

Supplementary Material

Facile synthesis of mono-, bis- and tris-aryl-substituted aniline derivatives in aqueous DMF

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Materials and methods

Unless otherwise noted, all the reactions were carried out under air. All aryl halides and arylboronic acids were purchased from Alfa Aesar, Avocado and used without purification. ^1H NMR spectra were recorded on a Varian Inova 400 spectrometer. Chemical shifts are reported in ppm relative to TMS. Mass spectroscopy data of the products were collected on a MS-EI instrument. HPLC yields were recorded on a Waters Alliance 2695-2996-2475 High Performance Liquid Chromatography. Other products were isolated by chromatography on a short silica gel (200-300 mesh) column using petroleum ether (60-90°C), unless otherwise noted. Compounds described in the literature were characterised by comparison of their ^1H NMR spectra with reported data.

The HPLC measurement was carried out using an XBridge C18 (2.1×150mm, 5 μm) column. Mobile phase consisted of H_2O (including 0.3% HOAc and 0.3% $\text{N}(\text{CH}_2\text{CH}_3)_3$) and MeOH, the gradient elution was adopted, the volume ratio of H_2O to MeOH was 30:70 at the beginning to 0:100 at the end, the flow rate was 0.3 mL/min. A variable wavelength UV detector at 246 nm was used. The value of time of retention was 14.2 min.

General procedure for the Suzuki reaction of aryl bromides with arylboronic acids. A mixture of 2,4,6-tribromoaniline (0.25 mmol), aryl boronic acid (1.125 mmol), $K_3PO_4 \cdot 7H_2O$ (1.25 mmol), $Pd(OAc)_2$ (1.0 mol%), DMF (2.7 mL) and distilled water (1.3 mL) was stirred at 80°C under air for the indicated time. The mixture was added to brine (15 mL) and extracted three times with ethyl acetate (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by chromatography on a short silica gel (200-300 mesh) column.

A mixture of 2,6-dibromo-4-nitroaniline (0.25 mmol), aryl boronic acid (0.75 mmol), $K_3PO_4 \cdot 7H_2O$ (0.75 mmol), $Pd(OAc)_2$ (0.5 mol%), DMF (2.7 mL) and distilled water (1.3 mL) was stirred at 80°C under air for the indicated time. The mixture was added to brine (15 mL) and extracted three times with ethyl acetate (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by chromatography on a short silica gel (200-300 mesh) column.

A mixture of 2,6-dibromoaniline (0.5 mmol), aryl boronic acid (1.5 mmol), $K_3PO_4 \cdot 7H_2O$ (1.5 mmol), $Pd(OAc)_2$ (0.5 mol%), DMF (2.7 mL) and distilled water (1.3 mL) was stirred at 80°C under air for the indicated time. The mixture was added to brine (15 mL) and extracted three times with ethyl acetate (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by chromatography on a short silica gel (200-300 mesh) column.

A mixture of 4-bromoaniline (0.5 mmol), aryl boronic acid (0.75 mmol), $K_3PO_4 \cdot 7H_2O$ (1.0 mmol), $Pd(OAc)_2$ (0.5 mol%), DMF (2.7 mL) and distilled water (1.3 mL) was stirred at 80°C under air for the indicated time. The mixture was added to brine (15 mL) and extracted three times with ethyl acetate (3×15 mL). The solvent was concentrated under vacuum and the product was isolated by chromatography on a short silica gel (200-300 mesh) column.

Characterization data

2,4,6-Triphenylaniline (Table 3, entry 1). 1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.56 (m, 6H, Ph), 7.48 (t, J 7.6 Hz, 4H, Ph), 7.41-7.37 (m, 6H, Ph), 7.26 (t, J 7.2 Hz, 1H, Ph), 3.91 (s, 2H, NH_2), ppm.

2,4,6-Tris(4-methylphenyl)aniline (Table 3, entry 2). 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.49-7.46 (m, 6H, Ph), 7.38 (s, 2H, Ph), 7.29 (d, J 8.0 Hz, 4H, Ph), 7.20 (d, J 8.0 Hz, 2H, Ph), 2.41 (s, 6H, $2 \times CH_3$), 2.37 (s, 3H, CH_3), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 140.07 (Ph), 138.16 (Ph), 137.13 ($2 \times$ Ph), 136.81 ($2 \times$ Ph), 136.01 (Ph), 131.22 (Ph), 129.65 ($4 \times$ Ph), 129.47 ($2 \times$ Ph), 129.30 ($4 \times$ Ph), 128.40 ($2 \times$ Ph), 128.13 ($2 \times$ Ph), 126.34 ($2 \times$ Ph), 21.19 ($2 \times$ CH₃), 21.11 (CH₃); MS (EI) m/z : calculated value: 363.1987, found value: 363.1990 (M^+); Mp 113.1-114.0°C.

2,4,6-Tris(3-methylphenyl)aniline (Table 3, entry 3). 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.41-7.35 (m, 10H, Ph), 7.27 (t, J 7.4 Hz, 1H, Ph), 7.21-7.17 (m, 2H, Ph), 7.07 (d, J 7.2 Hz, 1H, Ph), 3.91 (s, 2H, NH_2), 2.41 (s, 6H, $2 \times CH_3$), 2.37 (s, 3H, CH_3), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 140.99 (Ph), 140.07 (Ph), 139.77 ($2 \times$ Ph), 138.70 ($2 \times$ Ph), 138.31 (Ph), 131.39

(Ph), 130.22 (2×Ph), 128.94 (2×Ph), 128.75 (Ph), 128.66 (Ph), 128.39 (2×Ph), 128.29 (2×Ph), 127.36 (Ph), 127.26 (Ph), 126.48 (2×Ph), 123.67 (2×Ph), 21.70 (CH₃), 21.65 (2×CH₃) ppm; MS (EI) *m/z*: calculated value: 363.1987, found value: 363.1990 (M⁺); mp 96.8-97.4°C.

2,4,6-Tris(4-methoxyphenyl)aniline (Table 3, entry 4). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.52-7.47 (m, 6H, Ph), 7.31 (s, 2H, Ph), 7.01 (d, *J* 8.8 Hz, 4H, Ph), 6.93 (d, *J* 8.8 Hz, 2H, Ph), 3.87 (s, 6H, 2×OCH₃), 3.85 (s, 2H, NH₂), 3.83 (s, 3H, OCH₃), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 158.92 (2×Ph), 158.47 (Ph), 140.19 (Ph), 133.68 (Ph), 132.02 (2×Ph), 130.81 (Ph), 130.49 (4×Ph), 128.00 (2×Ph), 127.80 (2×Ph), 127.45 (2×Ph), 114.30 (4×Ph), 114.14 (2×Ph), 55.36 (3×OCH₃) ppm; MS (EI) *m/z*: calculated value: 411.1834, found value: 411.1844 (M⁺); mp 154.0-154.8°C.

2,4,6-Tris(4-fluorophenyl)aniline (Table 3, entry 5). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.53-7.49 (m, 6H, Ph), 7.30 (s, 2H, Ph), 7.17 (t, *J* 8.8 Hz, 4H, Ph), 7.08 (t, *J* 8.8 Hz, 2H, Ph), 3.81 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 162.40 (d, *J*_{CF} 245 Hz, 2×Ph), 162.15 (d, *J*_{CF} 244 Hz, Ph), 140.52 (Ph), 136.92 (d, *J*_{CCCCF} 3 Hz, Ph), 135.40 (d, *J*_{CCCCF} 2 Hz, 2×Ph), 131.15 (d, *J*_{CCCF} 8 Hz, 4×Ph), 130.44 (Ph), 128.52 (2×Ph), 128.03 (d, *J*_{CCCF} 8 Hz, 2×Ph), 127.57 (2×Ph), 116.08 (d, *J*_{CCF} 21 Hz, 4×Ph), 115.71 (d, *J*_{CCF} 21 Hz, 2×Ph), ppm; MS (EI) *m/z*: calculated value: 375.1235, found value: 375.1241 (M⁺); mp 127.6-129.4°C.

2,4,6-Tris(3,4-difluorophenyl)aniline (Table 3, entry 6). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.38-7.16 (m, 11H, Ph), 3.87 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 150.55 (dd, *J* 248, 12 Hz, 3×Ph), 149.96 (dd, *J* 248, 12 Hz, 2×Ph), 149.50 (dd, *J* 247, 12 Hz, Ph), 140.57 (Ph), 137.48 (dd, *J* 6, 4 Hz, Ph), 135.84 (dd, *J* 6, 5 Hz, Ph), 129.33 (Ph), 128.55 (2×Ph), 126.50 (2×Ph), 125.49 (dd, *J* 6, 4 Hz, 2×Ph), 122.14 (dd, *J* 6, 4 Hz, 2×Ph), 118.41 (d, *J* 17 Hz, 2×Ph), 117.98 (d, *J* 17 Hz, 2×Ph), 117.53 (d, *J* 17 Hz, Ph), 115.16 (d, *J* 18 Hz, Ph), ppm; MS (EI) *m/z*: calculated value: 429.0952, found value: 429.0955 (M⁺); mp 194.0-194.4°C.

2,4,6-Tris(4-chlorophenyl)aniline (Table 3, entry 7). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.50-7.44 (m, 10H, Ph), 7.35 (d, *J* 8.4 Hz, 2H, Ph), 7.31 (s, 2H, Ph), 3.86 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 140.47 (Ph), 138.97 (Ph), 137.65 (2×Ph), 133.65 (2×Ph), 132.55 (Ph), 130.69 (4×Ph), 130.06 (Ph), 129.25 (4×Ph), 128.90 (2×Ph), 128.36 (2×Ph), 127.58 (2×Ph), 127.27 (2×Ph), ppm; MS (EI) *m/z*: calculated value: 423.0348, found value: 423.0343 (M⁺); mp 152.0-153.1°C.

2,6-Bis(4-methylphenyl)-4-nitroaniline (Table 4, entry 3). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.02 (s, 2H, Ph), 7.36 (d, *J* 7.6 Hz, 4H, Ph), 7.30 (d, *J* 8.0 Hz, 4H, Ph), 4.58 (s, 2H, NH₂), 2.42 (s, 6H, 2×CH₃), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 147.68 (Ph), 138.65 (Ph), 138.23 (2×Ph), 134.39 (2×Ph), 130.03 (4×Ph), 128.91 (4×Ph), 126.73 (2×Ph), 125.61 (2×Ph), 21.25 (2×CH₃), ppm; MS (EI) *m/z*: calculated value: 318.1368, found value: 318.1371 (M⁺); mp

180.2-182.1°C.

4-Nitro-2,6-diphenylaniline (Table 4, entry 4).² ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.06 (s, 2H, Ph), 7.53-7.47 (m, 8H, Ph), 7.45-7.42 (m, 2H, Ph), 4.58 (s, 2H, NH₂), ppm.

2,6-Bis(4-formylphenyl)-4-nitroaniline (Table 4, entry 5). ¹H NMR (400 MHz, CDCl₃, TMS): δ 10.10 (s, 2H, 2×CHO), 8.11 (s, 2H, Ph), 8.05 (d, *J* 8.4 Hz, 4H, Ph), 7.70 (d, *J* 8.0 Hz, 4H, Ph), 4.57 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): δ 193.29 (2×CHO), 149.42 (Ph), 143.75 (2×Ph), 137.14 (Ph), 136.08 (2×Ph), 130.80 (4×Ph), 130.40 (4×Ph), 126.49 (2×Ph), 125.60 (2×Ph), ppm; MS (EI) *m/z*: calculated value: 346.0954, found value: 346.0959 (M⁺); mp 226.9-228.3°C.

2,6-Bis(4-fluorophenyl)-4-nitroaniline (Table 4, entry 6). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.03 (s, 2H, Ph), 7.47-7.44 (m, 4H, Ph), 7.21 (t, *J* 8.6 Hz, 4H, Ph), 4.47 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 162.68 (d, *J*_{CF} 247 Hz, 2×Ph), 147.47 (Ph), 138.72 (Ph), 133.06 (d, *J*_{CCCCF} 3 Hz, 2×Ph), 130.93 (d, *J*_{CCCCF} 9 Hz, 4×Ph), 125.93 (2×Ph), 125.87 (2×Ph), 116.47 (d, *J*_{CCF} 21 Hz, 4×Ph), ppm; MS (EI) *m/z*: calculated value: 326.0867, found value: 326.0875 (M⁺); mp 215.9-216.5°C.

2,6-Bis(3,4-difluorophenyl)-4-nitroaniline (Table 4, entry 7). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.03 (s, 2H, Ph), 7.36-7.30 (m, 4H, Ph), 7.23-7.20 (m, 2H, Ph), 4.49 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 150.76 (dd, *J* 250, 13 Hz, 2×Ph), 150.45 (dd, *J* 250, 13 Hz, 2×Ph), 146.96 (Ph), 138.84 (Ph), 133.72 (dd, *J* 7, 5 Hz, 2×Ph), 126.16 (2×Ph), 125.49 (dd, *J* 8, 3 Hz, 2×Ph), 124.95 (2×Ph), 118.45 (2×Ph), 118.45 (d, *J* 34 Hz, 2×Ph), ppm; MS (EI) *m/z*: calculated value: 326.0678, found value: 326.0676 (M⁺); mp 221.6-222.3°C.

2,6-Bis(3,4,5-trifluorophenyl)-4-nitroaniline (Table 4, entry 8). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.03 (s, 2H, Ph), 7.17-7.09 (m, 4H, Ph), 4.51 (s, 2H, NH₂), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 151.83 (ddd, *J* 252, 10, 4 Hz, 4×Ph), 146.56 (Ph), 139.96 (dt, *J* 253, 15 Hz, 2×Ph), 138.88 (Ph), 132.64-132.44 (m, 2×Ph), 126.34 (2×Ph), 124.20 (2×Ph), 113.65 (dd, *J* 9, 6 Hz, 4×Ph), ppm; MS (EI) *m/z*: calculated value: 398.0490, found value: 398.0490 (M⁺); mp 209.2-210.2°C.

2,6-Diphenylaniline (Table 5, entry 1).³ ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.52-7.50 (m, 4H, Ph), 7.47-7.43 (m, 4H, Ph), 7.37-7.33 (m, 2H, Ph), 7.12 (d, *J* 7.6 Hz, 2H, Ph), 6.88 (t, *J* 7.4 Hz, 1H, Ph), 3.85 (s, 2H, NH₂), ppm.

2,6-Bis(4-methylphenyl)aniline (Table 5, entry 2). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.33 (dd, *J* 48.4, 8.0 Hz, 8H, Ph), 7.10 (d, *J* 7.6 Hz, 2H, Ph), 6.86 (t, *J* 7.6 Hz, 1H, Ph), 3.85 (s, 2H, NH₂), 2.40 (s, 6H, 2×CH₃), ppm; ¹³C NMR (100 MHz, CDCl₃, TMS): δ 141.01 (Ph), 136.95

(2×Ph), 136.92 (2×Ph), 129.68 (2×Ph), 129.60 (4×Ph), 129.28 (4×Ph), 127.95 (Ph), 118.18 (2×Ph), 21.29 (2×CH₃), ppm; MS (EI) *m/z*: calculated value: 273.1517, found value: 273.1510 (M⁺); mp 118.2-119.1 °C.

2,6-Bis(4-methoxyphenyl)aniline (Table 5, entry 3).⁴¹H NMR (400 MHz, CDCl₃, TMS): δ 7.45-7.42 (m, 4H, Ph), 7.08 (d, *J* 7.6 Hz, 2H, Ph), 7.01-6.97 (m, 4H, Ph), 6.85 (t, *J* 7.4 Hz, 1H, Ph), 3.85 (s, 6H, 2×OCH₃), 3.82 (s, 2H, NH₂), ppm.

2,6-Bis(2-methylphenyl)aniline (Table 5, entry 4).⁴ ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.29-7.25 (m, 8H, Ph), 7.02-6.99 (m, 2H, Ph), 6.85-6.80 (m, 1H, Ph), 3.28 (s, 2H, NH₂), 2.20 (d, *J* 4.0 Hz, 6H, 2×CH₃), ppm.

2,6-Bis(4-fluorophenyl)aniline (Table 5, entry 5). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.48-7.45 (m, 4H, Ph), 7.17-7.12 (m, 4H, Ph), 7.09 (d, *J* 7.6 Hz, 2H, Ph), 6.87 (t, *J* 7.6 Hz, 1H, Ph), 3.75 (s, 2H, NH₂), ppm, ¹³C NMR (100 MHz, CDCl₃, TMS): δ 162.16 (d, *J*_{CF} 245 Hz, 2×Ph), 140.93 (Ph), 135.50 (d, *J*_{CCCCF} 3 Hz, 2×Ph), 131.01 (d, *J*_{CCCF} 8 Hz, 4×Ph), 129.95 (2×Ph), 127.03 (Ph), 118.30 (2×Ph), 115.84 (d, *J*_{CCF} 21 Hz, 4×Ph), ppm; MS (EI) *m/z*: calculated value: 281.1016, found value: 281.1018 (M⁺); mp 146.0-147.6 °C.

2,6-Bis(3,4-difluorophenyl)aniline (Table 5, entry 6). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.33-7.29 (m, 2H, Ph), 7.27-7.19 (m, 4H, Ph), 7.08 (d, *J* 7.6 Hz, 2H, Ph), 6.87 (t, *J* 7.6 Hz, 1H, Ph), 3.77 (s, 2H, NH₂), ppm, ¹³C NMR (100 MHz, CDCl₃, TMS): δ 150.46 (dd, *J* 248, 12 Hz, 2×Ph), 149.77 (dd, *J* 248, 12 Hz, 2×Ph), 140.64 (Ph), 136.28 (dd, *J* 6, 4 Hz, 2×Ph), 130.19 (2×Ph), 126.06 (Ph), 125.47 (dd, *J* 6, 4 Hz, 2×Ph), 118.45 (2×Ph), 118.37 (d, *J* 17 Hz, 2×Ph), 117.78 (d, *J* 17 Hz, 2×Ph), ppm; MS (EI) *m/z*: calculated value: 317.0828, found value: 317.0818 (M⁺); mp 88.2-89.0 °C.

2,6-Bis(3,4,5-trifluorophenyl)aniline (Table 5, entry 7). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.16-7.07 (m, 6H, Ph), 6.87 (t, *J* 7.6 Hz, 1H, Ph), 3.78 (s, 2H, NH₂), ppm, ¹³C NMR (100 MHz, CDCl₃, TMS): δ 151.46 (ddd, *J* 250, 10, 4 Hz, 4×Ph), 140.37 (Ph), 139.21 (dt, *J* 251, 5 Hz, 2×Ph), 135.25-135.04 (m, 2×Ph), 130.42 (2×Ph), 125.25 (Ph), 118.67 (2×Ph), 113.52 (dd, *J* 16, 6 Hz, 4×Ph), ppm; MS (EI) *m/z*: calculated value: 353.0639, found value: 353.0637 (M⁺); mp 92.5-93.1 °C.

4-Phenylaniline (Table 6, entry 1).⁵ ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.55-7.52 (m, 2H, Ph), 7.43-7.37 (m, 4H, Ph), 7.29-7.25 (m, 1H, Ph), 6.77-6.74 (m, 2H, Ph), 3.71 (s, 2H, NH₂), ppm.

4-(4-Methylphenyl)aniline (Table 6, entry 2).⁶ ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.44-7.38 (m, 4H, Ph), 7.20 (d, *J* 8.0 Hz, 2H, Ph), 6.76-6.73 (m, 2H, Ph), 3.69 (s, 2H, NH₂), 2.37 (s, 3H,

CH_3), ppm.

4-(2-Methylphenyl)aniline (Table 6, entry 3).⁷ 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.24-7.20 (m, 4H, Ph), 7.12 (d, J 8.8 Hz, 2H, Ph), 6.72-6.69 (m, 2H, Ph), 3.66 (s, 2H, NH_2), 2.28 (s, 3H, CH_3), ppm.

4-(2-Methoxyphenyl)aniline (Table 6, entry 4).¹ 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.34 (d, J 8.4 Hz, 2H, Ph), 7.29-7.21 (m, 2H, Ph), 6.99 (t, J 7.4 Hz, 1H, Ph), 6.94 (d, J 8.0 Hz, 1H, Ph), 6.70 (d, J 8.4 Hz, 2H, Ph), 3.79 (s, 3H, CH_3), 3.66 (s, 2H, NH_2), ppm.

4-(4-Cyanophenyl)aniline (Table 6, entry 5).⁸ 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.80 (s, 1H, Ph), 7.76-7.73 (m, 1H, Ph), 7.55-7.52 (m, 1H, Ph), 7.48 (t, J 8.0 Hz, 1H, Ph), 7.40-7.37 (m, 2H, Ph), 6.79-6.75 (m, 2H, Ph), 3.82 (s, 2H, NH_2), ppm.

4-(4-Fluorophenyl)aniline (Table 6, entry 6). 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.49-7.44 (m, 2H, Ph), 7.37-7.33 (m, 2H, Ph), 7.10-7.05 (m, 2H, Ph), 6.77-6.73 (m, 2H, Ph), 3.72 (s, 2H, NH_2), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.88 (d, J_{CF} 244 Hz, Ph), 145.85 (Ph), 137.35 (d, J_{CCCCF} 3 Hz, Ph), 130.64 (Ph), 127.90 (2 \times Ph), 127.82 (2 \times Ph), 115.46 (d, J_{CCF} 21 Hz, 2 \times Ph), 115.42 (2 \times Ph), ppm; MS (EI) m/z : calculated value: 187.0797, found value: 187.0795 (M^+); mp 120.2-121.1 $^{\circ}C$.

4-(3,4-Difluorophenyl)aniline (Table 6, entry 7). 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.32-7.28 (m, 3H, Ph), 7.23-7.13 (m, 2H, Ph), 6.76-6.73 (m, 2H, Ph), 3.76 (s, 2H, NH_2), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 150.48 (dd, J 245, 13 Hz, Ph), 149.23 (dd, J 245, 13 Hz, Ph), 146.37 (Ph), 138.39 (dd, J 6, 4 Hz, Ph), 129.36 (Ph), 127.87 (2 \times Ph), 122.07 (dd, J 6, 4 Hz, Ph), 117.34 (d, J 17 Hz, Ph), 115.40 (2 \times Ph), 115.07 (d, J 17 Hz, Ph), ppm; MS (EI) m/z : calculated value: 205.0703, found value: 205.0694 (M^+); mp 88.3-89.2 $^{\circ}C$.

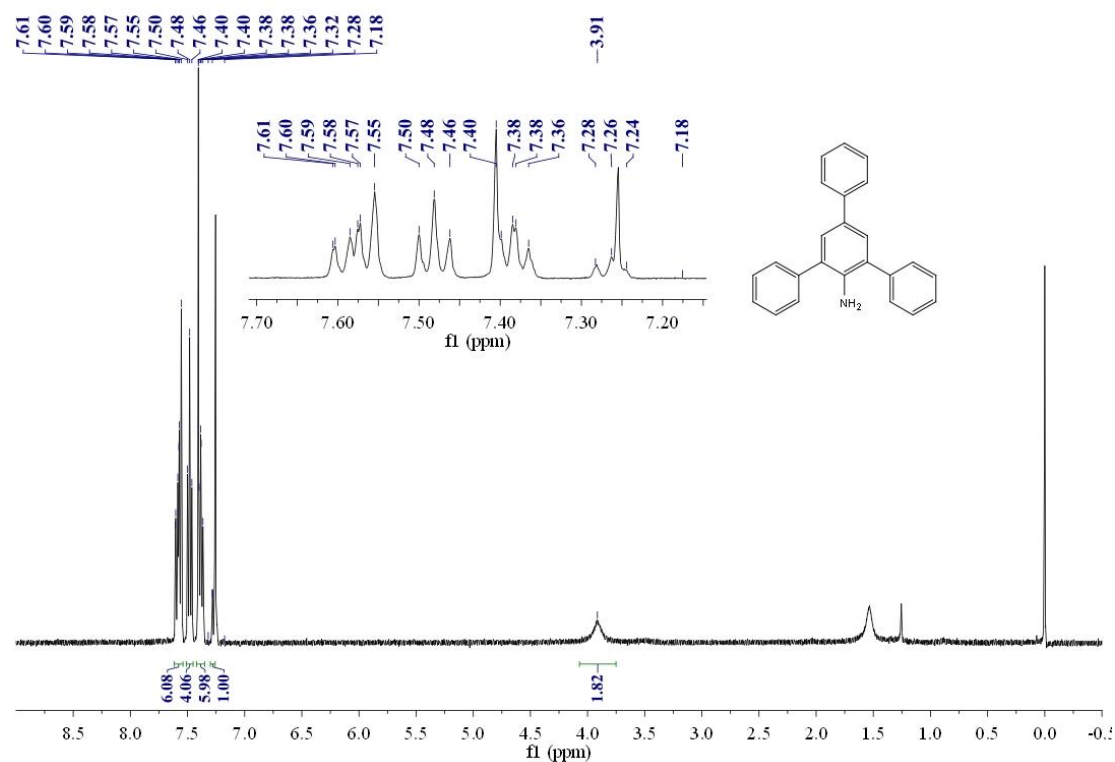
4-(3,4,5-Trifluorophenyl)aniline (Table 6, entry 8). 1H NMR (400 MHz, $CDCl_3$, TMS): δ 7.32-7.29 (m, 2H, Ph), 7.13-7.07 (m, 2H, Ph), 6.75-6.72 (m, 2H, Ph), 3.80 (s, 2H, NH_2), ppm; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 151.38 (ddd, J 247, 10, 5 Hz, 2 \times Ph), 146.84 (Ph), 139.85-137.06 (m, 2 \times Ph), 128.25 (Ph), 127.78 (2 \times Ph), 115.35 (2 \times Ph), 109.95 (dd, J 16, 6 Hz, 2 \times Ph), ppm; MS (EI) m/z : calculated value: 223.0609, found value: 223.0599 (M^+); mp 83.6-84.1 $^{\circ}C$.

References

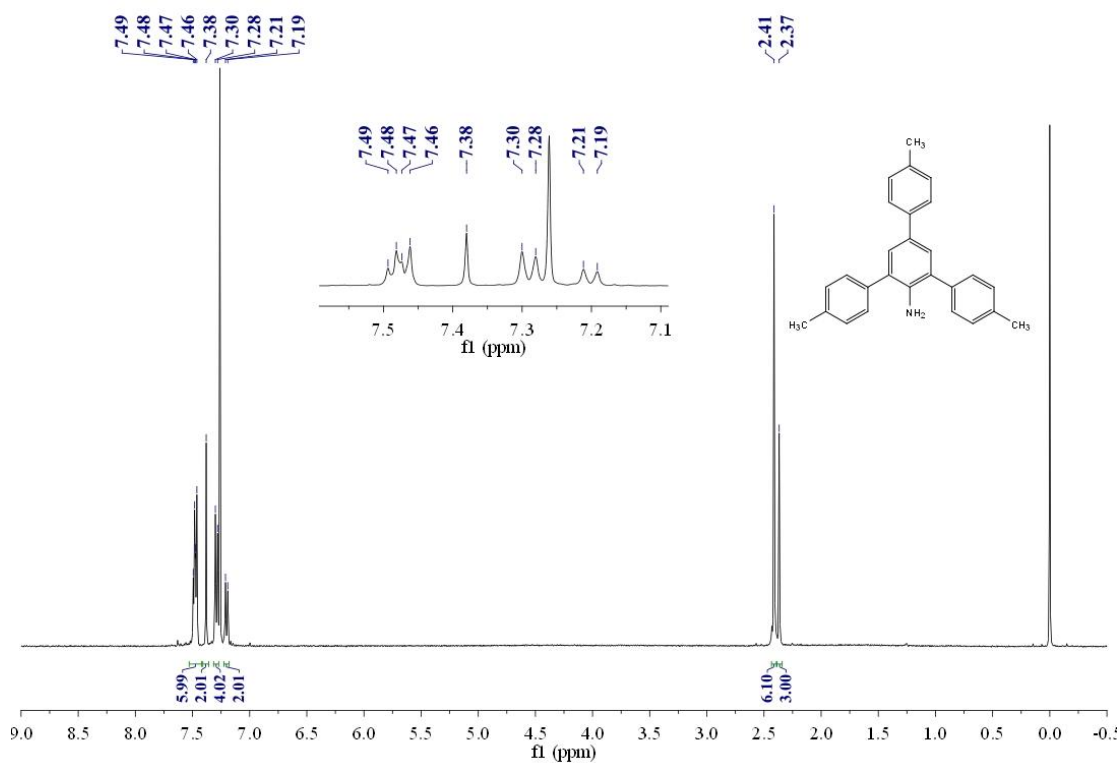
- 1 Bollige, J. L.; Frech, C. M. *Adv. Synth. Catal.* **2010**, 352, 1075.
- 2 Meinhard, D.; Wegner, M.; Kipiani, G.; Hearley, A.; Reuter, P.; Fischer, S.; Mart, O.; Rieger, B. *J. Am. Chem. Soc.* **2007**, 129, 9182.
- 3 Miura, Y.; Oka, H.; Momoki, M. *Synthesis* **1995**, 1419.
- 4 Lee, D.; Jung, J.; Jin, M. *Chem. Commun.* **2010**, 46, 9046.
- 5 Liu, L.; Zhang, Y.; Wang, Y. *J. Org. Chem.* **2005**, 70, 6122.
- 6 Inada, K.; Miyaura, N. *Tetrahedron* **2000**, 56, 8657.
- 7 Song, C.; Ma, Y.; Chai, Q.; Ma, C.; Jiang, W.; Andrus, M. B. *Tetrahedron* **2005**, 61, 7438.
- 8 Manolikakes, G.; Hernandez, C. M.; Schade, M. A.; Metzger, A.; Knochel, P. *J. Org. Chem.* **2008**, 73, 8422.

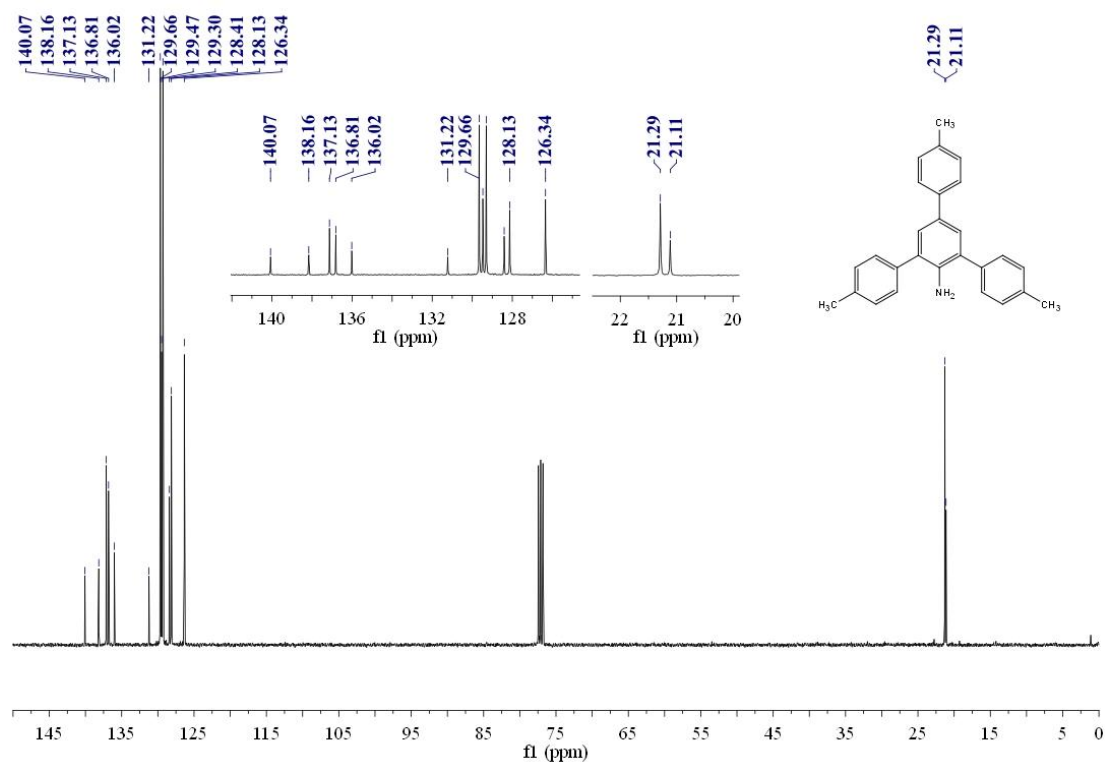
NMR Spectra for all Cross-Coupling Products

2,4,6-triphenylaniline

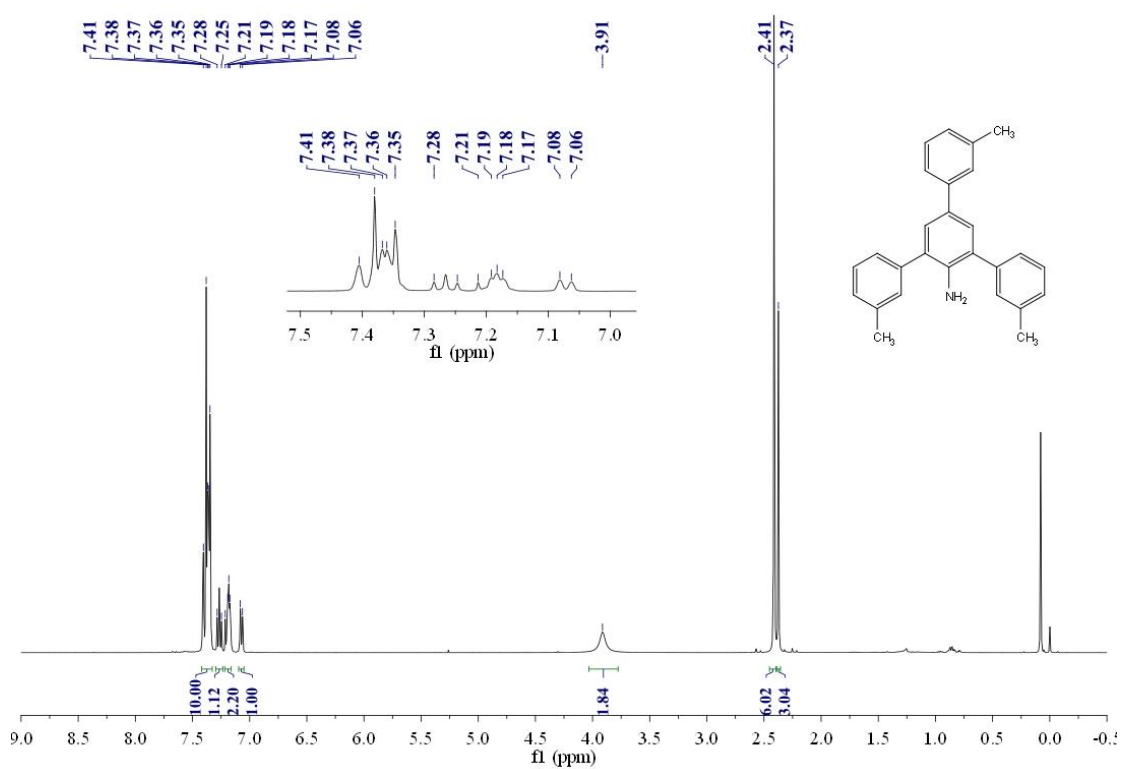


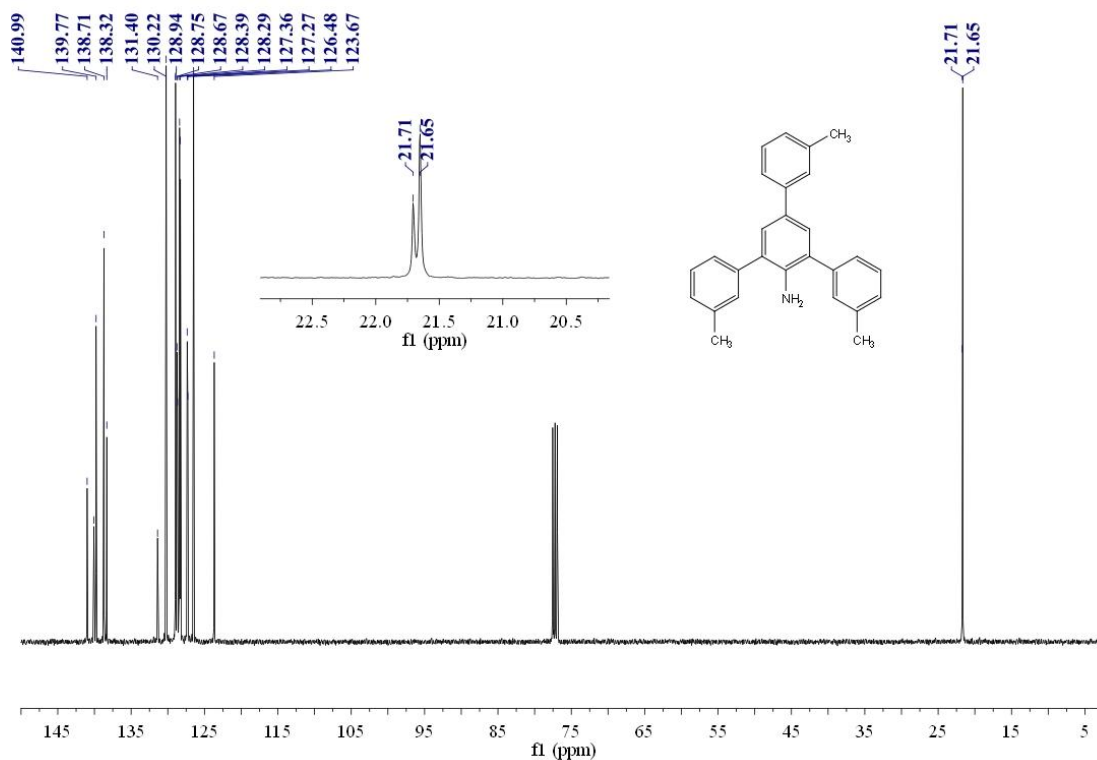
2,4,6-tris(4-methylphenyl)aniline



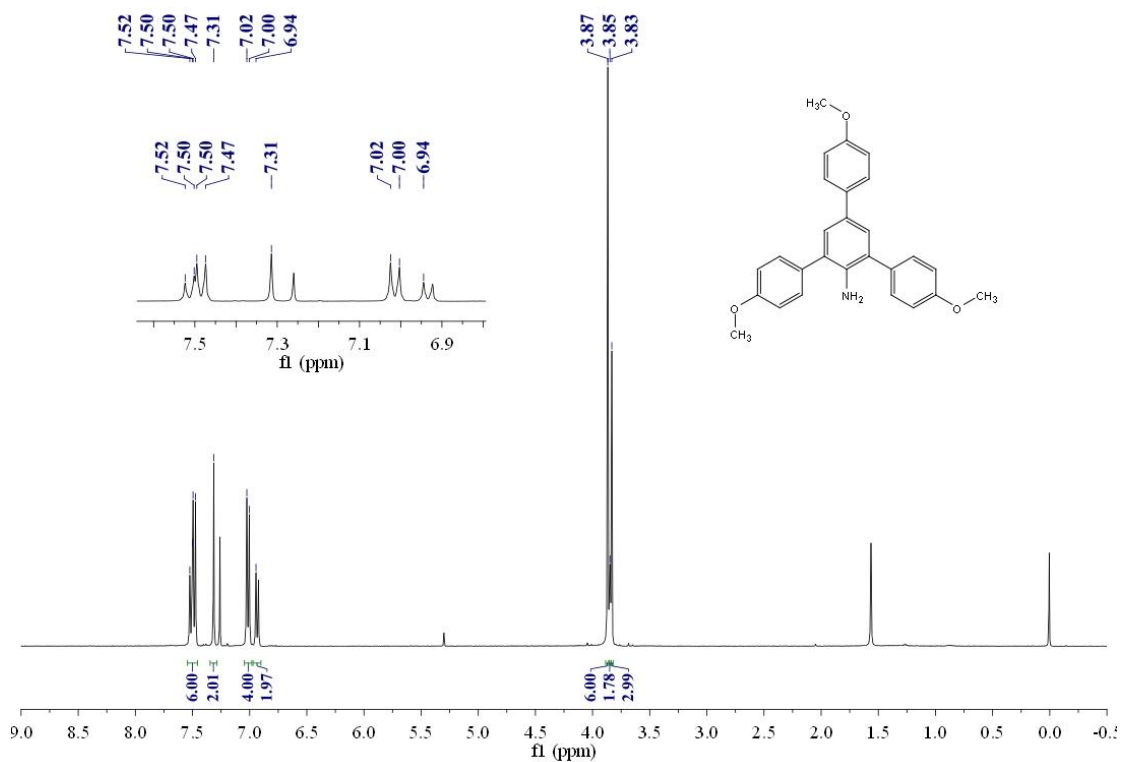


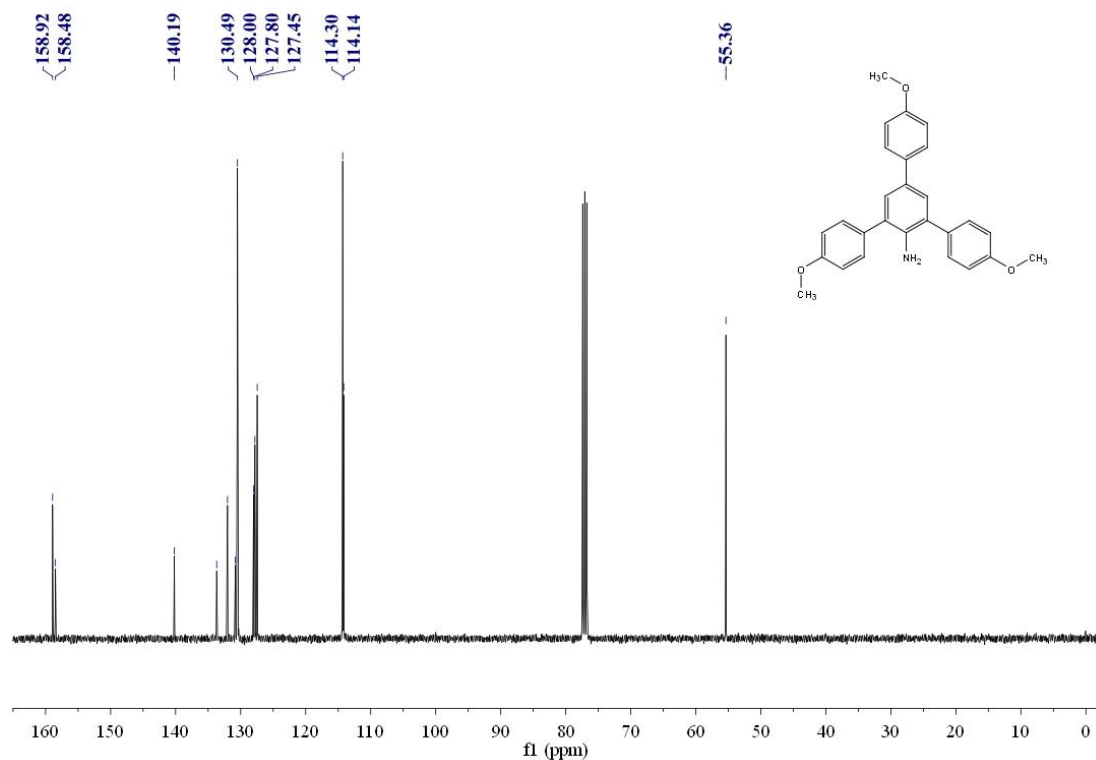
2,4,6-tris(3-methylphenyl)aniline



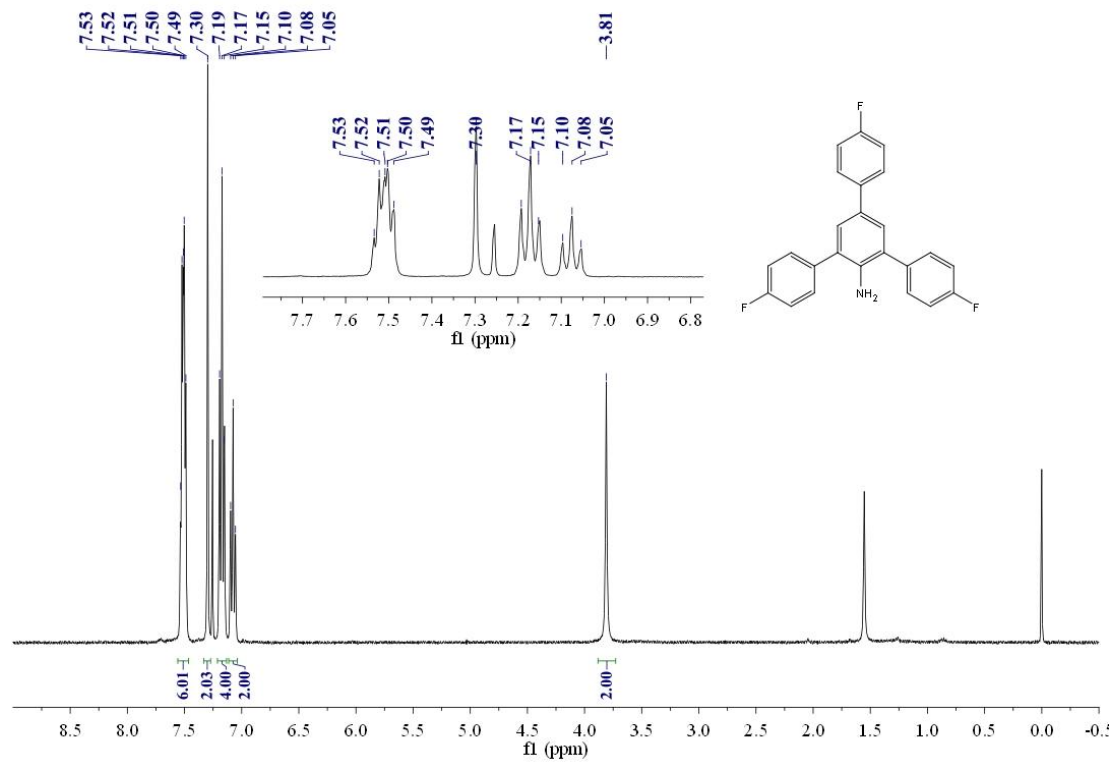


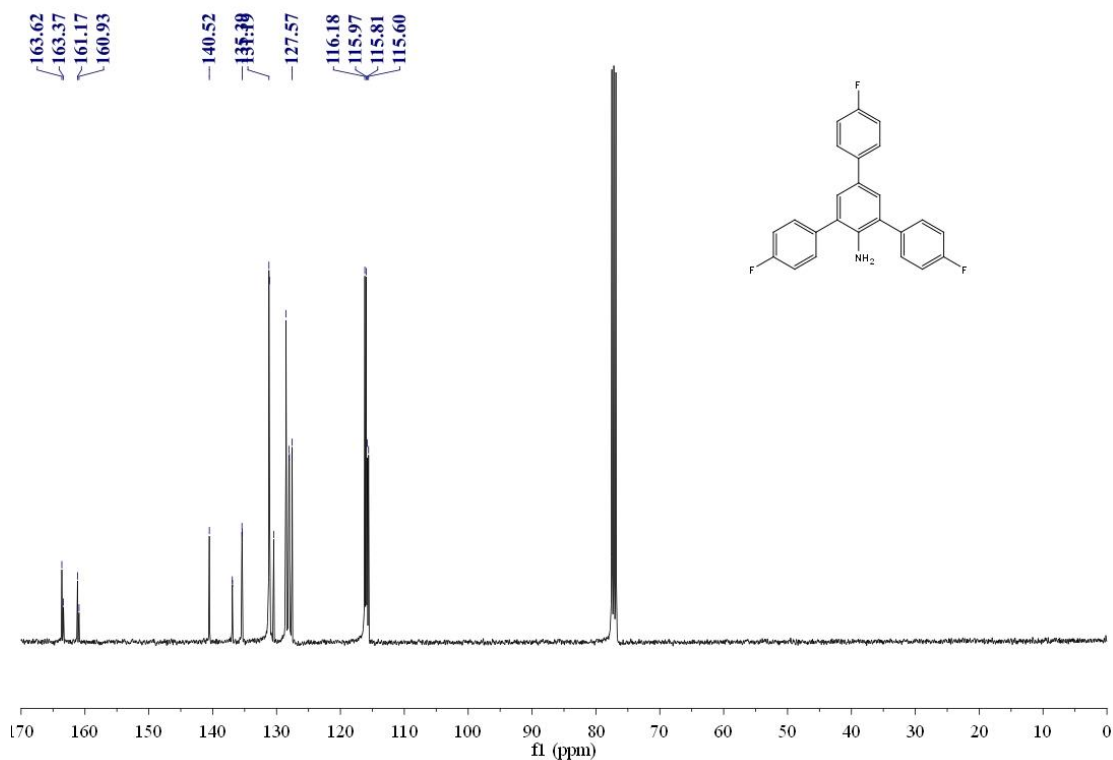
2,4,6-tris(4-methoxyphenyl)aniline



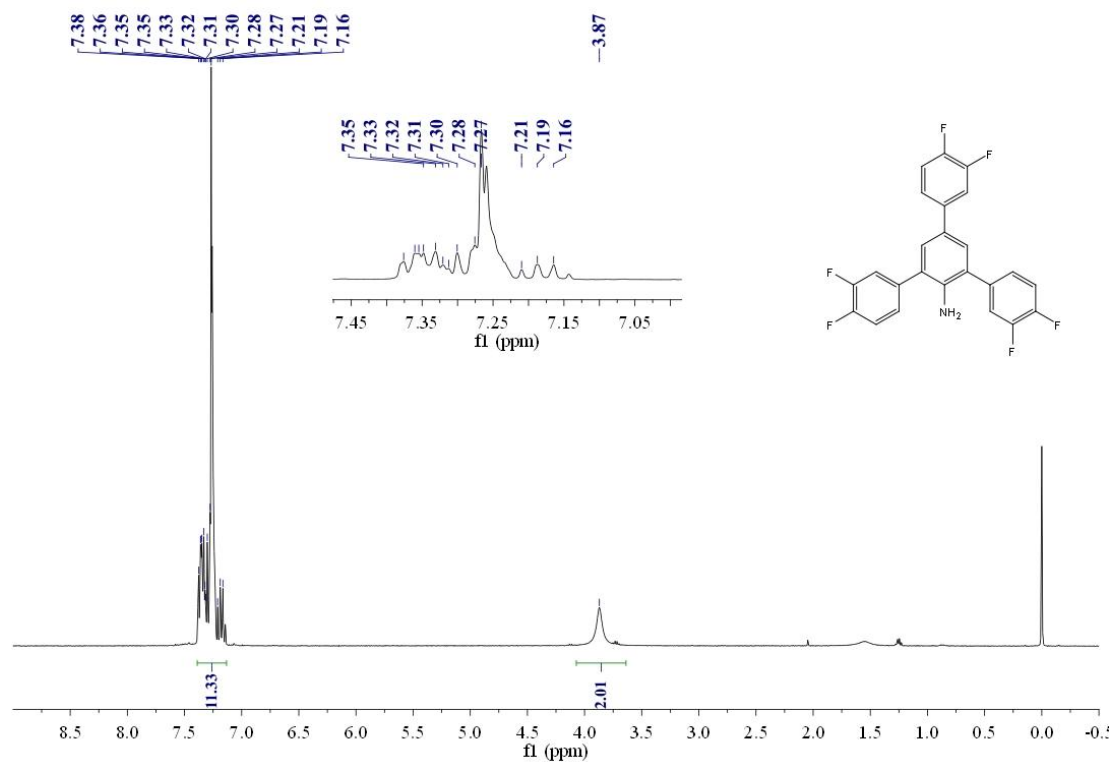


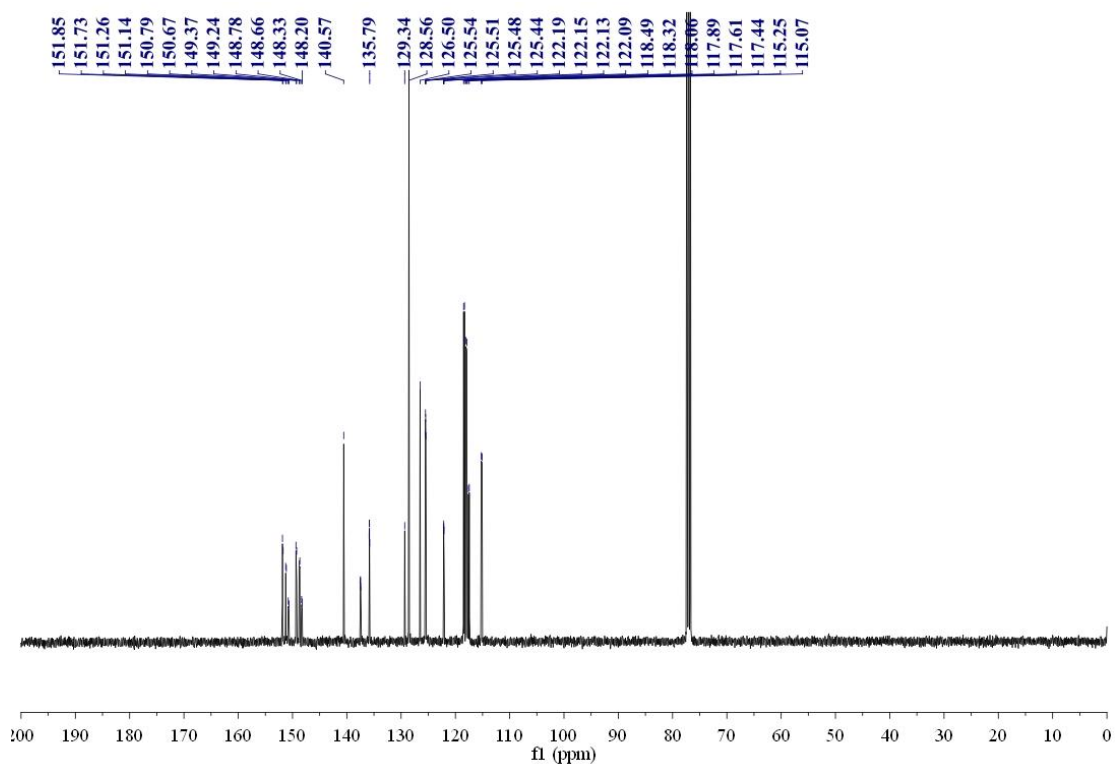
2,4,6-tris(4-fluorophenyl)aniline



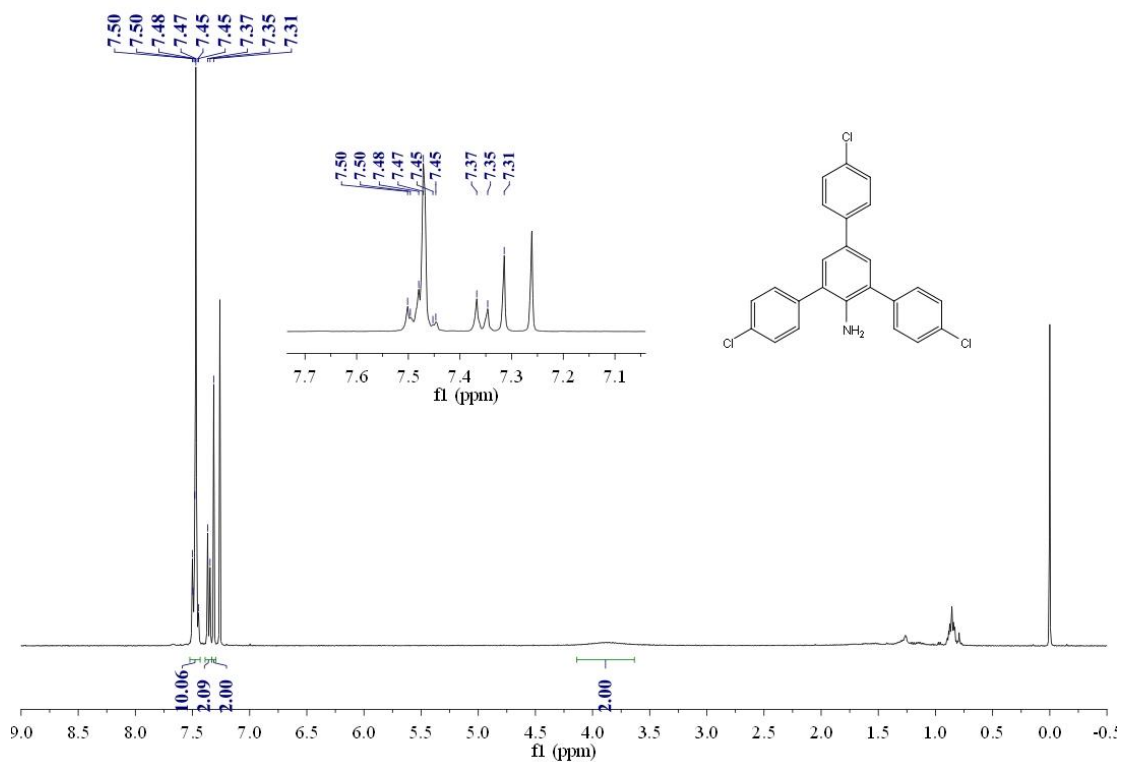


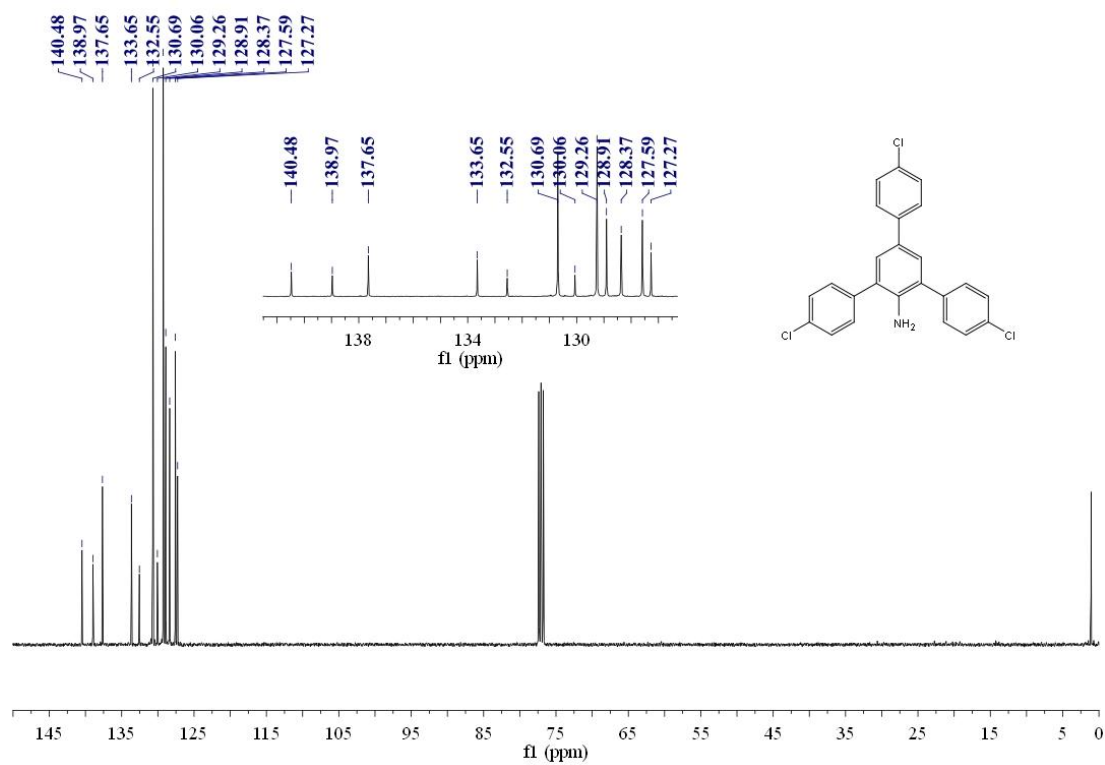
2,4,6-tris(3,4-difluorophenyl)aniline



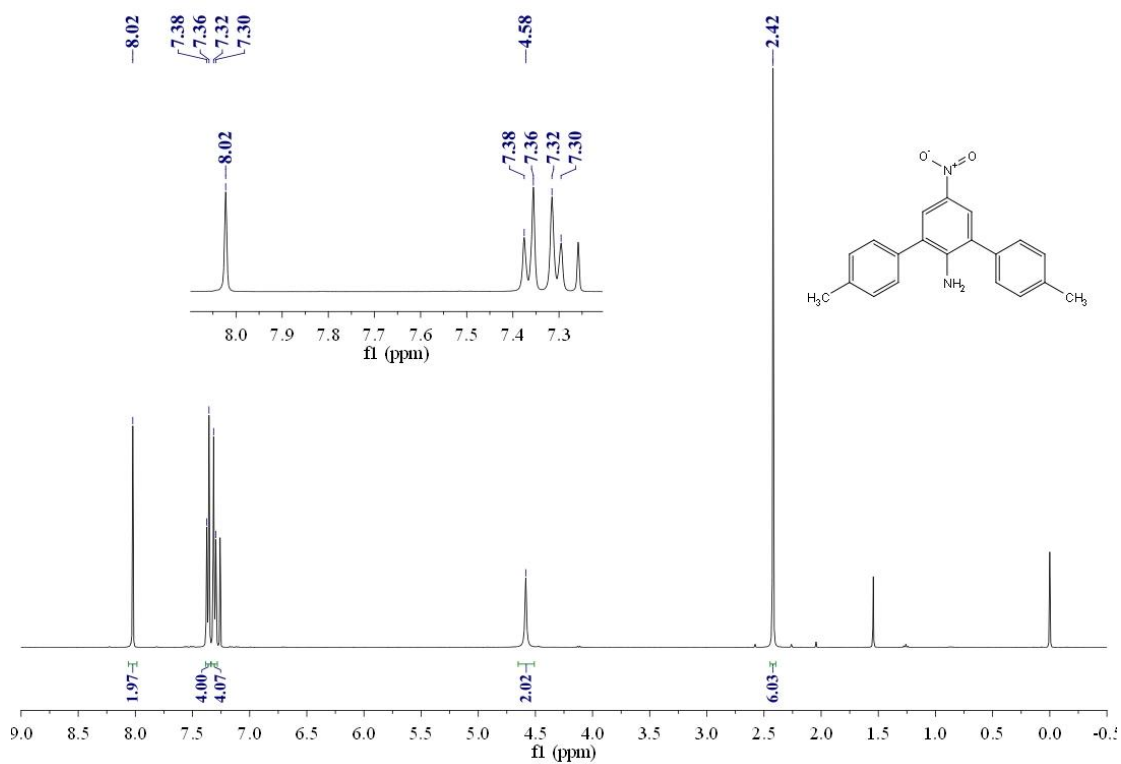


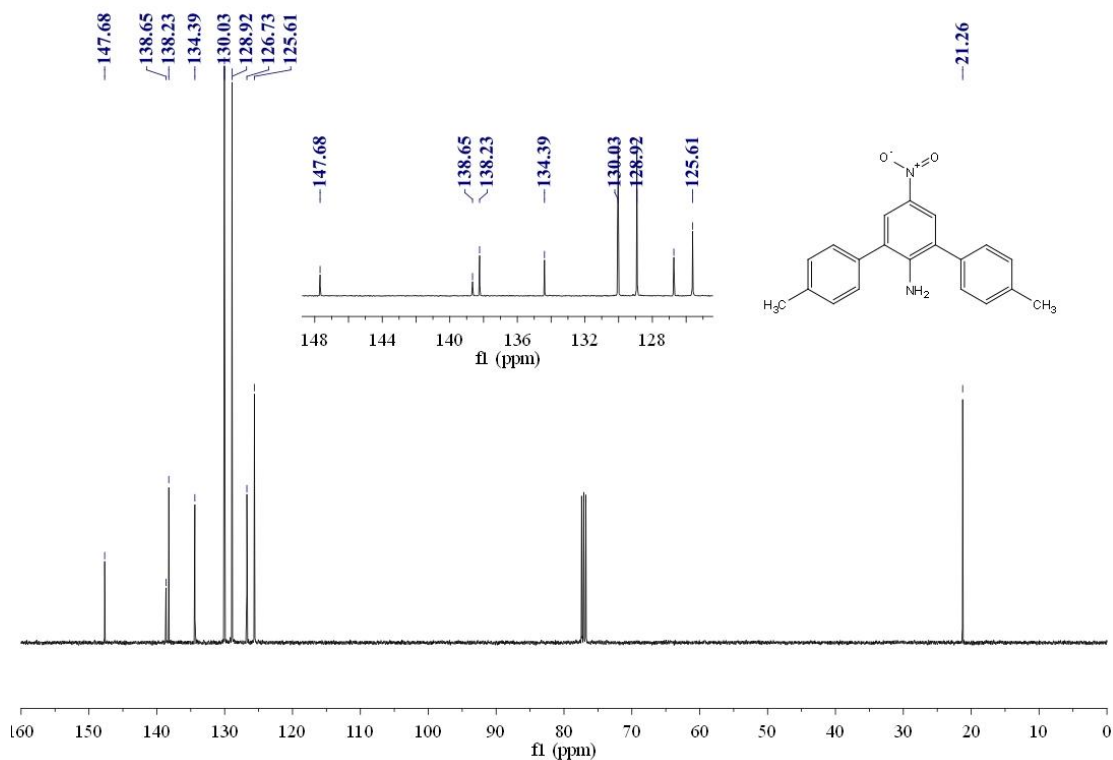
2,4,6-tris(4-chlorophenyl)aniline



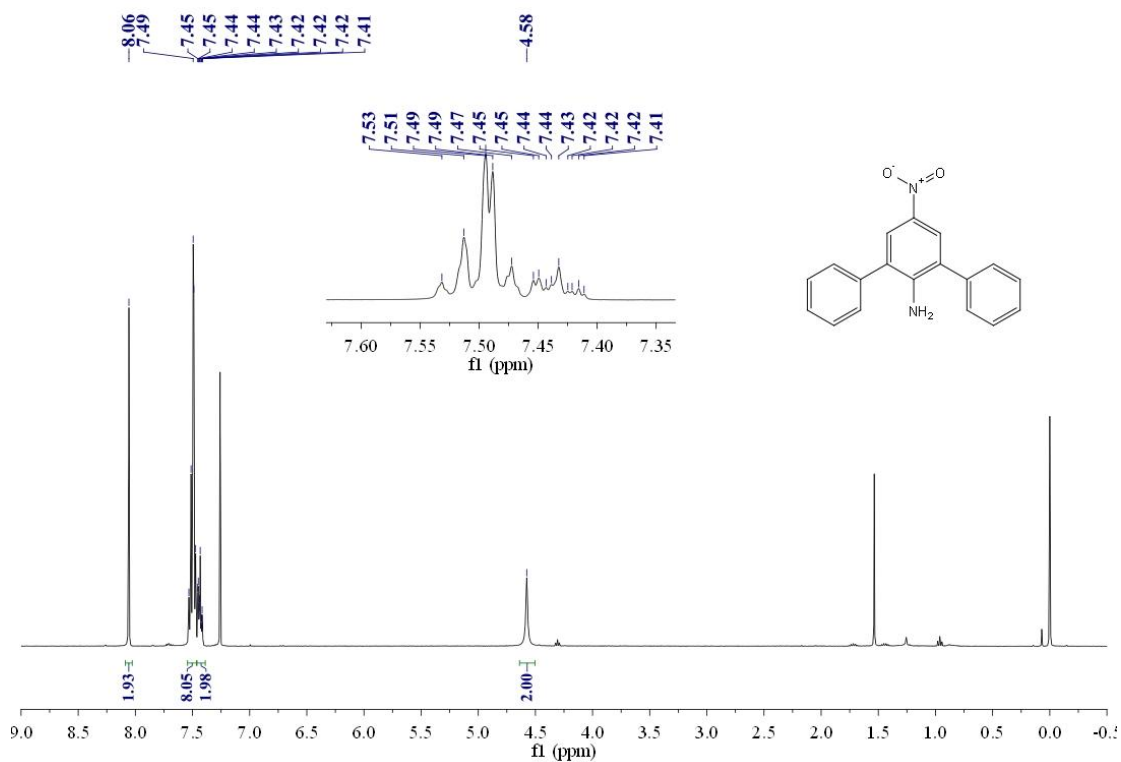


2,6-bis(4-methylphenyl)-4-nitroaniline

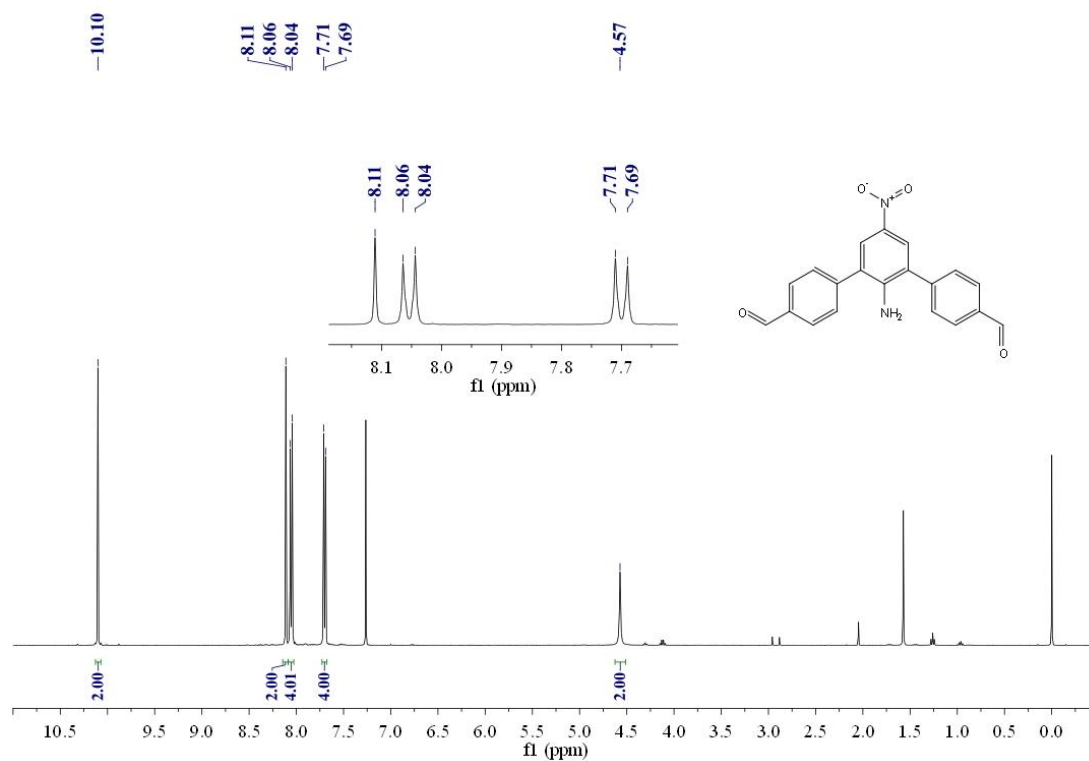




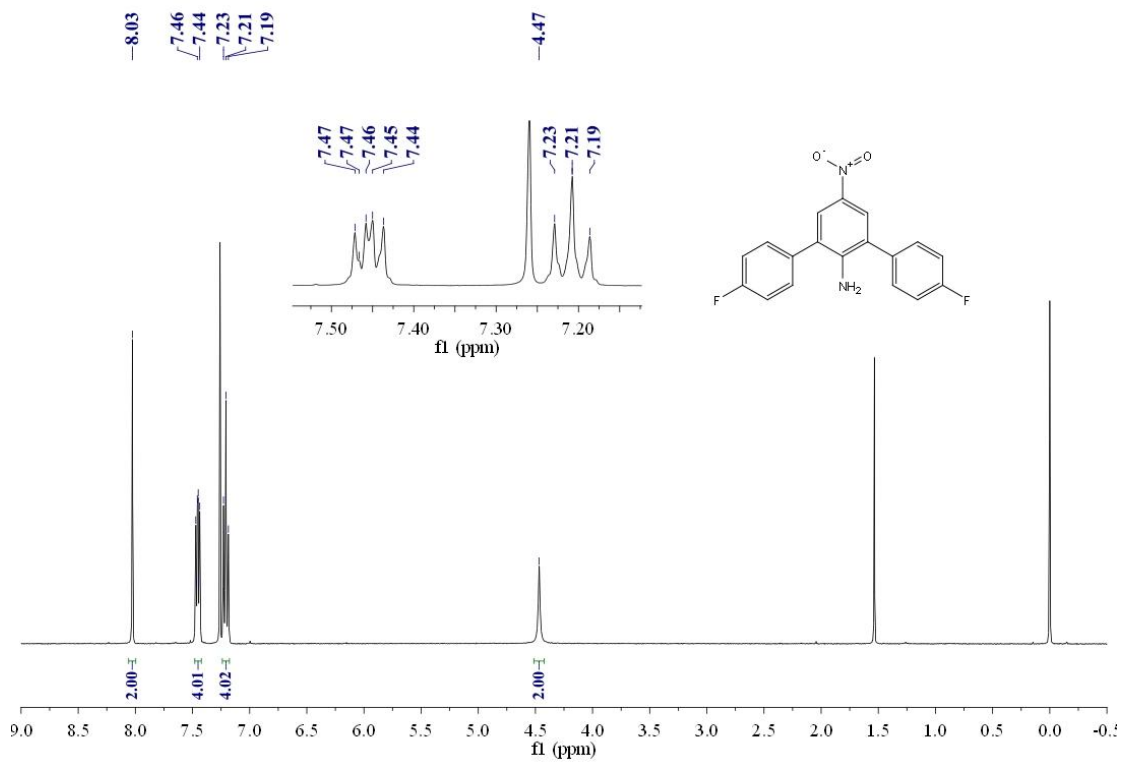
4-nitro-2,6-diphenylaniline

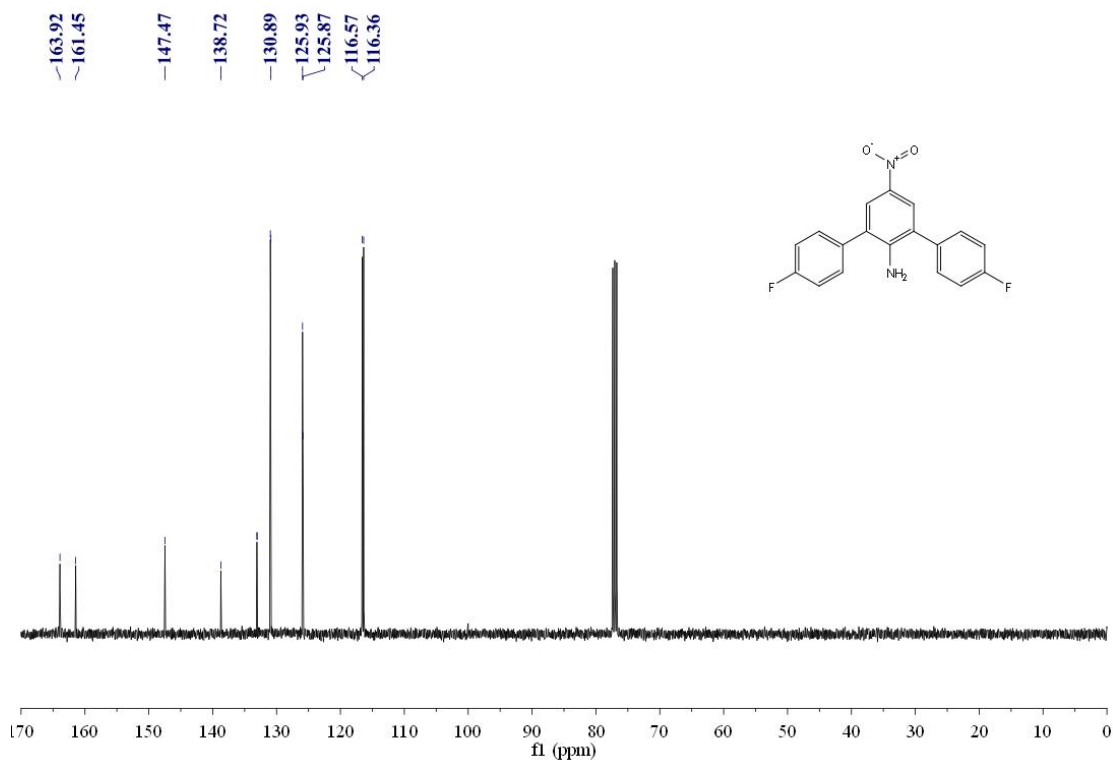


2,6-bis(4-formylphenyl)-4-nitroaniline

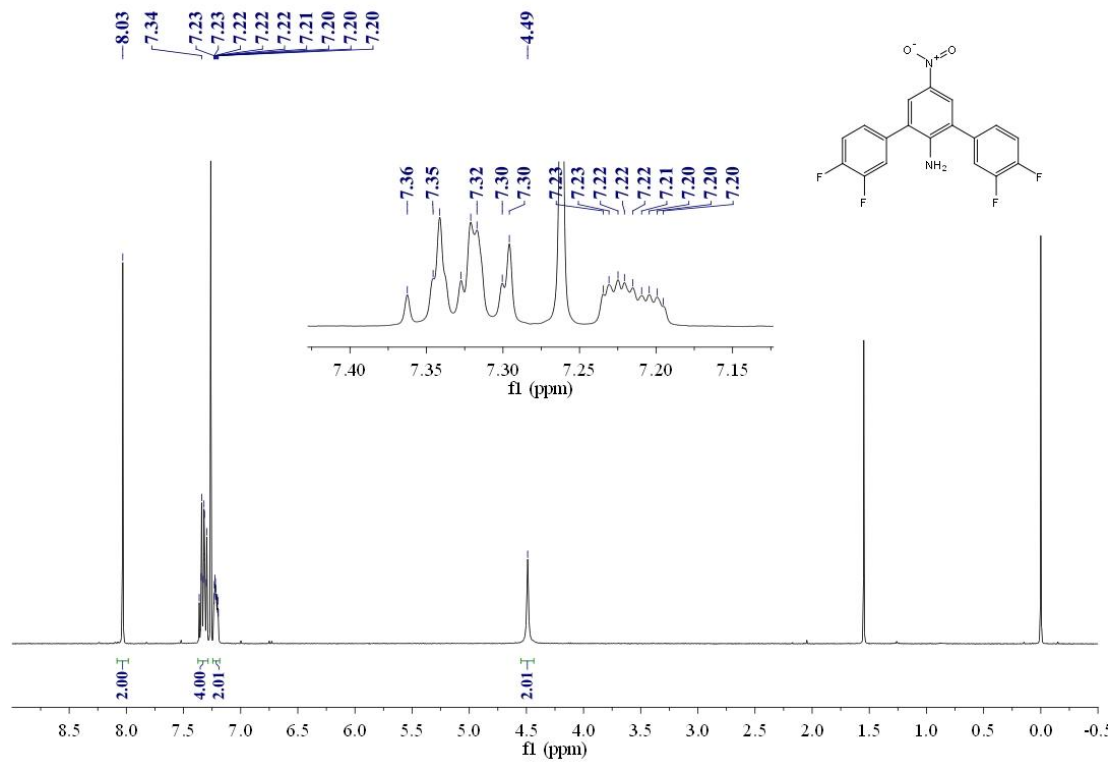


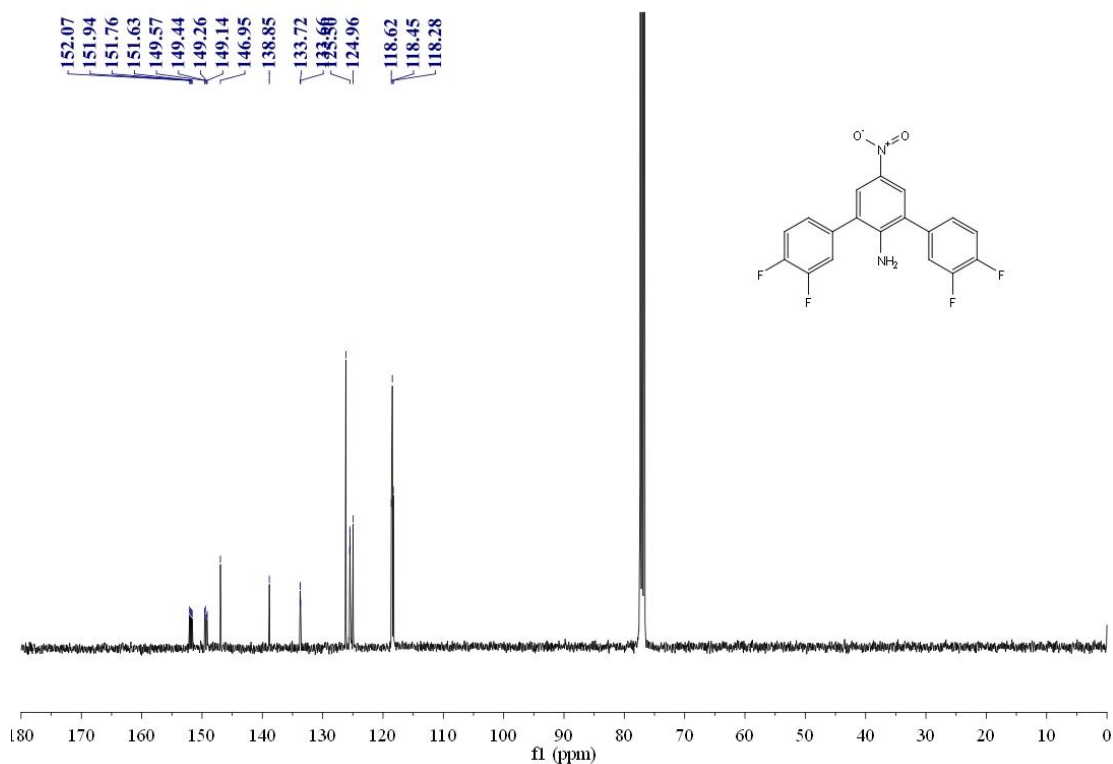
2,6-bis(4-fluorophenyl)-4-nitroaniline



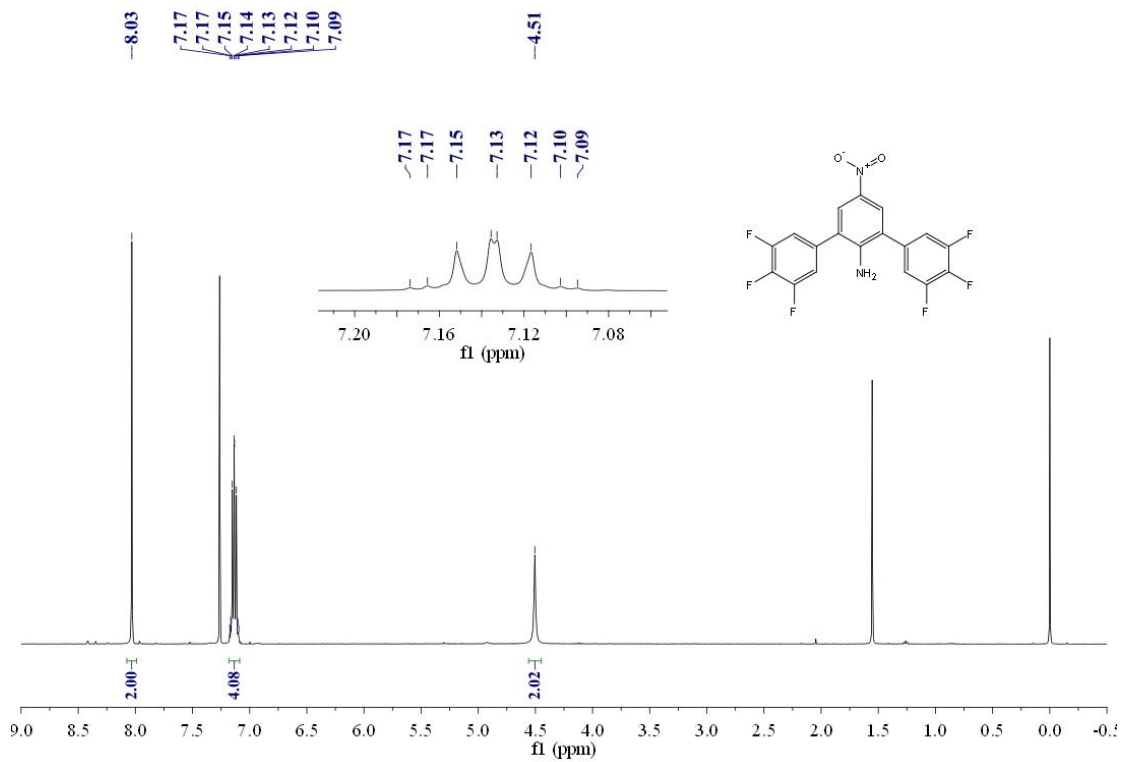


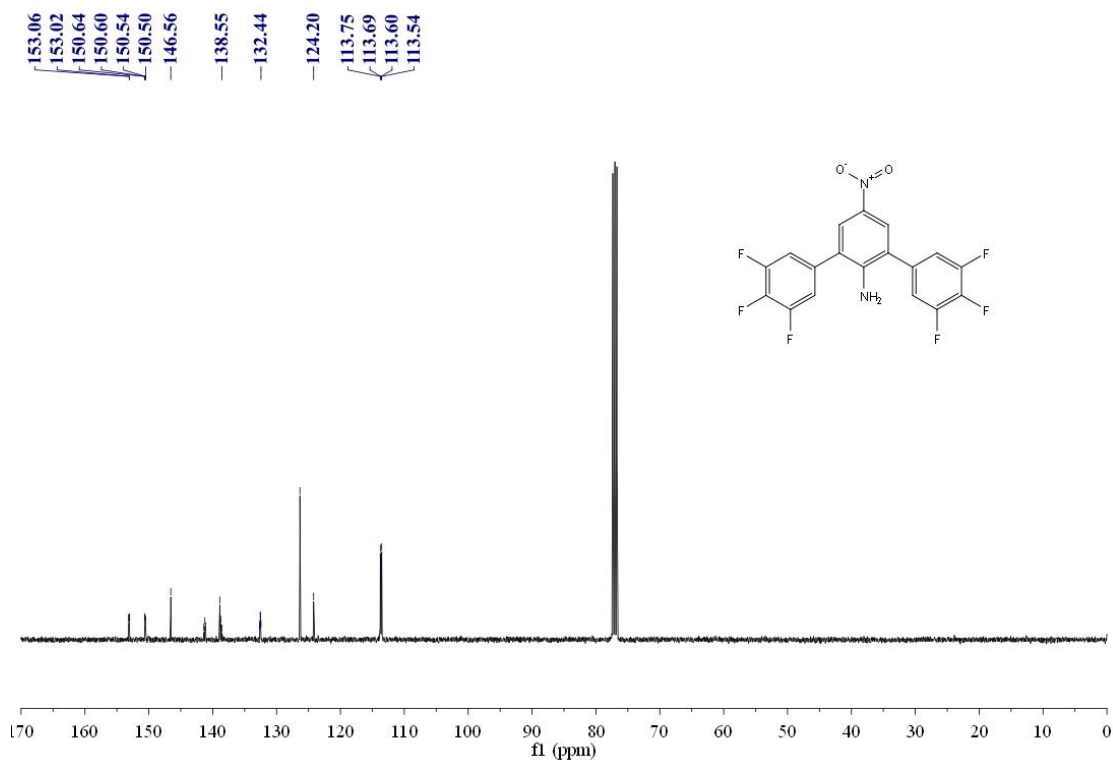
2,6-bis(3,4-difluorophenyl)-4-nitroaniline



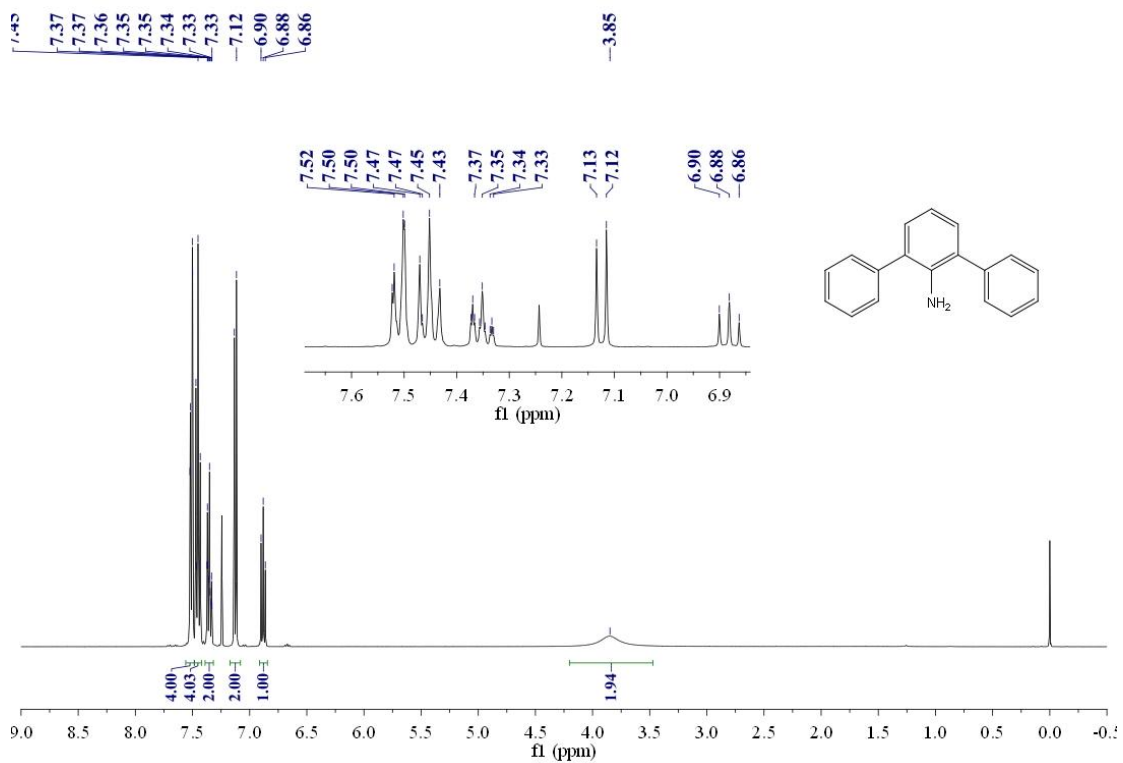


2,6-bis(3,4,5-trifluorophenyl)-4-nitroaniline

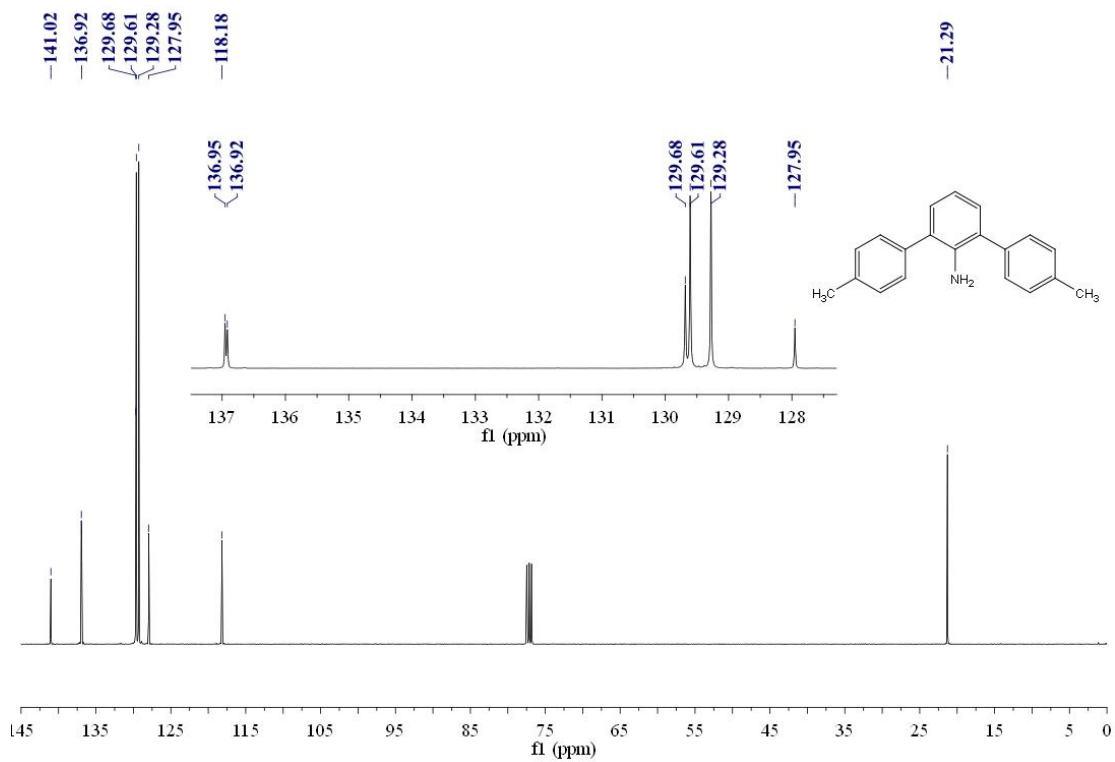
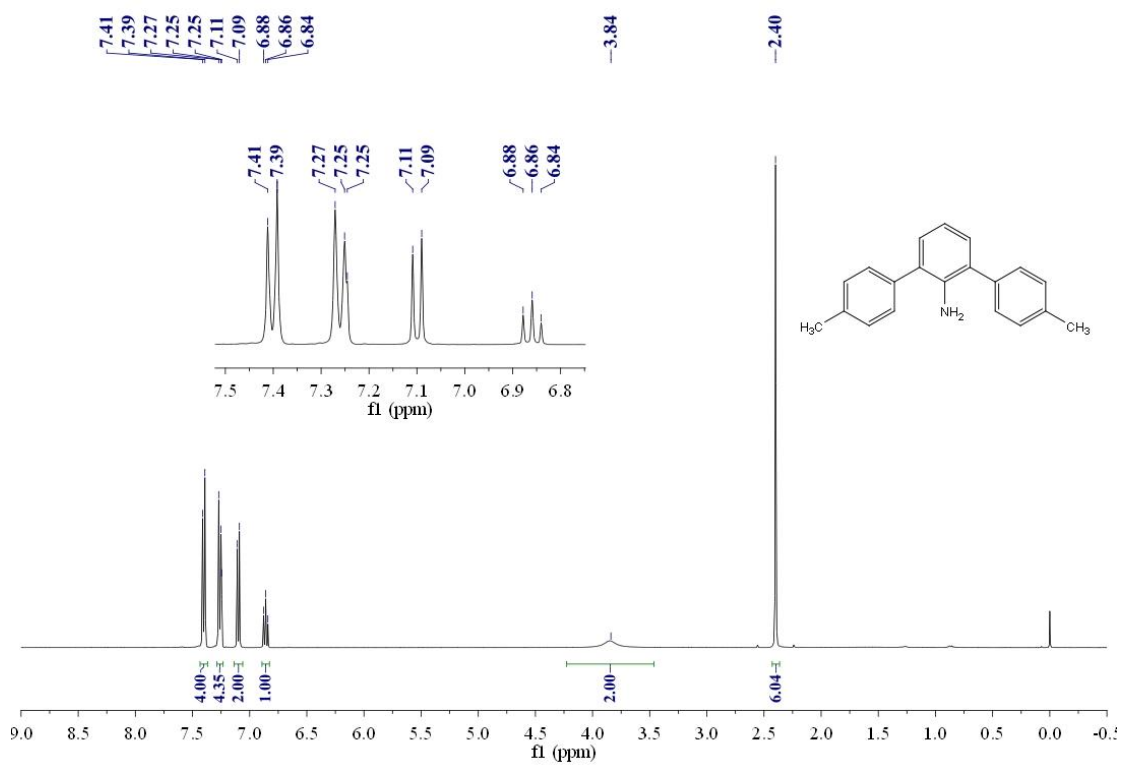




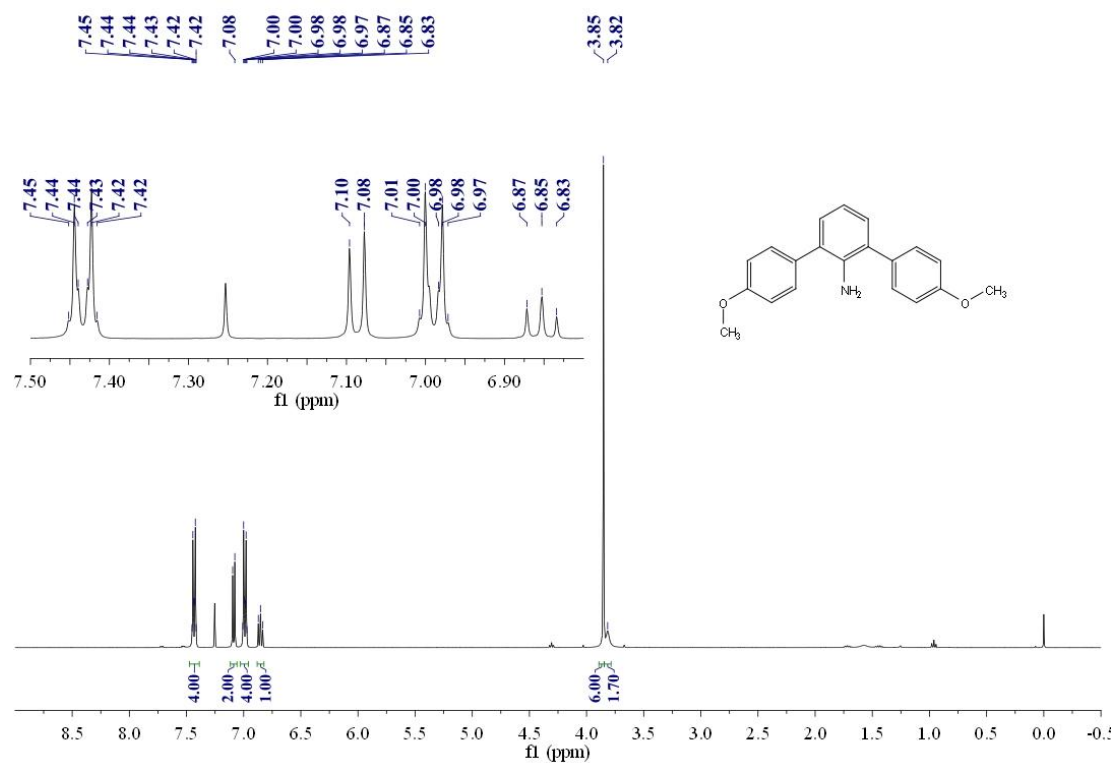
2,6-diphenylaniline



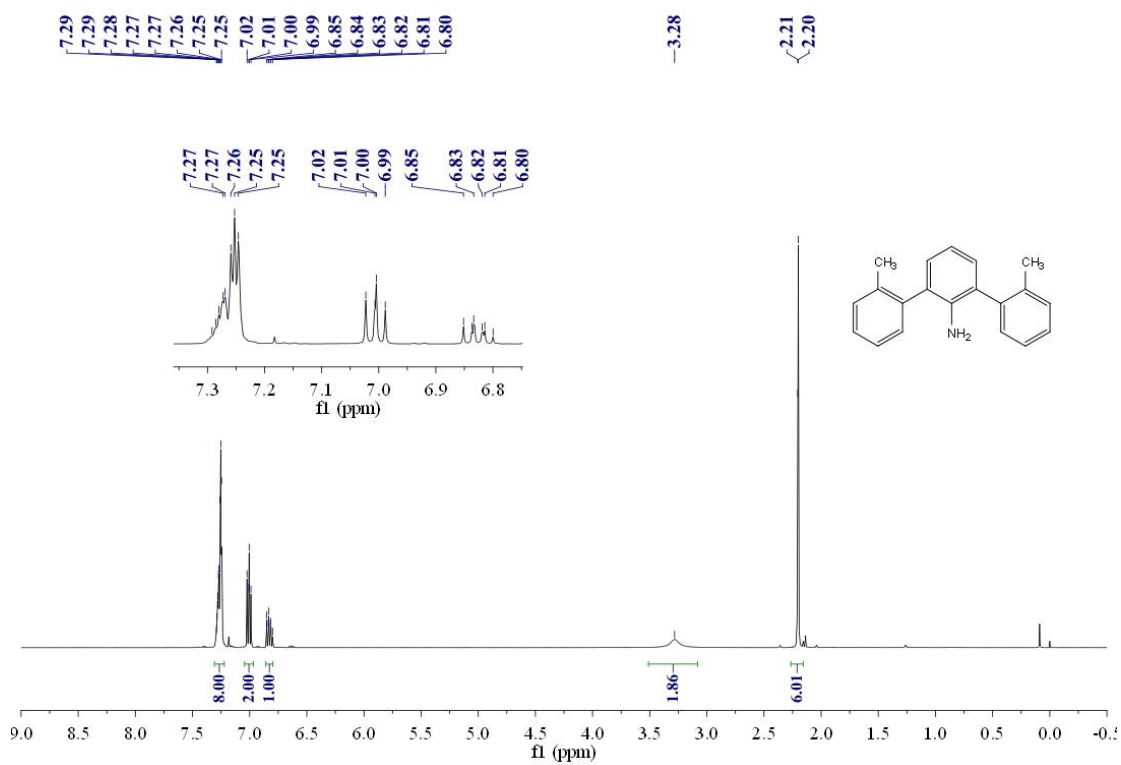
2,6-bis(4-methylphenyl)aniline



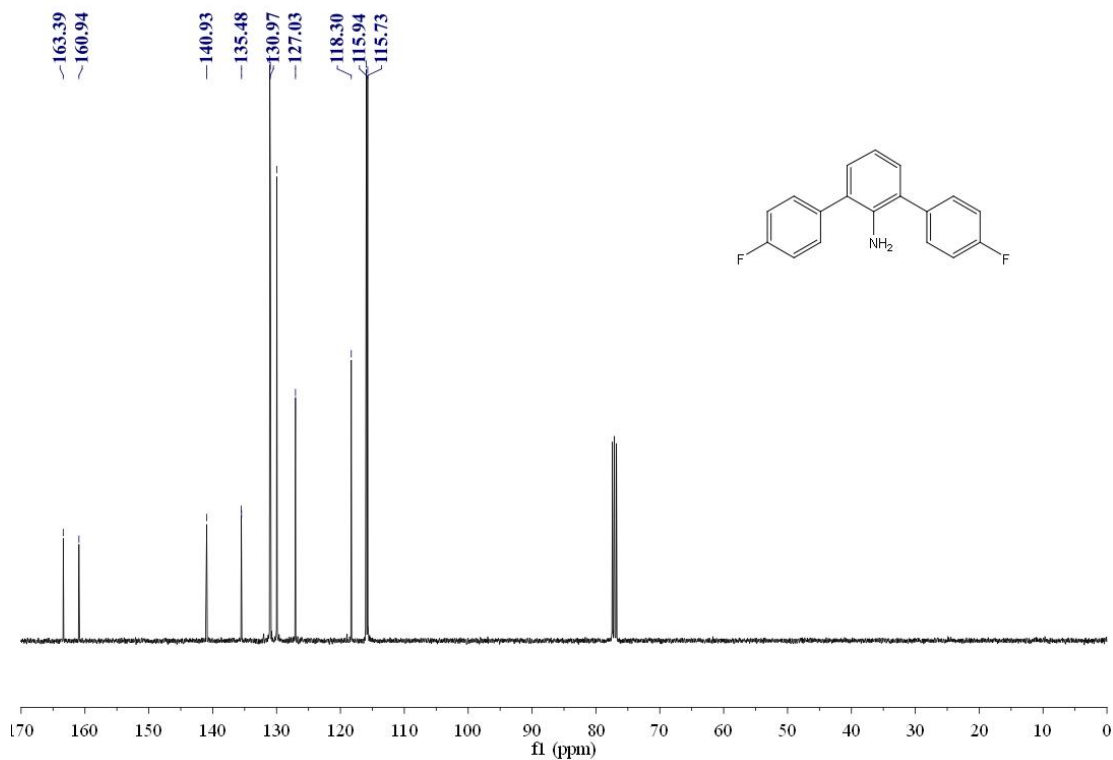
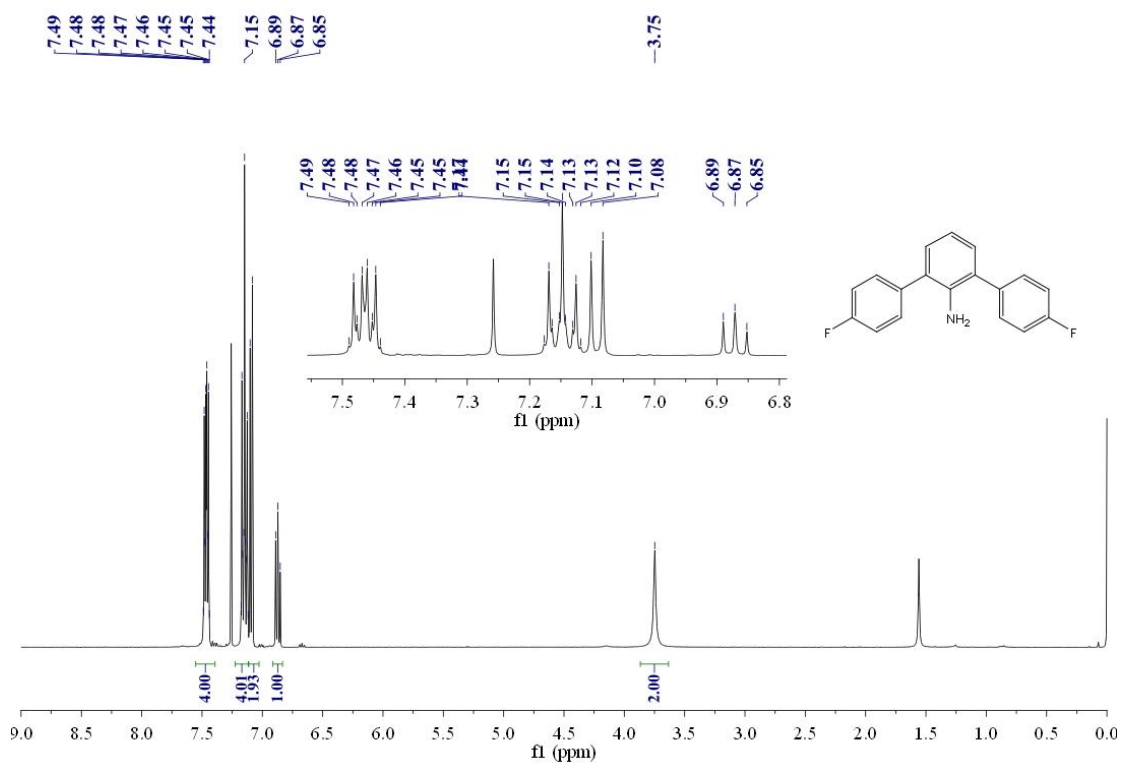
2,6-bis(4-methoxyphenyl)aniline



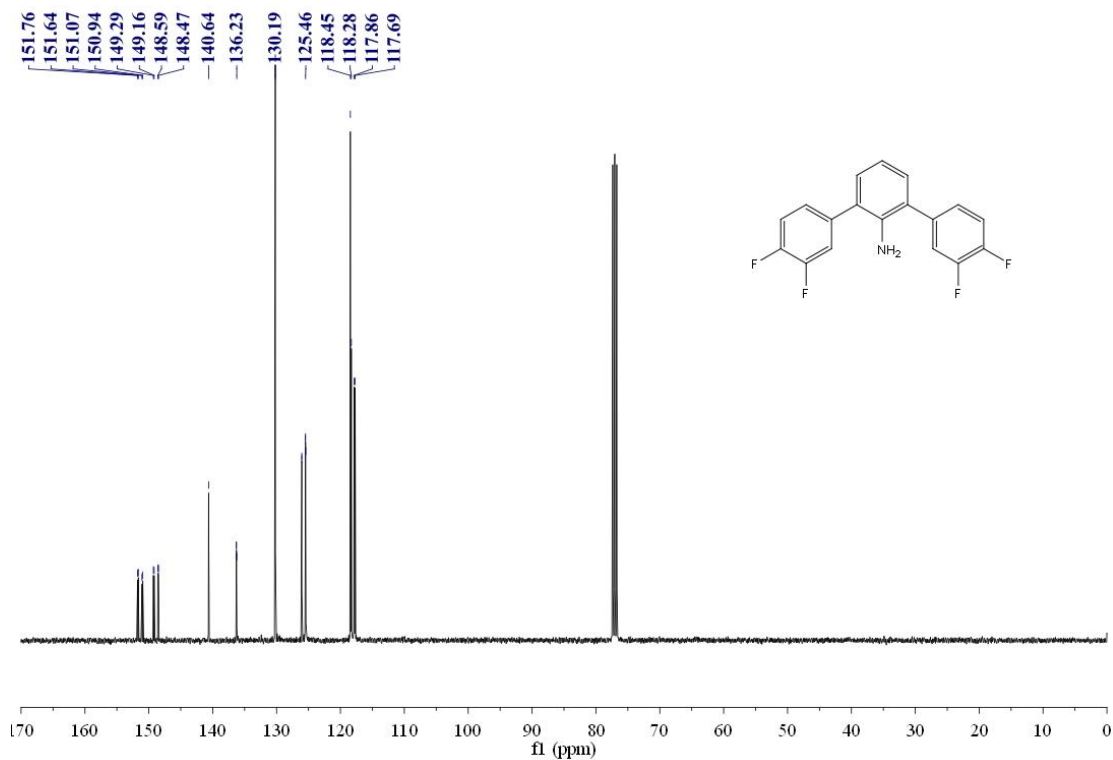
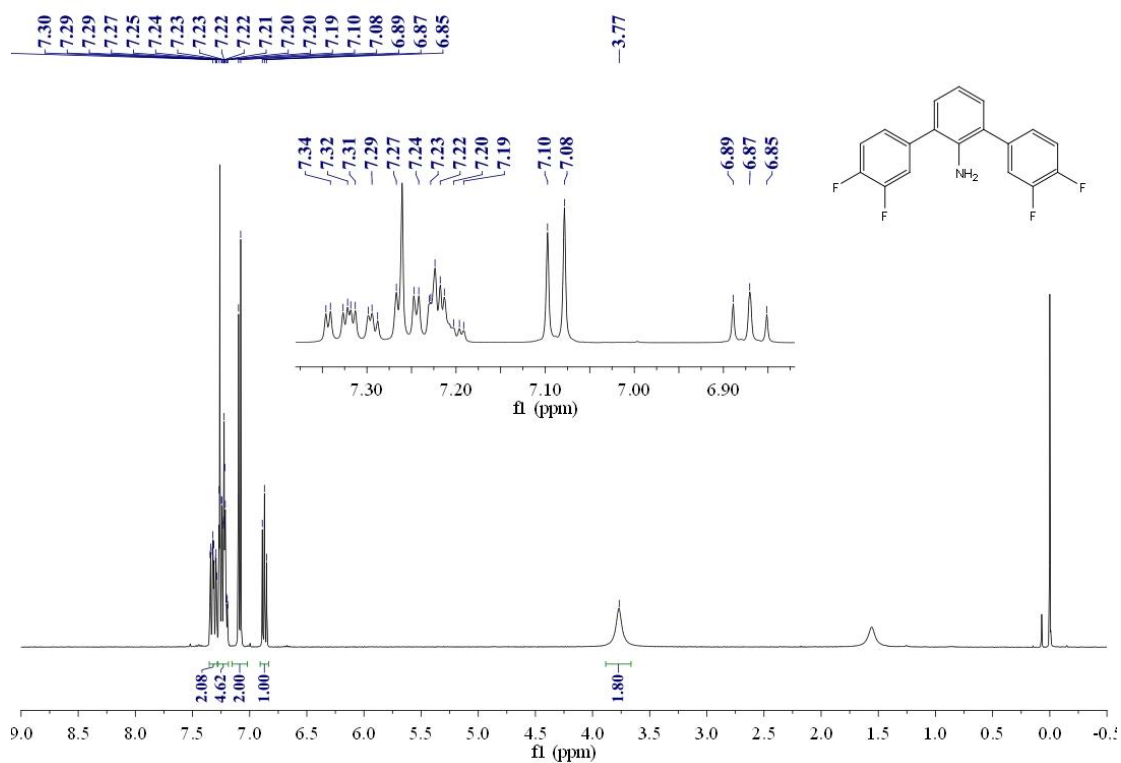
2,6-bis(2-methylphenyl)aniline



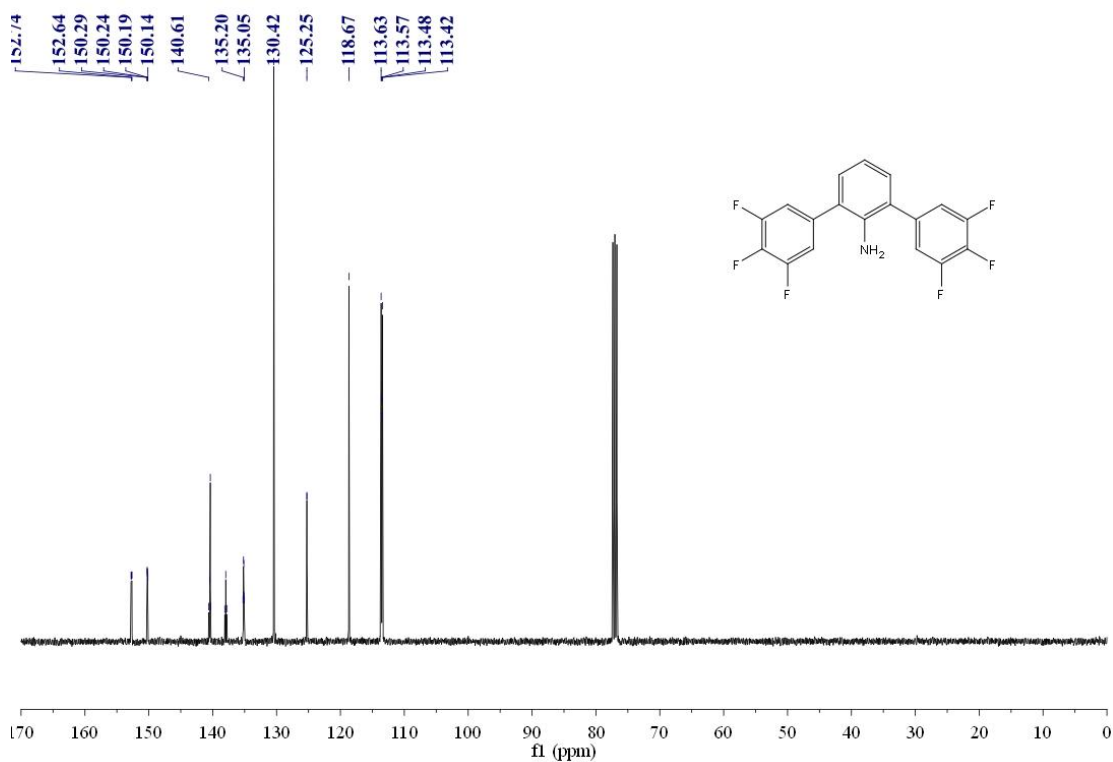
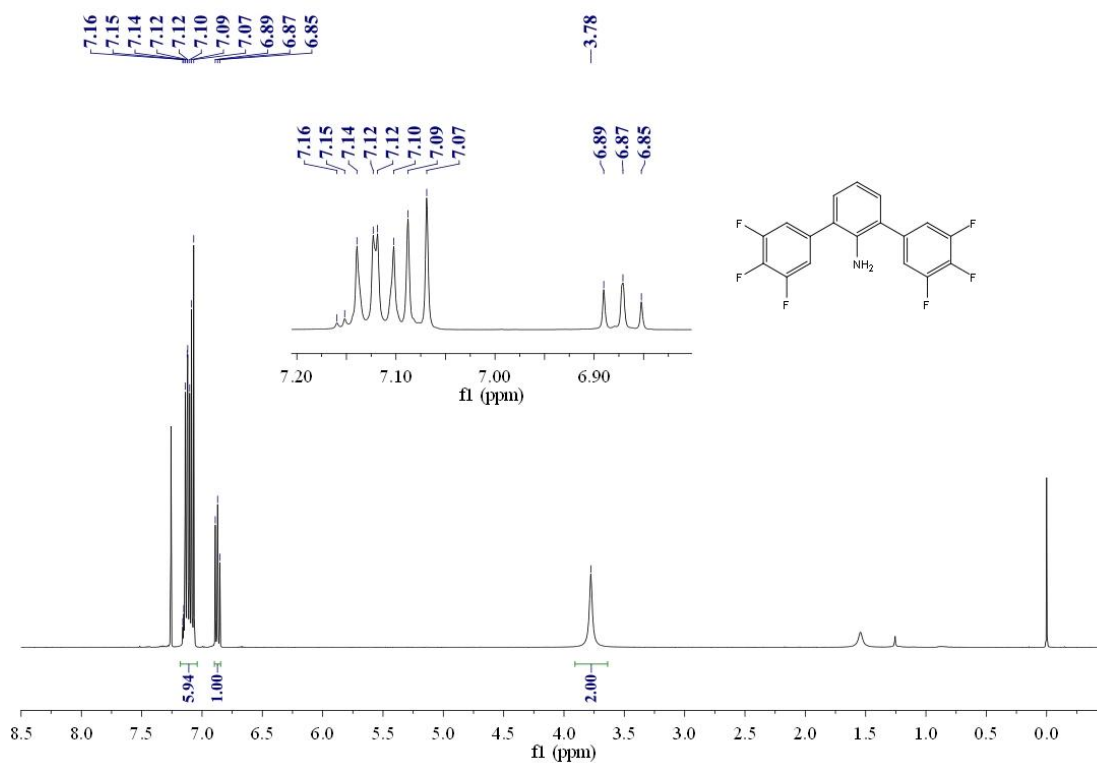
2,6-bis(4-fluorophenyl)aniline



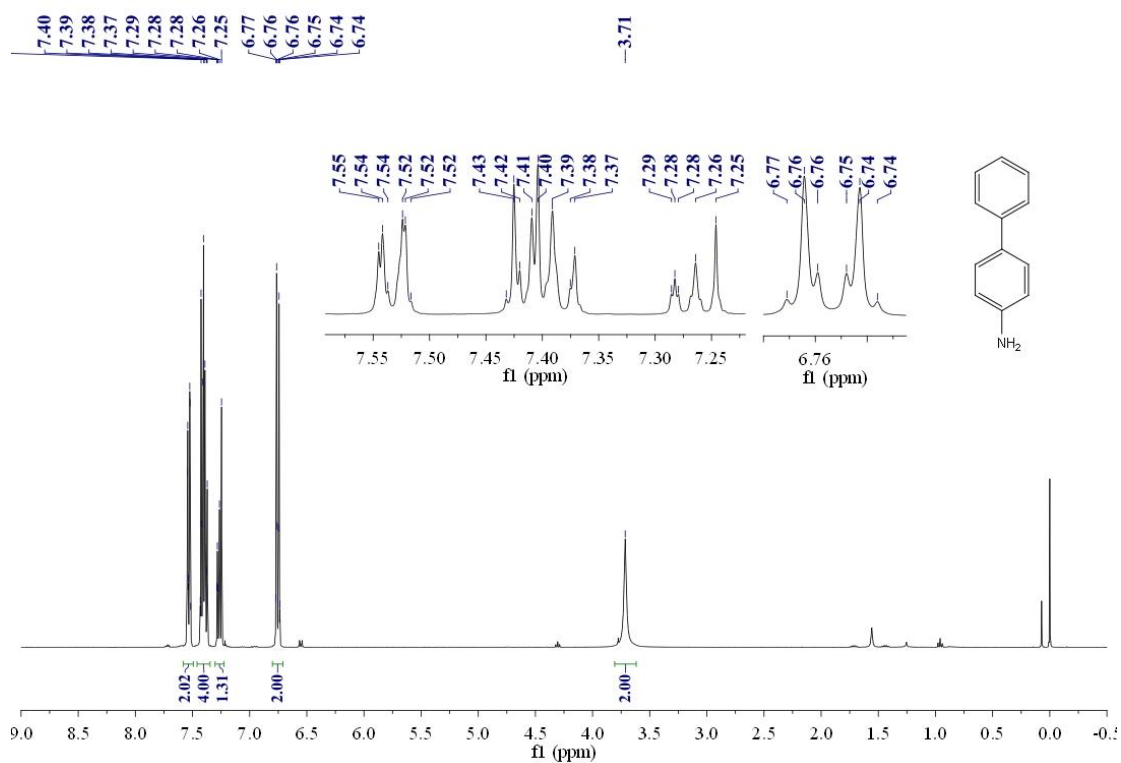
2,6-bis(3,4-difluorophenyl)aniline



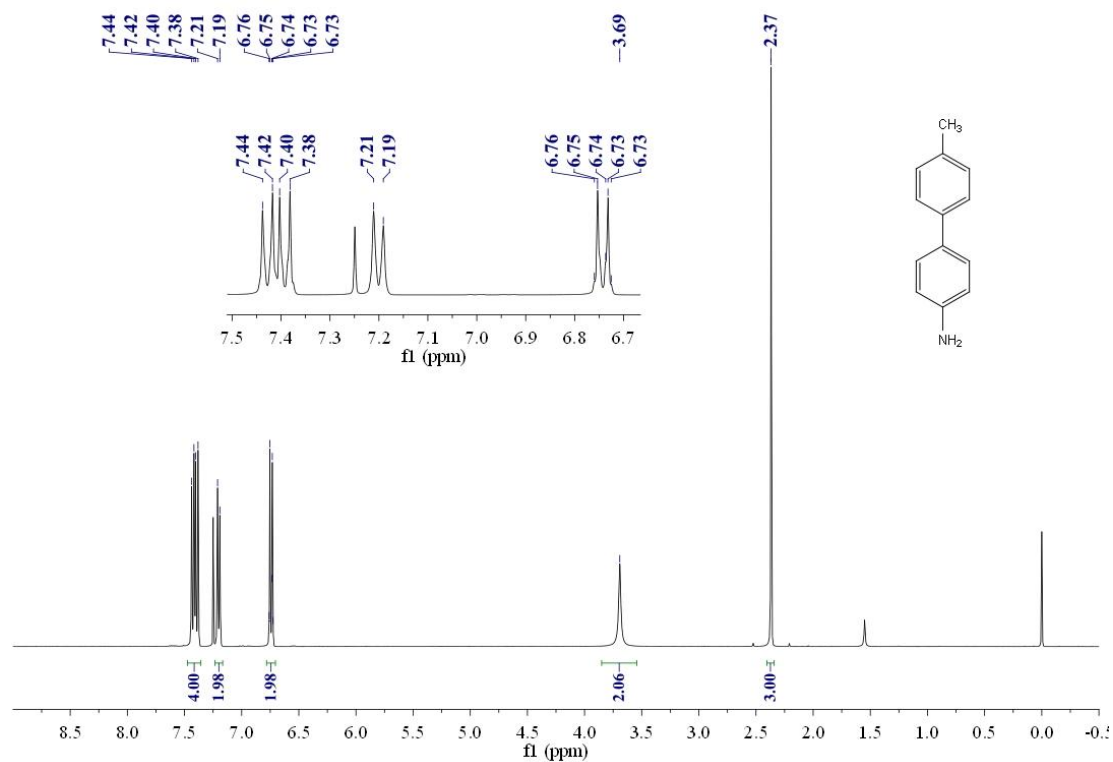
2,6-bis(3,4,5-trifluorophenyl)aniline



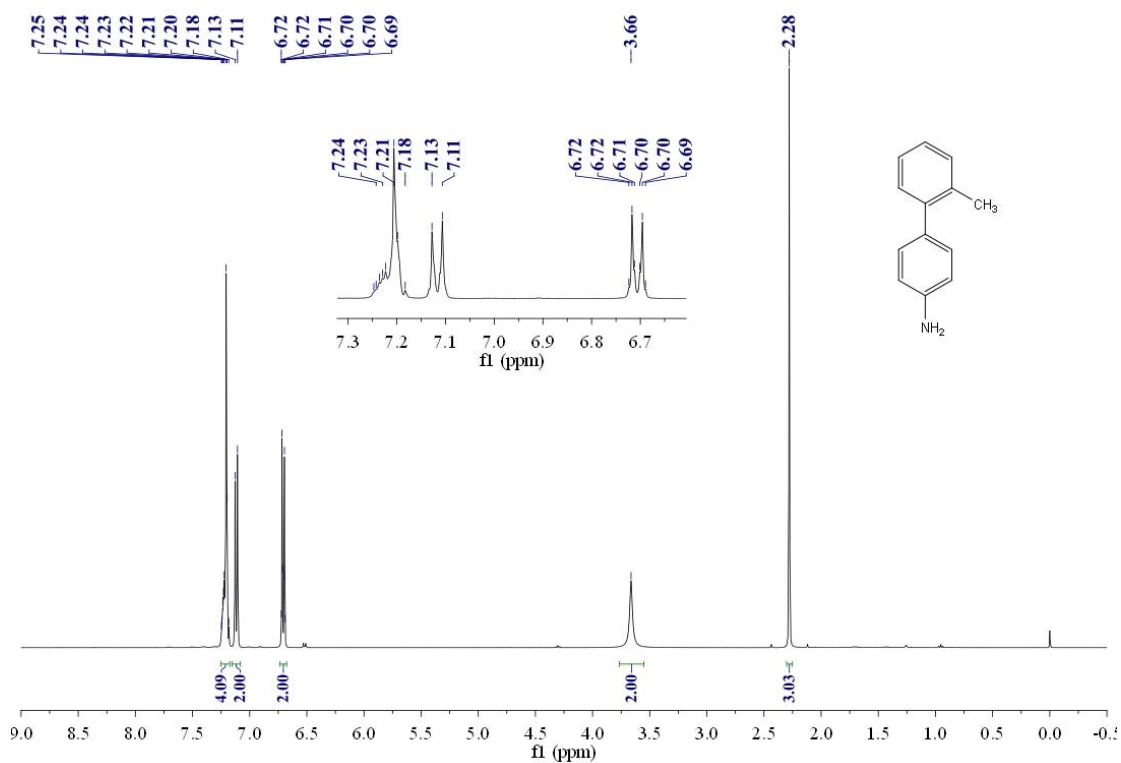
4-phenylaniline



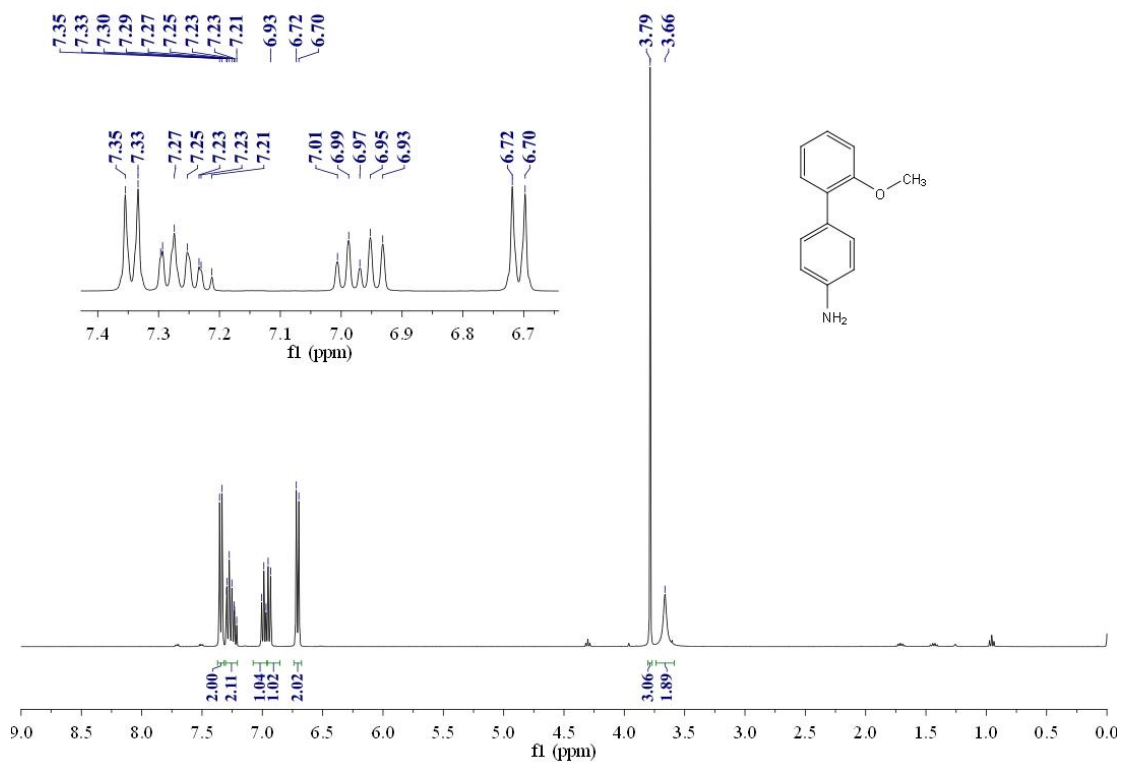
4-(4-methylphenyl)aniline



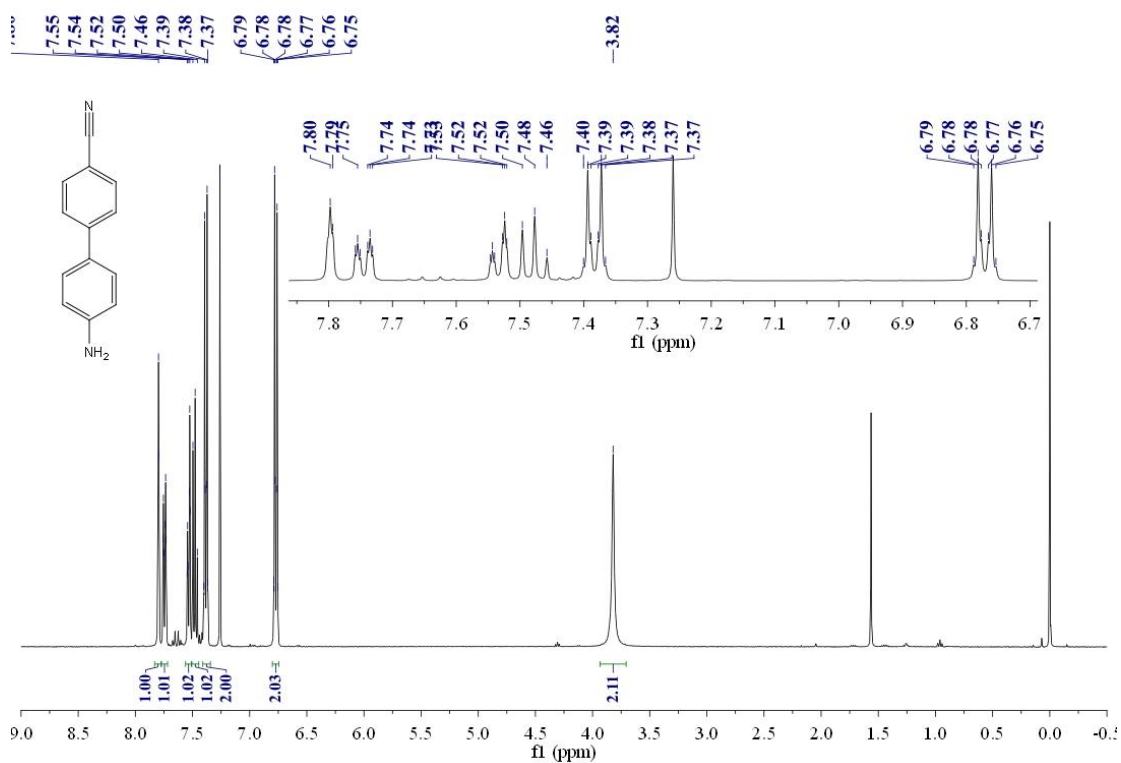
4-(2-methylphenyl)aniline



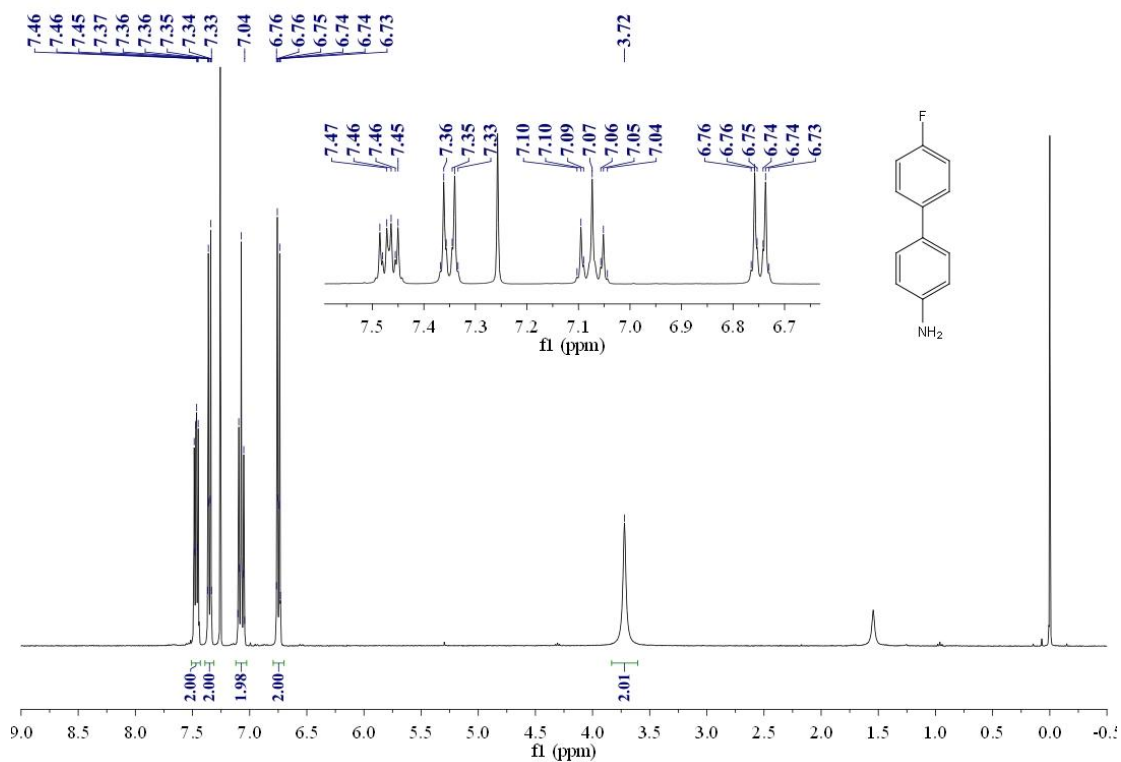
4-(2-methoxyphenyl)aniline

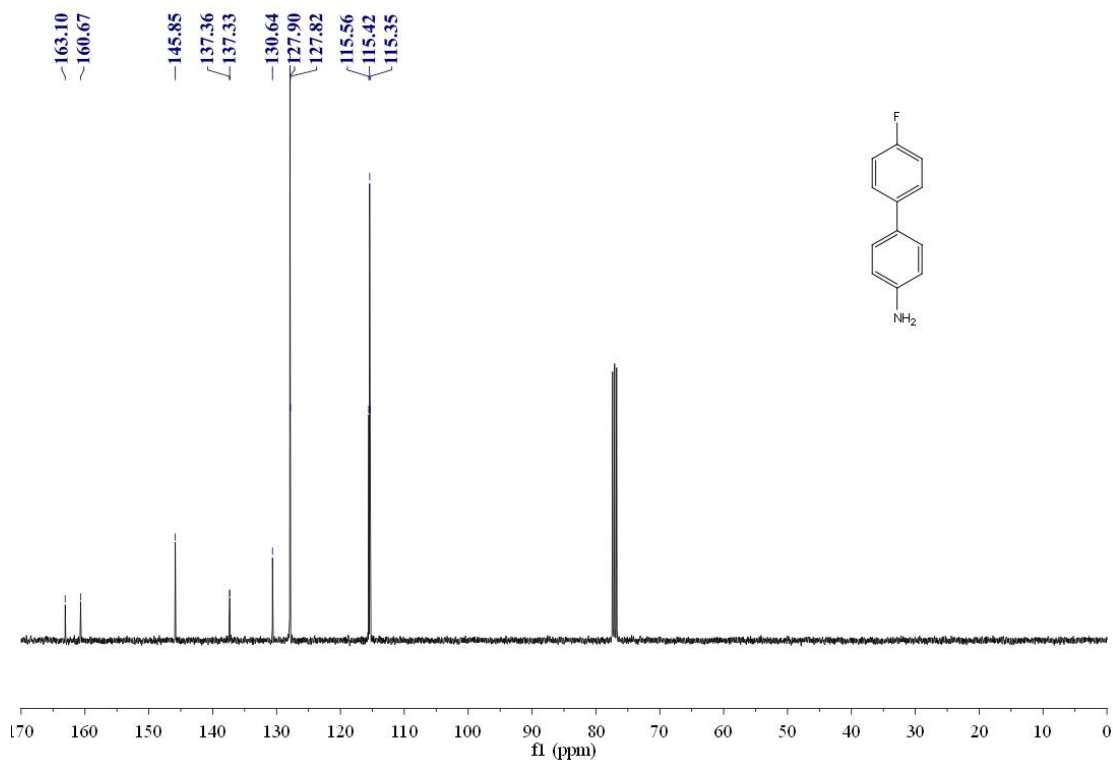


4-(4-cyanophenyl)aniline

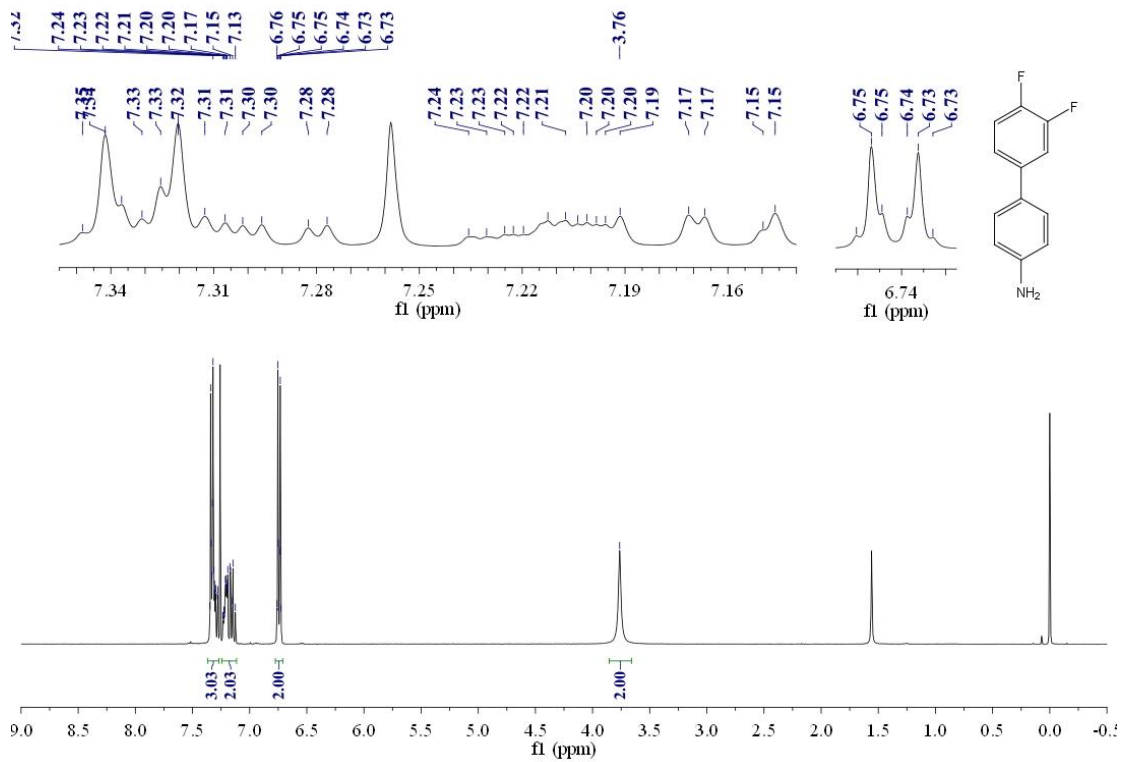


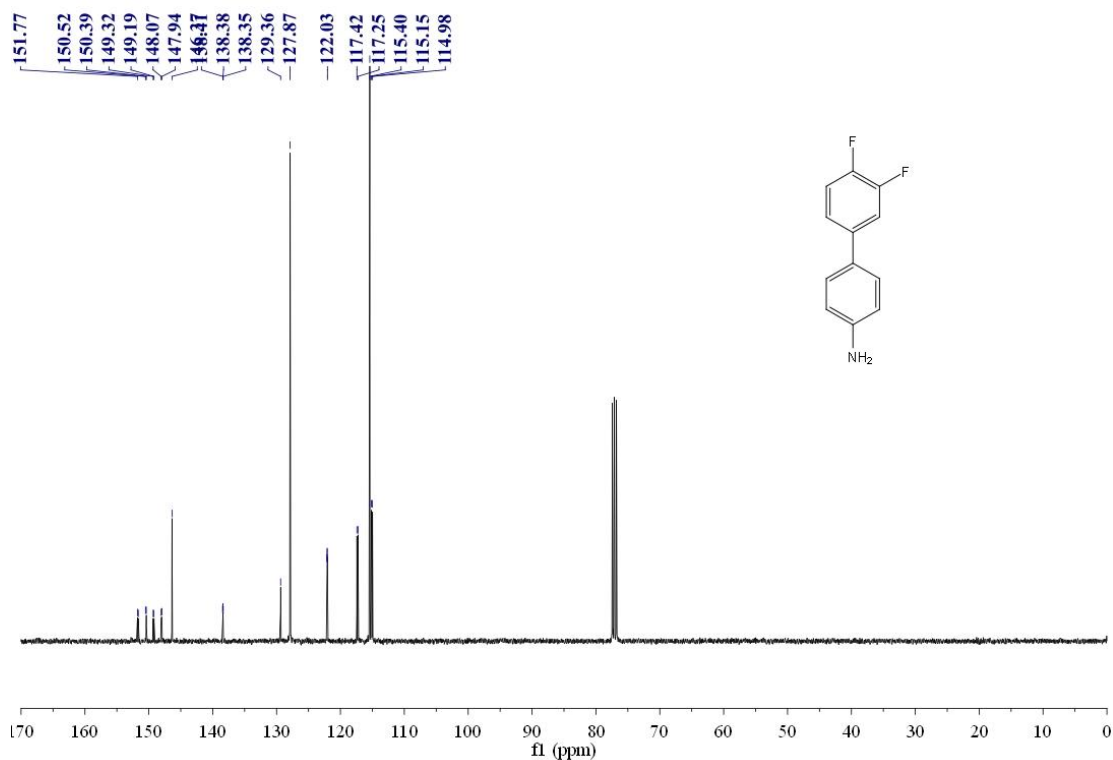
4-(4-fluorophenyl)aniline





4-(3,4-difluorophenyl)aniline





4-(3,4,5-trifluorophenyl)aniline

