

Supporting Information

Highly Z-selective synthesis of 1,3-oxathiol-2-ylidenes and 4-methylene-oxazolidine-2-thiones via atom specific 5-exo-dig cyclization of propargyl alcohol with isothiocyanate

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Supporting Information

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EXPERIMENTAL SECTION

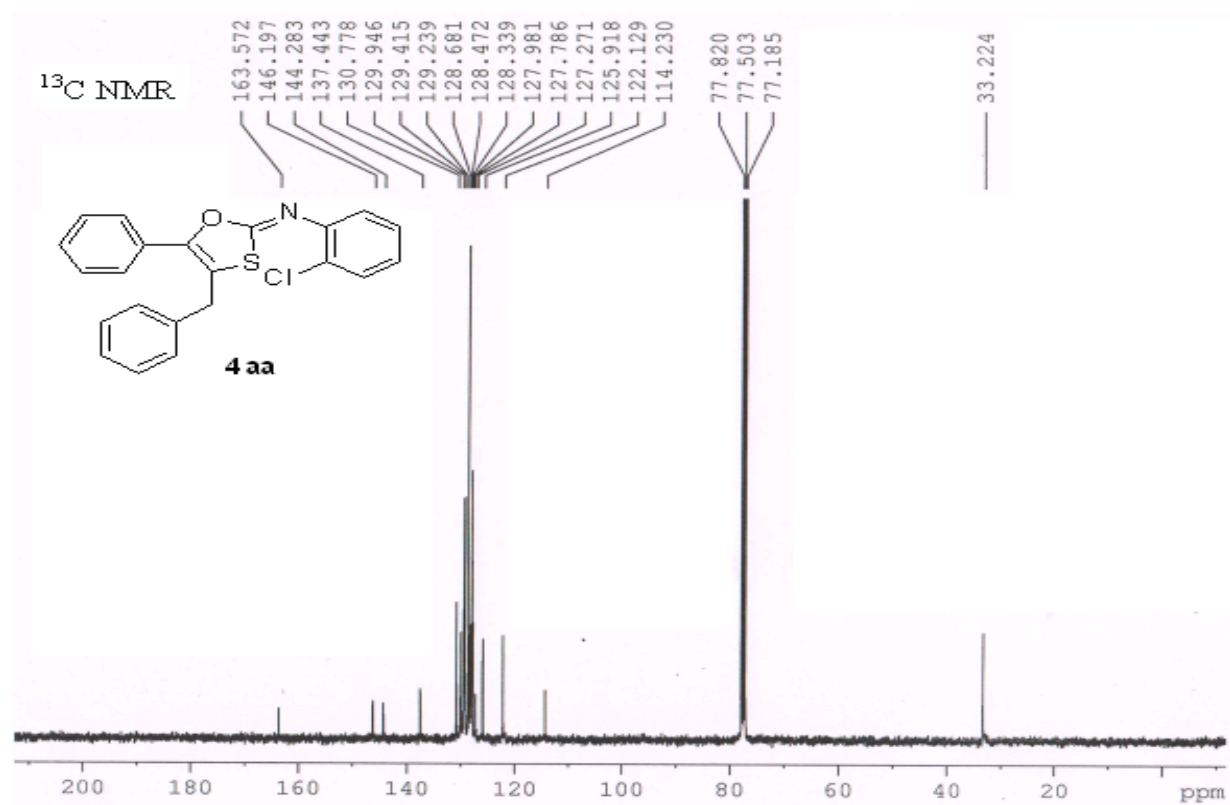
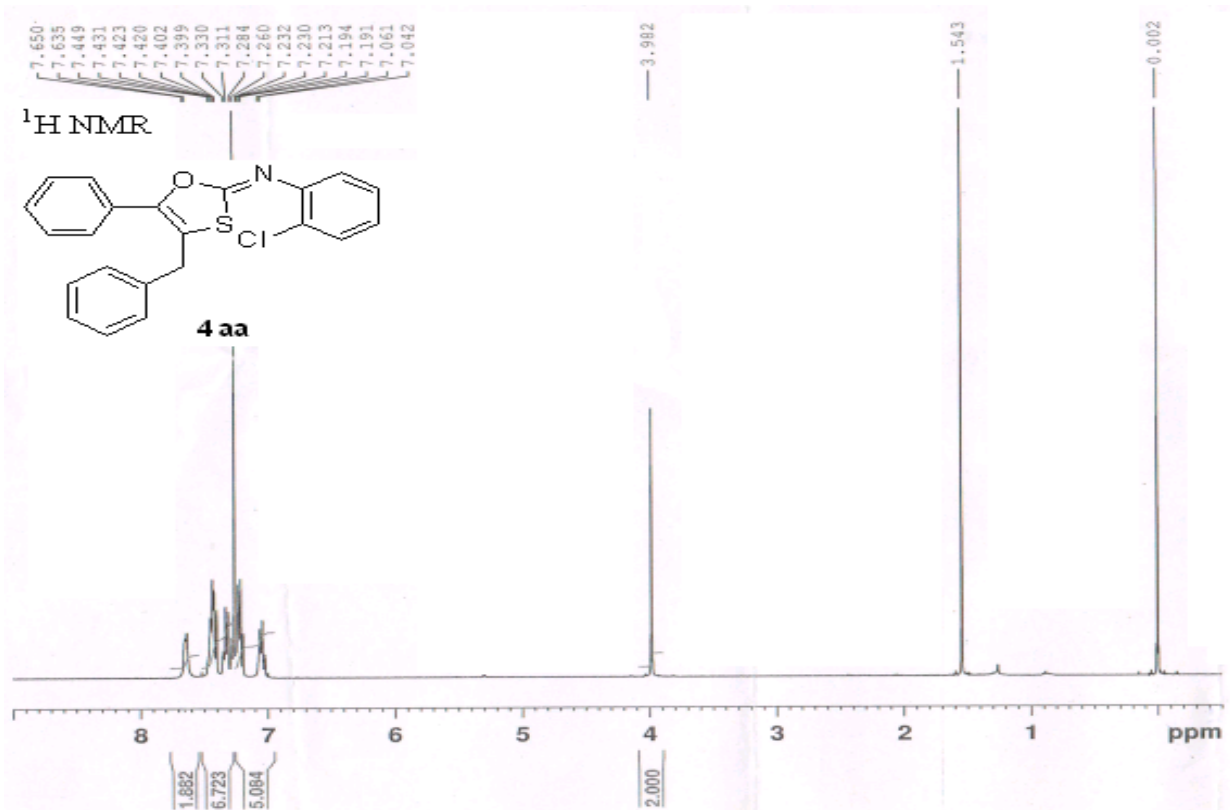
General : ^1H and ^{13}C NMR spectra were recorded at 300/ 400 (75/100) MHz spectrometers, respectively and the spectral data were reported in ppm relative to Tetramethylsilane (TMS) as the internal standard. Mass spectra were recorded by electron ionization. IR spectra were recorded on an FT-IR spectrometer, and major peaks were reported in cm^{-1} . TLC was performed by using commercially available 100-400 mesh silica gel plates (GF254). Unless and otherwise mentioned, the purchased chemicals were used without further purification.

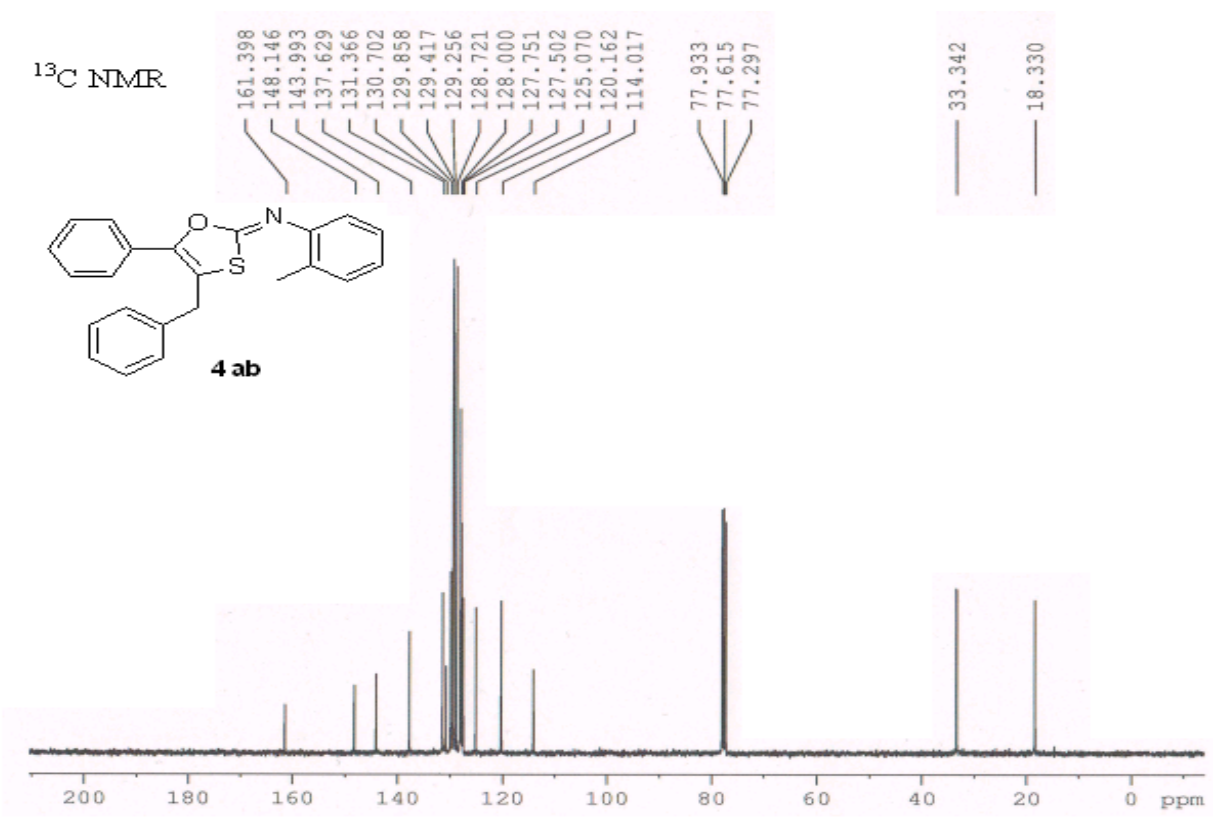
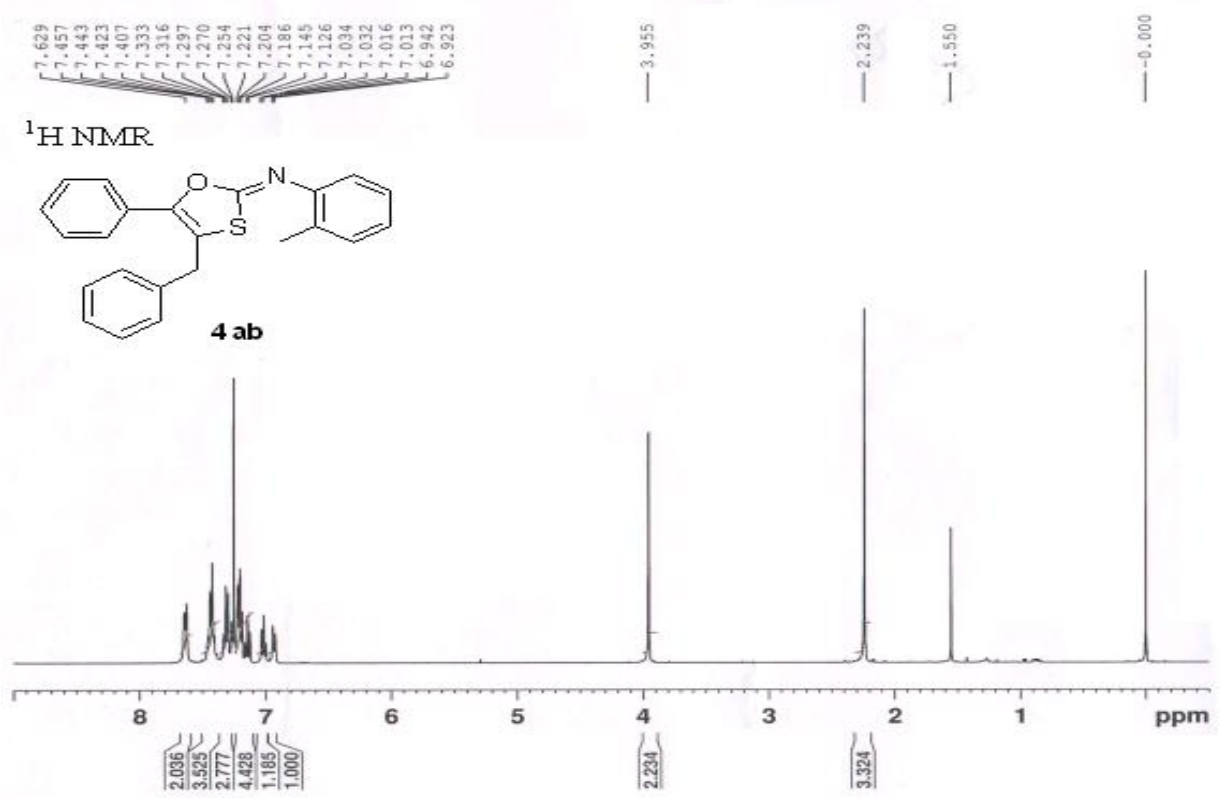
General procedure for the synthesis of secondary propargyl alcohols (1a-1m). To an oven dried multi-necked round bottom flask (RBF) were added corresponding phenyl acetylene (0.100mol) and tetrahydrofuran (THF), sequentially under nitrogen atmosphere. The reaction mixture was cooled to $-70\text{ }^\circ\text{C}$. 2.0M solution of *n*-BuLi in hexane (0.090mol) at $-70\text{ }^\circ\text{C}$ was added and the reaction mixture was stirred at the same temperature for about 20 minutes. Then a solution of corresponding benzaldehyde (0.067mol) in tetrahydrofuran at $-70\text{ }^\circ\text{C}$ was added to the reaction mixture which was stirred at the same temperature for about 10 minutes. The progress of the reaction was monitored by thin layer chromatogram (TLC) and at the completion of the reaction the reaction mixture was quenched with aqueous NH_4Cl solution and then extracted with ethyl acetate. The organic layer washed with aqueous NH_4Cl solution, dried over Na_2SO_4 , filtered and concentrated at reduced pressure to give a light brown liquid. The crude sample was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give the desired secondary propargyl alcohols.

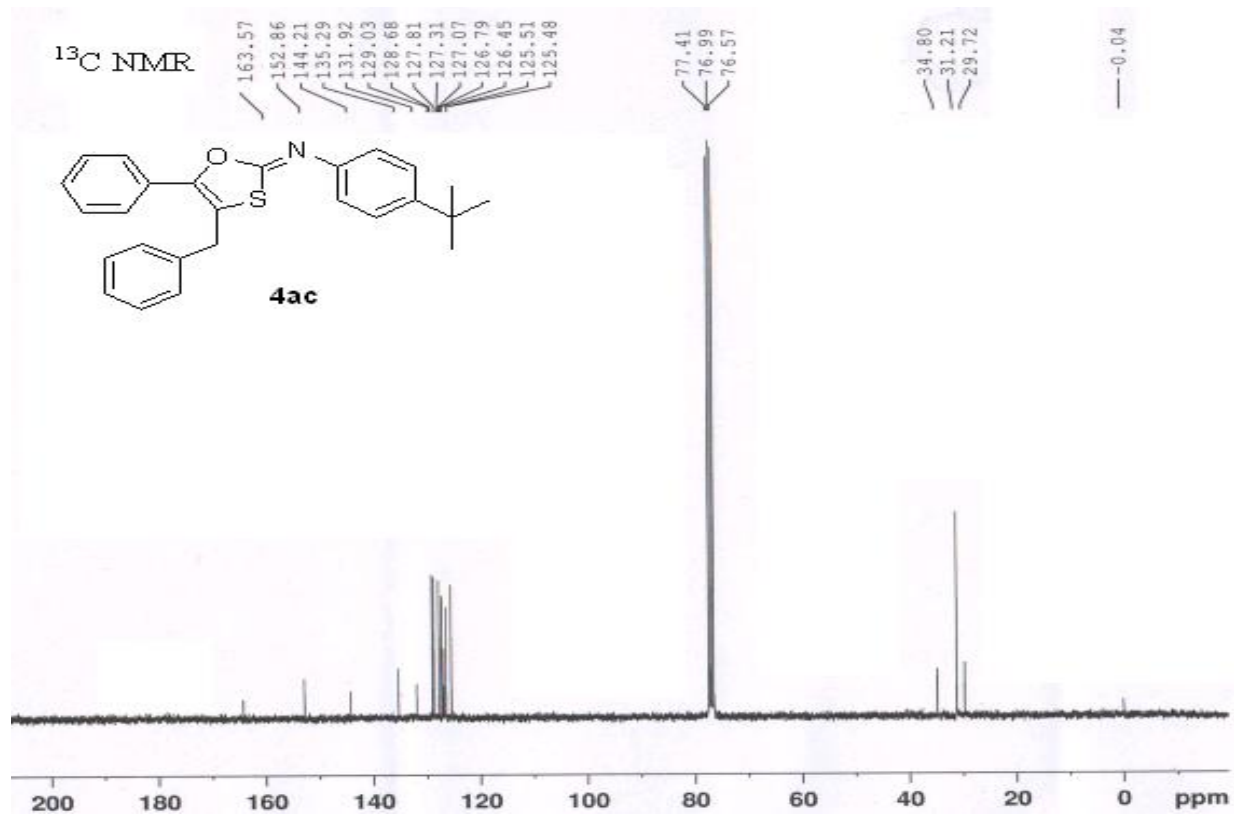
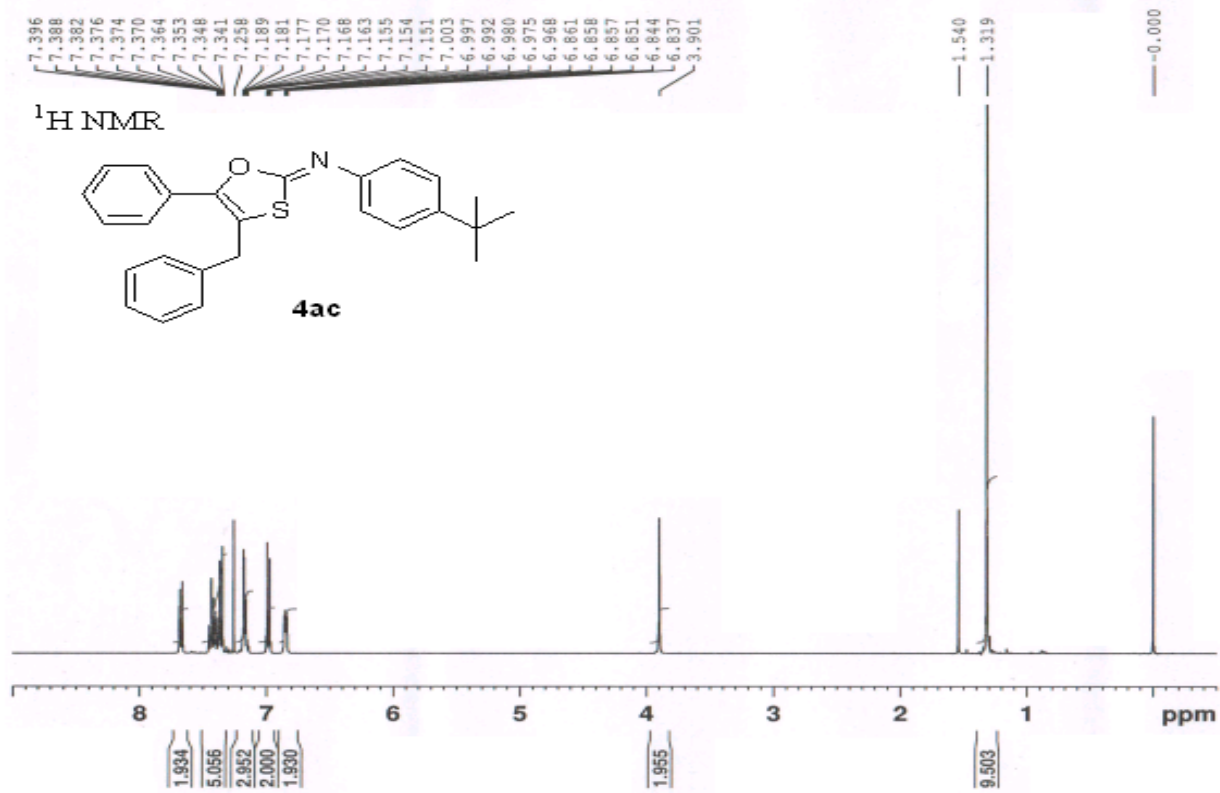
General procedure for the synthesis of primary propargyl alcohols (1n-1u). To an oven dried multi-necked RBF were added corresponding iodobenzene (0.057mol), prop-2-yn-1-ol (0.085mol), acetonitrile (ACN), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2.844mmol), CuI (2.844 mmol) and triethyl amine (0.142mol) were successively added under nitrogen atmosphere at room temperature. The reaction mixture was heated to $80\text{ }^\circ\text{C}$ and stirred at the same temperature for 2 h. Completion of the reaction was asserted by TLC and then the reaction mixture was quenched with aqueous ammonia solution. The reaction mixture was

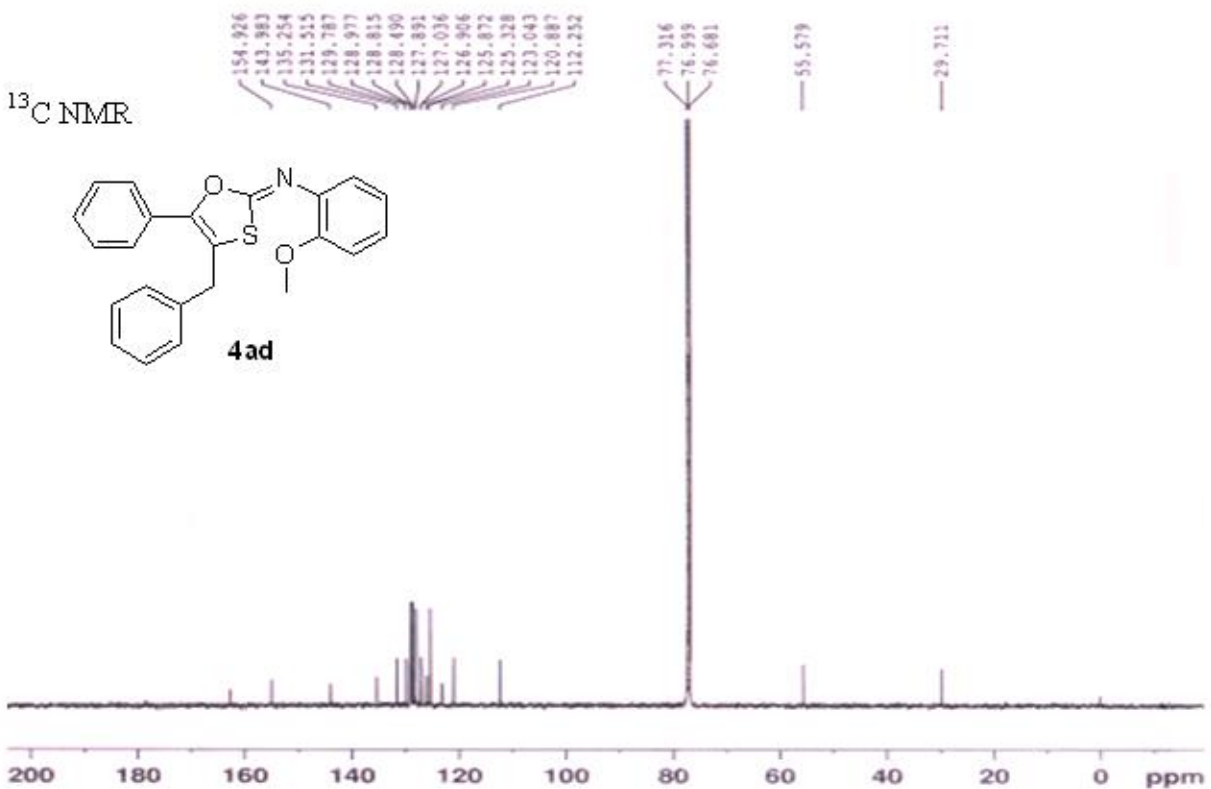
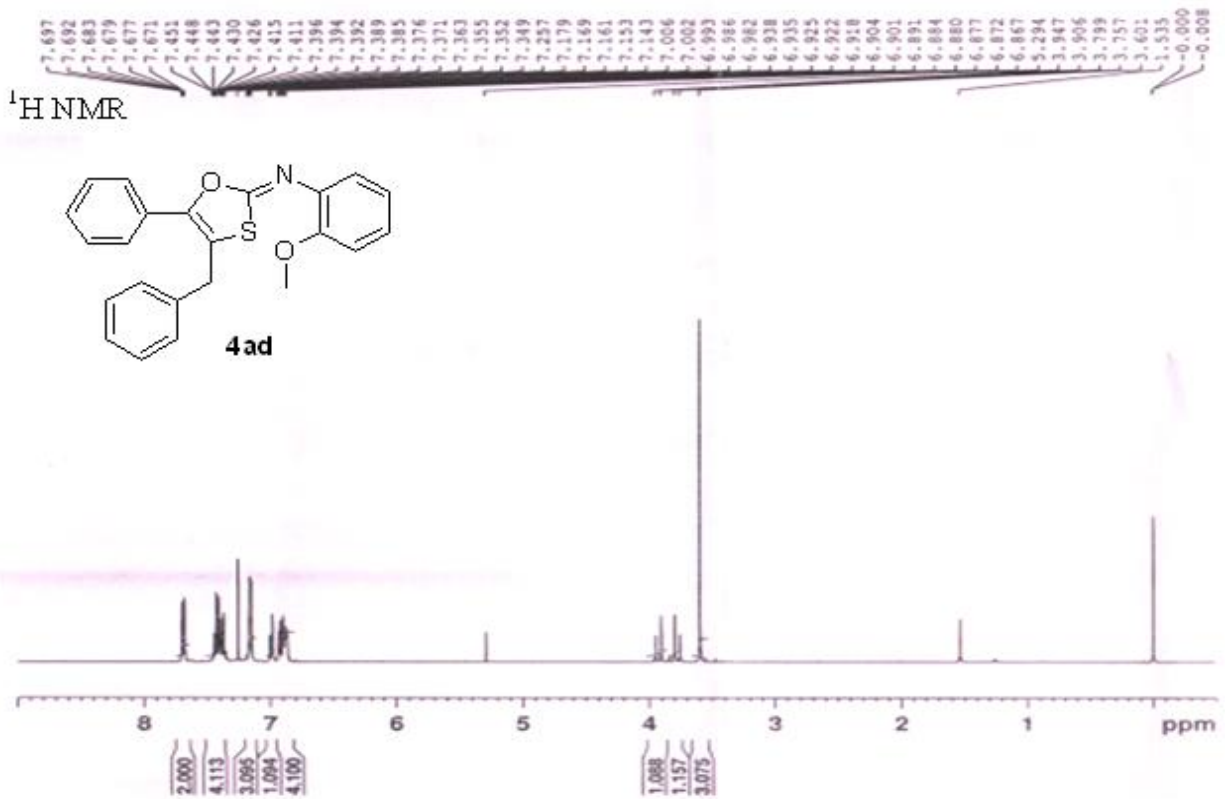
extracted with ethyl acetate, and the organic layer washed with brine solution, dried over Na_2SO_4 , filtered and concentrated at reduced pressure to give a dark brown liquid. The crude sample was purified by chromatography on silica gel (petroleum ether/ ethyl acetate = 1/1) to give the desired primary propargyl alcohols.

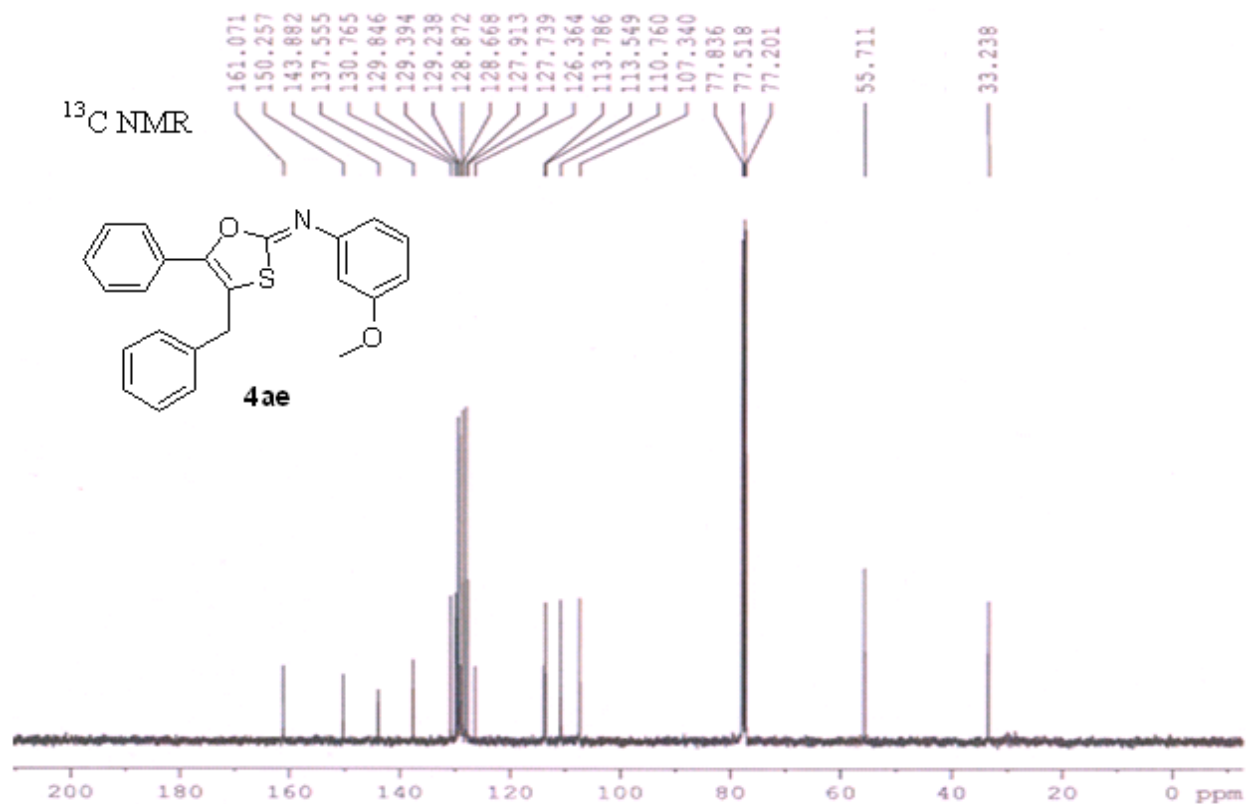
NMR spectra

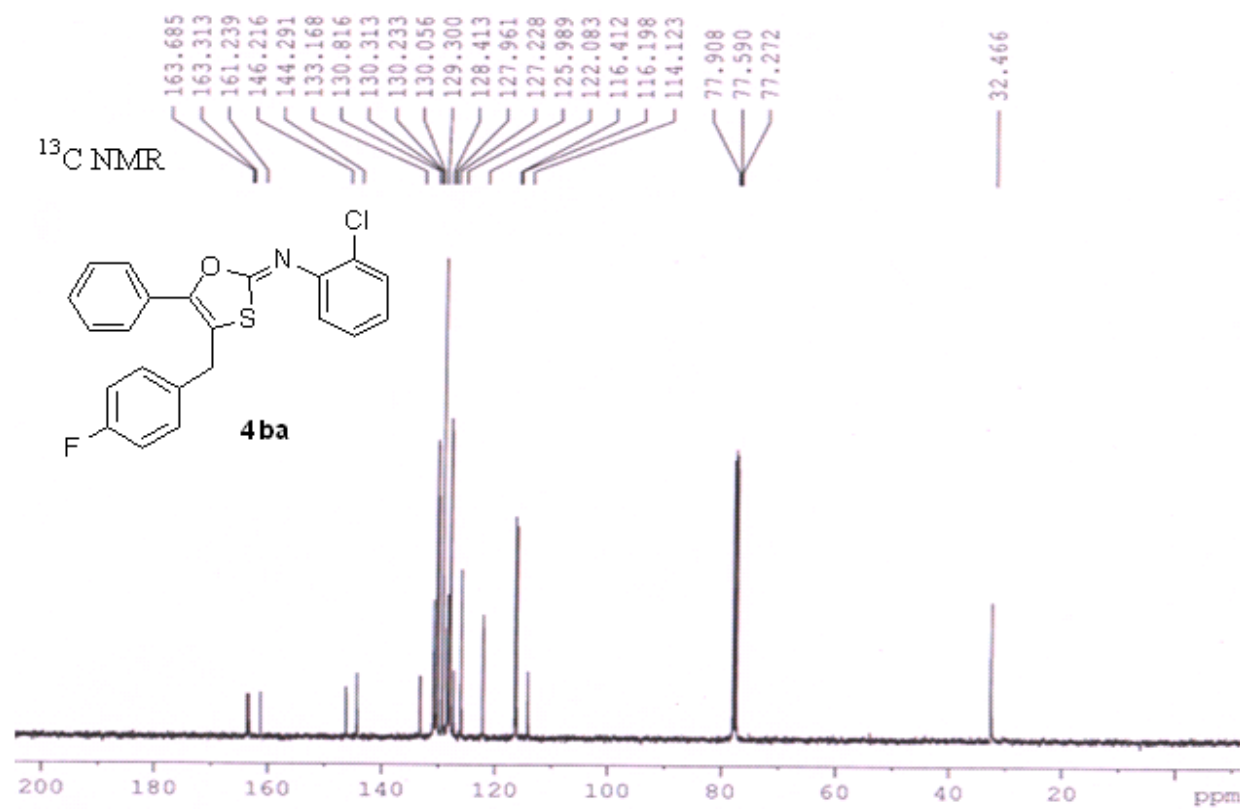
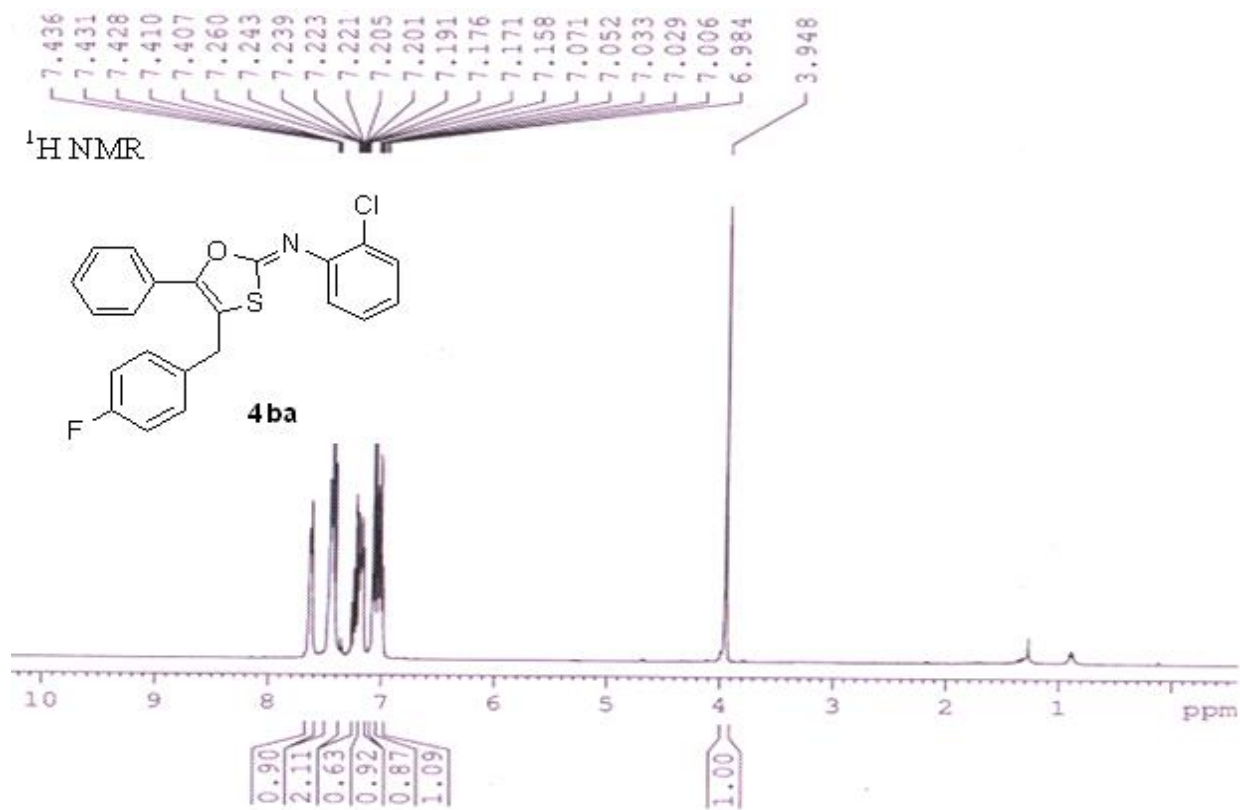


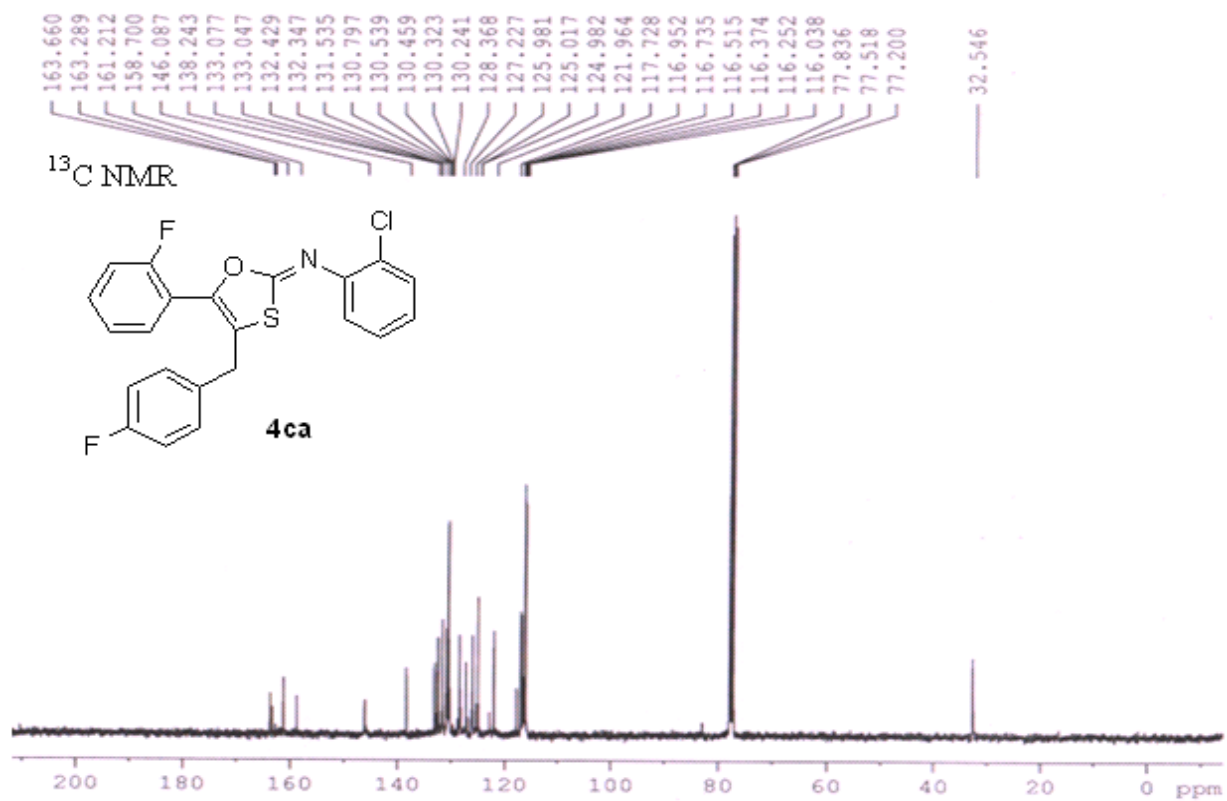
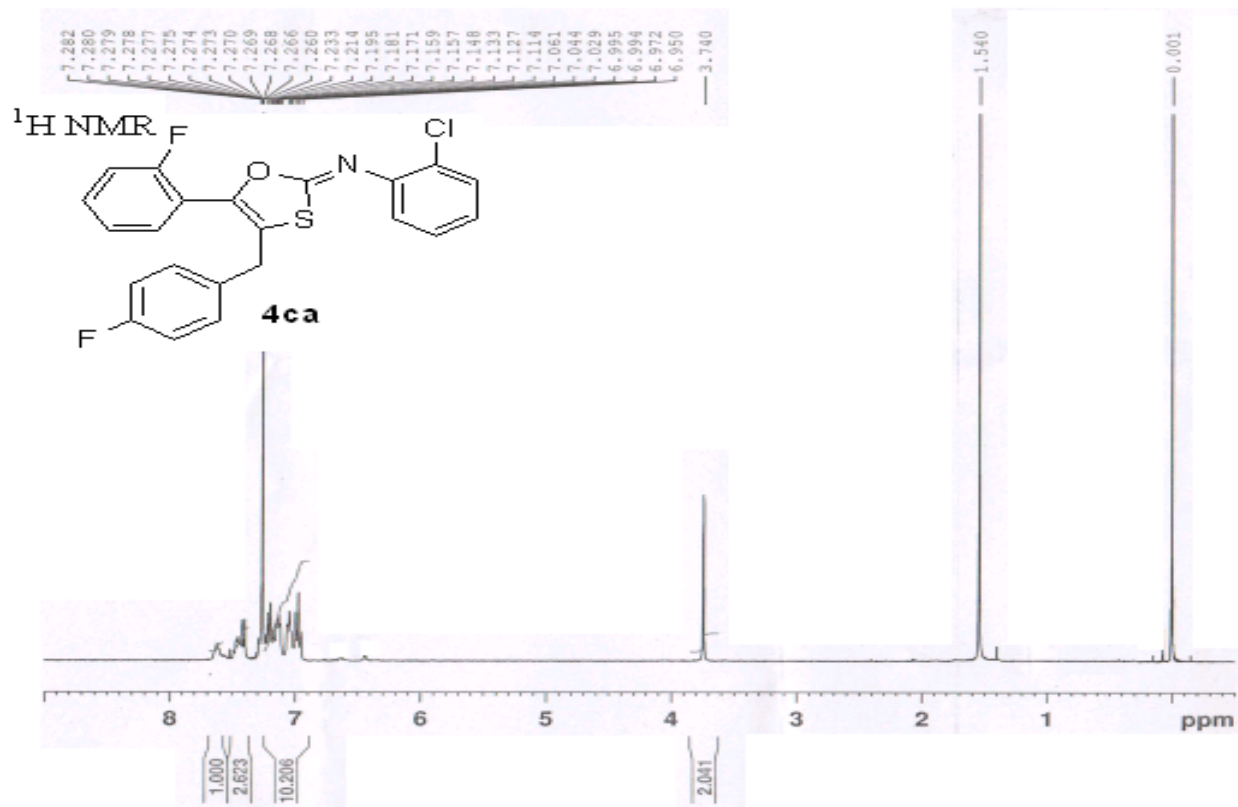


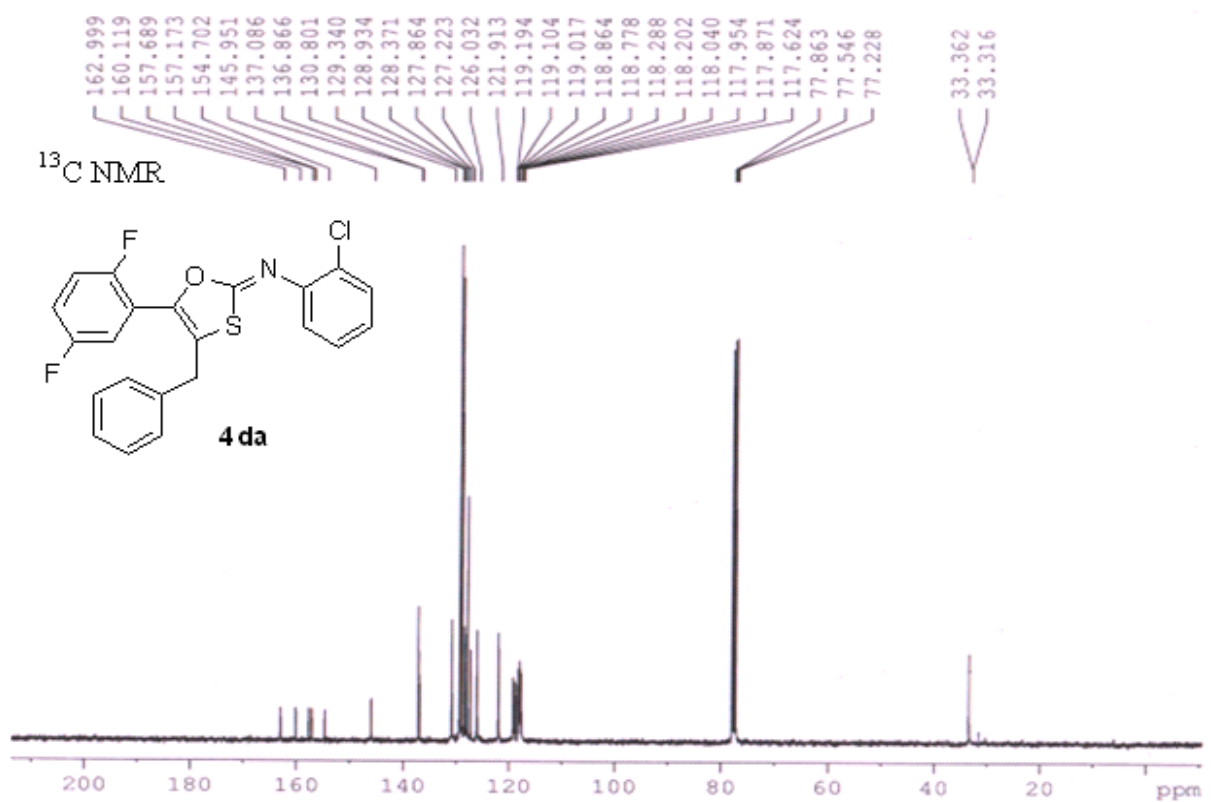
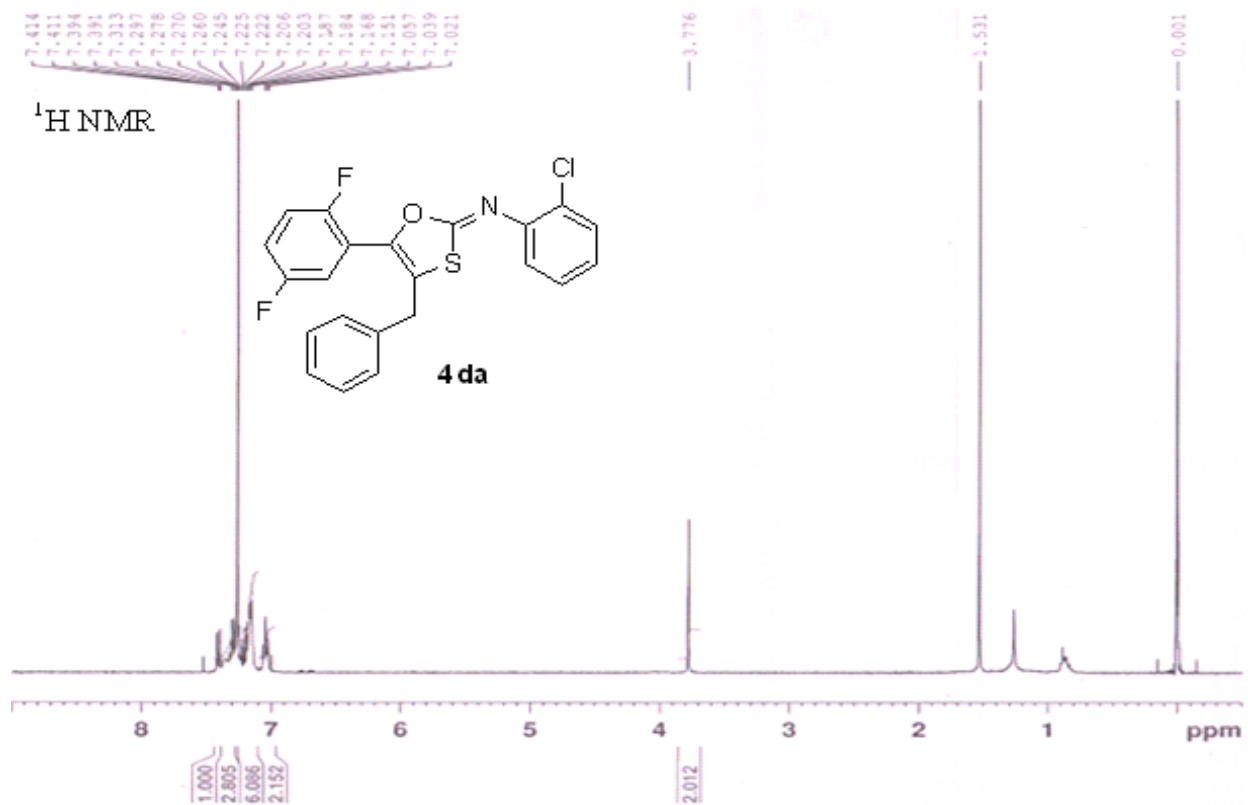


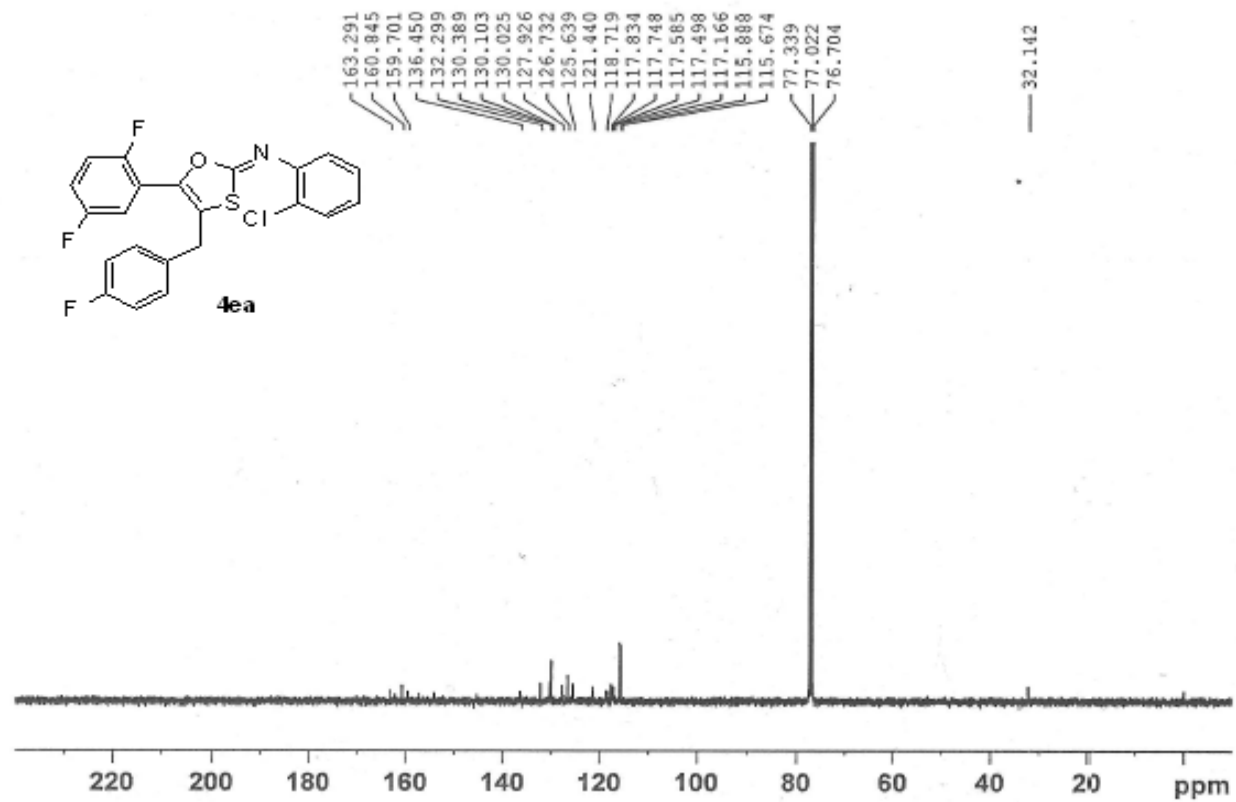
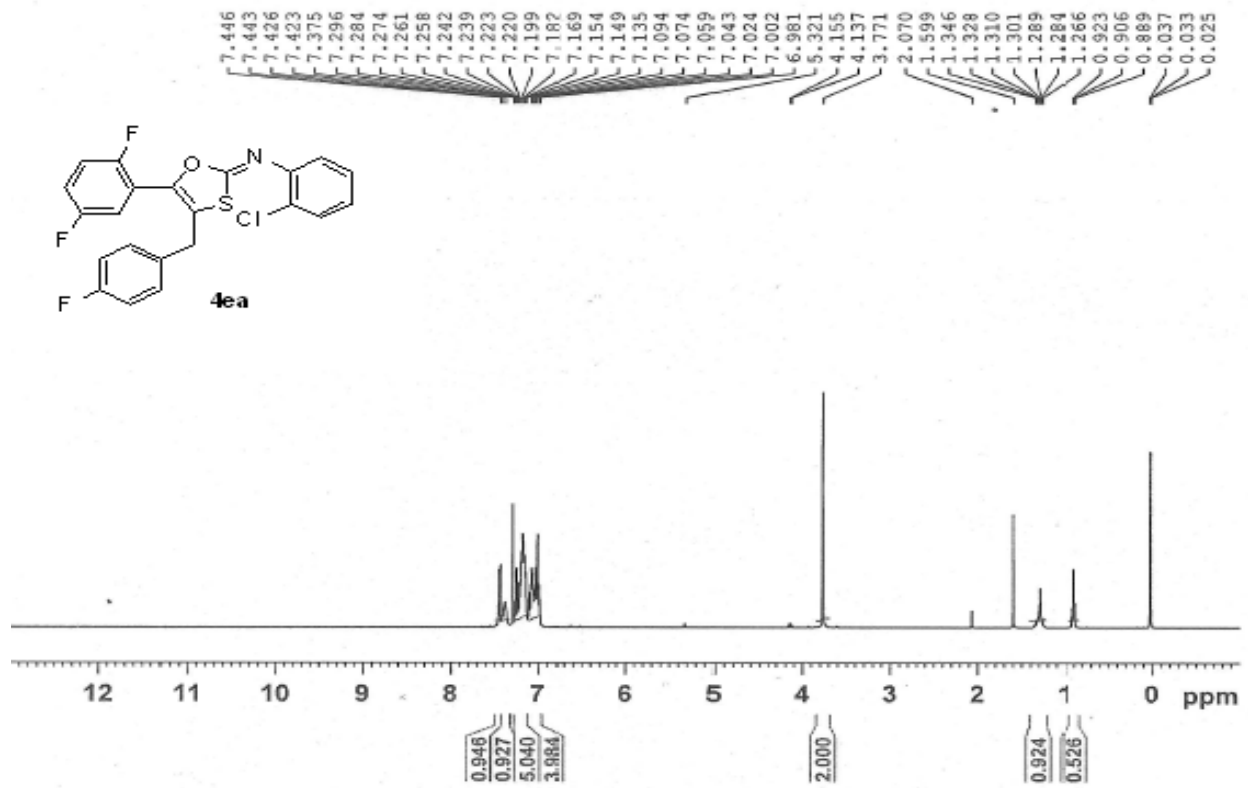


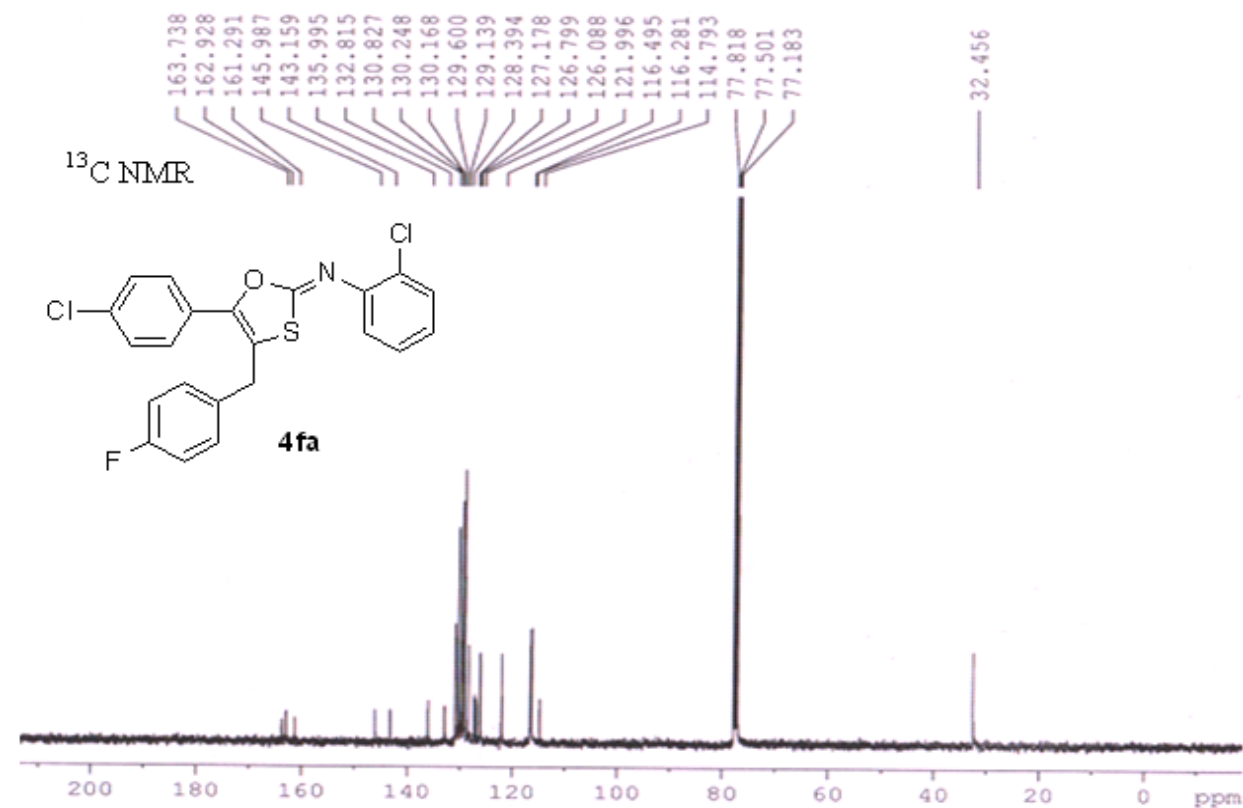
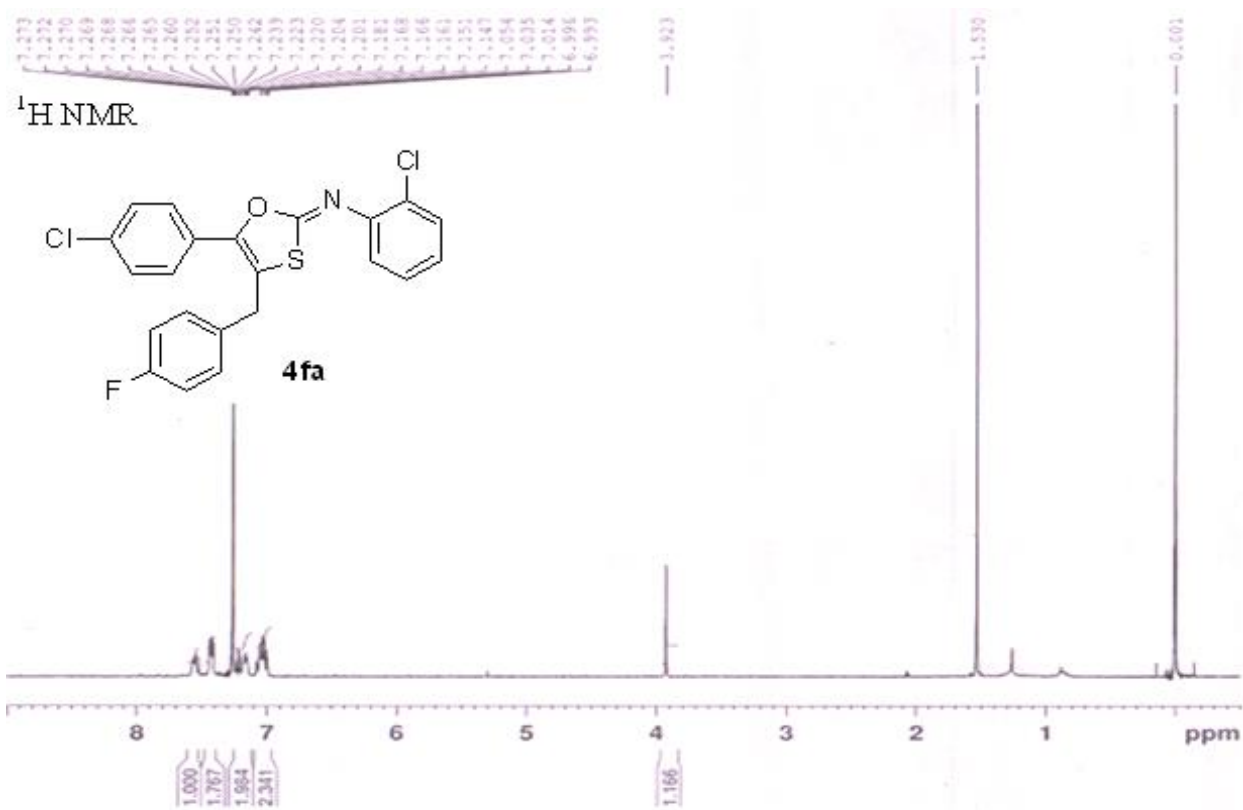


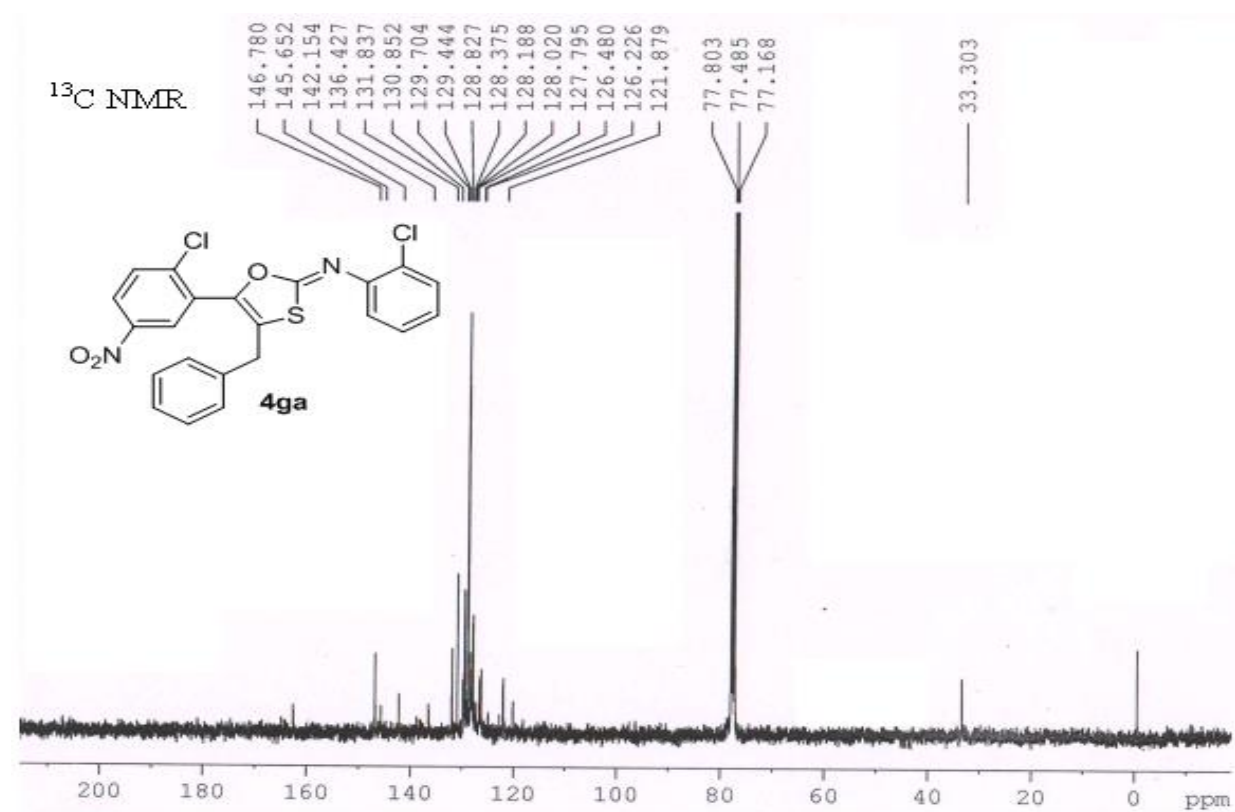
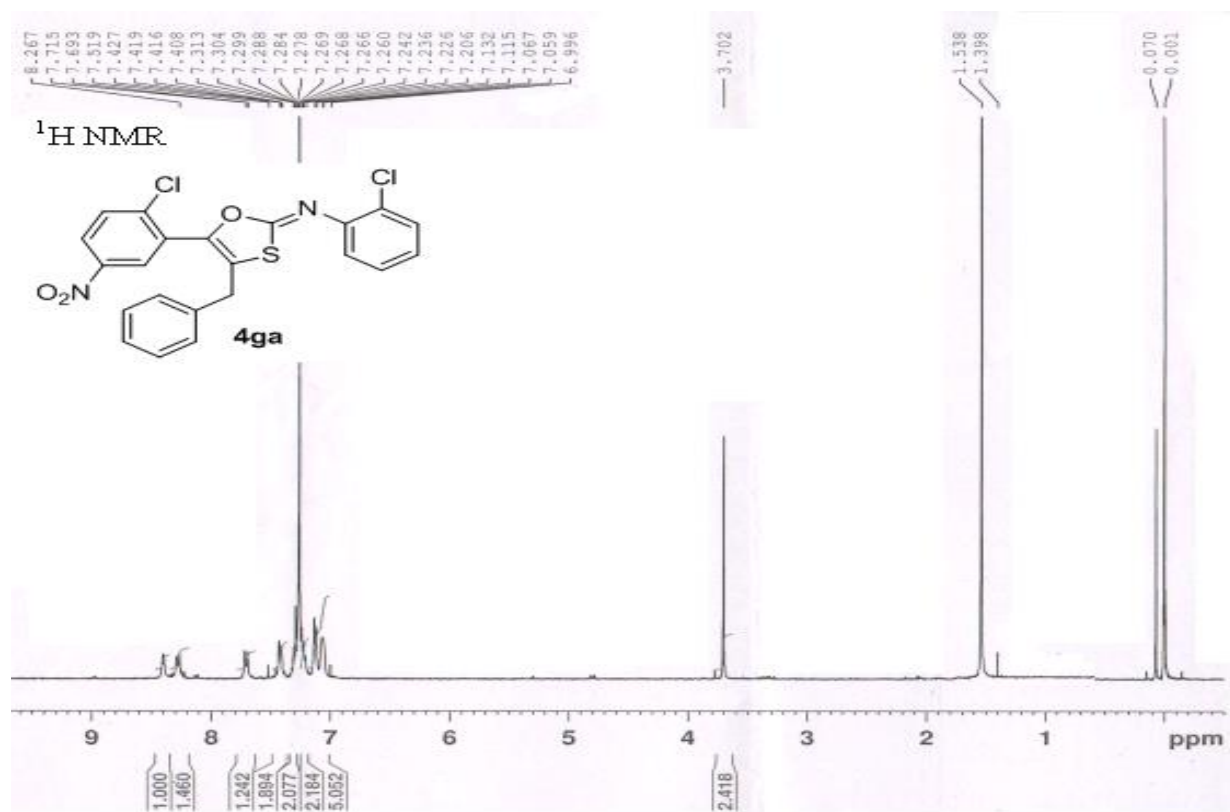


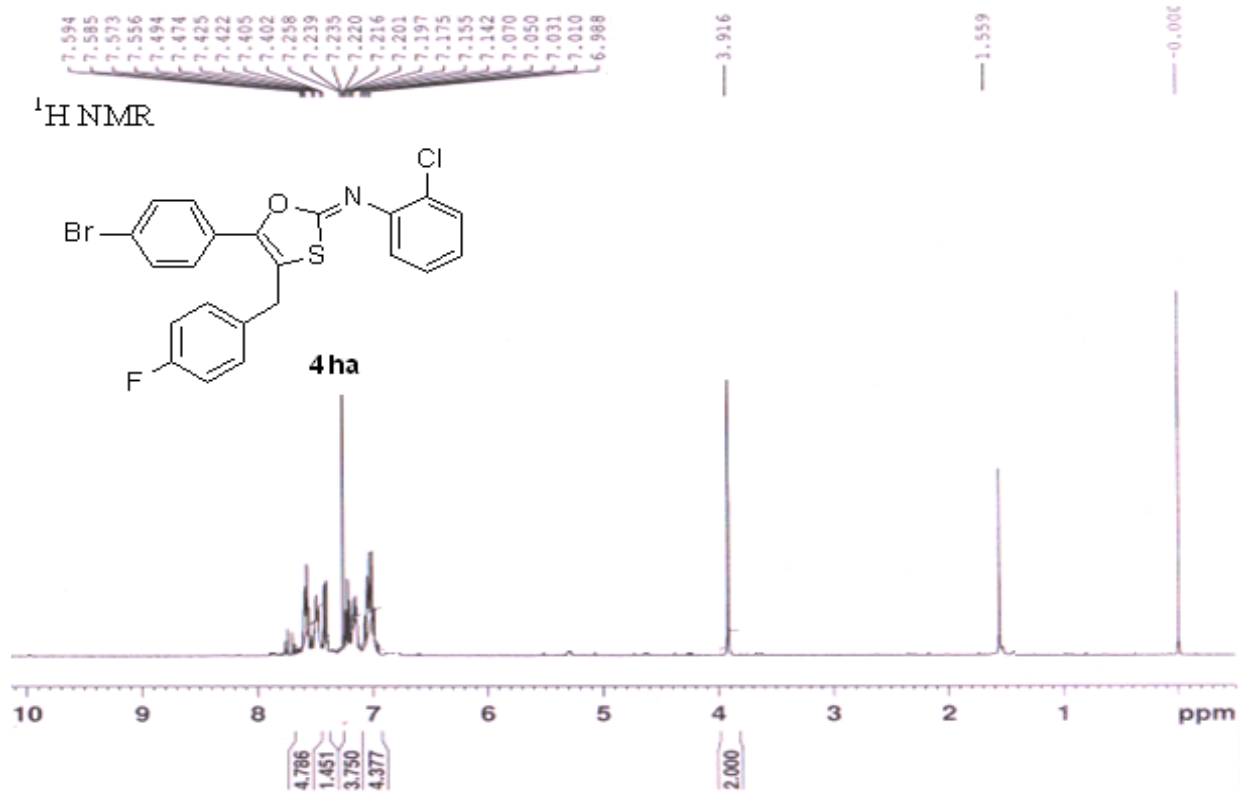


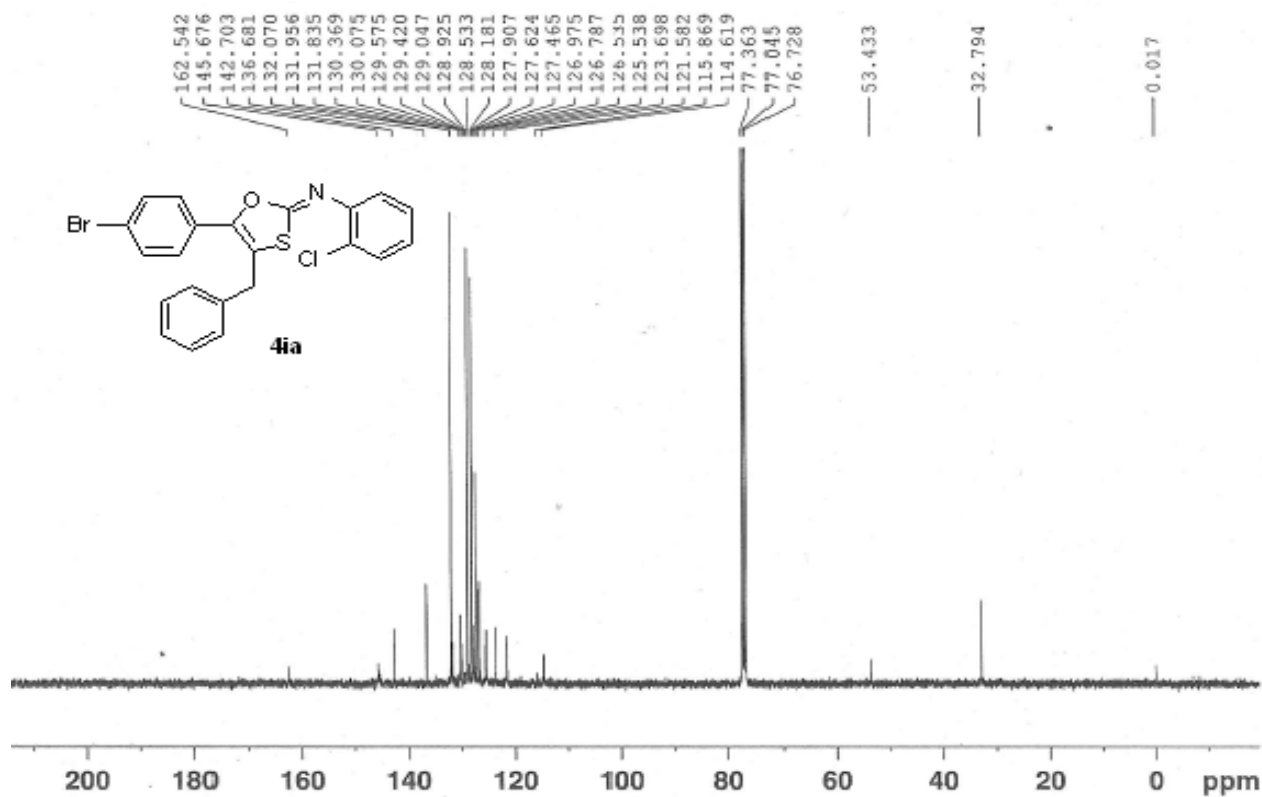
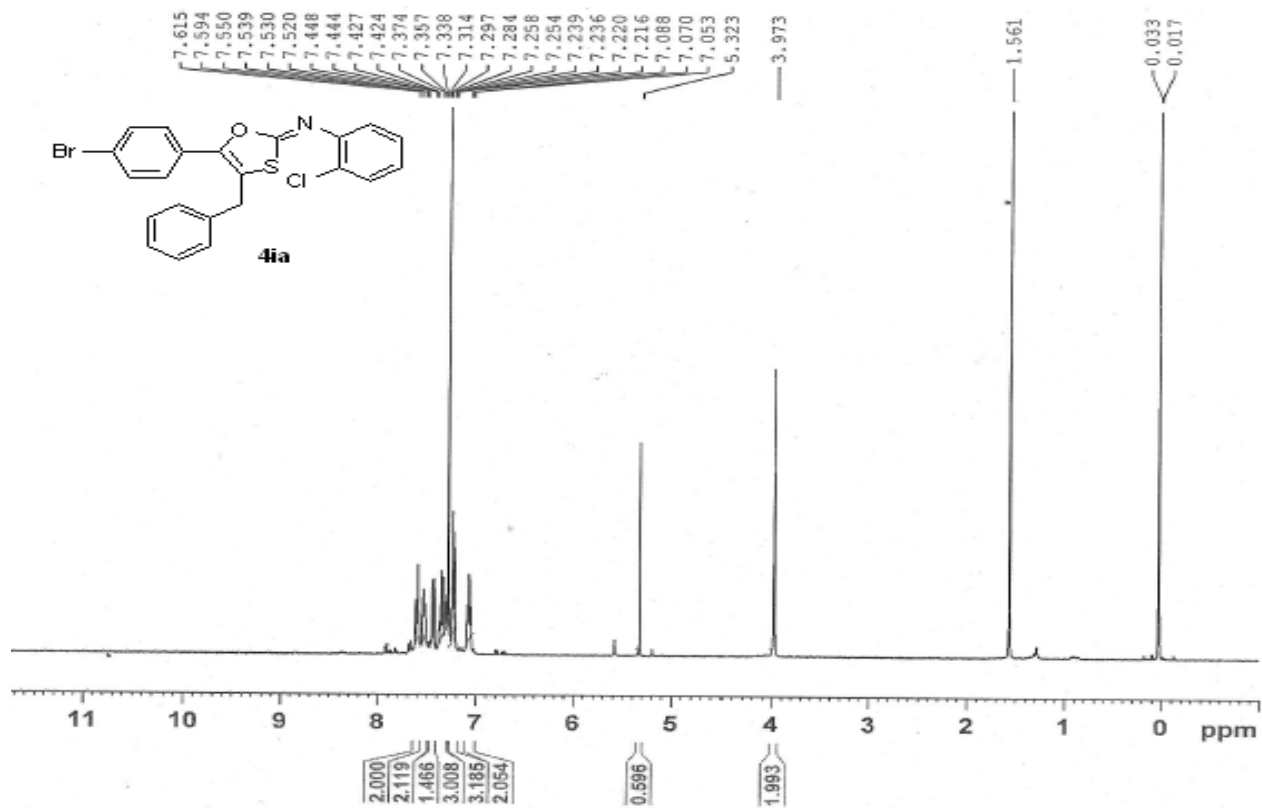


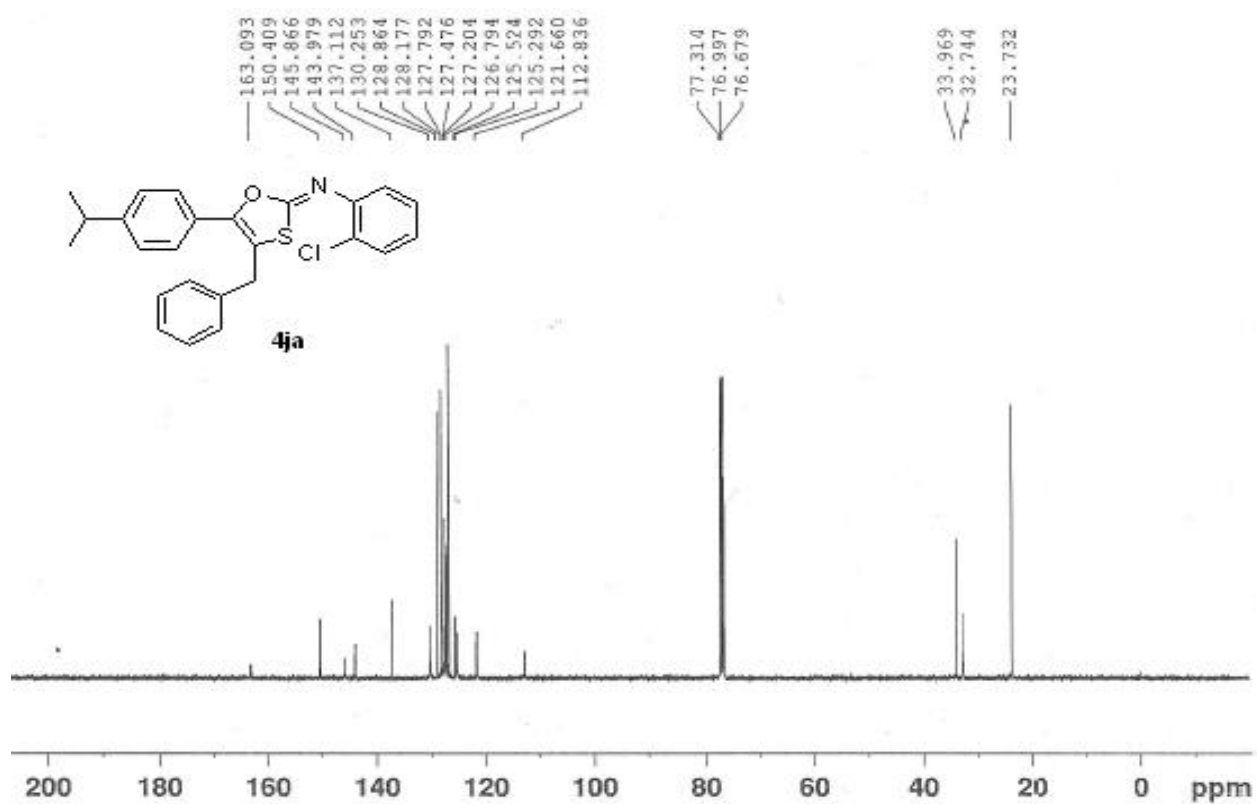
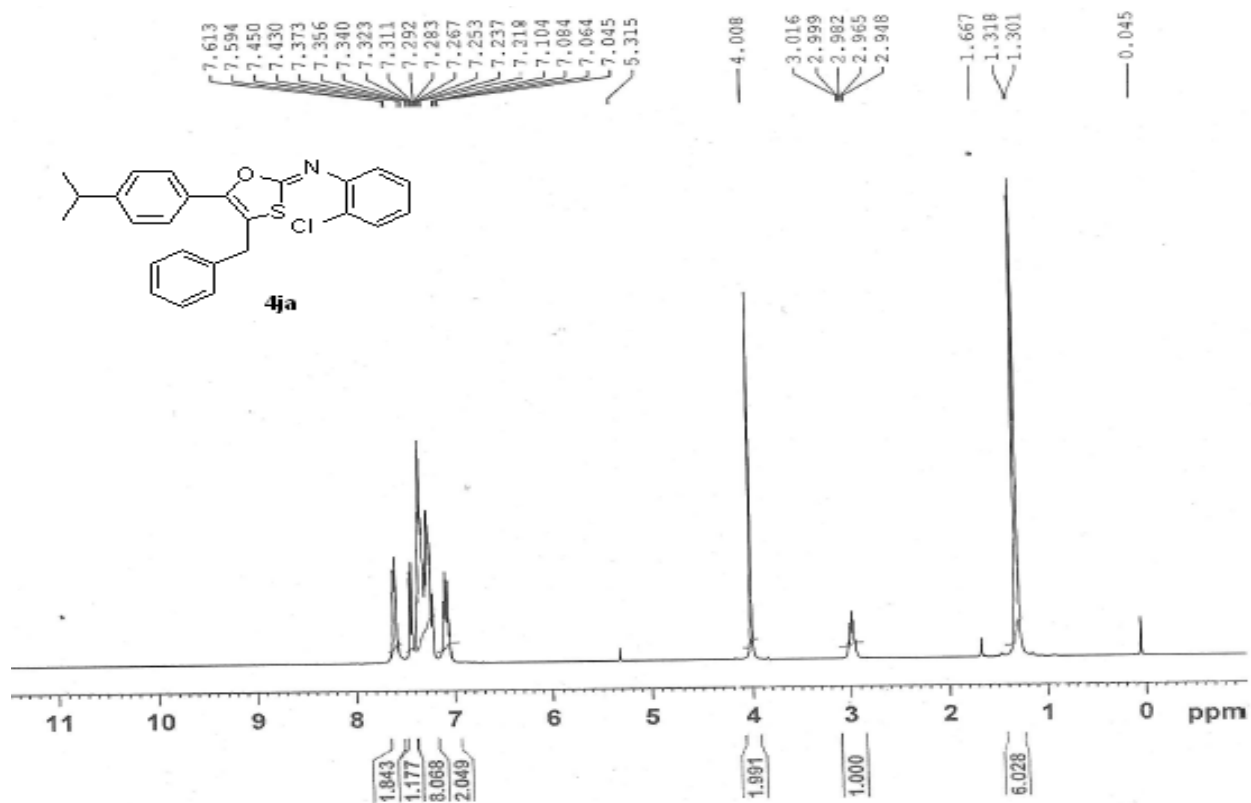


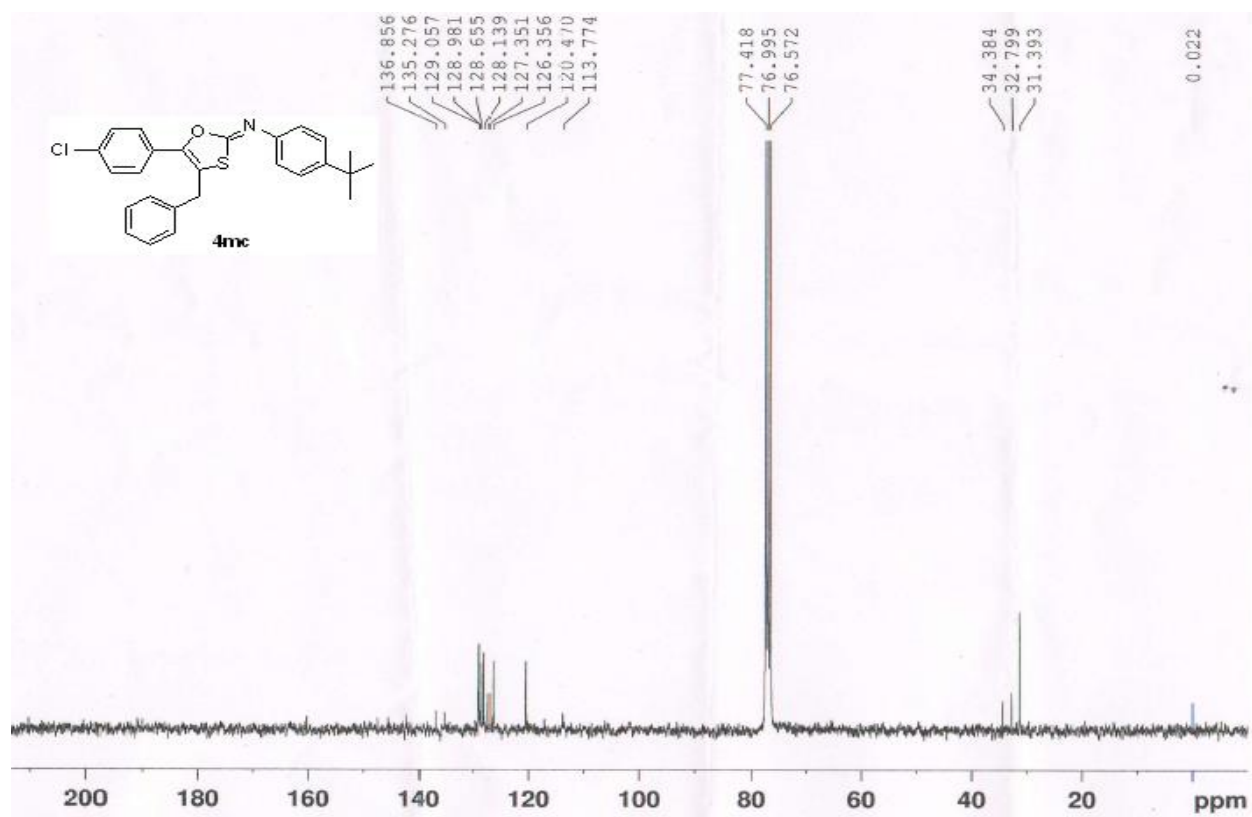
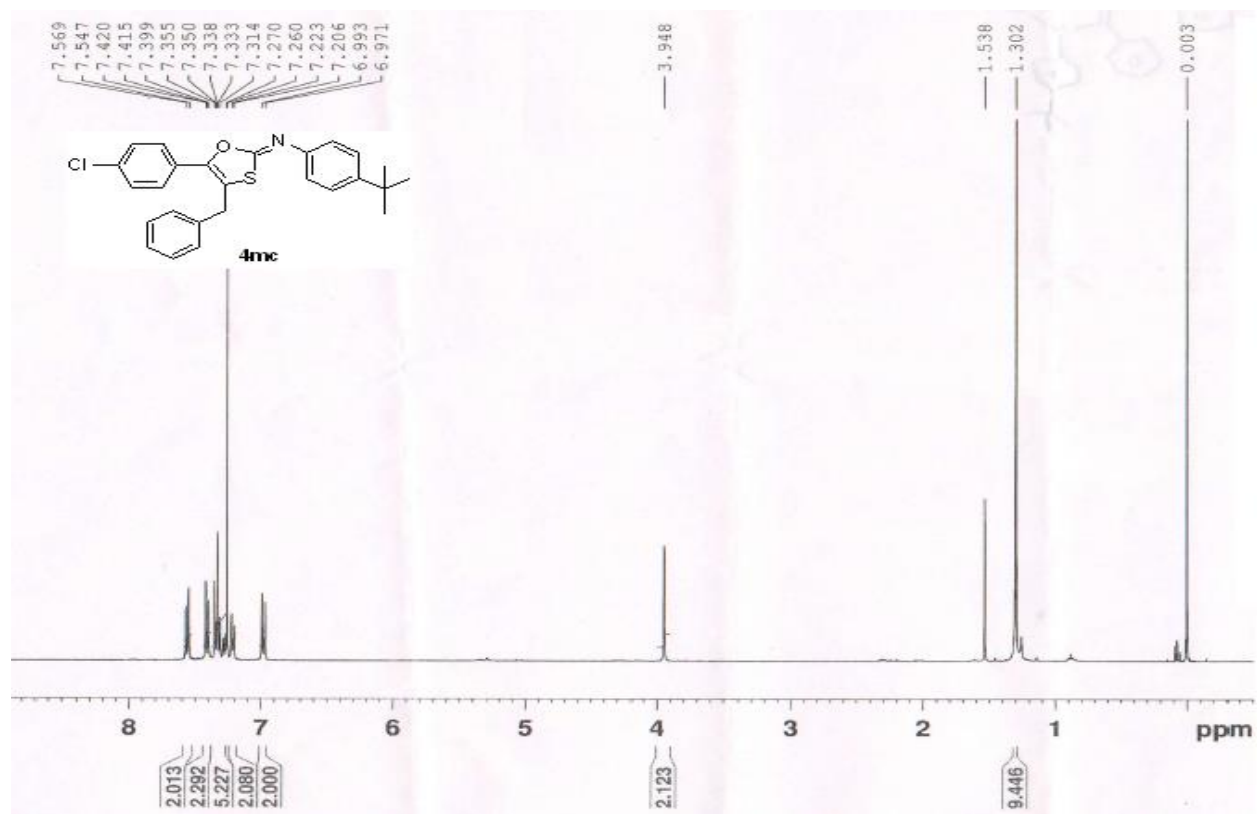


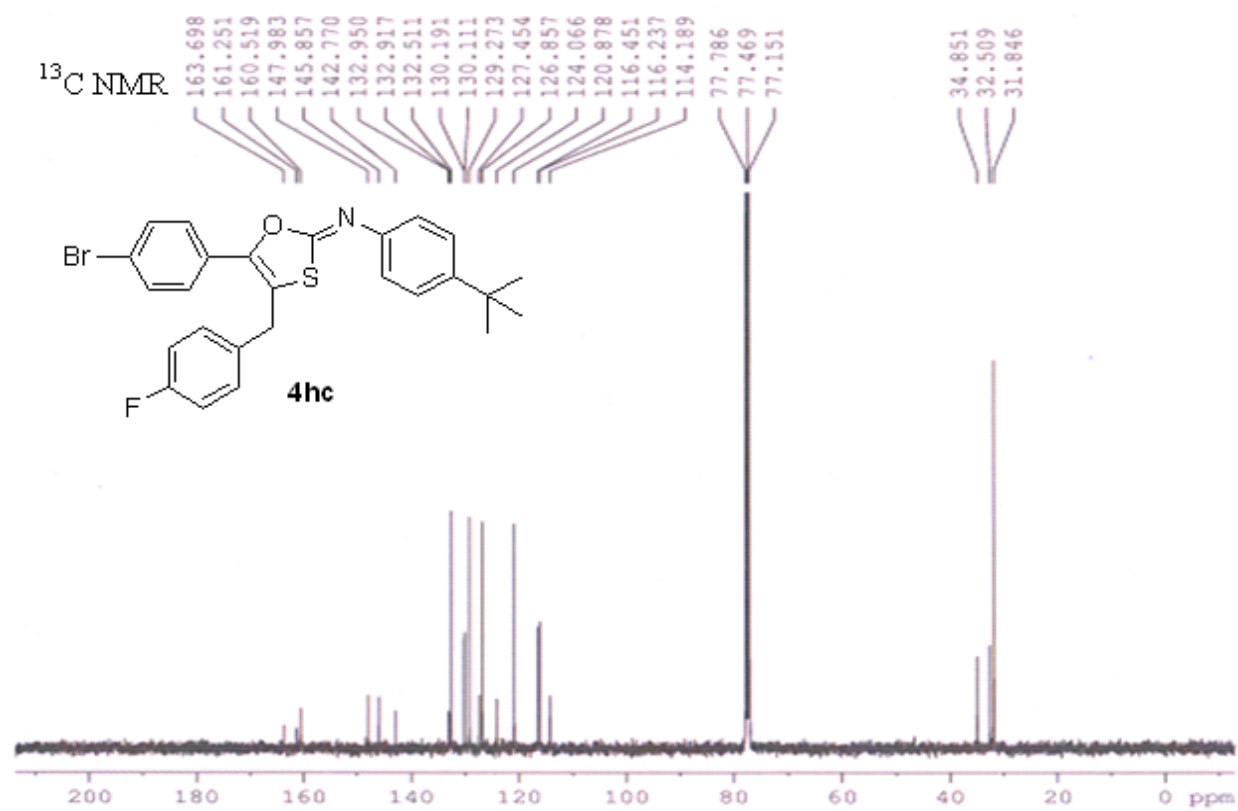
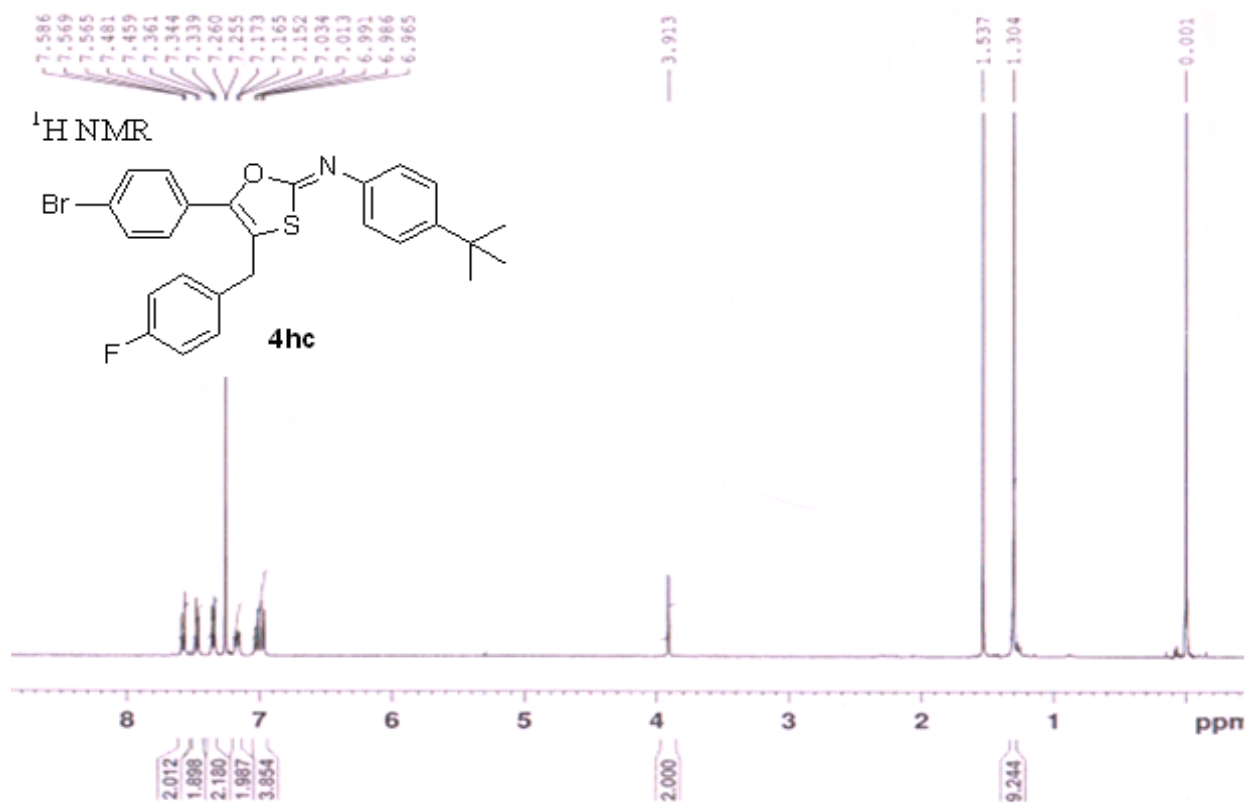


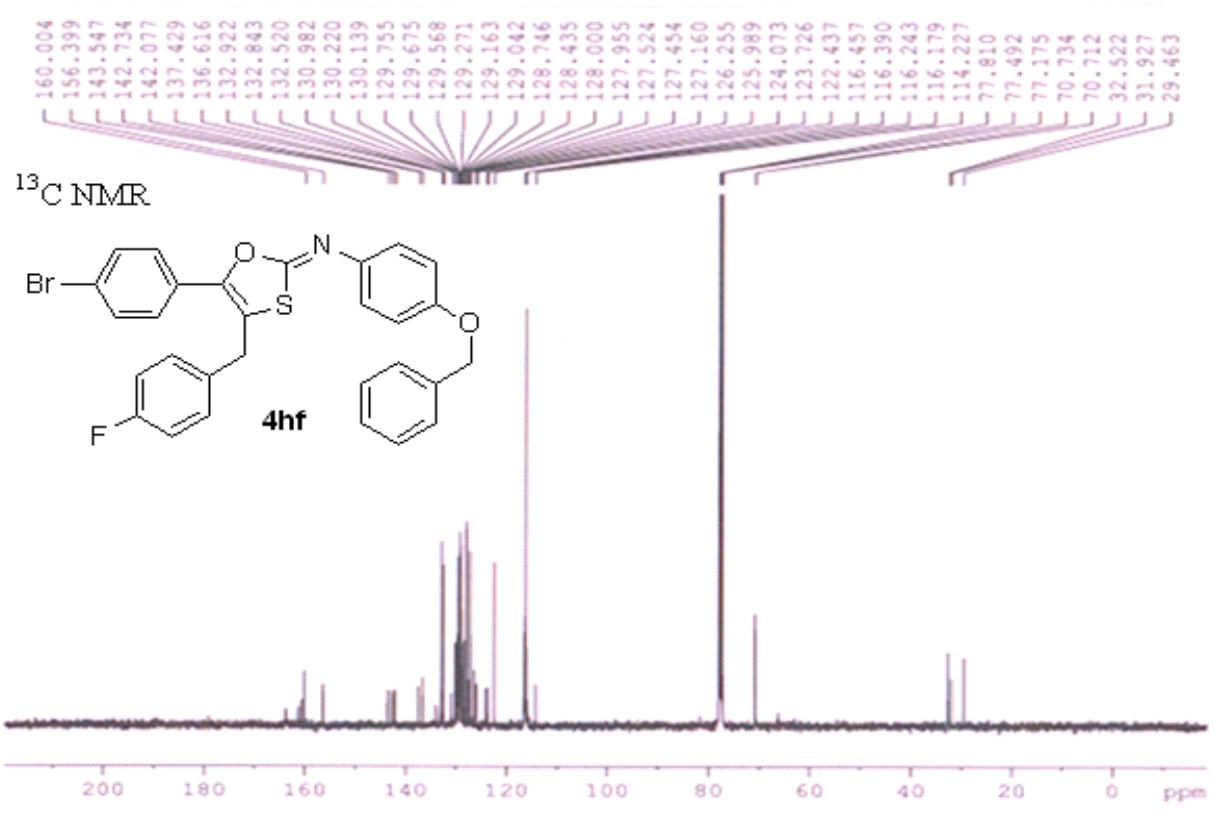
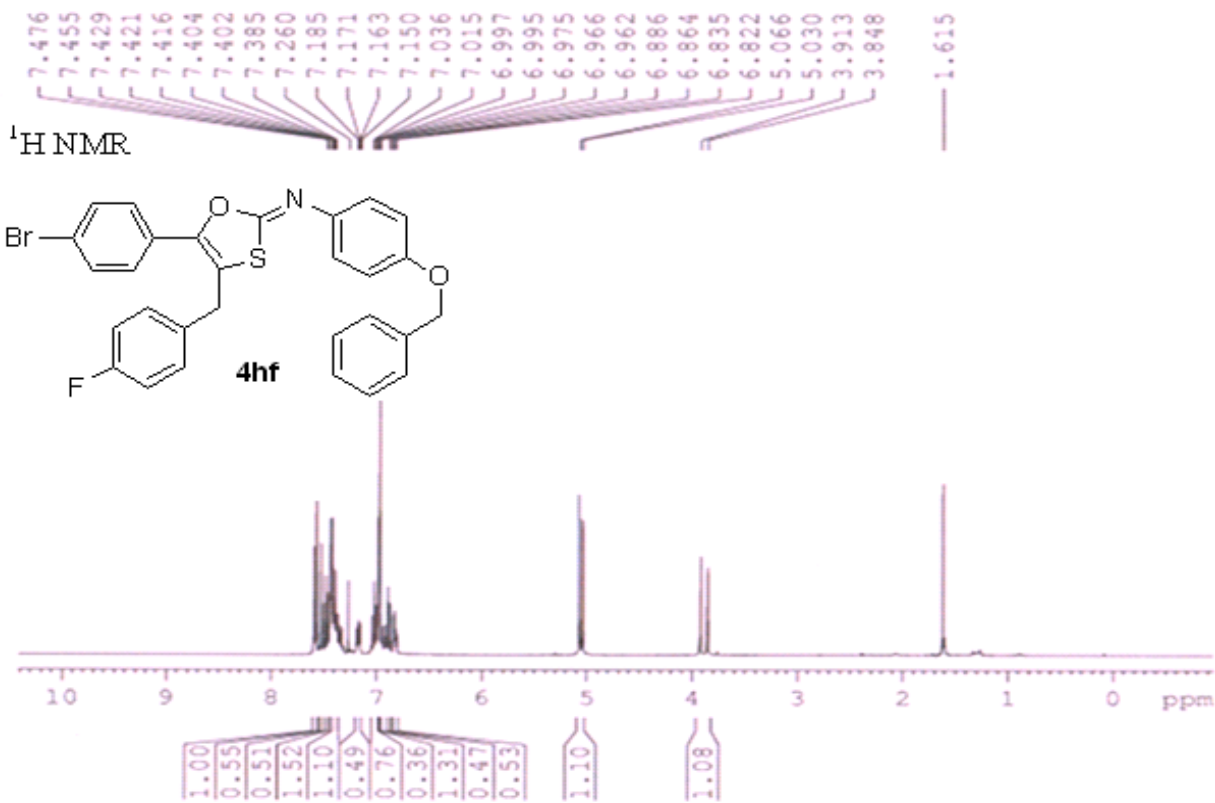


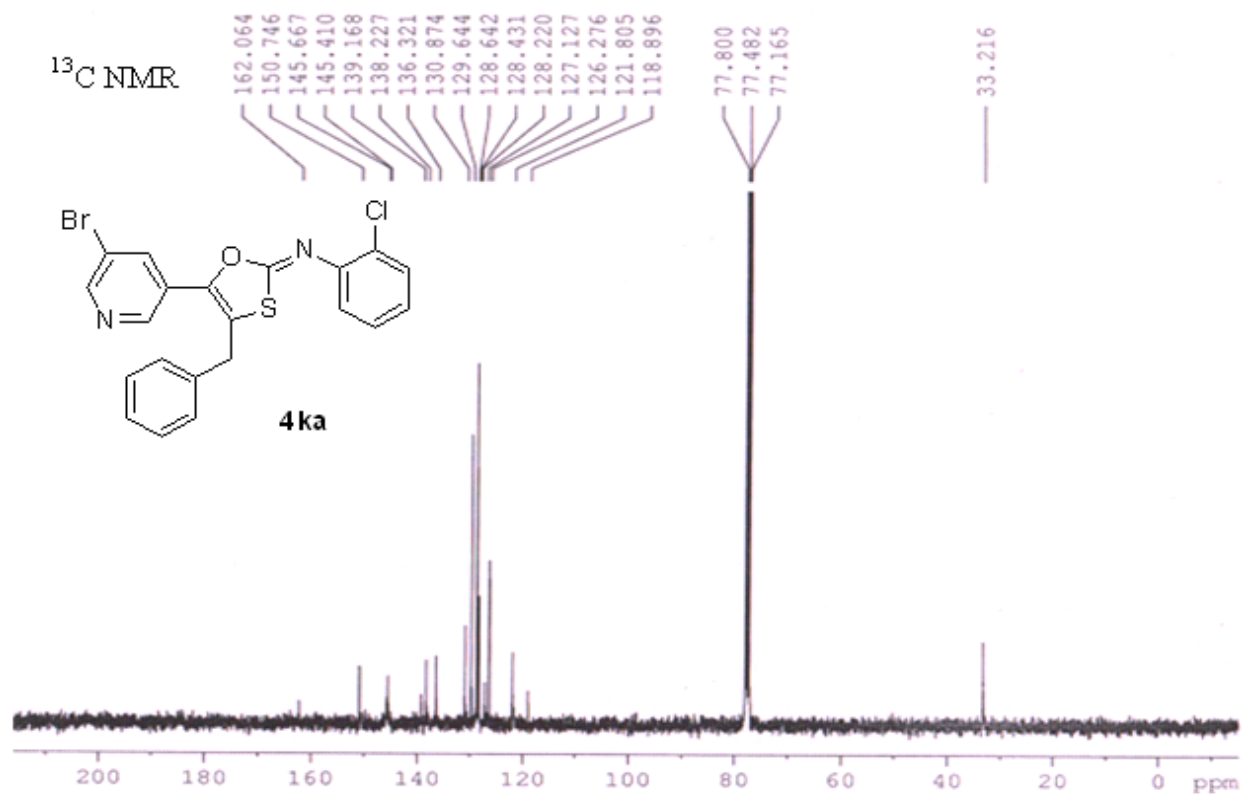
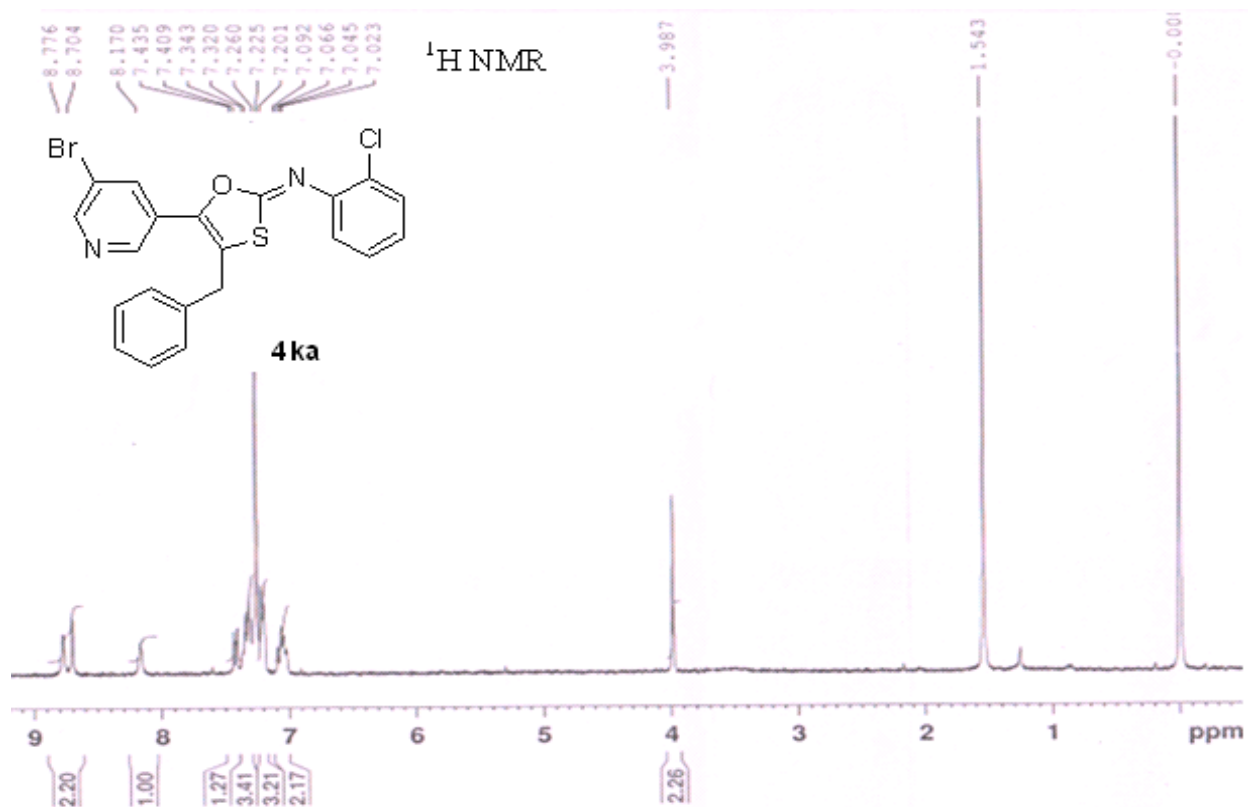


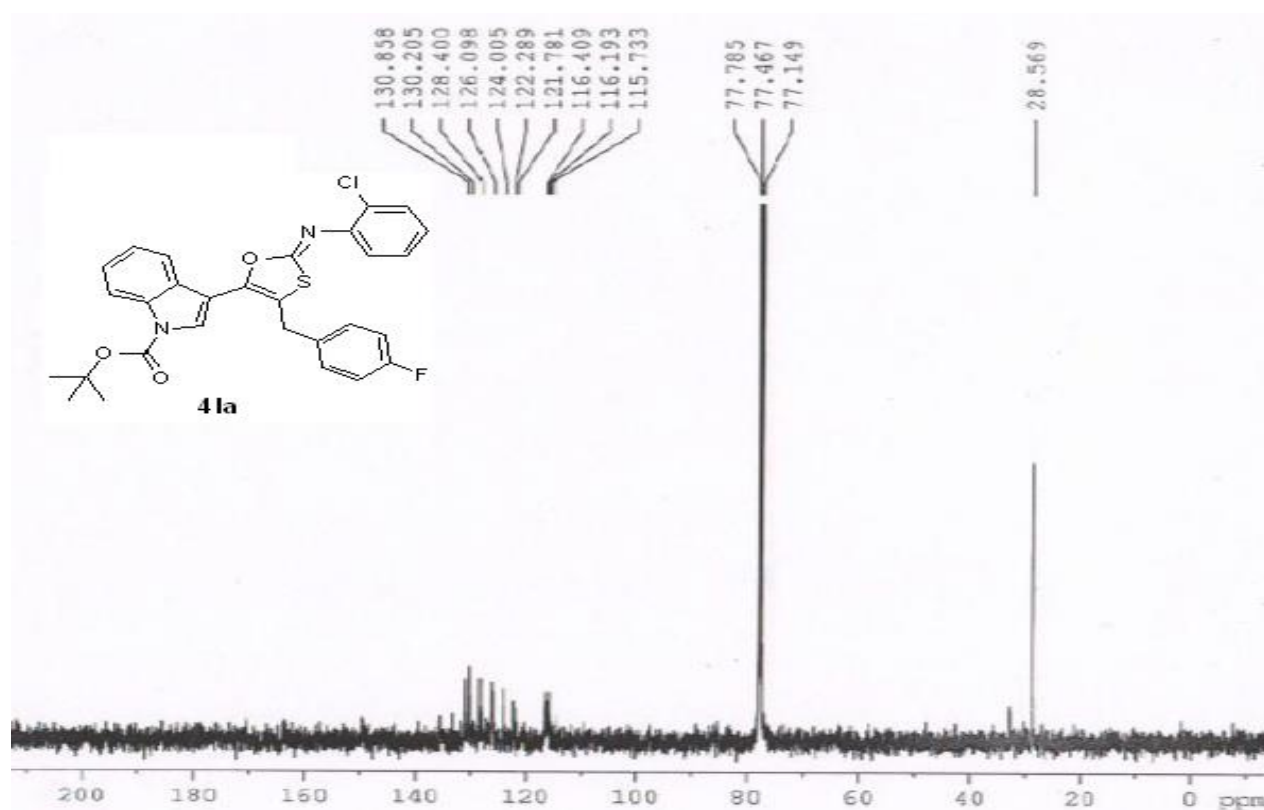
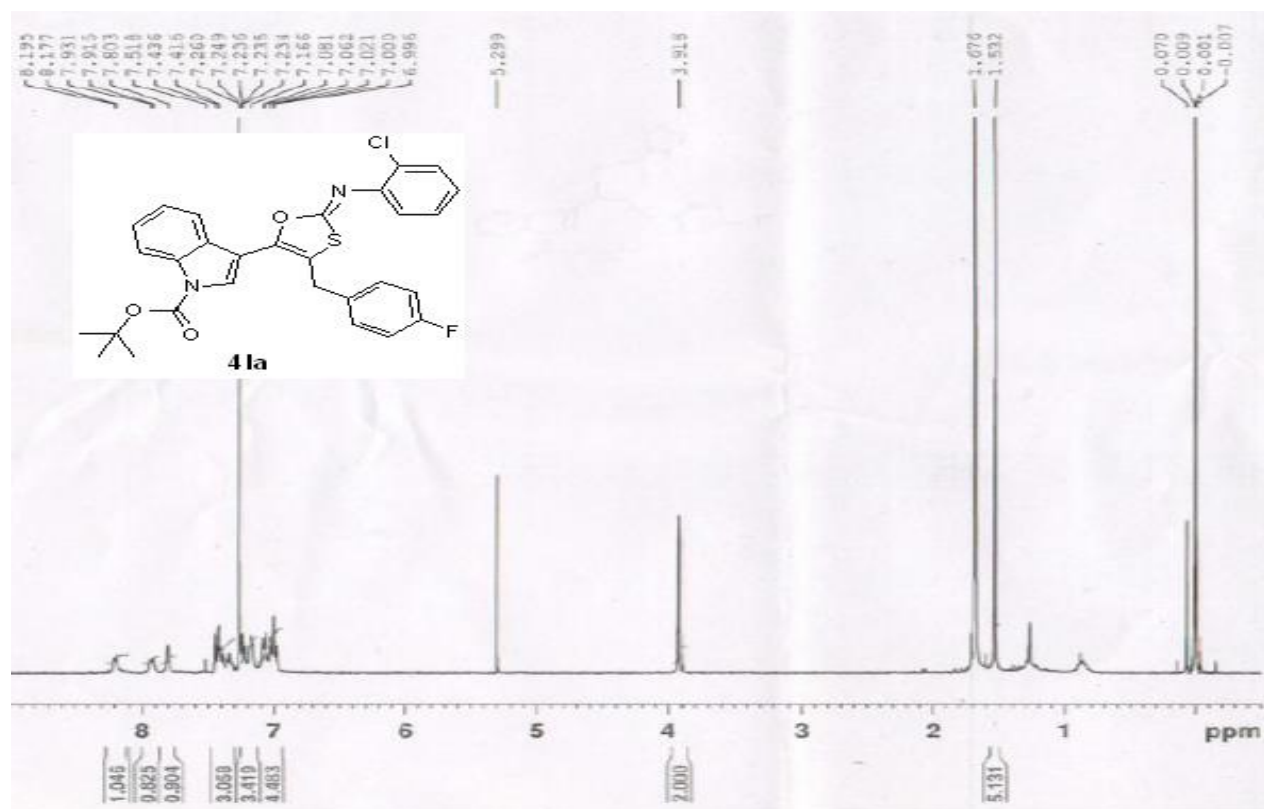


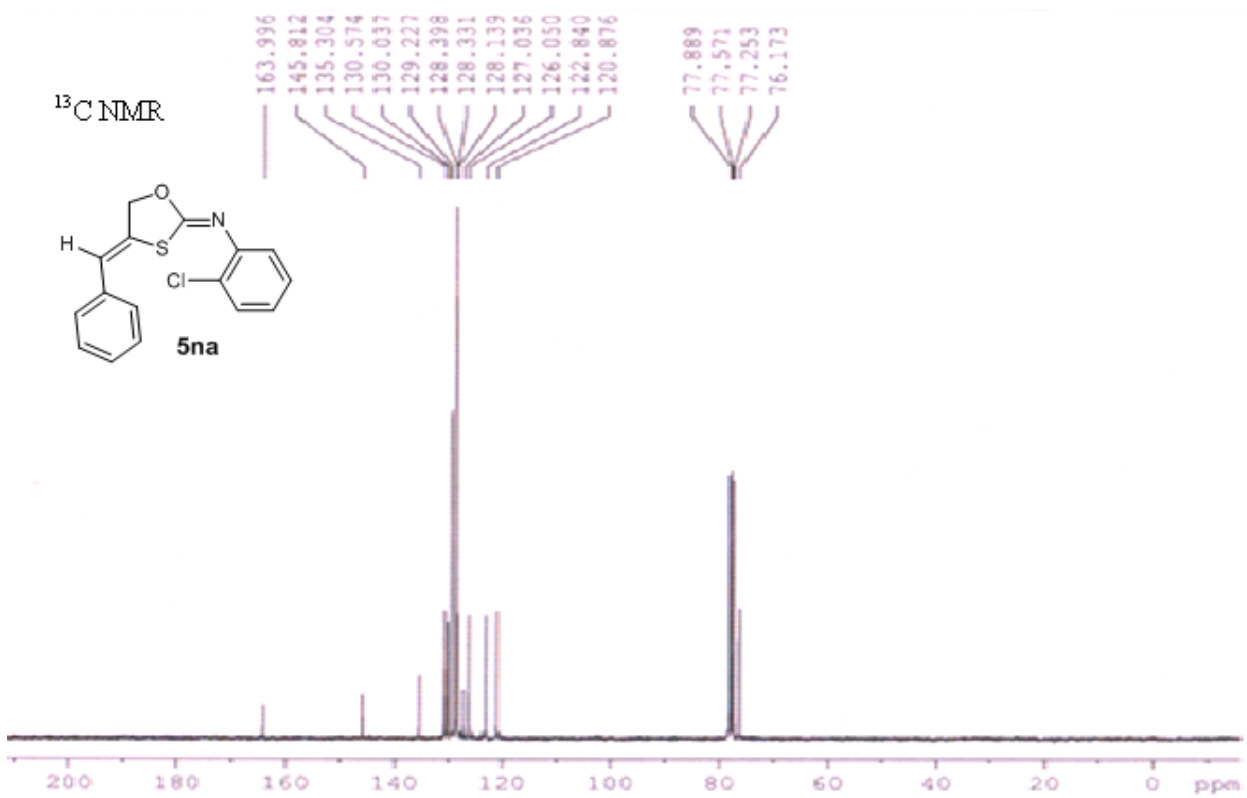
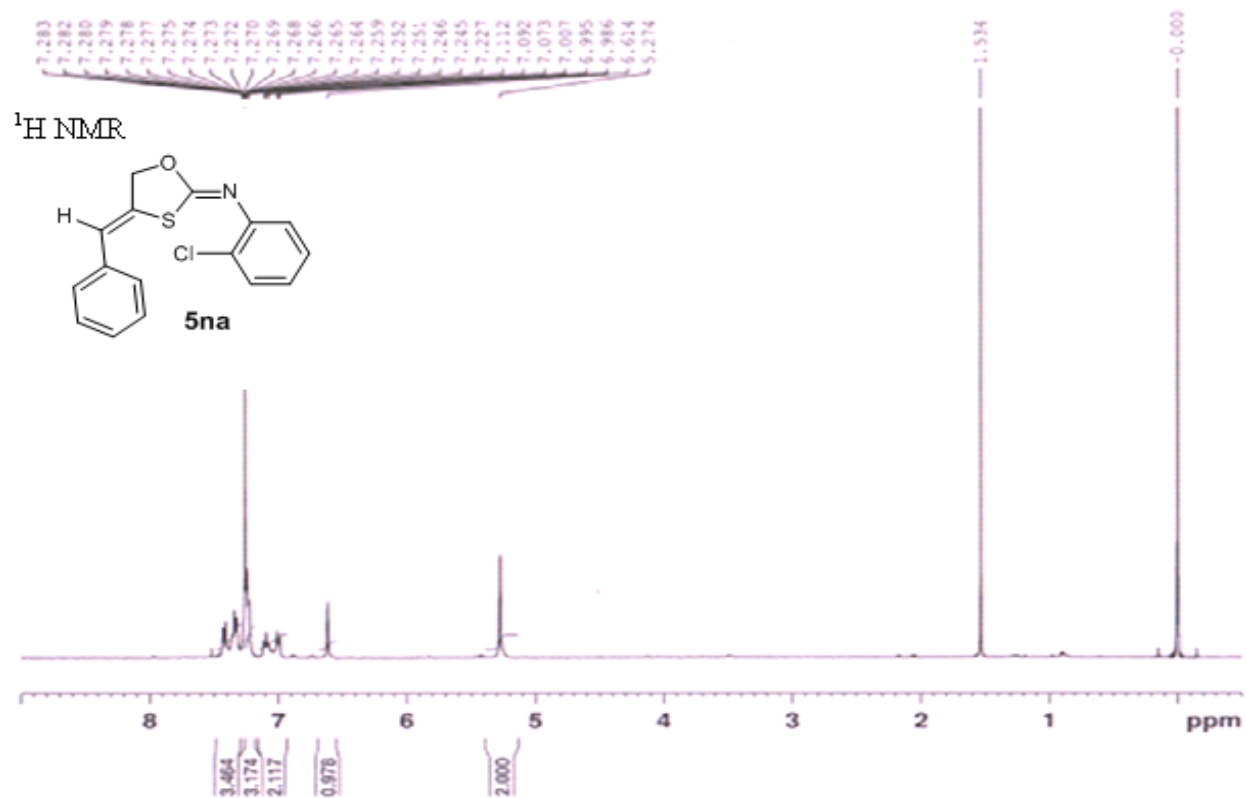


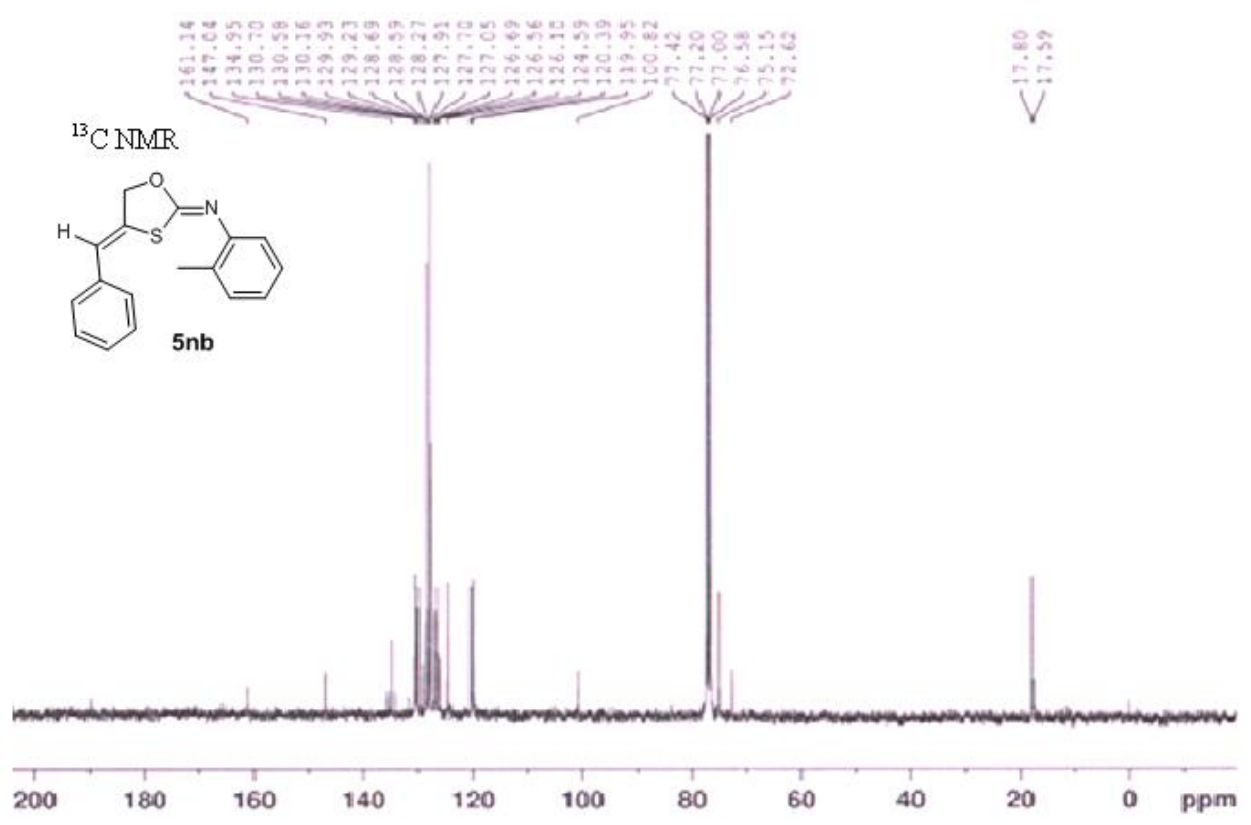
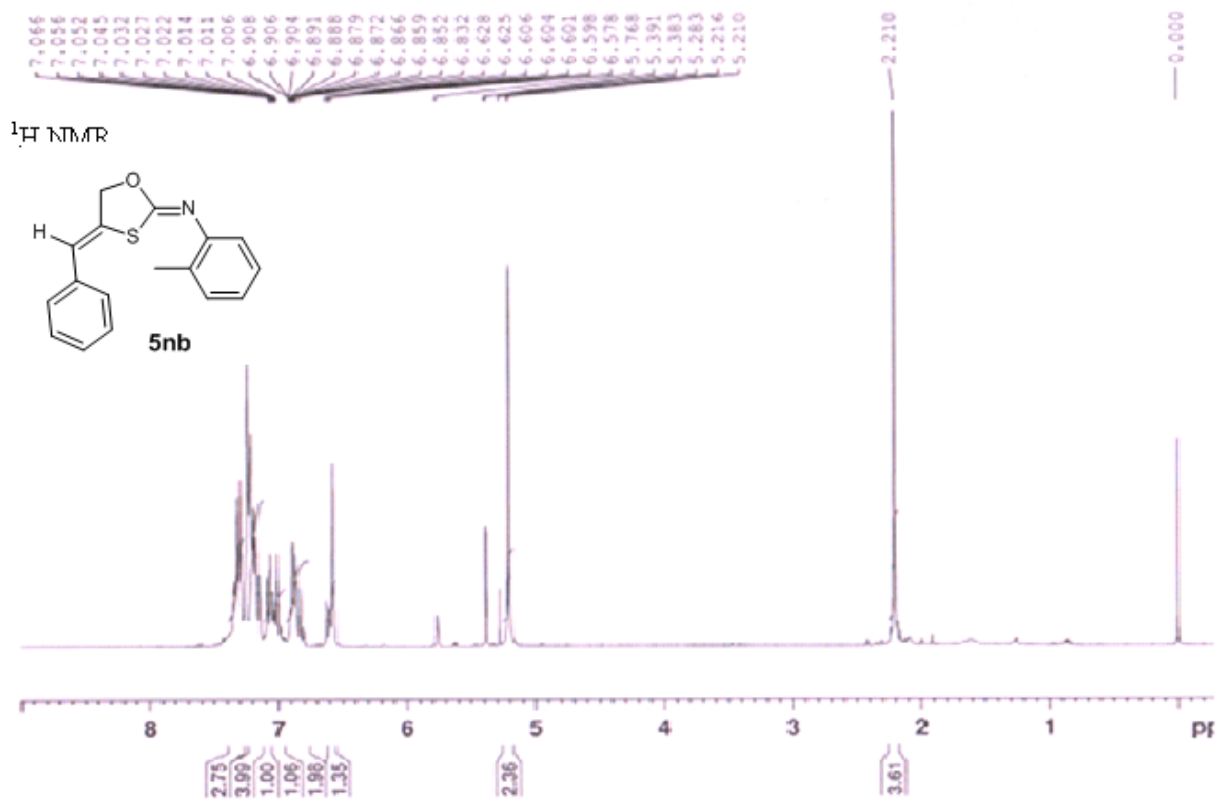


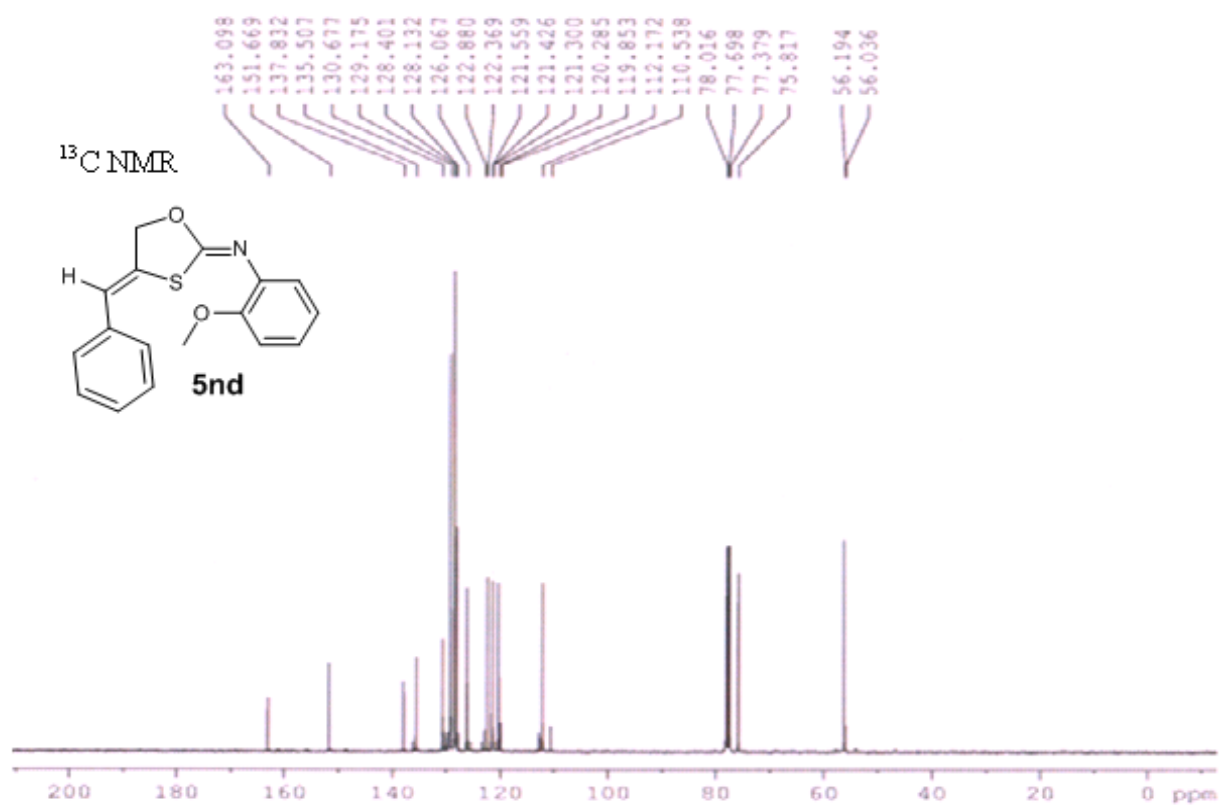
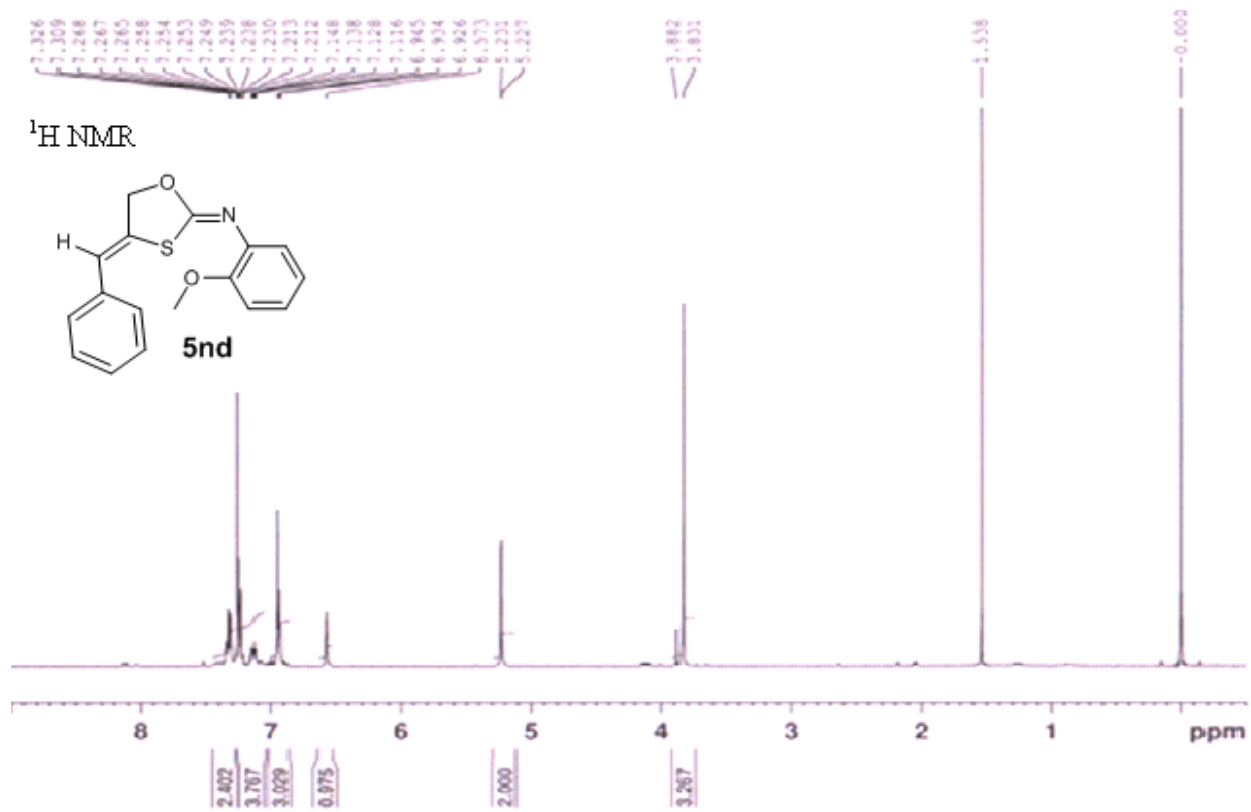


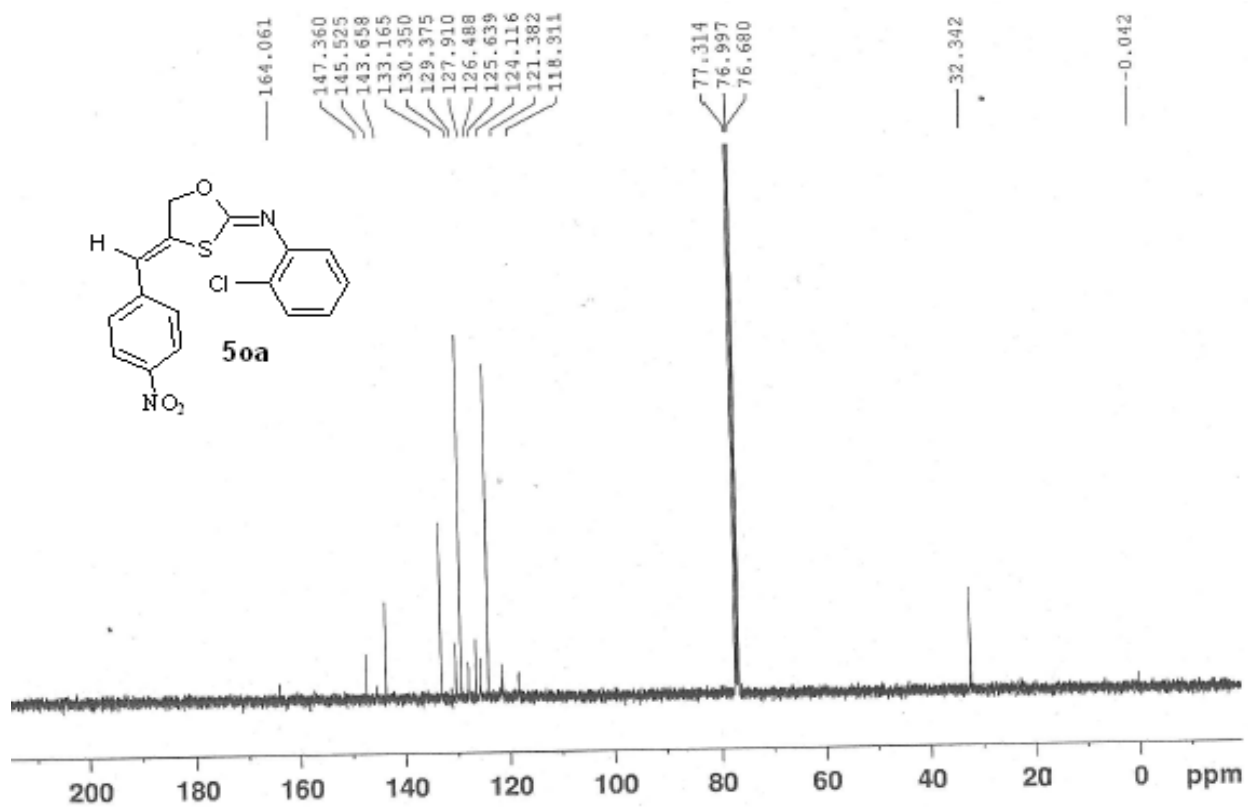
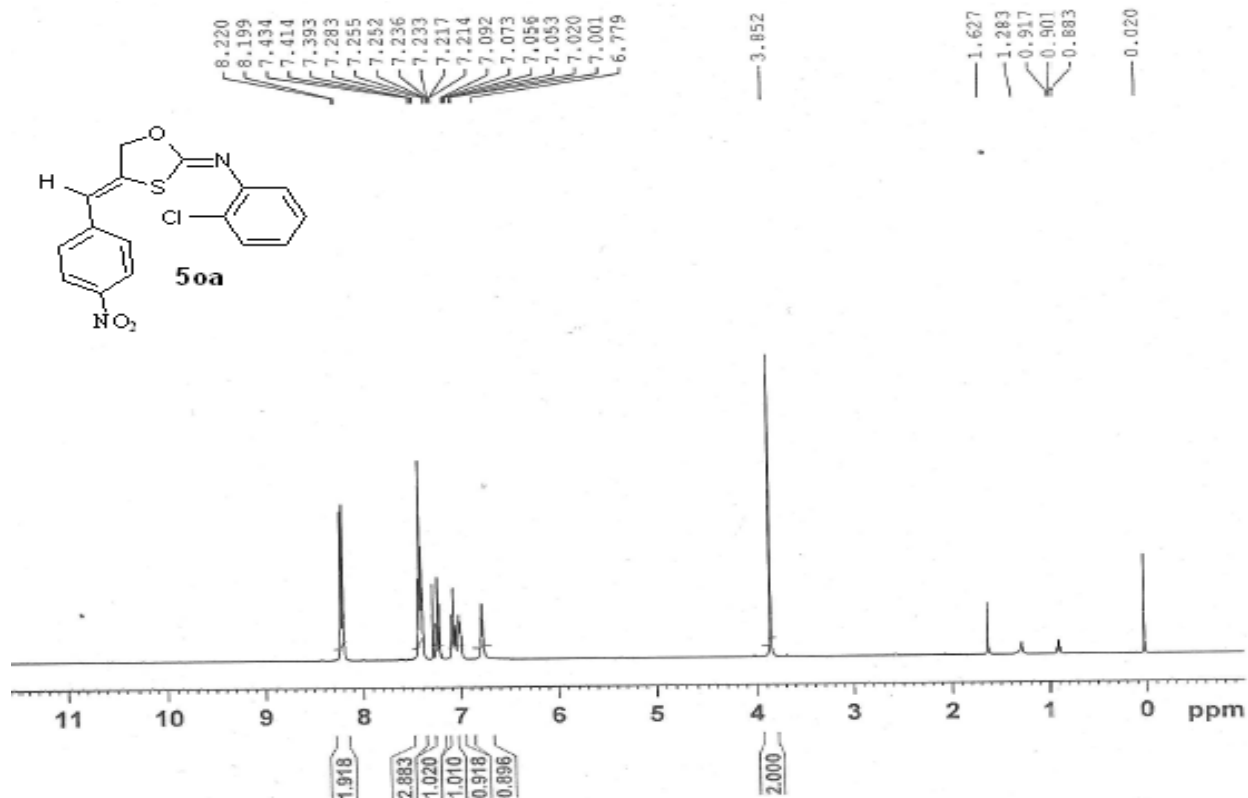


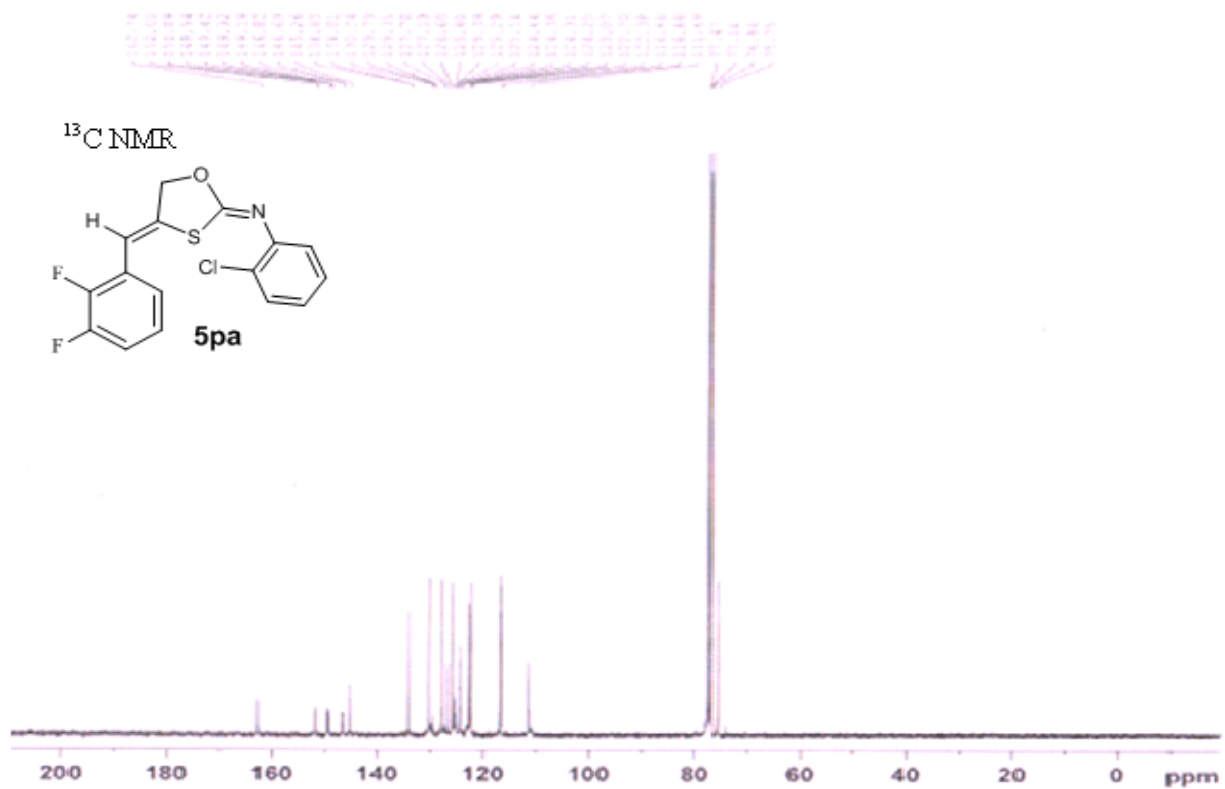
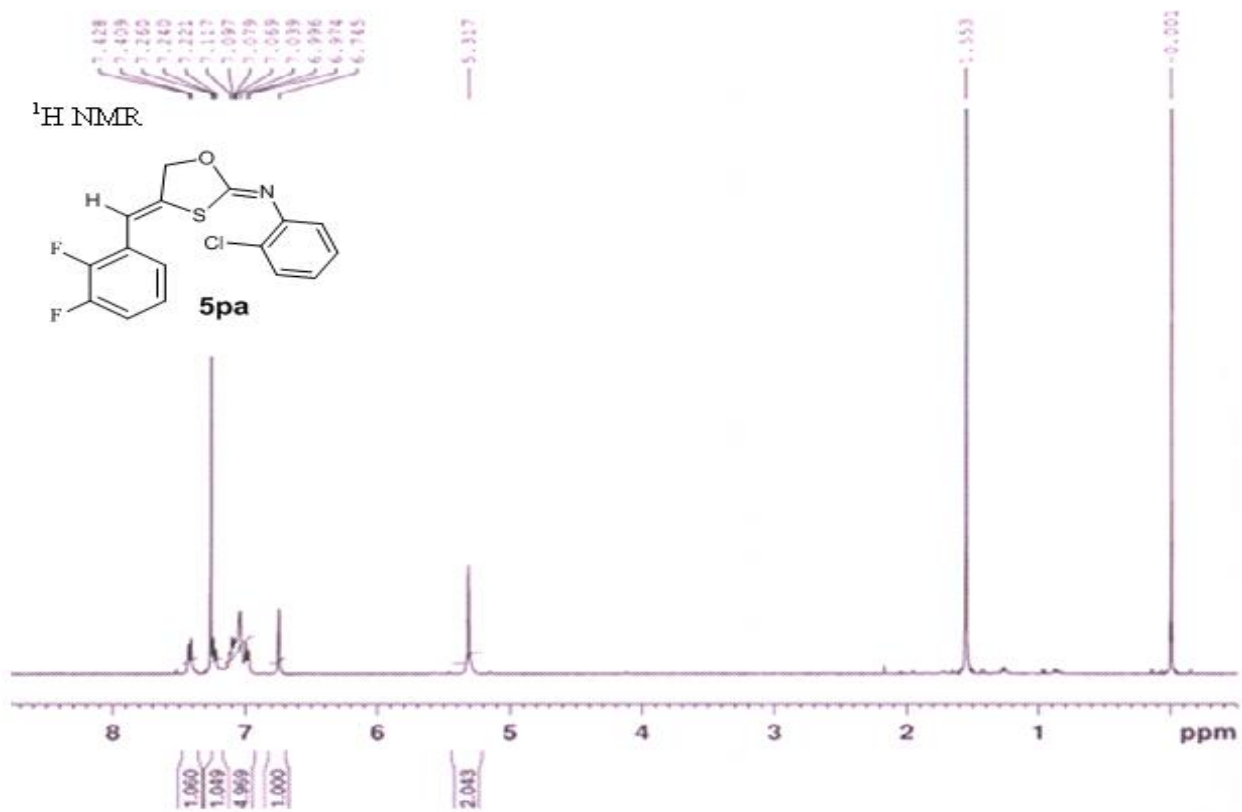


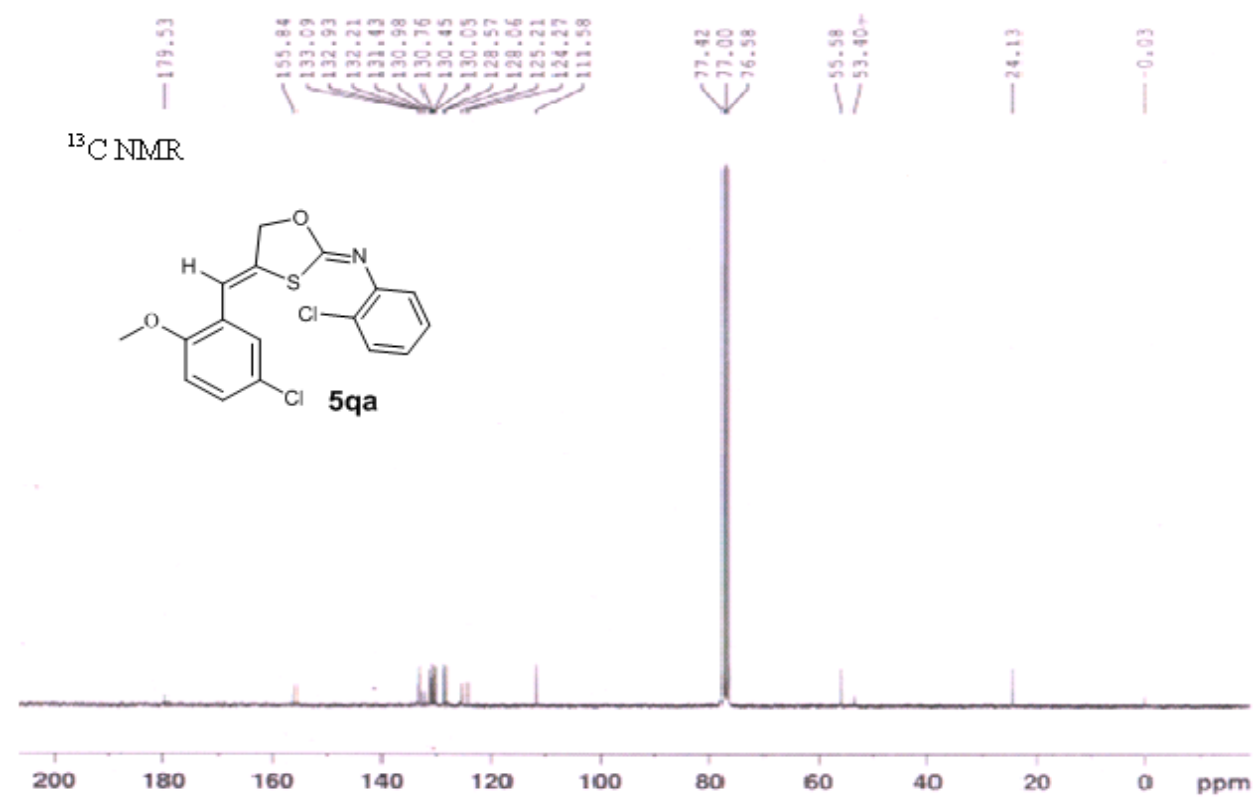
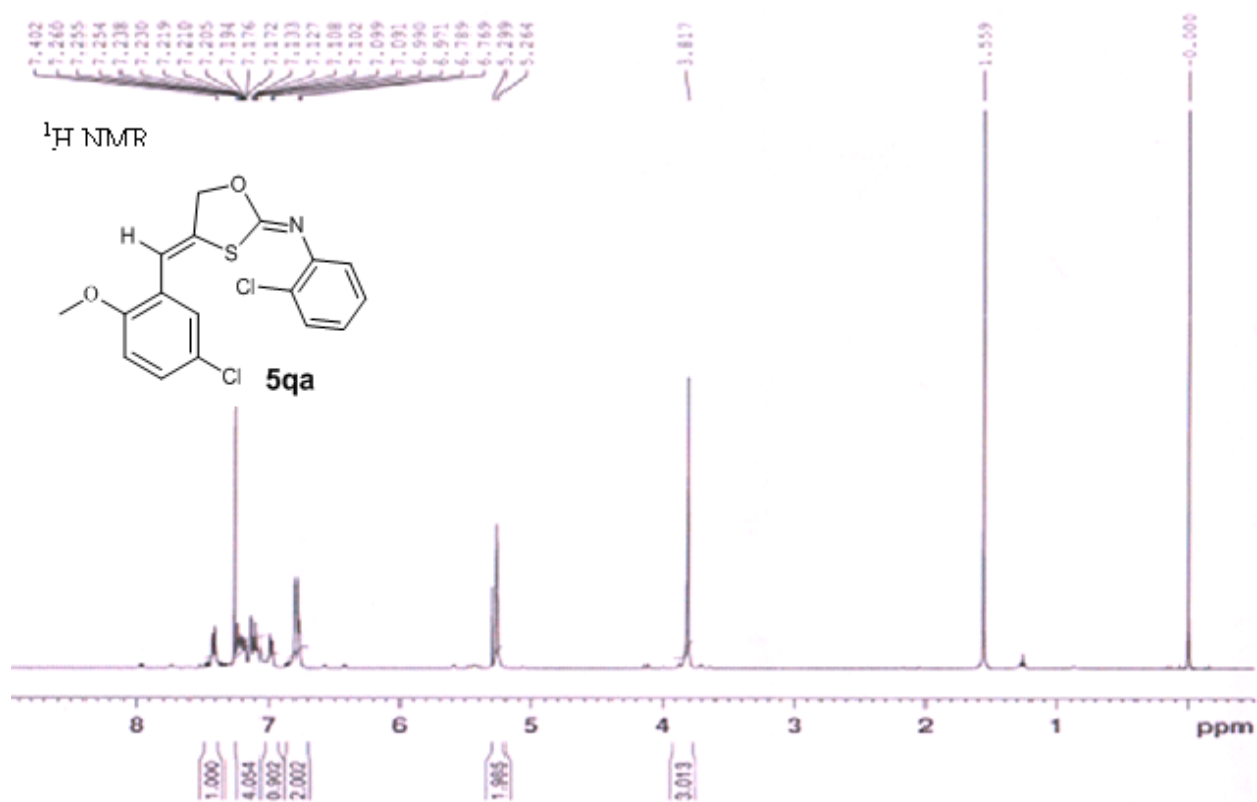


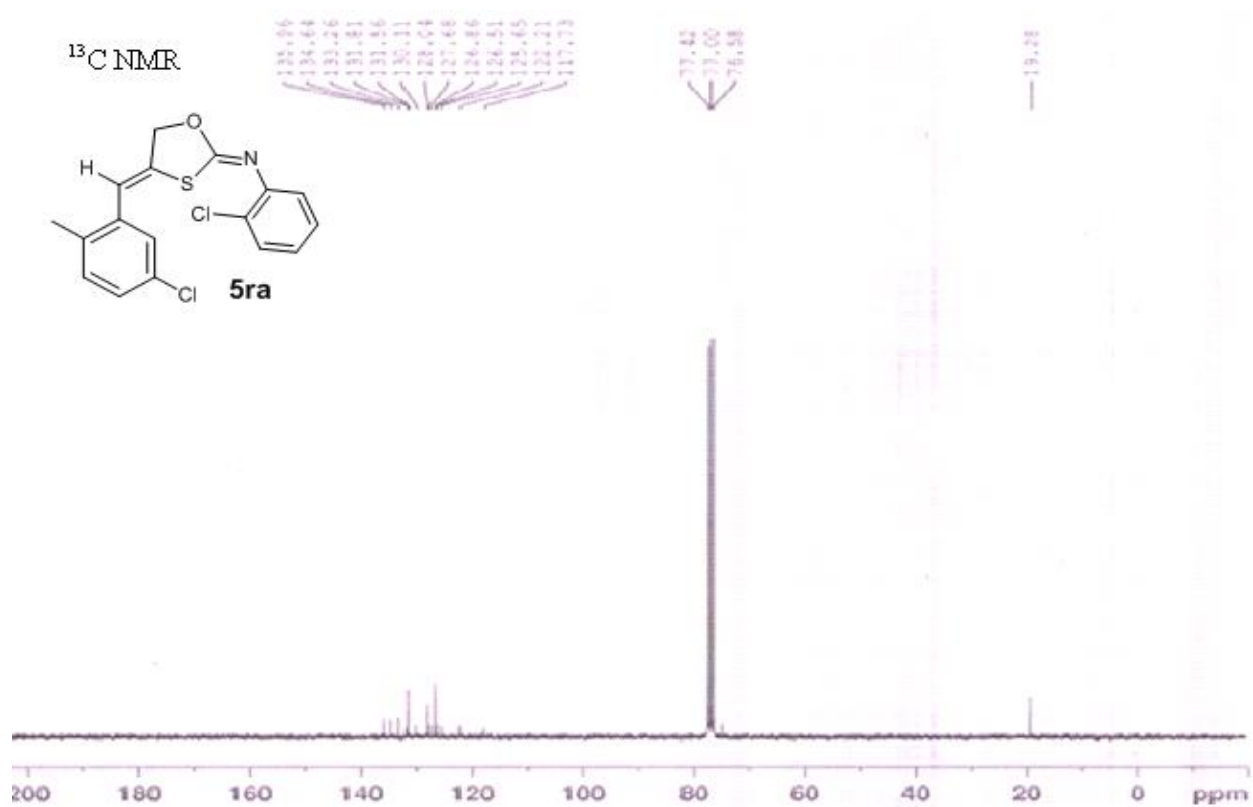
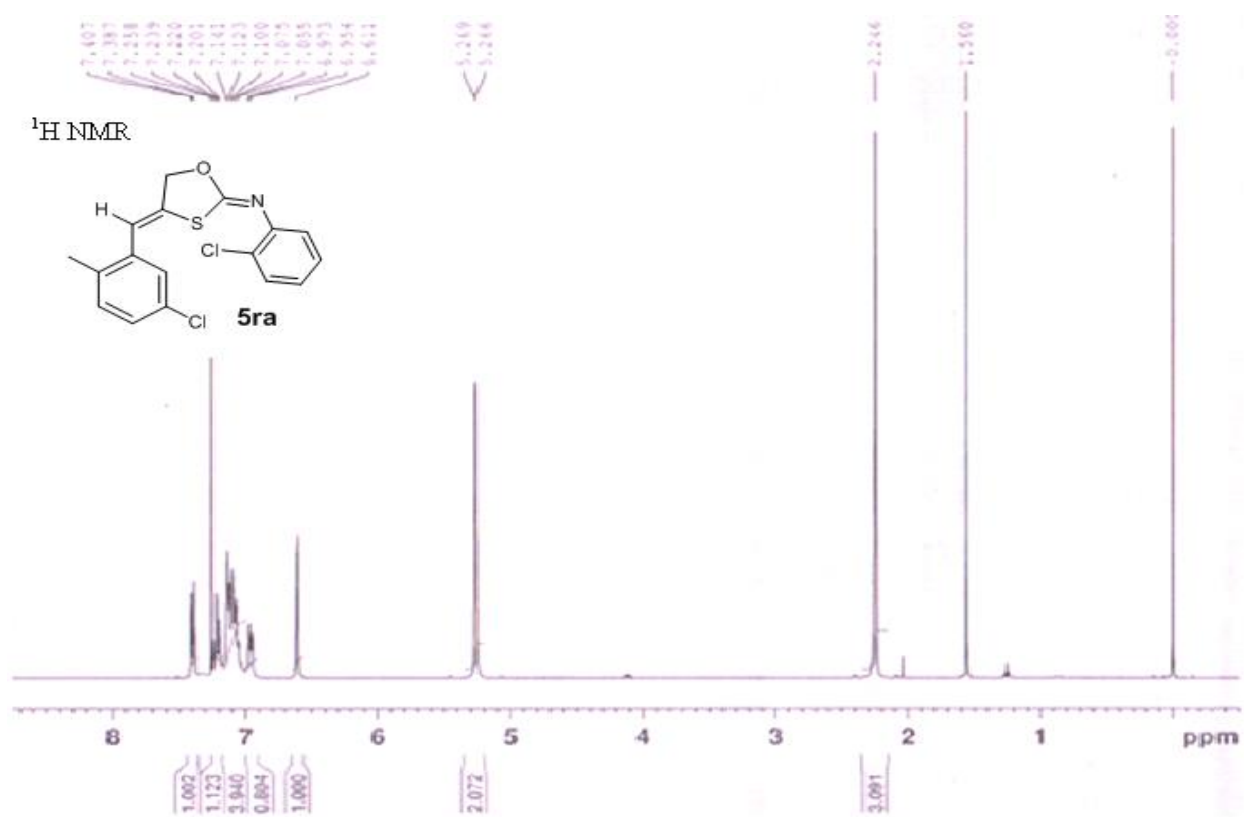


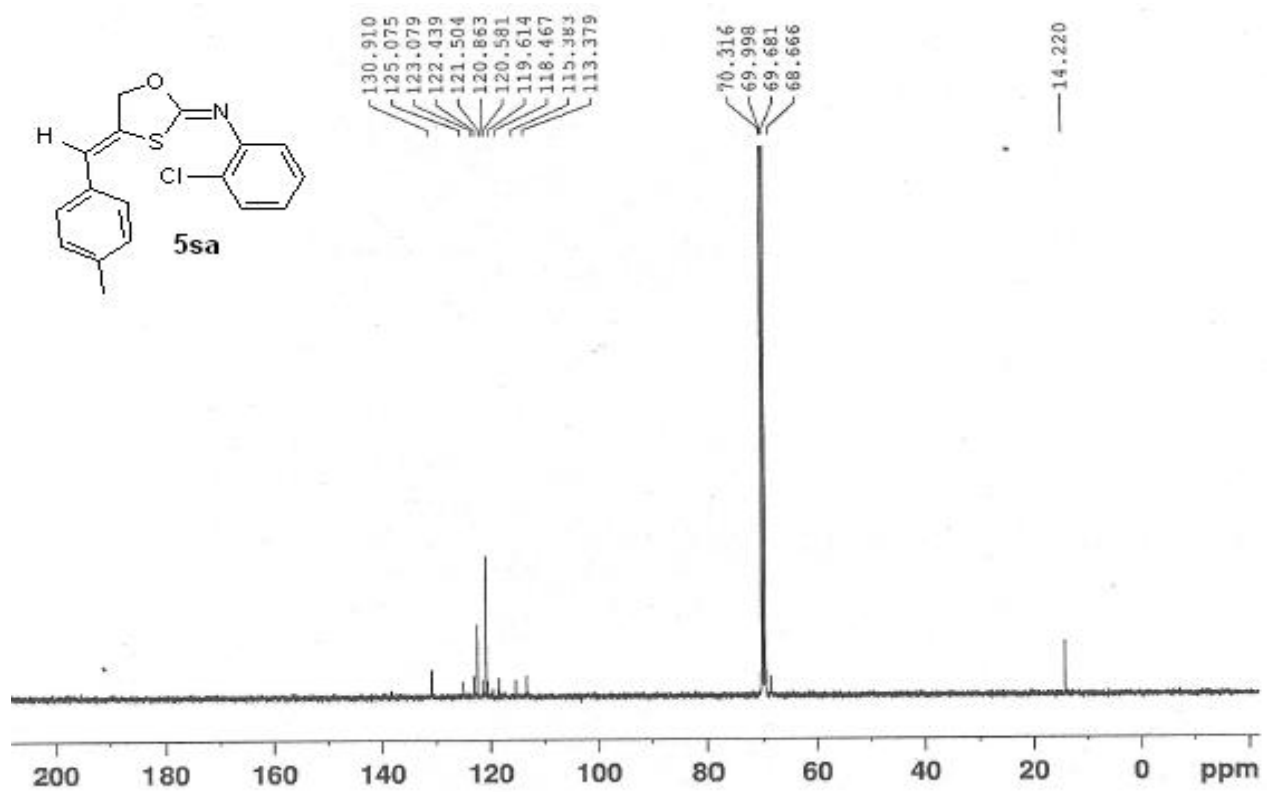
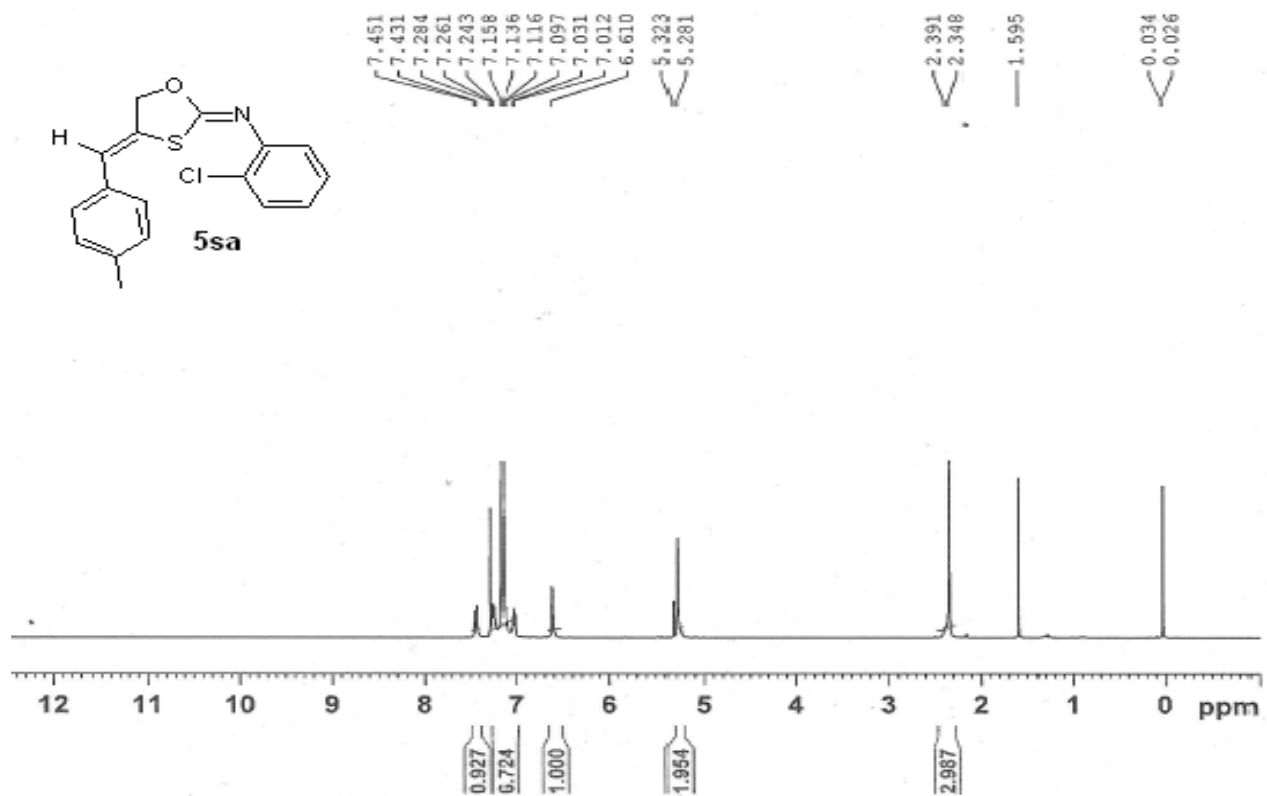


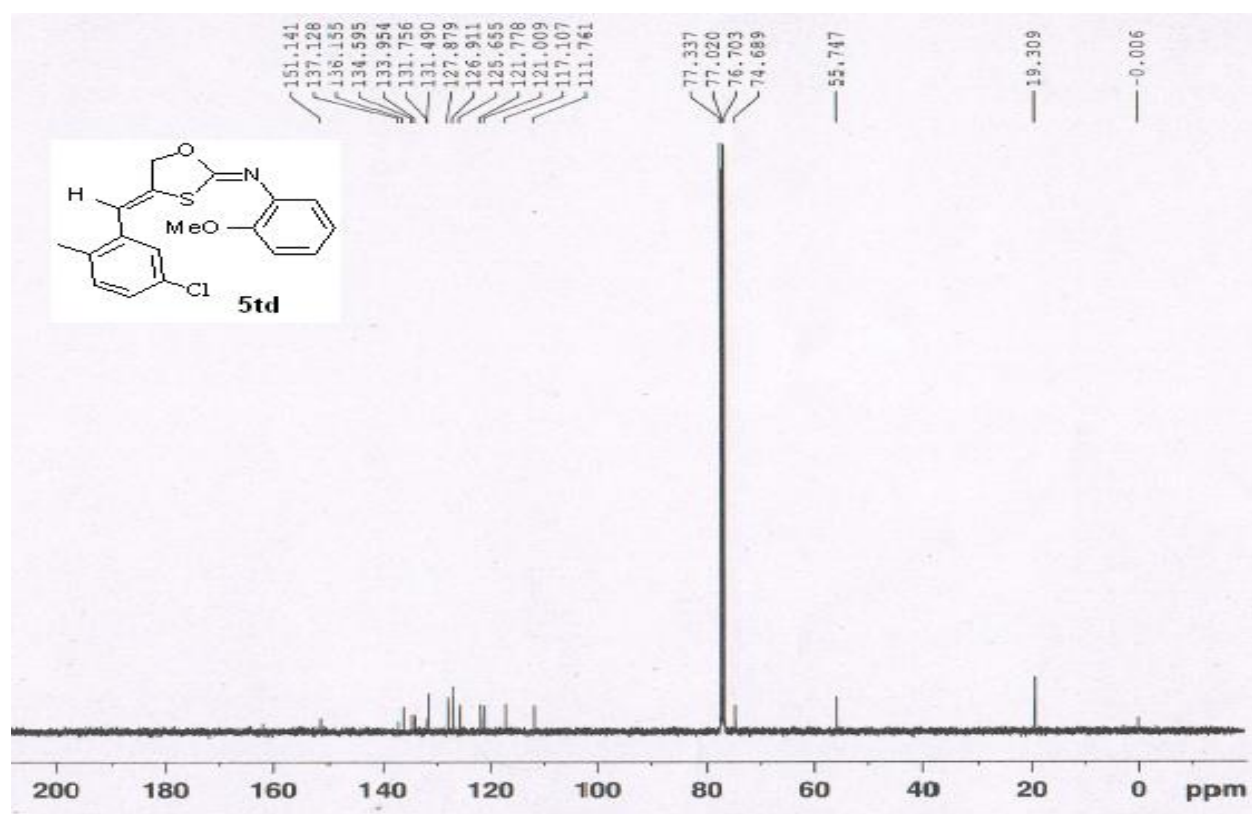
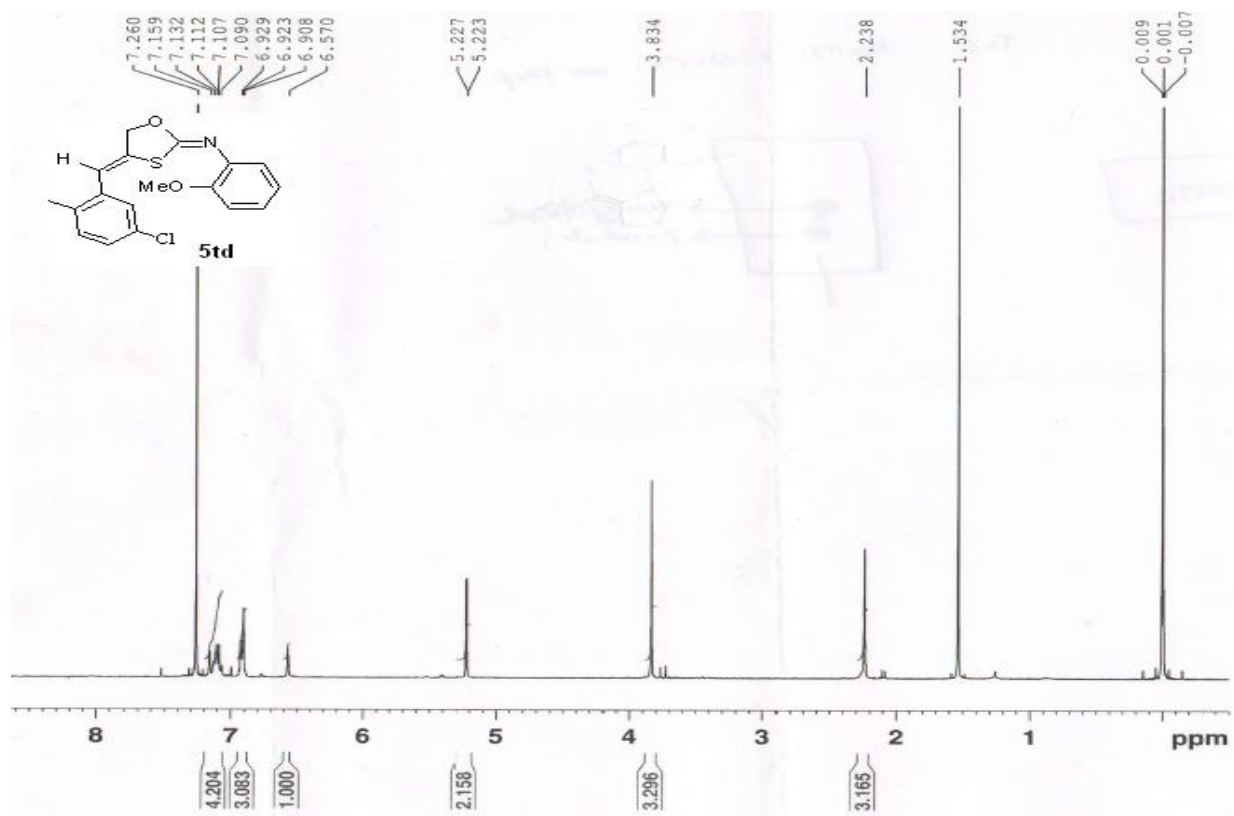


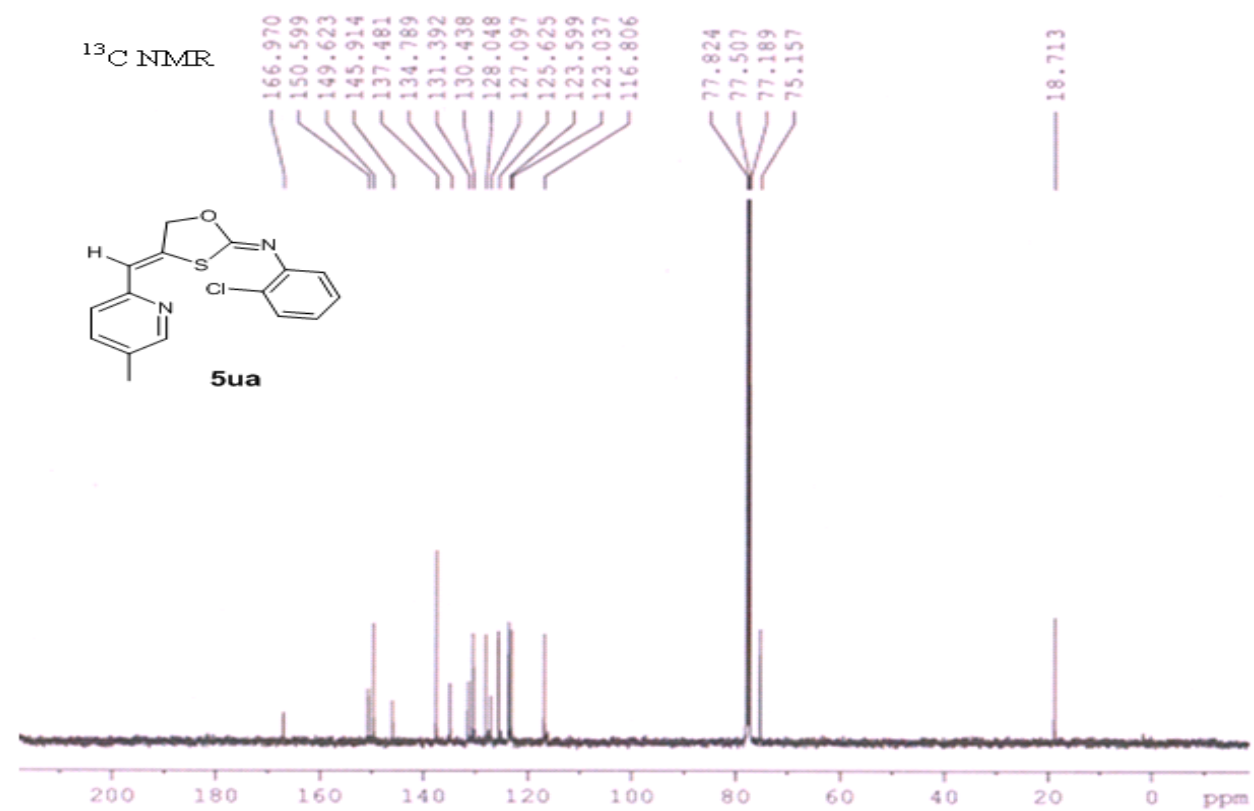
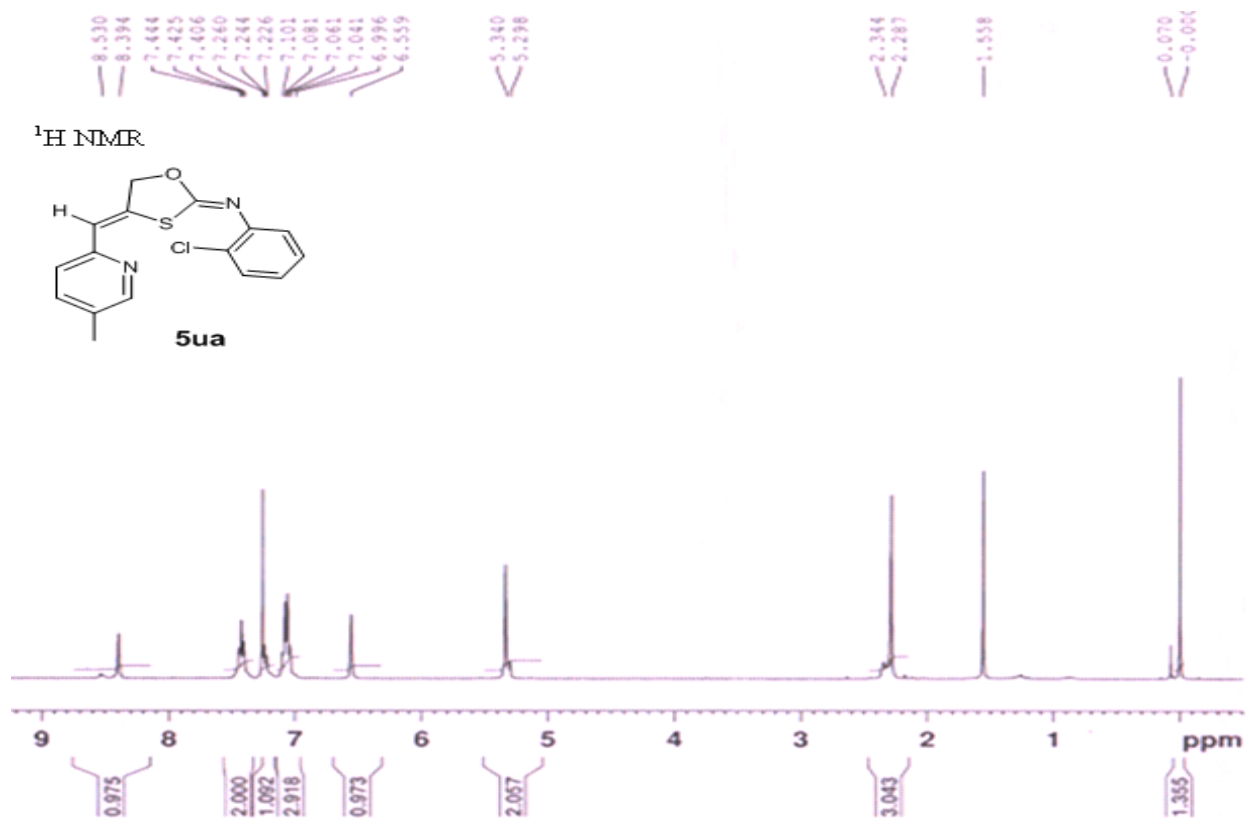


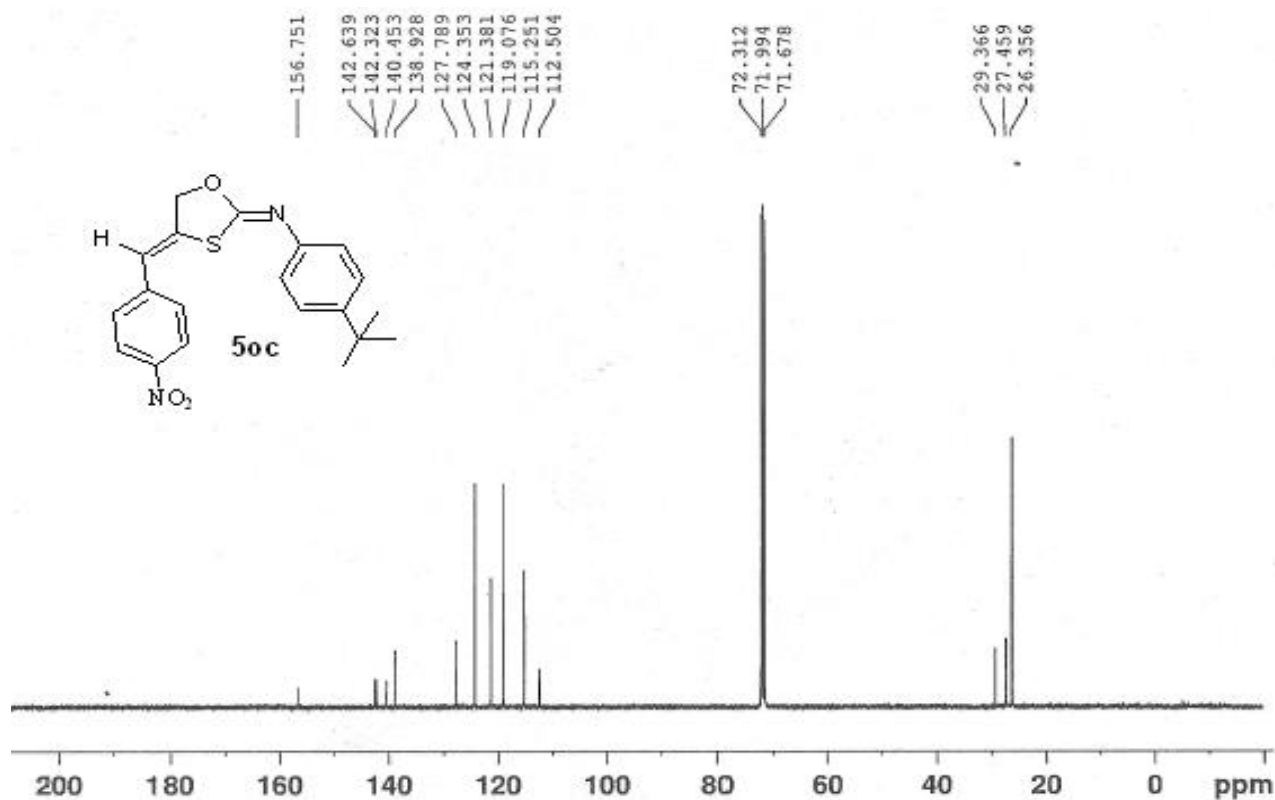
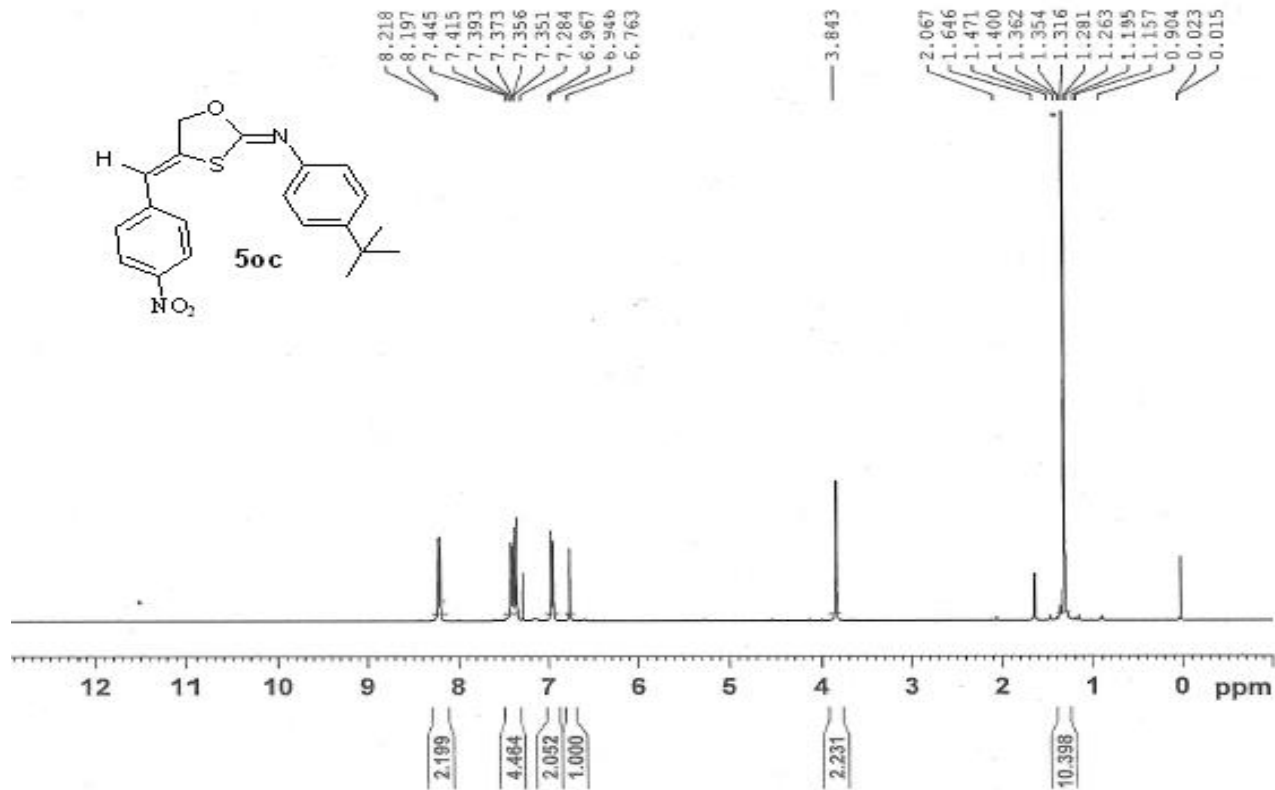


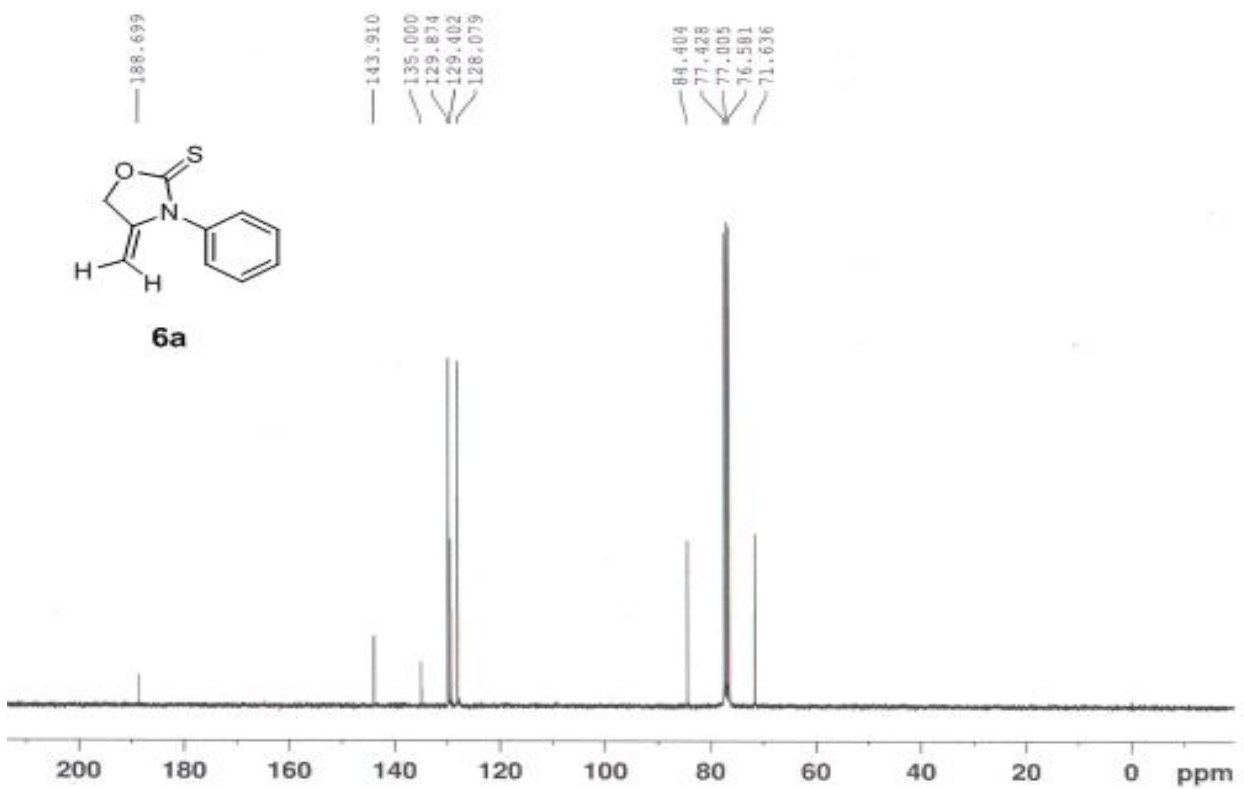
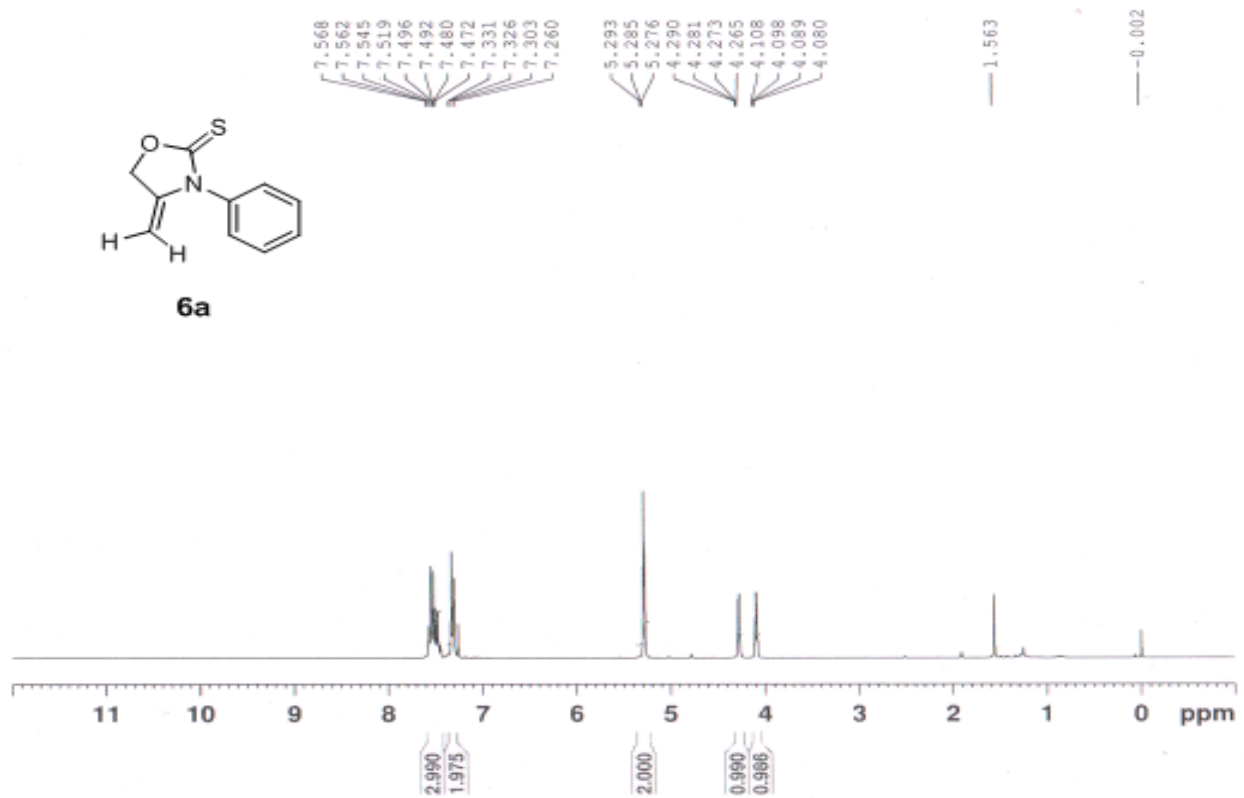


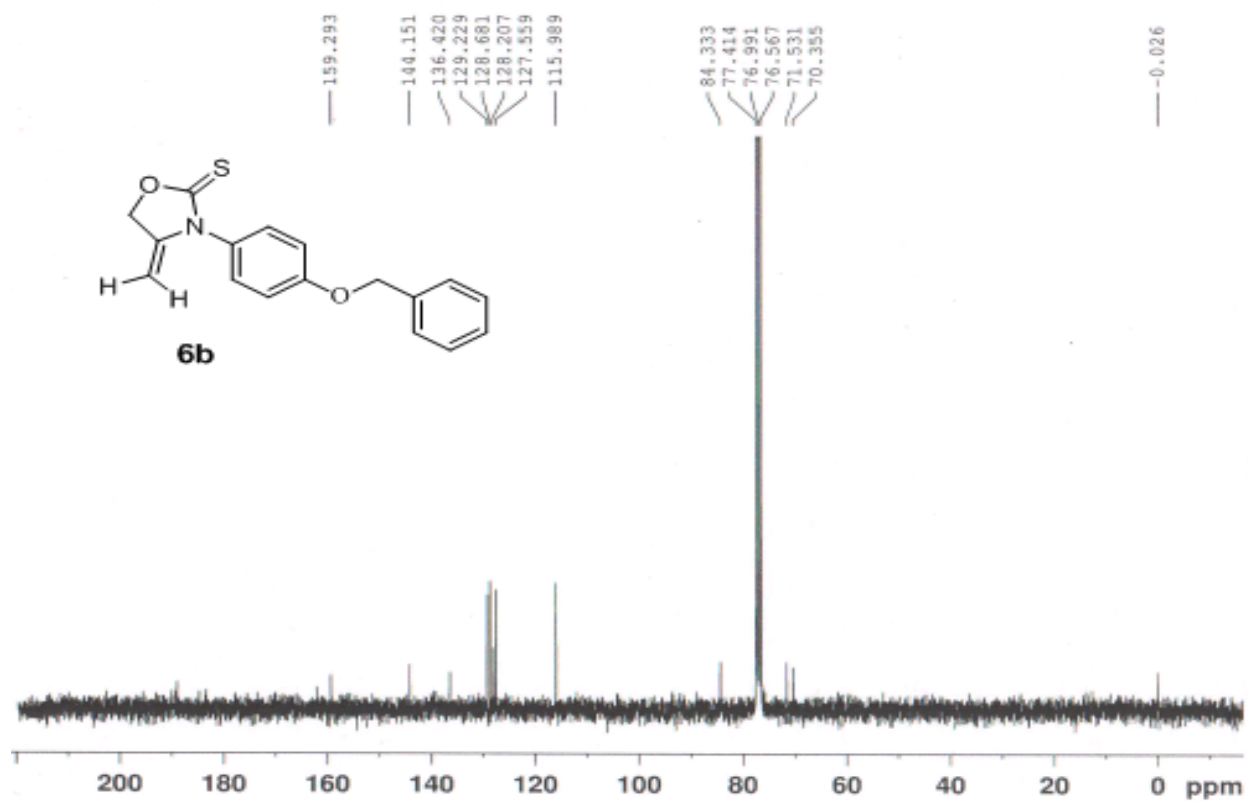
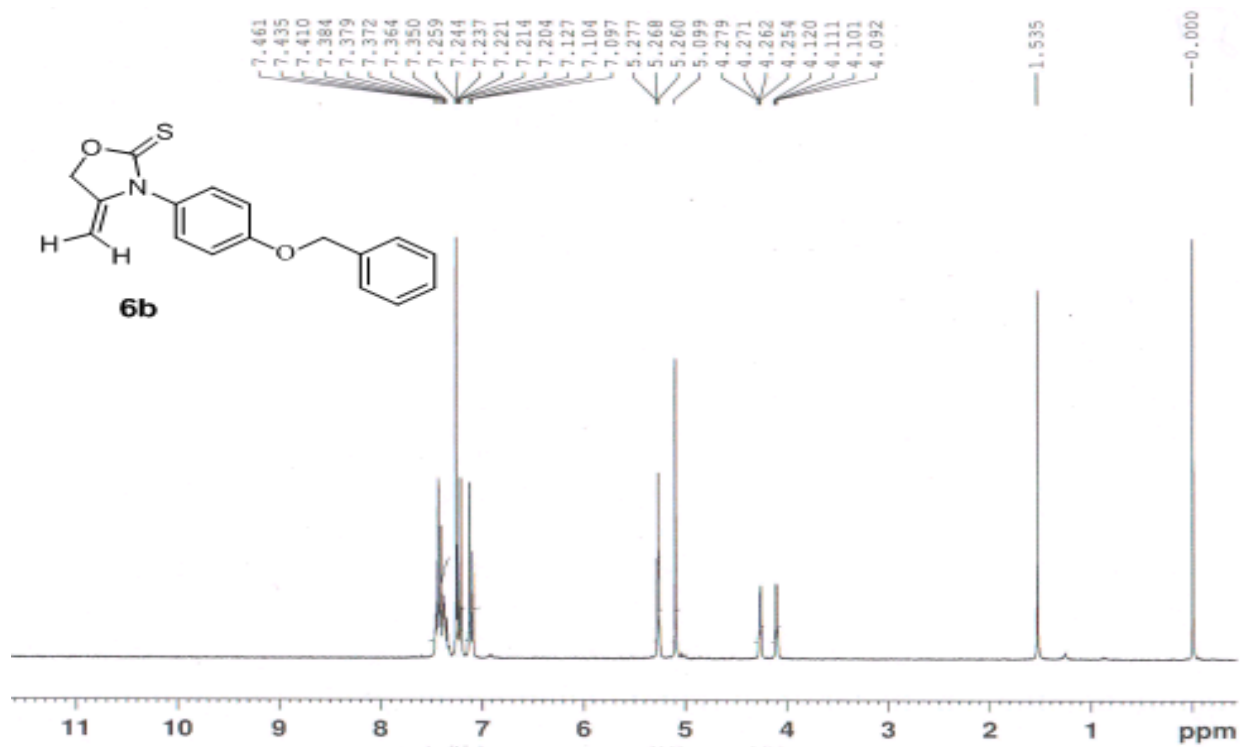


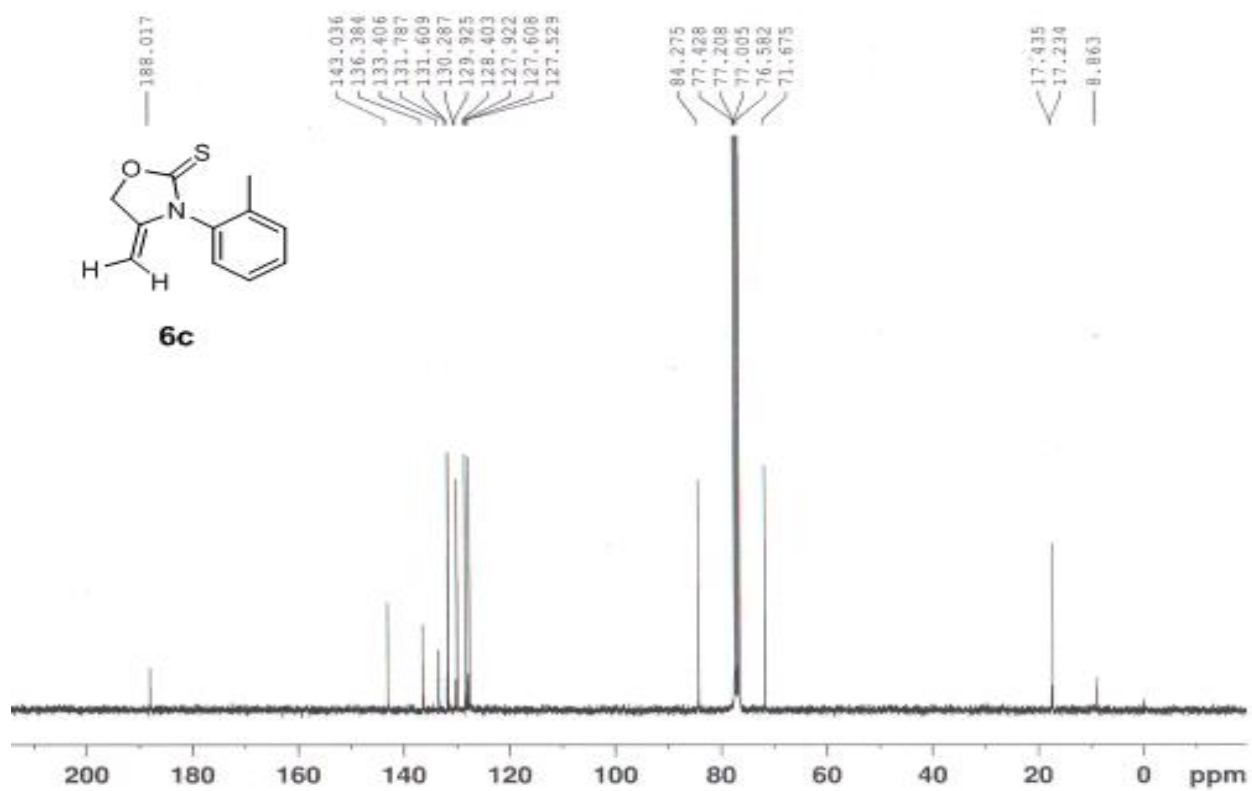
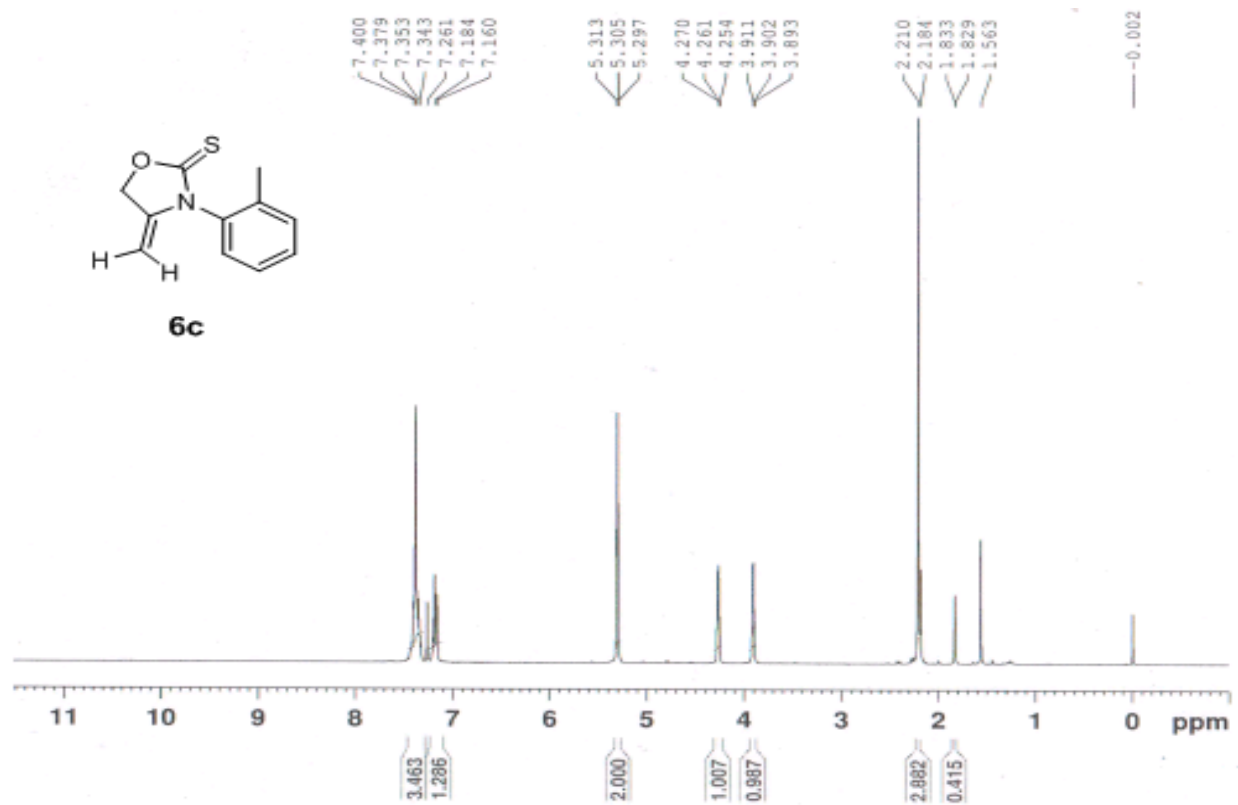


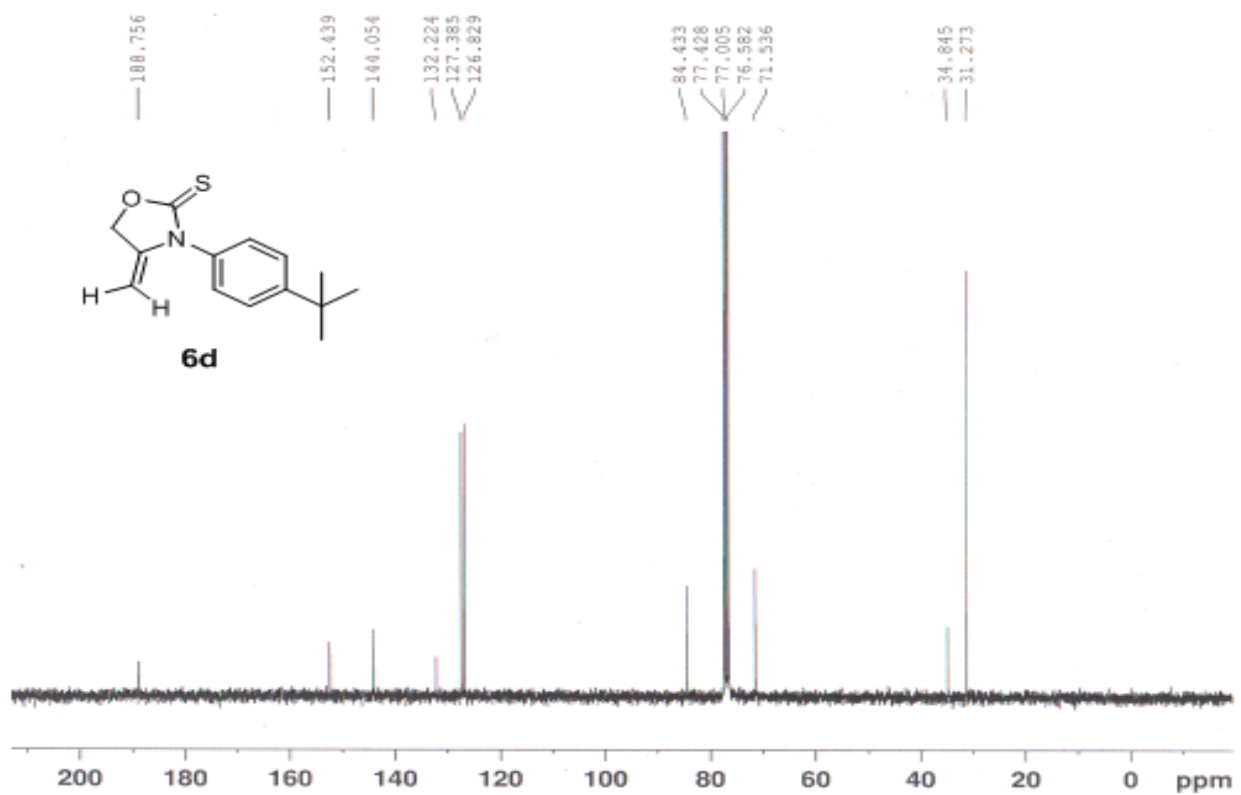
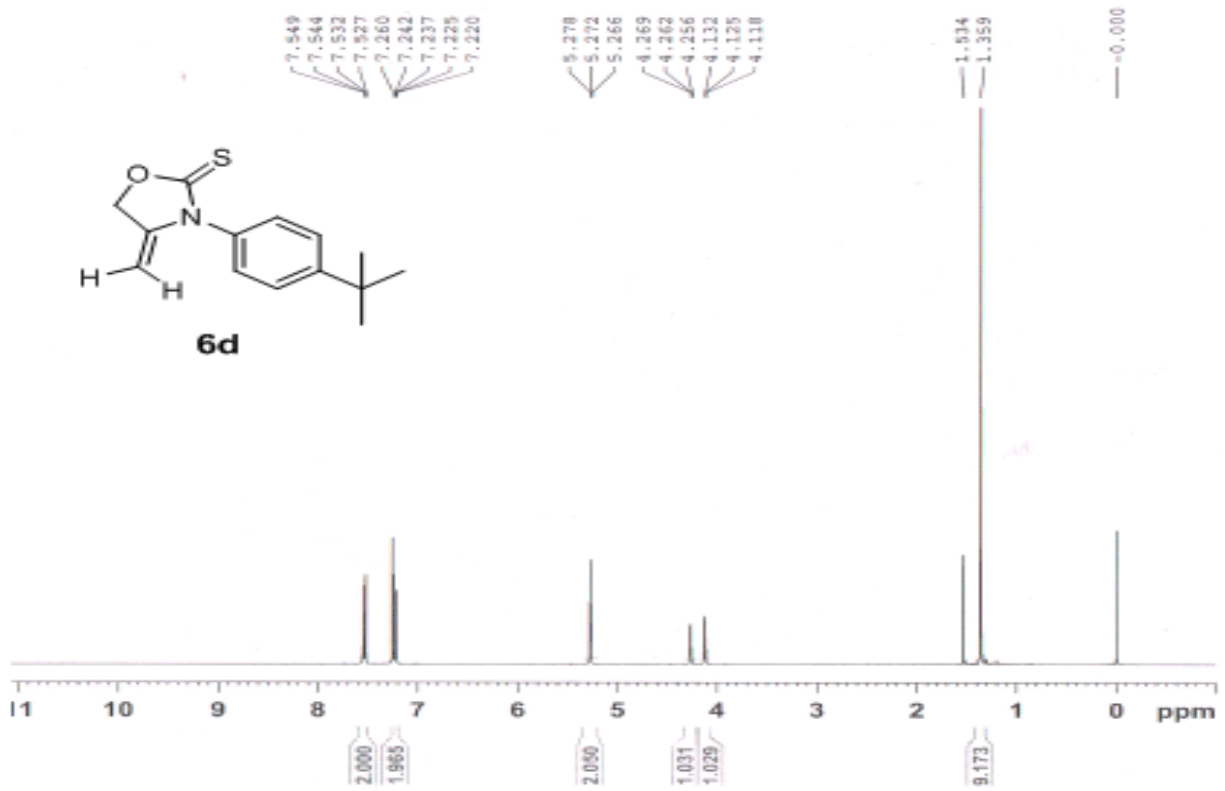


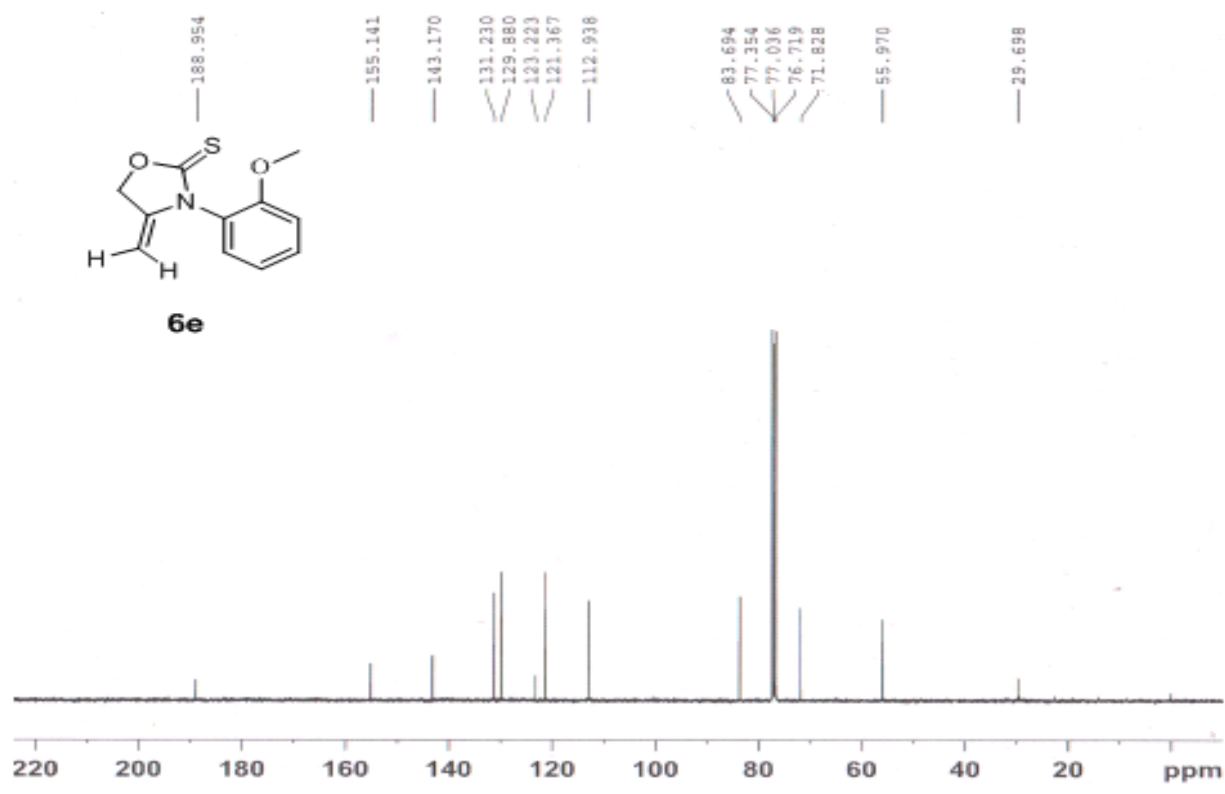
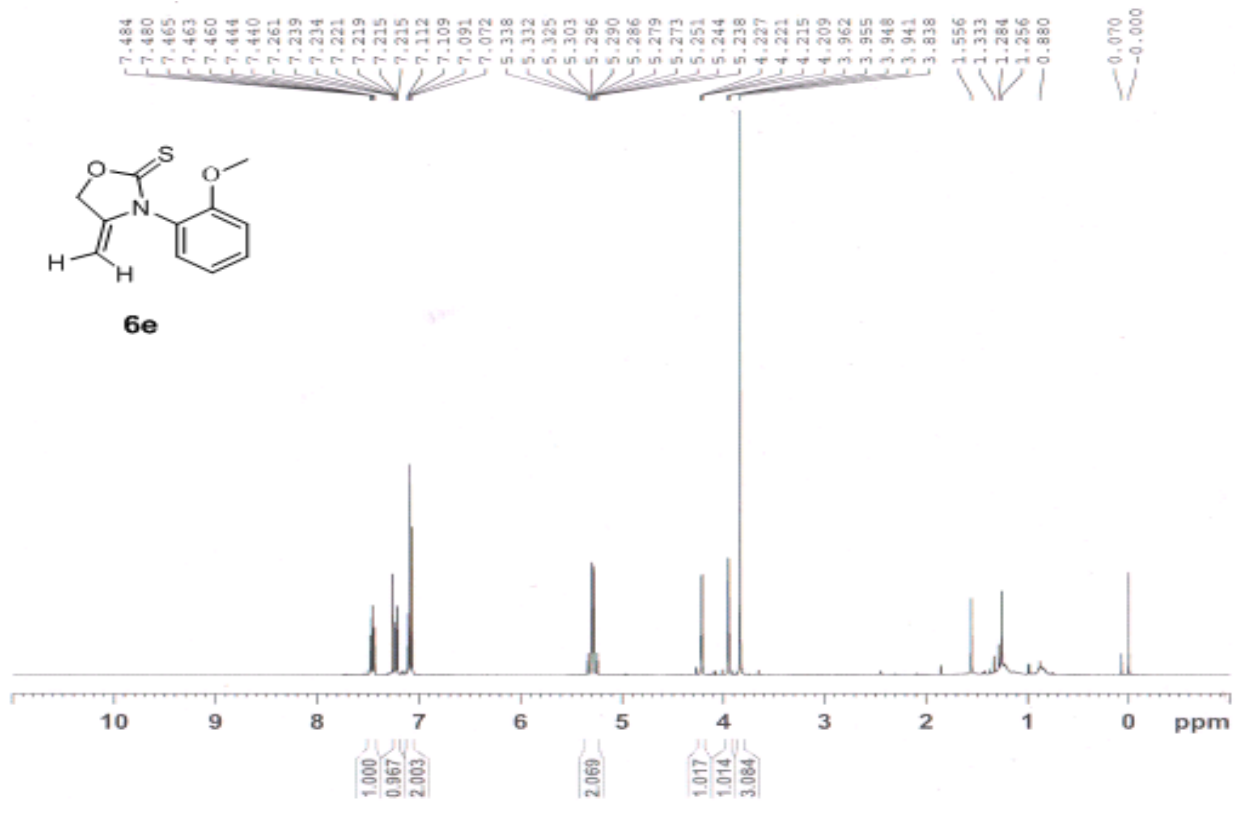


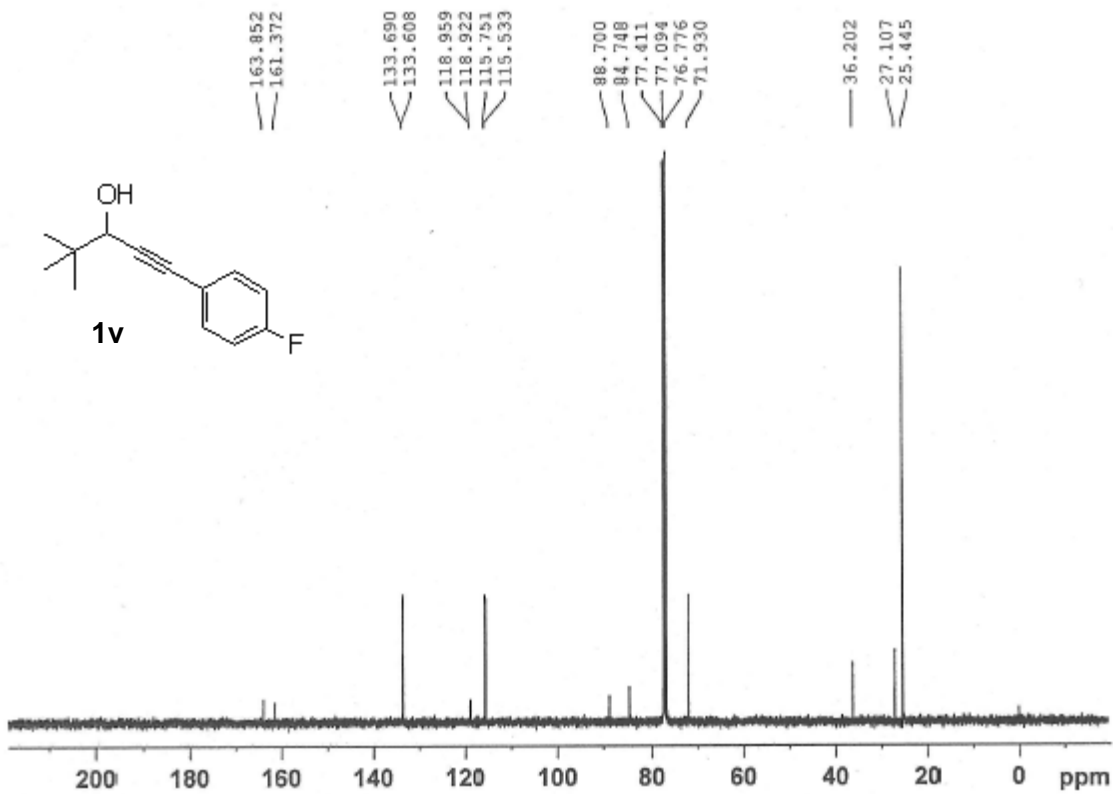
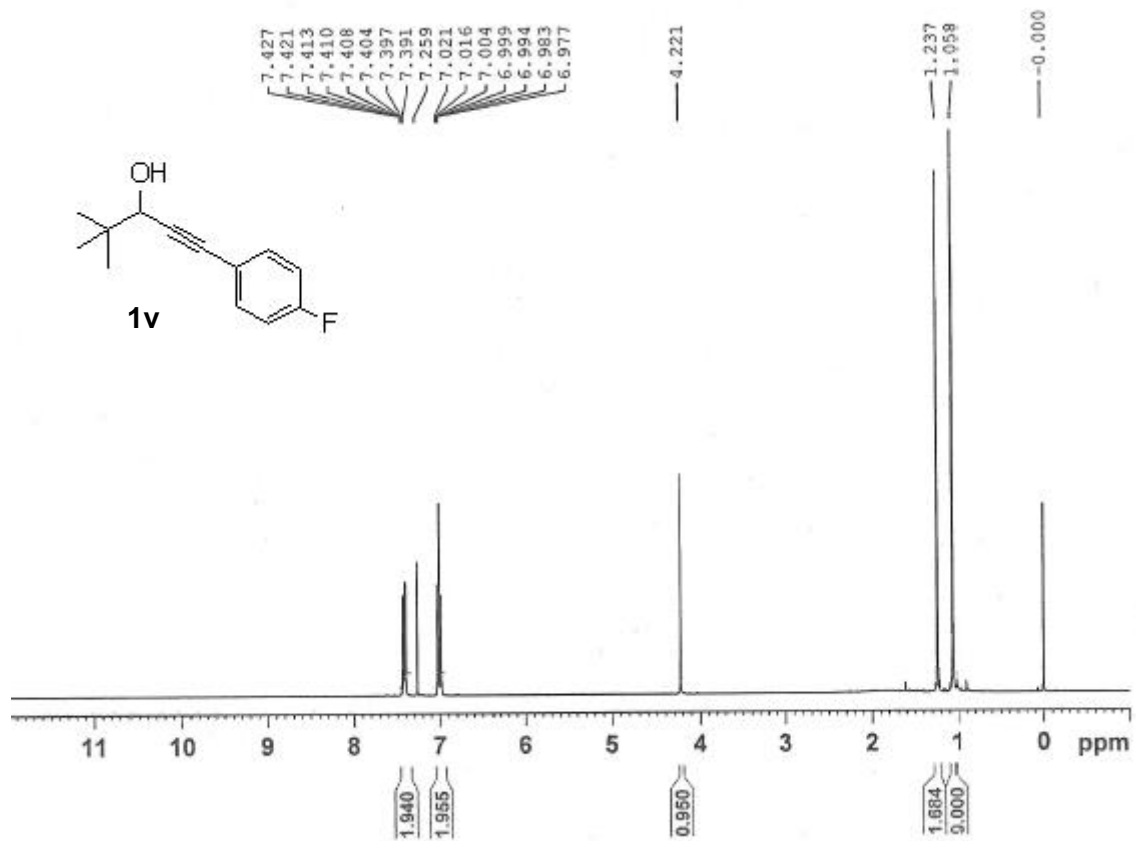


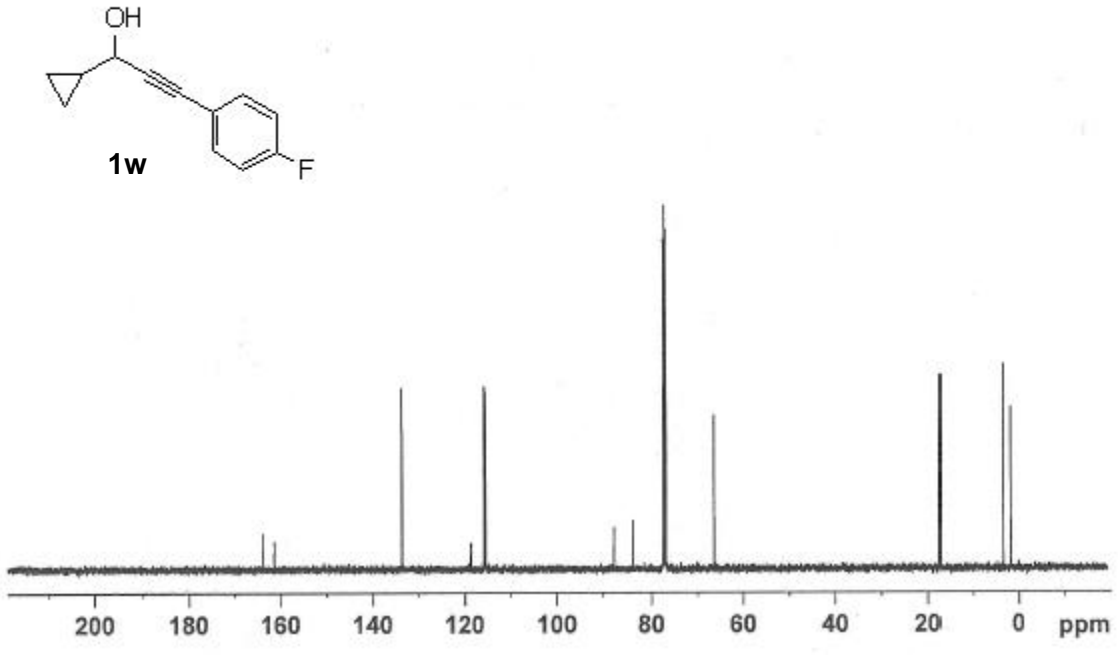
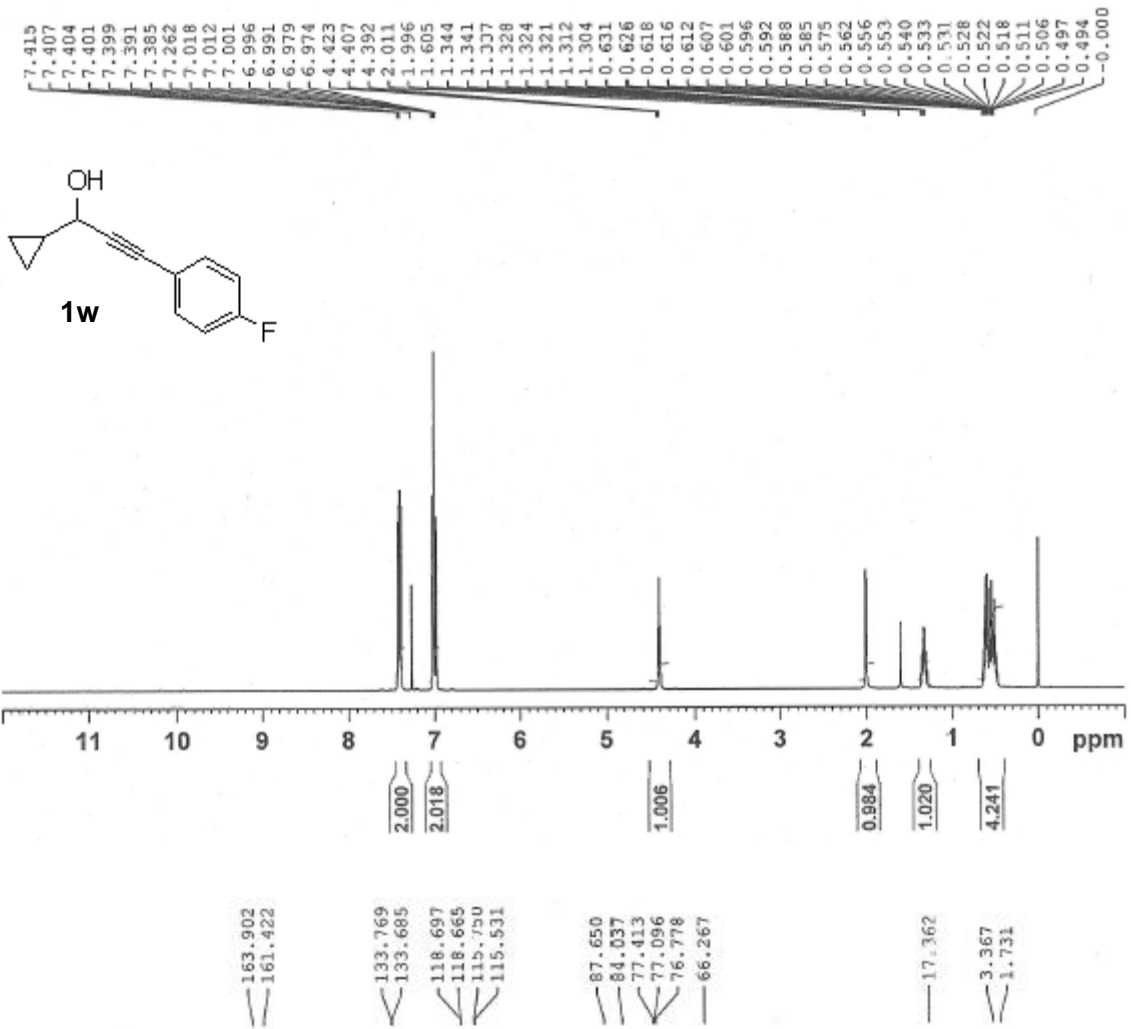




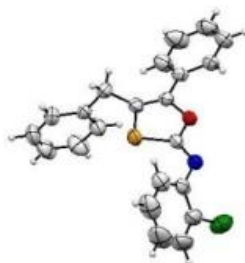




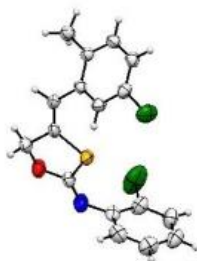




Single crystal structure of the prepared (Z)-N-(4-benzyl-5-phenyl-1,3-oxathiol-2-ylidene)-2-chloroaniline (4aa) (CCDC 1879214) : These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



Single crystal structure of the prepared (Z)-2-chloro-N-((Z)-4-(5-chloro-2-methylbenzylidene)-1,3-oxathiolan-2-ylidene)aniline (5ra) (CCDC 1879222) : These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



Single crystal structure of the prepared 3-(4-(benzyloxy)phenyl) 4-methyleneoxazolidine-2-thione (6b) (CCDC 1870970) : These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

