Electronic Supplementary Material (ESI) for Chemical Communications

Selective One-pot Synthesis of Symmetrical and Unsymmetrical Di- and Triarylamines with a Ligandless Copper Catalytic System

Anis Tlili[a], Florian Monnier*[a], Marc Taillefer[a]*

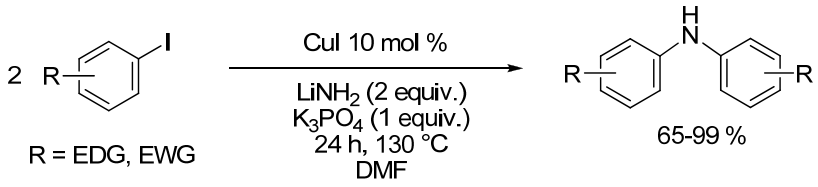
[a] CNRS, UMR 5253, Institut Charles Gerhardt Montpellier AM_2N
Architectures Moléculaires et Matériaux Nanostructurés, Ecole Nationale Supérieure de Chimie de Montpellier
8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France
Fax: (+33)467144319
E-mail: marc.taillefer@enscm.fr, florian.monnier@enscm.fr

Supporting Information

General Experimental Procedures

All reactions were carried out in 35 mL Schlenk tubes or in Carousel "reaction stations RR98030" Radley tubes, under a pure and dry nitrogen atmosphere. DMF was distilled and was stored on 4 Å activated molecular sieves under a nitrogen atmosphere. Other solvents were distilled and stored under a nitrogen atmosphere. Lithium amide 95% (Alfa Aesar), Cesium carbonate 99% metals basis (Alfa Aesar), Potassium phosphate, anhydrous, 97% (Alfa Aesar), CuI 99.999% metals basis (Aldrich) and all other solid materials were stored in the presence of P_4O_{10} in a bench-top desiccator under vacuum at room temperature and weighed in the air without further purification. Aryl iodide and aryl bromides were purchased from commercial sources. If solids, they were recrystallized in an appropriate solvent.[1] If liquids, they were distilled under vacuum and stored under an atmosphere of nitrogen. Column chromatography was performed with SDS 60 A C.C silica gel (35-70 µm). Thin layer chromatography was carried out using Merck silica gel 60 F_{254} plates. All products were characterized by their NMR, GC/MS spectra. NMR spectra were recorded at 20°C on a Bruker AC 400 MHz or on a DRX-250 spectrometer working respectively at 400 MHz for ^1H, at 100 MHz for ^{13}C. Chemical shifts are reported in ppm/TMS for ^1H and $\{^1H\}^{13}C$ (δ 77.00 for $\underline{C}DCl_3$ signal). The first-order peak patterns are indicated as s (singulet), d (doublet), t (triplet), q (quadruplet). Complex non-first-order signals are indicated as m (multiplet). Gas chromatography - mass spectra (GC/MS) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973 N mass detector (EI) and a HP5-MS 30 m x 0.25 mm capillary apolar column (Stationary phase: 5 % diphenyldimethylpolysiloxane film, 0.25 µm). GC/MS method: Initial temperature: 45°C; Initial time: 2 min; Ramp: 2°C/min until 50°C then 10 °C/min; Final temperature: 250°C; Final time: 10 min. HRMS were recorded on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a *m*-nitrobenzylalcohol matrix. Melting points were obtained on a Büchi B-540 melting point apparatus and are uncorrected.

General Procedure for synthesis of biarylamines 1-10 (1 mmol scale) : (Conditions A, Scheme 2).



Protocol A: After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel "reaction stations RR98030") or a Schlenk tube equipped with a magnetic stirring bar was charged with CuI (0.1 mmol), $LiNH_2$ (2 mmol), K_3PO_4(1 mmol) and the aryl halide (1 mmol). The tube was evacuated, back-filled with nitrogen. Then anhydrous and degassed DMF (2.0 mL) was added under a stream of nitrogen by syringe at room temperature. The tube was sealed under a positive pressure of nitrogen, stirred and heated to 130 °C for 24 h. After cooling to room temperature, 10 ml of dichloromethane and 130 µL of 1,3-dimethoxybenzene (internal standard) were added. The filtrate is washed twice with water. Gathered aqueous phases were extracted with dichloromethane five times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product (a small sample of the crude was analyzed by gas chromatography). The obtained crude was purified by silica gel chromatography using heptanes as eluent. All products are known compounds (except products **2, 5** and **10**) and characterized by comparison of their NMR data with published information. The GC yields were determined by obtaining the correction factors using authentic samples of the expected products.

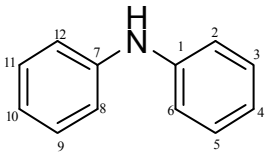
Experimental procedures and characterization data

Diphenylamine 1[1]

Experimental procedure

Following the general procedure **Protocol A**, iodobenzene (112µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 90% yield desired product as a white solid (eluent: ethyl acetate/heptane =20/80).

Identification



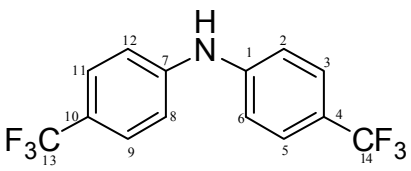
Mp: 52-54 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17-7.21 (m, 4H, $H_{3,5,9,11}$), 6.98-7.01 (m, 2H, $H_{2,6,8,12}$), 6.83-6.87 (m, 2H, $H_{4,10}$), 5.61 (1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1 ($C_{1,7}$), 129.3 ($C_{3,5,9,11}$), 121.0 ($C_{4,10}$), 117.8 ($C_{2,6,8,12}$).
GC/MS: rt = 17.90 min, M/Z = 169.
HRMS calculated for $C_{12}H_{12}N$ (M+H) 170.0970. Found: 170.0976

- **bis(4-(trifluoromethyl)phenyl)amine 2**

Experimental procedure

Following the general procedure **Protocol A**, 4-Iodobenzotrifluoride (147µL, 1.0 mmol) was coupled with $LiNH_2$, in the presence of 0.5 mmol of DMEDA to afford 74% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification



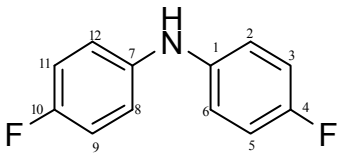
Mp: 56-58 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.48 (d, J = 8.4 Hz, 4H, $H_{3,5,9,11}$), 7.08-7.10 (d, J = 8.4 Hz, 4H, $H_{3,5,9,11}$), 6.04 (br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 ($C_{1,7}$), 126.8 (q, J = 3.6 Hz,$C_{13,14}$), 119.0 ($C_{4,10}$), 117.4 ($C_{2,3,5,6,9,11,12}$).
GC/MS: rt = 17.80 min, M/Z = 305.
HRMS calculated for $C_{14}H_{10}F_6N$ (M+H) 306.0717. Found: 306.0717

- **bis(4-fluorophenyl)amine 3**[2]

Experimental procedure

Following the general procedure **Protocol A**, 4-Fluoroiodobenzene (115µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 82% yield desired product as a white solid (eluent: ethyl acetate/heptane =20/80).

Identification



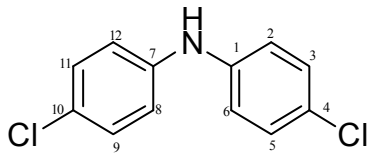
Mp: 38-40 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93-6.95 (m, 8H, $H_{2,3,5,6,8,9,11,12}$), 5.44 (br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8 (d, J_{C-F} = 239.7 Hz, $C_{4,10}$), 139.7 ($C_{1,7}$), 119.4 (d, J_{C-F} = 7.6 Hz ,$C_{2,6,8,12}$), 115.9 (d, J_{C-F} = 22.4 Hz, $C_{3,5,9,11}$).
GC/MS: rt = 18.12 min, M/Z = 205.
HRMS calculated for $C_{12}H_9F_2N$ (M+H) 206.781. Found: 206.0782

- **bis(4-chlorophenyl)amine 4**[2]

Experimental procedure

Following the general procedure **Protocol A**, 4-Chloroiodobenzene (239 mg, 1.0 mmol) was coupled with $LiNH_2$ to afford 65% yield desired product as a white solid (eluent: ethyl acetate/heptane =20/80).

Identification



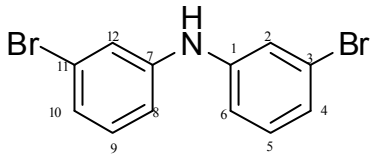
Mp: 77-79 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.20 (d, *J* = 8.8 Hz, 4H, $H_{3,5,9,11}$), 6.95-6.97 (d, *J* = 8.8 Hz, 4H, $H_{2,6,8,12}$), 5.53(br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7 ($C_{1,7}$), 129.46 ($C_{3,5,9,11}$), 128.5 ($C_{4,10}$), 125.2 ($C_{2,6,8,12}$).
GC/MS: rt = 20.50 min, M/Z = 237.
HRMS calculated for $C_{12}H_9Cl_2N$ (M+H) 238.0190. Found: 238.0215.

- **bis(3-bromophenyl)amine 5**

Experimental procedure

Following the general procedure **Protocol A**, 3-Bromoiodobenzene (127 µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 76% yield desired product as a brown oil (eluent: ethyl acetate/heptane =20/80).

Identification



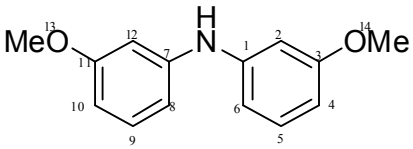
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.13 (m, 2H, $H_{6,8}$), 7.05-7.07 (d, *J* = 7.6 Hz, 2H, $H_{4,10}$), 7.00-7.02 (m, 2H, $H_{5,9}$), 6.90-6.92 (m, 2H, $H_{2,12}$), 5.64 (br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0 ($C_{1,7}$), 130.9 ($C_{5,9}$), 124.6 ($C_{4,10}$), 123.2 ($C_{3,11}$), 120.8 ($C_{6,8}$), 116.7 ($C_{2,12}$).
GC/MS: rt = 22.01 min, M/Z = 324.
HRMS calculated for $C_{12}H_9Br_2N$ (M+H) 325.9180 Found: 325.9173

- **bis(3-methoxyphenyl)amine 6**[3]

Experimental procedure

Following the general procedure **Protocol A,** 3-Iodoanisole (132µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 87% yield desired product as a brown oil (eluent: ethyl acetate/heptane=10/90).

Identification



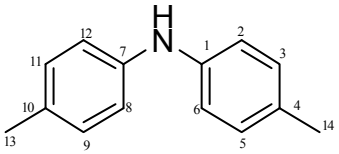
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.11 (t, *J* = 8.0 Hz, 2H, $H_{5,9}$), 6.57-6.58 (m, 4H, $H_{2,6,10,12}$), 6.40-6.43 (ddd, *J* = 0.8, 2.4, 8.0 Hz, 2H, $H_{6,8}$), 5.63 (br s, 1H, NH), 3.70 (s, 6H, $H_{13,14}$). .
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5 ($C_{3,11}$), 144.1 ($C_{1,7}$), 130.1 ($C_{5,9}$), 110.4 ($C_{4,10}$), 106.4 ($C_{4,8}$), 103.7 ($C_{2,12}$), 20.4 ($C_{13,14}$).
GC/MS: rt = 21.86 min, M/Z = 229.
HRMS calculated for $C_{14}H_{16}O_2N$ (M+H) 230.1181 Found: 230.1182

- **di-p-tolylamine 7[3]**

Experimental procedure

Following the general procedure **Protocol A**, 4-iodotoluene (218 mg, 1.0 mmol) was coupled with $LiNH_2$ to afford 93% yield desired product as a white solid (eluent: ethyl acetate/heptane =20/80).

Identification



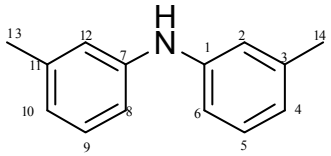
Mp: 79-81 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98-7.00 (d, *J* = 8 Hz, 4H, $H_{2,6,8,12}$), 6.86-6.88 (d, *J* = 8 Hz, 4H, $H_{3,5,9,11}$), 5.43(br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0 ($C_{1,7}$), 130.0 ($C_{3,5,9,11}$), 128.4 ($C_{4,10}$), 118.2 ($C_{2,6,8,12}$).
GC/MS: rt = 20.25 min, M/Z = 197.
HRMS calculated for $C_{14}H_{16}N$ (M+H) 198.1283 Found: 198.1288

- **di-*m*-tolylamine 8[3]**

Experimental procedure

Following the general procedure **Protocol A**, 3-Iodotoluene (128µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 94% yield desired product as a yellow oil (eluent: ethyl acetate/heptane =20/80).

Identification



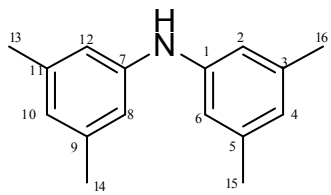
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05-7.09 (dd, *J* = 8.8, 1.2 Hz, 2H, $H_{5,9}$), 6.80-6.81 (m, 4H, $H_{2,6,10,12}$), 6.66-6.68 (d, *J* = 8.8 Hz, 2H, $H_{4,10}$), 5.53 (br s, 1H, NH), 2.23 (s, 6H, $H_{13,14}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5 ($C_{1,7}$), 138.6 ($C_{3,11}$), 128.4 ($C_{5,9}$), 120.7 ($C_{4,10}$)117.9 ($C_{4,8}$), 114.0 ($C_{2,12}$), 20.4 ($C_{13,14}$).
GC/MS: rt = 20.62 min, M/Z = 197.
HRMS calculated for $C_{14}H_{16}N$ (M+H) 198.1283 Found: 198.1275

- **bis(3,5-dimethylphenyl)amine 9[3]**

Experimental procedure

Following the general procedure **Protocol A,** 3,5-Iodo-*m*-xylene (128µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 77% yield desired product as a brown oil (eluent: ethyl acetate/heptane=10/90).

Identification



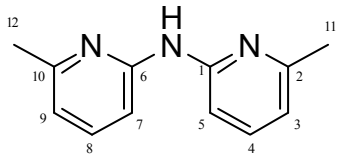
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (m, 4H, $H_{2,6,8,12}$), 6.50 (m, 2H, $H_{4,10}$), 5.55(br s, 1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2 ($C_{1,7}$), 138.9 ($C_{3,5,9,11}$), 122.7 ($C_{4,10}$), 115.7 ($C_{2,6,8,12}$), 21.4($C_{2,6,8,12}$).
GC/MS: rt = 21.34 min, M/Z = 225.
HRMS calculated for $C_{16}H_{20}N$ (M+H) 226.1596. Found: 226.1595.

- **bis(6-methylpyridin-2-yl)amine 10**

Experimental procedure

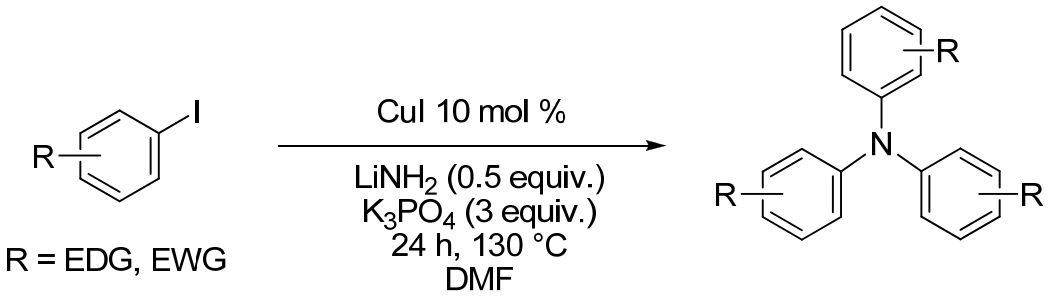
Following the general procedure **Protocol A,** 2-bromo-6-methylpyridine (128µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 64% yield desired product as a yellow solid (eluent: ethyl acetate/heptane=20/80).

Identification



Mp: 82-84 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.43 (t, *J* = 8.0 Hz, 2H, $H_{4,8}$), 7.28-7.30 (d, *J* = 8.0 Hz, 6H, $H_{3,9}$), 7.10 (br s, 1H, NH), 6.62-6.63 (d, *J* = 8.0 Hz, 2H, $H_{5,7}$), 2.39 (s, 6H, $H_{16,17}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7 ($C_{2,10}$), 153.3 ($C_{1,6}$), 138.0 ($C_{4,8}$), 115.5 ($C_{3,9}$), 108.2 ($C_{5,7}$), 24.2 ($C_{16,17}$).
GC/MS: rt = 17.98 min, M/Z = 200.
HRMS calculated for $C_{12}H_{14}N_3$ (M+H) 200.1188. Found: 200.1176

General Procedure for synthesis of symmetrical triarylamines 11-18 (1 mmol scale): (Conditions B, Scheme 2).



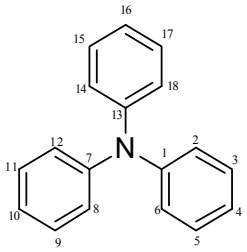
Protocol B: After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel "reaction stations RR98030") or a Schlenk tube equipped with a magnetic stirring bar was charged with CuI (0.1 mmol), $LiNH_2$ (0.5 mmol), K_3PO_4 (3 mmol) and the aryl halide (1 mmol). The tube was evacuated, back-filled with nitrogen. Then anhydrous and degassed DMF (2.0 mL) was added under a stream of nitrogen by syringe at room temperature. The tube was sealed under a positive pressure of nitrogen, stirred and heated to 130 °C for 24 h. After cooling to room temperature, 10 ml of dichloromethane and 130 µL of 1,3-dimethoxybenzene (internal standard) were added. The filtrate is washed twice with water. Gathered aqueous phases were extracted with dichloromethane five times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product (a small sample of the crude was analyzed by gas chromatography).The obtained crude was purified by silica gel chromatography using heptanes as eluent heptanes. All products are known compounds (except products **13**, **14, 15, 16, 17 and 18**) and characterized by comparison of their NMR data with published information. The GC yields were determined by obtaining the correction factors using authentic samples of the expected products.

- **Triphenylamine 11[4]**

Experimental procedure

Following the general procedure **Protocol B**, iodobenzene (112µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 79% yield desired product as a white solid (eluent: ethyl acetate/heptane =10/90).

Identification



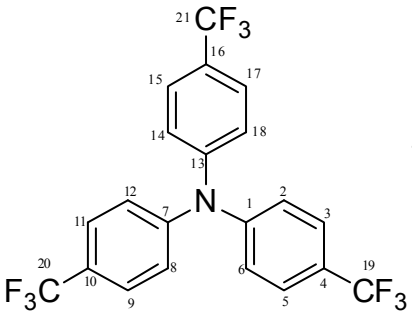
Mp: 126-128 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.18 (t, J = 8.3 Hz, 6H, $H_{3,5,9,11,15,17}$), 6.98-7.01 (d, J = 8.3 Hz, 6H, $H_{2,6,8,12,14,18}$), 6.90-6.94 (t, J = 8.3, Hz, 3H, $H_{4,10,16}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0 ($C_{1,7,13}$), 129.3 ($C_{3,5,9,11,15,17}$), 124.3 ($C_{2,6,8,12,14,18}$), 122.9 ($C_{4,10,16}$).
GC/MS: rt = 22.00 min, M/Z = 245.
HRMS calculated for $C_{18}H_{15}N$ (M+H) 245.1204. Found: 245.1208

- **tris(4-(trifluoromethyl)phenyl)amine 12[3]**

Experimental procedure

Following the general procedure **Protocol A**, 4-Iodobenzotrifluoride (147µL, 1.0 mmol) was coupled with $LiNH_2$, in the presence of 0.5 mmol of DMEDA, to afford 86% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification



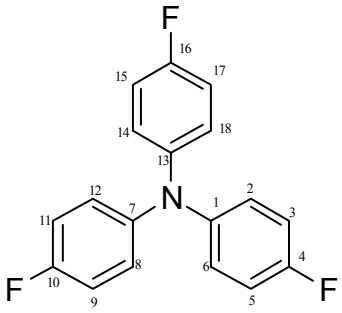
Mp : 62-64°C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.52 (d, J = 8.5 Hz, 6H, $H_{3,5,9,11,15,17}$), 7.15-7.17 (d, J = 8.5 Hz, 6H, $H_{2,6,8,12,14,18}$) .
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5 ($C_{1,7,13}$), 126.9 (q, $J_{C\text{-}F}$ = 3.6 Hz,$C_{19,20,21}$), 124.2 ($C_{2,3,5,6,8,9,11,12,14,15,17,18}$), 121.7 ($C_{4,10,16}$).
GC/MS: rt = 21.61 min, M/Z = 449.
HRMS calculated for $C_{18}H_{13}NCl_3$ (M+H) 449.3123. Found: 449.3128.

- **tris(4-fluorophenyl)amine 13[6]**

Experimental procedure

Following the general procedure **Protocol B**, 4-Fluoroiodobenzene (115 µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 83% yield desired product as a white solid (eluent: ethyl acetate/heptane =10/90).

Identification



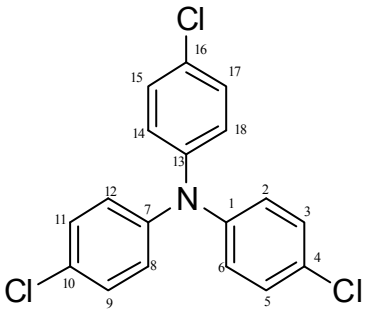
Mp : 122-124 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84-6.92 (m, 12H, $H_{2,3,5,6,8,9,11,12,14,15,17,18}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8 (d, $J_{C\text{-}F}$ = 238.3 Hz,$C_{4,10,16}$), 144.0 (d, $J_{C\text{-}F}$ = 3.0 Hz $C_{1,7,13}$), 125.2(d, $J_{C\text{-}F}$ = 7.8 Hz, $C_{2,6,8,12,14,18}$), 116.1 (d, $J_{C\text{-}F}$ = 23 Hz $C_{3,5,9,11,15,17}$).
GC/MS: rt = 21.69 min, M/Z = 299.
HRMS calculated for $C_{18}H_{13}NCl_3$ (M+H) 300.0922. Found: 300.0918.

- **tris(4-chlorophenyl)amine 14**

Experimental procedure

Following the general procedure **Protocol B**, 4-Cloroiodobenzene (239 mg, 1.0 mmol) was coupled with $LiNH_2$ to afford 98% yield desired product as a white solid (eluent : heptane).

Identification



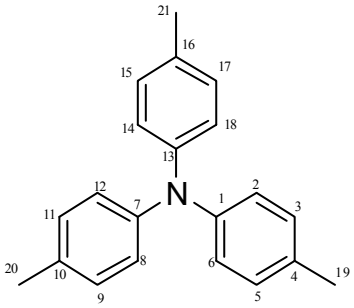
Mp: 147-149 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.22 (d, 6H, *J* = 8.8 Hz, $H_{3,5,9,11,15,17}$), 6.96-6.98 (d, *J* = 8.8 Hz, 6H, $H_{2,6,8,12,15,17}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7 ($C_{1,7,13}$), 129.6 ($C_{2,6,8,12,15,17}$), 128.4($C_{4,10,16}$), 125.3 ($C_{3,5,9,11,15,17}$).
GC/MS: rt = 28.78 min, M/Z = 347.
HRMS calculated for $C_{18}H_{13}NCl_3$ (M+H) 348.0114. Found: 348.0104.

- **tri-p-tolylamine 15**

Experimental procedure

Following the general procedure **Protocol B**, 4-Iodotoluene (239 mg, 1.0 mmol) was coupled with $LiNH_2$ to afford 78% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification



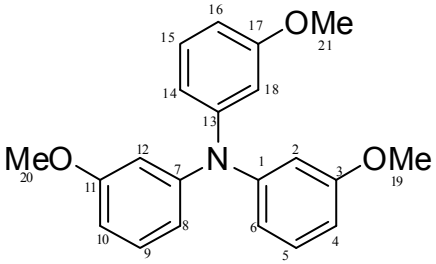
Mp: 112-114 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-6.99 (m, 6H, $H_{3,5,9,11,15,17}$), 6.96-6.98 (m, 6H, $H_{2,6,8,12,15,17}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1 ($C_{1,7,13}$), 131.8 ($C_{2,6,8,12,15,17}$), 129.8($C_{4,10,16}$), 12.7 ($C_{3,5,9,11,15,17}$).
GC/MS: rt = 24.67 min, M/Z = 287.
HRMS calculated for $C_{21}H_{22}N$ (M+H) 288.1752. Found: 288.1741.

- **tris(3-methoxyphenyl)amine 16**

Experimental procedure

Following the general procedure **Protocol B**, 3-Iodoanisole (132 µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 84% yield desired product as a brown oil (eluent : ethyl acetate/heptane = 50/50).

Identification



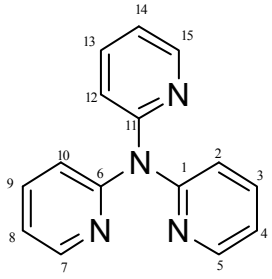
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05-7.09 (t, *J* = 8.0 Hz, 3H, $H_{5,9,15}$), 6.59-6.61 (dd, *J* = 8, 1.5 Hz, 3H, $H_{4,10,16}$), 6.56-6.57 (t, *J* = 2.2 Hz, 3H, $H_{6,8,14}$), 6.48-6.51 (dd, *J* = 8, 2.2, Hz, 3H, $H_{2,12,18}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 ($C_{3,11,17}$), 149.1 ($C_{1,7,13}$), 130.0 ($C_{6,8,14}$), 117.2 ($C_{5,9,15}$), 110.5 ($C_{4,10,16}$). 108.6 ($C_{2,12,18}$).
GC/MS: rt = 28.21 min, M/Z = 335.
HRMS calculated for $C_{21}H_{21}NO_3$ (M+H) 336.1586. Found: 336.1587.

- **Tri(pyridin-2-yl)amine 17**

Experimental procedure

Following the general procedure **Protocol B**, 2-Bromopyridine (96 µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 99% yield desired product as a yellow solid (eluent: ethyl acetate/heptane =50/50).

Identification



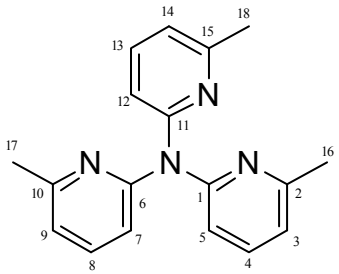
Mp : 139-131 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (br s, 3H, $H_{5,7,15}$), 7.54-7.59 (m, 3H, $H_{3,9,13}$), 7.00-7.03 (m, 3H, $H_{4,8,14}$), 6.94-6.97 (m, 3H, $H_{2,10,12}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4 ($C_{1,6,11}$), 129.3 ($C_{5,7,15}$), 119.4 ($C_{3,9,13}$), 117.8 ($C_{2,10,12}$).
GC/MS: rt = 24.04 min, M/Z = 247.
HRMS calculated for $C_{15}H_{12}N_4$ (M+H) 249.1140. Found: 249.1154

- **tris(6-methylpyridin-2-yl)amine 18**

Experimental procedure

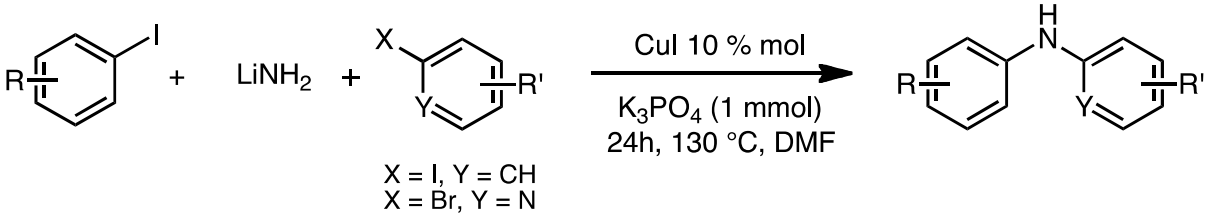
Following the general procedure **Protocol A** (2 mmol of K_3PO_4 were used), 2-bromo-6-methylpyridine (96 µL, 1.0 mmol) was coupled with $LiNH_2$ to afford 94% yield desired product as a yellow oil (eluent: ethyl acetate/heptane =20/80 to 80/20).

Identification



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.41 (t, , *J* = 8.0 Hz, 3H, $H_{4,8,13}$), 6.75-6.77 (d, , *J* = 8.0 Hz, 6H, $H_{3,5,7,9,12,14}$), 2.33 (s, 9H, $H_{16,17,18}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 ($C_{2,10,15}$), 157.0 ($C_{1,6,11}$), 137.5 ($C_{4,8,13}$), 118.3 ($C_{3,9,13}$), 116.5 ($C_{5,7,12}$), 24.4 ($C_{16,17,18}$).
GC/MS: rt = 17.98 min, M/Z = 289.
HRMS calculated for $C_{18}H_{19}N_4$ (M+H) 291.1610. Found: 291.1606

General Procedure for synthesis of unsymmetrical diarylamines 19-30 (1 mmol scale) : (Scheme 3).

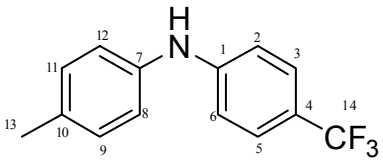


Protocol C: After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel "reaction stations RR98030") or a Schlenk tube equipped with a magnetic stirring bar was charged with CuI (0.1 mmol), $LiNH_2$ (2 mmol), K_3PO_4 (1 mmol) and the first aryl halide RC_6H_4I (1 mmol). The tube was evacuated, back-filled with nitrogen. Then anhydrous and degassed DMF (2.0 mL) was added under a stream of nitrogen by syringe at room temperature. The tube was sealed under a positive pressure of nitrogen, stirred and heated to 130 °C. Then after 6 h at 130 °C, the second aryl halide $R'C_6H_4X$ (0.7 mmol) was added under a stream of nitrogen and the
reaction was heated for an additional 18h at 130°C. After cooling to room temperature, 10 ml of dichloromethane and 130 µL of 1,3-dimethoxybenzene (internal standard) were added. The filtrate is washed twice with water. Gathered aqueous phases were extracted with dichloromethane five times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product (a small sample of the crude was analyzed by gas chromatography). The obtained crude was purified by silica gel chromatography using heptanes as eluent. All products are known compounds (except products **19**, **20**, **23**, **24**, **26**, **29** and **30**) and characterized by comparison of their NMR data with published information. The GC yields were determined by obtaining the correction factors using authentic samples of the expected products.

- **4-methyl-N-(4-(trifluoromethyl)phenyl)aniline 19**

Following the general procedure **Protocol C**, 4-Iodotoluene (218 mg, 1.0 mmol) was coupled with $LiNH_2$ and 4-trifluoromethylidobenzene (103µL, 0.7 mmol) to afford 74% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification

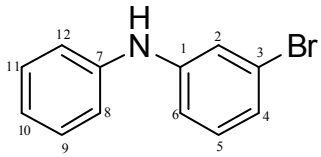


Mp : 76-78 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.45 (d, *J* = 8.2 Hz, 2H, $H_{2,6}$), 7.15-7.13 (d, *J* = 8.2 Hz, 2H, $H_{3,5}$), 7.04-7.07 (d, *J* = 8.5 Hz, 2H, $H_{8,12}$), 6.95-6.97 (d, *J* = 8.5 Hz, 2H, $H_{9,11}$), 5.82 (1H, NH), 2.33 (s, 3H, H_{13}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2 (C_1), 138.3 (C_7), 133.0 (C_{10}), 130.0 ($C_{9,11}$), 129.8 ($C_{3,5}$), 126.7 (q, *J* = 3.4 Hz,C_{14}), 121.2 (C_4), 120.9 ($C_{2,6}$), 114.8 ($C_{8,12}$), 21.0 (C_{13}).
GC/MS: rt = 19.70 min, M/Z = 251.
HRMS calculated for $C_{14}H_{13}F_3N$ (M+H) 252.1000. Found: 252.1019.

- **3-bromo-N-phenylaniline 20**

Following the general procedure **Protocol C**, Iodobenzene (112 µL, 1.0 mmol) was coupled with $LiNH_2$ and 3-Bromo-Iodobenzene (89 µL, 0.7 mmol) to afford 87% yield desired product as a colorless oil (eluent : ethyl acetate/heptane =20/80).

Identification

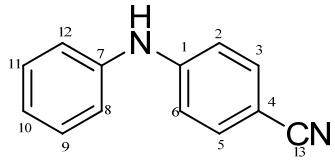


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.24 (m, 1H, $H_{8,12}$), 7.17 (br s, 1H, H_6), 6.99-7.02 (m, 3H, $H_{9,11,5}$), 6.92-6.94 (d, *J* = 7.5 Hz, 1H, H_4), 6.83-6.87 (t, *J* = 7.6 Hz 2H, $H_{2,10}$), 5.63 (1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9 (C_7), 143.1 (C_1), 129.5 (C_5), 129.4 ($C_{9,11}$), 123.1 (C_3), 122.2 (C_4), 121.1 (C_{10}), 119.0 (C_6), 117.8 ($C_{8,12}$), 115.6 (C_2).
GC/MS: rt = 21.65 min, M/Z = 247.
HRMS calculated for $C_{12}H_{13}BrN$ (M+H) 248.0075. Found: 248.0058.

- **4-(phenylamino)benzonitrile 21[4]**

Following the general procedure **Protocol C**, Iodobenzene (112µL, 1.0 mmol) was coupled with $LiNH_2$ and 4-Iodobenzonitrile (160.3 mg, 0.7 mmol) to afford 81% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification

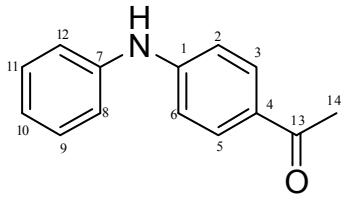


Mp : 98-100 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.42 (d, *J* = 8.5 Hz, 2H, $H_{3,5}$), 7.27-7.31 (t, *J* = 8.5 Hz, 2H, $H_{8,12}$), 7.09-7.11 (d, *J* = 8.5 Hz, 2H, $H_{9,11}$), 7.01-7.06 (t, *J* = 8.5 Hz, 1H, H_{10}), 6.89-6.91 (d, *J* = 8.5 Hz, 2H, $H_{2,6}$), 5.98 (1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0 (C_1), 139.3 (C_7), 133.8 ($C_{3,5}$), 129.7 ($C_{9,11}$), 124.1 (C_{10}), 121.3 ($C_{8,12}$), 119.8 (C_4), 115.0 ($C_{2,6}$), 101.7 (C_{13}).
GC/MS: rt = 23.70 min, M/Z = 194.
HRMS calculated for $C_{13}H_{11}N_2$ (M+H) 195.0922. Found: 195.0921

- **1-(4-(phenylamino)phenyl)ethanone 22[1]**

Following the general procedure **Protocol C**, iodobenzene (112µL, 1.0 mmol) was coupled with $LiNH_2$ and 4-Iodoacetophenone (172.2 mg, 0.7 mmol) to afford 63% yield desired product as a white solid (eluent: ethyl acetate/heptane =20/80).

Identification

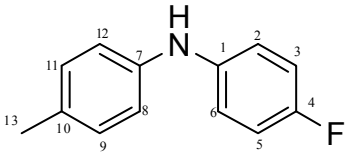


Mp : 104-106 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.81 (d, *J* = 8.8 Hz, 2H, $H_{3,5}$), 7.26-7.30 (m, 2H, $H_{2,6}$), 7.14-7.13 (m, 2H, $H_{8,12}$), 7.00-7.04 (t, *J* = 8.0 Hz, 1H, H_{10}), 6.92-6.94 (d, *J* = 8.0 Hz, 2H, $H_{9,11}$), 6.01 (1H, NH), 2.46 (s, 3H, H_{14}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2 (C_{13}), 147.6 (C_1), 140.5 (C_7), 130.6 ($C_{3,5}$), 130.2 (C_4), 129.7 ($C_{9,11}$), 123.6 (C_{10}), 120.7 ($C_{8,12}$), 114.7 ($C_{2,6}$), 30.2 (C_{14}).
GC/MS: rt = 24.07 min, M/Z = 212.
HRMS calculated for $C_{14}H_{14}NO$ (M+H) 212.1075. Found: 212.1081.

- **4-fluoro-N-(p-tolyl)aniline 23**

Following the general procedure **Protocol C**, 4-Iodotoluene (218 mg, 1.0 mmol) was coupled with $LiNH_2$ and 4-Fluoroiodobenzene (160.3 mg, 0.7 mmol) to afford 44% yield desired product as a colorless oil (eluent : ethyl acetate/heptane =20/80).

Identification

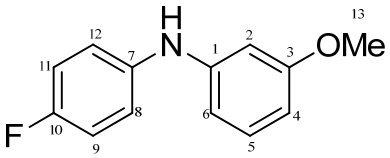


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.45 (d, *J* = 8.2 Hz, 2H, $H_{2,6}$), 7.15-7.13 (d, *J* = 8.2 Hz, 2H, $H_{3,5}$), 7.04-7.07 (d, *J* = 8.5 Hz, 2H, $H_{8,12}$), 6.95-6.97 (d, *J* = 8.5 Hz, 2H, $H_{9,11}$), 5.82 (1H, NH), 2.33 (s, 3H, H_{13}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2 (C_1), 138.3 (C_7), 133.0 (C_{10}), 130.0 ($C_{9,11}$), 129.8 ($C_{3,5}$), 121.2 (C_4), 120.9 ($C_{2,6}$), 114.8 ($C_{8,12}$), 21.0 (C_{13}).
GC/MS: rt = 19.70 min, M/Z = 201.
HRMS calculated for $C_{13}H_{13}FN$ (M+H) 202.1032. Found: 202.1040.

- **3-methoxy-N-(4-(Fluoro)phenyl)aniline 24**

Following the general procedure **Protocol C**, 4-Fluoroiodobenzene (115µL, 1.0 mmol) was coupled with $LiNH_2$ and 3-Iodoanisole (92.4 µL, 0.7 mmol) to afford 81% yield desired product as a yellow solid (eluent : ethyl acetate/heptane =20/80).

Identification

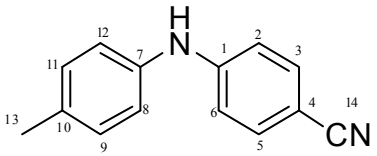


Mp : 58-60 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05-7.09 (t, *J* = 8.2 Hz, 1H, H_6), 6.97-7.01 (m, 2H, $H_{8,12}$), 6.91-6.93 (m, 2H, $H_{9,11}$), 6.46-6.49 (ddd, *J* = 0.7, 2.0, 8.0 Hz, 1H, H_5), 6.44-6.55 (t, *J* = 2.0 Hz, 1H, H_4), 6.37-6.39 (ddd, *J* = 0.7, 2.5, 8.0 Hz, 1H, H_5) 5.51 (1H, NH), 3.70 (s, 3H, H_{13}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (C_3), 159.4 (C_{10}), 145.4 (C_1), 138.7 (C_7), 130.1 (C_5), 121.2 (d, $J_{C\text{-}F}$ = 7.9 Hz, $C_{8,12}$), 115.9 (d, $J_{C\text{-}F}$ = 22.4 Hz, $C_{9,11}$), 109.2 (C_4), 105.6 (C_6), 102.4 (C_2), 55.4 (C_{13}).
GC/MS: rt = 19.20 min, M/Z = 217.
HRMS calculated for $C_{13}H_{13}NOF$ (M+H) 218.0981. Found: 218.0999

- **4-(p-tolylamino)benzonitrile 25[5]**

Following the general procedure **Protocol C**, 4-Iodotoluene (218 mg, 1.0 mmol) was coupled with $LiNH_2$ and 4-Iodobenzonitrile (160.3 mg, 0.7 mmol) to afford 61% yield desired product as a yelow solid (eluent : ethyl acetate/heptane =20/80).

Identification



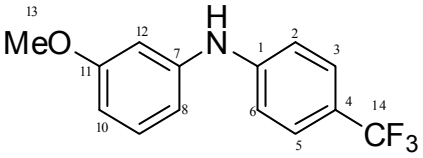
Mp : 102-104 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.39 (d, *J* = 7.5 Hz, 2H, $H_{2,6}$), 7.08-7.11 (d, *J* = 7.8 Hz, 2H, $H_{8,12}$), 6.98-7.00 (d, *J* = 7.8 Hz, 2H, $H_{9,11}$), 6.81-6.83 (d, *J* = 7.5 Hz, 2H, $H_{2,6}$), 5.89 (1H, NH), 2.28 (s, 3H, H_{13}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7 (C_1), 137.2 (C_7), 134.1 (C_{10}), 133.8 ($C_{3,5}$), 130.2 ($C_{9,11}$), 122.1 ($C_{2,6}$), 121.2 (C_4), 120.0 (C_{14}), 114.4 ($C_{8,12}$), 100.0 (C_4), 21.7 (C_4).

GC/MS: rt = 23.10 min, M/Z = 208.
HRMS calculated for $C_{14}H_{13}N_2$ (M+H) 209.1079. Found: 209.1076.

- **3-methoxy-N-(4-(trifluoromethyl)phenyl)aniline 26**

Following the general procedure **Protocol C**, 3-Iodoanisole (132µL, 1.0 mmol) was coupled with $LiNH_2$ and 4-trifluoromethylidobenzene (103µL, 0.7 mmol)to afford 72% yield desired product as a yellow solid (eluent : ethyl acetate/heptane =20/80).

Identification:

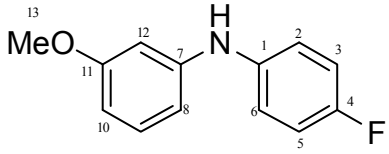


Mp : 68-70°C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.40 (d, *J* = 8.5 Hz, 1H, H_9), 7.11-7.17 (m, 2H, $H_{2,6}$), 6.97-7.00 (d, *J* = 8.5 Hz, 1H, H_{12}), 6.60-6.64 (m, 2H, $H_{3,5}$), 6.57-6.58 (m, 1H, H_{10}), 6.40-6.43 (m, 1H, H_8) 5.84 (1H, NH), 3.70 (s, 3H, H_{13}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (C_{11}), 144.2 (C_1), 142.5 (C_7), 130.1 (C_9), 127.0 (C_4), 126.7 (q, *J* = 3.7 Hz,C_{14}), 115.8 ($C_{3,5}$), 110.6 (C_{10}), 106.5 ($C_{2,6}$), 105.6 (C_8), 103.8 (C_{12}), 55.2 (C_{13}).
GC/MS: rt = 22.85 min, M/Z = 267.
HRMS calculated for $C_{14}H_{13}F_3NO$ (M+H) 268.0871. Found: 268.0875.

- **N-(4-fluorophenyl)-3-methoxyaniline 24**

Following the general procedure **Protocol C**, 3-Iodoanisole (132µL, 1.0 mmol) was coupled with $LiNH_2$ and 4-Fluoroiodobenzene (80.5µL, 0.7 mmol) to afford 92% yield desired product as a yellow solid (eluent : ethyl acetate/heptane =20/80).

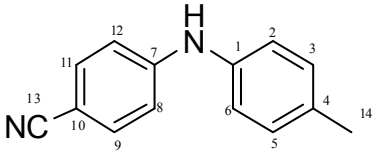
Identification: (^{1}H and ^{13}C NMR spectra are the same as those for the product **24**)



- **4-(p-tolylamino)benzonitrile 25**

Following the general procedure **Protocol C**, 4-Iodobenzonitrile (229 mg, 1.0 mmol) was coupled with $LiNH_2$ and 4-Iodotoluene (152.6 mg, 0.7 mmol) to afford 61% yield desired product as a yelow solid (eluent : ethyl acetate/heptane =20/80).

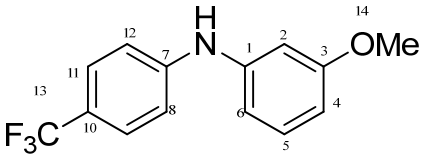
Identification (^{1}H and ^{13}C NMR spectra are the same as those for the product **25**)



- **3-methoxy-N-(4-(trifluoromethyl)phenyl)aniline 26**

Following the general procedure **Protocol C**, 4-trifluoromethyliodobenzene (147 µL, 0.7 mmol) was coupled with $LiNH_2$ and 3-Iodoanisole (92.4 µL, 1.0 mmol) to afford 77% yield desired product as a yellow solid (eluent : ethyl acetate/heptane =20/80).

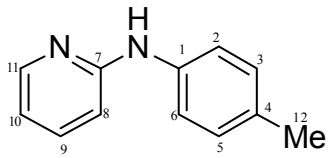
Identification (^1H and ^{13}C NMR spectra are the same as those for the product **26**)



- **N-(p-tolyl)pyridin-2-amine 27**[5]

Following the general procedure **Protocol C**, 4-Iodotoluene (218 mg, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 83% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification

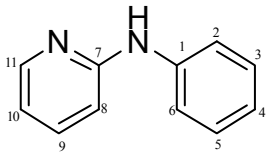


Mp : 110-112**°C**
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (brs, 1H, H_{11}), 7.37-7.41 (t, *J* = 5.2, Hz, 1H, H_{10}), 7.12-7.14 (d, *J* = 8.3 Hz, 2H, $H_{2,6}$), 7.06-7.08 (d, *J* = 8.3 Hz, 2H, $H_{3,5}$), 6.94-6.98 (d, *J* = 7.4, 1H, H_8), 6.61-6.64 (t, *J* = 5.2 Hz, 2H, $H_{9,11}$), 6.37 (1H, NH), 2.27 (s, 3H, C_{13}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (C_7), 148.4 (C_{11}), 137.6 (C_{11}), 137.5 (C_1), 132.8 (C_1), 129.8 ($C_{3,5}$), 121.2 ($C_{2,6}$), 114.7 (C_{10}), 107.7 (C_8).
GC/MS: rt = 18.90 min, M/Z = 184.
HRMS calculated for $C_{12}H_{13}N_2$ (M+H) 185.1079. Found: 185.1095.

- **N-phenylpyridin-2-amine 28**[6]

Following the general procedure **Protocol C**, iodobenzene (112µL, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 98% yield desired product as a white solid (eluent: ethyl acetate/heptane =20/80).

Identification

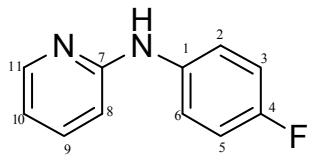


Mp: 106-108 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.14 (m, 1H, H_{11}), 7.40-7.44 (m, 1H, H_9), 7.25-7.26 (m, 1H, H_8), 6.95-7.00 (m, 2H, $H_{2,6}$), 6.79-6.81 (d, *J* = 8.4 Hz, 1H, H_9), 6.65-6.68 (m, 1H, H_{10}), 6.49 (1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (C_7), 148.7 (C_{11}), 140.6 (C_1), 138.0 (C_9), 129.2 ($C_{3,5}$), 123.0 (C_4), 120.3 ($C_{2,6}$), 115.2 (C_{10}), 108.2 (C8).
GC/MS: rt = 18.80 min, M/Z = 169.
HRMS calculated for $C_{11}H_{11}N_2$ (M+H) 171.0922. Found: 171.0947.

- **N-(4-fluorophenyl)pyridin-2-amine 29**

Following the general procedure **Protocol C**, 4-Fluoroiodobenzne (115 µL, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 99% yield desired product as a white solid (eluent : ethyl acetate/heptane =20/80).

Identification

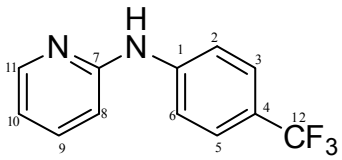


Mp : 102-104 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.112 (m, 1H, H_{11}), 7.38-7.34 (m, 1H,H_9), 7.21-7.25 (m, 2H, $H_{3,5}$), 6.94-6.98 (m, 2H, $H_{2,6}$), 6.64-6.67 (m, 2H, $H_{9,11}$), 6.34 (1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1 (C_4), 159.7 (C_7), 148.4 (C_{11}), 137.7 (C_9), 136.3 (C_1), 122.8 (d, J_{C-F} = 8.9 Hz, $C_{2,6}$), 115.9 (d, J_{C-F} = 22.9 Hz, $C_{3,5}$), 115.0 (C_{10}), 107.9 (C8).
GC/MS: rt = 19.70 min, M/Z = 188.
HRMS calculated for $C_{11}H_{10}N_2F$ (M+H) 189.0828. Found: 189.0849.

- **N-(4-(trifluoromethyl)phenyl)pyridin-2-amine 30**

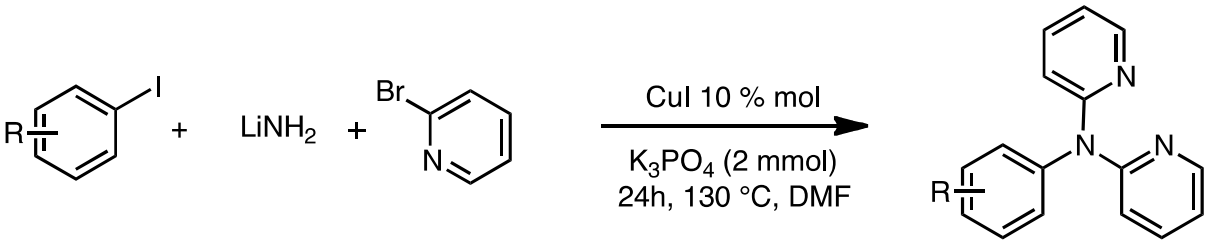
Following the general procedure **Protocol C**, 1-iodo-4-(trifluoromethyl)benzene (148 µL, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 94% yield desired product as a yelow oil (eluent : ethyl acetate/heptane =20/80).

Identification



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (m, 1H, H_{11}), 7.46-7.57 (m, 5H, $H_{2,3,5,6,9}$), 6.82-6.89 (m, 2H, $H_{8,10}$), 6.75 (1H, NH).
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6 (C_7), 148.2 (C_{11}), 145.9 (C_1), 139.4 (C_4), 137.9 ($C_{3,5}$), 126.4 (q, J_{C-F} = 3.6 Hz, C_{12}), 118.1 ($C_{2,6}$), 116.2 (C_{10}), 109.8 (C8).
GC/MS: rt = 19.80 min, M/Z = 238.
HRMS calculated for $C_{12}H_{10}F_3N_2$ (M+H) 239.0718. Found: 239.0732.

General Procedure for synthesis of triarylamine 31-34 (1 mmol scale) : Protocol D (Scheme 4).



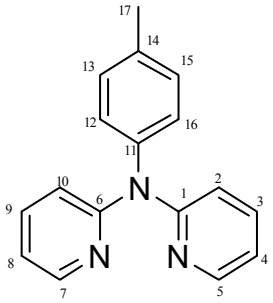
Protocol D: After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel "reaction stations RR98030") or a Schlenk tube equipped with a magnetic stirring bar was charged with CuI (0.1 mmol), $LiNH_2$ (2 mmol), K_3PO_4 (2 mmol) and the aryl halide R-C_6H_4-I (1 mmol). The tube was evacuated, back-filled with nitrogen. Then anhydrous and degassed DMF (2.0 mL) was added under a stream of nitrogen by syringe at room temperature. The tube was sealed under a positive pressure of nitrogen, stirred and heated to 130 °C. Then after 6 h at 130 °C, R'-C_6H_4-Br (0.7 mmol) was added under a stream of nitrogen and the reaction was heated for an additional 18h at 130°C. After cooling to room temperature, 10 ml of dichloromethane and 130 µL of 1,3-dimethoxybenzene (internal standard) were added. The filtrate is washed twice with water. Gathered aqueous phases were extracted with dichloromethane five times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product (a small sample of the crude was analyzed by gas chromatography).The obtained crude was purified by silica gel chromatography using heptanes as eluent.

- **N-(pyridin-2-yl)-N-(p-tolyl)pyridin-2-amine 31**

Experimental procedure

Following the general procedure **Protocol D**, 4-Iodotoluene (218 mg, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 96% yield desired product as a white solid (eluent: heptanes to heptanes/ethyl acetate : 80/20).

Identification



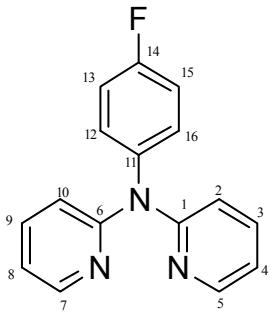
Mp : 124-126°C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23-8,24 (m, 2H, $H_{5,7}$), 7.43-7.48 (m, 2H, $H_{3,9}$), 7.10-7.13 (m, 2H, $H_{13,15}$), 7.01-7.03 (m, 2H, $H_{5,7}$), 6-90-6.92 (m, 2H, $H_{2,10}$), 6.82-6.84 (m, 2H, $H_{12,16}$), 2.30 (s, 3H, H_{17}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3 ($C_{1,6}$), 148.7 ($C_{5,7}$), 142.0 (C_{11}), 137.5 ($C_{3,9}$), 135.6 (C_{14}), 130.8 ($C_{13,15}$), 127.3($C_{2,10}$), 117.9 ($C_{12,16}$), 116.4($C_{4,8}$).
GC/MS: rt = 20.72 min, M/Z = 261.
HRMS calculated for $C_{17}H_{16}N_3$ (M+H) 262.1353. Found: 262.1344.

- **N-(4-fluorophenyl)-N-(pyridin-2-yl)pyridin-2-amine 32**

Experimental procedure

Following the general procedure **Protocol B**, 4-Fluoroiodobenzene (115 µL, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 98% yield desired product as a white solid (eluent : heptane).

Identification



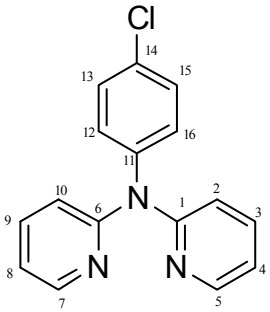
Mp : 120-122°C
^{1}H NMR (400 MHz, $CDCl_3$): 8.23-8,24 (m, 2H, $H_{5,7}$), 7.46-7.50 (m, 2H, $H_{3,9}$), 7.09-7.12 (m, 2H, $H_{13,15}$), 7.00-7.02 (m, 2H, $H_{5,7}$), 6-90-6.92 (m, 2H, $H_{2,10}$), 6.83-6.86 (m, 2H, $H_{12,16}$).
^{13}C NMR (100 MHz, $CDCl_3$): 160.7 ($C_{1,6}$), 159.3 (C_{11}), 148.4 ($C_{5,7}$), 137.5 ($C_{3,9}$), 129.2 (d, J = 8.5 Hz, $C_{13,15}$), 118.1 ($C_{4,8}$), 116.7 ($C_{2,10}$), 115.9 (d, J = 8.5 Hz, $C_{12,16}$).
107.9 (C8).**GC/MS:** rt = 20.30 min, M/Z = 265.
HRMS calculated for $C_{16}H_{13}N_3F$ (M+H) 266.1094. Found: 266.1096.

- **N-(4-Chlorophenyl)-N-(pyridin-2-yl)pyridin-2-amine 33**

Experimental procedure

Following the general procedure **Protocol B**, 4-Chloroiodobenzene (239 mg, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 82% yield desired product as a white solid (eluent : heptane).

Identification



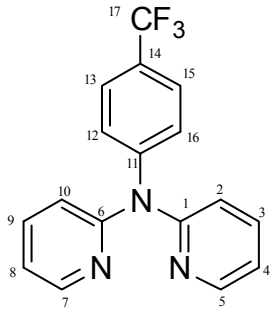
Mp : 132-134°C
^{1}H NMR (400 MHz, $CDCl_3$): 8.28-8,29 (m, 2H, $H_{5,7}$), 7.49-7.54 (m, 2H, $H_{3,9}$), 7.26-7.29 (d, J = 8.7 Hz ,2H, $H_{13,15}$), 7.05-7.07 (m, 2H, $H_{5,7}$), 6.88-6.92 (m, 4H, $H_{2,10,12,16}$).
^{13}C NMR (100 MHz, $CDCl_3$): 166.3 ($C_{1,6}$), 153.9 (C_{11}), 148.3 ($C_{5,7}$), 138.0 ($C_{3,9}$), 129.9 ($C_{13,15}$), 128.4 ($C_{12,16}$), 118.5 ($C_{4,8}$), 116.8 (d, $C_{2,10}$).
GC/MS: rt = 22.40 min, M/Z = 281.
HRMS calculated for $C_{16}H_{13}N_3F$ (M+H) 282.0803. Found: 282.0803.

- **N-(pyridin-2-yl)-N-(4-(trifluoromethyl)phenyl)pyridin-2-amine 34**

Experimental procedure

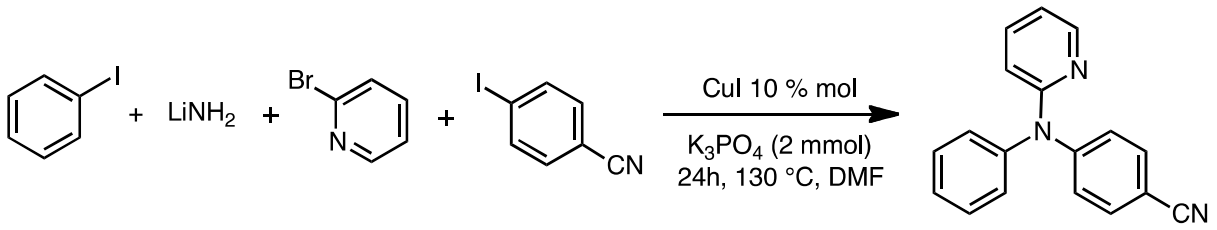
Following the general procedure **Protocol D**, 4-trifluoromethyliodobenzene (147 µL, 1.0 mmol) was coupled with $LiNH_2$ and 2-Bromopyridine (67µL, 0.7 mmol) to afford 93% yield desired product as a yellow oil (eluent : heptanes/ethyl acetate : 8/2).

Identification



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28-8.30(m, 2H , $H_{5,7}$), 7.49-7.56(m, 4H , $H_{3,9,13,15}$), 7.15-7.17 (d, J = 8.0 Hz, 2H , $H_{12,16}$), 6.92-6.96 (m, 4H, $H_{2,4,8,10}$).
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7 ($C_{1,6}$), 148.9 ($C_{5,7}$), 139.8 (C_{11}), 138.0 ($C_{3,9}$), 127.4.6 (C_{14}), 126.6 (q, $J_{C\text{-}F}$ = 3.4 Hz,C_{17}), 125.8($C_{13,15}$), 119.2 ($C_{12,16}$), 117.7($C_{4,2,8,10}$).
GC/MS: rt = 20.34 min, M/Z = 315.
HRMS calculated for $C_{17}H_{13}N_3F_3$ (M+H) 316.1062. Found: 316.56.

General Procedure for synthesis of unsymmetrical triarylamine 35 (1 mmol scale) : Protocol E (table 3).



35 42%

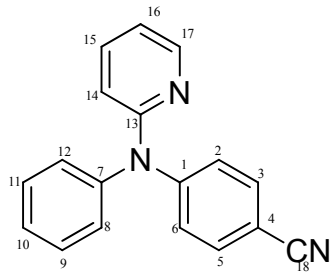
Protocol E: After standard cycles of evacuation and back-filling with dry and pure nitrogen, an oven-dried Radley tube (Carousel "reaction stations RR98030") or a Schlenk tube equipped with a magnetic stirring bar was charged with CuI (0.1 mmol), $LiNH_2$ (2 mmol), K_3PO_4 (2 mmol) and the Iodobenzene (1 mmol). The tube was evacuated, back-filled with nitrogen. Then anhydrous and degassed DMF (2.0 mL) was added under a stream of nitrogen by syringe at room temperature. The tube was sealed under a positive pressure of nitrogen, stirred and heated to 130 °C. Then after 6 h at 130 °C, 4-Iodobenzonitrile (0.7 mmol) and 2-Bromopyridine (0.7 mmol) werre added under a stream of nitrogen and the reaction was heated for an additional 18h at 130°C. After cooling to room temperature, 10 ml of dichloromethane and 130 µL of 1,3-dimethoxybenzene (internal standard) were added. The filtrate is washed twice with water. Gathered aqueous phases were extracted with dichloromethane for five times. Organic layers were gathered, dried over Na_2SO_4, filtered and concentrated in vacuum to yield the crude product (a small sample of the crude was analyzed by gas chromatography).The obtained crude was purified by silica gel chromatography.

- **4-(phenyl(pyridin-2-yl)amino)benzonitrile 35**

Experimental procedure

Following the general procedure **Protocol E**, Iodobenzene (112 µL, 1.0 mmol), 2-Bromopyridine (67,2 µL, 0.7 mmol) and 4-Iodobenzonitrile (160.3 mg, 0.7 mmol) was coupled with $LiNH_2$ to afford 51% yield desired product as a white solid (eluent : ethyl acetate/heptane =50/50).

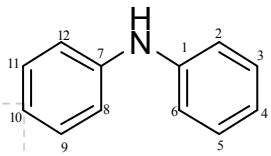
Identification

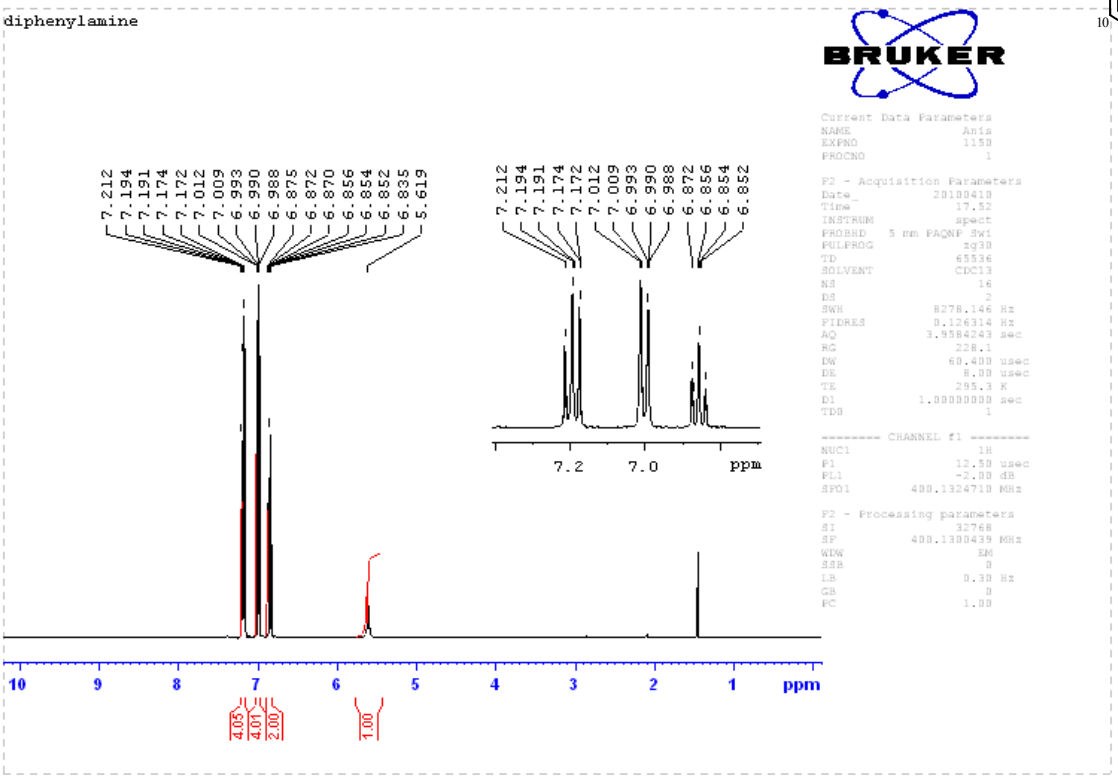


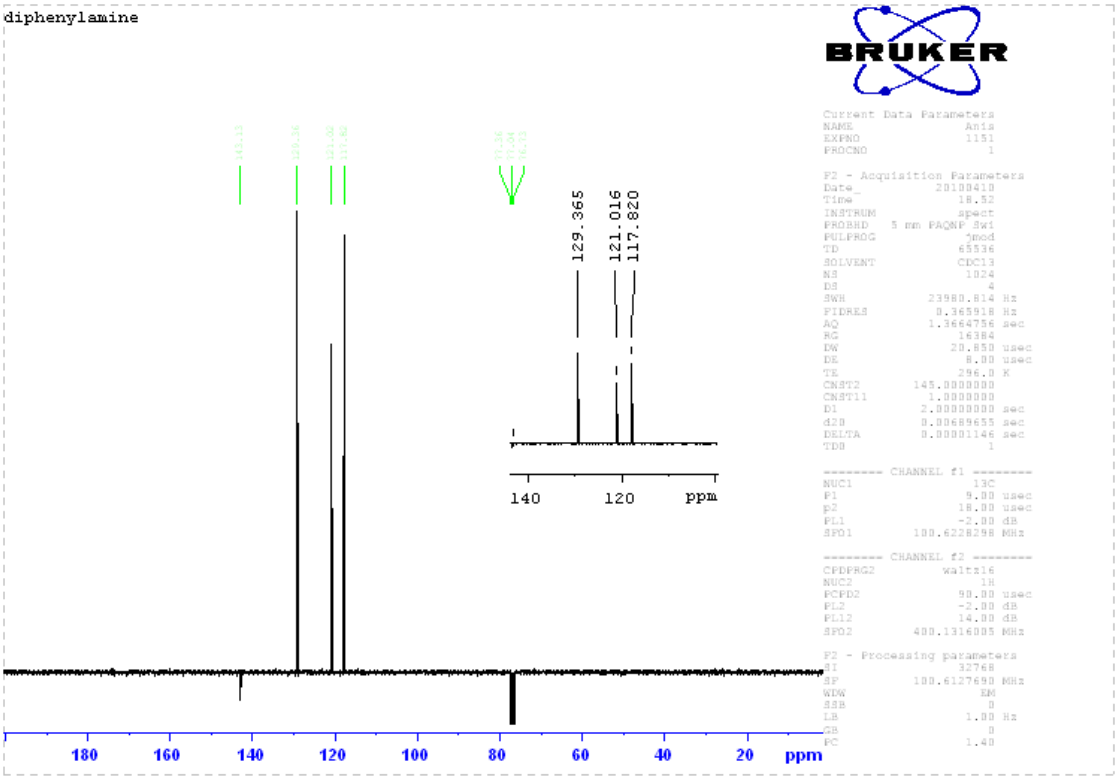
Mp : 112-114°C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br, 1H, H_{17}), 7.47-7.49 (m, 1H, H_{15}), 7.42-7.44 (d, J = 8.8 Hz, 2H, $H_{3,5}$), 7.31-7.35 (t, J = 7.6 Hz, 2H, $H_{9,11}$), 7.18-7.21 (m, 1H, H_{10}), 7.06-7.12 (dd, J = 8.8, 16,4 Hz, 4H,, $H_{2,6,8,12}$), 6.87-6.89 (d, J = 8.8 Hz ,1H, H_{16}), 6.71-6.73 (m, 1H, H_{14}).
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1 (C_{13}), 150.0 (C_1), 148.6 (C_{17}), 144.9 (C_7), 138.1 (C_{13}), 133.1 ($C_{3,5}$), 130.0 ($C_{9,11}$), 127.6 ($C_{8,12}$), 126.4 (C_{10}), 123.1 ($C_{2,6}$), 119.5 (C_{18}), 118.5 (C_{16}), 116.2 (C_{14}), 105.0 (C_4).
GC/MS: rt = 24.88 min, M/Z = 271.
HRMS calculated for $C_{18}H_{14}N_3$ (M+H) 272.1188. Found: 272.1195

Below are given some selected ^{1}H and ^{13}C NMR spectra:

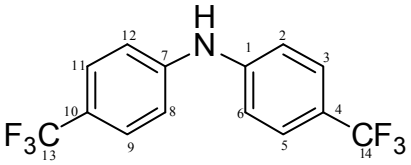
Diphenylamine 1

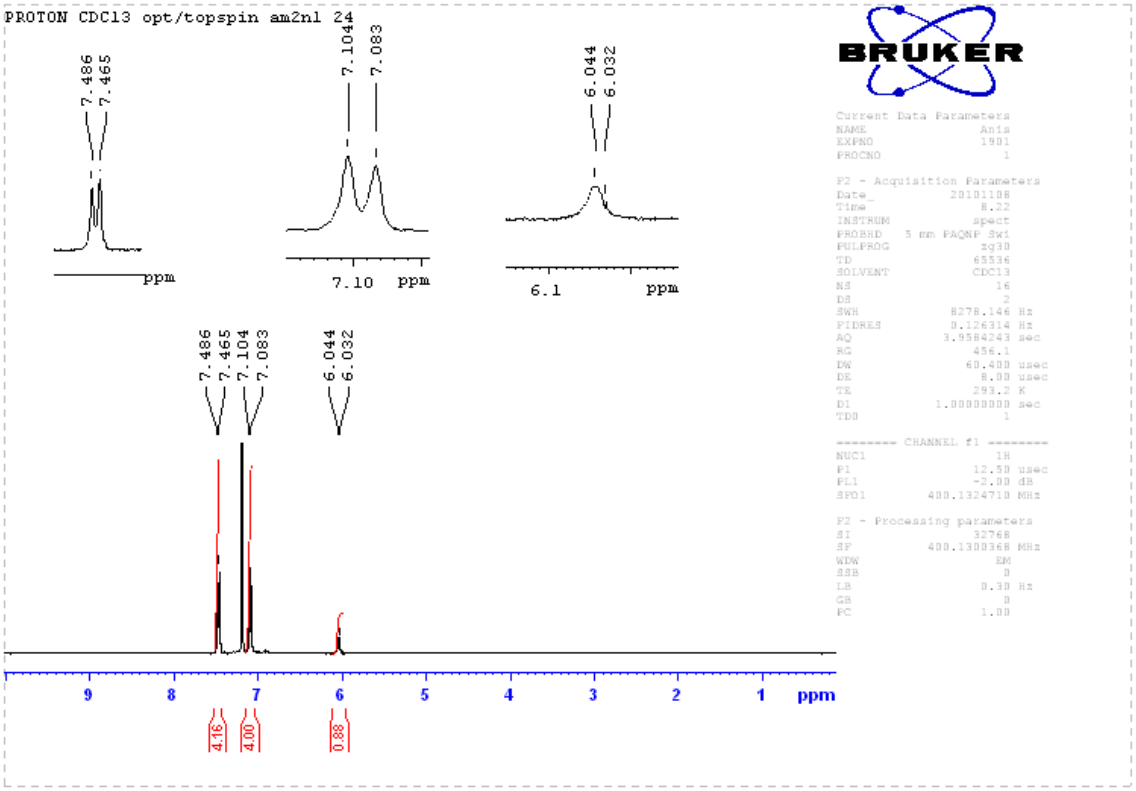


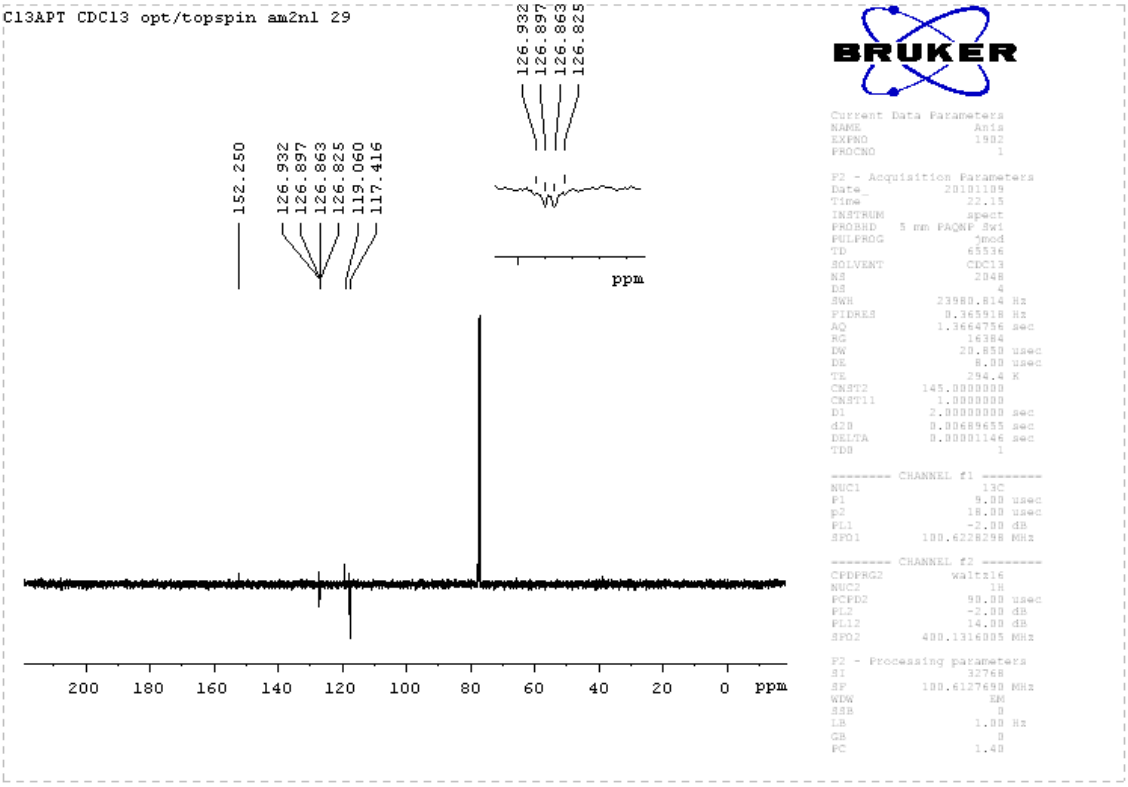




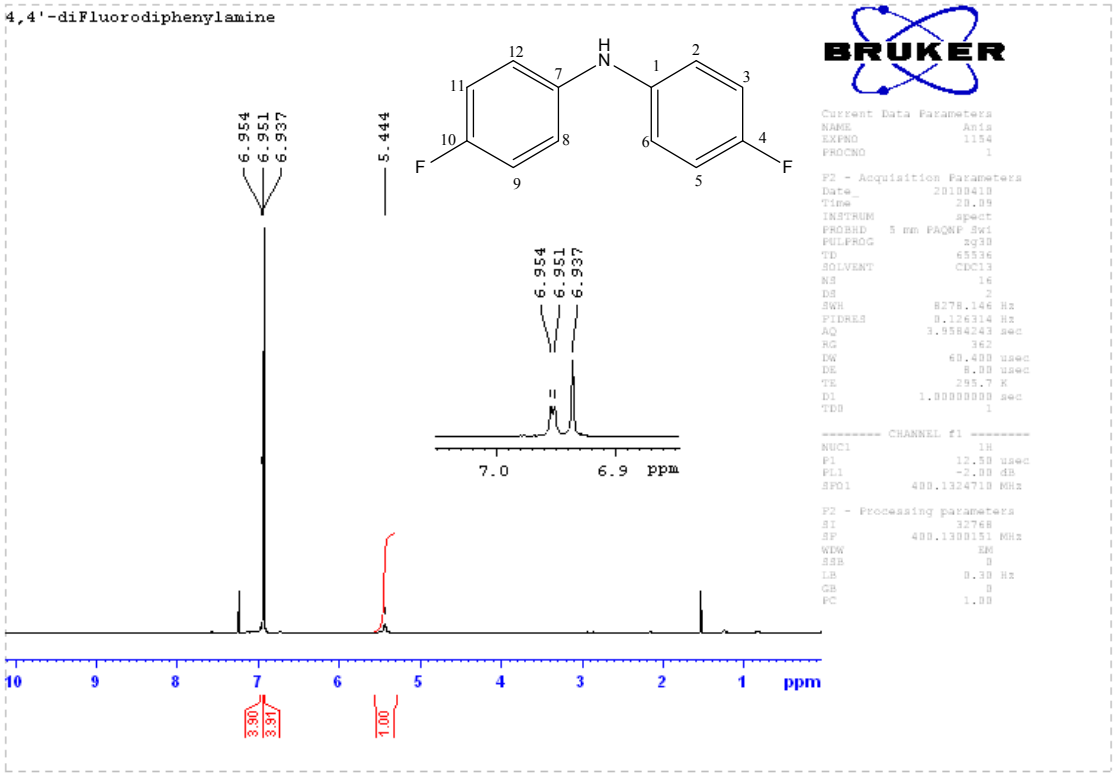
bis(4-(trifluoromethyl)phenyl)amine 2

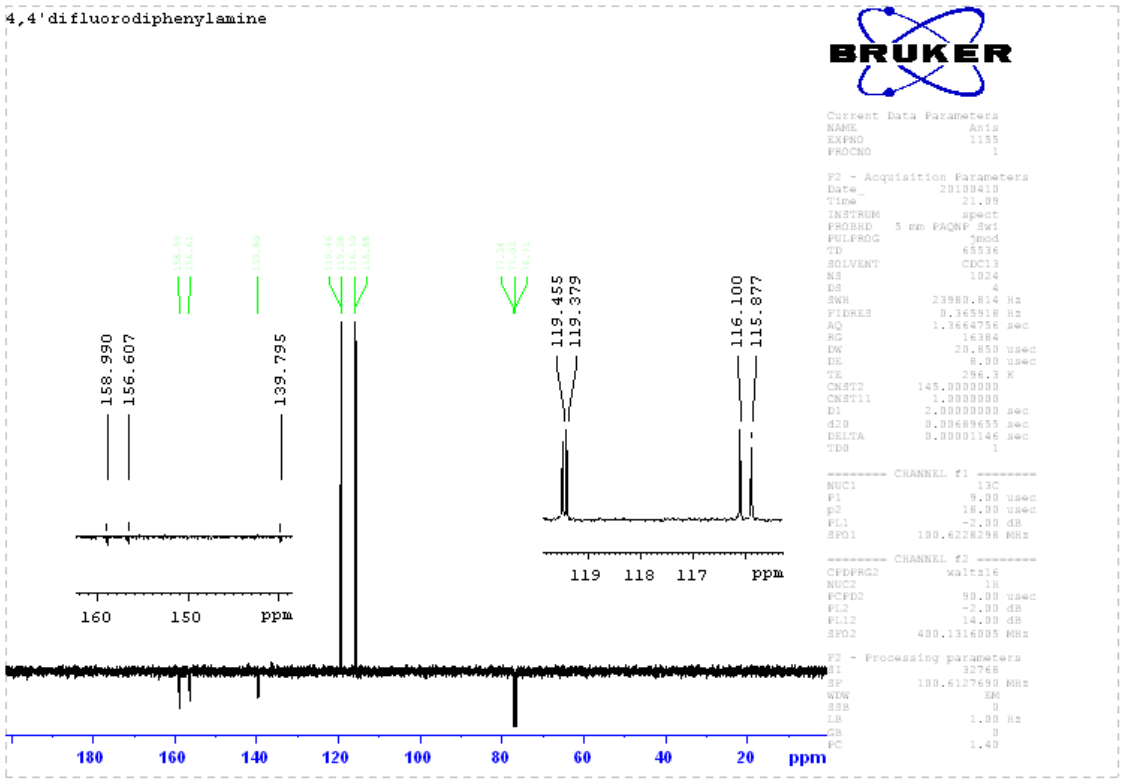




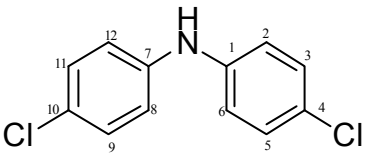


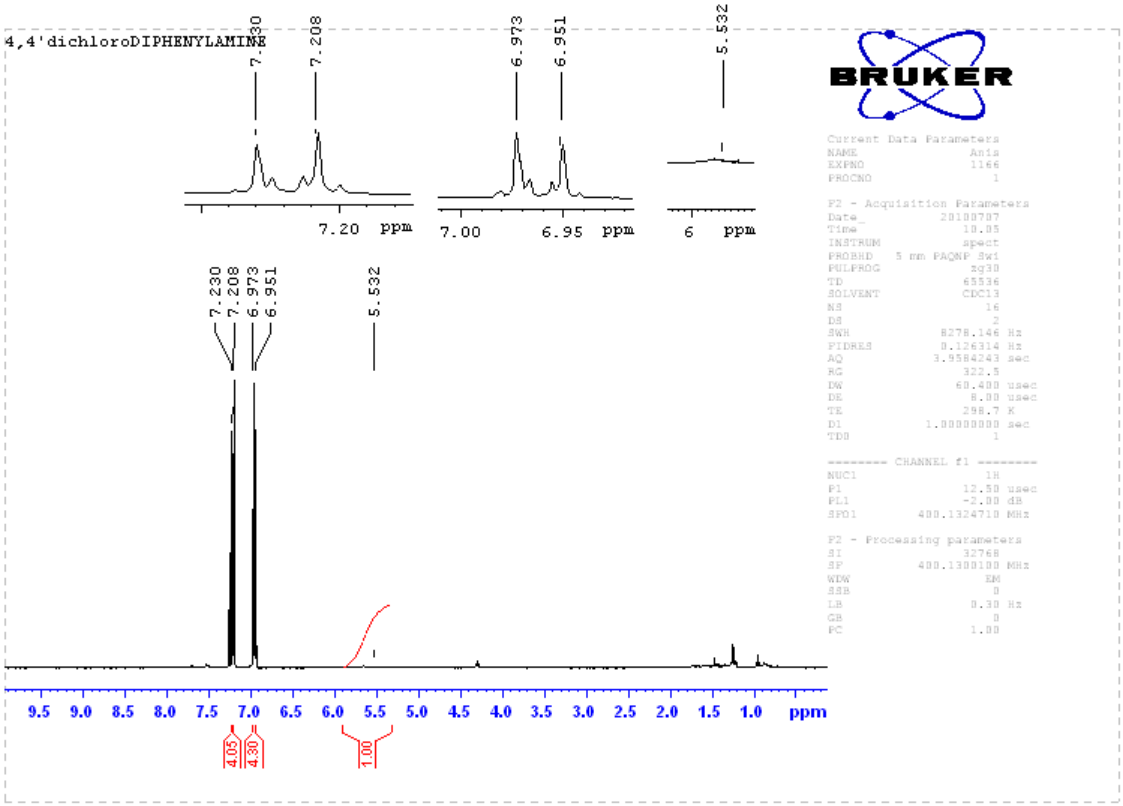
bis(4-fluorophenyl)amine 3

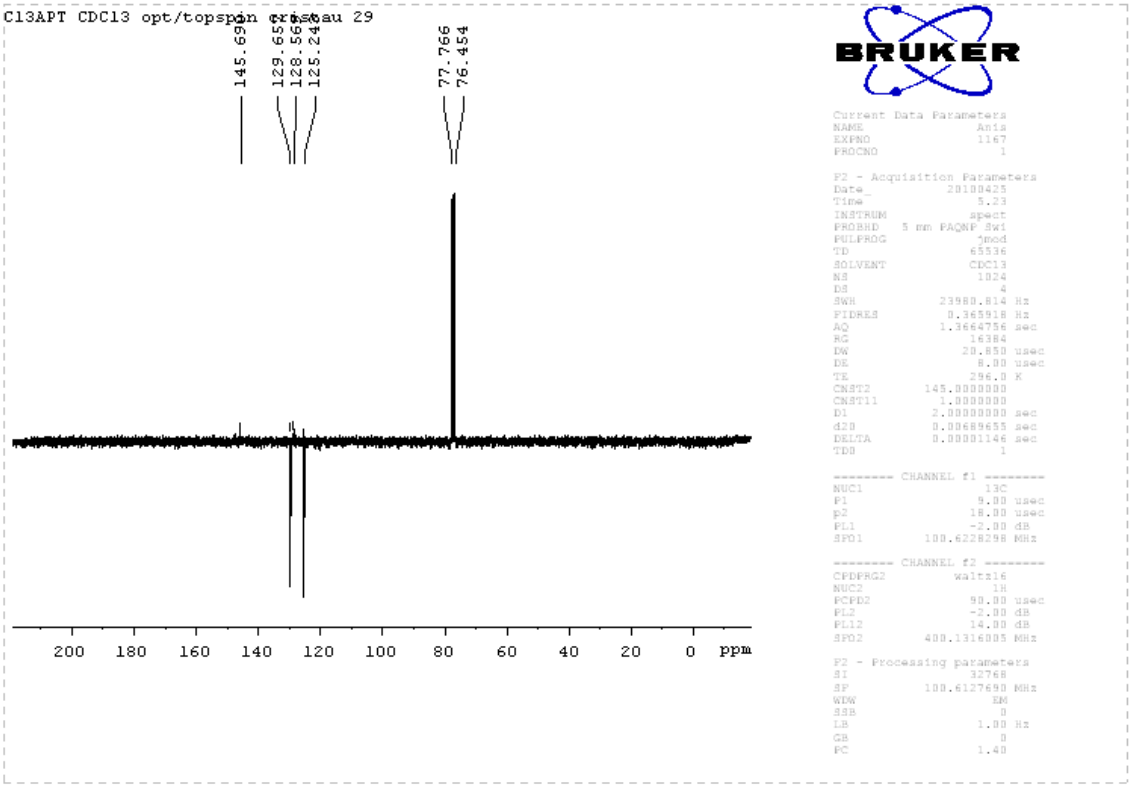




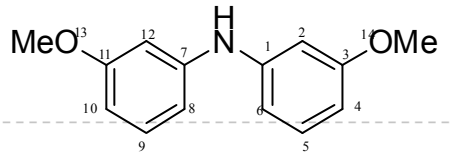
bis(4-clorophenyl)amine 4

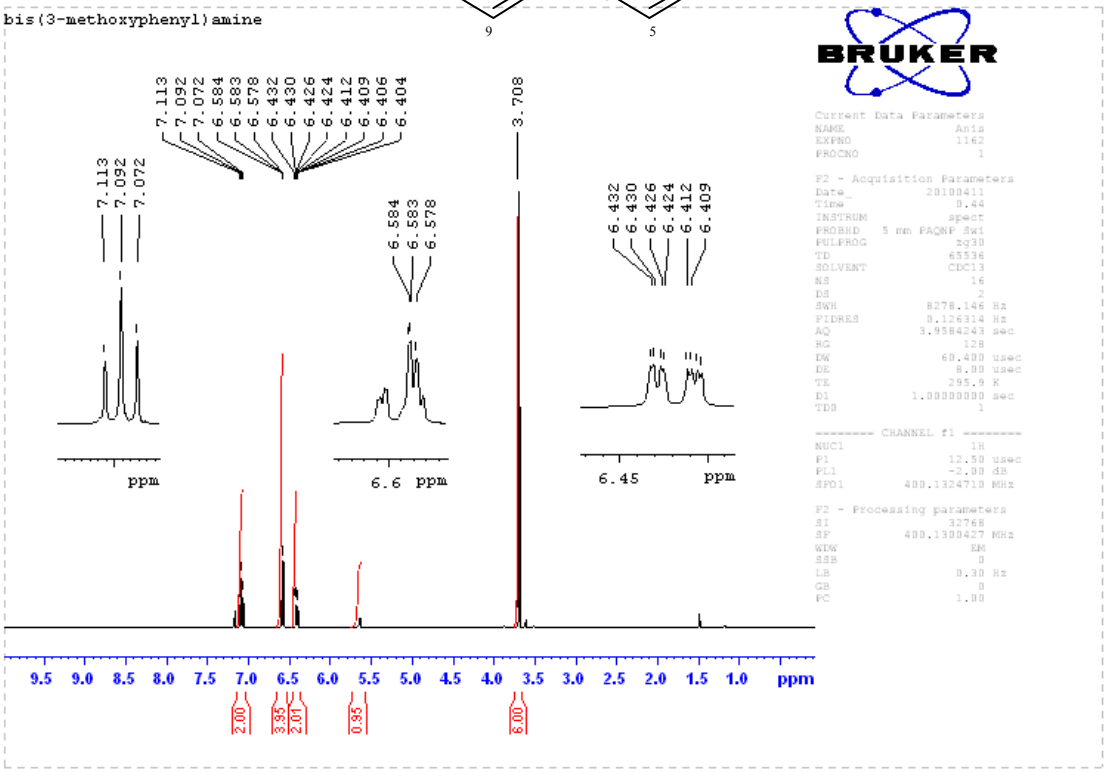


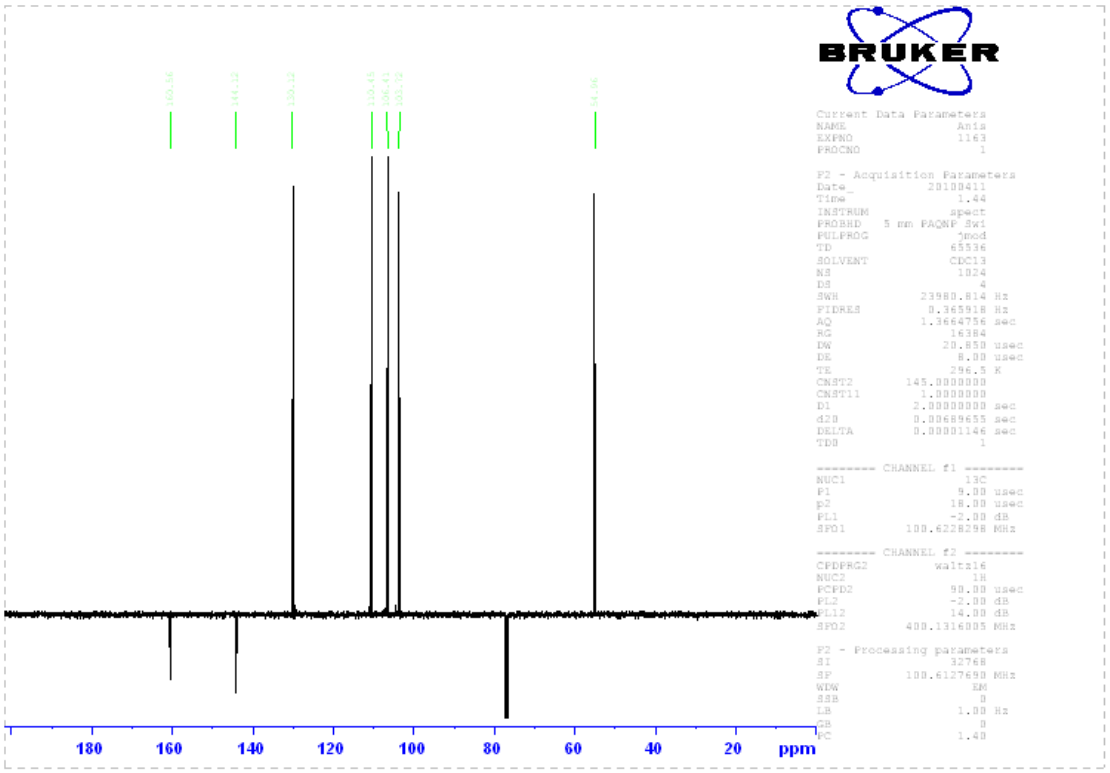




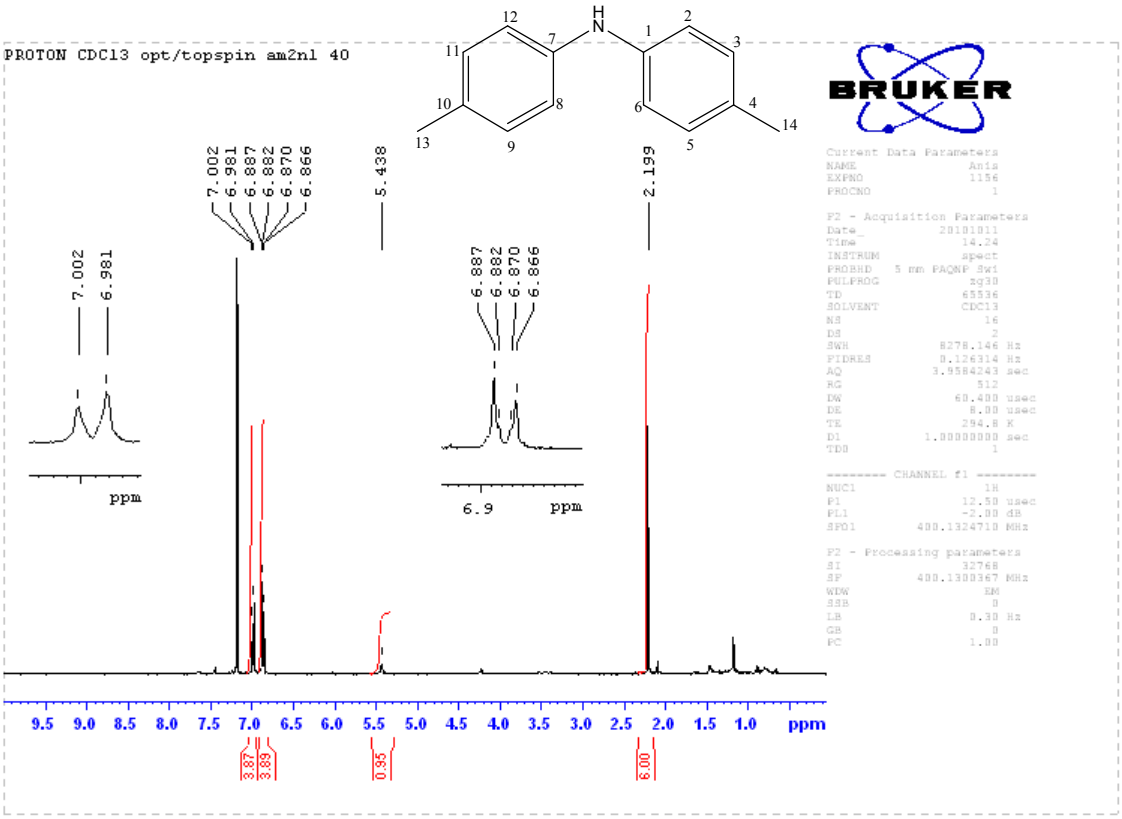
bis(3-methoxyphenyl)amine 6

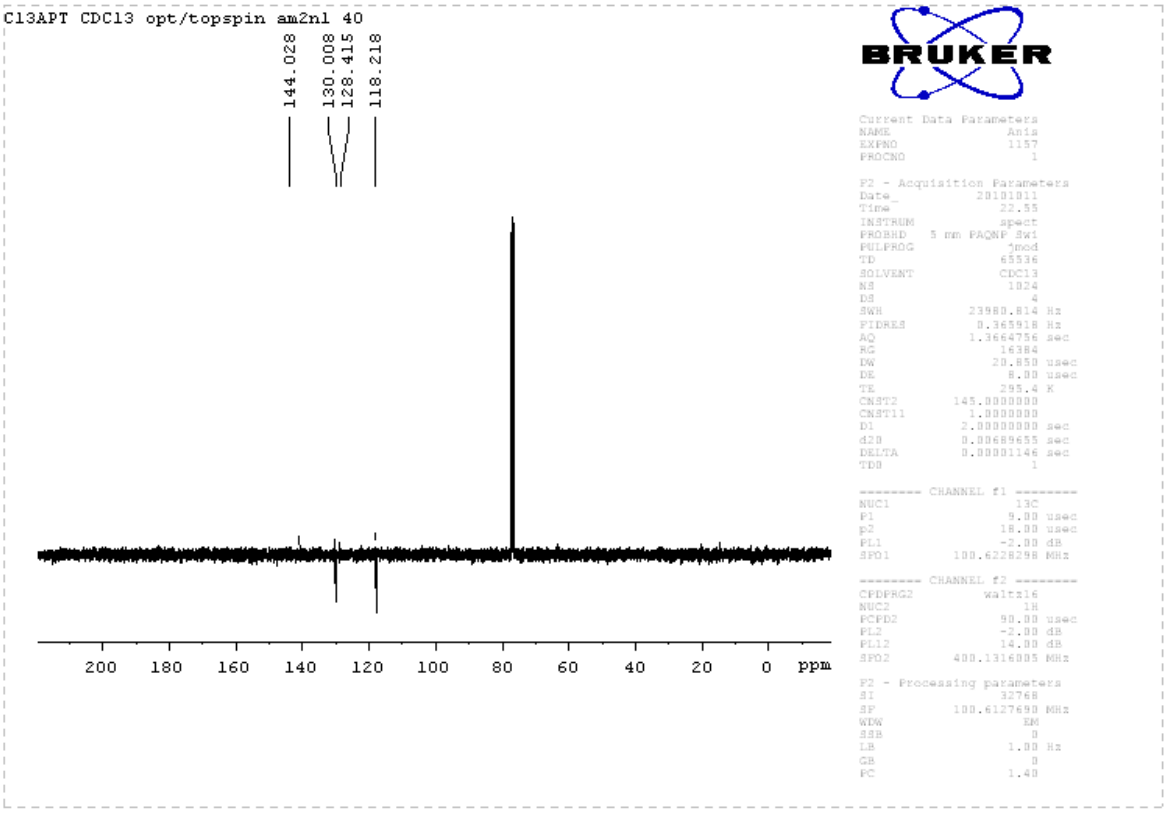




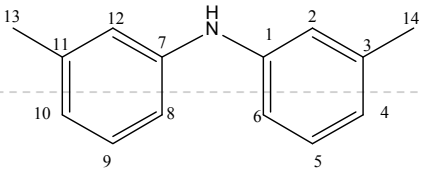


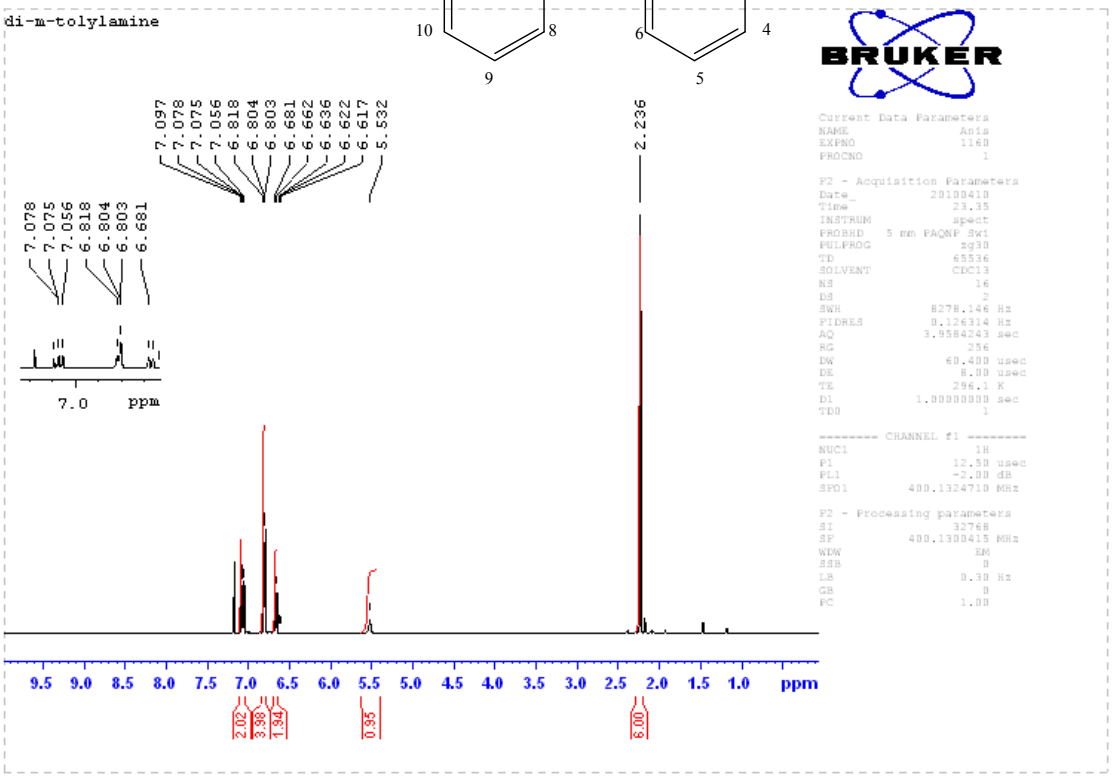
di-p-tolylamine 7

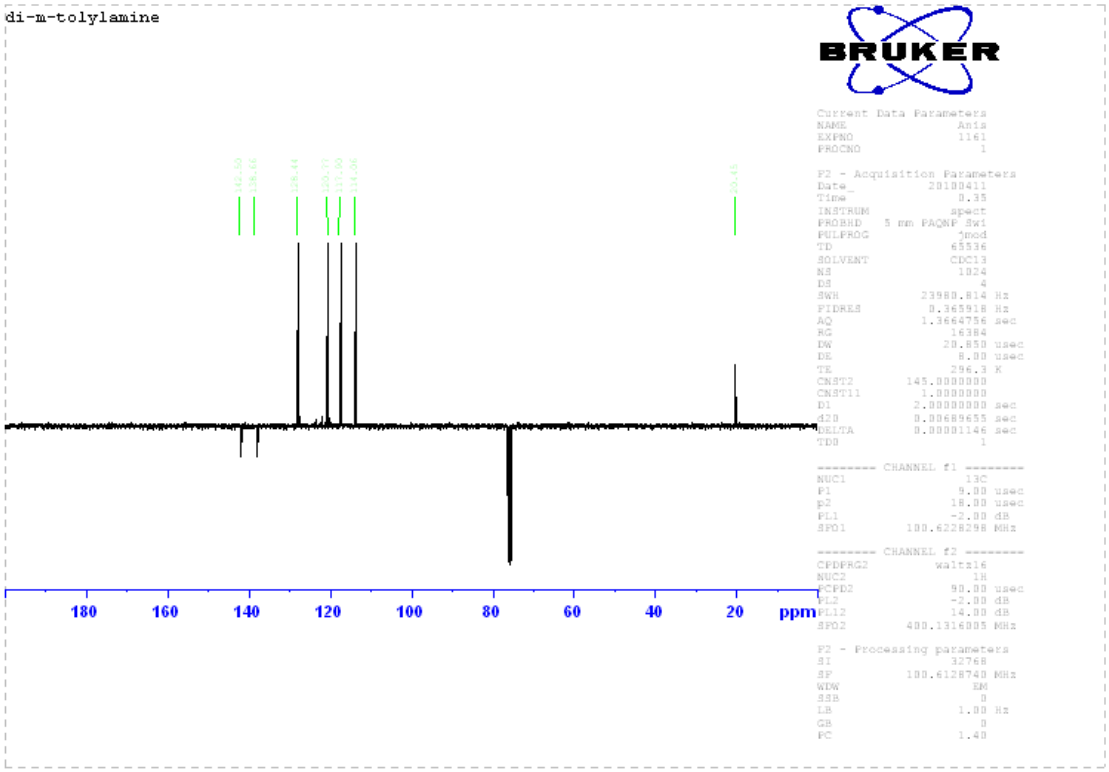




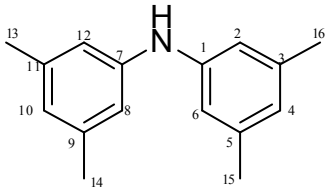
di-*m*-tolylamine 8

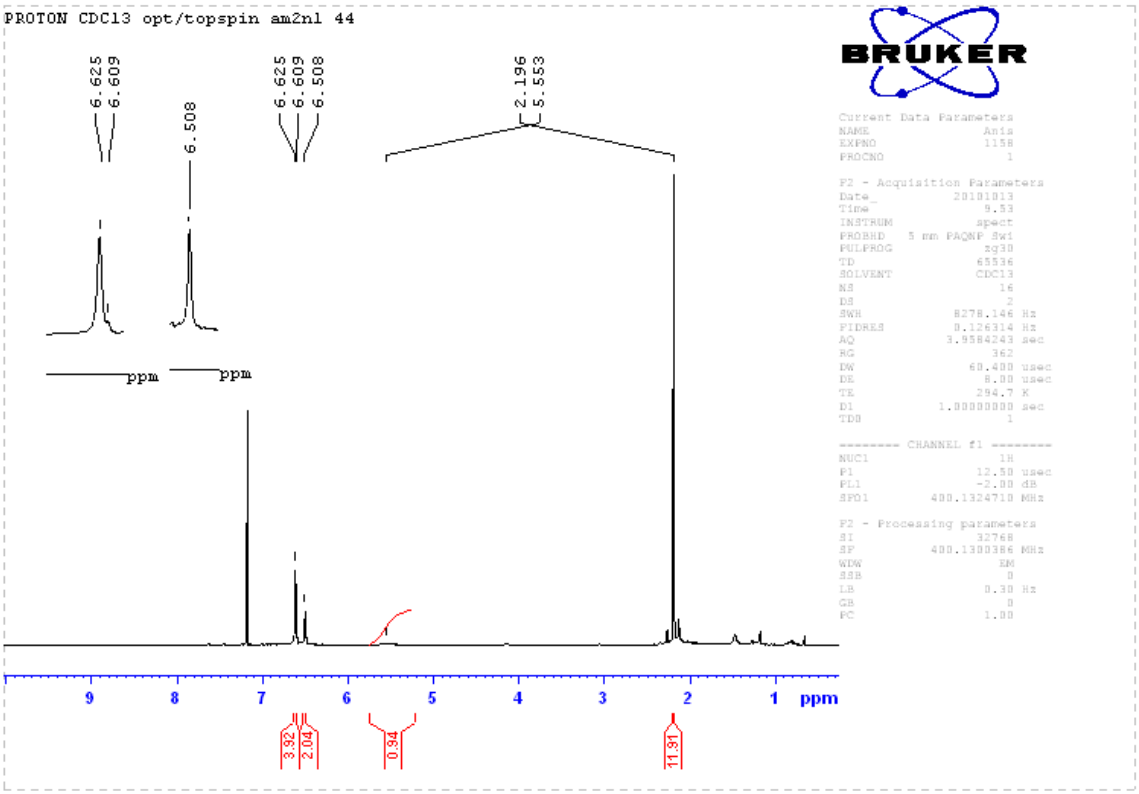


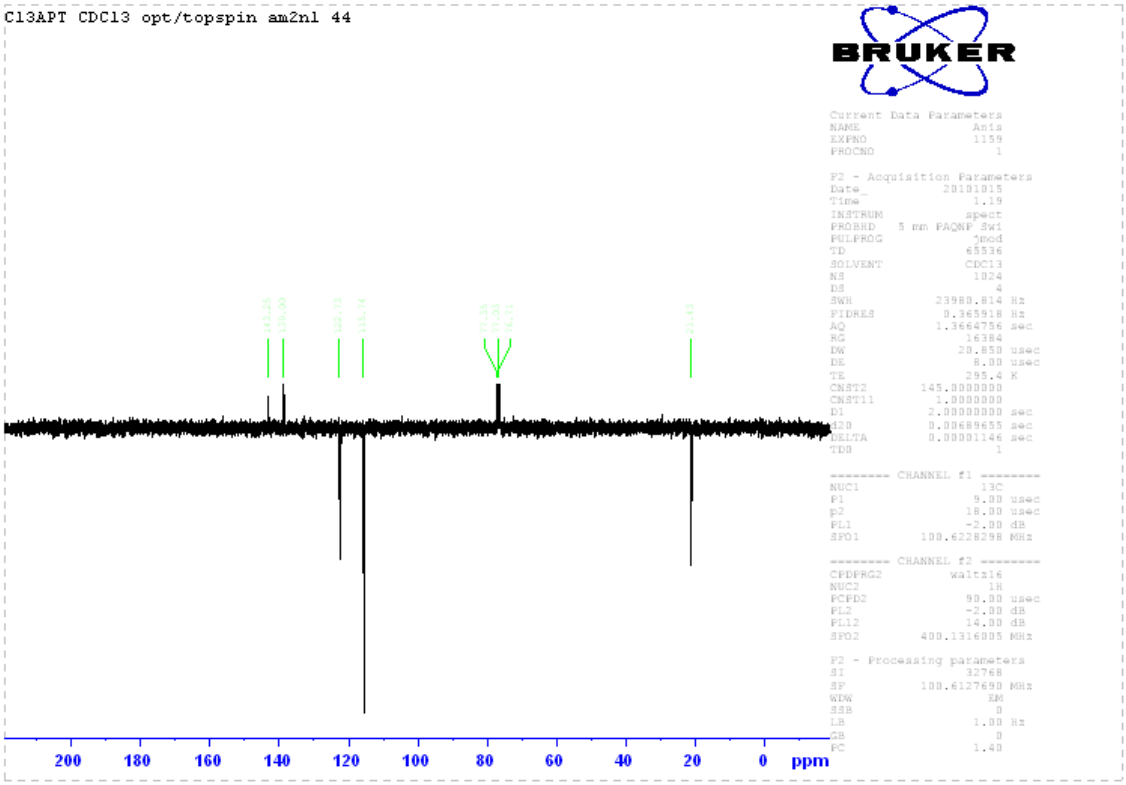




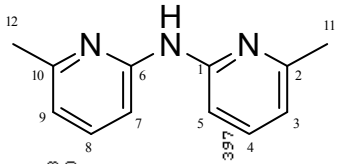
bis(3,5-dimethylphenyl)amine 9

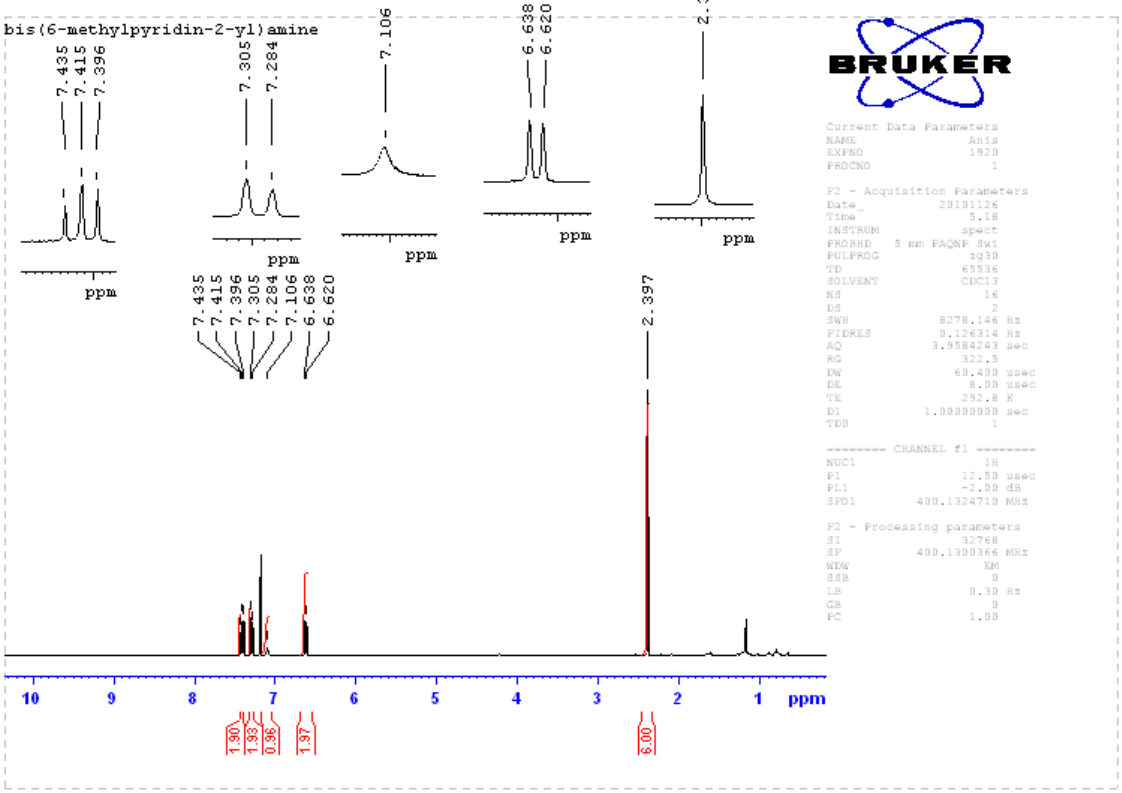


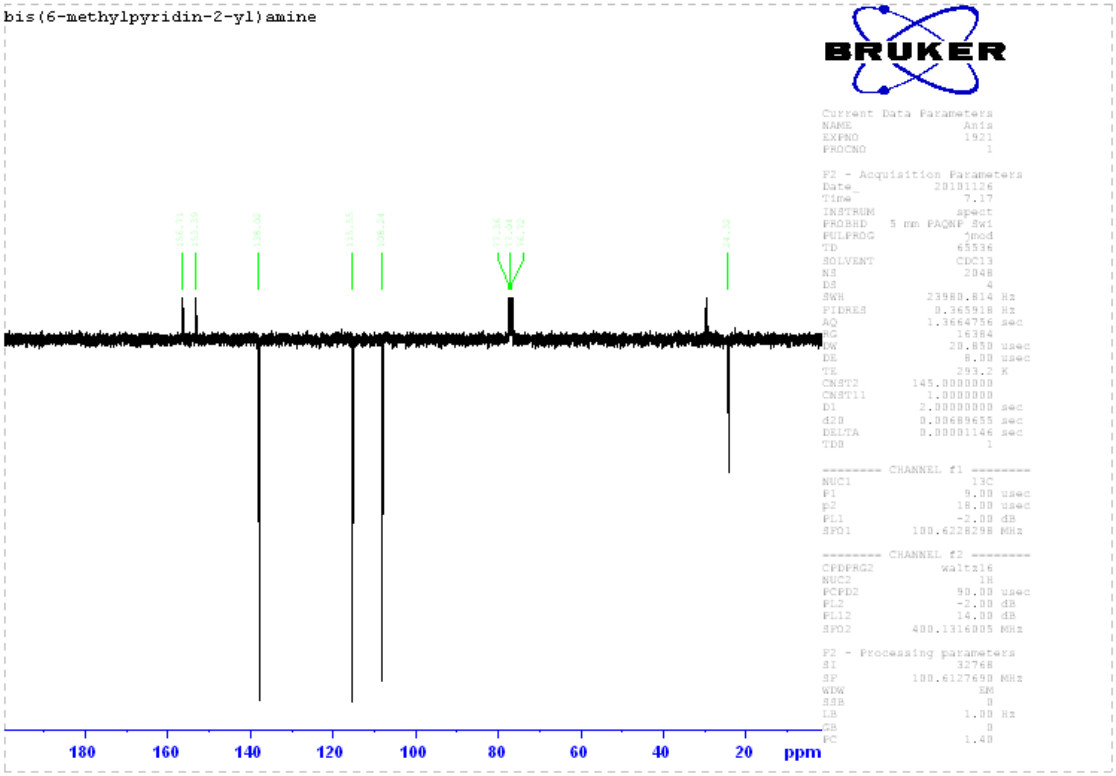




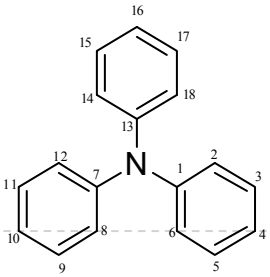
bis(3-methylpyridin-2-yl)amine 10

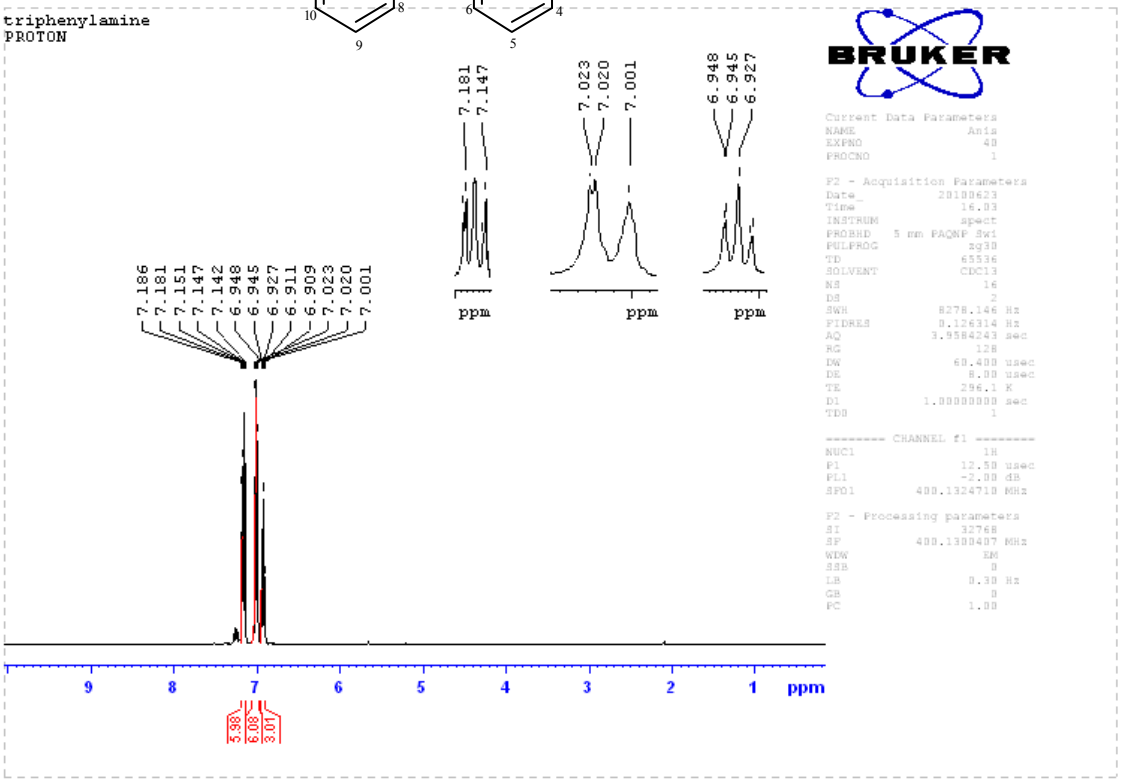


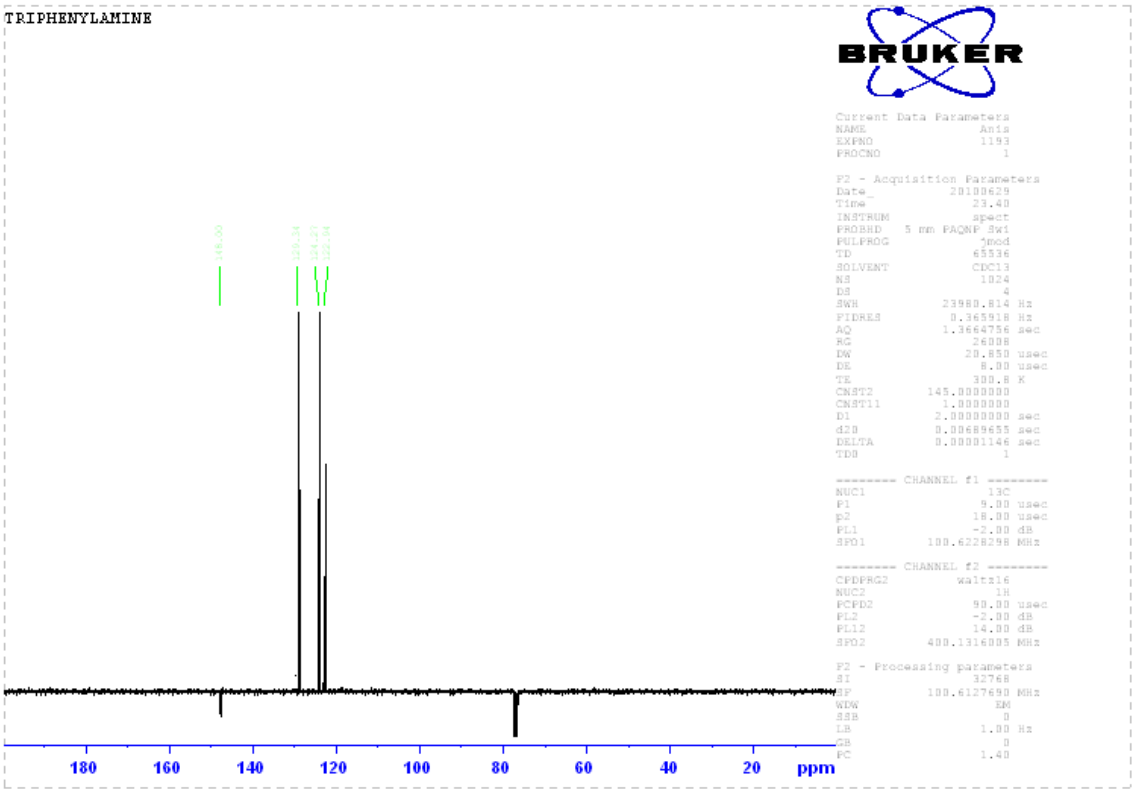




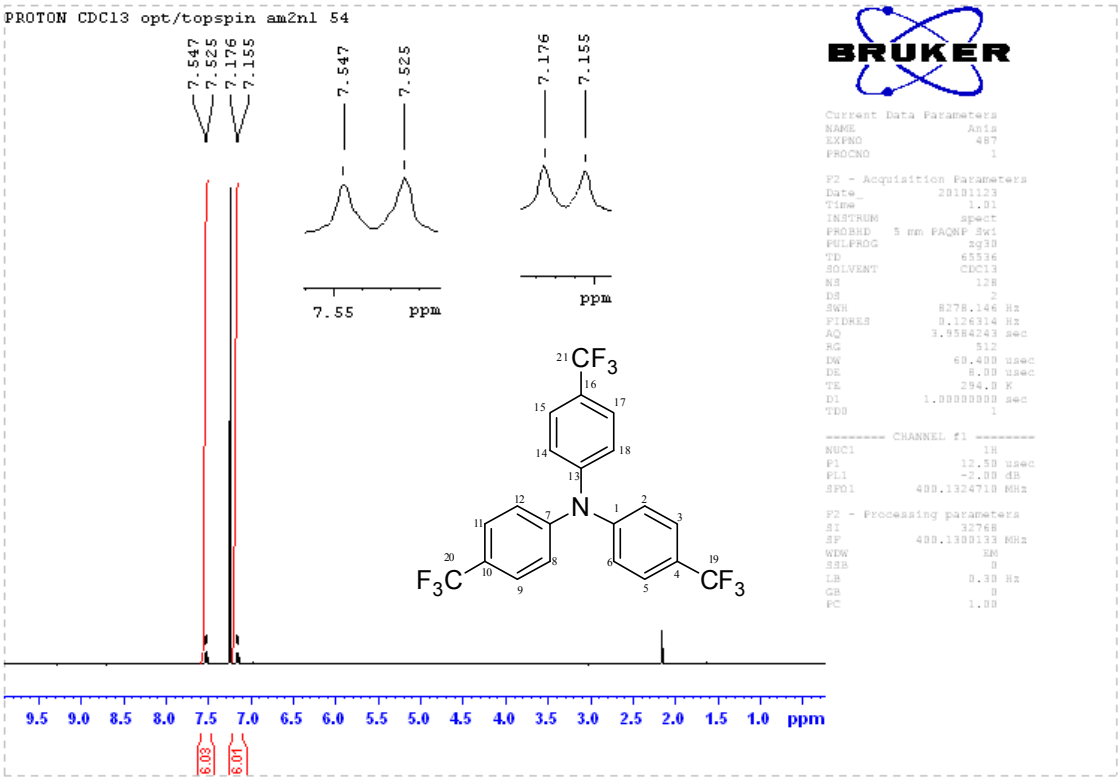
Triphenylamine 11

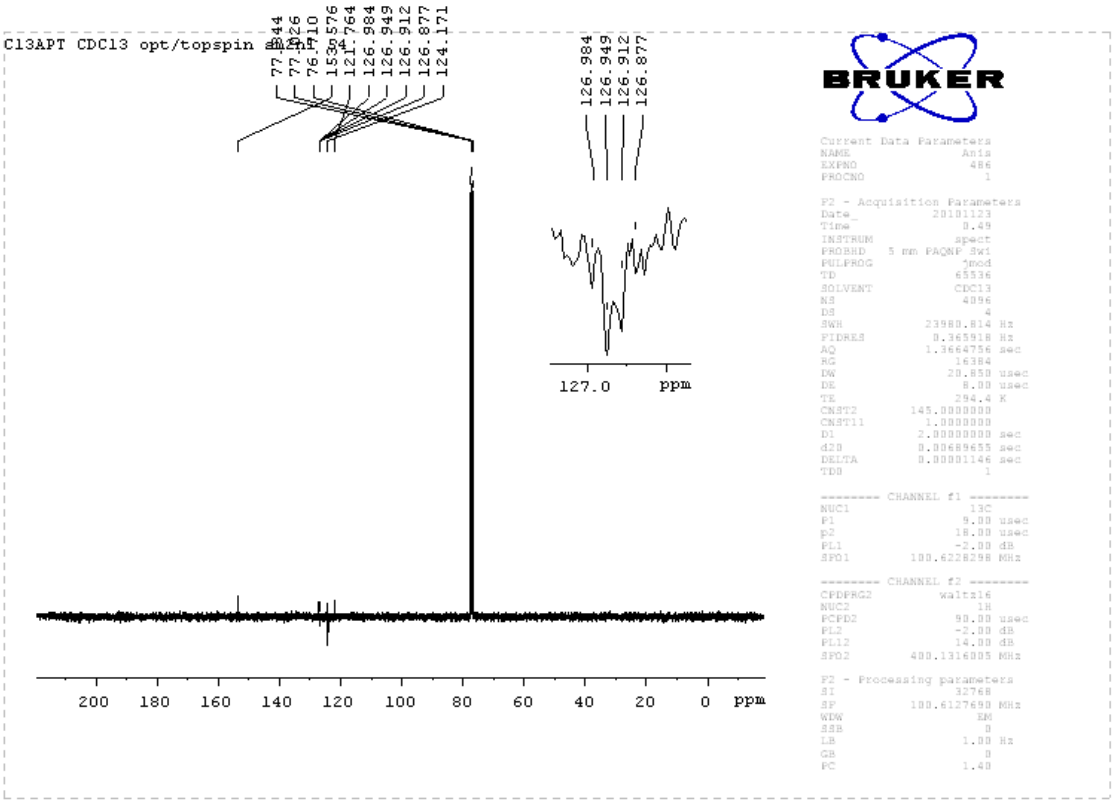




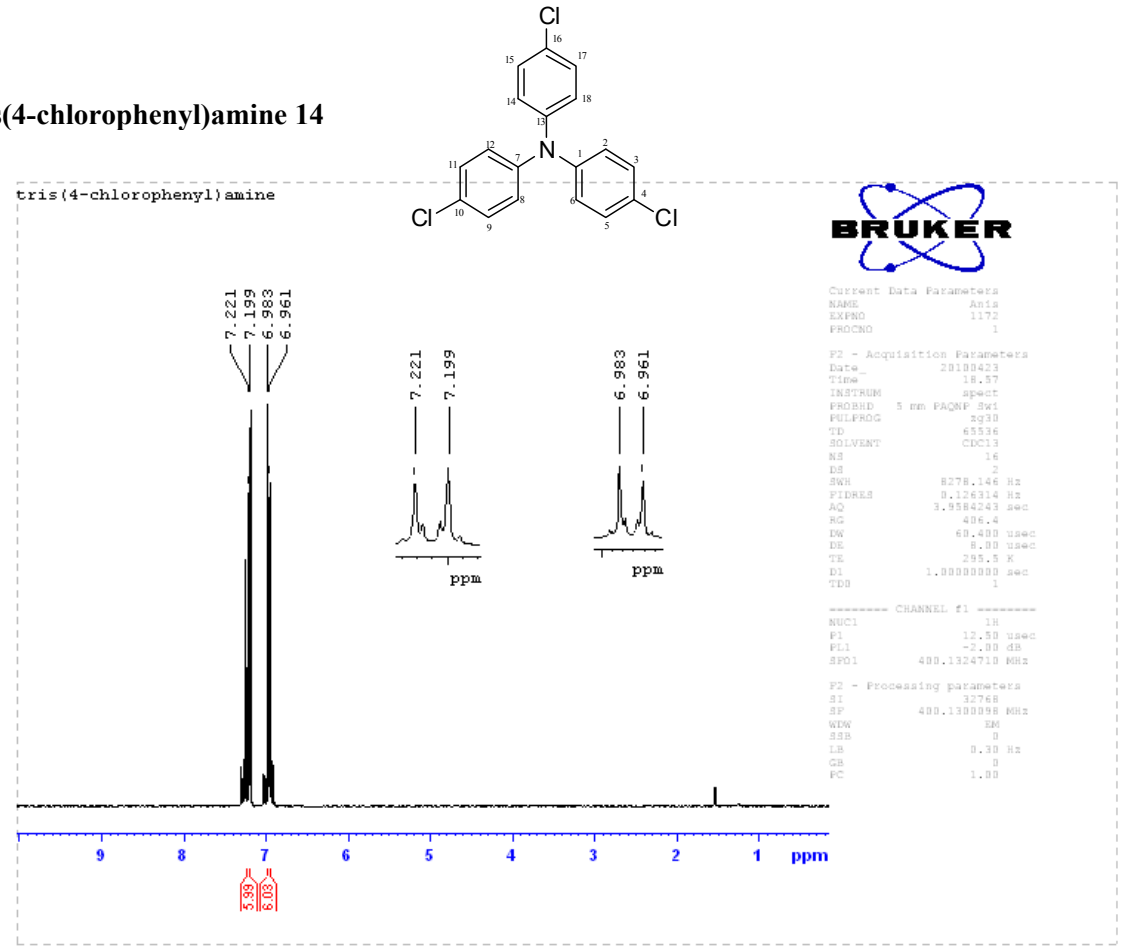


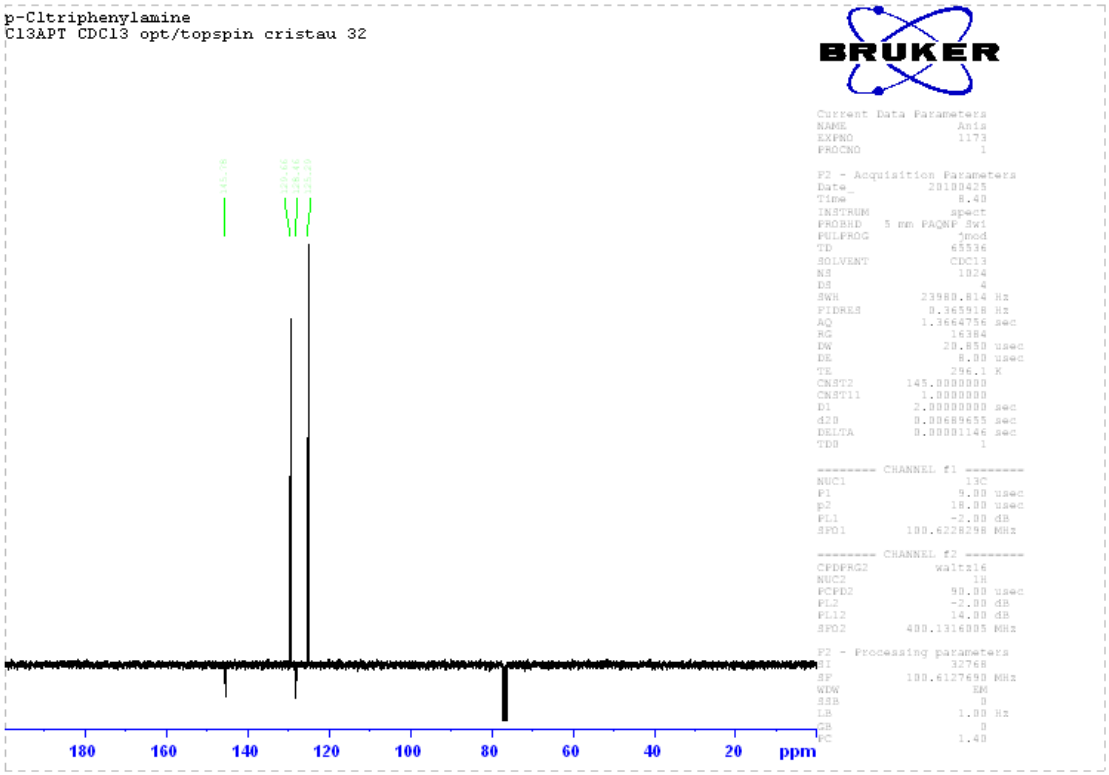
tris(4-(trifluoromethyl)phenyl)amine 12



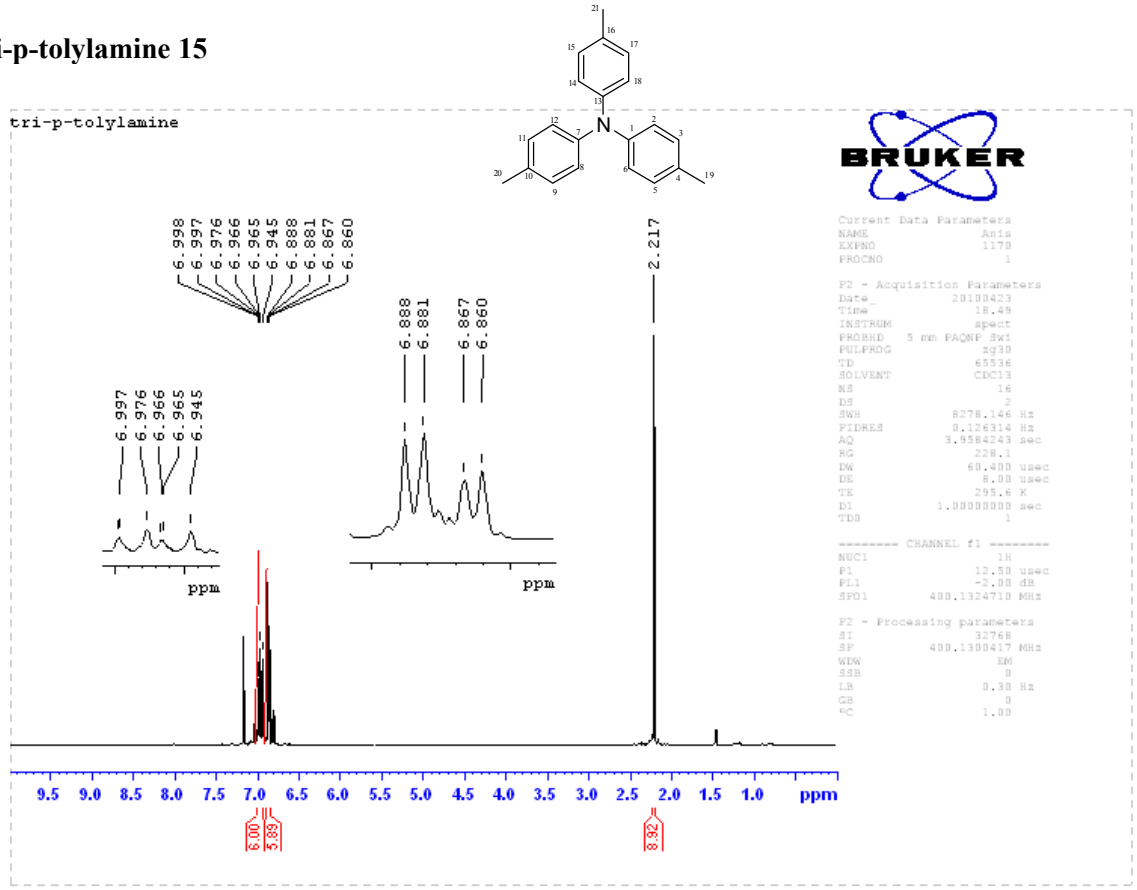


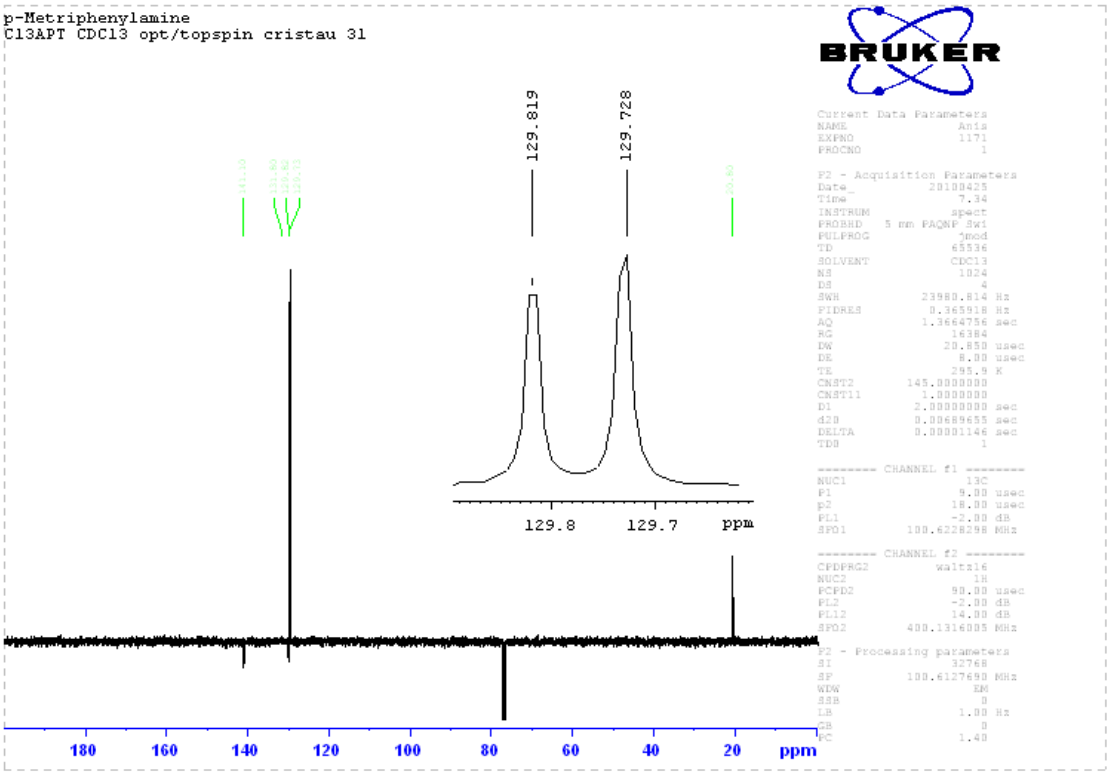
tris(4-chlorophenyl)amine 14



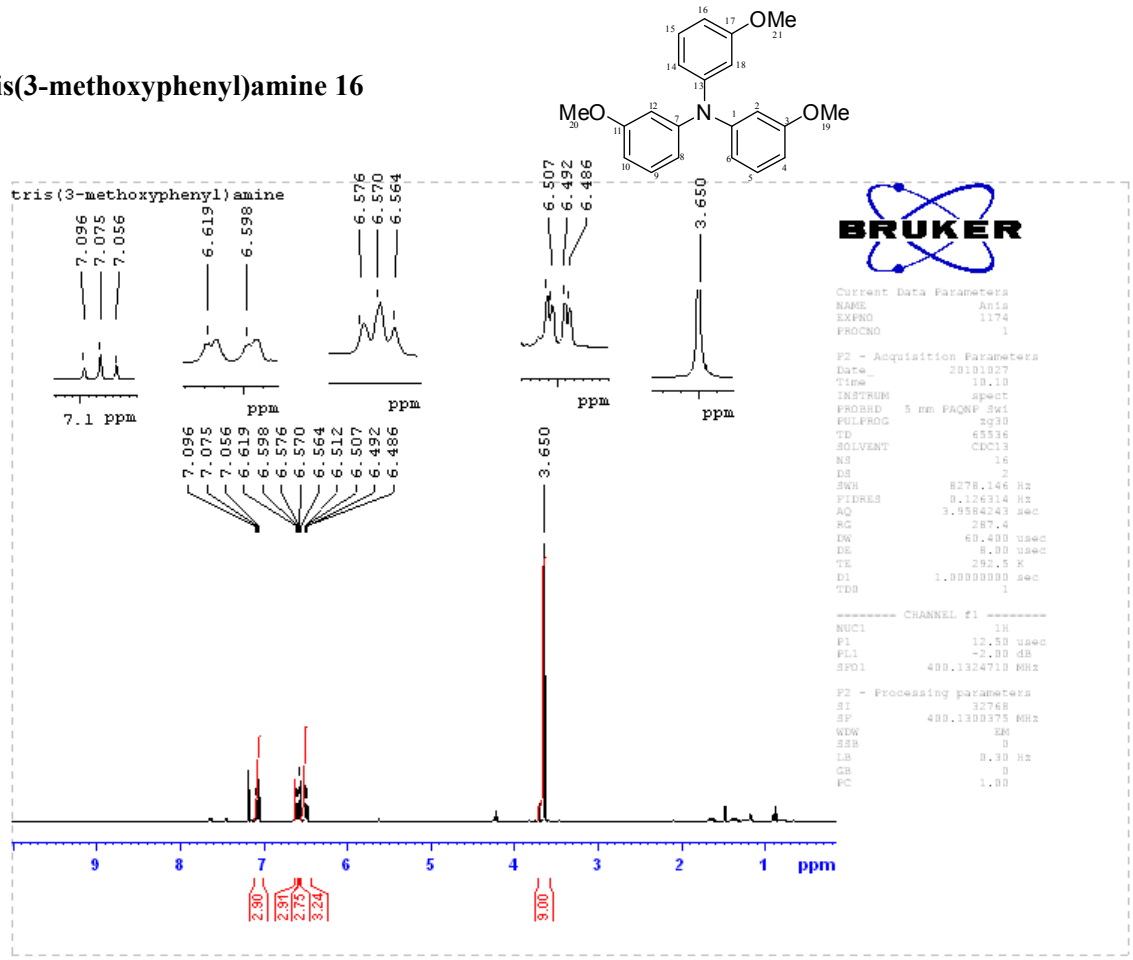


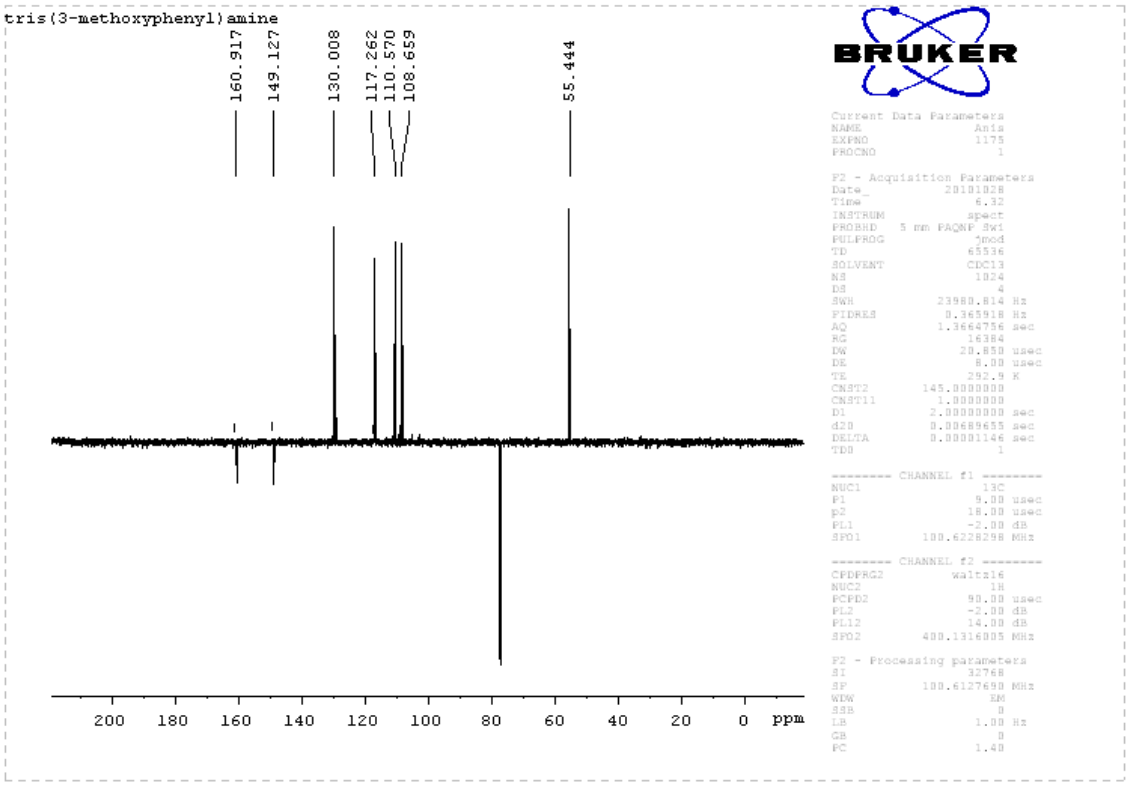
tri-p-tolylamine 15



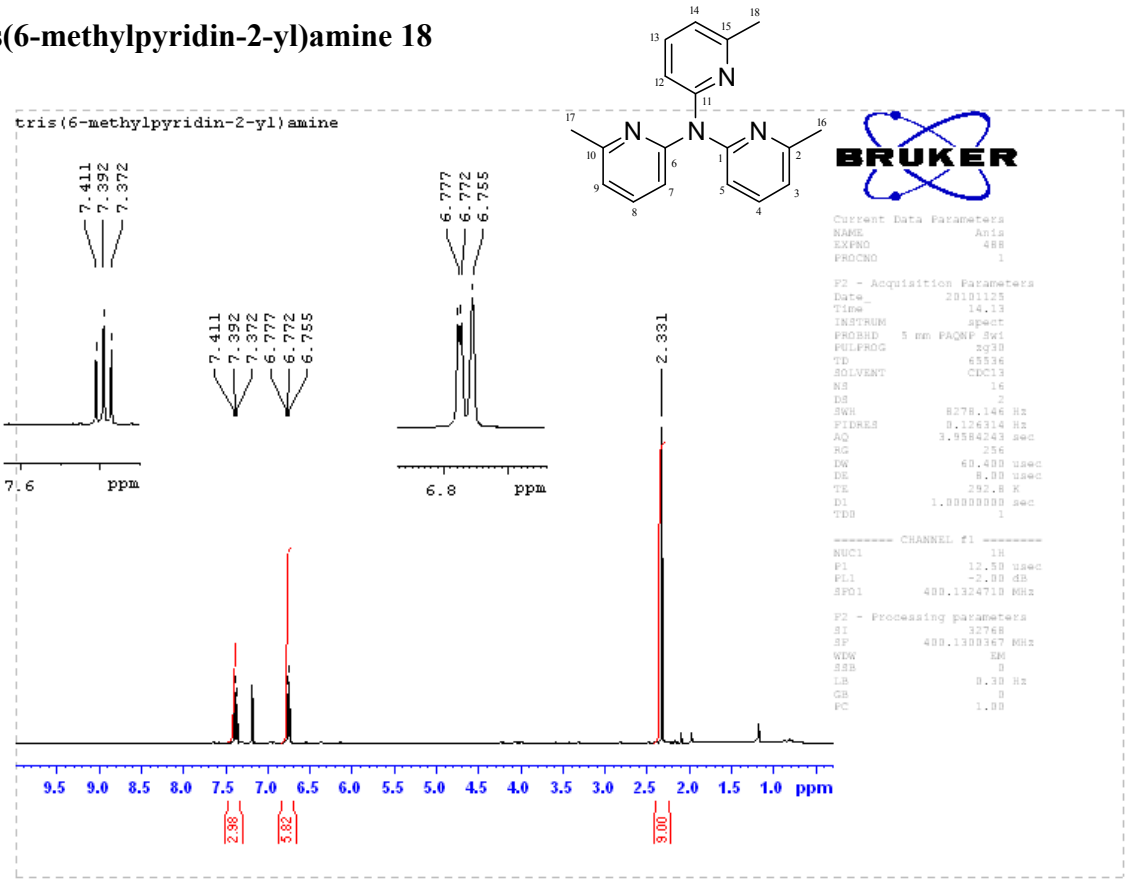


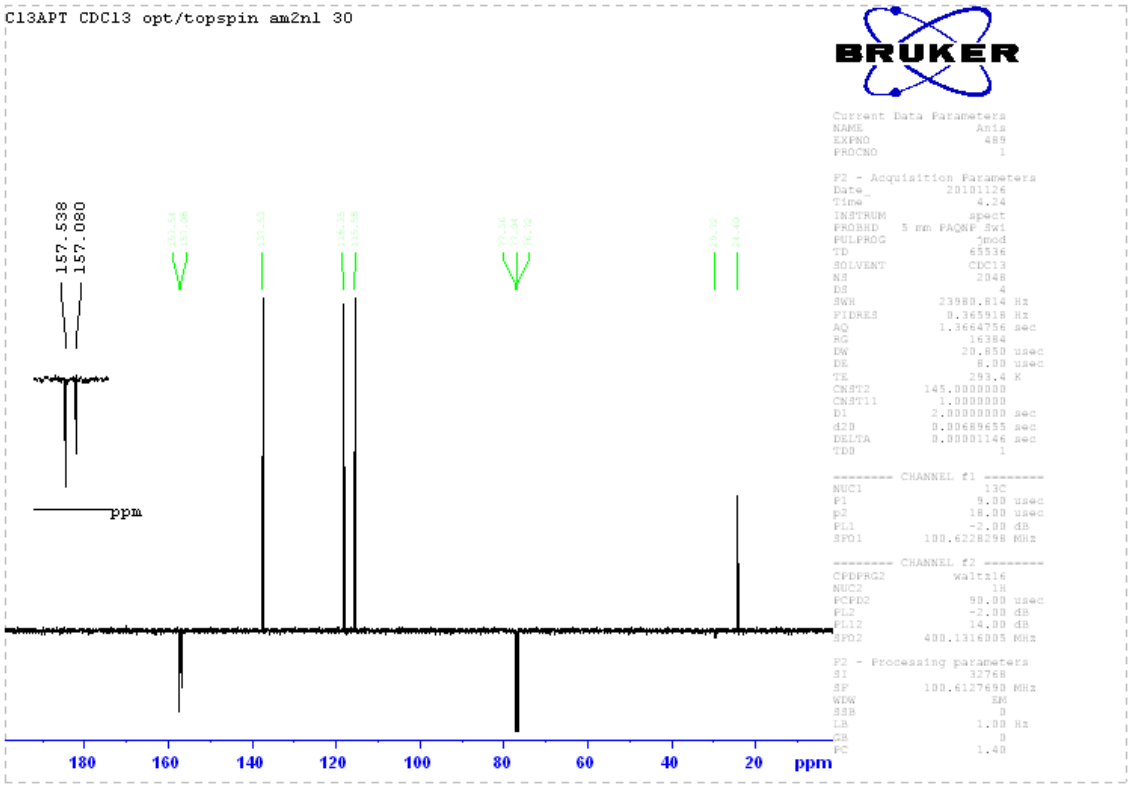
tris(3-methoxyphenyl)amine 16



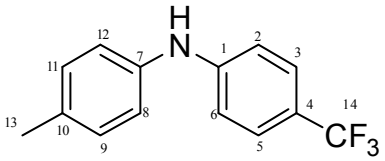


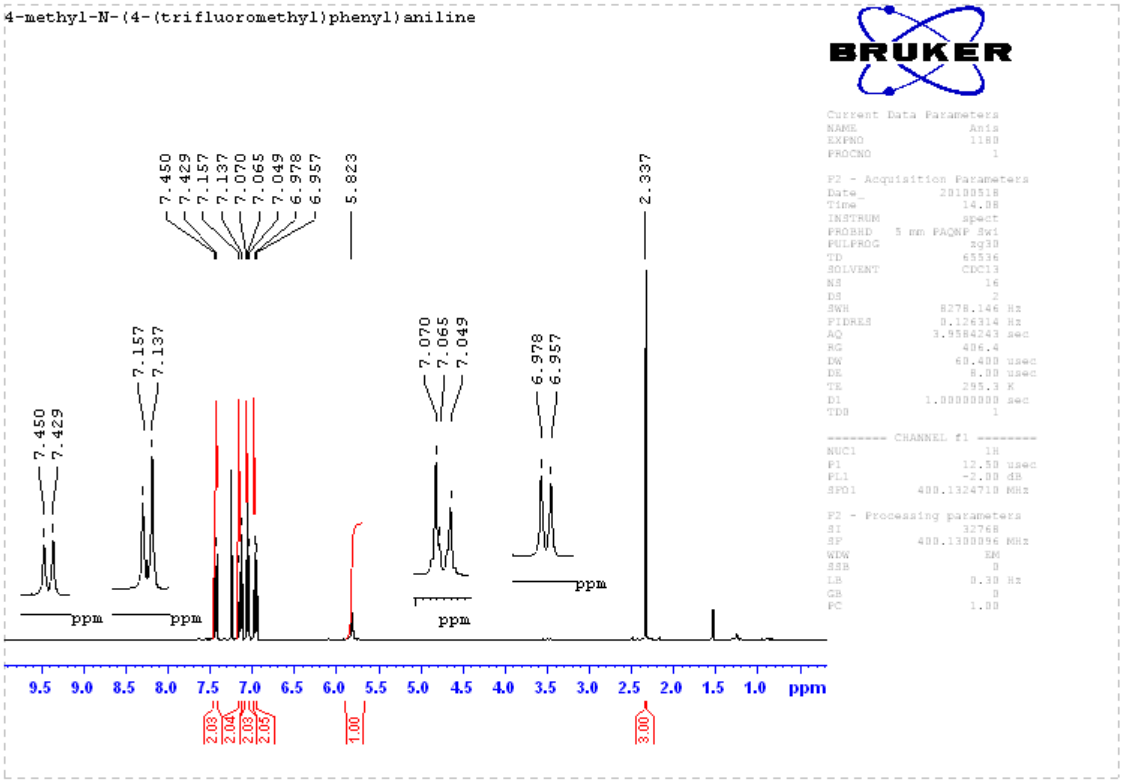
tris(6-methylpyridin-2-yl)amine 18

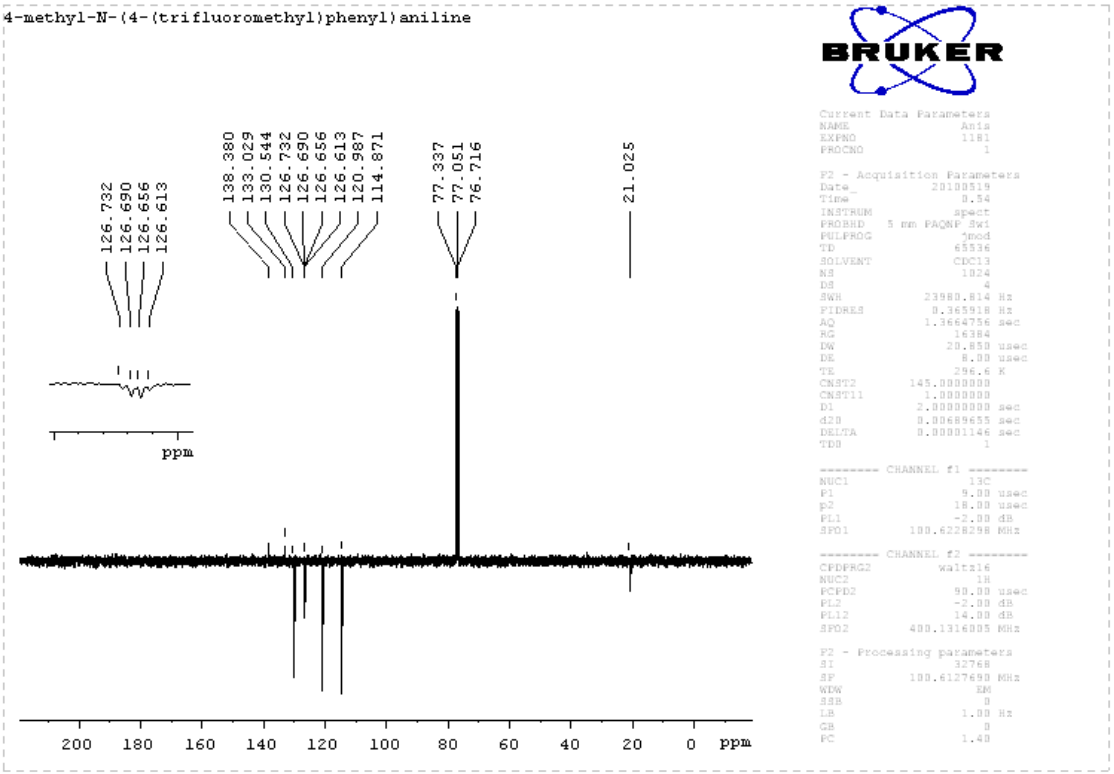




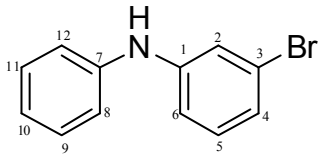
4-methyl-N-(4-(trifluoromethyl)phenyl)aniline 19

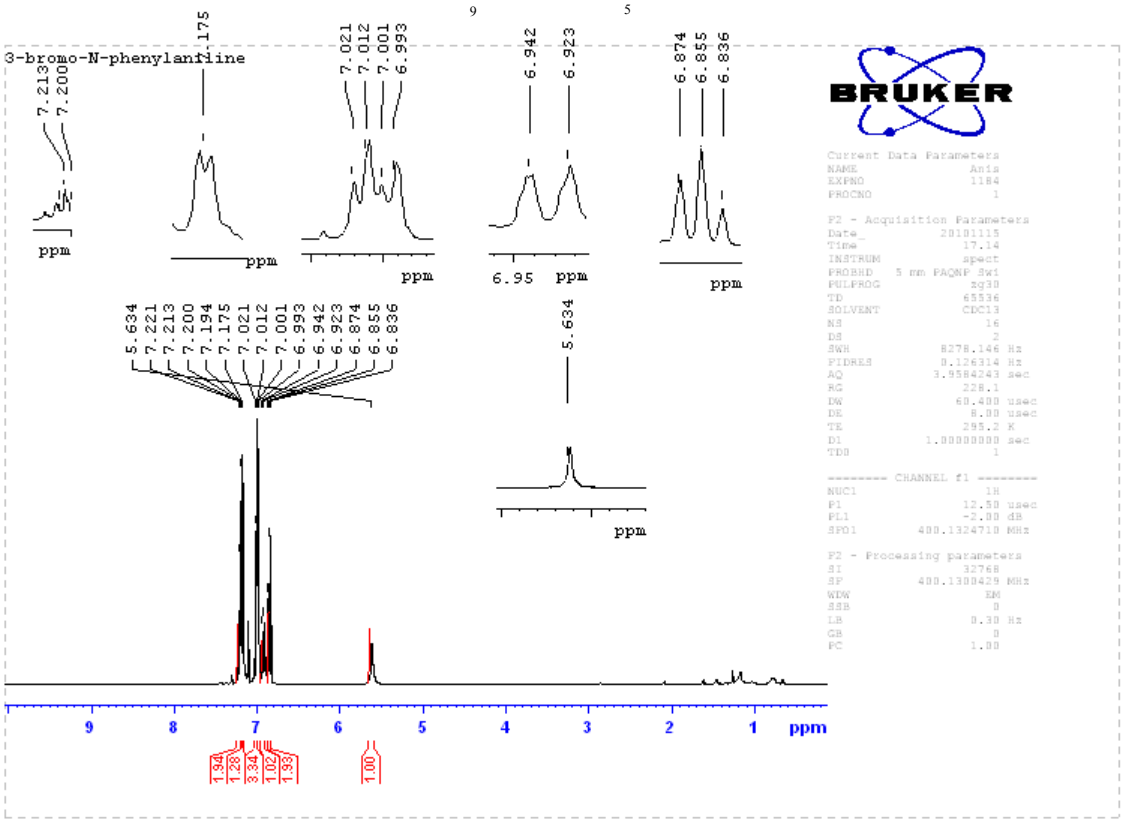


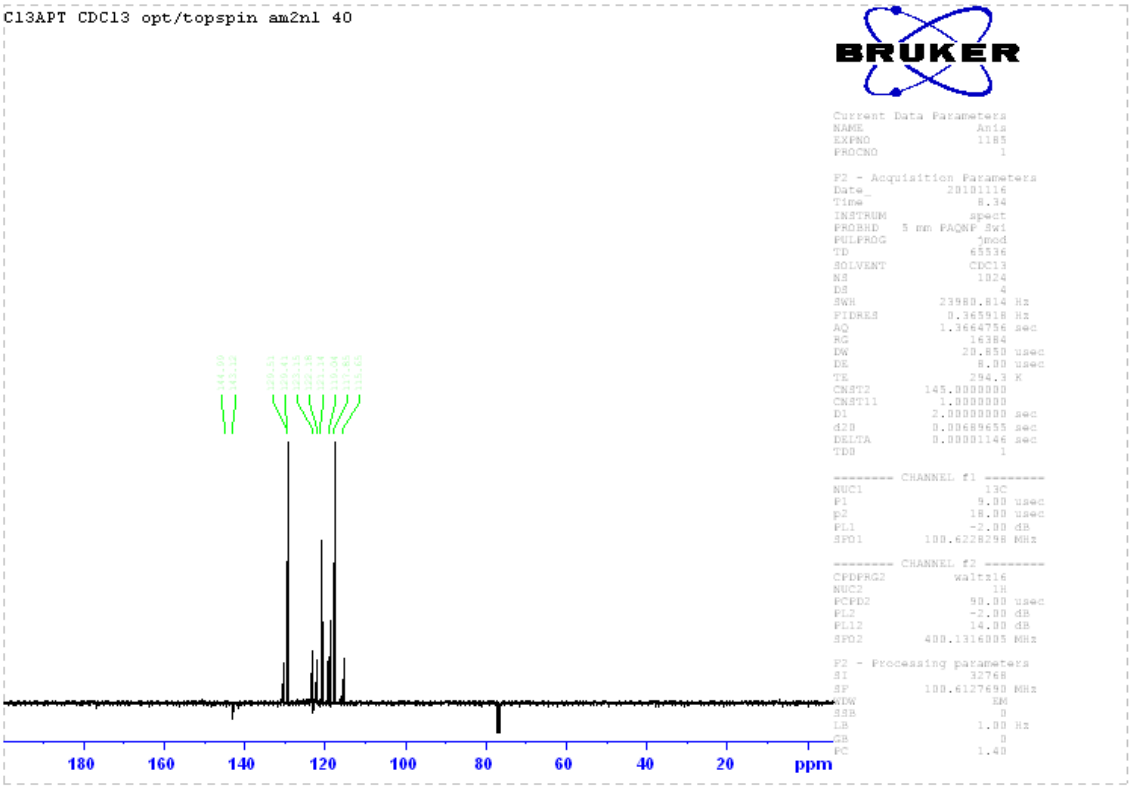




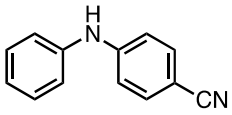
3-bromo-N-phenylaniline 20

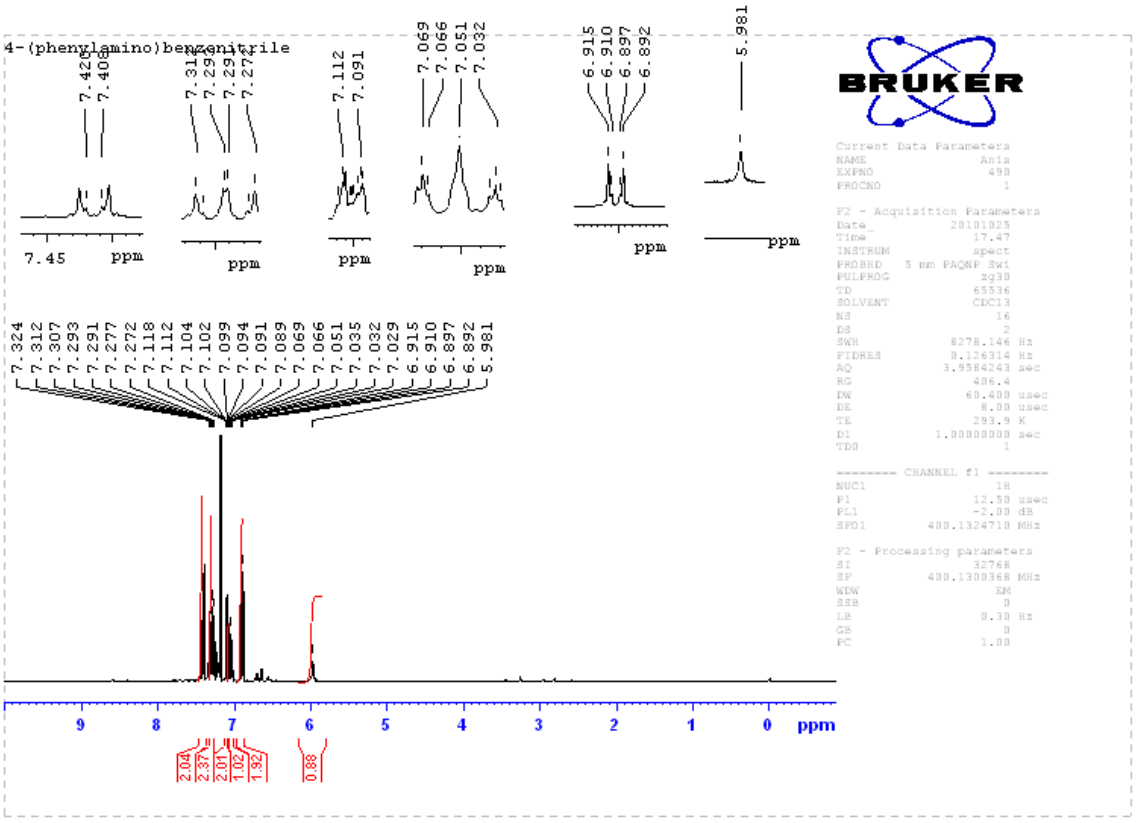


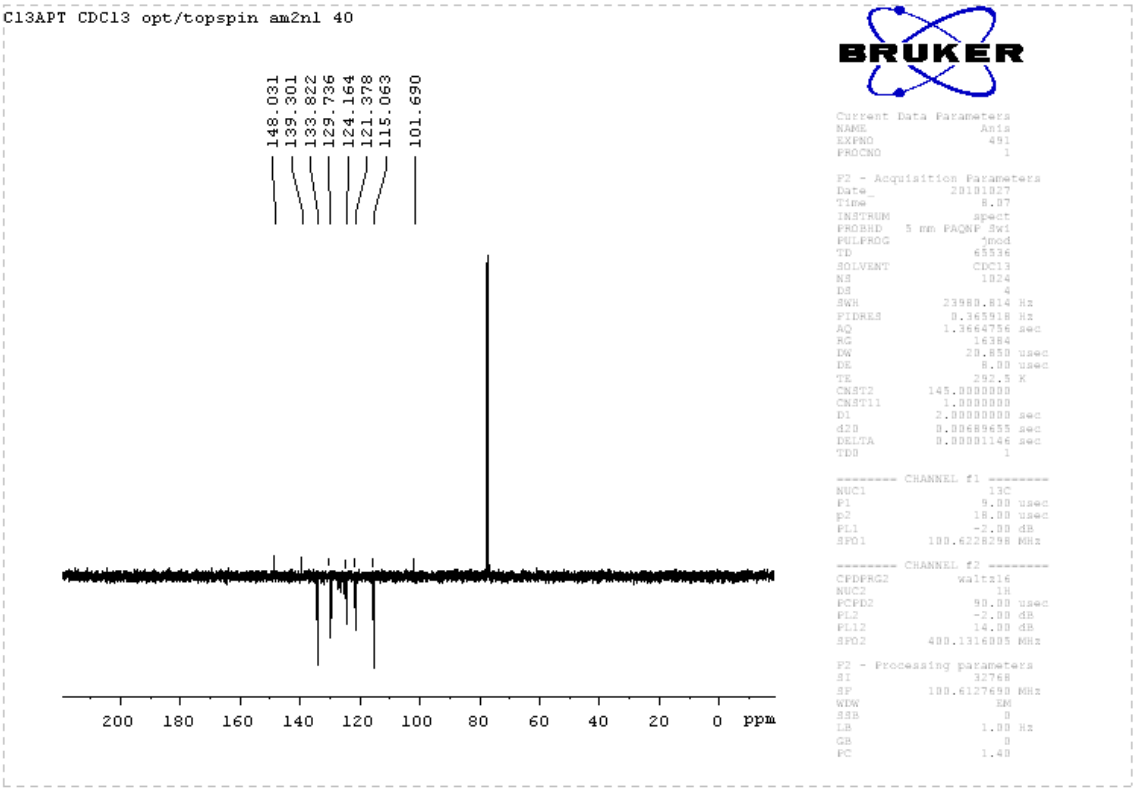




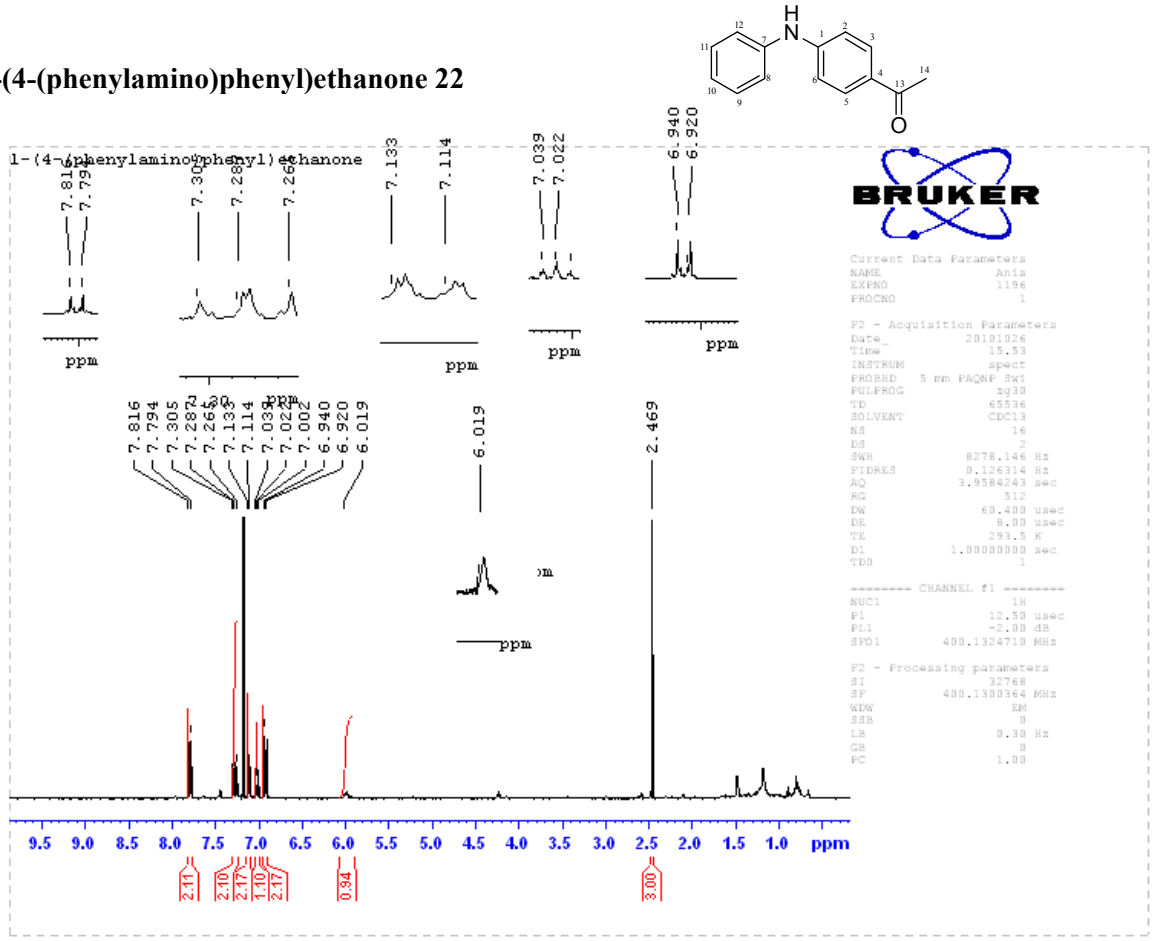
4-(phenylamino)benzonitrile 21

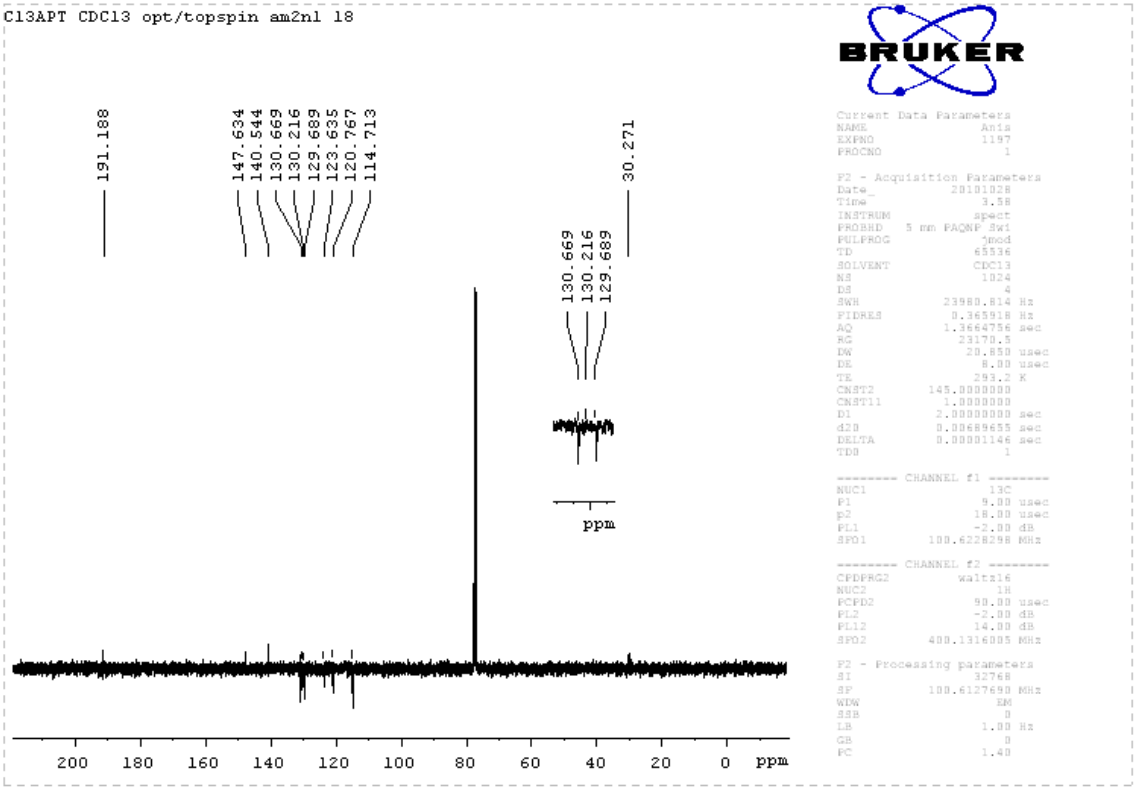


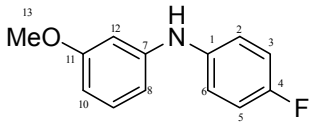




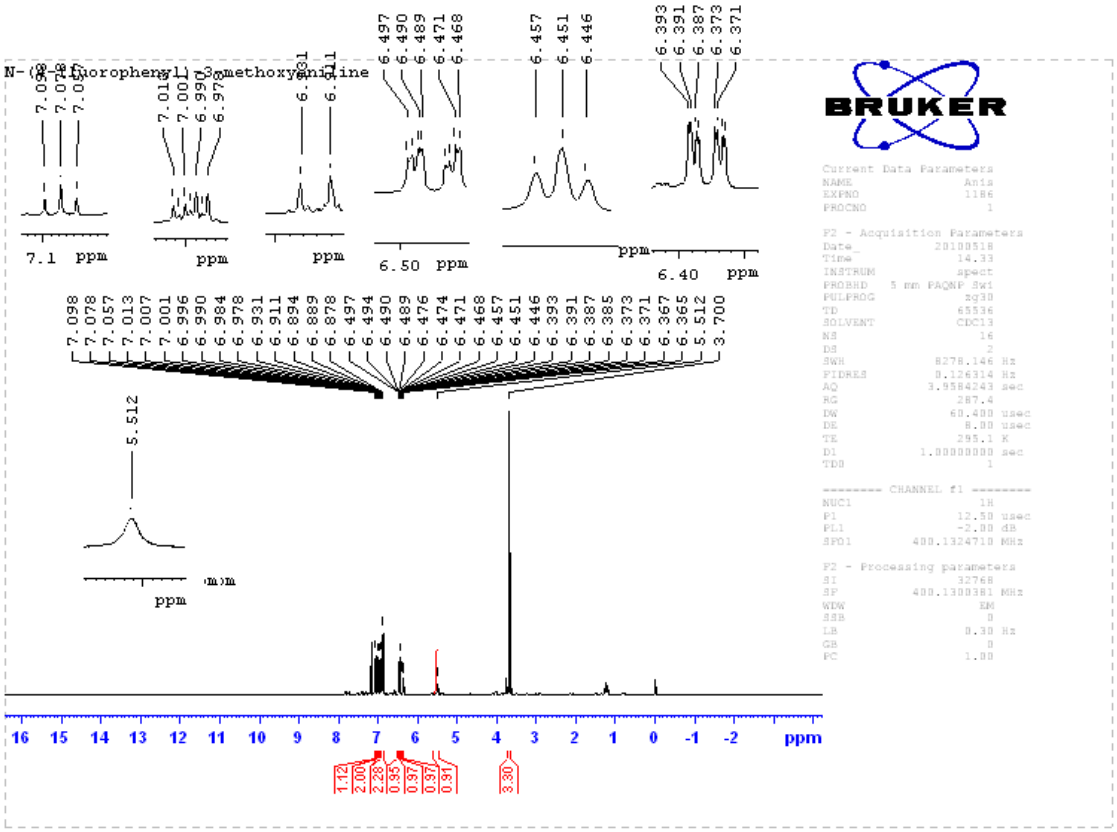
1-(4-(phenylamino)phenyl)ethanone 22

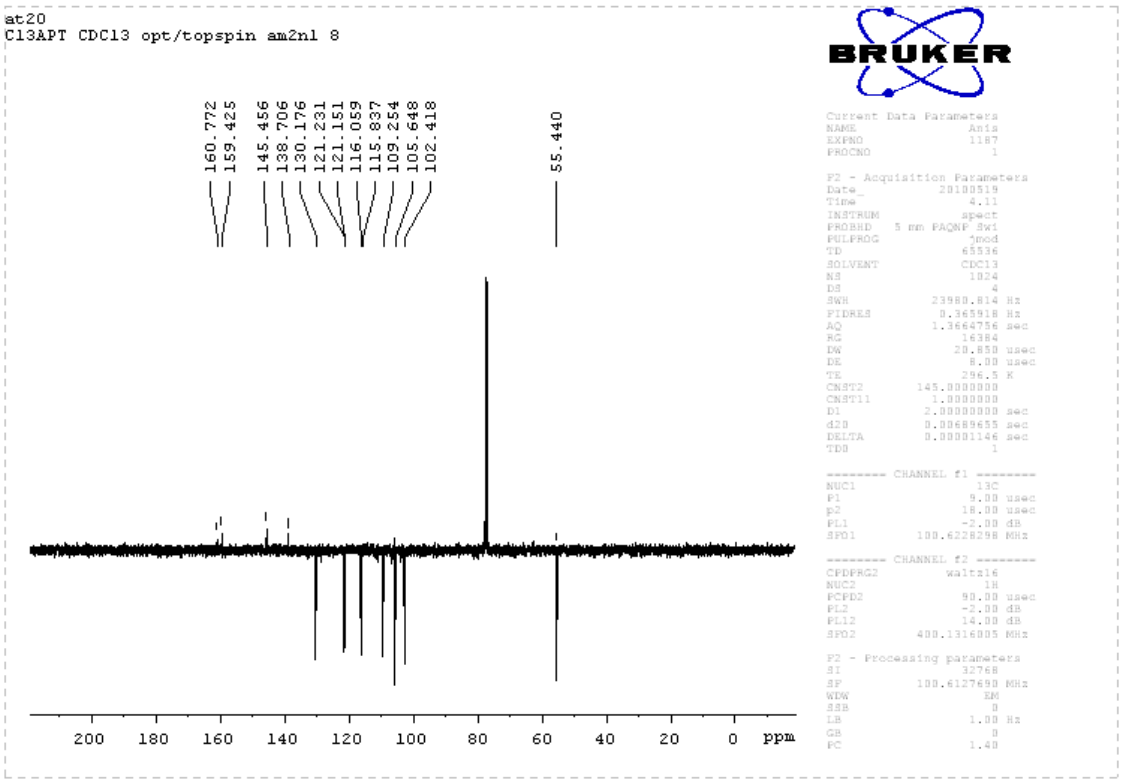




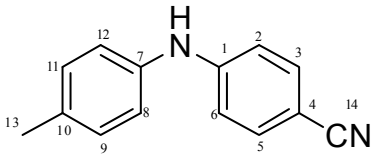


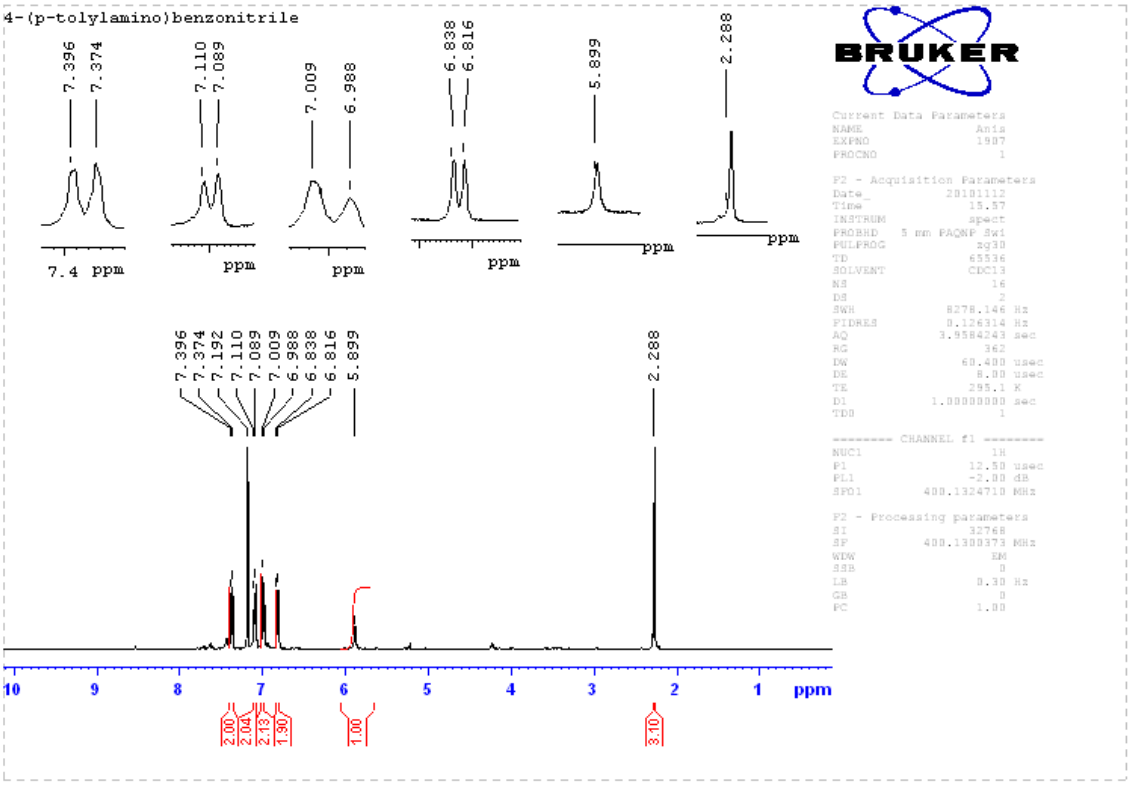
3-methoxy-N-(4-(Fluoro)phenyl)aniline 24

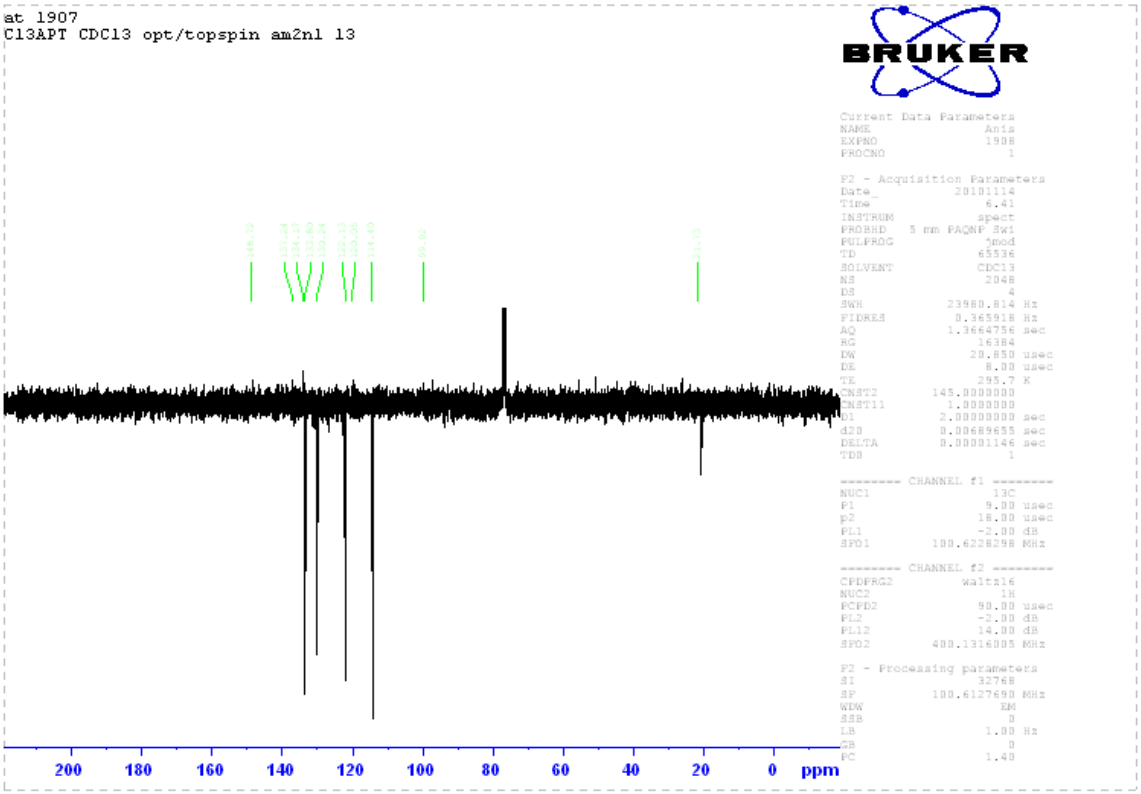




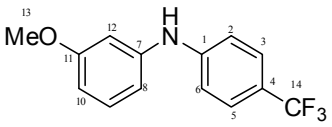
4-(p-tolylamino)benzonitrile 25

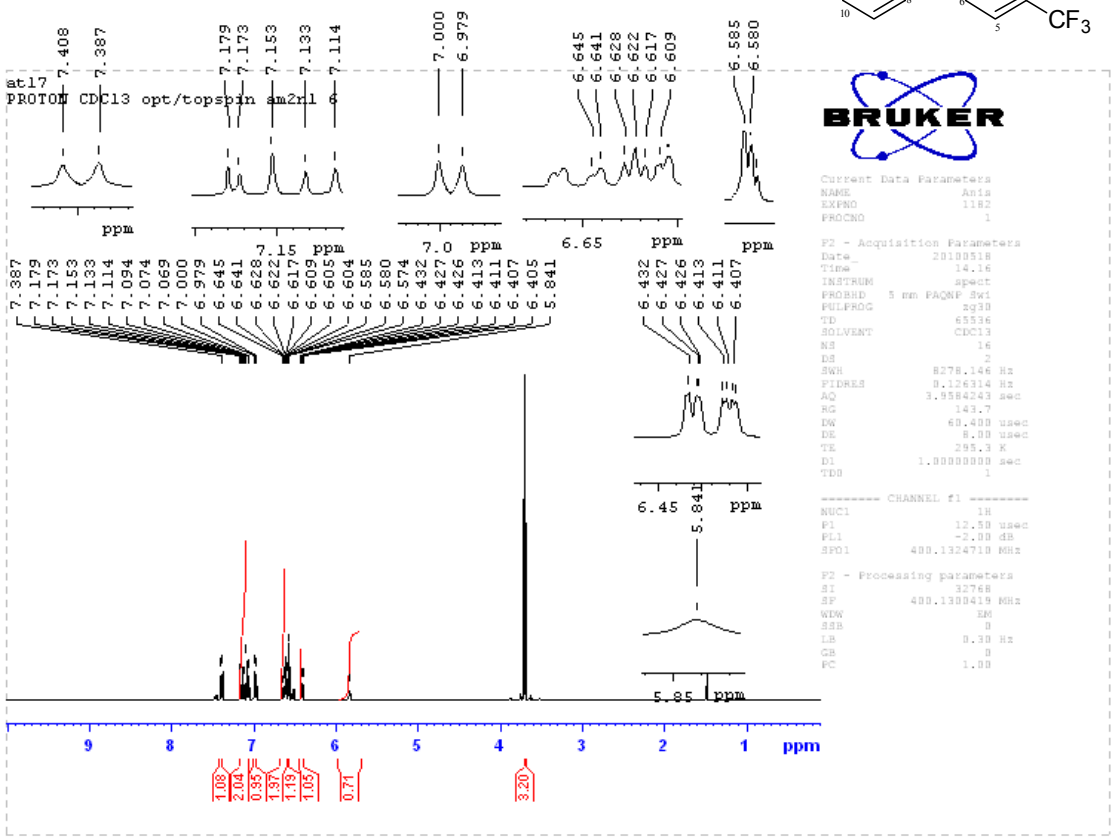


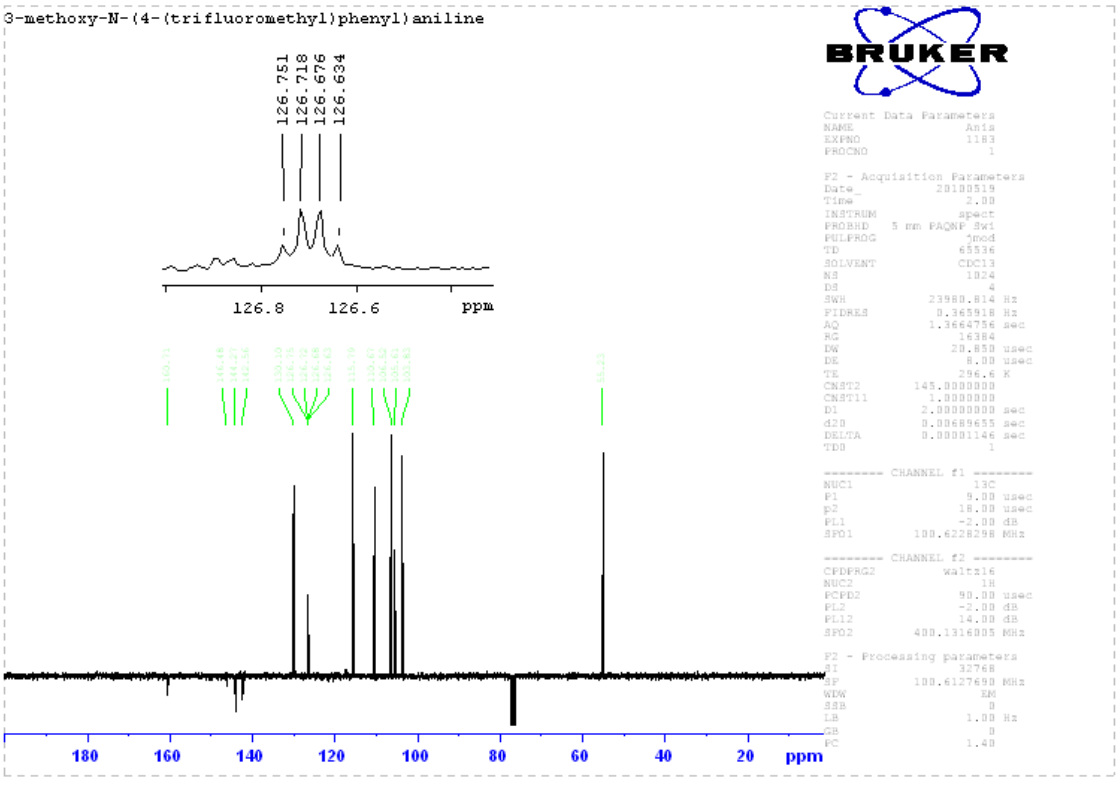




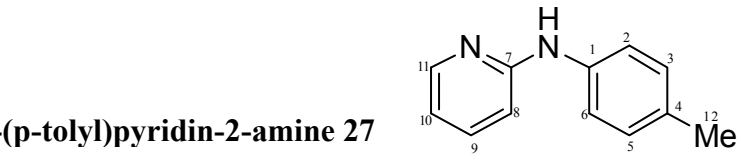
3-methoxy-N-(4-(trifluoromethyl)phenyl)aniline 26

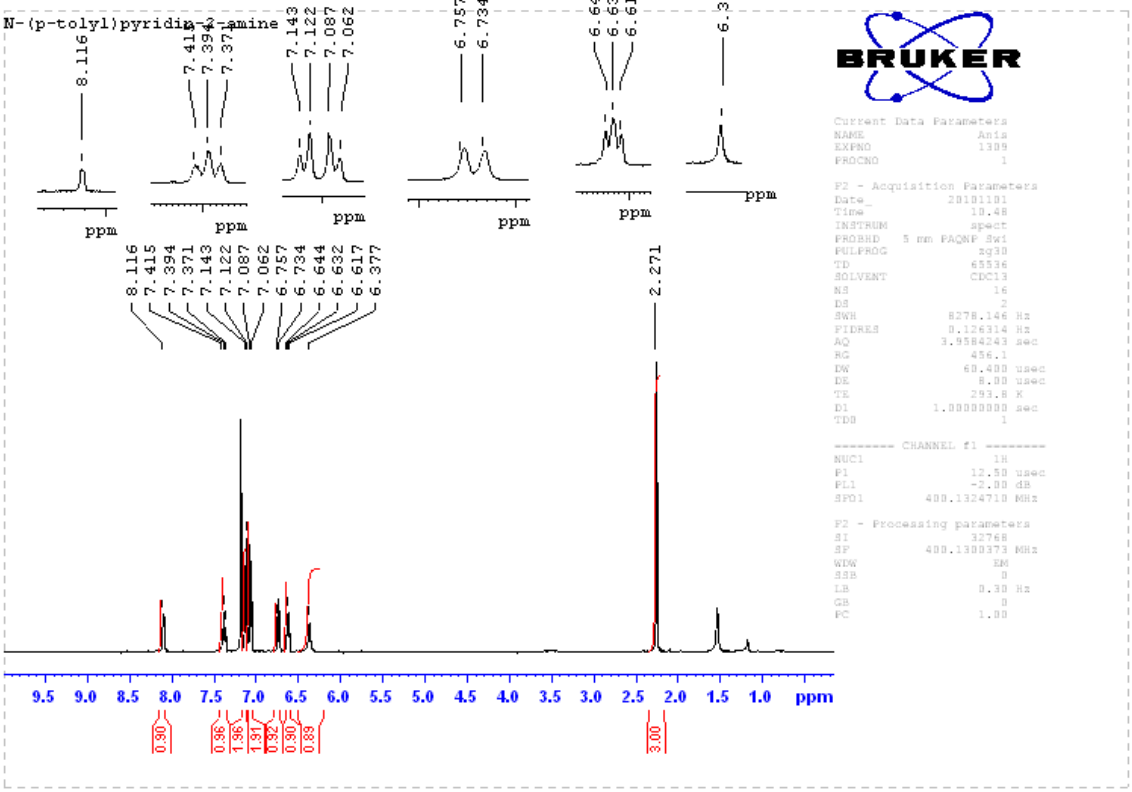


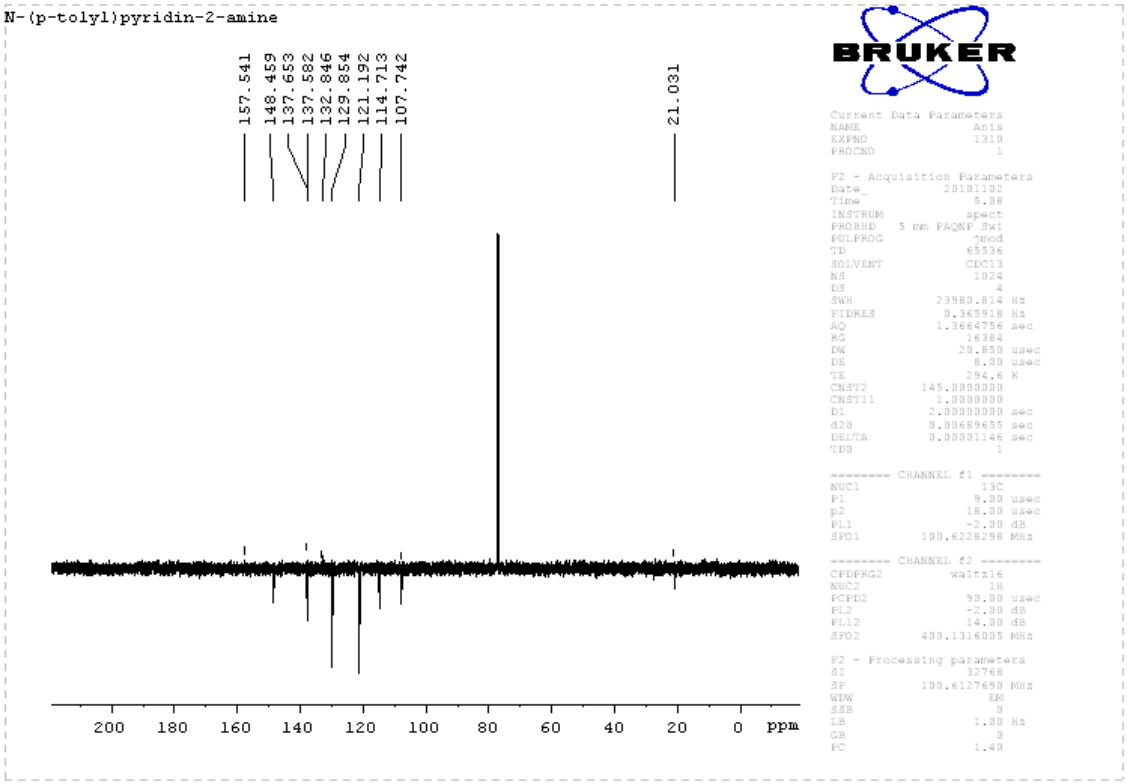




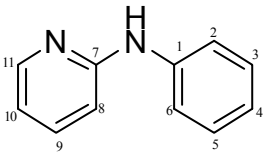
N-(p-tolyl)pyridin-2-amine 27

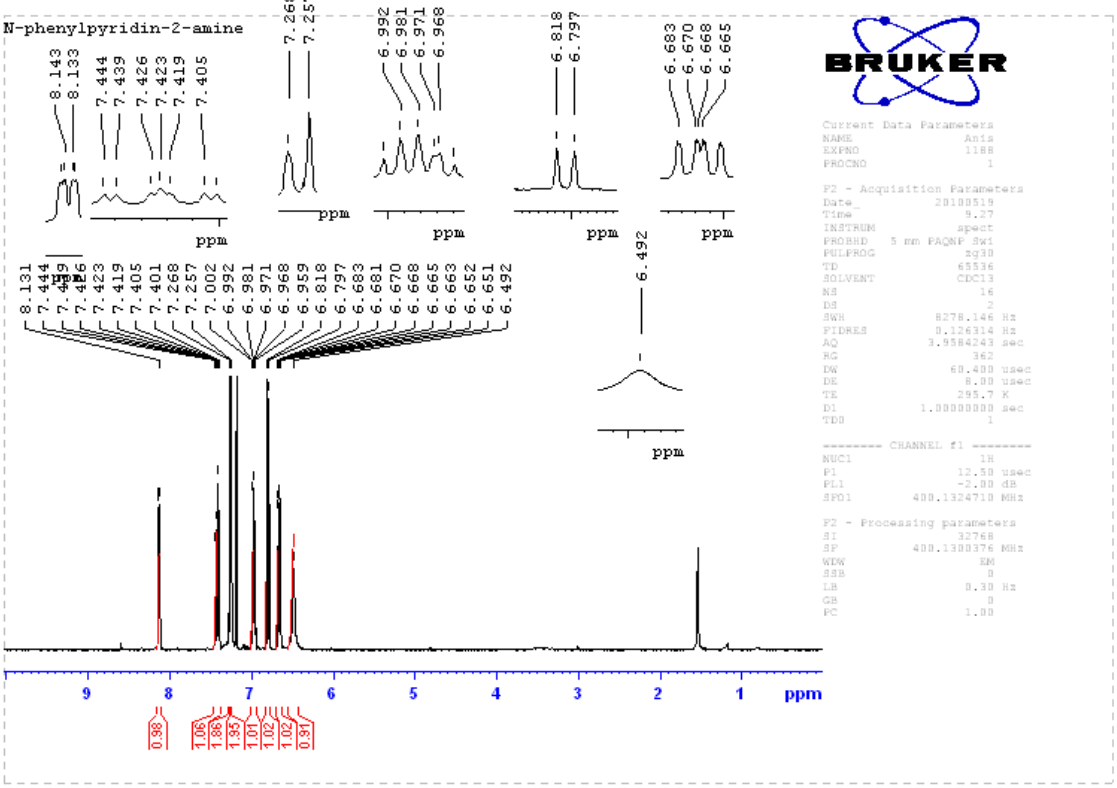


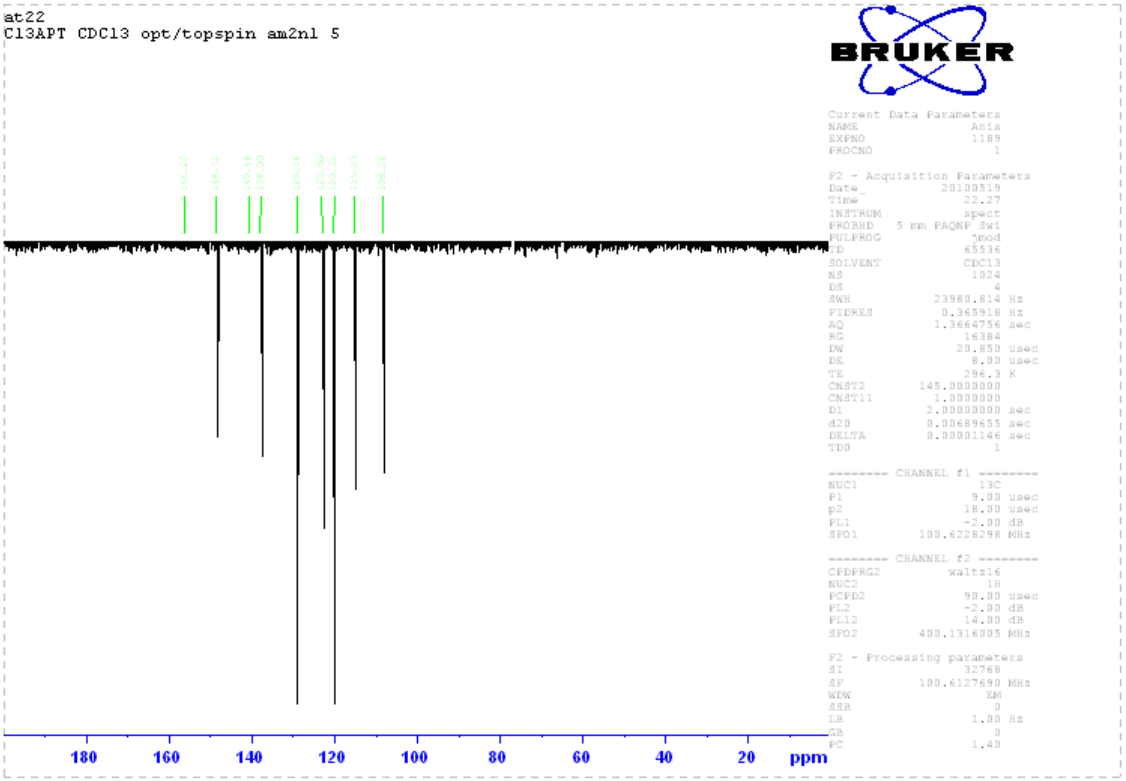




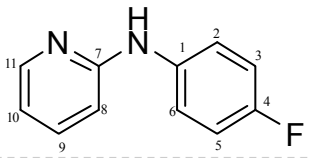
N-phenylpyridin-2-amine 28

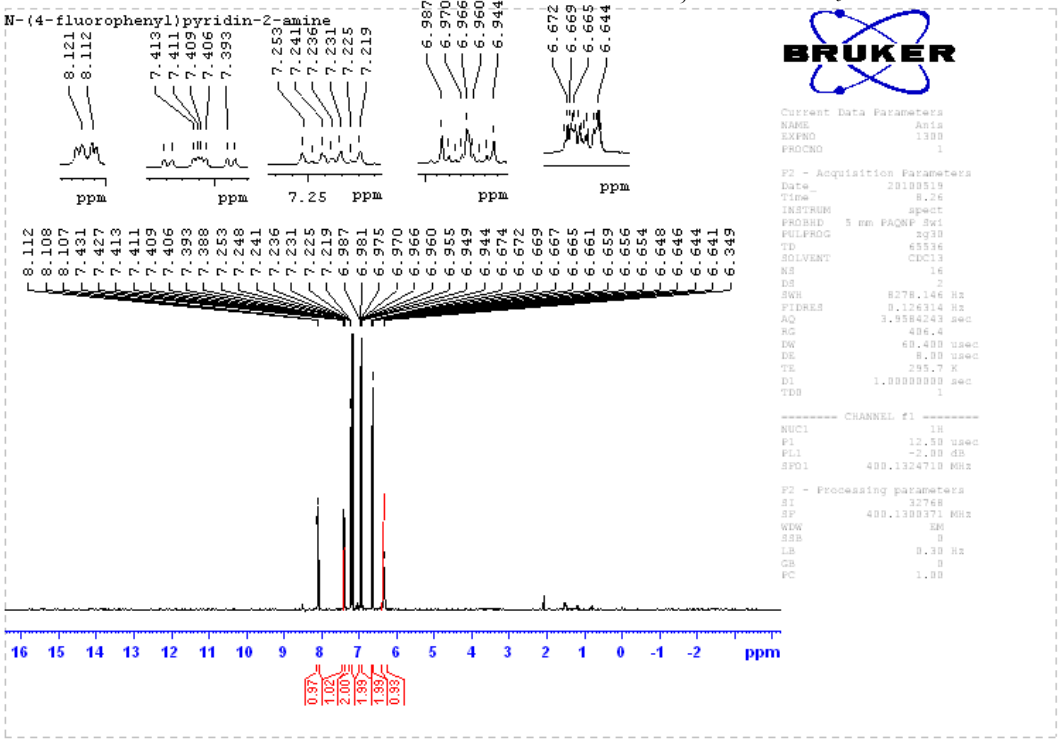


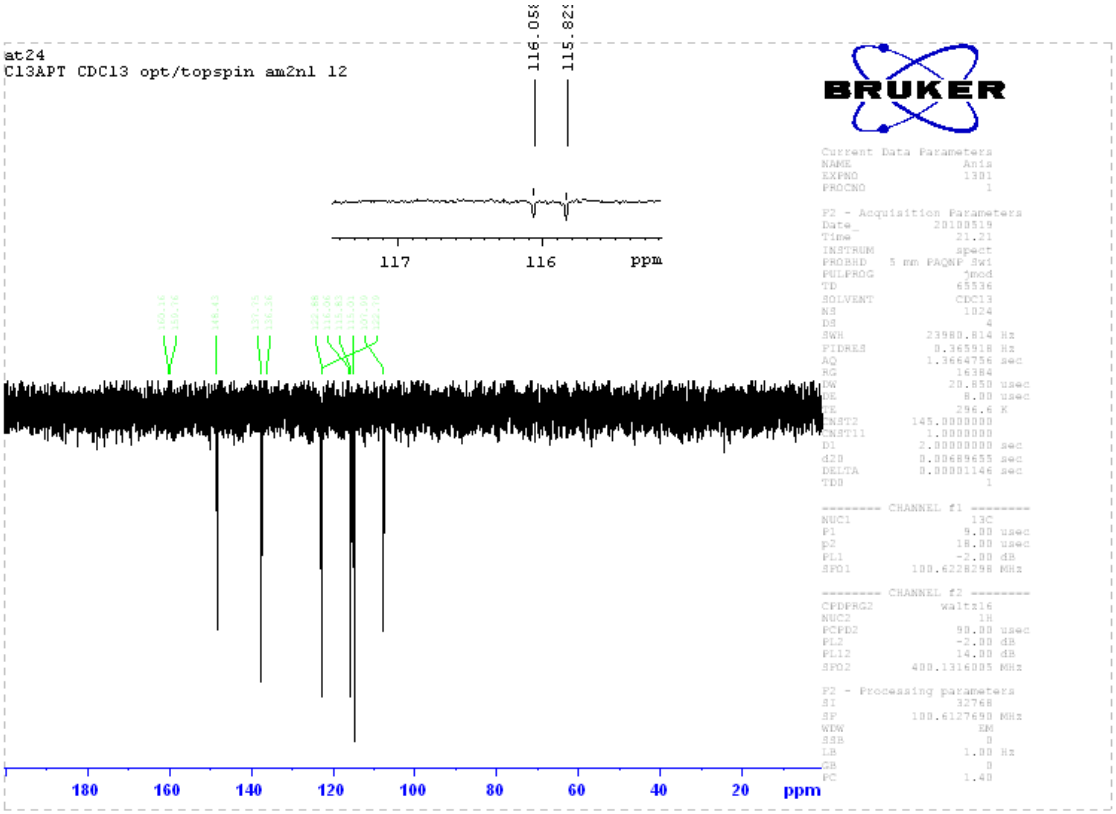




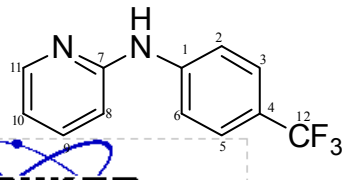
N-(4-fluorophenyl)pyridin-2-amine 29

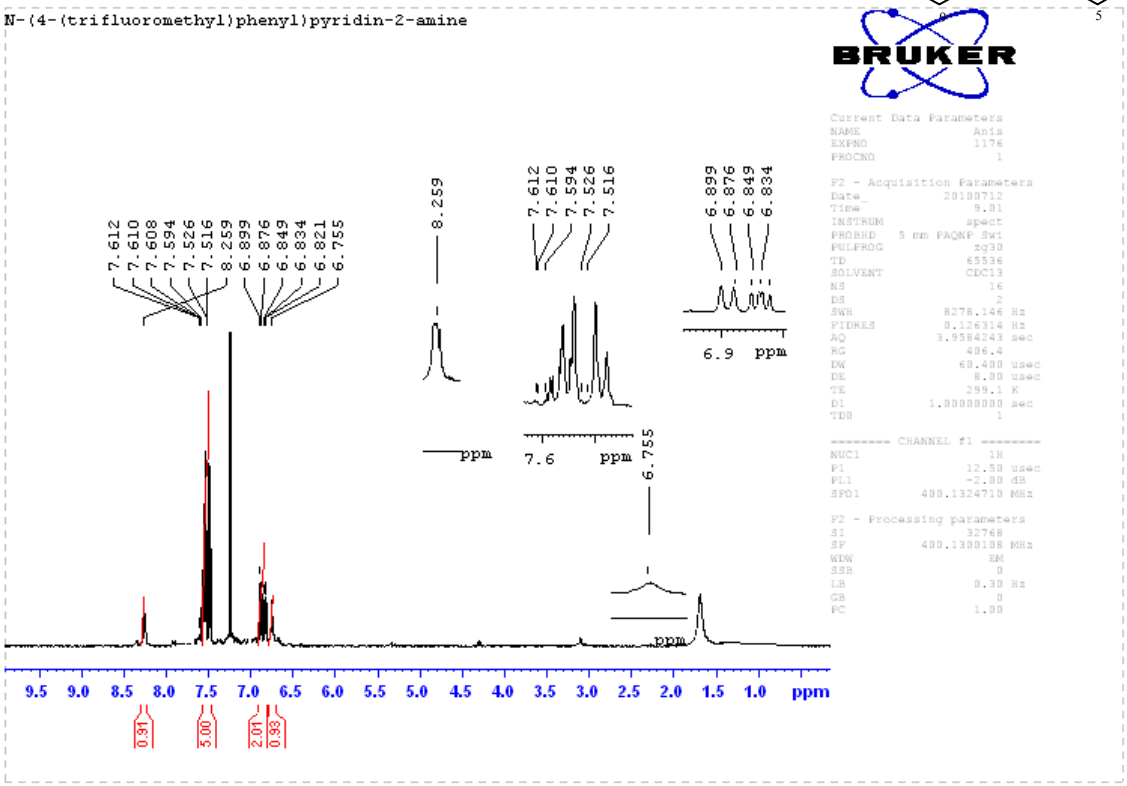


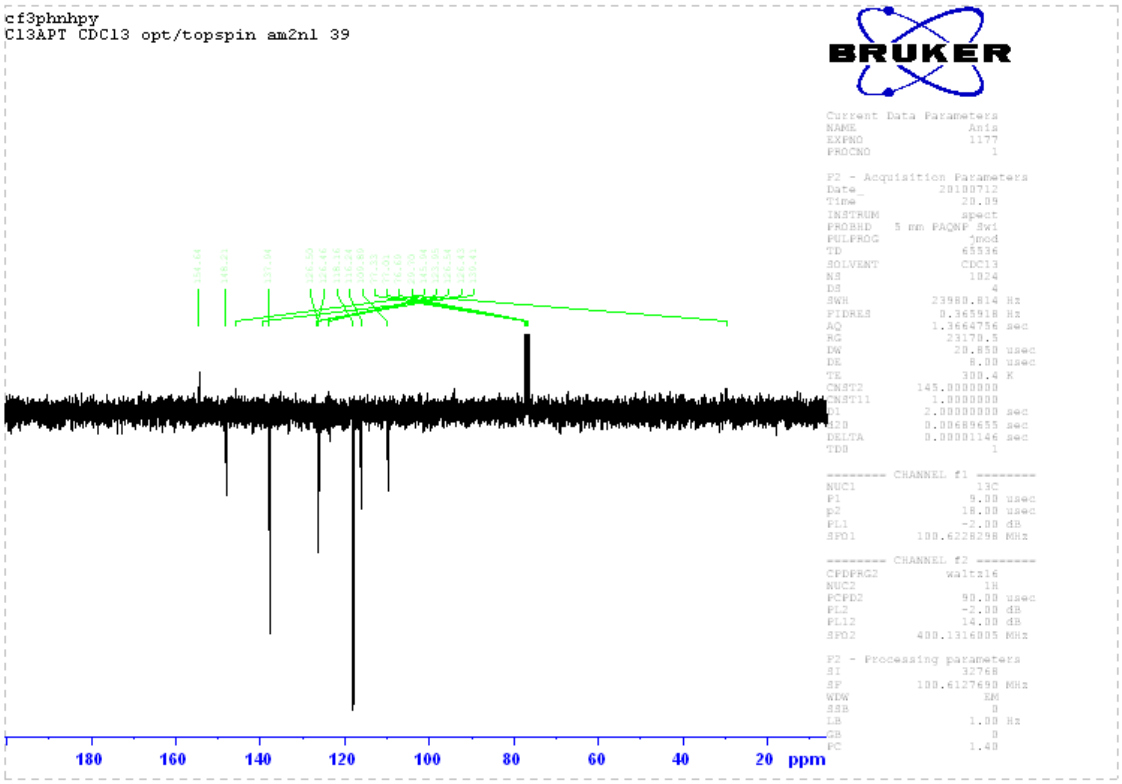




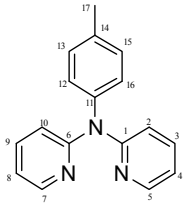
N-(4-(trifluoromethyl)phenyl)pyridin-2-amine 30

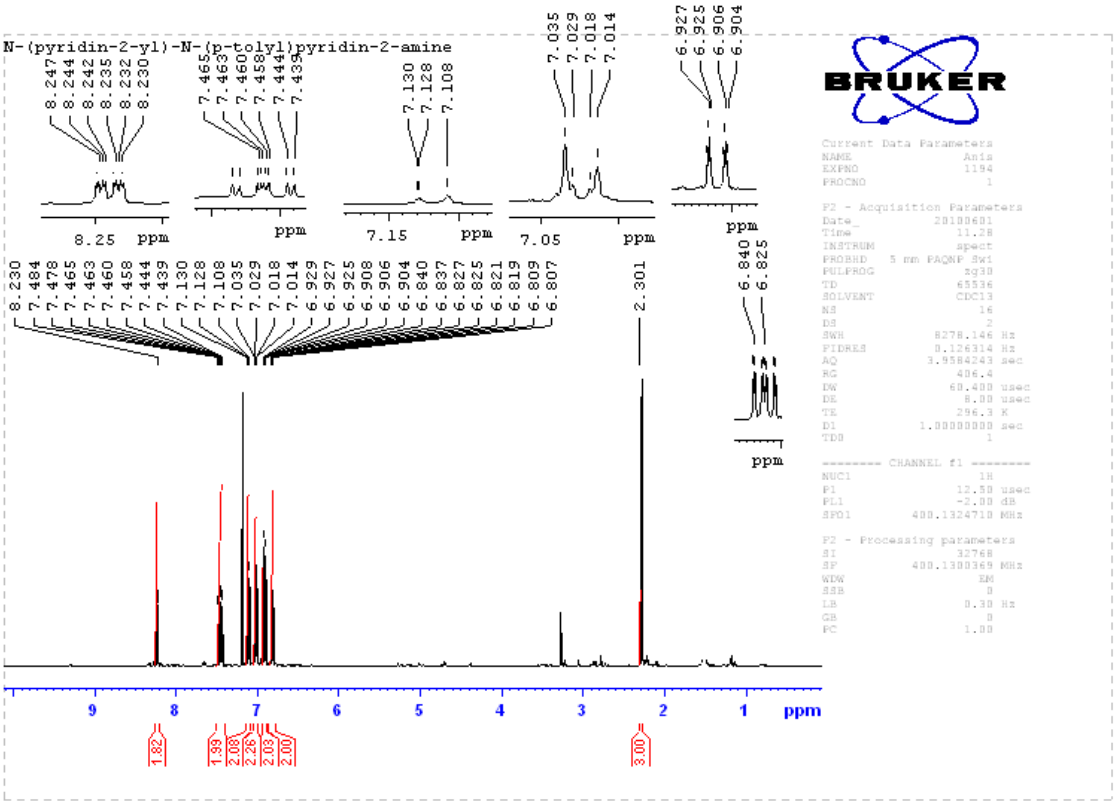


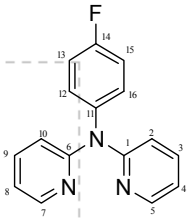


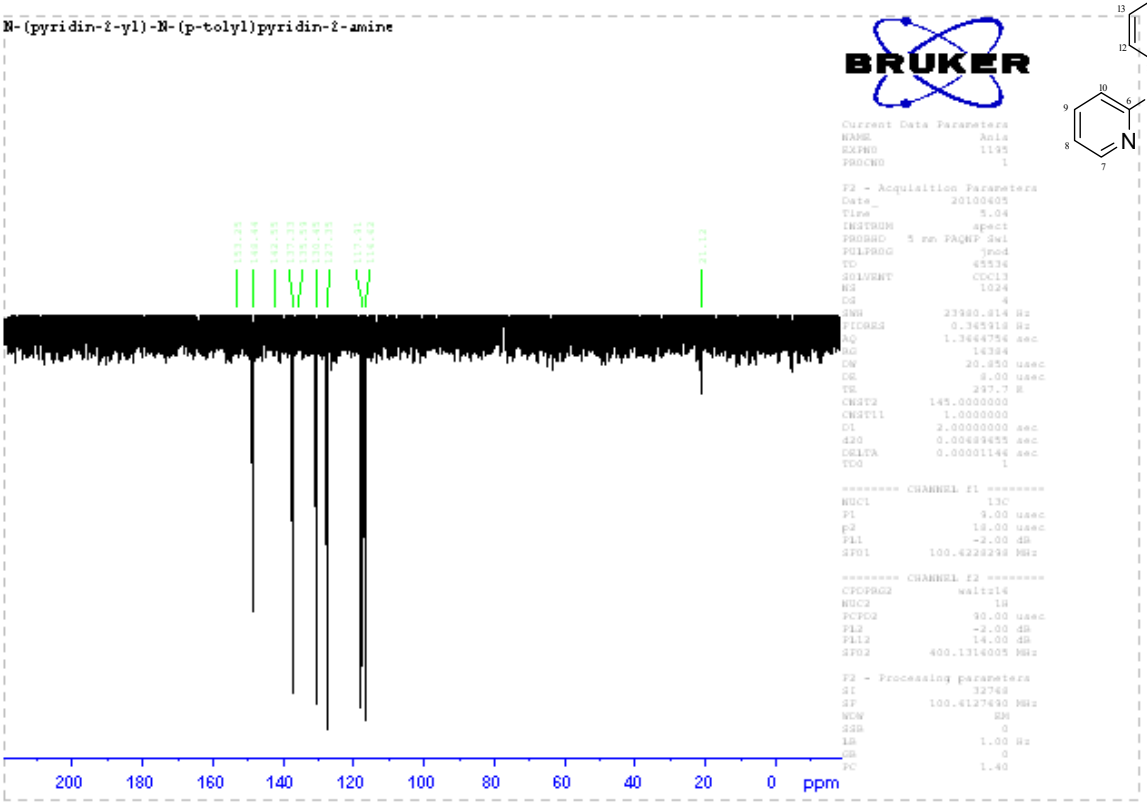


N-(pyridin-2-yl)-N-(p-tolyl)pyridin-2-amine 31

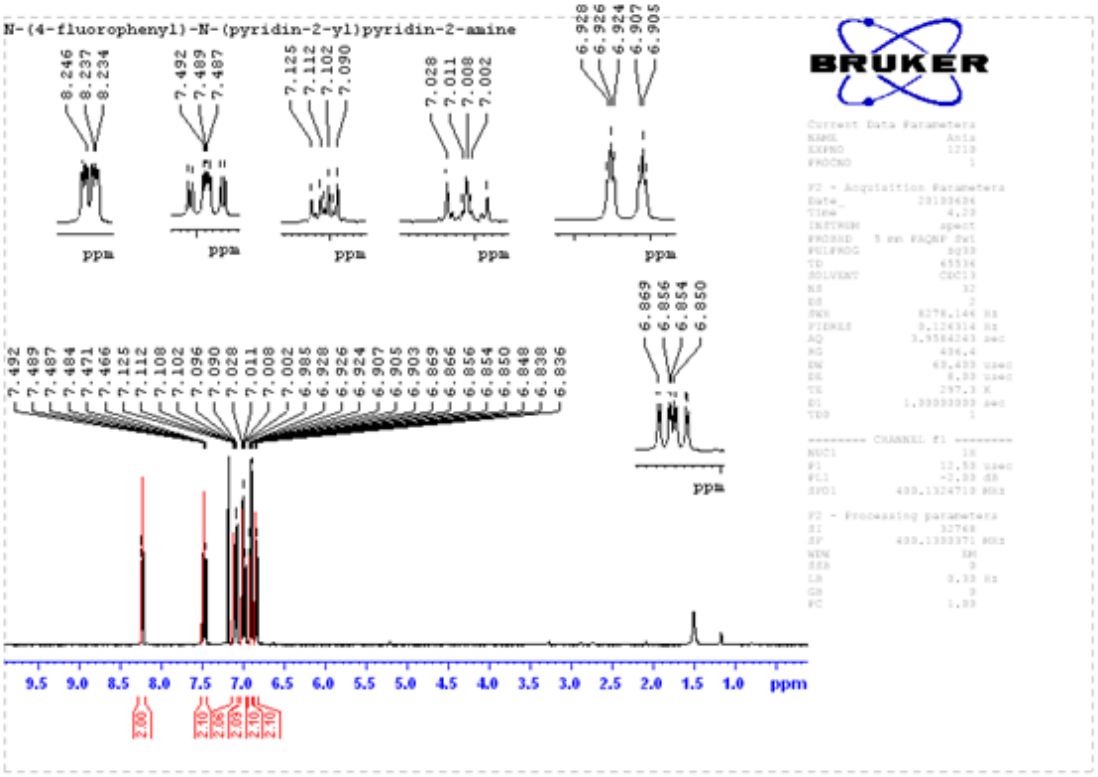


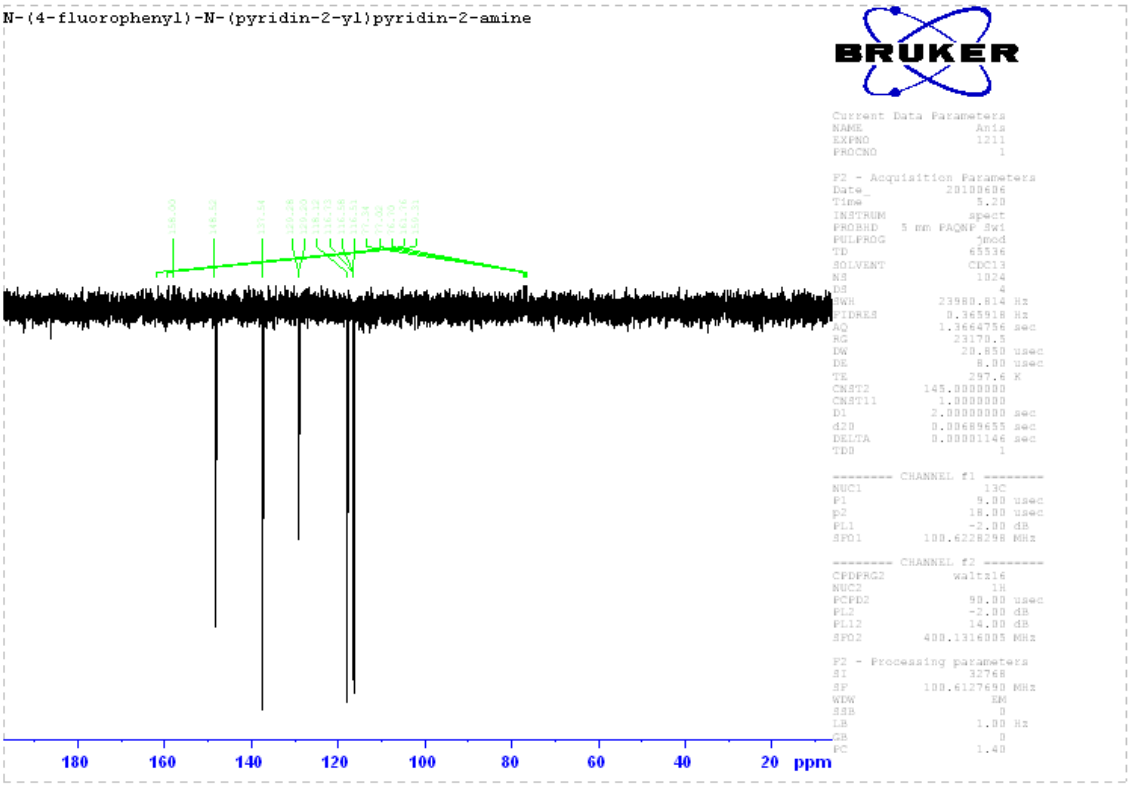




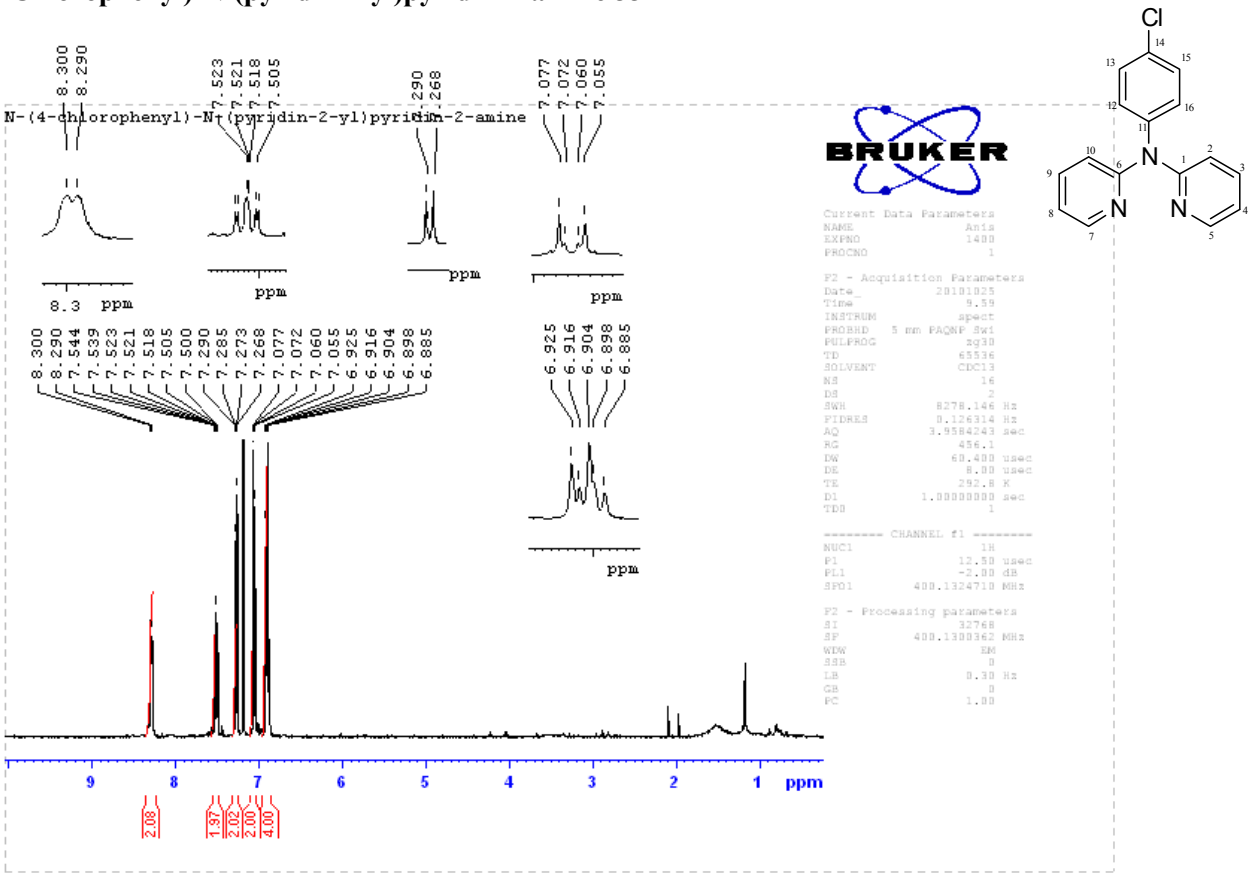


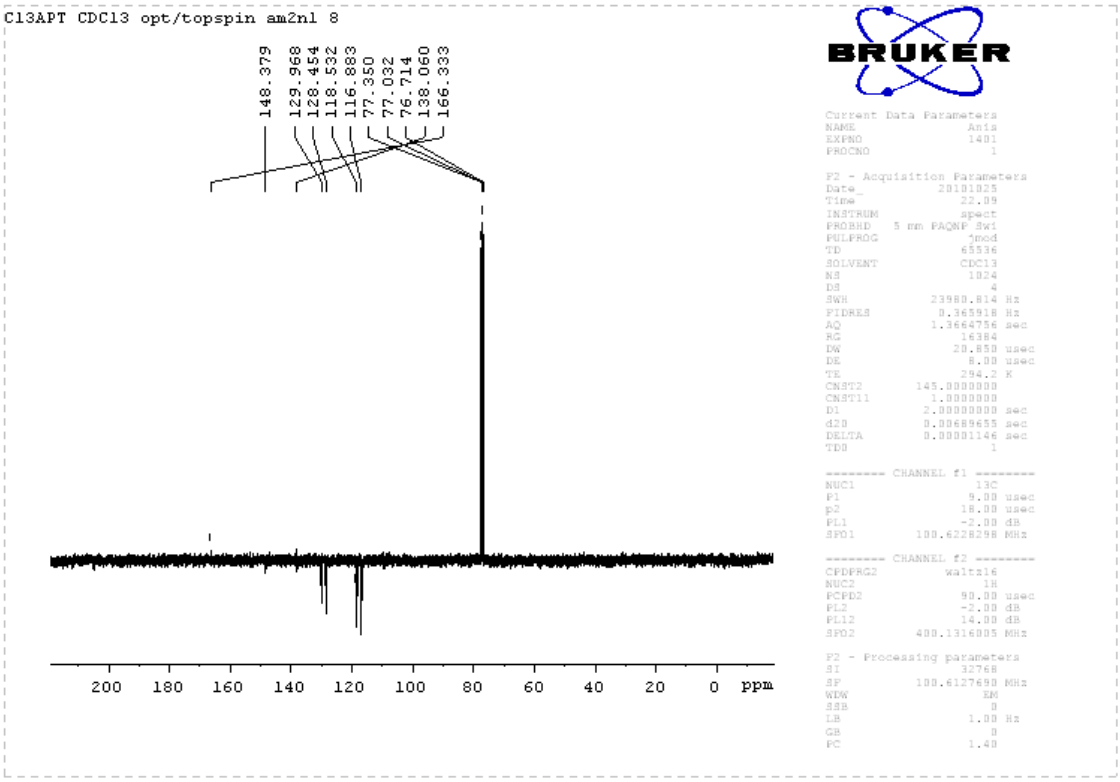
N-(4-fluorophenyl)-N-(pyridin-2-yl)pyridin-2-amine 32



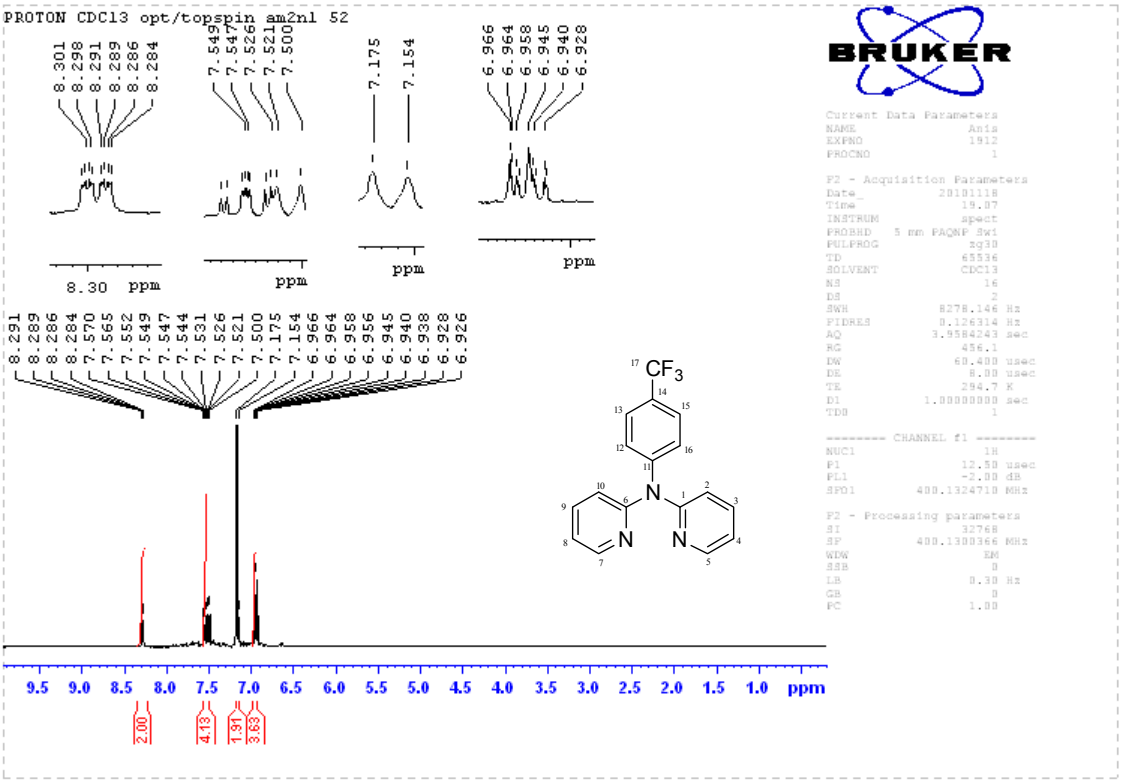


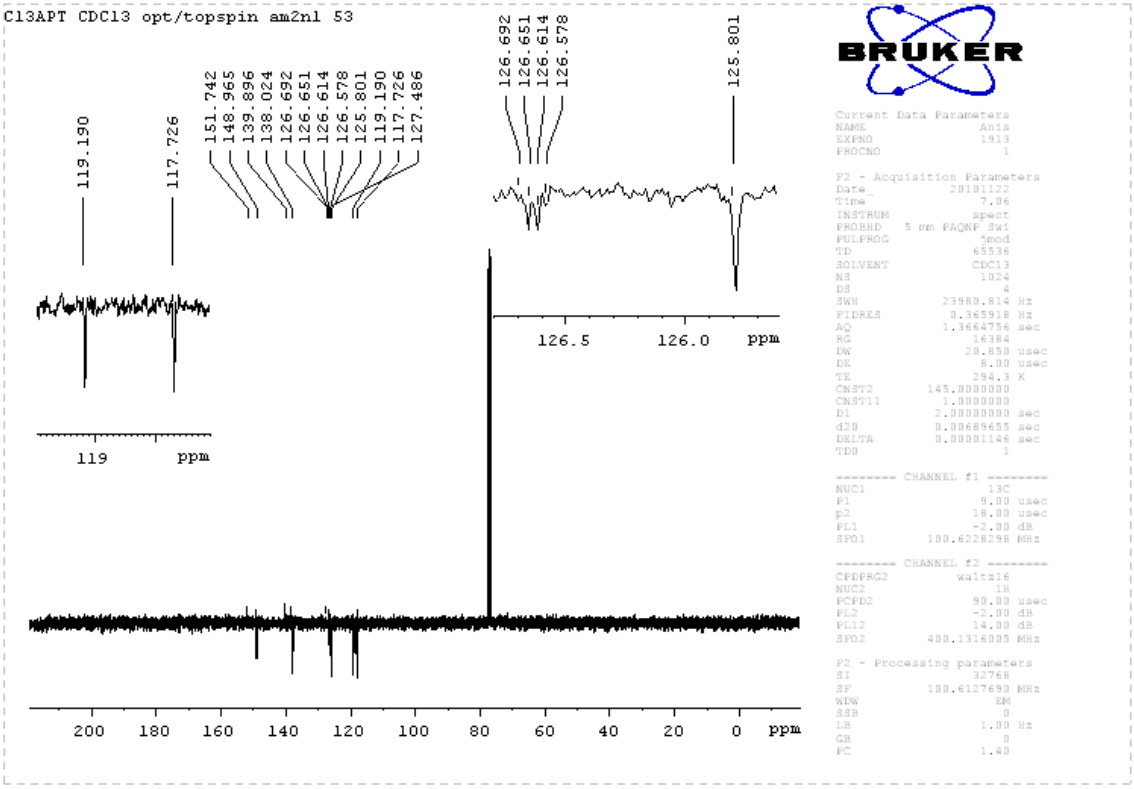
N-(4-Chlorophenyl)-N-(pyridin-2-yl)pyridin-2-amine 33



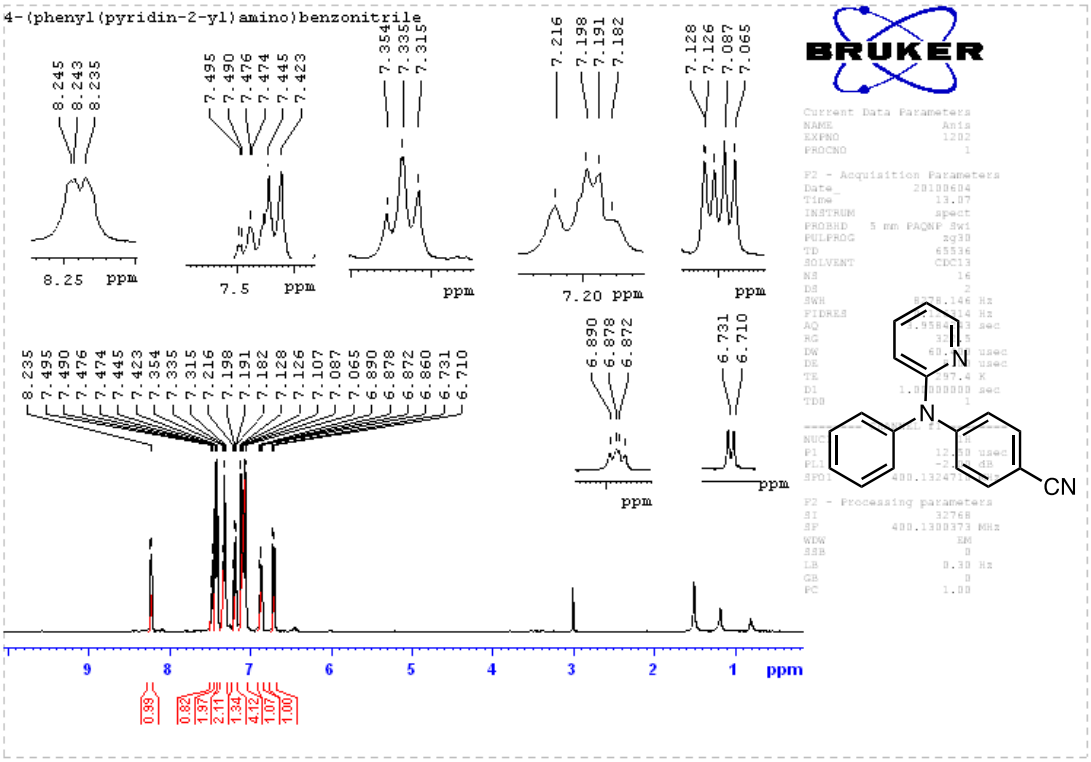


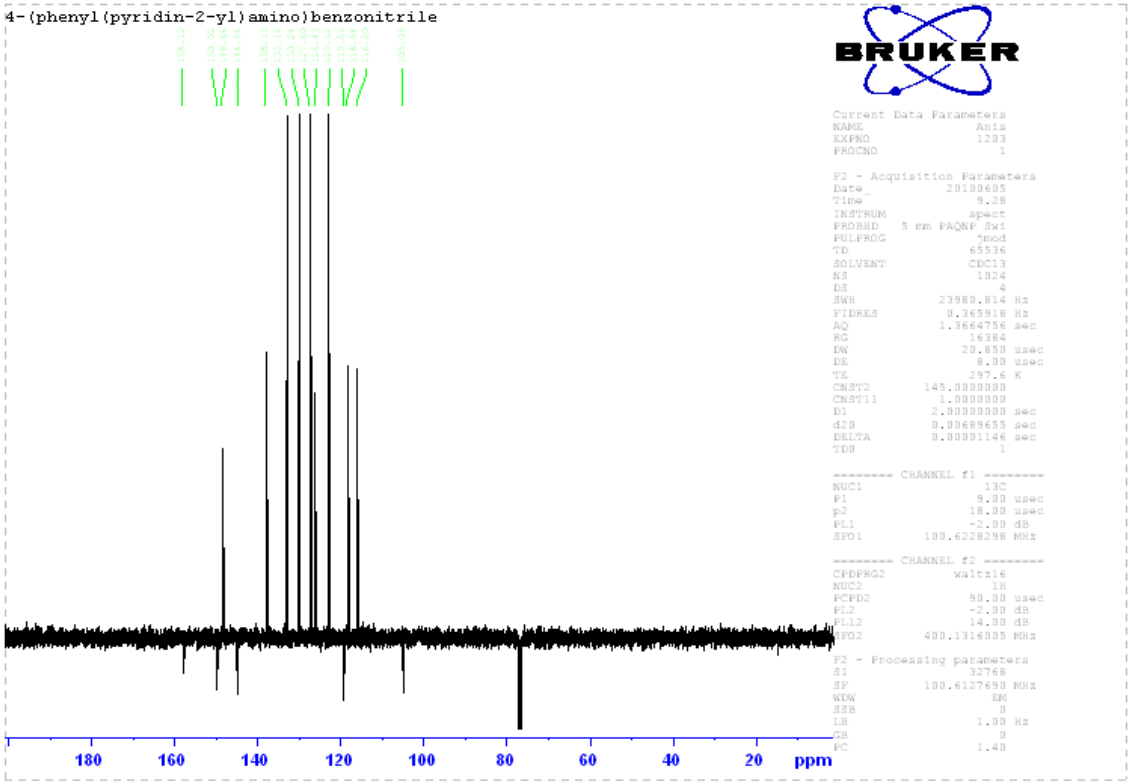
N-(pyridin-2-yl)-N-(4-(trifluoromethyl)phenyl)pyridin-2-amine 34





4-(phenyl(pyridin-2-yl)amino)benzonitrile 35





[1] Kuwano, R.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem*. **2002**, *67*, 6479.
[2] Changfeng Z.; Dongpeng Y.; Xiaofei J.; Lixue Z.; Jiang C., *Synlett*. 2009, 19, 3198.
[3] Surry, D. S.; Buchwald, S.L, *J. Am. Chem. Soc*, **2007**, 129, 10354.
[4] Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553.
[5] Wolfe, J. P ; Buchwald, S.L. *J. Org. Chem*. **2000**, *65*, 1155.
[6] Shen, Q.; Ogata, T.; Hartwig; J. F. *J. Am. Chem. Soc*, **2008**, 130, 6586.