Supporting Information

Ammonium Salts as an Inexpensive and Convenient Nitrogen Source in the Cu-Catalyzed Amination of Aryl Halides at Room Temperature

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General information: Unless otherwise stated, all commercial reagents and solvents were used as purchased without additional purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid or anisaldehyde stain followed by heating. Flash column chromatography was undertaken on silica gel (Merck Kieselgel 60 F_{254} 400-630 mesh). ^{1}H NMR was recorded on Bruker FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Brucker FT AM 400 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell on Bruker EQUINOX 55. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. Melting point was measured by Barnstead Electrothermal.

General procedure for Table 1: A mixture of 4'-iodoacetophenone (0.5 mmol), NH_4Cl (0.5 mmol), copper (0.05 mmol), ligand (0.1 mmol) and K_2CO_3 (3 mmol) in 1 mL of solvent in a flame-dried flask was allowed to react at the indicated temperature under argon atmosphere. After the reaction was completed monitored by TLC, the mixture was partitioned between ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with

ethyl acetate twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with EtOAc/Hx (1:1) to afford the desired product.

Reaction profile for the CuI/proline-catalyzed C-N cross coupling of aryl halides with either NH_4Cl or aqueous NH_3. A mixture of 4'-iodoacetophenone (0.5 mmol), NH_4Cl (0.5 mmol) or aqueous NH_3 (28 %, 0.5 mmol), CuI (0.1 mmol), L-proline (0.2 mmol) and 1.5 mmol of K_2CO_3 in DMSO (1 mL, and 0.034 mL of H_2O when NH_4Cl was employed) was stirred at room temperature. An aliquot was taken over time from the reaction mixture, and conversion and yield of the reaction were monitored by ^1H NMR using an internal standard (1,1,2,2-tetrachloroethane) in the period of 15 min, 30 min, 1 h, 2 h, 4 h, 6 h, 8 h and 12 h. The results are presented in the below figure (Figure S1).

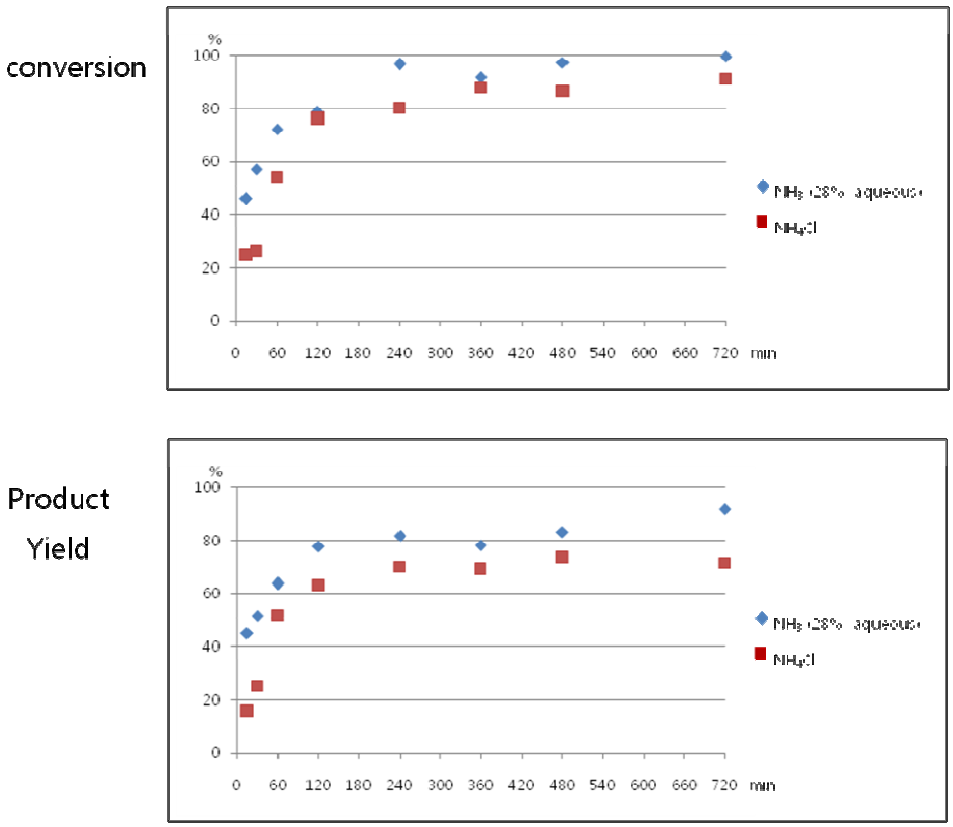
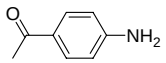


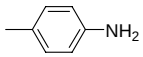
Figure S1 Conversion and product yield in the CuI/proline-catalyzed reactions of 4'-iodoacetophenone with either NH_4Cl or aqueous NH_3 solution

General procedure for the CuI/proline-catalyzed C-N cross coupling of aryl halides with NH_4Cl or aqueous NH_3 solution (Table 2-4). A mixture of aryl halide (0.5 mmol), NH_4Cl

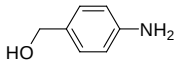
(0.65 mmol) or aqueous NH_3 (28%, 0.75 mmol), CuI (0.1 mmol), L-proline (0.2 mmol) and 1.5 mmol of K_2CO_3 in 1 mL of DMSO (0.05 mL of H_2O was added when NH_4Cl was employed) was stirred under argon atmosphere at room temperature (in case of aryl bromides, at the reaction temperature was 80 ^oC) After the reaction was completed monitored by TLC, the mixture was partitioned between ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residual oil was loaded on a silica gel column and eluted with ethyl acetate/hexane to afford the product. All products obtained herein are known compounds, and melting point, ^1H NMR, ^{13}C NMR and IR data are presented below.



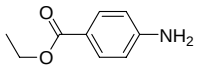
4-Aminoacetophenone[1] **(Table 1):** brown solid; m.p. 105–106 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 4.15 (br, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 151.1, 130.7, 127.8, 113.7, 26.0; IR (NaCl) ν 3396, 3336, 3226, 1651, 1600 cm^{-1}.



4-Aminotoluene[2] **(entry 1, Table 2):** black solid; m.p. 42–43 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.1 Hz, 2H), 6.60 (d, *J* = 8.3 Hz, 2H), 3.47 (br, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 129.7, 127.7, 115.2, 20.4; IR (NaCl) ν 3417, 3337, 3222, 2921, 1623, 1516 cm^{-1}.

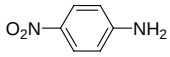


4-Aminobenzylalcohol[3] **(entry 2, Table 2):** brown solid; m.p. 62–63 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 8.3 Hz, 2H), 4.50 (s, 2H), 3.25 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 131.0, 128.7, 115.1, 65.1; IR (NaCl) ν 3582, 3333, 3227, 2924, 1613 cm^{-1}.

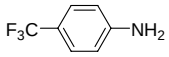


Ethyl 4-aminobenzoate[2] **(entry 4, Table 2):** white solid; m.p. 89–90 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.07 (s,

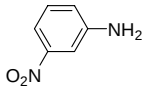
2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 150.8, 131.5, 119.9, 113.7, 60.2, 14.4; IR (NaCl) ν 3422, 3342, 1685, 1281 cm^{-1}.



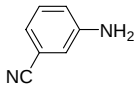
4-Nitroaniline[2] **(entry 5, Table 2):** bright yellow solid; m.p. 145–146 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.0 Hz, 2H), 6.61 (d, J = 6.9 Hz, 2H), 4.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 139.2, 126.3, 113.4; IR (NaCl) ν 3585, 3481, 3363, 1627, 1477, 1354 cm^{-1}.



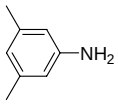
4-Trifluoromethylaniline[2] **(entry 6, Table 2):** brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 3.92 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 126.7 (q, J_3 = 3.8 Hz), 124.8 (q, J_1 = 268.7 Hz), 119.9 (q, J_2 = 32.6 Hz), 114.1; IR (NaCl) ν 2923, 2853, 1618, 1323 cm^{-1}.



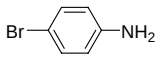
3-Nitroaniline[2] **(entry 7, Table 2):** yellow solid; m.p. 112–113 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.1, 2.0 Hz 1H), 7.46 (t, J = 2.2 Hz, 1H), 7.26 (t, J = 8.1 Hz, 1H), 6.92 (dd, J = 8.0, 2.3 Hz 1H), 3.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 147.4, 129.9, 120.6, 113.1, 109.0; IR (NaCl) ν 3433, 3327, 1624, 1483, 1349 cm^{-1}.



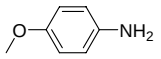
3-Aminobenzonitrile[2] **(entry 8, Table 2):** yellow solid; m.p. 52–53 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 6.87 (s, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 130.0, 121.8, 119.2 119.1, 117.3, 112.7; IR (NaCl) ν 3465, 3373, 3227, 2229, 1602 cm^{-1}.



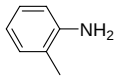
3,5-Dimethylaniline[4] **(entry 9, Table 2):** brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 6.35 (s, 2H), 3.55 (br, 2H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 138.9, 120.3, 113.0, 21.2; IR (NaCl) ν 3554, 3440, 3353, 2919, 1619, 1478 cm^{-1}.



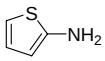
4-Bromoaniline[5] **(entry 10, Table 2):** yellow solid; m.p. 61–62 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.7 Hz, 2H), 3.57 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 131.9, 116.7, 110.1; IR (NaCl) ν 3475, 3383, 1614 cm^{-1}.



4-Aminoanisole[2] **(entry 11, Table 2):** dark brown solid; m.p. 56–57 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 6.6 Hz, 2H), 6.63 (d, *J* = 6.6 Hz, 2H), 3.73 (s, 3H), 3.40 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 139.9, 116.4, 114.8, 55.7; IR (NaCl) ν 3385, 3310, 3215, 2836, 1235 cm^{-1}.

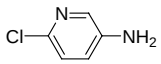


2-Aminotoluene[6] **(entry 12, Table 2):** brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.4 Hz, 2H), 6.82 (t, *J* = 7.0 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 3.63 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 130.2, 126.8, 122.1, 118.4, 114.7, 17.1; IR (NaCl) ν 3449, 3364, 3218, 2972, 1620 cm^{-1}.

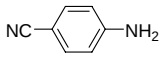


2-Aminothiophene[7] **(entry 1, Table 4):** brown liquid; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.53 (dd, *J* = 2.8, 1.7 Hz, 1H), 6.31 (dd, *J* = 2.8, 0.7 Hz, 1H), 5.85 (dd, *J* = 1.7, 0.7 Hz, 1H), 5.38 (br, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 152.0, 124.1, 106.8, 102.1; IR (NaCl) ν 3448, 1647 cm^{-1}.

3-Aminothiophene[7] **(entry 3, Table 4):** black solid; m.p. 75–76 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 5.1, 3.1 Hz, 1H), 6.63 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.15 (dd, *J* = 3.1, 1.5 Hz, 1H), 3.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 125.3, 121.1, 100.2; IR (NaCl) ν 2922, 2853, 1609 cm^{-1}.



5-Amino-2-chloropyridin[7] **(entry 5, Table 4):** brown solid; m.p. 81–82 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.9 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.90 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 139.6, 136.0, 124.7, 124.0; IR (NaCl) ν 3316, 3197, 1573, 1466, 1412 cm^{-1}.



4-Aminobenzonitile[2] **(entry 7, Table 4):** yellow solid; m.p. 85–86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.8 Hz, 2H), 6.62 (d, *J* = 6.8 Hz, 2H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 133.7, 120.1, 114.4, 100.1; IR (NaCl) ν 3478, 3374, 3214, 2218, 1603 cm^{-1}.

References

1 (*a*) D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.*, 1964, **29**, 3252. (*b*) A. A. Trabanco, J. A. Vega and M. A. Ferna´ndez, *J. Org. Chem.*, 2007, **72**, 8146.

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7 These products are commercially available and the obtained analytical data were identical to the those of the commercial compounds.

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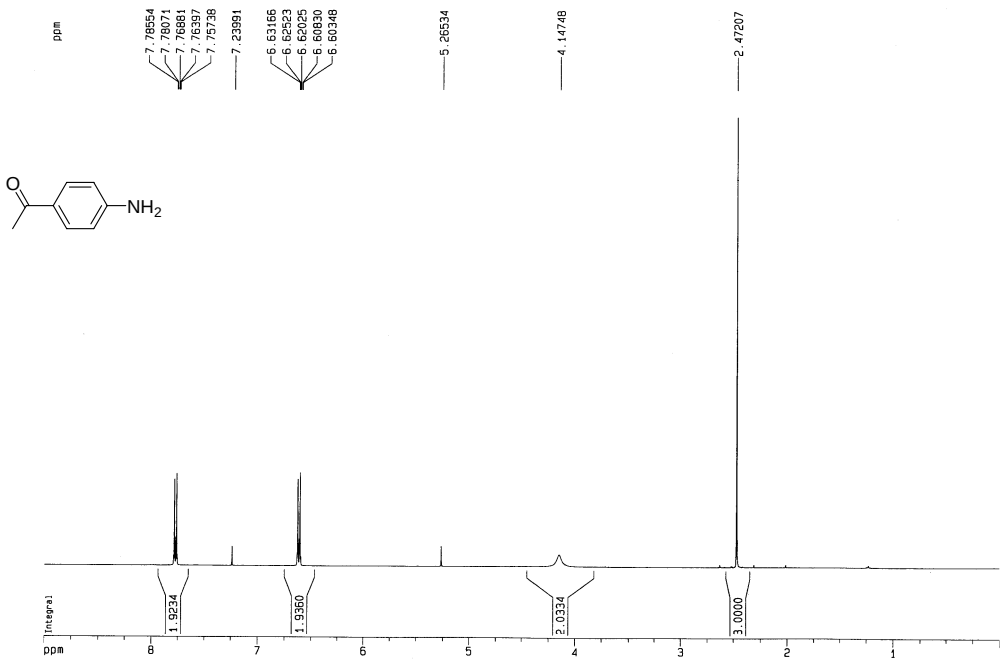
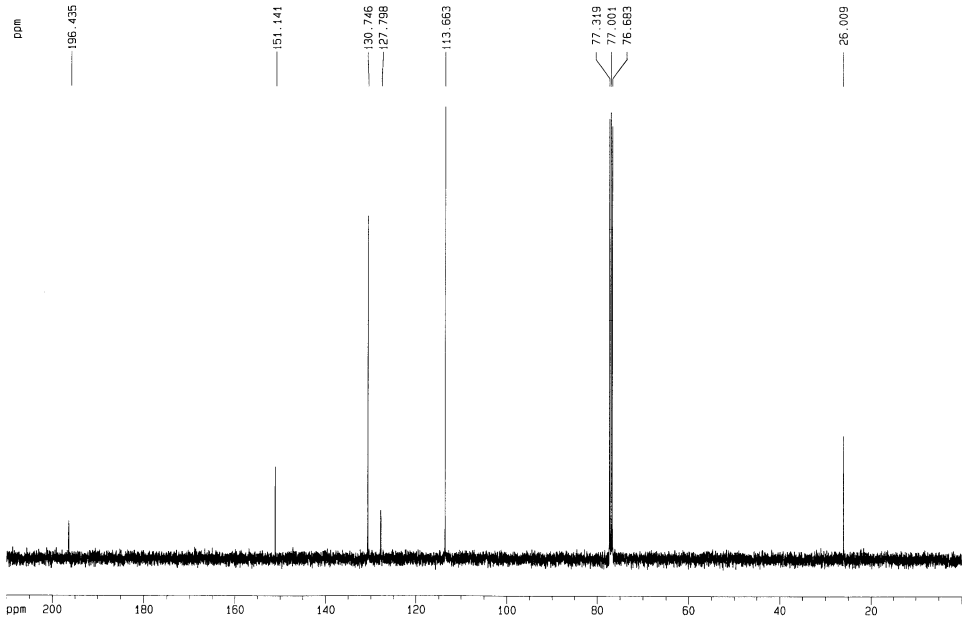
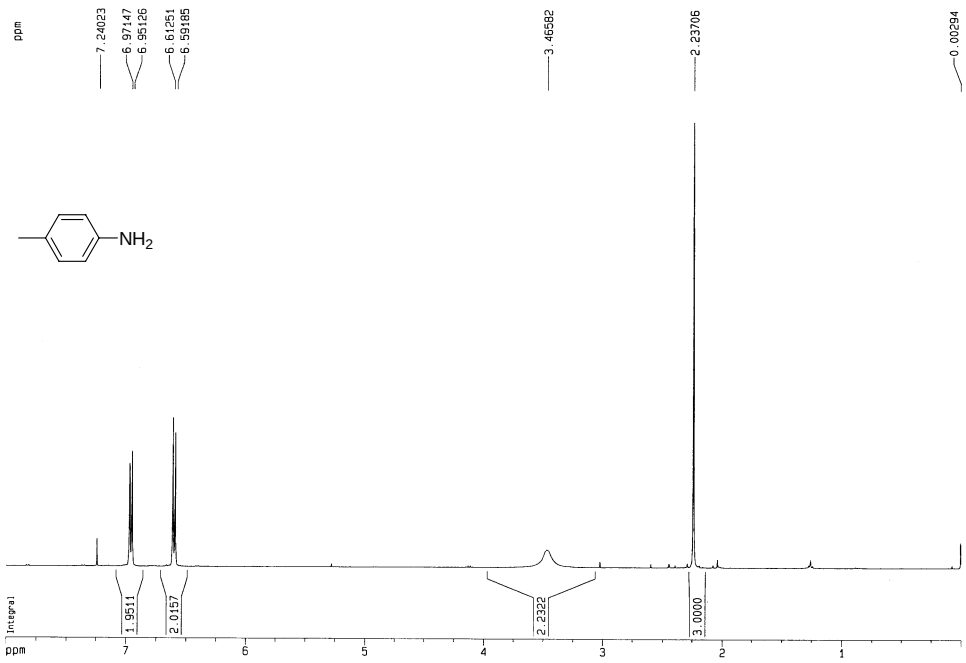
Spectral Copies of ^{1}H and ^{13}C NMR of Products Obtained in this Study

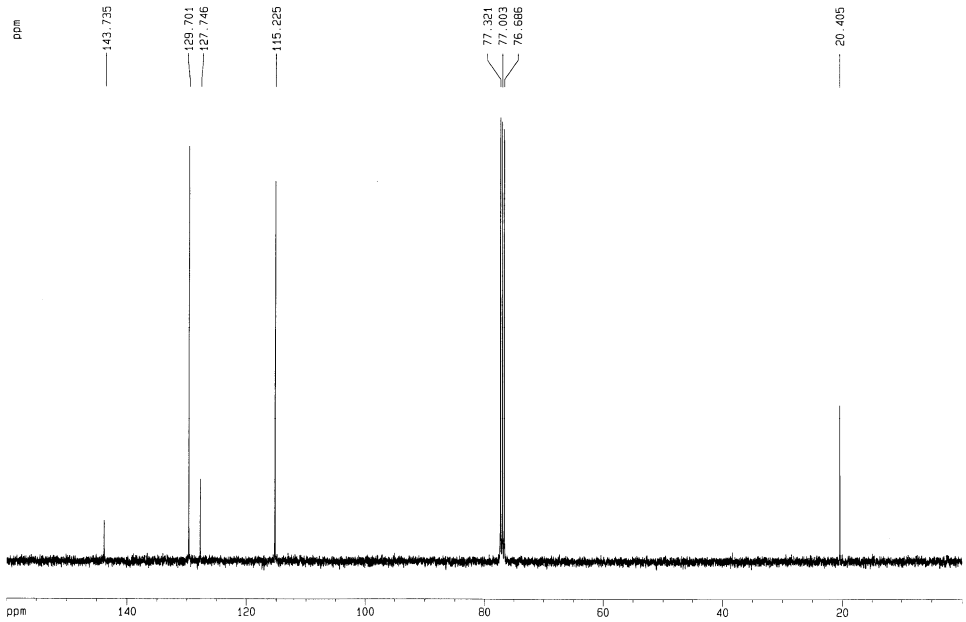
4-Aminoacetophenone (Table 1)



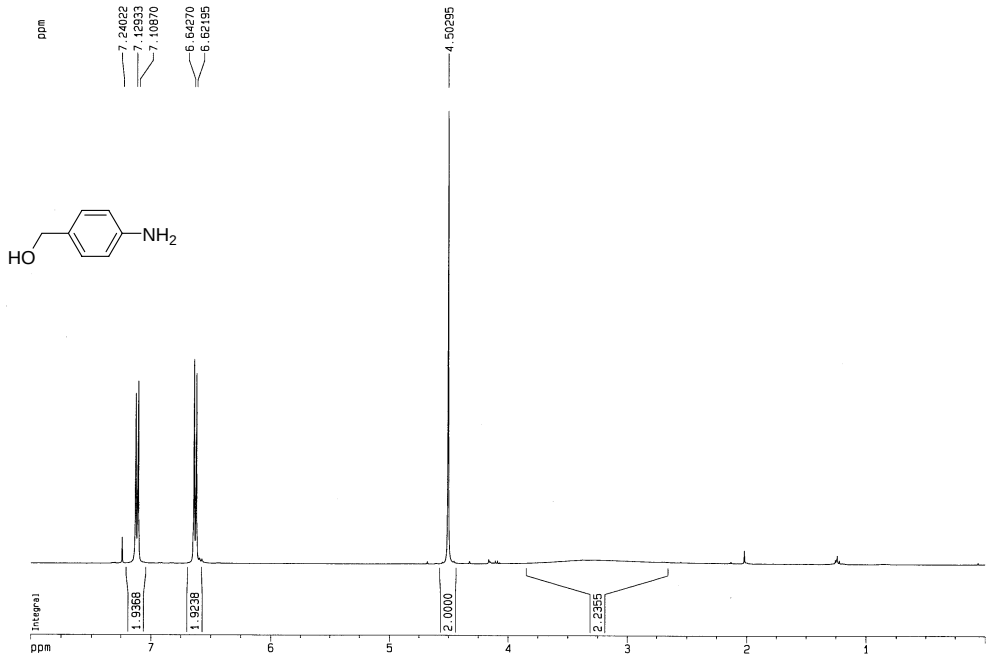


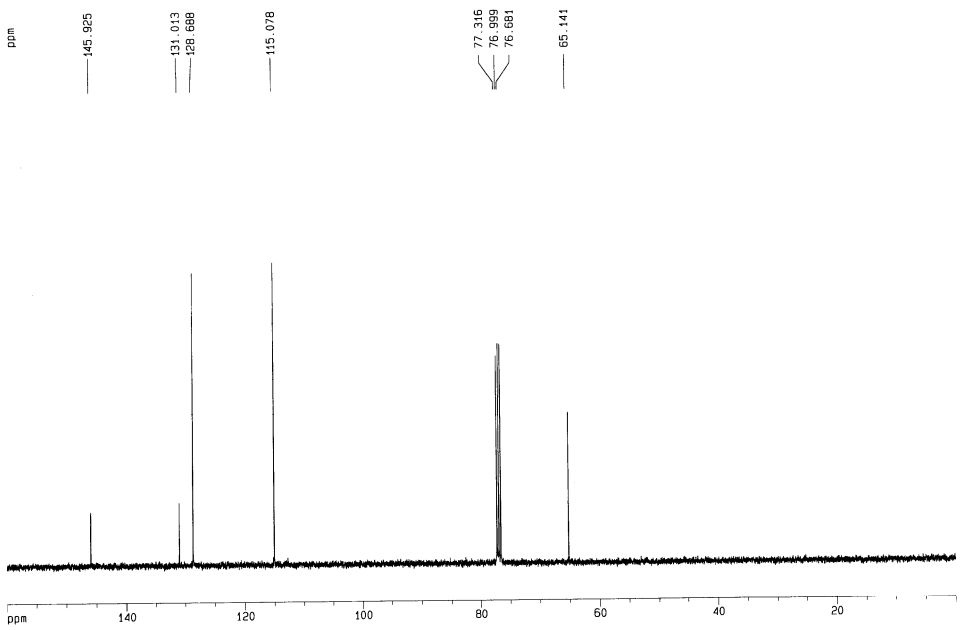
4-Aminotoluene (entry 1, Table 2)



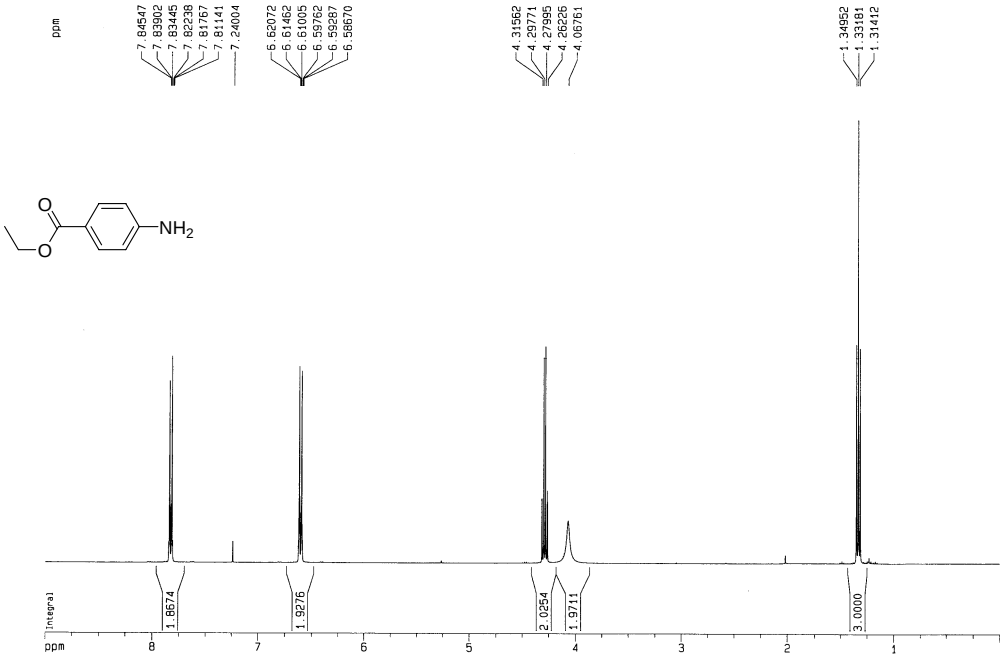


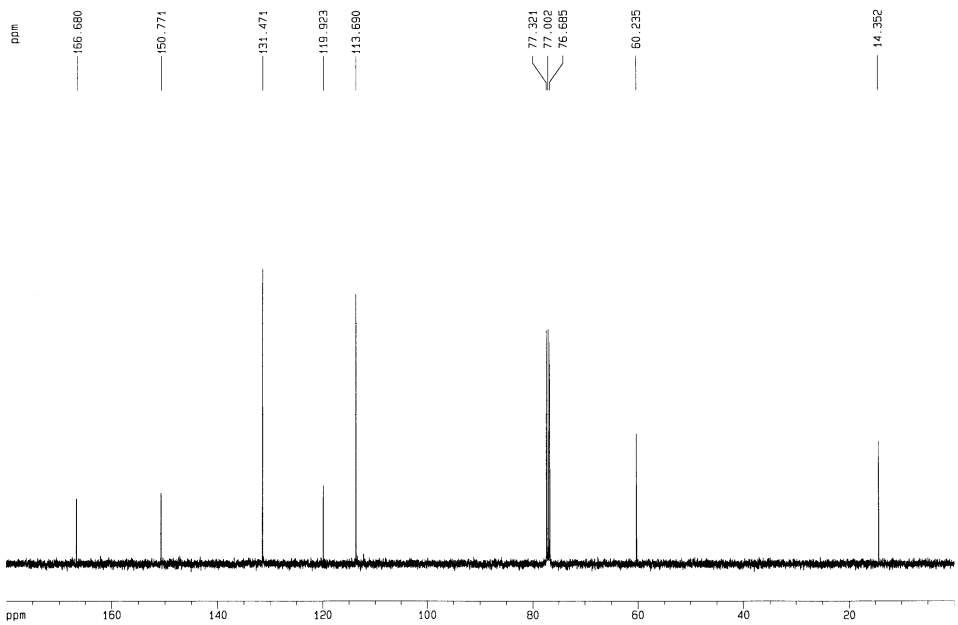
4-Aminobenzylalcohol (entry 2, Table 2)



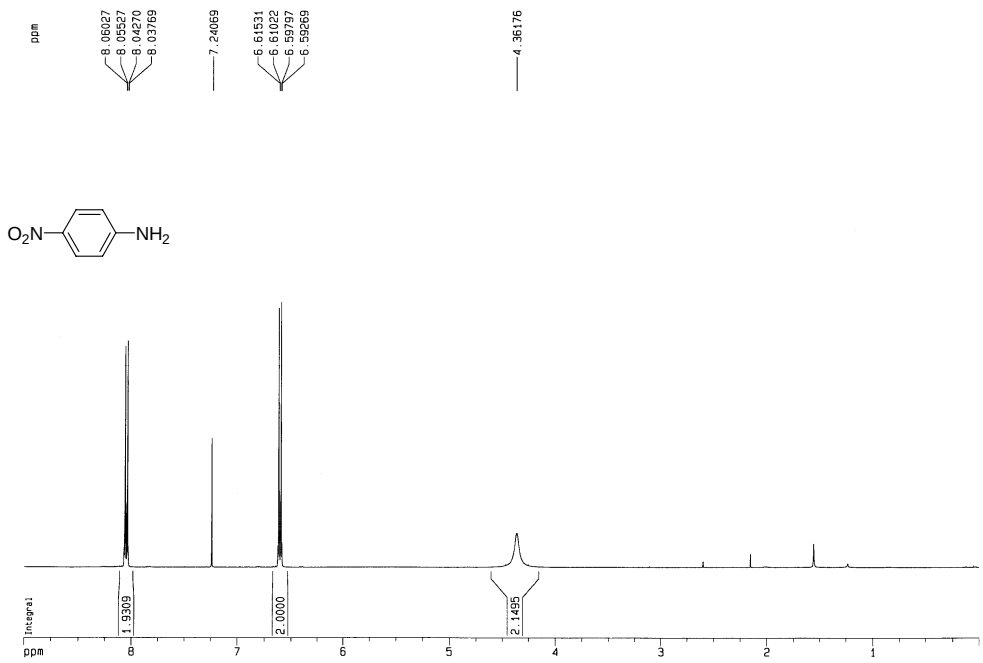


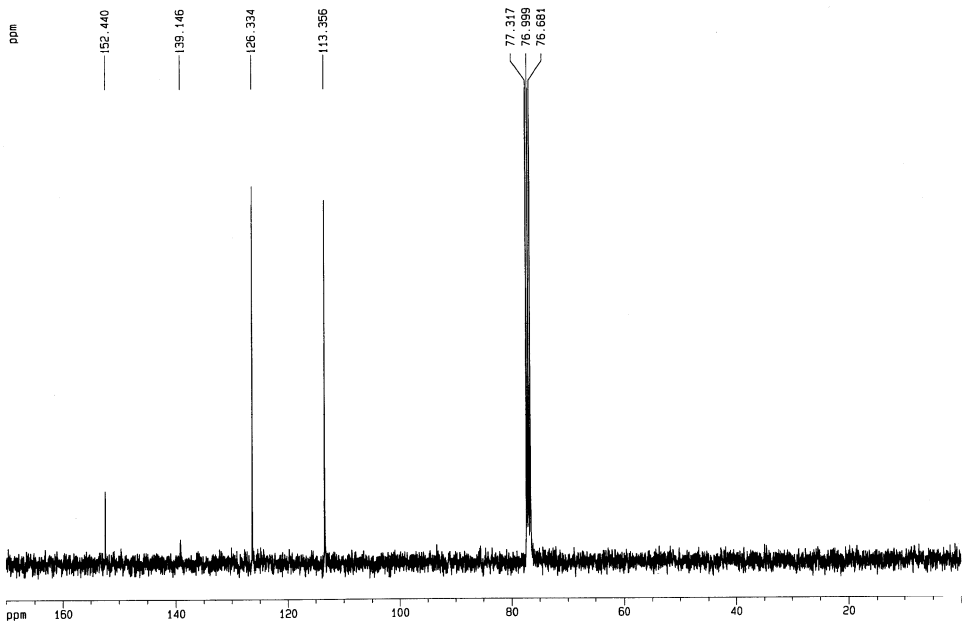
Ethyl 4-aminobenzoate (entry 4, Table 2)



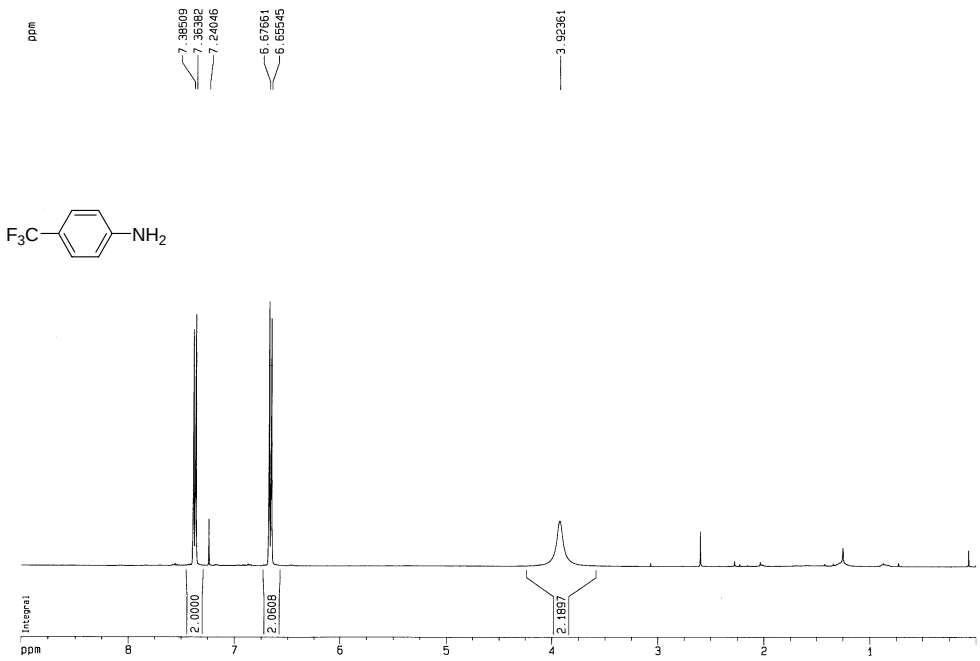


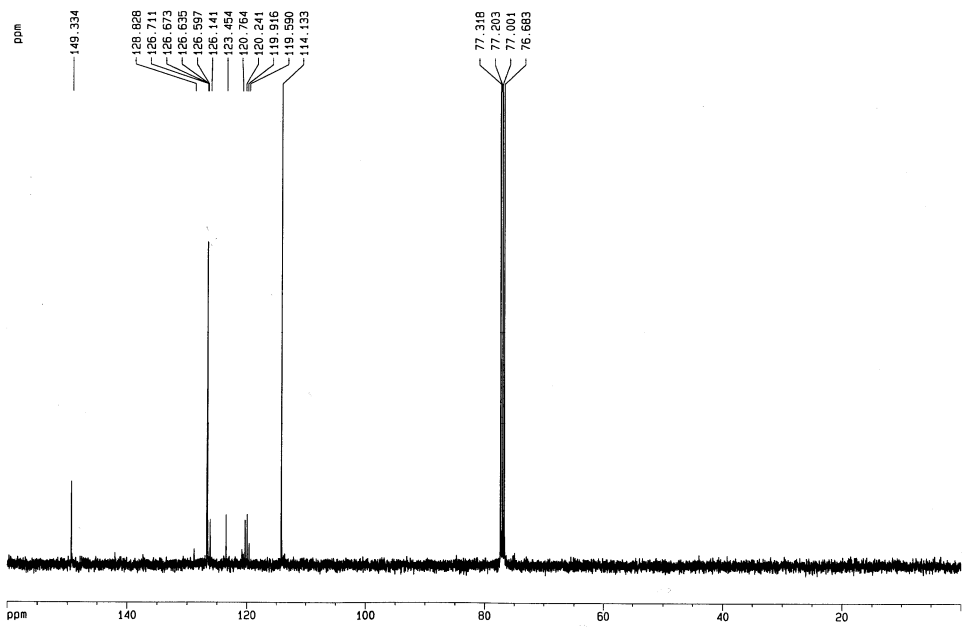
4-Nitroaniline (entry 5, Table 2)



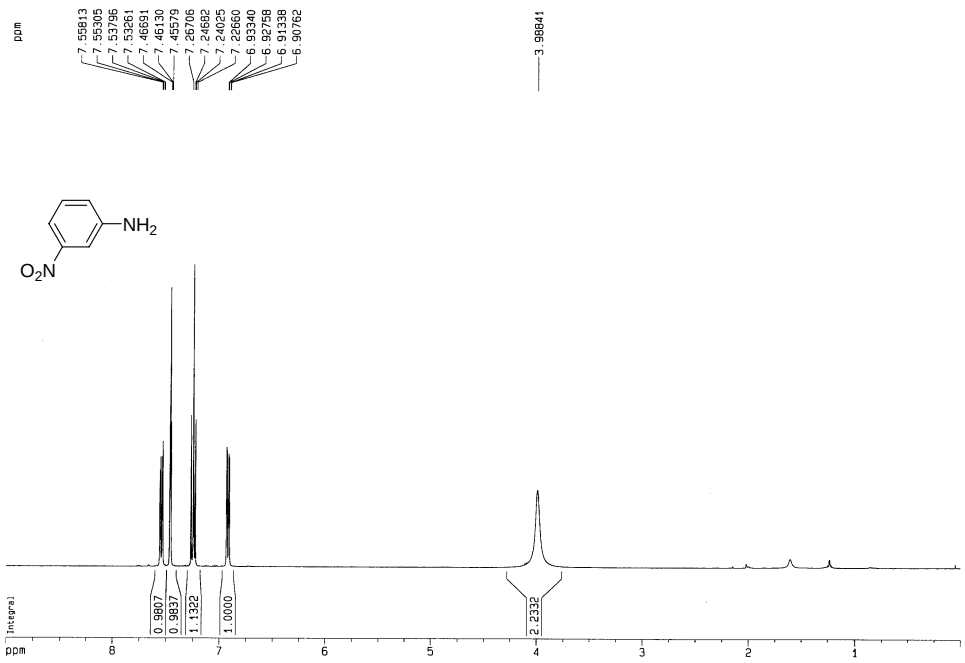


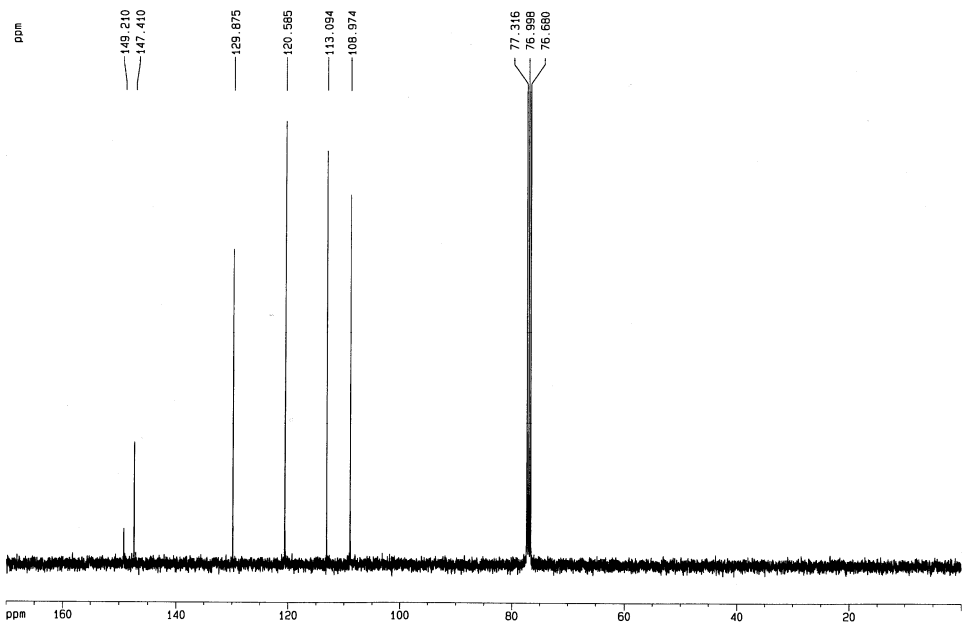
4-Trifluoromethylaniline (entry 6, Table 2)



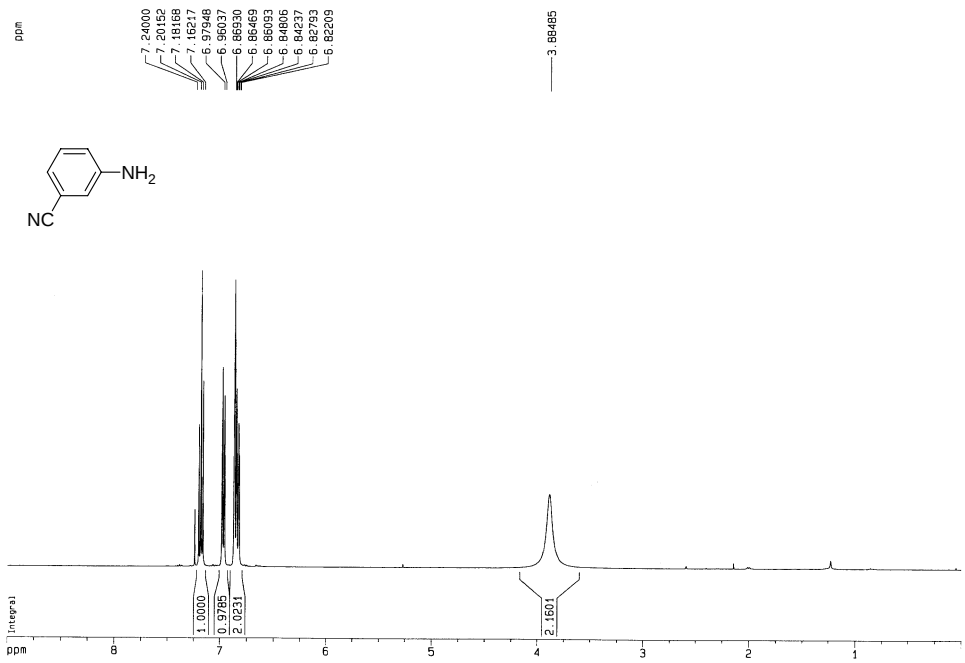


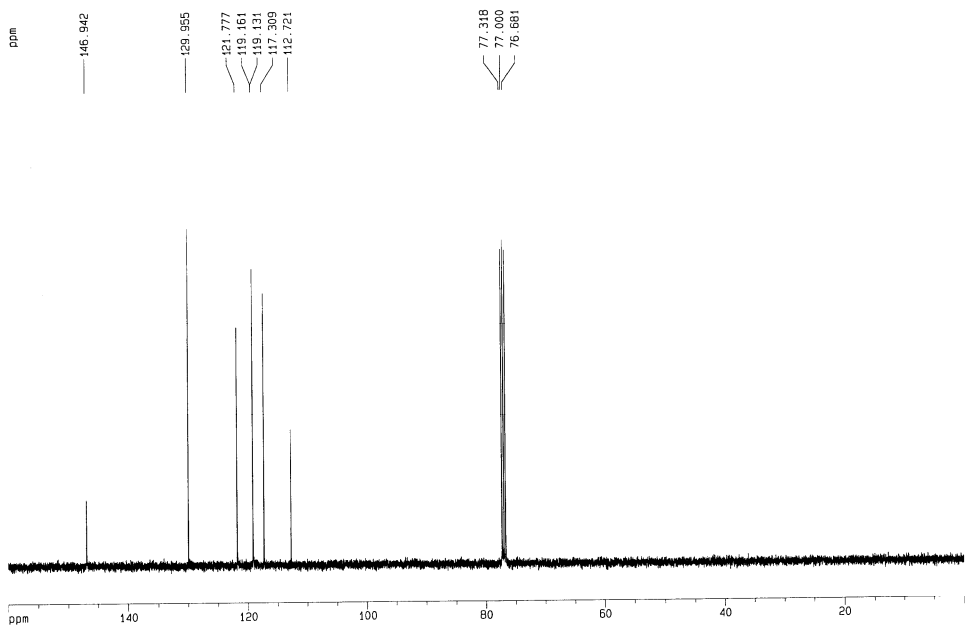
3-Nitroaniline (entry 7, Table 2)



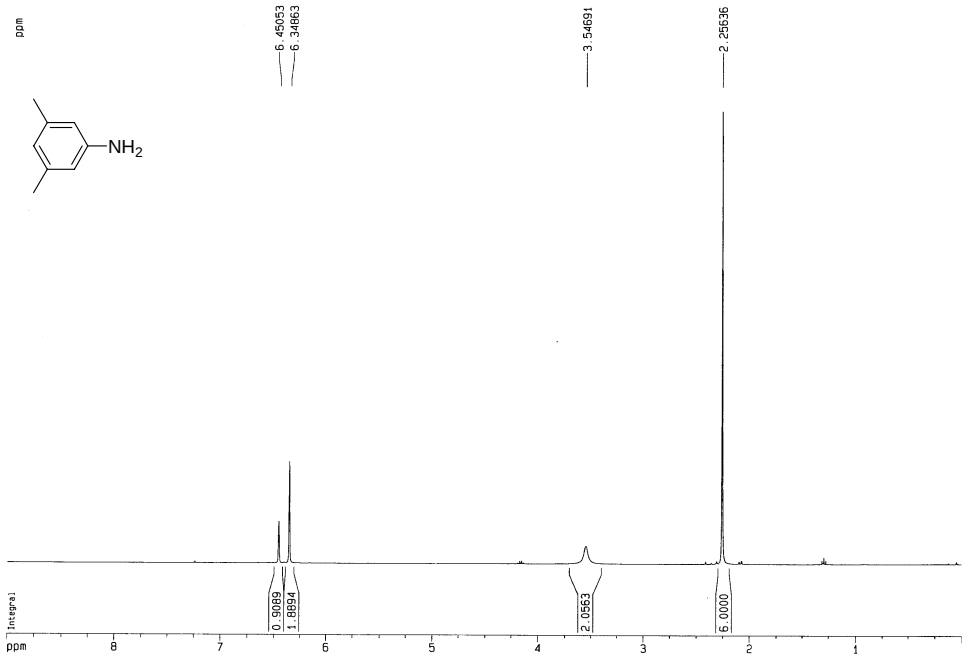


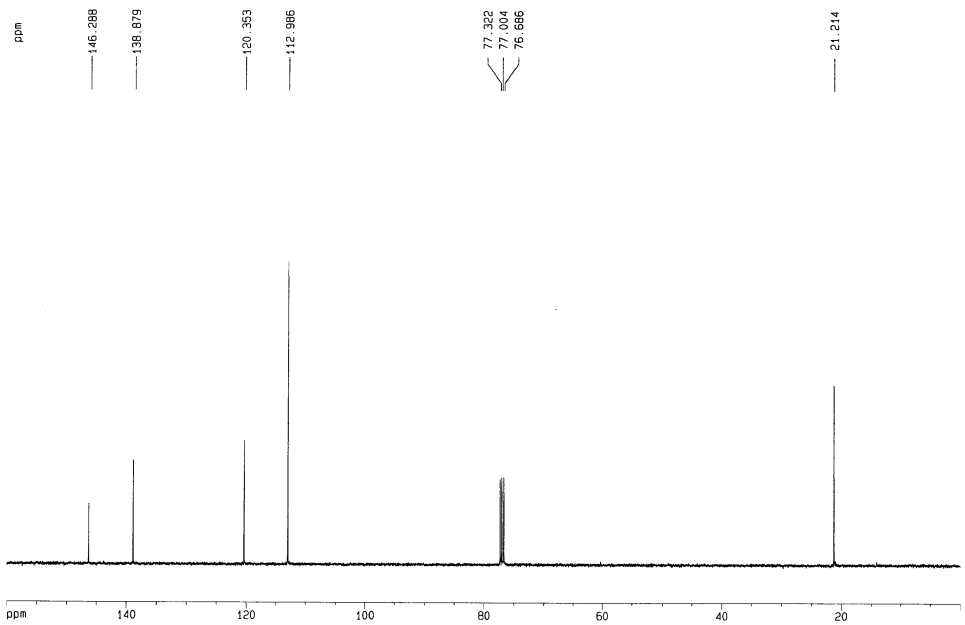
3-Aminobenzonitrile (entry 8, Table 2)



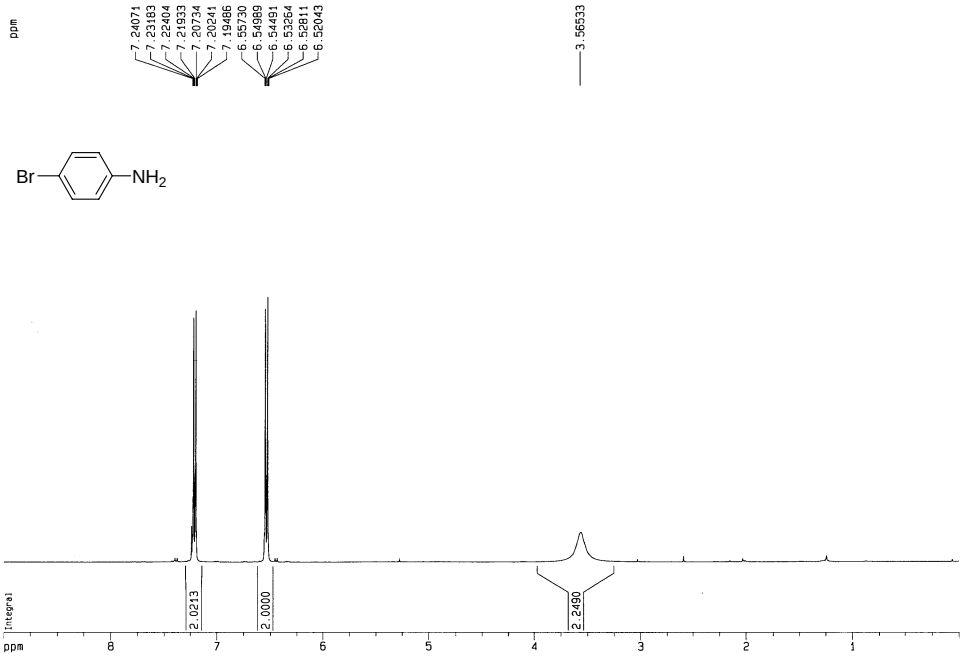


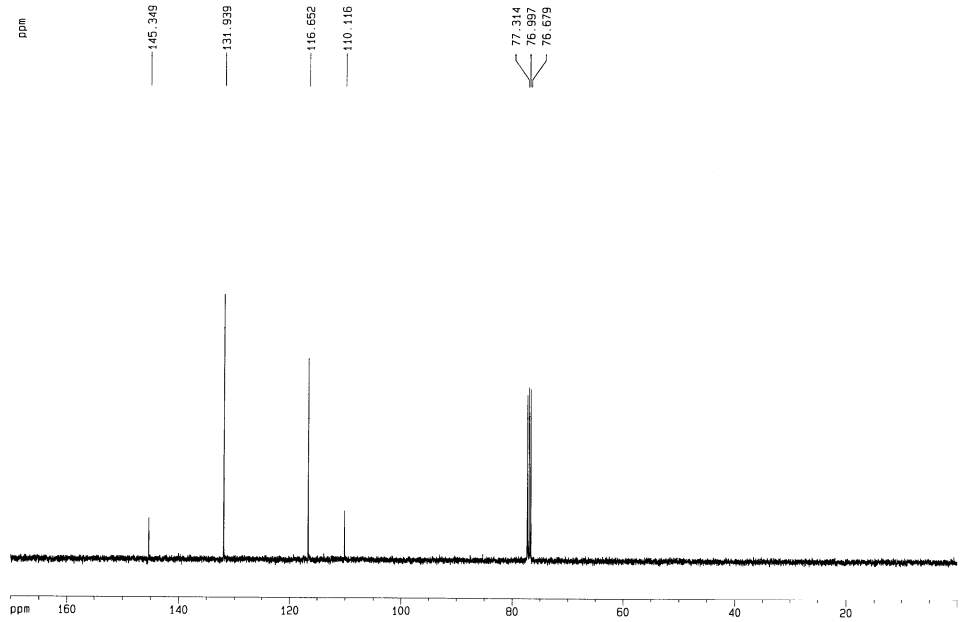
3,5-Dimethylaniline (entry 9, Table 2)



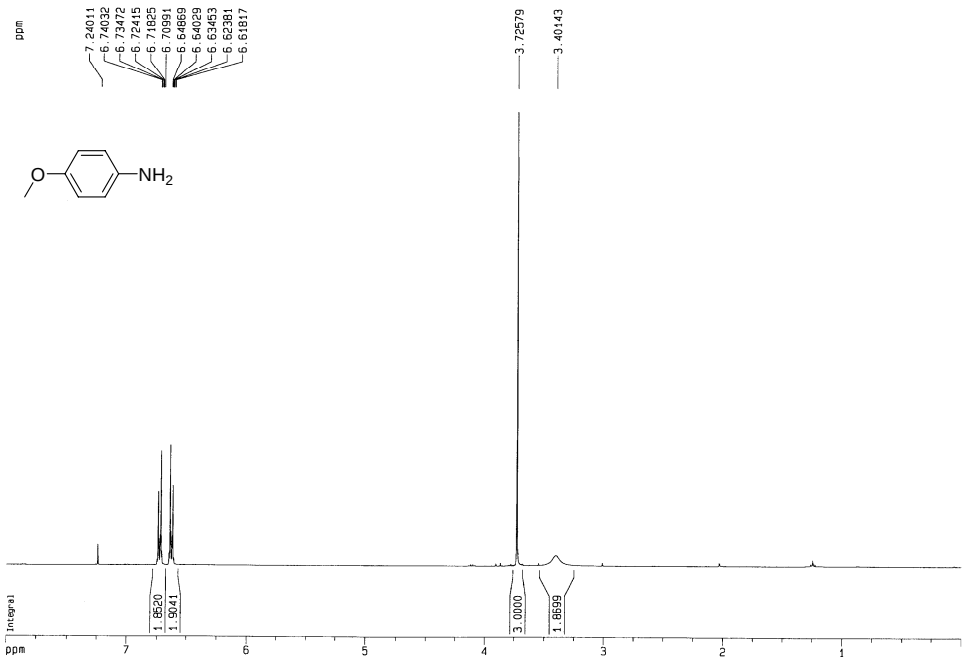


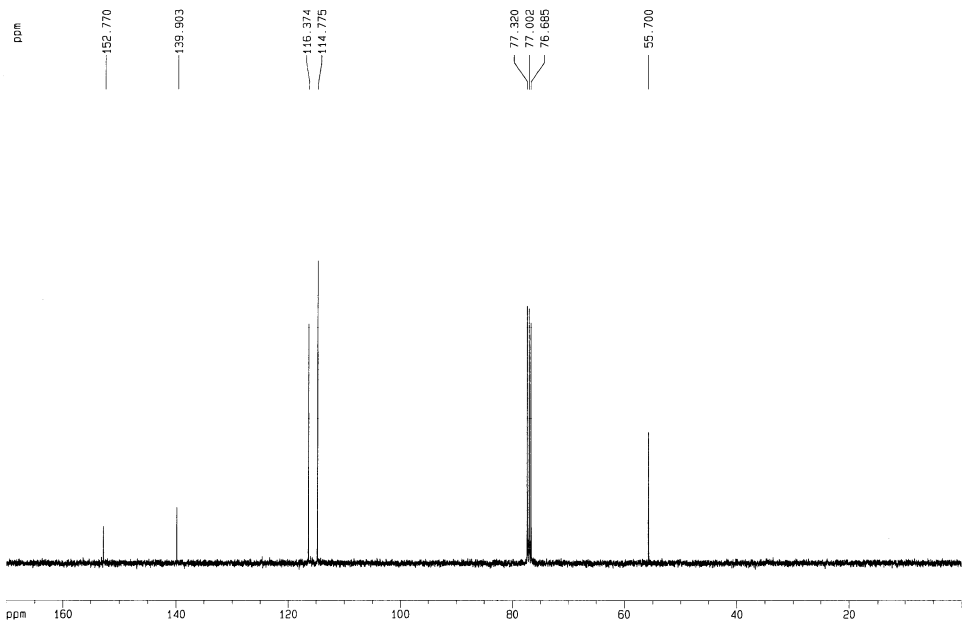
4-Bromoaniline (entry 10, Table 2)



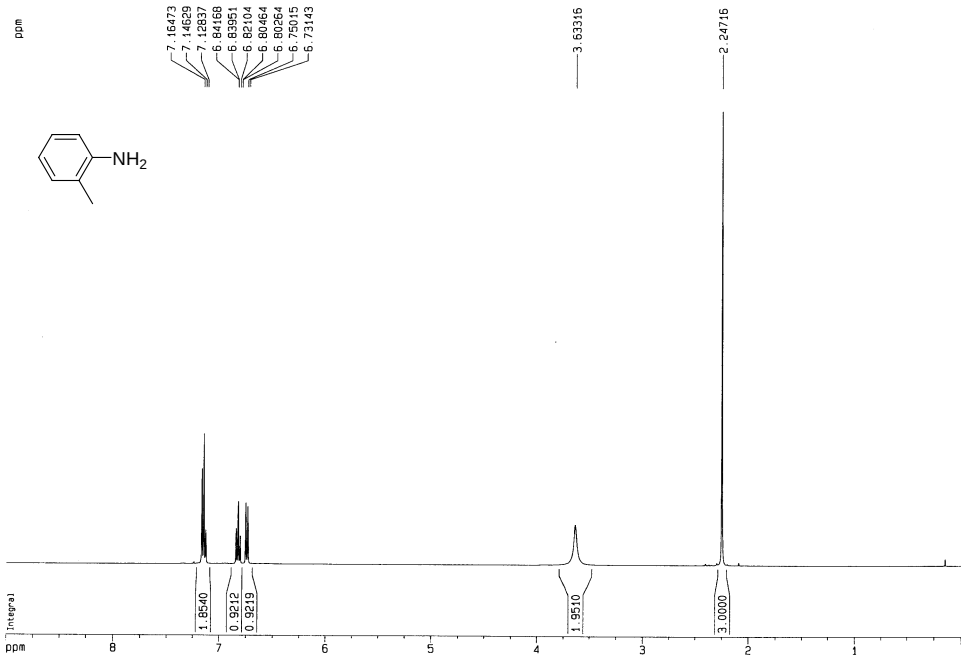


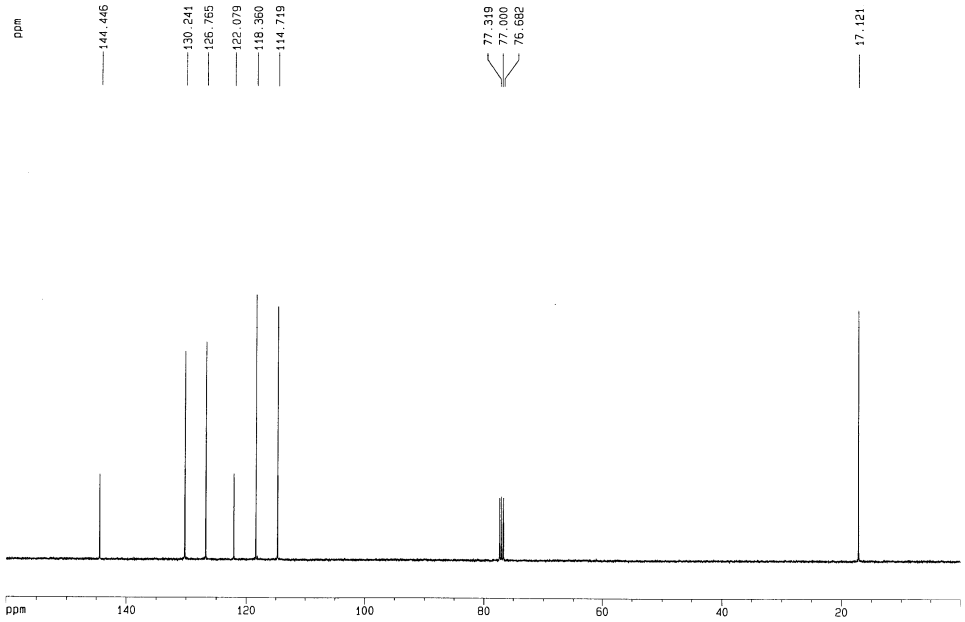
4-Aminoanisole (entry 11, Table 2)



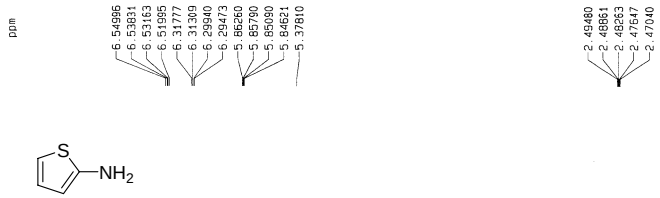


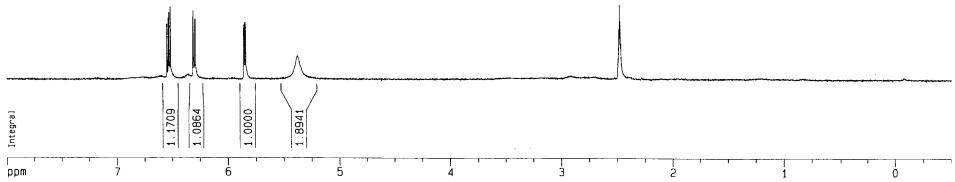
2-Aminotoluene (entry 12, Table 2)

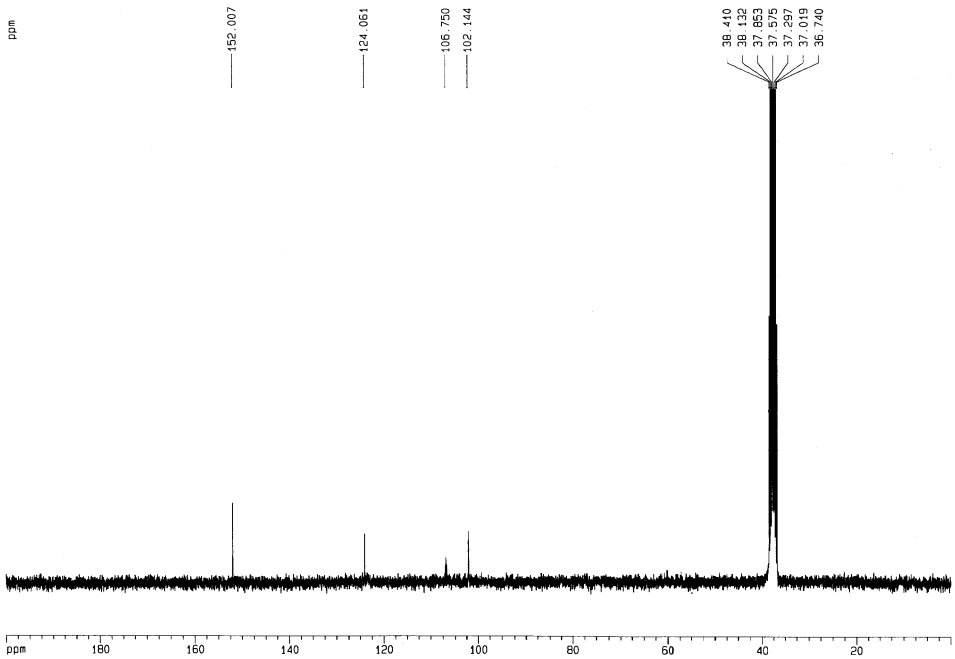




2-Aminothiophene (entry 1, Table 4)







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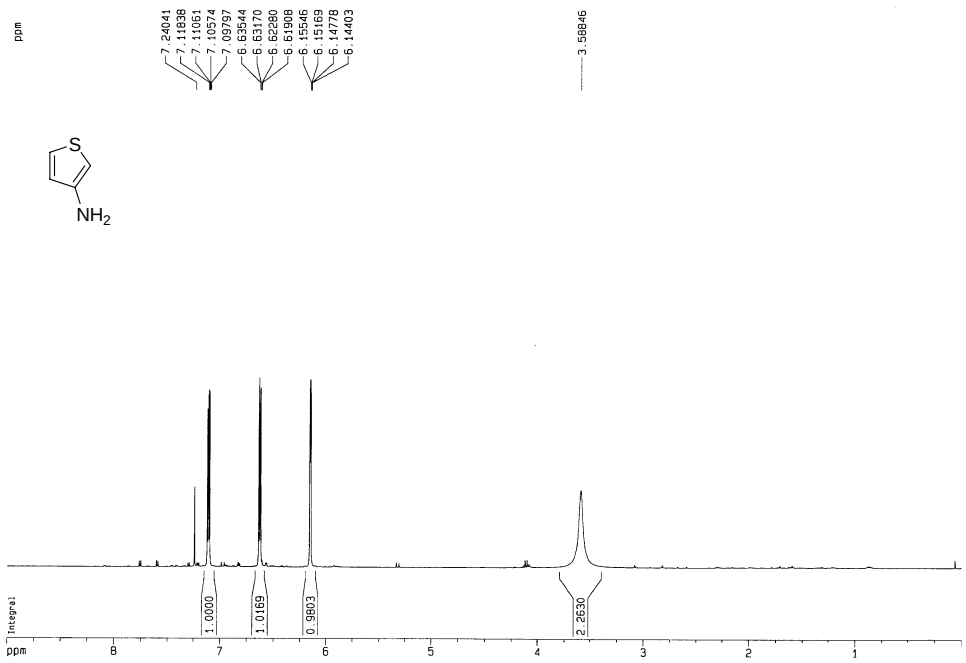
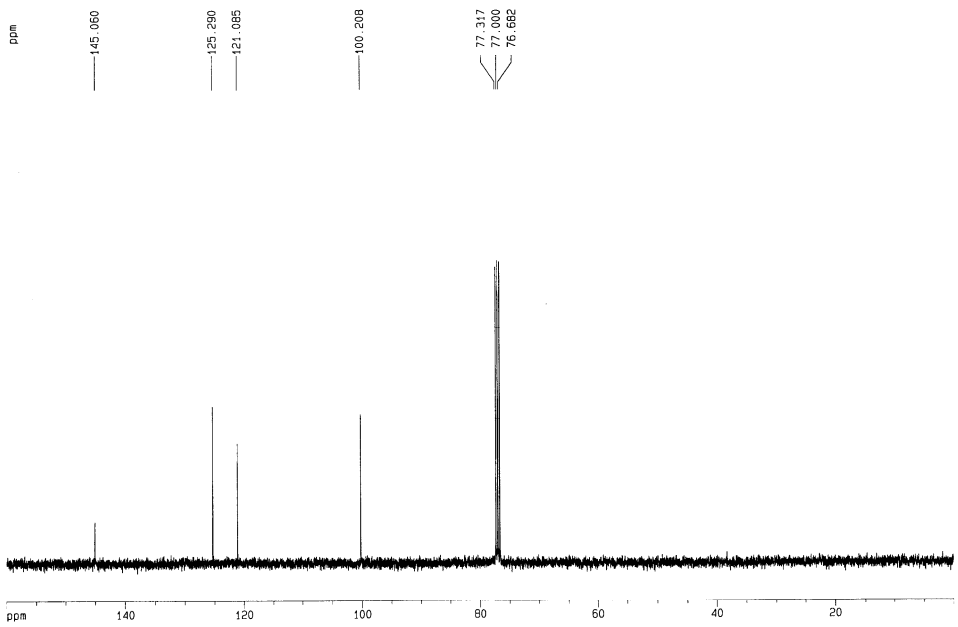
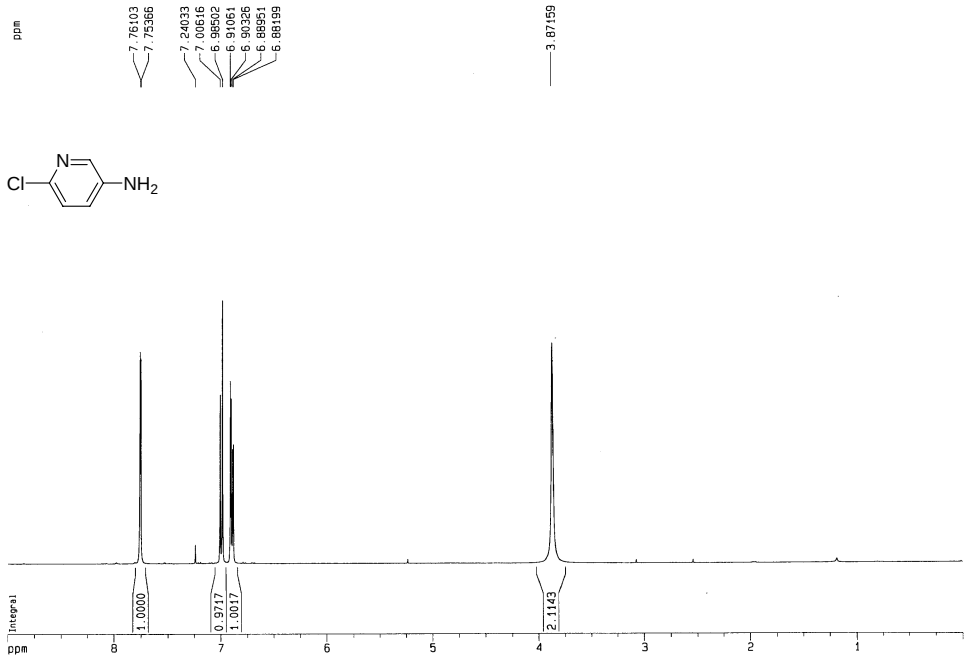
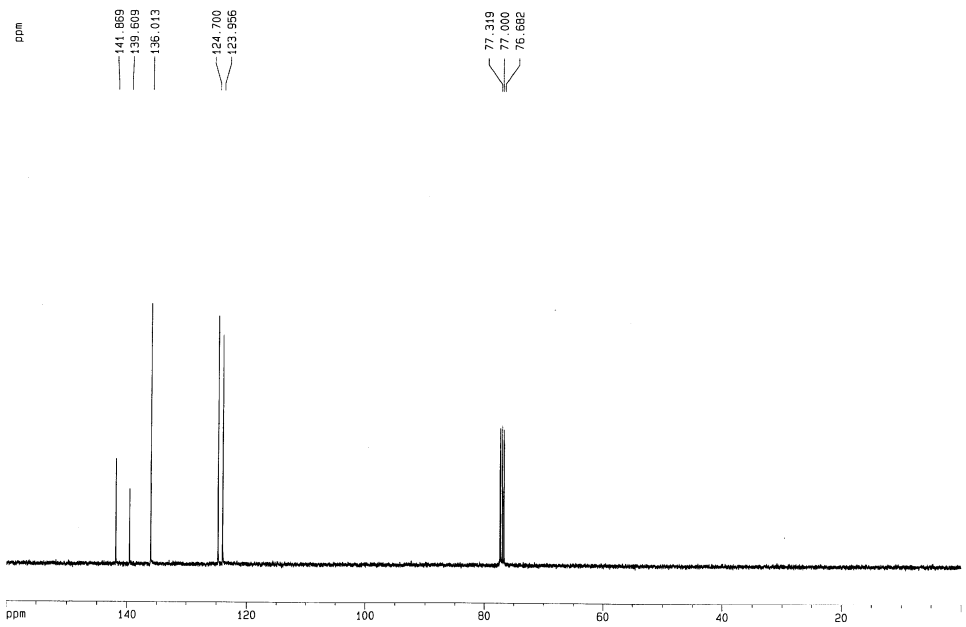
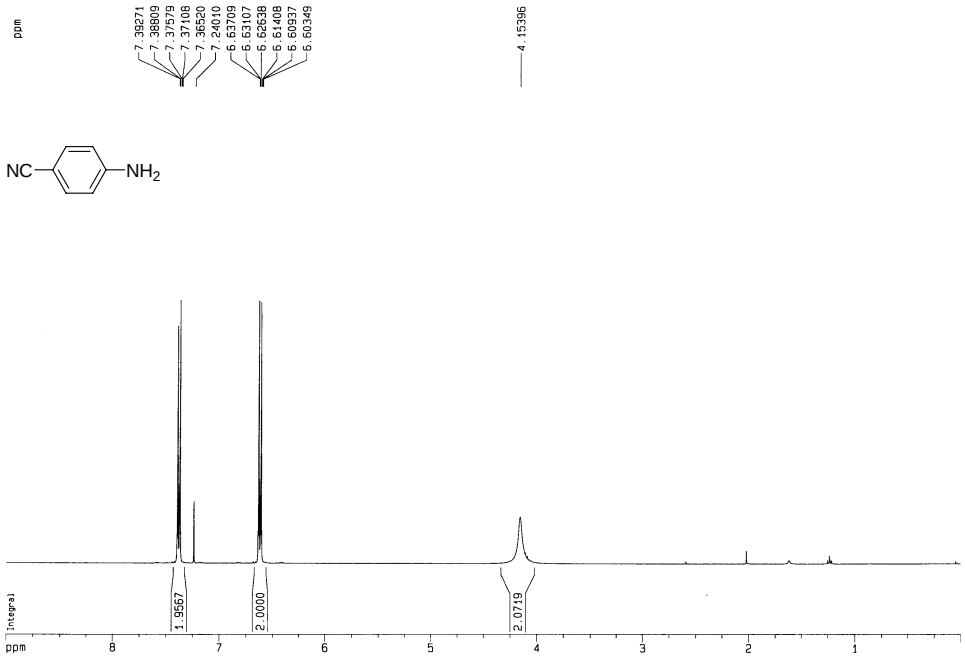
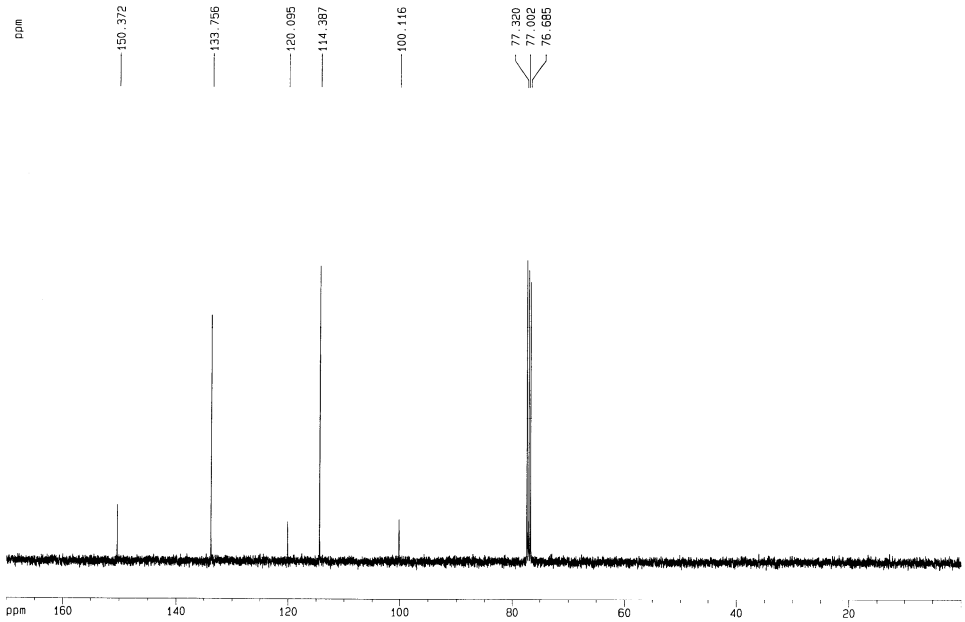
3-Aminothiophene (entry 3, Table 4)





5-Amino-2-chloropyridin (entry 5, Table 4)





4-Aminobenzonitile (entry 7, Table 4)