Electronic Supplementary Material (ESI) for ChemComm.

Modular Access to Sulfur Substituted Analogues of Isocytosine *via* Photoredox Catalysis.

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1. **General information:**

Materials: All the reagents except Propargyl Chlorides were purchased commercially and used as received. Reactions were carried out in oven-dried glassware. The solvents used for chromatography were purified by distillation.

NMR spectra: ^{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.

High-Resolution Mass Spectrometry (HRMS): All were recorded by using a QTOF-LC/MS spectrometer using electron spray ionization.

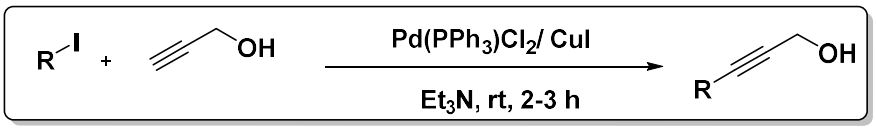
Electrochemical measurements: Electrochemical measurements were carried out using Bio-Logic SAS potentiostat (Model SP-150) with the glassy carbon as working, platinum wire as counter, and Ag/AgCl(3M NaCl) as reference electrode, in CH_3CN solvent using NBu_4PF_6 as supporting electrolyte over a scan rate of 100 mV/s.

Set-up for Photochemical reaction: The Penn PhD Photoreactor M2 (450 nm) is used for reaction irradiation, which was commercially purchased from Sigma-Aldrich. LED intensity for irradiation is generally 100% with stirring at 200 RPM and 4000 RPM fan speed. The reaction was performed at room temperature (25 ^{o}C) under this setting.

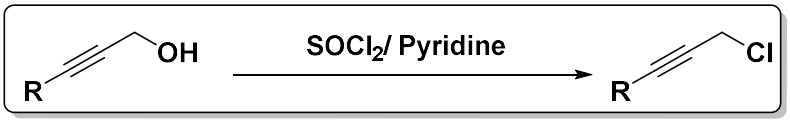
Figure **S1**: The Penn PhD Photoreactor M2

2. General Synthesis of Phenyl Propargyl Chlorides:

2.1. General Procedure for the Sonogashira Coupling of Propargyl Alcohol with Aryl Iodides (GP1): General procedure reported from the previous literature.[1] Iodobenzene (1 equiv.) was added to an oven-dried 50 mL round bottom flask and dissolved in Triethylamine (10 mL), $Pd(PPh_3)_2Cl_2$ (0.01 mol%), CuI (0.02 mol%), and propargyl alcohol (1.5 equiv.) were added to the flask and the mixture was cooled to 0 ºC. After 2-4 hours, TLC analysis showed consumption of the iodobenzene. Evaporating the solvent under reduced pressure yielded a thick brown paste which was filtered through a plug of silica gel (100% EtOAc). The crude material was then purified by column chromatography with hexane/ethyl acetate as solvent system.

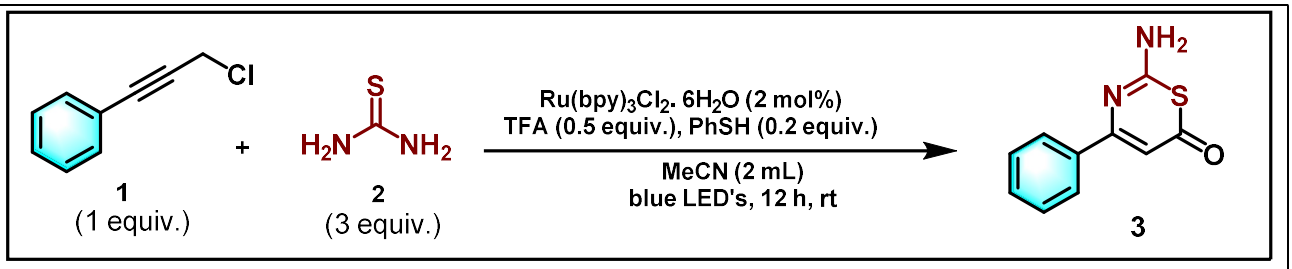


2.2. Functional group interconversion of Propargyl Alcohols to Propargyl Chlorides (GP2): General procedure was reported from the previous literature.[2] A 50 mL round-bottom flask was charged with anhydrous CH_2Cl_2 (20 mL), propargyl alcohol (1 equiv.) and Pyridine (1.2 equiv.), and the mixture was cooled with an ice bath. To the solution, $SOCl_2$ (1.1 equiv.) was added dropwise and the mixture was stirred at 0 ^oC for 30 minutes. The mixture was allowed to warm up to room temperature and stirred overnight at room temperature. The resulting mixture was diluted with ether (20 mL) and washed with 1N HCl Solution (15 mL×3). The water layer was extracted with Et_2O (20 mL×3). The combined organic extracts were washed with saturated $NaHCO_3$ aq. (15 mL ×3). The organic layer was dried over $MgSO_4$. After filtration and removal of the solvents in vacuo, the crude material was then purified by column chromatography using hexane as solvent to obtain the desired product.



3. **General procedure for the synthesis of sulfur analogues of isocytosine (GP3):**
To an oven-dried 30 ml glass vial was added 3-chloro-1-phenyl-1-propyne **1** (100 µL, 0.67 mmol) in 2 mL ACN followed by addition of $Ru(bpy)_3Cl_2$ (10 mg, 2 mol%), thiourea **2** (152.7 mg, 2.01 mmol), thiophenol (15 µL, 0.13 mmol) and trifluoroacetic acid (38.2 µL, 0.33 mmol) with continuous stirring under air. The reaction mixture was then irradiated under blue light sourced from Penn PhD Photoreactor M2 for 12 h. After the completion of the reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate and water. The aqueous layers were washed with sodium bicarbonate ($NaHCO_3$) and 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 column chromatography to obtain product **3** as a brownish liquid (106.6 µL, 78% yield) using distilled hexane/ethyl acetate (80:20) as a solvent system.

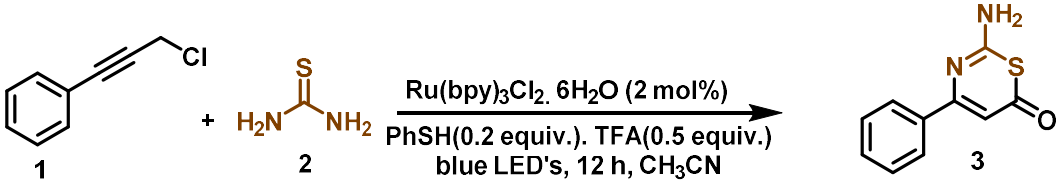
4. Optimization Table (Table S1):



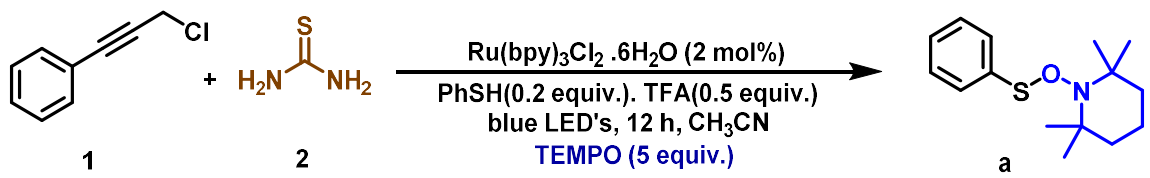
Entry	Deviation from standard conditions	Yield (%)
1	none	78
2	Mes-Acr^{+}ClO$_4^{-}$ as photocatalyst	traces
3	Rose Bengal as photocatalyst	16
4	eosin-Y as photocatalyst	23
5	DMSO instead of CH_3CN	32
6	MeOH instead of CH_3CN	41
7	DCM, DCE, DMF instead of CH_3CN	traces
8	no light, TFA, photocatalyst or thiophenol	n.d

5. Control Experiments:

Table **S2:**



Entry	Deviation	Yield[3] (%)
1	+ TEMPO (5 eq.)	traces
2	+Benzoquinone (3 eq.)	traces
3	Degassed/ Inert Atmosphere	traces
4	Dry ACN under O_2 atmosphere	72
5	Dry TFA	68



HRMS (ESI) (m/z) of compound **a**

Elemental Composition Report **Page 1**

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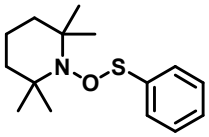
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-15 H: 0-100 N: 0-1 O: 0-1 S: 0-1

$[M+H]^+$ found for $C_{15}H_{24}NOS$ = 266.1576

TEMPO-1
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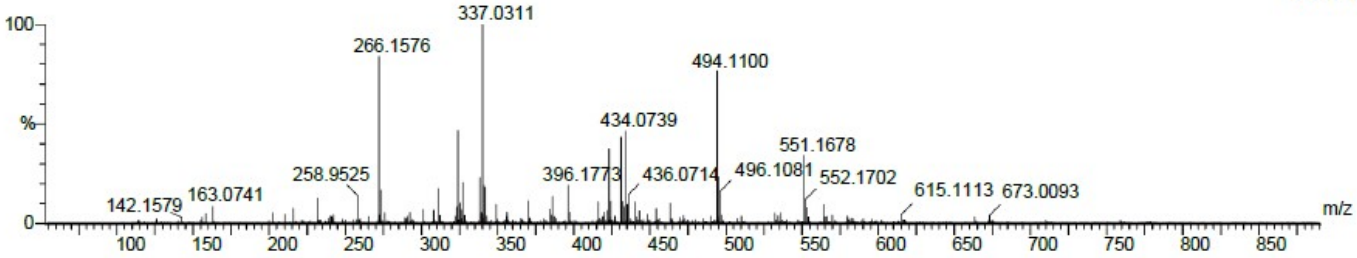

Minimum:			-1.5				
Maximum:		2.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
266.1576	266.1573	0.3	-5.1	6.5	1172.1	n/a	n/a	C15 H24 N O S

HRMS (ESI) (m/z) of Intermediate **III**

Elemental Composition Report **Page 1**

Single Mass Analysis
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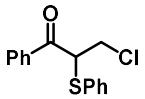
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)
Elements Used:
C: 0-15 H: 0-100 O: 0-1 S: 0-1 Cl: 0-1

$[M+H]^+$ found for $C_{15}H_{14}OSCl$ = 277.0436

TC-2
081123_09 17 (0.363)

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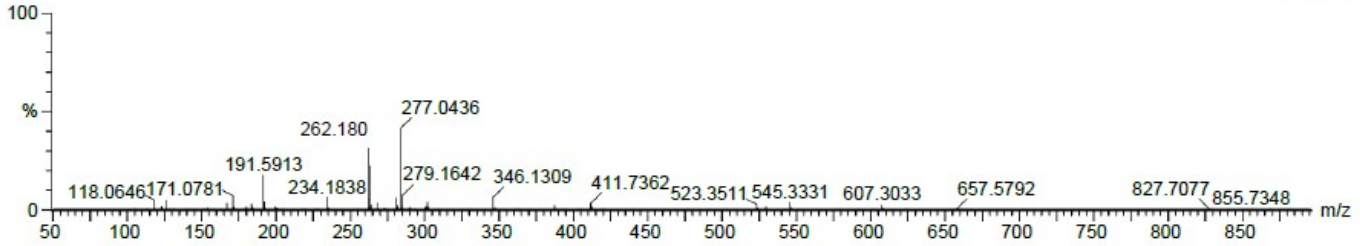
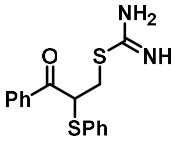


Minimum:			-1.5				
Maximum:		2.0	100.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
277.0436	277.0454	-1.8	-6.5	8.5	50.1	n/a	n/a	C15 H14 O S Cl

HRMS (ESI) (m/z) of Intermediate **IV**

Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



$[M+H]^+$ found for $C_{16}H_{17}N_2OS_2$ = 317.0779

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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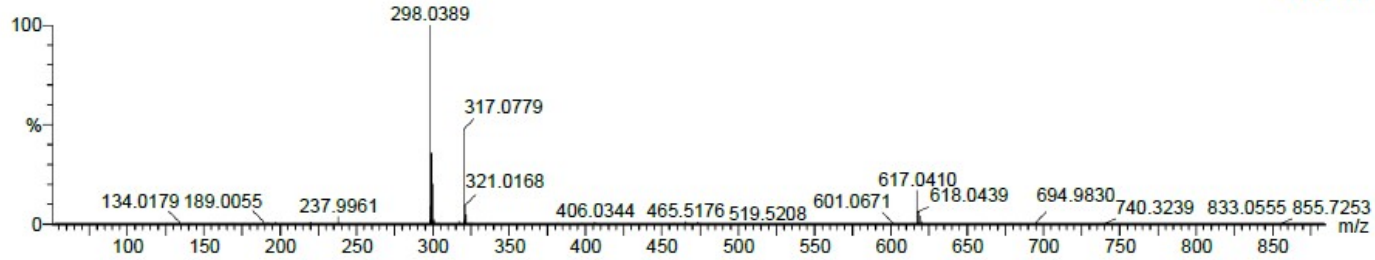

Minimum:				-1.5				
Maximum:		2.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
317.0779	317.0777	0.2	9.7	11.5	922.6	n/a	n/a	C16 H17 N2 O S2

HRMS (ESI) (m/z) of Intermediate **VI**

Elemental Composition Report Page 1

Single Mass Analysis
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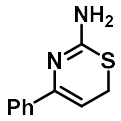

$[M+H]^+$ found for $C_{10}H_{11}N_2S$ = 191.0617

Monoisotopic Mass, Even Electron Ions
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Elements Used:
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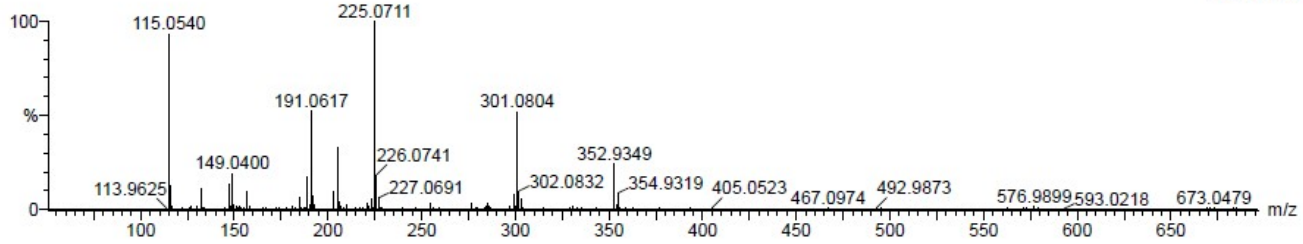


Minimum:				-1.5				
Maximum:		2.0	50.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
191.0617	191.0643	-2.6	-13.6	6.5	1947.9	n/a	n/a	C10 H11 N2 S

6. Photoredox Studies:

6.1. Absorption Studies: Absorption changes were monitored by adding reactants (independently) to the fixed concentration (5 μM) of photocatalyst $[Ru(bpy)_3]Cl_2$ as binary mixtures in acetonitrile (ACN) solvent at room temperature. All these binary mixtures were titrated with increasing concentration of reactants under blue LED irradiation. The observed changes in the absorption profile of $[Ru(bpy)_3]Cl_2$ with thiophenol (PhSH), thiourea (TU) and propargyl chloride (PC) can be corroborated with their relative propensity towards single electron transfer reaction. The binding propensity was quantified using the ***Benesi–Hildebrand equation***.

$$\frac{\mathbf{1}}{(\mathbf{A} - \mathbf{A_0})} = \frac{\mathbf{1}}{(\mathbf{A}_{max} - \mathbf{A})} + \frac{\mathbf{1}}{\mathbf{K}(\mathbf{A}_{max} - \mathbf{A})[\mathbf{M}]}$$

From the data analysis, it can be seen that the propensity of thiophenol to the $[Ru(bpy)_3]Cl_2$ catalyst is higher than other reactants confirming thiophenol as a primer reactant for single electron transfer reaction with excited photo excited $[Ru(bpy)_3]Cl_2$ catalyst as shown in the reaction mechanism.

6.2. Fluorescence Studies: Fluorescence quenching studies were carried out using 5 μM of $[Ru(bpy)_3]Cl_2$ and increasing concentrations of reactants (PhSH, PC, TU) as quenchers in ACN at room temperature. The solutions were irradiated with blue LED light at an excitation wavelength of λ= 450 nm and the fluorescence 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 **S2**. The calculated quenching constants were in good agreement with absorption results and further confirm thiophenol to be an effective reagent for initiating single electron transfer reaction with photoexcited $[Ru(bpy)_3]Cl_2$ catalyst.

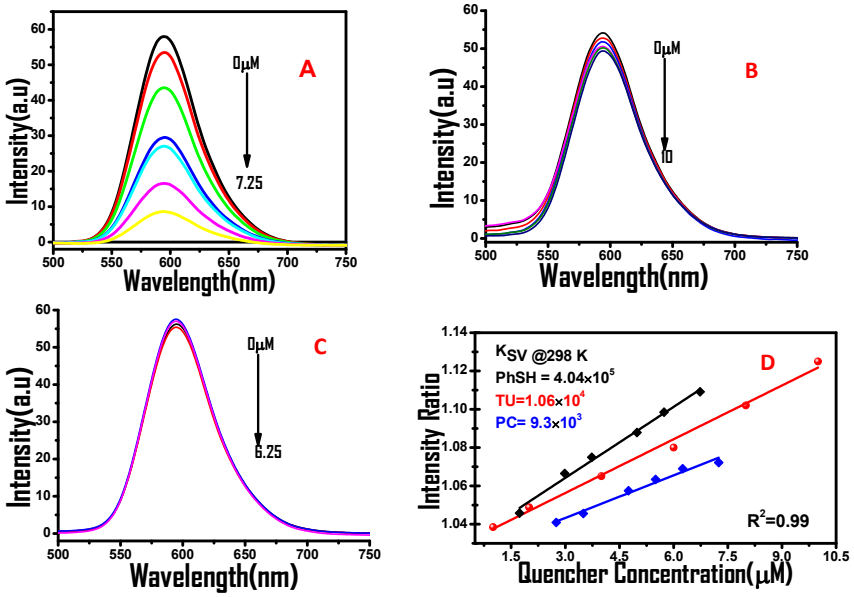


Figure **S2**: Photoredox studies: (A-C) fluorescence quenching studies of $[Ru(bpy)_3]Cl_2$ with reaction precursors, and (D) Their relative Stern-Volmer plots at room temperature.

The comparative Benesi–Hildebrand plots, describing the thermodynamic binding propensity of reaction ingredients towards the photocatalyst for electron transfer reaction under blue LED irradiation, predicted thiophenol (PhSH) > thiourea (TU) > phenyl propargyl chloride (PC). The corresponding Stern-Volmer plots corroborated the quenching order of reactants to their binding propensities predicted from Benesi–Hildebrand plots (Figure **S3**-C, D). The higher ther thermodynamic binding affinity and the significant quenching observed in the case of thiophenol (Figure **S3**-A) supports the proposed single electron transfer of photoexcited $[Ru(bpy)_3]Cl_2$ photocatalyst with thiophenol as the initial step of the reaction mechanism. The reduction of photo-excited $[Ru^{II}(bpy)_3]Cl_2$ by thiophenol to $[Ru^{I}(bpy)_3]Cl_2$ was validated from the observed reduction peak current changes in the cyclic voltammograms upon thiophenol addition (Figure S**3**-B). In addition, the results of the light on-off experiment imply an essential requirement for continuous irradiation (Figure **S4**). The light on-off experiment emphasizes the necessity of continuous irradiation with blue LED light for the progression of reaction (Figure S4).

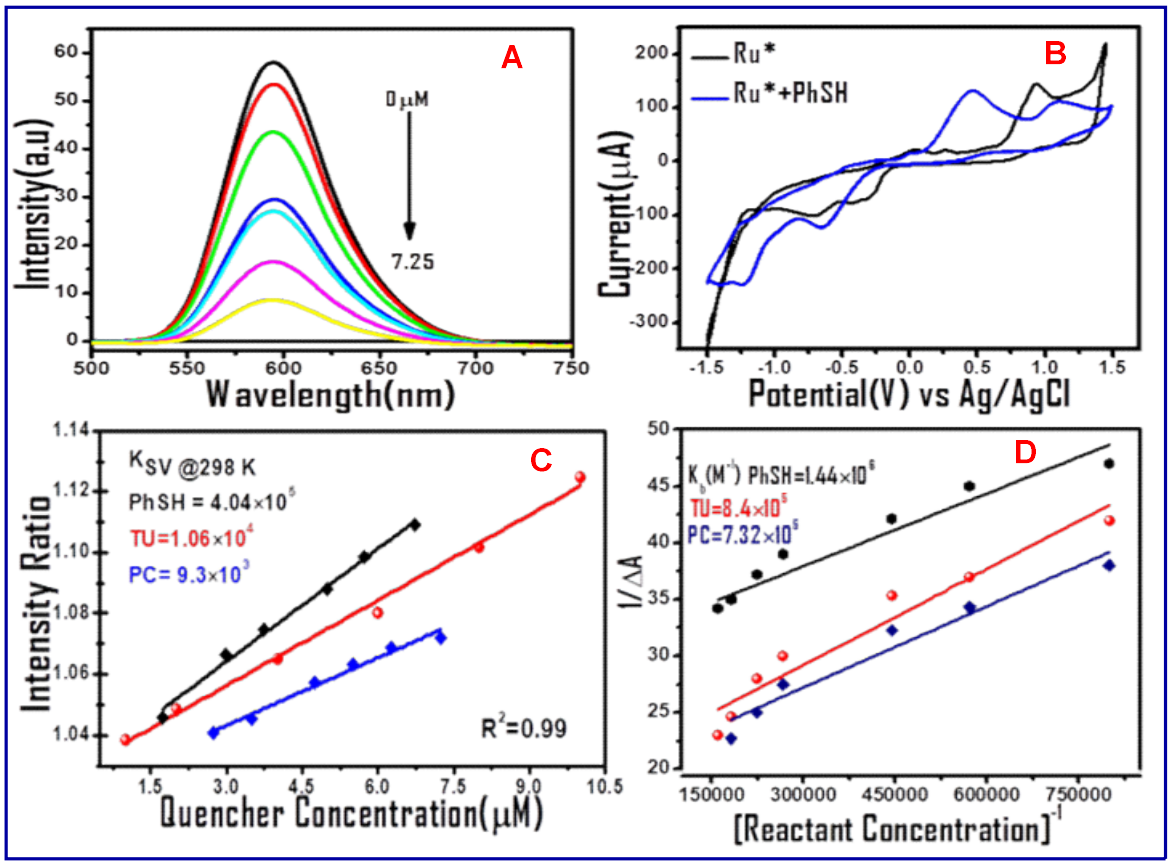


Figure **S3:** A) fluorescence quenching profile of $[Ru(bpy)_3]Cl_2$ with thiophenol (PhSH); B) cyclic voltammogram profiles of $[Ru(bpy)_3]Cl_2$ upon PhSH addition; C) comparative Stern-Volmer plots; D) comparative Benesi–Hildebrand plots of reactant binding affinity to $[Ru(bpy)_3]Cl_2$

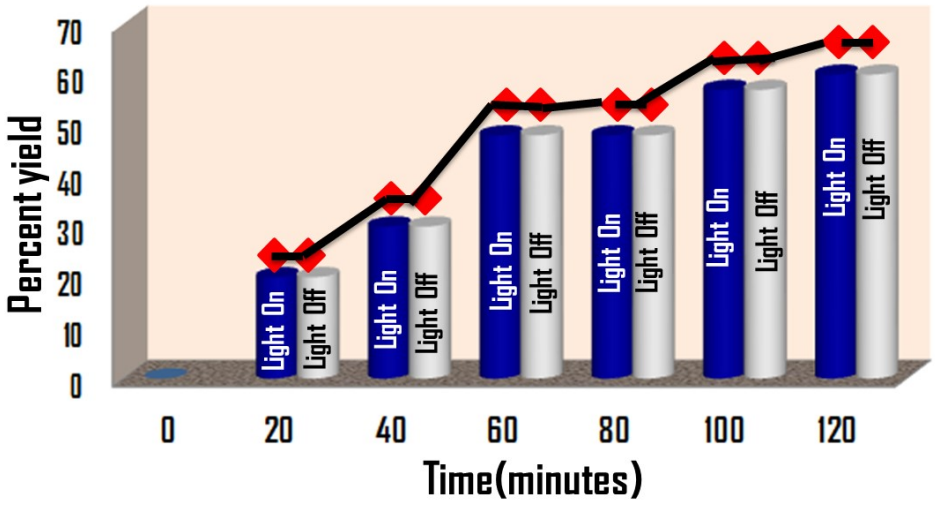


Figure **S4**: Light on-off experiment implies requirement of continuous irradiation of blue LED.

6.3. Electrochemical Studies: Electrochemical measurements were conducted using a Bio-Logic SAS potentiostat (Model SP-150) with a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl reference electrode. The scan rate employed was 100 mV/s, in acetonitrile (ACN) solvent and $NBuPF_6$ as the supporting electrolyte. All the measurements were carried out using fixed concentration of $[Ru(bpy)_3]Cl_2 .6H_2O$ (5 µM) under blue irradiation under increasing concentrations of reactants. The well-defined redox potential of $[Ru(bpy)_3]Cl_2 .6H_2O$ exhibited a notable shift towards higher potential with an increase in peak current upon the addition of 3 µM thiophenol(Figure **S4** A). This observed shift in peak potentials aligns with the notion of single electron reduction of the photocatalyst by thiophenol. However, no significant changes in the redox behavior of $[Ru(bpy)_3]Cl_2 .6H_2O$ were observed upon the addition of propargyl chloride and thiourea, both individually and as their respective binary combinations (Figure **S4** B&C). The lack of observable changes suggests that these reactants may not significantly influence the redox behaviour of the photocatalyst under the experimental conditions. In summary, the electrochemical measurements, particularly the shift in redox potential with thiophenol addition, provide further evidence supporting the proposed reaction mechanism involving the single electron reduction of the photocatalyst. Conversely, propargyl chloride and thiourea seem to have limited impact on the redox behavior of $[Ru(bpy)_3]Cl_2 .6H_2O$ under the investigated conditions.

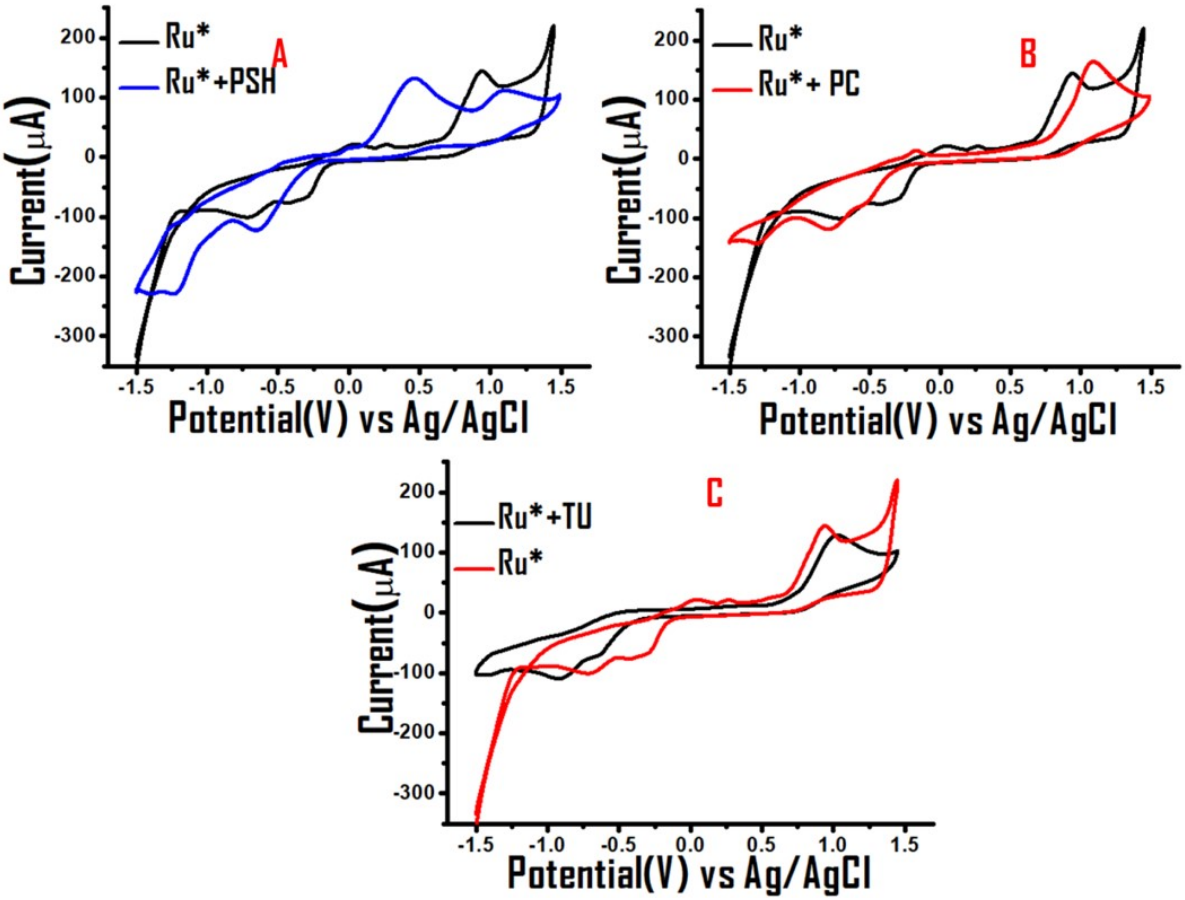


Figure **S5**: Cyclic voltammograms of photocatalyst with binary reaction combinations

7. Determination of the reaction quantum yield:

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

Step 1: The potassium ferrioxalate actinometer method published in literature[3-7] 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[5]. 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 the dark place.

The actinometer measurement was done as follows:

After irradiation of 2.0 mL 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 Beer's Laws using the equation:

$$\text{moles of } Fe^{2+} = \frac{\boldsymbol{V(L) \times \Delta A(510)nm}}{\boldsymbol{l(cm) \times \varepsilon(Lmol^{-1}\,cm^{-1})}} = \mathbf{4.29 \times 10^{-7}}$$

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 [5] at λ 510 nm (11,100 L $mol^{-1}cm^{-1}$). The photon flux of the Blue LED was calculated as under:

$$\boldsymbol{Photon\ flux} = \frac{\boldsymbol{moles\ of\ Fe^{2+}}}{\boldsymbol{\emptyset \times t \times f}} = \mathbf{4.29 \times 10^{-9}}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (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}.

Step 2:

3-chloro-1-phenyl-1-propyne (20 μL, 0.133 mmol, 1.0 equiv.), thiourea (30.3 mg, 0.39 mmol, 3 equiv.), thiophenol (2.92 μL, 0.026 mmol, 0.2 equiv.), trifluoroacetic acid (7.6 μL, 0.066 mmol, 0.5 equiv.) and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.99 mg, 0.0026 mmol) were placed in a quartz cuvette. The sample was stirred and irradiated for 90s. After irradiation, the yield of product **3** formed was determined using the peak area analysis method of the Gas Chromatography technique.[8] The yield of product **3** formed after the 90s of irradiation as determined from quantitative analysis by gas chromatography was found to be 0.12%, corresponding to (1x10^{-6} mol). The reaction quantum yield (Φ) was then arrived at using the equation:

$$\emptyset = \frac{\boldsymbol{moles\ of\ product\ formed}}{\boldsymbol{photon\ flux \times t \times f}} = \mathbf{0.43}$$

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.[9]The reaction quantum yield (Φ) was determined to be 0.43, indicating radical non chain process.[10]

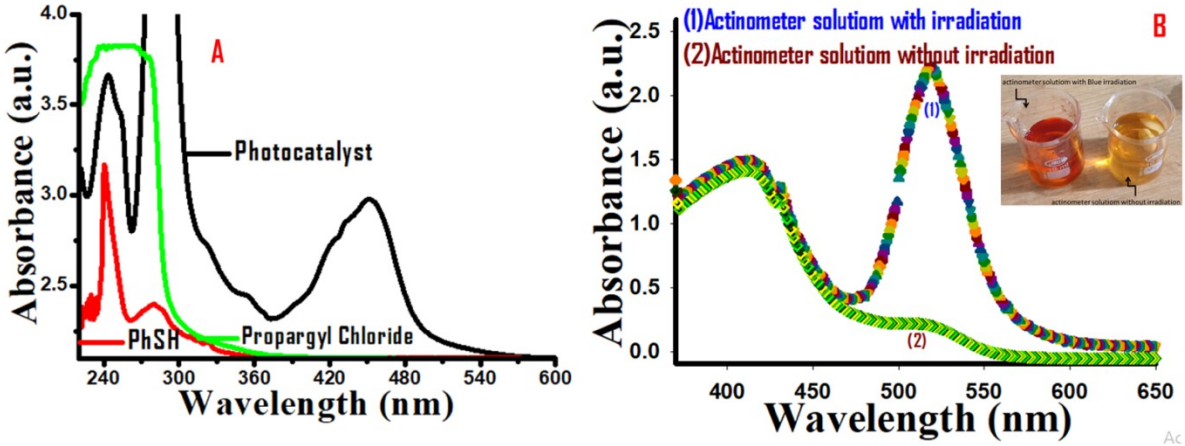
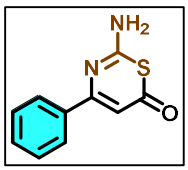


Figure S6: A: Initial absorption spectra of reaction mixture showing absorption. B: Absorption spectra's of actinometer solution without and after irradiation for 90s

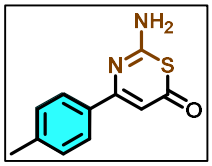
8. Characterization data:

2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (3):



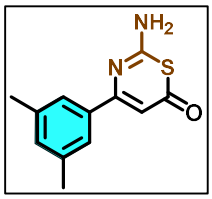
Following the general procedure (**GP3**) the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), thiourea (152.7 mg, 2.01 mmol), thiophenol (15 µL, 0.13 mmol), TFA (38 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as brownish liquid (106.6 µL, 78% yield). ^1H NMR (400 MHz, $CDCl_3$) : δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.29 (s, 1H), 6.15 (br s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.7 , 168.2, 150.0, 137.8, 132.5, 129.6, 128.3, 120.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_9N_2OS^+$, 205.0430; found: 205.0434

2-amino-4-(p-tolyl)-6*H*-1,3-thiazin-6-one (4):



Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-methylbenzene (100 µL, 0.61 mmol), thiourea (139.1 mg, 1.83 mmol), thiophenol (13µL, 0.12 mmol), TFA (35 µL, 0.30 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (9.1mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as light brown solid (m.p 123-125 °C) (107.7 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.77 (m, 2H), 7.27 (s, 1H), 7.26-7.20 (m, 2H), 6.02 (br s, 2H, NH_2), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.5, 168.2, 150.2, 143.3, 135.1, 129.8, 129.0, 119.9, 21.7. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_{11}N_2OS^+$: 219.0587; found: 219.0596

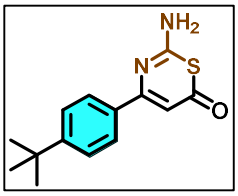
2-amino-4-(3,5-dimethylphenyl)-6*H*-1,3-thiazin-6-one (5):



Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3,5-dimethylbenzene (100 µL, 0.56 mmol), thiourea (128.1 mg, 1.68 mmol), thiophenol (12 µL, 0.12 mmol), TFA (32.0 µL, 0.28 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8.4 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as

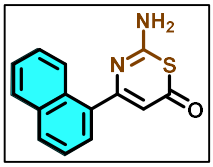
brown solid (m.p 150-152 °C) (98.7 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 2H), 7.13 (d, *J* = 3.3 Hz, 2H), 2.29 (d, *J* = 3.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 188.1, 168.6, 149.1, 138.0, 137.7, 134.2, 127.1, 120.3, 21.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{13}N_2OS^+$: 233.0743; found: 233.0744

2-amino-4-(4-(tert-butyl)phenyl)-6*H*-1,3-thiazin-6-one (6):



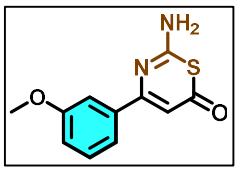
Following the general procedure (**GP3**) the reaction was carried out with 1-(tert-butyl)-4-(3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.49 mmol), thiourea (111.7 mg, 1.47 mmol), thiophenol (11 µL, 0.09 mmol), TFA (28 µL, 0.24 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (7.3 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as brown solid (m.p 119-121 °C) (93 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.22 (s, 1H), 1.35 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 189.1, 161.1, 144.3, 137.7, 133.3, 129.5, 123.0, 39.0, 34.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{17}N_2OS^+$: 261.1056; found: 261.1055

2-amino-4-(naphthalen-1-yl)-6*H*-1,3-thiazin-6-one (7):



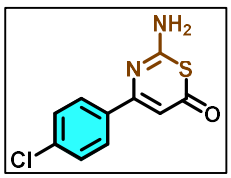
Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)naphthalene (100 µL, 0.50 mmol), thiourea (114.0 mg, 1.5 mmol), thiophenol (11.0 µL, 0.10 mmol), TFA (29 µL, 0.25 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (7.5 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as light brown solid (m.p 161-163 °C) (97.8 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 8.02 (m, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.63 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.02 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 193.2, 154.6, 139.6, 137.6, 135.5, 134.6, 132.3, 131.3, 130.4, 129.1, 128.1, 126.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{11}N_2OS^+$: 255.0587; found: 255.0592

2-amino-4-(3-methoxyphenyl)-6*H*-1,3-thiazin-6-one (8):



Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3-methoxybenzene (100 µL, 0.56 mmol), thiourea (127.68 mg, 1.68 mmol), thiophenol (12 µL, 0.11 mmol), TFA (32 µL, 0.28 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8.4 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 79:21) as brownish liquid (87.8 µL, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.23 (s, 1H), 7.14 (dd, *J* = 8.1, 2.6 Hz, 1H), 3.85 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 186.0, 169.0, 159.6, 146.2, 138.2, 129.5, 122.0, 119.9, 119.2, 114.0, 55.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_{11}N_2O_2S^+$: 235.0536; found: 235.0539

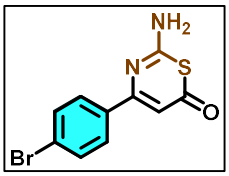
2-amino-4-(4-chlorophenyl)-6*H*-1,3-thiazin-6-one (9):



Following the general procedure (**GP3**) the reaction was carried out with 1-chloro-4-(3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.54 mmol), thiourea (123.12 mg, 1.62 mmol), thiophenol (12 µL, 0.11 mmol), TFA (31 µL, 0.27 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8.1 mg, 2 mol%) and

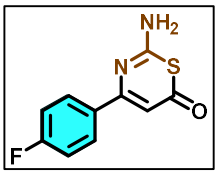
purified by column chromatography (hexane/ethyl acetate = 83:17) as cream coloured solid (m.p 151-153 °C) (95.1 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.34 (s, 1H), 5.70 (br s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.1, 167.7, 150.1, 139.0, 136.0, 131.3, 128.6, 120.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_2OSCl^+$: 239.0040; found: 239.0047

2-amino-4-(4-bromophenyl)-6*H*-1,3-thiazin-6-one (10):



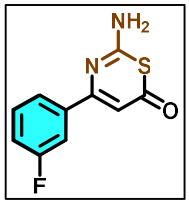
Following the general procedure (**GP3)** the reaction was carried out with 1-bromo-4-(3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.44 mmol), thiourea (100.3 mg, 1.32 mmol), thiophenol (10.0 µL, 0.09 mmol), TFA (25 µL, 0.22 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (6.6 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as light brown solid (m.p 156-158 °C) (89.3 mg, 72% yield). ^{1}H NMR (400 MHz, Acetone-D_6): δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.49 (s, 1H), 4.87 (br s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, Acetone-D_6): δ 184.1, 165.5, 146.8, 136.4, 131.7, 131. 4, 127.0, 118.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_2OSBr^+$: 282.9535; found: 282.9546

2-amino-4-(4-fluorophenyl)-6*H*-1,3-thiazin-6-one (11):



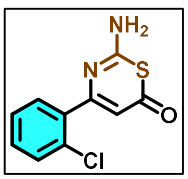
Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-fluorobenzene (100 µL, 0.60 mmol), thiourea (137 mg, 1.80 mmol), thiophenol (13 µL, 0.12 mmol), TFA (34 µL, 0.30 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (9 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 82:18) as brownish liquid (101.7 µL, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 8.03 (m, 2H), 7.34 (s, 1H), 7.15 (t, *J* = 8.7 Hz, 2H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.9, 168.2, 165.5 (d, *J* = 254.2 Hz), 149.0, 133.7, 132.4 (d, *J* = 9.1 Hz), 129.1, 120.0, 115.5 (d, *J* = 21.9 Hz). ^{19}F NMR (400 MHz, $CDCl_3$): δ -105.5 (s). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_2OSF^+$: 223.0336; found: 223.0347

2-amino-4-(3-fluorophenyl)-6*H*-1,3-thiazin-6-one (12):



Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3-fluorobenzene (100 µL, 0.60 mmol), thiourea (137.0 mg, 1.80 mmol), thiophenol (13 µL, 0.12 mmol), TFA (34 µL, 0.30 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (9 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 80:20) as brownish liquid (91.9 µL , 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.70 (dd, *J* = 9.4, 3.9 Hz, 1H), 7.46 (td, *J* = 8.0, 5.6 Hz, 1H), 7.36 (s, 1H), 7.28 (d, *J* = 13.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.1, 168.0, 162.4 (d, *J* = 247.4 Hz),149.8, 139.7 (d, *J* = 6.6 Hz), 130.0 (d, *J* = 7.7 Hz), 125.5 (d, *J* = 3.0 Hz), 120.6, 119.6, 119.4, 116.7, 116.5. ^{19}F NMR (400 MHz, $CDCl_3$): δ -105.5 (s). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_2OSF^+$: 223.0336; found: 223.0347

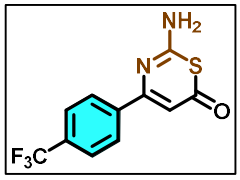
2-amino-4-(2-chlorophenyl)-6*H*-1,3-thiazin-6-one (13):



Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-fluorobenzene (100 µL, 0.54 mmol), thiourea (123.12 mg, 1.62 mmol), thiophenol (12 µL, 0.11 mmol), TFA

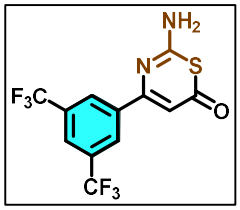
(31 µL, 0.27 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8.1 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 70:30) as white solid (m.p 126-128 °C) (91.2 mg, 71% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.40 (m, 3H), 7.37 – 7.33 (m, 1H), 7.12 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.8, 168.5, 150.4, 138.2, 131.4, 130.2, 129.1, 126.5, 122.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_2OSCl^+$: 239.0040; found: 239.0046

2-amino-4-(4-(trifluoromethyl)phenyl)-6*H*-1,3-thiazin-6-one (14):



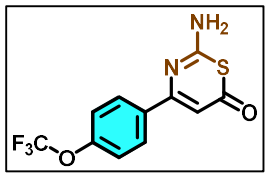
Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-(trifluoromethyl)benzene (100 µL, 0.46 mmol), thiourea (104.9 mg, 1.38 mmol), thiophenol (10 µL, 0.09 mmol), TFA (26 µL, 0.23 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (6.9 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 81:19) as light brown solid (m.p 122-124 °C) (86.3 mg, 69% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.32 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.1, 168.4, 149.0, 140.6, 134.0, 133.7, 133.42, 130.0, 125.4 (q, J = 3.7 Hz), 125.0, 122.3, 121.0. ^{19}F NMR (400 MHz, $CDCl_3$): δ -64.5 (s). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_8N_2OSF_3^+$: 273.0304; found: 273.0317

2-amino-4-(3,5-bis(trifluoromethyl)phenyl)-6*H*-1,3-thiazin-6-one (15):



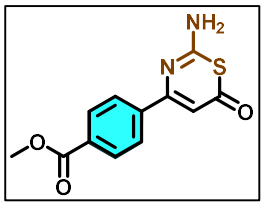
Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-3,5-bis(trifluoromethyl)benzene (100 µL, 0.35 mmol), thiourea (79.8 mg, 1.05 mmol), thiophenol (8 µL, 0.07 mmol), TFA (20 µL, 0.17 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (5.2 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 84:16) as orange brown solid (m.p 148-150 °C) (86.9 mg, 73% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 2H), 8.07 (s, 1H), 7.53 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 183.9, 167.8, 149.2, 139.1, 132.2, 131.9, 131.6, 131.2, 130.2 (d, J = 2.9 Hz), 125.7 (q, J = 3.7 Hz), 124.4, 121.6, 121.1. ^{19}F NMR (400 MHz, $CDCl_3$): δ -62.9 (s). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_7N_2OSF_6^+$: 341.0178; found: 341.0187

2-amino-4-(4-(trifluoromethoxy)phenyl)-6*H*-1,3-thiazin-6-one (16):



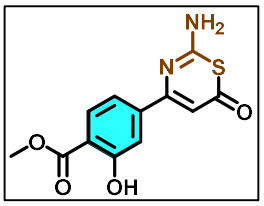
Following the general procedure (**GP3**) the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-(trifluoromethoxy)benzene (100 µL, 0.43 mmol), thiourea (97.58 mg, 1.28 mmol), thiophenol (10 µL, 0.08 mmol), TFA (24 µL, 0.21 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (6.4 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 77:23) as light brownish solid (m.p 125-127 °C) (84.2 mg, 68% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.1 Hz, 2H), 7.39 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 5.57 (br s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.7, 167.4, 152.2, 150.0, 135.9, 131.9, 121.66 (q, J = 5.9 Hz), 121.5. ^{19}F NMR (400 MHz, $CDCl_3$): δ -57.5 (s). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_8N_2O_2SF_3^+$: 289.0253; found: 289.0259

methyl 4-(2-amino-6-oxo-6*H*-1,3-thiazin-4-yl)benzoate (17):



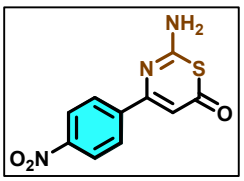
Following the general procedure (**GP3)** the reaction was carried out with methyl 4-(3-chloroprop-1-yn-1-yl)benzoate (100 µL, 0.48 mmol), thiourea (109.44 mg, 1.44 mmol), thiophenol (11µL, 0.10 mmol), TFA (27 µL, 0.24 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (7.2 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 68:32) as yellow solid (m.p 132-134 ^oC) (80.4 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.34 (s, 1H), 3.96 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.0, 166.5, 166.3, 149.6, 141.4, 133.1, 129.4, 121.0, 52.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{11}N_2O_3S^+$: 263.0485; found: 263.0496

methyl 4-(2-amino-6-oxo-6*H*-1,3-thiazin-4-yl)-2-hydroxybenzoate (18):



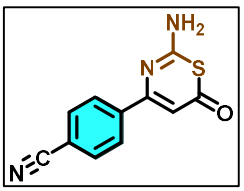
Following the general procedure (**GP3)** the reaction was carried out with methyl 4-(3-chloroprop-1-yn-1-yl)-2-hydroxybenzoate (100 µL, 0.45 mmol), thiourea (102.6 mg, 1.35 mmol), thiophenol (10 µL, 0.09 mmol), TFA (26 µL, 0.22 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (6.7 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 68:32) as yellow solid (m.p 168-170 ^oC) (76.3 mg, 61% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 8.2, 3.8 Hz, 1H), 7.41 (d, *J* = 5.3 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.24 (d, *J* = 3.8 Hz, 1H), 3.93 (d, *J* = 4.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.5, 169.9, 168.7, 160.8, 148.9, 143.8, 130.1, 121.4, 119.5, 118.4, 115.0, 52.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{12}H_{11}N_2O_4S^+$: 279.0434; found: 279.0443

2-amino-4-(4-nitrophenyl)-6*H*-1,3-thiazin-6-one(19):



Following the general procedure (**GP3)** the reaction was carried out with 1-(3-chloroprop-1-yn-1-yl)-4-nitrobenzene (100 µL, 0.51 mmol), thiourea (116.9 mg, 1.54 mmol), thiophenol (11 µL, 0.10 mmol), TFA (30 µL, 0.26 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (7.7 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 68:32) as yellow solid (m.p 173-175 ^oC) (73.6 mg, 58% yield). ^1H NMR (400 MHz, DMSO): δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 8.3 Hz, 2H), 7.62 (s, 1H), 7.37 (br s, 2H, NH_2). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO): δ 185.8, 168.9, 149.7, 149.6 143.6, 131.2, 123.7, 121.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_3O_3S^+$: 250.0281; found: 250.0279

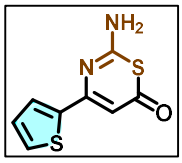
4-(2-amino-6-oxo-6*H*-1,3-thiazin-4-yl)benzonitrile (20):



Following the general procedure (**GP3)** the reaction was carried out with 4-(3-chloroprop-1-yn-1-yl)benzonitrile (100 µL, 0.57 mmol), thiourea (130 mg, 1.71 mmol), thiophenol (10 µL, 0.11mmol), TFA (32 µL, 0.28 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (8.5 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 68:32) as yellow solid (m.p 177-179 ^oC) (70.48 mg, 54% yield). ^1H NMR

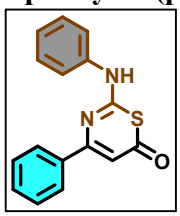
(400 MHz, DMSO): δ 8.24 (d, J = 8.6 Hz, 2H), 8.08 (d, J = 8.6 Hz, 2H), 7.55 (s, 1H), 7.36 (br s, 2H, NH_2).$^{13}C\{^1H\}$(100 MHz, DMSO): δ 190.5, 173.6, 154.2, 146.7, 137.4, 135.3, 125.6, 123.5, 119.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_8N_3O_3S^+$: 250.0281; found: 250.0279

2-amino-4-(thiophen-2-yl)-6*H*-1,3-thiazin-6-one (21):



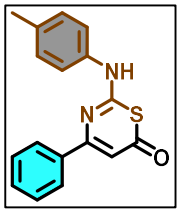
Following the general procedure (**GP3)** the reaction was carried out with 2-(3-chloroprop-1-yn-1-yl)thiophene (100 µL, 0.64 mmol), thiourea (145.9 mg, 1.92 mmol), thiophenol (14 µL, 0.13 mmol), TFA (37 µL, 0.32 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (9.6 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 74:26) as blackish solid (m.p 141-143 °C) (90 mg, 67% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.34 (dd, J = 3.8, 1.2 Hz, 1H), 7.69 (dd, J = 5.0, 1.2 Hz, 1H), 7.57 (s, 1H), 7.17 (dd, J = 4.9, 3.8 Hz, 1H), 5.36 (br s, 2H, NH_2). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.0, 167.0, 149.9, 142.6, 135.5, 134.7, 127.9, 118.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_8H_7N_2OS_2^+$: 210.9994; found: 211.0005

4-phenyl-2-(phenylamino)-6*H*-1,3-thiazin-6-one (22):



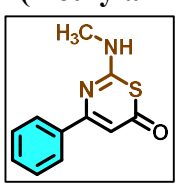
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), N-phenylthiourea (305.9 mg, 2.01 mmol), thiophenol (15 µL, 0.13 mmol), TFA (38 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 90:10) as brownish solid (m.p 135-137 °C) (136.9 mg, 73% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.6 Hz, 2H), 7.86 (br s, 1H, NH), 7.59 (t, J = 7.4 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.40 – 7.34 (m, 4H), 7.15 – 7.09 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.5, 165.0, 150.3, 139.8, 137.6, 132.7, 130.0, 129.7, 128.2, 123.9, 119.0, 118.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{13}N_2OS^+$: 281.0743; found: 281.0752

4-phenyl-2-(p-tolylamino)-6*H*-1,3-thiazin-6-one (23):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), N-(p-tolyl)thiourea (334.06 mg, 2.01 mmol), thiophenol (15 µL, 0.13 mmol), TFA (38 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 93:07) as brown solid (m.p 147-149 °C) (139.8 mg, 71% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, J = 8.4, 1.3 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 7.40 (s, 1H), 7.23 – 7.19 (m, 2H), 7.14 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.5, 166.2, 150.4, 137.7, 137.5, 133.9, 132.6, 130.1, 130.0, 128.2 119.9, 118.4 , 20.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{15}N_2OS^+$: 295.0900; found: 295.0909

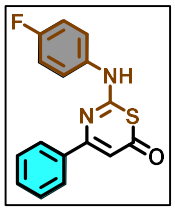
2-(methylamino)-4-phenyl-6*H*-1,3-thiazin-6-one (24):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), N-methylthiourea (180.9 mg, 2.01 mmol), thiophenol (15 µL, 0.13 mmol), TFA (38. µL,

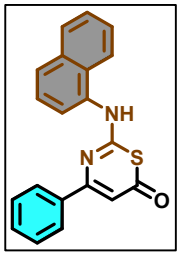
0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 89:11) as blackish solid (m.p 156-158 ^oC) (100.8 mg, 69% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J*=8.3, 1.3 Hz, 2H), 7.88 (br s, 1H, NH), 7.61 – 7.57 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.22 (s, 1H), 3.03 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 188.0, 171.7, 150.8, 138.1, 132.3, 129.6, 128.3, 118.2, 32.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{11}H_{11}N_2OS^+$: 219.0587 found: 219.0594

2-((4-fluorophenyl)amino)-4-phenyl-6*H*-1,3-thiazin-6-one (25):



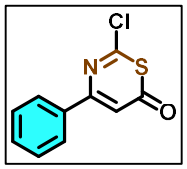
Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.67 mmol), N-(4-fluorophenyl)thiourea (341.7 mg, 2.01 mmol thiophenol (15 µL, 0.13 mmol), TFA (38 µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 89:11) as blackish viscous liquid (131.8 µL, 66% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.36 (s, 1H), 7.28 (dd, *J* = 4.5, 2.3 Hz, 2H), 7.01 (dd, *J* = 14.6, 6.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.3, 166.6, 159.5 (d, *J* = 243.7 Hz), 150.0, 137.5, 136.2, 132.7, 129.9, 128.3, 122.1 (d, *J* = 8.0 Hz), 118.6, 116.3 (d, *J* = 22.7 Hz). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{12}N_2OSF^+$: 299.0649 found: 299.0655

2-(naphthalen-1-ylamino)-4-phenyl-6*H*-1,3-thiazin-6-one (26):



Following the general procedure (**GP3)** the reaction was carried out with (3-chloroprop-1-yn-1-yl)benzene (100 µL, 0.66 mmol), N-naphthylthiourea (406.18 mg, 2.01 mmol), thiophenol (15 µL, 0.13 mmol), TFA (38. µL, 0.33 mmol), $[Ru(bpy)_3]Cl_2.6H_2O$ (10 mg, 2 mol%) and purified by column chromatography (hexane/ethyl acetate = 92:08) as blackish viscous liquid (139.3 µL, 63% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.77 (dd, *J* = 13.8, 7.8 Hz, 3H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.14 (t, *J* = 2.2 Hz, 1H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 187.0, 169.2, 149.3, 137.4, 136.0, 134.6, 132.6, 129.7, 128.6, 128.3, 126.8, 125.8, 121.8, 120.5, 118.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{20}H_{15}N_2OS^+$: 331.0900 found: 331.0910

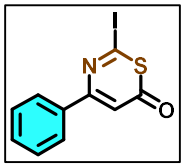
Synthesis of 2-chloro-4-phenyl-6*H*-1,3-thiazin-6-one (27)



2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (50 µL, 0.33 mmol, 1 equiv.) was introduced into a 50 ml round-bottom flask, followed by the addition of concentrated H_2SO_4 (65 µL, 0.66 mmol, 2 equiv.) and sodium nitrite (22.7 mg, 0.33 mmol, 1 equiv.) in water at 0 °C. The resulting diazonium salt of compound **3** at 0 °C was then subjected to continuous stirring with the addition of CuCl (44.3 mg, 0.33 mmol, 1 equiv.) for one hour at room temperature. 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 column chromatography using (hexane/ethyl acetate 97:03) as a

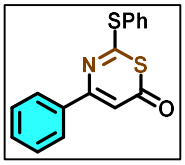
yellow liquid(67 µL, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (dd, *J*= 8.3, 1.1 Hz, 2H), 8.15 (s, 1H), 7.61 (m, 1H), 7.51 (t, *J*= 7.6 Hz, 2H).^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.7, 152.7, 151.8, 136.5, 133.3, 130.5, 129.6, 128.4. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_7NOSCl^+$: 223.9931, found: 223.9934

Synthesis of 2-iodo-4-phenyl-6*H*-1,3-thiazin-6-one (28)



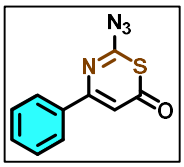
2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (50 µL, 0.33 mmol, 1 equiv.) was introduced into a 50 ml round-bottom flask, followed by the addition of concentrated H_2SO_4 (65 µL, 0.66 mmol, 2 equiv.) and sodium nitrite (22.7 mg, 0.33 mmol, 1 equiv.) in water at 0 °C. The resulting diazonium salt of compound **3** at 0 °C was then subjected to continuous stirring with the addition of KI (54.7 mg, 0.33 mmol, 1 equiv.) for one hour at room temperature. 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 column chromatography using (hexane/ethyl acetate 98:02) as a white powdery solid (m.p 137-139 °C) (91.47 mg , 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 2.3 Hz, 2H), 8.08 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 185.4, 156.4, 136.6, 134.0, 133.3, 130.5, 128.4, 100.6. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_7NOSI^+$: 315.9288 found: 315.9286

Synthesis of 4-phenyl-2-(phenylthio)-6*H*-1,3-thiazin-6-one (29)



2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (50 µL, 0.33 mmol, 1 equiv.) was introduced into a 50 ml round-bottom flask, followed by the addition of concentrated H_2SO_4 (65 µL, 0.66 mmol, 2 equiv.) and sodium nitrite (22.7 mg, 0.33 mmol, 1 equiv.) in water at 0 °C. The resulting diazonium salt of compound **3** at 0 °C was then subjected to continuous stirring with the addition of thiophenol (36 µL, 0.33 mmol, 1 equiv.) for 2 hours at room temperature. 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 column chromatography using (hexane/ethyl acetate 97:03) as a viscous liquid (80.37 µL, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.2 Hz 2H), 7.95 (s, 1H), 7.60 (dd, *J* = 7.1, 1.6 Hz, 2H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.38 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 186.5, 168.0, 154.8, 137.0, 134.8, 133.0, 130.6, 130.5, 130.3, 130.1, 128.7, 128.2. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{16}H_{12}NOS_2^+$: 298.0355 found: 298.0389

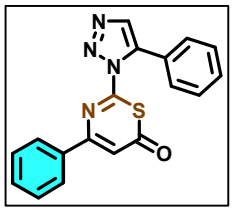
Synthesis of 2-azido-4-phenyl-6*H*-1,3-thiazin-6-one (30)



2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (50 µL, 0.33 mmol, 1 equiv.) was introduced into a 50 ml round-bottom flask, followed by the addition of concentrated H_2SO_4 (65.2 µL, 0.66 mmol, 2 equiv.) and sodium nitrite (22.7 mg, 0.33 mmol, 1 equiv.) in water at 0 °C. The

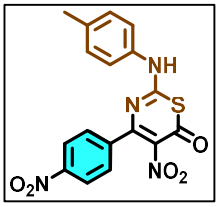
resulting diazonium salt of compound **3** at 0 °C was then subjected to continuous stirring with the addition of sodium azide (21.45 mg, 0.33 mmol, 1equiv.) for 30 minutes at room temperature. After the completion of the reaction, as monitored by TLC, the reaction mixture was extracted with ethyl acetate 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 column chromatography using (hexane/ethyl acetate 97:03) as a viscous liquid (69.8 µL, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 2H), 7.80 (s, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.1 (s), 162.7 (s), 151.4 (s), 136.8 (s), 133.1 (s), 130.4 (s), 128.3 (s), 125.0 (s). HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{10}H_7N_4OS^+$: 231.0355 found: 231.0338

Synthesis of 4-phenyl-2-(5-phenyl-1*H*-1,2,3-triazol-1-yl)-6*H*-1,3-thiazin-6-one (31)



2-azido-4-phenyl-6*H*-1,3-thiazin-6-one (50 µL, 0.22 mmol, 1 equiv.) was subjected to click reaction with phenylacetylene (22 µL ,0.217 mmol, 1 equiv), CuI (7.6 mg ,0.04 mmol, 0.2 equiv.), DIPEA (1 µL ,0.0087 mmol, 0.04 equiv.), AcOH (0.5 µL ,0.0087 mmol, 0.04 equiv.) in DCM for 1 hour. 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 column chromatography using (hexane/ethyl acetate 87:13) as a white solid (m.p 143-145 °C) (69.16 mg , 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.07 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.04 (s, 1H), 7.85 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.58 (m, 1H), 7.47 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 186.4, 156.8, 151.5, 148.9, 136.7, 133.3, 130.3, 129.1, 128.5, 126.6, 126.1, 117.1. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{13}N_4OS^+$: 333.0805 found: 333.0809.

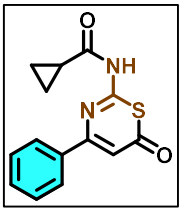
Synthesis of 5-nitro-4-(4-nitrophenyl)-2-(p-tolylamino)-6*H*-1,3-thiazin-6-one (32)



4-phenyl-2-(p-tolylamino)-6*H*-1,3-thiazin-6-one (50 mg, 0.17 mmol, 1 equiv.) was introduced into a 50 ml round-bottom flask, followed by the addition of concentrated H_2SO_4 (33 µL, 0.34 mmol, 2 equiv.) and sodium nitrite (19 mg, 0.17 mmol. 2 equiv.) in water at 0 °C. The resulting diazonium salt of compound **3** at 0 °C was then subjected to continuous stirring for 40 minutes at room temperature. 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 column chromatography using (hexane/ethyl acetate 91:09) as a yellow solid (m.p 192-194 °C) (49.6 mg, 76% yield). ^{1}H NMR (400 MHz, DMSO): δ 11.58 (br s, 1H, NH), 7.88 (d, *J* = 8.2 Hz, 3H), 7.79 – 7.73 (m, 2H), 7.59 (t, *J* = 7.8 Hz, 3H), 2.36 (s, 3H).

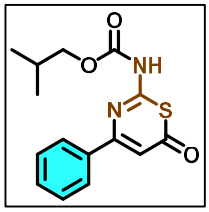
$^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO): δ 194.4, 172.9, 157.9, 146.9, 142.2, 140.5, 140.3, 139.1, 134.5,134.1 131.0, 130.7, 25.3 . HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{17}H_{13}N_4O_5S$: 385.0607 found: 385.0641.

Synthesis of N-(6-oxo-4-phenyl-6*H*-1,3-thiazin-2-yl)cyclopropanecarboxamide (33)



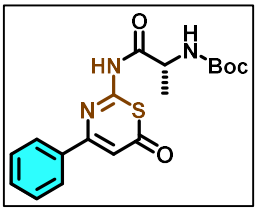
Cyclopropane carboxylic acid (50 mg, 0.58 mmol, 1 equiv.) was first treated with oxalyl chloride (147 µL, 1.16 mmol, 2 equiv.) at 0 °C to yield the corresponding acid chloride. Subsequently, this acid chloride was further reacted with 2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (118 µL, 0.58 mmol, 1 equiv.) in presence of triethylamine (117 µL,1.16 mmol, 2 equiv.) and the resulting reaction was subjected to continuous stirring for 2 hours at room temperature. 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 column chromatography using (hexane/ethyl acetate 97:03) as a viscous liquid (132.5 µL, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.85 (br s, 1H, NH), 7.89 (d, *J* = 7.1 Hz, 2H), 7.64 (s, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 1.63-1.57 (m, 1H), 1.09 – 1.04 (m, 2H), 0.85 (td, *J* = 7.4, 4.1 Hz, 2H).$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 187.6, 172.8, 159.1, 147.8, 137.4, 132.9, 129.8, 128.4), 124.2, 14.87, 9.5. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{14}H_{13}N_2O_2S^+$: 273.0692 found: 273.0688.

Synthesis of Isobutyl (6-oxo-4-phenyl-6*H*-1,3-thiazin-2-yl)carbamate (34)



2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (50 µL, 0.33 mmol, 1 equiv.) when treated with isobutyl chloroformate (45 µL, 0.33 mmol, 1 equiv.) in the presence of NMM (100µL, 0.99 mmol, 3 equiv.), followed by continuous stirring for 2 hours at room temperature. 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 column chromatography using (hexane/ethyl acetate 96:04) as a viscous liquid (77.27 µL, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.48 (br s, 1H, NH), 7.94 (d, *J* = 7.1 Hz, 2H), 7.67 (s, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 3.88 (d, *J* = 6.7 Hz, 2H), 1.84 (m, 1H), 0.82 (d, *J* = 6.7 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 187.2, 160.0, 153.6, 148.9, 137.4, 132.8, 130.0, 128.2, 123.3, 72.7, 27.8, 18.9. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{15}H_{17}N_2O_3S^+$: 305.0960, found: 305.0968.

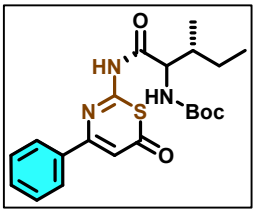
Synthesis of tert-butyl (R)-(1-oxo-1-((6-oxo-4-phenyl-6*H*-1,3-thiazin-2-yl)amino)propan-2-yl)carbamate (35)



To a cooled (0 °C) solution of Boc-l-Alanine (50 mg, 0.26 mmol, 1 equiv.), EDC.HCl (49.8 mg, 0.26 mmol, 1 equiv.), HOBt (35.13 mg, 0.26 mmol, 1 equiv.) and DIPEA (134 µL, 1.04 mmol, 4 equiv.) in dry DCM was added 2-amino-4-phenyl-6*H*-1,3-thiazin-

6-one (53 µL, 0.26 mmol, 1 equiv.) under dry conditions with continuous stirring for 24 hours at room temperature. 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 column chromatography using (hexane/ethyl acetate = 92:08) as a yellowish viscous liquid (65.3 µL, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.02 (br s, 1H, NH), 7.97 (d, *J* = 7.5 Hz, 2H), 7.73 (s, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 5.33 (br s, 1H, NH), 4.58 (s, 1H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.45 (s, 9H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.7, 172.1, 158.4, 155.6, 148.3, 137.4, 132.8, 129.9, 128.4, 124.3, 80.7, 50.5, 28.3, 18.0. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{22}N_3O_4S^+$: 376.1326, found: 376.1331.

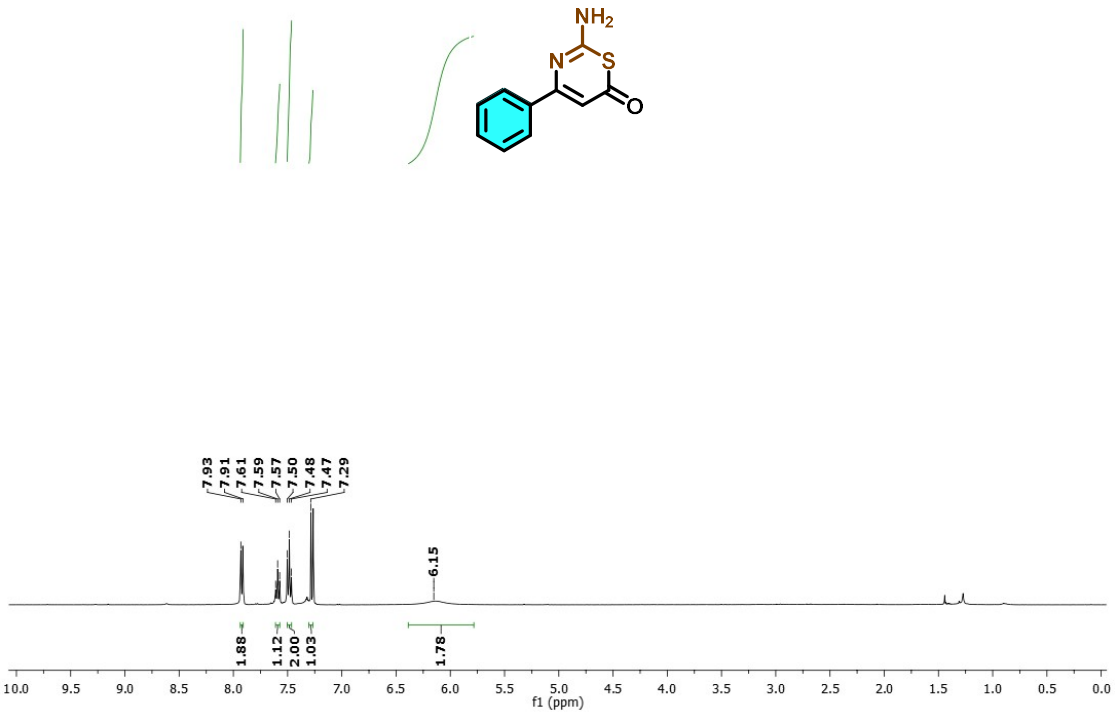
Synthesis of tert-butyl ((3R)-3-methyl-1-oxo-1-((6-oxo-4-phenyl-6*H*-1,3-thiazin-2-yl)amino)pentan-2-yl)carbamate (36)



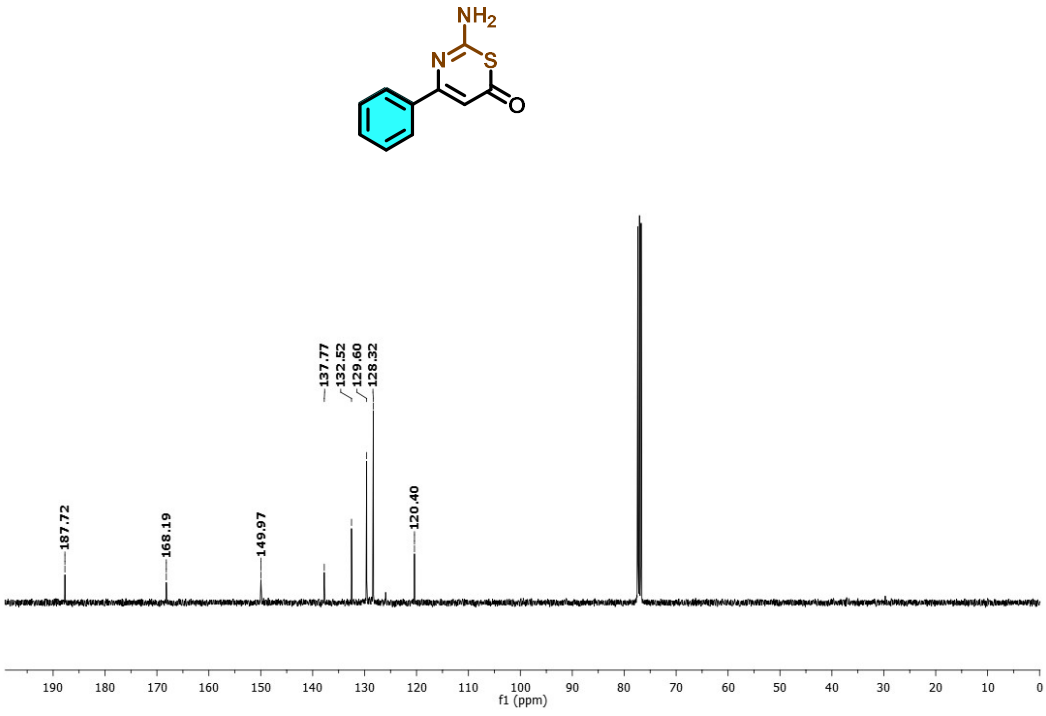
To a cooled (0 °C) solution of Boc-l-isoleucine (50 mg, 0.21 mmol, 1 equiv.), EDC.HCl (40.2 mg, 0.21 mmol, 1 equiv.), HOBt (28.4 mg, 0.21 mmol, 1 equiv.) and DIPEA (108 µL, 0.84 mmol, 4 equiv.) in dry DCM was added 2-amino-4-phenyl-6*H*-1,3-thiazin-6-one (43 µL, 0.21 mmol, 1 equiv.) under dry conditions with continuous stirring for 24 hours at room temperature. 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 column chromatography using (hexane/ethyl acetate = 92:08) as a yellowish viscous liquid (61.33 µL, 70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.56 (br s, 1H, nh), 7.93 (d, *J* = 7.2 Hz, 2H), 7.66 (s, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 5.14 (br s, 1H, NH), 4.32 (s, 1H), 2.00 – 1.94 (m, 1H), 1.50 – 1.41 (m, 2H), 1.36 (s, 9H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 187.6, 171.0, 157.6, 156.0, 148.6, 137.5, 132.7, 130.0, 128.3, 124.1, 80.8, 59.4, 37.1, 28.3, 24.8, 15.6, 11.3. HRMS (ESI) (m/z): $[M+H]^+$ calculated for $C_{18}H_{22}N_3O_4S^+$: 418.1795, found: 418.1798.

9. NMR Spectra:

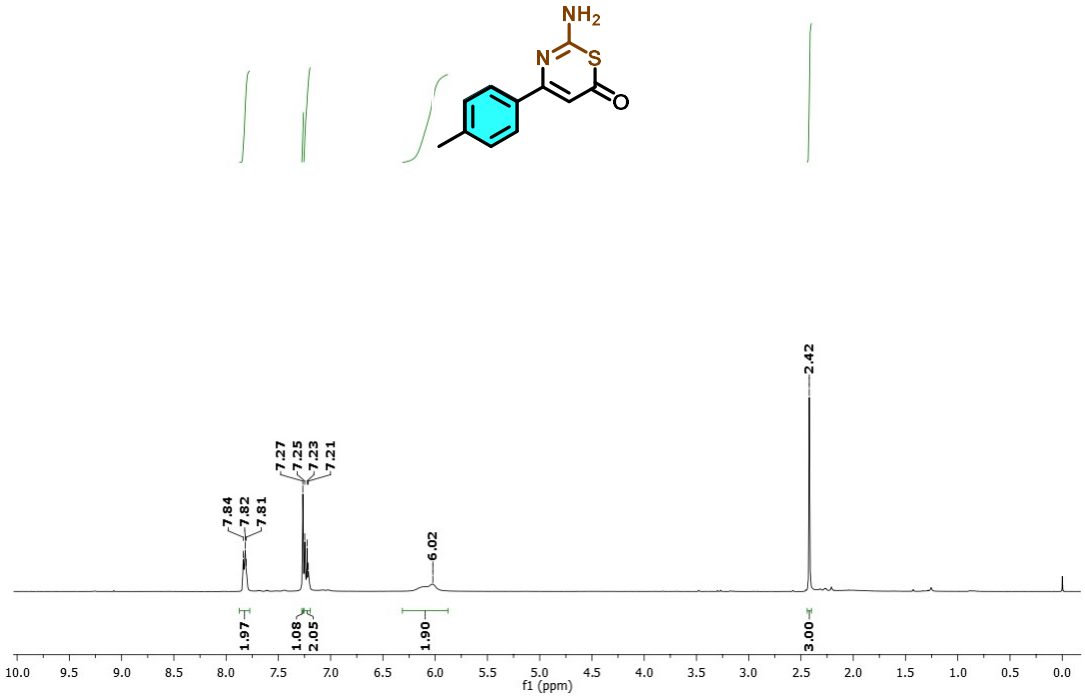
^{1}H-NMR (400 MHz, $CDCl_3$) of Compound **3**



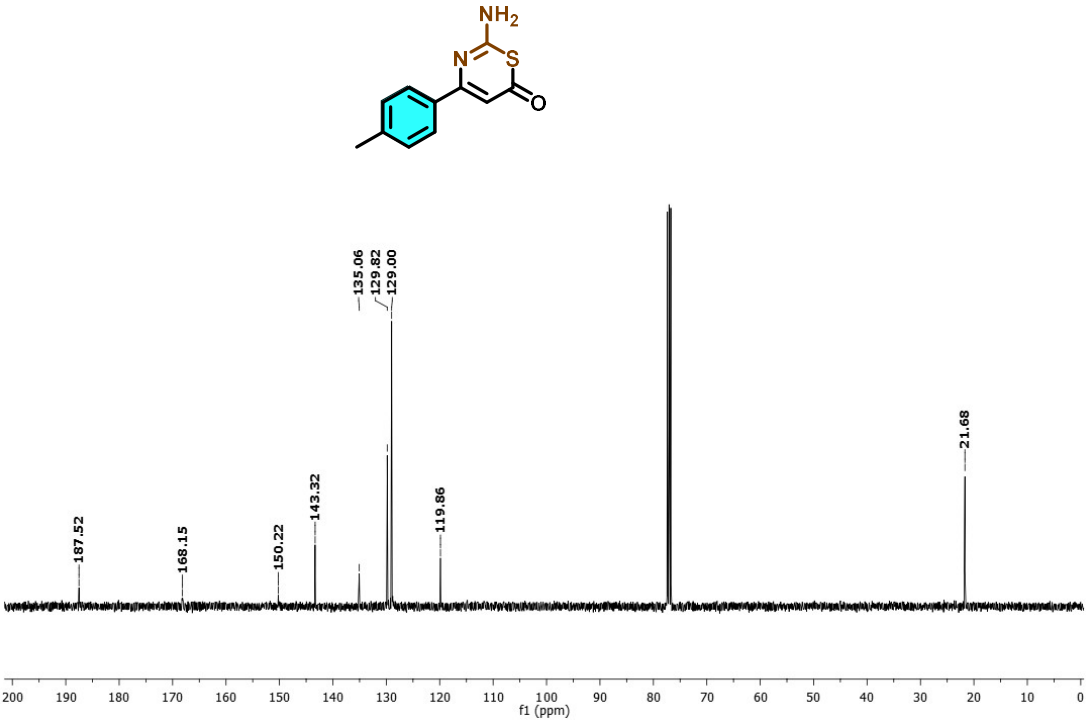
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) of Compound **3**



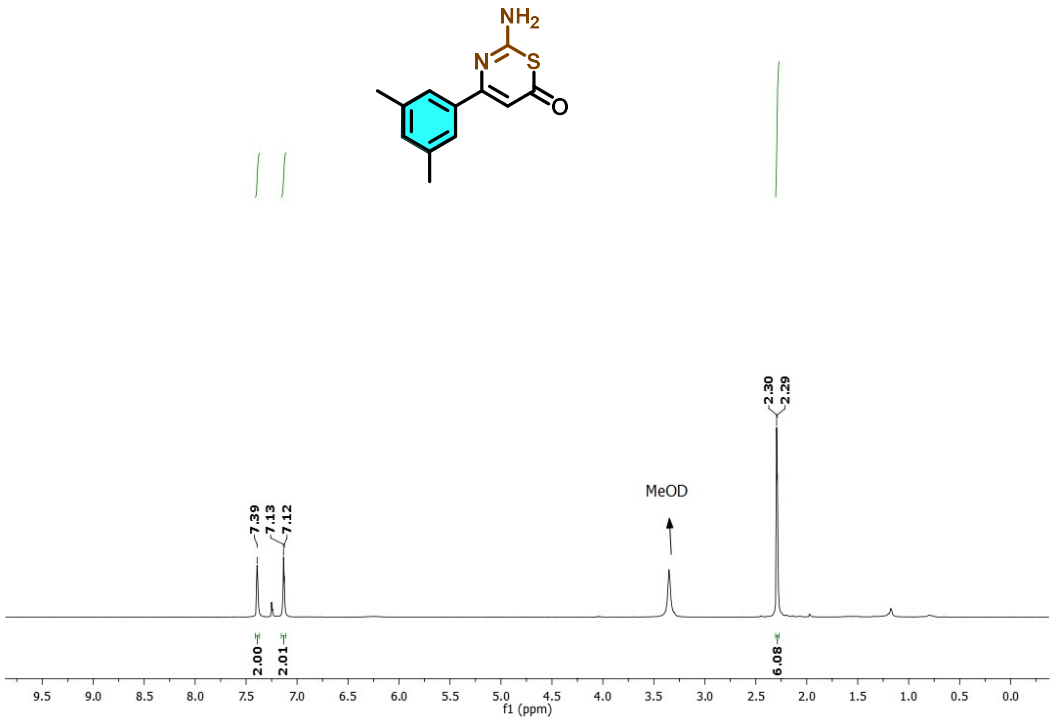
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **4**



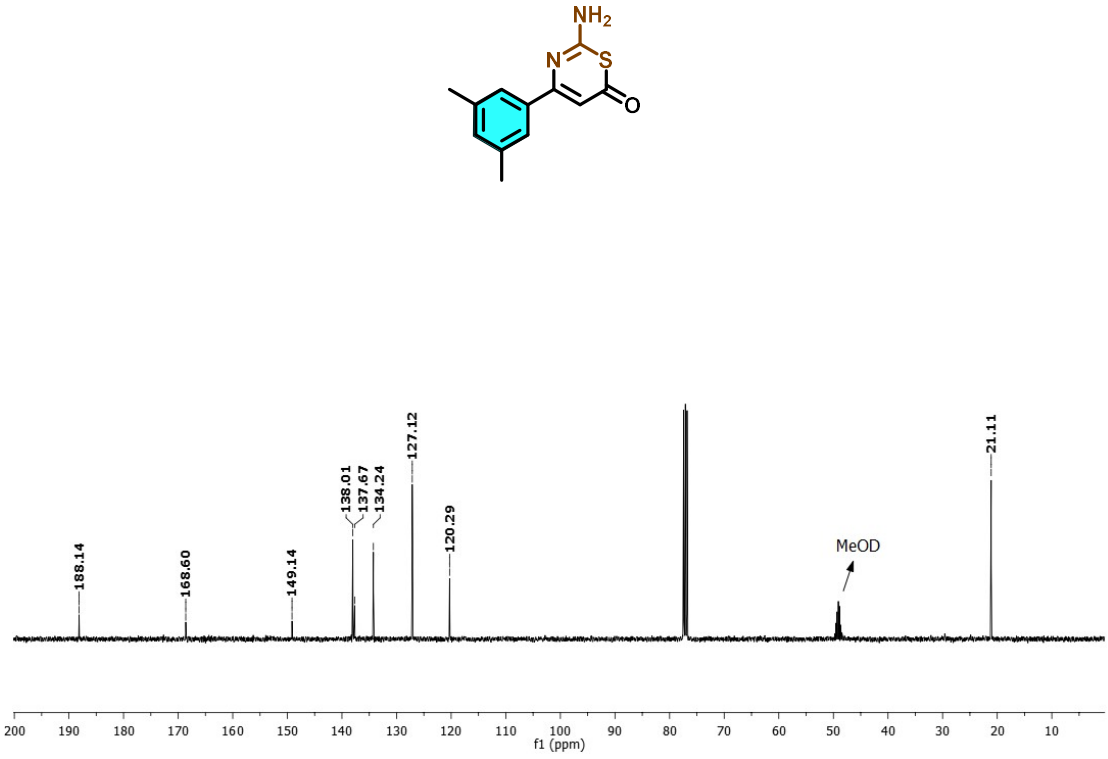
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **4**



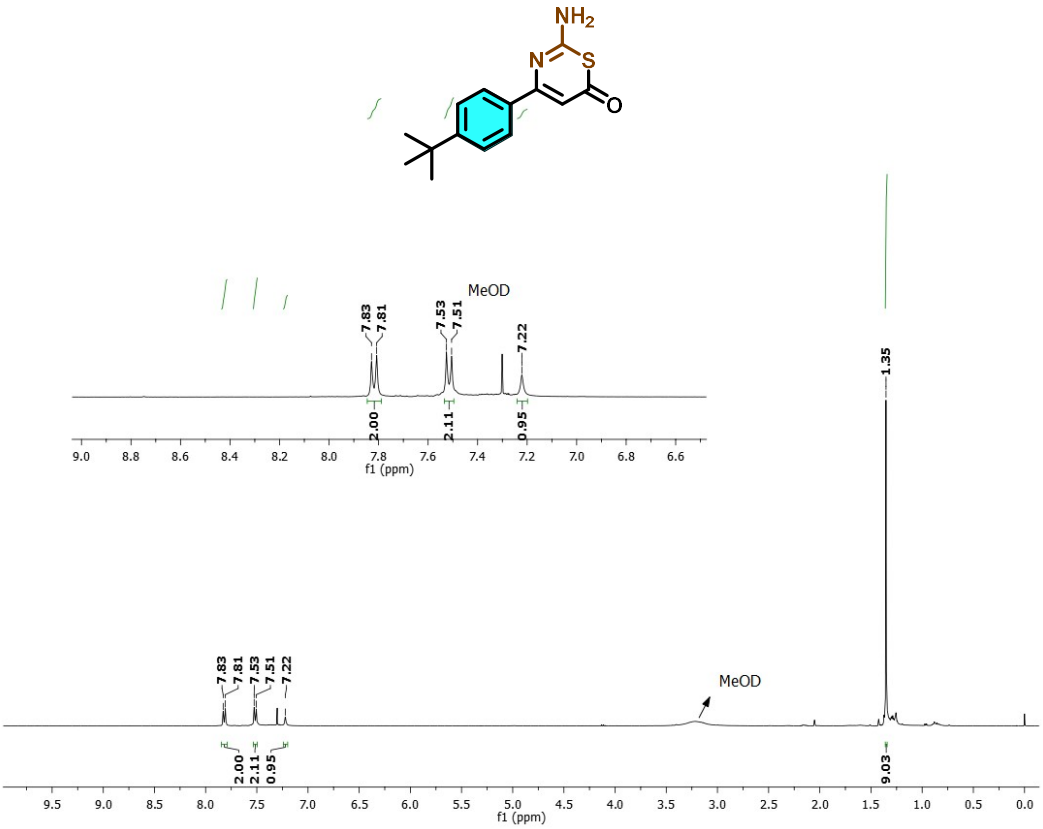
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **5**



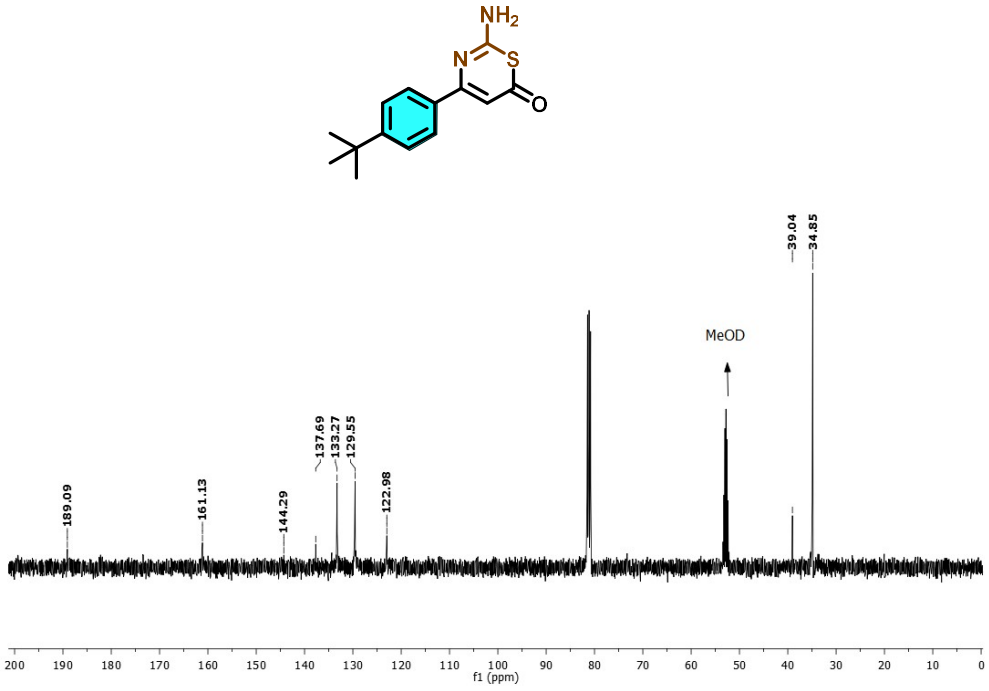
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **5**



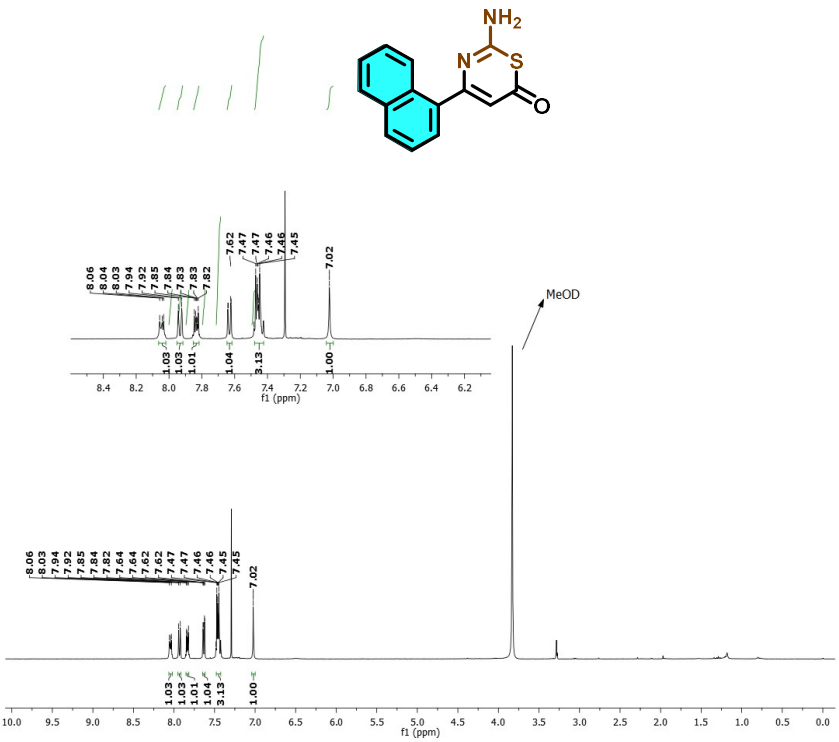
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **6**



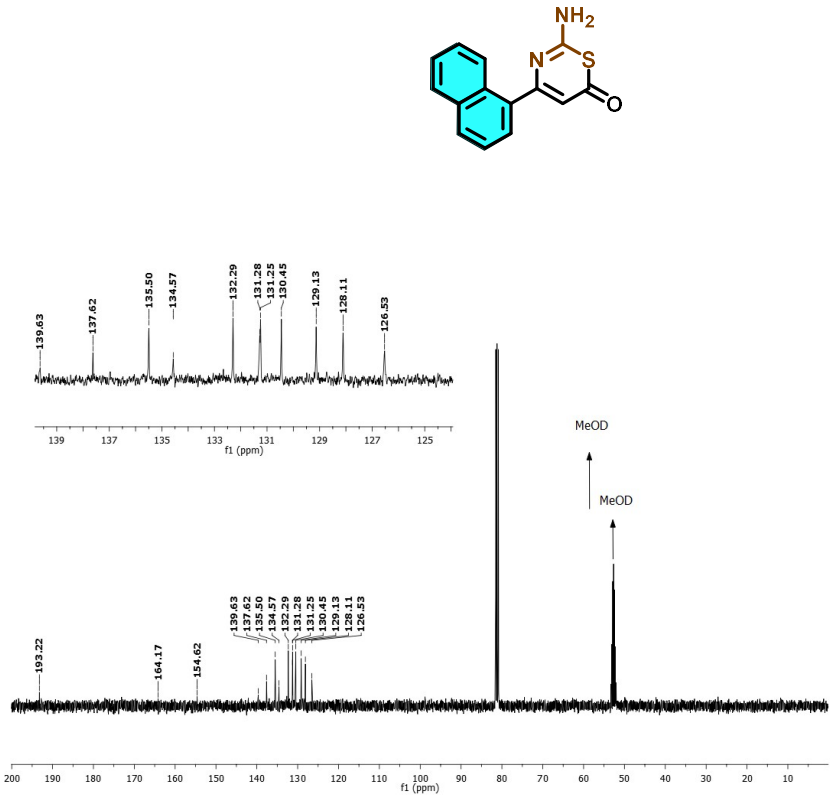
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **6**



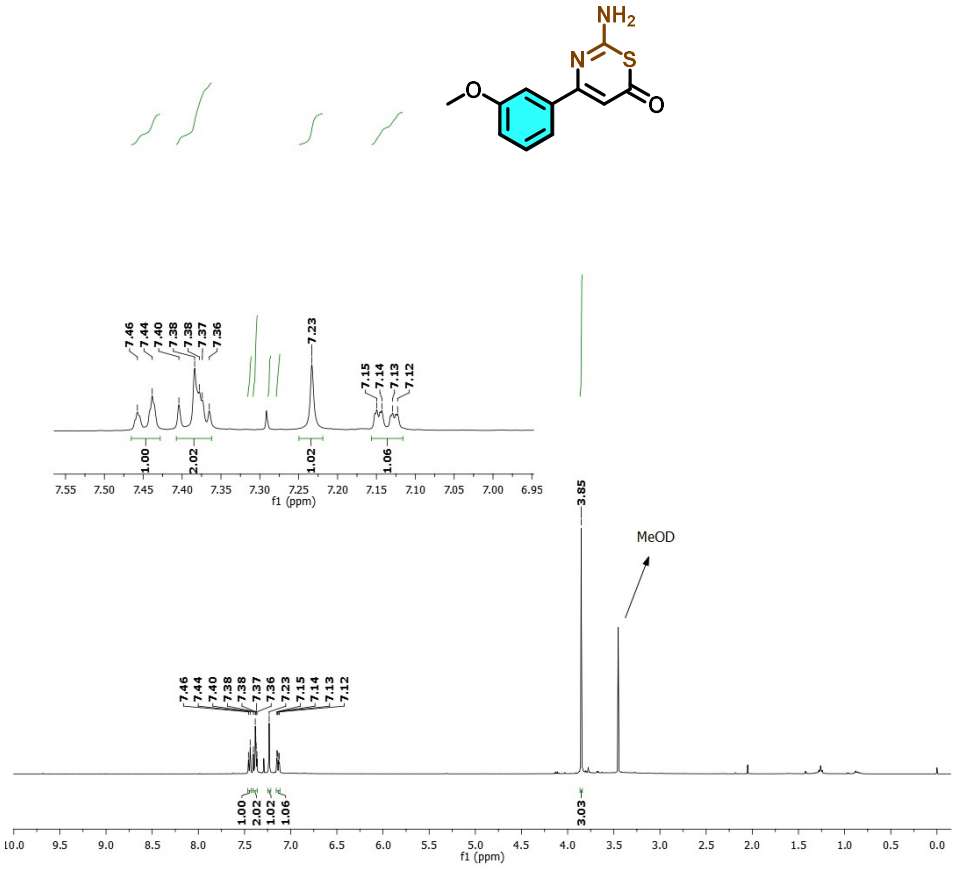
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **7**



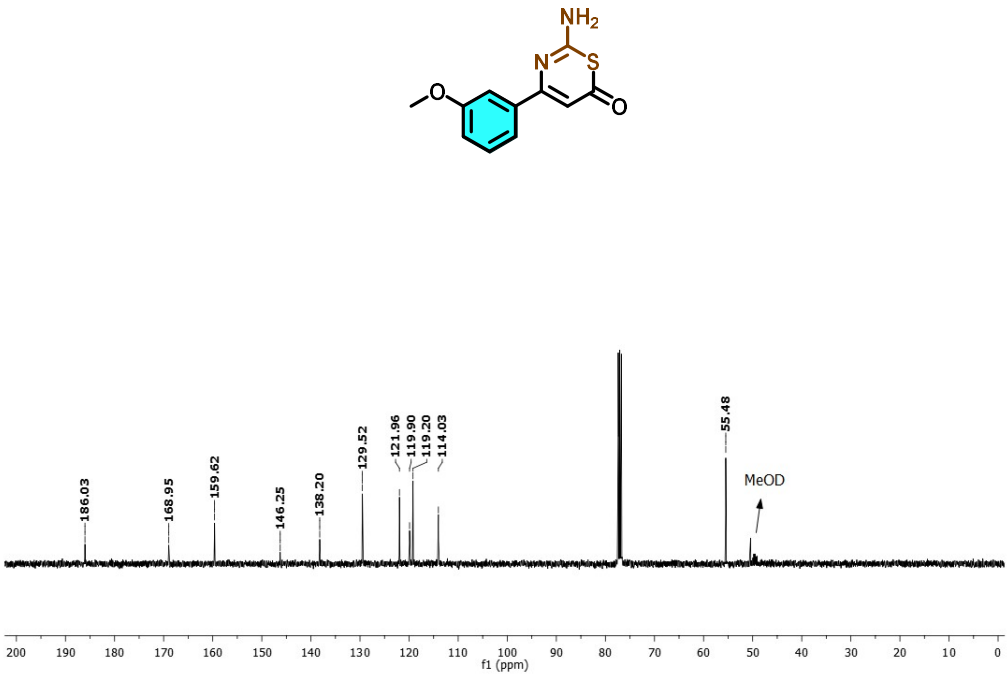
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) of Compound **7**



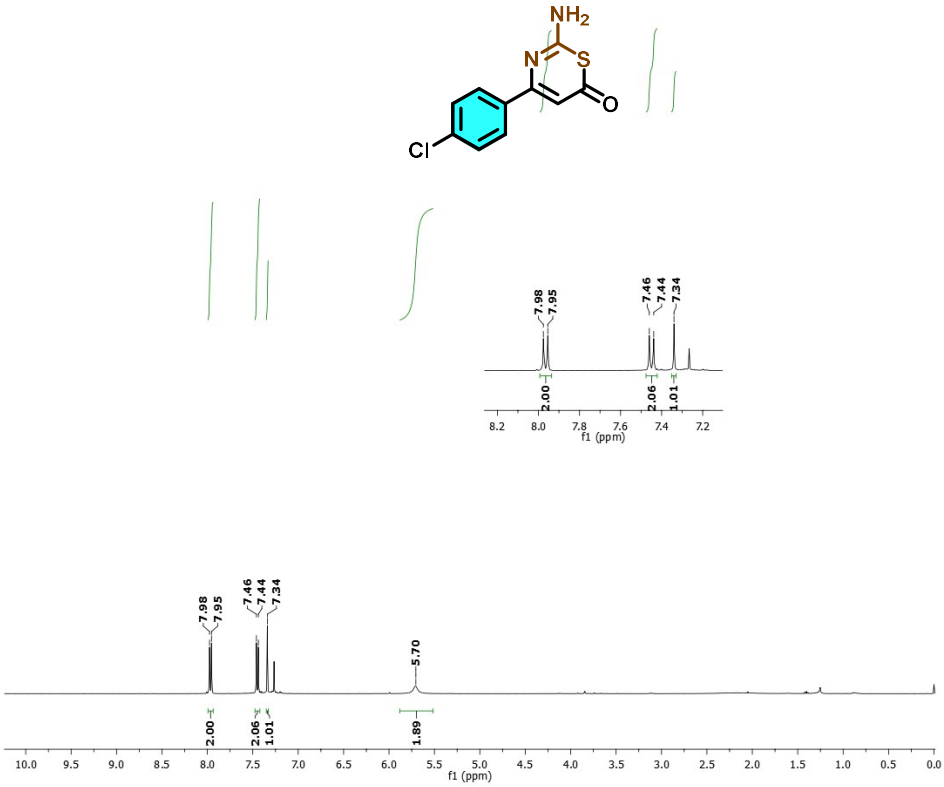
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **8**



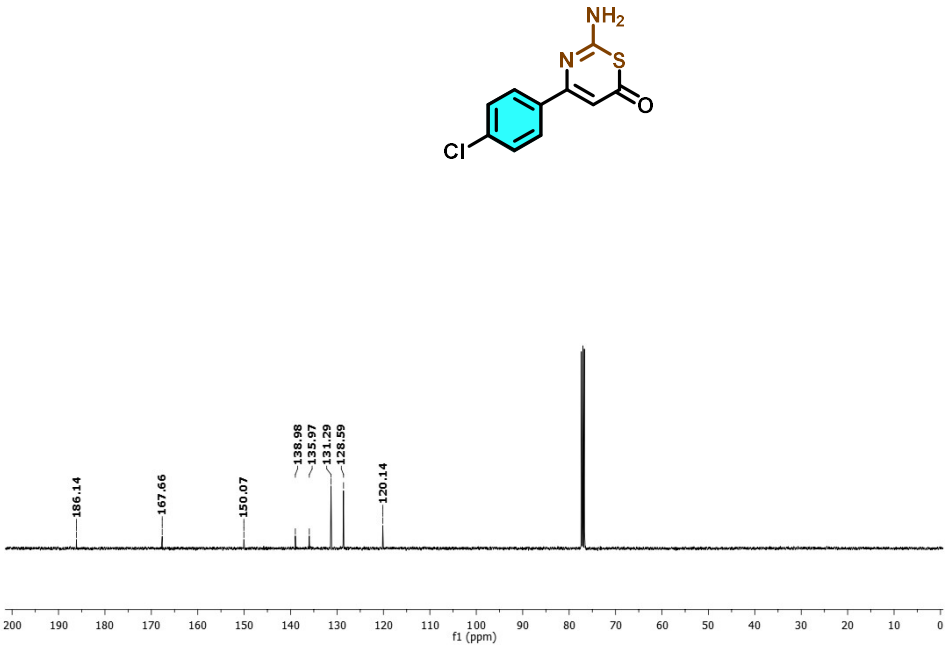
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **8**



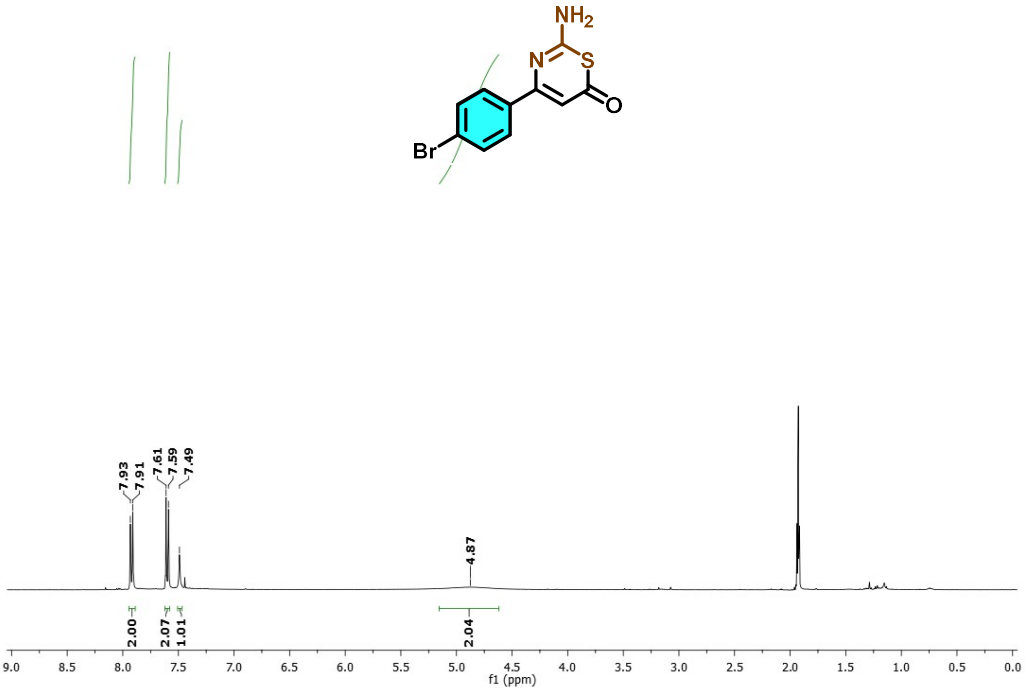
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **9**



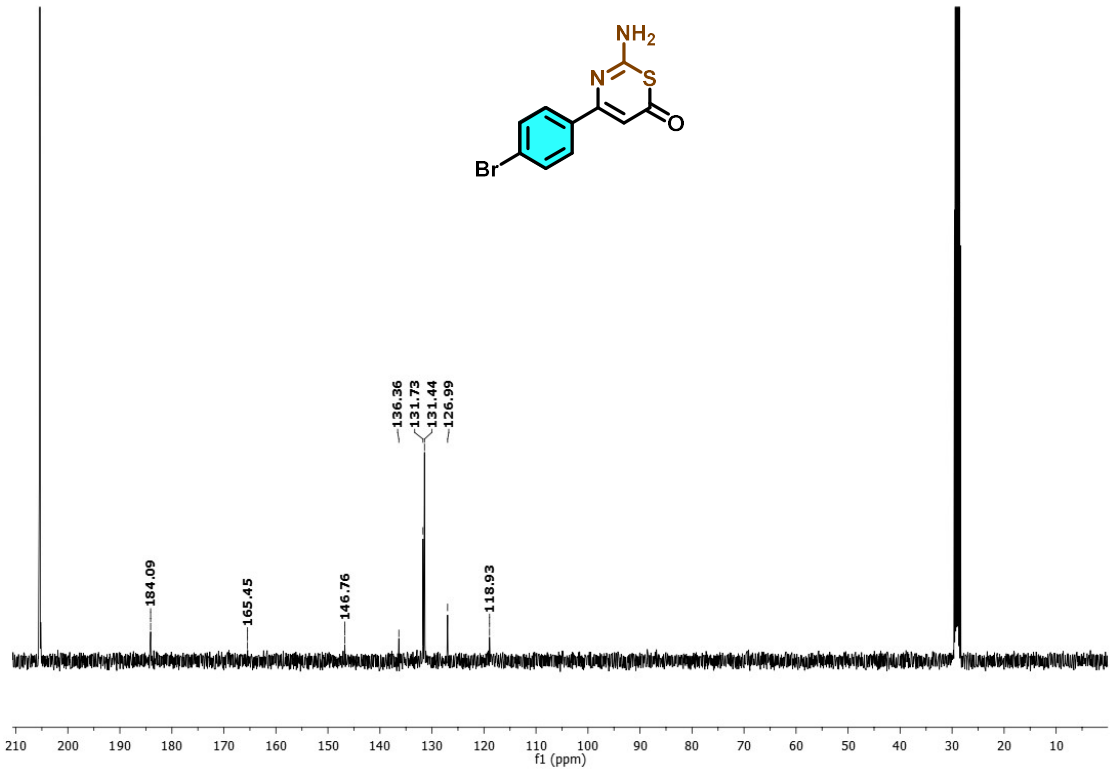
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **9**



^{1}H-NMR (400 MHz, Acetone-D_6) spectrum of Compound **10**

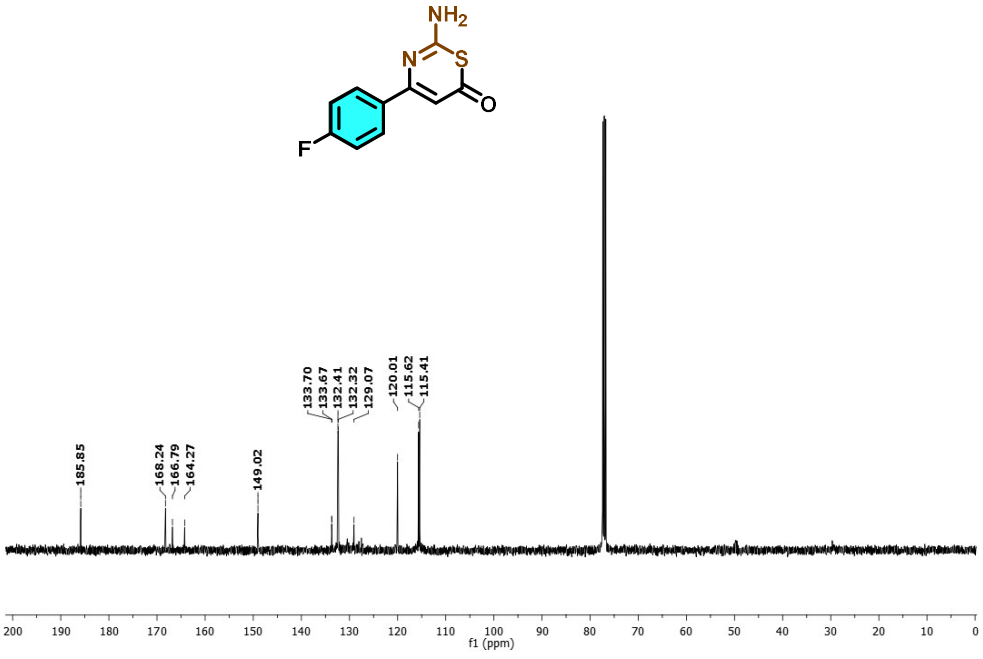


^{13}C{^{1}H}-NMR (100 MHz, Acetone-D_6) spectrum of Compound **10**

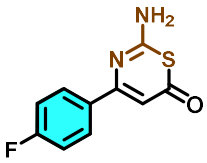


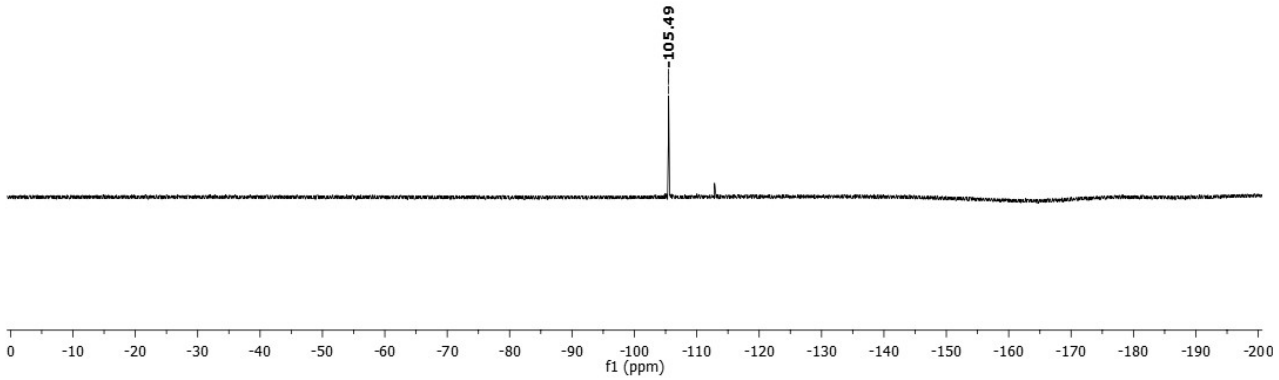
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **11**

^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **11**

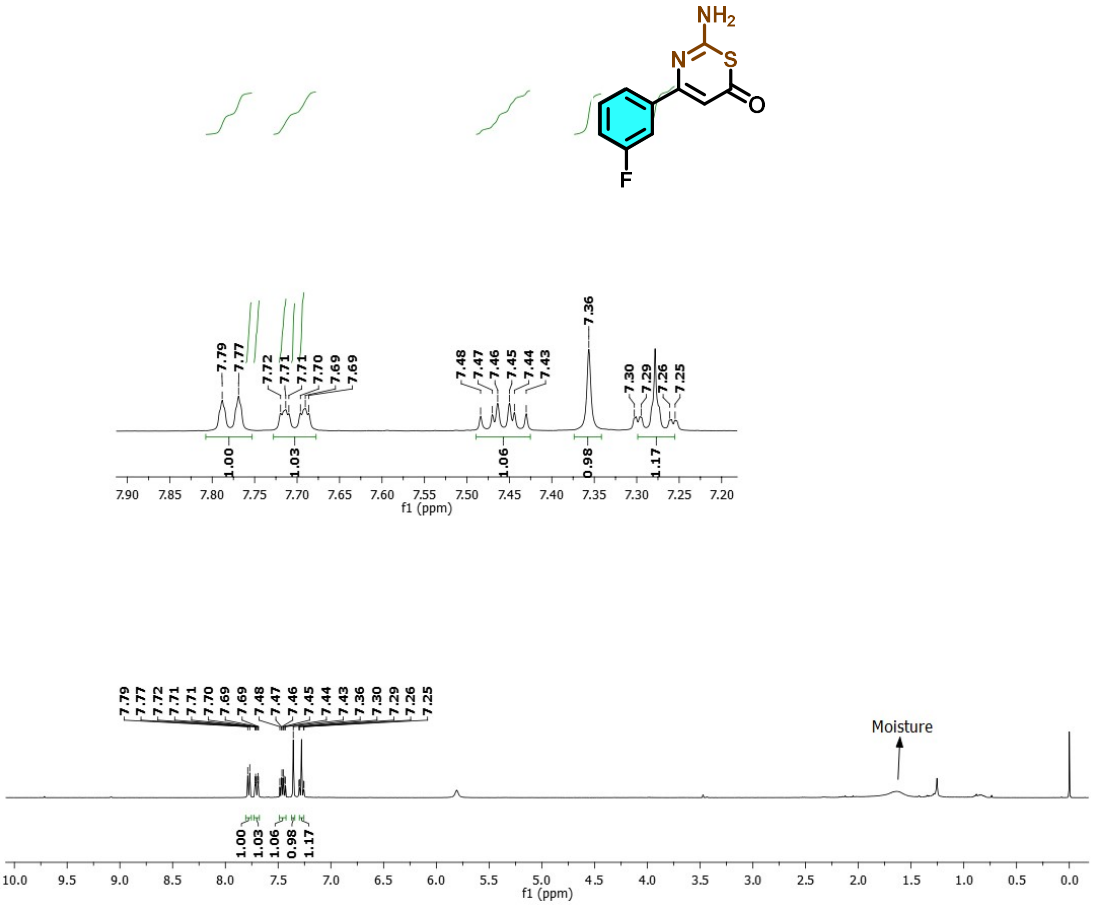


^{19}F-NMR (400 MHz, $CDCl_3$) spectrum of Compound **11**

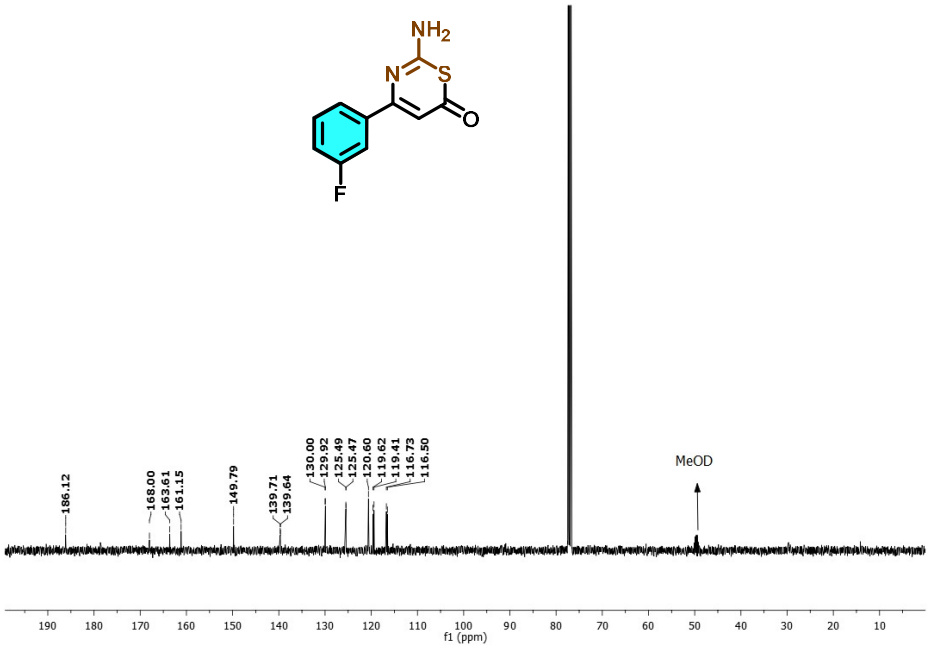




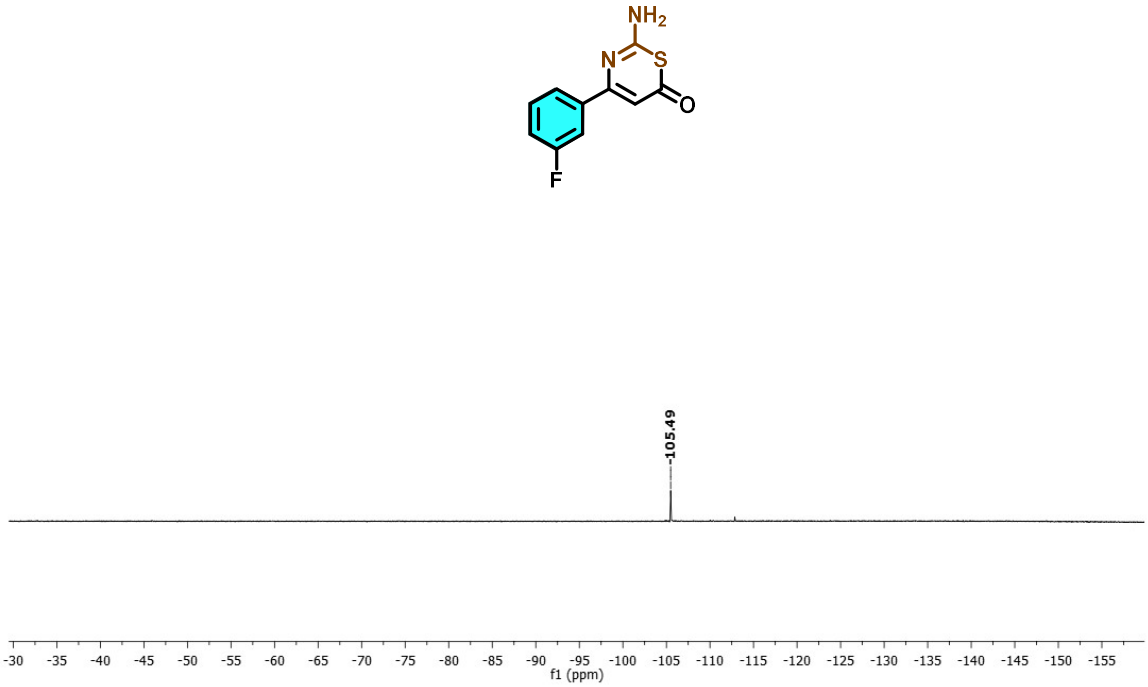
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **12**



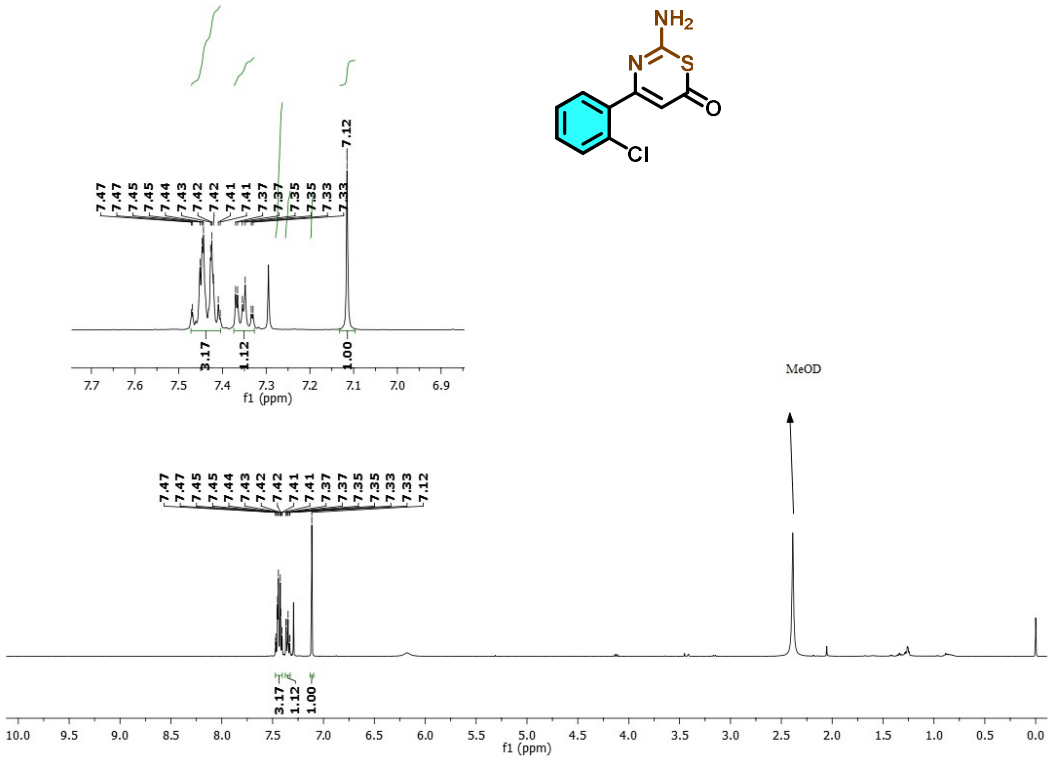
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **12**



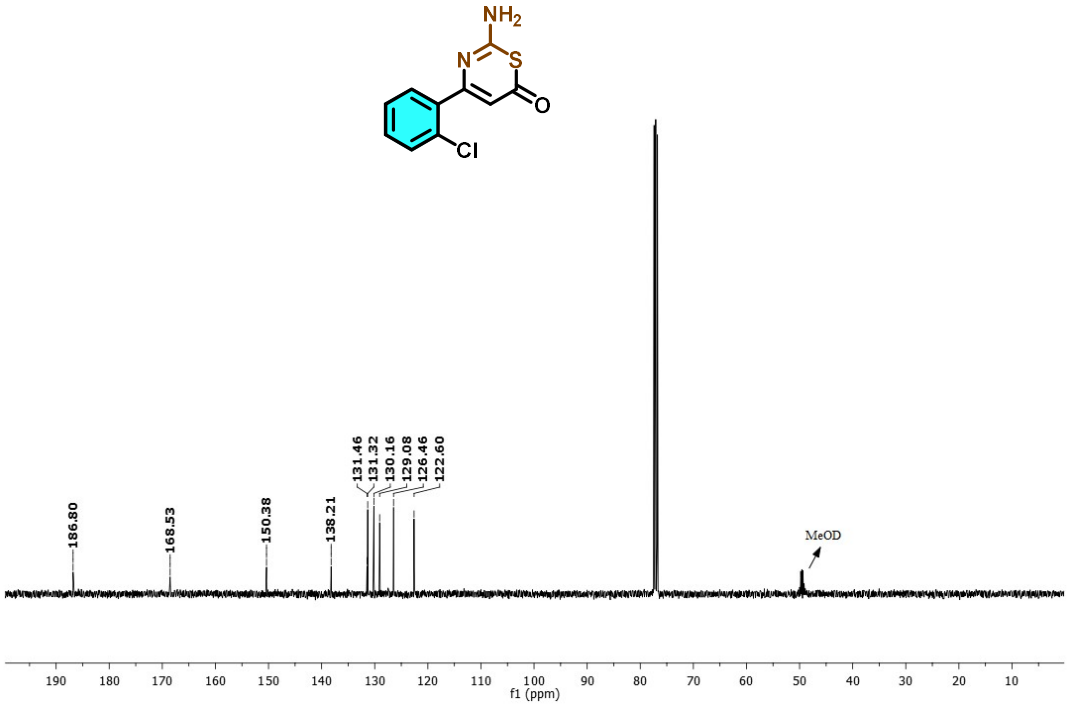
^{19}F-NMR (400 MHz, $CDCl_3$) spectrum of Compound **12**



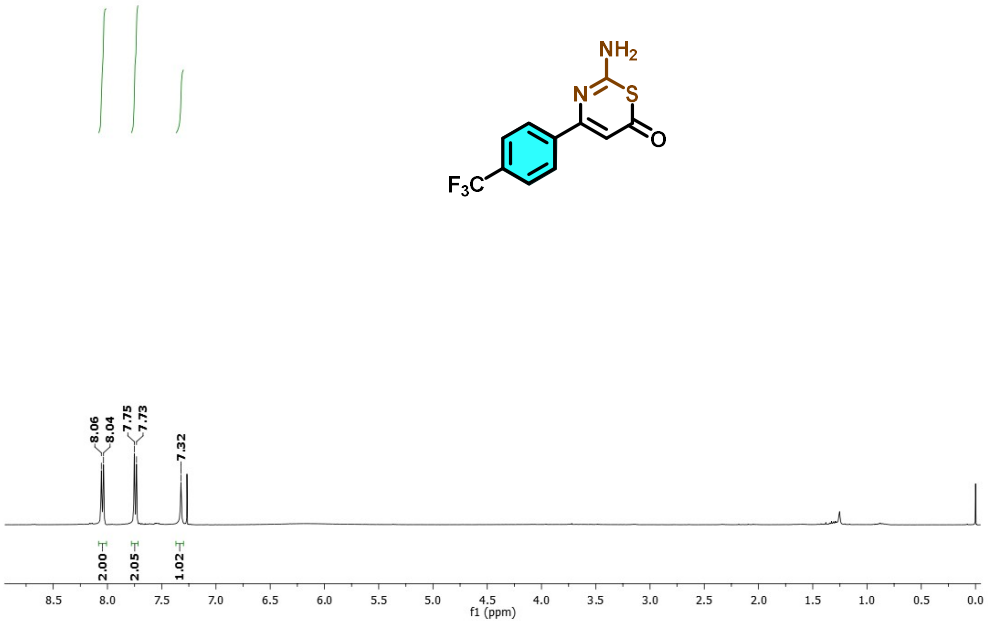
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **13**



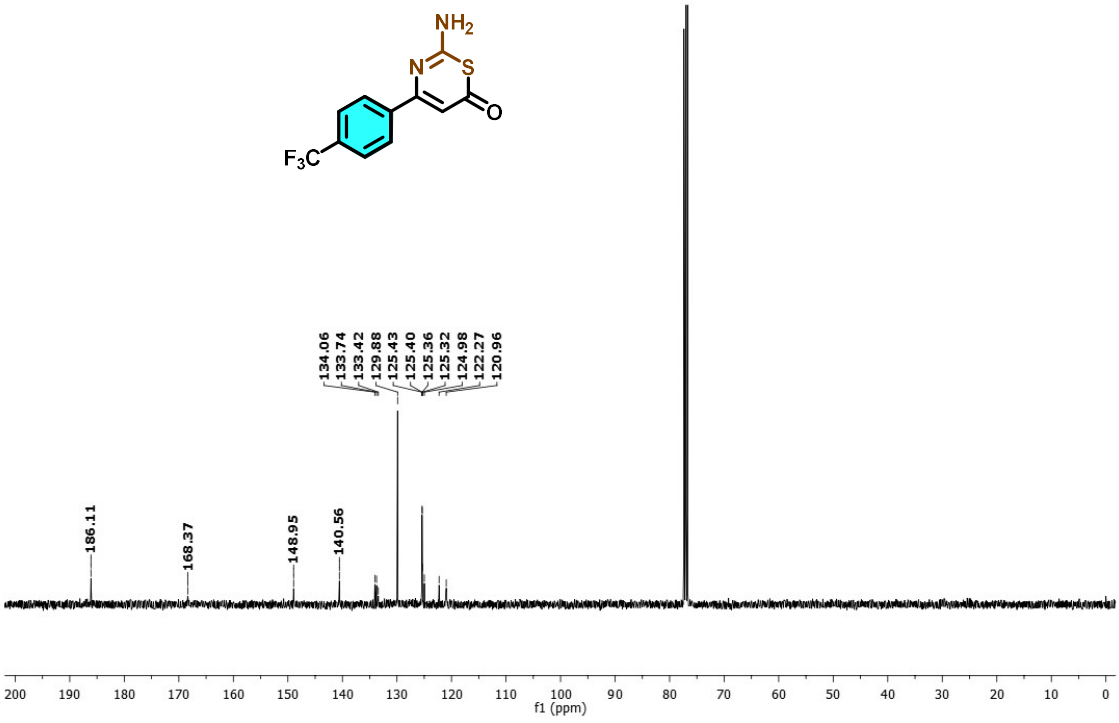
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **13**



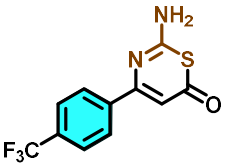
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **14**

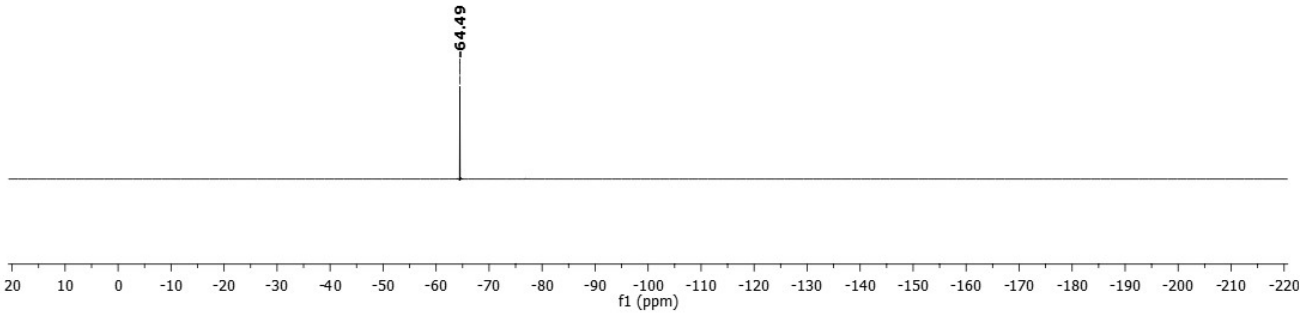


^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) of Compound **14**

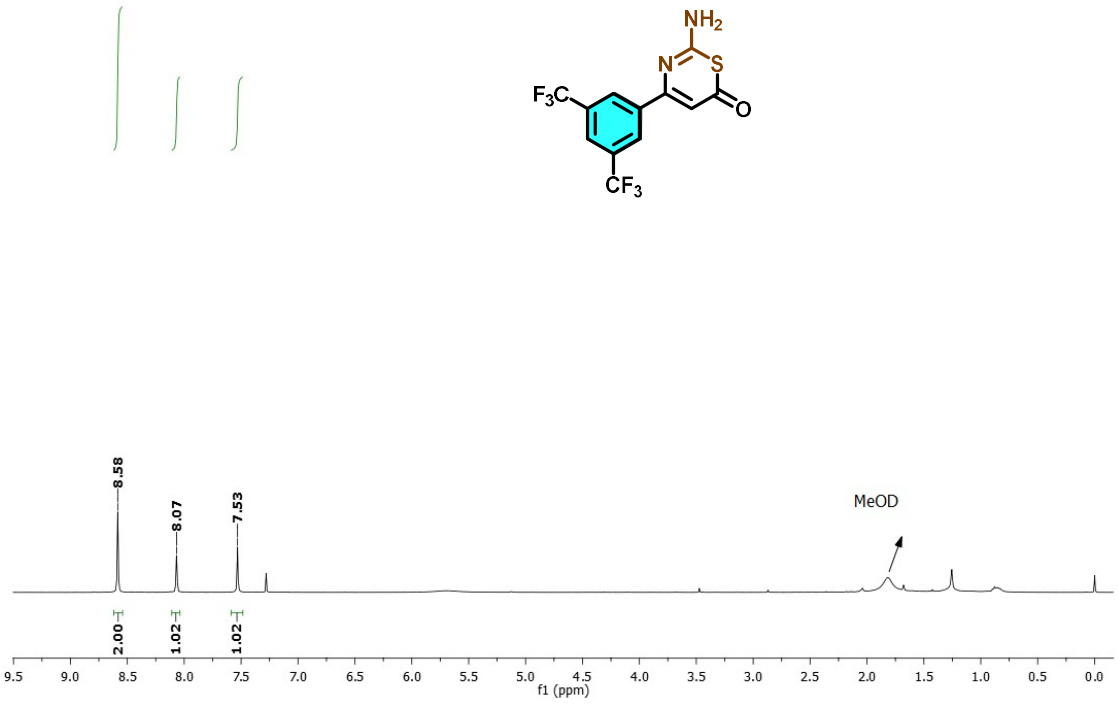


^{19}F-NMR (400 MHz, $CDCl_3$) spectrum of Compound **14**

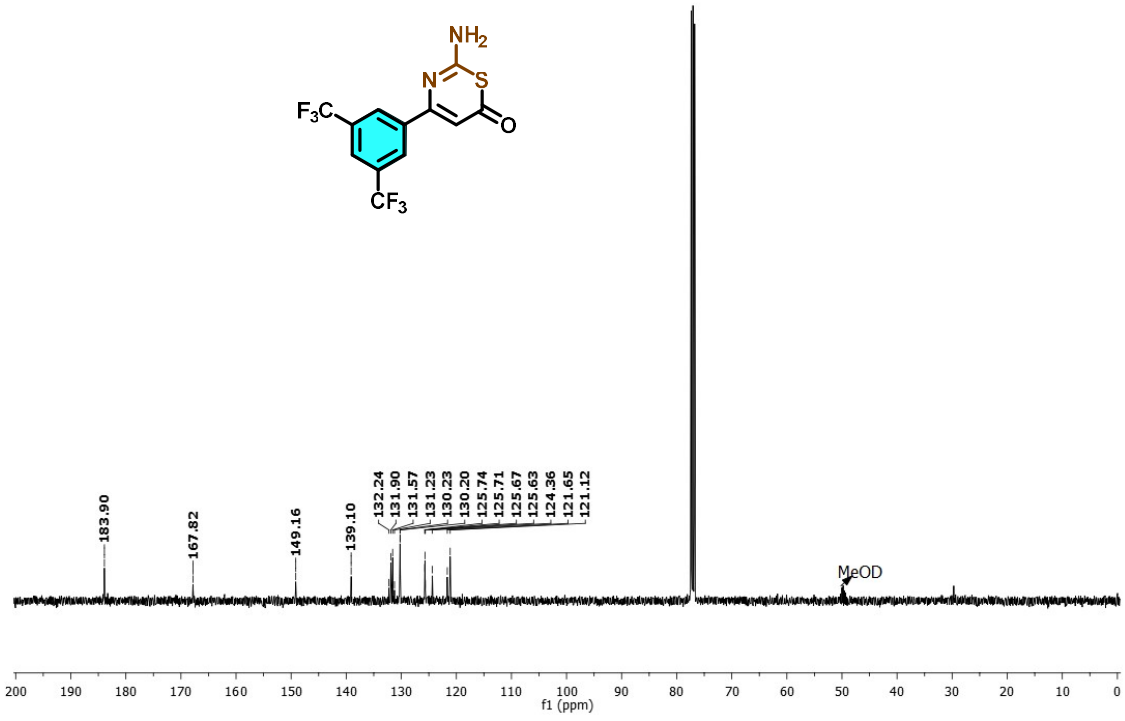




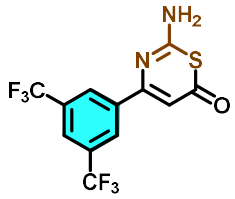
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **15**

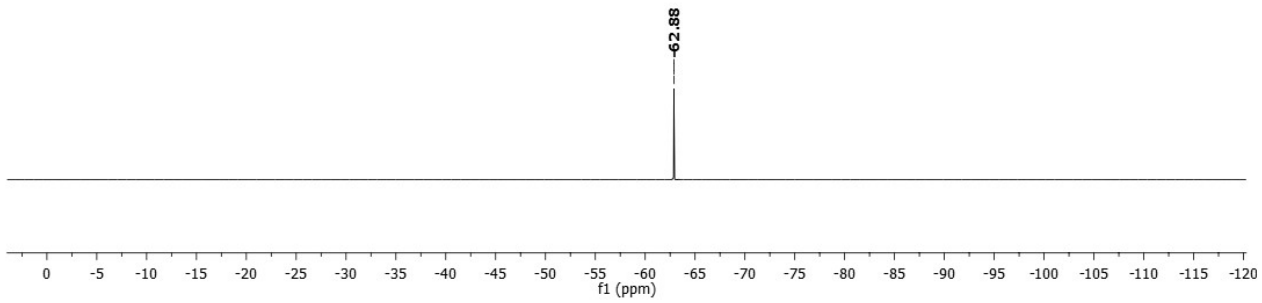


^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **15**

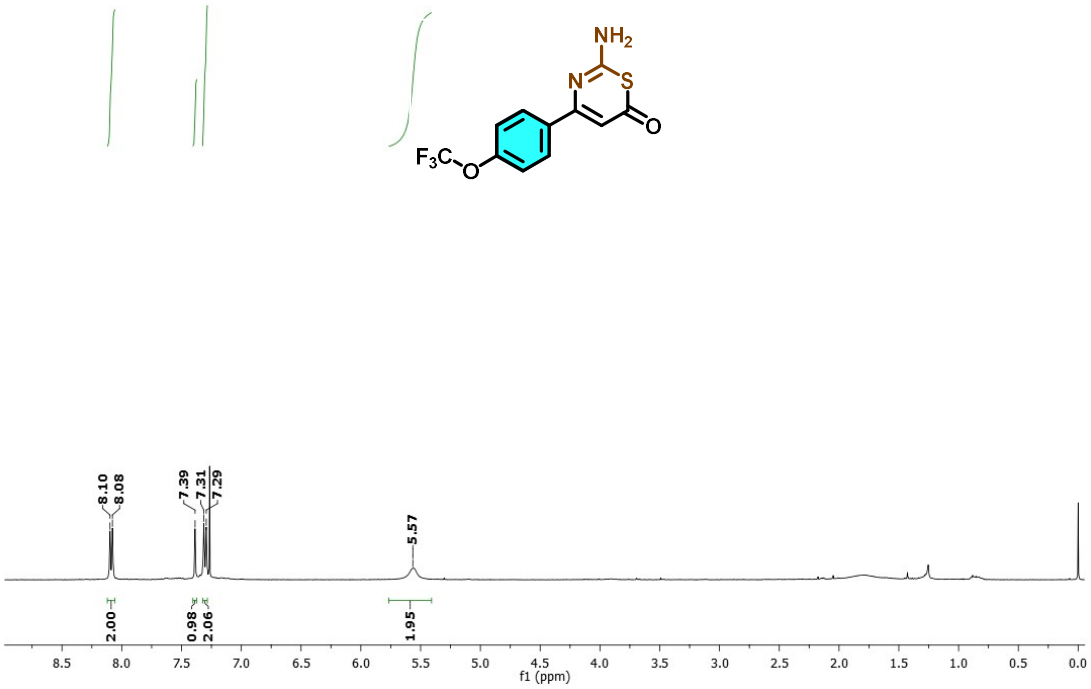


^{19}F-NMR (400 MHz, $CDCl_3$) spectrum of Compound **15**

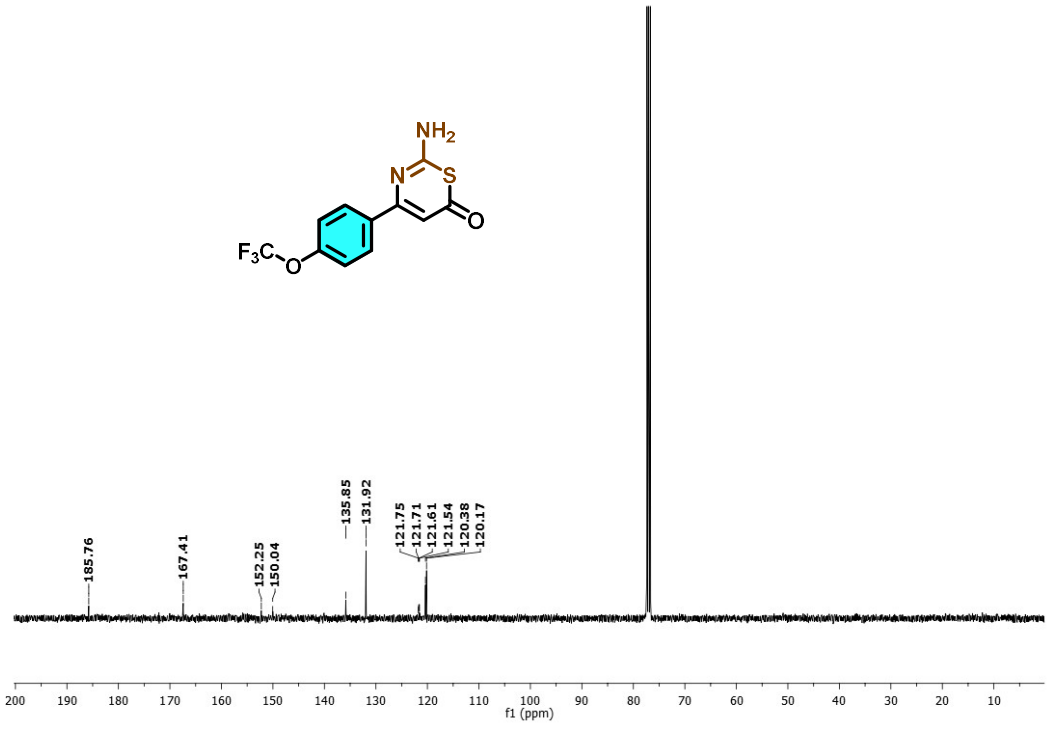




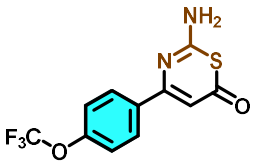
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **16**

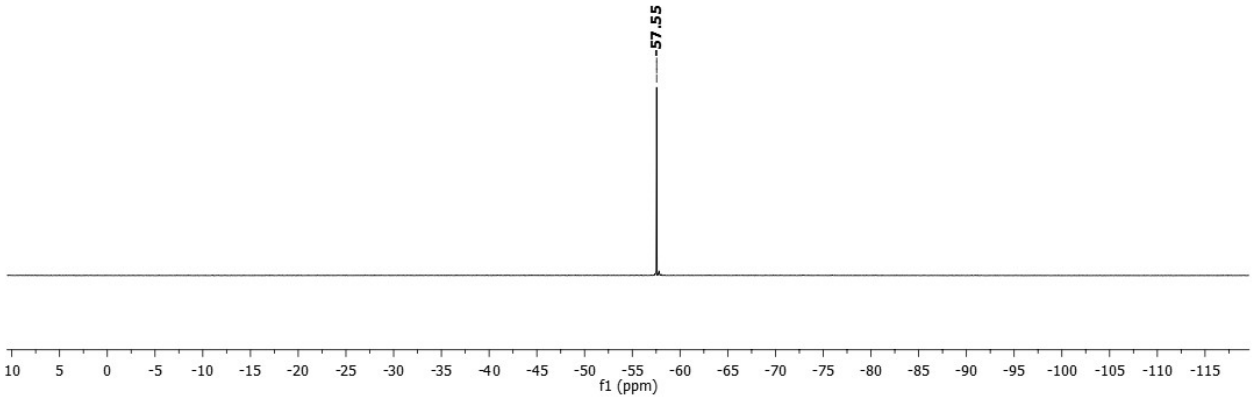


^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **16**

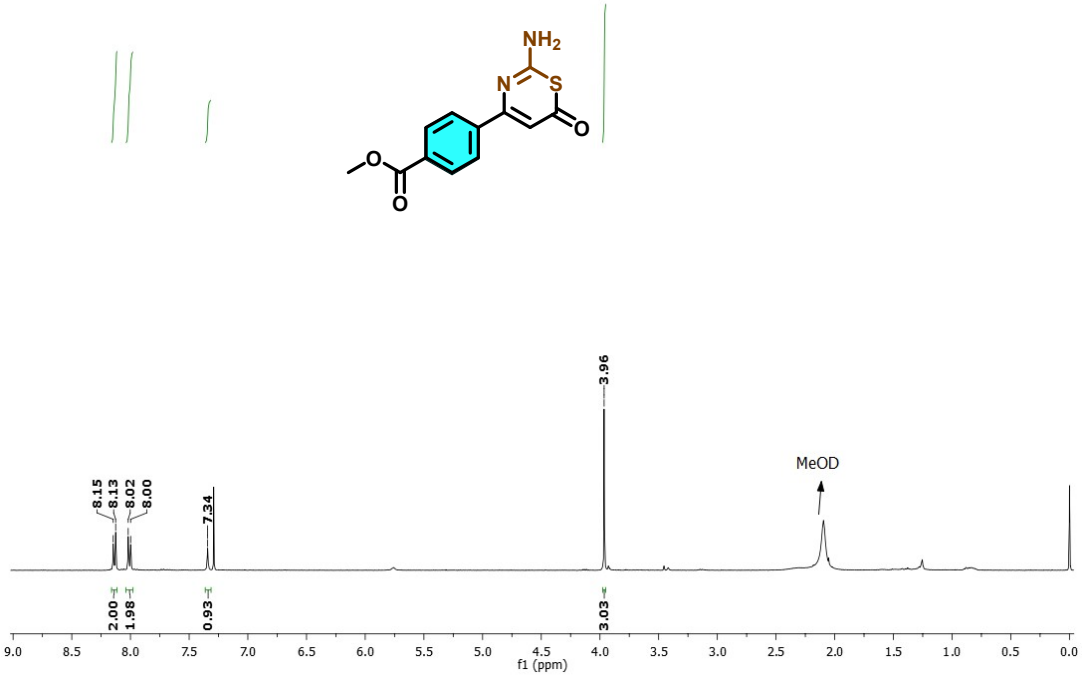


^{19}F-NMR (400 MHz, $CDCl_3$) spectrum of Compound **16**

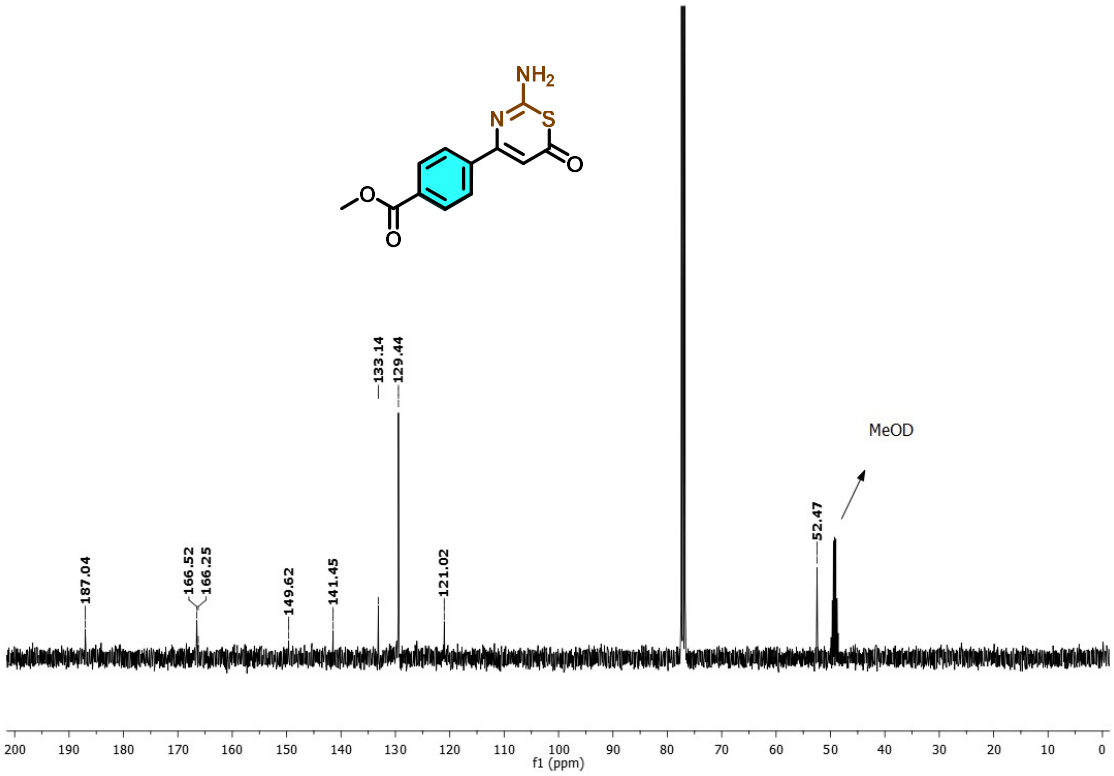




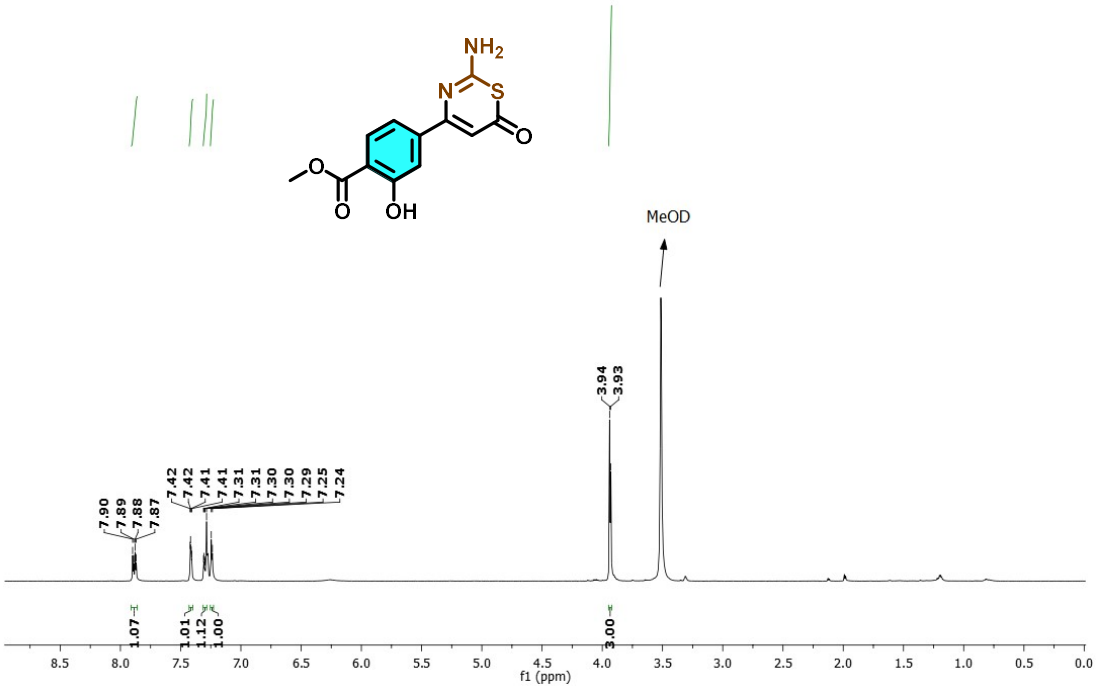
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **17**



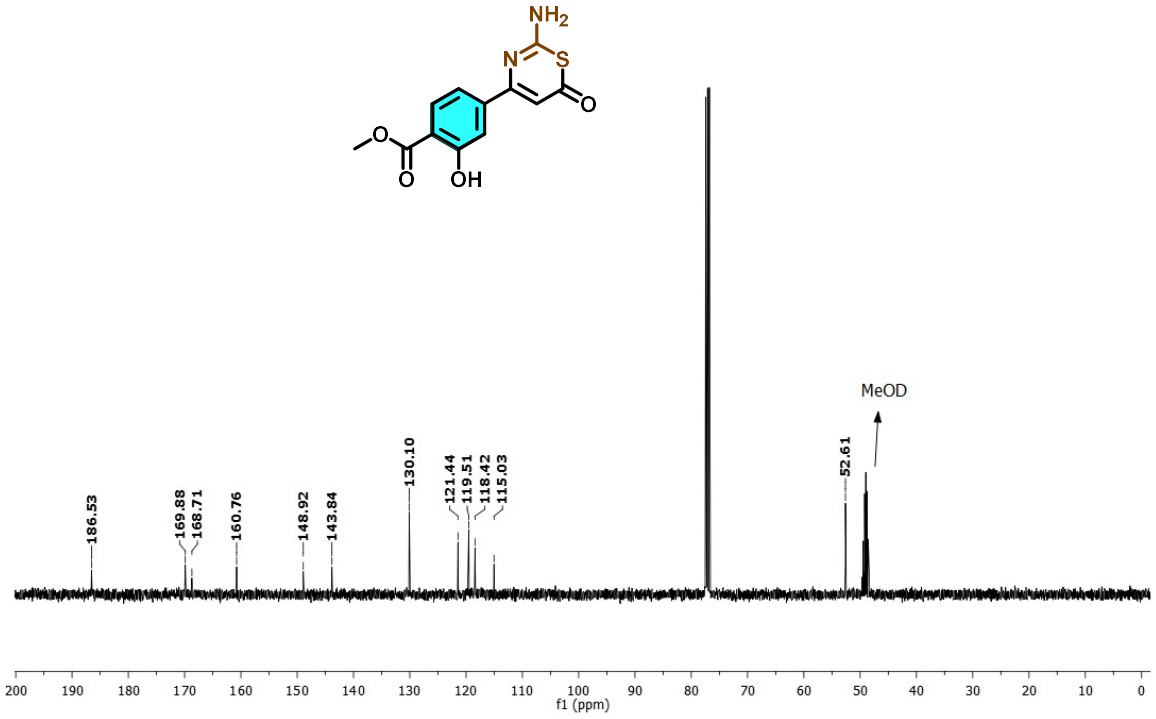
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **17**



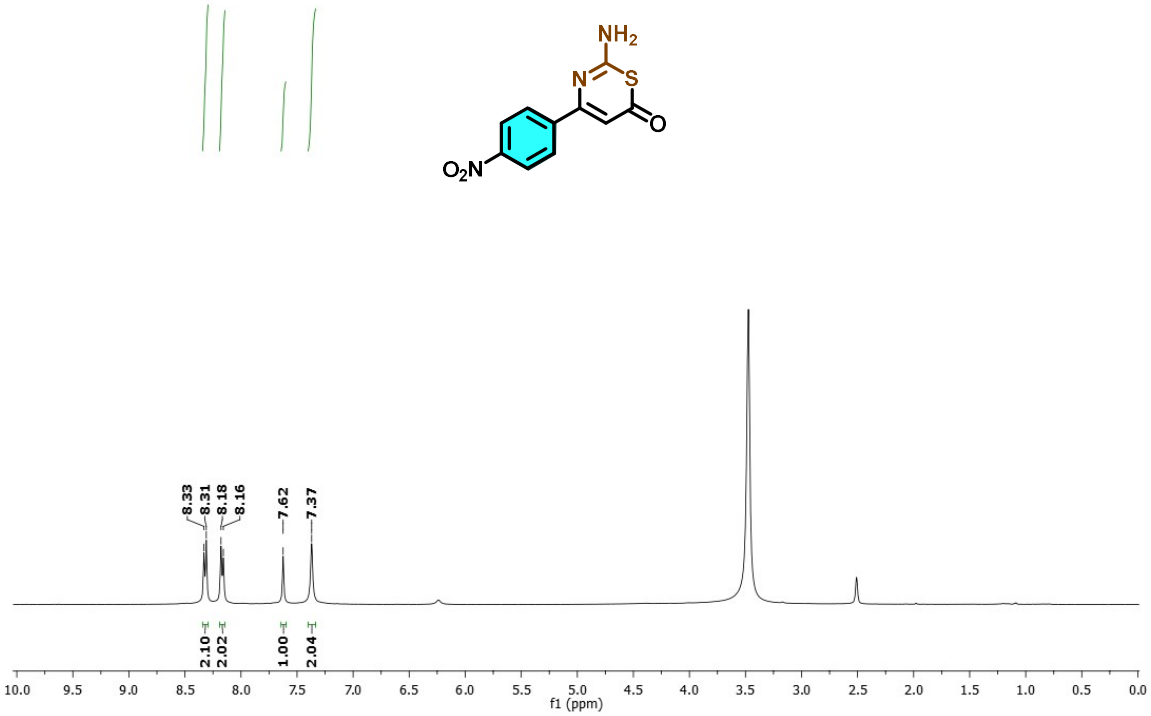
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **18**



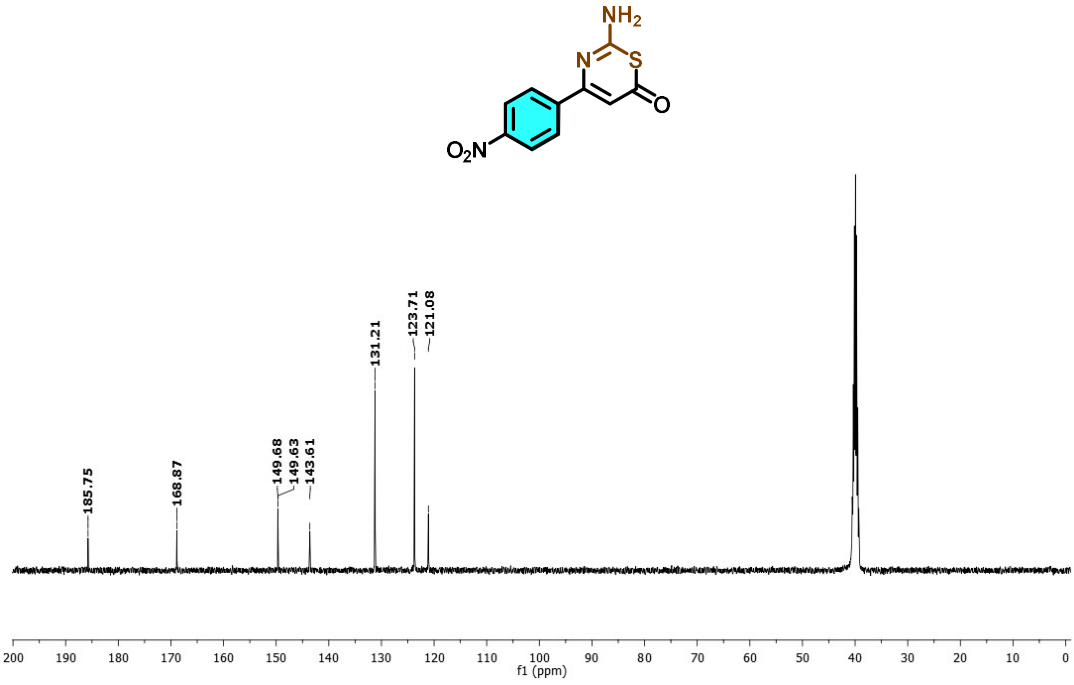
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **18**



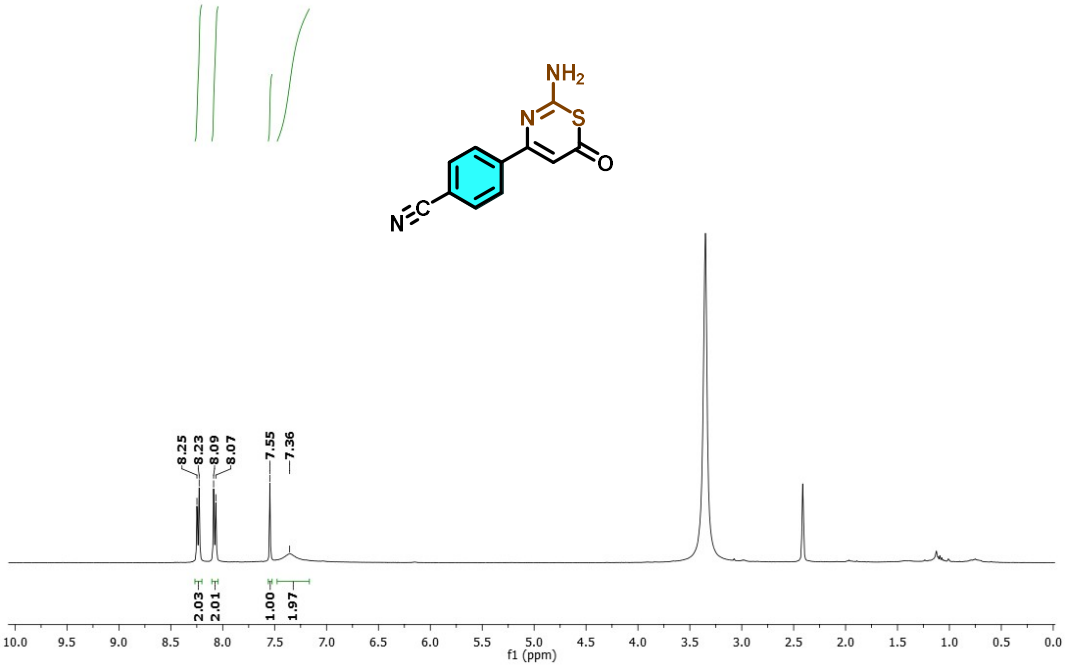
^{1}H-NMR (400 MHz,DMSO) spectrum of Compound **19**



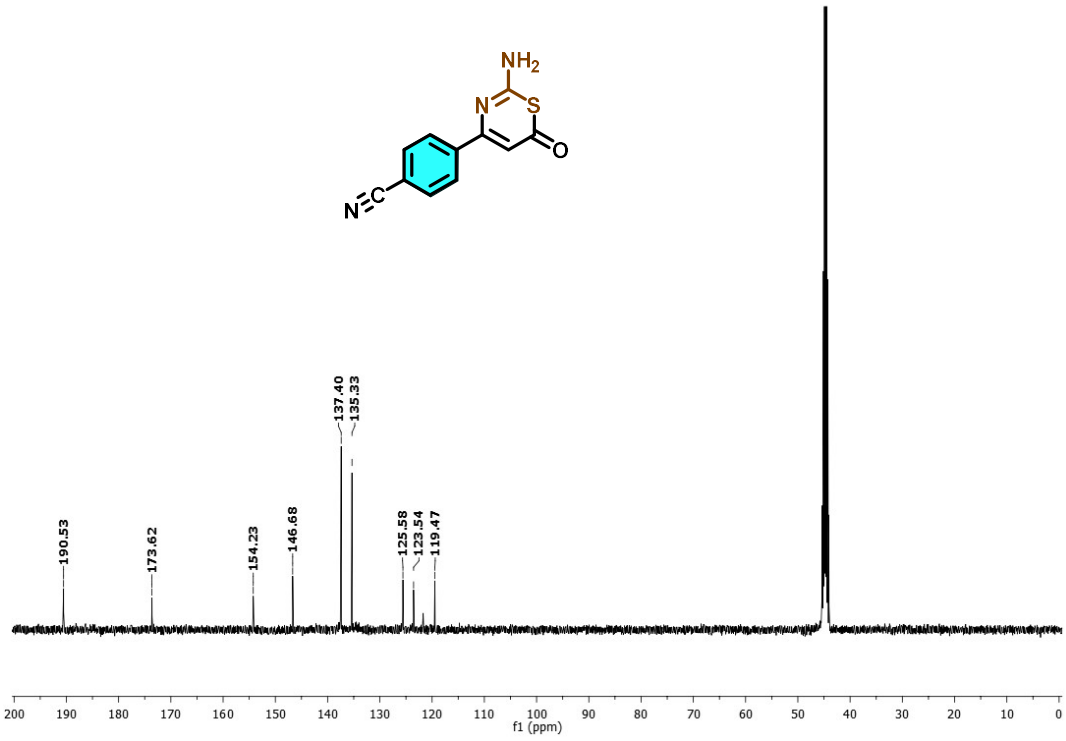
^{13}C{^{1}H}-NMR (100 MHz, DMSO) spectrum of Compound **19**



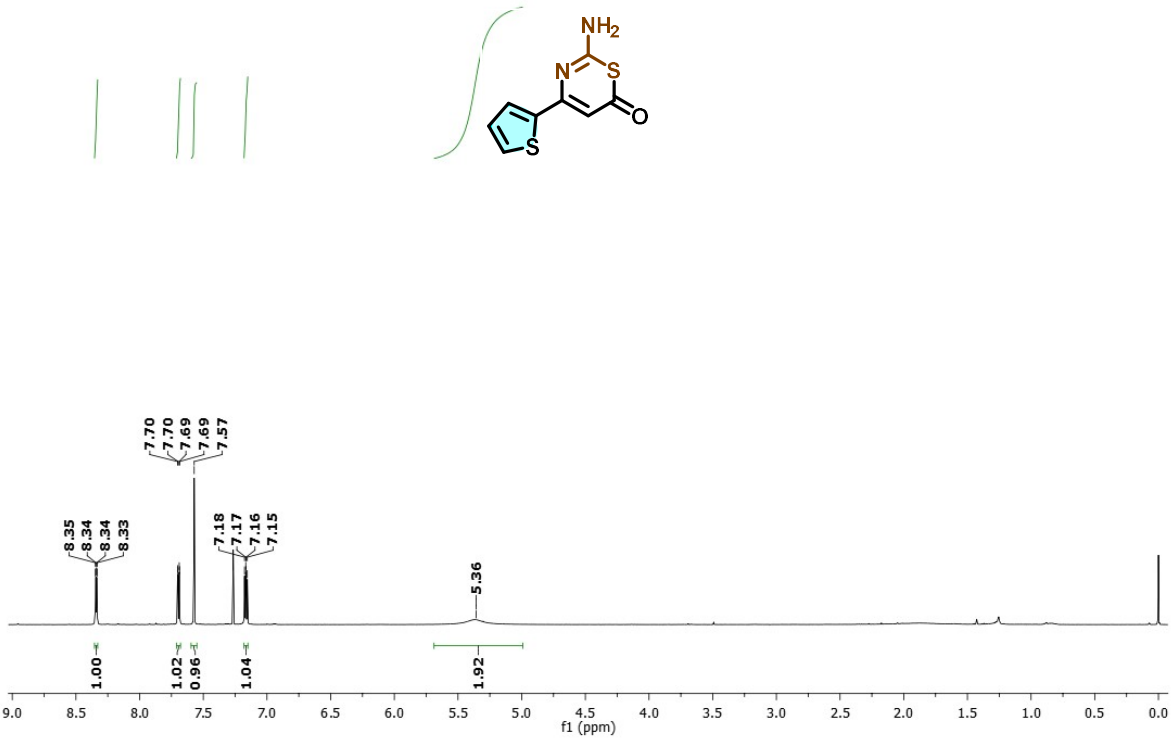
^{1}H-NMR (400 MHz,DMSO) spectrum of Compound **20**



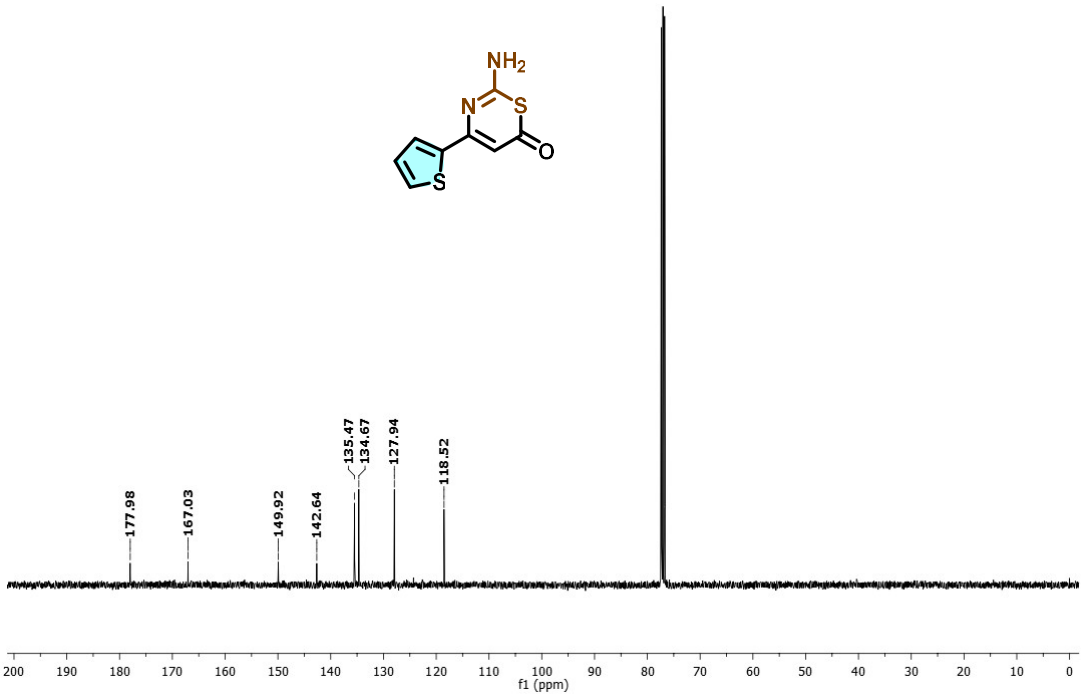
^{13}C{^{1}H}-NMR (100 MHz, DMSO) spectrum of Compound **20**



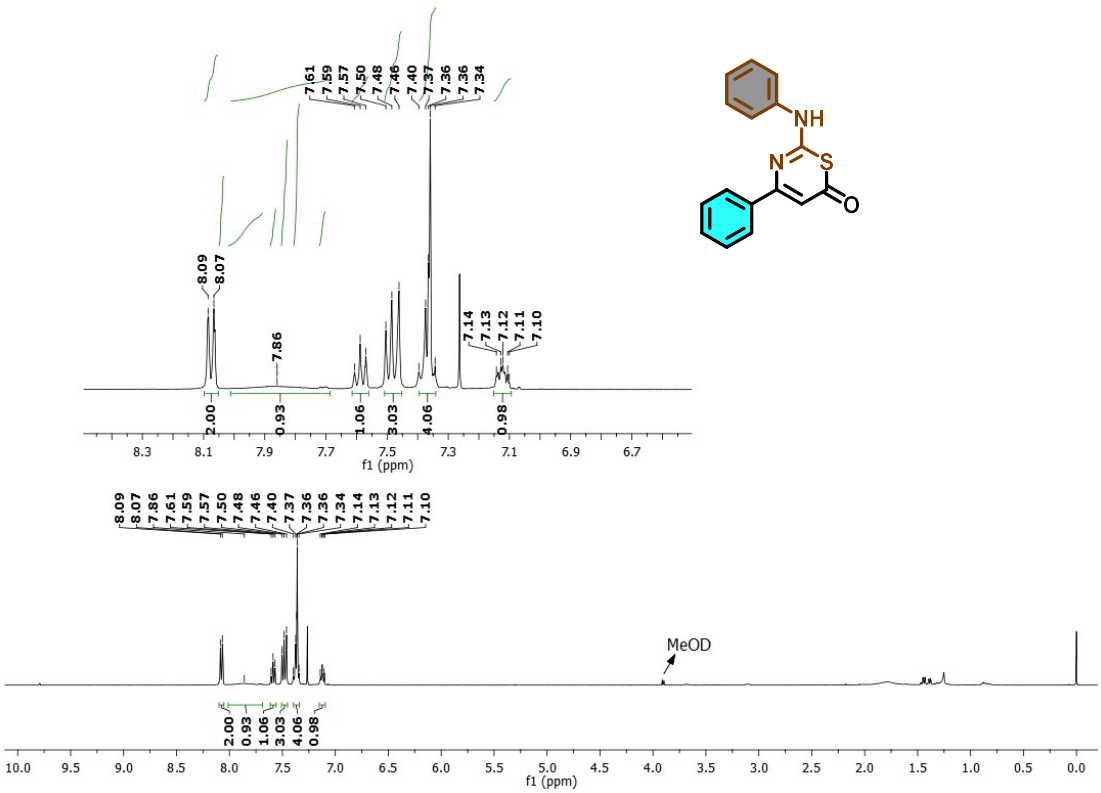
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **21**



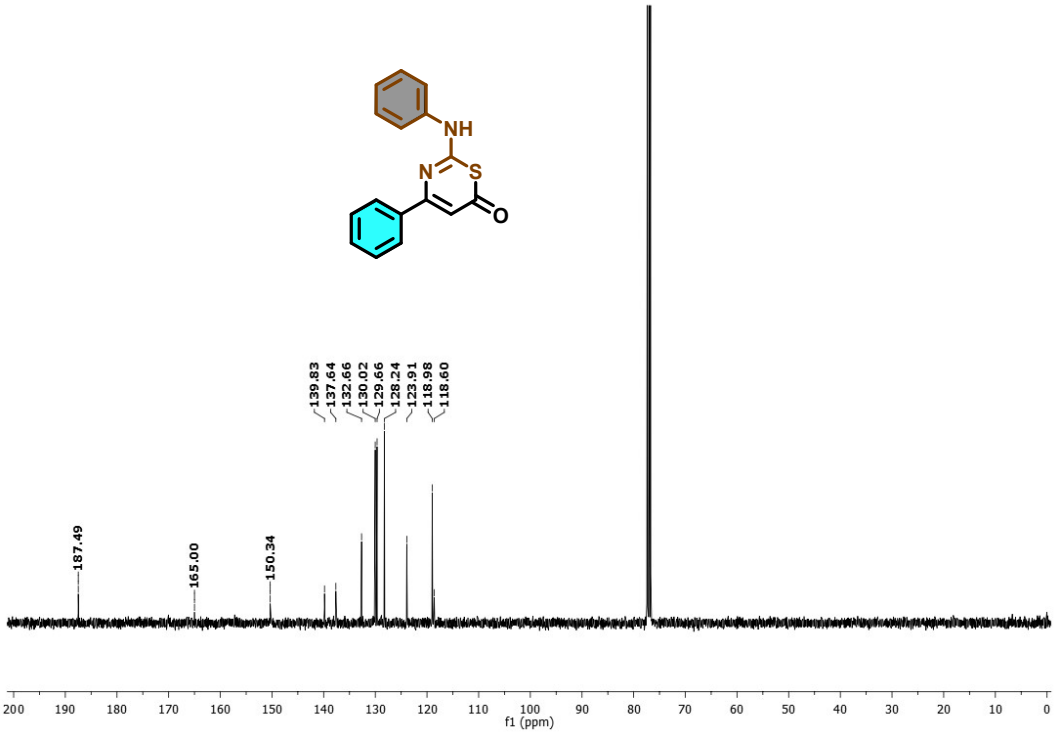
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **21**



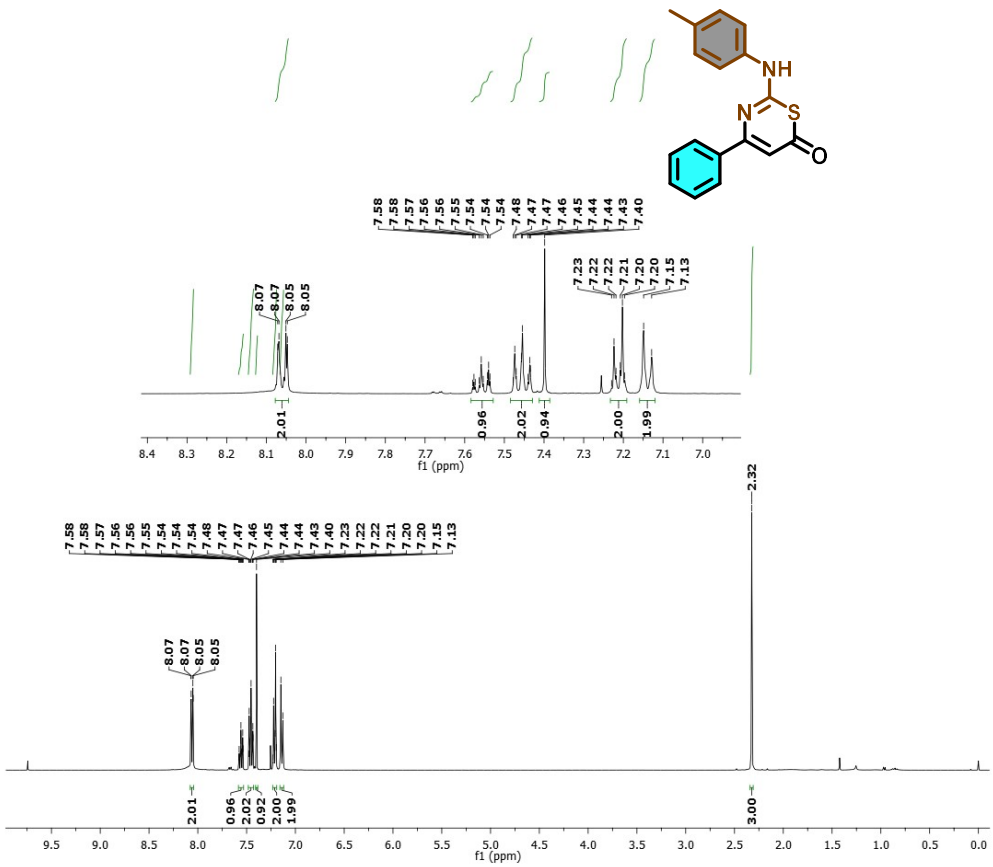
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **22**



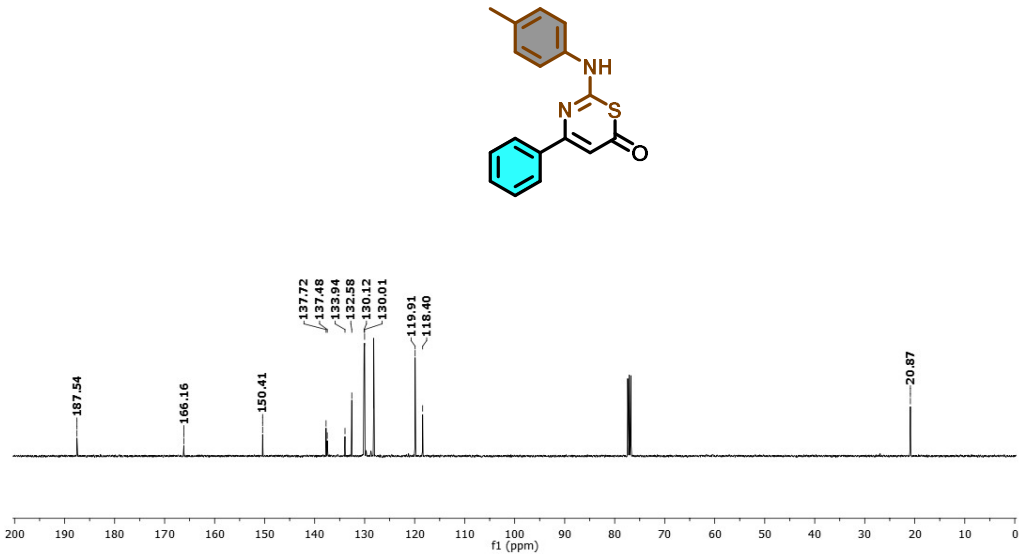
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **22**



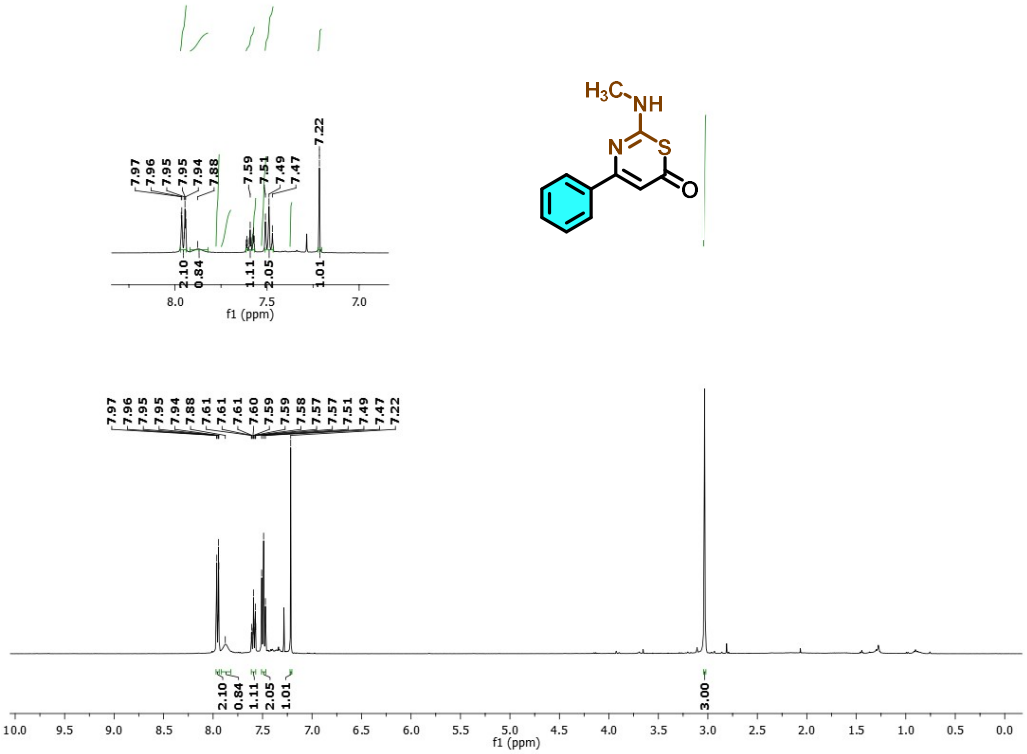
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **23**



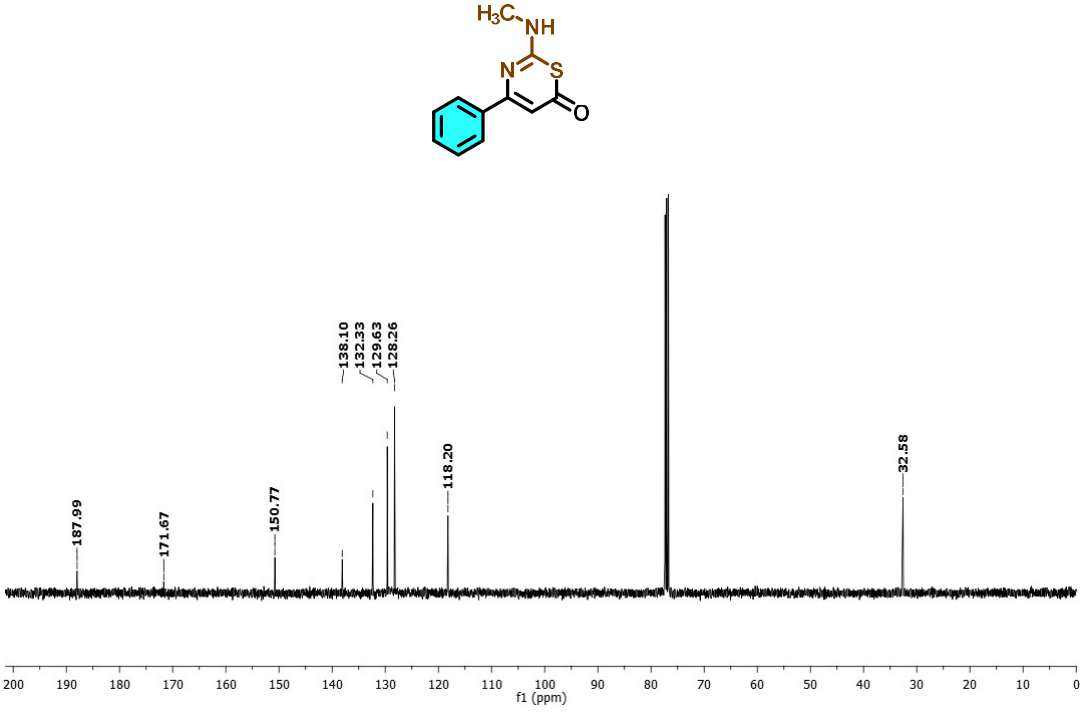
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **23**



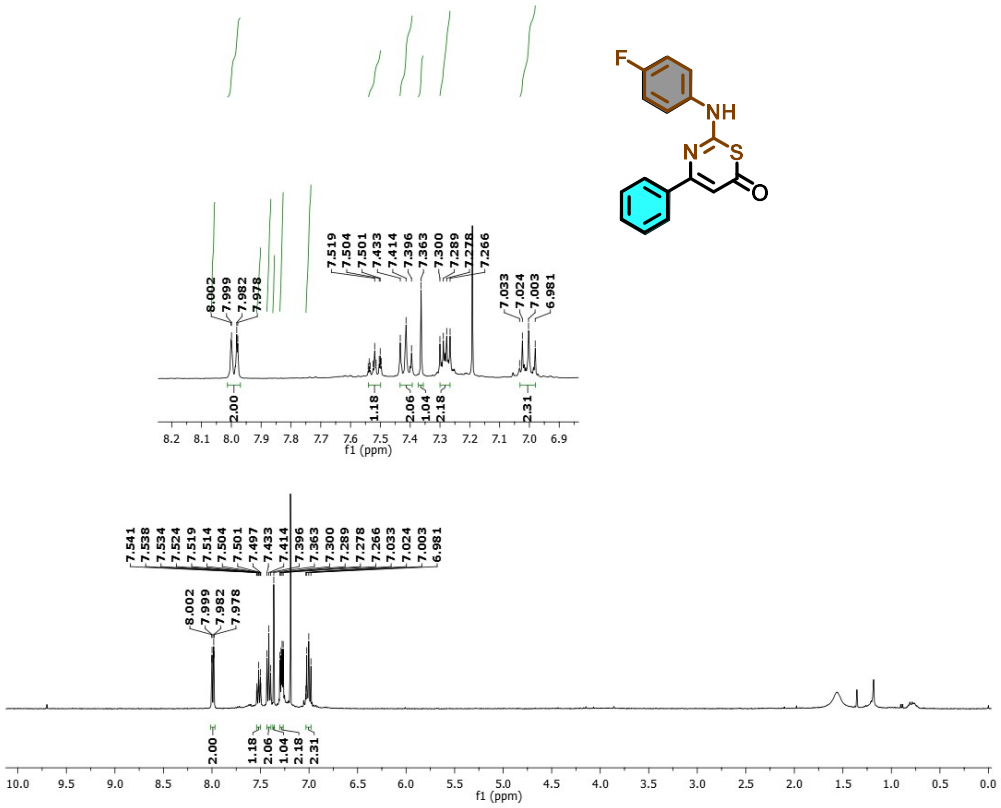
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **24**



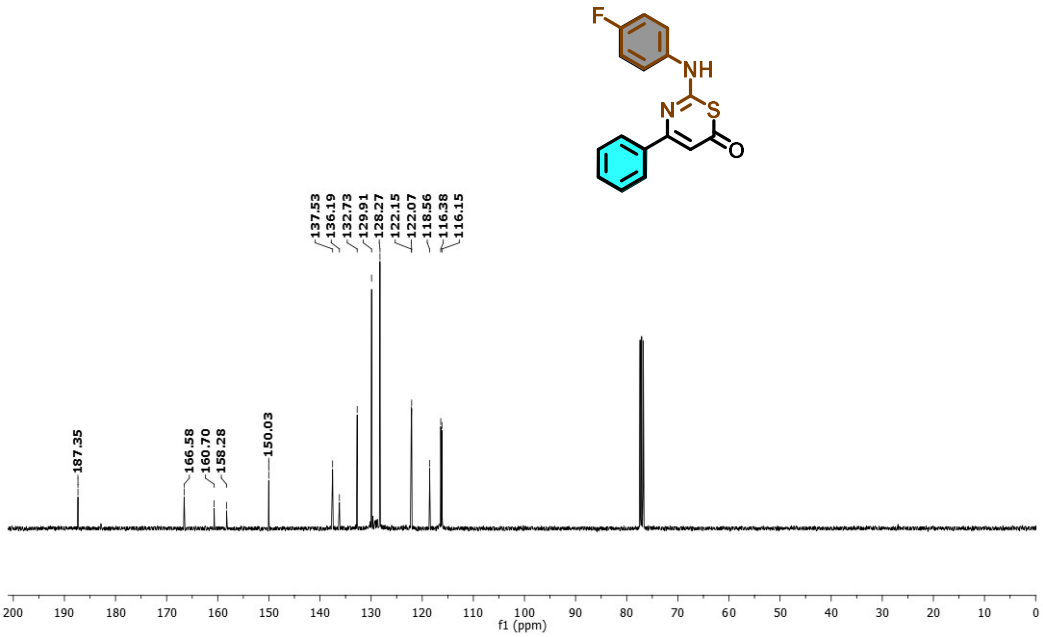
^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$) spectrum of Compound **24**



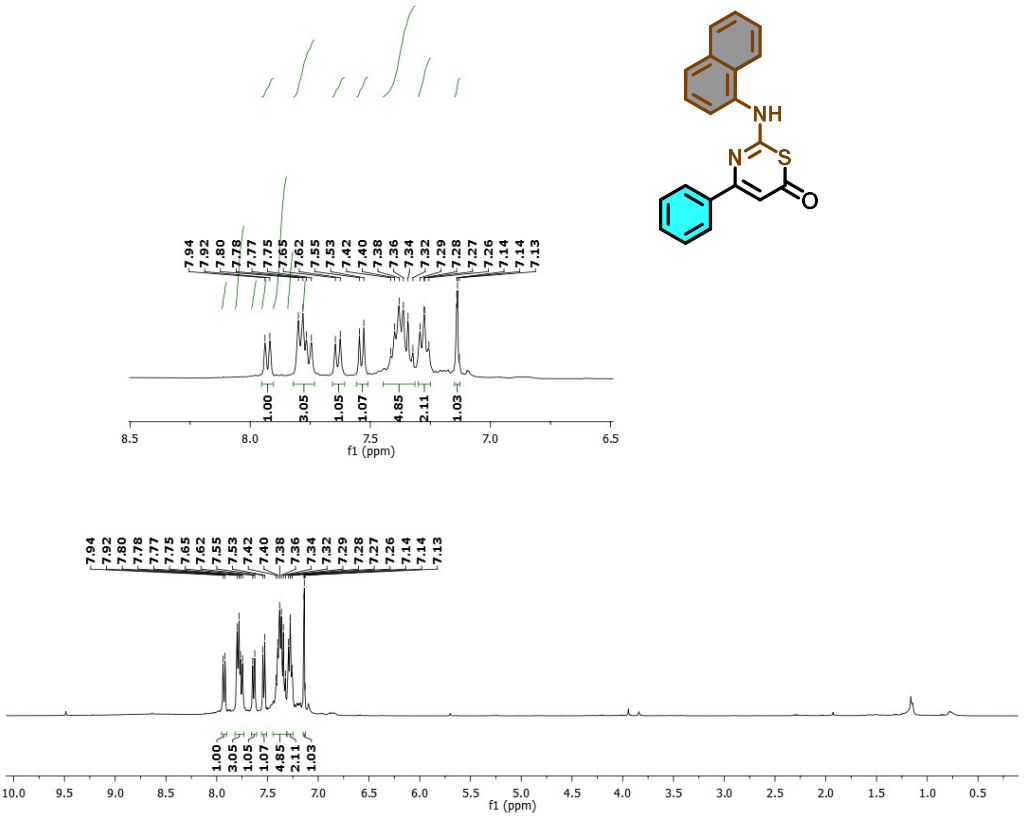
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **25**



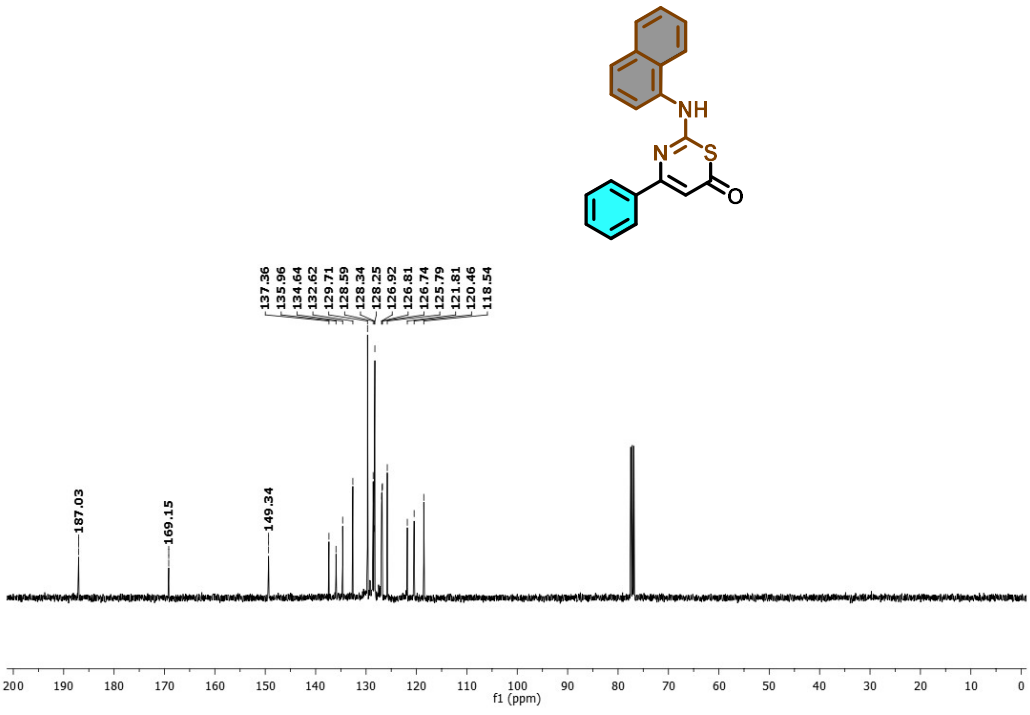
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **25**



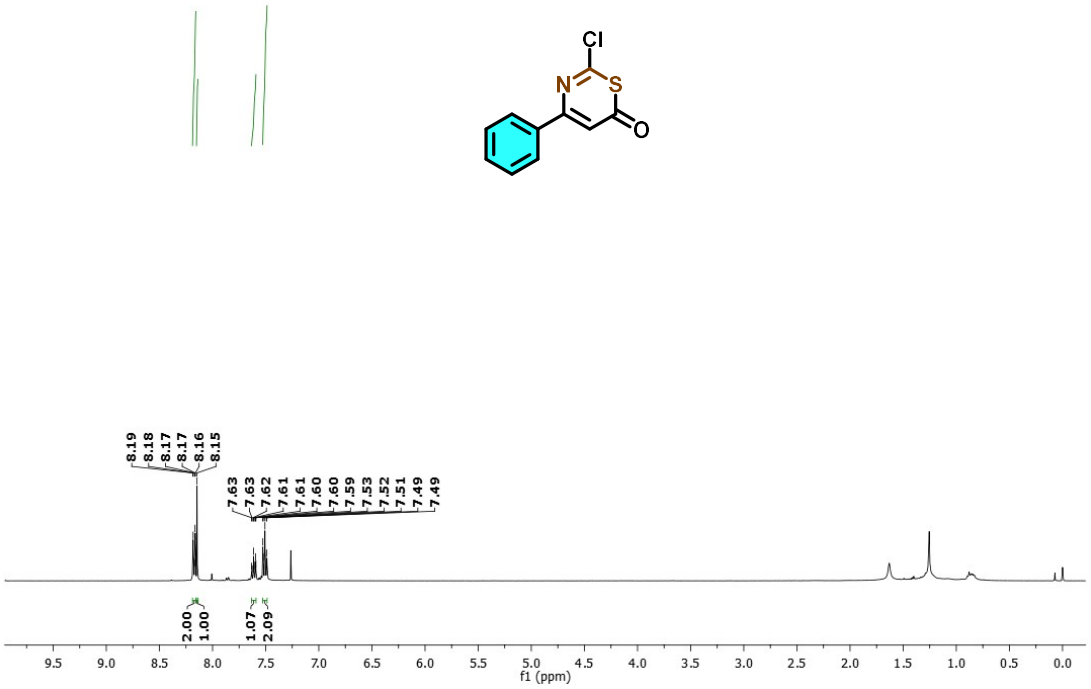
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **26**



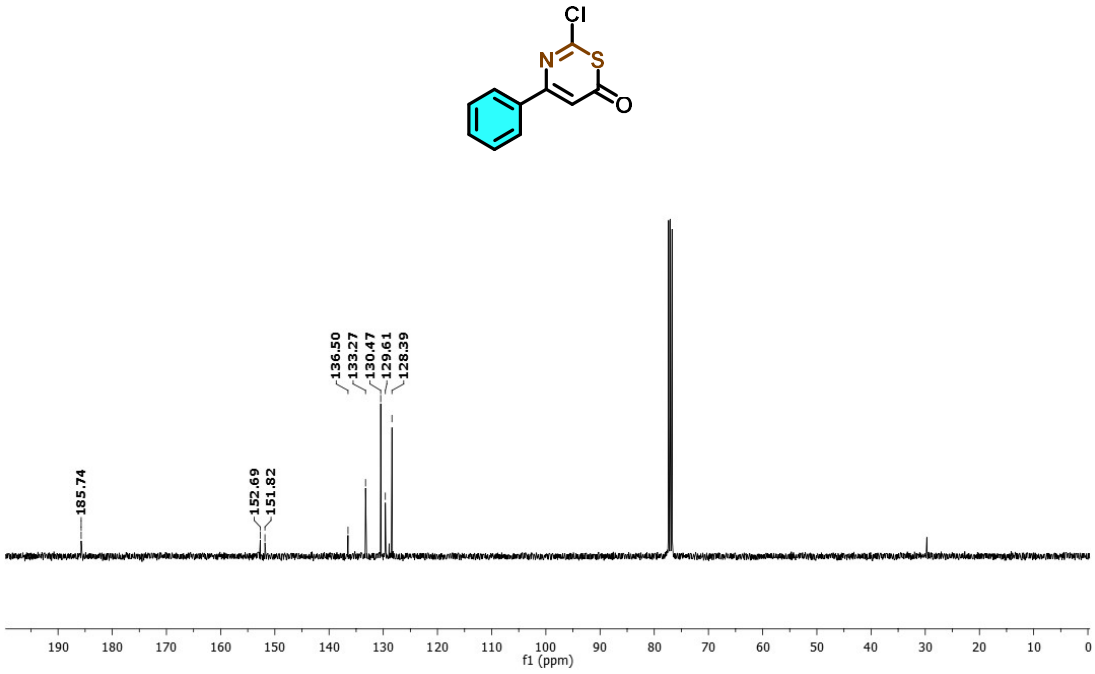
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **26**



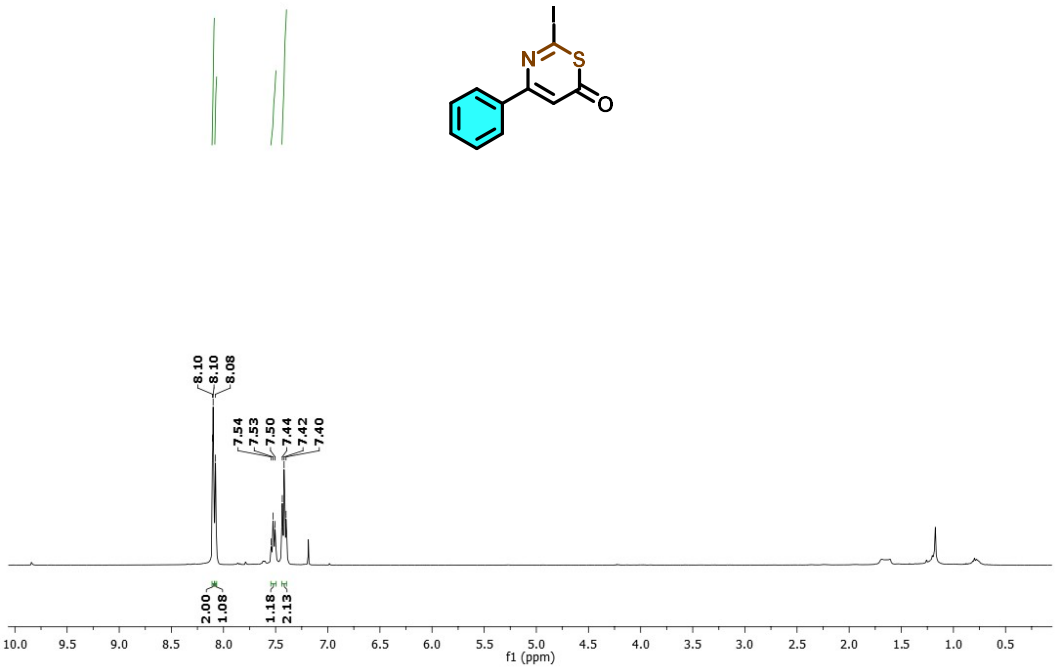
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **27**



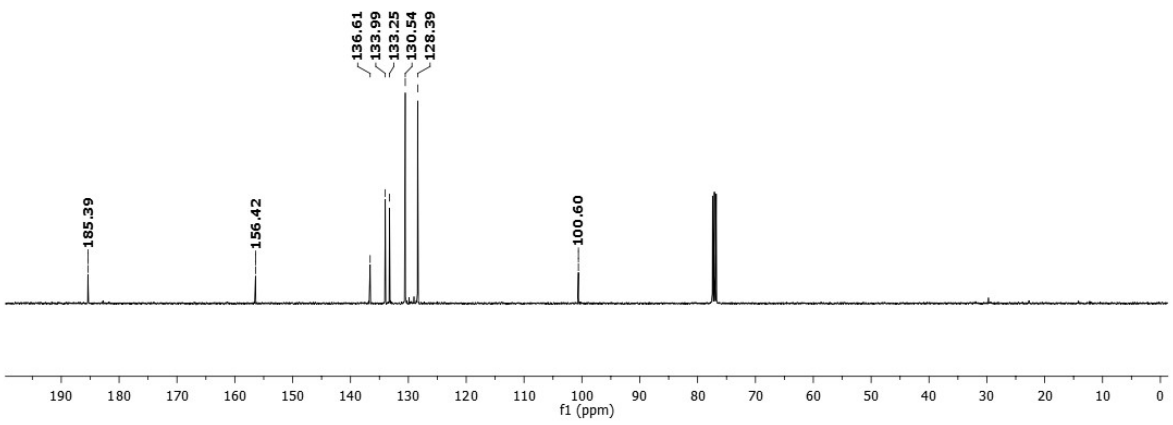
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **27**



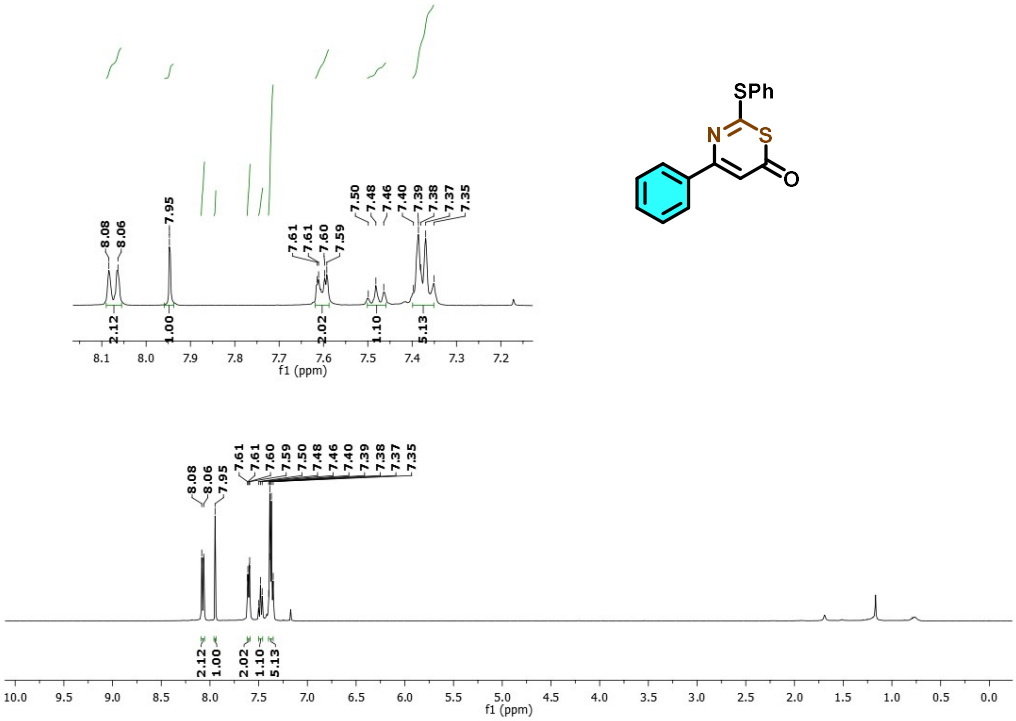
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **28**



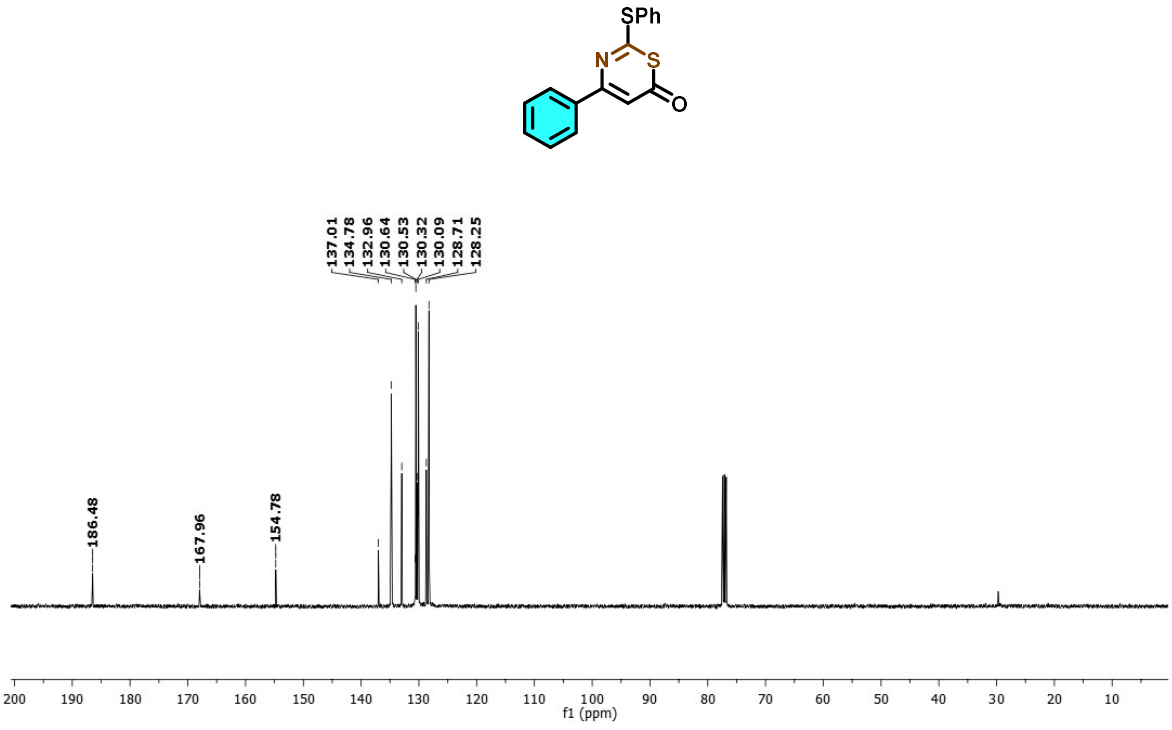
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **28**



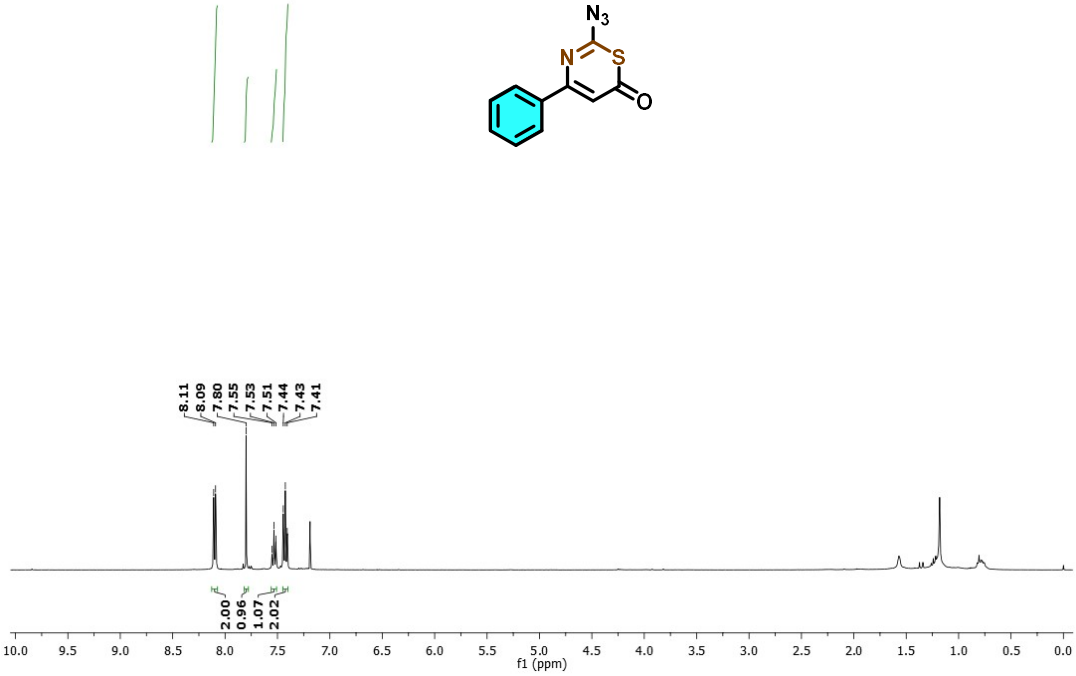
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **29**



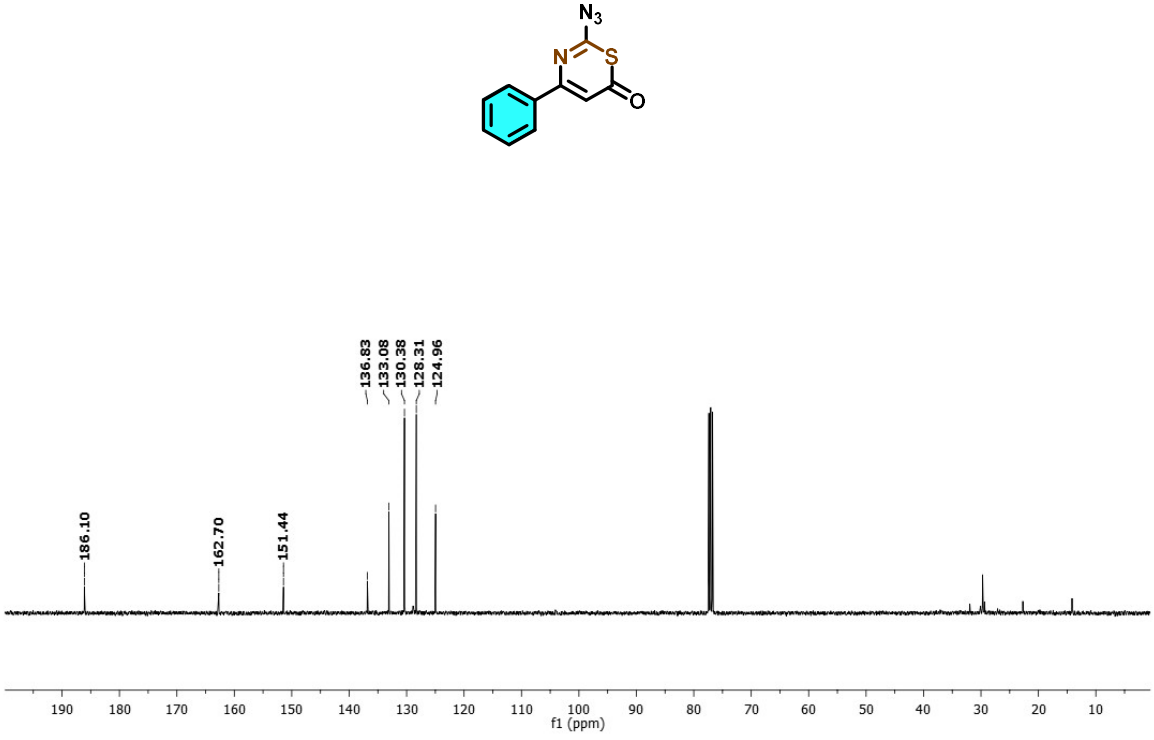
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **29**



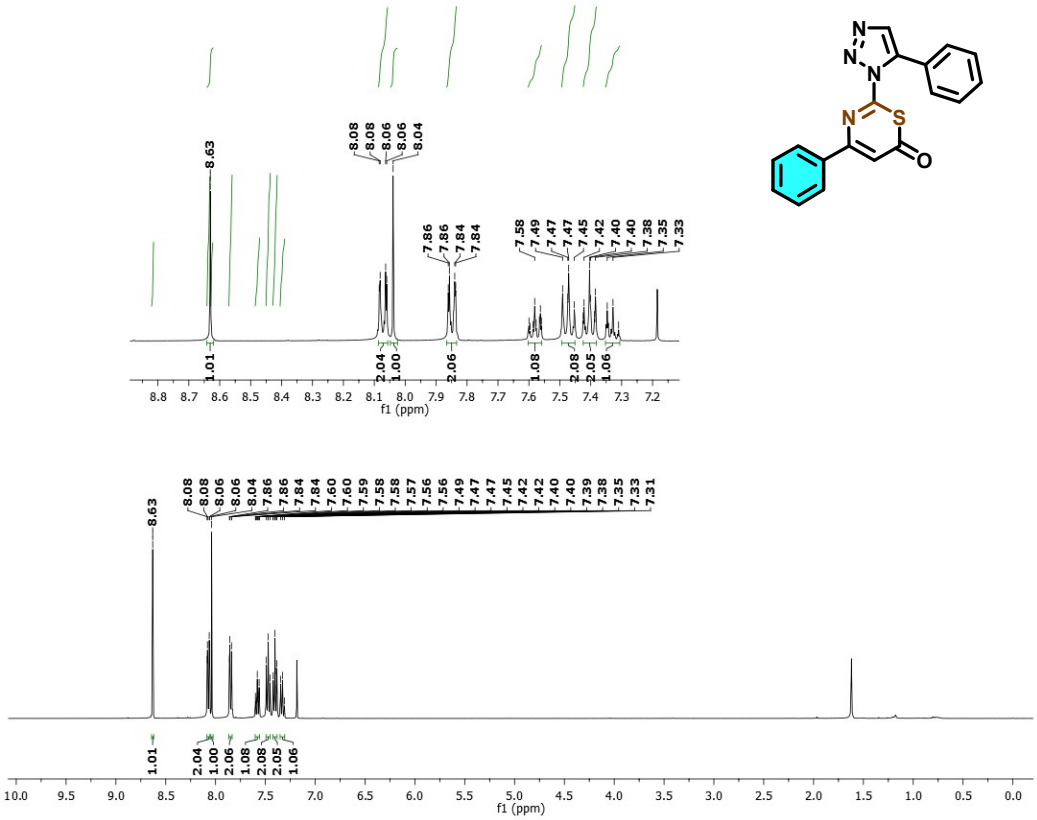
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **30**



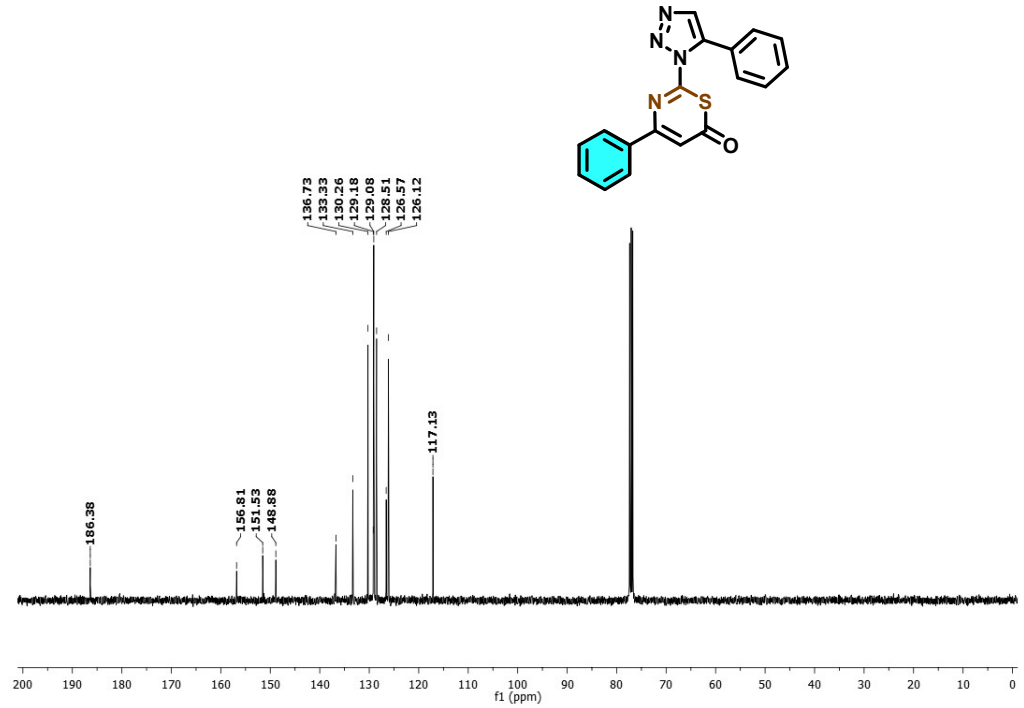
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **30**



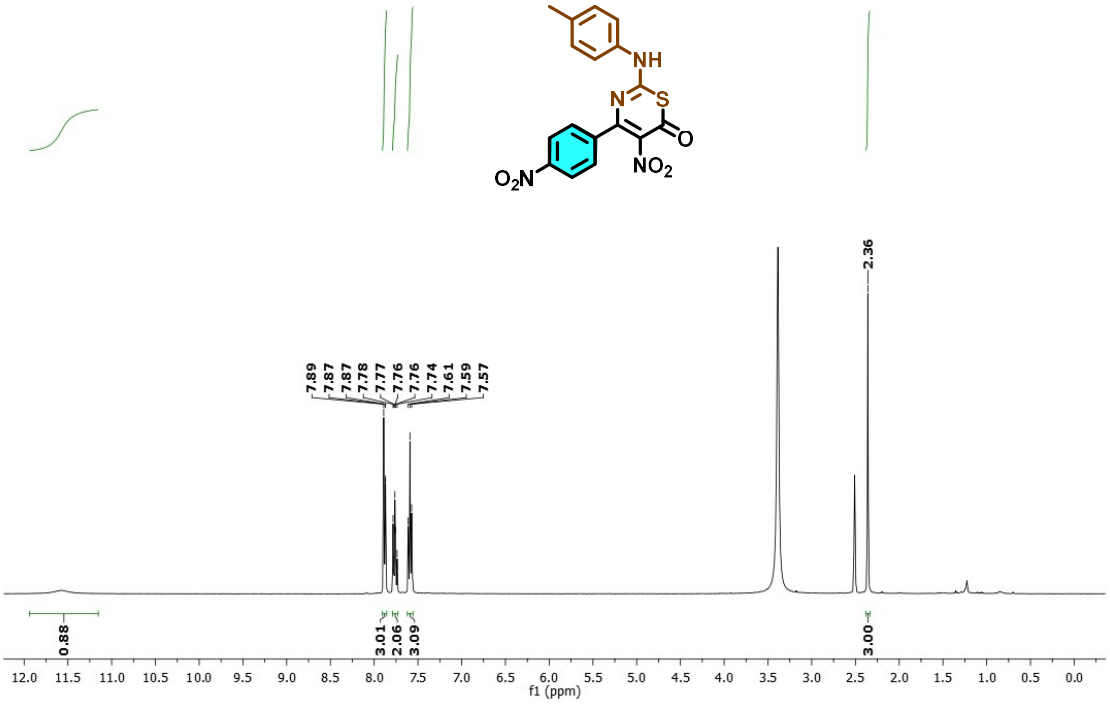
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **31**



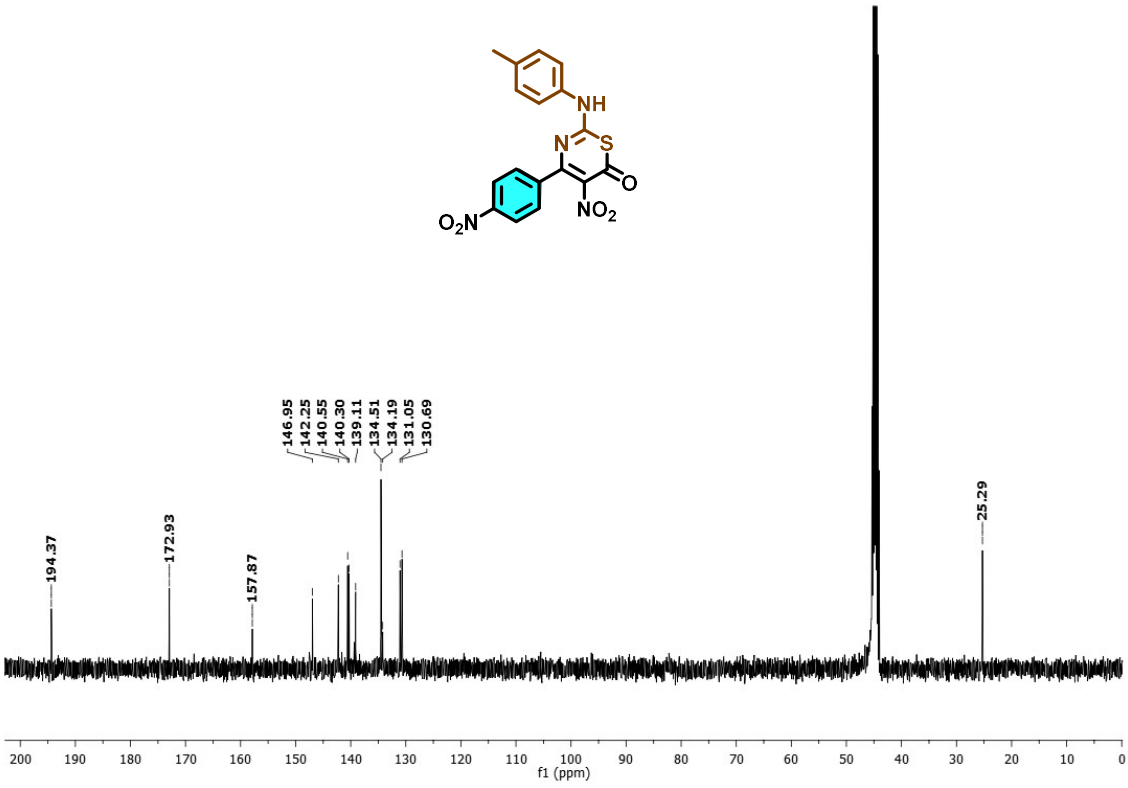
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **31**



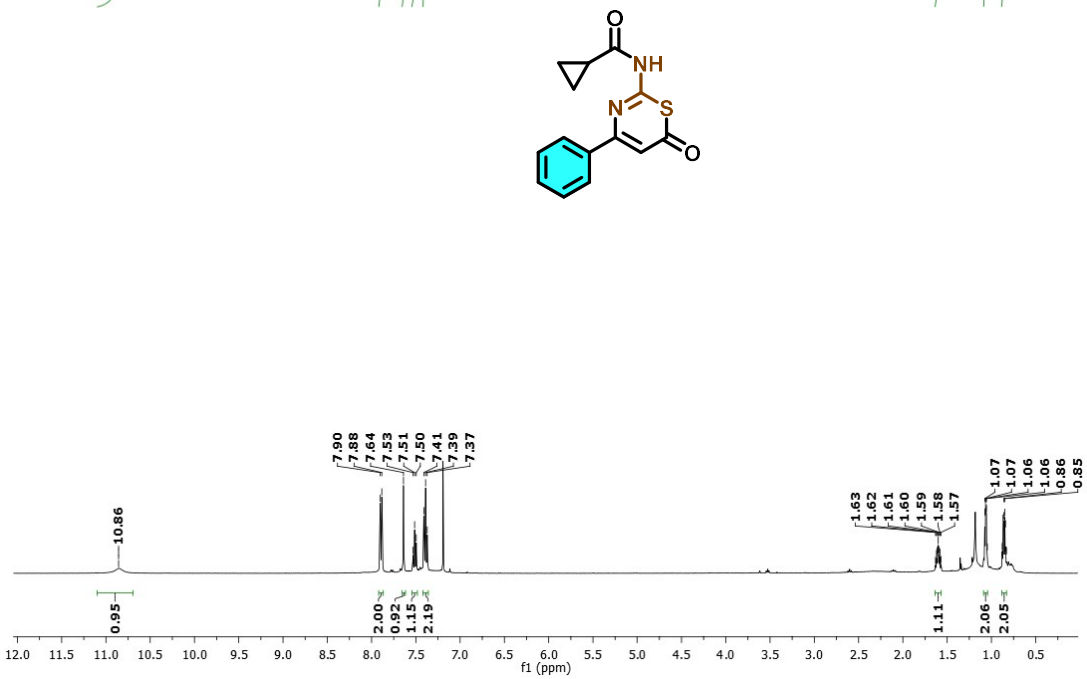
^{1}H-NMR (400 MHz, DMSO) spectrum of Compound **32**



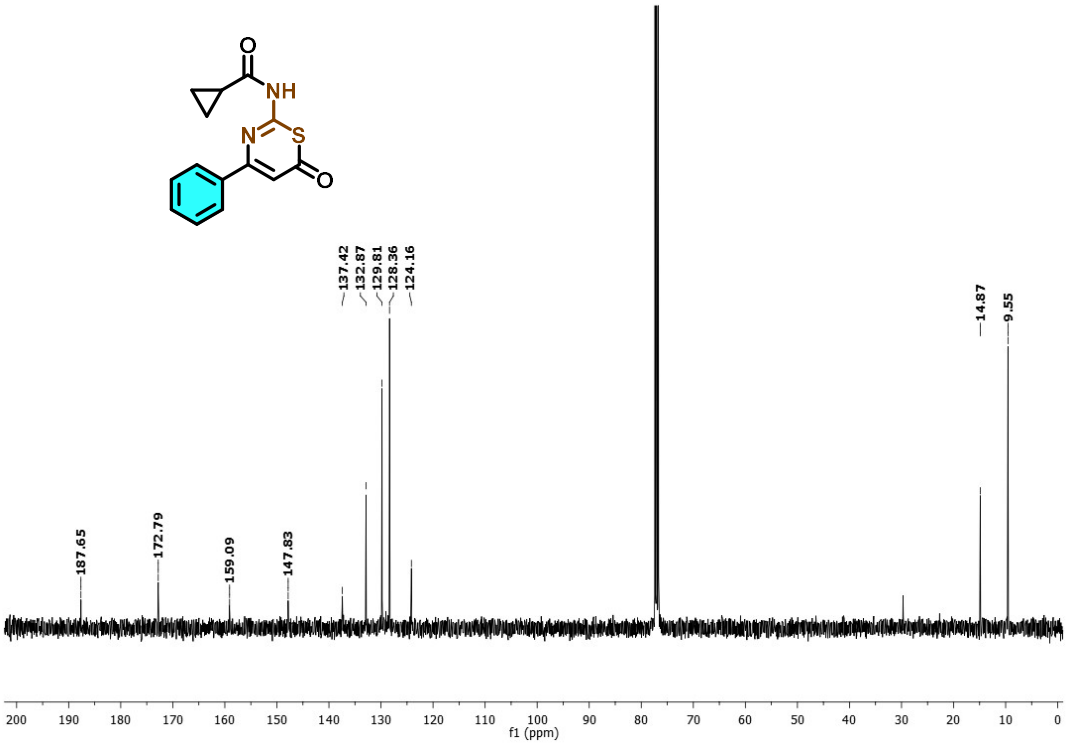
^{13}C{^{1}H} -NMR (100 MHz, DMSO) spectrum of Compound **32**



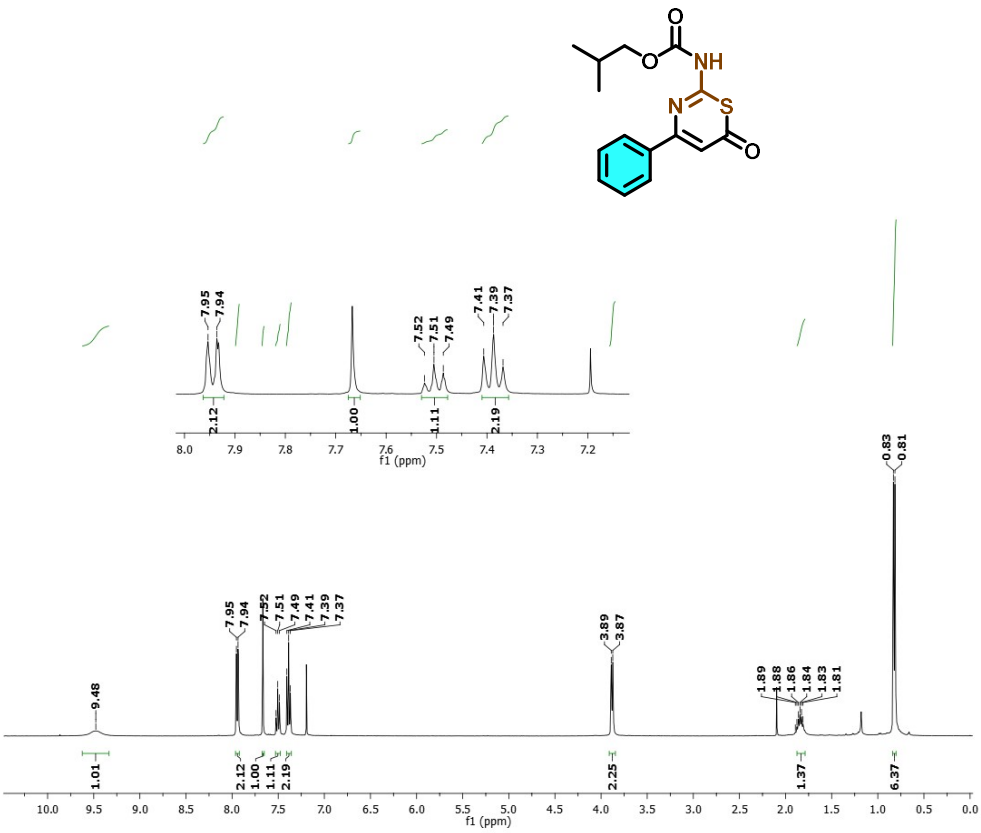
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **33**



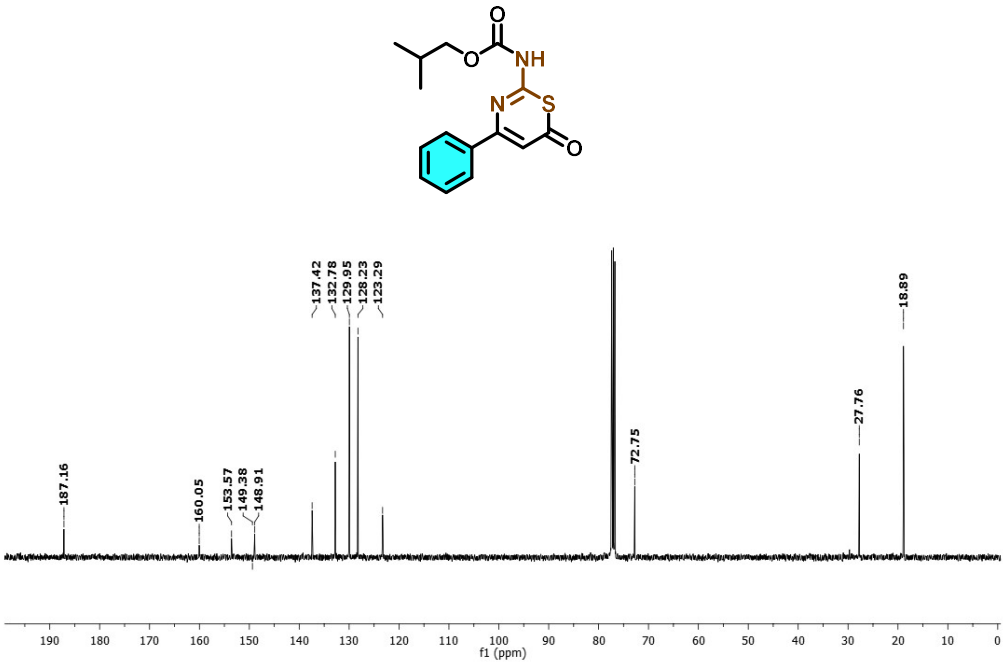
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **33**



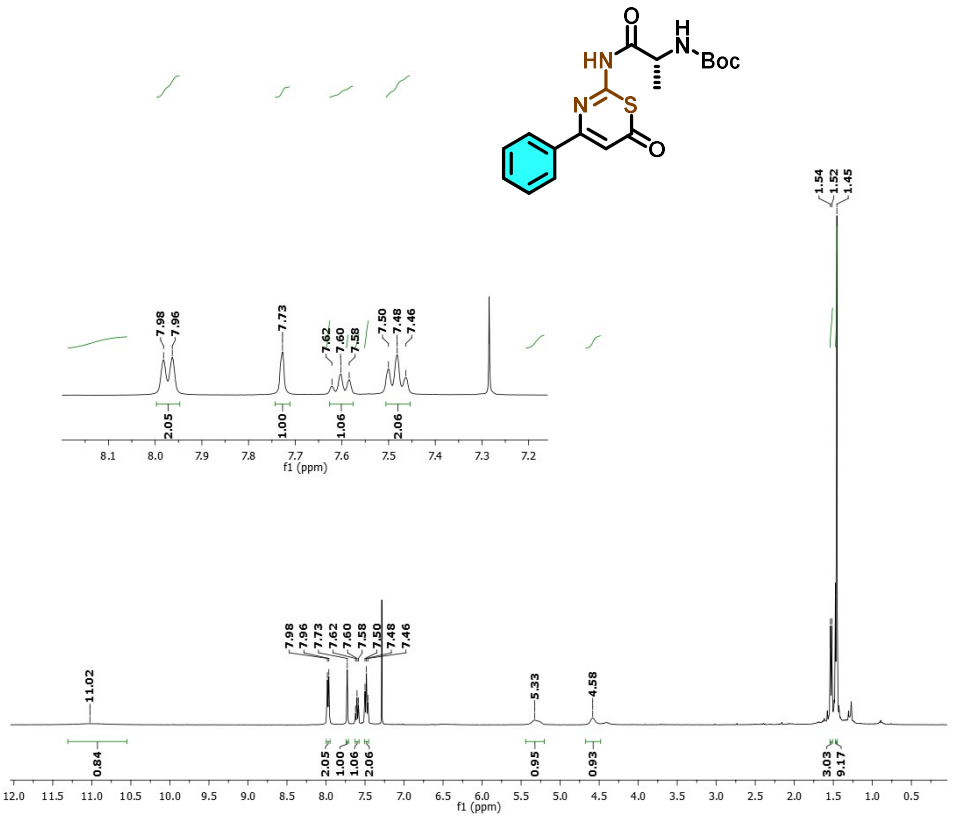
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **34**



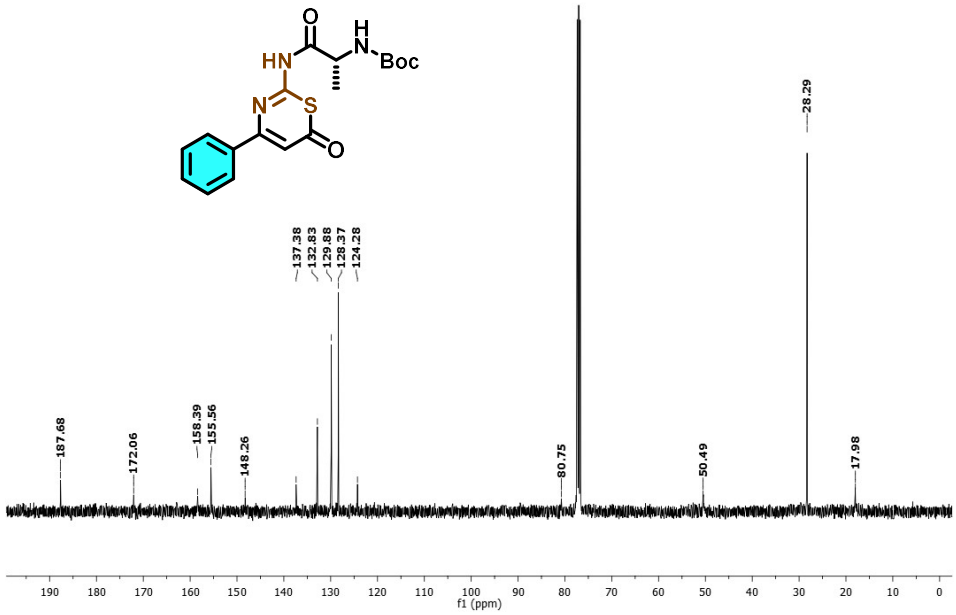
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **34**



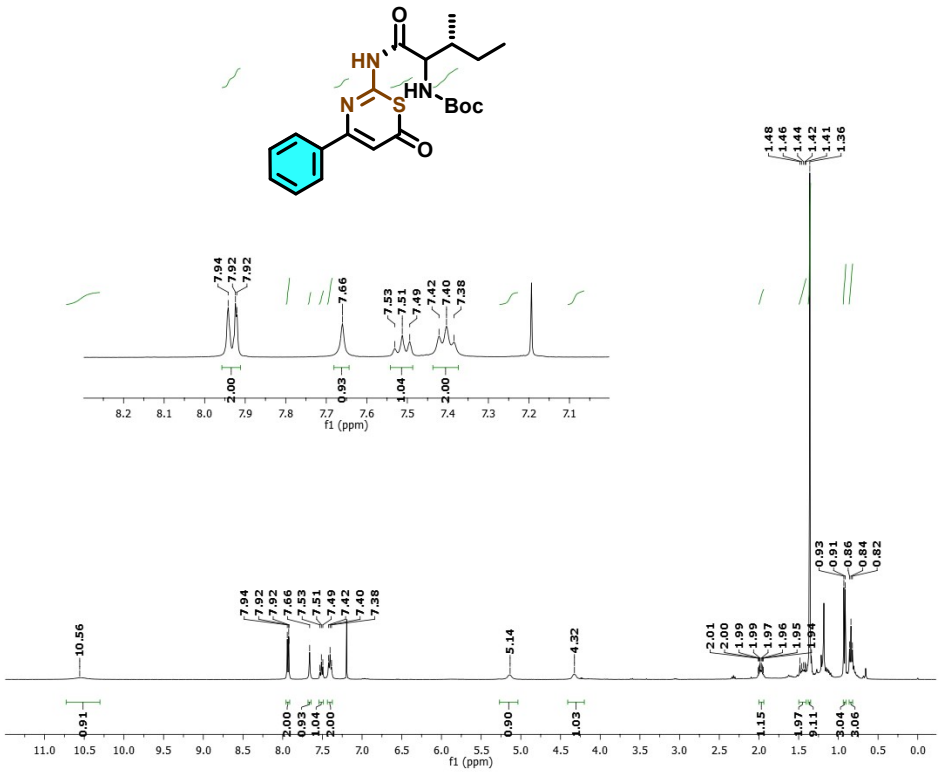
^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **35**



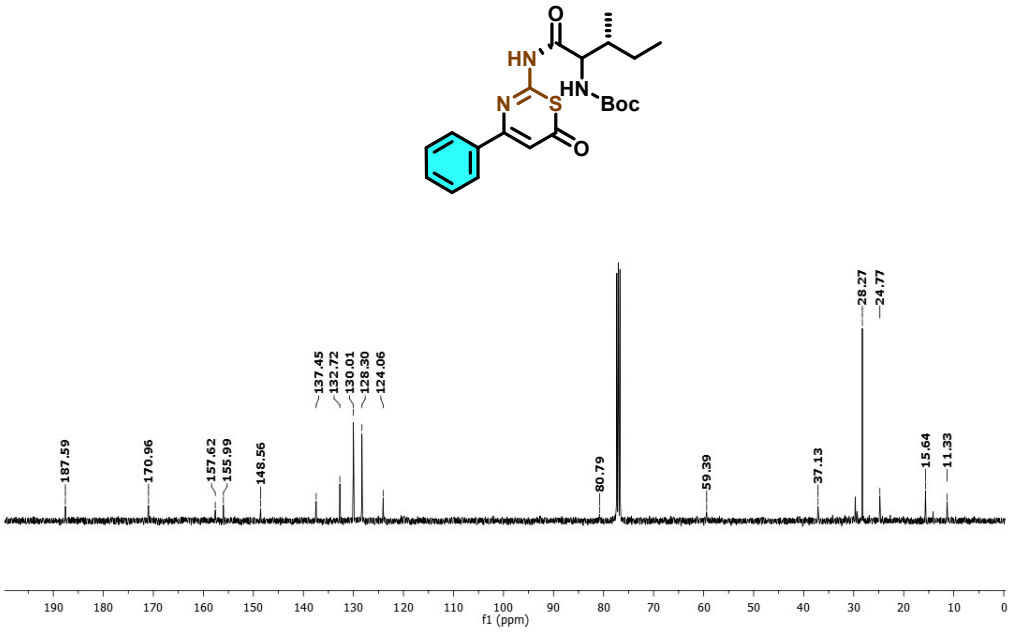
^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **35**



^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of Compound **36**



^{13}C{^{1}H} -NMR (100 MHz, $CDCl_3$) spectrum of Compound **36**



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