Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Catalyst- and Solvent-Free Efficient Access to *N*-Alkylated Amines via Reductive Amination using HBpin

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General experimental information:

All reactions were performed under an argon atmosphere using glove box or standard Schlenk techniques unless stated otherwise. NMR spectra were recorded on the Bruker 400 and 500 MHz FT-NMR spectrometer at room temperature. All the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced internally to the residual solvent signals. ^{19}F NMR spectra were referenced to α,α,α-trifluorotoluene (0.05% in $CDCl_3$; $\delta = -63.73$ ppm). High resolution ESI-MS mass and GC-MS were recorded with an Agilent 6545A Q-TOF and Shimadzu GCMS-QP2020 spectrometer, respectively. HBpin was purchased from Alfa Aesar and all other chemicals were purchased from the commercial sources and used as it is without further purification.

General procedure for the synthesis secondary amines:

Method A: An oven dried schlenk tube (5 mL) was charged with 4 Å molecular sieve, aldehyde (0.5 mmol, 1 equiv.), and aniline (0.525 mmol, 1.05 equiv.) using standard Schlenk line and stirred for 30 mins at ambient temperature. After that the pinacolborane (0.65 or 0.75 mmol) was added, and allowed to stir at room temperature for 6 to 24 hours under an inert atmosphere. The products were isolated by column chromatography over silica gel using ethyl acetate-hexane mixture as eluent.

Method B (for solid aldehyde and aniline): An oven dried schlenk tube (5 mL) was charged with 4 Å molecular sieve, aldehyde (0.5 mmol, 1 equiv.), and aniline (0.525 mmol, 1.05 equiv.) followed by the addition of 0.3 mL of DCM. The resulting mixture was stirred for 30 mins at room temperature. After removal of the volatiles, pinacolborane (0.65 or 0.75 mmol) was added and the reaction mixture was allowed to stir at ambient temperature for 6 to 24 hours under an inert atmosphere. The products were isolated via column chromatography over silica gel using ethyl acetate-hexane mixture as eluent.

Analytical data for the Secondary Amine products:

*N-benzylaniline (Compound-**3aa**)*: Compound **3aa** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 6 h at room temperature. Yield: 83 mg (0.453 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.16 (m, 5H), 7.07 (t, J = 7.8 Hz, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 8.2 Hz, 2H), 4.15 (s, 2H), 3.81 (s, 1H, NH) ppm. $^{13}C\{^{1}H\}$

NMR (101 MHz, $CDCl_3$) δ 148.2, 139.5, 129.3, 128.6, 127.5, 127.2, 117.5, 112.8, 48.2 ppm. HRMS (ESI): calcd. for $C_{13}H_{13}NH$ ($[M+H]^+$): 184.1126, found: 184.1128.

*N-(4-methylbenzyl)aniline (Compound-**3ba**)*: Compound **3ba** was synthesized following the general procedure (method A) by reacting 4-methylbenzaldehyde (60 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 6 h at room temperature. Yield: 95 mg (0.481 mmol, 96%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.8 Hz, 2H), 7.15-7.10 (m, 4H), 6.68 (t, J = 6.9 Hz, 1H), 6.57 (d, J = 8.5 Hz, 2H), 4.21 (s, 2H), 3.89 (s, 1H, NH), 2.31 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.3, 136.9, 136.5, 129.4, 129.3, 127.6, 117.5, 112.9, 48.1, 21.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NH$ ($[M+H]^+$): 198.1283, found: 198.1282.

*N-(4-methoxybenzyl)aniline (Compound-**3ca**)*: Compound **3ca** was synthesized following the general procedure (method A) by reacting 4-methoxybenzaldehyde (68 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 99 mg (0.464 mmol, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.8 Hz, 2H), 7.13 (t, J = 7.2 Hz, 2H), 6.83 (d, J = 7.9 Hz, 2H), 6.67 (t, J = 6.9 Hz, 1H), 6.57 (d, J = 7.5 Hz, 2H), 4.18 (s, 2H), 3.88 (s, 1H, NH), 3.73 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.9, 148.3, 131.5, 129.3, 128.8, 117.5, 114.1, 112.9, 55.3, 47.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NOH$ ($[M+H]^+$): 214.1232, found: 214.1232.

*N-(4-chlorobenzyl)aniline (Compound-**3da**)*: Compound **3da** was synthesized following the general procedure (method A) by reacting 4-chlorobenzaldehyde (70 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 104 mg (0.477 mmol, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.20 (m, 4H), 7.12 (t, J = 7.9 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.8 Hz, 2H), 4.18 (s, 2H), 3.93 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 138.1, 132.8, 129.3, 128.8, 128.7, 117.8, 112.9, 47.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}ClNH$ ($[M+H]^+$): 218.0737, found: 218.0736.

*N-(4-fluorobenzyl)aniline (Compound-**3ea**)*: Compound **3ea** was synthesized following the general procedure (method A) by reacting 4-fluorobenzaldehyde (62 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 6 h at room temperature. Yield: 95 mg (0.472 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 7.12 (t, J = 7.7 Hz, 2H), 6.95 (t, J = 8.6 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 8.2 Hz, 2H), 4.21 (s, 2H), 3.92 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.1 (d, J = 245.1 Hz), 148.0, 135.3 (d, J = 3.3 Hz), 129.4, 129.1 (d, J = 8.1 Hz), 117.8, 115.5 (d, J = 21.5 Hz), 113.0, 47.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}NFH$ ($[M+H]^+$): 202.1032, found: 202.1032.

*N-(3-bromobenzyl)aniline (Compound-**3fa**)*: Compound **3fa** was synthesized following the general procedure (method A) by reacting 3-bromobenzaldehyde (92.5 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 6 h at room temperature. Yield: 124 mg (0.473 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.13-7.09 (m, 3H), 6.67 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.9 Hz, 2H), 4.18 (s, 2H), 3.95 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.8, 142.1, 130.3, 130.3, 130.2, 129.3, 125.9, 122.8, 117.8, 112.9, 47.7 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}BrNH$ ($[M+H]^+$): 262.0231, found: 262.0232.

*N-(3-chlorobenzyl)aniline (Compound-**3ga**)*: Compound **3ga** was synthesized following the general procedure (method A) by reacting 3-chlorobenzaldehyde (70 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 6 h at room temperature. Yield: 105 mg (0.482 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.18-7.15 (m, 3H), 7.11 (t, J = 7.8 Hz, 2H), 6.67 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.9 Hz, 2H), 4.19 (s, 2H), 3.95 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.8, 141.8, 134.5, 129.9, 129.4, 127.4, 127.4, 125.4, 117.9, 112.9, 47.7 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}ClNH$ ($[M+H]^+$): 218.0737, found: 218.0737.

*N-(pyridin-2-ylmethyl)aniline (Compound-**3ha**)*: Compound **3ha** was synthesized following the general procedure (method A) by reacting 2-pyridinecarboxaldehyde (53.5 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at 60 ºC. Yield: 37 mg (0.200 mmol, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 4.7 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.8 Hz, 3H), 6.73 (t, J = 13.3, 5.9 Hz, 1H), 6.68 (d, J = 7.9 Hz, 2H), 4.78 (s, 1H, NH), 4.47 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.6, 149.3, 148.0, 136.7, 129.3, 122.2, 121.7, 117.6, 113.1, 49.3 ppm. HRMS (ESI): calcd. for $C_{12}H_{12}N_2H$ ($[M+H]^+$): 185.1079, found: 185.1071.

*4-methoxy-N-(4-methoxybenzyl)aniline (Compound-**3ib**)*: Compound **3ib** was synthesized following the general procedure (method B) by reacting 4-methoxybenzaldehyde (68 mg, 0.5 mmol), 4-methoxyaniline (65 mg, 0.525 mmol), and pinacolborane (96 mg, 0.75 mmol) for 12 h at room temperature. Yield: 104 mg (0.427 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.11 (s, 2H), 3.70 (s, 3H), 3.65 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.8, 152.1, 142.6, 131.7, 128.8, 114.9, 114.1, 114.0, 55.7, 55.2, 48.6 ppm. HRMS (ESI): calcd. for $C_{15}H_{17}NO_2H$ ($[M+H]^+$): 244.1338, found: 244.1340.

*4-chloro-N-(4-chlorobenzyl)aniline (Compound-**3jc**)*: Compound **3jc** was synthesized following the general procedure (method B) by reacting 4-chlorobenzaldehyde (70 mg, 0.5 mmol), 4-chloroaniline (67 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 116 mg (0.460 mmol, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.44 (d, J = 8.6 Hz, 2H), 4.19 (s, 1H), 4.02 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.4, 137.6, 133.0, 129.2, 128.9, 128.7, 122.3, 114.0, 47.6 ppm. HRMS (ESI): calcd. for $C_{13}H_{11}Cl_2NH$ ($[M+H]^+$): 252.0347, found: 252.0350.

*N-((5-bromothiophen-2-yl)methyl)aniline (Compound-**3ka**)*: Compound **3ka** was synthesized following the general procedure (method A) by reacting 5-bromo-2-thiophenecarbaldehyde (96 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 95 mg (0.354 mmol, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 7.8 Hz, 2H), 6.87 (d, J = 3.6 Hz, 1H), 6.74 (t, J = 7.2 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 4.40 (s, 2H), 4.02 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.4, 145.2, 129.7, 129.4, 125.2, 118.5, 113.3, 111.0, 43.9 ppm. HRMS (ESI): calcd. for $C_{11}H_{10}BrNSH$ ($[M+H]^+$): 269.9775, found: 269.9778.

*N-(furan-2-ylmethyl)aniline (Compound-**3la**)*: Compound **3la** was synthesized following the general procedure (method A) by reacting furfural (48 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 75.5 mg (0.435 mmol, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.14 (t, J = 7.8 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 8.1 Hz, 2H), 6.27 (s, 1H), 6.18 (s, 1H), 4.24 (s, 2H), 3.94 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.9, 147.8, 142.0, 129.3, 118.1, 113.3, 110.5, 107.1, 41.5 ppm. HRMS (ESI): calcd. for $C_{11}H_{11}NOH$ ($[M+H]^+$): 174.0919, found: 174.0913.

*N-(naphthalen-1-ylmethyl)aniline (Compound-**3ma**)*: Compound **3ma** was synthesized following the general procedure (method A) by reacting 1-naphthaldehyde (78 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 6 h at room temperature. Yield: 112 mg (0.480 mmol, 96%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 9.3 Hz, 1H), 7.81 (d, J = 9.4 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.46–7.38 (m, 3H), 7.33 (t, J = 7.6 Hz, 1H), 7.13 (t, J = 7.7 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 8.2 Hz, 2H), 4.60 (s, 2H), 3.85 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 148.3, 134.4, 133.9, 131.6, 129.4, 128.9, 128.2, 126.4, 126.1, 125.9, 125.6, 123.7, 117.6, 112.8, 46.4 ppm. HRMS (ESI): calcd. for C$_{17}$H$_{15}$NH ([M+H]$^+$): 234.1283, found: 234.1284.

4-methoxy-*N*-(naphthalen-1-ylmethyl)aniline *(Compound-**3mb**)*: Compound **3mb** was synthesized following the general procedure (method B) by reacting 1-naphthaldehyde (78 mg, 0.5 mmol), 4-methoxyaniline (65 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 121 mg (0.459 mmol, 92%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99-7.96 (m, 1H), 7.81-7.78 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.43-7.41 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.55 (s, 2H), 3.65 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 152.2, 142.6, 134.7, 133.9, 131.6, 128.8, 128.1, 126.3, 126.0, 125.8, 125.6, 123.7, 115.0, 114.0, 55.8, 47.2 ppm. HRMS (ESI): calcd. for C$_{18}$H$_{17}$NOH ([M+H]$^+$): 264.1388, found: 264.1378.

*N-(4-chlorobenzyl)-3,5-dimethylaniline (Compound-**3dd**)*: Compound **3dd** was synthesized following the general procedure (method A) by reacting 4-chlorobenzaldehyde (70 mg, 0.5 mmol), 3,5-dimethylaniline (64 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 112 mg (0.455 mmol, 91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23-7.18 (m, 4H), 6.34 (s, 1H), 6.18 (s, 2H), 4.17 (s, 2H), 3.81 (s, 1H, NH), 2.17 (s, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 148.1, 139.0, 138.3, 132.8, 128.7, 119.9, 110.9, 47.6, 21.6 ppm. HRMS (ESI): calcd. for C$_{15}$H$_{16}$ClNH ([M+H]$^+$): 246.1050, found: 246.1041.

*N-(4-chlorobenzyl)-4-methoxyaniline (Compound-**3db**)*: Compound **3db** was synthesized following the general procedure (method B) by reacting 4-chlorobenzaldehyde (70 mg, 0.5 mmol), 4-methoxyaniline (65 mg, 0.525 mmol), and pinacolborane (96 mg, 0.75 mmol) for 12 h at room temperature. Yield: 105 mg (0.423 mmol, 85%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26-7.22 (m, 4H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 2H), 4.19 (s, 2H),3.76 (s, 1H, NH) 3.68 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 152.4, 142.2, 138.4, 132.8, 128.8, 128.7, 115.0, 114.2, 55.8, 48.5 ppm. HRMS (ESI): calcd. for C$_{14}$H$_{14}$ClNOH ([M+H]$^+$): 248.0842, found: 248.0842.

*N, N'-(1,4-phenylenebis(methylene))dianiline (Compound-**3na**)*: Compound **3na** was synthesized following the general procedure (method B) by reacting terephthaldehyde (67 mg, 0.5 mmol), aniline (98 mg, 0.525 mmol), and pinacolborane (166 mg, 1.30 mmol) for 12 h at 60 ºC. Yield: 137 mg (0.475 mmol, 95%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25-7.22 (m, 4H), 7.11 (t, *J* = 7.4 Hz, 4H), 6.67-6.64 (m, 2H), 6.54 (d, *J* = 7.8 Hz, 4H), 4.21 (s, 4H), 3.90 (s, 2H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.1, 138.5, 129.3, 127.8, 127.0, 117.6, 112.9, 48.0 ppm. HRMS (ESI): calcd. for $C_{20}H_{20}N_2H$ ($[M+H]^+$): 289.1705, found: 289.1710.

*N-cinnamylaniline (Compound-**3oa**)*: Compound **3oa** was synthesized following the general procedure (method A) by reacting cinnamic aldehyde (66 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 78 mg (0.372 mmol, 74%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.23–7.17 (m, 3H), 6.72 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.6 Hz, 2H), 6.61 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 5.8 Hz, 1H), 3.93 (dd, J = 5.8, 1.5 Hz, 2H), 3.82 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.2, 137.0, 131.7, 129.4, 128.7, 127.7, 127.2, 126.5, 117.8, 113.2, 46.4 ppm. HRMS (ESI): calcd. for $C_{15}H_{15}NH$ ($[M+H]^+$): 210.1283, found: 210.1288.

*N,N-dimethyl-4-((phenylamino)methyl)aniline (Compound-**3pa**)*: Compound **3pa** was synthesized following the general procedure (method B) by reacting 4-(dimethylamino)benzaldehyde (74.5 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 82 mg (0.362 mmol, 72%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.1 Hz, 2H), 7.16 (t, J = 7.5 Hz, 2H), 6.72-6.70 (m, 3H), 6.62 (d, J = 7.8 Hz, 2H), 4.18 (s, 2H), 3.85 (s, 1H, NH), 2.92 (s, 6H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.2, 148.5, 129.3, 128.8, 127.8, 127.2, 117.4, 112.9, 48.0, 40.8 ppm. HRMS (ESI): calcd. for $C_{15}H_{18}N_2H$ ($[M+H]^+$): 227.1548, found: 227.1552.

*N-butylaniline (Compound-**3qa**)*: Compound **3qa** was synthesized following the general procedure (method A) by reacting butyraldehyde (36 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 60 mg (0.402 mmol, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 7.7 Hz, 2H), 6.67 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 8.2 Hz, 2H), 3.56 (s, 1H, NH), 3.08 (t, J = 7.1 Hz, 2H), 1.61-1.54 (m, 2H), 1.45-1.36 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.6, 129.3, 117.1, 112.7, 43.7, 31.7, 20.5, 14.1 ppm. HRMS (ESI): calcd. for $C_{10}H_{15}NH$ ($[M+H]^+$): 150.1283, found: 150.1283.

*4-((phenylamino)methyl)benzonitrile (Compound-**3ra**)*: Compound **3ra** was synthesized following the general procedure (method A) by reacting 4-cyanobenzaldehyde (66 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 96 mg (0.461 mmol, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.18 (t, J = 7.4 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.59 (d, J

= 7.9 Hz, 2H), 4.43 (s, 2H), 4.24 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.5, 145.5, 132.5, 129.4, 127.8, 119.0, 118.2, 113.0, 110.9, 47.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{12}N_2H$ ([M+H]$^+$): 209.1079, found: 209.1072.

*N-(4-nitrobenzyl)aniline (Compound-**3sa**)*: Compound **3sa** was synthesized following the general procedure (method A) by reacting 4-nitrobenzaldehyde (76 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 104 mg (0.455 mmol, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.11 (t, J = 7.6 Hz, 2H), 6.69 (d, J = 7.3 Hz, 1H), 6.53 (d, J = 7.9 Hz, 2H), 4.40 (s, 2H), 4.26 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.7, 147.4, 147.1, 129.4, 127.7, 123.8, 118.1, 112.9, 47.5 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}N_2O_2H$ ([M+H]$^+$): 229.0977, found: 229.0977.

*N-(cyclohexylmethyl)aniline (Compound-**3ta**)*: Compound **3ta** was synthesized following the general procedure (method A) by reacting cyclohexanecarboxaldehyde (56 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 80 mg (0.422 mmol, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 –7.12 (m, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 8.1 Hz, 2H), 3.65 (s, 1H, NH), 2.92 (d, 2H), 1.80–1.78 (m, 2H), 1.74–1.71 (m, 2H), 1.68–1.65 (m, 1H), 1.59–1.51 (m, 1H), 1.27–1.14 (m, 3H), 0.99–0.92 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) 148.7, 129.3, 116.9, 112.7, 50.7, 37.6, 31.4, 26.7, 26.1 ppm. HRMS (ESI): calcd. for $C_{13}H_{19}NH$ ([M+H]$^+$): 190.1596, found: 190.1584.

*N-((1-methyl-1H-indol-2-yl)methyl)aniline (Compound-**3ua**)*: Compound **3ua** was synthesized following the general procedure (method B) by reacting 1-methylindole-2-carbaldehyde (80 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 71 mg (0.300 mmol, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.17 (t, J = 7.9 Hz, 3H), 7.06 (t, J = 7.4 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 8.0 Hz, 2H), 6.41 (s, 1H), 4.30 (s, 2H), 3.69 (s, 1H, NH), 3.62 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.9, 137.9, 137.2, 129.4, 127.4, 121.6, 120.5, 118.1, 113.1, 109.1, 101.3, 41.0, 29.8 ppm. HRMS (ESI): calcd. for $C_{16}H_{16}N_2H$ ([M+H]$^+$): 237.1392, found: 237.1393.

*N-benzyl-4-methoxyaniline (Compound-**3ab**)*: Compound **3ab** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 4-methoxylaniline (65 mg, 0.525 mmol), and pinacolborane (96 mg, 0.75 mmol) for 12 h at room temperature.

Yield: 92 mg (0.431 mmol, 86%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 2H), 4.18 (s, 2H), 3.88 (s, 1H, NH), 3.73 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 158.9, 148.3, 131.5, 129.3, 128.8, 117.5, 114.1, 112.9, 55.3, 47.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NOH$ ([M+H]$^+$): 214.1232, found: 214.1233.

*N-benzyl-4-chloroaniline (Compound-**3ac**)*: Compound **3ac** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 4-chloroaniline (67 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 96 mg (0.441 mmol, 88%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31-7.29 (m, 4H), 7.26-7.22 (m, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 4.23 (s, 2H), 3.99 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 146.8, 139.1, 129.2, 128.8, 127.5, 127.5, 122.2, 114.0, 48.4 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}ClNH$ ([M+H]$^+$): 218.0737, found: 218.0728.

*N-benzyl-4-methylaniline (Compound-**3ae**)*: Compound **3ae** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 4-methylaniline (56 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 81 mg (0.410 mmol, 82%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31-7.25 (m, 4H), 7.22-7.18 (m, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 2H), 4.22 (s, 2H), 3.80 (s, 1H, NH), 2.19 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 146.0, 139.8, 129.8, 128.7, 127.6, 127.2, 126.7, 113.1, 48.7, 20.5 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NH$ ([M+H]$^+$): 198.1283, found: 198.1284.

*N-benzyl-4-bromoaniline (Compound-**3af**)*: Compound **3af** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 4-bromolaniline (67 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 110 mg (0.420 mmol, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31-7.23 (m, 5H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 8.7 Hz, 2H), 4.21 (s, 2H), 3.99 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 147.1, 138.9, 132.0, 128.8, 127.4, 114.5, 109.1, 48.2 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}BrNH$ ([M+H]$^+$): 262.0231, found: 262.0233.

*N-benzyl-4-(trifluoromethyl) aniline (Compound-**3ag**)*: Compound **3ag** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 4-(trifluoromethyl)aniline (84.5 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 104 mg (0.414 mmol, 83%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.28-7.23 (m, 5H), 6.54 (d, *J* = 8.6 Hz, 2H), 4.27 (s, 3H, -NCH_2- and NH) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.6, 138.6, 128.9, 127.6, 127.5, 126.7 (q, J = 3.6 Hz), 125.2 (q, J = 270.0 Hz), 119.1 (q, J = 32.5 Hz), 118.7, 47.9 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{12}F_3NH$ ($[M+H]^+$): 252.1000, found: 252.1004.

*N-benzyl-2-methylaniline (Compound-**3ah**)*: Compound **3ah** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 2-methylaniline (56 mg, 0.525mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 87 mg (0.441 mmol, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 4H), 7.23 (t, J = 7.0 Hz, 1H), 7.07-7.02 (m, 2H), 6.64 (t, J = 7.4 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 4.30 (s, 2H), 3.79 (s, 1H, NH), 2.11 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.1, 139.6, 130.2, 128.7, 127.6, 127.3, 127.2, 122.0, 117.3, 110.1, 48.3, 17.6 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NH$ ($[M+H]^+$): 198.1283, found: 198.1274.

*N-benzyl-2-chloroaniline (Compound-**3ai**)*: Compound **3ai** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 2-chloroaniline (67 mg, 0.525 mmol), pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 97 mg (0.445 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 3.6 Hz, 4H), 7.21 (d, J = 7.5 Hz, 2H), 7.02 (t, J = 7.7 Hz, 1H), 6.57 (t, J = 7.8 Hz, 2H), 4.68 (s, 1H, NH), 4.31 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.9, 138.8, 129.2, 128.8, 127.9, 127.4, 127.3, 119.2, 117.5, 111.6, 47.9 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}ClNH$ ($[M+H]^+$): 218.0737, found: 218.0728.

*N-benzyl-3-methoxyaniline (Compound-**3aj**)*: Compound **3aj** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 3-methoxyaniline (65 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 57 mg (0.267 mmol, 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.26-7.23 (m, 1H), 7.05 (t, J = 8.1 Hz, 1H), 6.27-6.21 (m, 2H), 6.16 (t, J = 2.1 Hz, 1H), 4.27 (s, 2H), 4.02 (s, 1H, NH), 3.71 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.9, 149.6, 139.4, 130.1, 128.7, 127.6, 127.3, 106.1, 102.7, 98.9, 55.1, 48.4 ppm. HRMS (ESI): calcd. for $C_{14}H_{15}NOH$ ($[M+H]^+$): 214.1232, found: 214.1224.

*N-benzyl-3-bromoaniline (Compound-**3ak**)*: Compound **3ak** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 3-Bromoaniline (90 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 108 mg (0.411 mmol, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 5H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 6.45 (d, *J* = 8.2 Hz, 1H), 4.20 (s, 2H), 4.00 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.4, 138.8, 130.6, 128.8, 127.5, 123.3, 120.3, 115.4, 111.6, 48.1 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}BrNH$ ($[M+H]^+$): 262.0231, found: 262.0222.

*N1, N4-dibenzylbenzene-1,4-diamine (Compound-**3al**)*: Compound **3al** was synthesized following the general procedure (method B) by reacting benzaldehyde (53 mg, 0.5 mmol), *p*-phenylenediamine (57 mg, 0.525 mmol), and pinacolborane (166 mg, 1.30 mmol) for 12 h at 60 ºC. Yield: 116 mg (0.402 mmol, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 8H), 7.31 (t, *J* = 7.0 Hz, 2H), 6.62 (s, 4H), 4.30 (s, 4H), 3.65 (s, 2H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.8, 140.1, 128.6, 127.7, 127.2, 114.7, 49.6 ppm. HRMS (ESI): calcd. for $C_{20}H_{20}N_2H$ ($[M+H]^+$): 289.1705, found: 289.1705.

*N-benzylnaphthalen-1-amine (Compound-**3am**)*: Compound **3am** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 1-naphthylamine (75 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 12 h at room temperature. Yield: 105 mg (0.450 mmol, 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.35-7.29 (m, 3H), 7.28-7.24 (m, 3H), 7.21 (m, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 6.50 (d, *J* = 7.4 Hz, 1H), 4.52 (s, 1H NH), 4.32 (s, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.3, 139.2, 134.4, 128.8, 127.8, 127.4, 126.7, 125.8, 124.8, 123.5, 120.0, 117.7, 104.8, 48.6 ppm. HRMS (ESI): calcd. for $C_{17}H_{15}NH$ ($[M+H]^+$): 234.1283, found: 234.1275.

*N-benzyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (Compound-**3an**)*: Compound **3an** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 2,3-dihydrobenzo[b][1,4]dioxin-6-amine (79 mg, 0.525mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 102 mg (0.422 mmol, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.35 (m, 4H), 7.30 (t, *J* = 6.5 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.24–6.20 (m, 2H), 4.27 (s, 2H), 4.24–4.22 (m, 2H), 4.19–4.17 (m, 2H), 3.82 (s, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 144.1, 143.3, 139.6, 135.7, 128.6, 127.6, 127.2, 117.7, 106.8, 101.6, 64.8, 64.2, 49.0 ppm. HRMS (ESI): calcd. for $C_{15}H_{15}NO_2H$ ($[M+H]^+$): 242.1181, found: 242.1180.

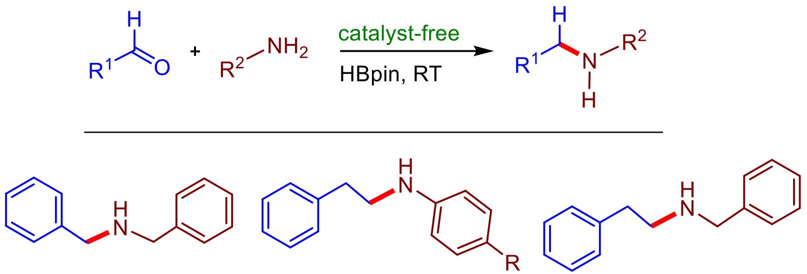
*N-benzylbenzo[d][1,3]dioxol-5-amine (Compound-**3ao**)*: Compound **3ao** was synthesized following the general procedure (method A) by reacting benzaldehyde (53 mg, 0.5 mmol), 1,3-benzodioxol-5-amine (80 mg, 0.525mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 91 mg (0.400 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.28 (m, 4H), 7.24–7.19 (m, 1H), 6.59 (d, J = 8.3 Hz, 1H), 6.19 (d, J = 2.2 Hz, 1H), 6.00 (dd, J = 8.3, 2.3 Hz, 1H), 5.74 (s, 2H), 4.17 (s, 2H), 3.78 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.3, 144.0, 139.7, 139.5, 128.6, 127.5, 127.2, 108.6, 104.4, 100.6, 96.0, 49.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{13}NO_2H$ ($[M+H]^+$): 228.1025, found: 228.1010.

*N-benzyl-4-nitroaniline (Compound-**3ap**)*: Compound **3ap** was synthesized following the general procedure (method B) by reacting benzaldehyde (78 mg, 0.5 mmol), 4-nitroaniline (72.5 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 87 mg (0.382 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.9 Hz, 2H), 7.39-7.32 (m, 5H), 6.57 (d, J = 8.9 Hz, 2H), 4.95 (s, 1H), 4.43 (s, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.2, 138.4, 137.5, 129.1, 128.0, 127.5, 126.5, 111.5, 47.7 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}N_2O_2Na$ ($[M+Na]^+$): 251.0796, found: 251.0794.

*1-(4-(benzylamino)phenyl)ethan-1-one (Compound-**3aq**)*: Compound **3aq** was synthesized following the general procedure (method B) by reacting benzaldehyde (78 mg, 0.5 mmol), 4-aminoacetophenone (49 mg, 0.525 mmol), and pinacolborane (83 mg, 0.65 mmol) for 24 h at room temperature. Yield: 81 mg (0.359 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.6 Hz, 2H), 7.34-7.22 (m, 5H), 6.56 (d, J = 8.6 Hz, 2H), 4.78 (s, 1H, NH), 4.36 (s, 2H), 2.44 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.6, 152.1, 138.3, 130.9, 128.8, 127.6, 127.4, 126.8, 111.6, 47.5, 26.1 ppm. HRMS (ESI): calcd. for $C_{15}H_{15}NOH$ ($[M+H]^+$): 226.1232, found: 226.1237.

*N1-(4-fluorobenzyl)-3-nitrobenzene-1,4-diamine (Compound-**3es**)*: Compound **3es** was synthesized following the general procedure (method A) by reacting the 4-fluorobenzaldehyde (62 mg, 0.5 mmol), 2-nitro-1,4-phenylenediamine (80 mg, 0.525 mmol), and pinacolborane (96 mg, 0.75 mmol) for 24 h at room temperature. Yield: 103 mg (0.394 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.28 (s, 1H), 7.03 (m, 2H), 6.84 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 8.9 Hz, 1H), 5.75 (s, 2H, -NH_2), 4.25 (s, 2H), 3.82 (s, 1H, NH) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.2 (d, J = 246.1 Hz), 139.4, 138.4, 134.5 (d, J = 3.3 Hz), 132.5, 129.3 (d, J = 8.0 Hz), 125.5, 120.2, 115.7 (d, J = 21.4 Hz), 105.9, 48.3 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.2 ppm. HRMS (ESI): calcd. for $C_{13}H_{12}FN_3O_2H$ ($[M+H]^+$): 262.0992, found: 262.0989.

Table S1. Substrate scope for biologically relevant molecules[a]



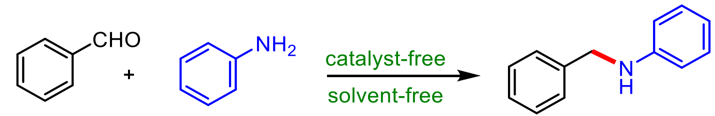
3ar (89%)

R = H, **3va** (65%)
= Br, **3vg** (49%)[b]

3vr (65%)[b,c]

[a] Reaction condition: aldehyde (0.5 mmol), amine (0.525 mmol), HBpin (0.75 mmol), RT, 24 h. Yields were determined by GC-MS using mesitylene as internal standard. [b] DCM (0.3 mL) was used. [c] Reactions were performed at 60 ºC for 12 h.

Scheme S1. Reductive amination reaction in gram scale.



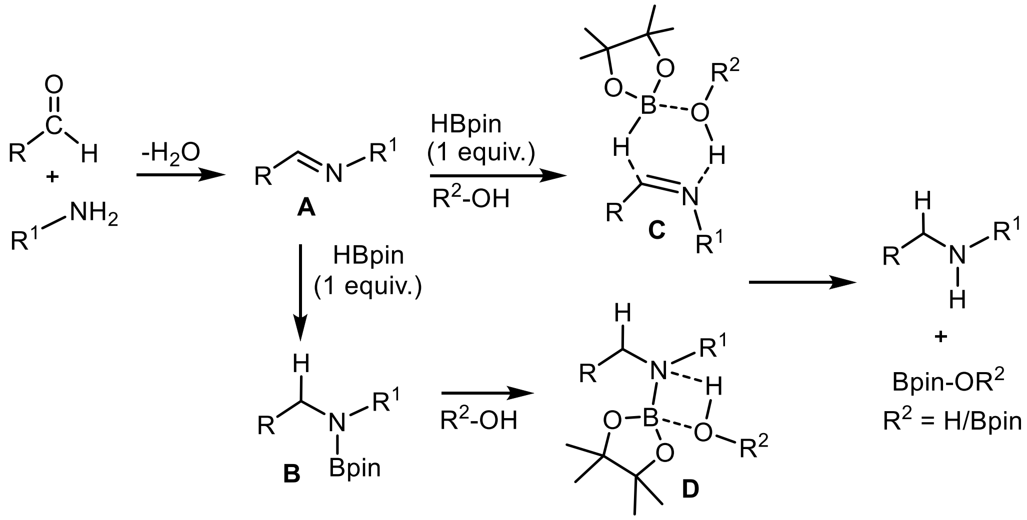
1a 9.42 mmol

2a 9.89 mmol

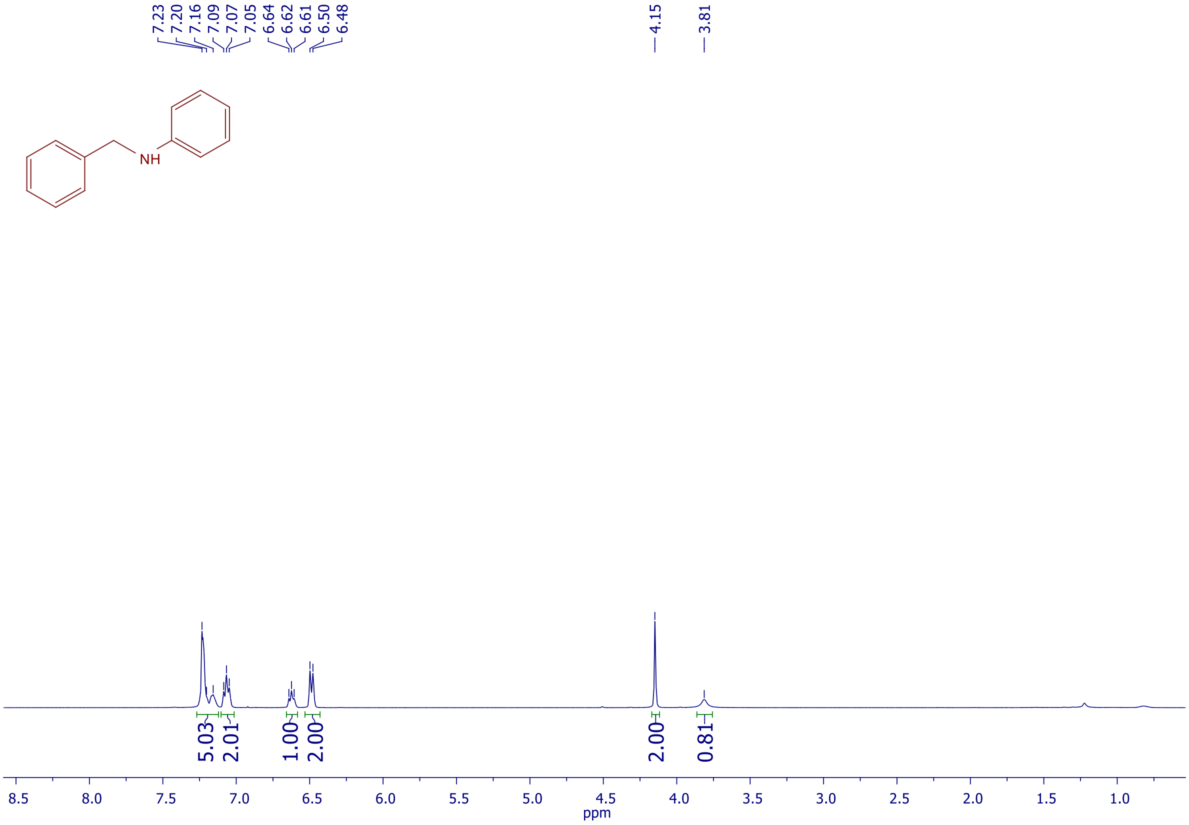
3aa, 1.42 g
7.74 mmol, 82%

Compound **3aa** was synthesized in gram scale following the general procedure by reacting benzaldehyde (1.0 g, 9.42 mmol), aniline (0.921 g, 9.89 mmol), and pinacolborane (1.567 g, 12.246 mmol) for 6 h at room temperature. Yield: 1.42 g (7.74 mmol, 82%).

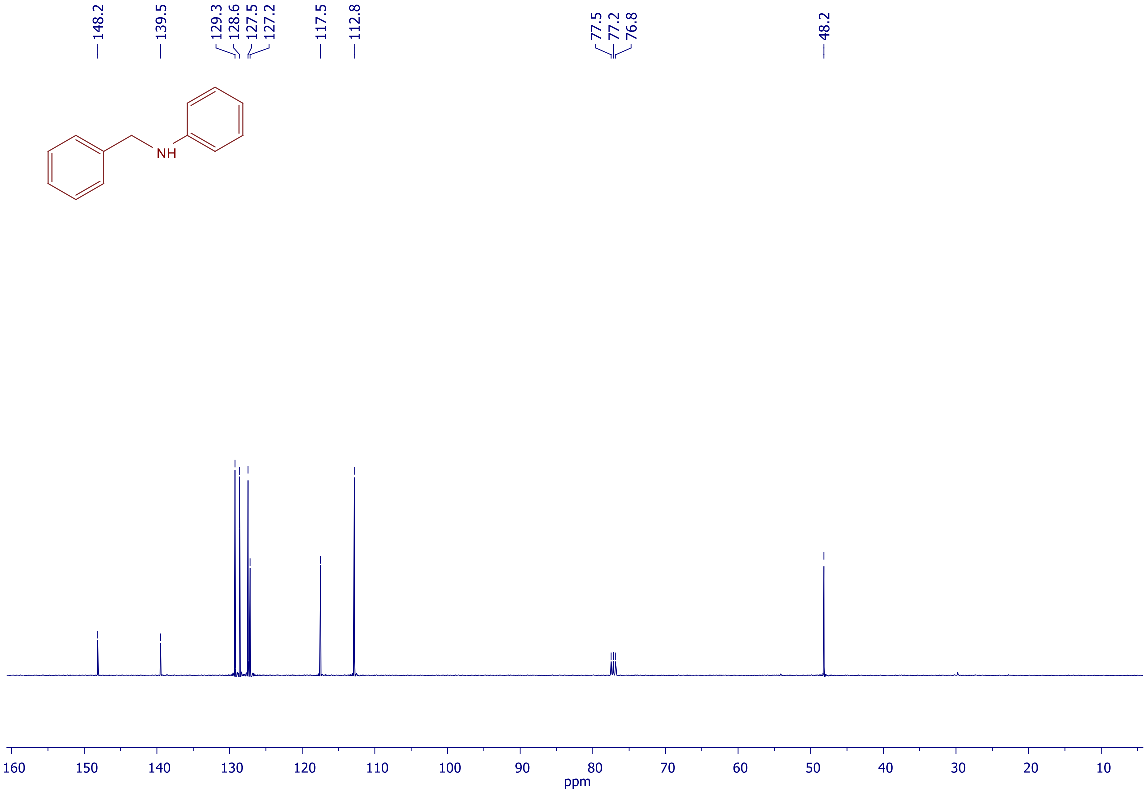
Scheme S2. A plausible mechanism for the reductive amination process.



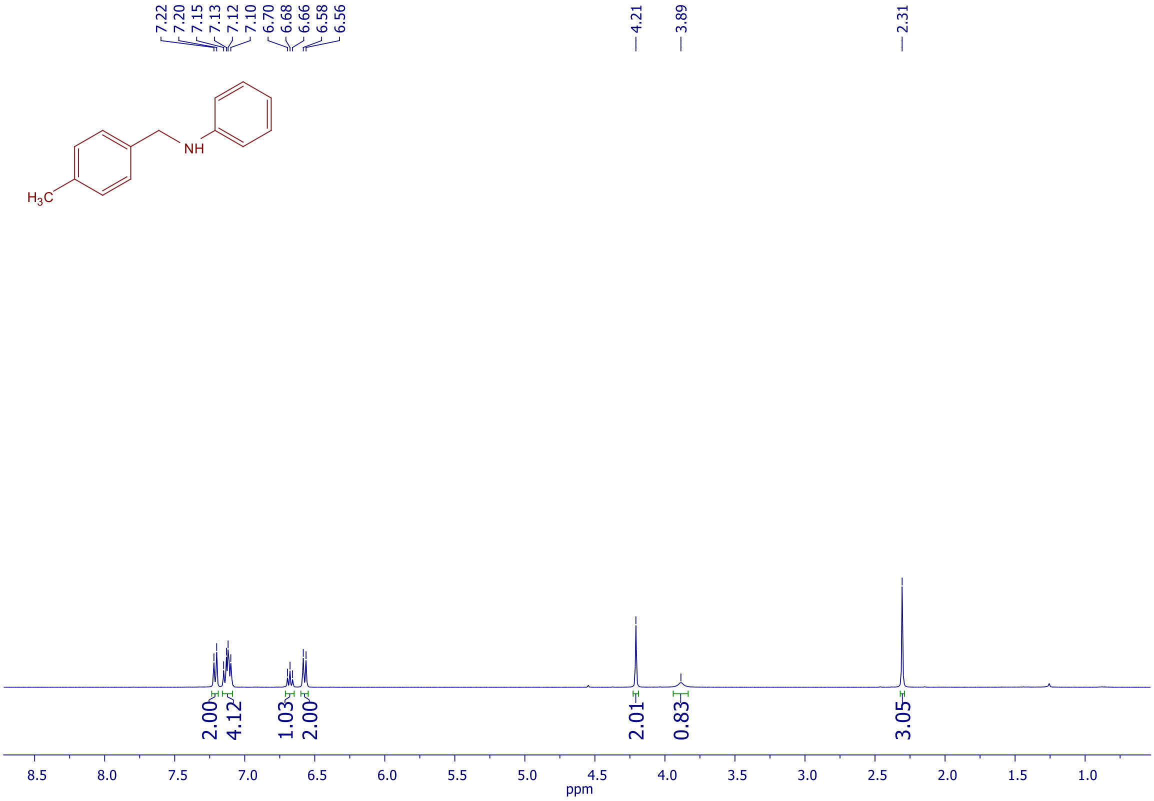
NMR spectra of the isolated secondary amines in $CDCl_3$:



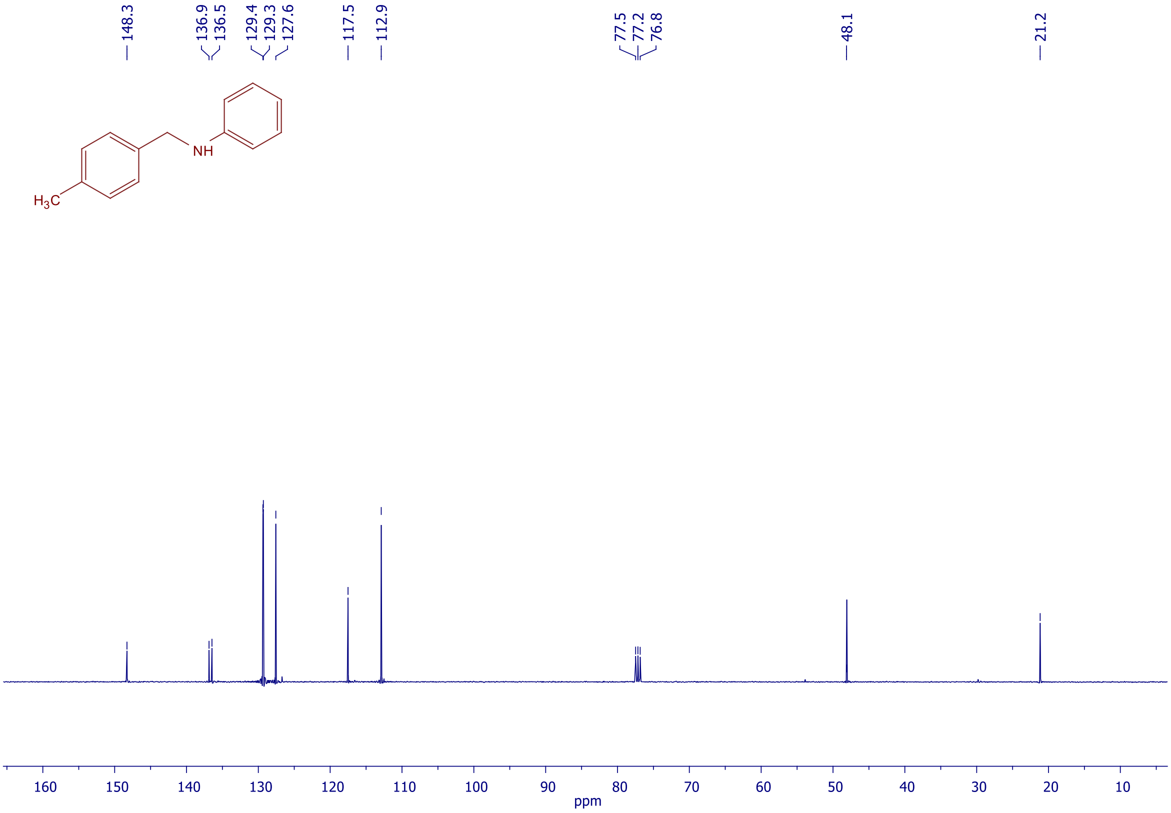
*^1H NMR of N-benzylaniline (Compound-**3aa**)*



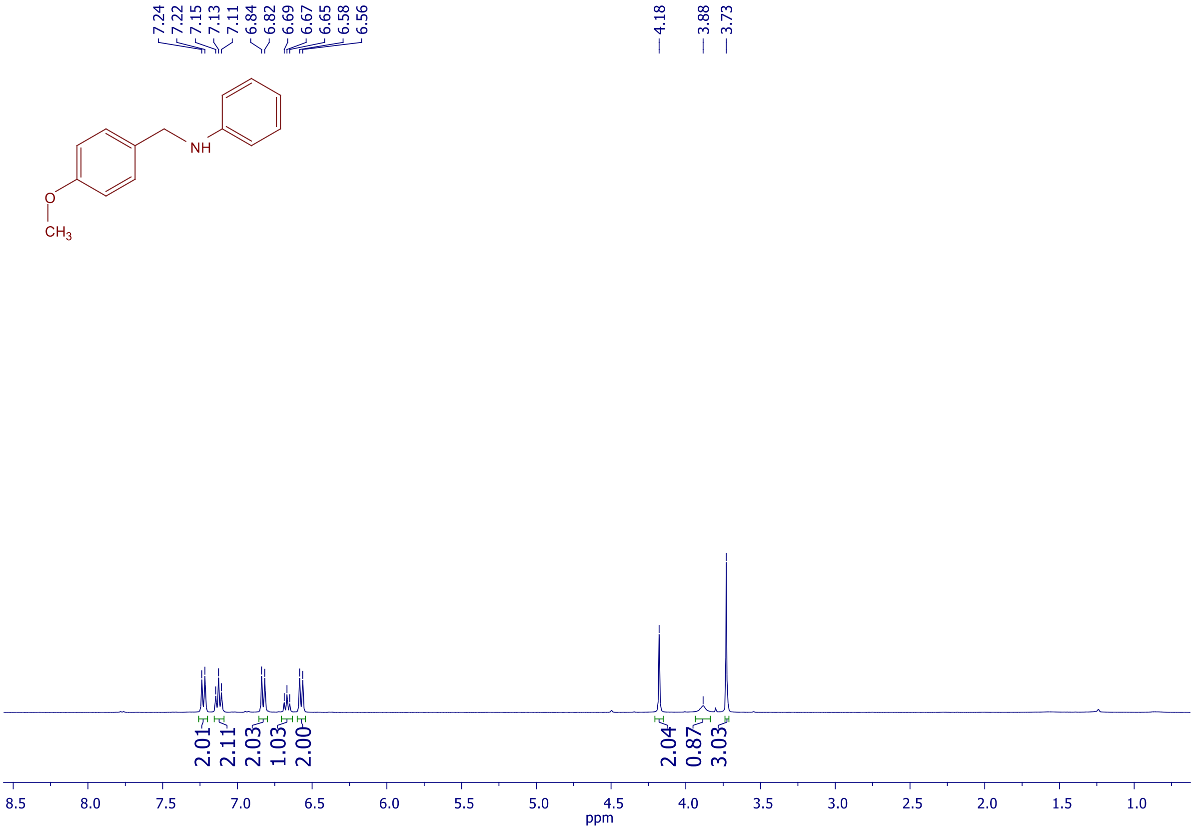
*$^{13}C\{^1H\}$ NMR of N-benzylaniline (Compound-**3aa**)*



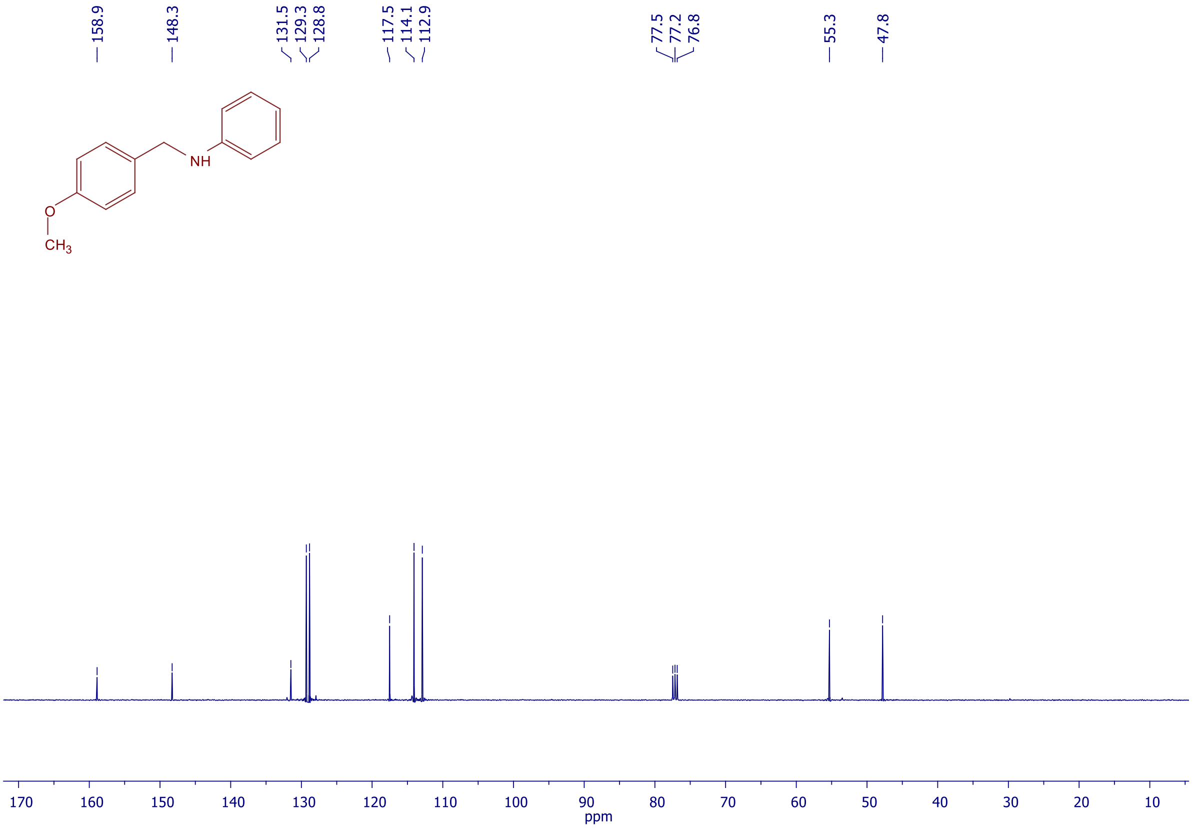
^{1}H NMR of N-(4-methylbenzyl)aniline (Compound-**3ba**)



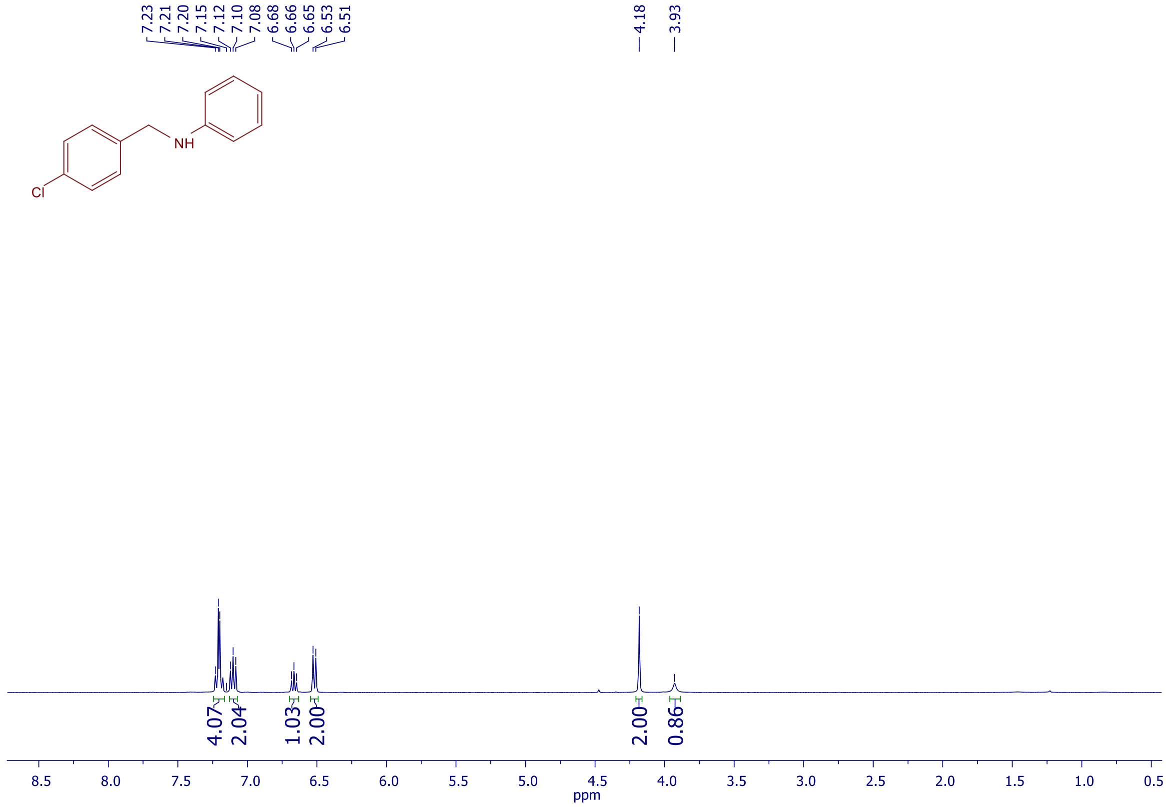
^{13}C{^{1}H} NMR of N-(4-methylbenzyl)aniline (Compound-**3ba**)



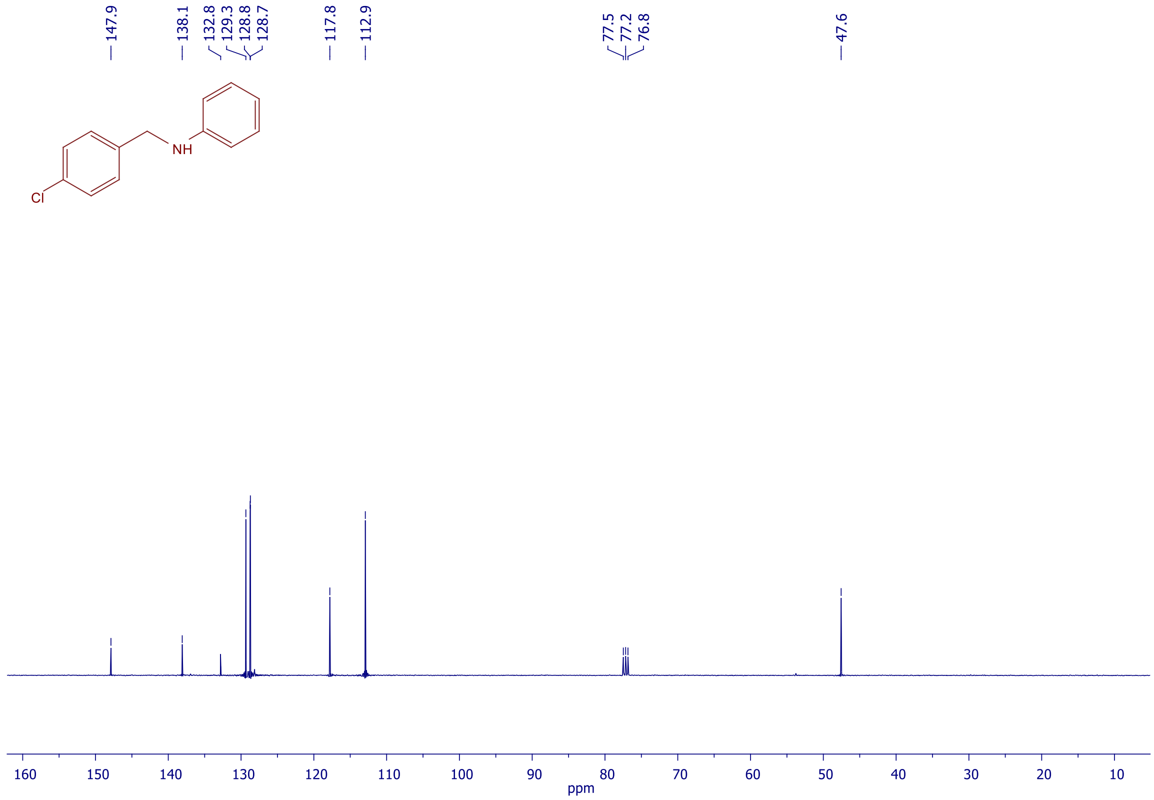
^{1}*H NMR of N-(4-methoxybenzyl)aniline (Compound-**3ca**)*



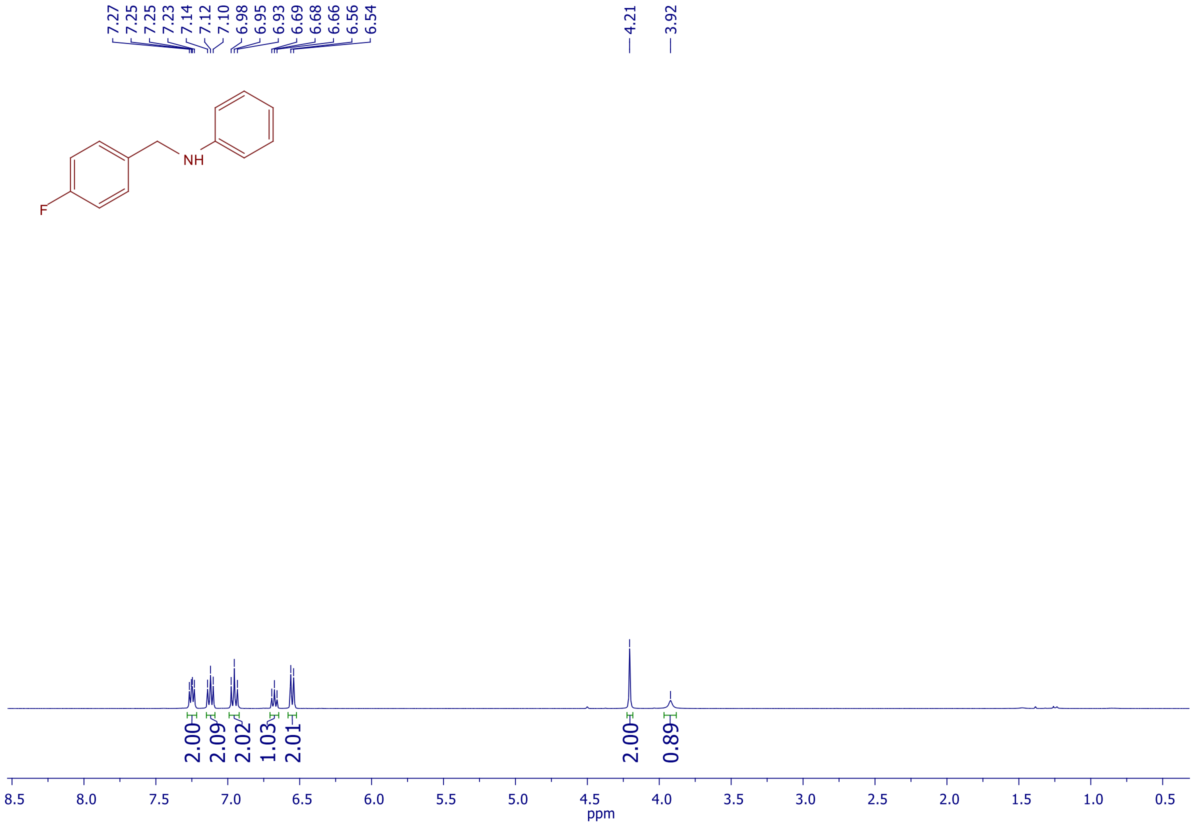
^{13}*C{^{1}H} NMR of N-(4-methoxybenzyl)aniline (Compound-**3ca**)*



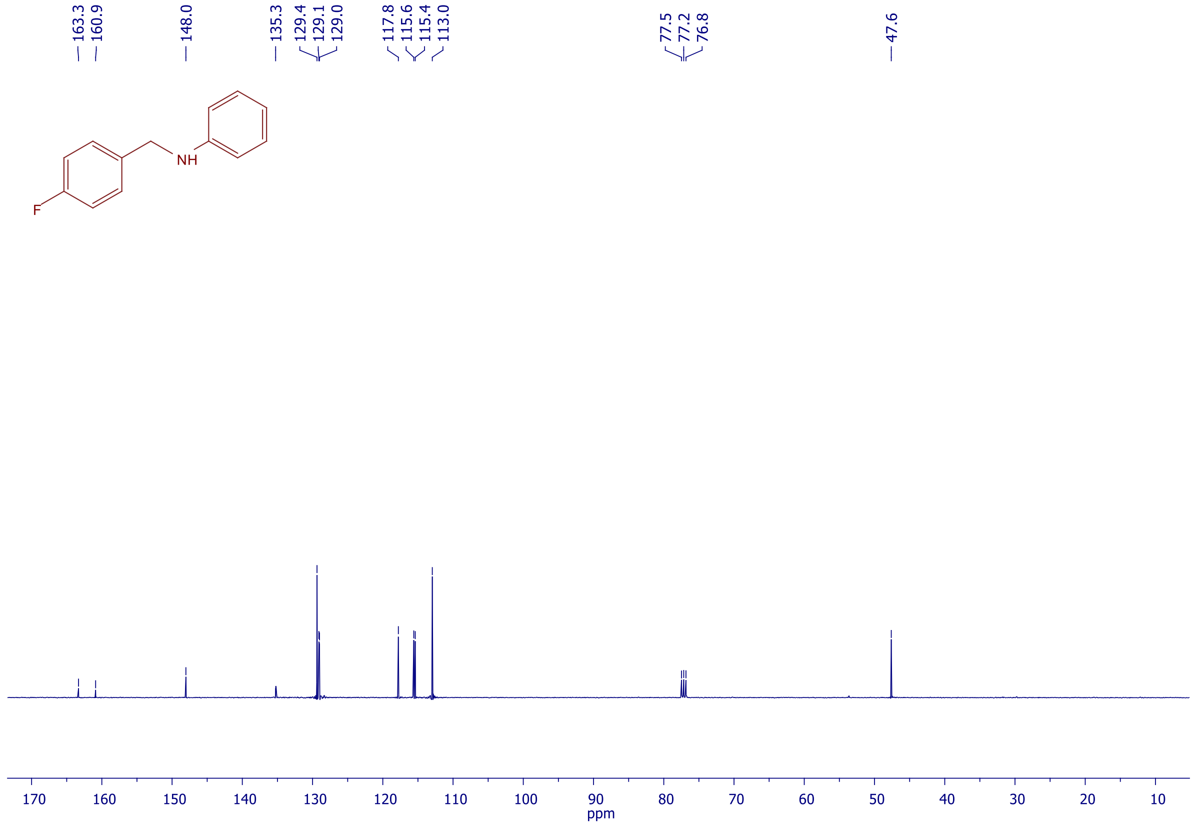
^{1}H NMR of N-(4-chlorobenzyl)aniline (Compound-**3da**)



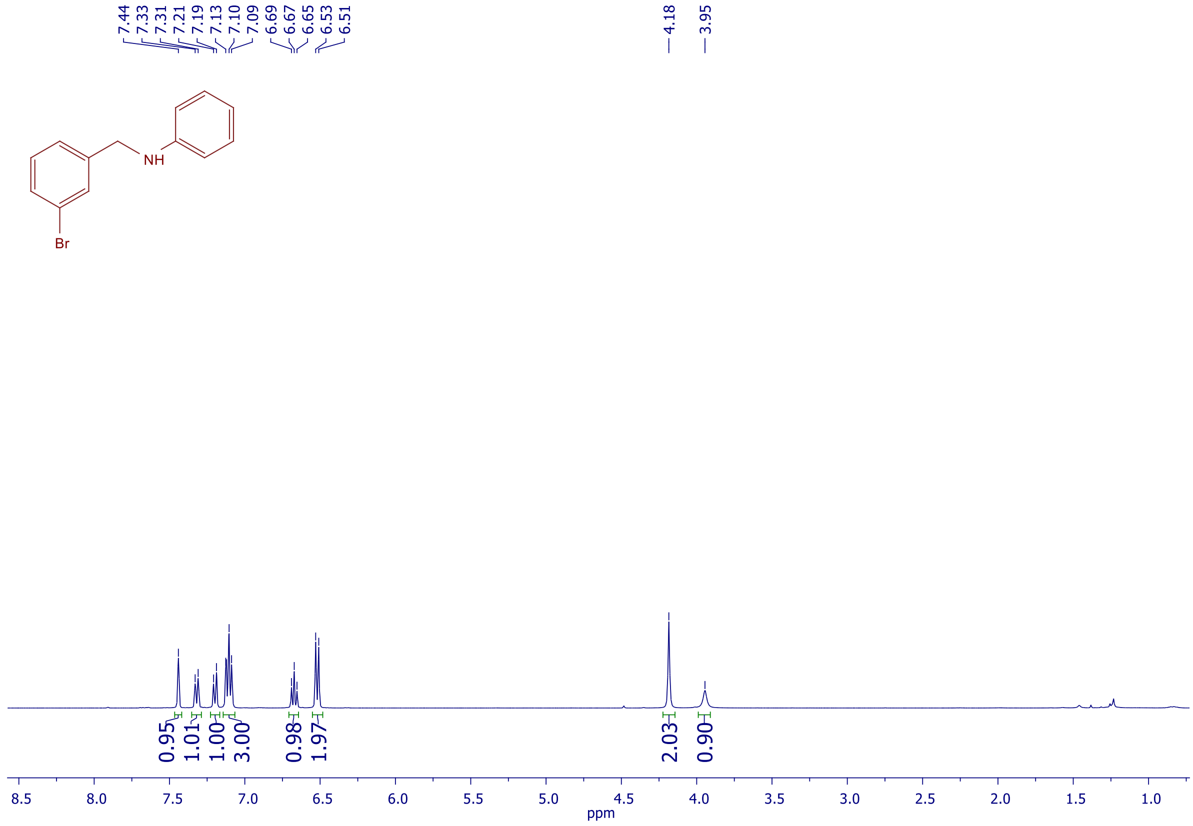
^{13}C{^{1}H} NMR of N-(4-chlorobenzyl)aniline (Compound-**3da**)



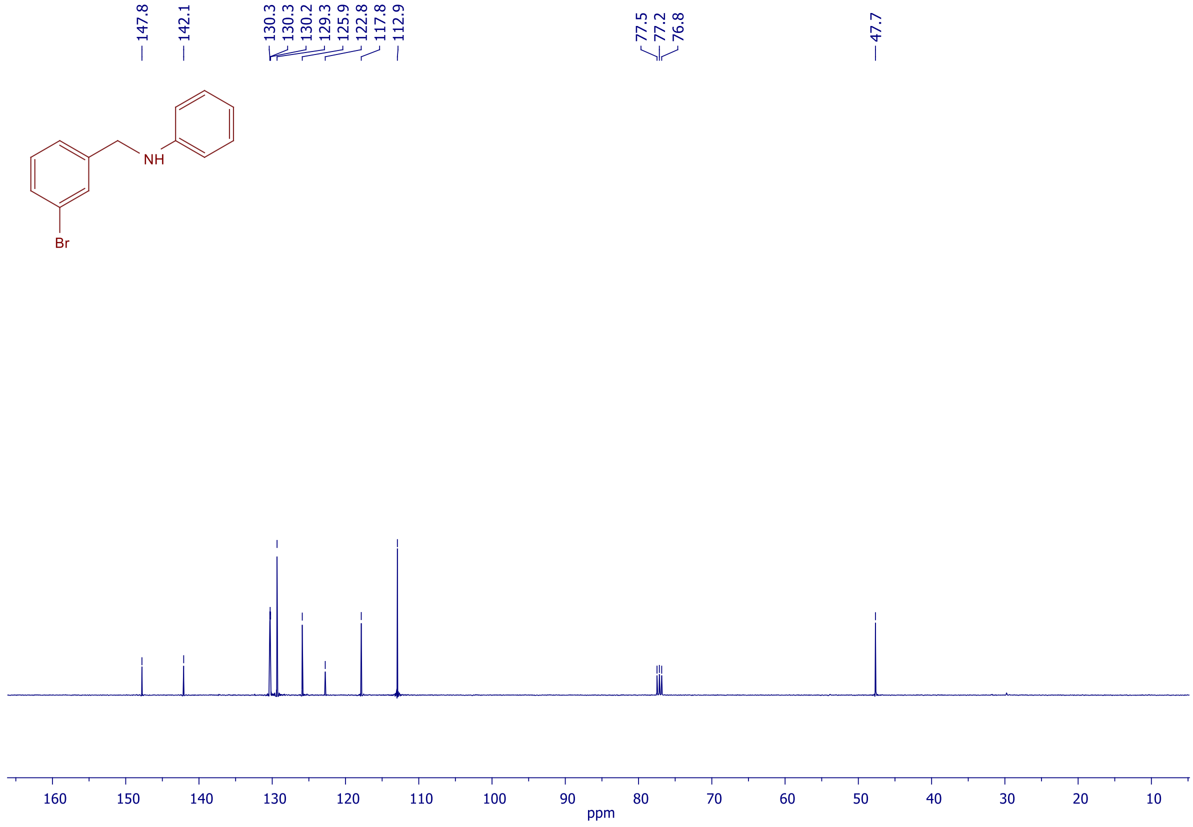
^{1}H NMR of *N*-(4-fluorobenzyl)aniline (Compound-**3ea**)



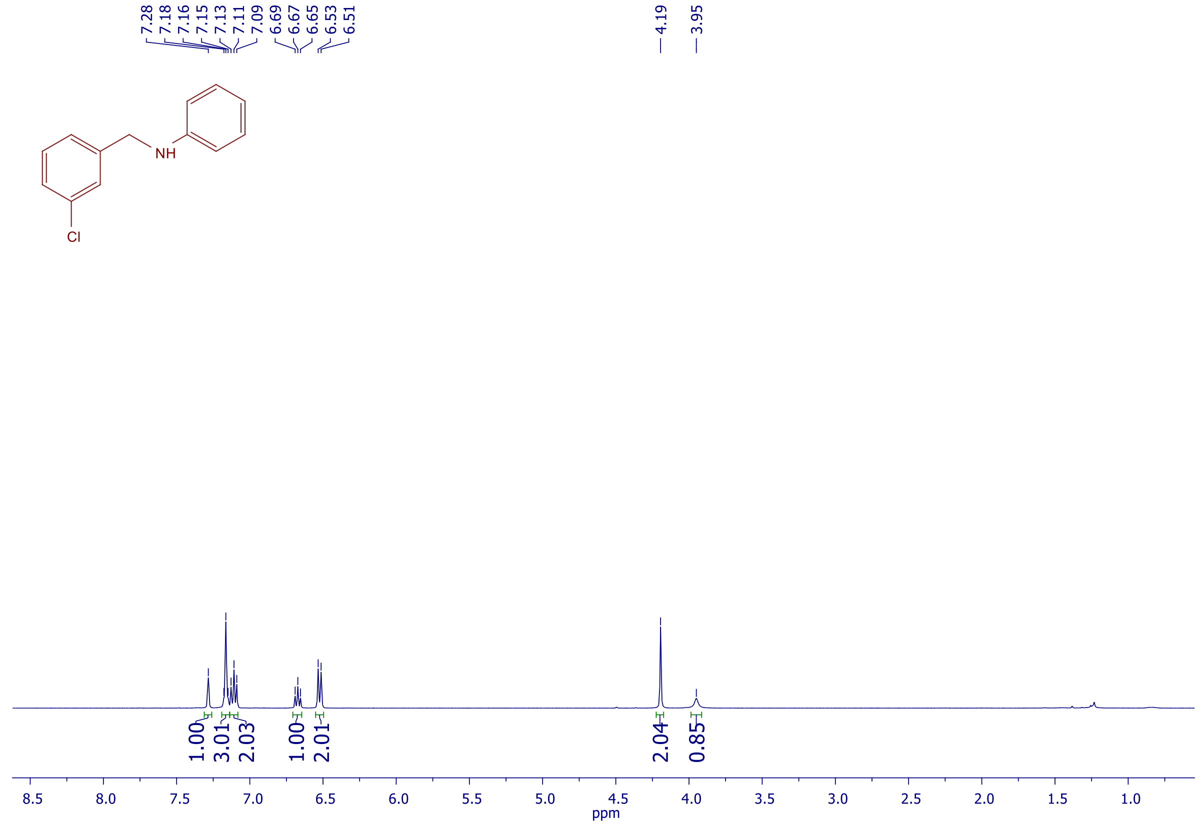
^{13}C{^{1}H} NMR of *N*-(4-fluorobenzyl)aniline (Compound-**3ea**)



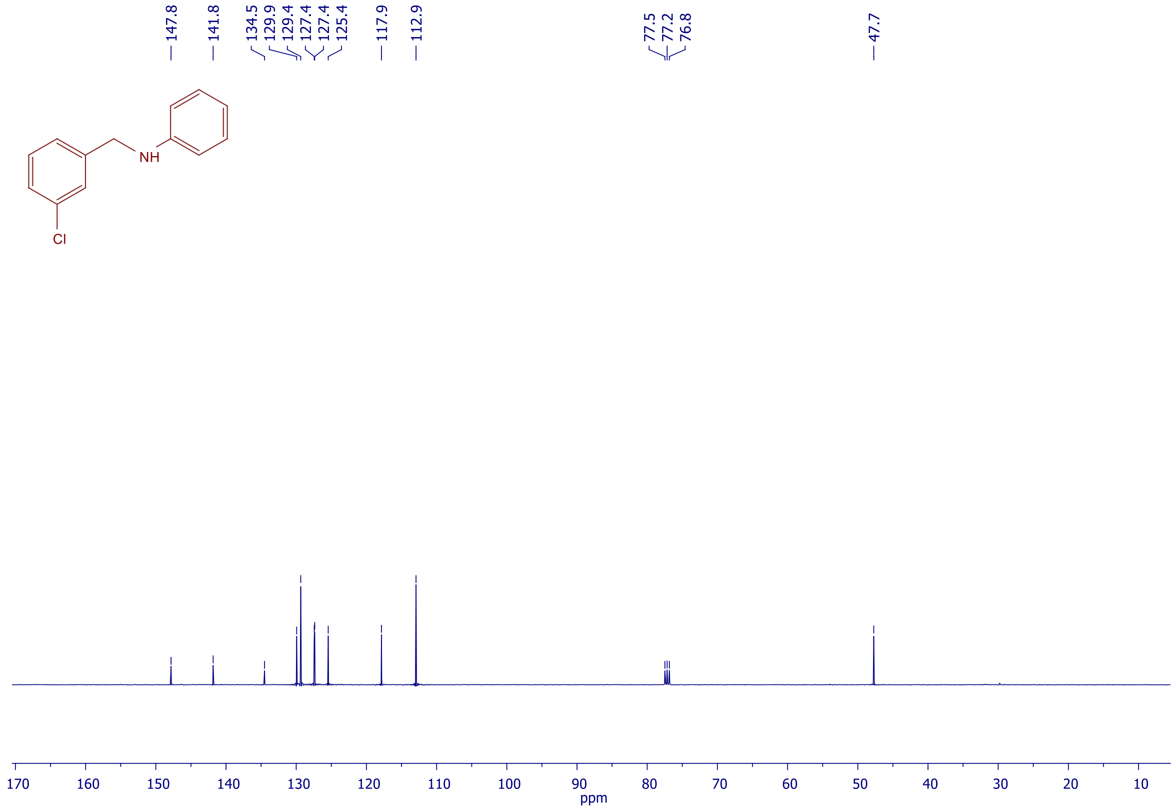
^{1}*H NMR of N-(3-bromobenzyl)aniline (Compound-**3fa**)*



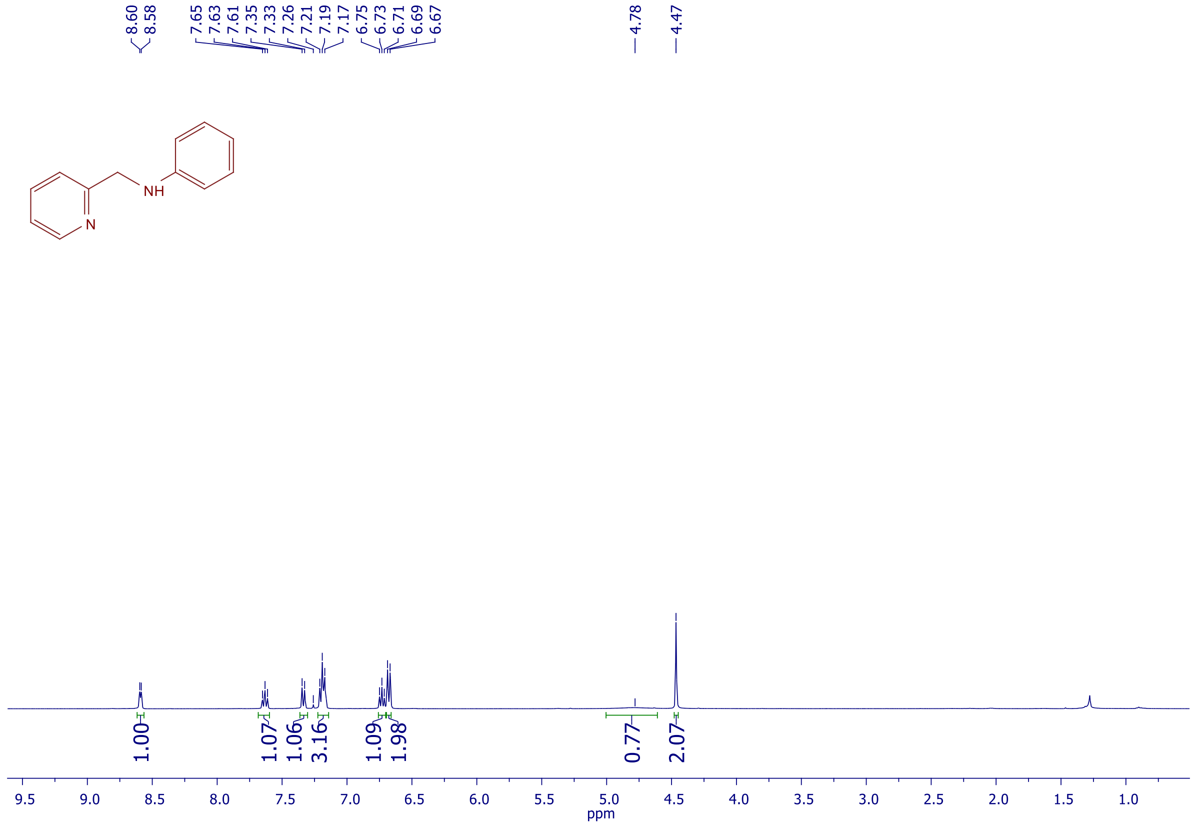
^{13}*C{^{1}H} NMR of N-(3-bromobenzyl)aniline (Compound-**3fa**)*



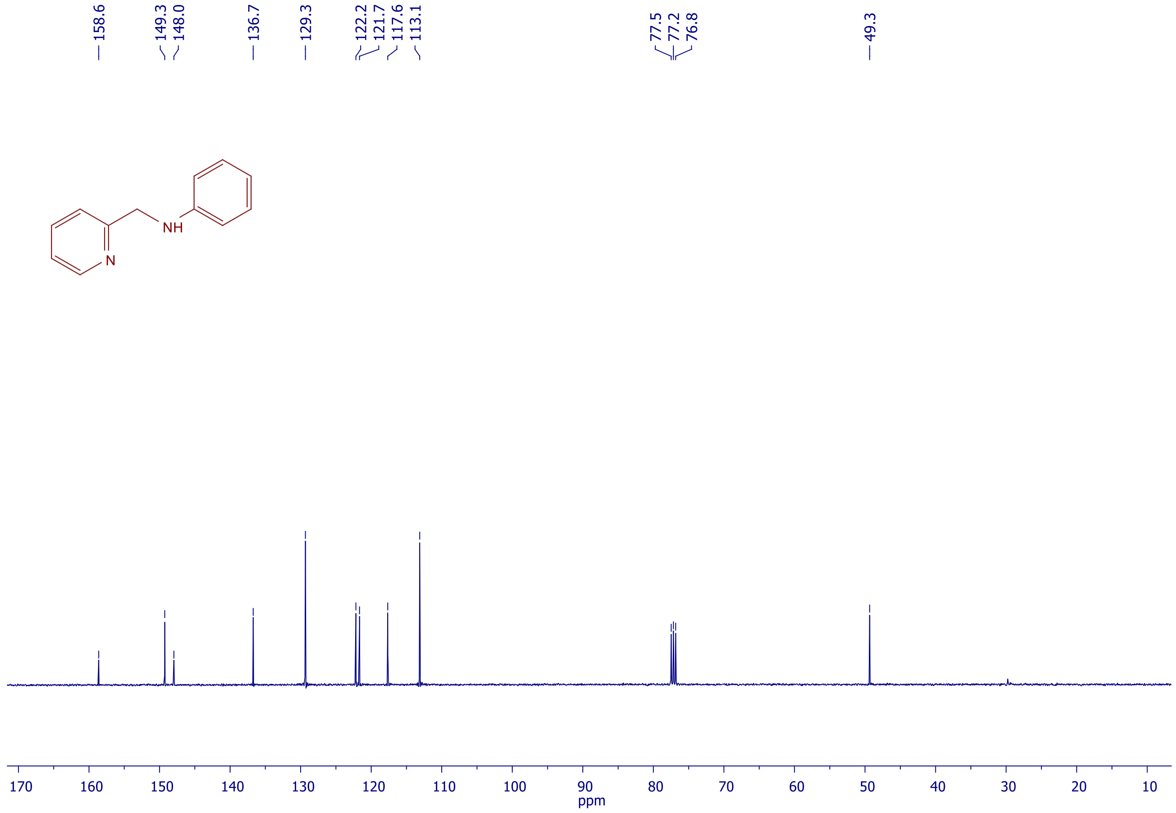
*^{1}H NMR of N-(3-chlorobenzyl)aniline (Compound-**3ga**)*



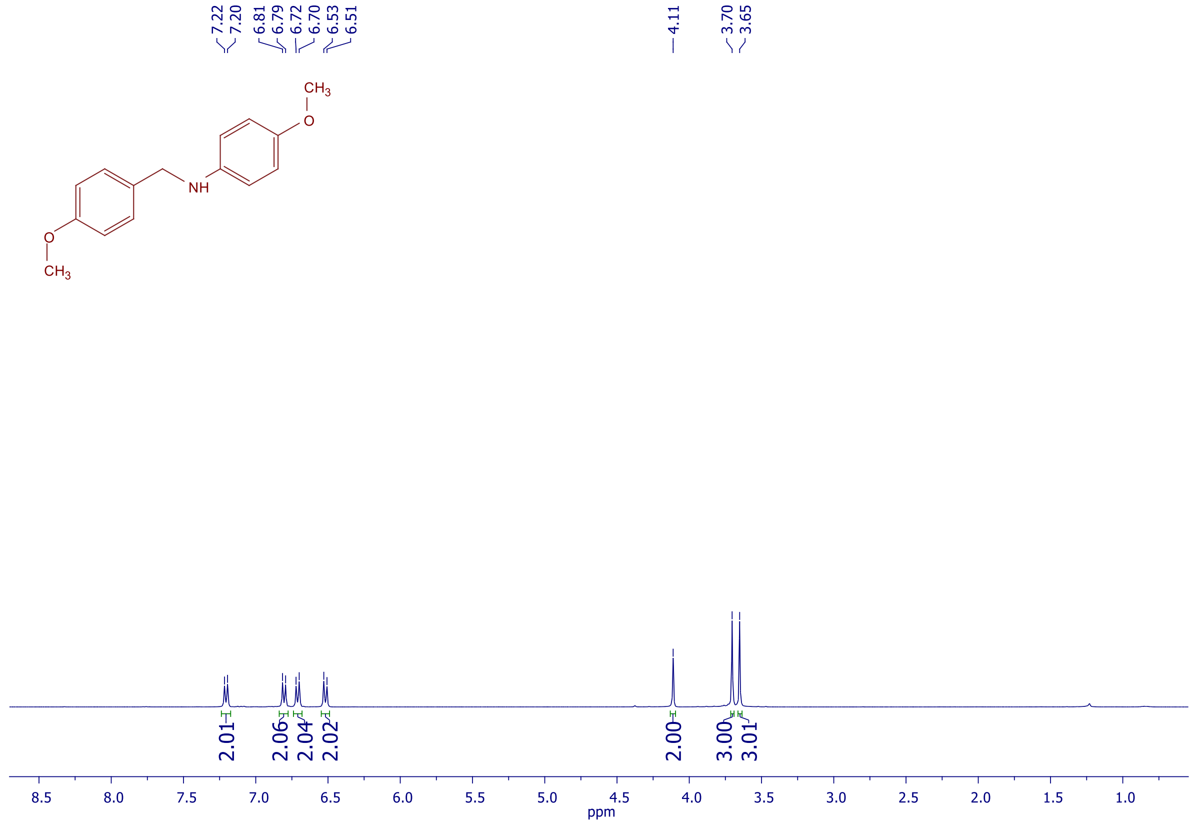
*^{13}C{^{1}H} NMR of N-(3-chlorobenzyl)aniline (Compound-**3ga**)*



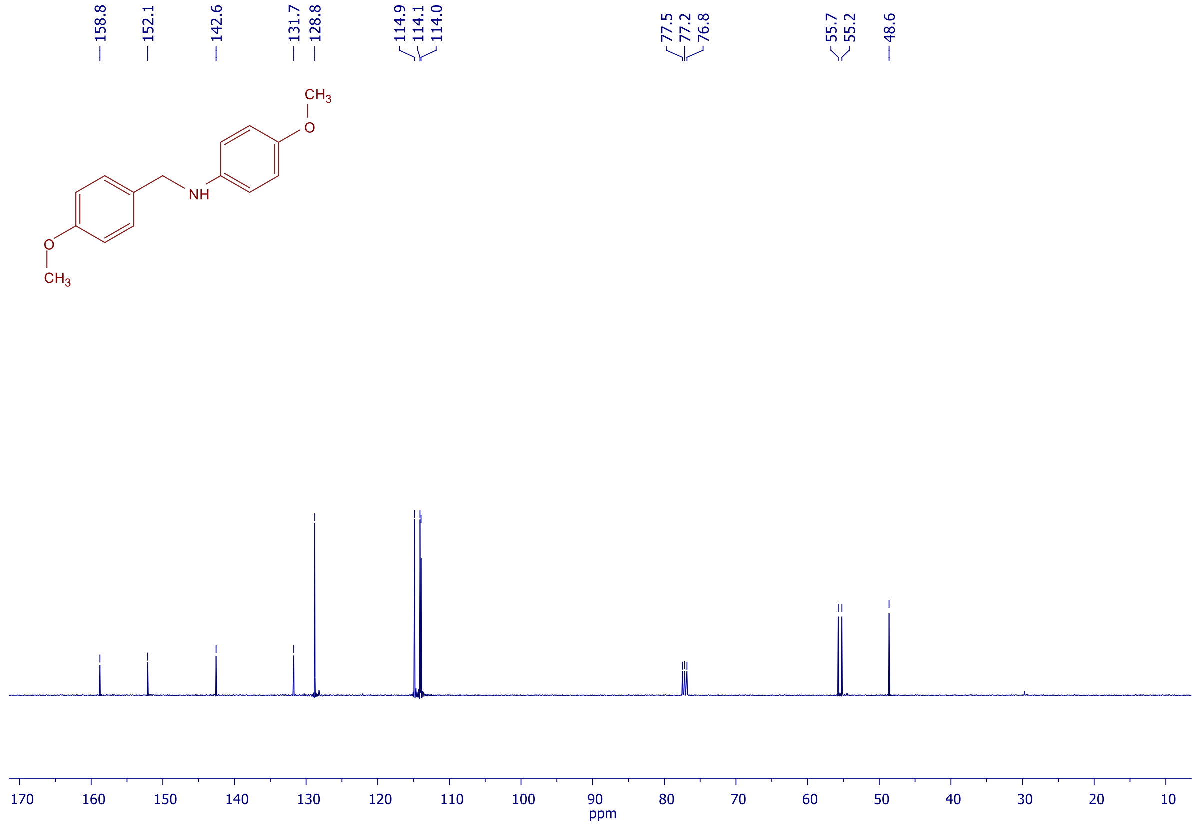
*^{1}H NMR of N-(pyridin-2-ylmethyl)aniline (Compound-**3ha**)*



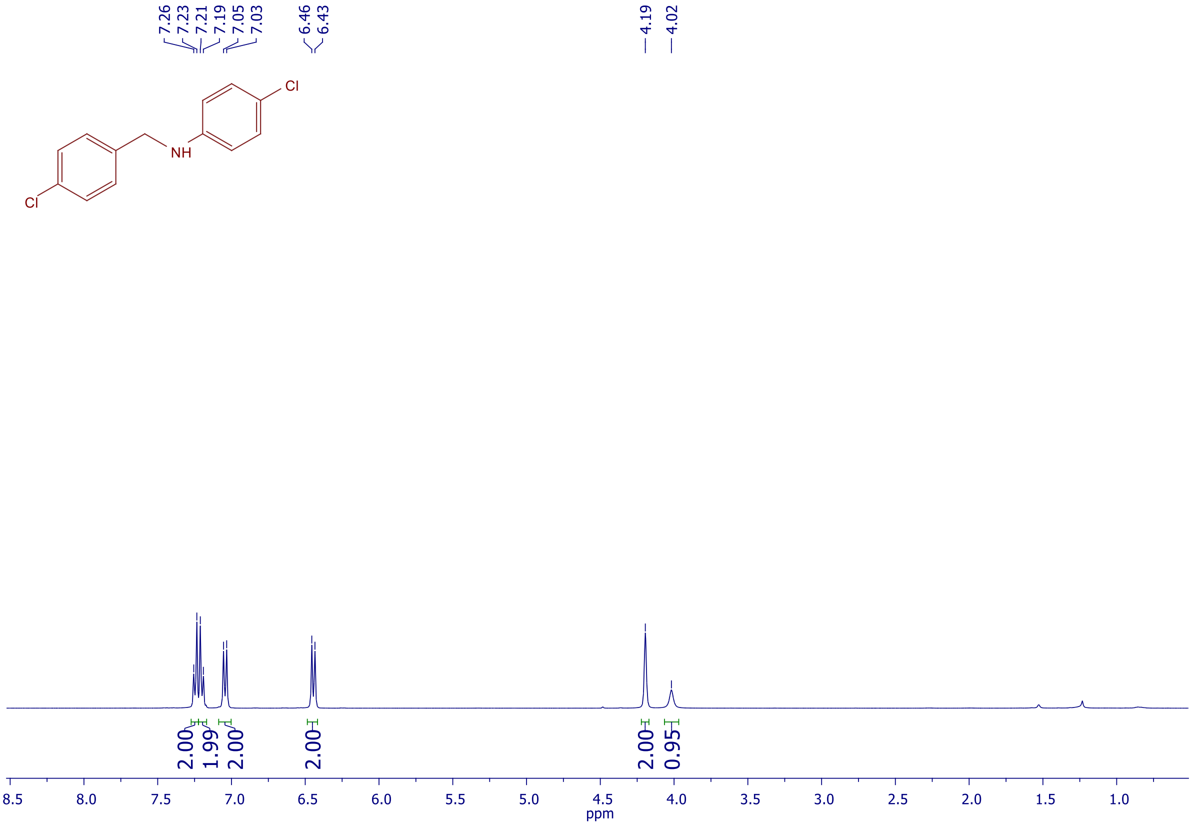
*^{13}C{^{1}H} NMR of N-(pyridin-2-ylmethyl)aniline (Compound-**3ha**)*



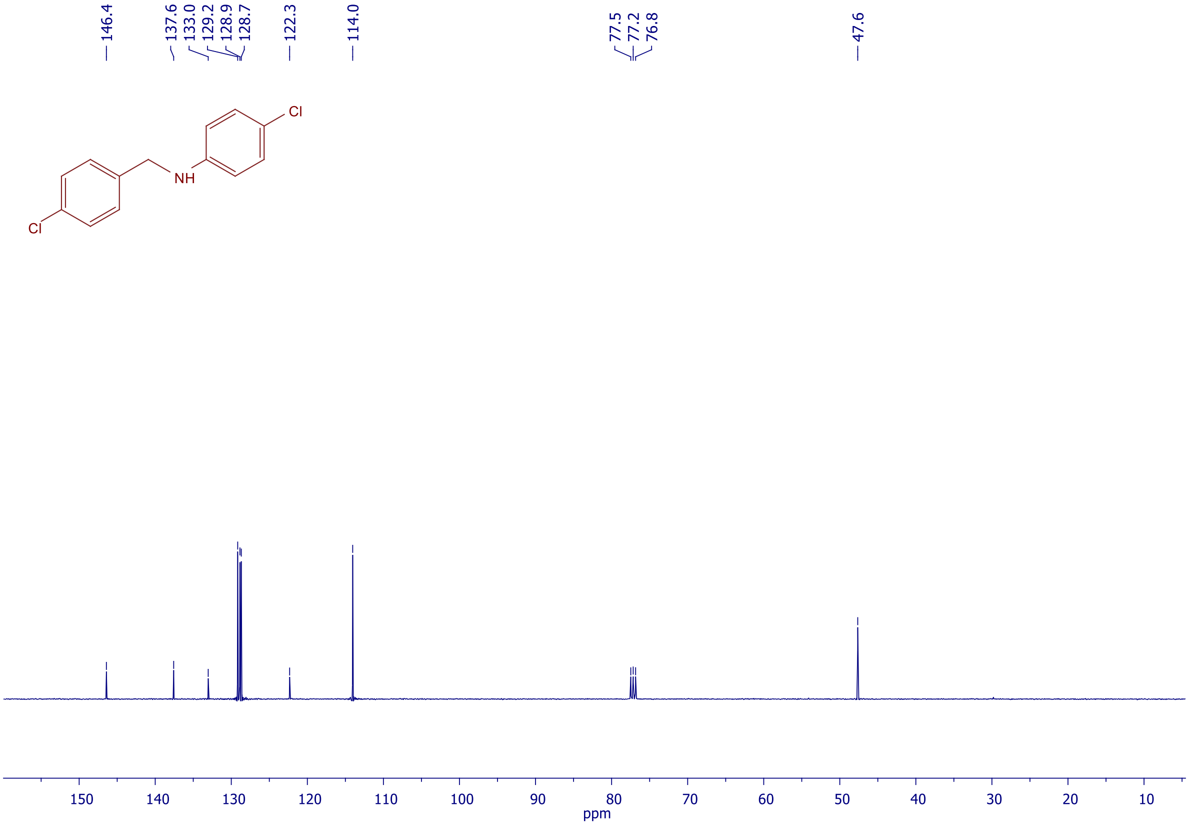
*^{1}H NMR of 4-methoxy-N-(4-methoxybenzyl)aniline (Compound-**3ib**)*



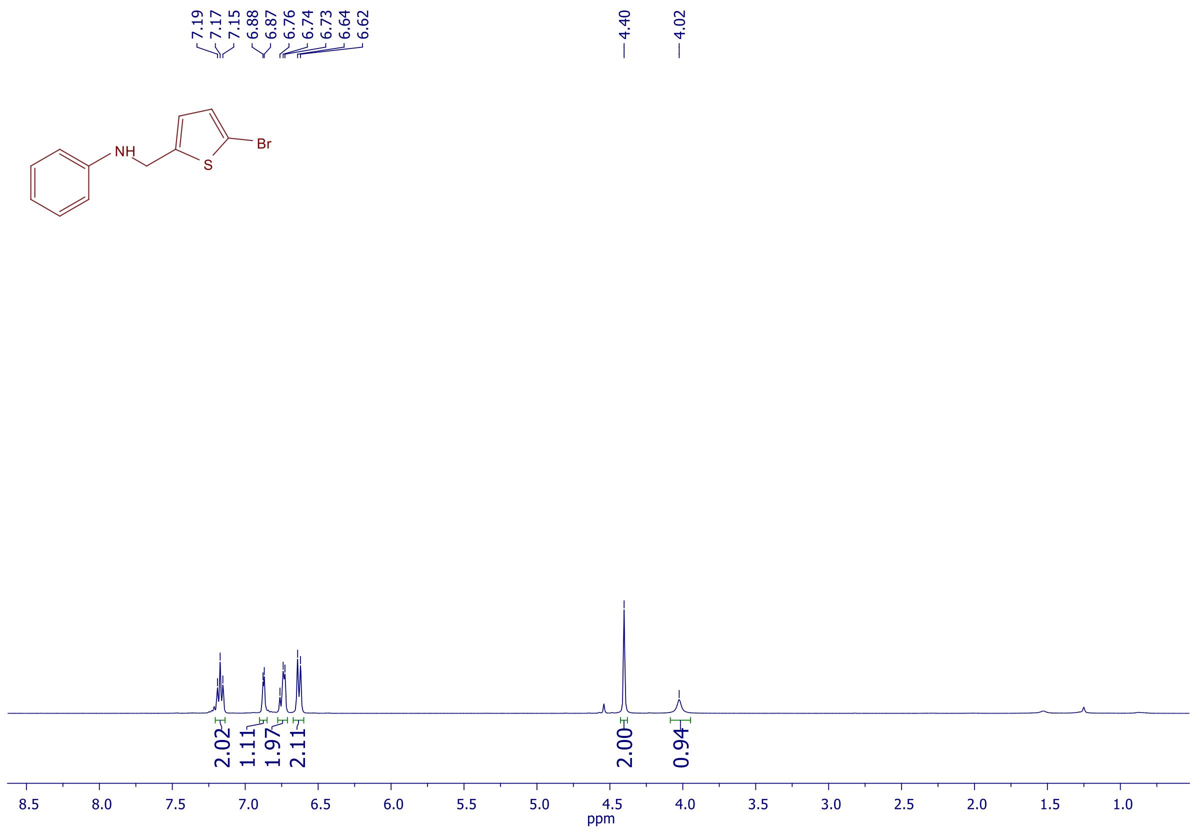
*^{13}C{^{1}H} NMR of 4-methoxy-N-(4-methoxybenzyl)aniline (Compound-**3ib**)*



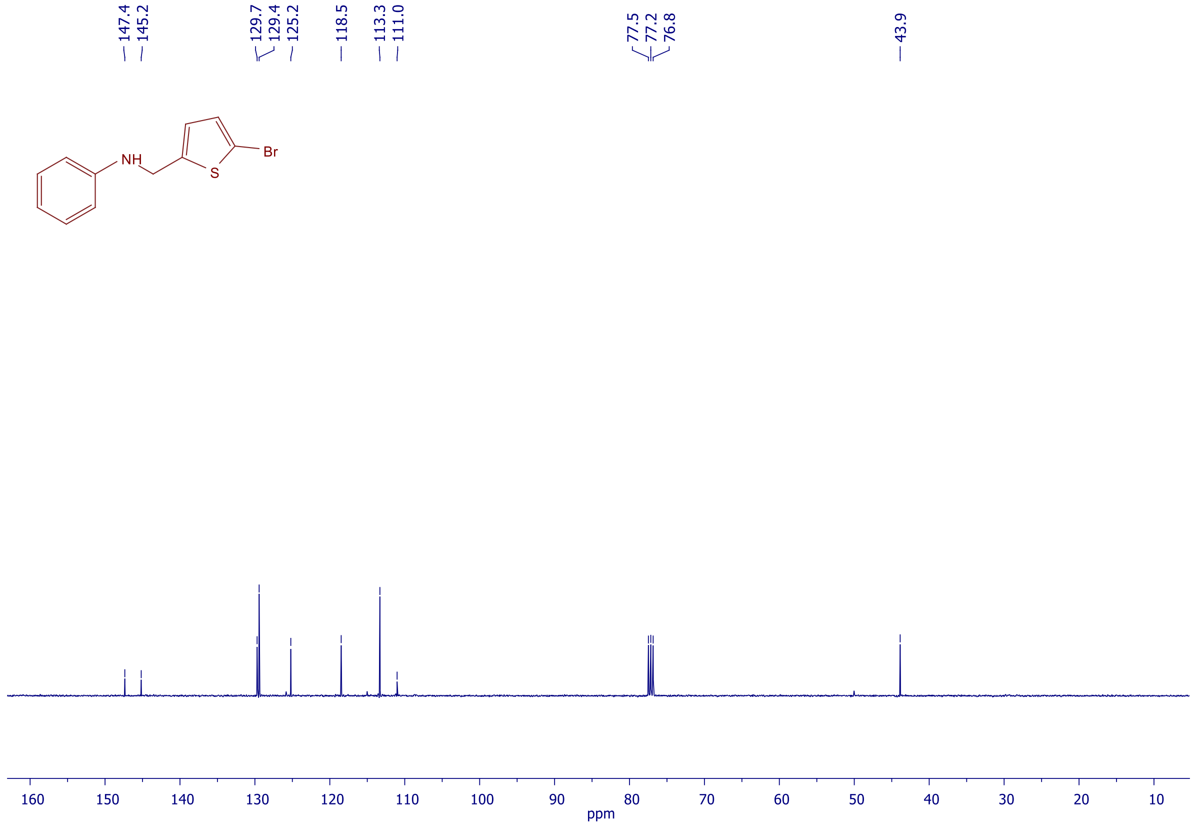
^{1}H NMR of 4-chloro-N-(4-chlorobenzyl)aniline (Compound-**3jc**)



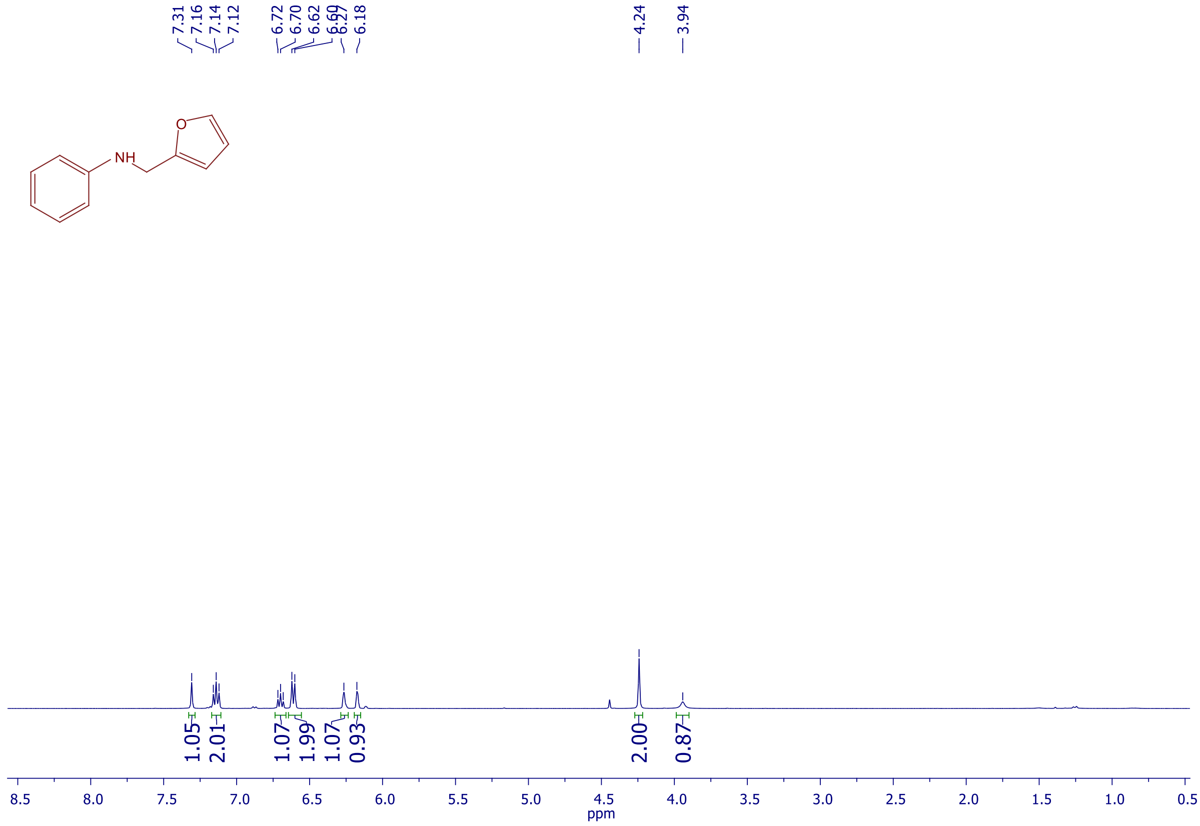
^{13}C{^{1}H} NMR of 4-chloro-N-(4-chlorobenzyl)aniline (Compound-**3jc**)



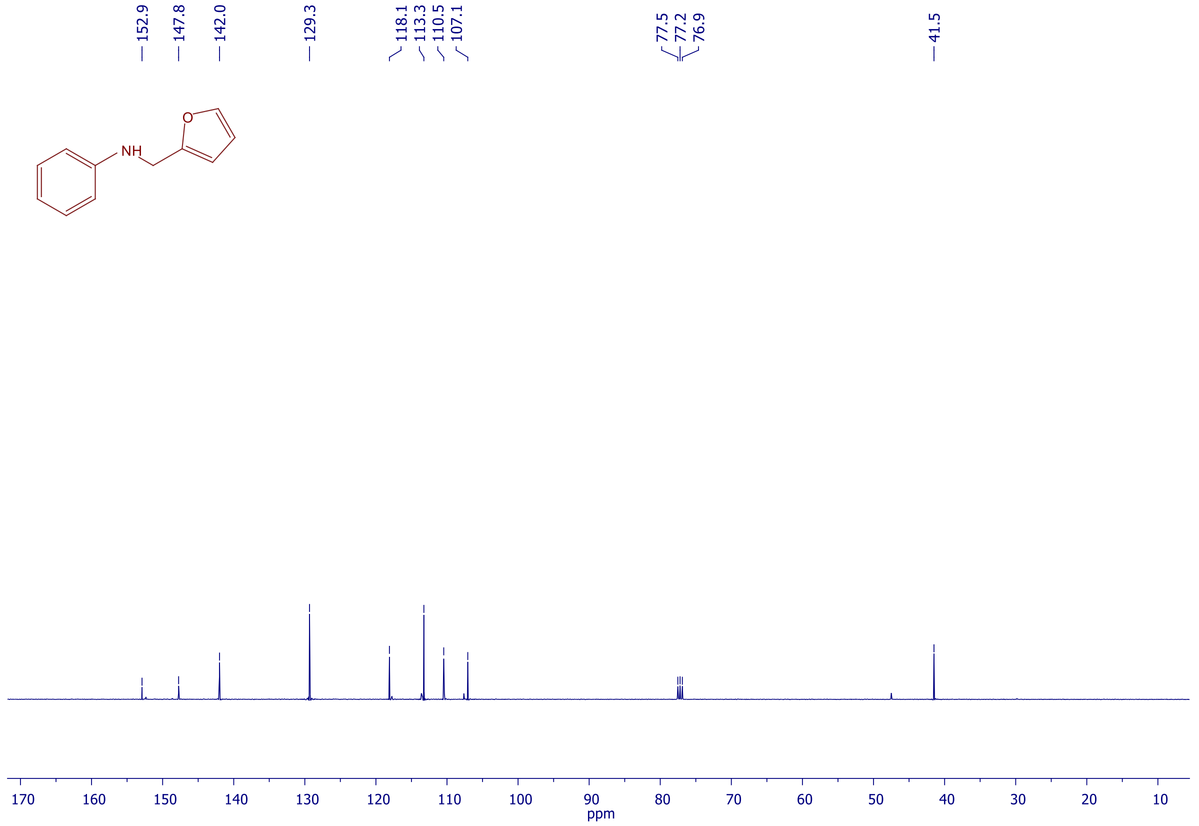
^{1}*H NMR of N-((5-bromothiophen-2-yl)methyl)aniline (Compound-**3ka**)*



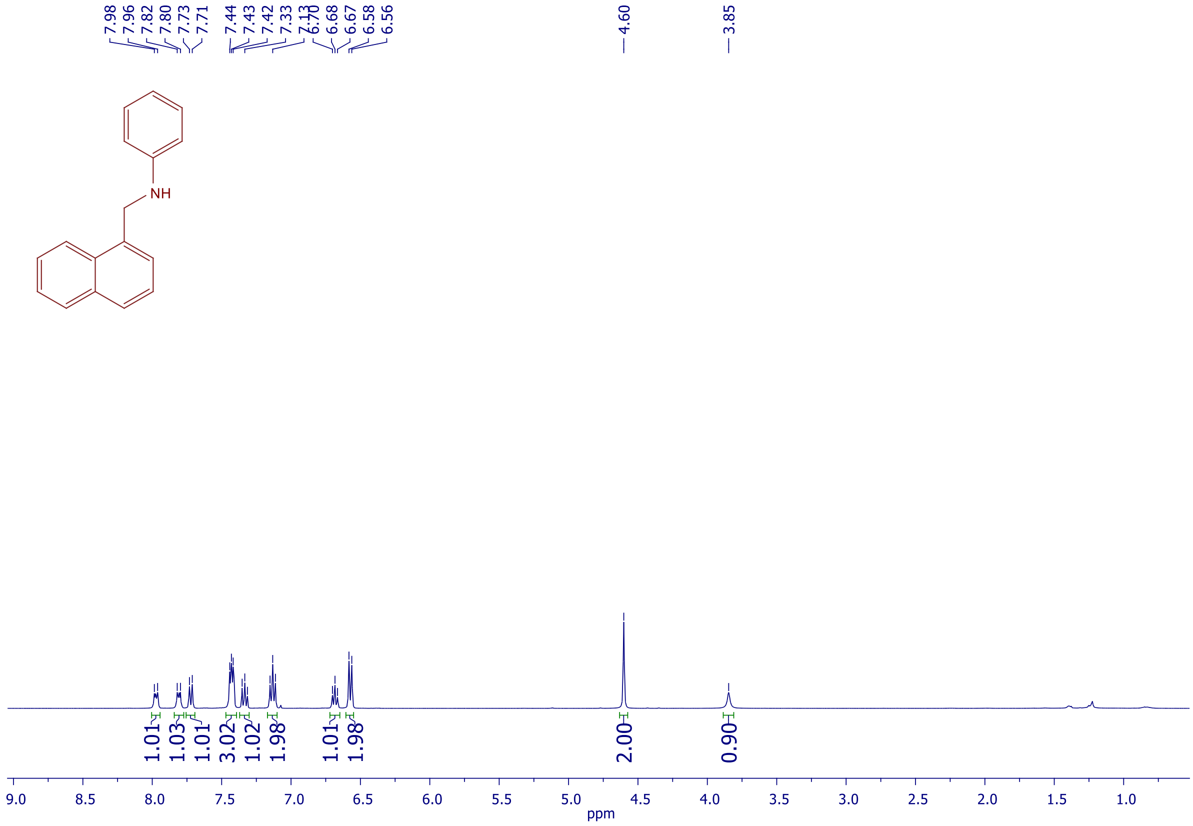
^{13}*C{^{1}H} NMR of N-((5-bromothiophen-2-yl)methyl)aniline (Compound-**3ka**)*



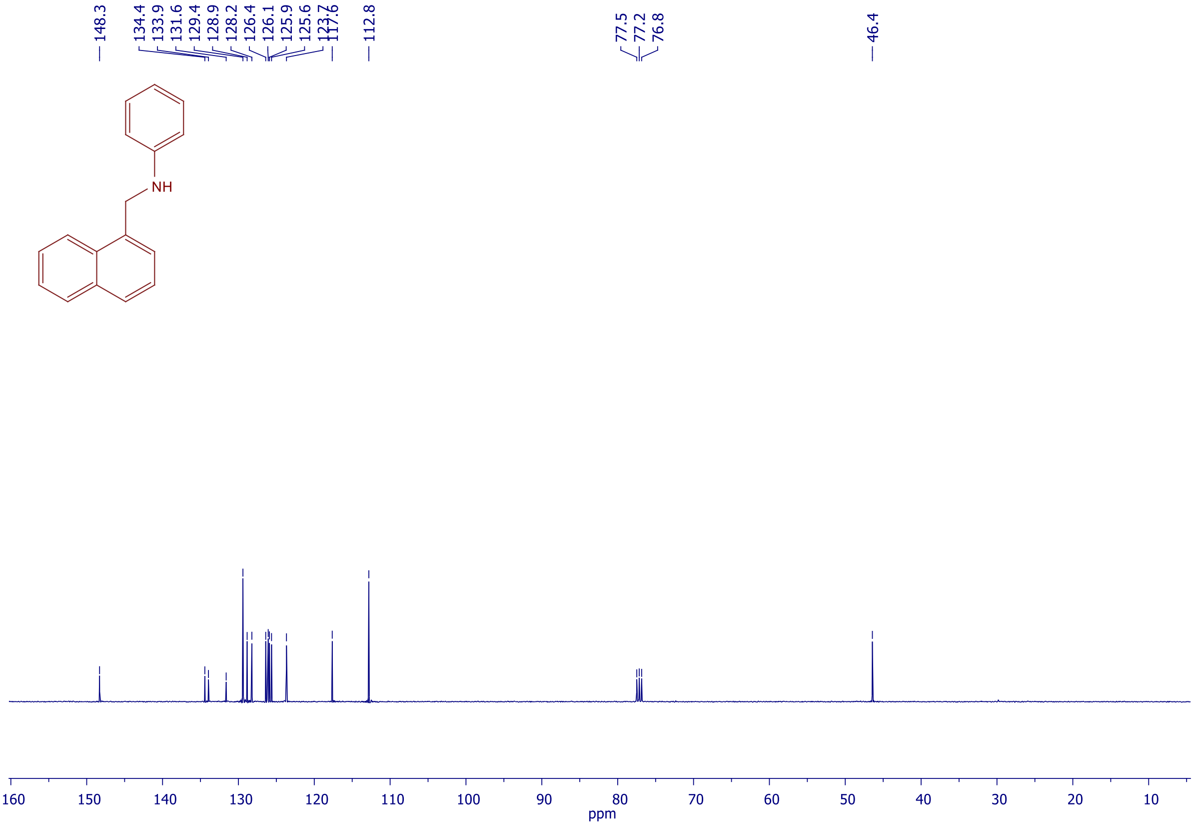
*^{1}H NMR of N-(furan-2-ylmethyl)aniline (Compound-**3la**)*



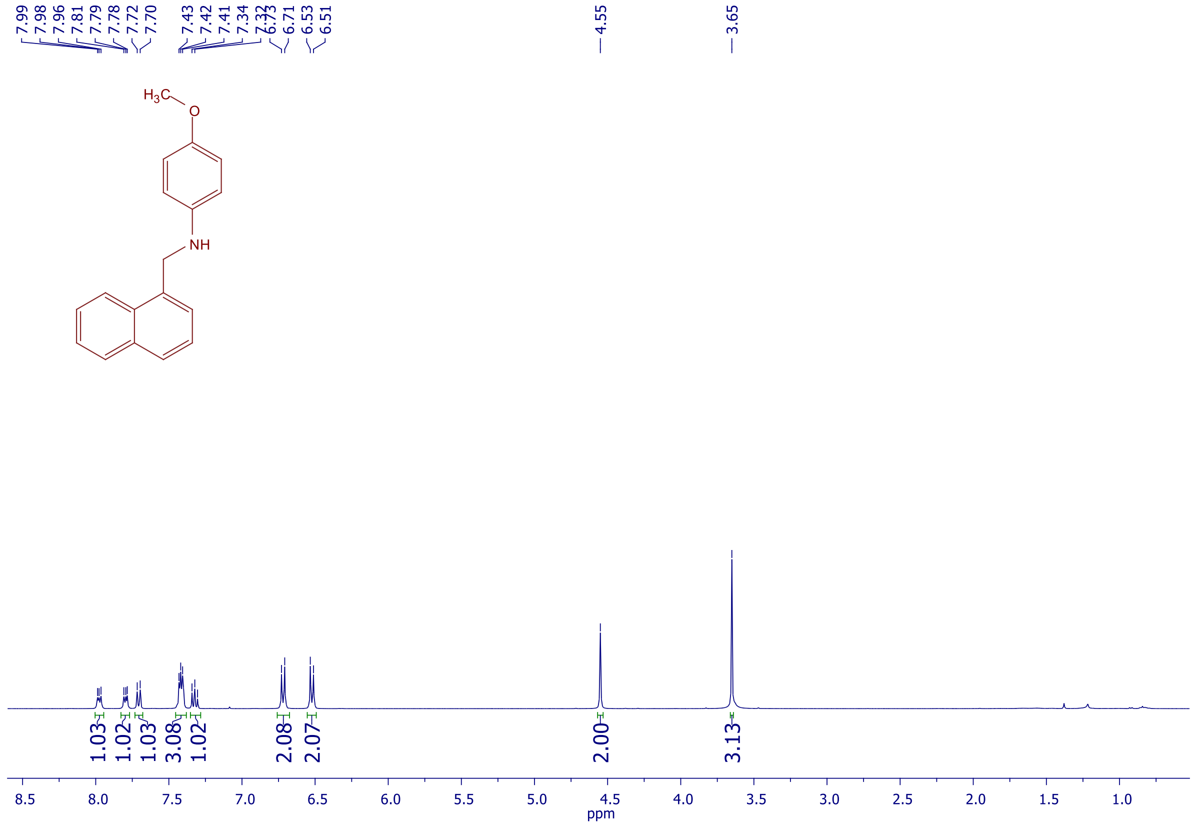
*^{13}C{^{1}H} NMR of N-(furan-2-ylmethyl)aniline (Compound-**3la**)*



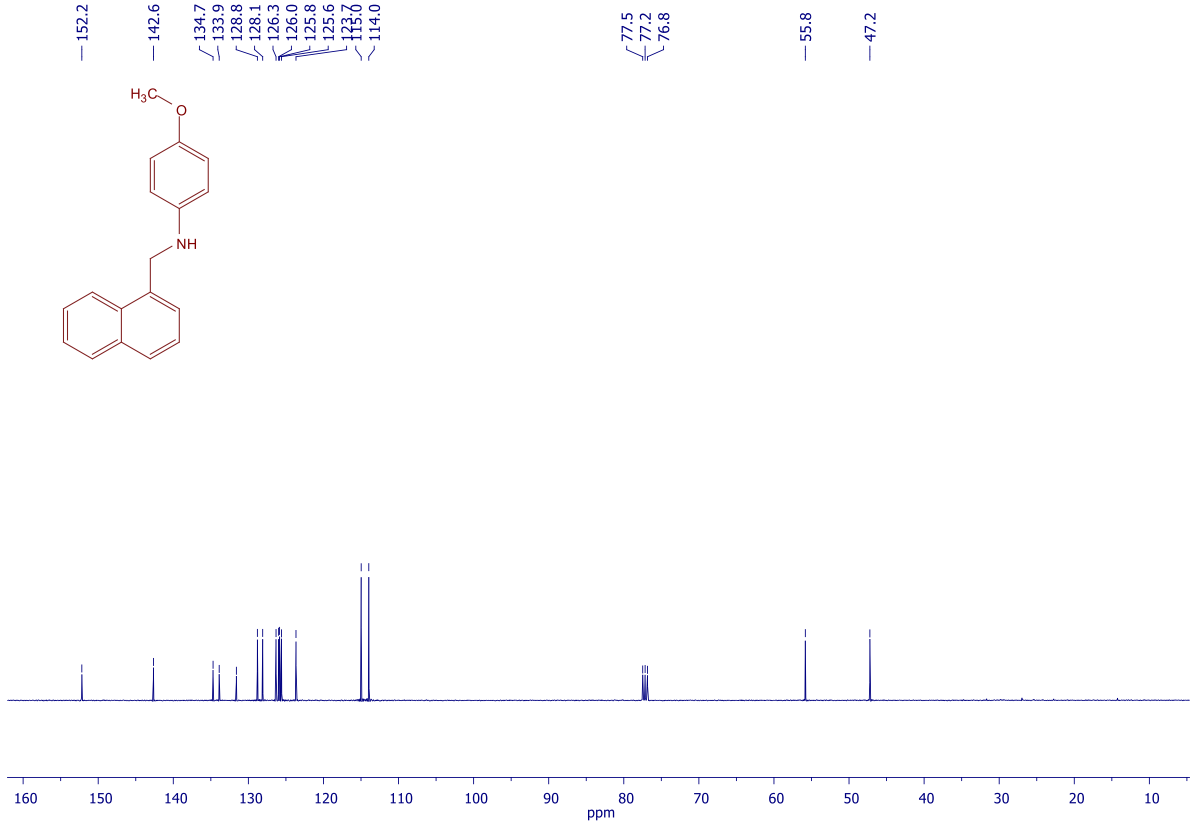
^{1}H NMR of N-(naphthalen-1-ylmethyl)aniline (Compound-**3ma**)



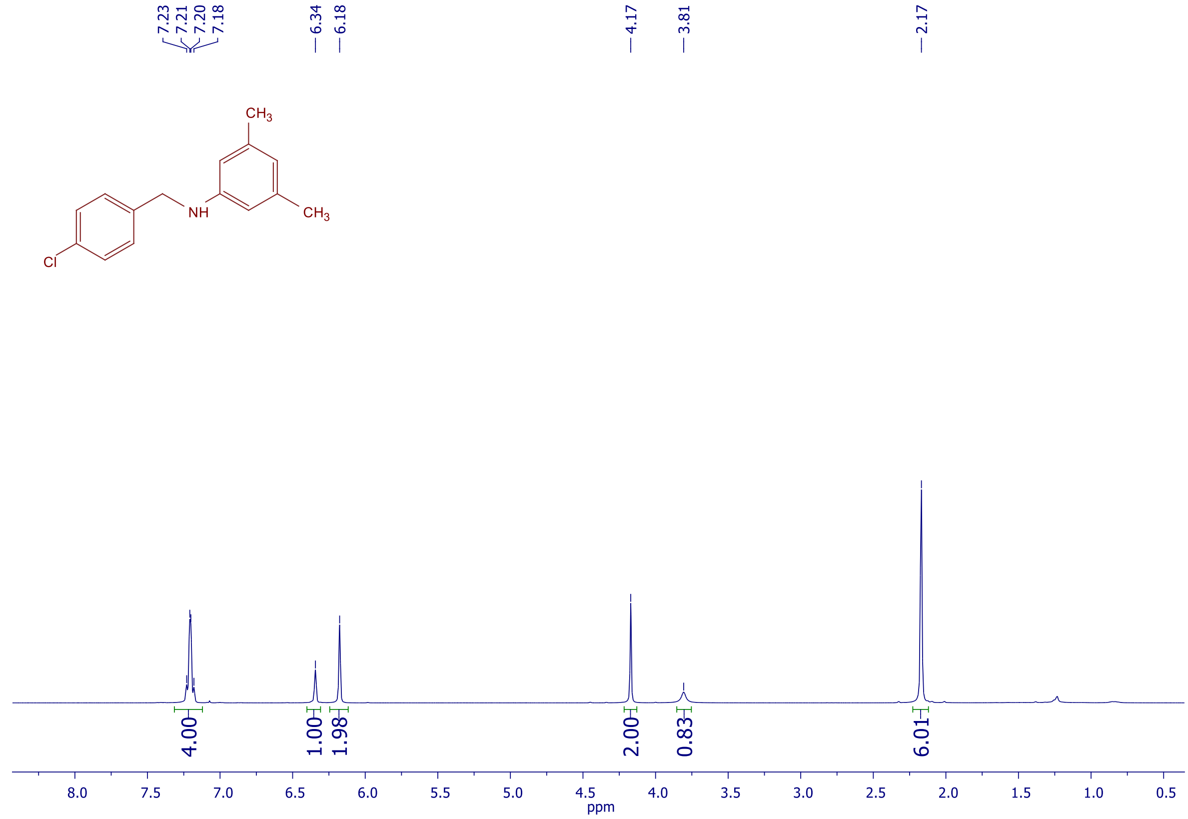
^{13}C{^{1}H} NMR of N-(naphthalen-1-ylmethyl)aniline (Compound-**3ma**)



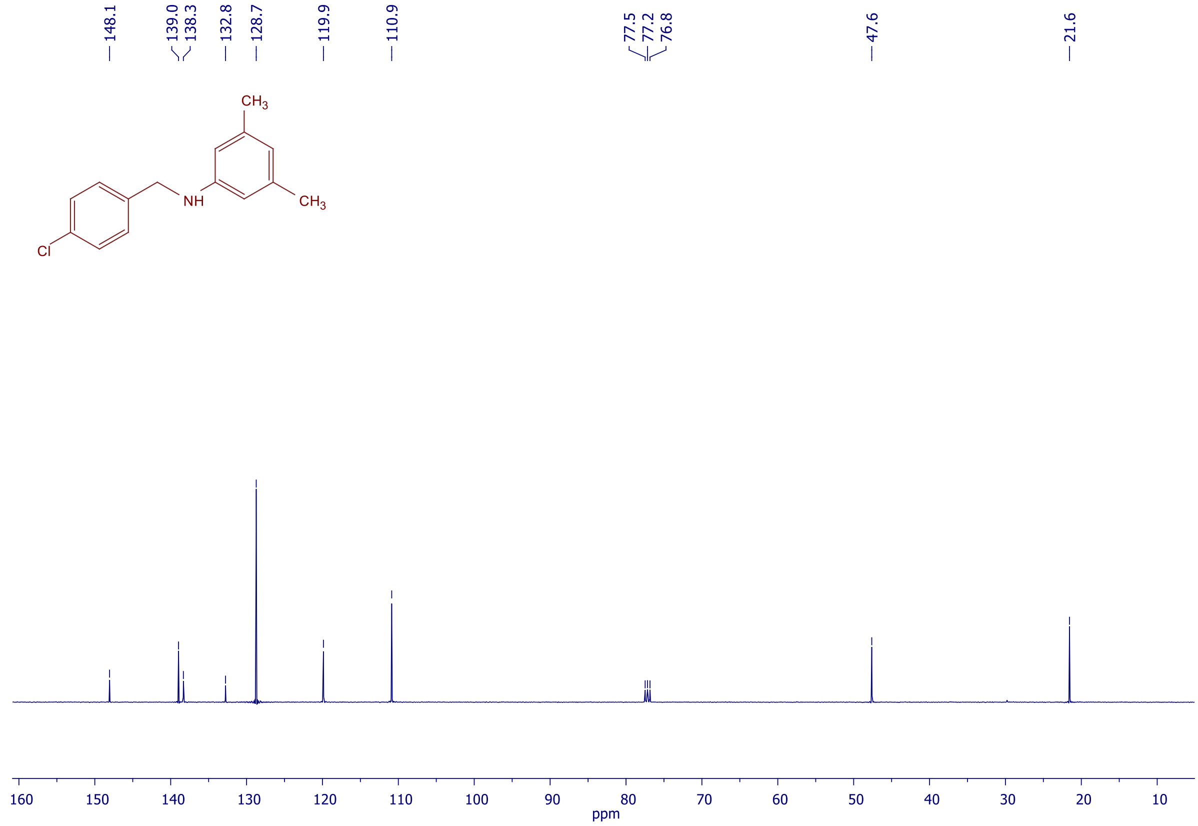
^{1}H NMR of 4-methoxy-N-(naphthalen-1-ylmethyl)aniline *(Compound-**3mb**)*



^{13}C{^{1}H} NMR of 4-methoxy-N-(naphthalen-1-ylmethyl)aniline *(Compound-**3mb**)*

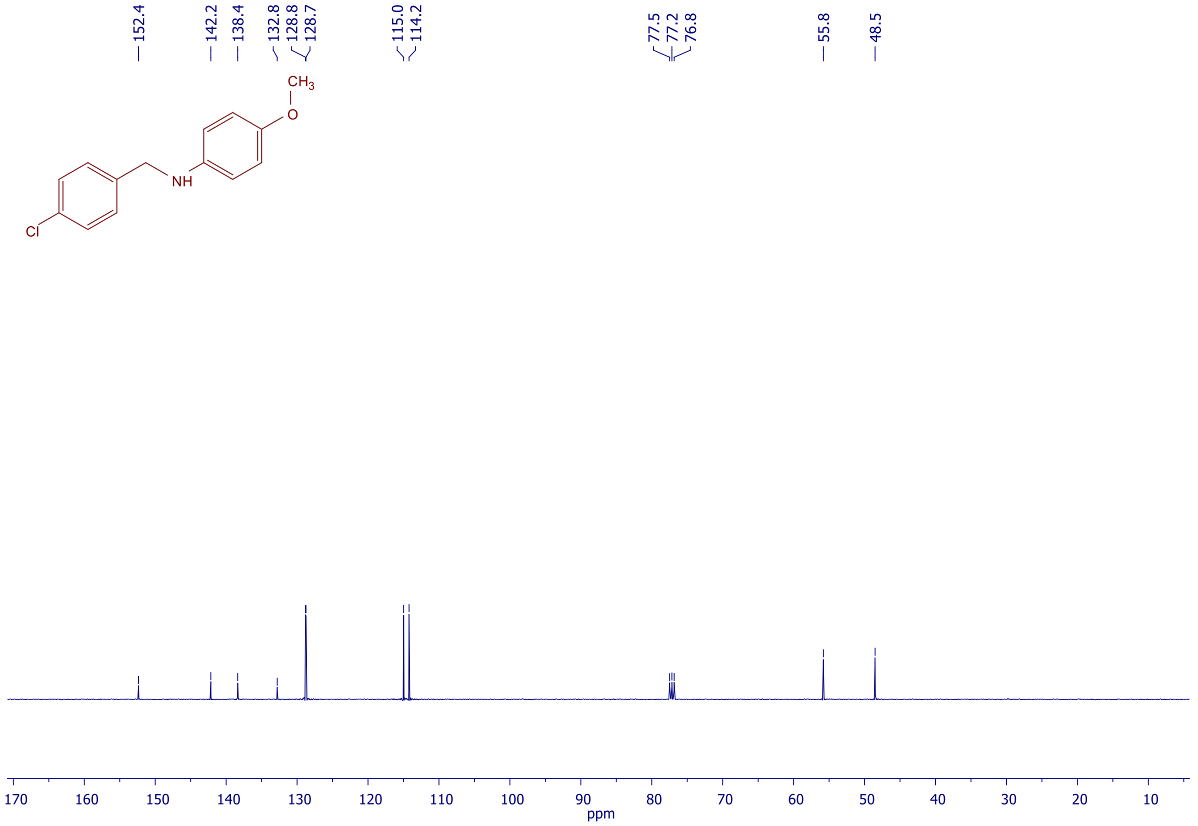


*^{1}H NMR of N-(4-chlorobenzyl)-3,5-dimethylaniline (Compound-**3dd**)*

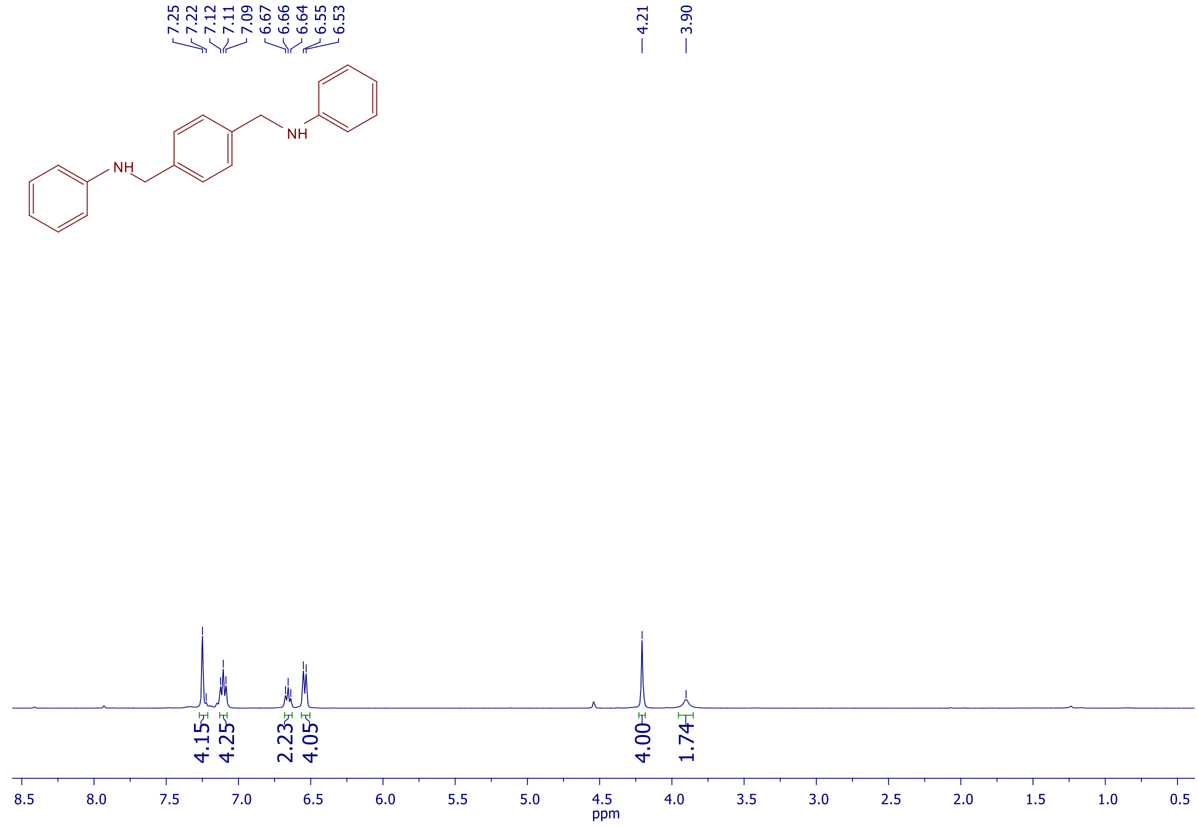


*^{13}C{^{1}H} NMR of N-(4-chlorobenzyl)-3,5-dimethylaniline (Compound-**3dd**)*

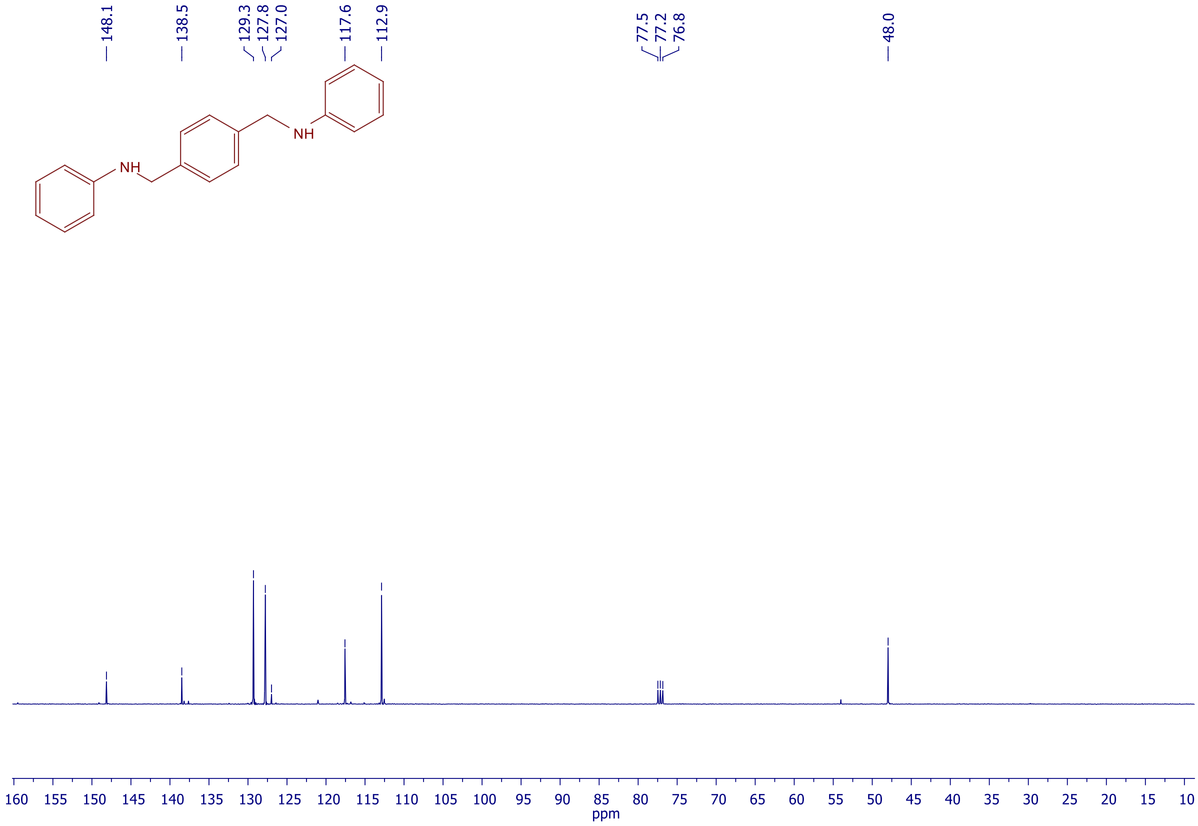
*^{1}H NMR of N-(4-chlorobenzyl)-4-methoxyaniline (Compound-**3db**)*



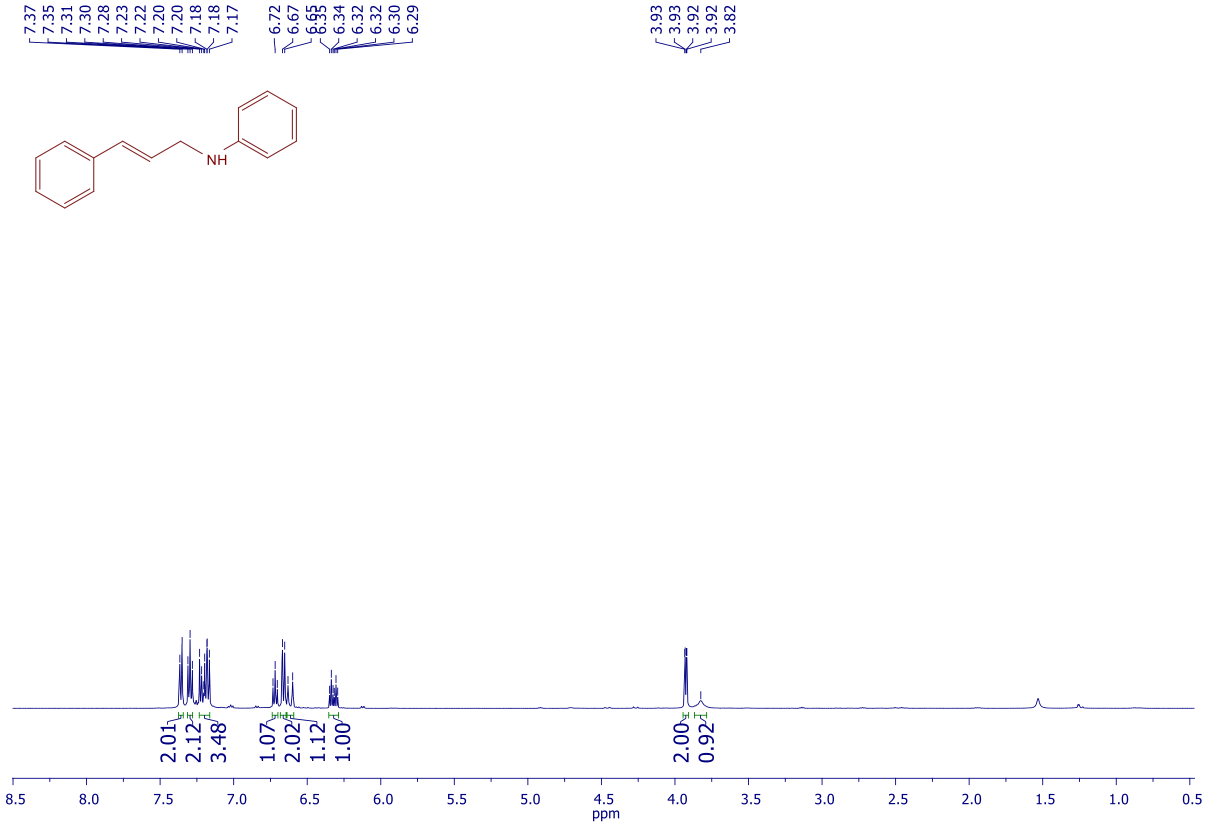
*^{13}C{^{1}H} NMR of N-(4-chlorobenzyl)-4-methoxyaniline (Compound-**3db**)*



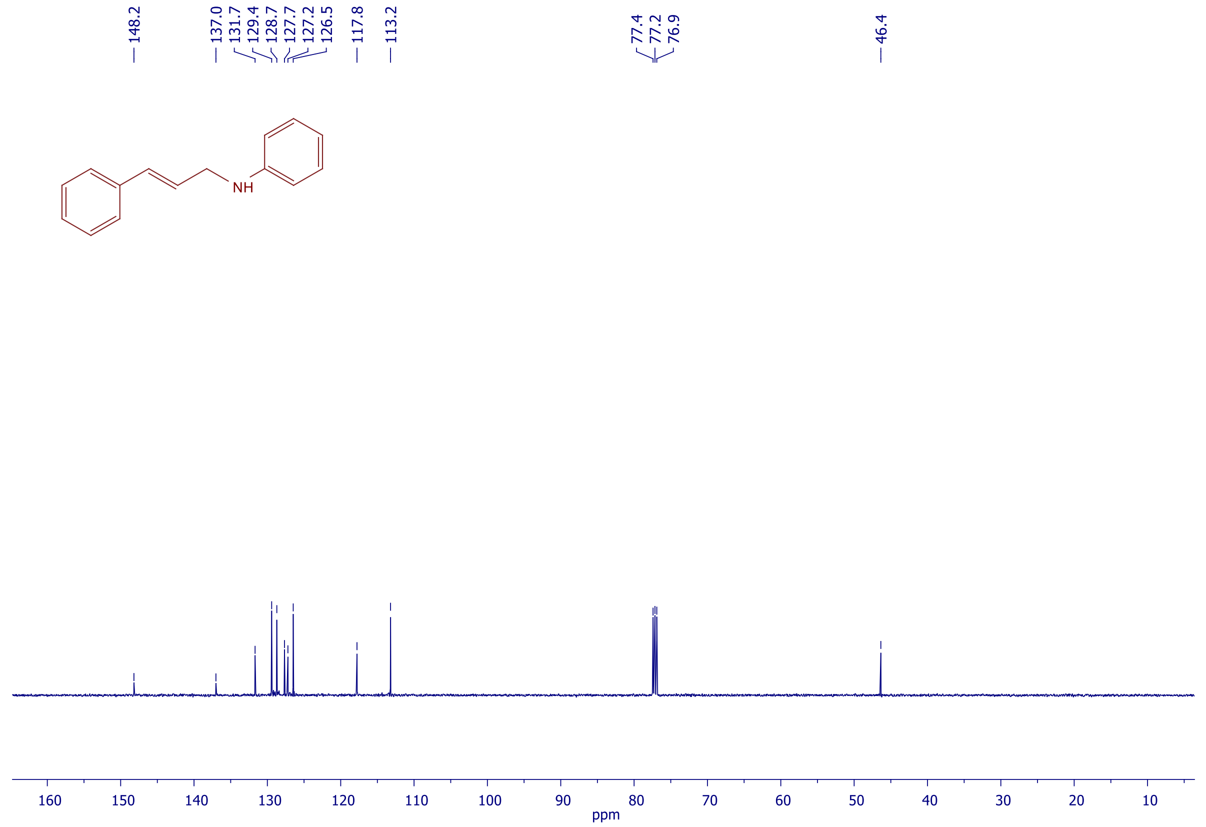
*^{1}H NMR of N,N'-(1,4-phenylenebis(methylene))dianiline (Compound-**3na**)*



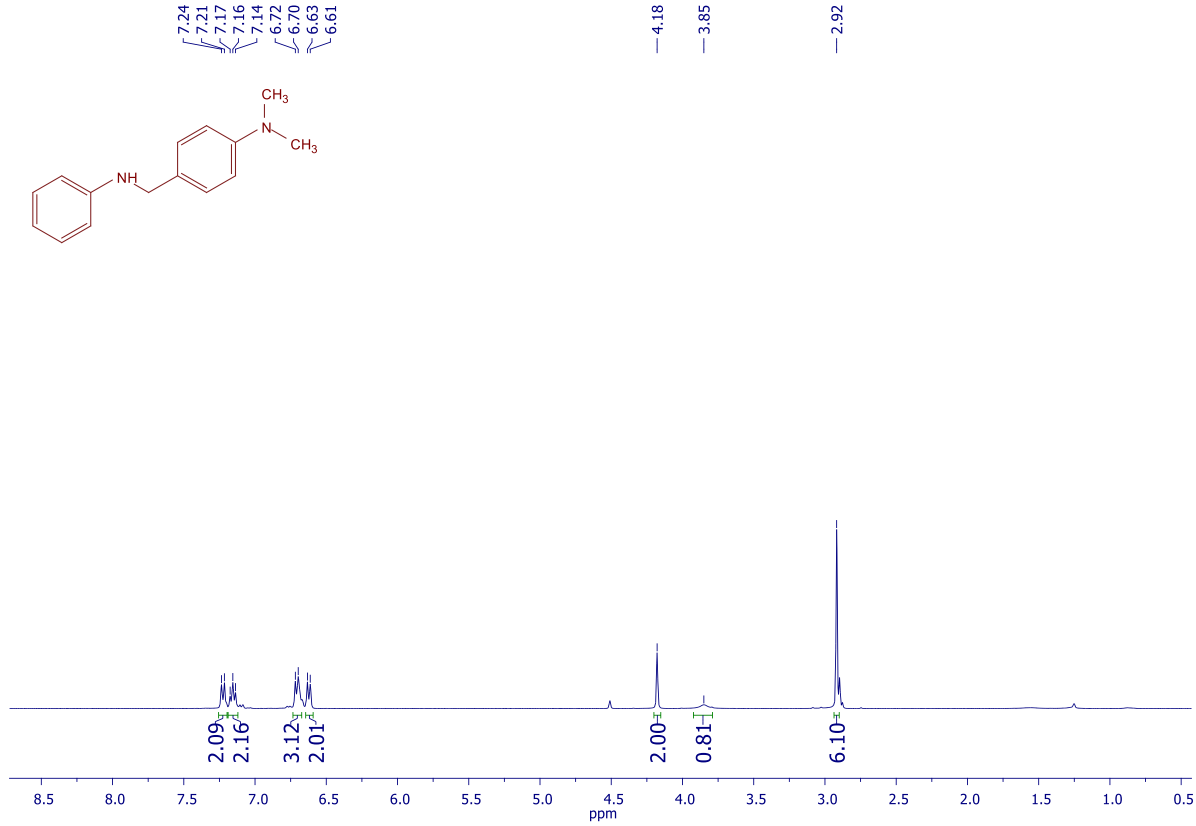
*^{13}C{^{1}H} NMR of N,N'-(1,4-phenylenebis(methylene))dianiline (Compound-**3na**)*



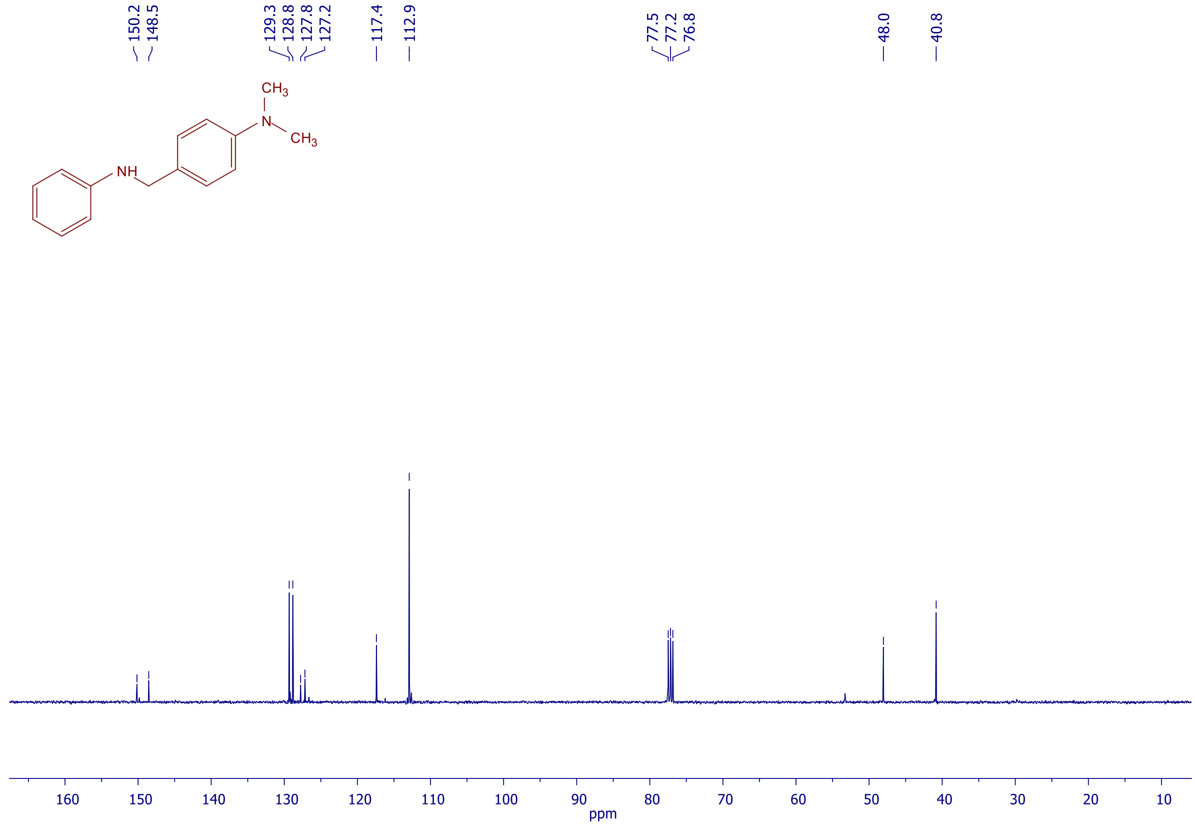
*^{1}H NMR of N-cinnamylaniline (Compound-**3oa**)*



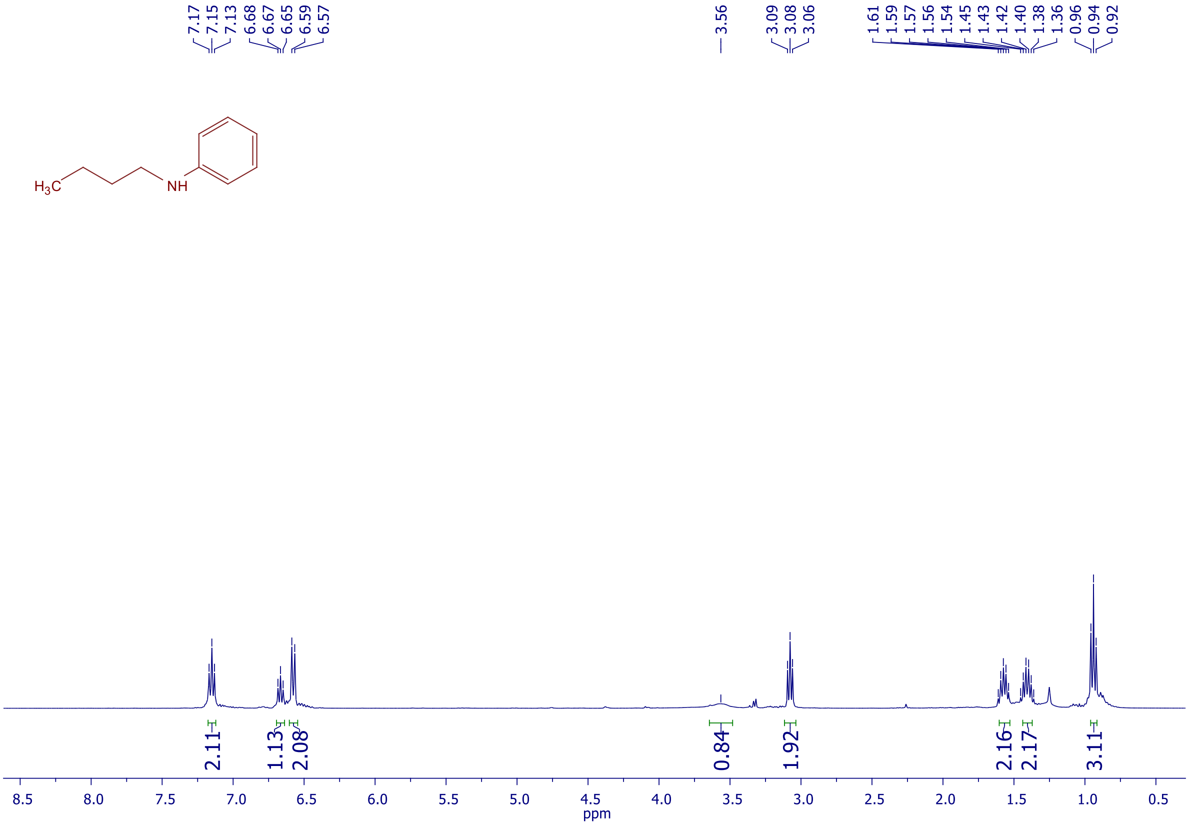
*^{13}C{^{1}H} NMR of N-cinnamylaniline (Compound-**3oa**)*



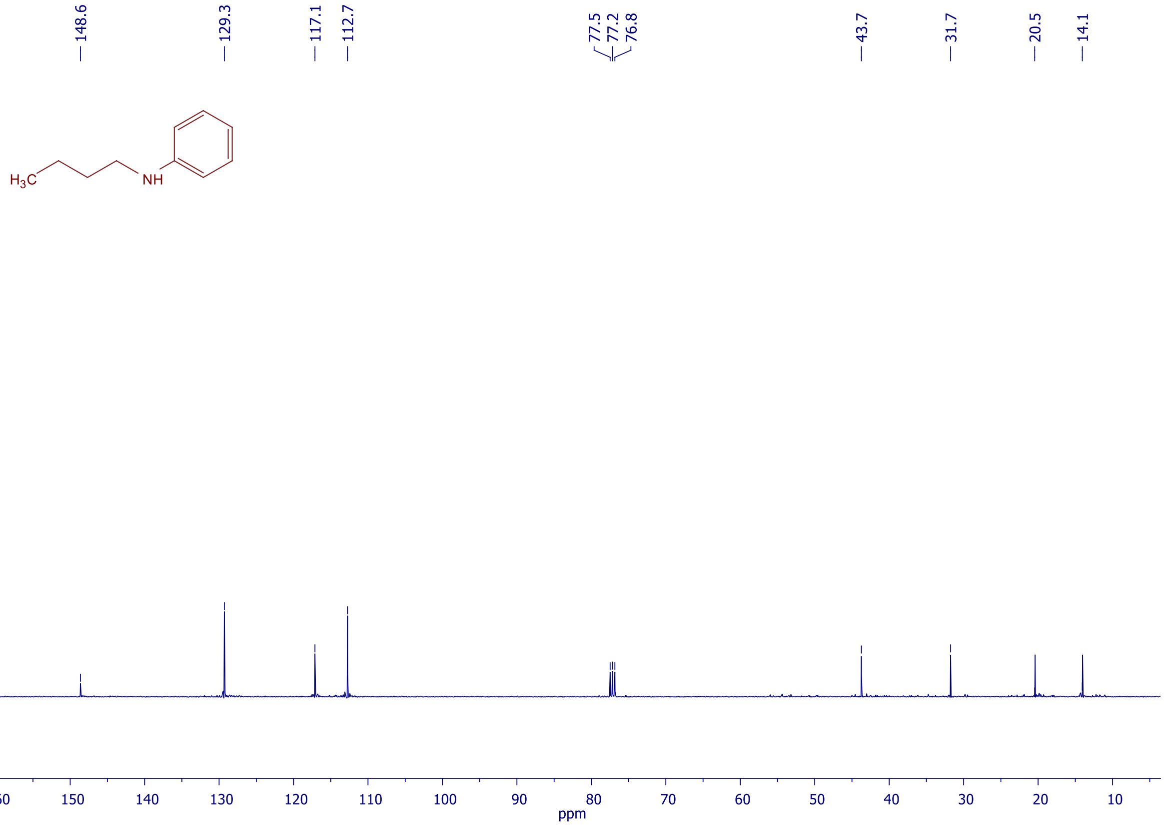
^{1}H NMR of N,N-dimethyl-4-((phenylamino)methyl)aniline (Compound-**3pa**)



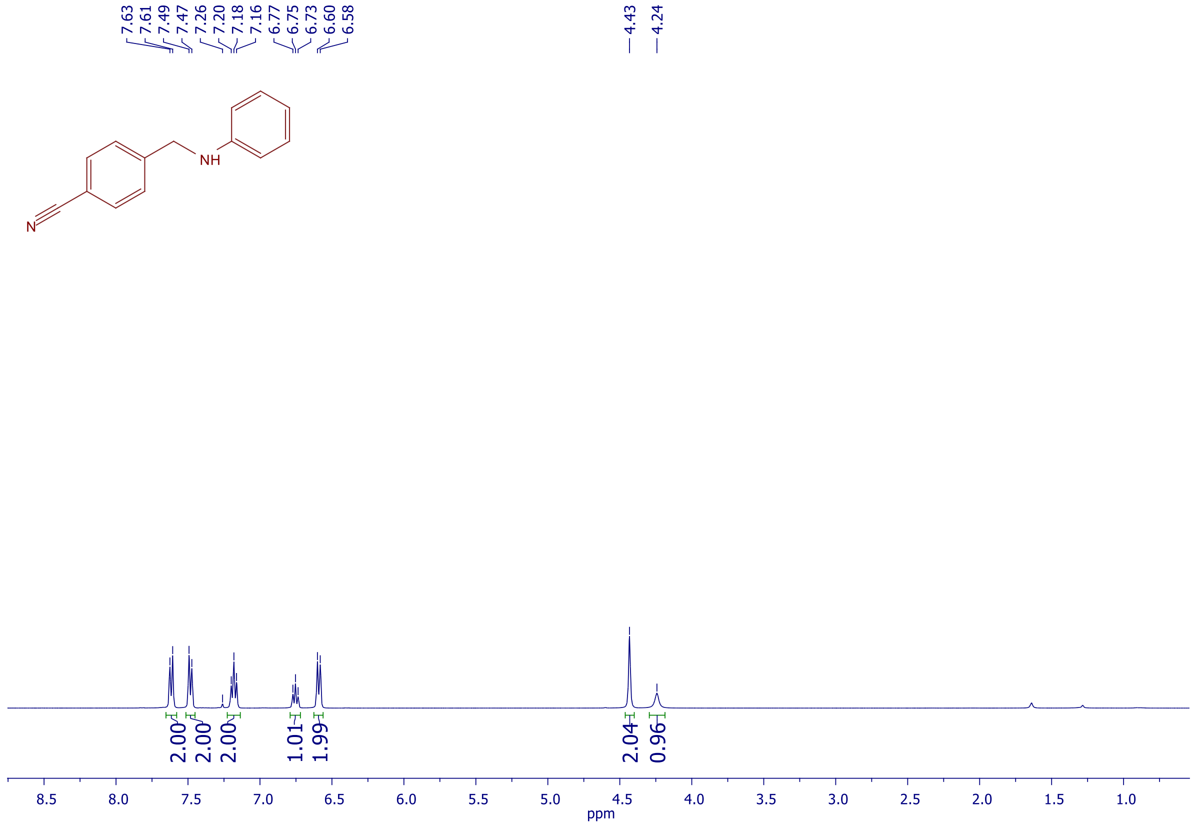
^{13}C{^{1}H} NMR of N,N-dimethyl-4-((phenylamino)methyl)aniline (Compound-**3pa**)



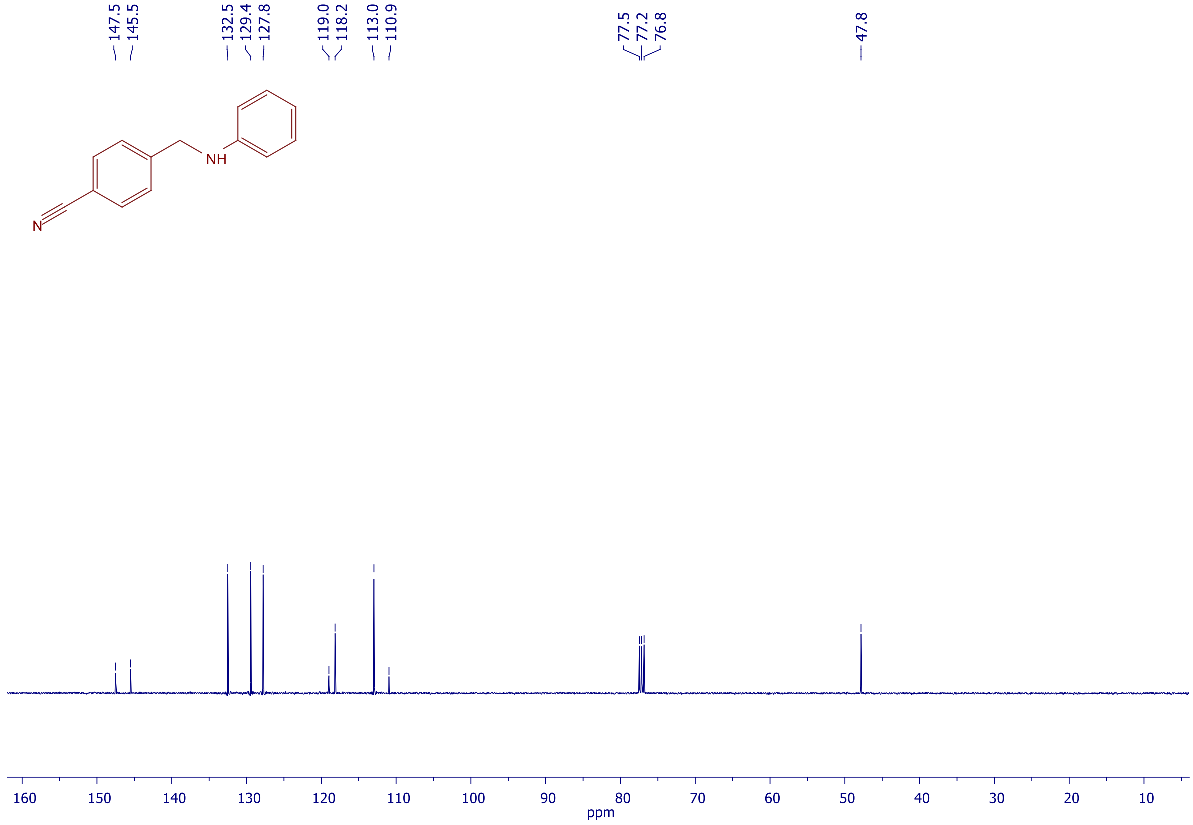
^{1}H NMR of N-butylaniline (Compound-**3qa**)



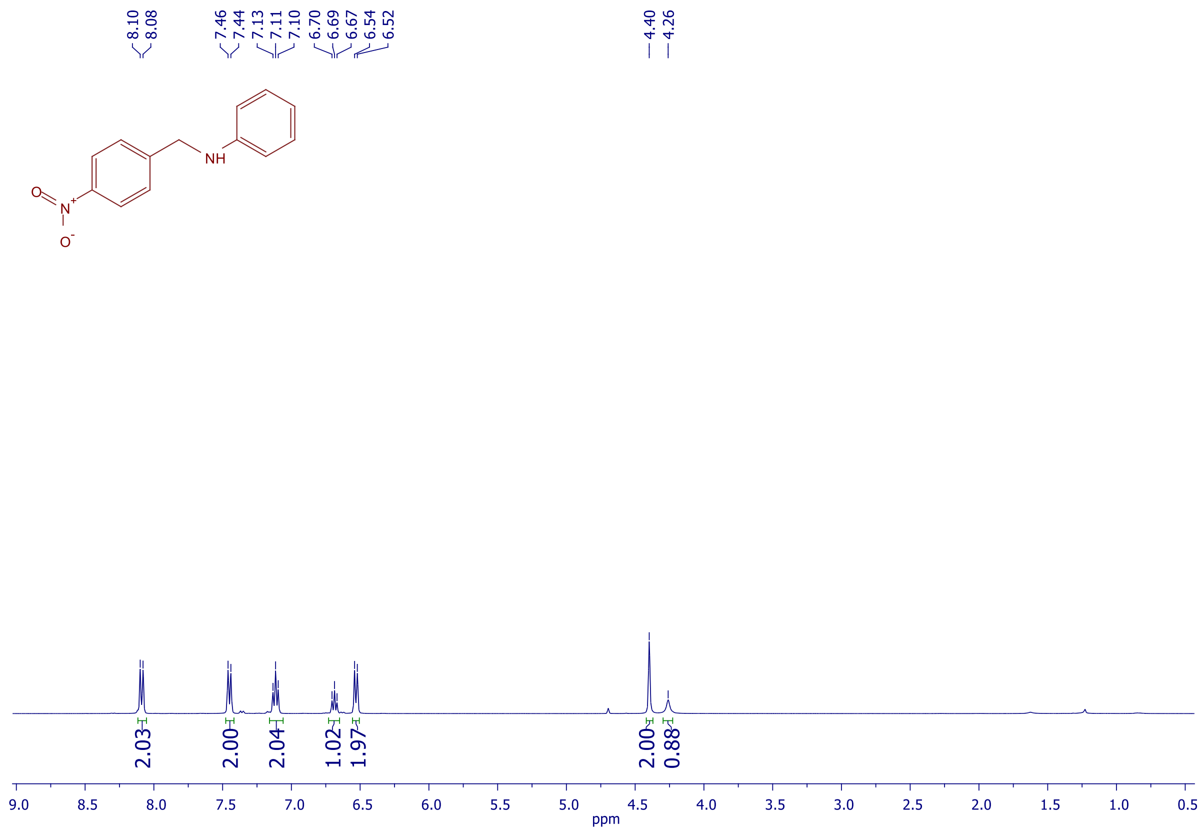
^{13}C{^{1}H} NMR of N-butylaniline (Compound-**3qa**)



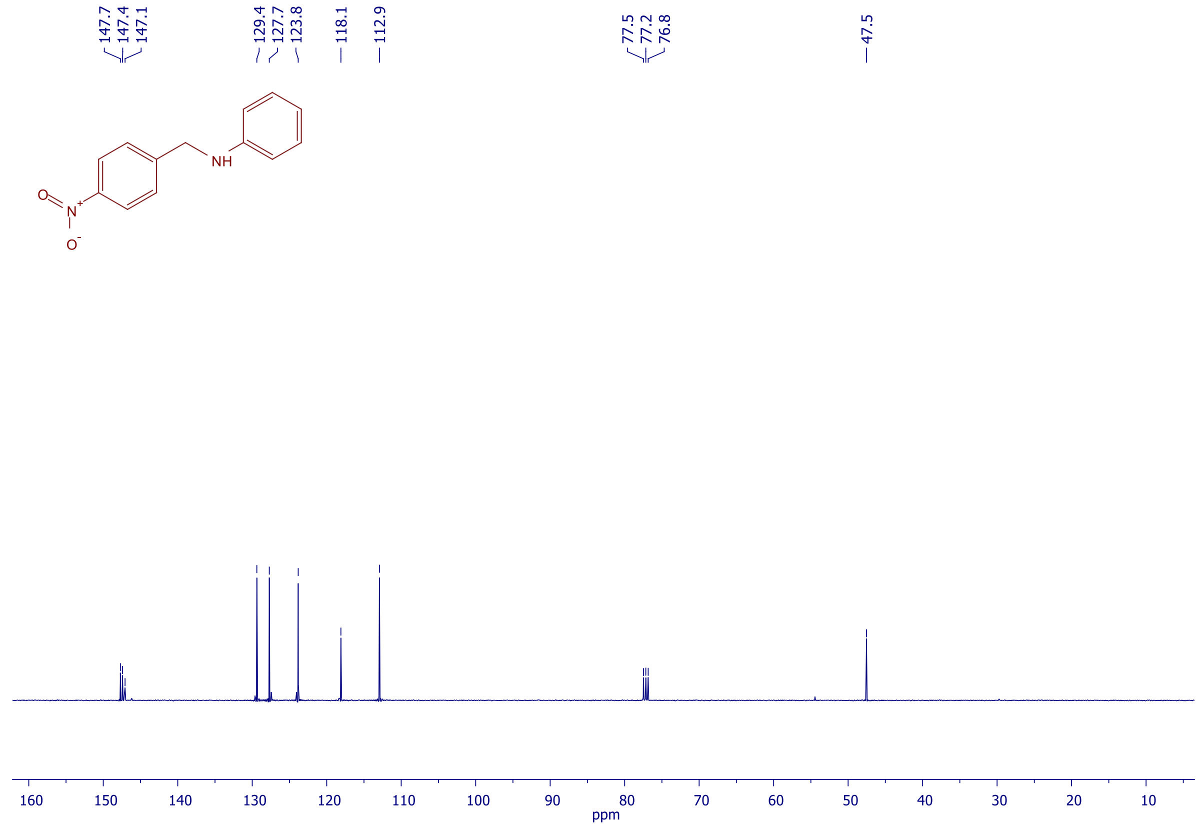
^{1}*H NMR of 4-((phenylamino)methyl)benzonitrile (Compound-**3ra**)*



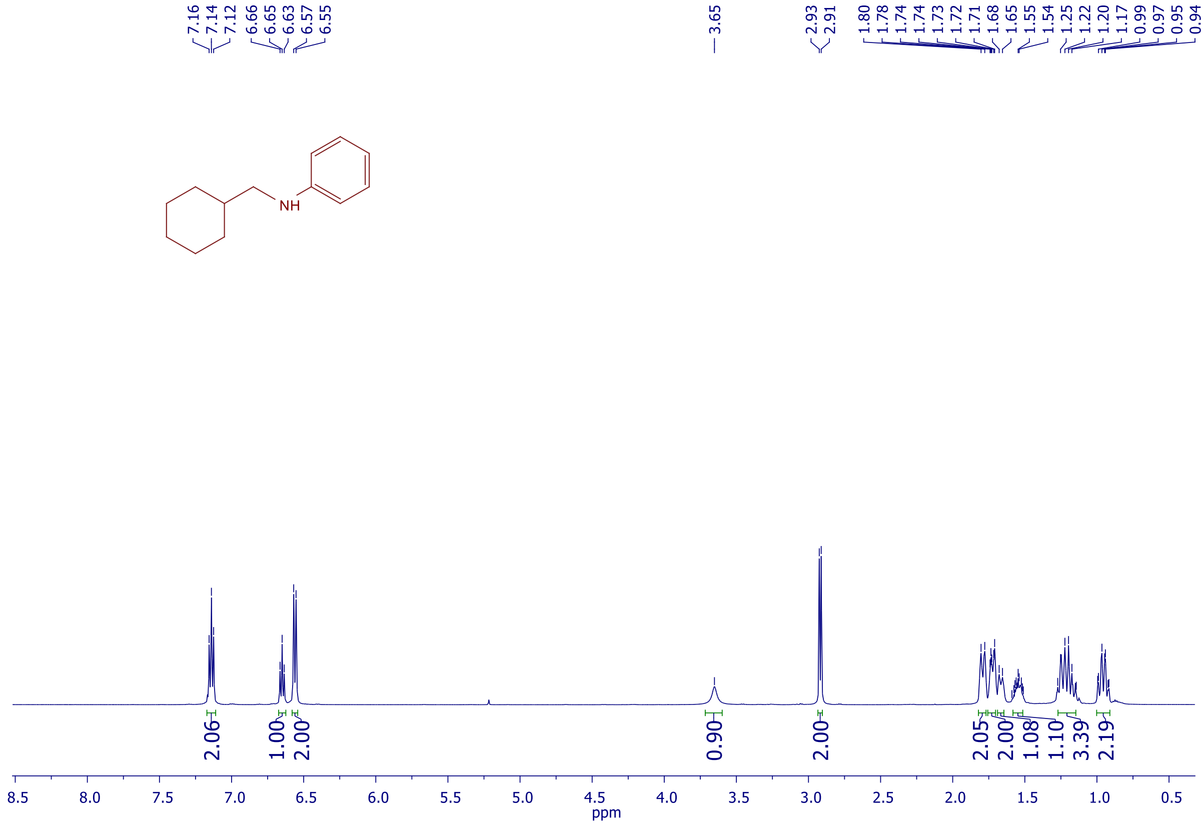
^{13}*C{^{1}H} NMR of 4-((phenylamino)methyl)benzonitrile (Compound-**3ra**)*



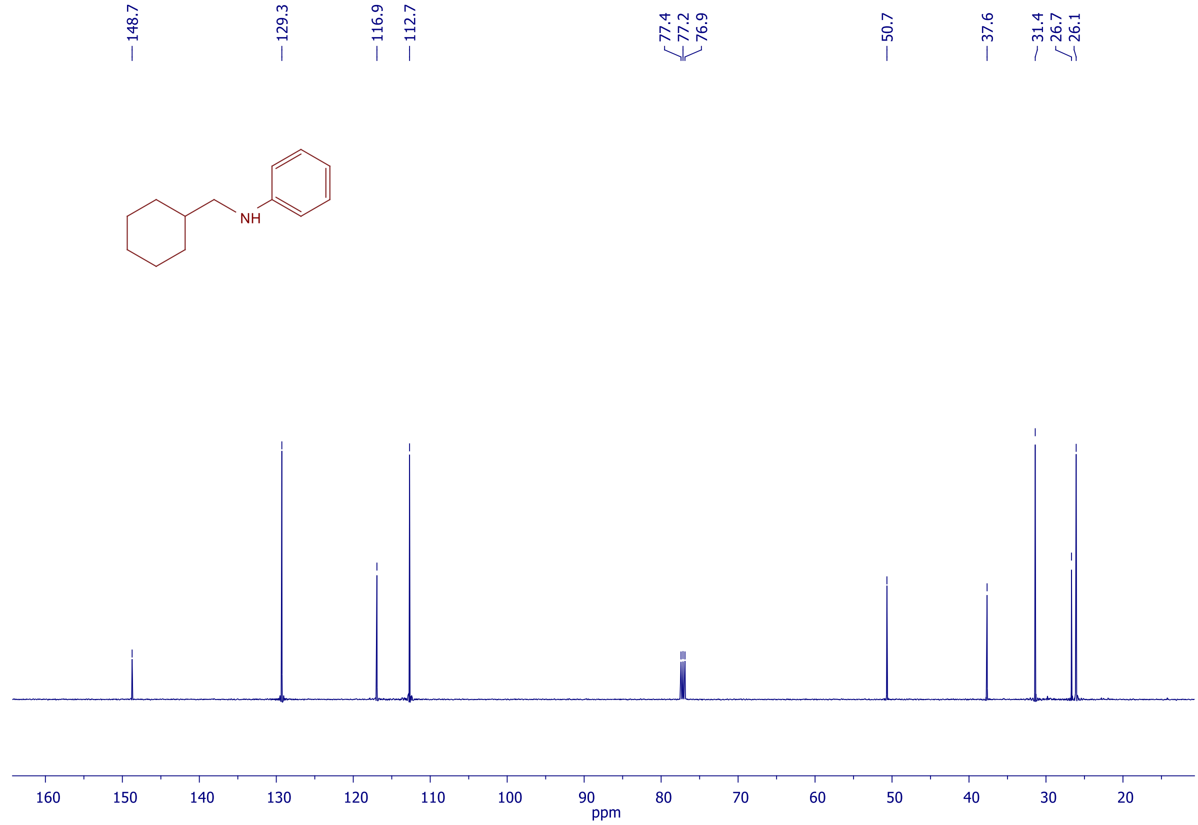
^{1}H NMR of N-(4-nitrobenzyl)aniline (Compound-**3sa**)



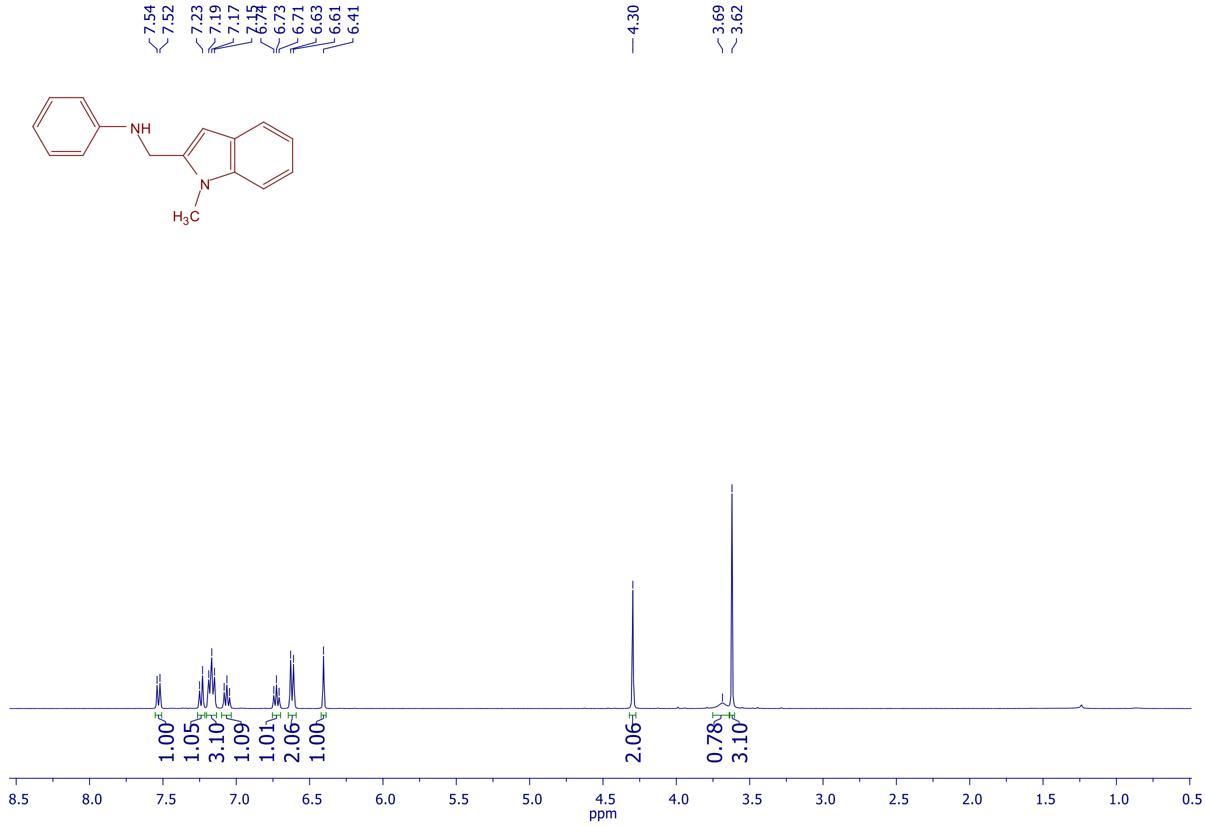
^{13}C{^{1}H} NMR of N-(4-nitrobenzyl)aniline (Compound-**3sa**)



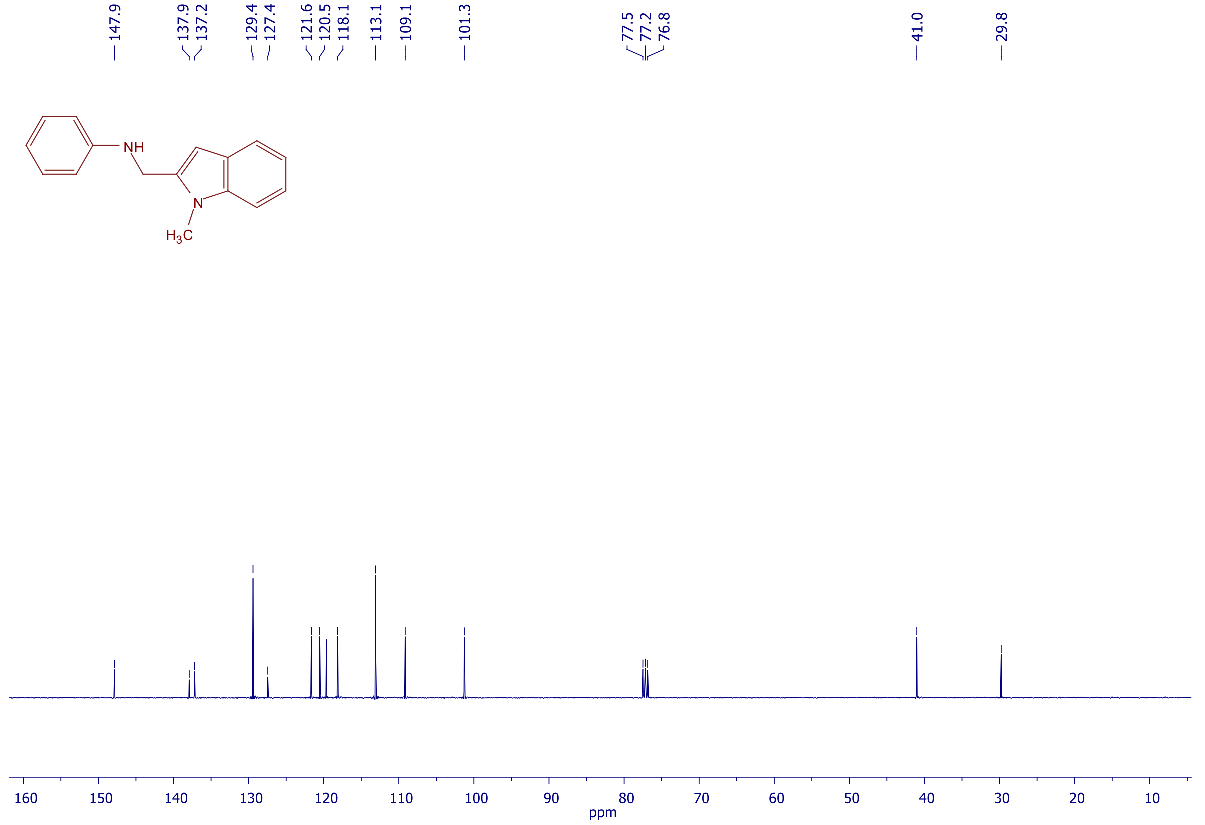
^{1}*H NMR of N-(cyclohexylmethyl)aniline (Compound-**3ta**)*



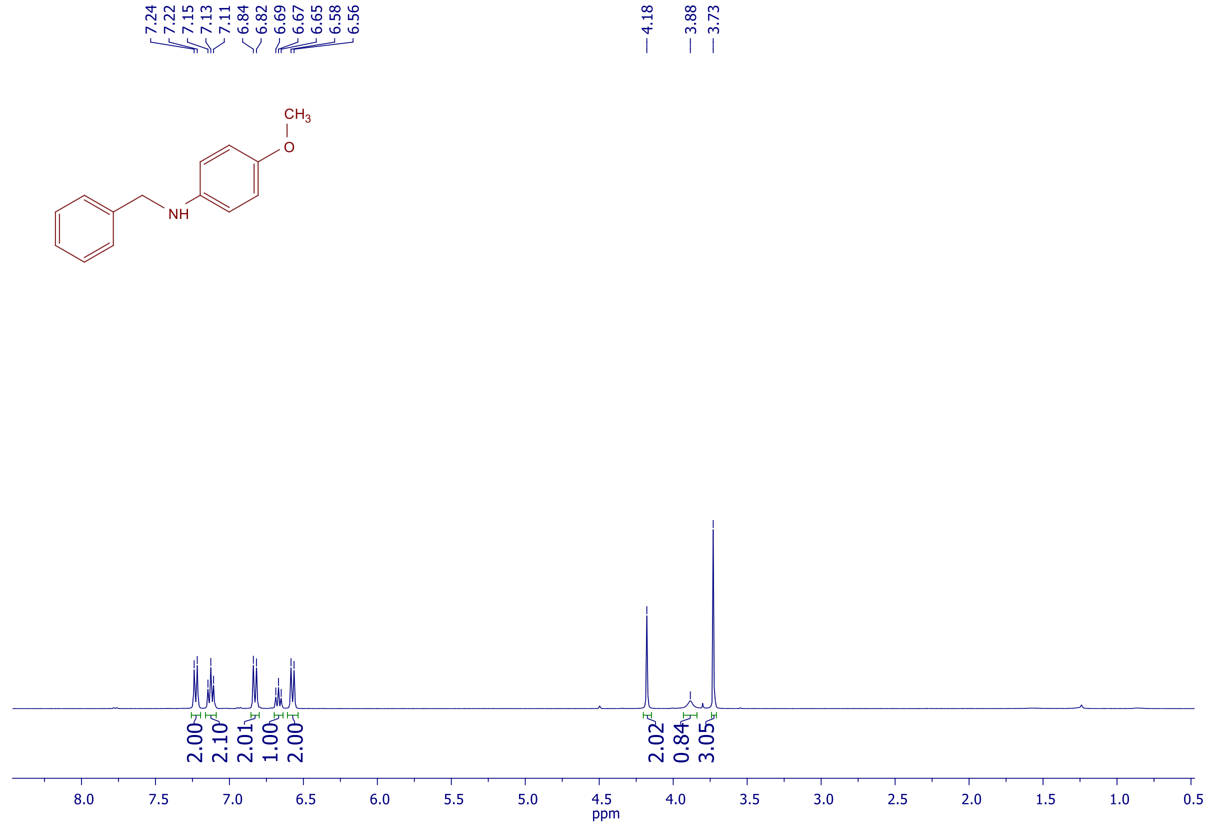
^{13}*C{^{1}H} NMR of N-(cyclohexylmethyl)aniline (Compound-**3ta**)*



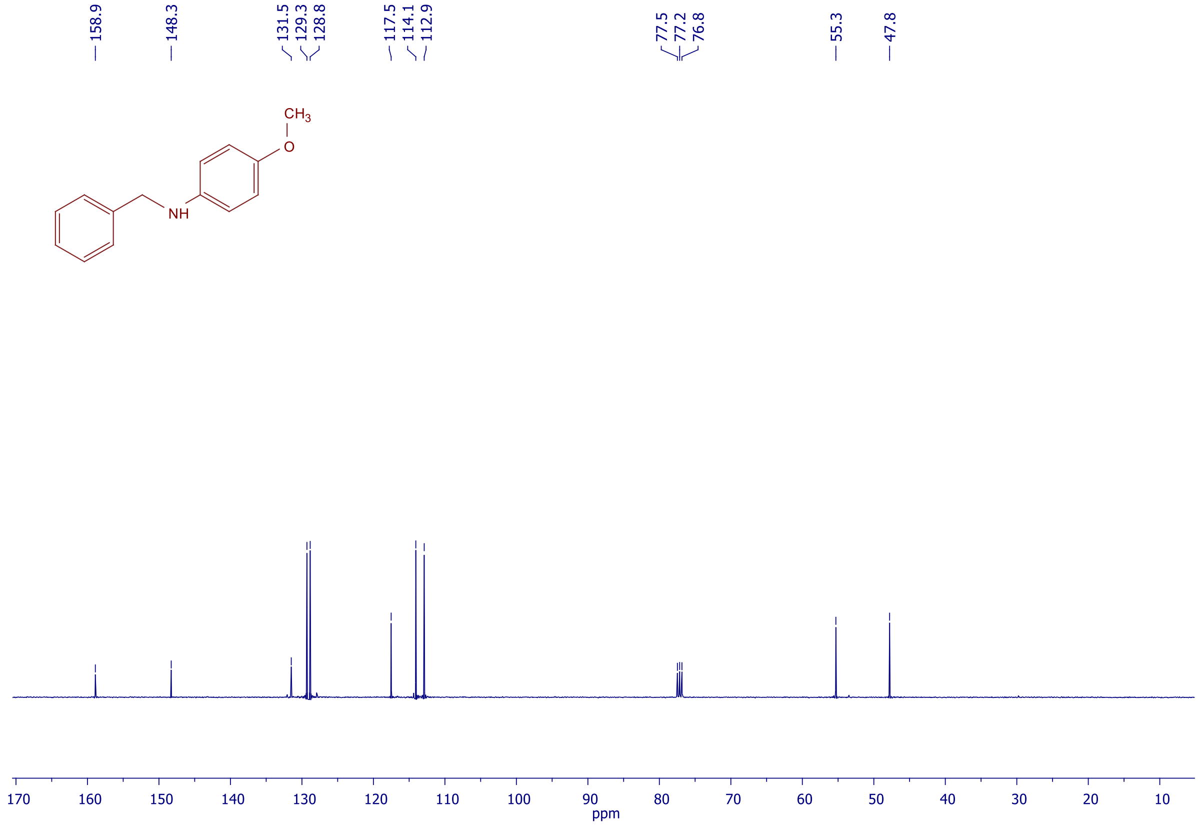
^{1}*H NMR of N-((1-methyl-1H-indol-2-yl)methyl)aniline (Compound-**3ua**)*



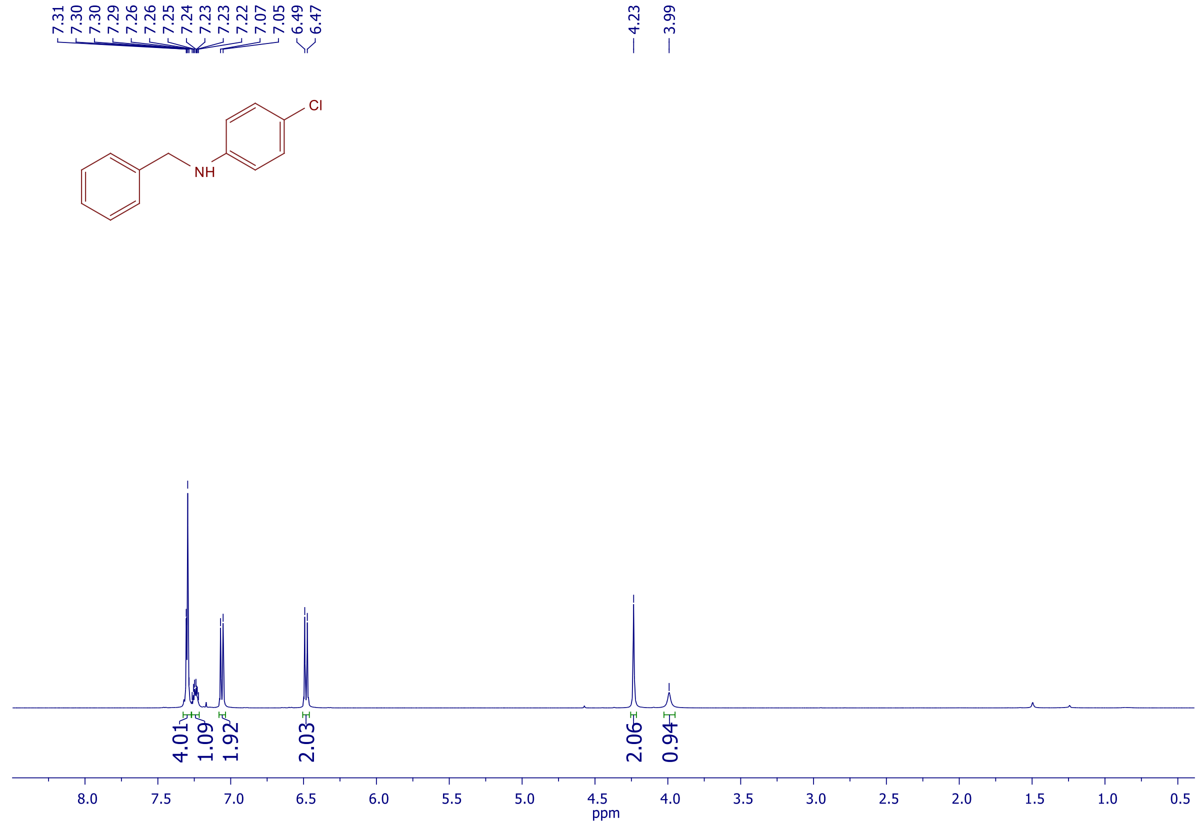
^{13}*C{^{1}H} NMR of N-((1-methyl-1H-indol-2-yl)methyl)aniline (Compound-**3ua**)*



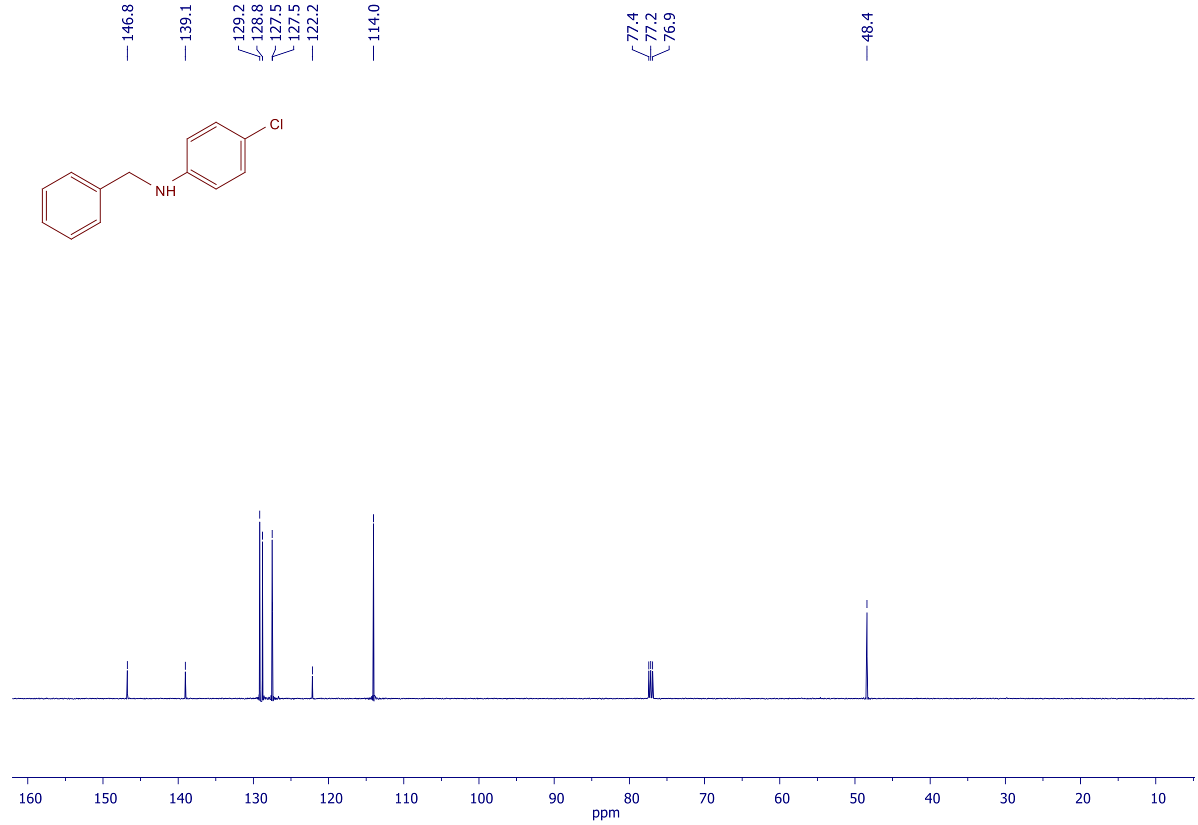
^{1}*H NMR of N-benzyl-4-methoxyaniline (Compound-**3ab**)*



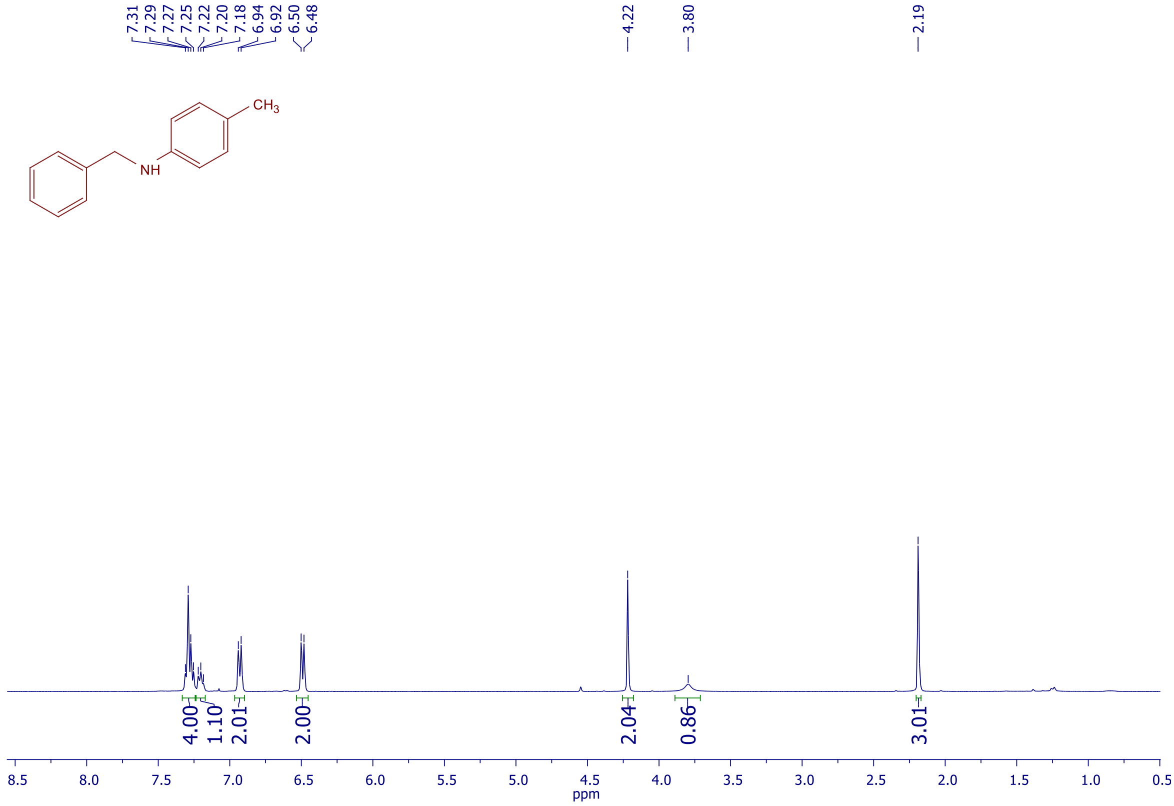
^{13}*C{^{1}H} NMR of N-benzyl-4-methoxyaniline (Compound-**3ab**)*



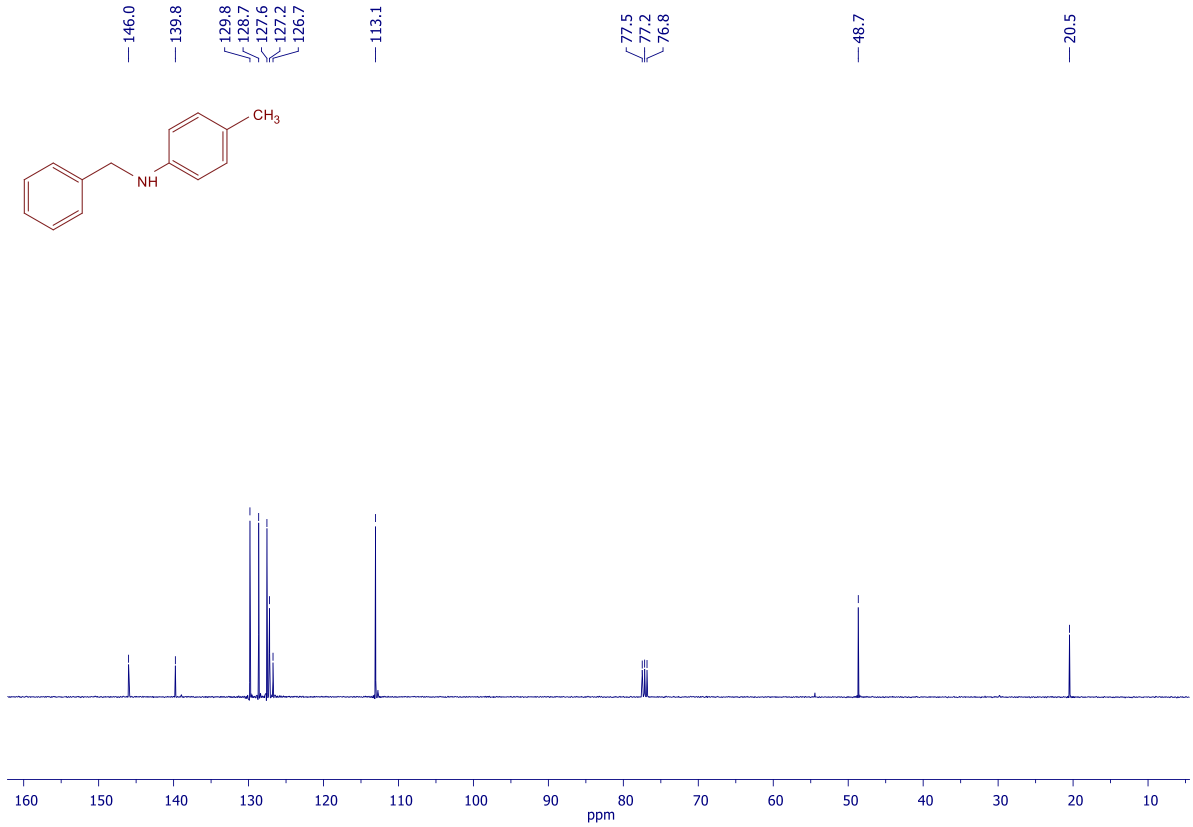
*^{1}H NMR of N-benzyl-4-chloroaniline (Compound-**3ac**)*



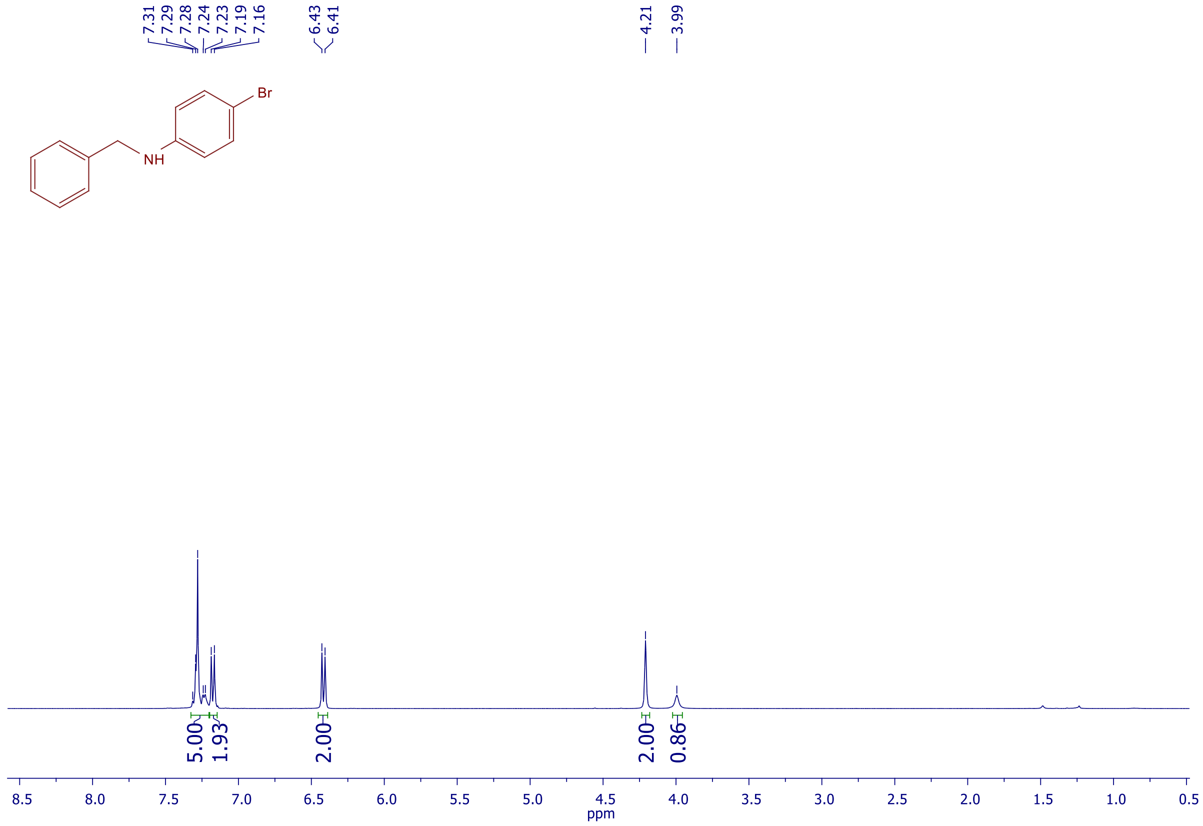
*^{13}C{^{1}H} NMR of N-benzyl-4-chloroaniline (Compound-**3ac**)*



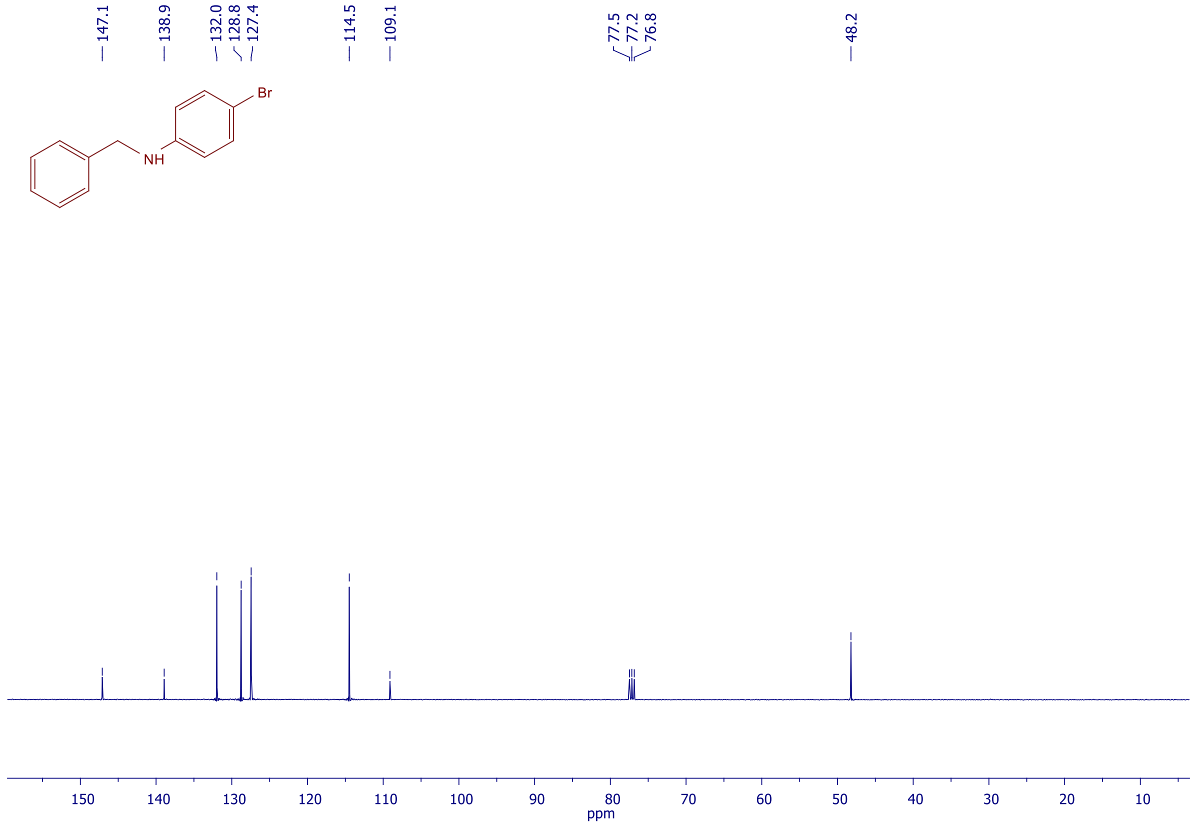
*^{1}H NMR of N-benzyl-4-methylaniline (Compound-**3ae**)*



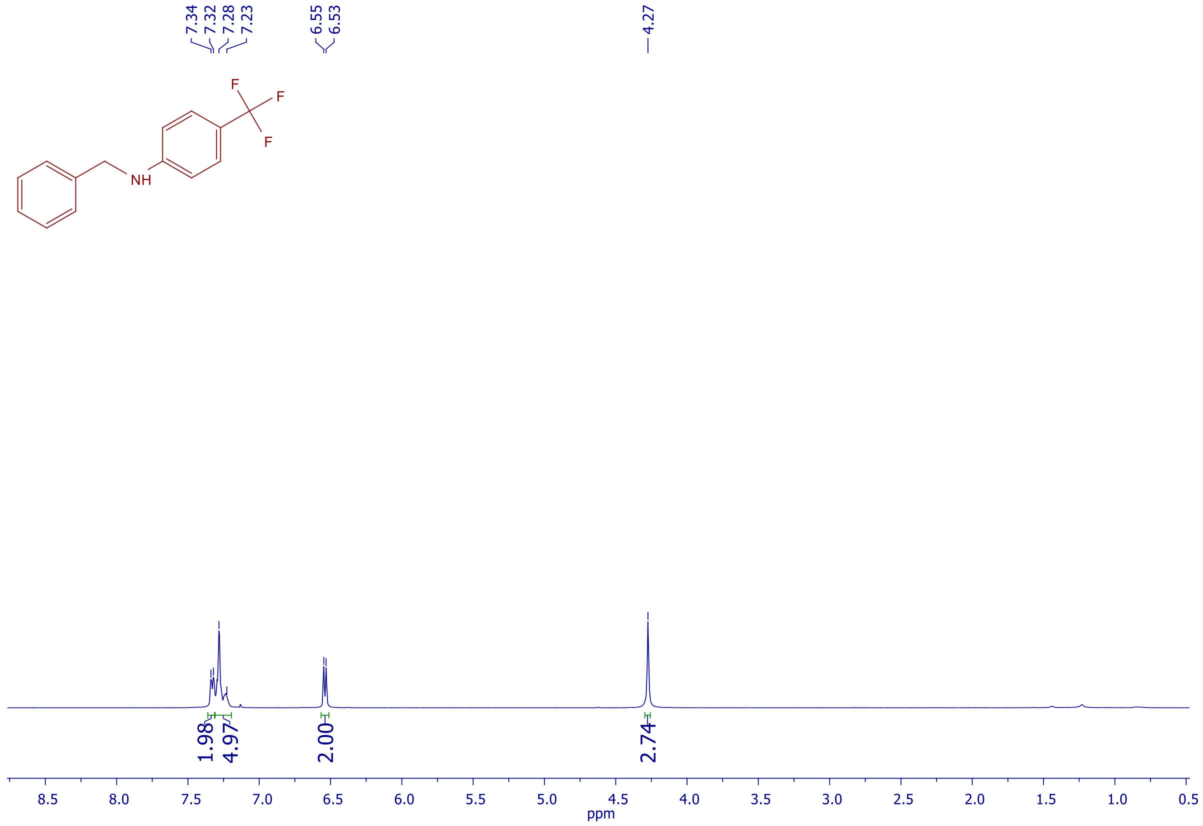
*^{13}C{^{1}H} NMR of N-benzyl-4-methylaniline (Compound-**3ae**)*



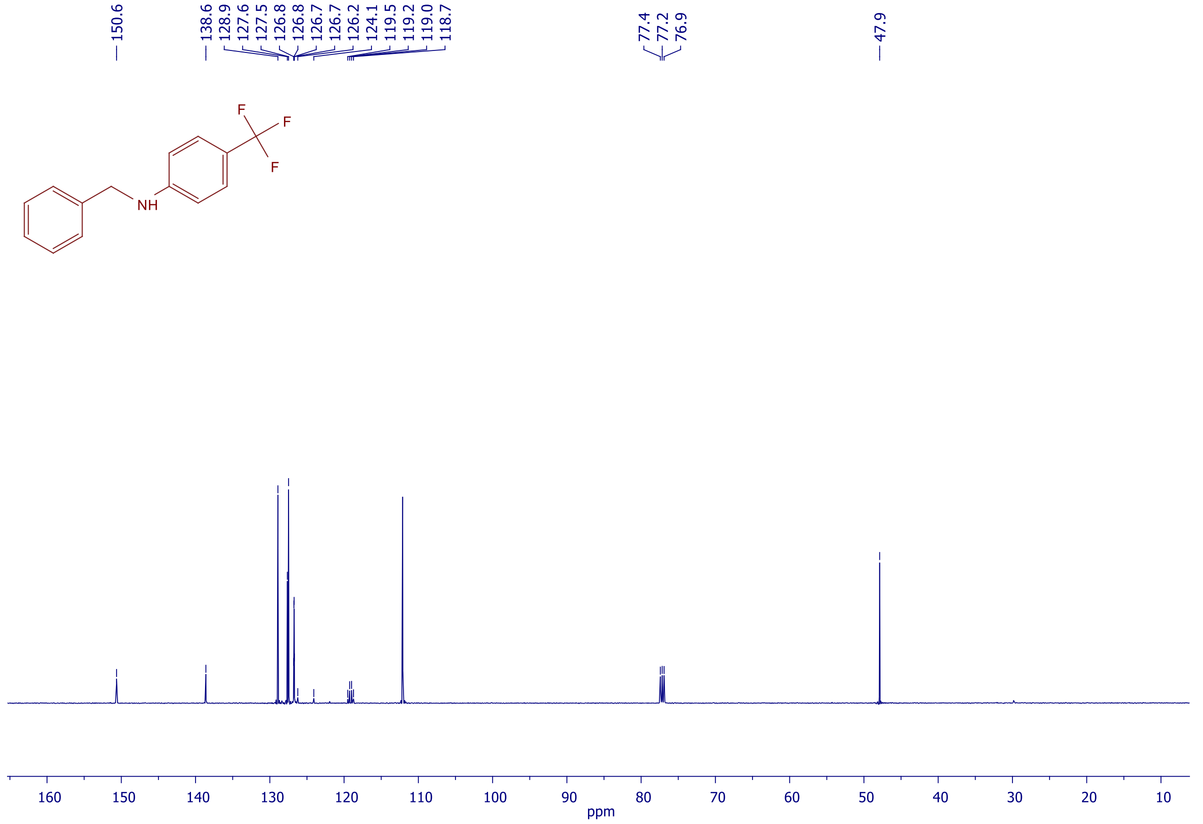
^{1}*H NMR of N-benzyl-4-bromoaniline (Compound-**3af**)*



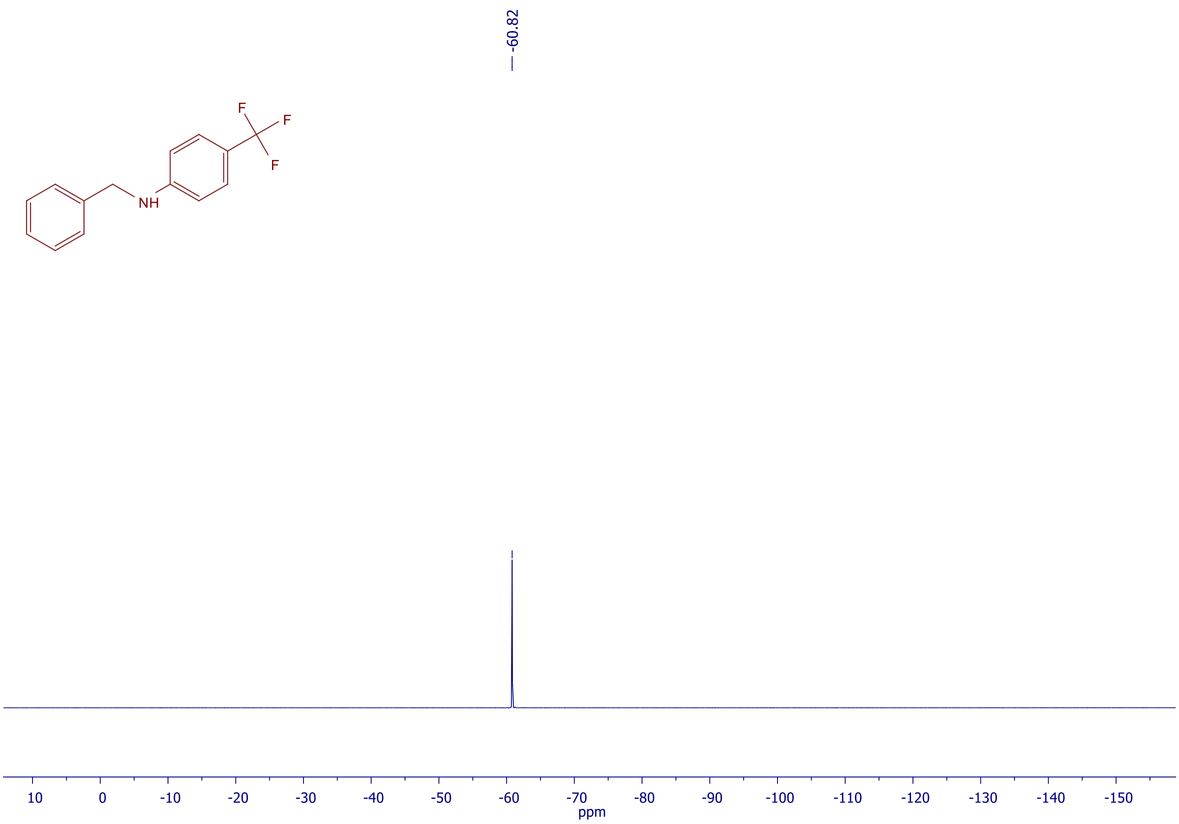
^{13}*C{^{1}H} NMR of N-benzyl-4-bromoaniline (Compound-**3af**)*



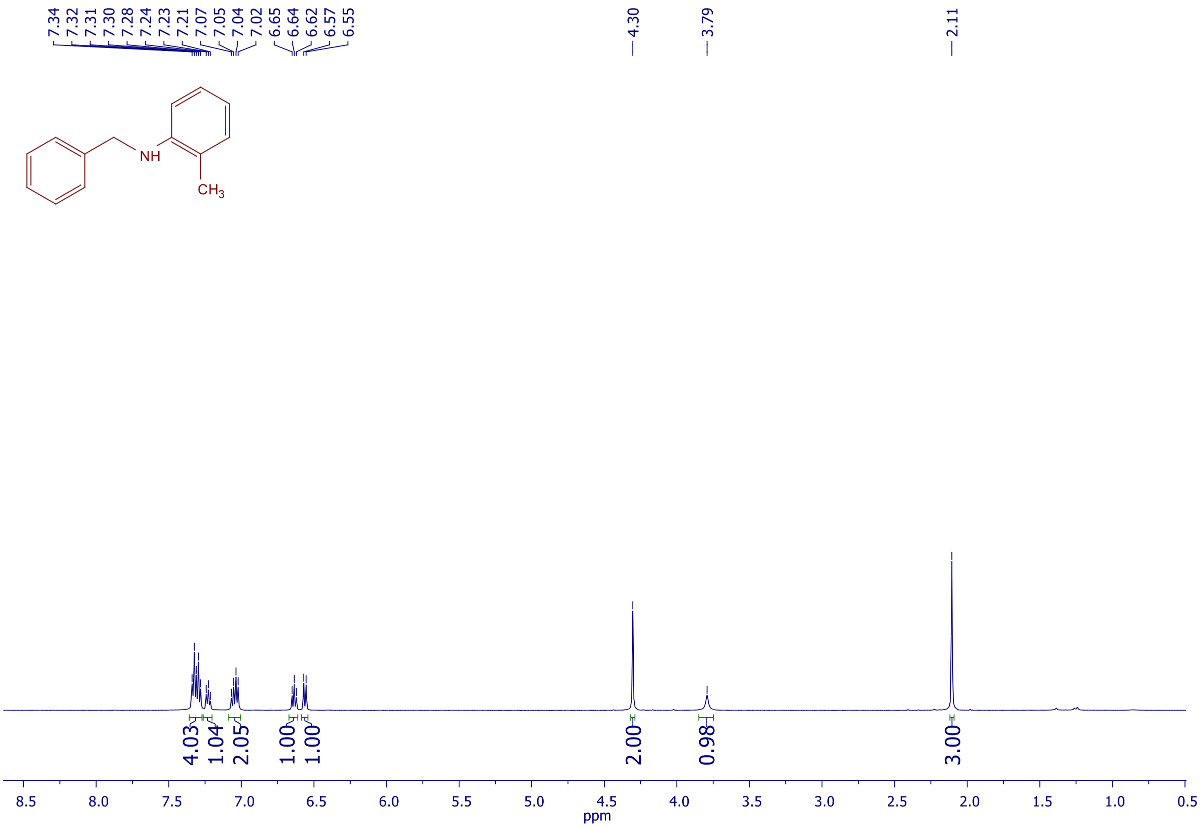
^{1}*H NMR of N-benzyl-4-(trifluoromethyl) aniline (Compound-**3ag**)*



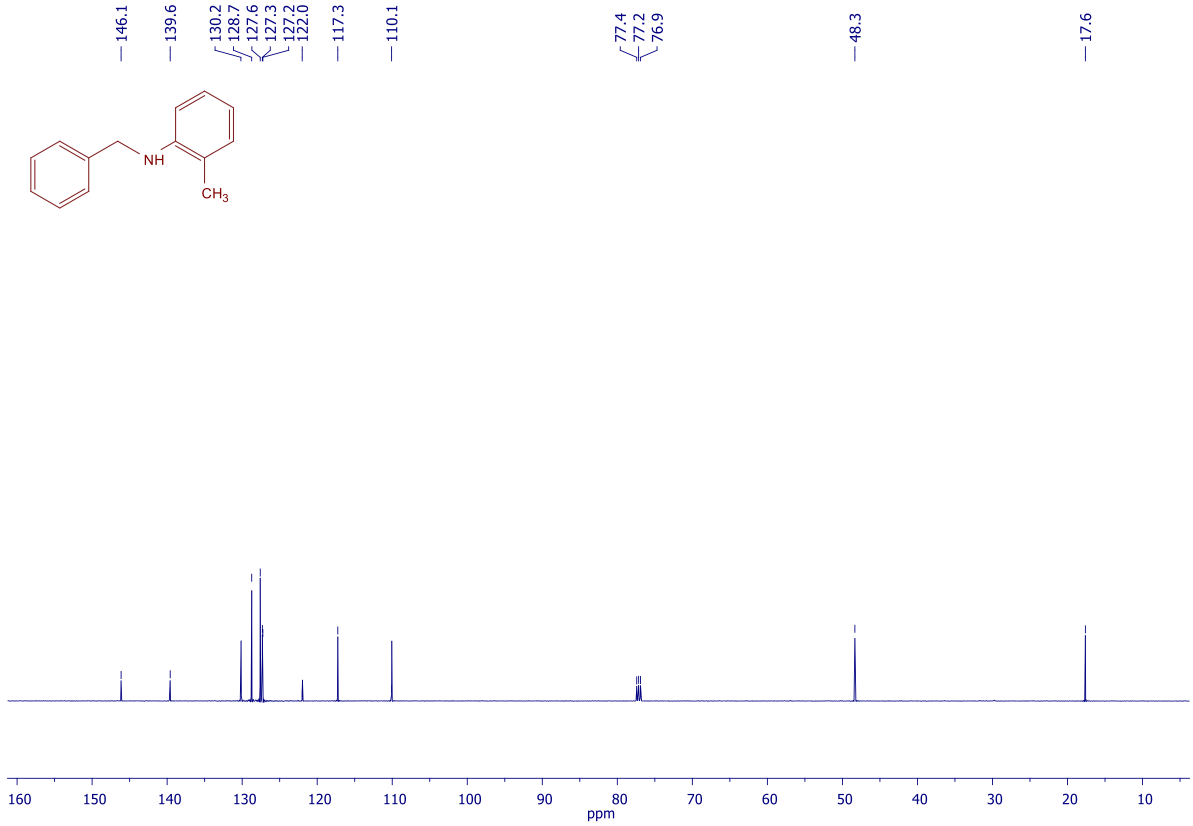
^{13}*C{^{1}H} NMR of N-benzyl-4-(trifluoromethyl) aniline (Compound-**3ag**)*



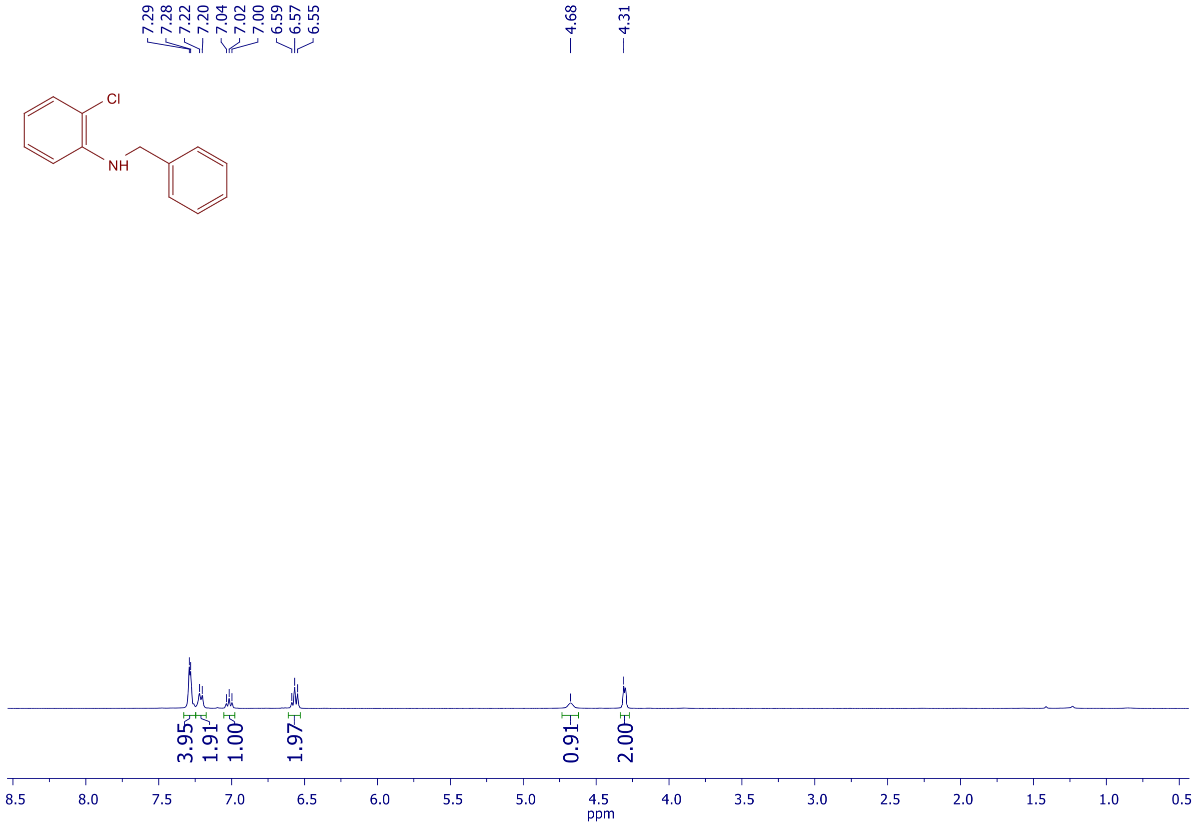
^{19}*F NMR of N-benzyl-4-(trifluoromethyl) aniline (Compound-**3ag**)*



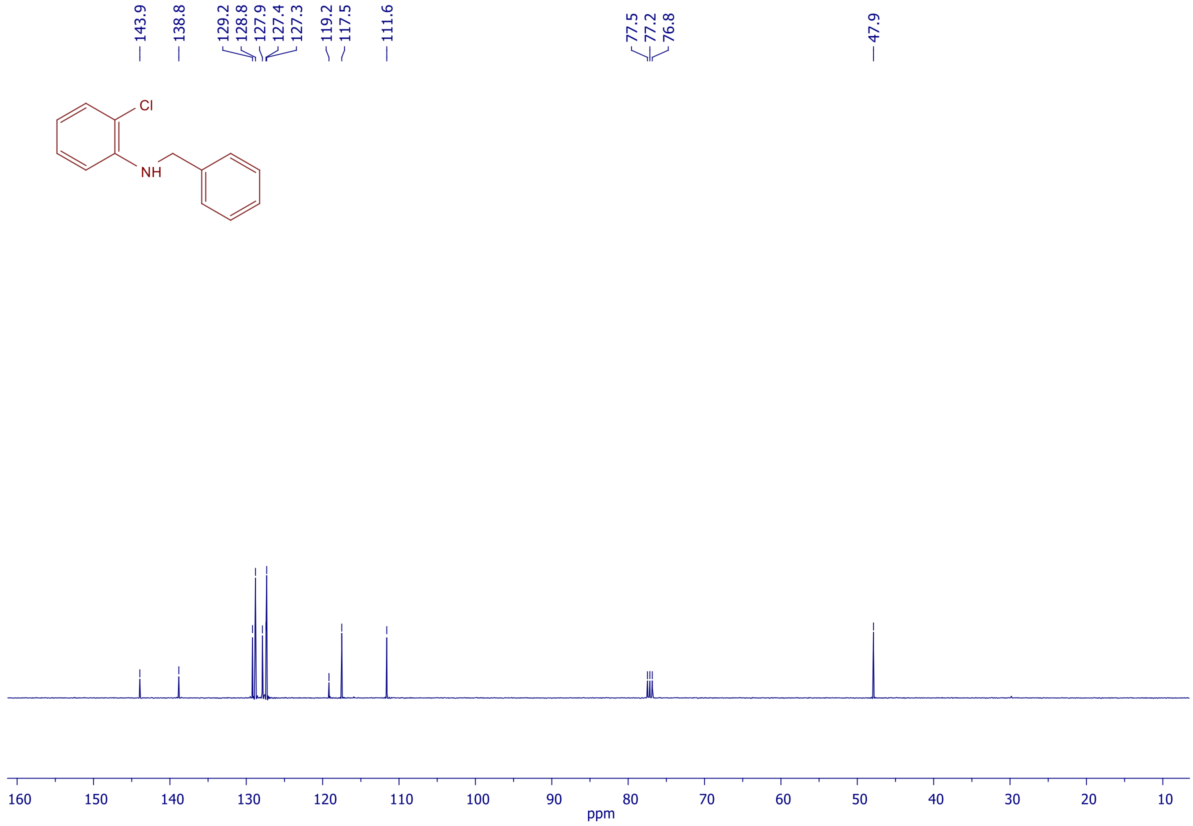
^{1}*H NMR of N-benzyl-2-methylaniline (Compound-**3ah**)*



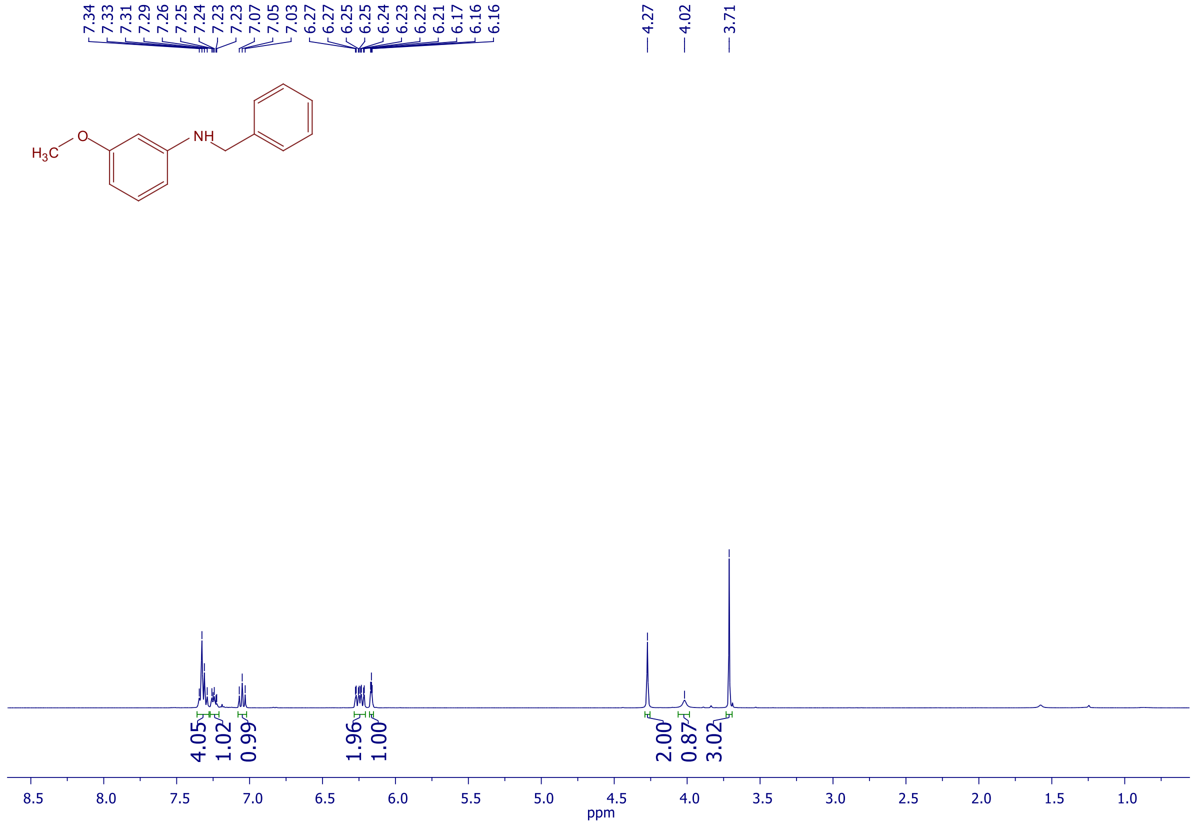
^{13}C{^{1}H} *NMR of N-benzyl-2-methylaniline (Compound-**3ah**)*



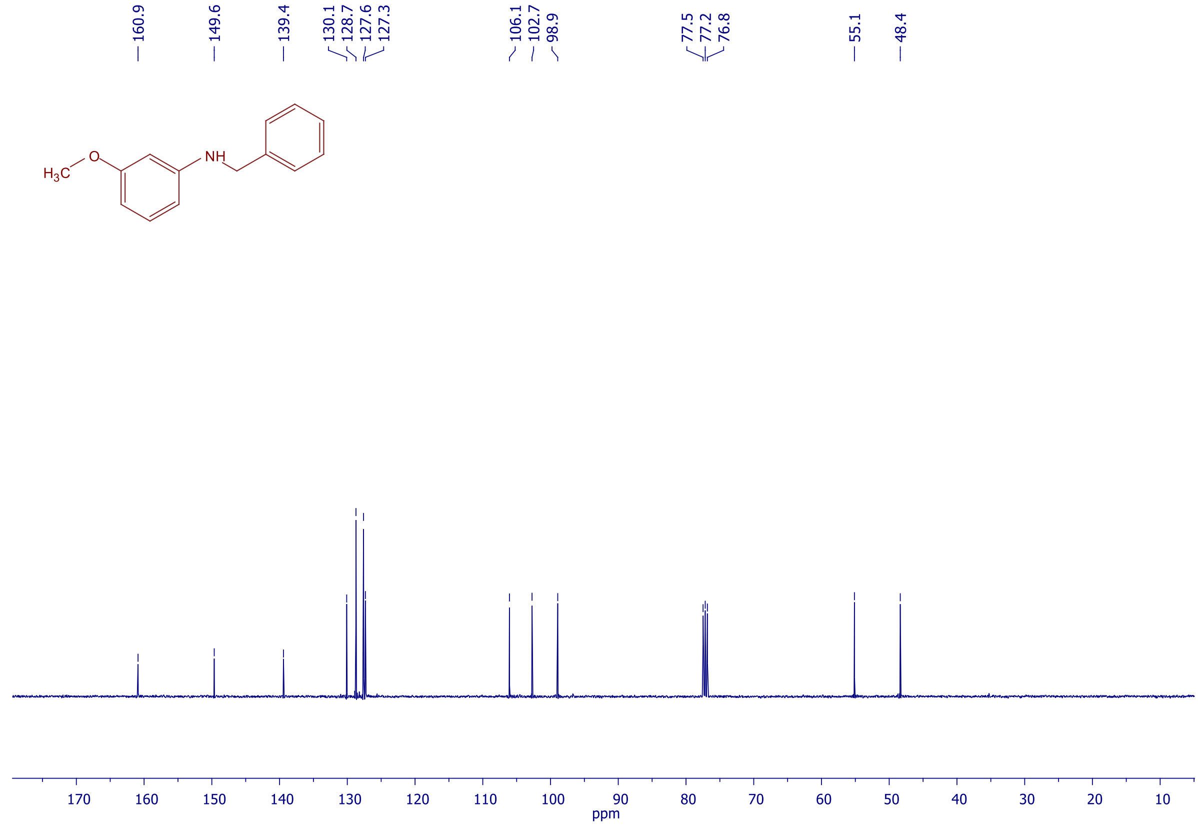
^{1}H *NMR of N-benzyl-2-chloroaniline (Compound-**3ai**)*



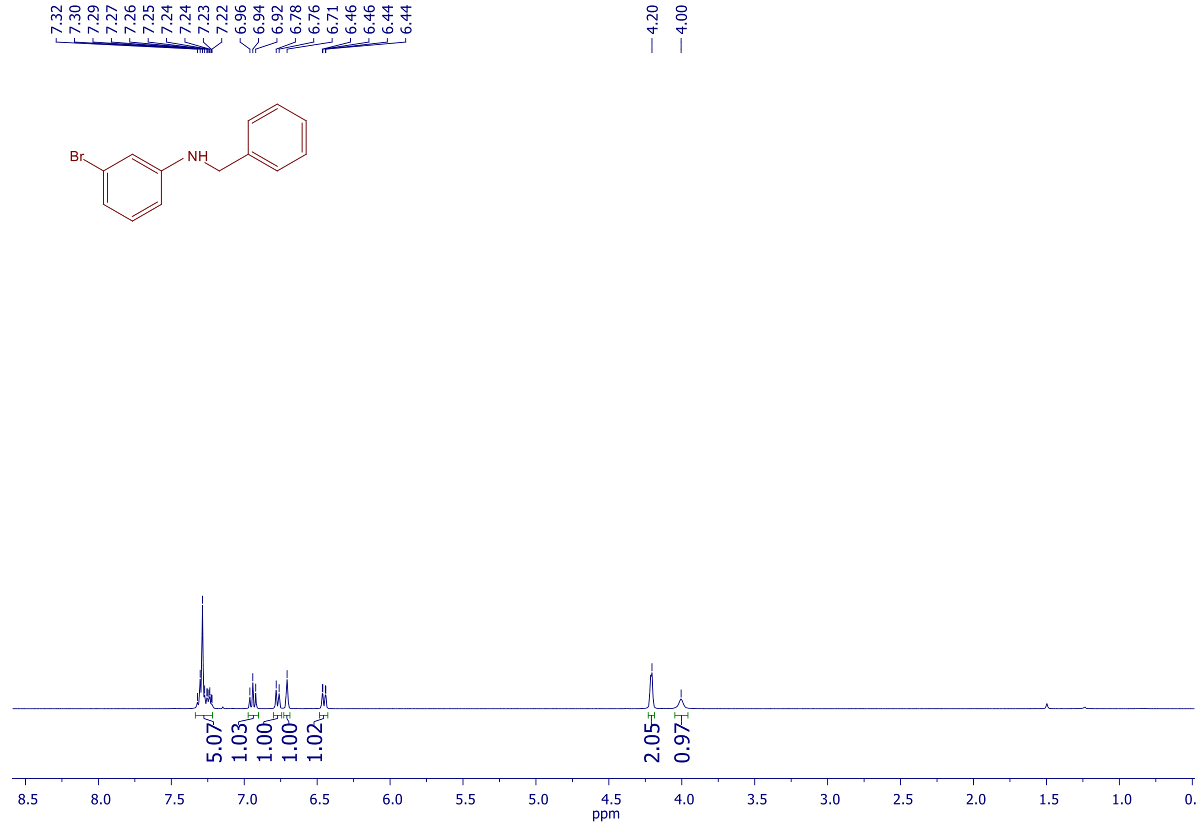
*^{13}C{^{1}H} NMR of N-benzyl-2-chloroaniline (Compound-**3ai**)*



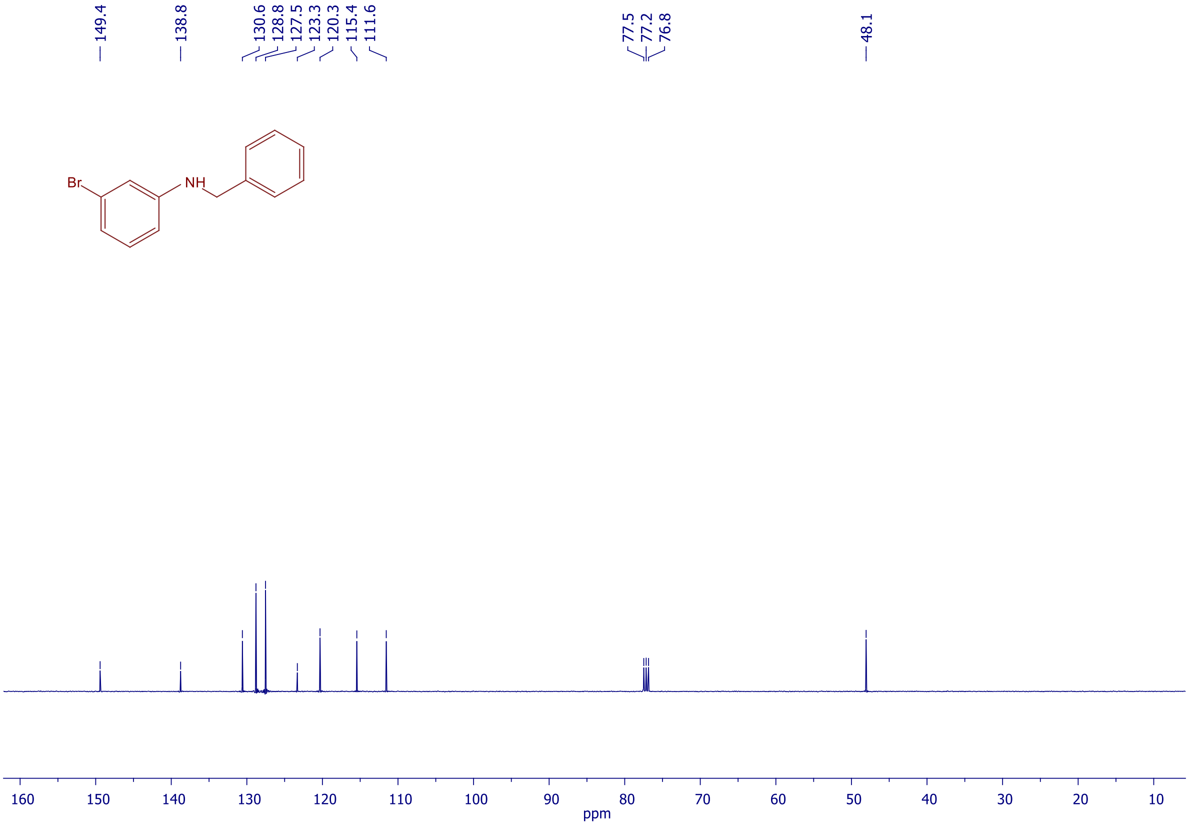
*^{1}H NMR of N-benzyl-3-methoxyaniline (Compound-**3aj**)*



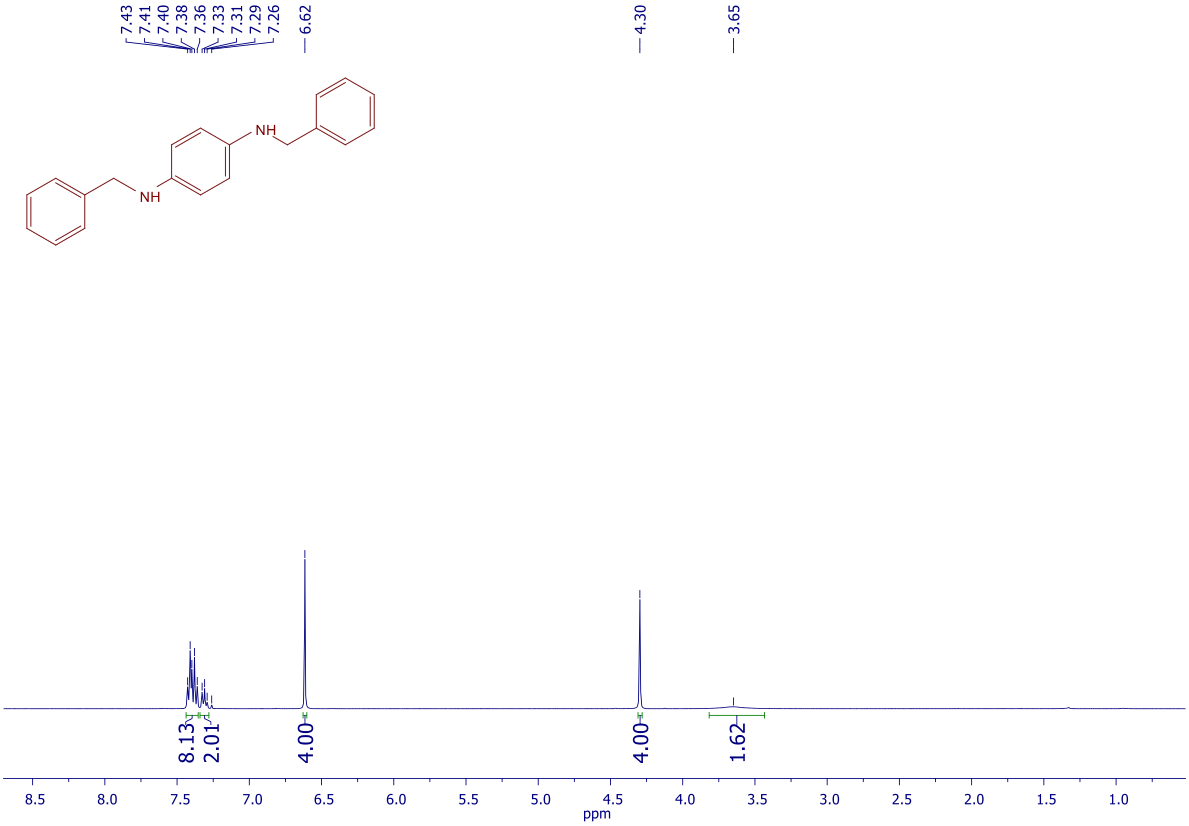
^{13}C{^{1}H} *NMR of N-benzyl-3-methoxyaniline (Compound-**3aj**)*



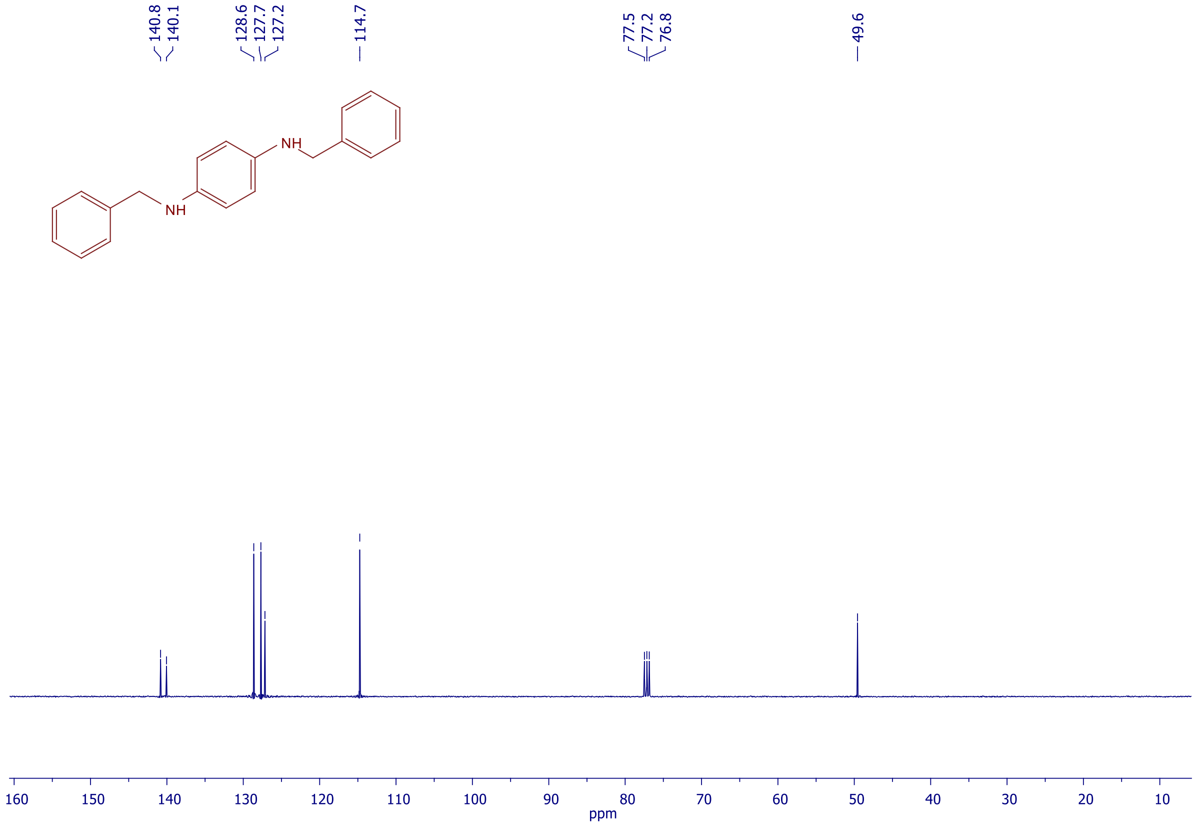
^{1}H *NMR of N-benzyl-3-bromoaniline (Compound-**3ak**)*



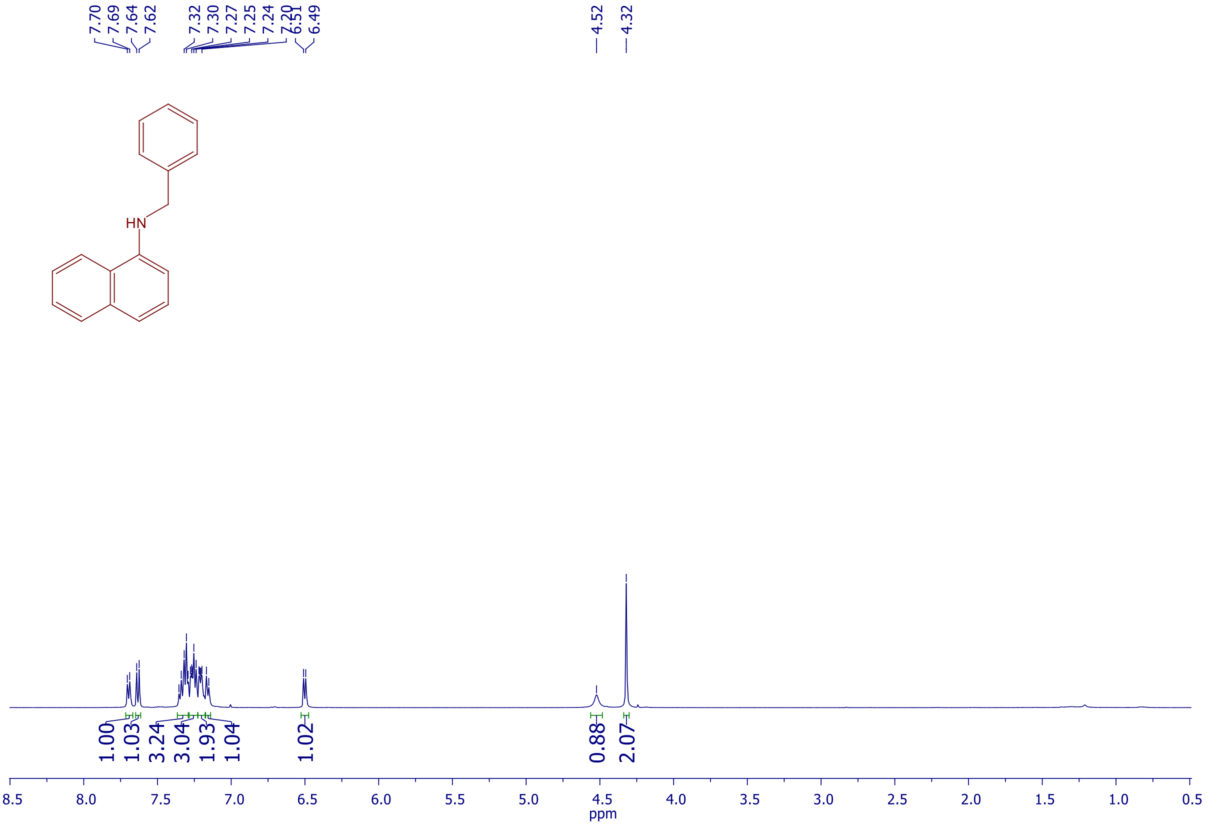
^{13}*C{*^{1}*H} NMR of N-benzyl-3-bromoaniline (Compound-**3ak**)*



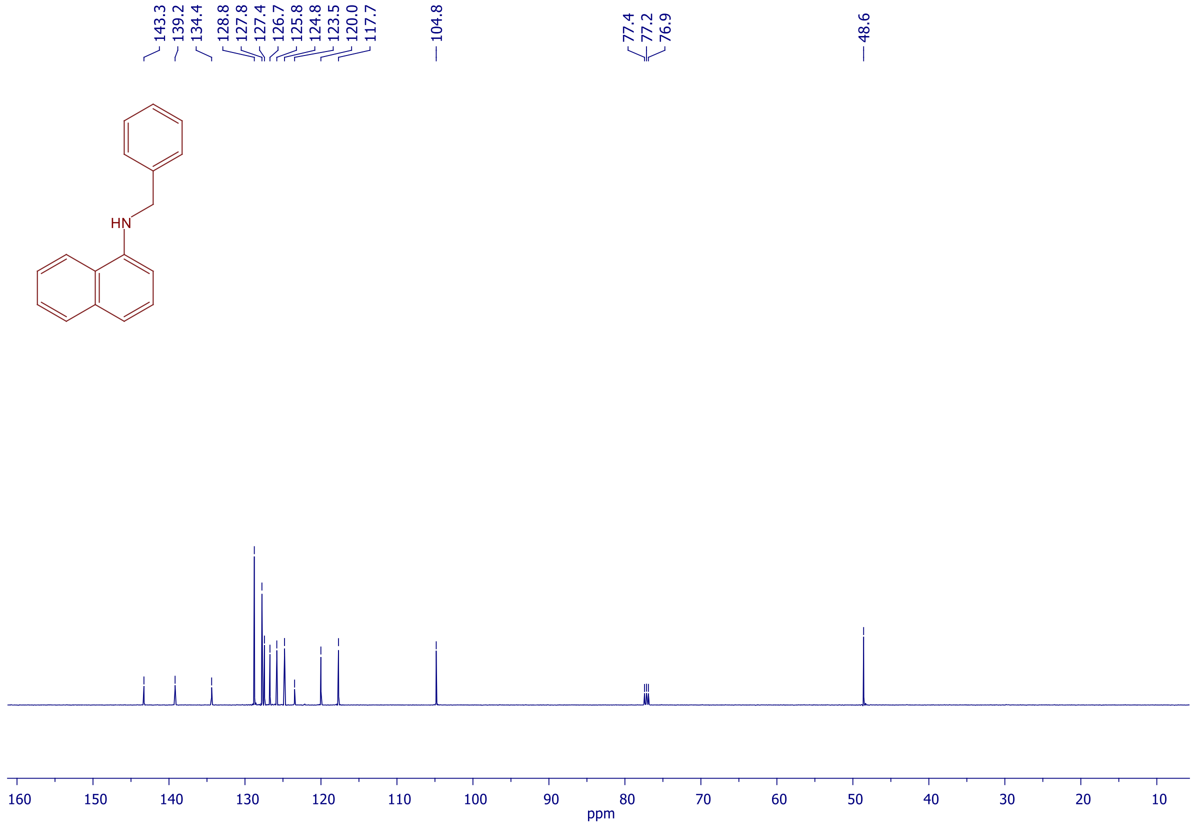
^{1}*H NMR of N1, N4-dibenzylbenzene-1,4-diamine (Compound-**3al**)*



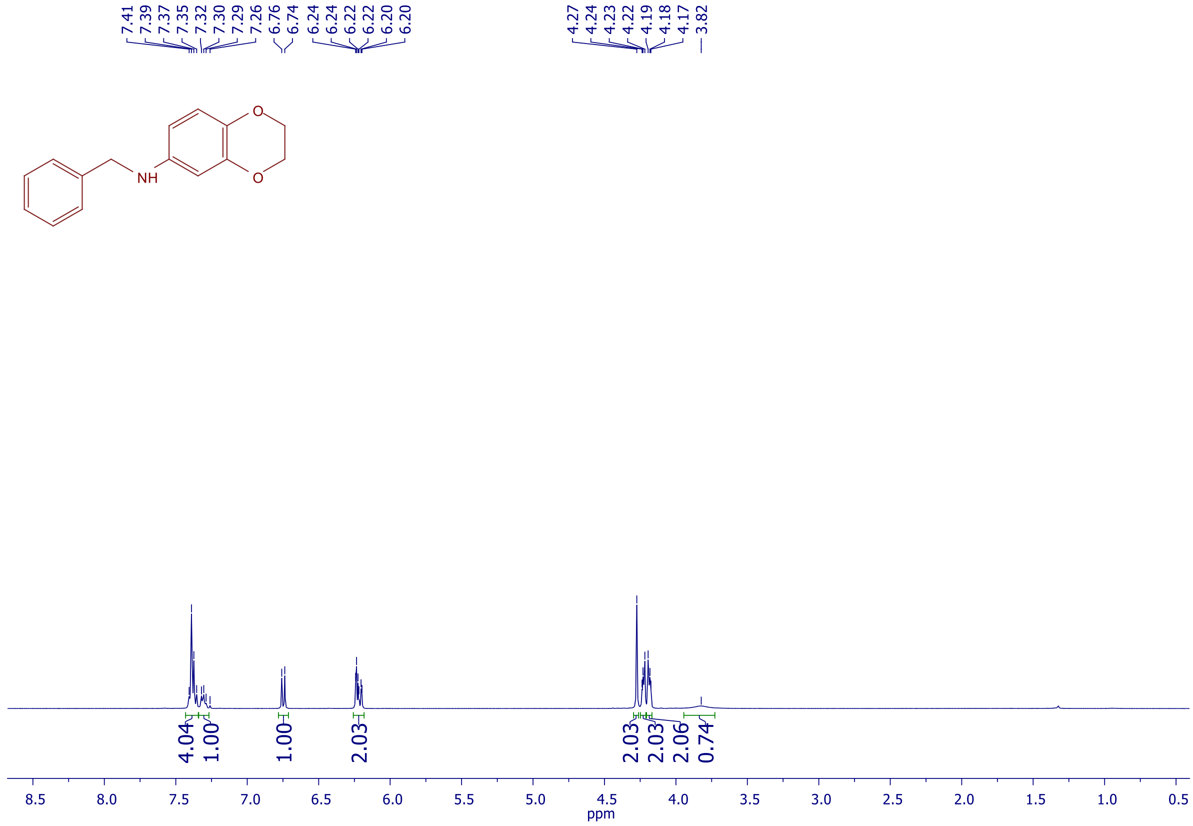
$^{13}C\{^{1}H\}$ *NMR of N1, N4-dibenzylbenzene-1,4-diamine (Compound-**3al**)*



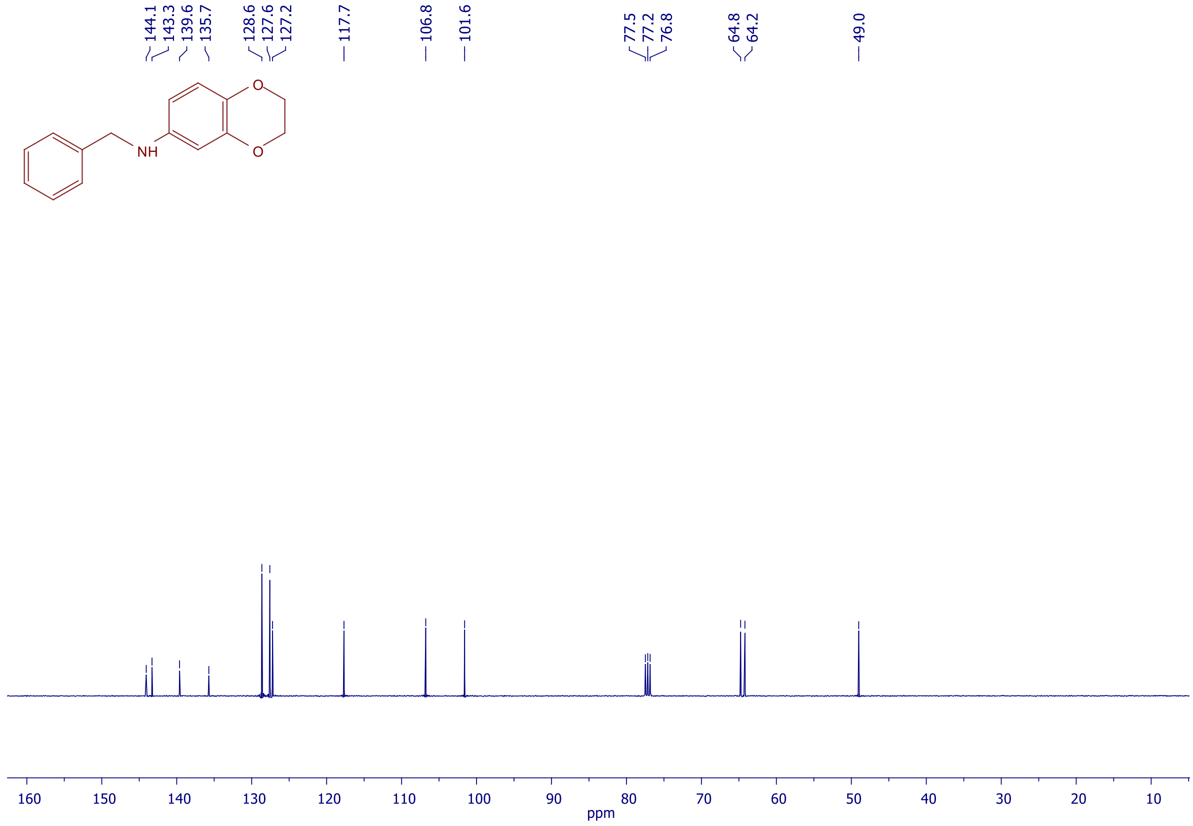
^{1}H *NMR of N-benzylnaphthalen-1-amine (Compound-**3am**)*



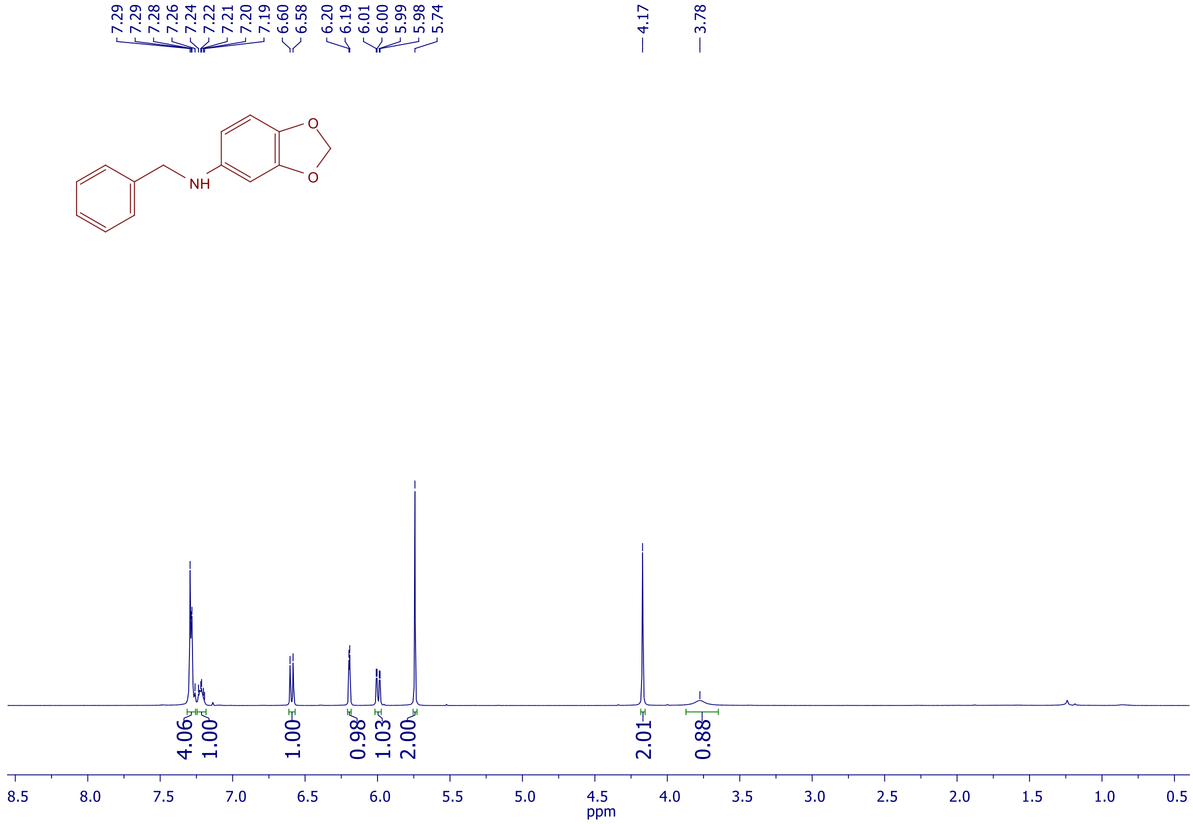
$^{13}C\{^{1}H\}$ *NMR of N-benzylnaphthalen-1-amine (Compound-**3am**)*



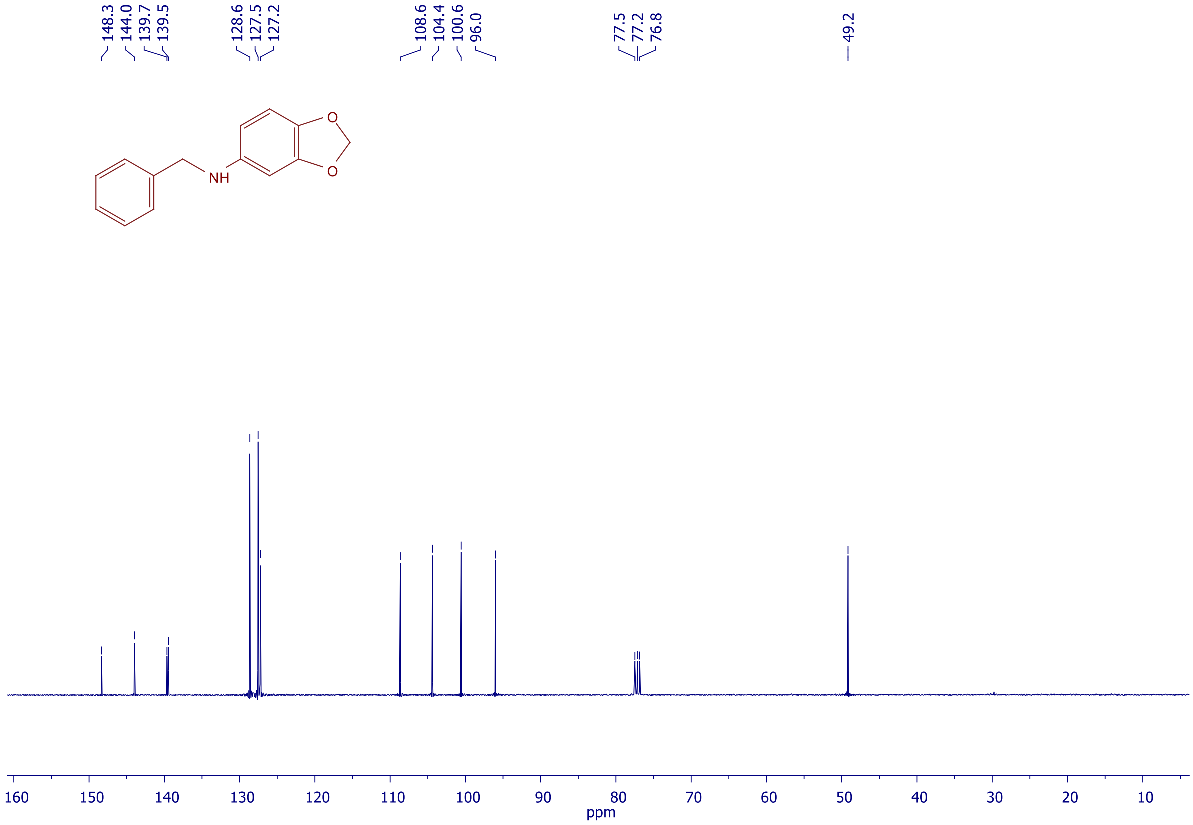
^{1}H *NMR of N-benzyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (Compound-**3an**)*



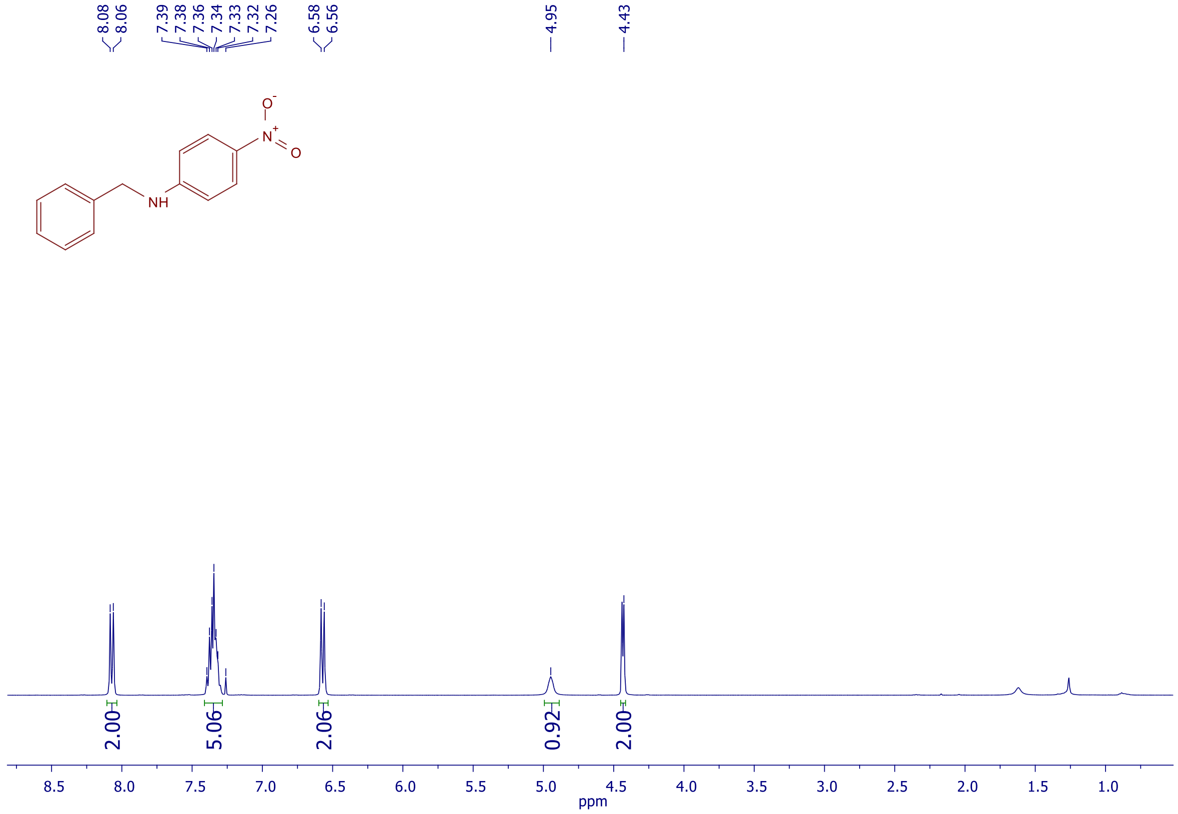
*^{13}C{^{1}H} NMR of N-benzyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine (Compound-**3an**)*



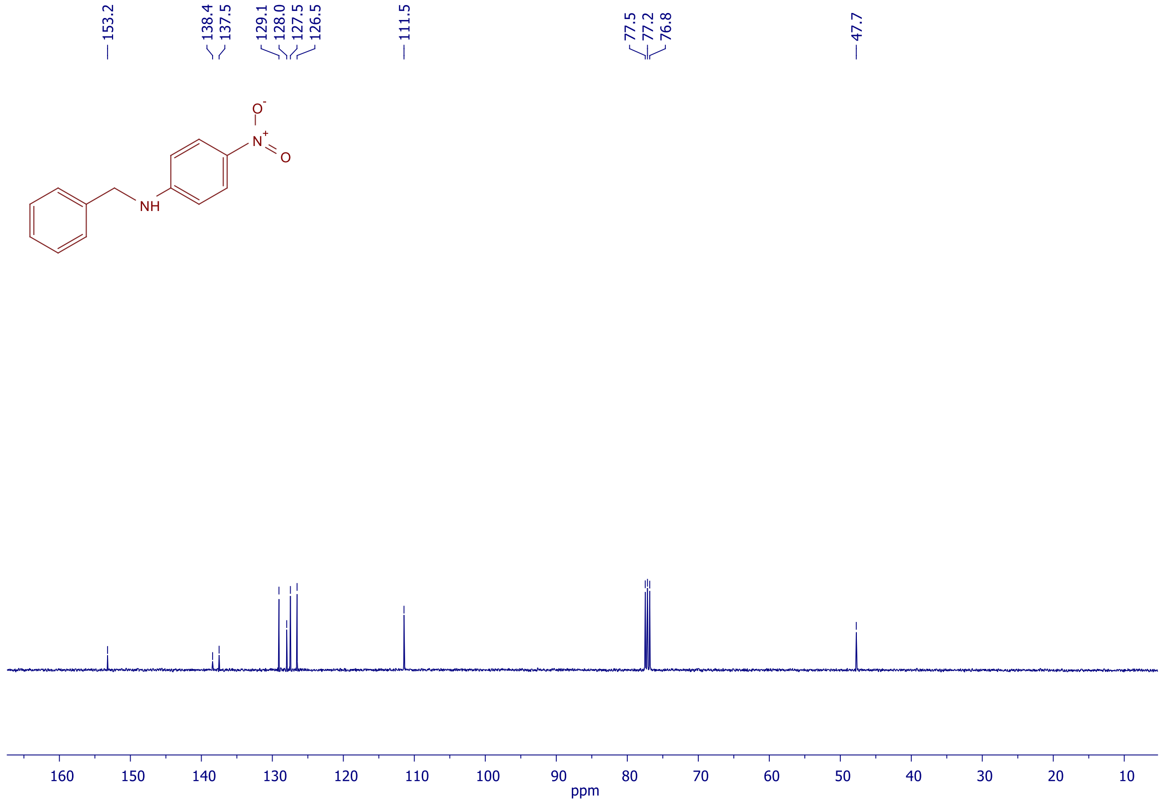
*^{1}H NMR of N-benzylbenzo[d][1,3]dioxol-5-amine (Compound-**3ao**)*



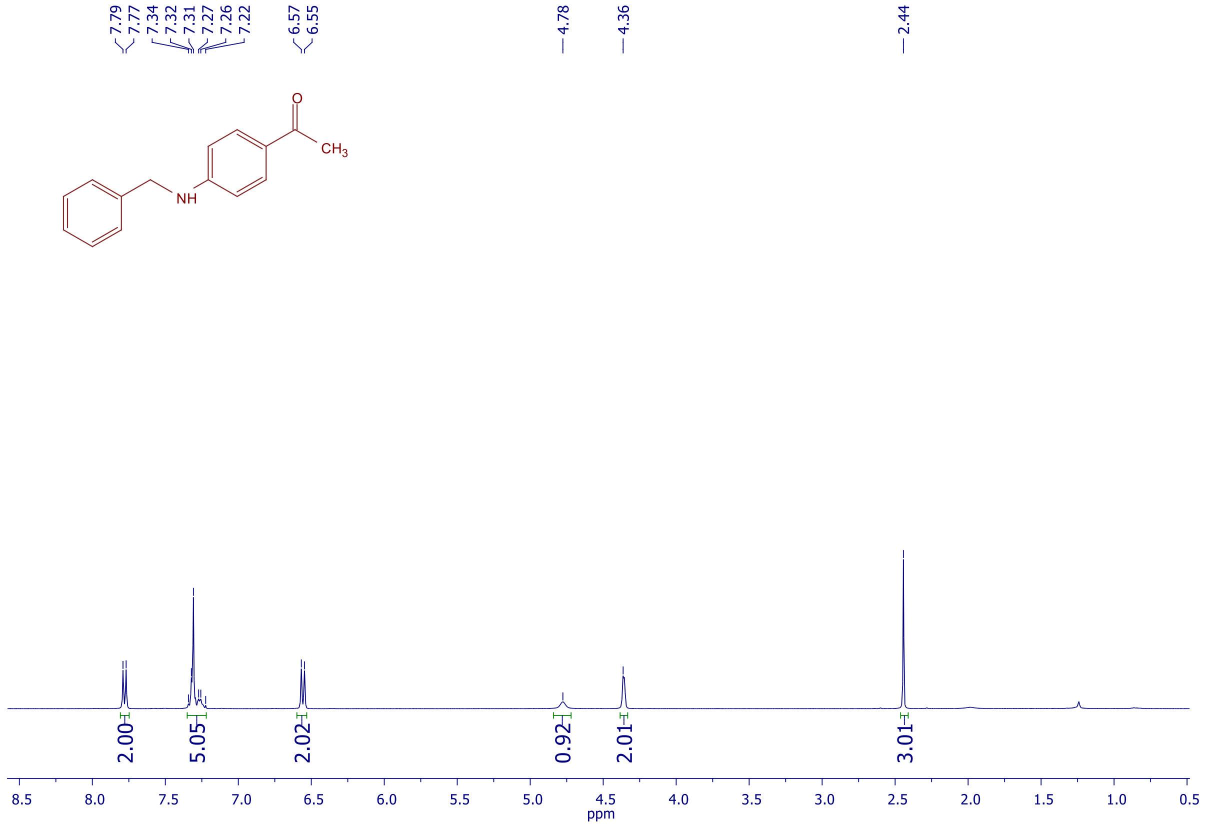
^{13}C{^{1}H} *NMR of N-benzylbenzo[d][1,3]dioxol-5-amine (Compound-**3ao**)*



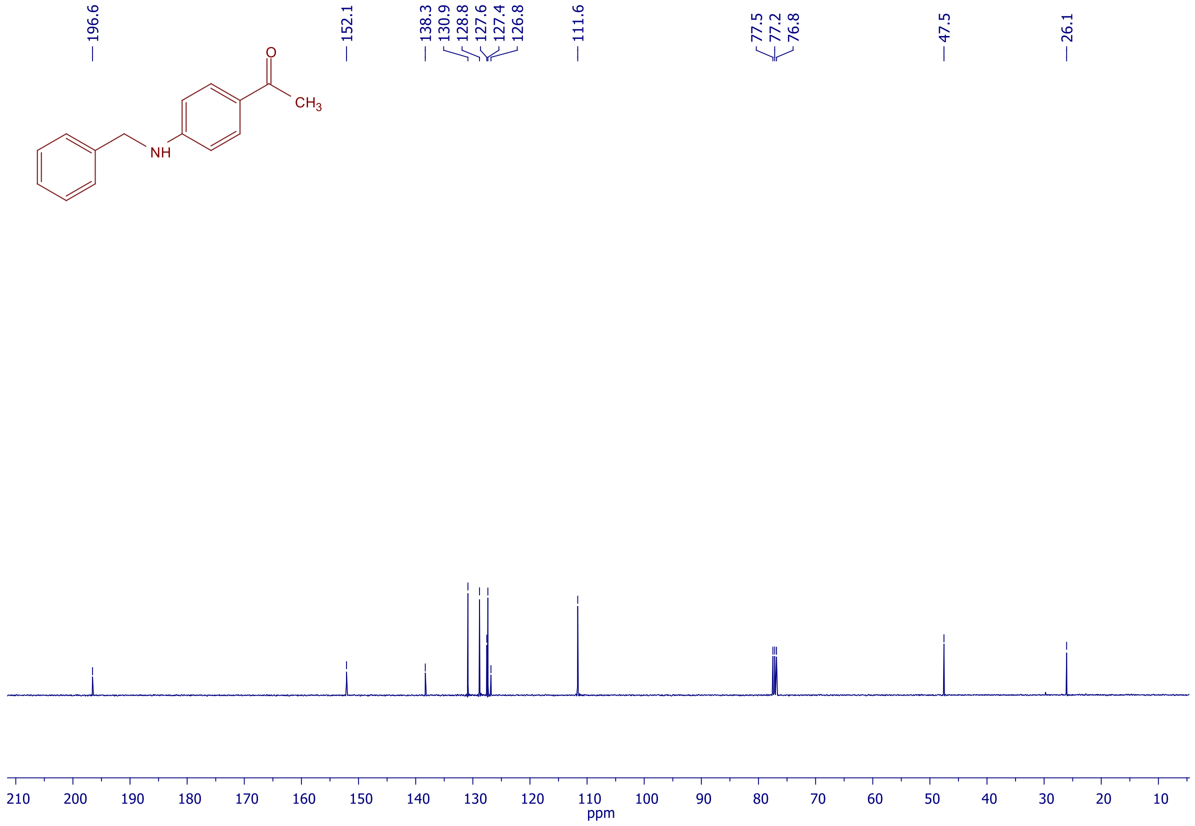
^{1}H *NMR of N-benzyl-4-nitroaniline (Compound-**3ap**)*



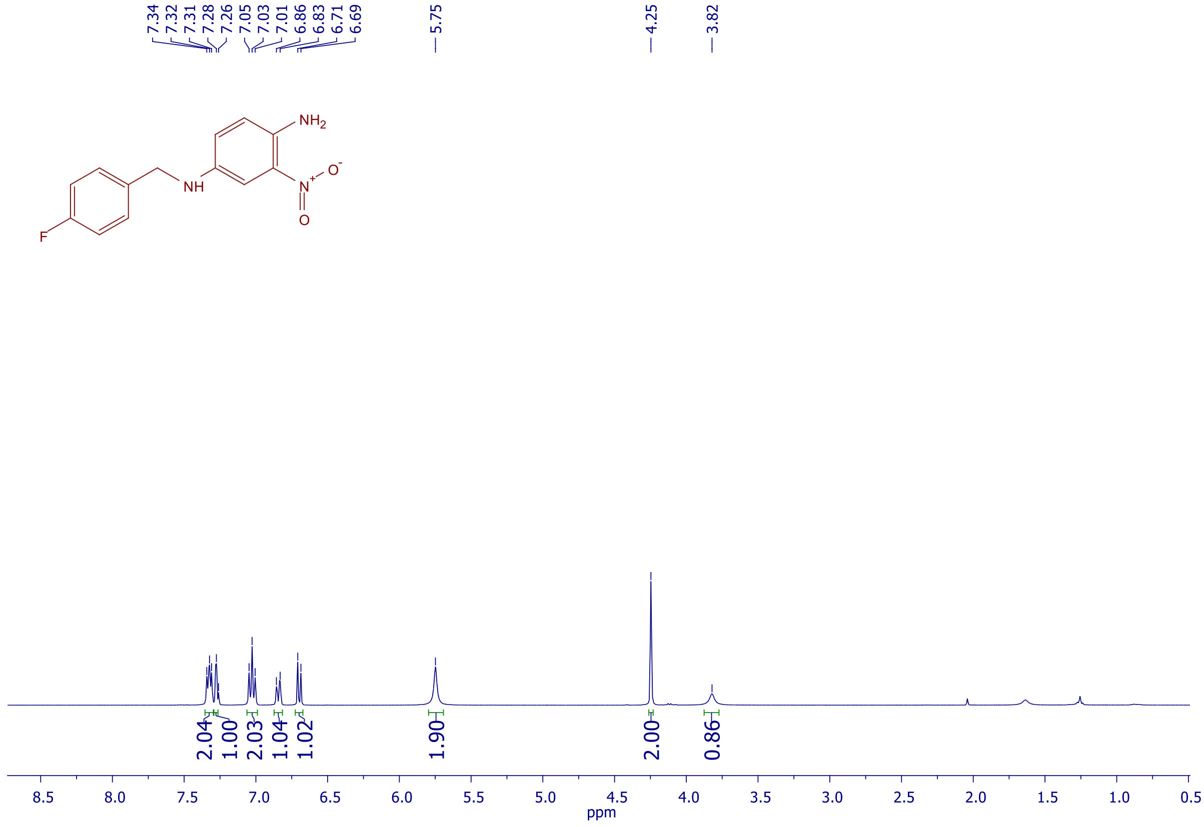
^{13}C{^{1}H} *NMR of N-benzyl-4-nitroaniline (Compound-****3ap****)*



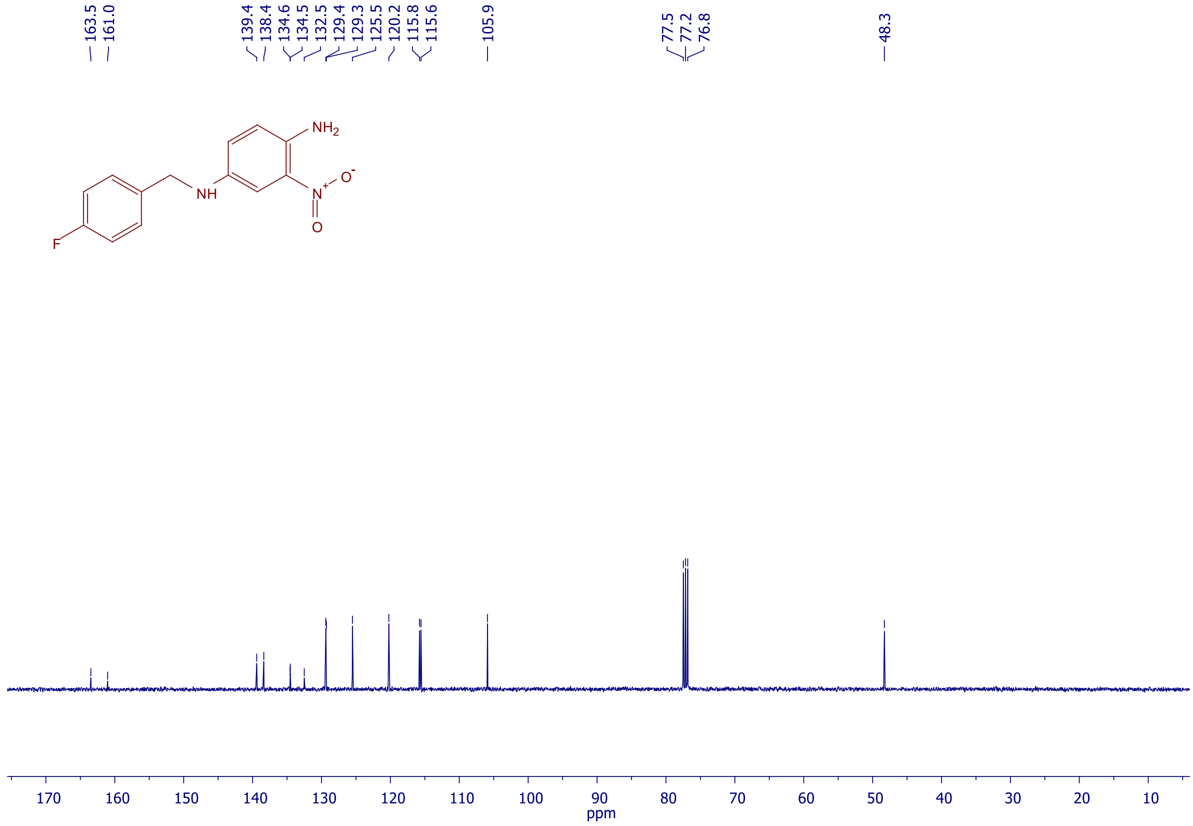
^{1}H *NMR of 1-(4-(benzylamino)phenyl)ethan-1-one (Compound-****3aq****)*



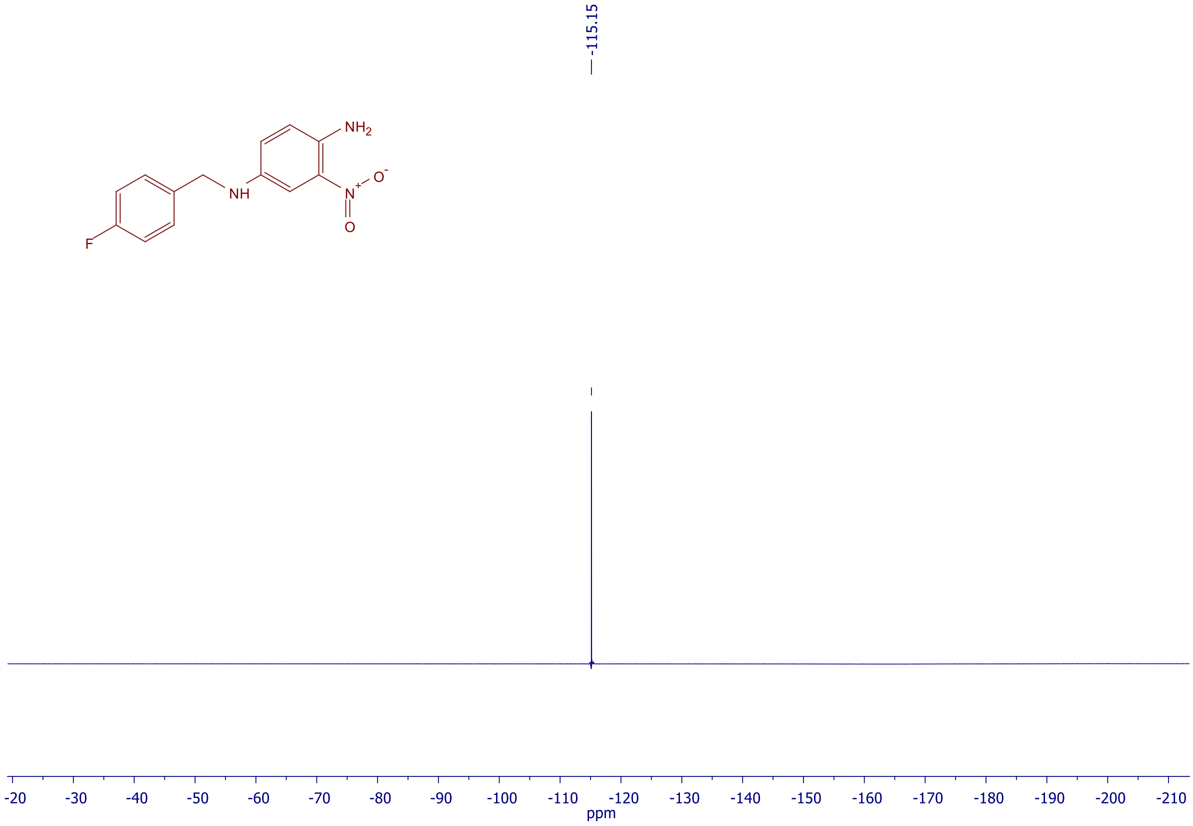
^{13}C{^{1}H} *NMR of1-(4-(benzylamino)phenyl)ethan-1-one (Compound-**3aq**)*



^{1}H *NMR of N1-(4-fluorobenzyl)-3-nitrobenzene-1,4-diamine (Compound-**3es**)*



*$^{13}C\{^{1}H\}$ NMR of N1-(4-fluorobenzyl)-3-nitrobenzene-1,4-diamine (Compound-**3es**)*



*^{19}F NMR of N1-(4-fluorobenzyl)-3-nitrobenzene-1,4-diamine (Compound-**3es**)*

Procedure for the chemo selective formation of *N*-benzylaniline:

Benzaldehyde, aniline and acetophenone: An oven dried schlenk tube (5 mL) was charged with 4 Å molecular sieve, aldehyde (53 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and acetophenone (60 mg, 0.5 mmol) under inert condition and stirred for 30 minutes at room temperature. After that the schlenk tube was taken into a glove box, pinacolborane (70 mg, 0.55 mmol) was added and the reaction mixture was allowed to stir at room temperature for 6 h. Upon completion of the reaction, $CDCl_3$ and nitro methane (0.5 mmol) were added to the reaction mixture and ^1H NMR of the reaction mixture was recorded which shows the presence of only *N*-benzylaniline and the unreacted starting materials.

Benzaldehyde, aniline and benzamide: An oven dried schlenk tube (5 mL) was charged with 4 Å molecular sieve, aldehyde (53 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and benzamide (60 mg, 0.5 mmol) under inert condition and stirred for 30 minutes at room temperature. After that the schlenk tube was taken into a glove box, pinacolborane (77 mg, 0.60 mmol) was added and the reaction mixture was allowed to stir at room temperature for 6 hours. Upon completion of the reaction, $CDCl_3$ and nitro methane (0.5 mmol) were added to the reaction mixture and ^1H NMR of the reaction mixture was recorded which shows the presence of only *N*-benzylaniline and the unreacted starting materials.

Benzaldehyde, aniline and N-methylaniline: An oven dried schlenk tube (5 mL) was charged with 4 Å molecular sieve, aldehyde (53 mg, 0.5 mmol), aniline (49 mg, 0.525 mmol), and *N*-methylaniline (53.5 mg, 0.5 mmol) under inert condition and stirred for 30 minutes at room temperature. After that the schlenk tube was taken into a glove box, pinacolborane (70 mg, 0.55 mmol) was added and the reaction mixture was allowed to stir at room temperature for 6 hours. Upon completion of the reaction, $CDCl_3$ and nitro methane (0.5 mmol) were added to the reaction mixture and ^1H NMR of the reaction mixture was recorded which shows the presence of only *N*-benzylaniline and the unreacted starting materials.

^{1}H NMR spectra of the chemoselectivity experiments:

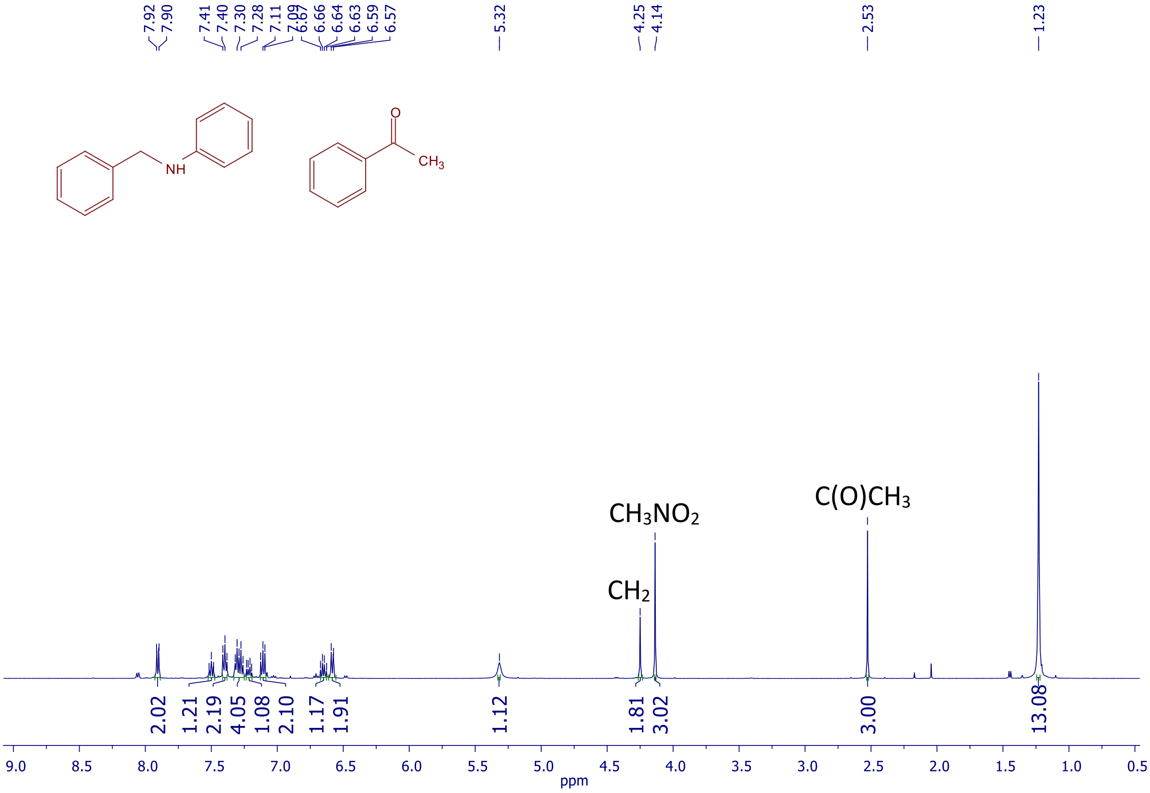


Figure S1. *^{1}H NMR of the chemoselectivity experiment involving benzaldehyde, aniline, and acetophenone. $MeNO_2$ is used as an internal standard.*

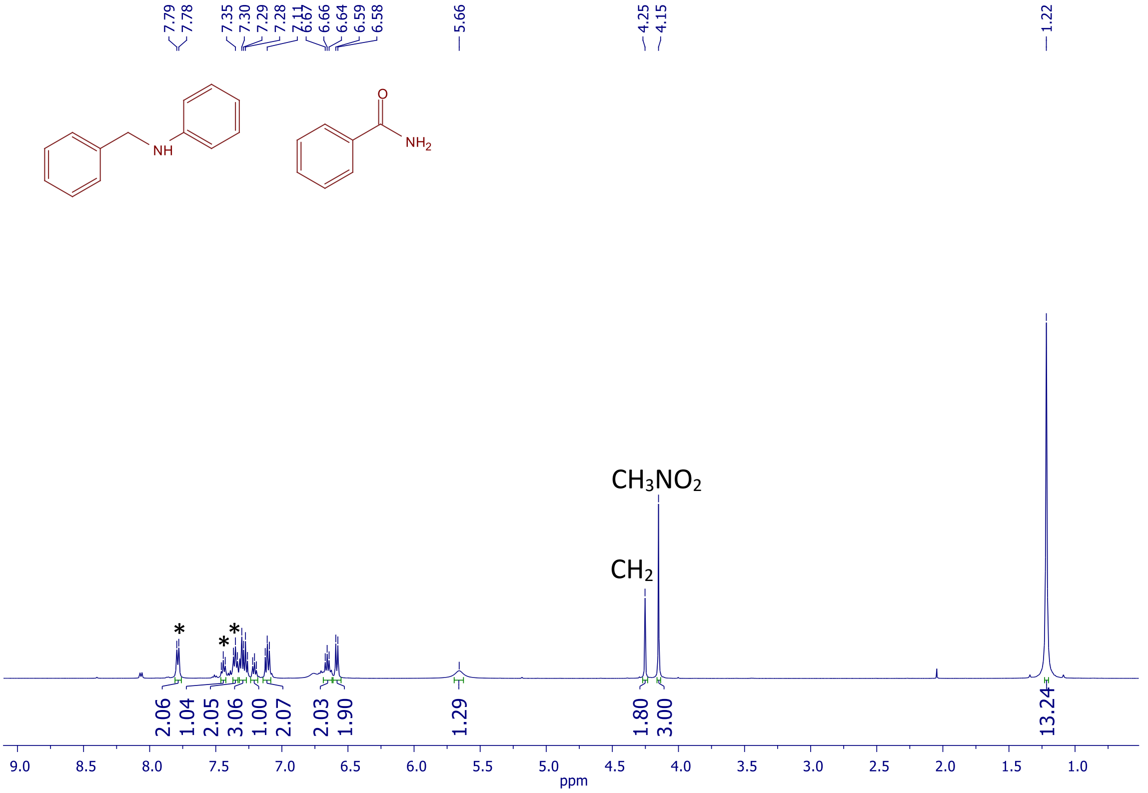


Figure S2. *^{1}H NMR of chemoselectivity experiment involving benzaldehyde, aniline, and benzamide. $MeNO_2$ is used as an internal standard. * represents the peaks corresponding to benzamide.*

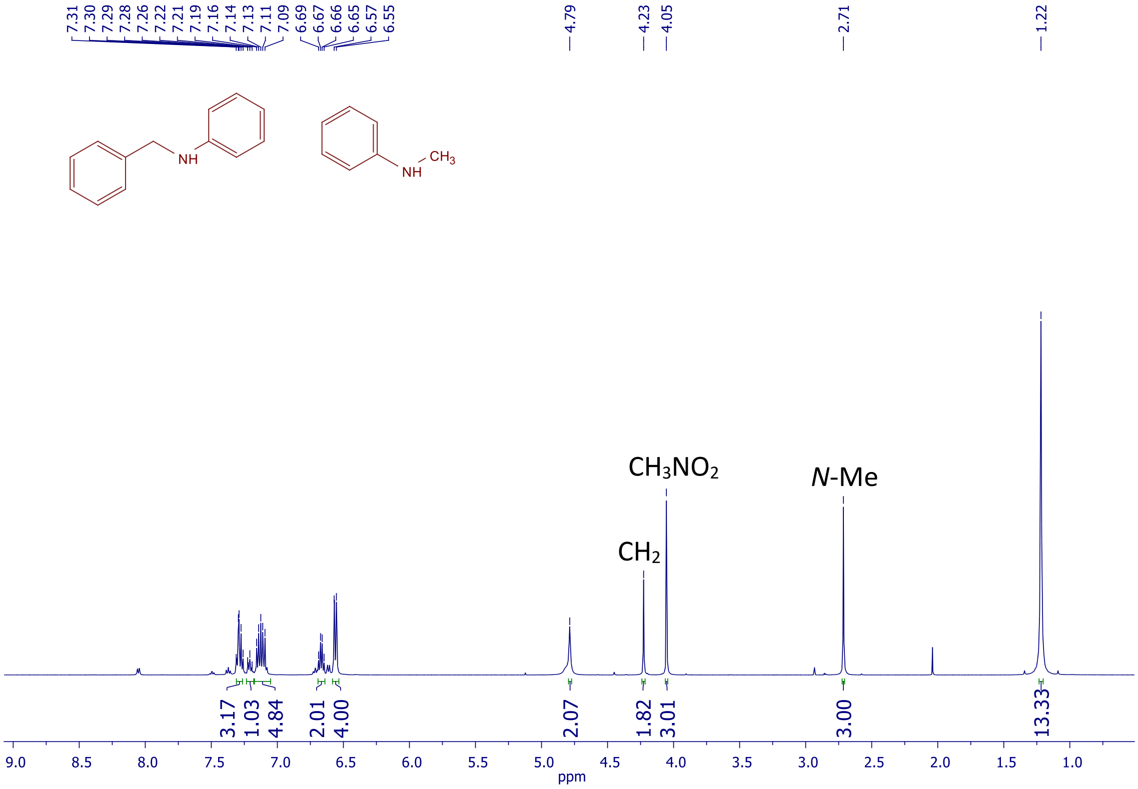
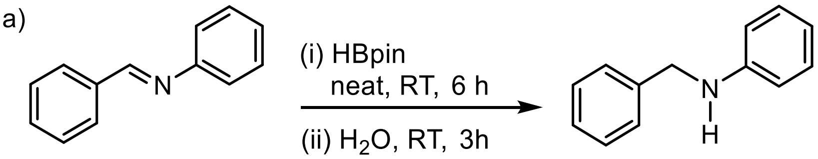


Figure S3. *^{1}H NMR of chemoselectivity experiment involving benzaldehyde, aniline, and N-methylaniline. $MeNO_2$ is used as an internal standard.*

^{1}H NMR spectra of the mechanistic studies:



An oven dried schlenk tube (5 mL) was charged with *N*-benzylidene aniline (0.5 mmol) and pinacolborane (0.65 mmol) and the resulting mixture was stirred for 6 h at room temperature. After the completion of the reaction, 0.3 mL of H_2O was added and stirred at RT for 3 h. After that $CDCl_3$ was added to the reaction mixture and NMR spectra were recorded.

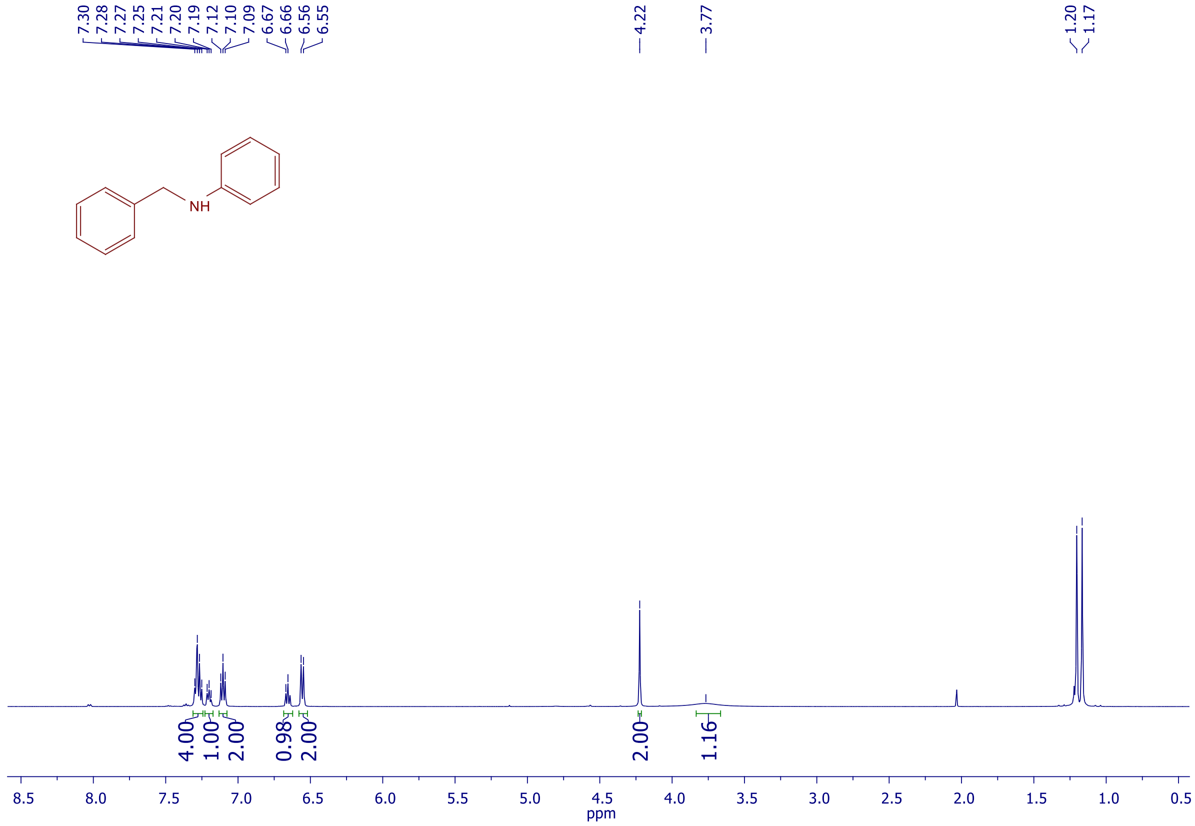


Figure S4. *^{1}H NMR spectrum of the imine hydroboration followed by hydrolysis with H_2O.*

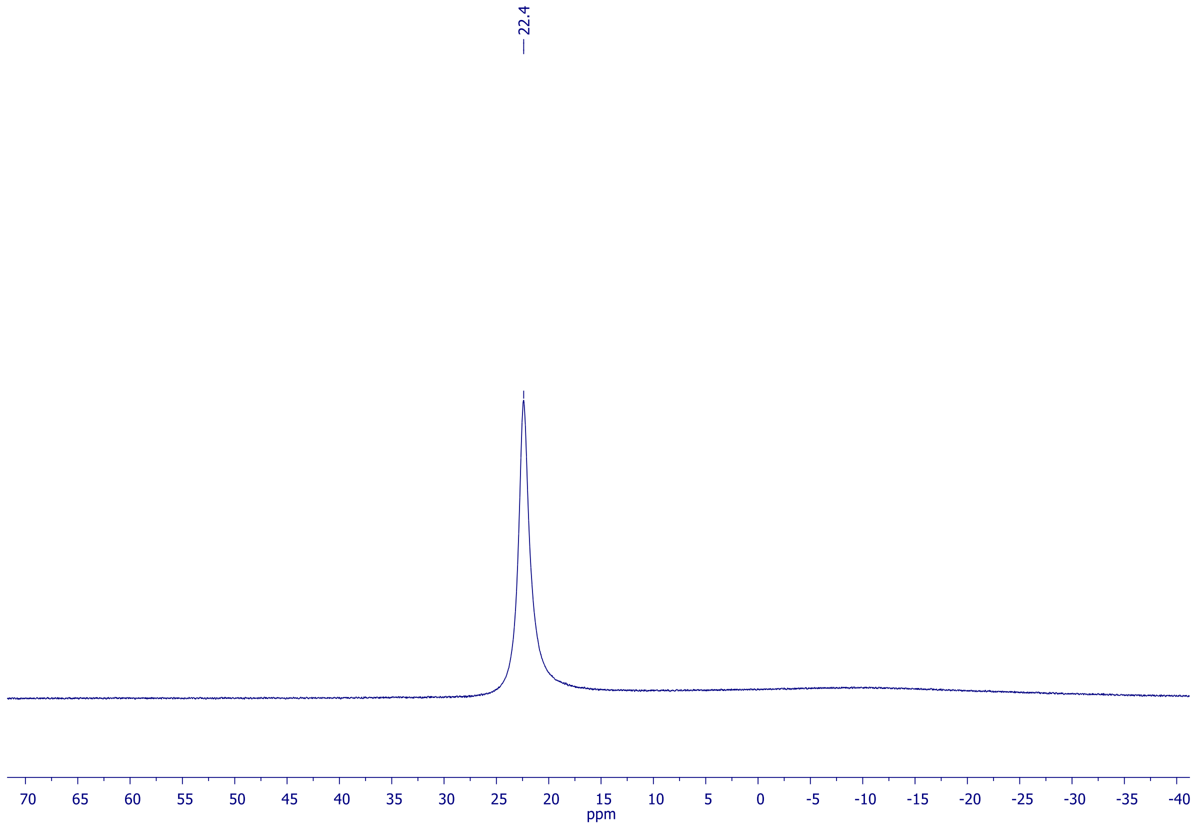
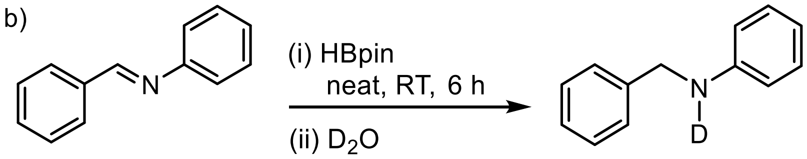


Figure S5. *^{11}B{^{1}H} NMR spectrum of the reaction mixture of imine hydroboration followed by hydrolysis with H_2O.*



An oven dried schlenk tube (5 mL) was charged with *N*-benzylidene aniline (0.5 mmol) and pinacolborane (0.65 mmol) and the resulting mixture was stirred for 6 h at room temperature. After the completion of the reaction, 0.3 mL of D_2O was added and stirred at RT for 3 h. After that $CDCl_3$ was added to the reaction mixture and NMR spectra were recorded.

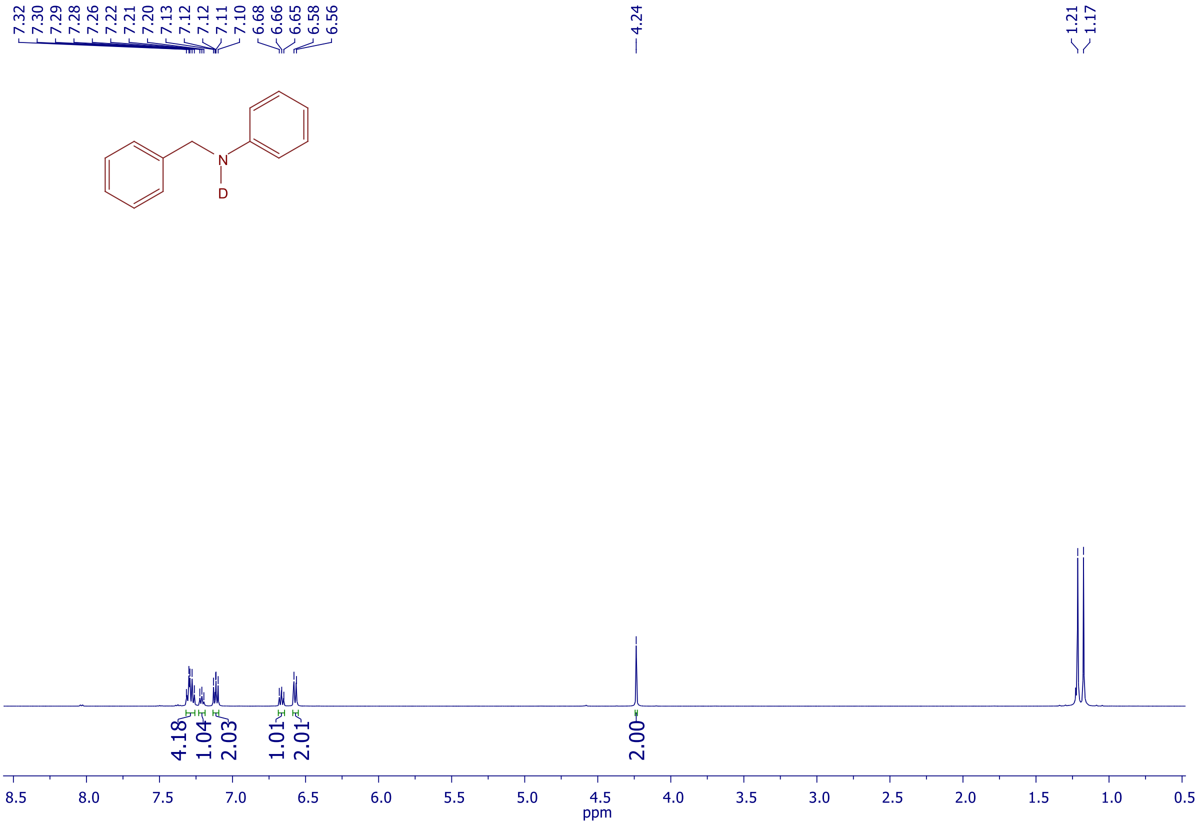


Figure S6. *^{1}H NMR spectrum of the imine hydroboration followed by hydrolysis with D_2O.*

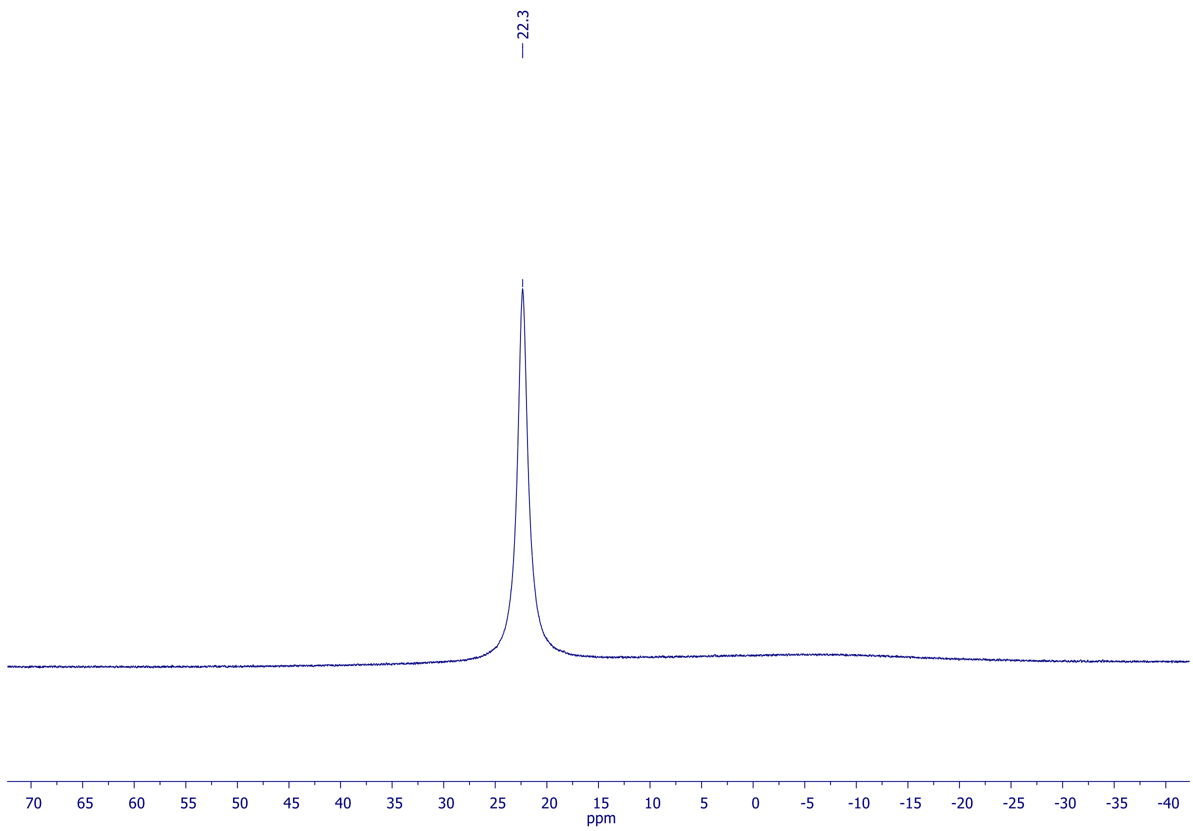
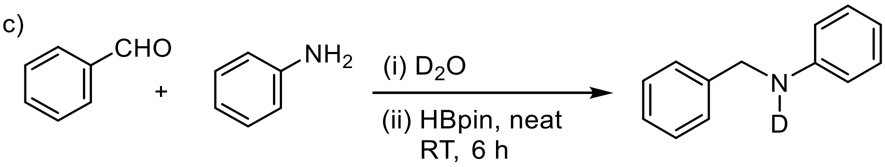


Figure S7. *$^{11}B\{^1H\}$ NMR spectrum of the reaction mixture of imine hydroboration followed by hydrolysis with D_2O.*



An oven dried schlenk tube (5 mL) was charged with 4 Å molecular sieve, aldehyde (0.5 mmol) and aniline (0.525 mmol, 1.05 equiv.) under inert atmosphere using standard Schlenk line and stirred for 30 mins at ambient temperature. After that D_2O (0.1 mL) was added to the schlenk tube and stirred for some time before the addition of pinacolborane (0.65 mmol). The reaction mixture was then stirred at room temperature for 6 h and after the completion of the reaction, $CDCl_3$ was added to a portion of the reaction mixture and NMR spectra were recorded.

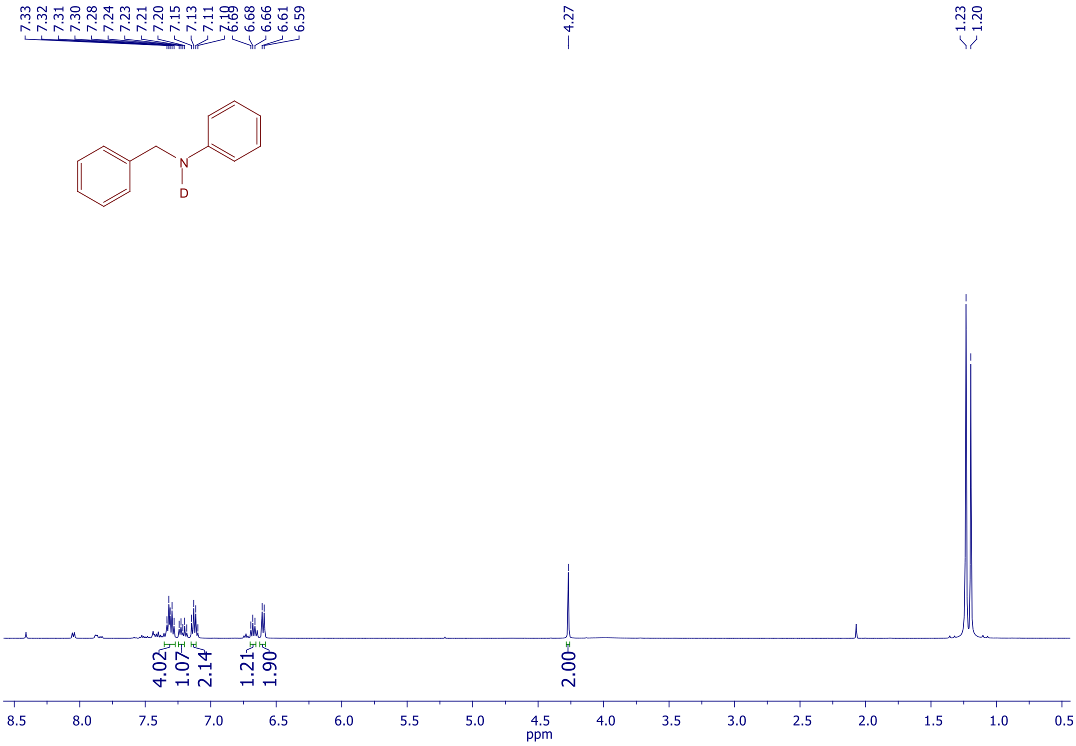


Figure S8. *^{1}H NMR spectrum of the reaction performed under our optimized conditions in the presence of D_2O.*

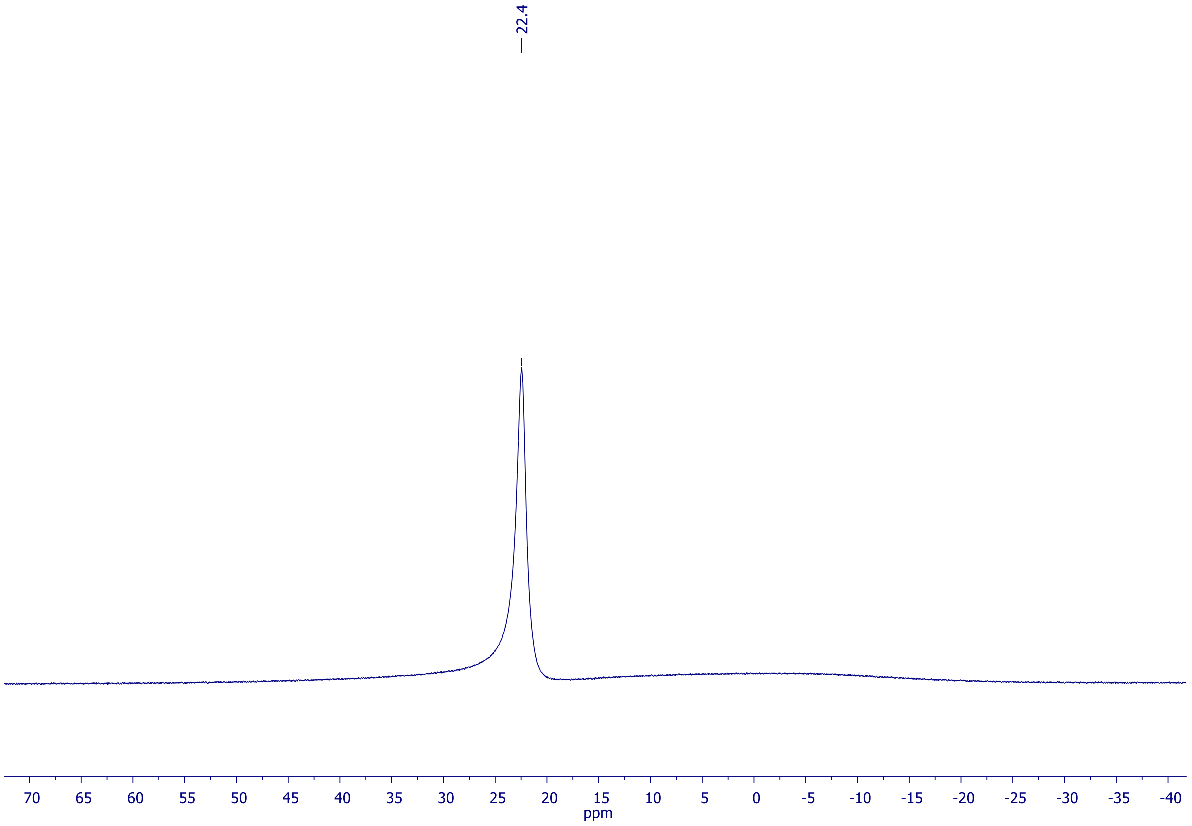


Figure S9. *$^{11}B\{^1H\}$ NMR spectrum of the reaction performed under our optimized conditions in the presence of D_2O.*

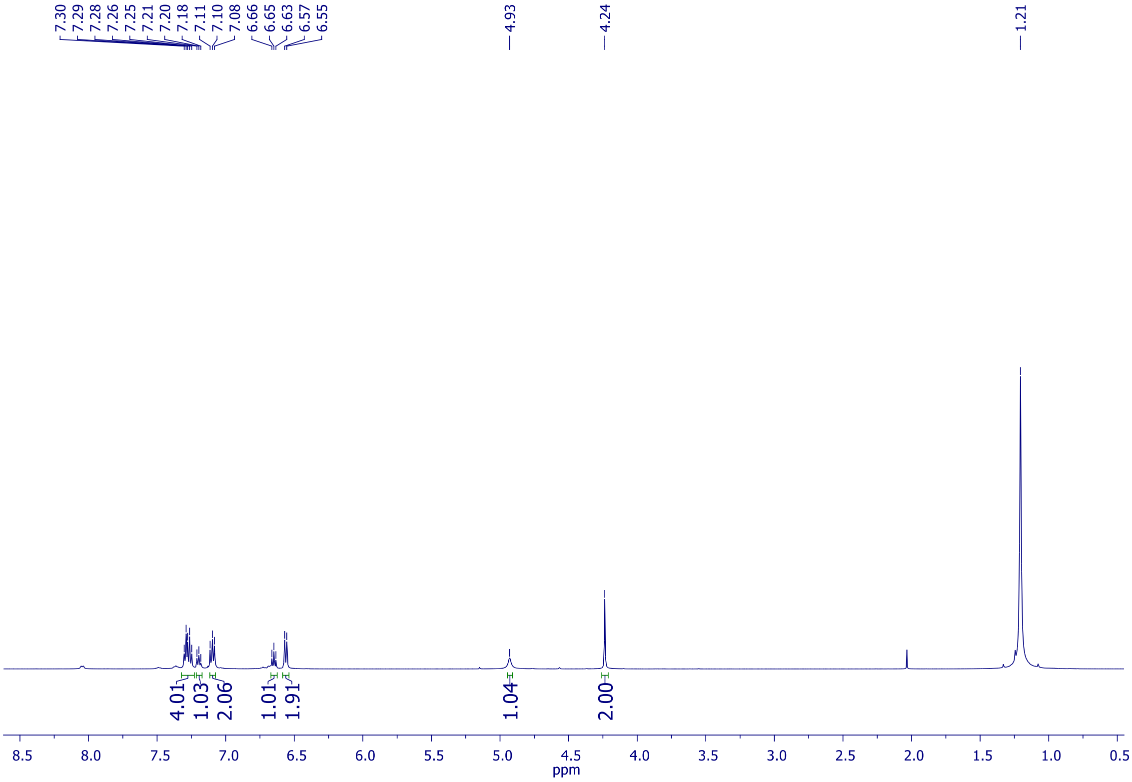


Figure S10. *^{1}H NMR spectrum of the reaction between aniline and benzaldehyde performed under our optimized conditions.*

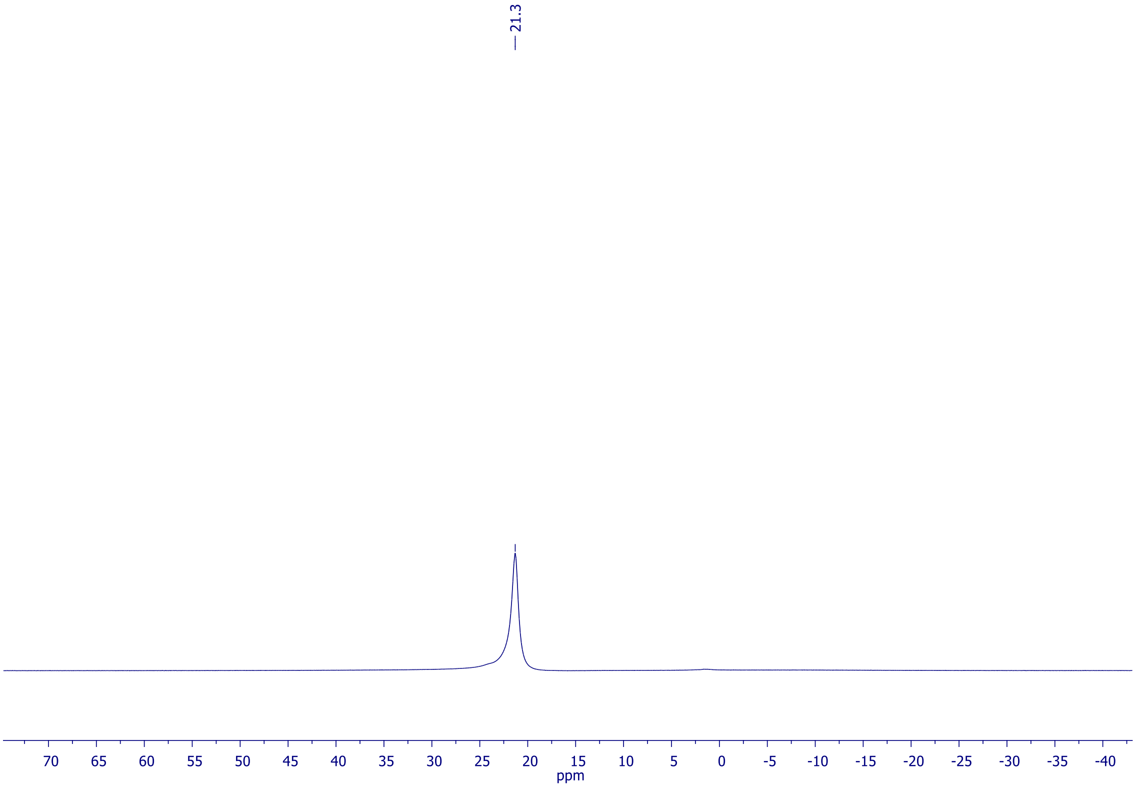


Figure S10. *^{11}B{^{1}H} NMR spectrum of the reaction between aniline and benzaldehyde performed under our optimized conditions.*