

Supporting Information for:

Bulky Alkylphosphines with Neopentyl Substituents as Ligands in the Amination of Aryl Bromides and Chlorides

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Experimental Details and Characterization Data

General Procedures. TTBP, DTBNpP, TBDNpP, and TNpP were obtained from FMC, Lithium Division as 10-15% (w/w) solutions in toluene. These were stored and dispensed in a nitrogen filled glove box. DTBNpP·HBF₄ was also obtained from FMC, Lithium Division. Palladium sources, aryl halides, and amines were obtained from commercial sources and were used as received. Toluene and xylenes were distilled from molten sodium under nitrogen. All coupling reactions were carried out under nitrogen in septum-sealed reaction vessels.

Typical procedure for the coupling of aryl bromides and aniline derivatives (Method A). Pd₂(dba)₃ (2-4 μmol), DTBNpP (10% solution in toluene) or DTBNpP·HBF₄ (4-8 μmol, 1 eq/Pd), sodium *t*-butoxide (0.85 mmol), and toluene (2 mL) were added to a round bottom flask in a glove box. Upon removing the septum sealed flask from the drybox, the aryl bromide (0.80 mmol) and aniline derivative (**8** or **10**, 0.82-1.0 mmol) were added by syringe and the reaction was allowed to stir for 1-6 hours at room temperature until judged complete by GC. The reaction mixture was then adsorbed on silica gel and purified by flash chromatography.

Typical procedure for the coupling of aryl chlorides and aniline derivatives (Method B). Pd₂(dba)₃ (2-20 μmol), DTBNpP (10% solution in toluene) or DTBNpP·HBF₄ (4-40 μmol, 1 eq/Pd), sodium *t*-butoxide (0.85 mmol), and solvent (toluene or xylenes) (2 mL) were added to a round bottom flask in a glove box. Upon removing the septum sealed flask from the drybox, the aryl chloride (0.80 mmol) and aniline derivative (**8** or **10**, 0.82-1.0 mmol) were added by syringe. The flask was placed in a preheated oil bath at the indicated temperature and stirred for 2-24 hours until judged complete by GC. The reaction mixture was then adsorbed on silica gel and purified by flash chromatography.

***N*-(4-Fluorophenyl)aniline (Table 3, entry 1).** 1-Bromo-4-fluorobenzene (140 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(4-fluorophenyl)aniline (84%, 126 mg) as a low-melting solid. ¹H NMR (500 MHz, CDCl₃): δ 7.26 (dd, 7.27, 8.48 Hz, 2H), 7.04-7.07 (m, 2H), 6.97-7.01 (m, 4H), 6.91 (tt, 1.11, 7.44 Hz, 1H), 5.58 (brs, 1H). ¹³C NMR (90.6 MHz, DMSO): δ 155.9 (d, *J* = 235.5 Hz), 143.5, 139.3 (d, *J*_{C-F} = 2.67), 128.7, 118.9, 118.4 (d, *J*_{C-F} = 7.34), 115.6, 115.1 (d, *J*_{C-F} = 22.0). The ¹H NMR spectrum was consistent with previously reported data.¹

***N*-(4-Trifluoromethylphenyl)aniline (Table 3, entry 2).** 4-Bromobenzotrifluoride (179 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(4-(trifluoromethyl)phenyl)aniline (96%, 182 mg). ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.68 (s, 1H), 7.50 (d, *J* = 8.83 Hz, 2H), 7.31 (t, *J* = 7.97 Hz, 2H), 7.16 (d, *J* = 7.50 Hz, 2H), 7.13 (d, *J* = 8.45 Hz, 2H), 6.97 (t, *J* = 7.25 Hz, 1H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 148.0, 142.0, 129.8, 126.9 (q, *J*_{C-F} = 3.71 Hz), 125.4 (q, *J*_{C-F} = 270.4 Hz), 122.1, 119.5, 119 (q, *J*_{C-F} = 32.1 Hz), 115.1. The NMR spectral data was consistent with the previously reported data.² mp: 63-65 °C (lit. mp: 63-64 °C).³

***N*-Phenyl-*p*-toluidine (Table 3, entry 3; Table 6, entry 1).** 4-Bromotoluene (138 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-phenyl-*p*-toluidine (125

mg, 86%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.21 (m, 5H), 6.82 (t, *J* = 7.60 Hz, 1H), 6.59 (d, *J* = 7.88 Hz, 2H), 5.24 (s, 1H), 2.31 (s, 6H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 146.5, 138.4, 136.1, 129.4, 128.7, 125.9, 118.4, 113.7, 18.5. The NMR spectral data was consistent with previously reported data.⁴ mp: 87 °C (lit. mp: 87-88 °C).⁵

Alternatively, 4-Chlorotoluene (101 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method B at 120 °C in xylenes to afford 120 mg of *N*-phenyl-*p*-toluidine (86%).

***N*-Phenyl-*p*-anisidine (Table 3, entry 4; Table 6, entry 2).** 4-Bromoanisole (150 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-phenyl-*p*-anisidine (92%, 138 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.26 (d, *J* = 7.89 Hz, 2H), 7.12 (d, *J* = 8.82 Hz, 2H), 6.96 (d, *J* = 7.64 Hz, 2H), 6.90 (m, 3H), 5.53 (s, 1H), 3.85 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 155.2, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.5. The NMR spectral data was consistent with previously reported data.⁶ mp: 98-100 °C (lit. mp: 102-103 °C).⁷

Alternatively, 4-Chloroanisole (114 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method B at 140 °C in xylenes to afford 141 mg of *N*-phenyl-*p*-anisidine (89%).

Bis(4-methoxyphenyl)amine (Table 3, entry 5). 4-Bromoanisole (150 mg, 0.80 mmol) and anisidine (126 mg, 1.04 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (methylene chloride) to afford bis(4-methoxyphenyl)amine (92%, 138 mg). ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.50 (s, 1H), 6.91 (d, *J* = 8.94 Hz, 4H), 6.80 (d, *J* = 8.93

Hz, 4H), 3.68 (s, 6H). ^{13}C NMR (90.6 MHz, DMSO- d_6): δ 152.7, 138.9, 117.9, 114.4, 55.1.
mp: 98 °C (lit. mp: 96.8 °C).⁸

***N,N*-Dimethyl-*N'*-phenyl-1,4-benzenediamine (Table 3, entry 6).** 4-Bromo-*N,N*-dimethylaniline (159 mg, 0.78 mmol) and aniline (93 mg, 1.0 mmol) were coupled using $\text{Pd}_2(\text{dba})_3$ (3.7 mg, 4.0 μmol) and DTBNpP· HBF_4 (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N,N*-dimethyl-*N'*-phenylbenzene-1,4-diamine (78%, 129 mg). ^1H NMR (500 MHz, C_6D_6): δ 7.11-7.15 (m, 2H), 6.98 (d, 8.93 Hz, 2H), 6.77-6.81 (m, 3H), 6.57 (d, 8.93 Hz, 2H), 5.21 (brs, 1H), 2.53 (s, 6H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 147.0, 146.0, 132.1, 128.9, 123.0, 118.5, 114.7, 113.7, 40.9, 29.4. The NMR spectral data was consistent with previously reported data.⁹ mp: 115 °C.

***N*-Phenyl-*o*-toluidine (Table 3, entry 7; Table 6, entry 3).** 2-Bromotoluene (137 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using $\text{Pd}_2(\text{dba})_3$ (3.7 mg, 4.0 μmol) and DTBNpP· HBF_4 (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-phenyl-*o*-toluidine (117.1 mg, 80%) as an oil. ^1H NMR (500 MHz, CDCl_3): δ 7.32 (t, $J = 8.00$ Hz, 3H), 7.28 (d, $J = 7.46$ Hz, 1H), 7.21 (t, $J = 7.54$ Hz, 1H), 7.03 (m, 3H), 6.98 (t, $J = 7.94$ Hz, 1H), 5.44 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 144.0, 141.2, 130.9, 129.3, 128.3, 126.7, 122.0, 120.4, 118.9, 117.4, 17.8. The NMR spectral data was consistent with previously reported data.¹⁰

Alternatively, 2-Chlorotoluene (102 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using $\text{Pd}_2(\text{dba})_3$ (3.7 mg, 4.0 μmol) and DTBNpP· HBF_4 (2.3 mg, 8.0 μmol) according to Method B at 120 °C in xylenes to afford 139 mg of *N*-phenyl-*o*-toluidine (95%).

2,6-Dimethyl-*N*-phenylaniline (Table 3, entry 8). 2-Bromo-*m*-xylene (148 mg, 0.80 mmol) and aniline (93 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford 2,6-dimethyl-*N*-phenylaniline (122.1 mg, 77%) as an oil. ¹H NMR (500 MHz, CDCl₃): δ 7.21 (m, 5H), 6.82 (t, *J* = 7.60, 1H), 6.59 (d, *J* = 7.88, 2H), 5.24 (s, 1H), 2.31 (s, 6H). ¹³C NMR (90.6 MHz, CDCl₃): δ 146.5, 138.4, 136.1, 129.4, 128.7, 125.9, 118.4, 113.7, 18.5. The NMR spectral data was consistent with previously reported data.¹⁰

2,4,6-Trimethyl-*N*-(4-methylphenyl)aniline (Table 3, entry 9). 4-Bromotoluene (137 mg, 0.80 mmol) and 2,4,6-trimethylaniline (135 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford 2,4,6-trimethyl-*N*-(4-methylphenyl)aniline (60%, 106 mg). ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.96 (s, 1H), 6.90 (s, 2H), 6.85 (d, *J* = 8.13 Hz, 2H), 6.28 (d, *J* = 8.12 Hz, 2H), 2.23 (s, 3H), 2.13 (s, 3H), 2.07 (s, 6H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 144.9, 136.2, 135.3, 133.9, 129.3, 128.8, 124.6, 112.3, 20.4, 20.0, 17.9. The ¹H NMR spectrum was consistent with previously reported data.¹¹ mp: 61-63 °C (lit. mp: 66-67 °C).¹¹

2,6-Diisopropyl-*N*-(4-methylphenyl)aniline (Table 3, entry 10).¹² 4-Bromotoluene (137 mg, 0.80 mmol) and 2,6-diisopropylaniline (177 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford 109 mg of crude 2,6-diisopropyl-*N*-(4-methylphenyl)aniline contaminated with 8% (w/w) of 2,6-diisopropylamine that could not be removed. The yield of 2,6-diisopropyl-*N*-(4-

methylphenyl)aniline was estimated to be 100 mg (47%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.21 (m, 3H), 7.05 (s, 1H), 6.83 (d, *J* = 8.09 Hz, 2H), 6.30 (d, *J* = 7.56 Hz, 2H), 3.17 (sept, *J* = 6.94 Hz, 2H), 2.13 (s, 3H), 1.06 (d, *J* = 6.96 Hz, 12H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 147.7, 147.1, 136.3, 129.8, 127.1, 124.2, 123.9, 112.4, 28.0, 24.2, 20.5.

2,4,6-Trimethyl-*N*-(2-methylphenyl)aniline (Table 3, entry 11). 2-Bromotoluene (120 mg, 0.80 mmol) and 2,4,6-trimethylaniline (135 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μmol) and DTBNpP·HBF₄ (2.3 mg, 8.0 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford 2,4,6-trimethyl-*N*-(2-methylphenyl)aniline (78%, 141 mg). ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.01 (d, *J* = 6.97 Hz, 1H), 6.94 (s, 2H), 6.82 (t, *J* = 7.71 Hz, 1H), 6.51 (t, *J* = 7.75 Hz, 1H), 6.34 (s, 1H), 5.84 (d, *J* = 7.78 Hz, 1H), 2.26 (s, 6H), 2.06 (s, 6H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 144.8, 136.1, 135.6, 134.0, 129.8, 128.6, 126.2, 121.6, 116.1, 109.9, 20.3, 17.6, 17.5. The ¹H NMR spectrum was consistent with previously reported data.¹¹ mp 76-78 °C (lit. mp: 78.5-79.5 °C).¹¹

2,4,6-Trimethyl-*N*-(2,6-dimethylphenyl)aniline (Table 3, entry 12). 2-Bromo-*m*-xylene (135 mg, 0.80 mmol) and 2,4,6-trimethylaniline (135 mg, 1.0 mmol) were coupled using Pd₂(dba)₃ (7.4 mg, 8.0 μmol) and DTBNpP·HBF₄ (4.6 mg, 16 μmol) according to Method A. The reaction was heated at 50 °C. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford 2,4,6-trimethyl-*N*-(2,6-dimethylphenyl)aniline (75%, 143 mg). ¹H NMR (500 MHz, DMSO-*d*₆): δ 6.88 (d, *J* = 7.21 Hz, 2H), 6.74 (s, 2H), 6.69 (t, *J* = 7.41 Hz, 1H), 5.99 (s, 1H), 2.17 (s, 3H), 1.91 (s, 12H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 143.3, 140.2, 130.9, 130.6, 128.3, 128.9, 128.8, 120.8, 20.7, 19.5, 19.4. The ¹H NMR spectrum was consistent with previously reported data.¹³ mp 97 °C (lit. mp: 97-99 °C).¹³

4-(*N*-Methyl-*N*-phenylamino)benzotrile (Table 4, entry 1; Table 6, entry 4). 4-Bromobenzotrile (146 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4 μmol) according to Method A. The crude product was purified by column chromatography (10% ethyl acetate/90% hexanes) to afford 4-(*N*-methyl-*N*-phenylamino)benzotrile (165 mg, 99%) as a pale yellow oil. ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.46 (m, 4H), 7.25 (m, 3H), 6.76 (d, *J* = 9.31 Hz, 2H), 3.38 (s, 3H). ¹³C NMR (90.6 MHz, DMSO-*d*₆): δ 152.0, 146.8, 133.2, 130.1, 126.4, 126.2, 120.3, 113.9, 99.4, 40.2. The NMR spectral data was identical to previously reported data.¹⁴

Alternatively, 4-Chlorobenzotrile (110 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4.0 μmol) according to Method B at 50 °C in toluene to afford 160 mg of 4-(*N*-methyl-*N*-phenylamino)benzotrile (97%).

***N*-(4-Fluorophenyl)-*N*-methylaniline (Table 4, entry 2).** 1-Bromo-4-fluorobenzene (140 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(4-fluorophenyl)-*N*-methylaniline (149 mg, 93%) as a light yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.22 (dd, *J* = 8.83, 7.27 Hz, 2H), 7.00 (m, 4H), 6.87 (m, 3H), 3.25 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 158.7 (d, *J*_{C-F} = 242.0 Hz), 149.4, 145.3 (d, *J*_{C-F} = 2.79 Hz), 129.2, 124.2, 124.4, 120.1, 118.1, 116.0 (d *J*_{C-F} = 20.2 Hz), 40.6.

***N*-(4-Trifluoromethylphenyl)-*N*-methylaniline (Table 4, entry 3).** 4-Bromobenzotrifluoride (180 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4 μmol) according to Method A. The crude

product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(4-trifluoromethylphenyl)-*N*-methylaniline (189 mg, 93%) as a light yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.45 (m, 4H), 7.23 (m, 3H), 6.88 (d, *J* = 8.49 Hz, 2H), 6.82 (m, 3H), 3.39 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 151.5, 147.8, 129.8, 126.2, 125.3, 125.0, 122.5 (q, *J*_{C-F} = 269 Hz), 119.8, 114.8, 40.2. The NMR spectral data was identical to previously reported data.¹⁵

***N*-Methyl-*N*-phenyl-*p*-toluidine (Table 4, entry 4; Table 6, entry 5).** 4-Bromotoluene (138 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4 μmol) according to Method A. The crude product was purified by column chromatography (2.5% ethyl acetate/97.5% hexanes) to afford *N*-methyl-*N*-phenyl-*p*-toluidine (148 mg, 93%) as a light yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.31 (t, *J* = 8.51 Hz, 2H), 7.19 (d, *J* = 8.57 Hz, 2H), 7.07 (d, *J* = 8.08 Hz, 2H), 7.00 (d, *J* = 8.59 Hz, 2H), 6.94 (t, *J* = 7.38 Hz, 1H), 3.36 (s, 3H), 2.40 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 149.4, 146.7, 132.0, 129.9, 129.1, 122.6, 119.8, 118.2, 40.4, 20.8. The NMR spectral data was identical to literature values.¹⁰

Alternatively, 4-Chlorotoluene (101 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4.0 μmol) according to Method B at 100 °C in toluene to afford 109 mg of *N*-methyl-*N*-phenyl-*p*-toluidine (70%).

***N*-Methyl-*N*-phenyl-*p*-anisidine (Table 4, entry 5; Table 6, entry 6).** 4-Bromoanisole (138 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using Pd₂(dba)₃ (1.9 mg, 2.0 μmol) and DTBNpP·HBF₄ (1.2 mg, 4 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-methyl-*N*-phenyl-*p*-anisidine (148 mg, 93%) as a light yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.25

(m, 2H), 7.13 (d, $J = 9.01$ Hz, 2H), 6.93 (d, $J = 9.17$ Hz, 2H), 6.82 (m, 3H), 3.85 (s, 3H), 3.30 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 156.3, 149.8, 142.3, 129.0, 126.2, 118.4, 115.8, 114.8, 55.5, 40.5. The NMR spectral data was identical to literature values.¹⁰

Alternatively, 4-Chloroanisole (114 mg, 0.80 mmol) and *N*-methylaniline (88.0 mg, 0.82 mmol) were coupled using $\text{Pd}_2(\text{dba})_3$ (19 mg, 20 μmol) and DTBNpP· HBF_4 (12 mg, 40 μmol) according to Method B at 100 °C in toluene for 18 hours to afford 168 mg of *N*-methyl-*N*-phenyl-*p*-anisidine (99%).

***N,N,N'*-Trimethyl-*N'*-phenyl-1,4-benzenediamine (Table 4, entry 6).** 4-Bromo-*N,N*-dimethylaniline (160 mg, 0.80 mmol) and *N*-methylaniline (88 mg, 1.0 mmol) were coupled using $\text{Pd}_2(\text{dba})_3$ (1.9 mg, 2.0 μmol) and DTBNpP· HBF_4 (1.2 mg, 4 μmol) according to Method A. The crude product was purified by column chromatography (25% methylene chloride/75% hexanes) to afford *N,N,N'*-trimethyl-*N'*-phenyl-1,4-benzenediamine (163 mg, 89%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.25 (t, $J = 7.25$ Hz, 2H), 7.15 (d, $J = 8.80$ Hz, 2H), 6.82 (m, 5H), 3.32 (s, 3H), 3.02 (s, 6H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 150.1, 148.1, 138.8, 128.9, 126.9, 117.5, 114.7, 113.8, 41.0, 40.5. The NMR spectral data was identical to literature values.¹⁶

***N*-Methyl-*N*-phenyl-*o*-toluidine (Table 4, entry 7).** 2-Bromotoluene (138 mg, 0.80 mmol) and *N*-methylaniline (88 mg, 1.0 mmol) were coupled using $\text{Pd}_2(\text{dba})_3$ (1.9 mg, 2.0 μmol) and DTBNpP· HBF_4 (1.2 mg, 4 μmol) according to Method A. The crude product was purified by column chromatography (2.5% ethyl acetate/97.5% hexanes) to afford *N*-methyl-*N*-phenyl-*o*-toluidine (141 mg, 90%) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.17 (m, 6H), 6.69 (t, $J = 7.28$ Hz, 1H), 6.52 (d, $J = 7.83$ Hz, 2H), 3.21 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (90.6 MHz,

CDCl₃): δ 149.2, 146.9, 136.9, 131.4, 129.0, 128.4, 127.6, 126.5, 116.9, 112.9, 39.1, 17.9. The NMR spectral data was identical to literature values.¹⁵

***N,N*-Diphenyl-*p*-toluidine (Table 4, entry 9).** 4-Bromotoluene (138 mg, 0.80 mmol) and diphenylamine (132 mg, 0.78 mmol) were coupled using Pd₂(dba)₃ (7.3 mg, 8.0 μ mol) and DTBNpP·HBF₄ (4.9 mg, 16 μ mol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N,N*-diphenyl-*p*-toluidine (200 mg, 97%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 7.25 (m, 4H), 7.09 (m, 6H), 7.02 (m, 4H), 2.34 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 148.1, 145.3, 132.7, 129.9, 129.1, 124.9, 123.6, 122.2, 20.8. The NMR spectral data was identical to literature values.¹⁰ mp: 67-68 °C (lit. mp: 69-70 °C).¹⁷

***N,N*-Diphenyl-*p*-anisidine (Table 4, entry 10).** 4-Bromoanisole (150 mg, 0.80 mmol) and diphenylamine (132 mg, 0.78 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μ mol) and DTBNpP·HBF₄ (2.4 mg, 8 μ mol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N,N*-diphenyl-*p*-anisidine (179 mg, 83%). ¹H NMR (500 MHz, CDCl₃): 7.23 (m, 4H), 7.07 (m, 6H), 6.97 (t, *J* = 7.22 Hz, 2H), 6.86 (d, *J* = 9.12 Hz, 2H), 3.83 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 156.2, 148.2, 140.8, 129.1, 127.3, 122.9, 121.8, 114.8, 55.5. The NMR spectral data was identical to literature values.¹⁰ mp: 97-99 °C (lit. mp: 98-100 °C).¹⁷

***N,N*-Diphenyl-*o*-toluidine (Table 4, entry 11).** 4-Bromotoluene (138 mg, 0.80 mmol) and diphenylamine (132 mg, 0.78 mmol) were coupled using Pd₂(dba)₃ (3.7 mg, 4.0 μ mol) and DTBNpP·HBF₄ (2.4 mg, 8 μ mol) according to Method A. The crude product was purified by column chromatography (2.5% ethyl acetate/97.5% hexanes) and then by recrystallization from hot ethanol to afford 109 mg of *N,N*-diphenyl-*o*-toluidine contaminated with diphenyl amine

(18% by weight). The yield of *N,N*-diphenyl-*o*-toluidine was estimated to be 89.4 mg (44%). ¹H NMR (500 MHz, CDCl₃): δ 7.23 (m, 9H), 6.99 (d, *J* = 8.54 Hz, 3H), 6.95 (t, *J* = 7.28 Hz, 2H), 2.07 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 147.5, 145.4, 136.5, 131.7, 129.6, 129.0, 127.4, 126.0, 121.5, 121.4, 18.6. The NMR spectral data was identical to literature values.¹⁰ mp: 50-53 °C (lit. mp: 55-56 °C).¹⁷

Typical procedure for the coupling of aryl bromides and secondary alkylamines (Method

A). Pd(OAc)₂ (10 μmol), DTBNpP (10% solution in toluene) or DTBNpP·HBF₄ (10 μmol, 1 eq/Pd), sodium *t*-butoxide (1.5 mmol), and toluene (2.5 mL) were added to a round bottom flask in a glove box. Upon removing the septum sealed flask from the drybox, the aryl bromide (1.0 mmol) and amine **12a** or **12b** (1.0 mmol) were added by syringe and the reaction was allowed to stir for 2 hours at 50 °C. The reaction mixture was then adsorbed on silica gel and purified by flash chromatography.

Typical procedure for the coupling of aryl chlorides and secondary alkylamines (Method

B). Pd(OAc)₂ (10-50 μmol), DTBNpP (10% solution in toluene) or DTBNpP·HBF₄ (10-50 μmol, 1 eq/Pd), sodium *t*-butoxide (1.5 mmol), and toluene (2.5 mL) were added to a round bottom flask in a glove box. Upon removing the septum sealed flask from the drybox, the aryl chloride (1.0 mmol) and amine **12a** or **12b** (1.0 mmol) were added by syringe. The flask was placed in a preheated oil bath at 80 °C and stirred until judged complete by GC. The reaction mixture was then adsorbed on silica gel and purified by flash chromatography.

***N*-(4-Trifluoromethylphenyl)morpholine (Table 5, entry 1).** 4-Bromobenzotrifluoride (113 mg, 0.5 mmol) and morpholine (43 mg, 0.5 mmol) were coupled using Pd(OAc)₂ (1.1 mg, 5 μmol) and DTBNpP·HBF₄ (1.5 mg, 5 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(4-

trifluoromethylphenyl)morpholine (108 mg, 93%) as a white solid. ^1H NMR (360 MHz, DMSO): δ 7.51 (d, J = 8.48 Hz, 2H), 7.05 (d, J = 8.74 Hz, 2H), 3.74 (t, J = 4.87 Hz, 4H), 3.22 (t, J = 4.87 Hz, 4H). ^{13}C NMR (90.6 MHz, DMSO): δ 153.3, 126.0 (q, $J_{\text{C-F}}$ = 3.68 Hz), 124.9 (q, $J_{\text{C-F}}$ = 270.3 Hz), 118.2 (q, $J_{\text{C-F}}$ = 31.7 Hz), 113.9, 65.8, 47.1. The ^1H NMR spectral data was identical to literature values.¹⁸ mp: 64-66 °C (lit. mp: 58 °C).¹⁸

***N*-(4-Methylphenyl)morpholine (Table 5, entry 2; Table 6, entry 8).** 4-Bromotoluene (123 μL , 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (2.2 mg, 10 μmol) and DTBNpP· HBF_4 (3.0 mg, 10 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(4-methylphenyl)morpholine (158 mg, 89%) as a white solid. ^1H NMR (360 MHz, CDCl_3): δ 7.09 (d, J = 8.24 Hz, 2H), 6.83 (d, J = 8.58 Hz, 2H), 3.85 (t, J = 4.80 Hz, 4H), 3.10 (t, J = 4.80 Hz, 4H), 2.27 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 149.3, 129.8, 129.7, 116.2, 67.1, 50.1, 20.5. The NMR spectral data was identical to literature values.¹⁰ mp: 45-48 °C (lit. mp: 49.8-50.4 °C).¹⁹

Alternatively, 4-chlorotoluene (118 μL , 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (4.4 mg, 20 μmol) and DTBNpP· HBF_4 (6.0 mg, 20 μmol) according to Method B to give 153 mg of *N*-(4-methylphenyl)morpholine (86%).

***N*-(4-Methoxyphenyl)morpholine (Table 5, entry 3; Table 6, entry 9).** 4-Bromoanisole (125 μL , 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (2.2 mg, 10 μmol) and DTBNpP· HBF_4 (3.0 mg, 10 μmol) according to Method A. The crude product was purified by column chromatography (10% ethyl acetate/90% hexanes) to afford *N*-(4-methoxyphenyl)morpholine (187 mg, 97%) as a white solid. ^1H NMR (360 MHz, CDCl_3): δ 6.89 (d, J = 9.40 Hz, 2H), 6.85 (d, J = 9.40 Hz, 2H), 3.85 (t, J = 4.75 Hz, 4H), 3.77 (s, 3H), 3.05

(t, $J = 4.75$ Hz, 4H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 154.0, 145.7, 117.9, 114.5, 67.1, 55.6, 50.9. The NMR spectral data was identical to literature values.¹⁰ mp: 69-71 °C (lit. mp: 71 °C).¹⁹

Alternatively, 4-chloroanisole (122 μL , 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (11.2 mg, 50 μmol) and DTBNpP-HBF₄ (15 mg, 50 μmol) according to Method B to give 153 mg of *N*-(4-methoxyphenyl)morpholine (79%).

***N*-(4-(*N,N'*-Dimethylamino)phenyl)morpholine (Table 5, entry 4).** 4-Bromo-*N,N'*-dimethylaniline (200 mg, 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (2.2 mg, 10 μmol) and DTBNpP-HBF₄ (3.0 mg, 10 μmol) according to Method A. The crude product was purified by column chromatography (10% ethyl acetate/90% methylene chloride) to afford *N*-(4-methoxyphenyl)morpholine (187 mg, 97%) as an off-white solid. ^1H NMR (360 MHz, CDCl_3): δ 6.89 (d, $J = 9.08$ Hz, 2 H), 6.75 (d, $J = 9.08$ Hz, 2 H), 3.85 (t, $J = 4.75$ Hz, 4H), 3.03 (t, $J = 4.75$ Hz, 4 H), 2.87 (s, 3 H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 145.9, 143.3, 118.1, 114.6, 67.2, 51.2, 41.6. The NMR spectral data was identical to literature values.²⁰ mp: 117-120 °C.

***N*-(2-Methylphenyl)morpholine (Table 5, entry 5).** 4-Bromotoluene (120 μL , 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (2.2 mg, 10 μmol) and DTBNpP-HBF₄ (3.0 mg, 10 μmol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(2-methylphenyl)morpholine (165 mg, 93%) as a colorless oil. ^1H NMR (360 MHz, CDCl_3): δ 7.20-7.16 (m, 2H), 7.02-6.97 (m, 2H), 3.85 (t, $J = 4.52$ Hz, 4H), 2.90 (t, $J = 4.52$ Hz, 4H), 2.32 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 151.4, 132.7, 131.3, 126.8, 123.5, 119.1, 67.6, 52.4, 18.0. The NMR spectral data was identical to literature values.¹⁴

***N*-(2,4-Dimethylphenyl)morpholine (Table 5, entry 6).** 4-Bromo-*m*-xylene (135 μ L, 1.00 mmol) and morpholine (87 μ L, 1.0 mmol) were coupled using Pd(OAc)₂ (2.2 mg, 10 μ mol) and DTBNpP·HBF₄ (3.0 mg, 10 μ mol) according to Method A. The crude product was purified by column chromatography (5% ethyl acetate/95% hexanes) to afford *N*-(2,4-dimethylphenyl)morpholine (168 mg, 88%) as a colorless oil. ¹H NMR (360 MHz, CDCl₃): δ 7.01-6.97 (m, 2H), 6.93-6.91 (m 1H), 3.83 (t, *J* = 4.55 Hz, 4H), 2.89 (t, *J* = 4.55 Hz, 4H), 2.28 (s, 3H), 2.27 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 148.9, 132.9, 132.7, 132.0, 127.2, 119.0, 67.6, 52.6, 20.8, 17.8.

***N,N*-Dibutyl-*p*-toluidine (Table 5, entry 6; Table 6, entry 10).** 4-Bromotoluene (123 μ L, 1.00 mmol) and dibutylamine (169 μ L, 1.0 mmol) were coupled using Pd(OAc)₂ (2.2 mg, 10 μ mol) and DTBNpP·HBF₄ (3.0 mg, 10 μ mol) according to Method A. The crude product was purified by column chromatography (2.5% ethyl acetate/97.5% hexanes) to afford *N,N*-dibutyl-*p*-toluidine (168 mg, 88%) as a pale yellow oil. ¹H NMR (360 MHz, CDCl₃): δ 7.01 (d, *J* = 8.26 Hz, 2H), 6.57 (d, *J* = 8.69 Hz, 2H), 3.21 (t, *J* = 7.60 Hz, 4H), 2.37 (s, 3H), 1.58-1.49 (m, 4H), 1.38-1.28 (m, 4H), 0.93 (t, *J* = 7.32 Hz, 6H). ¹³C NMR (90.6 MHz, CDCl₃): δ 146.3, 129.8, 124.4, 112.3, 51.1, 29.6, 20.5, 20.3 14.1. The NMR spectral data was identical to literature values.¹⁹

Alternatively, 4-chlorotoluene (118 μ L, 1.00 mmol) and dibutylamine (169 μ L, 1.0 mmol) were coupled using Pd(OAc)₂ (4.4 mg, 20 μ mol) and DTBNpP·HBF₄ (6.1 mg, 20 μ mol) according to Method B to give 216 mg of *N,N*-dibutyl-*p*-toluidine (98%).

***N,N*-Dibutyl-*p*-anisidine (Table 5, entry 7).** 4-Bromoanisole (125 μ L, 1.00 mmol) and dibutylamine (169 μ L, 1.0 mmol) were coupled using Pd(OAc)₂ (2.2 mg, 10 μ mol) and DTBNpP·HBF₄ (3.0 mg, 10 μ mol) according to Method A. The crude product was purified by

column chromatography (2.5% ethyl acetate/97.5% hexanes) to afford *N,N*-dibutyl-*p*-anisidine (168 mg, 88%) as a pale yellow oil. ^1H NMR (360 MHz, CDCl_3): δ 6.81 (d, $J = 9.12$ Hz, 2H), 6.64 (d, $J = 9.12$ Hz), 3.74 (s, 3H), 3.17 (t, $J = 7.60$ Hz, 4H), 1.56-1.47 (m, 4H), 1.34-1.28 (m, 4H), 0.93 (t, $J = 7.32$ Hz, 6H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 151.1, 143.4, 114.9, 114.5, 55.9, 51.8, 29.6, 20.6, 14.2. The NMR spectral data was identical to literature values.²¹

Alternatively, 4-chlorotoluene (118 μL , 1.00 mmol) and dibutylamine (169 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (11 mg, 50 μmol) and DTBNpP· HBF_4 (15 mg, 50 μmol) according to Method B to give 206 mg of *N,N*-dibutyl-*p*-anisidine (86%).

***N*-(4-Cyanophenyl)morpholine (Table 6, entry 7).** 4-Chlorobenzonitrile (138 mg, 1.00 mmol) and morpholine (87 μL , 1.0 mmol) were coupled using $\text{Pd}(\text{OAc})_2$ (2.2 mg, 10 μmol) and DTBNpP· HBF_4 (3.0 mg, 10 μmol) according to Method B at 80 $^\circ\text{C}$. The crude product was purified by column chromatography (20% ethyl acetate/80% hexanes) to afford *N*-(4-cyanophenyl)morpholine (132 mg, 70%) as a pale yellow solid. ^1H NMR (360 MHz, CDCl_3): δ 7.52 (d, $J = 9.05$ Hz, 2H), 6.86 (d, $J = 9.05$ Hz, 2H), 3.85 (t, $J = 4.94$ Hz, 4H), 3.28 (t, $J = 4.94$ Hz, 4H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 153.6, 133.6, 119.9, 114.2, 101.1, 66.6, 47.4. The NMR spectral data was identical to literature values.²² mp: 77-81 $^\circ\text{C}$ (lit. mp: 77-78 $^\circ\text{C}$).²²

Structure optimization and determination of cone angles. Geometries were optimized at the LDFT level with the polarized double zeta DZVP2 basis set on all atoms except Pd.²³ We used the Stuttgart relativistic pseudopotential and the associated basis set for Pd.²⁴ There are 28 electrons in the core of the ECP and the basis set for Pd is contracted to [6s5p3d]. The LDFT calculations were done with the potential fit of Vosko, Wilk and Nusair for the correlation functional²⁵ and the exchange functional of Slater.²⁶ The bond energies were calculated at the gradient-corrected level at the LDA optimized geometries with the B3LYP exchange-correlation

functional with the above basis sets.^{27,28} The calculations were done with the program Gaussian03²⁹ on Cray XD-1 and Silicon Graphics Altix computers at the Alabama Supercomputing Center. The cone angles were calculated from the LDA optimized geometries for the (phosphine)Pd⁰ complex by using the STERIC program and the volumetric parameters for the atoms therein with the Pd atom set at the origin.^{30,31}

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Computational Data.

Pd, L and (L)Pd Total Electronic Energies and Zero Point Energies (ZPE) in a.u.

Species	E(B3LYP/DGDZVP2)	ZPE(SVWN5/DGDZVP2)
Pd	-127.886371	0.000000
TTBP	-814.998386	0.356952
DTBNpP	-854.338499	0.382832
TBDNpP	-893.671314	0.409430
TnpP	-933.000191	0.437614
(i-Pr) ₃ P	-697.056917	0.275630
(n-Bu) ₃ P	-815.041528	0.358265
Ph ₃ P	-1036.423898	0.266275
Pd(TTBP)	-942.944770	0.357467
Pd(DTBNpP)	-982.282697	0.383567
Pd(TBDNpP)	-1021.613819	0.409441
Pd(TNpP)	-1060.940079	0.437486
Pd[(i-Pr) ₃ P]	-825.006197	0.276806
Pd[(n-Bu) ₃ P]	-942.991629	0.359467
Pd(Ph ₃ P)	-1164.370427	0.267315

The local DFT optimized geometries (coordinates) of TTBP, DTBNpP, TBDNpP, TNpP, (TTBP)Pd, (DTBNpP), (TBDNpP)Pd, and (TNpP)Pd in x,y,z format in Å.

TTBP

P	0.000000	0.000000	0.731735
C	0.000000	1.760795	0.005384
C	0.387261	1.923952	-1.457653
C	-1.381020	2.373965	0.208669
C	0.944757	2.590608	0.875305
C	1.524893	-0.880398	0.005384
C	1.472560	-1.297354	-1.457653
C	2.746424	0.009016	0.208669
C	1.771154	-2.113488	0.875305
C	-1.524893	-0.880398	0.005384
C	-1.859822	-0.626598	-1.457653
C	-1.365404	-2.382981	0.208669
C	-2.715911	-0.477120	0.875305
H	0.664235	2.515749	1.941537
H	0.870211	3.654450	0.572857
H	2.000154	2.290041	0.782846
H	-1.729228	2.262393	1.252426

H	-2.144951	1.948780	-0.464901
H	-1.317371	3.459086	-0.007709
H	1.426858	1.610178	-1.657075
H	0.313657	2.995406	-1.735203
H	-0.276644	1.358039	-2.133677
H	1.846585	-1.833119	1.941537
H	2.729741	-2.580850	0.572857
H	0.983157	-2.877205	0.782846
H	2.823904	0.366359	1.252426
H	2.760168	0.883192	-0.464901
H	3.654341	-0.588666	-0.007709
H	0.681026	-2.040785	-1.657075
H	2.437269	-1.769338	-1.735203
H	1.314418	-0.439438	-2.133677
H	-2.510820	-0.682630	1.941537
H	-3.599952	-1.073600	0.572857
H	-2.983311	0.587164	0.782846
H	-1.094676	-2.628752	1.252426
H	-0.615217	-2.831972	-0.464901
H	-2.336971	-2.870419	-0.007709
H	-2.107884	0.430606	-1.657075
H	-2.750926	-1.226068	-1.735203
H	-1.037774	-0.918601	-2.133677

DTBNpP

P	-0.330400	0.000687	-0.532911
C	-1.272577	1.543395	0.026447
C	-1.868078	1.501063	1.422468
C	-0.283387	2.698912	-0.051759
C	-2.366670	1.816123	-0.998703
C	-1.312623	-1.523315	0.014213
C	-1.444155	-1.775852	1.508556
C	-2.699370	-1.472288	-0.608324
C	-0.553747	-2.692470	-0.603251
C	2.489957	-0.013560	0.019851
C	2.687849	-1.230749	-0.870263
C	2.675035	1.241631	-0.817833
C	3.525379	-0.030990	1.134083
H	-1.946176	1.875872	-2.019102
H	-2.855544	2.784482	-0.771778
H	-3.148040	1.037730	-1.000705
H	0.201961	2.756401	-1.043792
H	0.513085	2.627327	0.711024
H	-0.825427	3.649873	0.119005
H	-2.711684	0.790707	1.489357
H	-2.261051	2.502979	1.689953

H	-1.119248	1.223560	2.188421
H	-0.477722	-2.590544	-1.701412
H	-1.081510	-3.639939	-0.375365
H	0.473799	-2.775311	-0.201559
H	-2.656508	-1.205321	-1.681035
H	-3.357147	-0.746573	-0.095735
H	-3.179313	-2.467630	-0.524491
H	-0.463225	-1.893040	2.004412
H	-1.997256	-2.723308	1.667835
H	-1.993270	-0.974573	2.029143
H	3.419846	0.853336	1.790530
H	4.550910	-0.023888	0.719502
H	3.420674	-0.935844	1.762161
H	2.576155	2.156642	-0.204255
H	1.918999	1.284673	-1.625452
H	3.678074	1.249005	-1.283581
H	2.631610	-2.168772	-0.284548
H	3.678135	-1.196628	-1.361219
H	1.911227	-1.268606	-1.658673
C	1.095338	-0.057069	0.660274
H	0.996859	0.771193	1.391500
H	1.020079	-0.993098	1.248958

TBDNpP

P	0.027790	0.404776	-0.387793
C	2.538032	-0.935981	0.023181
C	1.823963	-2.277308	-0.008585
C	2.994185	-0.571980	-1.381721
C	3.748342	-1.032771	0.940018
C	-0.264936	2.218935	0.036556
C	-0.086803	2.545632	1.509632
C	0.724049	3.020095	-0.797935
C	-1.673549	2.594596	-0.389234
C	-2.279248	-1.291308	0.023551
C	-3.137141	-0.409986	-0.870240
C	-1.665365	-2.392509	-0.827789
C	-3.155735	-1.920916	1.096566
H	4.288669	-0.068667	0.991044
H	4.457145	-1.799671	0.575297
H	3.448772	-1.309065	1.968629
H	3.566080	0.375745	-1.378567
H	2.123399	-0.440972	-2.051525
H	3.644710	-1.361609	-1.801122
H	1.460117	-2.562375	0.998023
H	2.504618	-3.074600	-0.360988
H	0.952753	-2.246810	-0.689645

H	-1.858736	2.350828	-1.451882
H	-1.824046	3.683906	-0.255740
H	-2.439534	2.076188	0.216730
H	0.583185	2.825811	-1.877013
H	1.775496	2.783522	-0.548218
H	0.577603	4.103641	-0.620411
H	-0.773083	1.959971	2.150318
H	-0.310483	3.616838	1.685276
H	0.945230	2.362542	1.858413
H	-2.566185	-2.590146	1.751211
H	-3.965627	-2.520660	0.640261
H	-3.625074	-1.147857	1.733713
H	-1.062258	-3.086846	-0.212689
H	-1.011387	-1.960744	-1.610006
H	-2.457296	-2.979326	-1.329650
H	-3.659969	0.372929	-0.289681
H	-3.903365	-1.017834	-1.386152
H	-2.518384	0.088591	-1.641250
C	-1.182932	-0.476527	0.721002
H	-0.592499	-1.161714	1.362271
H	-1.656185	0.260635	1.403230
C	1.608481	0.151352	0.562591
H	1.374194	-0.046931	1.629473
H	2.157235	1.115110	0.531976

TNpP

P	0.000000	0.000000	0.095653
C	0.000000	2.852099	-0.014138
C	-1.474064	2.818018	0.361843
C	0.838836	2.947159	1.252166
C	0.271338	4.062350	-0.893920
C	2.469990	-1.426049	-0.014138
C	3.382430	-2.266161	-0.893920
C	3.177507	-0.132432	0.361843
C	2.132897	-2.200033	1.252166
C	-2.469990	-1.426049	-0.014138
C	-1.703443	-2.685586	0.361843
C	-2.971733	-0.747126	1.252166
C	-3.653768	-1.796189	-0.893920
H	1.336182	4.106555	-1.190111
H	0.028295	5.000793	-0.361042
H	-0.336557	4.027854	-1.817536
H	1.916578	3.013165	1.008321
H	0.685463	2.054089	1.888137
H	0.566438	3.843915	1.839058
H	-2.116775	2.750762	-0.537357

H	-1.756924	3.734941	0.911419
H	-1.700288	1.949938	1.013107
H	1.436162	-1.620673	1.888137
H	3.045709	-2.412507	1.839058
H	1.651188	-3.166388	1.008321
H	2.538840	0.497524	1.013107
H	3.440617	0.457800	-0.537357
H	4.113015	-0.345930	0.911419
H	2.888290	-3.210445	-1.190111
H	4.316666	-2.524901	-0.361042
H	3.656502	-1.722460	-1.817536
H	-4.224472	-0.896110	-1.190111
H	-4.344961	-2.475892	-0.361042
H	-3.319946	-2.305394	-1.817536
H	-3.567766	0.153223	1.008321
H	-2.121625	-0.433416	1.888137
H	-3.612146	-1.431408	1.839058
H	-1.323842	-3.208561	-0.537357
H	-2.356092	-3.389011	0.911419
H	-0.838552	-2.447462	1.013107
C	-1.568767	-0.460746	-0.786611
H	-2.125172	0.480984	-0.965992
H	-1.316720	-0.883128	-1.782311
C	0.385366	1.588965	-0.786611
H	-0.106451	1.581877	-1.782311
H	1.479130	1.599961	-0.965992
C	1.183402	-1.128219	-0.786611
H	0.646042	-2.080945	-0.965992
H	1.423171	-0.698749	-1.782311

(i-Pr)₃P

P	0.033956	0.025746	-0.697990
C	1.692815	-0.077525	0.147891
C	2.350903	-1.400713	-0.213409
C	2.587305	1.059903	-0.320620
C	-0.951075	1.235857	0.343531
C	-0.136046	2.377366	0.922865
C	-2.076521	1.794226	-0.515362
C	-0.730494	-1.578100	-0.106756
C	-0.594537	-1.860918	1.379415
C	-2.187202	-1.648320	-0.535317
H	2.723053	1.007716	-1.417281
H	3.587436	0.983730	0.147396
H	2.178163	2.056104	-0.084343
H	2.385307	-1.527372	-1.313395
H	1.828701	-2.276738	0.210533

H	3.395246	-1.420877	0.151272
H	-1.658020	2.396100	-1.343645
H	-2.740895	2.449011	0.080909
H	-2.695681	1.001510	-0.971091
H	0.306848	2.996745	0.119599
H	0.680640	2.031394	1.581756
H	-0.791039	3.042587	1.517515
H	-2.312217	-1.427512	-1.611332
H	-2.802354	-0.923647	0.032306
H	-2.606388	-2.652671	-0.338242
H	0.456762	-1.851116	1.720742
H	-1.020001	-2.852815	1.624879
H	-1.149135	-1.117562	1.983364
H	-1.387859	0.661079	1.187352
H	1.553375	-0.019921	1.248460
H	-0.172180	-2.352584	-0.670334

(n-Bu)₃P

P	-0.020652	0.006604	-0.756144
C	0.178120	-1.622313	0.101244
C	1.482585	-2.317624	-0.241167
H	-0.671058	-2.263122	-0.210353
H	0.087565	-1.477903	1.199898
C	1.626450	-3.672998	0.425897
H	1.562118	-2.437678	-1.341474
H	2.341874	-1.680255	0.054113
C	2.936541	-4.355039	0.078705
H	1.542196	-3.548479	1.524107
H	0.773360	-4.315157	0.127687
H	3.037228	-5.337099	0.572848
H	3.021262	-4.517190	-1.011815
H	3.799774	-3.735588	0.385595
C	1.273364	0.964564	0.153499
C	1.306944	2.427112	-0.248312
H	2.253656	0.496303	-0.068442
H	1.107300	0.864278	1.248109
C	2.400900	3.212333	0.452340
H	1.440575	2.505881	-1.346757
H	0.327775	2.903585	-0.030863
C	2.413800	4.674819	0.049122
H	2.269157	3.121339	1.549302
H	3.381505	2.747415	0.225636
H	3.210792	5.240351	0.562654
H	2.572667	4.783309	-1.039780
H	1.449752	5.160533	0.289243
C	-1.507815	0.621591	0.156131

C	-2.783063	-0.098779	-0.240728
H	-1.610081	1.702999	-0.067508
H	-1.332303	0.532885	1.250036
C	-4.015328	0.441548	0.461324
H	-2.923666	-0.026616	-1.338875
H	-2.691094	-1.183081	-0.020557
C	-5.281839	-0.287252	0.053548
H	-3.871302	0.368608	1.558013
H	-4.112095	1.523542	0.239861
H	-6.174418	0.113145	0.565082
H	-5.453087	-0.203977	-1.035744
H	-5.213621	-1.364866	0.292526

Ph₃P

P	0.000369	-0.004156	-1.316219
C	3.695977	-1.888047	0.747135
C	1.463966	-0.696847	-0.467415
C	3.100937	-2.488239	-0.366643
C	1.997889	-1.889497	-0.975410
C	2.065130	-0.099932	0.647416
C	3.178321	-0.691814	1.247815
H	4.569616	-2.351070	1.220536
H	3.506922	-3.423837	-0.769158
H	3.643735	-0.216407	2.119649
H	1.540671	-2.351931	-1.860631
H	1.652442	0.836398	1.045500
C	-3.492926	-2.243990	0.742848
C	-1.335606	-0.924136	-0.473449
C	-3.712317	-1.409770	-0.357558
C	-2.637771	-0.762538	-0.967312
C	-1.121989	-1.761517	0.628066
C	-2.196020	-2.421776	1.228789
H	-4.334833	-2.761582	1.217166
H	-4.727359	-1.271201	-0.748340
H	-2.019054	-3.077072	2.090168
H	-2.808437	-0.119315	-1.841187
H	-0.103006	-1.892009	1.015888
C	-0.199462	4.142228	0.739287
C	-0.133677	1.613142	-0.474928
C	0.643246	3.911194	-0.352126
C	0.667176	2.656428	-0.960668
C	-0.975260	1.850373	0.618153
C	-1.010521	3.111227	1.217737
H	-0.227754	5.130383	1.213049
H	1.278552	4.717896	-0.736614
H	-1.673611	3.288521	2.073070

H	1.318643	2.478503	-1.826961
H	-1.604619	1.036130	1.000739

PdL

Pd(TTBP)

P	-0.136381	0.000175	0.000450
C	-0.800467	-1.268949	-1.246951
C	-2.265848	-1.647428	-1.085264
C	-0.572068	-0.713966	-2.647256
C	0.071637	-2.518595	-1.150527
C	-0.806522	-0.454132	1.719103
C	-2.277796	-0.144586	1.954003
C	-0.560307	-1.940936	1.937992
C	0.049666	0.266182	2.757248
C	-0.822907	1.708969	-0.469855
C	-2.289574	1.742973	-0.874853
C	-0.602252	2.648463	0.708849
C	0.041796	2.258395	-1.601972
H	1.143023	-2.229798	-1.182081
H	-0.154782	-3.176361	-2.013094
H	-0.092017	-3.097385	-0.228431
H	0.478782	-0.388038	-2.771927
H	-1.240931	0.128317	-2.894266
H	-0.770659	-1.522395	-3.377784
H	-2.460313	-2.178324	-0.136567
H	-2.546243	-2.337785	-1.905557
H	-2.941357	-0.775903	-1.139751
H	1.124124	0.087789	2.544578
H	-0.195971	-0.135495	3.760451
H	-0.110699	1.355126	2.776683
H	0.492317	-2.199693	1.711391
H	-1.225783	-2.584134	1.336496
H	-0.748955	-2.172374	3.004630
H	-2.486328	0.939987	1.941619
H	-2.563637	-0.516606	2.957954
H	-2.941144	-0.632872	1.218683
H	1.113636	2.177724	-1.326034
H	-0.215567	3.324843	-1.759634
H	-0.097092	1.728878	-2.557357
H	0.449773	2.606127	1.051358
H	-1.267415	2.437855	1.563904
H	-0.811392	3.682726	0.371789
H	-2.482948	1.177820	-1.803627
H	-2.578616	2.794840	-1.069859
H	-2.959606	1.355407	-0.087400

Pd 2.024856 0.011495 0.000087

Pd(DTBNpP)

P	0.407935	0.195914	0.011149
C	1.342879	0.494445	1.616706
C	1.990761	1.863920	1.719825
C	0.327630	0.319322	2.736663
C	2.387714	-0.601903	1.776484
C	1.414581	0.793445	-1.464764
C	1.630631	2.296866	-1.551506
C	2.755650	0.078073	-1.463730
C	0.622759	0.333706	-2.681897
C	-2.427515	0.869698	0.054080
C	-2.705132	0.139761	-1.250461
C	-2.684339	-0.085665	1.207378
C	-3.358120	2.068589	0.173719
H	1.909132	-1.594889	1.656614
H	2.838536	-0.534424	2.786166
H	3.198803	-0.528881	1.032825
H	-0.193751	-0.652720	2.640289
H	-0.433960	1.120044	2.754921
H	0.860237	0.338020	3.707264
H	2.848950	1.966729	1.031269
H	2.378842	2.005429	2.747881
H	1.280023	2.688241	1.519526
H	0.464297	-0.763048	-2.645012
H	1.180641	0.596531	-3.602428
H	-0.374587	0.810098	-2.738592
H	2.618948	-1.008788	-1.299193
H	3.435375	0.470953	-0.685490
H	3.250515	0.224278	-2.443787
H	0.682021	2.861317	-1.606159
H	2.188810	2.520409	-2.481791
H	2.217126	2.695755	-0.707605
H	-3.192681	2.609206	1.125085
H	-4.415200	1.744863	0.148097
H	-3.202368	2.783462	-0.656841
H	-2.506749	0.392441	2.188783
H	-2.004135	-0.969579	1.114428
H	-3.729790	-0.444894	1.179752
H	-2.574347	0.805410	-2.125852
H	-3.740983	-0.246889	-1.263579
H	-2.004819	-0.725879	-1.351807
C	-0.988425	1.411155	0.063049
H	-0.842898	2.058320	0.952535
H	-0.874272	2.071386	-0.820053

Pd -0.200765 -1.872176 -0.172560

Pd(TBDNpP)

P	0.027947	0.472701	0.264608
C	2.553648	-0.875577	0.720084
C	1.819455	-2.205947	0.687436
C	3.099590	-0.569522	-0.665297
C	3.704711	-0.952391	1.712614
C	-0.263983	2.307369	0.503410
C	-0.091057	2.731760	1.953112
C	0.733570	3.030870	-0.387146
C	-1.668008	2.634525	0.028196
C	-2.307404	-1.218025	0.737618
C	-3.149775	-0.421148	-0.244535
C	-1.711396	-2.408844	0.003797
C	-3.189779	-1.720139	1.872681
H	4.248017	0.009689	1.770941
H	4.428078	-1.731754	1.408872
H	3.341575	-1.202140	2.727900
H	3.692758	0.365127	-0.666204
H	2.247556	-0.438054	-1.383597
H	3.742989	-1.393292	-1.025355
H	1.365142	-2.445427	1.669161
H	2.514761	-3.025074	0.425470
H	1.015364	-2.177450	-0.076424
H	-1.819739	2.285269	-1.011228
H	-1.822728	3.730507	0.060819
H	-2.443197	2.165777	0.662396
H	0.619176	2.694986	-1.436355
H	1.782146	2.843817	-0.088783
H	0.558534	4.123044	-0.334356
H	-0.788613	2.204466	2.630910
H	-0.302475	3.814762	2.047473
H	0.937182	2.561849	2.318749
H	-2.606363	-2.315656	2.600253
H	-3.999049	-2.363056	1.479327
H	-3.659086	-0.878596	2.417348
H	-1.075844	-3.023849	0.669043
H	-1.079521	-2.046610	-0.848372
H	-2.515008	-3.048729	-0.405338
H	-3.647521	0.439895	0.240164
H	-3.933274	-1.066576	-0.683141
H	-2.504794	-0.043411	-1.070415
C	-1.205686	-0.355004	1.370666
H	-0.621991	-0.991786	2.065972
H	-1.679079	0.435127	1.991098

C	1.619662	0.249053	1.179413
H	1.377424	0.115971	2.254672
H	2.167881	1.209439	1.091674
Pd	0.008244	-0.201319	-1.789219

Pd(TNpP)

P	0.000000	0.000000	-0.488098
C	1.321729	2.561929	-0.565284
C	0.000000	3.206692	-0.174107
C	2.145760	2.313382	0.688663
C	2.087301	3.490738	-1.496101
C	1.557831	-2.425615	-0.565284
C	1.979418	-3.553025	-1.496101
C	2.777076	-1.603346	-0.174107
C	0.930568	-3.014973	0.688663
C	-2.879560	-0.136313	-0.565284
C	-2.777076	-1.603346	-0.174107
C	-3.076327	0.701591	0.688663
C	-4.066718	0.062286	-1.496101
H	3.048531	3.039791	-1.806951
H	2.310646	4.450472	-0.994008
H	1.502735	3.711805	-2.409480
H	3.136962	1.888673	0.439086
H	1.611700	1.581420	1.351765
H	2.298166	3.252774	1.251429
H	-0.638898	3.396497	-1.058865
H	0.179286	4.176170	0.326747
H	-0.551983	2.553254	0.534901
H	0.563700	-2.186483	1.351765
H	1.667902	-3.616657	1.251429
H	0.067158	-3.661025	0.439086
H	2.487174	-0.798596	0.534901
H	3.260902	-1.144947	-1.058865
H	3.527026	-2.243351	0.326747
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H	2.463150	-3.157310	-2.409480
H	-4.156802	1.120210	-1.806951
H	-5.009544	-0.224158	-0.994008
H	-3.965885	-0.554496	-2.409480
H	-3.204119	1.772352	0.439086
H	-2.175400	0.605063	1.351765
H	-3.966068	0.363883	1.251429
H	-2.622004	-2.251551	-1.058865
H	-3.706312	-1.932819	0.326747
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C	-1.620346	0.320288	-1.310606
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H	0.654825	1.447265	-2.313508
H	2.063099	0.743779	-1.474797
C	0.532796	-1.563405	-1.310606
H	-0.387418	-2.158586	-1.474797
H	0.925956	-1.290728	-2.313508
Pd	0.000000	0.000000	1.678616

Pd[(i-Pr)₃P]

P	0.32200800	0.06425100	0.04136600
C	0.78051700	1.85399700	0.22824600
C	0.96321400	2.47535300	-1.14724200
C	-0.32027500	2.60084000	0.96493600
C	0.83953600	-0.77446700	1.61916900
C	0.53171600	0.05523800	2.85208300
C	0.14384100	-2.12248700	1.71906600
C	1.56524900	-0.54509400	-1.19959600
C	3.00887800	-0.25791400	-0.82690900
C	1.34650800	-2.01323100	-1.51616700
H	-1.27816900	2.44920300	0.42703000
H	-0.09284000	3.68332400	0.99485300
H	-0.46984000	2.24776900	1.99820100
H	0.05754900	2.29586600	-1.76110600
H	1.83593500	2.07866200	-1.69508800
H	1.09114400	3.56945900	-1.05214800
H	-0.95309800	-1.96794300	1.66811000
H	0.39652800	-2.61812700	2.67590300
H	0.40761500	-2.80458900	0.89326200
H	-0.55598300	0.24693000	2.92719100
H	1.05860500	1.02579800	2.86103200
H	0.83329600	-0.50172700	3.75900500
H	0.27204700	-2.21764200	-1.68899600
H	1.69214000	-2.65924200	-0.68751000
H	1.91626300	-2.30572200	-2.41749300
H	3.19086800	0.81036900	-0.60807100
H	3.68236100	-0.54784600	-1.65527900
H	3.32199000	-0.84341300	0.05781000
H	1.93832600	-0.91942700	1.54943400
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H	1.29933600	0.03771300	-2.10361100
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C	1.953688	-1.973735	-0.553390
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H	1.363196	-0.637109	-2.173667
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H	1.991181	-1.924822	0.555962
H	1.182712	-2.734914	-0.793839
C	3.695639	-3.796386	-0.580001
H	3.245668	-2.450275	-2.212609
H	4.063653	-1.681309	-0.844728
H	4.671578	-4.121582	-0.979884
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H	2.948547	-4.564457	-0.852901
C	-1.302498	-1.007198	-1.077773
C	-2.691578	-0.691355	-0.557177
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H	-2.961915	0.356920	-0.802070
C	-5.142707	-1.281465	-0.578308
H	-3.754427	-1.576779	-2.211346
H	-3.498492	-2.663557	-0.838389
H	-5.915219	-1.962725	-0.974785
H	-5.172142	-1.344488	0.524931
H	-5.430627	-0.250320	-0.854830
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C	0.743921	2.679882	-0.544157
H	-1.267652	1.954683	-0.849263
H	-0.138997	1.515320	-2.163553
C	0.469603	4.070936	-1.084507
H	0.694307	2.680746	0.565774
H	1.785412	2.391870	-0.797855
C	1.460250	5.097418	-0.567685
H	0.492767	4.047335	-2.192616
H	-0.562214	4.366998	-0.808428
H	1.252866	6.108126	-0.959581
H	1.432681	5.151638	0.536039
H	2.493675	4.830841	-0.856656
Pd	-0.002309	-0.012833	1.872976

Pd(Ph₃P)

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P	0.005321	-0.000543	0.417892
C	-1.748716	3.776936	-1.576932

C	-0.621261	1.514881	-0.377908
C	-2.275585	3.284238	-0.378992
C	-1.707348	2.162702	0.222266
C	-0.093154	2.010489	-1.575057
C	-0.654744	3.142569	-2.168933
H	-2.186674	4.666899	-2.044579
H	-3.127744	3.787257	0.093653
H	-0.234003	3.534072	-3.103099
H	-2.083920	1.776175	1.181690
H	0.768255	1.508552	-2.037252
C	-2.427391	-3.384139	-1.572614
C	-1.000164	-1.295637	-0.378029
C	-1.733531	-3.604194	-0.378637
C	-1.029784	-2.560838	0.220362
C	-1.696973	-1.076336	-1.571190
C	-2.412076	-2.119104	-2.163221
H	-2.992419	-4.200863	-2.037629
H	-1.753499	-4.593877	0.093288
H	-2.964588	-1.942343	-3.094033
H	-0.504456	-2.700275	1.177565
H	-1.684505	-0.078742	-2.031709
C	4.145935	-0.393583	-1.590478
C	1.626292	-0.218335	-0.386476
C	3.985276	0.332628	-0.406491
C	2.731866	0.411416	0.197489
C	1.788716	-0.945943	-1.570783
C	3.048318	-1.035969	-2.166728
H	5.134504	-0.467795	-2.059270
H	4.847821	0.829107	0.054086
H	3.174643	-1.614349	-3.090009
H	2.588314	0.948213	1.147586
H	0.924180	-1.452374	-2.021877

^1H and ^{13}C NMR Spectra of Amine Products

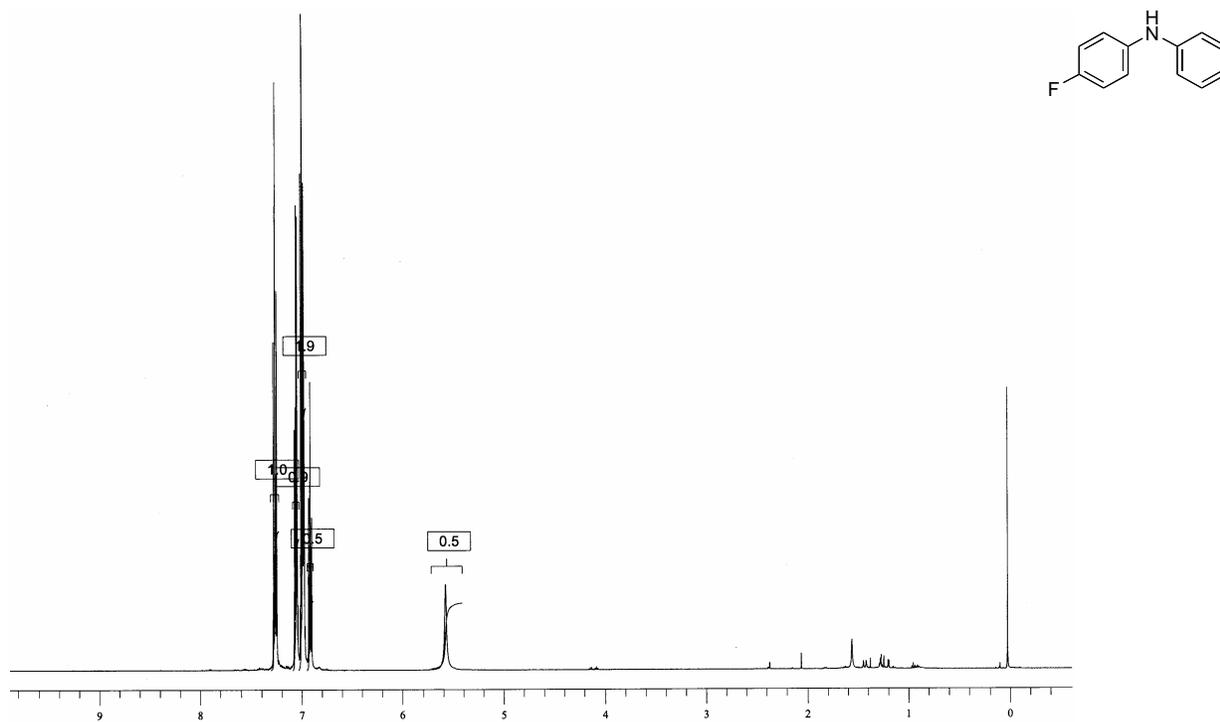


Figure S1. ^1H NMR spectrum (CDCl_3 , 500 MHz) of *N*-(4-fluorophenyl)aniline (Table 3, entry 1).

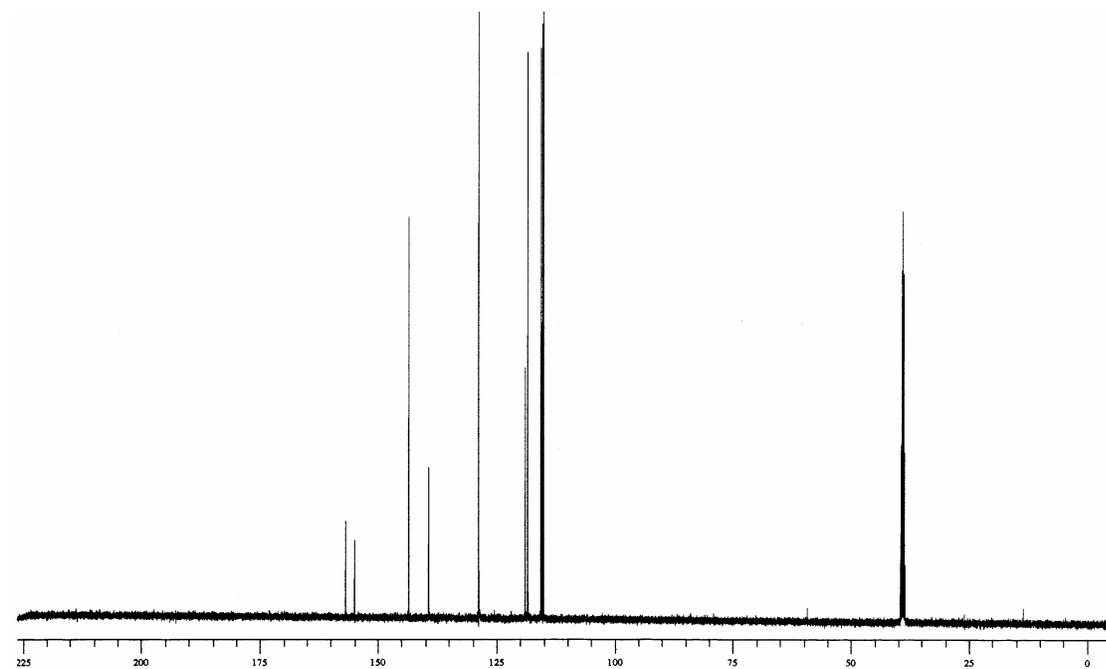


Figure S2. ^{13}C NMR spectrum ($\text{DMSO-}d_6$, 90.6 MHz) of *N*-(4-fluorophenyl)aniline (Table 3, entry 1).

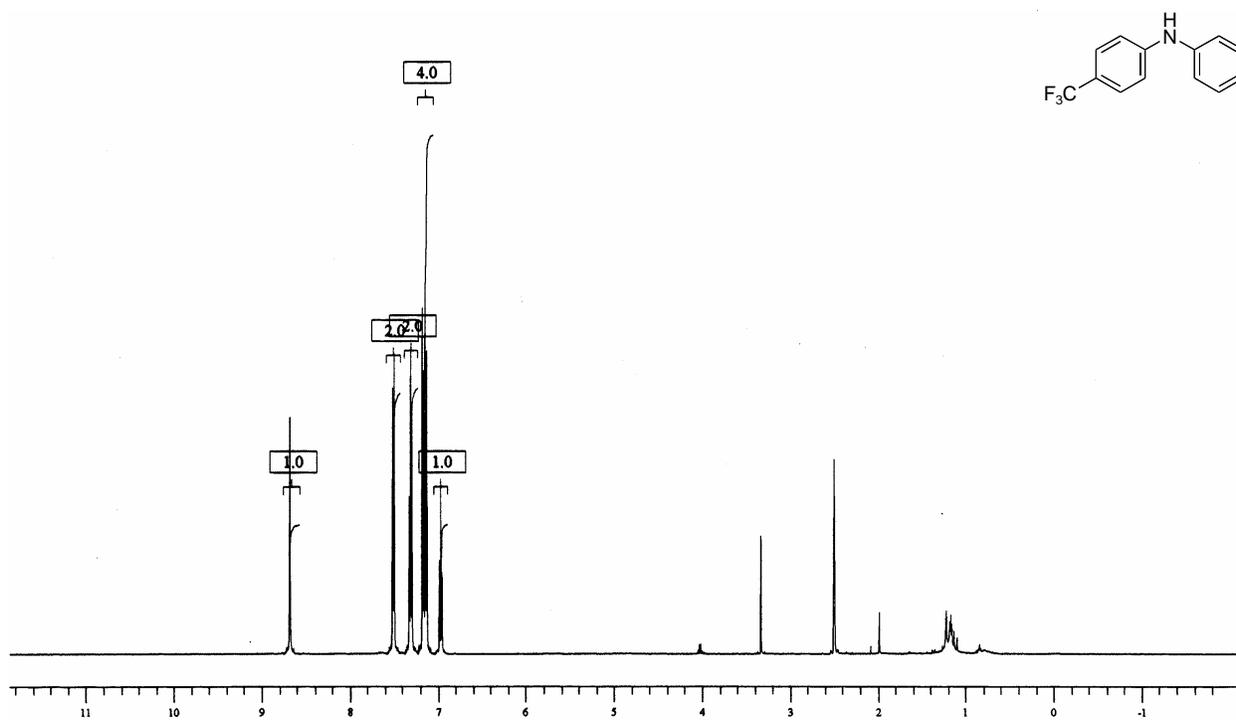


Figure S3. ¹H NMR spectrum (DMSO-*d*₆, 500 MHz) of *N*-(4-trifluoromethylphenyl)aniline (Table 3, entry 2).

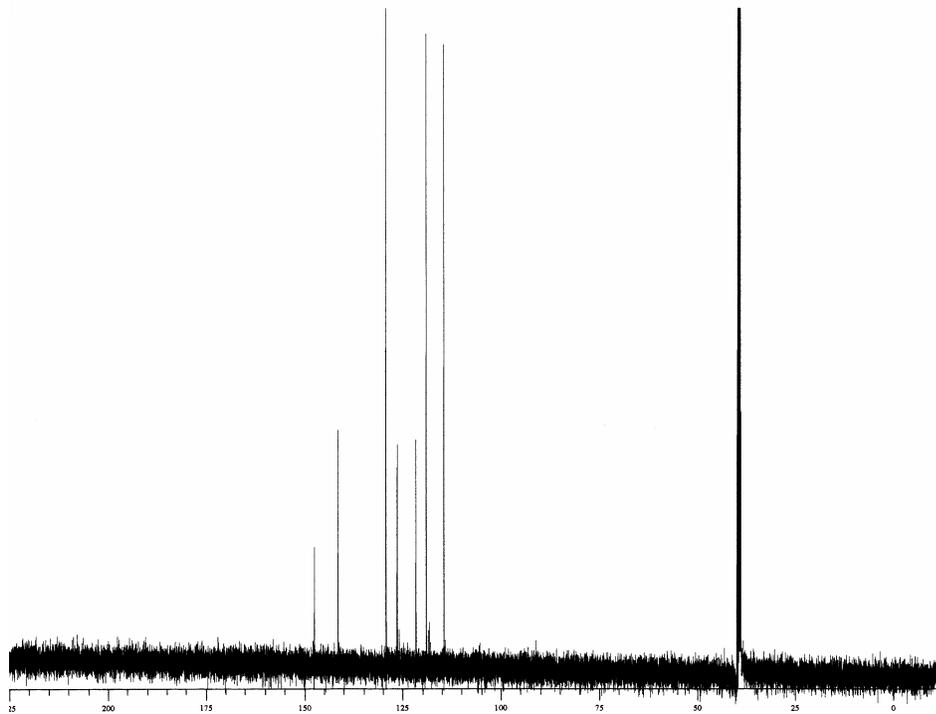


Figure S4. ¹³C NMR spectrum (DMSO-*d*₆, 90.6 MHz) of *N*-(4-trifluoromethylphenyl)aniline (Table 3, entry 2).

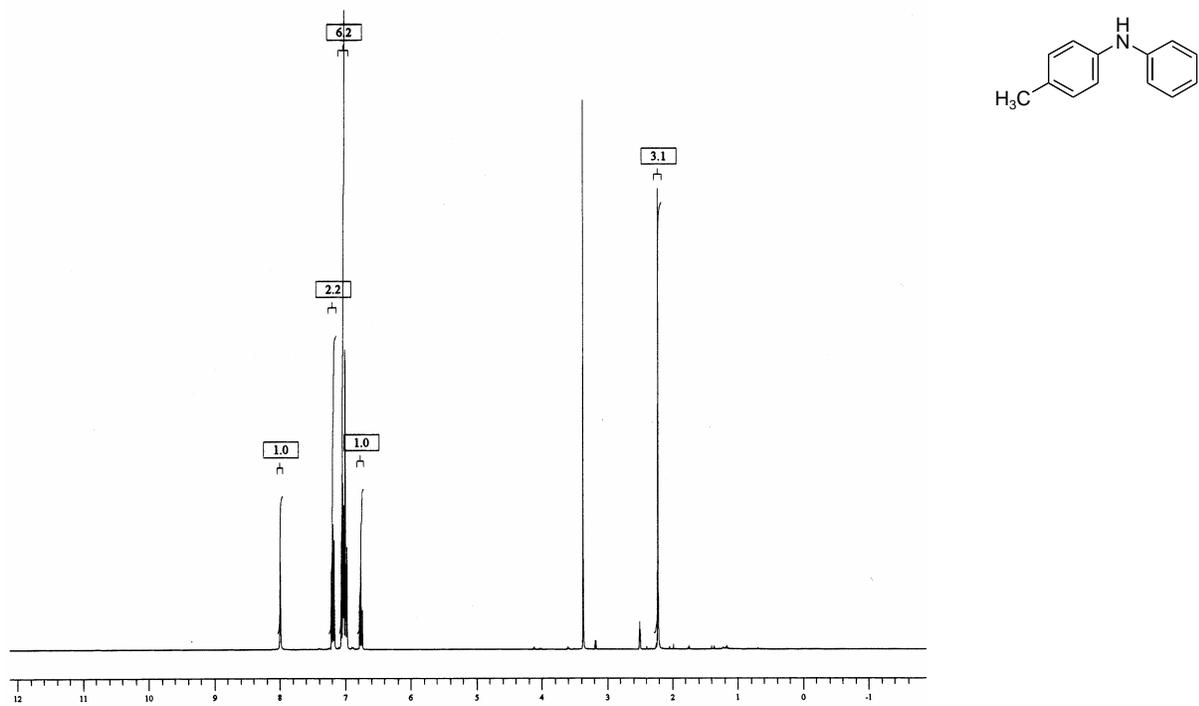


Figure S5. ^1H NMR spectrum ($\text{DMSO-}d_6$, 500 MHz) of *N*-(4-methylphenyl)aniline (Table 3, entry 3).

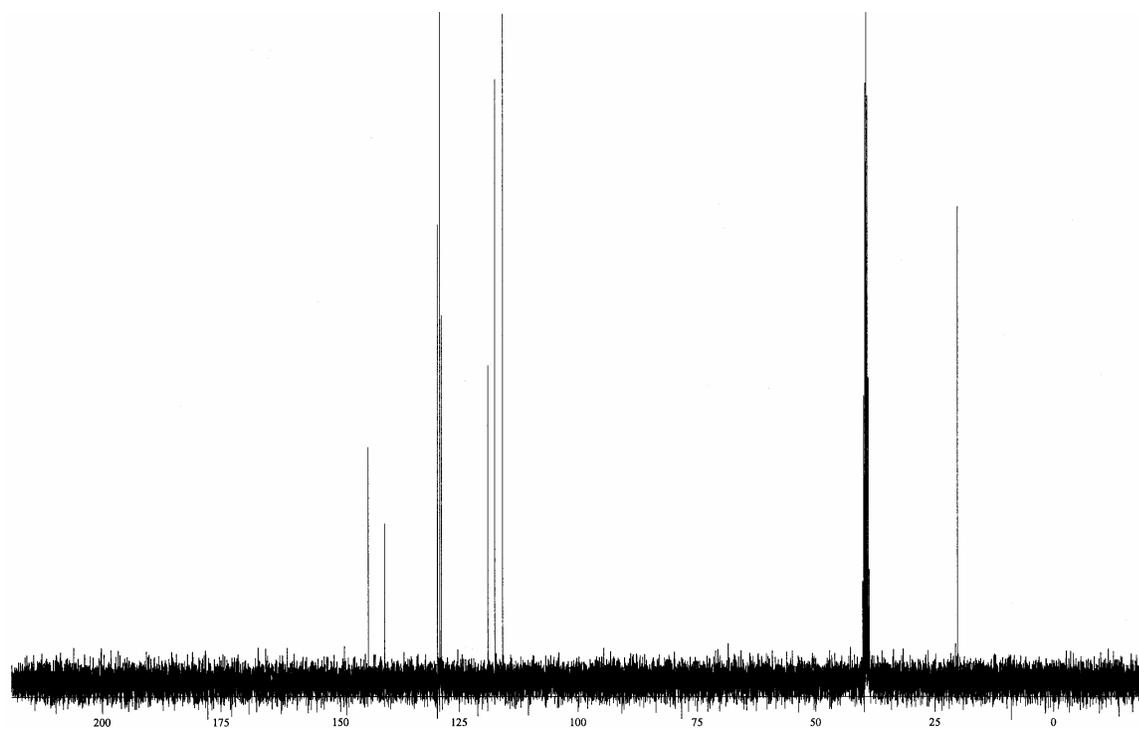


Figure S6. ^{13}C NMR spectrum ($\text{DMSO-}d_6$, 90.6 MHz) of *N*-(4-methylphenyl)aniline (Table 3, entry 3).

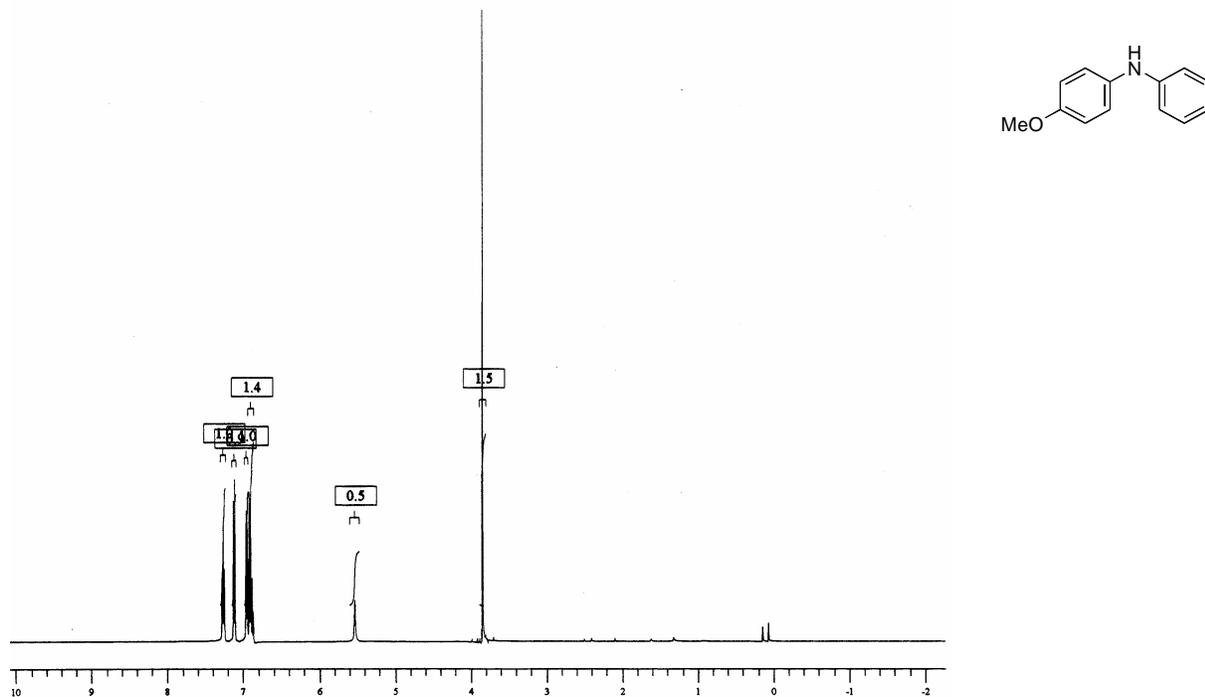


Figure S7. ¹H NMR spectrum (CDCl₃, 500 MHz) of *N*-(4-methoxyphenyl)aniline (Table 3, entry 4).

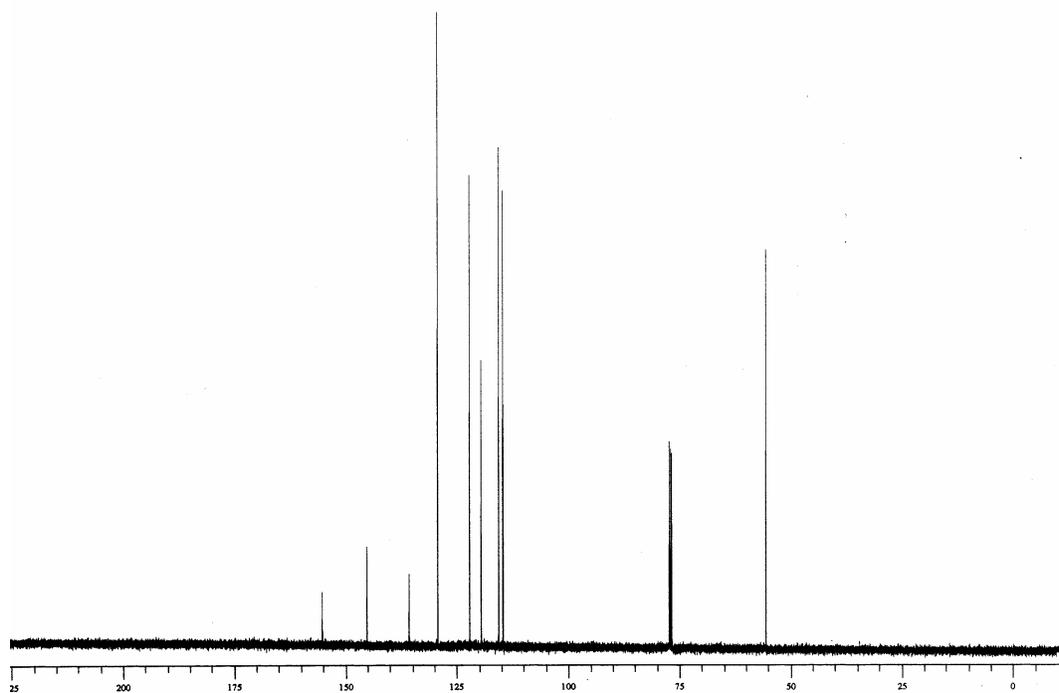


Figure S8. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-(4-methoxyphenyl)aniline (Table 3, entry 4).

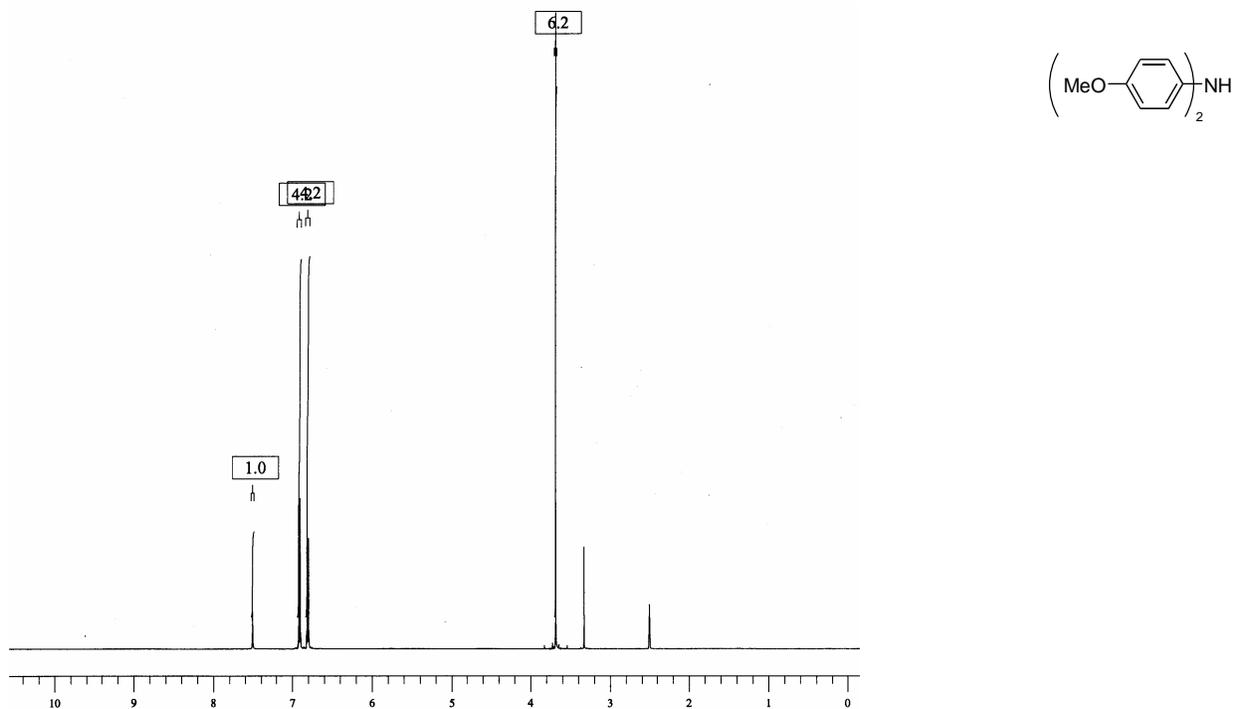


Figure S9. ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of bis(4-methoxyphenyl)amine (Table 3, entry 5).

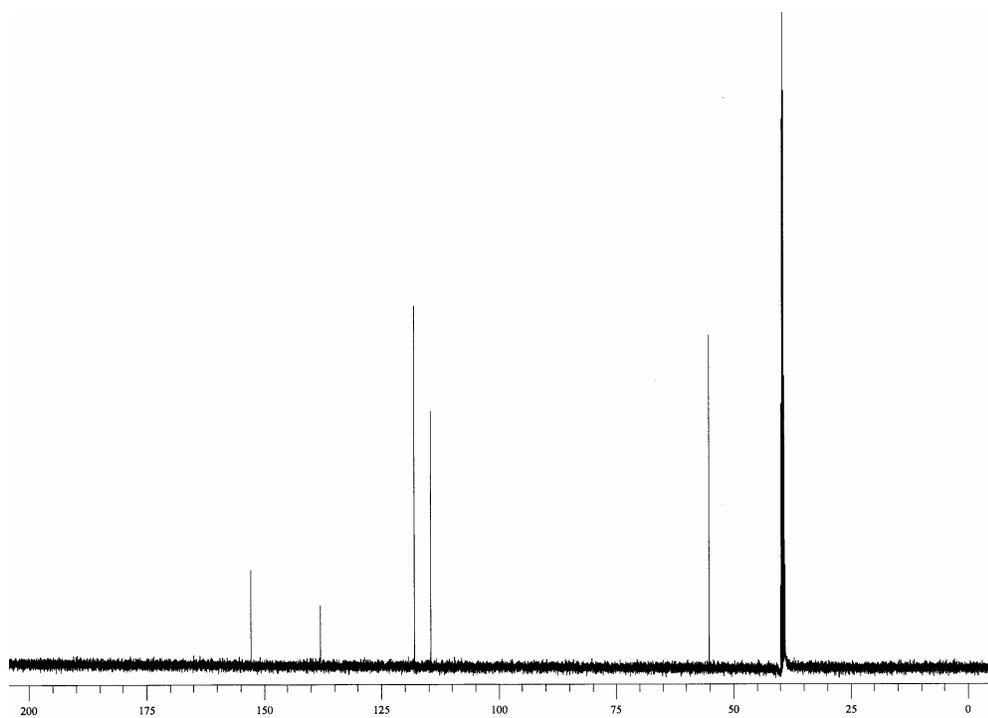


Figure S10. ^{13}C NMR spectrum (DMSO- d_6 , 90.6 MHz) of bis(4-methoxyphenyl)amine (Table 3, entry 5).

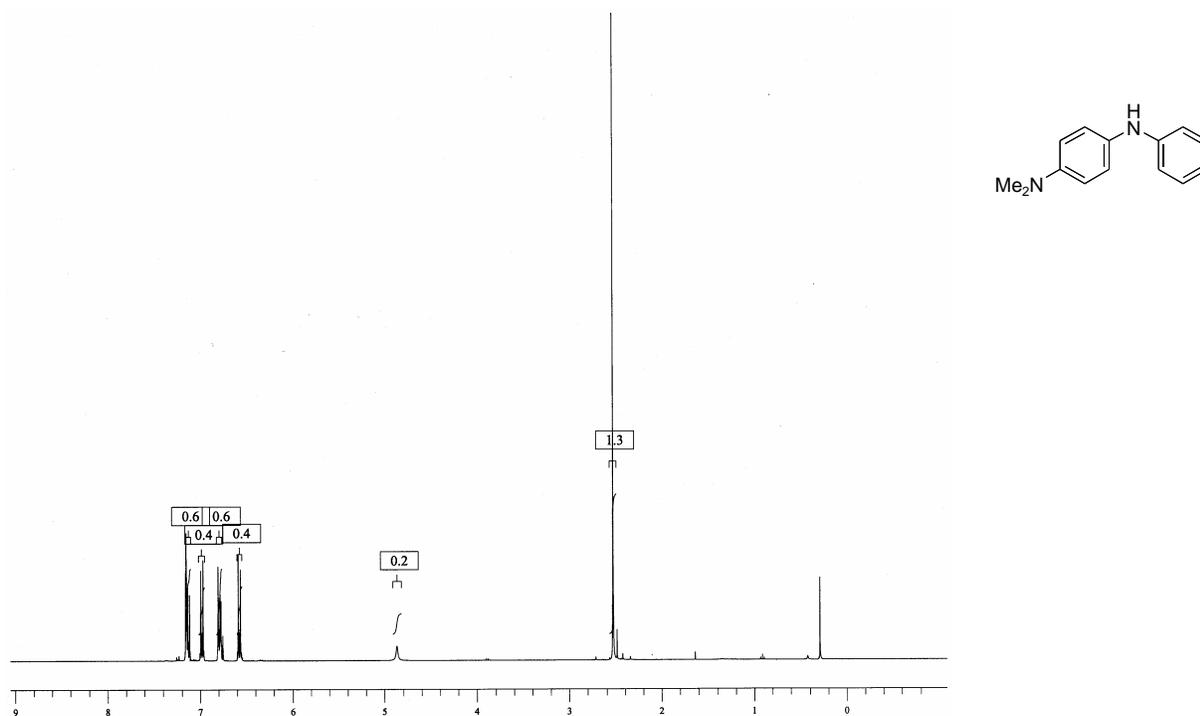


Figure S11. ^1H NMR spectrum (C_6D_6 , 500 MHz) of *N,N*-dimethyl-*N'*-phenyl-1,4-benzenediamine (Table 3, entry 6).

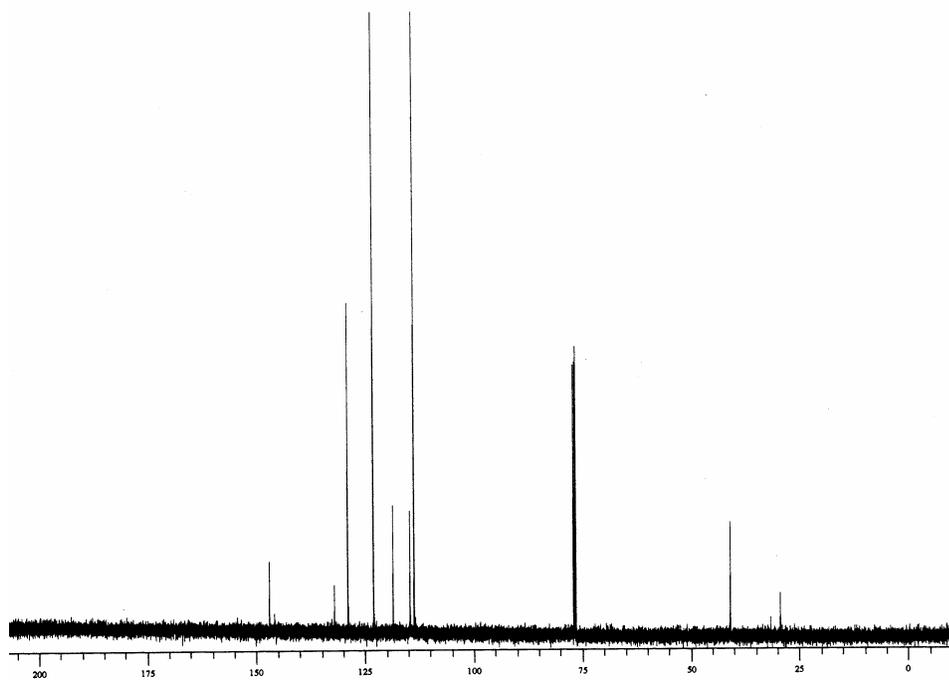


Figure S12. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N,N*-dimethyl-*N'*-phenyl-1,4-benzenediamine (Table 3, entry 6).

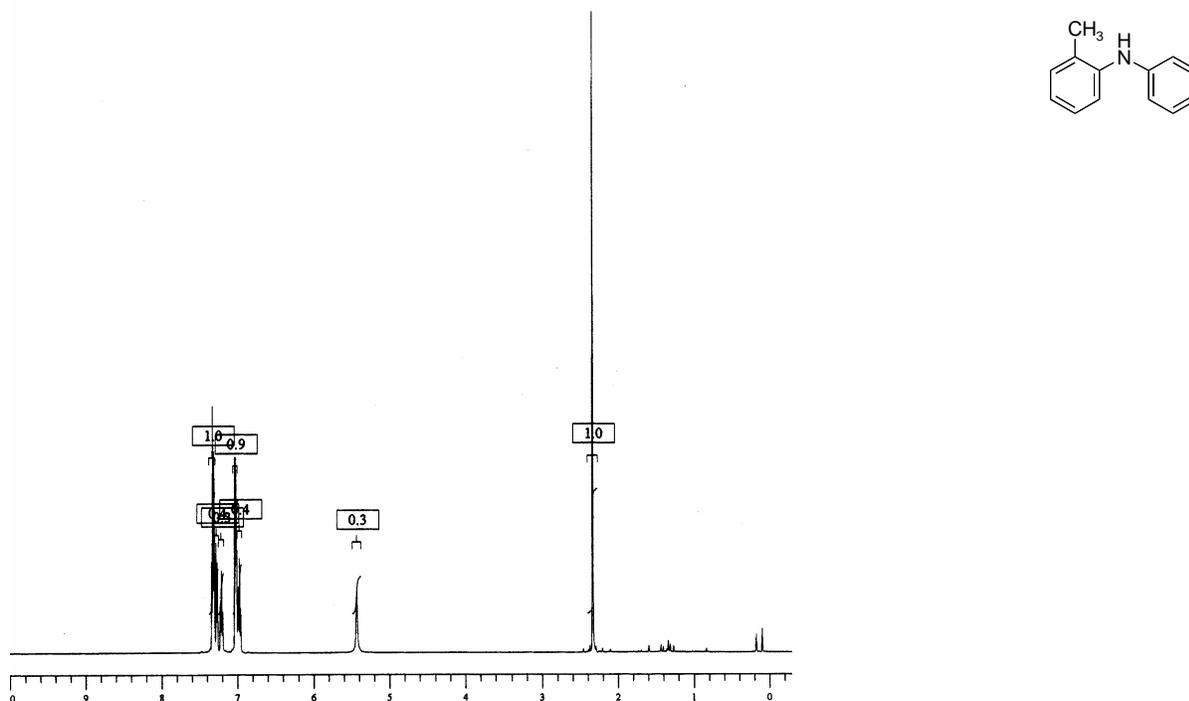


Figure S13. ¹H NMR spectrum (CDCl₃, 500 MHz) of *N*-(2-methylphenyl)aniline (Table 3, entry 7).

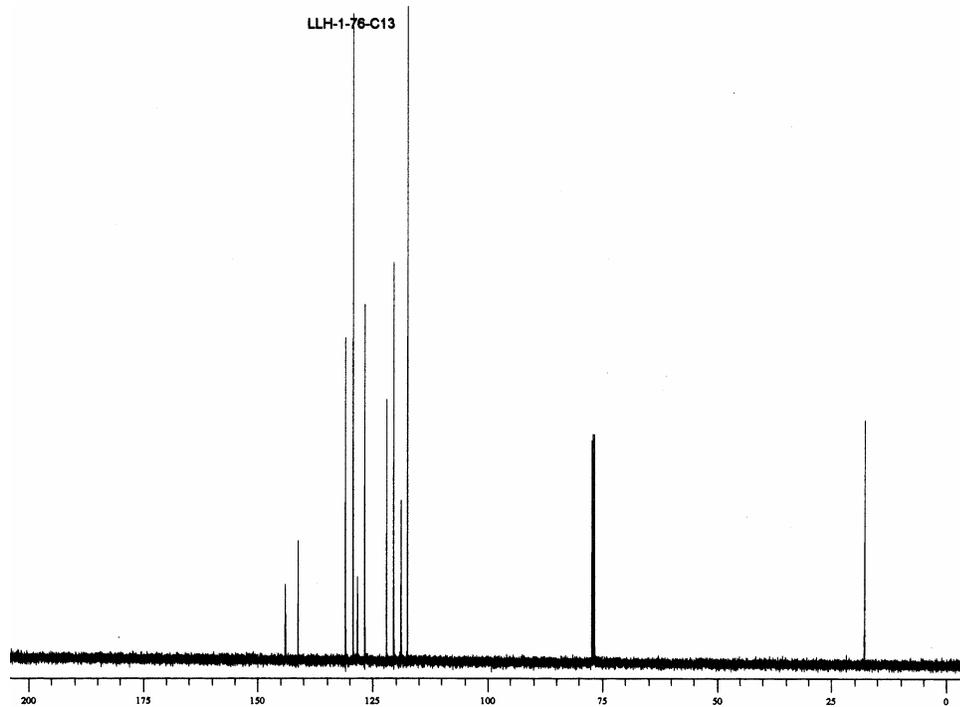


Figure S14. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-(2-methylphenyl)aniline (Table 3, entry 7).

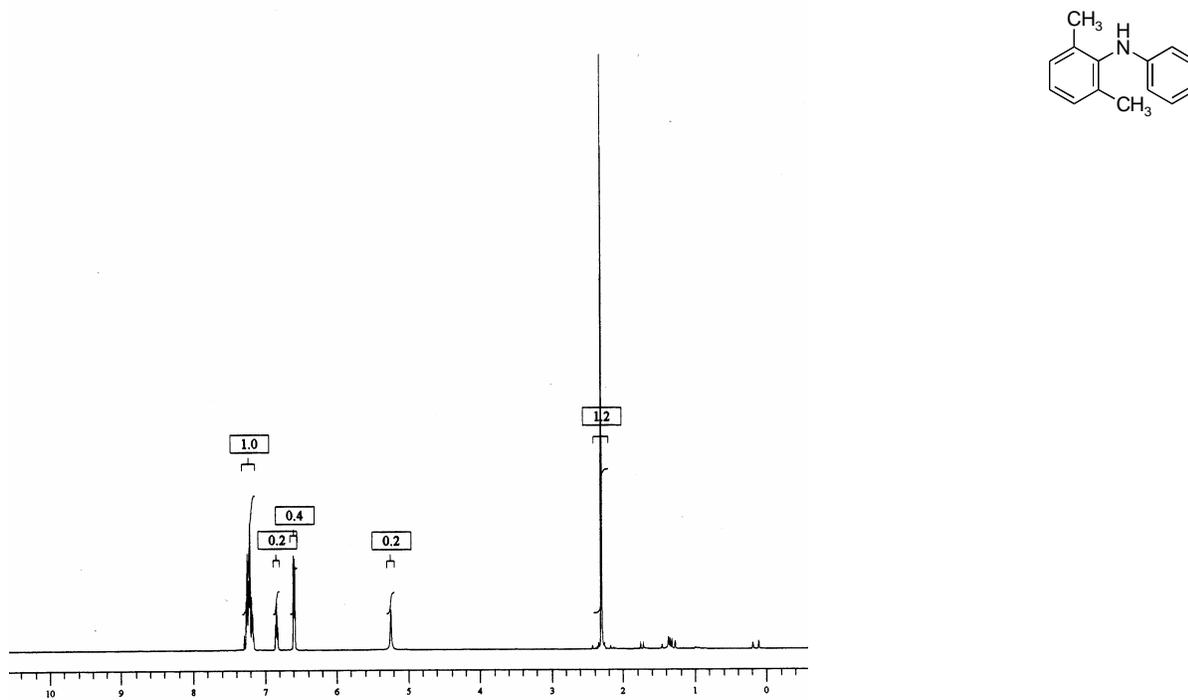


Figure S15. ¹H NMR spectrum (CDCl₃, 500 MHz) of *N*-(2,6-dimethylphenyl)aniline (Table 3, entry 8).

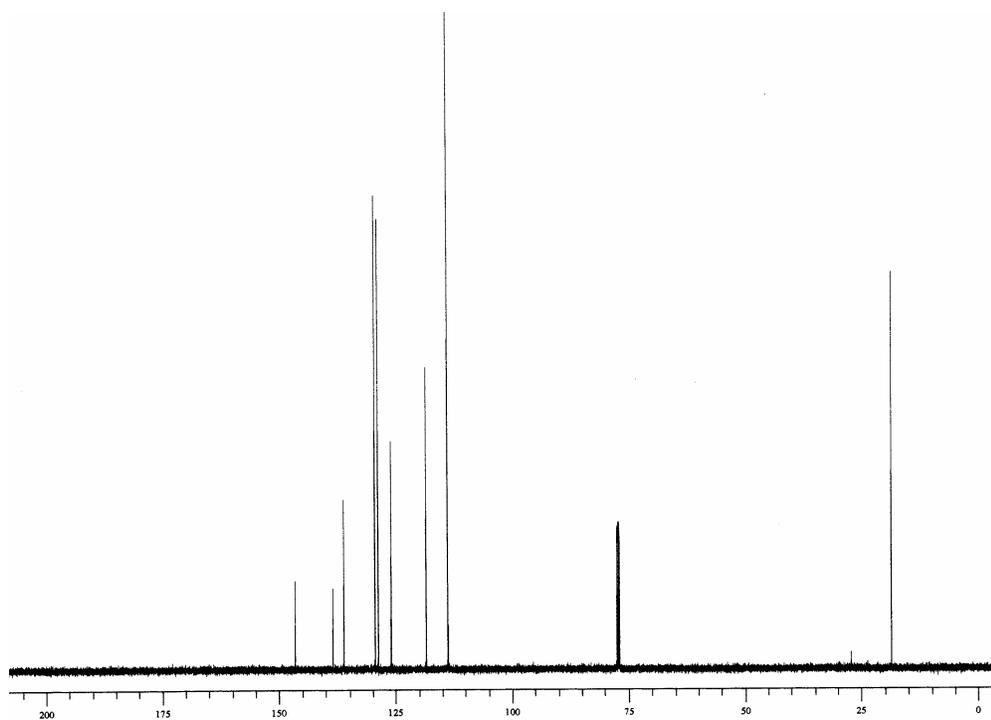


Figure S16. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-(2,6-dimethylphenyl)aniline (Table 3, entry 8).

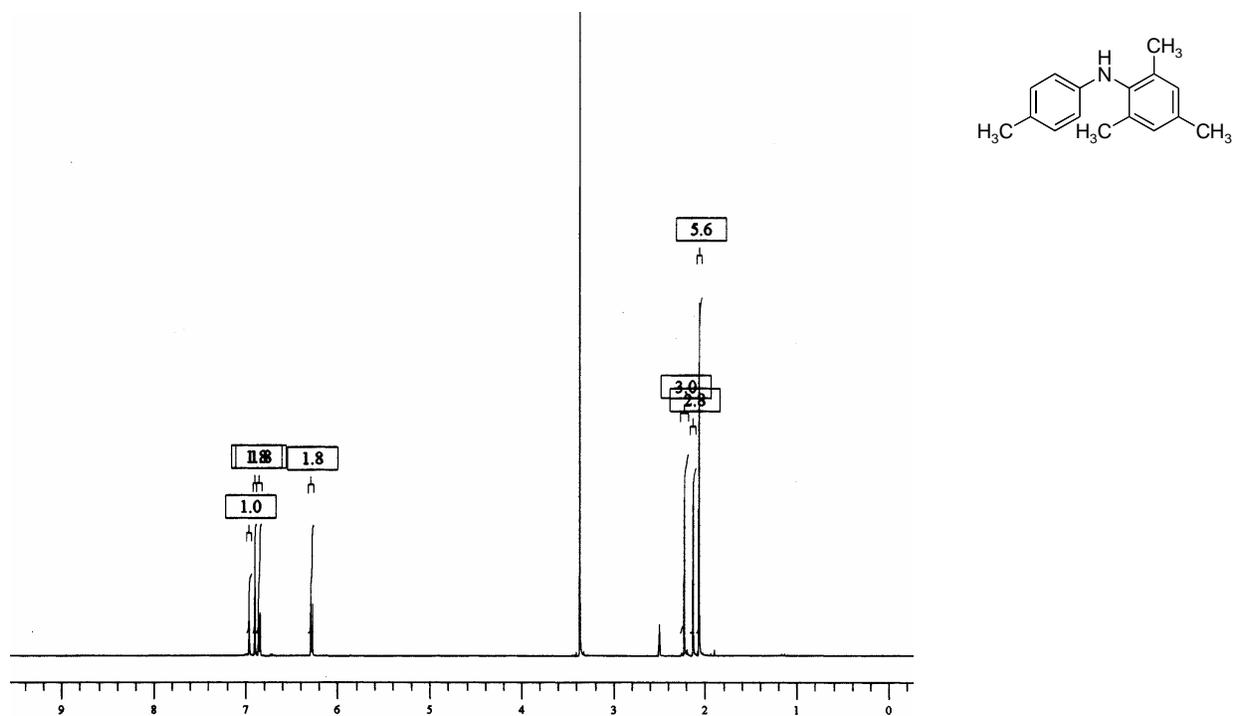


Figure S17. ¹H NMR spectrum (DMSO-*d*₆, 500 MHz) of 2,4,6-trimethyl-*N*-(4-methylphenyl)aniline (Table 3, entry 9).

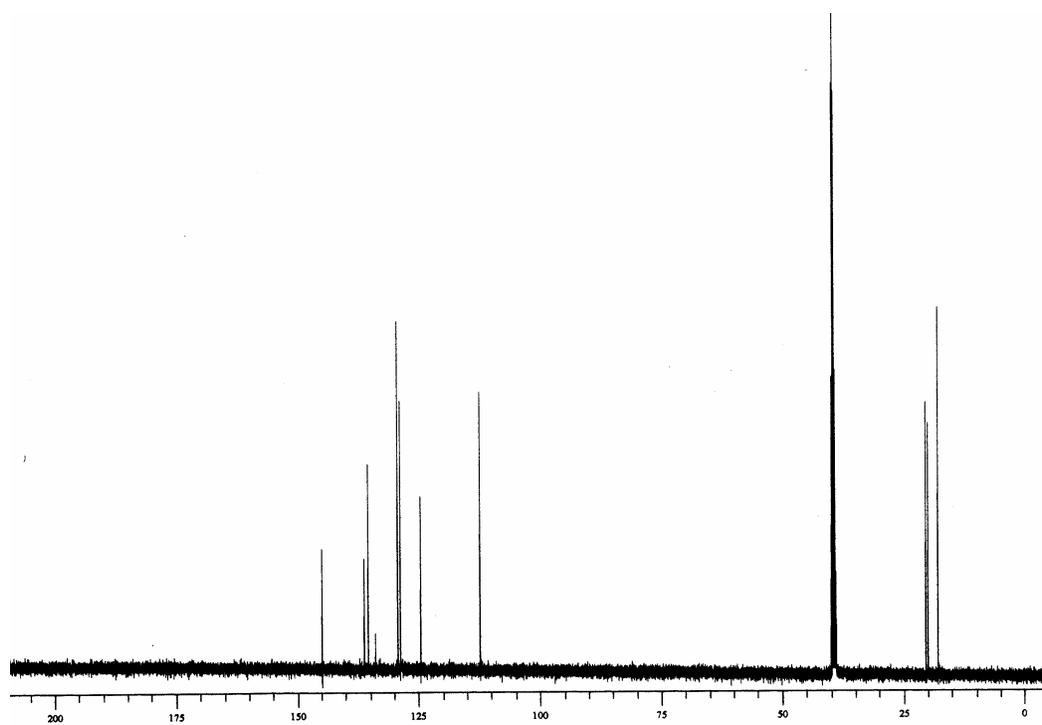


Figure S18. ¹³C NMR spectrum (DMSO-*d*₆, 90.6 MHz) of 2,4,6-trimethyl-*N*-(4-methylphenyl)aniline (Table 3, entry 9).

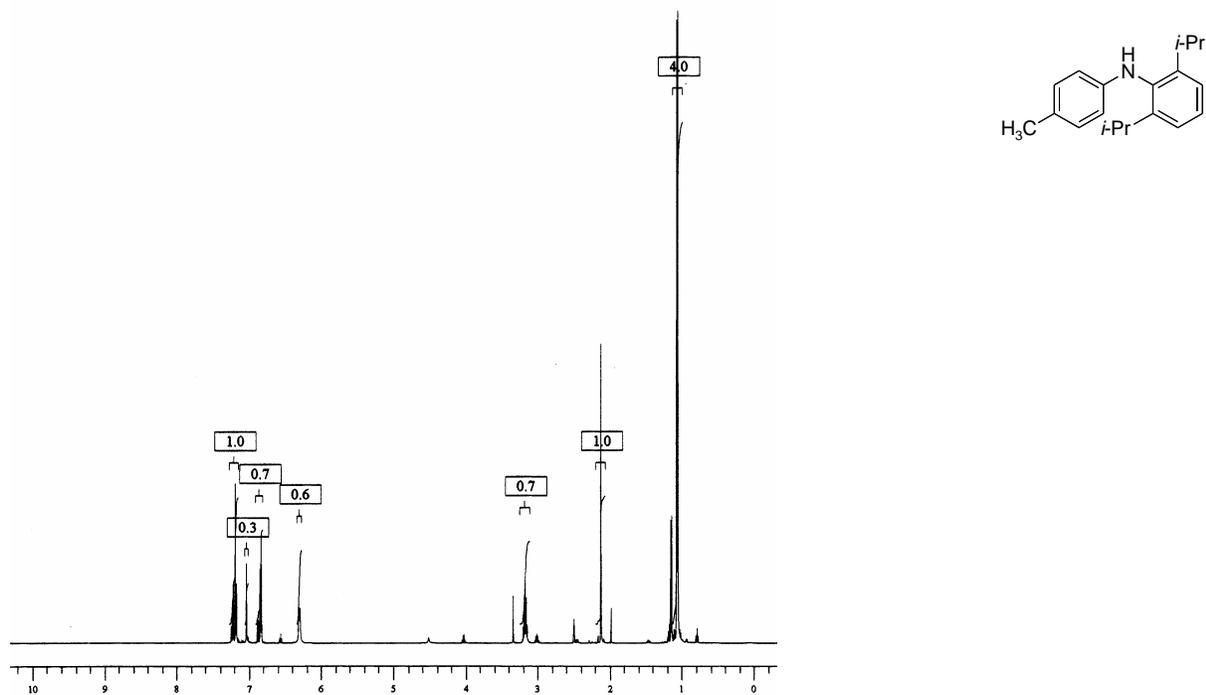


Figure S19. ¹H NMR spectrum (DMSO-*d*₆, 500 MHz) of 2,6-diisopropyl-*N*-(4-methylphenyl)aniline (Table 3, entry 10).

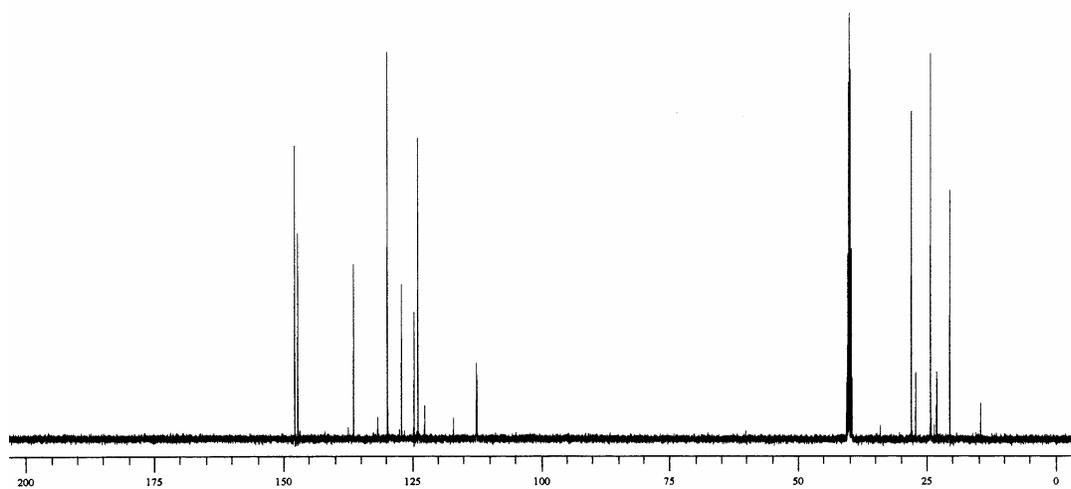


Figure S20. ¹³C NMR spectrum (DMSO-*d*₆, 90.6 MHz) of 2,6-diisopropyl-*N*-(4-methylphenyl)aniline (Table 3, entry 10).

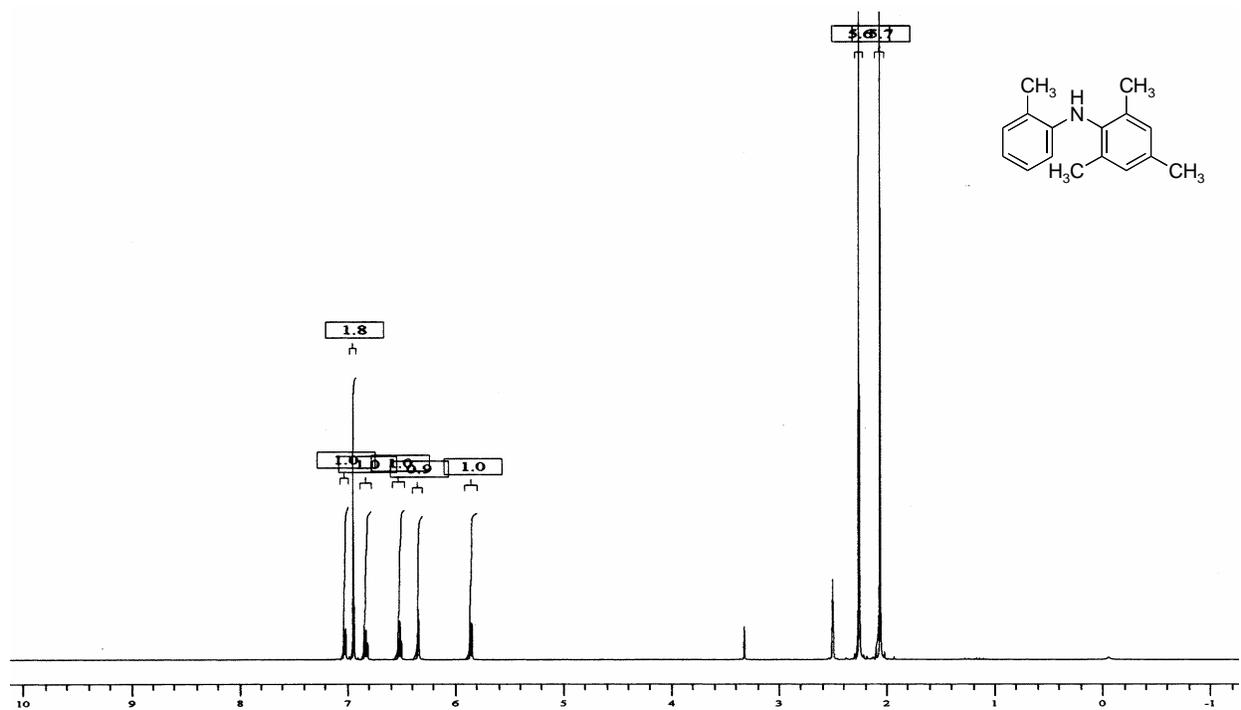


Figure S21. ^1H NMR spectrum (CDCl_3 , 500 MHz) of 2,4,6-trimethyl-*N*-(2-methylphenyl)aniline (Table 3, entry 11).

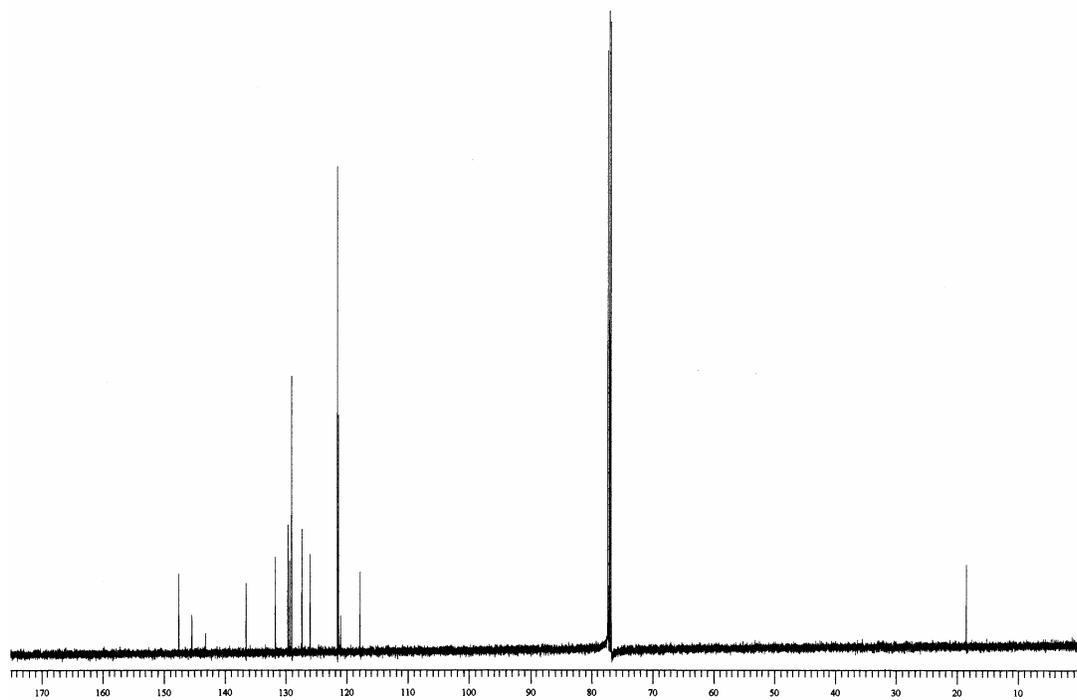


Figure S22. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of 2,4,6-trimethyl-*N*-(2-methylphenyl)aniline (Table 3, entry 11).

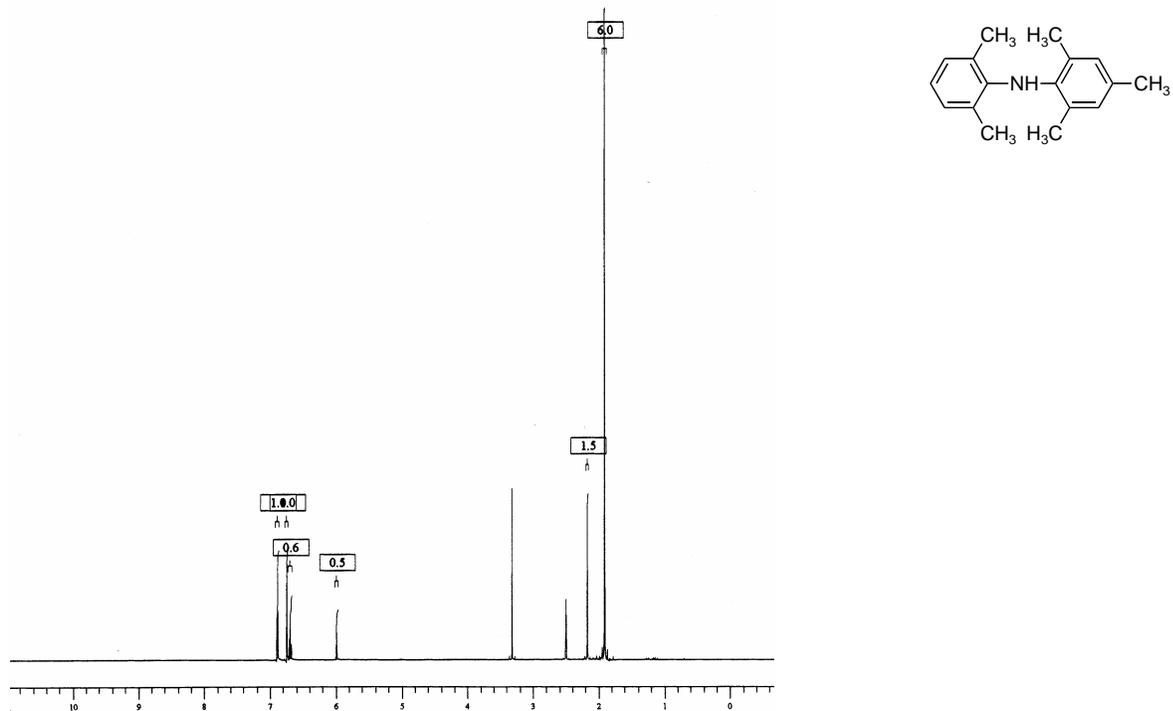


Figure S23. ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of 2,4,6-trimethyl-*N*-(2,6-dimethylphenyl)aniline (Table 3, entry 12).

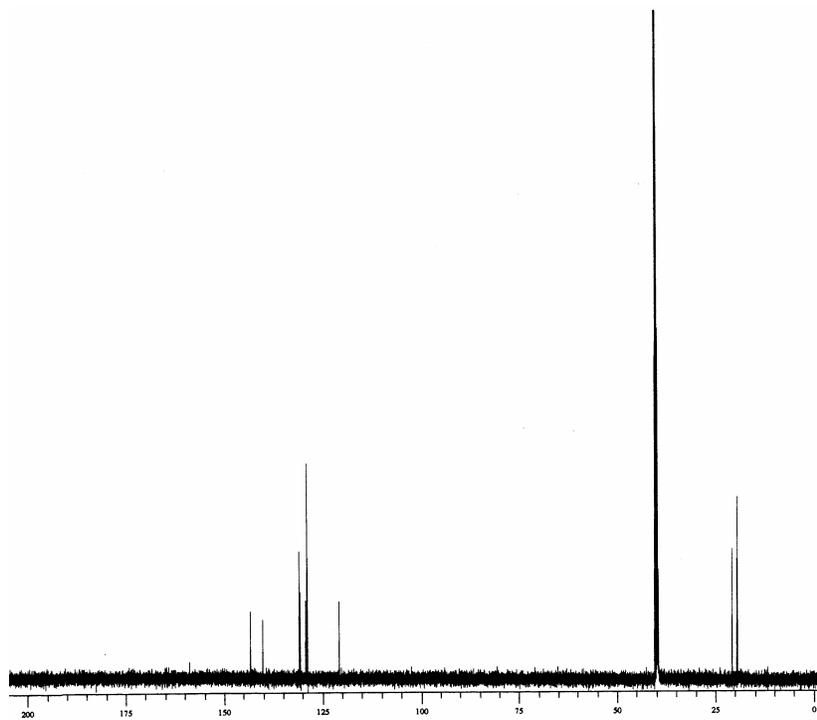


Figure S24. ^{13}C NMR spectrum (DMSO- d_6 , 90.6 MHz) of 2,4,6-trimethyl-*N*-(2,6-dimethylphenyl)aniline (Table 3, entry 12).

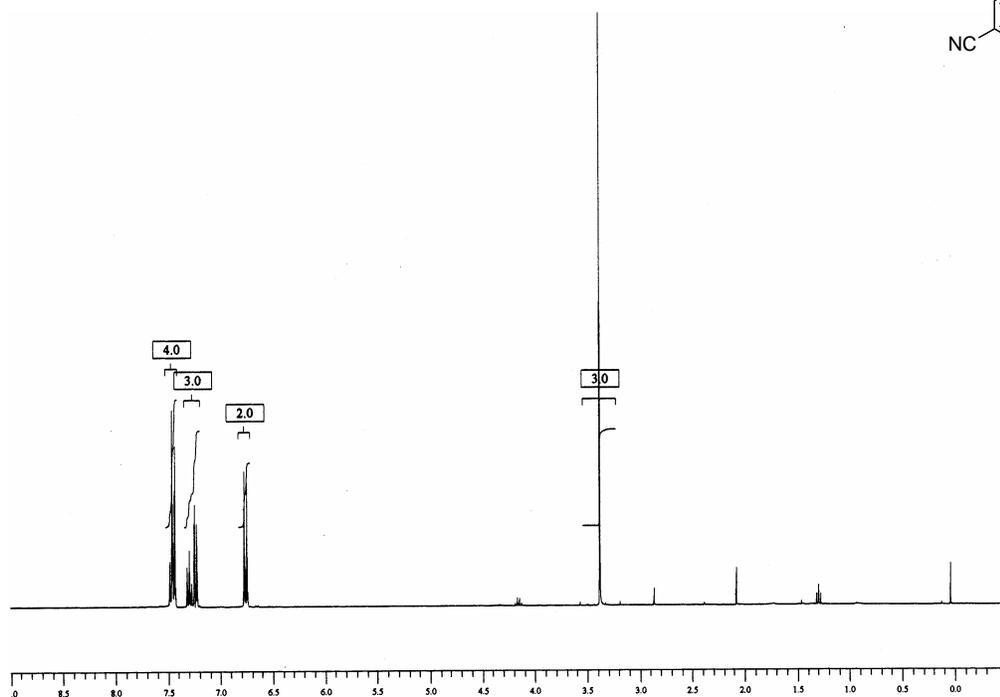
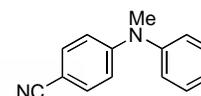


Figure S25. ^1H NMR spectrum (CDCl_3 , 360 MHz) of 4-(*N*-methyl-*N*-phenylamino)benzonitrile (Table 4, entry 1).

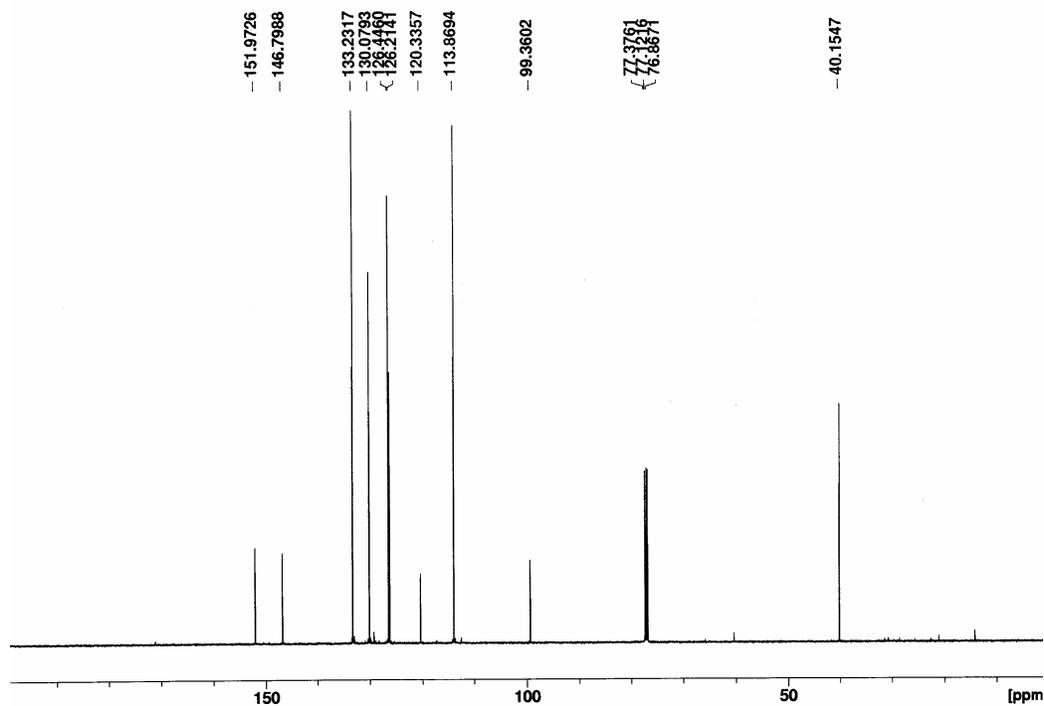


Figure S26. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of 4-(*N*-methyl-*N*-phenylamino)benzonitrile (Table 4, entry 1).

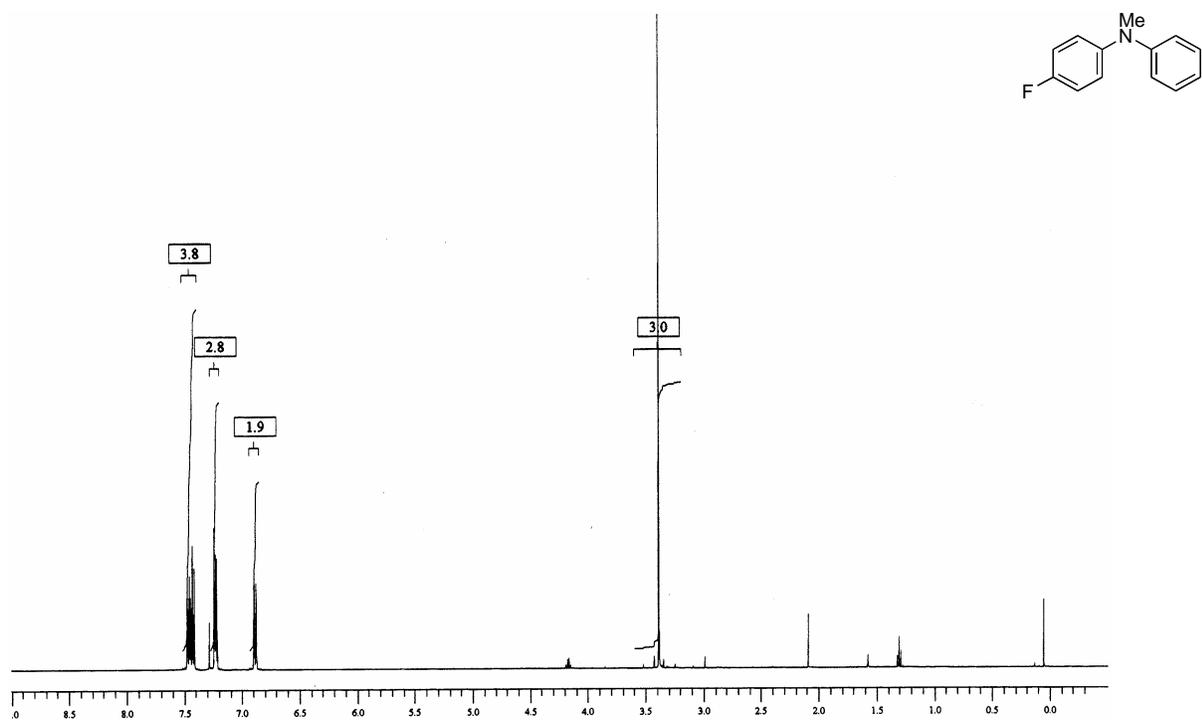


Figure S27. ¹H NMR spectrum (CDCl₃, 360 MHz) of *N*-(4-fluorophenyl)-*N*-methylaniline (Table 4, entry 2).

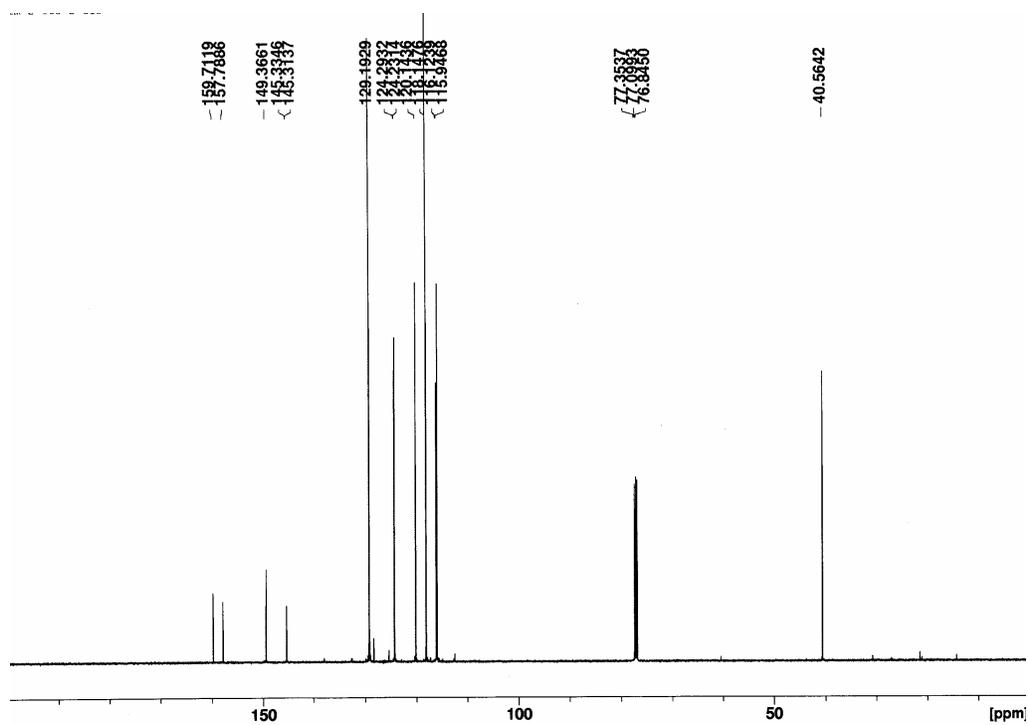


Figure S28. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-(4-fluorophenyl)-*N*-methylaniline (Table 4, entry 2).

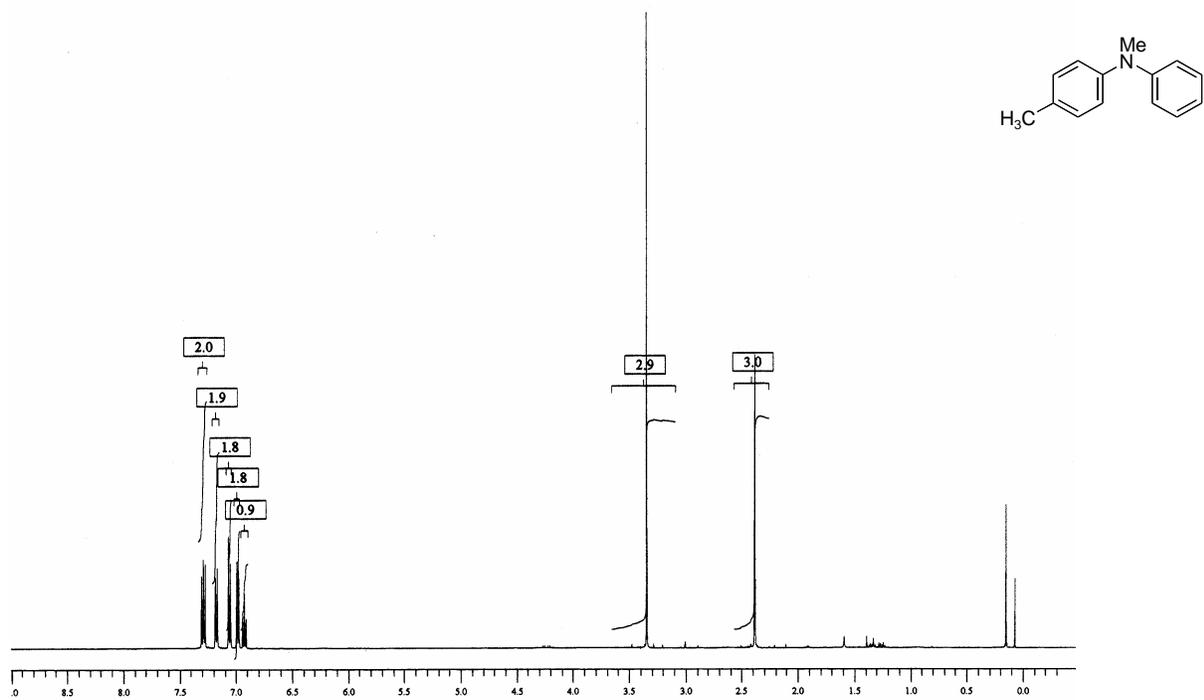


Figure S31. ¹H NMR spectrum (CDCl₃, 360 MHz) of *N*-methyl-*N*-phenyl-*p*-toluidine (Table 4, entry 4).

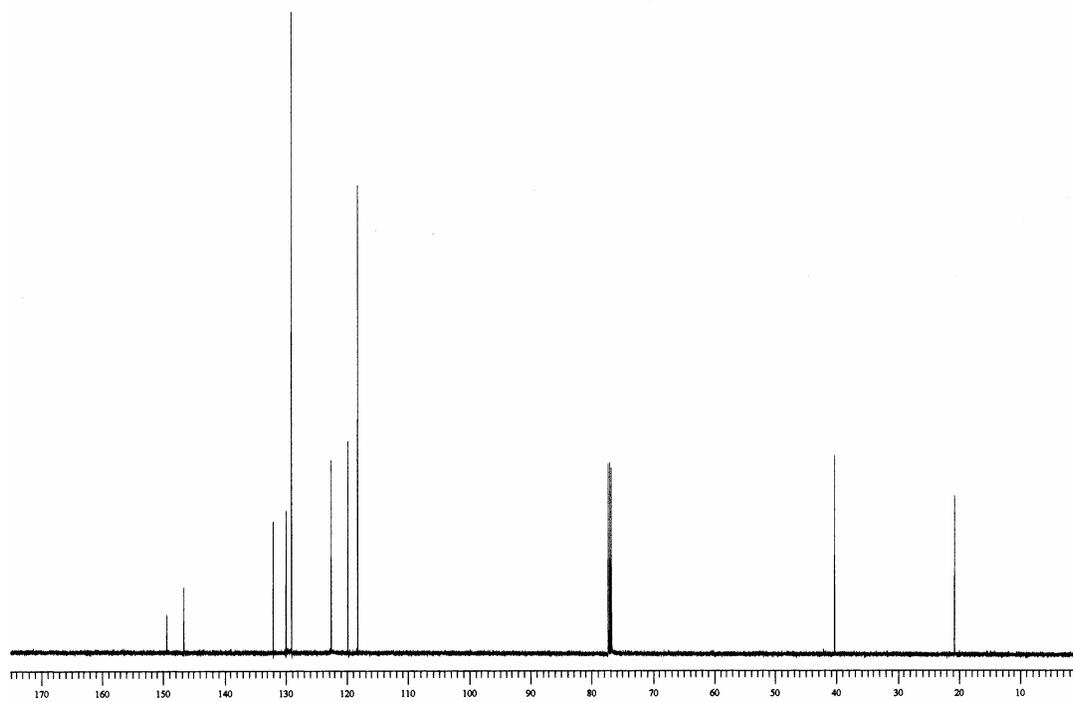


Figure S32. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-methyl-*N*-phenyl-*p*-toluidine (Table 4, entry 4).

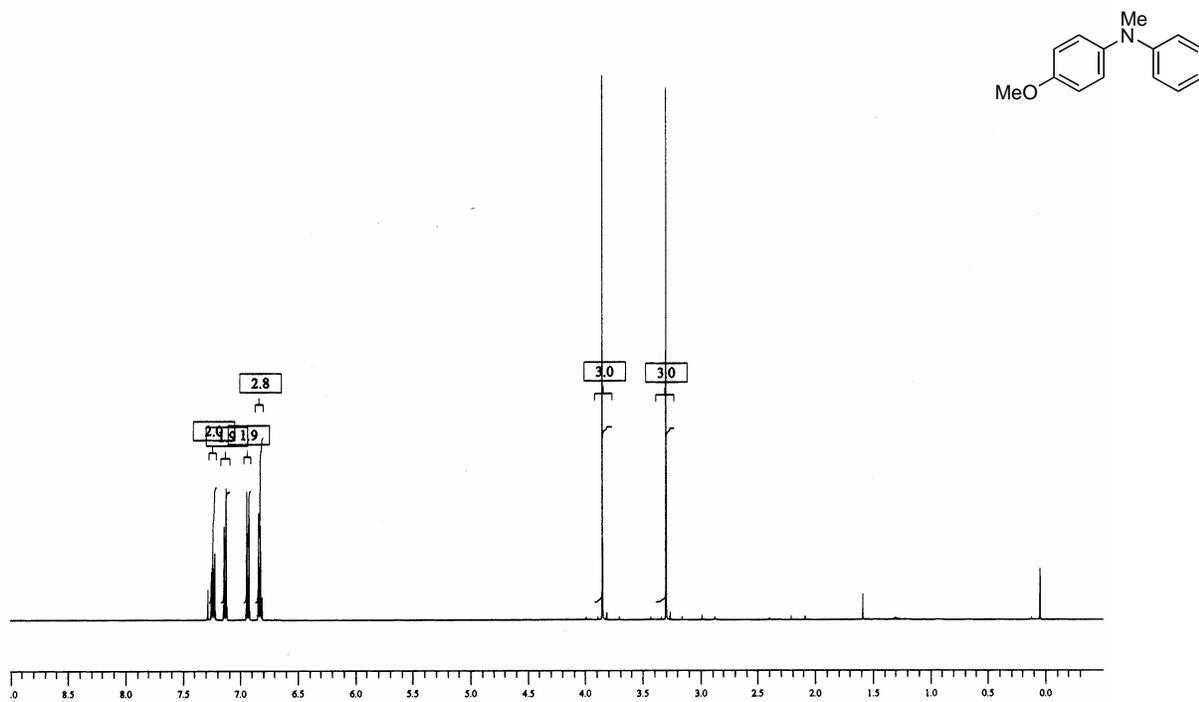


Figure S33. ¹H NMR spectrum (CDCl₃, 360 MHz) of *N*-methyl-*N*-phenyl-*p*-anisidine (Table 4, entry 5).

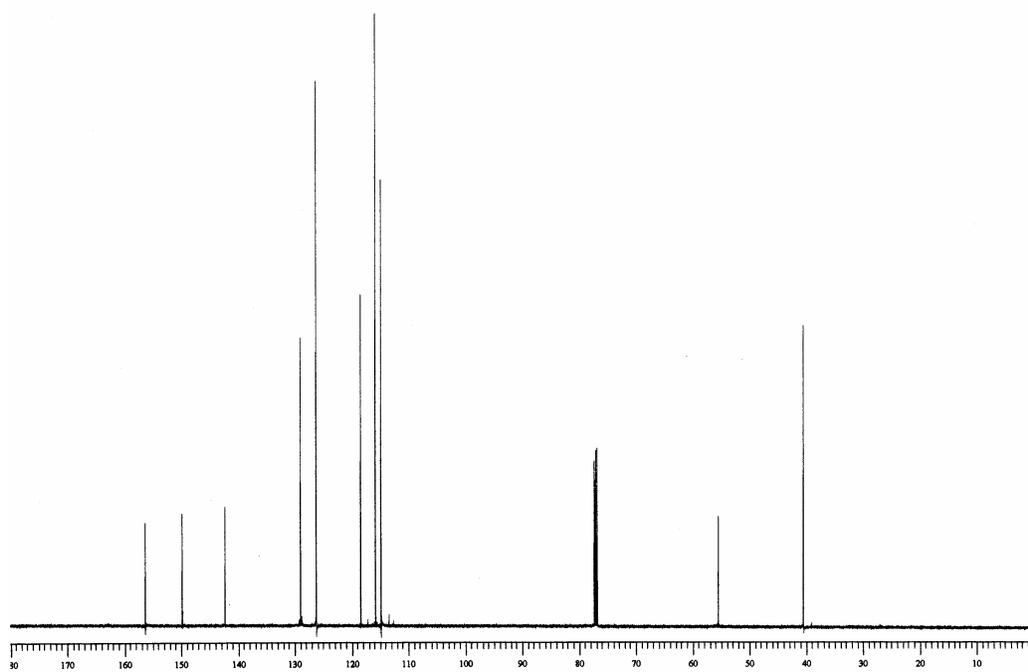


Figure S34. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-methyl-*N*-phenyl-*p*-anisidine (Table 4, entry 5).

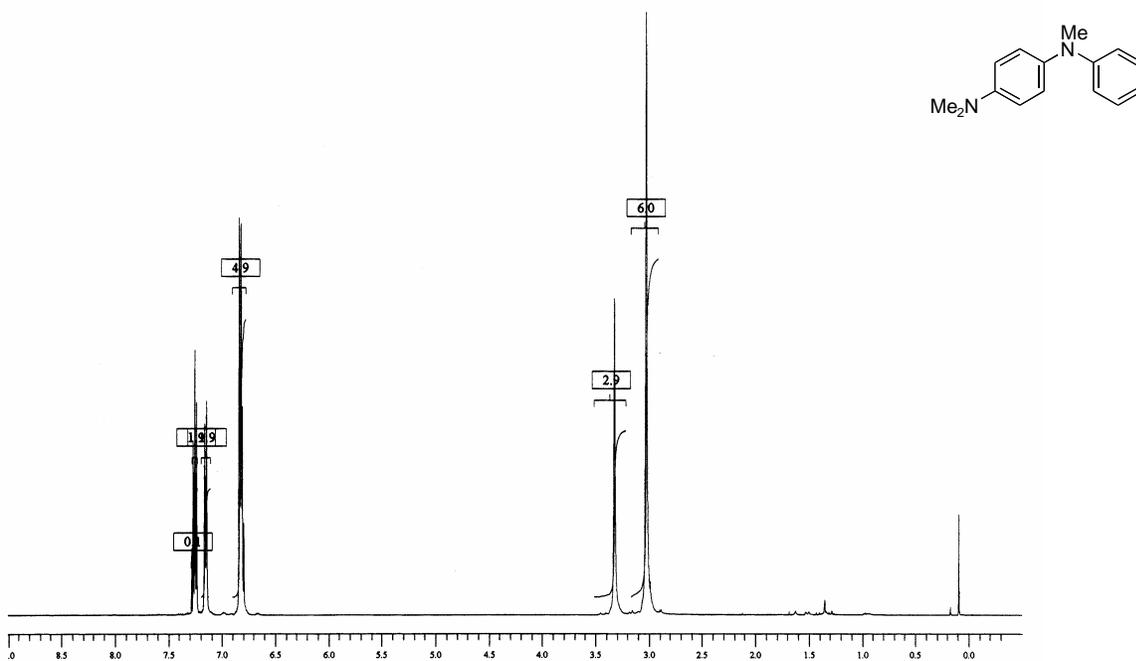


Figure S35. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N,N,N'*-trimethyl-*N'*-phenylbenzene-1,4-diamine (Table 4, entry 6).

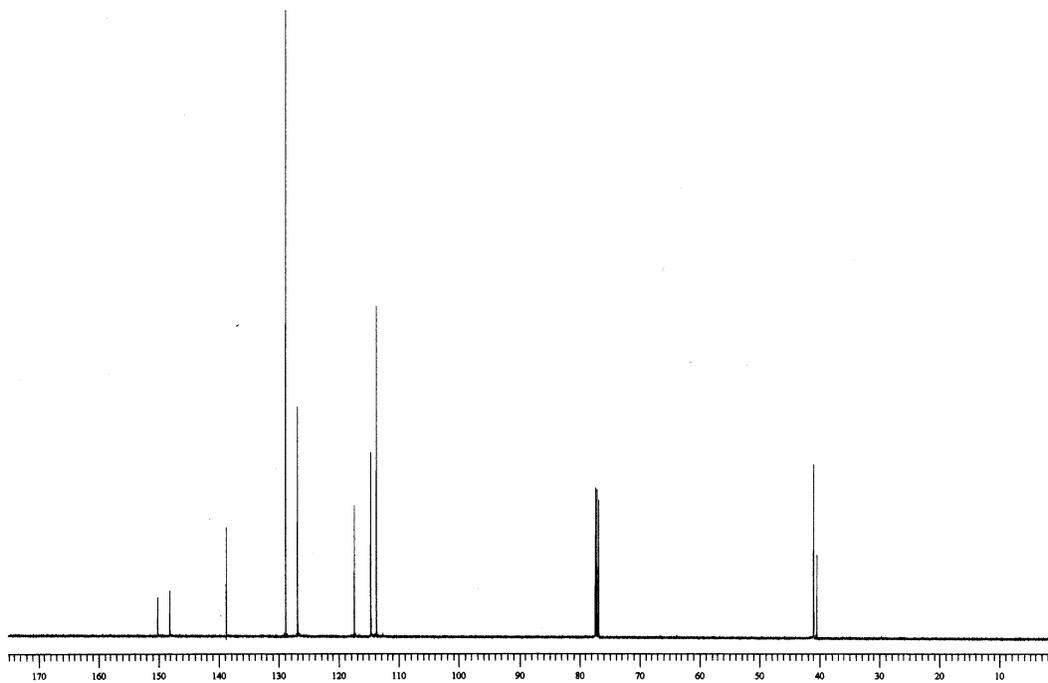


Figure S36. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N,N,N'*-trimethyl-*N'*-phenylbenzene-1,4-diamine (Table 4, entry 6).

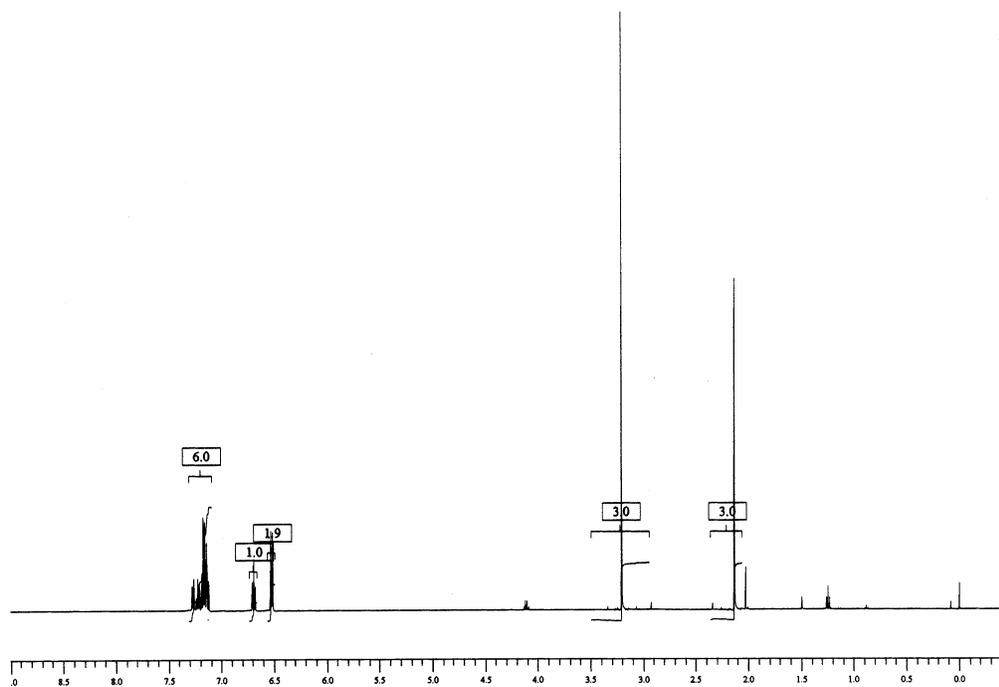
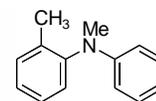


Figure S37. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-methyl-*N*-phenyl-*o*-toluidine (Table 4, entry 7).

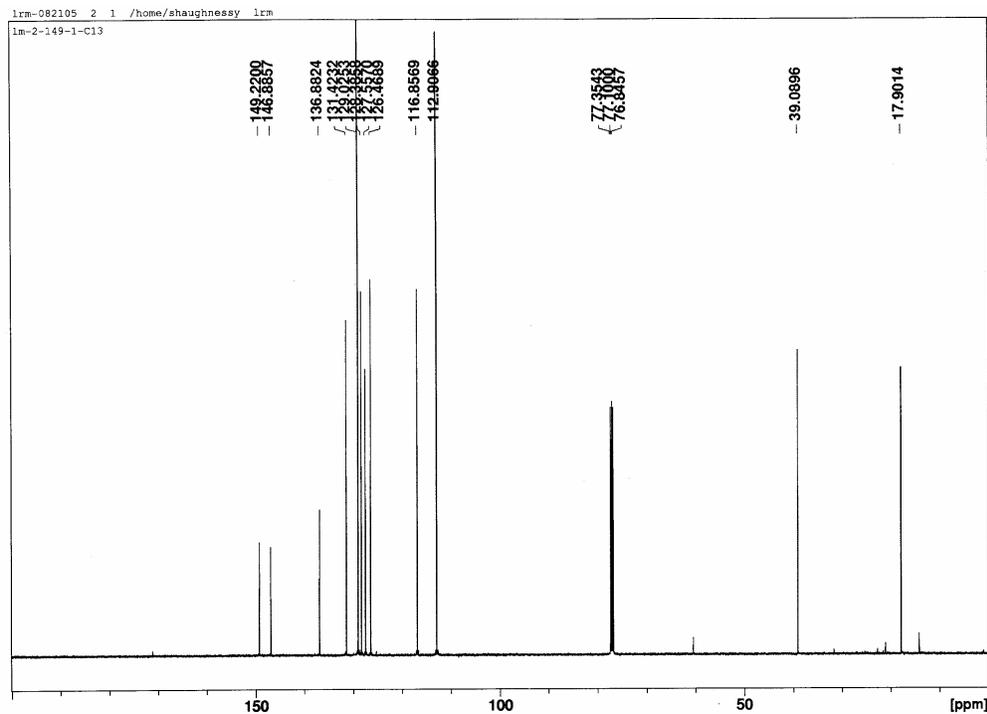


Figure S38. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-methyl-*N*-phenyl-*o*-toluidine (Table 4, entry 7).

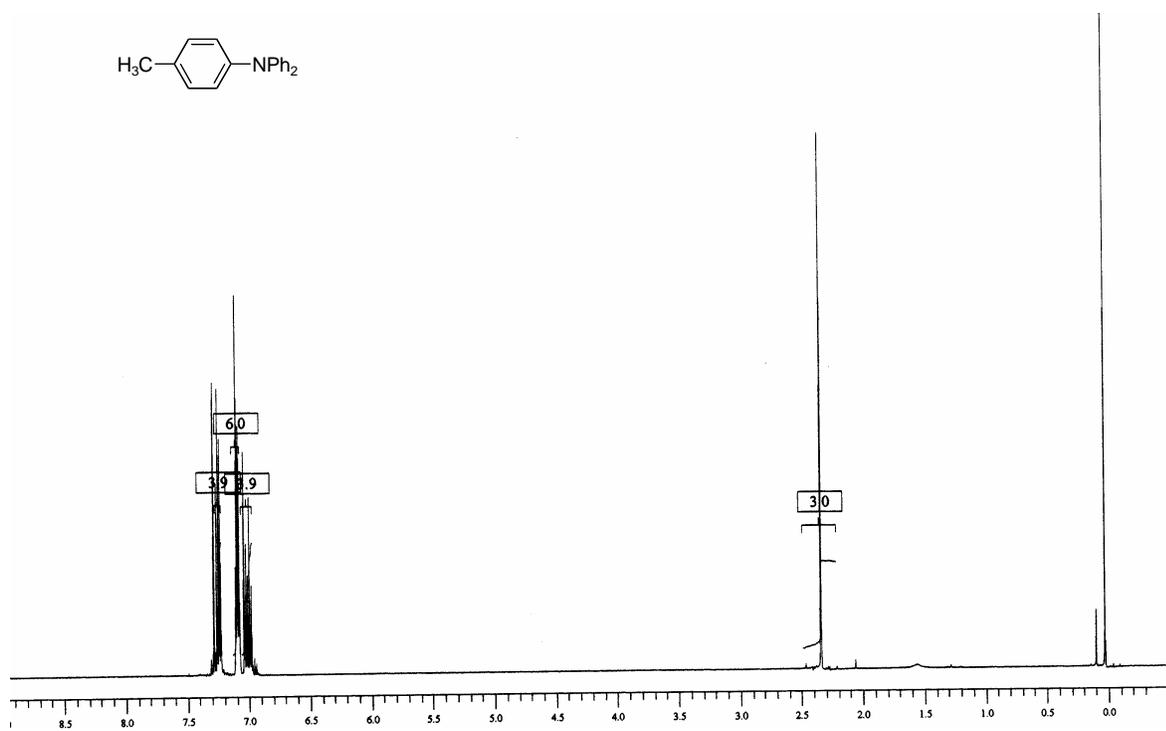


Figure S39. ¹H NMR spectrum (CDCl₃, 360 MHz) of *N,N*-diphenyl-*p*-toluidine (Table 4, entry 9).

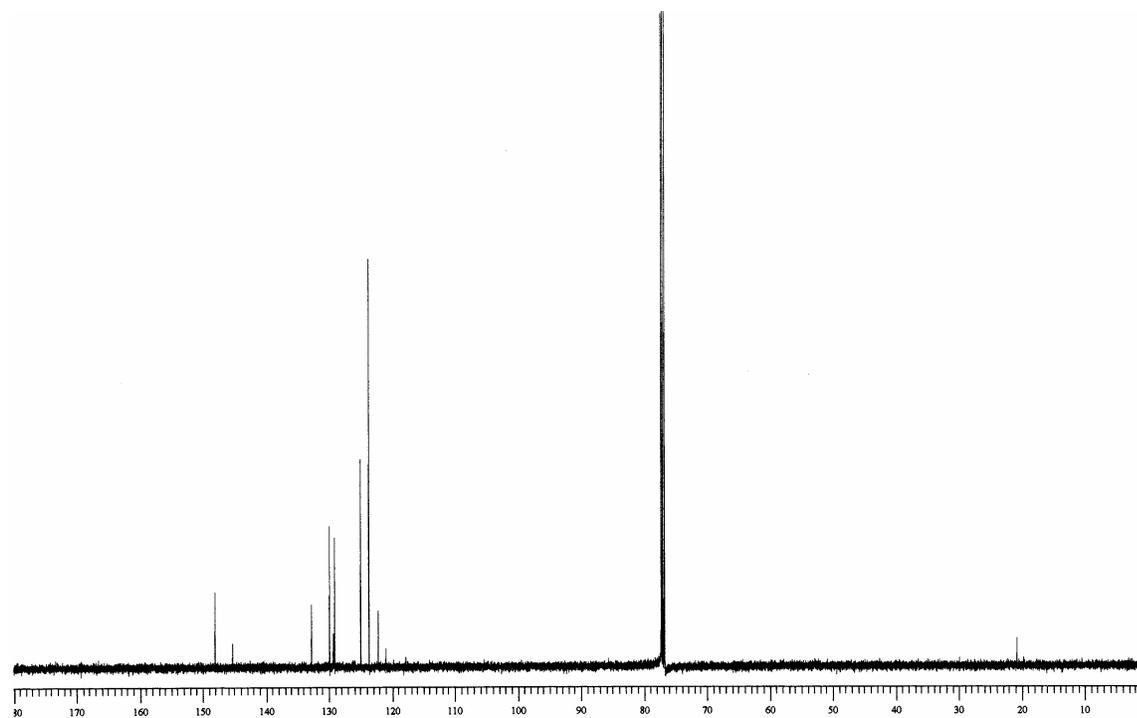


Figure S40. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N,N*-diphenyl-*p*-toluidine (Table 4, entry 9).

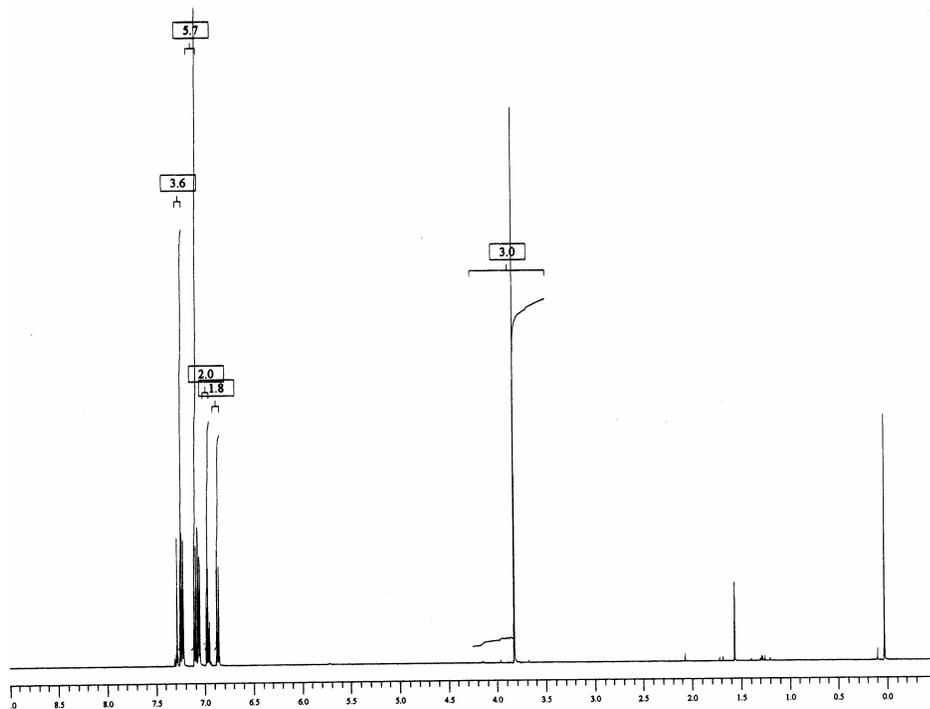


Figure S41. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N,N*-diphenyl-*p*-anisidine (Table 4, entry 10).

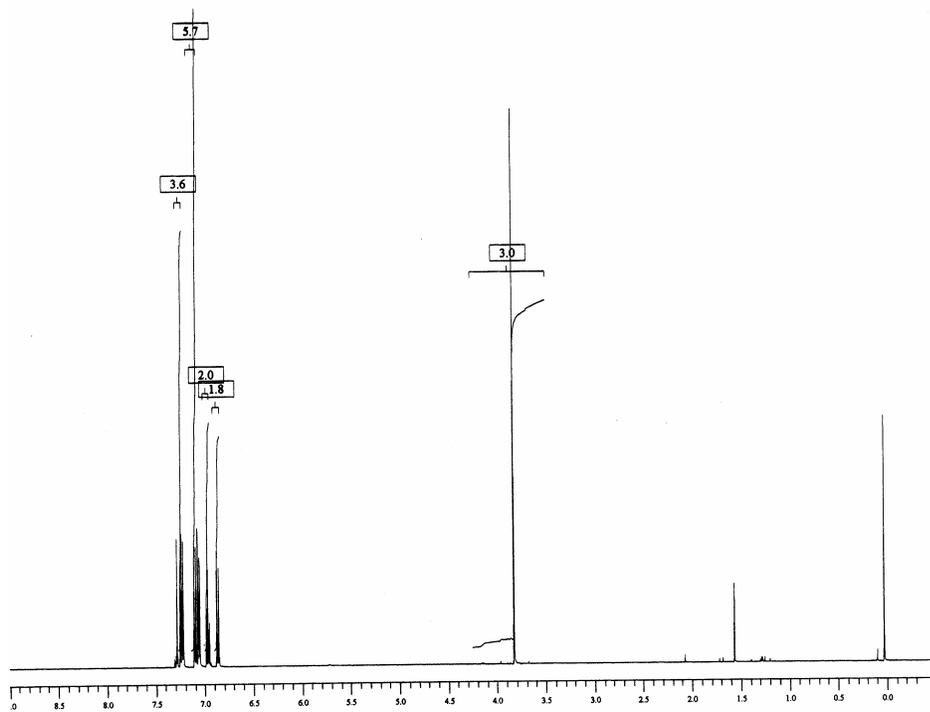


Figure S42. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N,N*-diphenyl-*p*-anisidine (Table 4, entry 10).

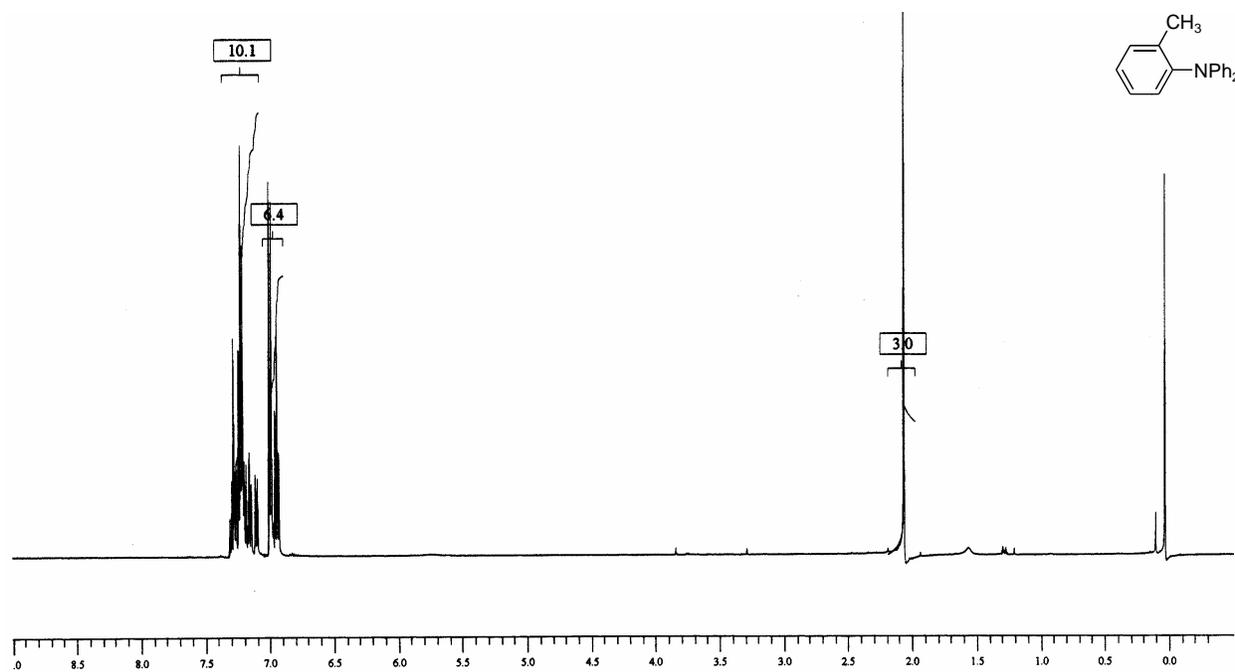


Figure S43. ¹H NMR spectrum (CDCl₃, 360 MHz) of *N,N*-diphenyl-*o*-toluidine (Table 4, entry 11).

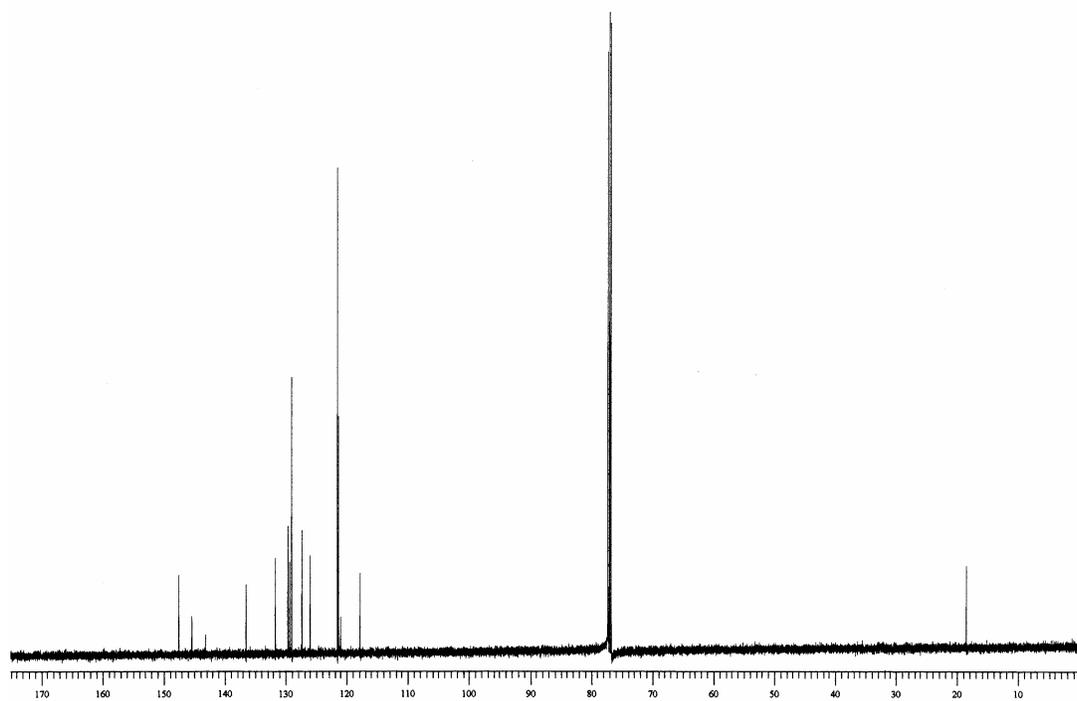


Figure S44. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N,N*-diphenyl-*o*-toluidine (Table 4, entry 11).

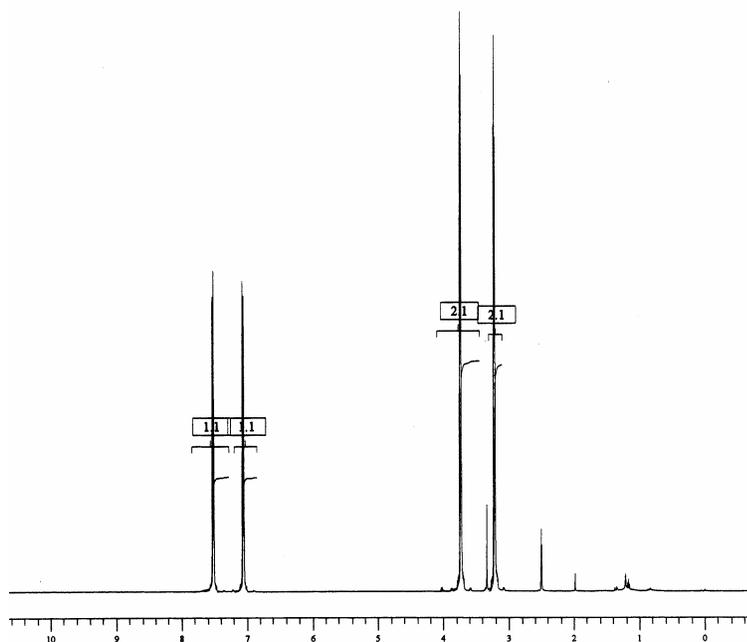
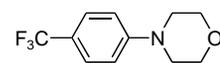


Figure S45. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-(4-trifluoromethylphenyl)morpholine (Table 5, entry 1).

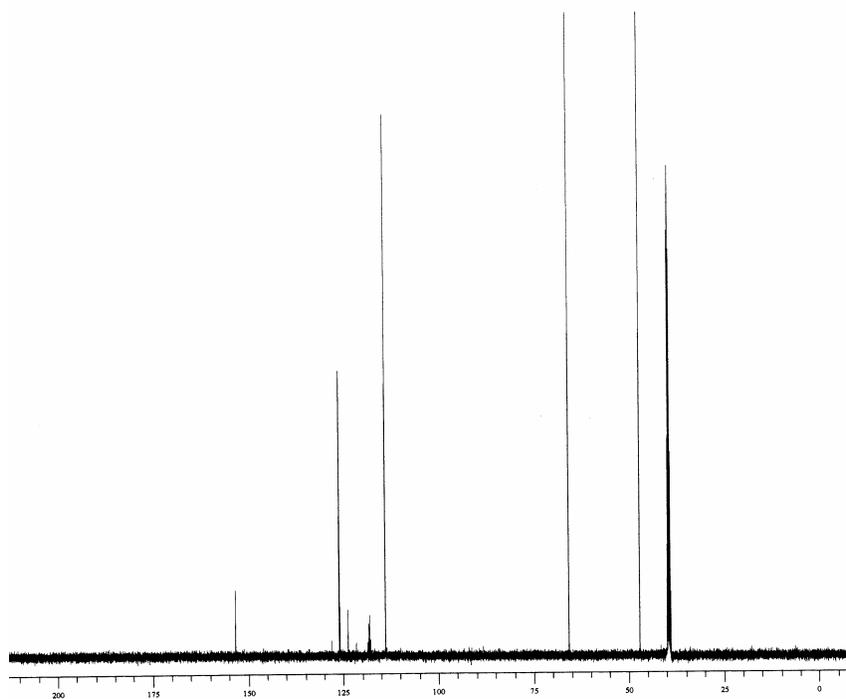


Figure S46. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-(4-trifluoromethylphenyl)morpholine (Table 5, entry 1).

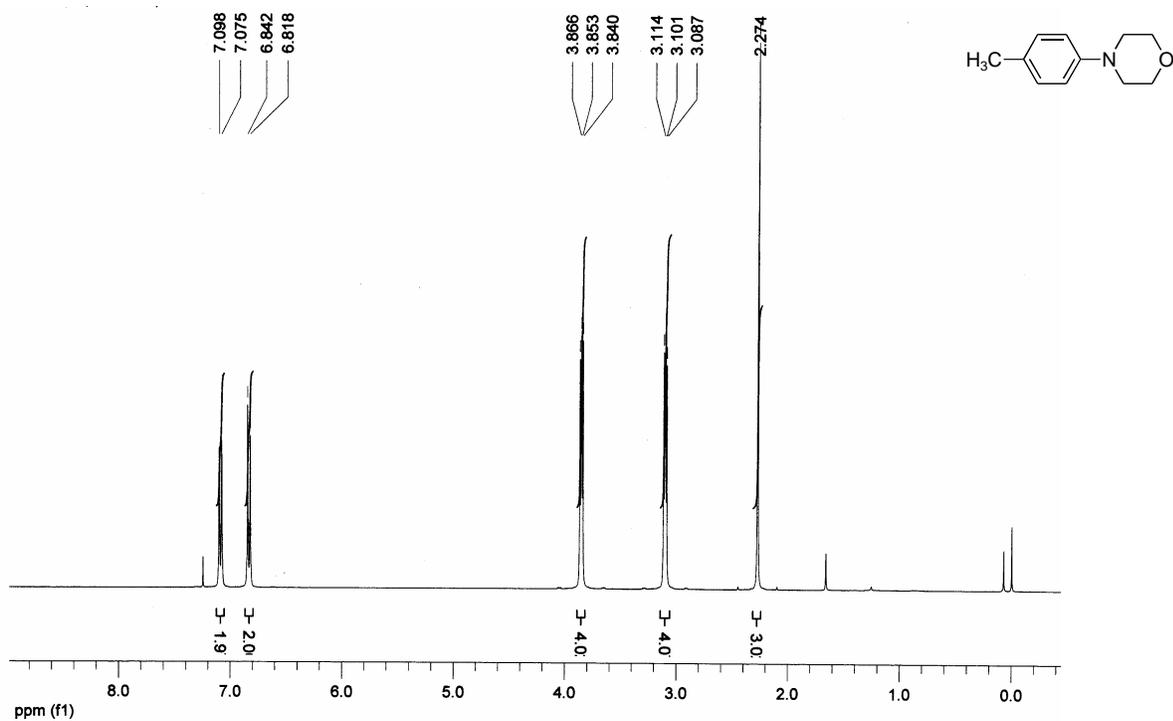


Figure S47. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-(4-methylphenyl)morpholine (Table 5, entry 2).

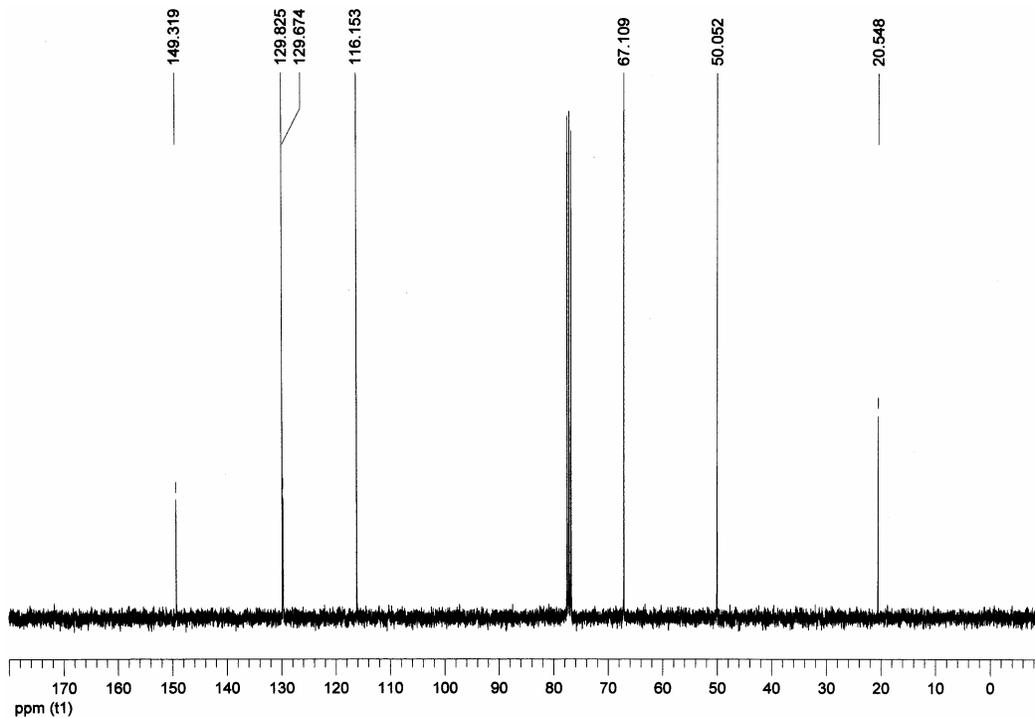


Figure S48. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-(4-methylphenyl)morpholine (Table 5, entry 2).

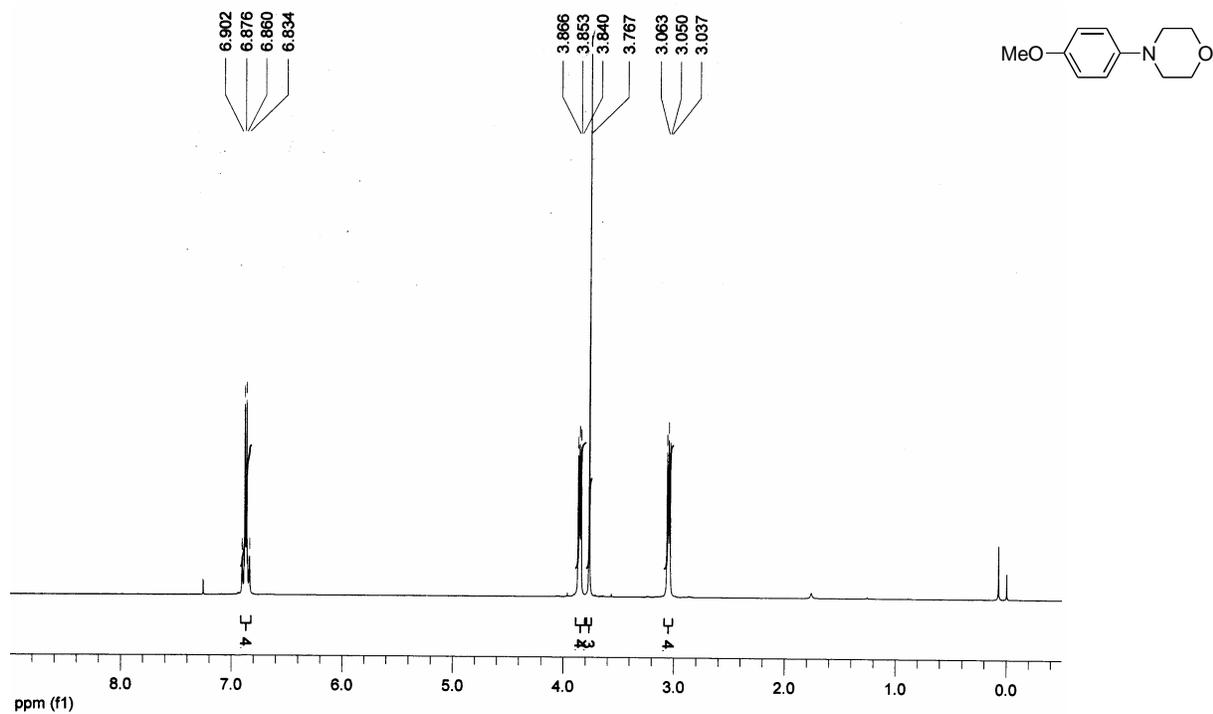


Figure S49. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-(4-methoxyphenyl)morpholine (Table 5, entry 3).

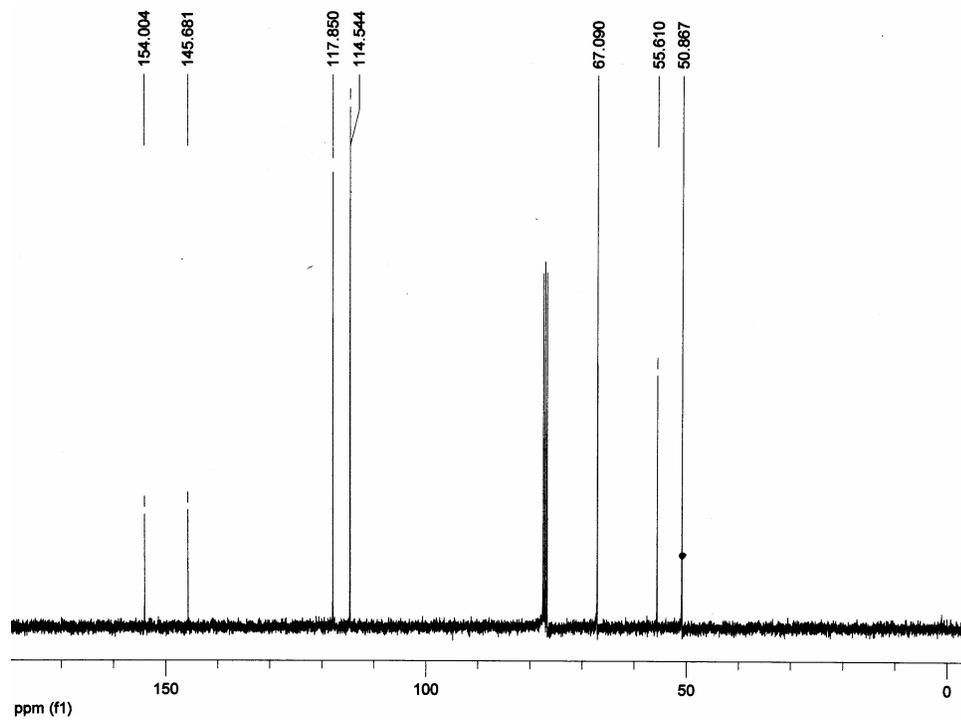


Figure S50. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-(4-methoxyphenyl)morpholine (Table 5, entry 3).

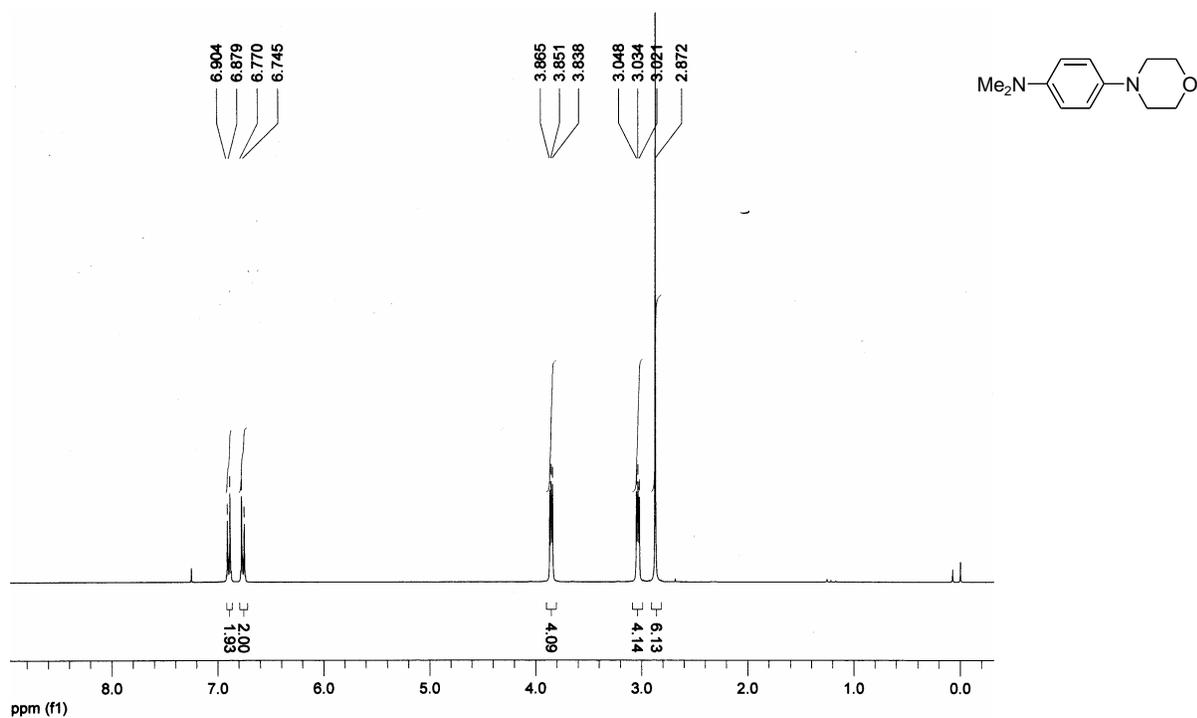


Figure S51. ¹H NMR spectrum (CDCl₃, 360 MHz) of *N*-(4-*N,N'*-dimethylamino)phenyl)morpholine (Table 5, entry 4).

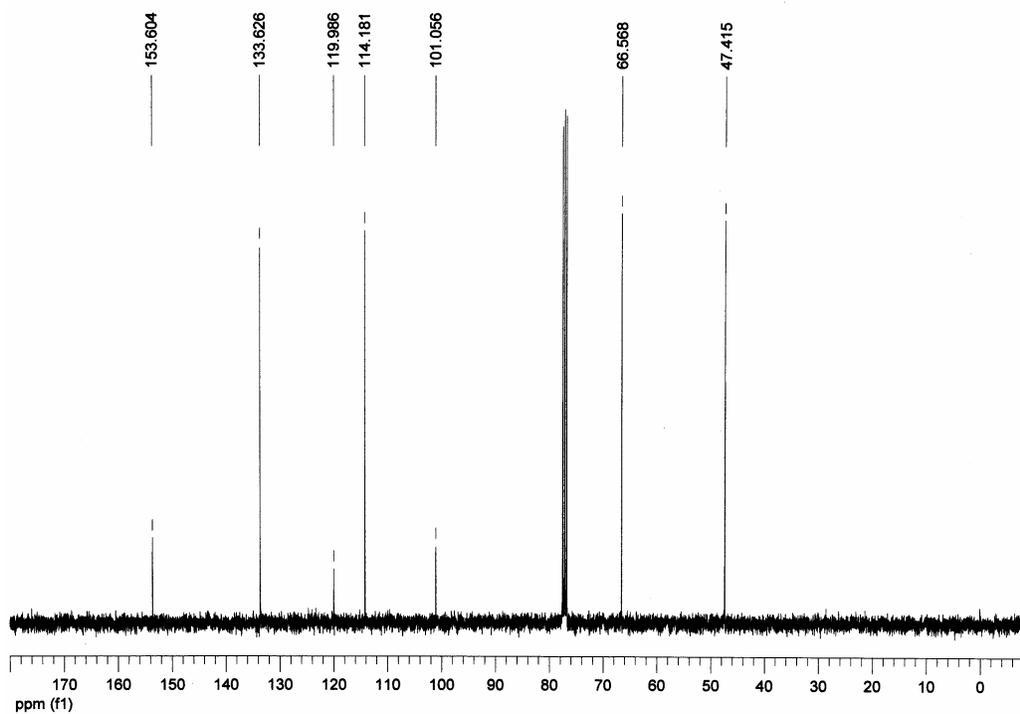


Figure S52. ¹³C NMR spectrum (CDCl₃, 90.6 MHz) of *N*-(4-*N,N'*-dimethylamino)phenyl)morpholine (Table 5, entry 4).

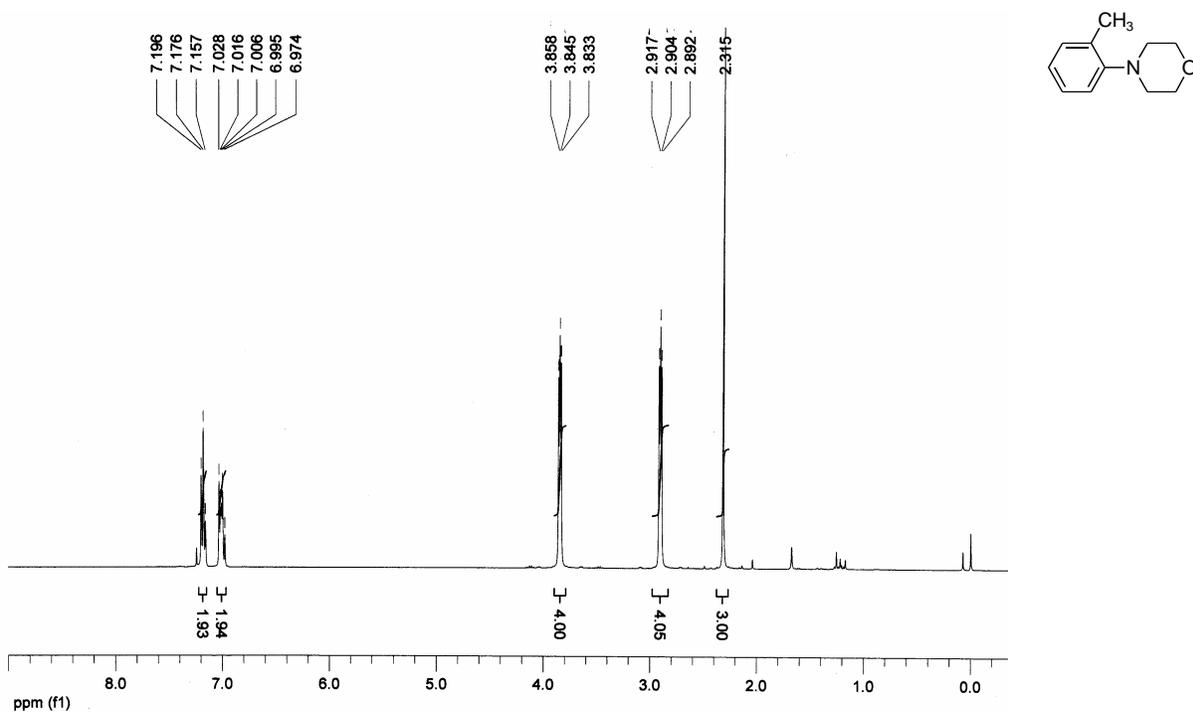


Figure S53. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-(2-methylphenyl)morpholine (Table 5, entry 5).

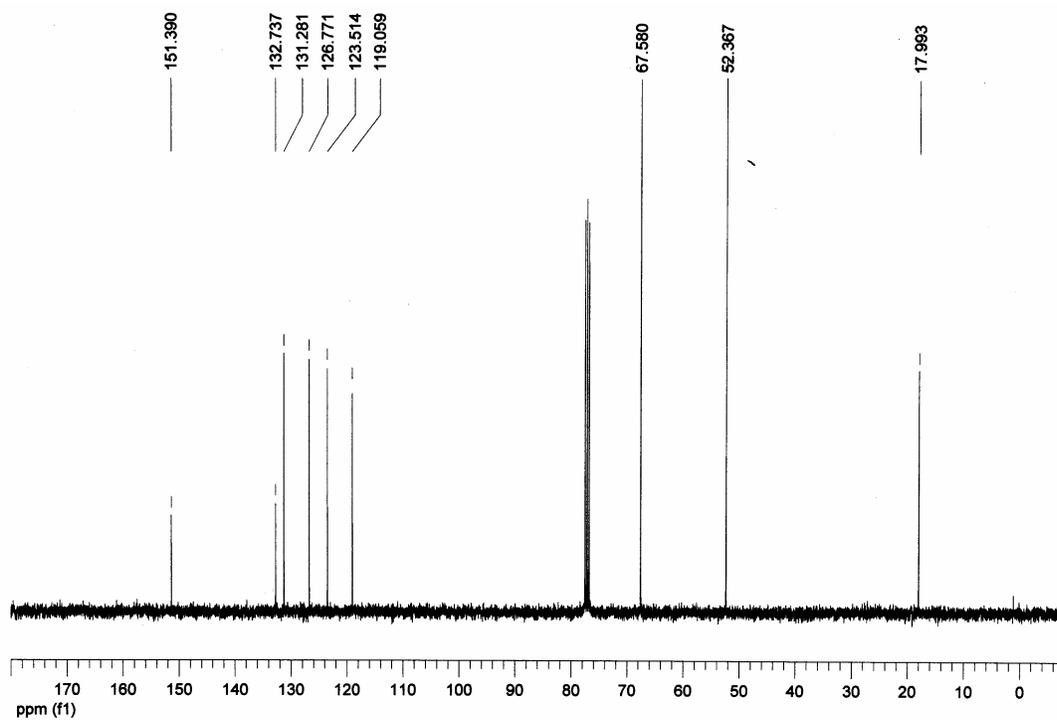


Figure S54. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-(2-methylphenyl)morpholine (Table 5, entry 5).

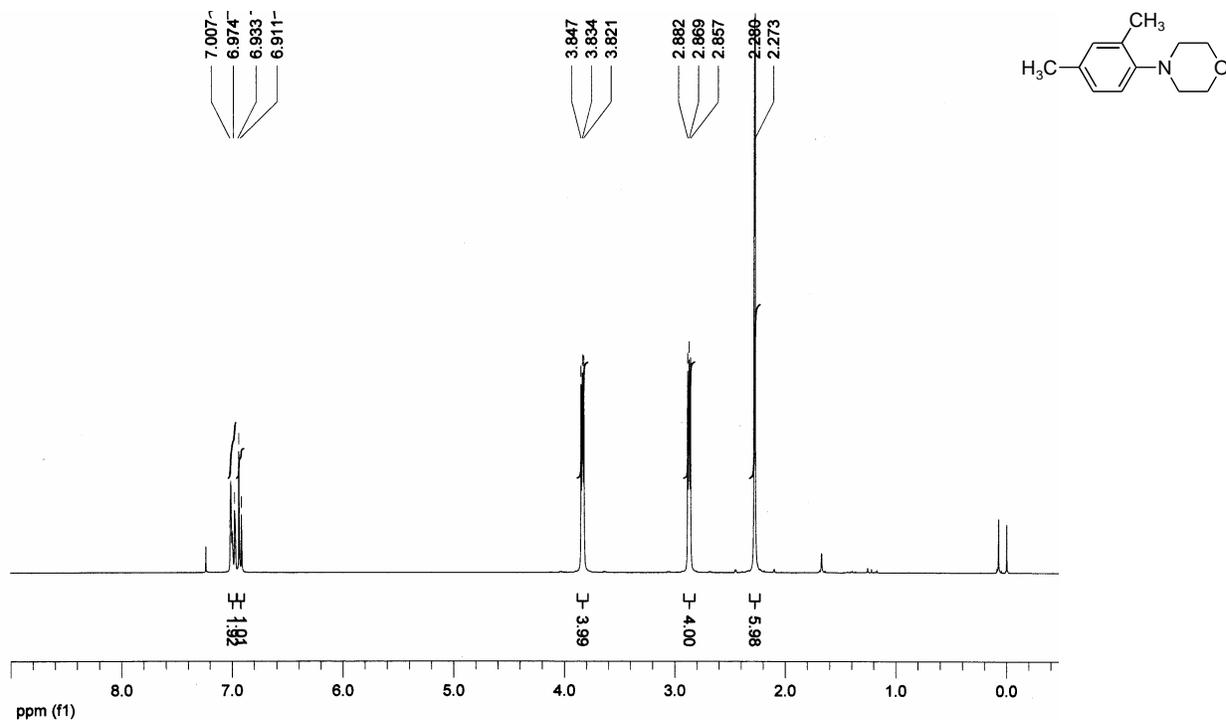


Figure S55. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-(2,4-dimethylphenyl)morpholine (Table 5, entry 6).

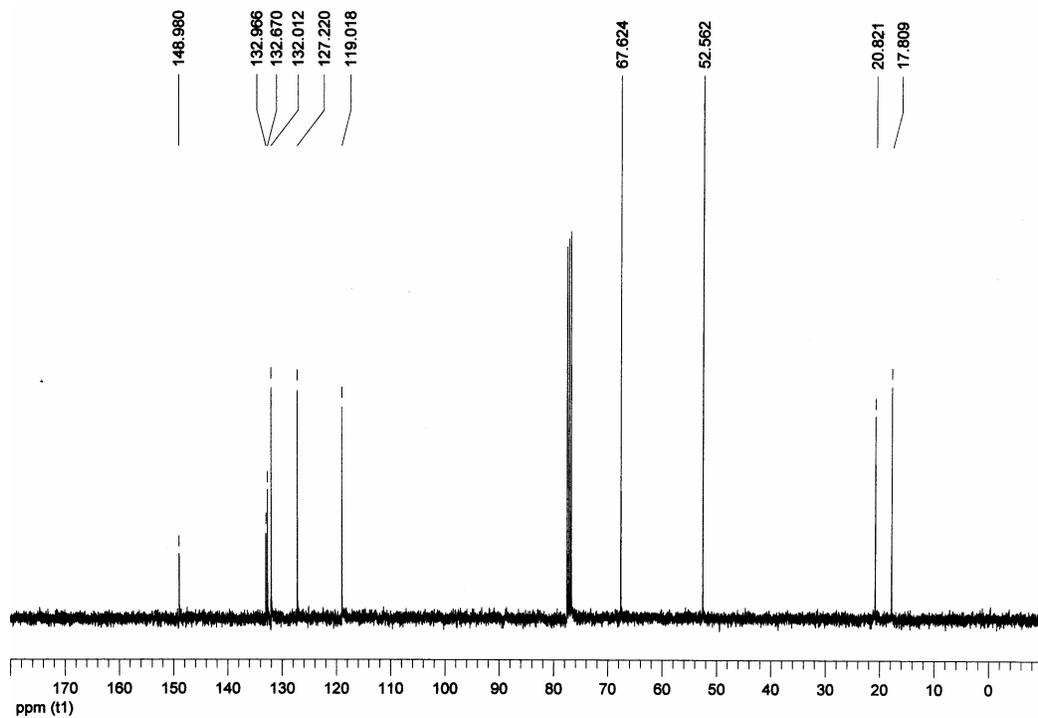


Figure S56. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-(2,4-dimethylphenyl)morpholine (Table 5, entry 6).

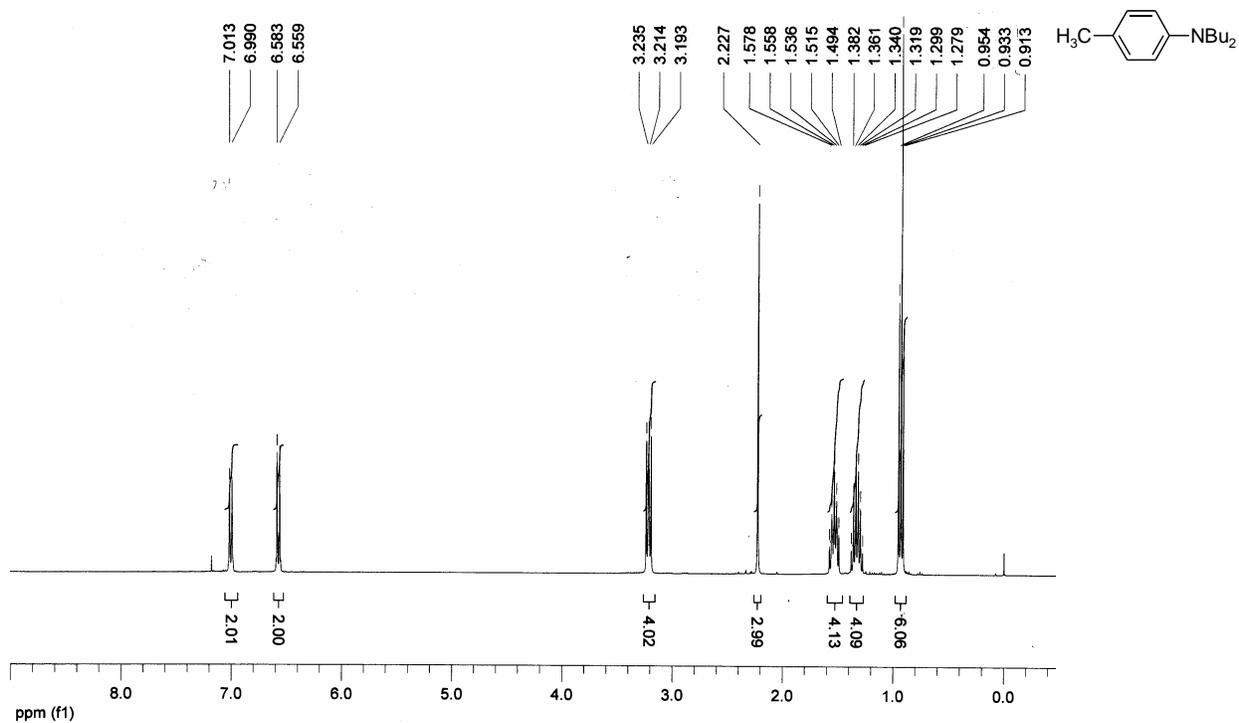


Figure S57. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N,N*-dibutyl-*p*-toluidine (Table 5, entry 7).

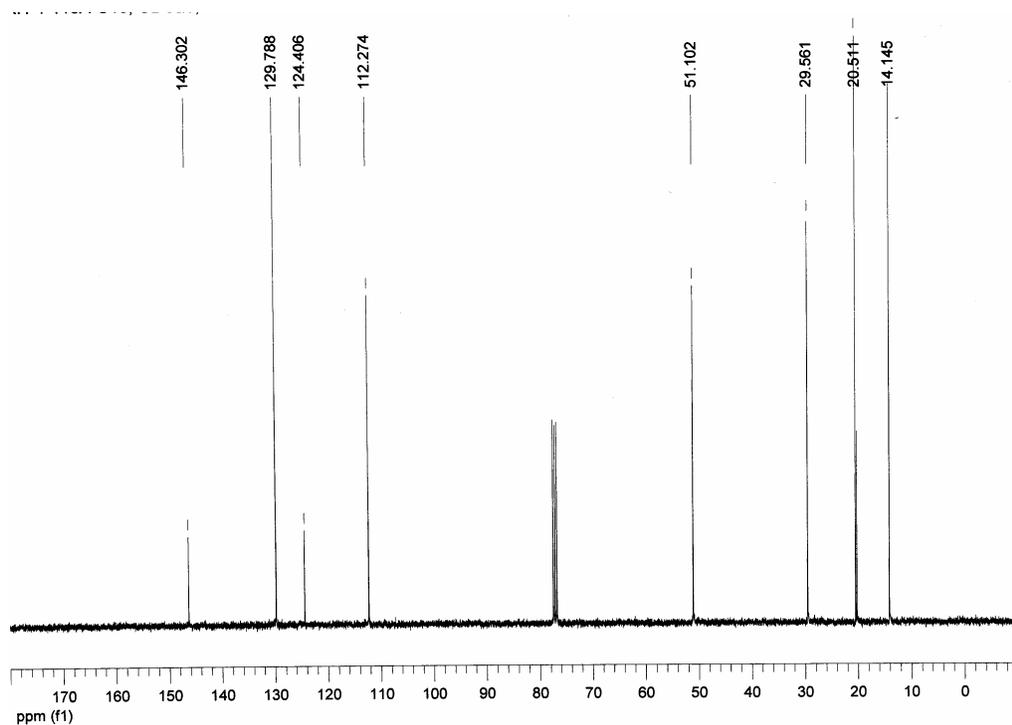


Figure S57. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N,N*-dibutyl-*p*-toluidine (Table 5, entry 7).

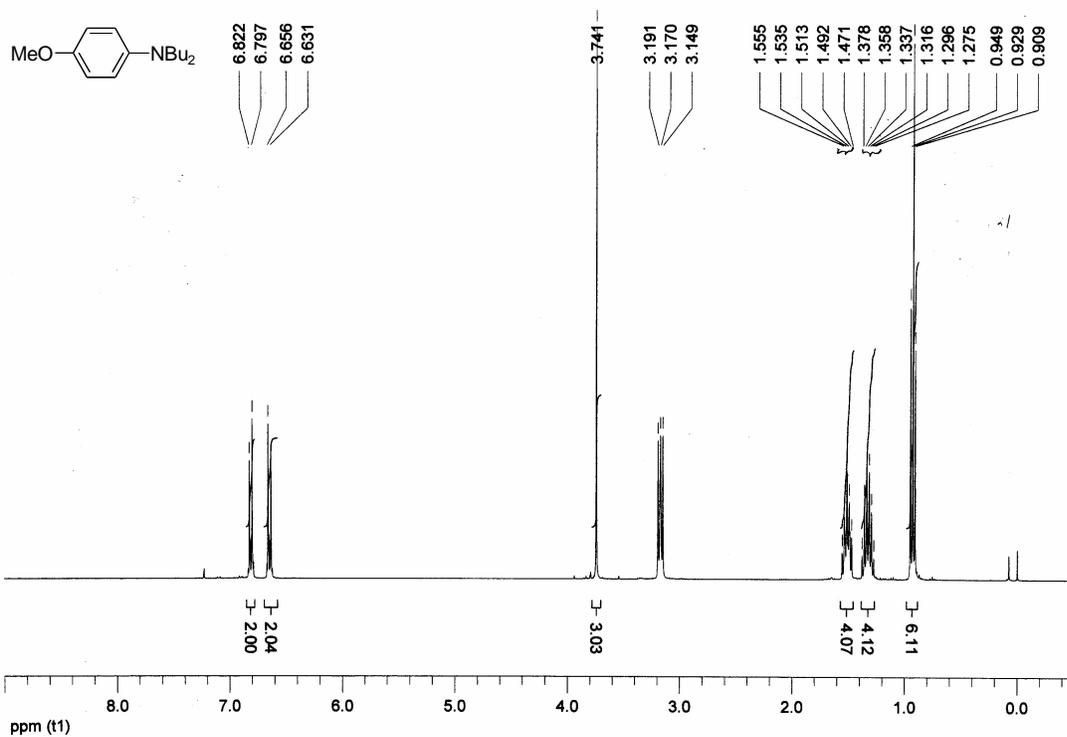


Figure S59. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N,N*-dibutyl-*p*-anisidine (Table 5, entry 8).

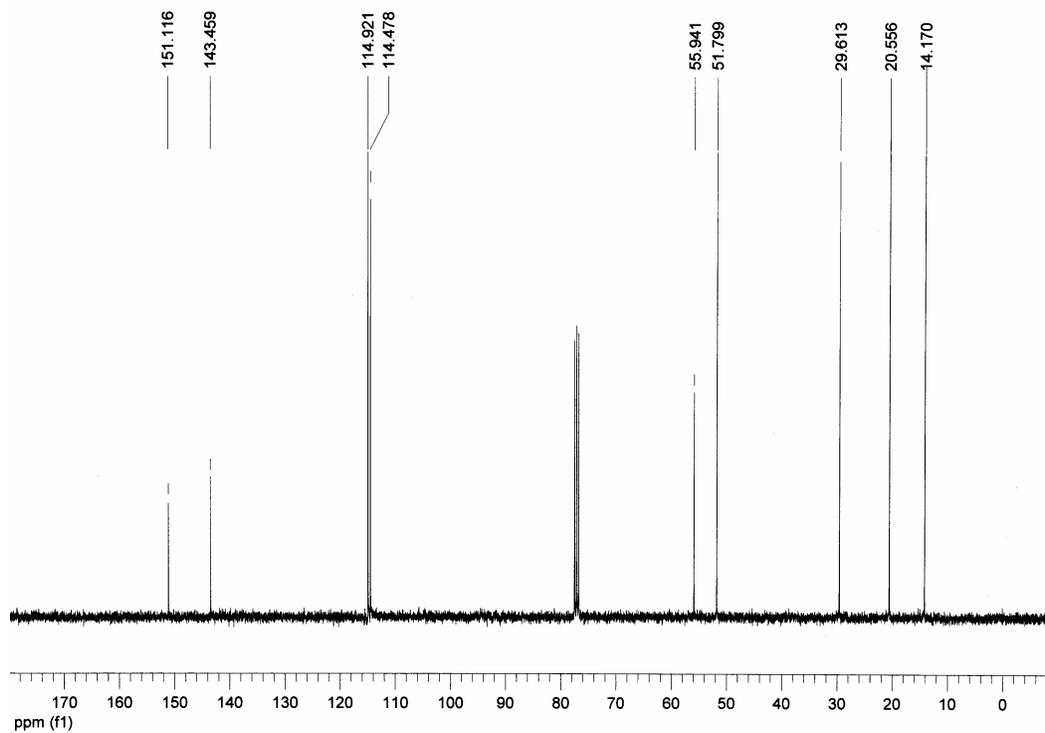


Figure S60. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N,N*-dibutyl-*p*-anisidine (Table 5, entry 7).

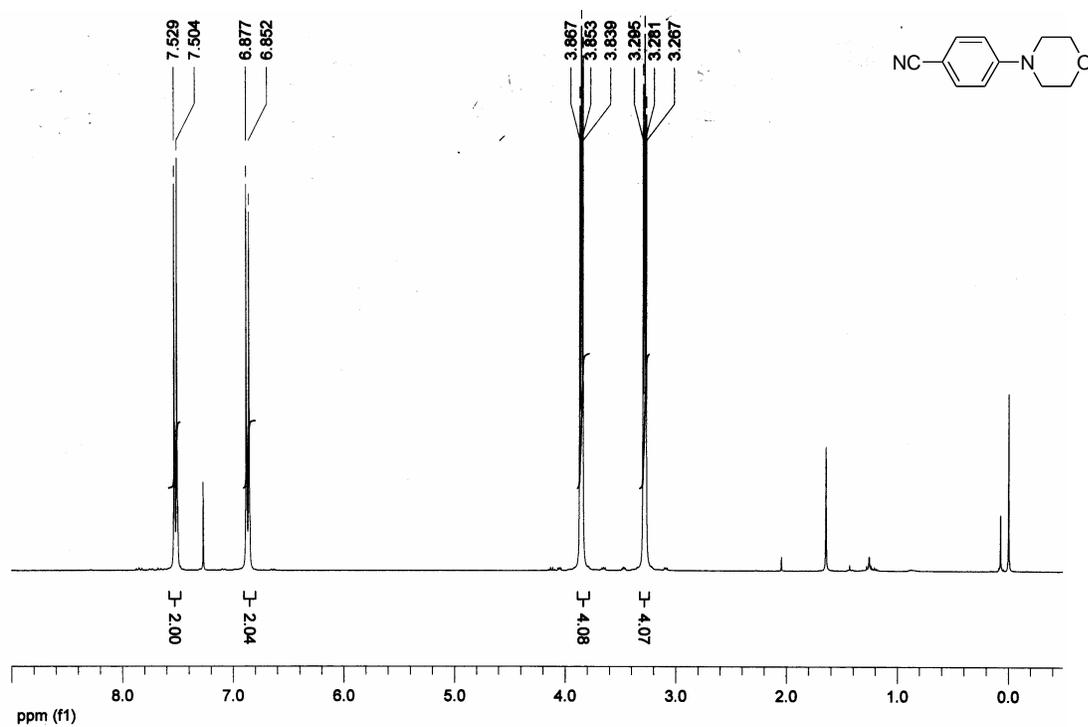


Figure S61. ^1H NMR spectrum (CDCl_3 , 360 MHz) of *N*-(4-cyanophenyl)morpholine (Table 6, entry 7).

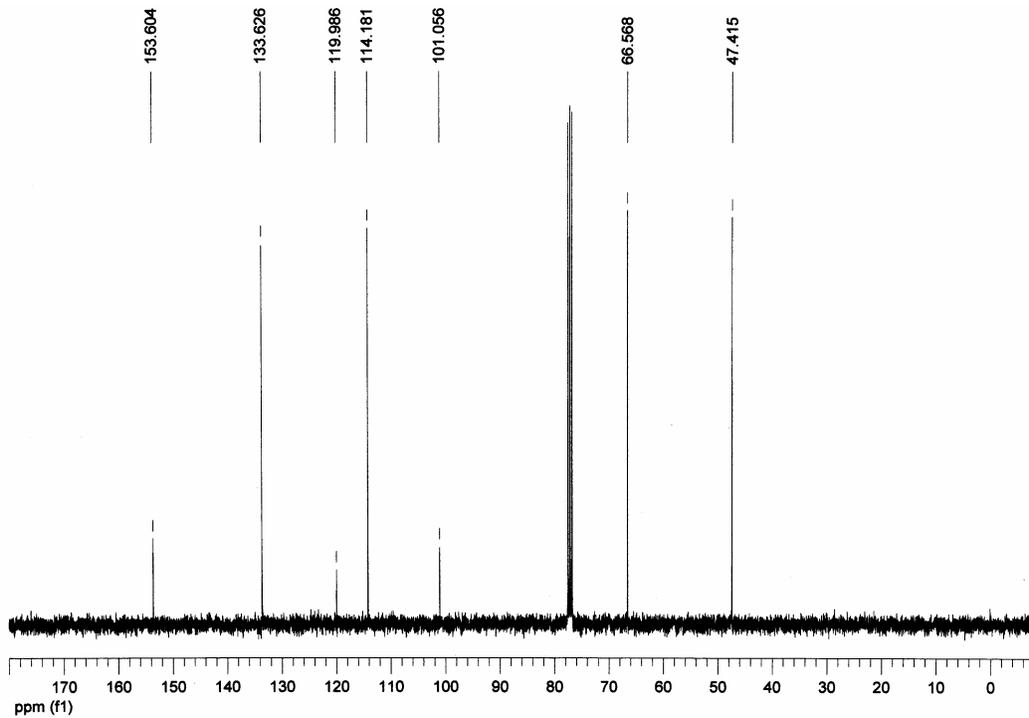


Figure S61. ^{13}C NMR spectrum (CDCl_3 , 90.6 MHz) of *N*-(4-cyanophenyl)morpholine (Table 6, entry 7).