Straightforward solvent-free heterogeneous palladium catalyzed synthesis of arylamines from non-aromatic substrates by dehydrogenative alkylation

Marc Sutter, Marie-Christine Duclos, Boris Guicheret, Yann Raoul, Estelle Métay and Marc Lemaire*

SUPPORTING INFORMATION

Table of Contents

Experimental procedures S**2**
Products characterizations S**5**
NMR ^{1}H and ^{13}C Spectra S**16**
References S**45**

Experimental

General

General Information

Amines, nitro compounds, cyclohexanone and tetralone derivatives were purchased from Acros, Sigma-Aldrich, Alfa Aesar and TCI. All reagents were used as received from the chemical company without further purification, excepted for aniline and nitrobenzene which were distilled prior to use. Pd/C (5%) on activated carbon, reduced and dry (Escat 1431) and all the supported catalysts were purchased from Strem Chemicals and Sigma-Aldrich.

^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER DRX 300 or BRUKER ALS 300 (^{1}H 300 MHz, ^{13}C 75 MHz) in $CDCl_3$ (except when mentioned) and chemical shifts are given in ppm. *J* values are given in Hertz (Hz). Abbreviations are defined as follows: *br* = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, m = multiplet.

IR spectra were recorded on a Spectro Nicolet IS10 Smart ITR with an ATR diamond.

The HRMS-ESI mass spectra were recorded in positive-ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The flow of spray gas was at 0.6 bar and the capillary voltage was 4.5kV. The solutions were infused at 180µL/h in a mixture of solvents (methanol / dichloromethane / water 45/40/15). The mass range of the analysis was 50-1000m/z and the calibration was done with sodium formate.

The HRMS-CI (Chemical Ionization) and HRMS-EI (Electron Ionization) mass spectra were recorded on a high resolution double-focusing (reversed Nier-Johns B/E geometry) mass spectrometer (ThermoFinnigan MAT95XL, Bremen, Germany) equipped with a chemical ionization (CI) and an electron ionization (EI) ion sources. The reagent gas for the CI was isobutane and the calibration for high resolution mass spectra was done with perfluorotrybutylamine (FC43). For the EI an electron energy of 70eV was used and the calibration was done with perfluorokerozene (PFK).

The GC-MS analysis were performed on a Focus GC (Thermo Electron Corporation, Bremen, Germany) equipped with a DB-5MS capillary column (30m, 0.25mm i.d, 0.25µm film thickness) and a DSQ mass spectrometer as a detector (Thermo Electron corporation, Bremen, Germany). The carrier gas was helium, at a flow rate of 1 mL/min. Column temperature was initially 70°C for 2 min, then gradually increased to 310°C at 15°C/min and finally kept at 310°C for 10min. The injector temperature was 220°C and the transfer line temperature was 280°C. For GC-MS detection an electron ionization system was used with electron energy of 70 eV, and the mass analyzer was a simple quadrupole.

Dehydrogenative alkylation of α-tetralone with amines (A):

In a sealed tube under argon, 3 mmol of α-tetralone derivative were added to 15 mmol of amine. Next, 64 mg of Pd/C (5%) (0.03 mmol, 1 mol%) were added to the mixture, under an inert argon atmosphere. The medium was stirred at 130 °C for 16-36 h at 800 rpm, depending on the substrate. Thereafter, the crude was dissolved in a mixture of CH_2Cl_2 and CH_3OH and filtered off (Millipore Durapore filter 0.01 μm). The solvents were evaporated under reduced pressure and the crude product was finally purified by flash chromatography on silica gel to afford the desired naphthylamine (eluent: cyclohexane/ethyl acetate = 100:0~9:1).

Dehydrogenative alkylation of functionalized cyclohexanones and β-tetralones in non-aerobic conditions (B):

The same procedure as (A) was followed, but two molar equivalents of 1-octene were added under an inert argon atmosphere. The medium was stirred at 800 rpm at 130 °C for 16-36 h, depending on the substrate.

Dehydrogenative alkylation of functionalized cyclohexanones and β-tetralones in aerobic conditions (B):

The same procedure as (A) was followed, but the reaction was carried out in a round-bottom flask equipped with a condenser fitted with a $CaCl_2$ guard. The medium was stirred at 800 rpm at 130 °C for 16-48 h, depending on the substrate.

Cross-dehydrogenative alkylation of functionalized cyclohexanones with nitro compounds (C):

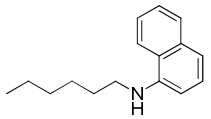
In a sealed tube under argon, 30 mmol of cyclohexanone derivative were added to 3 mmol of nitro compound. Next, 160 mg of Pd/C (5%) (0.075 mmol, 2.5 mol%) were added to the mixture, under an inert argon atmosphere. The medium was stirred at 150 °C for 16-36 h at 800 rpm, depending on the substrate. Thereafter, the crude was dissolved in a mixture of CH_2Cl_2 and CH_3OH and filtered off (Millipore Durapore filter 0.01 μm). The solvents were evaporated under reduced pressure and the crude product was finally purified by flash chromatography on silica gel to afford the desired arylamine (eluent: cyclohexane/ethyl acetate = 100:0~9:1).

Procedure for the Pd/C catalyst recycling:

After each reaction, the crude was dissolved in CH_2Cl_2 and MeOH and filtered off under argon atmosphere (Millipore Durapore filter 0.01 μm). The Pd/C catalyst was carefully washed three times with a mixture of CH_2Cl_2 and MeOH under argon atmosphere before being transferred in a reactor. To limit flammability and deactivation risks, it is recommended to work under an argon flow and to transfer the

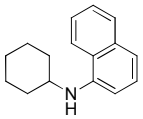
catalyst in the reactor with a small amount of solvent. Then, the reactor was left under an argon flow for 2 h at room temperature. After evaporation of the solvents, both substrates (amine and cyclohexanone derivative) were added to the catalyst in order to start a new reaction.

***N*-hexylnaphthalen-1-amine [87619-72-5] (3aa)**[1]



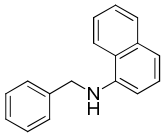
Colorless oil; ^{1}H NMR: δ = 0.92 (t, *J* = 7.1 Hz, 3H, CH_3), 1.35-1.45 (m, 4H, 2×CH_2), 1.47-1.55 (m, 2H, CH_2), 1.74-1.83 (m, 2H, CH_2), 3.28 (t, *J* = 7.2 Hz, 2H, CH_2), 6.62 (d, *J* = 7.5 Hz, 1H, CH_{arom}), 7.22-7.26 (m, 1H, CH_{arom}), 7.33-7.38 (m, 1H, CH_{arom}), 7.42-7.47 (m, 2H, 2×CH_{arom}), 7.78-7.83 (m, 2H, 2×CH_{arom}); ^{13}C NMR (100 MHz): δ = 14.2 (CH_3), 22.8 (CH_2), 27.2 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 44.4 (CH_2), 104.3 (CH_{arom}), 117.2 (CH_{arom}), 119.9 (CH_{arom}), 123.4 (C_q), 124.7 (CH_{arom}), 125.7 (CH_{arom}), 126.8 (CH_{arom}), 128.8 (CH_{arom}), 134.4 (C_q), 143.8 (C_q); IR (ATR): ν_{max} = 3429, 3052, 2925, 2854, 1581, 1524, 1476, 1407, 1280, 764 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{22}N$: 228.1747 found: 228.1738; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{22}N$: 228.1747 found: 228.1738.

***N*-cyclohexylnaphthalen-1-amine [26863-63-8] (3ba)**[2]



Colorless oil; ^{1}H NMR: δ = 1.25-1.84 (m, 8H, 4×CH_2), 2.16-2.20 (m, 2H, CH_2), 3.44-3.52 (m, 1H, CH), 4.32 (*br*, 1H, NH), 6.61-6.69 (m, 1H, CH_{arom}), 7.19-7.25 (m, 1H, CH_{arom}), 7.30-7.36 (m, 1H, CH_{arom}), 7.39-7.46 (m, 2H, 2×CH_{arom}), 7.76-7.81 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 25.2 (2×CH_2), 26.2 (CH_2), 33.4 (2×CH_2), 51.9 (CH), 104.8 (CH_{arom}), 116.7 (CH_{arom}), 119.9 (CH_{arom}), 123.5 (C_q), 124.6 (CH_{arom}), 125.7 (CH_{arom}), 126.7 (CH_{arom}), 128.8 (CH_{arom}), 134.7 (C_q), 142.4 (C_q); IR (ATR): ν_{max} = 3418, 3052, 2926, 2851, 1579, 1525, 1479, 1407, 1120, 765 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{20}N$: 226.1590 found: 226.1601.

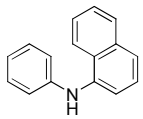
***N*-benzylnaphthalen-1-amine [6361-33-7] (3ca)**[3]



Light yellow oil; ^{1}H NMR (400 MHz): δ = 4.52 (s, CH_2), 4.79 (*br*, 1H, NH), 6.66 (d, *J* = 7.3 Hz, 1H, CH_{arom}), 7.26-7.49 (m, 9H, 9×CH_{arom}), 7.81-7.86 (m, 2H, 2×CH_{arom}); ^{13}C NMR (100 MHz): δ = 48.7 (CH_2), 104.9 (CH_{arom}), 117.8 (CH_{arom}), 120.0 (CH_{arom}), 123.5 (C_q), 124.9 (CH_{arom}), 125.9 (CH_{arom}), 126.7

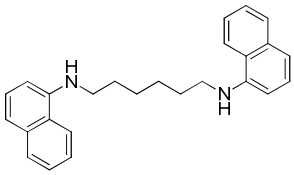
(CH_{arom}), 127.5 (CH_{arom}), 127.8 (2×CH_{arom}), 128.8 (2×CH_{arom}), 128.8 (CH_{arom}), 134.4 (C_q), 139.1 (C_q), 143.2 (C_q); IR (ATR): ν_{max} = 3444, 3047, 1574, 1526, 1480, 1407, 1285, 1119, 765 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{17}H_{16}N$: 234.1277 found: 234.1274.

_N_-phenylnaphtalen-1-amine [90-30-2] (3da)[4]



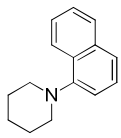
Light yellow solid; Mp = 60-62 °C; ^1H NMR: δ = 5.81 (*br*, 1H, NH), 6.80 (t, *J* = 7.5 Hz, 1H, CH_{arom}), 6.85-6.89 (m, 2H, 2×CH_{arom}), 7.11-7.18 (m, 2H, 2×CH_{arom}), 7.24-7.31 (m, 2H, 2×CH_{arom}), 7.32-7.42 (m, 2H, 2×CH_{arom}), 7.46 (dd, J^3 = 7.3 Hz, J^4 = 1 Hz, 1H, CH_{arom}), 7.75 (dd, J^3 = 7.4 Hz, J^4 = 1 Hz, 1H, CH_{arom}), 7.90 (dd, J^3 = 7.4 Hz, J^4 = 1 Hz, 1H, CH_{arom}); ^{13}C NMR: δ = 116.0 (CH_{arom}), 117.4 (2×CH_{arom}), 120.5 (CH_{arom}), 121.9 (CH_{arom}), 123.1 (CH_{arom}), 125.8 (CH_{arom}), 126.1 (CH_{arom}), 126.2 (CH_{arom}), 127.8 (C_q), 128.6 (CH_{arom}), 129.4 (2×CH_{arom}), 134.8 (C_q), 138.8 (C_q), 144.8 (C_q); IR (ATR): ν_{max} = 3409, 3052, 1587, 1573, 1523, 1305, 732 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{14}N$: 220.1122 found: 220.1121.

N^1,N^6-di(naphthalen-1-yl)hexane-1,6-diamine [185736-50-9] (3ea)



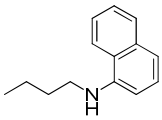
Beige solid; Mp = 117-120 °C; ^1H NMR: δ = 1.54-1.64 (m, 4H, 2×CH_2), 1.80-1.88 (m, 4H, 2×CH_2), 3.31 (t, *J* = 7.1 Hz, 4H, 2×CH_2), 4.32 (*br*, 2H, 2×NH), 6.62 (d, *J* = 7.4 Hz, 2H, 2×CH_{arom}), 7.21-7.26 (m, 2H, 2×CH_{arom}), 7.32-7.38 (m, 2H, 2×CH_{arom}), 7.41-7.46 (m, 4H, 4×CH_{arom}), 7.77-7.82 (m, 4H, 4×CH_{arom}); ^{13}C NMR: δ = 27.3 (CH_2), 29.5 (CH_2), 44.2 (CH_2), 104.3 (CH_{arom}), 117.2 (CH_{arom}), 119.9 (CH_{arom}), 123.4 (C_q), 124.7 (CH_{arom}), 125.8 (CH_{arom}), 126.8 (CH_{arom}), 128.8 (CH_{arom}), 134.4 (C_q), 143.7 (C_q); IR (ATR): ν_{max} = 3415, 3057, 2934, 2857, 1575, 1523, 1477, 1407, 1279, 1111, 766 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{26}H_{29}N_2$: 369.2325 found: 369.2309.

1-(naphthalen-1-yl)piperidine [62062-39-9] (3fa)



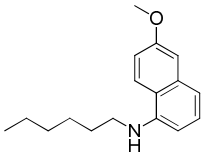
Colorless oil; ^{1}H NMR (400 MHz): δ = 1.55-1.72 (m, 2H, CH_2), 1.77-1.89 (m, 4H, 2×CH_2), 2.90-3.20 (m, 4H, 2×CH_2), 7.06 (dd, J^3 = 7.4 Hz, J^4 = 0.9 Hz, 1H, CH_{arom}), 7.37-7.54 (m, 4H, 4×CH_{arom}), 7.80-7.83 (m, 1H, CH_{arom}), 8.20 (dd, J^3 = 7.3 Hz, J^4 = 0.8 Hz, 1H, CH_{arom}); ^{13}C NMR (100 MHz): δ = 24.8 (CH_2), 26.8 (2×CH_2), 54.8 (2×CH_2), 114.6 (CH_{arom}), 123.0 (CH_{arom}), 124.0 (CH_{arom}), 125.3 (CH_{arom}), 125.8 (CH_{arom}), 126.0 (CH_{arom}), 128.4 (CH_{arom}), 129.2 (C_q), 134.9 (C_q), 151.2 (C_q); IR (ATR): ν_{max} = 3011, 2930, 1576, 1517, 1466, 1448, 1427, 1402, 1386, 1154, 990, 771 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{15}H_{18}N$: 212.1434 found: 212.1430.

***N*-butylnaphthalen-1-amine [6281-00-1] (3ga)**[2]



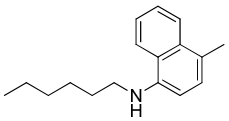
Colorless oil; ^{1}H NMR: δ = 1.02 (t, *J* = 7.3 Hz, 3H, CH_3), 1.49-1.57 (m, 2H, CH_2), 1.73-1.83 (m, 2H, CH_2), 3.29 (t, *J* = 7.1 Hz, 2H, CH_2), 4.41 (*br*, 1H, NH), 6.64 (d, *J* = 7.5 Hz, 1H, CH_{arom}), 7.22-7.26 (m, 1H, CH_{arom}), 7.33-7.39 (m, 1H, CH_{arom}), 7.40-7.48 (m, 2H, 2×CH_{arom}), 7.78-7.83 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 14.1 (CH_3), 20.6 (CH_2), 31.6 (CH_2), 44.0 (CH_2), 104.2 (CH_{arom}), 117.1 (CH_{arom}), 119.9 (CH_{arom}), 123.4 (C_q), 124.7 (CH_{arom}), 125.7 (CH_{arom}), 126.8 (CH_{arom}), 128.8 (CH_{arom}), 134.4 (C_q), 143.8 (C_q); IR (ATR): ν_{max} = 3427, 3053, 2954, 2926, 2858, 1623, 1581, 1524, 1475, 1407, 1281, 1136, 764 cm^{-1}; HRMS-CI: *m/z* $[MH]^+$ calcd for $C_{14}H_{18}N$: 200.1434 found: 200.1433.

***N*-hexyl-6-methoxynaphthalen-1-amine [No CAS Number] (3ab)**



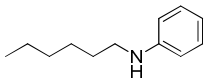
White solid; Mp = 75-79 °C; ^{1}H NMR (500 MHz): δ = 0.93 (t, *J* = 6.9 Hz, 3H, CH_3), 1.34-1.39 (m, 4H, 2×CH_2), 1.47-1.52 (m, 2H, CH_2), 1.73-1.80 (m, 2H, CH_2), 3.26 (t, *J* = 7.3 Hz, 2H, CH_2), 3.92 (s, 3H, CH_3), 4.29 (*br*, 1H, NH), 6.50 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 7.07-7.14 (m, 3H, 3×CH_{arom}), 7.30-7.33 (m, 1H, CH_{arom}), 7.72 (d, *J* = 8.9 Hz, 1H, CH_{arom}); ^{13}C NMR (125 MHz): δ = 14.2 (CH_3), 22.8 (CH_2), 27.2 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 44.5 (CH_3), 55.4 (CH_2), 102.9 (CH_{arom}), 107.0 (CH_{arom}), 116.4 (CH_{arom}), 116.9 (CH_{arom}), 118.7 (C_q), 121.7 (CH_{arom}), 127.6 (CH_{arom}), 135.8 (C_q), 143.9 (C_q), 157.6 (C_q); IR (ATR): ν_{max} = 3417, 2954, 2927, 2845, 1621, 1583, 1531, 1476, 1433, 1381, 1220, 1033, 770, 728 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{17}H_{24}NO$: 258.1852 found: 258.1844.

***N*-hexyl-4-methylnaphthalen-1-amine [No CAS Number] (3ac)**



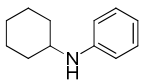
White solid; Mp = 62-64 °C; ^{1}H NMR: δ = 0.93 (t, *J* = 7.0 Hz, 3H, CH_3), 1.35-1.46 (m, 4H, 2×CH_2), 1.47-1.54 (m, 2H, CH_2), 1.73-1.83 (m, 2H, CH_2), 2.59 (s, 3H, CH_3), 3.25 (t, *J* = 7.0 Hz, 2H, CH_2), 4.17 (*br*, 1H, NH), 6.54 (d, *J* = 7.5 Hz, 1H, CH_{arom}), 7.19 (d, *J* = 7.5 Hz, 1H, CH_{arom}), 7.43-7.55 (m, 2H, 2×CH_{arom}), 7.84-7.87 (m, 1H, CH_{arom}), 7.96 (d, *J* = 8.3 Hz, 1H, CH_{arom}); ^{13}C NMR (125 MHz): δ = 14.2 (CH_3), 19.1 (CH_3), 22.8 (CH_2), 27.1 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 45.5 (CH_2), 106.2 (CH_{arom}), 120.7 (CH_{arom}), 124.3 (C_q), 124.8 (CH_{arom}), 125.1 (CH_{arom}), 125.8, (CH_{arom}), 127.1 (CH_{arom}), 133.3 (C_q), 141.1 (C_q); IR (ATR): ν_{max} = 3432, 2947, 2924, 2851, 1585, 1520, 1476, 1425, 1342, 1134, 798, 748, 732 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{17}H_{24}N$: 242.1903 found: 242.1899.

***N*-hexylaniline [4746-32-1] (3ad)**[1]



Colorless oil; ^{1}H NMR (400 MHz): δ = 0.90 (t, *J* = 7.1 Hz, 3H, CH_3), 1.25-1.38 (m, 4H, 2×CH_2), 1.39-1.44 (m, 2H, CH_2), 1.58-1.66 (m, 2H, CH_2), 3.10 (t, *J* = 7.1 Hz, 2H, CH_2), 3.64 (*br*, 1H, NH), 6.61 (dd, J^3 = 8.6 Hz, J^4 = 0.8 Hz, 2H, 2×CH_{arom}), 6.67-6.71 (m, 1H, CH_{arom}), 7.15-7.20 (m, 2H, CH_{arom}); ^{13}C NMR (100 MHz): δ = 14.2 (CH_3), 22.8 (CH_2), 27.0 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 44.2 (CH_2), 112.8 (2×CH_{arom}), 117.2 (CH_{arom}), 129.4 (2×CH_{arom}), 148.6 (C_q); IR (ATR): ν_{max} = 3411, 3051, 2925, 2855, 1601, 1504, 1466, 1318, 1254, 745, 690 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{12}H_{20}N$: 178.1590 found: 178.1587.

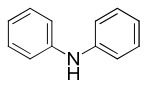
***N*-cyclohexylaniline [1821-36-9] (3bd)**[5]



Colorless oil; ^{1}H NMR: δ = 1.08-1.69 (m, 6H, 3×CH_2), 1.73-1.80 (m, 2H, CH_2), 2.03-2.08 (m, 2H, CH_2), 3.21-3.30 (m, 1H, CH), 3.51 (*br*, 1H, NH), 6.59 (dd, J^3 = 8.5 Hz, J^4 = 0.9 Hz, 2H, 2×CH_{arom}), 6.63-6.68 (m, 1H, CH_{arom}), 7.12-7.18 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 25.1 (2×CH_2), 26.0 (CH_2), 33.5 (2×CH_2),

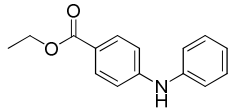
51.7 (CH), 113.2 (2×CH_{arom}), 116.9 (CH_{arom}), 129.3 (2×CH_{arom}), 147.5 (C_q); IR (ATR): ν_{max} = 3398, 3050, 295, 2851, 1599, 1501, 1448, 1318, 1254, 1116, 744, 690 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{12}H_{18}N$: 176.1434 found: 176.1432.

Diphenylamine [122-39-4] (3dd)[4]



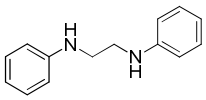
White solid; Mp = 50-53 °C; ^{1}H NMR: δ = 5.70 (*br*, 1H, NH), 6.91-6.96 (m, 2H, 2×CH_{arom}), 7.06-7.10 (m, 4H, 4×CH_{arom}), 7.24-7.31 (m, 4H, 4×CH_{arom}); ^{13}C NMR: δ = 117.9 (4×CH_{arom}), 121.1 (2×CH_{arom}), 129.5 (4×CH_{arom}), 143.2 (2×C_q); IR (ATR): ν_{max} = 3382, 3041, 1587, 1514, 1492, 1457, 1316, 1172, 875, 741, 687 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{12}H_{12}N$: 170.0964 found: 170.0964.

Ethyl 4-(phenylamino)benzoate [64678-66-6] (3hd)[4]



White solid; Mp = 114-115 °C; ^{1}H NMR: δ = 1.38 (t, *J* = 7.2 Hz, 3H, CH_3), 4.34 (q, *J* = 7.1 Hz, 2H, CH_2), 6.14 (*br*, 1H, NH), 7.00 (d, *J* = 8.7 Hz, 2H, 2×CH_{arom}), 7.03-7.09 (m, 1H, CH_{arom}), 7.17 (d, *J* = 7.6 Hz, 2H, 2×CH_{arom}), 7.31-7.36 (m, 2H, 2×CH_{arom}), 7.93 (d, *J* = 8.7 Hz, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 14.5 (CH_3), 60.6 (CH_2), 114.7 (2×CH_{arom}), 120.4 (2×CH_{arom}), 121.5 (C_q), 123.1 (CH_{arom}), 129.6 (2×CH_{arom}), 131.5 (2×CH_{arom}), 141.0 (C_q), 148.1 (C_q), 166.7 (C_q); IR (ATR): ν_{max} = 3358, 3334, 2982, 1687, 1676, 1587, 1528, 1495, 1475, 1335, 1272, 1249, 1173, 1110, 767, 692 cm^{-1}; HRMS-ESI: *m/z* $[MNa]^+$ calcd for $C_{15}H_{15}NaO_2$: 264.0995 found: 264.0988.

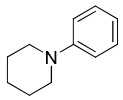
***N*^{1},*N*^{2}-diphenylethane-1,2-diamine [150-61-8] (3id)**[6]



Beige solid; Mp = 65-67 °C; ^{1}H NMR: δ = 3.41 (s, 4H, 2×CH_2), 3.87 (*br*, 1H, NH), 6.67 (d, *J* = 7.7 Hz, 4H, 4×CH_{arom}), 6.73-6.78 (m, 2H, 2×CH_{arom}), 7.18-7.25 (m, 4H, 4×CH_{arom}); ^{13}C NMR: δ = 43.4 (2×CH_2), 113.1 (4×CH_{arom}), 117.9 (2×CH_{arom}), 129.4 (4×CH_{arom}), 148.1 (2×C_q); IR (ATR): ν_{max} = 3415, 3050,

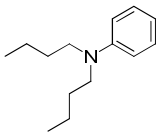
2945, 2921, 2867, 1594, 1512, 1495, 1341, 1263, 1096, 740, 690 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{14}H_{17}N_2$: 213.1386 found: 213.1379.

1-phenylpiperidine [4096-20-2] (3fd)[7]



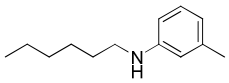
Yellow oil; ^1H NMR: δ = 1.51-1.61 (m, 2H, CH_2), 1.68-1.76 (m, 4H, 2×CH_2), 3.16 (t, *J* = 5.4 Hz, 4H, 2×CH_2), 6.80-6.85 (m, 1H, CH_{arom}), 6.95 (t, *J* = 8.1 Hz, 2H, 2×CH_{arom}), 7.23-7.28 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 24.4 (CH_2), 26.0 (2×CH_2), 50.9 (2×CH_2), 116.7 (2×CH_{arom}), 119.4 (CH_{arom}), 129.1 (2×CH_{arom}), 152.3 (C_q); IR (ATR): ν_{max} = 3023, 2931, 2851, 2791, 1596, 1493, 1449, 1234, 1130, 1024, 916, 753, 690 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{11}H_{16}N$: 162.1277 found: 162.1276.

***N*,*N*-dibutylaniline [613-29-6] (3gd)**[8]



Colorless oil; ^1H NMR: δ = 0.95 (t, *J* = 7.3 Hz, 6H, 2×CH_3), 1.22-1.41 (m, 4H, 2×CH_2), 1.51-1.62 (m, 4H, 2×CH_2), 3.26 (t, *J* = 7.6 Hz, 4H, 2×CH_2), 6.59-6.66 (m, 3H, 3×CH_{arom}), 7.17-7.23 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 14.2 (2×CH_3), 20.5 (2×CH_2), 29.5 (2×CH_2), 50.9 (2×CH_2), 111.8 (2×CH_{arom}), 115.2 (CH_{arom}), 129.3 (2×CH_{arom}), 148.3 (C_q); IR (ATR): ν_{max} = 3025, 2955, 2930, 2871, 1595, 15003, 1464, 1360, 1217, 1187, 742, 690 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{14}H_{24}N$: 206.1903 found: 206.1898.

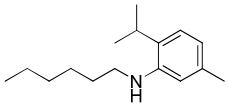
***N*-hexyl-3-methylaniline [145567-64-2] (3af)**[9]



Orange oil; ^1H NMR (400 MHz): δ = 0.90 (t, *J* = 6.9 Hz, 3H, CH_3), 1.30-1.42 (m, 6H, 3×CH_2), 1.57-1.65 (m, 2H, CH_2), 2.28 (s, 3H, CH_3), 3.09 (t, *J* = 7.1 Hz, 2H, CH_2), 3.56 (*br*, 1H, NH), 6.41-6.44 (m, 2H, 2×CH_{arom}), 6.52 (d, *J* = 7.2 Hz, 1H, CH_{arom}), 7.05-7.09 (m, 1H, CH_{arom}); ^{13}C NMR (100 MHz): δ = 14.2 (CH_3), 21.8 (CH_3), 22.8 (CH_2), 27.0 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 44.2 (CH_2), 110.0 (CH_{arom}), 113.6 (CH_{arom}), 118.2 (CH_{arom}), 129.2 (CH_{arom}), 139.1 (C_q), 148.7 (C_q); IR (ATR): ν_{max} = 3409, 2954, 2924, 2855, 1604, 1588, 1508, 1490, 1326, 1179, 765 cm^{-1}; HRMS-ESI: *m/z* $[MH]^{+\cdot}$ calcd for $C_{13}H_{22}N$:

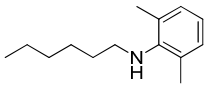
192.1747 found: 192.1747.

***N*-hexyl-2-isopropyl-5-methylaniline [No CAS Number] (3ag)**



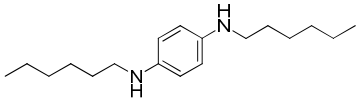
Colorless oil; ^{1}H NMR: δ = 0.94 (t, *J* = 6.9 Hz, 3H, CH_3), 1.26 (d, *J* = 6.8 Hz, 6H, 2×CH_3), 1.30-1.50 (m, 6H, 3×CH_2), 1.64-1.74 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.77-2.89 (m, 1H, CH), 3.16 (t, *J* = 7.0 Hz, 2H, CH_2), 3.60 (*br*, 1H, NH), 6.49 (s, 1H, CH_{arom}), 6.57 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.05 (d, *J* = 7.7 Hz, 1H, CH_{arom}); ^{13}C NMR: δ = 14.2 (CH_3), 21.6 (CH_3), 22.5 (2×CH_3), 22.8 (CH_2), 27.0 (CH), 27.1 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 44.3 (CH_2), 111.4 (CH_{arom}), 117.7 (CH_{arom}), 124.9 (CH_{arom}), 129.2 (C_q), 136.4 (C_q), 145.2 (C_q); IR (ATR): ν_{max} = 3409, 3010, 2957, 2925, 2857, 1613, 1579, 1517, 1456, 1300, 907, 797, 730 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{28}N$: 234.2216 found: 234.2215.

***N*-hexyl-2,6-dimethylaniline [213697-52-0] (3ah)**[10]



Colorless oil; ^{1}H NMR: δ = 0.88 (t, *J* = 6.8 Hz, 3H, CH_3), 1.27-1.45 (m, 6H, 3×CH_2), 1.53-1.62 (m, 2H, CH_2), 2.28 (s, 6H, 2×CH_3), 2.97 (t, *J* = 7.2 Hz, 2H, CH_2), 2.99 (*br*, 1H, NH), 6.77-6.83 (m, 1H, CH_{arom}), 6.98 (d, *J* = 7.5 Hz, 2H, CH_{arom}); ^{13}C NMR: δ = 14.2 (CH_3), 18.7 (2×CH_3), 22.8 (CH_2), 27.0 (CH_2), 31.3 (CH_2), 31.9 (CH_2), 48.8 (CH_2), 121.6 (CH_{arom}), 128.9 (2×CH_{arom}), 129.2 (2×C_q), 146.6 (C_q); IR (ATR): ν_{max} = 3381, 3032, 2919, 2850, 1590, 1472, 1375, 1260, 1214, 1096, 756, 719 cm^{-1}; HRMS-ESI: *m/z* $[MH]^{+\cdot}$calcd for $C_{14}H_{24}N$: 206.1903 found: 206.1905.

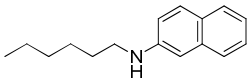
***N*^{1},*N*^{4}-dihexylbenzene-1,4-diamine [51833-32-0] (3ai)**[11]



White solid; Mp = 70-72 °C; ^{1}H NMR: δ = 0.89 (t, *J* = 6.7 Hz, 6H, 2×CH_3), 1.28-1.41 (m, 12H, 6×CH_2), 1.54-1.61 (m, 4H, 2×CH_2), 3.04 (t, *J* = 7.0 Hz, 4H, 2×CH_2), 3.17 (*br*, 2H, 2×NH), 6.55 (s, 4H, 4×CH_{arom}); ^{13}C NMR (100 MHz): δ = 14.2 (2×CH_3), 22.8 (2×CH_2), 27.1 (2×CH_2), 29.9 (2×CH_2), 31.9 (2×CH_2), 45.6

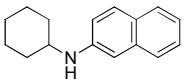
(2×CH_2), 114.9 (4×CH_{arom}), 141.1 (2×C_q); IR (ATR): ν_{max} = 3363, 2953, 2918, 2851, 1520, 1467, 1291, 1245, 1218, 1139, 1088, 800 cm^{-1}; HRMS-CI: *m/z* $[MH]^+$ calcd for $C_{18}H_{33}N_2$: 277.2638 found: 277.2637.

***N*-hexylnaphthalen-2-amine [58533-06-5] (3ae)**[12]



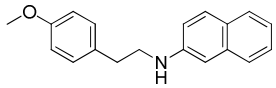
White solid; Mp = 44-46 °C; ^{1}H NMR (500 MHz): δ = 0.93 (t, *J* = 7.1 Hz, 3H, CH_3), 1.34-1.39 (m, 4H, 2×CH_2), 1.43-1.49 (m, 2H, CH_2), 1.66-1.72 (m, 2H, CH_2), 3.22 (t, *J* = 7.1 Hz, 2H, CH_2), 3.79 (*br*, 1H, NH), 6.81 (d, J^4 = 2.2 Hz, 1H, CH_{arom}), 6.88 (dd, J^3 = 8.8 Hz, J^4 = 2.5 Hz, 1H, CH_{arom}), 7.18-7.21 (m, 1H, CH_{arom}), 7.35-7.38 (m, 1H, CH_{arom}), 7.61-7.64 (m, 2H, 2×CH_{arom}), 7.67 (d, *J* = 7.6 Hz, 1H, CH_{arom}); ^{13}C NMR (125 MHz): δ = 14.2 (CH_3), 22.8 (CH_2), 27.1 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 44.2 (CH_2), 104.3 (CH_{arom}), 118.1 (CH_{arom}), 121.9 (CH_{arom}), 126.0 (CH_{arom}), 126.4 (CH_{arom}), 127.5 (C_q), 127.8 (CH_{arom}), 129.0 (CH_{arom}), 135.4 (C_q), 146.3 (C_q); IR (ATR): ν_{max} = 3373, 3053, 2965, 2950, 2923, 2849, 1628, 1601, 1492, 1423, 1303, 1135, 843, 800, 751 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{22}N$: 228.1747 found: 228.1741.

***N*-cyclohexylnaphthalen-2-amine [23761-52-6] (3be)**[13]



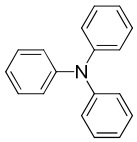
White solid; Mp = 177-180 °C; ^{1}H NMR (500 MHz): δ = 1.23-1.69 (m, 6H, 3×CH_2), 1.76-1.81 (m, 2H, CH_2), 2.12-2.16 (m, 2H, CH_2), 3.36-3.41 (m, 1H, CH), 6.94-6.97 (m, 2H, 2×CH_{arom}), 7.18-7.22 (m, 1H, CH_{arom}), 7.33-7.37 (m, 1H, CH_{arom}), 7.60-7.66 (m, 3H, 3×CH_{arom}); ^{13}C NMR (125 MHz): δ = 25.1 (2×CH_2), 25.9 (CH_2), 32.9 (2×CH_2), 53.3 (CH), 107.2 (CH_{arom}), 118.8 (CH_{arom}), 122.5 (CH_{arom}), 126.2 (CH_{arom}), 126.5 (CH_{arom}), 127.8 (CH_{arom}), 128.1 (C_q), 129.2 (CH_{arom}), 135.1 (C_q), 143.3 (C_q); IR (ATR): ν_{max} = 3421, 3050, 2921, 2854; 1625, 1600, 1522, 1452, 1222, 1144, 1106, 826, 752 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{20}N$: 226.1590 found: 226.1595.

***N*-(4-methoxyphenethyl)naphthalen-2-amine [No CAS Number] (3je)**



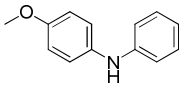
Orange gel; ^{1}H NMR (400 MHz): δ = 2.95 (t, *J* = 7.0 Hz, 2H, CH_2), 3.48 (t, *J* = 7.0 Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 6.85-6.91 (m, 4H, 4×CH_{arom}), 7.16 (dd, J^3 = 11.3 Hz, J^4 = 2.8 Hz, 2H, 2×CH_{arom}), 7.19-7.23 (m, 1H, CH_{arom}), 7.35-7.39 (m, 1H, CH_{arom}), 7.63 (d, J^3 = 8.5 Hz, 2H, 2×CH_{arom}), 7.67 (d, J^3 = 8.0 Hz, 1H, CH_{arom}); ^{13}C NMR: δ = 34.3 (CH_2), 45.7 (CH_2), 55.4 (CH_3), 105.5 (CH_{arom}), 114.2 (2×CH_{arom}), 118.3 (CH_{arom}), 122.3 (CH_{arom}), 126.1 (CH_{arom}), 126.5 (CH_{arom}), 127.8 (CH_{arom}), 127.9 (C_q), 129.1 (CH_{arom}), 129.9 (2×CH_{arom}), 131.2 (C_q), 135.3 (C_q), 145.3 (C_q), 158.4 (C_q); IR (ATR): ν_{max} = 3401, 3048, 2929, 2835, 1627, 1602, 1510, 1464, 1440, 1225, 1176, 1031, 823, 807, 743 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{19}H_{20}NO$: 278.1539 found: 278.1534.

Triphenylamine [603-34-9] (12dd)[15]



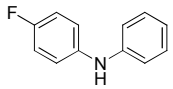
White solid; Mp = 128-130 °C ^{1}H NMR: δ = 6.97-7.03 (m, 3H, 3×CH_{arom}), 7.05-10 (m, 6H, 6×CH_{arom}), 7.20-7.27 (m, 6H, 6×CH_{arom}); ^{13}C NMR: δ = 122.8 (3×CH_{arom}), 124.3 (6×CH_{arom}), 129.3 (6×CH_{arom}), 148.0 (3×C_q); IR (ATR): ν_{max} = 3033, 1582, 1483, 1273, 1172, 1074, 1027, 746, 690 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{18}H_{16}N$: 246.1277 found: 246.1277.

4-methoxy-*N*-phenylaniline [1208-86-2] (3kd)[4]



White solid; Mp = 104-106 °C; ^{1}H NMR: δ = 3.80 (s, 3H, CH_3), 5.49 (*br*, 1H, NH), 6.80-6.92 (m, 5H, 5×CH_{arom}), 7.05-7.09 (m, 2H, 2×CH_{arom}), 7.18-7.24 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 55.7 (CH_3), 114.7 (2×CH_{arom}), 115.7 (2×CH_{arom}), 119.6 (CH_{arom}), 122.3 (2×CH_{arom}), 129.4 (2×CH_{arom}), 135.8 (C_q), 145.3 (C_q), 155.3 (C_{arom}).; IR (ATR): ν_{max} = 3386, 3035, 2910, 1594, 1461, 1235, 1032, 748 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{13}H_{14}NO$: 200.1073 found: 200.1070.

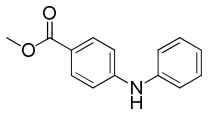
4-Fluoro-*N*-phenylaniline [330-83-6] (3ld)[4]



Light yellow solid; Mp = 34-38 °C; ^{1}H NMR: δ = 5.59 (*br*, 1H, NH), 6.94-7.11 (m, 7H, 7×CH_{arom}), 7.31

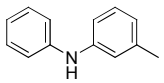
(t, J = 7.8 Hz, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 116.1 (d, J = 22 Hz, CH_{arom}), 116.9 (CH_{arom}), 120.6 (d, J = 7.7 Hz, CH_{arom}), 129.5 (CH_{arom}), 139.0 (d, J = 2.8 Hz, C_q), 144.0 (C_q), 158.1 (d, J = 238.9 Hz, C_q); IR (ATR): ν_{max} = 3395, 3032, 1594, 1492, 1311, 1211, 742 cm^{-1}; HRMS-ESI: *m/z* $[MH]^{+\cdot}$calcd for $C_{12}H_{11}FN$: 188.0870 found: 188.0870.

Methyl 4-(phenylamino)benzoate [4058-18-8] (3md)[4]



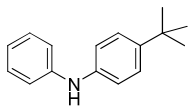
White solid; Mp = 109-112 °C; ^{1}H NMR: δ = 3.88 (s, 3H, CH_3), 6.48 (*br*, 1H, NH), 6.99 (d, J = 8.7 Hz, 2H, 2×CH_{arom}), 7.04-7.06 (m, 1H, CH_{arom}), 7.17 (d, J = 7.7 Hz, 2H, 2×CH_{arom}), 7.33 (t, J = 7.8 Hz, 2H, 2×CH_{arom}), 7.94 (d, J = 8.7 Hz, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 51.8 (CH_3), 114.6 (2×CH_{arom}), 120.5 (2×CH_{arom}), 121.0 (C_q), 123.1 (CH_{arom}), 129.6 (2×CH_{arom}), 131.6 (2×CH_{arom}), 140.9 (C_q), 148.2 (C_q), 167.1 (C_q); IR (ATR): ν_{max} = 3331, 1680, 1587, 1531, 1495, 1272, 745 cm^{-1}; HRMS-ESI: *m/z* $[MNa]^+$ calcd for $C_{14}H_{13}NNaO_2$: 250.0829 found: 250.0838.

3-methyl-*N*-phenylaniline [1205-64-7] (3df)[4]



Colorless oil; ^{1}H NMR: δ = 2.32 (s, 3H, CH_3), 5.66 (*br*, 1H, NH), 6.76 (d, J = 7.3 Hz, 1H, CH_{arom}), 6.88-6.95 (m, 3H, 3×CH_{arom}), 7.07 (d, J = 7.5 Hz, 2H, 2×CH_{arom}), 7.16 (t, J = 8.1 Hz, 1H, CH_{arom}), 7.24-7.30 (m, 2H, 2×CH_{arom}); ^{13}C NMR: δ = 21.6 (CH_3), 115.0 (CH_{arom}), 117.9 (2×CH_{arom}), 118.6 (CH_{arom}), 120.9 (CH_{arom}), 121.9 (CH_{arom}), 129.2 (CH_{arom}), 129.4 (2×CH_{arom}), 139.2 (C_q), 143.1 (C_q), 143.3 (C_q); IR (ATR): ν_{max} = 3391, 3035, 2917, 1587, 1512, 1492, 1312, 742 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{13}H_{14}N$: 184.1122 found: 184.1121.

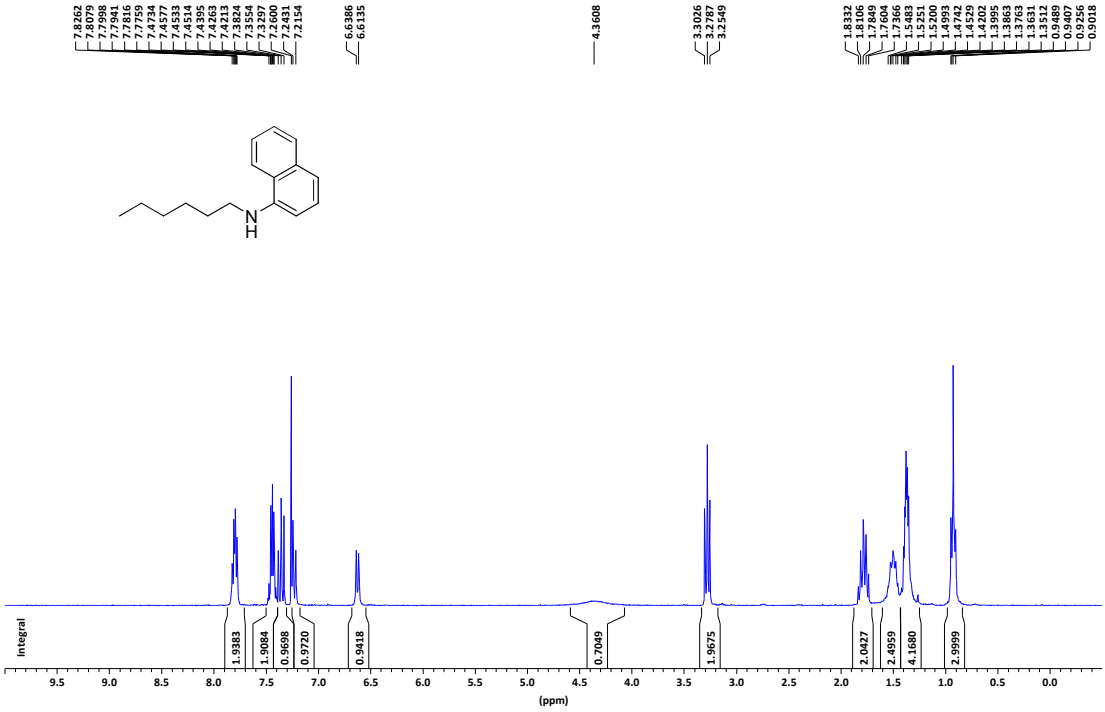
4-*tert*butyl-*N*-phénylaniline [4496-49-5] (3dk)[4]

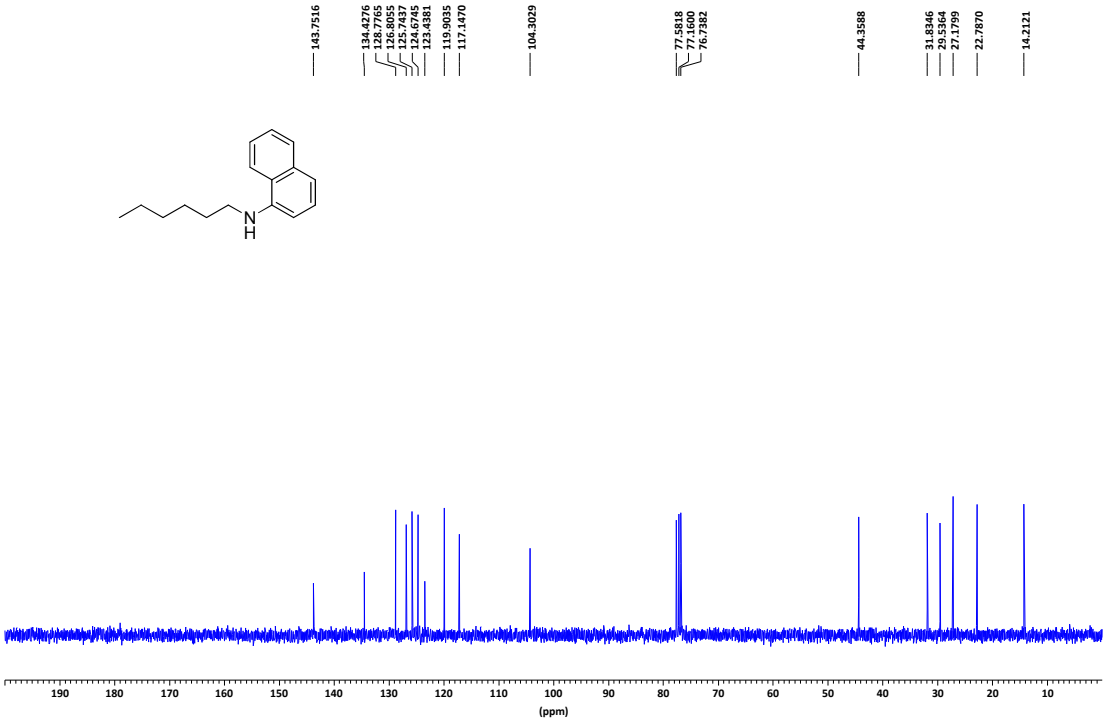


Yellow solid; Mp = 64-66 °C; ^{1}H NMR: δ = 1.31 (s, 9H, 3×CH_3), 5.61 (*br*, 1H, NH), 6.88 (t, J = 7.2 Hz, 1H, CH_{arom}), 7.02 (d, J = 8.5 Hz, 4H, 4×CH_{arom}), 7.20-7.30 (m, 4H, 4×CH_{arom}); ^{13}C NMR: δ = 31.6

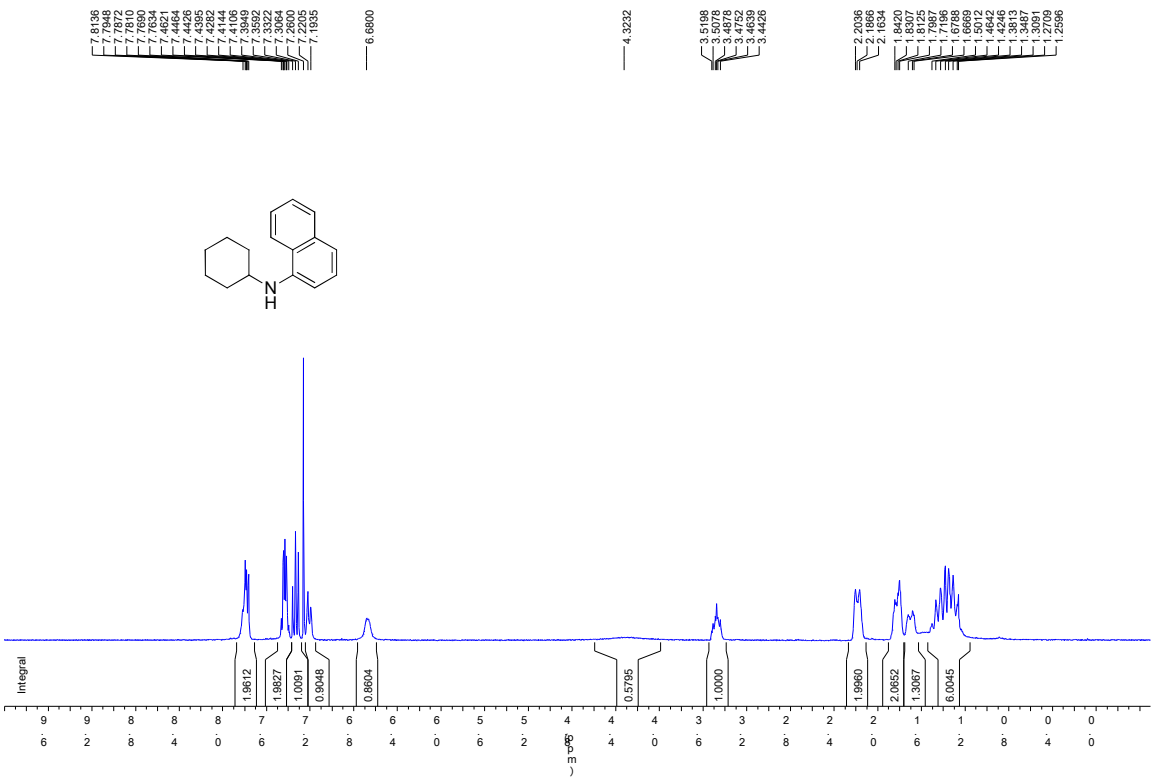
($3\times CH_3$), 34.3 (C_q), 117.2 ($2\times CH_{arom}$), 118.2 ($2\times CH_{arom}$), 120.5 (C_q), 126.2 ($2\times CH_{arom}$), 129.4 ($2\times CH_{arom}$), 140.4 (C_q), 143.8 (C_q), 144.2 (CH_{arom}); IR (ATR): ν_{max} = 3385, 3032, 2960, 1593, 1469, 1305, 740 cm^{-1}; HRMS-ESI: *m/z* $[MH]^+$ calcd for $C_{16}H_{20}N$: 226.1586 found: 226.1590.

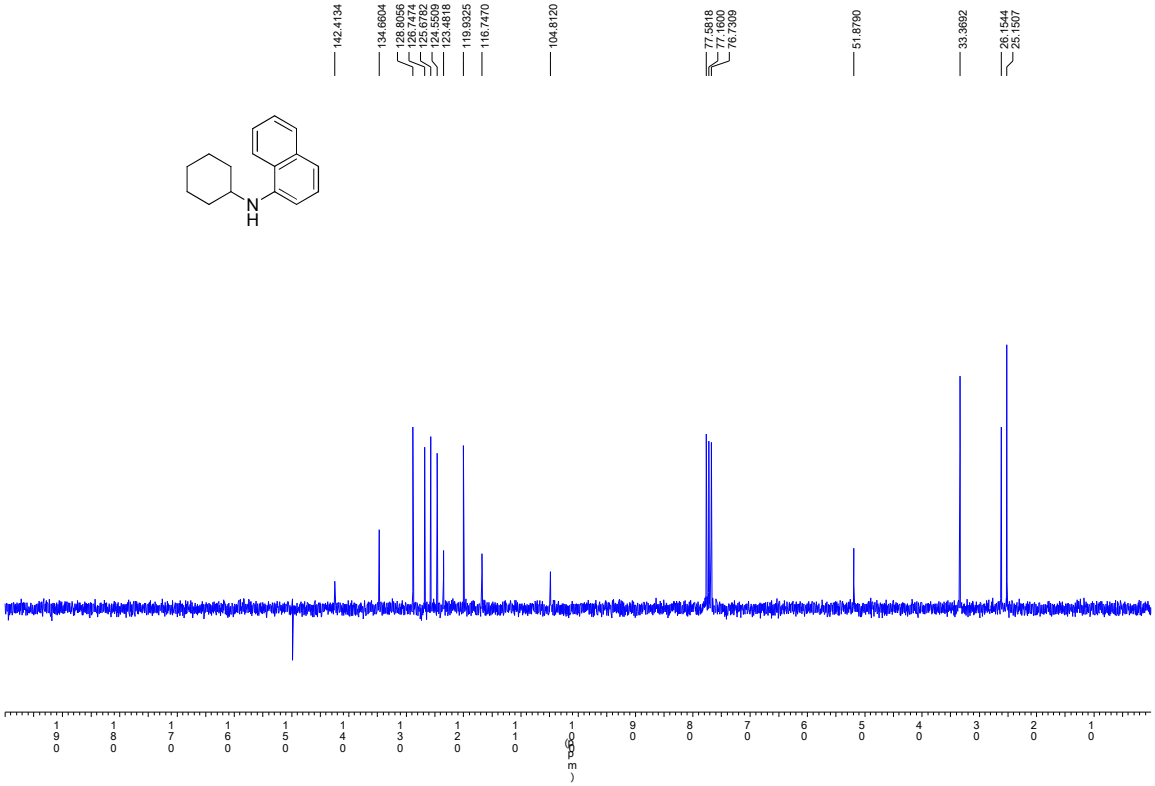
N-hexylnaphthalen-1-amine [87619-72-5] (3aa)



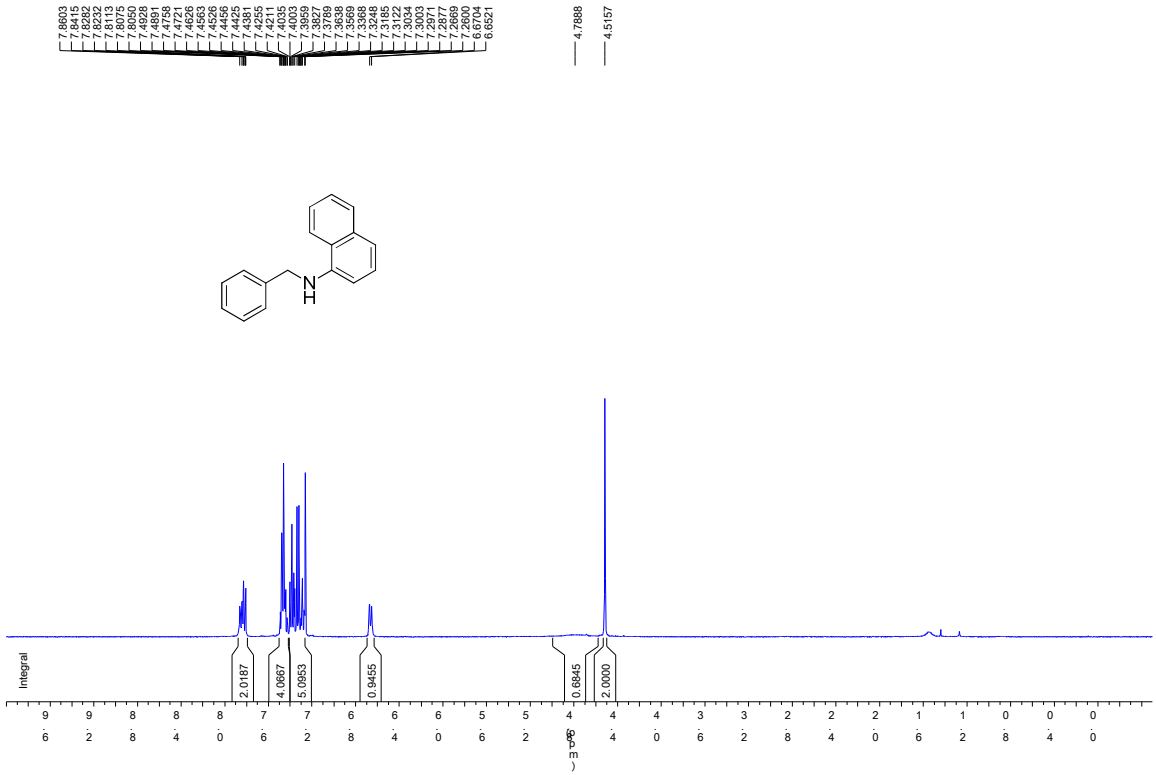


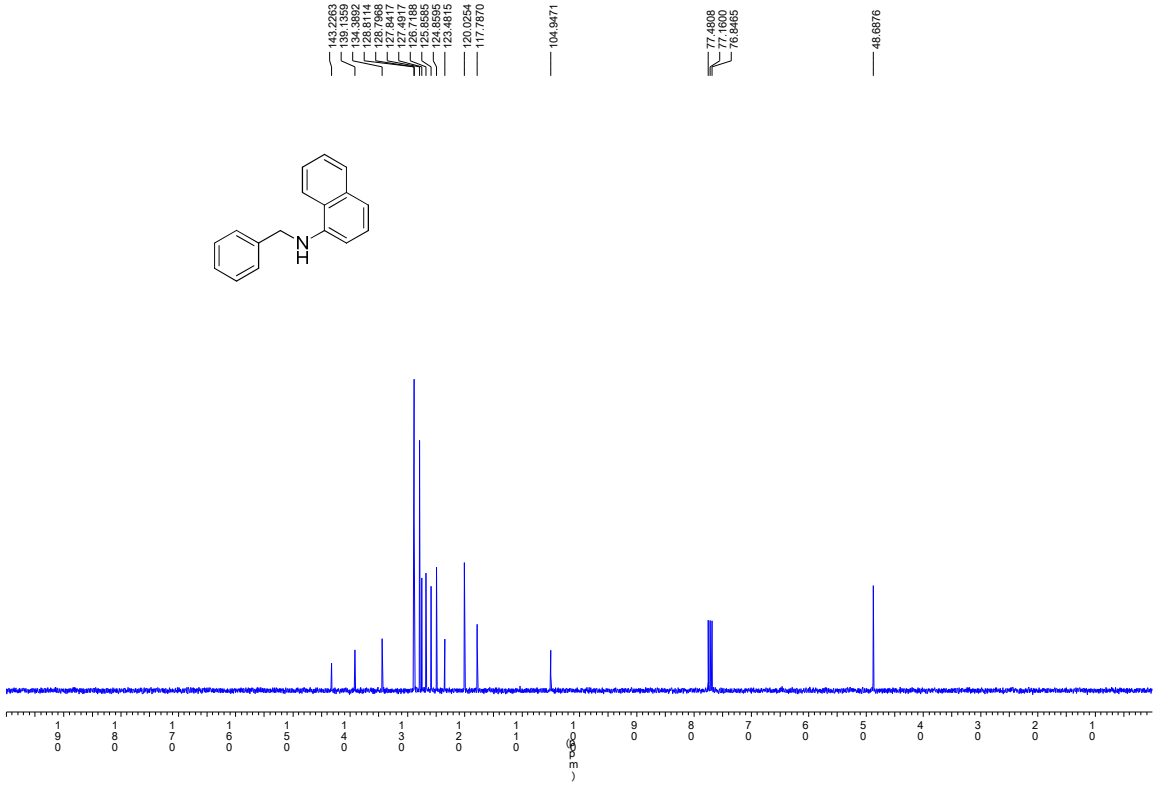
N-cyclohexylnaphthalen-1-amine [26863-63-8] (3ba)



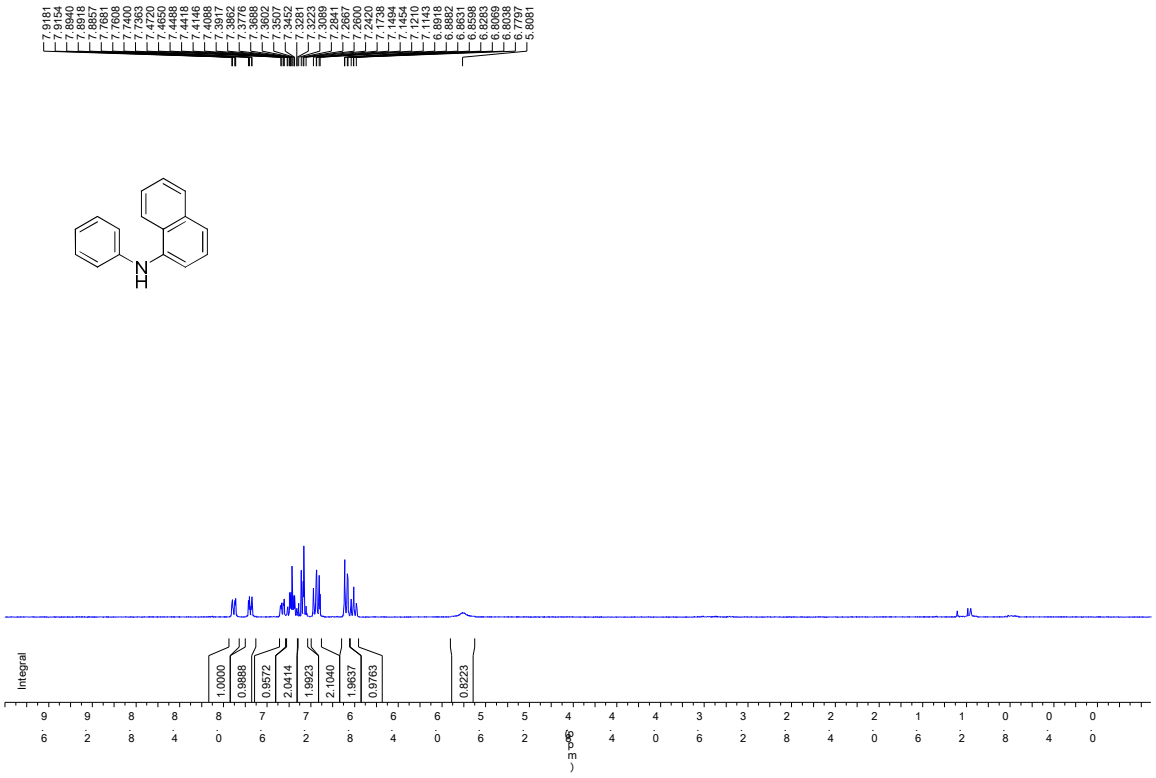


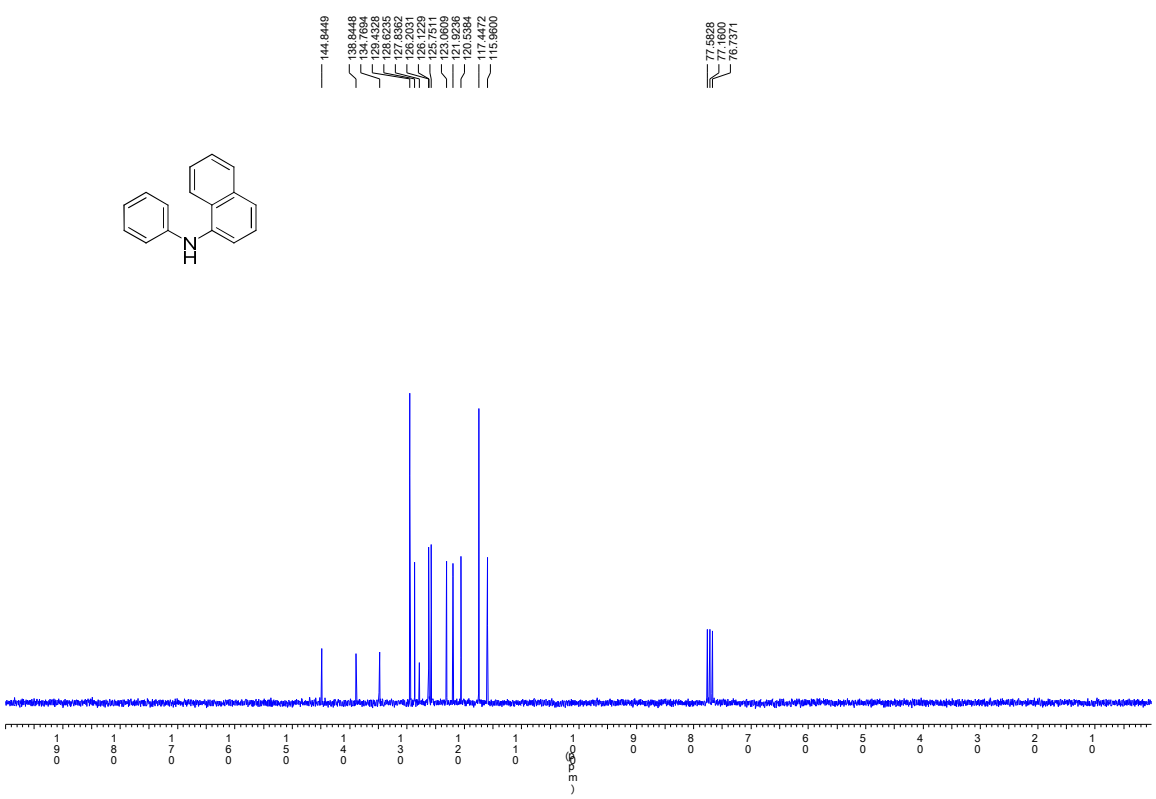
N-benzylnaphthalen-1-amine [6361-33-7] (3ca)



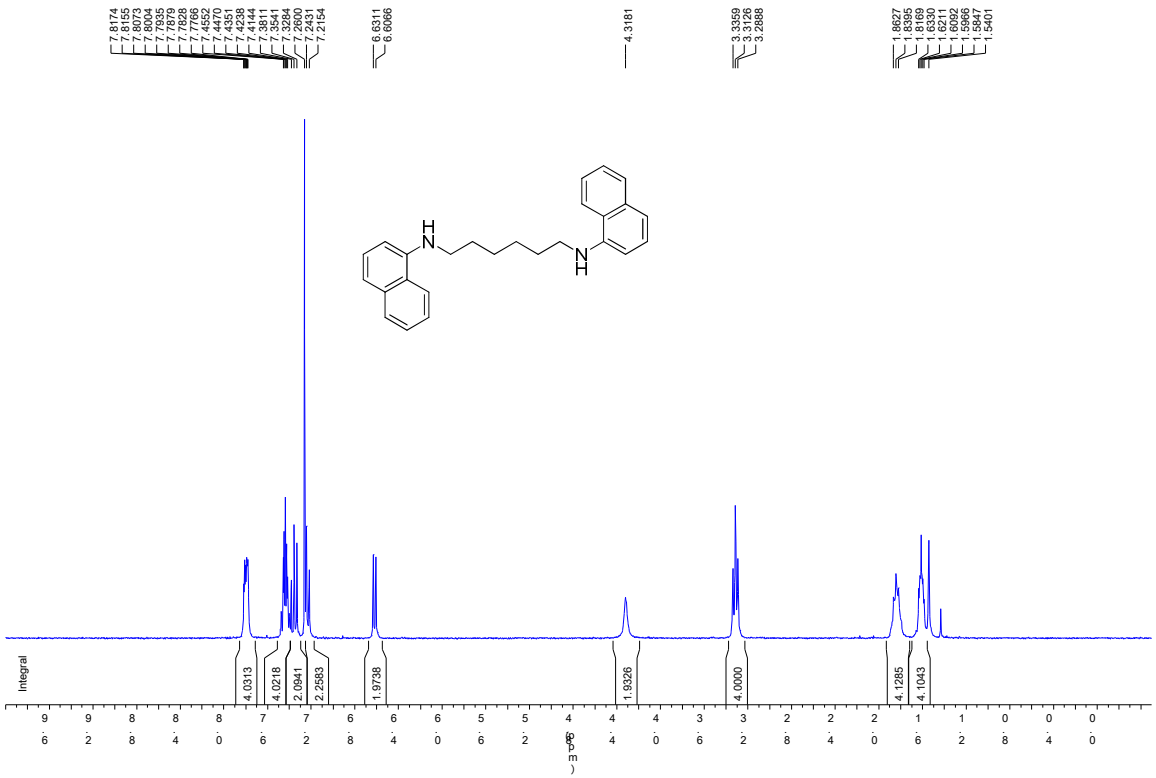


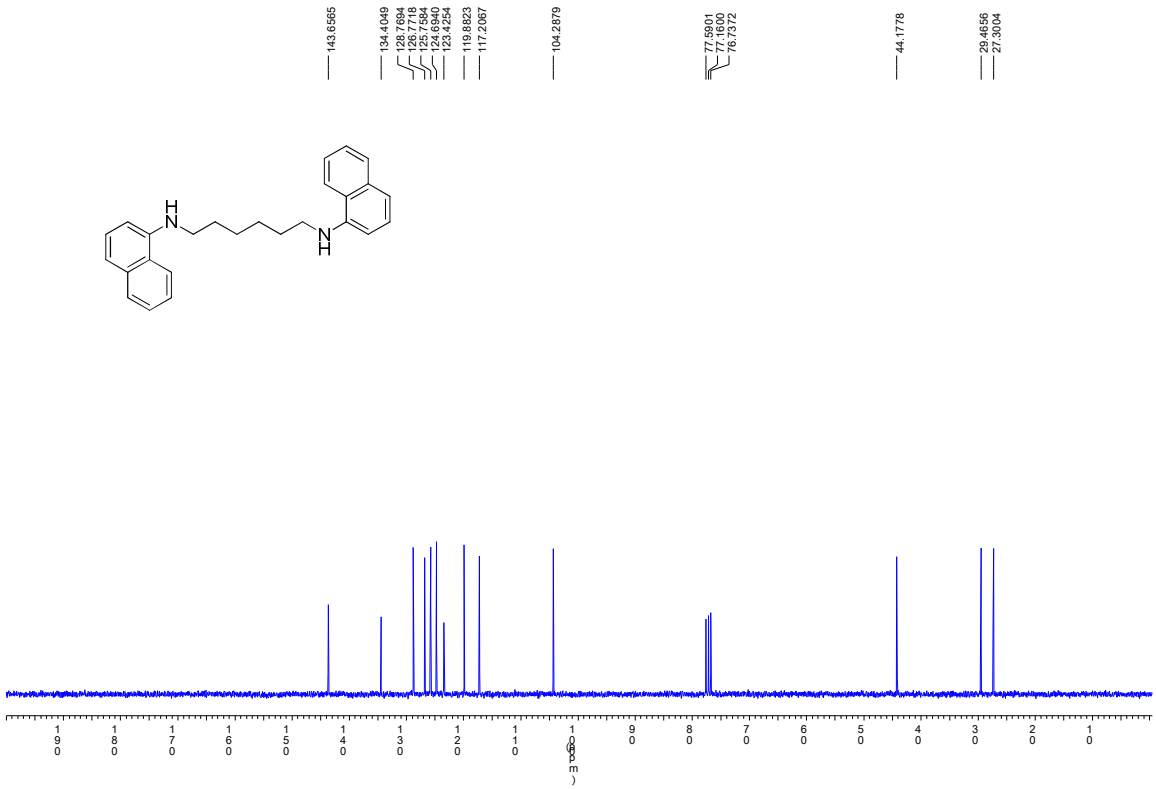
N-phenylnaphtalen-1-amine [90-30-2] (3da)



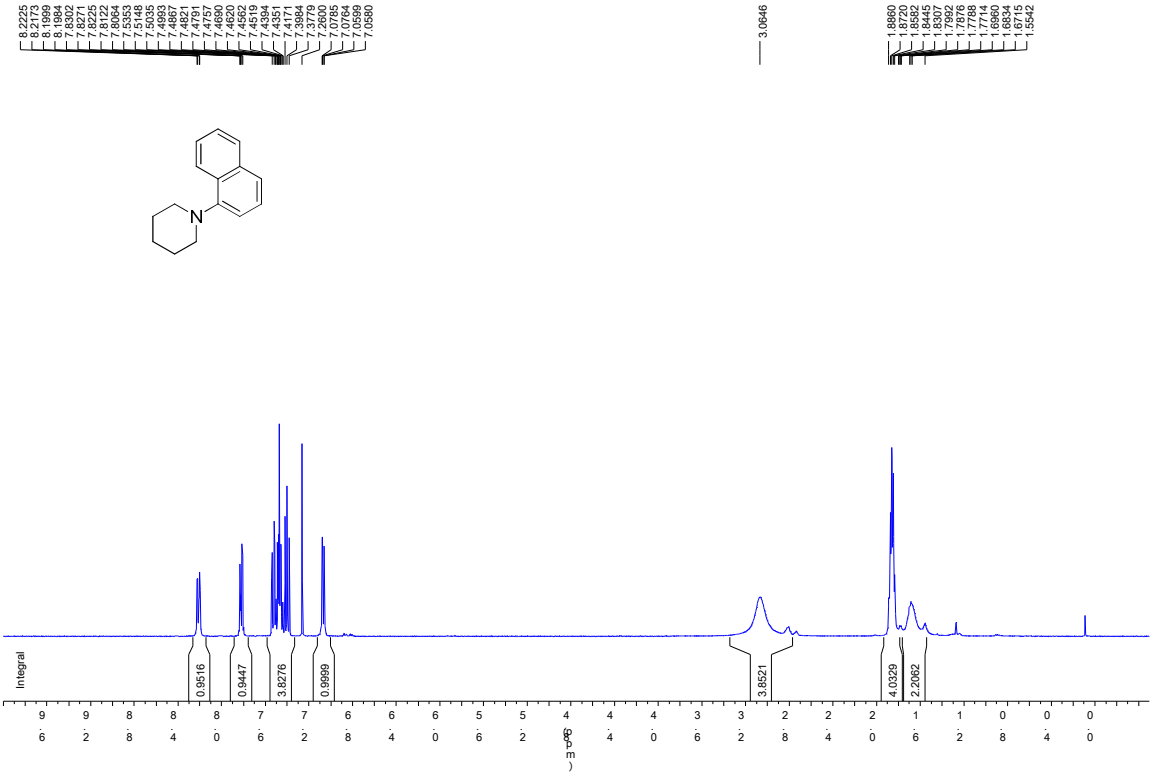


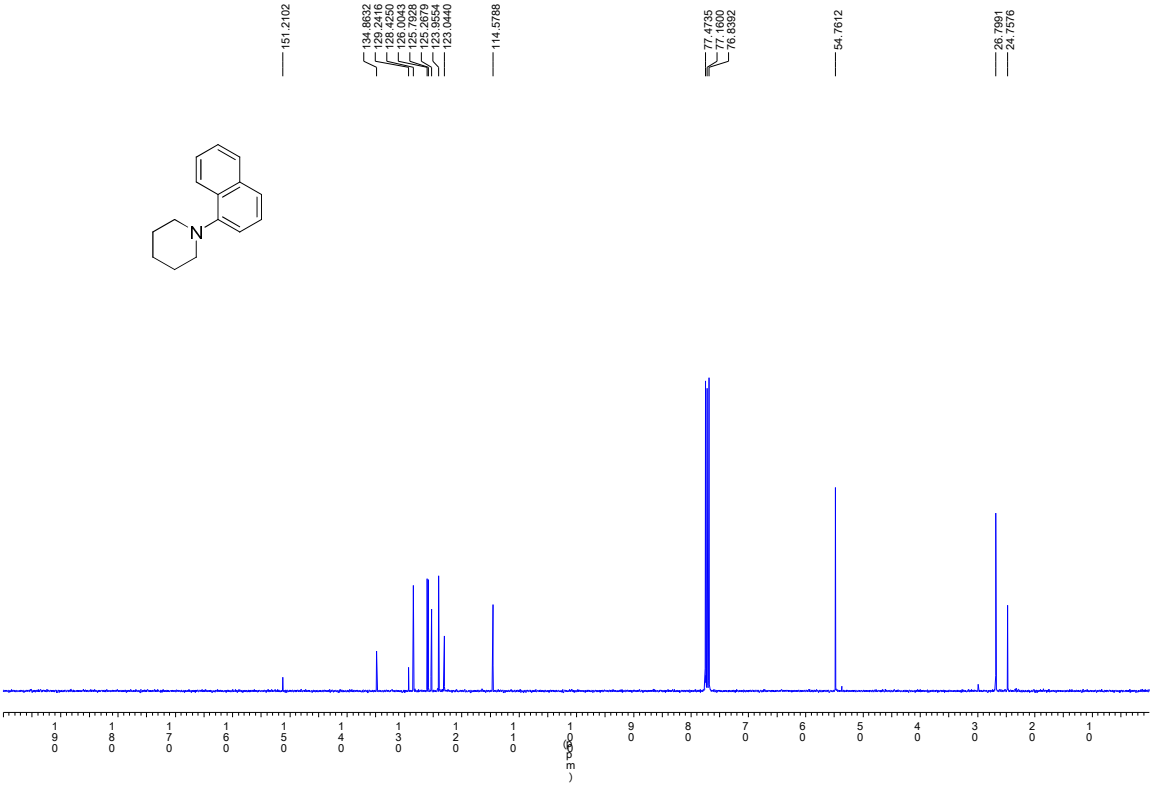
N^1,N^6-di(naphthalen-1-yl)hexane-1,6-diamine [185736-50-9] (3ea)



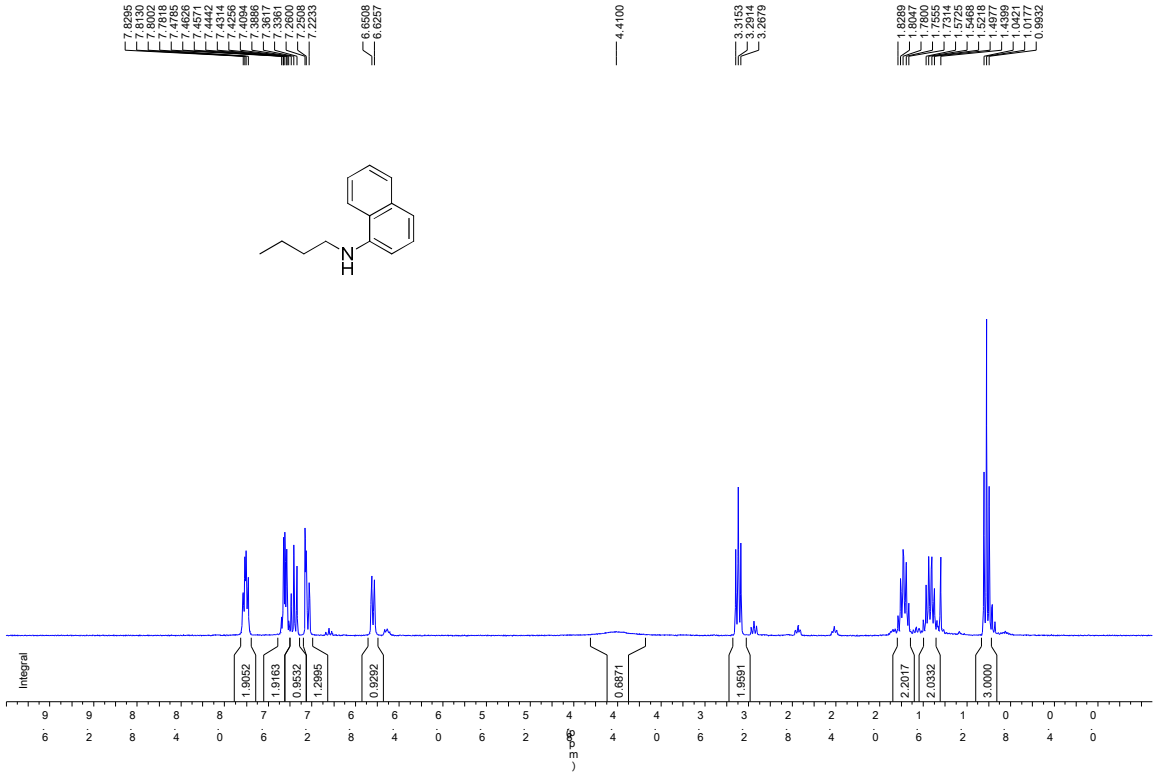


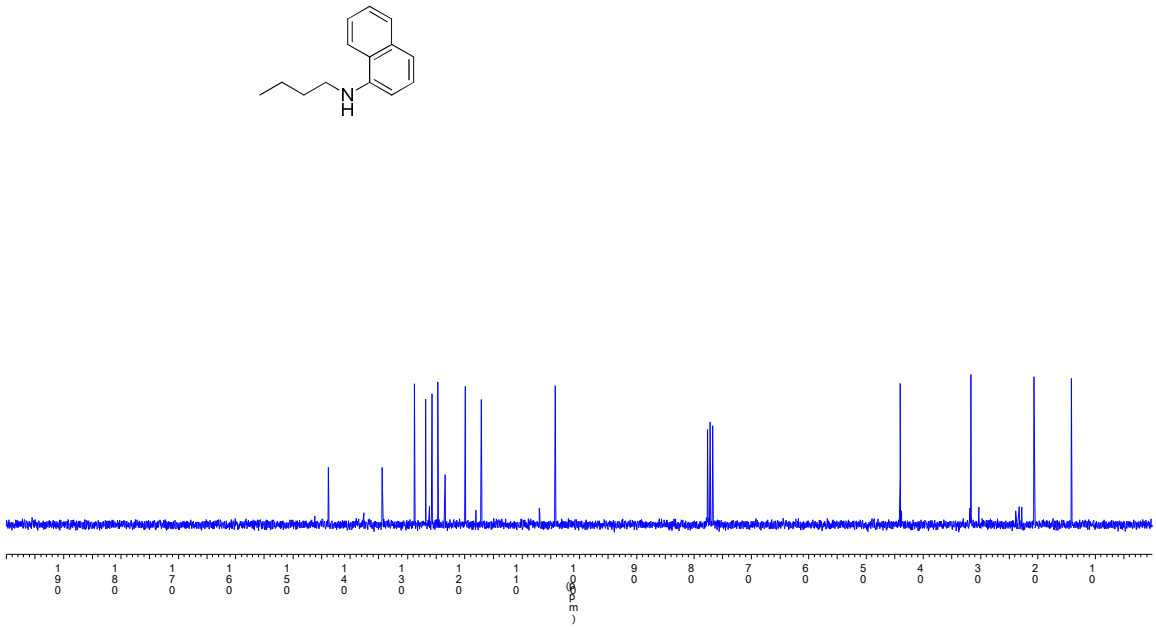
1-(naphthalen-1-yl)piperidine [62062-39-9] (3fa)



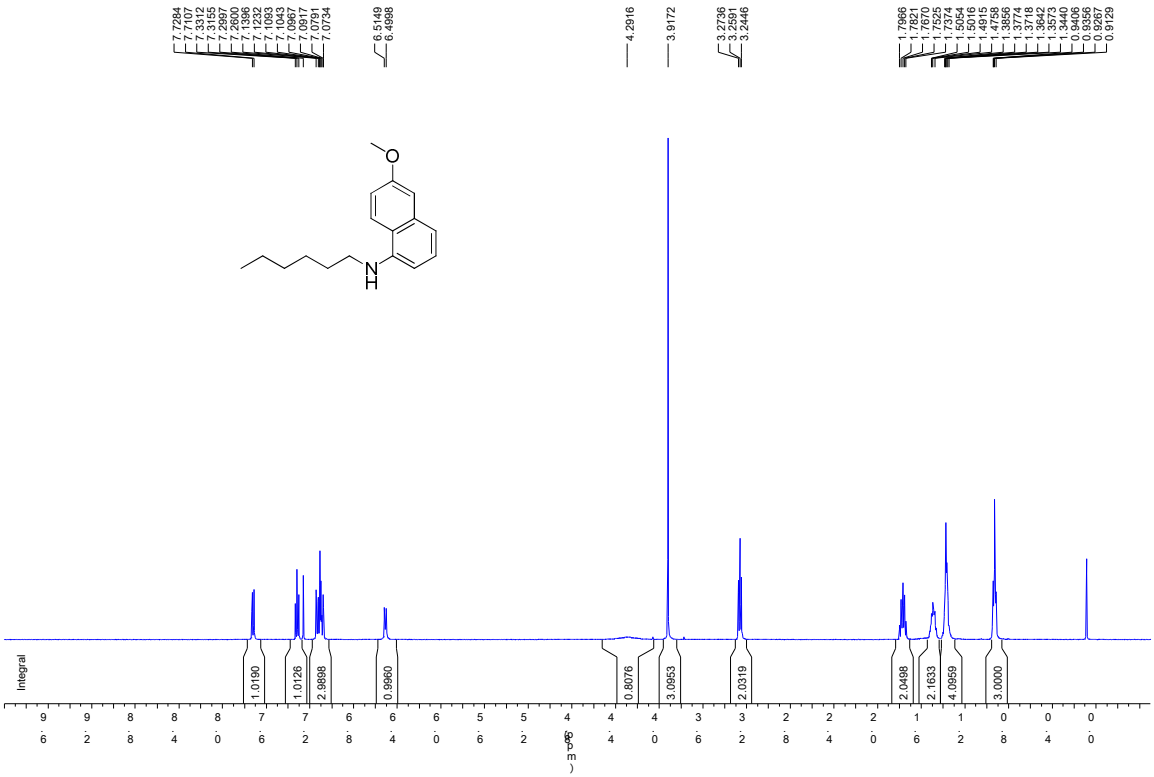


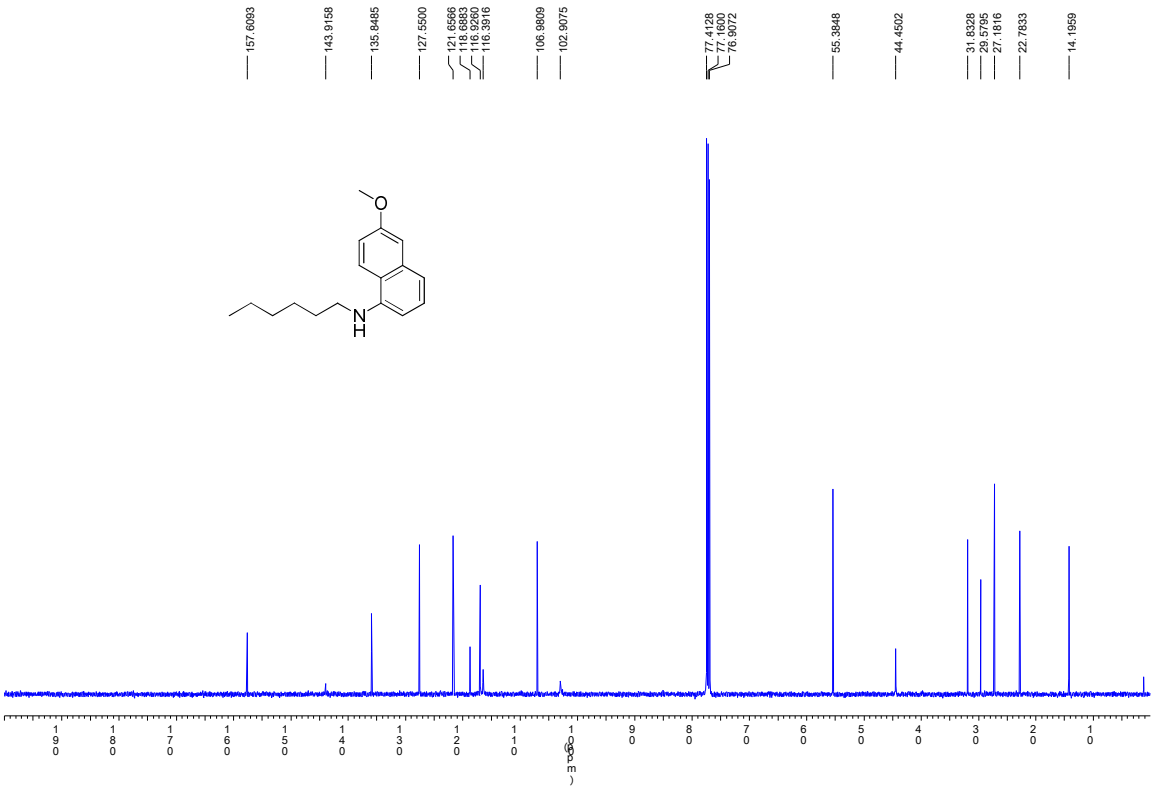
N-butylnaphthalen-1-amine [6281-00-1] (3ga)



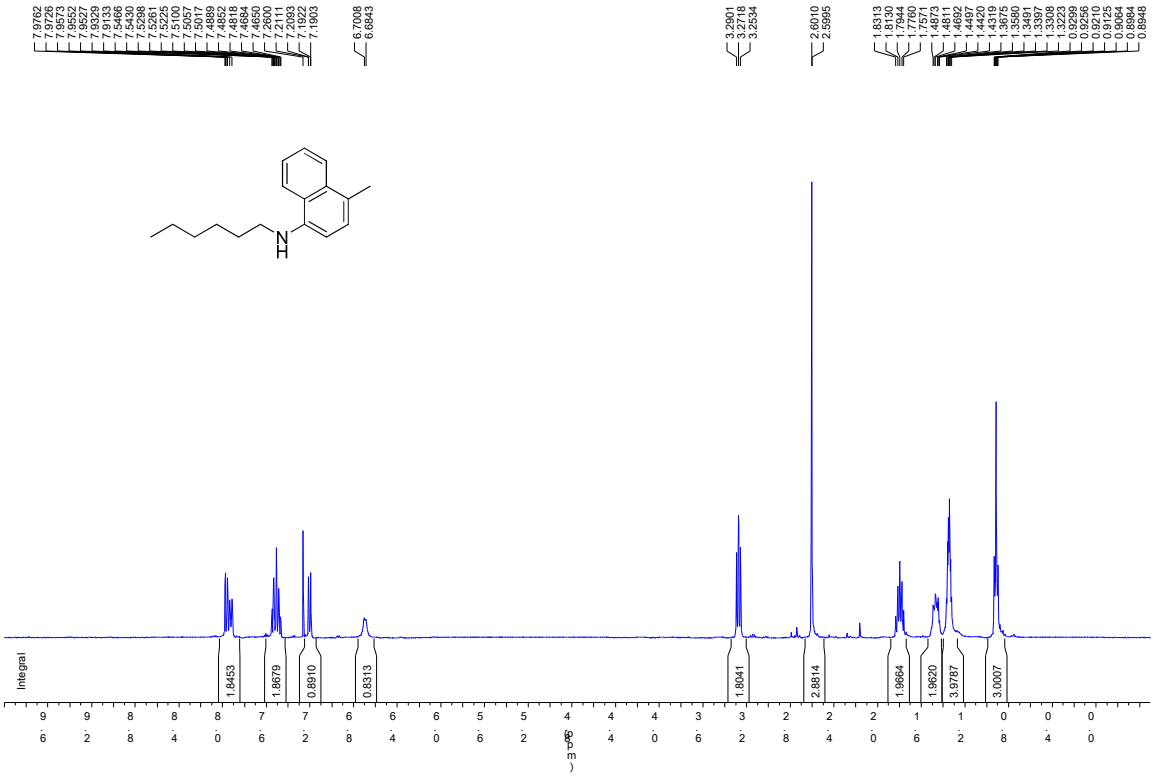


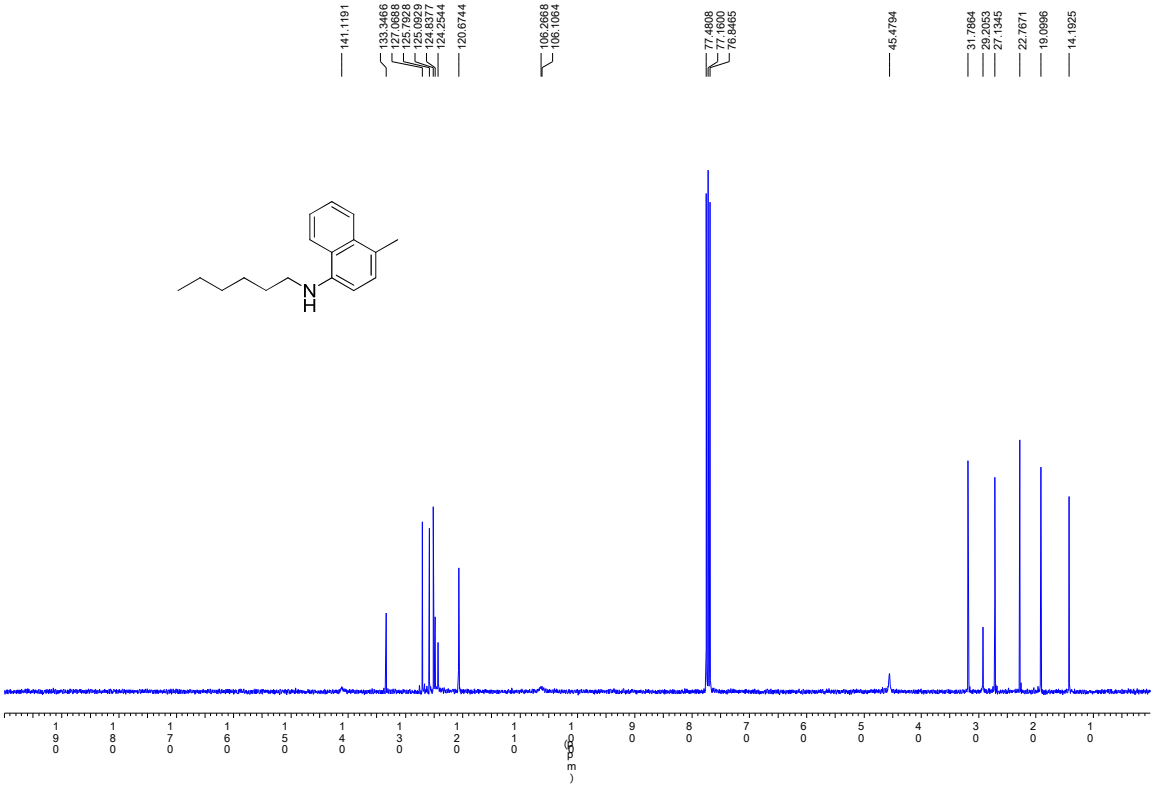
N-hexyl-6-methoxynaphthalen-1-amine [No CAS Number] (3ab)



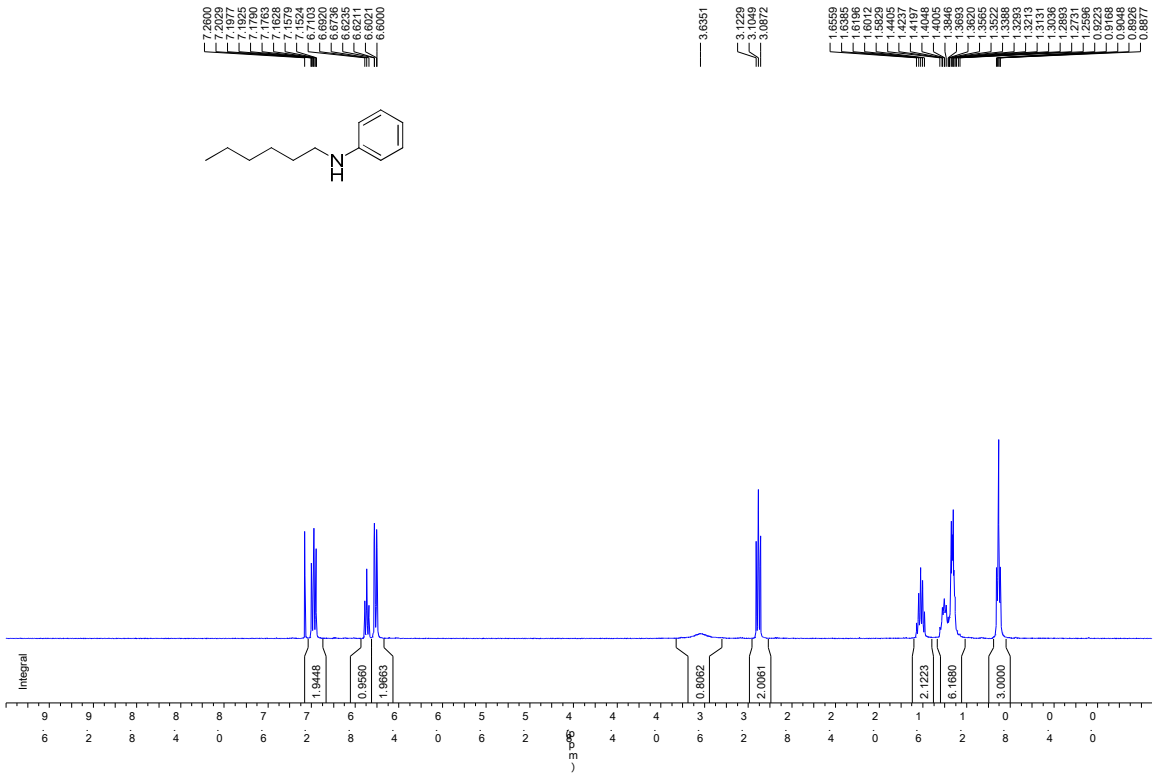


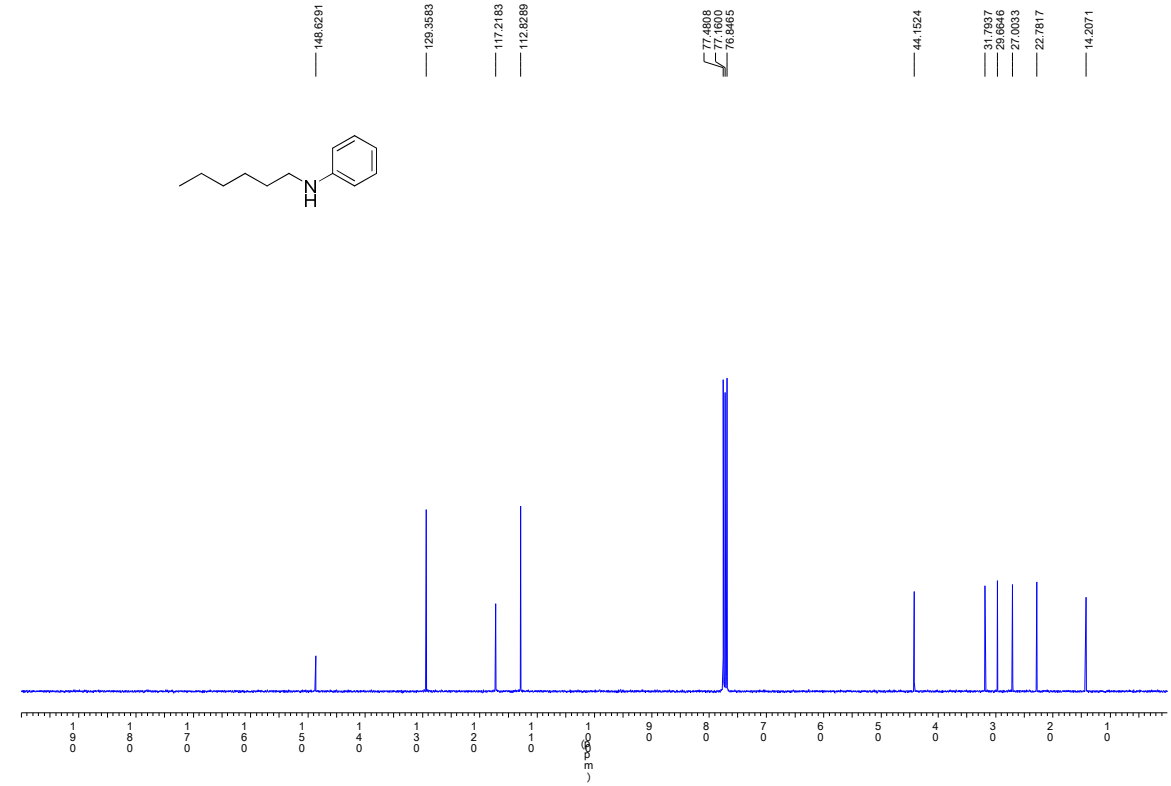
N-hexyl-4-methylnaphthalen-1-amine [No CAS Number] (3ac)



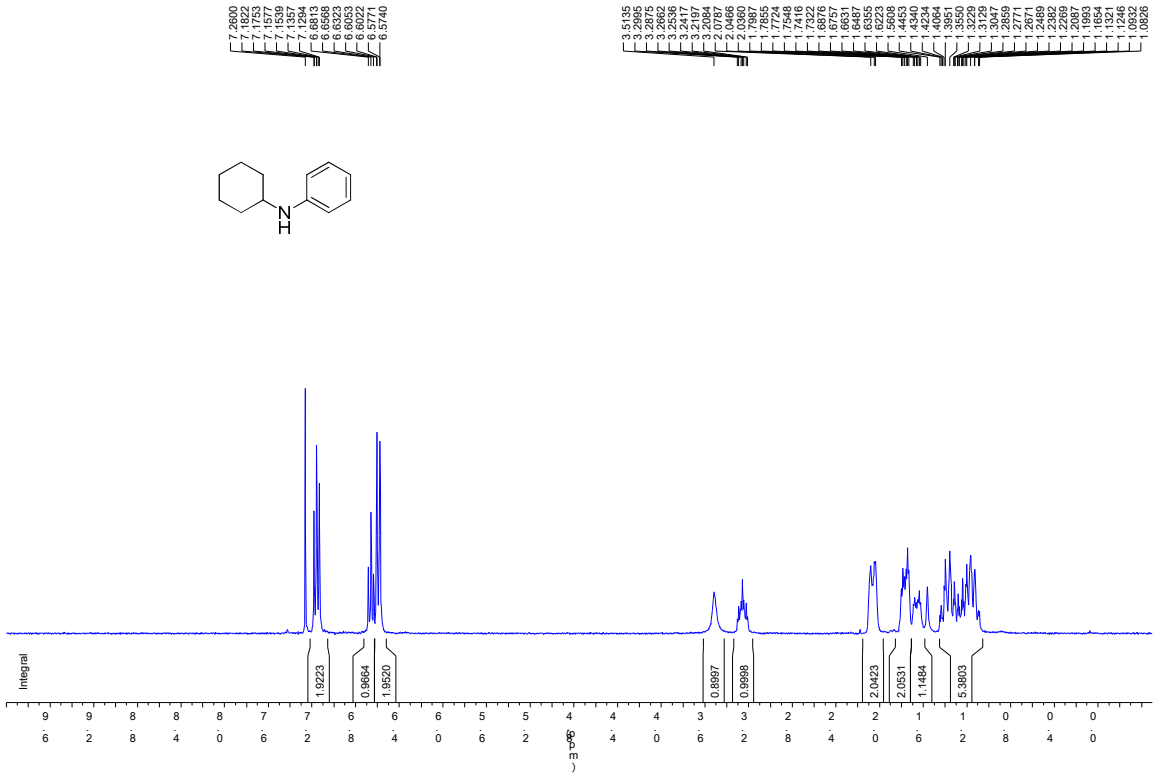


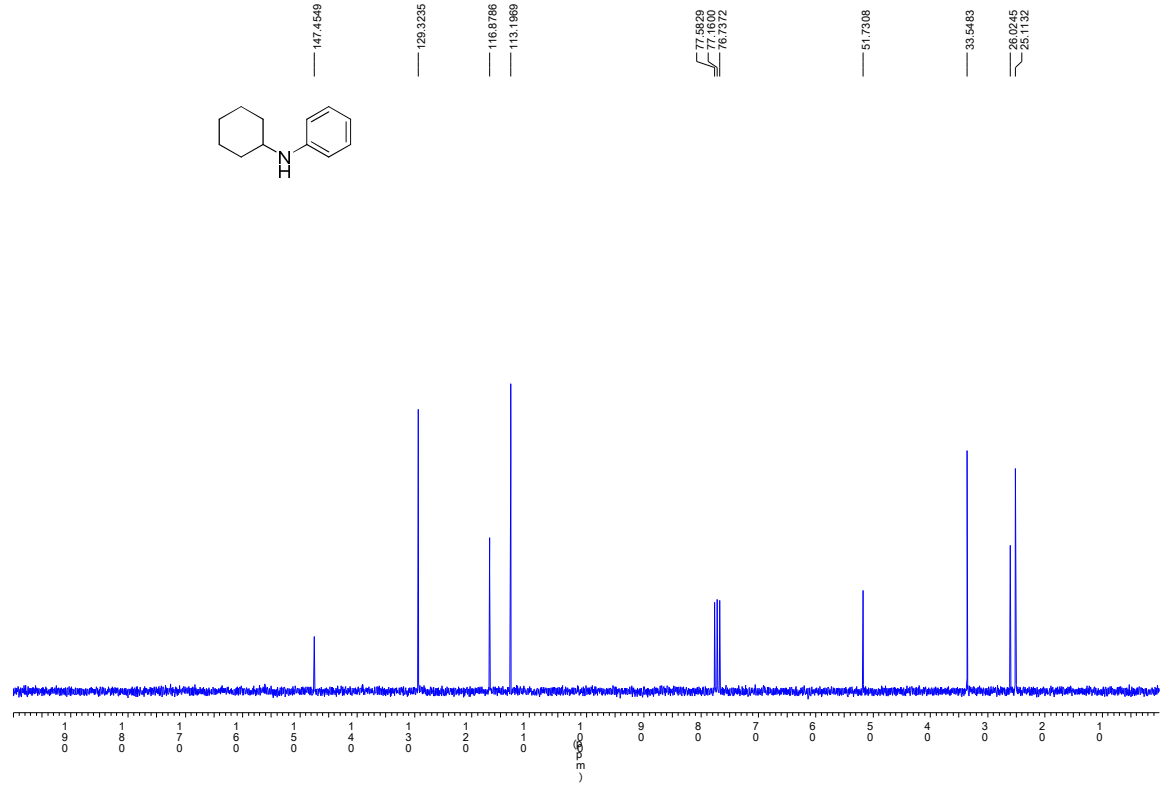
N-hexylaniline [4746-32-1] (3ad)



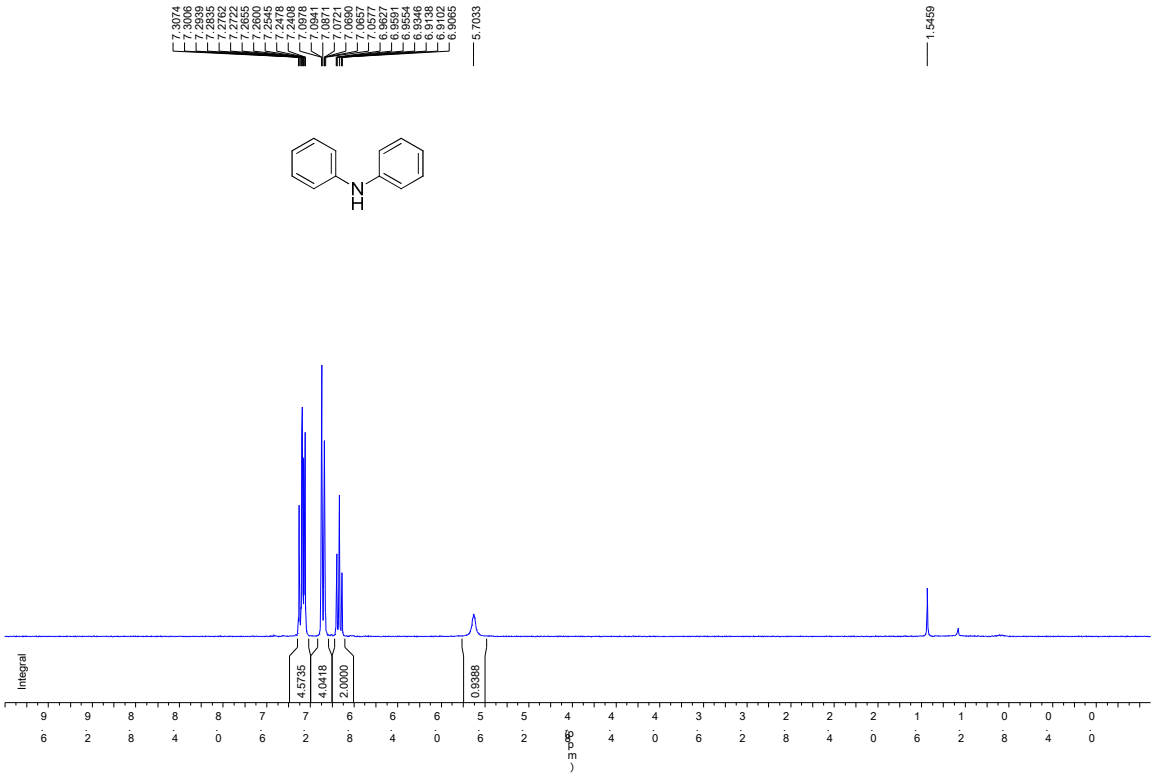


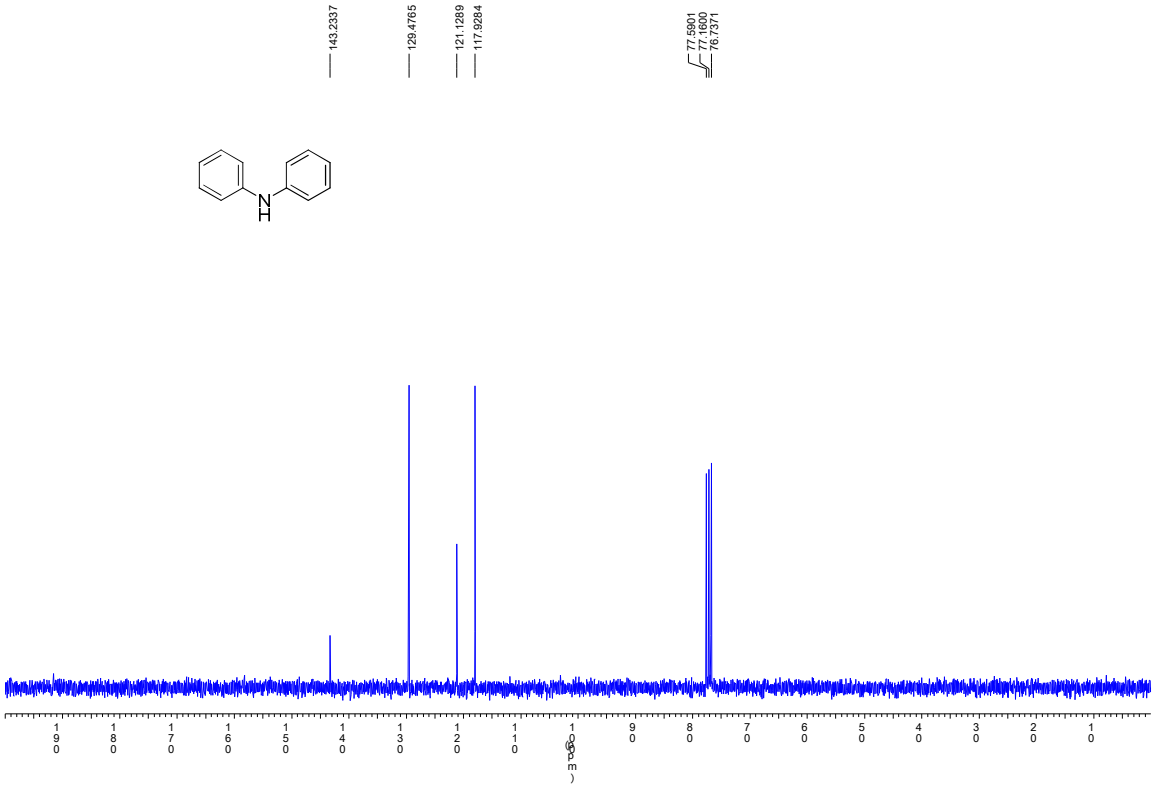
N-cyclohexylaniline [1821-36-9] (3bd)



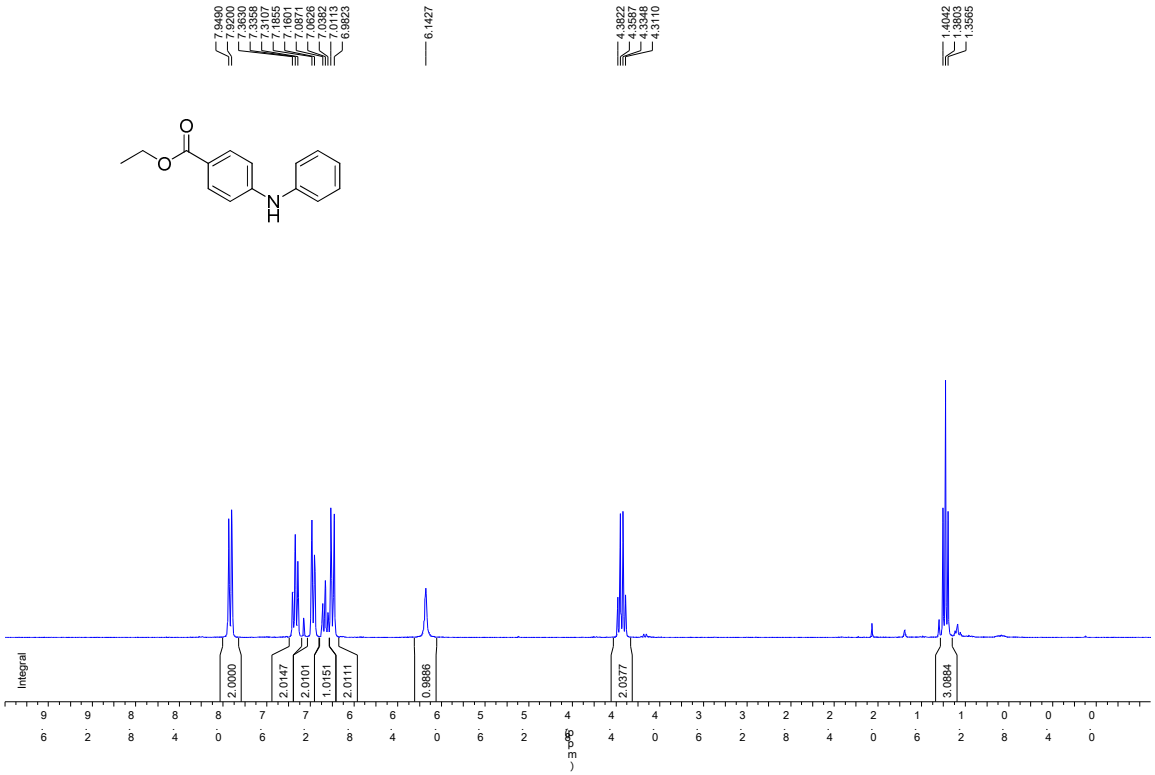


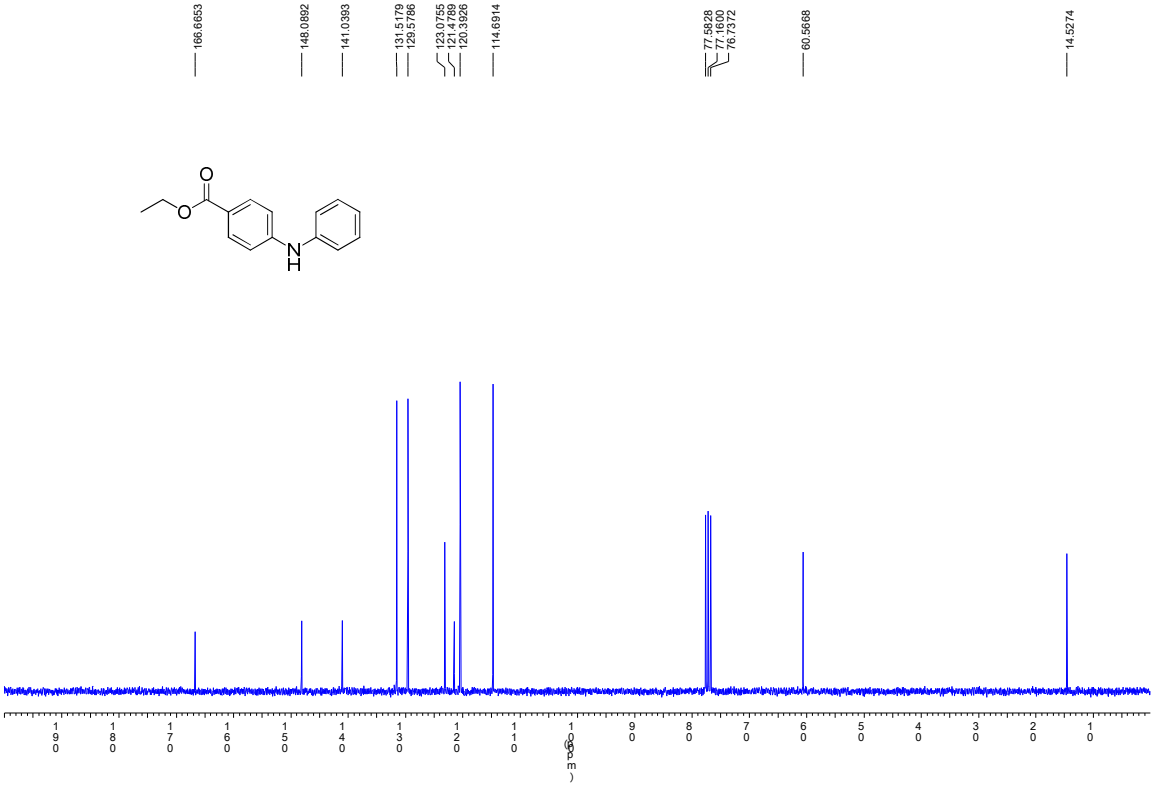
Diphenylamine [122-39-4] (3dd)



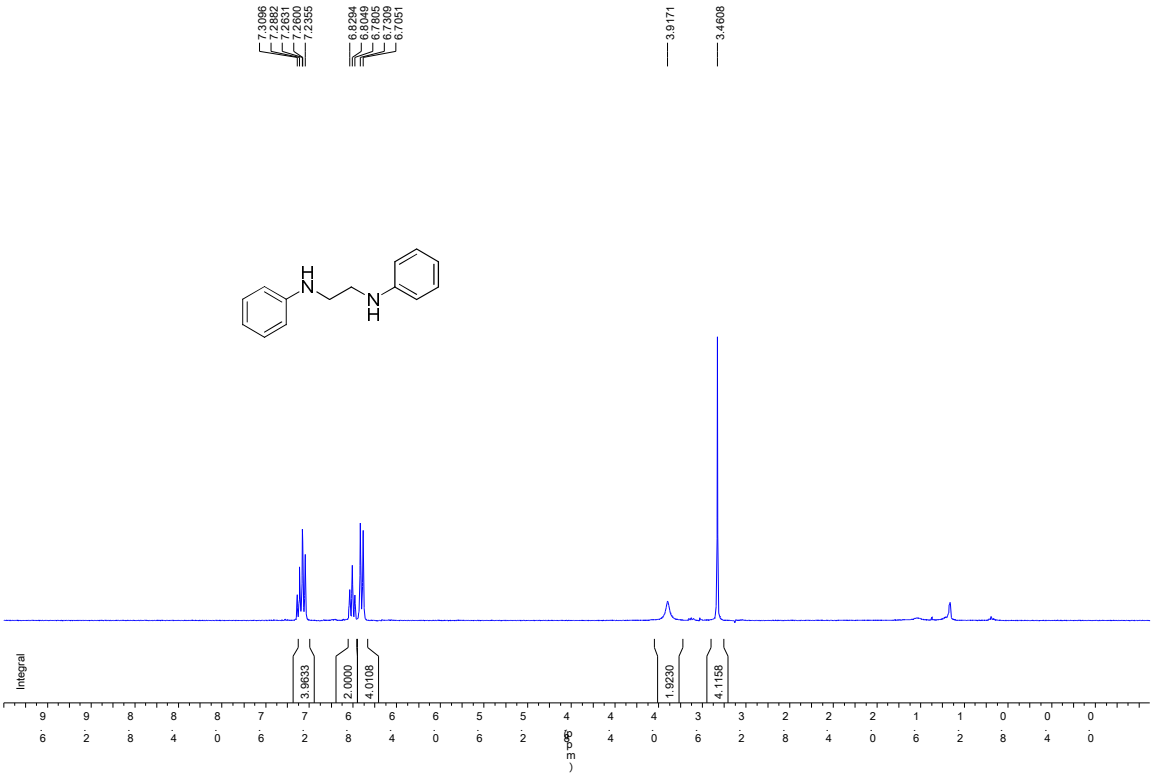


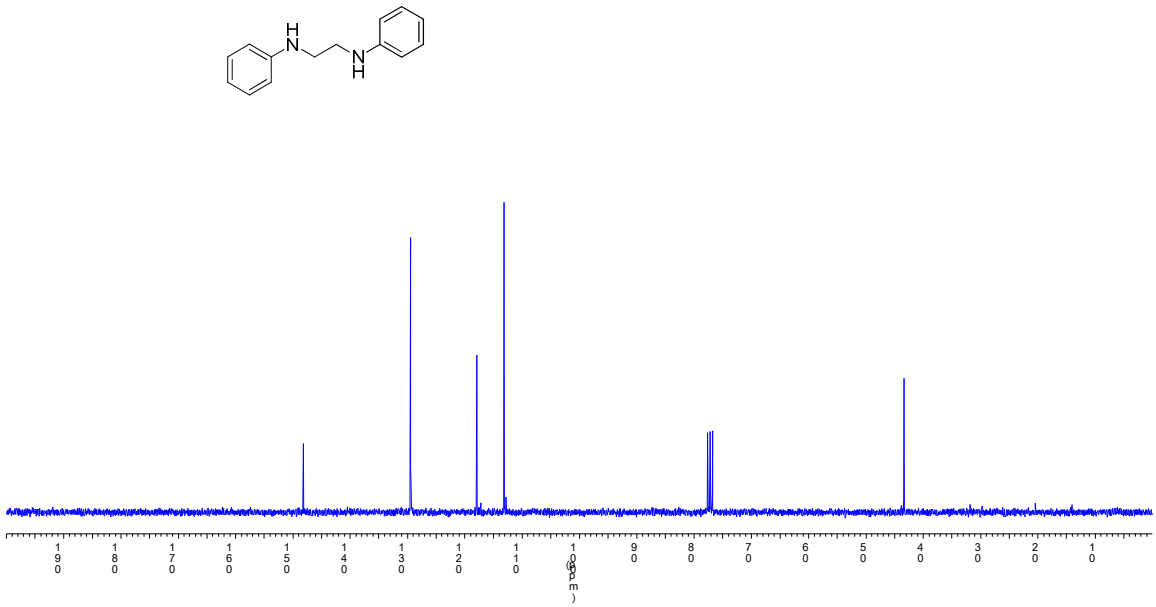
Ethyl 4-(phenylamino)benzoate [64678-66-6] (3hd)



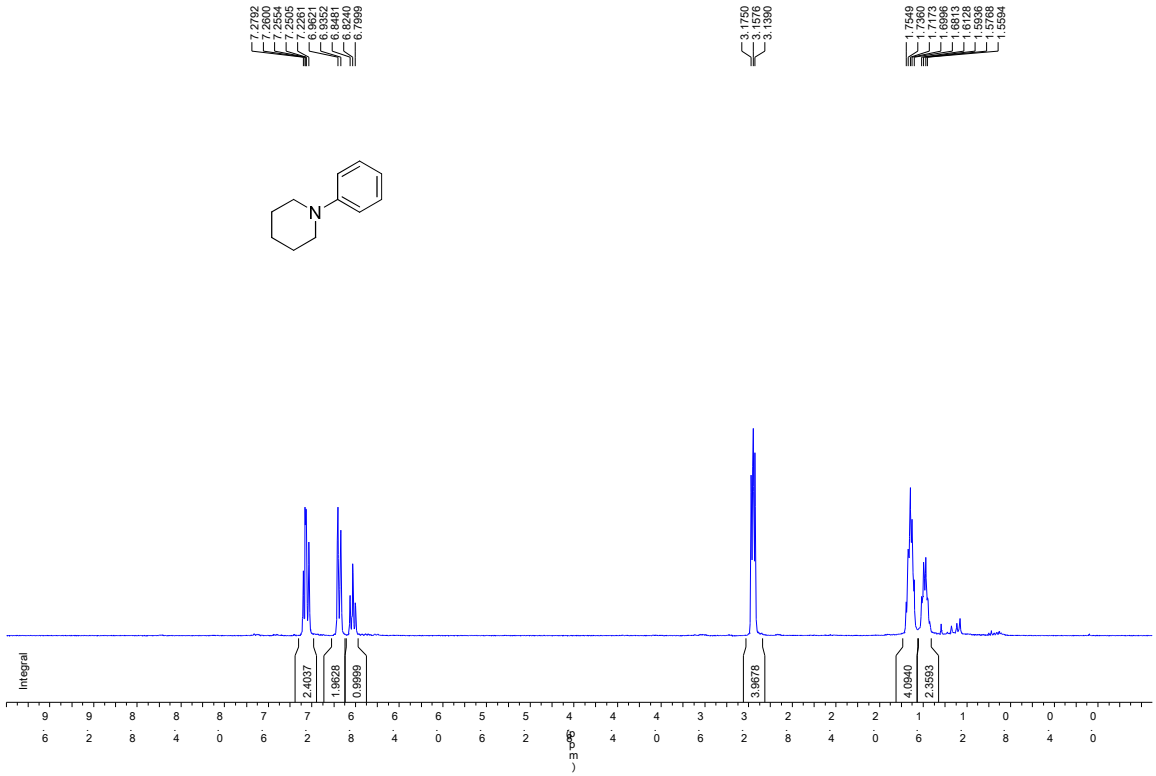


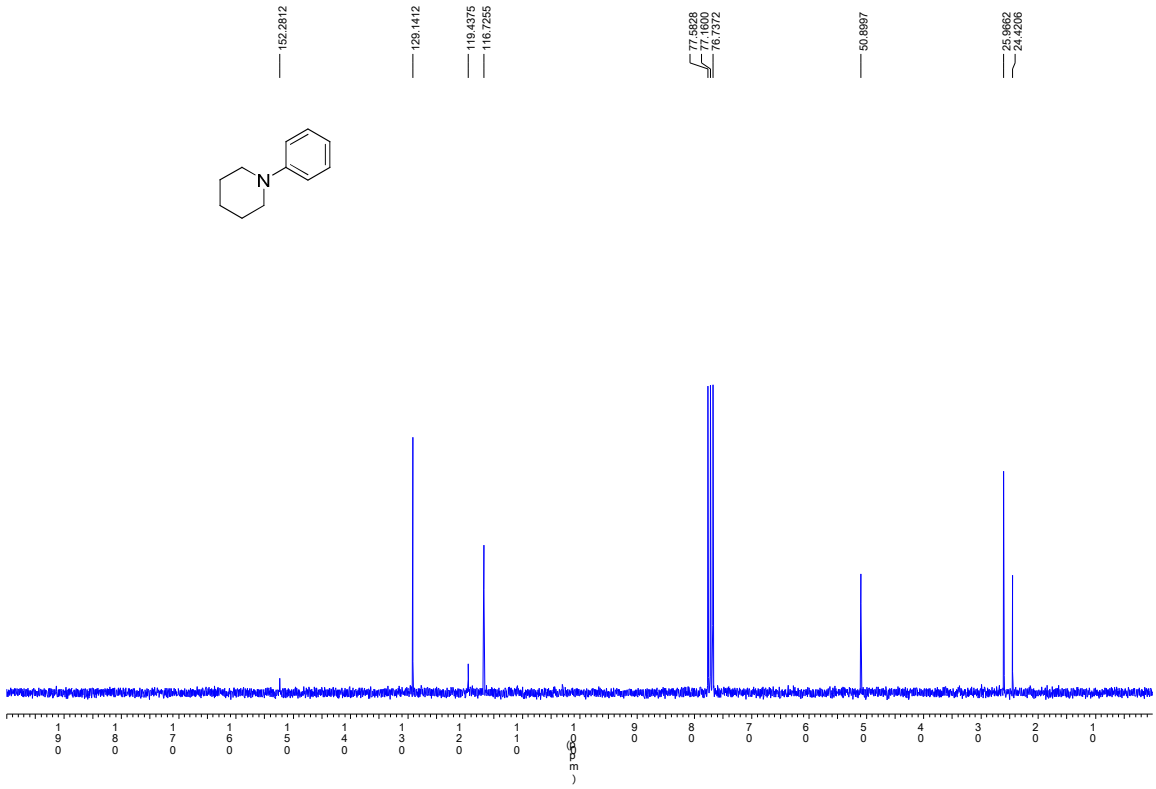
N^1,N^2-diphenylethane-1,2-diamine [150-61-8] (3id)



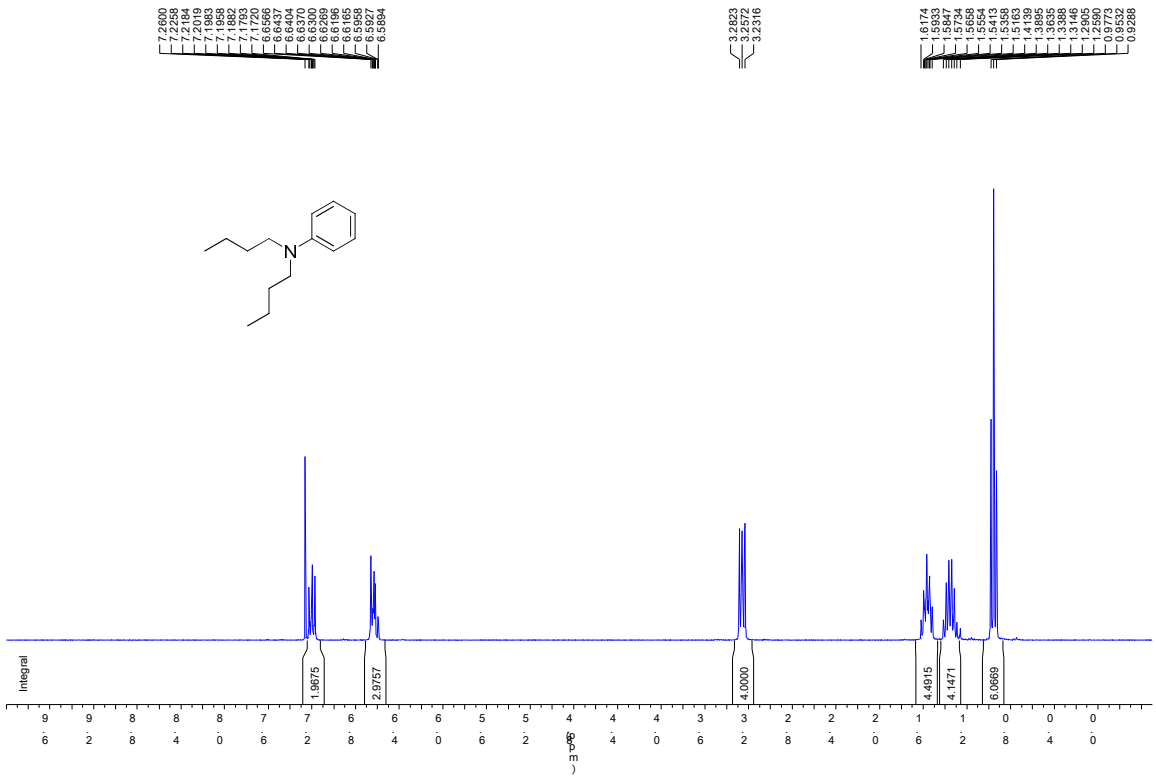


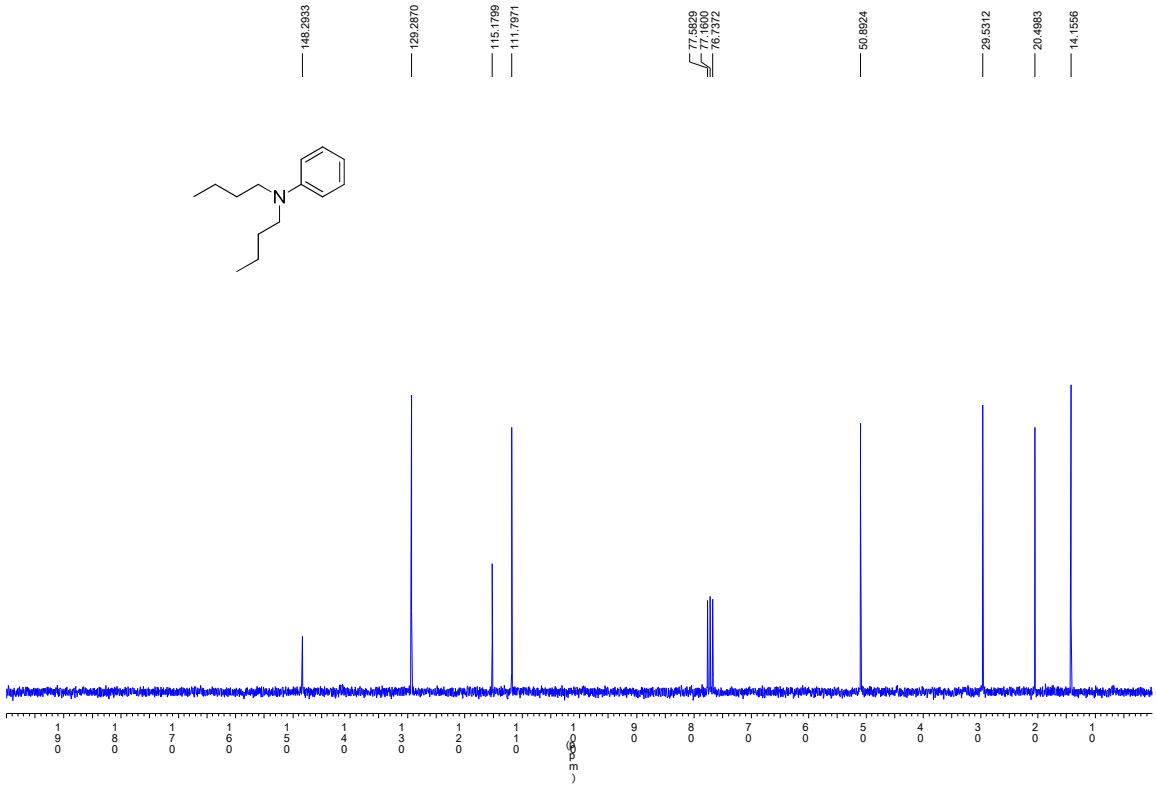
1-phenylpiperidine [4096-20-2] (3fd)



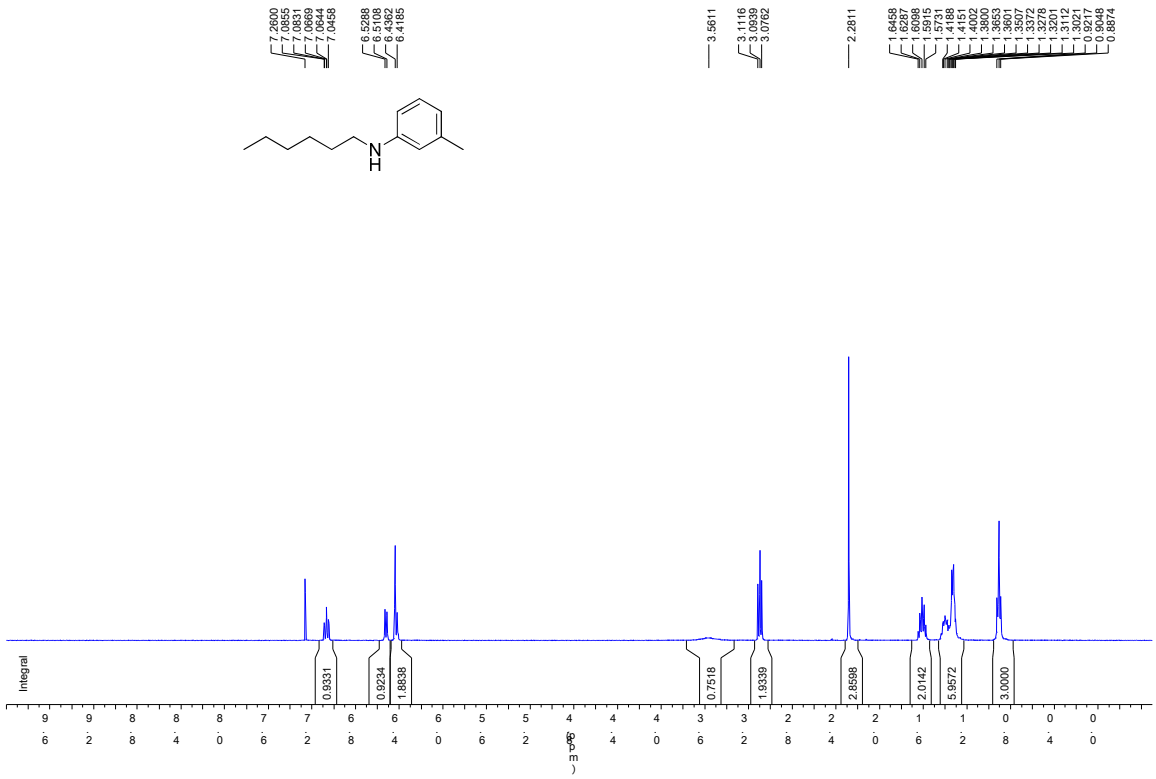


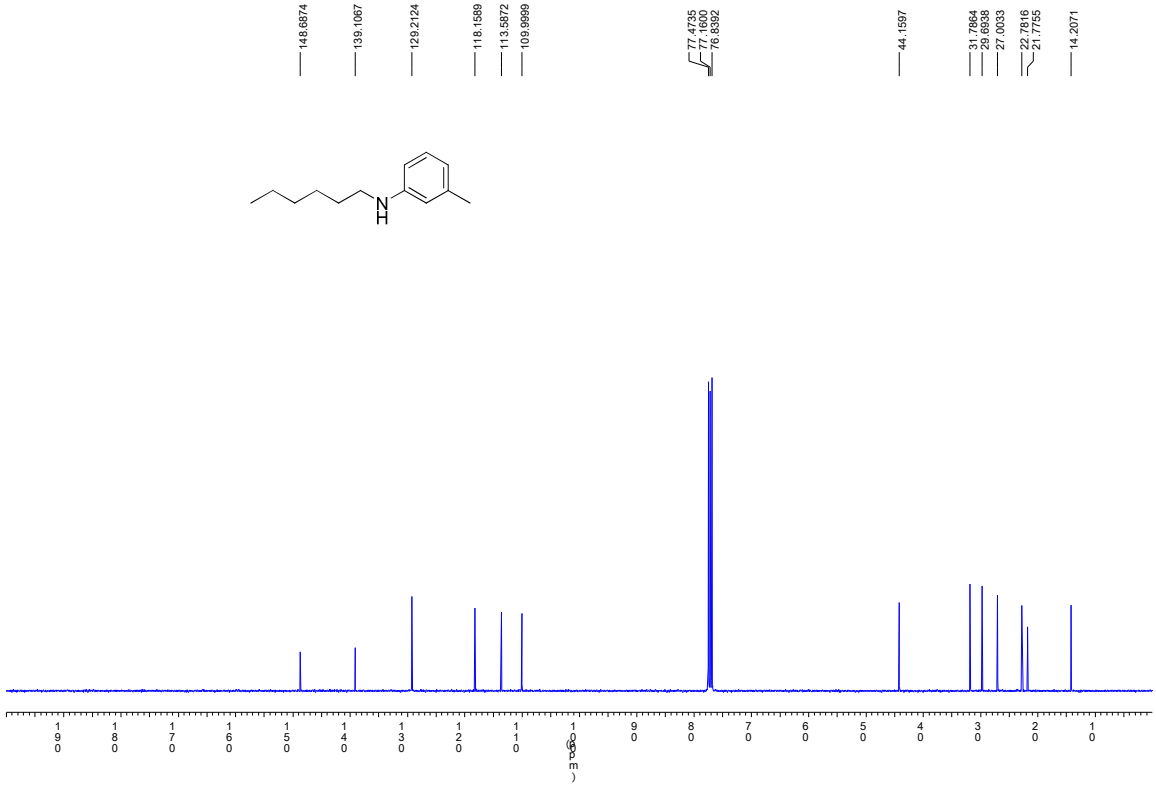
N,*N*-dibutylaniline [613-29-6] (3gd)



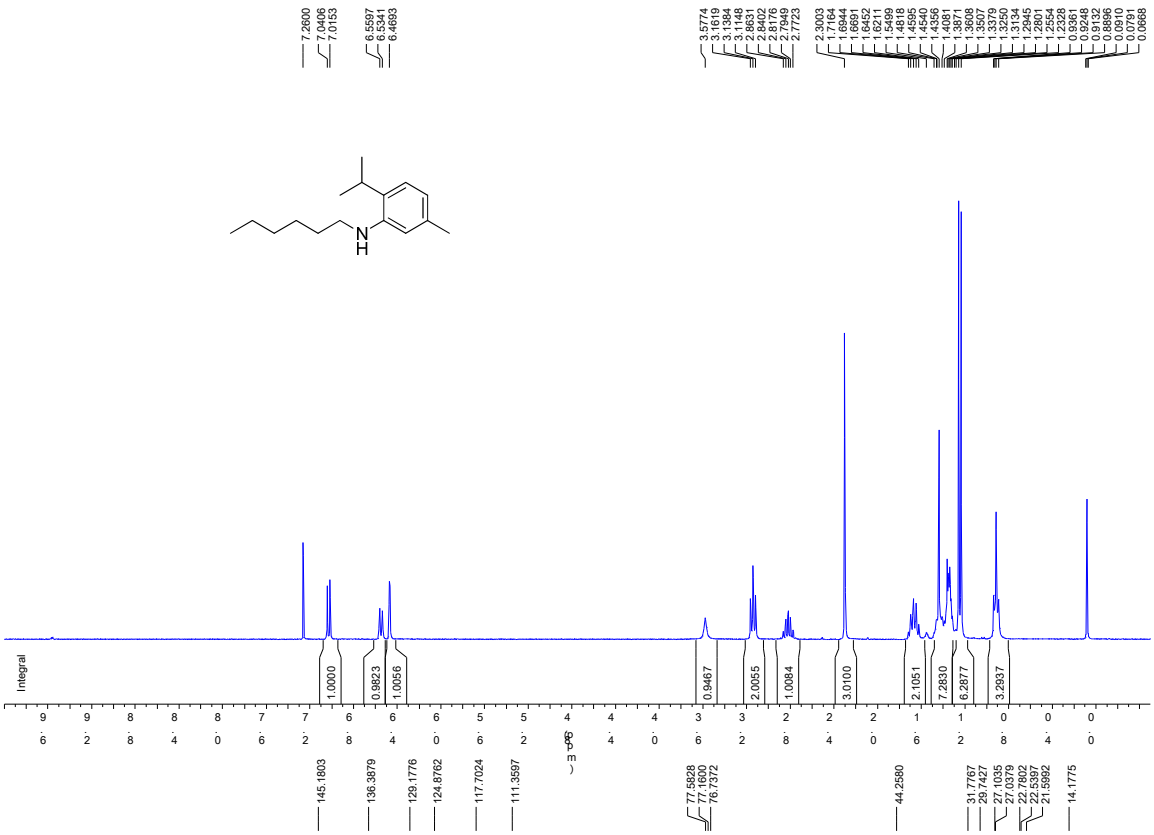


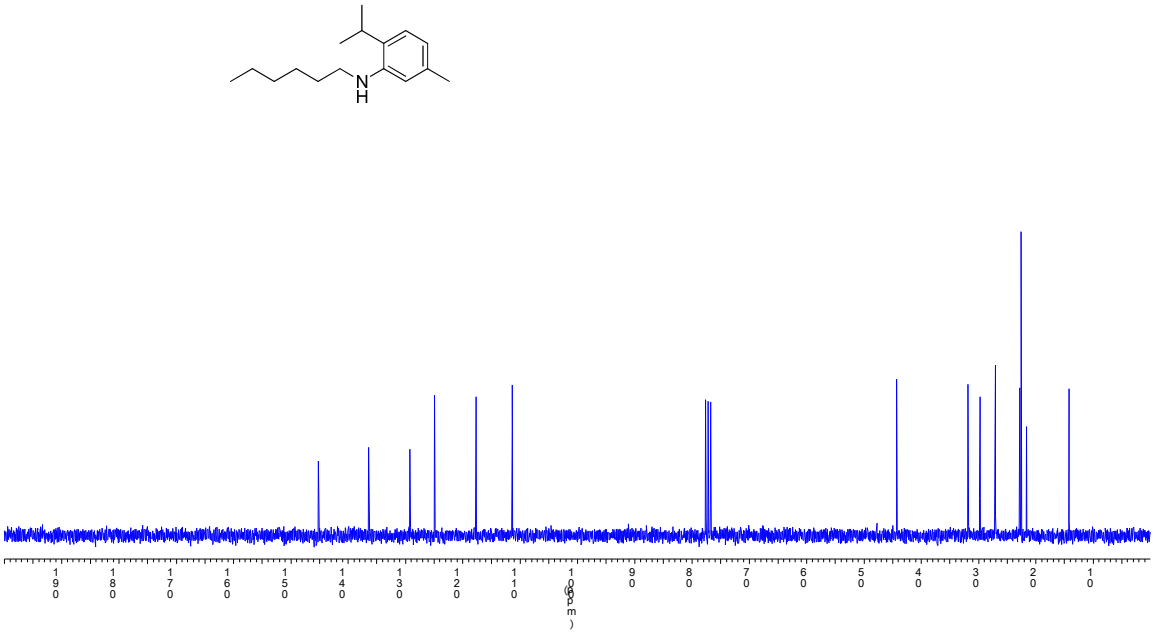
N-hexyl-3-methylaniline [145567-64-2] (3af)



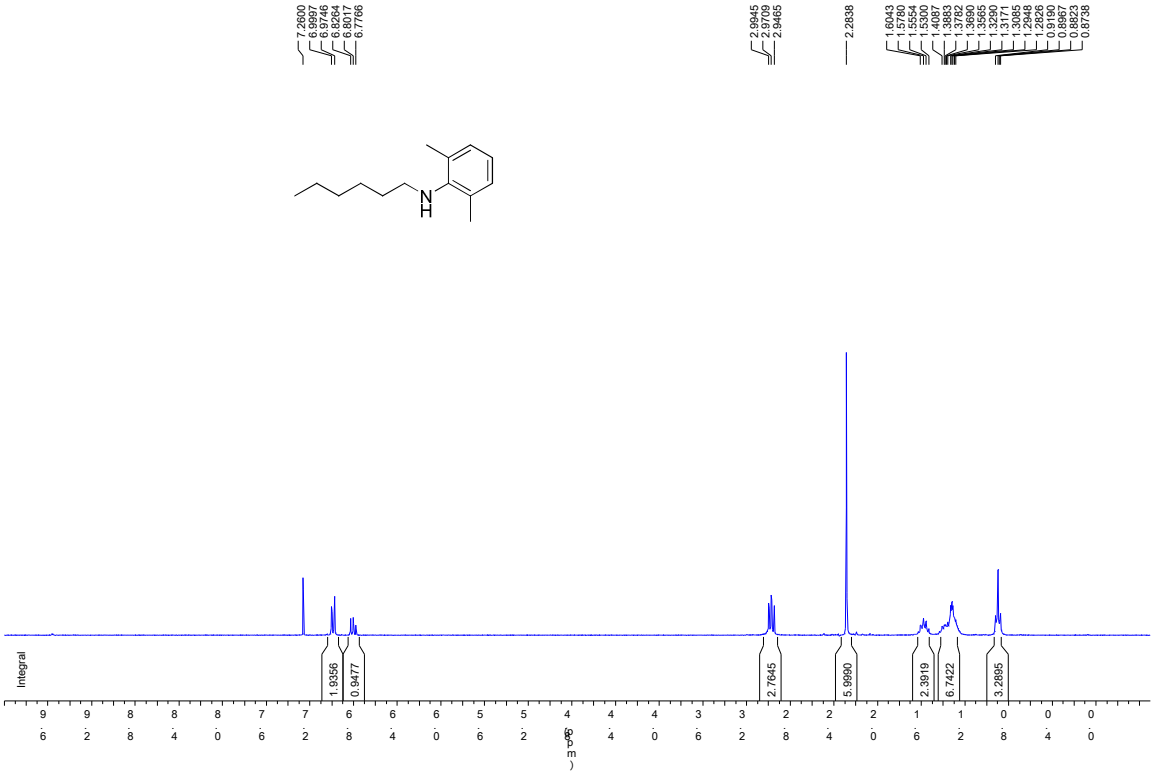


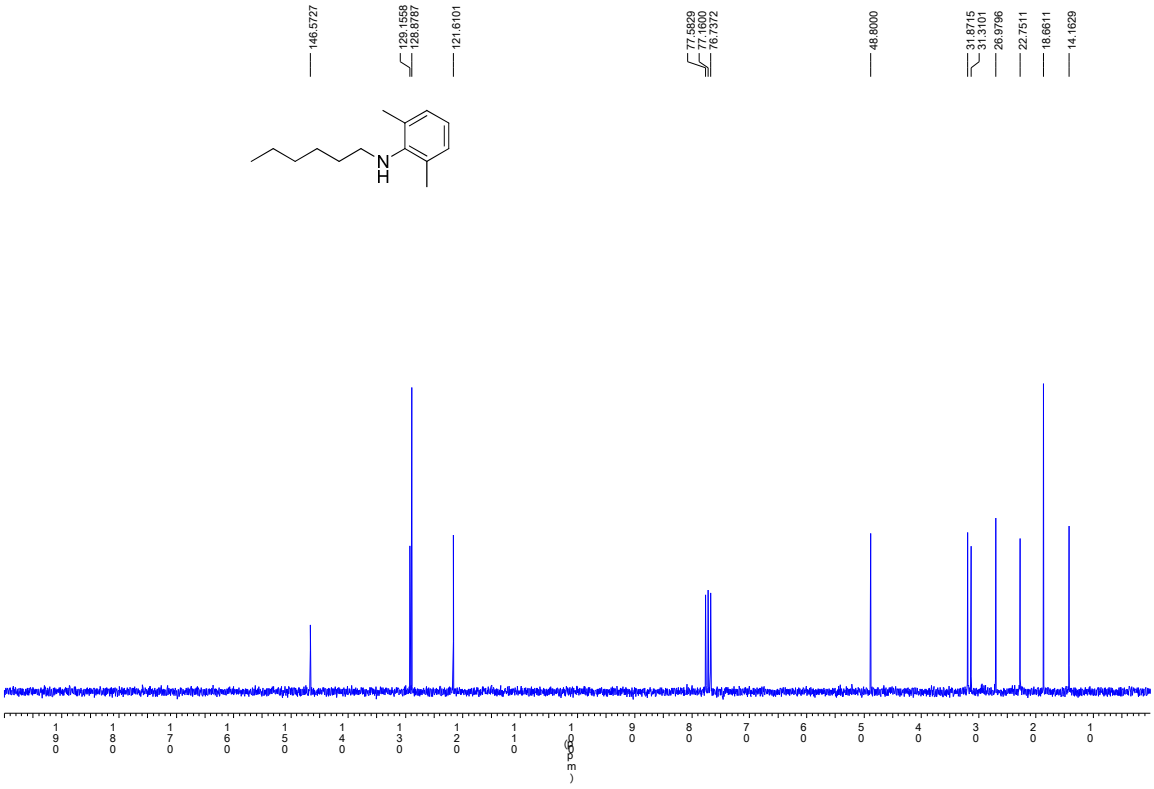
N-hexyl-2-isopropyl-5-methylaniline [No CAS Number] (3ag)



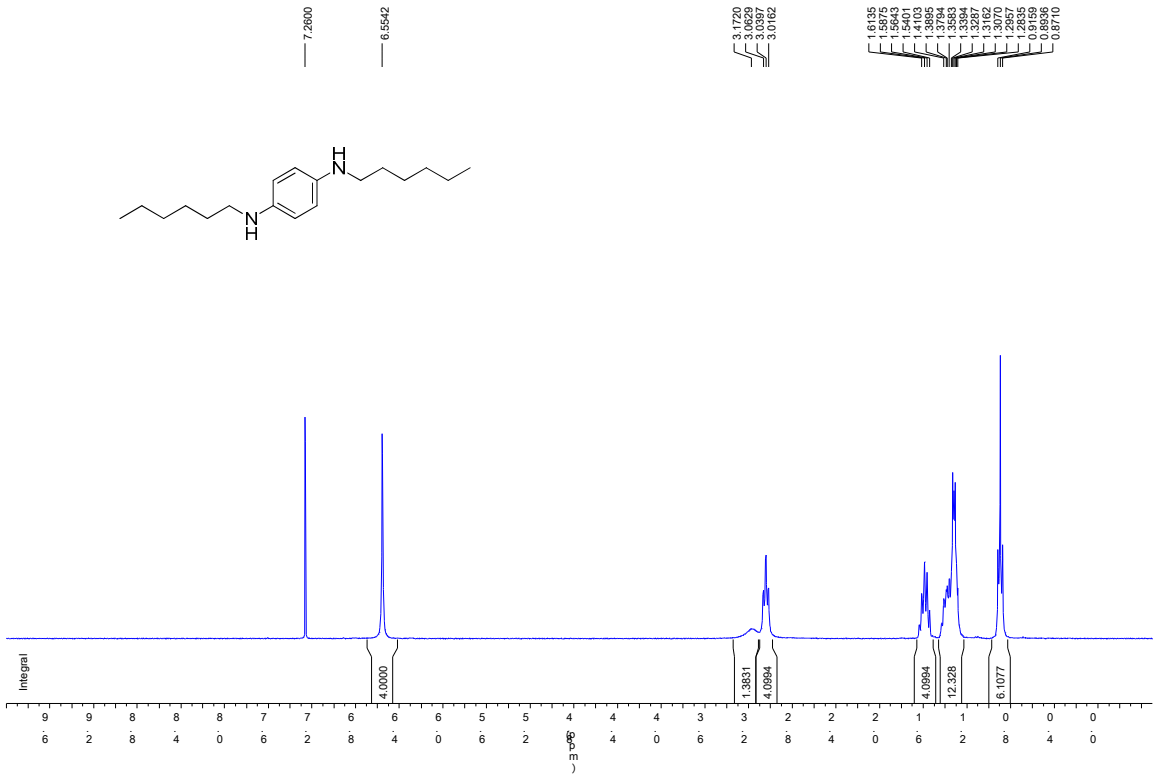


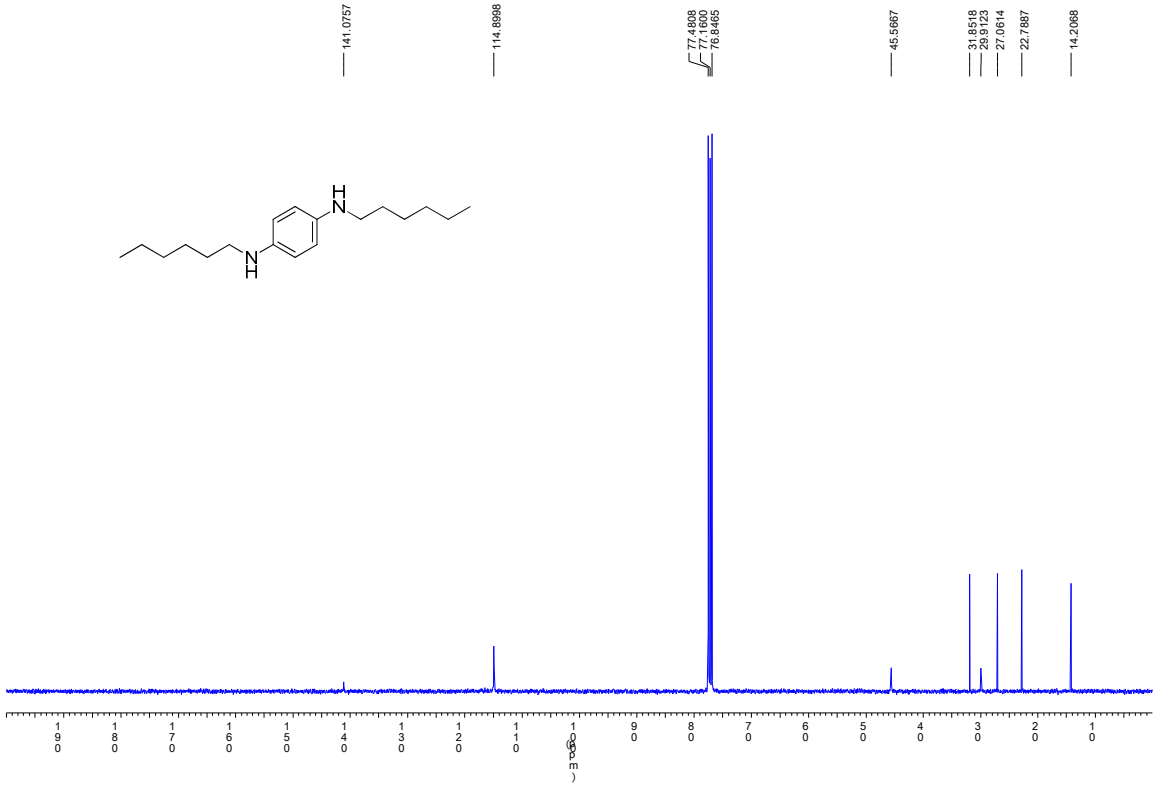
N-hexyl-2,6-dimethylaniline [213697-52-0] (3ah)



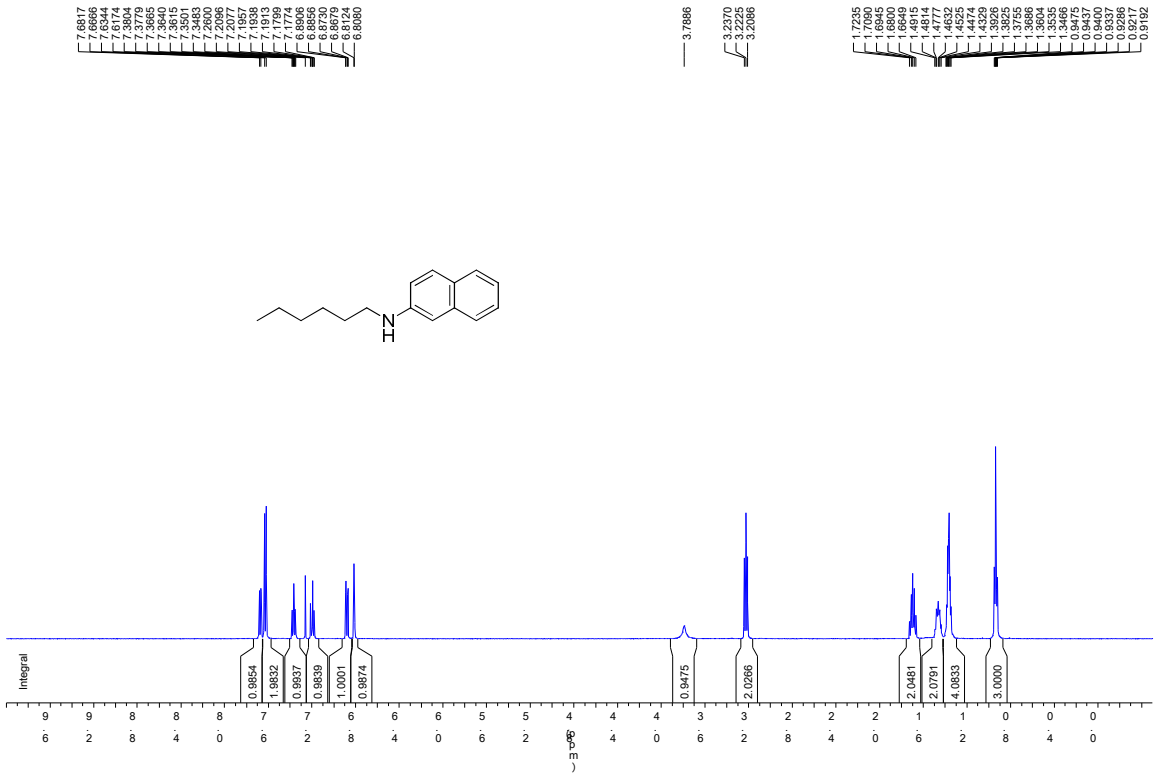


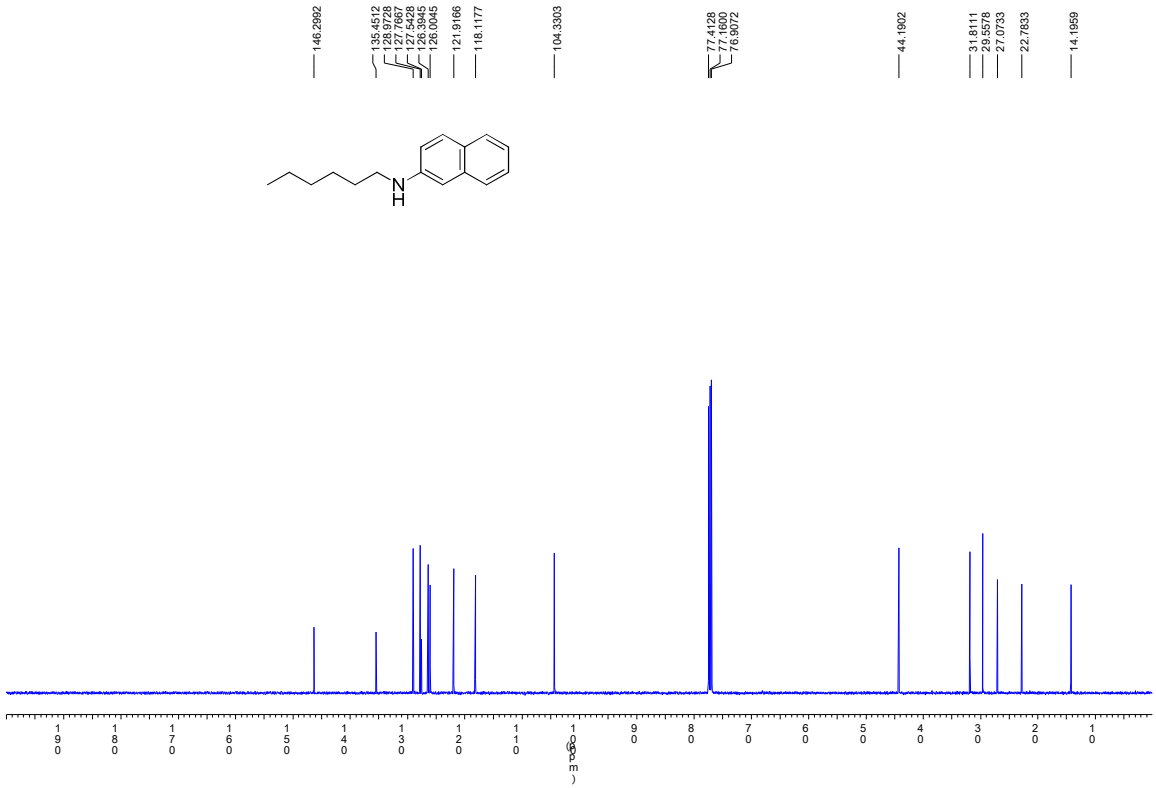
N^1,N^4-dihexylbenzene-1,4-diamine [51833-32-0] (3ai)



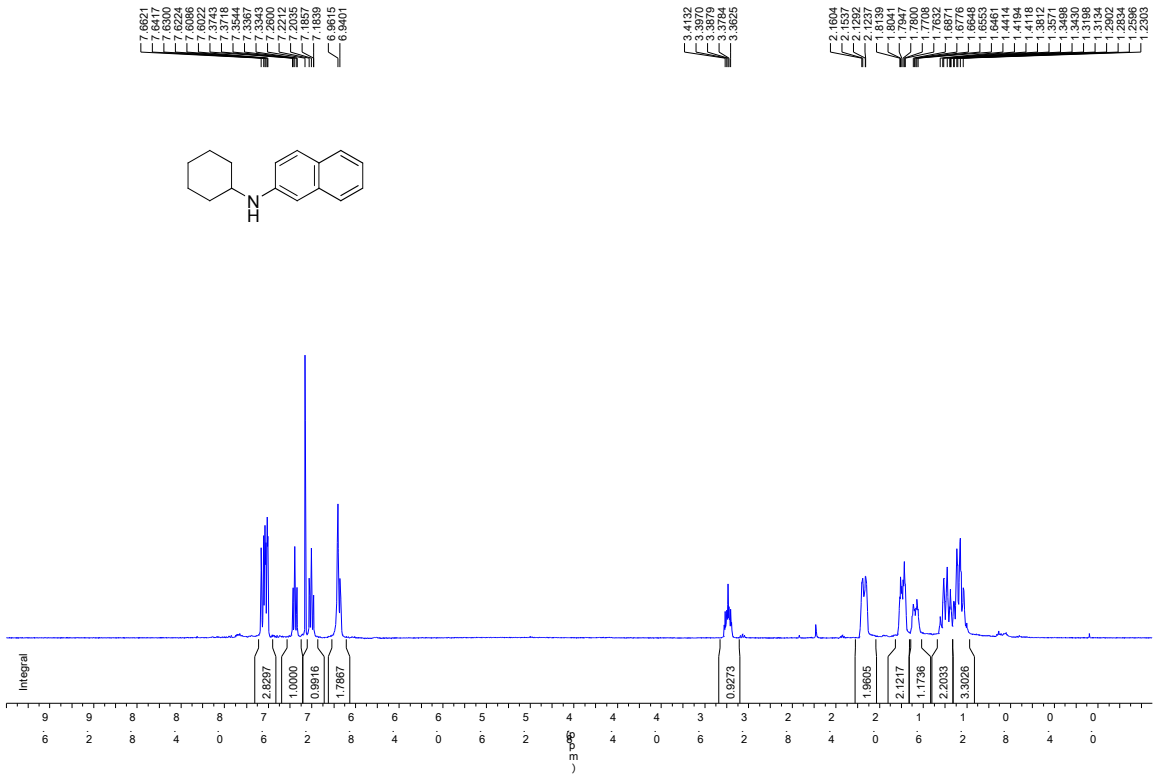


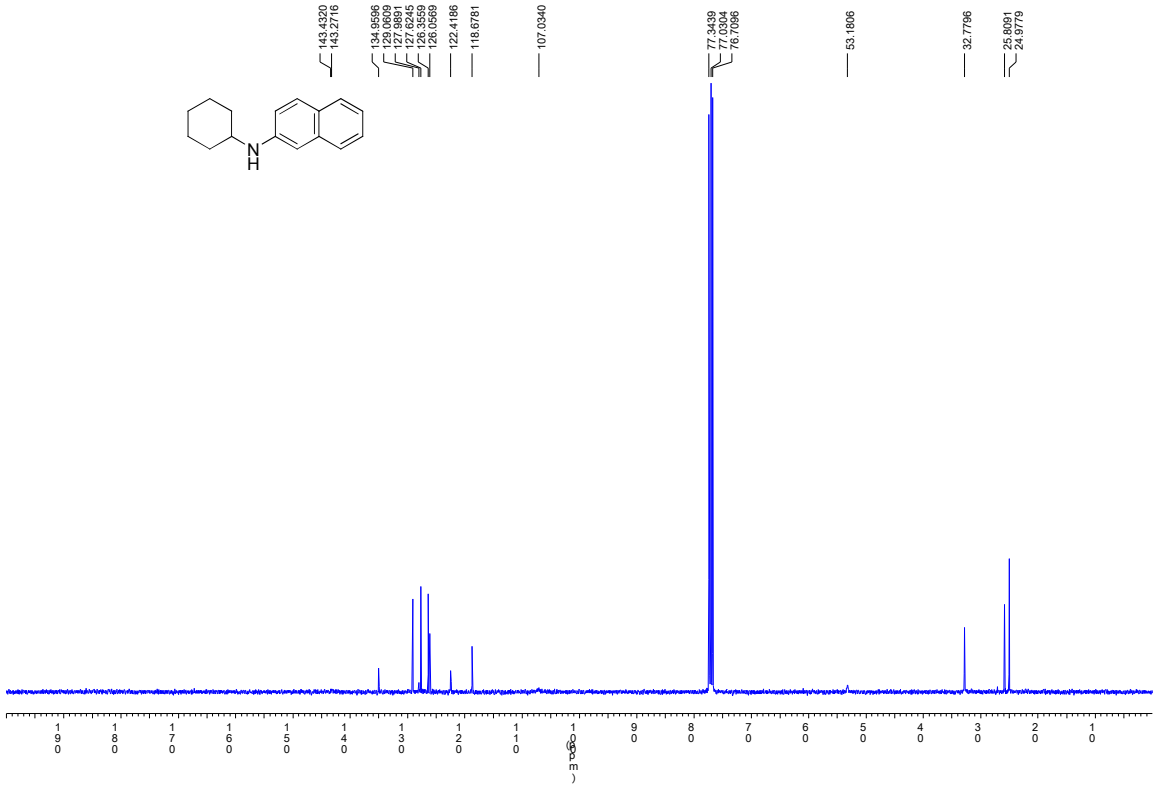
N-hexylnaphthalen-2-amine [58533-06-5] (3ae)



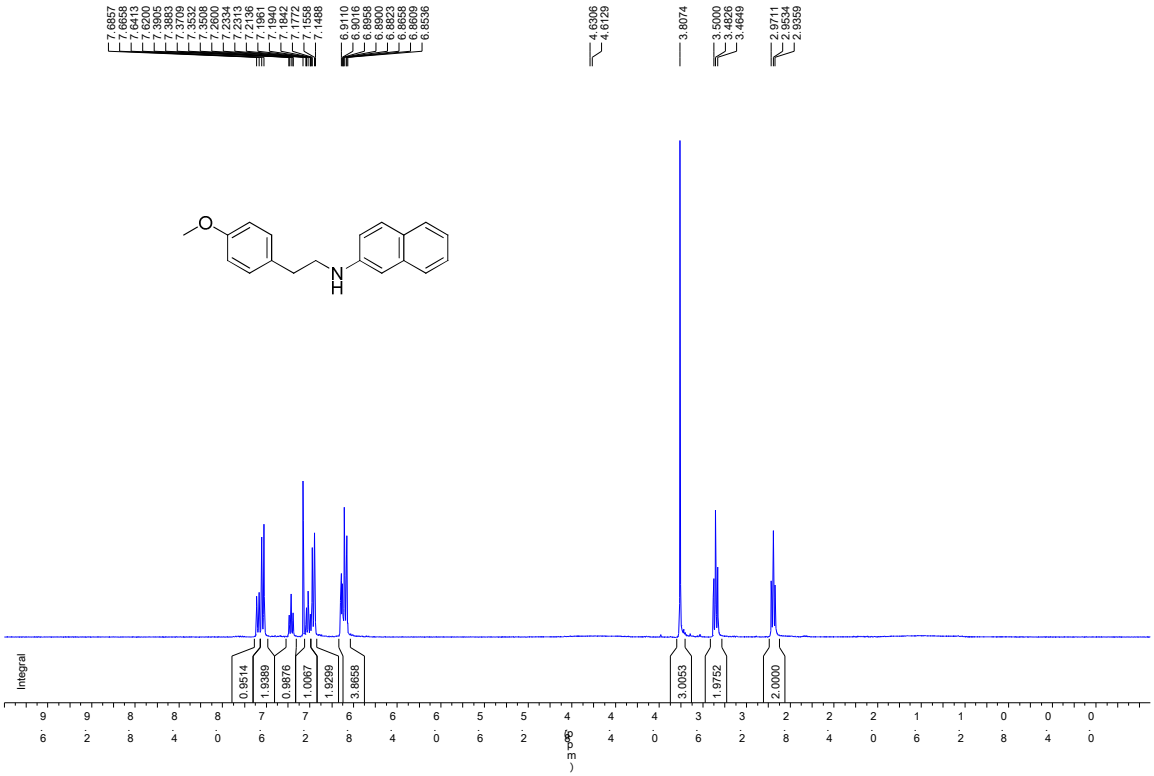


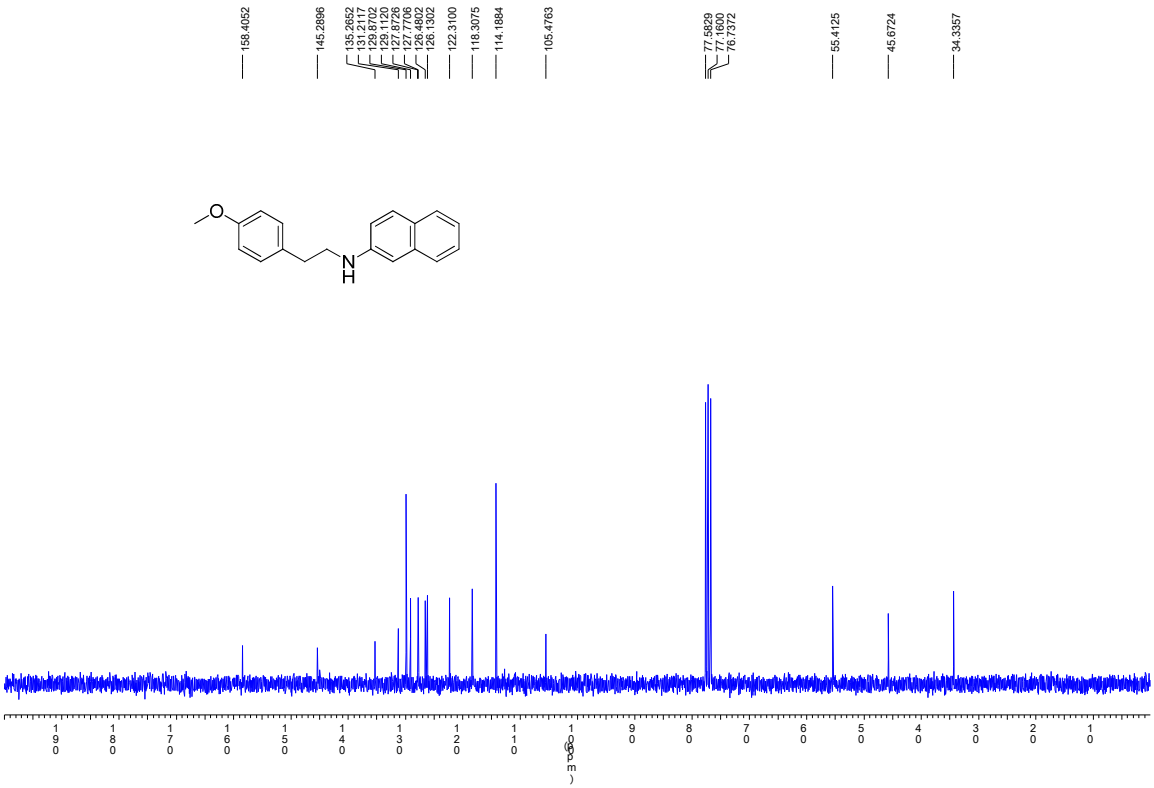
N-cyclohexylnaphthalen-2-amine [23761-52-6] (3be)



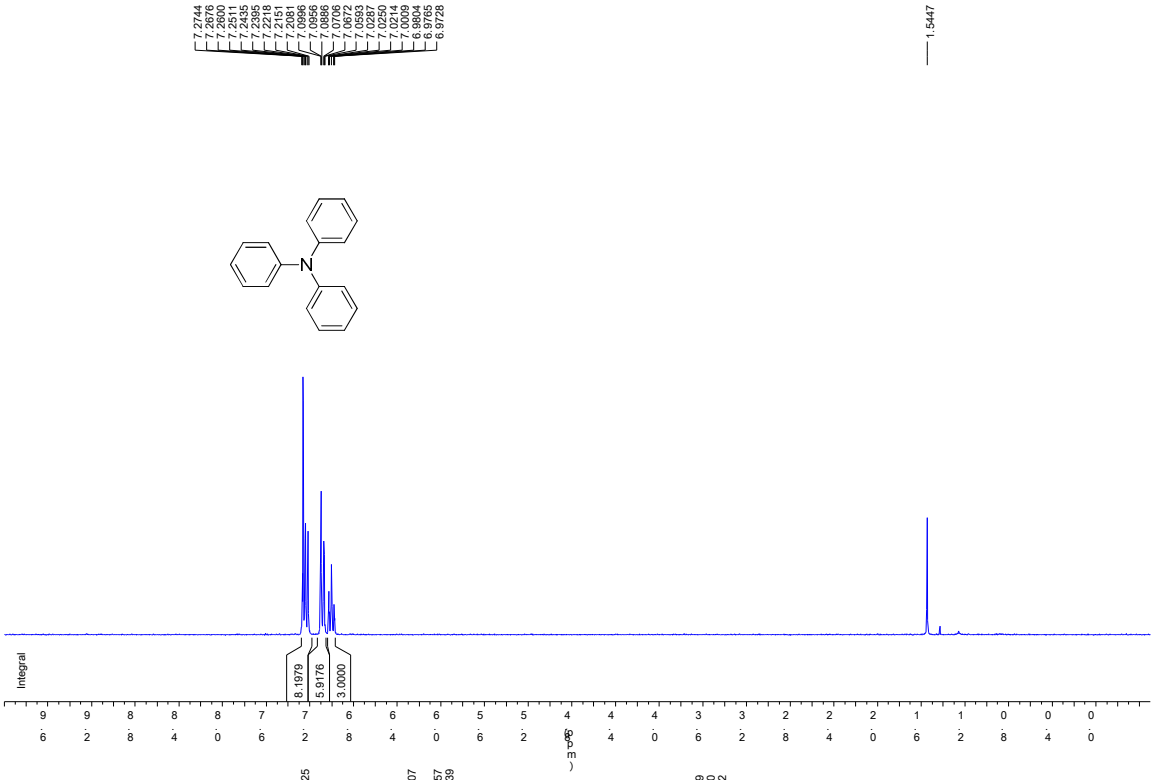


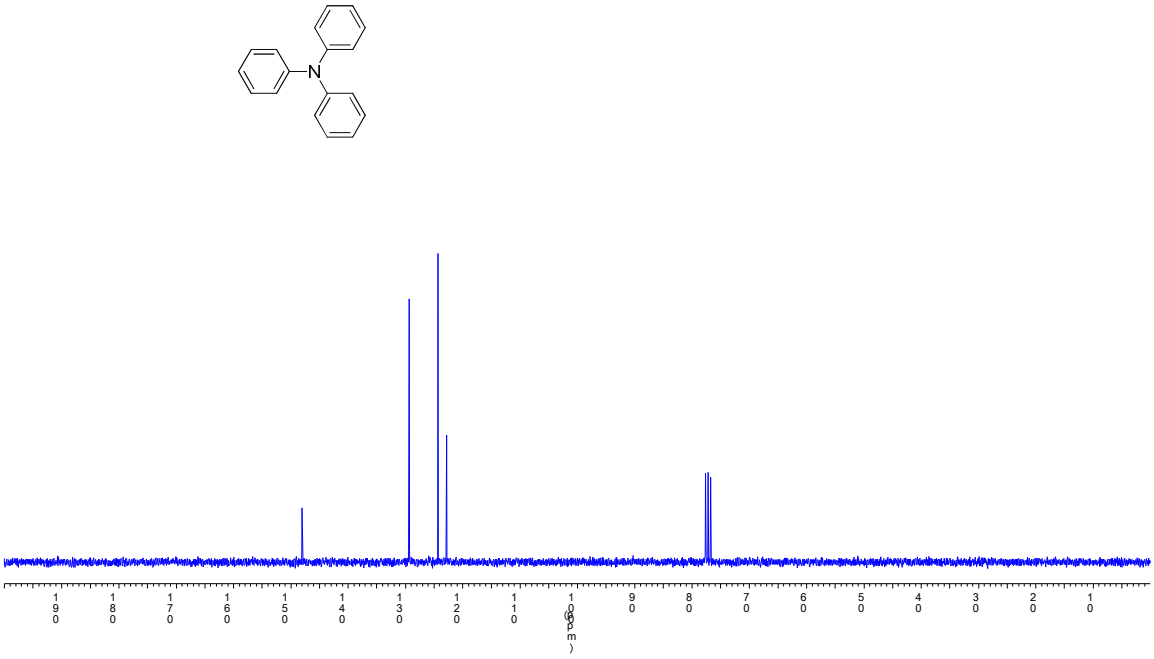
N-(4-methoxyphenethyl)naphthalen-2-amine [No CAS Number] (3je)



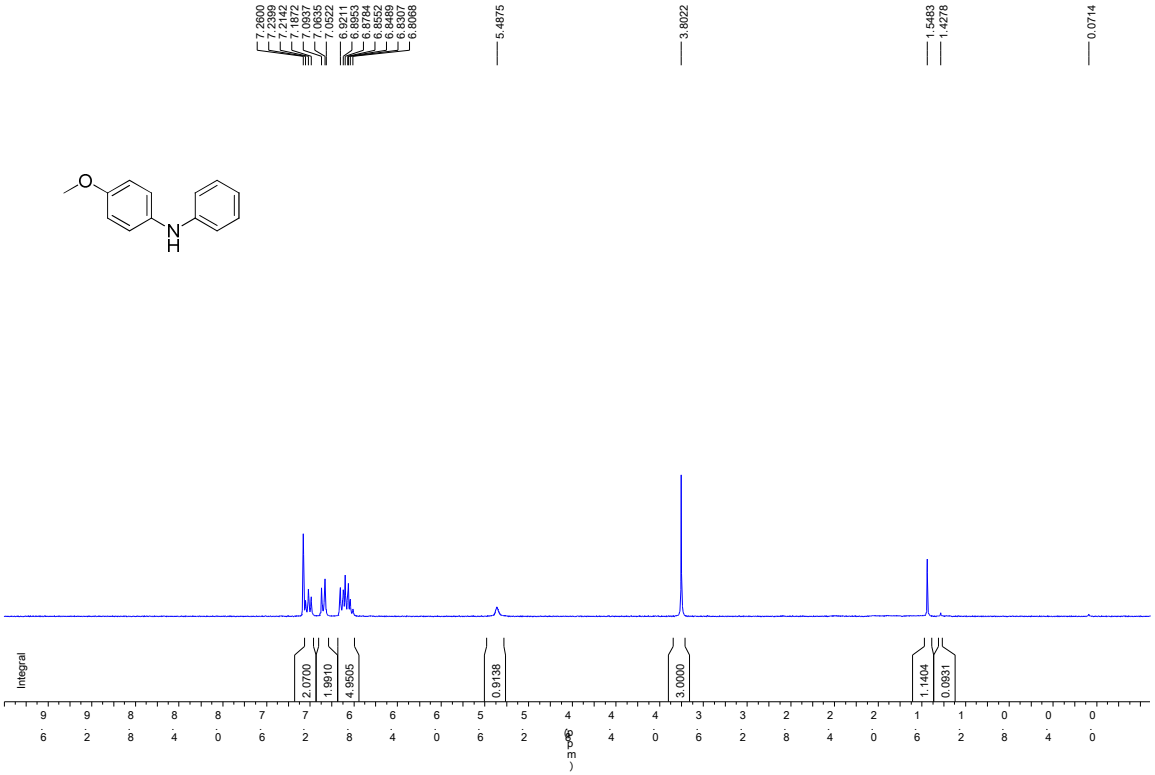


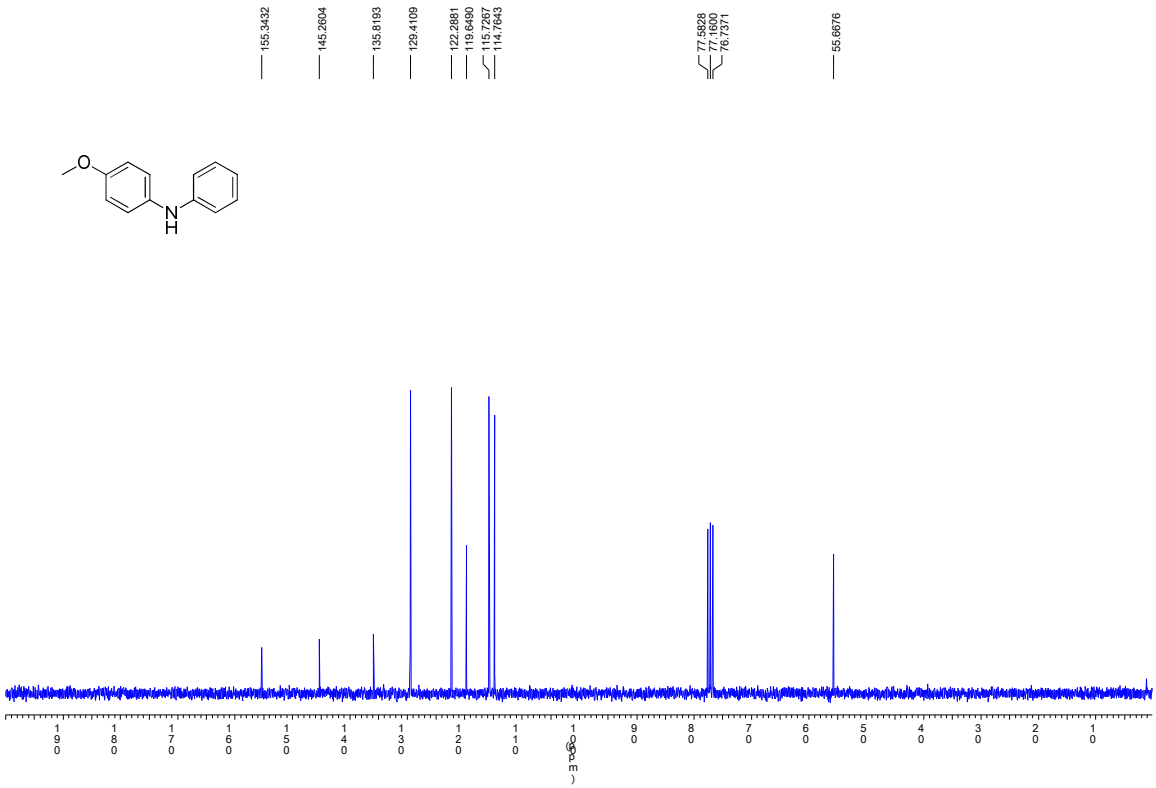
Triphenylamine [603-34-9] (6dd)



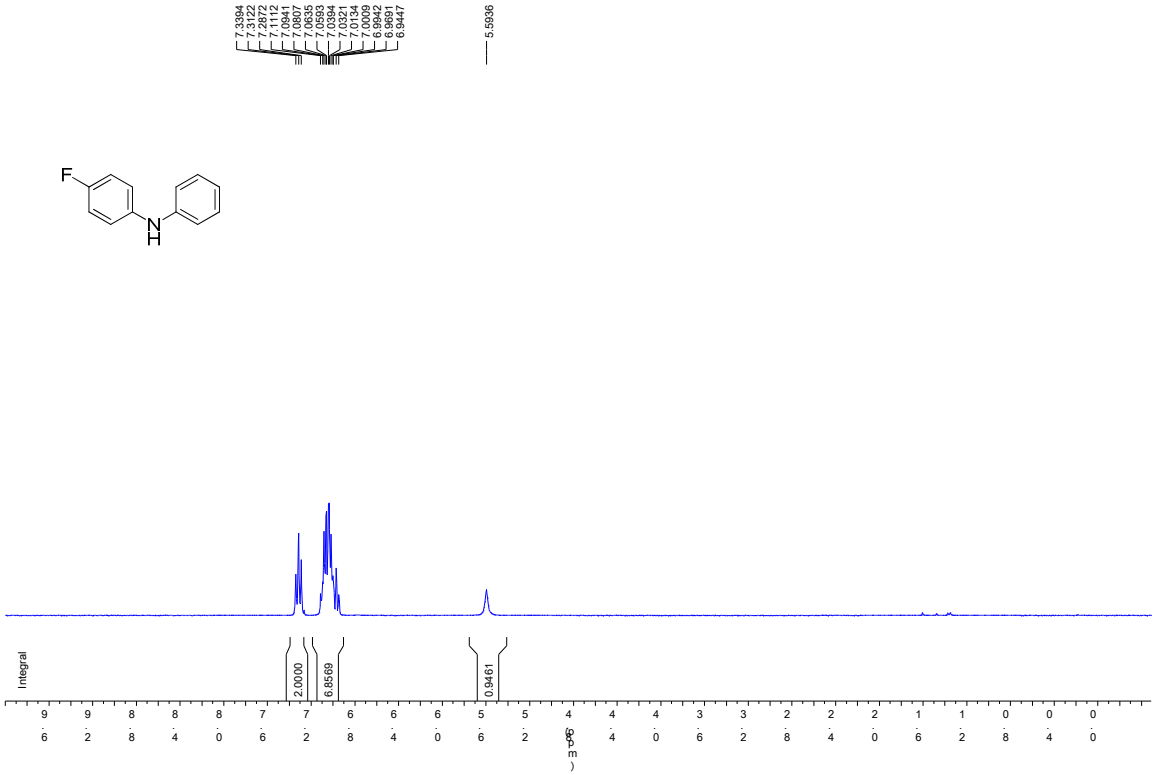


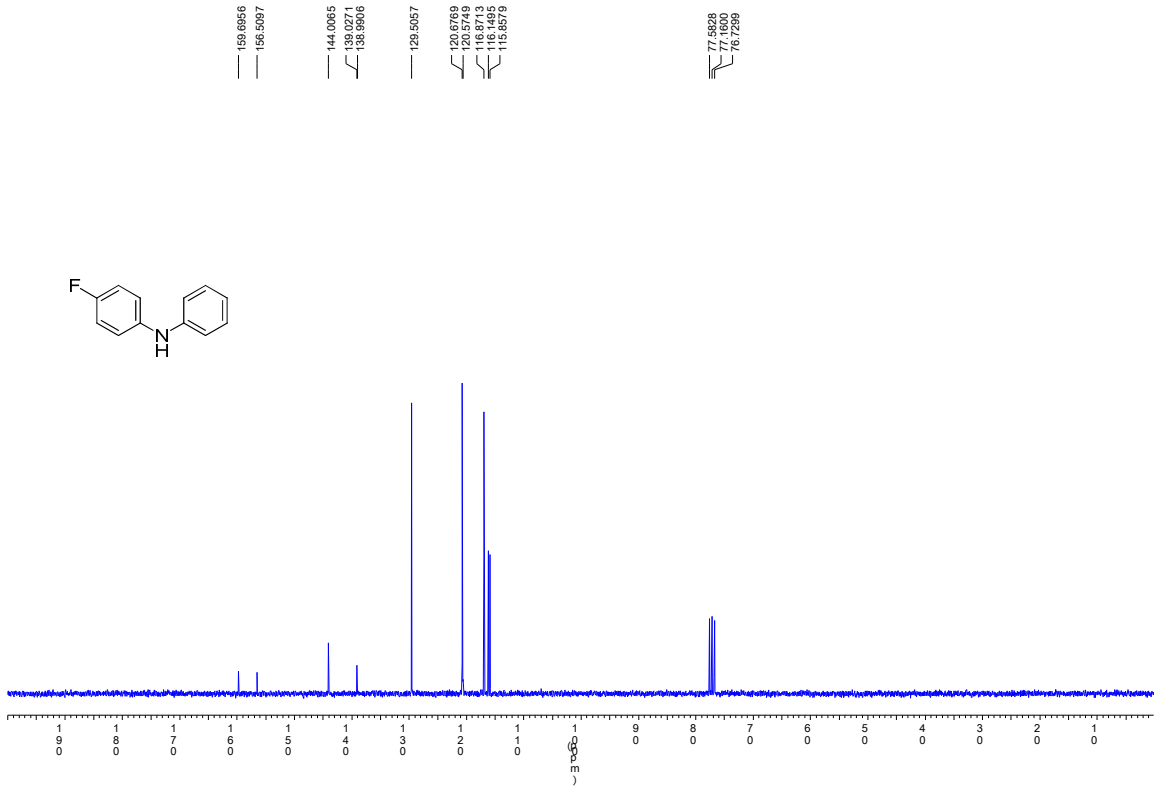
4-methoxy-*N*-phenylaniline [1208-86-2] (3kd)



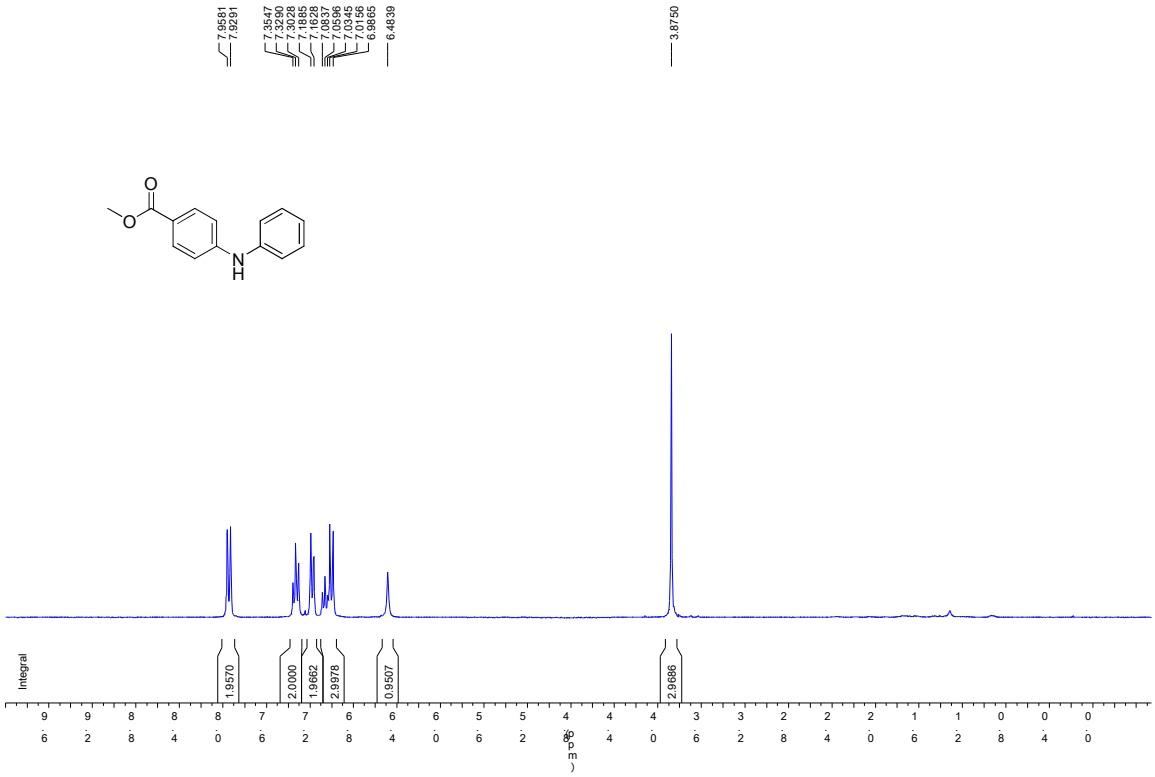


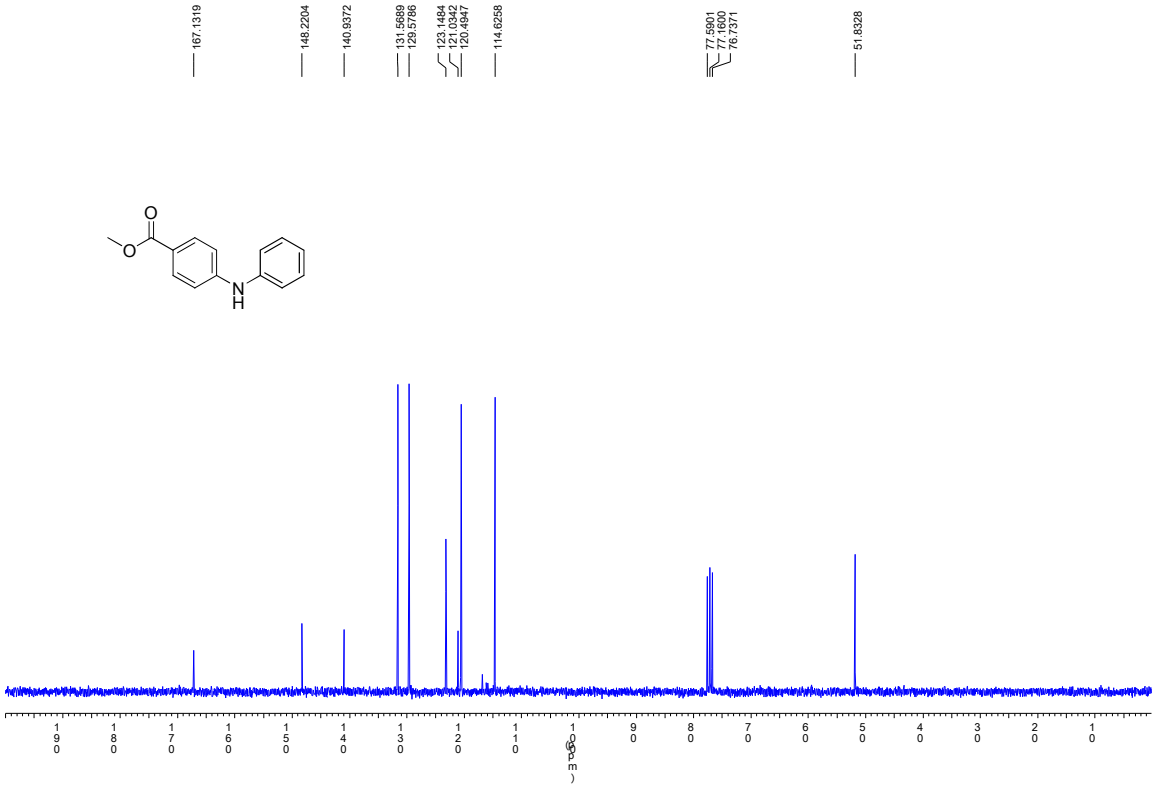
4-Fluoro-*N*-phenylaniline [330-83-6] (3ld)



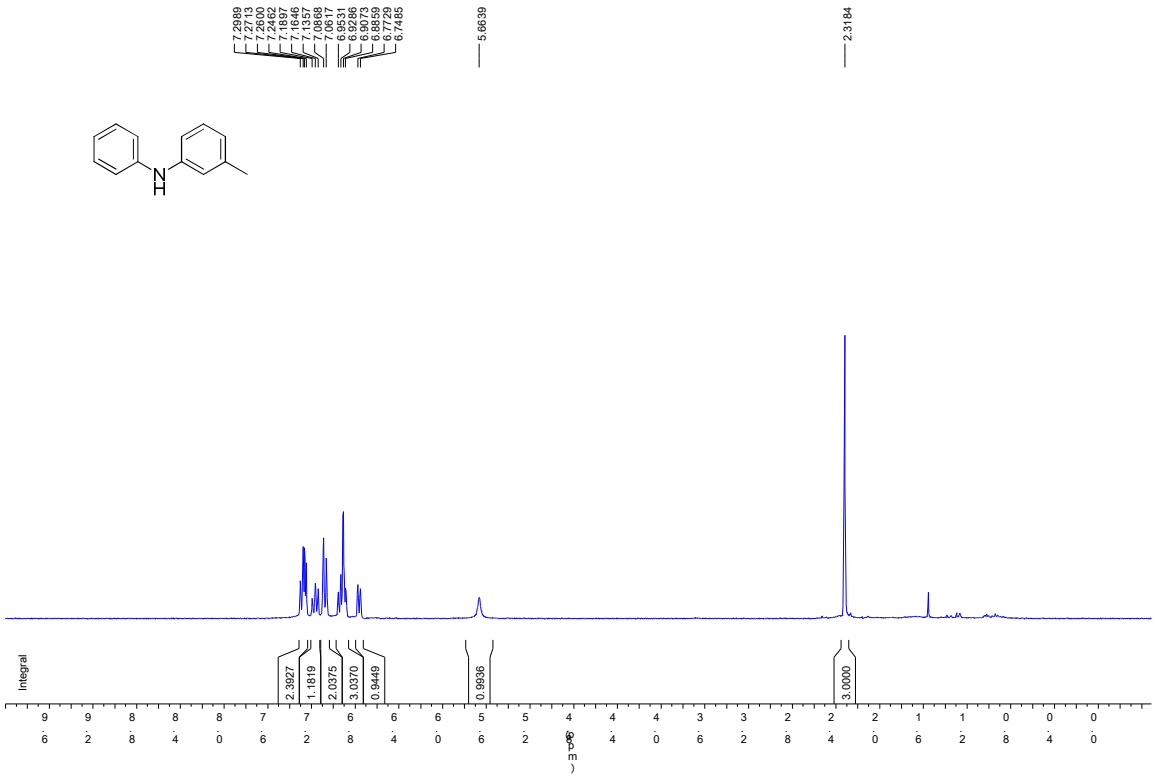


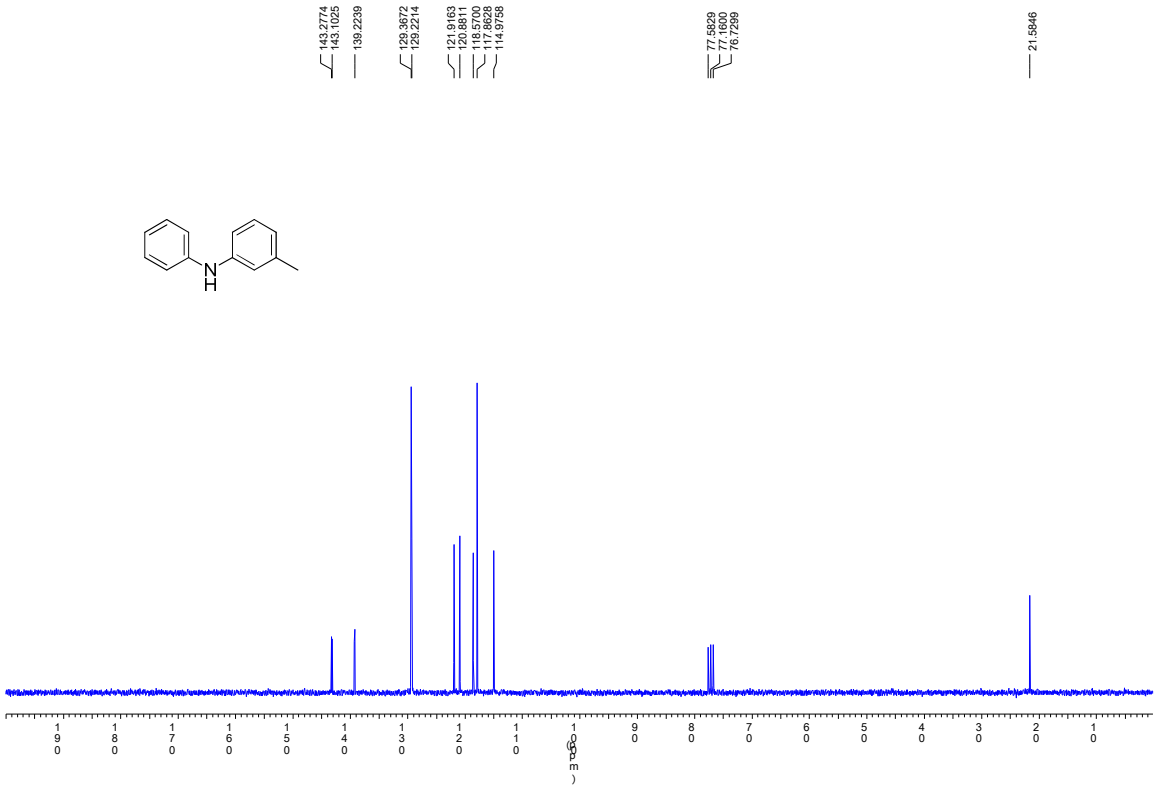
Methyl 4-(phenylamino)benzoate [4058-18-8] (3md)



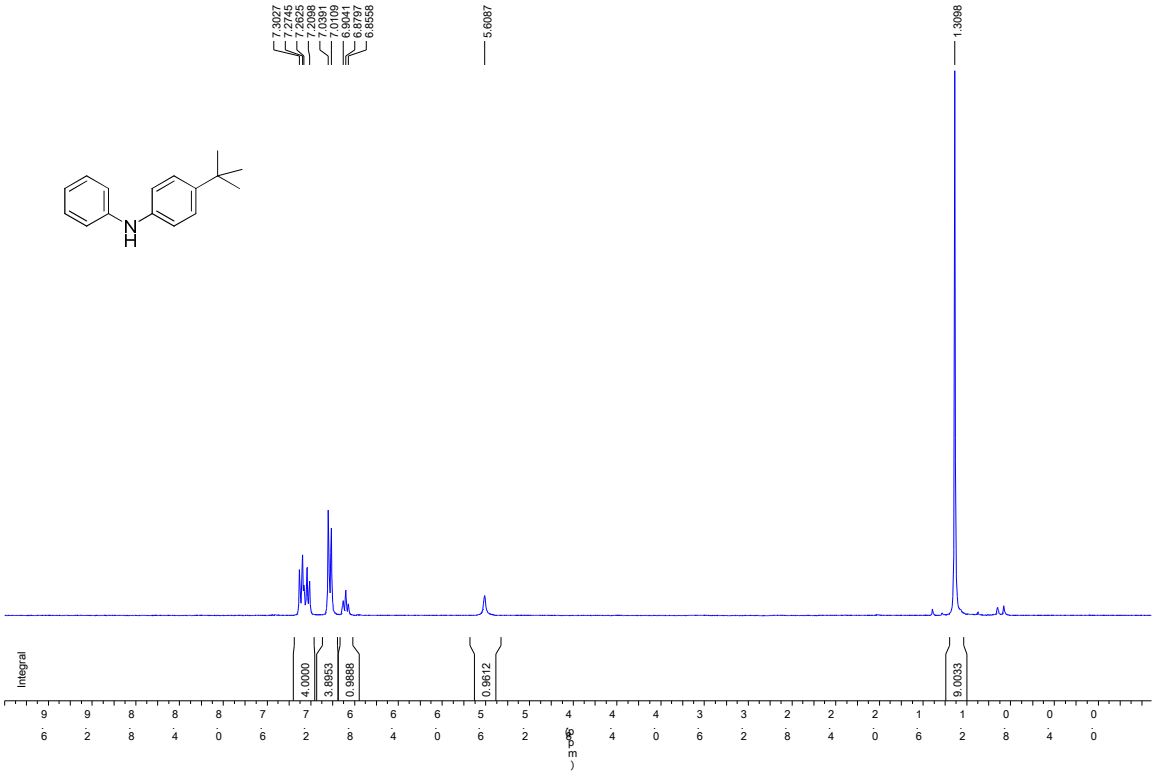


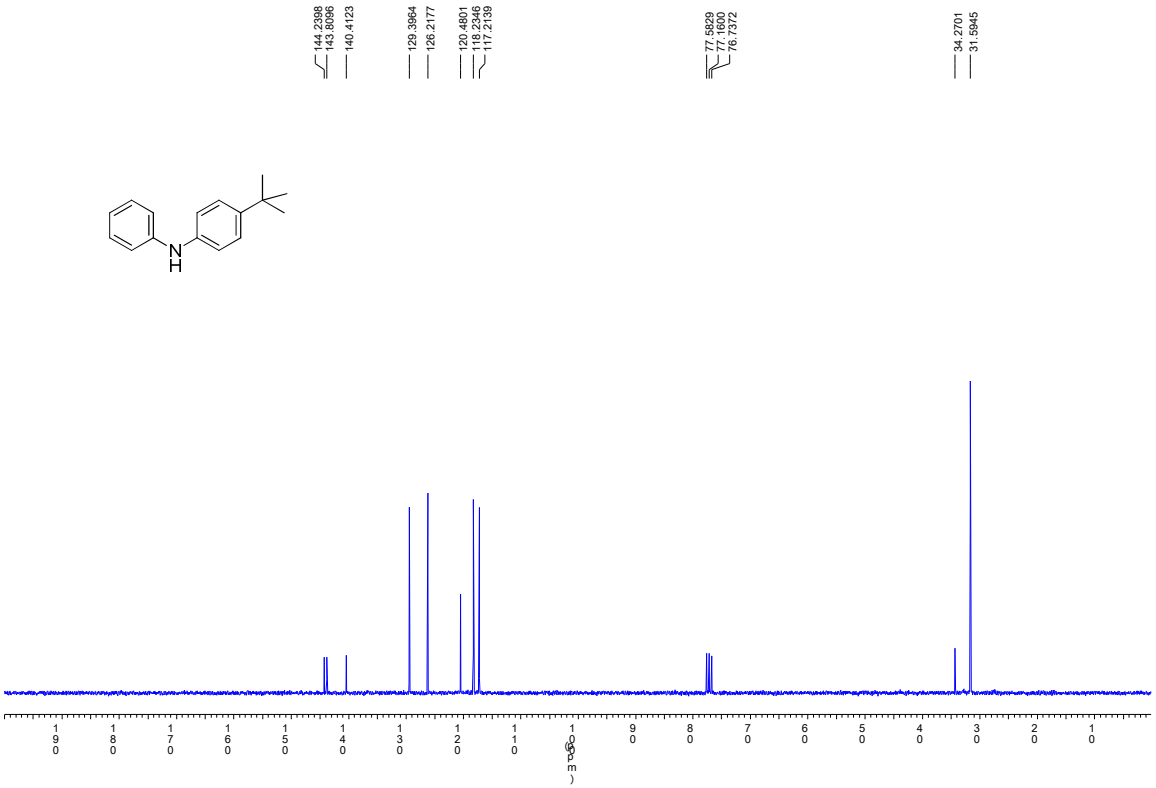
3-methyl-*N*-phenylaniline [1205-64-7] (3df)





4-tertbutyl-*N*-phénylaniline [4496-49-5] (3dk)





References

[1] Sutter, M.; Sotto, N.; Raoul, Y.; Métay, E.; Lemaire, *Green Chem.*, **2013**, *15*, 347-352.

[2] N. Shankaraiah, N. Markandeya, V. Srinivasulu, K. Sreekanth, C. S. Reddy, L. S. Santos, A. Kamal, *J. Org. Chem.*, **2011**, *76*, 7017-7026.

[3] C.-T. Yang, Y. Fu, Y.-B. Huang, J. Yi, Q.-X. Guo, L. Liu, *Angew. Chem., Int. Ed.*, **2009**, *48*, 7398-7401.

[4] Y. Xie, S. Liu, Y. Liu, Y. Wen, G.-J. Deng, *Org. Lett.*, **2012**, *14*, 1692-1695.

[5] D. Hollmann, S. Bähn, A. Tillack, M. Beller, *Angew. Chem., Int. Ed.*, **2007**, *46*, 8291-8294.

[6] C. A. Caputo, J. T. Price, M. C. Jennings, R. McDonald, N. D. Jones, *Dalton Trans.*, **2008**, 3461-3469.

[7] S. A. Girard, X. Hu, T. Knauber, F. Zhou, M.-O. Simon, G.-J. Deng, C.-J. Li, *Org. Lett.,* **2012**, *14*, 5606-5609.

[8] C. He, C. Chen, J. Cheng, C. Liu, W. Liu, Q. Li, A. Lei, *Angew. Chem., Int. Ed.*, **2008**, *47*, 6414-6417.

[9] B. Lü, P. Li, C. Fu, L. Xue, Z. Lin, S. Ma, *Adv. Synth. Catal.*, **2011**, *353*, 100-112.

[10] L. Ackermann, J. H. Spatz, C. J. Gschrei, R. Born, A. Althammer, *Angew. Chem., Int. Ed.*, **2006**, *45*, 7627-7630.

[11] L. T. Higham, K. Konno, J. L. Scott, C. R. Strauss, T. Yamaguchi, *Green Chem.*, **2007**, *9*, 80-84.

[12] L. Ackermann, R. Sandmann, W. Song, *Org. Lett.*, **2011**, *13*, 1784-1786.

[13] X. Li, D. Yang, Y. Jiang, H. Fu, *Green Chem.*, **2010**, *12*, 1097-1105.

[15] Y. Hirai, Y. Uozumi, *Chem. Commun.*, **2010**, *46*, 1103-1105.