

## Supporting Information

# Ligand-free Pd/C-catalyzed Suzuki-Miyaura Coupling Reaction for the Synthesis of Heterobiaryl Derivatives

*Yoshiaki Kitamura, Satoko Sako, Takahiro Udzu, Azusa Tsutsui, Tomohiro Maegawa,*

*Yasunari Monguchi, Hironao Sajiki\**

Laboratory of Medicinal Chemistry, Gifu Pharmaceutical University

5-6-1, Mitahora-higashi, Gifu, 502-8585, Japan

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## Experimental Section

**General.** All reactions were carried out under an argon atmosphere, unless otherwise noted. Aryl bromides were purchased from Tokyo Chemical Industry Co., Ltd., Aldrich Chemical Co., Inc. or Wako Pure Chemical Industries, Ltd. Aryl boronic acid esters were purchased from Aldrich Chemical Co., Inc. or Tokyo Chemical Industry Co., Ltd. Pd/C was gifted by N. E. Chemcat Co. Bases and solvents were purchased from Nacalai Tasque, Inc. or Wako Pure Chemical Industries, Ltd. All these materials were used without further purification.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM EX-400 or JEOL JNM AL-400 spectrometer (400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$  NMR). All NMR samples were prepared as  $\text{CDCl}_3$  solutions. Chemical shifts ( $\delta$ ) are expressed in ppm and are internally referenced (0.00 ppm for TMS- $\text{CDCl}_3$  for  $^1\text{H}$  NMR and 77.0 ppm for  $^{13}\text{C}$  NMR). EI Mass spectra were taken on a JEOL JMS-SX102A instrument. Elemental analyses were performed by YANACO MT-5 instrument. Flash column chromatography was performed using silica gel 60N [spherical neutral (63-210  $\mu\text{m}$ )] from Kanto Chemical Co., Inc.

## General Procedure of Suzuki-Miyaura Cross-Coupling Reaction

### Method A: (eq 1; Table 1, entries 1-8; Table 2, entries 1-5, 7, 9 and 11):

To a test tube with a stir bar were added aryl bromide (250  $\mu\text{mol}$ ), arylboronic acid (375  $\mu\text{mol}$ ),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (333 mg, 875  $\mu\text{mol}$ ), 10% Pd/C (9.3 mg, 8.75  $\mu\text{mol}$ ),  $\text{H}_2\text{O}$  (0.5 mL), and *i*-PrOH (0.5 mL) and the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles and the mixture was stirred at 80 °C. After a certain period, the mixture was diluted with  $\text{H}_2\text{O}$  (25 mL) and EtOAc (or Et<sub>2</sub>O) (25 mL), and passed through a membrane filter (Millipore, Millex<sup>®</sup>-LH, 0.45  $\mu\text{m}$ ). The filtrate was separated into two layers and the aqueous layer was extracted with EtOAc (or Et<sub>2</sub>O) (2  $\times$  25 mL). The combined organic layers were washed with brine (25 mL), dried over  $\text{Na}_2\text{SO}_4$  (or  $\text{MgSO}_4$ ), and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the corresponding biaryl.

**Method B (Table 2, entries 6,8,10 and 12):**

To a test tube with a stir bar were added aryl bromide (250 µmol), arylboronic acid (375 µmol),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (333 mg, 875 µmol), 10% Pd/C (9.3 mg, 8.75 µmol), *i*-PrOH (1.0 mL) and the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles and the mixture was stirred at 80 °C. After a certain period, the mixture was diluted with  $\text{H}_2\text{O}$  (25 mL) and  $\text{Et}_2\text{O}$  (25 mL), and passed through a membrane filter (Millipore, Millex®-LH, 0.45 µm). The filtrate was separated into two layers and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  ( $2 \times 25$  mL). The combined organic layers were washed with brine (25 mL), dried over  $\text{MgSO}_4$ , and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the corresponding biaryl.

**Method C (Table 3, entries 1-6):**

To a test tube with a stir bar were added aryl bromide (500 µmol), arylboronic acid (750 µmol),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (285 mg, 750 µmol), 10% Pd/C (8.0 mg, 7.50 µmol), *i*-PrOH (2.0 mL) and the system was sealed with a septum. The air inside was replaced with argon (balloon) by three vacuum/argon cycles and the mixture was stirred at 80 °C. After a certain period, the mixture was diluted with  $\text{H}_2\text{O}$  (50 mL) and  $\text{EtOAc}$  (50 mL), and passed through a membrane filter (Millipore, Millex®-LH, 0.45 µm). The filtrate was separated into two layers and the aqueous layer was extracted with  $\text{EtOAc}$  ( $2 \times 50$  mL). The combined organic layers were washed with brine (50 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give the corresponding biaryl.

**4-(4'-Nitrophenyl)dibenzofuran**

Yellow solid; mp 174–176 °C,  $^1\text{H}$  NMR  $\delta$  8.34 (d,  $J = 8.8$  Hz, 2H), 8.06 (d,  $J = 8.8$  Hz, 2H), 8.00 (d,  $J = 7.6$  Hz, 1H), 7.99 (d,  $J = 7.6$  Hz, 1H), 7.60 (d,  $J = 8.2$  Hz, 1H), 7.59 (d,  $J = 8.2$  Hz, 1H), 7.49 (t,  $J = 8.2$  Hz, 1H), 7.45 (t,  $J = 8.2$  Hz, 1H), 7.38 (t,  $J = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  156.1, 153.1, 147.0, 142.9, 129.4, 127.7, 126.7, 125.4, 123.8, 123.7, 123.4, 123.3, 123.2, 121.3, 120.8, 111.8; MS (EI)  $m/z$  289 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{18}\text{H}_{11}\text{NO}_3$  ( $\text{M}^+$ ) 289.0739. Found 289.0744. Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{NO}_3 \cdot 1/3\text{H}_2\text{O}$ : C, 73.21; H, 3.98; N, 4.74. Found: C, 73.25; H, 4.04; N, 4.63.

**2-(4'-Nitrophenyl)benzofuran<sup>1</sup>**

Yellow solid;  $^1\text{H}$  NMR  $\delta$  8.30 (d,  $J = 8.8$  Hz, 2H), 7.99 (d,  $J = 8.8$  Hz, 2H), 7.64 (d,  $J =$

8.0 Hz, 1H), 7.55 (d,  $J$  = 8.0 Hz, 1H), 7.37 (t,  $J$  = 8.0 Hz, 1H), 7.30–7.23 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  155.4, 153.2, 147.3, 136.3, 128.6, 125.8, 125.2, 124.3, 123.5, 121.6, 111.5, 105.1; MS (EI)  $m/z$  239 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_3$  ( $\text{M}^+$ ) 239.0583. Found 239.0588.

### **2-(4'-Nitrophenyl)benzothiophene<sup>2</sup>**

Yellow solid;  $^1\text{H}$  NMR  $\delta$  8.27 (d,  $J$  = 8.8 Hz, 2H), 7.87–7.84 (m, 4H), 7.70 (s, 1H), 7.42–7.38 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  147.2, 141.2, 140.6, 140.3, 140.2, 126.8, 125.6, 125.1, 124.4, 124.3, 122.4, 122.4; MS (EI)  $m/z$  255 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{14}\text{H}_9\text{NO}_2\text{S}$  ( $\text{M}^+$ ) 255.0354. Found 255.0360.

### **4-(4'-Acetylphenyl)dibenzofuran**

Colorless solid; mp 109–111 °C,  $^1\text{H}$  NMR  $\delta$  8.08 (d,  $J$  = 8.0 Hz, 2H), 7.98 (d,  $J$  = 8.0 Hz, 2H), 7.96 (d,  $J$  = 8.0 Hz, 1H), 7.94 (d,  $J$  = 8.0 Hz, 1H), 7.59 (d,  $J$  = 8.0 Hz, 1H), 7.58 (d,  $J$  = 8.0 Hz, 1H), 7.45 (t,  $J$  = 8.0 Hz, 1H), 7.40 (t,  $J$  = 8.0 Hz, 1H), 7.35 (t,  $J$  = 8.0 Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  197.6, 156.1, 153.3, 141.1, 136.1, 128.8, 128.6, 127.4, 126.7, 125.1, 124.5, 123.9, 123.2, 122.9, 120.7, 120.5, 111.8, 26.6; MS (EI)  $m/z$  286 ( $\text{M}^+$ , 81%); HRMS (EI) Calcd for  $\text{C}_{20}\text{H}_{14}\text{O}_2$  ( $\text{M}^+$ ) 286.0994. Found 286.0987. Anal. Calcd for  $\text{C}_{20}\text{H}_{14}\text{O}_2$ : C, 83.90; H, 4.93. Found: C, 83.75; H, 5.08.

### **2-(4'-Acetylphenyl)benzofuran**

Colorless solid; mp 177–179 °C,  $^1\text{H}$  NMR  $\delta$  8.00 (d,  $J$  = 8.6 Hz, 2H), 7.90 (d,  $J$  = 8.6 Hz, 2H), 7.59 (d,  $J$  = 8.4 Hz, 1H), 7.52 (d,  $J$  = 8.4 Hz, 1H), 7.32 (t,  $J$  = 8.4 Hz, 1H), 7.22 (t,  $J$  = 8.4 Hz, 1H), 2.60 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  197.2, 155.2, 154.5, 136.5, 134.5, 128.9, 125.1, 124.7, 123.2, 121.3, 111.3, 103.6, 26.6; MS (EI)  $m/z$  236 ( $\text{M}^+$ , 90%); HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2$  ( $\text{M}^+$ ) 236.0837. Found 236.0830. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{O}_2 \cdot 1/7 \text{H}_2\text{O}$ : C, 80.46; H, 5.18. Found: C, 80.85; H, 5.26.

### **4-(4'-Methoxyphenyl)dibenzofuran**

Colorless solid; mp 86–88 °C,  $^1\text{H}$  NMR  $\delta$  7.97 (d,  $J$  = 8.0 Hz, 1H), 7.89–7.85 (m, 3H), 7.59 (d,  $J$  = 8.0 Hz, 2H), 7.56 (d,  $J$  = 8.0 Hz, 2H), 7.45 (t,  $J$  = 8.0 Hz, 1H), 7.39 (t,  $J$  = 8.0 Hz, 1H), 7.34 (t,  $J$  = 8.0 Hz, 1H), 7.07 (d, 2H);  $^{13}\text{C}$  NMR  $\delta$  159.3, 156.1, 153.3, 129.9, 128.8, 127.1, 126.4, 125.5, 124.8, 124.3, 123.1, 122.7, 120.6, 119.0, 114.1, 111.8, 55.3; MS (EI)  $m/z$  289 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_2$  ( $\text{M}^+$ ) 274.0994. Found 274.0998. Anal. Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_2 \cdot 1/6.5 \text{H}_2\text{O}$ : C, 82.36; H, 5.20. Found: C, 82.36; H, 5.21.

#### 4-(2'-Tolyl)dibenzofuran

Colorless oil;  $^1\text{H}$  NMR  $\delta$  7.97 (d,  $J = 7.8$  Hz, 1H), 7.94 (d,  $J = 7.8$  Hz, 1H) 7.50 (d,  $J = 7.8$  Hz, 1H), 7.43–7.31 (m, 8H), 2.24 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  156.2, 153.6, 136.8, 136.4, 130.3, 130.2, 128.3, 128.1, 127.1, 126.3, 125.7, 124.3, 124.2, 122.7, 122.7, 120.7, 119.6, 111.8, 20.2; MS (EI)  $m/z$  258 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}$  ( $\text{M}^+$ ) 258.1045. Found 258.1055. Anal. Calcd for  $\text{C}_{19}\text{H}_{14}\text{O}$ : C, 88.34; H, 5.46. Found: C, 88.10; H, 5.68.

#### 2-Phenylpyridine<sup>3</sup>

Colorless oil;  $^1\text{H}$  NMR  $\delta$  8.65–8.64 (m, 1H), 7.99–7.96 (m, 2H), 7.63–7.57 (m, 2H), 7.44–7.33 (m, 3H), 7.22–7.08 (m, 1H);  $^{13}\text{C}$  NMR  $\delta$  157.1, 149.4, 139.1, 136.4, 128.7, 128.5, 126.6, 121.8, 120.2; MS (EI)  $m/z$  155 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_9\text{N}$  ( $\text{M}^+$ ) 155.0735. Found 155.07447.

#### 2-(4'-Tolyl)pyridine<sup>3</sup>

Colorless oil;  $^1\text{H}$  NMR  $\delta$  8.66 (d,  $J = 4.8$  Hz, 1H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.68–7.67 (m, 2H), 7.26 (d,  $J = 8.0$  Hz, 2H), 7.18–7.14 (m, 1H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  157.4, 149.5, 138.8, 136.6, 136.5, 129.4, 126.7, 121.7, 120.1, 21.2; MS (EI)  $m/z$  169 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{11}\text{N}$  ( $\text{M}^+$ ) 169.0892. Found 169.0897.

#### 2-(4'-Methoxyphenyl)pyridine<sup>3</sup>

Colorless solid;  $^1\text{H}$  NMR  $\delta$  8.63 (d,  $J = 4.8$  Hz, 1H), 7.94 (d,  $J = 8.8$  Hz, 2H), 7.68–7.62(m, 2H), 7.15–7.11 (m, 1H), 7.02 (d,  $J = 8.8$  Hz, 2H), 3.82 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  160.4, 157.0, 149.4, 136.5, 131.9, 128.0, 121.3, 119.6, 114.0, 55.2; MS (EI)  $m/z$  185 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{11}\text{NO}$  ( $\text{M}^+$ ) 185.0841. Found 185.0838.

#### 2-(3',4'-Methylenedioxy)pyridine

Colorless oil;  $^1\text{H}$  NMR  $\delta$  8.63 (d,  $J = 4.8$  Hz, 1H), 7.68 (t,  $J = 7.4$  Hz, 1H), 7.61 (d,  $J = 7.4$  Hz, 1H), 7.52 (s, 1H), 7.48 (d,  $J = 8.4$  Hz, 1H), 7.16 (dd,  $J = 7.4$  Hz, 4.8 Hz, 1H), 6.89 (d,  $J = 8.4$  Hz, 1H), 6.00 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  156.8, 149.4, 148.4, 148.2, 136.6, 133.8, 121.6, 120.8, 119.9, 108.3, 107.3, 101.2; MS (EI)  $m/z$  199 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_9\text{NO}_2$  ( $\text{M}^+$ ) 199.0633. Found 199.0640. Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{NO}_2 \cdot 1/9 \text{H}_2\text{O}$ : C, 71.63; H, 4.62; N, 6.96. Found: C, 71.78; H, 4.59; N, 6.93.

#### 2-(4'-Chlorophenyl)pyridine<sup>3</sup>

Colorless oil;  $^1\text{H}$  NMR  $\delta$  8.69 (d,  $J = 4.0$  Hz, 1H), 7.94 (d,  $J = 8.6$  Hz, 2H), 7.75(t,  $J =$

7.6 Hz, 1H), 7.69 (d,  $J$  = 7.6 Hz, 1H), 7.45 (d,  $J$  = 8.6 Hz, 2H), 7.02 (dd,  $J$  = 7.6 Hz, 4.0 Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  156.9, 150.4, 138.5, 137.5, 135.8, 129.6, 128.8, 123.0, 121.0; MS (EI)  $m/z$  189 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_8\text{ClN}$  ( $\text{M}^+$ ) 189.0345. Found 189.0347.

**3-(4'-Methoxyphenyl)pyridine<sup>3</sup>**

Colorless solid;  $^1\text{H}$  NMR  $\delta$  8.83 (s, 1H), 8.55 (d,  $J$  = 4.7 Hz, 1H), 7.82 (d,  $J$  = 7.7 Hz, 1H), 7.50 (d,  $J$  = 8.6 Hz, 2H), 7.32 (dd,  $J$  = 4.7 Hz, 7.7 Hz, 1H), 7.00 (d,  $J$  = 8.6 Hz, 2H), 3.84 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  159.7, 147.5, 147.4, 136.3, 133.9, 130.0, 128.1, 123.5, 114.5, 55.2; MS (EI)  $m/z$  185 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{11}\text{NO}$  ( $\text{M}^+$ ) 185.0841. Found 185.0832.

**4-(4'-Methoxyphenyl)pyridine<sup>3</sup>**

Colorless solid;  $^1\text{H}$  NMR  $\delta$  8.62 (d,  $J$  = 5.8 Hz, 2H), 7.57 (d,  $J$  = 8.8 Hz, 2H), 7.45 (d,  $J$  = 5.8 Hz, 2H), 6.98 (d,  $J$  = 8.8 Hz, 2H), 3.84 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  160.5, 149.7, 147.9, 130.1, 128.0, 121.0, 114.5, 55.3; MS (EI)  $m/z$  185 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_{11}\text{NO}$  ( $\text{M}^+$ ) 185.0841. Found 185.0831.

**5-(4'-Methoxyphenyl)pyrimidine<sup>4</sup>**

Colorless solid;  $^1\text{H}$  NMR  $\delta$  9.16 (s, 1H), 8.92 (s, 2H), 7.52 (d,  $J$  = 8.4 Hz, 2H), 7.04 (d,  $J$  = 8.4 Hz, 2H), 3.87 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  160.4, 156.7, 154.3, 133.8, 128.0, 126.4, 114.8, 55.3; MS (EI)  $m/z$  186 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$  ( $\text{M}^+$ ) 186.0793. Found 186.0798.

**2-(3'-Quinolyl)benzofuran**

Colorless solid; mp 134–136 °C,  $^1\text{H}$  NMR  $\delta$  9.31 (s, 1H), 8.50 (s, 1H), 8.10 (d,  $J$  = 8.2 Hz, 1H), 7.84 (d,  $J$  = 8.2 Hz, 1H), 7.68 (t,  $J$  = 8.2 Hz, 1H), 7.60 (d,  $J$  = 7.8 Hz, 1H), 7.55–7.51 (m, 2H), 7.31 (t,  $J$  = 7.8 Hz, 1H), 7.24 (t,  $J$  = 7.8 Hz, 1H), 7.17 (s, 1H);  $^{13}\text{C}$  NMR  $\delta$  155.1, 153.1, 147.6, 147.5, 130.7, 129.7, 129.3, 128.8, 128.1, 127.7, 127.3, 125.0, 123.6, 123.3, 121.2, 111.2, 102.9; MS (EI)  $m/z$  245 ( $\text{M}^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{17}\text{H}_{11}\text{NO}$  ( $\text{M}^+$ ) 245.0841. Found 245.0835. Anal. Calcd for  $\text{C}_{17}\text{H}_{11}\text{NO}$ : C, 83.25; H, 4.52; N, 5.71. Found: C, 82.97; H, 4.77; N, 5.62.

**4-(3'-Quinolyl)dibenzofuran**

Colorless solid; mp 145–147 °C,  $^1\text{H}$  NMR  $\delta$  9.46 (s, 1H), 8.59 (s, 1H), 8.18 (d,  $J$  = 8.8 Hz, 1H), 7.93 (t,  $J$  = 6.4 Hz, 2H), 7.88 (d,  $J$  = 8.0 Hz, 1H), 7.23 (t,  $J$  = 7.4 Hz, 1H), 7.66

(d,  $J = 8.0$  Hz, 1H), 7.58–7.54 (m, 2H), 7.50–7.40 (m, 2H), 7.34 (t,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  156.0, 153.3, 150.6, 147.3, 135.0, 129.5, 129.2, 129.1, 128.0, 127.8, 127.3, 126.8, 126.5, 125.0, 123.8, 123.3, 122.8, 122.2, 120.6, 120.4, 111.7; MS (EI)  $m/z$  295 ( $M^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{21}\text{H}_{13}\text{NO}$  ( $M^+$ ) 295.0997. Found 295.0986. Anal. Calcd for  $\text{C}_{21}\text{H}_{13}\text{NO} \cdot 1/11 \text{H}_2\text{O}$ : C, 84.93; H, 4.47; N, 4.72. Found: C, 84.98; H, 4.60; N, 4.71.

### 3-(2'-Thienyl)quinoline<sup>4</sup>

Colorless solid;  $^1\text{H}$  NMR  $\delta$  9.17 (s, 1H), 8.21 (s, 1H), 8.07 (d,  $J = 8.2$  Hz, 1H), 7.77 (d,  $J = 8.2$  Hz, 1H), 7.65 (t,  $J = 8.2$  Hz, 1H), 7.51 (t,  $J = 8.2$  Hz, 1H), 7.45 (d,  $J = 3.6$  Hz, 1H), 7.35 (d,  $J = 5.2$  Hz, 1H), 7.12 (dd,  $J = 5.2$  Hz, 3.6 Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  148.6, 147.3, 140.8, 131.4, 129.3, 129.3, 128.4, 127.9, 127.8, 127.6, 127.3, 126.1, 124.4; MS (EI)  $m/z$  211 ( $M^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{13}\text{H}_9\text{NS}$  ( $M^+$ ) 211.0456. Found 211.0461.

### 2-(5'-Pyrimidyl)benzofuran<sup>5</sup>

Colorless solid;  $^1\text{H}$  NMR  $\delta$  9.15 (s, 1H), 9.10 (s, 1H), 7.57 (d,  $J = 7.8$  Hz, 2H), 7.51 (d,  $J = 7.8$  Hz, 2H), 7.32 (t,  $J = 7.8$  Hz, 1H), 7.24 (t,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR  $\delta$  157.6, 155.0, 152.4, 149.4, 128.0, 125.4, 124.6, 123.4, 121.2, 111.2, 103.9; MS (EI)  $m/z$  196 ( $M^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}$  ( $M^+$ ) 196.0637. Found 196.0642.

### 2-[2'-(5'-Methyl)thienyl]benzofuran

Colorless solid; mp 85–87 °C,  $^1\text{H}$  NMR  $\delta$  7.48 (d,  $J = 7.0$  Hz, 1H), 7.45 (d,  $J = 7.0$  Hz, 1H), 7.25 (d,  $J = 4.0$  Hz, 1H), 7.23–7.18 (m, 2H), 6.73 (s, 1H), 6.72 (d,  $J = 4.0$  Hz, 1H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  154.4, 151.5, 140.8, 130.9, 129.2, 126.1, 124.6, 123.9, 123.0, 120.5, 110.9, 100.2, 15.3; MS (EI)  $m/z$  214 ( $M^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{13}\text{H}_{10}\text{OS}$  ( $M^+$ ) 214.0452. Found 214.0444. Anal. Calcd for  $\text{C}_{13}\text{H}_{10}\text{OS}$ : C, 72.87; H, 4.70. Found: C, 72.92; H, 4.81.

### 2-(5'-Indoyl)benzofuran

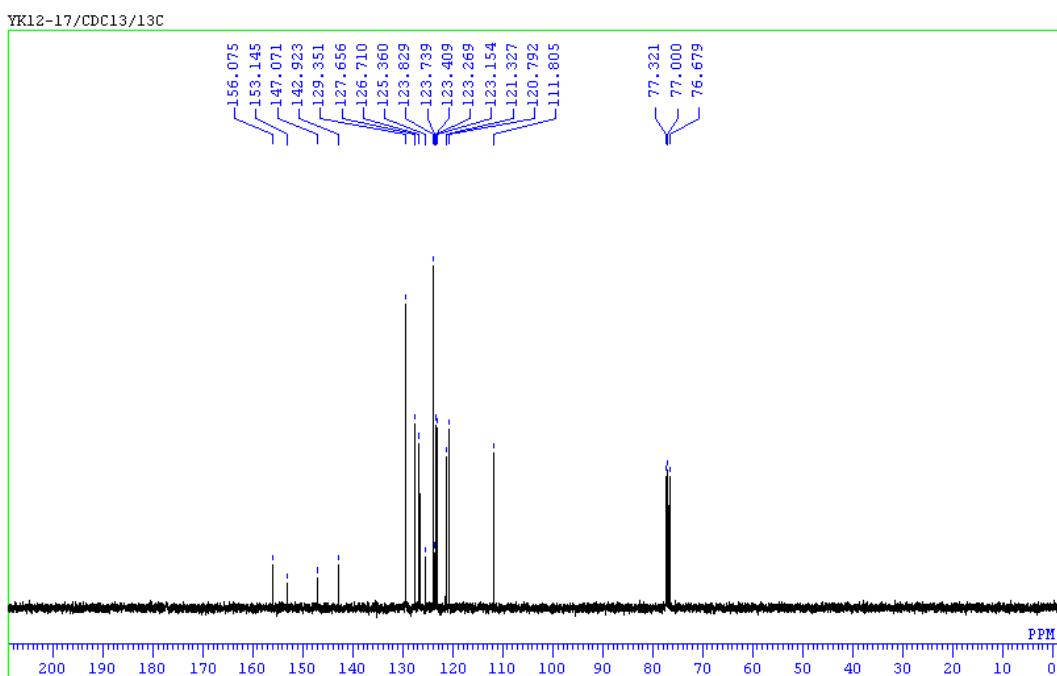
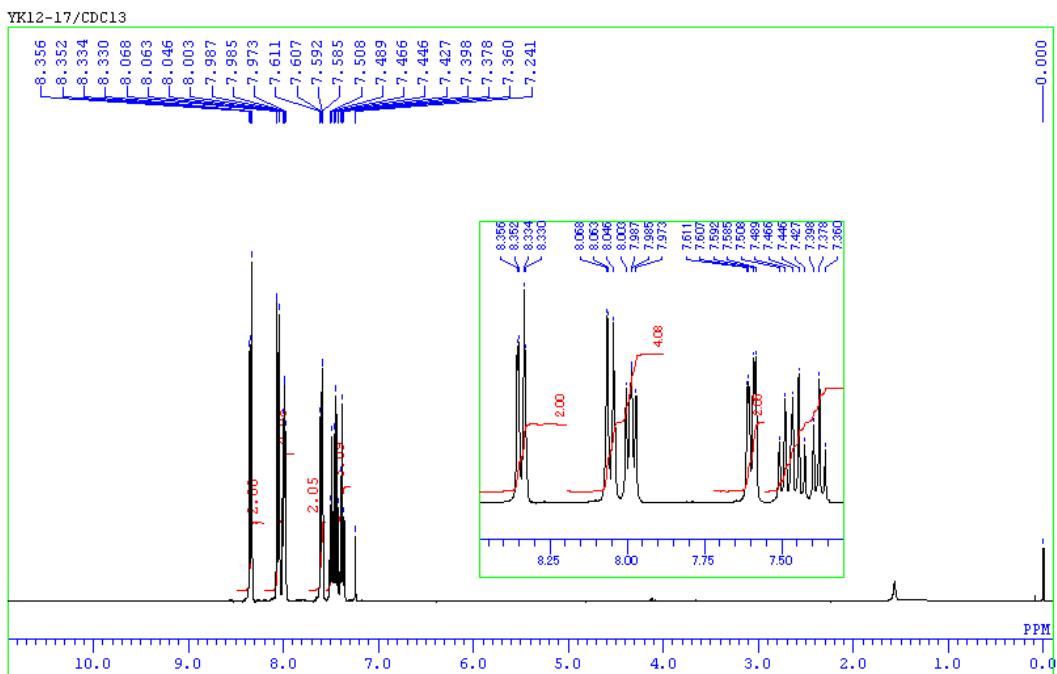
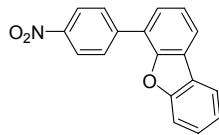
Colorless solid; mp 156–158 °C,  $^1\text{H}$  NMR  $\delta$  8.18 (s, 1H), 8.05 (brs, 1H), 7.68 (d,  $J = 8.8$  Hz, 1H), 7.54 (d,  $J = 7.2$  Hz, 1H), 7.52 (d,  $J = 7.2$  Hz, 1H), 7.35 (d,  $J = 8.8$  Hz, 1H), 7.26–7.18 (m, 3H), 7.15 (t,  $J = 7.2$  Hz, 1H), 6.93 (s, 1H), 6.60–6.59 (m, 1H);  $^{13}\text{C}$  NMR  $\delta$  157.6, 154.7, 135.9, 129.7, 128.1, 125.1, 123.5, 122.7, 122.6, 120.4, 119.7, 117.6, 111.4, 110.9, 103.3, 99.4; MS (EI)  $m/z$  233 ( $M^+$ , 100%); HRMS (EI) Calcd for  $\text{C}_{16}\text{H}_{11}\text{NO}$  ( $M^+$ ) 233.0841. Found 233.0835. Anal. Calcd for  $\text{C}_{16}\text{H}_{11}\text{NO} \cdot 1/3 \text{H}_2\text{O}$ : C,

80.32; H, 4.91; N, 5.85. Found: C, 80.46; H, 4.90, N, 5.82.

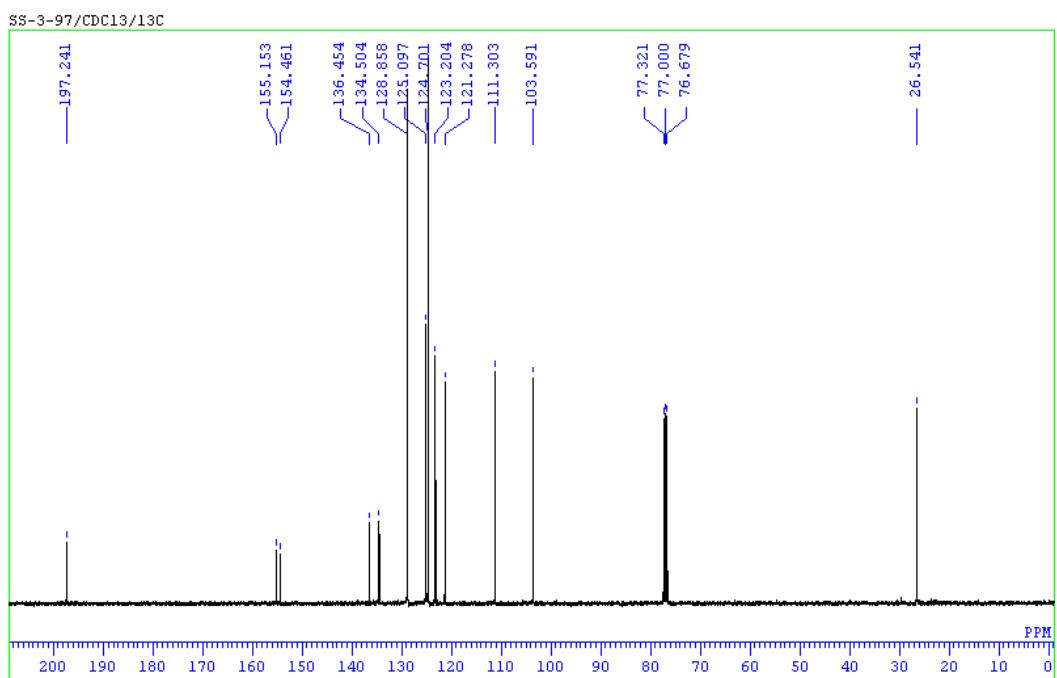
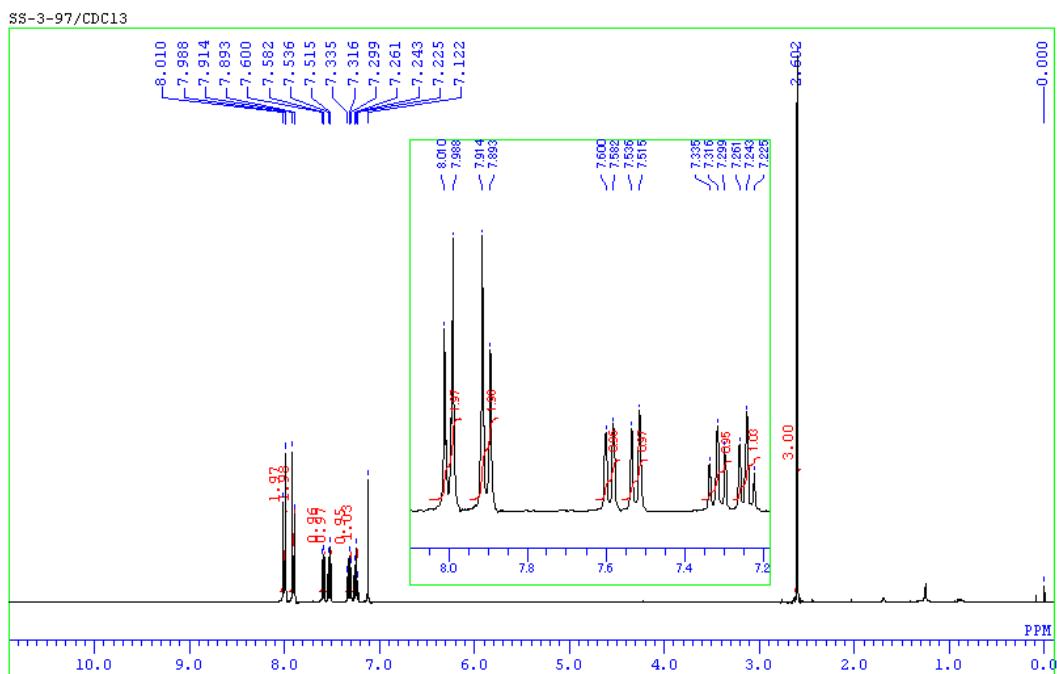
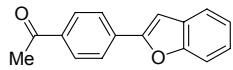
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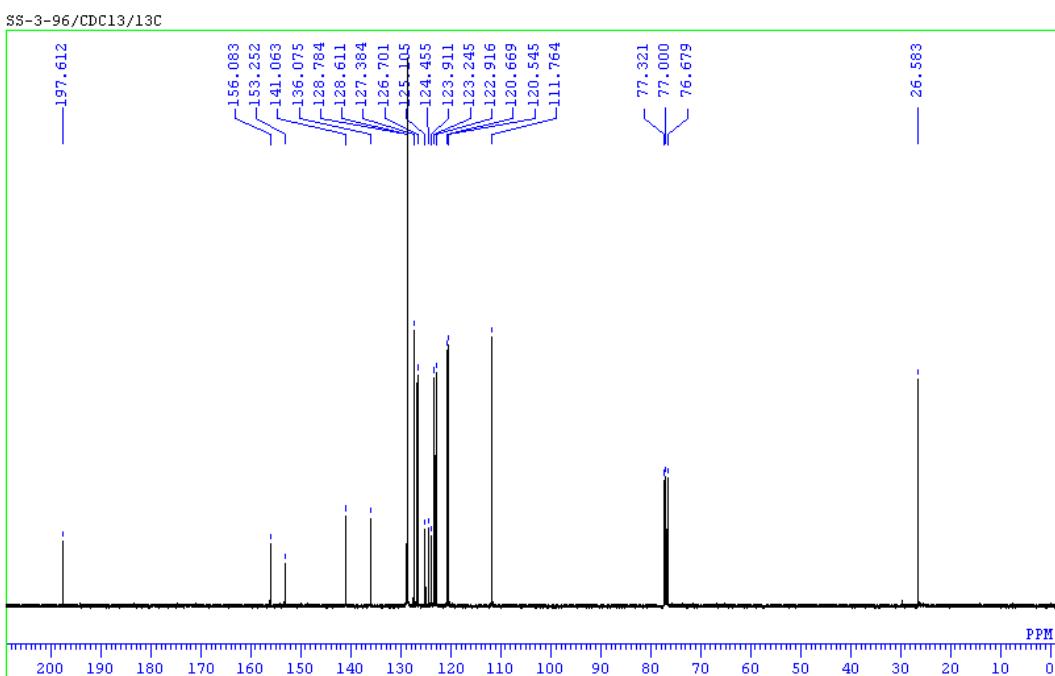
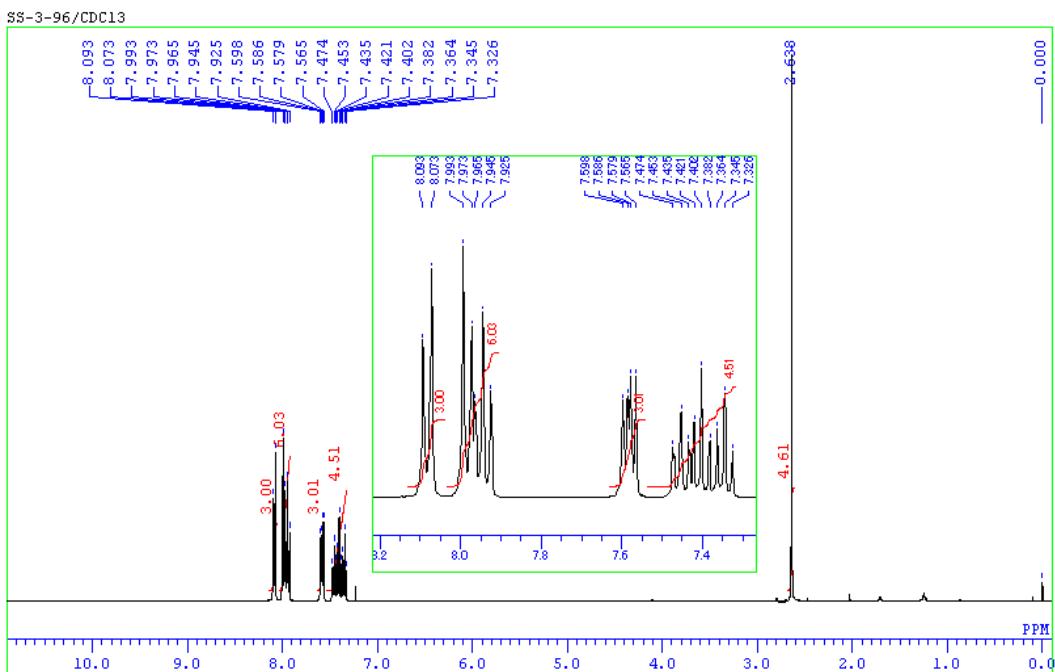
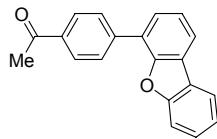
**4-(4'-Nitrophenyl)dibenzofuran**



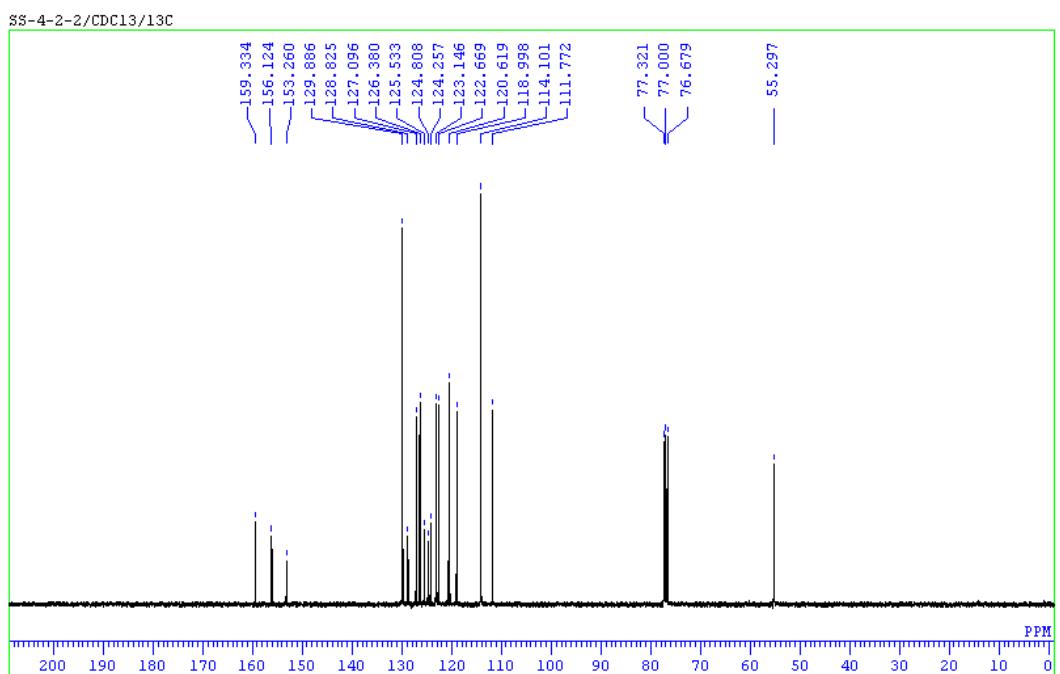
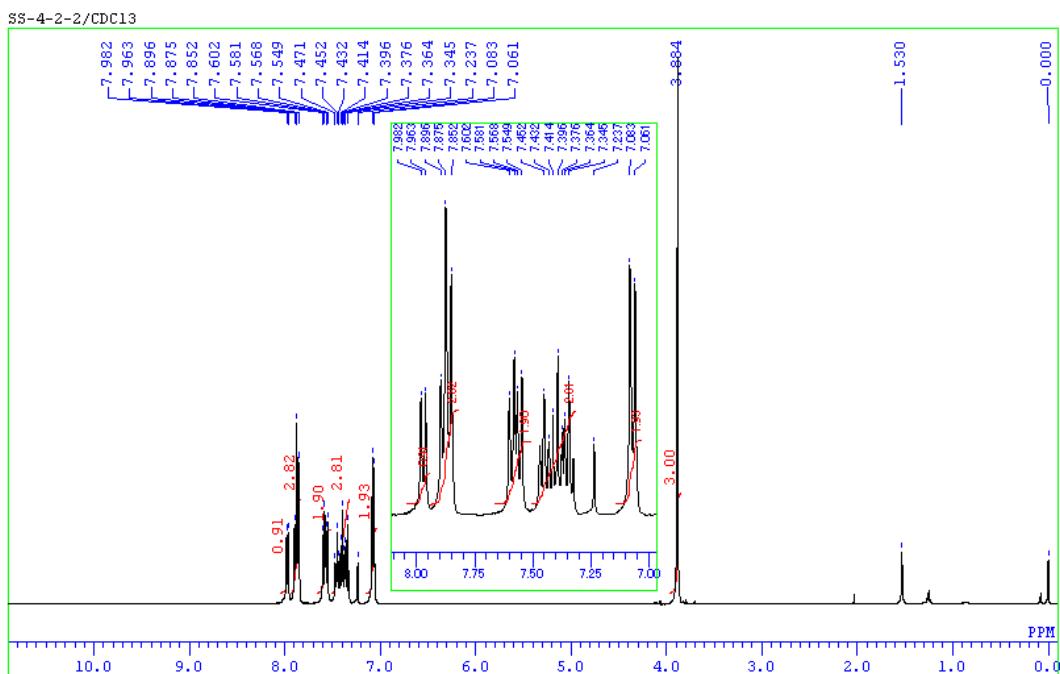
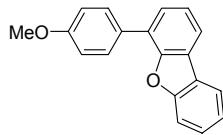
### **2-(4'-Acetylphenyl)benzofuran**



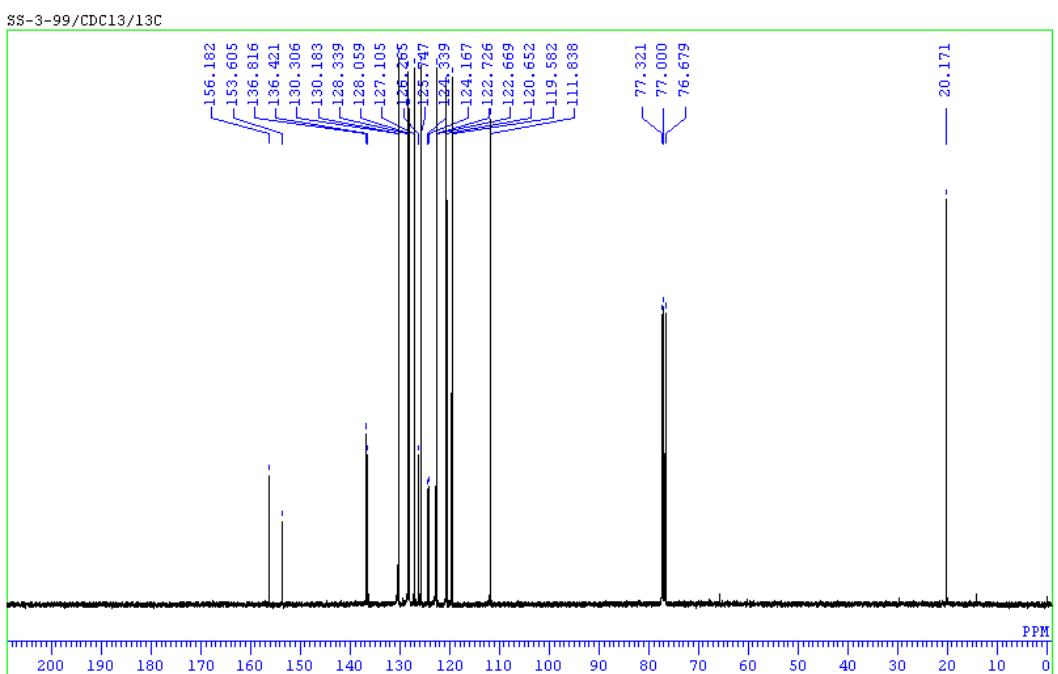
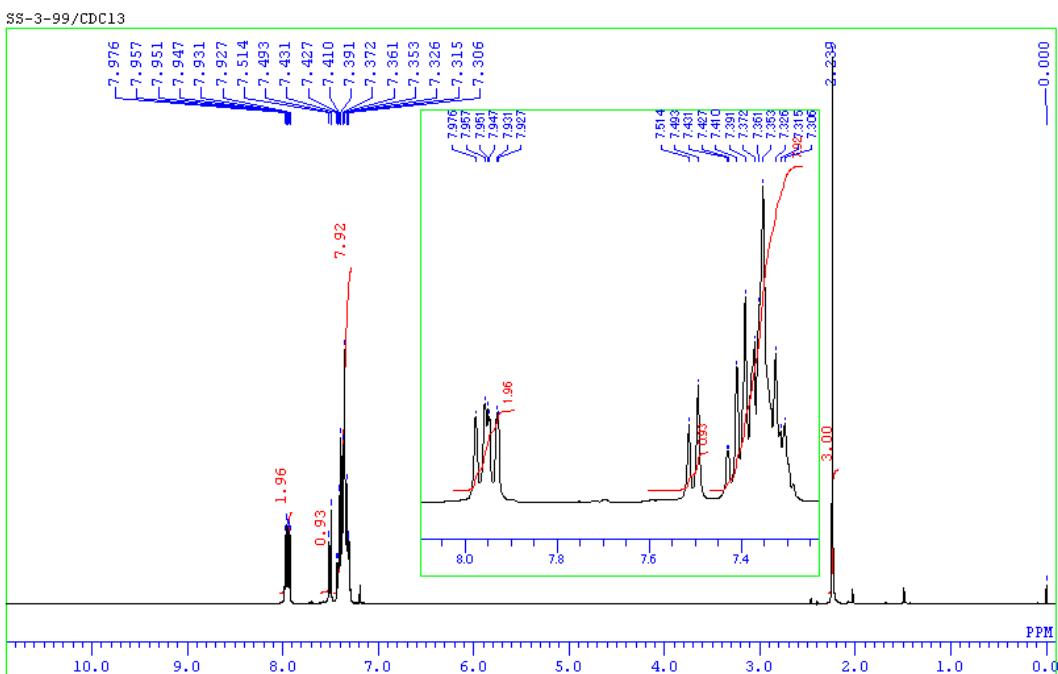
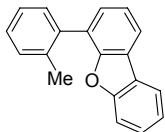
**4-(4'-Acetylphenyl)dibenzofuran**



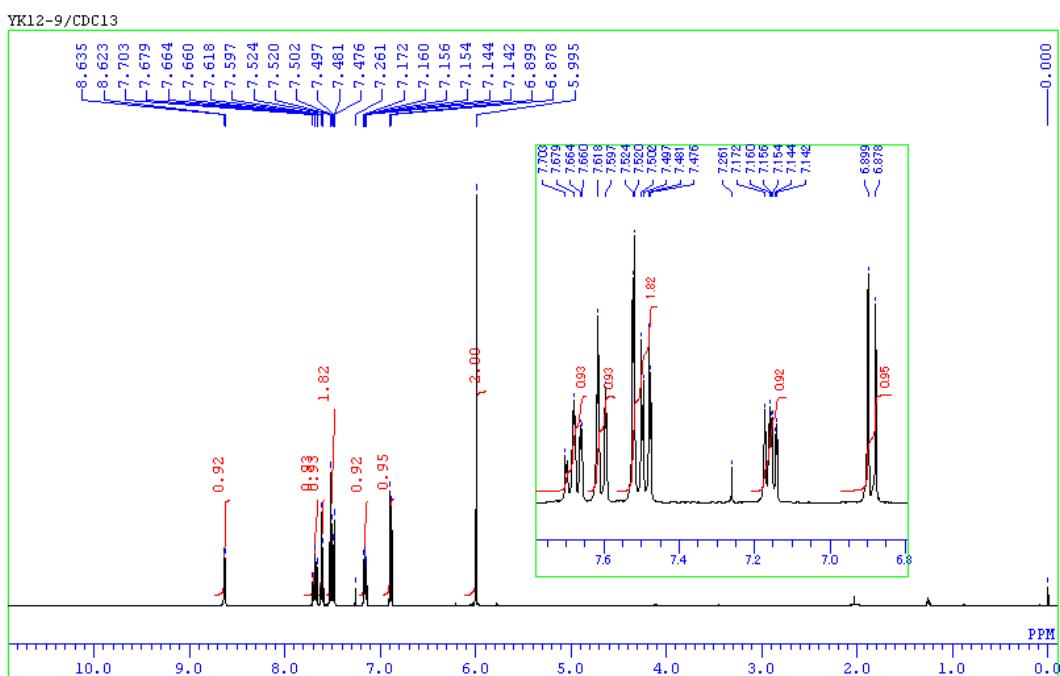
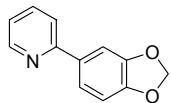
**4-(4'-Methoxyphenyl)dibenzofuran**



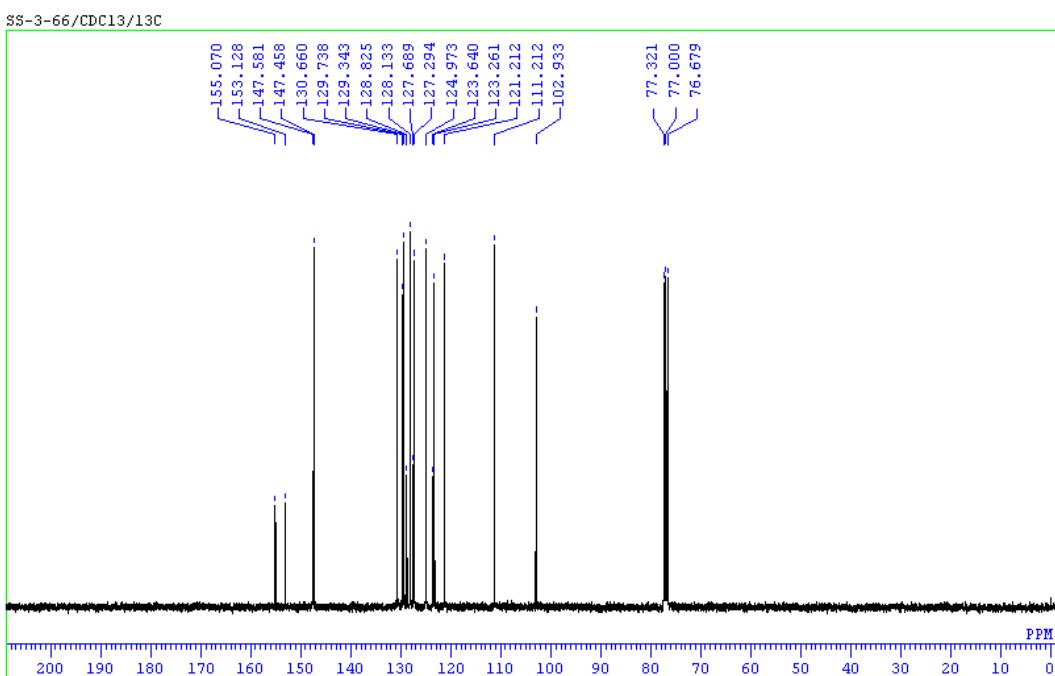
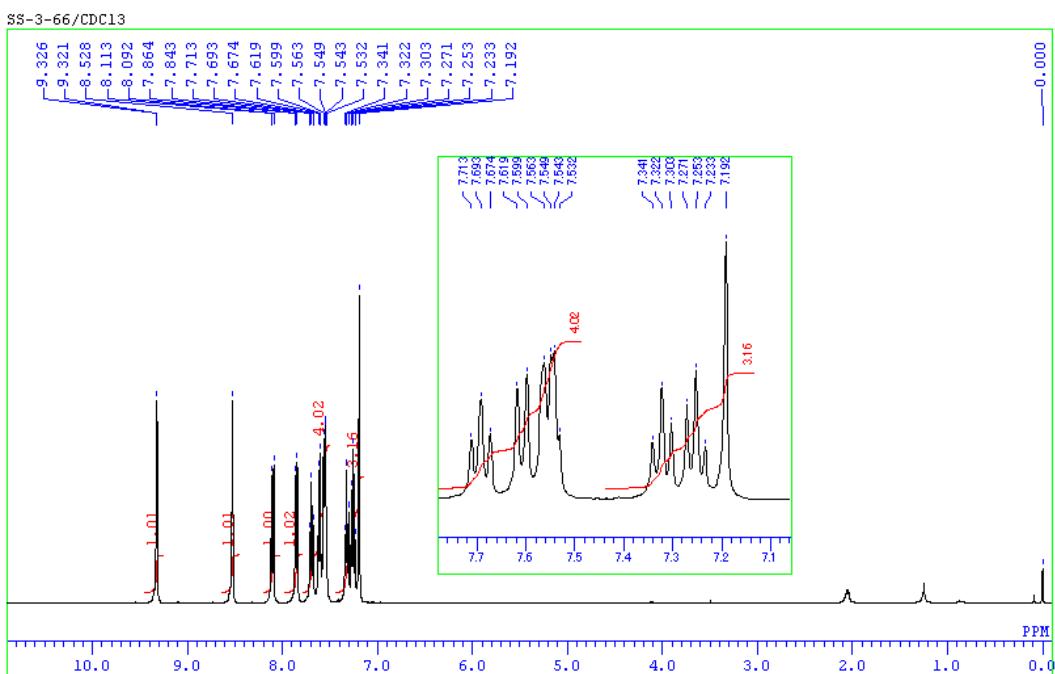
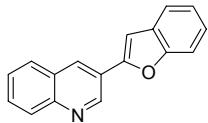
**4-(2'-Tolyl)dibenzofuran**



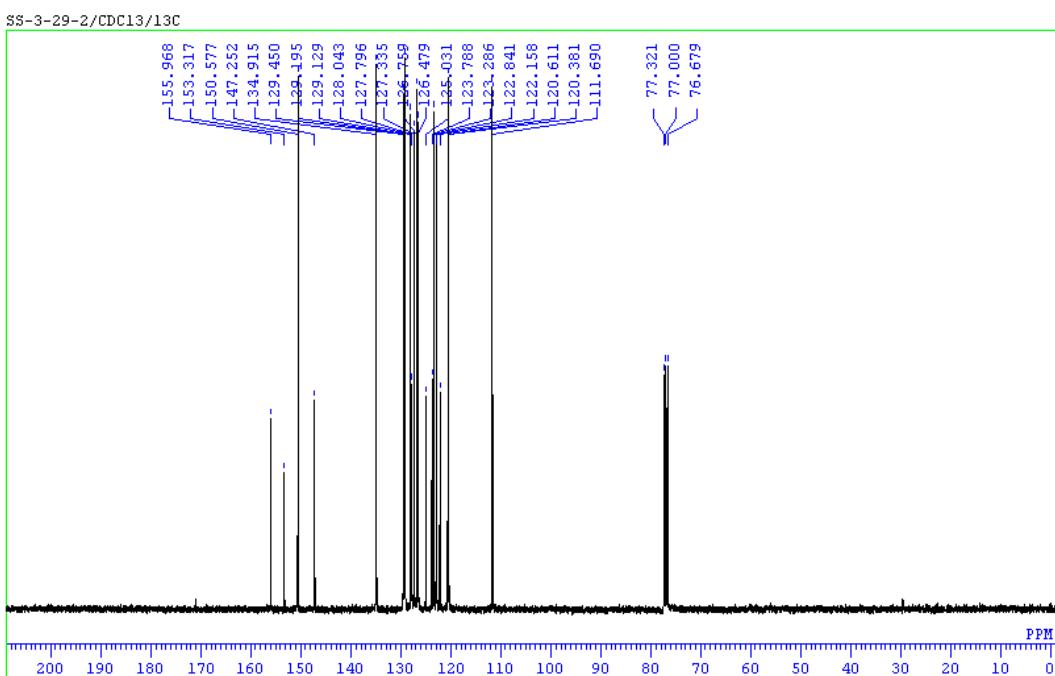
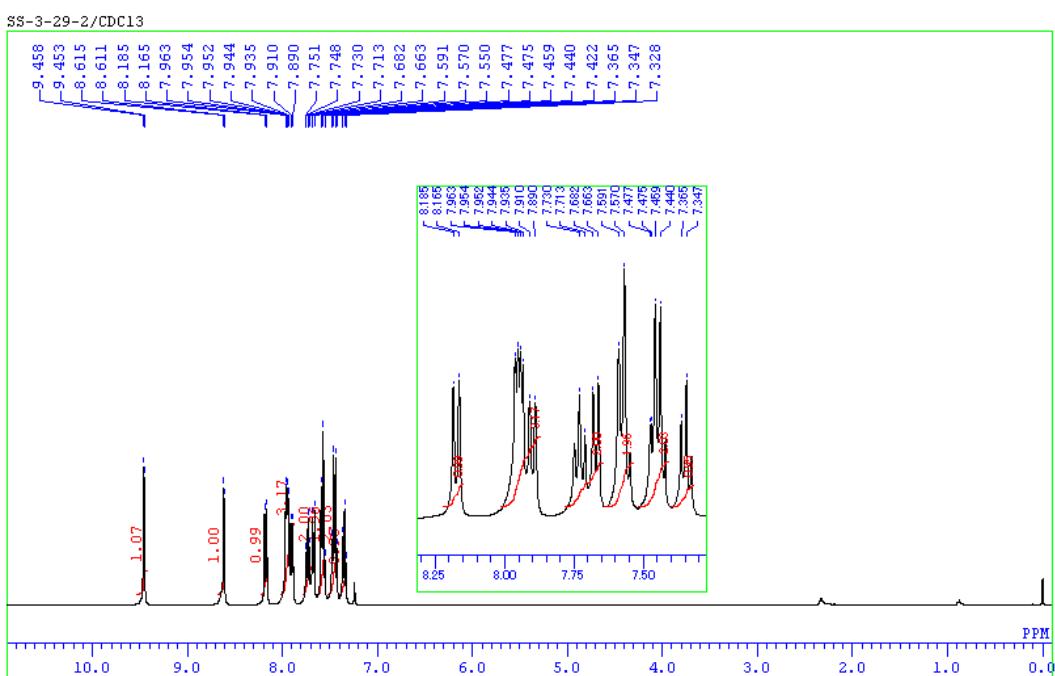
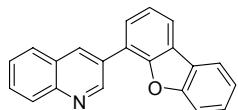
**2-(3',4'-Methylenedioxy)pyridine**



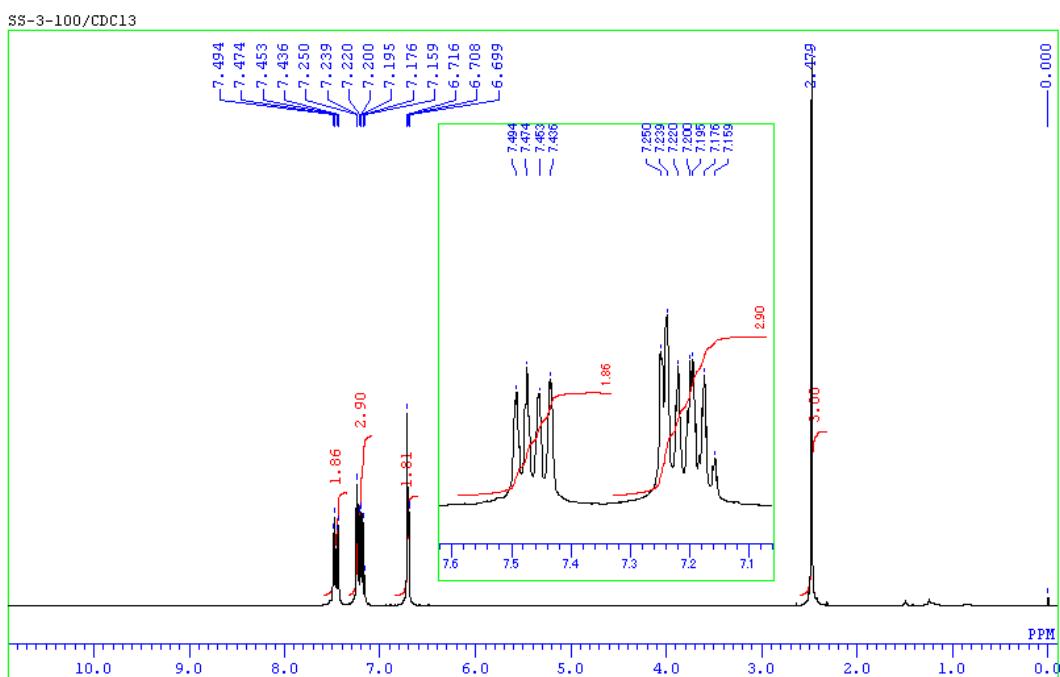
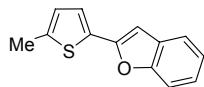
**2-(3'-Quinolyl)benzofuran**



## 4-(3'-Quinolyl)dibenzofuran



**2-[2'-(5'-Methyl)thienyl]benzofuran**



**2-(5'-Indoyl)benzofuran**

