

Supporting information

Iron-catalysed tandem isomerisation/hydrosilylation reaction of allylic alcohols with amines

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I. General information.

All reagents were obtained from commercial sources and used as received. All reactions were carried out with flame-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. Dicholoromethane, toluene and THF were dried over Braun MB-SPS-800 solvent purification system. Ethanol is distilled under reduced pressure and stored in the presence of molecular sieves. Technical grade petroleum ether (40-60 °C bp.) and diethylether were used for chromatography column. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 µm, 60 Å).

¹H NMR spectra were recorded in CDCl₃ at ambient temperature on Bruker AVANCE 300 and 400 spectrometers at 300.1, and 400.1 MHz, respectively, using the solvent as internal standard (CDCl₃ 7.26 ppm). ¹³C NMR spectra were obtained at 75 or 100 MHz and referenced to the internal solvent signals (CDCl₃, central peak is 77.16 ppm, C₆D₆ 128.06 ppm). Chemical shifts and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet, and br. for broad).

GC analyses were performed with GC-2014 (Shimadzu) 2010 equipped with a 30-m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 m × 0.25 mm × 0.25 mm film thickness), which was used with N₂/air as the vector gas. The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 10 °C/min. until 220 °C and 220 °C for 15 minutes.

GC-MS were measured by GCMS-QP2010S (Shimadzu) with GC-2010 equipped with a 30-m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 m × 0.25 mm × 0.25 mm film thickness), which was used with helium as the vector gas. The following GC-MS conditions were used: initial temperature 100 °C, for 2 minutes, then rate 10 °C/min. until 250 °C and 250 °C for 10 minutes.

HR-MS spectra and elemental analysis were carried out by the corresponding facilities at the CRMPO (Centre Régional de Mesure Physiques de l'Ouest), University Rennes 1.

Visible light irradiation experiments were performed using a 24 Watt compact fluorescent lamp.

II- General experimental procedures:

A 20 mL oven dried Schlenk tube containing a stirring bar, was charged with Fe(cod)(CO)₃ (3.1 mg, 0.0125 mmol) and then purged with argon/vacuum three times. Ethanol (1 mL), aniline derivative (0.25 mmol, 1 equiv.), allylic alcohol or homoallylic alcohol (1.0-1.5 equiv.), PMHS (45 µL, 3 equiv.) were added under argon. The reaction mixture was stirred in a preheated oil bath for 20 h under visible light irradiation. The reaction mixture was condensed under reduced pressure. The residue was then purified by silica gel column chromatography using a mixture of diethylether/petroleum ether as the eluent to afford the desired product.

Procedure A: allylic alcohol or homoallylic alcohol (0.375 mmol, 1.5 equiv.), heated at 50 °C.

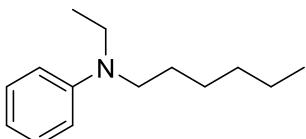
Procedure B: allylic alcohol (0.313 mmol, 1.25 equiv.), heated at 70 °C.

Procedure C: allylic alcohol (0.25 mmol, 1.0 equiv.), heated at 70 °C.

Procedure D: allylic alcohol (0.313 mmol, 1.25 equiv.), heated at 100 °C.

III- Characterization data for the aniline derivatives

N-Ethyl-*N*-hexylaniline (Table 2, Entries 1, 2, 10)¹

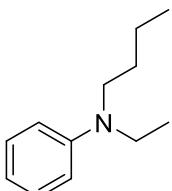


The compound was prepared as described using the *procedure A* ($m = 43$ mg, 86% isolated yield).

¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, 2H, $J = 7.9$), 6.70-6.59 (m, 3H), 3.36 (q, 2H, $J = 7.0$), 3.25 (t, 2H, $J = 7.7$), 1.59 (m, 2H), 1.33 (m, 6H), 1.15 (t, 3H, $J = 6.9$), 0.91 (t, 3H, $J = 6.5$).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.0, 129.2, 115.2, 111.7, 50.5, 44.9, 31.8, 27.5, 26.9, 22.7, 14.0, 12.3.

N-Butyl-*N*-ethylaniline (Table 2, Entries 3, 9)¹

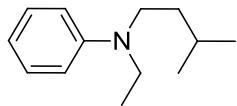


The compound was prepared as described using the *procedure A* ($m = 36$ mg, 81% isolated yield).

¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, 2H, $J = 7.6$), 6.70-6.60 (m, 3H), 3.36 (q, 2H, $J = 7.1$), 3.25 (t, 2H, $J = 7.4$), 1.63 – 1.51 (m, 2H), 1.42 – 1.31 (m, 2H), 1.15 (t, 3H, $J = 7.0$), 0.96 (t, 3H, $J = 7.3$).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 148.0, 129.2, 115.2, 111.8, 50.2, 44.9, 29.7, 20.4, 14.0, 12.3.

N-Ethyl-*N*-isopentylaniline (Table 2, Entries 4, 11)



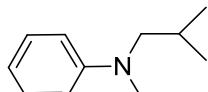
The compound was prepared as described using the *procedure A* ($m = 39$ mg, 82% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.20 (t, 2H, $J = 7.6$), 6.70-6.60 (m, 3H), 3.35 (q, 2H, $J = 7.1$), 3.27 (t, 2H, 7.8), 1.70 – 1.56 (m, 1H), 1.48 (m, 2H), 1.15 (t, $J = 7.0$ Hz), 0.96 (d, $J = 6.6$ Hz).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.0, 129.2, 115.2, 111.8, 48.7, 44.8, 36.2, 26.4, 22.7, 12.4.

MS (EI): m/z: 191 (8, M+), 134 (100), 120 (12), 106 (28), 77 (15).

N-Ethyl-*N*-isobutyylaniline (Table 2, Entry 5)²

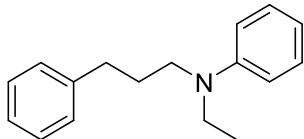


The compound was prepared as described using the *procedure A* ($m = 42$ mg, 95% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 7.26-7.16 (m, 2H), 6.81-6.54 (m, 3H), 3.41 (q, 2H, $J = 7.2$), 3.05 (d, 2H, $J = 7.3$), 2.12-2.19 (m, 1H), 1.14 (t, 3H, $J = 7.2$), 0.95 (d, 6H, $J = 6.2$).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 148.3, 129.1, 115.2, 112.0, 58.5, 45.8, 27.2, 20.4, 11.6.

N-Ethyl-*N*-(3-phenylpropyl)aniline (Table 2, Entry 6)¹

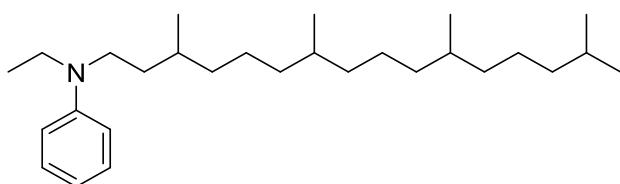


The compound was prepared as described using the *procedure A* ($m = 45$ mg, 75% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.30 (m, 2H), 7.24-7.16 (m, 5H), 6.68-6.10 (m, 3H), 3.37 (q, 2H, $J = 6.9$), 3.30 (t, 2H, $J = 6.5$), 2.68 (t, 2H, $J = 7.6$), 2.00–1.88 (m, 2H), 1.15 (t, 1H, $J = 6.9$)

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.0, 141.8, 129.2, 128.40, 128.37, 125.9, 115.5, 112.0, 50.0, 45.0, 33.4, 29.0, 12.4.

N-Ethyl-*N*-(3,7,11,15-tetramethylhexadecyl)aniline (Table 2, Entry 8)¹

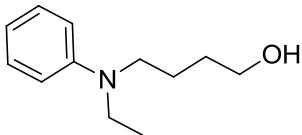


The compound was prepared as described using the *procedure A* ($m = 65$ mg, 65% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 7.25-7.17 (m, 2H), 6.74-6.59 (m, 3H), 3.37 (q, 2H, $J = 7.1$), 3.20-3.19 (m, 2H), 1.74-1.01 (m, 27H), 0.97 (d, 3H, $J = 6.4$), 0.93-0.81 (m, 12H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.0, 129.2, 115.2, 111.8, 48.6, 44.8, 39.4, 37.5-37.3, 34.3, 34.2, 32.8, 31.2, 28.0, 24.8, 24.5, 24.4, 22.7, 22.6, 19.8-19.7, 12.4.

4-[Ethyl-phenyl-amino]butan-1-ol (Table 2, Entry 7)

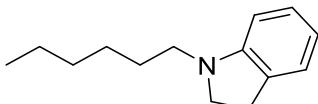


The compound was prepared as described using the *procedure A* ($m = 43$ mg, 89% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.26-7.18 (m, 2H), 6.75-6.65 (m, 3H), 3.67 (t, 2H, $J = 6.3$), 3.36 (q, 2H, $J = 7.2$), 3.29 (t, 2H, $J = 7.2$), 1.96 (br s, 1H), 1.64-1.57 (m, 4H), 1.16 (t, 3H, $J = 7.2$)

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.0, 129.3, 116.1, 112.7, 62.8, 50.4, 45.4, 30.5, 24.2, 12.2, MS (EI): m/z: 239 (12, M^+), 134 (100), 120 (12), 106 (27), 91 (16), 77 (18).

N-Hexyl-2,3-dihydro-1*H*-indole (Table 2, Entry 12)⁵

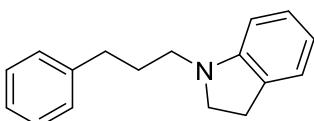


The compound was prepared as described using the *procedure A* ($m = 41$ mg, 81% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.10-7.03 (m, 2H), 6.68-6.60 (m, 1H), 6.46 (d, 1H, $J = 7.4$), 3.34 (t, 2H, $J = 8.2$), 3.04 (t, 2H, $J = 7.2$), 2.96 (t, 2H, $J = 8.2$), 1.72-1.51 (m, 2H), 1.49-1.22 (m, 6H), 0.92 (t, 3H, $J = 6.2$).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 152.7, 130.0, 127.3, 124.4, 117.3, 106.9, 53.1, 49.4, 31.8, 28.6, 27.3, 27.0, 22.7, 14.1.

N-(3-Phenylpropyl)indoline (Table 2, Entry 13)³

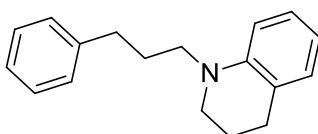


The compound was prepared as described using the *procedure A* ($m = 41$ mg, 70% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.35-7.27 (m, 2H), 7.25-7.18 (m, 3H), 7.12-7.02 (m, 2H), 6.53 (t, 1H, $J = 7.6$), 6.42 (d, 1H, $J = 8.0$), 3.36 (t, 2H, $J = 8.2$), 3.09 (t, 2H, $J = 7.0$), 2.98 (t, 2H, $J = 8.2$), 2.75 (t, 2H, $J = 7.8$), 1.95 (quint, 2H, $J = 7.4$).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 151.7, 140.9, 129.0, 127.5, 127.4, 126.3, 124.8, 123.4, 116.4, 105.9, 52.1, 47.7, 32.3, 28.1, 27.6.

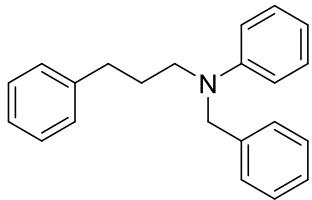
N-(3-Phenylpropyl)-1,2,3,4-tetrahydroquinoline (Table 2, Entry 14)⁴



The compound was prepared as described using the *procedure A* ($m = 60$ mg, 96% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.34-7.27 (m, 2H), 7.24-7.17 (m, 3H), 7.02 (t, 1H, $J = 7.6$), 6.94 (d, 1H, $J = 7.2$), 6.55 (t, 1H, $J = 7.2$), 6.50 (d, 1H, $J = 8.0$), 3.32-3.23 (m, 4H), 2.76 (t, 2H, $J = 6.2$), 2.67 (t, 2H, $J = 7.8$), 2.00-1.89 (m, 4H). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 145.3, 141.8, 129.1, 128.34, 128.32, 127.0, 125.8, 122.3, 115.4, 110.5, 50.9, 49.4, 33.4, 28.2, 27.7, 22.3.

N-Benzyl-N-(3-phenylpropyl)aniline (Table 2, Entry 15)



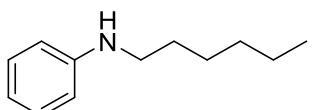
The compound was prepared as described using the *procedure A* ($m = 59$ mg, 75% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.35-7.27 (m, 3H), 7.25-7.14 (m, 9H), 6.71-6.61 (m, 3H), 4.55 (s, 2H), 3.44 (t, 2H, $J = 7.6$), 2.67 (t, 2H, $J = 7.6$), 2.08-1.95 (m, 2H).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 148.6, 141.7, 139.1, 129.2, 128.6, 128.44, 128.37, 126.8, 126.6, 126.0, 116.2, 112.3, 54.6, 50.8, 33.4, 28.6.

MS (EI): m/z: 301 (10, M^+), 196 (23), 106 (6), 91 (100), 77 (9).

N-Hexylaniline (Table 4, Entry 1)¹

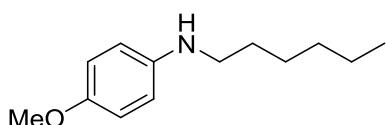


The compound was prepared as described using the *procedure B* ($m = 29$ mg, 88% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 7.18 (t, 2H, $J = 7.3$), 6.69 (t, 1H, $J = 7.3$), 6.61 (d, 2H, $J = 7.3$), 3.63 (br s, 1H), 3.11 (t, 2H, $J = 7.2$), 1.62 (m, 2H), 1.52-1.21 (m, 6H), 0.91 (t, 3H, $J = 6.4$).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 148.6, 129.2, 117.1, 112.7, 44.0, 31.7, 29.6, 26.9, 22.6, 14.1.

N-Hexyl-4-methoxyaniline (Table 4, Entry 2)⁶

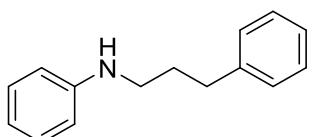


The compound was prepared as described using the *procedure C* ($m = 37$ mg, 72% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 6.78 (d, 2H, $J = 9.0$), 6.58 (d, 2H, $J = 9.0$), 3.80 (br s, 1H), 3.75 (s, 3H), 3.06 (t, 2H, $J = 7.2$), 1.60 (quint, 2H, $J = 7.1$), 1.48-1.14 (m, 6H), 0.90 (t, 3H, $J = 6.8$).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 152.0, 142.9, 114.9, 114.0, 55.9, 45.1, 31.7, 29.7, 26.9, 22.7, 14.1.

N-(3-Phenylpropyl)aniline (Table 4, Entry 3)¹

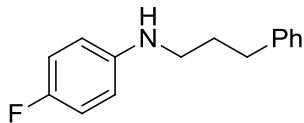


The compound was prepared as described using the *procedure B* ($m = 41$ mg, 81% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.36-7.14 (m, 7H), 6.71 (t, 1H, $J = 7.2$), 6.59 (d, 2H, $J = 8.0$), 3.63 (br s, 1H), 3.17 (t, 2H, $J = 7.0$), 2.76 (t, 2H, $J = 7.6$), 2.0-1.9 (m, 2H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.4, 141.7, 129.3, 128.5, 128.4, 126.0, 117.3, 112.8, 43.5, 33.5, 31.1.

N-(3-Phenylpropyl)-4-fluoro-aniline (Table 4, Entry 4)



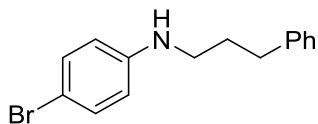
The compound was prepared as described using the *procedure B* ($m = 39$ mg, 68% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.31 (m, 2H), 7.25-7.17 (m, 3H), 6.93-6.84 (m, 2H), 6.56-6.46 (m, 2H), 3.48 (br s, 1H), 3.12 (t, 2H, $J = 7.0$), 2.75 (t, 2H, $J = 7.4$), 2.0-1.9 (m, 2H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 155.8 (d, $J_{\text{CF}} = 234.6$) 144.7, 141.6, 128.5 (d, $J_{\text{CF}} = 6.8$), 126.0, 115.6 (d, $J_{\text{CF}} = 22.3$), 113.6 (d, $J_{\text{CF}} = 7.3$), 44.2, 33.4, 31.1.

MS (EI): m/z: 229 (18, M^+), 124 (100), 111 (13), 91 (13), 77 (6).

N-(3-Phenylpropyl)-4-bromo-aniline (Table 4, Entry 5)



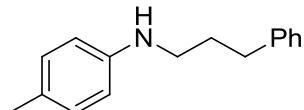
The compound was prepared as described using the *procedure B* ($m = 55$ mg, 76% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.34-7.16 (m, 7H), 6.43 (d, 2H, $J = 8.4$), 3.62 (br s, 1H), 3.11 (t, 2H, $J = 6.8$), 2.73 (t, 2H, 7.5), 2.0-1.9 (m, 2H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.3, 141.5, 131.9, 128.5, 128.4, 126.1, 114.3, 108.7, 43.4, 33.4, 30.9.

MS (EI): m/z: 291 (35, M^+), 289 (37, M^+), 186 (91), 184 (100), 173 (16), 171 (17), 157 (5), 155 (5), 117 (16), 105 (51), 91 (67), 77 (24), 65 (27), 51 (15).

N-(3-Phenylpropyl)-4-methyl-aniline (Table 4, Entry 7)⁸

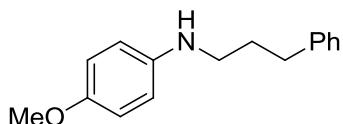


The compound was prepared as described using the *procedure C* ($m = 51$ mg, 91% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.32-7.25 (m, 2H), 7.22-7.15 (m, 3H), 6.99 (d, 2H, $J = 7.2$), 6.55 (d, 2H, $J = 7.6$), 3.48 (br s, 1H), 3.14 (t, 2H, $J = 7.0$), 2.74 (t, 2H, $J = 7.6$), 2.25 (s, 3H), 2.01-1.89 (m, 2H).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 146.1, 141.8, 129.8, 128.5, 126.5, 126.0, 113.1, 43.9, 33.5, 31.2, 20.5.

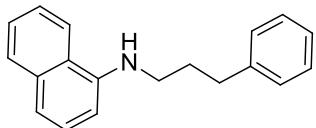
N-(3-Phenylpropyl)-4-methoxy-aniline (Table 4, Entry 8)⁷



The compound was prepared as described using the *procedure C* ($m = 40$ mg, 66% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 7.38-7.13 (m, 5H), 6.79 (d, 2H, $J = 8.8$), 6.56 (d, 2H, $J = 8.7$), 3.76 (s, 3H), 3.12 (t, 2H, $J = 6.9$), 2.75 (t, 2H, $J = 7.7$), 2.0-1.9 (m, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 152.1, 142.7, 141.8, 128.44, 128.43, 125.9, 115.0, 114.1, 55.9, 44.5, 33.5, 31.2.

N-(3-Phenylpropyl)naphthalen-1-amine (Table 4, Entry 9)

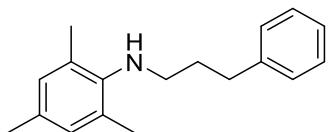


The compound was prepared as described using the *procedure B* ($m = 48$ mg, 74% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, 1H, $J = 7.6$), 7.59 (d, 1H, $J = 8.0$), 7.39-7.28 (m, 2H), 7.25-7.08 (m, 7H), 6.47 (d, 1H, $J = 7.6$), 4.20 (br s, 1H), 3.23 (t, 2H, $J = 6.8$), 2.74 (t, 2H, $J = 7.4$), 2.03 (quint, 2H, $J = 7.2$). $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.4, 141.6, 134.3, 128.6, 128.5, 128.4, 126.6, 126.0, 125.6, 124.6, 123.3, 119.7, 117.2, 104.2, 43.7, 33.7, 30.8.

ESI-HR-MS: $[\text{M}+\text{H}]^+$ ($\text{C}_{19}\text{H}_{20}\text{N}$) Theoretical m/z: 262.1596 Found m/z: 262.1593.

N-(3-Phenylpropyl)-2,4,6-trimethyl-aniline (Table 4, Entry 10)



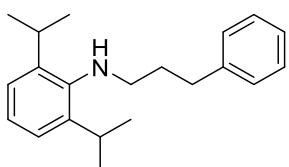
The compound was prepared as described using the *procedure B* ($m = 45$ mg, 71% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.34-7.28 (m, 2H), 7.24-7.17 (m, 3H), 6.83 (s, 2H), 2.99 (t, 2H, $J = 7.2$), 2.81 (br s, 1H), 2.74 (t, 2H, $J = 7.8$), 2.25 (s, 9H), 1.93 (m, 2H).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.6, 141.9, 131.2, 129.6, 129.4, 128.4, 125.9, 48.5, 33.6, 32.9, 20.7, 18.4.

ESI-HR-MS: $[\text{M}+\text{H}]^+$ ($\text{C}_{18}\text{H}_{24}\text{N}$) Theoretical m/z: 254.1909 Found m/z: 254.1907.

N-(3-Phenylpropyl)-2,6-diisopropylaniline (Table 4, Entry 11)



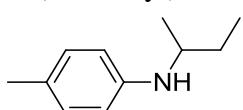
The compound was prepared as described using the *procedure B* ($m = 56$ mg, 76% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 7.35-7.27 (m, 2H), 7.25-7.16 (m, 3H), 7.13-6.98 (m, 3H), 3.32-3.13 (m, 2H), 2.90 (t, 2H, $J = 7.1$), 2.78 (t, 2H, $J = 7.7$), 2.10-1.88 (m, 2H), 1.22 (d, 12H, $J = 7.0$).

$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.5, 142.3, 141.8, 128.4, 125.9, 123.6, 123.5, 51.5, 33.5, 32.5, 27.7, 24.2.

ESI-HR-MS: $[\text{M}+\text{H}]^+$ ($\text{C}_{21}\text{H}_{30}\text{N}$) Theoretical m/z: 296.2378 Found m/z: 296.2379.

N-(*sec*-Butyl)-4-methylaniline (Table 4, Entry 12)⁹

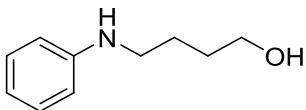


The compound was prepared as described using the procedure D ($m = 38$ mg, 91% isolated yield).

^1H NMR (300 MHz, CDCl_3) δ 7.02 (d, 2H, $J = 8.4$), 6.55 (d, 2H, $J = 8.4$), 3.49-3.33 (m, 1H), 3.32 (br s, 1H), 2.28 (s, 3H), 1.75-1.40 (m, 2H), 1.20 (d, 3H, $J = 6.3$), 0.99 (t, 3H, $J = 7.4$).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 145.4, 129.7, 125.9, 113.3, 50.1, 29.6, 20.3, 20.2, 10.3.

4-(Phenylamino)butan-1-ol (Table 4, Entry 13)¹⁰

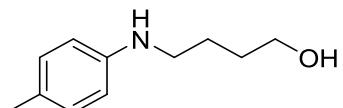


The compound was prepared as described using the procedure B ($m = 29$ mg, 71% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.18 (t, 2H, $J = 7.4$), 6.70 (t, 1H, $J = 7.2$), 6.63 (d, 2H, $J = 8.0$), 3.70 (t, 2H, $J = 5.6$), 3.16 (t, 2H, $J = 5.6$), 2.63 (br s, 2H), 1.71 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.3, 129.2, 117.5, 112.9, 62.7, 43.9, 30.4, 26.1.

4-(*p*-Tolylamino)butan-1-ol (Table 4, Entry 14)¹¹

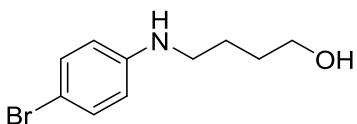


The compound was prepared as described using the procedure B ($m = 32$ mg, 72% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 6.99 (d, 2H, $J = 7.6$), 6.55 (d, 2H, $J = 7.6$), 3.69 (m, 2H), 3.14 (m, 2H), 2.58 (br s, 2H), 2.23 (s, 3H), 1.70 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 146.1, 146.0, 129.82, 129.75, 126.8, 113.3, 62.7, 44.4, 30.5, 26.3, 20.4.

4-[(4-Bromophenyl)amino]butan-1-ol (Table 4, Entry 15)



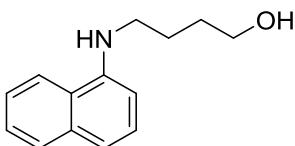
The compound was prepared as described using the procedure B ($m = 56$ mg, 92% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, 2H, $J = 8.8$), 6.47 (d, 2H, $J = 8.8$), 3.68 (t, 2H, $J = 5.5$), 3.11 (t, 2H, $J = 7.0$), 2.62 (br s, 2H), 1.68 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.3, 131.9, 114.4, 108.8, 62.6, 43.9, 30.2, 25.9.

MS (EI): m/z: 245 (25, M+), 243 (25, M+), 186 (93), 184 (100), 105 (47).

4-(Naphthalen-1-ylamino)butan-1-ol (Table 4, Entry 16)



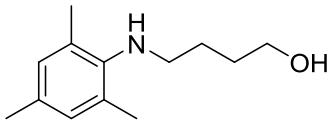
The compound was prepared as described using the procedure B ($m = 33$ mg, 61% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 7.87-7.75 (m, 2H), 7.49-7.39 (m, 2H), 7.35 (t, 1H, $J = 7.5$), 7.26-7.20 (m, 1H), 6.62 (d, 1H, $J = 7.6$), 3.75 (t, 2H, $J = 6.0$), 3.33 (t, 2H, $J = 6.8$), 1.95-1.83 (m, 2H), 1.83-1.72 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 143.5, 134.3, 128.7, 126.6, 125.7, 124.7, 123.5, 119.8, 117.4, 104.4, 62.7, 44.1, 30.6, 25.9.

MS (EI): m/z: 215 (36, M+), 156 (100), 143 (11), 129 (53), 115 (18), 77 (10).

4-(Mesitylamino)butan-1-ol (Table 4, Entry 17)



The compound was prepared as described using the procedure B ($m = 33$ mg, 64% isolated yield).

^1H NMR (400 MHz, CDCl_3) δ 6.82 (s, 2H), 3.68 (t, 2H, $J = 6.2$), 2.94 (t, 2H, $J = 6.2$), 2.59 (br s, 2H), 2.26 (s, 6H), 2.23 (s, 3H), 1.71 (m, 4H).

$^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ 143.1, 131.8, 129.9, 129.5, 62.9, 48.9, 31.0, 28.3, 20.6, 18.3.

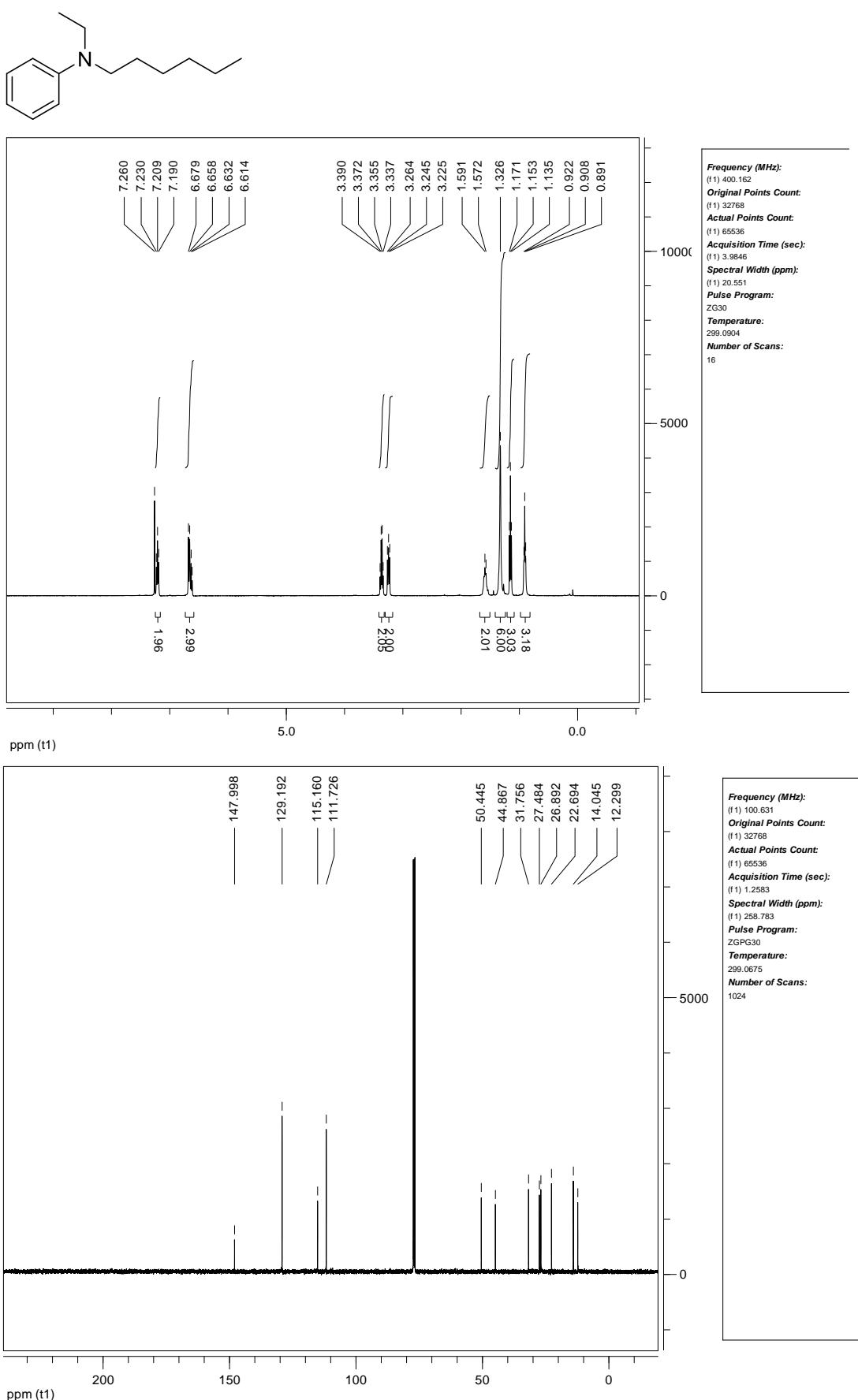
MS (EI): m/z: 207 (13, M^+), 148 (100), 134 (8), 119 (10), 91 (10), 77 (6).

References

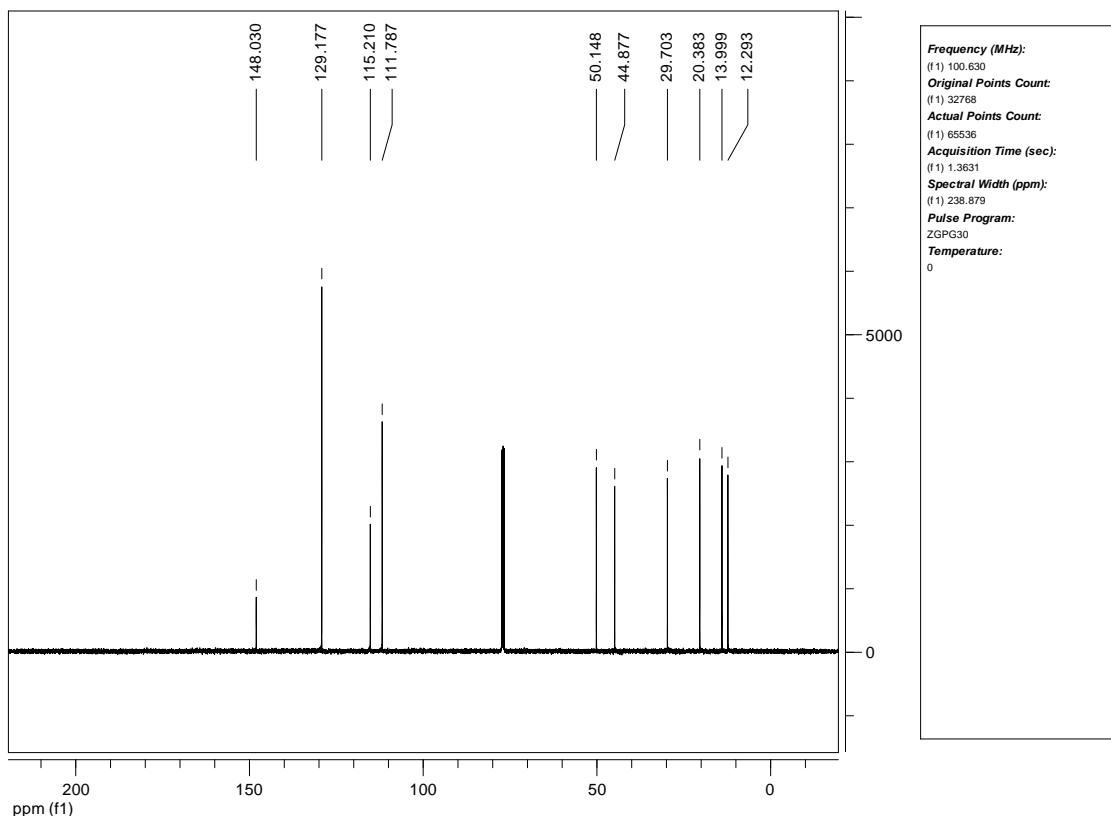
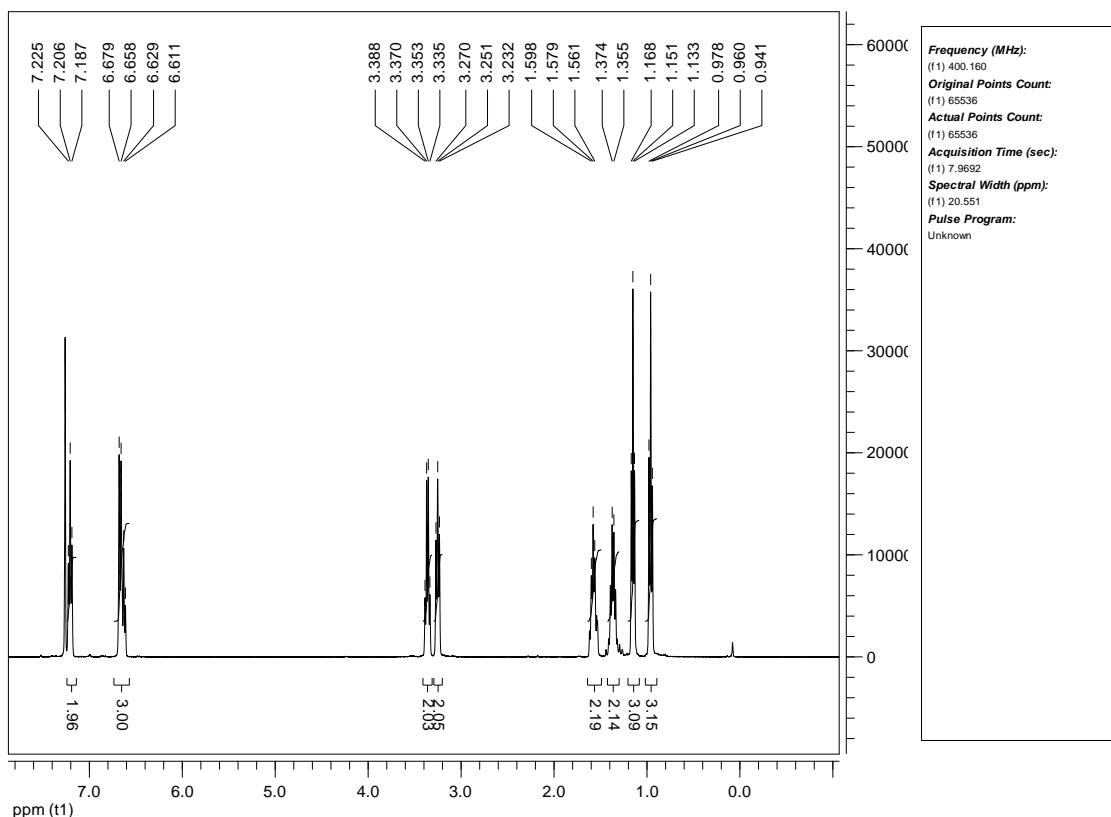
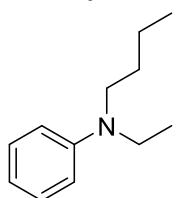
- (1) Z. Sahli, B. Sundararaju, M. Achard, and C. Bruneau, *Org. Lett.*, 2011, **13**, 3964-3967.
- (2) H. C. Brown, M. Zaidlewicz, and P. V. Dalvi, *Organometallics*, 1998, **17**, 4202-4205.
- (3) T. Ikeda, and R. W. Stevens, PCT Int. Appl. (1994), WO 9402459 A1 19940203.
- (4) F. I. McGonagle, D. S. MacMillan, J. Murray, H. F. Sneddon, C. Jamieson, and A. J. B. Watson, *Green. Chem.*, 2013, **15**, 1159-1165.
- (5) M. Ahmed, R. P. J. Bronger; R: Jackstell, P. C. J. Kamer, P. W. N. M. van Leeuwen, and M. Beller, *Chem. Eur. J.*, 2006, **12**, 8979-8988.
- (6) A. Wetzel, S. Wöckel, M. Schelwies, M. K. Brinks, F. Rominger, P. Hofmann, and M. Limbach, *Org. Lett.*, 2013, **15**, 266-269.
- (7) J. Dörfler, and S. Doye, *Angew. Chem. Int. Ed.*, 2013, **52**, 1806-1809.
- (8) A. Heutling, F. Pohlki, I. Bytschkov, and S. Doye, *Angew. Chem. Int. Ed.*, 2005, **44**, 2951-2954.
- (9) Q. Shen, T. Ogata, and J. F. Hartwig, *J. Am. Chem. Soc.*, 2008, **130**, 6586-6596.
- (10) M. Ito, T. Ootsuka, R. Watari, A. Shiibashi, A. Himizu, and T. Ikariya, *J. Am. Chem. Soc.*, 2011, **133**, 4240-4242.
- (11) A. Shafir, P. A. Lichtor, and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3490-3491.

¹H NMR and ¹³C NMR spectra

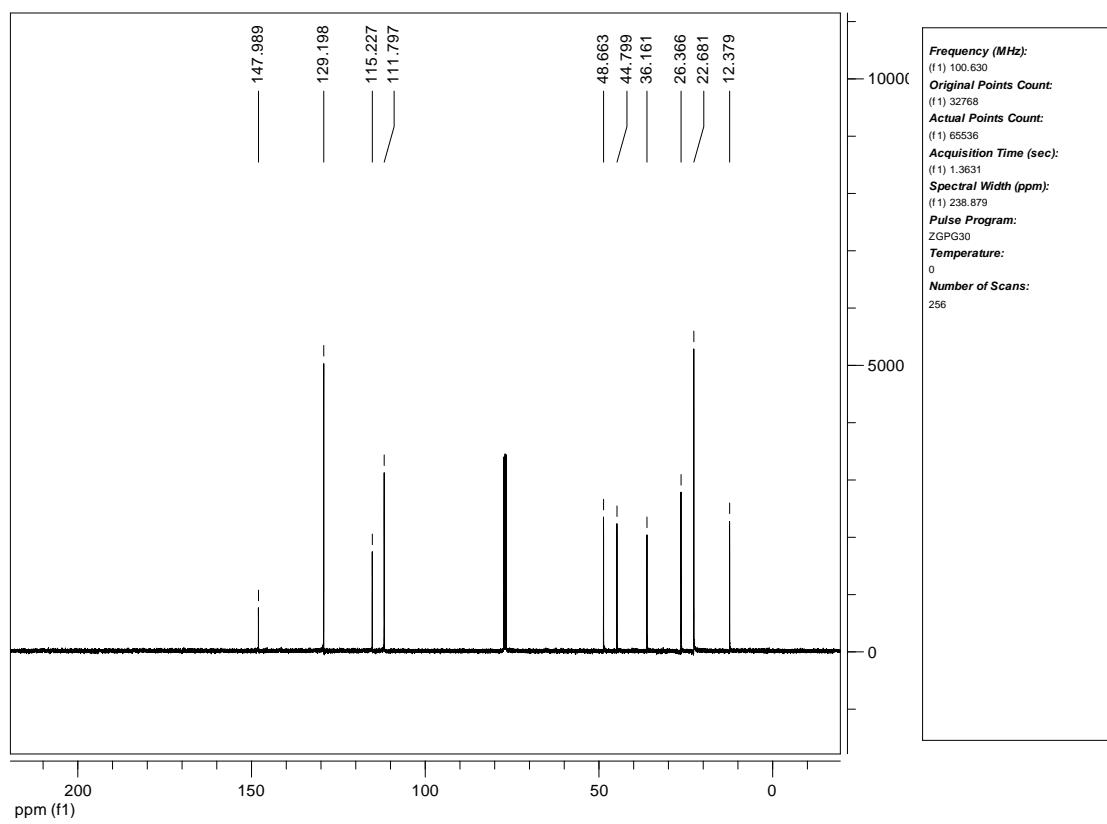
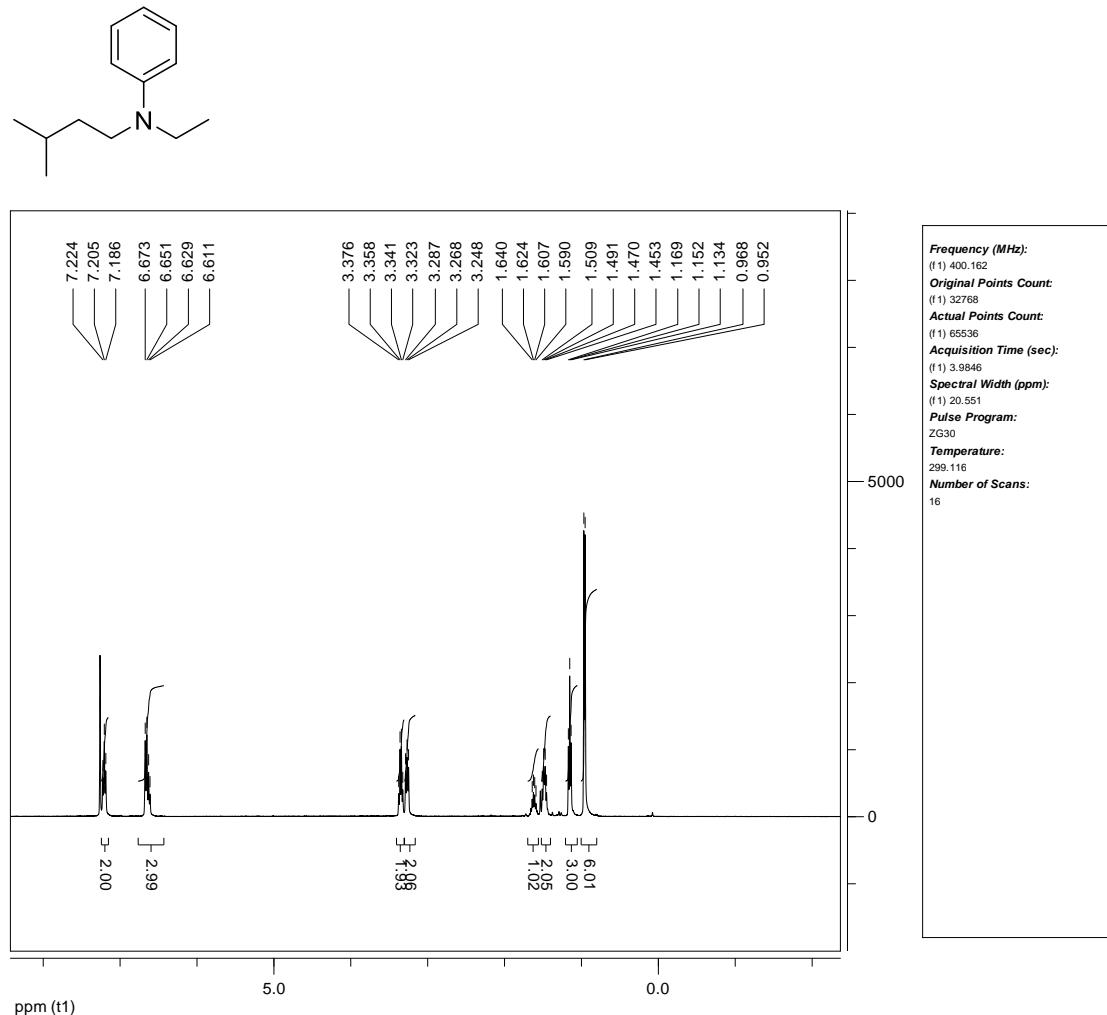
N-Ethyl-N-hexylaniline (Table 3, Entries 1, 2, 10)



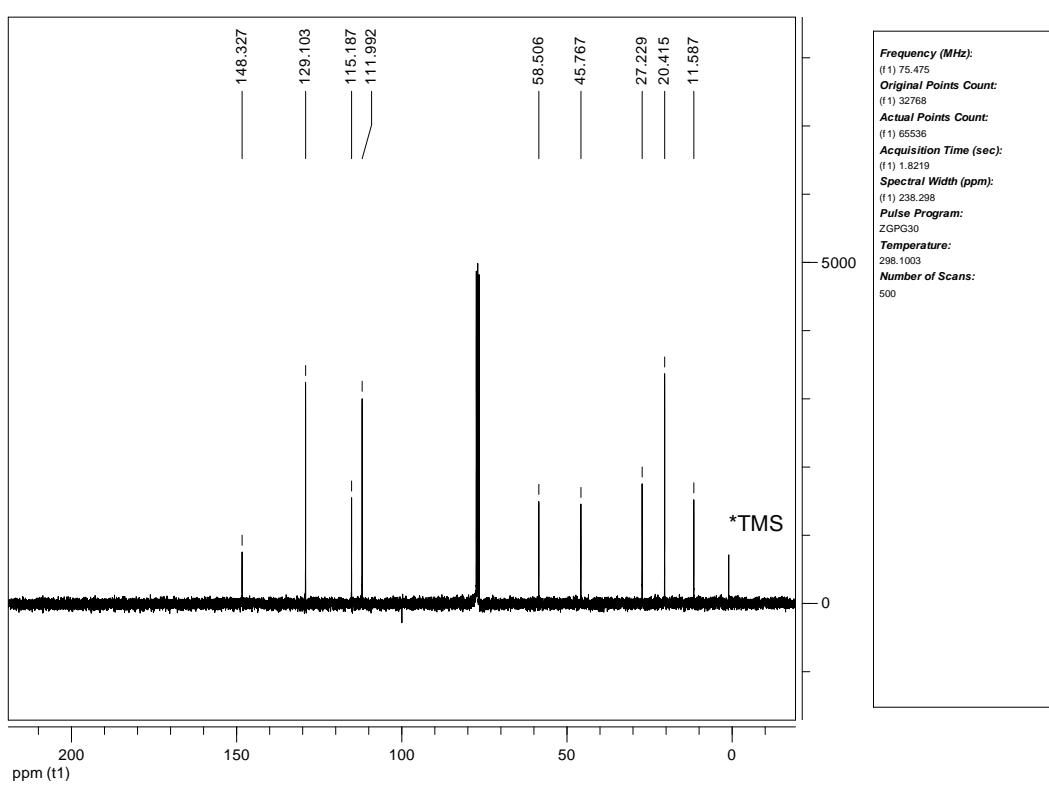
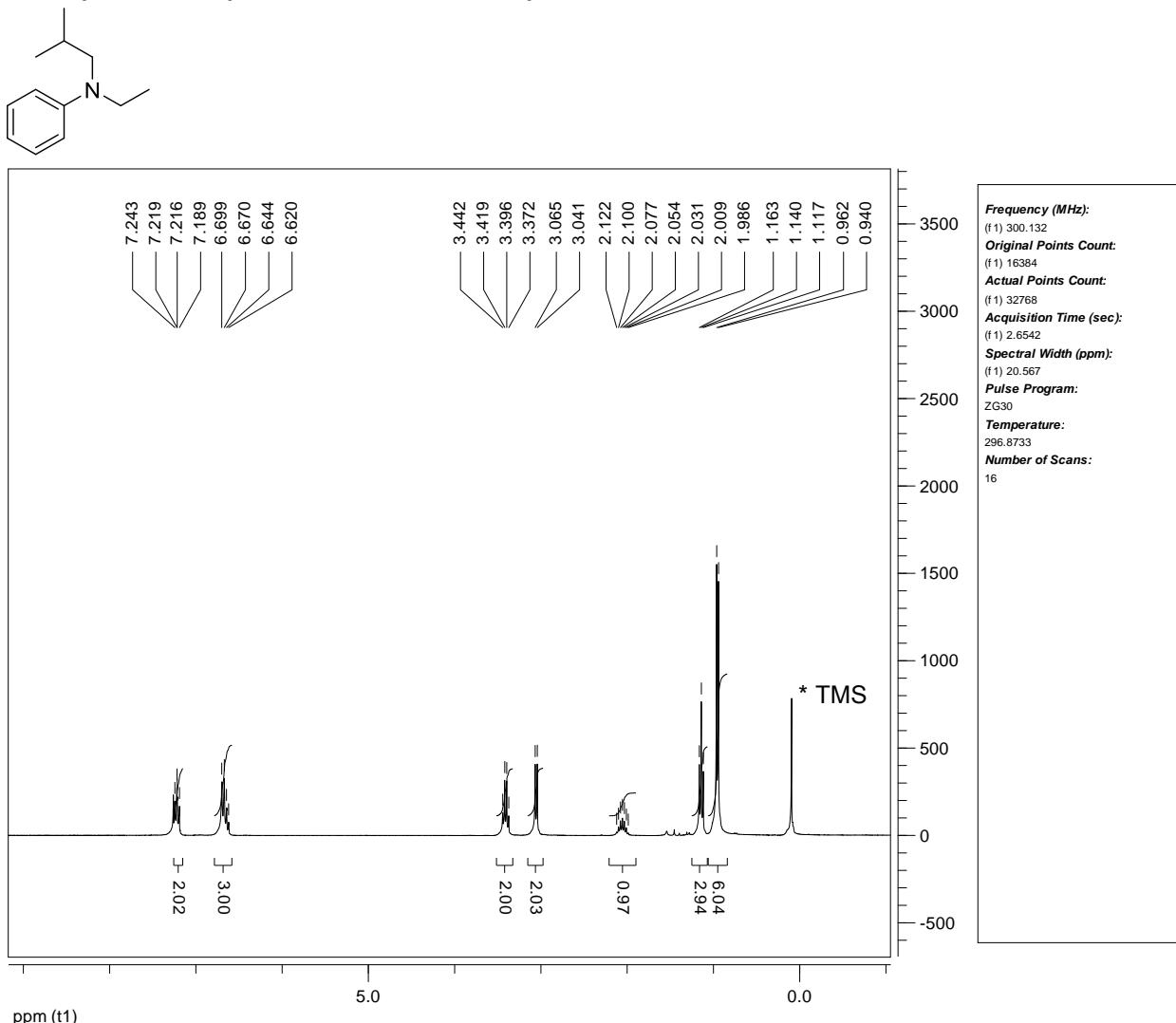
N-Butyl-N-ethylaniline (Table 3, Entries 3, 9)



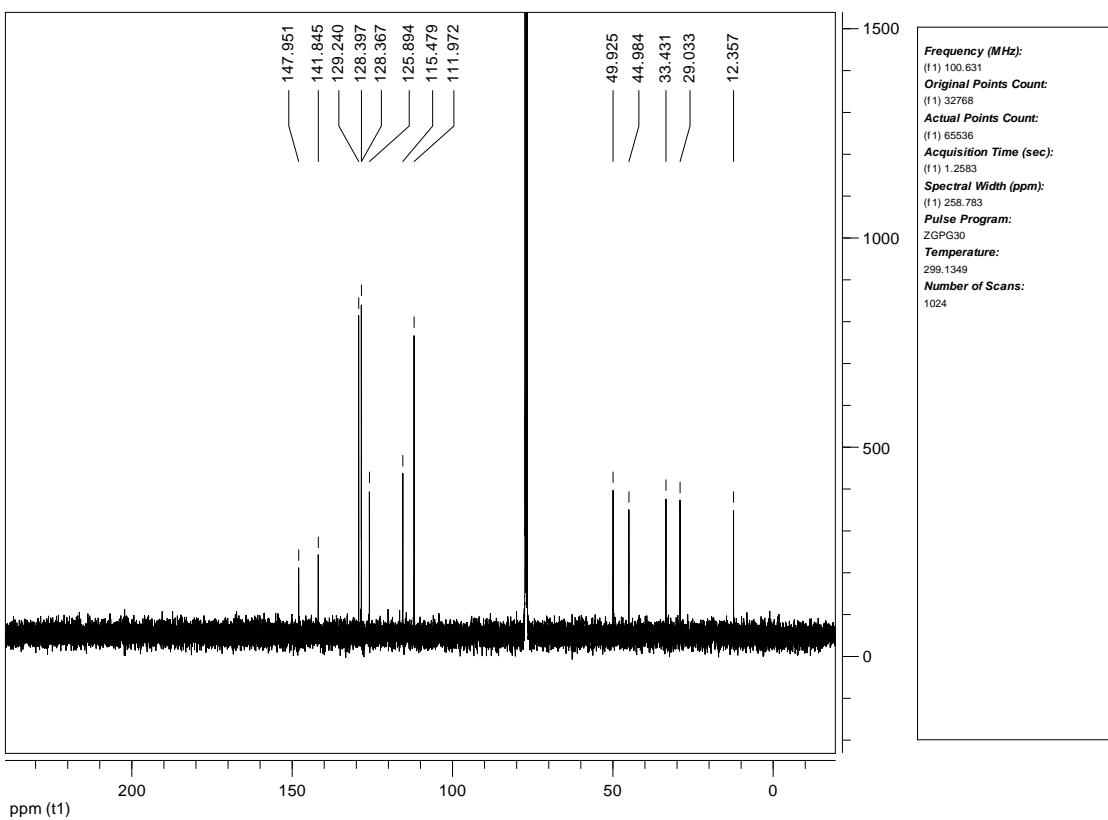
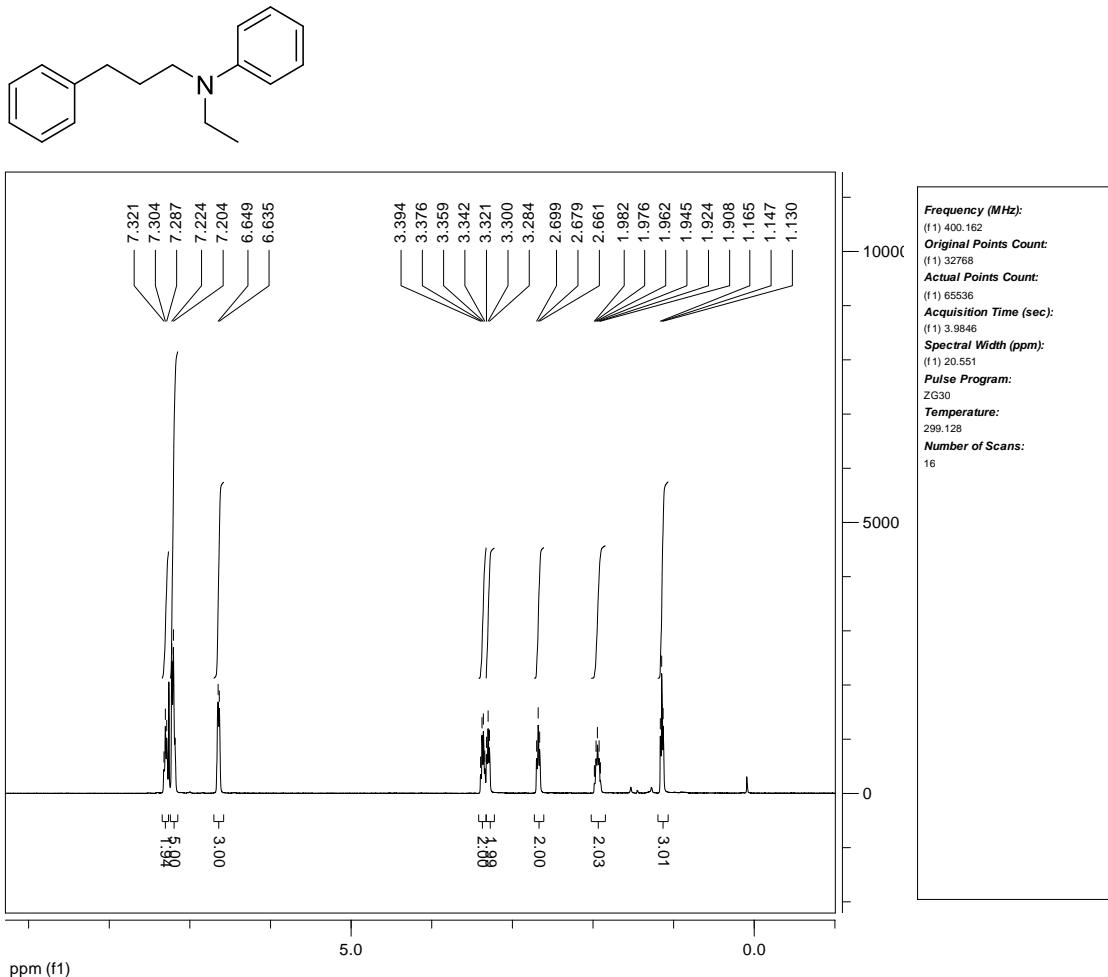
N-Ethyl-N-isopentylaniline (Table 3, Entry 4, 11)



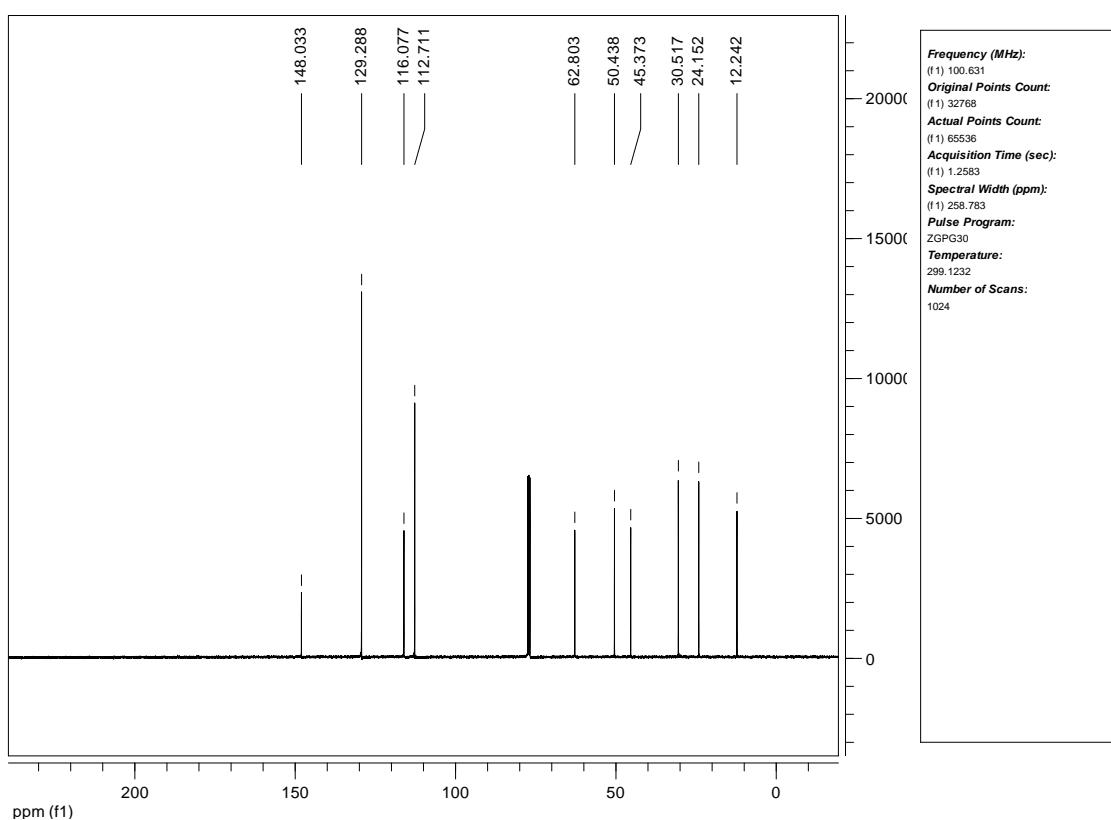
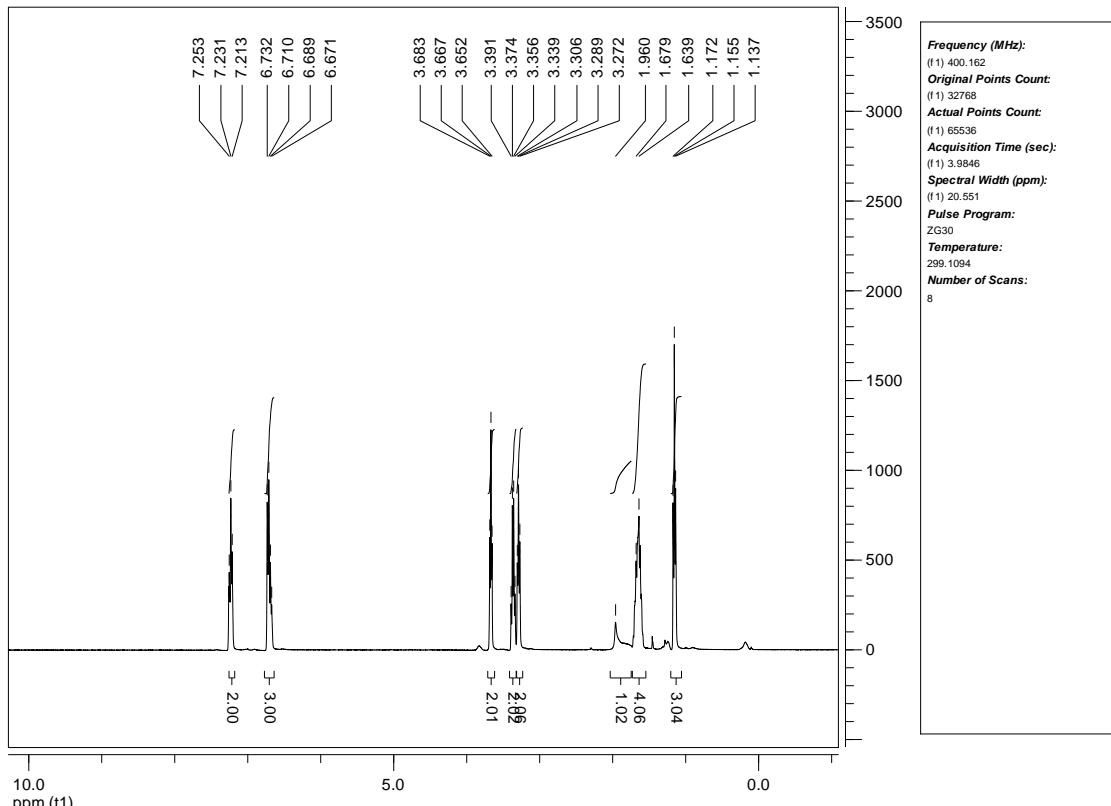
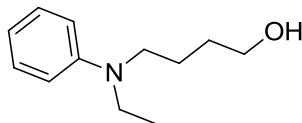
N-Ethyl-N-isobutylaniline (Table 3, Entry 5)



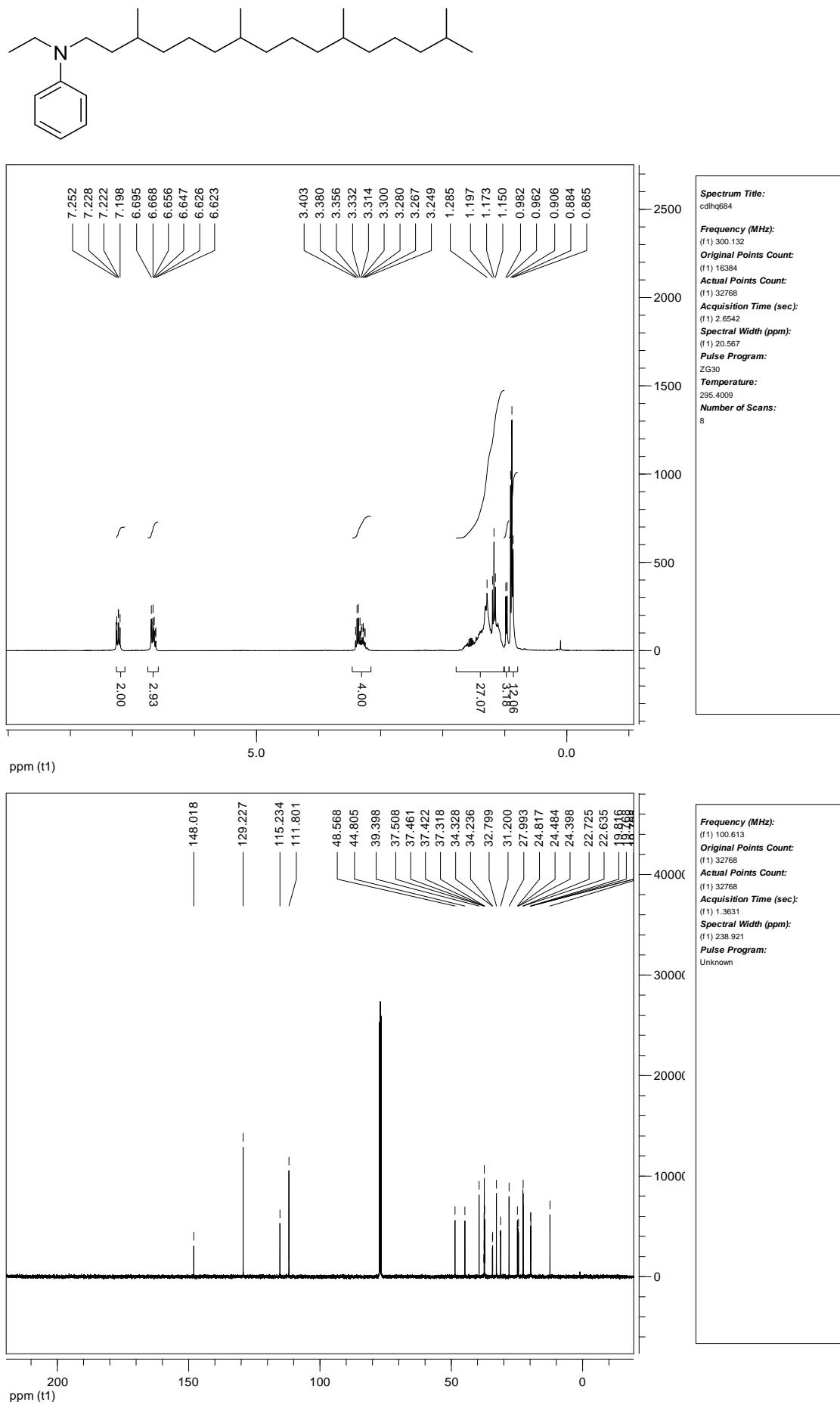
N-Ethyl-N-(3-phenylpropyl)aniline (Table 3, Entry 6)

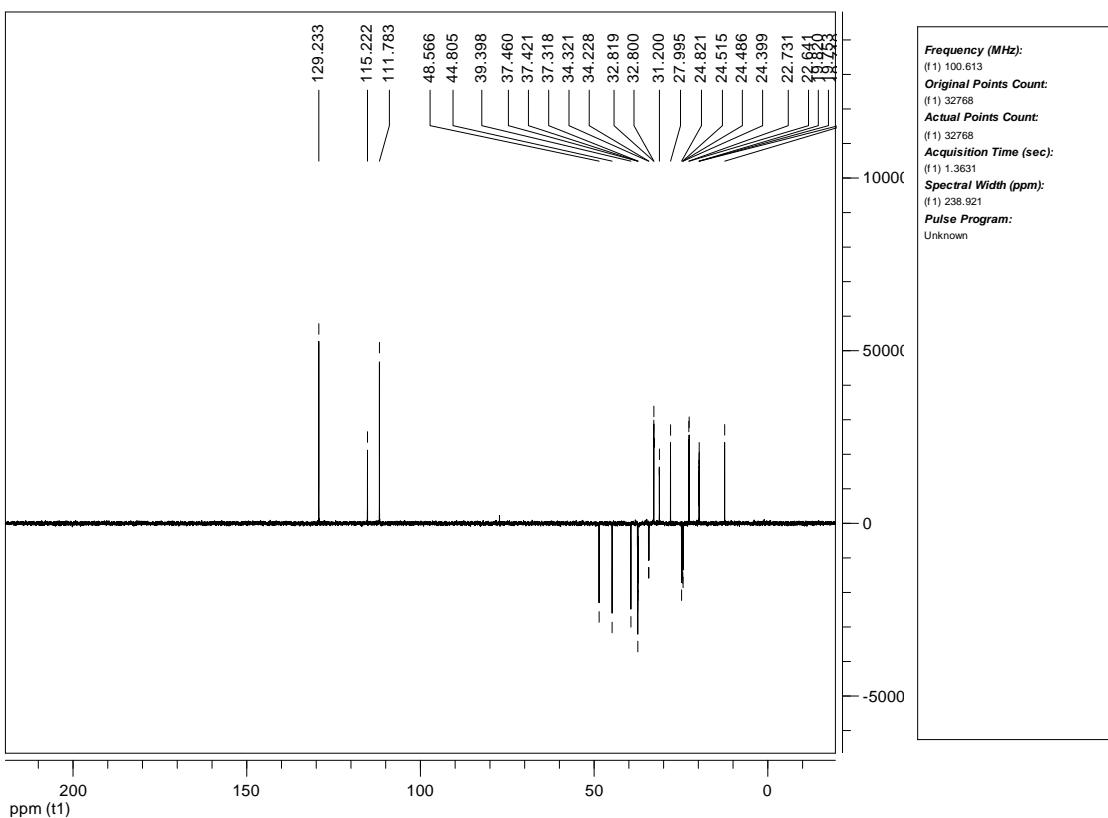


4-[Ethyl(phenyl)amino]butan-1-ol (Table 3, Entry 7)

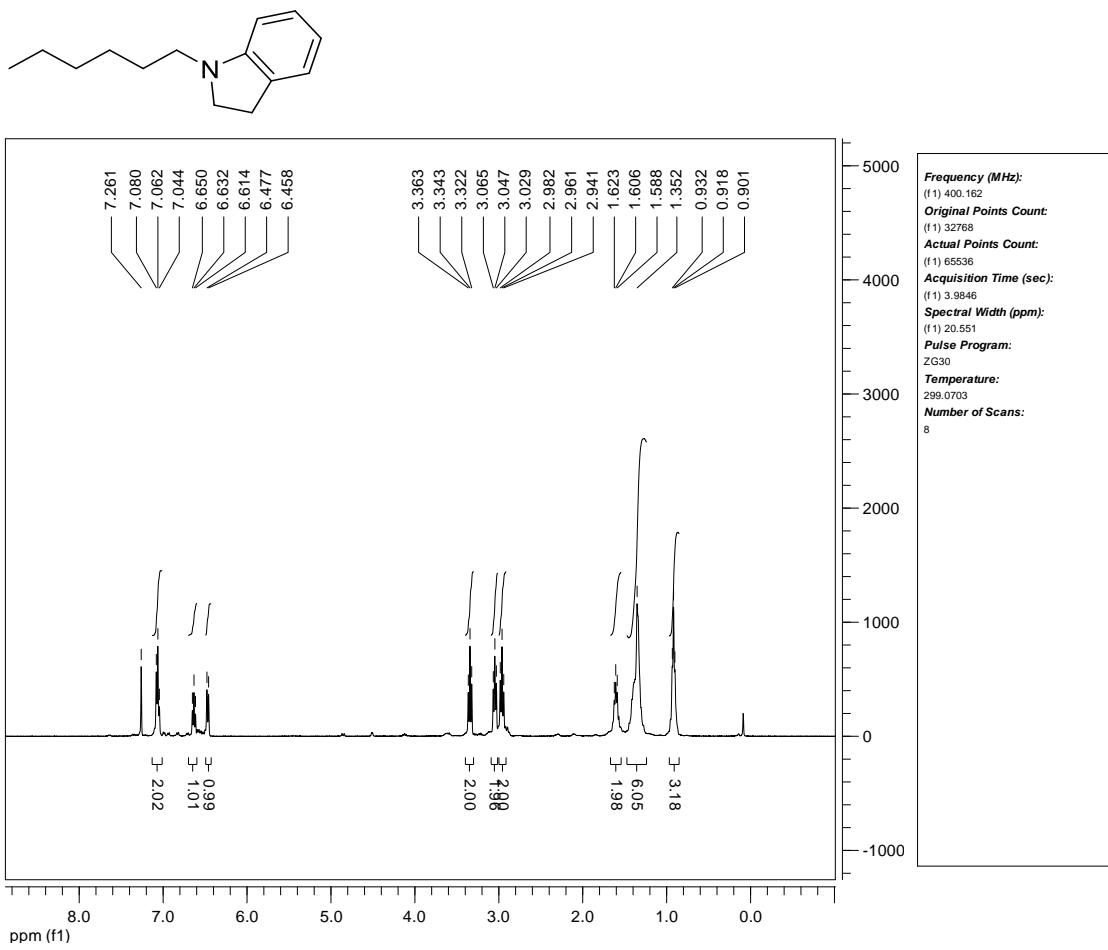


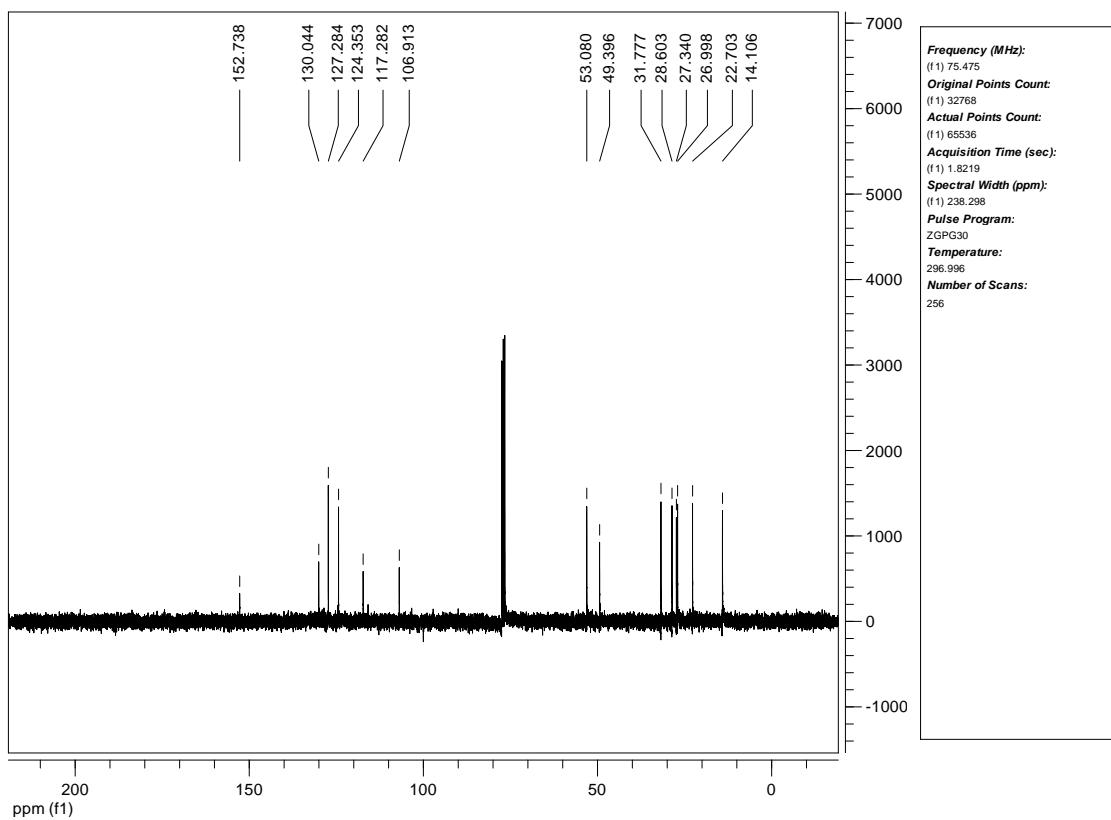
N-Ethyl-N-(3,7,11,15-tetramethylhexadecyl)aniline (Table 3, Entry 8)



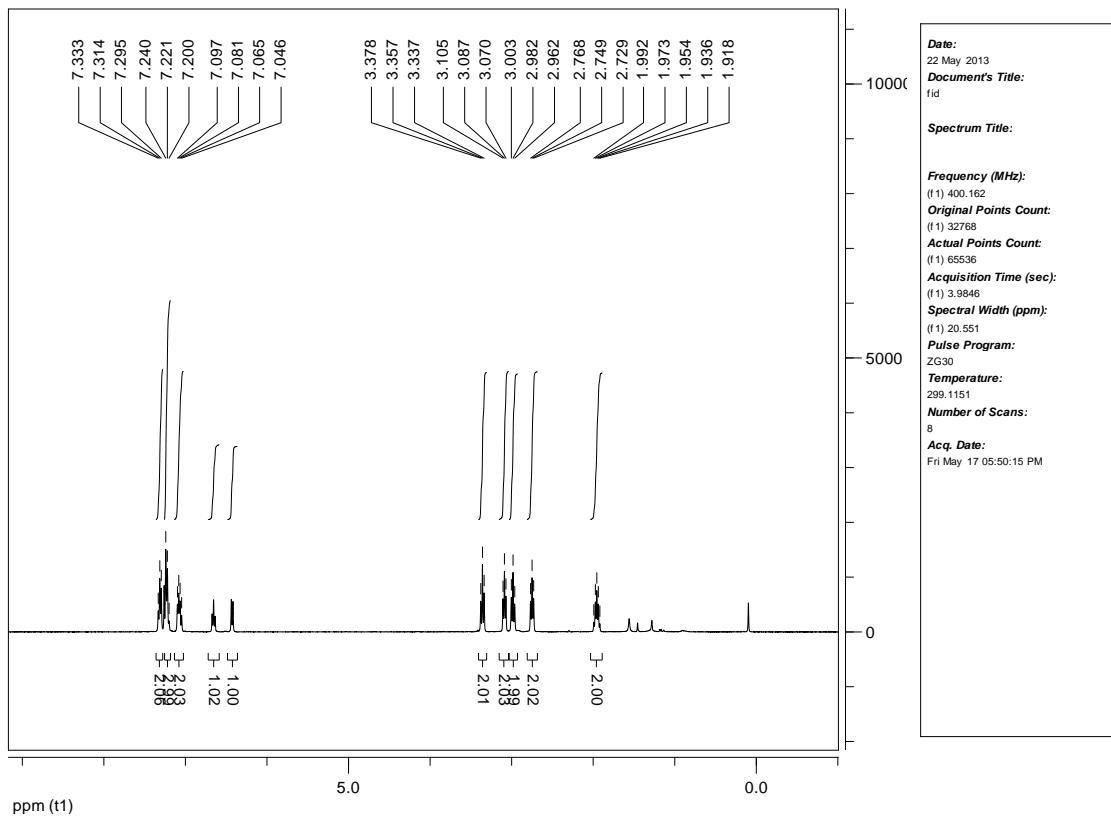
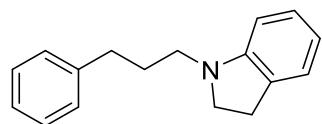


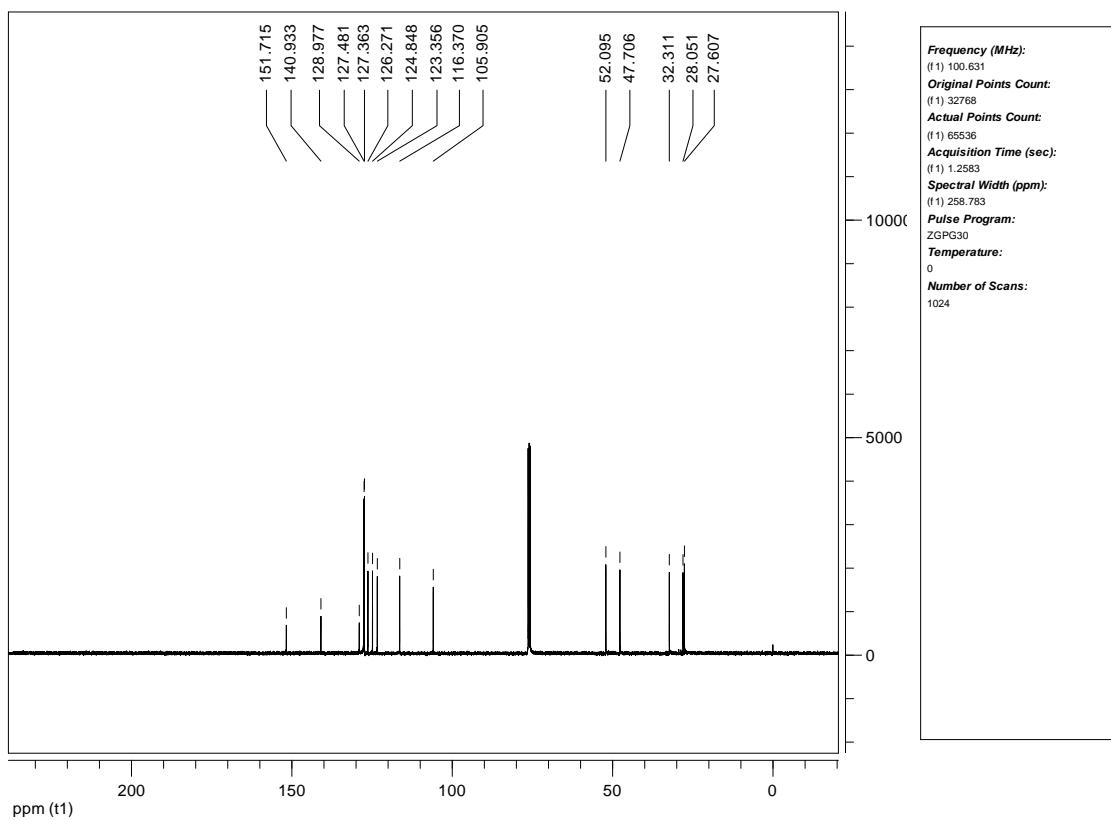
N-Hexylindoline (Table 3, Entry 12)



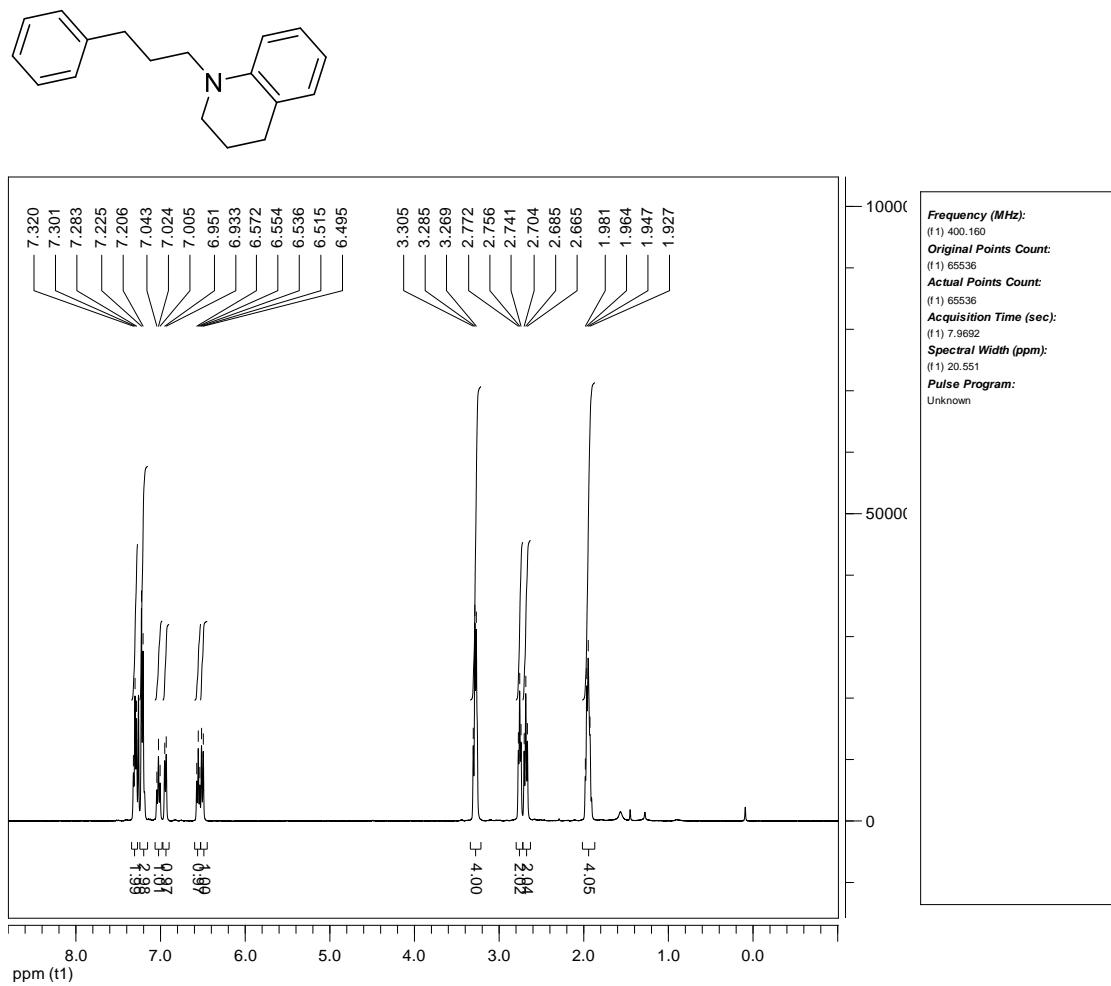


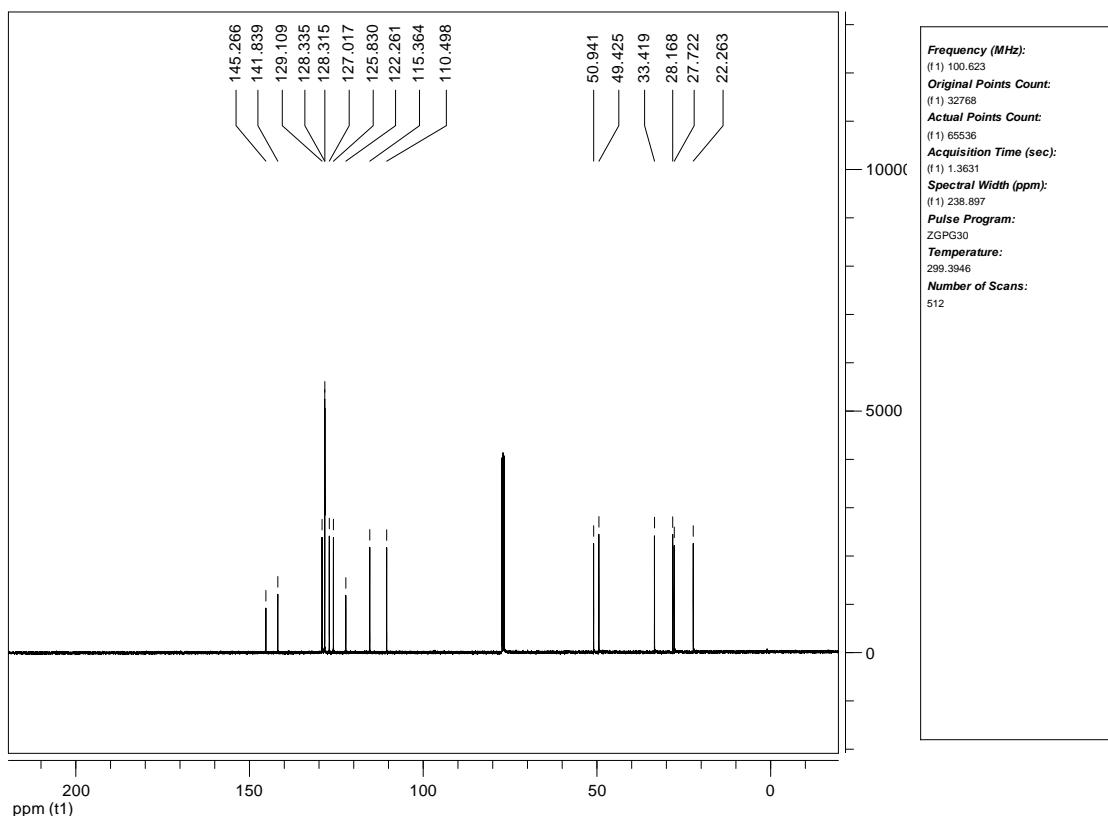
N-(3-Phenylpropyl)indoline (Table 3, Entry 13)



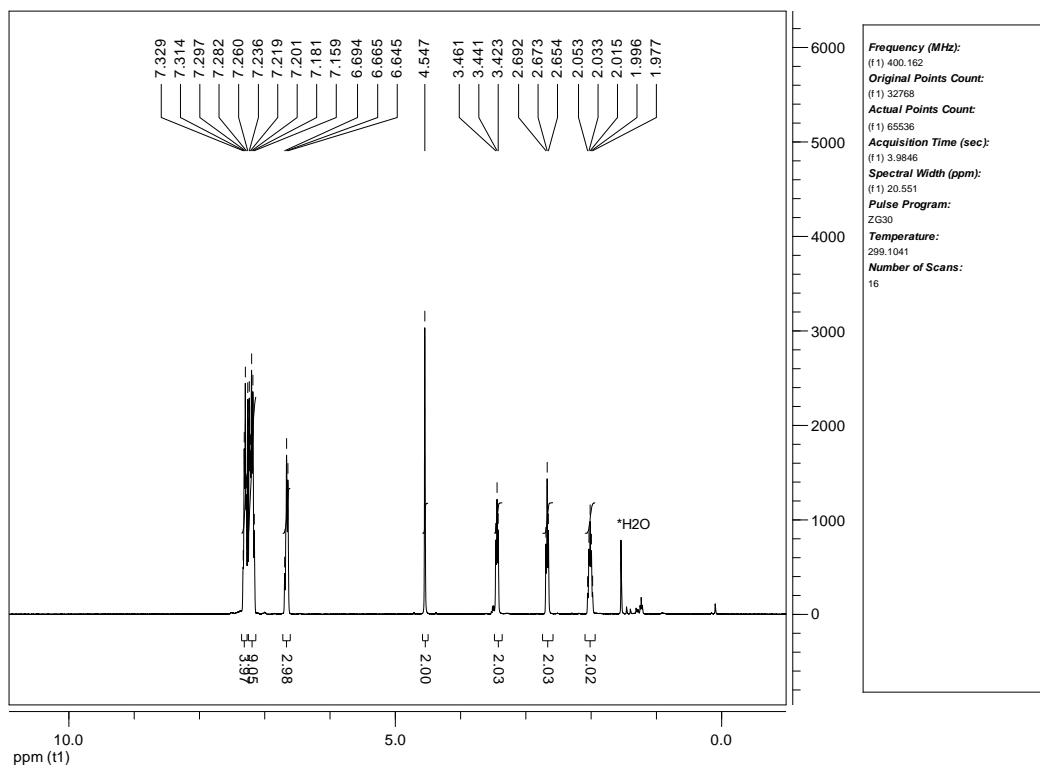
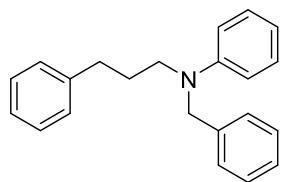


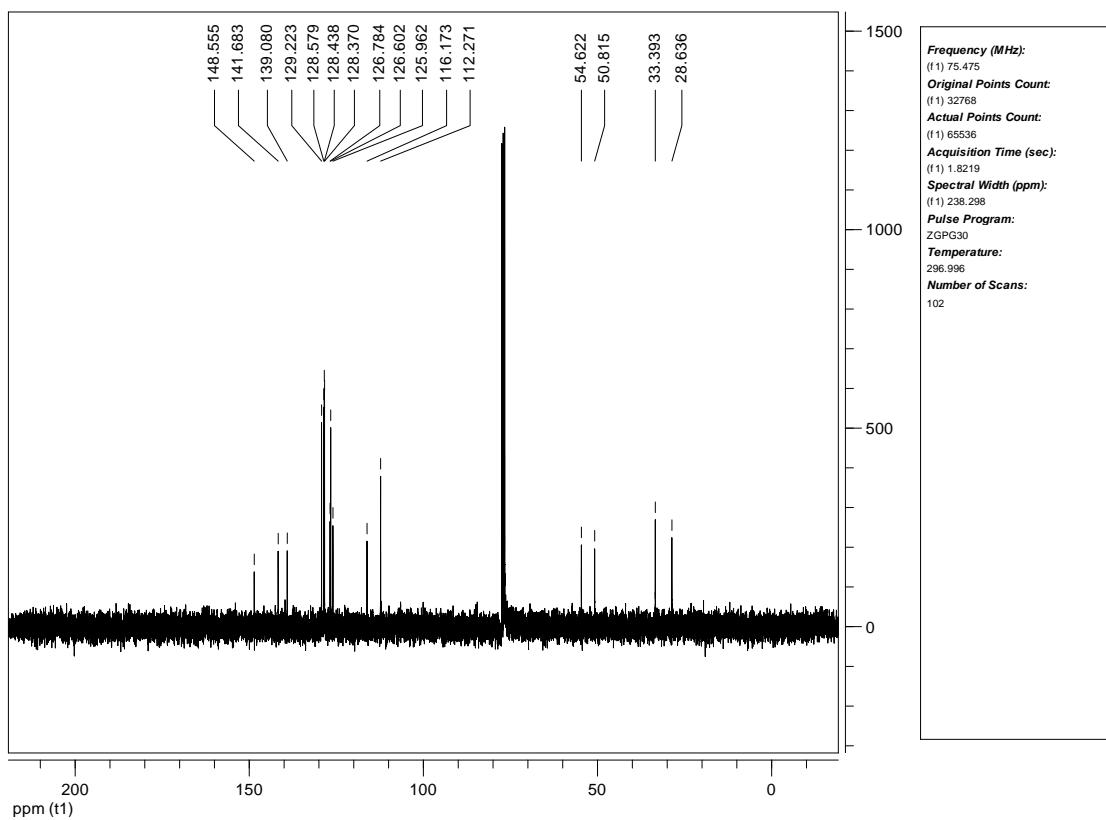
N-(3-Phenylpropyl)-1,2,3,4-tetrahydroquinoline (Table 3, Entry 14)



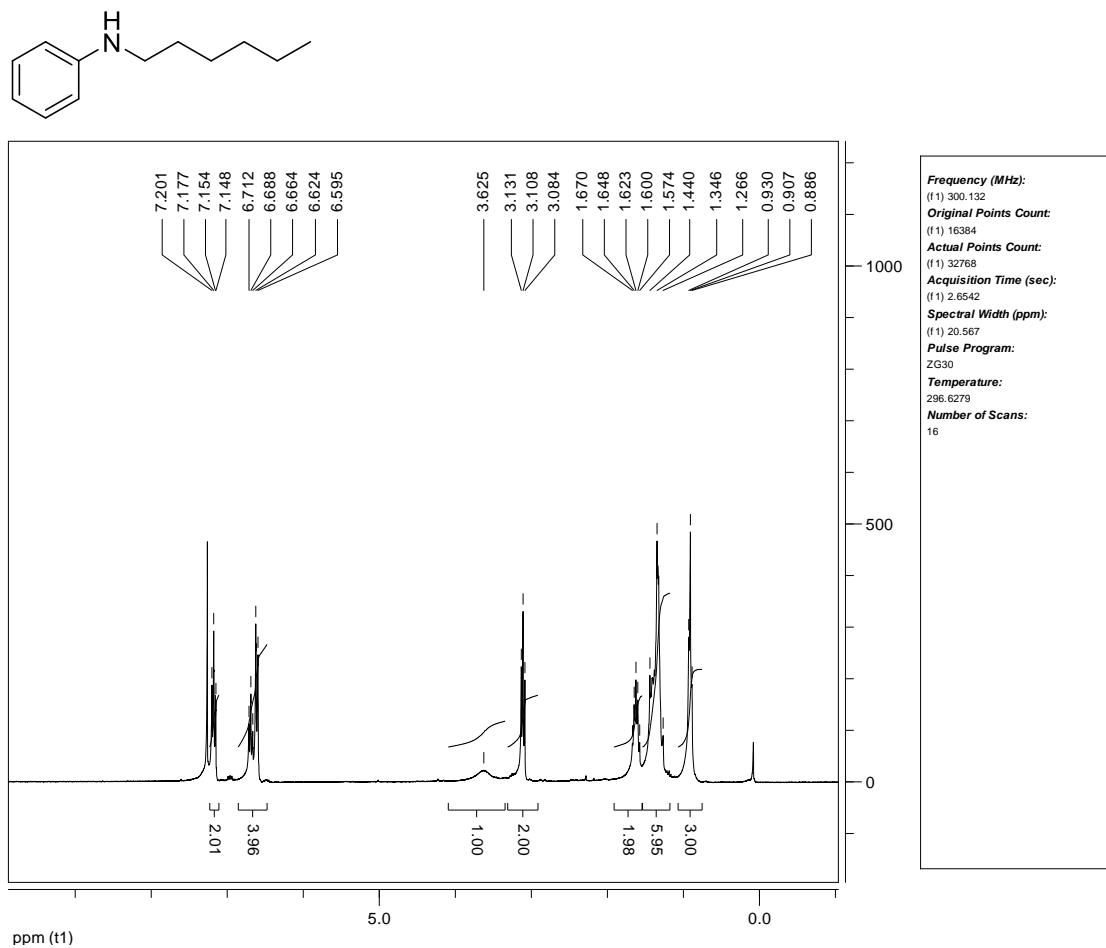


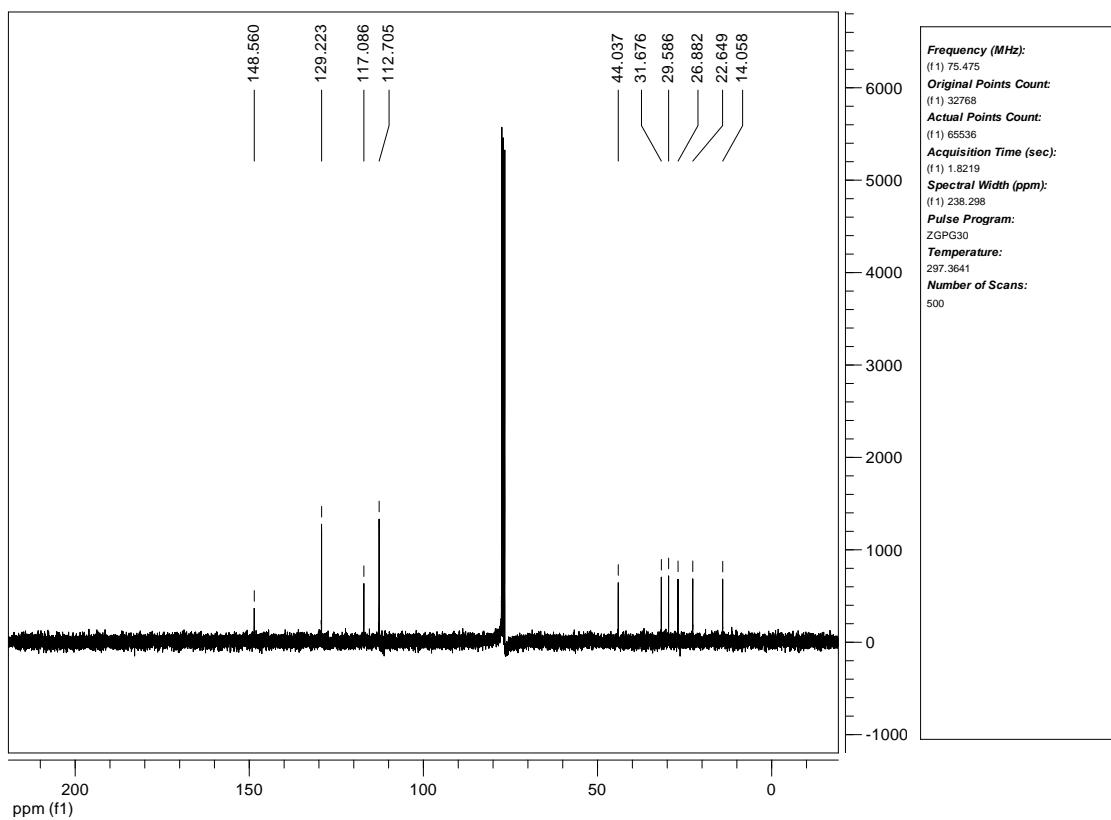
N-Benzyl-N-(3-phenylpropyl)aniline (Table 3, Entry 15)



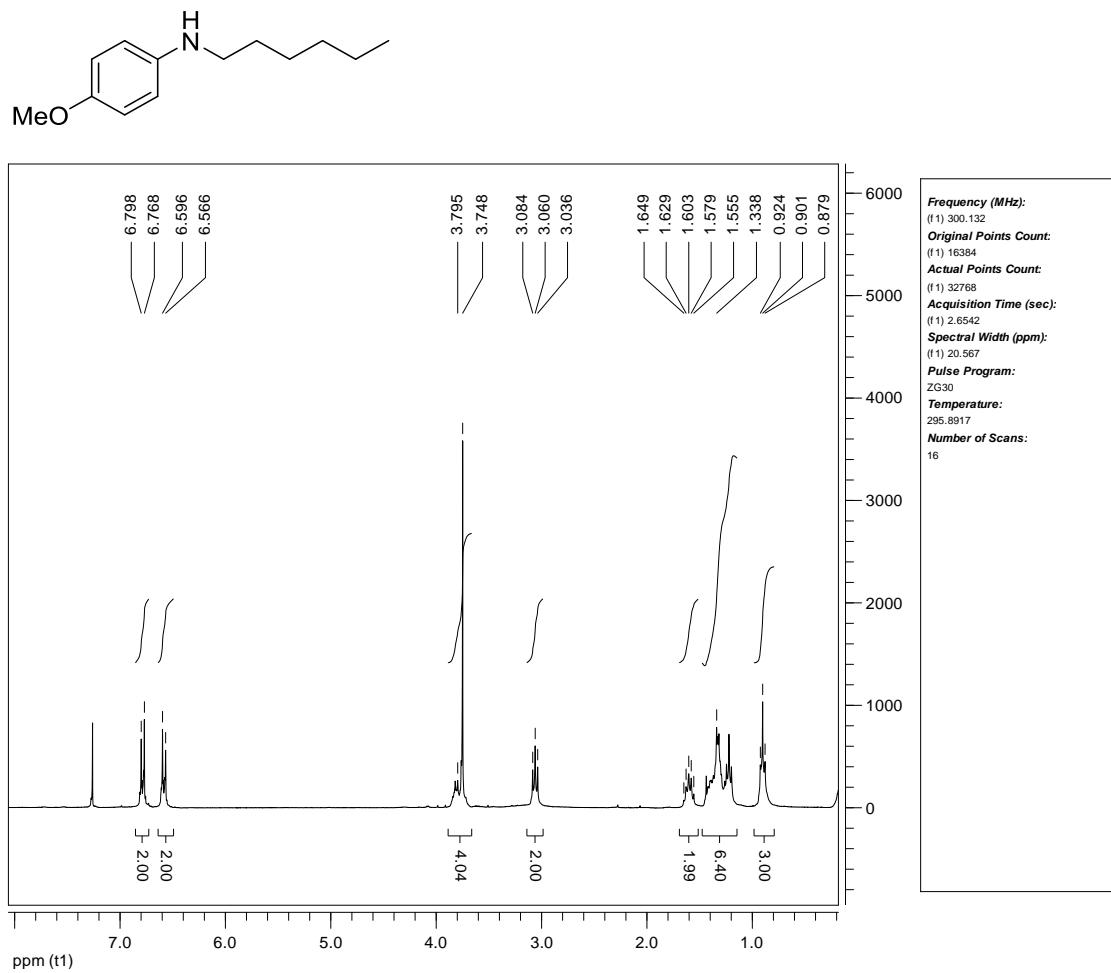


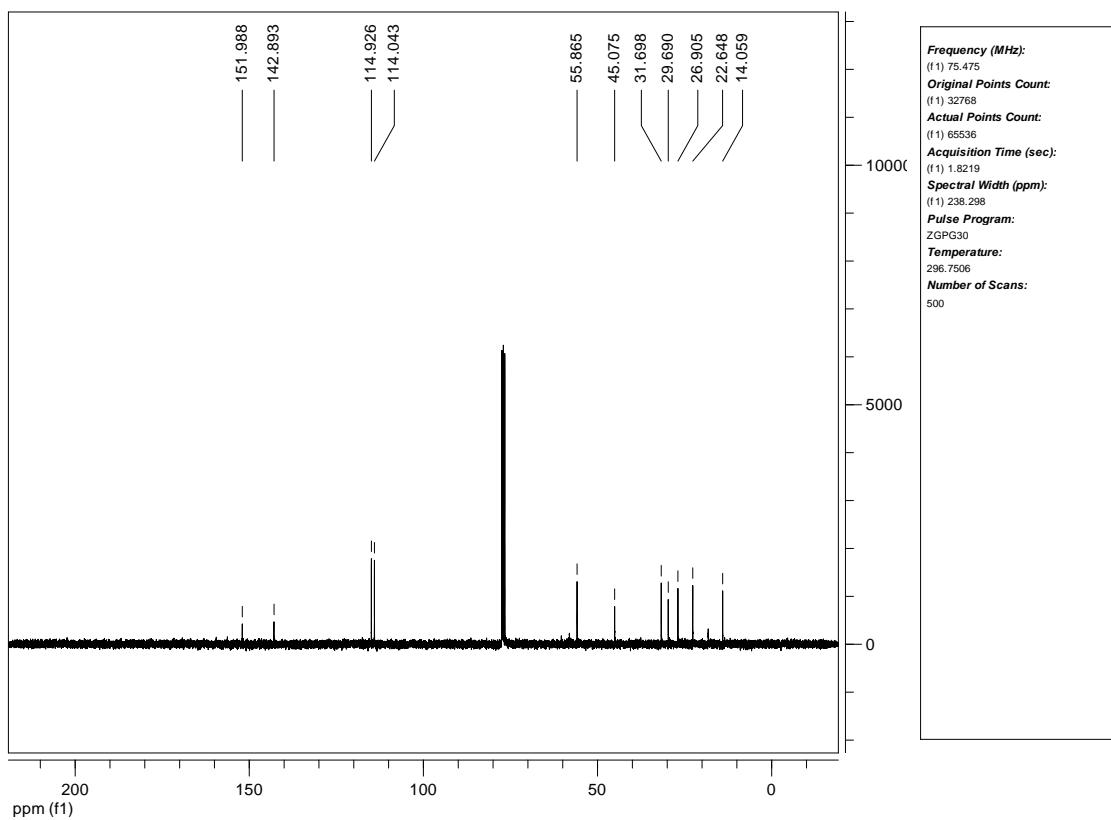
N-Hexylaniline (Table 4, Entry 1)



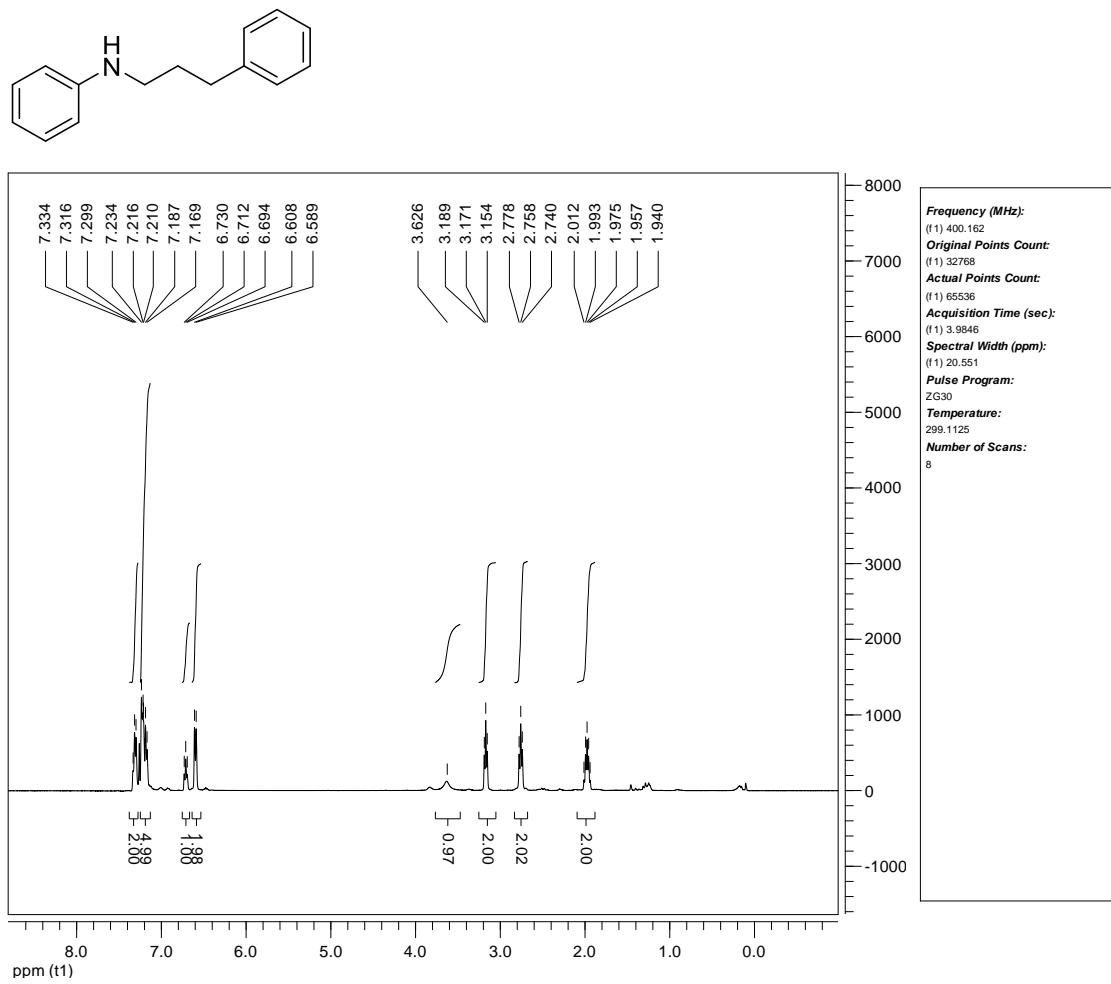


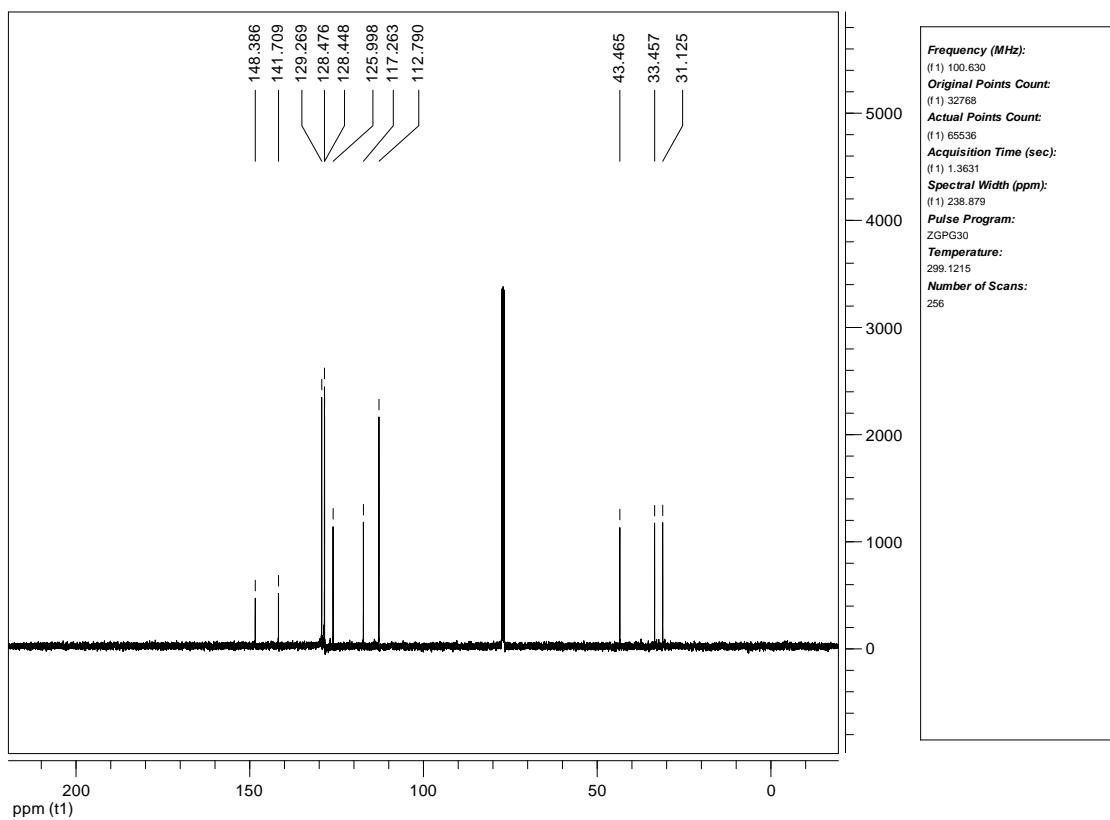
N-Hexyl-4-methoxyaniline (Table 4, Entry 2)



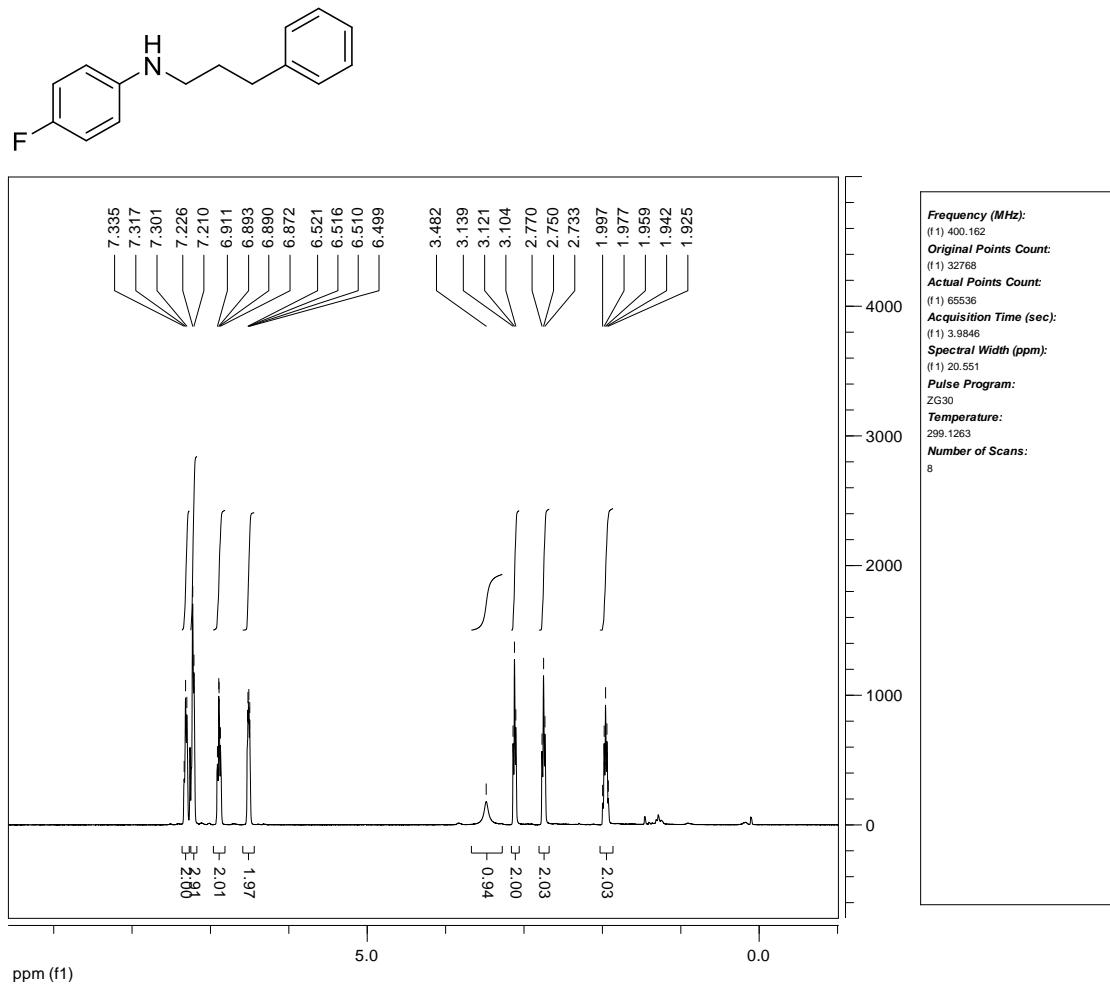


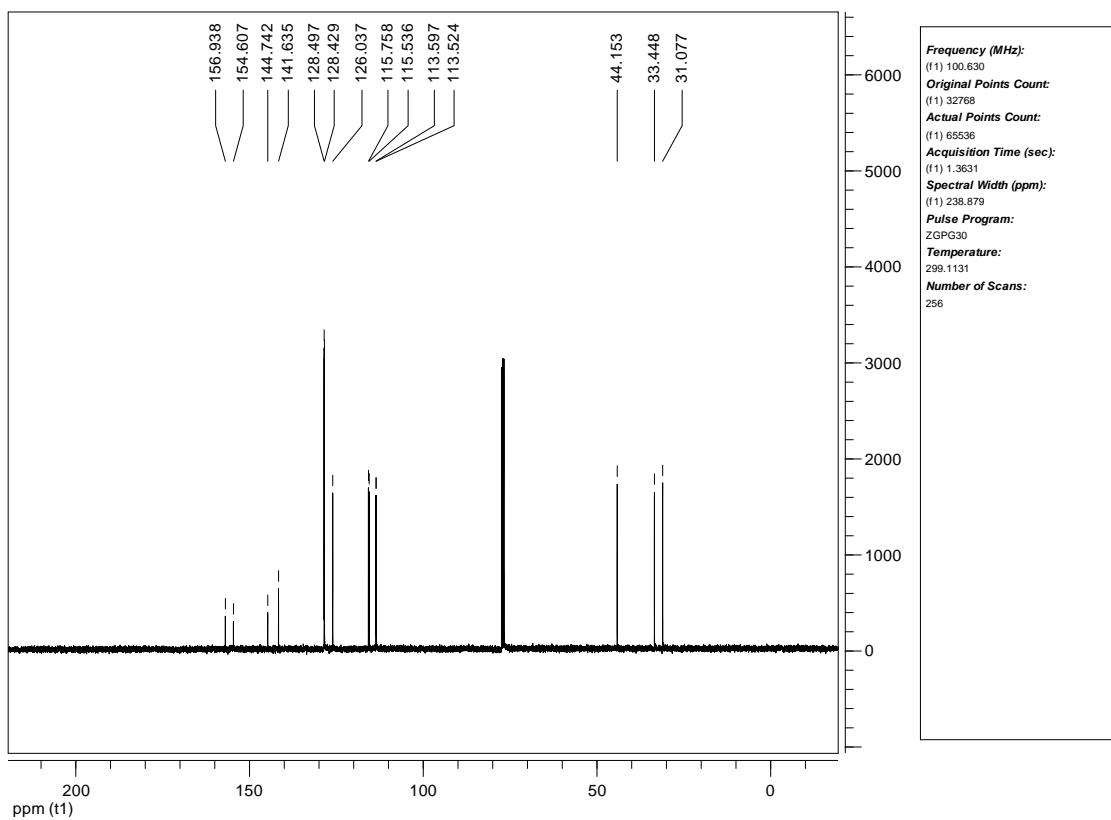
N-(3-Phenylpropyl)aniline (Table 4, Entry 3)



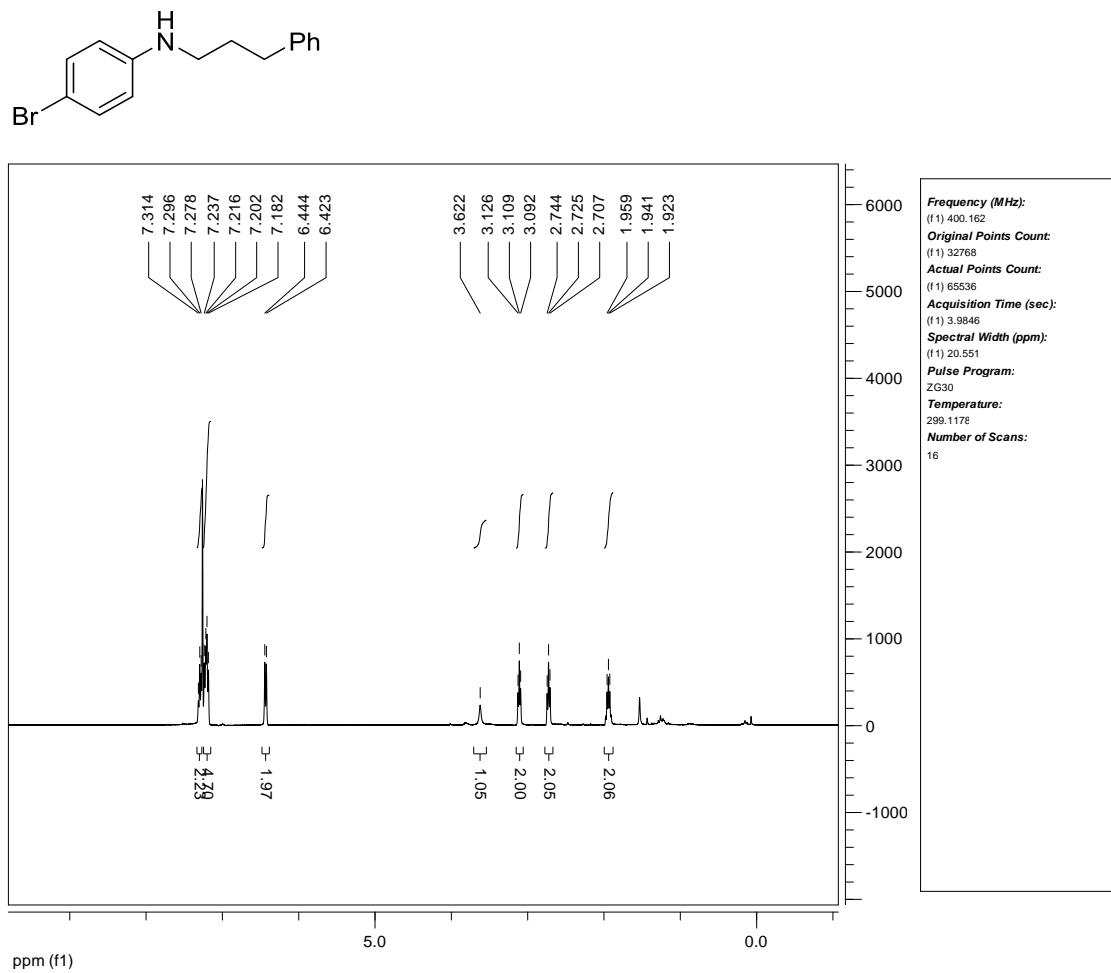


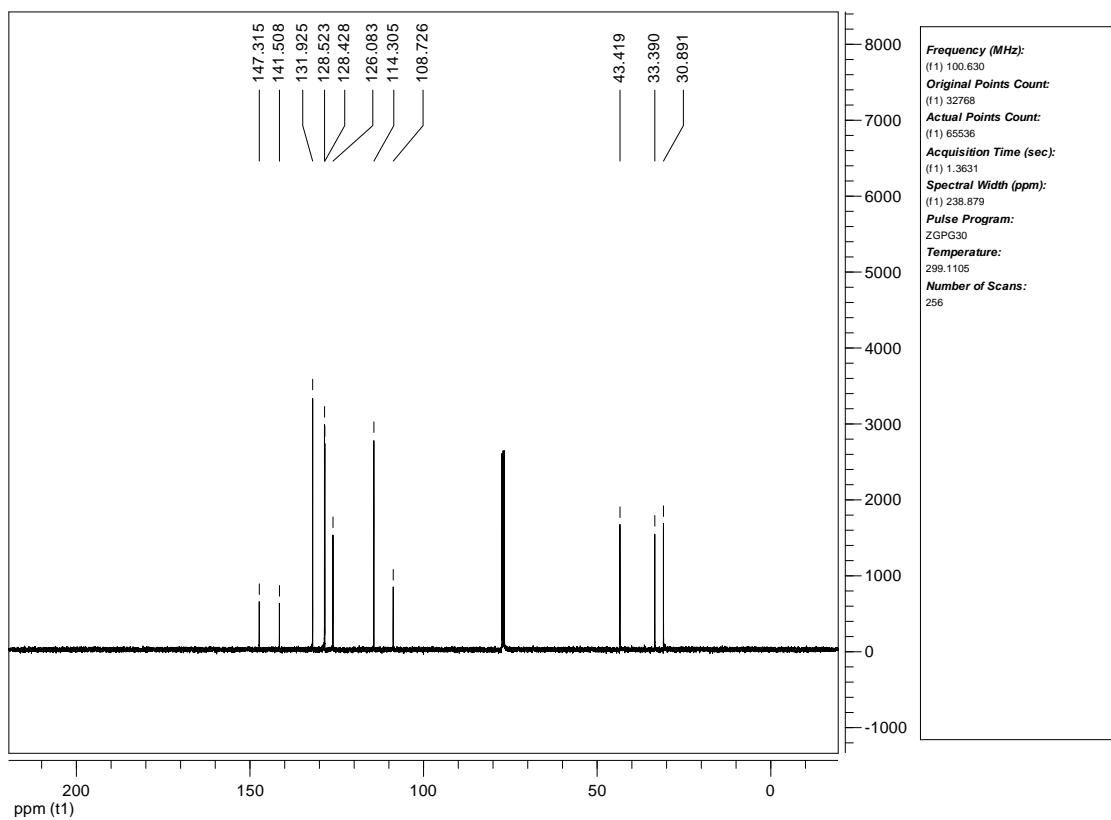
4-Fluoro-N-(3-phenylpropyl)aniline (Table 4, Entry 4)



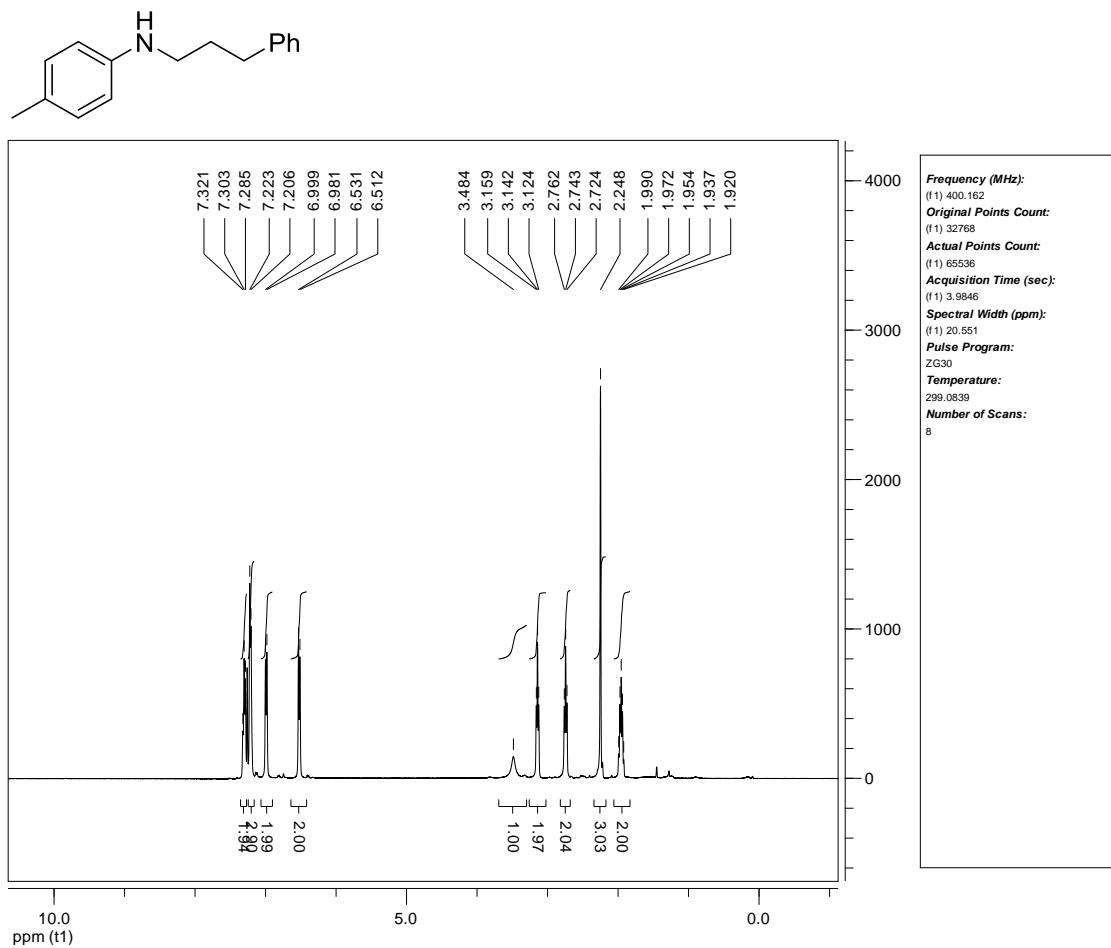


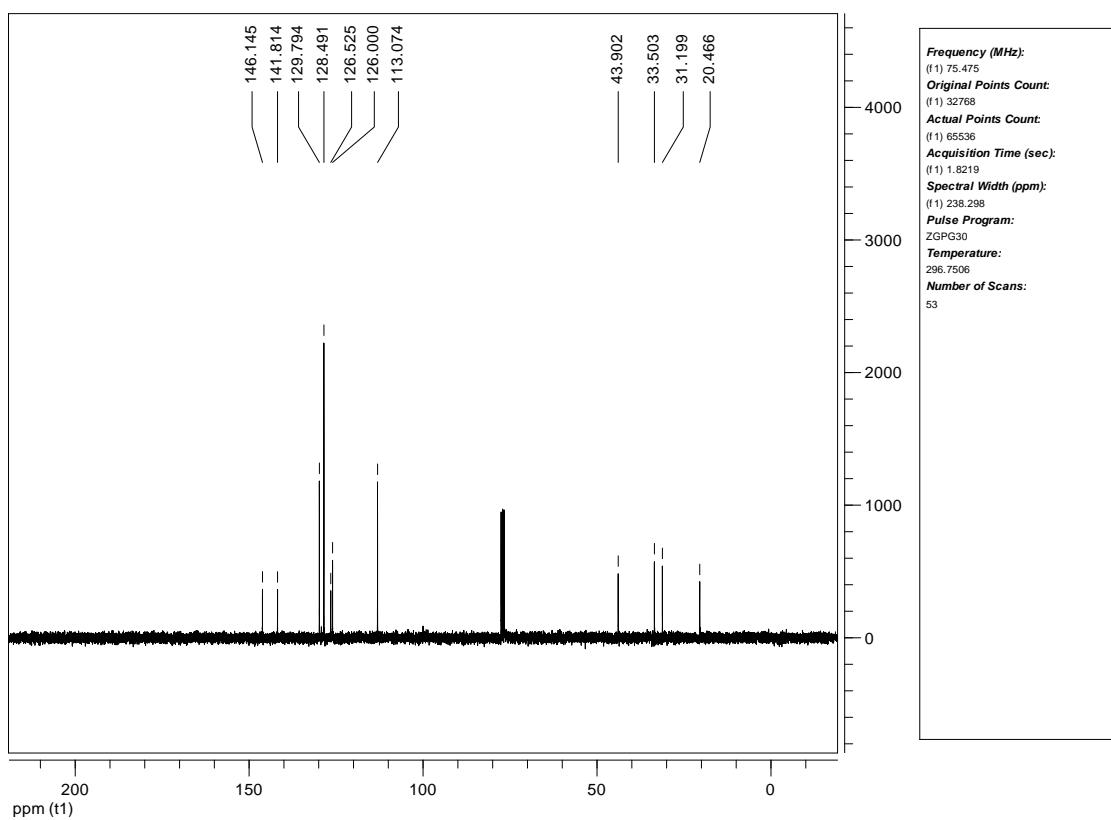
4-Bromo-N-(3-phenylpropyl)aniline (Table 4, Entry 5)



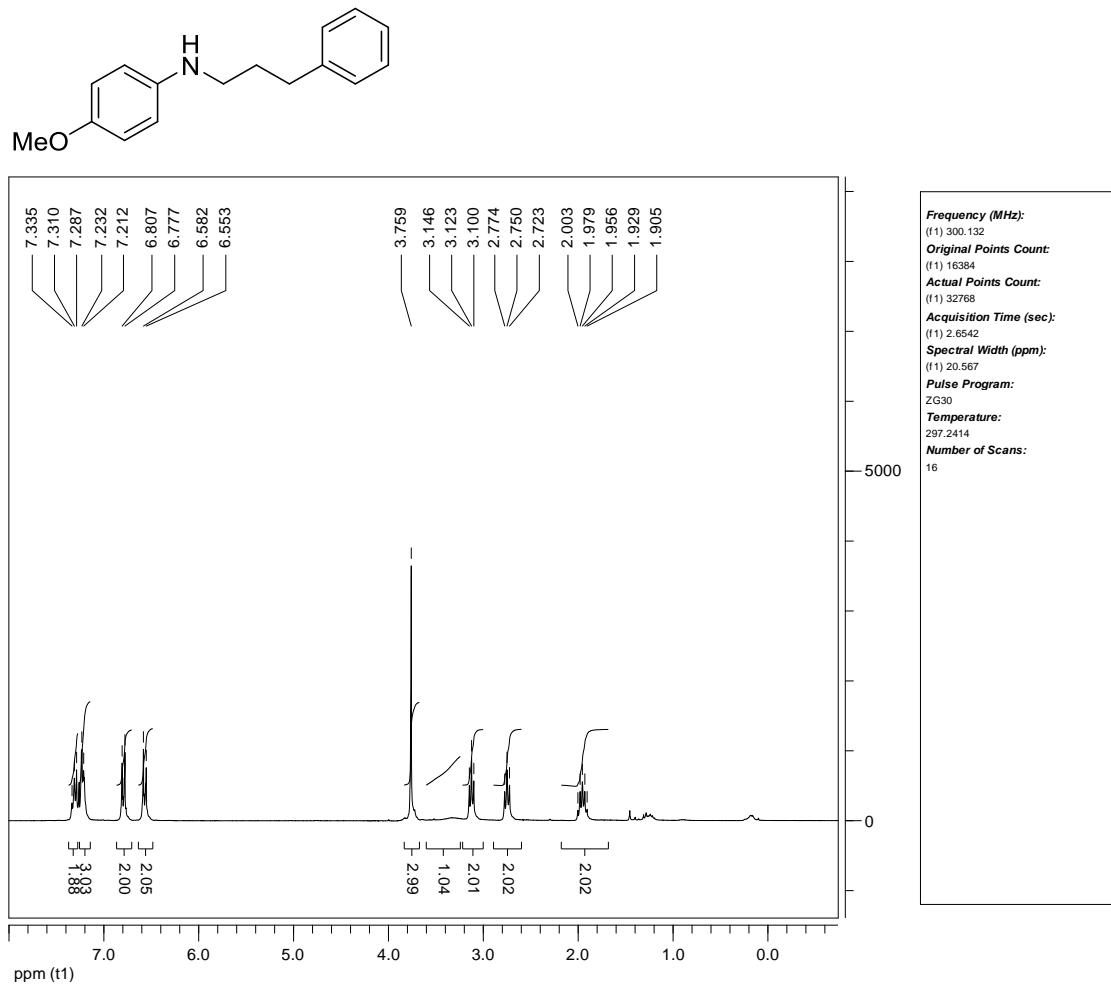


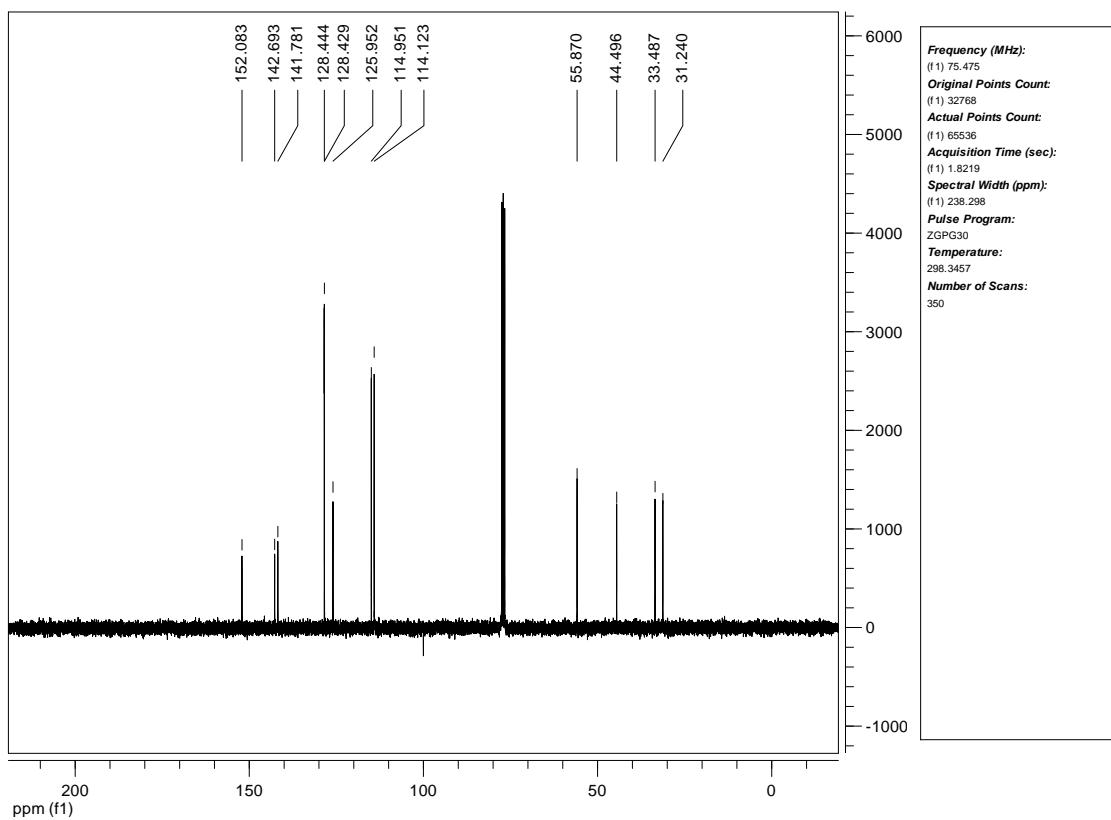
4-Methyl-N-(3-phenylpropyl)aniline (Table 4, Entry 7)



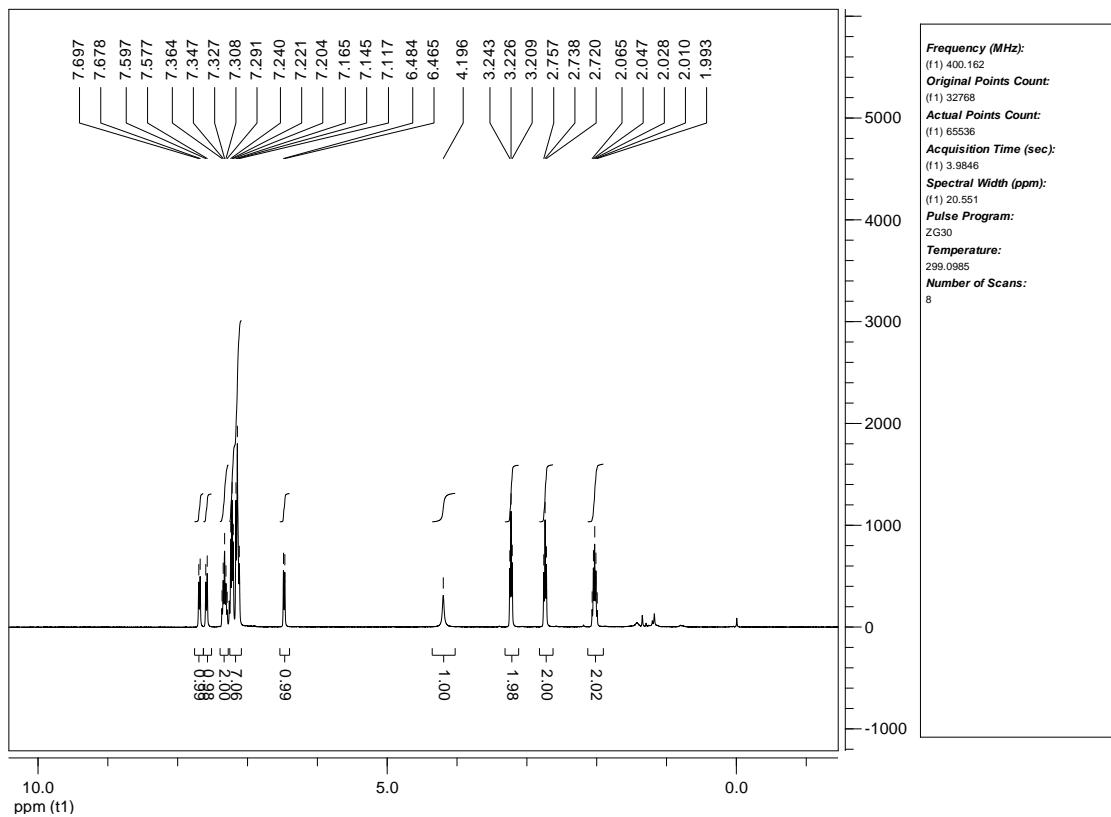
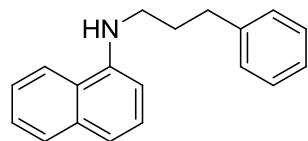


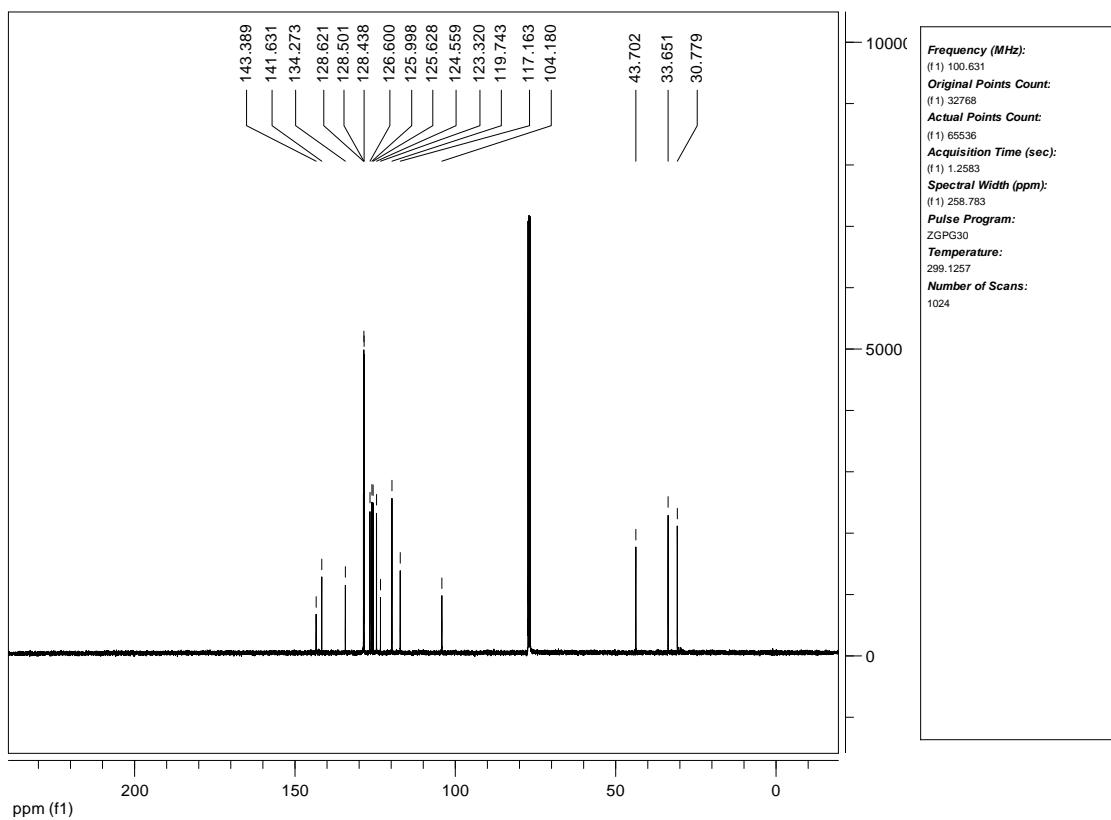
4-Methoxy-N-(3-phenylpropyl)aniline (Table 4, Entry 8)



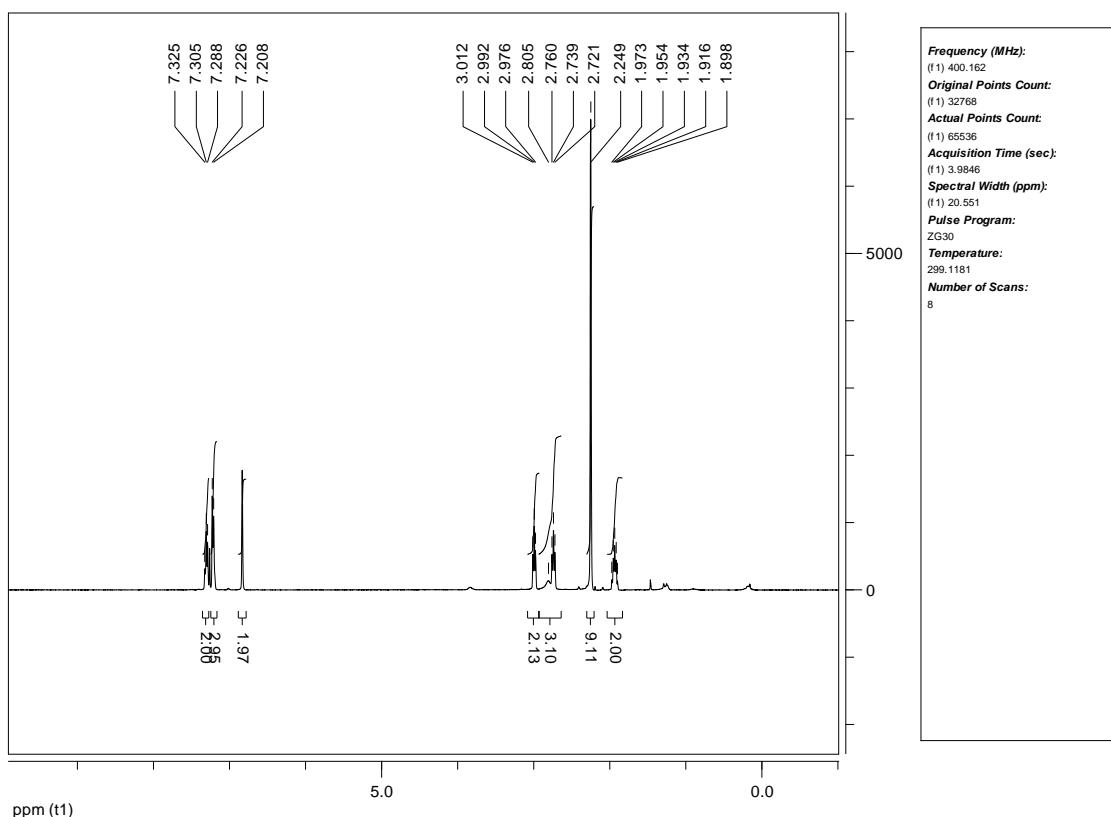


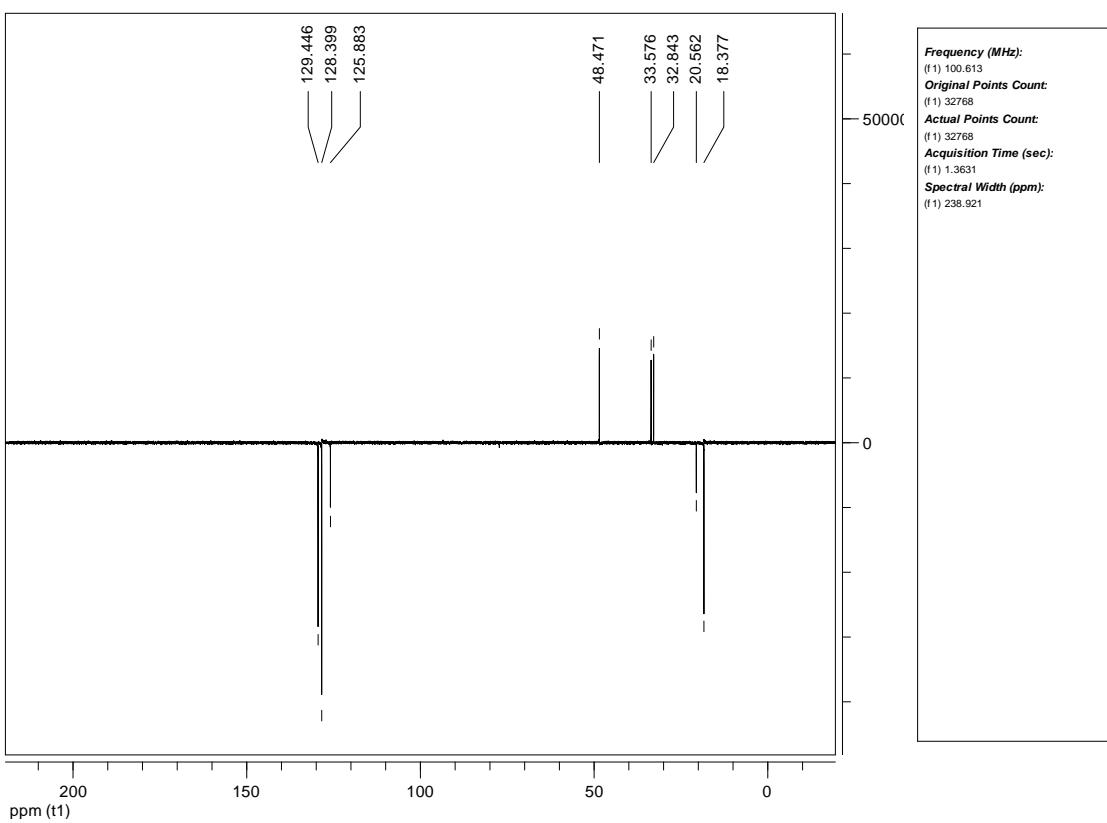
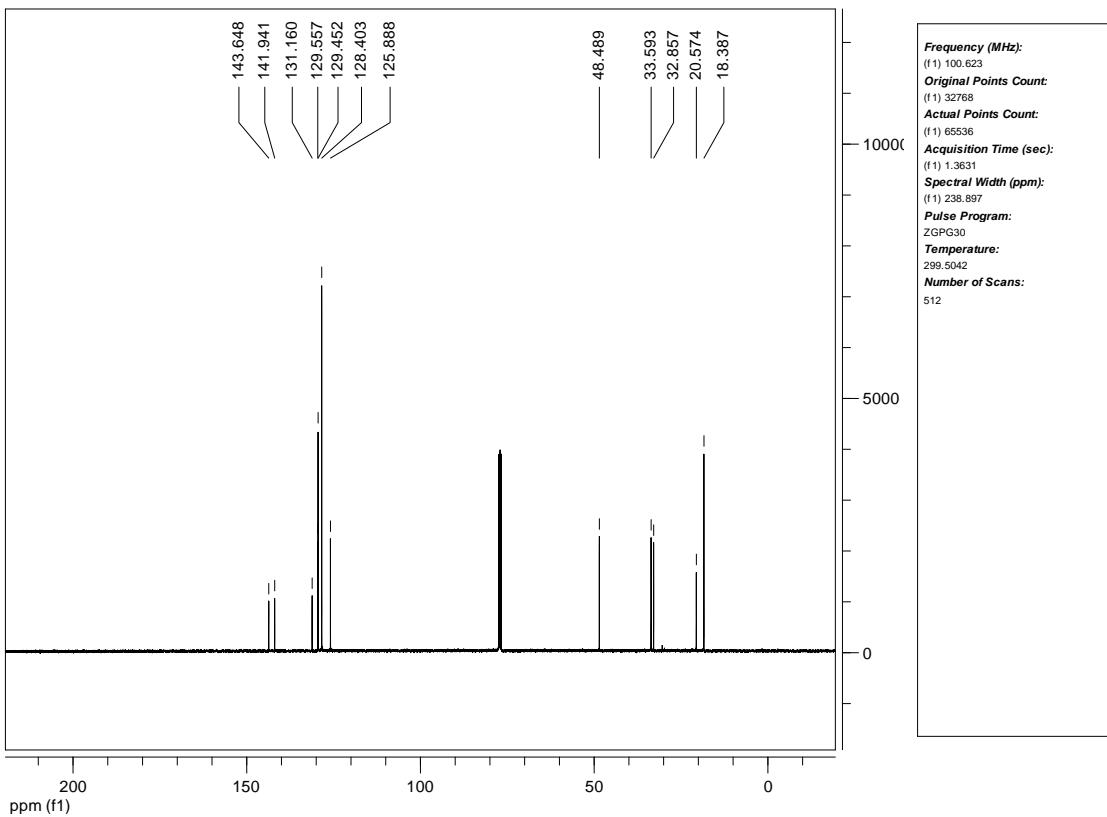
N-(3-Phenylpropyl)naphthalen-1-amine (Table 4, Entry 9)



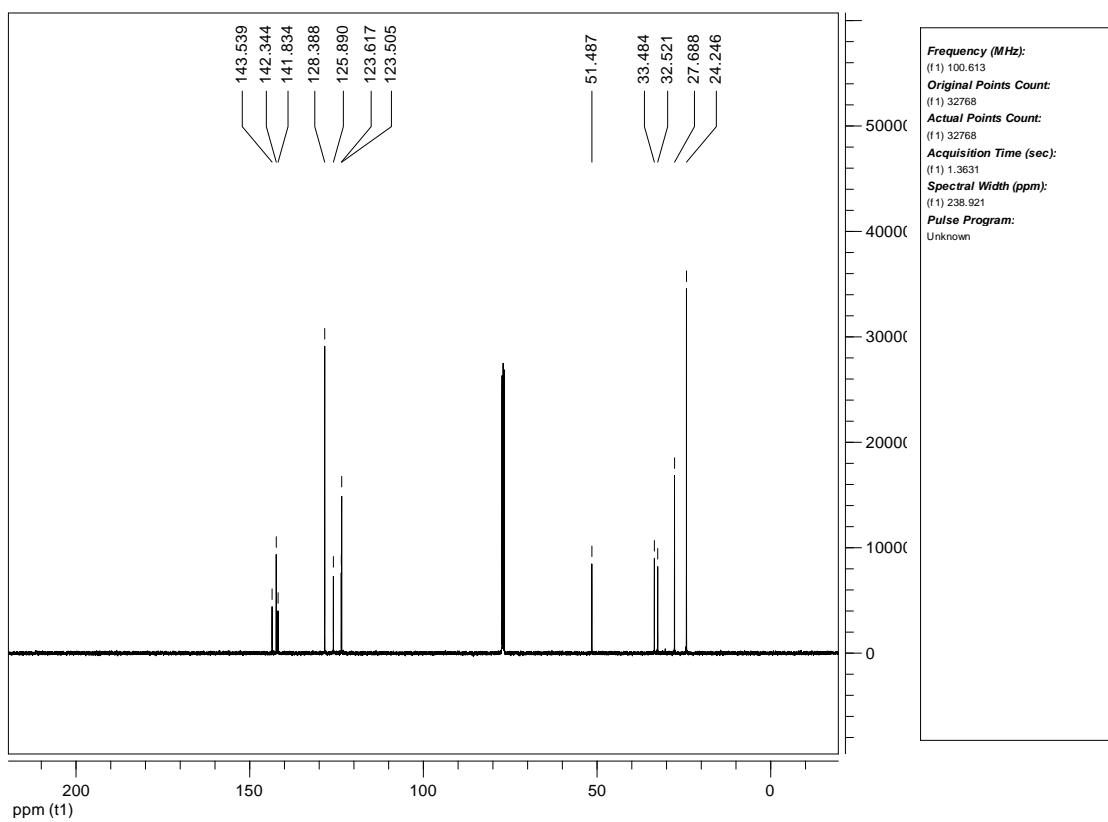
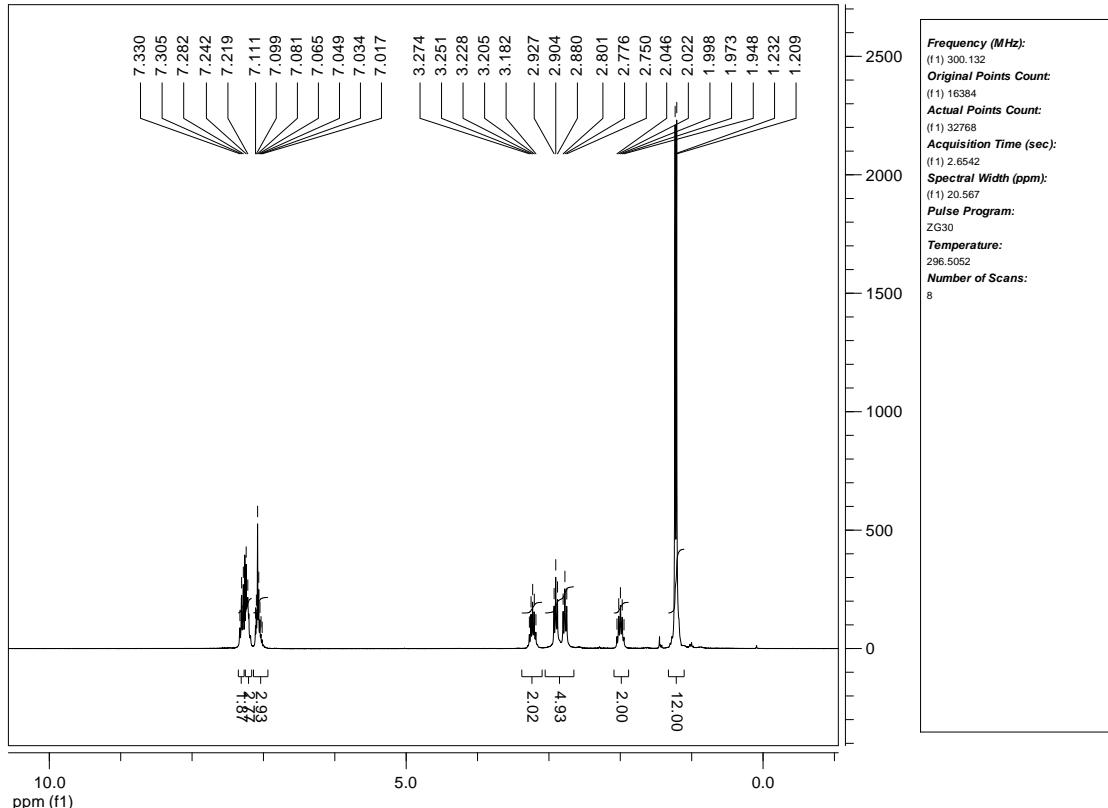
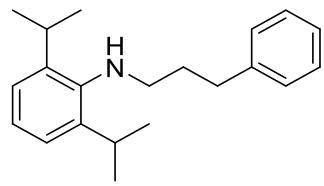


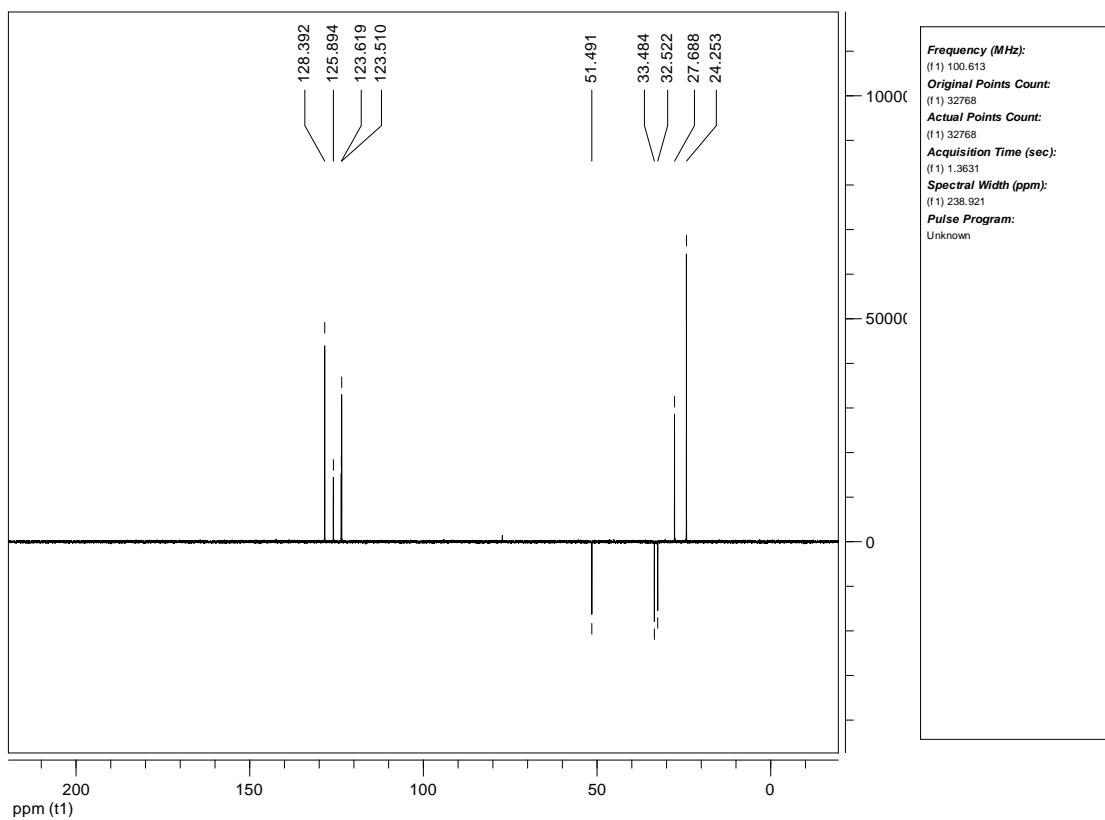
N-(3-phenylpropyl)-2,4,6-trimethyl aniline (Table 4, Entry 10)



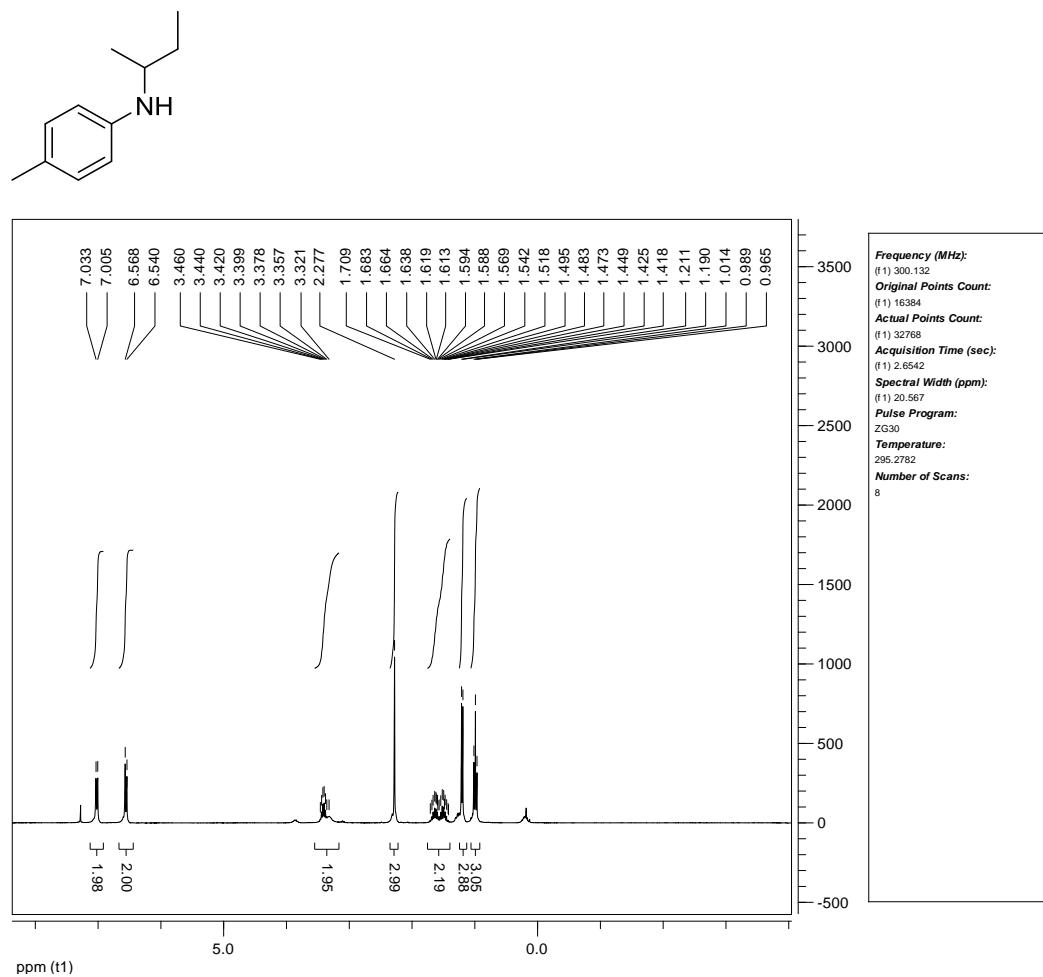


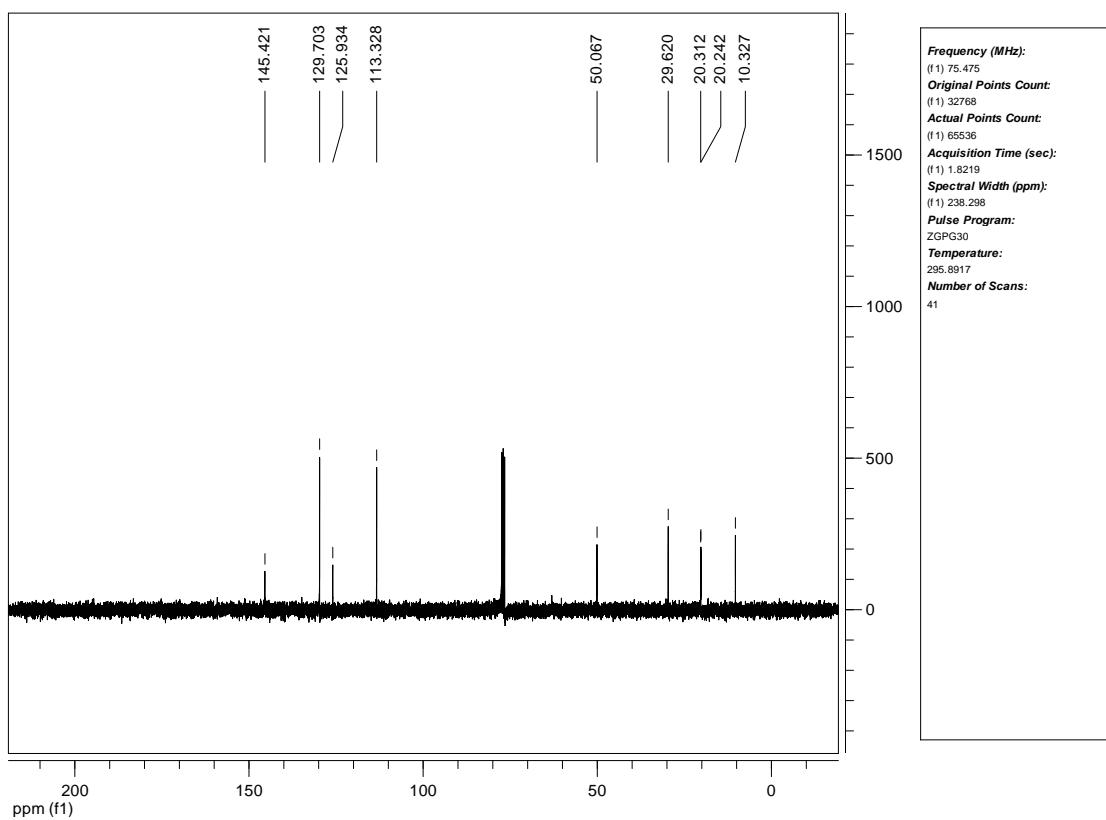
2,6-Diisopropyl-N-(3-phenylpropyl)aniline (Table 4, Entry 11)



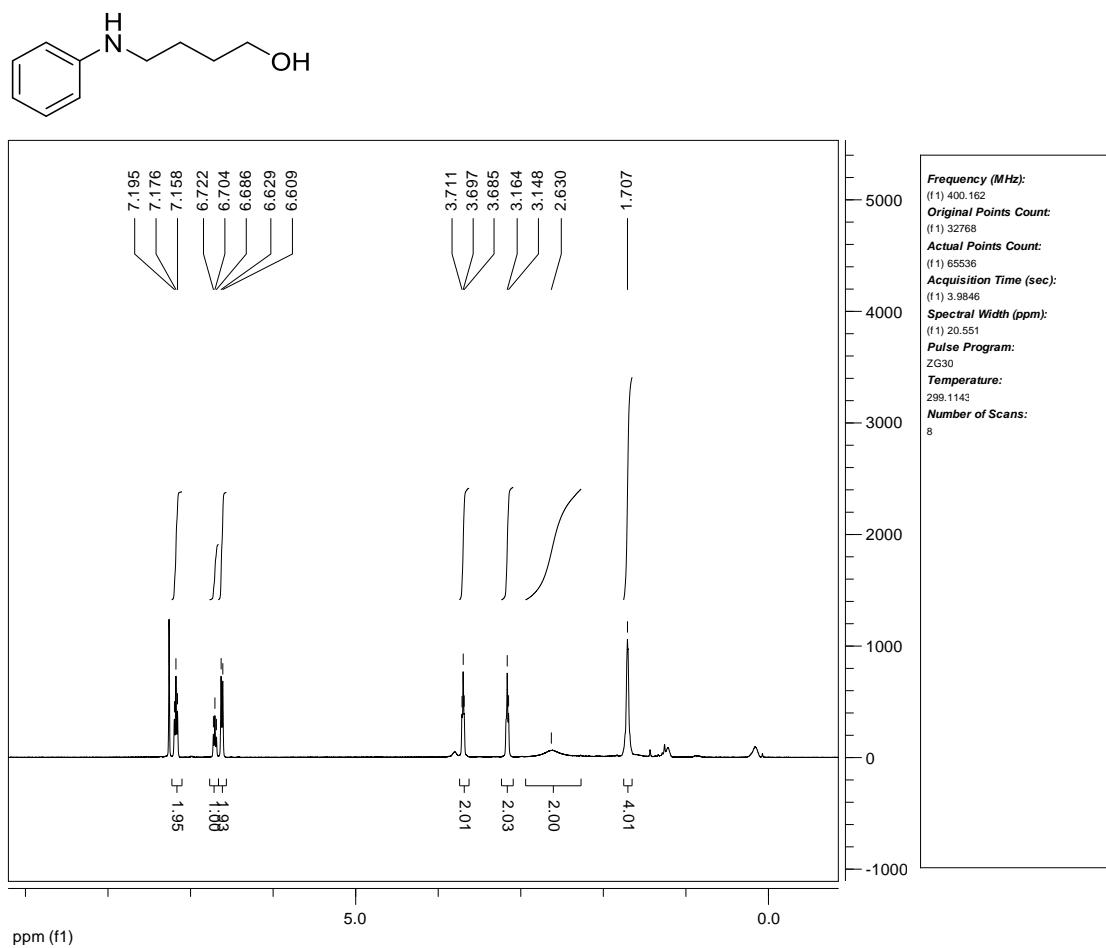


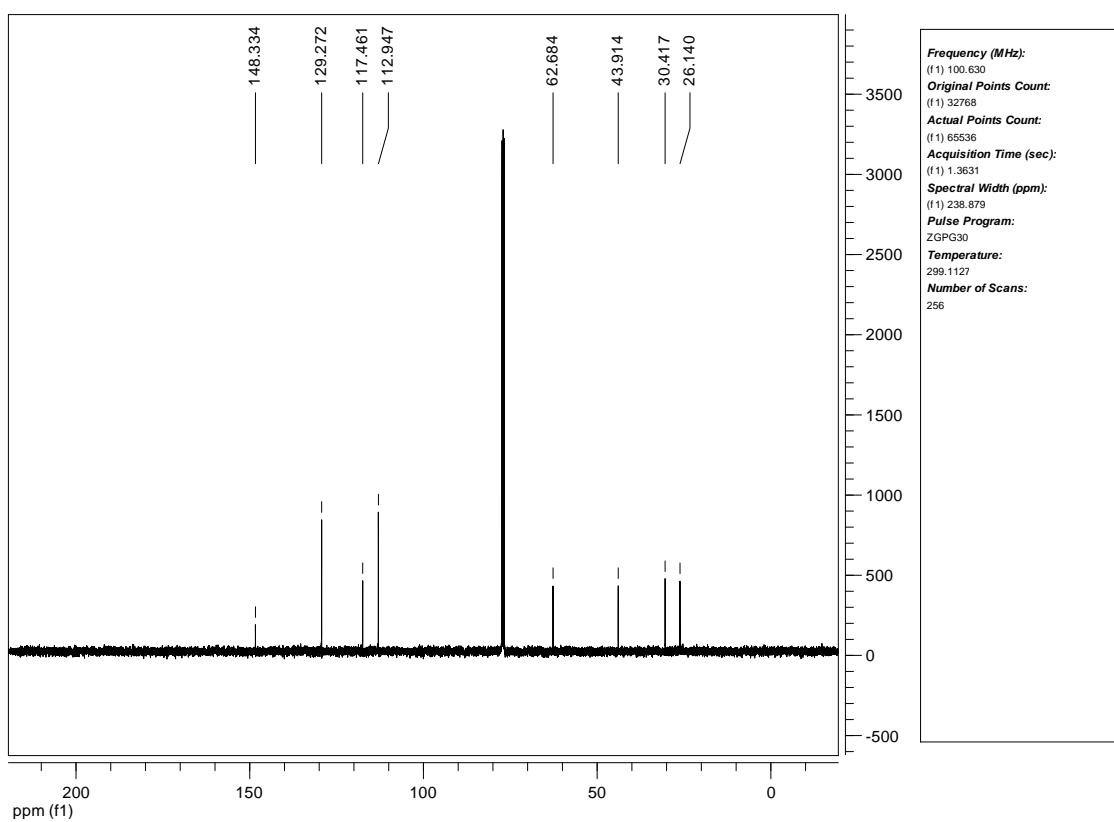
N-(*sec*-Butyl)-4-methylaniline (Table 4, Entry 12)



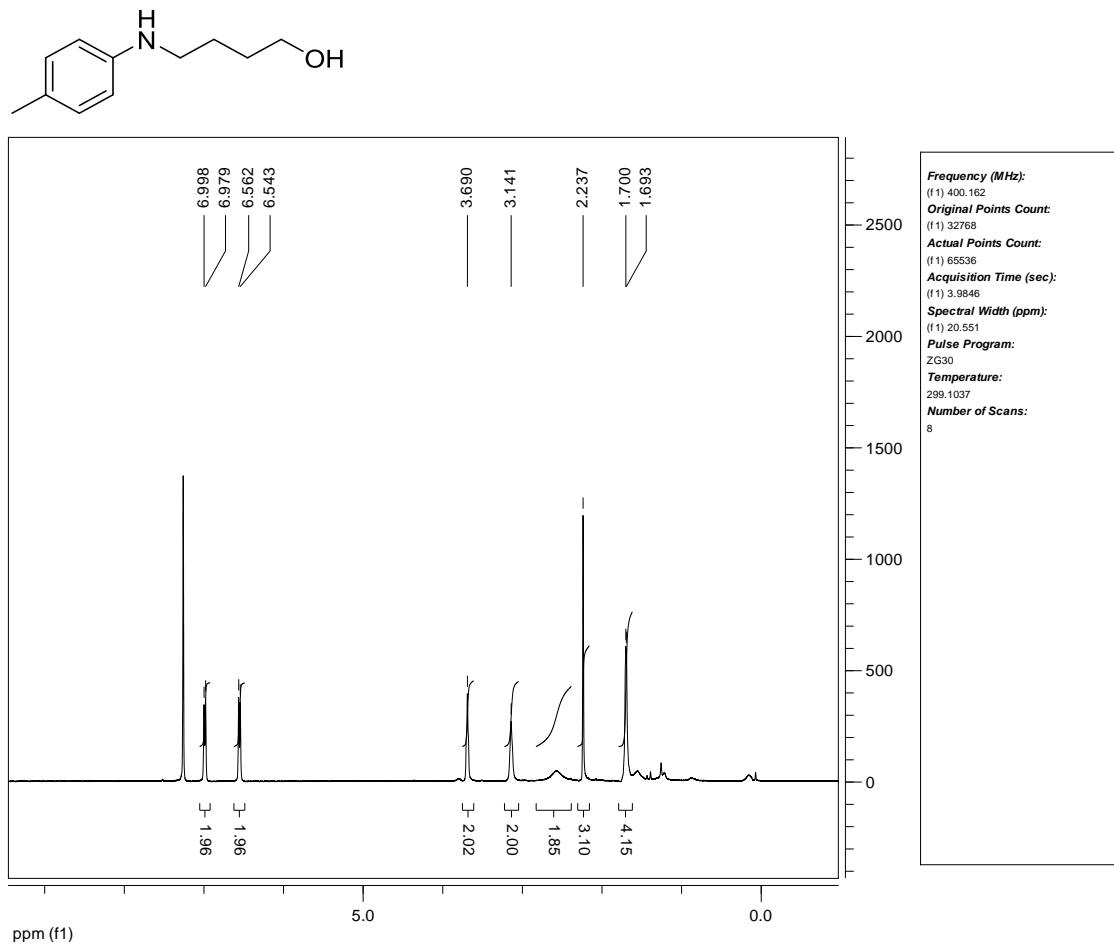


4-(phenylamino)butan-1-ol (Table 4, Entry 13)

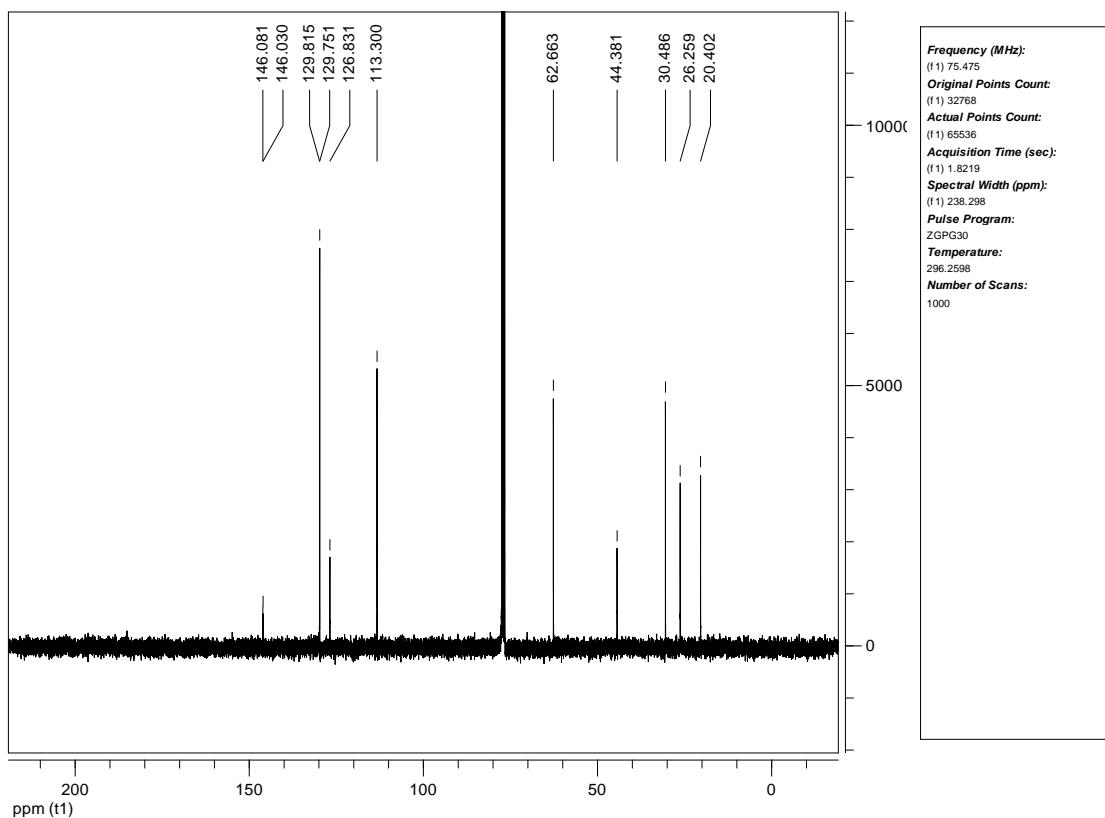




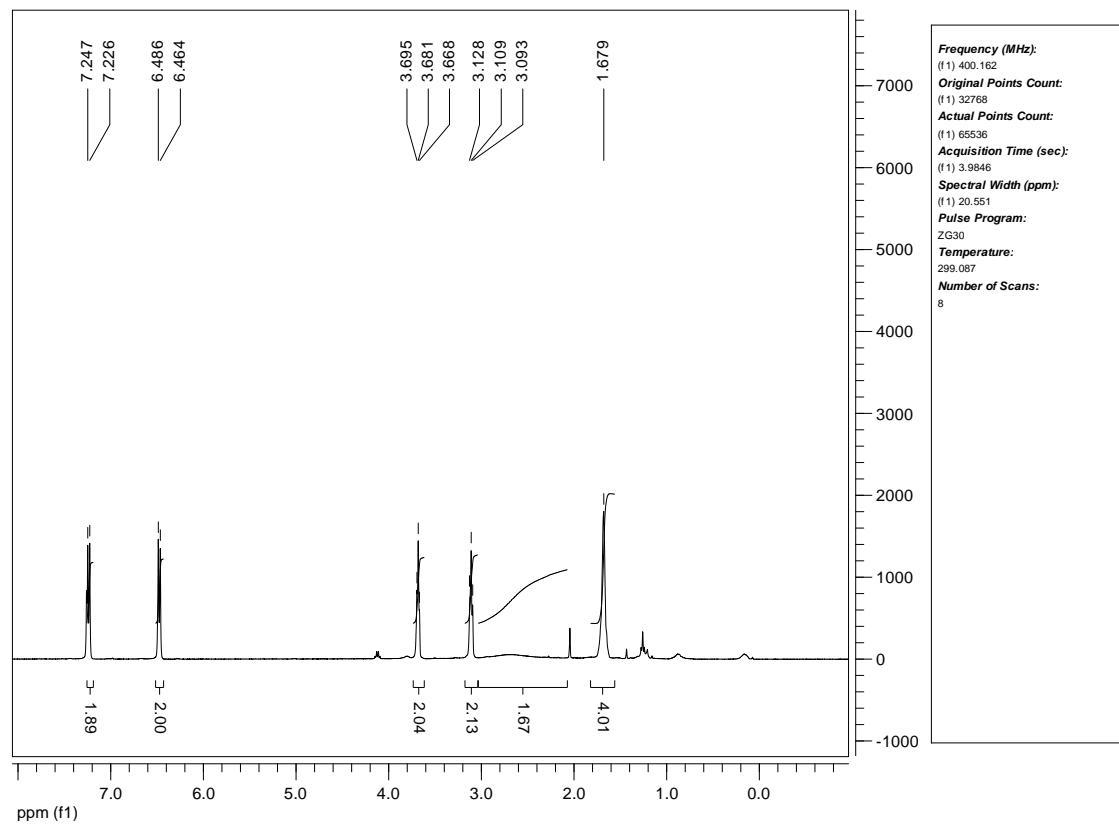
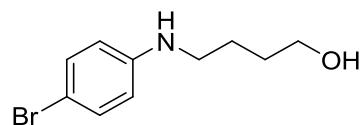
4-(*p*-Tolylamino)butan-1-ol (Table 4, Entry 14)

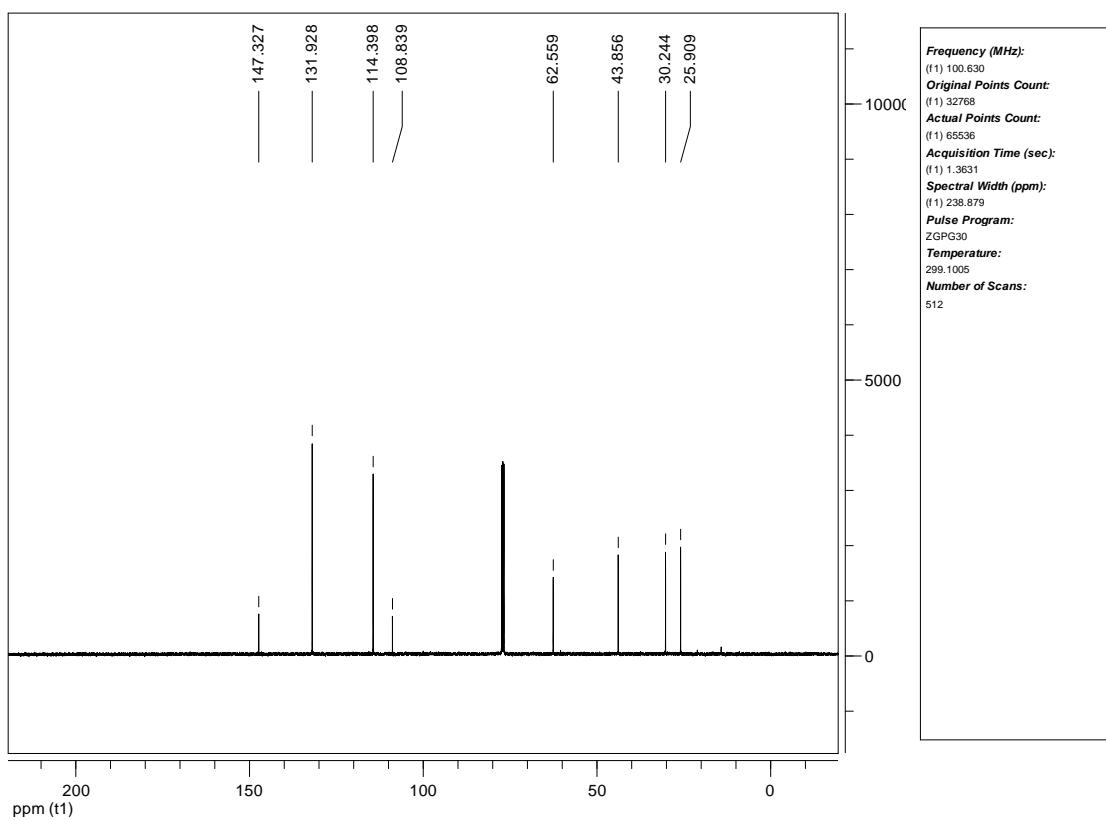


ppm (f1)

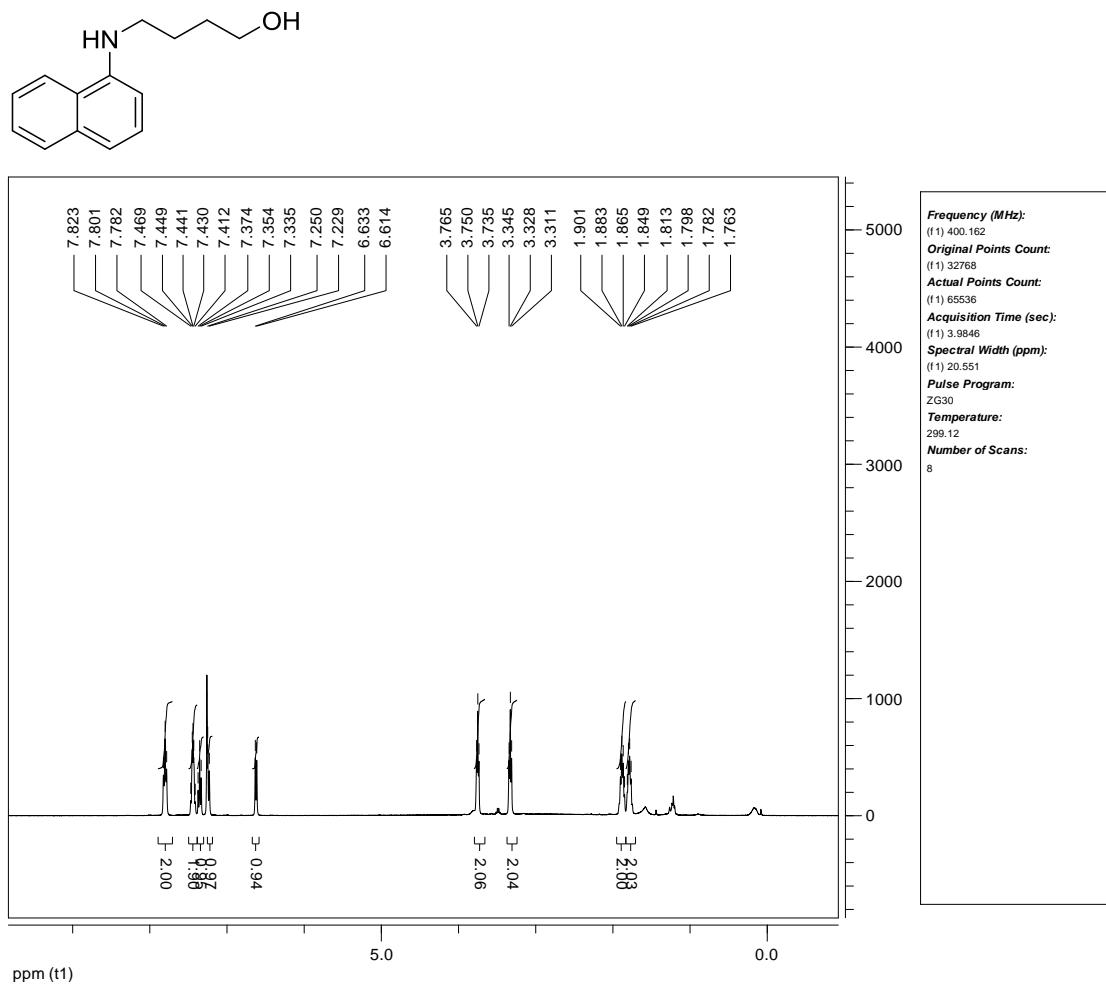


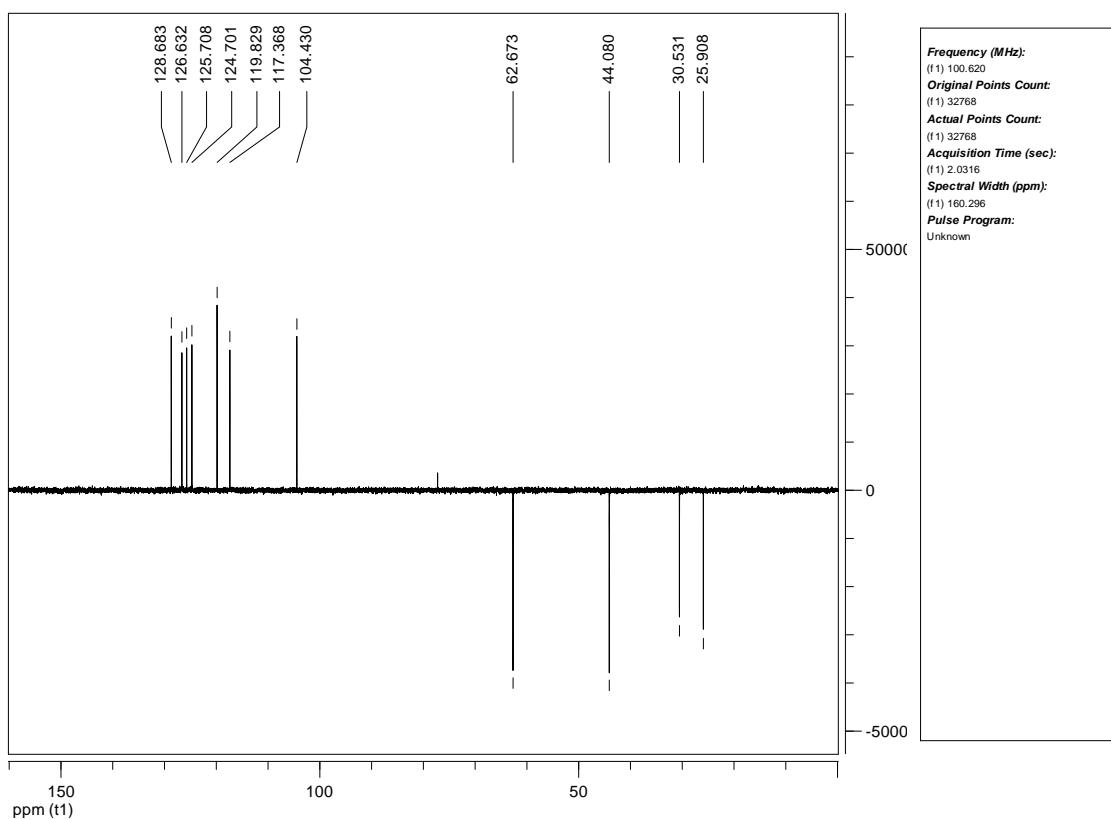
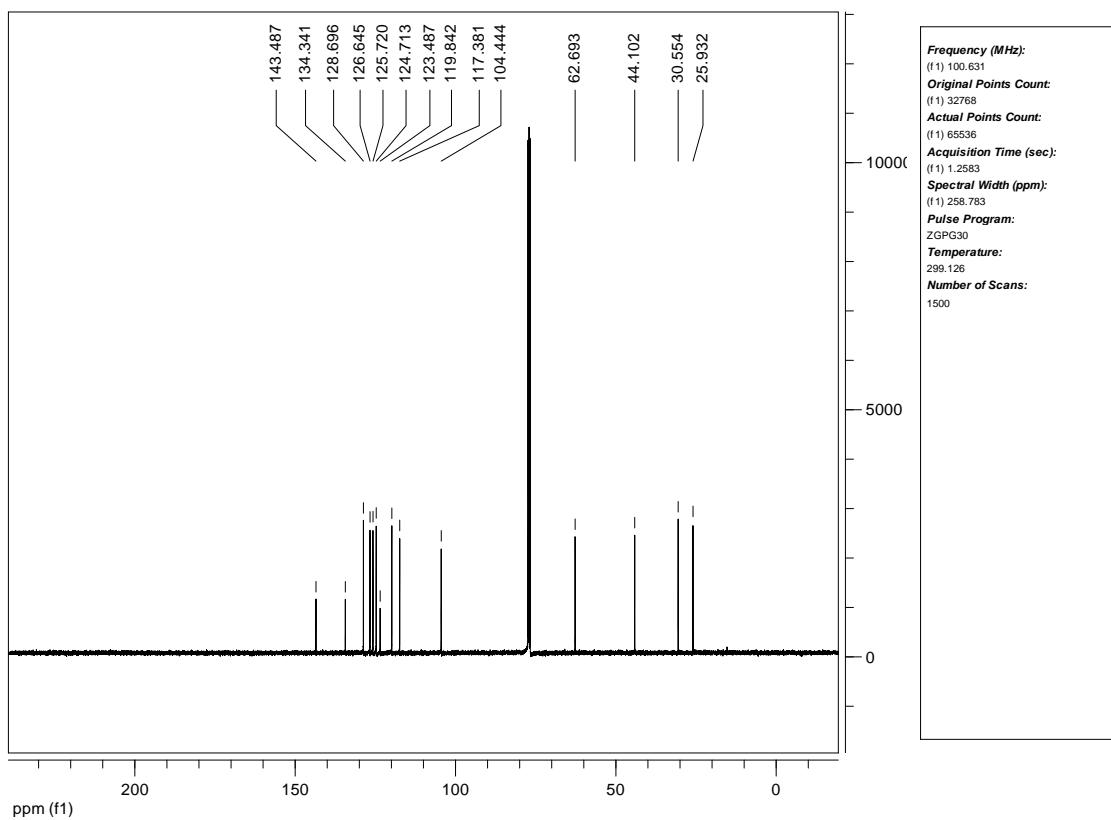
4-[(4-Bromophenyl)amino]butan-1-ol (**Table 4, Entry 15**)





4-(Naphthalen-1-ylamino)butan-1-ol (**Table 4, Entry 16**)





4-(Mesitylamino)butan-1-ol (Table 4, Entry 17)

