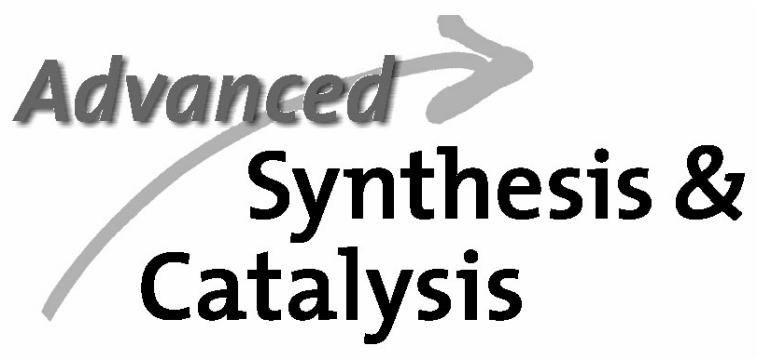



Supporting Information

Supporting Information for

# A New Hybrid Phosphine Ligand for Palladium-Catalyzed Amination of Aryl Halides

Ken Suzuki,* Yoji Hori and Tohru Kobayashi

## General Information:

All reactions were carried out under nitrogen atmosphere. All solvents and reagents were used without further purification from commercial sources. $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were taken on Varian Mercury Plus3004N (300 MHz) or Bruker DRX-500 (500 MHz) spectrameters. Chemical shifts are reported in parts per million (δ value) relative to tetramethylsilane (δ = 0 ppm for 1H), the middle peaks of the solvent ($CDCl_3$) (δ = 77.00 ppm for $^{13}C$), the middle peaks of the solvent ($CD_2Cl_2$) (δ = 53.73 ppm for $^{13}C$) or phosphoric acid (δ = 0 ppm for $^{31}P$). All high-resolution mass spectra were taken on a Shimadzu LCMS-IT-TOF spectrameter.

## Typical procedure for the Preparation of Phosphine 6:

### 1-Chloro-2,2-diphenyl-1-methylcyclopropane (7):

Butyllithium (1513 mL, 1.54 M in hexane, 2.33 mol) was added dropwise to a solution of 1,1-dichloroethane (461 g, 4.66 mol) and 1,1-diphenylethylene (210 g, 1.17 mol) in CPME (1260 mL) at -35 to -40 °C. After the solution was stirred for 30 min, the reaction was quenched by the addition of water (1000 mL) at 0 °C. The organic phase was then separated, washed with water (1000 mL x 2) and concentrated under reduced pressure. The concentrate was purified by recrystallization from MeOH (1000 mL) to give the title compound (218 g, 77 %) as a white solid.

$^{1}H$ NMR (300 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.67 (d, *J* = 6.7 Hz, 1H), 1.87 (d, *J* = 6.7 Hz, 1H), 7.12-7.32 (m, 6H), 7.42 (br d, *J* = 6.9, Hz, 2H), 7.50 (dt, *J* = 7.2 Hz, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 27.0, 28.3, 42.5, 48.6, 126.6, 126.7, 128.1, 128.6, 129.1, 129.8, 142.2, 142.9.

### 2,2-Diphenyl-1-(di-*tert*-butylphosphino)-1-methylcyclopropane (6):

A small amount of iodine and *t*-BuMgCl were added to a solution of magnesium turnings (18.2 g, 0.754 mmol) in THF (73 mL) at rt. After stirring for 3 h, a solution of compound **8** (174 g, 0.718 mol) in THF (523 mL) was added dropwise to the premixed solution.

The reaction solution was stirred at 65 °C for overnight and cooled to rt. The resulting solution was added dropwise to a solution of CuI (145 g, 0.761 mol), LiBr (68.6 g, 0.790 mol) and di-*tert*-butylchlorophosphine (143., 0.790 mol) in THF (699 mL) at 55 °C. After stirring for 6 h, hexane (900 mL) was added at 35 °C and the mixed solution was cooled to 10 °C. A generated copper salt was separated by filtration and dissolved with toluene. The toluene solution was washed with aqueous ammonia under air until the color of the solution change from blue to colorless. After washing with water, the solution was concentrated under reduced pressure. The concentrate was purified from methanol (930 mL) to give the title compound (162 g, 64%) as a white solid.
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 13.1 Hz, 9H), 1.28-1.33 (m, 1H), 1.31 (d, *J* = 6.3 Hz, 9H), 1.36 (d, *J* = 1.2 Hz, 3H), 2.27 (dd, *J* = 5.2, 12.6 Hz, 1H), 7.06 (tt, *J* = 1.2, 7.3 Hz, 1H), 7.13-7.20 (m, 3H), 7.28 (br t, *J* = 7.7 Hz, 2H), 7.34 (br d, *J* = 7.2 Hz, 2H), 7.43 (br d, *J* = 8.3 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 24.9 (d, *J* = 4.1 Hz), 26.6 (d, *J* = 33.7 Hz), 28.4 (d, *J* = 8.4 Hz), 31.5 (d, *J* = 13.9 Hz), 32.3 (d, *J* = 13.6 Hz), 33.5 (d, *J* = 26.5 Hz), 34.8 (d, *J* = 27.9 Hz), 40.6 (d, *J* = 13.1 Hz), 125.5, 126.1, 127.1, 128.1, 130.3 (d, *J* = 4.2 Hz), 131.2 (d, *J* = 1.6 Hz), 142.6 (d, *J* = 6.9 Hz), 144.0; $^{31}$P NMR (202 MHz, $CDCl_3$) δ 39.25; HRMS (ESI) *m/z* calcd for $C_{24}H_{33}P$ $[M+H]^+$ 353.2398, found $[M+H]^+$ 353.2403.

**Typical Procedure for the Coupling Reaction of Aryl Halides with Amines.**
Aryl halide (1.1 equiv) and amine (1 equiv) were added to a solution of NaO*t*-Bu (1.2 equiv), $[(\pi\text{-allyl})PdCl]_2$ (0.5 mol%) and lingand **6** (2.0 mol%) in toluene (0.5 M) at rt. The mixture was stirred at 100-120 °C for the time specified. After cooling to rt, the reaction solution was diluted with toluene, washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the concentrate by column chromatography on silica gel and/or recrystallization gave the coupling product.

**N-(4-Anisyl)-N,N-diphenylamine (Scheme 2 and Table 1, entry 3):**
Purification by flash chromatography (hexane/toluene = 2/1) gave a white solid.
$^{1}$H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.84 (dt, *J* = 9.3, 2.9 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 2H), 6.98-7.11 (m, 6H), 7.16-7.27 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 55.4, 114.7, 121.8, 122.9, 127.3, 129.0, 140.8, 148.2, 156.1; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}NO$ $[M+H]^+$ 276.1388, found $[M+H]^+$ 276.1394.

**N-(3,4-Methylenedioxyphenyl)diphenylamine (Table 1, entry 1):**
Purification by flash chromatography (hexane/toluene = 2/1) gave a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 5.94 (s, 2H), 6.58 (dd, *J* = 2.2, 8.3 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.69-6.75 (m, 1H), 6.91-7.07 (m, 6H), 7.17-7.27 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 101.2, 107.5, 108.6, 119.1, 122.0, 123.1, 129.1, 142.1, 144.0, 148.0, 148.3; HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO$ $[M+H]^+$ 290.1181, found $[M+H]^+$ 290.1174.

**N-(2-Tolyl)-N,N-diphenylamine (Table 1, entry 2):**

Purification by flash chromatography (hexane/toluene = 8/1) gave a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 3H), 6.87-7.00 (m, 6H), 7.09-7.27 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 18.8, 121.6, 121.8, 126.2, 127.6, 129.2, 129.9, 131.9, 136.7, 145.6, 147.7; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N$ $[M+H]^+$ 260.1439, found $[M+H]^+$ 260.1429.

**1,4-(Diphenylamino)benzene (Table 1, entry 4):**

Purification by flash chromatography (hexane/toluene = 4/1) and the following recrystallization (haxane/toluene = 2/1) gave a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.94-7.02 (m, 8H), 7.06-7.13 (m, 8H), 7.19-7.28 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 122.4, 123.7, 125.4, 129.2, 142.8, 147.8; HRMS (ESI) *m/z* calcd for $C_{30}H_{24}N_2$ $[M+H]^+$ 413.2018, found $[M+H]^+$ 143.2033.

**N-(1-Naphthyl)-N-(3-tolyl)aniline (Table 1, entry 5):**

Purification by flash chromatography (hexane/toluene = 8/1) gave a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 2.21 (s, 3H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.79.7.02 (m, 5H., 7.07 (t, *J* = 7.8 Hz, 1H), 7.11-7.21 (m, 2H), 7.27-7.38 (m, 2H), 7.40-7.50 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CD_2Cl_2$) δ 21.5, 119.6, 121.7, 121.9, 123.0, 123.1, 124.5, 126.4, 126.6, 126.68, 126.70, 127.6, 128.7, 129.2, 129.3, 131.7, 135.7, 139.4, 144.0, 148.8, 148.0; HRMS.ESI. *m/z* calcd for $C_{23}H_{19}N$ $[M+H]^+$ 310.1596, found $[M+H]^+$ 310.1582.

**N,N-[di-(3.4-Methylenedioxyphenyl)]aniline (Table 1, entry 6):**

Purification by flash chromatography (hexane/toluene = 1/1) gave a white solid.

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 5.93 (s, 4H), 6.54 (dd, *J* = 2.1, 8.4 Hz, 2H), 6.62 (d, *J* = 2.1 Hz, 2H), 6.67-6.73 (m, 2H), 6.85-6.99 (m, 3H), 7.13-7.23 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 101.2, 106.8, 108.5, 118.1, 121.2, 121.7, 129.0, 142.4, 143.6, 148.2, 148.5; HRMS (ESI) *m/z* calcd for $C_{20}H_{15}NO_4$ $[M+H]^+$ 334.1079, found $[M+H]^+$ 334.1066.

**N,N-di-(4-Anisyl)aniline (Table 1, entry 7):**

Purification by flash chromatography (hexane/AcOEt = 8/1) gave a white solid.

$^1$H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 6H), 6.72-6.97 (m, 7H), 7.04 (br d, *J* = 9.0 Hz, 4H), 7.12-7.20 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 55.4, 114.6, 120.5, 120.9, 126.3, 128.9, 141.1, 148.7, 155.6; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_2$ $[M+H]^+$ 306.1494, found $[M+H]^+$ 306.1485.

**N-Phenylindole[1] (Table 1, entry 8):**

Purification by flash chromatography (hexane/toluene = 8/1) gave a colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$) δ 6.68 (d, *J* = 3.3 Hz, 1H), 7.13-7.26 (m, 2H), 7.31-7.41 (m, 2H), 7.47-7.60 (m, 5H), 7.66-7.72 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 103.5, 110.5, 120.3, 121.1, 122.3, 124.4, 126.4, 127.9, 129.2, 129.6, 135.8, 139.8.

**N-(4-Tolyl)indole[2] (Table 1, entry 9):**

Purification by flash chromatography (hexane/toluene = 8/1) gave a colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 6.66 (d, *J* = 3.3 Hz, 1H), 7.11-7.42 (m, 7H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 6.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.0, 103.2, 110.5, 120.1, 121.0, 122.2, 124.3, 128.0, 129.1, 130.1, 136.0, 136.3, 137.3.

**N-Phenylcarbazole (Table 2, entry 1):**

Purification by flash chromatography (hexane/toluene =8/1) gave a white solid.

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.23-7.34 (m, 2H), 7.36-7.51 (m, 5H), 7.52-7.64 (m, 4H), 8.14 (d, *J* = 7.8 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 109.7, 119.9, 120.3, 123.3, 125.9, 127.1, 127.4, 129.8, 137.7, 140.9.

**N-(4-Cyanophenyl)carbazole (Table 2, entry 3):**

Purification by flash chromatography (hexane/toluene = 1/1) gave a white solid.

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.28-7.49 (m, 6H), 7.72 (dt, *J* = 8.7, 2.1 Hz, 2H), 7.89 (dt, *J* = 8.7, 2.1 Hz, 2H), 8.14 (br d, *J* = 7.8 Hz, 2H) ; $^{13}$C NMR (75 MHz, $CDCl_3$) δ 109.5, 110.4, 118.3, 120.6, 121.0, 124.0, 126.3, 127.1, 133.9, 139.9, 142.0; HRMS (ESI) *m/z* calcd for $C_{19}H_{12}N_2$ $[M+Na]^+$ 291.0898, found $[M+Na]^+$ 291.0905.

**N-(4-Tolyl)carbazole (Table 2, entry 4):**

Purification by flash chromatography (hexane/toluene = 16/1) gave a white solid.

$^1$H NMR (300 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.21-7.32 (m, 2H), 7.33-7.47 (m, 8H), 8.13

(br d, *J* =7.5 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 21.2, 109.8, 119.7, 120.2, 123.2, 125.8, 127.0, 130.4, 135.0, 137.3, 141.1; HRMS (ESI) *m/z* calcd for $C_{19}H_{15}N$ $[M+H]^+$ 258.1283, found $[M+H]^+$ 258.1288.

**N-(3-Anisyl)carbazole (Table 2, entry 5):**

Purification by flash chromatography (hexane/toluene = 8/1) gave a white solid.

$^1$H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H), 7.00 (dd, *J* = 2.7, 8.4 Hz, 1H), 7.10 (t, *J* = 2.0 Hz, 1H), 7.16 (dt, *J* = 1.0, 8.1 Hz, 1H), 7.22-7.32 (m, 2H), 7.36-7.54 (m, 5H), 8.14 (dd, *J* = 0.8, 7.7 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 55.5, 109.9, 112.6, 113.2, 119.3, 119.9, 120.3, 123.3, 125.9, 130.5, 138.8, 140.8, 160.8; HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO$ $[M+H]^+$ 274.1232, found $[M+H]^+$ 274.1234.

**1,3,5-Tricarbazolebenzene (Table2, entry 6):**

Recrystallization from toluene gave a white solid.

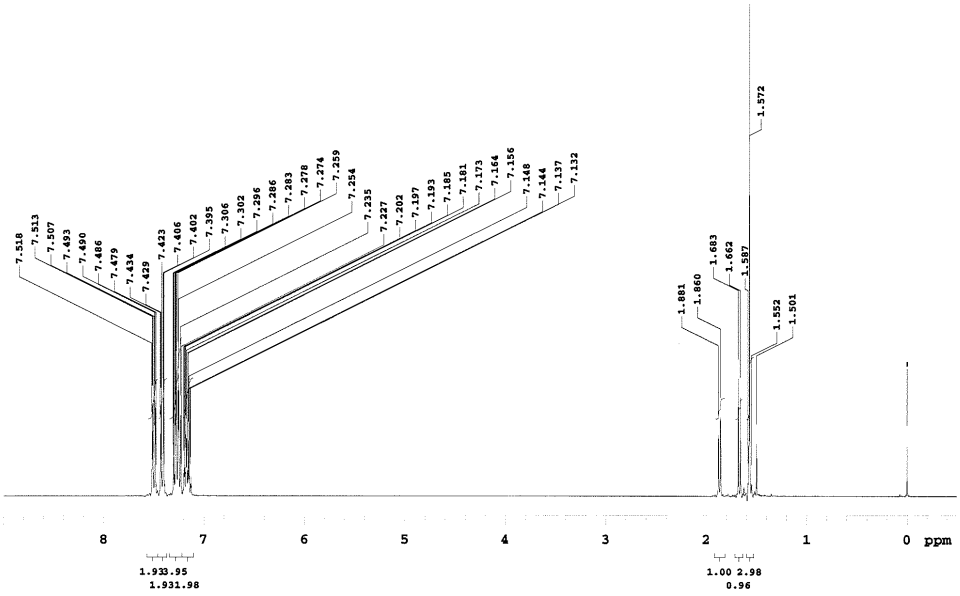
$^1$H NMR (300 MHz, $CDCl_3$) δ 7.33 (br d, *J* = 7.5 Hz, 6H), 7.47 (dt, *J* = 1.2, 7.8 Hz, 6H), 7.67 (d, *J* = 8.1 Hz, 6H), 7.96 (s, 3H), 8.16 (d, *J* = 7.5 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 109.7, 120.6, 120.7, 123.5, 123.8, 126.4, 140.3, 140.8; HRMS (ESI) *m/z* calcd for $C_{42}H_{27}N_3$ $[M+H]^+$ 574.2283, found $[M+H]^+$ 574.2288.

**References:**

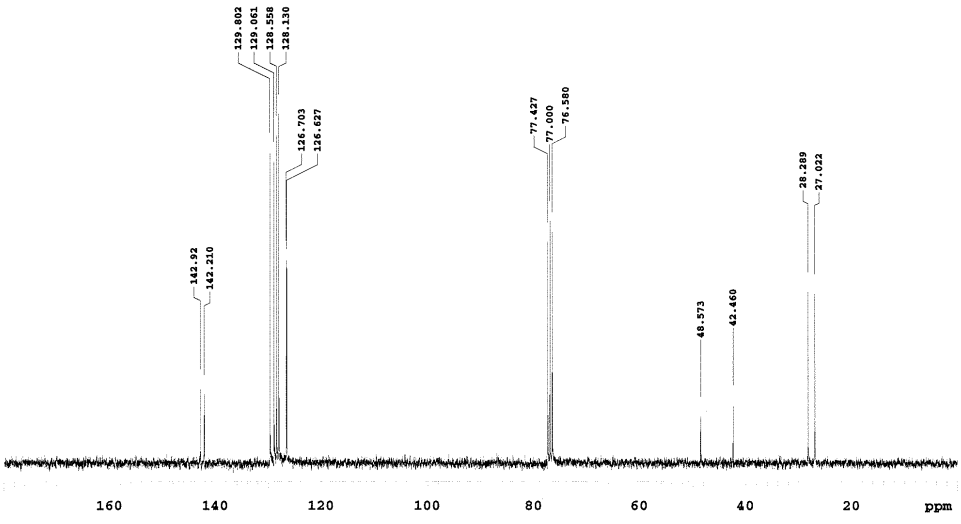
(1) Ma, H.-C.; Jiang, X.-Z. *J. Org. Chem.* **2007**, *72*, asap.

(2) Hartwig, H. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575.

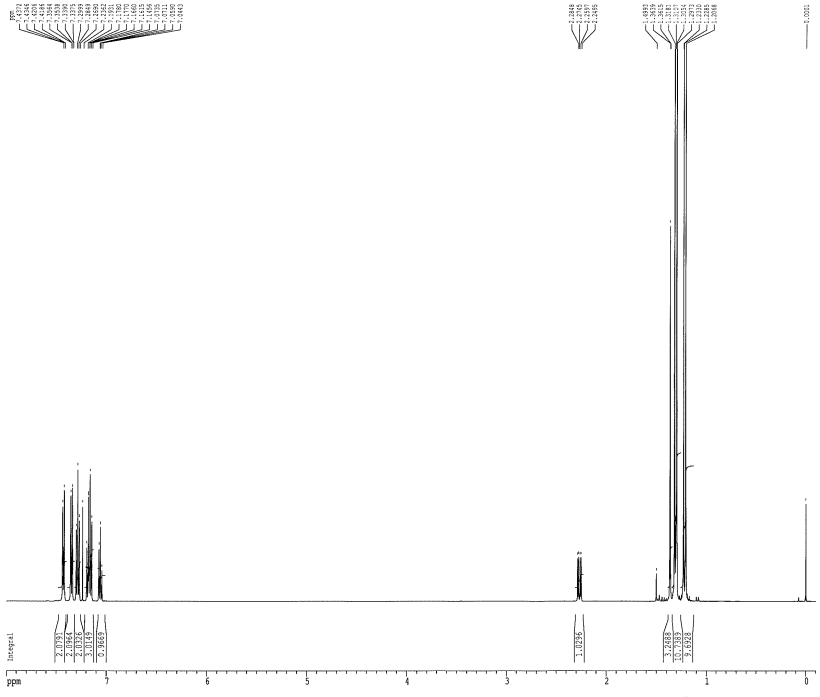
$^1$H NMR of compound **7** in $CDCl_3$



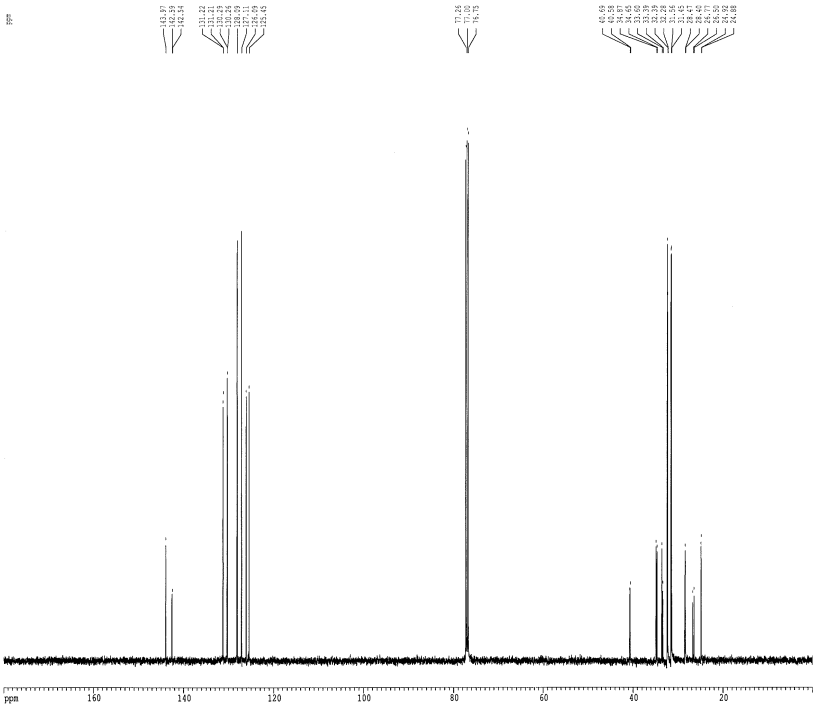

$^{13}$C NMR of compound **7** in $CDCl_3$



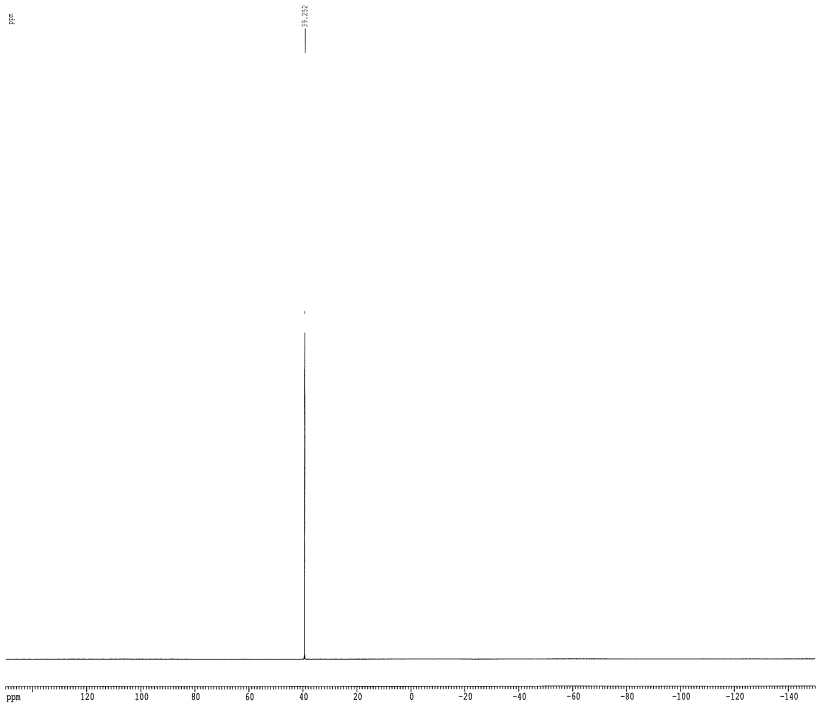

$^{1}$H NMR of MOHOS **6** in $CDCl_3$



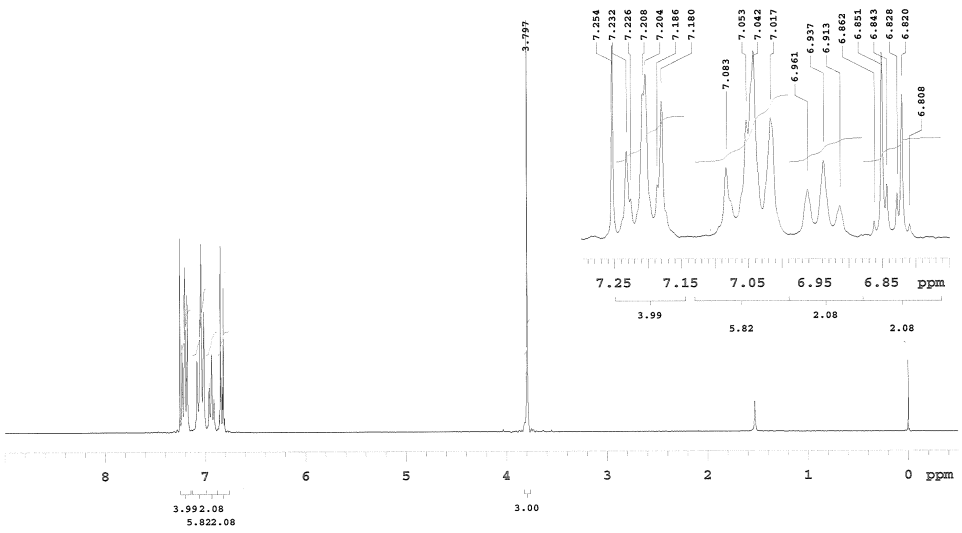
$^{13}$C NMR of MOHOS **6** in $CDCl_3$



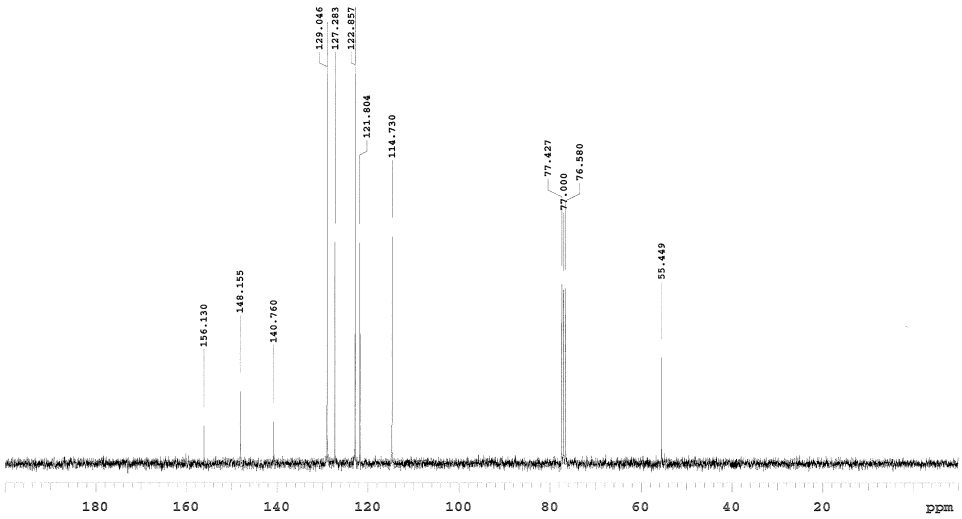
$^{31}$P NMR of MOHOS **6** in $CDCl_3$



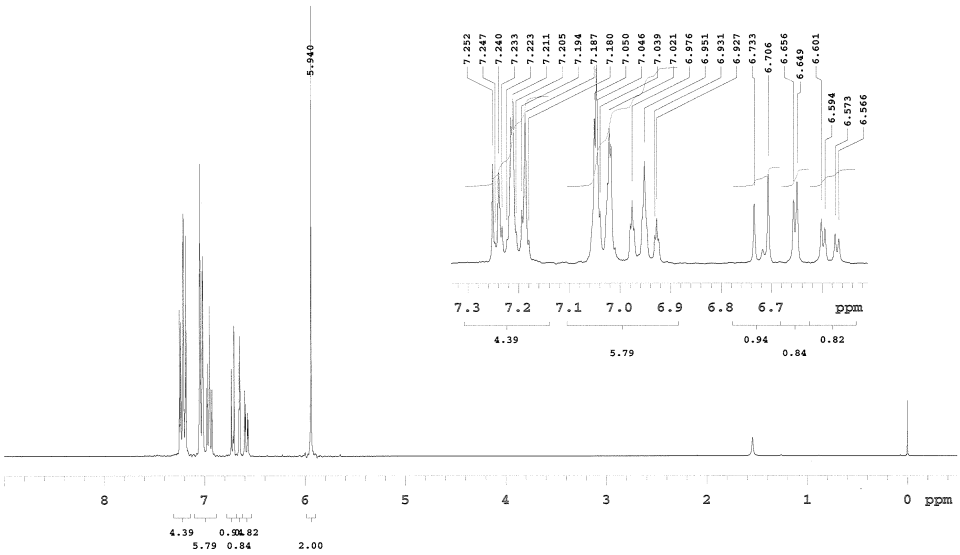

$^{1}$H NMR of **N-(4-Anisyl)-N,N-diphenylamine (Table 1, entry 3)** in $CDCl_3$:



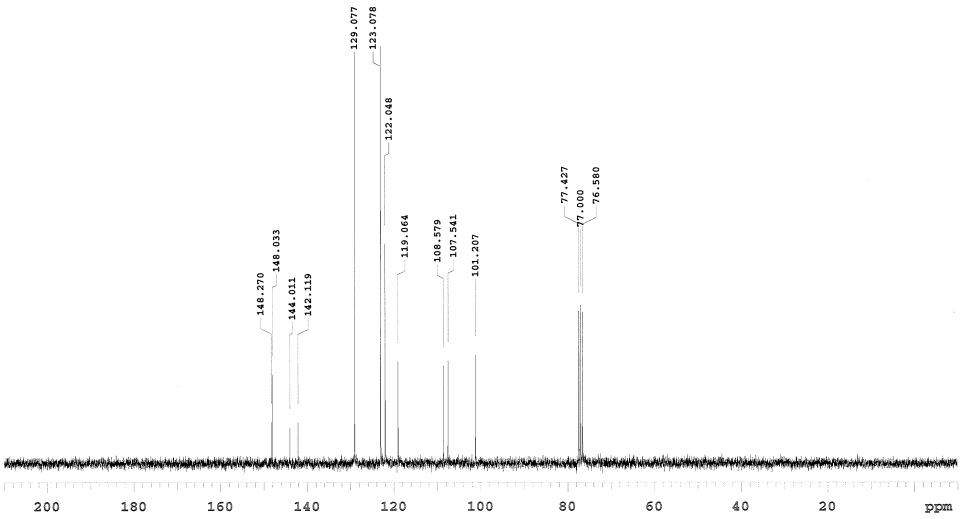

$^{13}$C NMR of **N-(4-Anisyl)-N,N-diphenylamine (Table 1, entry 3)** in $CDCl_3$:



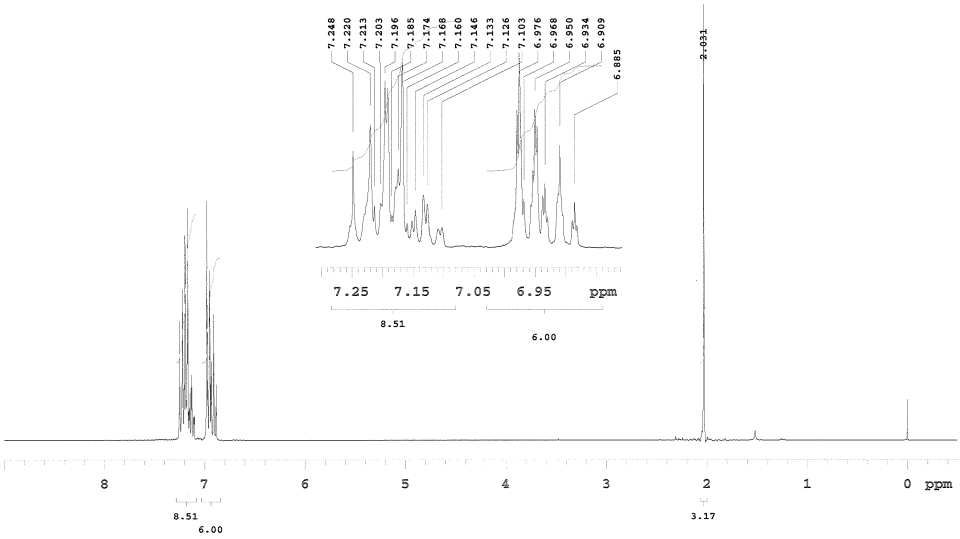

$^{1}$H NMR of **N-(3,4-Methylenedioxyphenyl)diphenylamine (Table 1, entry 1)** in $CDCl_3$:



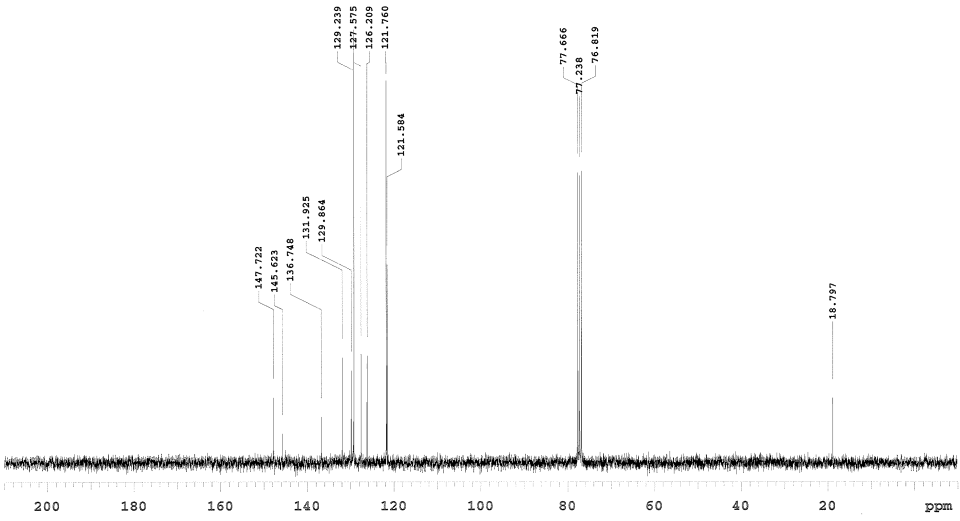

$^{13}$C NMR of **N-(3,4-Methylenedioxyphenyl)diphenylamine (Table 1, entry 1)** in $CDCl_3$:



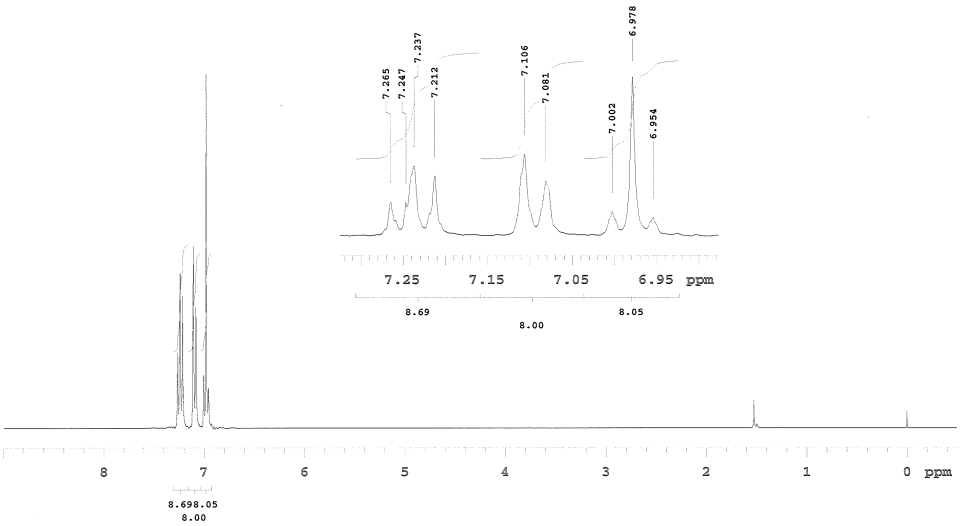

**N-(2-Tolyl)-N,N-diphenylamine (Table 1, entry 2)** in $CDCl_3$:



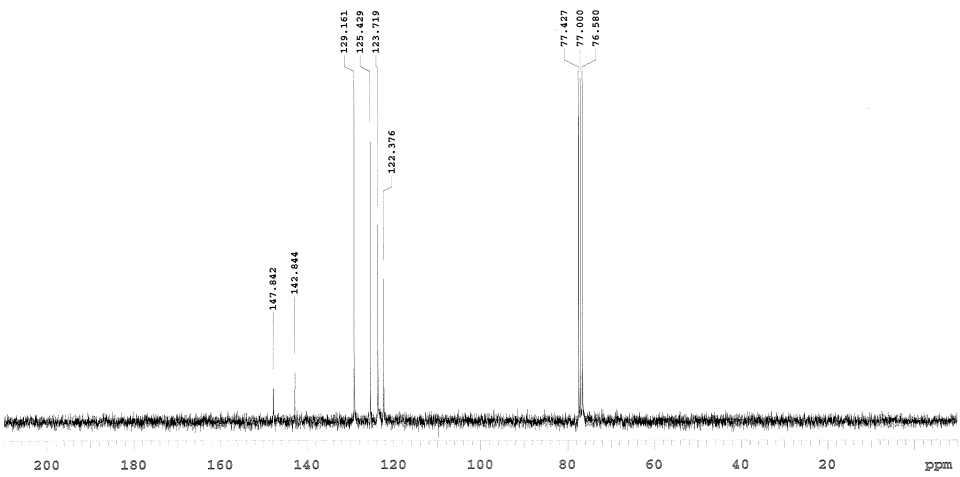

$^{13}$C NMR of **N-(2-Tolyl)-N,N-diphenylamine (Table 1, entry 2)** in $CDCl_3$:



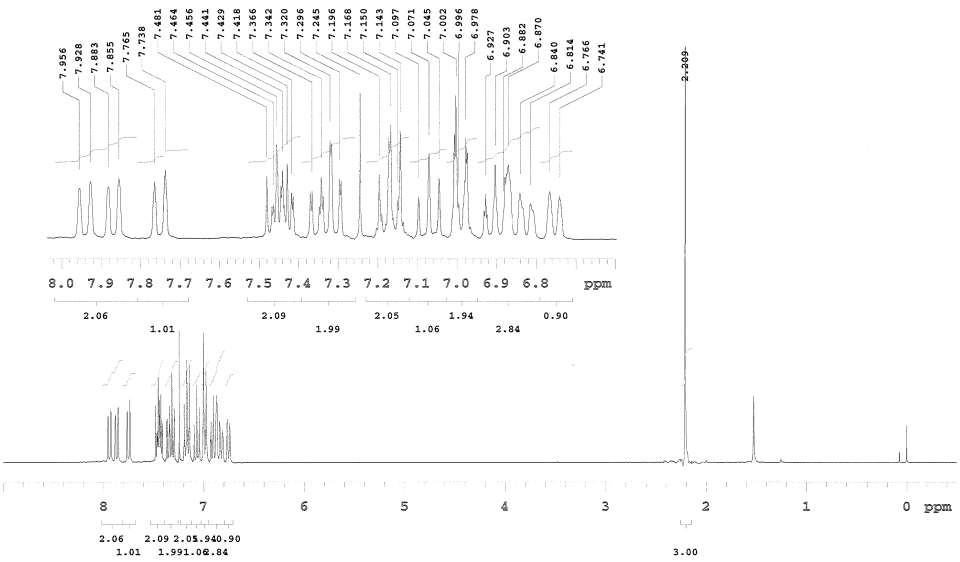

$^{1}$H NMR of **1,4-(Diphenylamino)benzene (Table 1, entry 4)** in $CDCl_3$:



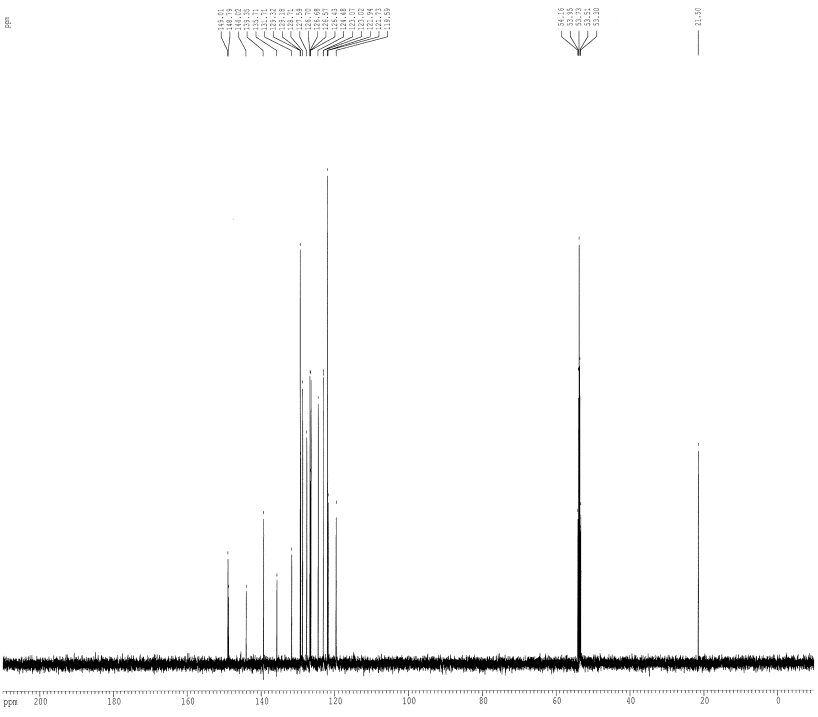

$^{13}$C NMR of **1,4-(Diphenylamino)benzene (Table 1, entry 4)** in $CDCl_3$:



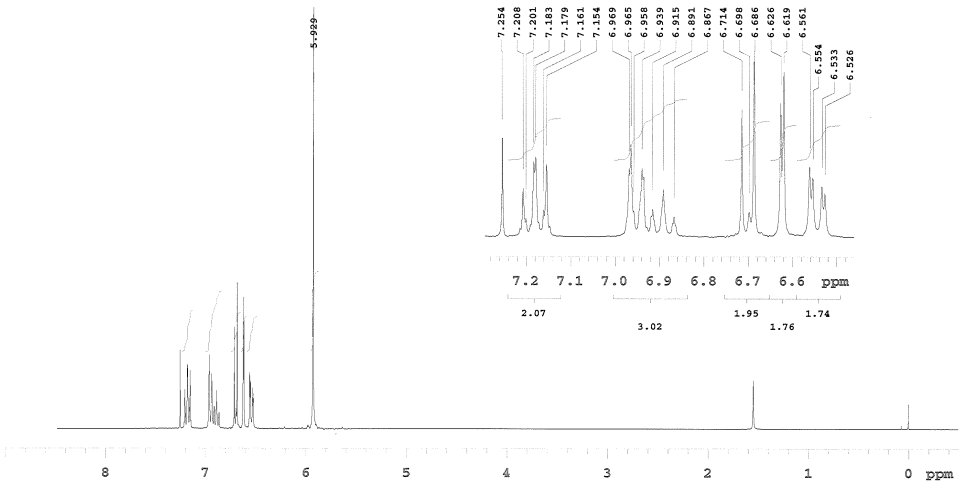

$^{1}$H NMR of **N-(1-Naphthyl)-N-(3-tolyl)aniline (Table 1, entry 5)** in $CDCl_3$:



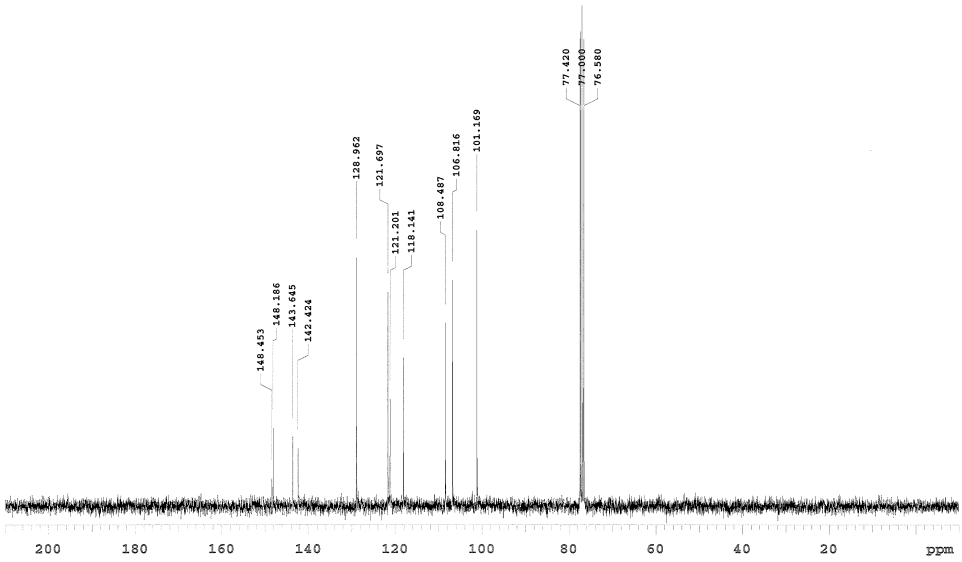
$^{13}$C NMR of **N-(1-Naphthyl)-N-(3-tolyl)aniline (Table 1, entry 5)** in $CD_2Cl_2$:



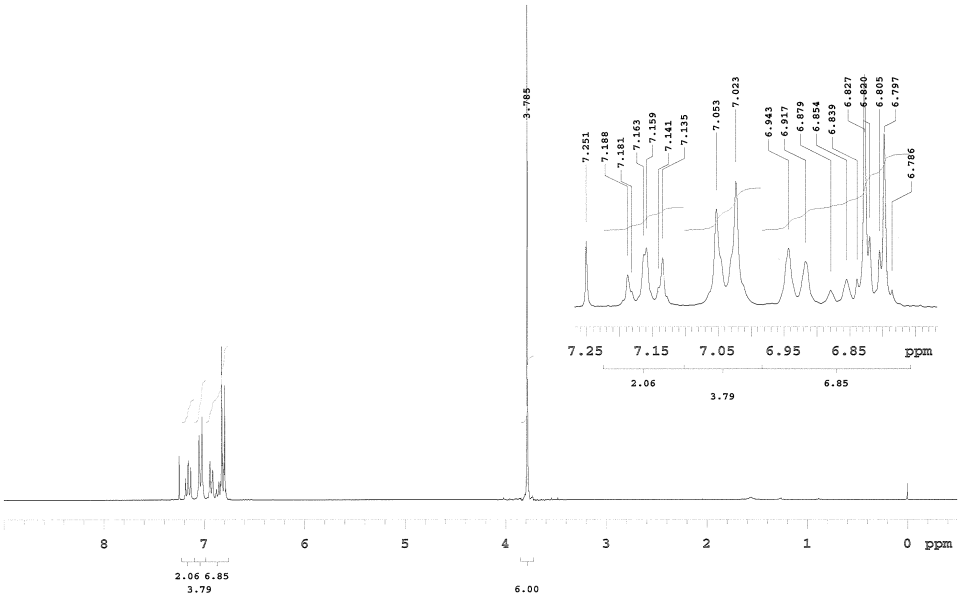
$^{1}$H NMR of **N,N-[Bis-(3.4-methylenedioxyphenyl)]aniline (Table 1, entry 6)** in $CDCl_3$:



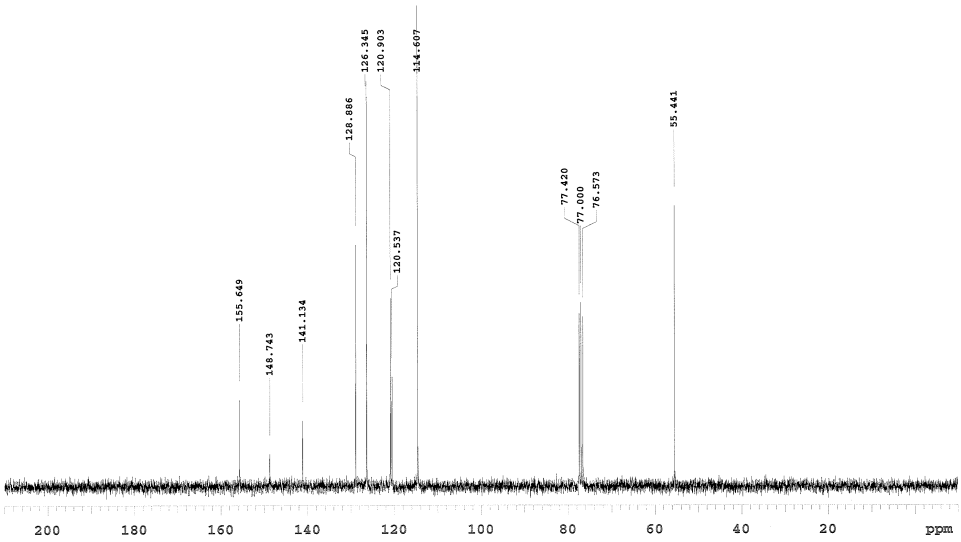

$^{13}$C NMR of **N,N-[Bis-(3.4-methylenedioxyphenyl)]aniline (Table 1, entry 6)** in $CDCl_3$:



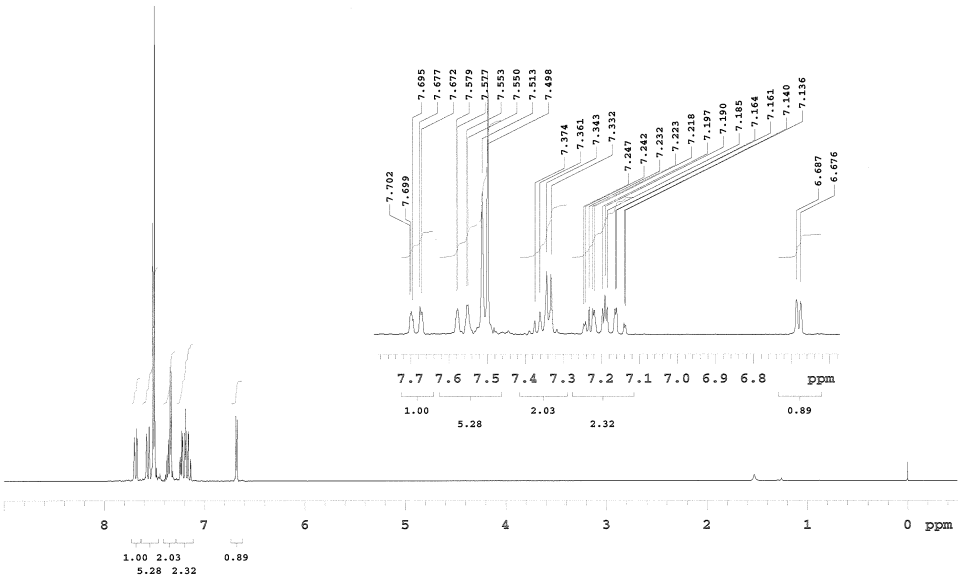

$^{1}$H NMR of **N,N-di-(4-Anisyl)aniline (Table 1, entry 7)** in $CDCl_3$:



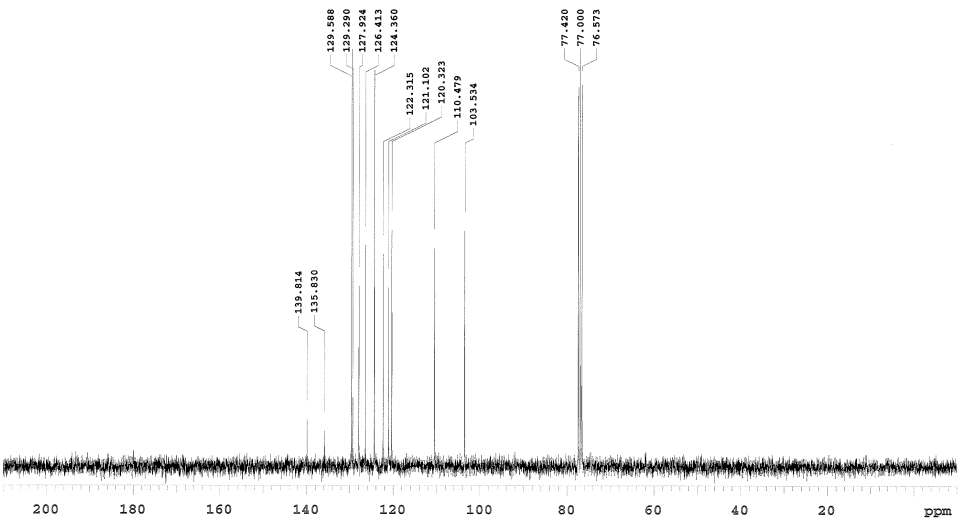

$^{13}$C NMR of **N,N-di-(4-Anisyl)aniline (Table 1, entry 7)** in $CDCl_3$:



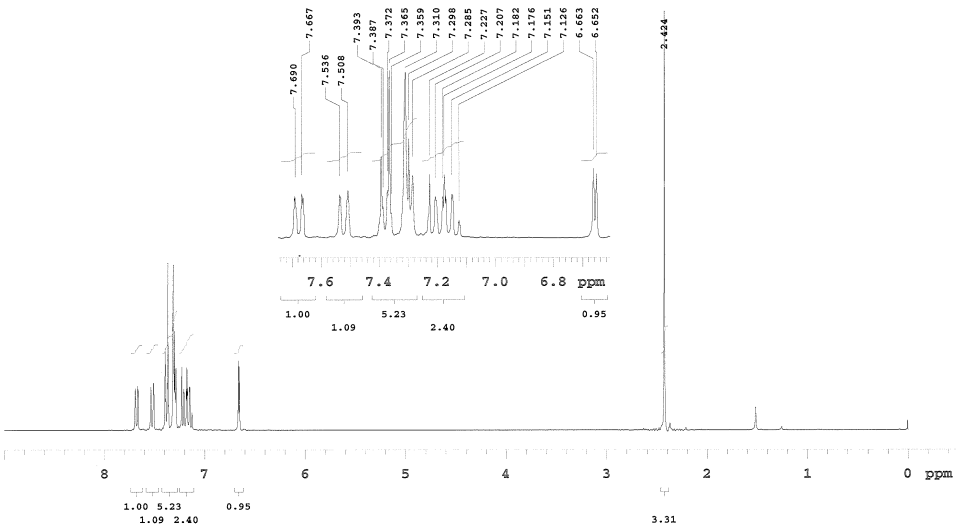

$^{1}$H NMR of **N-Phenylindole (Table 1, entry 8)** in $CDCl_3$:



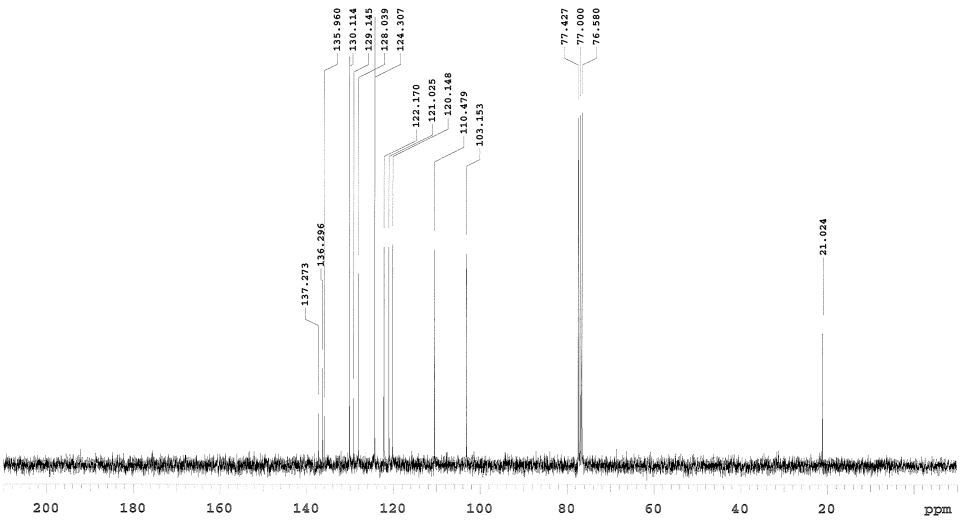

$^{13}$C NMR of **N-Phenylindole (Table 1, entry 8)** in $CDCl_3$:



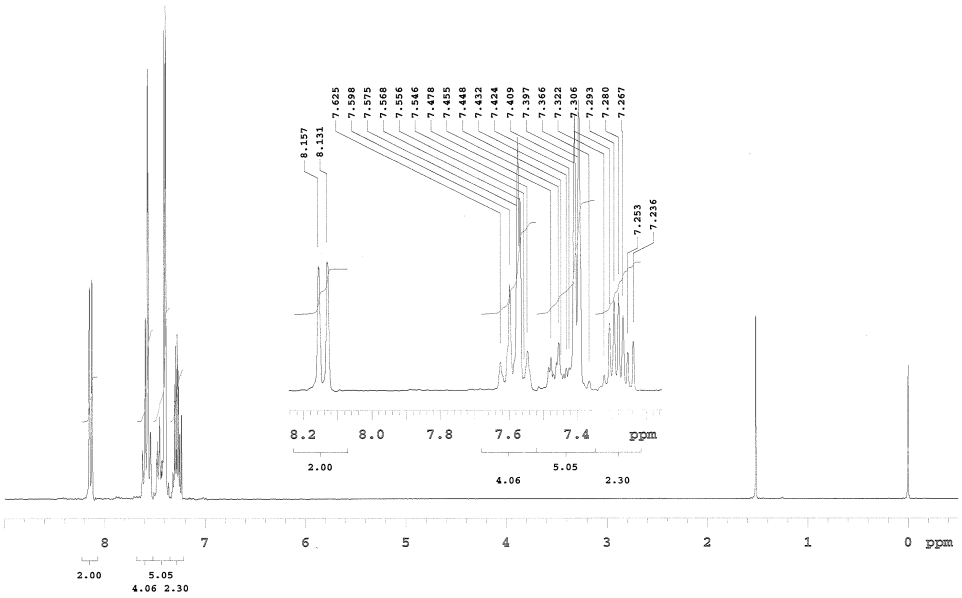

$^{1}$H NMR of **N-(4-Tolyl)indole (Table 1, entry 9)** in $CDCl_3$:



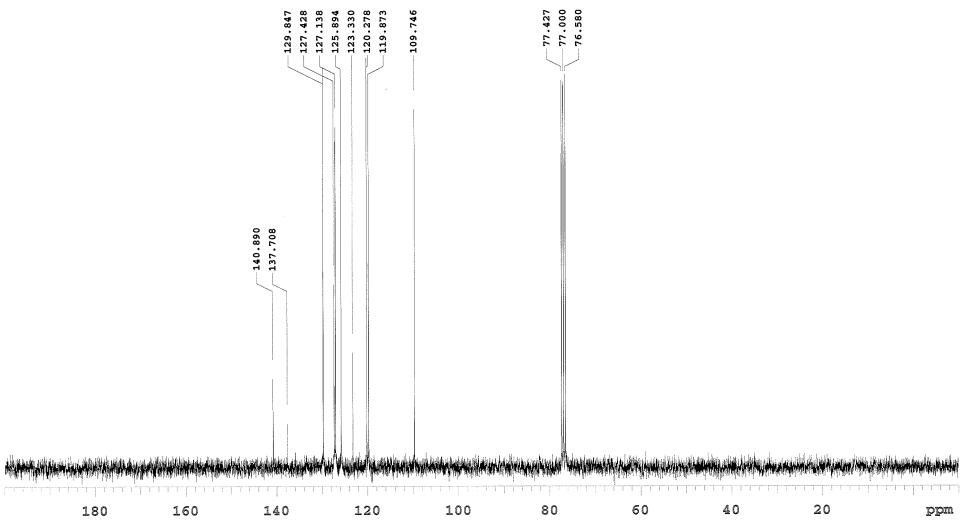

$^{13}$C NMR of **N-(4-Tolyl)indole (Table 1, entry 9)** in $CDCl_3$:



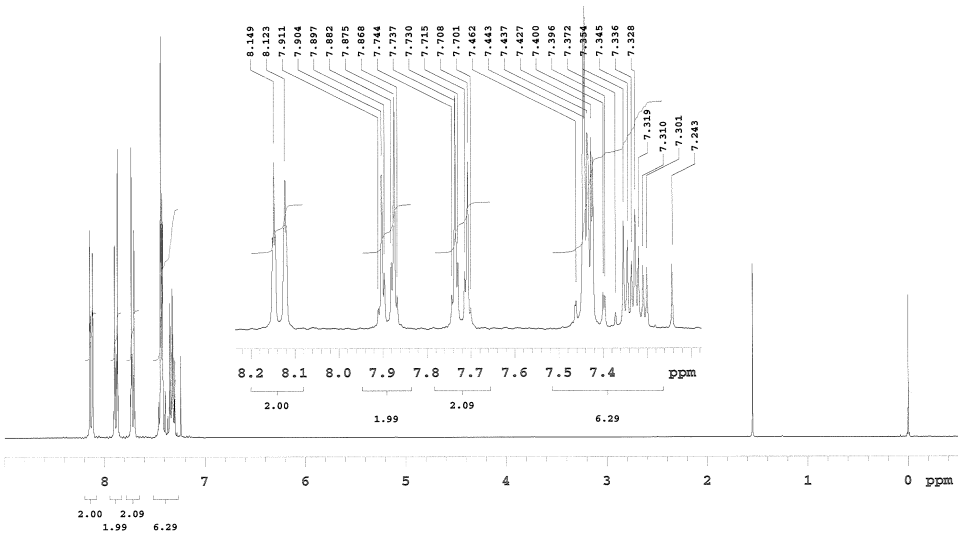

$^{1}$H NMR of **N-Phenylcarbazole (Table 2, entry 1)** in $CDCl_3$:



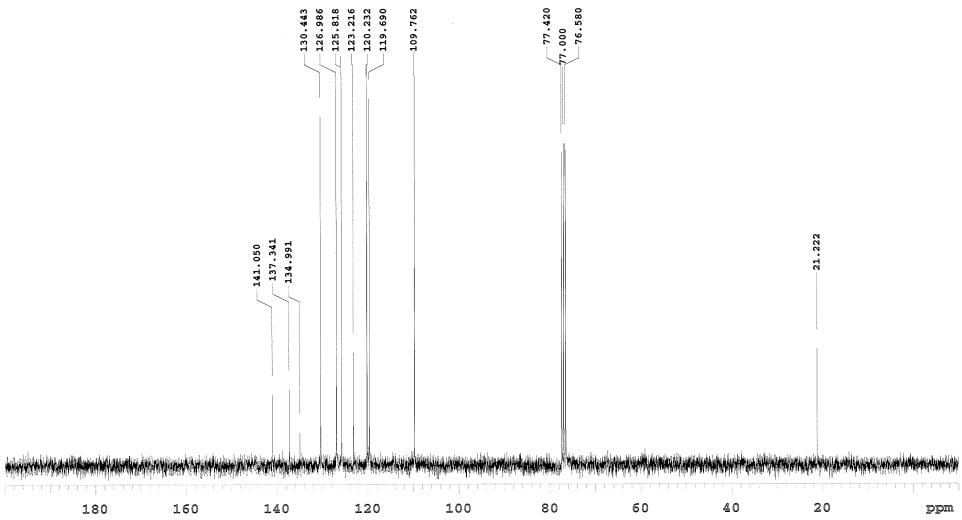

$^{13}$C NMR of **N-Phenylcarbazole (Table 2, entry 1)** in $CDCl_3$:



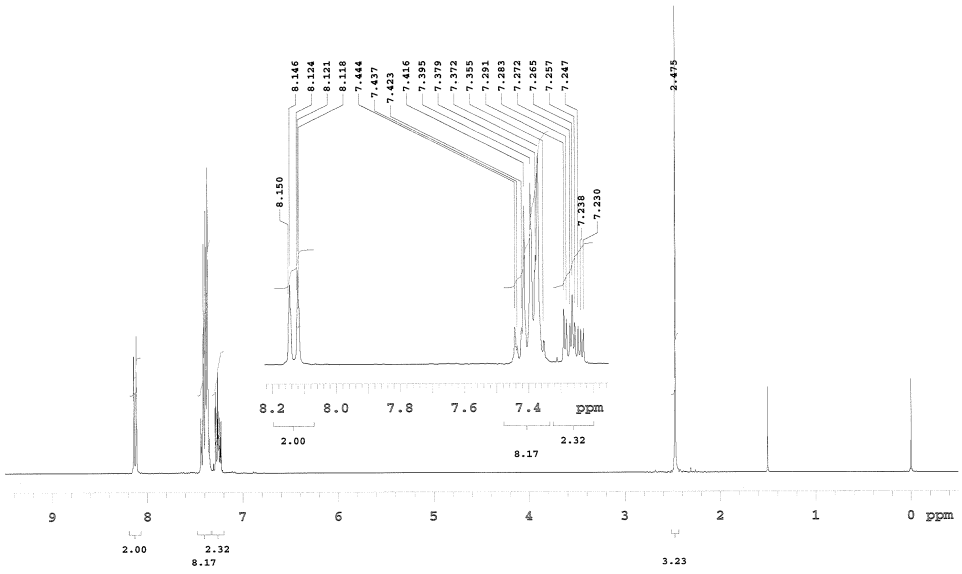

$^{1}$H NMR of **N-(4-Cyanophenyl)carbazole (Table 2, entry 3)** in $CDCl_3$:



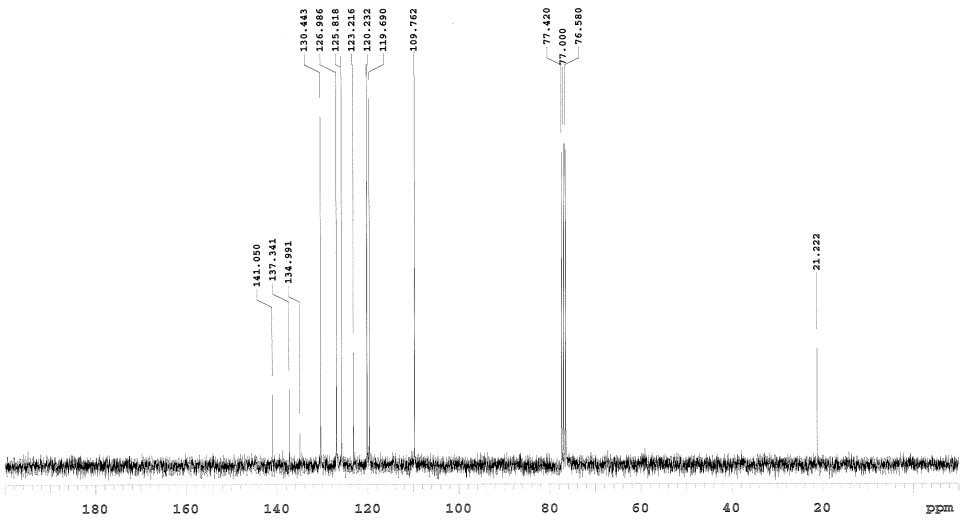

$^{13}$C NMR of **N-(4-Cyanophenyl)carbazole (Table 2, entry 3)** in $CDCl_3$:



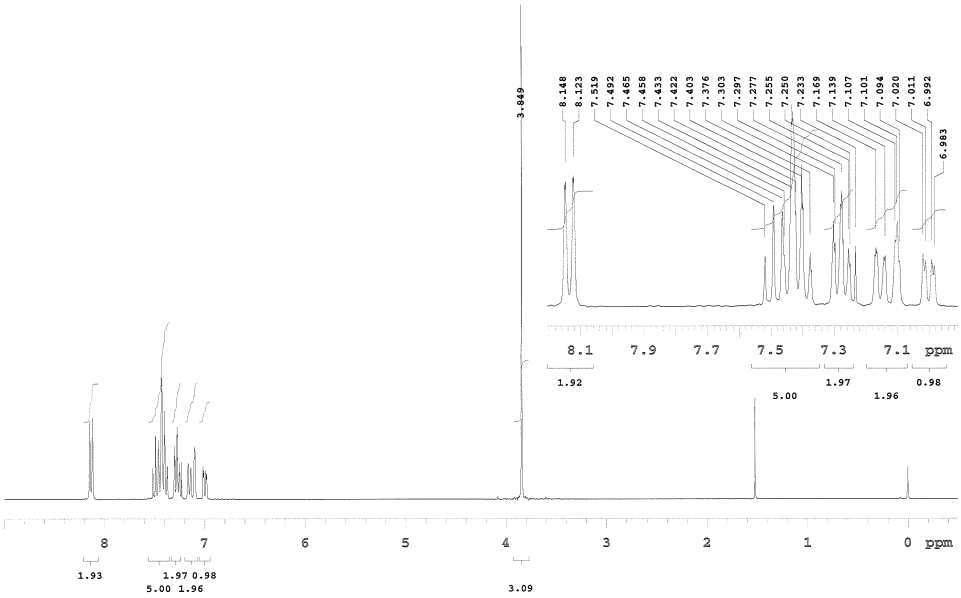

$^{1}$H NMR of **N-(4-Tolyl)carbazole (Table 2, entry 4)** in $CDCl_3$:



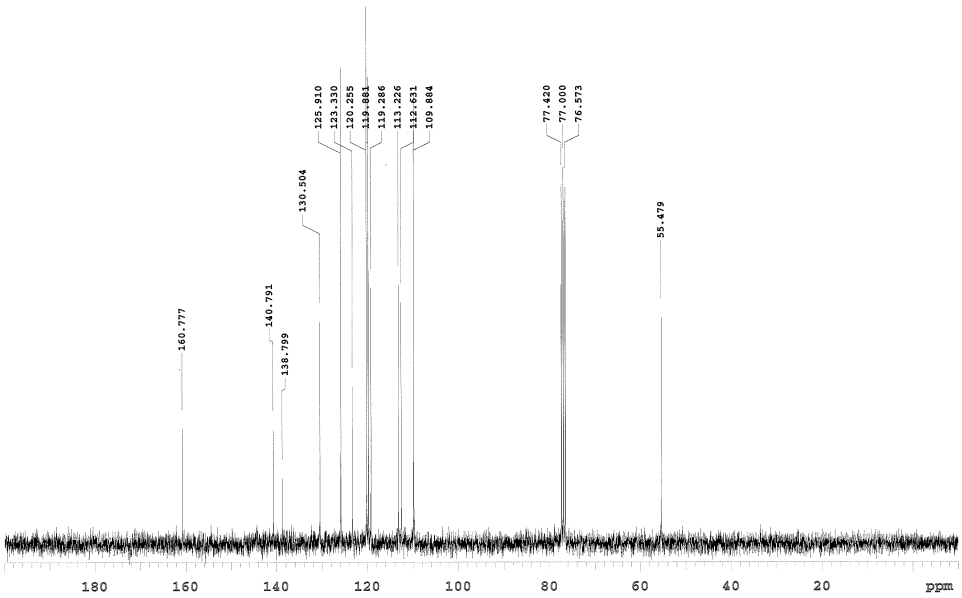

$^{13}$C NMR of **N-(4-Tolyl)carbazole (Table 2, entry 4)** in $CDCl_3$:



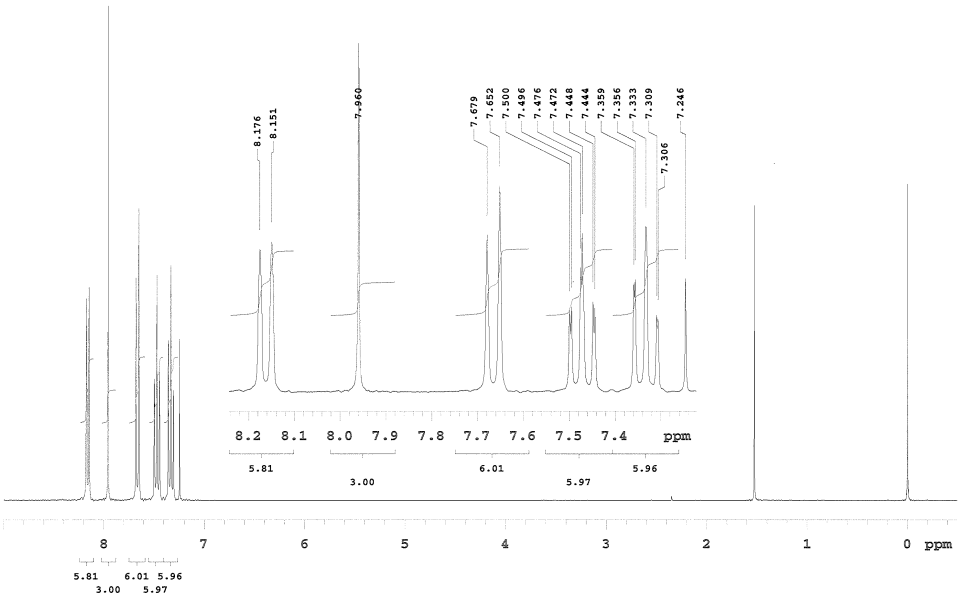

$^{1}$H NMR of **N-(3-Anisyl)carbazole (Table 2, entry 5)** in $CDCl_3$:




$^{13}$C NMR of **N-(3-Anisyl)carbazole (Table 2, entry 5)** in $CDCl_3$:




$^{1}$H NMR of **1,3,5-Tricarbazolebenzene (Table2, entry 6)** in $CDCl_3$:




$^{13}$C NMR of **1,3,5-Tricarbazolebenzene (Table2, entry 6)** in $CDCl_3$: