Highly Efficient Cyanoimidation of Aldehydes

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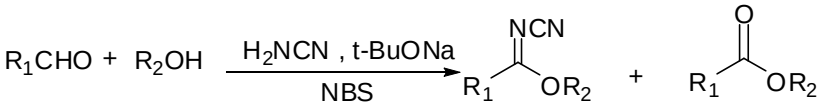
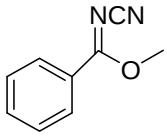
Supporting information

1. General Experimental Section

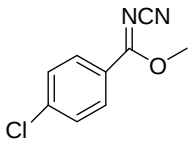
The Silica gel F_{254} plates were used for thin layer chromatography (TLC) in which the spots were examined under UV light at 254 nm and then developed by an iodine vapor. Flash chromatography was performed on silica gel H. Solvents were purified according to standard procedures. NMR spectra were recorded on Bruker AC-E 200 MHz and Varian Mercury 400 MHz spectrometer. The mass spectra (ESI / HRMS) were recorded on a Bruker Daltonics Data analysis 3.2 mass spectrometer.

2． Procedure and Characterization of Compounds



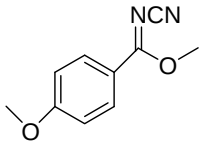


Preparation of methyl N-cyanobenzimidate(3a): To a 25 ml flask with a mixture of benzaidehyde (106 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3a**(87% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10-8.08 (d, J = 8.4Hz, 2H), 7.65-7.61 (t, J = 7.6Hz, 1H), 7.54-7.50 (t, J = 7.6Hz, 2H), 4.07(s,3H); **^{13}C NMR (400 MHz, CDCl3)** δ 175.1, 133.9, 129.5, 129.0, 128.8, 113.5, 57.0; **HRMS (ESI) Calcd for $C_9H_8N_2NaO_1$:** $[M+Na]^+$, 183.0529.**Found:** m/z 183.0524.

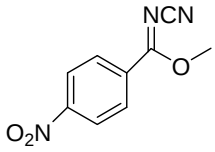


Preparation of methyl 4-chloro-N-cyanobenzimidate (3b): To a 25 ml flask with a mixture of 4-chlorobenzaldehyde (140 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and t-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The

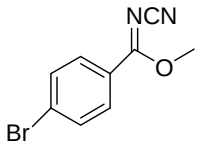
mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3b**(85% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06-8.04 (d, J = 8.4Hz, 2H),7.50-7.48 (d, J = 8.4Hz, 2H),4.06 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.6, 140.4, 130.1, 129.3, 127.6, 113.1, 57.0; **HRMS (ESI) Calcd $C_9H_8Cl_1N_1O_2$ for :**$[M]^+$ 195.0320. **Found:** m/z 195.0312.



Preparation of methyl N-cyano-4-methoxybenzimidate (3c): To a 25 ml flask with a mixture of 4-methoxybenzaldehyde (136 mg, 1mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 6 h at room temperature. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-20:1) as eluent to give **3c**(82% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17-8.15 (d, J = 8.8Hz, 2H), 6.99-6.97 (d, J = 8.8Hz, 2H), 4.03 (s, 3H), 3.89 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.7, 163.9, 131.1, 121.6, 114.1, 113.9, 56.5, 55.6; **HRMS (ESI) Calcd for $C_{10}H_{10}N_1Na_1O_2$:**$[M+Na]^+$, 213.0634.**Found:** m/z 213.0647.

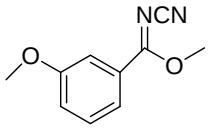


Preparation of methyl N-cyano-4-nitrobenzimidate (3d): To a 25 ml flask with a mixture of 4-nitrobenzaldehyde (151 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml), then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (50:1-10:1) as eluent to give **3d**(67% yield) .**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39-8.37 (d, J = 8.8Hz, 2H), 8.27-8.24 (d, J = 8.8Hz, 2H), 4.15 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.0, 150.4, 134.3, 130.0, 124.0, 112.4, 57.6; **HRMS (ESI) Calcd for $C_9H_7N_3Na_1O_3$:**$[M+Na]^+$, 228.0380.**Found:** m/z 228.0374.

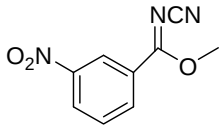


Preparation of methyl 4-bromo-N-cyanobenzimidate (3e): To a 25 ml flask with a mixture of 4-bromobenzaldehyde (185 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and t-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature,

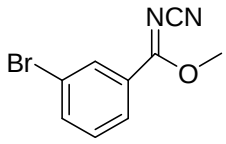
then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3e** (76% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99-7.97 (d, J =8.4 Hz, 2H), 7.68-7.66 (d, J = 8.4Hz, 2H), 4.06 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.7, 132.3, 130.1, 129.0, 128.1, 113.0, 57.0; **HRMS (ESI) Calcd for $C_9H_7N_2NaO_1$:** $[M+Na]^+$, 260.9634.**Found:** m/z 260.9634.



Preparation of methyl N-cyano-3-methoxybenzimidate (3f): To a 25 ml flask with a mixture of 3-methoxybenzaldehyde (136 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-30:1) as eluent to give **3f**(58% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69-7.67 (d, J = 8.0Hz, 1H), 7.57(s,1H), 7.44-7.40 (t, J = 8.0Hz, 1H), 7.17-7.14(m, 1H), 4.05 (s, 3H), 3.87 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ174.7, 159.7, 130.4, 130.0, 121.0, 120.2, 113.3, 112.8, 56.8, 55.6; **HRMS (ESI) Calcd for $C_{10}H_{10}N_2Na_1O_2$:**$[M+Na]^+$, 213.0634.**Found:** m/z 213.0643.

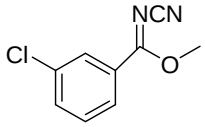


Preparation of methyl N-cyano-3-nitrobenzimidate (3g): To a 25 ml flask with a mixture of 3-nitrobenzaldehyde (151 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml), then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (50:1-20:1) as eluent to give **3g**(72% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.82-8.81 (t, J = 2.0Hz, 1H), 8.58-8.56 (d, J = 8.0Hz, 1H), 8.51-8.48 (m, 1H), 7.79-7.75 (t, J = 8.0Hz, 1H), 4.16 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ172.4, 148.3, 134.2, 130.7, 130.4, 128.0, 123.8, 112.4, 57.6; **HRMS (ESI) Calcd for $C_9H_7N_3Na_1O_3$:**$[M+Na]^+$, 228.0380.**Found:** m/z 228.0386.

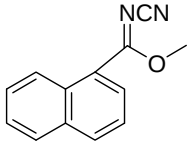


Preparation of methyl 3-bromo-N-cyanobenzimidate (3h): To a 25 ml flask

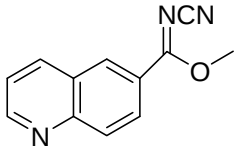
with a mixture of 3-bromobenzaldehyde (185 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3h**(94% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.14-8.11 (m, 2H), 7.77-7.75 (m, 1H), 7.43-7.39(t, J = 8.0Hz, 1H), 4.08 (s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ173.2, 136.7, 131.5, 131.0, 130.4, 127.3, 122.9, 112.7, 57.1; **HRMS (ESI) Calcd for $C_9H_7Br_1N_2Na_1O_1$:**$[M+Na]^+$, 260.9634.**Found:** m/z 260.9643.



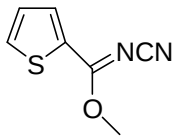
Preparation of methyl 3-chloro-N-cyanobenzimidate (3i): To a 25 ml flask with a mixture of 3-chlorobenzaldehyde (140 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3i**(83% yield).**^{1}H NMR (400 MHz, d_6-DMSO)** δ 7.97 (s, 1H), 7.95-7.93 (d, J = 8.0Hz, 1H), 7.81-7.79(d, J = 8.0Hz, 1H), 7.67-7.63(t, J = 8.0Hz, 1H); **^{13}C NMR (400 MHz, d_6-DMSO)** δ174.9, 134.0, 133.9, 131.6, 131.4, 128.6, 127.5, 113.4, 58.0; **HRMS (ESI) Calcd for $C_9H_7Cl_1N_2Na_1O_1$:**$[M+Na]^+$, 217.0139.**Found:** m/z 217.0129.



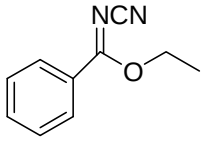
Preparation of methyl N-cyano-1-naphthimidate (3j): To a 25 ml flask with a mixture of 1-naphthaldehyde (140mg, 1 mmol) and H_2NCN (156 mg, 3 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3j**(76% yield).**^{1}H NMR (400 MHz, d_6-DMSO)** δ 8.24-8.22 (d, J = 8.0Hz, 1H), 8.10-8.09 (d, J = 6.8Hz, 1H), 7.88(s, 2H), 7.68(s, 3H), 4.20(s, 3H); **^{13}C NMR (400 MHz, d_6-DMSO)** δ 180.3, 133.4, 132.8, 129.2, 128.8, 128.6, 128.5, 127.6, 127.5, 125.5, 124.7, 113.6, 58.3; **HRMS (ESI) Calcd for $C_{13}H_{10}N_2Na_1O_1$:** $[M+Na]^+$, 233.0685.**Found:** m/z 233.0692.



Preparation of methyl N-cyanoquinoline-6- carbimidate(3k): To a 25 ml flask with a mixture of quinoline-6-carbaldehyde (157 mg, 1 mmol) and H_2NCN (156 mg, 3 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 2 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (20:1-5:1) as eluent to give **3k**(80% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.10-9.06 (m, 1H), 8.79-8.78 (d, J = 1.6Hz, 1H), 8.35-8.30(m, 1H), 8.28-8.22(m, 2H), 7.56-7.53(q, J = 4.0Hz, 1H), 4.15(s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 174.1, 153.3, 149.8, 137.7, 130.7, 130.5, 127.6, 122.5, 113.2, 57.2; **HRMS (ESI) Calcd for $C_{13}H_9N_3O_1$:**$[M]^+$, 212.0818.**Found:** m/z 212.0831.

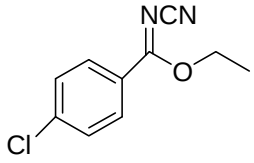


Preparation of methyl N-cyanothiophene-2-carbimidate (3l): To a 25 ml flask with a mixture of thiophene-2-carbaldehyde (112 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3l**(49% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59-8.58 (dd, J_1 = 4.0Hz, J_2 = 1.2Hz, 1H), 7.71-7.10 (dd, J_1 = 4.8Hz, J2 = 1.2Hz, 1H), 7.23-7.21 (m, 1H), 4.03(s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 168.1, 135.3, 134.2, 131.3, 128.7, 113.5, 56.6; **HRMS (ESI) Calcd for $C_7H_7N_2O_1S_1$:**$[M]^+$, 167.0274.**Found:** m/z 167.0266.

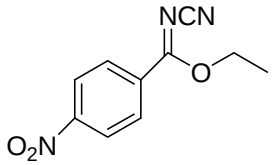


Preparation of ethyl N-cyanobenzimidate (3m): To a 25 ml flask with a mixture of benzaidehyde (106 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in EtOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3m**(74% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08-8.07 (d, J = 5.2Hz, 2H), 7.63-7.61 (t, J = 5.2Hz, 1H), 7.53-7.50 (t, J = 5.2Hz, 2H), 4.50-4.47(q, J = 4.8Hz, 2H), 1.47-1.45(t, J = 4.8Hz, 3H);

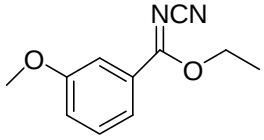
^{13}C NMR (400 MHz, $CDCl_3$) δ 174.5, 133.6, 129.6, 128.8, 128.6, 113.6, 66.3, 13.8; **HRMS (ESI) Calcd for $C_{10}H_{10}N_2Na_1O_1$:**$[M+Na]^+$, 197.0685.**Found:** m/z 197.0699.



Preparation of ethyl 4-chloro-N-cyanobenzimidate (3n): To a 25 ml flask with a mixture of 4-chlorobenzaldehyde (140 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in EtOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3n**(79% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07-8.03 (dt, J_1 = 9.2Hz, J_2 = 2.4Hz, 2H), 7.51-7.47 (dt, J_1 = 9.2Hz, J_2 = 2.4Hz, 2H), 4.52-4.46(q, J = 7.2Hz, 2H), 1.48-1.45(t, J = 7.2Hz, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.2, 140.2, 130.1, 129.2, 127.9, 113.3, 66.5, 13.8; **HRMS (ESI) Calcd for $C_{10}H_9Cl_1N_2Na_1O_1$:**$[M+Na]^+$, 231.0296.**Found:** m/z 231.0286.

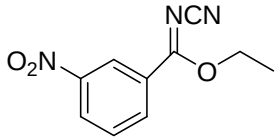


Preparation of ethyl N-cyano-4-nitrobenzimidate (3p): To a 25 ml flask with a mixture of 4-nitrobenzaldehyde (151mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in EtOH (8 ml), then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (50:1-20:1) as eluent to give **3p**(84% yield).**^{1}H NMR (400 MHz, d_6-DMSO)** δ 8.45-8.42 (d, J = 8.4Hz, 2H), 8.19-8.17 (d, J = 8.4Hz, 2H), 4.54-4.49 (q, J = 6.8Hz, 2H), 1.43-4.39 (t, J = 6.8Hz, 3H); **^{13}C NMR (200 MHz, d_6-DMSO)** δ 174.2, 150.1, 135.0, 130.2, 124.1, 113.0, 57.4, 13.9; **HRMS (ESI) Calcd for $C_{10}H_9N_3Na_1O_3$:**$[M+Na]^+$, 242.0536.**Found:** m/z 242.0528.

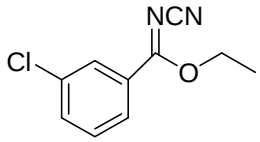


Preparation of ethyl N-cyano-3-methoxybenzimidate (3q): To a 25 ml flask with a mixture of 3-methoxybenzaldehyde (136 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in EtOH (8 ml),the mixture was stirred for 0.5h at room

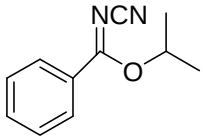
temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 24h at room temperature. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-30:1) as eluent to give **3q**(77% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68-7.66(d, J = 8.0Hz, 1H), 7.57-7.56(t, J = 2.0Hz, 1H), 7.44-7.40(t, J = 8.0Hz, 1H), 7.17-7.14(m,1H), 4.51-4.45(q, J = 7.2Hz, 2H), 1.48-1.44(t, J = 7.2Hz, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 174.3, 159.7, 130.7, 129.9, 121.0, 120.0, 113.5, 113.4, 66.3, 55.6, 13.8; **HRMS (ESI) Calcd for $C_{11}H_{12}N_2Na_1O_2$:**$[M+Na]^+$, 227.0791.**Found:** m/z 227.0784.



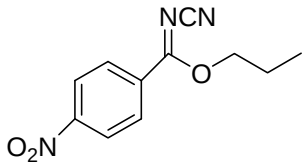
Preparation of ethyl N-cyano-3-nitrobenzimidate (3r): To a 25 ml flask with a mixture of 3-nitrobenzaldehyde (151 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in EtOH (8 ml), then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (50:1-20:1) as eluent to give **3r**(81% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.81-8.80(t, J = 2.0Hz, 1H), 8.55-8.52(m,1H), 8.50-8.47(m, 1H), 7.80-7.76(t, J = 8.0Hz, 1H), 4.61-4.56(q, J = 7.2Hz, 2H), 1.54-1.51(t, J = 7.2Hz, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 171.9, 148.3, 134.2, 131.0, 130.3, 127.9, 123.8, 112.6, 67.3, 13.8; **HRMS (ESI) Calcd for $C_{10}H_9N_3Na_1O_3$:**$[M+Na]^+$, 242.0536.**Found:** m/z 242.0540.



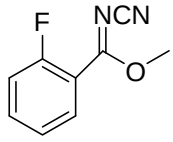
Preparation of ethyl 3-chloro-N-cyanobenzimidate (3s): To a 25 ml flask with a mixture of 3-chlorobenzaldehyde (140 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in EtOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3s**(92% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07-8.05(d, J = 8.0Hz, 1H), 7.96-7.95(t, J = 2.0Hz, 1H), 7.61-7.59 (dt,J_1 = 8.0Hz, J_2 = 0.8Hz, 1H), 7.49-7.45(t, J = 8.0Hz, 1H), 4.53-4.47(q, J = 7.2Hz, 2H), 1.49-1.45(t, J = 7.2Hz, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 172.9, 135.1, 133.7, 131.1, 130.2, 128.6, 126.8, 113.0, 66.7,13.8; **HRMS(ESI) Calcd for $C_{10}H_9Cl_1N_2Na_1O_1$:** $[M+Na]^+$, 231.0296.**Found:** m/z 231.0308.



Preparation of isopropyl N-cyanobenzimidate (3t): To a 25 ml flask with a mixture of benzaldehyde (106 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in i-PrOH(8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 24 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-50:1) as eluent to give **3t** (20% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06-8.03(m, 2H), 7.64-7.59(m, 1H), 7.54-7.49(m, 2H); **HRMS (ESI) Calcd for $C_{11}H_{12}N_2Na_1O_1$:**$[M+Na]^+$, 211.0842.**Found:** m/z 211.0838.

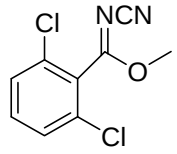


Preparation of propyl N-cyano-4- nitrobenzimidate (3u): To a 25 ml flask with a mixture of 4-nitrobenzaldehyde (140 mg, 1 mmol) and H_2NCN (168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) in n-PrOH(8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-10:1) as eluent to give **3u**(51% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.38-8.36(m, 2H), 8.25-8.22(m, 2H), 4.47-4.44 (t, 2H, J = 6.8Hz), 1.94-1.85(m, 2H), 1.09-1.05(t, 3H, J = 7.2Hz); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 172.5, 150.4, 134.7, 129.9, 124.0, 112.6, 72.8, 21.6, 10.4; **HRMS (ESI) Calcd for $C_{11}H_{11}N_3Na_1O_3$:**$[M+Na]^+$, 256.0693.**Found:** m/z 256.0697.

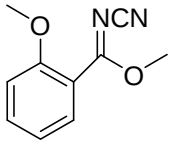


Preparation of methyl N-cyano-2-fluorobenzimidate (3v): To a 25 ml flask with a mixture of 2-fluorobenzaldehyde (124 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (50:1) as eluent to give **3v**(90% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63-7.53 (m, 2H), 7.28-7.18 (m, 2H), 4.06(s,3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 174.7, 160.6, 158.0, 134.8, 134.7, 129.6, 124.6, 124.5,

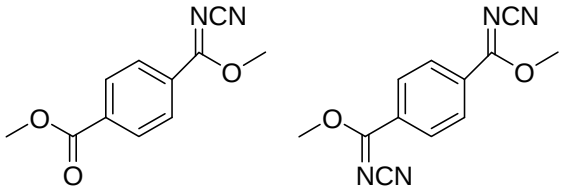
118.6, 118.5, 117.1, 116.8, 112.7, 57.3; **HRMS (ESI) Calcd for $C_9H_8F_1N_2O_1$:** $[M]^+$, 179.0615.**Found:** m/z 179.0624.



Preparation of methyl 2,6-dichloro-N-cyanobenzimidate (3w): To a 25 ml flask with a mixture of 2,6-dichlorobenzaldehyde (174 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1-25:1) as eluent to give **3v**(84% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.41 (t, 3H), 4.14(s,3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 175.6, 132.7,132.3, 130.6, 128.3, 111.8, 57.6 ; **HRMS (ESI) Calcd for $C_9H_7Cl_2N_2O_1$:** $[M]^+$, 228.9930.**Found:** m/z 228.9922.

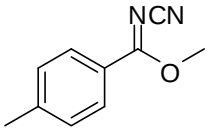


Preparation of methyl N-cyano- 2-methoxybenzi- midate (3x): To a 25 ml flask with a mixture of 2-methoxybenzaldehyde (136 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv.) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (40:1) as eluent to give **3x**(85% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54-7.49 (m, 1H), 7.40-7.38(dd, 1H, J_1 = 8.0Hz, J_2 = 2.0Hz), 7.04-7.01(m, 2H),4.04(s, 3H), 3.94(s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 177.1, 157.1, 133.9, 129.1, 120.5, 119.7, 113.4, 112.0, 56.8, 55.8; **HRMS (ESI) Calcd for $C_{10}H_{10}N_2Na_1O_2$:** $[M+Na]^+$, 213.0634.**Found:** m/z 213.0633.

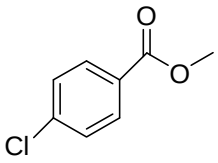


Preparation of methyl 4-(N-cyano(methoxy) carbonoimidoyl) benzoate (3I) and methyl 4-(N-cyano(methoxy) carbonoimidoyl) N-cyanobenzimidate(4I): To a 25 ml flask with a mixture of terephthalaldehydee (134 mg, 1 mmol) and H_2NCN(264 mg, 6 equiv) and *t*-BuONa (576 mg,6 equiv) in MeOH (16 ml),the mixture was stirred for 0.5h at room temperature, then NBS (1068 mg, 3 equiv.) was added. The

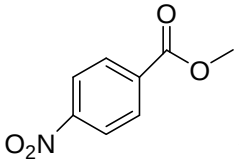
resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (20:1-5:1) as eluent to give **3I** (37% yield) and **4I** (40% yield). **3I ^{1}H NMR (400 MHz, d_6-DMSO)** δ 8.16-8.14(d, J = 8.4Hz, 2H), 8.09-8.07(d, J = 8.4Hz, 2H), 4.08(s, 3H), 3.91(s, 3H); **^{13}C NMR (400 MHz, d_6-DMSO)** δ 175.7, 165.7, 134.1, 133.6, 130.0, 129.3, 128.9, 127.5, 113.4, 58.1, 53.1; **HRMS (ESI) Calcd for $C_{11}H_{10}N_2Na_1O_3$:** $[M+Na]^+$, 241.0584.**Found:** m/z 241.0594. **4I ^{1}H NMR (400 MHz, d_6-DMSO)** δ 8.14(s, 4H), 4.08(s, 6H); **^{13}C NMR (400 MHz, d_6-DMSO)** 179.9, 133.7, 129.3, 113.4, 58.2; **HRMS (ESI) Calcd for $C_{12}H_{10}N_4Na_1O_2$:** $[M+Na]^+$,265.0696. .**Found:** m/z 265.0693.



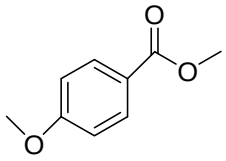
Preparation of methyl N-cyano-4-methylbenzimidate (3II): To a 25 ml flask with a mixture of 4-methylbenzaldehyde (120 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa (388 mg,4 equiv) in MeOH (8 ml),the mixture was stirred for 0.5h at room temperature, then NBS (708 mg, 4 equiv) was added. The resulting mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (30:1) as eluent to give **3II** (72% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02-8.00 (d, 2H, J = 8.0Hz), 7.32-7.30(d, 2H, J = 8.0Hz), 4.04(s, 3H), 2.43(s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.6, 143.8, 128.5, 127.7, 125.5, 112.5, 55.6, 20.7.



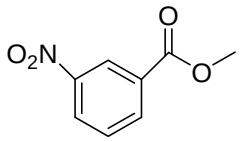
Preparation of methyl 4-chlorobenzoate (4b)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (d, 2H, J = 8.4Hz), 7.43-7.41(d, 2H, J = 8.4Hz), 3.92(s, 3H);**^{13}C NMR (400 MHz, $CDCl_3$)** δ 166.2, 139.4, 131.0, 128.7, 128.6, 52.3.



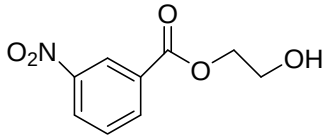
Preparation of methyl 4-methoxybenzoate (4d) [2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.29m (d, 2H, J = 8.8Hz), 8.23-8.21(d, 2H, J = 8.8Hz), 3.99(s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 165.2, 150.5, 135.5, 130.7, 123.5, 52.8.



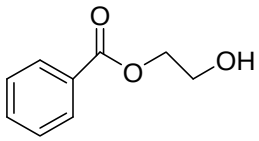
Preparation of methyl 4-nitrobenzoate (4f) [2]**:** **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00-7.98(d, 2H, J = 8.8Hz), 6.93-6.90(d, 2H, J = 8.8Hz);**^{13}C NMR (400 MHz, $CDCl_3$)** δ 179.2, 166.8, 163.3, 131.6, 113.6, 55.4, 51.8.



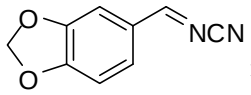
Preparation of methyl 3-nitrobenzoate (4g) [3]**: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87(s, 1H), 8.44-8.37(m, 2H), 7.69-7.65(t, 1H, J = 8.0Hz), 4.00(s, 3H);**^{13}C NMR (400 MHz, $CDCl_3$)** δ 164.9, 148.3, 135.2, 131.9, 129.6, 127.4, 124.6, 52.8.



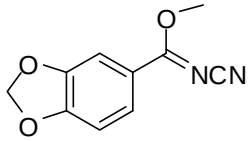
Preparation of 2-hydroxyethyl 3-nitrobenzoate (4y) [4] **:**To a 25 ml flask with a mixture of 4-nitrobenzaldehyde (151 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) and NBS (708 mg, 4 equiv.) was added in glycol (8 ml), The mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10:1-5:1) as eluent to give **4y**(67% yield).**^{1}H NMR (400 MHz, d_6-DMSO)** δ 8.37-8.35(d, 2H, J = 8.8Hz), 8.24-8.22(d, 2H, J = 8.8Hz),5.01-4.99(t, 1H, J = 5.6Hz) 4.36-4.34(t, 2H, J = 5.2Hz),3.76-3.72(q, 2H, J =5.2Hz);**^{13}C NMR (400 MHz, d_6-DMSO)** δ 164.9, 150.7, 135.7, 131.2, 124.3, 67.9, 57.4.



Preparation of 2-hydroxyethyl benzoate (4z)[5]**:** To a 25 ml flask with a mixture of benzaidehyde (106 mg, 1 mmol) and H_2NCN(168 mg, 4 equiv) and *t*-BuONa(388 mg,4 equiv) and NBS (708 mg, 4 equiv.) was added in glycol (8 ml), The mixture was stirred for 12 h at 50°C. The mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10:1-5:1) as eluent to give **4z**(68% yield).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.08-8.06(d, 2H, J = 7.2Hz), 7.60-7.56(t, 1H, J = 7.2Hz),7.47-7.43(t, 2H, J = 7.2Hz) 4.47-4.46(t, 2H, J = 8.4Hz),3.98-3.96(t, 2H, J = 8.4Hz), 2.04(br, 1H);**^{13}C NMR (400 MHz, $CDCl_3$)** δ 167.0, 133.2, 129.9, 129.7, 128.4, 66.6, 61.2.

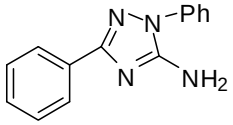


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84, 7.44-7.43(d, 1H, J = 1.6Hz), 7.38-7.35(dd, 1H, J_1 = 8.0Hz, J_2 = 1.6Hz), 6.95-6.93(d, 1H, 8.0Hz), 6.13(s, 2H); **HRMS (ESI) Calcd for $C_9H_6N_2O_2$:** $[M+Na]^+$ 197.0321.**Found:** m/z 197.0322.

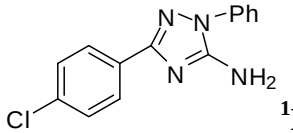


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83(dd, 1H, J_1 = 8.4Hz, J_2 = 2.0Hz), 7.54-7.53(d, 1H, J = 2.0Hz), 6.92-6.90(d, 1H, J = 8.4Hz), 4.02(s, 3H); **^{13}C NMR (400 MHz, $CDCl_3$)** δ 173.3, 152.3, 148.1, 125.3, 123.0, 113.6, 108.7, 108.4, 102.3, 56.7; **HRMS (ESI) Calcd for $C_{10}H_8N_2NaO_3$:** $[M+Na]^+$ 227.0427. **Found:** m/z 227.0434.

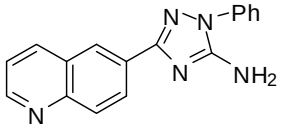
General procedure of 3-amino-l, 2, 4-triazole derivants: A mixture of N-Cyanoimidates (1mmol), phenylhydrazine (1.2mmol) and methanol (3ml) was refluxed for 4h. Then the reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography to obtain the final product.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.02(m, 2H), 7.62-7.59(m, 2H), 7.54-7.50(m, 2H), 7.44-7.36(m, 4H), 5.45(br, 2H); M.p. 158-159□ (lit.[6]160℃)

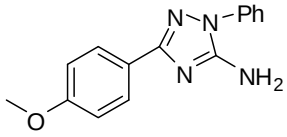


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01(s, 1H), 7.99(s, 1H), 7.62-7.53(m, 4H), 7.46-7.40(m, 3H), 4.90(br, 2H); **^{13}C NMR (400 MHz, $CDCl_3$)** 158.4, 154.4, 136.8, 135.0, 129.9, 129.5, 128.8, 128.3, 127.5, 123.5; **HRMS (ESI) Calcd for $C_{14}H_{11}ClN_4$:** $[M+H]^+$ 271.07482.**Found:** m/z 271.07450.

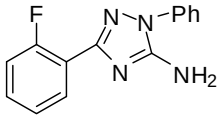


^{1}H NMR (400 MHz, d_6-DMSO) δ 8.91-8.90(d, 1H,J = 3.2Hz), 8.55(s,1H), 8.50-8.48(d, 1H, J = 8.0Hz), 8.36-8.33(d, 1H, J = 8.8Hz), 8.09-8.07(d, 1H, J= 8.8Hz), 7.69-7.67(d, 2H, J = 8.0Hz), 7.59-7.55(t, 3H, J = 7.2Hz), 7.44-7.40(t, 1H, 7.2Hz), 6.68(br,1H); **^{13}C NMR (400**

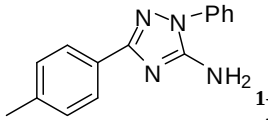
MHz, d_6-DMSO) δ 157.7, 155.6, 150.8, 147.9, 137.2, 136.5, 129.5, 129.3, 129.2, 127.9, 127.3, 127.0, 124.7, 123.0, 121.9; **HRMS (ESI) Calcd for $C_{17}H_{13}N_5$:** $[M+H]^+$ 288.12456. **Found:** m/z 288.12437.



^{1}H NMR (400 MHz, d_6-DMSO) δ 7.89-7.87(d, 2H, J = 8.4Hz), 7.63-7.61(d, 2H, J = 8.0Hz), 7.55-7.51(t, 2H, J = 7.6Hz), 7.40-7.37(t, 2H, J = 7.2Hz), 7.01-6.99(d, 1H, J = 8.4Hz), 6.21(br, 2H), 3.80(s, 3H); **^{13}C NMR (400 MHz, d_6-DMSO)** δ 159.8, 158.1, 155.2, 137.3, 129.4, 127.0, 126.9, 124.0, 122.7, 113.9, 55.1; **HRMS (ESI) Calcd for $C_{15}H_{14}N_4O$:** $[M+H]^+$267.12462**, Found:** m/z 267.12404.



^{1}H NMR (400 MHz, d_6-DMSO) δ 7.99-7.97(t, 1H, J = 5.2Hz), 7.64-7.62(d, 1H, J = 5.2Hz), 7.57-7.54(t, 2H, J = 5.2Hz), 7.47-7.42(m, 2H), 7.31-7.28(m, 2H), 6.62(s, 2H); **^{13}C NMR (400 MHz, d_6-DMSO)** δ 160.3, 158.7, 155.0 , 154.9, 137.1, 130.6, 130.5, 129.7, 129.4, 127.2, 124.3, 123.0, 119.2, 119.2, 116.5, 116.4; **HRMS (ESI) Calcd for $C_{14}H_{11}FN_4$:** $[M+H]^+$ 255.10455. **Found:** m/z 255.10405.



^{1}H NMR (400 MHz, d_6-DMSO) δ 7.87-7.84(d, 2H, J = 9.6Hz), 7.63-7.62(d, 2H, J = 5.2Hz), 7.55-7.52(t, 2H, J = 9.6Hz), 7.40-7.38(t, 1H, J = 5.2Hz), 7.25-7.24(d, 2H, J = 5.2Hz), 2.34(s, 3H); **HRMS (ESI) Calcd for $C_{15}H_{14}N_4$:** $[M+H]^+$ 251.12951. **Found:** m/z 251.12912

Reference:

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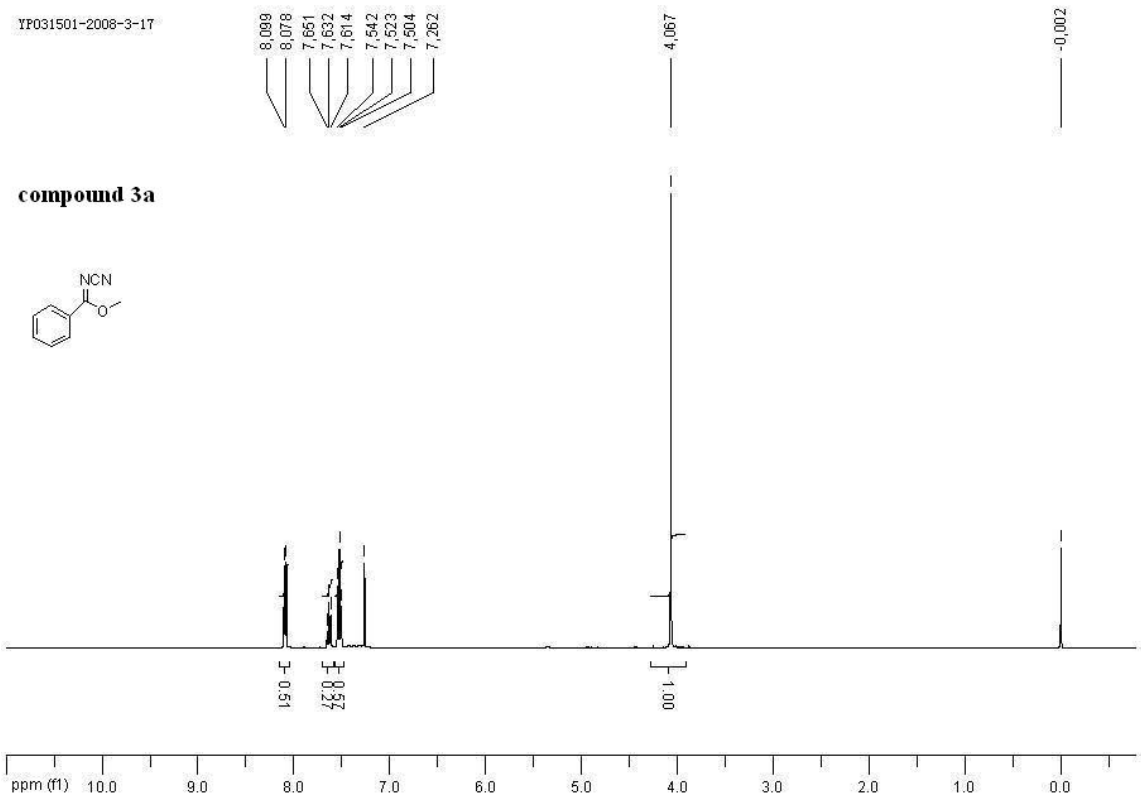
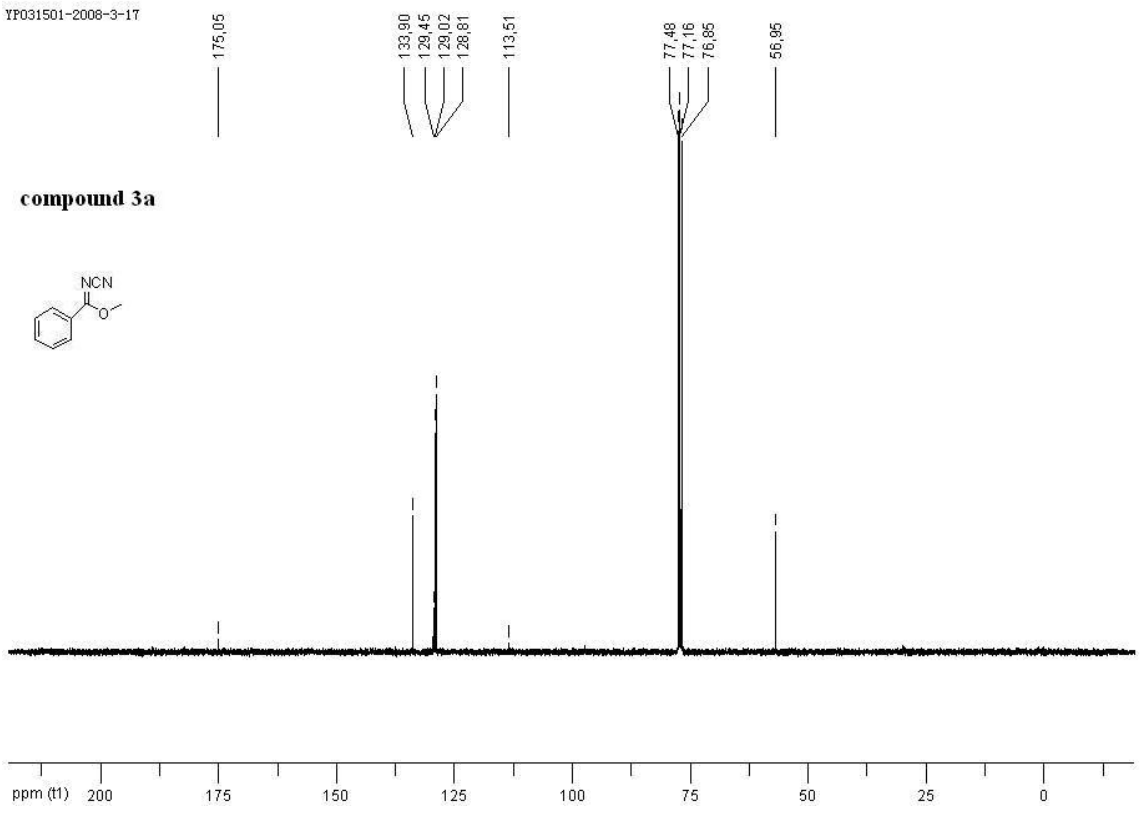
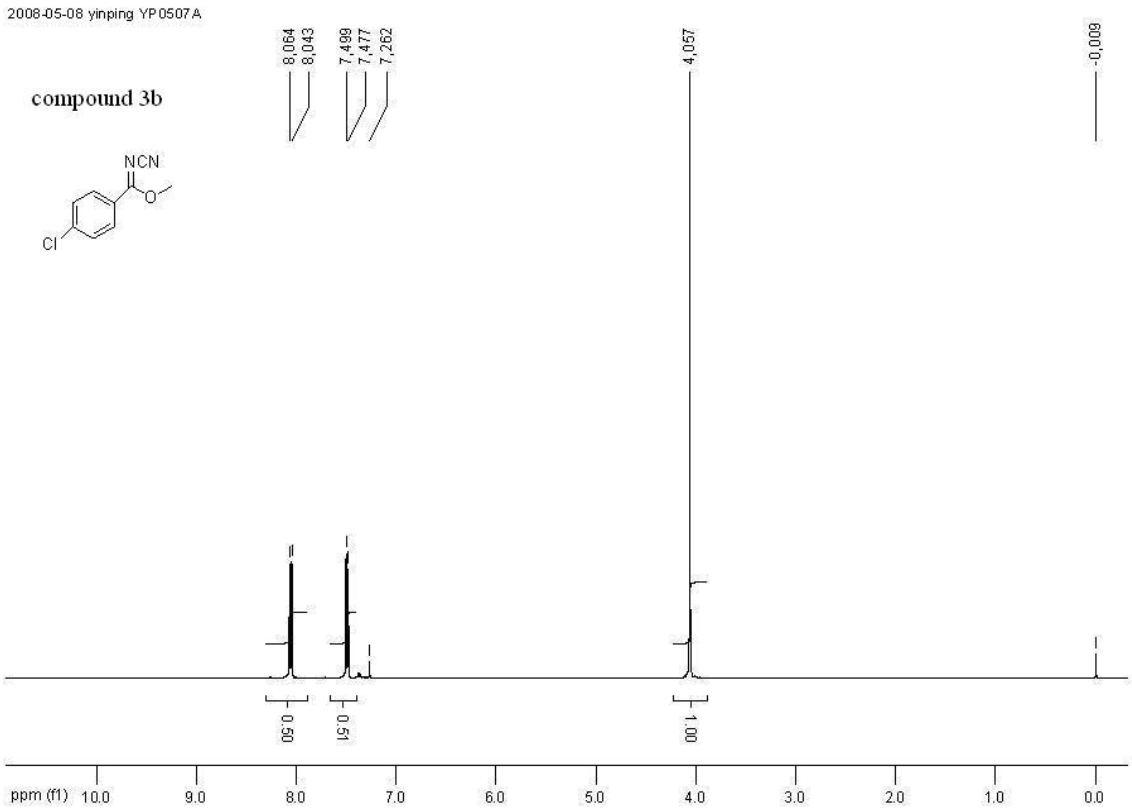
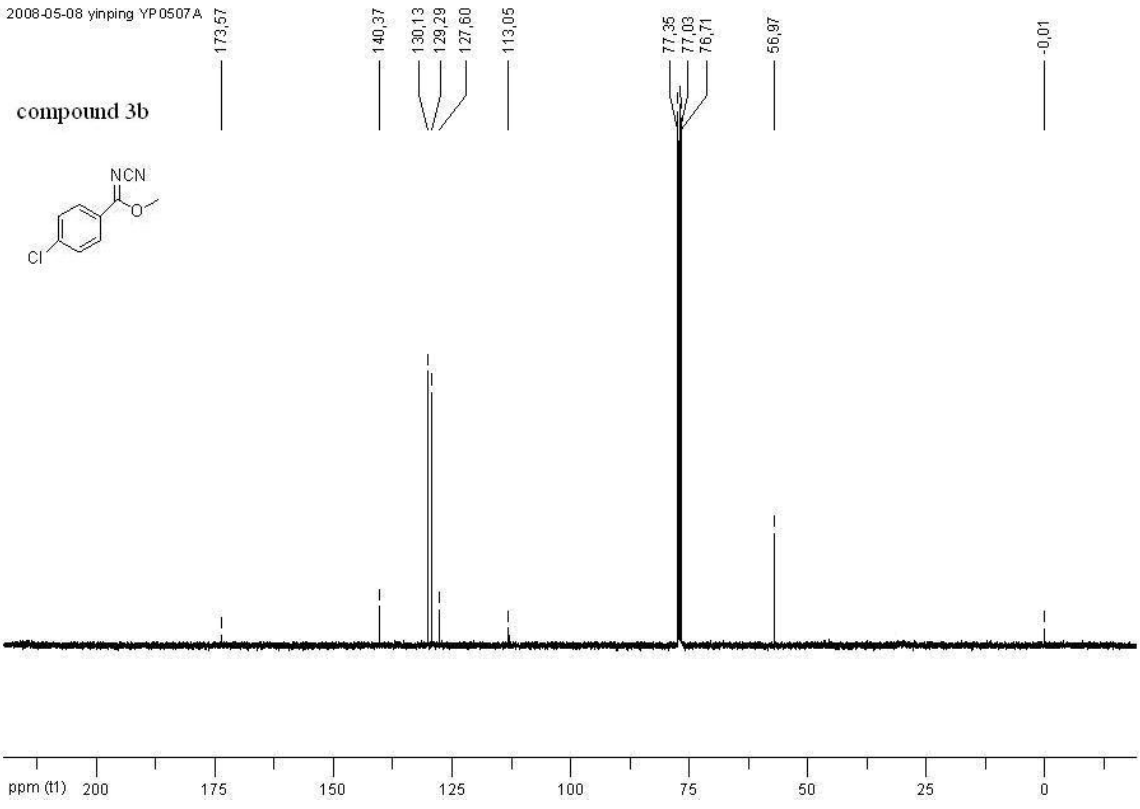
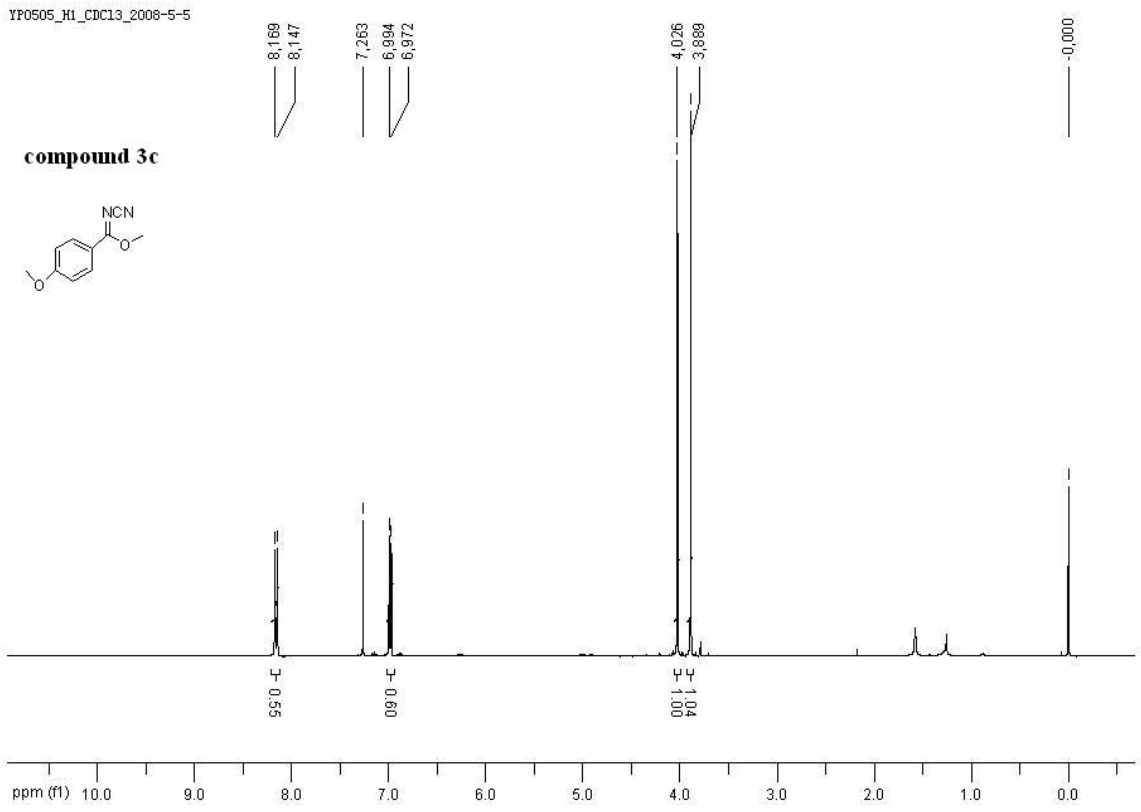
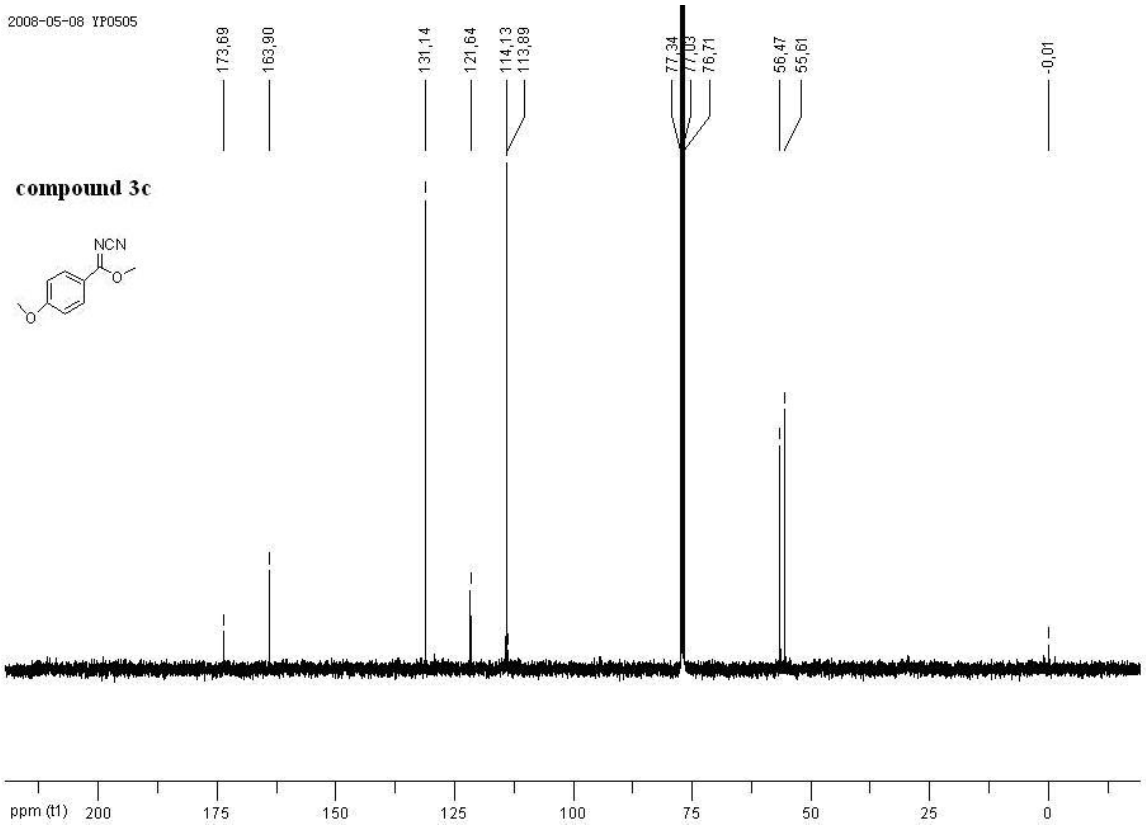

YP031501-2008-3-17
8,099
8,078
7,651
7,632
7,614
7,542
7,523
7,504
7,262
4,067
-0,002
compound 3a
NCN
O
0.51
0.27
1.00
ppm (f1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

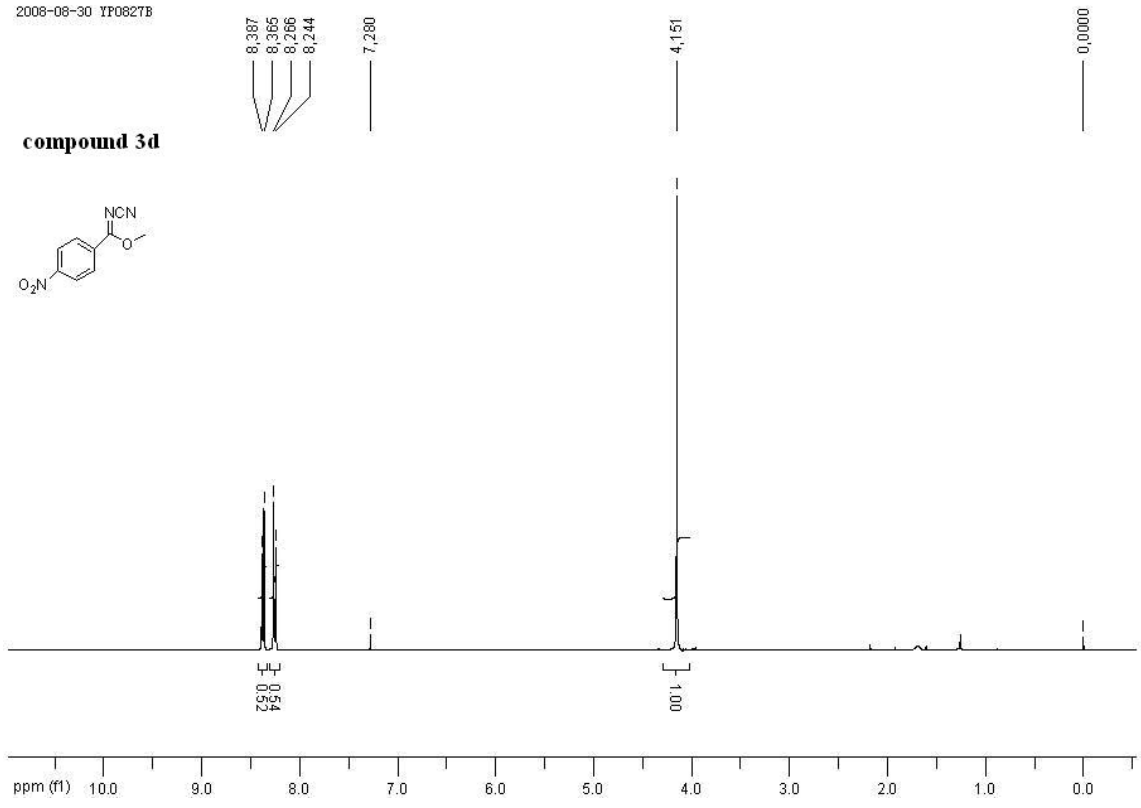

YP031501-2008-3-17
175,05
133,90
129,45
129,02
128,81
113,51
77,48
77,16
76,85
56,95
compound 3a
NCN
O
ppm (f1)
200
175
150
125
100
75
50
25
0

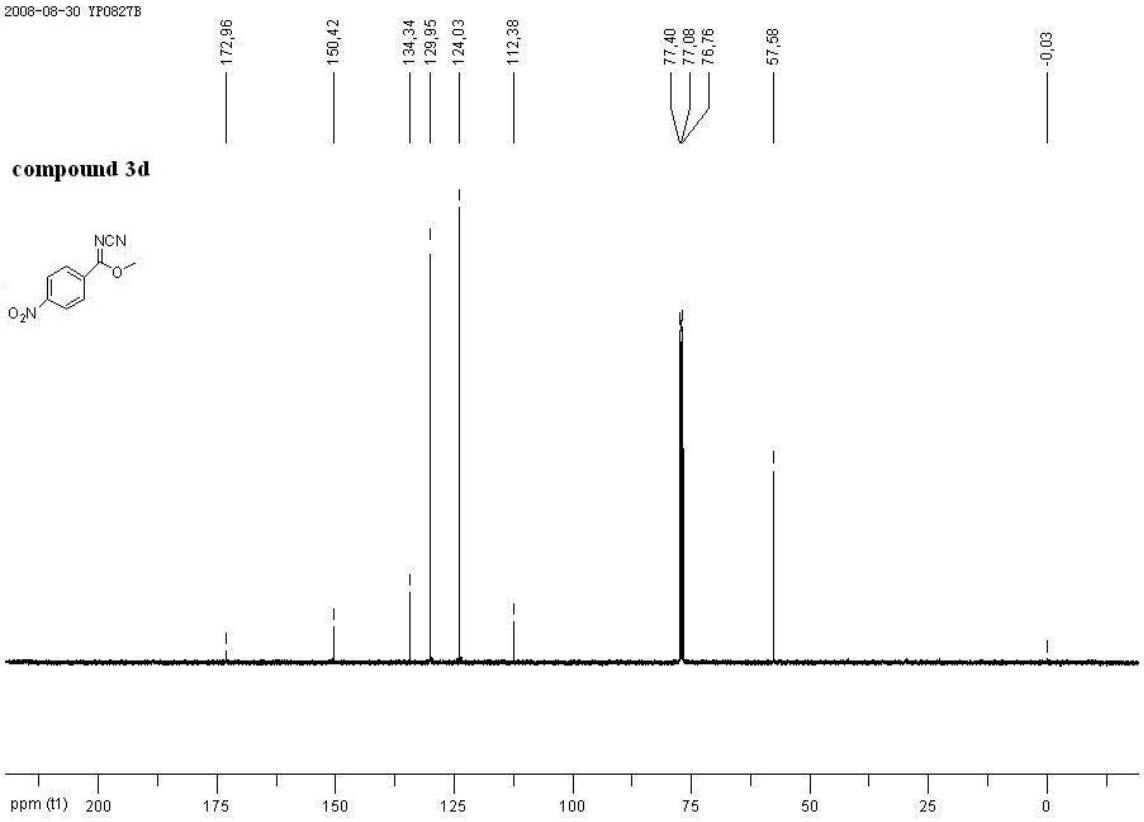

2008-05-08 yinping YP0507A
compound 3b
NCN
O
Cl
8,064
8,043
7,499
7,477
7,262
4,057
-0,009
0,50
0,51
1,00
ppm (f1) 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

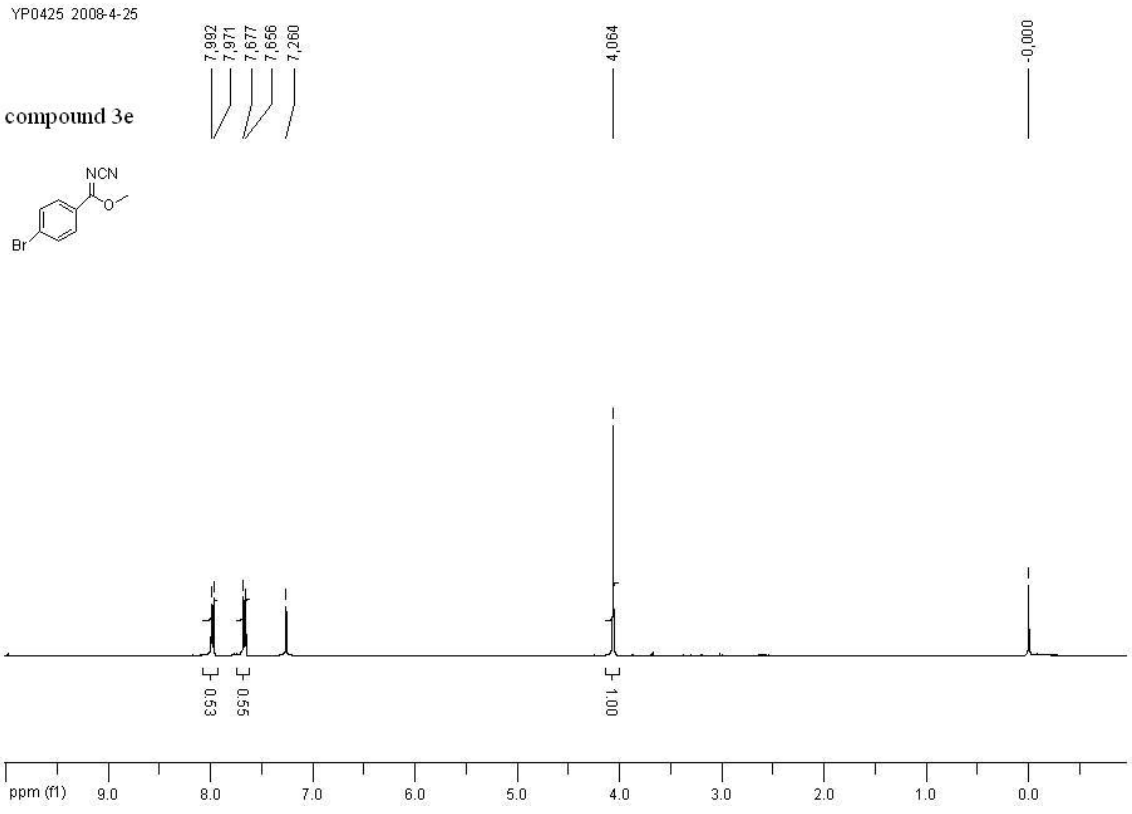

2008-05-08 yinping YP0507A
compound 3b
NCN
O
Cl
173,57
140,37
130,13
129,29
127,60
113,05
77,35
77,03
76,71
56,97
-0,01
ppm (t1) 200 175 150 125 100 75 50 25 0

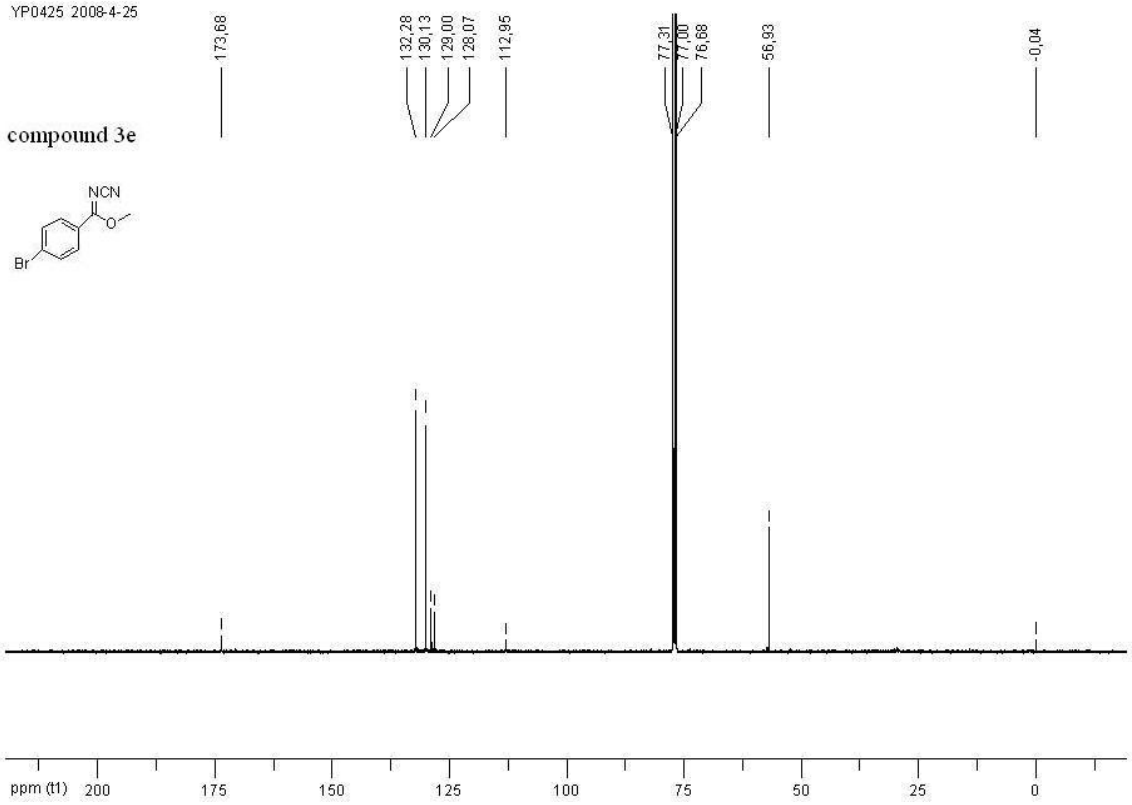

YP0505_H1_CDCl3_2008-5-5
8,169
8,147
7,263
6,994
6,972
4,026
3,889
-0,000
compound 3c
NCN
O
O
3- 0,56
3- 0,60
3- 1,04
3- 1,00
ppm (f1) 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

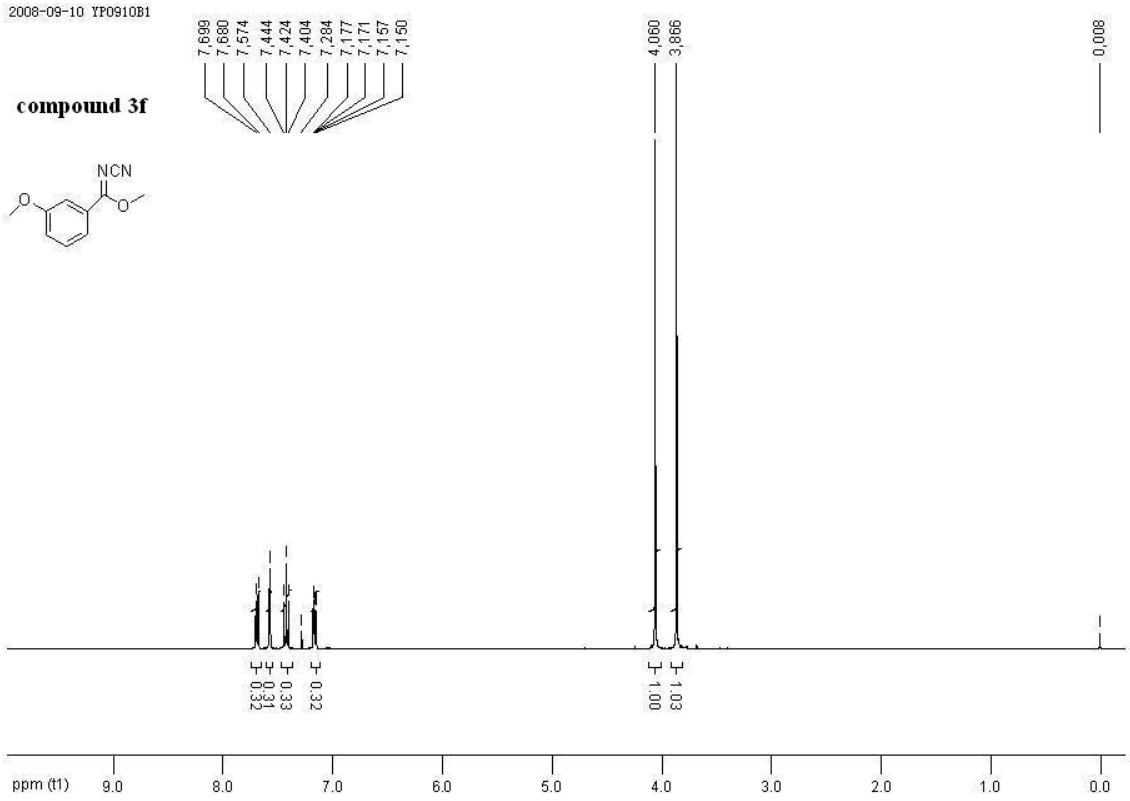

2008-05-08 YP0505
173,69
163,90
131,14
121,64
114,13
113,89
77,34
77,03
76,71
56,47
55,61
-0,01
compound 3c
NCN
O
O
ppm (f1) 200 175 150 125 100 75 50 25 0

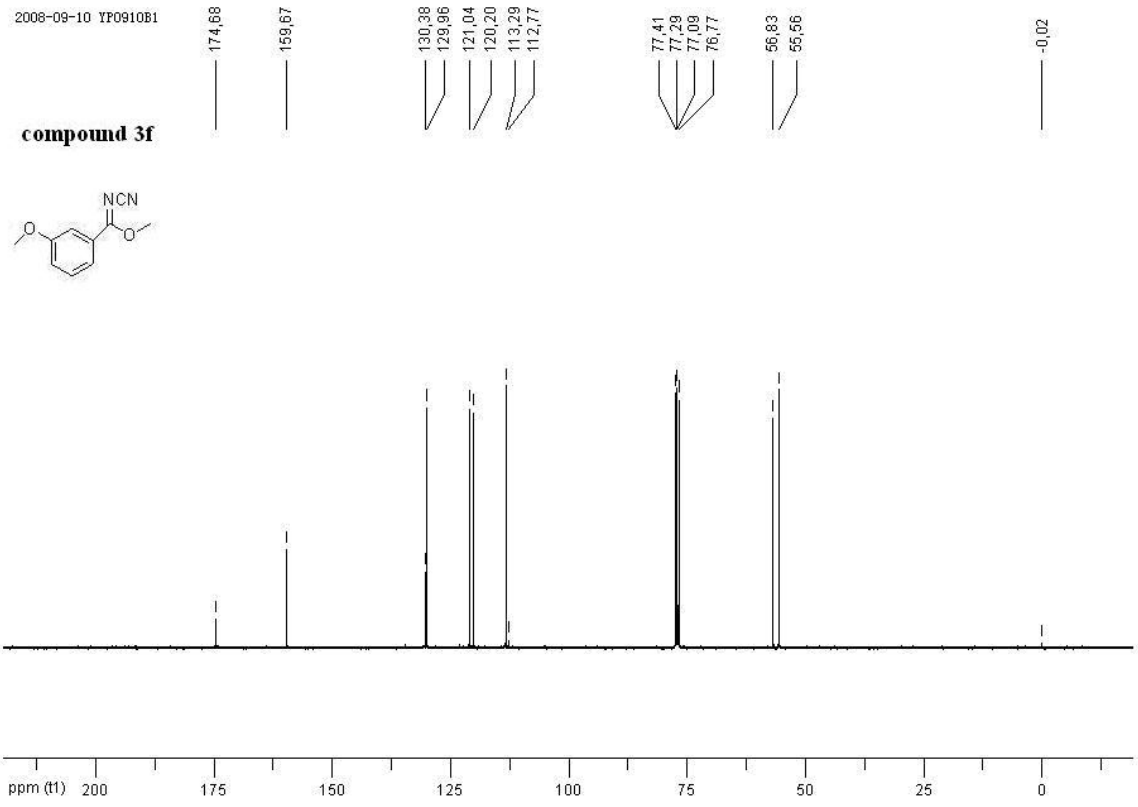

2008-08-30 YP0827B
8,387
8,365
8,266
8,244
7,280
4,151
0,0000
compound 3d
NCN
O
O_2N
0,52
0,54
1,00
ppm (f1) 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


2008-08-30 YP0827B
172,96
150,42
134,34
129,95
124,03
112,38
77,40
77,08
76,76
57,58
-0,03
compound 3d
NCN
O
O_2N
ppm (f1) 200 175 150 125 100 75 50 25 0


YP0425 2008-4-25
7,992
7,971
7,677
7,656
7,260
4,064
-0,000
compound 3e
NCN
O
Br
3,063
3,055
4,100
ppm (f1) 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


YP0425 2008-4-25
173,68
132,28
130,13
129,00
128,07
112,95
77,31
77,00
76,68
56,93
-0,04
compound 3e
NCN
O
Br
ppm (f1) 200 175 150 125 100 75 50 25 0


2008-09-10 YP0910B1
compound 3f
NCN
7,699
7,680
7,574
7,444
7,424
7,404
7,284
7,177
7,171
7,157
7,150
4,060
3,866
0,008
0,32
0,33
0,31
0,32
1,00
1,03
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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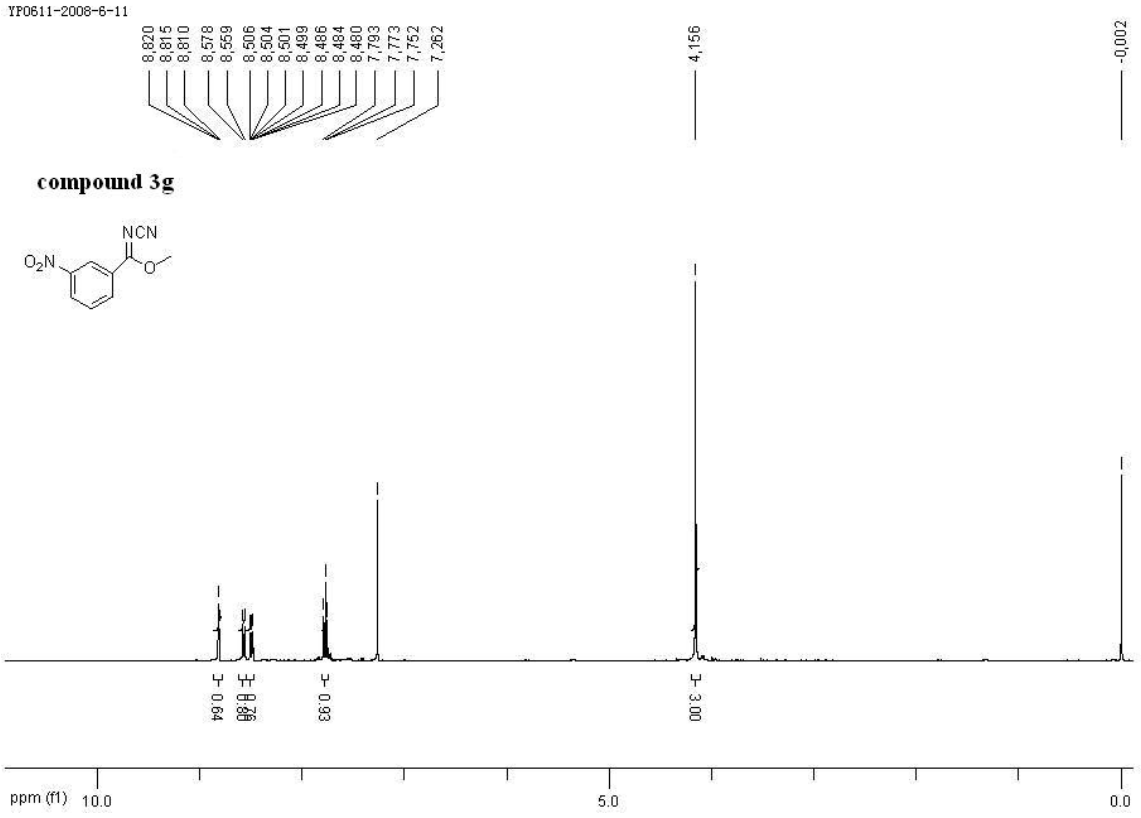
compound 3f
NCN
174,68
159,67
130,38
129,96
121,04
120,20
113,29
112,77
77,41
77,29
77,09
76,77
56,83
55,56
-0,02
ppm (t1)
200
175
150
125
100
75
50
25
0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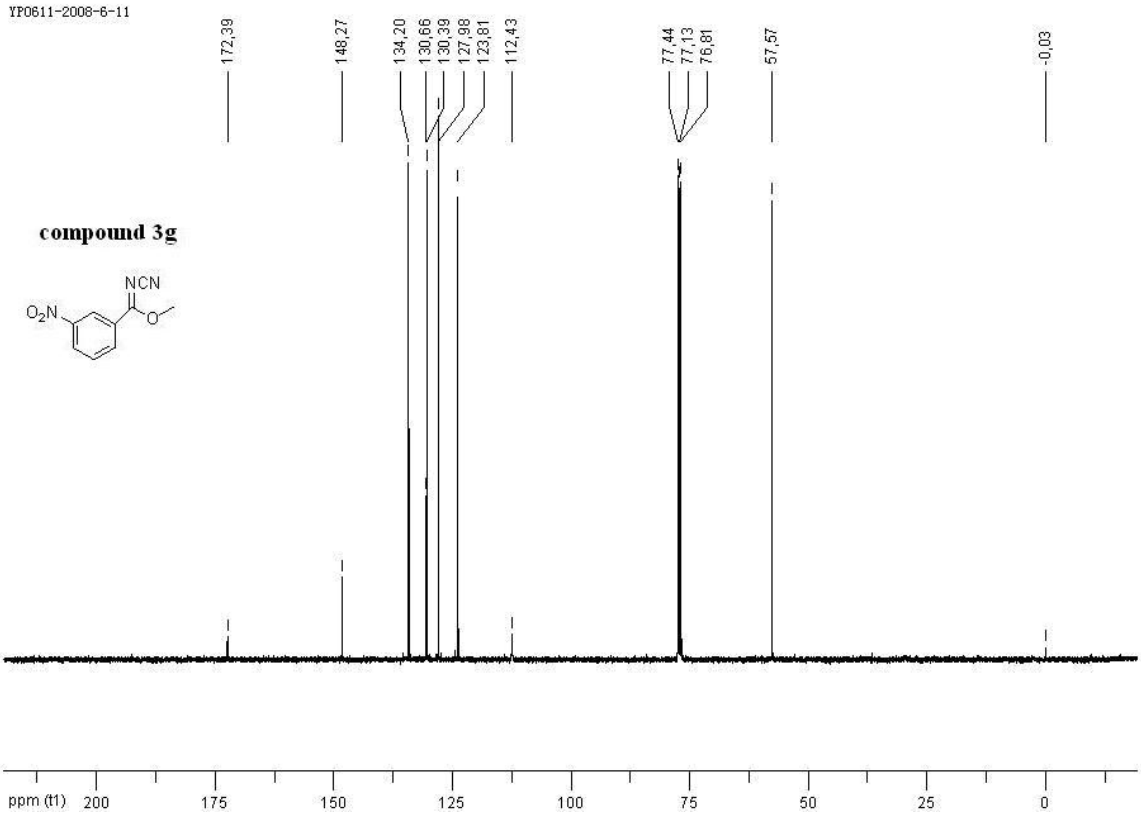
8,820
8,815
8,810
8,578
8,559
8,506
8,504
8,501
8,499
8,486
8,484
8,480
7,793
7,773
7,752
7,262
4,156
-0,002
compound 3g
NCN
O2N
O
3- 0.64
3- 0.93
3- 3.00
ppm (f1)
10.0
5.0
0.0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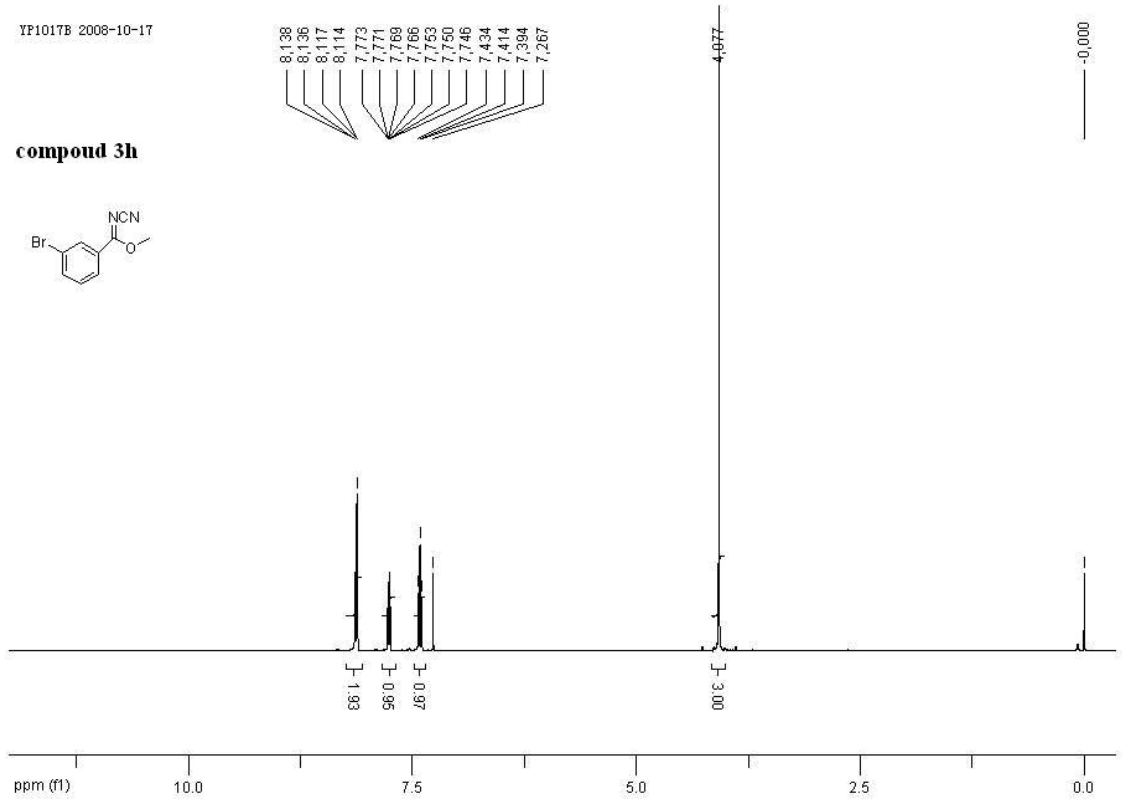
172,39
148,27
134,20
130,66
130,39
127,98
123,81
112,43
77,44
77,13
76,81
57,57
-0,03
compound 3g
NCN
O2N
O
ppm (f1)
200
175
150
125
100
75
50
25
0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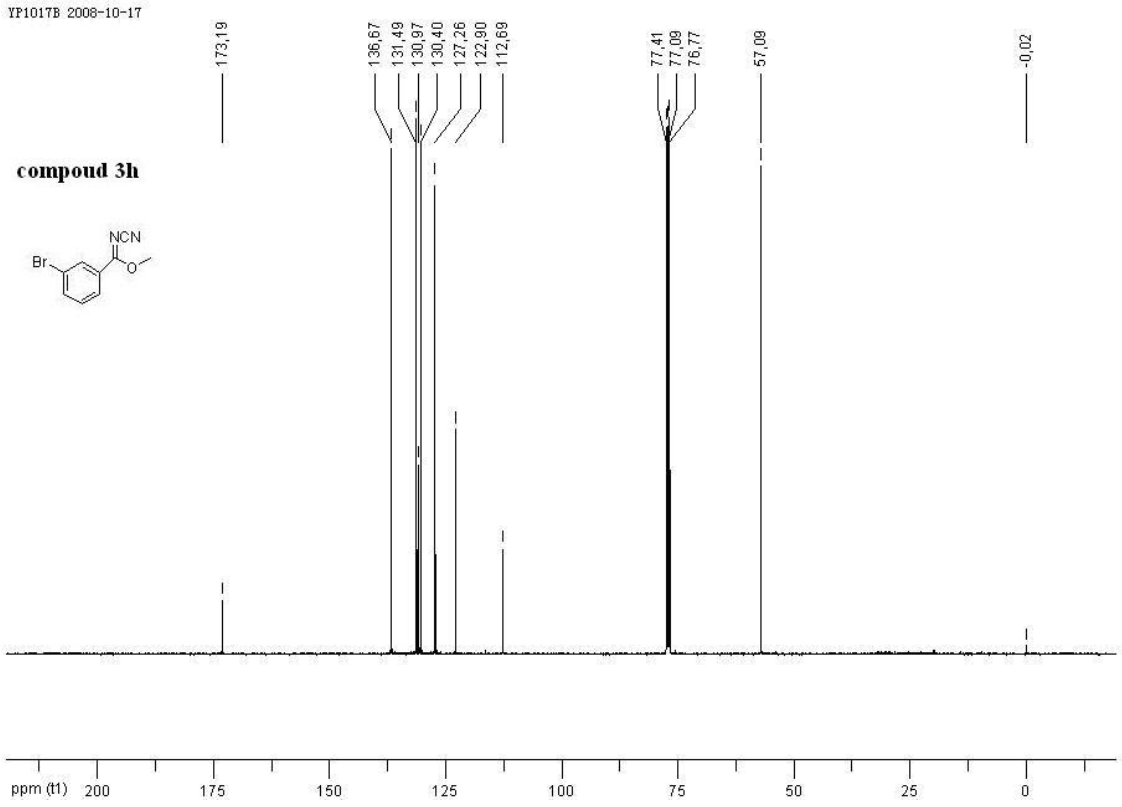
8,138
8,136
8,117
8,114
7,773
7,771
7,769
7,766
7,753
7,750
7,746
7,434
7,414
7,394
7,267
4,077
-0,000
compoud 3h
NCN
Br
O
1,93
0,96
0,97
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0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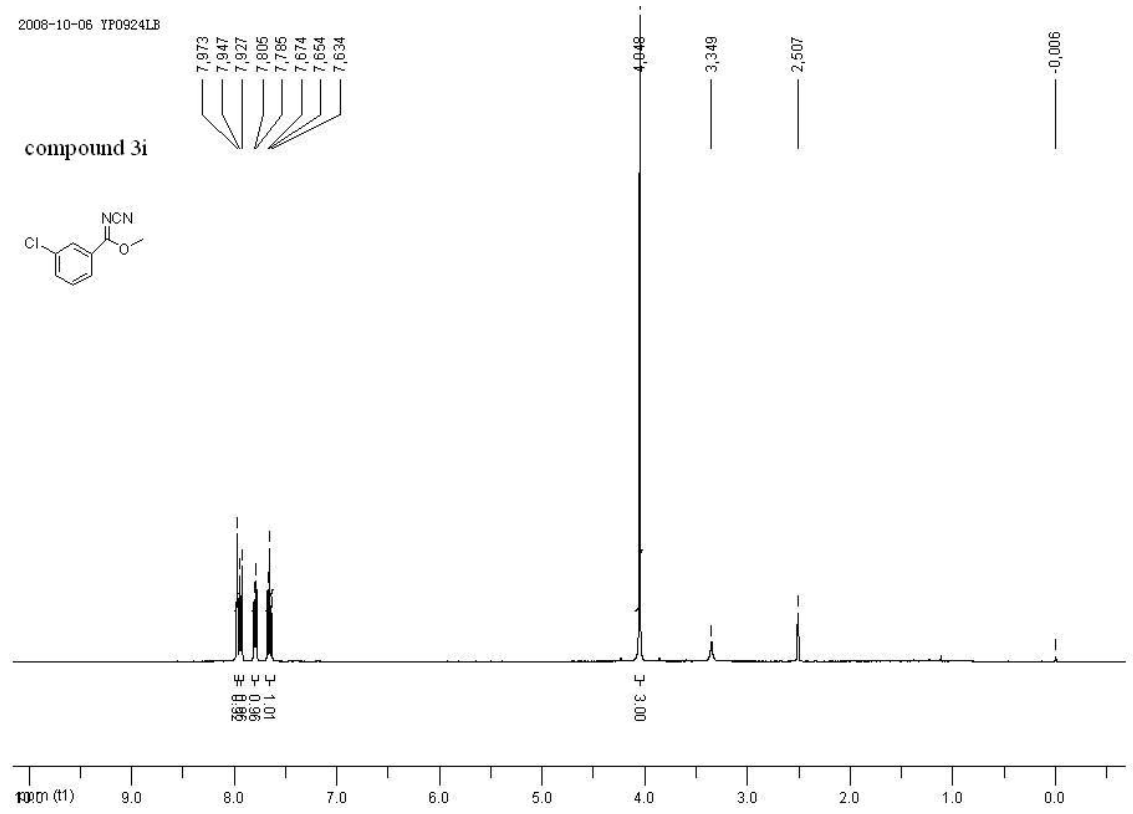
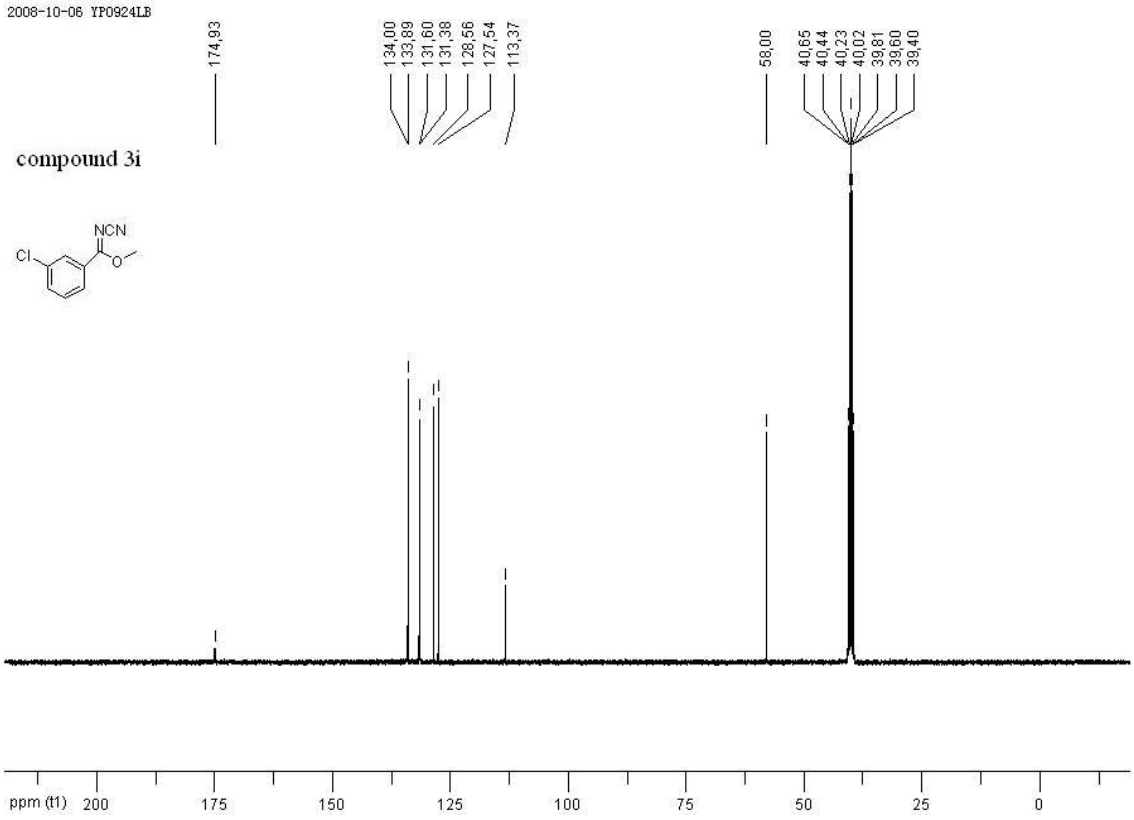
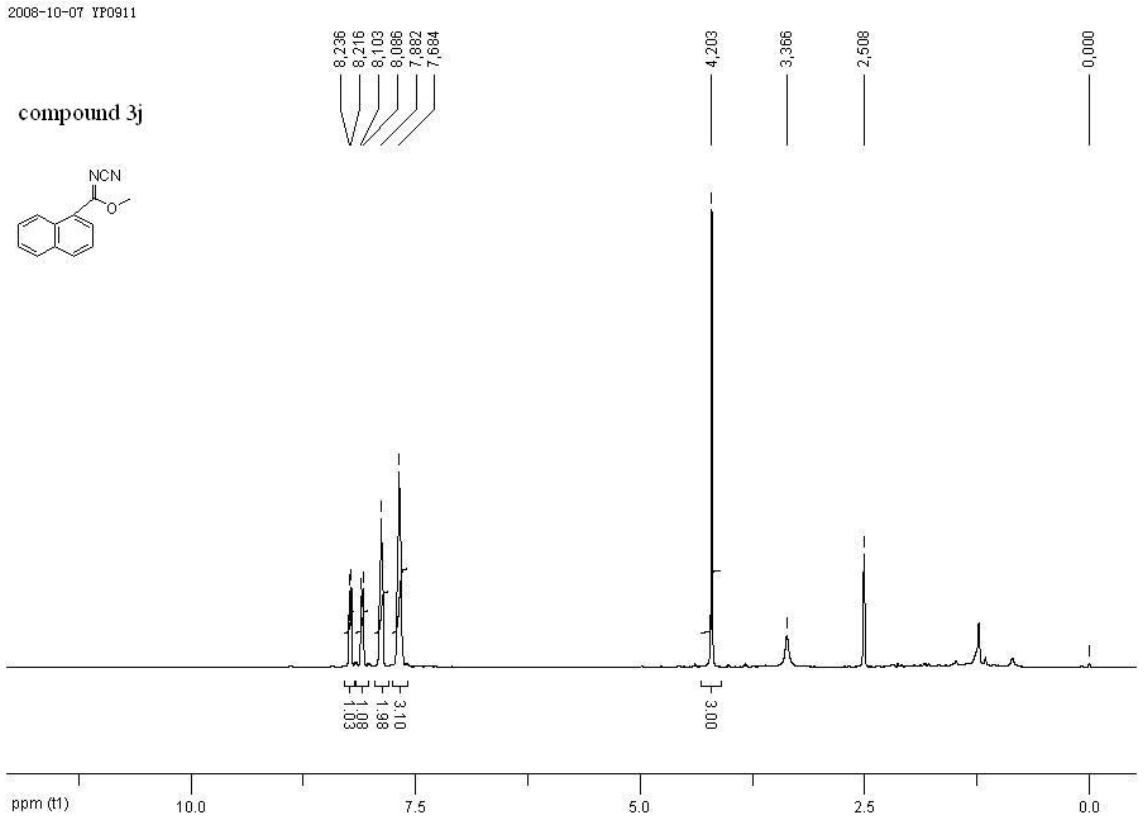
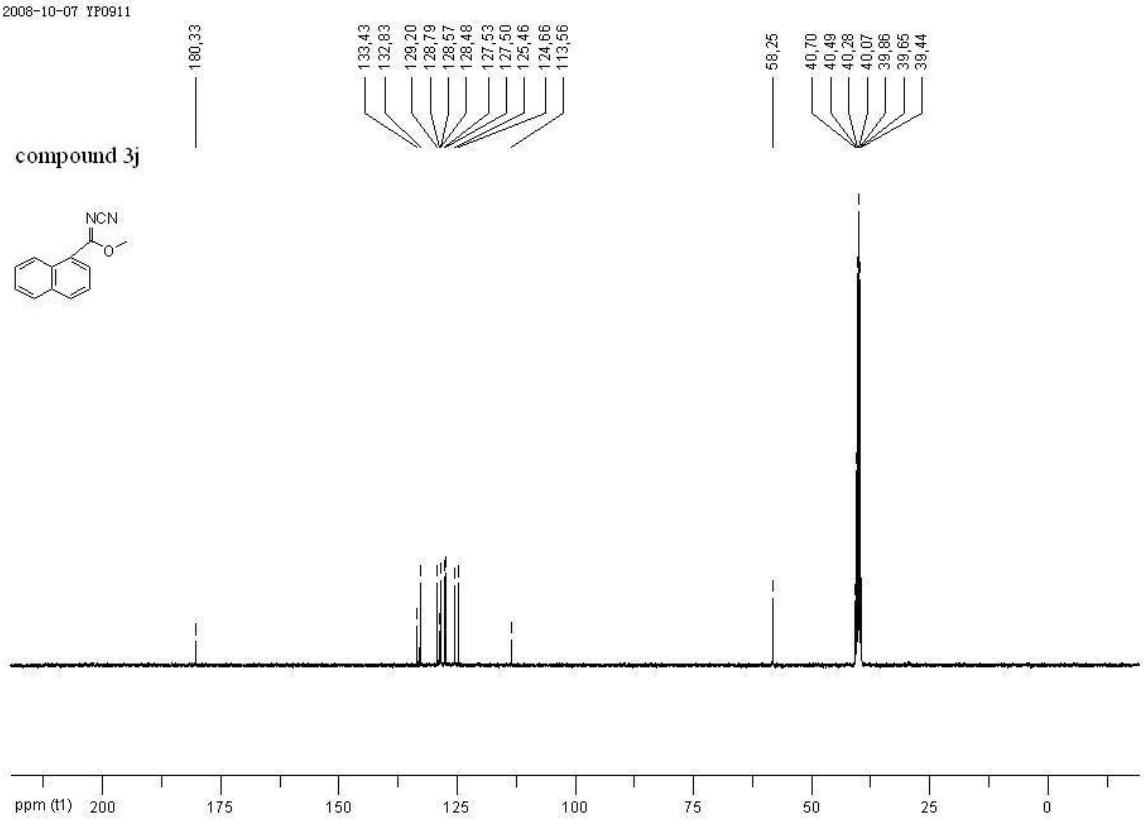
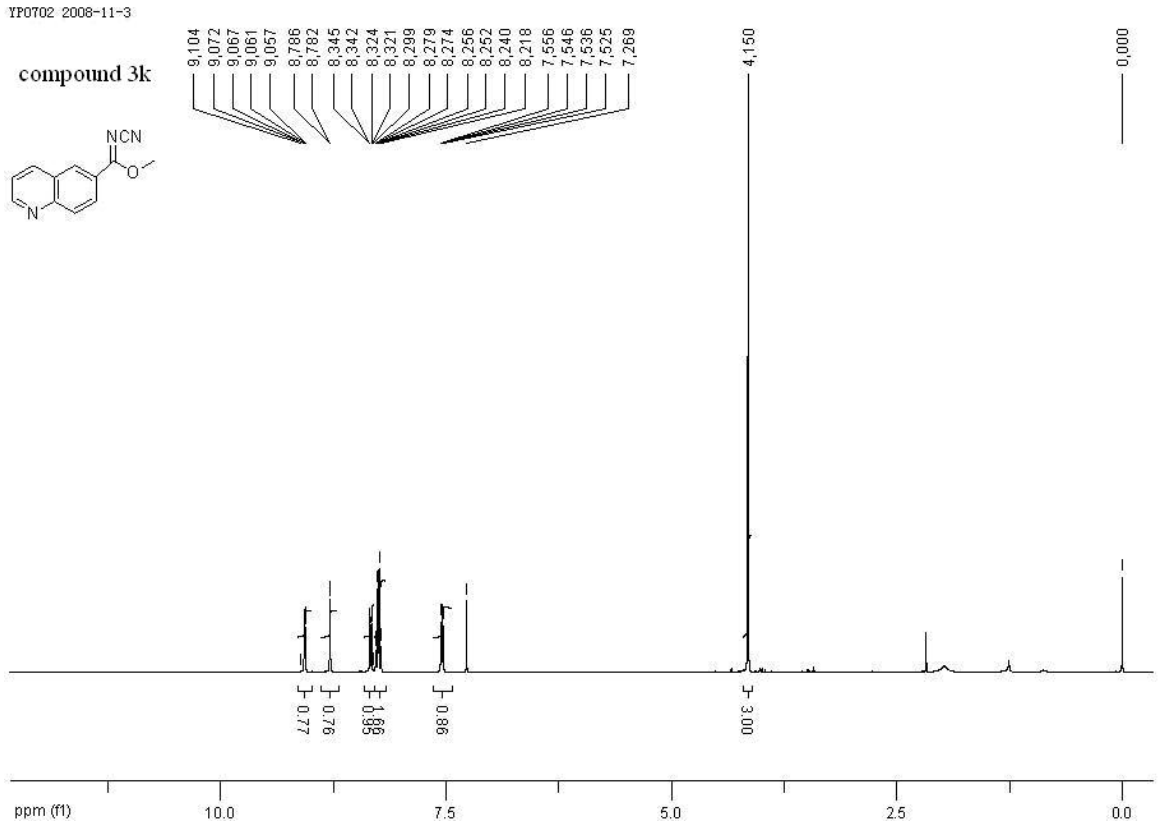
136,67
131,49
130,97
130,40
127,26
122,90
112,69
77,41
77,09
76,77
57,09
-0,02
compoud 3h
NCN
Br
O
ppm (f1)
200
175
150
125
100
75
50
25
0

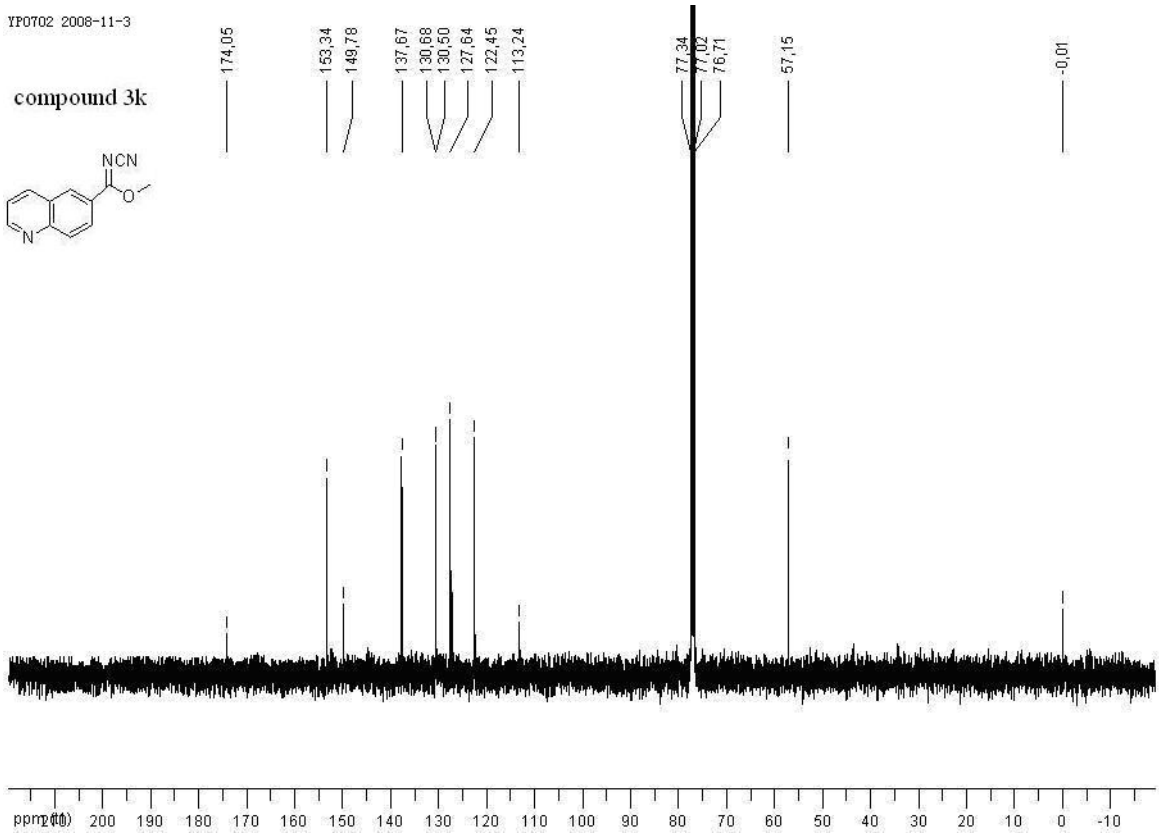

2008-10-06 YP0924LB
7,973
7,947
7,927
7,805
7,785
7,674
7,654
7,634
4,049
3,349
2,507
-0,006
compound 3i
NCN
Cl
O
3,00
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

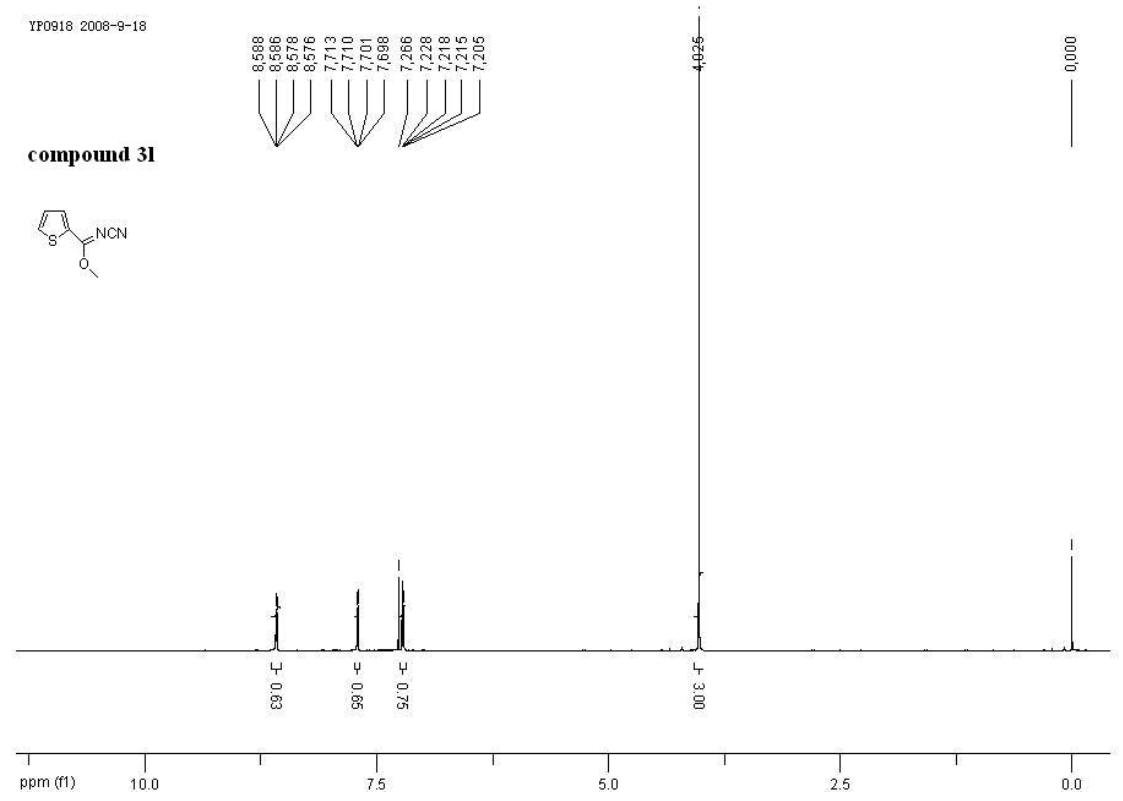

2008-10-06 YP0924LB
174,93
134,00
133,89
131,60
131,38
128,56
127,54
113,37
58,00
40,65
40,44
40,23
40,02
39,81
39,60
39,40
compound 3i
NCN
Cl
O
ppm (t1)
200
175
150
125
100
75
50
25
0

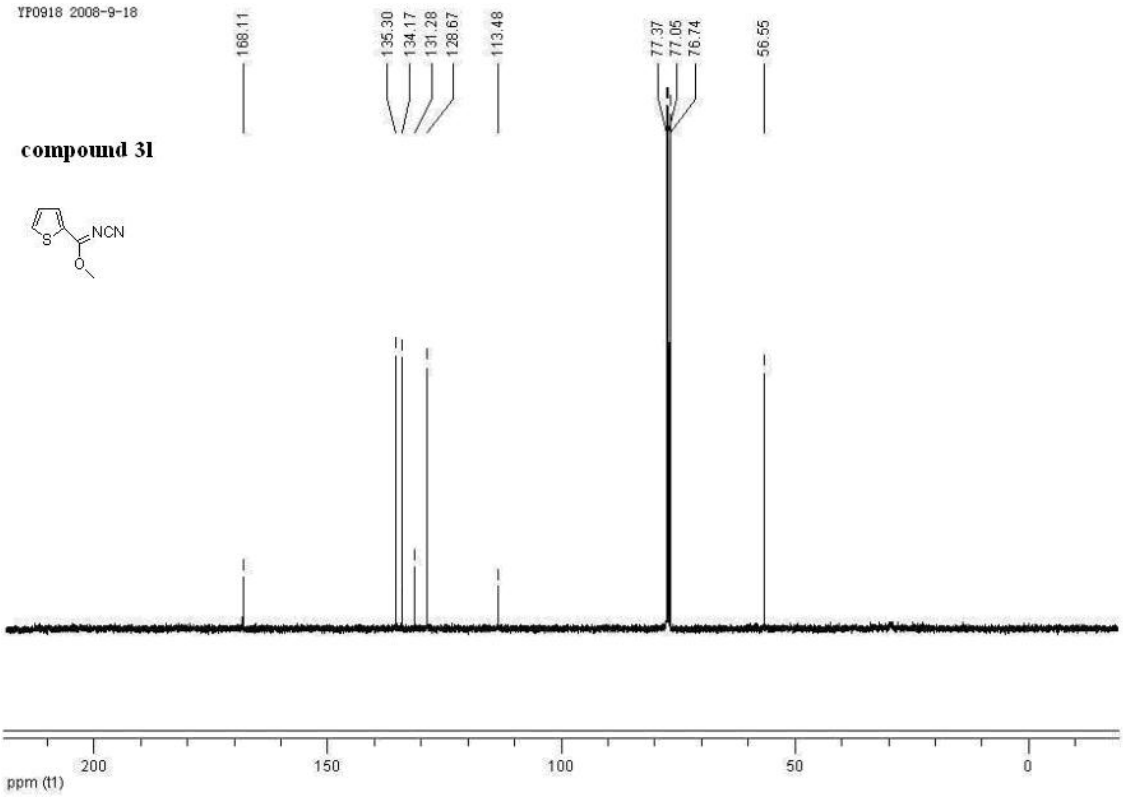

2008-10-07 YP0911
compound 3j
NCN
O
8,236
8,216
8,103
8,086
7,882
7,684
4,203
3,366
2,508
0,000
1,03
1,08
1,98
3,10
3,00
ppm (t1)
10.0
7.5
5.0
2.5
0.0

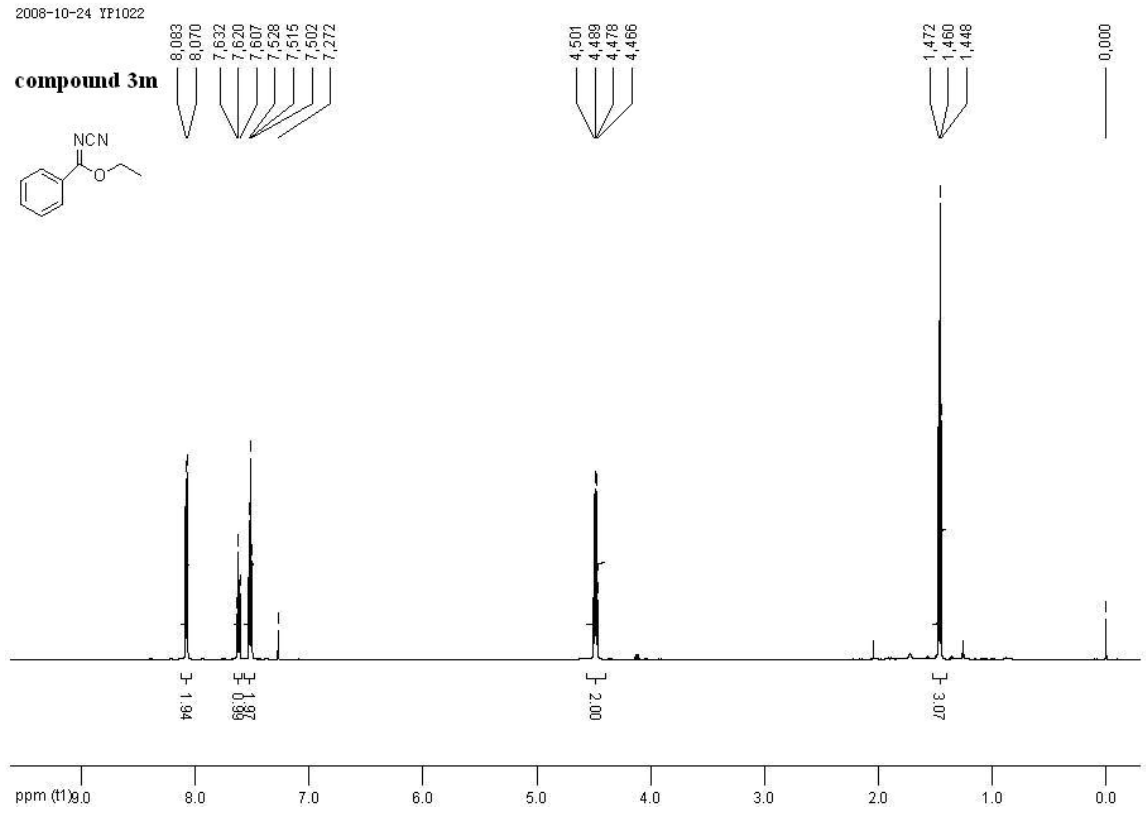

2008-10-07 YP0911
compound 3j
NCN
O
180,33
133,43
132,83
129,20
128,79
128,57
128,48
127,53
127,50
125,46
124,66
113,56
58,25
40,70
40,49
40,28
40,07
39,86
39,65
39,44
ppm (t1)
200
175
150
125
100
75
50
25
0

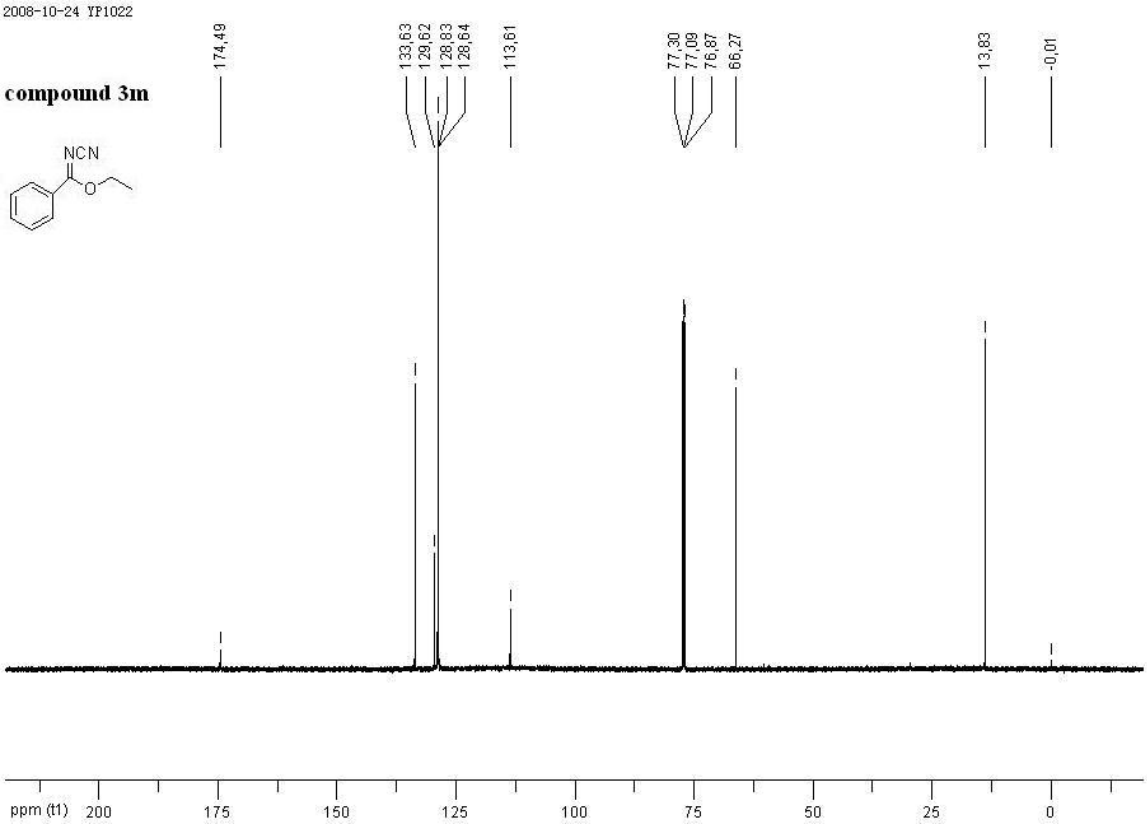

YP0702 2008-11-3
compound 3k
NCN
O
N
9,104
9,072
9,067
9,061
9,057
8,786
8,782
8,345
8,342
8,324
8,321
8,299
8,279
8,274
8,256
8,252
8,240
8,218
7,556
7,546
7,536
7,525
7,269
4,150
0,000
0,77
0,76
0,95
1,00
0,86
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0

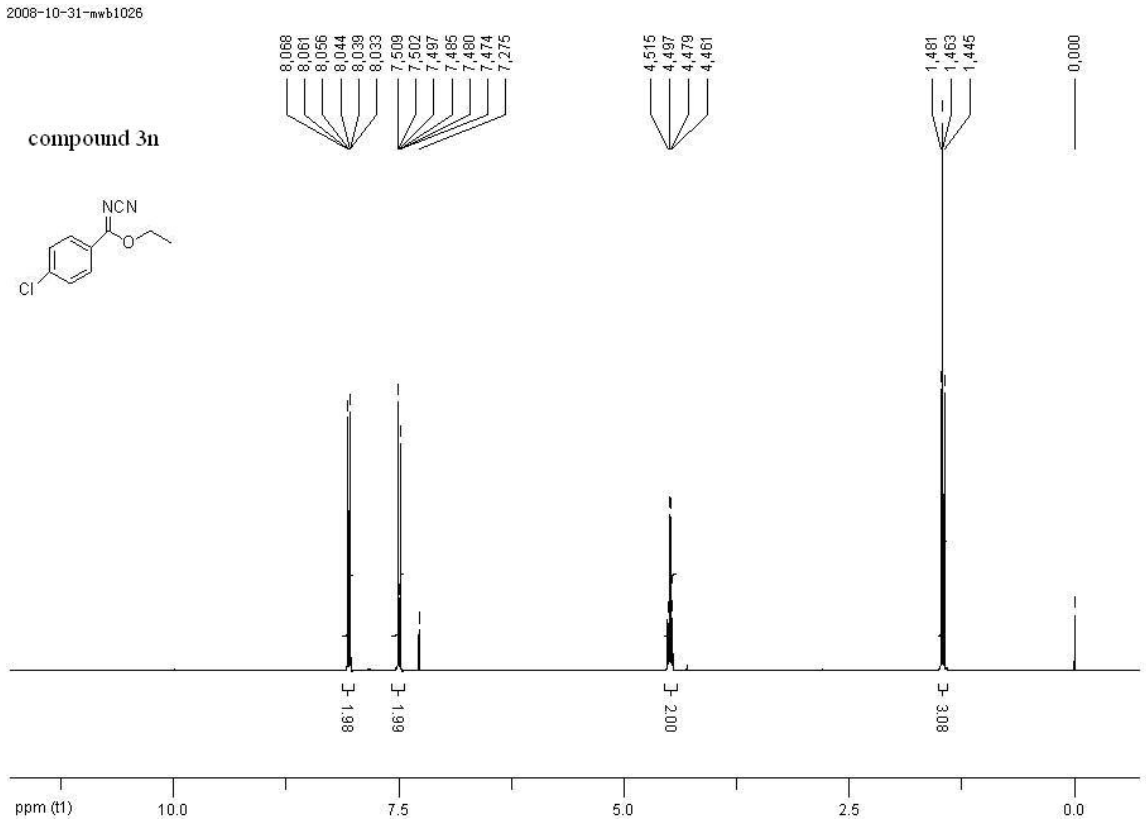

YP0702 2008-11-3
compound 3k
NCN
O
N
174,05
153,34
149,78
137,67
130,68
130,50
127,64
122,45
113,24
77,34
77,02
76,71
57,15
-0,01
ppm (f1)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

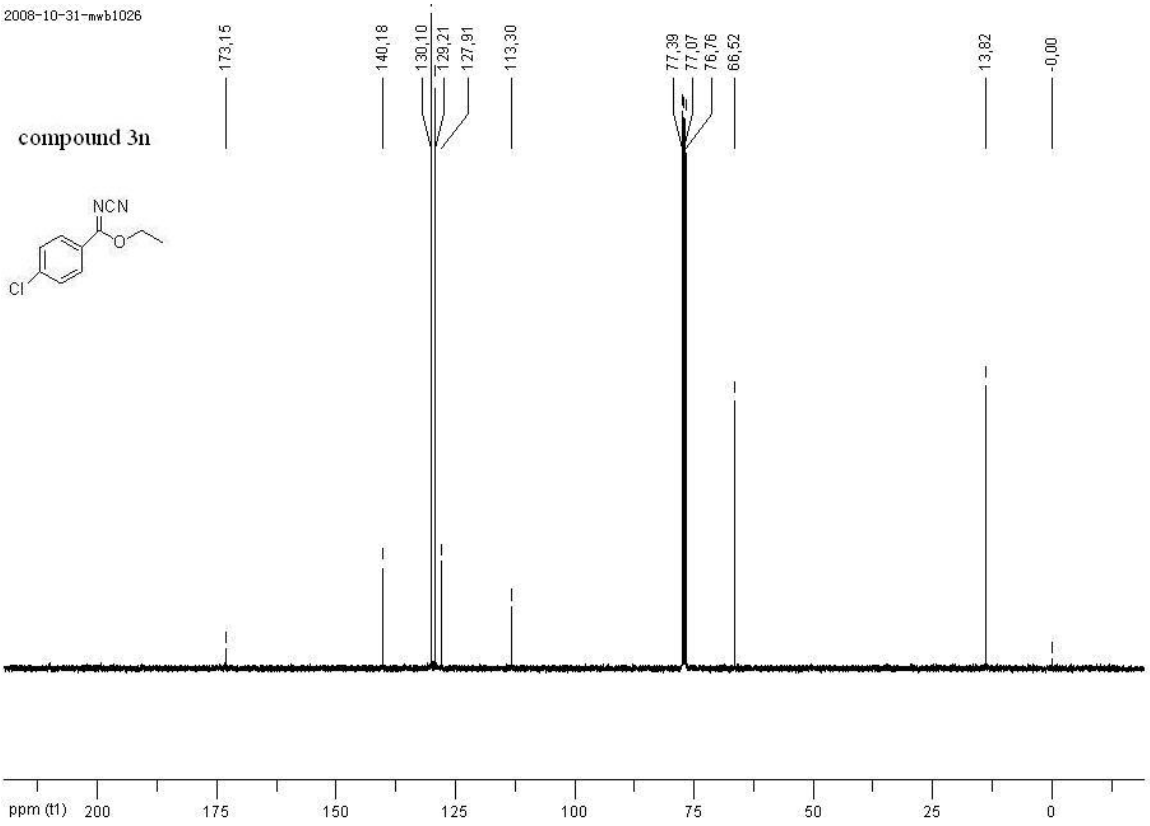

YP0918 2008-9-18
8.588
8.586
8.578
8.576
7.713
7.710
7.701
7.698
7.266
7.228
7.218
7.215
7.205
4.026
0.000
compound 3l
NCN
O
0.63
0.66
0.75
3.00
ppm (f1)
10.0
7.5
5.0
2.5
0.0

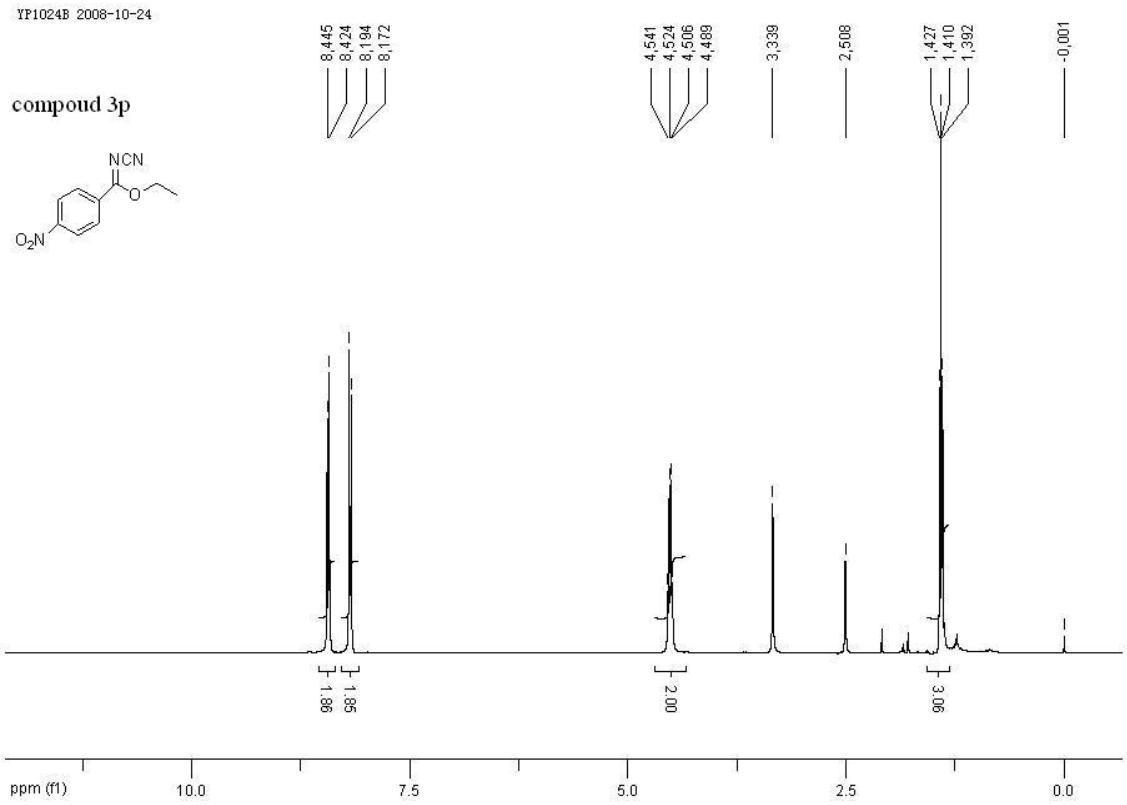

YP0918 2008-9-18
168.11
135.30
134.17
131.28
128.67
113.48
77.37
77.05
76.74
56.55
compound 3l
NCN
O
ppm (f1)
200
150
100
50
0

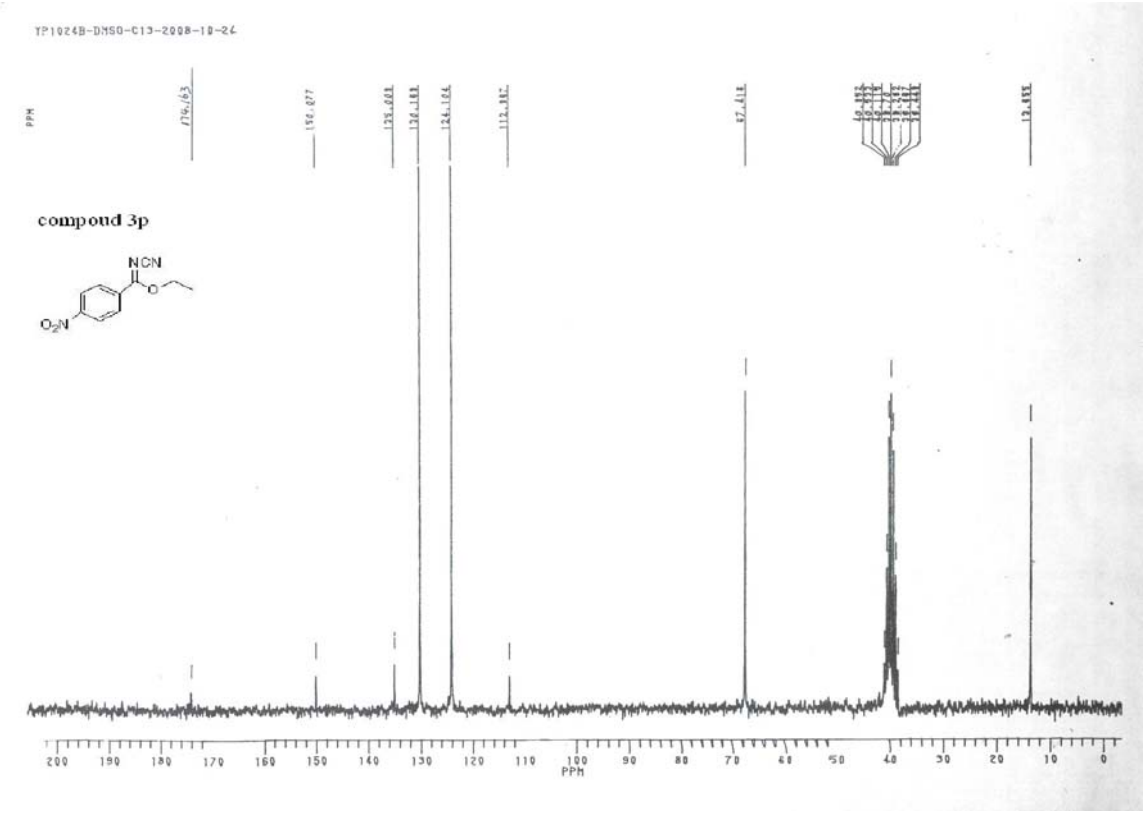

2008-10-24 YP1022
compound 3m
NCN
O
8,083
8,070
7,632
7,620
7,607
7,528
7,515
7,502
7,272
4,501
4,489
4,478
4,466
1,472
1,460
1,448
0,000
1,94
0,98
1,97
2,00
3,07
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

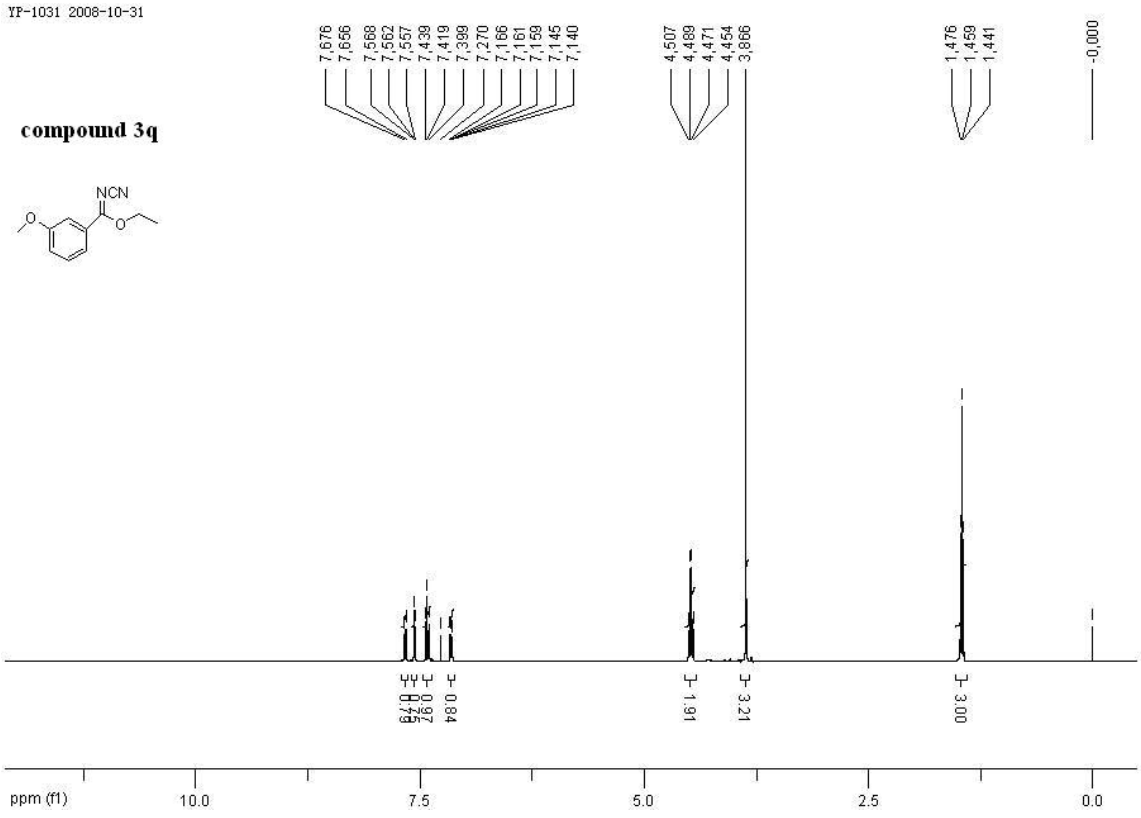

2008-10-24 YP1022
compound 3m
NCN
O
174,49
133,63
129,62
128,83
128,64
113,61
77,30
77,09
76,87
66,27
13,83
-0,01
ppm (t1)
200
175
150
125
100
75
50
25
0

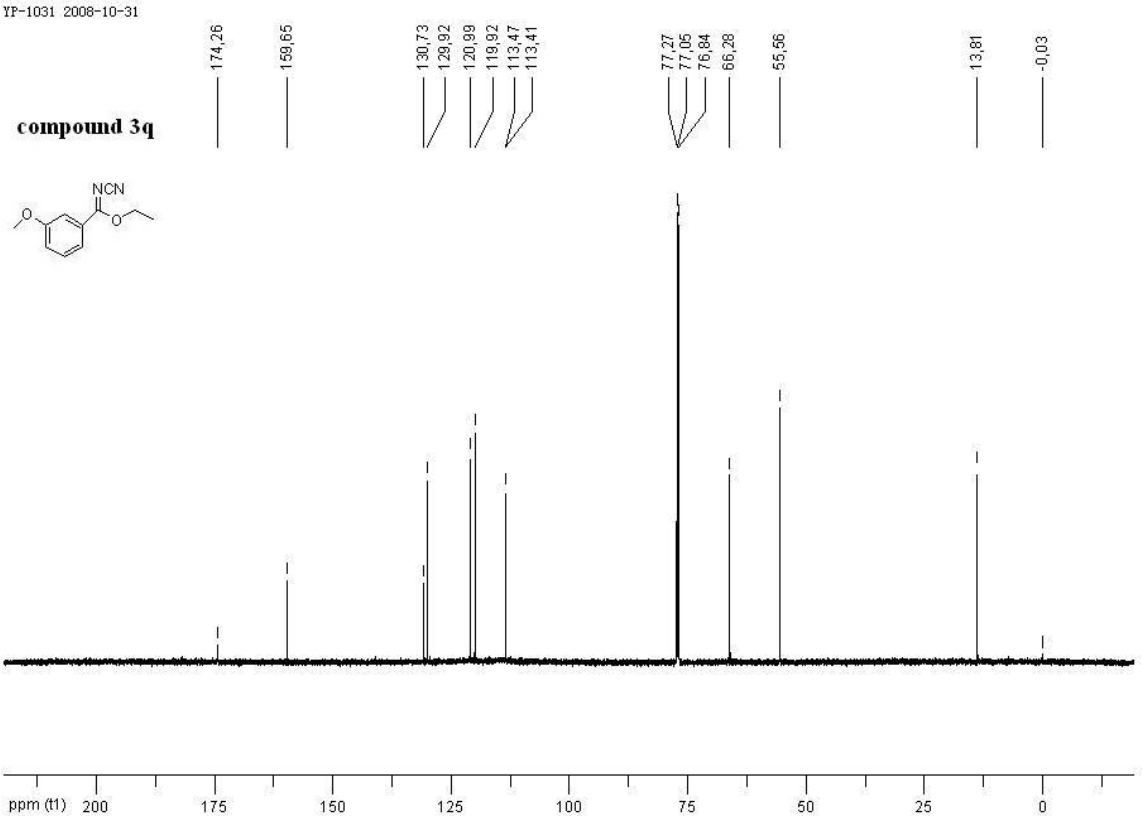

2008-10-31-mwb1026
compound 3n
NCN
O
Cl
8,068
8,061
8,056
8,044
8,039
8,033
7,509
7,502
7,497
7,485
7,480
7,474
7,275
4,515
4,497
4,479
4,461
1,481
1,463
1,445
0,000
1,98
1,99
2,00
3,08
ppm (t1)
10.0
7.5
5.0
2.5
0.0

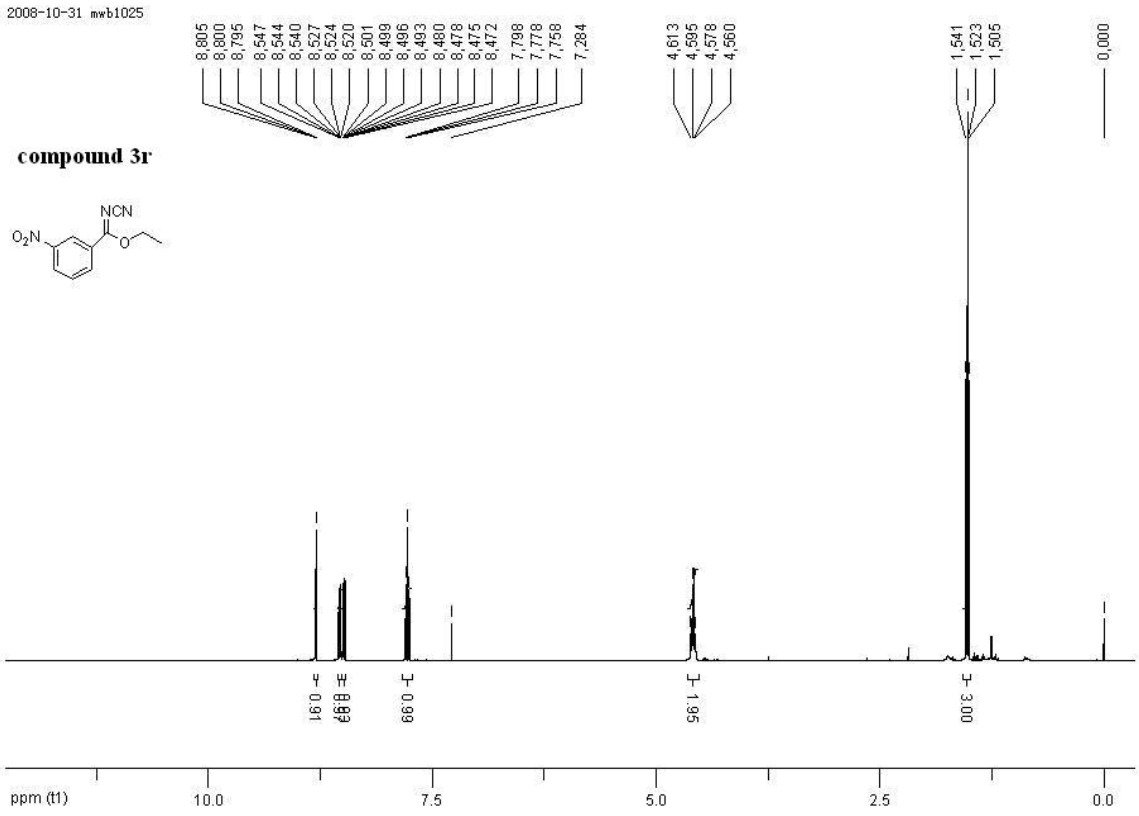

2008-10-31-mwb1026
compound 3n
NCN
O
Cl
173,15
140,18
130,10
129,21
127,91
113,30
77,39
77,07
76,76
66,52
13,82
-0,00
ppm (t1)
200
175
150
125
100
75
50
25
0

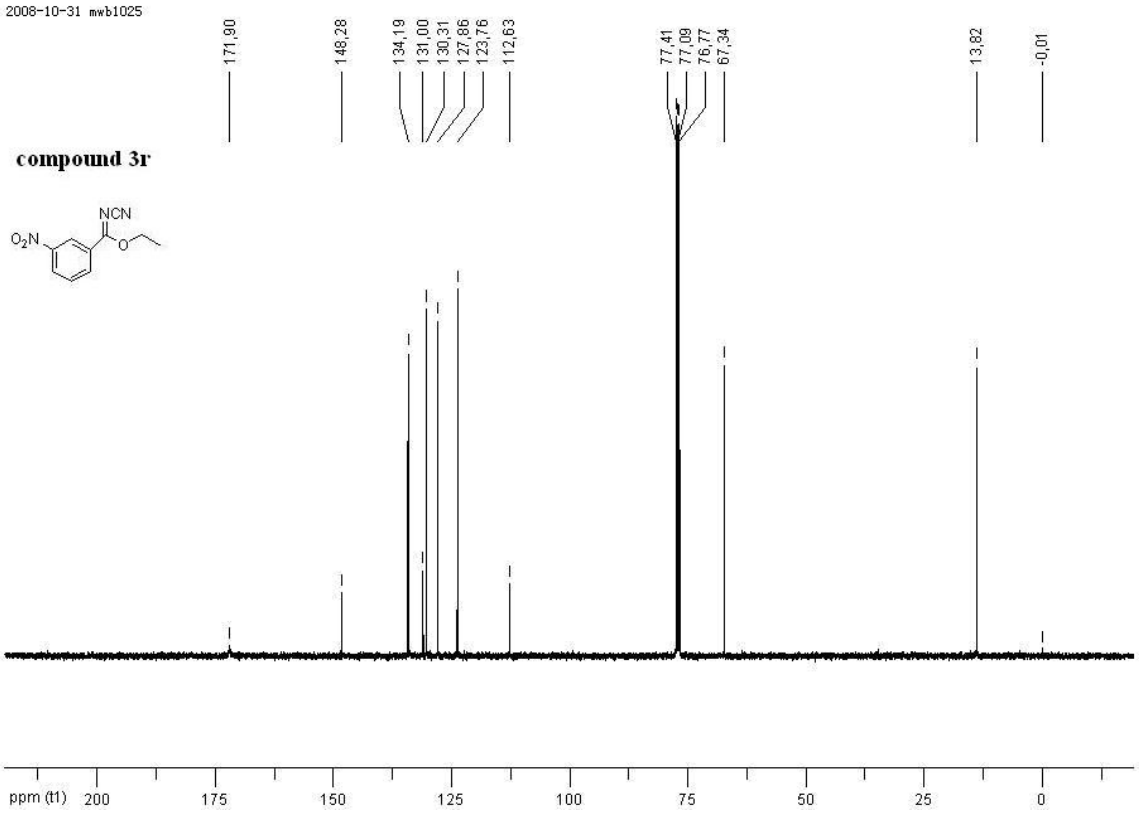

YP1024B 2008-10-24
compoud 3p
NCN
O
O2N
8,445
8,424
8,194
8,172
4,541
4,524
4,506
4,489
3,339
2,508
1,427
1,410
1,392
-0,001
1.86
1.85
2.00
3.06
ppm (f1)
10.0
7.5
5.0
2.5
0.0

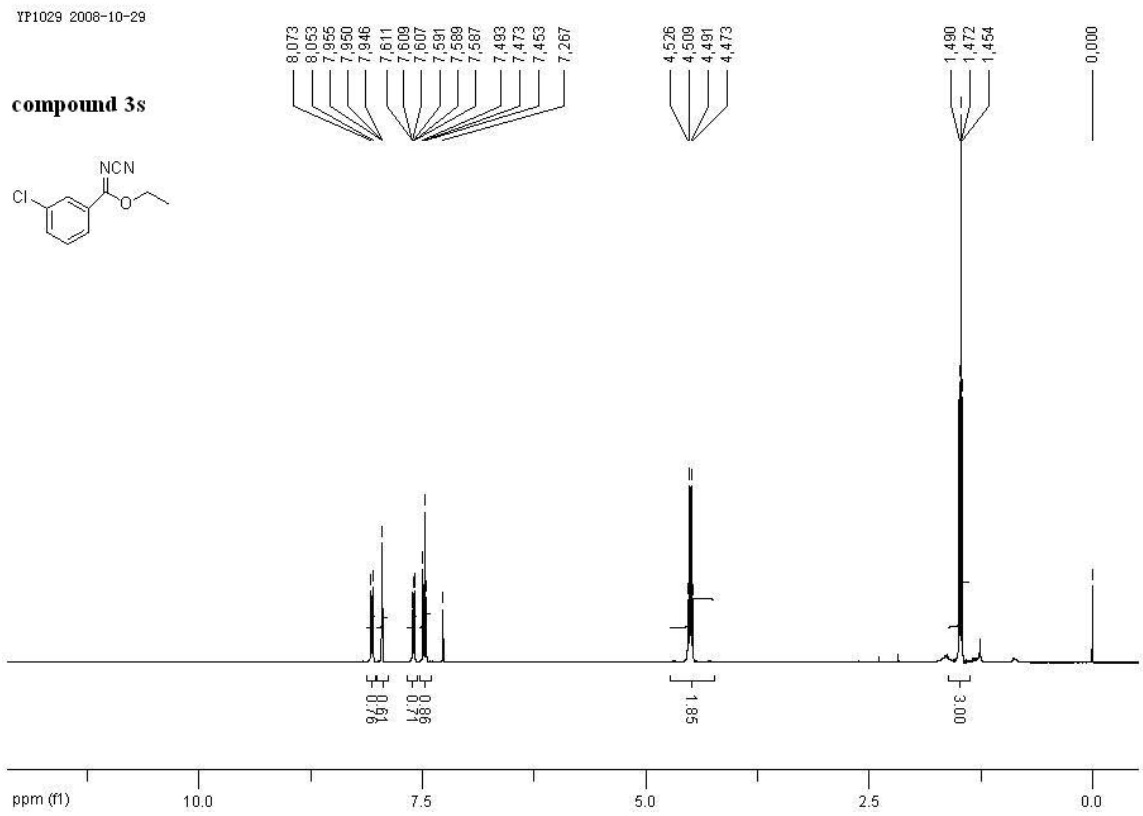

YP1024B-DMSO-C13-2008-10-24
compoud 3p
NCN
O
O2N
PPM

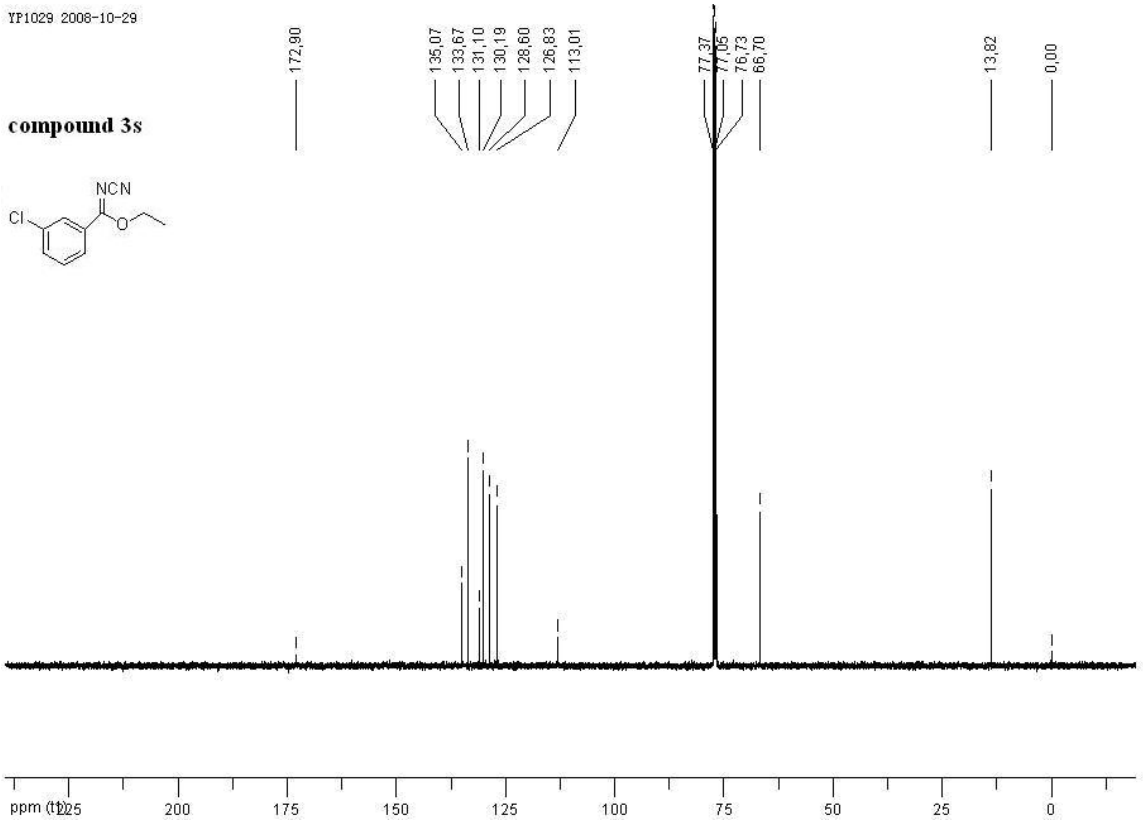

YP-1031 2008-10-31
compound 3q
7,676
7,656
7,568
7,562
7,557
7,439
7,419
7,399
7,270
7,166
7,161
7,159
7,145
7,140
4,507
4,489
4,471
4,454
3,866
1,476
1,459
1,441
-0,000
0,84
1,91
3,21
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0


YP-1031 2008-10-31
compound 3q
174,26
159,65
130,73
129,92
120,99
119,92
113,47
113,41
77,27
77,05
76,84
66,28
55,56
13,81
-0,03
ppm (f1)
200
175
150
125
100
75
50
25
0

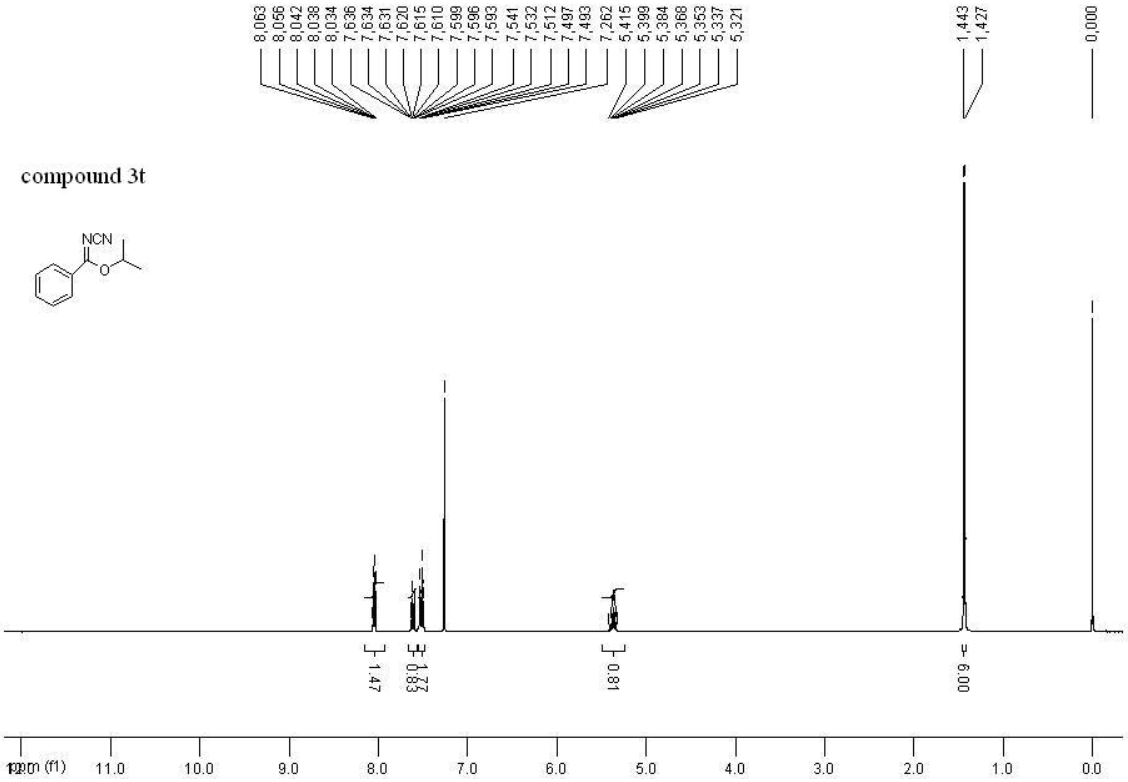

2008-10-31 mwb1025
8,805
8,800
8,795
8,547
8,544
8,540
8,527
8,524
8,520
8,501
8,499
8,496
8,493
8,480
8,478
8,475
8,472
7,798
7,778
7,758
7,284
4,613
4,595
4,578
4,560
1,541
1,523
1,505
0,000
compound 3r
NCN
O2N
O
0,91
1,99
0,99
1,95
3,00
ppm (t1)
10.0
7.5
5.0
2.5
0.0


2008-10-31 mwb1025
171,90
148,28
134,19
131,00
130,31
127,86
123,76
112,63
77,41
77,09
76,77
67,34
13,82
-0,01
compound 3r
NCN
O2N
O
ppm (t1)
200
175
150
125
100
75
50
25
0

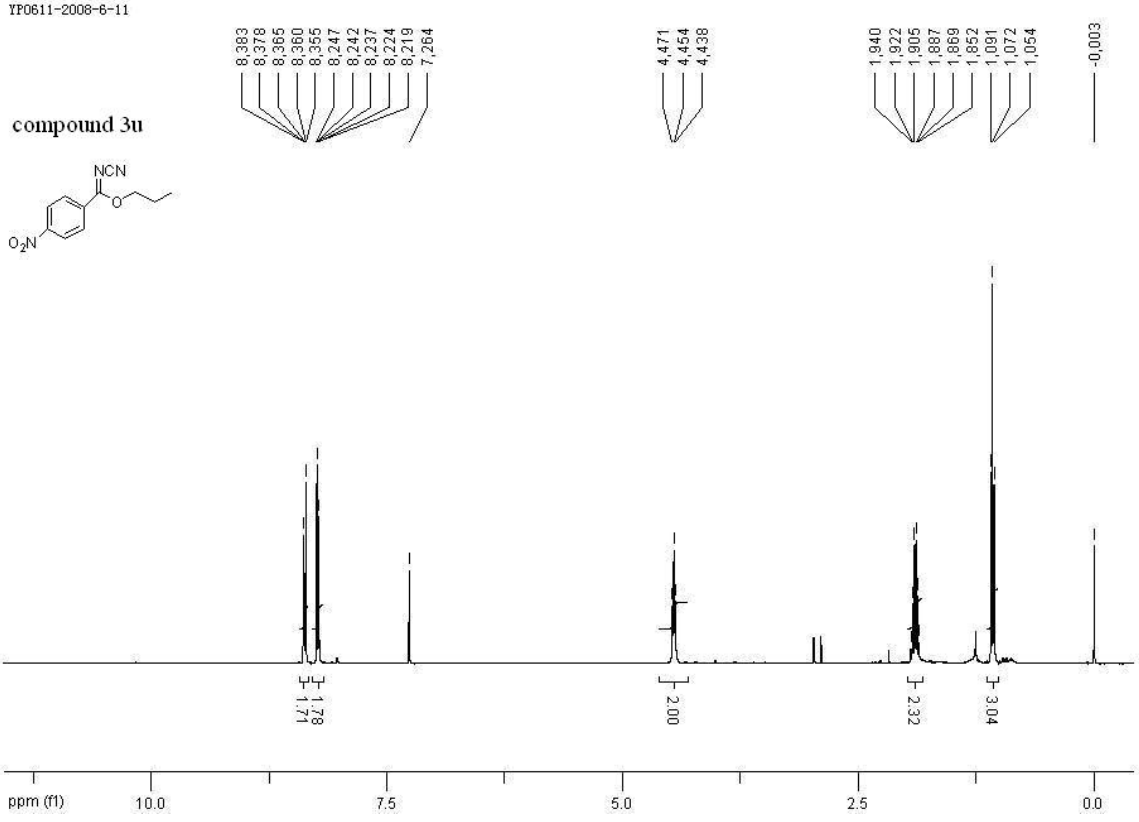

YP1029 2008-10-29
compound 3s
8,073
8,053
7,956
7,950
7,946
7,611
7,609
7,607
7,591
7,589
7,587
7,493
7,473
7,453
7,267
4,526
4,509
4,491
4,473
1,490
1,472
1,454
0,000
0,96
1,00
0,98
0,71
0,98
1,86
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0


YP1029 2008-10-29
compound 3s
172,90
135,07
133,67
131,10
130,19
128,60
126,83
113,01
77,37
77,05
76,73
66,70
13,82
0,00
ppm (f1)
225
200
175
150
125
100
75
50
25
0

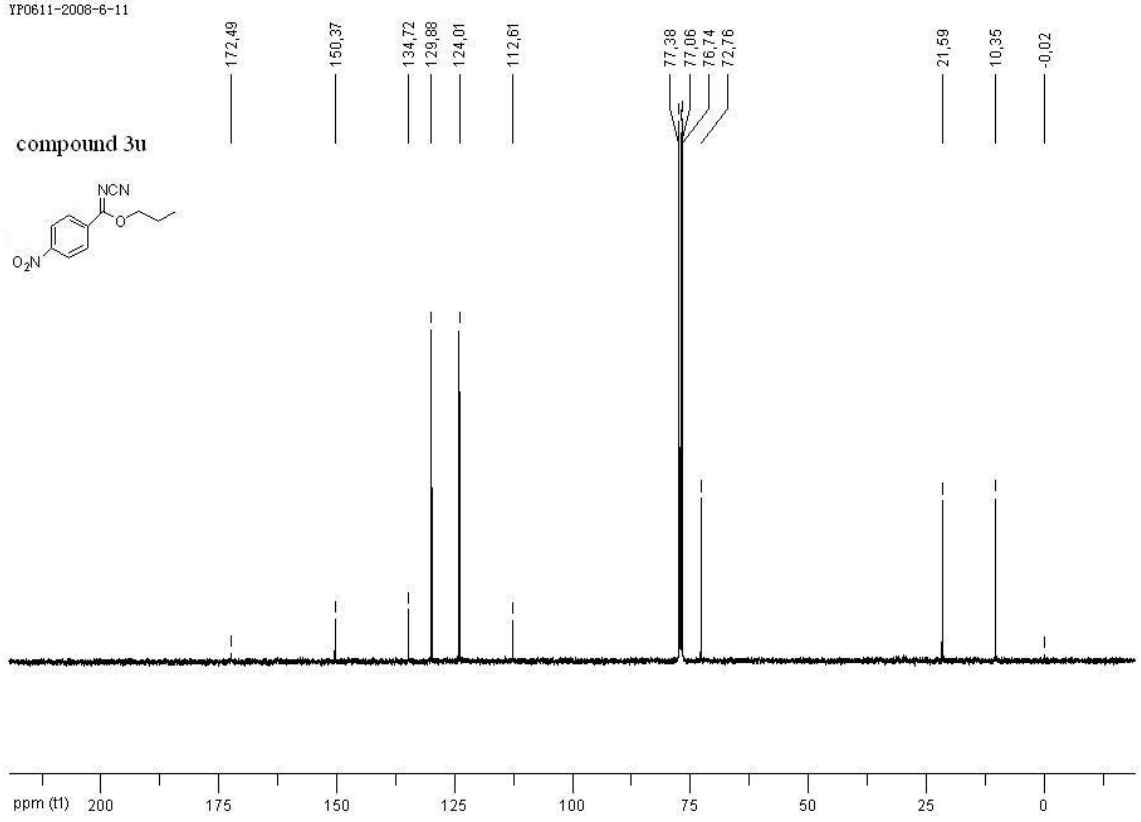
YP1103 2008-11-3



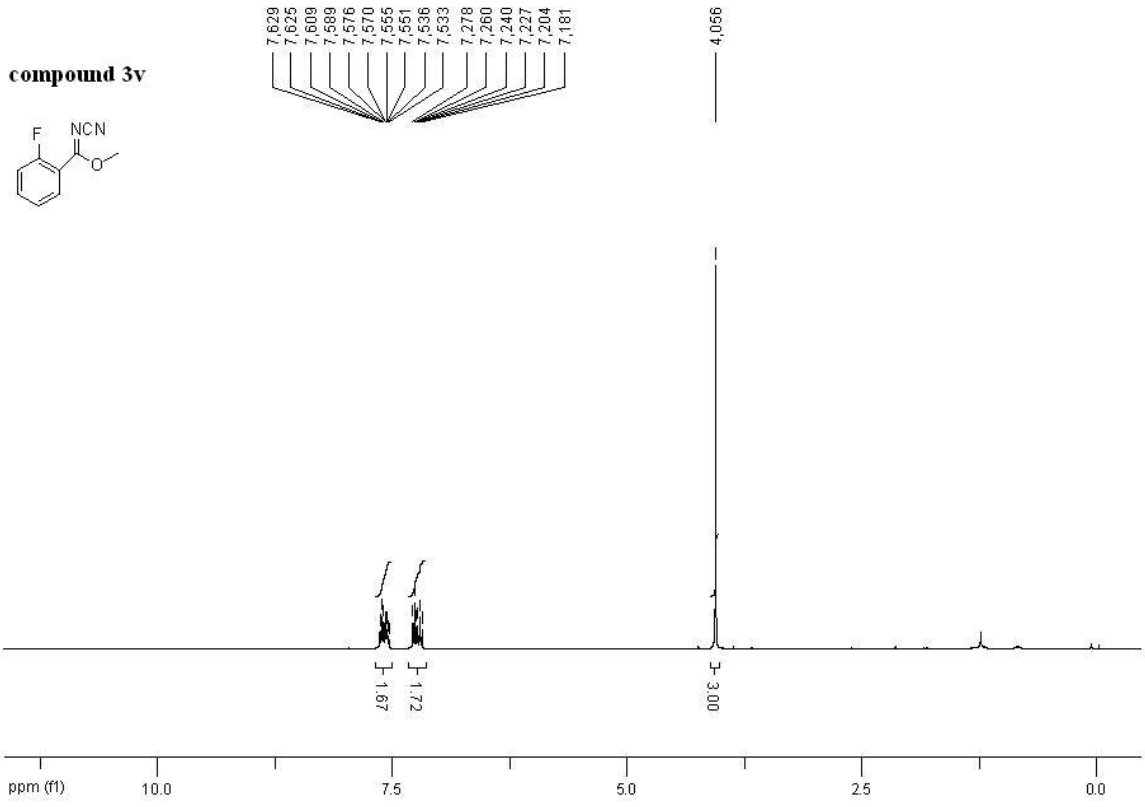
YP0611-2008-6-11



YP0611-2008-6-11



YP1128B 2008-12-2

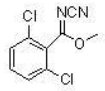


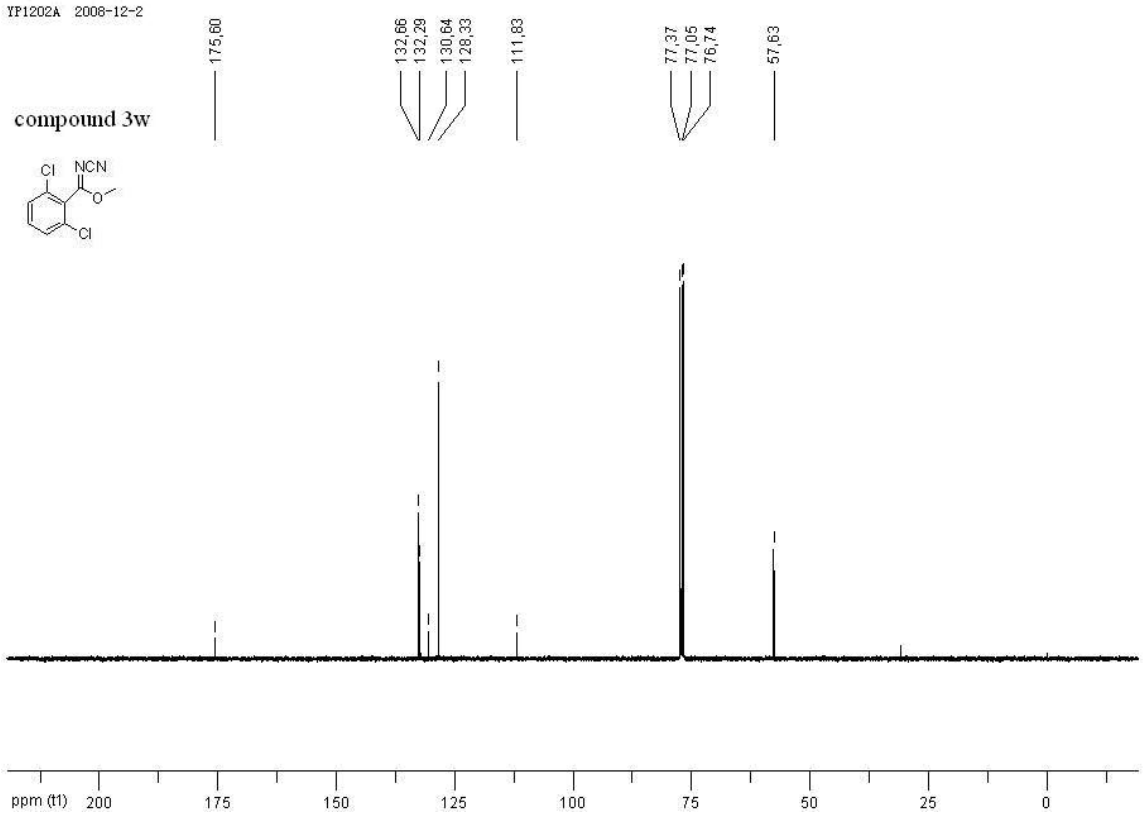
YP1128B 2008-12-2

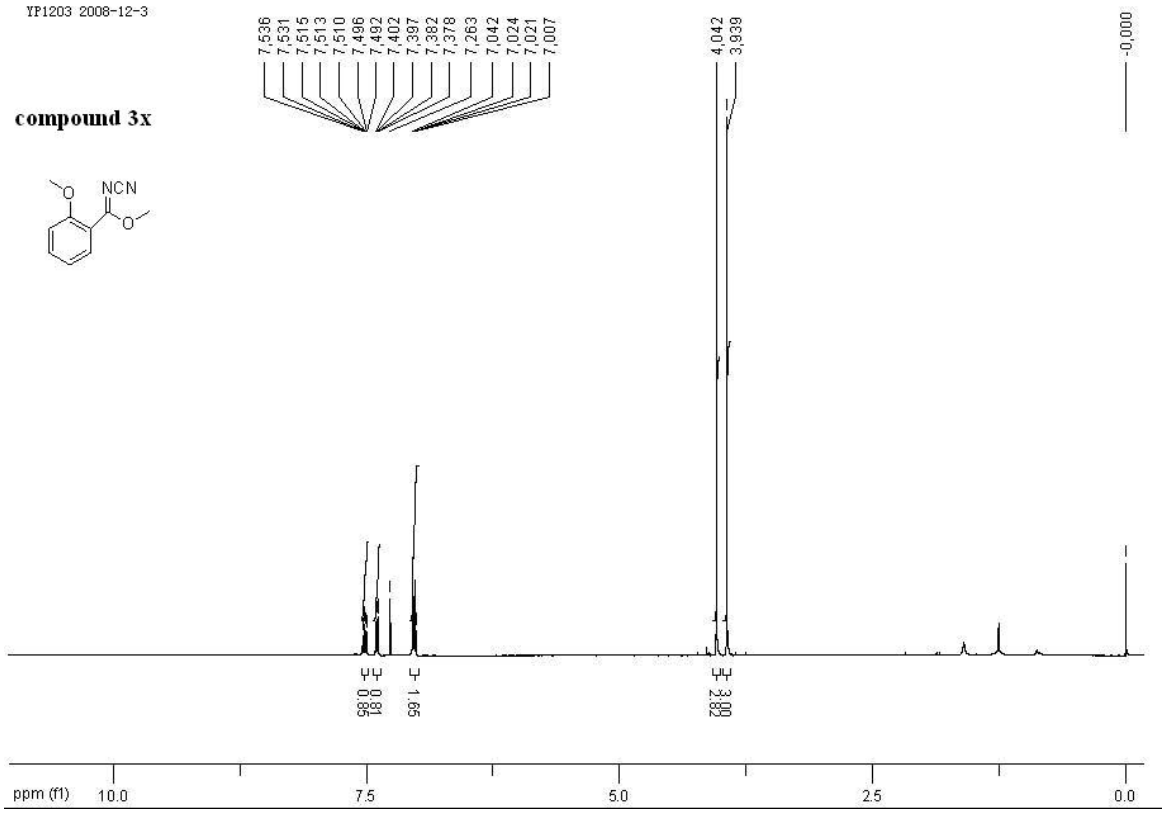
compound 3v

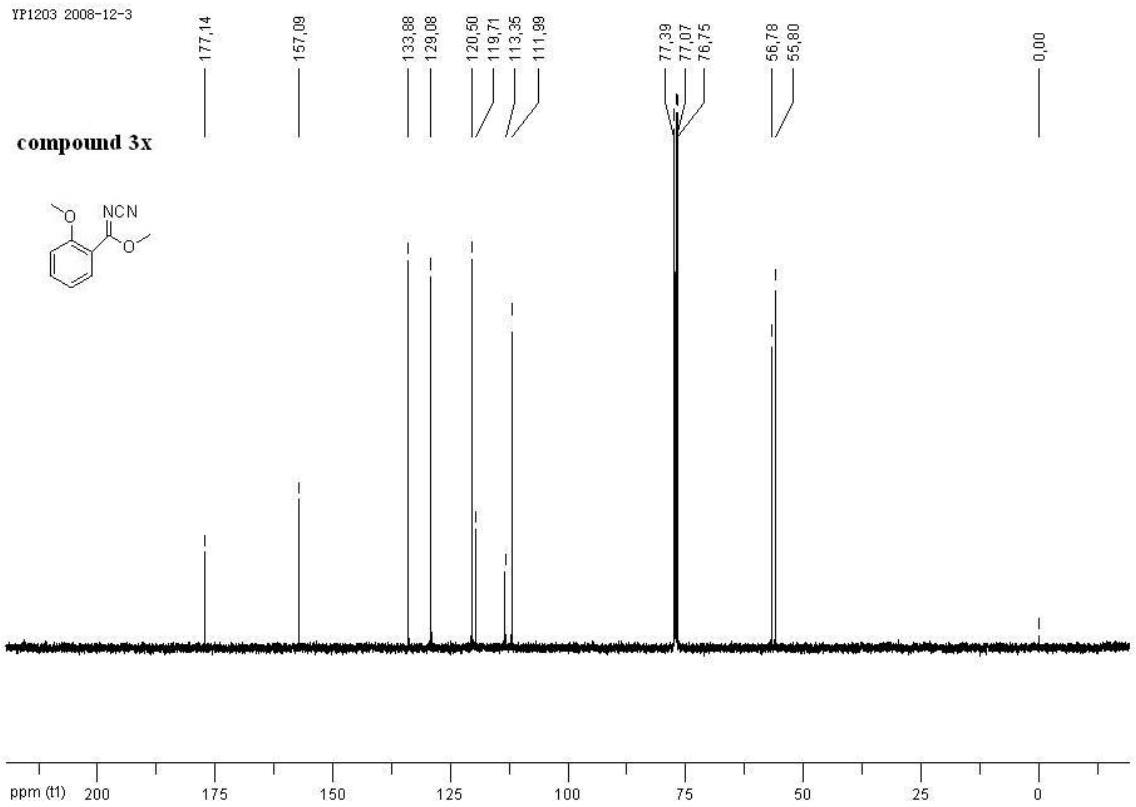
YP1202A 2008-12-2

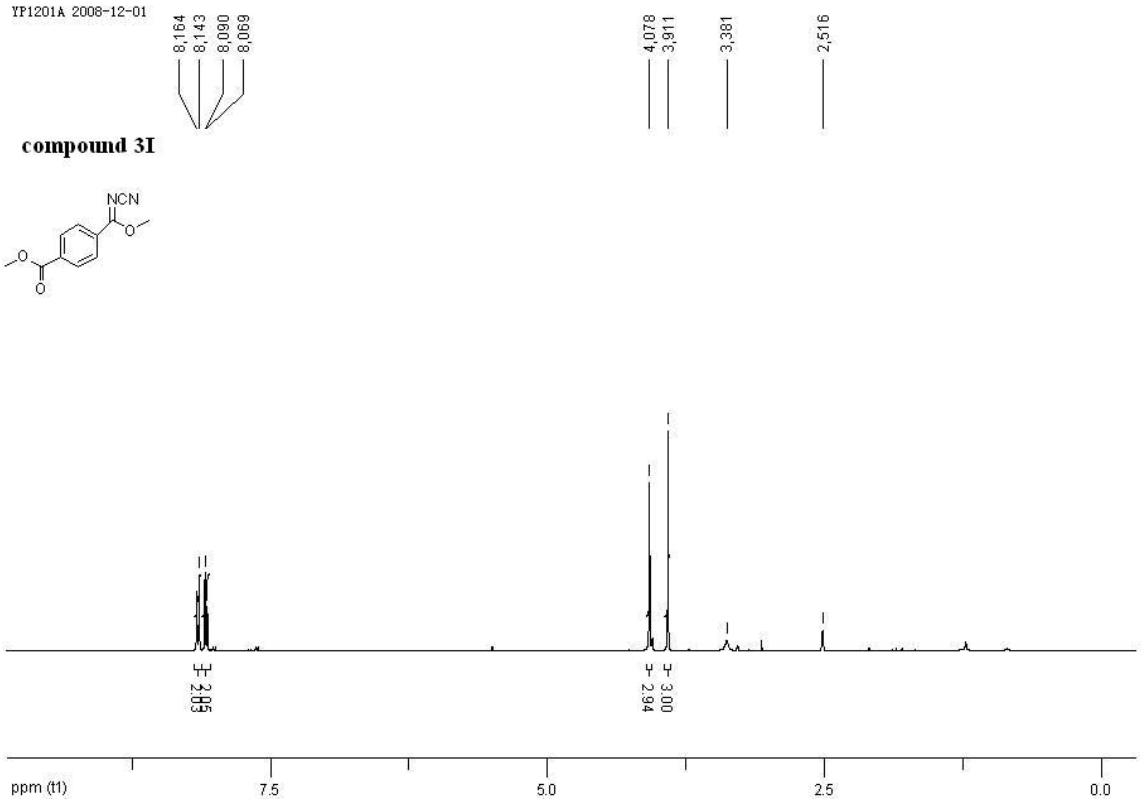
compound 3w




YP1202A 2008-12-2
175,60
132,66
132,29
130,64
128,33
111,83
77,37
77,05
76,74
57,63
compound 3w
Cl
NCN
O
Cl
ppm (f1)
200
175
150
125
100
75
50
25
0


YP1203 2008-12-3
7,536
7,531
7,515
7,513
7,510
7,496
7,492
7,402
7,397
7,382
7,378
7,263
7,042
7,024
7,021
7,007
4,042
3,939
-0,000
compound 3x
NCN
O
O
0,86
1,00
1,66
2,82
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0

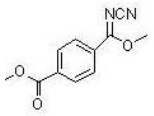

YP1203 2008-12-3
177,14
157,09
133,88
129,08
120,50
119,71
113,35
111,99
77,39
77,07
76,75
56,78
55,80
0,00
compound 3x
NCN
O
O
ppm (t1)
200
175
150
125
100
75
50
25
0


YP1201A 2008-12-01
8,164
8,143
8,090
8,069
4,078
3,911
3,381
2,516
compound 3I
NCN
O
O
O
2,05
2,94
3,00
ppm (t1)
7.5
5.0
2.5
0.0

YP1201A 2008-12-01

175,67
165,66
134,11
133,56
129,97
129,29
128,89
127,51
113,37
58,05
53,08
40,61
40,41
40,20
39,99
39,78
39,57
39,36

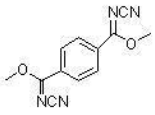
compound 3I

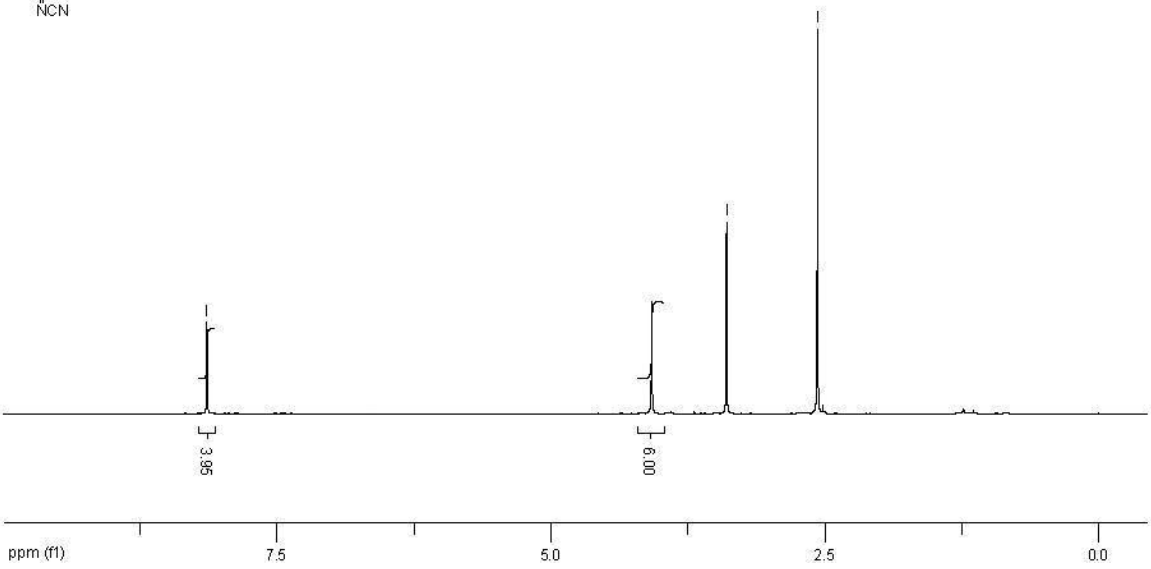


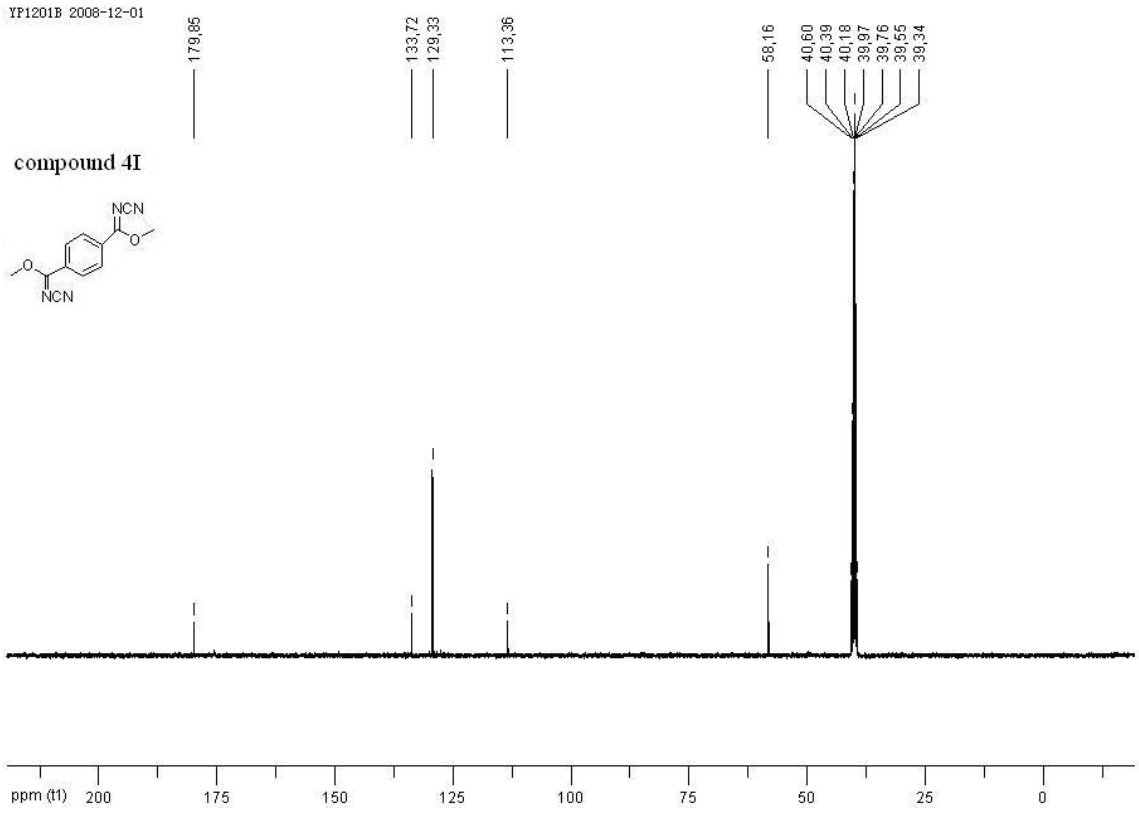
YP1201B 2008-12-01

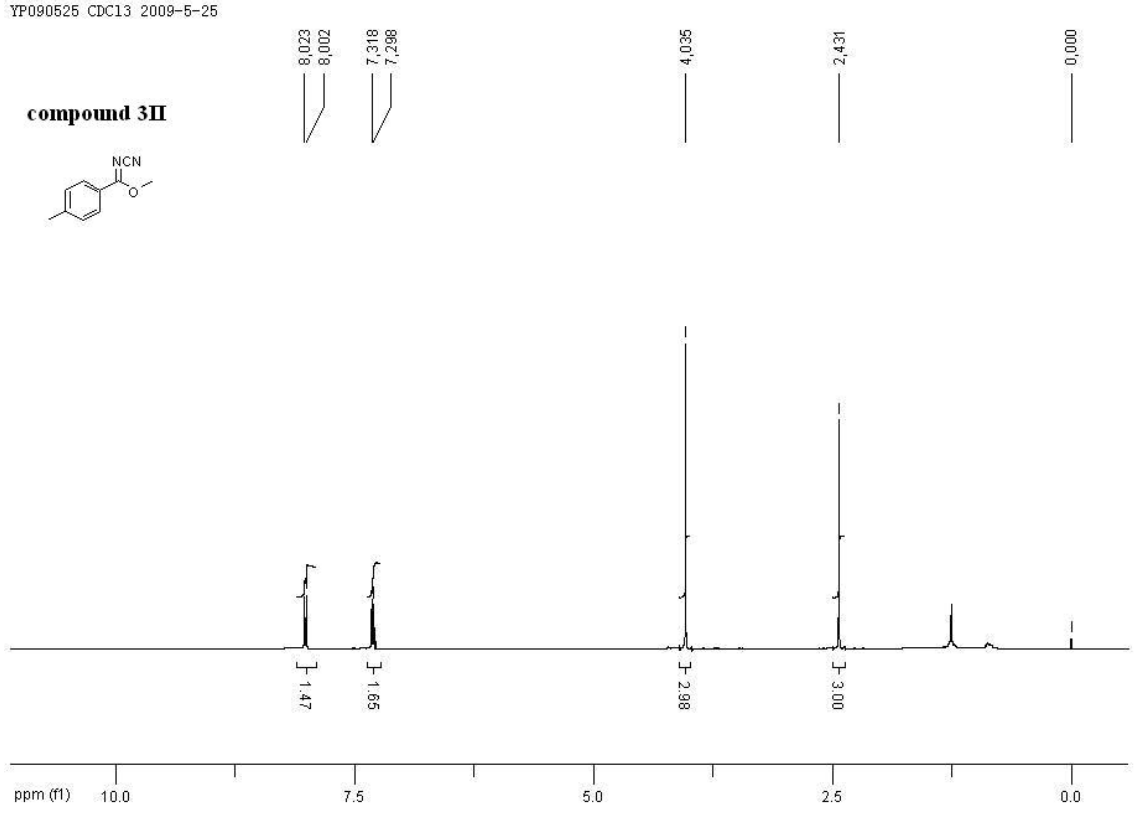
8,139
4,080
3,397
2,567

compound 4I

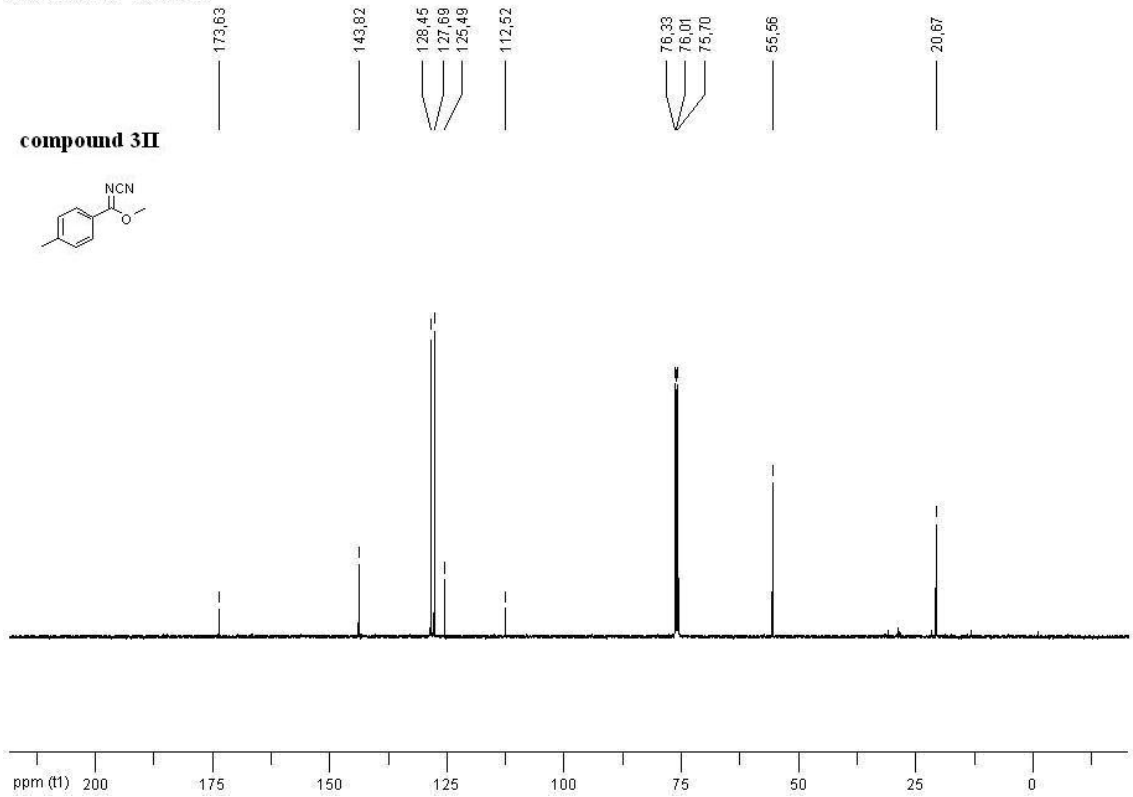





YP1201B 2008-12-01
179,85
133,72
129,33
113,36
58,16
40,60
40,39
40,18
39,97
39,76
39,55
39,34
compound 4I
NCN
NCN
ppm (t1) 200 175 150 125 100 75 50 25 0

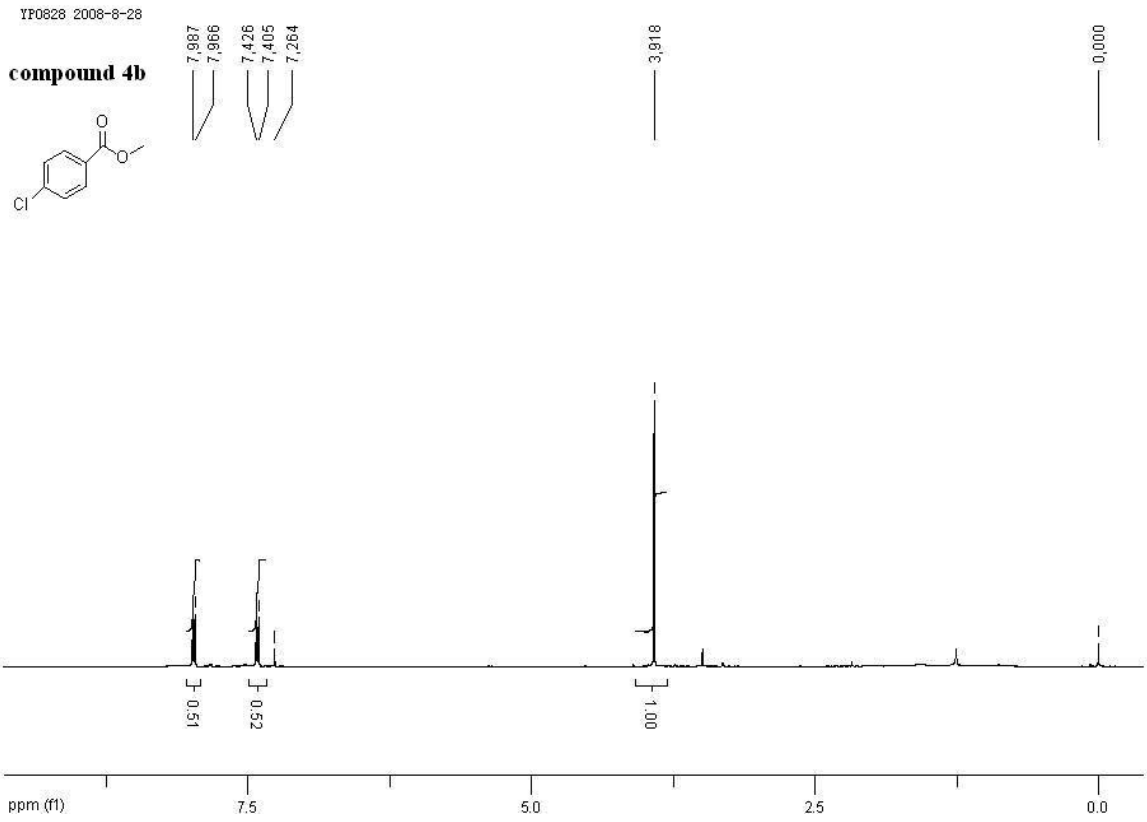

YP090525 CDC13 2009-5-25
8,023
8,002
7,318
7,298
4,035
2,431
0,000
compound 3II
NCN
1.47
1.69
2.88
3.00
ppm (f1) 10.0 7.5 5.0 2.5 0.0

YP090525 CDC13 2009-5-25

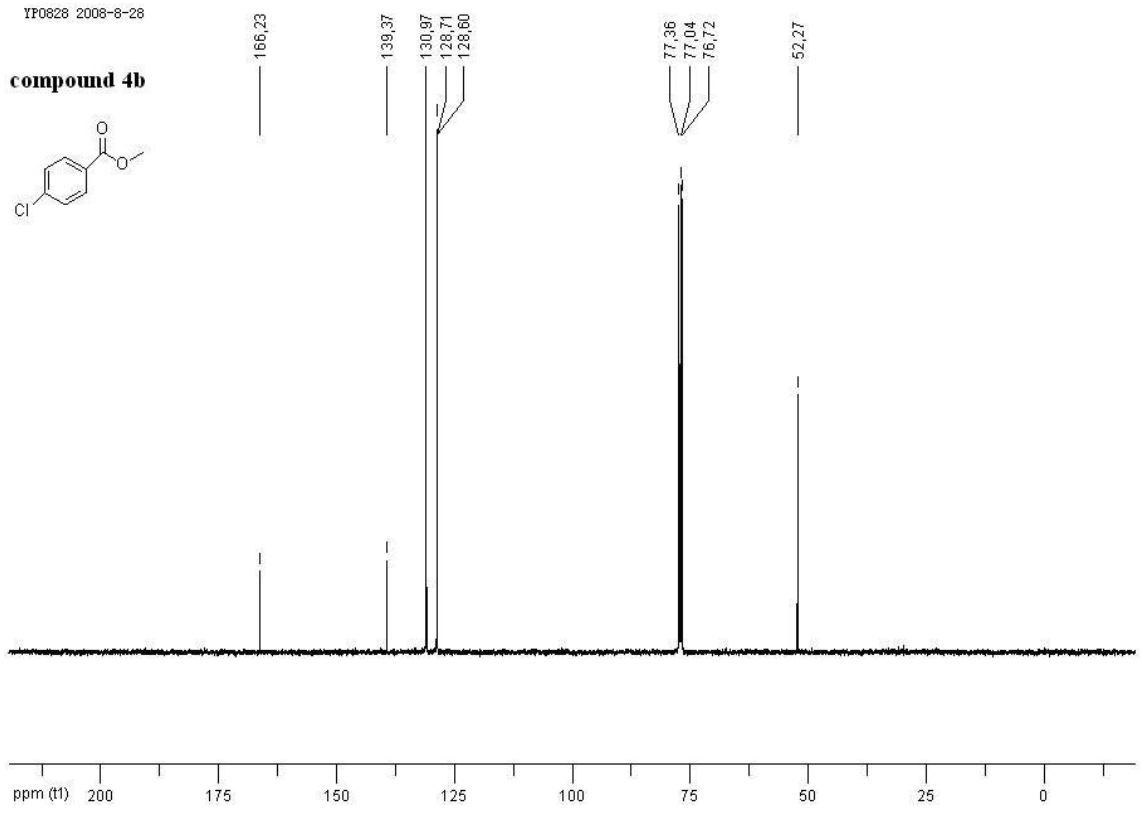


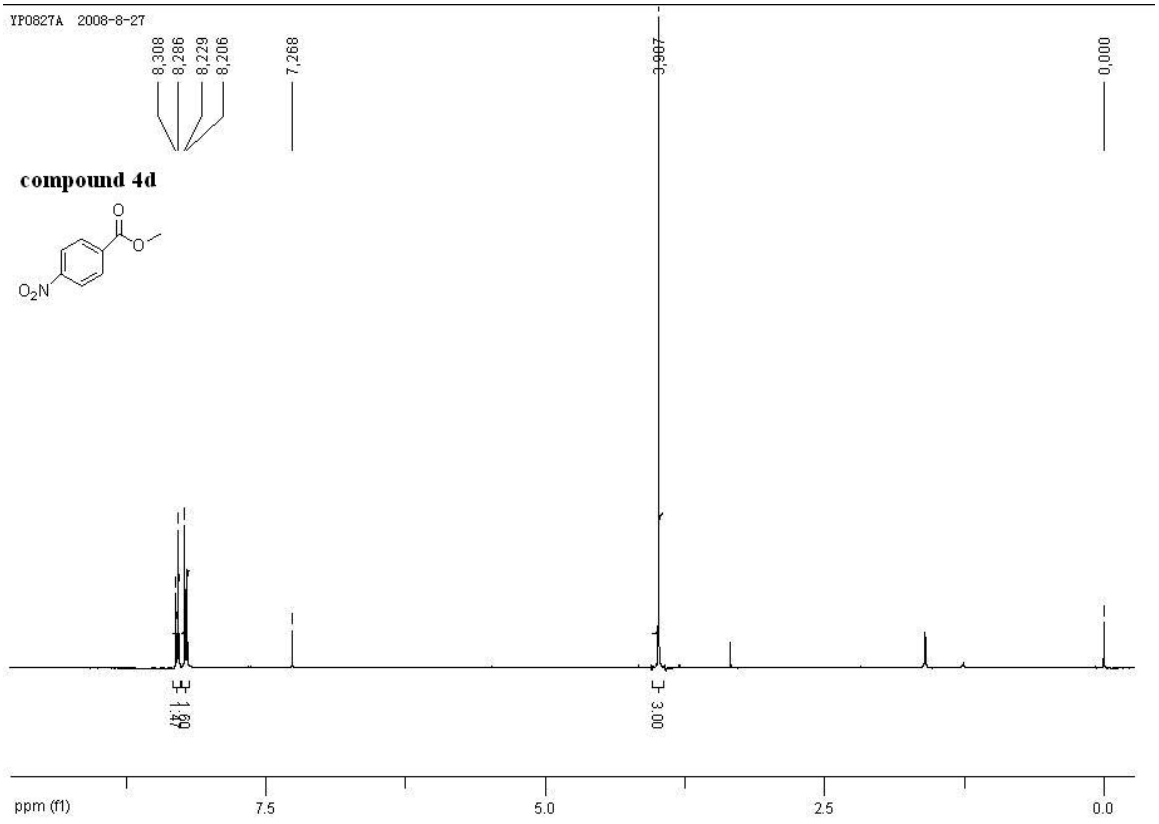
compound 3II

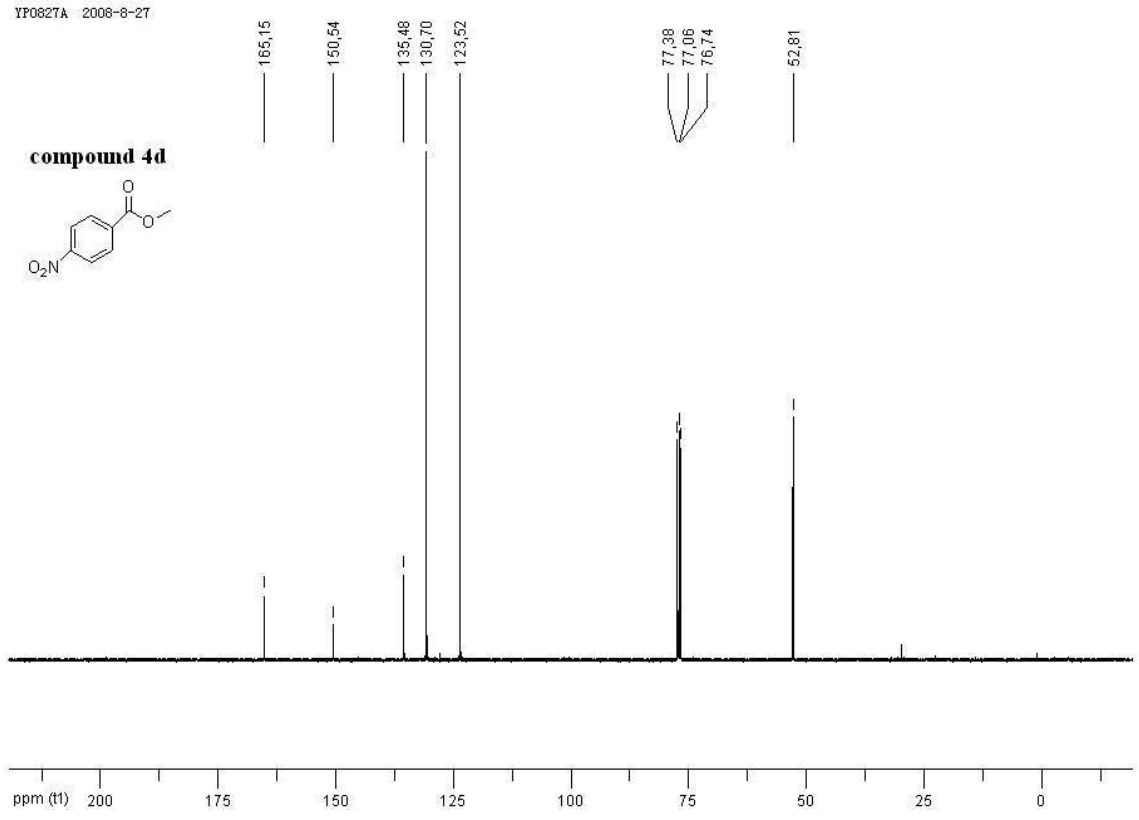
YP0828 2008-8-28

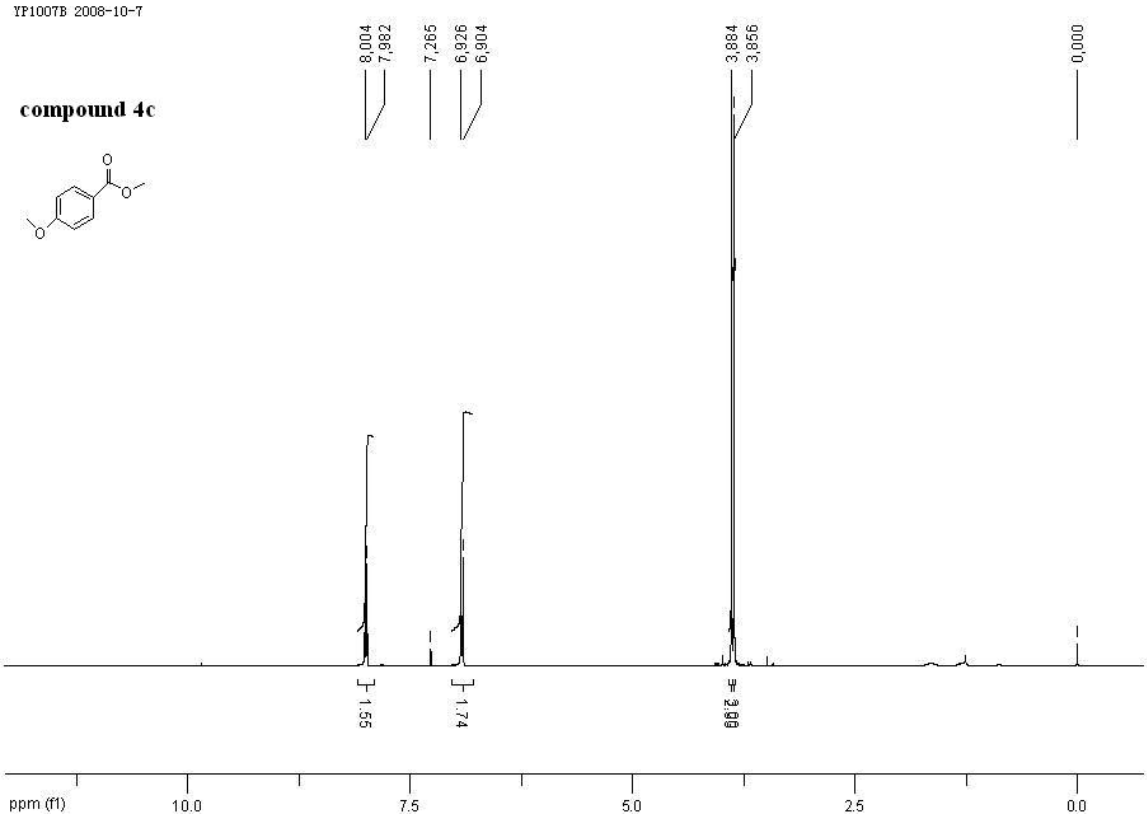


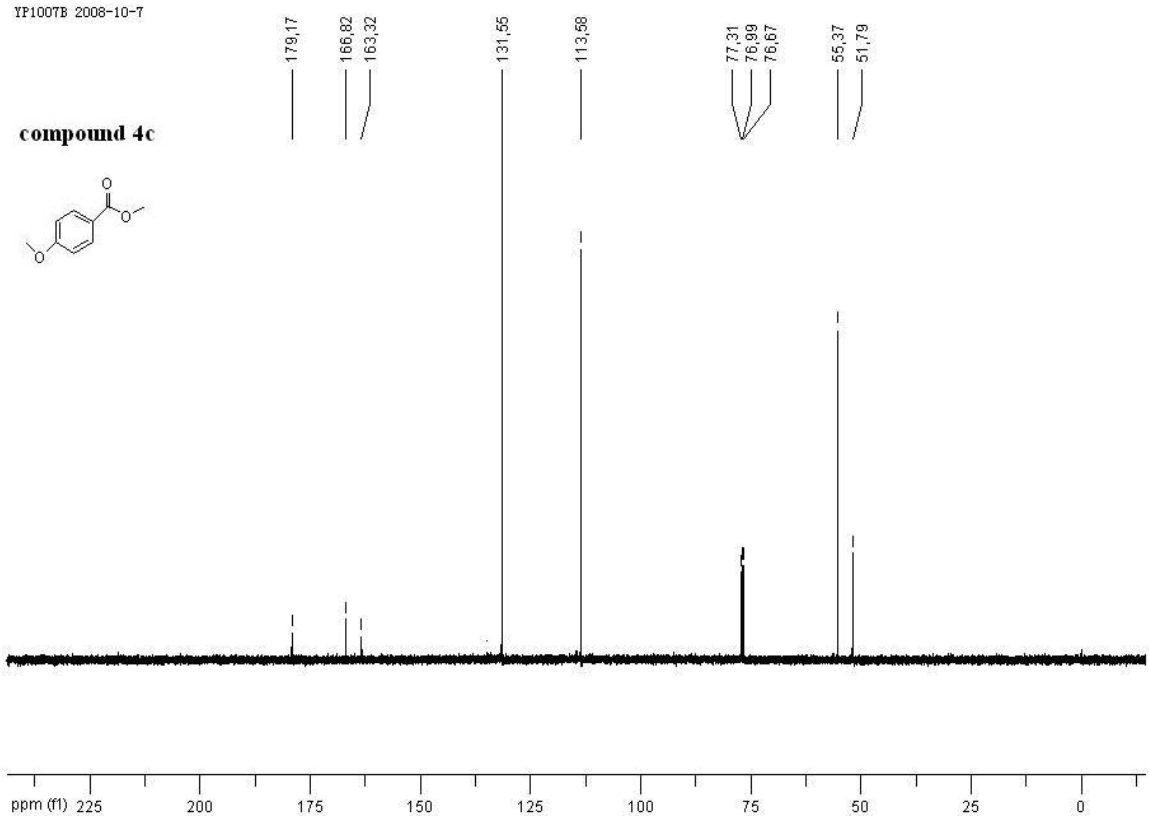
compound 4b

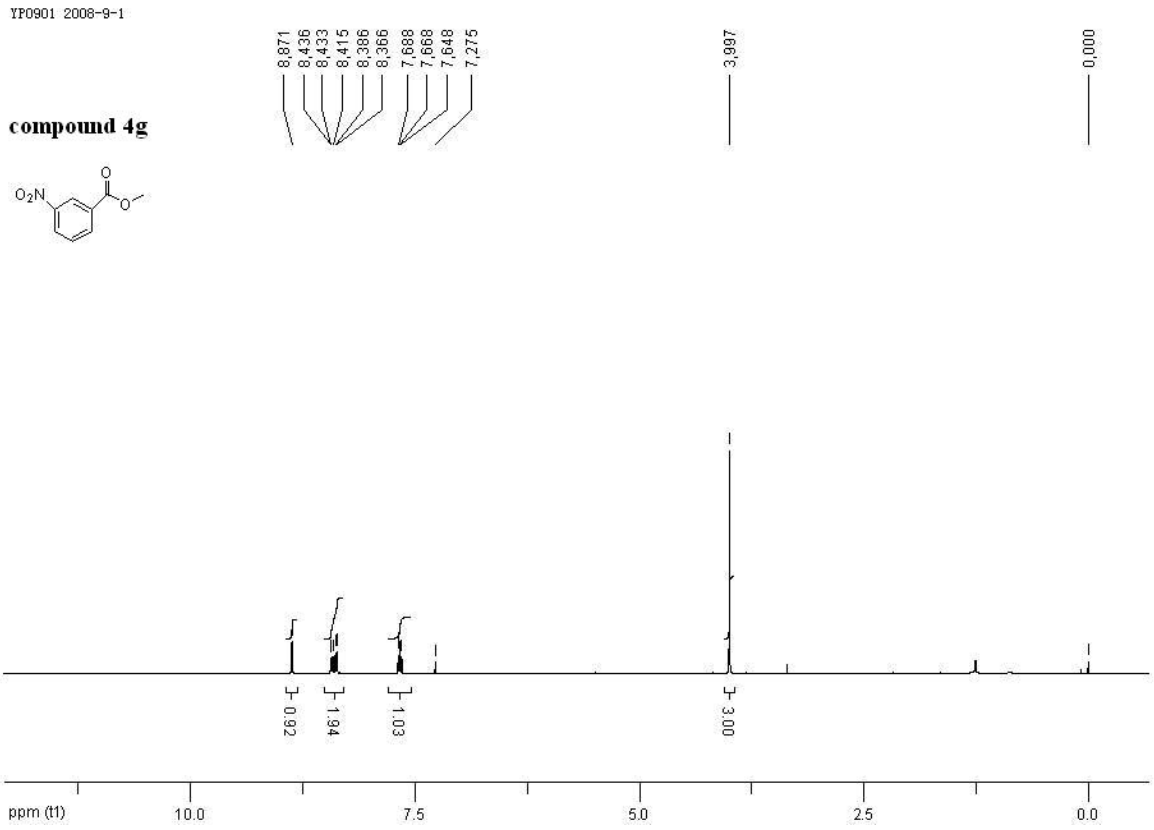

YP0828 2008-8-28
compound 4b
166,23
139,37
130,97
128,71
128,60
77,36
77,04
76,72
52,27
Cl
O
O
ppm (t1)
200
175
150
125
100
75
50
25
0

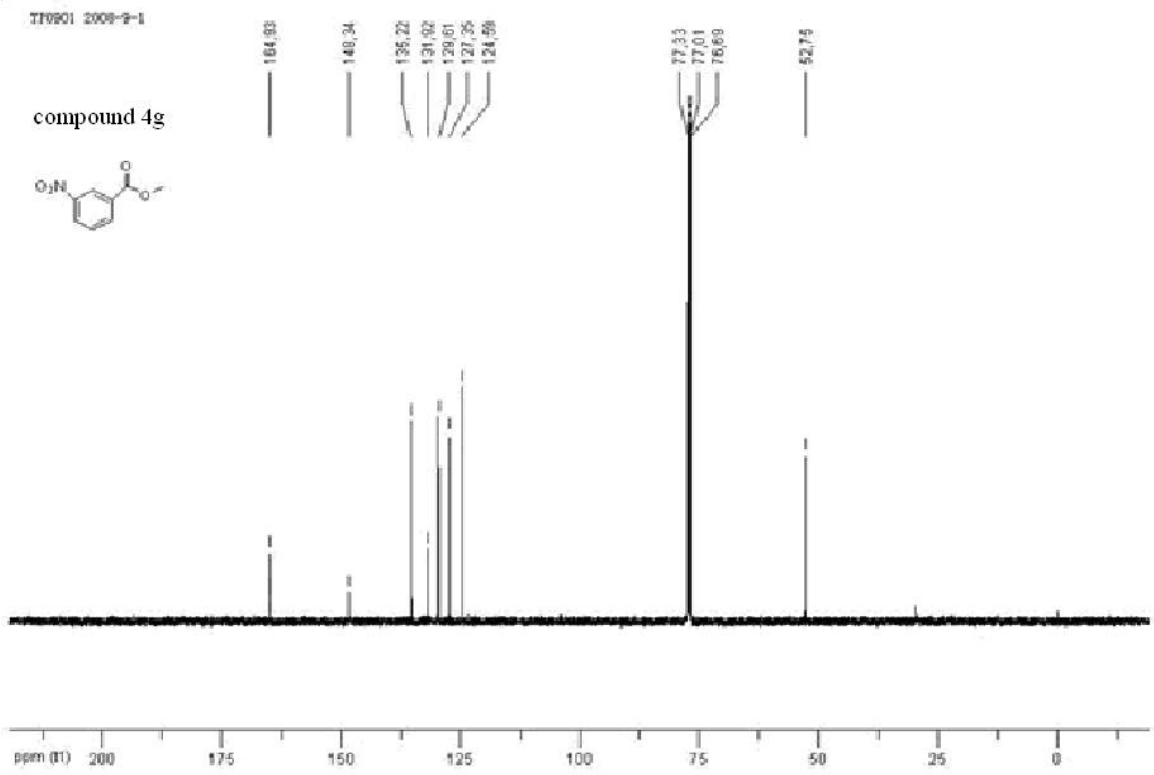

YP0827A 2008-8-27
8,308
8,286
8,229
8,206
7,268
3,907
0,000
compound 4d
O
O
O2N
1,87
3,00
ppm (f1)
7.5
5.0
2.5
0.0

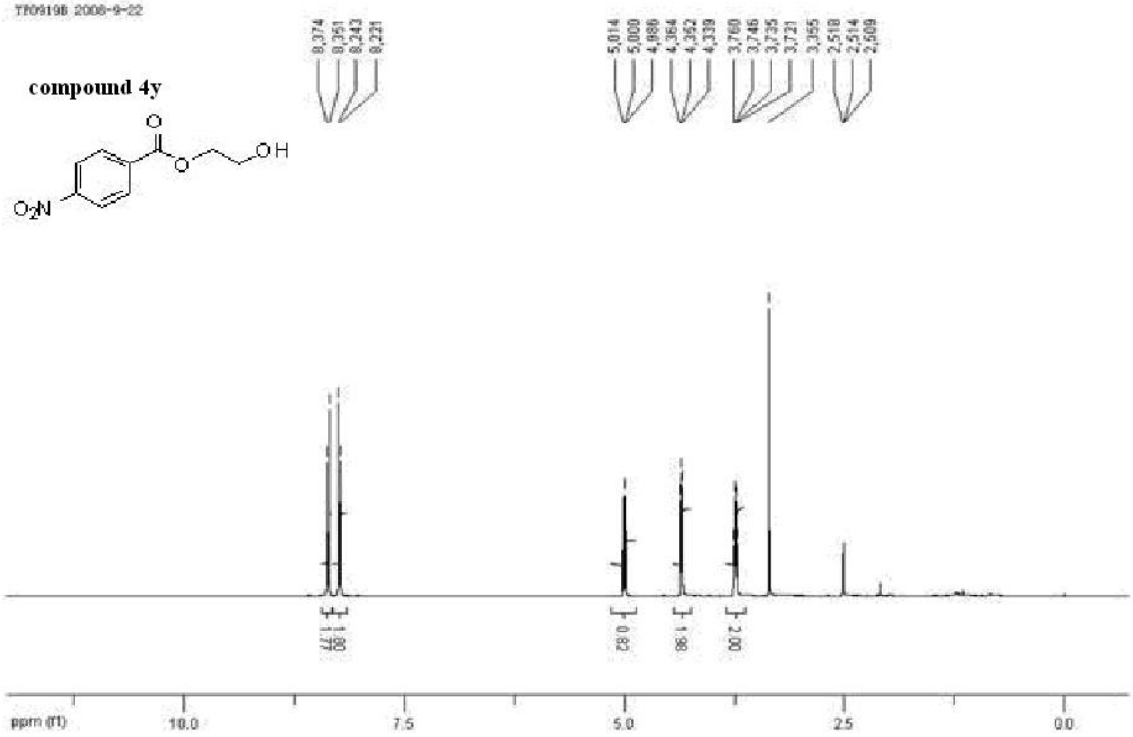

YP0827A 2008-8-27
165,15
150,54
135,48
130,70
123,52
77,38
77,06
76,74
52,81
compound 4d
O
O
O2N
ppm (f1)
200
175
150
125
100
75
50
25
0

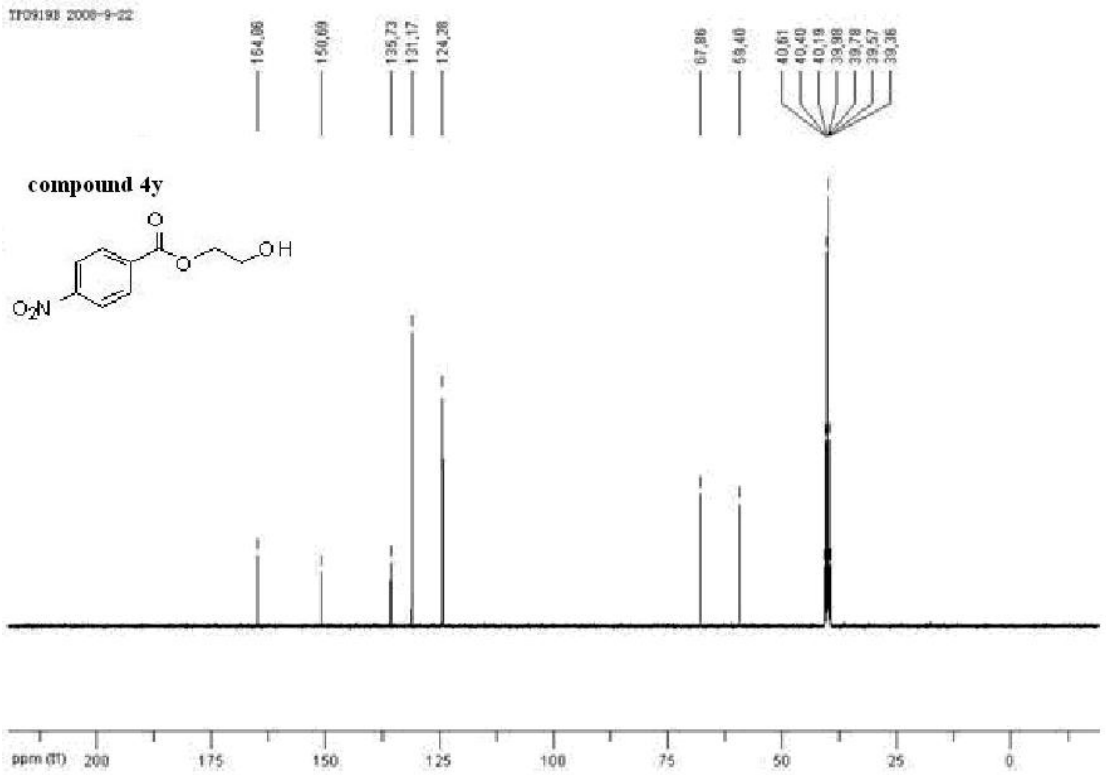

YP1007B 2008-10-7
8,004
7,982
7,265
6,926
6,904
3,884
3,856
0,000
compound 4c
O
O
O
1,55
1,74
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0

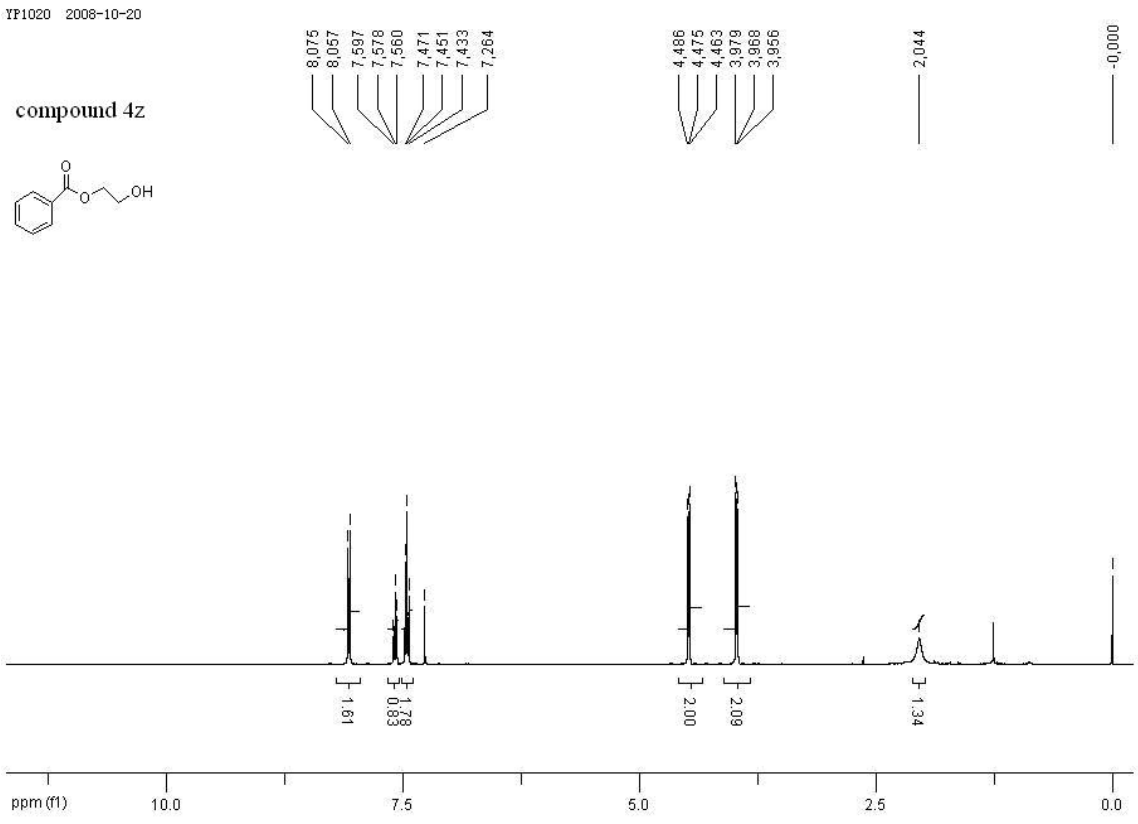

YP1007B 2008-10-7
compound 4c
179,17
166,82
163,32
131,55
113,58
77,31
76,99
76,67
55,37
51,79
ppm (f1) 225
200
175
150
125
100
75
50
25
0

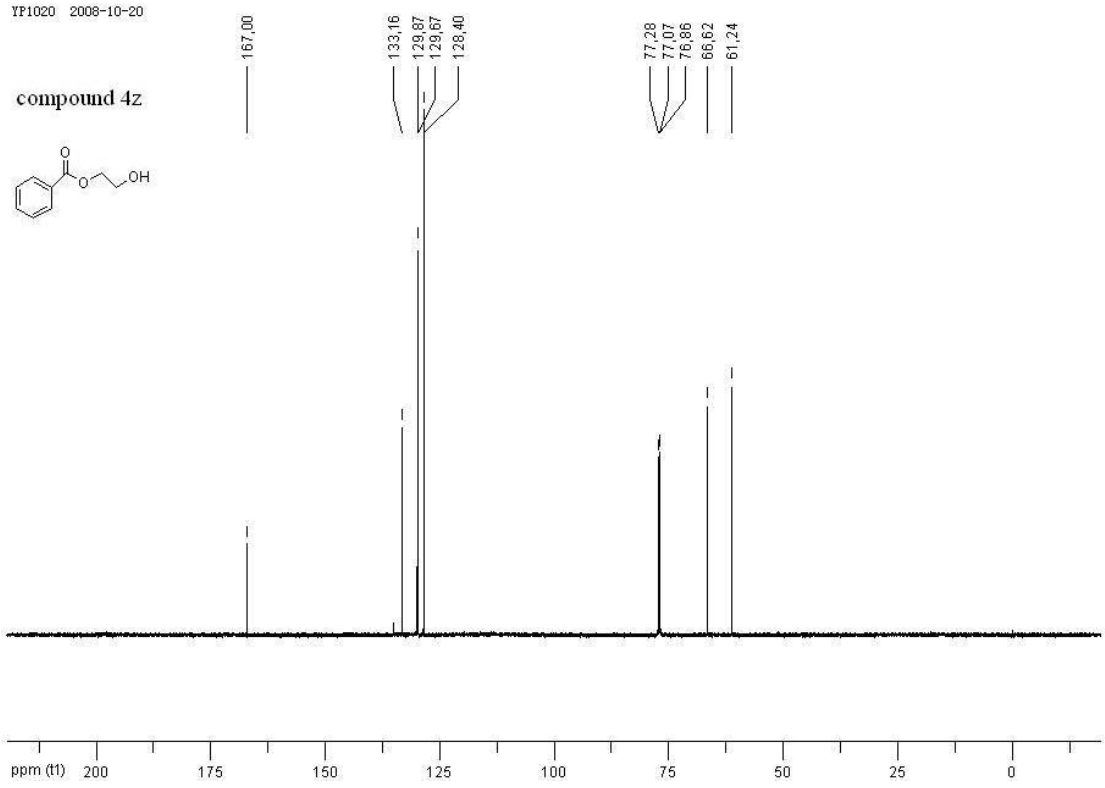

YP0901 2008-9-1
compound 4g
8,871
8,436
8,433
8,415
8,386
8,366
7,688
7,668
7,648
7,275
3,997
0,000
0,92
1,94
1,03
3,00
ppm (f1)
10.0
7.5
5.0
2.5
0.0

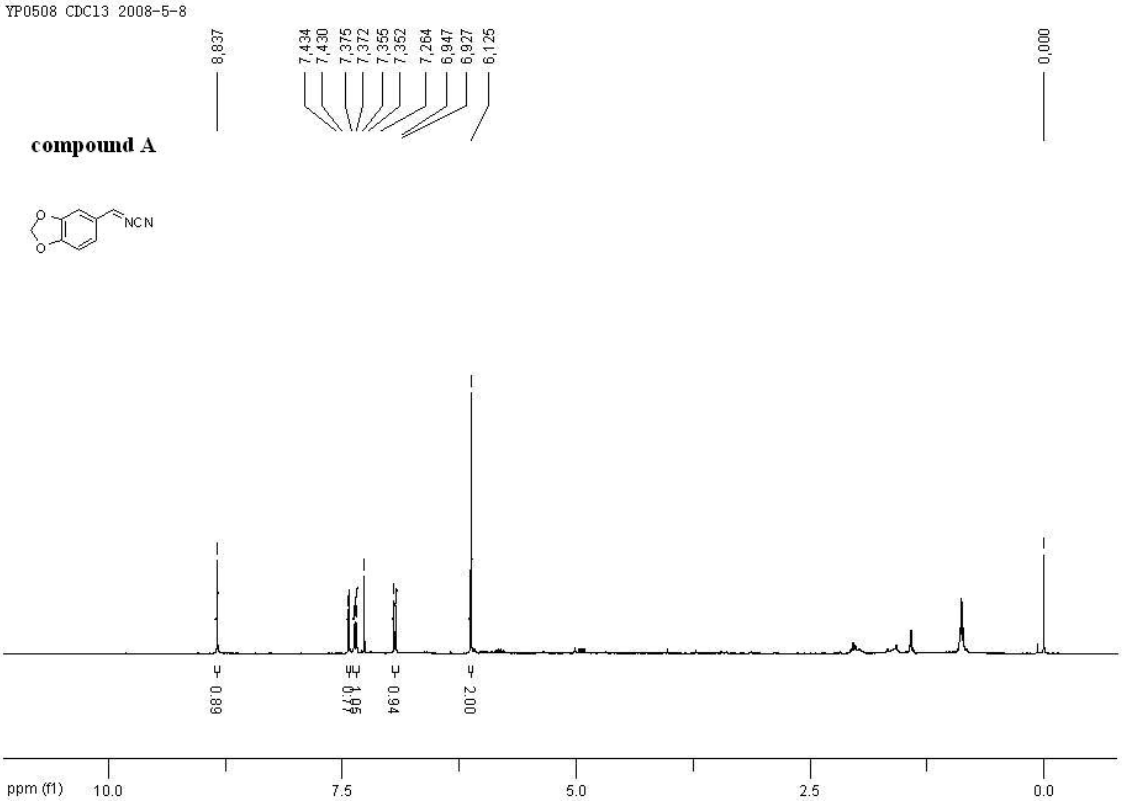

compound 4g
164,93
149,34
135,22
131,92
129,61
127,25
124,58
77,33
77,01
76,69
52,75
ppm (f1) 200 175 150 125 100 75 50 25 0


compound 4y
8,374
8,351
8,243
8,221
5,014
5,000
4,988
4,364
4,352
4,339
3,760
3,746
3,735
3,721
3,355
2,518
2,514
2,509
1,80
1,77
0,82
1,98
2,00
ppm (f1) 10.0 7.5 5.0 2.5 0.0

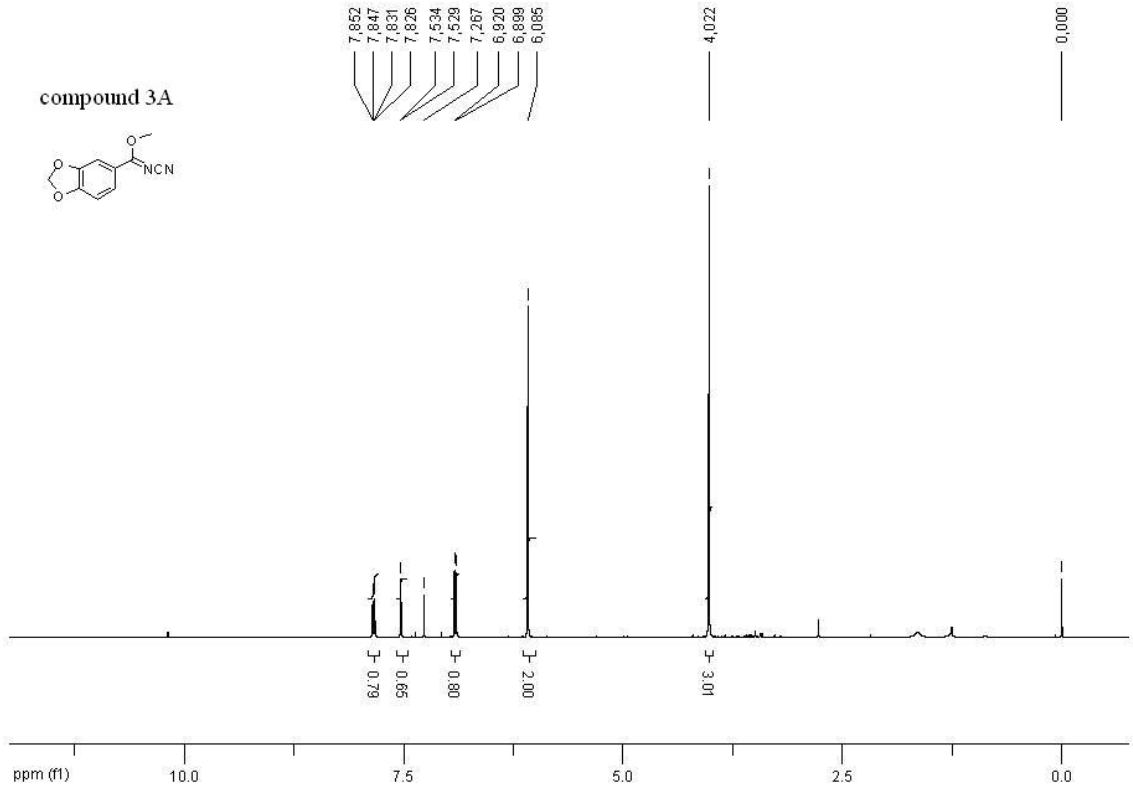

TF09198 2008-9-22
164,86
150,69
135,73
131,17
124,28
67,86
59,40
40,61
40,40
40,19
39,98
39,78
39,57
39,36
compound 4y
O
O
OH
O2N
ppm (f1) 200
175
150
125
100
75
50
25
0


YP1020 2008-10-20
8,075
8,057
7,597
7,578
7,560
7,471
7,451
7,433
7,264
4,486
4,475
4,463
3,979
3,968
3,956
2,044
0,000
compound 4z
O
O
OH
1,61
0,83
1,78
2,00
2,09
1,34
ppm (f1)
10.0
7.5
5.0
2.5
0.0

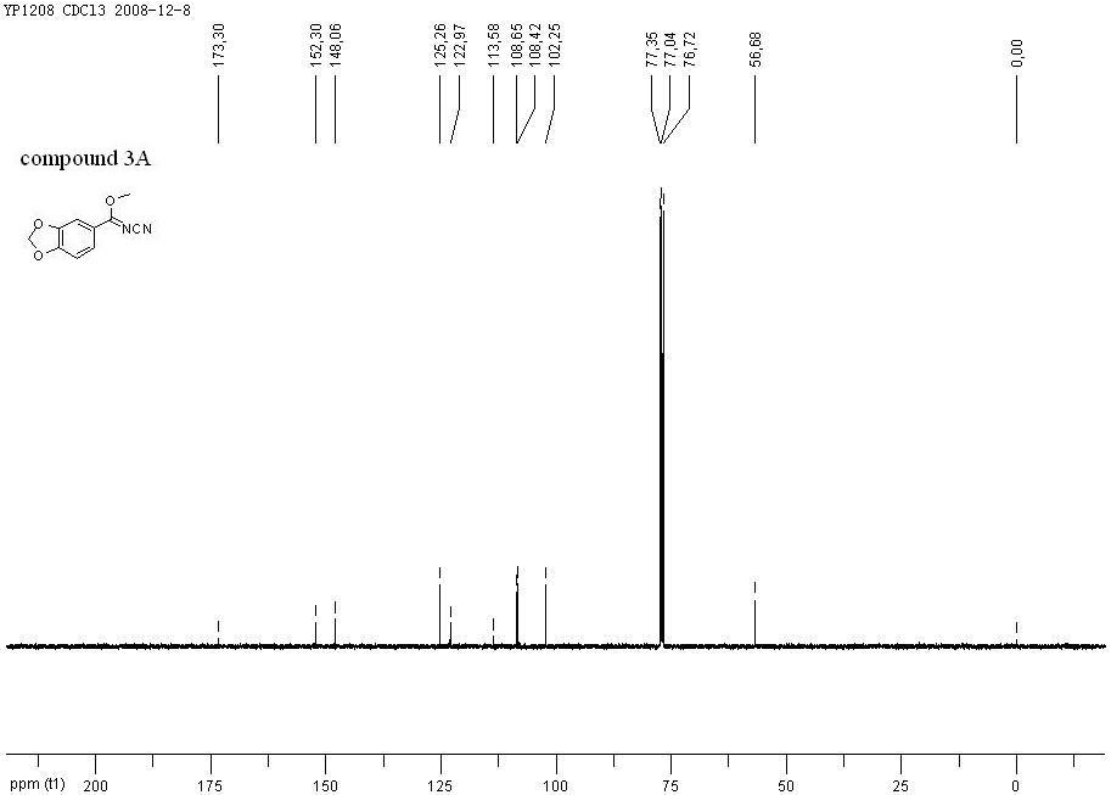

YP1020 2008-10-20
compound 4z
167,00
133,16
129,87
129,67
128,40
77,28
77,07
76,86
66,62
61,24
OH
ppm (t1) 200 175 150 125 100 75 50 25 0


YP0508 CDCl3 2008-5-8
8,837
7,434
7,430
7,375
7,372
7,355
7,352
7,264
6,947
6,927
6,125
0,000
compound A
NCN
0,89
0,95
0,94
2,00
ppm (f1) 10.0 7.5 5.0 2.5 0.0

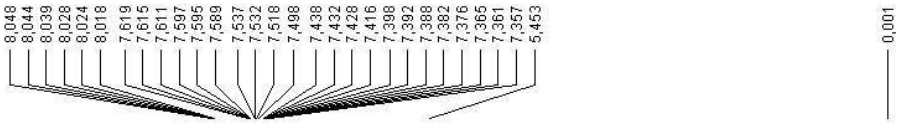
YP1208 CDC13 2008-12-8



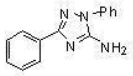
YP1208 CDC13 2008-12-8

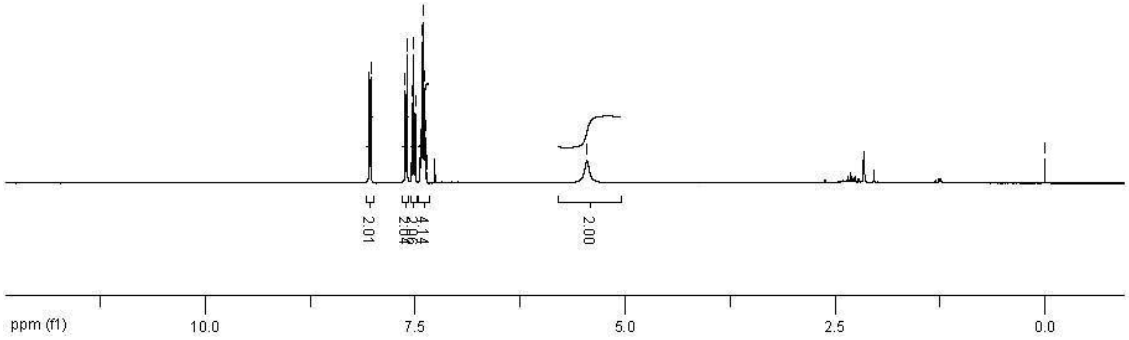


YP090710 2009-7-10

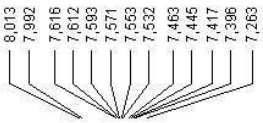


compound 5a

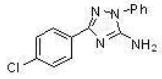


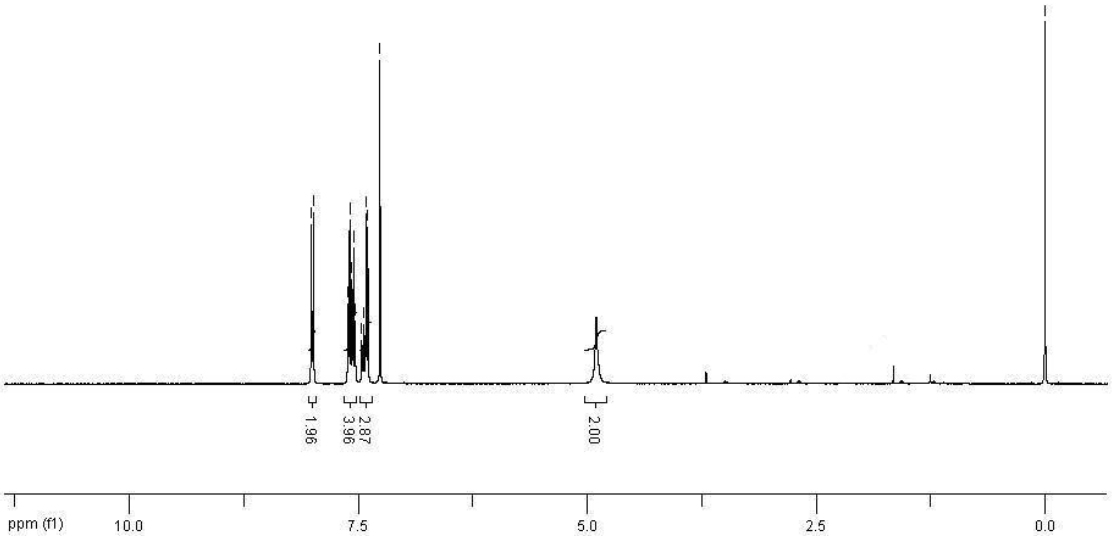


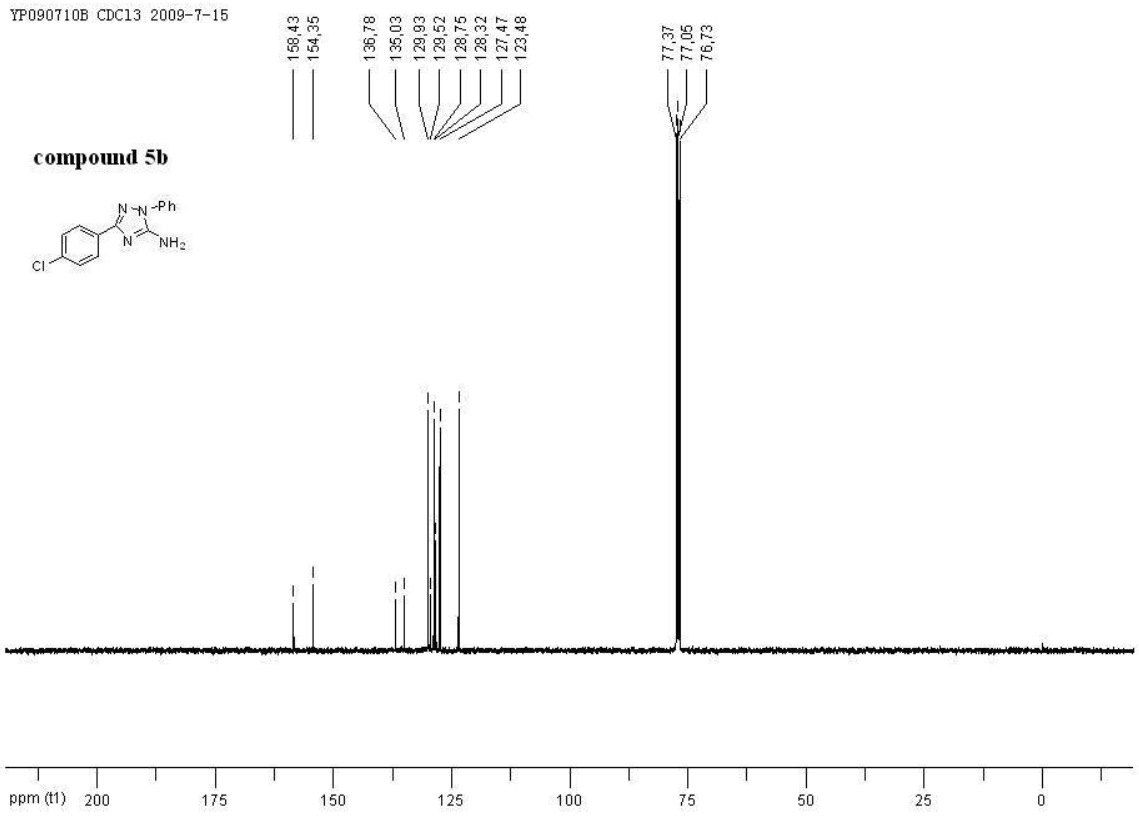
YP0910B-H1-CDCl3-2009-7-10

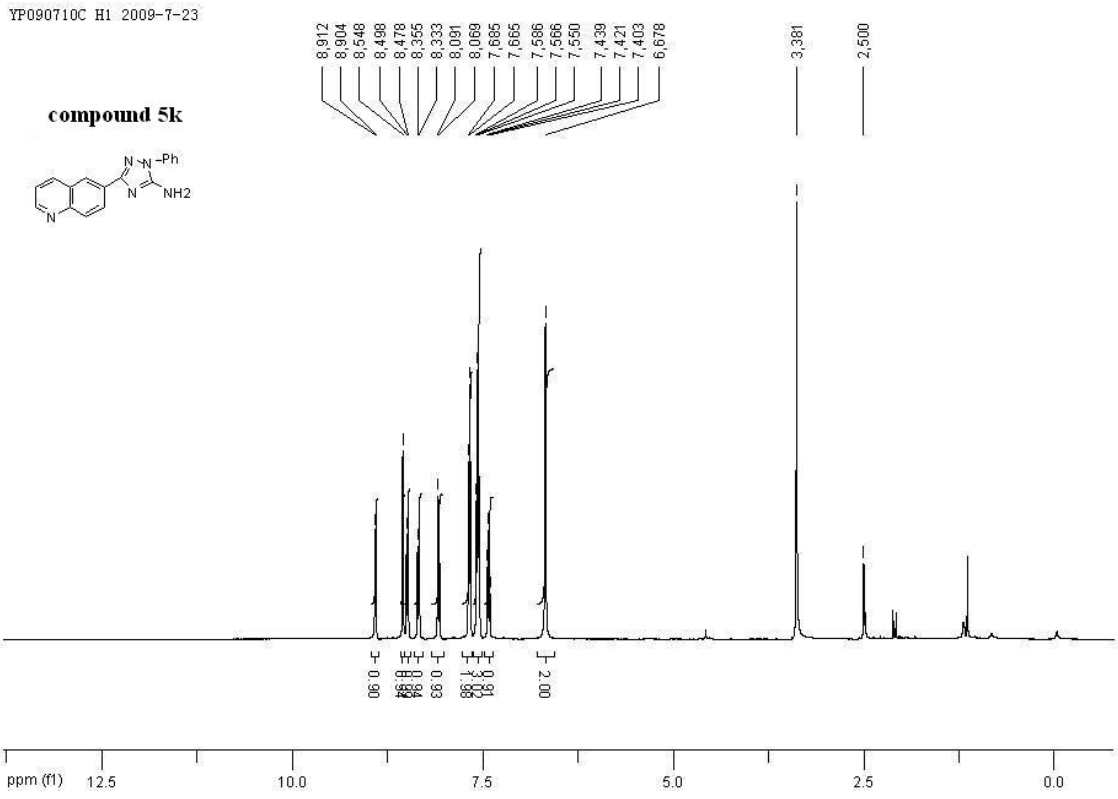


compound 5b






YP090710B CDC13 2009-7-15
158,43
154,35
136,78
135,03
129,93
129,52
128,75
128,32
127,47
123,48
77,37
77,05
76,73
compound 5b
-Ph
NH2
Cl
ppm (t1)
200
175
150
125
100
75
50
25
0

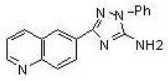

YP090710C H1 2009-7-23
8,912
8,904
8,548
8,498
8,478
8,355
8,333
8,091
8,069
7,685
7,665
7,586
7,566
7,550
7,439
7,421
7,403
6,678
3,381
2,500
compound 5k
-Ph
NH2
N
0.90
0.93
2.00
ppm (f1)
12.5
10.0
7.5
5.0
2.5
0.0

YP090710C H1 2009-7-23

157,71
155,57
150,75
147,90
137,16
136,49
129,46
129,30
129,23
127,87
127,25
127,00
124,70
122,96
121,88

39,88
39,74
39,60
39,46
39,32
39,18
39,04

compound 5k



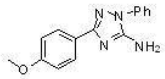
ppm (t1) 200 175 150 125 100 75 50 25 0

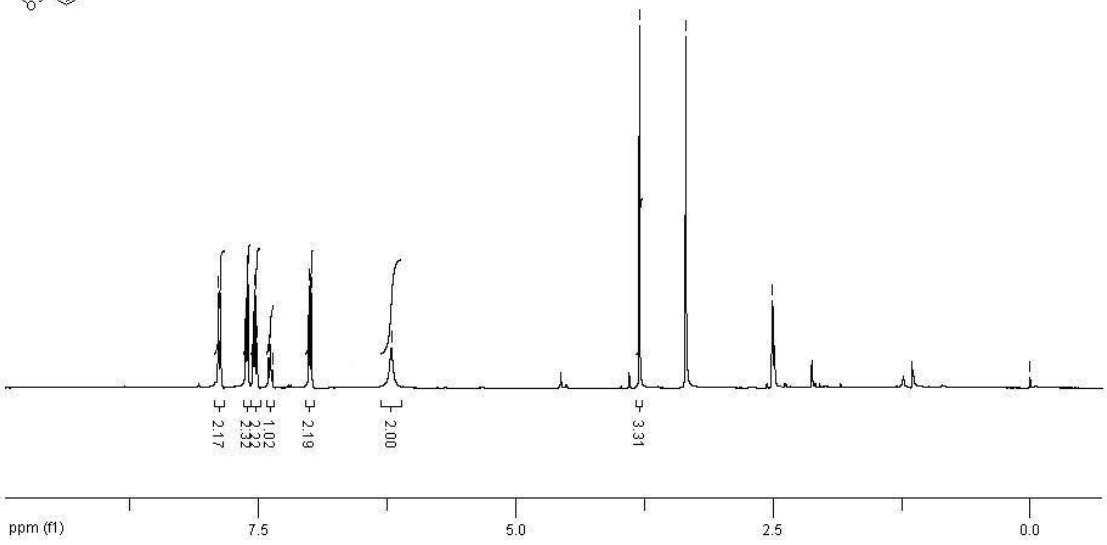
YP090710D 20090728

7,896
7,869
7,625
7,605
7,552
7,533
7,514
7,402
7,384
7,366
7,009
6,988
6,210

3,798
3,348
2,504
0,000

compound 5c





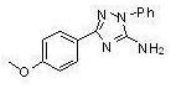
2,17
2,32
1,02
2,19
2,00
3,31

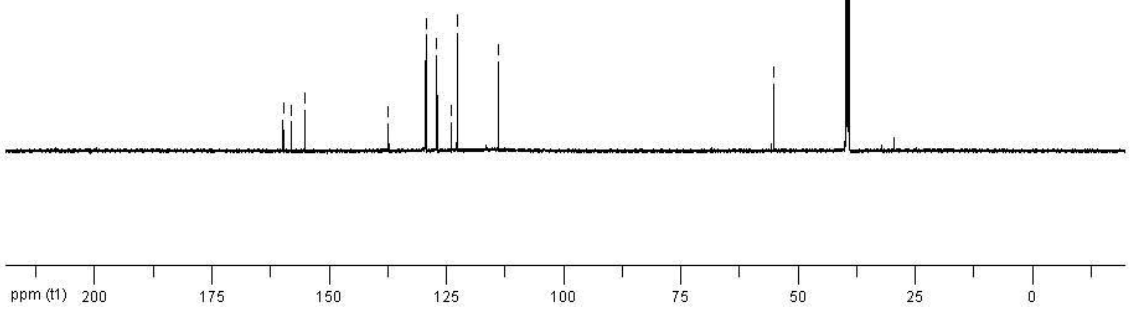
ppm (f1) 7.5 5.0 2.5 0.0

YP090710D 20090728

159,79
158,07
155,16
137,32
129,37
127,00
126,88
123,95
122,67
113,88
55,10
39,88
39,74
39,60
39,46
39,32
39,18
39,04

compound 5c

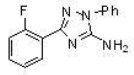


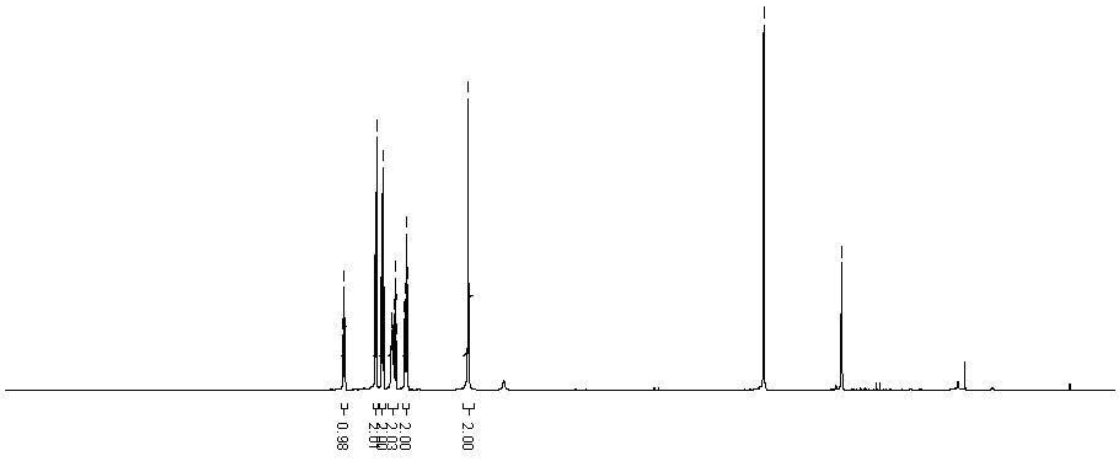


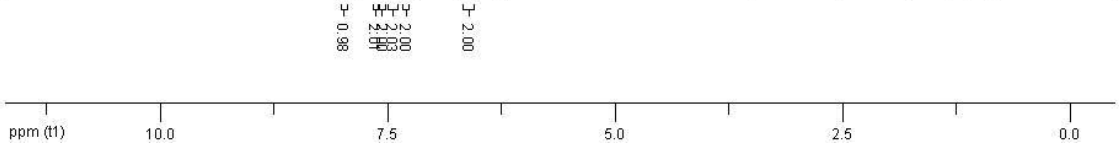
YP090710E 2009-7-28

7,992
7,979
7,966
7,636
7,622
7,567
7,555
7,543
7,471
7,459
7,448
7,437
7,429
7,416
7,404
7,314
7,303
7,293
7,280
6,615
3,365
2,511
2,508

compound 5v





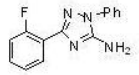


YP090710E 2009-7-28

160,33
158,65
154,99
154,94
137,09
130,60
130,54
129,67
129,42
127,23
124,34
122,96
119,25
119,17
116,51
116,37

39,89
39,75
39,61
39,47
39,33
39,19
39,06

compound 5v

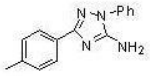


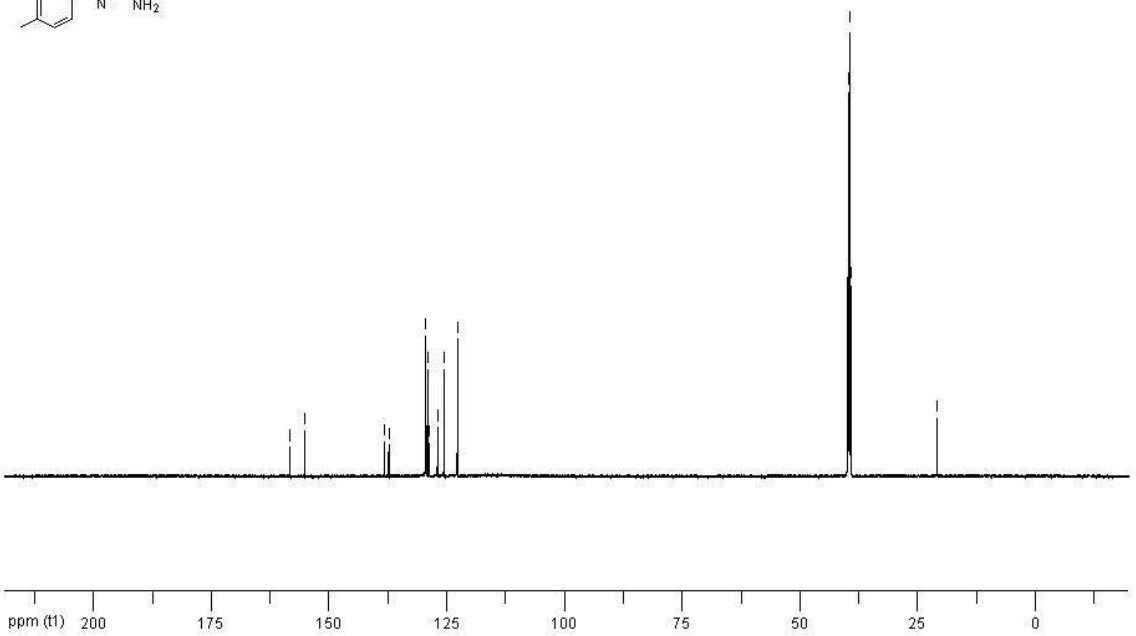
YP090710F 2009-7-29

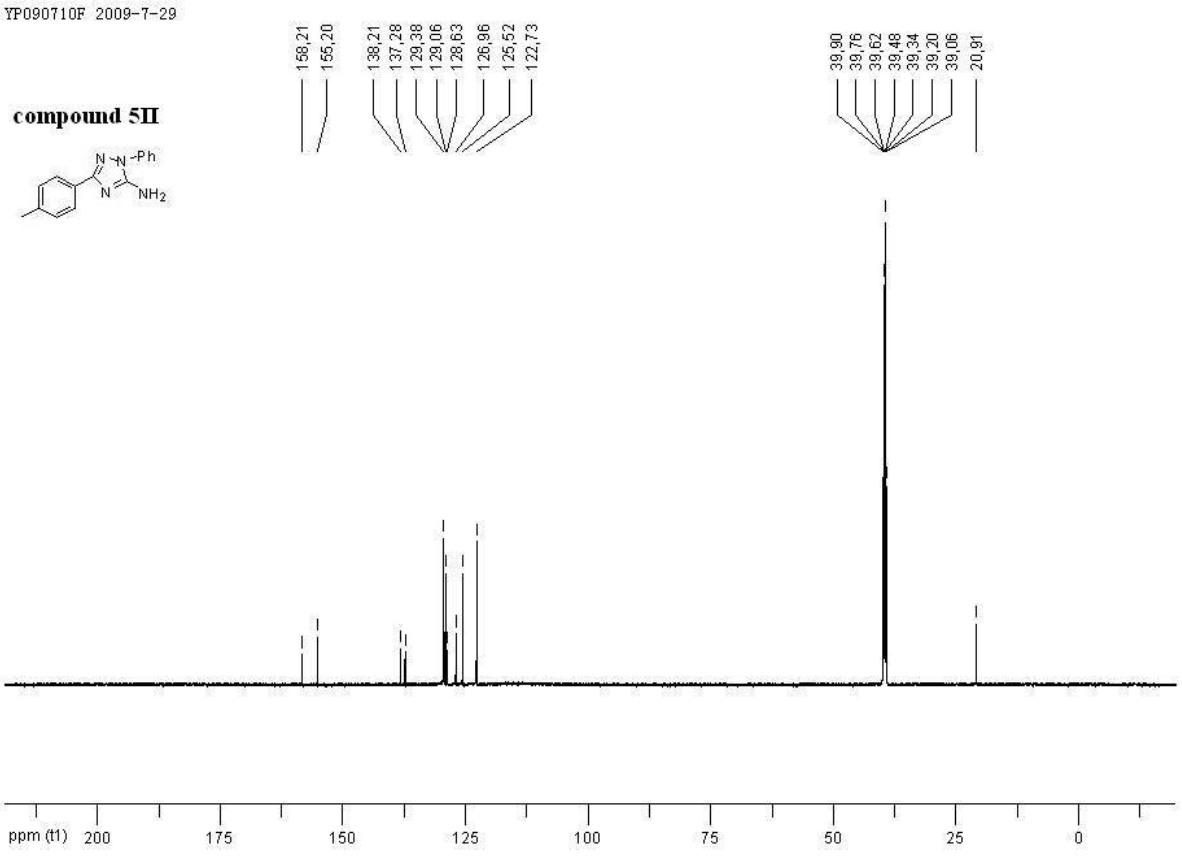
158,21
155,20
138,21
137,28
129,38
129,06
128,63
126,86
125,52
122,73

39,90
39,76
39,62
39,48
39,34
39,20
39,06
20,91

compound 5II






YP090710F 2009-7-29
compound 5II
158,21
155,20
138,21
137,28
129,38
129,06
128,63
126,96
125,52
122,73
39,90
39,76
39,62
39,48
39,34
39,20
39,06
20,91
ppm (t1)
200
175
150
125
100
75
50
25
0