Supplementary Material (ESI) for Chemical Communications

Supporting Information

Title: The Reductive Amination of Aldehydes and Ketones by Catalytic Use of Dibutylchlorotin Hydride Complex

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General:

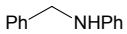
IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All ^{1}H and ^{13}C-NMR spectra were recorded with a JEOL JNM-GSX-270 (270 and 67 MHz, respectively) or JEOL JMTC-400/54/SS (400 and 100 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using Fuji Davison silica gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel.

A typical experimental procedure for Reductive Amination:

To the solution of Bu_2SnH_2 (0.025 mmol) and Bu_2SnCl_2 (0.025 mmol) in 2.5 mL of THF was added pyridine *N*-oxide (0.05 mmol). The mixture was stirred at room temperature for 5 min. To the solution were added carbonyl compound (2.5 mmol), amine (2.5 mmol) and hydrosilane (2.7 mmol), and the resulting mixture was stirred at room temperature for 2 h. After quenching with H_2O (5 mL), the reaction mixture was extracted with ether (10 mL x 2). The combined organic layer was dried over $MgSO_4$ and concentrated. The residue was subjected to column chromatography eluting with hexane/EtOAc. Tin or silane residue and Pyridine *N*-Oxide were removed by this treatment. Further purification was performed by TLC eluting with hexane/Et_2O. Product was determined by ^{1}H NMR.

***N*-Benzylaniline (3a)**

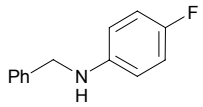
Reference : T. Kawakami, T. Sugimoto, I. Shibata, A. Baba, H. Matsuda and N. Sonoda, *J. Org. Chem.,* 1995, **60**, 2677-2682.



White solid; mp 35.5-37.8 ^{o}C (lit. 36-37.2 ^{o}C); IR (KBr) 3400, 1320cm^{-1}; ^{1}H NMR ($CDC1_3$, 400 MHz) δ 3.88 (br, 1H), 4.23 (s, 2H), 6.55-7.32 (m, 10H); ^{13}C NMR ($CDC1_3$, 100.6 MHz) δ 48.1, 112.7, 117.4, 127.1,127.4, 128.5, 129.2, 139.4, 148.1; HRMS calcd for $C_{13}H_{13}N$, 183.1049, found 183.1033.

lit.**)** K. A. Schellenberg, *J. Org. Chem.,* 1963, **28**, 3259-3261.

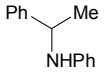
_N_-Benzyl-_p_-fluoroaniline (3b)



Yellow liquid; IR (neat) 3421cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.93 (br, 1H), 4.28 (s, 2H), 6.55 (dd, *J*=4.39 and 8.78 Hz, 2H), 6.87 (t, *J*=8.78 Hz, 2H), 7.27-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 48.4, 113.0 (d, $J_{C\text{-}F}$=7 Hz), 115.1 (d, $J_{C\text{-}F}$=22 Hz), 126.7, 126.9, 128.1, 138.6, 143.9, 155.2 (d, $J_{C\text{-}F}$=234 Hz); MS (m/z) 201 (49), 124 (8), 91 (100); HRMS calcd for $C_{13}H_{12}FN$: 201.0954, found: 201.0965 (+1.1 mmu); Anal calcd for $C_{13}H_{12}FN$: C, 77.59; H, 6.01; N, 6.96; F, 9.44, found: C, 77.42; H, 6.09; N, 6.98; F, 9.49.

N-α-Phenethylphenylamine (3c)

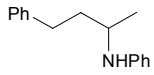
Reference : T. Kawakami, T. Sugimoto, I. Shibata, A. Baba, H. Matsuda and N. Sonoda, *J. Org. Chem.,* 1995, **60**, 2677-2682.



Colorless liquid; IR (neat) 3380, 1305cm^{-1}; ^{1}H NMR ($CDC1_3$ 400 MHz) δ 1.48 (d, *J*=6.84 Hz, 3H,), 3.99 (br, 1H), 4.46 (q, *J*=6.84 Hz, 1H), 6.47-7.36 (m, 10H); ^{13}C NMR ($CDC1_3$, 100.6 MHz) δ 25.0, 53.4, 113.2, 117.2, 125.8, 126.8, 128.6, 129.0, 145.2,147.2; HRMS calcd for $C_{14}H_{15}N$ 197.1206, found 197.1199 (-0.7 mmu).

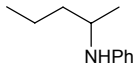
***N*-2-(4-Phenylbutyl)aniline (3d)**

Reference : T. Suwa, E. Sugiyama, I. Shibata and A. Baba, *Synthesis*, 2000, 789–800.



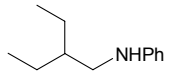
Colorless liquid; IR (neat) 3402 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.21 (d, *J*=6.4 Hz, 3H), 1.69-1.94 (m, 2H), 2.72 (t, *J*=7.8 Hz, 2H), 3.42 (br,1H), 3.48 (tq, *J*=6.4 and 6.4 Hz, 1H), 6.50 (d, *J*=7.8 Hz, 2H), 6.65 (t, , *J*=7.8 Hz, 1H), 7.10-7.29 (m, 7H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.8, 32.5, 38.8, 47.9, 113.2, 116.9, 125.8, 128.4, 128.4, 129.3, 142.0, 147.6; HRMS calcd for $C_{16}H_{19}N$ 225.1519, found 225.1515 (-0.4 mmu).

_N_-2-Pentylaniline (3e)



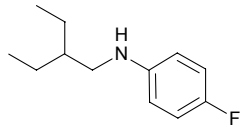
Yellow liquid; IR (neat) 3405 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.92 (t, *J*=7.08 Hz, 3H), 1.16 (d, *J*=6.10 Hz, 3H), 1.33-1.61(m, 4H), 3.42-3.49 (m, 2H), 6.56 (d, *J*=8.05 Hz, 2H), 6.65 (t, *J*=7.32 Hz, 1H), 7.15 (dd, J=7.32 and 8.05 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 14.1, 19.3, 20.8, 39.4, 48.1, 112.9, 116.6, 129.1, 147.6; MS (m/z) 163 (13), 120 (100), 77 (7); HRMS calcd for $C_{11}H_{17}N$: 163.1361, found: 163.1356 (-0.5 mmu); Anal calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58, found: C, 80.67; H, 10.47; N, 8.43.

_N_-(2-Ethylbutyl)aniline (3f)



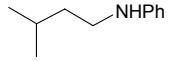
Colorless liquid; IR (neat) 3421cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.91 (t, *J*=7.32 Hz, 6H), 1.34-1.55 (m, 5H), 3.01 (d, *J*=5.86 Hz, 2H), 3.58 (br, 1H), 6.59 (d, *J*=8.54 Hz, 2H), 6.66 (t, *J*=7.32 Hz, 1H), 7.16 (dd, J=7.32 and 8.54 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 10.9, 24.0, 40.5, 46.5, 112.5, 116.8, 129.1, 148.6; MS (m/z) 177 (2), 106 (100), 77 (7); HRMS calcd for $C_{12}H_{19}N$: 177.1517, found: 177.1522 (+0.5 mmu); Anal calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.92, found: C, 81.03; H, 10.68; N, 7.82.

_N_-(2-Ethylbutyl)-_p_-fluoroaniline (3g)



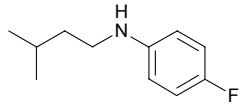
Yellow liquid; IR (neat) 3428cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.90 (t, *J*=7.08 Hz, 6H), 1.34-1.53 (m, 5H), 2.96 (d, *J*=5.86 Hz, 2H), 3.47 (br, 1H), 6.52 (dd, *J*=4.39 and 8.78 Hz, 2H), 6.87 (t, *J*=8.78 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 10.9, 23.9, 40.5, 47.3, 113.2 (d, J_{C-F}=7 Hz), 115.5 (d, J_{C-F}=22 Hz), 145.0, 155.4 (d, J_{C-F}=233 Hz); MS (m/z) 195 (2), 124 (100), 95 (3); HRMS calcd for $C_{12}H_{18}FN$: 195.2765, found: 195.2765 (+0.0 mmu); Anal calcd for $C_{12}H_{18}FN$: C, 73.81; H, 9.29; N, 7.17; F, 9.73, found: C, 74.08; H, 9.28; N, 7.23; F, 9.78.

_N_-(3-Methylbutyl)aniline (3h)



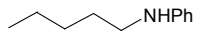
Colorless liquid; IR (neat) 3409 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.94 (d, *J*=6.59 Hz, 6H), 1.50 (dt, *J*=6.83 and 7.32 Hz, 2H), 1.64-1.79 (m, 1H), 3.11 (t, *J*=7.32 Hz, 2H), 3.53 (br, 1H), 6.59 (d, *J*=8.30 Hz, 2H), 6.68 (t, *J*=7.32 Hz, 1H), 7.16 (dd, *J*=7.32 and 8.30 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 22.6. 26.0, 38.5, 42.1, 112.6, 117.0, 129.1, 148.4; MS (m/z) 163 (2), 106 (100), 77 (9); HRMS calcd for $C_{11}H_{17}N$: 163.1361, found: 163.1346 (-1.5 mmu); Anal calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50; N, 8.58, found: C, 80.80; H, 10.42; N, 8.40.

_N_-(3-Methylbutyl)-*p*-fluoroaniline (3i)



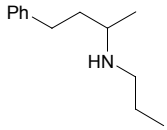
Yellow liquid; IR (neat) 3417cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.94 (d, *J*=6.83 Hz, 6H), 1.48 (dt, *J*=6.83 and 7.32 Hz, 2H), 1.63-1.75 (m, 1H), 3.05 (t, *J*=7.32 Hz, 2H), 3.45 (br, 1H), 6.49-6.55 (m, 2H), 6.84-6.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 22.6, 26.0, 38.5, 42.8, 113.3 (d, J_{C-F}=7 Hz), 115.5 (d, J_{C-F}=22 Hz), 144.8, 155.5 (d, J_{C-F}=234 Hz); MS (m/z) 181 (19), 124 (100), 95 (4); HRMS calcd for $C_{11}H_{16}FN$: 181.1267, found: 181.1268 (+0.1 mmu); Anal calcd for $C_{11}H_{16}FN$: C, 72.89; H, 8.90; N, 7.73; F, 10.48, found: C, 72.73; H, 8.75; N, 7.71; F, 10.50.

_N_-1-Pentylaniline (3j)



Yellow liquid; IR (neat) 3409 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.91 (t, *J*=6.83 Hz, 3H), 1.35-1.38 (m, 4H), 1.59-1.64(m, 2H), 3.09 (t, *J*=7.08 Hz, 2H), 3.62 (br, 1H), 6.60 (d, *J*=7.56 Hz, 2H), 6.68 (t, *J*=7.32 Hz, 1H), 7.14-7.19 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 14.0, 22.5, 29.2, 29.3, 43.9, 112.6, 116.9, 129.1, 148.4; MS (m/z) 163 (18), 106 (100), 77 (8); HRMS calcd for $C_{11}H_{17}N$: 163.1361, found: 163.1353 (-0.8 mmu).

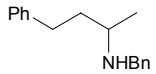
_N_-Propyl-4-phenyl-2-butylamine (3k)



Yellow liquid; IR (neat) 3309 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, *J*=7.24 Hz, 3H), 1.09 (d, *J*=6.27 Hz, 3H), 1.47 (tq, *J*=7.24 and 7.36 Hz, 2H), 1.61 (ddt, *J*=6.52 and 13.76 and 9.90 Hz, 1H), 1.78 (ddt, *J*=6.27 and 13.76 and 9.90 Hz, 1H) 2.47-2.70 (m, 5H), 7.15-7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 11.8, 20.3, 23.5, 32.3, 38.7, 49.1, 52.6, 125.6, 128.2, 128.2, 142.4; MS (m/z) 191 (3), 91 (25), 86 (100); HRMS calcd for $C_{13}H_{21}N$: 191.1674, found: 191.1661 (-1.3 mmu).

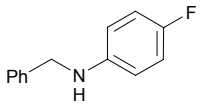
_N_-Benzyl-2-(4-phenyl)-butylamine (3l)

Reference : T. Suwa, E. Sugiyama, I. Shibata and A. Baba, *Synlett*, 2000, 556-558.

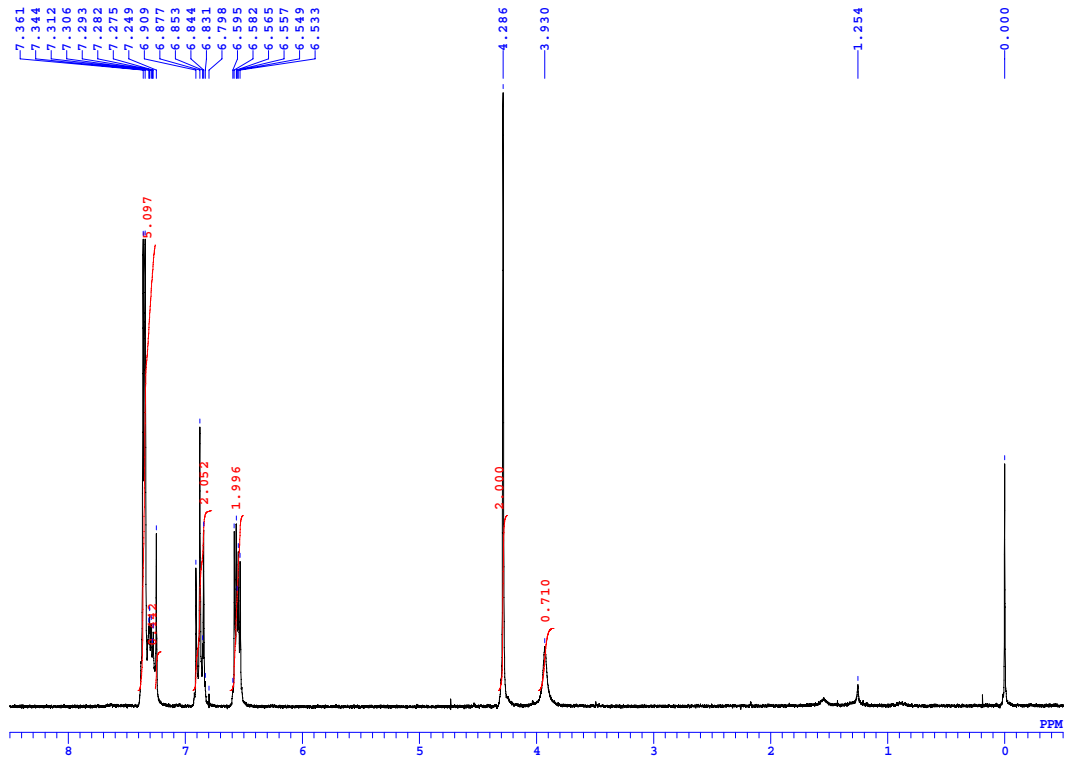


Colorless liquid; IR (neat) 3325 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.13 (d, *J*=6.4 Hz, 3H), 1.36 (br,1H), 1.65 (dt, *J*=6.8 and 6.8 Hz, 1H), 1.80 (dt, *J*=6.8 and 6.8 Hz, 1H), 2.64 (t, *J*=6.8 Hz, 2H), 2.71 (tq, *J*=6.4 and 6.8 Hz, 1H), 3.71 (d, *J*=13.2 Hz, 1H), 3.81 (d, *J*=13.2 Hz, 1H), 7.14-7.30 (m, 10H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 20.3, 32.2, 38.7, 51.2, 52.0, 125.6, 126.8, 128.1, 128.3, 128.3, 140.8, 142.4; HRMS calcd for $C_{17}H_{21}N$ 239.1675, found 239.1676 (+0.1 mmu); Anal calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85, found: C, 84.98; H, 8.88; N, 5.99.

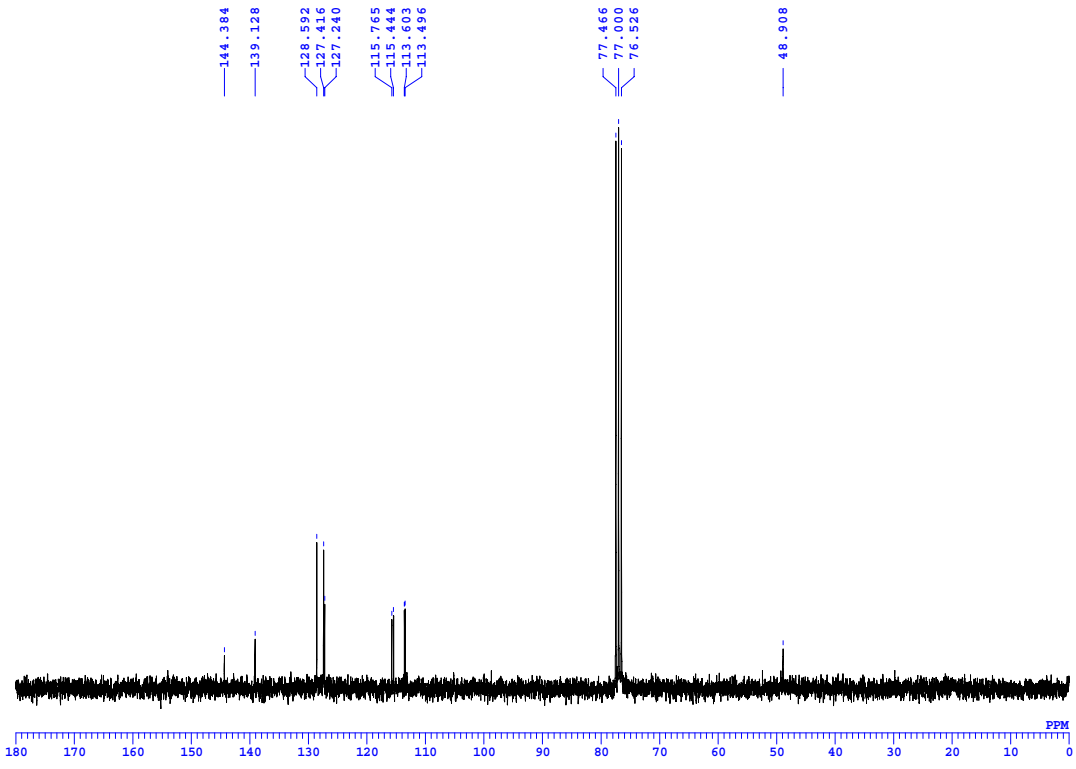
N-Benzyl-*p*-fluoroaniline (3b)



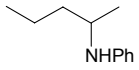
^{1}H NMR



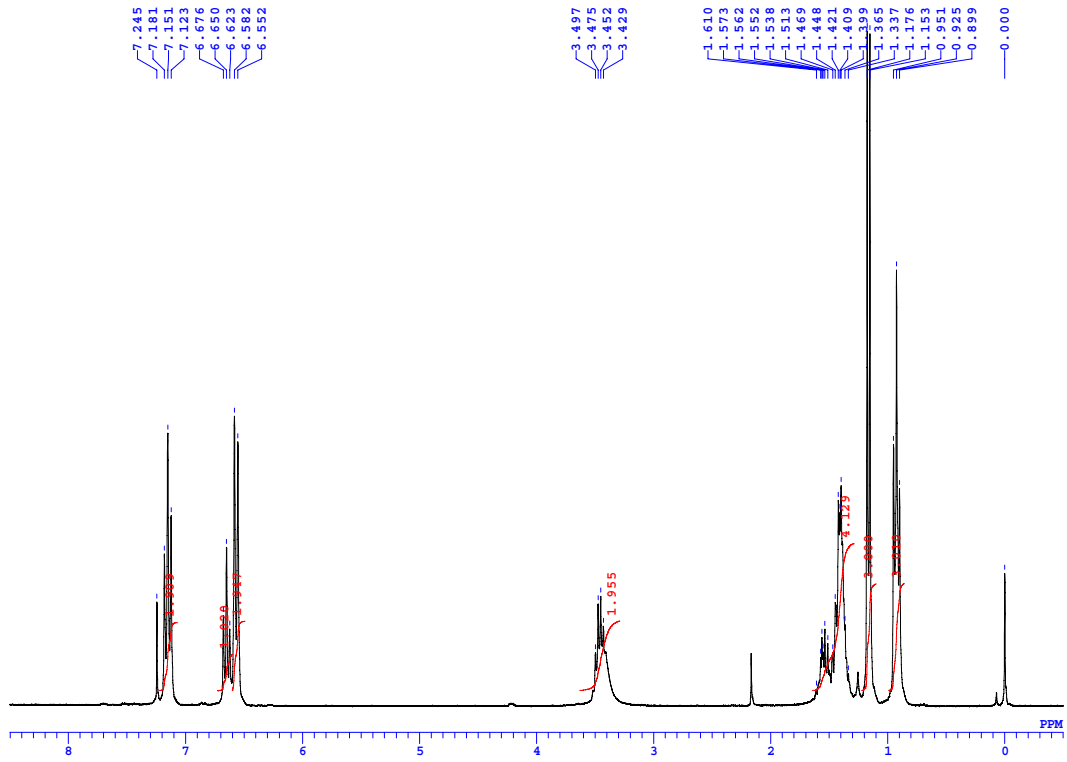
^{13}C NMR



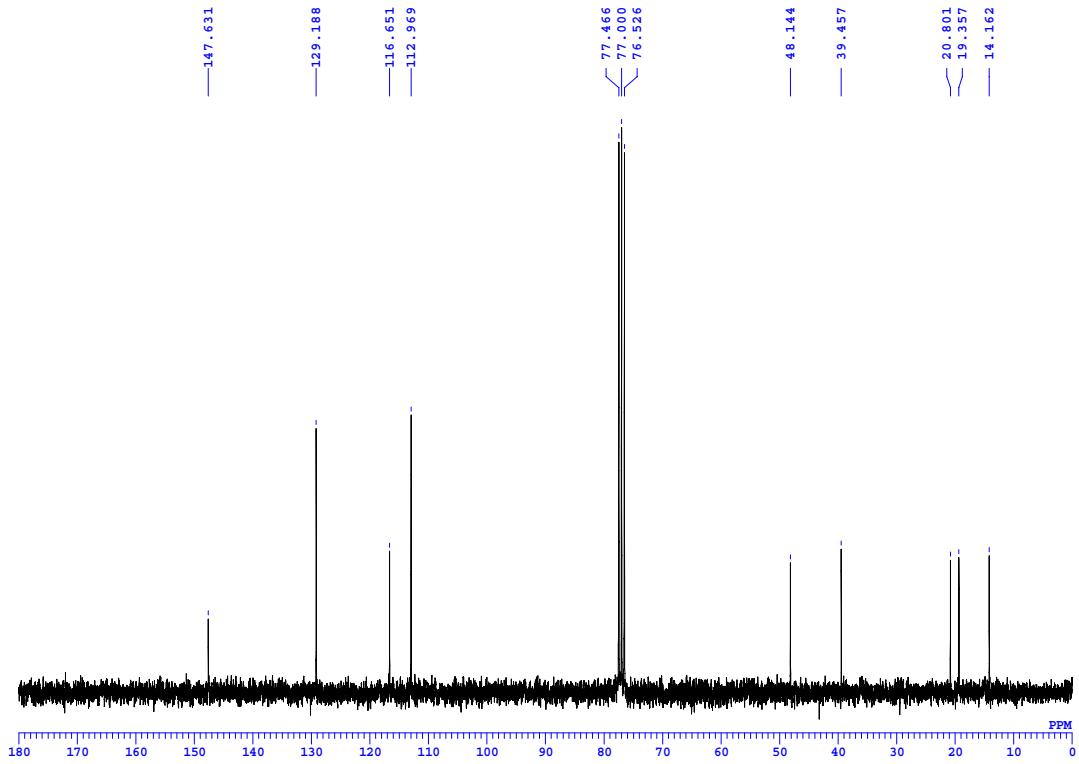
N-2-Pentylaniline (3e)



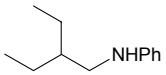
^{1}H NMR



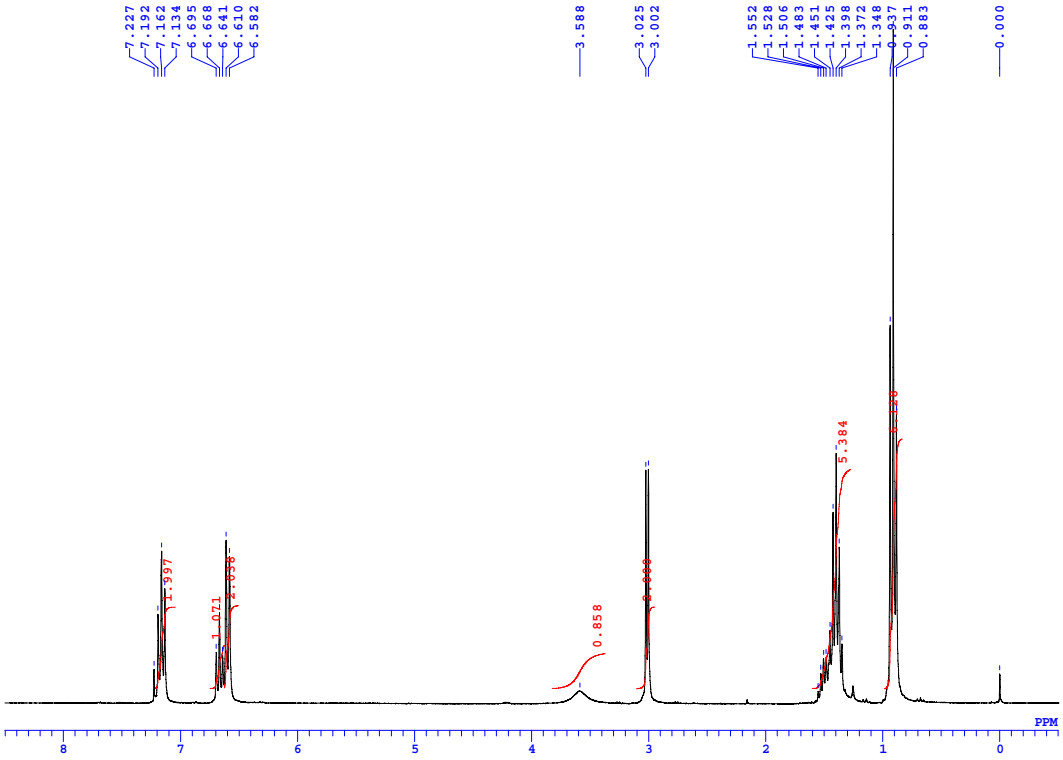
^{13}C NMR



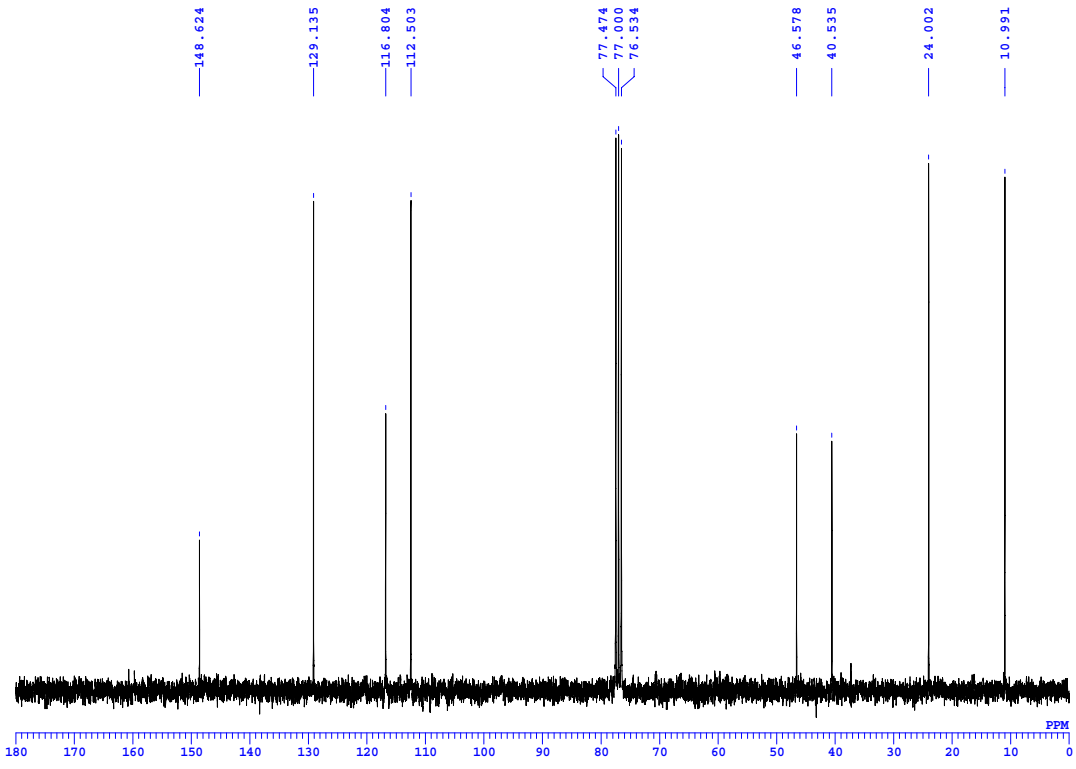
N-(2-Ethylbutyl)aniline (3f)



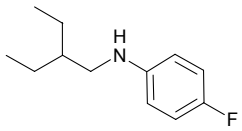
^{1}H NMR



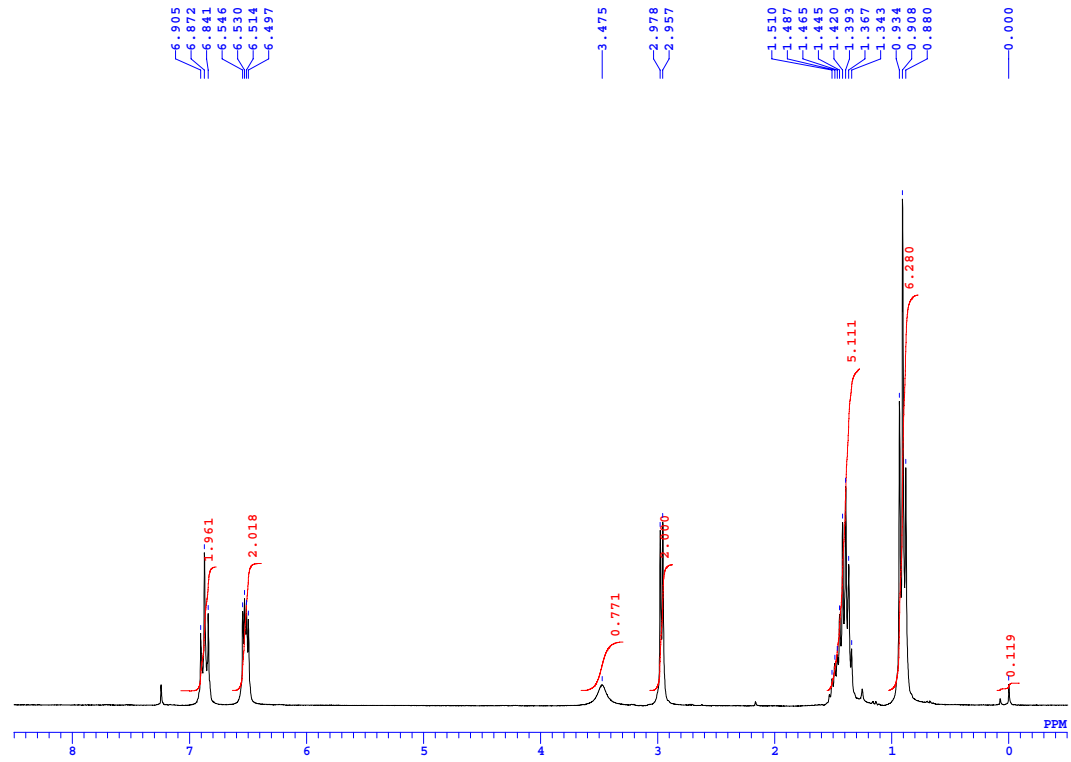
^{13}C NMR



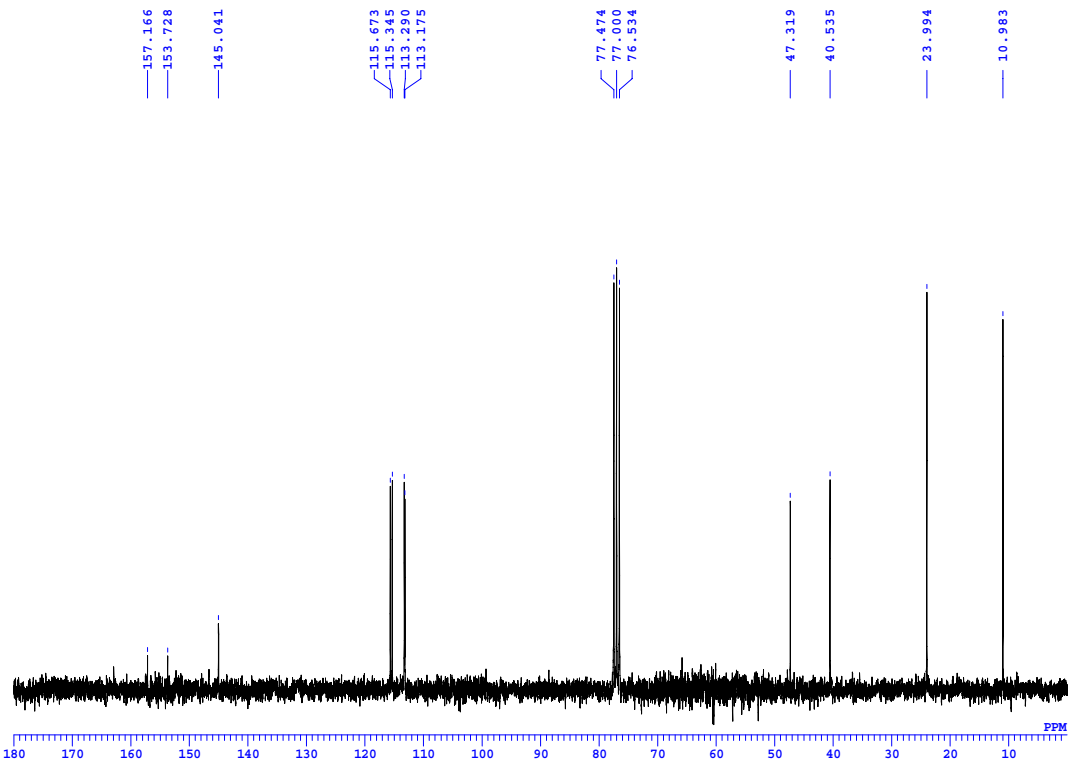
_N_-(2-Ethylbutyl)-_p_-fluoroaniline (3g)



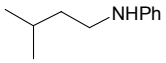
^{1}H NMR



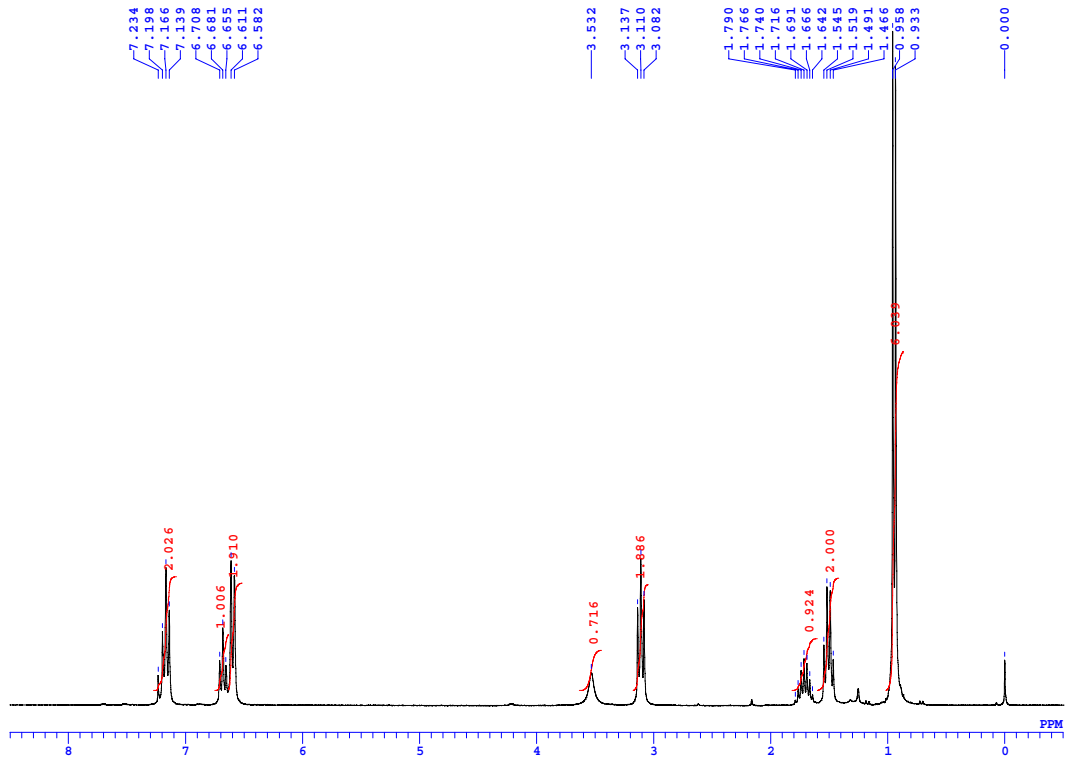
^{13}C NMR



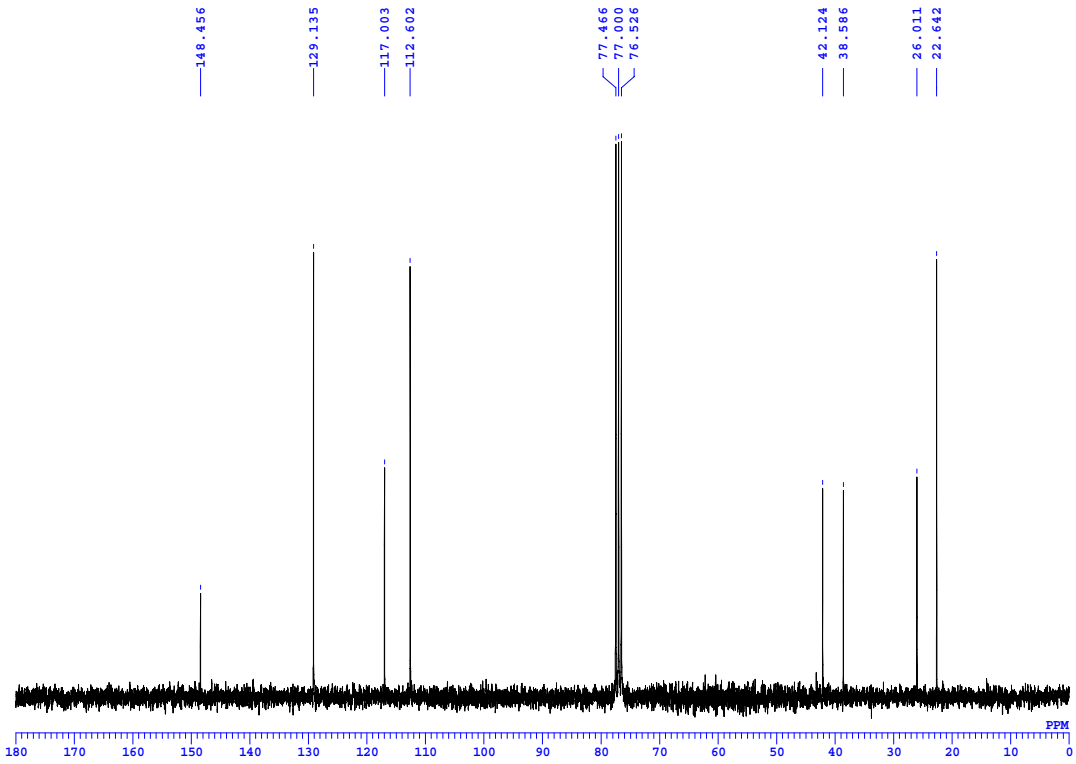
N-(3-Methylbutyl)aniline (3h)



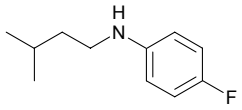
^{1}H NMR



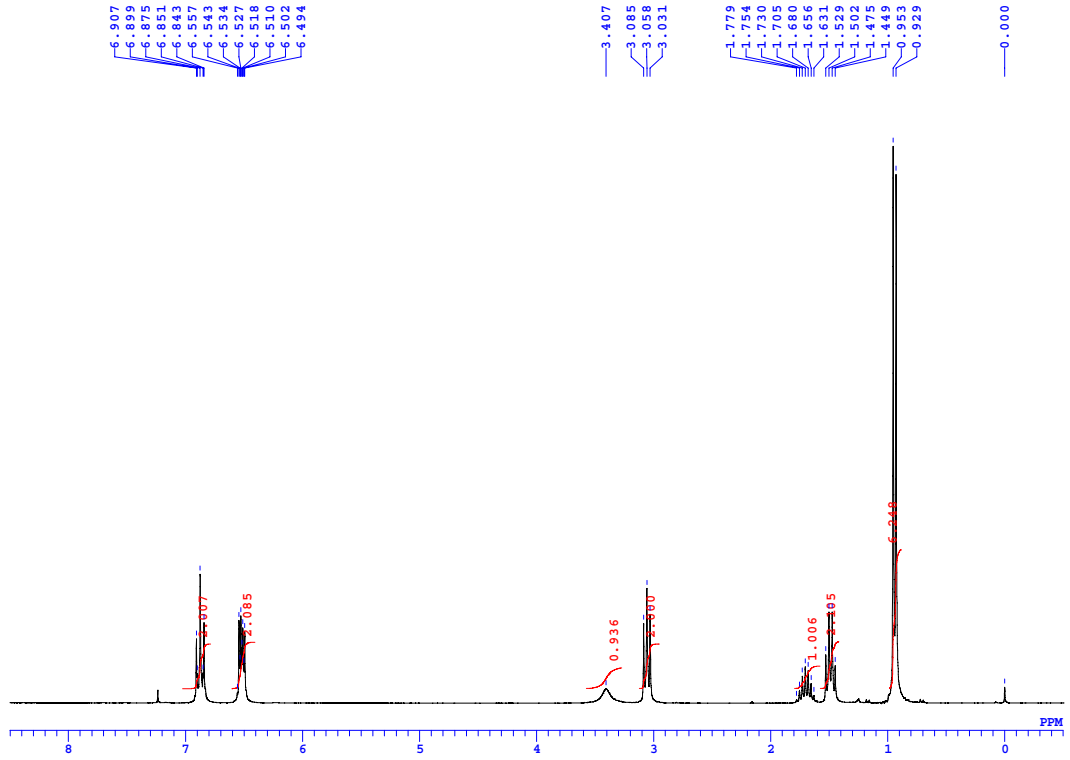
^{13}C NMR



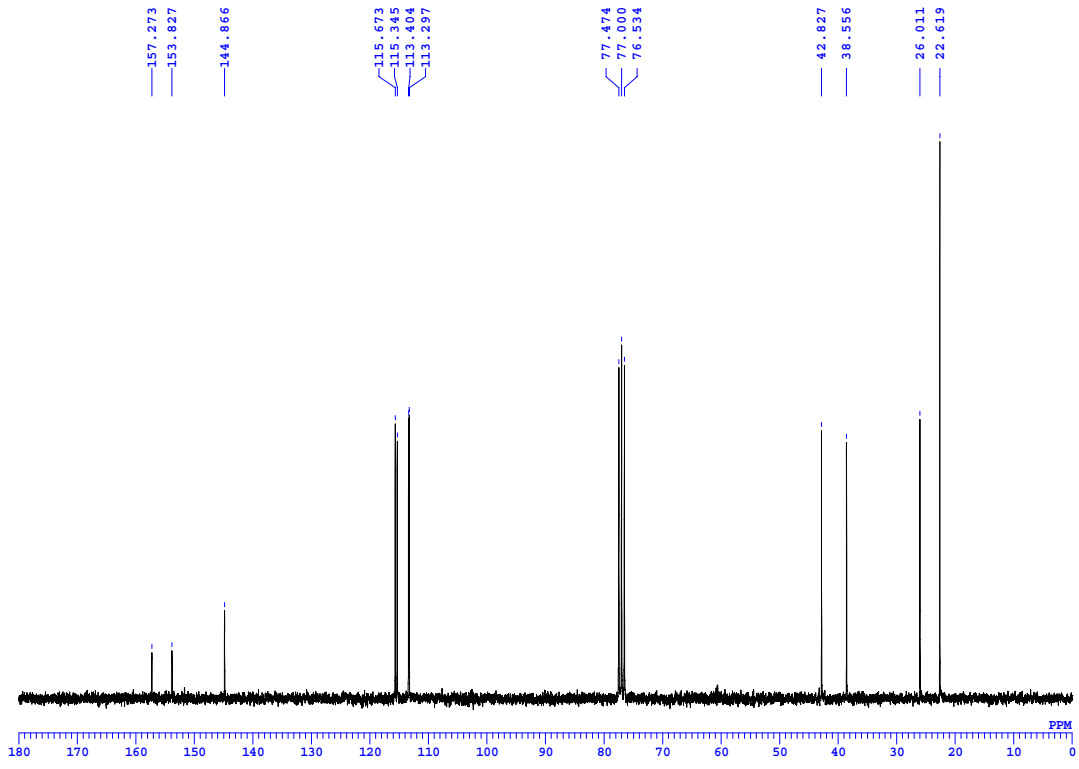
N-(3-Methylbutyl)-*p*-fluoroaniline (3i)



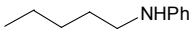
^{1}H NMR



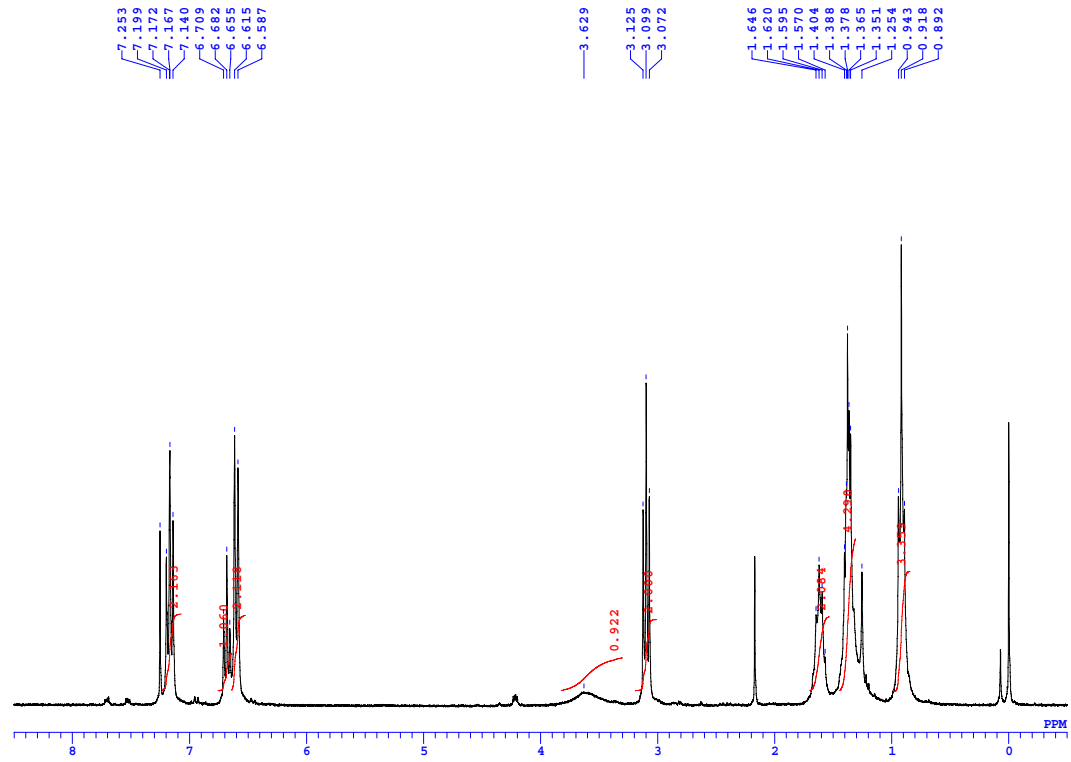
^{13}C NMR



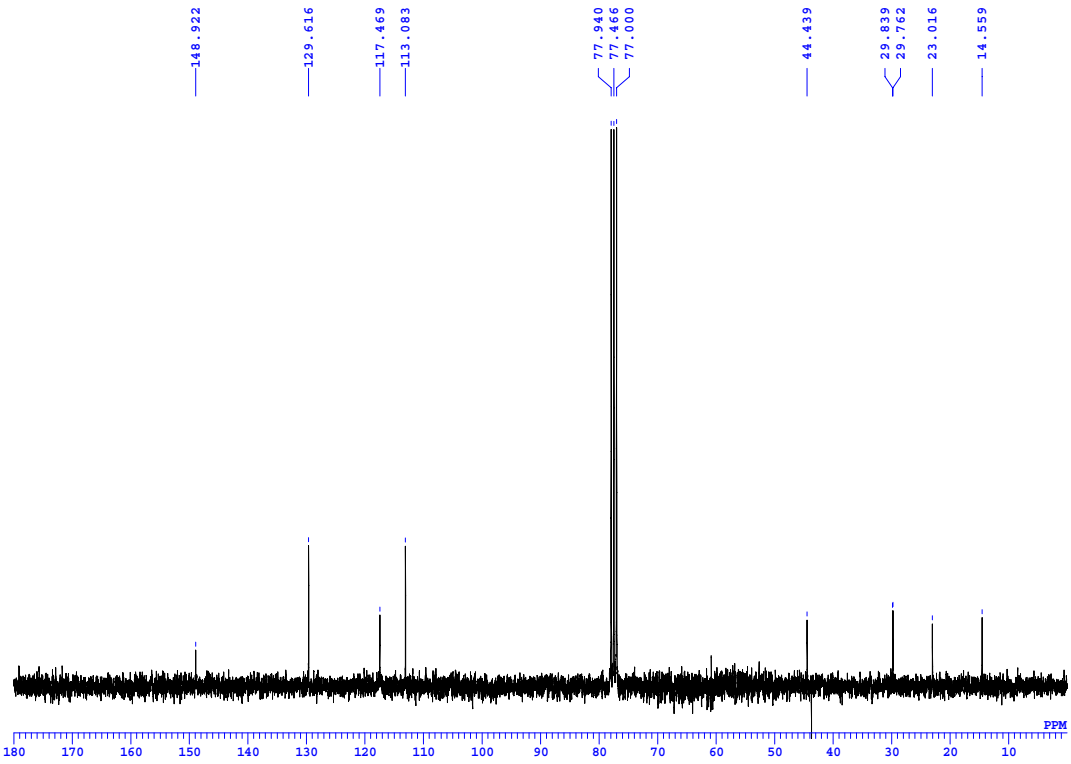
N-1-Pentylaniline (3j)



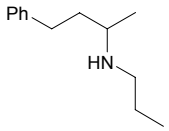
^{1}H NMR



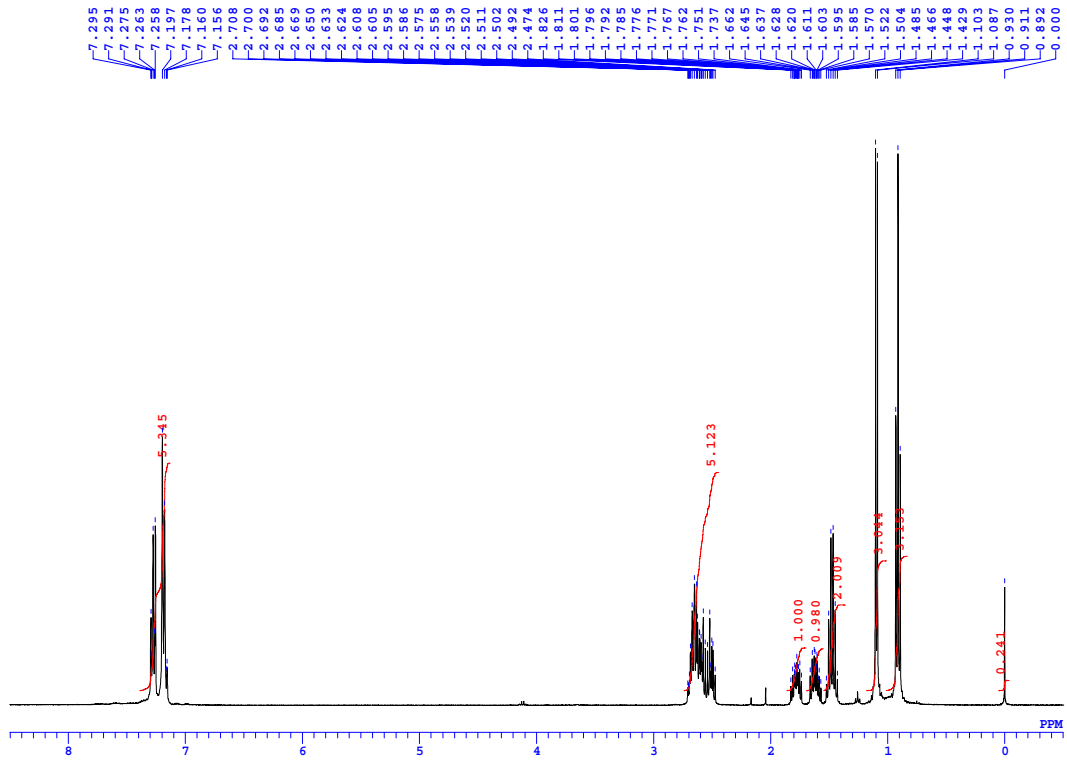
^{13}C NMR



N-Propyl-4-phenyl-2-butylamine (3k)



^{1}H NMR



^{13}C NMR