Supporting Information

An Efficient Cascade Synthesis of Various 2*H*-1,4-benzoxazin -3-(4*H*)-ones from *o*-Halophenols and 2-Halo-amides Catalyzed by CuI

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General Remarks.

All reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification, if not stated otherwise. 4-Substituted-*o*-iodophenols and *N*-substituted 2-halo amides were prepared according to the known literatures.[1a-c] All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ on a 400 M Hz instrument with TMS as internal standard. TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. The columns were hand packed with silica gel 60 (200-300). All reactions were carried out in an over-dried Schlenk tube equipped with a magnetic stir bar under N_2 atmosphere. Unknown compound was additionally confirmed by ^{13}C NMR and Elemental analysis. Mass spectra were obtained using EI ionization. IR spectrum were taken in ATR apparatus.

General procedure

General Procedure for the synthesis of 2*H*-1,4-benzoxazin-3-(4*H*)-ones

An oven-dried Schlenk tube equipped with a Teflon valve was charged with a magnetic stir bar, CuI (10 mg, 0.05 mmol, 10 mol%), Cs_2CO_3 (359 mg, 1.1 mmol),

2-halophenol **1** (0.60 mmol), 2-halo amides **2** (0.50 mmol), 1,10-phenanthroline (20 mg, 0.10 mmol, 20 mol%). The tube was evacuated and backfilled with N_2 (this procedure was repeated 3 times). Under a counter flow of N_2, dioxane (2.0 mL) was added by syringe and the mixture was stirred for about 24 h at 90°C. The reaction mixture was cooled to room temperature, Ethyl acetate (20 mL) were added, and the resulting suspension was filtered. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (PE-EtOAc=10:1~2:1, v/v) to provide the desired product **3**.

Spectroscopic and Analytical Data

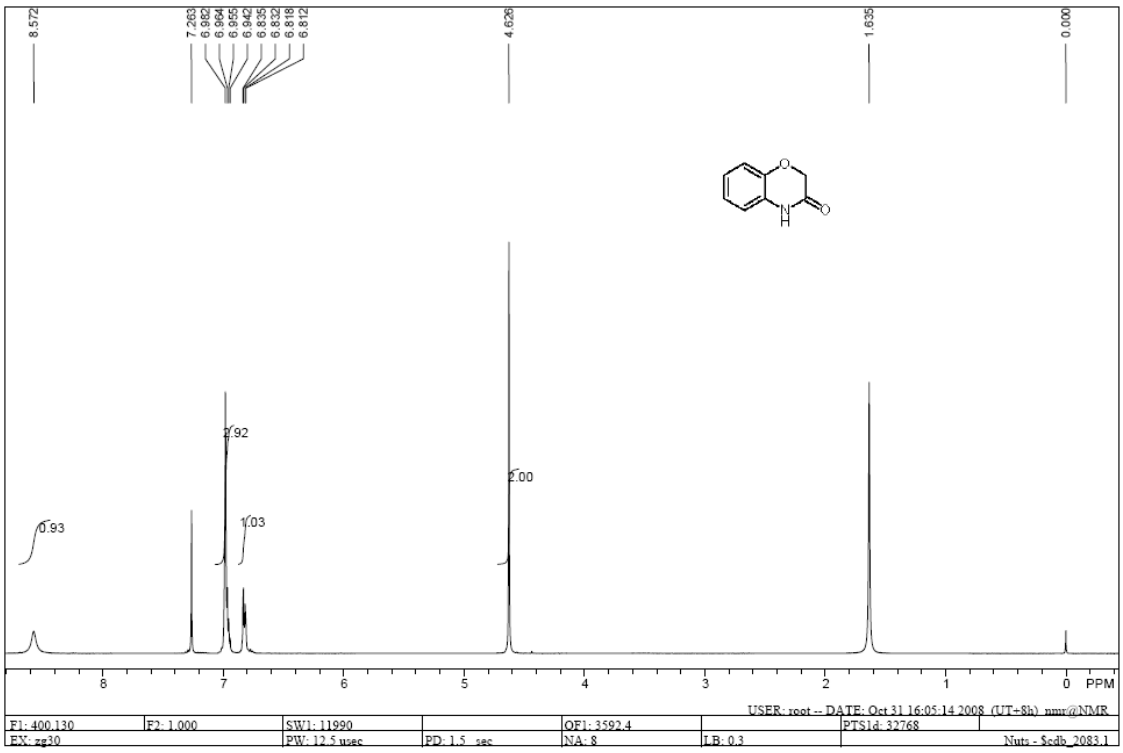
***N*-t-Butyl-2-(2-iodophenoxy)acetamide (4)**

A white solid; Mp 50-52°C; IR (neat) ν_{max}/cm^{-1} 3412.1, 3079.5, 2969.2, 1677.5, 1525.0, 1472.7, 1247.1, 1060.8 cm^{-1}. ^1H NMR (400M Hz, $CDCl_3$ /TMS): δ 7.78 (dd, *J* =7.6, 1.2 Hz, 1H), 7.35-7.28 (m, 1H), 6.96 (s, 1H), 6.81-6.75 (m, 2H), 4.40 (s, 2H), 1,45 (s, 9H) ppm. ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 166.2, 155.5, 139.2, 129.8, 123.6, 112.2, 86.1, 67.9, 51.3, 28.8 ppm. MS (EI) *m/z* 333 (M^+). Anal. Calcd for $C_{12}H_{16}INO_2$: C, 43.26; H, 4.84; N, 4.20; Found: C, 43.54; H, 4.71; N, 4.11.

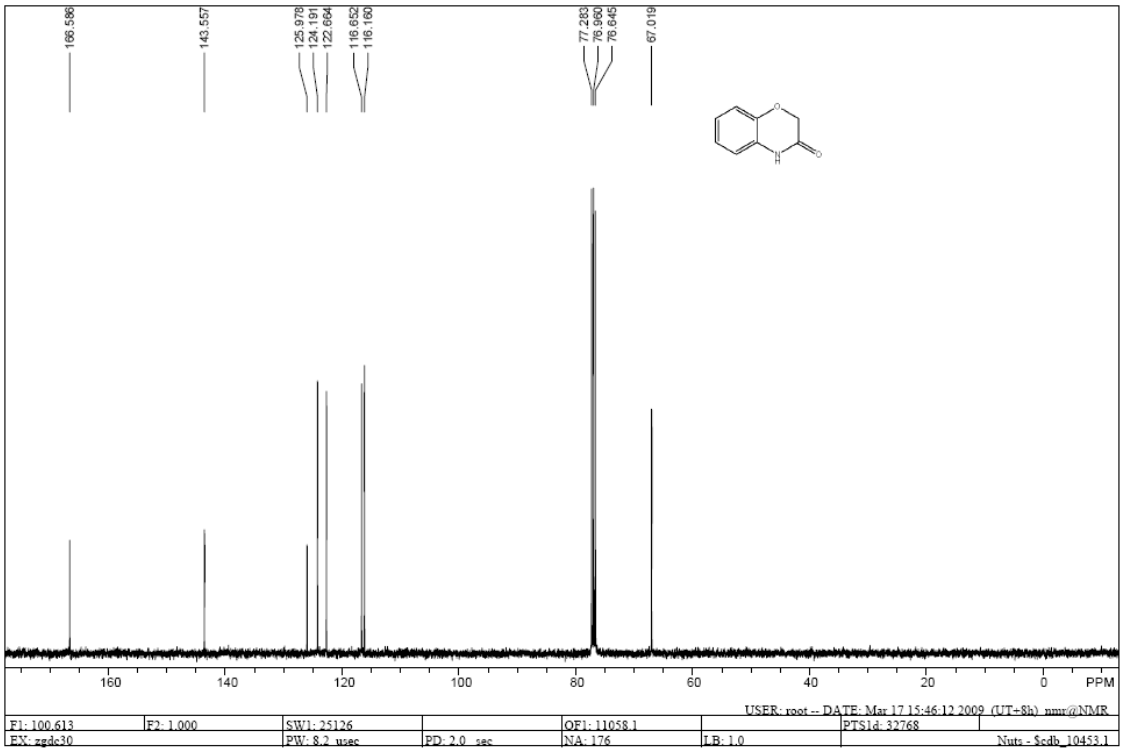
***N*-p-tolyl-2-(2-iodophenoxy)acetamide (5)**

A white solid; Mp 152-154°C; IR (neat) ν_{max}/cm^{-1} 3378.7, 3054.8, 2917.9, 1688.3, 1536.5, 1474.9, 1249.9, 1060.3 cm^{-1}. ^1H NMR (400M Hz, $CDCl_3$ /TMS): δ 8.77 (s, 1H), 7.81 (dd, *J* =8.0, 1.2 Hz, 1H), 7.55 (d, *J* =8.4 Hz, 2H), 7.38-7.33 (m, 1H), 7.16 (d, *J* =8.0 Hz, 2H), 6.84-6.81 (m, 2H), 4.61 (s, 2H), 2.33 (s, 3H) ppm. ^{13}C NMR (100M Hz, $CDCl_3$/TMS): 164.9, 155.4, 139.4, 134.5, 134.4, 130.0, 129.6, 124.0, 119.8, 112.5, 86.4, 67.9, 20.9 ppm. MS (EI) *m/z* 367 (M^+). Anal. Calcd for $C_{15}H_{14}INO_2$: C, 49.07; H, 3.84; N, 3.81; Found: C, 49.18 H, 3.92; N, 3.85.

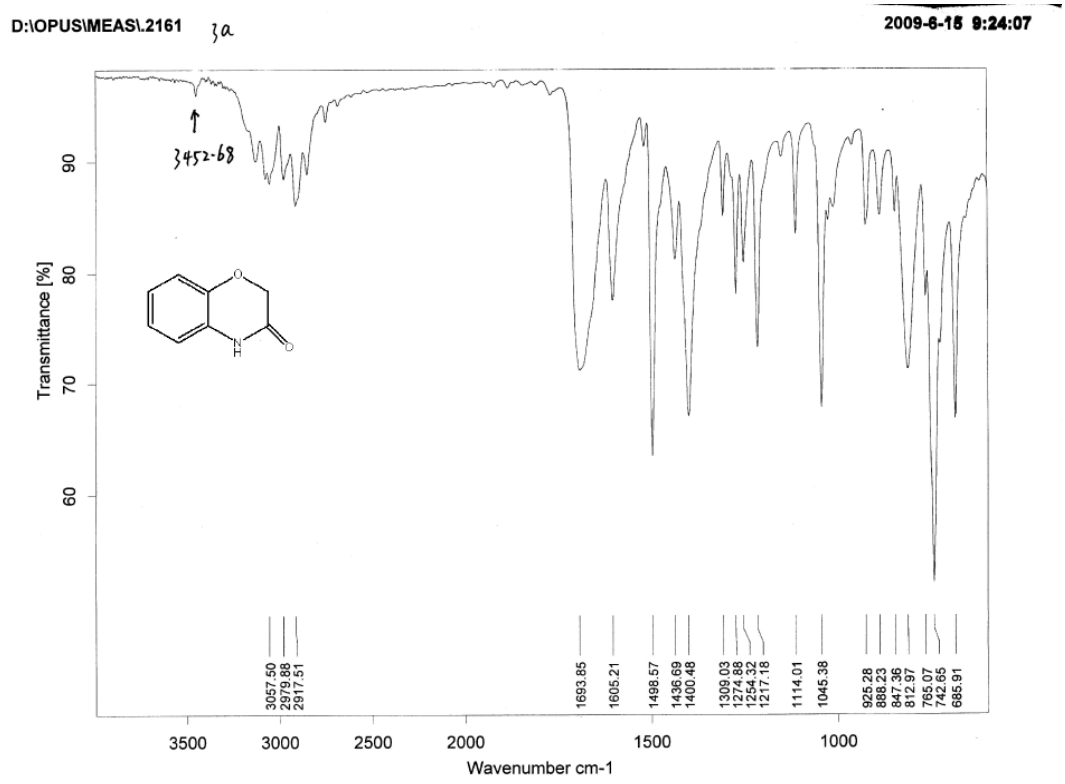
Copies of ^1H NMR , ^{13}C NMR and IR Spectrum of Compound



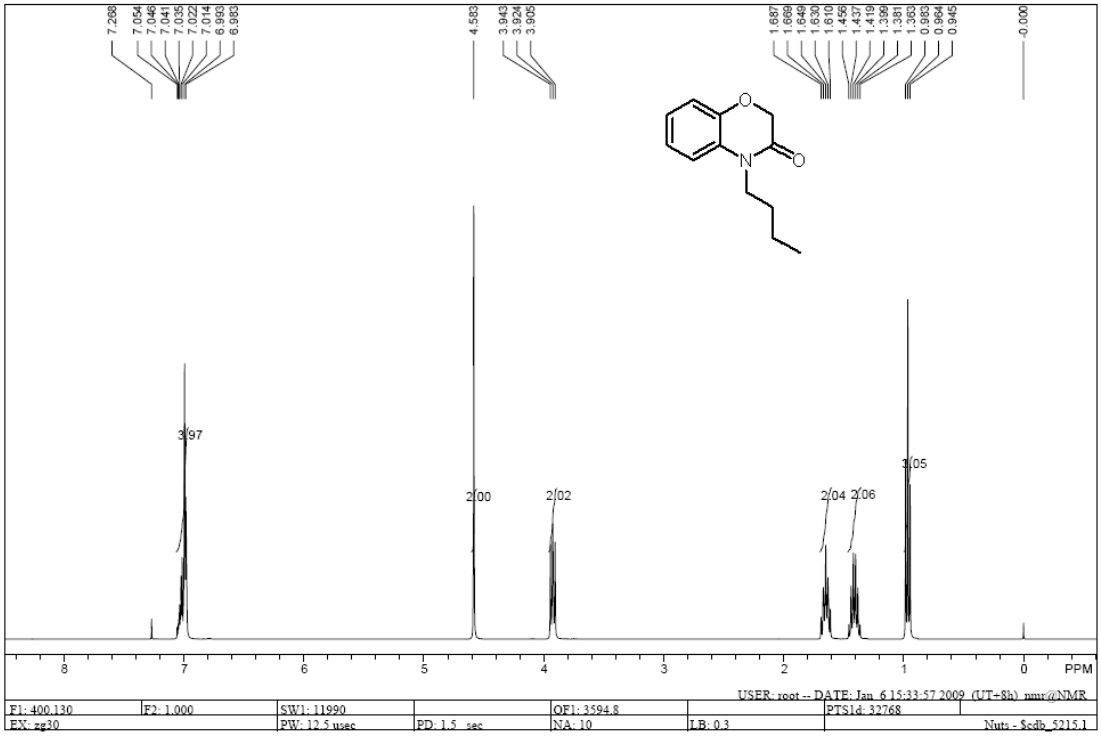
^{1}H NMR Spectrum of Compound 3a



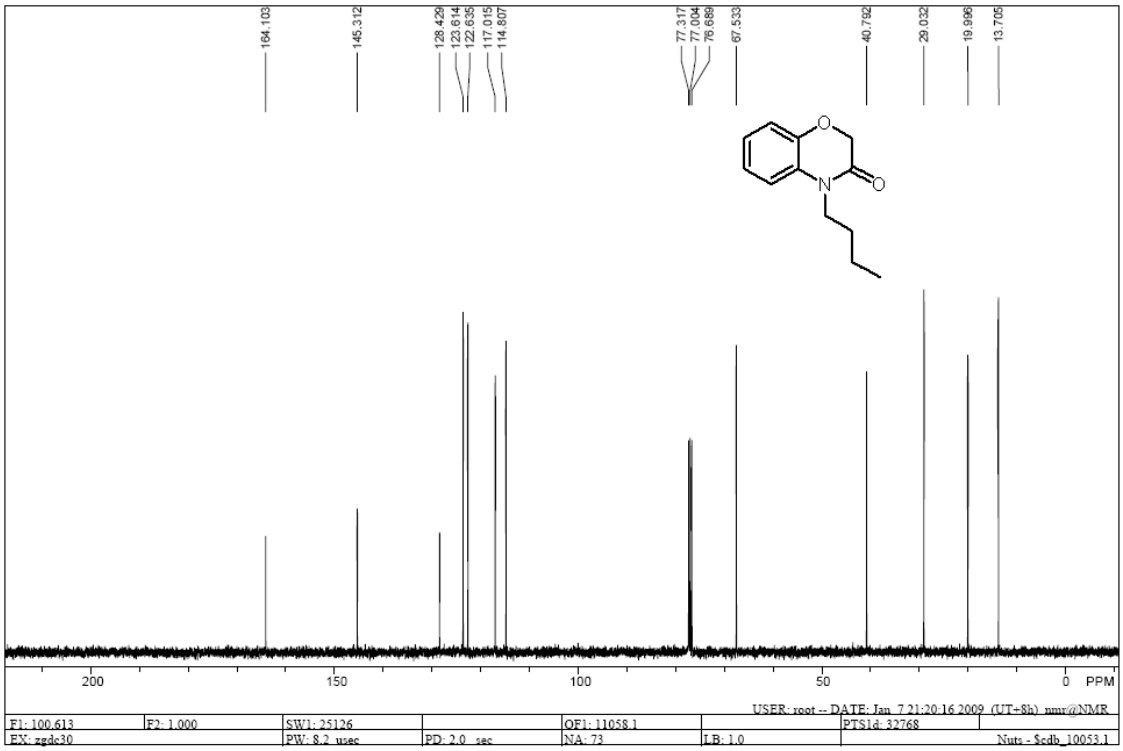
^{13}C NMR Spectrum of Compound 3a



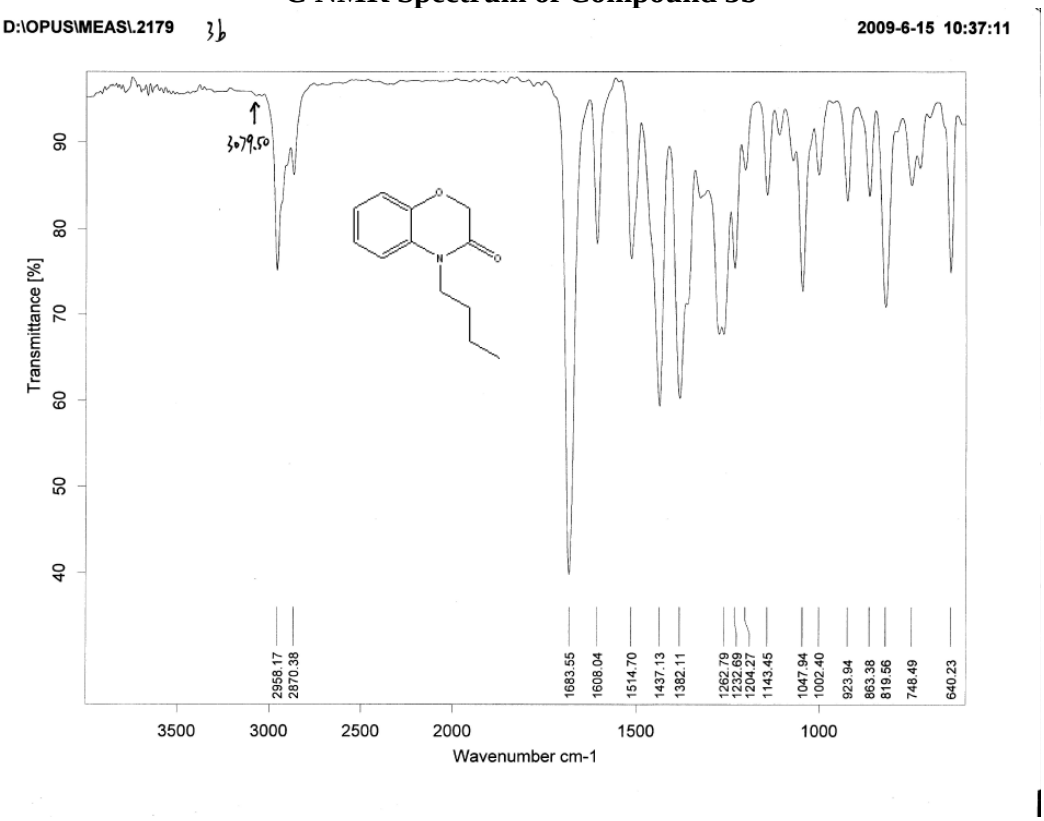
IR Spectrum of Compound 3a



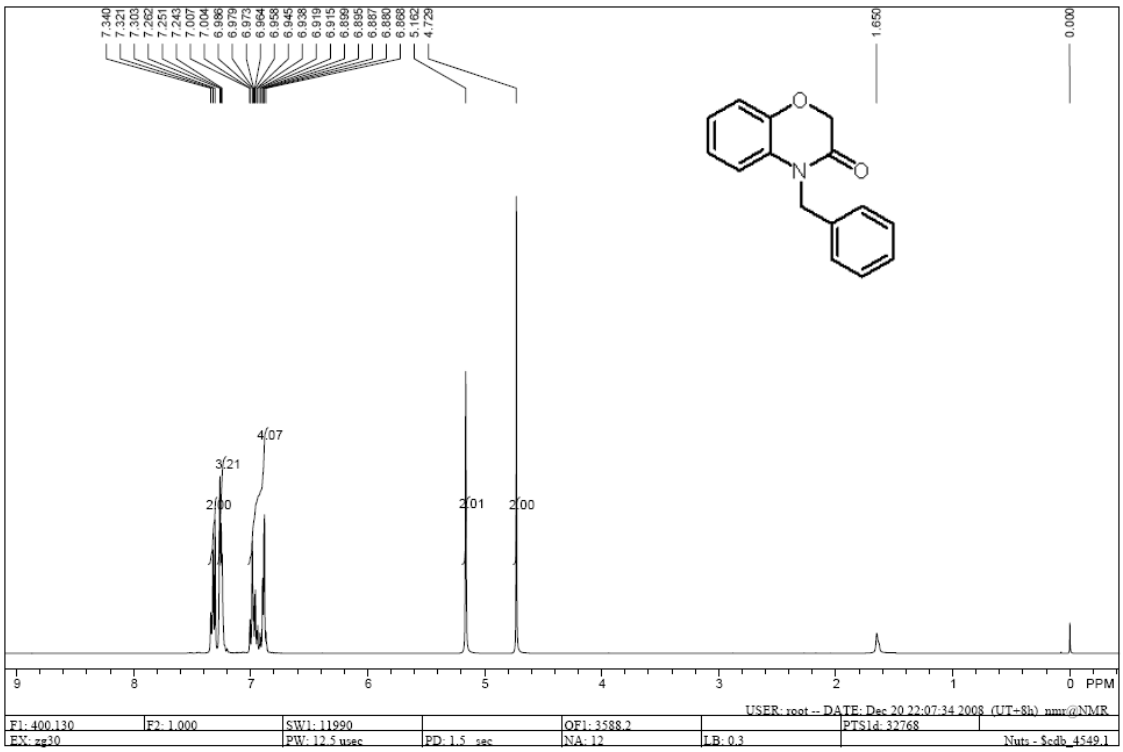
^{1}H NMR Spectrum of Compound 3b



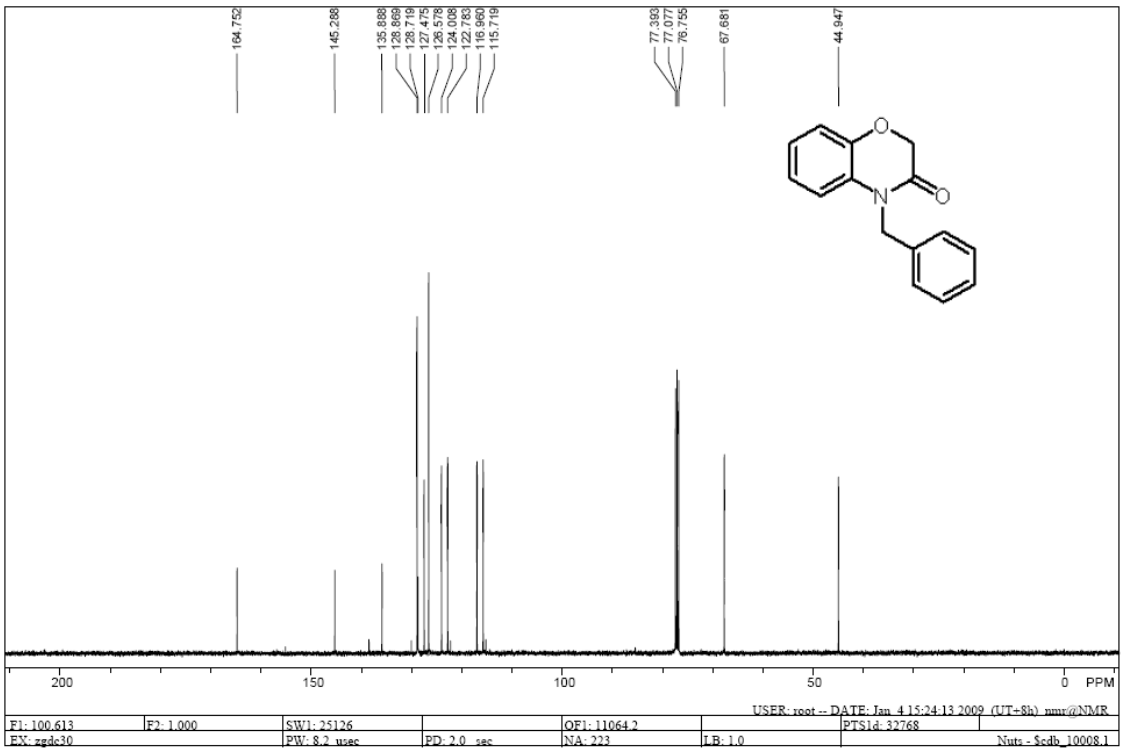
^{13}C NMR Spectrum of Compound 3b



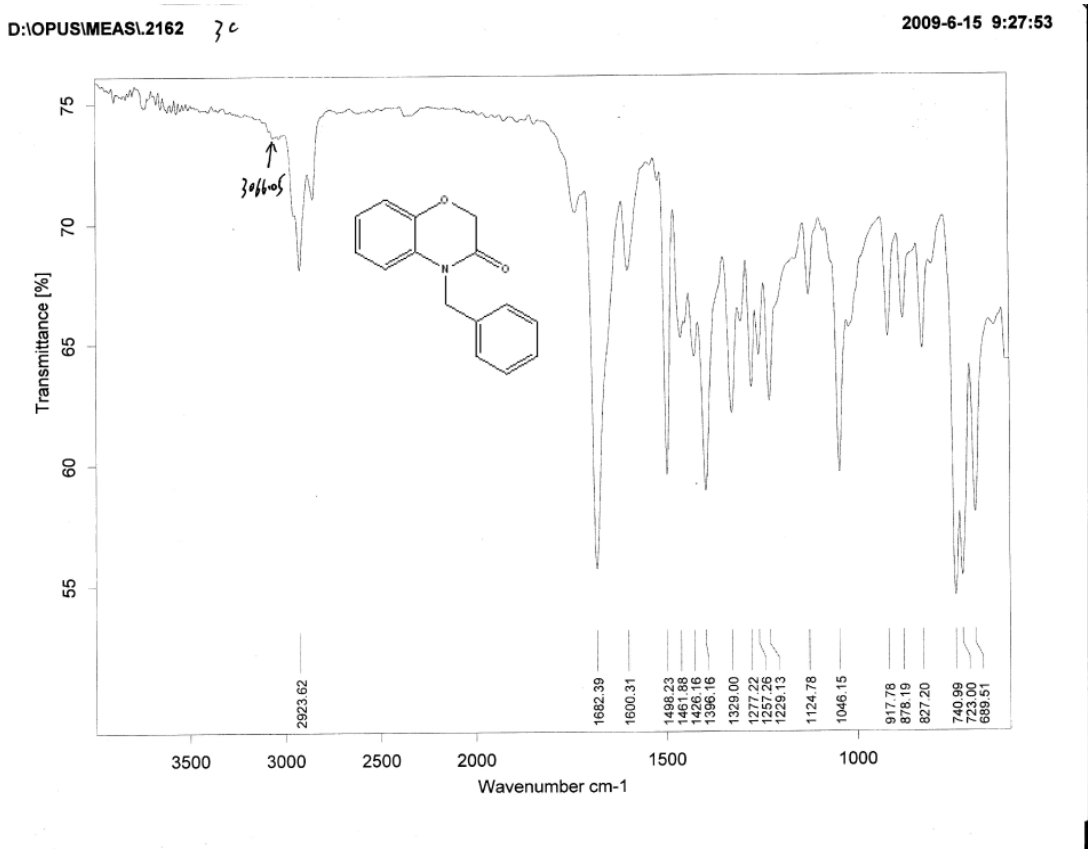
IR Spectrum of Compound 3b



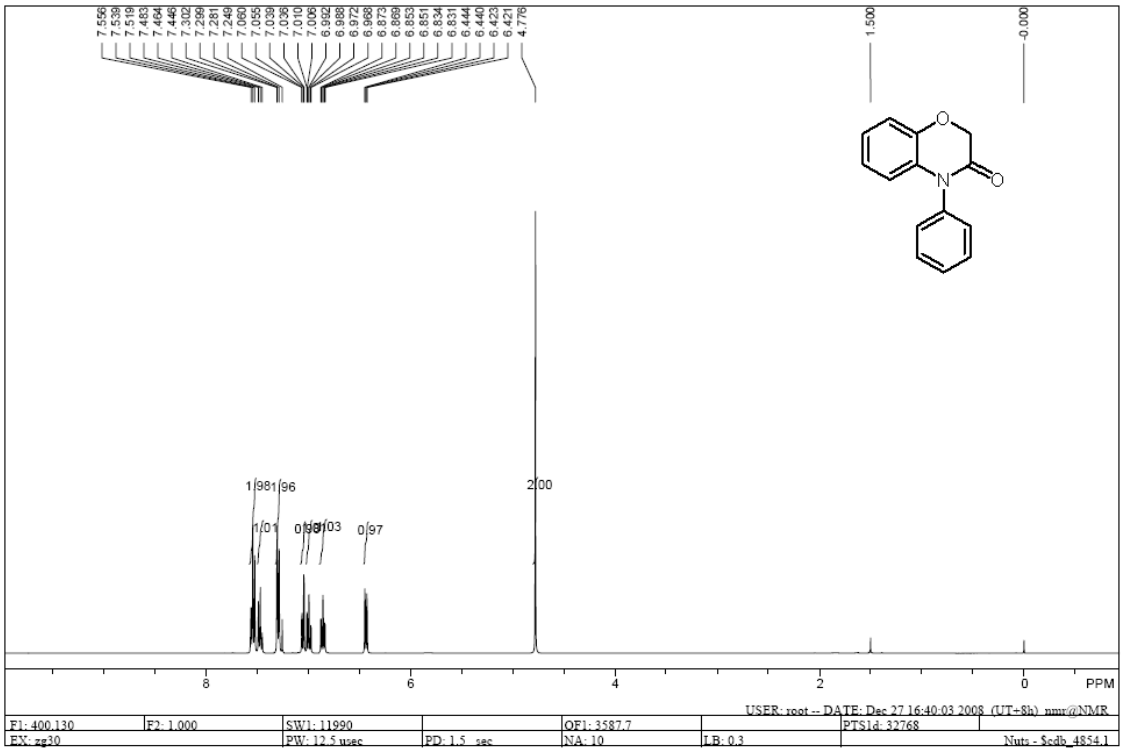
^{1}H NMR Spectrum of Compound 3c



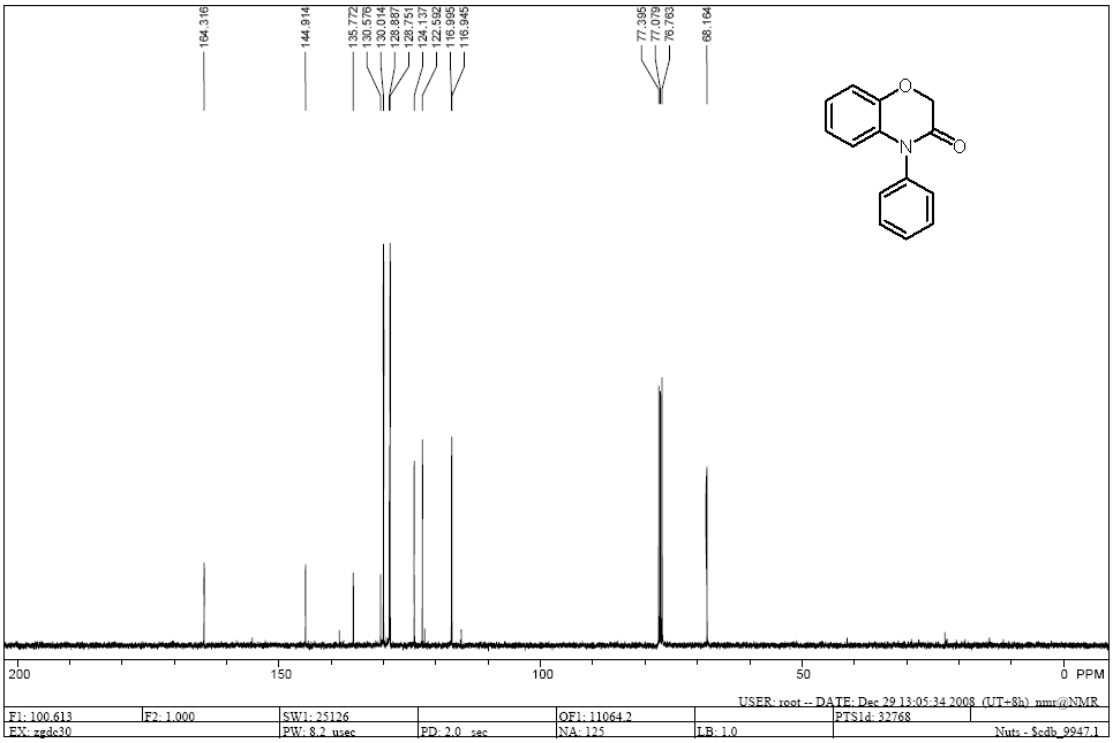
^{13}C NMR Spectrum of Compound 3c



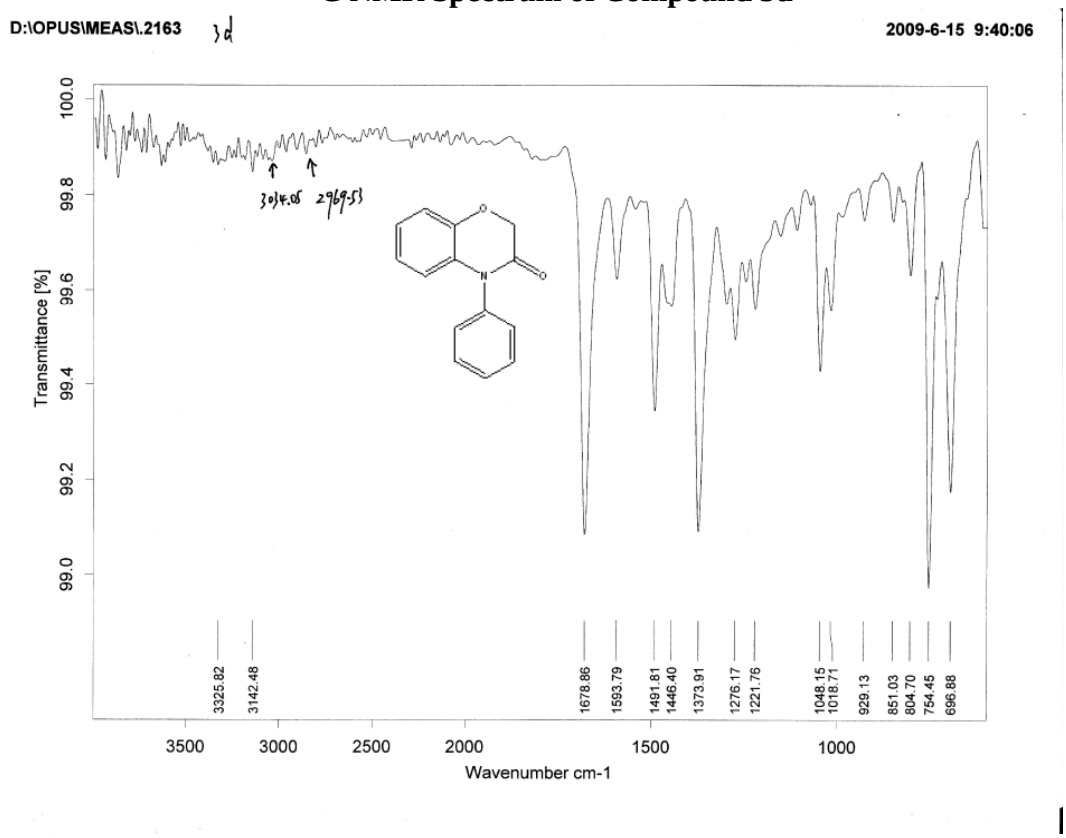
IR Spectrum of Compound 3c



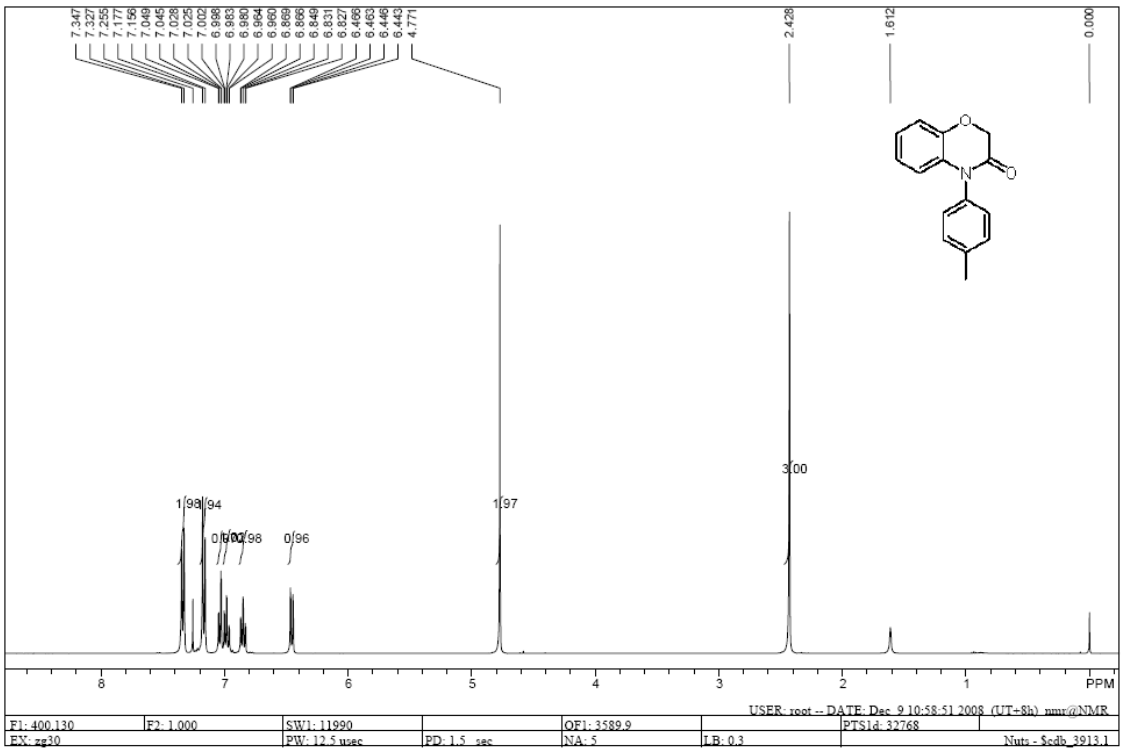
^{1}H NMR Spectrum of Compound 3d



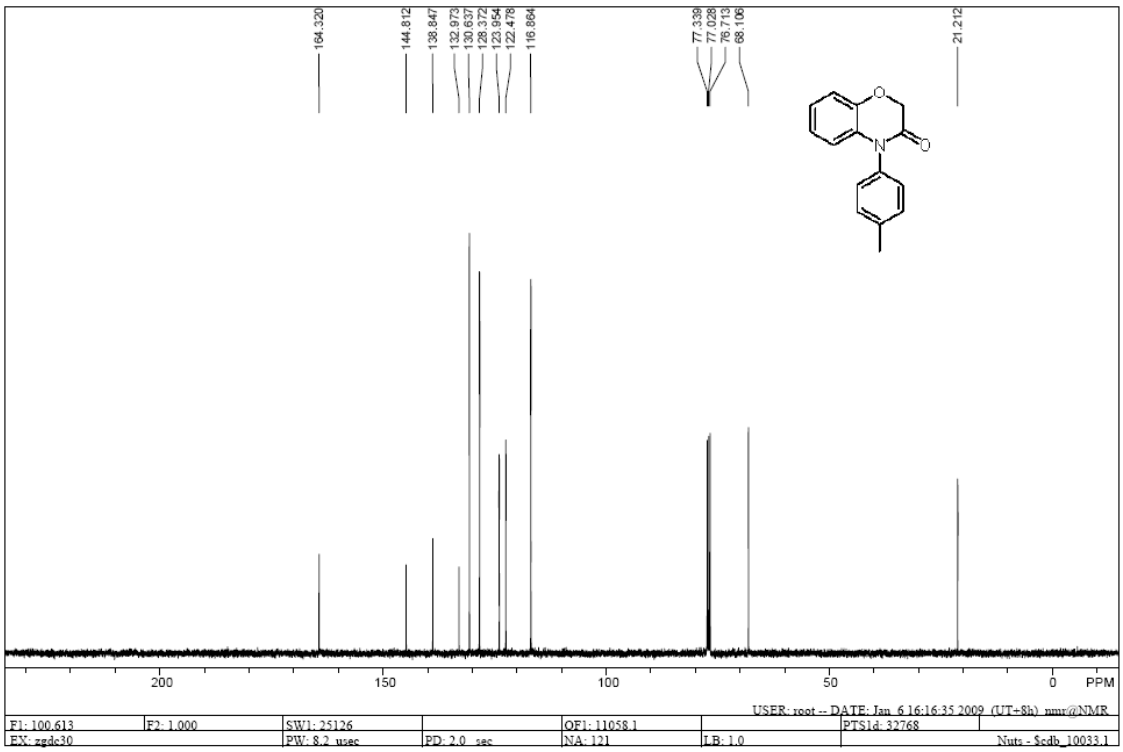
^{13}C NMR Spectrum of Compound 3d



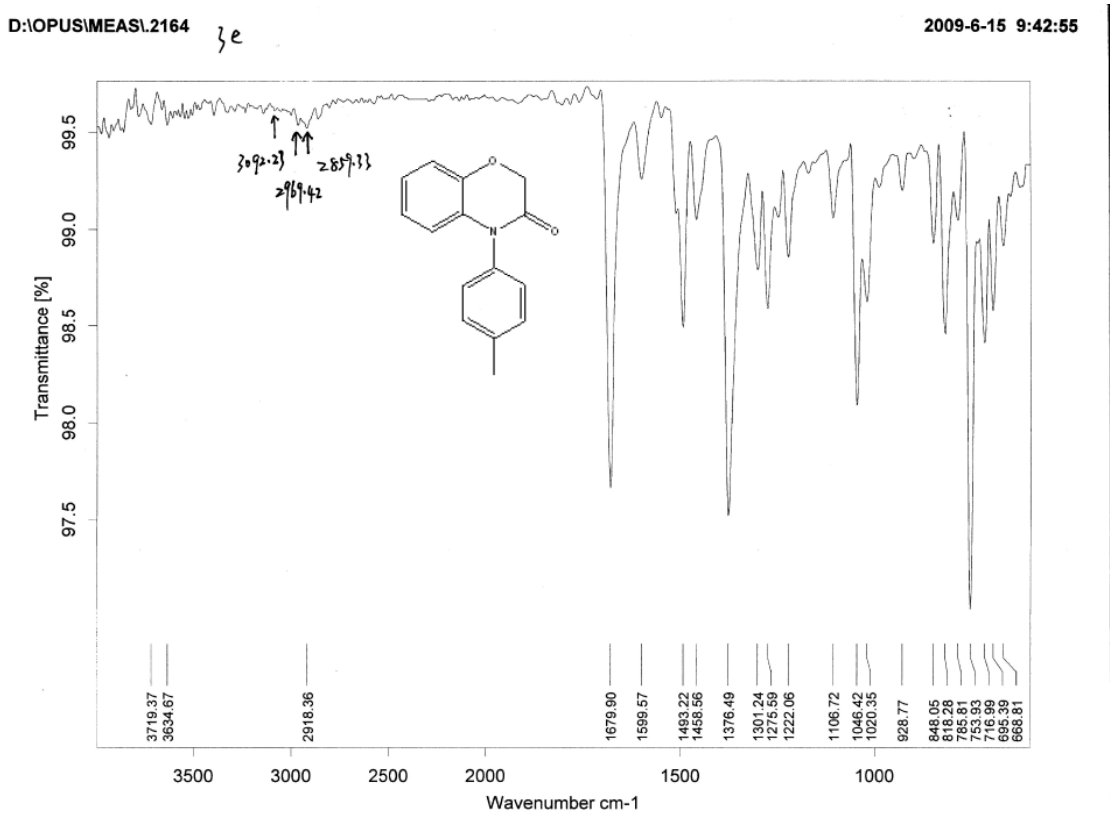
IR Spectrum of Compound 3d



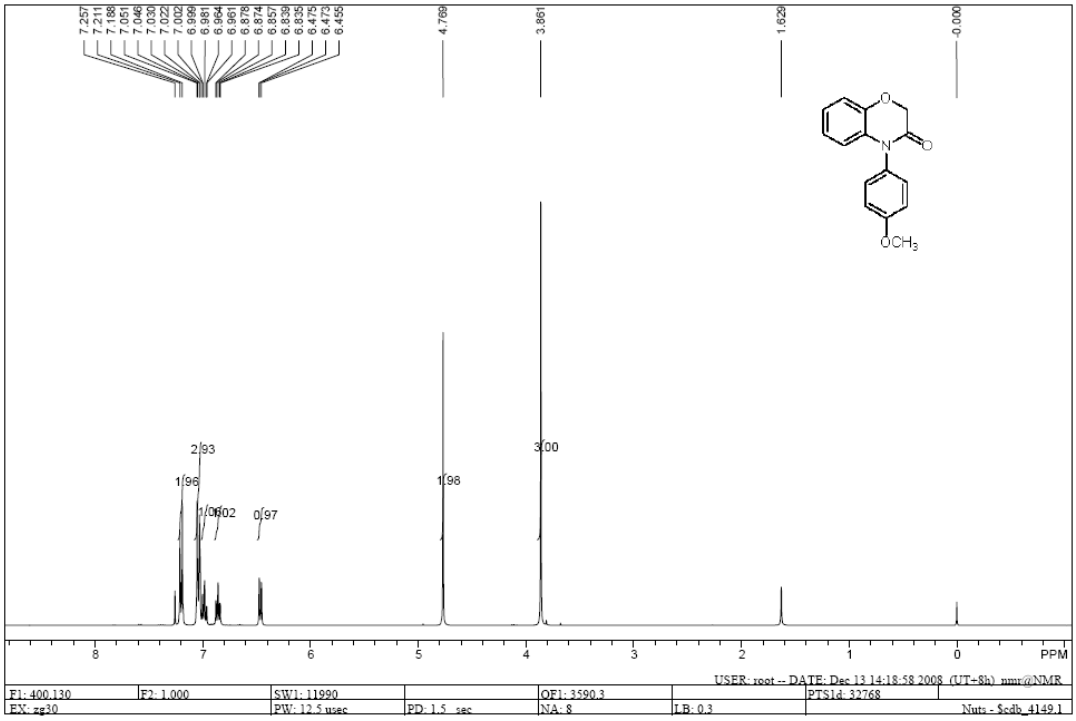
^{1}H NMR Spectrum of Compound 3e



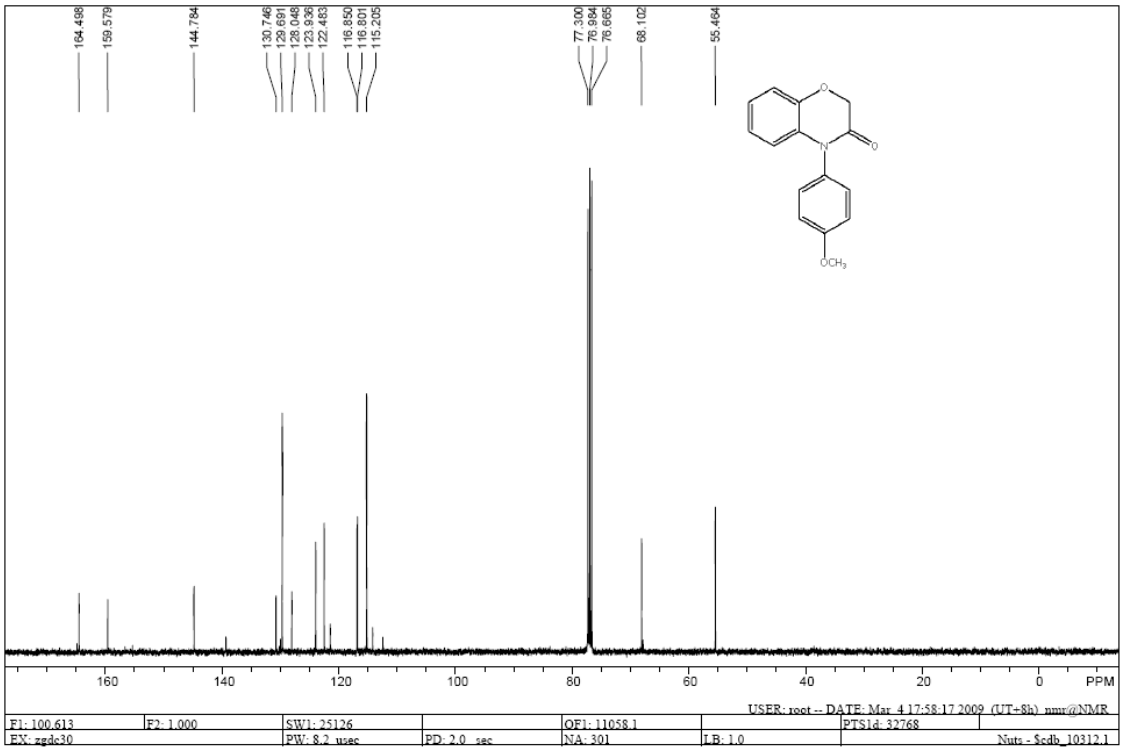
^{13}C NMR Spectrum of Compound 3e



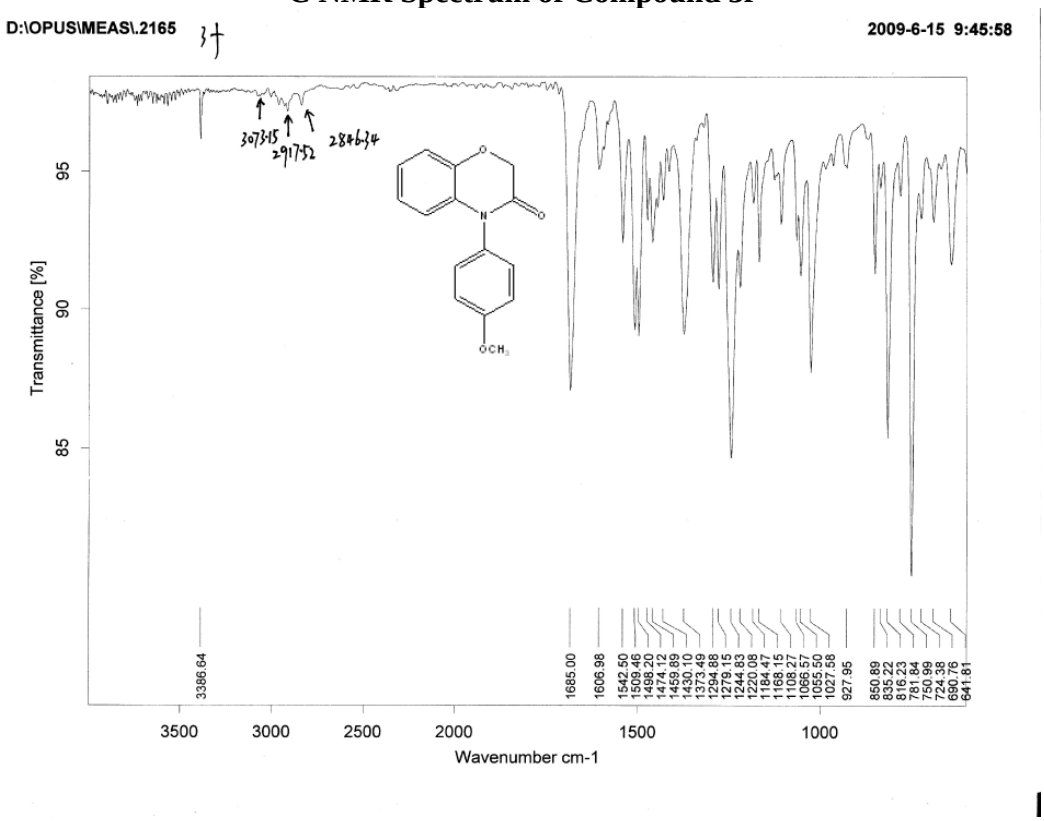
IR Spectrum of Compound 3e



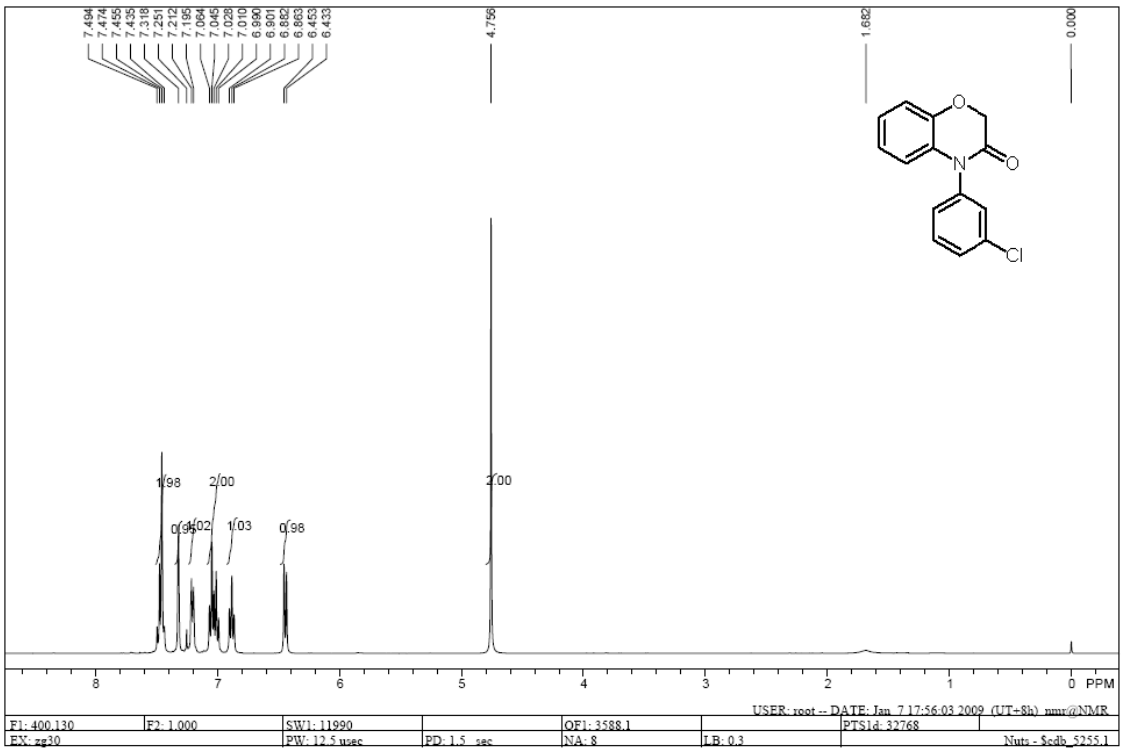
^{1}H NMR Spectrum of Compound 3f



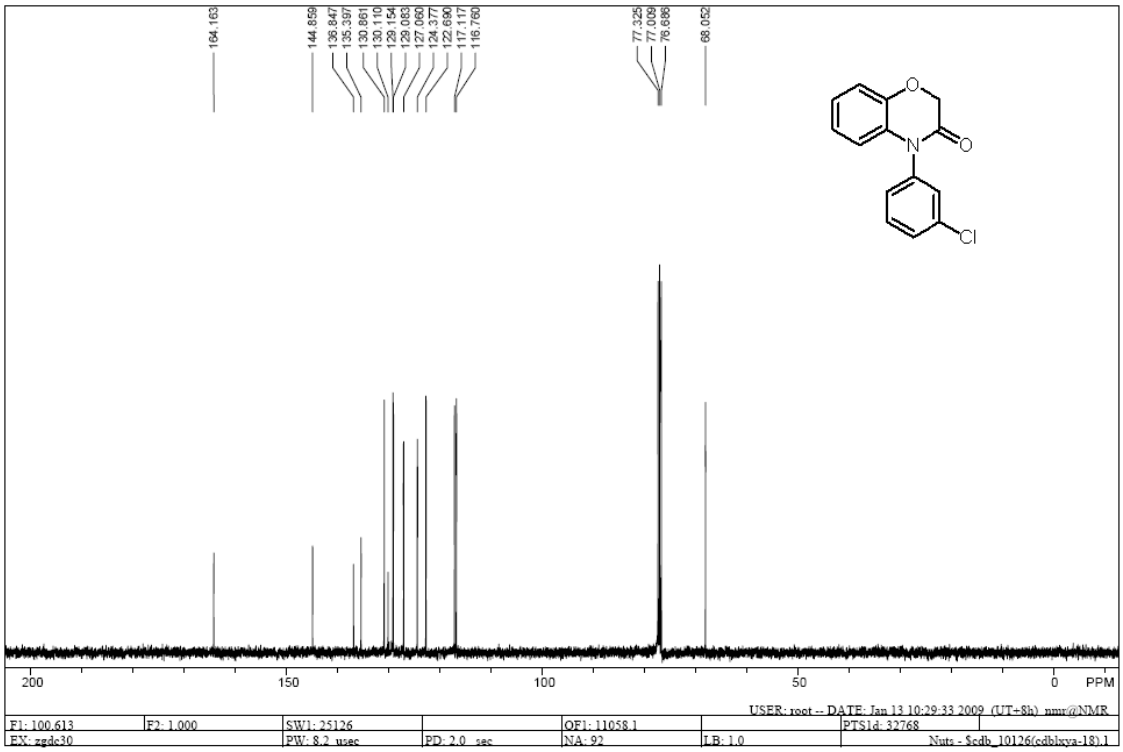
^{13}C NMR Spectrum of Compound 3f



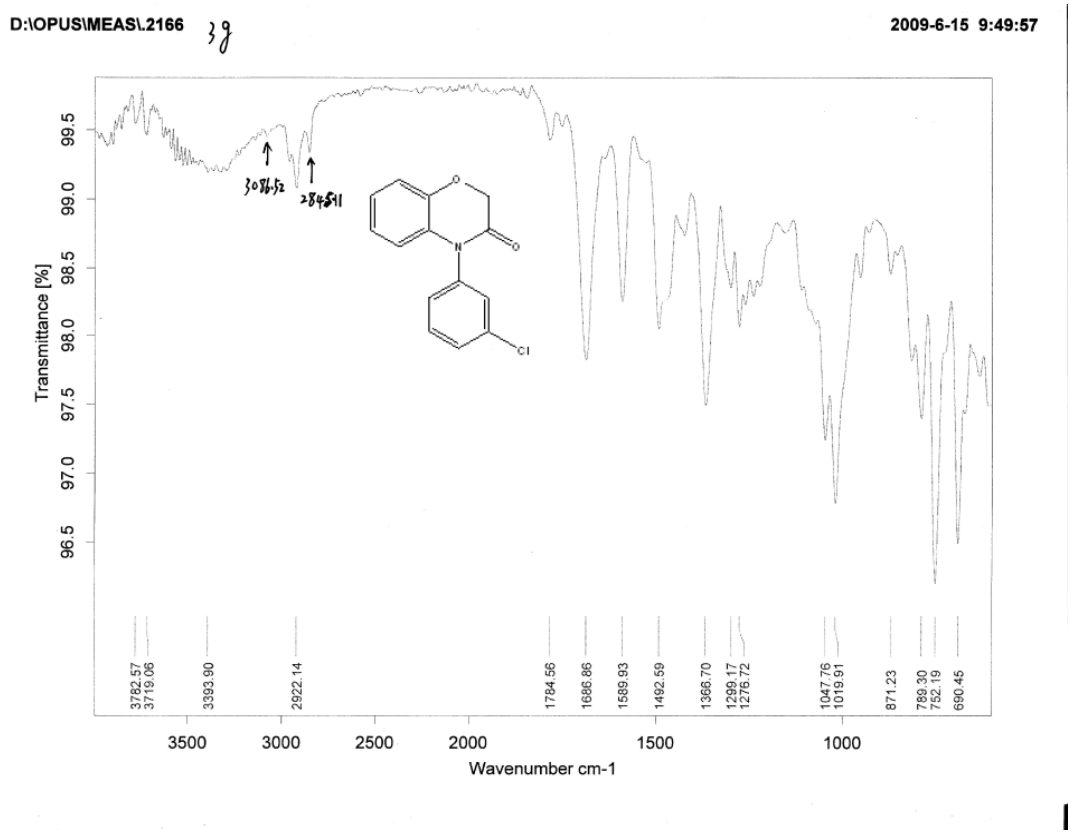
IR Spectrum of Compound 3f



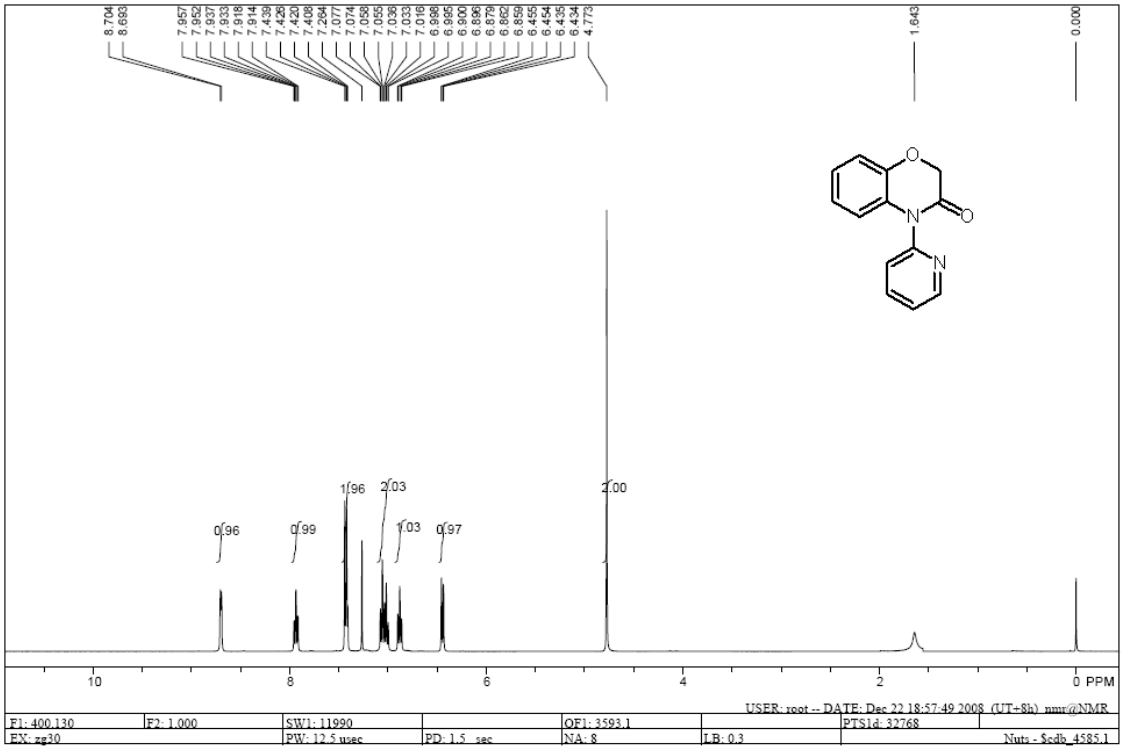
[1]H NMR Spectrum of Compound 3g



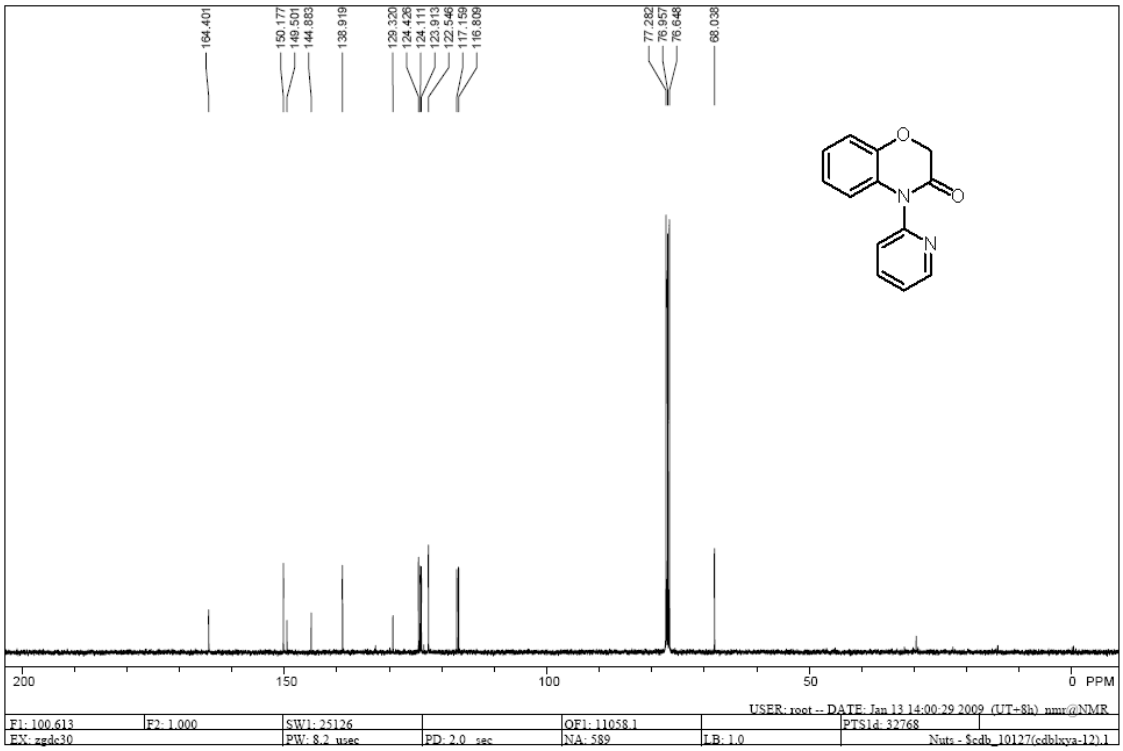
[13]C NMR Spectrum of Compound 3g



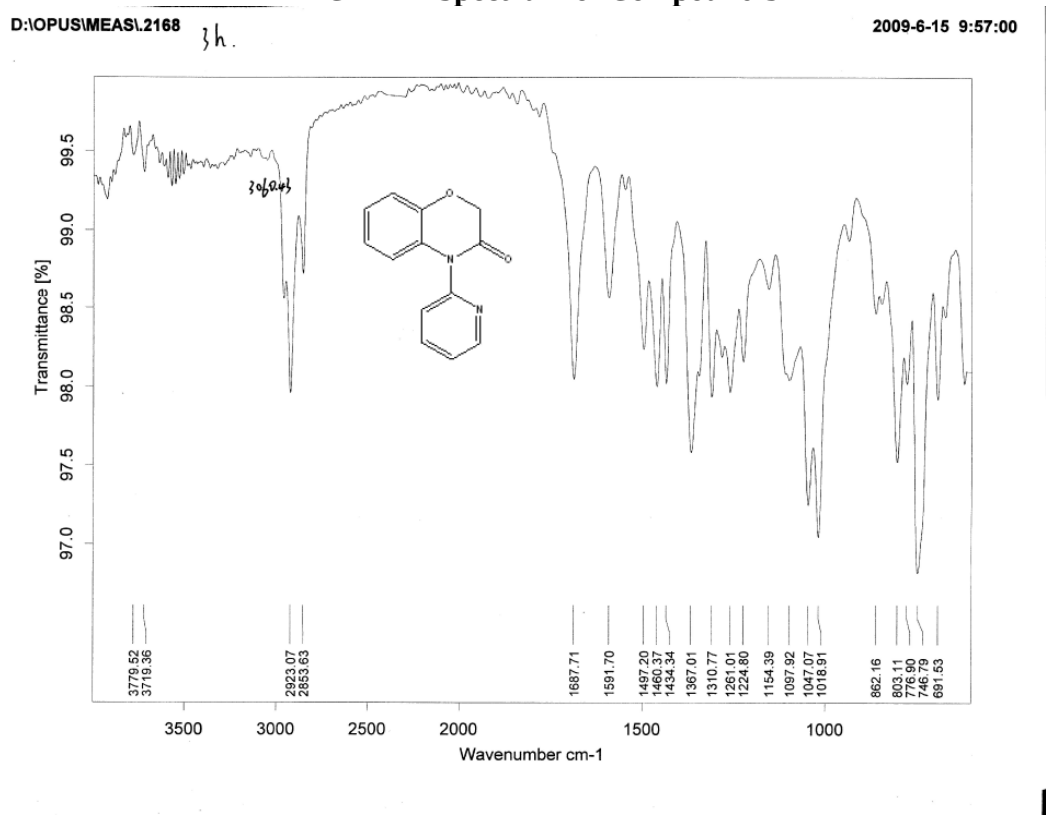
IR Spectrum of Compound 3g



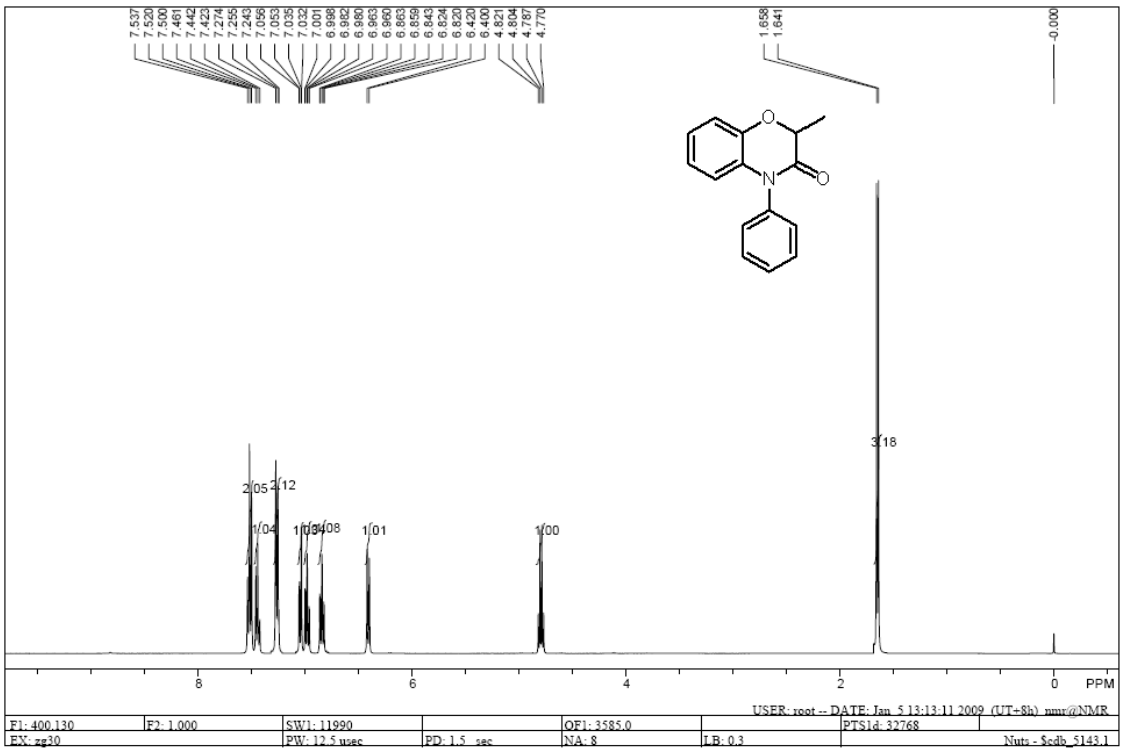
^{1}H NMR Spectrum of Compound 3h



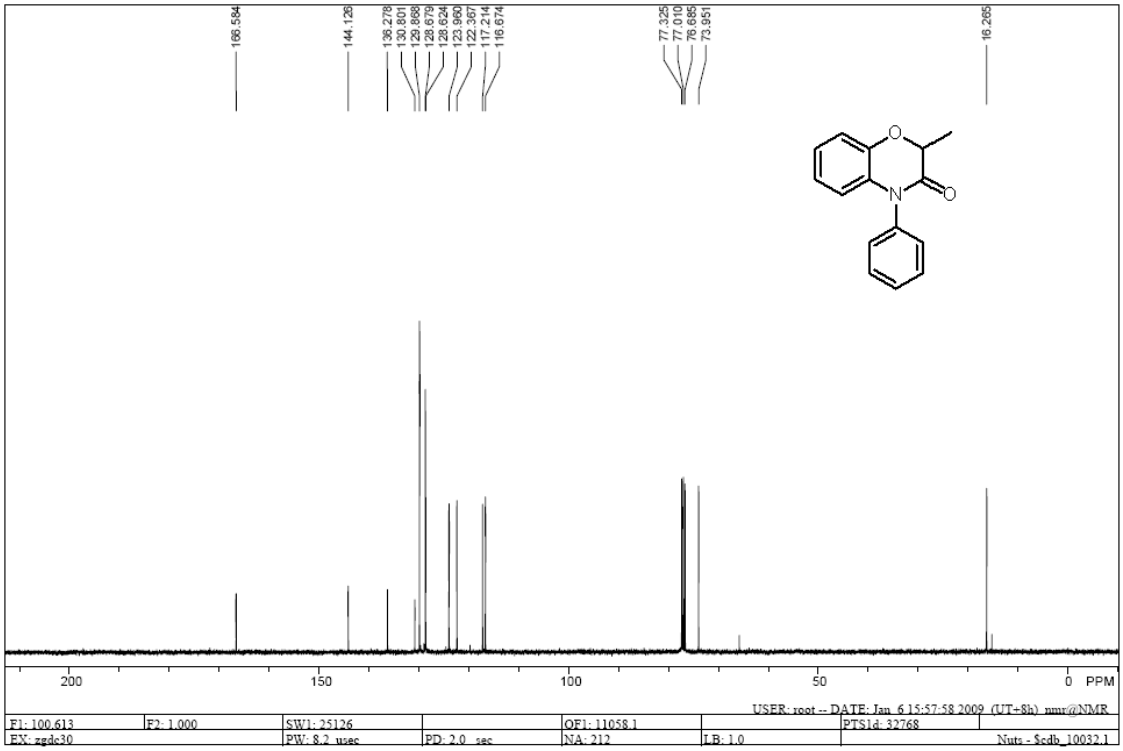
^{13}C NMR Spectrum of Compound 3h



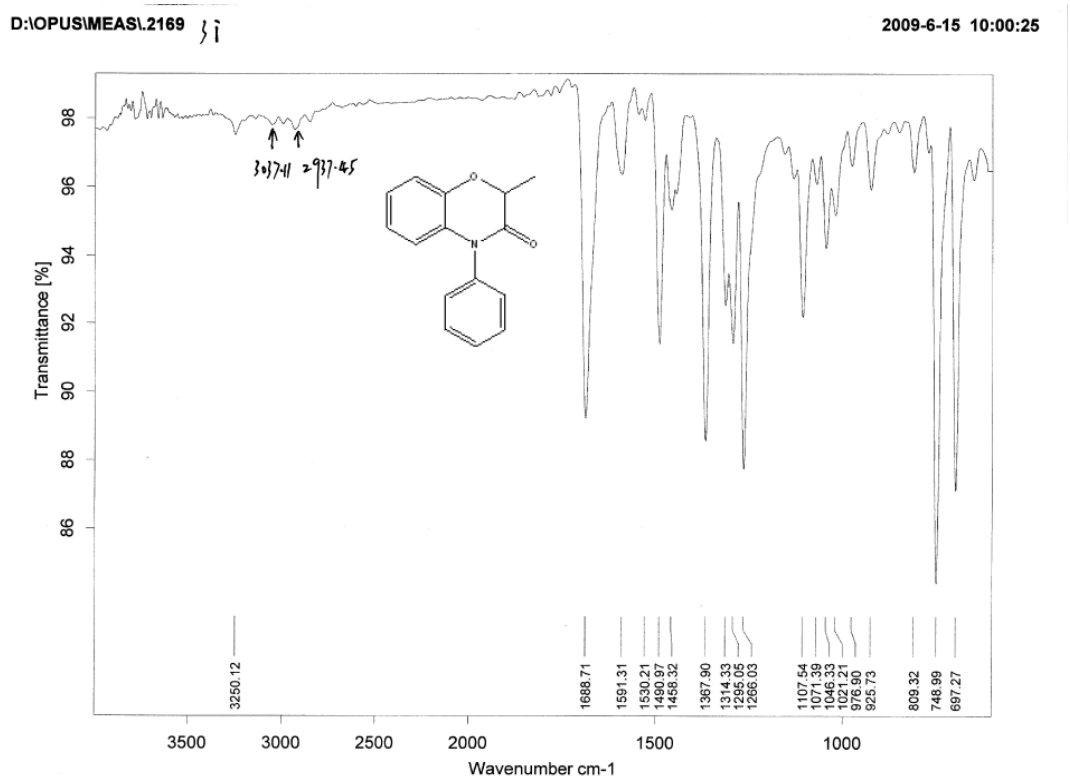
IR Spectrum of Compound 3h



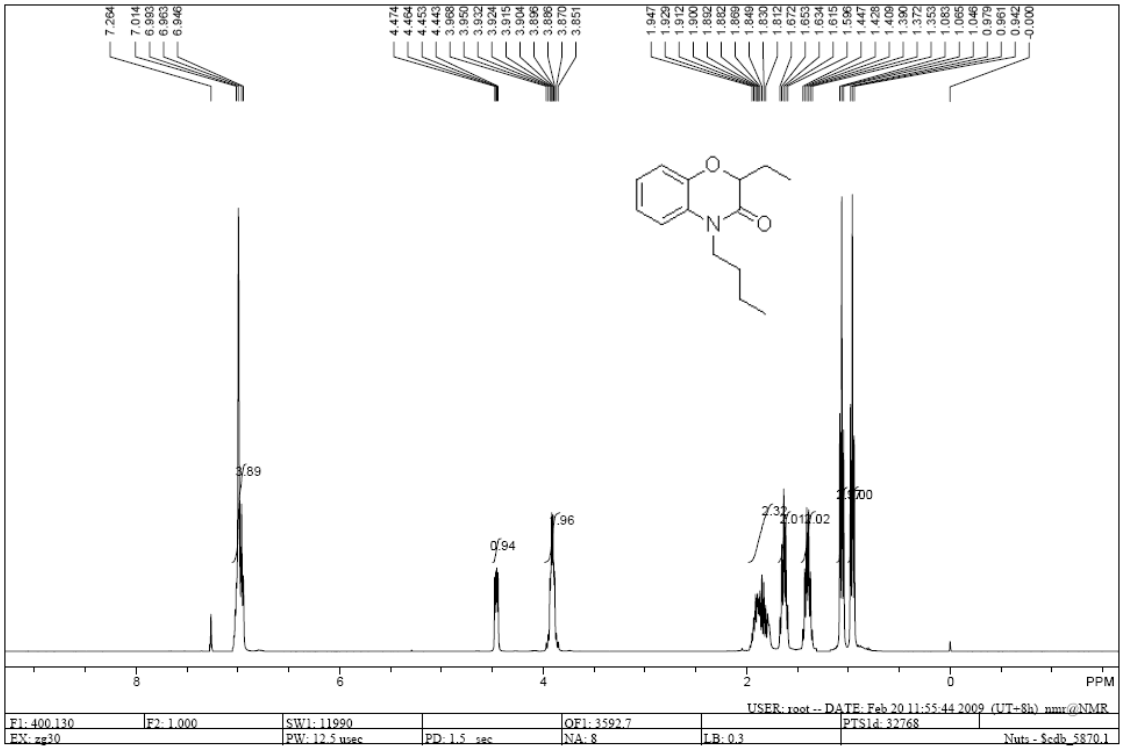
[1]H NMR Spectrum of Compound 3i



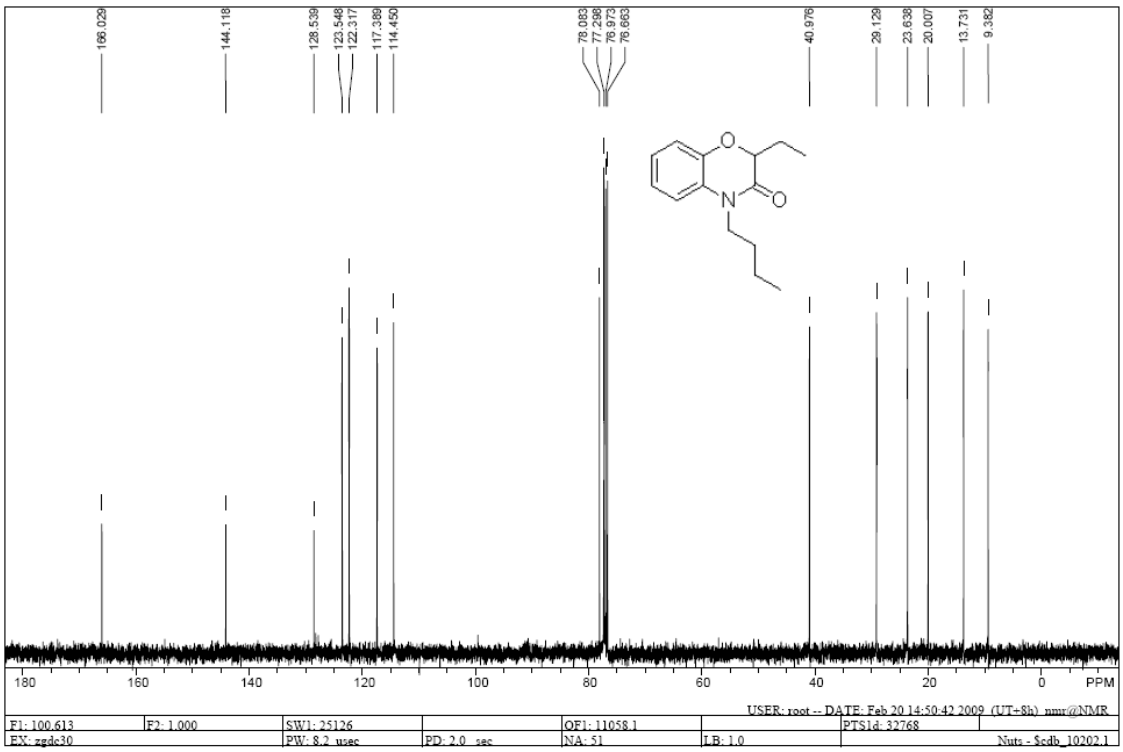
[13]C NMR Spectrum of Compound 3i



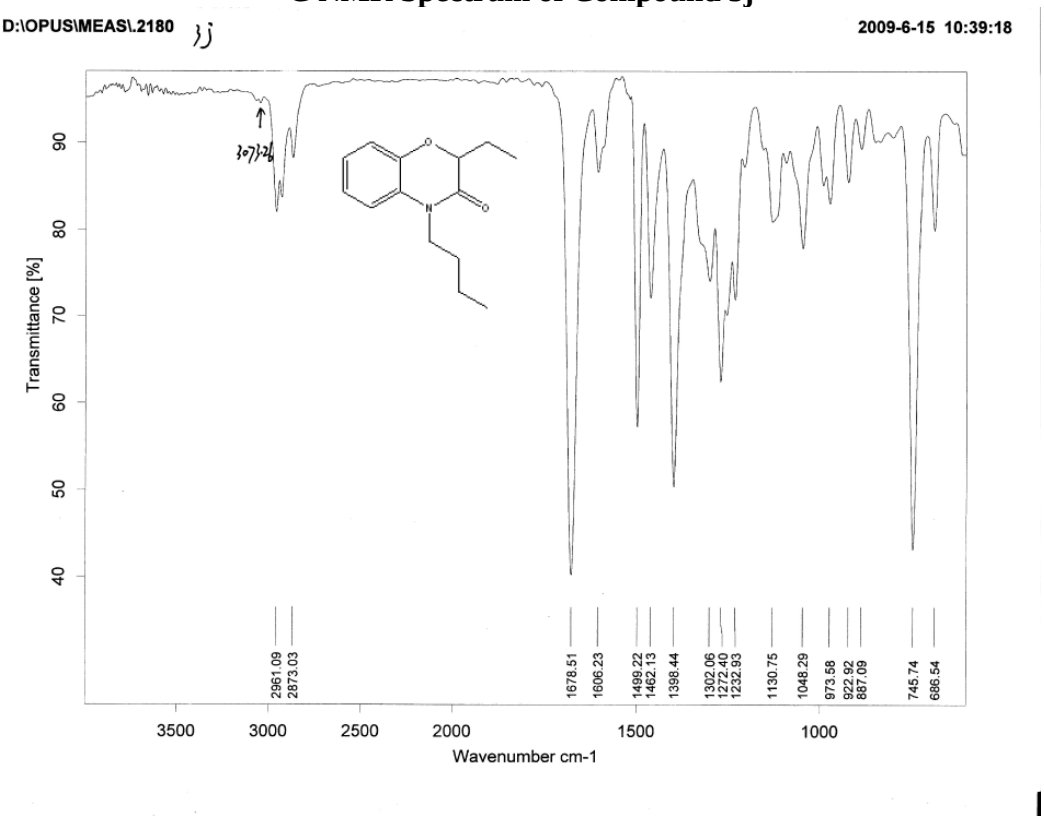
IR Spectrum of Compound 3i



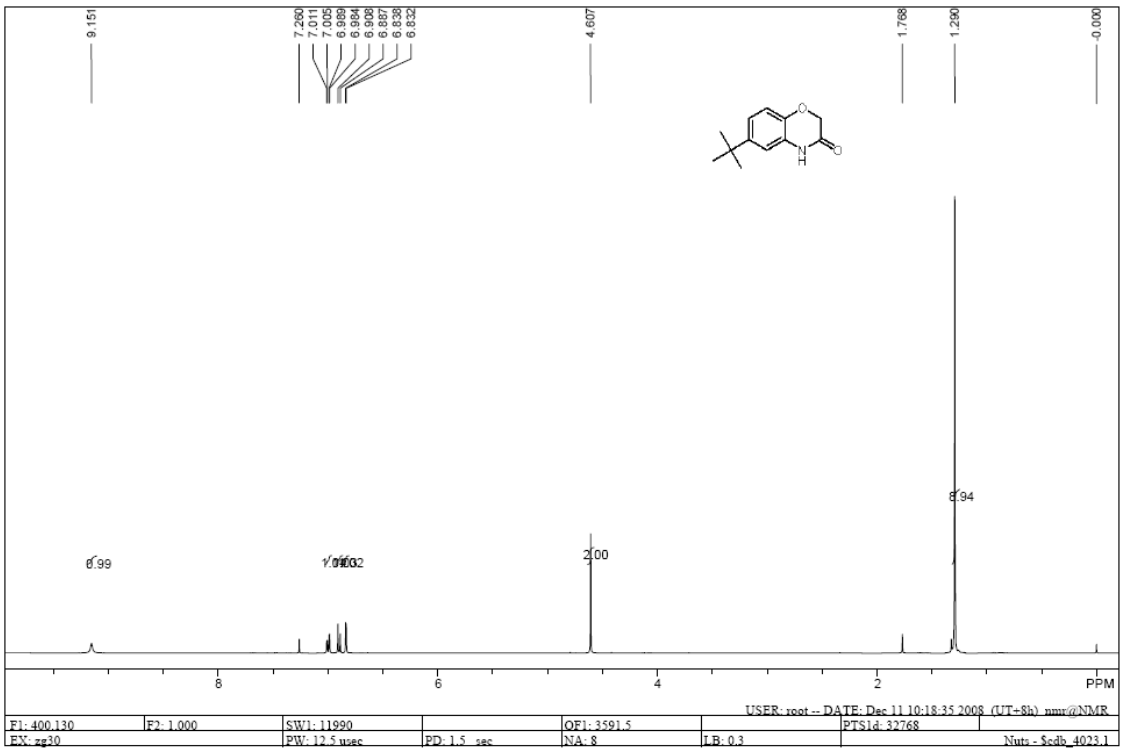
^{1}H NMR Spectrum of Compound 3j



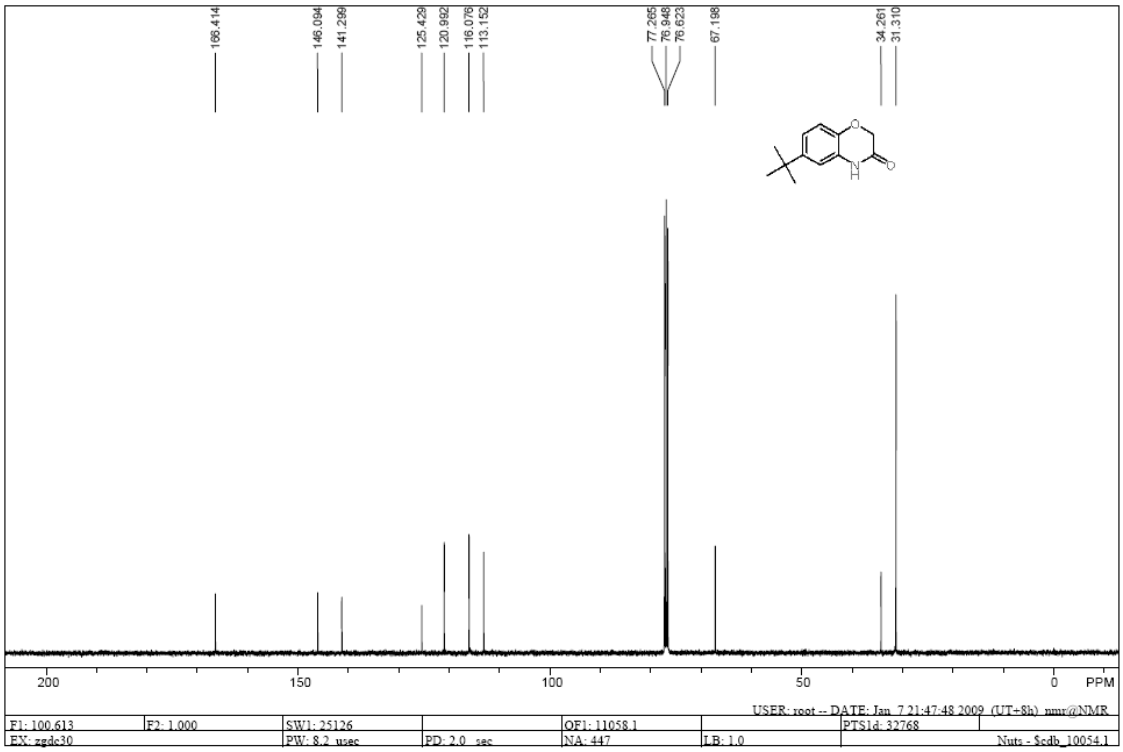
^{13}C NMR Spectrum of Compound 3j



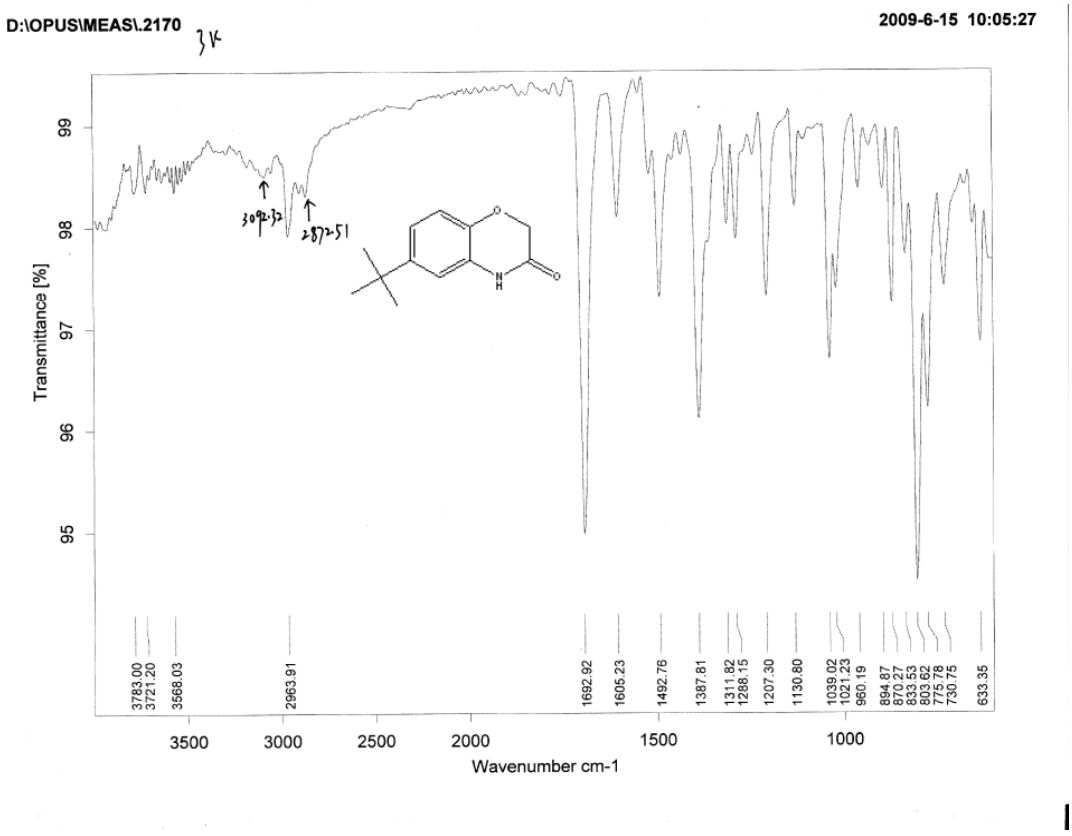
IR Spectrum of Compound 3j



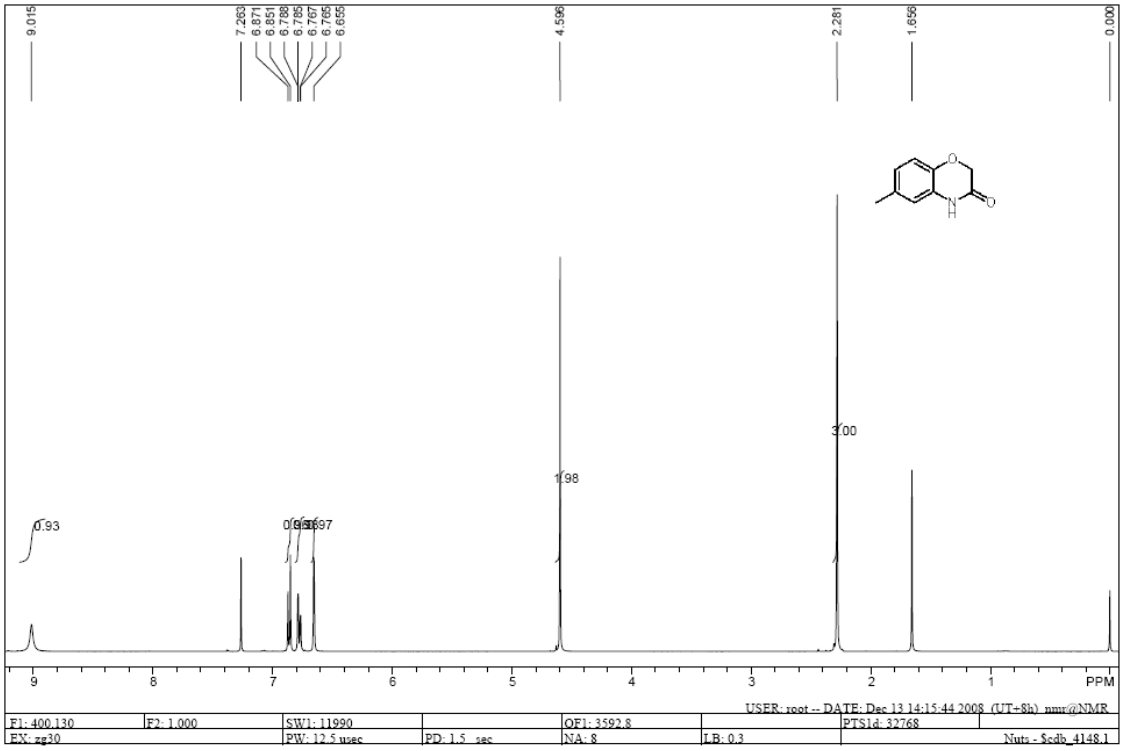
^{1}H NMR Spectrum of Compound 3k



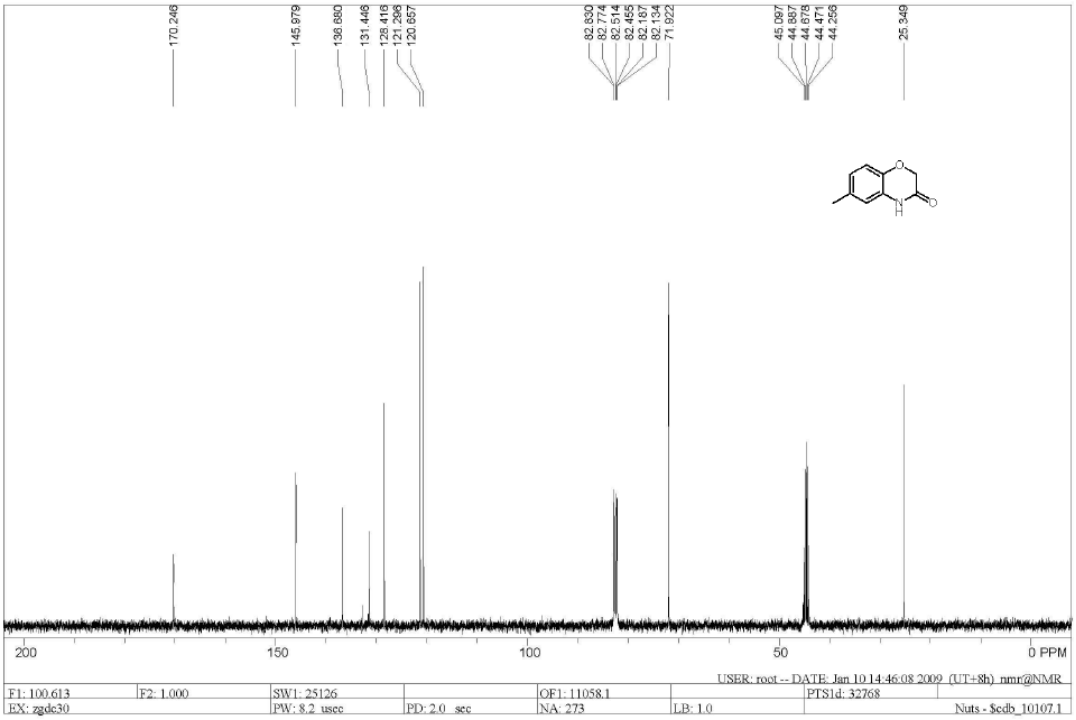
^{13}C NMR Spectrum of Compound 3k



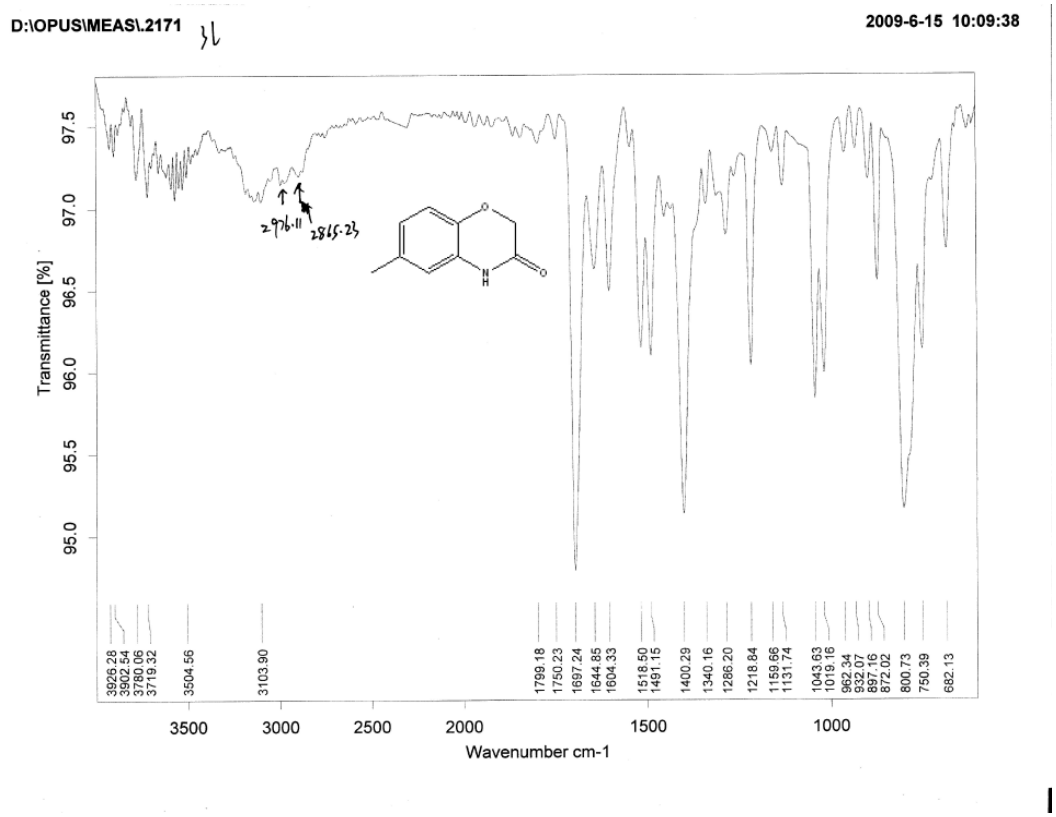
IR Spectrum of Compound 3k



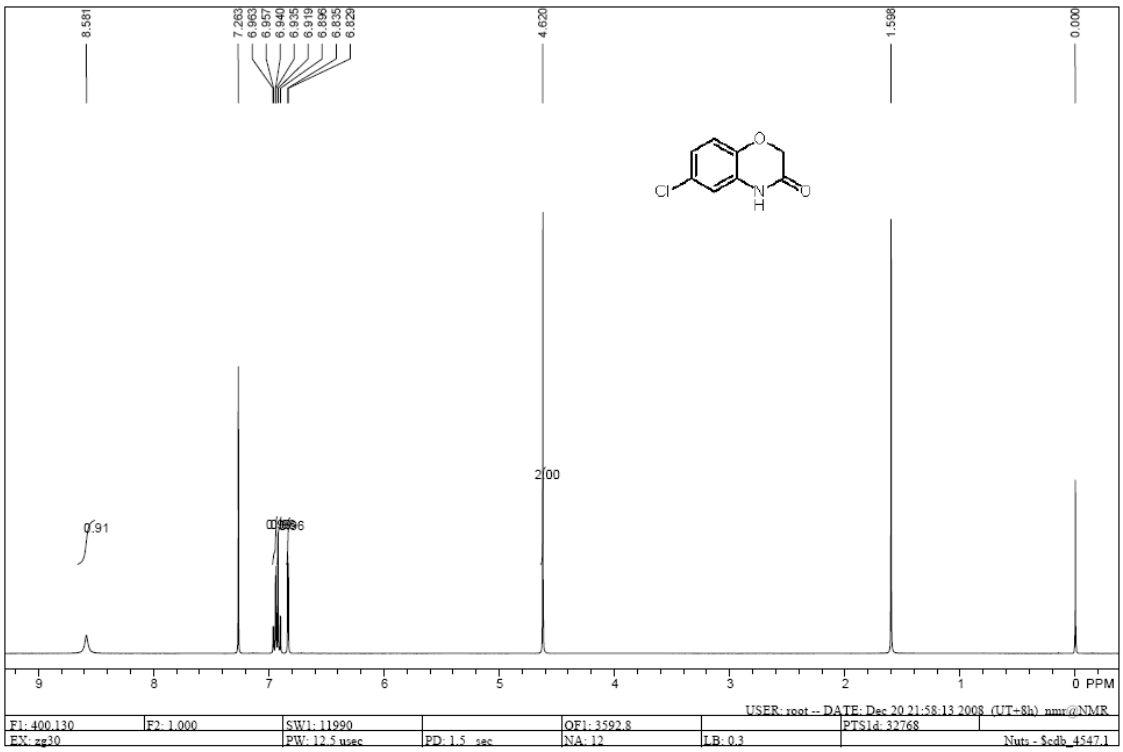
^{1}H NMR Spectrum of Compound 3l



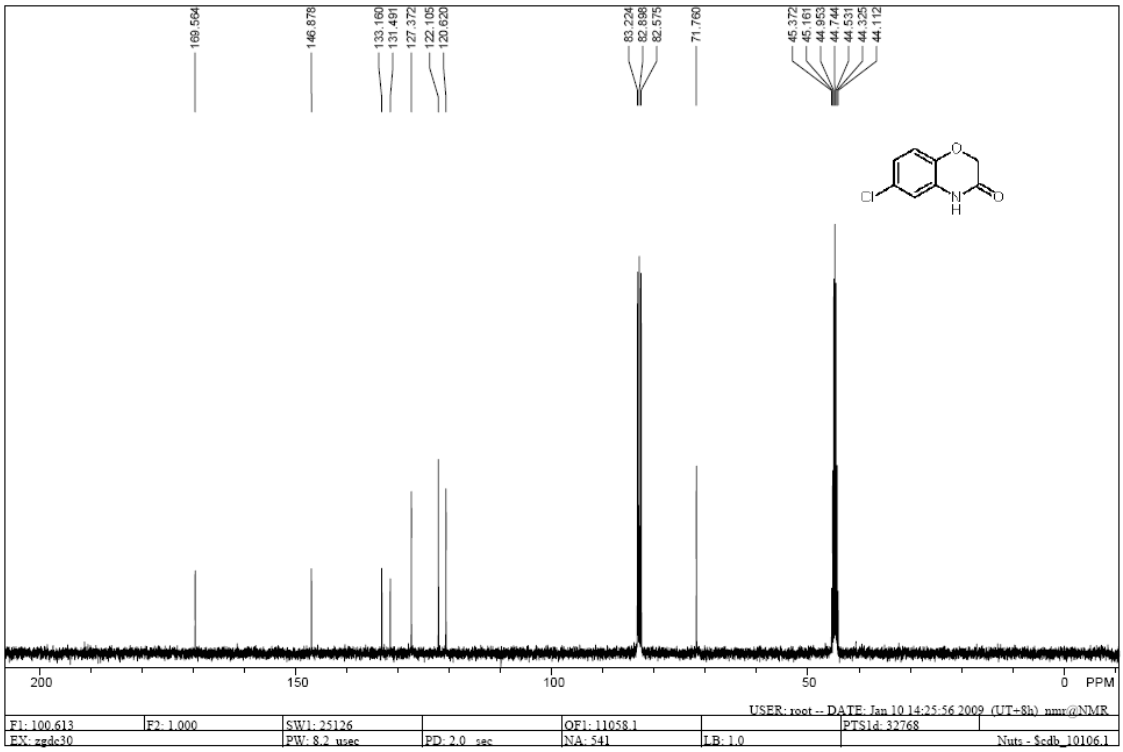
^{13}C NMR Spectrum of Compound 3l



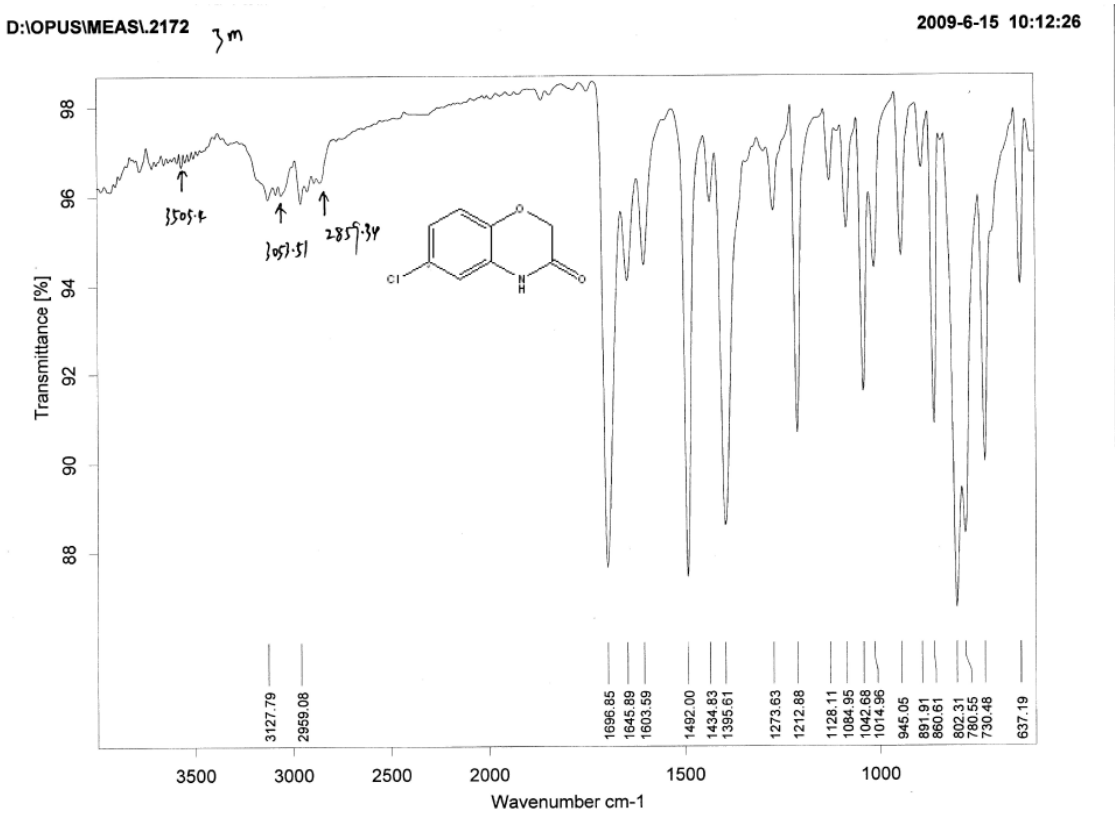
IR Spectrum of Compound 3l



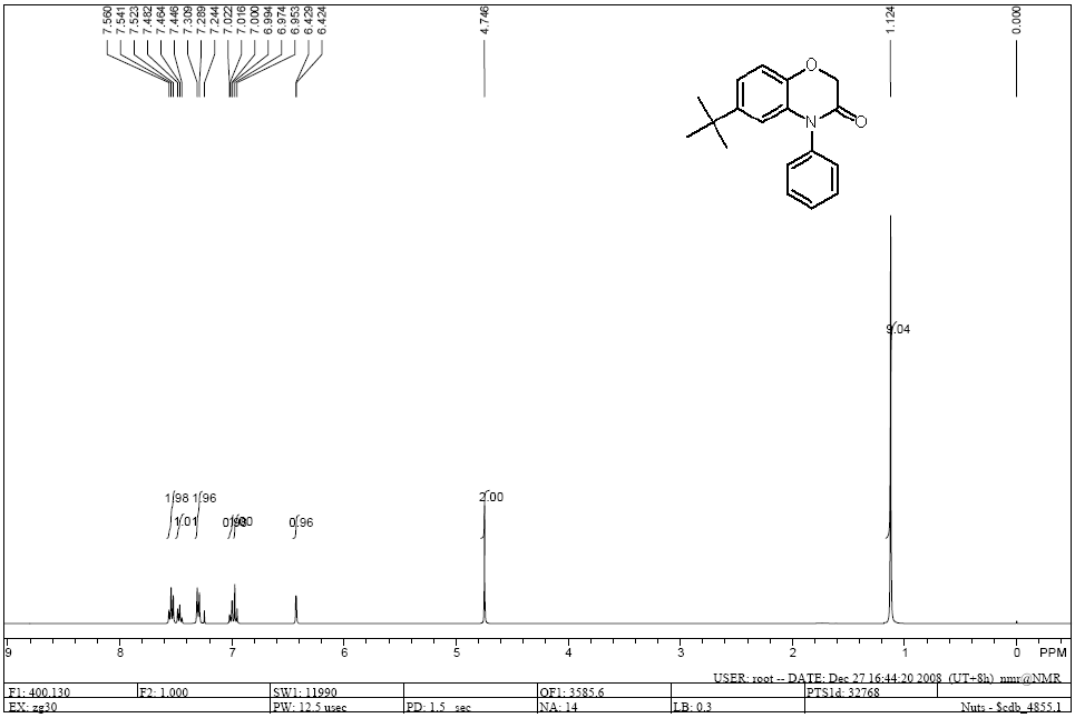
[1]H NMR Spectrum of Compound 3m



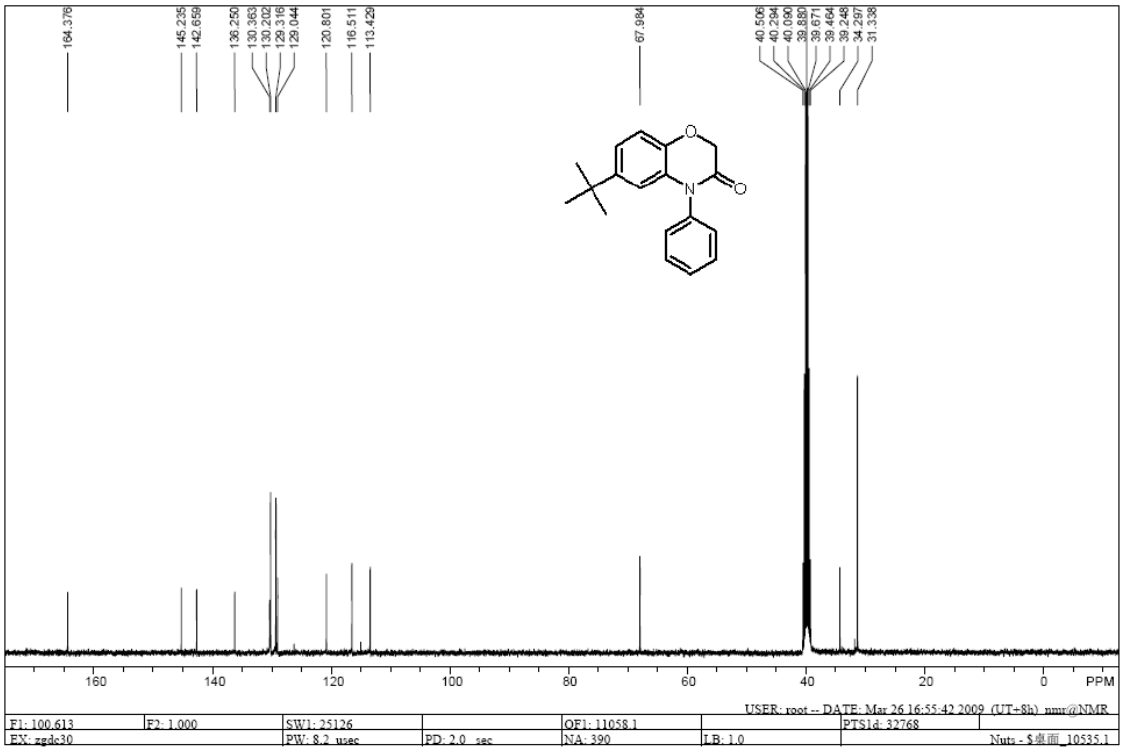
[13]C NMR Spectrum of Compound 3m



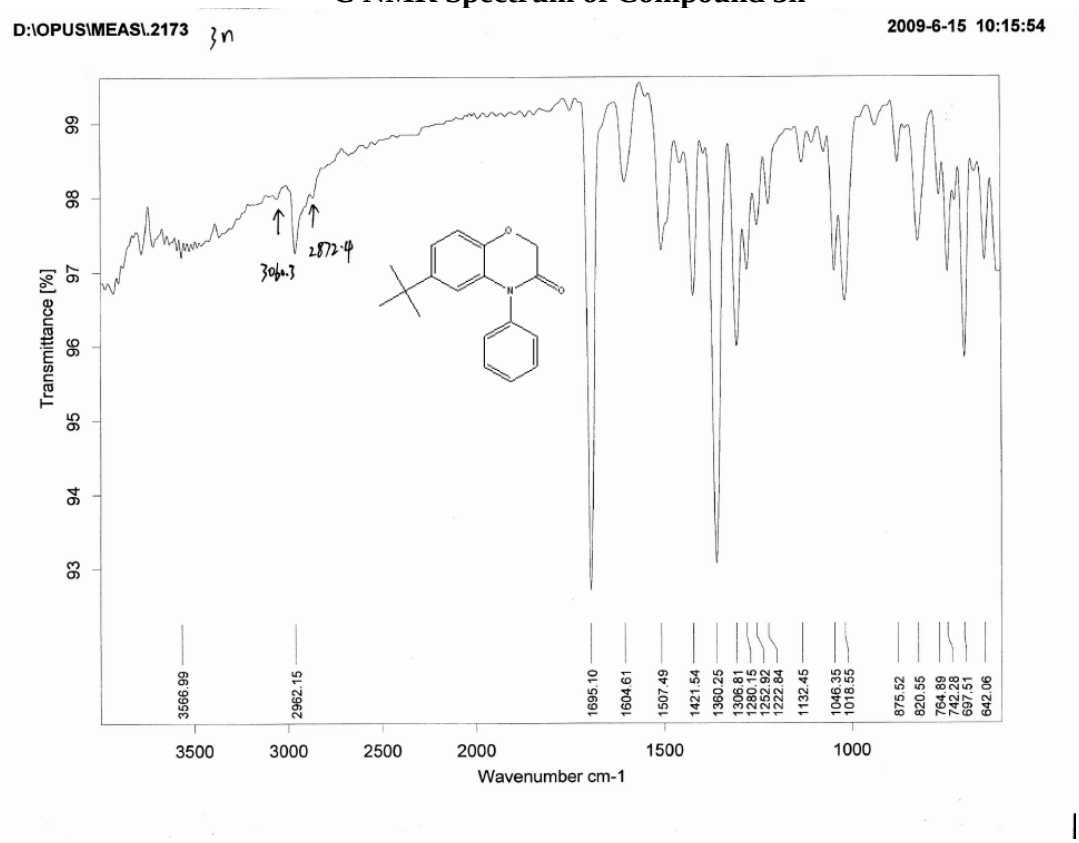
IR Spectrum of Compound 3m



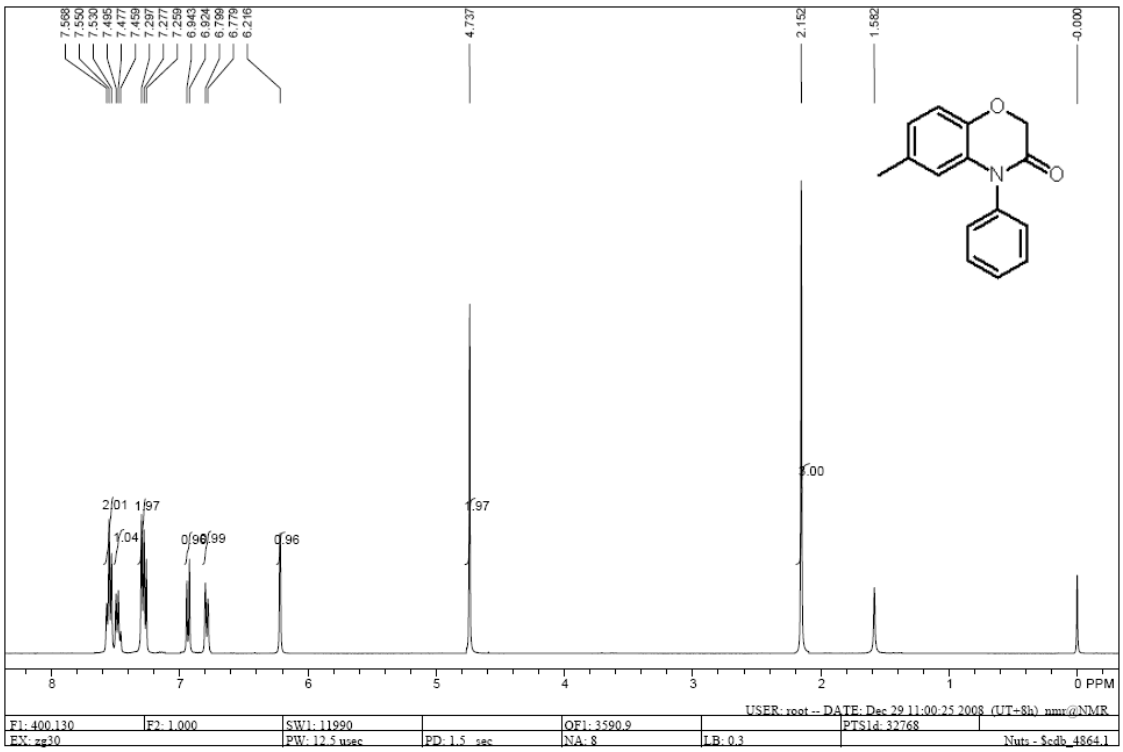
^{1}H NMR Spectrum of Compound 3n



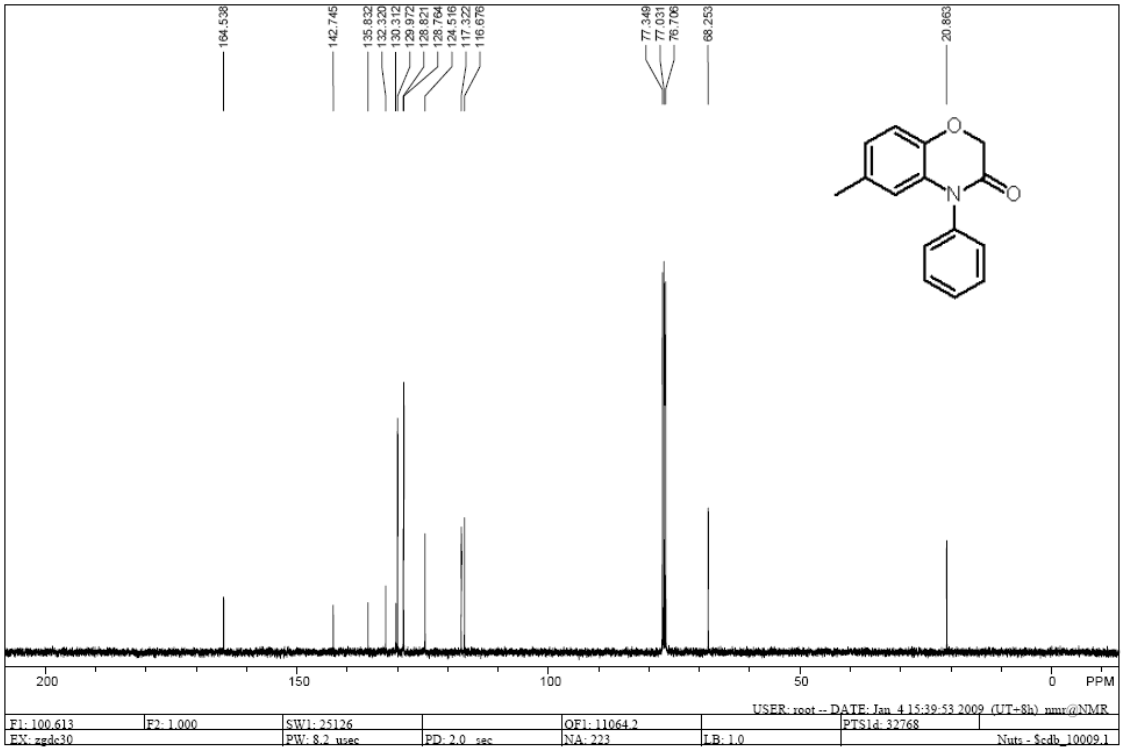
^{13}C NMR Spectrum of Compound 3n



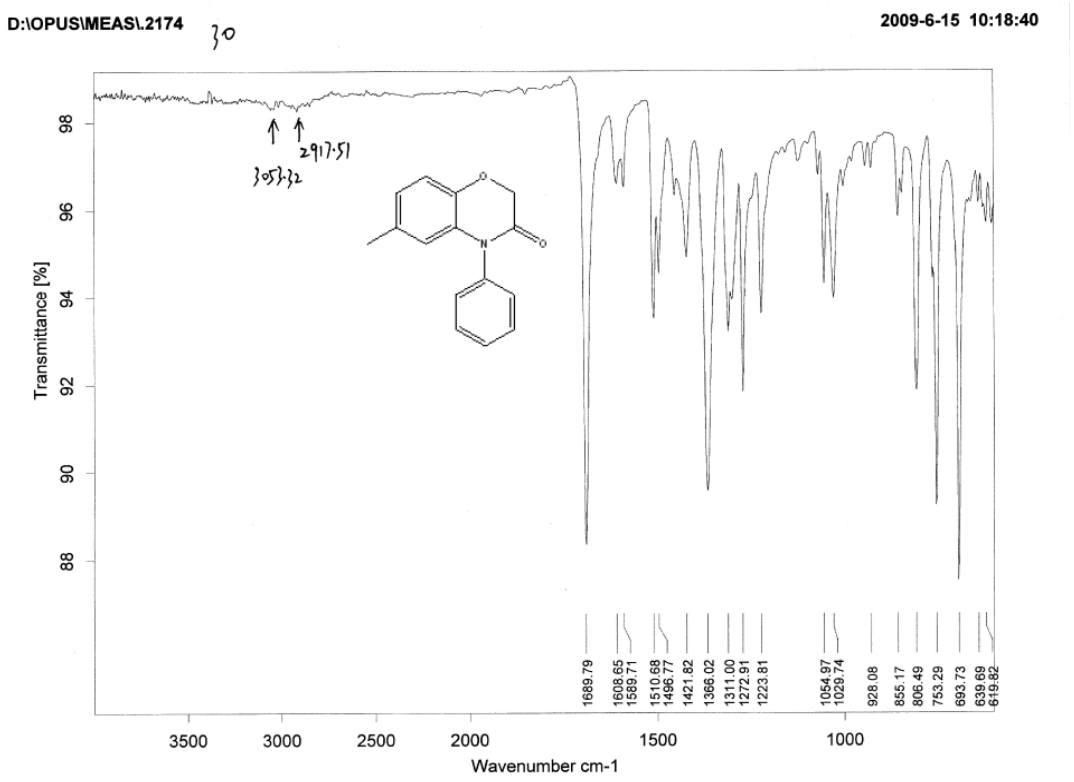
IR Spectrum of Compound 3n



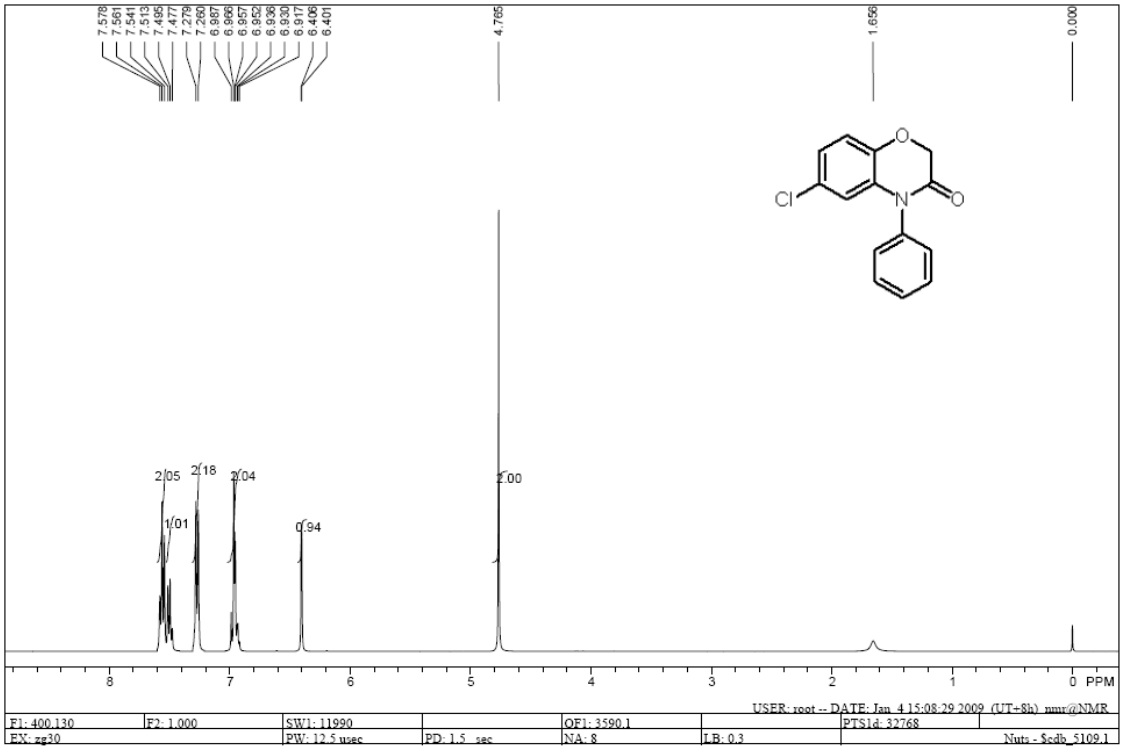
^{1}H NMR Spectrum of Compound 3o



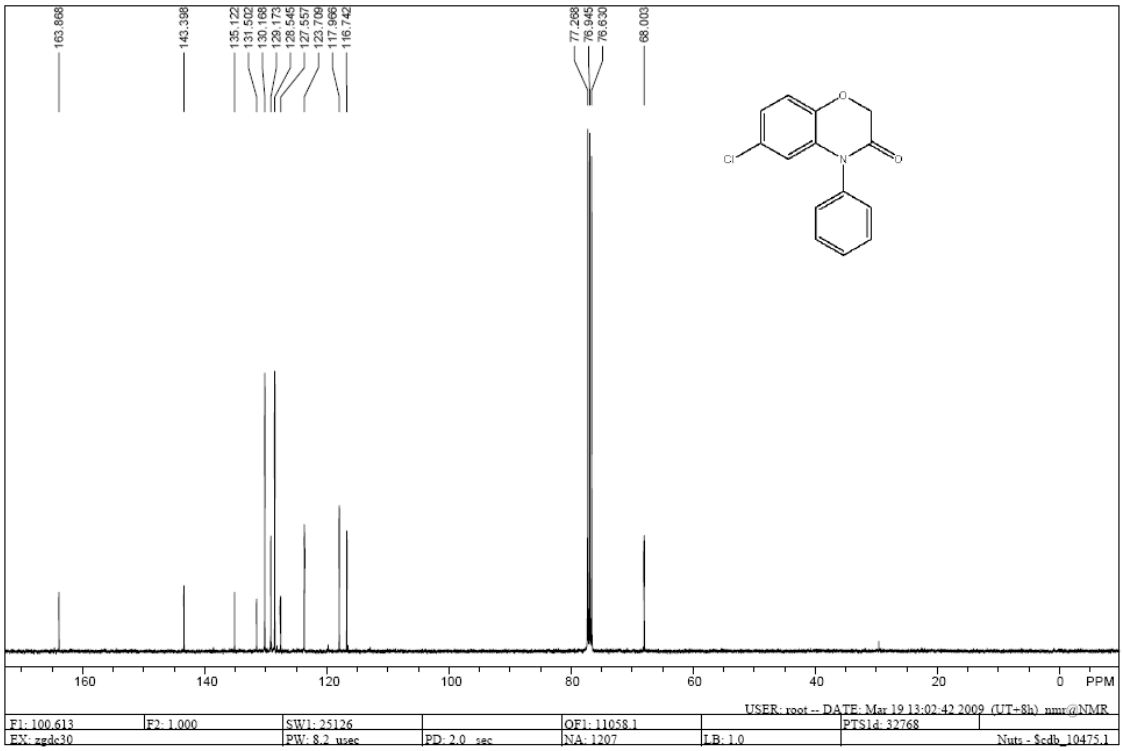
^{13}C NMR Spectrum of Compound 3o



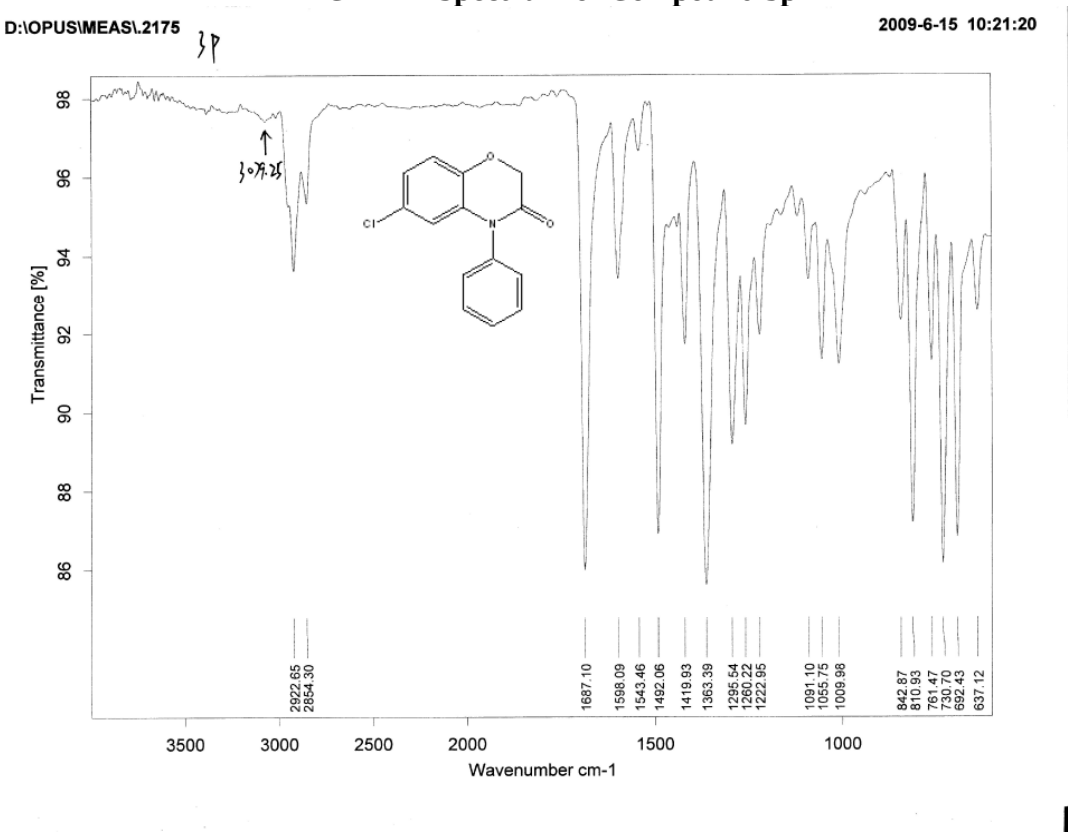
IR Spectrum of Compound 3o



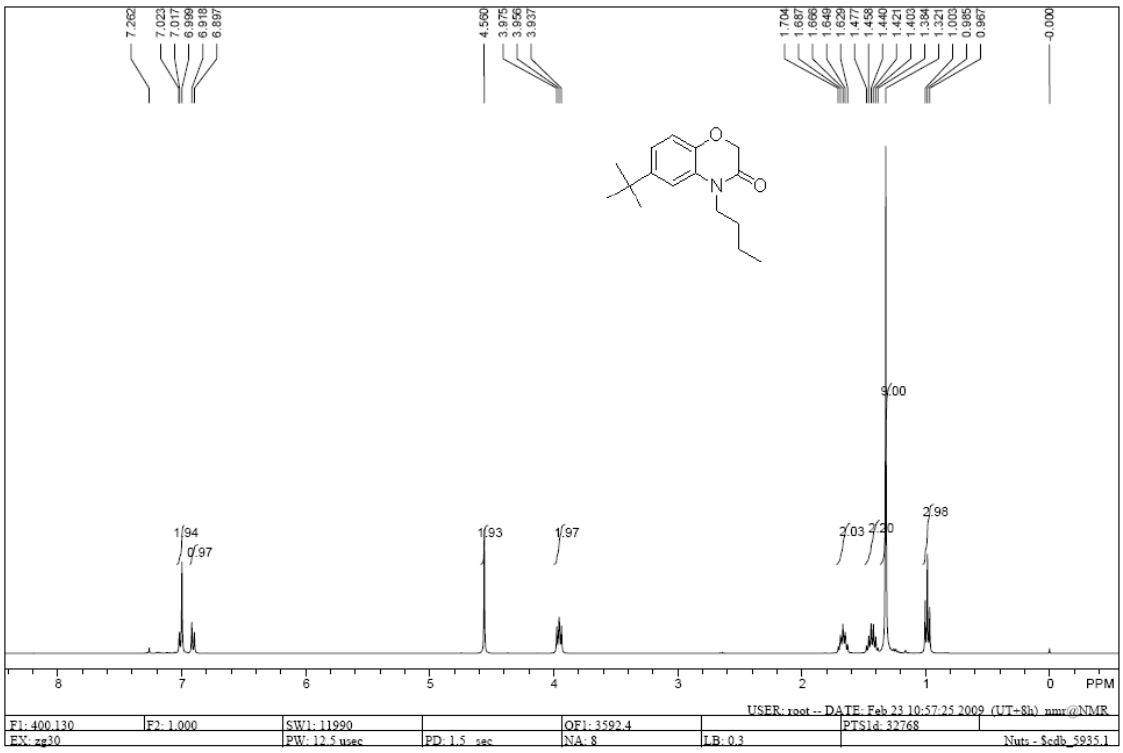
^{1}H NMR Spectrum of Compound 3p



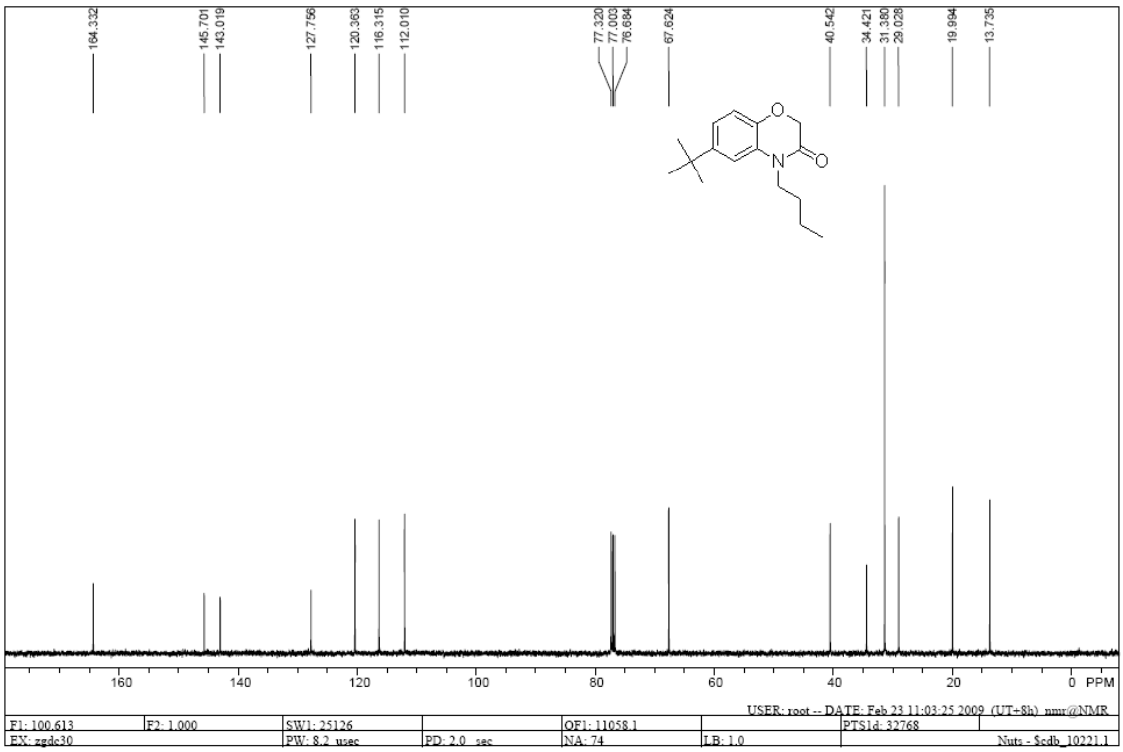
^{13}C NMR Spectrum of Compound 3p



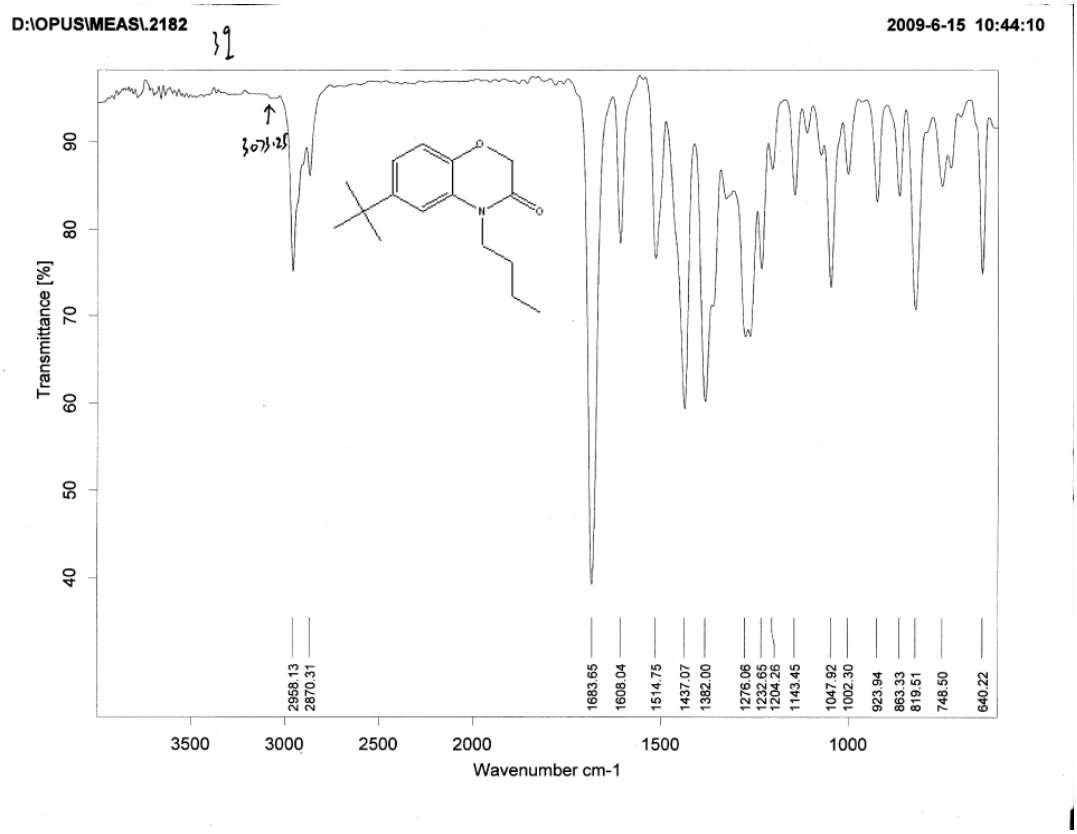
IR Spectrum of Compound 3p



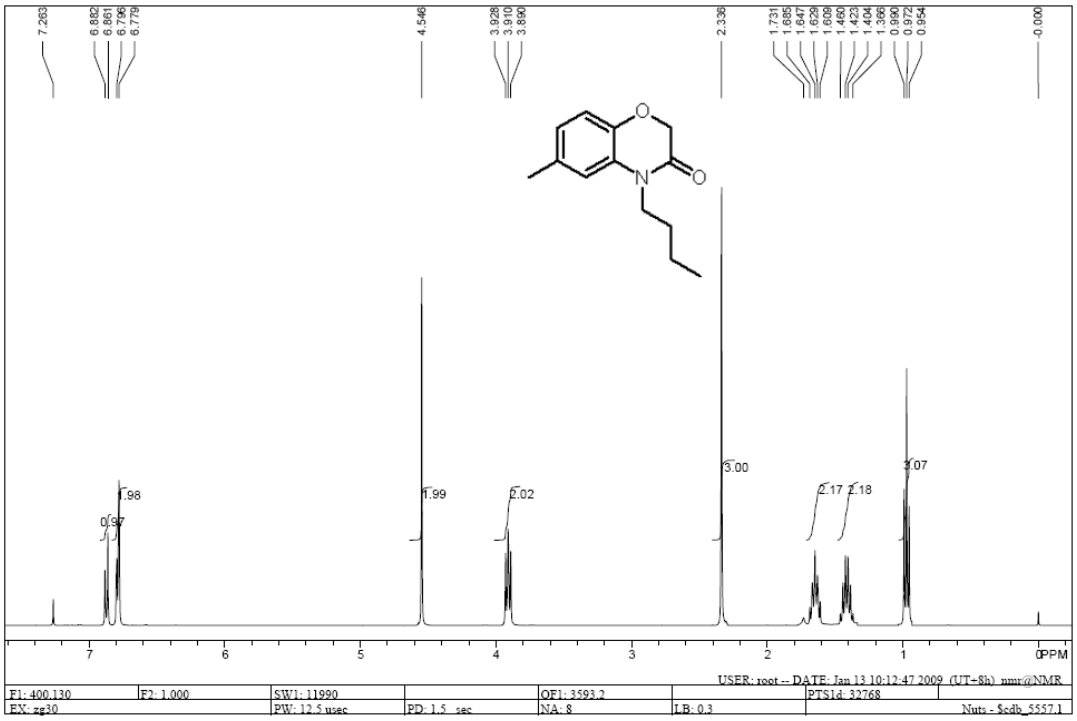
[1]H NMR Spectrum of Compound 3q



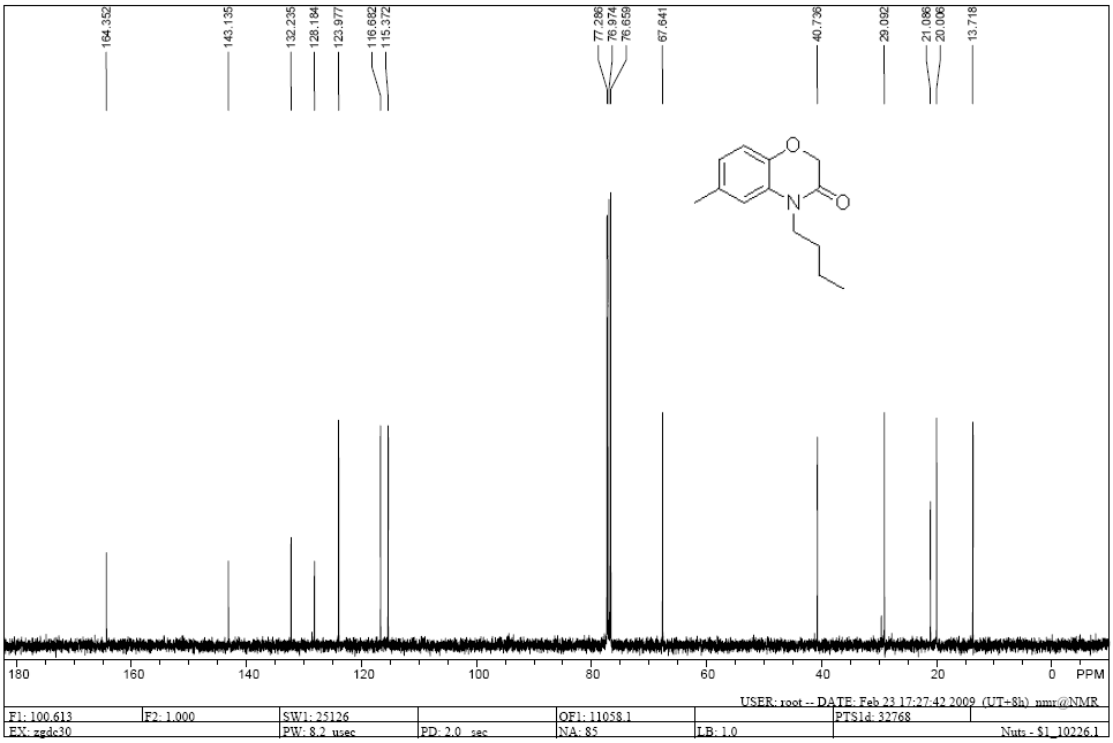
[13]C NMR Spectrum of Compound 3q



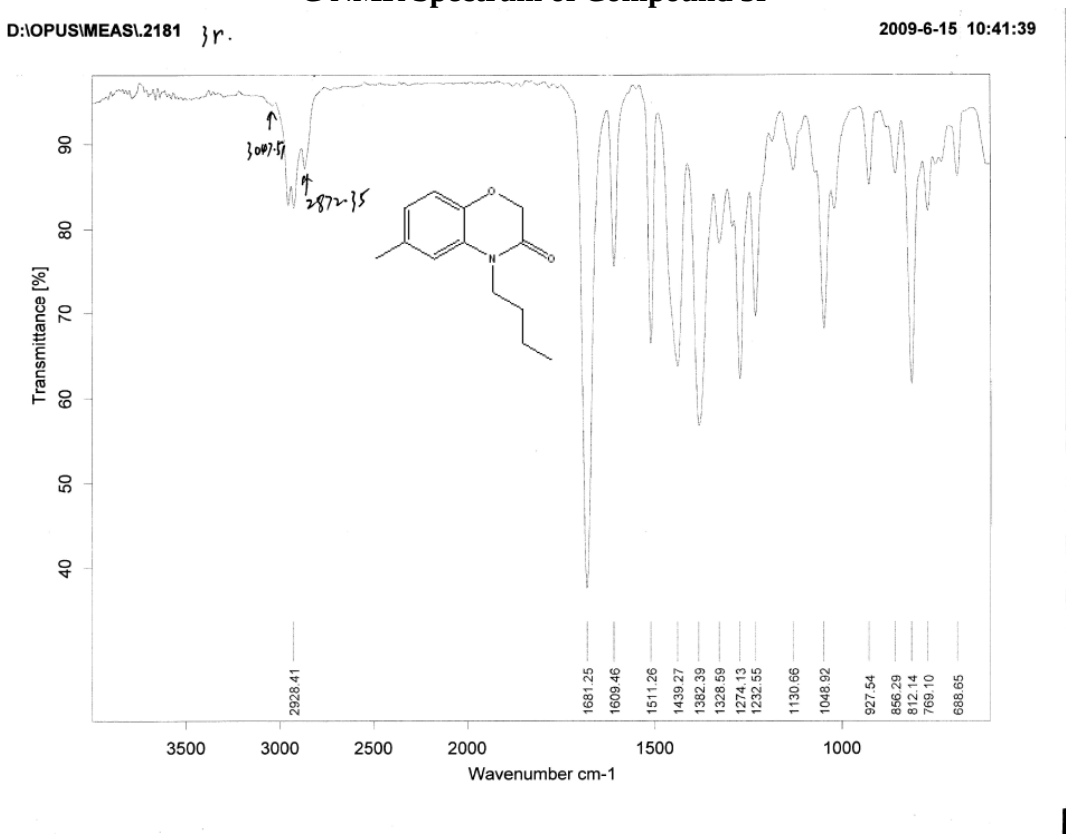
IR Spectrum of Compound 3q



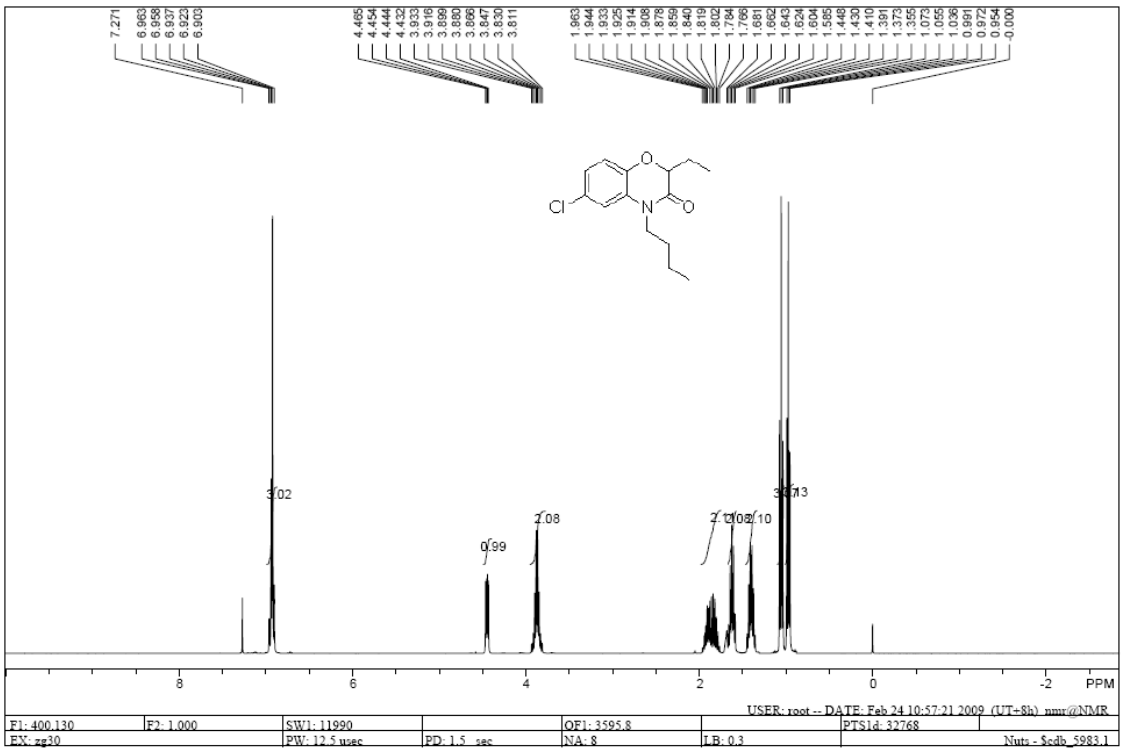
^{1}H NMR Spectrum of Compound 3r



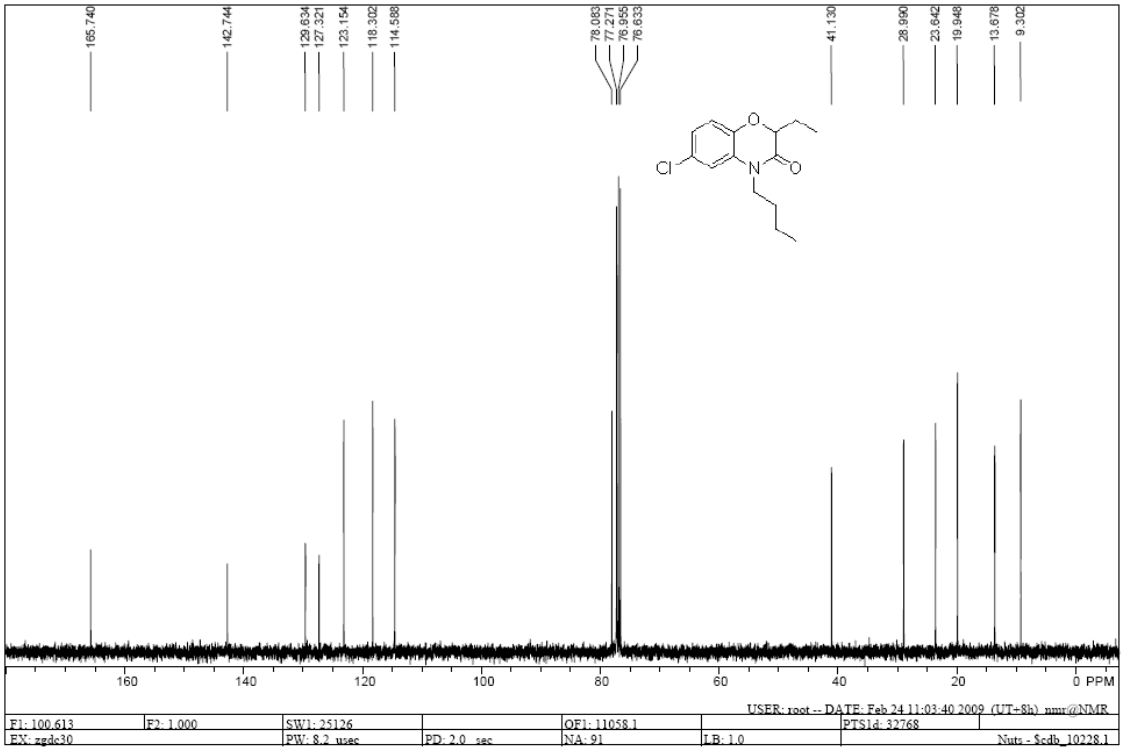
^{13}C NMR Spectrum of Compound 3r



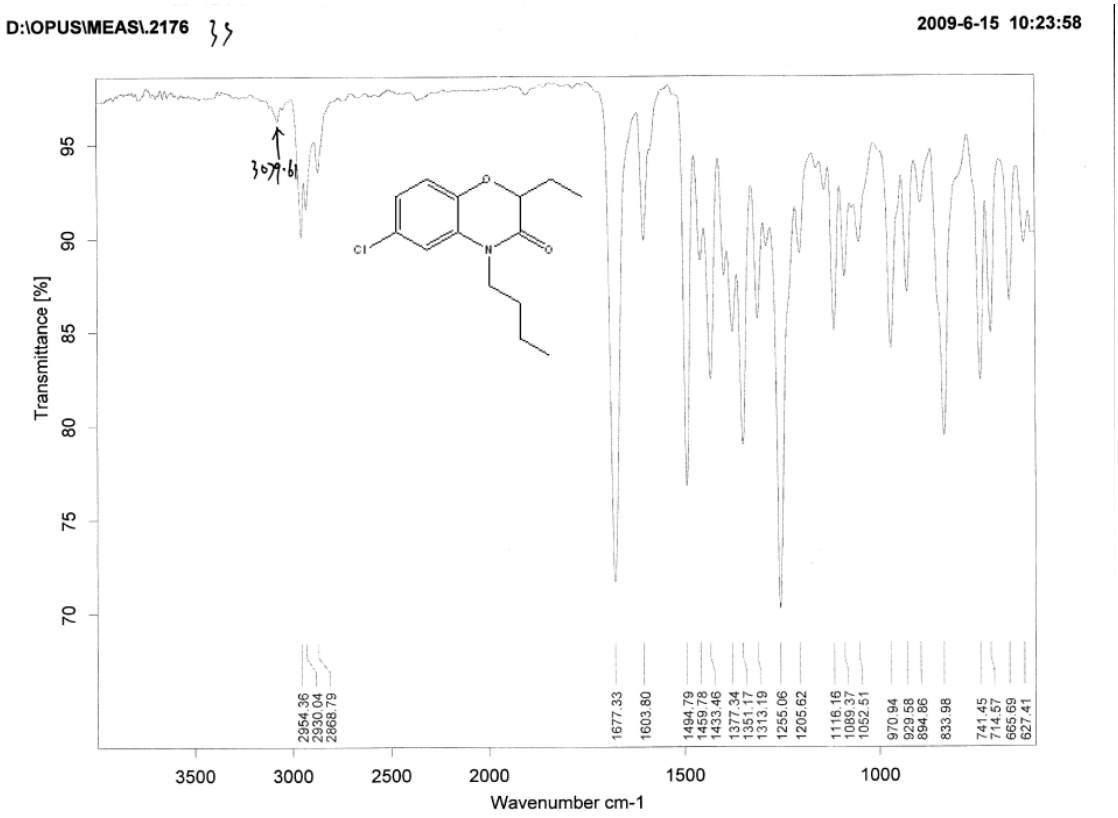
IR Spectrum of Compound 3r



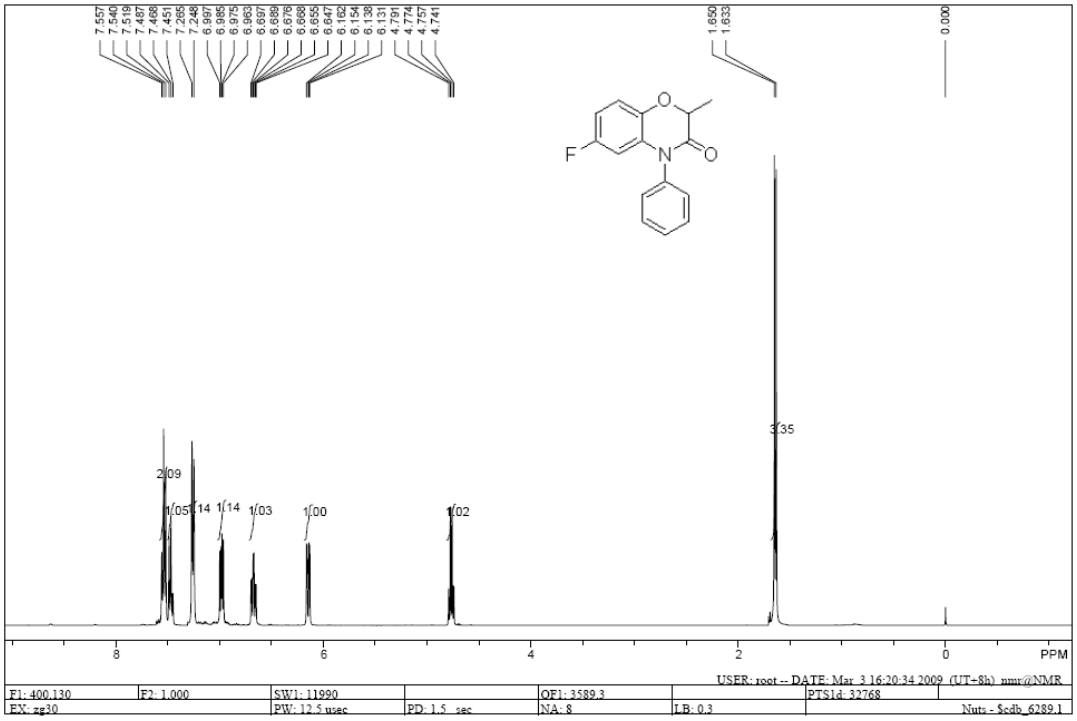
[1]H NMR Spectrum of Compound 3s



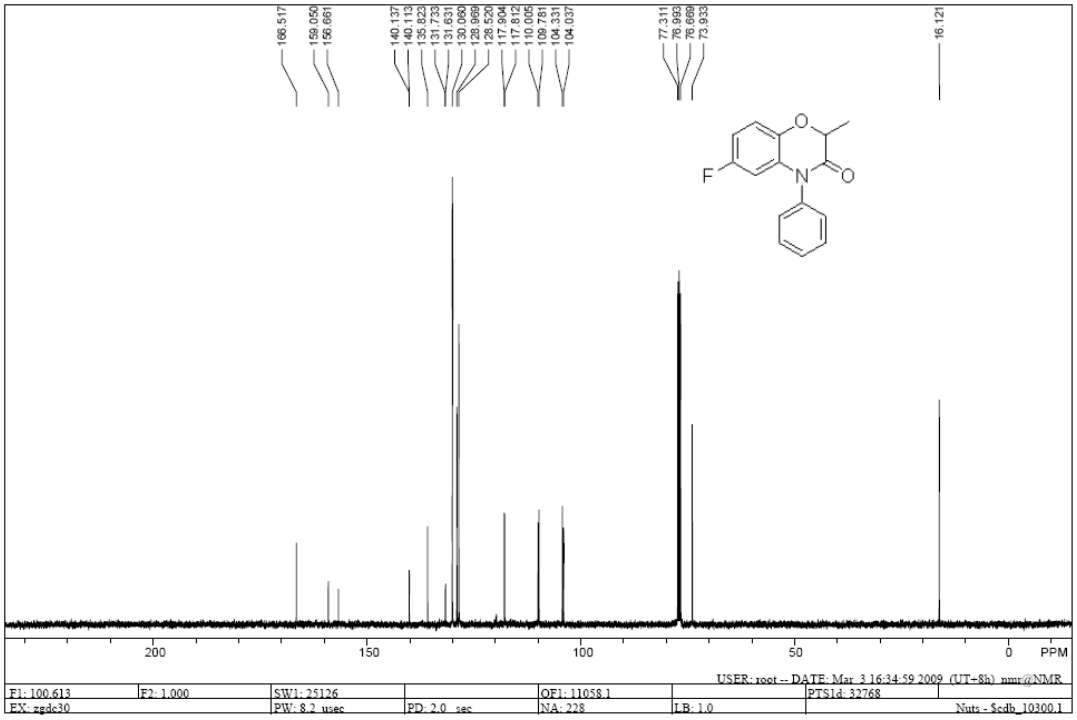
[13]C NMR Spectrum of Compound 3s



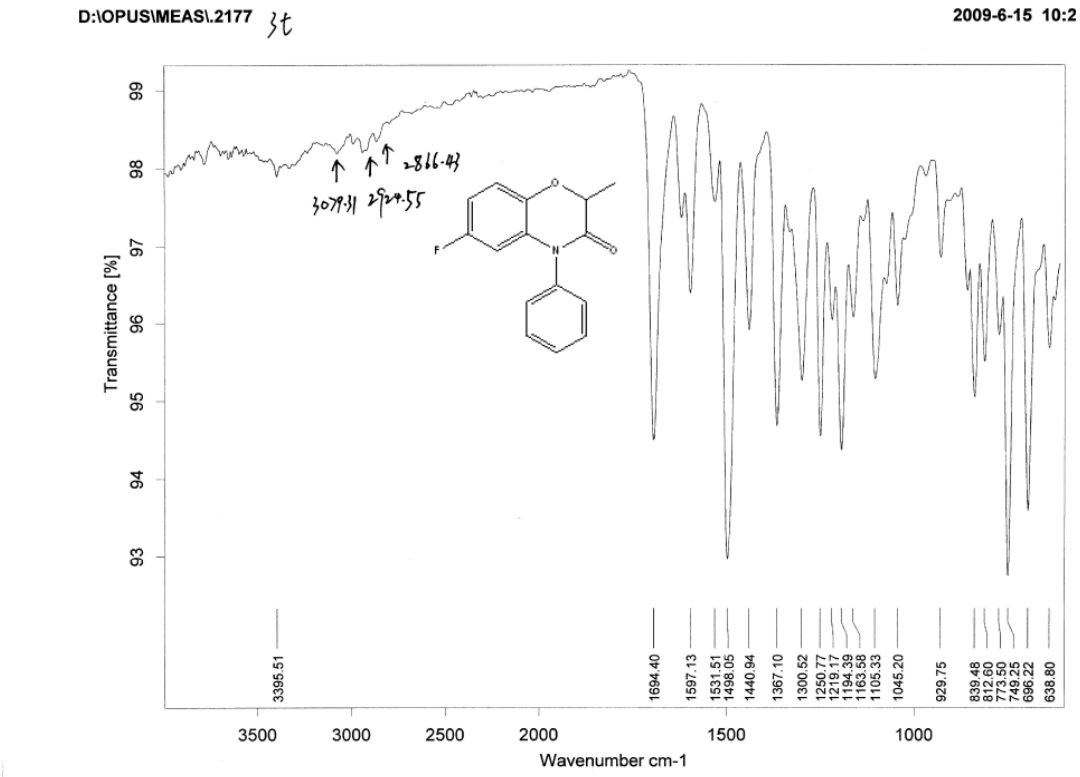
IR Spectrum of Compound 3s



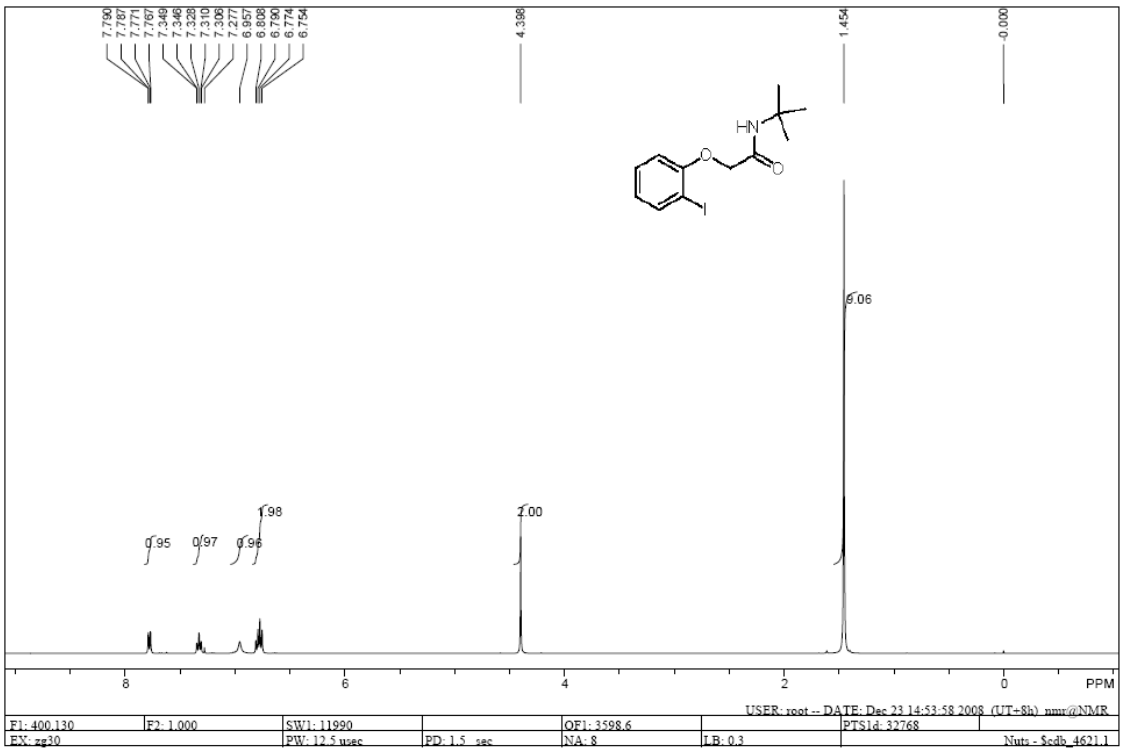
^{1}H NMR Spectrum of Compound 3t



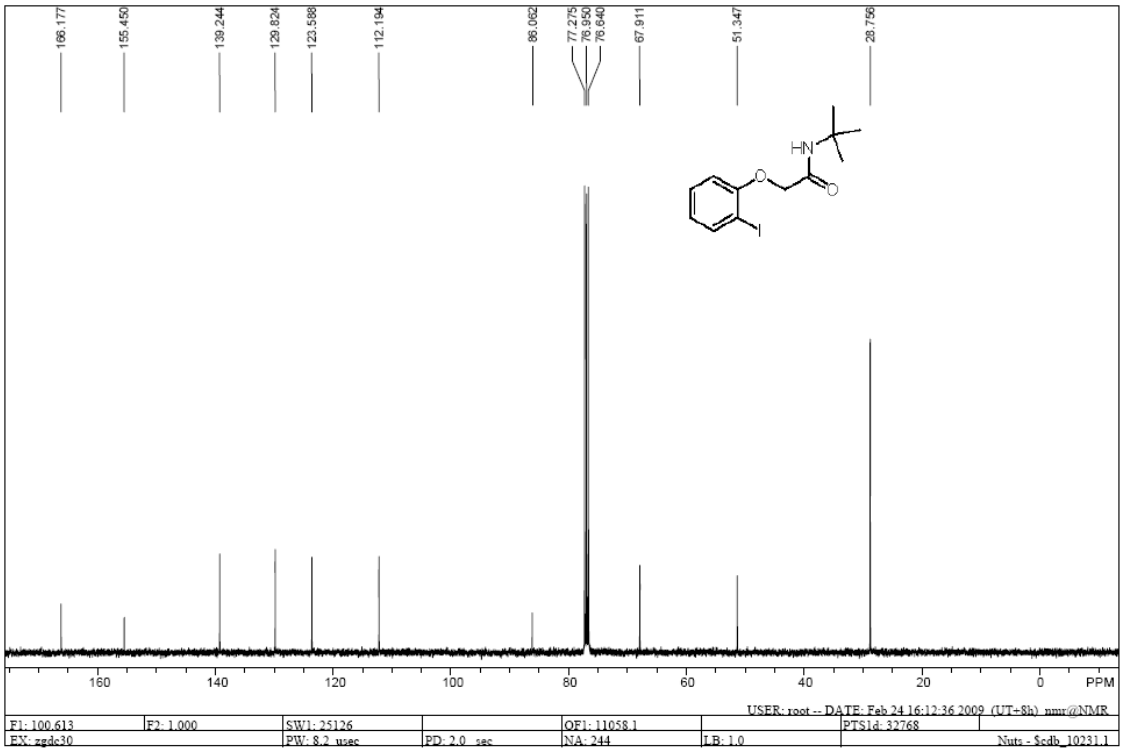
^{13}C NMR Spectrum of Compound 3t



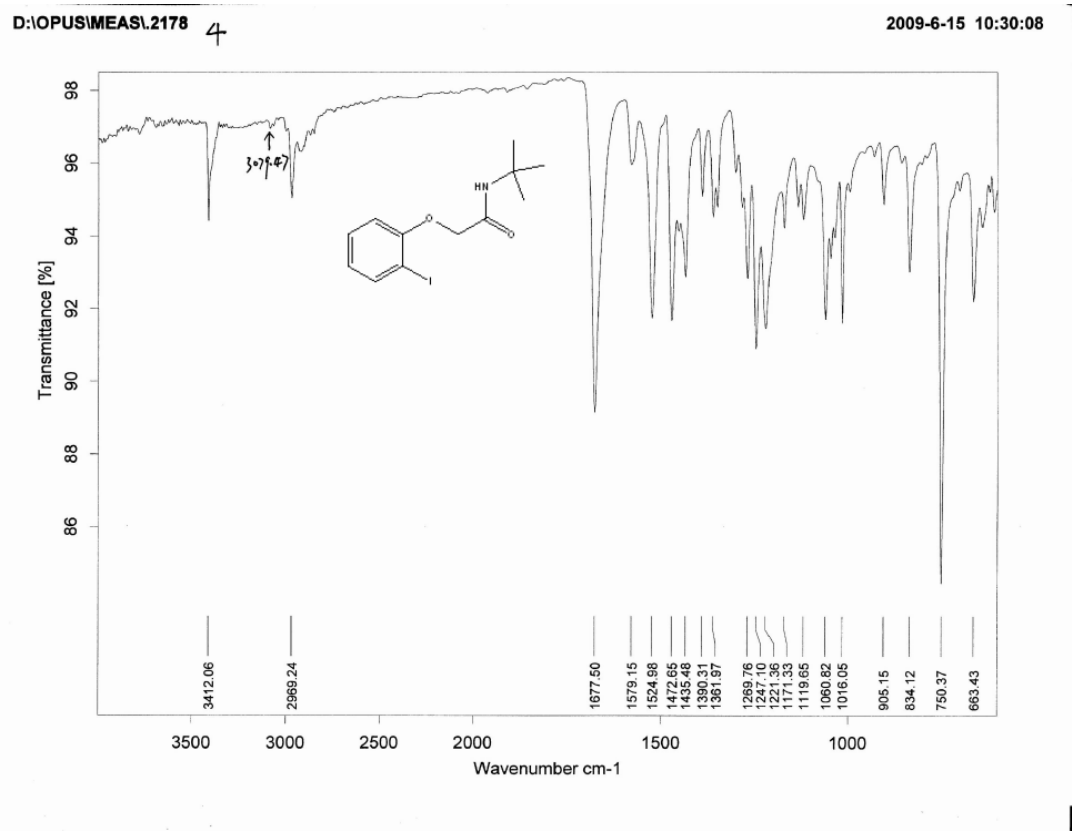
IR Spectrum of Compound 3t



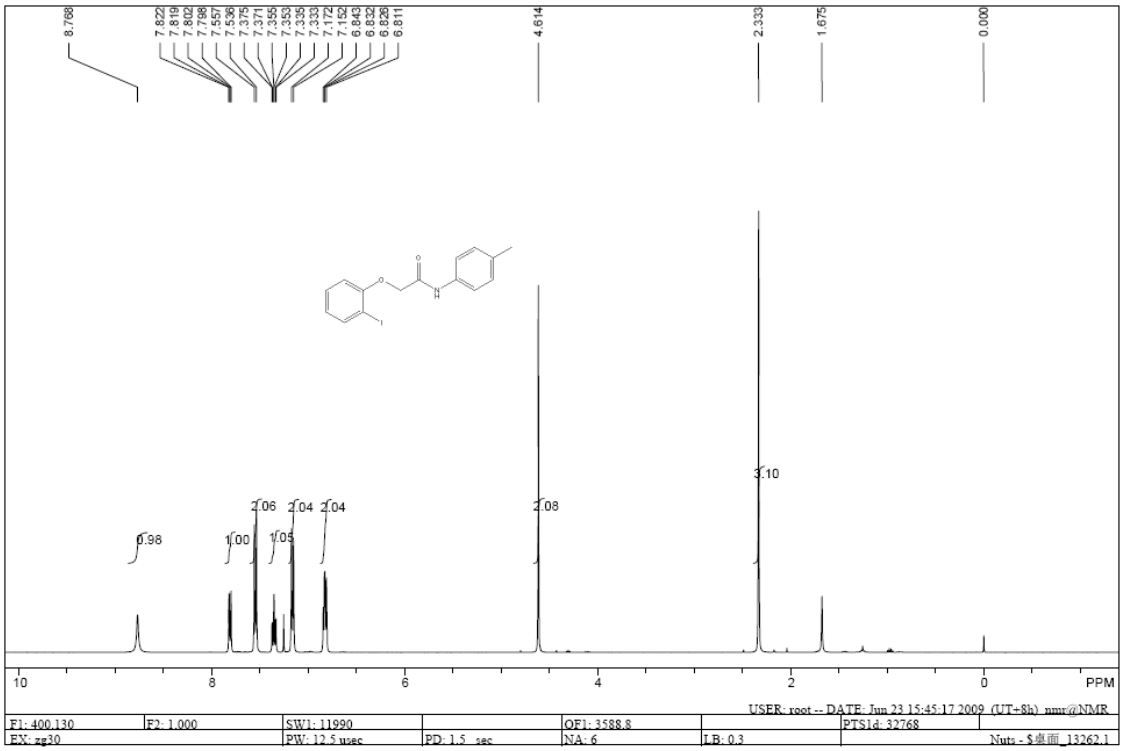
[1]H NMR Spectrum of Compound 4



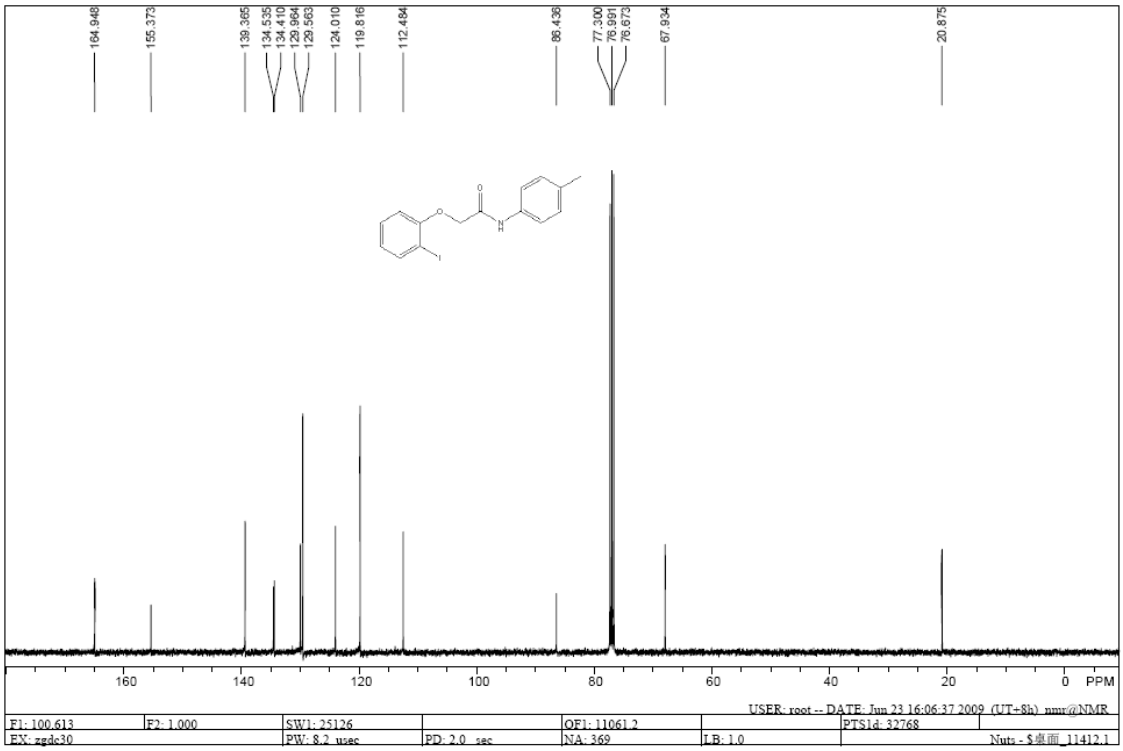
[13]C NMR Spectrum of Compound 4



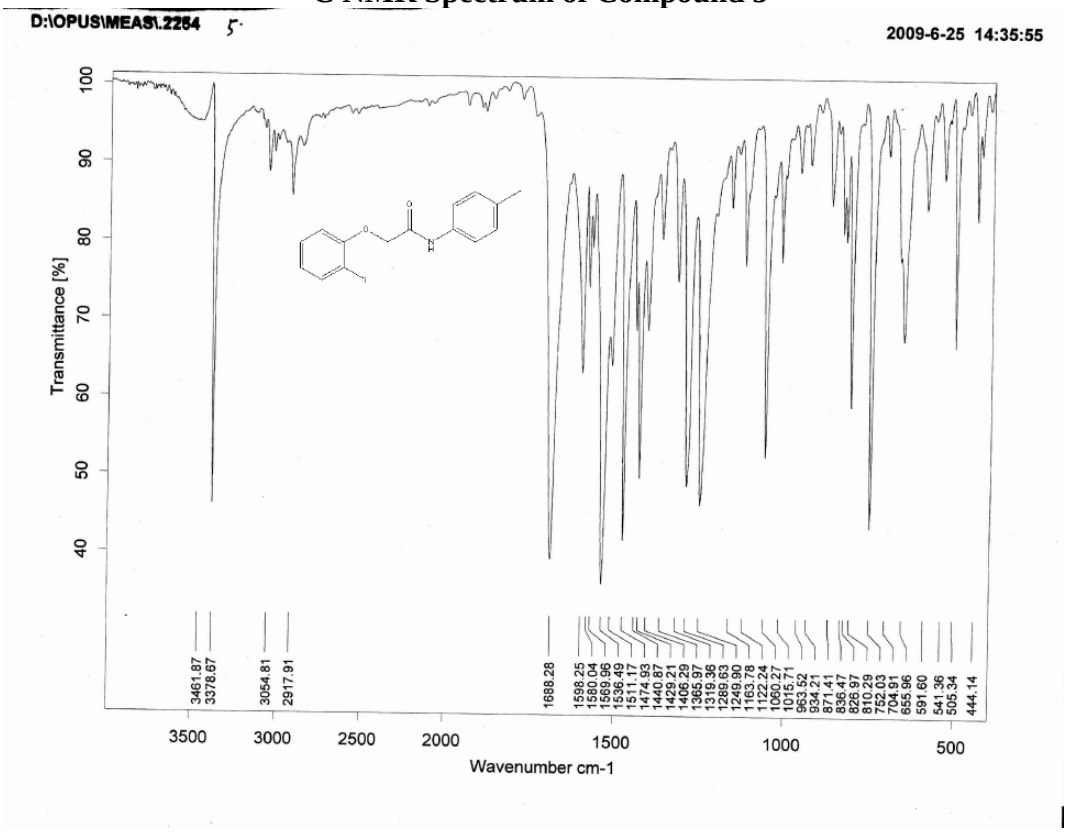
IR Spectrum of Compound 4



^{1}H NMR Spectrum of Compound 5



^{13}C NMR Spectrum of Compound 5



IR Spectrum of Compound 5

References:

1 4-Substituted-*o*-iodophenols were synthesized see : (a)K. J. Edgar, S. N. Falling *J. Org. Chem.*, 1990, **55**, 5287; N-substituted 2-halo amides were synthesized see: (b) M. Y. Chang, S. T. Chen, N. C. Chang *Tetrahedron*, 2002, **58**, 3623. (c) P. G. Baraldi, D. Preti, M. A. Tabrizi, F. Fruttarolo, G. Saponaro, S. Baraldi, R. Romagnoli, A. R. Moorman, A. Gessi, K. Varani, P. A. Barea *Bioorganic & Medicinal Chemistry,* 2007, **15**, 2514.