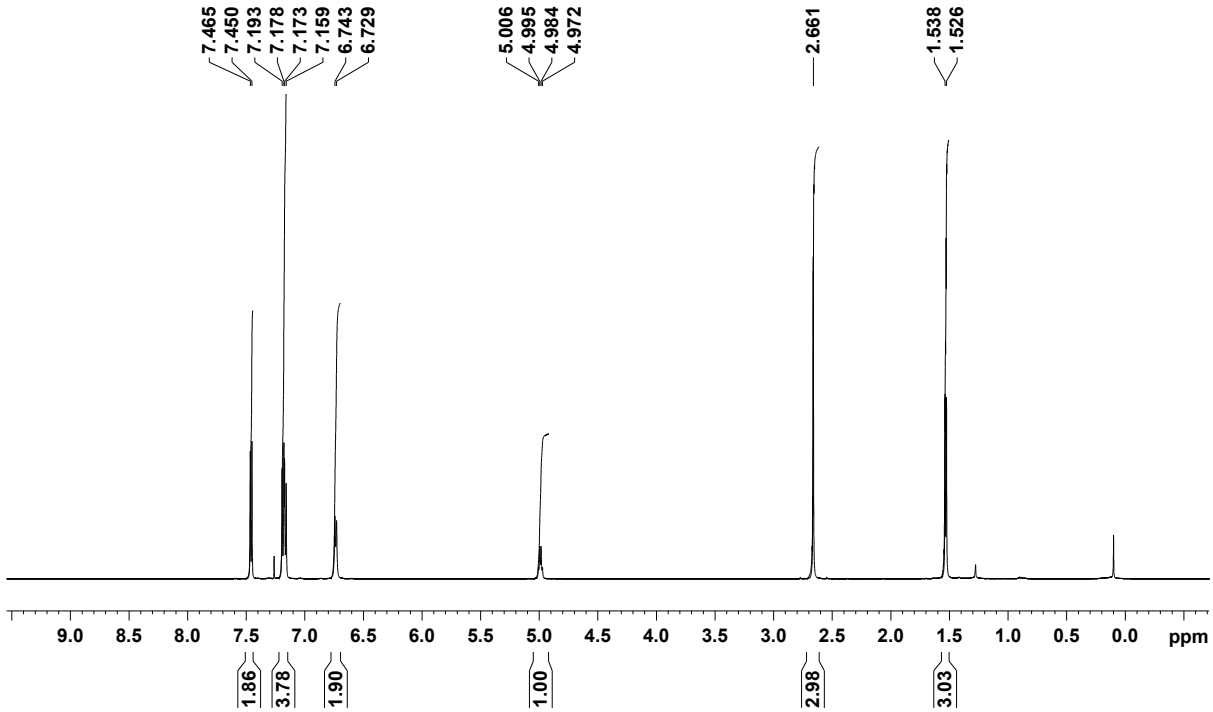


^{13}C NMR

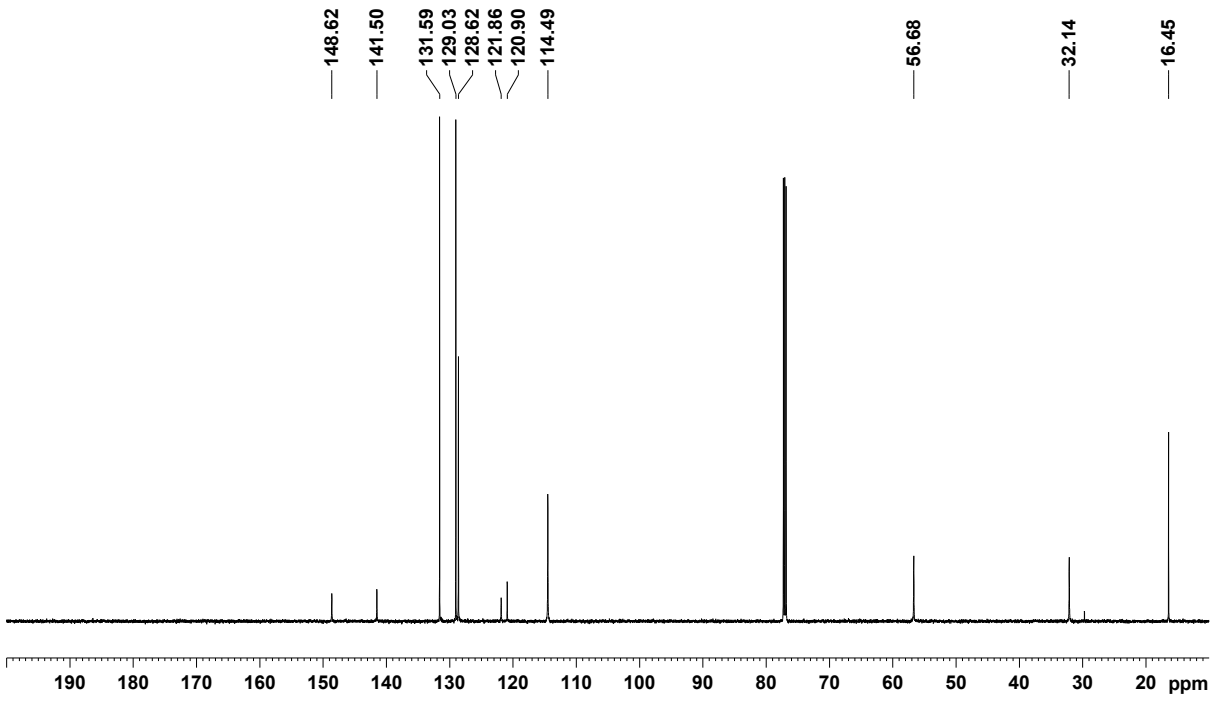


4-Chloro-*N*-1-(4-bromophenyl)ethyl-*N*-methylaniline (3b).

^{1}H NMR

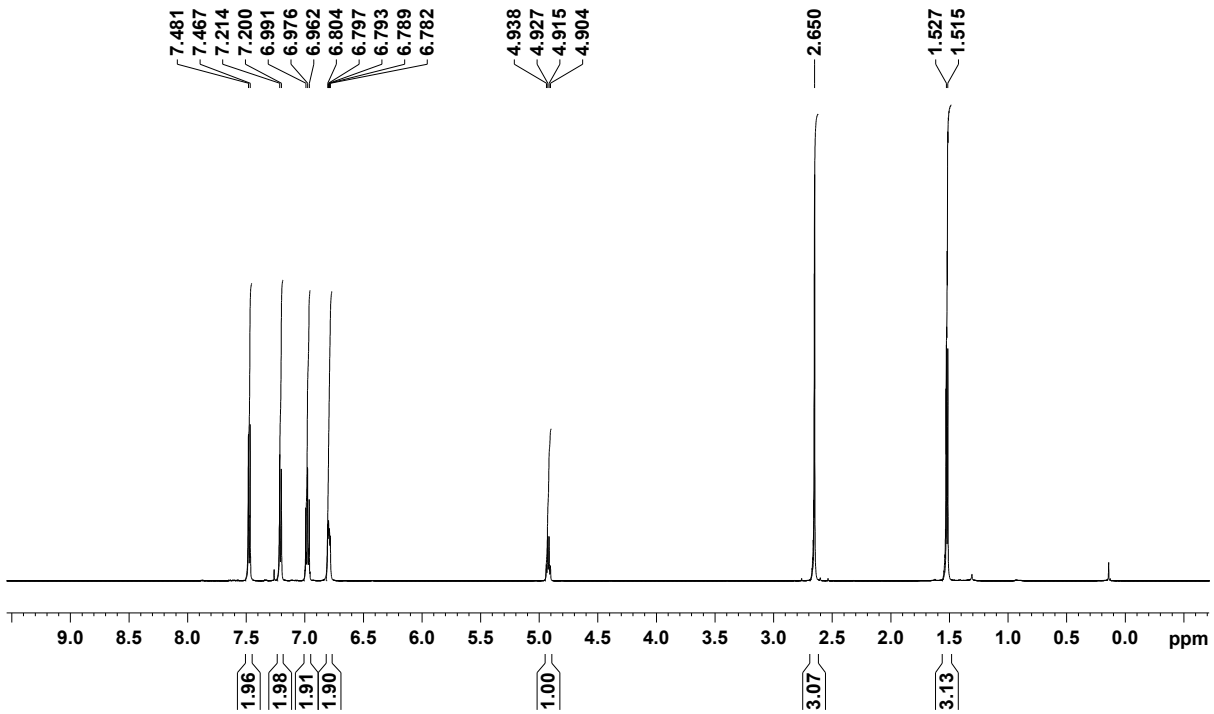


^{13}C NMR

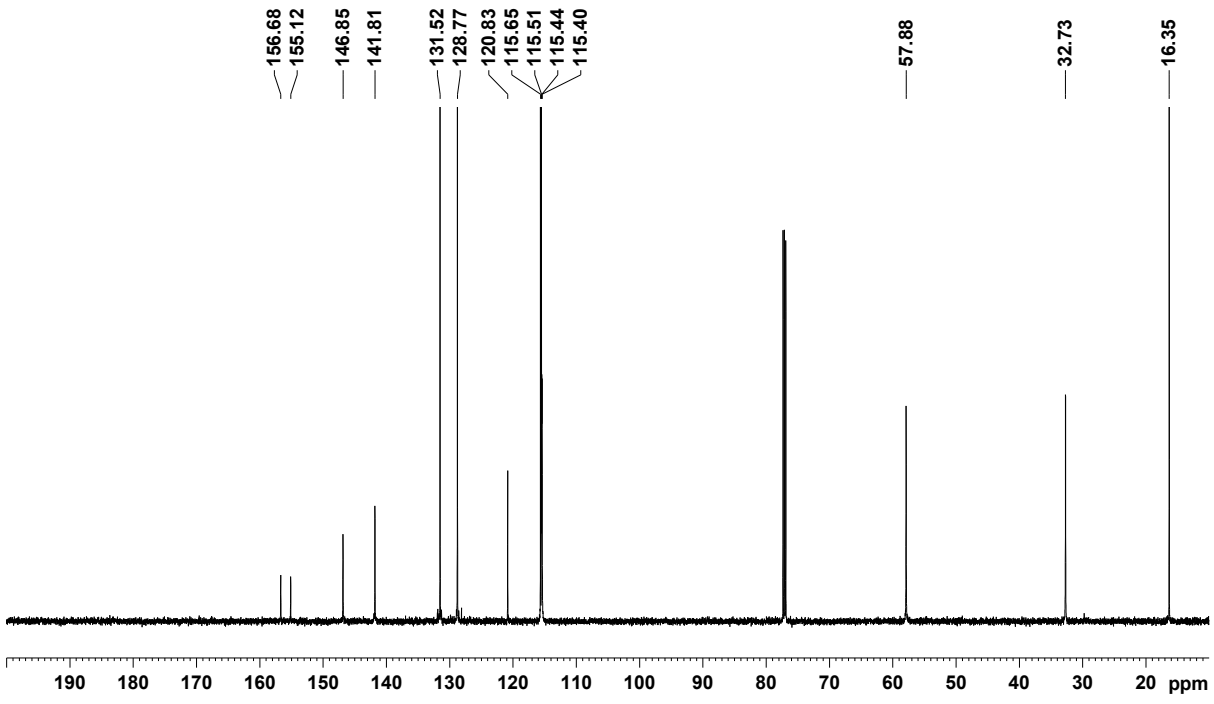


4-Fluoro-*N*-1-(4-bromophenyl)ethyl-*N*-methylaniline (3c).

^{1}H NMR

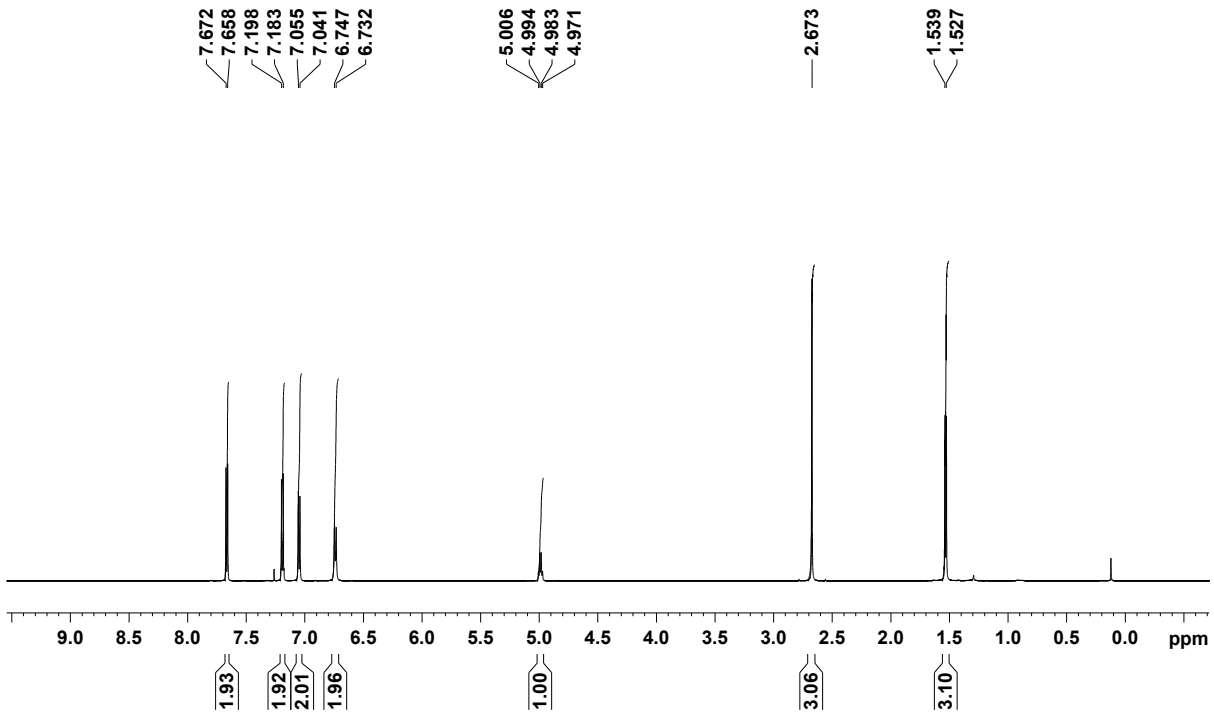


^{13}C NMR

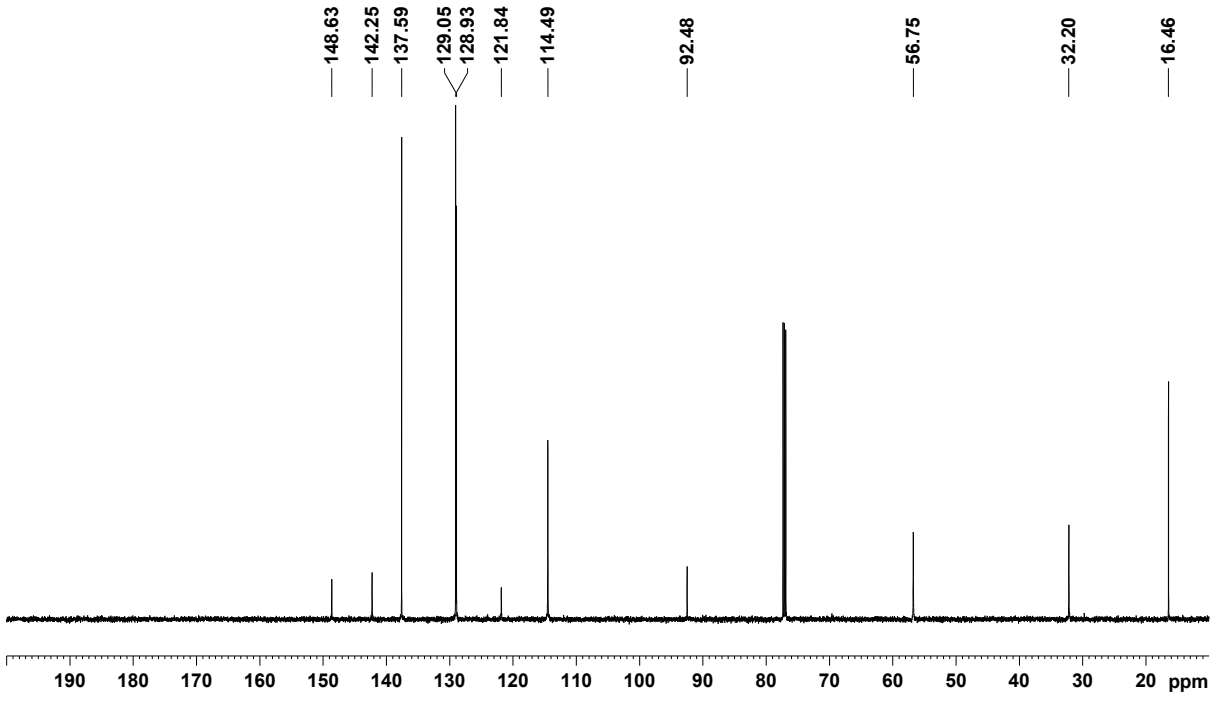


4-Chloro-*N*-1-(4-iodophenyl)ethyl-*N*-methylaniline (3d).

^{1}H NMR

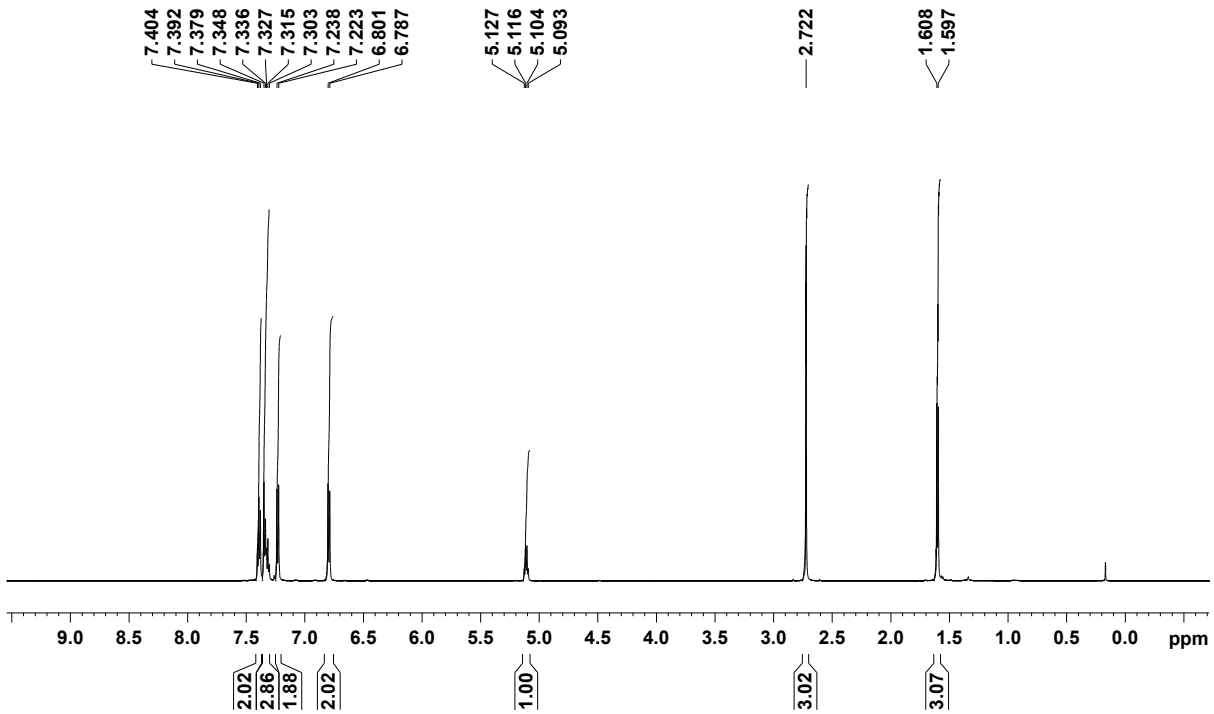


^{13}C NMR

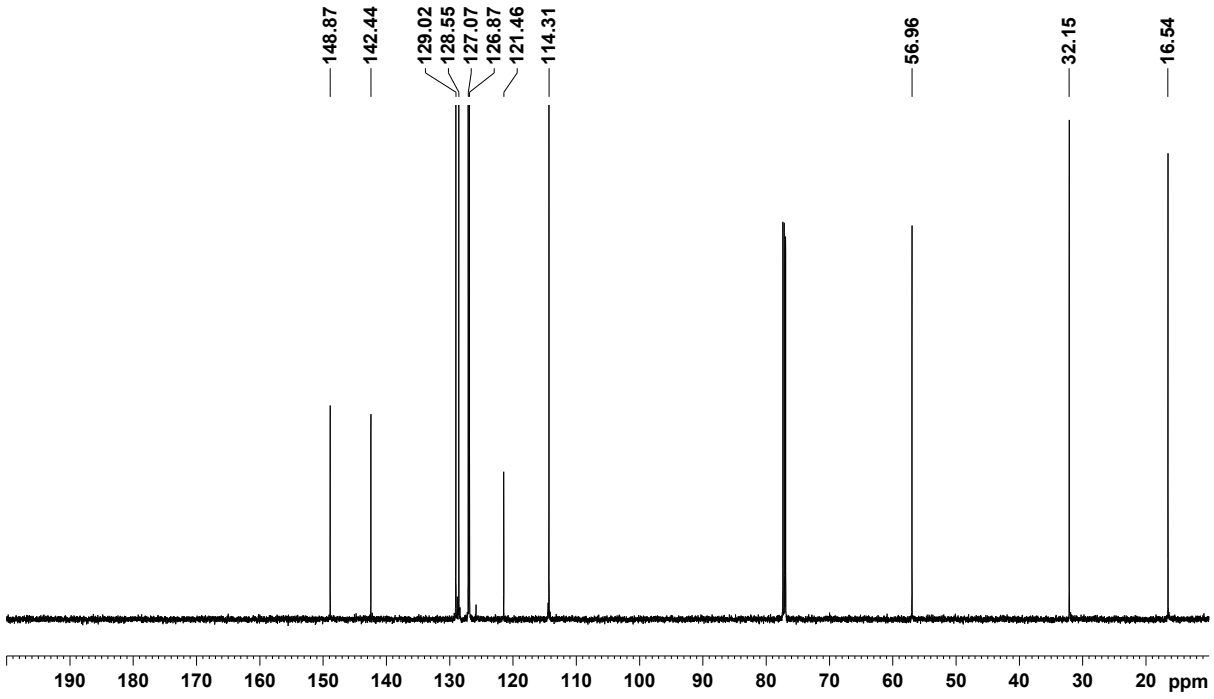


4-Chloro-*N*-1-phenylethyl-*N*-methylaniline (3e).

^{1}H NMR

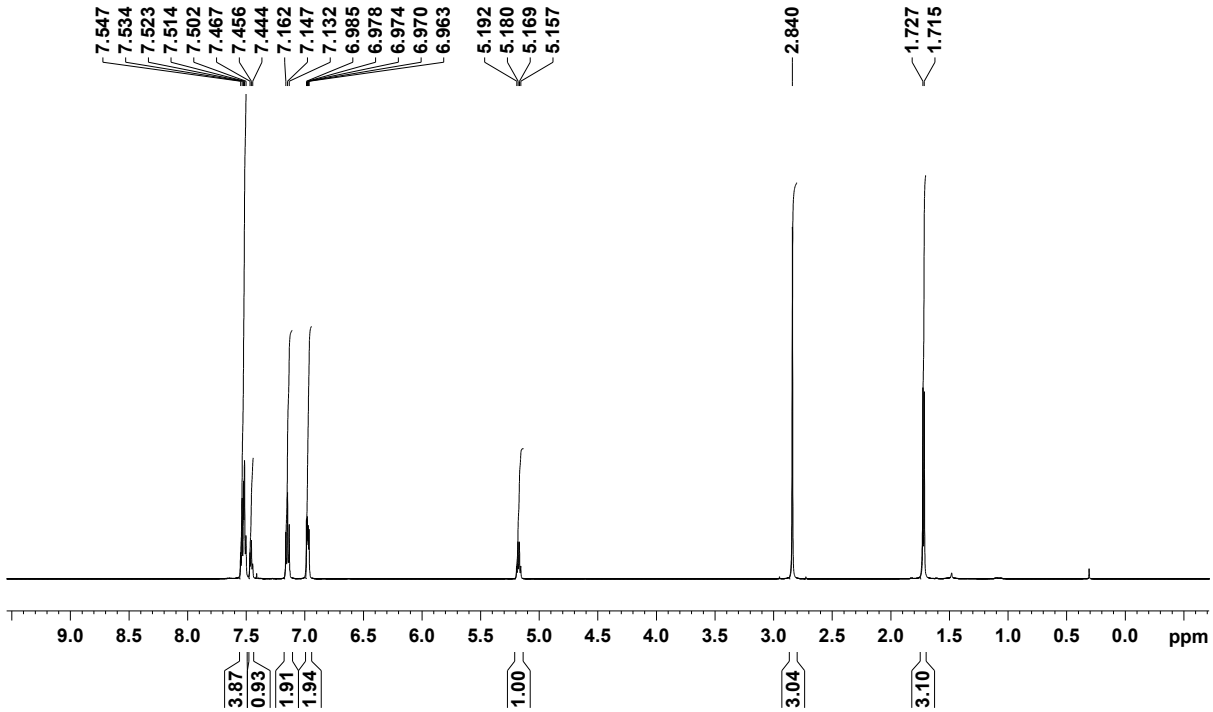


^{13}C NMR

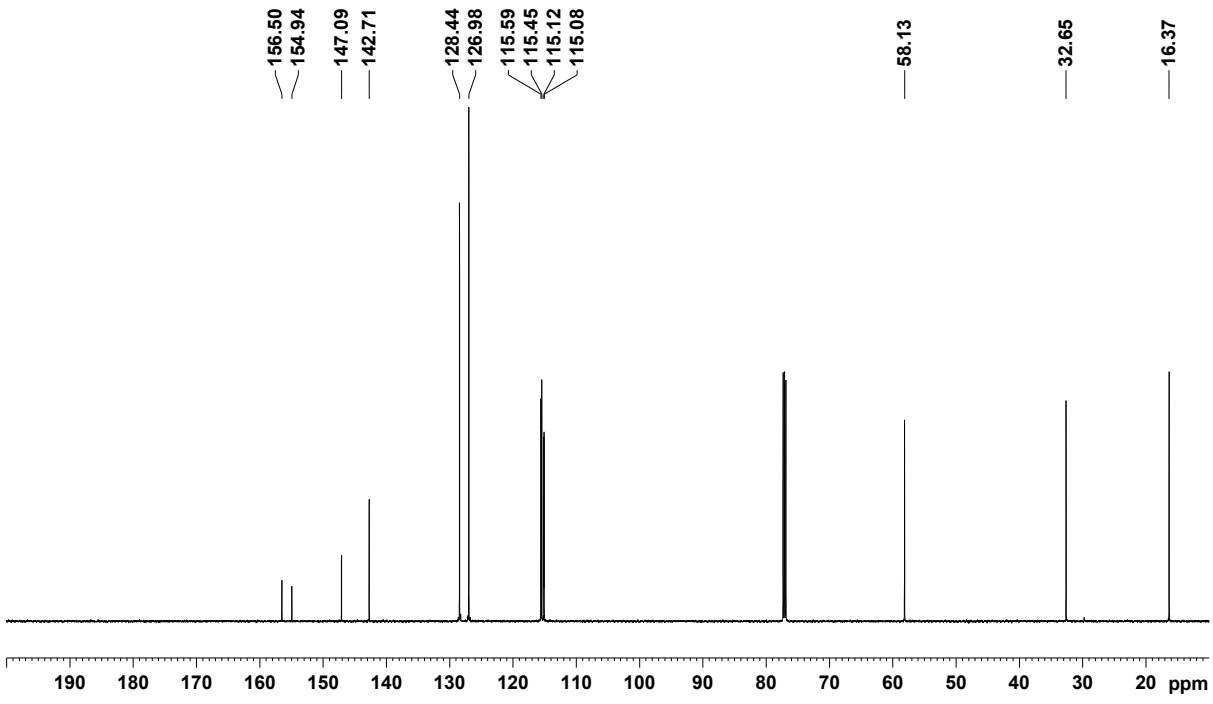


4-Fluoro-*N*-1-phenylethyl-*N*-methylaniline (3f).

^{1}H NMR

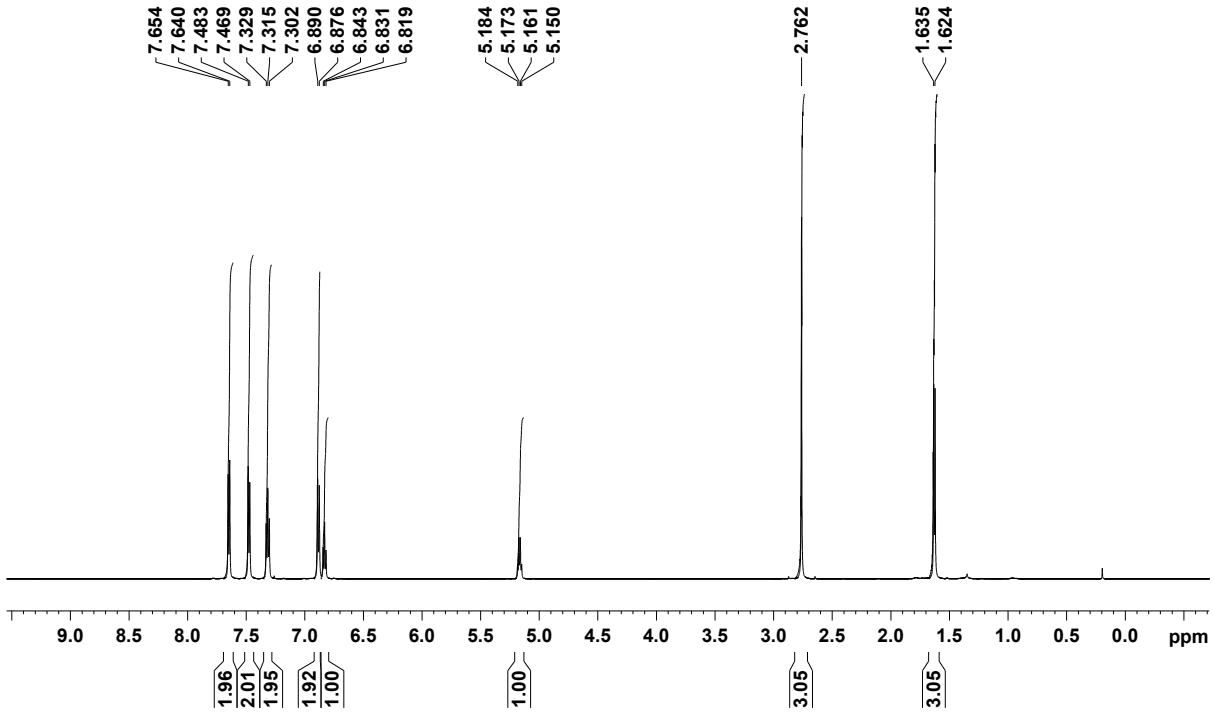


^{13}C NMR

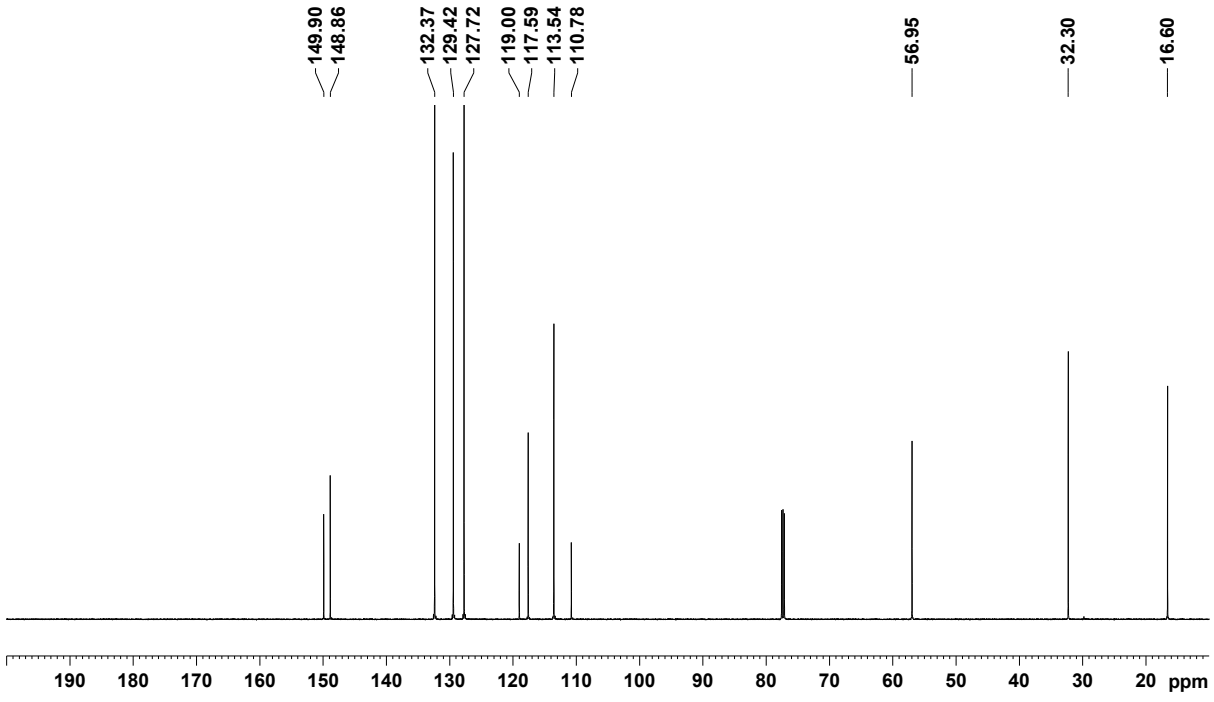


***N*-1-(4-Cyanophenyl)ethyl-*N*-methylaniline (3g).**

^{1}H NMR

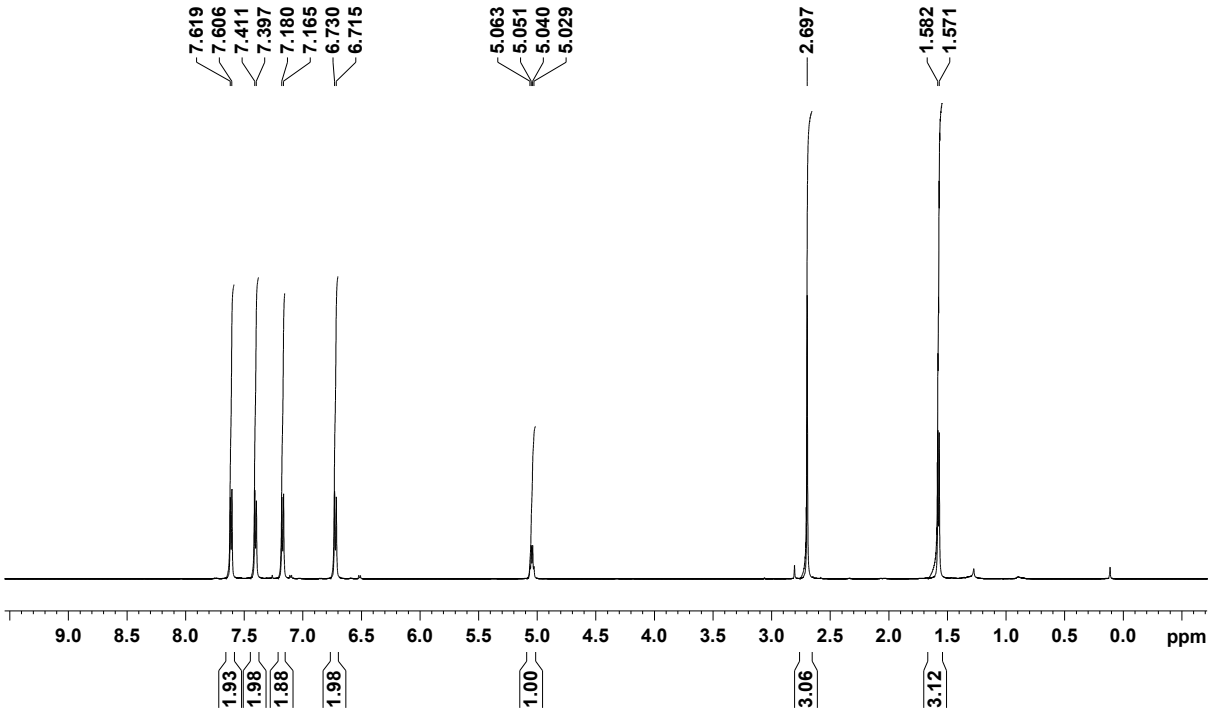


^{13}C NMR

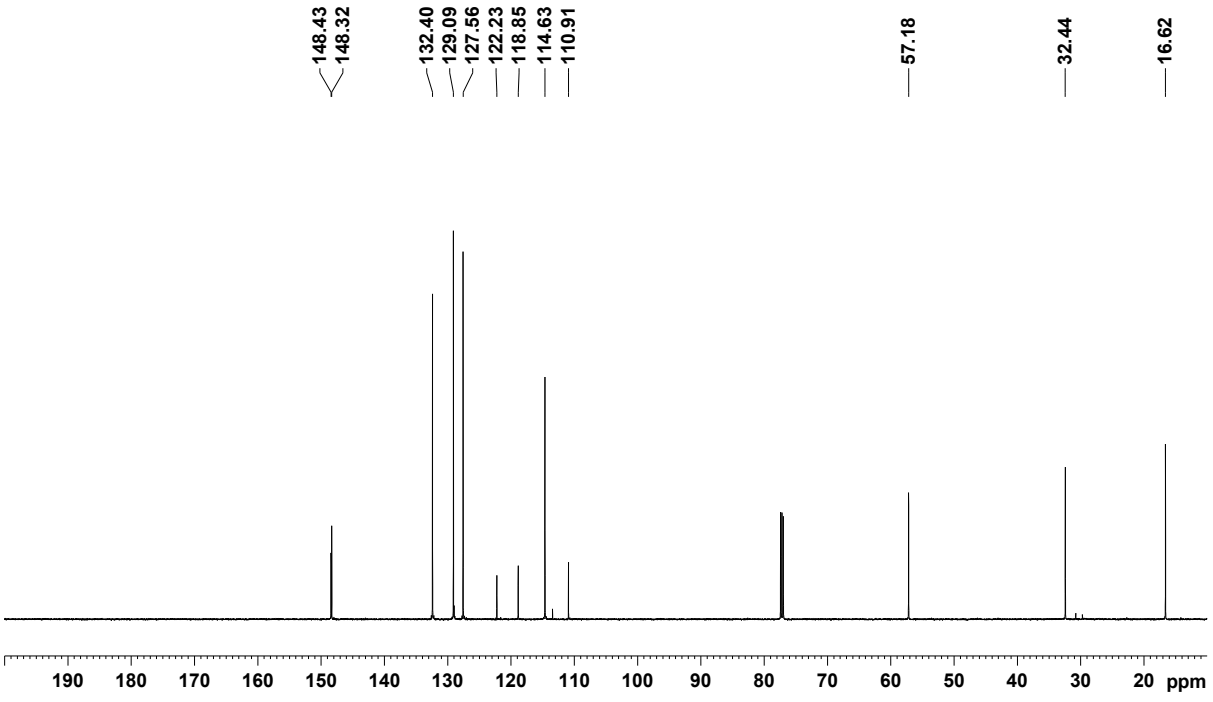


4-Chloro-*N*-1-(4-cyanophenyl)ethyl-*N*-methylaniline (3h).

^{1}H NMR

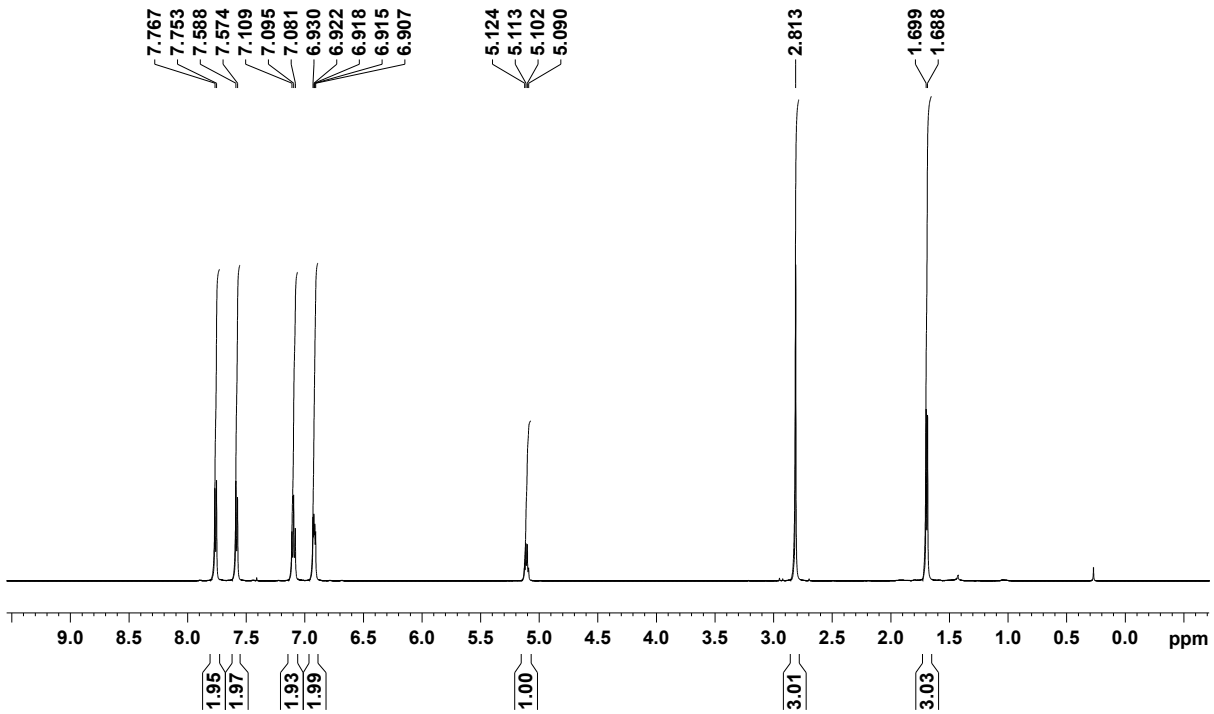


^{13}C NMR

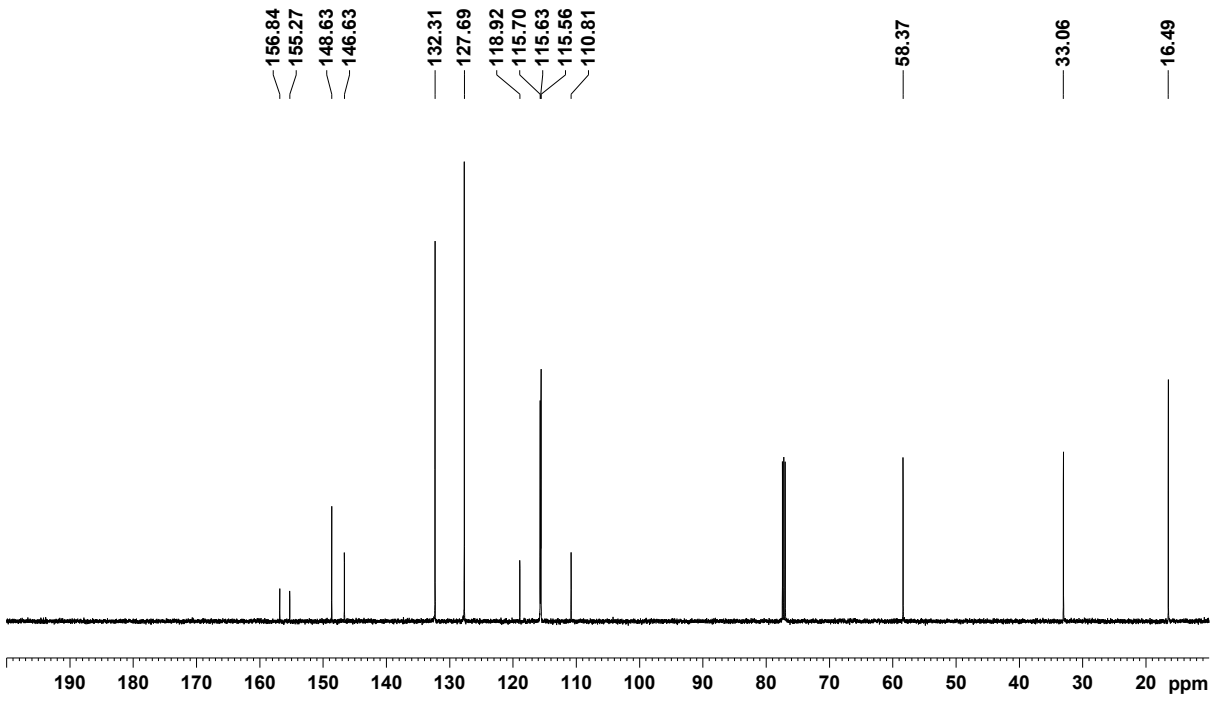


4-Fluoro-*N*-1-(4-cyanophenyl)ethyl-*N*-methylaniline (3i).

^{1}H NMR

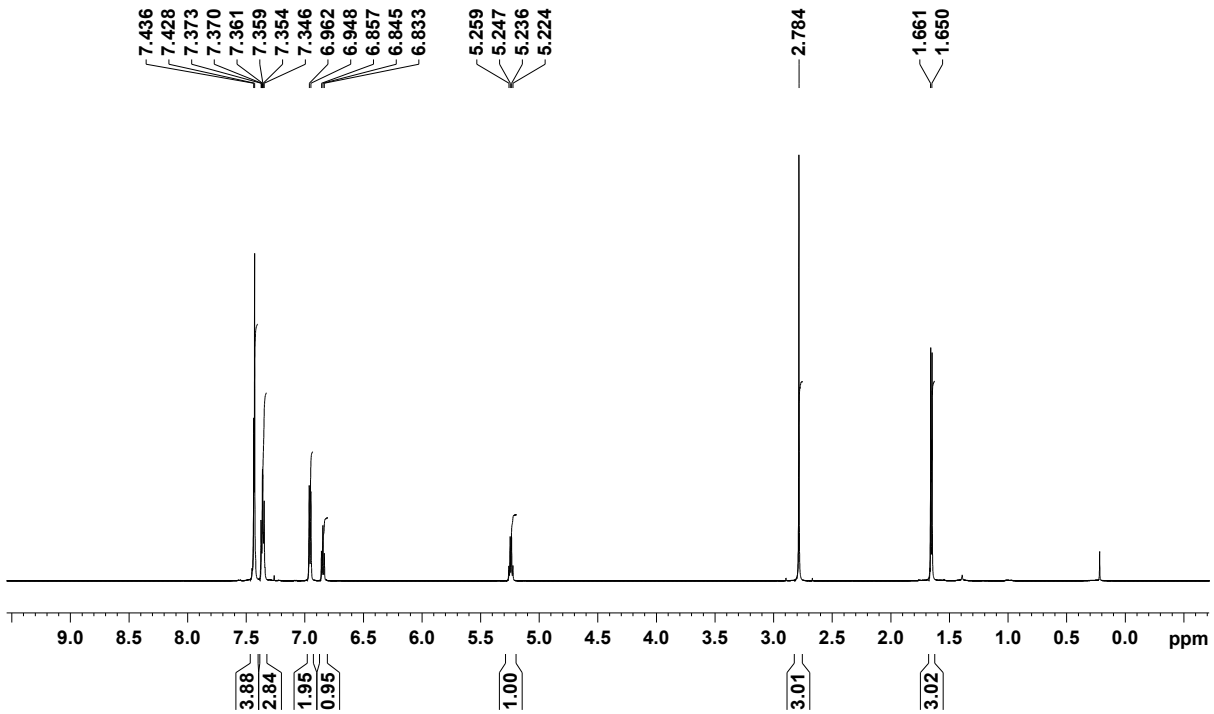


^{13}C NMR

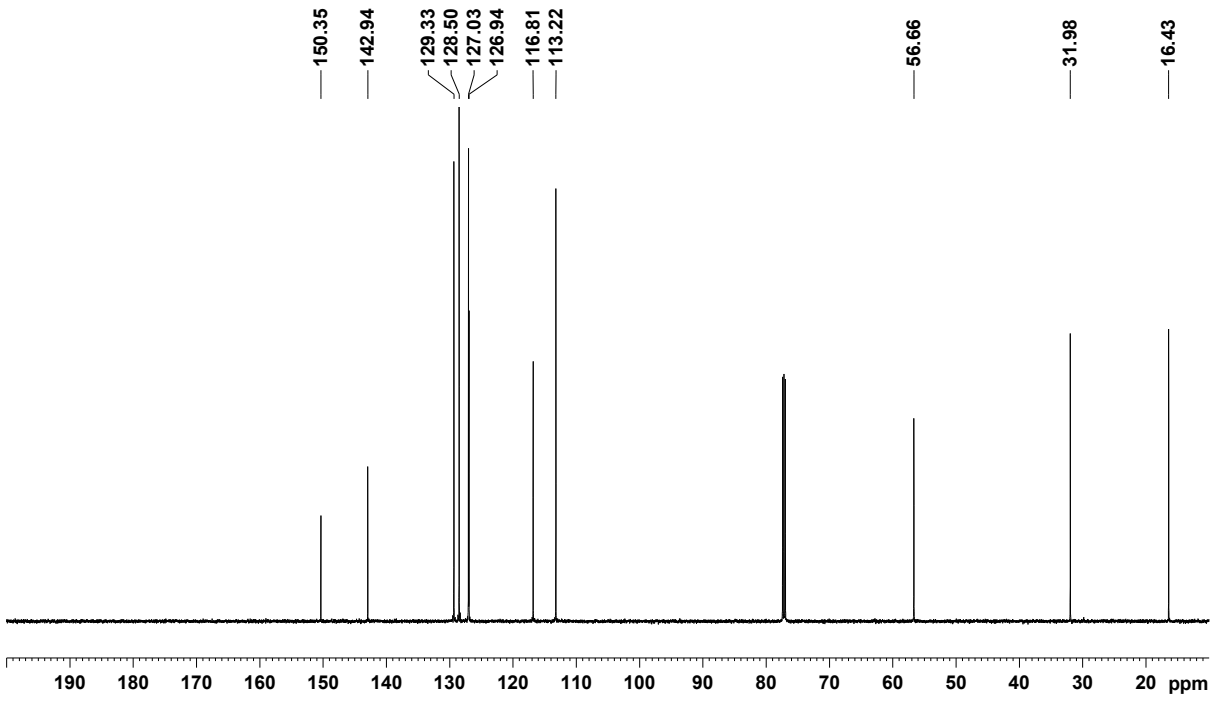


***N*-1-Phenylethyl-*N*-methylaniline (3j).**

^{1}H NMR

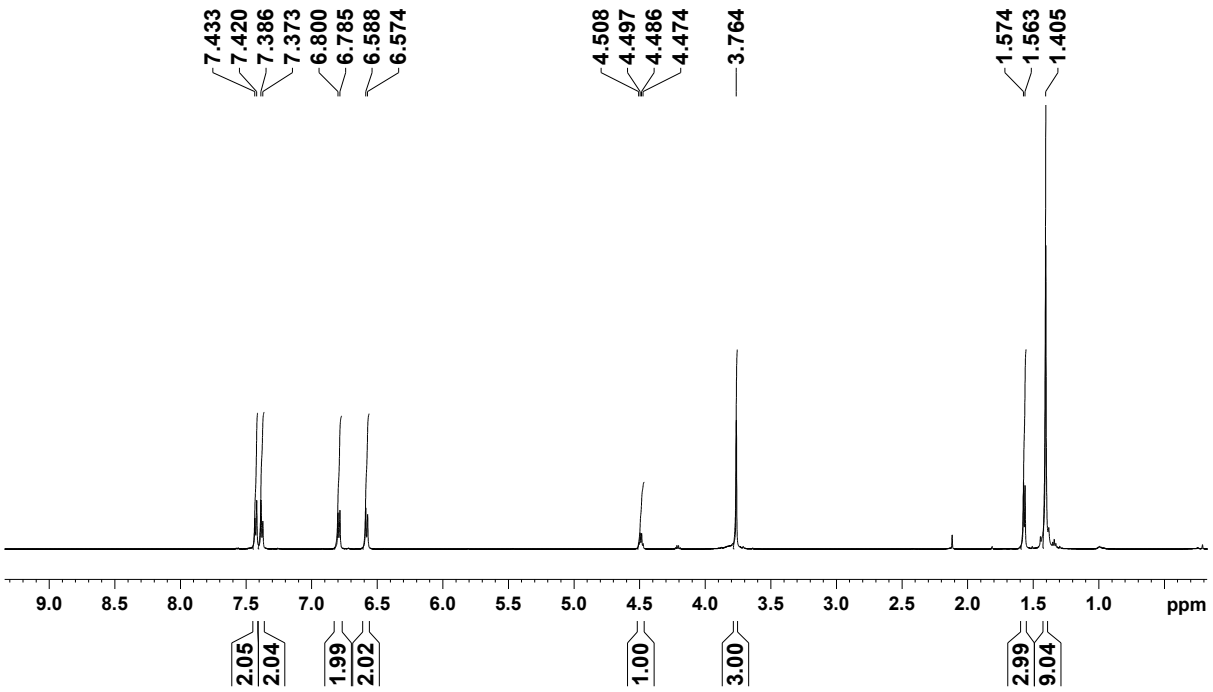


^{13}C NMR

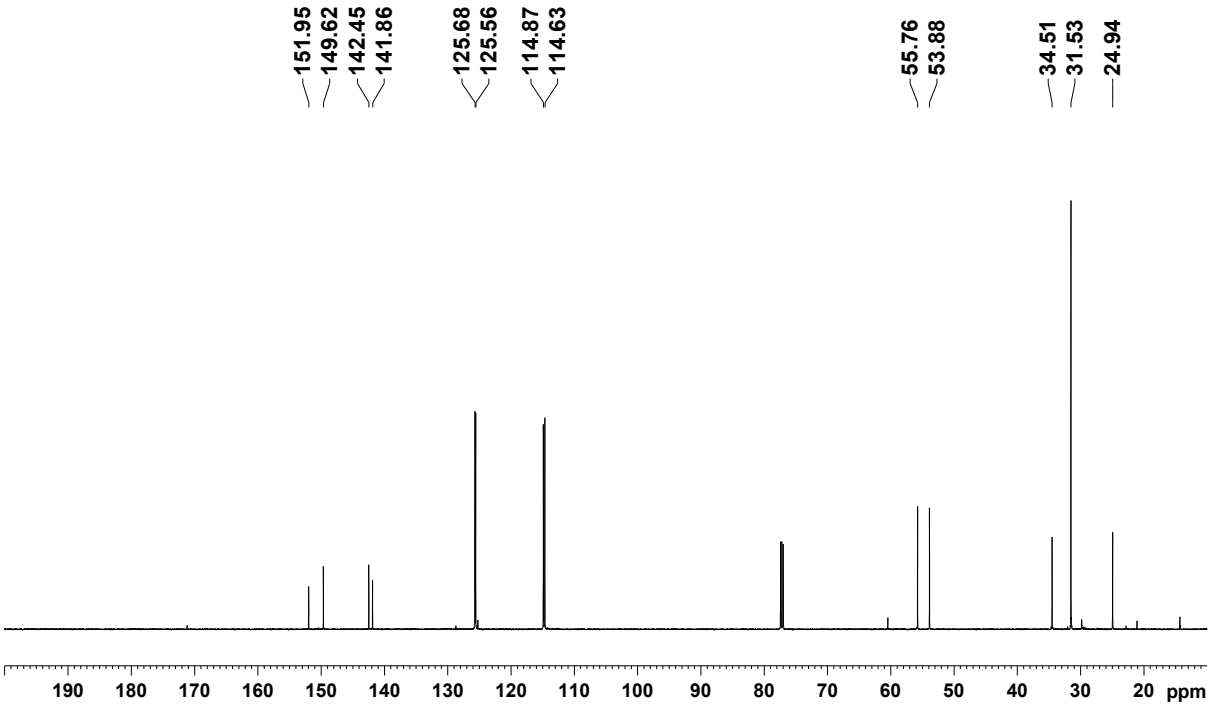


***N*-1-(4-methylphenyl)ethyl-*N*-methylaniline (3k).**

^{1}H NMR

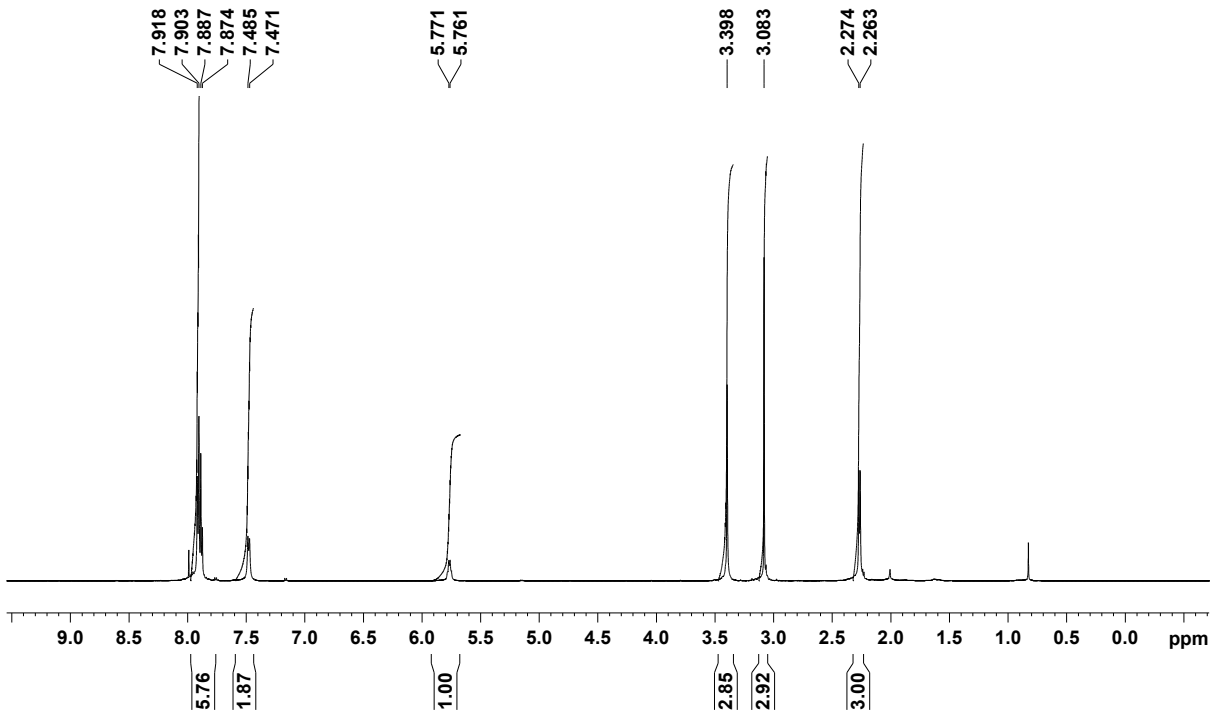


^{13}C NMR

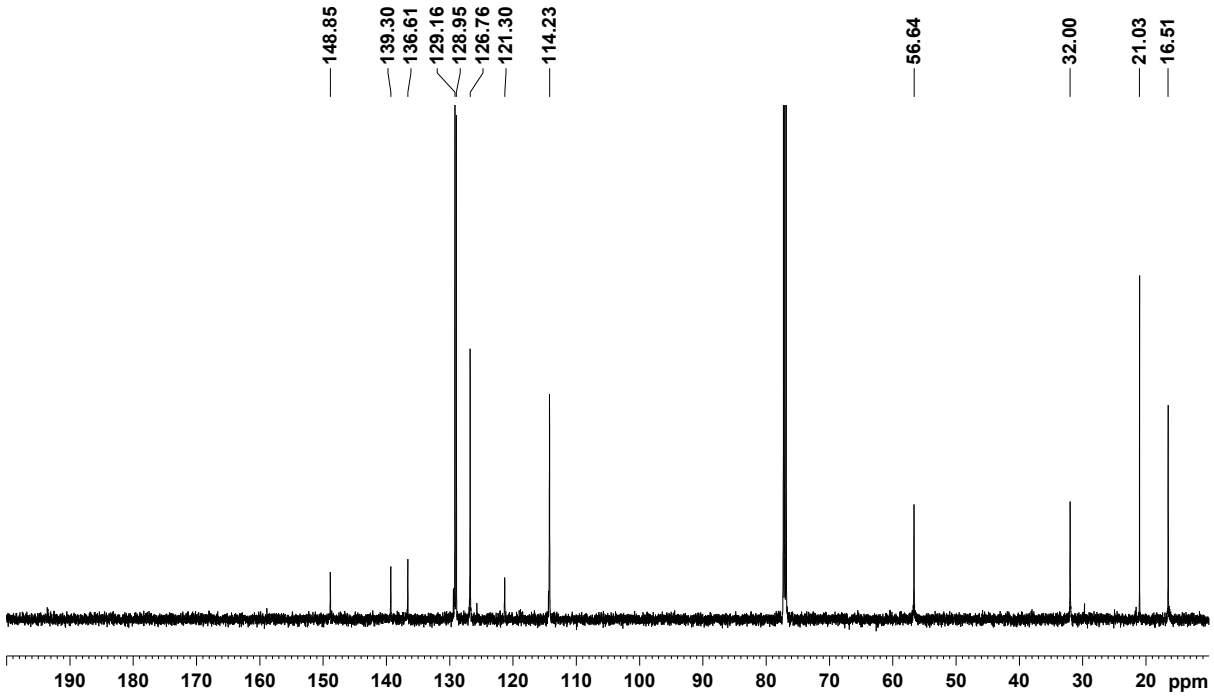


4-Chloro-*N*-1-(4-methylphenyl)ethyl-*N*-methylaniline (3l).

^{1}H NMR

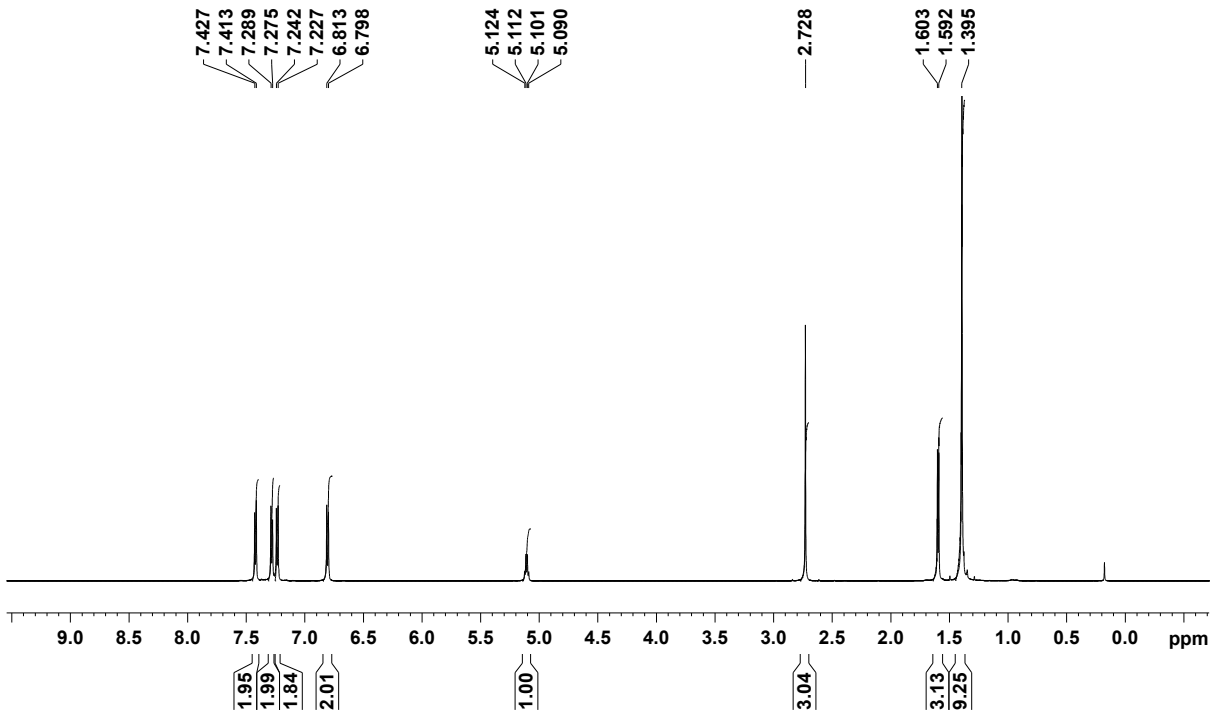


^{13}C NMR

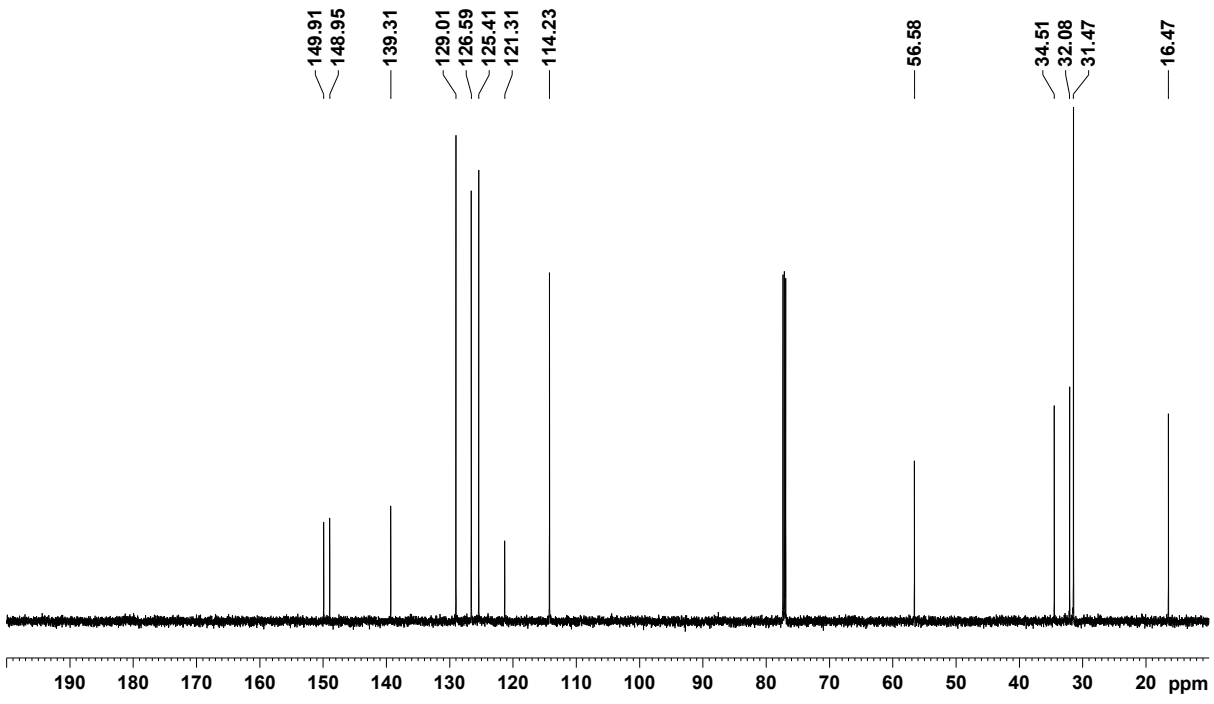


4-Chloro-*N*-1-(4-*tert*-butylphenyl)ethyl-*N*-methylaniline (3m).

^{1}H NMR

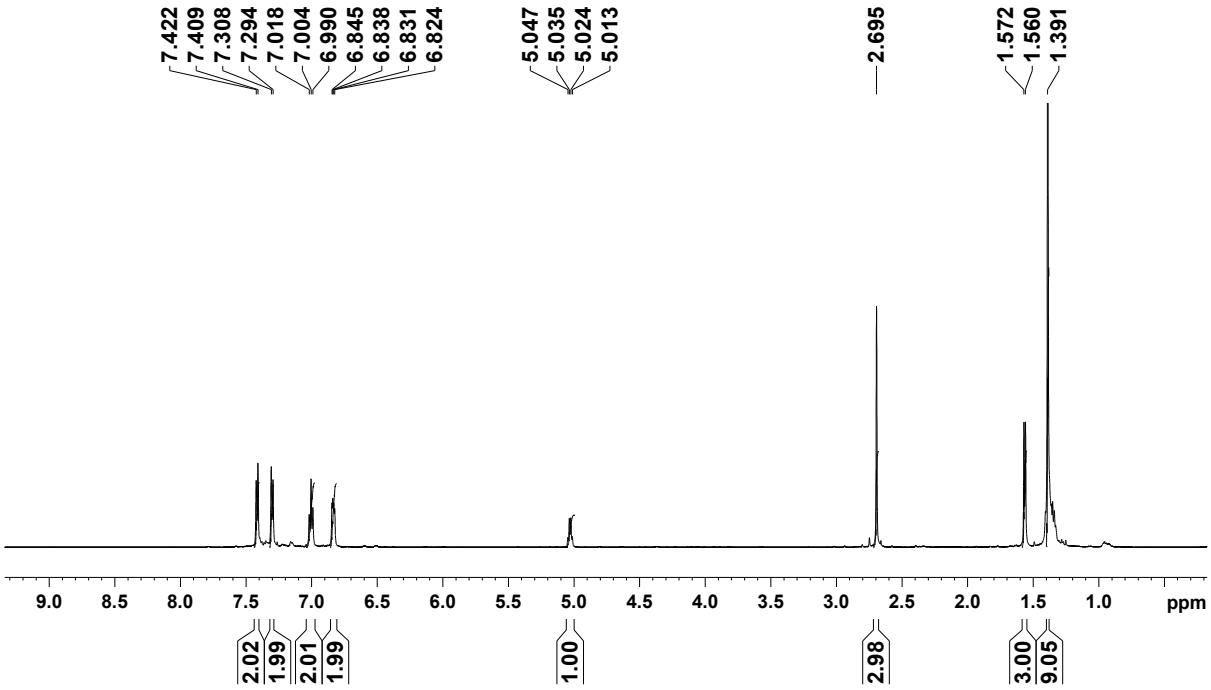


^{13}C NMR

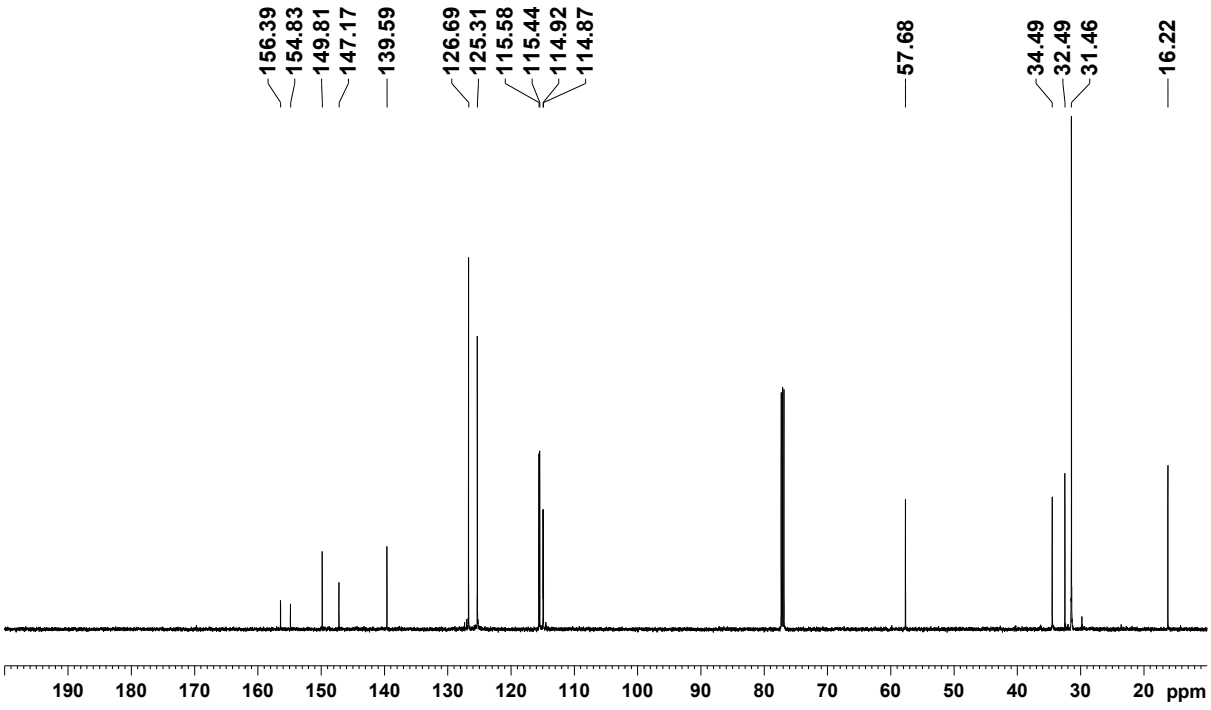


4-Fluoro-*N*-1-(4-*tert*-butylphenyl)ethyl-*N*-methylaniline (3n).

^{1}H NMR

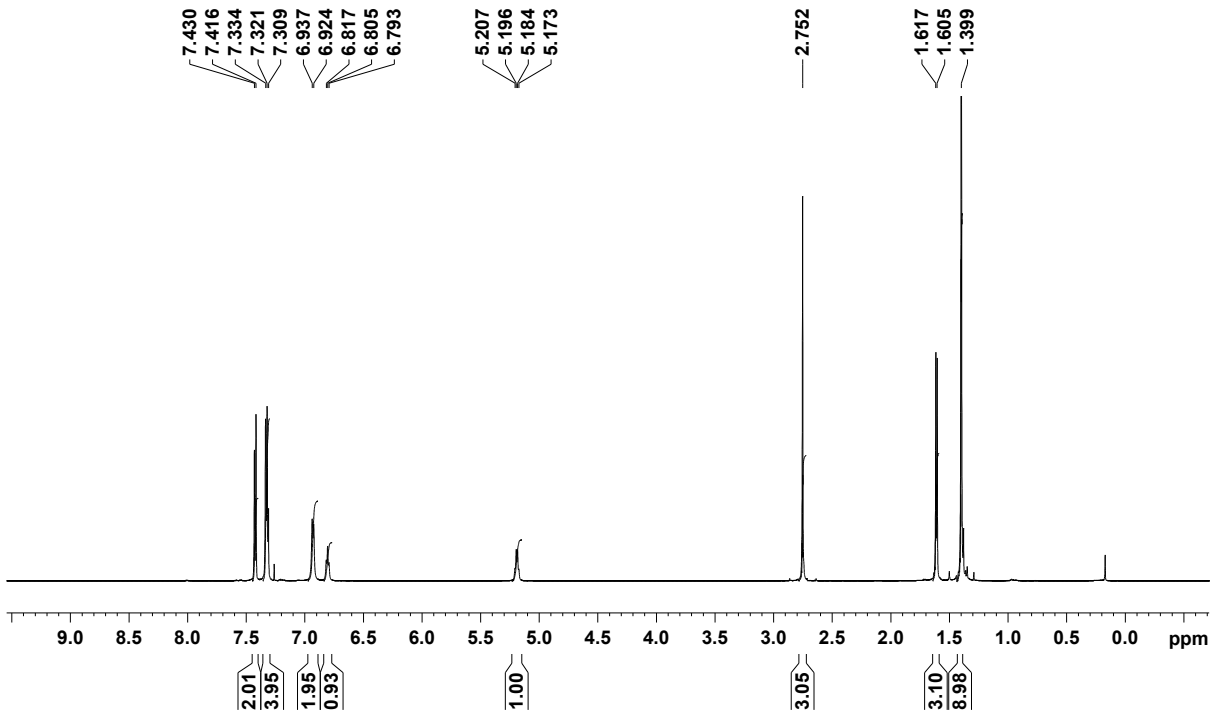


^{13}C NMR

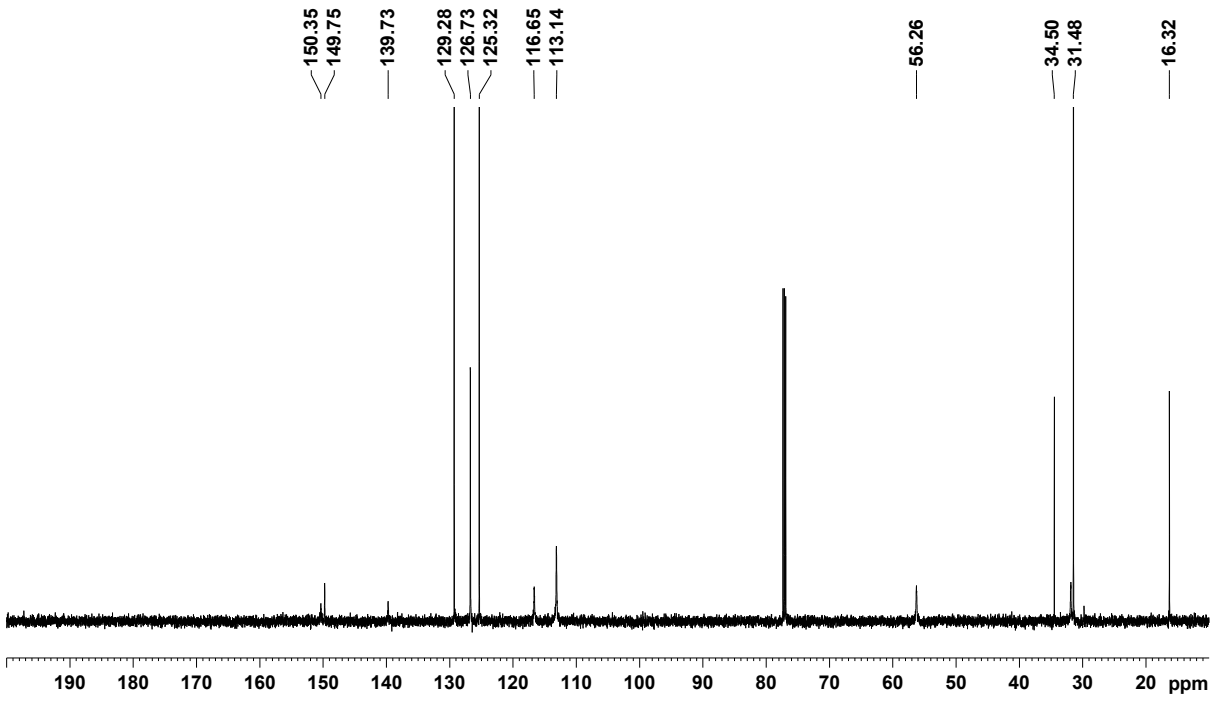


***N*-1-(4-*tert*-Butylphenyl)ethyl-*N*-methylaniline (3o).**

^{1}H NMR

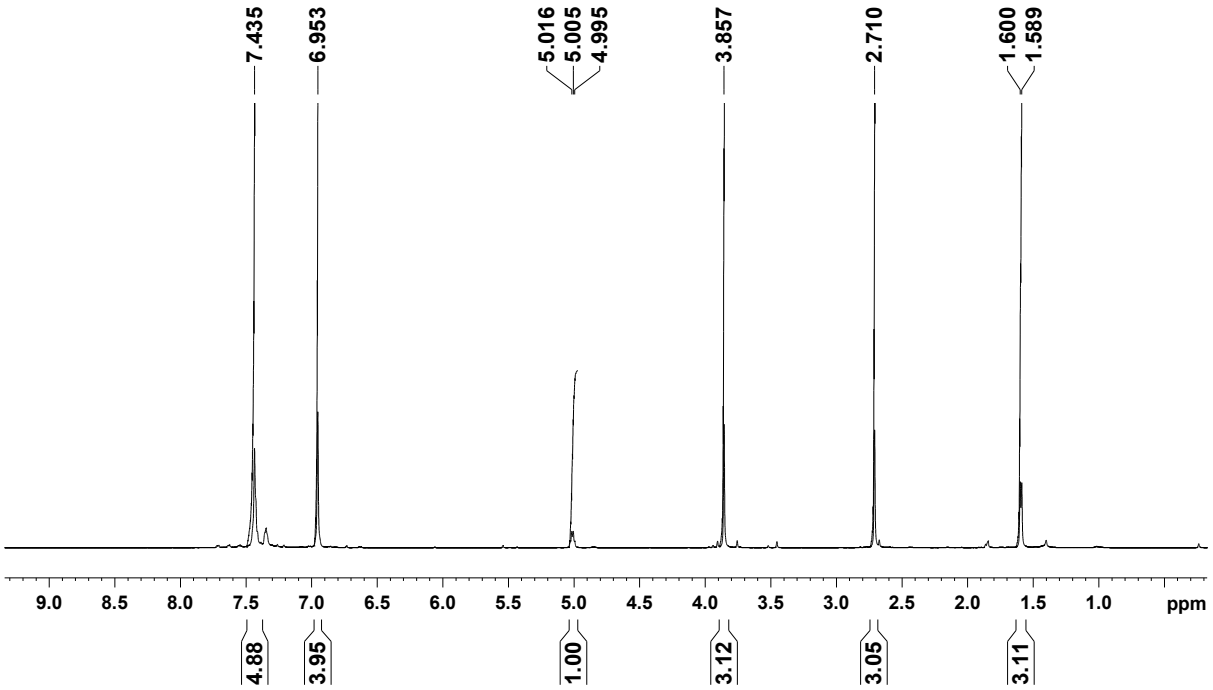


^{13}C NMR

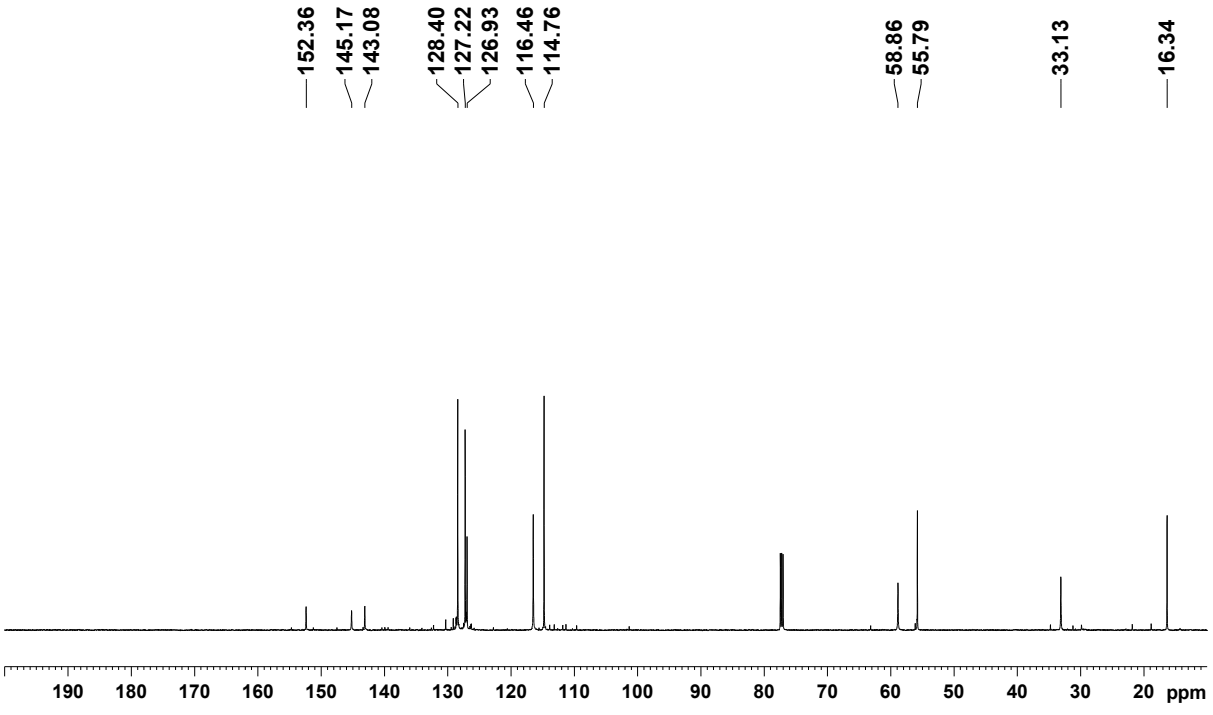


4-Methoxy-*N*-(1-phenylethyl)-*N*-methylaniline (3p).

^{1}H NMR

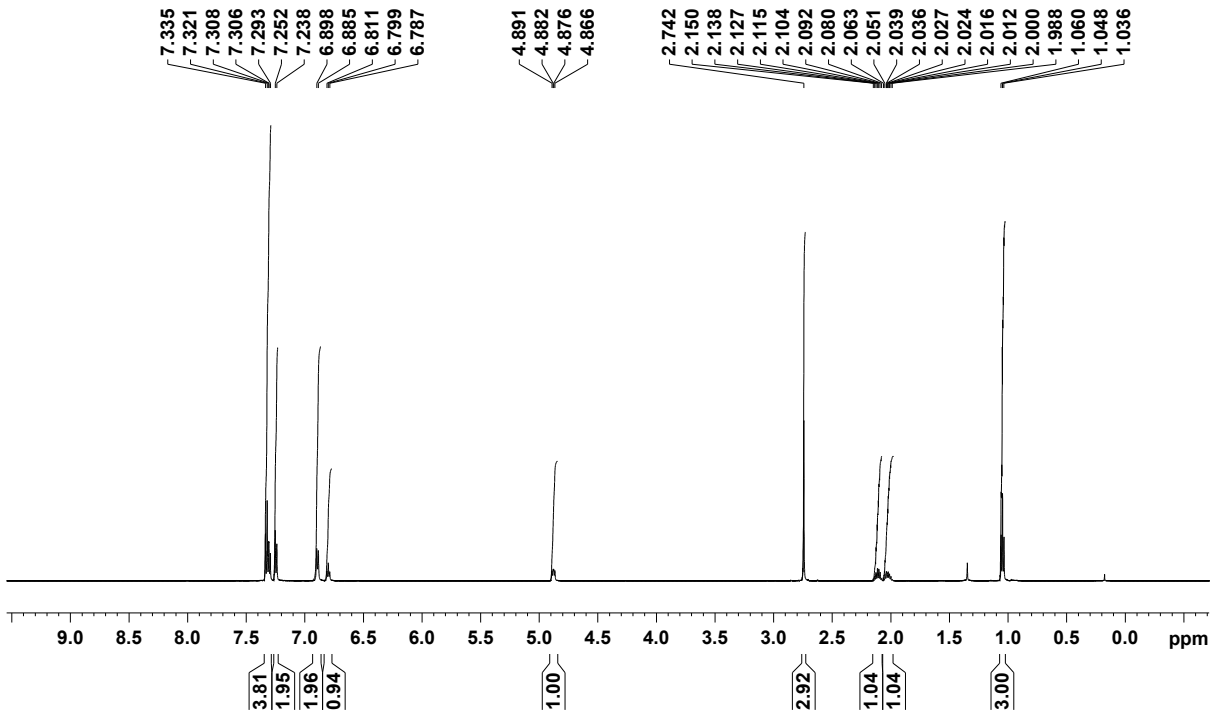


^{13}C NMR

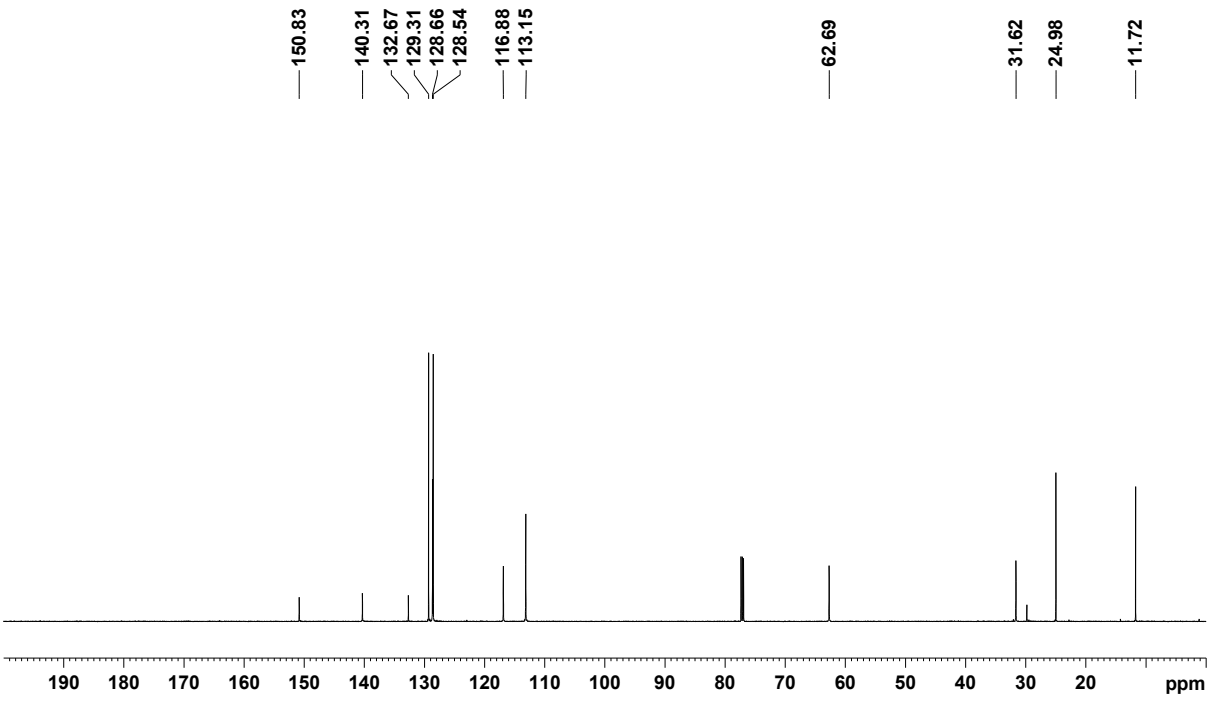


***N*-1-(4-Chlorophenyl)propyl-*N*-methylaniline (3q).**

^{1}H NMR

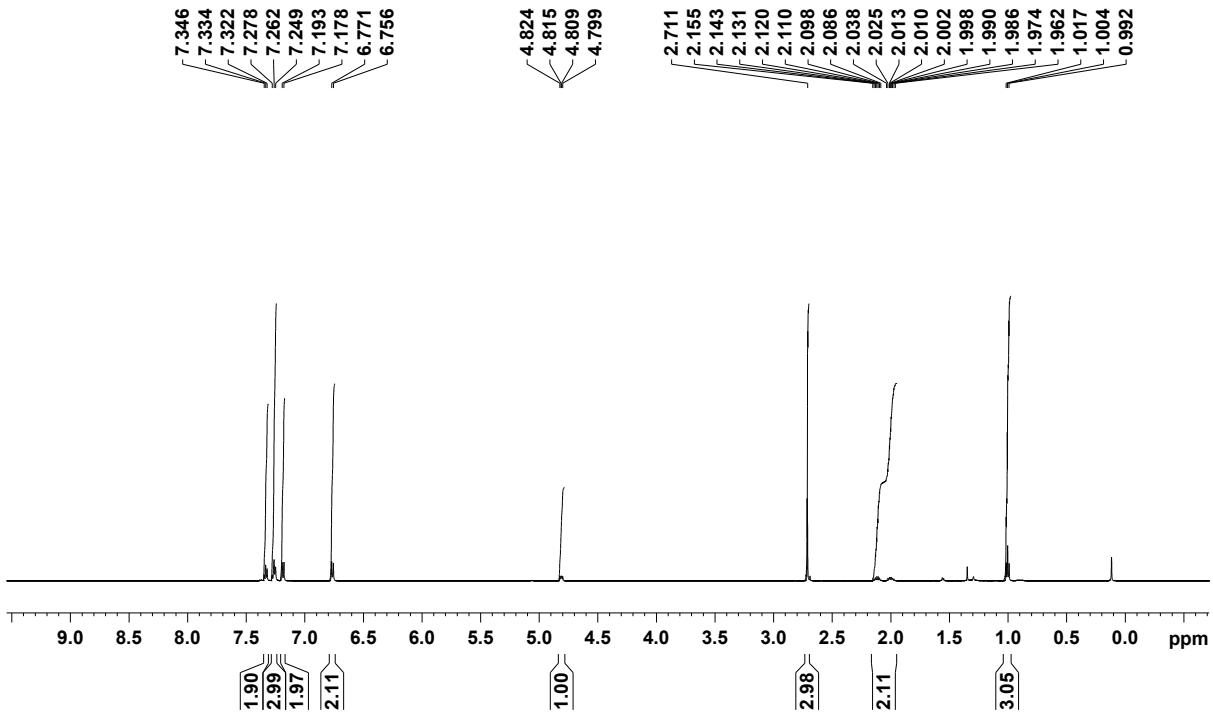


^{13}C NMR

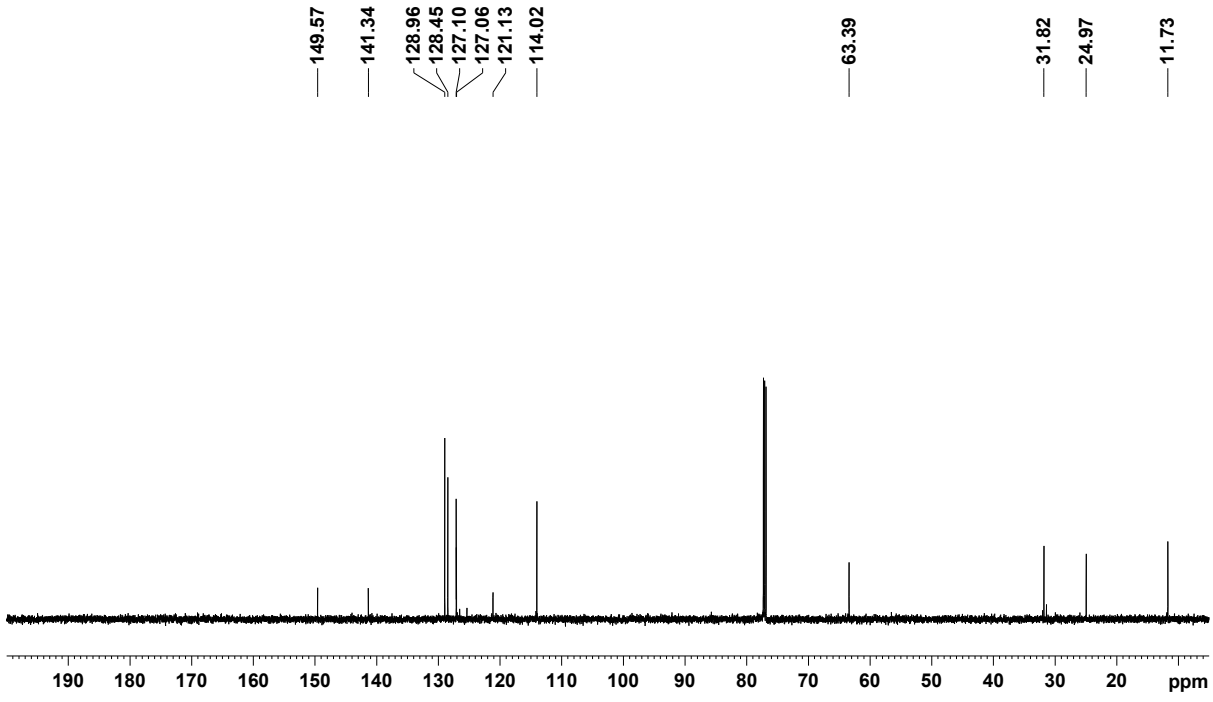


4-Chloro-*N*-1-(phenyl)propyl-*N*-methylaniline (3r).

^{1}H NMR

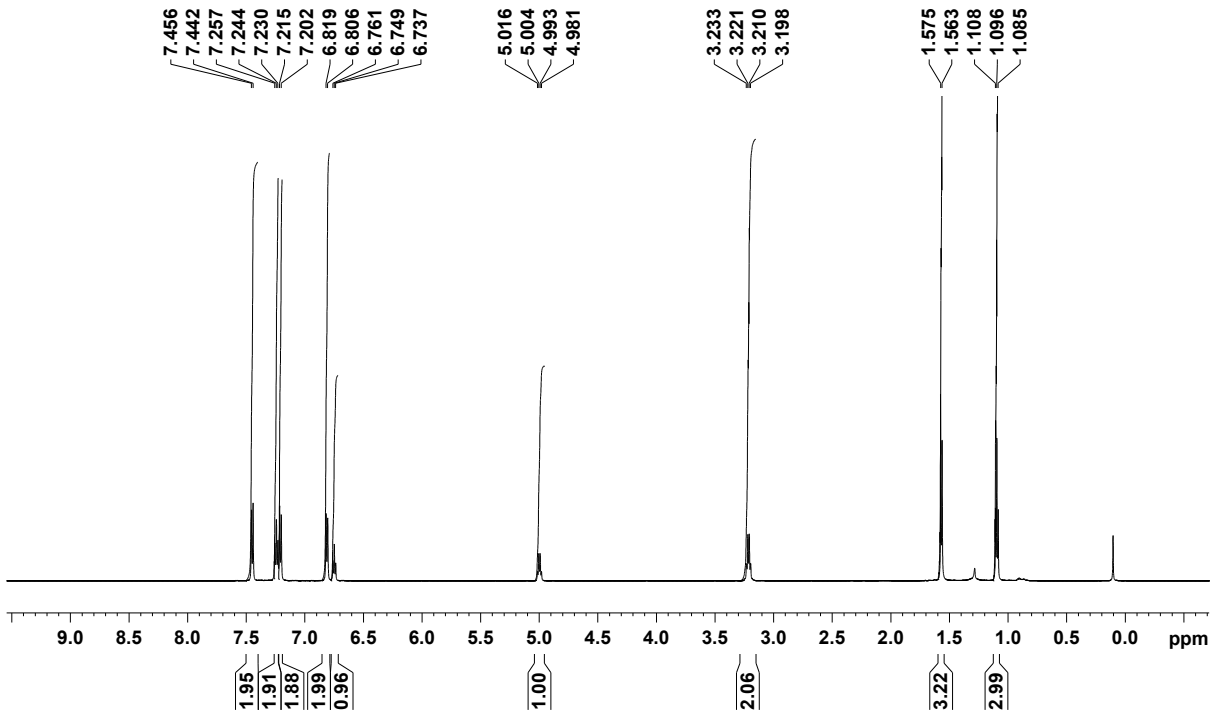


^{13}C NMR

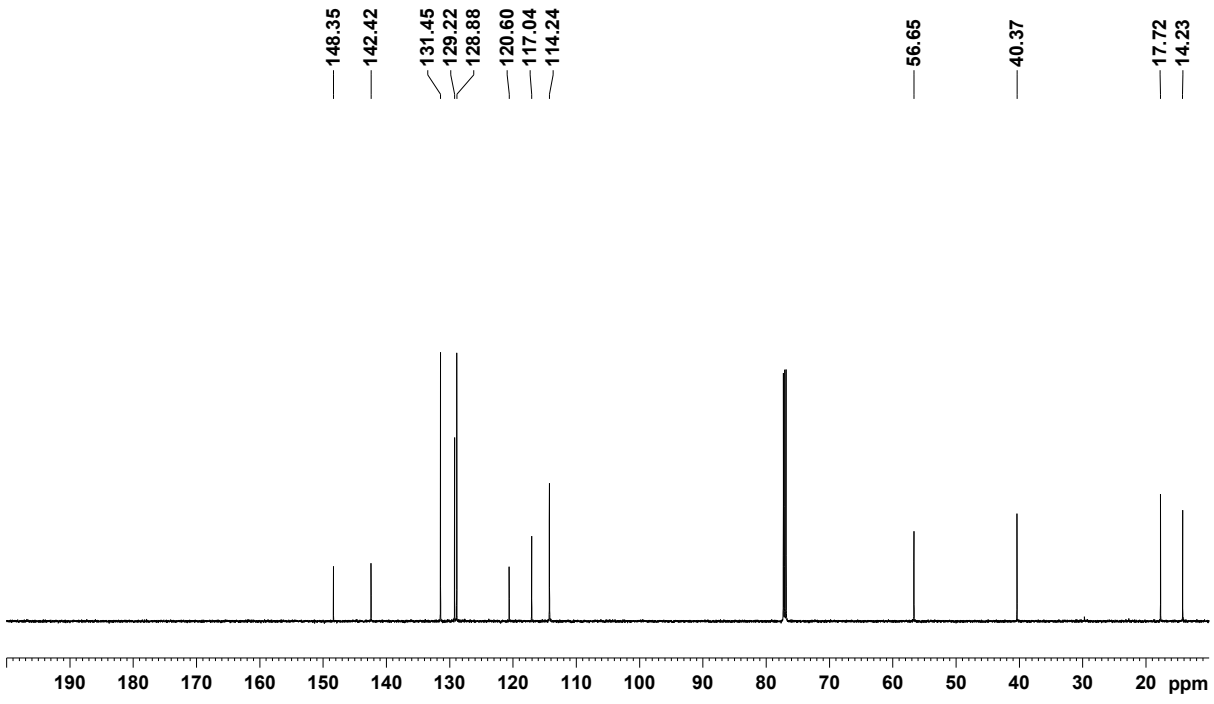


***N*-1-(4-Bromo phenyl)ethyl-*N*-ethylaniline (3s).**

^{1}H NMR

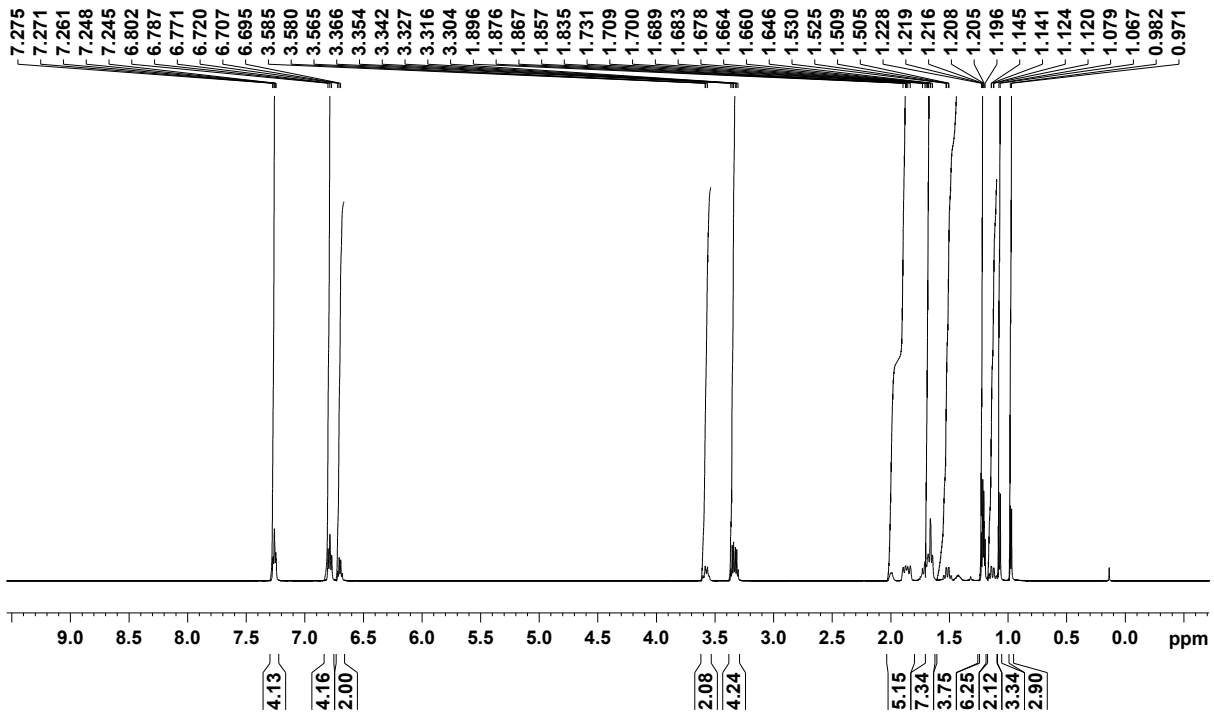


^{13}C NMR

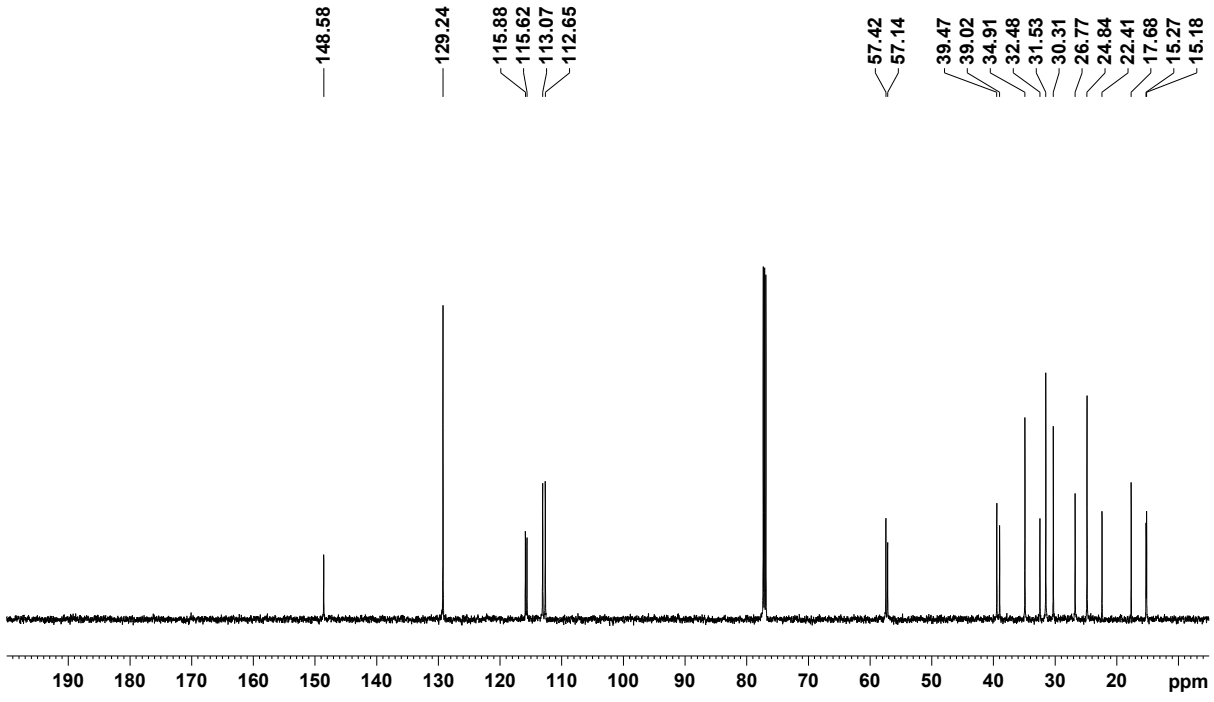


***N*-1- (4-Methylcyclohexyl)-*N*-ethylaniline (3t).**

^{1}H NMR

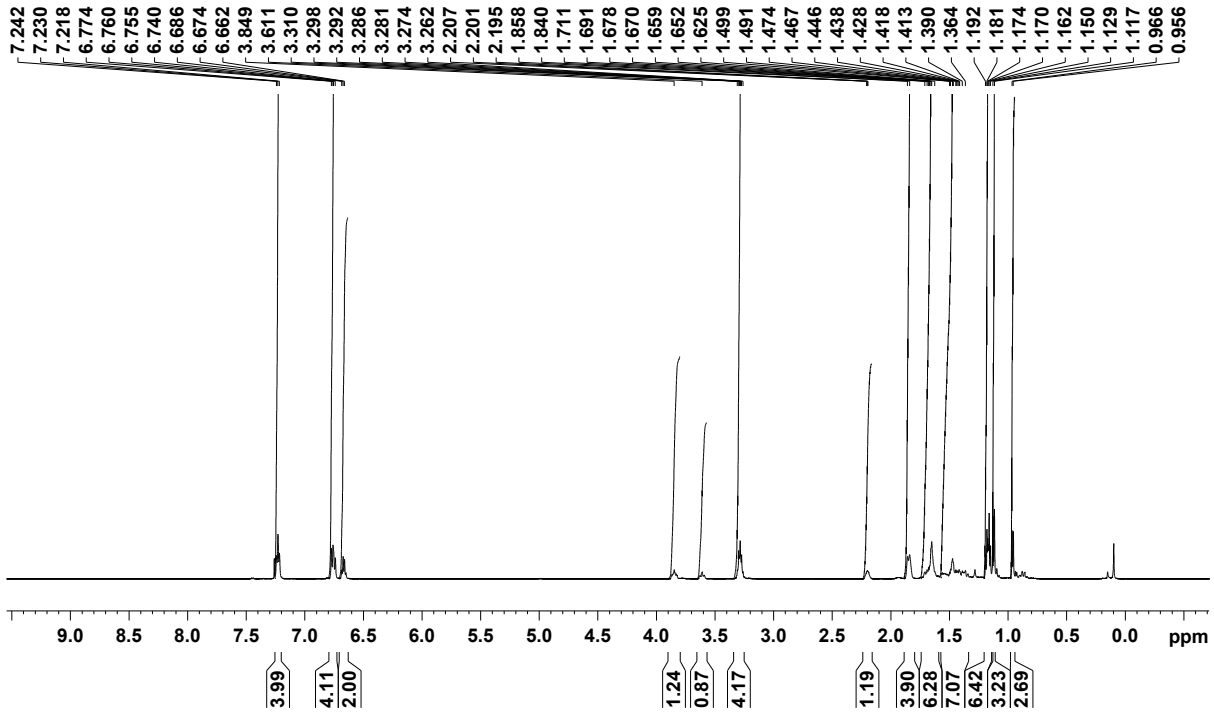


^{13}C NMR

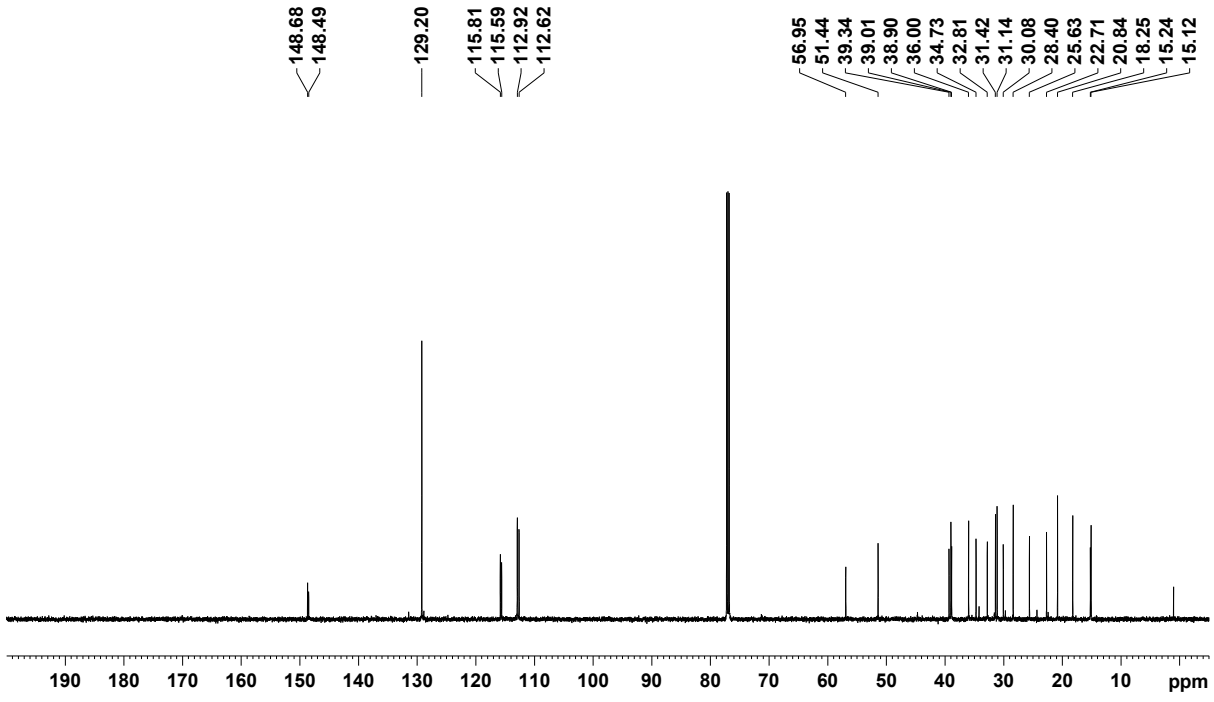


***N*-1- (3-Methylcyclohexyl)-*N*-ethylaniline (3u).**

^{1}H NMR

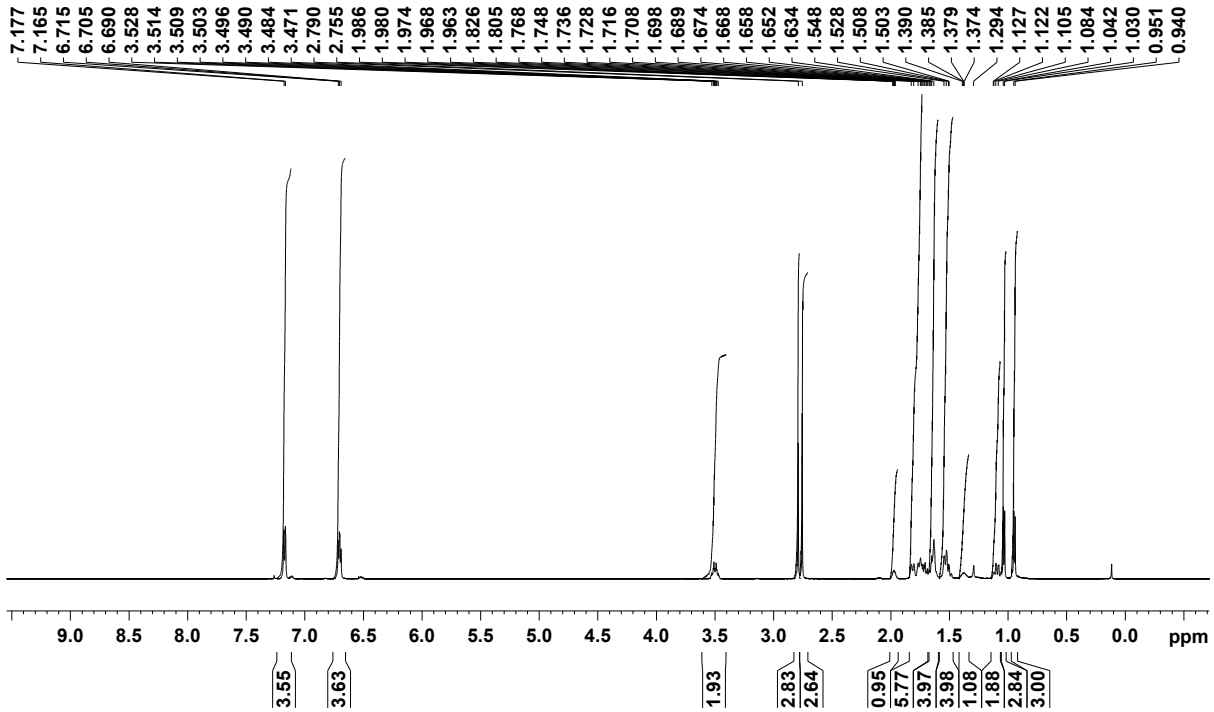


^{13}C NMR

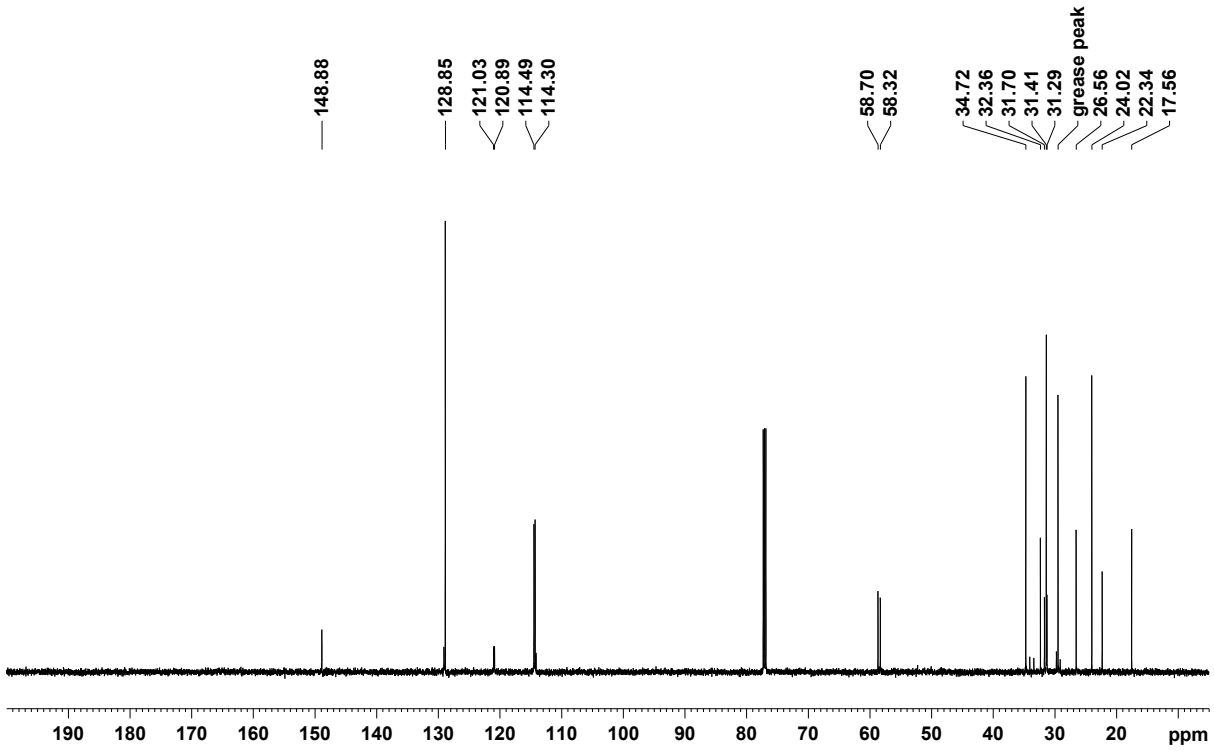


4-Chloro-*N*-4-methylcyclohexyl-*N*-methylaniline (3v).

^{1}H NMR

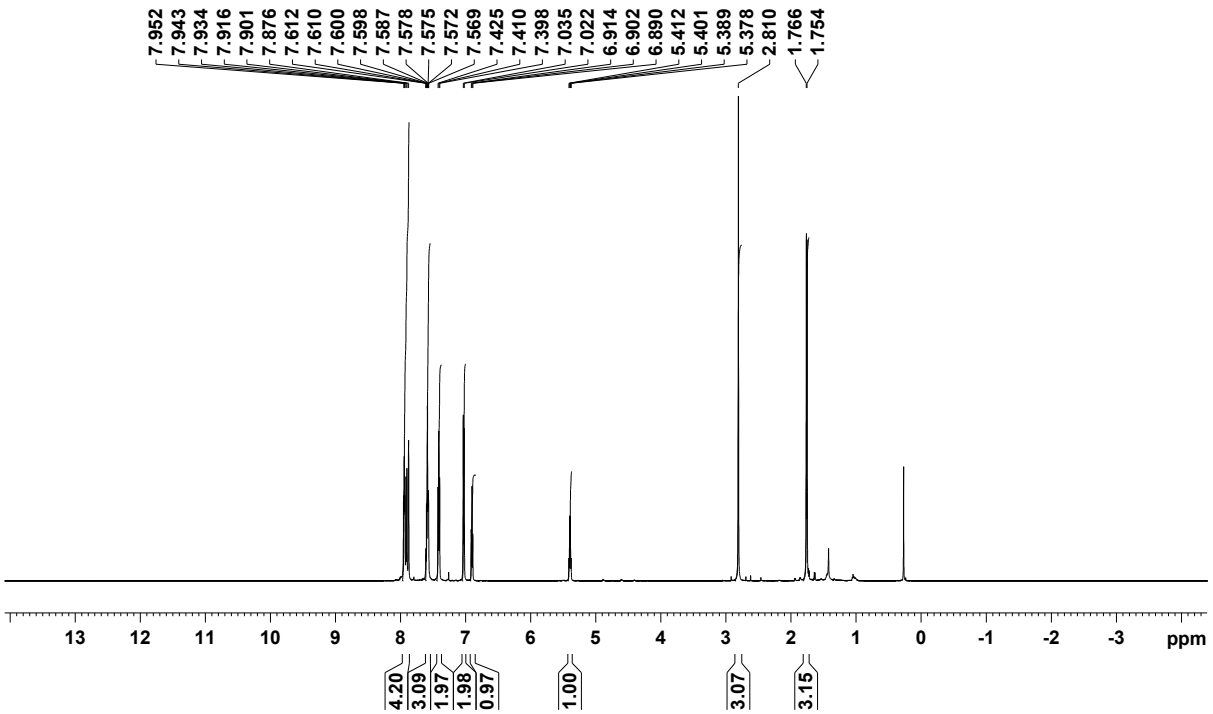


^{13}C NMR

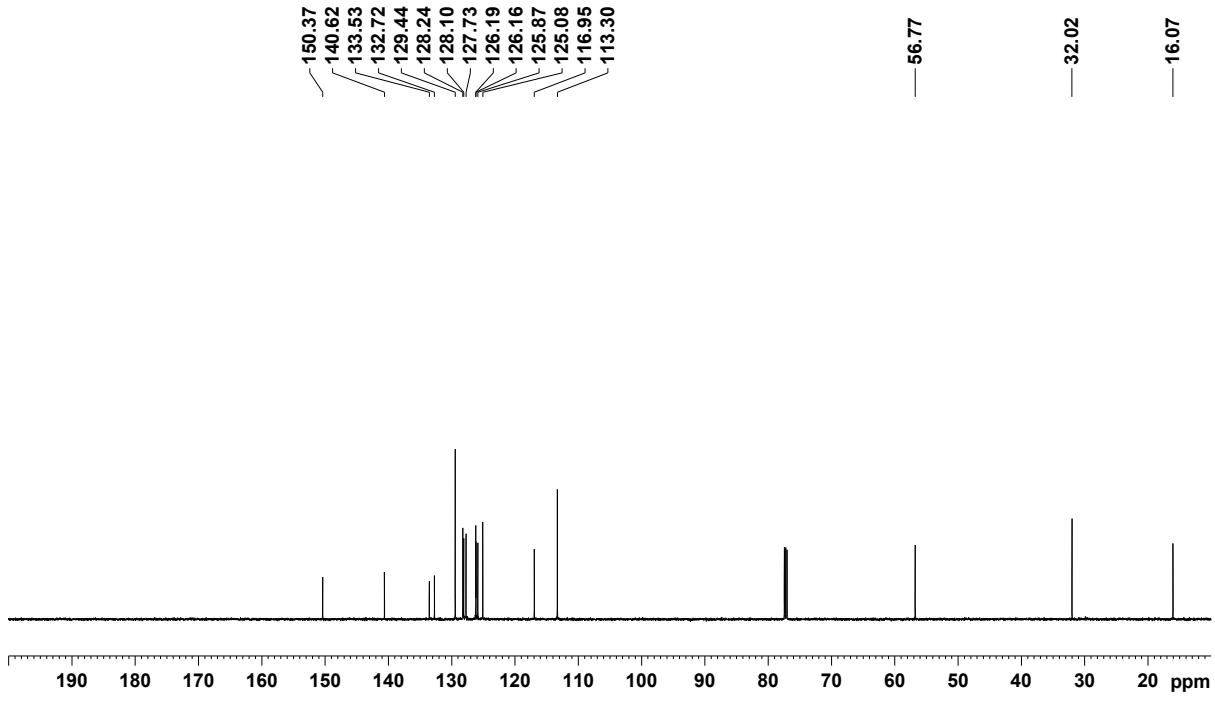


***N*-1-naphathylethyl-*N*-methylaniline (3w).**

^{1}H NMR

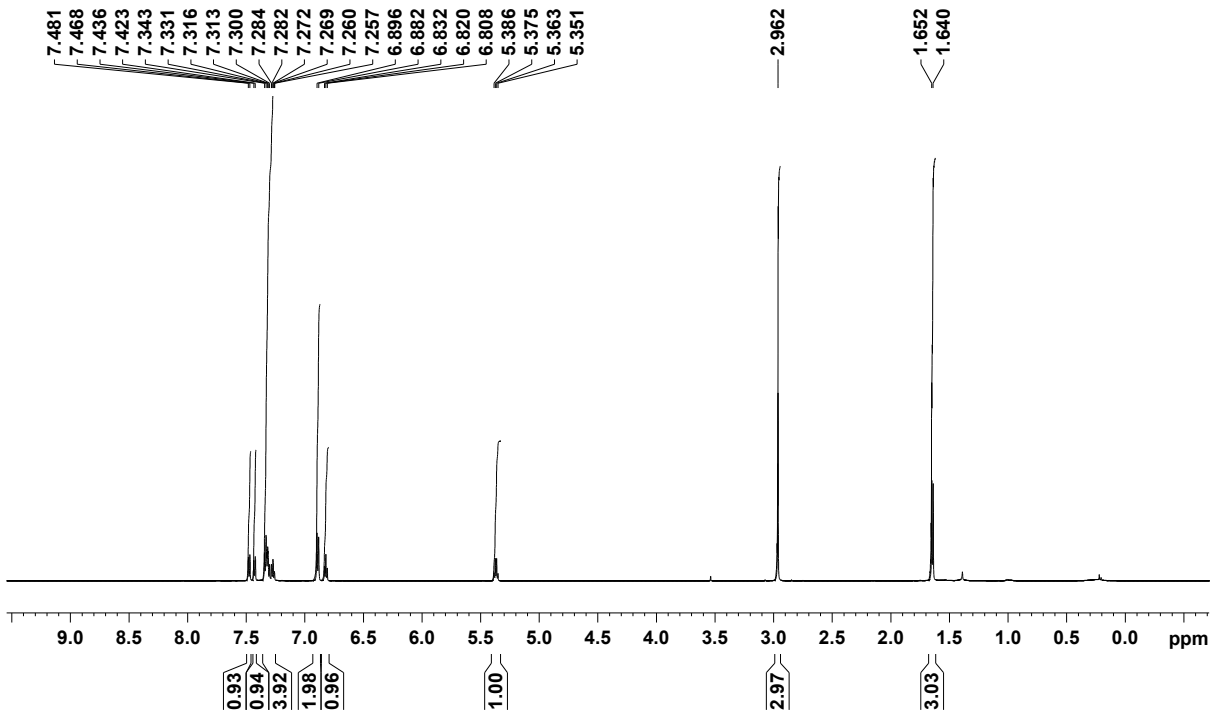


^{13}C NMR

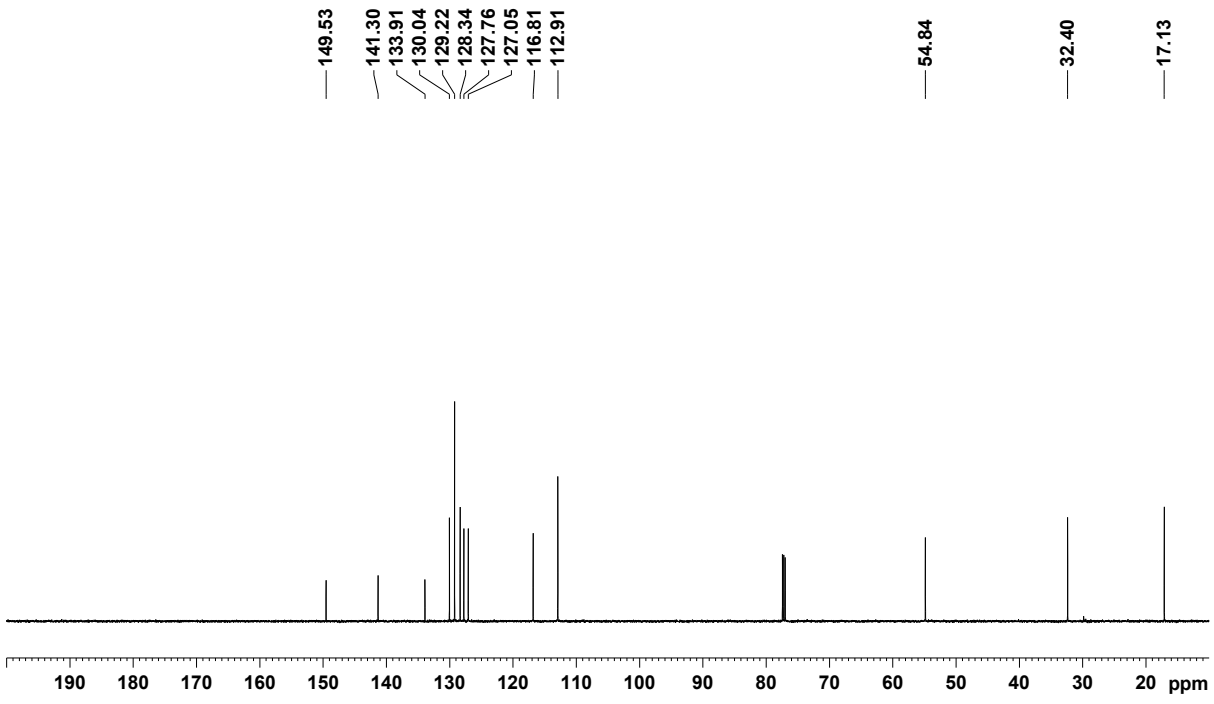


***N*-1-(2-Chlorophenyl)ethyl-*N*-methylaniline (3x).**

^{1}H NMR

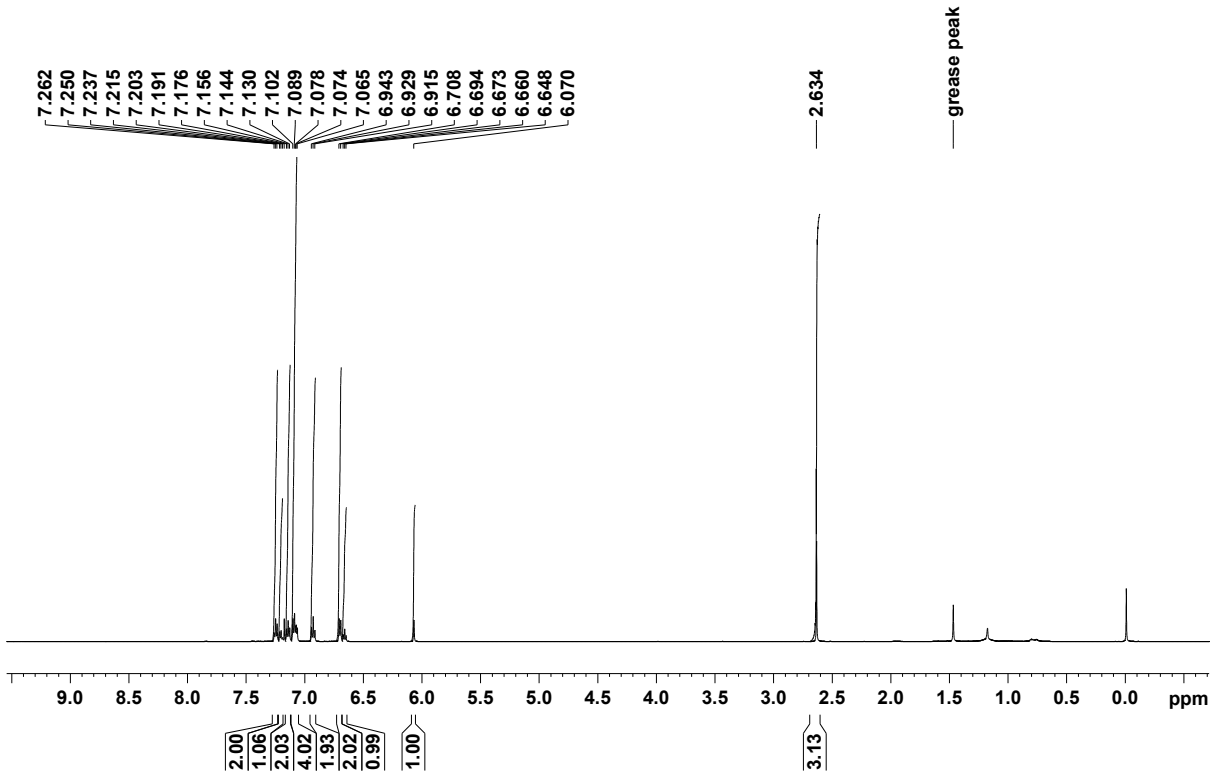


^{13}C NMR

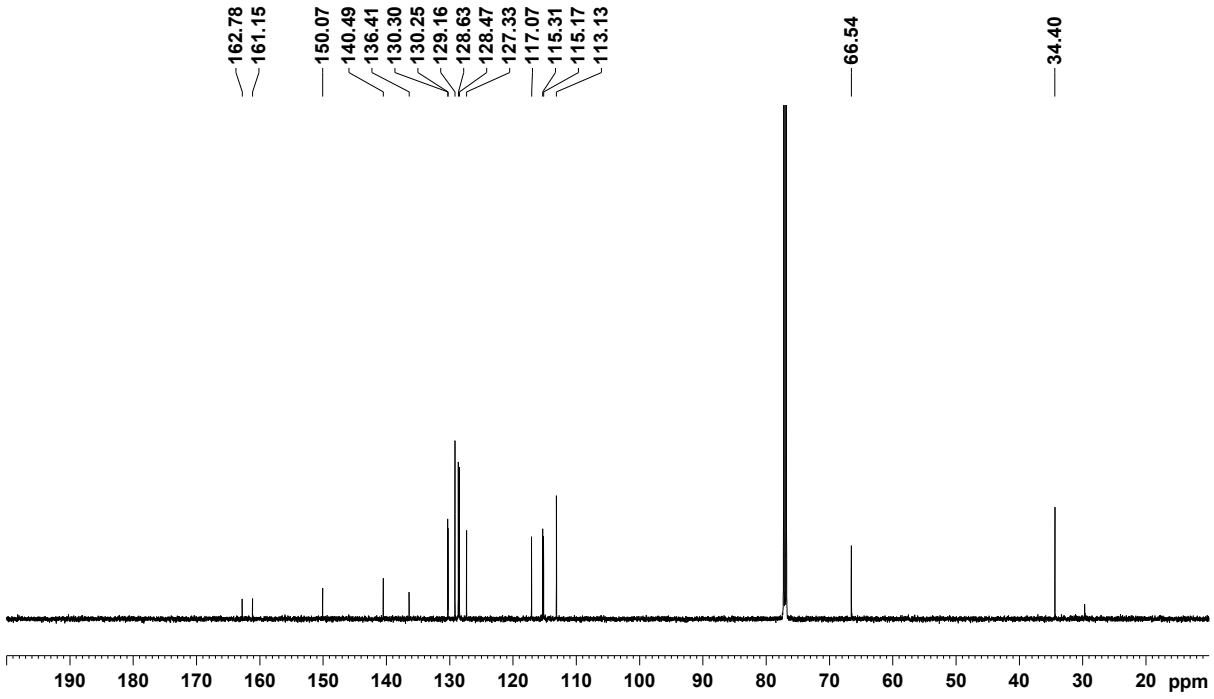


***N*-[(4-Fluoro-phenyl)phenylmethyl]-*N*-methylaniline(3y).**

^{1}H NMR

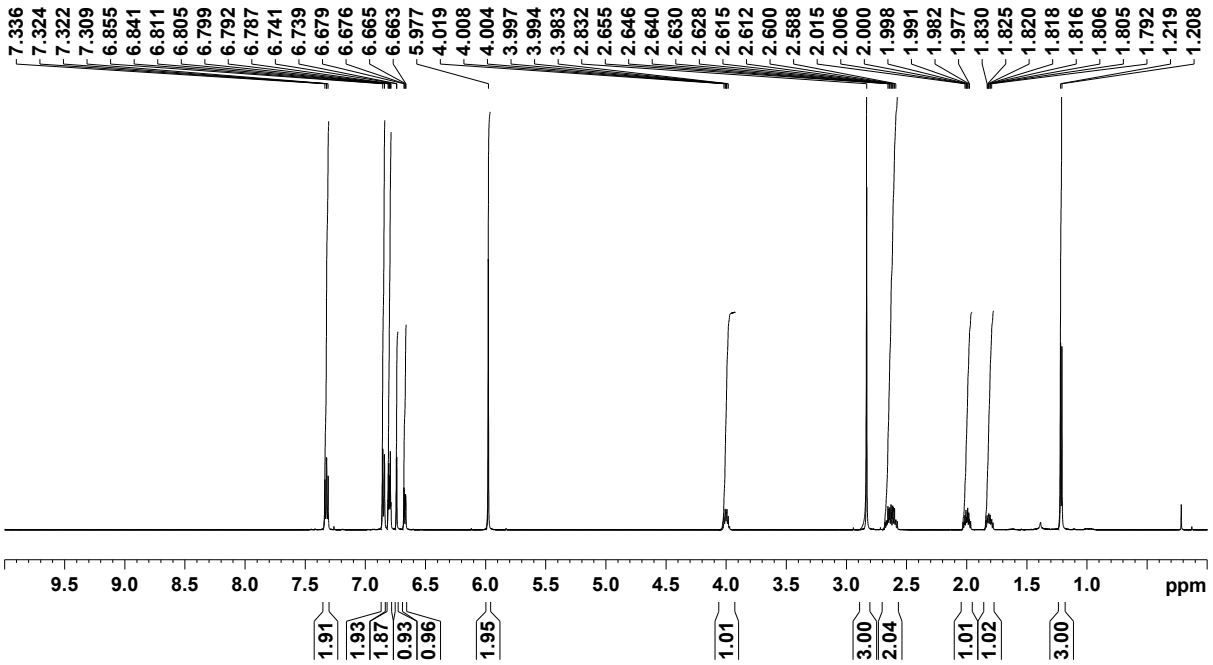


^{13}C NMR

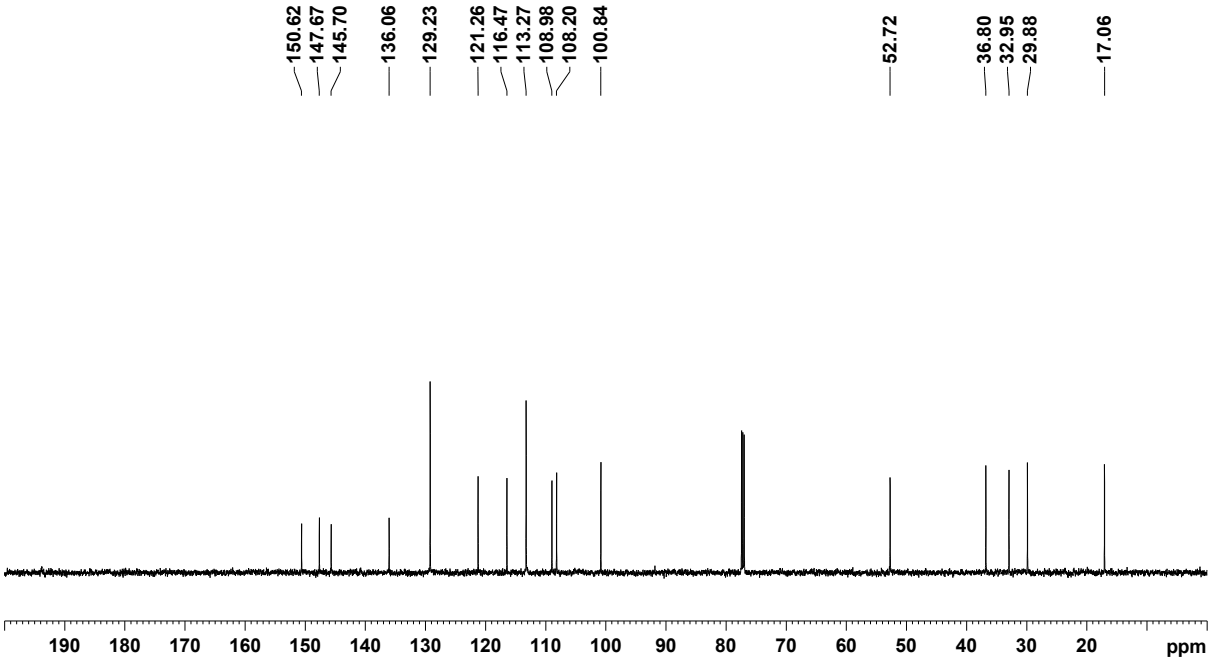


***N*-Methyl-*N*-phenyl-*N*, *α*-methyl- 1, 3-Benzodioxole-5-propanamine (3z).**

^{1}H NMR

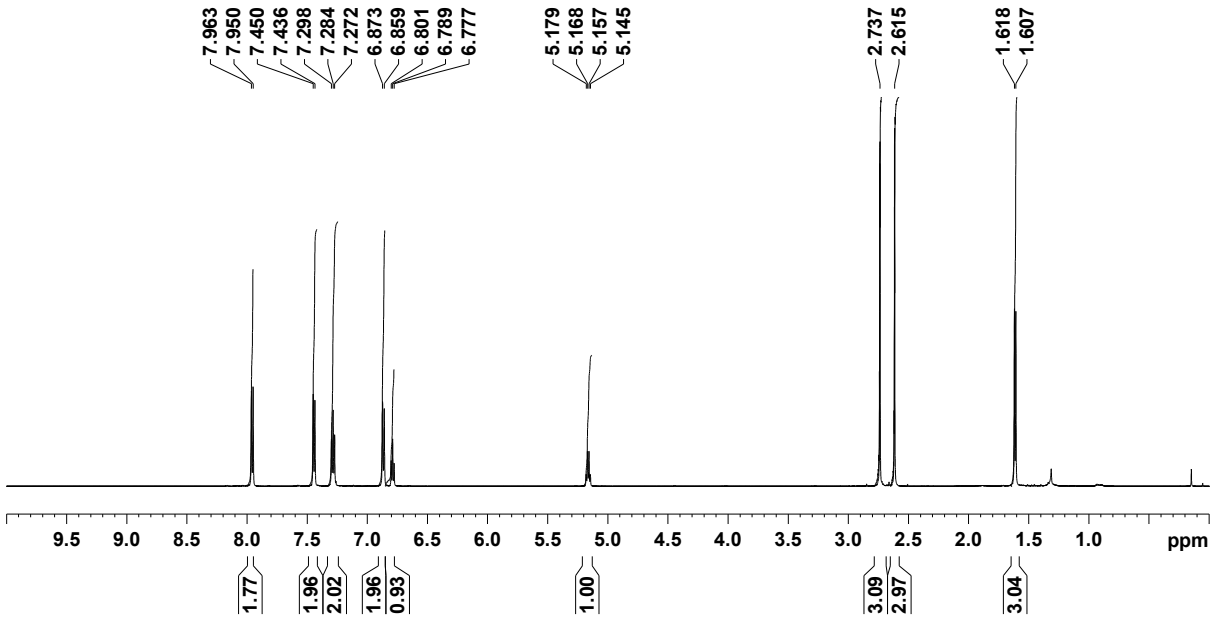


^{13}C NMR

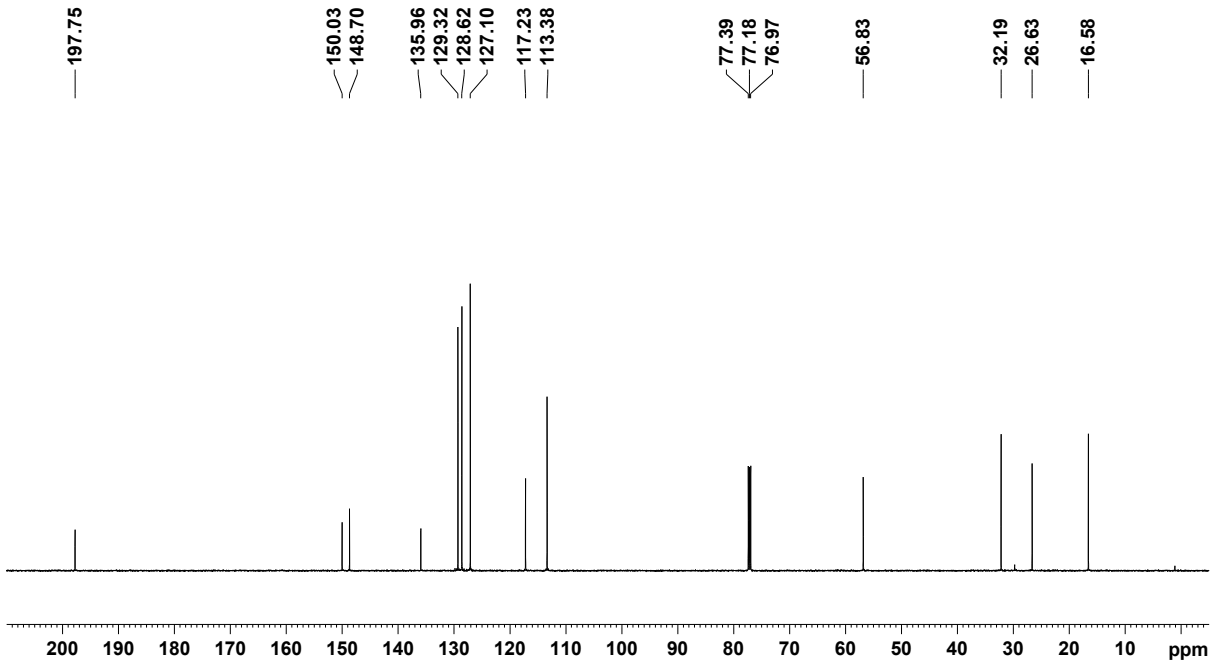


N-1-(4-Acetylphenyl)ethyl-N-methylaniline (3aa).

^{1}H NMR

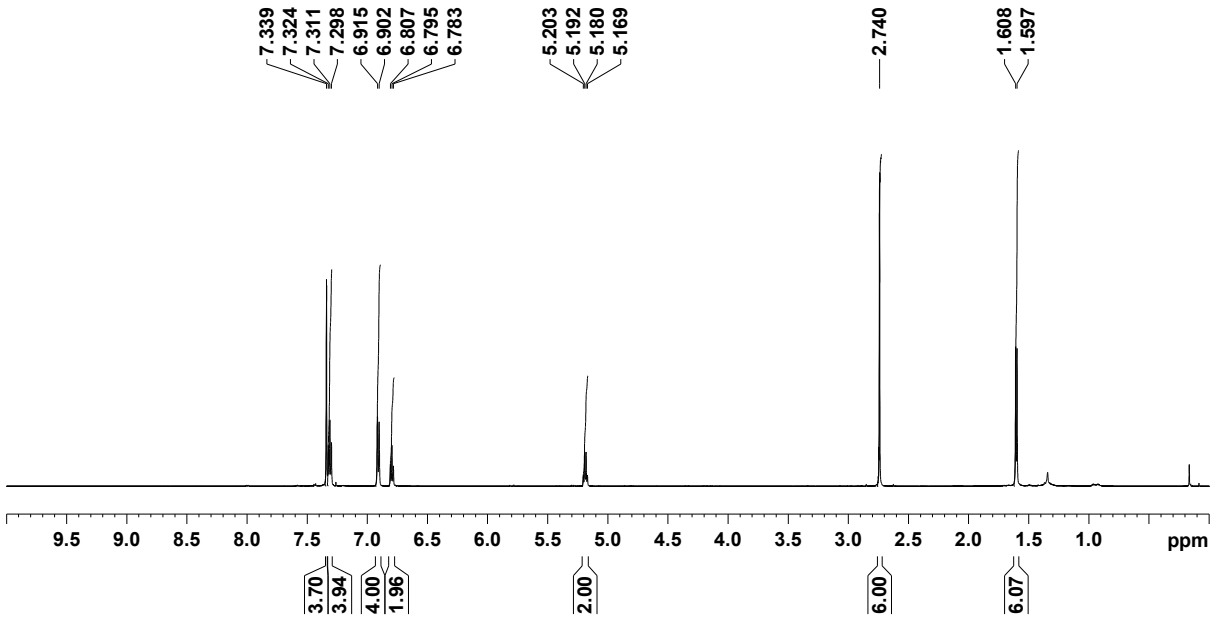


^{13}C NMR

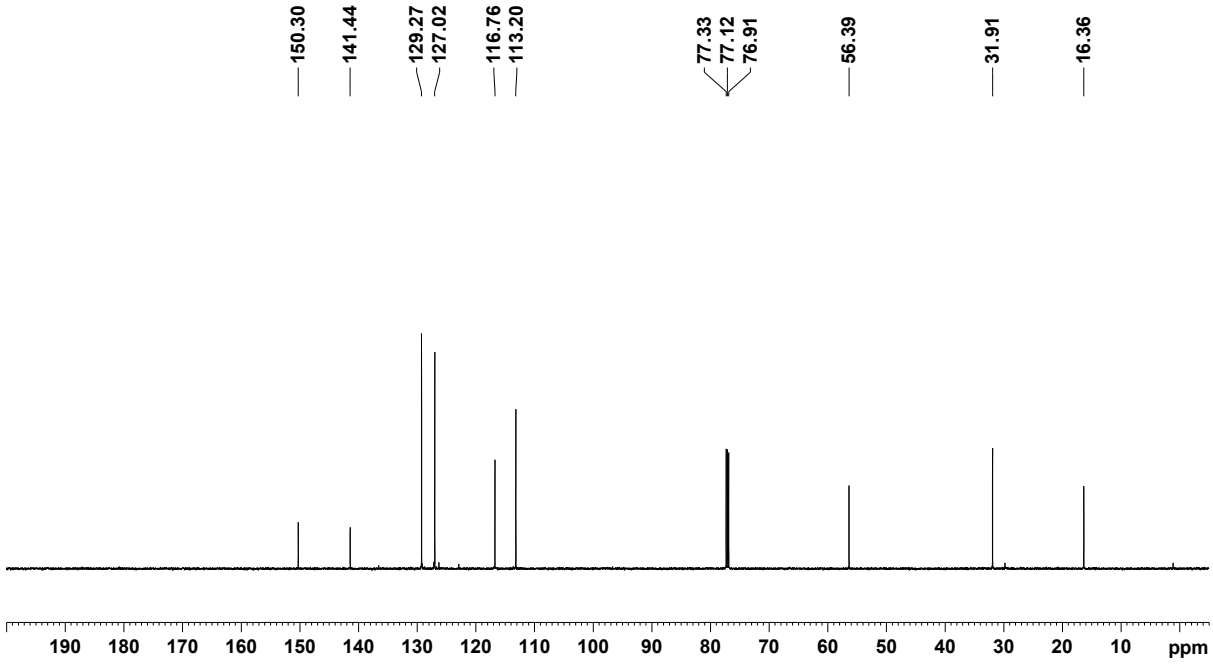


1, 4- bis (1-N-Methylphenylamineethyl)benzene (3ab).

^{1}H NMR

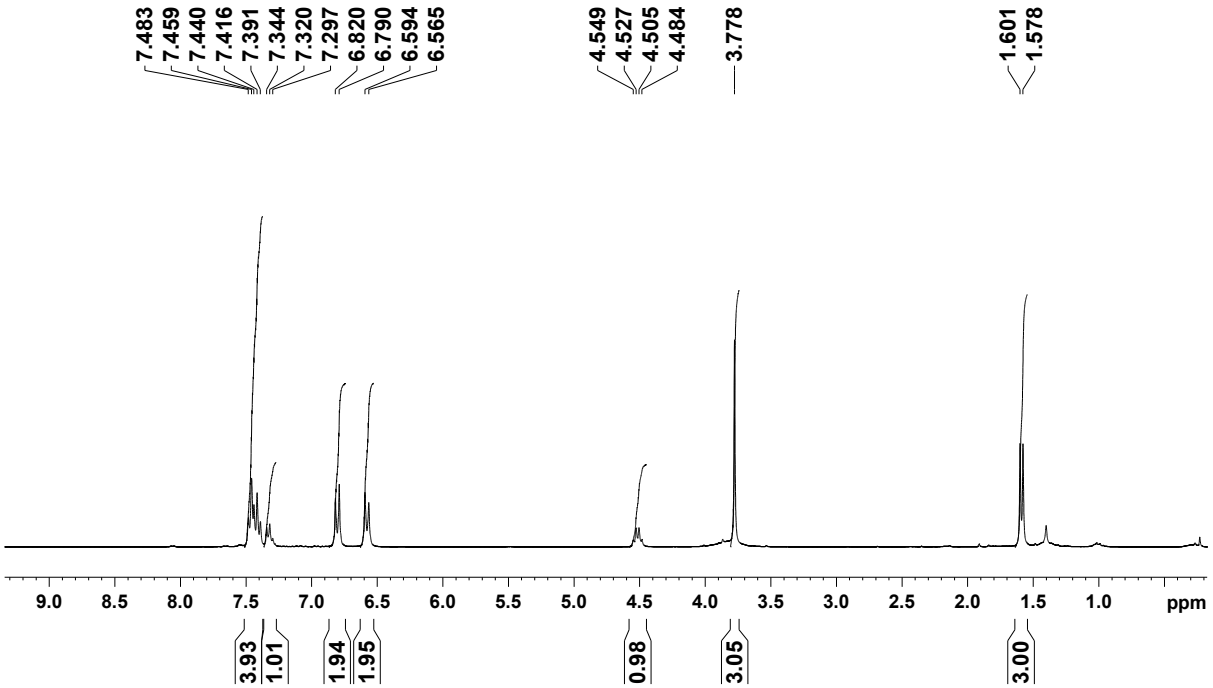


^{13}C NMR

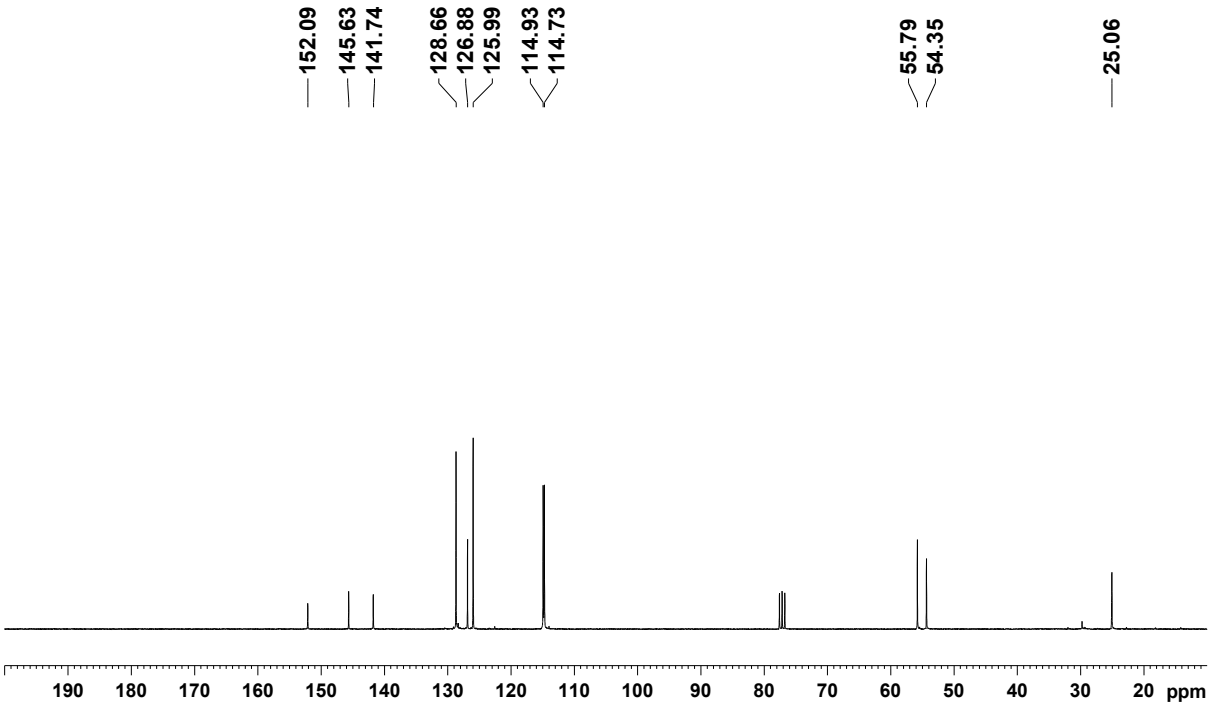


4-Methoxy-*N*-(1-phenylethyl)aniline (6a).

^{1}H NMR

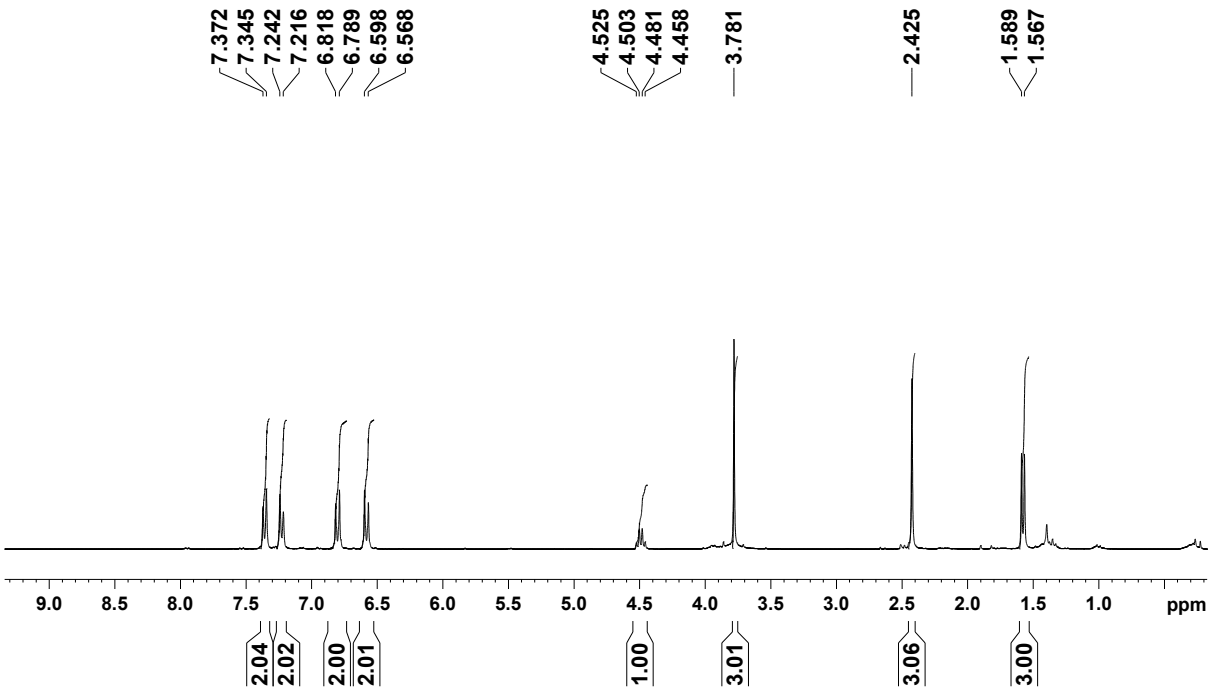


^{13}C NMR

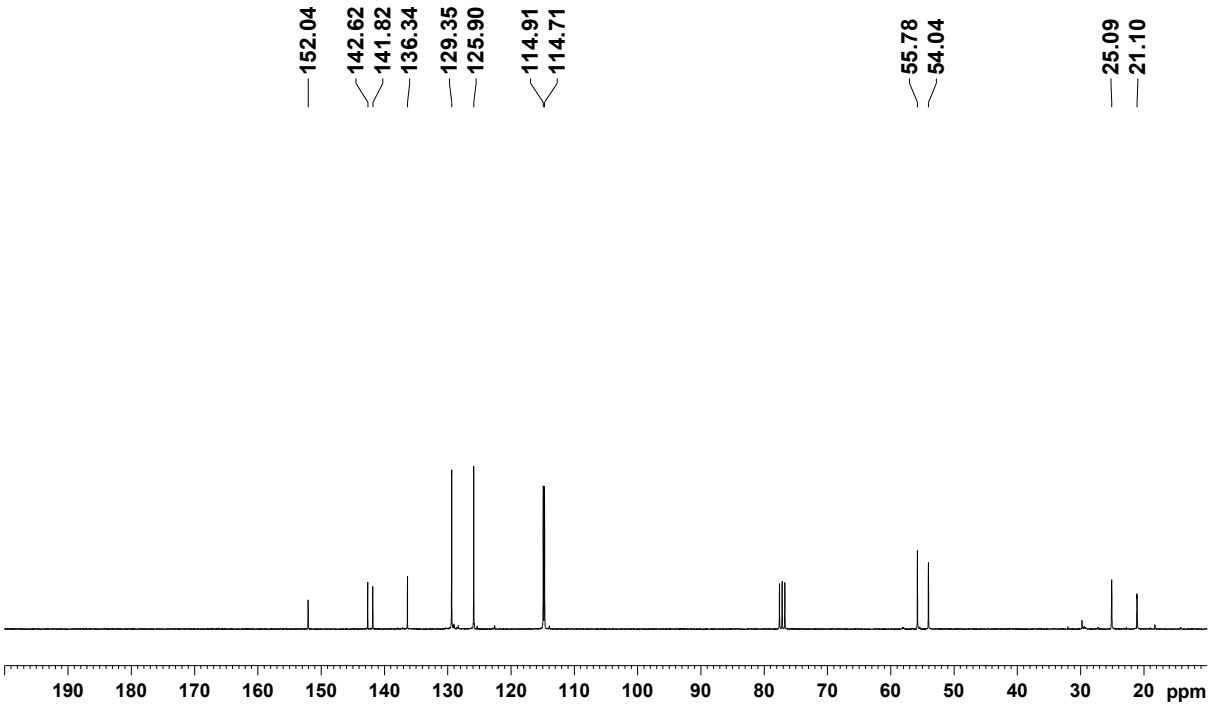


4-Methoxy-*N*-(1-*p*-tolylethyl)aniline (6b).

^{1}H NMR

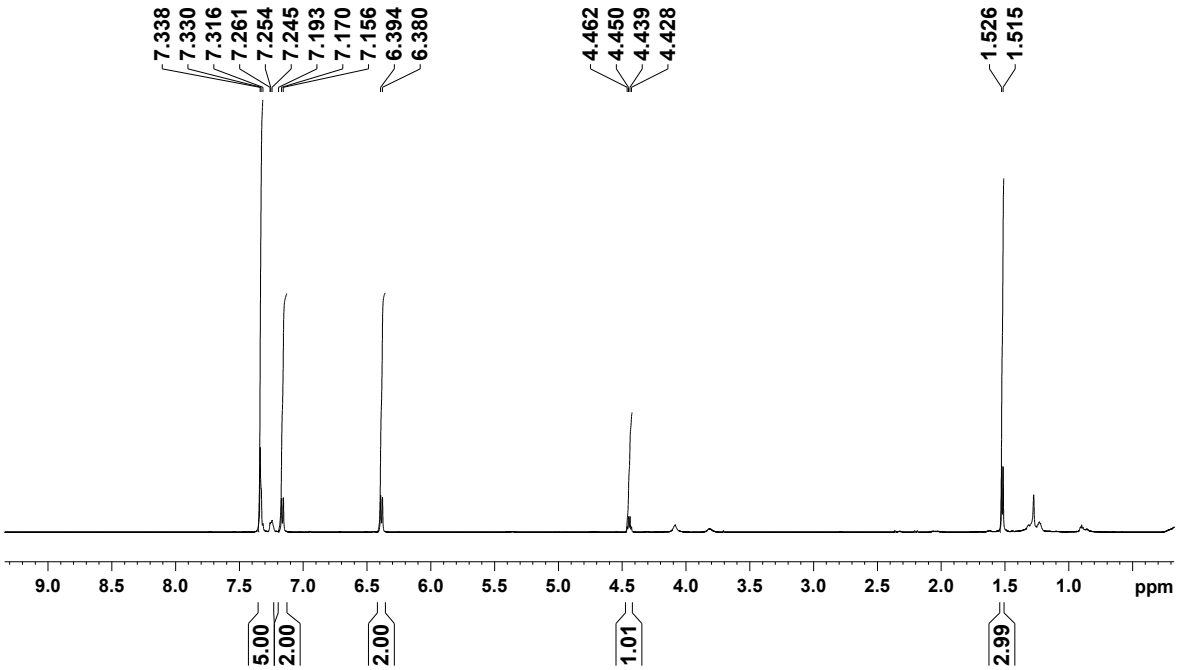


^{13}C NMR

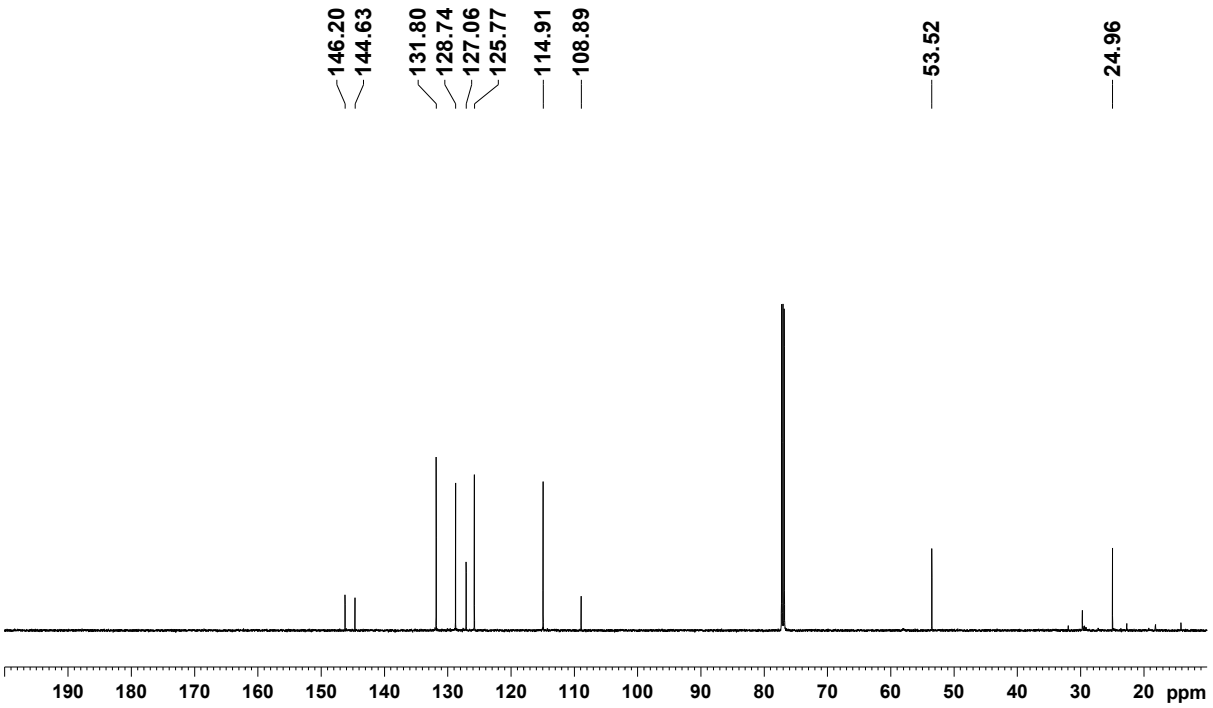


4-Bromo-*N*-(1-phenylethyl)aniline(6c).

^{1}H NMR

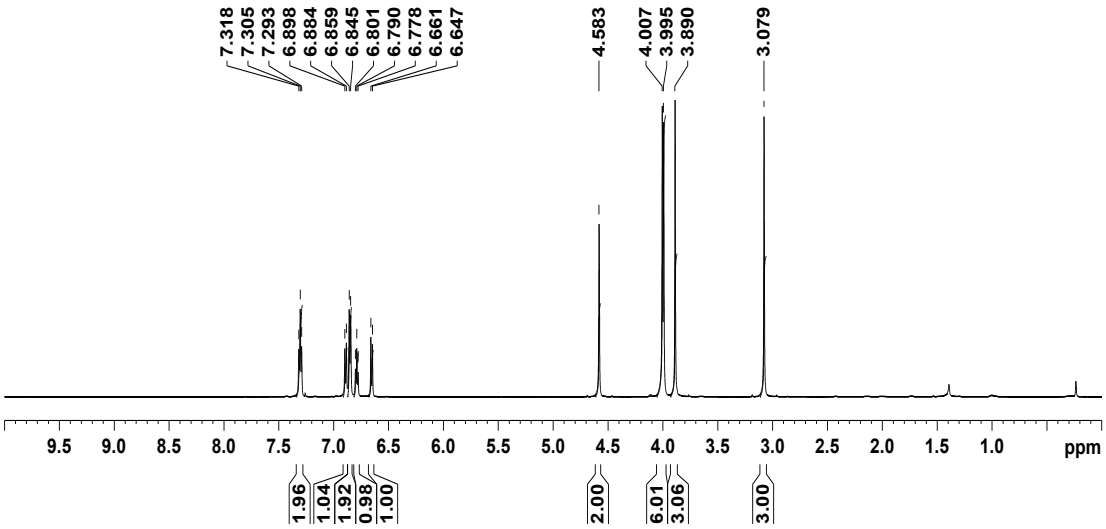


^{13}C NMR

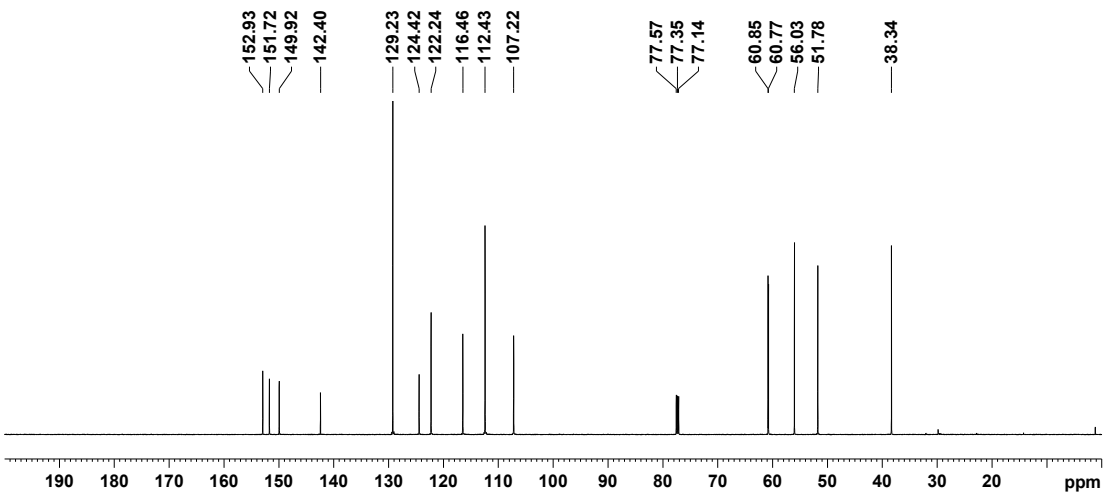


***N*-(2, 3, 4, -Trimethoxybenzyl)-*N*-methylaniline(9a)**

^{1}H NMR

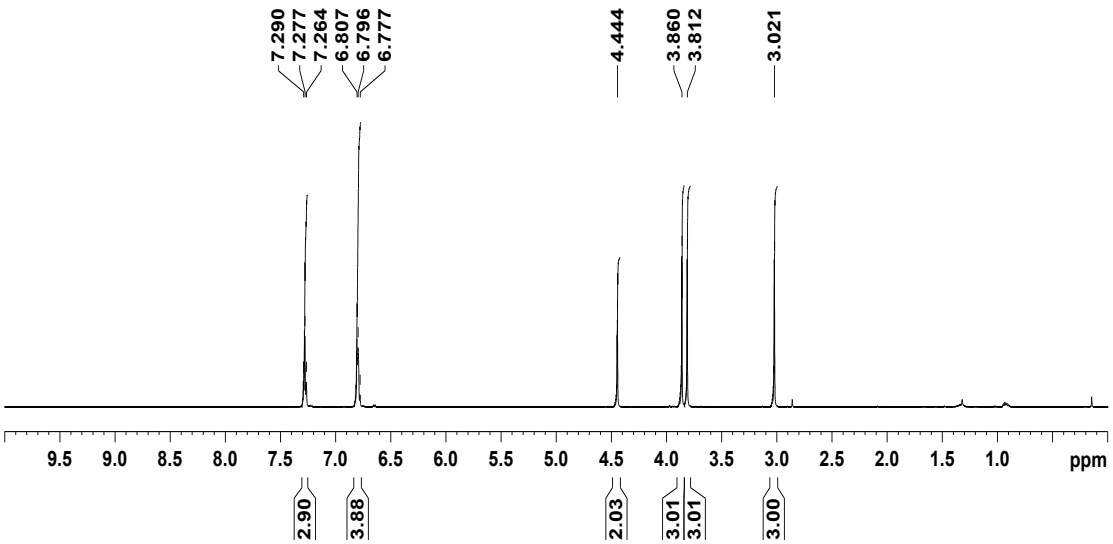


^{13}C NMR

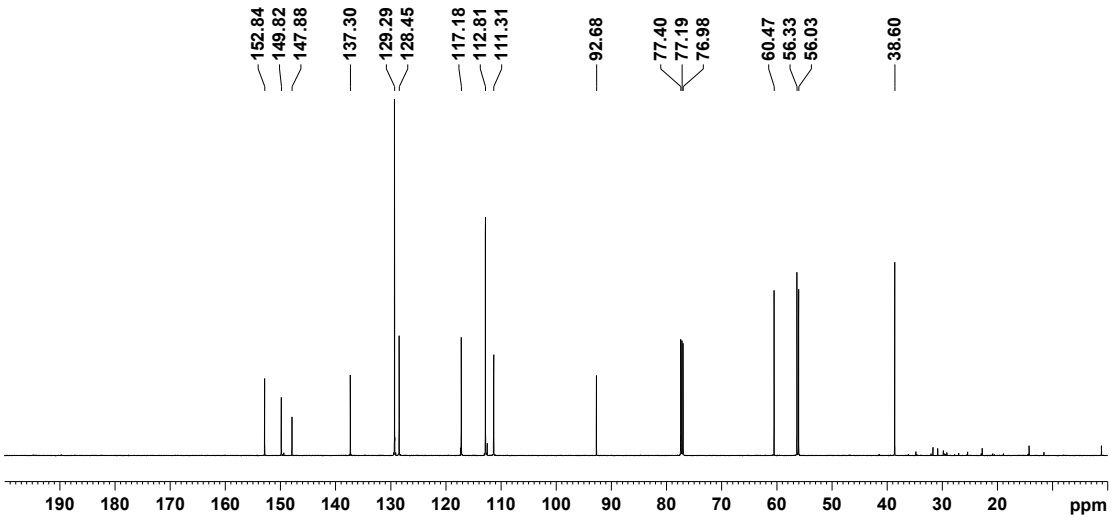


***N*-(3-Iodo-4,5-dimethoxybenzyl)-*N*-methylaniline** (**9b**).

^{1}H NMR

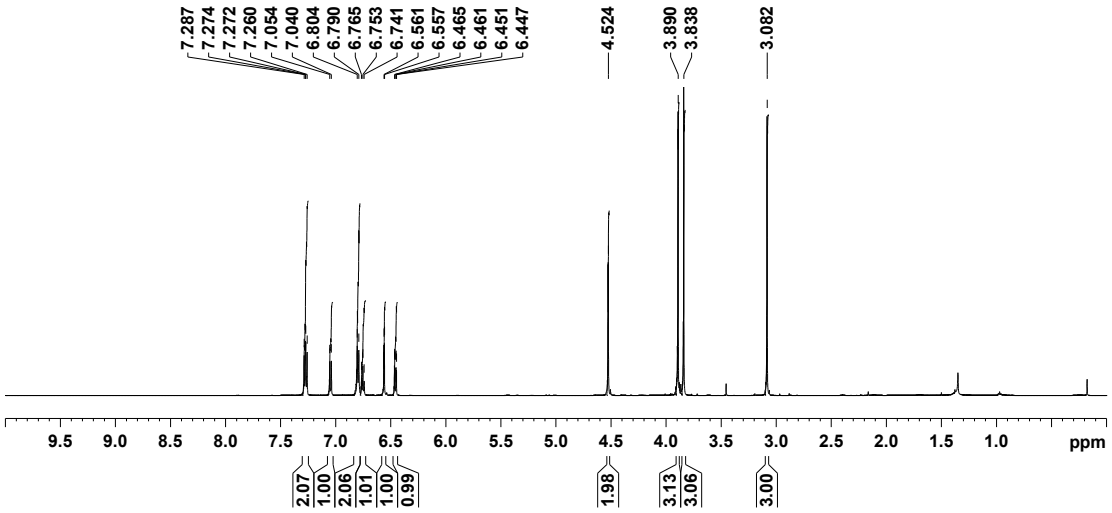


^{13}C NMR

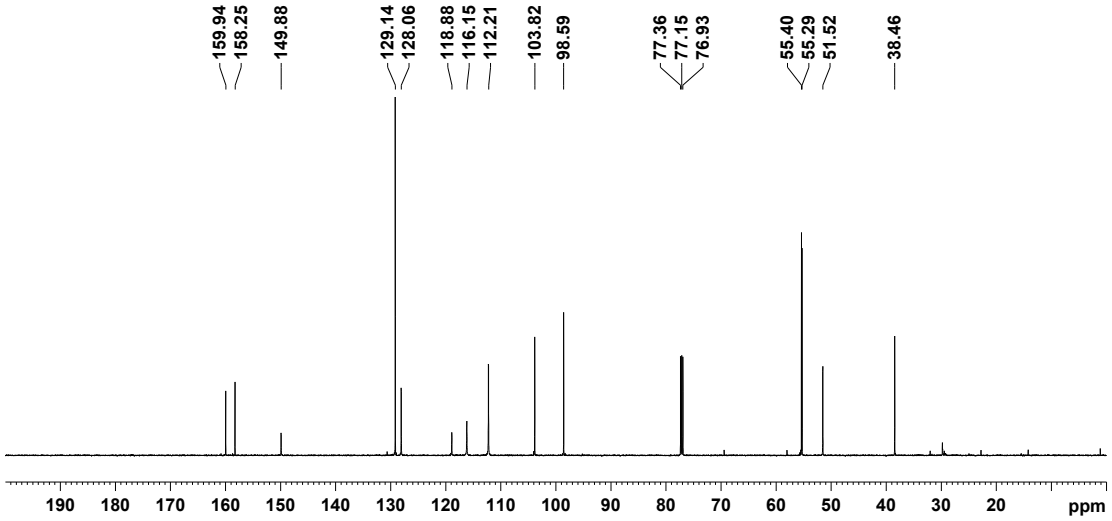


***N*-(2, 4-Dimethoxybenzyl)-*N*-methylaniline (9c)**

^{1}H NMR

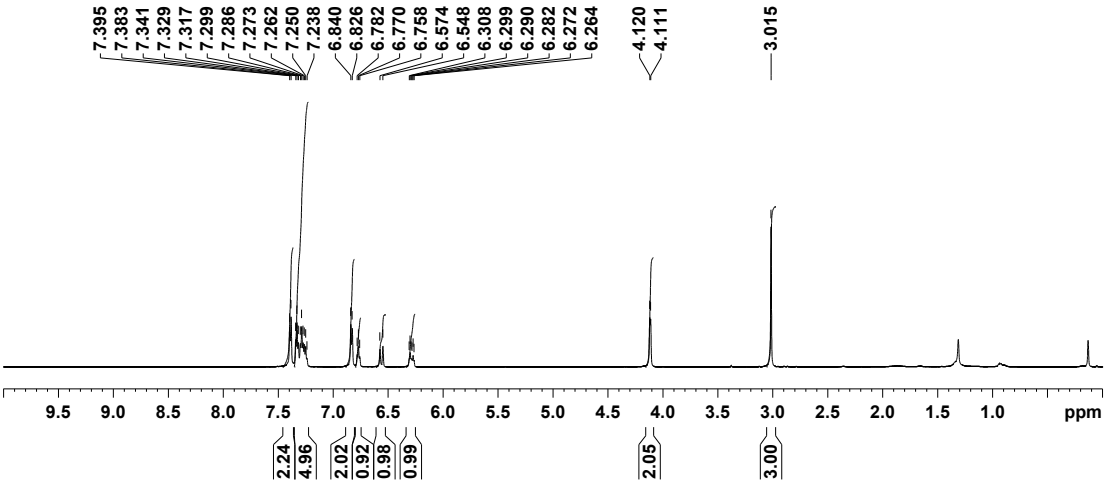


^{13}C NMR

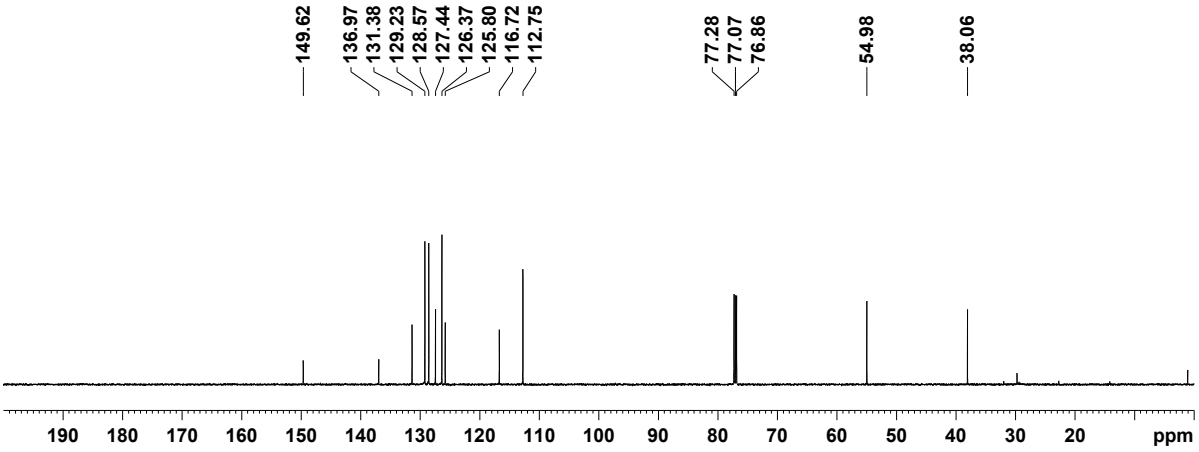


_N_-Cinnamyl-_N_-methylaniline (9d)

^{1}H NMR

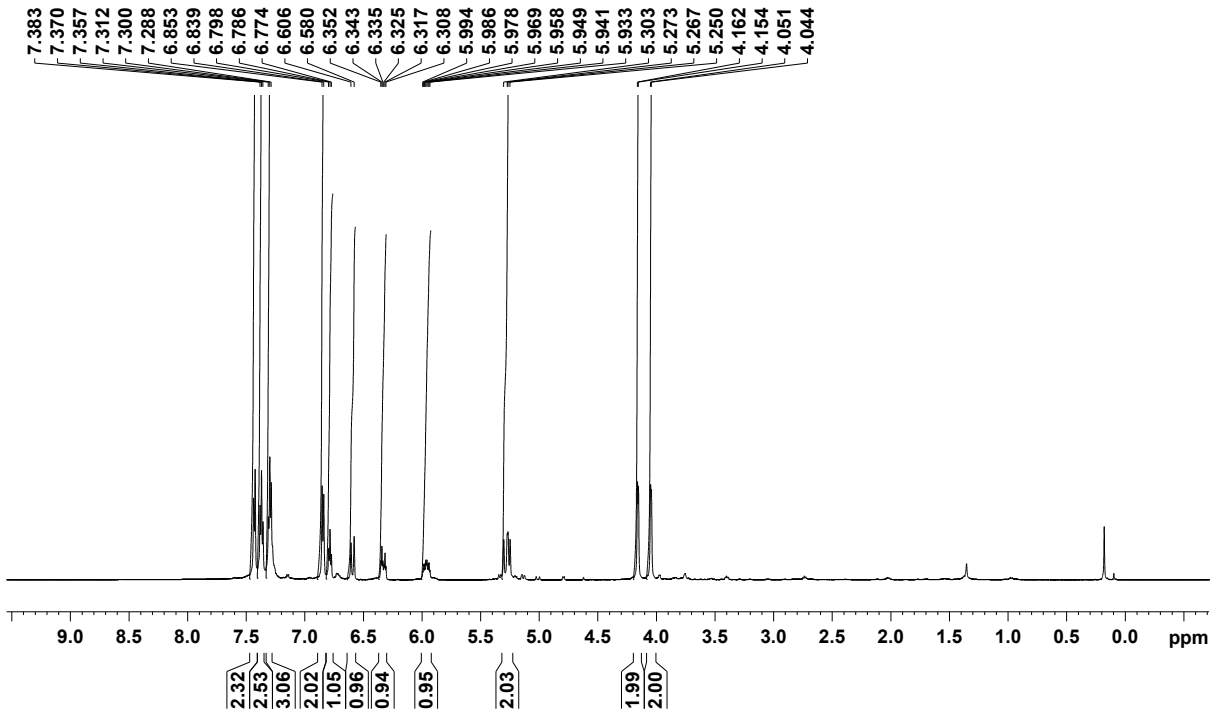


^{13}C NMR

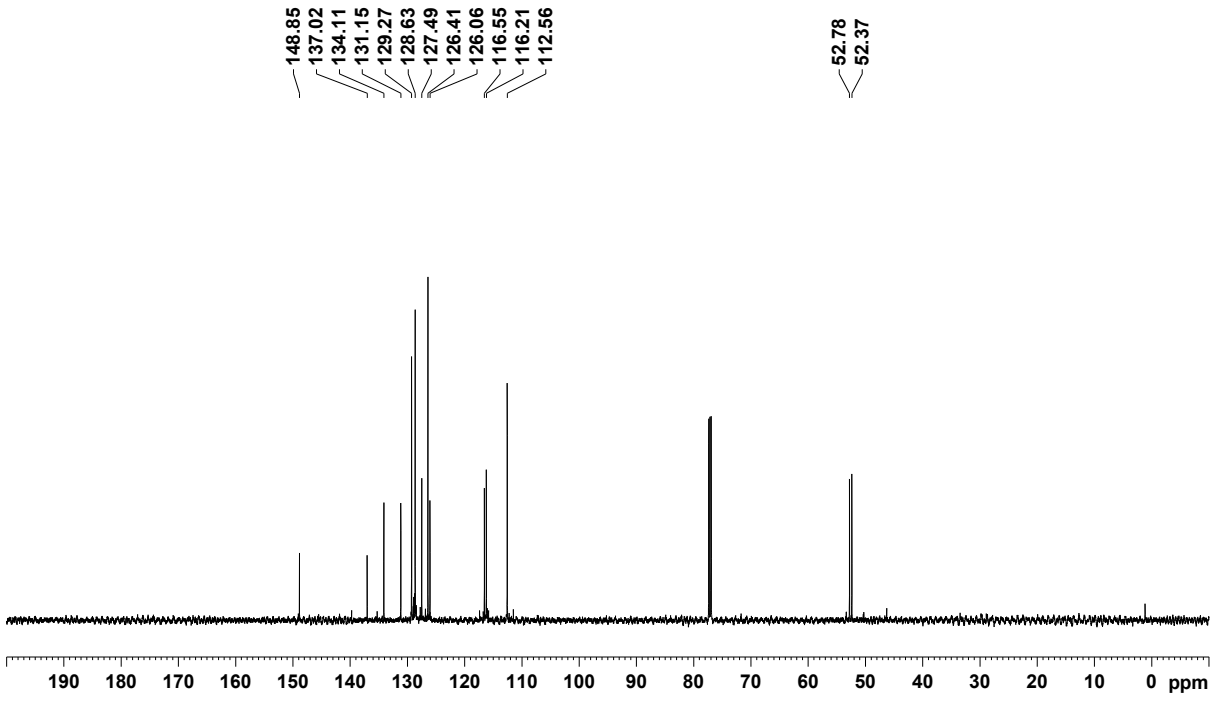


***N*- Cinnamyl-*N*-allylaniline (9e)**

^{1}H NMR

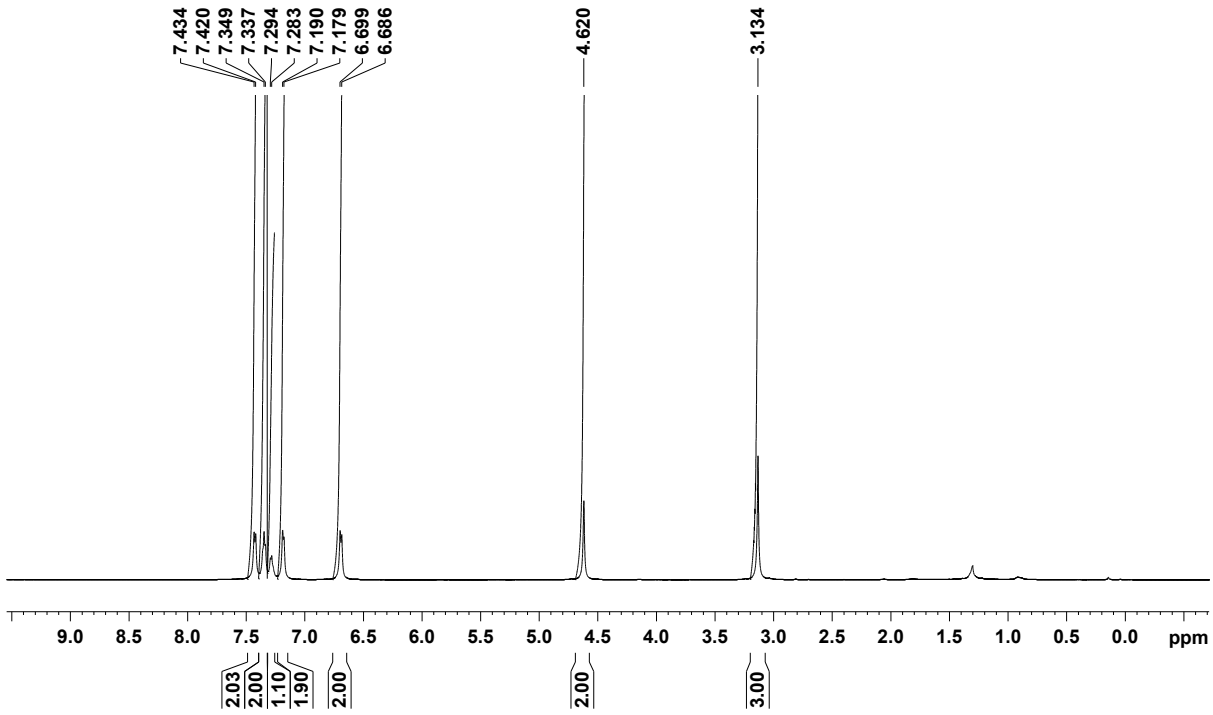


^{13}C NMR

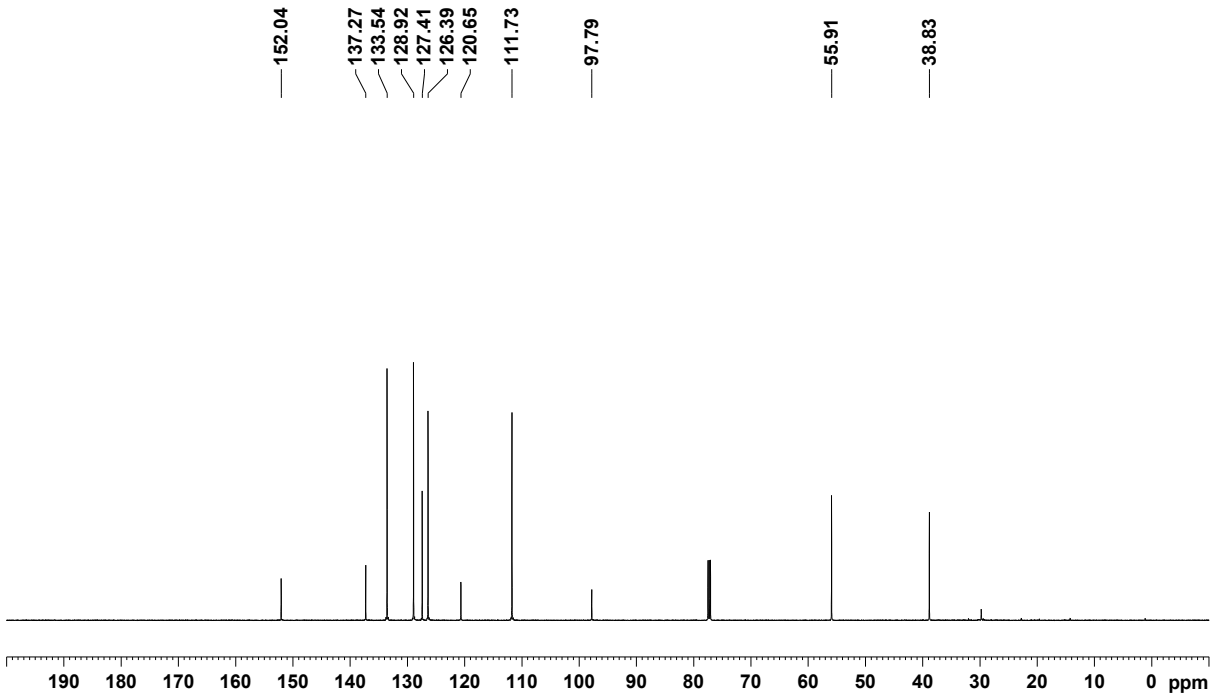


4-Cyano-N-methyl-N-benzylaniline (9f)

^{1}H NMR

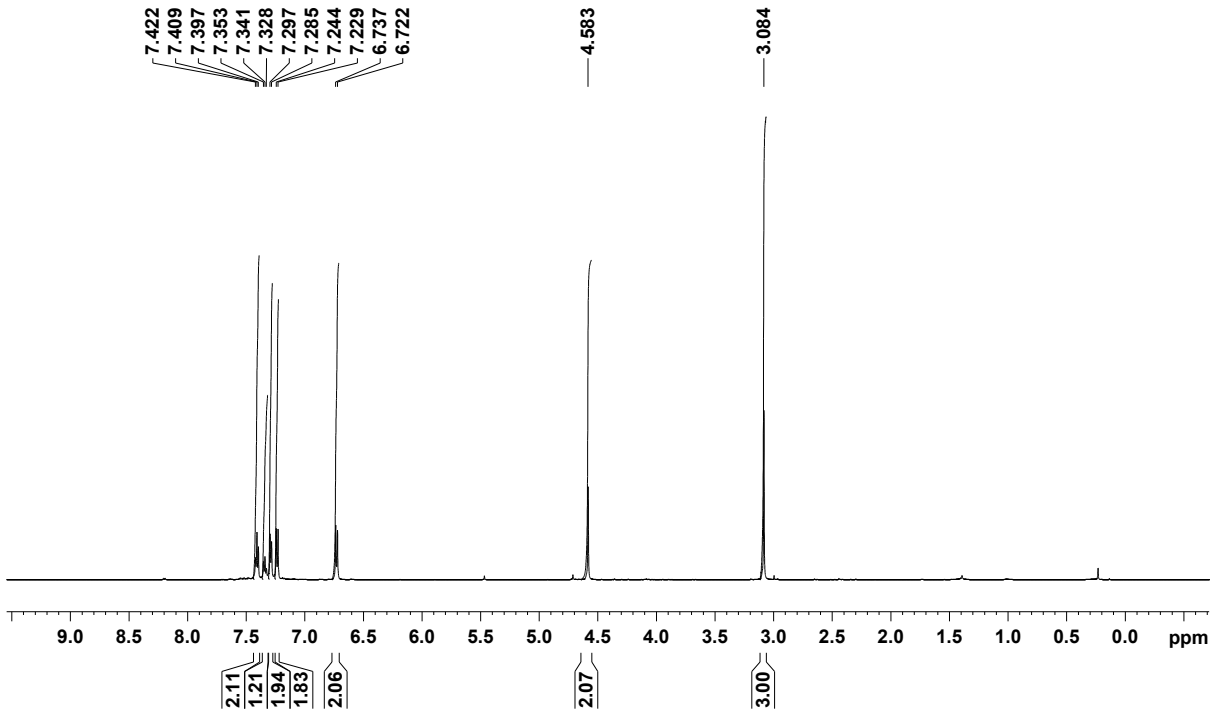


^{13}C NMR

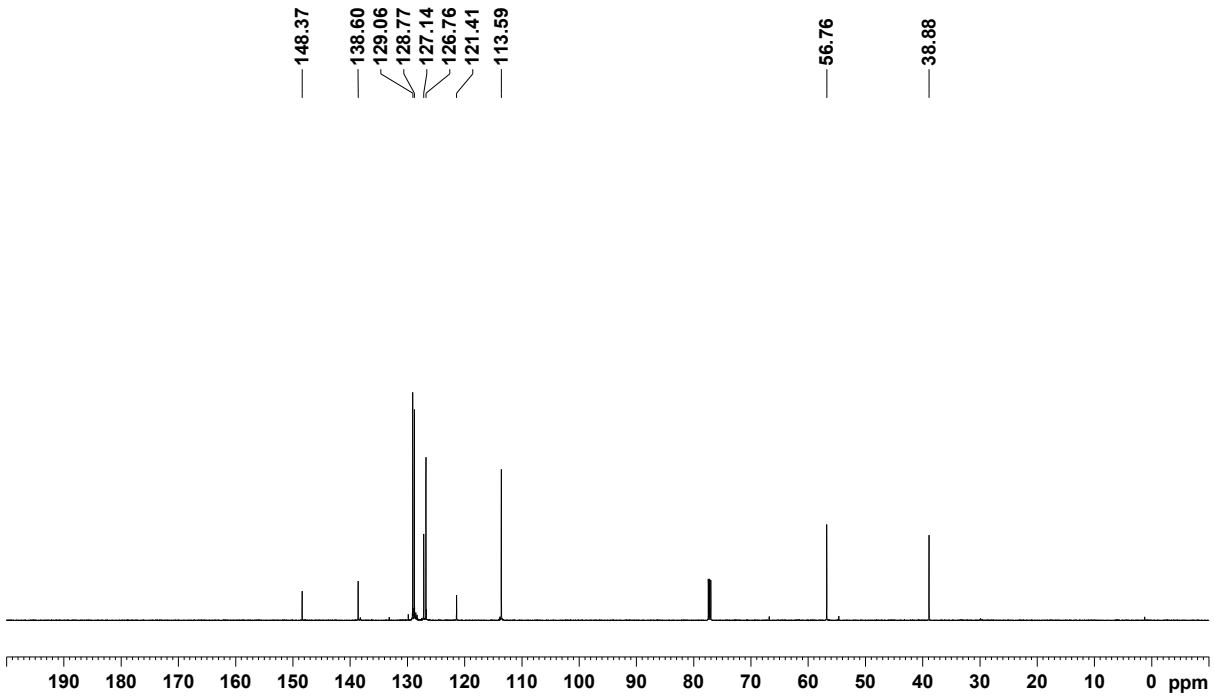


4-Chloro-*N*-methyl-*N*-benzylaniline (9g)

^{1}H NMR

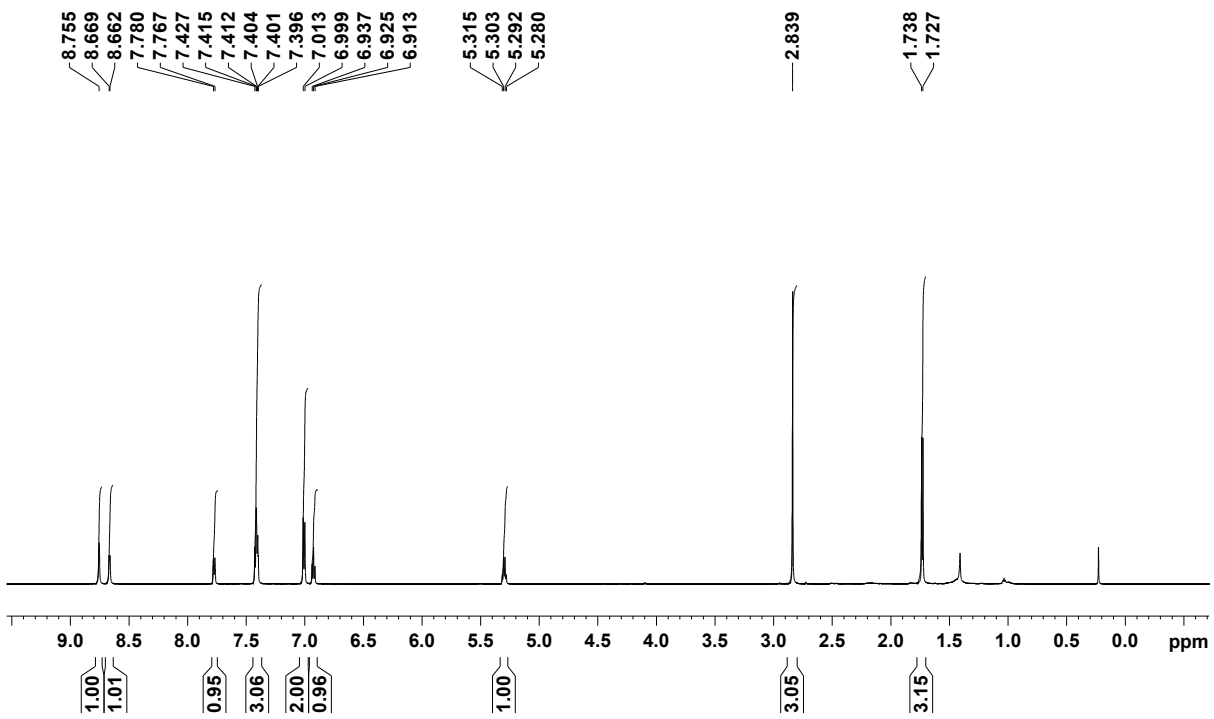


^{13}C NMR

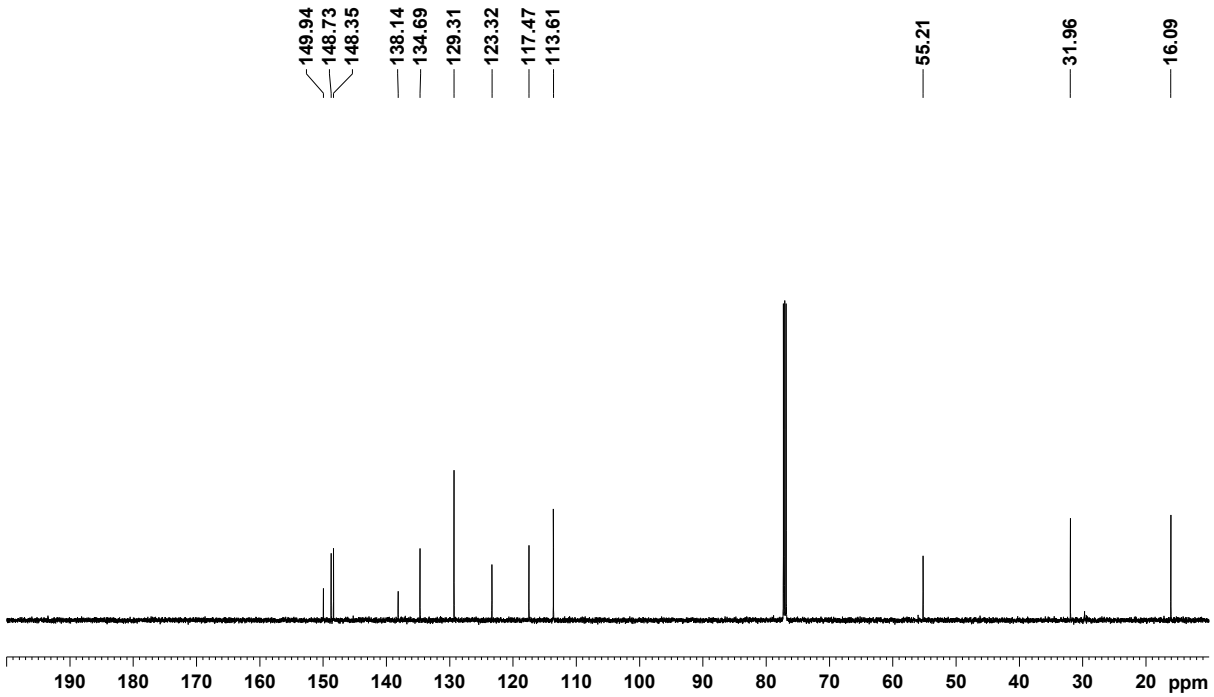


Methyl-phenyl-(1-pyridin-3-yl-ethyl)-amine (12a).

^{1}H NMR

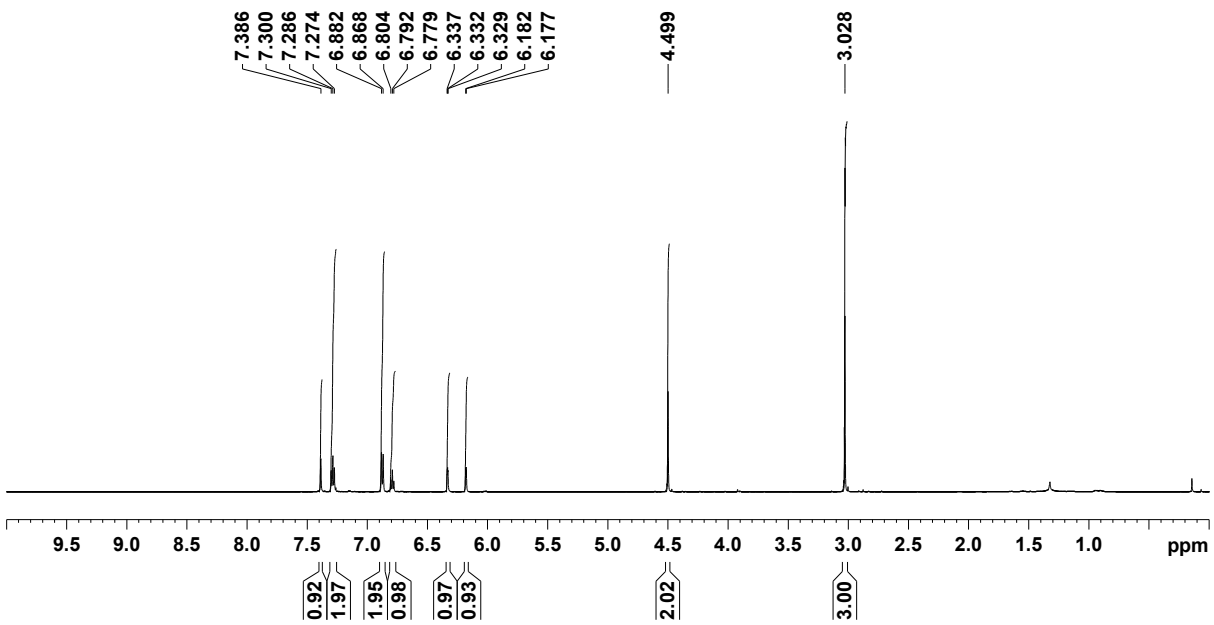


^{13}C NMR

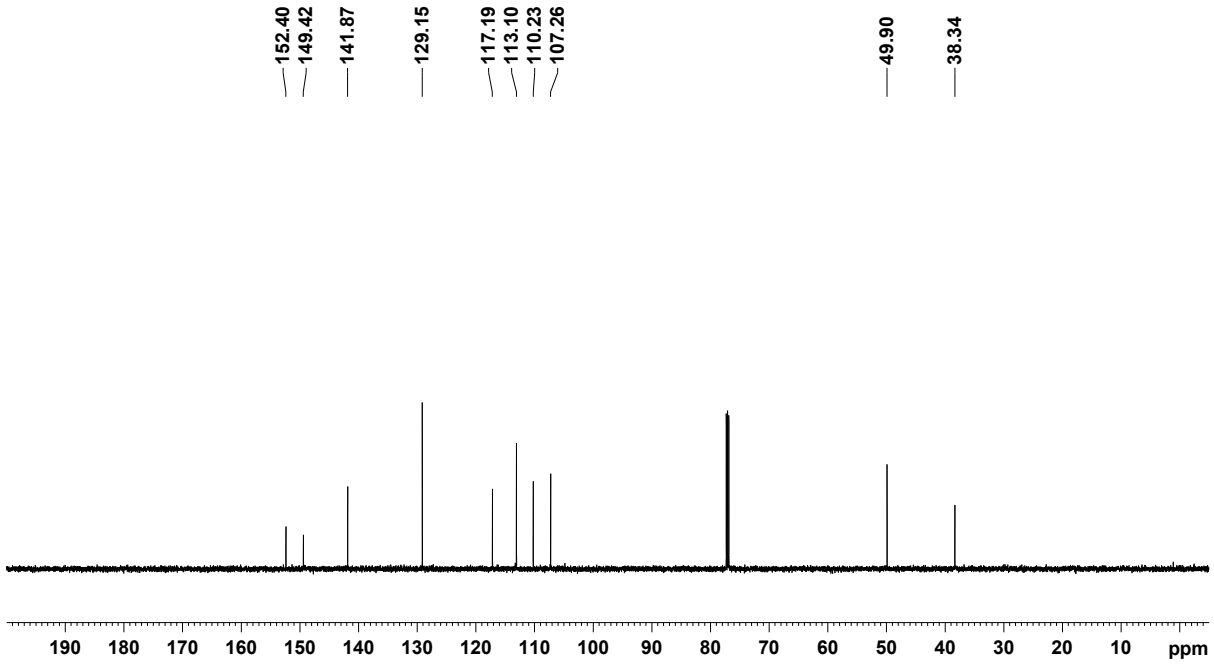


Tetrahydro-*N*-methyl-*N*-phenyl-2-furanmethanamine (12b).

^{1}H NMR

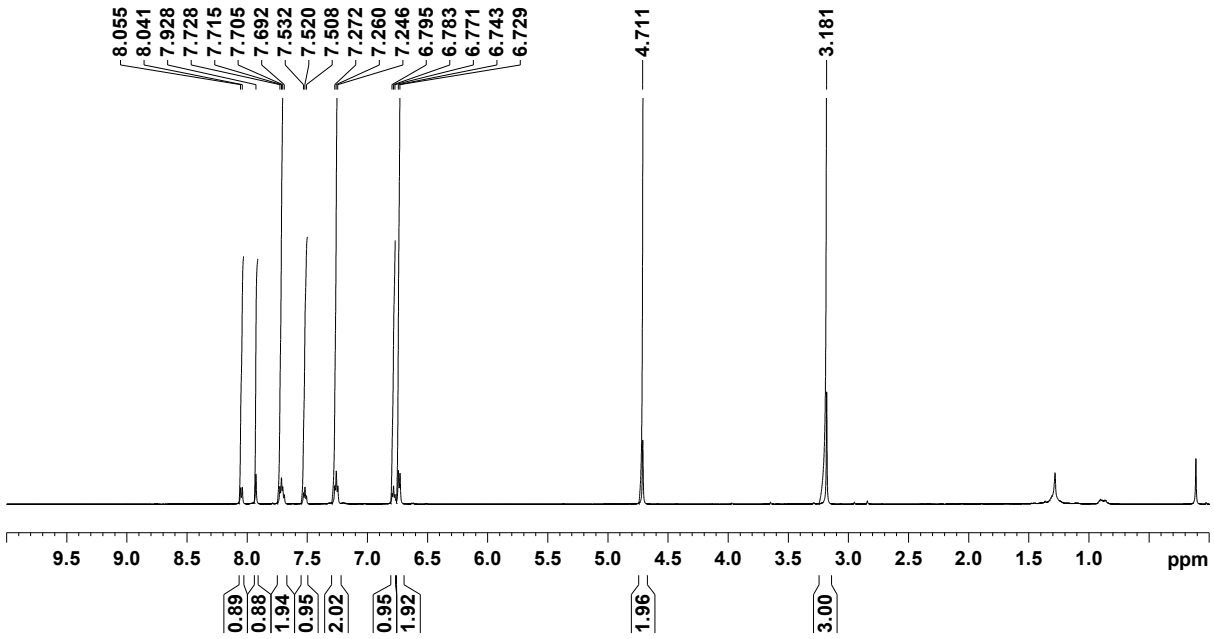


^{13}C NMR

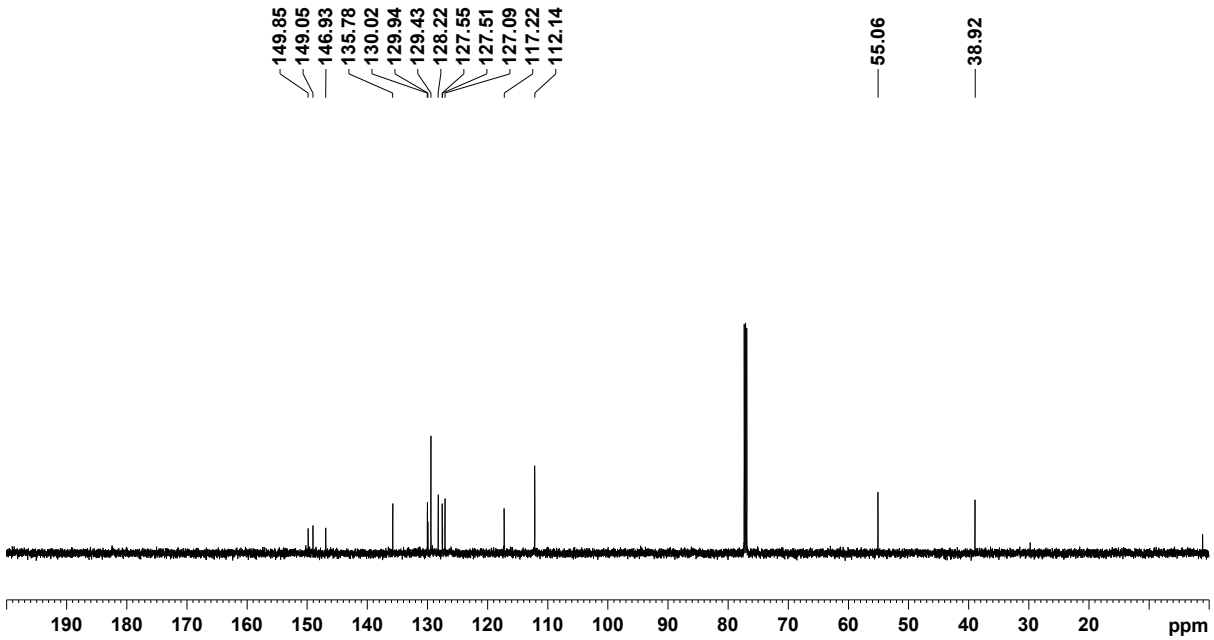


***N*-(phenylmethyl)-2-chloro-3-Quinolinemethanamine (12c).**

^{1}H NMR

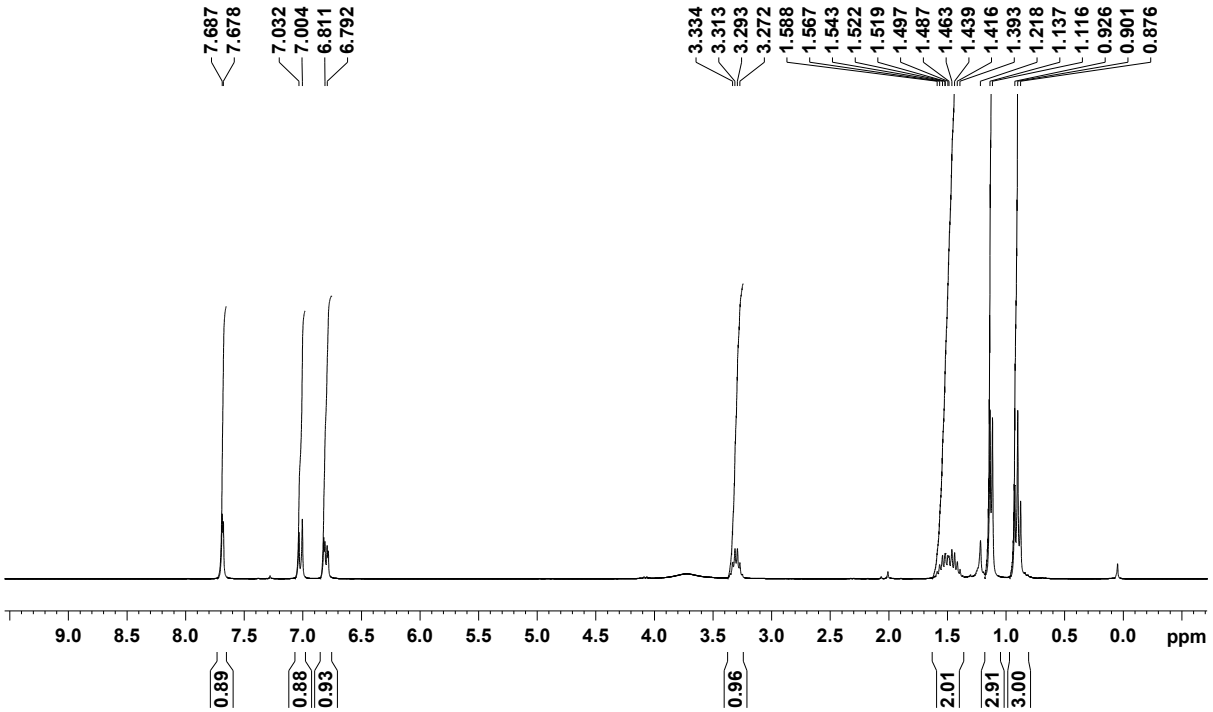


^{13}C NMR

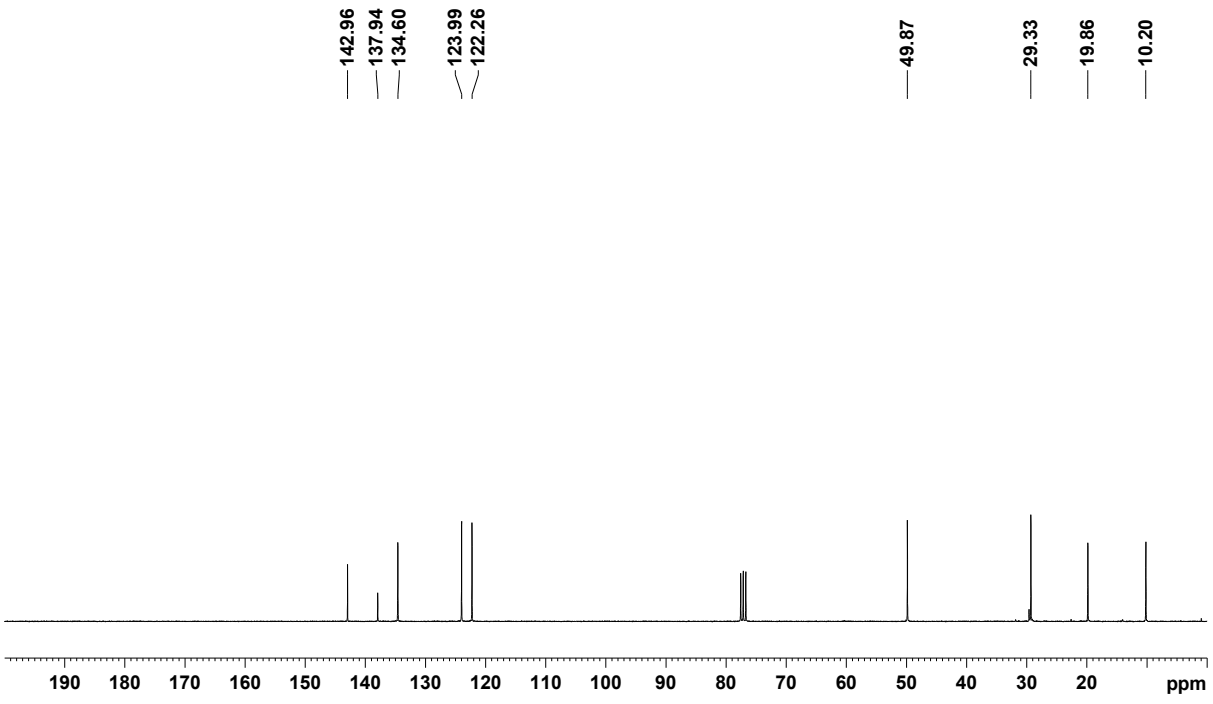


***Sec*-Butyl (6-chaloro-3-pyridyl)amine (12d).**

^{1}H NMR

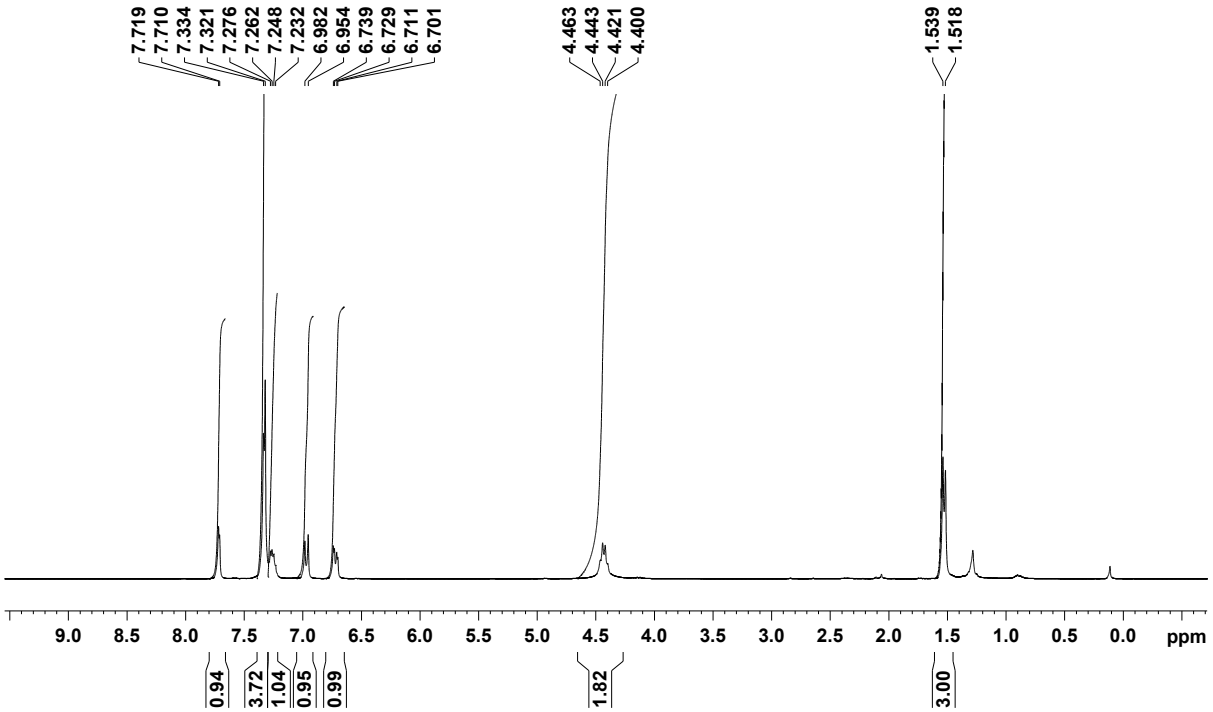


^{13}C NMR

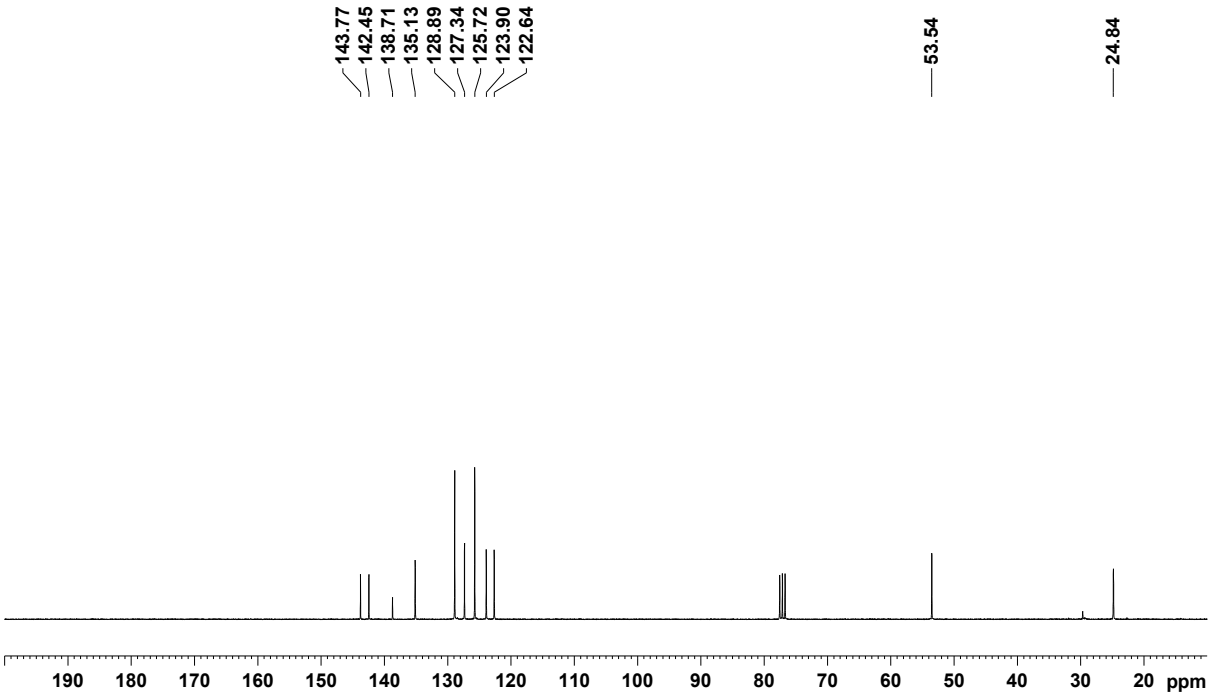


(6-Chloro-3-pyridinyl)-*N*-(1-phenyl-ethyl)amine (12e).

^{1}H NMR

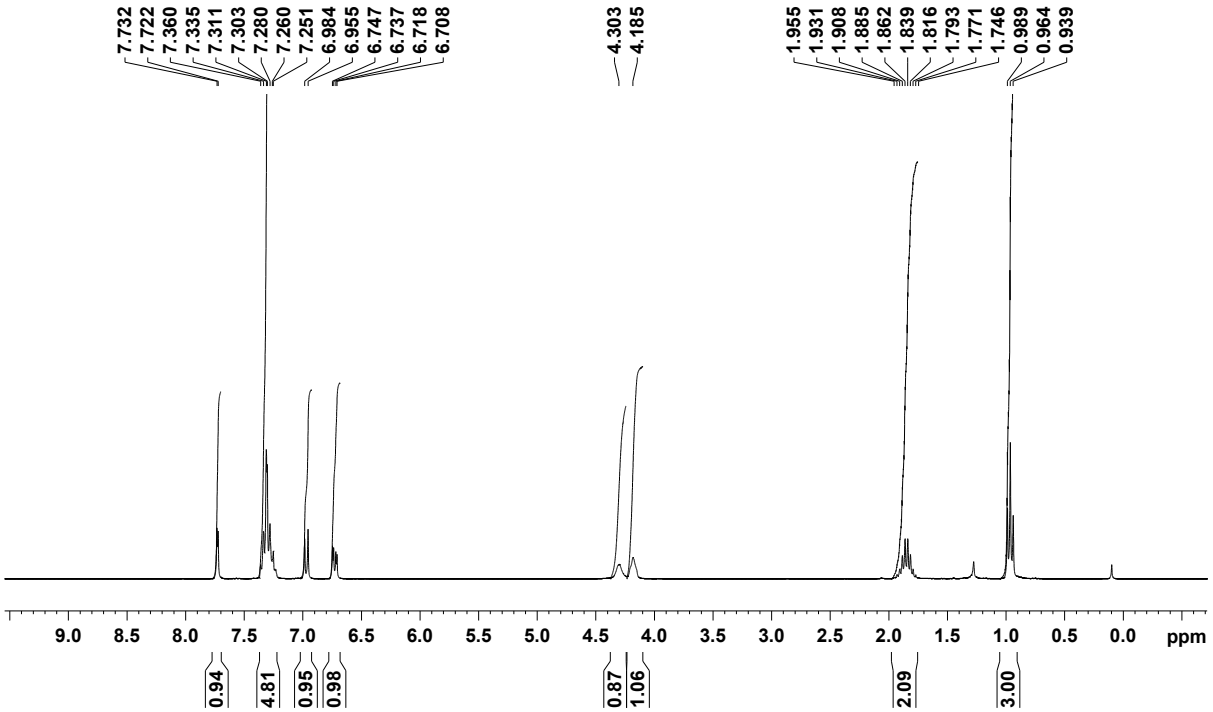


^{13}C NMR

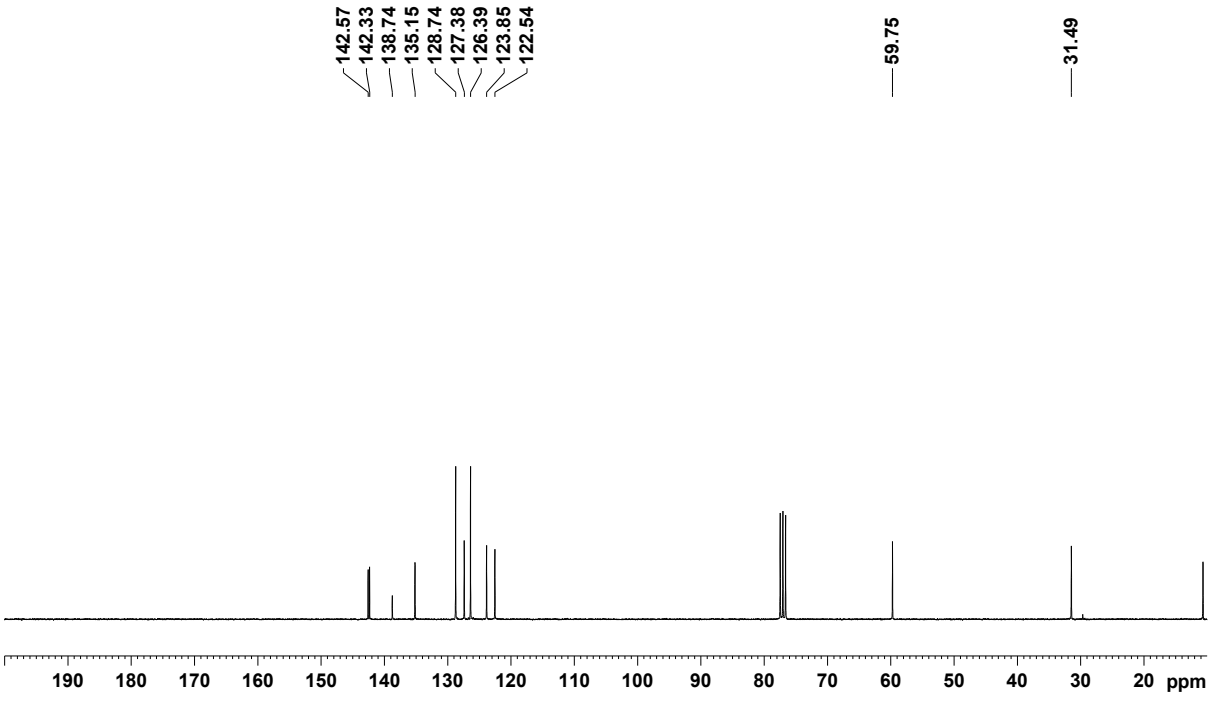


(6-Chloro-3-pyridinyl)-*N*-(1-phenyl-propyl)-amine (12f).

^{1}H NMR

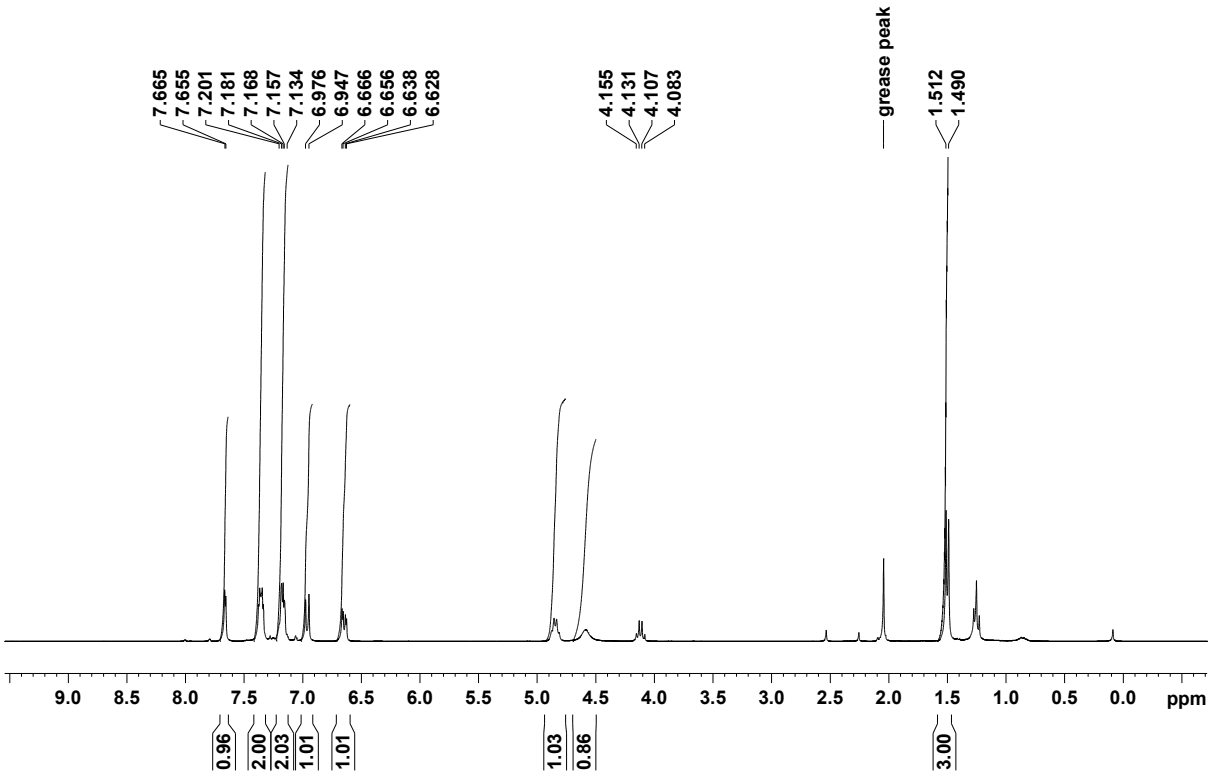


^{13}C NMR

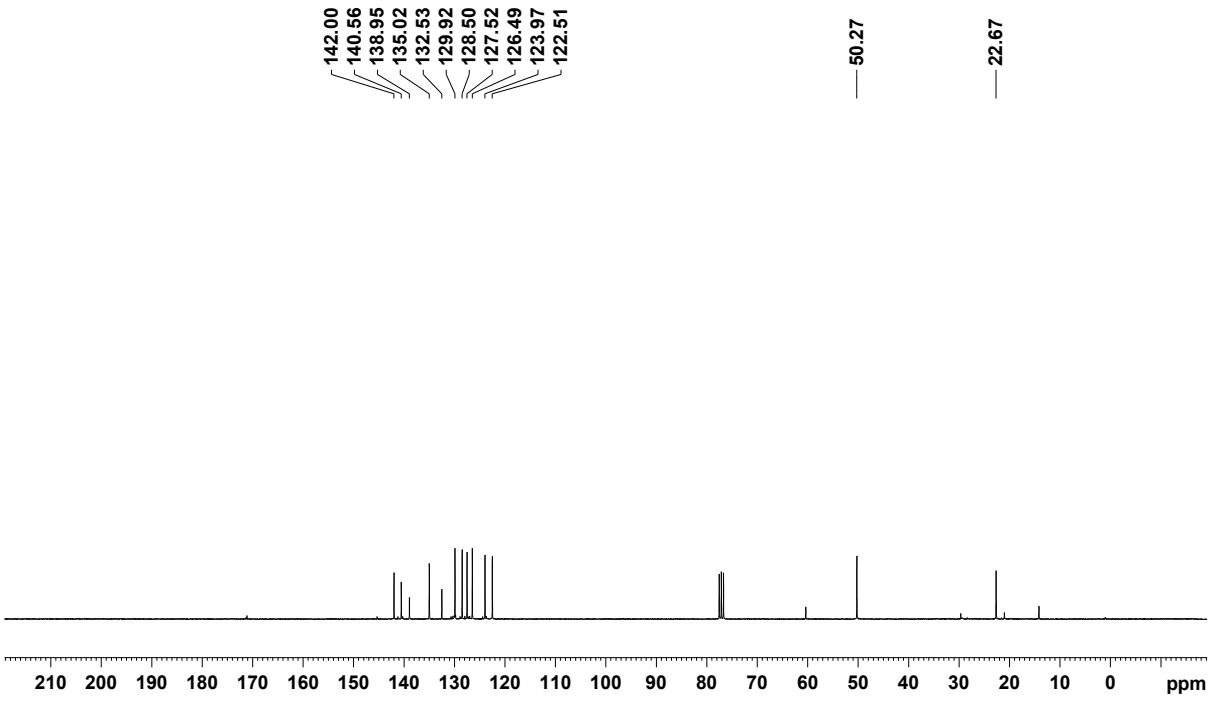


***N*-[1-(2-Chloro-phenyl)-ethyl]-(6-chloro-pyridin-3-yl)-amine (12g).**

^{1}H NMR

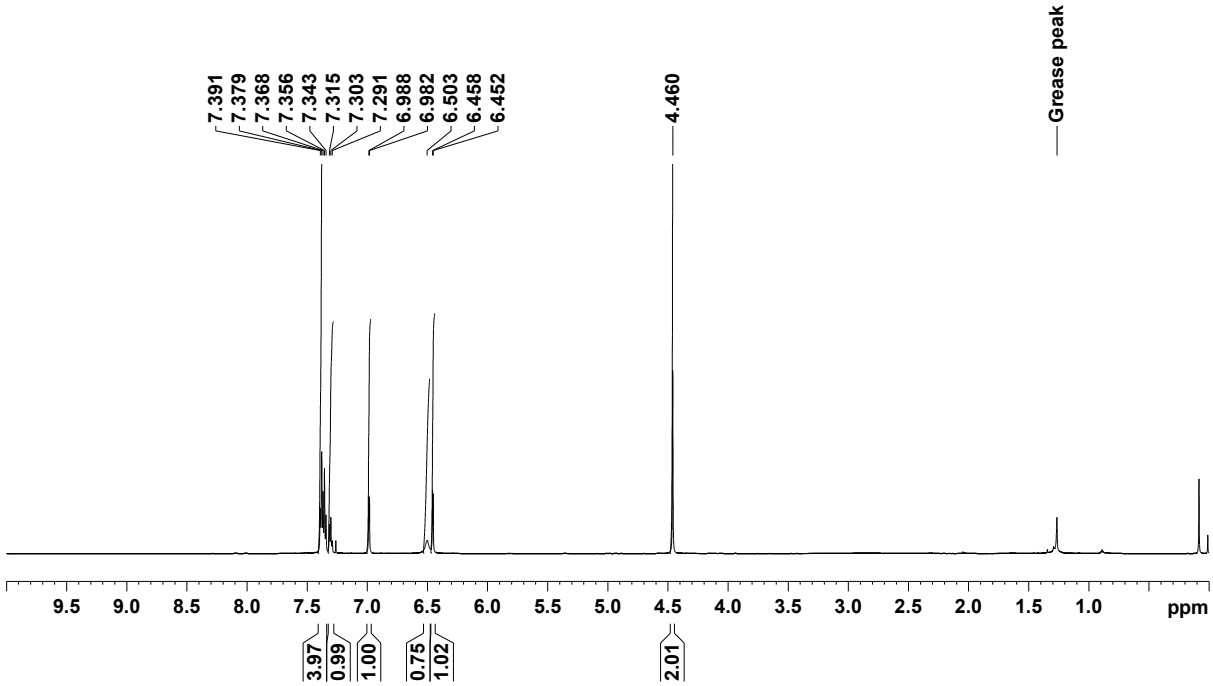


^{13}C NMR

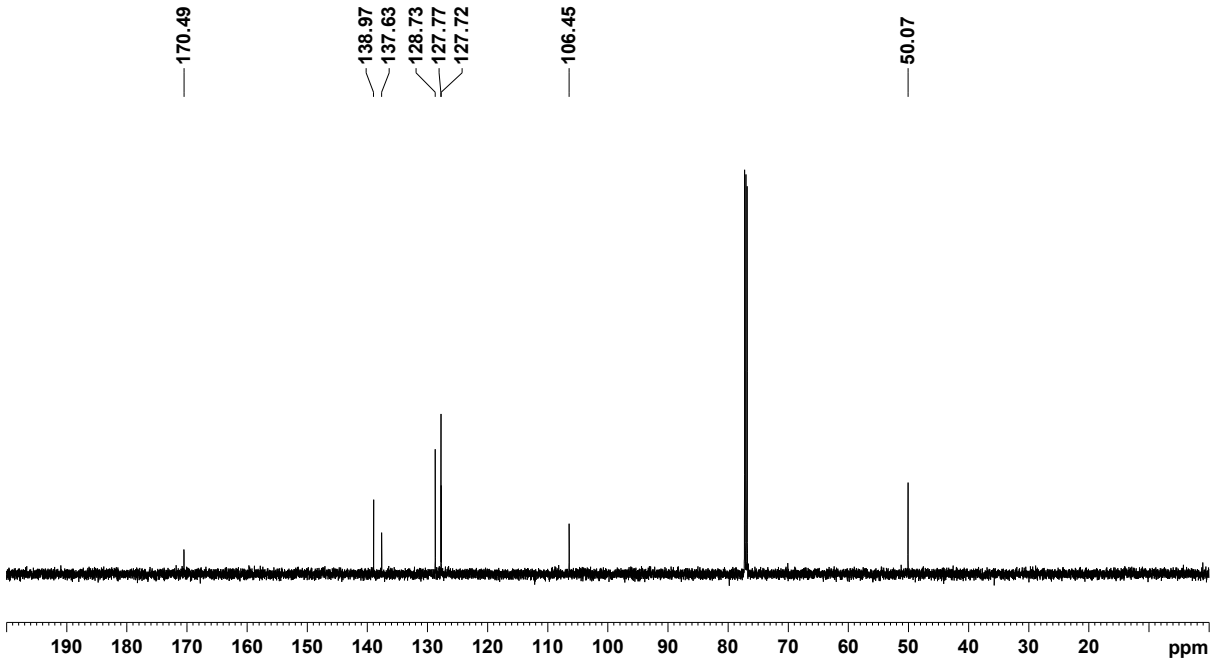


2-Thiazolamine-4,5-dihydro-*N*-benzylamine (12h).

^{1}H NMR

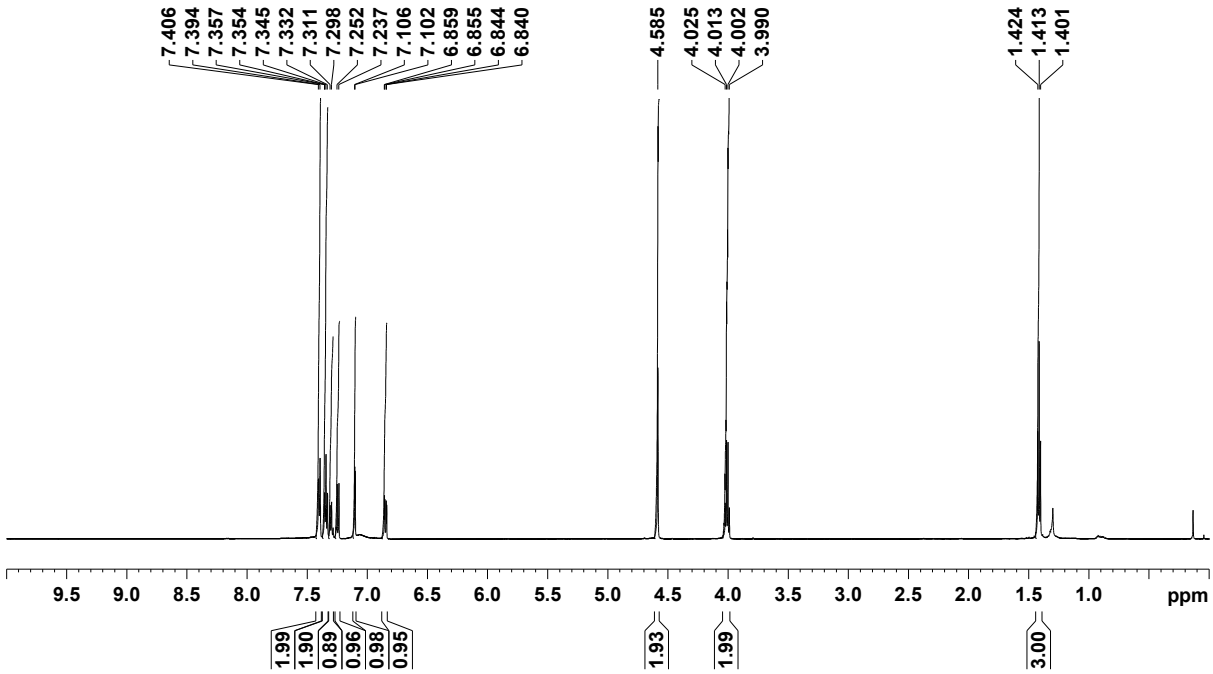


^{13}C NMR

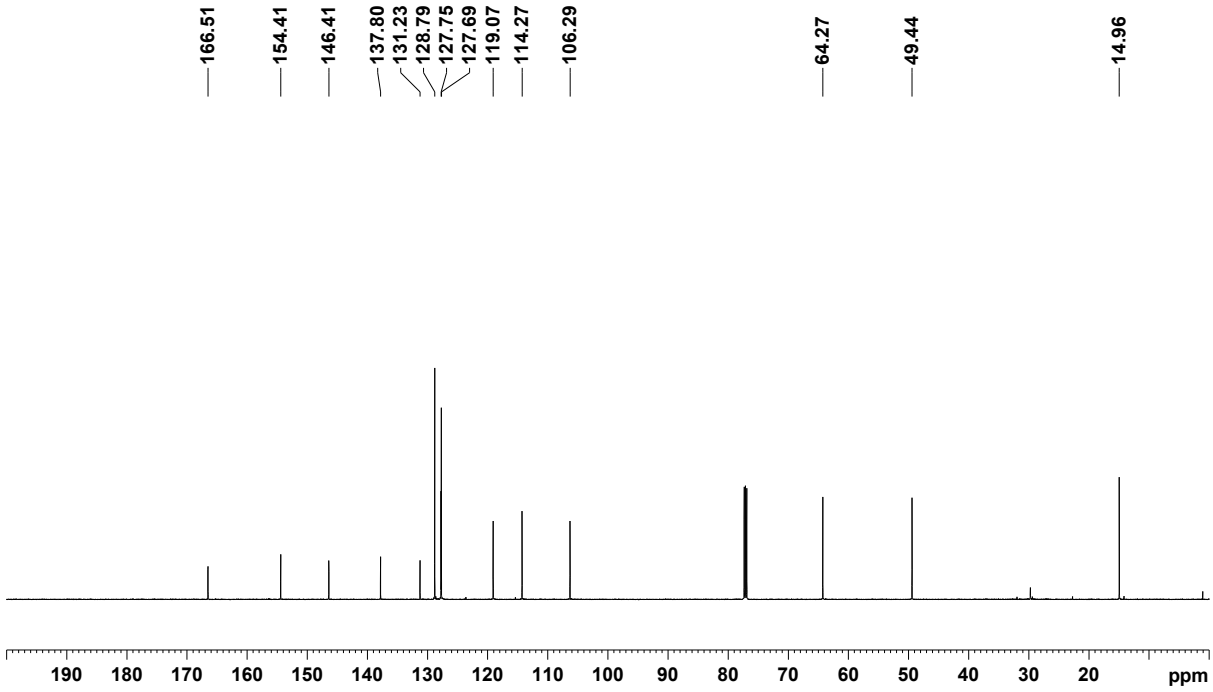


2-Benzothiazolamine-6-ethoxy-*N*-benzylamine (12i)

^{1}H NMR

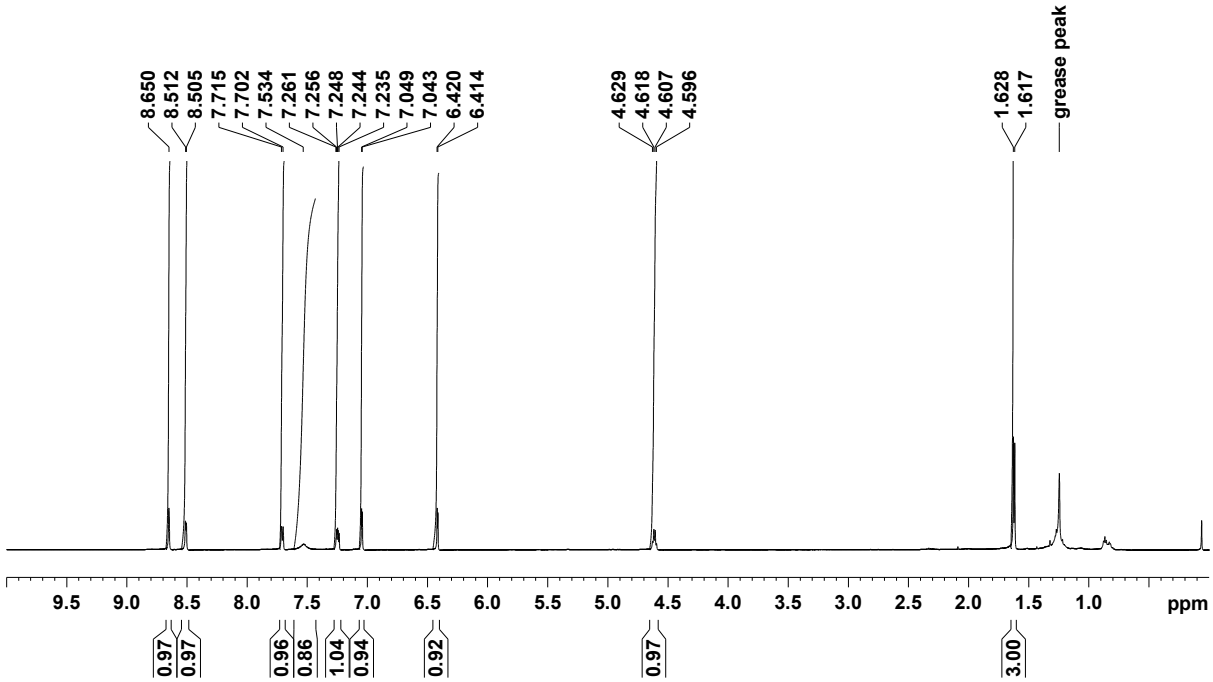


^{13}C NMR

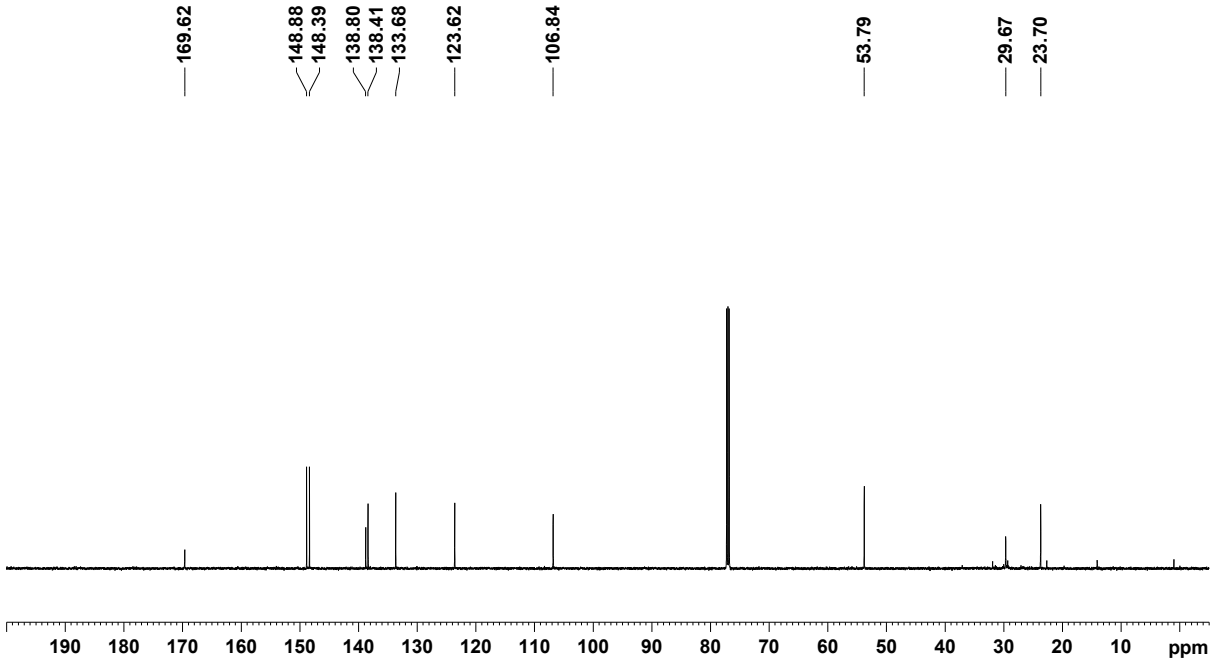


(1-Pyridin-3-yl-ethyl)-thiazol-5-yl-amine (12j).

^{1}H NMR

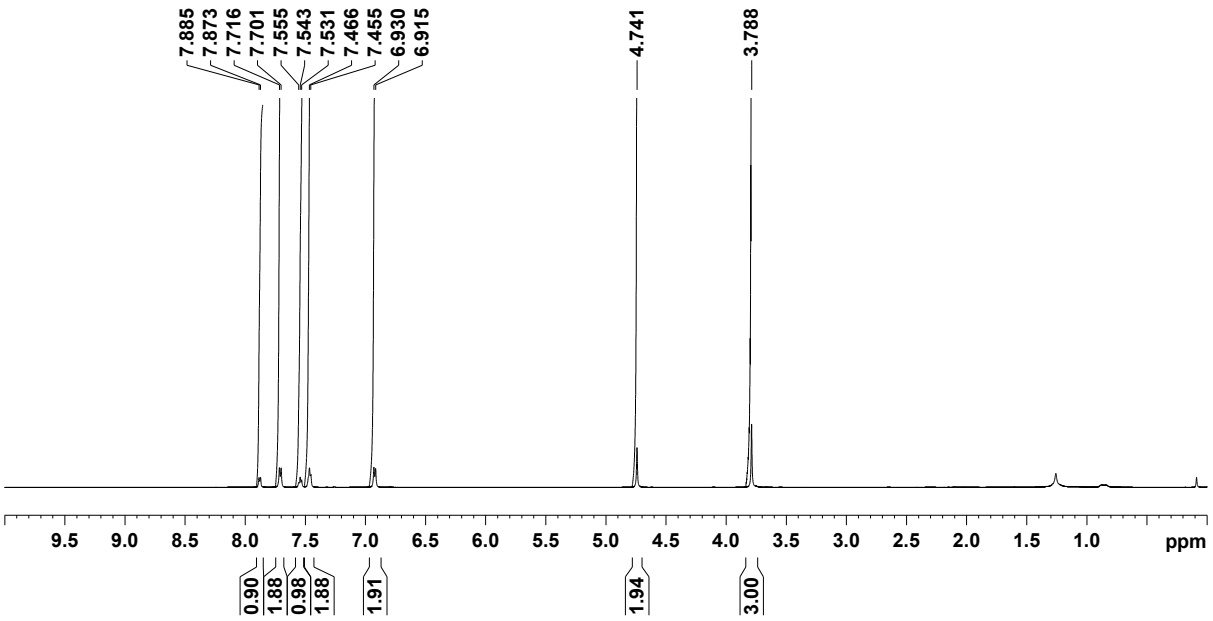


^{13}C NMR

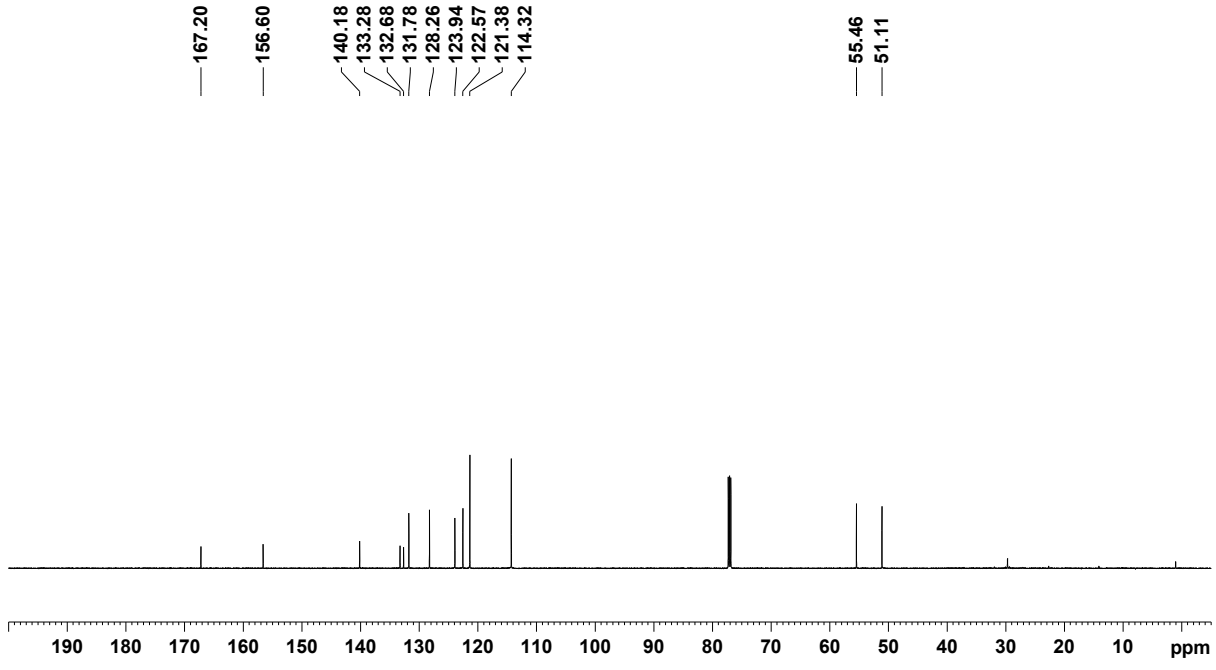


2-(4-Methoxy-phenyl) isoindol-1-one (15a).

^{1}H NMR

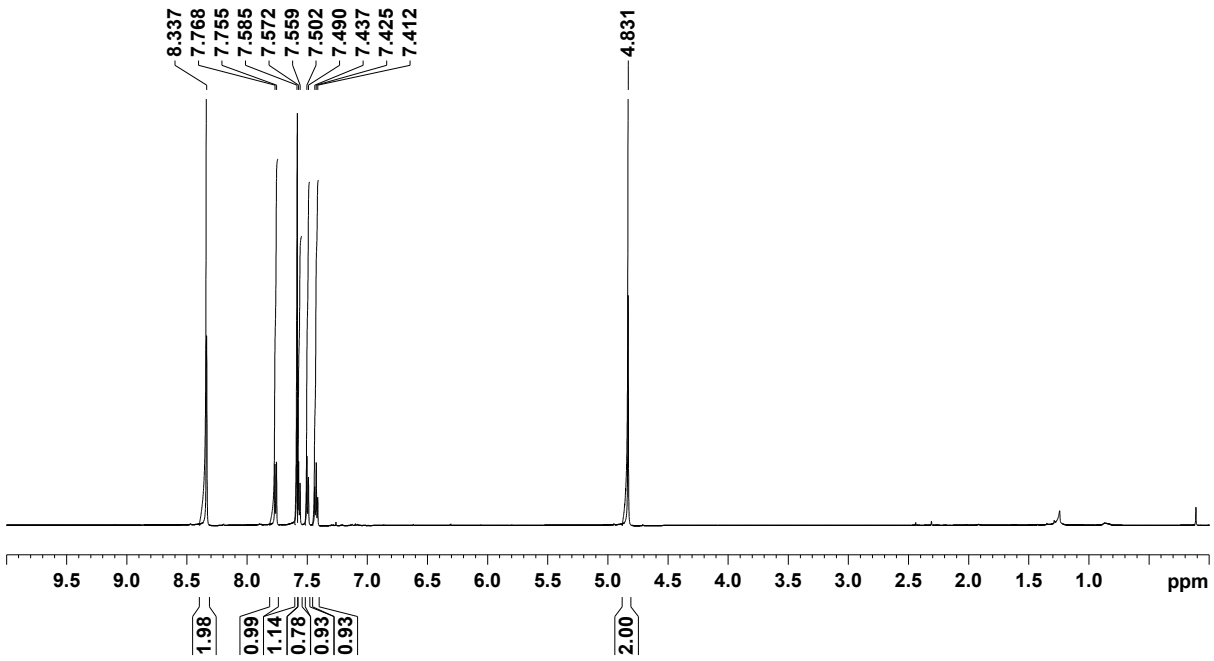


^{13}C NMR

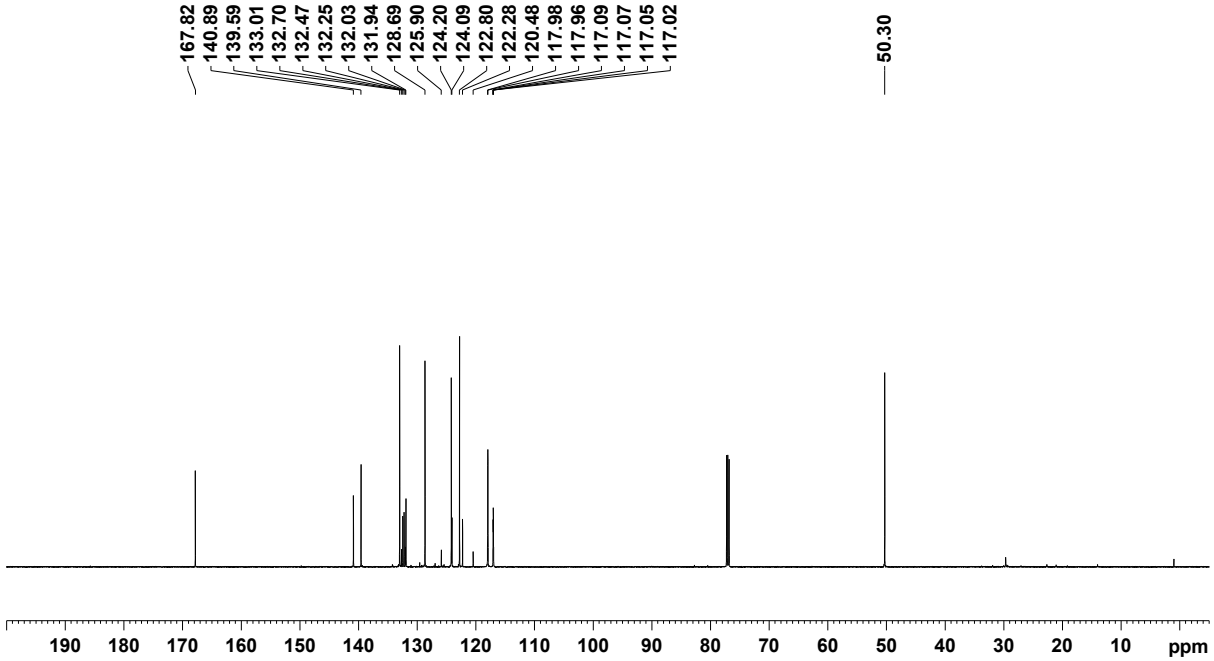


2-(3,5-Bis-trifluoromethyl-phenyl) isoindol-1-one (15b).

^{1}H NMR

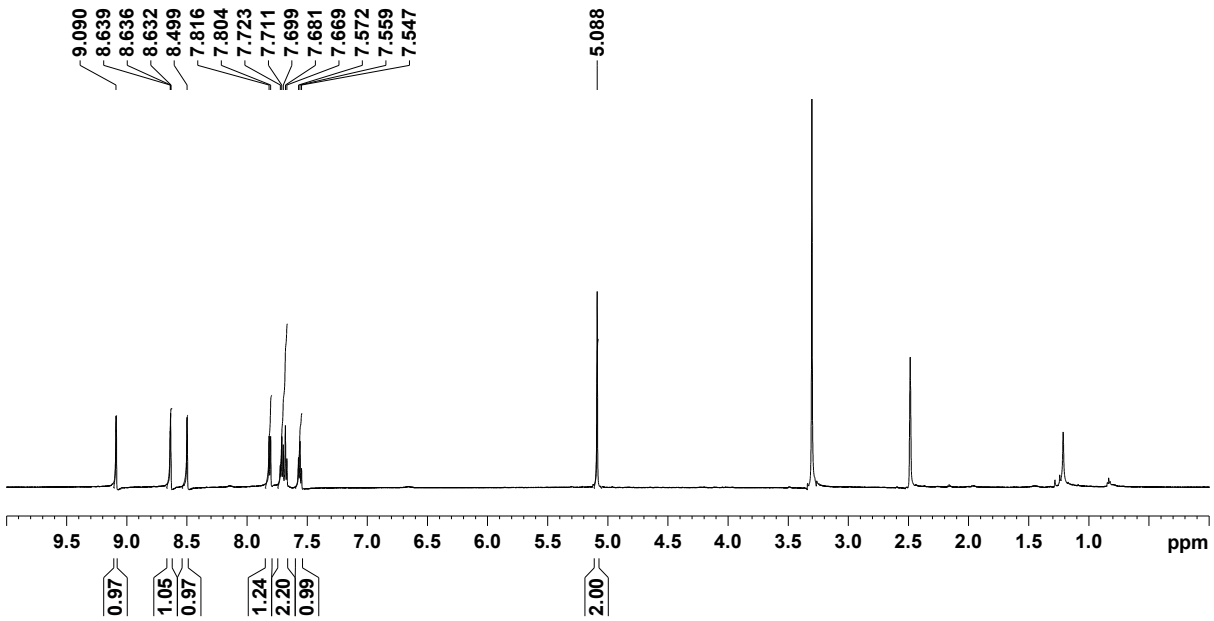


^{13}C NMR

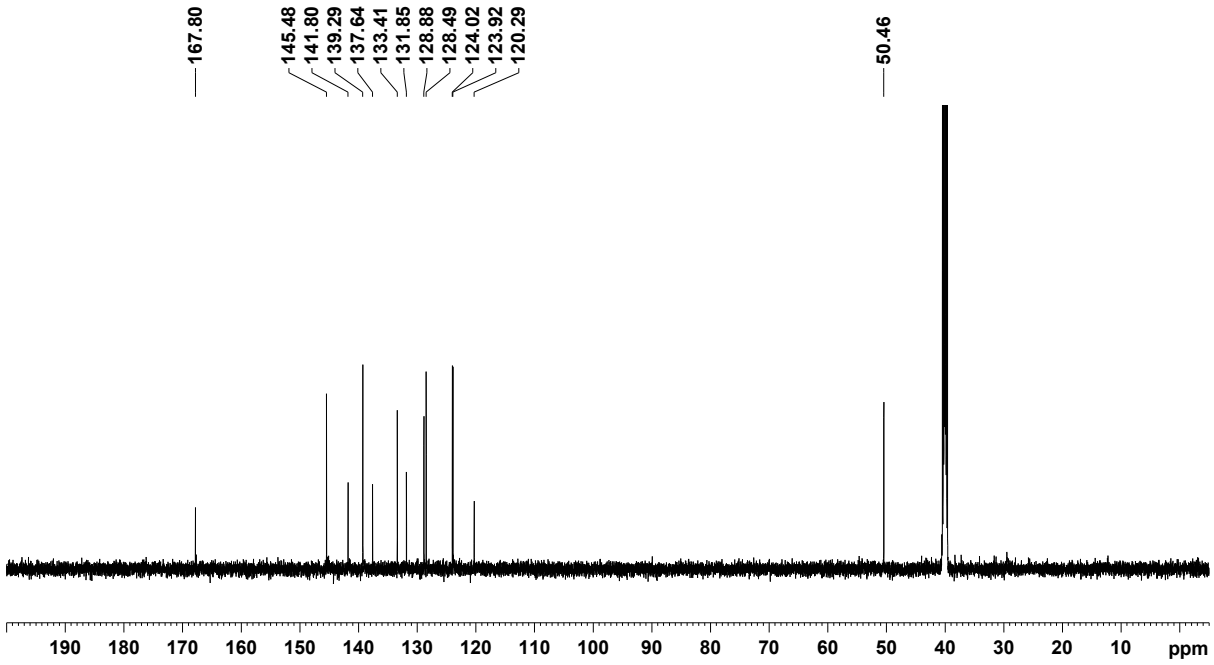


2-(2-Chloropyridyl) isoindolinonein DMSO-d_6(15c)

^{1}H NMR

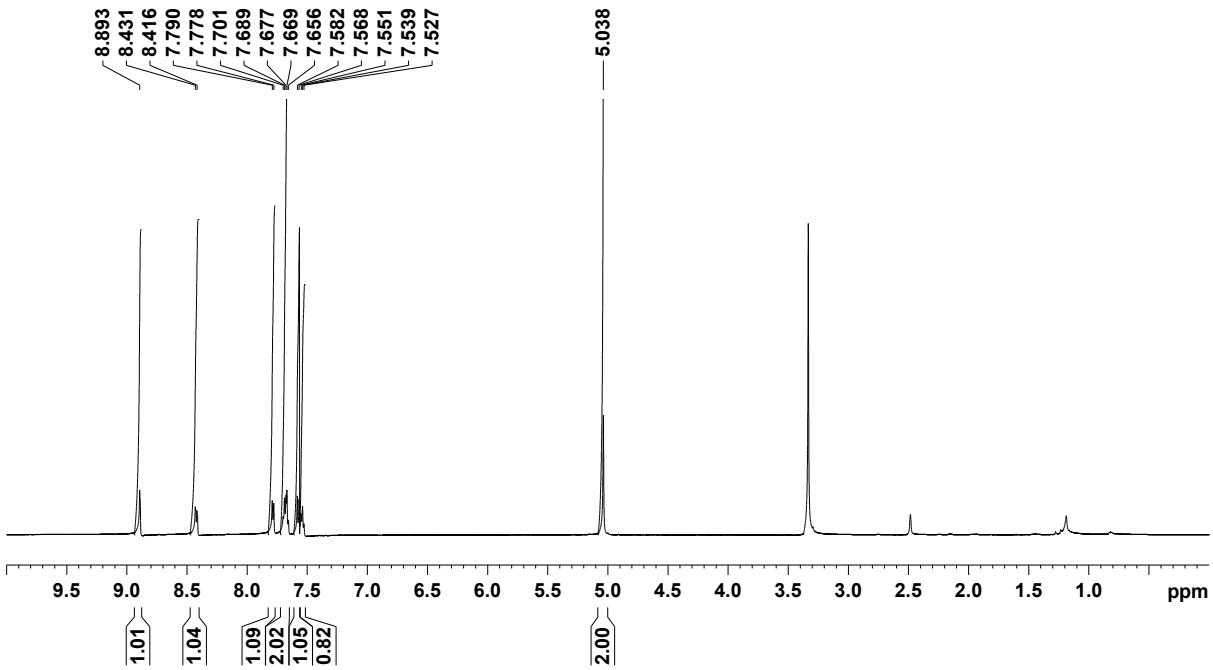


^{13}C NMR

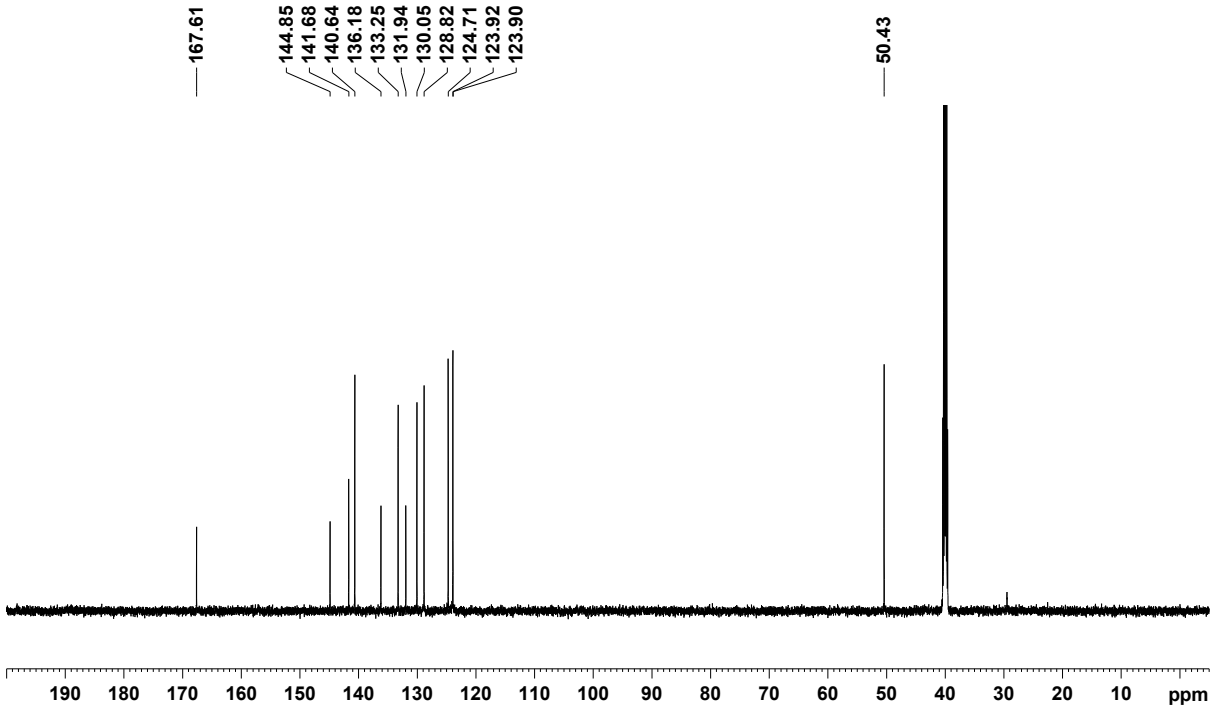


2-(3-Bromopyridyl) isoindolinone in DMSO-d_6 (15d).

^{1}H NMR

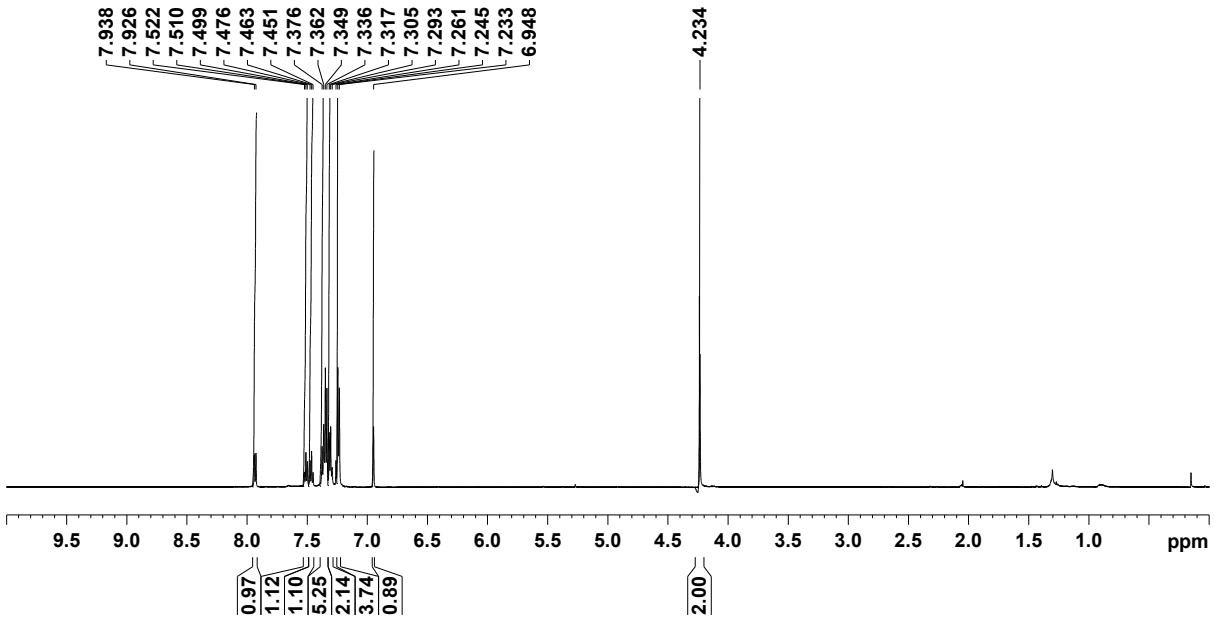


^{13}C NMR

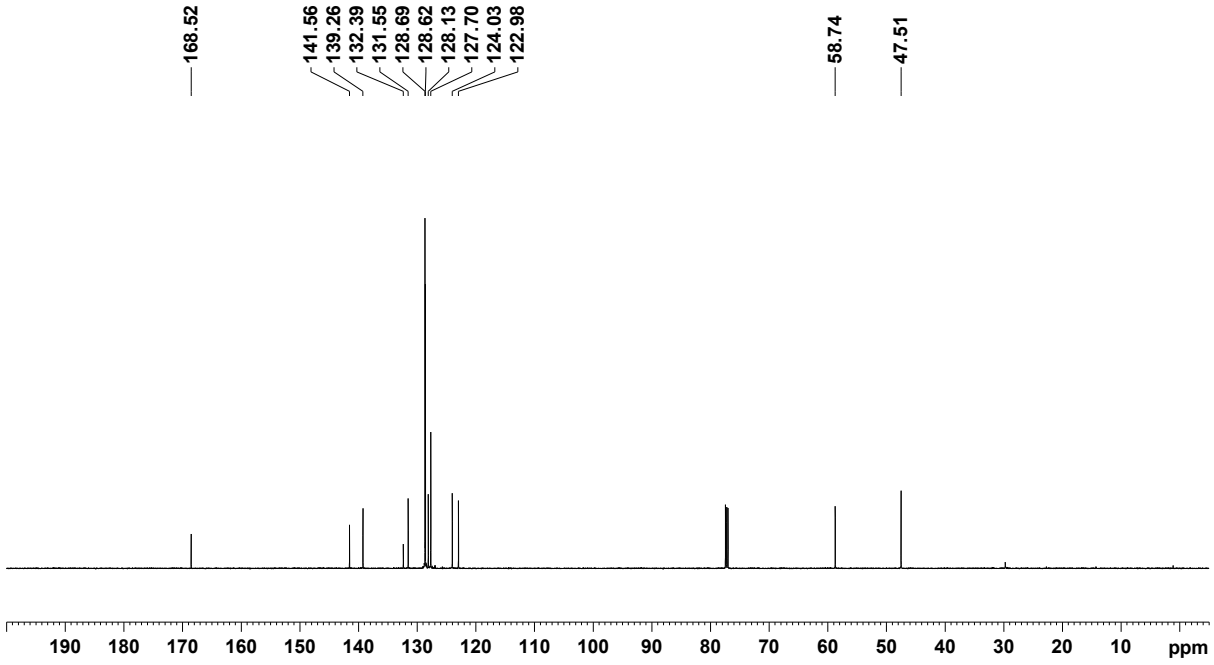


2-(Biphenylmethyl)isoindolinone (15e)

^{1}H NMR

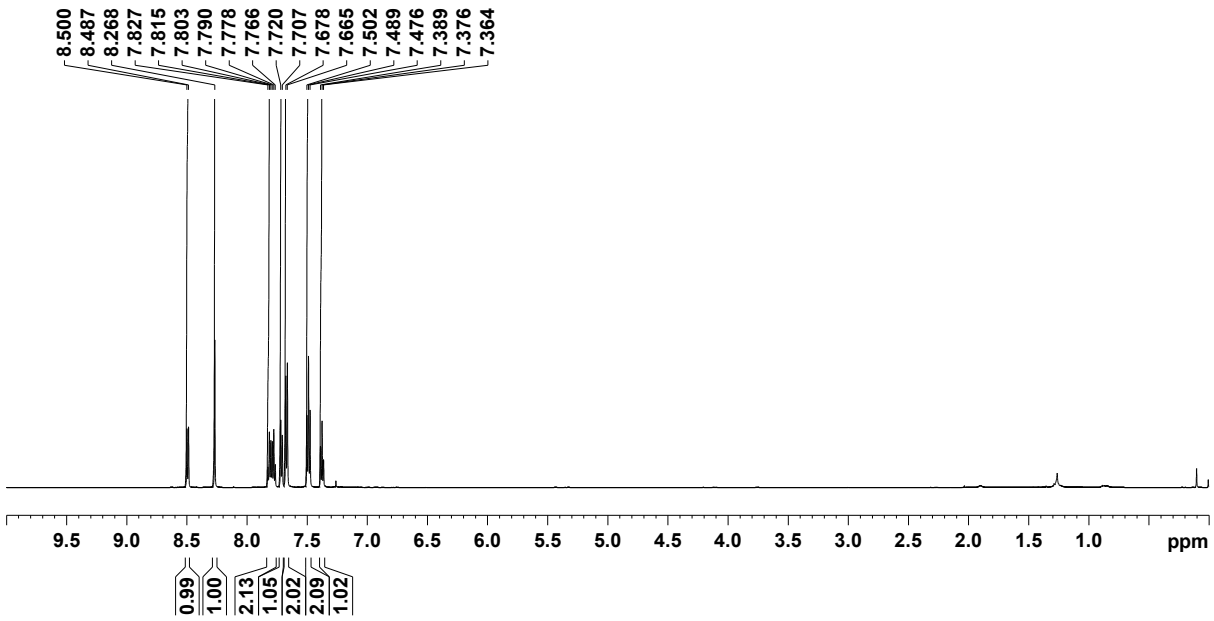


^{13}C NMR

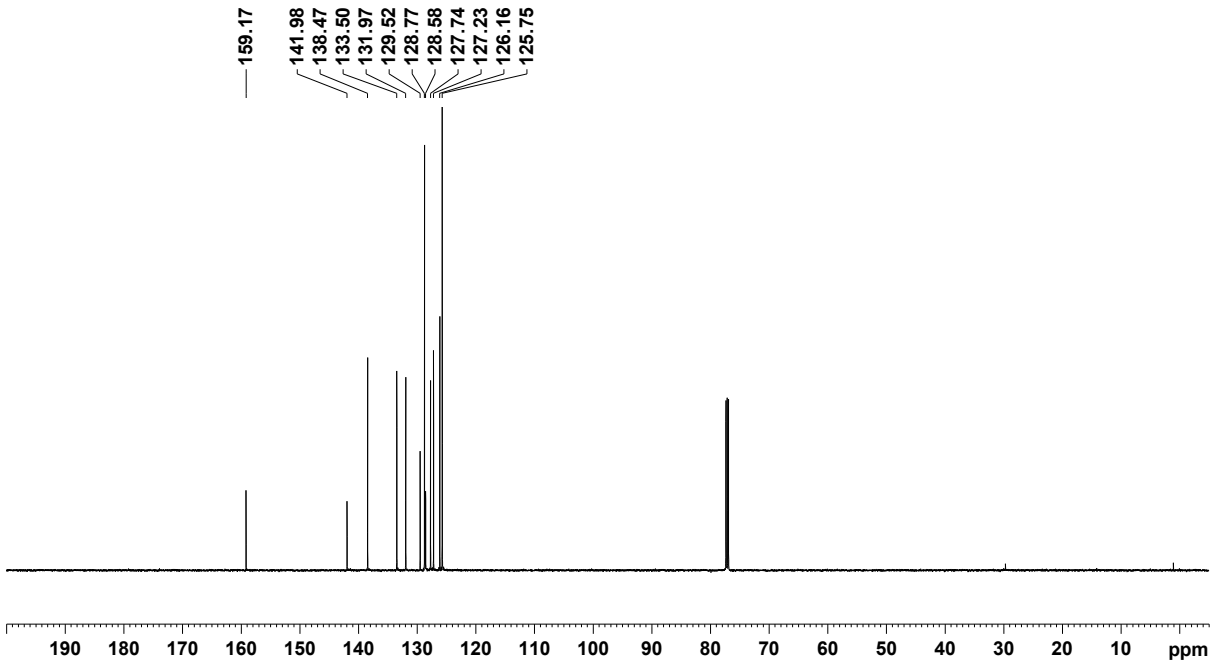


2-Phenylpthalazin-1-(2H)-one (15f).

^{1}H NMR

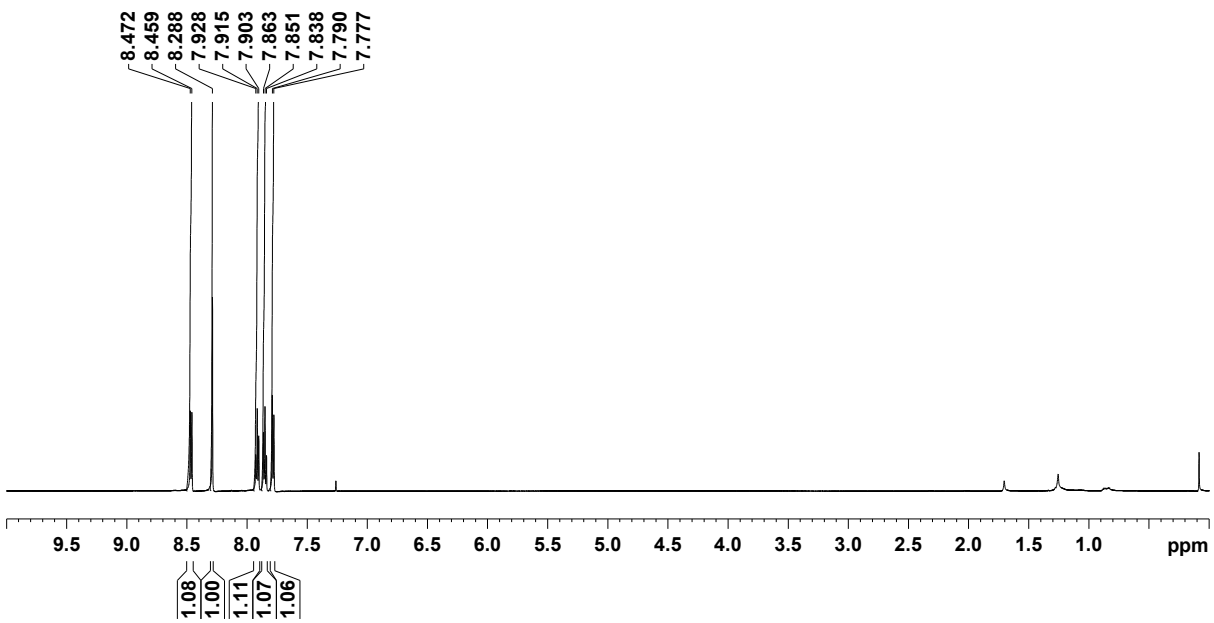


^{13}C NMR



2-Pentafluorophenylphthalazin-1-(2H)-one (15g).

^{1}H NMR



^{13}C NMR