Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Indirect Conversion of Ambient Pressure of CO_2 into Oxazolidin-2-ones by A Copper-Based Magnetic Nanocatalyst

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1. General Information

The starting materials were purchased commercially and were used without further purification. The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ^{o}C) and ethyl acetate.

All compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectroscopy, which are consistent with those reported in related literatures. NMR spectra were determined on Bruker 400 in $CDCl_3$. ^{1}H NMR chemical shifts were referenced to residual solvent as determined relative to $CDCl_3$ (7.26 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). ^{1}H NMR peaks are labelled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, are reported in Hertz (Hz). GC-MS data were performed on Agilent 7890A. GC analysis were performed on a Shimadzu GC-2014 equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector.

The FT-IR spectra were obtained by using a Fourier transform infrared (FT-IR) (4000 - 400 cm^{-1}) spectrometer (Burker VERTEX 80V) at 4 cm^{-1} resolution and 32 scans. And the samples were prepared by the KBr disc method. The weight percentage of copper in the catalyst FeDOPACu was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (SPECTRO ARCOS EOP) analysis. Size and morphology images of the nanoparticles were tested by a transmission electron microscope (TEM) (JEOL JEM-2100) operating at 100 kV after a drop of aqueous solution of the nanoparticles was deposited and dried on a copper grid. A scanning electron microscope (SEM) (JEOL JSM-7500F) was also used for confirming the sizes and morphologies of nanoparticles. The crystalline structure of the nanoparticles was detected by powder X-ray diffraction (XRD) (Bruker D8 Advance) with Cu supplying Kα radiation.

2. Experimental results

2.1 Synthesis of carbamic acid ammonium salts

The gaseous CO_2 in a balloon was bubbled into the liquid amine (20 mmol) which has been added to a reaction tube. The reaction is slightly exothermic. After about 5 min, the corresponding carbamic acid ammonium salt was synthesized as white solid.

2.2 Synthesis of magnetic nano-ferrites

In a 1000 mL beaker, $FeSO_4\cdot7H_2O$ (13.9 g) and $Fe_2(SO_4)_3$ (20 g) were dissolved in 500 mL water. Ammonium hydroxide (25 wt%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 60 ^{o}C. The precipitated nanoparticles were separated magnetically, washed with water until the pH reached 7, and then dried under vacuum at 60 ^{o}C for 2 h. This magnetic nano-ferrite (Fe_3O_4) was then used for further surface chemical modification.

2.3 Synthesis of magnetic FeDOPA

Nano-Fe_3O_4 (2 g) was dispersed in 25 mL water by sonication for 30 min. Dopamine hydrochloride (1 g) dissolved in 5 mL of water was added to this solution and sonicated for another 2 h. The amine-functionalized nanomaterial FeDOPA was then precipitated using acetone, isolated by centrifugation, and dried under vacuum at 60 °C for 2 h.

2.4 Synthesis of the catalyst FeDOPACu

The synthesized FeDOPA (1 g) was dispersed in water-methanol mixture (1:1). $CuCl_2 \cdot 2H_2O$ (0.1 g) solution in water was added to the reaction mixture. Hydrazine monohydrate solution in water was added dropwise to bring the pH of this mixture to 9, followed by the addition of 0.1 g of $NaBH_4$. Then the reaction mixture was stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and dried under vacuum at 60 °C for 2 h.[1]

2.5 Typical route for the synthesis of oxazolidin-2-ones

The copper catalyst (10 mol%), additive (10 mol%), solvent (0.2 mL), alkyne (2 mmol), aldehyde (2 mmol), and carbamate salt (1 mmol) were added to a 8 mL reaction tube equipped with magnetic stir bar. The reactions were carried out in screw cap vials with a Teflon seal at 100 °C for certain time. The reaction mixture was settled to cool to room temperature and the catalyst was separated by an external magnetic. The crude reaction mixture was further purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the desired product oxazolidin-2-ones.

2.6 Characterization of the catalysts

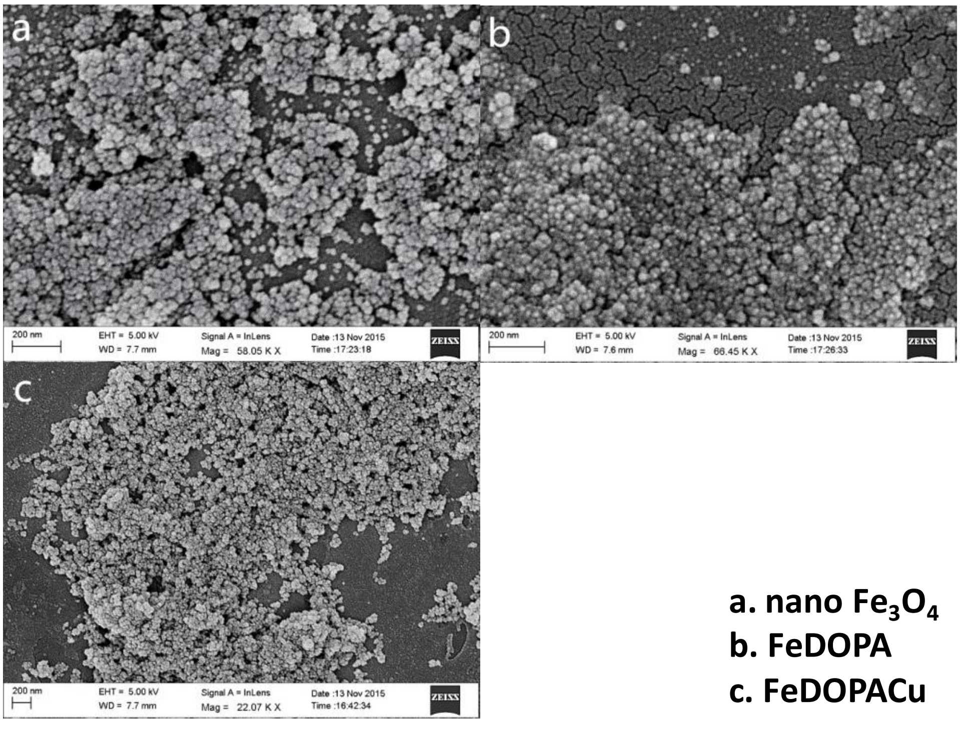
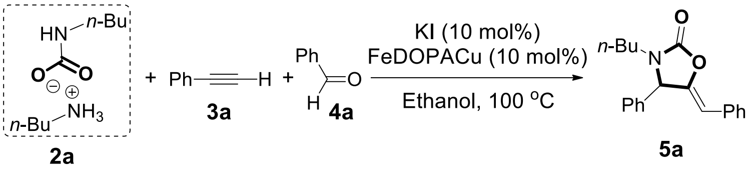


Figure S1 The scanning electron microscopy (SEM) images of: (a) bare nano Fe_3O_4, (b) FeDOPA, (c) FeDOPACu

Table S1 Recyclability of nano-FeDOPACu.[a]

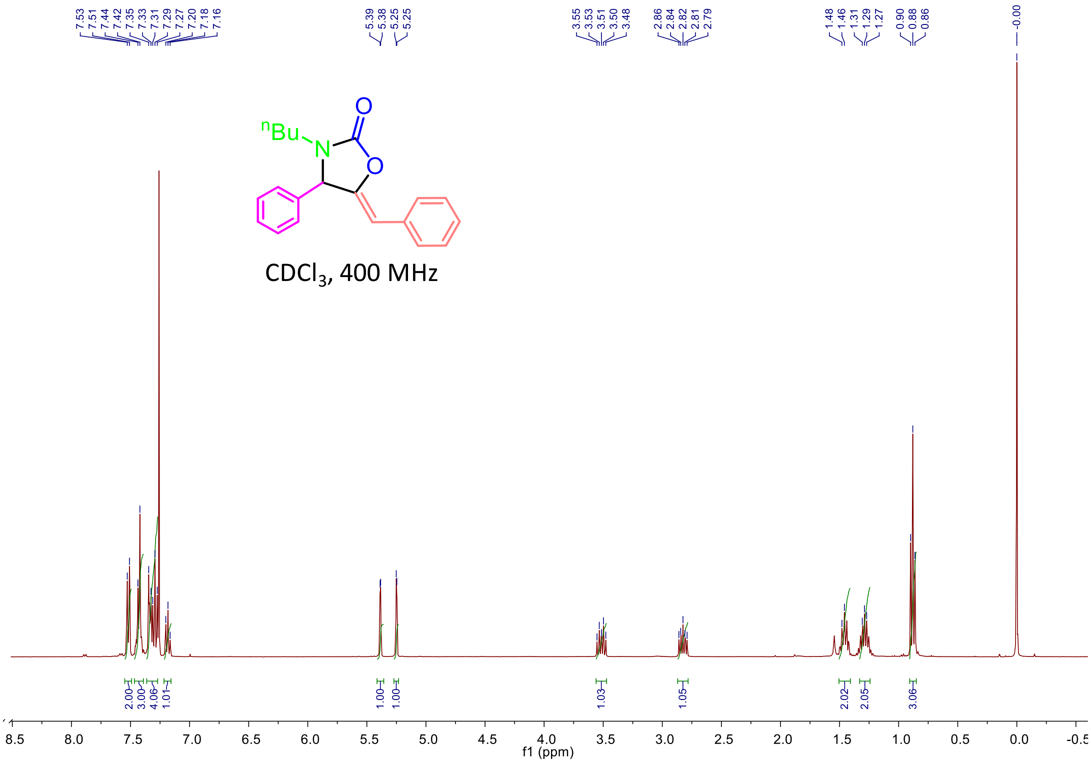


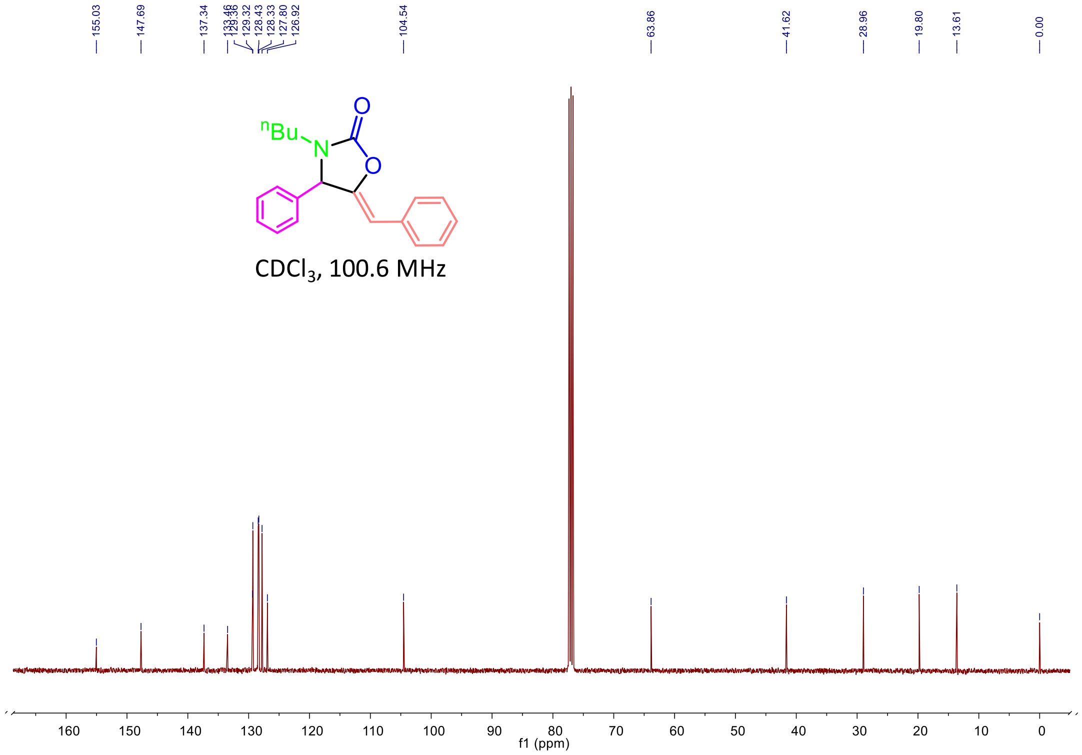
Cycle	Time [h]	Yield [%][b]
1st	4	99
2ed	4	82
3rd	5	83
2ed[c]	4	17

[a] *Reaction conditions:* Carbamic acid ammonium salts (1 mmol), aldehyde (2 mmol), alkyne (2 mmol), EtOH (0.2 ml), 100 °C. [b] The yields were determined by GC with biphenyl as the internal standard. [c] No KI was added in this second cycle reaction.

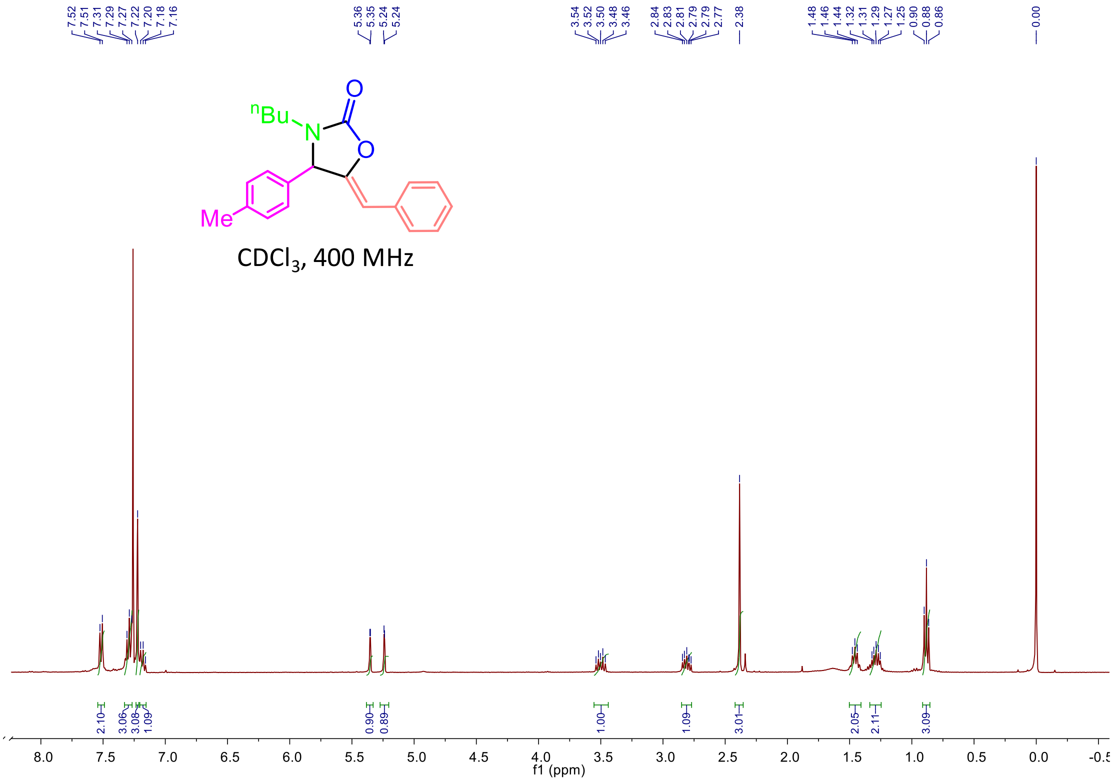
3. NMR Spectra

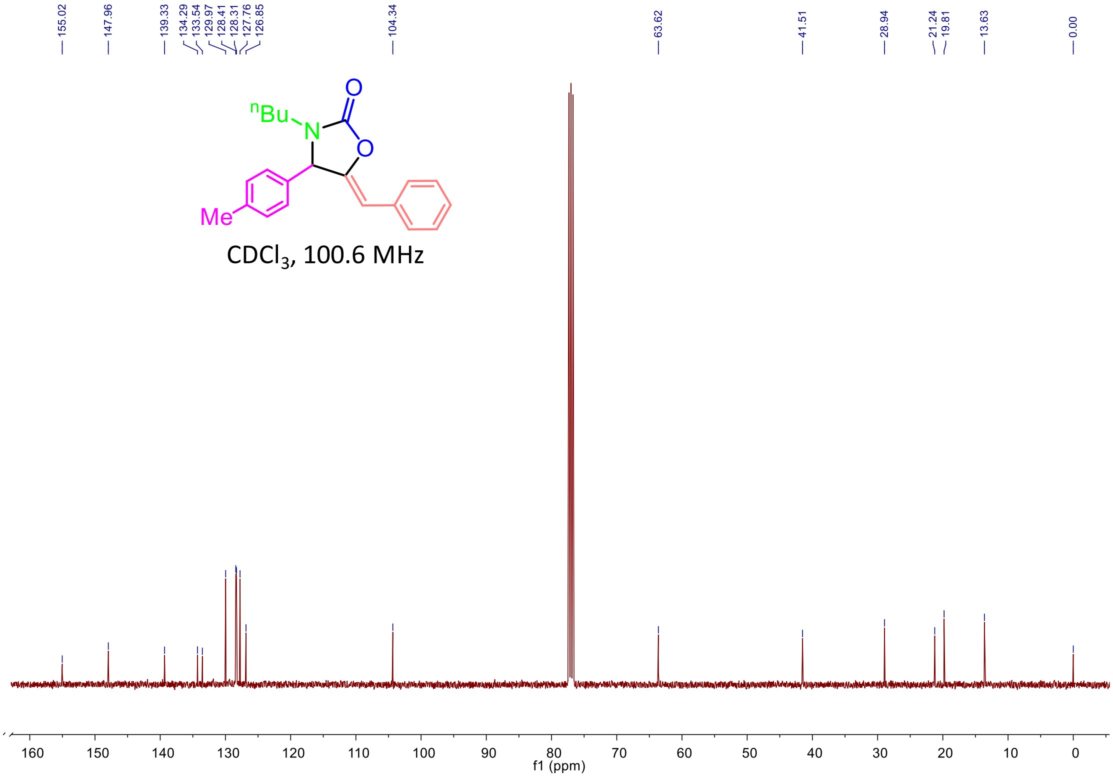
^{1}H NMR and ^{13}C NMR of compound **5a**



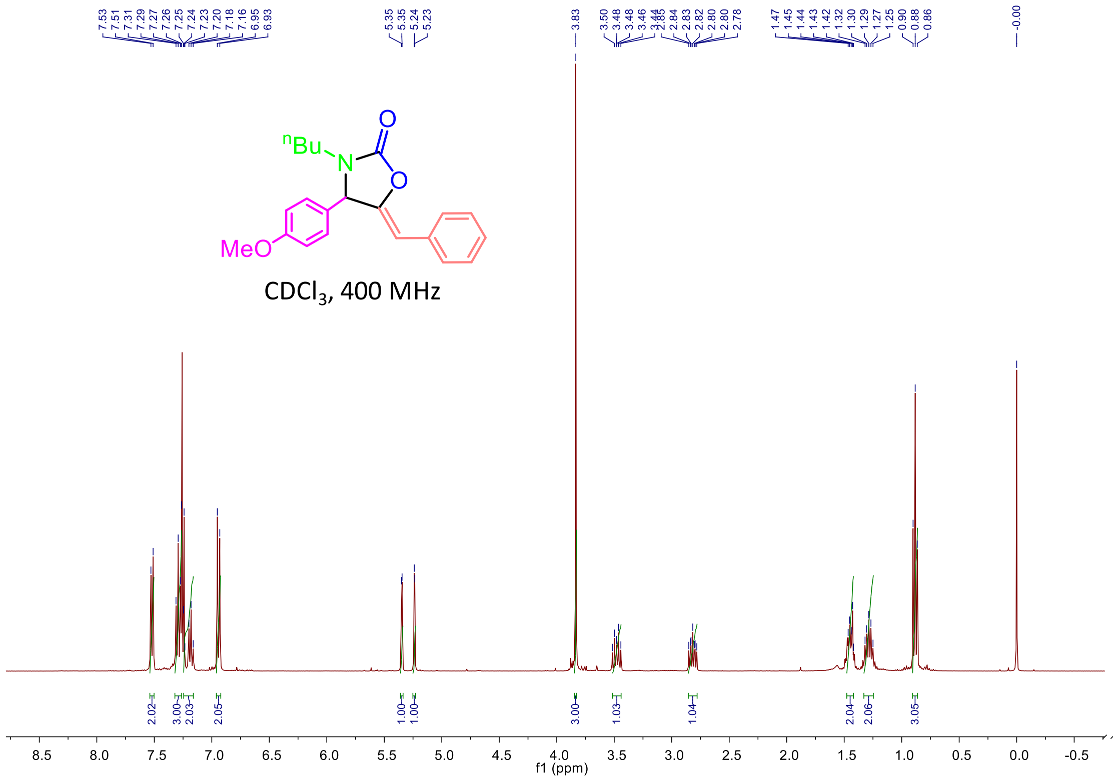


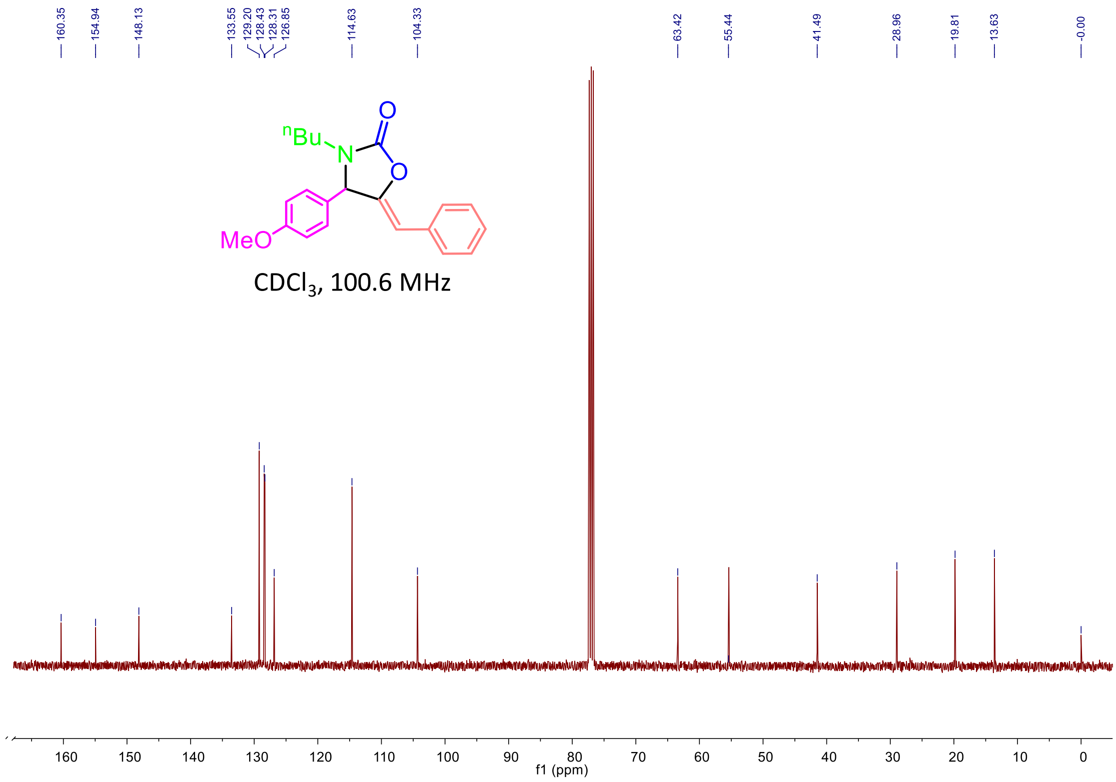
^{1}H NMR and ^{13}C NMR of compound **5b**



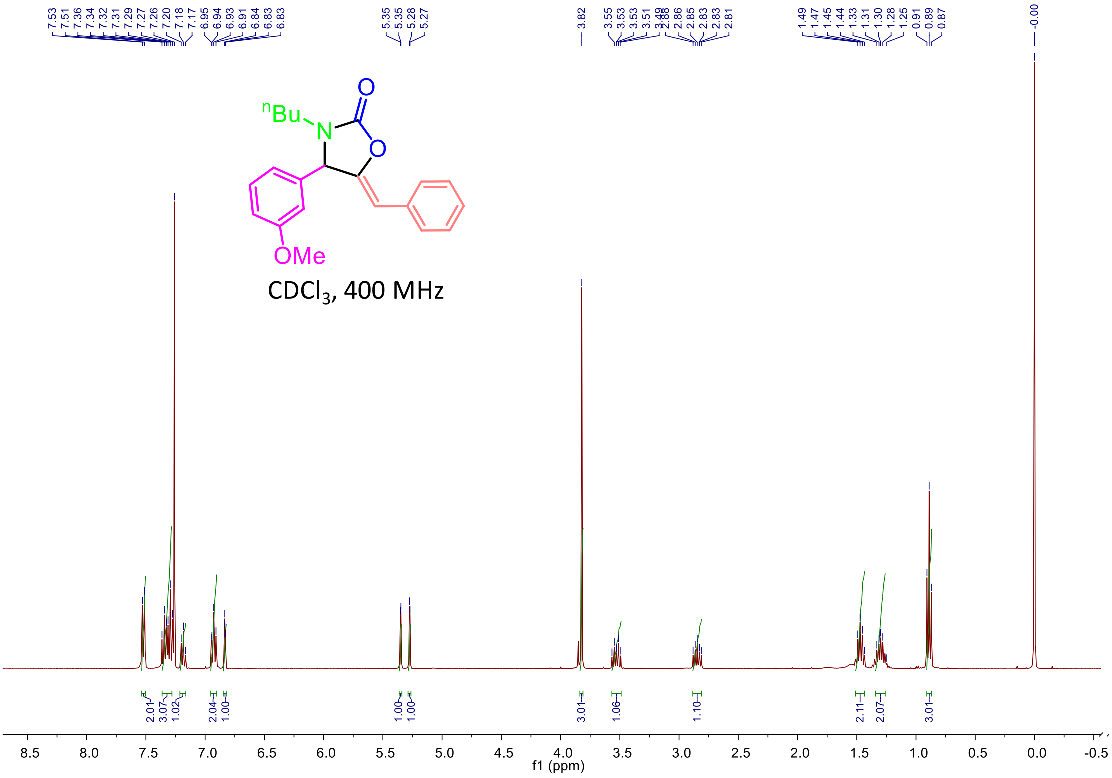


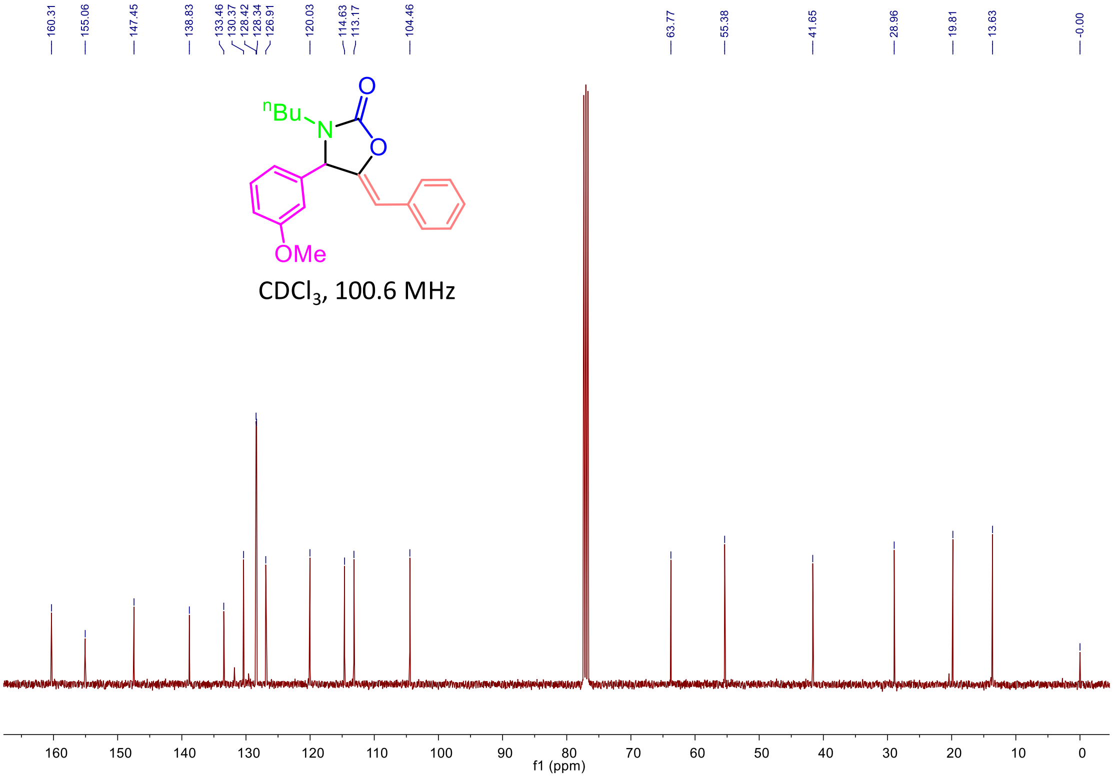
^{1}H NMR and ^{13}C NMR of compound **5c**



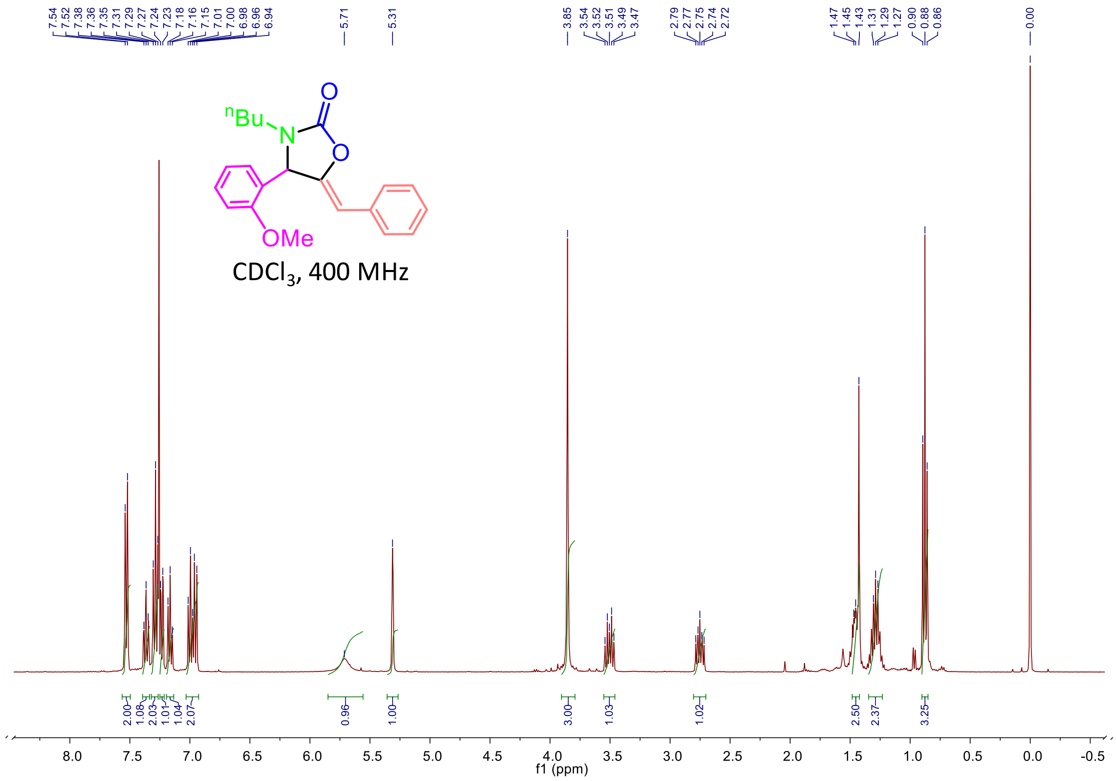


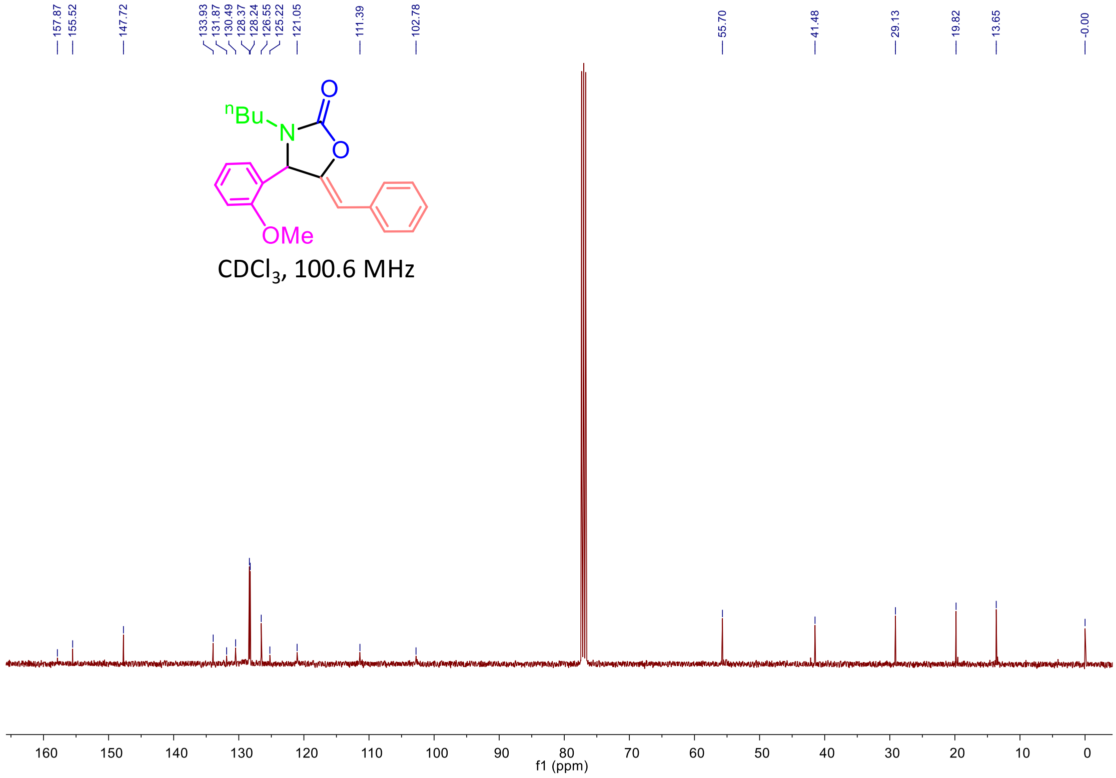
^{1}H NMR and ^{13}C NMR of compound **5d**



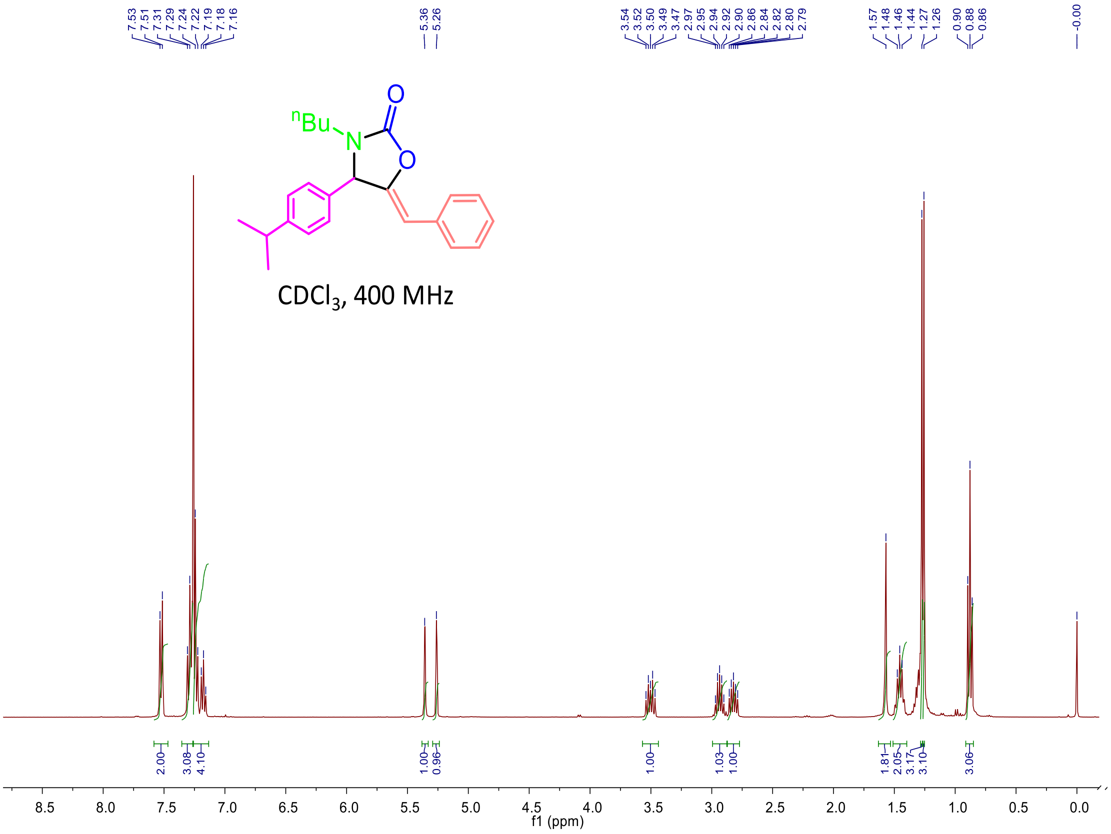


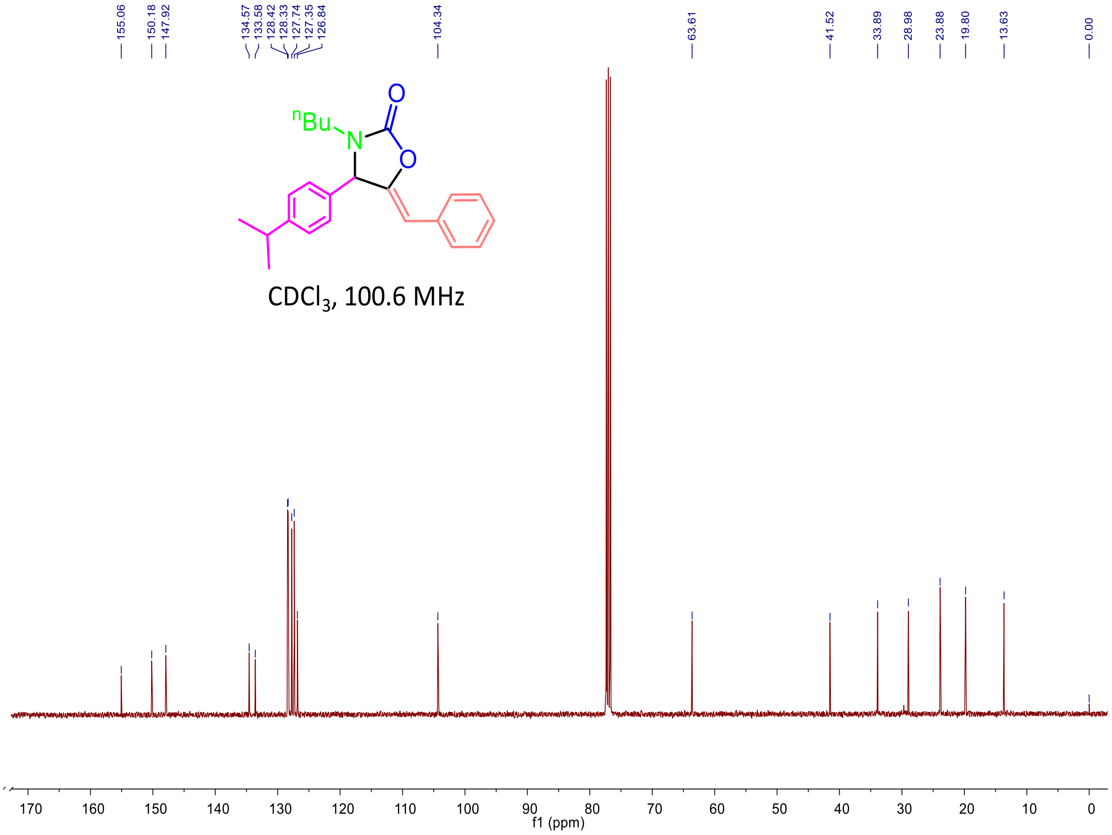
^{1}H NMR and ^{13}C NMR of compound **5e**



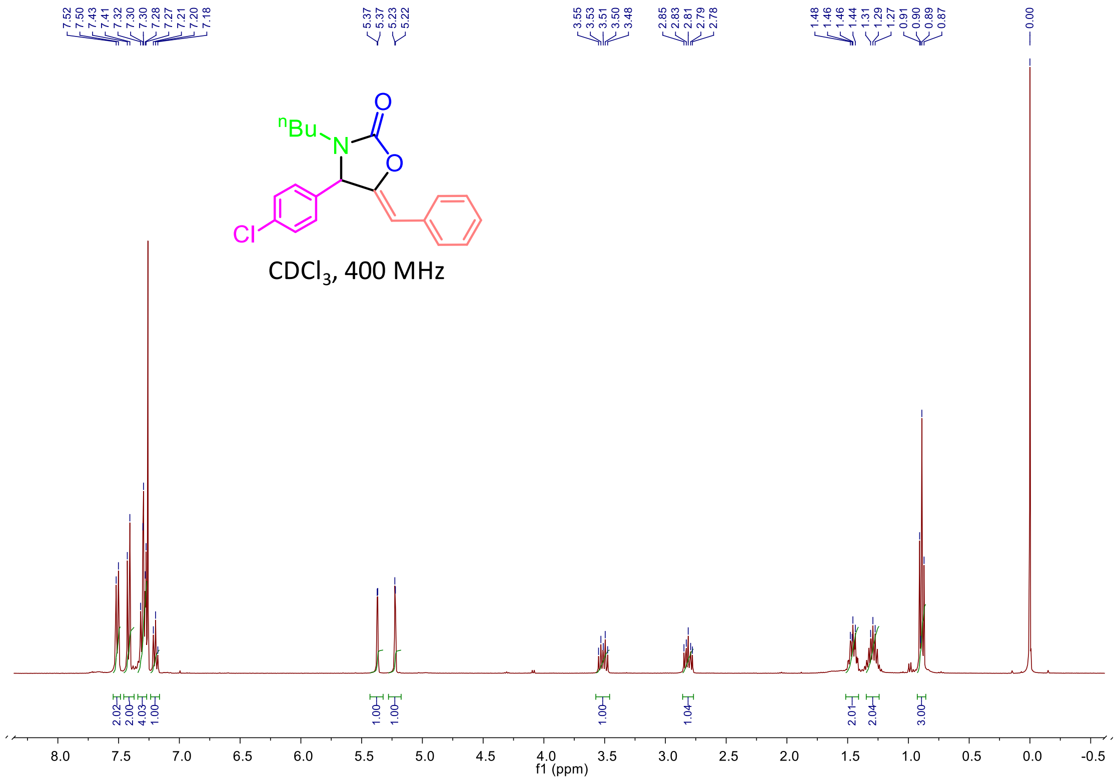


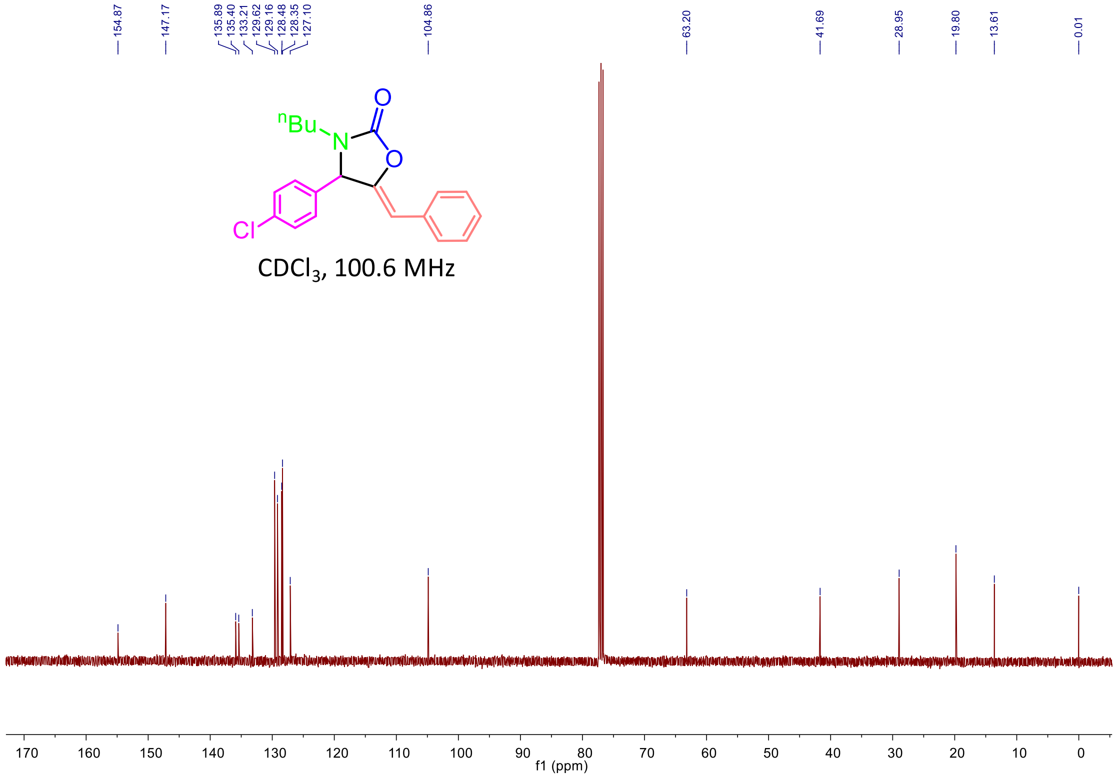
^{1}H NMR and ^{13}C NMR of compound **5f**



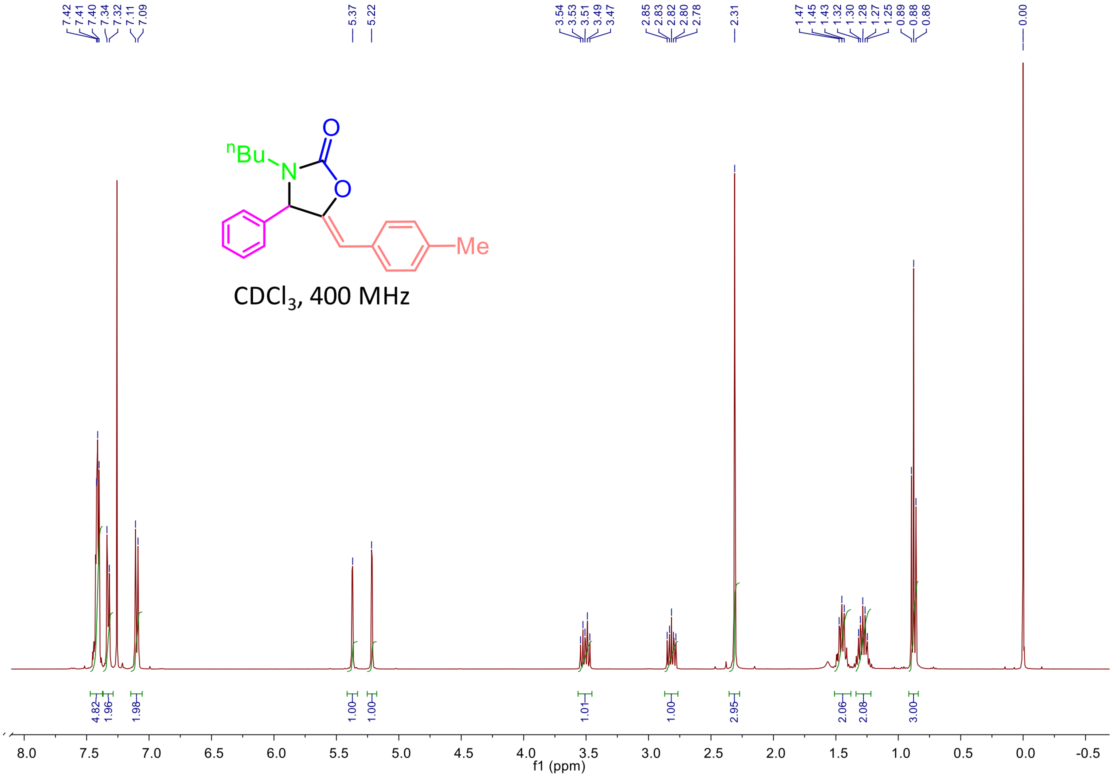


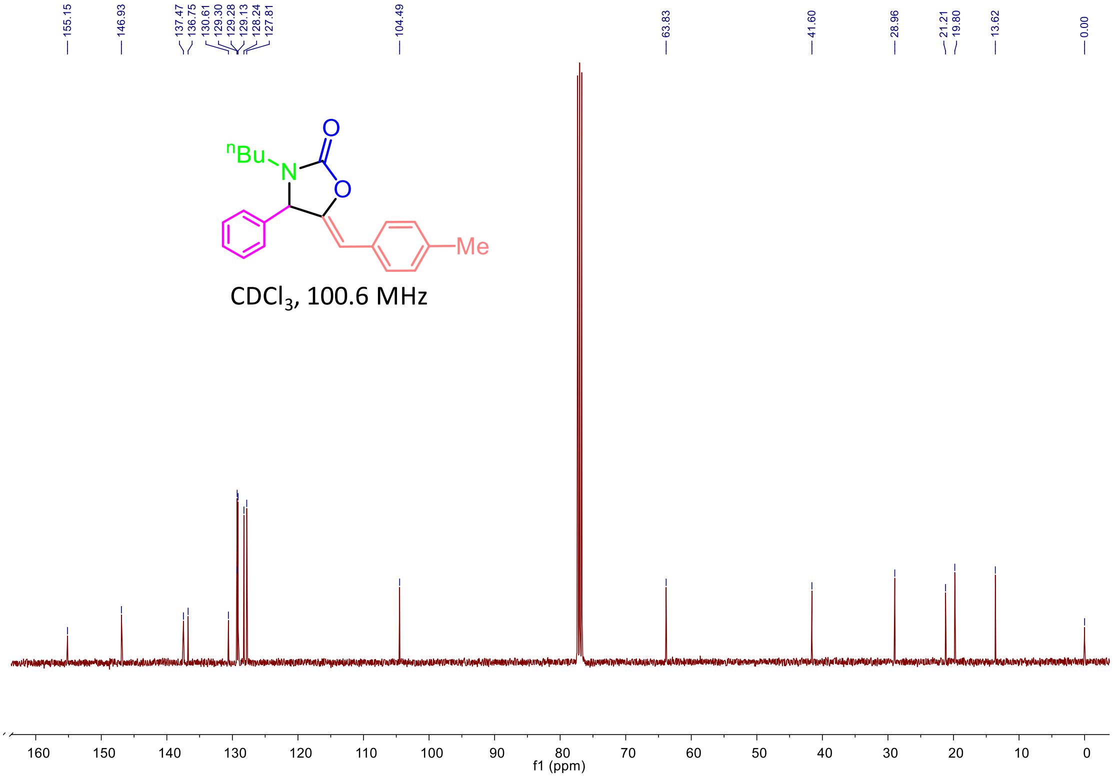
^{1}H NMR and ^{13}C NMR of compound **5g**



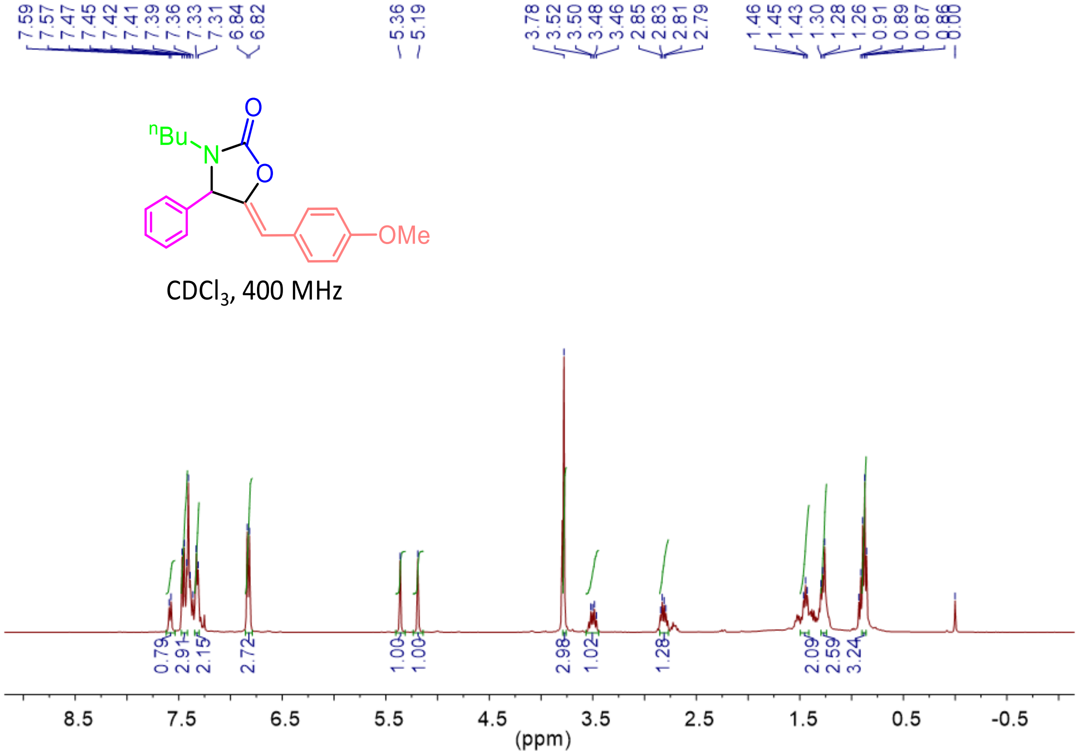


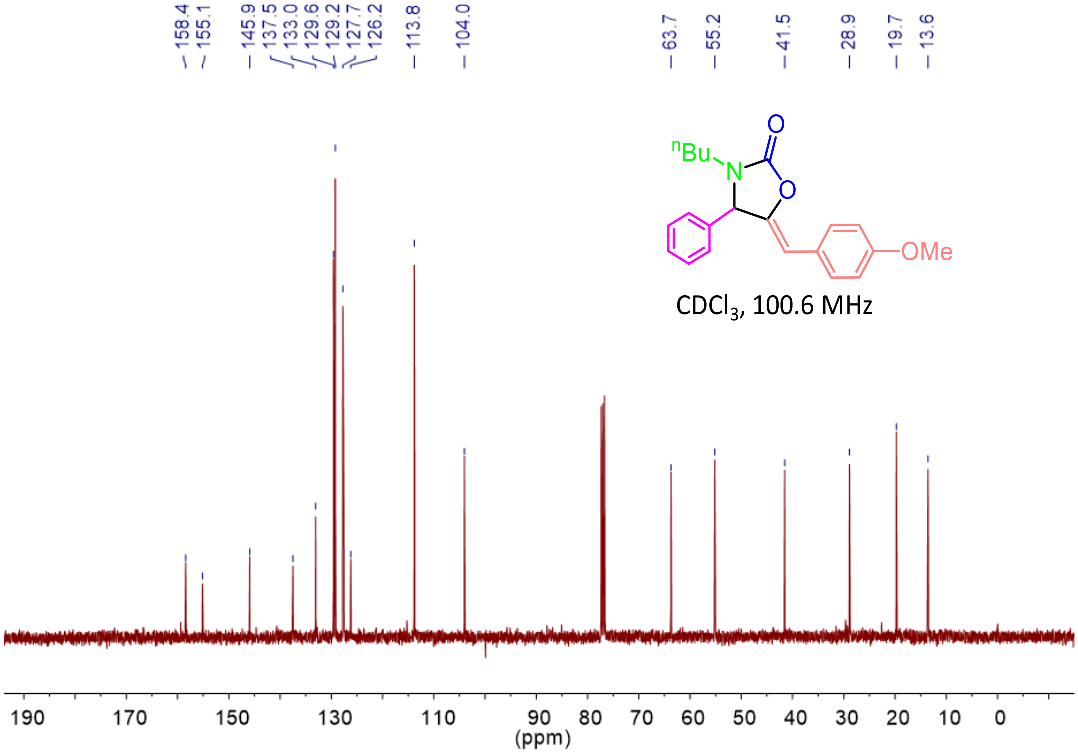
^{1}H NMR and ^{13}C NMR of compound **5h**



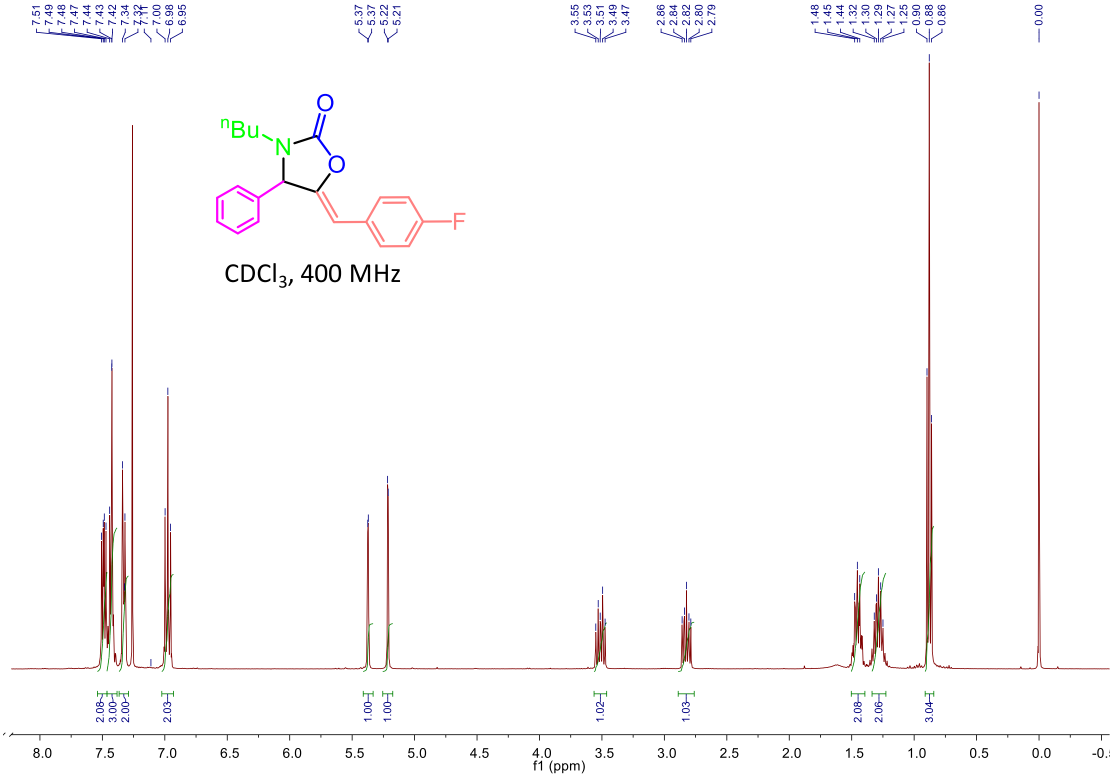


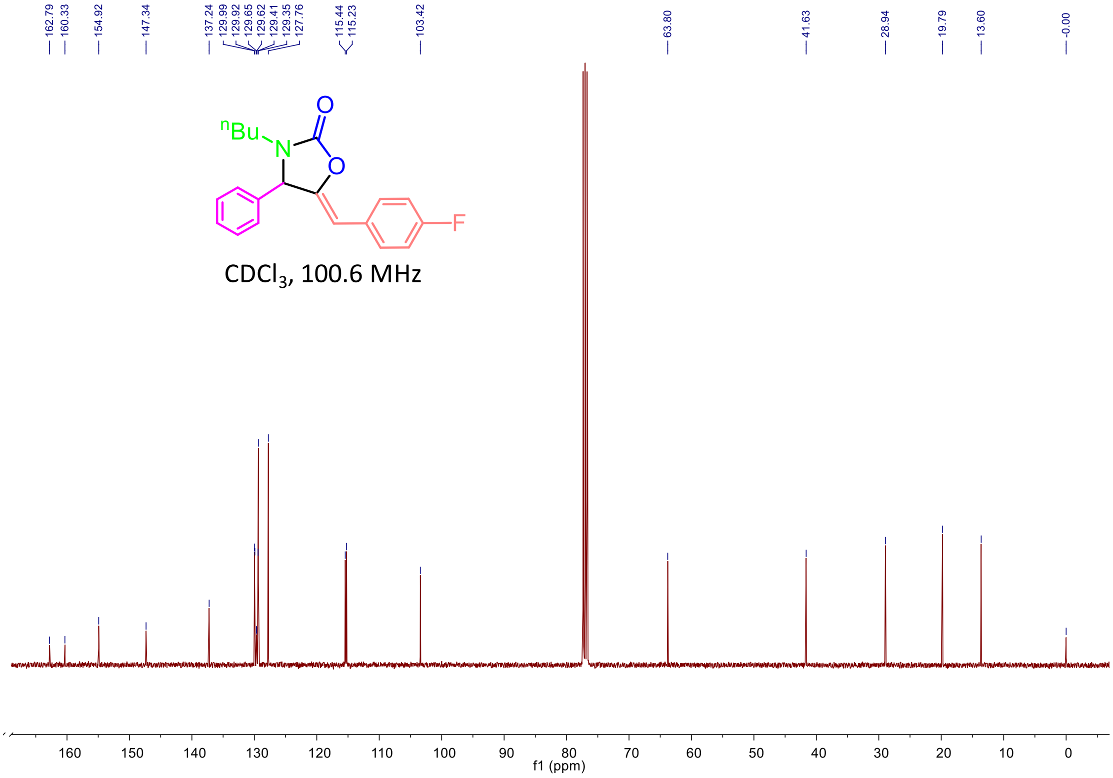
^{1}H NMR and ^{13}C NMR of compound **5i**



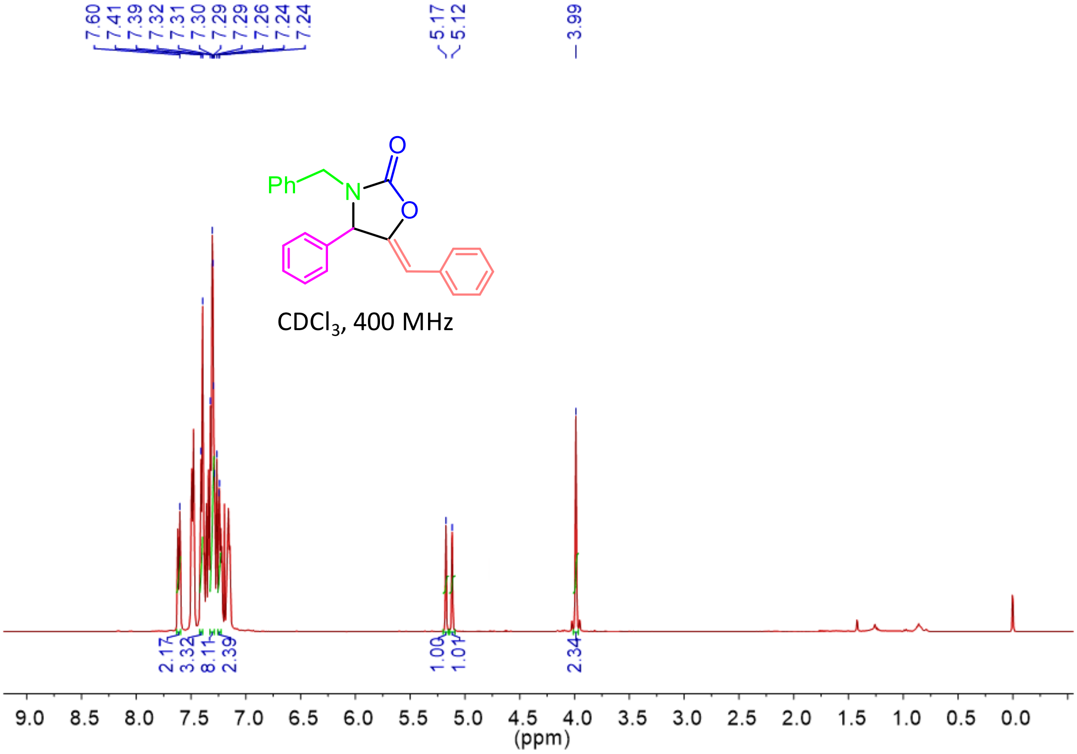


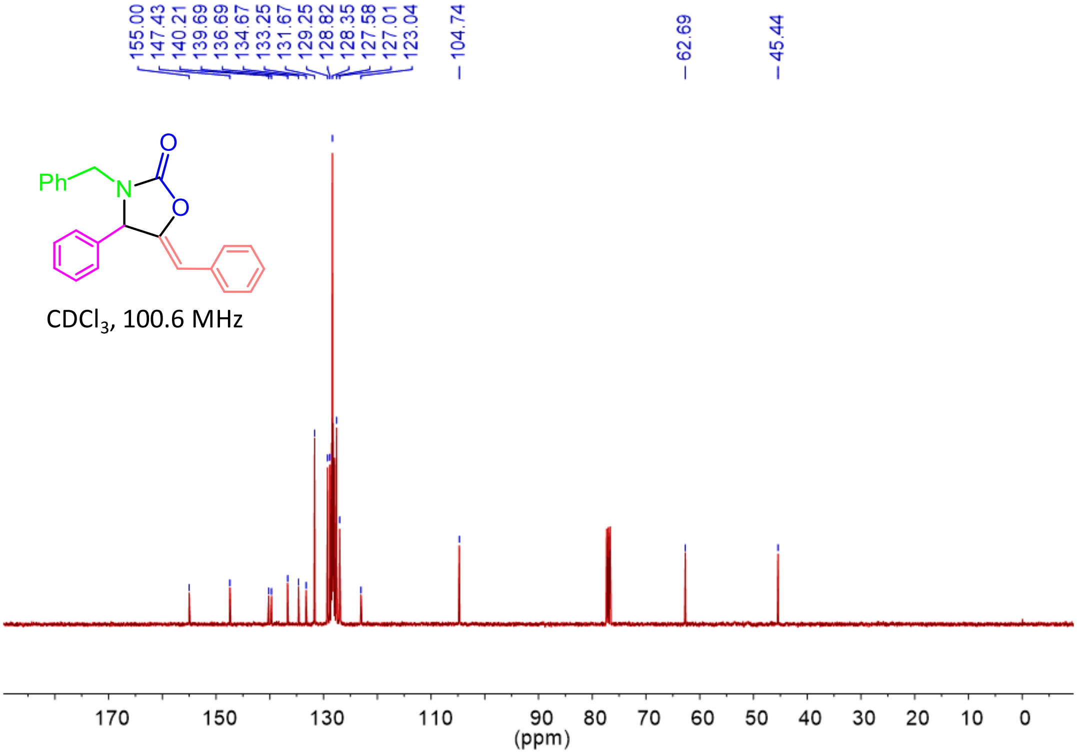
^{1}H NMR and ^{13}C NMR of compound **5j**



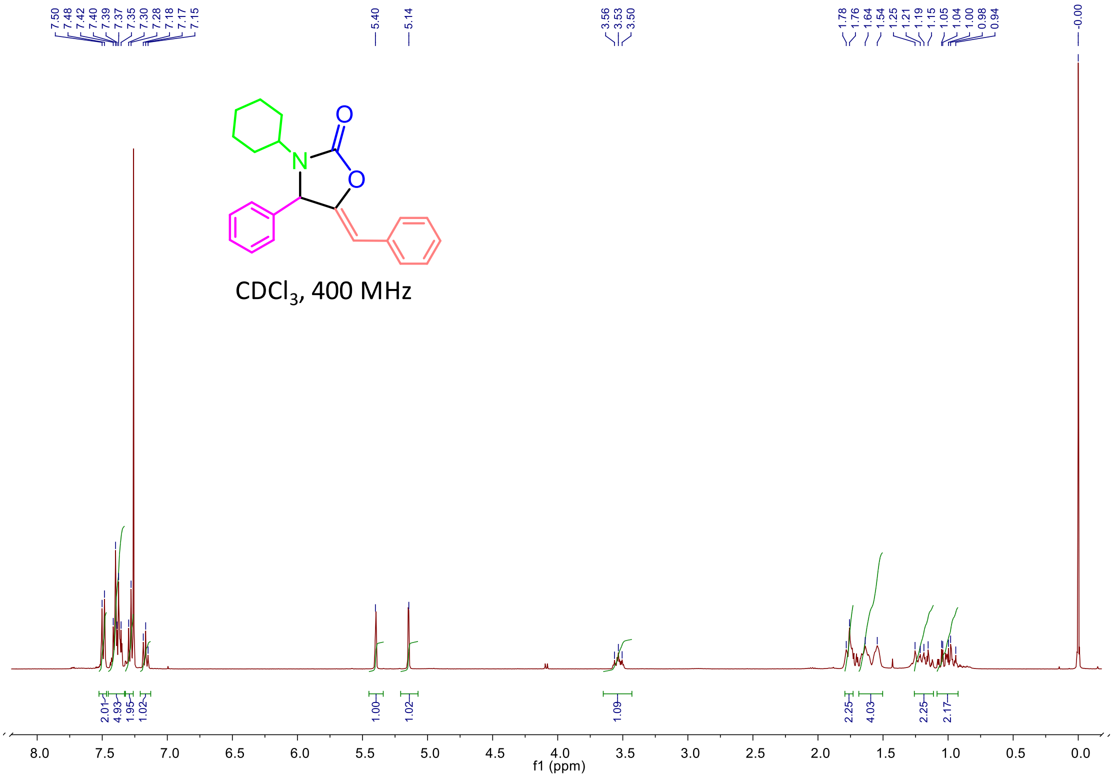


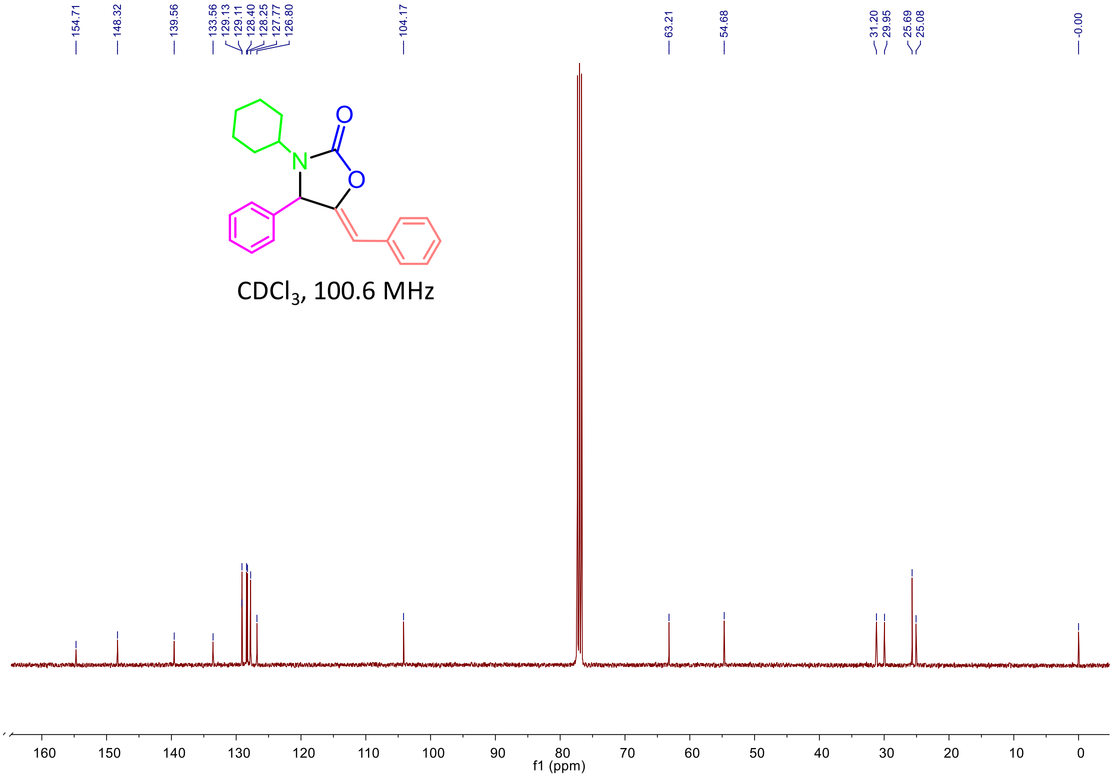
^{1}H NMR and ^{13}C NMR of compound **5k**



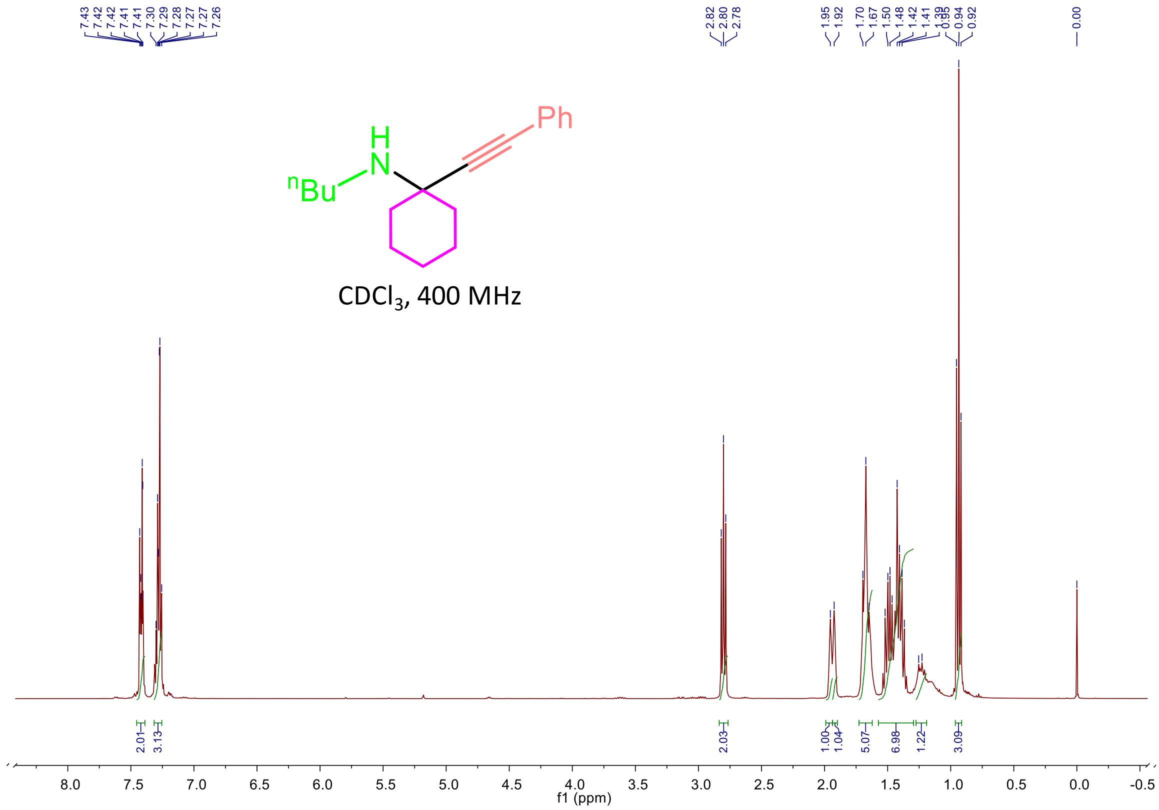


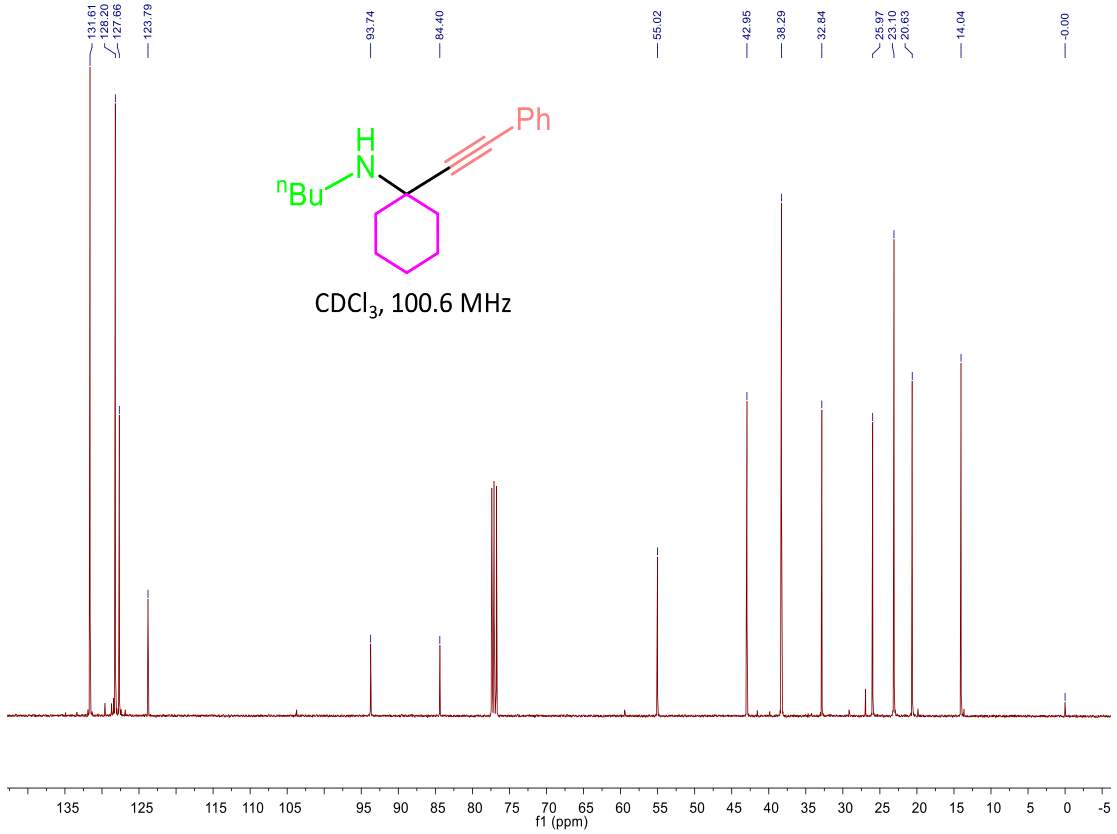
^{1}H NMR and ^{13}C NMR of compound **5l**





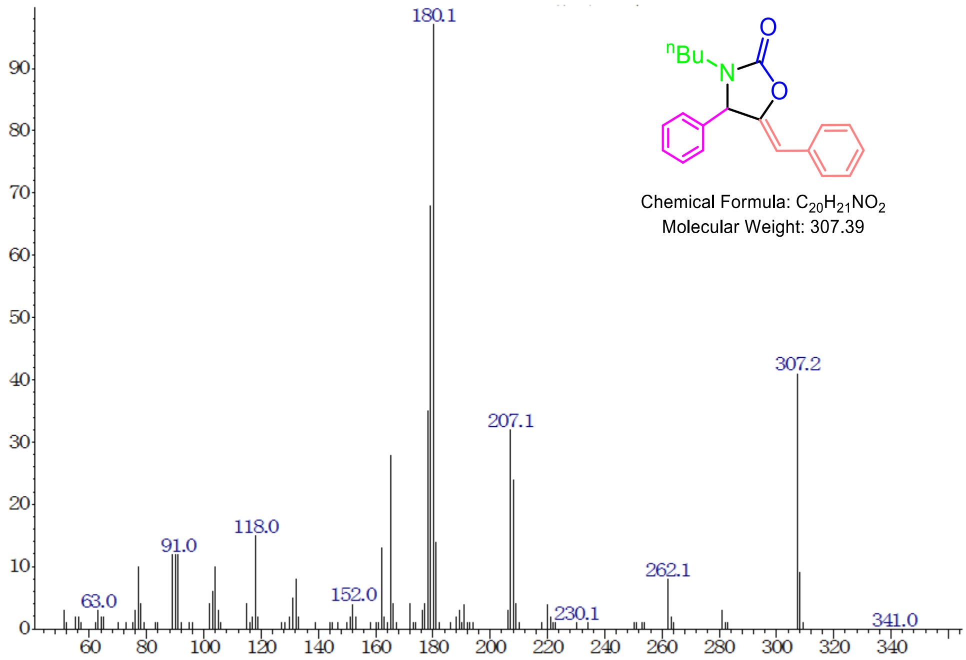
^{1}H NMR and ^{13}C NMR of compound **7a**



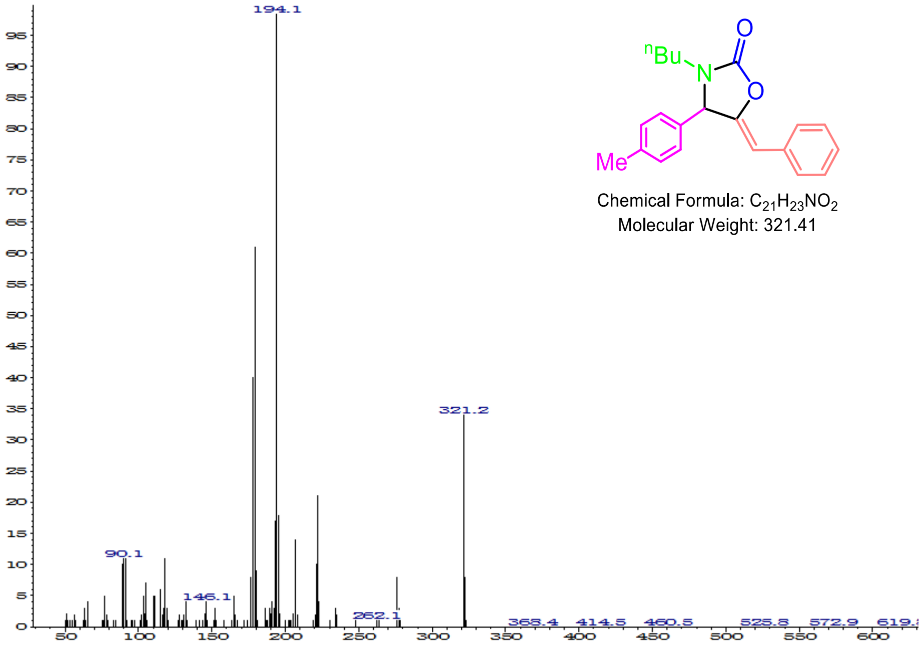


4. EI-MS Spectra

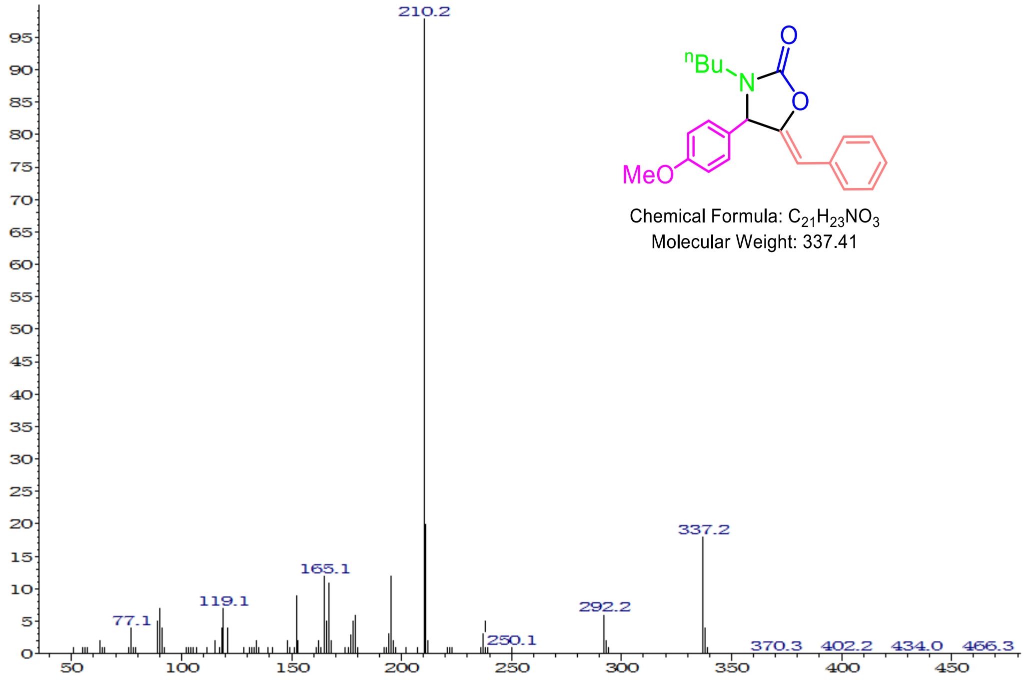
EI-MS spectra of compound **5a**



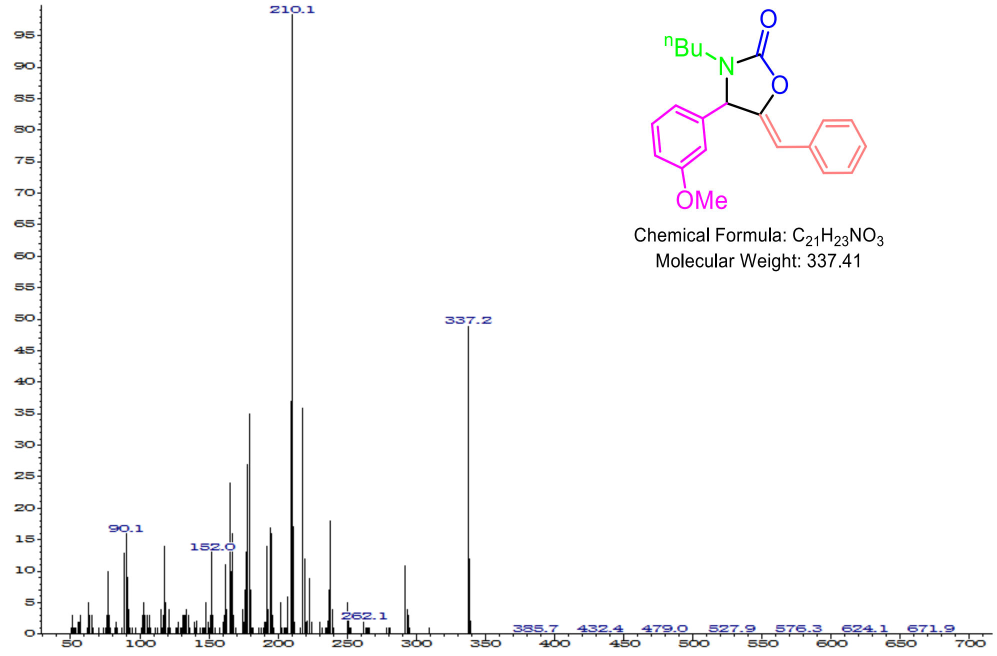
EI-MS spectra of compound **5b**



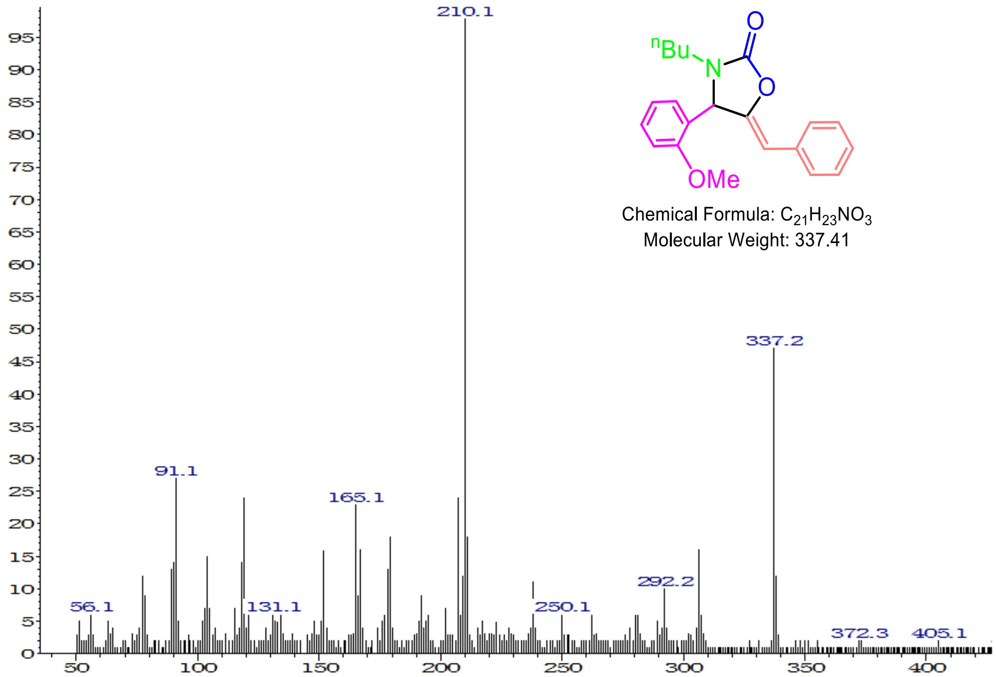
EI-MS spectra of compound **5c**



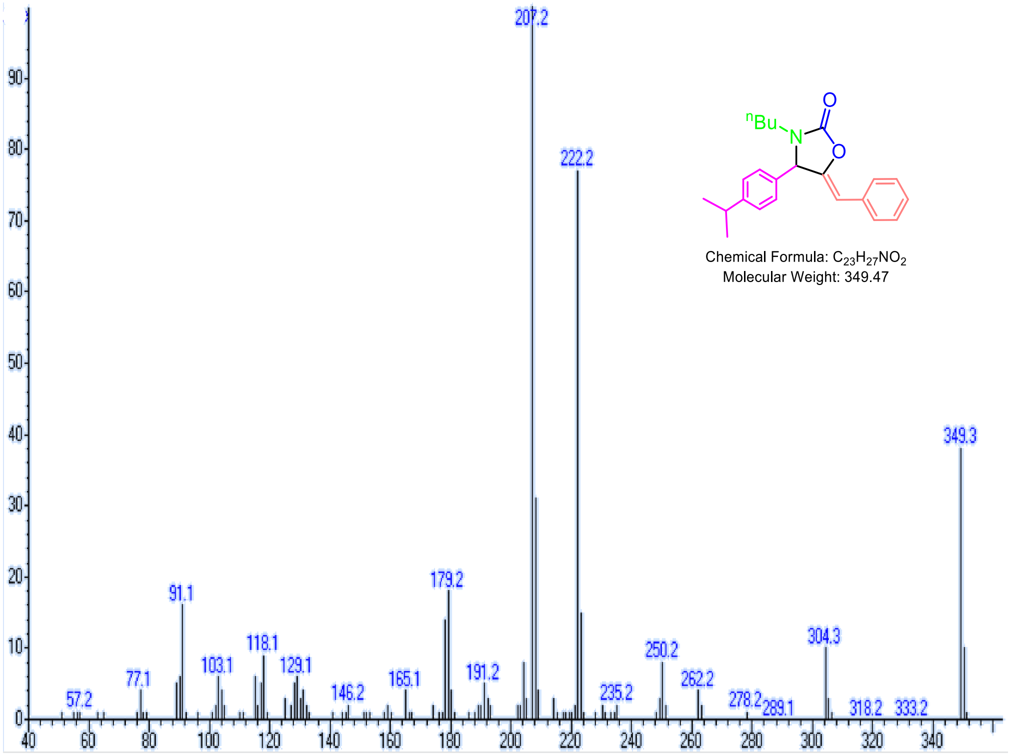
EI-MS spectra of compound **5d**



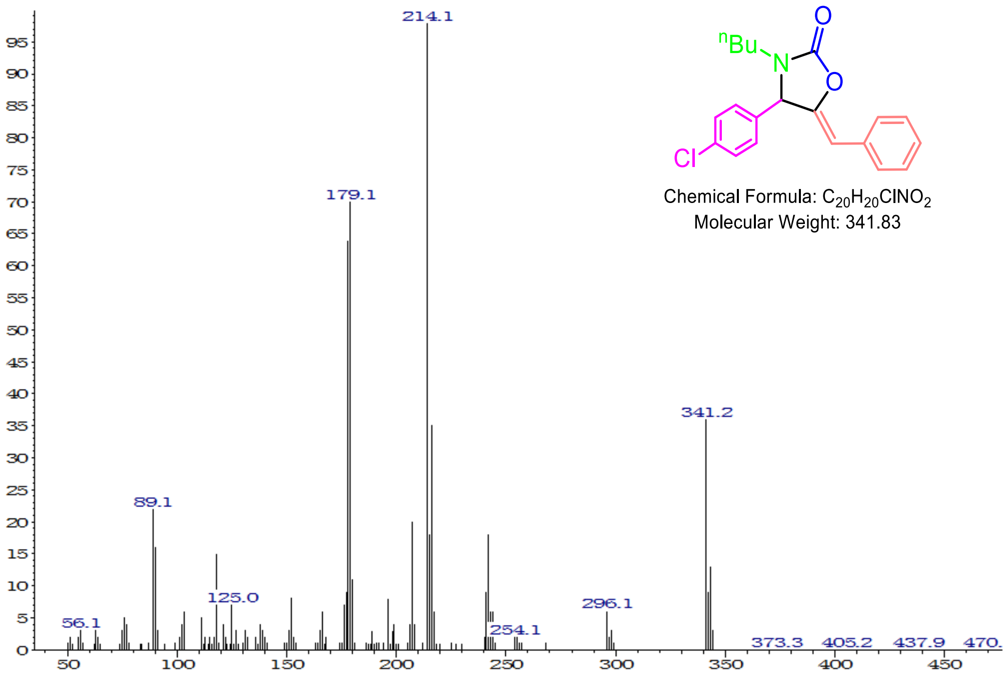
EI-MS spectra of compound **5e**



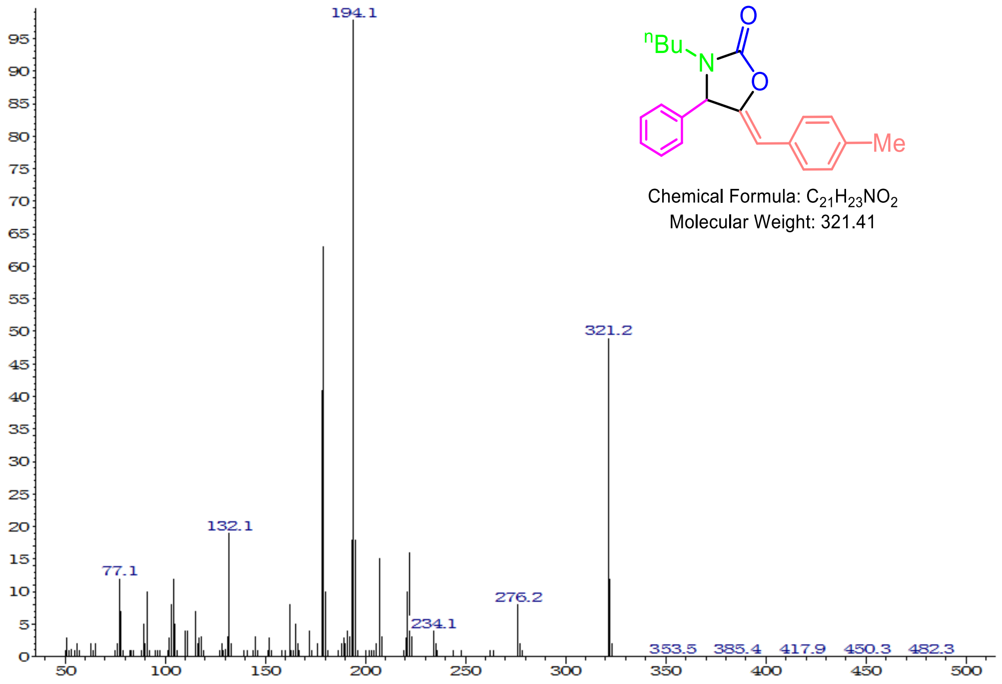
EI-MS spectra of compound **5f**



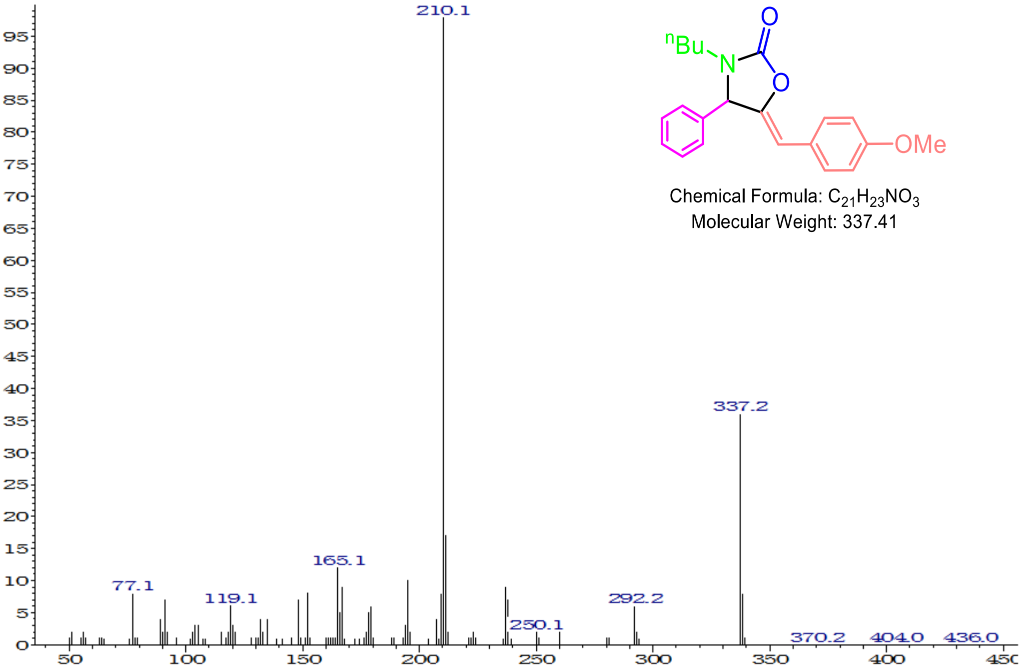
EI-MS spectra of compound **5g**



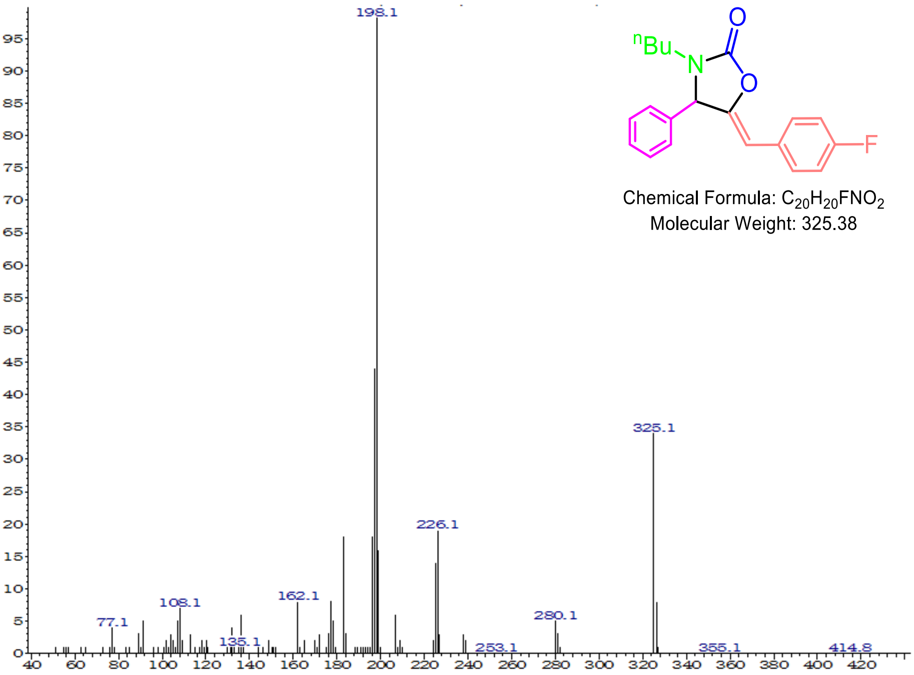
EI-MS spectra of compound **5h**



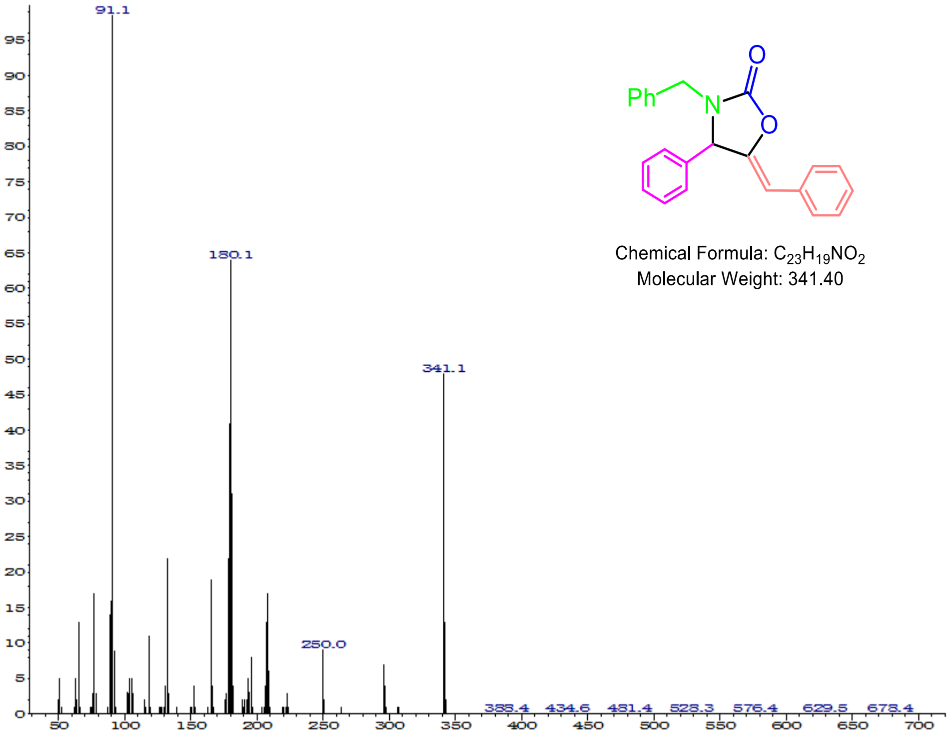
EI-MS spectra of compound **5i**



EI-MS spectra of compound **5j**



EI-MS spectra of compound **5k**



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Molecular Weight: 341.40

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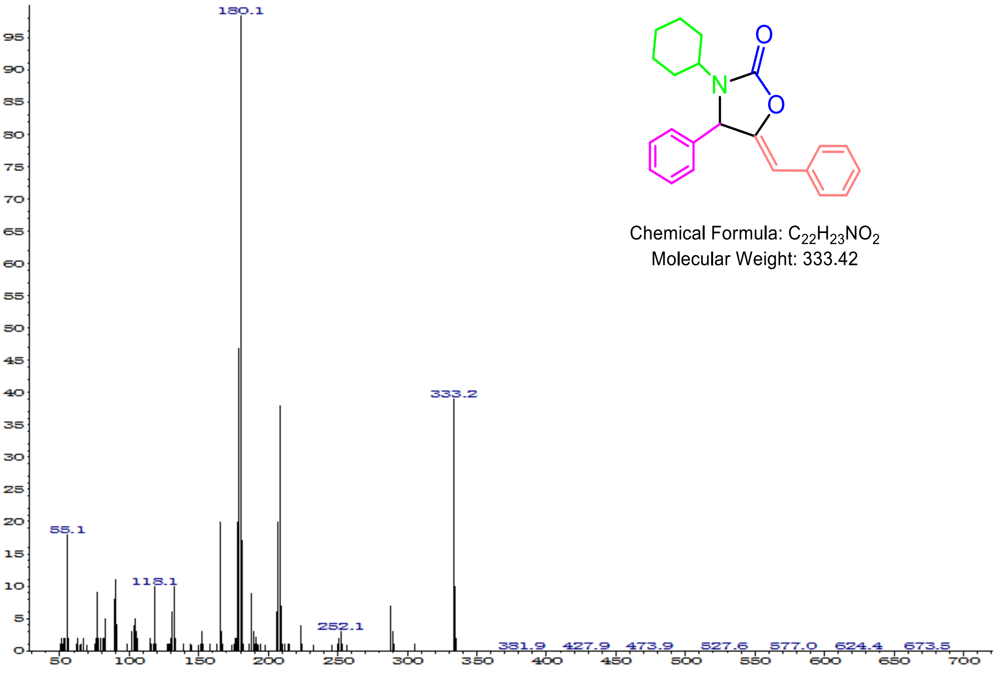

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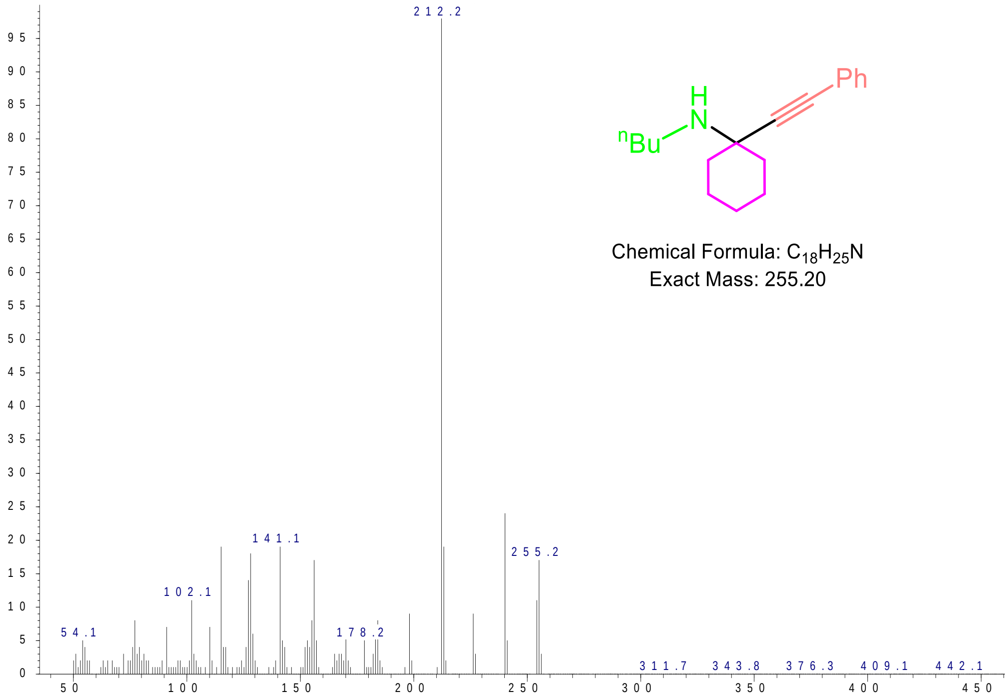
Molecular Weight: 333.42

EI-MS spectra of compound **7a**



1 R. B. Baig and R. S. Varma, *Chem Commun*, 2012, **48**, 2582-2584.