SUPPORTING INFORMATION

Synthesis of 1,2-oxazetidines with free -NH group via photoredox catalysis

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1. General information

All reactions were carried out in oven-dried glassware. The solvents used were purified by distillation. All reactions were irradiated using a blue light-emitting diode (LED)s purchased from the market (Manufacturer: GM Modular, Model: Zodion 5050SMD; 60 LEDs per meter, 14 Lumens per LED, 12V strip Light at 460 nm). ^{1}H and ^{13}C NMR spectra were recorded on FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. ^{19}F NMR spectra are not calibrated by an internal reference. Coupling constants (*J*) are quoted in Hz. Mass spectra were obtained by using Q-TOF-LC/MS spectrometer using electron spray ionization.

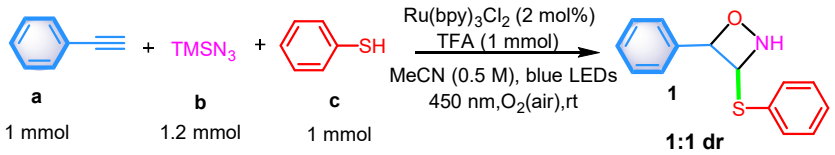
Note: Institutional Publication Number : CSIR-IIIM/IPR/00434

2. Synthesis of substituted oxazetidines

To an oven-dried 30 ml glass vial, containing starting compounds $Ru(bpy)_3Cl_2$ (2 mol%), alkyne (0.98 mmol) in CH_3CN, was added trimethylsilyl azide (1.17 mmol), thiophenol (0.98 mmol) and trifluoroacetic acid (0.98 mmol) with continuous stirring under air. The reaction mixture was then irradiated under blue light sourced from blue LED strips (40 mW/cm^2 at 460 nm). After the completion of the reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under a vacuum. The crude mixture was purified by silica gel colum chromatography to obtain product **1** as a yellow color oil (161 mg, 66% yield) using hexane/ethyl acetate as a solvent system.

3. Table S1. Optimization of Reaction Conditions[a]

We initiated our investigations by irradiating a mixture of phenylacetylene **a** (1 mmol), $TMSN_3$ **b** (1.2 mmol), and thiophenol **c** (1 mmol) as model substrates in the presence of $Ru(bpy)_3Cl_2$ as photocatalyst in CH_3CN under blue LEDs (Table **1**, entry **1**). The reaction led to the formation of oxazetidine **1** in 66% yields.

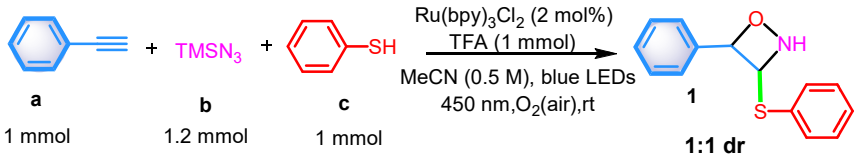


entry	Deviation from standard conditions	Yield (%) 1
1	none	66
2	Eosin-Y instead of $Ru(bpy)_3Cl_2$	20
3	Mes-Acr^+ BF_4^- instead of $Ru(bpy)_3Cl_2$	5
4	Rose-Bengal instead of $Ru(bpy)_3Cl_2$	traces
5	CH_3OH, DMF, THF instead of ACN	traces
6	DMSO, DCE instead of ACN	n.d
7	no photocatalyst, light, or TFA	n.d.

[a]Reaction conditions: phenylacetylene (1 mmol), thiophenol (1 mmol), $TMSN_3$ (1.2 mmol), TFA (1 mmol), photocatalyst (2 mol%), ACN (2ml), Blue LEDs, 12h.

Furthermore, the reaction in the presence of different photocatalysts eosin-Y, mesityl acridinium tetrafluoroborate (Mes-Acr^+ BF_4^-), and Rose-Bengal gave the product in lower yields (Table **1**, entries **2-4**). The change of solvent to CH_3OH, DMF, and THF led to the drop in the yields, and there was no product formation in DMSO and DCE (Table **1**, entry **6**). Besides, traces of the

product were observed in the absence of TFA, photocatalyst, and light, thereby highlighting their importance (Table **1,** entry **7**).Moreover,among the various acids screened TFA gave the best results.



Entry	Acids	Equiv.	Yields%
1	CF_3COOH	1	66
2	HCOOH	-	55
3	CH_3COOH	-	30
4	CF_3SO_3H	-	20
5	HCl	-	traces
6	H_2SO_4	-	traces

[a]Reaction conditions: phenylacetylene (1 mmol), thiophenol (1 mmol), $TMSN_3$ (1.2 mmol), TFA (1 mmol), photocatalyst (2 mol%), ACN (2ml), Blue LEDs, 12h

3. Photoredox Studies

The relative tendency of reactants towards the SET reaction of $[Ru(bpy)_3]Cl_2$ photocatalyst were examined (Figure **S1)**. The $[Ru(bpy)_3]Cl_2$ fluorescence quenching and corresponding Stern−Volmer plots depict reactant quenching in the order thiophenol (PSH)> phenylacetylene (PA) > TMS azide (Fig **S2)**

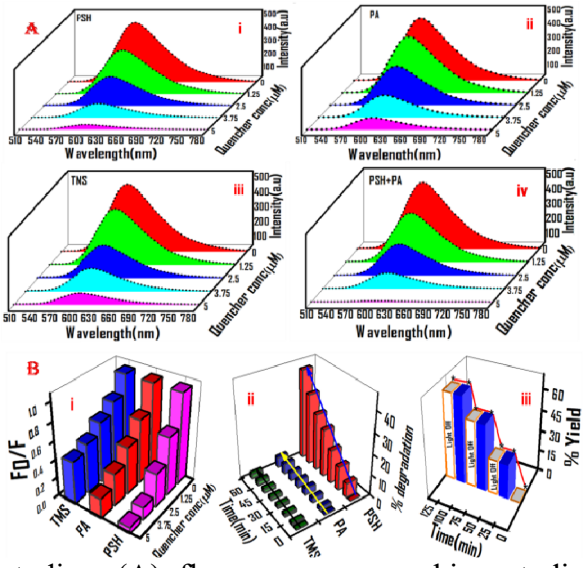


Figure S1. Photoredox studies: (A) fluorescence quenching studies of $[Ru(bpy)_3]Cl_2$ with reactants, (B) relative Stern-Volmer plots, absorption studies, and light on-off experiments

3.1. Luminescence Studies:

Fluorescence quenching studies were carried out using a fixed amount of $[Ru(bpy)_3]Cl_2$ and variable concentrations of reactants in MeCN at room temperature. The solutions were irradiated with blue LEDs light and the luminescence was measured at λ= 552 nm corresponding to the maximum emission wavelength of $[Ru(bpy)_3]Cl_2$ photocatalyst.Stern Volmer analysis of Fluorescence quenching data was attempted to calculate comparative quenching constants Figure S1 and the calculated values are summarized in Table S2. The calculated quenching constants were in good agreement with absorption results and further confirm thiophenol to be an effective reagent for starting a single electron transfer reaction with photoexcited $[Ru(bpy)_3]Cl_2$ catalyst. To observe the effect of other reaction ingredients on thiophenol quenching of $[Ru(bpy)_3]Cl_2$ catalyst, the approach of a ternary quenching system i.e. $Ru(bpy)_3Cl_2$ + PSH + reactant was designed. Among such ternary systems, $Ru(bpy)_3Cl_2$ + PSH + PA, showed positive feedback towards quenching thereby supporting the sequence of proposed mechanistic steps for the synthetic methodology.

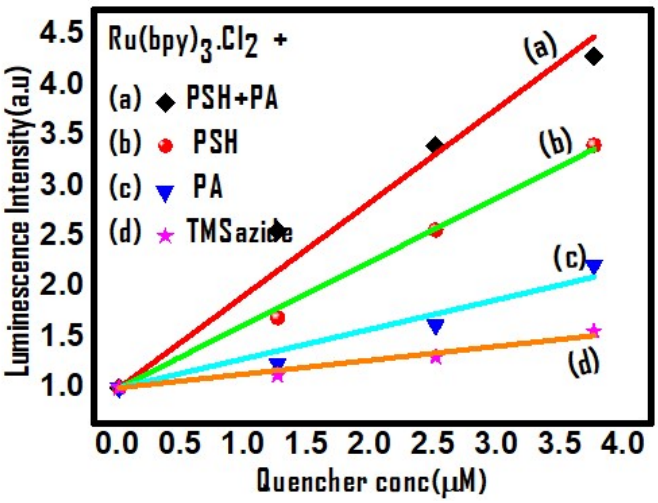


Figure S2. Comparative Stern Volmer plots for Luminescence quenching of photocatalyst with reactant combinations.

3.2. Absorption Studies:

Time-dependent absorption changes were monitored by adding uniform concentrations of thiophenol(PSH), phenylacetylene(PA), and trimethyl sodium azide(TMS) to the fixed concentration of photocatalyst $[Ru(bpy)_3]Cl_2$ in MeCN at room temperature. All these binary mixtures were kept under blue LED irradiation for 70 minutes and absorbances were recorded after every 10 minutes. Figure S2.The relative degradation data of $[Ru(bpy)_3]Cl_2$ by thiophenol(PSH),phenylacetylene(PA) and trimethyl sodium azide(TMS) solved in first order kinetics with the calculated first-order rate constant in the order: thiophenol > phenylacetylene > trimethyl sodium azide(TMS).This observed kinetic order can be corroborated with the relative propensity of reaction ingredients towards single electron transfer reaction with photoexcited $[Ru(bpy)_3]Cl_2$. From the data analysis of table S1 it can be seen that thiophenol is a major

reagent for such a single electron transfer reaction with excited photoexcited $[Ru(bpy)_3]Cl_2$ catalyst.

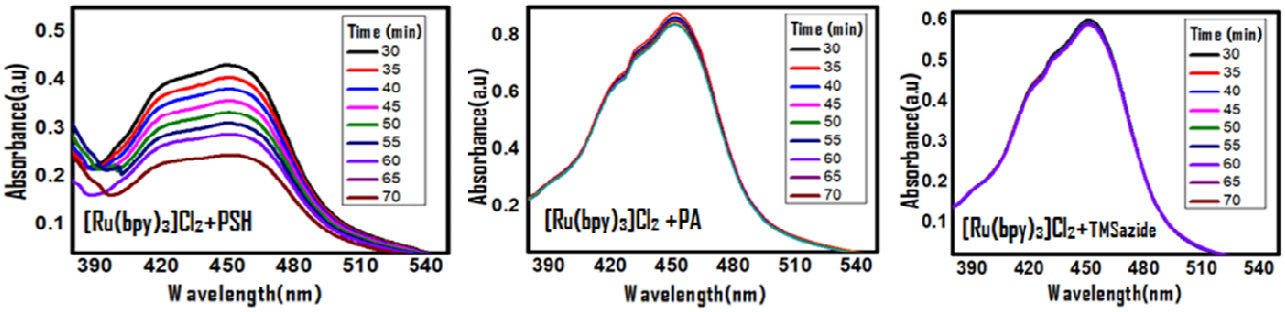


Figure S3. Kinetic plots for the photocatalytic degradation of $[Ru(bpy)_3]Cl_2$ with the reaction ingredients.

3.3. Cyclic Voltammetry Studies:

Electrochemical measurements were carried out with the glassy carbon as working, platinum wire as counter and Ag/AgCl(3M NaCl) as reference electrode, in CH_3CN solvent using NBu_4PF_6 as supporting electrolyte over a scan rate of 100 mV/s. The cyclic voltammogram's of individual reactants and their combinations were collected to observe changes in the peak pattern for corroboration with the absorption and luminescence data. Figure S3 Experimental data was analyzed by subtracting the electrolyte solution background current prior to identifying the peak current (Cp) and determining the potential ($E_{1/2}$) at half of its value (Cp/2). The calculated potentials were referenced to Ag/AgCl.

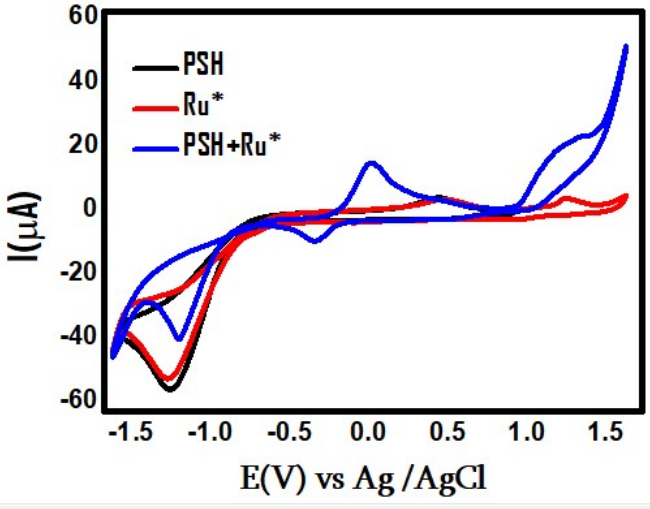


Figure S4. Cyclic voltammograms of photocatalyst with reactant combinations

As can be seen from CV plots, an oxidation and a reduction peak corresponding to $Ru(bpy)_3Cl_2$ catalyst were observed at 1.33 V and at –1.2 V respectively. Upon addition of 2 $x10^{-4}$ M of thiophenol (PSH), the CV plot of catalyst shows shifts in the oxidation peak (1.33 to 1.4 V) and reduction peak (–1.2 to –1.37), with emergence of two new peaks corresponding to oxidation potential of 0.08 V and reduction potential of 0.25V vs Ag/AgCl. The significant shift in potential coupled with decrease in the intensity of the reduction peak of $Ru(bpy)_3Cl_2$ upon

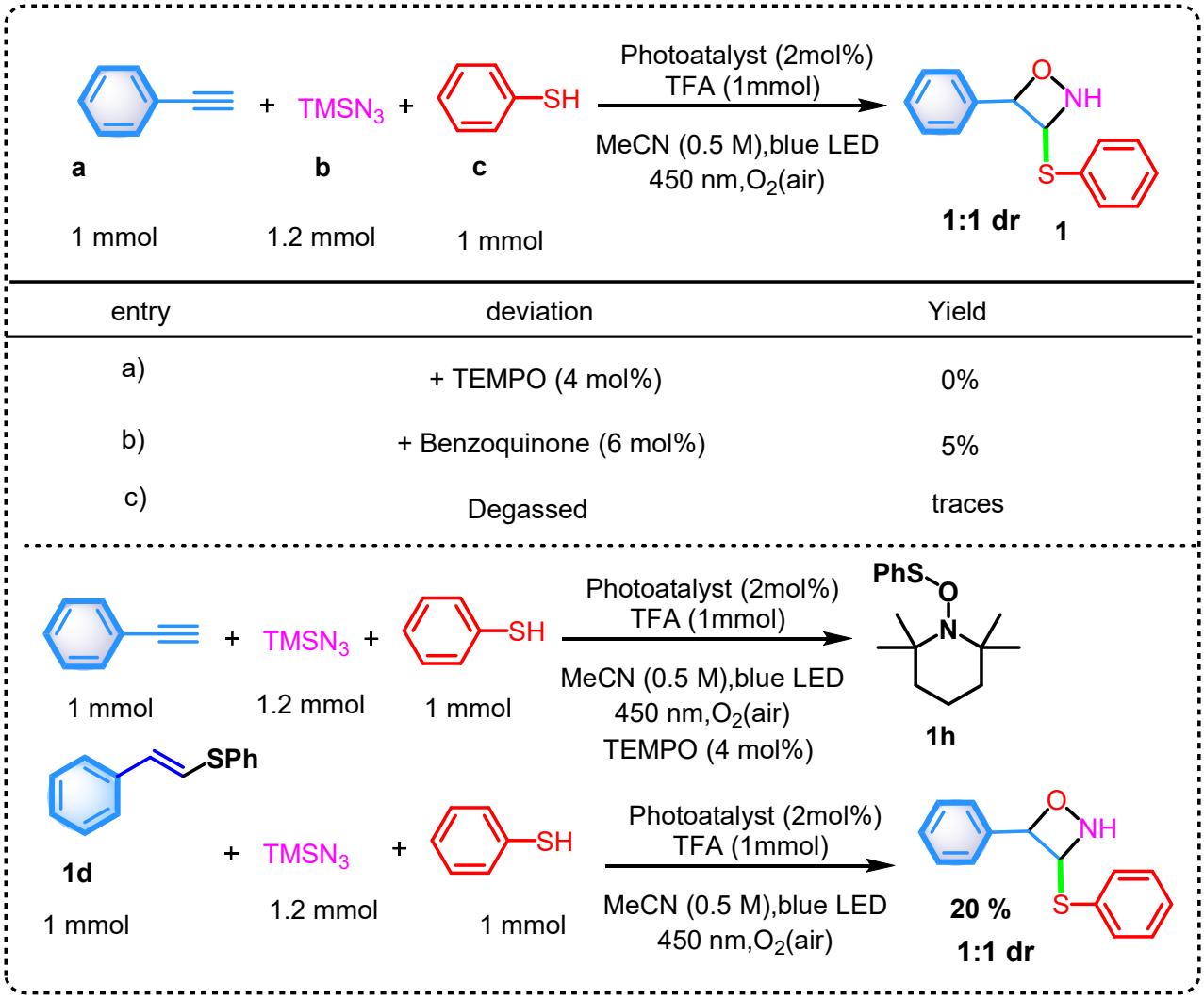
addition of thiophenol can be corroborated with the proposed reductive quenching/ single electron reduction of catalyst by thiophenol. Similarly, the newly emerged peaks can be ascribed to the oxidation of thiophenol by the photoexcited catalyst.Upon addition of equimolar concentration (2 x10^{-4}M) of Phenylacetylene (PA) to the binary system of catalyst + PSH, An observed shift (from 0.08 to 0.11 V) with decrease in current intensity of the oxidation peak ascribed to oxidized form of thiophenol(Thiyl radical) supports the second step of proposed reaction mechanism and also is in confirmation with absorbance and luminescence studies.

Table S2 : Mechanistic studies experimental data

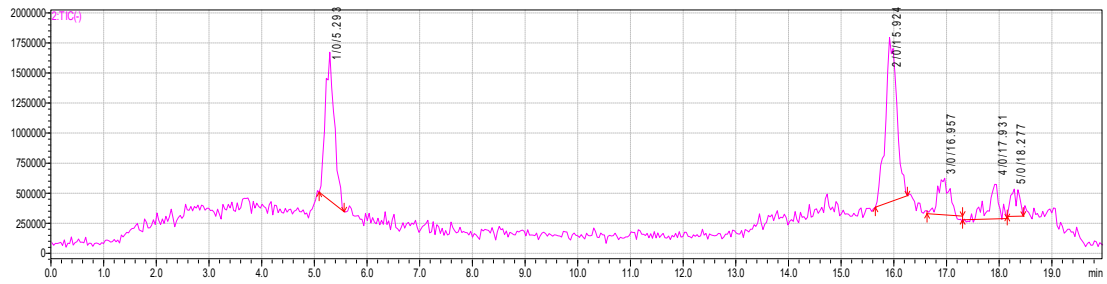
S.No	System	Absorption	Emission		CyclicVoltammetry	
		K (min^{-1})	Ksv (M^{-1}) ... x 10^5	% quenching	$E_{1/2}$ V Red	$E_{1/2}$ V Oxd
1	$[Ru(bpy)_3Cl_2]$ +PSH	.00845	6.8	80	–1.024 0.18	–0.064 1.216
2	$[Ru(bpy)_3Cl_2]$ +PA	.00087	2.9	60	–1.107	0.788
3	$[Ru(bpy)_3Cl_2]$ +TMS	.00023	1.3	52	– 0.963	0.822
4	$[Ru(bpy)_3Cl_2]$+PSH +PA	.00912	12	92	– 1.047 – 0.198	0.11 1.3

Figure S5. Control Experiments.

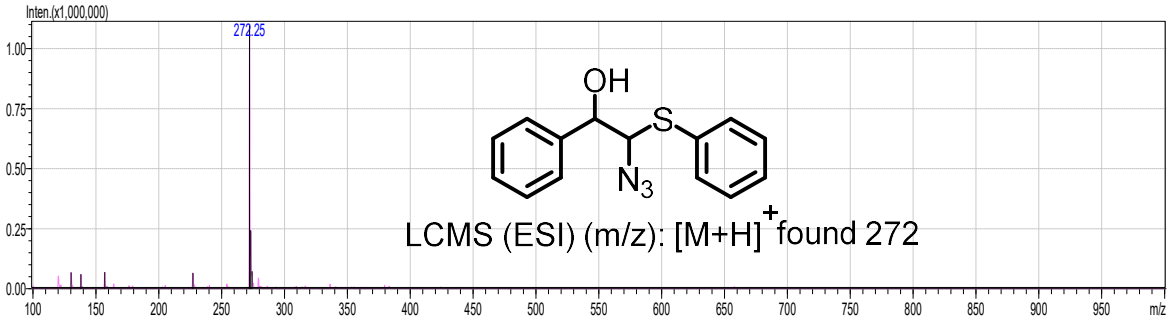
To gain the mechanistic insights some control experiments were performed. The reaction showed no product formation in the presence of TEMPO and benzoquinone, and in the absence of oxygen after degassing. In presence of TEMPO thiyl radical was trapped to afford **1h** product. Moreover, when intermediate **1d** was isolated and subjected to standard conditions it affords the product **1** in 20% yield therefore further solidifying the fact that reaction proceed through intermediate **1d**.



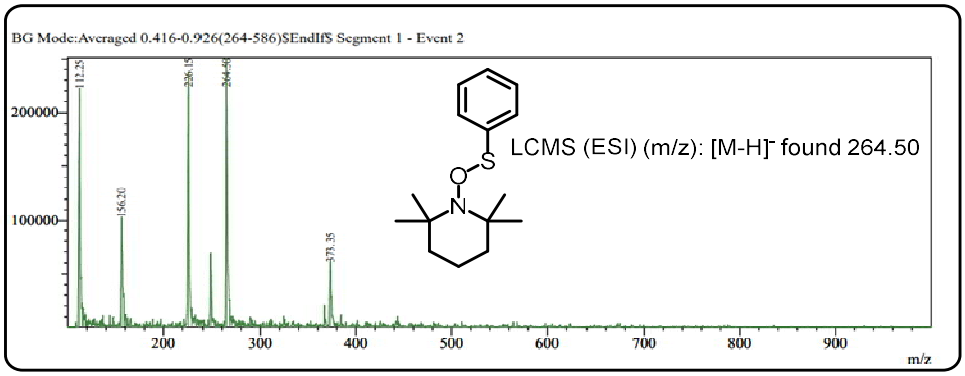
3.5. LCMS analysis of reaction mixture:

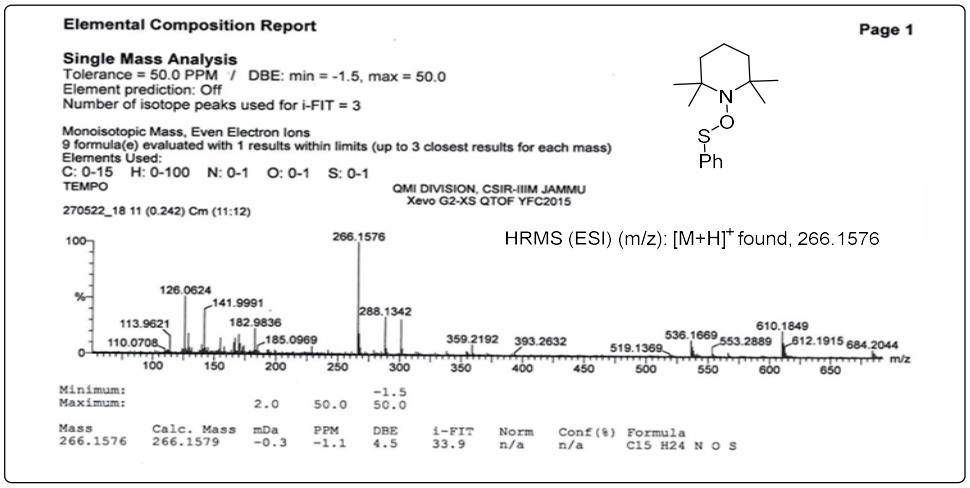


Ret. Time : [18.236->18.304]-[18.405->19.962] Scan# : [1079->1083]-[1089->1



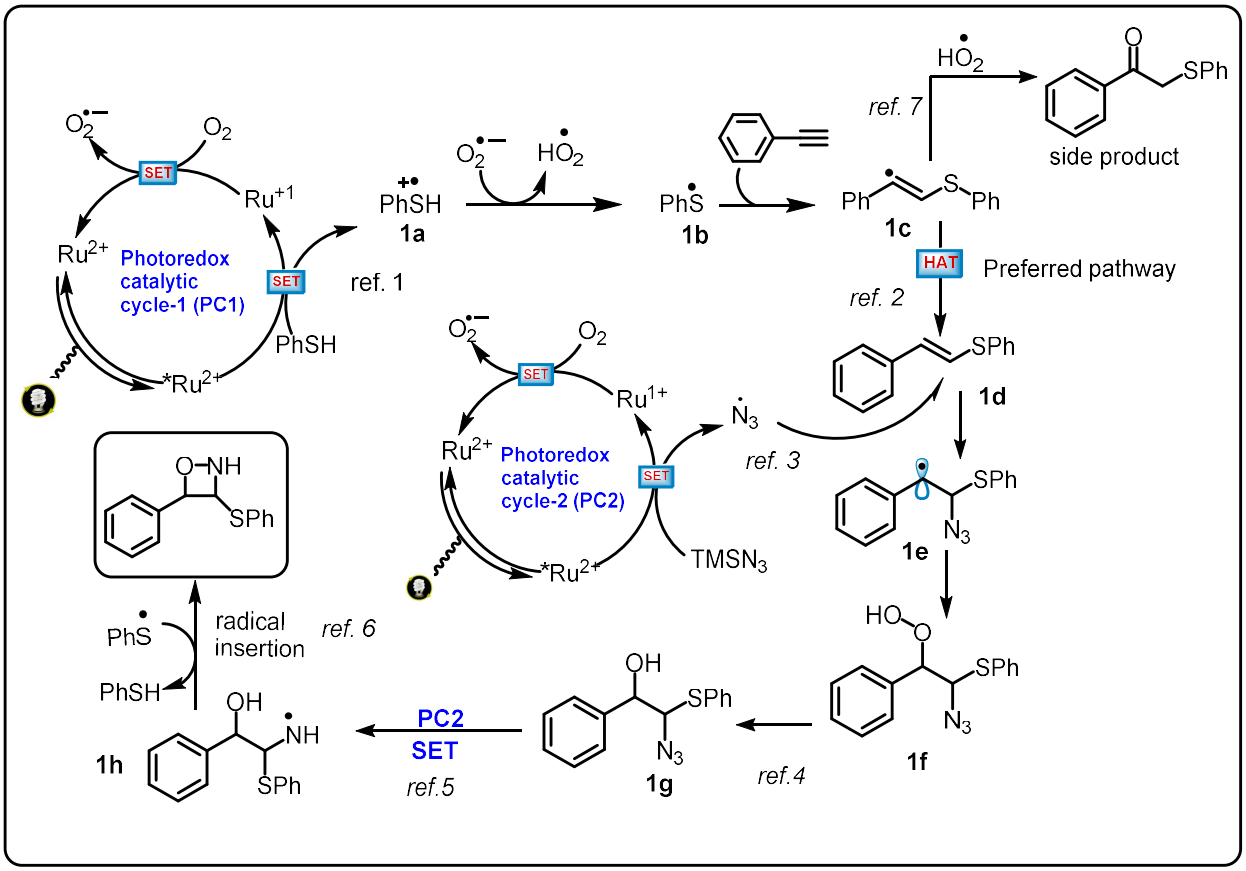
3.6. LCMS analysis of control experiment with TEMPO:





3.7 Alternative plausible mechanism (Scheme S1):

Based on LCMS analysis of the reaction mixture, we proposed an alternative mechanism Where the intermediate **If** undergo peroxide cleavage to afford intermediate **1g** as detected by LCMS. The intermediate **1g** after nitrogen extrusion and protonation affords aminyl radical intermediate **1h** which can undergo insertion to give the product.



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4. Determination of reaction quantum yield.

The quantum yield of the reaction was calculated in two steps:

1. The conventional potassium ferrioxalate actinometer method published in literature[1-6] was used to determine the photon flux of the blue LED. The iron(III) actinometer complex potassium trisoxalatoferrate (III) trihydrate was synthesized according to literature reports[3]. An experiment was set up to evaluate the light intensity by dissolving 0.737 g of potassium trisoxalato ferrate trihydrate complex in 10 mL of a 0.05 M H_2SO_4 solution to make a 0.15 M ferrioxalate actinometer solution. In a buffer solution made by dissolving 5.63 g sodium acetate in 25 mL of a 0.5 M solution H_2SO_4, a 0.2% by weight solution of 1, 10-phenanthroline ligand was prepared. Both solutions were kept in a dark place.
The actinometer measurement was done as follows:

After irradiation of 2.0mL actinometer solution for the 90s, 0.35 mL of the phenanthroline solution was added to the cuvette and the mixture was allowed to stir in the dark for 1.0 h to allow the complexation of the phenanthroline ligand with the produced ferrous to form a red-color $[Fe(phen)_3]^{2+}$ complex whose absorbance was measured at 510 nm against reagent blank after dilution (1:1) A non-irradiated sample (containing actinometer solution, buffer, and phenanthroline ligand in the same proportions as indicated but not irradiated) was also prepared and its absorbance at λ 510 nm was measured using similar conditions. The moles of Fe^{2+} formed can be determined according to the Beer's Laws using the equation:

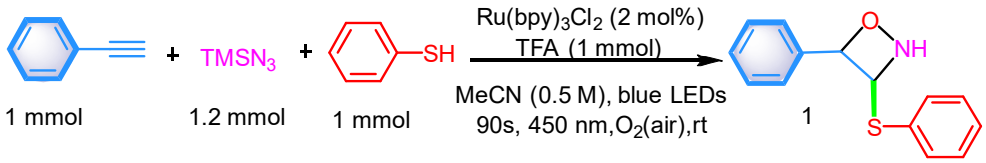
$$\text{moles of } Fe^{2+} = \frac{V\,(L) \times \Delta A\,(510)\,(5}{1\,(cm) \times \in (L\,mol^{-1}cm^{-1})} = 4.29 \times 10^{-7}$$

Where V is the total volume of the solution (0.00235 L) after the addition of all reagents, ΔA is the difference in absorbance at λ 510 nm between the irradiated and non-irradiated actinometer solutions (2.24 - 0.21). l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer[3] at λ 510 nm (11,100 L $mol^{-1}cm^{-1}$). The photon flux of the Blue LED was calculated as under:

$$\text{Photon flux} = \frac{\text{moles of } Fe^{2+}}{\Phi \times t \times f} = 4.2 \times 10^{-9}$$

Where Φ is the quantum yield for the ferrioxalateactinometer (1.12), t is the irradiation time (90 s), and f is the fraction of light absorbed by the ferrioxalate actinometer. An absorption spectrum gave an absorbance value of >3, indicating that the fraction of absorbed light (f) is >0.999. The photon flux was thus calculated(average of three experiments) to be 4.29 x 10^{-9} Einsteins s^{-1}.

2. Determination of the reaction quantum yield.



Phenylacetylene (20 µL, 0.196 mmol, 1.0 equiv), Thiophenol (21 µL, 0.196 mmol, 1.0 equiv),Trimethylsilyl azide(26 µL, 0.23 mmol, 1.2 equiv), Trifluoroacetic acid (22.54 µL, 0.196 mmol, 1.0 equiv) and $[Ru(bpy)_3]Cl_2$ (3 mg, 0.003 mmol) were placed in a quartz cuvette. The sample was stirred and irradiated for 90s. After irradiation,the yield of product **1** formed was determined using the peak area analysis method of Gas Chromatography technique.[7] The yield of the product **1** formed after 90s of irradiation as determined from quantitative analysis by gas chromatography was found to be 0.55% corresponding to (1x10^{-6} mol). The reaction quantum yield (Φ) was then arrived at using the equation:

$$\Phi = \frac{\text{moles of product formed}}{\text{photon flux x t x f}} = 2$$

Where the photon flux is 4.2 x 10^{-9} einsteins s^{-1} (as determined by actinometry in step 1), t is the reaction time (90s) and f is the fraction of incident light absorbed by the reaction mixture. An initial absorption spectrum of the aforementioned reaction mixture gave an absorbance value of >3 at 420 nm indicating that essentially all the incident light is absorbed by the photocatalyst in the reaction mixture, therefore (f) is > 0.999.[8]

The reaction quantum yield (Φ) was thus determined to be 2 indicating a possible short radical chain process[9].

A **B**

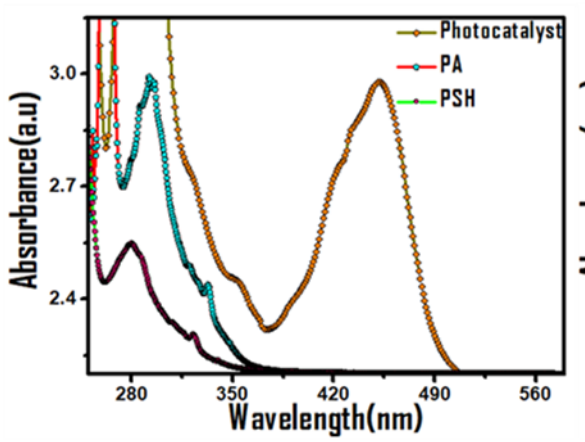


Figure 1A: Initial absorption spectra of reaction mixture showing absorption > 3 indicating that essentially all the incident light is absorbed by the photocatalyst and therefore (f ~0.999)[8]

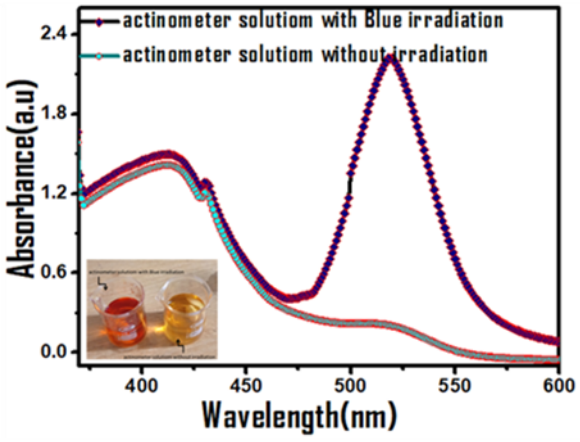


Figure 2B :Absorption spectra's of actinometer solution without and after irradiation for 90s

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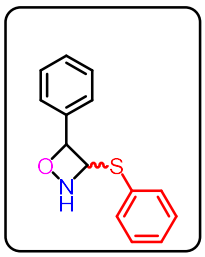
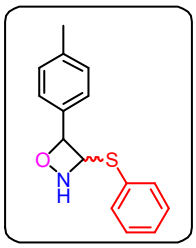
4. Spectral Data

4-phenyl-3-(phenylthio)-1,2-oxazetidine (1)



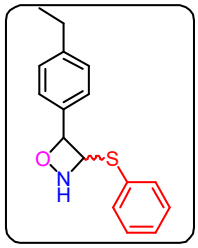
Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (134 µL, 1.17 mmol), thiophenol (107 µL, 0.98 mmol), TFA (112 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 98:2) as yellow oil (161 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.52 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.49 – 7.45 (m, 3H), 7.45 – 7.41 (m, 7H), 7.40 (d, *J* = 2.0 Hz, 2H), 7.38 (d, *J* = 2.0 Hz, 2H), 7.37 (d, *J* = 1.0 Hz, 1H), 7.36 – 7.34 (m, 3H), 4.95 (d, *J* = 4.8 Hz, 1H), 4.79 (dd, *J* = 5.9, 3.3 Hz, 2H), 4.75 (d, *J* = 6.5 Hz, 1H), 2.88 (s, 1H), 2.75 (s, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ - 139.2, 139.0, 134.0, 133.3, 132.1, 131.0, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.5, 126.9, 126.8, 126.7, 77.1, 76.3, 76.1, 75.0. HRMS (ESI) (m/z): $[M + H]^+$ calculated for $C_{14}H_{14}NOS$, 244.0791; found: 244.0774.

3-(phenylthio)-4-(p-tolyl)-1,2-oxazetidine (2)



Following the general procedure the reaction was carried out with 4-methyl phenylacetylene (100 µL, 0.86 mmol), trimethylsilyl azide (118 µL, 1.03 mmol), thiophenol (94 µL, 0.86 mmol), TFA (98 µL, 0.86 mmol), $Ru(bpy)_3Cl_2$ (12 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (185 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.55 – 7.52 (m, 1H), 7.48 (dd, *J* = 3.7, 2.0 Hz, 2H), 7.39 – 7.33 (m, 8H), 7.32 (s, 3H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.22 (s, 2H), 4.91 (d, *J* = 5.1 Hz, 1H), 4.80 – 4.76 (m, 2H), 4.71 (d, *J* = 6.5 Hz, 1H), 2.86 (s, 1H), 2.72 (s, 1H), 2.40 (s, 6H). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) δ - 138.5, 138.5, 136.6, 136.0, 133.4, 133.2, 132.2, 131.1, 129.4, 129.3, 129.8, 129.2, 128.7, 128.46, 126.8, 126.7, 76.9, 76.1, 76.0, 74.8, 21.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{16}NOS$ 258.0947; found: 258.0933.

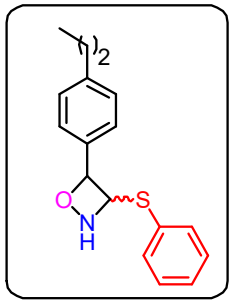
4-(4-ethylphenyl)-3-(phenylthio)-1,2-oxazetidine (3)



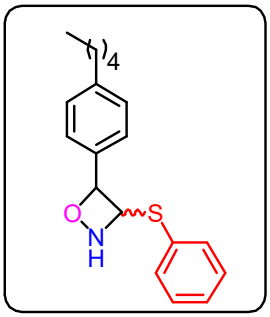
Following the general procedure the reaction was carried out with 4-ethyl-phenylacetylene (100 µL, 0.76 mmol), trimethylsilyl azide (105.8 µL, 0.92 mmol), thiophenol (83.6 µL, 0.76 mmol), TFA (86.64 µL, 0.76 mmol), $Ru(bpy)_3Cl_2$ (11.36 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (162 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.51 – 7.49 (m, 1H), 7.46 – 7.42 (m, 3H), 7.36 – 7.33 (m, 4H), 7.32 (d, *J* = 3.7 Hz, 7H), 7.22 (d, *J* = 7.8 Hz, 3H), 4.90 (d, *J* = 4.4 Hz, 1H), 4.76 (d, *J* = 5.9 Hz, 2H), 4.73 – 4.65 (m, 1H), 2.80 (s, 1H), 2.67 (t, *J* = 6.8 Hz, 4H), 1.59 (s, 1H), 1.25 (t, *J* = 7.5 Hz, 6H). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$) δ - 144.8, 136.5, 136.3, 133.8, 133.2, 132.3, 129.3, 129.7, 129.0, 128.7, 128.4, 128.0, 127.0, 126.8, 126.7, 77.1, 76.2, 76.16, 75.0, 28.4, 15.4, 15.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{18}NOS$ 272.1104; found: 272.1106.

3-(phenylthio)-4-(4-propylphenyl)-1,2-oxazetidine (4)

Following the general procedure the reaction was carried out with 4-n-propylphenylacetylene (100 µL, 0.69 mmol), trimethylsilyl azide (95.45 µL, 0.83 mmol), thiophenol (75.9 µL, 0.69 mmol), TFA (78 µL, 0.69 mmol), $Ru(bpy)_3Cl_2$ (10 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (176 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.50 – 7.48 (m, 1H), 7.44 (dd, *J* = 6.3, 3.0 Hz, 3H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 6H), 7.31 (s, 5H), 7.21 (s, 2H), 7.19 (s, 1H), 4.89 (d, *J* = 4.2 Hz, 1H), 4.76 (d, *J* = 5.6 Hz, 2H), 4.73 – 4.68 (m, 1H), 2.65 (d, *J* = 3.7 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 4H), 1.68 – 1.63 (m, 4H), 1.59 (s, 1H), 0.97 – 0.93 (m, 6H). ^{13}C{^{1}H} (125 MHz, $CDCl_3$) δ - 143.3, 143.3, 136.5, 136.2, 133.93, 133.3, 132.2, 131.2, 129.4, 129.3, 128.9, 128.7, 128.7, 128.6, 128.4, 126.8, 126.7, 77.1, 76.2, 76.1, 74.9, 37.8, 24.5, 24.5, 13.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{20}NOS$ 286.1260; found: 286.1249.

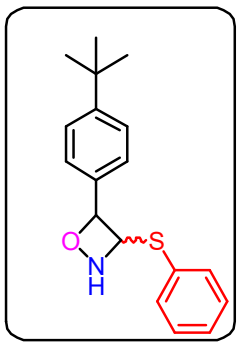


4-(4-pentylphenyl)-3-(phenylthio)-1,2-oxazetidine (5)



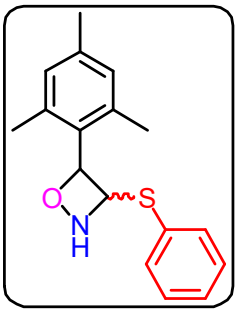
Following the general procedure the reaction was carried out with 4-n-pentylphenylacetylene (100 µL, 0.58 mmol), trimethylsilyl azide (79 µL, 0.69 mmol), thiophenol (63.8 µL, 0.58 mmol), TFA (66 µL, 0.58 mmol), $Ru(bpy)_3Cl_2$ (8 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (256 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.50 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.45 (dd, *J* = 4.5, 2.1 Hz, 2H), 7.35 (d, *J* = 2.3 Hz, 2H), 7.34 – 7.31 (m, 8H), 7.22 – 7.19 (m, 4H), 4.91 – 4.89 (m, 1H), 4.76 (d, *J* = 6.0 Hz, 2H), 4.71 (dd, *J* = 6.4, 2.4 Hz, 1H), 2.86 (d, *J* = 2.9 Hz, 1H), 2.73 (d, *J* = 3.7 Hz, 1H), 2.62 (d, *J* = 7.5 Hz, 4H), 1.66 – 1.62 (m, 4H), 1.37 – 1.32 (m, 8H), 0.91 (dd, *J* = 6.9, 5.5 Hz, 6H). ^{13}C{^{1}H} (125 MHz, $CDCl_3$) δ - 143.6, 143.5, 136.5, 136.2, 133.9, 133.2, 132.8, 131.2, 129.3, 129.3, 129.1, 128.7, 128.6, 128.6, 128.4, 126.8, 126.7, 77.1, 76.2, 76.1, 74.9, 35.7, 31.5, 31.1, 31.1, 22.6, 14.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{19}H_{24}NOS$ 314.1573; found: 314.1566.

4-(4-(*tert*-butyl)phenyl)-3-(phenylthio)-1,2-oxazetidine (6)



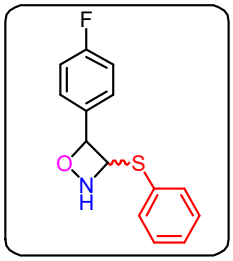
Following the general procedure the reaction was carried out with 4-*tert*-butyl-phenylacetylene (100 µL, 0.63 mmol), trimethylsilyl azide (86.2 µL, 0.75 mmol), thiophenol (69.3 µL, 0.63 mmol), TFA (71 µL, 0.63 mmol), $Ru(bpy)_3Cl_2$ (9 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (185 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.50 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.45 – 7.42 (m, 4H), 7.41 (s, 2H), 7.37 – 7.31 (m, 10H), 4.92 (s, 1H), 4.77 (dd, *J* = 5.7, 2.3 Hz, 2H), 4.73 (d, *J* = 6.1 Hz, 1H), 2.83 (s, 1H), 2.69 (s, 1H), 1.35 (d, *J* = 1.0 Hz, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ - 151.7, 151.7, 136.3, 136.0, 133.8, 133.2, 132.4, 131.9, 129.3, 129.2, 128.6, 128.4, 126.6, 126.5, 125.4, 125.42, 77.1, 76.2, 76.2, 75.0, 34.6, 31.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{22}NOS$ 300.1417; found: 300.1415.

4-mesityl-3-(phenylthio)-1,2-oxazetidine (7)



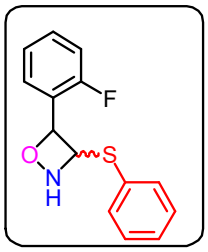
Following the general procedure the reaction was carried out with 2,4,6-trimethyl phenylacetylene (100 µL, 0.69 mmol), trimethylsilyl azide (94.62 µL, 0.83 mmol), thiophenol (75.9 µL, 0.69 mmol), TFA (78 µL, 0.69 mmol), $Ru(bpy)_3Cl_2$ (10 mg, 2 mol%) and purified by colum chromatography (hexane:EA = 99:1) as yellow oil (153 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.35 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.30 – 7.28 (m, 2H), 7.24 (dd, *J* = 6.4, 3.9 Hz, 3H), 7.20 (d, *J* = 2.3 Hz, 2H), 7.17 (s, 1H), 6.86 (d, *J* = 5.5 Hz, 2H), 5.04 (d, *J* = 5.5 Hz, 1H), 4.79 (d, *J* = 7.4 Hz, 1H), 4.74 (d, *J* = 7.4 Hz, 1H), 4.70 (d, *J* = 5.5 Hz, 1H), 2.15 (dd, *J* = 8.8, 6.8 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ - 134.0, 133.9, 133.3, 132.0, 131.9, 129.3, 129.3, 128.7, 128.4, 127.4, 76.9, 75.5, 72.7, 70.8, 19.4, 19.4, 18.7, 18.7. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{20}NOS$ 286.1260; found: 286.1258.

4-(4-fluorophenyl)-3-(phenylthio)-1,2-oxazetidine (8)



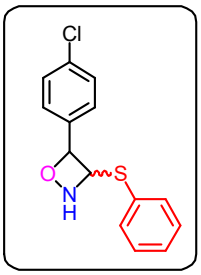
Following the general procedure the reaction was carried out with 4-fluorophenylacetylene (100 µL, 0.83 mmol), trimethylsilyl azide (113 µL, 0.99 mmol), thiophenol (91.3 µL, 0.83 mmol), TFA (94 µL, 0.83 mmol), $Ru(bpy)_3Cl_2$ (12 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (133 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.47 (s, 1H), 7.45 (d, *J* = 1.8 Hz, 2H), 7.43 (s, 1H), 7.39 (dd, *J* = 8.9, 3.9 Hz, 10H), 7.33 (s, 1H), 7.31 (s, 1H), 7.30 (s, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 4.92 (d, *J* = 4.5 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.71 (d, *J* = 5.4 Hz, 2H), 2.76 (s, 1H), 2.69 (s, 1H). ^{13}C{^{1}H}(100 MHz, $CDCl_3$) δ - 163.3 (d, *J* = 248 Hz), 163.1 (d, *J* = 248 Hz), 139.2, 139.1, 136.7 (d, *J* = 8.4 Hz), 136.1 (d, *J* = 8.4 Hz), 133.8, 130.3,129.4, 128.8, 128.7, 128.6, 128.5,126.9, 116.5 (d, *J* = 21.8 Hz), 116.5(d, *J* = 22 Hz),77.4, 76.6, 76.3, 75.1.^{19}F NMR (377 MHz, $CDCl_3$) δ - -117.9,-118; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}FNOS$ 262.0696; found: 262.0702.

4-(2-fluorophenyl)-3-(phenylthio)-1,2-oxazetidine(9)



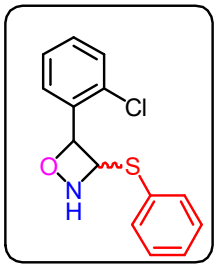
Following the general procedure the reaction was carried out with 2-fluorophenylacetylene (100 µL, 0.83 mmol), trimethylsilyl azide (113 µL, 0.99 mmol), thiophenol (91.3 µL, 0.83 mmol), TFA (94 µL, 0.83 mmol), $Ru(bpy)_3Cl_2$ (12 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (151 mg, 58% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.52 (dt, *J* = 7.4, 6.8 Hz, 2H), 7.46 – 7.43 (m, 2H), 7.39 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.30 – 7.25 (m, 8H), 7.18 – 7.13 (m, 2H), 7.03 – 6.97 (m, 2H), 5.24 (t, *J* = 4.4 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.82 (t, *J* = 5.3 Hz, 2H), 3.16 (d, *J* = 3.6 Hz, 1H), 3.09 (d, *J* = 4.3 Hz, 1H). ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ - 160.0 (d, *J* = 245 Hz), 159.8 (d, *J* = 244 Hz), 133.7, 133.3, 132.1, 131.6, 130.0 (d, *J* = 8 Hz), 130.0 (d, *J* = 8.4 Hz), 129.4, 128.6, 128.6, 128.3 (d, *J* = 3.8 Hz), 126.8 (d, *J* = 12.9 Hz), 126.5 (d, *J* = 12.9 Hz), 124.5, 124.4, 115.4 (d, *J* = 6.6 Hz), 115.3 (d, *J* = 6.8 Hz), 76.1, 74.7, 70.9, 69.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ- -106.3 ,-106.8; HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}FNOS$ 262.0696; found: 262.0685.

4-(4-chlorophenyl)-3-(phenylthio)-1,2-oxazetidine (10)



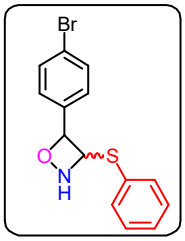
Following the general procedure the reaction was carried out with 4-chloro phenylacetylene (100 µL, 0.73 mmol), trimethylsilyl azide (101.2 µL, 0.73 mmol), thiophenol (80.3 µL, 0.73 mmol), TFA (83.22 µL, 0.73 mmol), $Ru(bpy)_3Cl_2$ (10.92 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (199 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$) δ - 7.51 – 7.48 (m, 2H), 7.45 – 7.42 (m, 3H), 7.37 (t, *J* = 2.6 Hz, 2H), 7.35 (d, *J* = 1.5 Hz, 8H), 7.34 (s, 1H), 7.33 (s, 1H), 7.33 – 7.32 (m, 1H), 4.87 (d, *J* = 5.3 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 2H), 4.70 – 4.64 (m, 1H), 2.90 (s, 1H), 2.74 (s, 1H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ - 139.1, 139.0, 135.4, 135.2, 134.8, 134.5, 130.7, 129.5, 129.5, 129.2, 129.2, 128.8, 128.7, 128.6, 128.6, 126.8, 77.1, 76.4, 76.0, 75.2. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}ClNOS$ 278.0401; found: 278.0391.

4-(2-chlorophenyl)-3-(phenylthio)-1,2-oxazetidine(11)



Following the general procedure the reaction was carried out with 2-chlorophenylacetylene (100 µL, 0.73 mmol), trimethylsilyl azide (101.2 µL, 0.73 mmol), thiophenol (80.3 µL, 0.73 mmol), TFA (83.22 µL, 0.73 mmol), $Ru(bpy)_3Cl_2$ (10.92 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (155 mg, 56% yield). ^1H NMR (400 MHz, $CDCl_3$) δ - 7.50 – 7.46 (m, 2H), 7.44 – 7.42 (m, 2H), 7.40 – 7.38 (m, 6H), 7.36 (dd, *J* = 2.7, 1.6 Hz, 2H), 7.34 (d, *J* = 2.1 Hz, 2H), 7.33 – 7.30 (m, 4H), 4.91 (d, *J* = 5.4 Hz, 1H), 4.78 – 4.68 (m, 3H), 2.86 (s, 2H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ - 137.1, 136.7, 133.3, 133.3, 132.3, 132.1, 131.8, 129.7, 129.6, 129.5, 129.4, 129.3, 128.9, 128.6, 128.4, 128.2, 127.1, 127.1, 75.9, 73.8, 73.4, 72.7. (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}ClNOS$ 278.0401; found: 278.0390.

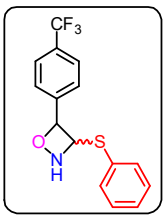
4-(4-bromophenyl)-3-(phenylthio)-1,2-oxazetidine (12)



Following the general procedure the reaction was carried out with 4-bromophenylacetylene (100 µL, 0.55 mmol), trimethylsilyl azide (77.05 µL, 0.67 mmol), thiophenol (60.5 µL, 0.55 mmol), TFA (62.7 µL, 0.55 mmol), $Ru(bpy)_3Cl_2$ (8.2 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (181 mg, 58% yield). ^1H NMR (400 MHz, $CDCl_3$) δ - 7.47 (s, 1H), 7.45 (d, *J* = 1.8 Hz, 2H), 7.43 (d, *J* = 3.1 Hz, 2H), 7.40 (t, *J* = 4.7 Hz, 9H), 7.33 (s, 1H), 7.31 (s, 1H), 7.30 (s, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 4.92 (d, *J* = 4.5 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.71 (d, *J* = 5.4 Hz, 2H), 2.76 (s, 1H), 2.69 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ - 139.0, 138.9, 135.5, 135.3, 135.2, 132.4, 131.9, 131.6, 131.4, 131.3, 130.5, 128.9, 128.6, 128.6, 126.8, 126.7, 122.9, 76.9, 76.5, 75.7. (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}BrNOS$ 321.9896; found: 321.9875.

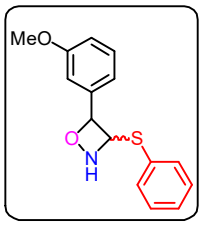
3-(phenylthio)-4-(4-(trifluoromethyl)phenyl)-1,2-oxazetidine (13)

Following the general procedure the reaction was carried out with 4-trifluoro-phenylacetylene (100 µL, 0.58 mmol), trimethylsilyl azide (80.04 µL, 0.696 mmol), thiophenol (63.8 µL, 0.58 mmol), TFA (66.12 µL, 0.58 mmol), $Ru(bpy)_3Cl_2$ (8.6 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil. (193 mg, 62% yield). ^1H NMR (400 MHz,



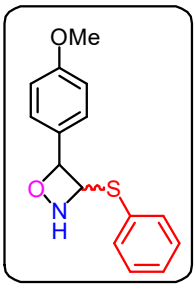
$CDCl_3$) δ - 7.64 – 7.60 (m, 4H), 7.51 (d, *J* = 7.3 Hz, 4H), 7.46 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.42 (dd, *J* = 4.2, 3.3 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.33 (s, 1H), 7.32 (dd, *J* = 5.1, 1.8 Hz, 3H), 4.94 (d, *J* = 5.3 Hz, 1H), 4.75 – 4.71 (m, 3H), 3.05 (s, 2H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ - 143.1, 142.9, 134.2, 133.4, 131.7, 130.9, 130.8, 130.6, 130.5, 130.5, 129.5,129.1, 128.8, 127.3, 127.3, 125.4 (dq, *J* = 7.5, 3.7 Hz), 77.0, 76.0, 75.7, 74.3.^{19}F NMR (377 MHz, $CDCl_3$) δ - 62.5, -62.6. (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{13}F_3NOS$ 312.0664; found: 312.0665.

4-(3-methoxyphenyl)-3-(phenylthio)-1,2-oxazetidine(14)



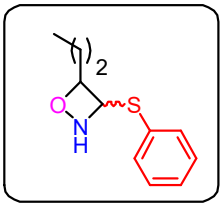
Following the general procedure the reaction was carried out with 3-methoxy-phenylacetylene (100 µL, 0.75 mmol), trimethylsilyl azide (104.53 µL, 0.90 mmol), thiophenol (82.5 µL, 0.75mmol), TFA (85.5, 0.75 mmol), $Ru(bpy)_3Cl_2$ (11.22 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (131 mg, 48% yield). ^1H NMR (400 MHz, $CDCl_3$) δ - 7.42 (d, *J* = 2.5 Hz, 1H), 7.40 (d, *J* = 1.9 Hz, 5H), 7.38 – 7.37 (m, 2H), 7.37 – 7.35 (m, 2H), 7.24 (dd, *J* = 6.0, 2.0 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.05 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.02 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 6.99 – 6.98 (m, 1H), 6.96 – 6.94 (m, 1H), 6.88 – 6.83 (m, 2H), 4.93 – 4.89 (m, 1H), 4.76 (dd, *J* = 5.5, 3.9 Hz, 3H), 3.77 (d, *J* = 1.0 Hz, 6H), 2.87 (s, 1H), 2.77 (s, 1H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ - 160.0, 139.2, 138.9, 133.3, 132.3, 130.1, 130.1, 128.7, 128.7, 128.5, 128.5, 126.9, 126.8, 125.8, 125.2, 118.7, 118.1, 114.7, 114.4, 77.1, 76.3, 76.0, 75.1, 55.4. (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{16}NO_2S$ 274.0896; found: 274.0889.

4-(4-methoxyphenyl)-3-(phenylthio)-1,2-oxazetidine(15)



Following the general procedure the reaction was carried out with 4-methoxy-phenylacetylene (100 µL, 0.75 mmol), trimethylsilyl azide (104.53 µL, 0.90 mmol), thiophenol (82.5 µL, 0.75 mmol), TFA (85.5, 0.75 mmol), $Ru(bpy)_3Cl_2$ (11.22 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (131 mg, 48% yield). ^1H NMR (400 MHz, $CDCl_3$) δ - 7.52 – 7.47 (m, 2H), 7.45 – 7.42 (m, 2H), 7.36 – 7.33 (m, 4H), 7.33 – 7.29 (m, 6H), 6.91 (d, *J* = 6.8 Hz, 4H), 4.85 (d, *J* = 5.4 Hz, 1H), 4.73 (d, *J* = 6.7 Hz, 2H), 4.66 (d, *J* = 6.5 Hz, 1H), 3.82 (d, *J* = 2.0 Hz, 6H), 2.79 (s, 1H), 2.65 (s, 1H). $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ - 159.8, 159.8, 133.9, 133.3, 132.1, 131.3, 131.1, 131.0, 129.4, 129.3, 128.8, 128.5, 128.1, 128.1, 113.9, 113.9, 77.1, 76.2, 75.8, 74.6, 55.3, 55.2. (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{16}NO_2S$ 274.0896; found: 274.0888.

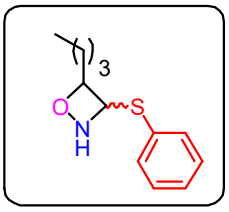
3-(phenylthio)-4-propyl-1,2-oxazetidine(16)



Following the general procedure the reaction was carried out with 1-Pentyne (100 µL, 1.47 mmol), trimethylsilyl azide (335µL, 2.94 mmol), thiophenol (161 µL, 1.47 mmol), TFA (169 µL, 1.47 mmol), $Ru(bpy)_3Cl_2$ (10.92 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (146 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) δ - 7.59 – 7.52 (m, 2H), 7.44 (ddd, *J* = 7.9, 5.5, 3.7 Hz, 3H), 7.36 – 7.34 (m, 2H), 7.28 (d, *J* = 1.6 Hz, 3H), 4.56 (t, *J* = 5.2 Hz, 1H), 4.46 (d, *J* = 3.9 Hz, 1H), 3.89 – 3.66 (m, 2H), 2.67 (d, *J* =

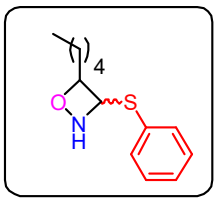
4.4 Hz, 1H), 2.26 (d, *J* = 39.2 Hz, 1H), 1.84 – 1.59 (m, 4H), 1.54 – 1.30 (m, 4H), 0.93 (ddd, *J* = 20.0, 10.9, 4.0 Hz, 6H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 133.6, 133.4, 132.8, 132.6, 129.2, 129.1, 128.1, 127.9, 75.5, 73.7, 73.0, 72.4, 66.9, 35.7, 35.4, 19.2, 18.8, 14.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_{16}NOS$ 210.0947; found: 210.0953.

4-butyl-3-(phenylthio)-1,2-oxazetidine(17)



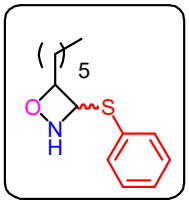
Following the general procedure the reaction was carried out with 1-Hexyne (100 µL, 1.21 mmol), trimethylsilyl azide (273µL, 2.94 mmol), thiophenol (133µL, 1.21mmol), TFA (139µL, 1.21mmol), $Ru(bpy)_3Cl_2$ (14mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (174 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 4H), 7.37 – 7.34 (m, 5H), 7.31 – 7.28 (m, 1H), 4.57 (t, *J* = 4.8 Hz, 2H), 3.82 – 3.76 (m, 1H), 3.71 (dd, *J* = 7.8, 4.4 Hz, 1H), 2.28 (s, 1H), 2.17 (s, 1H), 1.74 – 1.69 (m, 2H), 1.61 – 1.56 (m, 2H), 1.51 – 1.45 (m, 2H), 1.37 – 1.31 (m, 6H), 0.93 – 0.90 (m, 6H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 133.7, 133.4, 129.4, 129.4, 129.0, 128.6, 128.5, 127.5, 76.6, 75.5, 73.9, 73.2, 33.4, 33.0, 27.7, 27.6, 22.6, 22.6, 14.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{18}NOS$ 224.1104; found: 224.110.

4-pentyl-3-(phenylthio)-1,2-oxazetidine (18)



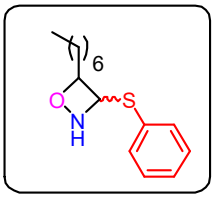
Following the general procedure the reaction was carried out with 1-Heptyne (100 µL, 1.04 mmol), trimethylsilyl azide (239µL, 2.08 mmol), thiophenol (114µL, 1.04mmol), TFA (118µL, 1.04mmol), $Ru(bpy)_3Cl_2$ (15mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (161 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 3H), 7.44 (dd, *J* = 5.3, 4.3 Hz, 2H), 7.34 (dd, *J* = 3.3, 1.9 Hz, 3H), 7.30 – 7.27 (m, 2H), 4.57 (t, *J* = 5.3 Hz, 2H), 3.81 – 3.77 (m, 1H), 3.72 (dd, *J* = 8.4, 4.2 Hz, 1H), 2.36 (d, *J* = 4.3 Hz, 1H), 2.27 (d, *J* = 4.9 Hz, 1H), 1.74 – 1.64 (m, 3H), 1.53 (ddd, *J* = 11.4, 11.0, 7.0 Hz, 3H), 1.30 (dd, *J* = 5.5, 1.6 Hz, 10H), 0.91 – 0.87 (m, 6H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 133.7, 133.4, 132.8, 132.6, 129.4, 129.2, 129.1, 128.6, 76.6, 75.5, 73.9, 73.2, 33.7, 33.3, 31.7, 31.7, 25.2, 25.2, 22.5, 14.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{13}H_{20}NOS$ 238.1260; found: 238.1266.

4-hexyl-3-(phenylthio)-1,2-oxazetidine(19)



Following the general procedure the reaction was carried out with octyne (100 µL, 0.90 mmol), trimethylsilyl azide (125.35 µL, 1.09 mmol), thiophenol (100 µL, 0.90 mmol), TFA (85.5, 0.75 mmol), $Ru(bpy)_3Cl_2$ (13 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (80 mg, 32% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.49 (dd, *J* = 5.9, 3.3 Hz, 4H), 7.30 – 7.28 (m, 5H), 7.23 (d, *J* = 6.7 Hz, 1H), 4.50 (t, *J* = 4.5 Hz, 2H), 3.74 – 3.70 (m, 1H), 3.64 (d, *J* = 3.8 Hz, 1H), 2.18 (s, 1H), 2.08 (s, 1H), 1.69 – 1.60 (m, 3H), 1.50 (ddd, *J* = 17.6, 9.0, 4.2 Hz, 5H), 1.39 (dd, *J* = 12.2, 6.7 Hz, 3H), 1.34 – 1.21 (m, 9H), 0.85 (t, *J* = 6.9 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ - 136.6, 133.7, 133.4, 133.2, 131.7, 129.7, 129.4, 129.4, 128.6, 128.5, 125.7, 125.0, 76.6, 75.5, 73.9, 73.2, 33.7, 33.2, 31.7, 25.1, 22.5, 14.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{22}NOS$ 252.1417; found: 252.1423.

4-heptyl-3-(phenylthio)-1,2-oxazetidine (20)



Following the general procedure the reaction was carried out with 1-nonyne (100 µL, 0.806 mmol), trimethylsilyl azide (185 µL, 1.61 mmol), thiophenol (88 µL, 0.806 mmol), TFA (91 µL, 0.806 mmol), $Ru(bpy)_3Cl_2$ (12 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (212 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 5.3, 2.3 Hz, 3H), 7.46 – 7.42 (m, 2H), 7.36 – 7.34 (m, 3H), 7.29 (d, *J* = 1.8 Hz, 2H), 4.57 (t, *J* = 4.9 Hz, 2H), 3.80 – 3.77 (m, 1H), 3.71 (d, *J* = 4.4 Hz, 1H), 2.28 (s, 1H), 2.18 (s, 1H), 1.85 – 1.62 (m, 5H), 1.60 – 1.42 (m, 5H), 1.30 – 1.25 (m, 14H), 0.90 – 0.87 (m, 6H). ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ - 133.7, 133.4, 132.8, 132.6, 129.4, 129.2, 129.1, 128.6, 75.5, 73.9, 73.3, 72.6, 33.7, 33.6, 33.3, 31.8, 29.5, 29.4, 29.2, 25.9, 25.5, 25.5, 22.7, 14.1. (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{24}NOS$ 266.1573; found: 266.1579

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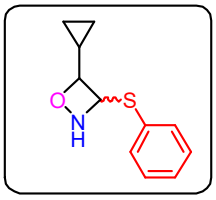
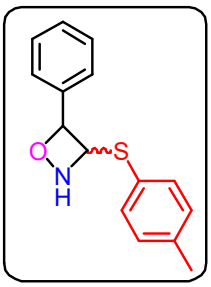
4-cyclopropyl-3-(phenylthio)-1,2-oxazetidine (21)



Following the general procedure the reaction was carried out with 1-nonyne(100 µL, 0.806 mmol), trimethylsilyl azide (185µL, 1.61mmol), thiophenol (88 µL, 0.806 mmol), TFA (91 µL, 0.806 mmol), $Ru(bpy)_3Cl_2$ (12 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (212 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 3H), 7.16 (s, 1H), 7.16 – 7.12 (m, 4H), 7.07 (dd, *J* = 11.0, 4.8 Hz, 2H), 4.47 (dd, *J* = 17.7, 4.1 Hz, 2H), 3.01 (ddd, *J* = 13.0, 8.3, 4.1 Hz, 2H), 2.18 (s, 1H), 1.09 – 0.90 (m, 2H), 0.49 – 0.35 (m, 4H), 0.32 – 0.07 (m, 4H). ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ 133.1, 132.7, 132.5, 132.3, 129.4, 129.2, 129.1, 128.3, 78.6, 78.6, 76.4, 75.2, 14.6, 14.3, 3.2, 3.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_{14}NOS$ 208.0791; found 208.0797

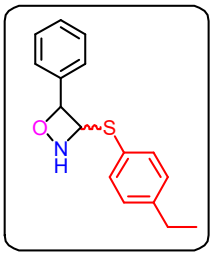
4-phenyl-3-(p-tolylthio)-1,2-oxazetidine (22)



Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (134 µL, 1.17 mmol), 4-methyl-thiophenol (121 µL, 0.98 mmol), TFA (111 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (154 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.39 (d, *J* = 6.0 Hz, 7H), 7.36 (s, 3H), 7.33 (d, *J* = 8.0 Hz, 4H), 7.17 – 7.12 (m, 4H), 4.88 (s, 1H), 4.74 – 4.68 (m, 2H), 4.64 (d, *J* = 6.6 Hz, 1H), 2.84 (s, 1H), 2.65 (s, 1H), 2.35 (d, *J* = 5.9 Hz, 6H). ^{13}C{^{1}H} (125 MHz, $CDCl_3$) δ - 139.3, 139.2, 134.5, 133.9, 130.2, 130.2, 130.1, 129.8, 128.6, 128.5, 128.5, 128.5, 128.2, 126.9, 126.8, 77.4, 76.5, 76.1, 74.7, 21.2, 21.2. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{16}NOS$ 258.0947; found: 258.0933.

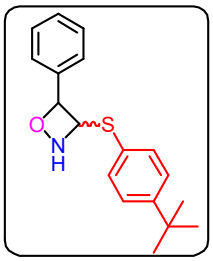
3-((4-ethylphenyl)thio)-4-phenyl-1,2-oxazetidine (23)

Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (134 µL, 1.17 mmol), 4-ethyl-thiophenol (135 µL, 0.98 mmol), TFA (111.7 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography



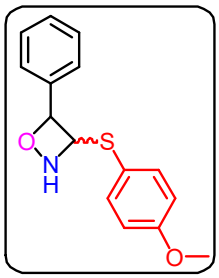
(hexane:EA = 99:1) as yellow oil (149 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.51 – 7.48 (m, 1H), 7.46 – 7.43 (m, 2H), 7.36 – 7.29 (m, 11H), 7.22 (d, *J* = 7.8 Hz, 4H), 4.90 (d, *J* = 4.4 Hz, 1H), 4.76 (d, *J* = 5.9 Hz, 2H), 4.68 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.77 (d, *J* = 23.1 Hz, 1H), 2.67 (d, *J* = 7.5 Hz, 4H), 1.59 (s, 1H), 1.24 (d, *J* = 7.6 Hz, 6H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 144.8, 136.5, 136.3, 133.8, 133.2, 132.3, 129.3, 129.3, 128.6, 128.4, 128.0, 128.0, 126.8, 126.8, 76.7, 76.2, 76.2, 75.0, 28.4, 15.2. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{18}NOS$ 272.1104; found:272.1106.

3-((4-(tert-butyl)phenyl)thio)-4-phenyl-1,2-oxazetidine (24)



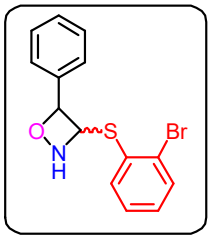
Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (135 µL, 1.176 mmol), 4-*tert*-butyl-thiophenol (162.68 µL, 0.98 mmol), TFA (111.72 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (193 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.47 – 7.45 (m, 2H), 7.44 (d, *J* = 3.8 Hz, 5H), 7.41 (d, *J* = 2.5 Hz, 3H), 7.39 (d, *J* = 4.9 Hz, 5H), 7.37 (d, *J* = 8.7 Hz, 3H), 4.93 (d, *J* = 5.0 Hz, 1H), 4.77 – 4.73 (m, 2H), 4.71 (d, *J* = 6.7 Hz, 1H), 2.95 (s, 1H), 2.78 (s, 1H), 1.35 (d, *J* = 3.4 Hz, 18H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 151.7, 151.7, 136.3, 136.0, 133.8, 133.2, 132.4, 131.5, 129.3, 129.2, 128.6, 128.4, 126.6, 126.5, 125.4, 125.4, 77.1, 76.2, 76.7, 75.0, 34.6, 31.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{22}NOS$ 300.1417; found: 300.1415.

3-((4-methoxyphenyl)thio)-4-phenyl-1,2-oxazetidine (25)



Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (135 µL, 1.176 mmol), 4-methoxy-thiophenol (137µL, 0.98mmol), TFA (111.72 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (114 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.46 (s, 1H), 7.43 (d, *J* = 3.3 Hz, 1H), 7.40 (d, *J* = 5.2 Hz, 7H), 7.37 (s, 4H), 6.87 (dd, *J* = 12.1, 8.7 Hz, 5H), 4.85 (d, *J* = 5.3 Hz, 1H), 4.66 (dd, *J* = 9.8, 6.4 Hz, 2H), 4.59 (d, *J* = 6.9 Hz, 1H), 3.82 (d, *J* = 5.4 Hz, 6H), 2.91 (s, 1H), 2.71 (s, 1H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 159.9, 159.8, 133.9, 133.3, 132.1, 131.2, 131.0, 129.4, 129.3, 128.7, 128.4, 128.1, 128.1, 113.9, 113.9, 77.1, 76.3, 75.8, 74.6, 55.3. (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{16}NO_2S$ 274.0896; found: 274.0888.

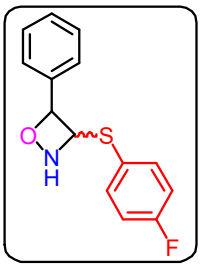
3-((2-bromophenyl)thio)-4-phenyl-1,2-oxazetidine (26)



Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (135 µL, 1.176 mmol), 2-br-thiophenol (137µL, 0.98 mmol), TFA (111.72 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (114 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.63 (d, *J* = 7.9 Hz, 2H), 7.56 (dd, *J* = 9.5, 3.5 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 3H), 7.42 (d, *J* = 4.3 Hz, 2H), 7.40 (s, 2H), 7.38 – 7.36 (m, 2H), 7.31 –

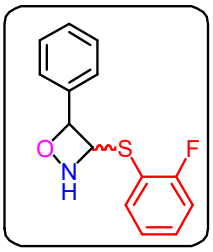
7.26 (m, 3H), 7.18 (ddd, J = 12.0, 5.9, 4.5 Hz, 2H), 5.09 (d, J = 3.7 Hz, 1H), 4.92 (d, J = 5.8 Hz, 1H), 4.83 (dd, J = 4.9, 3.1 Hz, 2H), 2.89 (s, 1H), 2.77 (s, 1H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 138.2, 138.0, 134.1, 133.4, 131.8, 131.7, 131.6, 130.7, 129.5, 129.4, 129.0, 128.7, 128.7, 128.6, 122.7, 122.6, 77.0, 76.1, 75.6, 74.4. (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}BrNOS$ 321.9896; found:321.9875.

3-((4-fluorophenyl)thio)-4-phenyl-1,2-oxazetidine (27)



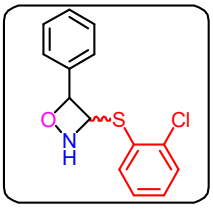
Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (135 µL, 1.176 mmol), 4-F-thiophenol (125.44 µL, 0.98 mmol), TFA (111.72 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (114 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.45 (d, J = 1.8 Hz, 2H), 7.43 (d, J = 3.1 Hz, 2H), 7.39 (dd, J = 8.9, 3.9 Hz, 9H), 7.33 (s, 1H), 7.31 (s, 1H), 7.30 (s, 1H), 7.27 (d, J = 1.9 Hz, 1H), 4.92 (d, J = 4.5 Hz, 1H), 4.76 (d, J = 6.0 Hz, 1H), 4.71 (d, J = 5.4 Hz, 2H), 2.76 (s, 1H), 2.69 (s, 1H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ 163.3 (d, J = 248 Hz), 163.1 (d, J = 248 Hz), 139.2, 139.1, 136.7 (d, J = 8.4 Hz), 136.1 (d, J = 8.4 Hz), 133.8, 130.3,129.4, 128.8, 128.7, 128.6, 128.5, 128.3,126.9, 116.5 (dd, J = 21.9, 3.4 Hz),77.4, 76.6, 76.3, 75.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ – 111.6, 112.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}FNOS$ 262.0696; found: 262.0688.

3-((2-fluorophenyl)thio)-4-phenyl-1,2-oxazetidine (28)



Following the general procedure the reaction was carried out with phenylacetylene (100 µL, 0.98 mmol), trimethylsilyl azide (135 µL, 1.176 mmol), 2-F-thiophenol (162.68 µL, 0.98 mmol), TFA (111.72 µL, 0.98 mmol), $Ru(bpy)_3Cl_2$ (14 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (115 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.53 – 7.50 (m, 2H), 7.48 – 7.44 (m, 2H), 7.37 – 7.33 (m, 8H), 7.24 (ddd, J = 7.5, 3.8, 2.7 Hz, 2H), 7.10 – 7.05 (m, 2H), 5.31 (d, J = 4.8 Hz, 1H), 5.16 (d, J = 5.7 Hz, 1H), 4.90 (t, J = 5.1 Hz, 2H), 2.98 (s, 2H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 160.0 (d, J = 244 Hz), δ 159.8 (d, J = 244 Hz), 133.6, 133.2, 132.2, 131.6, 130.1 (d, J = 8 Hz), 130.1 (d, J = 9 Hz), 129.4, 129.4, 128.6, 128.6, 128.3, 128.3, 126.8 (d, J = 12.7 Hz), 126.5 (d, J = 12.8 Hz), 124.5, 124.4, 115.4 (d, J = 21 Hz), 115.3 (d, J = 21.5 Hz), 76.1, 74.8, 70.9, 69.9. ^{19}F NMR (377 MHz, $CDCl_3$) δ -106.3, -106.9.HRMS (ESI) (m/z): $[M+H]^+$ calculated $C_{14}H_{13}FNOS$ 262.0696; found: 262.0690.

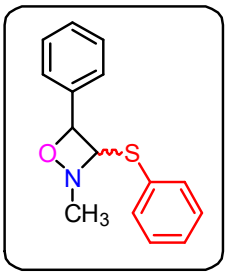
3-((2-chlorophenyl)thio)-4-phenyl-1,2-oxazetidine (29)



Following the general procedure the reaction was carried out with 2-chloro-phenylacetylene (100 µL, 0.73 mmol), trimethylsilyl azide (101.2 µL, 0.73 mmol), 2-Cl-thiophenol (80.3 µL, 0.73 mmol), TFA (83.22 µL, 0.73 mmol), $Ru(bpy)_3Cl_2$ (10.92 mg, 2 mol%) and purified by column chromatography (hexane:EA = 99:1) as yellow oil (155 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.4 Hz, 2H), 7.45 – 7.41 (m, 3H), 7.39 (dd, J = 3.6, 1.7

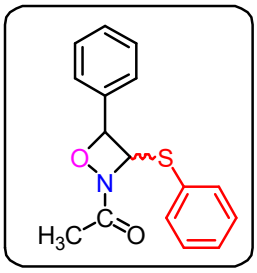
Hz, 6H), 7.36 (s, 1H), 7.34 (d, J = 2.1 Hz, 2H), 7.33 – 7.30 (m, 4H), 4.91 (d, J = 5.4 Hz, 1H), 4.75 (dd, J = 6.0, 2.5 Hz, 2H), 4.70 (d, J = 6.5 Hz, 1H), 2.86 (s, 2H). $^{13}C\{^{1}H\}$ (100 MHz, $CDCl_3$) δ - 139.2, 139.0., 134.0, 133.3, 132.1, 131.03, 129.3, 129.3, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 126.9, 126.8, 126.7, 77.1, 76.3, 76.1, 75.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}ClNOS$ 278.0401; found:278.0398.

2-methyl-4-phenyl-3-(phenylthio)-1,2-oxazetidine (30)



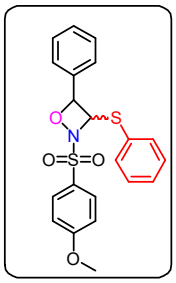
To an oven dried 50 ml glass vial, containing starting compound 4-phenyl-3-(phenylthio)-1,2-oxazetidine (50 µL, 0.2 mmol) in DMF was added methyl iodide (86 µL, 0.6 mmol) and pyridine (32 µL, 0.4 mmol) with continuous stirring under air at room temperature for 4 hours. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/ethyl acetate 99:1) as a as colourless oil (107 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.49 (dd, J = 6.6, 2.9 Hz, 2H), 7.46 – 7.42 (m, 3H), 7.41 (s, 5H), 7.39 (d, J = 2.1 Hz, 2H), 7.38 – 7.36 (m, 2H), 7.35 (d, J = 2.2 Hz, 2H), 7.32 (dd, J = 6.1, 2.9 Hz, 4H), 4.93 (d, J = 5.4 Hz, 1H), 4.76 (dd, J = 6.0, 2.4 Hz, 2H), 4.73 (d, J = 6.5 Hz, 1H), 2.95 (s, 3H), 2.88 (s, 3H). $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) δ - 139.3, 139.0, 134.0, 133.3, 132.1, 131.1, 129.4, 129.3, 128.8, 128.8, 128.7, 128.7, 128.5, 128.5, 126.9, 126.8, 77.1, 76.3, 76.1, 75.0, 36.6, 31.5. (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{16}NOS$ 258.0947; found: 258.0940.

1-(4-phenyl-3-(phenylthio)-1,2-oxazetidin-2-yl)ethan-1-one (31)



To an oven dried 50 ml glass vial, containing starting compound 4-phenyl-3-(phenylthio)-1,2-oxazetidine (50 µL, 0.2 mmol) in THF was added acetic anhydride (62 µL, 0.6 mmol) and triethylamine (60 µL, 0.6 mmol), with continuous stirring under air at 40 °C for 36 hours. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/ethyl acetate 96:4) as a colourless oil (114 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.43 (d, J = 10.6 Hz, 5H), 7.38 (s, 8H), 7.32 (s, 6H), 7.26 (s, 1H), 6.03 (dd, J = 6.2, 5.2 Hz, 2H), 4.82 (dd, J =5.2, 6.2 Hz, 2H), 2.17 (d, J = 5.2 Hz, 6H). $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) δ - 169.5, 169.4, 164.0, 163.9, 162.0, 161.9, 142.3, 133.4, 133.2, 132.2, 132.1, 131.8, 131.7, 131.6, 131.6, 129.4, 129.3, 129.2, 129.1, 129.0, 128.7, 128.7, 115.7, 115.6, 115.5, 115.43, 76.0, 75.6, 74.0, 73.4, 21.0, 20.8. (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{16}NO_2S$ 286.0896; found: 286.0883.

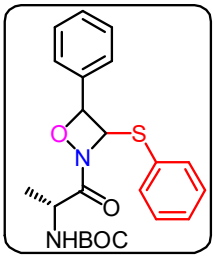
2-((4-methoxyphenyl)sulfonyl)-4-phenyl-3-(phenylthio)-1,2-oxazetidine(32)



To an oven dried 50 ml glass vial, containing starting compound 4-phenyl-3-(phenylthio)-1,2-oxazetidine (50 µL, 0.2 mmol) in DMF at -78 ^{0}C under inert conditions was added 4-methoxybenzenesulfonyl chloride (82 µL, 0.4 mmol) and pyridine base (47 µL, 0.6 mmol) with continuous stirring for 3 hours. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/ethyl acetate 80:20) as a colourless oil (144mg, 33% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.53 – 7.46 (m, 5H), 7.37 – 7.32 (m, 9H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.30 – 7.24 (m, 4H), 6.98 (t, *J* = 11.1 Hz, 6H), 6.87 (dd, *J* = 25.0, 8.2 Hz, 3H), 4.90 (t, *J* = 5.0 Hz, 2H), 4.77 (dd, *J* = 5.7, 3.5 Hz, 2H), 4.72 (d, *J* = 6.3 Hz, 1H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 139.3, 139.1, 133.6, 133.4, 130.3, 130.1, 128.84, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 126.9, 126.8, 126.2, 125.8, 125.1, 119.2, 118.7, 118.1, 115.4, 114.7, 114.4, 79.2, 76.3, 75.0, 75.2, 55.4. (ESI) (m/z): $[M+H]^+$ calculated for $C_{21}H_{20}NO_4S_2$ for 414.0828 found: 414.0820

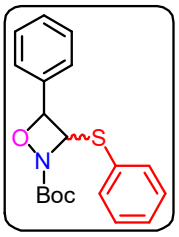
***tert*-butyl((2R)-1-oxo-1-(4-phenyl-3-(phenylthio)-1,2-oxazetidin-2-yl)propan-2-yl)carbamate (33)**

To a cooled (0 °C) solution of Boc Alanine (50 µL, 0.25 mmol)), HBTU (2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (193µL, 0.5 mmol) and NMM (*N*-Methylmorpholine) (123 µL, 0.6 mmol) in DMF were added under dry conditions. After stirring for 15 min, 4-phenyl-3-(phenylthio)-1,2-oxazetidine (61 µL, 0.25 mmol) was added with continuous stirring for 24 hours at room temperature. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/ethyl acetate 80:20) as a colourless oil (144 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.41 (d, *J* = 3.3 Hz, 4H), 7.36 (s, 5H), 7.32 (d, *J* = 8.1 Hz, 5H), 7.27 (t, *J* = 4.9 Hz, 6H), 4.90 (d, *J* = 4.9 Hz, 1H), 4.75 – 4.69 (m, 2H), 4.42 (s, 1H), 3.87 (d, *J* = 6.4 Hz, 2H), 3.82 (d, *J* = 6.6 Hz, 1H), 3.58 – 3.56 (m, 2H), 3.41 – 3.37 (m, 2H), 1.48 (s, 6H), 1.41 (s, 9H), 0.90 (d, *J* = 2.3 Hz, 3H), 0.88 (s, 3H).^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ - 155.6, 151.5, 139.8, 139.5, 133.6, 133.0, 132.6, 131.8, 129.3, 128.5, 128.5, 128.5, 128.4, 128.3, 126.9, 126.8, 84.8, 79.7, 77.0, 76.4, 76.0, 75.3, 71.8, 71.4, 66.2, 61.8, 46.8, 45.4, 28.4, 28.0, 27.7,19.0. (ESI) (m/z): $[M+H]^+$ calculated for $C_{22}H_{27}N_2O_4S$ 415.1686; found: 415.1675.



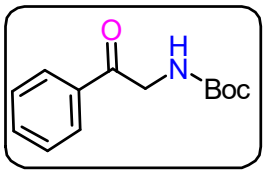
***tert*-butyl 4-phenyl-3-(phenylthio)-1,2-oxazetidine-2-carboxylate (34)**

To an oven dried 50 ml glass vial, containing starting compound 4-phenyl-3-(phenylthio)-1,2-oxazetidine (50 µL, 0.2 mmol) in THF was added Boc anhydride (87 µL, 0.40 mmol), triethylamine (20 µL, 0.20 mmol) and DMAP (20 µL, 0.20 mmol) with continuous stirring for



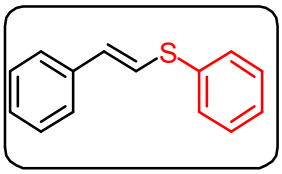
12 hours at room temperature. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/ethyl acetate 99:1) as a colourless oil (63 mg, 90% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ - 7.48 – 7.45 (m, 2H), 7.44 – 7.41 (m, 5H), 7.38 (dt, *J* = 7.9, 2.6 Hz, 8H), 7.32 (dd, *J* = 4.1, 2.1 Hz, 5H), 5.75 (d, *J* = 6.2 Hz, 1H), 5.72 (d, *J* = 5.7 Hz, 1H), 4.89 (d, *J* = 5.7 Hz, 1H), 4.86 (d, *J* = 6.2 Hz, 1H), 1.48 (s, 9H), 1.47 (s, 9H). ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ - 152.4, 152.3, 136.0, 135.8, 133.7, 133.4, 131.9, 131.9, 129.3, 129.1, 129.0, 128.8, 128.7, 128.7, 128.6, 128.5, 127.4, 127.3, 83.2, 83.1, 78.9, 78.6, 73.9, 73.7, 27.8, 27.7. (ESI) (m/z): $[M+Na]^+$ calculated for $C_{19}H_{21}NO_3NaS$ 366.1134; found: 366.1140

***tert*-butyl (2-oxo-2-phenylethyl)carbamate (35)**



To an oven-dried 50 ml glass vial, containing starting compound tert-butyl 4-phenyl-3-(phenylthio)-1,2-oxazetidine-2-carboxylate (50 µL, 0.145 mmol) in dry THF was added triphenylphosphine (76 µL, 0.29 mmol) under argon with continuous stirring for 12 hours at room temperature. After the completion of reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were then washed with sodium bicarbonate ($NaHCO_3$) and again extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by silica gel column chromatography using (hexane/ethyl acetate 99:1) as a white solid (24 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 2H), 7.54 (ddd, *J* = 6.9, 4.0, 1.2 Hz, 1H), 7.42 (dd, *J* = 10.6, 4.7 Hz, 2H), 5.49 (s, 1H), 4.60 (d, *J* = 4.5 Hz, 2H), 1.41 (s, 9H). ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ - 194.5, 155.8, 134.5, 134.0, 128.9, 127.8, 79.9, 47.5, 28.4. (ESI) (m/z): $[M+Na]^+$ calculated for $C_{13}H_{17}NO_3Na$ 258.1101; found: 258.1106

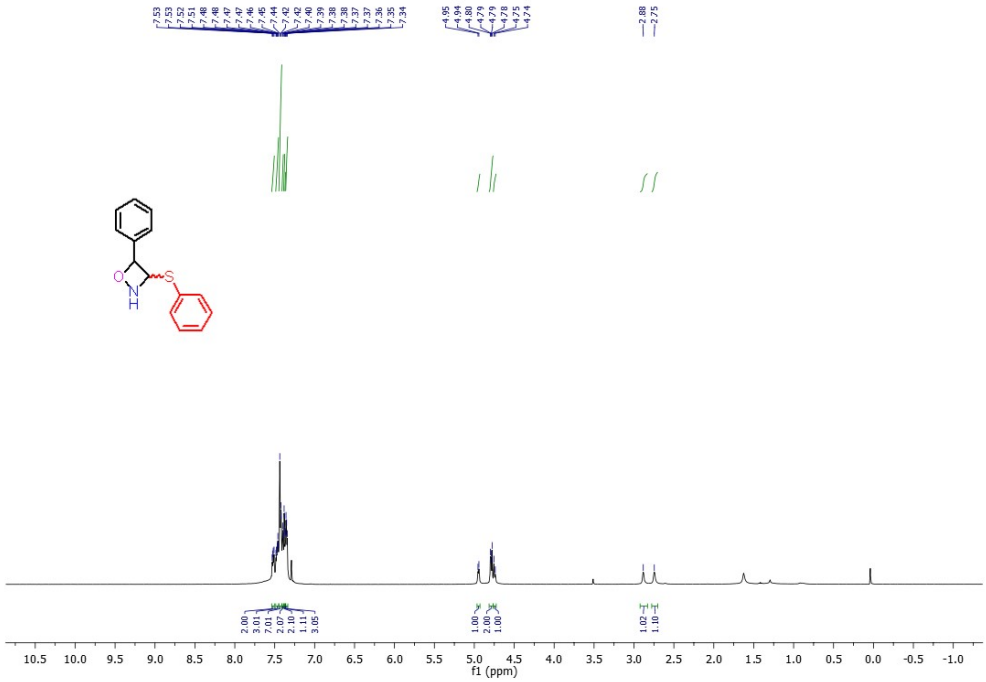
(E)-phenyl(styryl)sulfane (1d)



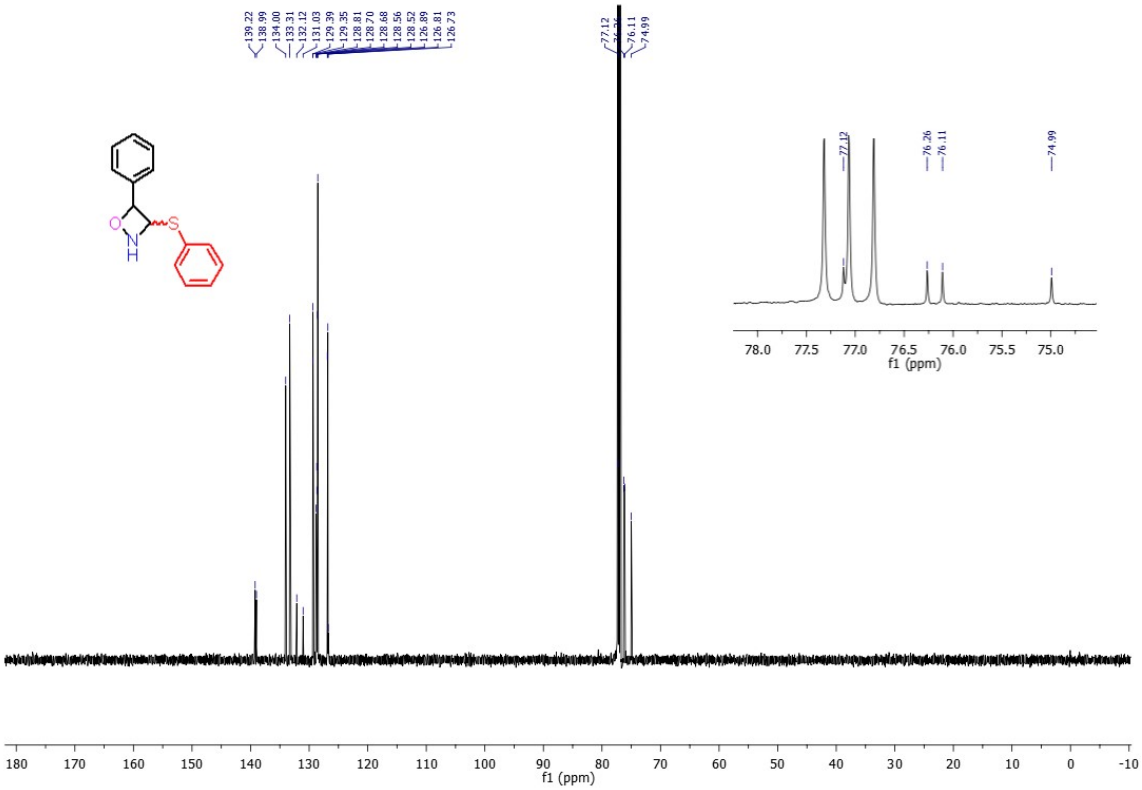
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.6, 3.7 Hz, 2H), 7.30 (dd, *J* = 8.3, 6.5 Hz, 6H), 7.24 – 7.19 (m, 2H), 6.89 – 6.81 (m, 1H), 6.74 – 6.66 (m, 1H). ^{13}C{^{1}H} (100 MHz, $CDCl_3$) δ - 136.6, 135.4, 131.9, 129.9, 129.3, 128.8, 127.7, 127.1, 126.1, 123.5. (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}S$ 213.0732; found: 213.0735

NMR Spectra

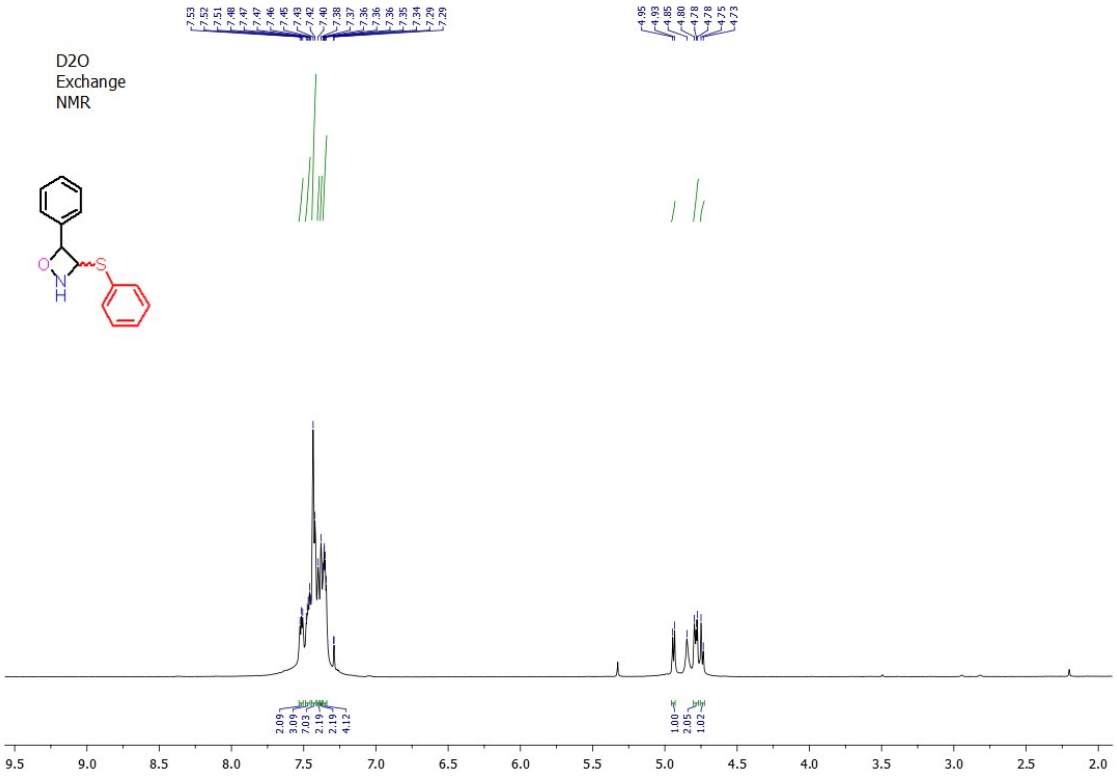
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **1**



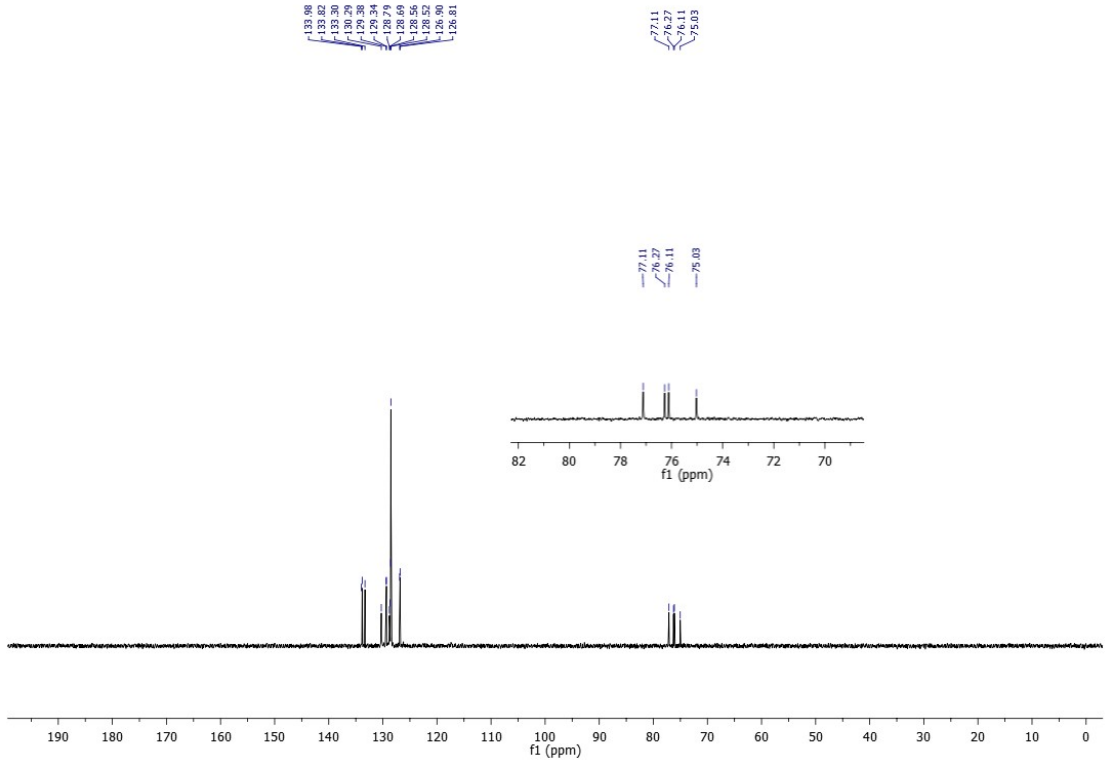
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **1**



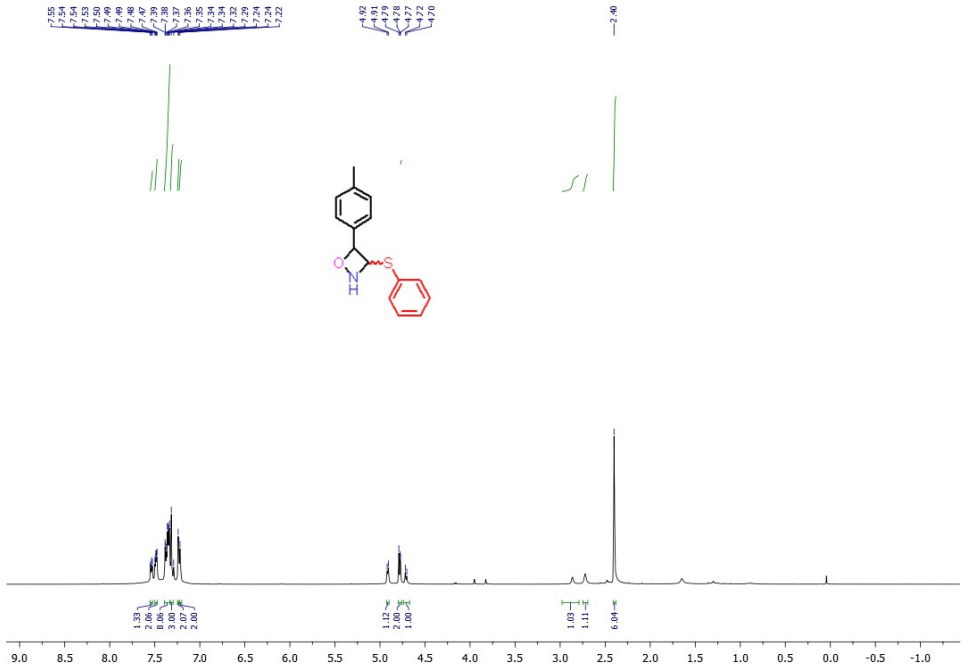
^{1}H-NMR (D_2O, 400 MHz) Spectra of compound **1**



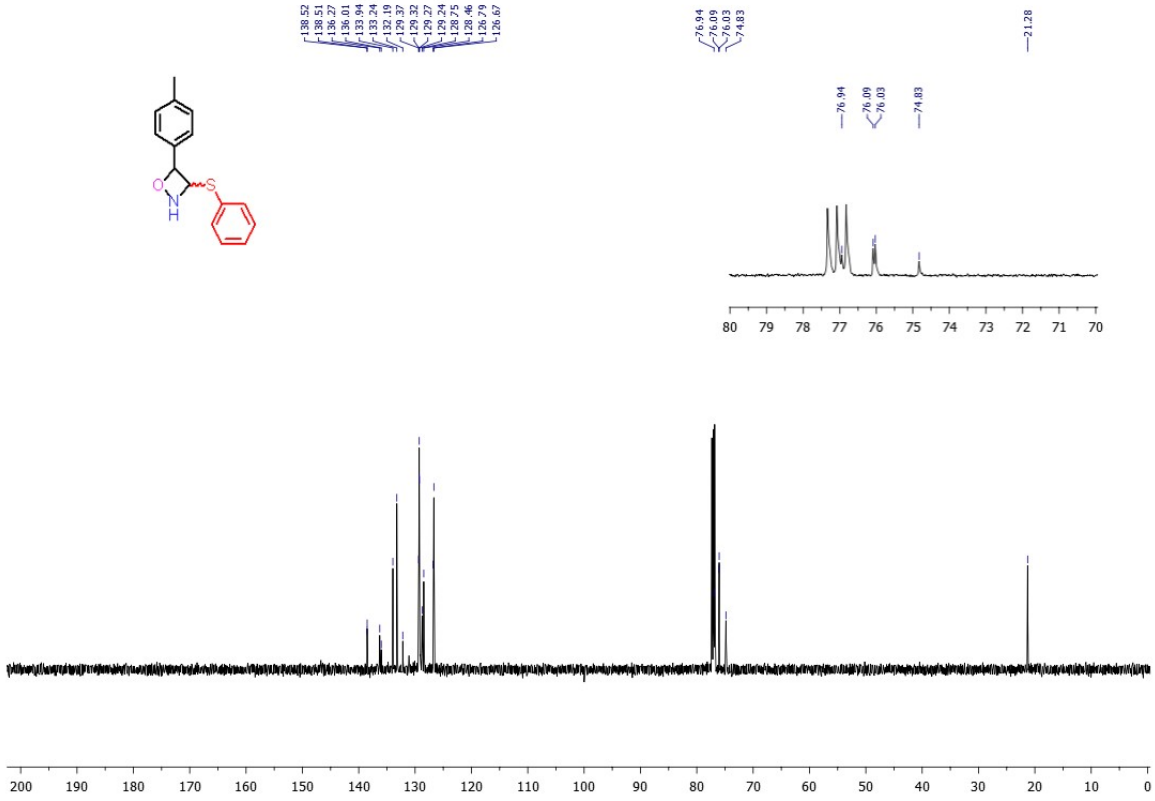
^{13}C DEPT NMR ($CDCl_3$, 125 MHz) spectra of compound **1**



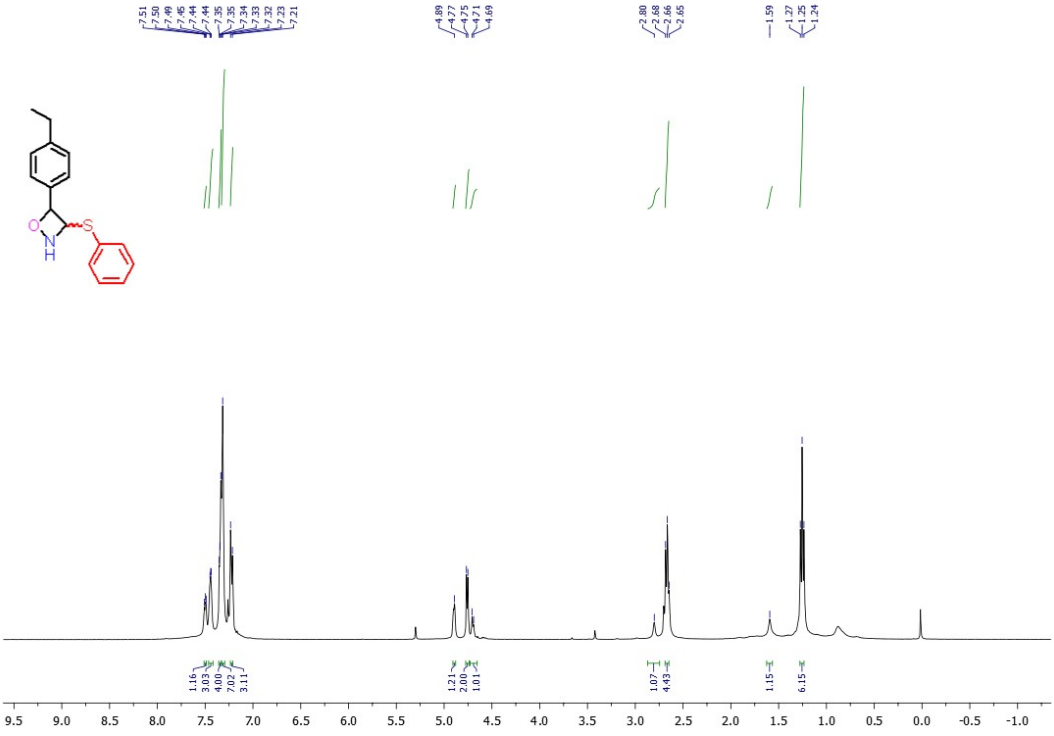
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **2**



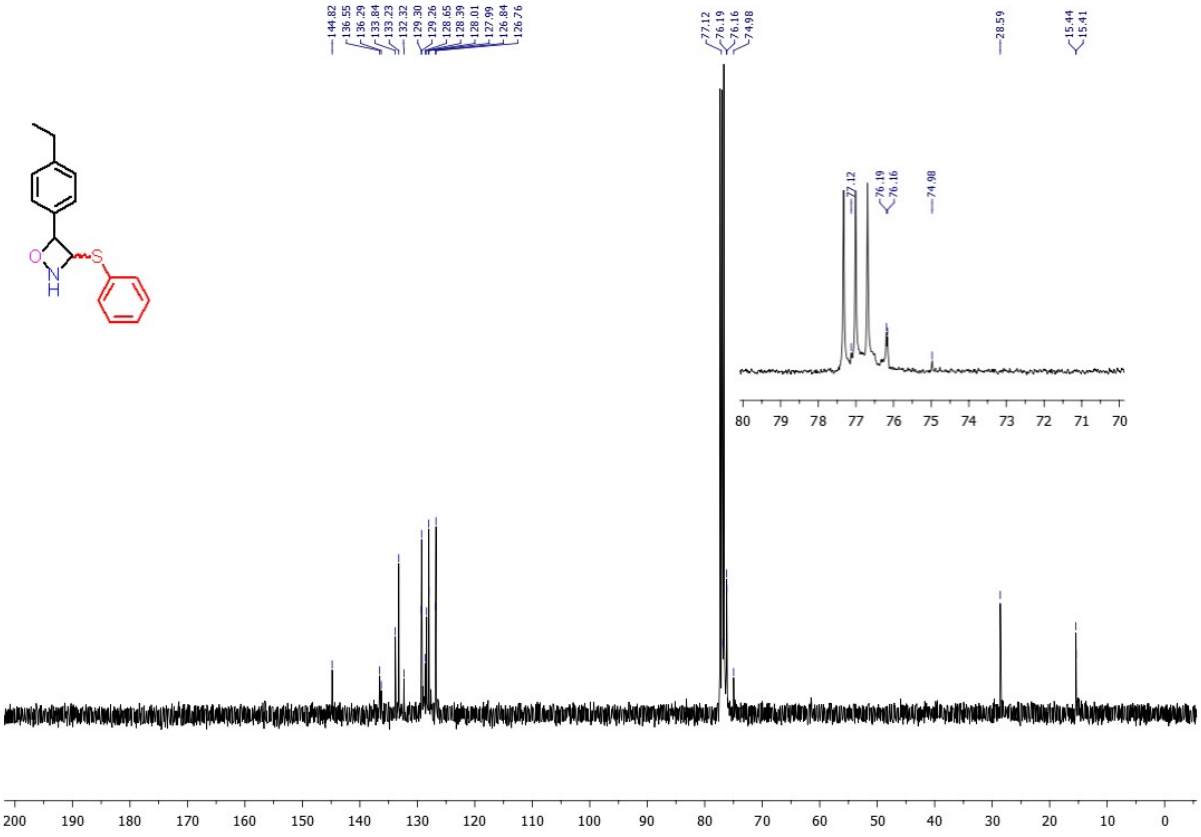
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound 2



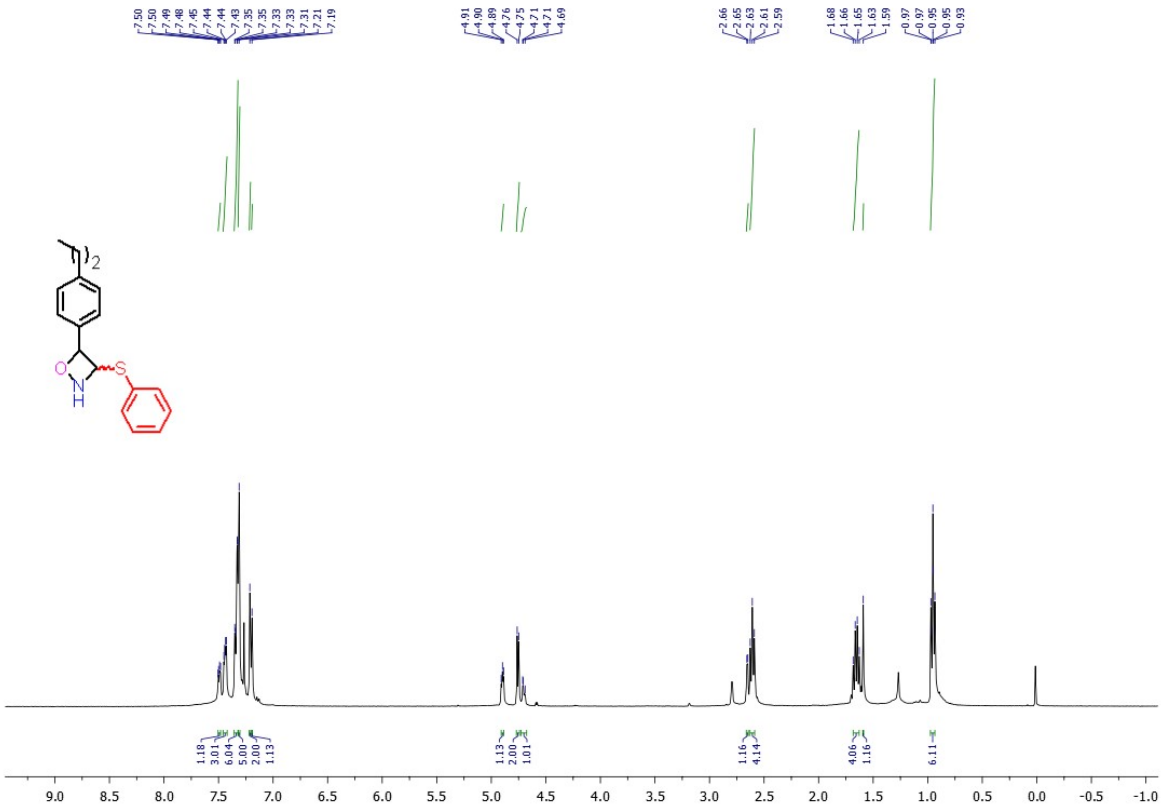
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **3**



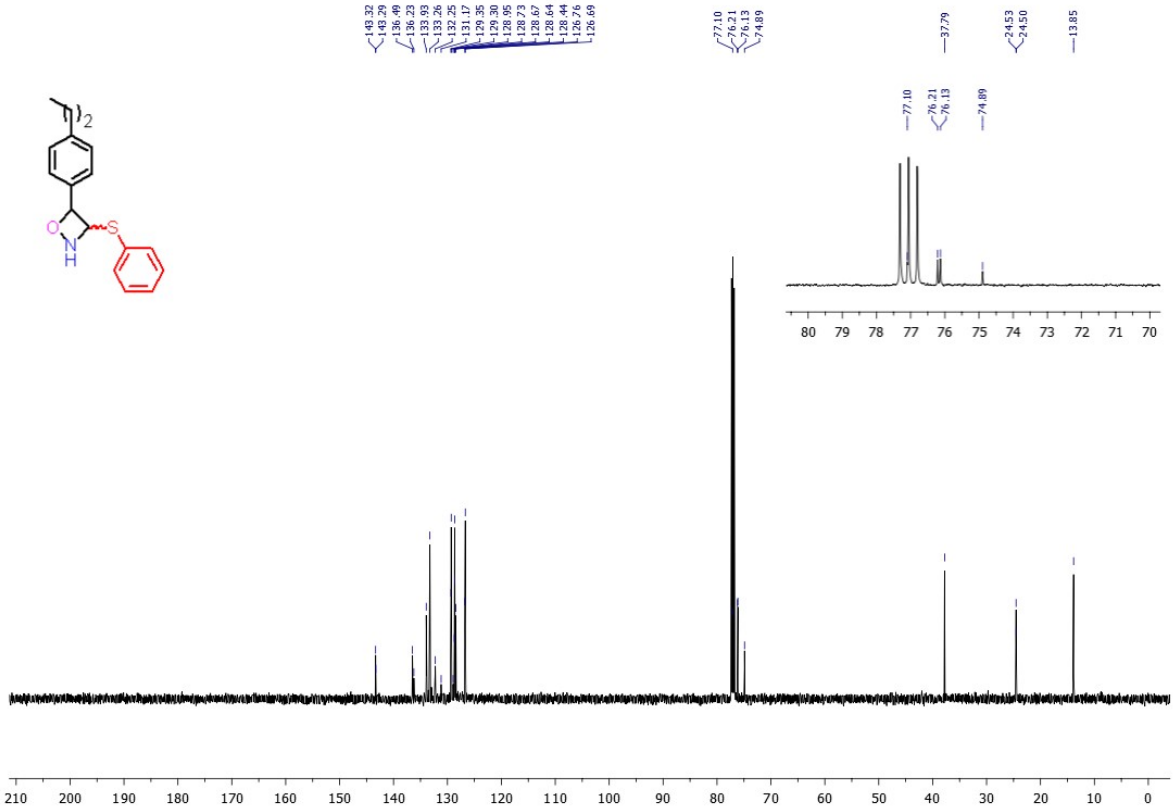
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of compound **3**



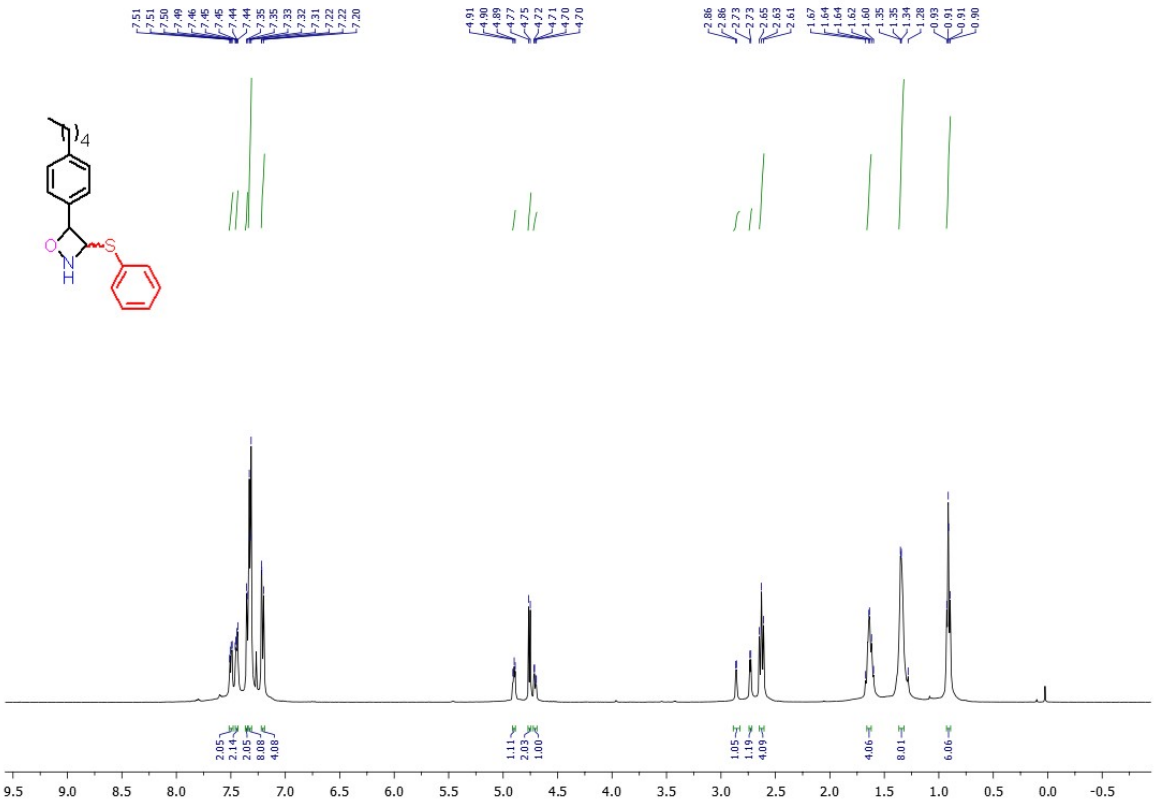
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **4**



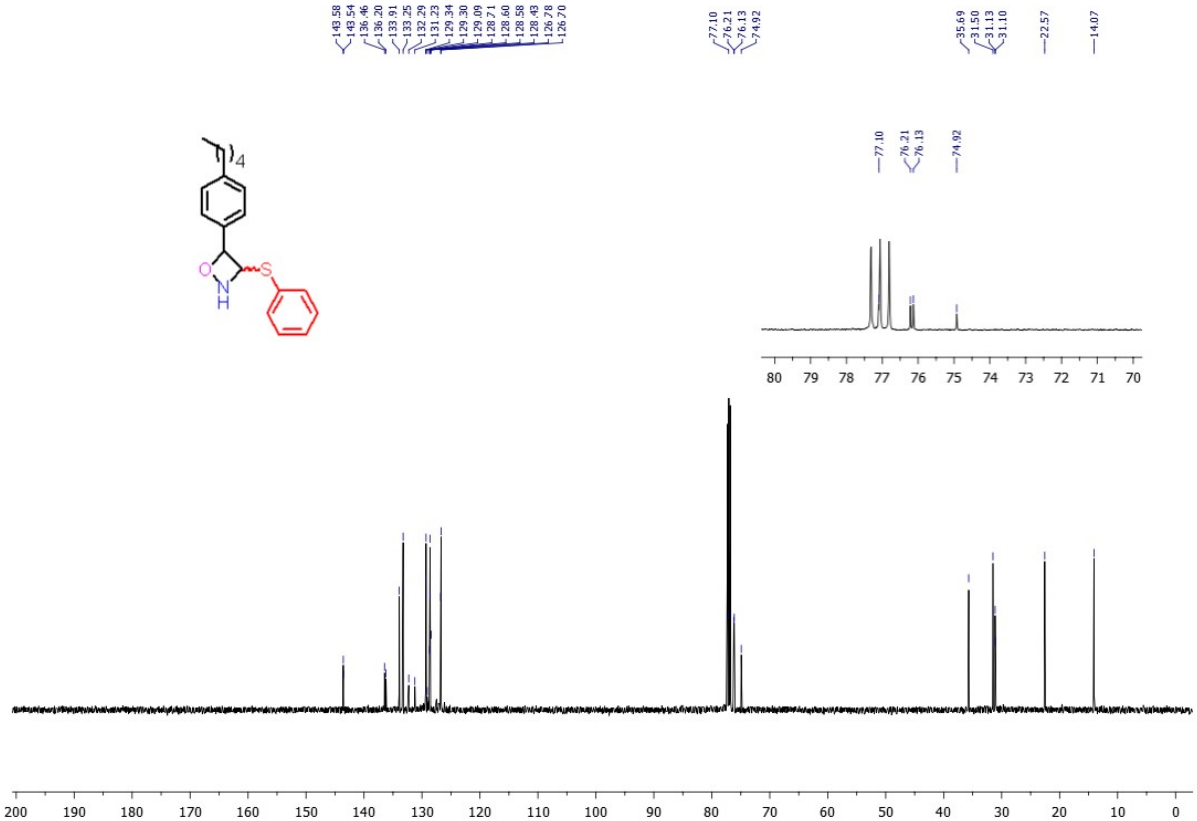
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of compound **4**



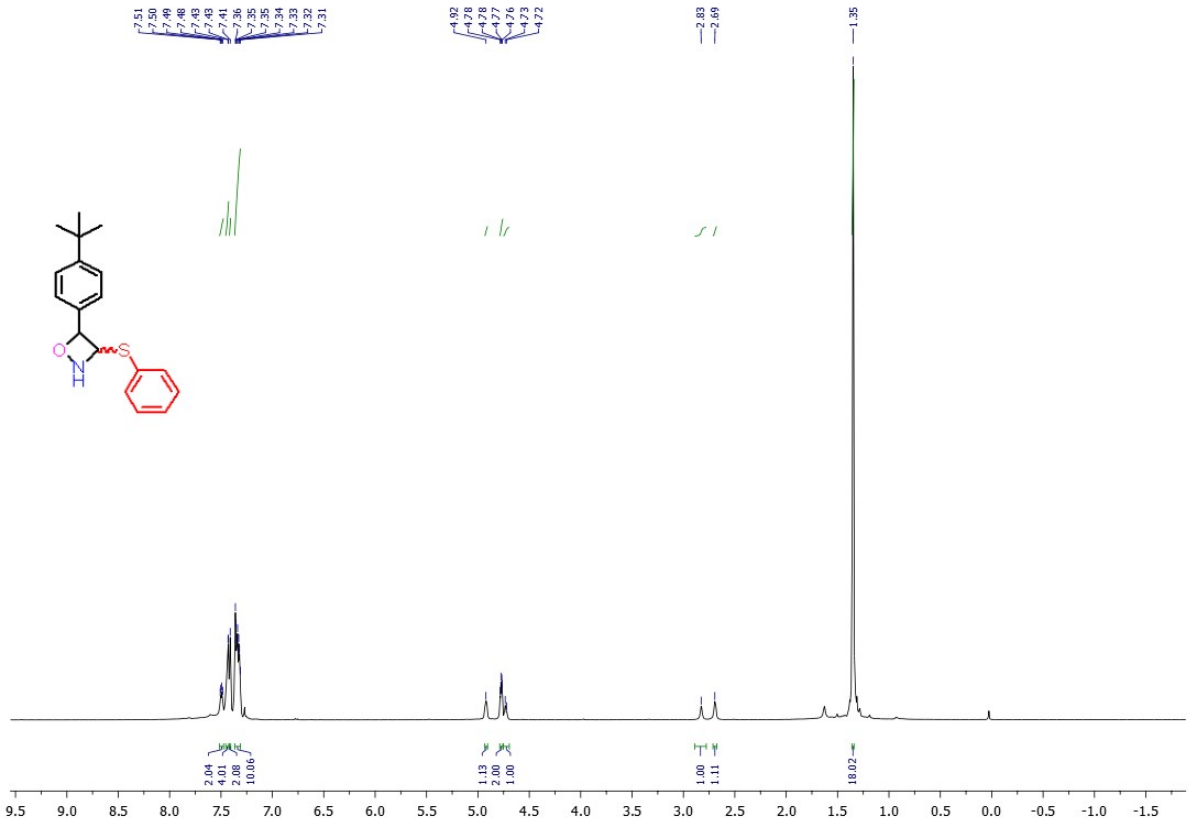
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **5**



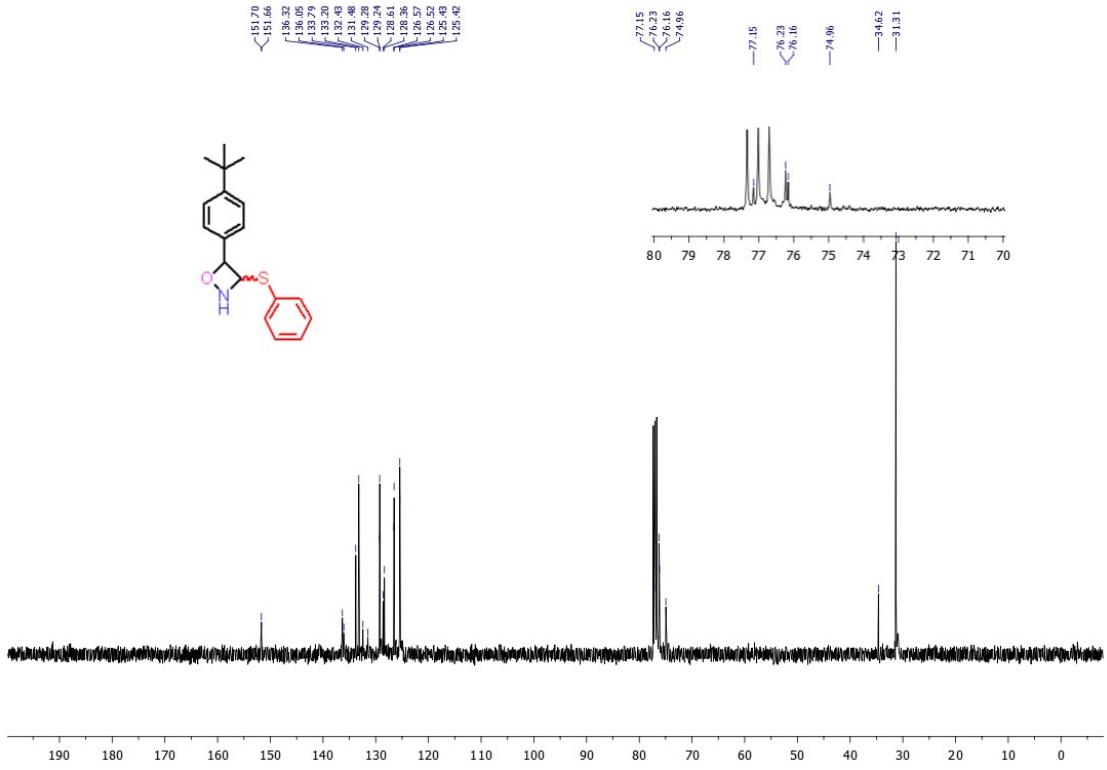
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of compound **5**



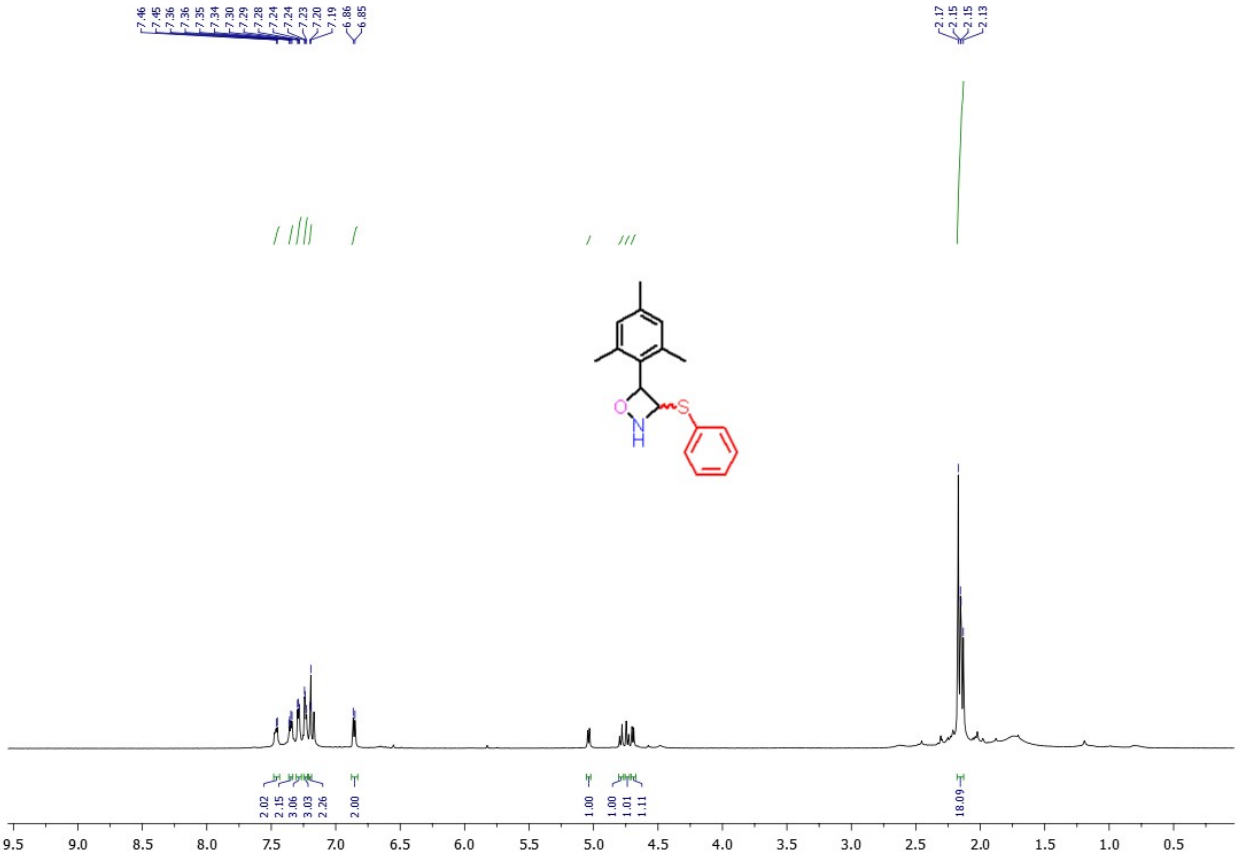
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **6**



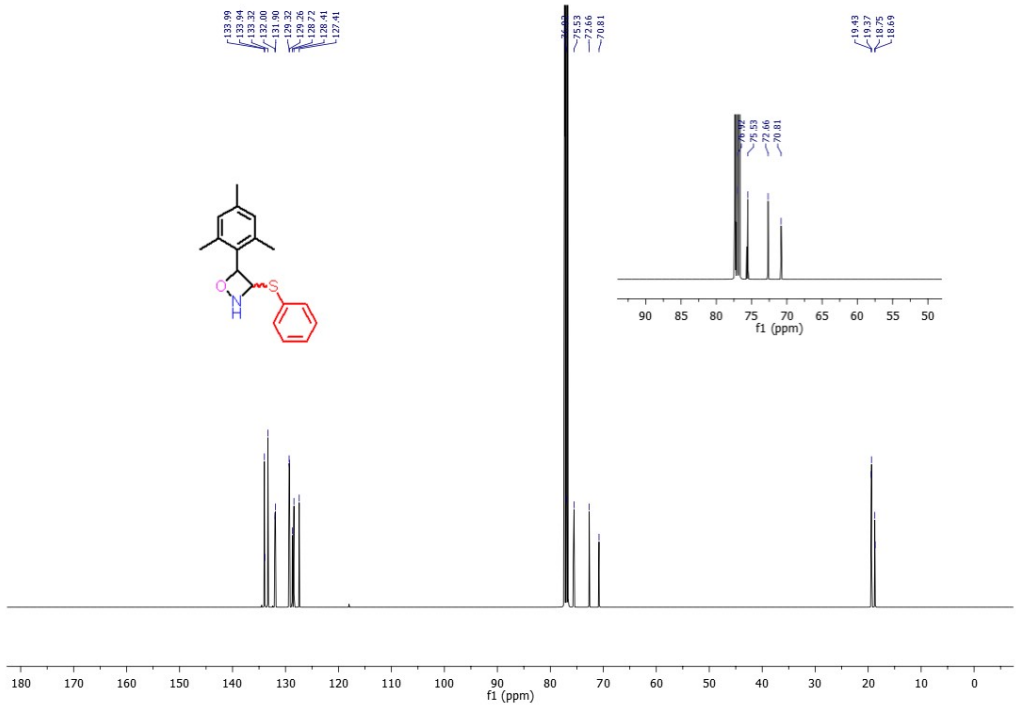
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **6**



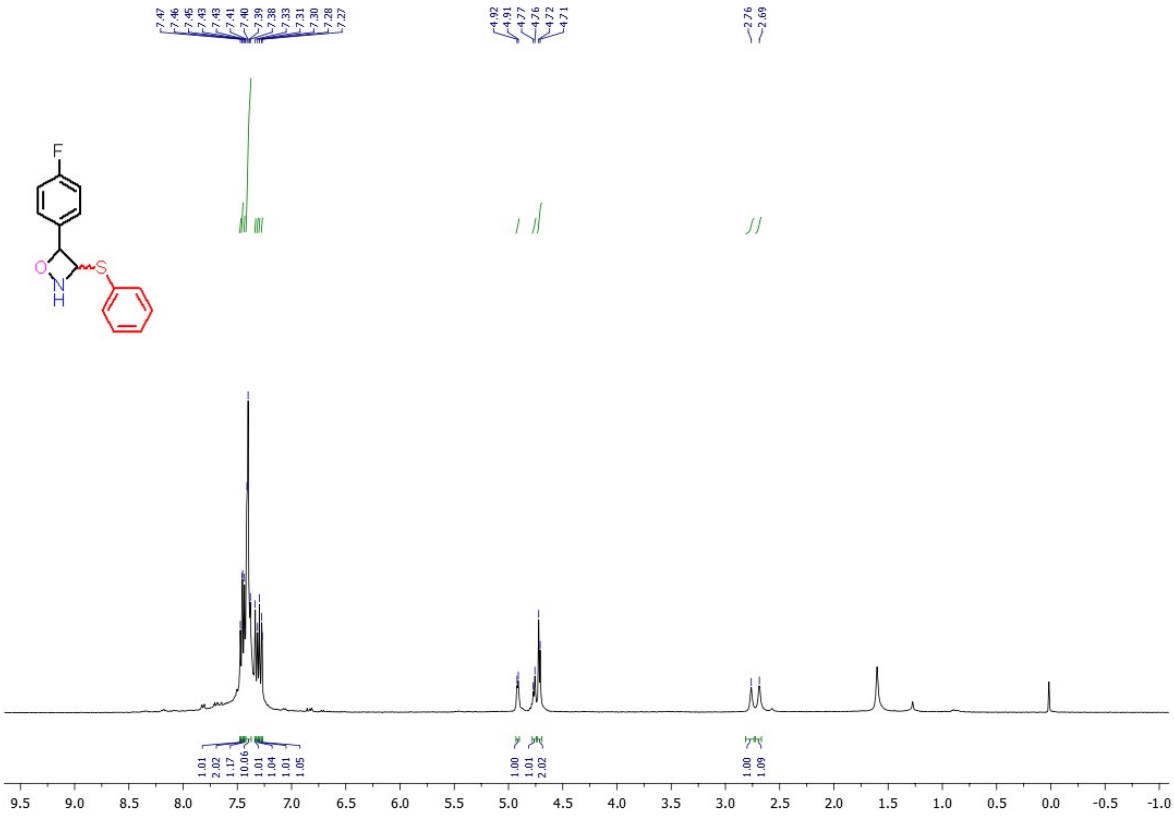
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **7**



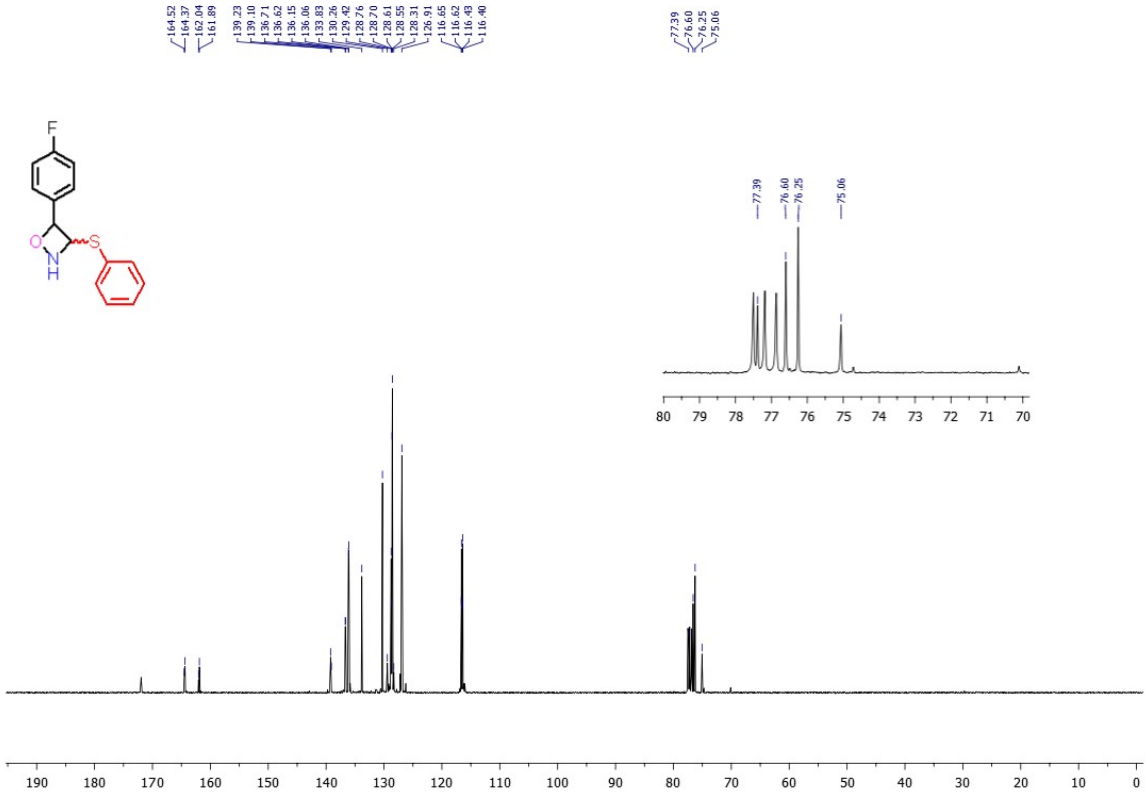
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **7**



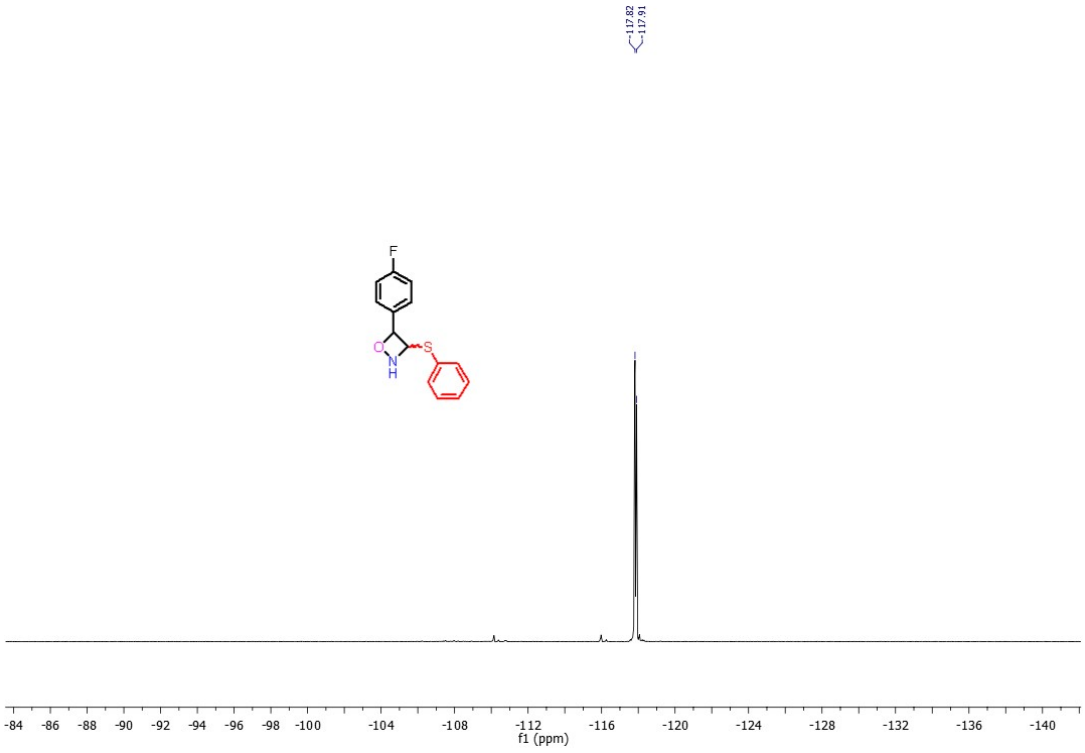
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **8**



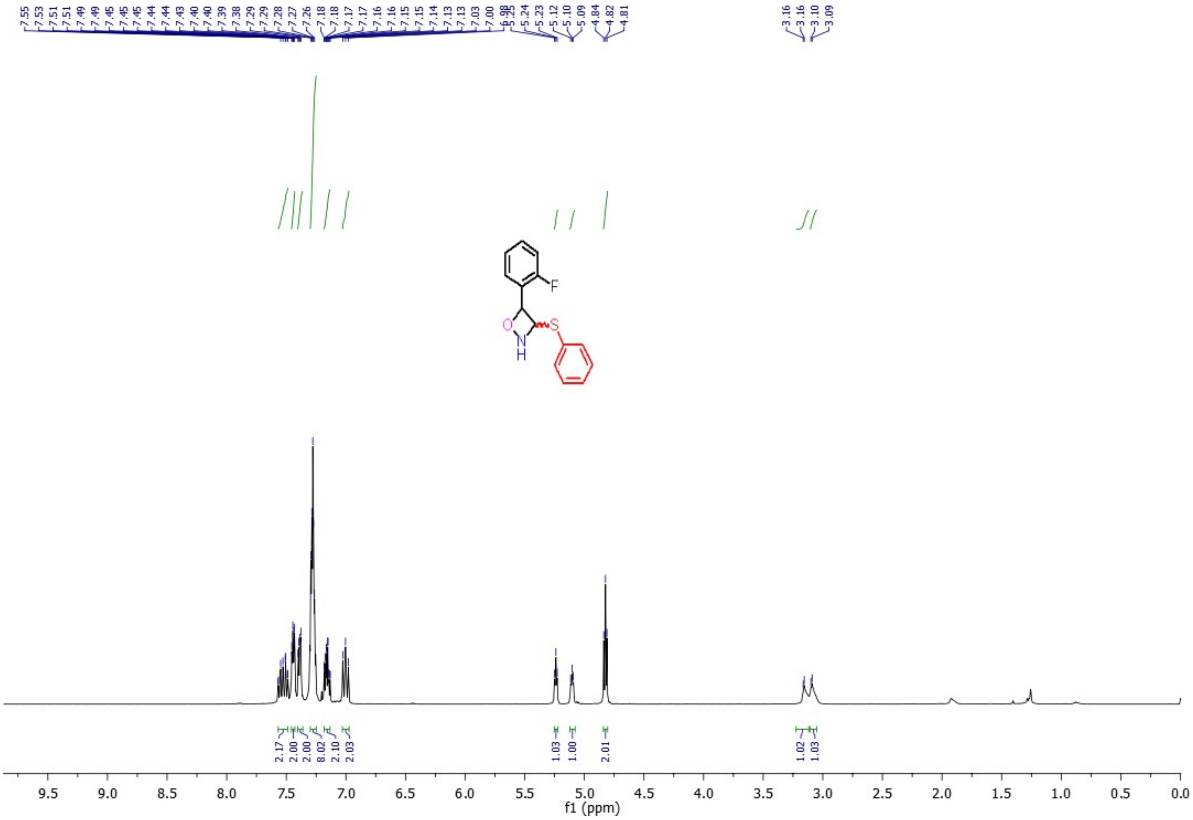
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **8**



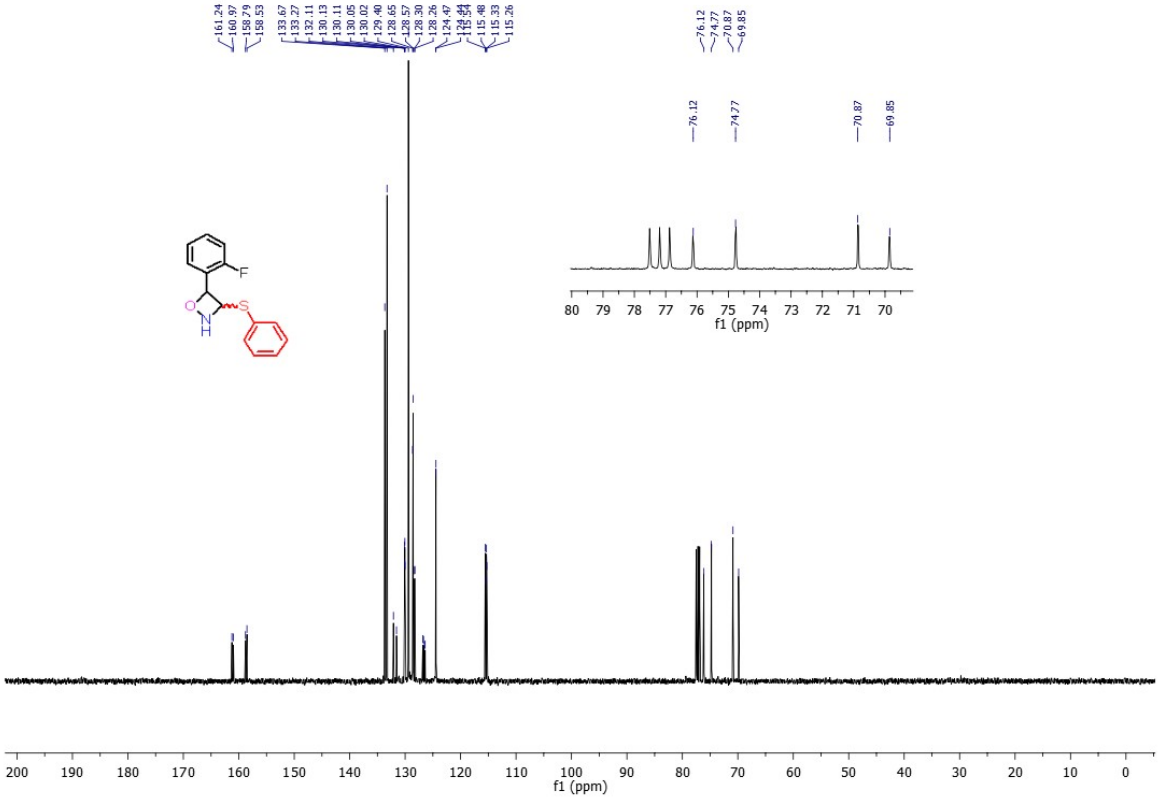
^{19}F-NMR ($CDCl_3$, 377 MHz) spectra of compound **8**



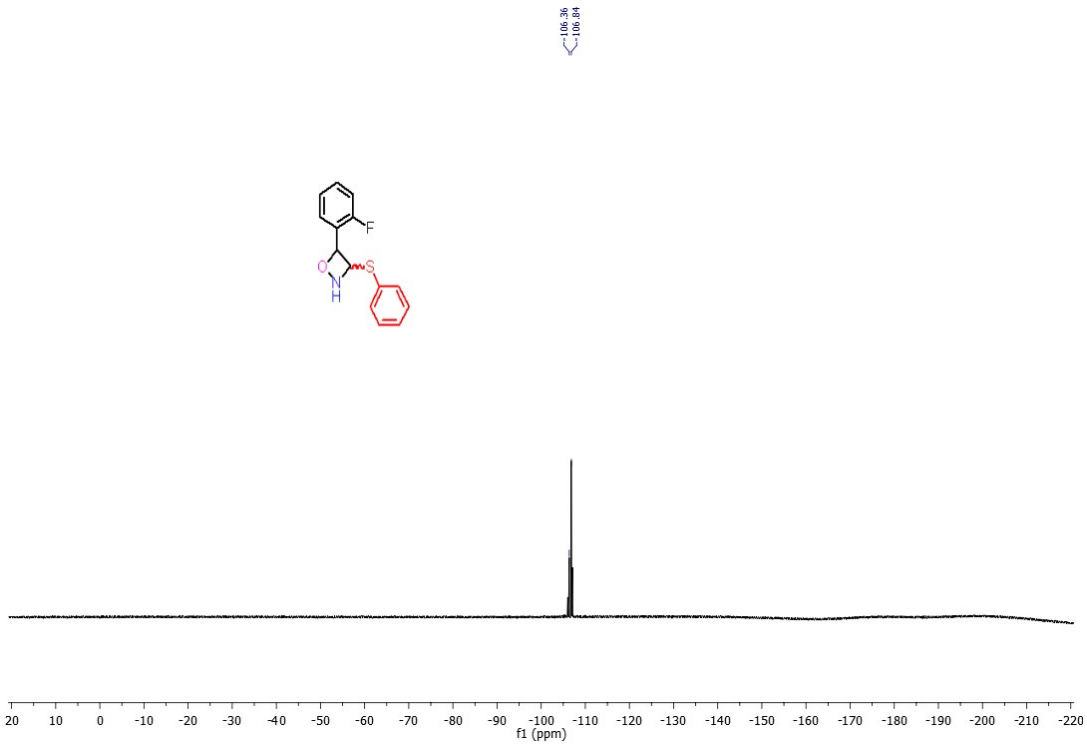
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **9**



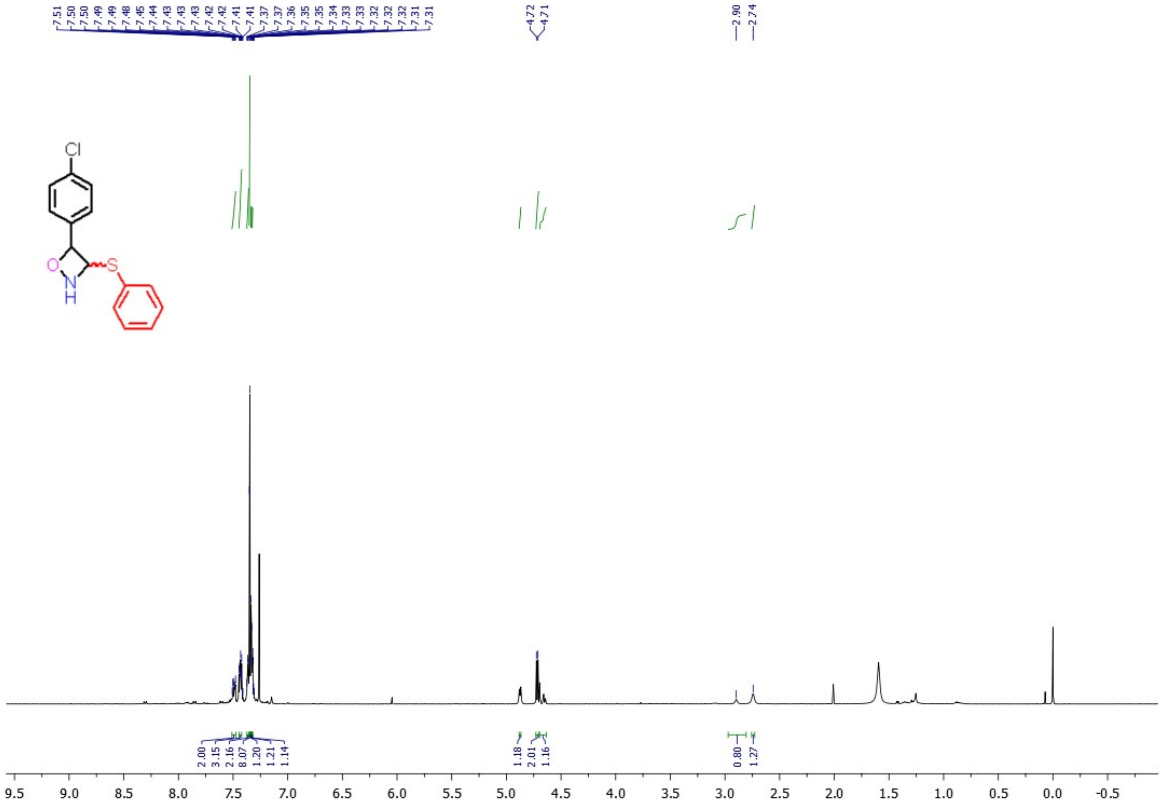
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **9**



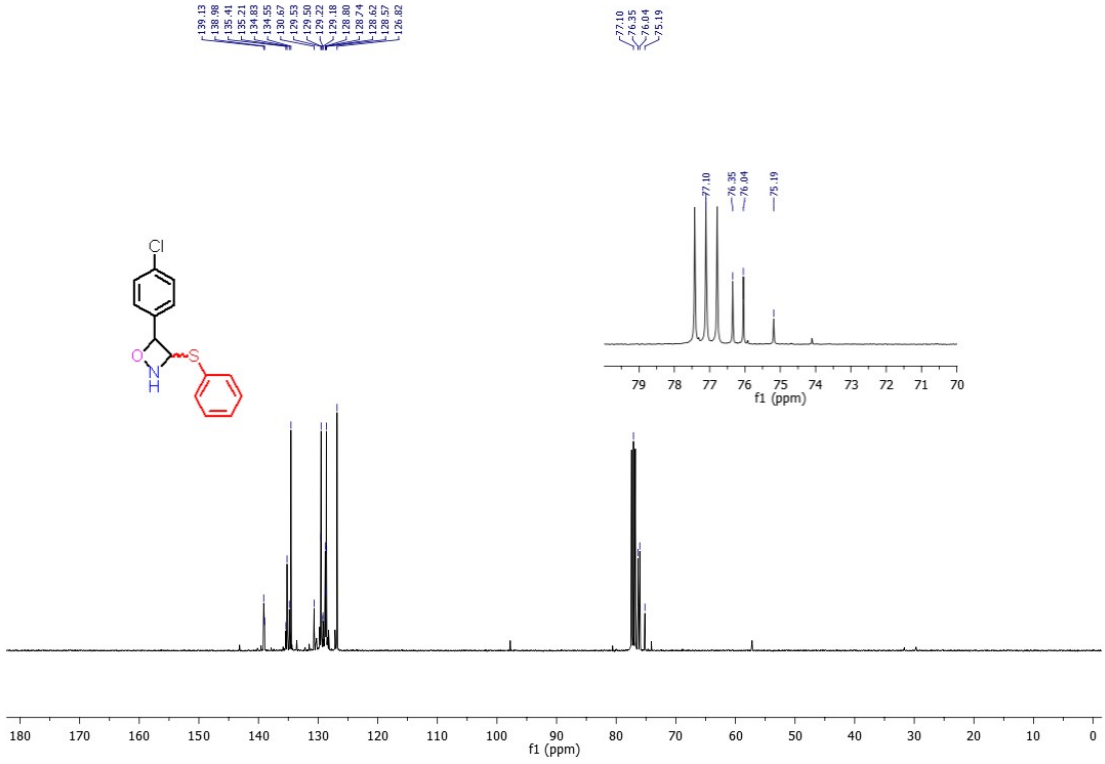
^{19}F-NMR ($CDCl_3$, 377 MHz) spectra of compound **9**



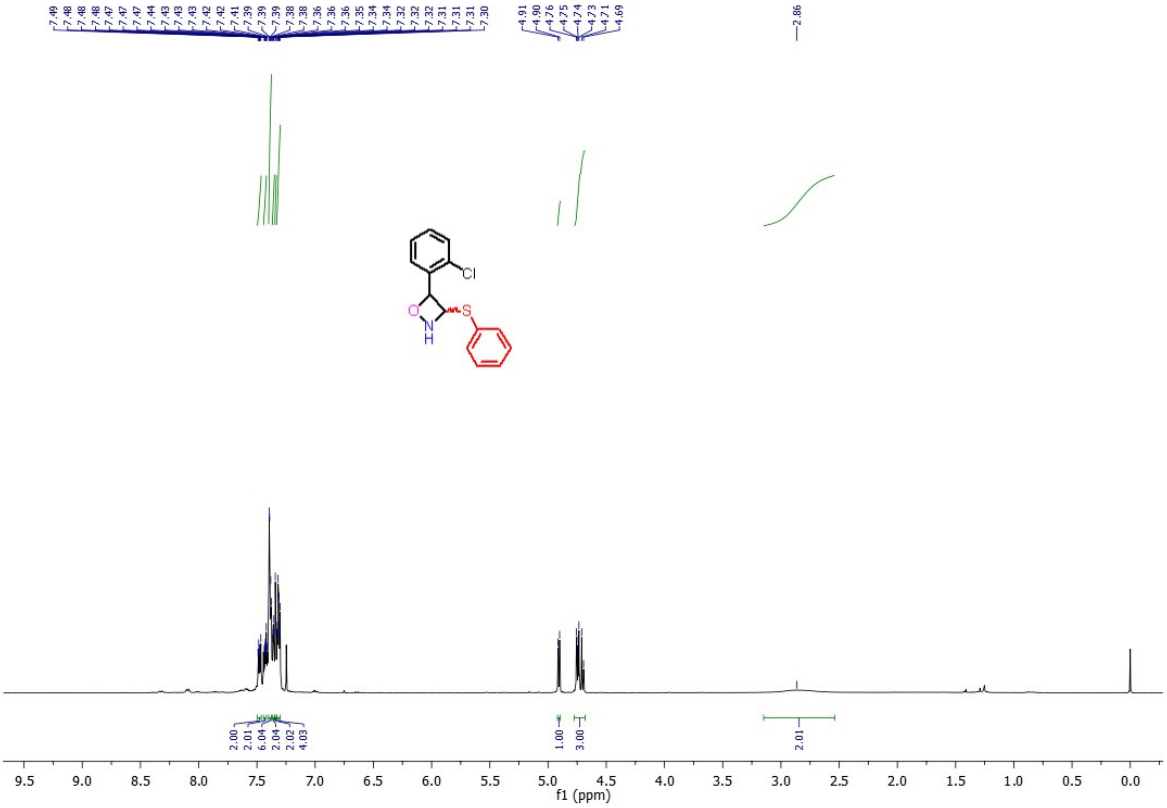
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **10**



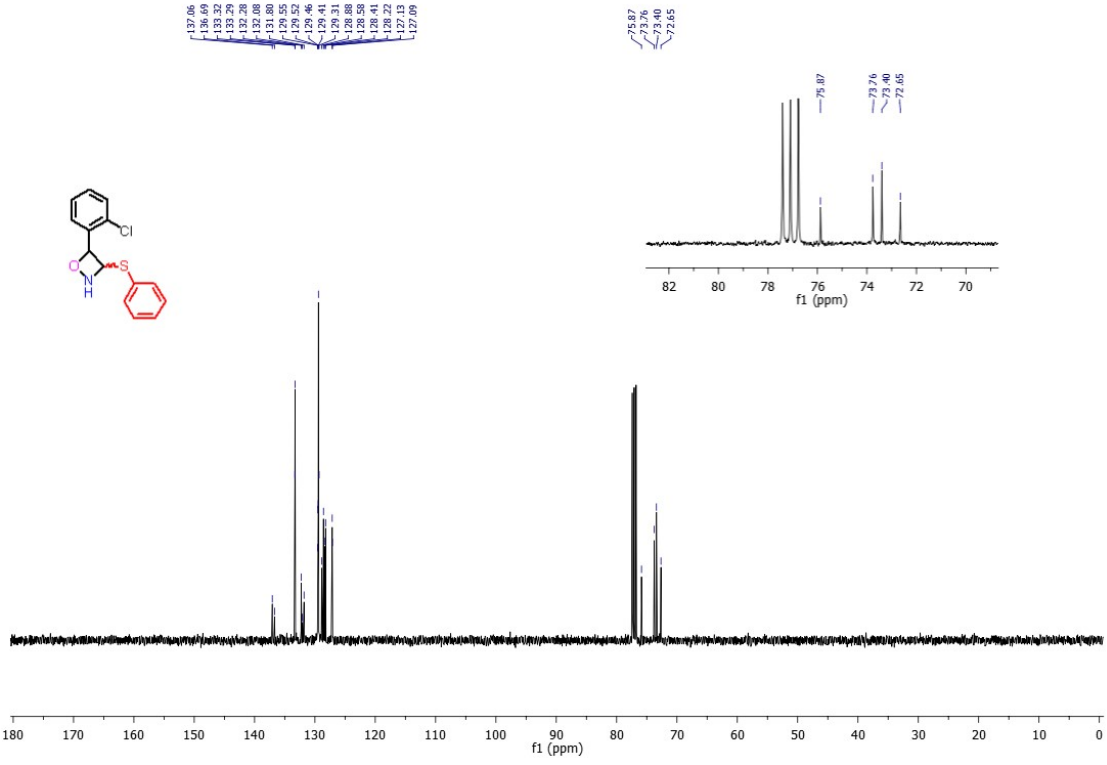
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **10**



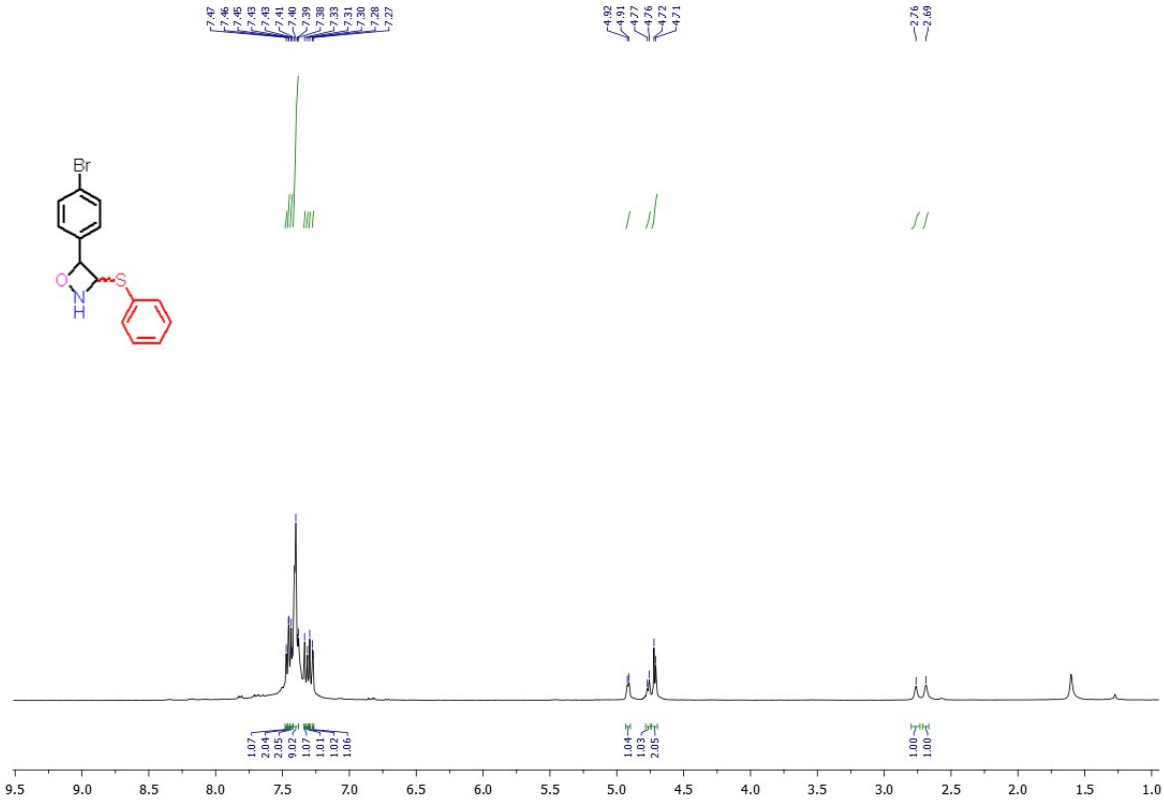
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **11**



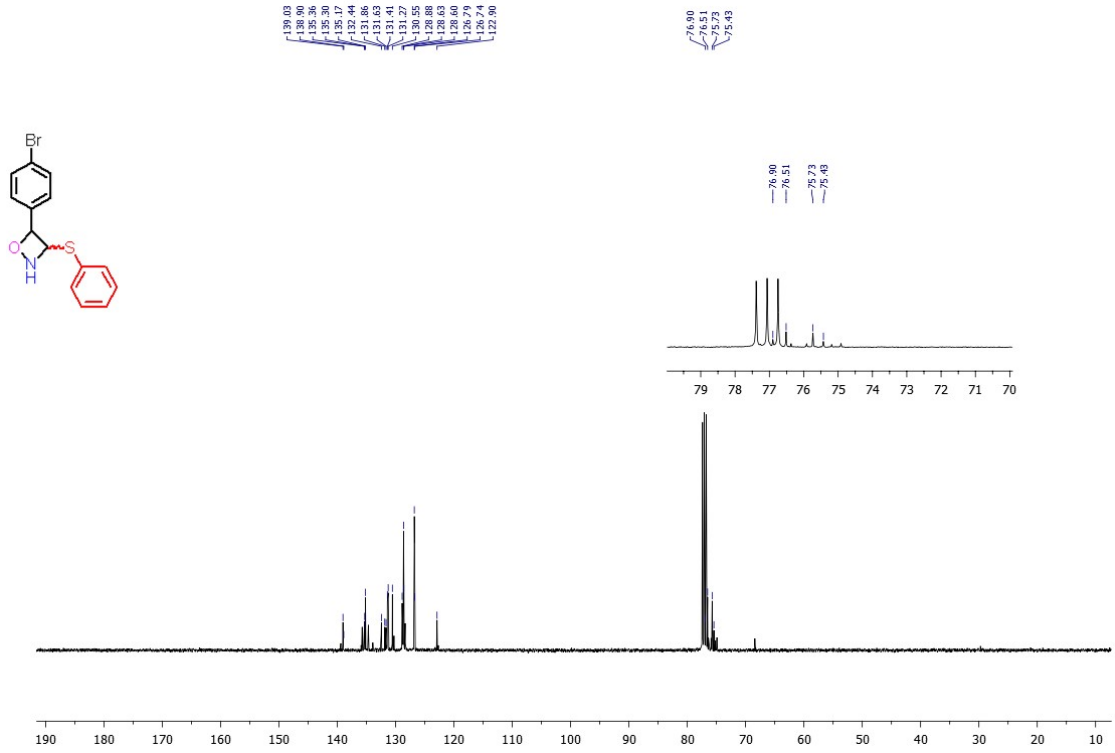
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **11**



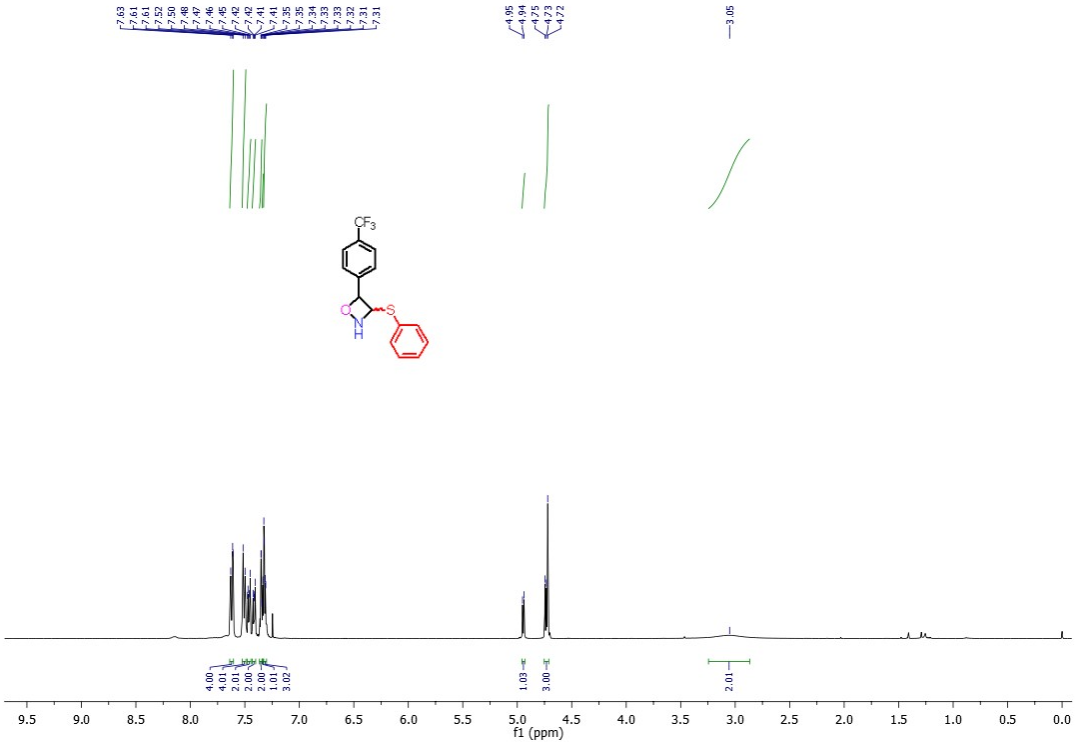
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **12**



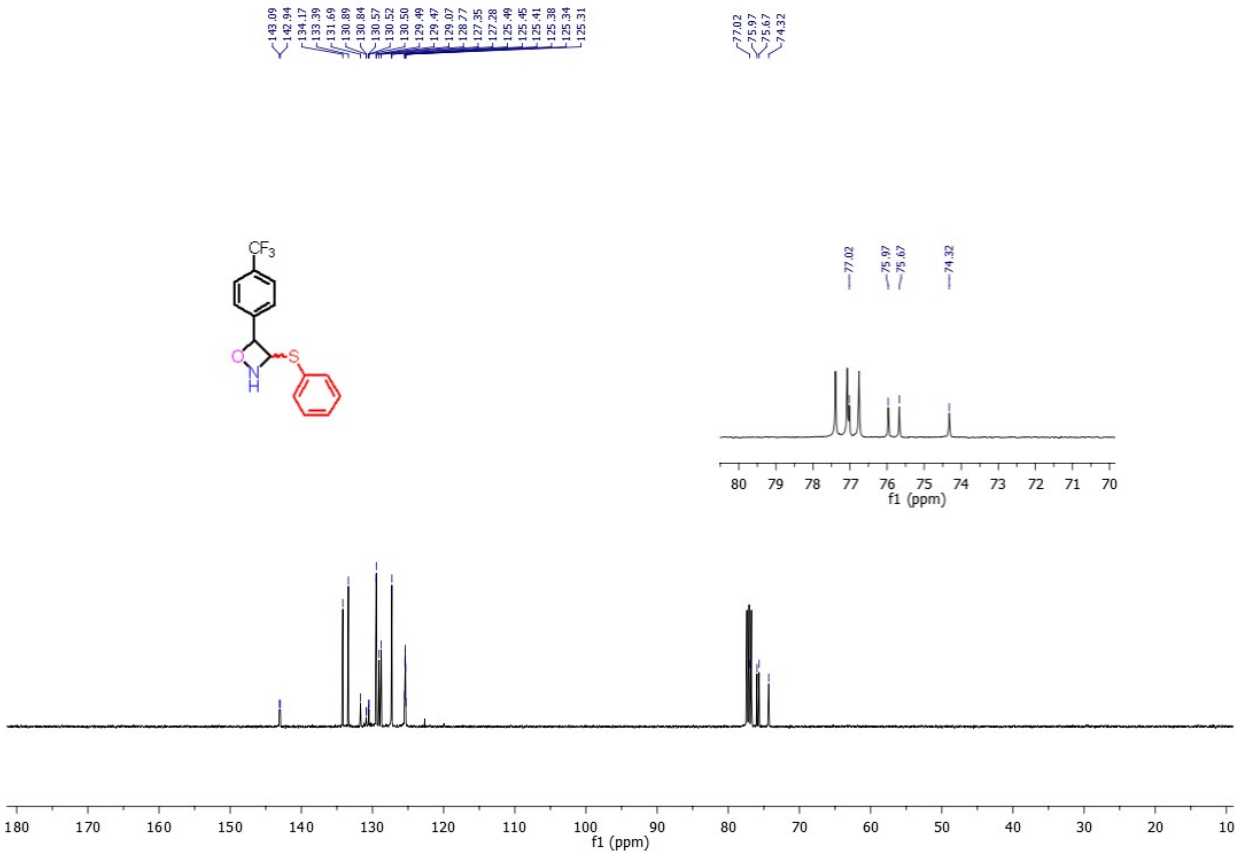
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **12**



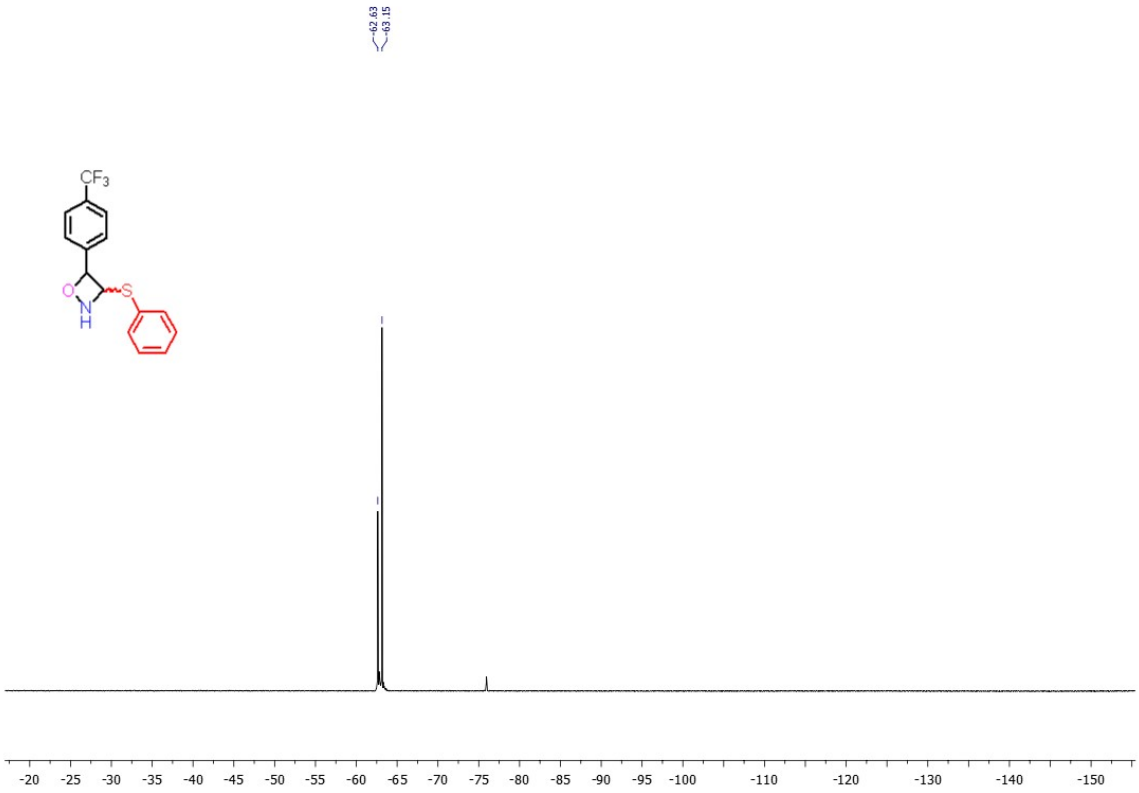
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **13**



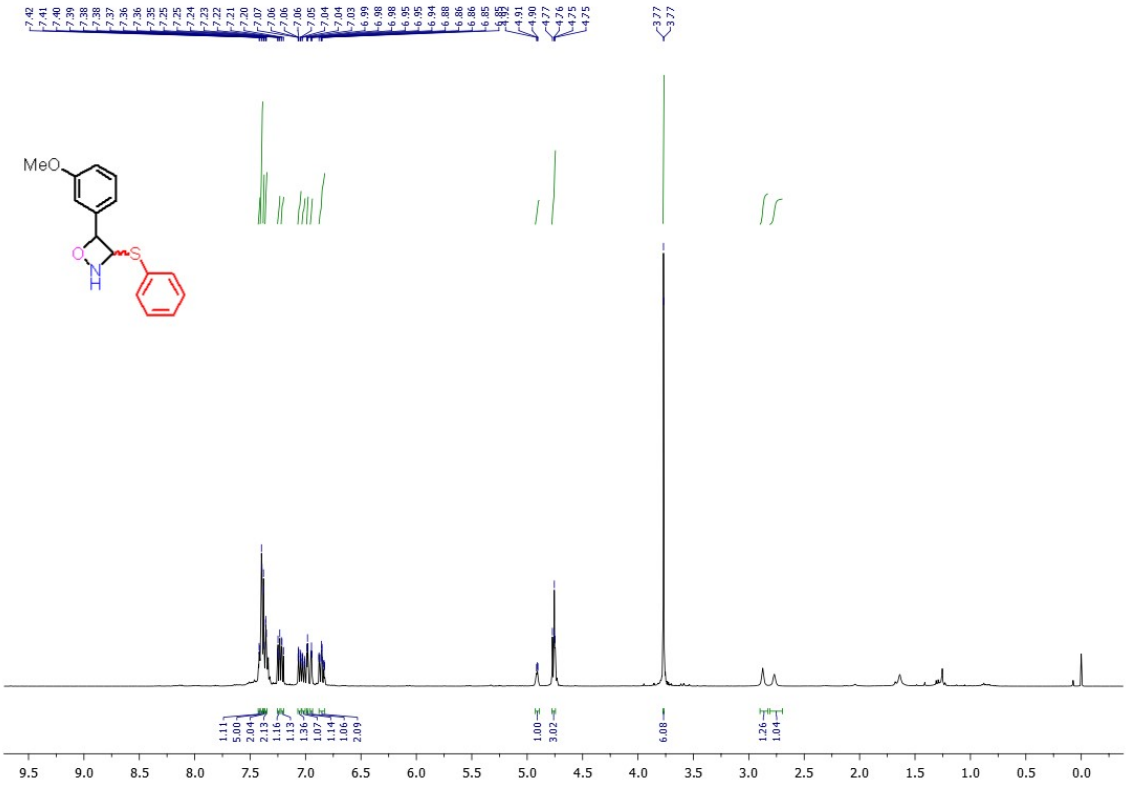
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **13**



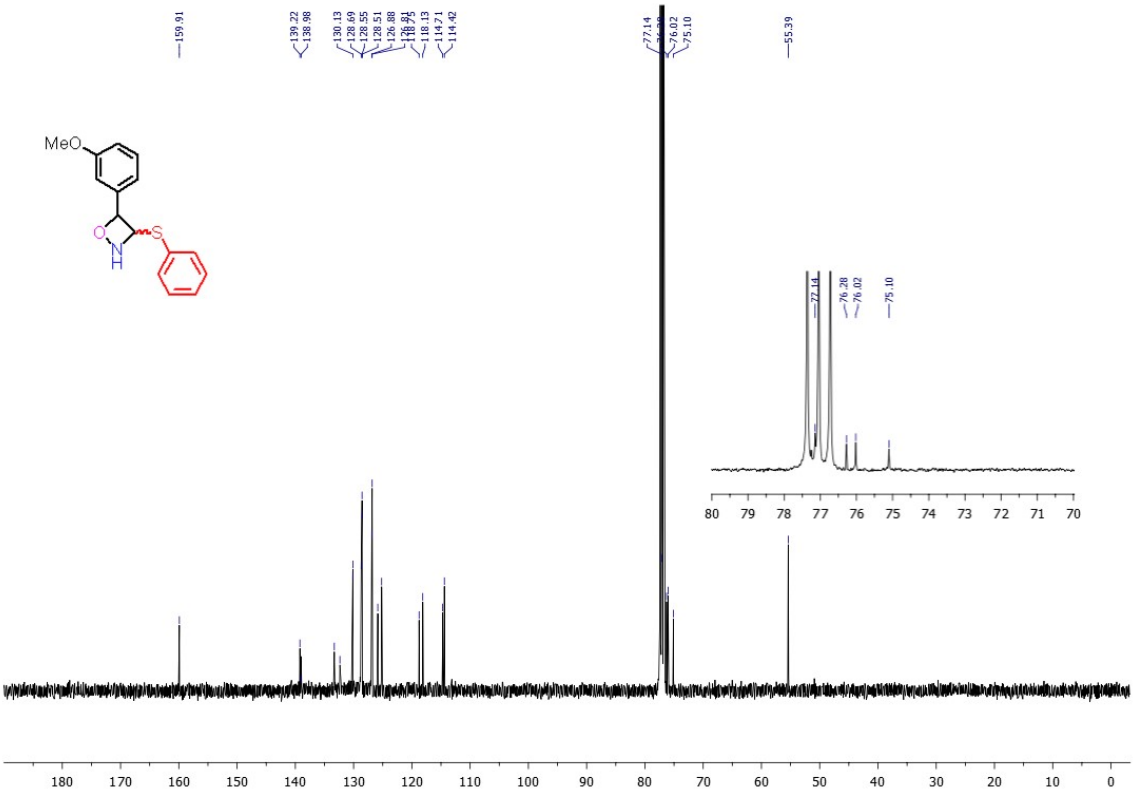
^{19}F-NMR ($CDCl_3$, 377 MHz) Spectra of compound **13**



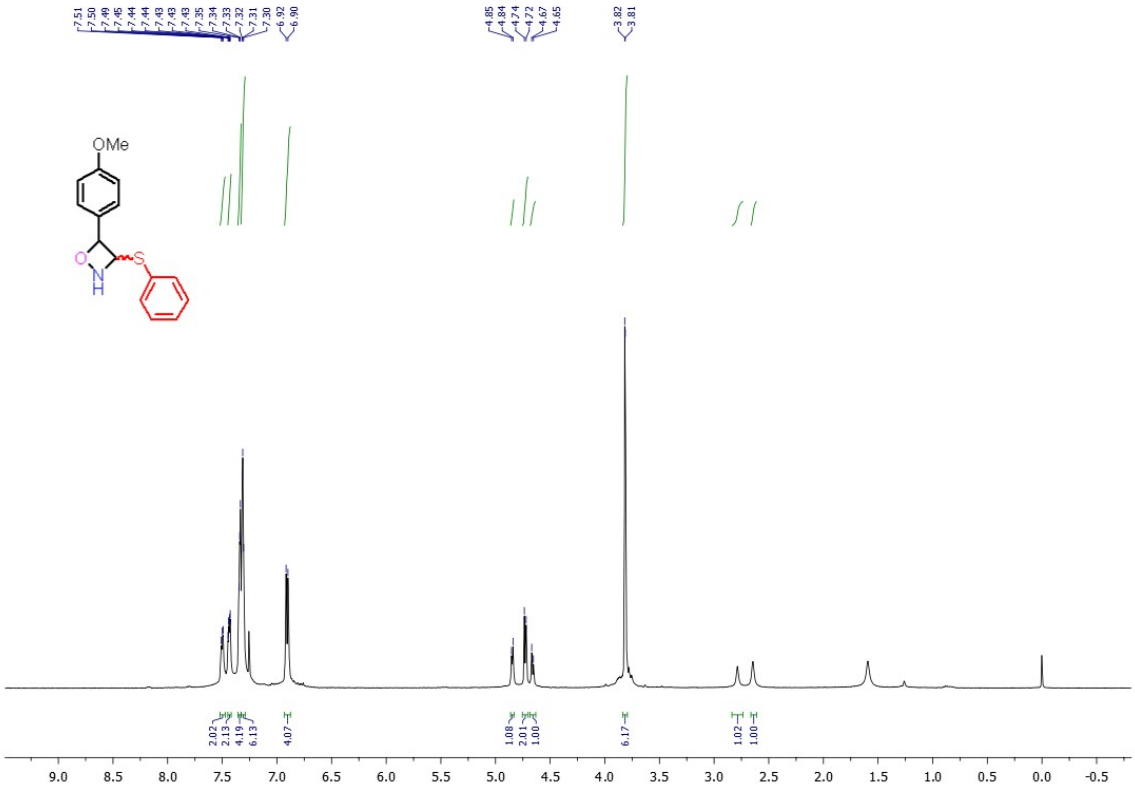
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **14**



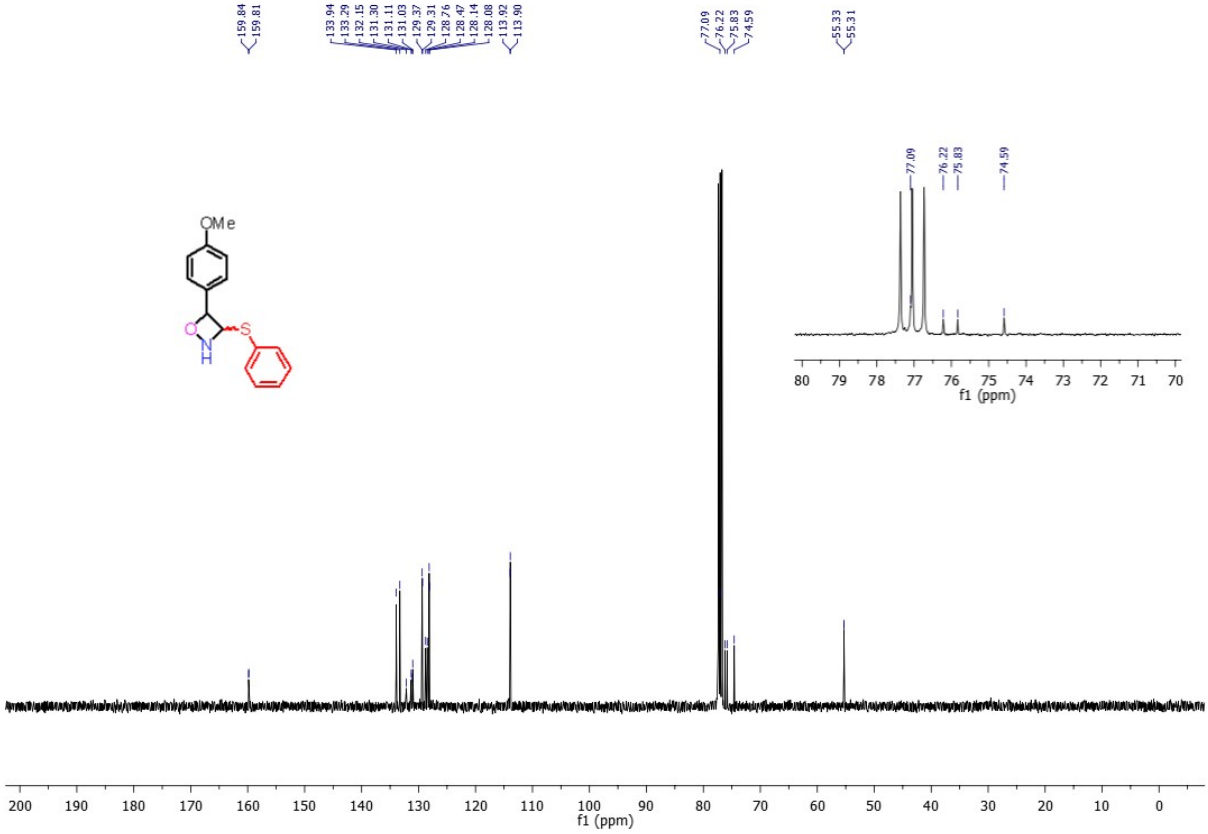
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **14**



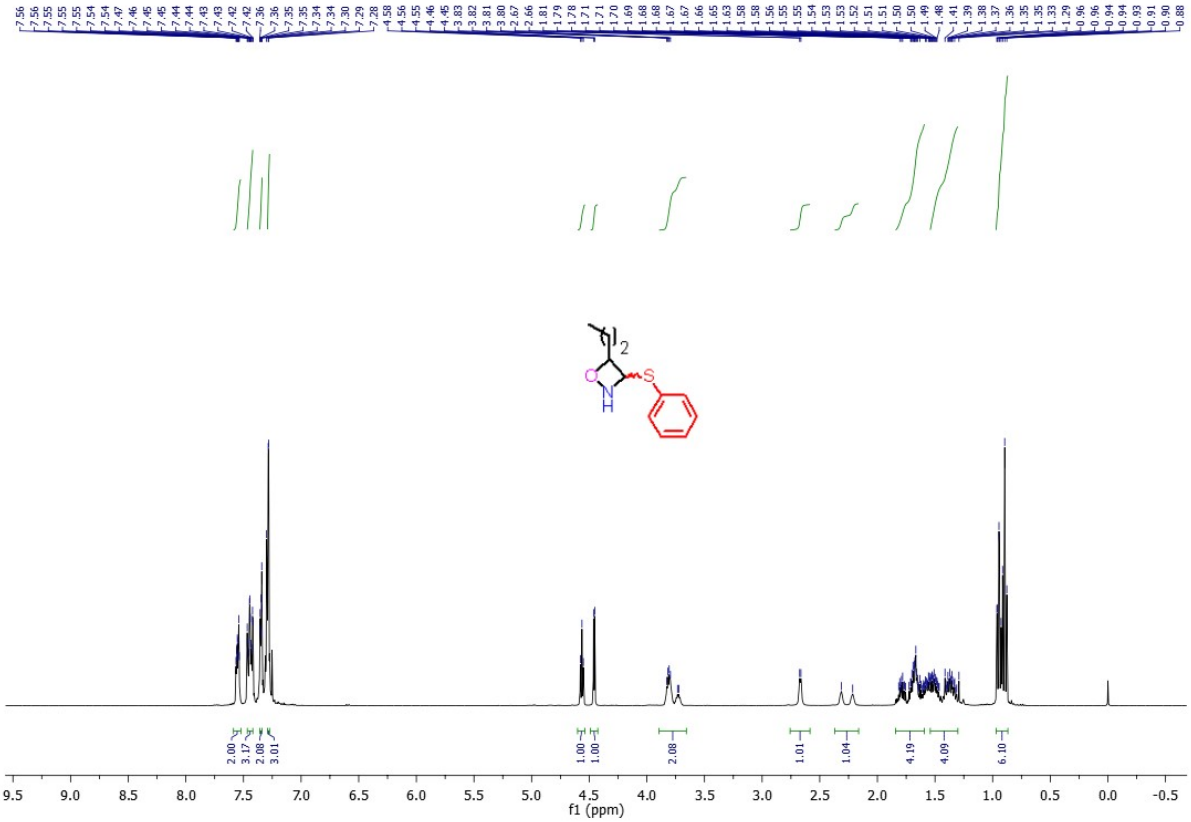
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **15**



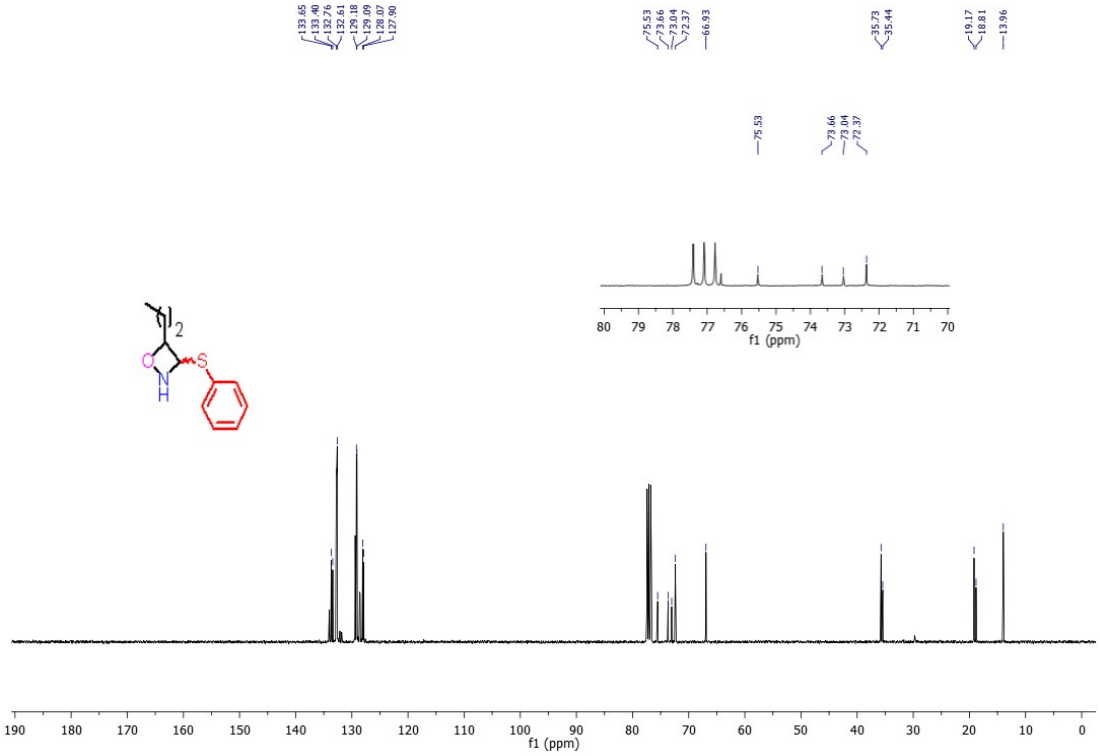
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **15**



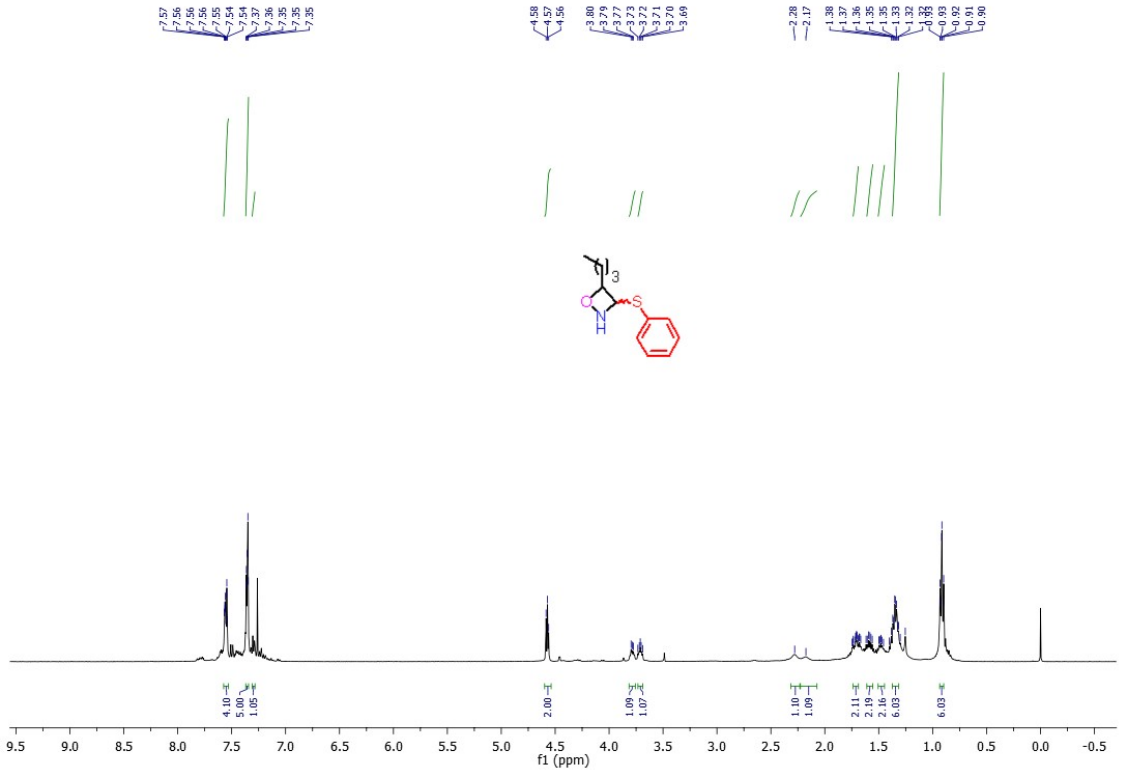
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **16**



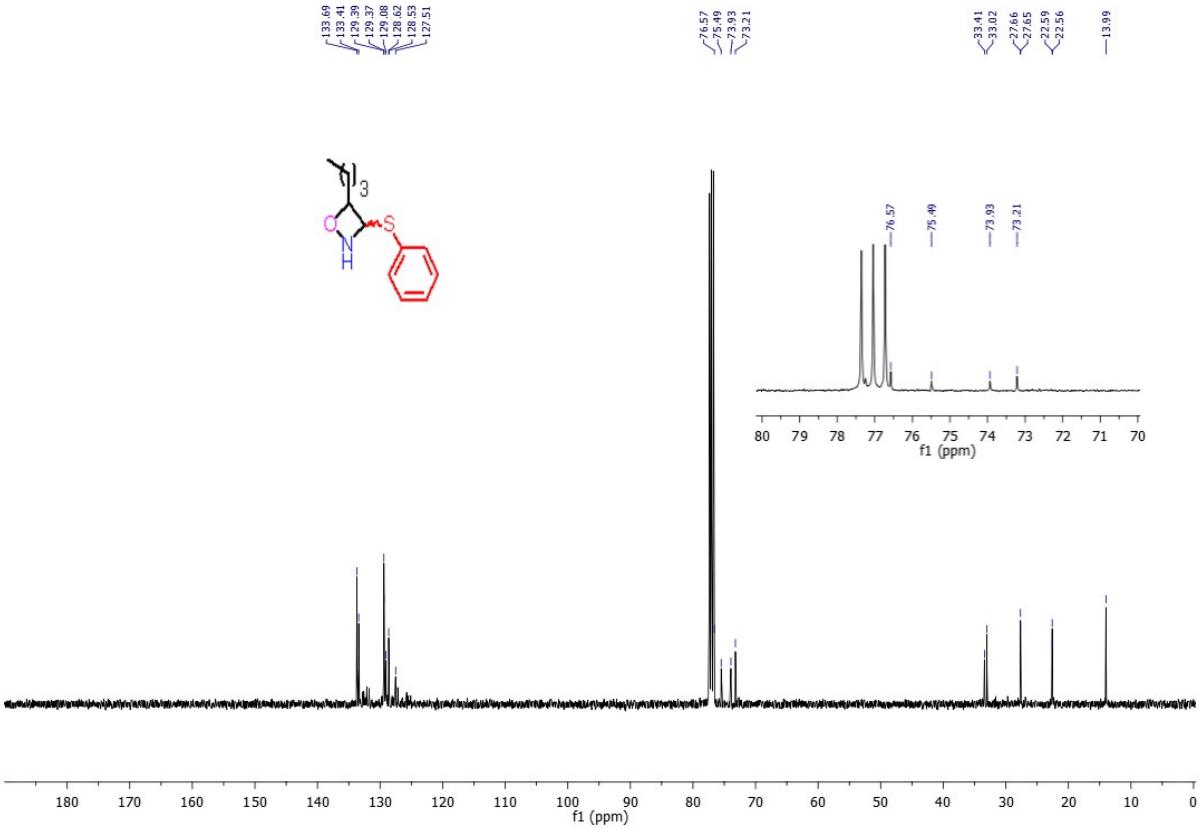
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **16**



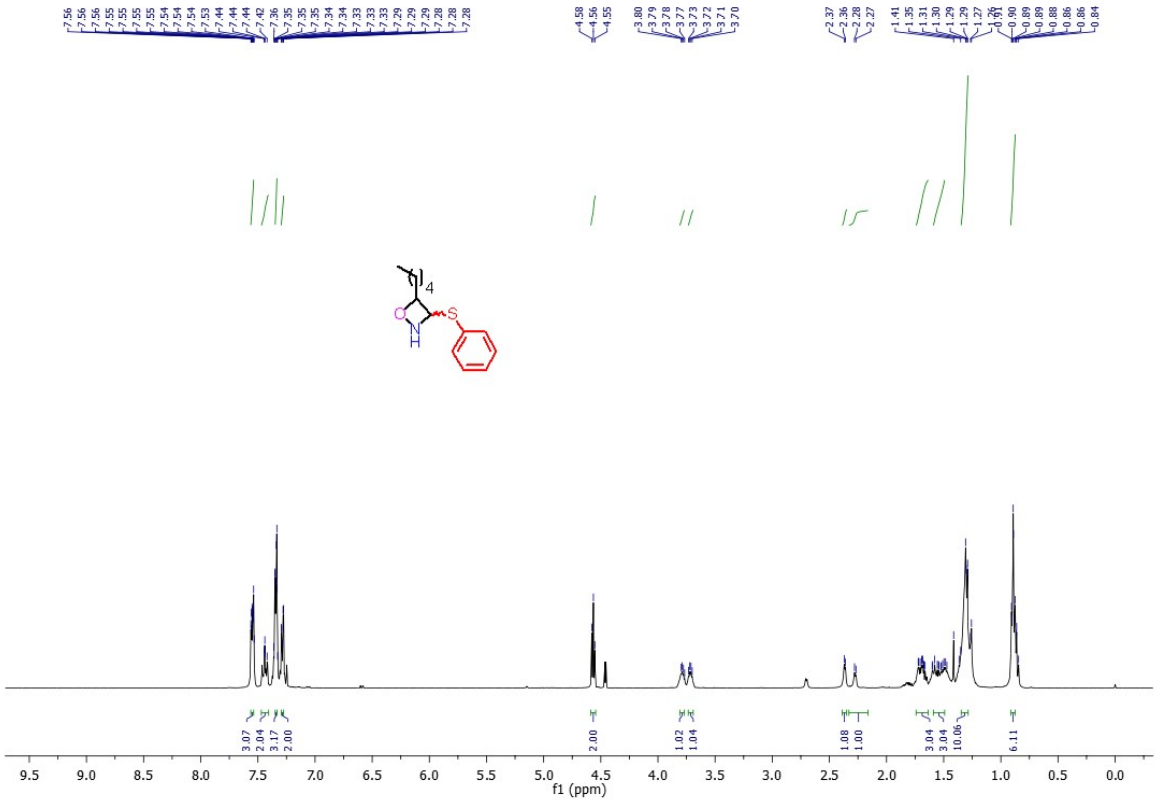
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **17**



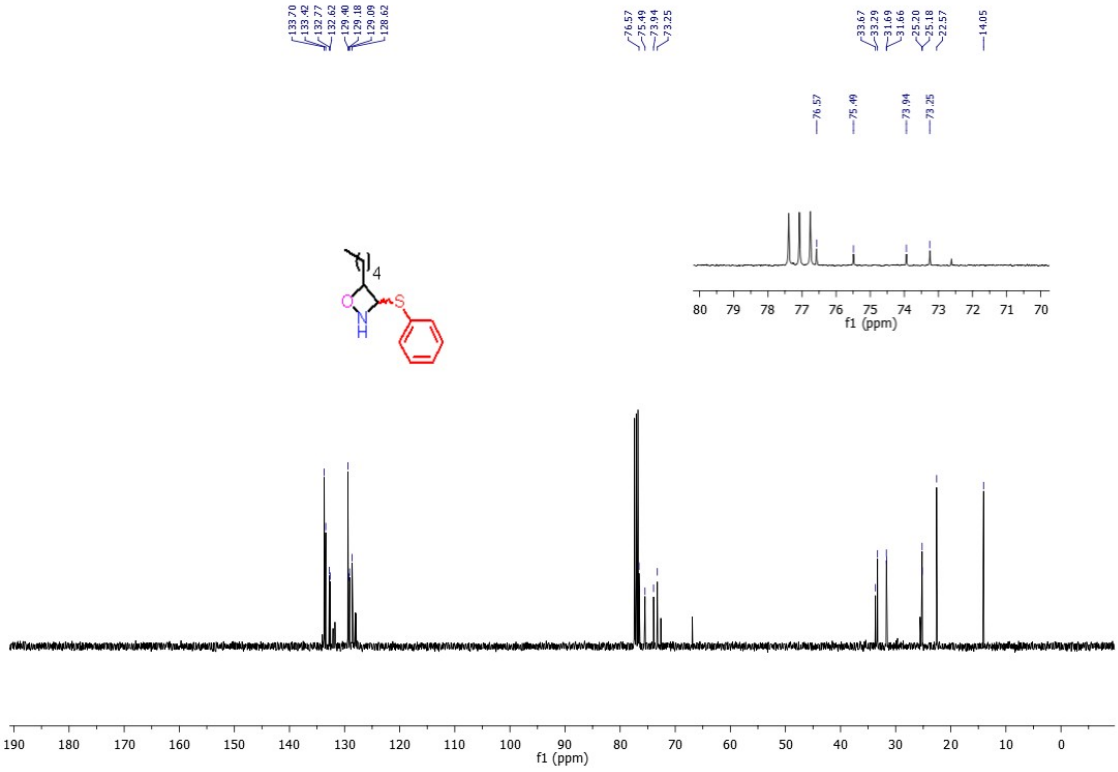
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **17**



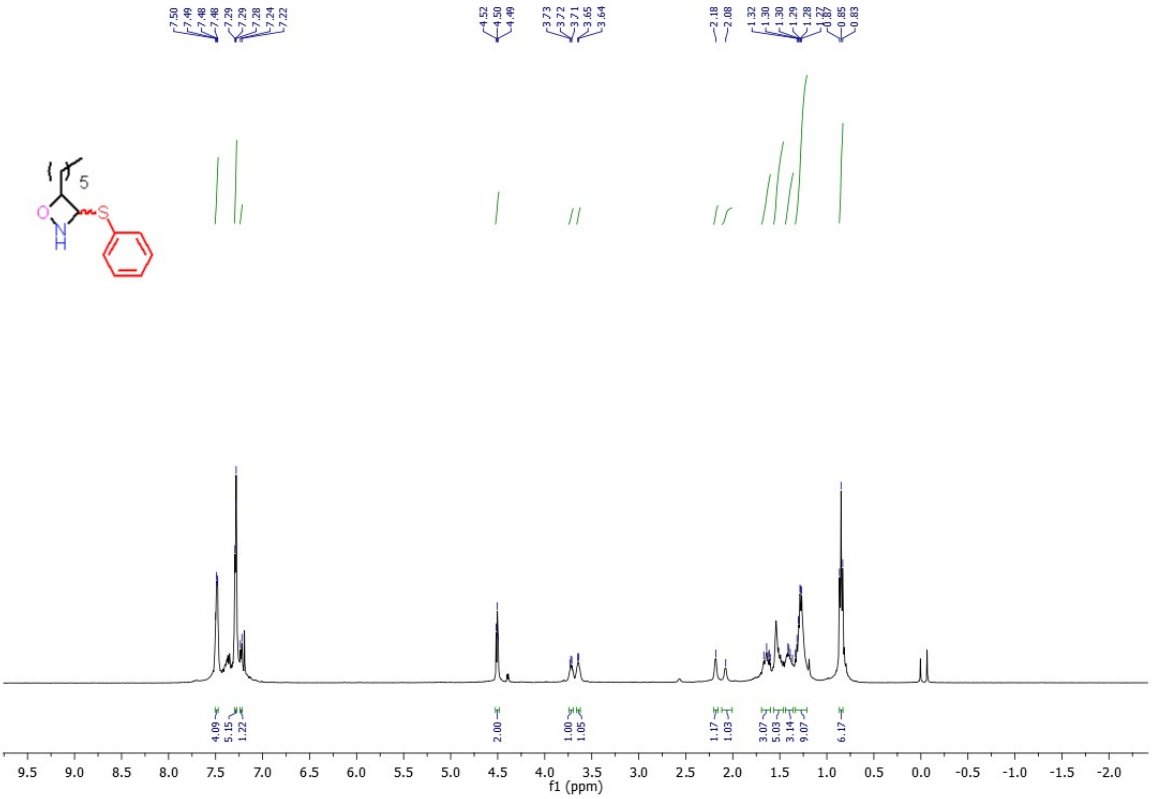
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **18**



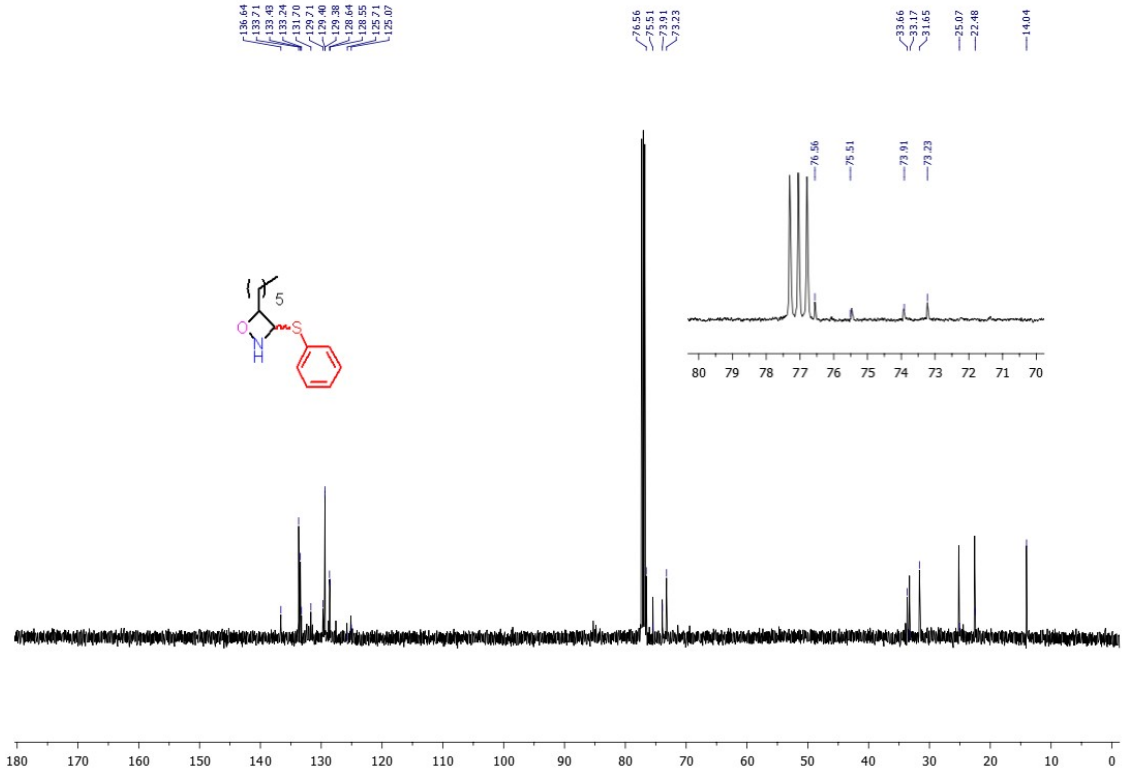
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **18**



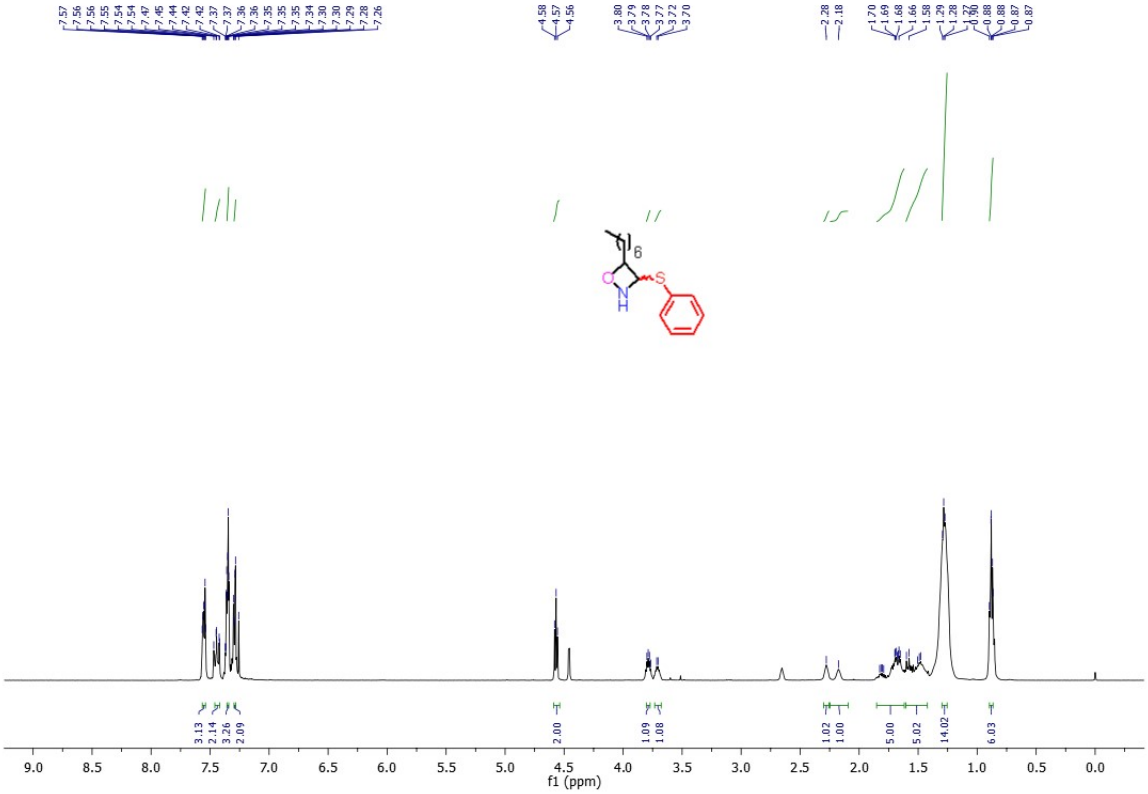
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **19**



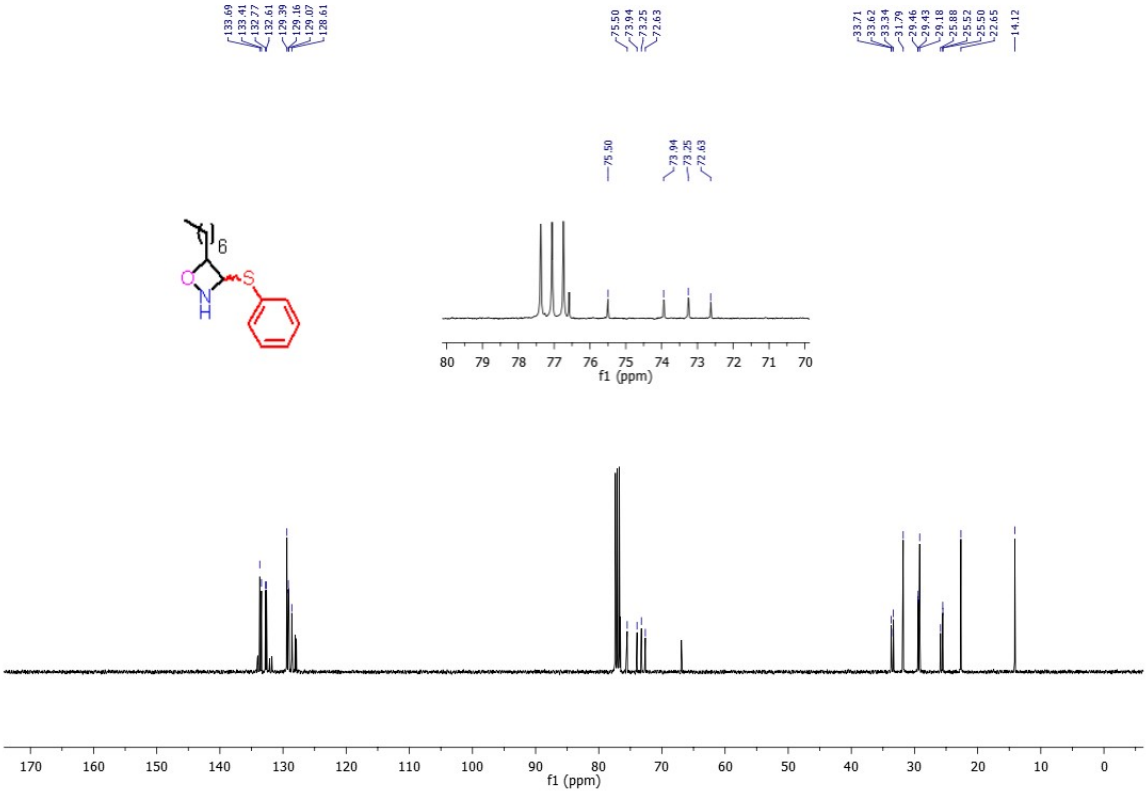
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **19**



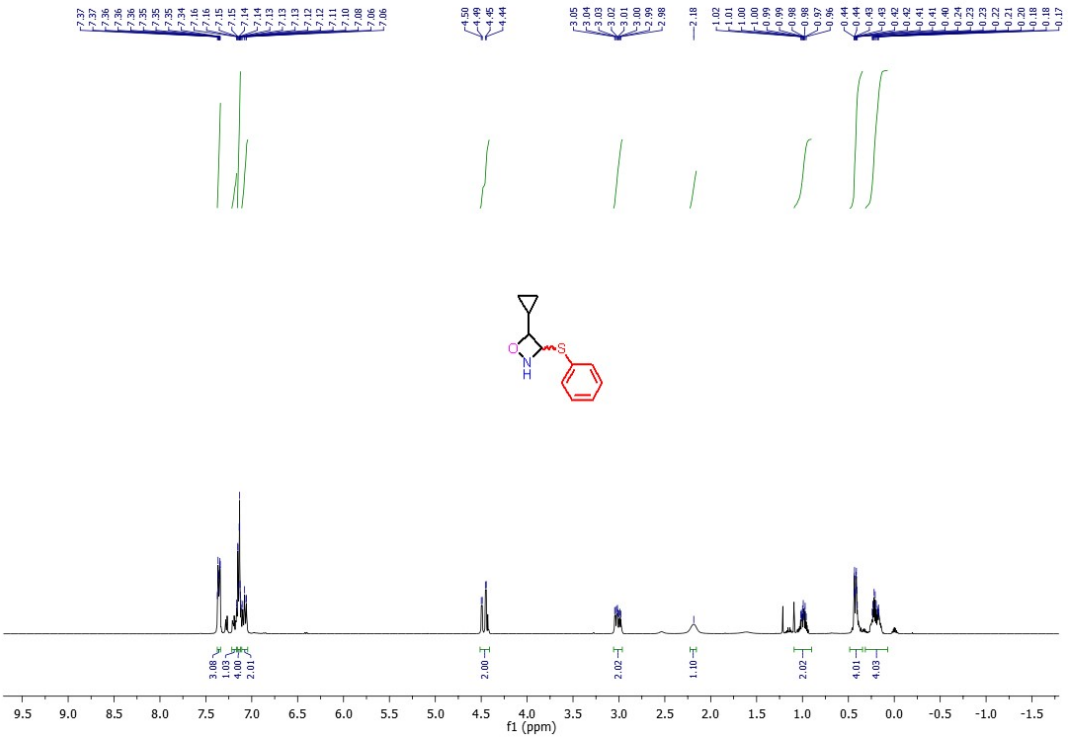
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **20**



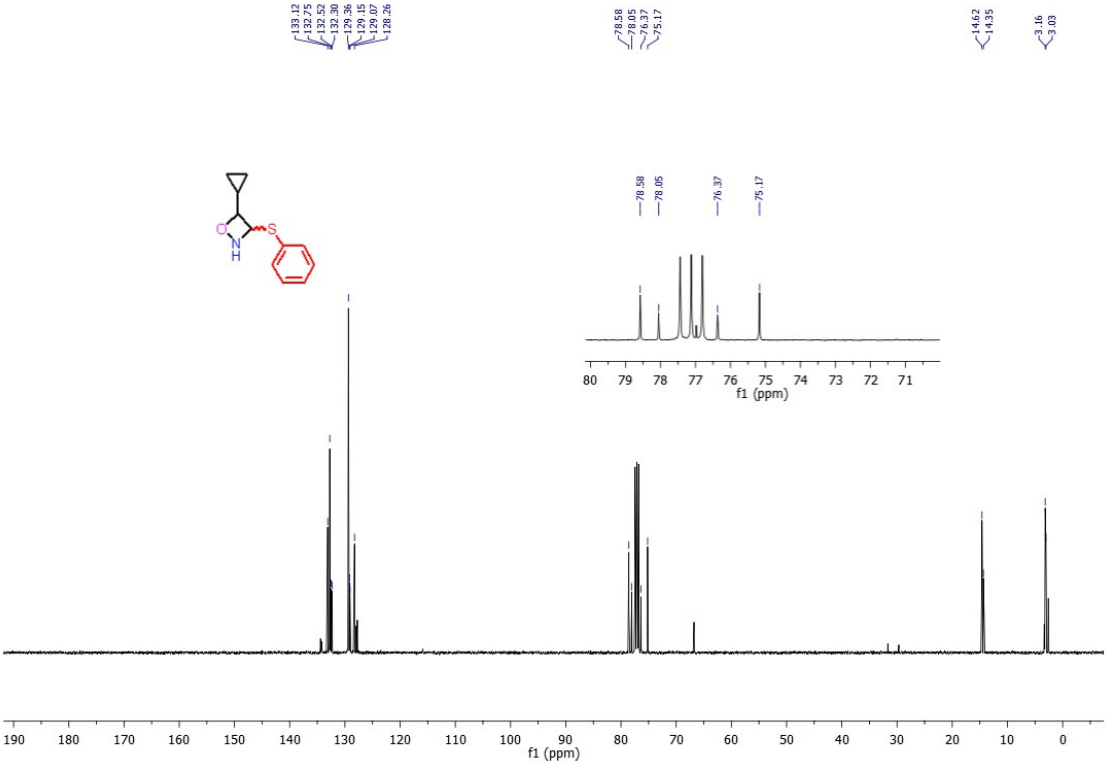
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **20**



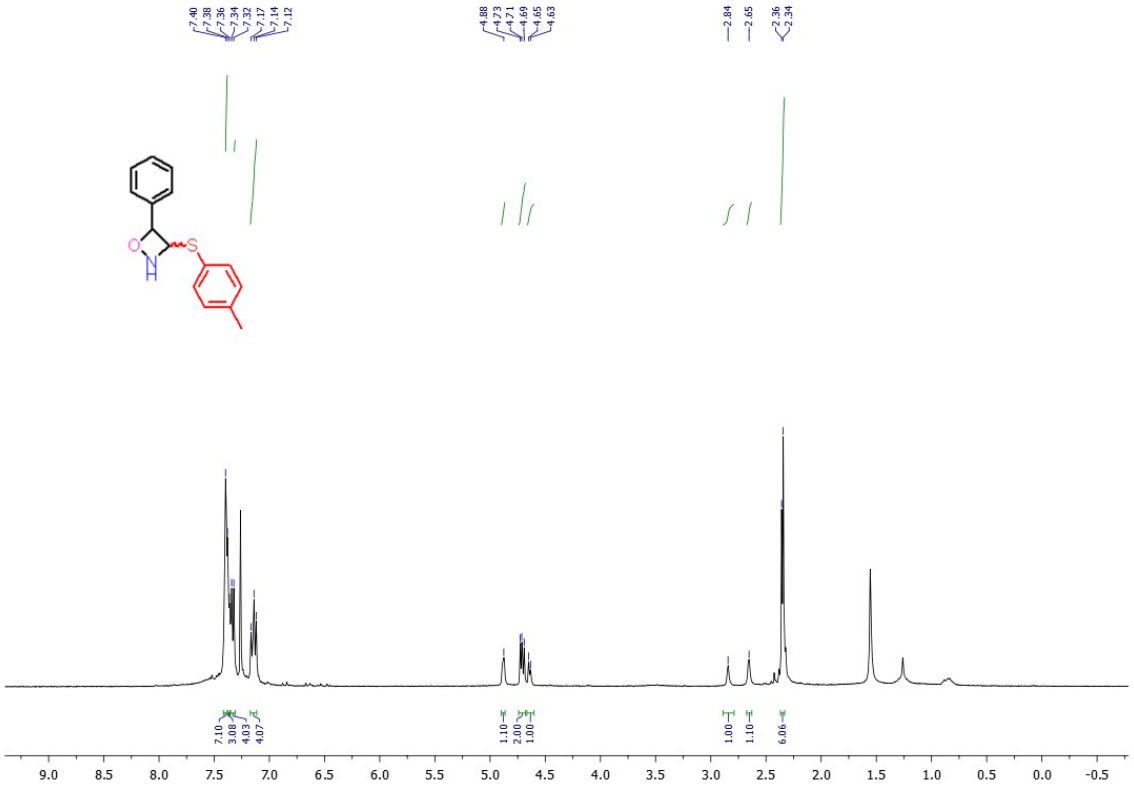
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **21**



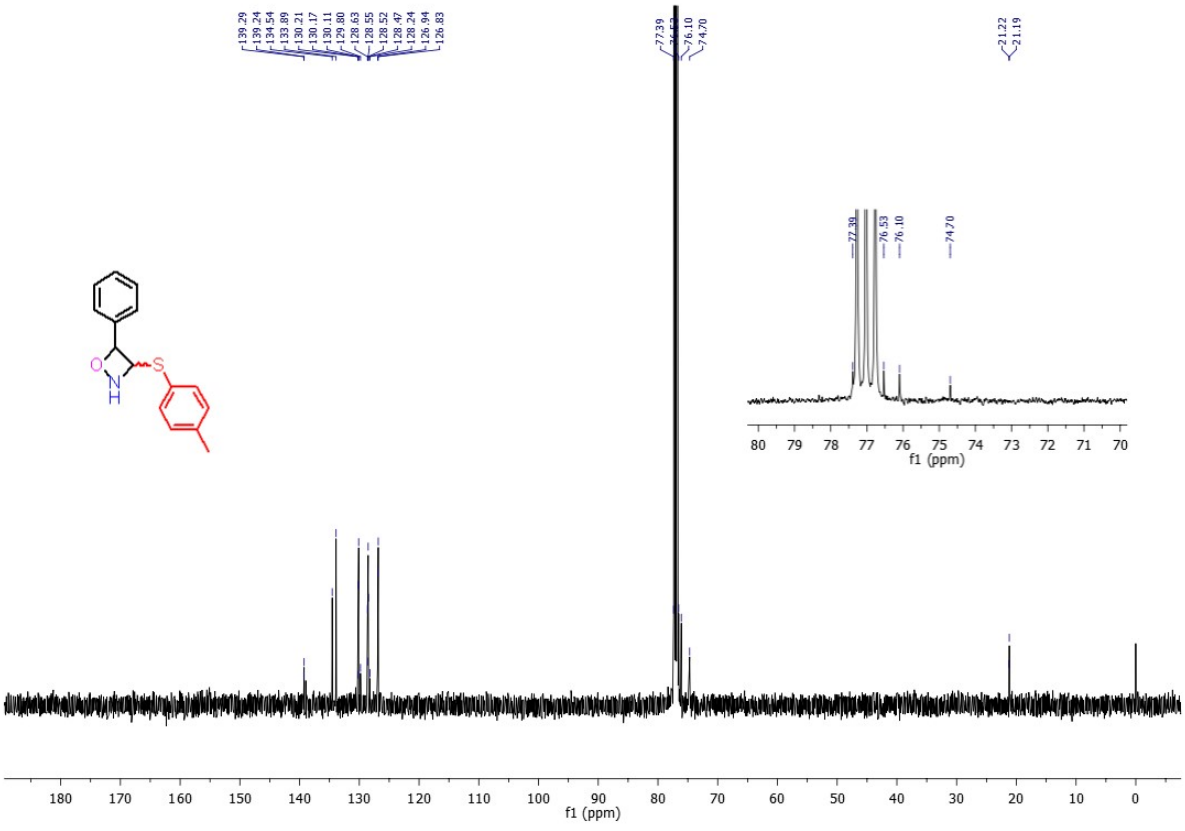
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **21**



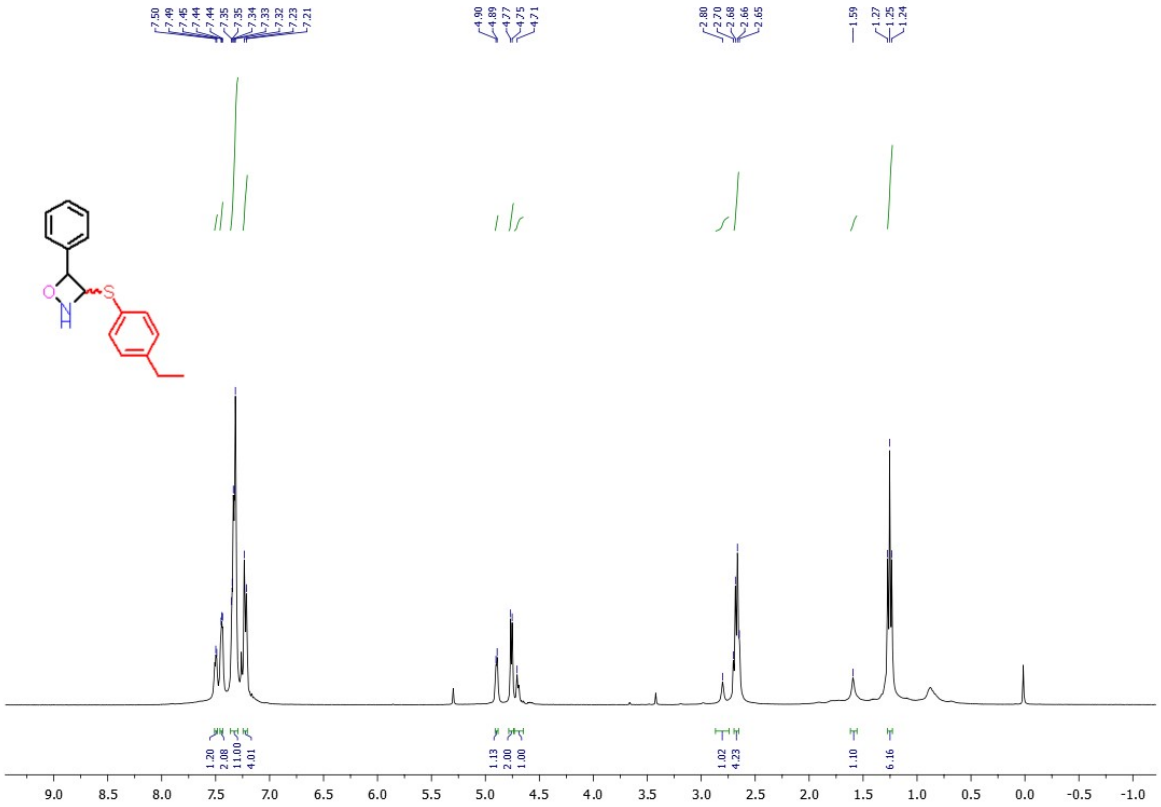
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **22**



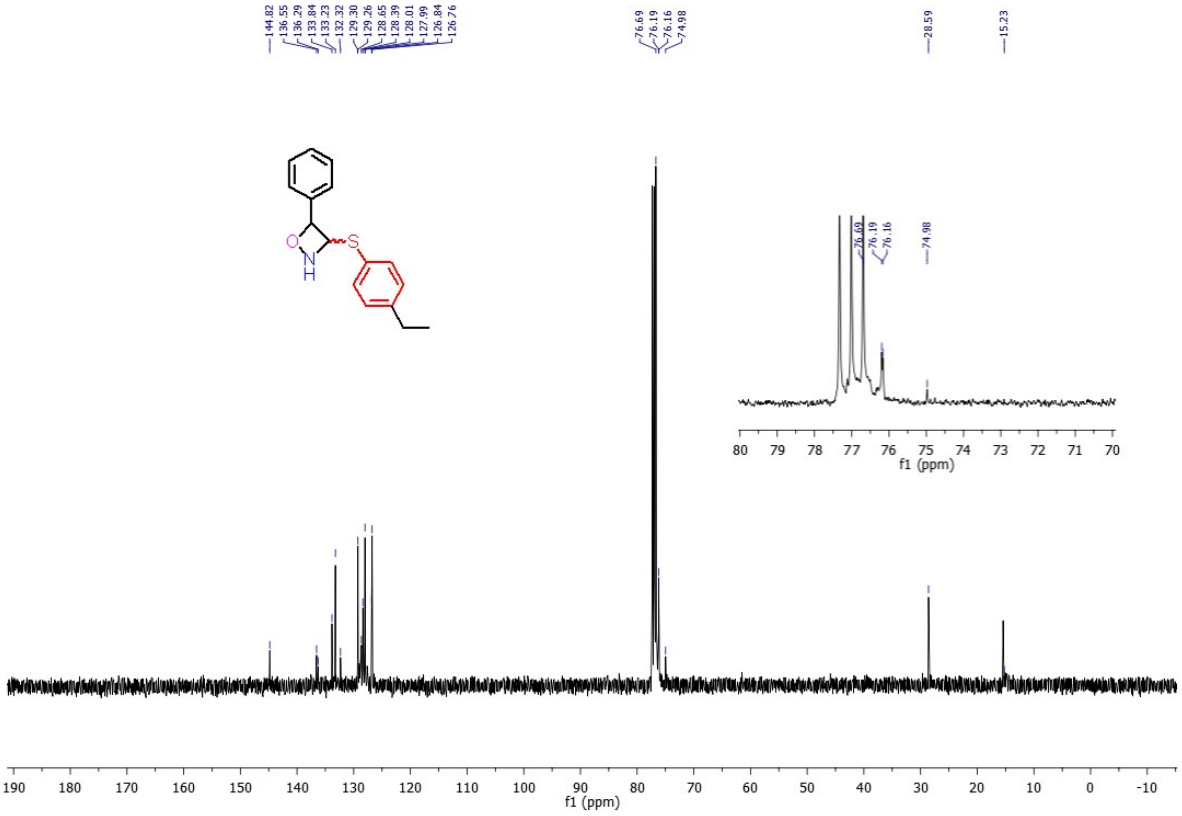
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **22**



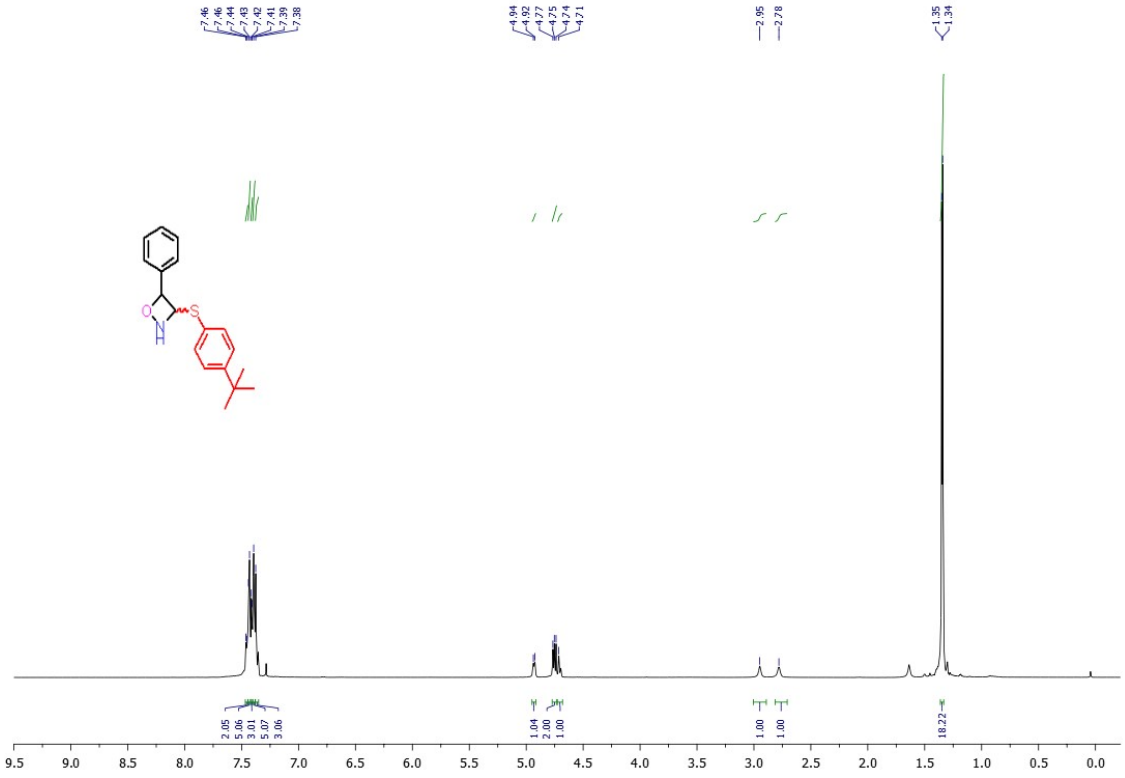
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **23**



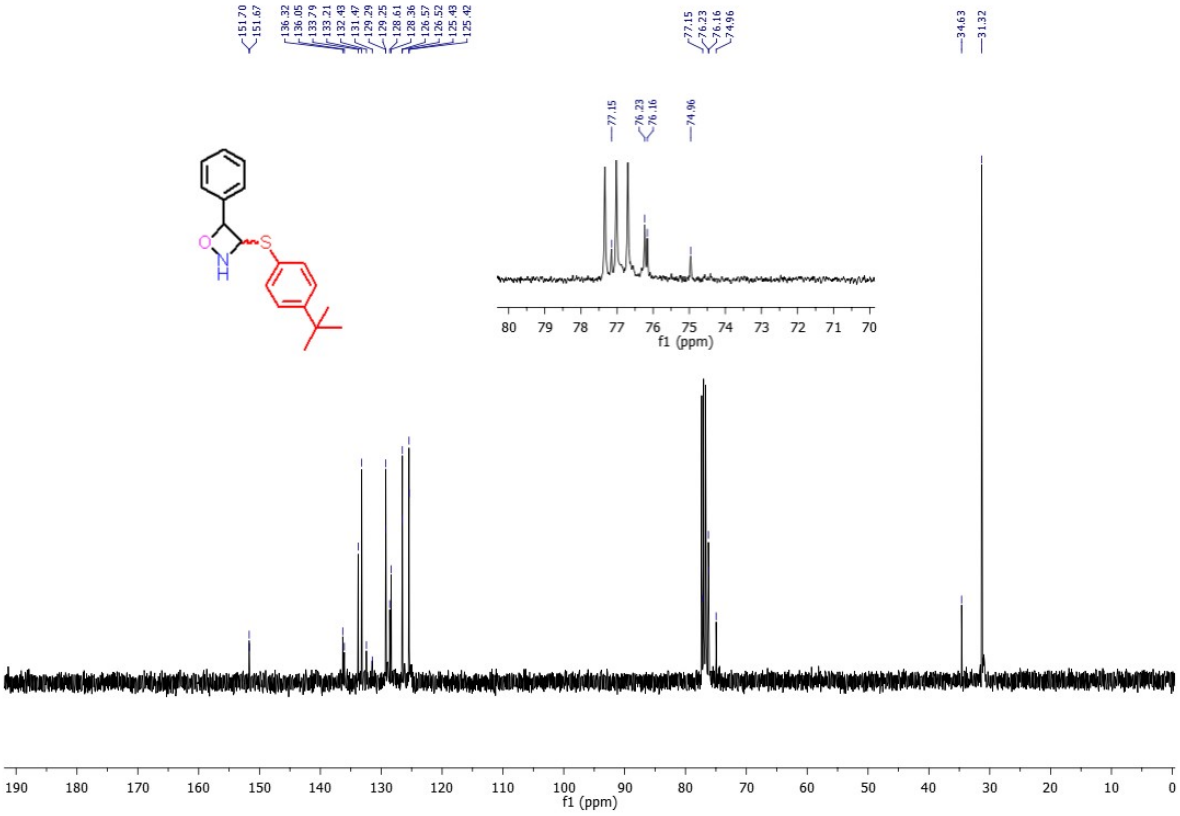
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **23**



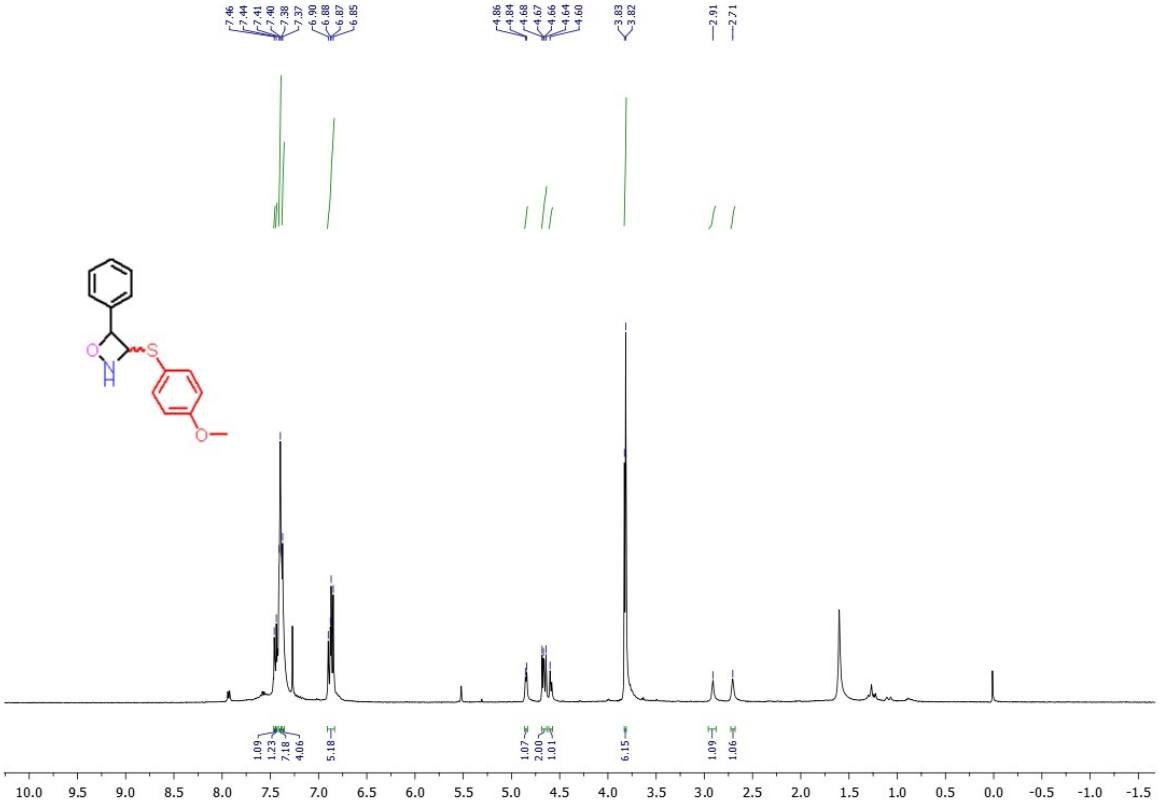
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **24**



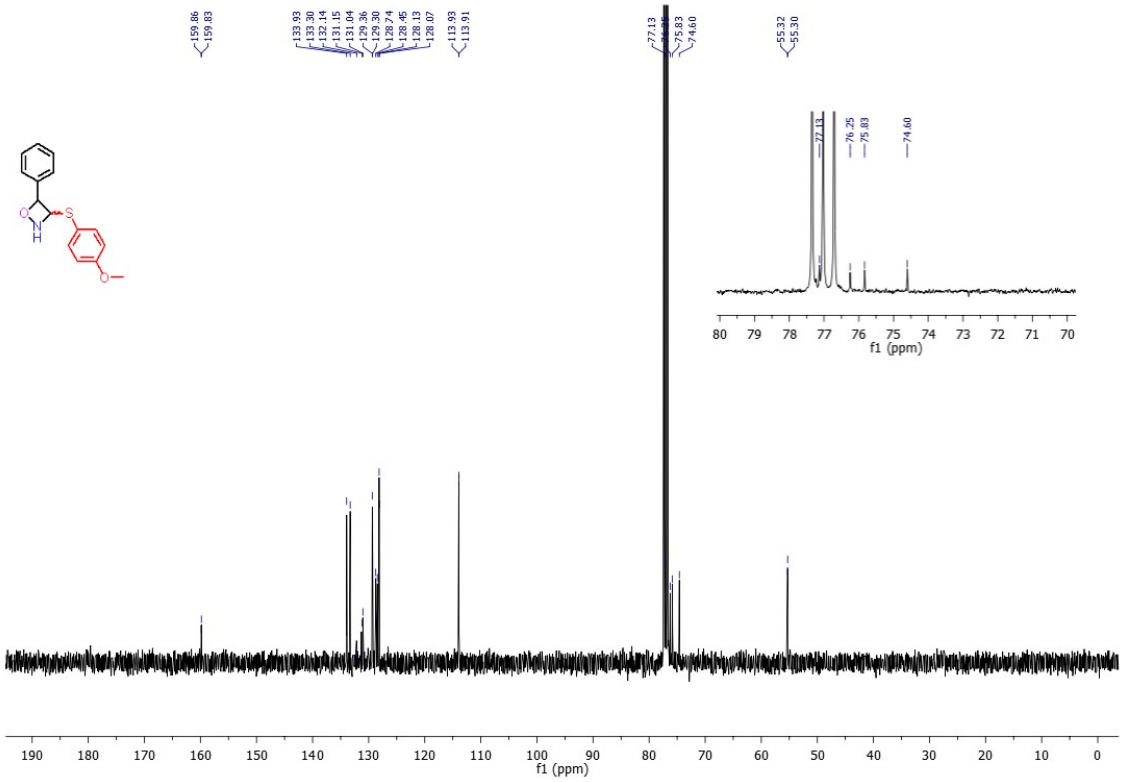
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **24**



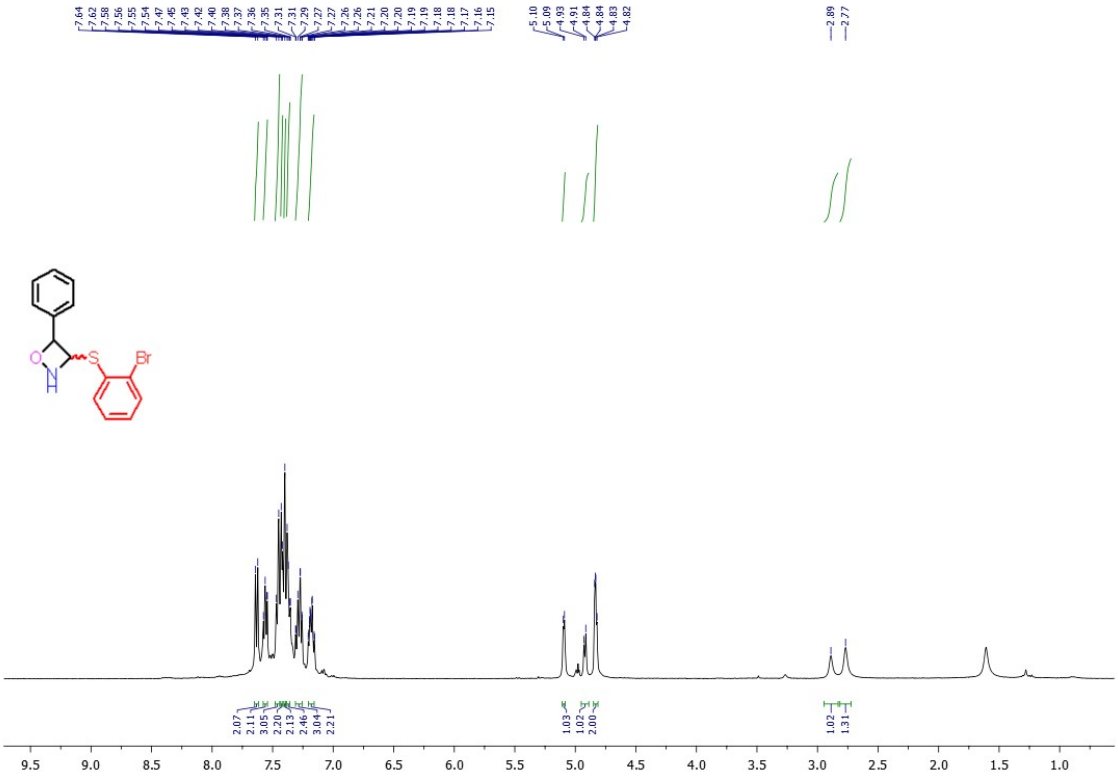
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **25**



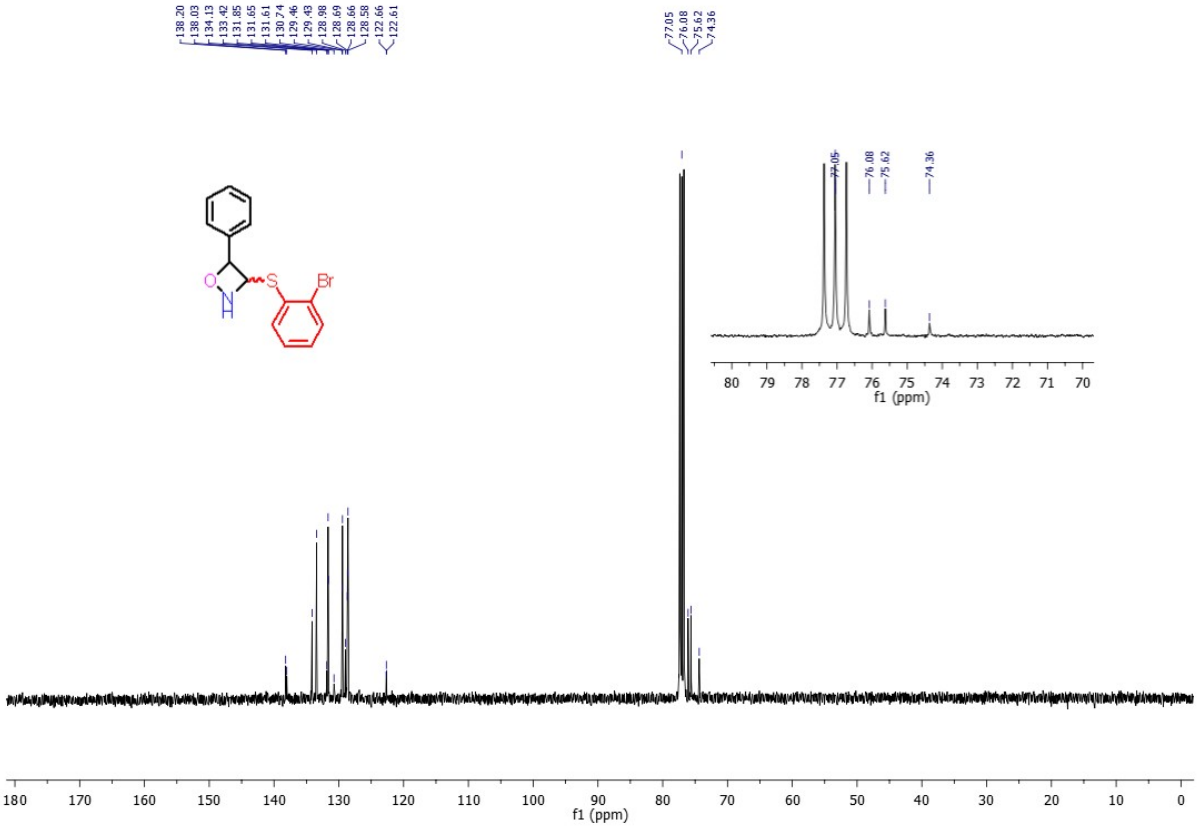
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **25**



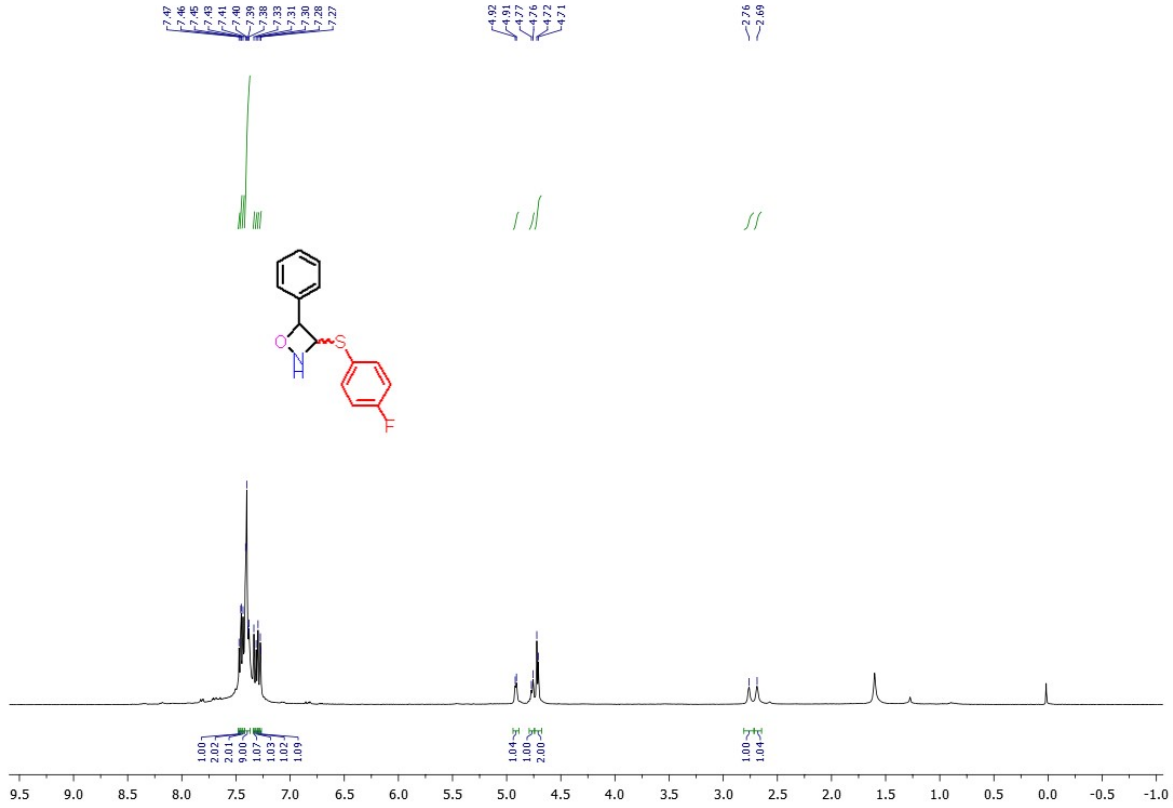
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **26**



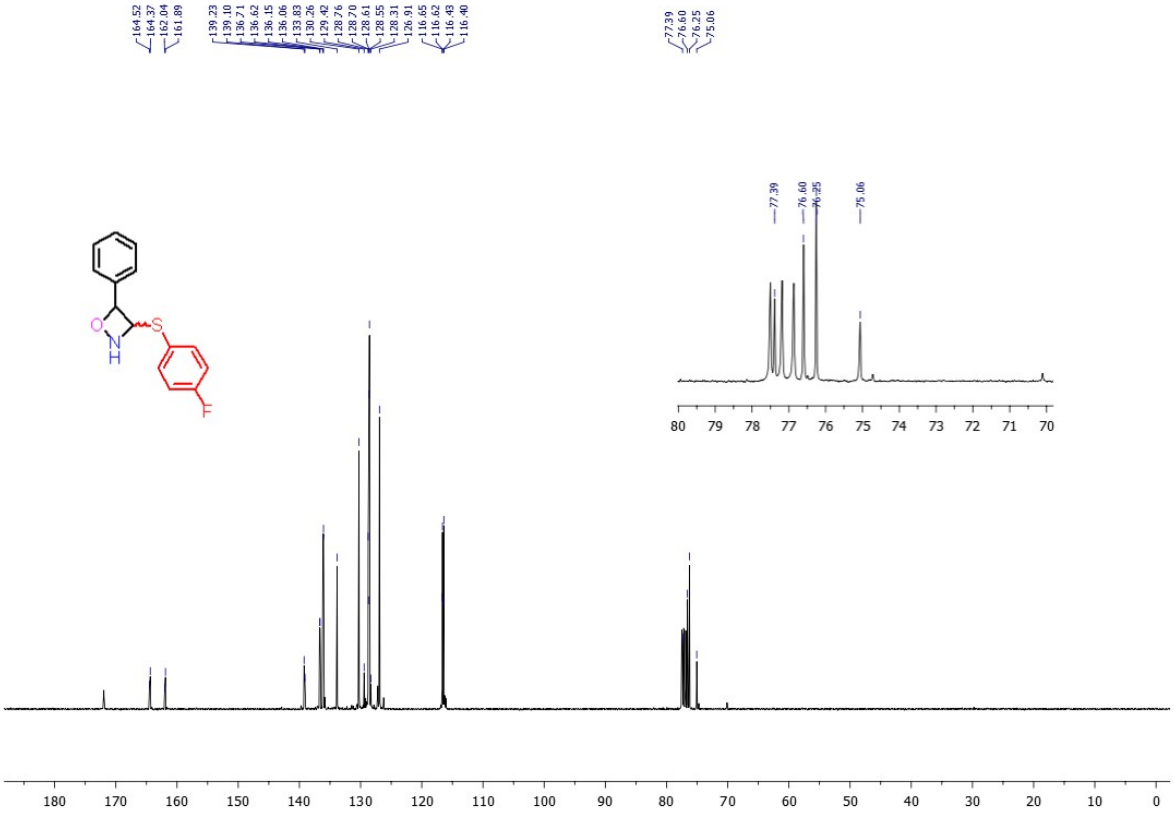
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **26**



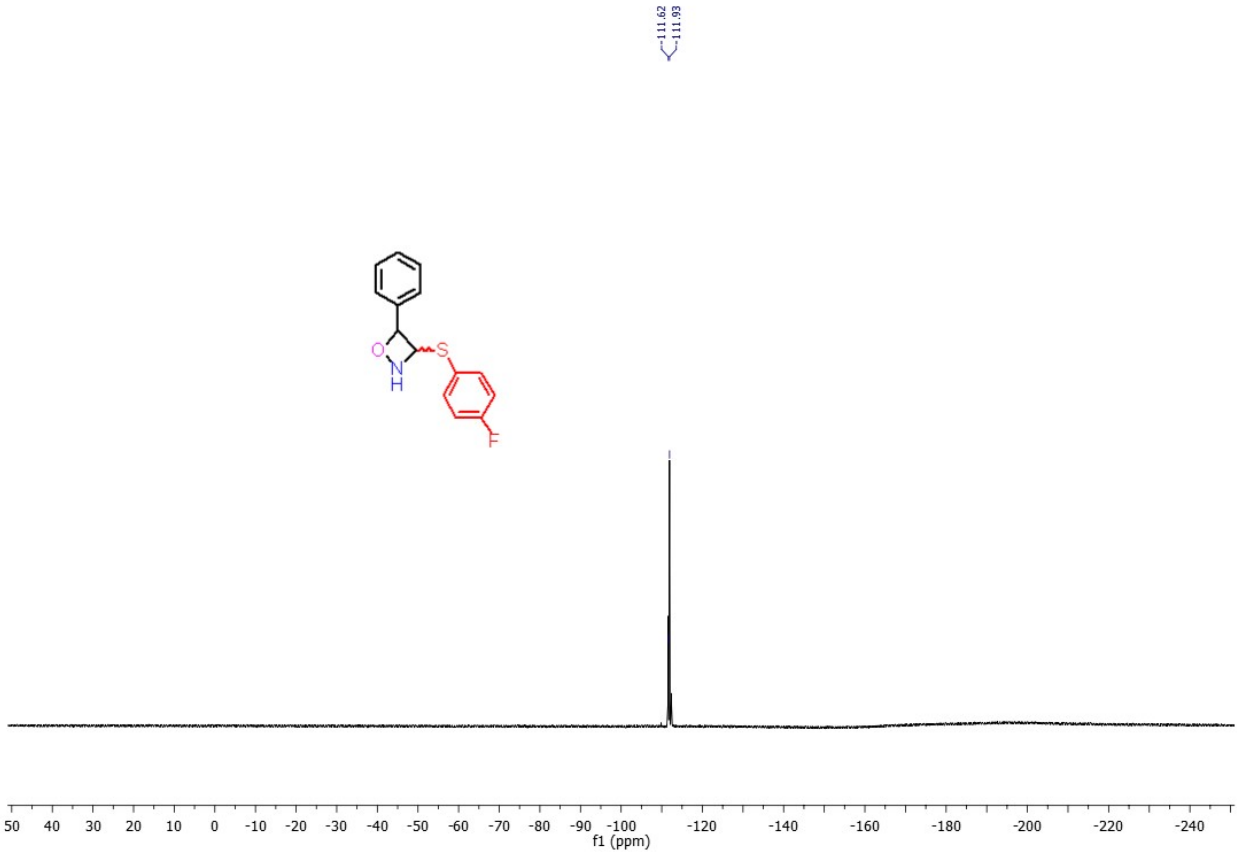
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **27**



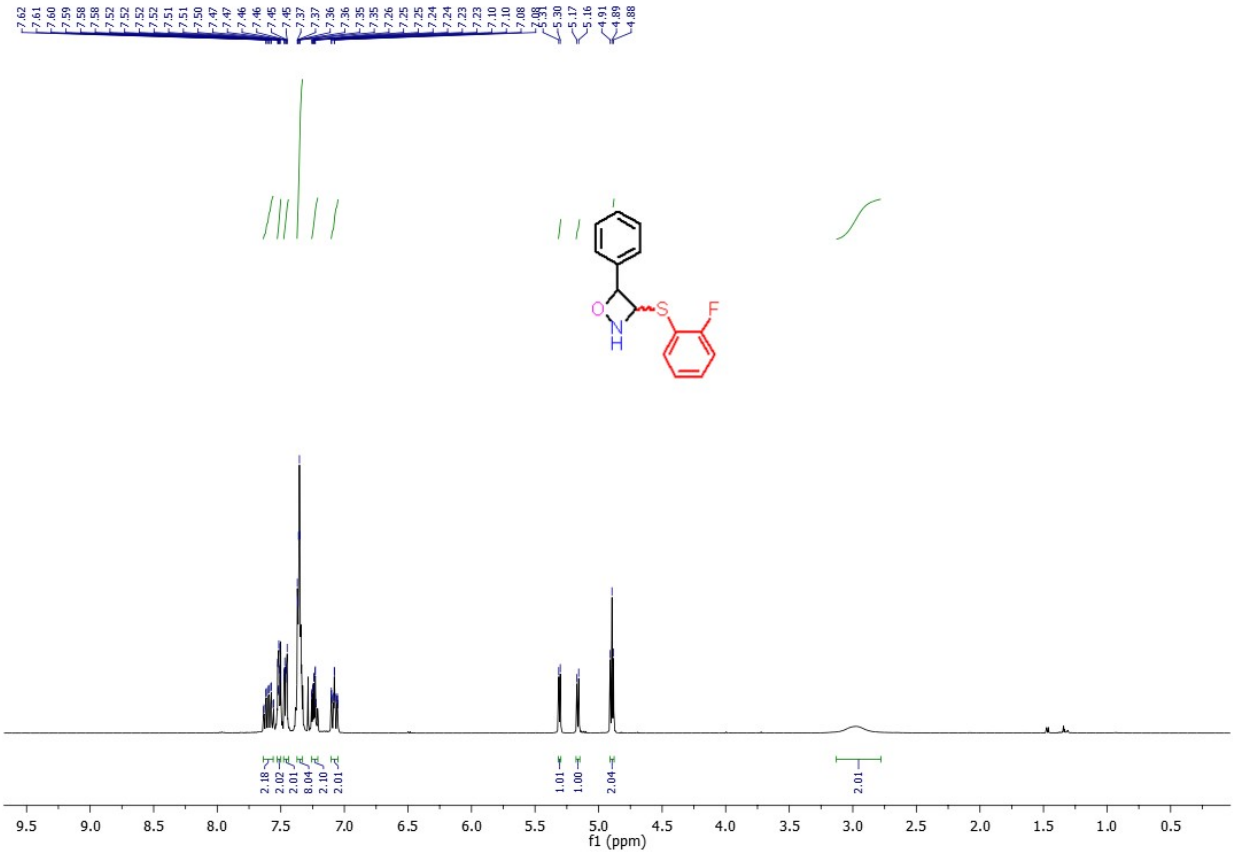
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **27**



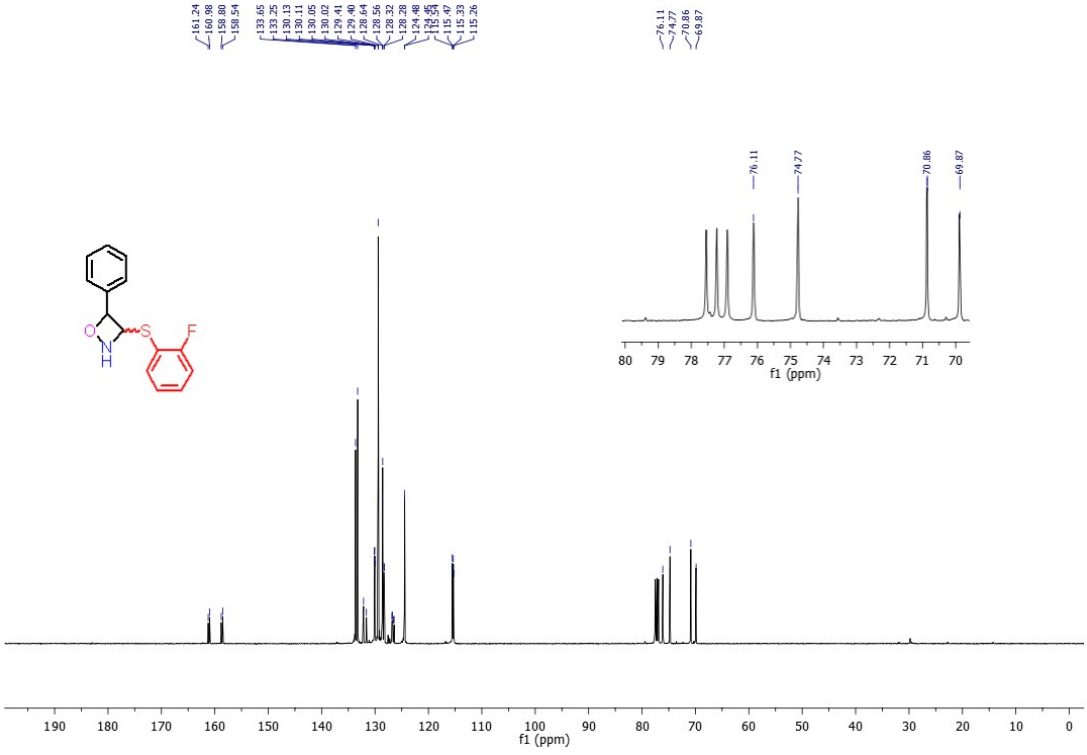
^{19}F-NMR ($CDCl_3$, 377 MHz) spectra of compound **27**



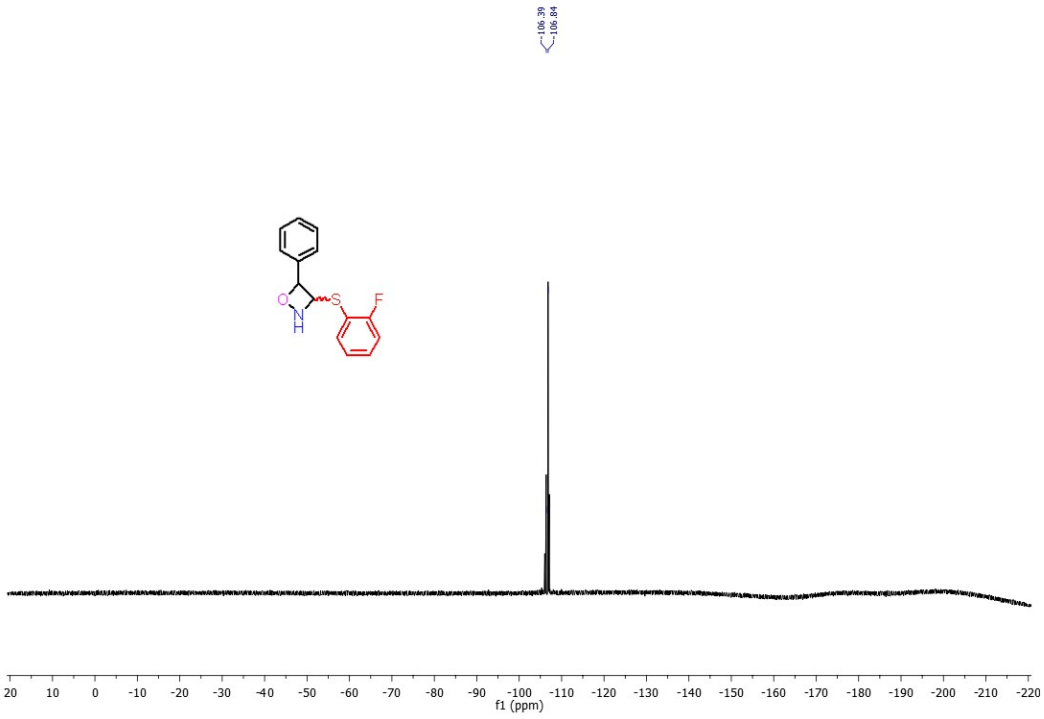
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **28**



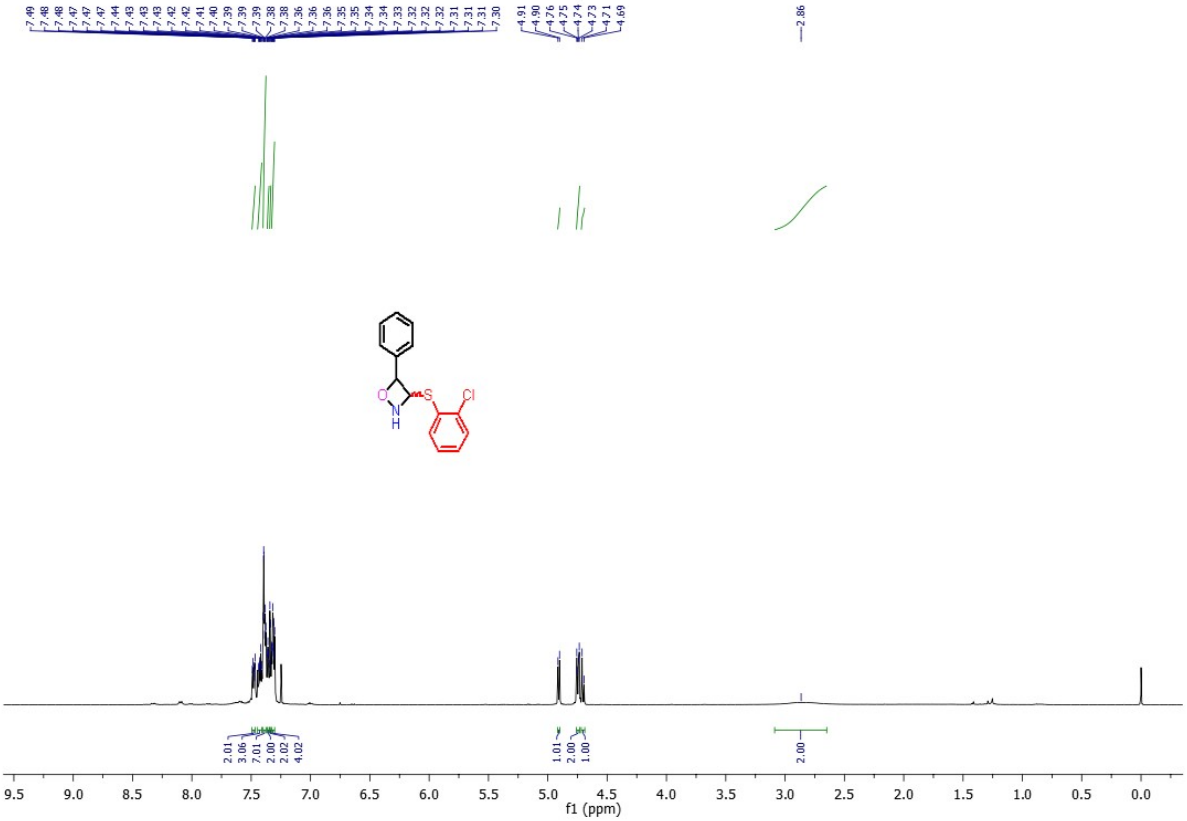
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **28**



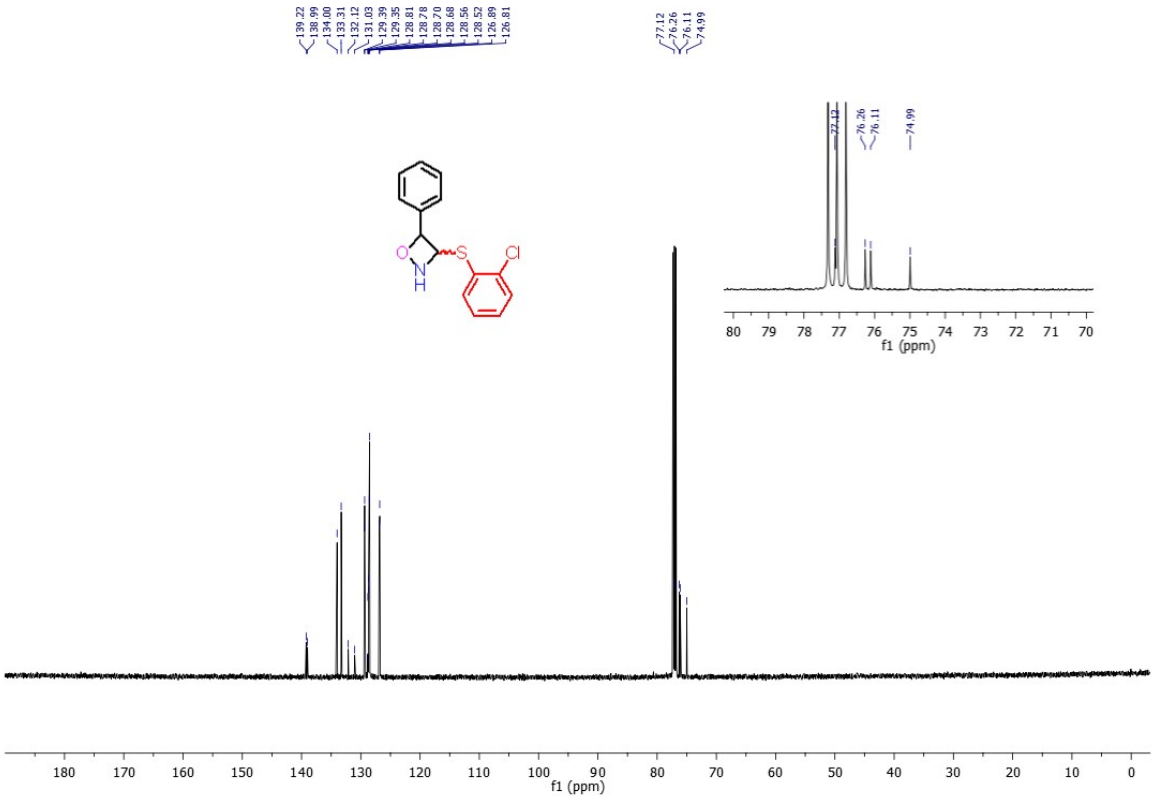
^{19}F-NMR ($CDCl_3$, 377 MHz) Spectra of compound **28**



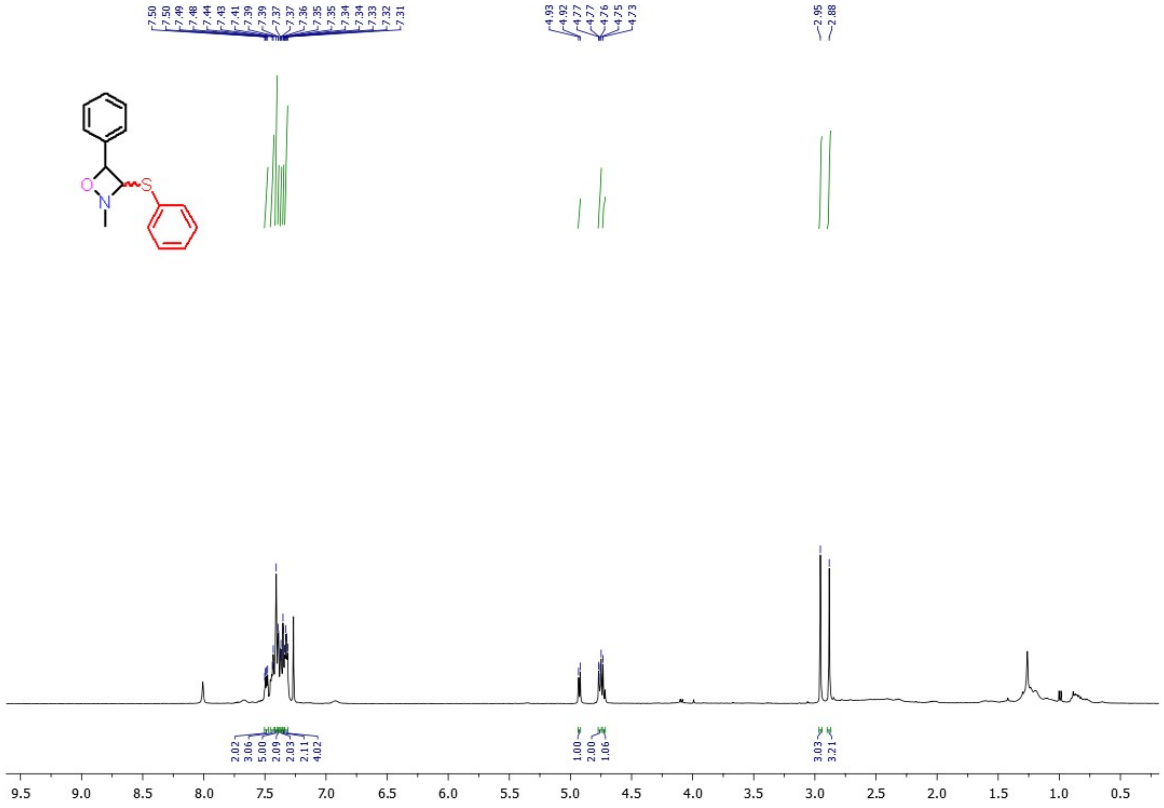
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **29**



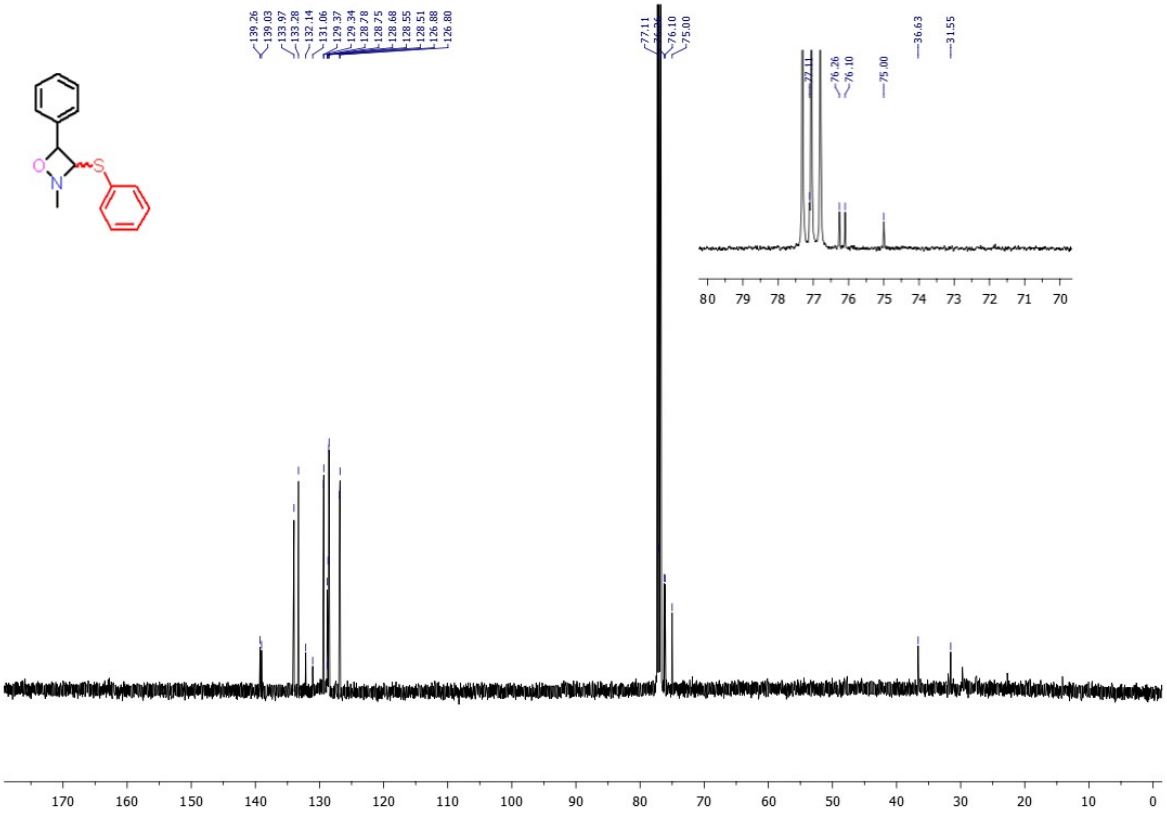
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectra of compound **29**



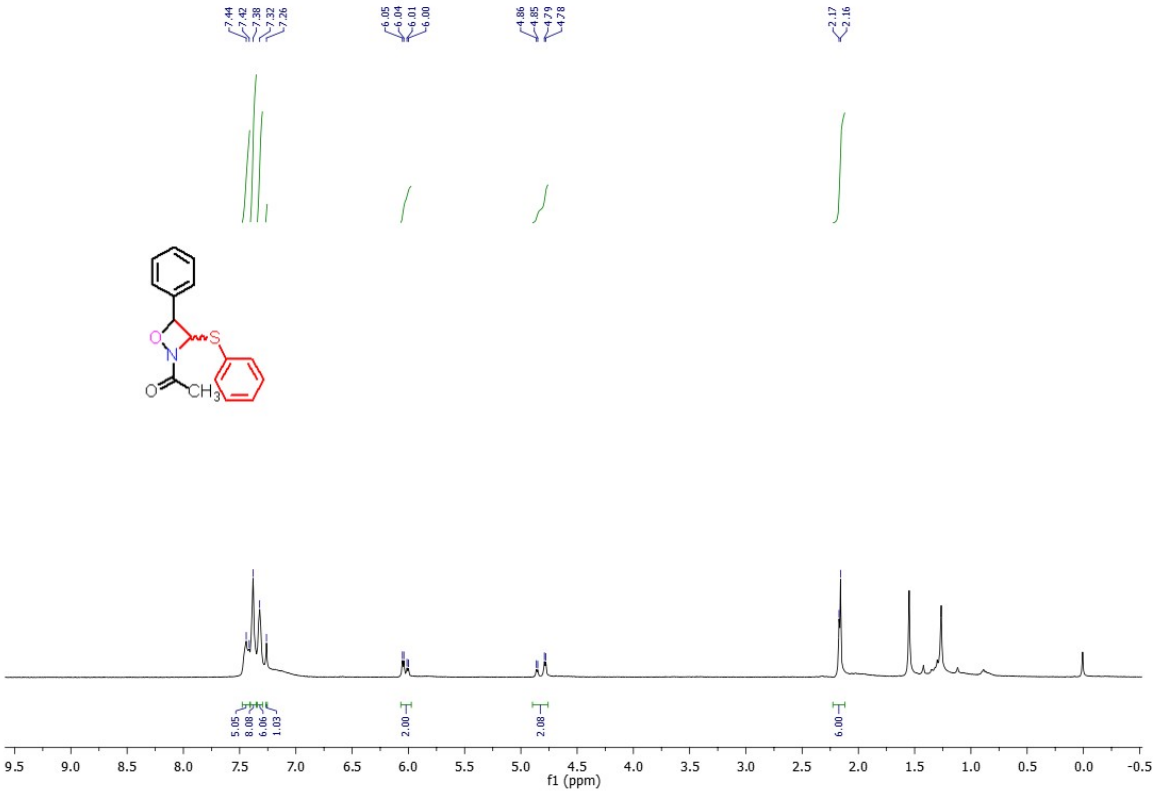
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **30**



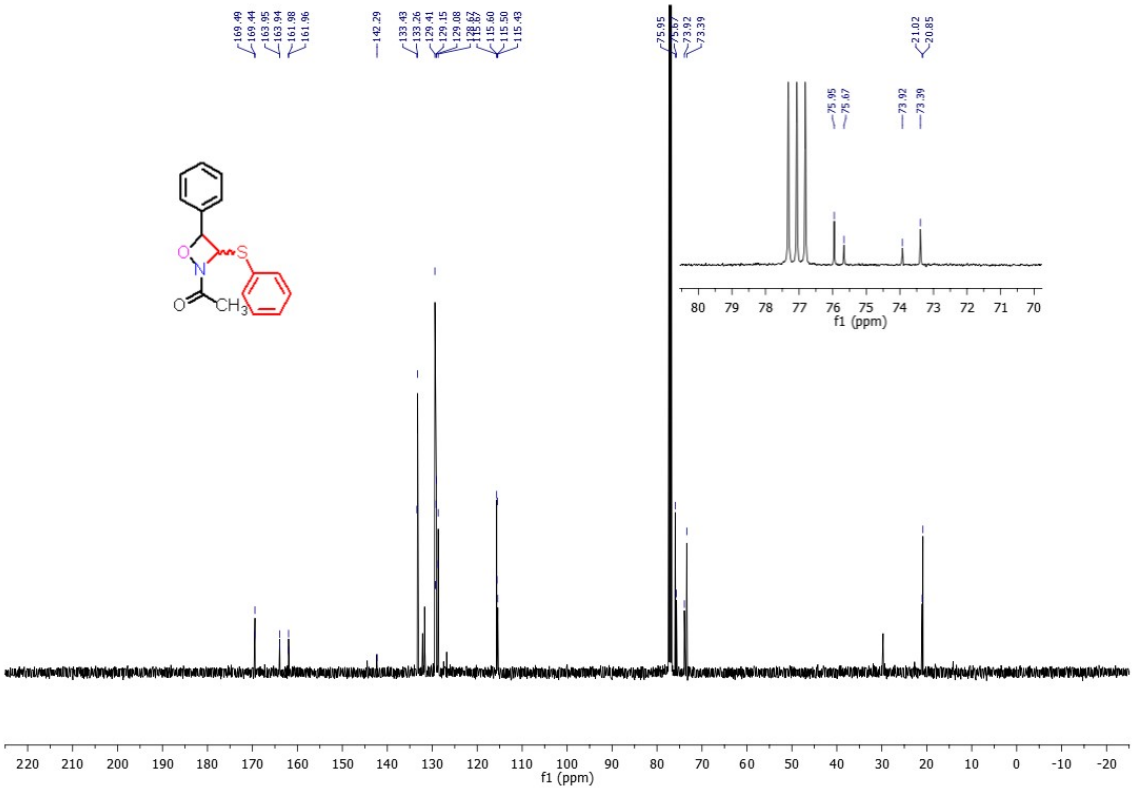
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **30**



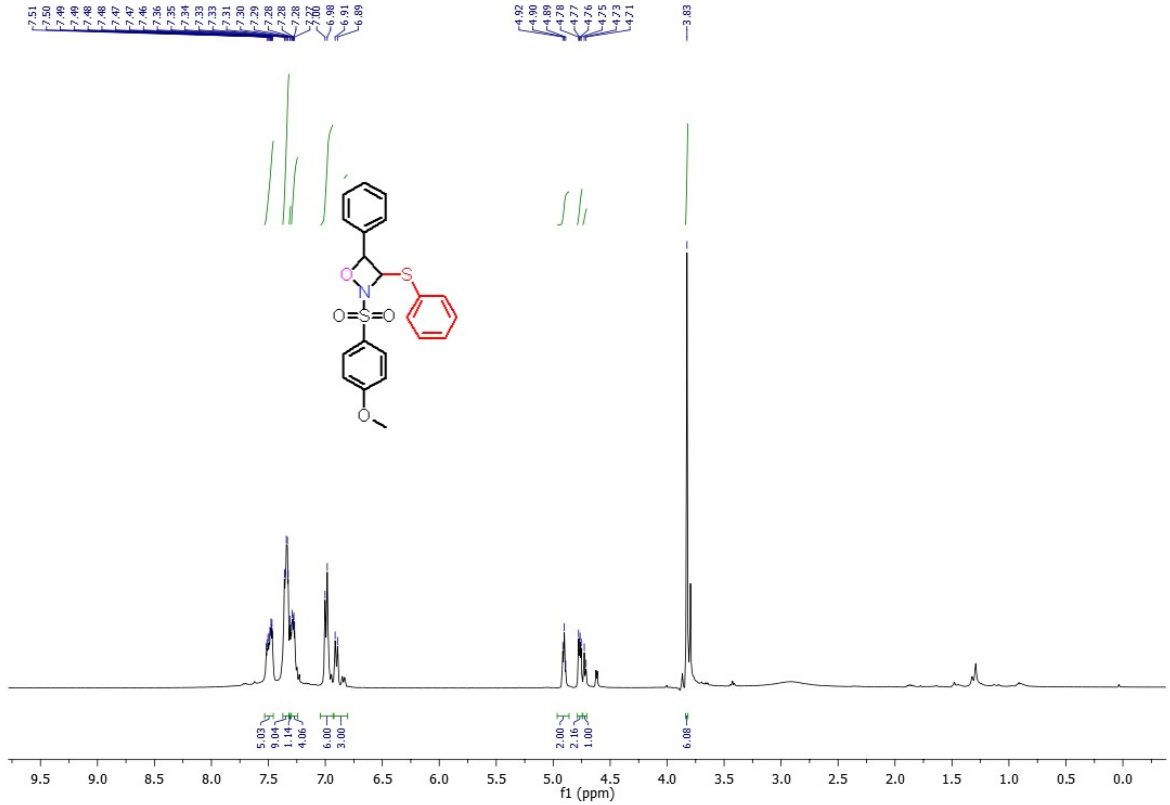
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **31**



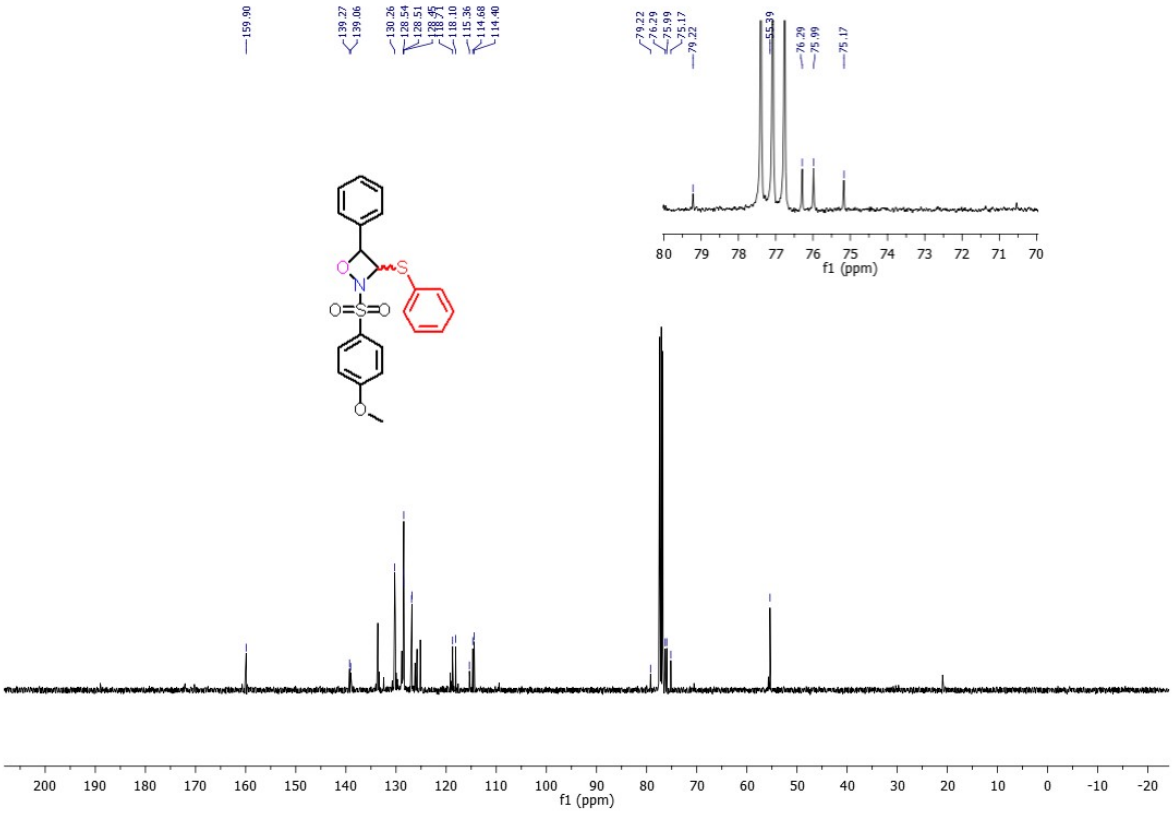
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **31**



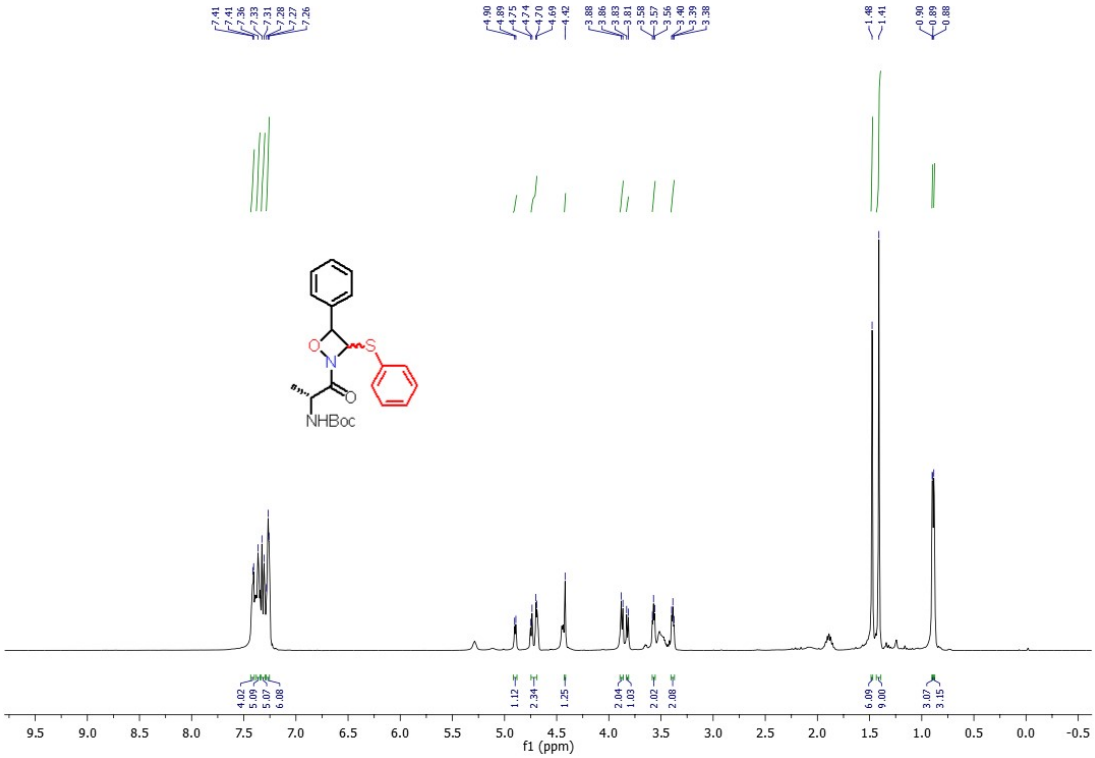
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **32**



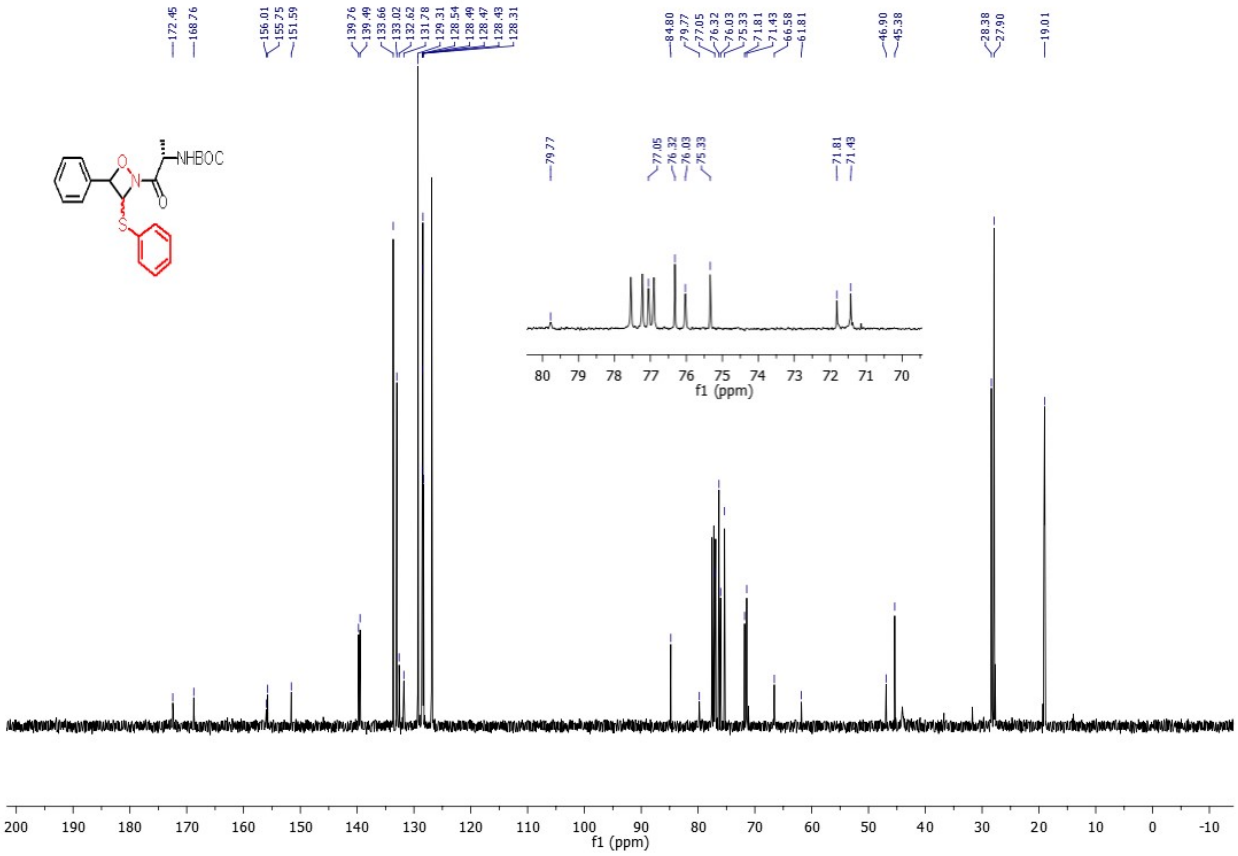
^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectra of compound **32**



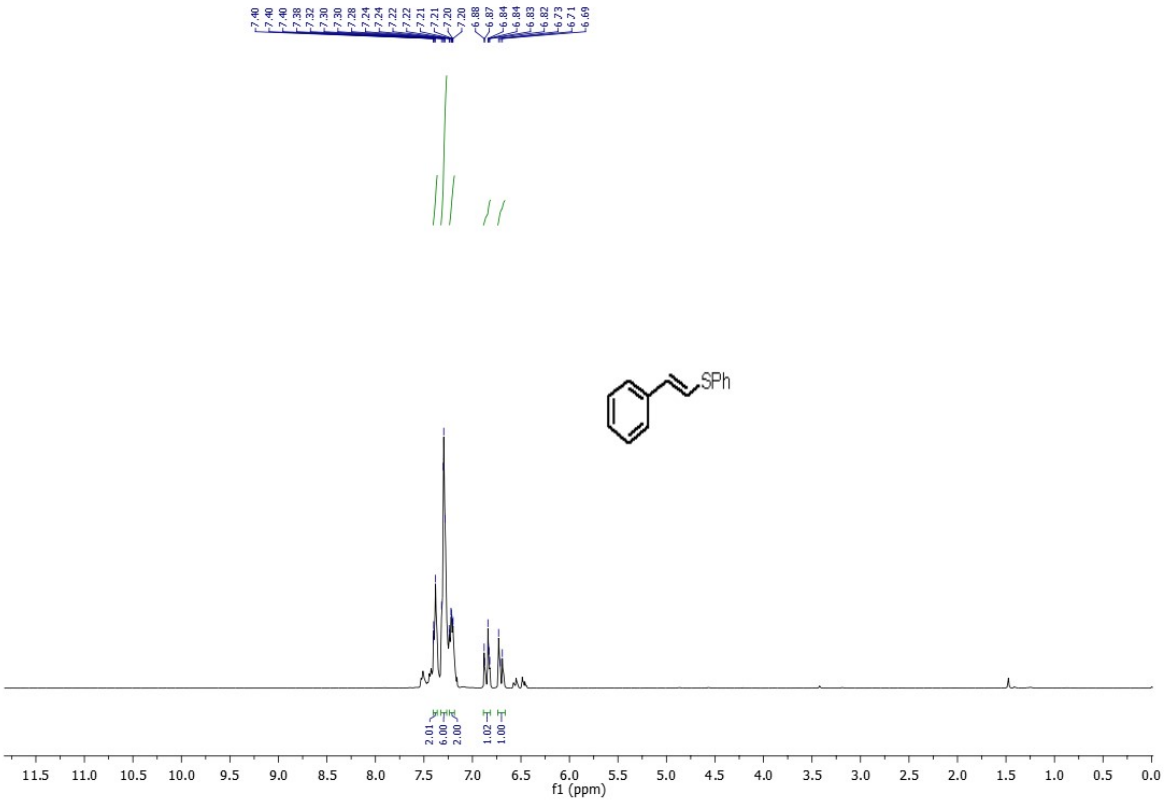
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **33**



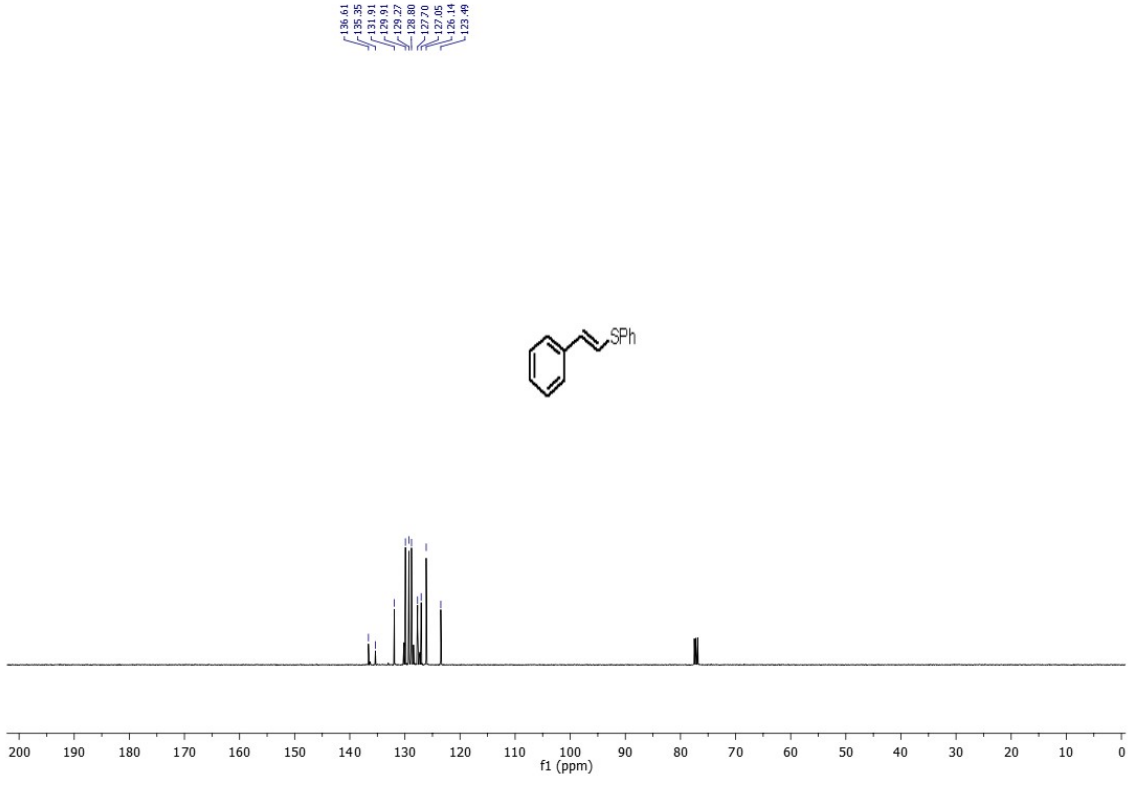
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz) spectra of compound **33**



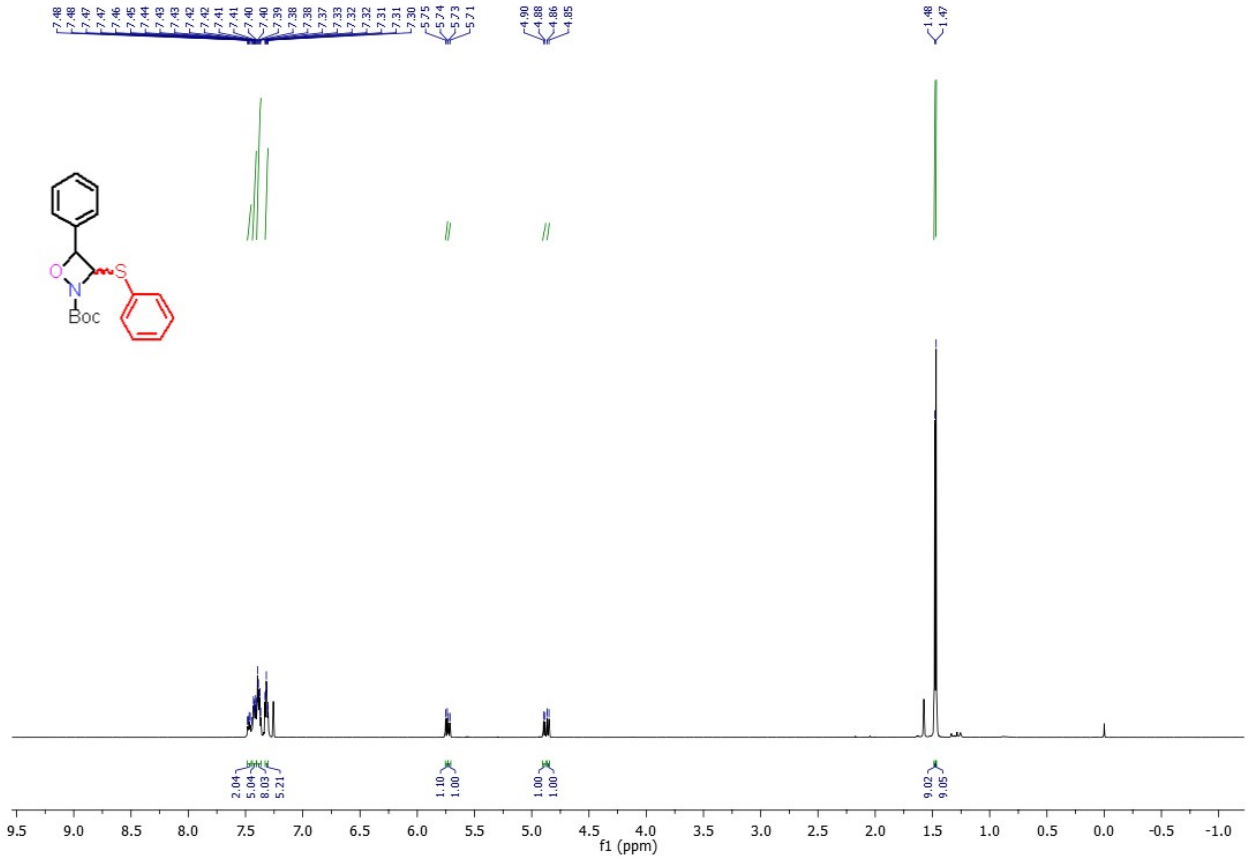
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **1d**



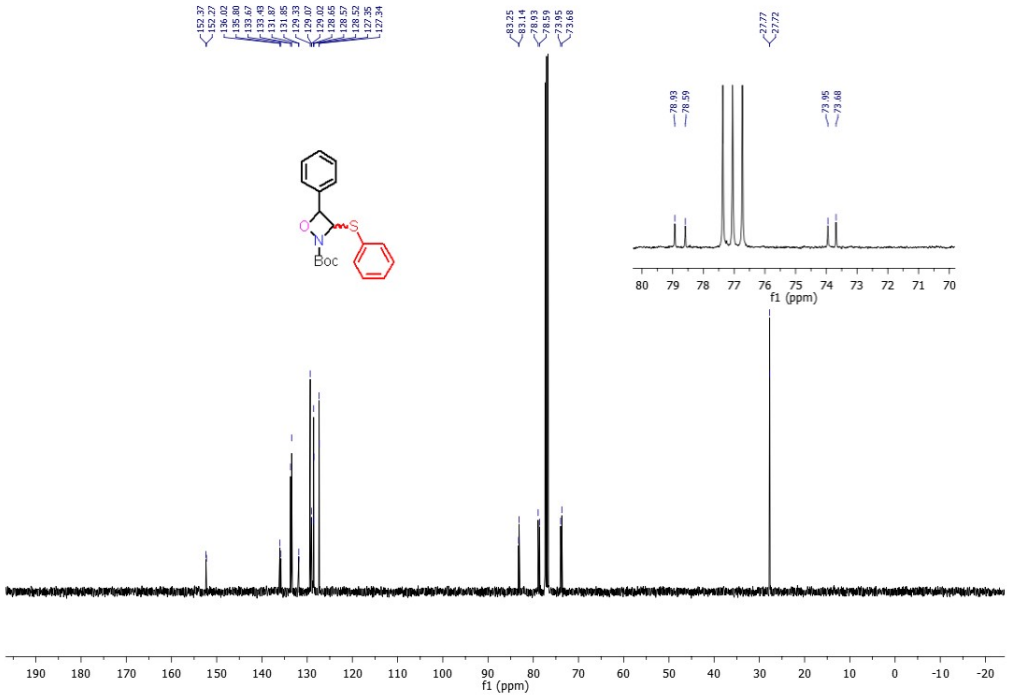
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **1d**



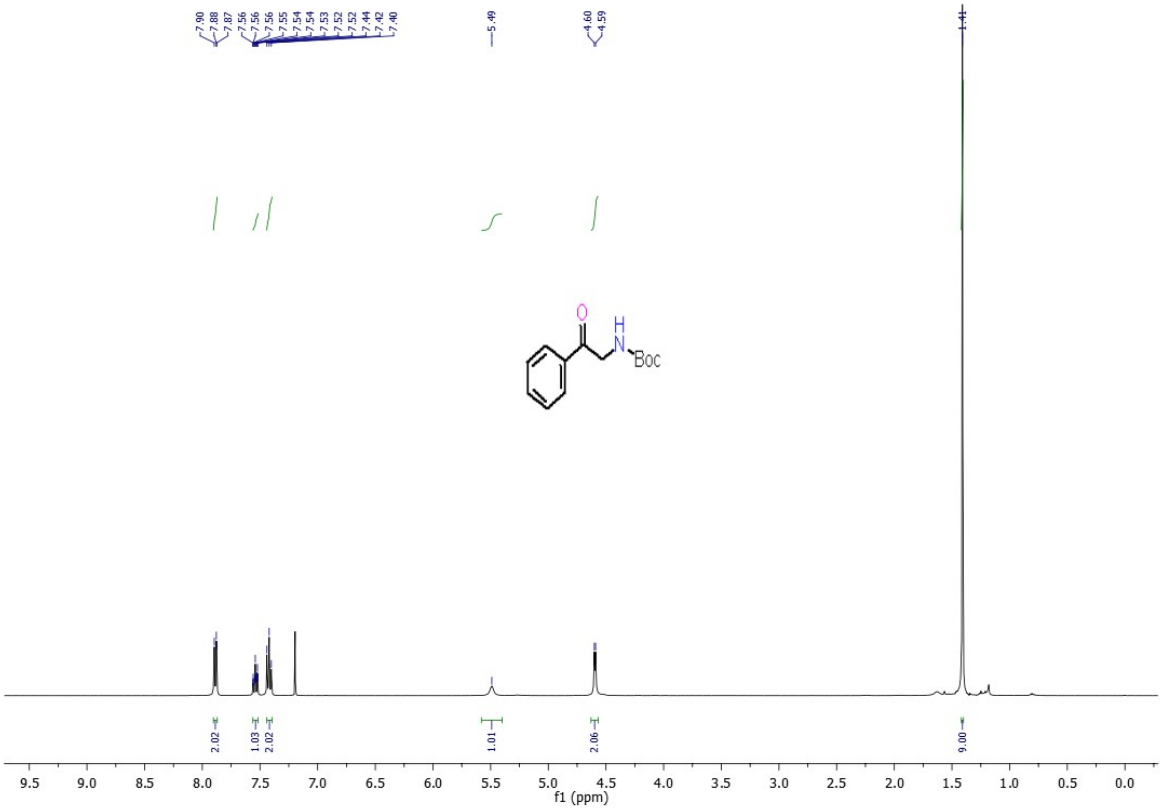
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **34**



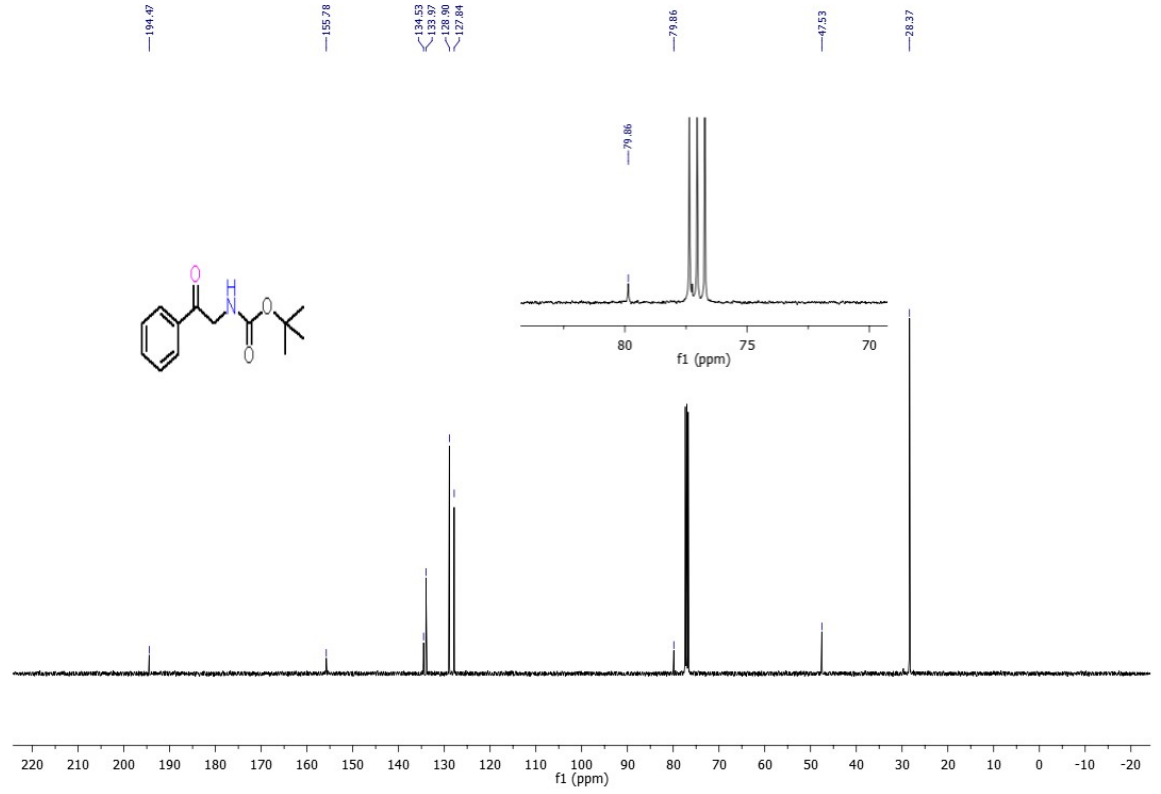
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **34**



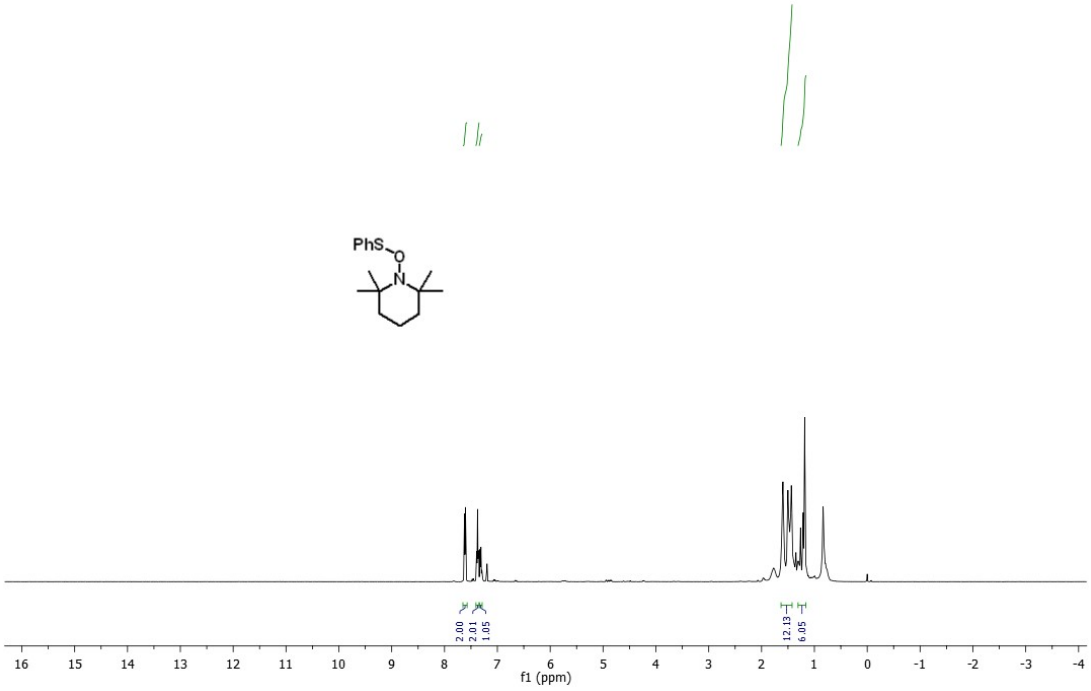
^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **35**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **35**



^{1}H-NMR ($CDCl_3$, 400 MHz) Spectra of compound **1h**



^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) spectra of compound **1h**