SUPPORTING INFORMATION

General Electron-Donor-Acceptor Complex Mediated Thioesterification Reaction *via* Site-Selective C-H Functionalization using Aryl Sulfonium Salts

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1. General Information

Chemicals: Commercially available reagents and analytical grade solvents were obtained from local suppliers and were used as received. Molecular Sieve 4Å (0.4 nm) (1.6 - 3 mm beads), were purchased from SRL chemicals (product code: 72866, CAS no: 70955-01-0) and were pre-heated in hot air oven for 2-hours prior to use.

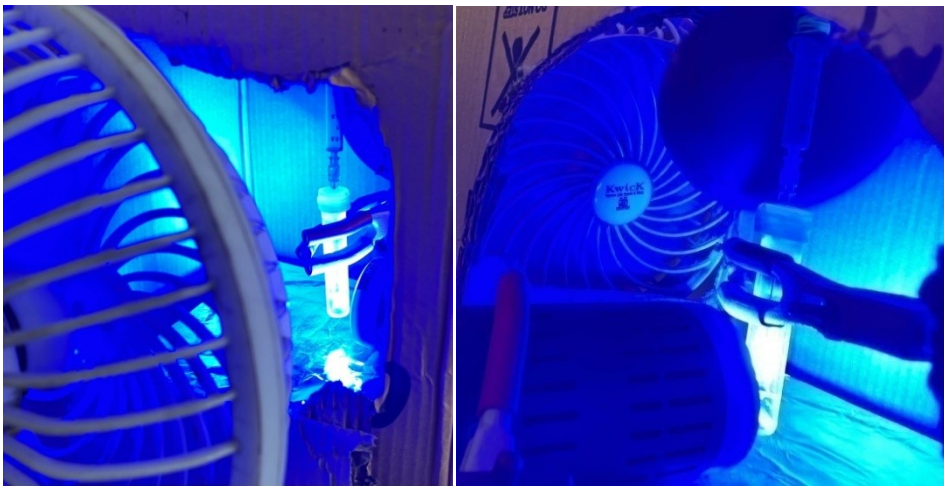
NMR Spectra: ^{1}H, ^{13}C and ^{19}F-NMR spectra were recorded on a JEOL (500 MHz ^{1}H, 126 MHz ^{13}C, 471 MHz ^{19}F) spectrometers using deuterated NMR solvents with tetramethylsilane (TMS) as internal standard. In the evaluation of ^{1}H-NMR spectra, chemical shift has been assigned in units of parts per million (ppm), wherein, “s” stands for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “qu” for quintet, “dd” for doublet of doublets”, “tt” for triplet of triplets, “dt” for doublet of triplets”, “td” for triplet of doublets” , ‘’sext’’ for (sextet) and “m” for multiplet. The units of coupling constant (J) has been assigned in Hz.

HRMS : High resolution mass spectra quadrupole time-of-flight (HRMS-QTOF) was obtained in ESI mode.

Chromatography: Reactions were monitored on Merck TLC silica gel 60 F254 plates and visualized using ultraviolet light of wavelength 254 nm. Column chromatography was performed on silica gel (100-200 mesh), eluted with hexane/ethyl acetate as mobile phase.

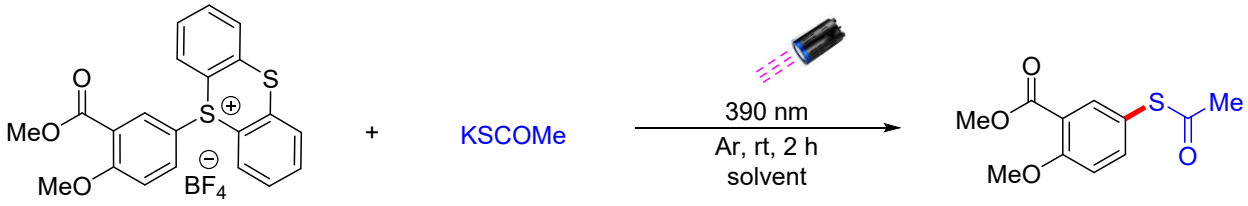
Melting points (mp): Measurements were recorded on a OptiMelt, automated melting point apparatus (Stanford Research Systems, Inc.).

Photoreactor: Visible light reaction was performed using a 40W Kessil PR160L lamp (427 nm), placed 3 cm away from reaction vials. The reaction setup was placed within a ventilated fume hood and using a fan to avoid overheating.



2. Optimization of Reaction Conditions

2.1 Screening of Solvent

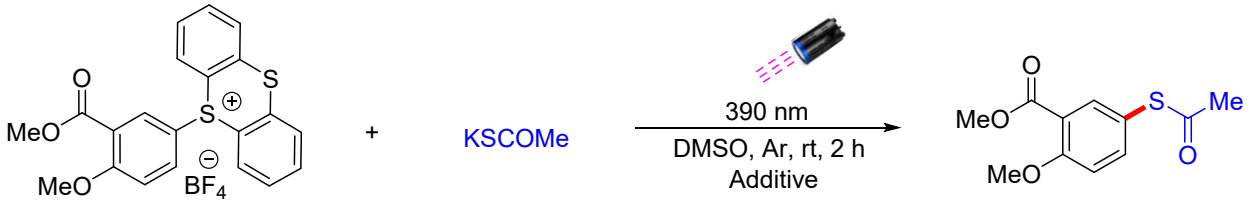


1a **2a** **3a**

Entry	Solvent	Isolated Yield (%)
1	DMSO	69%
2	MeCN	58%
3	DCM	37%
4	THF	25%
5	DMA	48%
6	DMF	43%
7	EtOAc	54%

Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv.) in solvent (0.8 mL) under purple Kessil (λ = 390 nm) irradiation for 2 h at rt under argon atmosphere.

2.2 Screening of Additive

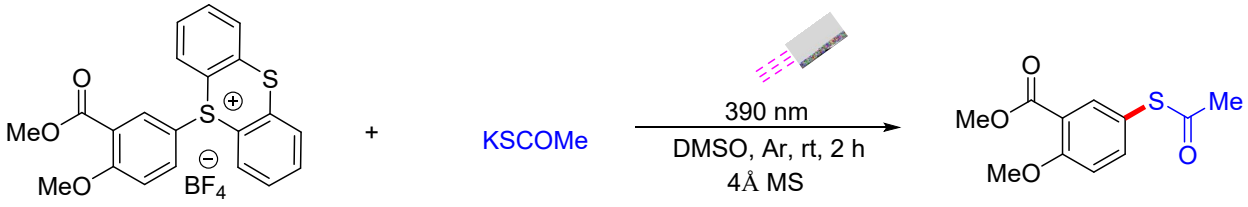


1a **2a** **3a**

Entry	Additive	Isolated Yield%
1	SiO_2 (20 mg)	72%
2	4Å MS (20 mg)	77%
3	3Å MS (20 mg)	70%
4	Basic alumia (20 mg)	73%
5	K_2CO_3	12%
6	Na_2CO_3	17%
7	K_2HPO_4	15%
8	Cs_2CO_3	21%

Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol, 2 equiv.), additive (0.2 mmol, 2 equiv.) in dry DMSO (0.8 mL) under purple Kessil (λ = 390 nm) irradiation for 2 h at rt under argon atmosphere.

2.3 Optimization of different equivalents of potassium thioacetate

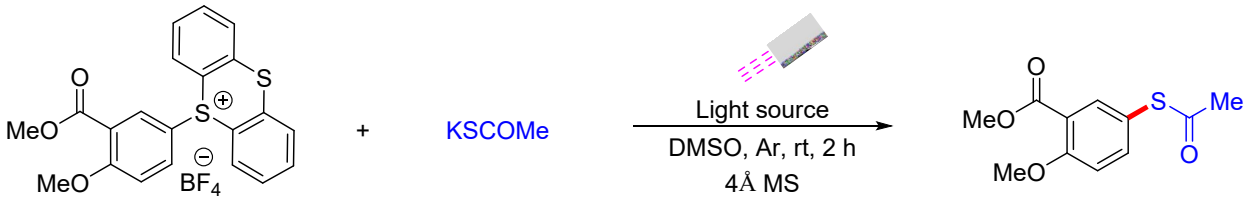


1a **2a** **3a**

Entry	**1a**	**2a**	Additive 4Å MS	Isolated Yield (%)
1	1 equiv.	1 equiv.	10 mg	57%
2	1 equiv.	2. equiv.	20 mg	77%
3	1 equiv.	2.5 equiv.	25 mg	77%

Reaction conditions: **1a** (0.1 mmol), **2** (x-equivalent), 4Å MS (x-mg) in dry DMSO (0.8 mL) under purple Kessil (λ = 390 nm) irradiation for 2 h at rt under argon atmosphere.

2.4 Screening of Light Irradiation



1a **2a** **3a**

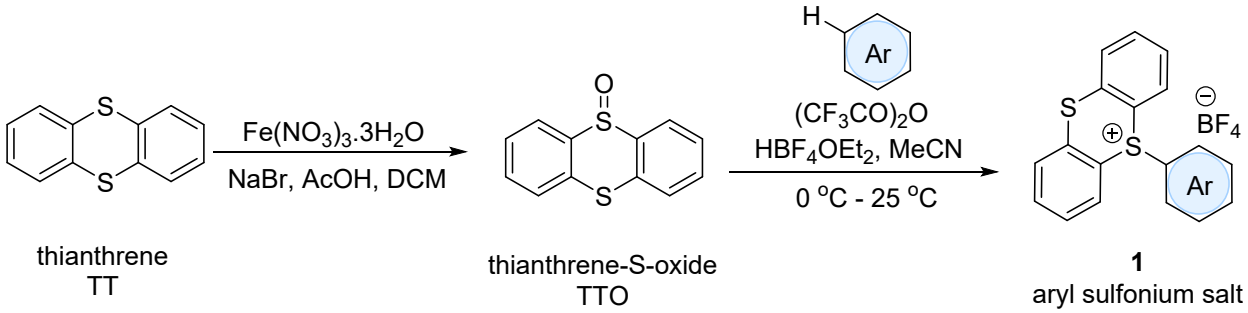
Entry	Light source	Isolated Yield[a]
1	390 nm Purple Kessil	77%
2	427 nm Blue Kessil	**85% (83%)[b]**
3	440 nm Blue Kessil	62%
4	456 nm Blue Kessil	50%
5	3W Green LED strips	trace
6	Dark (no light)	nr
7	427 nm Blue Kessil	72%[c]
8	427 nm Blue Kessil	83%[d]

[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.2 mmol, 2-equiv.), 4Å MS (20 mg) in dry DMSO (0.8 mL) under various light source for 2 h at rt under argon atmosphere. [b] **1a** (0.3 mmol), and **2a** (0.6 mmol, 2.0 equiv.), dry DMSO (1.5 mL), 4Å MS (60 mg), 2h; [c]open-to-air, [d] **1a** (0.3 mmol), and **2a** (0.6 mmol, 2.0 equiv.), dry DMSO (1.5 mL), 4Å MS (60 mg), 30 min; nr = no reaction.

3. General Procedure and Characterization of Products

3.1 General procedure for the synthesis of aryl sulfonium salts

The aryl sulfonium salts (1a-z) shown in Figure S1 were prepared according to previously described methods in the literature.[1]



(**step-1**) **Thianthrene to thianthrene-S-oxide synthesis**:[1] According to the modified procedure, 100 mL round-bottom flask was charged with thianthrene (1.081 g, 5.0 mmol, 1.0 equiv.), $Fe(NO_3)_3 \cdot 9H_2O$ (2.02 g, 5.0 mmol, 1.0 equiv.) and NaBr (20 mg, 4.0 mol%). DCM (20.0 mL) and AcOH (0.2 mL). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with H_2O (20 mL) and poured into a 125 mL separatory funnel. The aqueous and the organic layer were separated. The aqueous layer was extracted with DCM (ca. 10 mL x 2). The organic layers were combined, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting solid was recrystallized from EtOAc and dried in vacuo to afford thianthrene-S-oxide.

(**step-2**) **Thianthrene-S-oxide to aryl sulfonium salt synthesis**:[1]

Under an ambient atmosphere, a 50 mL round-bottom flask was charged with arene (2.0 mmol, 1.0 equiv.) and dry MeCN (5.0 mL). After cooling to 0 °C, $HBF_4 \cdot OEt_2$ (1.5 equiv.) was added to the vial while stirring the reaction mixture. After, thianthrenium-S-oxide (TTO) (2.0 mmol, 1.0 equiv.) was added in one portion to the solution at 0 ℃, leading to a suspension. Subsequently, trifluoroacetic anhydride (3.0 equiv.) was added in one portion, resulting in a color change to deep purple. The flask was sealed with a septum. The mixture was stirred at 0 ℃ for 1 h, subsequently the reaction mixture was warmed to 25 ℃ and stirred for 12 h. The solution was poured onto a mixture of 10 mL dichloromethane, 10 mL saturated aqueous Na_2CO_3 solution, and 10 mL water. After stirring for 5 min, the mixture was poured into a 125 mL separatory funnel, and the layers were separated. The organic layer was washed with aqueous $NaBF_4$ solution (2 × ca. 10 mL, 5 % w/w) and with water (2 × 10 mL). Then the organic layer was dried over Na_2SO_4, then filtered and concentrated under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM/MeOH and purified by precipitation with Et_2O/DCM, the solid was dried in vacuo to afford the aryl sulfonium salts.

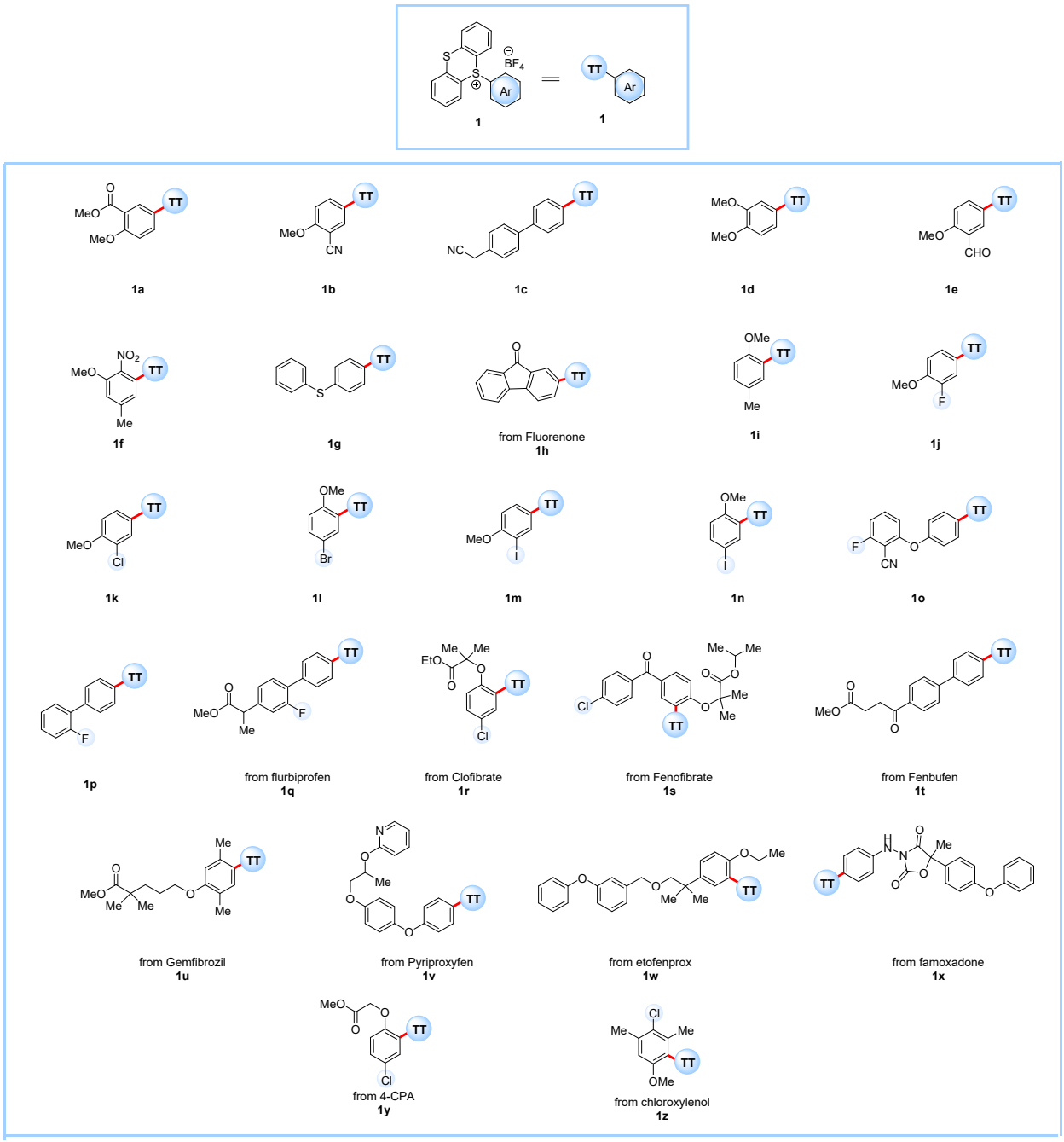
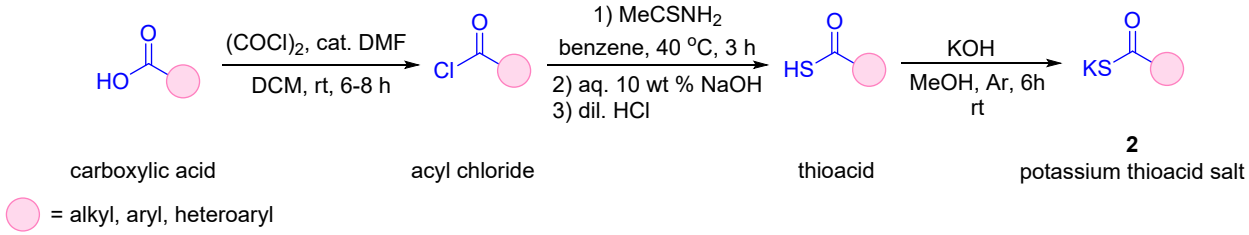


Figure 1. Various aryl sulfonium salts **1a-1z** used in this experiment

3.2 General procedure for the synthesis of potassium thioacid salts.



(**step-1**) **Carboxylic acid to acyl chloride synthesis**: To a oven dried 100 mL round-bottom flask, equipped with a magnetic stirrer, was charged with carboxylic acid (5 mmol), dried DCM (10 mL) followed by addition of catalytic amount of DMF (40 µL). The reaction mixture was cooled to 0 °C and stirred for 5 minutes, then oxalyl chloride $(COCl)_2$ (1.2 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 6-8 h. Later, the resulting reaction mixture was concentrated under reduced pressure to give access to acid chloride quantitatively, which was utilized for the next step directly without further purification.

(**step-2**) **Acyl chloride to thioacid synthesis**:[2] To the round bottom flask containing acyl chloride mixture, equipped with a magnetic stirrer, was added thioacetamide (5 mmol, 1 equiv.), followed by 20 mL benzene. The reaction flask was sealed with rubber septum, and stirred for 3 h at 40 °C in an oil bath. After completion of the reaction, aqueous solution of 10% NaOH (30 mL) was added and the reaction mixture was stirred for an additional 30 minutes. Thereafter, the reaction mixture was transfer to an 125 mL separation funnel and the aqueous layer was isolated and was acidified by dropwise addition of conc. HCl (to pH: 2). The reaction mixture was then extracted with ethyl acetate (2 x 20 mL) and the combined organic layers was dried over Na_2SO_4. The mixture was concentrated under reduced pressure to afford the required thioacid product, which was used for the next step without further purification.

(**step-3**) **Thioacid to potassium thioacid salt synthesis**:[3] To a oven dried 25 mL round-bottom flask, equipped with a magnetic stirrer, was charged with thioacid (2 mmol), followed by 10 mL methanol and potassium hydroxide (2 mmol, 1 equiv.). The reaction mixture was stirred under argon atmosphere at room temperature for 6 h. After completion, the solvent was removed under reduced pressure. The crude was the azeotropically dried with 10 mL benzene. This procedure was repeated 3 times and the desired product was used for the photochemical reaction without further purification.

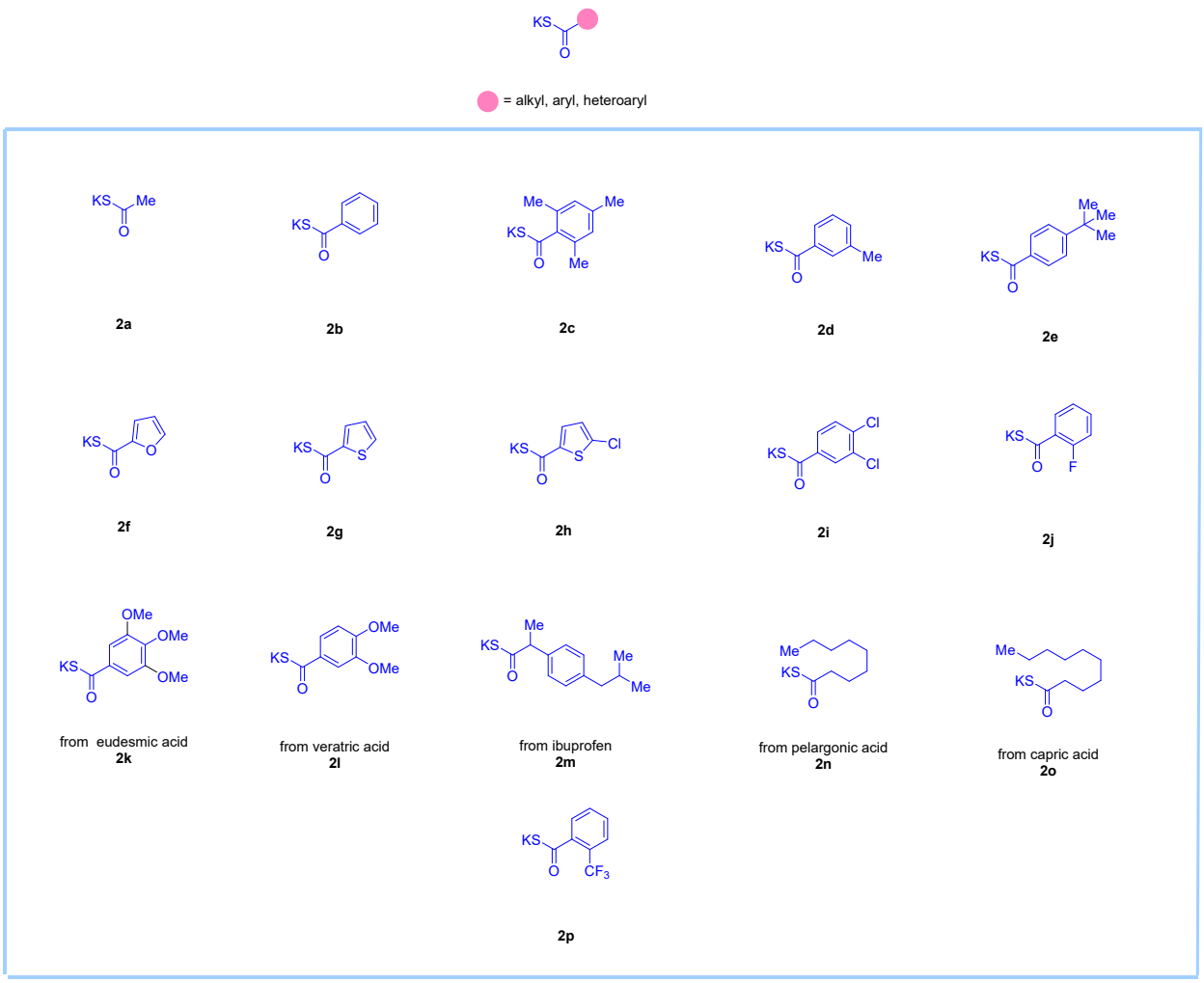
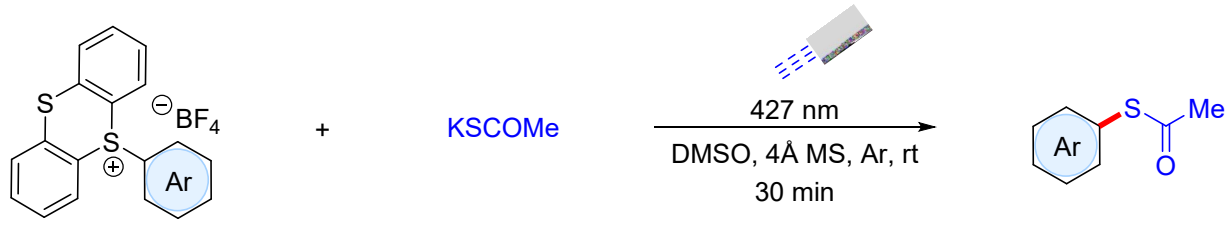


Figure 2. Various potassium thioacids **2a**-**2p** used in this experiment

Compound **2a** was purchased from local suppliers.
Compound **2b** was synthesis from corresponding thiobenzoic acid *via* **step-3**.
Compounds **2c**-**2e** was synthesis from corresponding acyl chlorides from **step-2**.
Compounds **2f**-**2p** was synthesis from corresponding carboxylic acids from **step-1**.

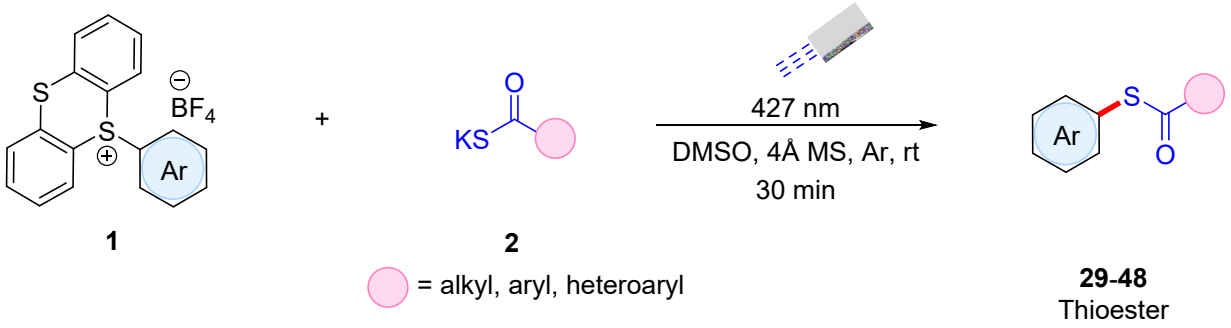
3.3 General procedure-A for the synthesis of aryl thioester using potassium thioacetate.



1 **2a** **3-28** Thioester

To a glass vial, charged with magnetic stir bar was added aryl thianthrenium salt **1** (0.3 mmol), potassium thioacetate **2a** (69 mg, 0.6 mmol, 2 equiv.), 60 mg 4Å MS and 1.5 mL dry DMSO. The glass vial was closed with septum and covered with Parafilm. The glass vial was purged with argon for 10 min. and placed in the reaction setup. The reaction was irradiated for 30 min (unless otherwise stated) with 40W Kessil lamp (λ_{max} = 427 nm, placed at a distance of 3 cm). After the completion of the reaction, the reaction was quenched with brine solution and the mixture was extracted with ethyl acetate. The combined organic layer was washed with H_2O, and then dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding desired thioester product.

3.4 General procedure-B for the synthesis of aryl thioester using different potassium thioacid salts.



1 **2**

= alkyl, aryl, heteroaryl

29-48 Thioester

To a glass vial, charged with magnetic stir bar was added aryl thianthrenium salt **1** (0.3 mmol), potassium thioacid **2** (0.6 mmol, 2 equiv.), 60 mg 4Å MS and 1.5 mL dry DMSO. The glass vial was closed with septum and covered with Parafilm. The glass vial was purged with argon for 10 min. and placed in the reaction setup. The reaction was irradiated for 30 min (unless otherwise stated) with 40W Kessil lamp (λ_{max} = 427nm, placed at a distance of 3 cm). After the completion of the reaction, the reaction was quenched with brine solution and the mixture was extracted with ethyl acetate. The combined organic layer was washed with saturated solution of $NaHCO_3$ (10 mL x2) and with H_2O (10 mL x2). Then, the

organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding desired thioester product.

3.5. Unsuitable substrates

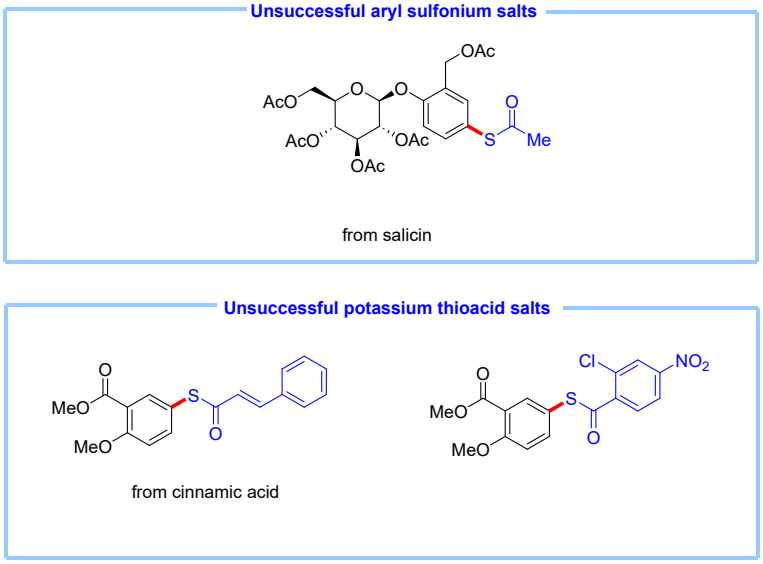


Figure 3. Unsuitable substrates

4. Mechanistic studies

4.1 UV-visible absorption spectra

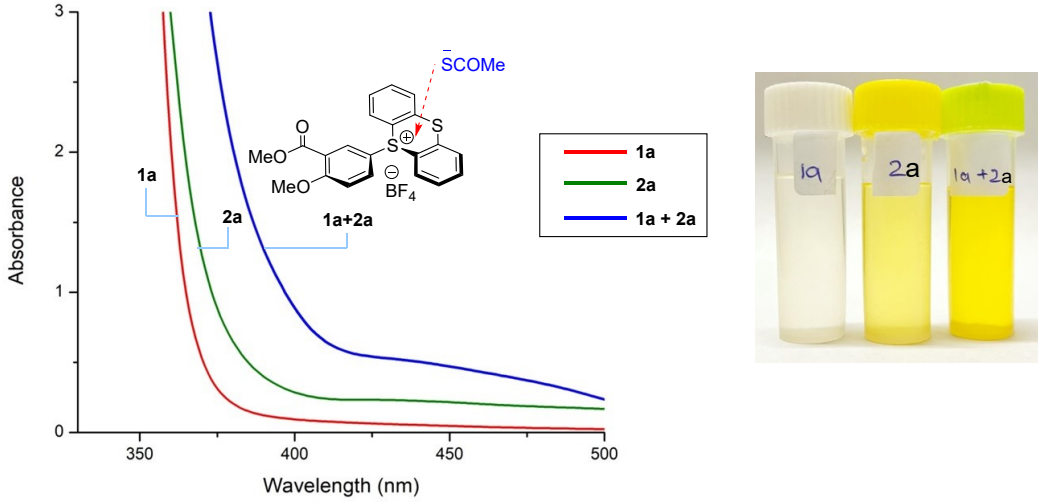
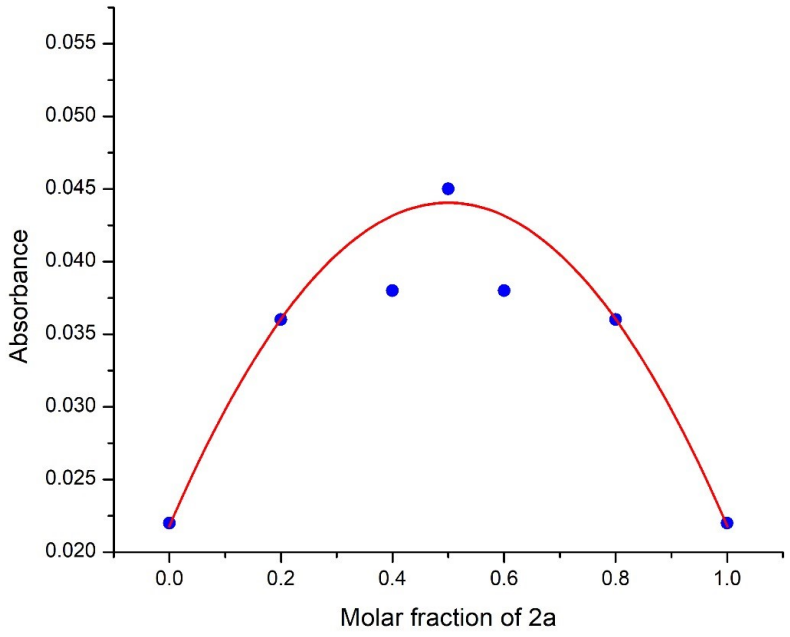


Figure 4: UV-visible spectra experiments measured in DMSO and visual appearance of individual components and reaction mixture.

UV/vis absorption spectra were recorded using Shimadzu UV-Vis 2600 spectrophotometer in the range of 200-800 nm in a 1 cm quartz cuvette. The UV/vis absorption spectra of the individual components and reaction mixture were thereof measured. A clear bathochromic shift was observed (blue band) of the reaction mixture (**1a + 2a**) in DMSO, which clearly indicates the formation of an electron donor-acceptor (EDA) complex. Moreover, the images show a clear transparent color of methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a**, a pale yellow color of potassium thioacetate **2a**, and an intense yellow color of the reaction mixture (**1a +2a**) in dried DMSO, which further speculate the formation of an EDA-complex aggregate.

4.2 Job's plot

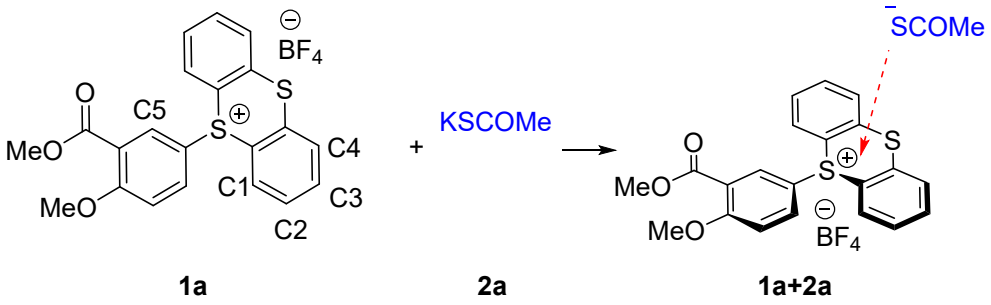
The absorbance values at 427 nm were monitored and plotted as a function of molar fraction of methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a**, and potassium thioacetate **2a** in DMSO. A parabolic curve with a maximum absorbance value at 50% mol fraction was obtained, indicating a 1:1 EDA complex between **1a** and potassium thioacetate **2a**.



4.3. ^{1}H-NMR titration experiment

^{1}H NMR spectra of mixtures of methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** and potassium thioacetate **2a** in DMSO-d_6 were recorded at 300 K. In an NMR tube, the total volume of the mixture was 0.6 mL, the concentration of methyl-2-methoxybenzoate-derived thianthrenium

tetrafluoroborate **1a** (0.03 mmol) was kept constant at 0.05 M, and that of potassium thioacetate **2a** was varied from 0 to 1.5 M. The molar ratios of methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a**: potassium thioacetate **2a** were 1:0, 1:1, 1:3, 1:9, 1:12 in DMSO-d_6. The ^{1}H NMR signal of C1-H in methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** shifted downfield along with increasing the amount of potassium thioacetate **2a**, while C4-H, C3-H, C2-H, and C5-H shifted upfield,[4] indicating the formation of EDA complex between methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** with potassium thioacetate **2a**.



1a **2a** **1a+2a**

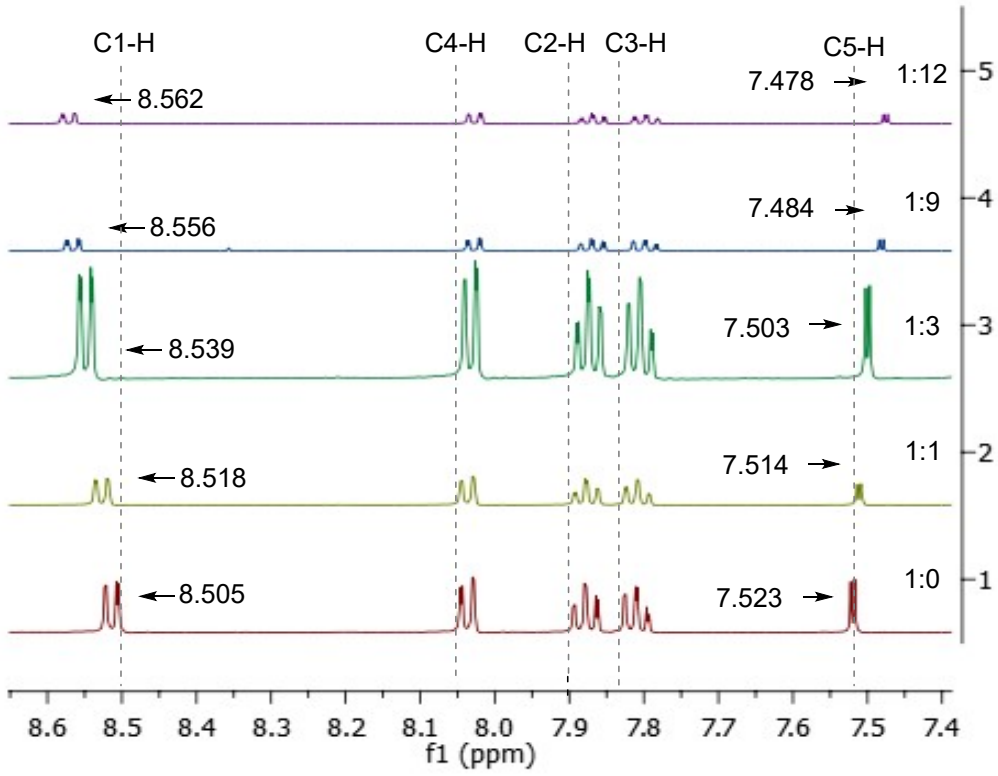
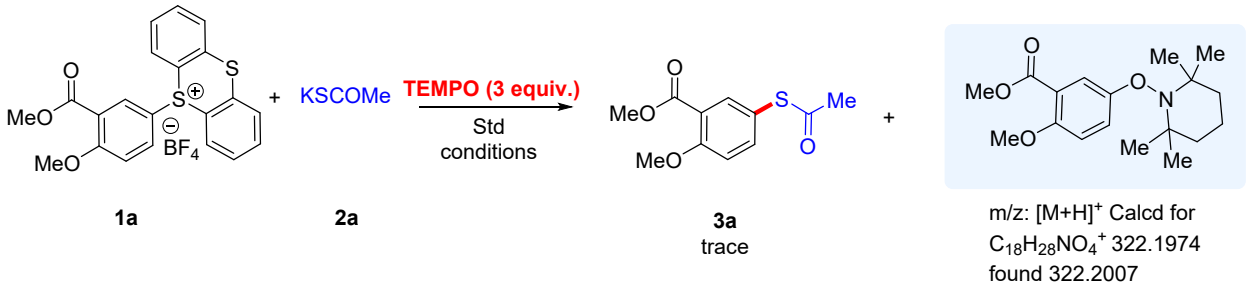


Figure 5: ^{1}H-NMR shift of methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1** with potassium thioacetate **2a**

4.4 Radical Trapping Experiments

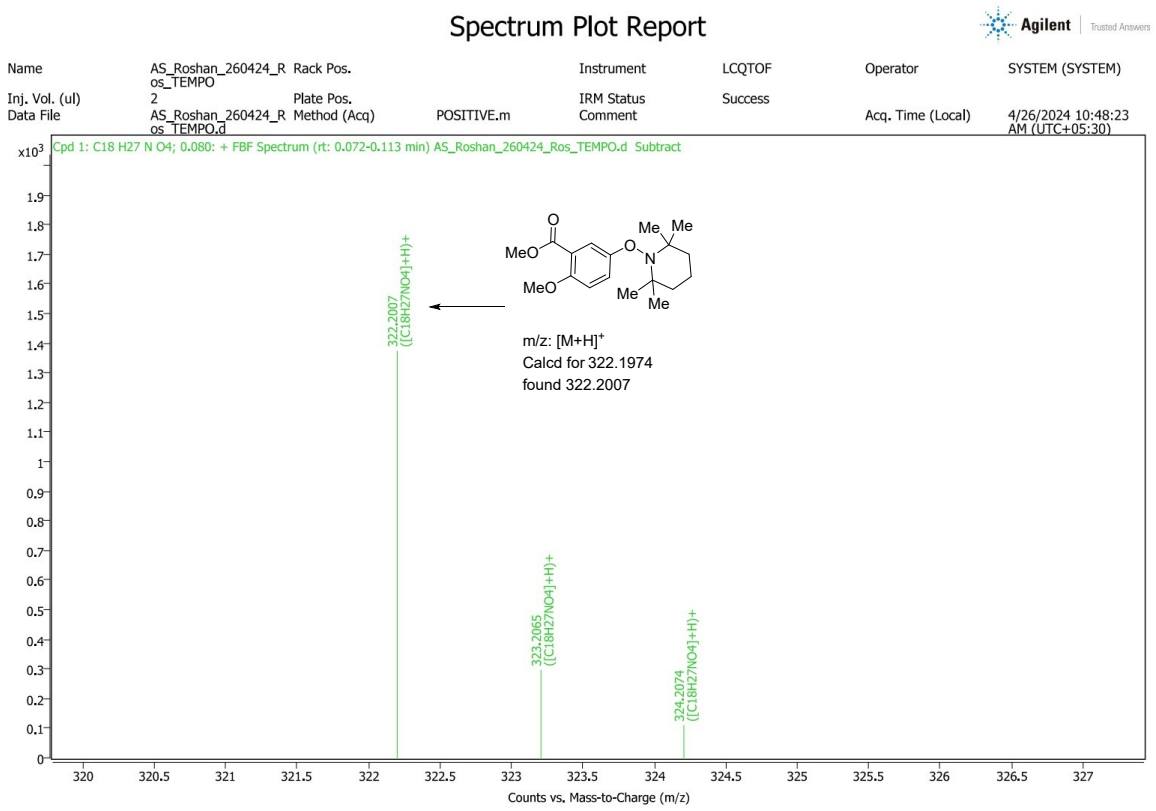
To a glass vial, charged with magnetic stir bar was added methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** (140 mg, 0.3 mmol), potassium thioacetate **2a** (69 mg, 0.6 mmol, 2.0 equiv.), TEMPO (141 mg, 0.9 mmol, 3.0 equiv), 60 mg 4Å MS. Then, dry DMSO (1.5 mL) was added and glass vial was closed with rubber septum. The glass vial was then purged with argon for 10 min, and reaction was stirred and irradiated with a 427 nm Kessil LED lamp (approximately 3 cm away from the light source) at room temperature for 30 min. The reaction was completely quenched and product **3a** was obtained in trace amount. Furthermore, the TEMPO-adduct was detected by HRMS. The TEMPO-adduct indicates the formation of an aryl radical intermediate in the reaction.

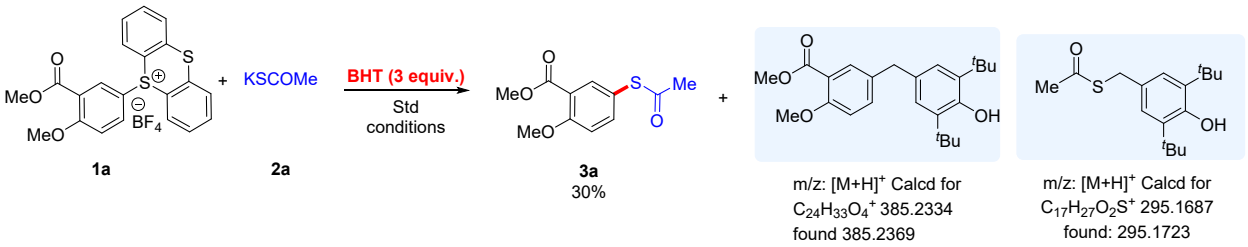


1a **2a** **3a** trace

m/z: $[M+H]^+$ Calcd for $C_{18}H_{28}NO_4^+$ 322.1974
found 322.2007

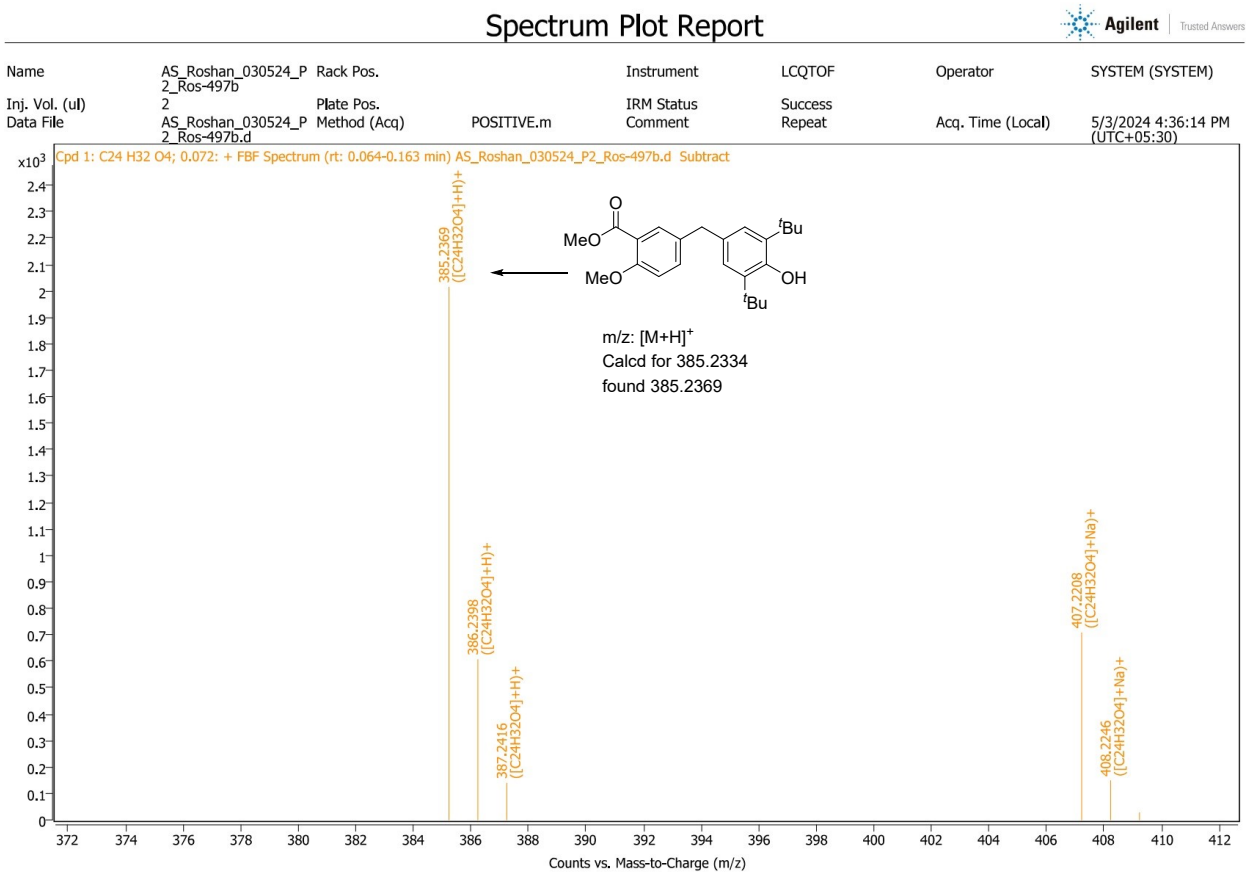
Scheme 1. Radical trapping experiment with TEMPO

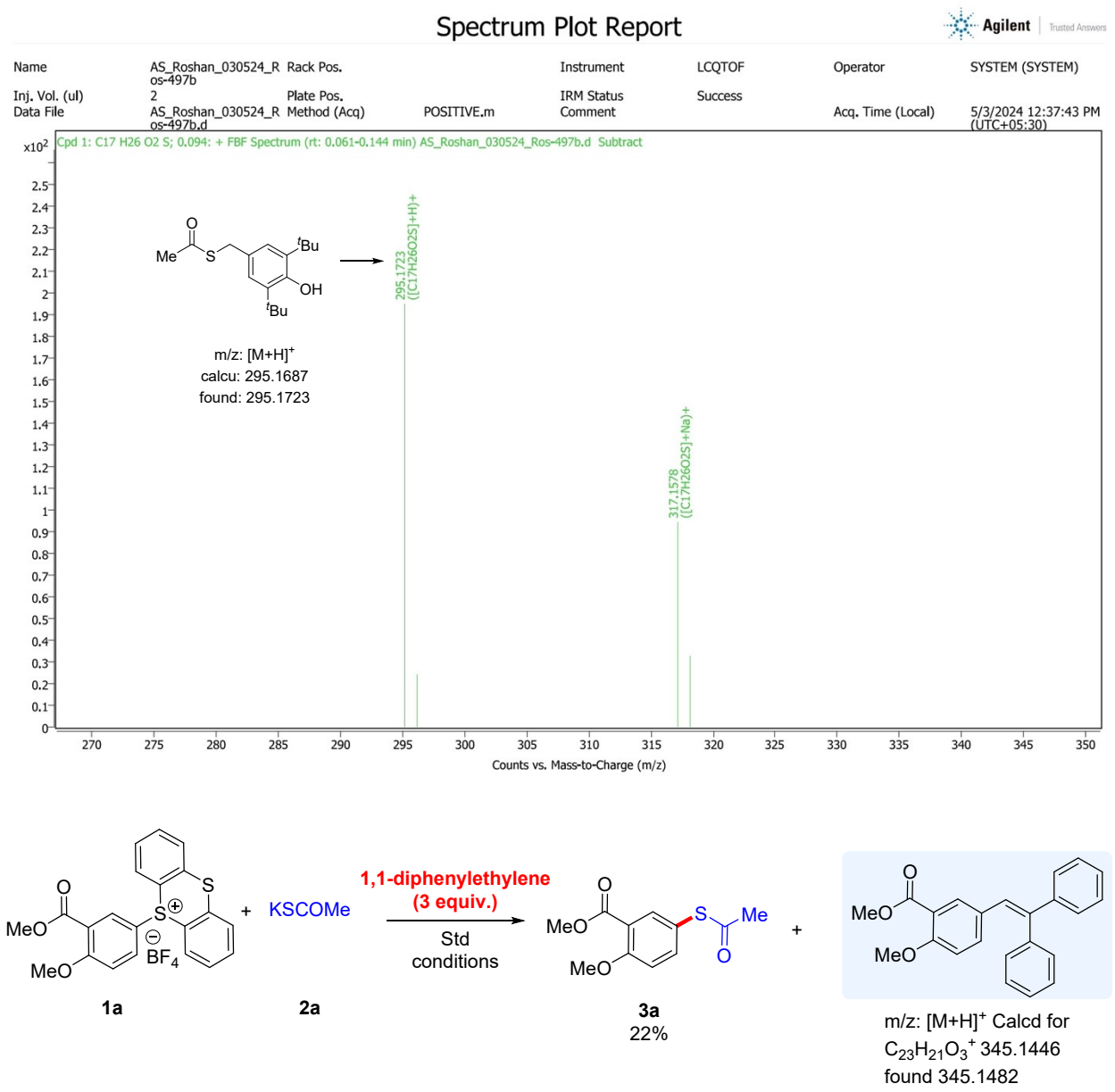




Scheme 2. Radical trapping experiment with BHT

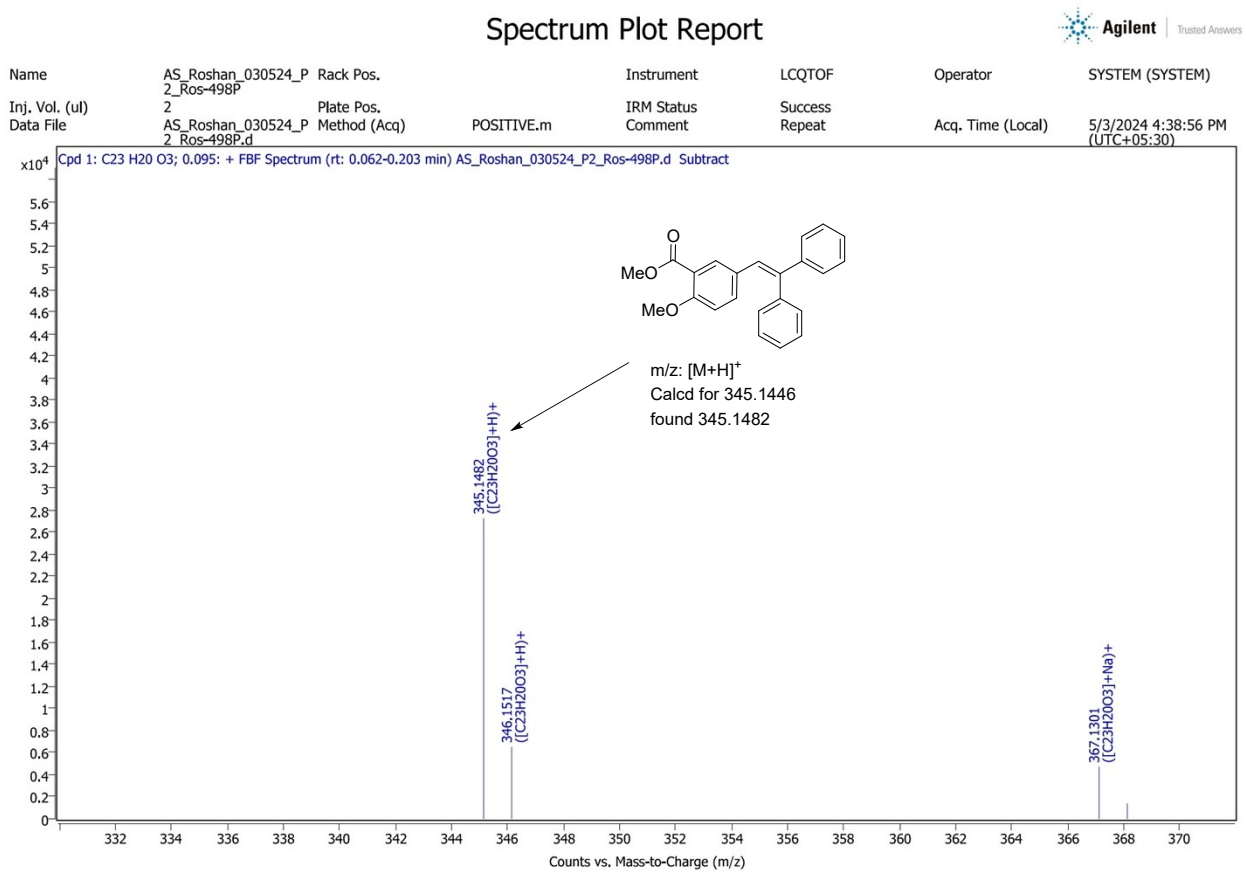
To a glass vial, charged with magnetic stir bar was added methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** (140 mg, 0.3 mmol), potassium thioacetate **2** (69 mg, 0.6 mmol, 2.0 equiv.), BHT (193 mg, 0.9 mmol, 3.0 equiv), 60 mg 4Å MS. Then, dry DMSO (1.5 mL) was added and glass vial was closed with rubber septum. The glass vial was then purged with argon for 10 min, and reaction was stirred and irradiated with a 427 nm Kessil LED lamp (approximately 3 cm away from the light source) at room temperature for 30 min. The reaction was completely quenched and product **3a** was obtained in 30% yield and the BHT-adducts was detected by HRMS. The BHT-adducts indicates the formation of an aryl radical intermediate as well as thiyl radical intermediate in the photochemical transformation.





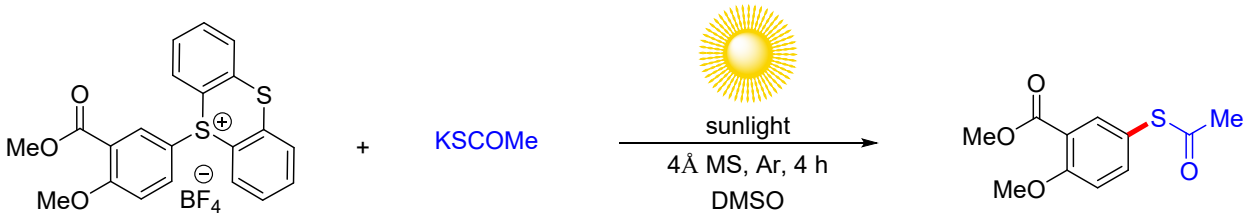
Scheme 3. Radical trapping experiment with 1,1-diphenylethylene

To a glass vial, charged with magnetic stir bar was added methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** (140 mg, 0.3 mmol), potassium thioacetate **2** (69 mg, 0.6 mmol, 2.0 equiv.), 1,1-diphenylethylene (162 mg, 0.9 mmol, 3.0 equiv), 60 mg 4Å MS. Then, dry DMSO (1.5 mL) was added and glass vial was closed with rubber septum. The glass vial was then purged with argon for 10 min, and reaction was stirred and irradiated with a 427 nm Kessil LED lamp (approximately 3 cm away from the light source) at room temperature for 30 min. The reaction was completely quenched and product **3a** was isolated in 22% yield and the 1,1-diphenyethylene-adduct was detected by HRMS.



4.5 Natural sunlight irradiation

Reaction setup under sunlight



1a
0.5 mmol

2a
(1.0 mmol)

3a
70%

To a glass vial, charged with magnetic stir bar was added methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a** (234.1 mg, 0.5 mmol), potassium thioacetate **2** (114.2 mg, 1.0 mmol, 2.0 equiv.), 100 mg 4Å MS. Then, dry DMSO (2.0 mL) was added and glass vial was closed with rubber septum. The glass vial was then purged with argon for 10 min. Then the reaction was carried out under natural sunlight for 4 h (from 11:00 am to 15:00 pm, 09/12/2023, Roorkee, IIT Roorkee, Uttarakhand, India, Temperature 21 °C -24 °C, location: 29°51'45''N 77°53'46''E). After the completion of the reaction, the reaction was quenched with brine solution and the mixture was extracted with ethyl acetate. The combined organic layer was washed with H_2O, and then dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding desired methyl 5-(acetylthio)-2-methoxybenzoate product **3a** in 70% yield (84 mg).

4.6. Quantum Yield (Φ)

A ferrioxalate actinometer solution was prepared following the Hammond variation of the Hatchard and Parker procedure[5] outlined in the Handbook of Photochemistry.[6] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The values of the quantum yield of potassium ferrioxalate are related to the concentration and wavelength.

The solutions were prepared and the flask was covered with aluminum foil:

1. Potassium ferrioxalate solution 0.012 M: Potassium ferrioxalate (147.4 mg) and 69.5 µL of sulfuric acid (96%) were added to a 25 mL volumetric flask and filled to the mark with water.

2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (50 mg in 25 mL).

3. Buffer solution: to a 100 mL volumetric flask, 4.94 g of NaOAc and 1.0 mL of sulfuric acid (96%) were added and filled to the mark with water.

A cuvette was loaded with 1.0 mL of potassium ferrioxalate solution and placed under 40W Kessil lamp (427 nm). The actinometer solution was irradiated for 90 s. After the irradiation, the actinometer

solution was carefully transferred into a 10 mL volumetric flask, then 0.5 mL of phenanthroline solution and 2.0 mL of buffer solution was added and the flask was filled up with water. The absorbance of the final solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

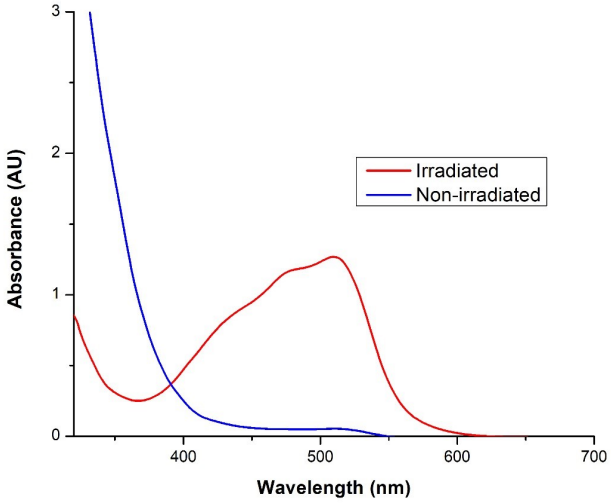


Figure 6. Absorption spectra for irradiated and non-irradiated samples of red $[Fe(phen)_3]^{+2}$

The moles of Fe^{2+} formed for the sample was determined using Beer's Law (Eq. 1):

$$mol\left(Fe^{+2}\right) = \frac{V1 \bullet V3 \bullet \Delta A\ (510\ nm)}{10^3 \bullet V2 \bullet I \bullet \epsilon\ (510\ nm)} \quad (4)$$

where V1 is the irradiated volume (1 mL), V2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), ΔA (510 nm) is the optical difference in absorbance between the irradiated solution and non-irradiated solution, ε (510 nm) is the extinction coefficient the complex $Fe(phen)_3^{2+}$ at 510 nm (11100 L mol^{-1} cm^1).

$$mol\left(Fe^{+2}\right) = \frac{1\ mL \bullet\ 10\ mL \bullet 1.215}{10^3 \bullet 1\ mL \bullet 1\ cm \bullet\ 11100\ L\ \ mol^{-1} cm^{-1}} = 1.094\ x\ 10^{-6}$$

fraction of light absorbed at 427 nm for the ferrioxalate solution are calculated by eq. 2

$$f = 1 - 10^{-A} \quad (2)$$

Absorption of ferrioxalate solution at 427 nm = 0.783

$$f = 1 - 10^{-0.783}$$

$$f = 0.835$$

The photon flux can be calculated using eq 3.

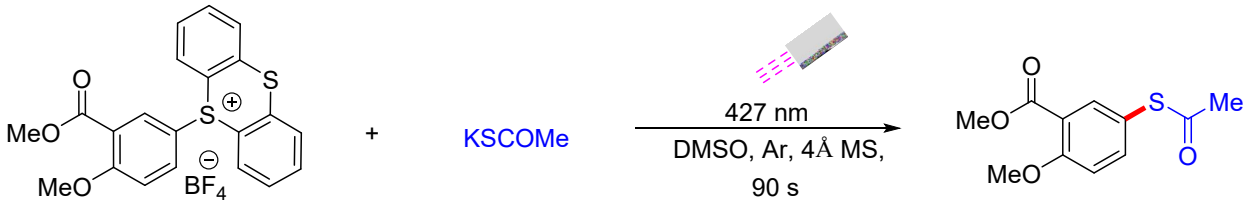
$$Photon\ flux = \frac{mol\ Fe^{+2}}{\Phi\left(Fe^{+2}\right) \bullet t \bullet f} \quad (3)$$

Φ (λ) = The quantum yield for Fe^{2+} formation at 427 nm is 1.11[7]

t = 90 s

$$Photon\ flux = \frac{1.094\ x\ 10^{-6}}{1.11 \bullet 90\ s \bullet 0.835} = 1.31x10^{-8}\ einstein\ s^{-1} \quad (3)$$

Quantum yield determination of photochemical reaction



1a **2a** **3a**

The reaction was performed under standard conditions with 90 second light irradiation, and the reaction produced 5 x 10^{-5} of the thioester product **3a**.

Therefore, the quantum yield of the reaction is determined to be:

$$Quantum\ yield\ \ (reaction\ at\ 427\ nm) = \frac{mol\ of\ formed\ product}{mol\ of\ photon\ flux \bullet t \bullet f} \quad (1)$$

Fraction of light absorbed at 427 nm for the photocatalytic reaction f = 1 – 10^{-A}

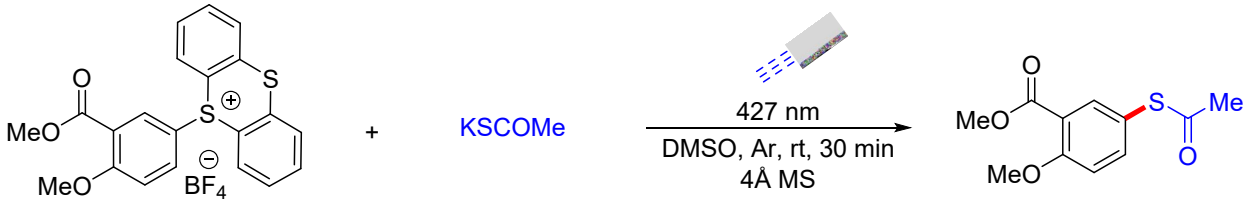
A = Absorption of photocatalytic reaction (1.575)

$$f = 1 - 10^{-1.575}$$

$$Quantum\ yield\ \ (reaction\ at\ 427\ nm) = \frac{f = 0.97}{\dfrac{5.0x10^{-5}\ mol}{1.31x10^{-8}\ einstein\ s^{-1} \bullet 90\ s \bullet 0.973}} = 44 \qquad (1)$$

The quantum yield studies indicate that this is a radical-chain process as evidenced by the **Φ** value.

4.7. Sensitivity assessment of reaction



1a **2** **3a**

1 equiv. 2 equiv.

Table 1. Preparation of sensitivity assessment of reaction

Entry	Parameter	Variation	Description	Yield[a]
1	High concentration (+10%)	*c* + 10% *c*	1.35 mL DMSO	83%
2	Low concentration (-10%)	*c* – 10% *c*	1.65 mL DMSO	81%
3	High H_2O	+H_2O; V_{H2O} = 1% V_{rxn}	10 µL H_2O in 1.5 mL DMSO	46%
4	O_2 level	O_2 ballon	O_2 ballon instead of Ar	64%
5	Low temperature (*T*)	*T* – 10 °C	15 °C	77%
6	High temperature (*T*)	*T* + 10 °C	cooling fan turned off	83%
7	Low intensity (*W*)	*d*. 4	Distance: 12 cm	70%
8	High intensity (*W*)	*d* / 4	Distance: 0.75 cm	82%
9	Big Scale	n.20	6 mmol of **1a**	48%

[a] Isolated yield.

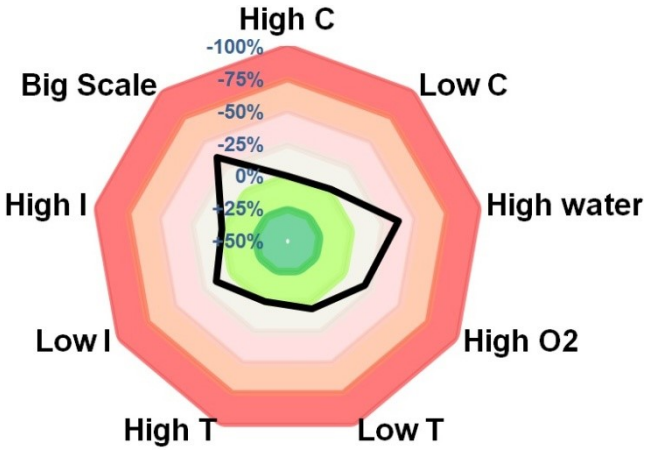
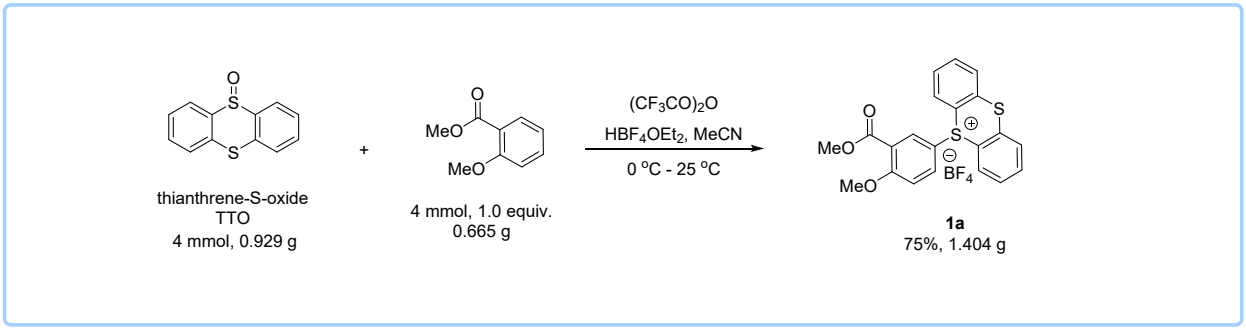


Figure 7: Sensitivity assessment of reaction towards concentration, water, oxygen, temperature, light intensity and large scale, is represented by a color-coded radar diagram. Deviation from standard reaction conditions is indicated by a black solid line.

4.8. Scale-up and recyclability of sulfonium salt



Synthesis of **1a**: The compound methyl-2-methoxybenzoate-derived thianthrenium tetrafluoroborate **1a**, was synthesized according general procedure 3.1, starting from thianthrene-S-oxide (0.929 g, 4 mmol) to yield the required compound **1a** in 75% yield (1.404 g), which was used for the photochemical scale-up reaction.

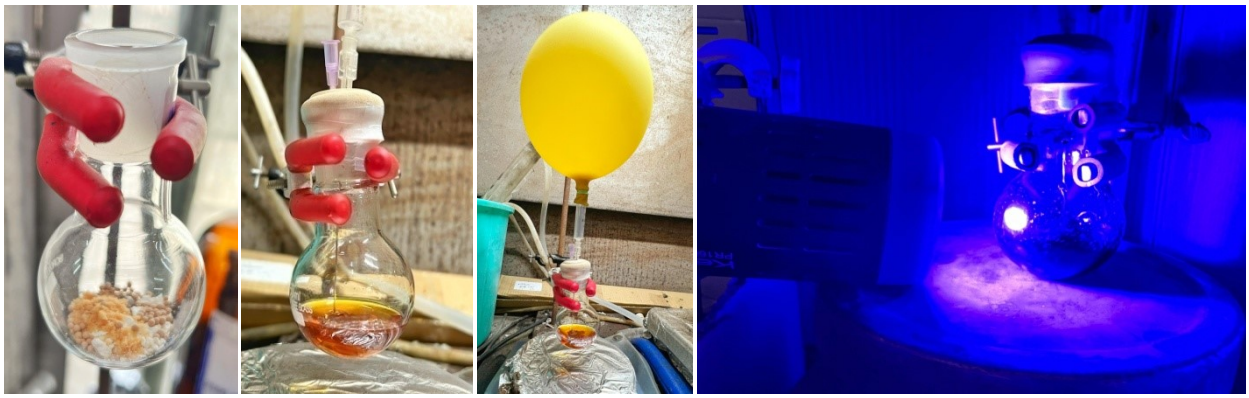
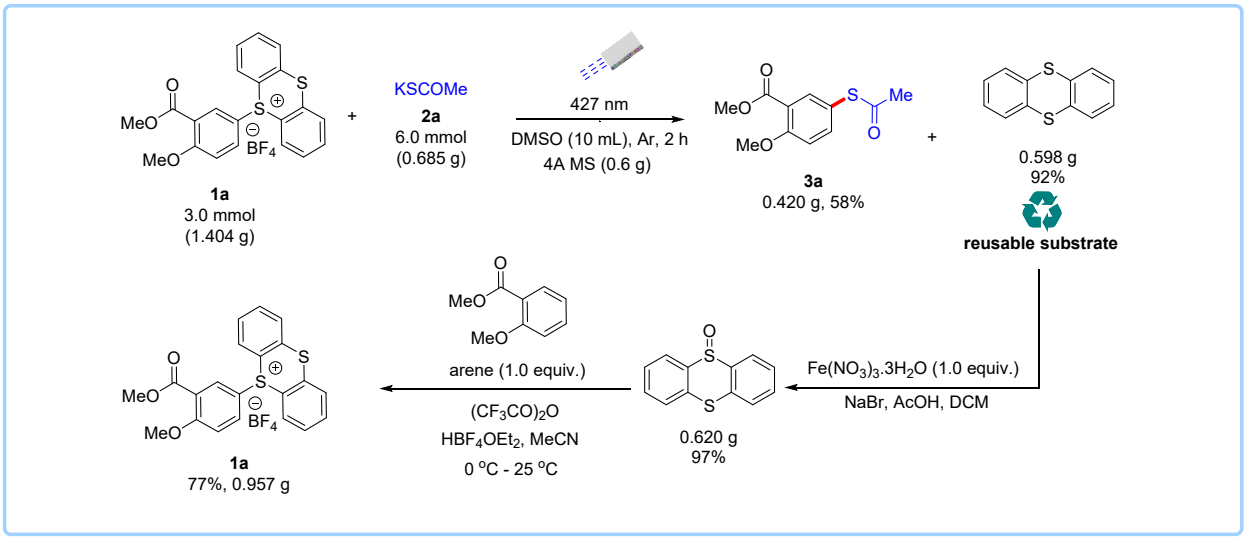


Figure 8. Gram scale synthesis reaction of compound **3a**.



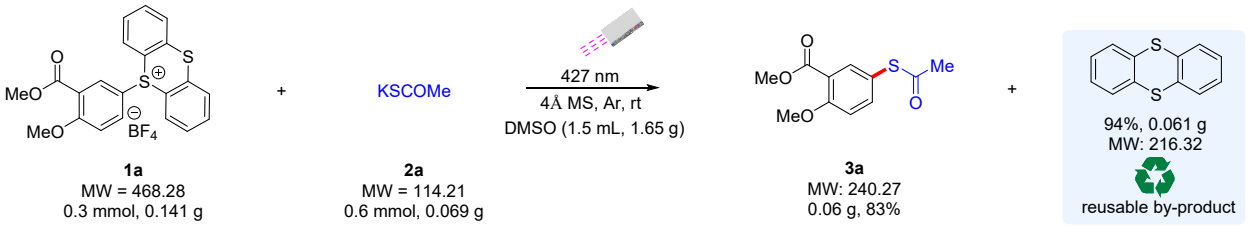
To a 25 mL round bottom flask equipped with a magnetic stir bar was added methyl-2-methoxybenzoate-derived sulfonium salt **1a** (1.404 g, 3.0 mmol), potassium thioacetate **2a** (0.685 g, 6.0 mmol, 2.0 equiv.), and 4Å molecular sieves (0.6 g). The flask was then charged with DMSO (10 mL) and was closed with a septum. The reaction mixture was purged with argon for 15 min and was irradiated for 2 h with a 40W Kessil LED lamp (λmax = 427 nm) with the temperature maintained by a fan. After irradiation, the mixture was quenched with brine solution, poured into a 250 mL separatory funnel, and extracted with EtOAc (20 mL x 3). The combined organic layer was washed with H_2O (20 mL x 3), and then dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified using column chromatography on silica gel, eluting with a hexane/ethyl acetate mixture, to yield methyl 5-(acetylthio)-2-methoxybenzoate **3a** at 58% yield (0.420 g). Moreover, thianthrene by-product was recovered in 92% yield (0.598 g).

To demonstrate the recyclability of thianthrene by-product, the recovered thianthrene (TT) is oxidized according to general procedure 3.1 to afford the thianthrene-S-oxide product in 97% yield (0.620 g). This

thianthrene-S-oxide is further converted to the required methyl-2-methoxybenzoate-derived sulfonium salt **1a** in 77% yield (0.957 g).

4.9. Calculations of Green Chemistry Metrics

(a) Procedure for the synthesis of compound 3a



To a glass vial, charged with magnetic stir bar was added methyl-2-methoxybenzoate-derived sulfonium salt **1a** (0.141 g, 0.3 mmol), potassium thioacetate **2** (0.069 g, 0.6 mmol, 2 equiv.), 0.06 g 4Å MS and dried DMSO (1.65 g, 1.5 mL). The glass vial was closed with septum and covered with Parafilm. The glass vial was then purged with argon for 10 min. The reaction was irradiated for 30 min with 40W Kessil lamp (λ_{max} = 427nm). After the completion of the reaction, the reaction was quenched with brine solution and the mixture was extracted with ethyl acetate. The combined organic layer was washed with H_2O, and then dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate to afford the corresponding desired thioester product **3a** (0.06 g, 83%) and corresponding thianthrene by-product (0.061 g, 94%).

(b) Investigations of green chemistry metrics

The green chemistry metrics including Atom Economy (AE), Carbon efficiency, Reaction Mass Efficiency (RME), Process Mass Intensity (PMI), *E*-factor were calculated according to literature.[8]

$$AE\ (\%) = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} \times 100 = \frac{240.05 + 216.32}{468.28 + 114.21} \times 100 = 78.34\%$$

$$Carbon\ efficiency\ (\%) = \frac{amount\ of\ carbon\ in\ product}{Total\ amount\ of\ carbon} \times 100 = \frac{11}{21 + 2 - 12} \times 100 = 100\%$$

$$RME\ (\%) = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100 = \frac{0.060\ g + 0.061}{0.141\ g + 0.069\ g} \times 100 = 57.62\%$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process\ (including\ solvents)}{Mass\ of\ product} = \frac{0.1}{} = 15.37$$

$$E - factor = \frac{Total\ mass\ of\ wastes}{mass\ of\ product} = \frac{0.141\ g + 0.069\ g + 1.65\ g + 0.07g - 0.060\ g - 0.061\ g}{0.060\ g + 0.061} = 14.95$$

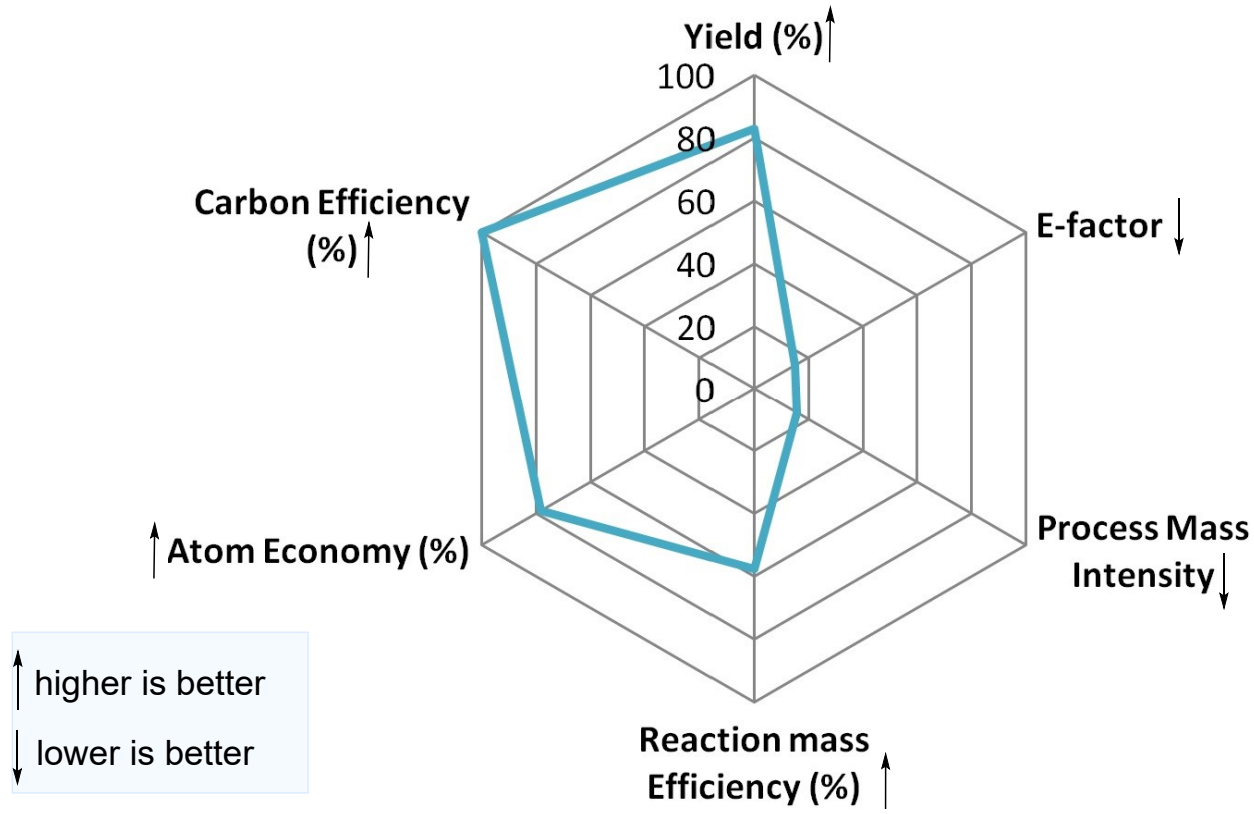


Figure 9: Summary of green metrics

(c) Calculations of EcoScale[8f]

Score on **EcoScale**: > 75, Excellent; >50, Acceptable; <50, Inadequate					
Parameters					**Penalty points**
Techniques					Visible light irradiation (this work)
Solvent					DMSO
Reaction yield % **Penalty points** = (100 - %yield)/2					83% 8.5
Chemical Components	mmol	MW	Price/ mmol	Price of component to obtain 10 mmol end product	
Methyl-2-methoxybenzoate-derived sulfonium salt	0.3 mmol	381.061	> $1	> $1	3
Potassium tioacetate	0.6 mmol	114.21	< $1	< $1	0
4Å molecular seive	0.06 g	-	< $1	< $1	0
DMSO	1.5 mL	78.13	< $1	< $1	0
3. Safety					
Methyl-2-methoxybenzoate-derived sulfonium salt					0
Potassium thioacetate					0
DMSO (T)					5
4. Technical Setup					
Unconventional activation technique (photochemical activation)					2
(inert) gas atmosphere- argon					1
5. Temperature/Time					

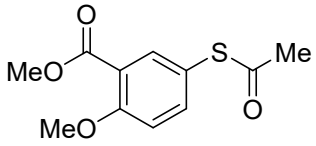
Room temperature, < 1 h	0
6. Workup and purification	
Classical chromatography	10
Penalty points total	29.5
EcoScale = 100 – sum of individual penalties	**70.5**
Ranking of reaction	**Acceptable synthesis**

EcoScale = 100 – sum of individual penalties
Score on **EcoScale**; > 75, Excellent; >50, Acceptable; <50, Inadequate
EcoScale score = 100 – 28 = 70.5 (< 75: it is an acceptable synthesis)

5. NMR data

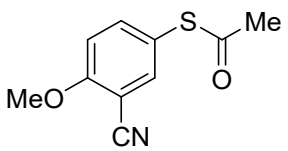
5.1 Characterization Data of Products

Methyl 5-(acetylthio)-2-methoxybenzoate (3):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 83% (60 mg)
R_f: 0.37 (Mobile phase: 15% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.84 (d, *J* = 2.5 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 2.41 (s, 3H)
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5, 165.7, 160.2, 140.0, 138.1, 120.8, 118.7, 113.0, 56.3, 52.3, 30.1.
HRMS-ESI (m/z) calc'd for $C_{11}H_{12}NaO_4S$: $[M+Na]^+$, 263.0354; Found, 263.0363.

S-(3-cyano-4-methoxyphenyl) ethanethioate (4):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.
Yield: 85% (53 mg).
R_f: 0.17 (Mobile phase: 10% EtOAc in Hexane).

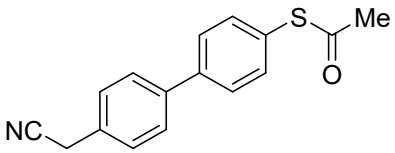
mp: 130-131°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.57-7.55 (m, 1H), 7.55-7.51 (m, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 3.94 (s, 3H), 2.41 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.7, 162.1, 141.0, 139.8, 119.8, 115.6, 112.3, 103.0, 56.5, 30.2.

HRMS-ESI (m/z) calc'd for $C_{10}H_9NaNO_2S$: $[M+Na]^+$, 230.0252; Found, 230.0252.

S-(4'-(cyanomethyl)-[1,1'-biphenyl]-4-yl) ethanethioate (5):



The titled compound was synthesized according to the general procedure **A** and obtained as a white solid.

Yield: 81% (65 mg).

R_f: 0.3 (Mobile phase: 20% EtOAc in Hexane).

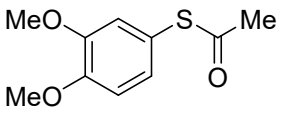
mp: 129-131°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.63-7.58 (m, 4H), 7.49 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 2H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.2, 141.4, 140.1, 135.0, 129.6, 128.6, 128.0, 127.9, 127.3, 117.9, 30.4, 23.4.

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}NNaOS$: $[M+Na]^+$, 290.0616; Found, 290.0624.

S-(3,4-dimethoxyphenyl) ethanethioate (6):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

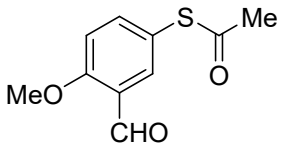
Yield: 86% (55 mg).

R_f: 0.2 (Mobile phase: 10% EtOAc in Hexane).

mp: 78-80°C

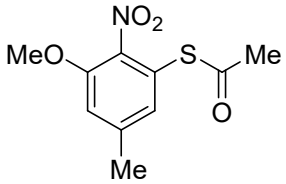
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.97 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.93-6.78 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.2, 150.3, 149.2, 127.8, 118.9, 117.3, 111.6, 56.0, 55.9, 30.0.
^{1}H and **^{13}C NMR** of the product are in agreement with the literature.[9]

S-(3-formyl-4-methoxyphenyl) ethanethioate (7):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 73% (45 mg)
R_f: 0.25 (Mobile phase: 10% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 10.43 (s, 1H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.57 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.05 (d, *J* = 8.5, Hz, 1H), 3.96 (s, 3H), 2.42 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.3, 188.8. 162.5, 142.2, 134.9, 125.5, 119.8, 112.8, 56.0, 30.1
HRMS-ESI (m/z) calc'd for $C_{10}H_{10}O_3S$: $[M+H]^+$, 211.0384; Found, 211.0423.

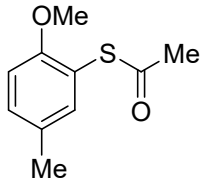
S-(3-methoxy-5-methyl-2-nitrophenyl) ethanethioate (8):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 82% (59 mg)
R_f: 0.32 (Mobile phase: 10% EtOAc in Hexane).

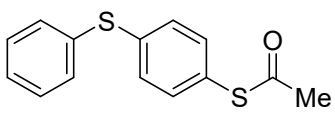
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (s, 1H), 7.02 (s, 1H), 3.96 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H)
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.1, 154.3, 150.3, 137.4, 133.4, 119.1, 115.5, 56.7, 30.2, 21.5.
HRMS-ESI (m/z) calc'd for $C_{10}H_{11}NNaO_4S$: $[M+Na]^+$, 264.0301; Found, 264.0315.

S-(2-methoxy-5-methylphenyl) ethanethioate (9):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 90% (53 mg).
R_f: 0.44 (Mobile phase: 10% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.22-7.19 (m, 2H) 6.87 (dd, *J* = 6.0, 3.0 Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.9, 157.2, 137.2, 132.3, 130.5, 115.7, 111.6, 56.2, 30.1, 20.4.
HRMS-ESI (m/z) calc'd for $C_{10}H_{12}NaO_2S$: $[M+Na]^+$, 219.0456; Found, 219.0455.

S-(4-(phenylthio)phenyl) ethanethioate (10):



The titled compound was synthesized according to the general procedure **A** and was obtained as a light brown oil

Yield: 79% (62 mg).

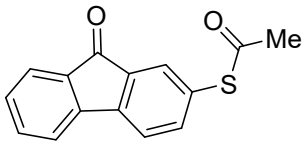
R_f: 0.58 (Mobile phase: 5% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.47-7.44 (m, 2H), 7.38-7.33 (m, 3H), 7.31-7.25 (m, 4H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.1, 139.6, 135.0, 133.6, 133.0, 129.7, 129.6, 128.3, 125.6, 30.3.

HRMS-ESI (m/z) calc'd for $C_{14}H_{12}NaOS_2$: $[M+Na]^+$, 283.0227; Found, 283.0217.

S-(9-oxo-9H-fluoren-2-yl) ethanethioate (11):



The titled compound was synthesized according to the general procedure **A** and was obtained as a yellow solid.

Yield: 71% (54 mg).

R_f: 0.43 (Mobile phase: 10% EtOAc in Hexane).

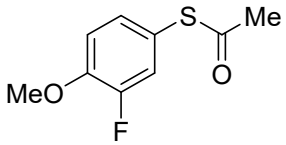
mp: 107-108 °C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.68-7.64 (m, 2H), 7.57-7.48 (m, 4H), 7.33 (t, *J* = 7.5 Hz, 1H), 2.45 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.4, 192.8, 145.4, 143.7, 140.8, 135.0, 134.2, 130.3, 129.8, 129.1, 128.5, 124.6, 121.0, 120.8, 30.4.

HRMS-ESI (m/z) calc'd for $C_{15}H_{10}NaO_2S$: $[M+Na]^+$, 277.0299; Found, 277.0303.

S-(3-fluoro-4-methoxyphenyl) ethanethioate (12):



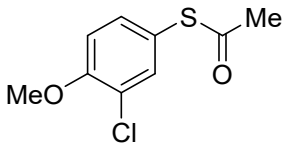
The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.

Yield: 85% (51 mg).

R_f: 0.52 (Mobile phase: 10% EtOAc in Hexane).

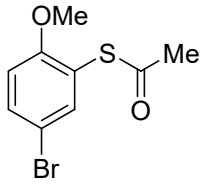
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.12-7.09 (m, 2H), 6.97 (t, *J* = 9.5 Hz, 1H), 3.88 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.4, 152.1 (d, *J* = 249.6 Hz), 149.0 (d, *J* = 10.7 Hz), 131.2 (d, *J* = 3.9 Hz), 122.3 (d, *J* = 19.4 Hz), 119.1 (d, *J* = 7.6 Hz), 113.6 (d, *J* = 3.2 Hz), 56.2, 30.0.
^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -133.45
HRMS-ESI (m/z) calc'd for $C_9H_9FNaO_2S$: $[M+Na]^+$, 223.0200; Found, 223.0199.

S-(3-chloro-4-methoxyphenyl) ethanethioate (13):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 82% (53 mg).
R_f: 0.21 (Mobile phase: 5% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.39 (d, *J* = 7.0 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.4, 156.2, 136.1, 134.6, 123.0, 119.6, 112.5, 56.3, 30.1.
HRMS-ESI (m/z) calc'd for $C_9H_9ClNaO_2S$: $[M+Na]^+$, 238.9909; Found, 238.9915.

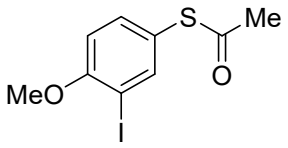
S-(5-bromo-2-methoxyphenyl) ethanethioate (14):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 72% (58 mg)
R_f = 0.37 (Mobile phase: 5% EtOAc in Hexane).

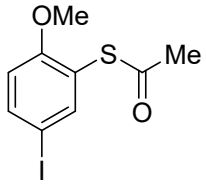
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.51 (d, *J* = 2.5 Hz, 1H), 7.49 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 3.82 (s, 3H), 2.41 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.5, 158.5. 138.8, 134.3, 118.3, 113.1, 112.7, 56.3, 30.2.
HRMS-ESI (m/z) calc'd for $C_9H_{10}BrO_2S$: $[M+H]^+$, 260.9540; Found, 260.9579.

S-(3-iodo-4-methoxyphenyl) ethanethioate (15):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.
Yield: 76% (70 mg).
R_f = 0.52 (Mobile phase: 5% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 2 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.40 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5, 159.2, 145.0, 136.3, 120.6, 111.3, 86.4, 56.6, 30.1.
HRMS-ESI (m/z) calc'd for $C_9H_9INaO_2S$: $[M+Na]^+$, 330.9266; Found, 330.9281.

S-(5-iodo-2-methoxyphenyl) ethanethioate (16):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.
Yield: 74% (68 mg).
R_f: 0.42 (Mobile phase: 5% EtOAc in Hexane).

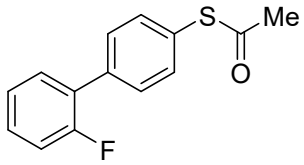
mp: 71-73°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.79 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.84 (d, *J*= 8.5 Hz, 1H), 3.89 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.5, 159.2, 145.0, 136.3, 120.6, 111.3, 86.4, 56.6, 30.1

HRMS-ESI (m/z) calc'd for $C_9H_9INaO_2S$: $[M+Na]^+$, 330.9266; Found, 330.9258.

S-(2'-fluoro-[1,1'-biphenyl]-4-yl) ethanethioate (17):



The titled compound was synthesized according to the general procedure **A** and was obtained as a white solid.

Yield: 75% (55 mg).

R_f = 0.71 (Mobile phase: 10% EtOAc in Hexane).

mp: 113-115°C

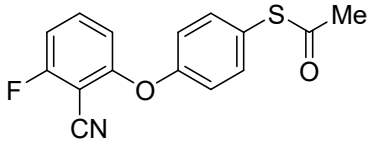
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.60 (dt, *J* = 6.5, 1.5 Hz, 2H), 7.50 (dt, *J* = 8.0, 2.5 Hz, 2H), 7.46 (td, *J* = 7.8, 1.5 Hz, 1H), 7.37-7.32 (m, 1H), 7.23 (td, *J* = 7.5, 1 Hz, 1H), 7.19-7.15 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.2, 159.8 (d, *J* = 249.0 Hz), 137.1, 134.5, 130.8 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 14.0 Hz), 129.6 (d, *J* = 8.4 Hz), 128.1 (d, *J* = 13.2 Hz), 127.4, 124.6 (d, *J* = 3.9 Hz), 116.3 (d, *J* = 22.7 Hz), 30.4.

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -117.53

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}FNaOS$: $[M+Na]^+$, 269.0412; Found, 269.0414.

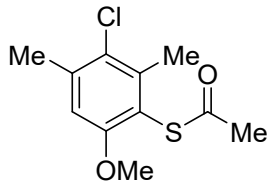
S-(4-(2-cyano-3-fluorophenoxy)phenyl) ethanethioate (18):



The titled compound was synthesized according to the general procedure **A** was obtained as white solid.

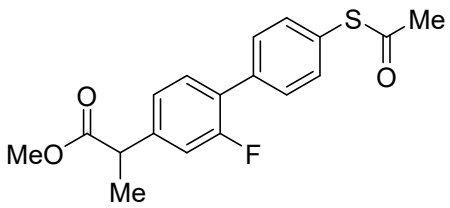
Yield: 79% (68 mg).
R_f = 0.25 (Mobile phase: 10% EtOAc in Hexane).
mp: 163-165°C
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.50 - 7.43 (m, 3H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.5 Hz, 1H), 2.44 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.9, 160.2 (d, *J* = 4.3 Hz), 155.7, 136.6, 135.1 (d, *J* = 10.5 Hz), 124.8, 120.8, 112.7 (d, *J* = 38.0 Hz), 110.5 (d, *J* = 19.7 Hz), 94.3 (d, *J* = 18.1 Hz), 30.4.
^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -104.16
HRMS-ESI (m/z) calc'd for $C_{15}H_{10}FNNaO_2S$: $[M+Na]^+$, 310.0314; Found, 310.0310.

S-(3-chloro-6-methoxy-2,4-dimethylphenyl) ethanethioate (19):



The titled compound was synthesized according to the general procedure **A** and was obtained as a pale yellow oil.
Yield: 62% (47 mg).
R_f: 0.31 (Mobile phase: 5% EtOAc in Hexane).
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 6.71 (s, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.0, 157.7, 141.4, 139.7, 127.3, 114.9, 111.5, 56.3, 30.1, 21.8, 19.4.
HRMS-ESI (m/z) calc'd for $C_{11}H_{13}ClNaO_2S$: $[M+Na]^+$, 267.0227; Found, 267.0215.

Methyl 2-(4'-(acetylthio)-2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (20):



The titled compound was synthesized according to the general procedure **A** and was obtained as a pale yellow oil.

Yield: 77% (77 mg).

$\mathbf{R_f}$ = 0.17 (Mobile phase: 5% EtOAc in Hexane).

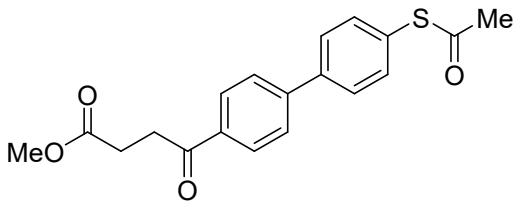
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.58 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.48 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.18 – 7.11 (m, 2H), 3.77 (q, *J* = 7.0 Hz, 1H), 3.70 (s, 3H), 2.44 (s, 3H), 1.54 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.1, 174.4, 159.8 (d, *J* = 249.6 Hz), 142.5 (d, *J* = 8.1 Hz), 136.7, 134.5, 130.8 (d, *J* = 4.0 Hz), 129.8 (d, *J* = 3.5 Hz), 127.4, 126.9 (d, *J* = 13.2 Hz), 123.8 (d, *J* = 3.8 Hz), 115.5 (d, *J* = 23.6 Hz), 52.4, 45.0, 30.4, 18.5.

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -117.0

HRMS-ESI (m/z) calc'd for $C_{18}H_{21}FNO_3S$: $[M+NH_4]^+$, 350.1226; Found, 350.1223.

Methyl 4-(4'-(acetylthio)-[1,1'-biphenyl]-4-yl)-4-oxobutanoate (21):



The titled compound was synthesized according to the general procedure **A** and was obtained as a off-white solid.

Yield: 73% (75 mg).

$\mathbf{R_f}$: 0.14 (Mobile phase: 10% EtOAc in Hexane).

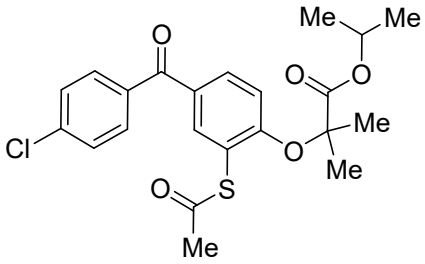
mp: 121-123°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.04 (d, *J* = 8.0 Hz, 2H), 7.69-7.60 (m, 4H), 7.49 (d. *J* = 8.5 Hz, 2H), 3.33 (t, *J* = 6.5 Hz, 2H), 3.70 (s, 3H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 197.6, 193.8, 173.4, 144.7, 140.9, 135.7, 134.9, 128.7, 128.1, 128.0, 127.3, 51.9, 33.5., 30.3, 28.1.

HRMS-ESI (m/z) calc'd for $C_{19}H_{18}NaO_4S$: $[M+Na]^+$, 365.0823; Found, 365.0818.

Isopropyl 2-(2-(acetylthio)-4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (21):



The titled compound was synthesized according to the general procedure **A** and was obtained as a colourless oil.

Yield: 41% (53 mg).

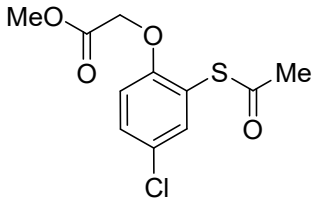
R_f: 0.29 (Mobile phase: 10% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.87 (d, *J* = 2.0 Hz, 1H), 7.79 (dd, *J* = 11.0, 2.0 Hz, 1H), 7.74 (d, *J* = 8.5, 2.5 Hz, 2H), 7.46 (dt, *J* = 8.5, 2.5 Hz, 2H), 6.8 (d, *J* = 8.5 Hz, 1H), 5.08 (quint, *J* = 6 Hz, 1H), 2.42 (S, 3H), 1.64 (S, 6H), 1.21 (d, *J* = 6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 193.5, 192.8, 172.9, 159.3, 139.1, 138.8, 135.9, 132.9, 131.4, 130.4, 128.8, 119.1, 115.7, 80.6, 69.7, 30.2, 25.1, 21.6.

HRMS-ESI (m/z) calc'd for $C_{22}H_{24}ClO_5S$: $[M+H]^+$, 435.0988; Found, 435.1028.

Methyl 2-(2-(acetylthio)-4-chlorophenoxy)acetate (23):



The titled compound was synthesized according to the general procedure **A** and was obtained as a brown oil.

Yield: 70% (71 mg)

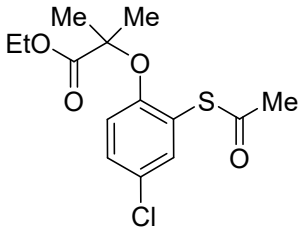
R_f: 0.28 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.41 (d, *J* = 3.5 Hz, 1H), 7.34-7.30 (m, 1H), 6.78 (d, *J* = 9.0 Hz, 1H), 4.64 (s, 2H), 3.77 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.6, 168.7, 156.3, 136.2, 131.3, 127.0, 119.1, 114.0, 66.3, 52.5, 30.3.

HRMS-ESI (m/z) calc'd for $C_{11}H_{11}ClNaO_4S$: $[M+Na]^+$, 296.9959; Found, 296.9959.

Ethyl 2-(2-(acetylthio)-4-chlorophenoxy)-2-methylpropanoate (20):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 65% (62 mg).

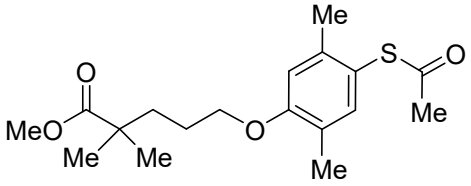
R_f: 0.25 (Mobile phase: 5% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.42 (d, *J* = 2.5 Hz, 1H), 7.24 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 1H), 4.22 (q, *J* = 7.5 Hz, 2H), 2.4 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.56 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 192.7, 173.8, 154.2, 135.9, 130.6, 126.9, 121.5, 118.5, 80.4, 61.7, 30.2, 25.0, 14.1.

HRMS-ESI (m/z) calc'd for $C_{14}H_{17}ClNaO_4S$: $[M+Na]^+$, 339.0434; Found, 339.0447.

Methyl 5-(4-(acetylthio)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (24):



The titled compound was synthesized according to the general procedure **A** under 2 hrs of light irradiation and was obtained as a light brown oil.

Yield: 74% (75 mg).

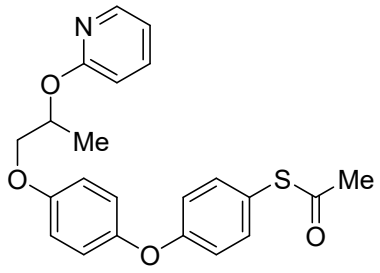
R_f: 0.37 (Mobile phase: 10% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.11 (s, 1H), 6.71 (s, 1H), 3.92 (t, *J* = 5.5 Hz, 2H), 3.65 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H), 1.74-1.67 (m, 4H), 1.21 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 195.1, 178.2, 158.6, 141.0, 137.7, 125.2, 117.3, 113.0, 68.0, 51.8, 42.1, 37.1, 30.0, 25.3, 25.2, 20.9, 15.7.

HRMS-ESI (m/z) calc'd for $C_{18}H_{26}NO_4S$: $[M+Na]^+$, 361.1449; Found, 361.1445.

S-(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl) ethanethioate (25):



The titled compound was synthesized according to the general procedure **A** under 2 hrs of light irradiation and was obtained as brown solid.

Yield: 72% (85 mg).

R_f: 0.37 (Mobile phase: 10% EtOAc in Hexane).

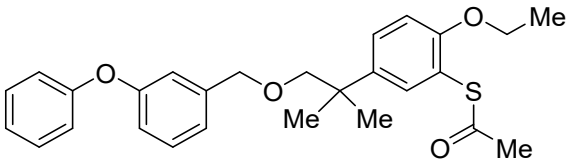
mp: 68-69°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.16 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.56 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.31 (dd, *J* = 6.5, 2.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.95 (dd, *J* = 9.0, 3.0 Hz, 4H), 6.85 (t, *J* = 6.5 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.61 (Sextet, *J* = 6.0 Hz, 1H), 4.22-4.07 (m, 2H), 2.39 (s, 3H), 1.48 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.7, 163.2, 160.0, 155.8, 149.2, 146.8, 138.7, 136.1, 121.5, 120.5, 117.8, 116.8, 116.0, 111.7, 71.1, 69.3, 30.0, 17.1.

HRMS-ESI (m/z) calc'd for $C_{22}H_{22}NO_4S$: $[M+H]^+$, 396.1225; Found, 396.1279.

S-(2-ethoxy-5-(2-methyl-1-((3-phenoxybenzyl)oxy)propan-2-yl)phenyl) ethanethioate (27):



The titled compound was synthesized according to the general procedure **A** and was obtained as a pale yellow oil.

Yield: 66% (89 mg).

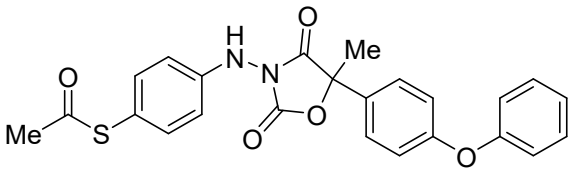
R_f: 0.72 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.41-7.33 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.0 (d, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.96 (s, 3H), 6.92 (dd, *J* = 8.25, 2.0 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 4.46 (s, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.42 (s, 2H), 2.40 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.33 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.0, 157.4, 157.3, 156.8, 141.0, 140.1, 134.4, 129.8, 129.7, 129.4, 123.3, 122.1, 119.1, 117.8, 117.7, 116.1, 112.2, 80.2, 72.8, 64.5, 38.7, 30.1, 26.1, 14.9.

HRMS-ESI (m/z) calc'd for $C_{27}H_{34}NO_4S$: $[M+NH_4]^+$, 468.2209; Found, 468.2202.

S-(4-((5-methyl-2,4-dioxo-5-(4-phenoxyphenyl)oxazolidin-3-yl)amino)phenyl) ethanethioate (28):



The titled compound was synthesized according to the general procedure **A** under 2 hrs of light irradiation and was obtained as a white solid.

Yield: 63% (85 mg).

R_f: 0.65 (Mobile phase: 40% EtOAc in Hexane).

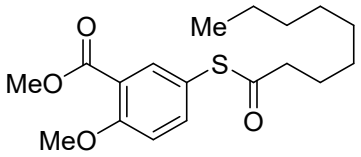
mp: 158-160^oC

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.54 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 - 7.25 (m, 2H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 9.0 Hz, 4H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.48 (s,1H), 2.39 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ (ppm) = 194.9, 172.0, 158.7, 156.2, 152.8, 145.5, 136.0, 130.1, 130.1, 126.2, 124.2, 121.2, 119.7, 118.7, 114.5, 85.3, 30.1, 25.6.

HRMS-ESI (m/z) calc'd for $C_{24}H_{24}N_3O_5S$: $[M+NH_4]^+$, 466.1437; Found, 466.1432.

Methyl 2-methoxy-5-(nonanoylthio)benzoate (29):



The titled compound was synthesized according to the general procedure **B** under 2 hrs of light irradiation and was obtained as a light brown oil.

Yield: 64% (65 mg)

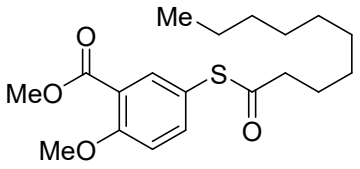
R_f: 0.22 (Mobile phase: 10% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.82 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.01 (d, *J* = 8.5 Hz 1H), 3.91 (s, 3H), 3.86 (s, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.39 -1.19 (m, 12H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 198.0, 165.7, 160.1, 140.1, 138.1, 120.7, 118.7, 112.9, 56.3, 52.2, 43.6, 31.9, 29.3, 29.2, 29.0, 25.6, 22.7, 14.2.

HRMS-ESI (m/z) calc'd for $C_{18}H_{26}NaO_4S$: $[M+Na]^+$, 361.1444; Found, 361.1447.

Methyl 5-(decanoylthio)-2-methoxybenzoate (30):



The titled compound was synthesized according to the general procedure **B** and was obtained as a brown oil.

Yield: 61% (65 mg).

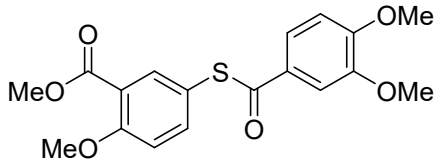
R_f: 0.29 (Mobile phase: 10% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.83 (d, *J* = 2.5 Hz, 1H), 7.48 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.69 (quint, *J* = 7.5 Hz, 2H), 1.34-1.23 (m, 12H), 0.87 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 198.0, 165.7, 160.1, 140.1, 138.1, 120.8, 118.8, 112.9, 56.3, 52.2, 43.7, 31.9, 29.8, 29.5, 29.3, 29.0, 25.6, 22.7, 14.2.

HRMS-ESI (m/z) calc'd for $C_{19}H_{28}NaO_4S$: $[M+Na]^+$, 375.1606; Found, 375.1597.

Methyl 5-((3,4-dimethoxybenzoyl)thio)-2-methoxybenzoate (31):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 69% (75 mg).

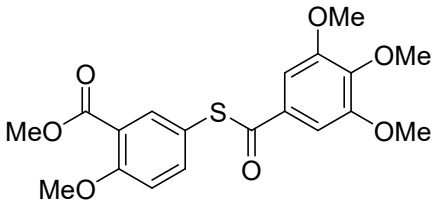
R_f: 0.15 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.92 (d, *J* = 2.5 Hz, 1H), 7.69 (dd, *J* = 8.5, 3.5 Hz, 1H), 7.56 (dd, *J* = 8.75, 2.0 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.0, 165.7, 160.3, 153.9, 149.1, 140.6, 138.7, 129.3, 122.1, 120.9, 118.4, 113.0, 110.4, 109.7, 56.3, 56.2, 56.1, 52.2.

HRMS-ESI (m/z) calc'd for $C_{18}H_{18}NaO_6S$: $[M+Na]^+$, 385.0716; Found, 385.0720.

Methyl 2-methoxy-5-((3,4,5-trimethoxybenzoyl)thio)benzoate (32):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 71% (84 mg).

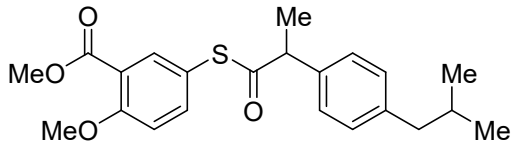
R_f: 0.17 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.97 (d, *J* = 2.5 Hz, 1H), 7.62 (dd, *J* = 8.75, 2.0 Hz, 1H), 7.29 (s, 2H), 7.10 (d, *J* = 8.5 Hz, 1H), 3.99 (s, 3H), 3.97-3.93 (m, 9H), 3.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 189.6, 165.7, 160.4, 153.3, 143.0, 140.6 138.7, 131.6, 121.0, 118.1, 113.1, 104.9, 61.1, 56.4, 56.3, 52.3.

HRMS-ESI (m/z) calc'd for $C_{19}H_{20}NaO_7S$: $[M+Na]^+$, 415.0827; Found, 415.0821.

Methyl 5-((2-(4-isobutylphenyl)propanoyl)thio)-2-methoxybenzoate (33):



The titled compound was synthesized according to the general procedure **B** under 2 hrs light irradiation and was obtained as a pale yellow oil.

Yield: 56% (65 mg).

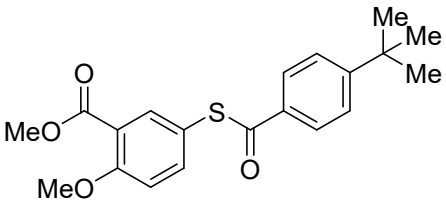
R_f: 0.54 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.78 (d, *J* = 2.5 Hz, 1H), 7.42 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.47 (d, *J* = 7.5 Hz, 2H), 1.91- 1.83 (M, 1H), 1.56 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 199.7, 165.7, 160.1, 141.3, 140.1, 138.1, 136.6, 129.6, 127.9, 120.8, 118.9, 112.9, 56.2, 53.7, 52.2, 45.2, 30.3, 22.5, 18.7.

HRMS-ESI (m/z) calc'd for $C_{22}H_{26}NaO_4S$: $[M+Na]^+$, 409.1449; Found, 409.1442.

Methyl 5-((4-(tert-butyl)benzoyl)thio)-2-methoxybenzoate (34):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 73% (78 mg).

R_f: 0.46 (Mobile phase: 20% EtOAc in Hexane).

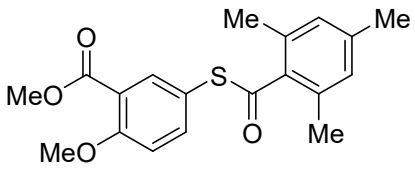
mp: 105-106°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.95-7.94 (m, 2H), 7.94 - 7.92 (m, 1H), 7.59 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.0, 165.7, 160.3, 157.8, 140.7, 138.8, 133.8, 127.8, 125.8, 120.8, 118.3, 113.0, 56.3, 52.3, 35.3, 31.2.

HRMS-ESI (m/z) calc'd for $C_{20}H_{22}NaO_4S$: $[M+Na]^+$, 381.1136; Found, 381.1124.

Methyl 2-methoxy-5-((2,4,6-trimethylbenzoyl)thio)benzoate (35):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 68% (70 mg).

R_f: 0.4 (Mobile phase: 20% EtOAc in Hexane).

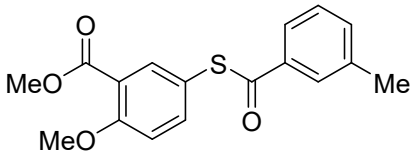
mp: 101-102°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.87 (s, 2H), 3.95 (s, 3H), 3.91 (s, 3H), 2.38 (s, 6H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 196.5, 165.8, 160.3, 140.0, 139.8, 138.0, 137.0, 133.8, 128.5, 121.0, 118.8, 113.1, 56.3, 52.3, 21.3, 19.2.

HRMS-ESI (m/z) calc'd for $C_{19}H_{20}NaO_4S$: $[M+Na]^+$, 367.0980; Found, 367.0978.

Methyl 2-methoxy-5-((3-methylbenzoyl)thio)benzoate (36):



The titled compound was synthesized according to the general procedure **B** and was obtained as a pale yellow oil.

Yield: 74% (70 mg).

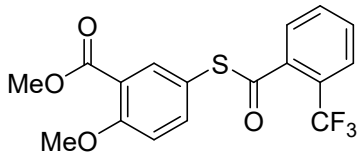
R_f: 0.37 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 2.5 Hz, 1H), 7.82-7.79 (m, 2H), 7.58 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.42-7.38 (m, 1H), 7.35 (t, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 3.9 (s, 3H), 3.87 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.6, 165.7, 160.3, 140.6, 138.8, 138.7, 136.5, 134.7, 128.8, 128.0, 124.8, 120.9, 118.2, 113.1, 56.3, 52.3, 21.4.

HRMS-ESI (m/z) calc'd for $C_{17}H_{16}NaO_4S$: $[M+Na]^+$, 339.0667; Found, 339.0665.

Methyl 2-methoxy-5-((2-(trifluoromethyl)benzoyl)thio)benzoate (37):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 62% (69 mg).

R_f: 0.46 (Mobile phase: 15% EtOAc in Hexane).

mp: 118-120°C

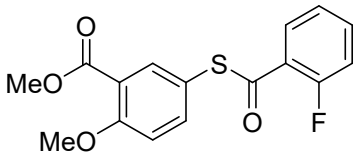
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 2.5 Hz, 1H), 7.81-7.73 (m, 2H), 7.65-7.57 (m, 3H), 7.07 (d, *J* = 9.0 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 191.6, 165.6. 160.6, 140.2, 138.2, 137.2, 131.9, 131.5, 128.5, 127.2 (q, *J* = 5.4 Hz), 124.4, 122.2, 121.1, 117.9, 113.3, 56.3, 52.3.

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -58.4.

HRMS-ESI (m/z) calc'd for $C_{17}H_{13}F_3NaO_4S$: $[M+Na]^+$, 393.0384; Found, 393.0382.

Methyl 5-((2-fluorobenzoyl)thio)-2-methoxybenzoate (38):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 67% (64 mg).

R_f: 0.17 (Mobile phase: 10% EtOAc in Hexane).

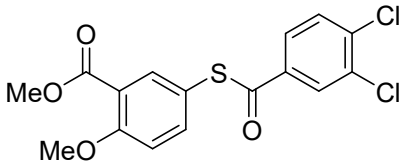
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.95 (d, *J* = 2.0 Hz, 1H), 7.90 (td, *J* = 7.8, 1.5 Hz, 1H), 7.60 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.57-7.52 (m, 1H), 7.25 (td, *J* = 7.8, 0.5 Hz, 1H), 7.18 .(t, *J* = 11.0 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H),3.95 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 187.5 (d, *J* = 5.8 Hz), 165.6, 161.7, 160.5, 159.6, 139.6 (d, *J* = 240.4 Hz), 134.9 (d, *J* = 36.5 Hz), 130.0, 124.9 (d, *J* = 11.8 Hz), 124.5 (d, *J* = 3.8 Hz), 120.9, 118.0 (d, *J* = 5.4 Hz), 117.0 (d, *J* = 22.4 Hz), 113.1, 56.3, 52.3.

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -109.51

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}NaFO_4S$: $[M+H]^+$, 343.0416; Found, 343.0412.

Methyl 5-((3,4-dichlorobenzoyl)thio)-2-methoxybenzoate (39):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid

Yield: 60% (67 mg).

R_f: 0.16 (Mobile phase: 10% EtOAc in Hexane).

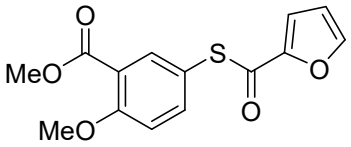
mp: 109-110°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.07 (d, *J* = 2.5 Hz, 1H), 7.93 (d, *J* = 2.5 Hz, 1H), 7.83 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.08 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.5, 165.6, 160.6, 140.5, 138.6, 138.4, 136.0, 133.6, 131.0, 129.4, 126.5, 121.1, 117.1, 113.2, 56.3, 52.3.

HRMS-ESI (m/z) calc'd for $C_{16}H_{12}Cl_2NaO_4S$: $[M+Na]^+$, 392.9731; Found, 392.9726.

Methyl 5-((furan-2-carbonyl)thio)-2-methoxybenzoate (40):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid;

Yield: 63% (55 mg).

R_f: 0.26 (Mobile phase: 20% EtOAc in Hexane).

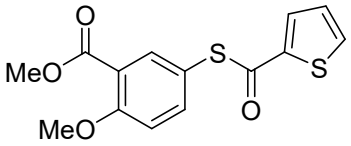
mp: 82-84^{o}C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 2.5 Hz, 1H), 7.62 (s, 1H), 7.57 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.57 (dd, *J* = 3.5, 1.5 Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 179.0, 165.6, 160.5, 150.3, 146.7, 140.7, 138.8, 120.9, 116.8, 116.5, 113.1, 112.6, 56.3, 52.3.

HRMS-ESI (m/z) calc'd for $C_{14}H_{12}NaO_5S$: $[M+Na]^+$, 315.0303; Found, 315.0299.

Methyl 2-methoxy-5-((thiophene-2-carbonyl)thio)benzoate (41):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 71% (65 mg).

R_f: 0.21 (Mobile phase: 20% EtOAc in Hexane).

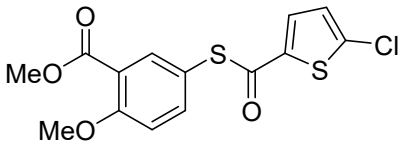
mp: 71-73^{o}C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.93 (d, *J* = 2.5 Hz, 1H), 7.86 (d, *J* = 3.0 Hz, 1H), 7.64 (d, *J* = 5.0 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.12 (t, *J* = 4.5 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 182.3, 165.6, 160.4, 141.1, 140.6, 138.7, 133.6, 131.8, 128.2, 120.9, 117.6, 113.1, 56.3, 52.2.

HRMS-ESI (m/z) calc'd for $C_{14}H_{12}NaO_4S_2$: $[M+Na]^+$, 331.0075; Found, 331.0069.

Methyl 5-((5-chlorothiophene-2-carbonyl)thio)-2-methoxybenzoate (42):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 52% (53 mg).

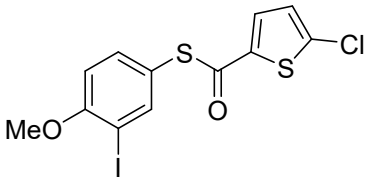
R_f: 0.37 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.94 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 4.5 Hz, 1H), 7.58 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 4.5 Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 181.6, 165.6, 160.6, 140.6, 139.5, 139.4, 138.8, 131.3, 127.6, 121.0, 117.0, 113.1, 56.3, 52.3.

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}ClNaO_4S_2$: $[M+Na]^+$, 364.9685; Found, 364.9686.

S-(3-iodo-4-methoxyphenyl) 5-chlorothiophene-2-carbothioate (43):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 44% (54 mg).

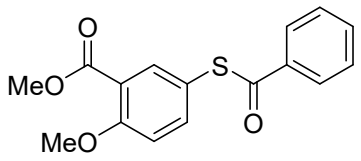
R_f: 0.4 (Mobile phase: 5% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 7.88 (d, *J* = 2.5 Hz, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.44 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.99 (d, *J* = 4.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 181.6, 159.6, 145.6, 139.5, 139.3, 136.9, 131.3, 127.6, 118.7, 111.3, 86.4, 56.6.

HRMS-ESI (m/z) calc'd for $C_{12}H_8ClNaIO_2S_2$: $[M+Na]^+$, 432.8597; Found, 432.8588.

Methyl 5-(benzoylthio)-2-methoxybenzoate (44):



The titled compound was synthesized according to the general procedure **B** was obtained as a white solid.

Yield: 81% (74 mg).

R_f: 0.48 (Mobile phase: 20% EtOAc in Hexane).

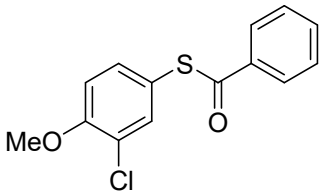
mp: 84-87°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.0 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.95 (d, *J* = 2.5 Hz, 1H), 7.61-7.57 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.5, 165.7, 160.4, 140.7, 138.7, 136.4, 133.9, 128.9, 127.6, 120.9, 118.0, 113.1, 56.3, 52.3.

HRMS-ESI (m/z) calc'd for $C_{16}H_{14}NaO_4S$: $[M+Na]^+$, 325.0510; Found, 325.0503.

S-(3-chloro-4-methoxyphenyl) benzothioate (45):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 79% (66 mg)

R_f: 0.45 (Mobile phase: 10% EtOAc in Hexane).

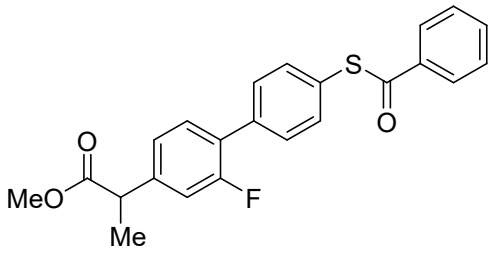
mp: 103-105°C

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.0 (d, *J* = 7.5 Hz, 2H), 7.61 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.49 (tt, *J* = 8.0, 1.5 Hz, 2H), 7.37 (dd, *J* = 8.25, 2.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.5, 156.3, 136.7, 136.4, 135.2, 133.9, 128.9, 127.6, 123.2, 118.9, 112.6, 56.4.

HRMS-ESI (m/z) calc'd for $C_{14}H_{11}ClNaO_2S$: $[M+Na]^+$, 301.0066; Found, 301.0075.

Methyl 2-(4'-(benzoylthio)-2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (46):



The titled compound was synthesized according to the general procedure **B** and was obtained as a white solid.

Yield: 76% (78 mg)

R_f: 0.19 (Mobile phase: 5% EtOAc in Hexane).

mp: 106-108°C

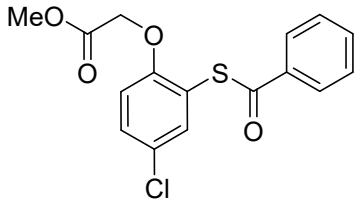
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.06 (d, *J* = 8.25 Hz, 2H), 7.65-7.58 (m, 5H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.20-7.13 (m, 2H), 3.78 (q, *J* = 7.0 Hz, 1H), 3.71 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.2, 174.5, 159.8 (d, *J*= 252.0 Hz), 142.49 (d, *J*= 31.5 Hz), 136.75 (d, *J*= 25.2 Hz), 135.2, 133.9, 130.88 (d, *J*= 4.2 Hz), 129.9 (d, *J*= 3.7 Hz), 128.9, 127.6, 127.0, 126.8 (d, *J*= 11.8 Hz), 123.8 (d, *J*= 3.7 Hz), 115.6, 115.4, 52.4, 45.0, 18.5.

^{19}F NMR (471 MHz, $CDCl_3$, 300 K): δ (ppm) = -116.9.

HRMS-ESI (m/z) calc'd for $C_{23}H_{20}FO_3S$: $[M+H]^+$, 395.1072; Found, 395.1116.

Methyl 2-(2-(benzoylthio)-4-chlorophenoxy)acetate (47):



The titled compound was synthesized according to the general procedure **B** and was obtained as a colourless oil.

Yield: 72% (73 mg)

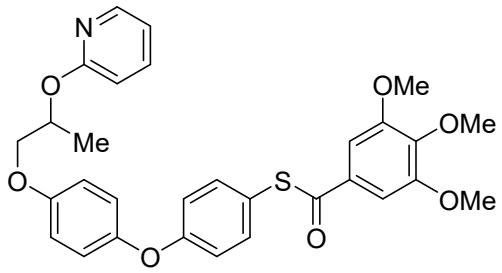
R_f: 0.28 (Mobile phase: 20% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.03 (dd, *J* = 8.25, 1.0 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.36 (dd, *J*= 9.0, 2.5 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 4.65 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 188.6, 168.7, 157.0, 136.7, 136.5, 133.9, 131.4, 128.9, 127.7, 127.0, 118.6, 114.3, 66.5, 52.4.

HRMS-ESI (m/z) calc'd for $C_{16}H_{13}ClNaO_4S$: $[M+Na]^+$, 359.0116; Found, 359.0118.

S-(4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl) 3,4,5-trimethoxybenzothioate (48):



The titled compound was synthesized according to the general procedure **B** under 2 hr light irradiation and was obtained as a light brown oil.

Yield: 60% (98 mg).

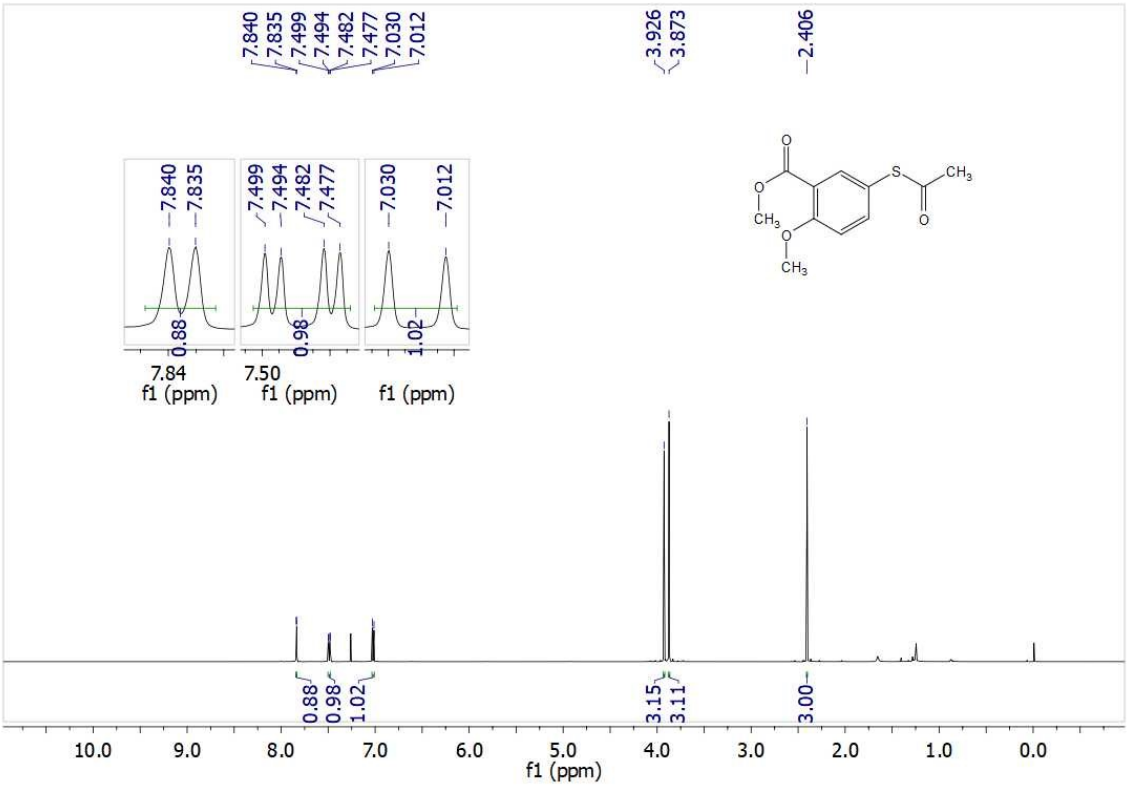
R_f: 0.53 (Mobile phase: 30% EtOAc in Hexane).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm) = 8.17-8.13 (m, 1H), 7.61-7.51 (m, 2H), 7.40 (dt, *J* = 8.5, 3.0 Hz, 2H), 7.27 (s, 1H), 7.03-6.97 (m, 6H), 6.87-6.84 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.59 (sx, *J* = 6.5 Hz, 1H), 4.20 (dd, *J* = 9.75, 5.5 Hz, 1H), 4.09 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.96-3.90 (m, 9H), 1.49 (d, *J* = 6.0 Hz, 3H).

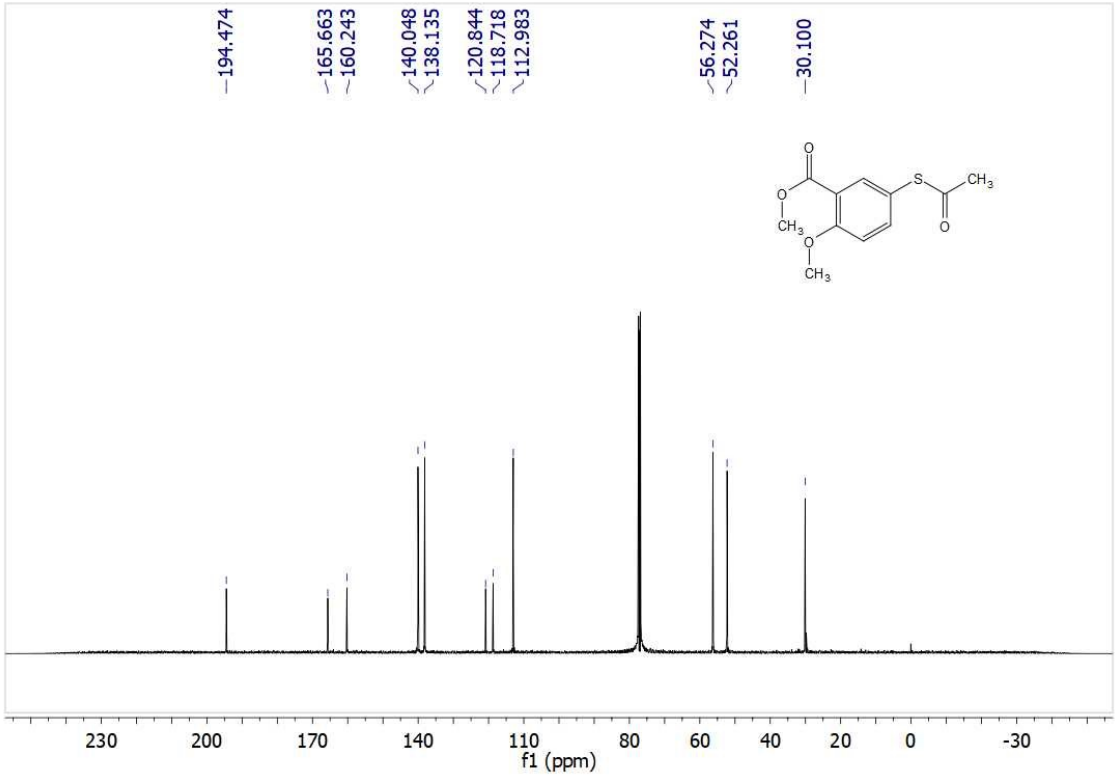
^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ (ppm) = 190.0, 163.2, 160.2, 155.8, 153.3, 149.2, 146.9, 142.9, 138.8, 136.7, 131.8, 121.5, 119.8, 117.9, 116.9, 116.0, 111.8, 104.8, 71.1, 69.3, 61.1, 56.4, 17.1.

HRMS-ESI (m/z) calc'd for $C_{30}H_{30}O_7S$: $[M+H]^+$, 548.1698; Found, 548.1734.

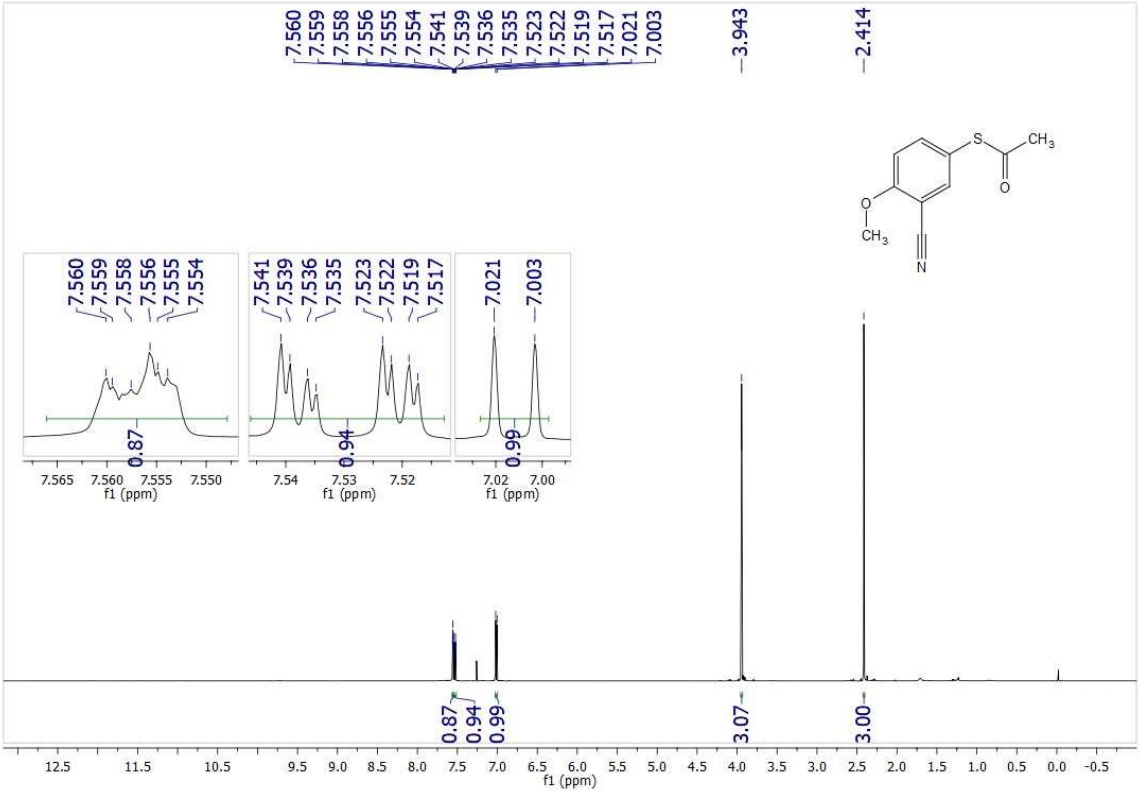
5.2. NMR spectra



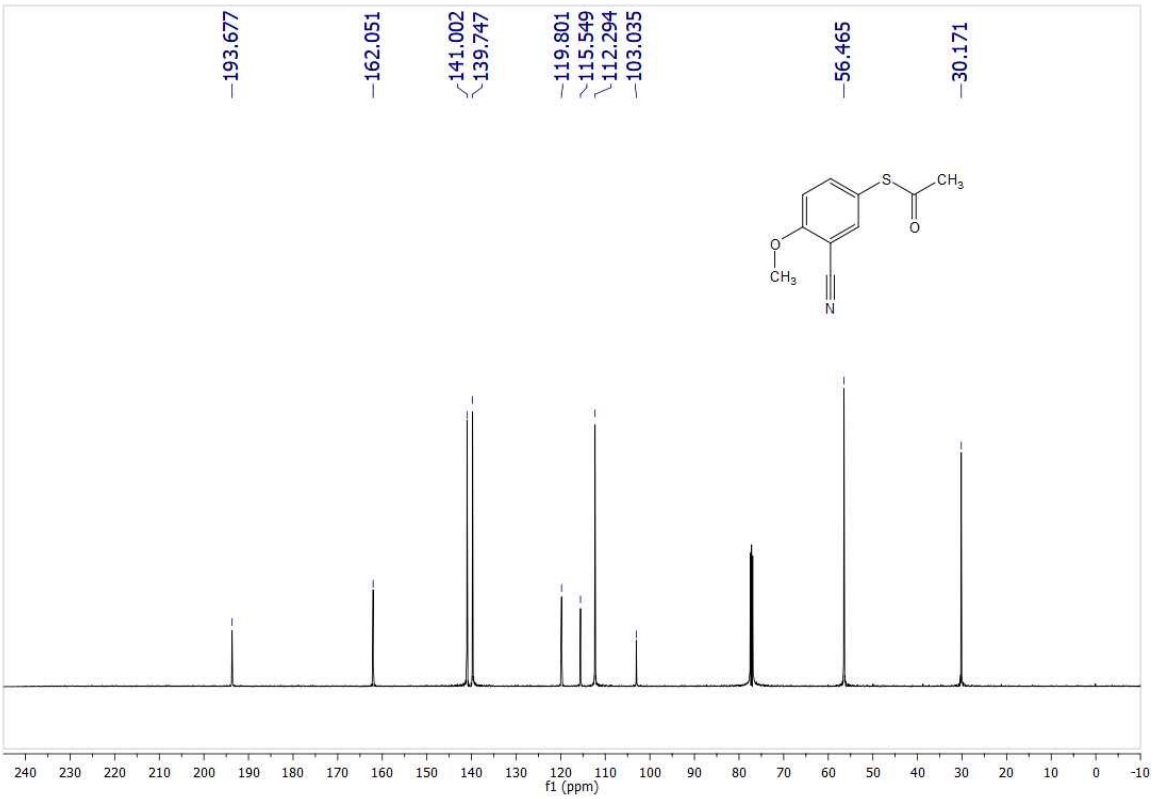
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3**.



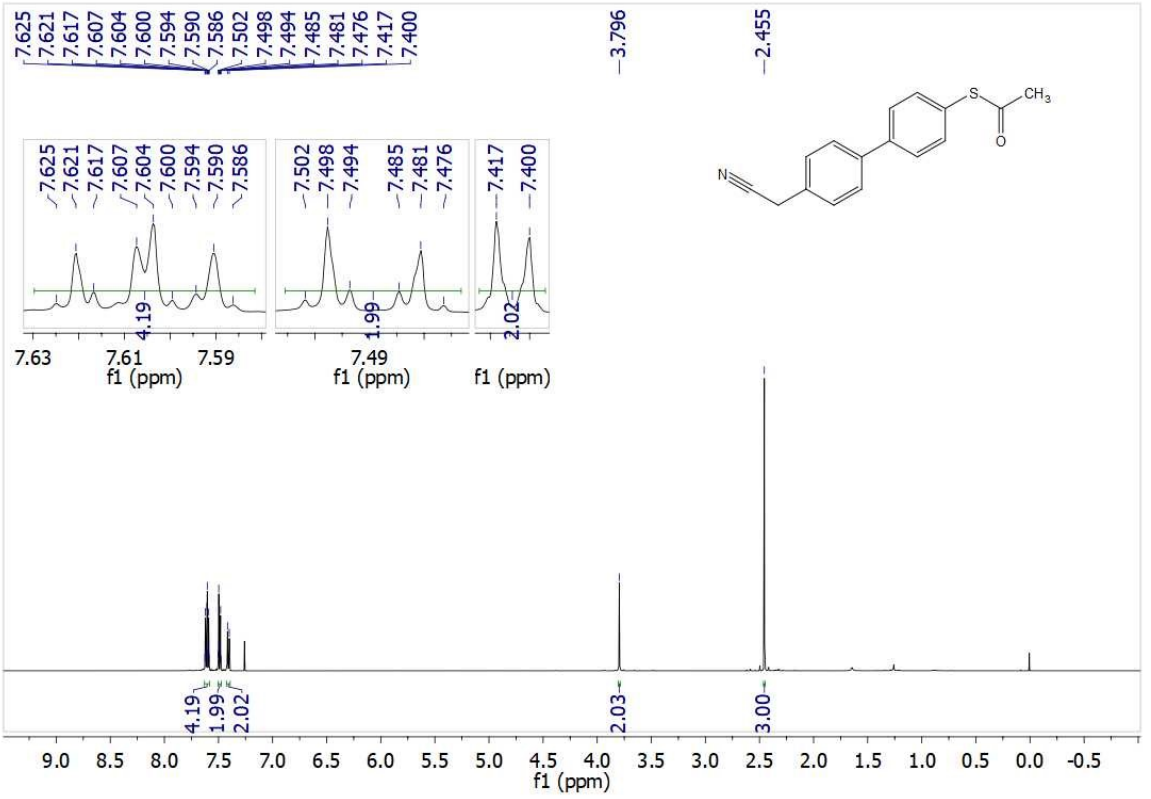
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3**.



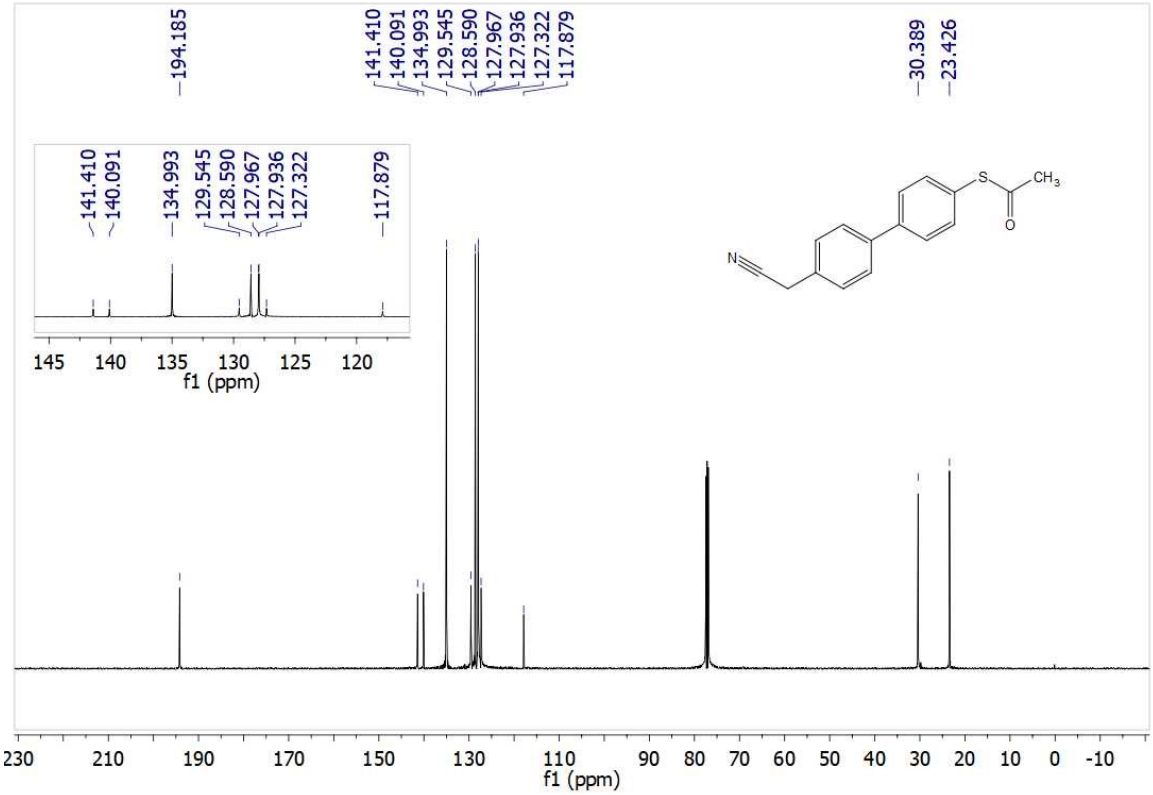
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4**.



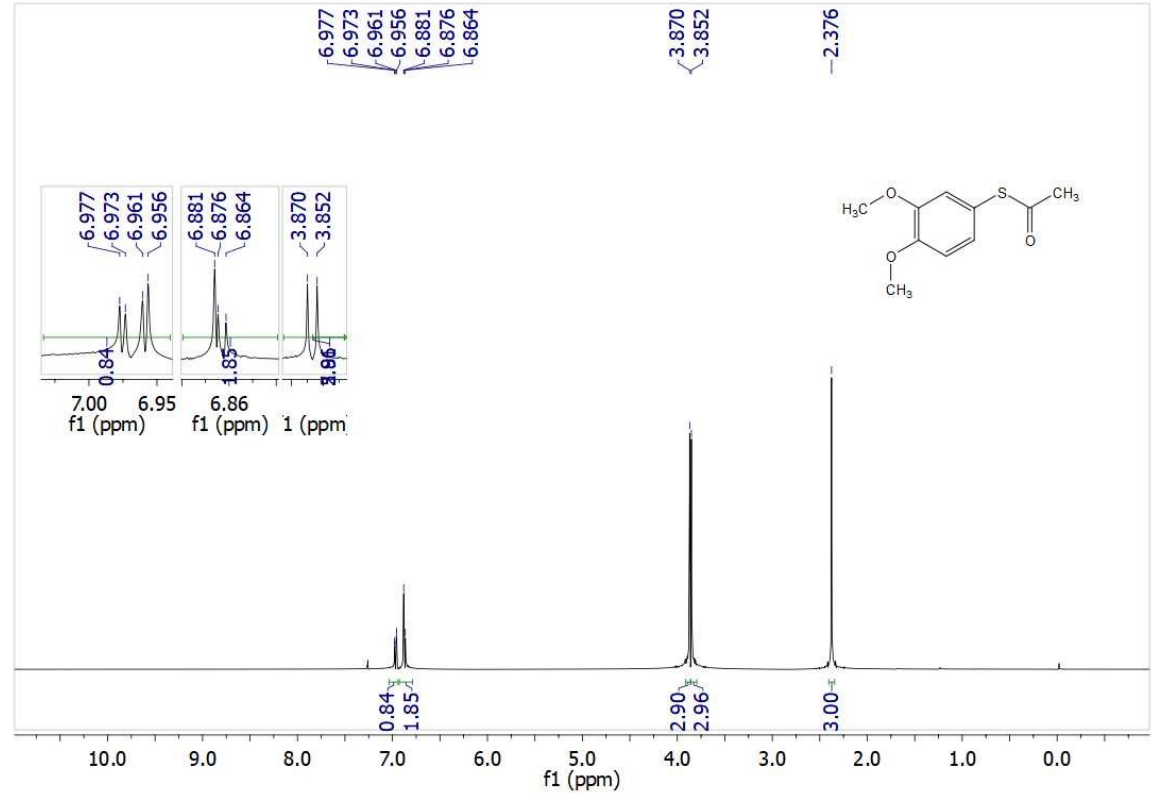
^{13}C NMR (126 MHz, $CDCl_3$) of compound **4**.



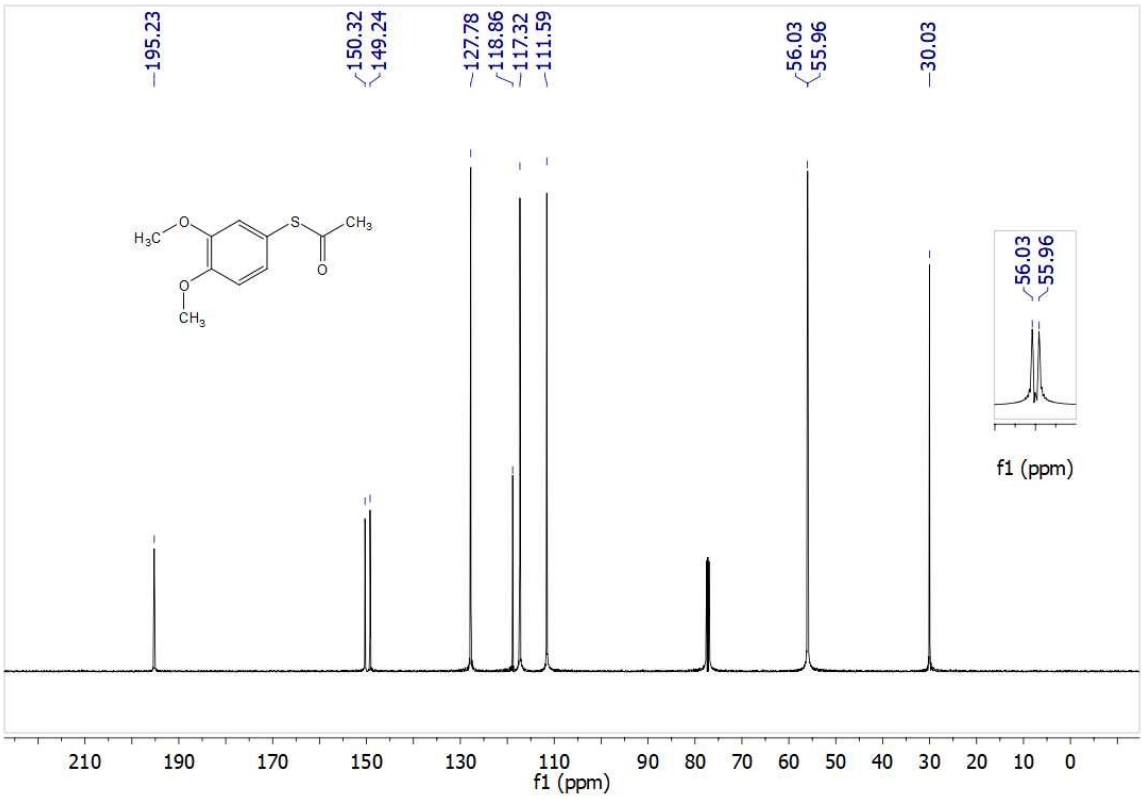
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**.



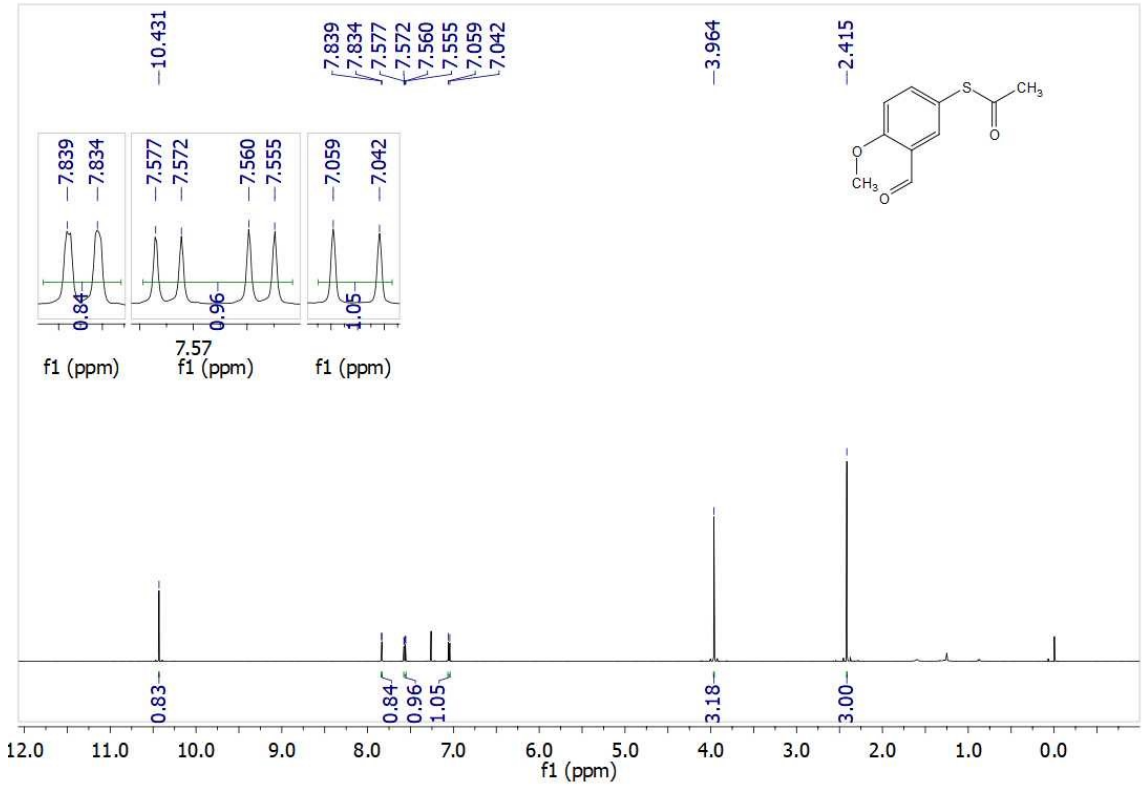
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5**.



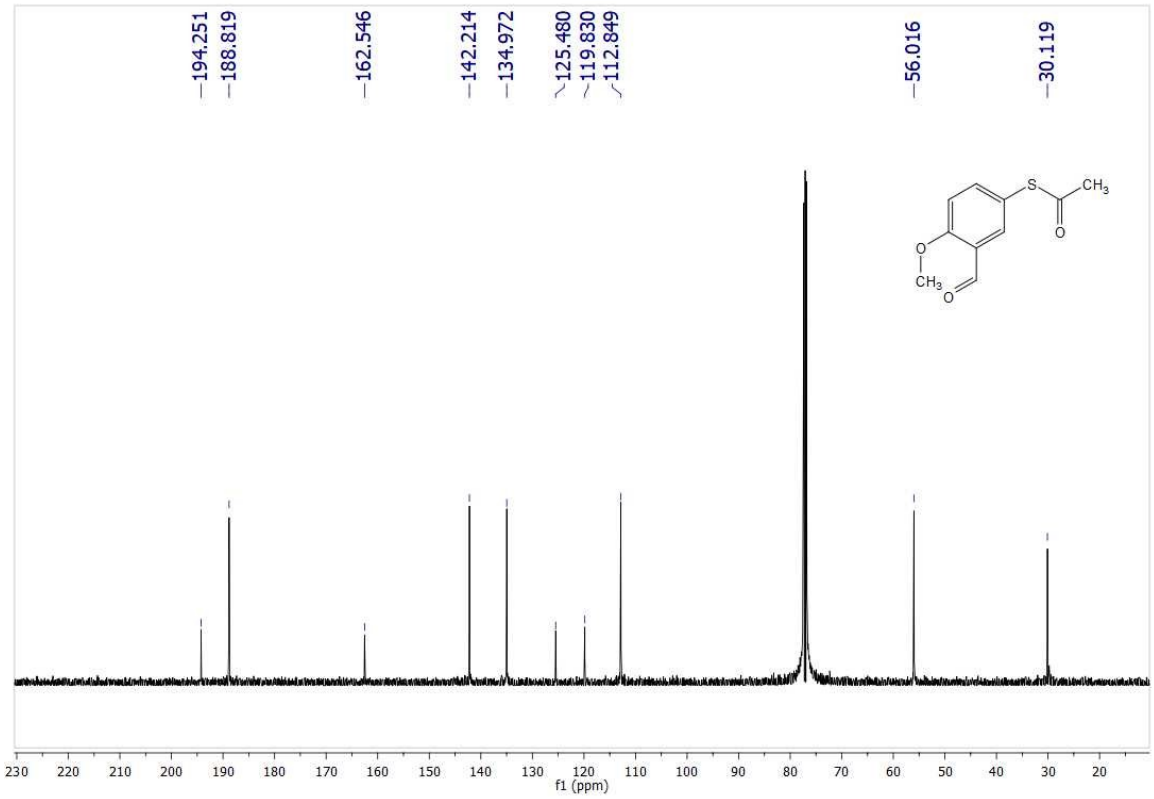
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



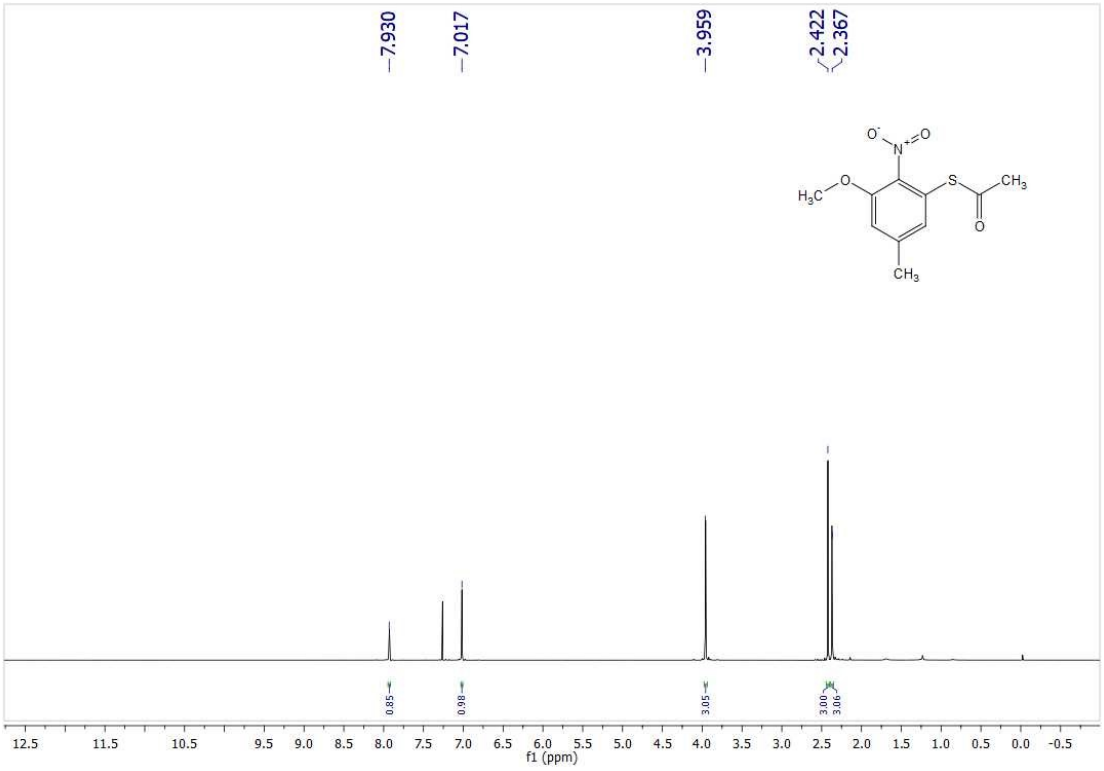
^{13}C NMR (126 MHz, $CDCl_3$) of compound **6**.



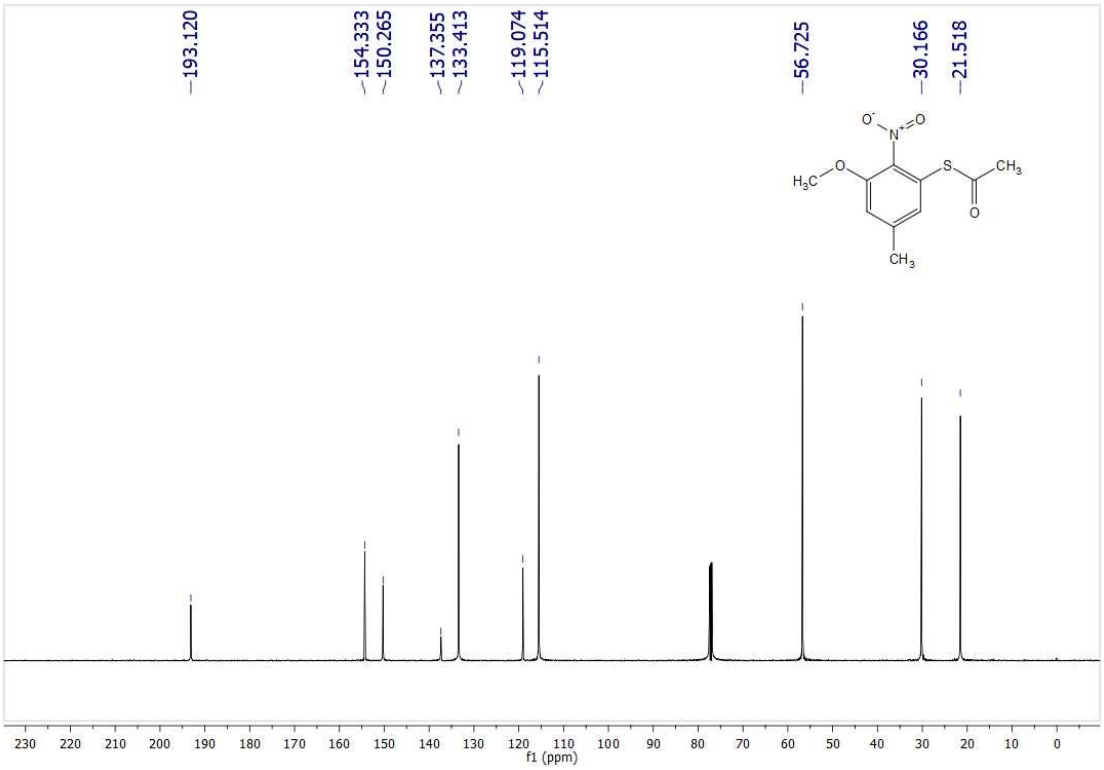
^{1}H NMR (500 MHz, $CDCl_3$) of compound **7**.



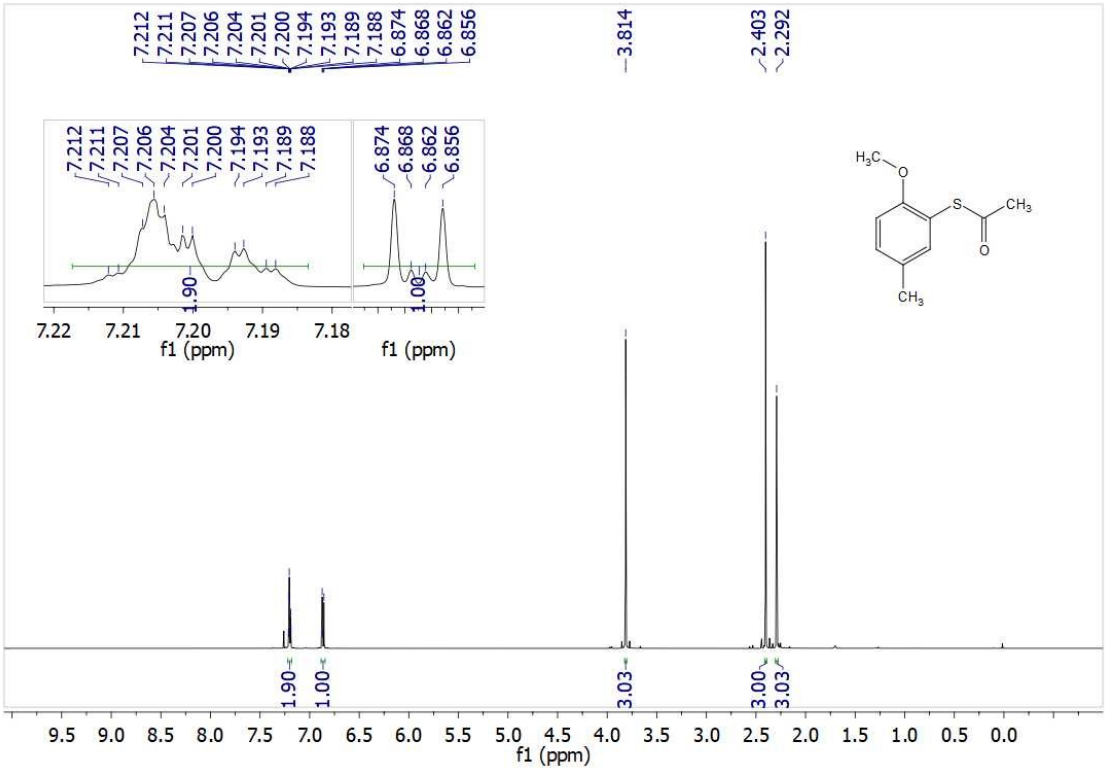
^{13}C NMR (126 MHz, $CDCl_3$) of compound **7**.



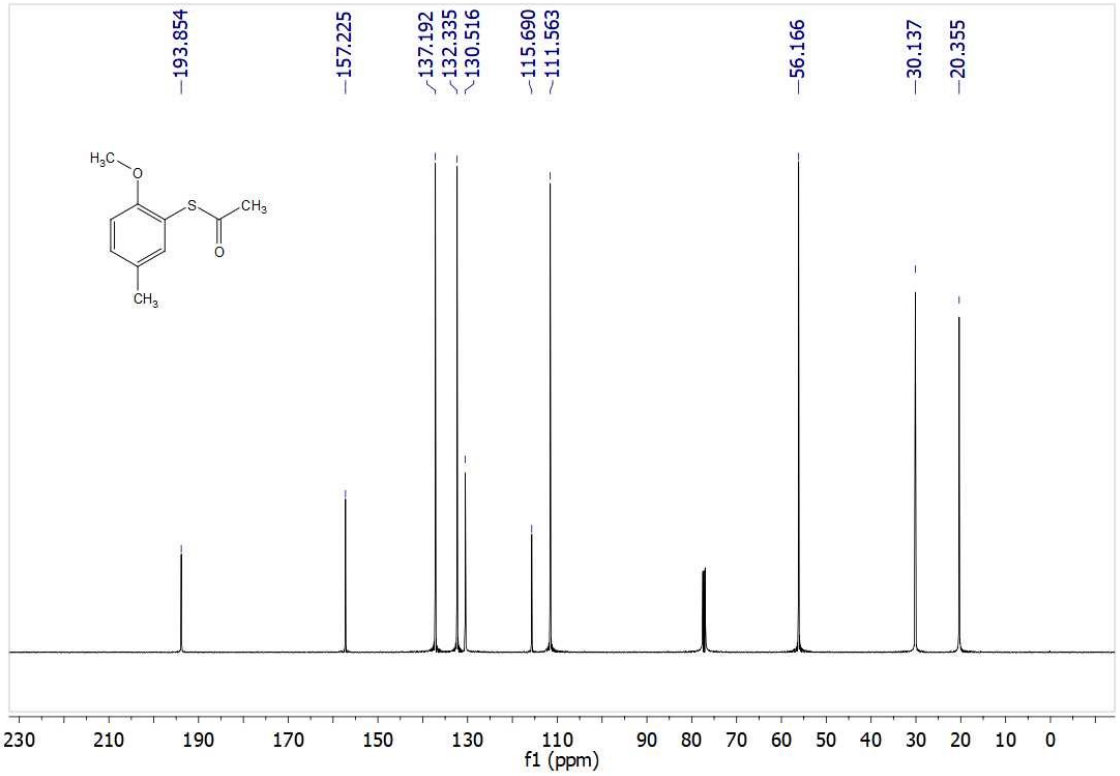
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



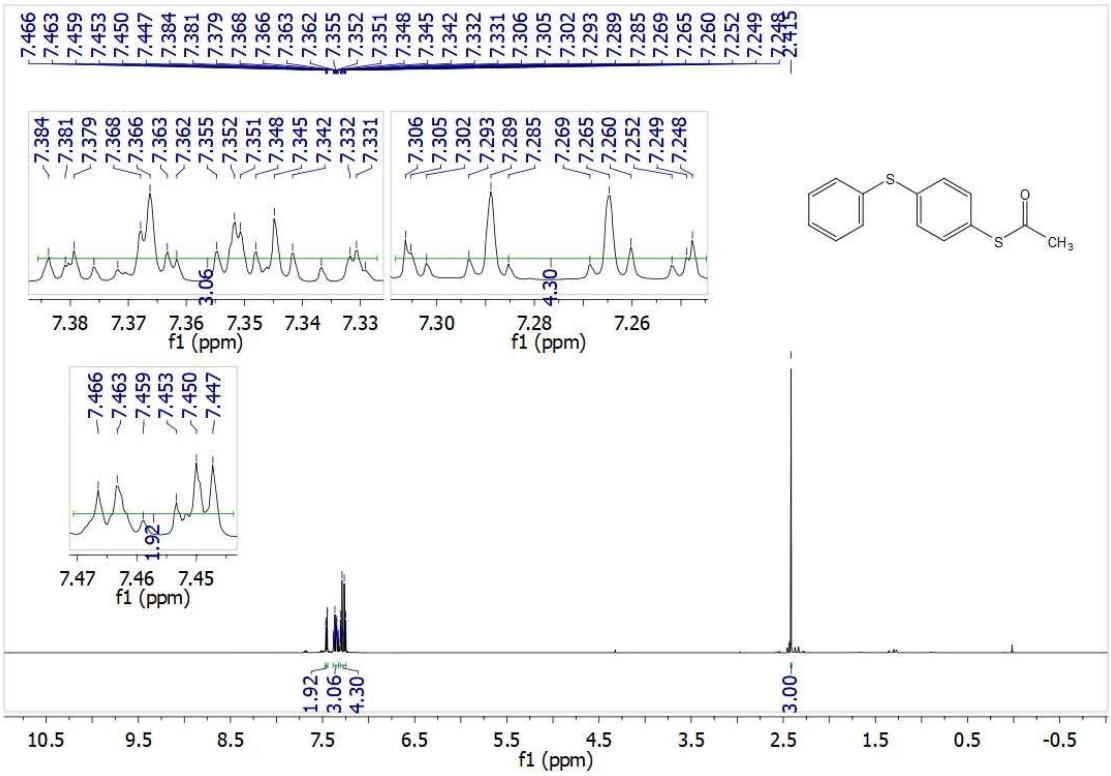
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8**.



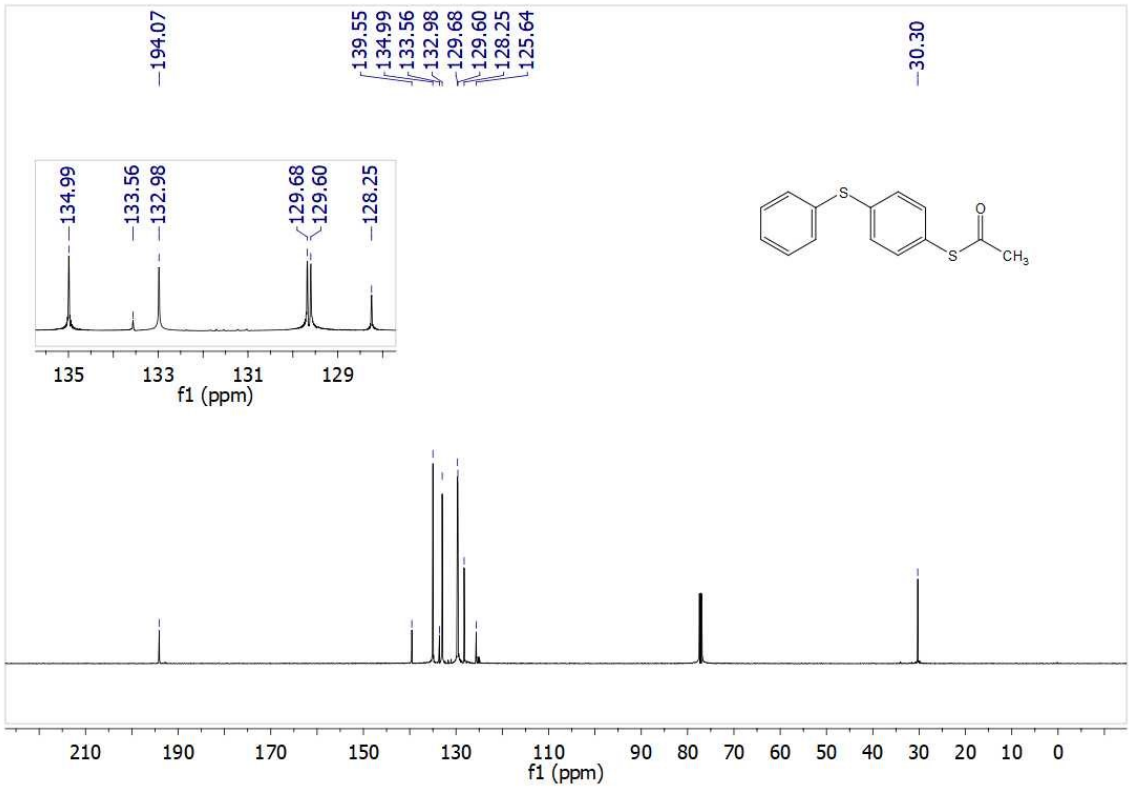
^{1}H NMR (500 MHz, $CDCl_3$) of compound **9**.



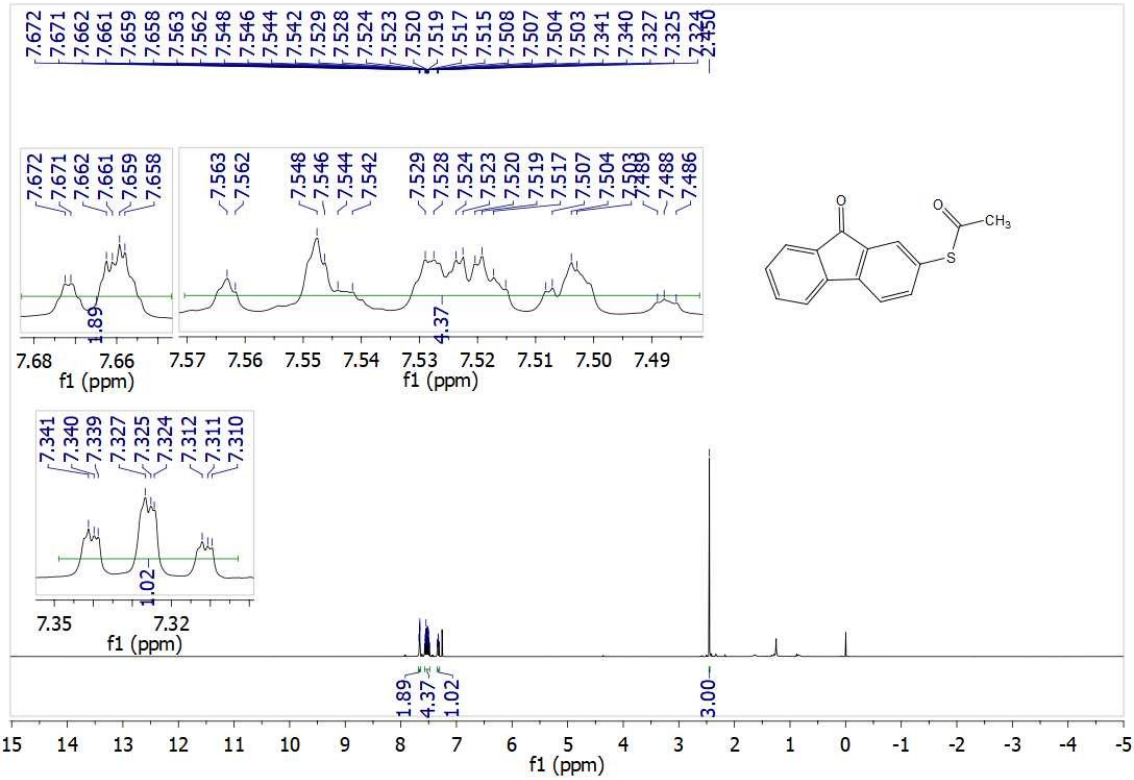
^{13}C NMR (126 MHz, $CDCl_3$) of compound **9**.



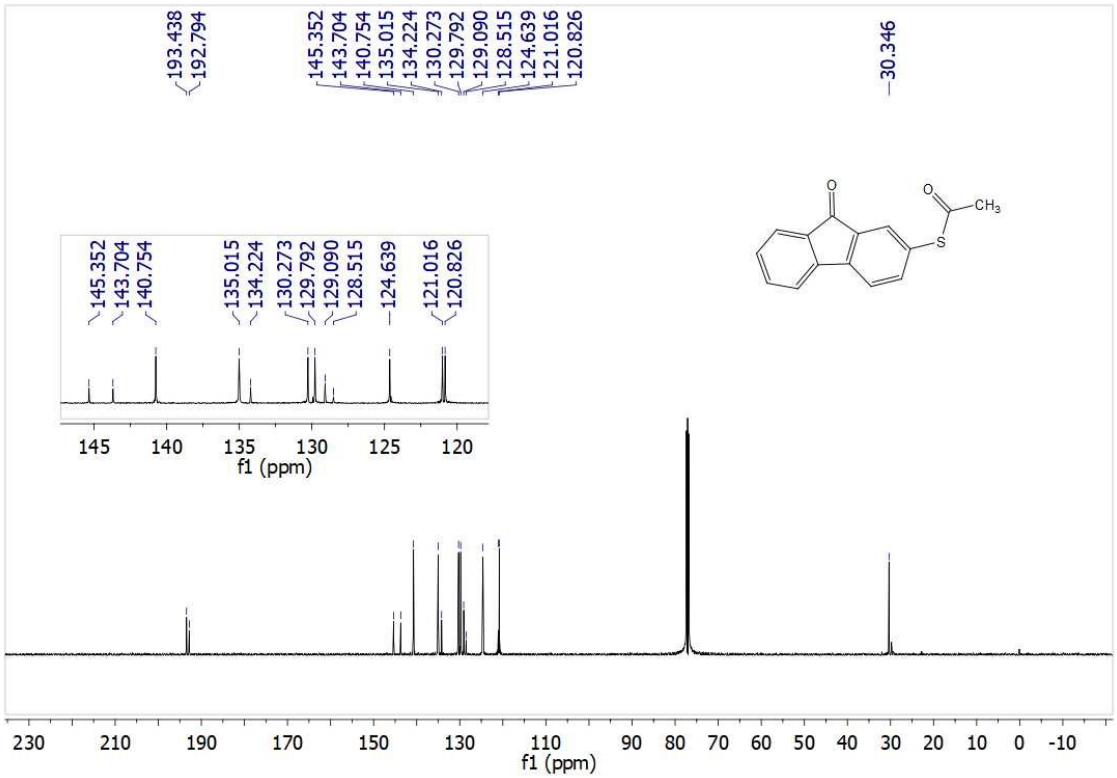
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**.



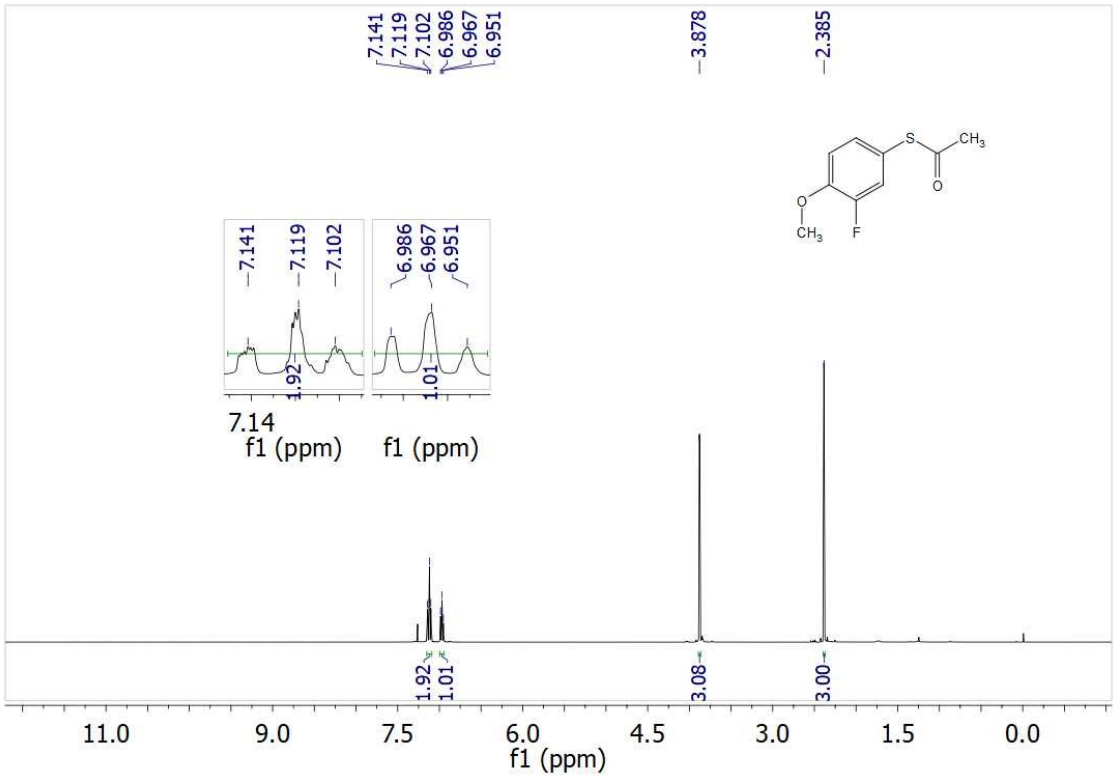
^{13}C NMR (126 MHz, $CDCl_3$) of compound **10**.



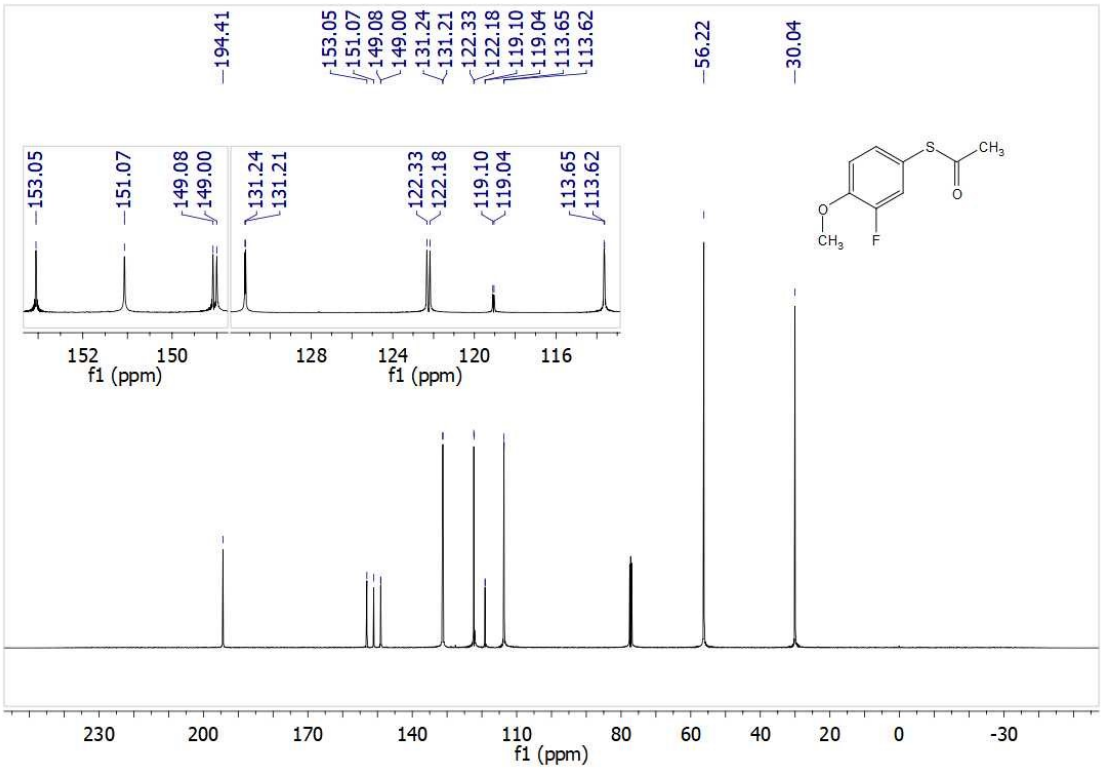
^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**.



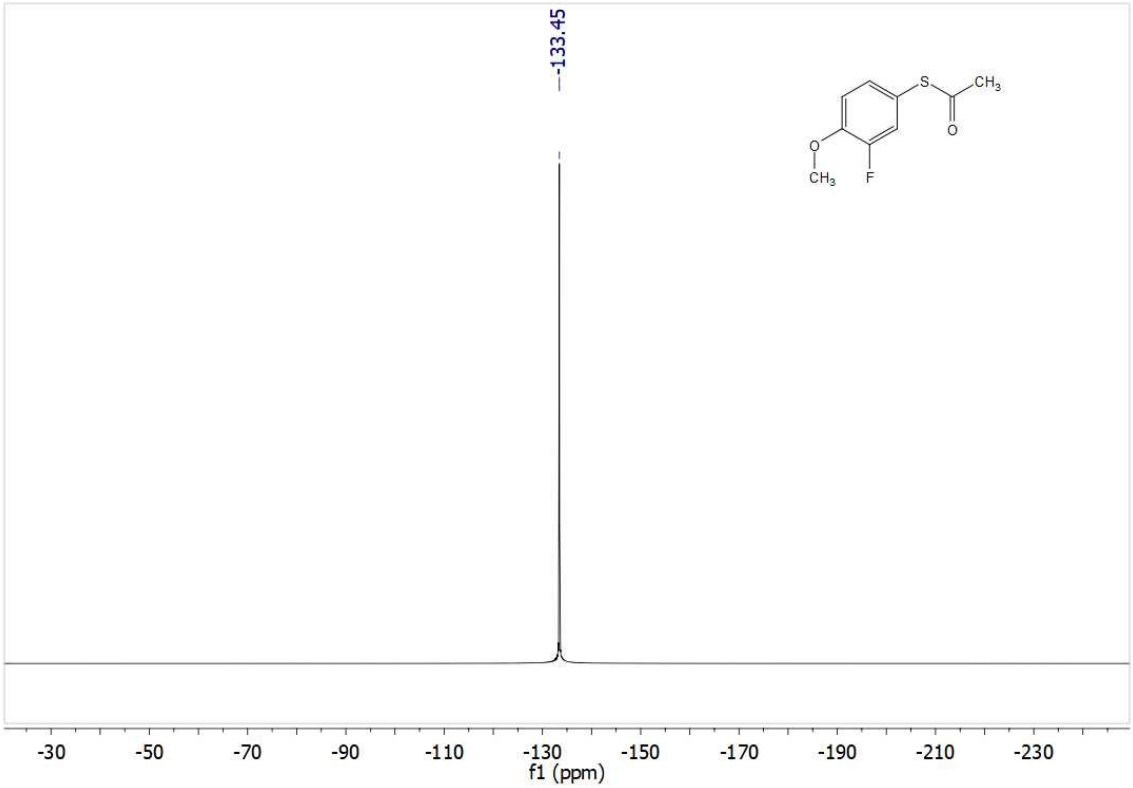
^{13}C NMR (126 MHz, $CDCl_3$) of compound **11**.



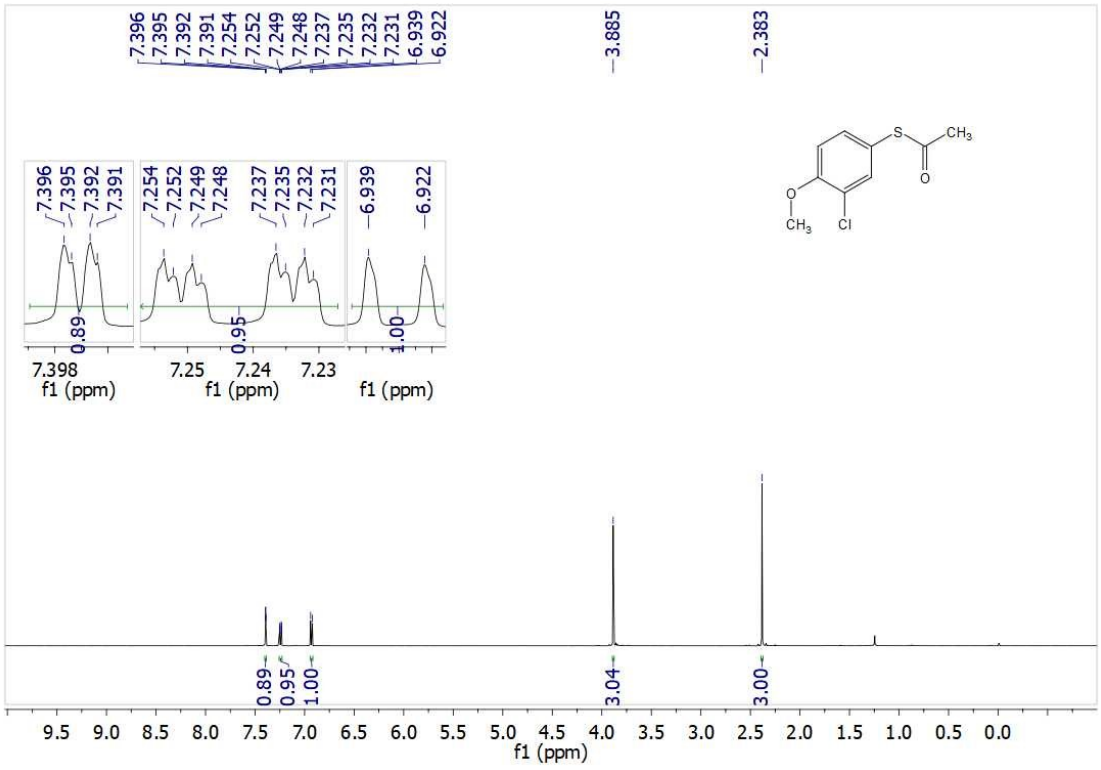
^{1}H NMR (500 MHz, $CDCl_3$) of compound **12**.



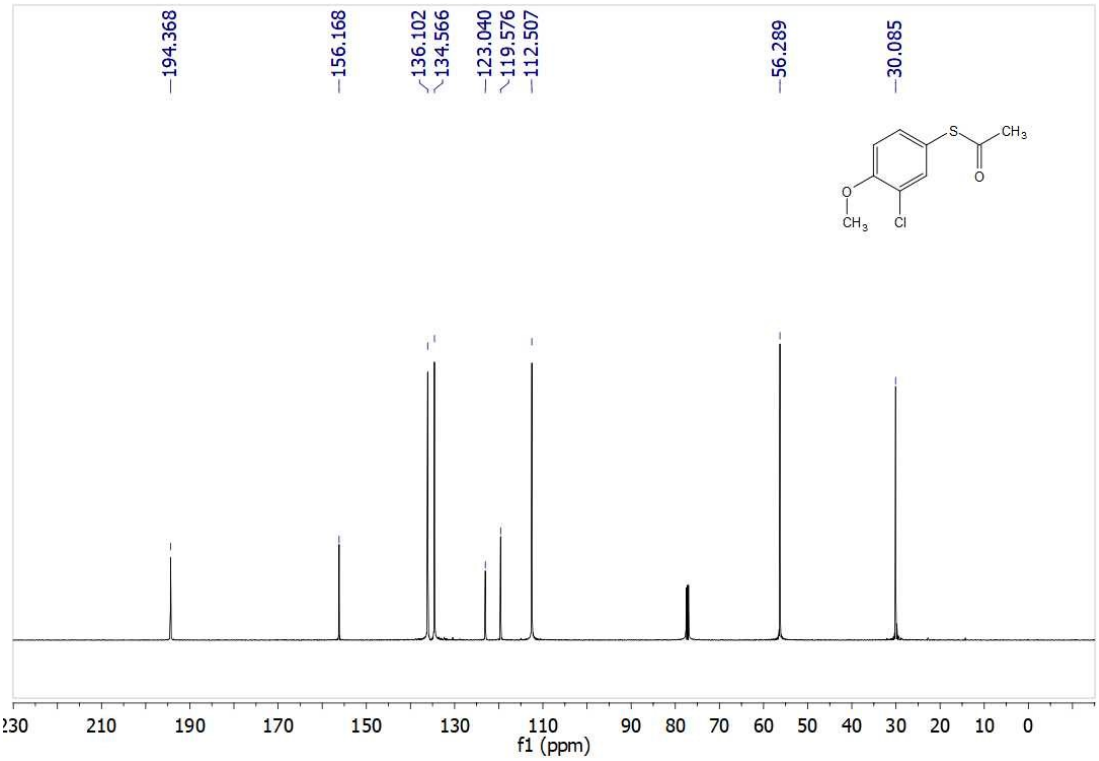
^{13}C NMR (126 MHz, $CDCl_3$) of compound **12**.



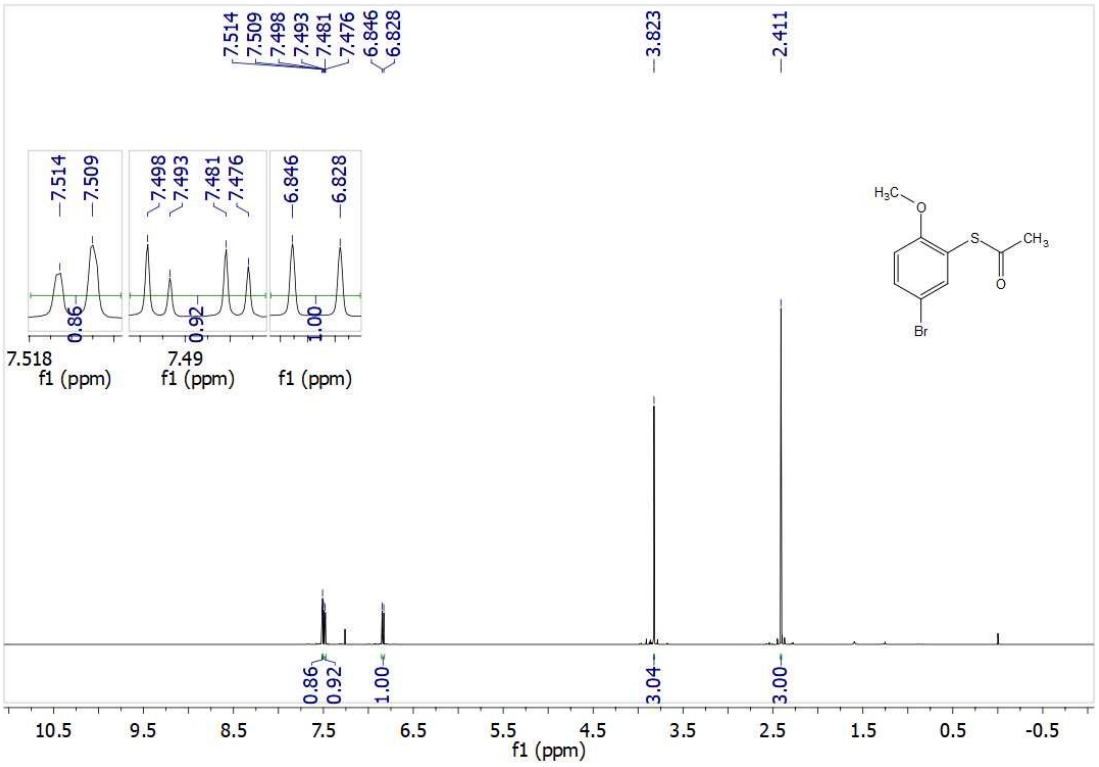
^{19}F NMR (472 MHz, $CDCl_3$) of compound **12**.



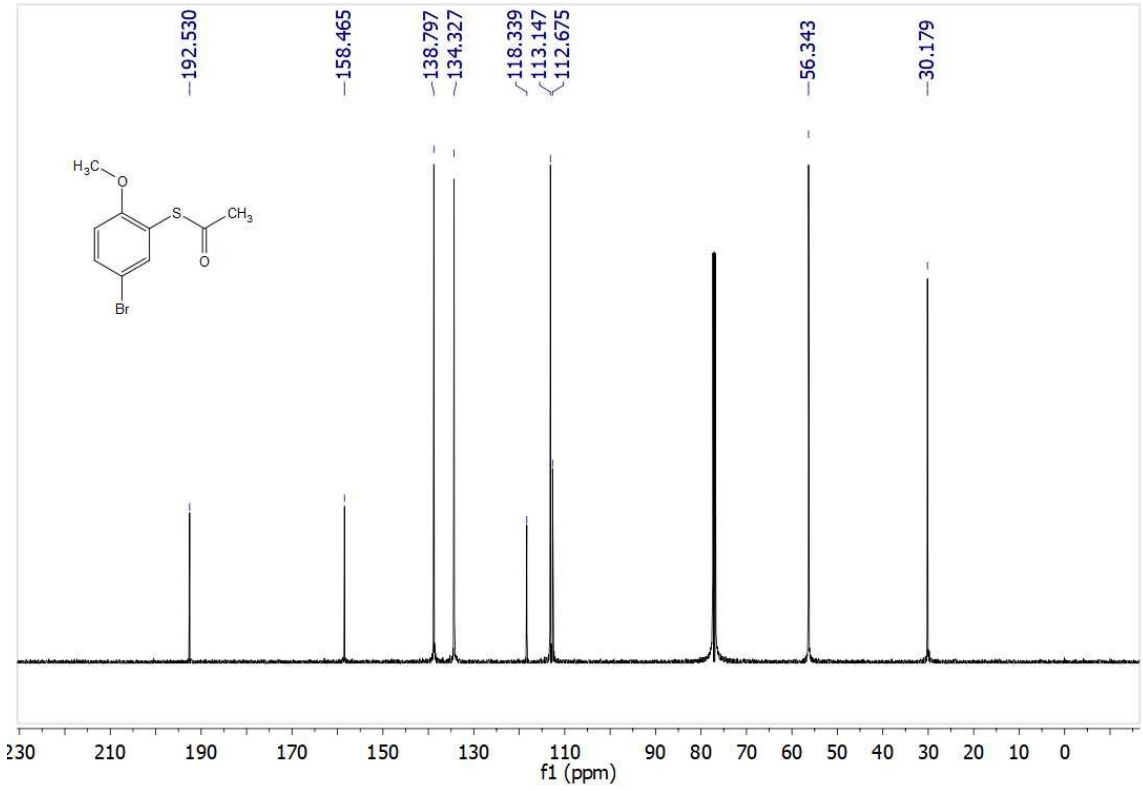
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13**.



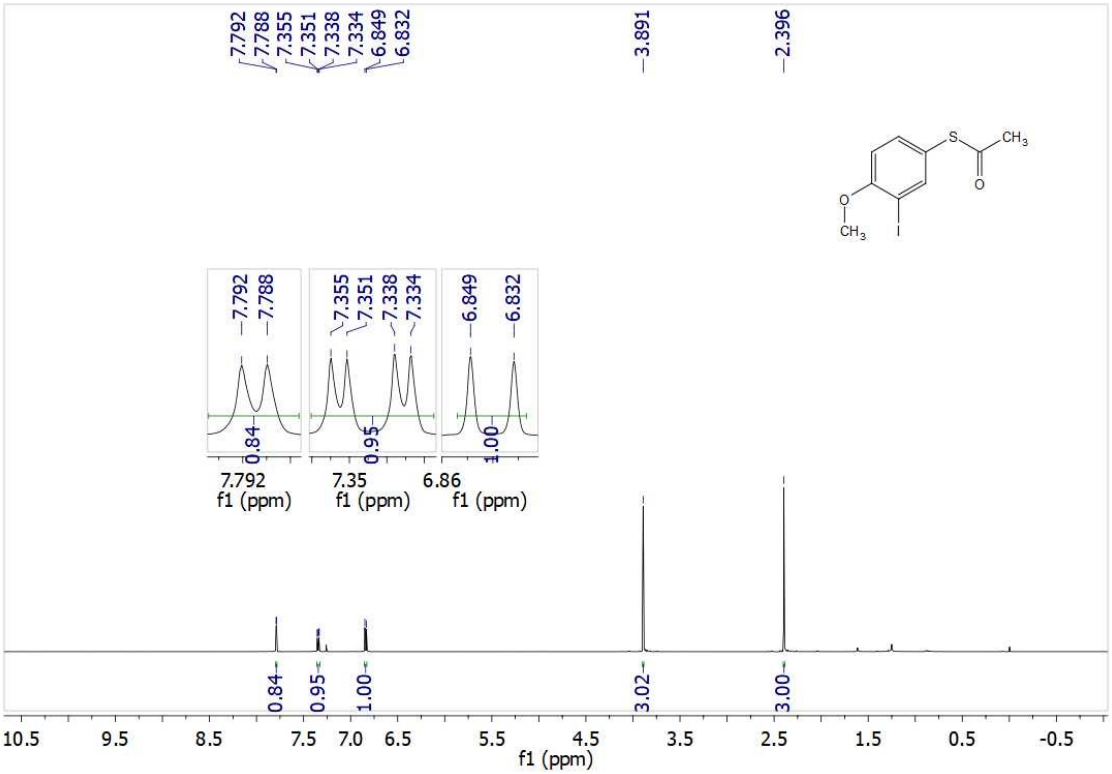
^{13}C NMR (126 MHz, $CDCl_3$) of compound **13**.



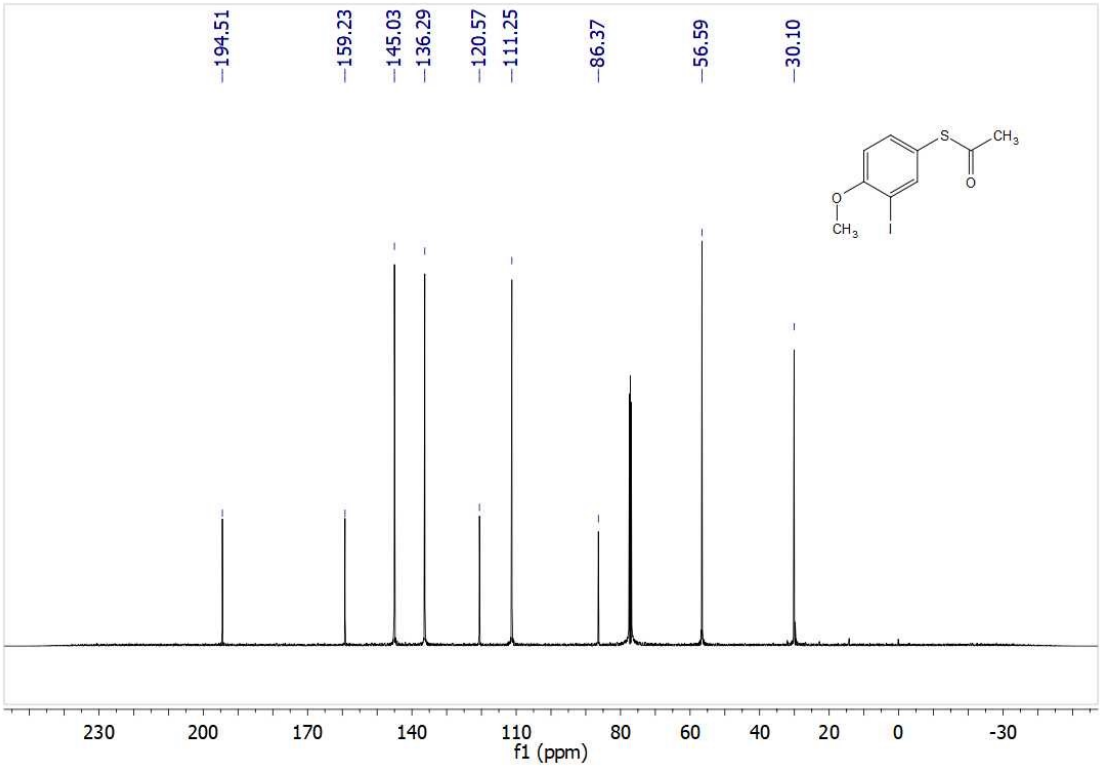
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14**.



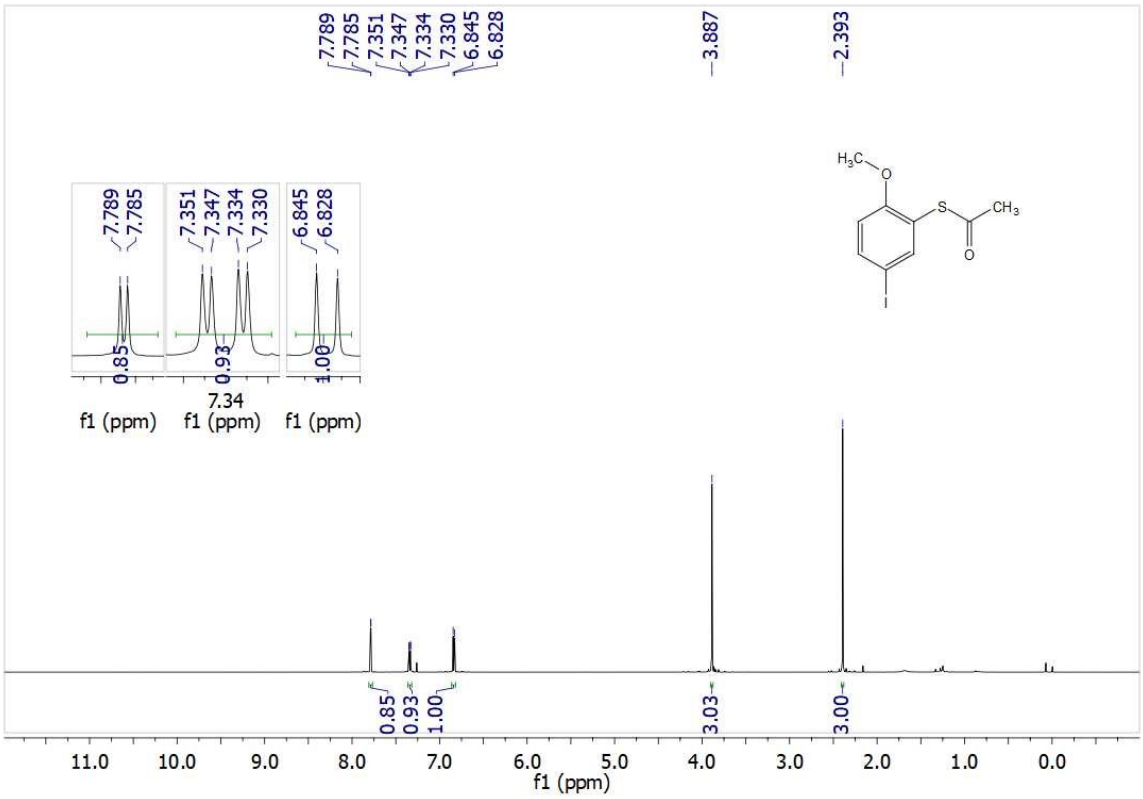
^{13}C NMR (126 MHz, $CDCl_3$) of compound **14**.



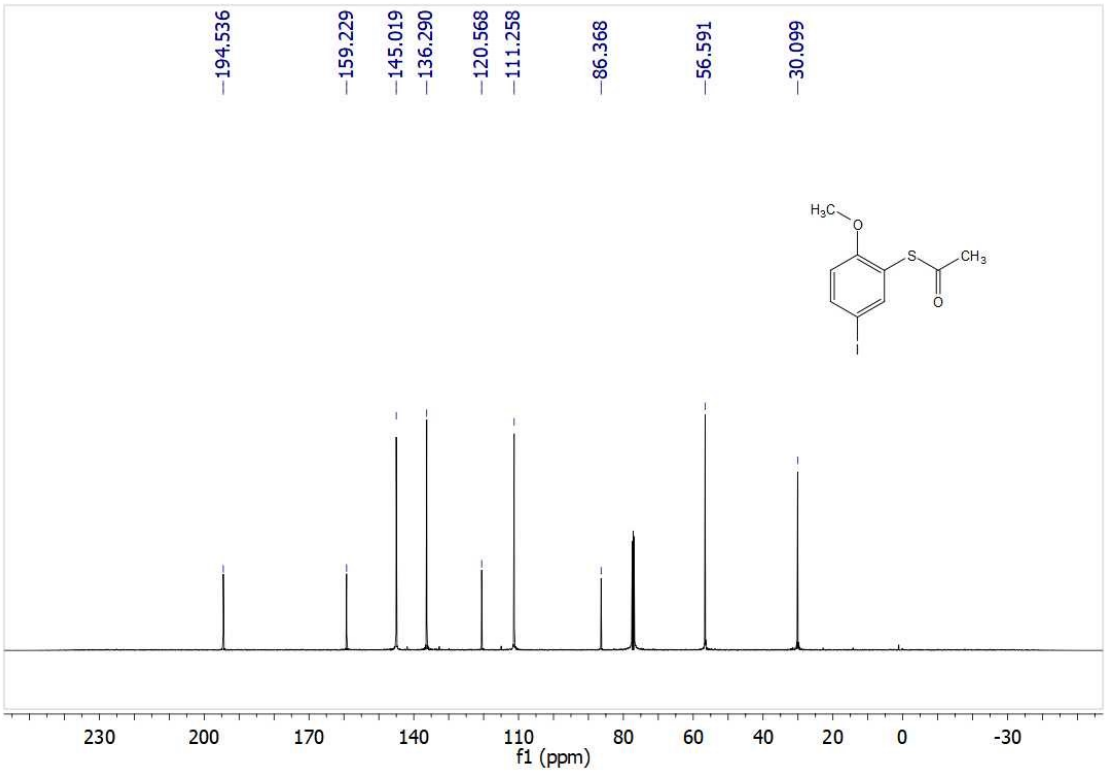
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15**.



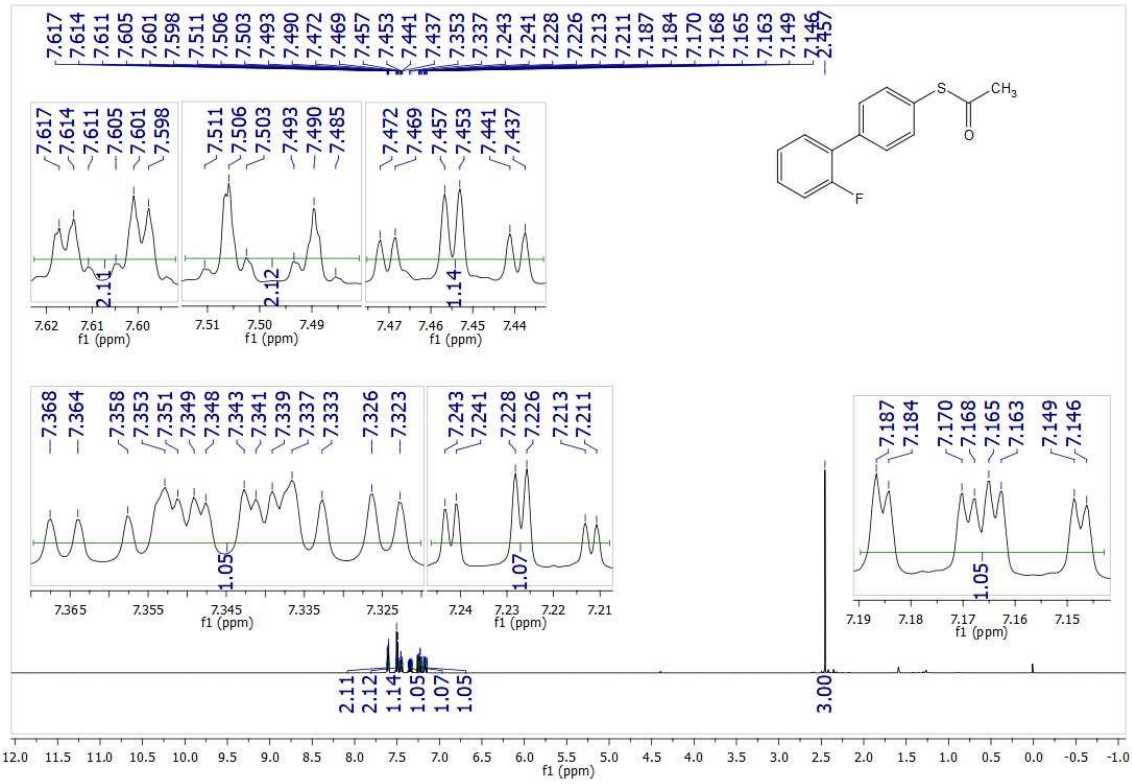
^{13}C NMR (126 MHz, $CDCl_3$) of compound **15**.



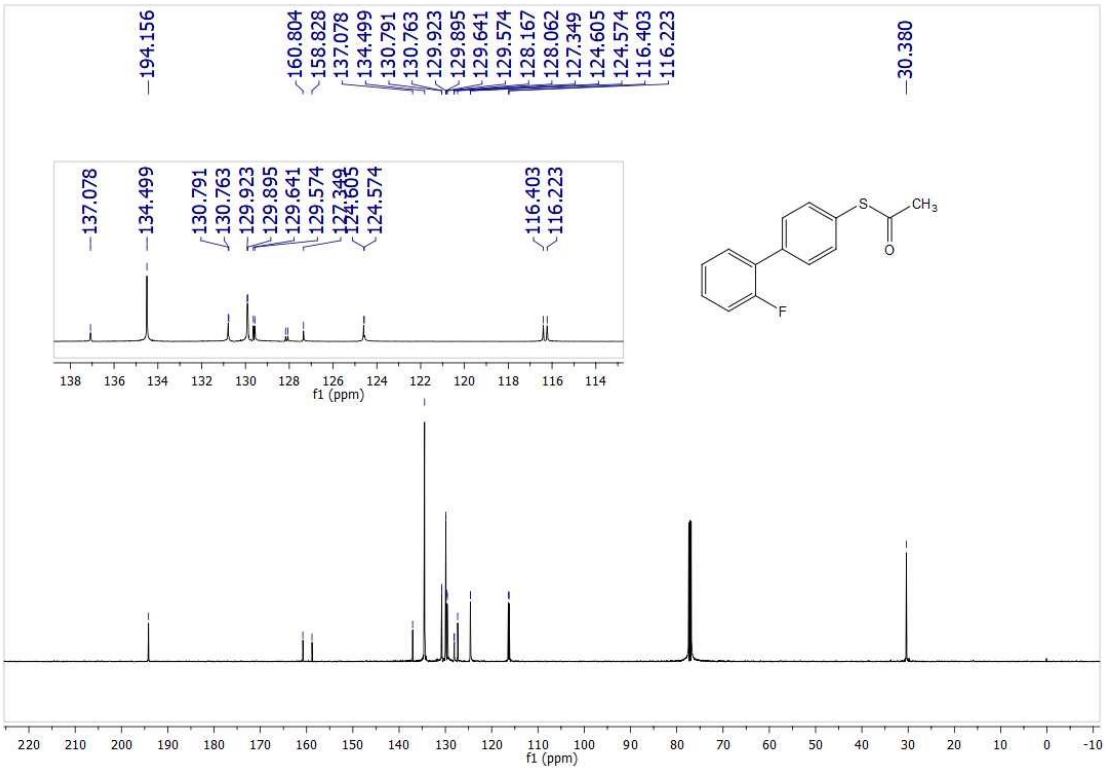
^{1}H NMR (500 MHz, $CDCl_3$) of compound **16**.



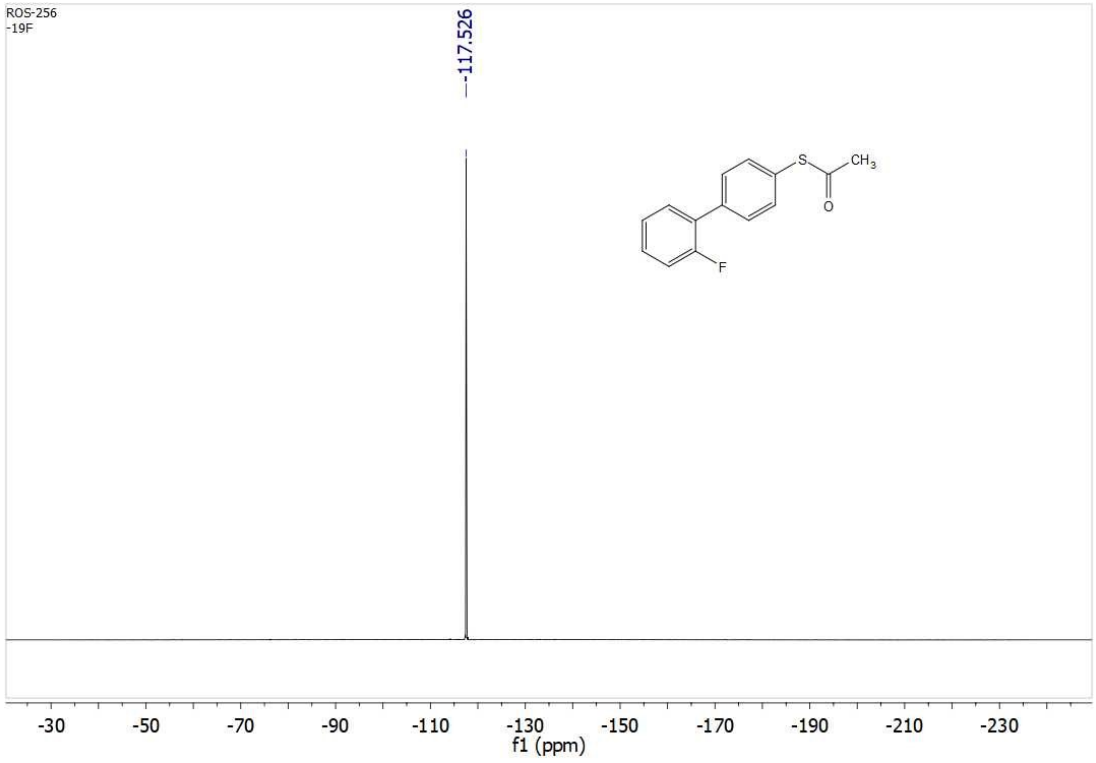
^{13}C NMR (126 MHz, $CDCl_3$) of compound **16**.



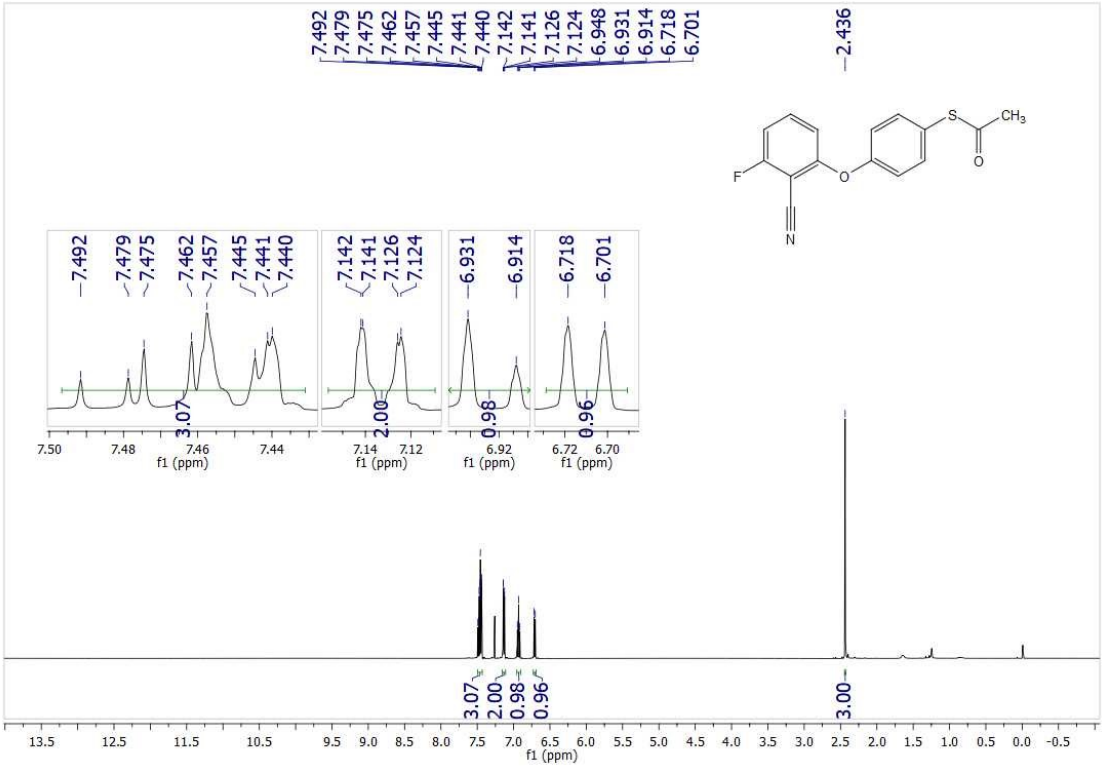
^{1}H NMR (500 MHz, $CDCl_3$) of compound **17**.



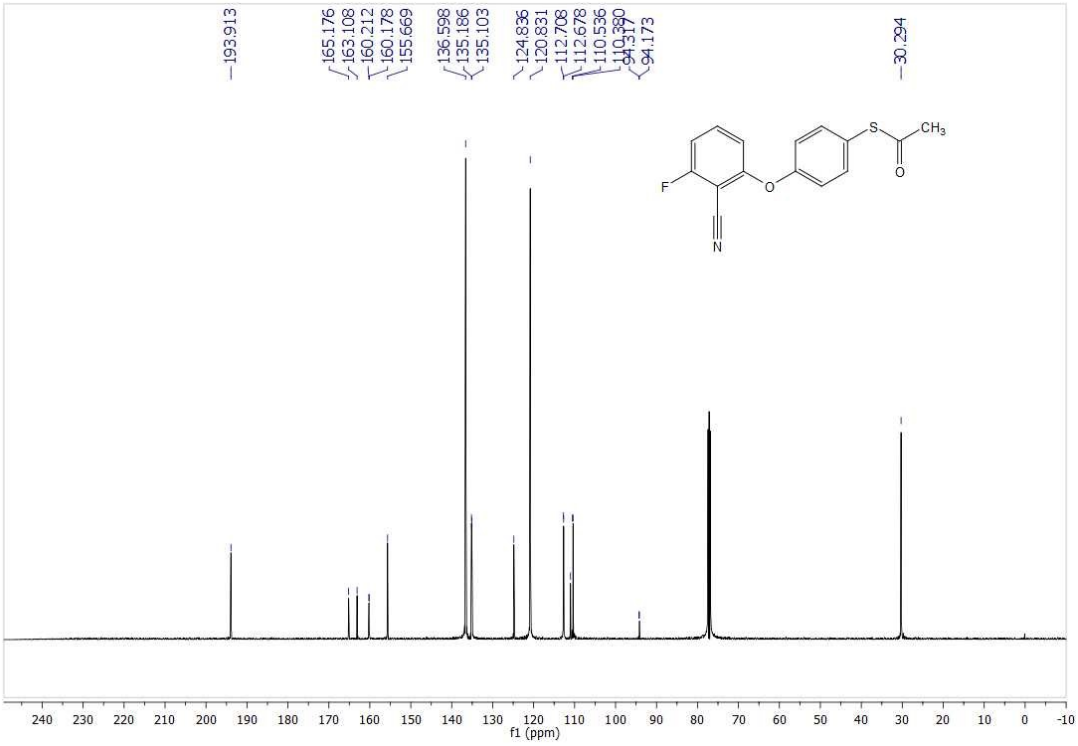
^{13}C NMR (126 MHz, $CDCl_3$) of compound **17**.



^{19}F NMR (472 MHz, $CDCl_3$) of compound **17**.

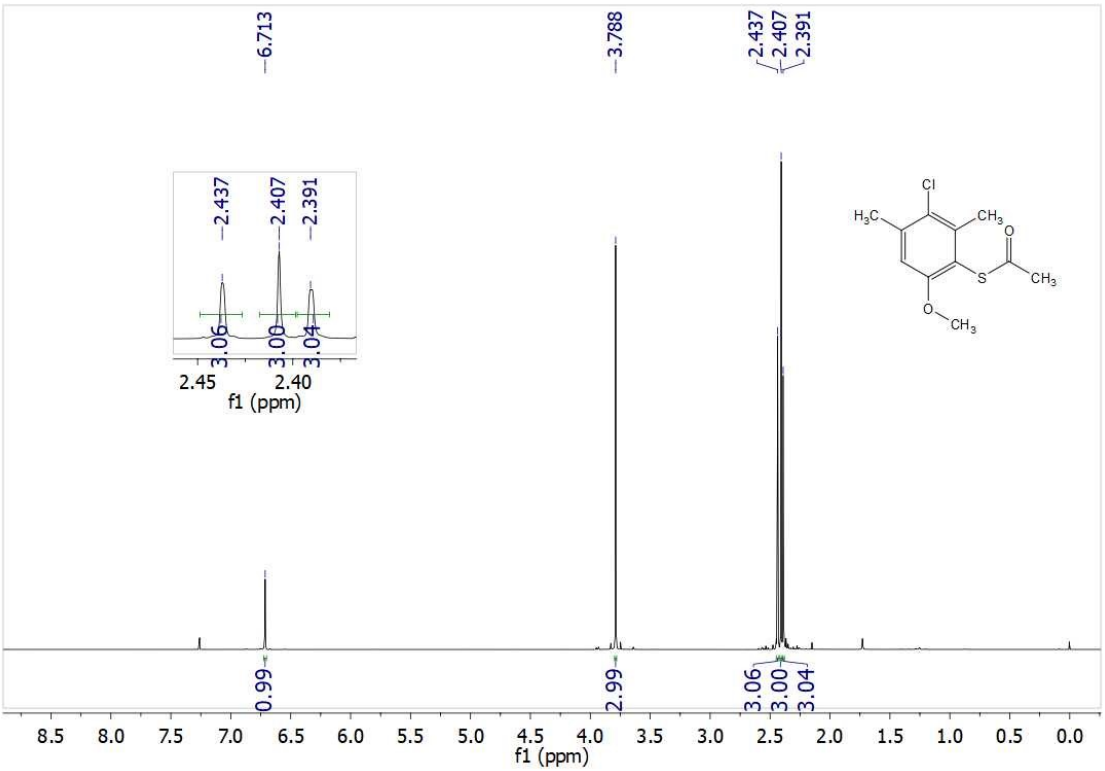


^{1}H NMR (500 MHz, $CDCl_3$) of compound **18**.

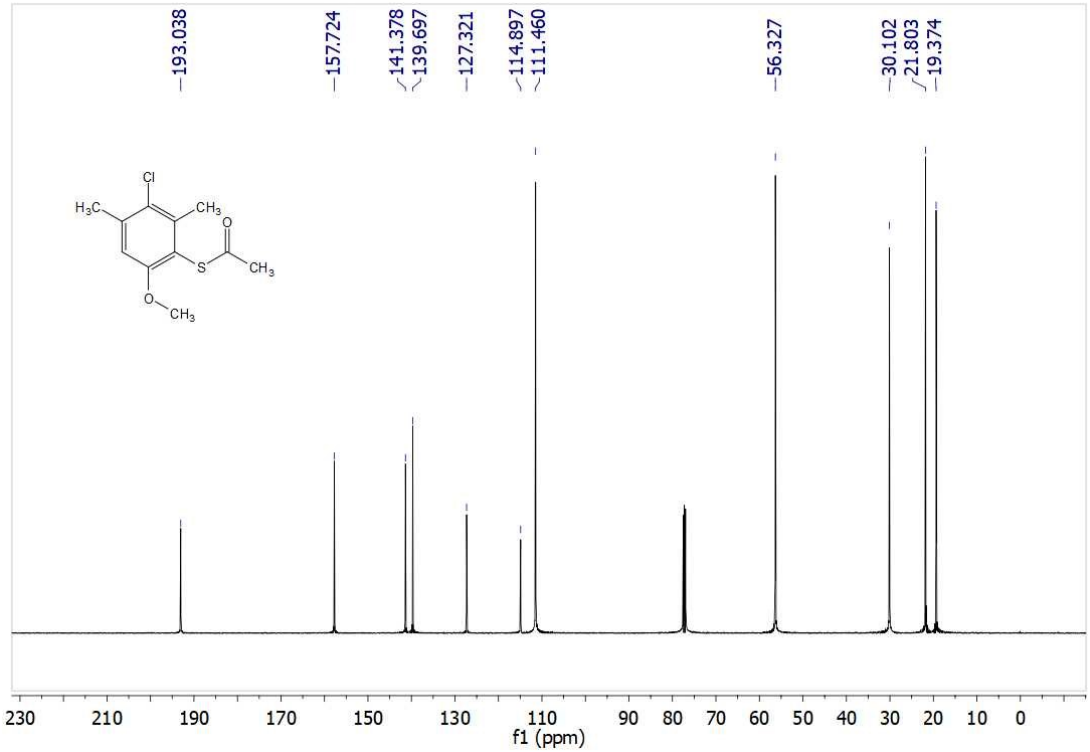


^{13}C NMR (126 MHz, $CDCl_3$) of compound **18**.

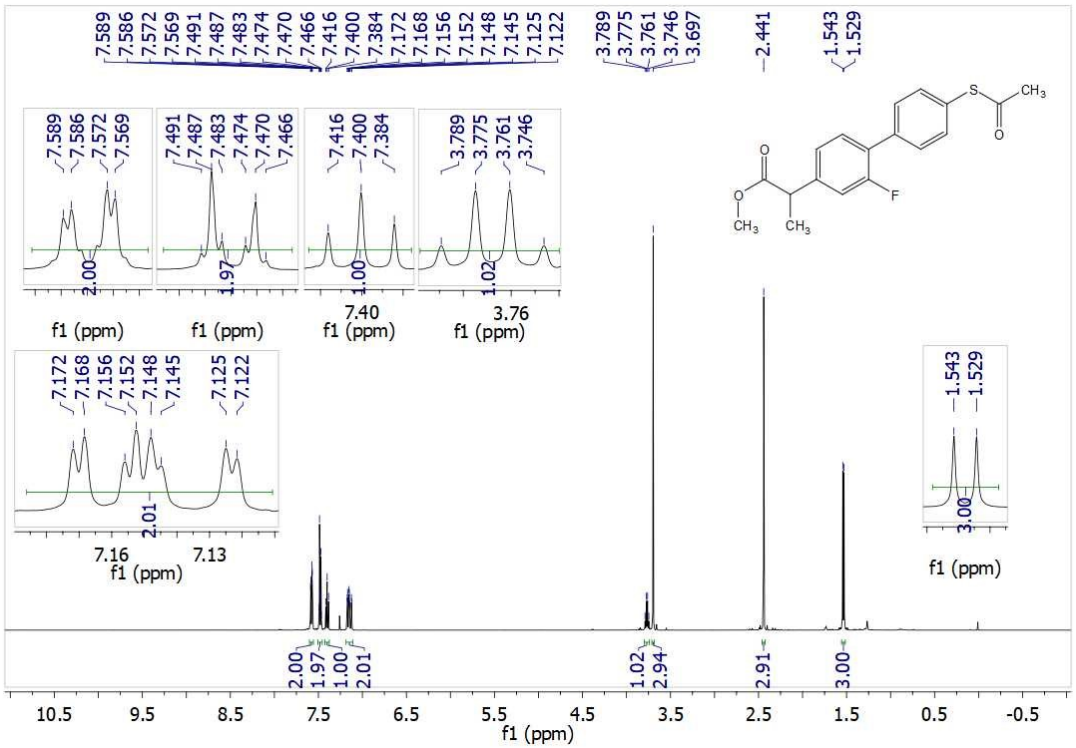
^{19}F NMR (472 MHz, $CDCl_3$) of compound **18**.



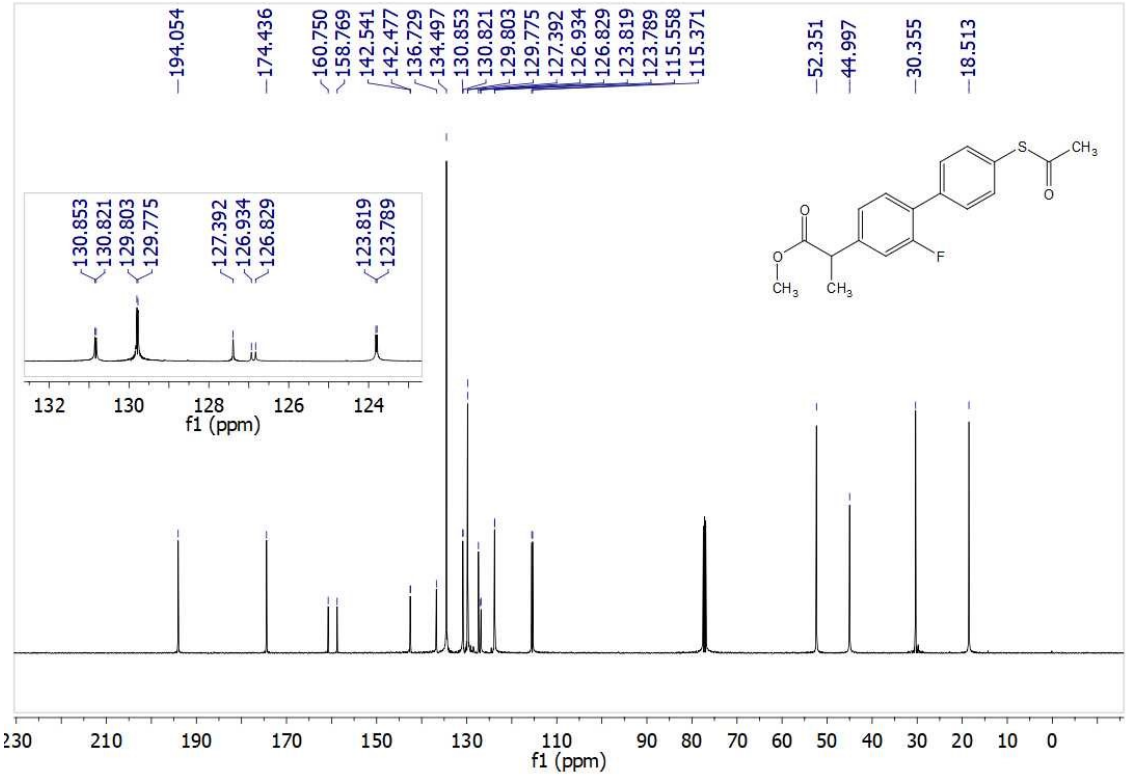
^{1}H NMR (500 MHz, $CDCl_3$) of compound **19**.



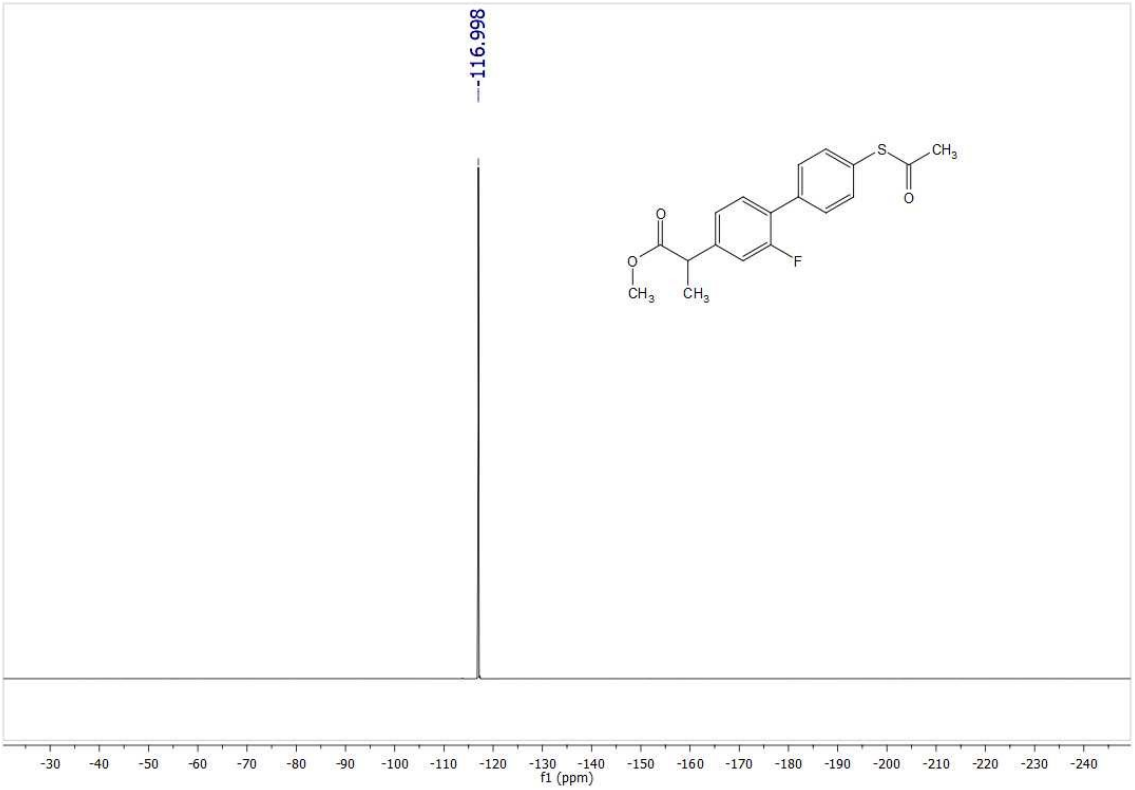
^{13}C NMR (126 MHz, $CDCl_3$) of compound **19**.



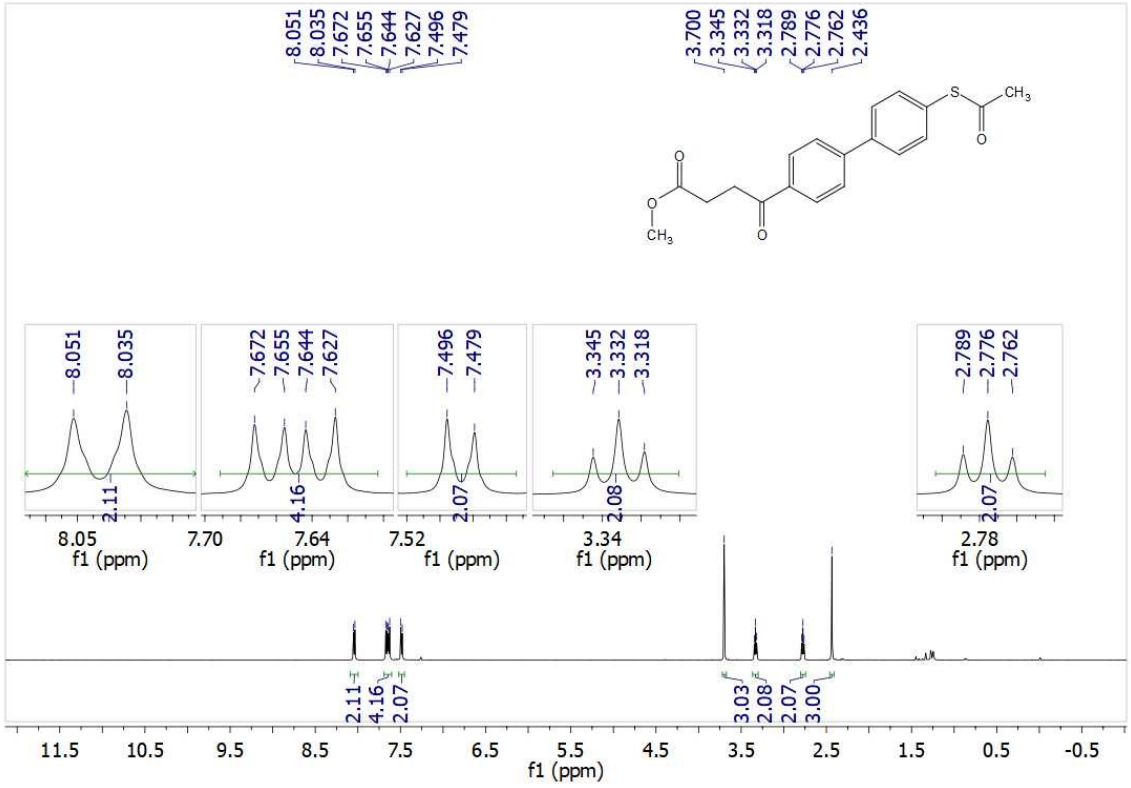
^{1}H NMR (500 MHz, $CDCl_3$) of compound **20**.



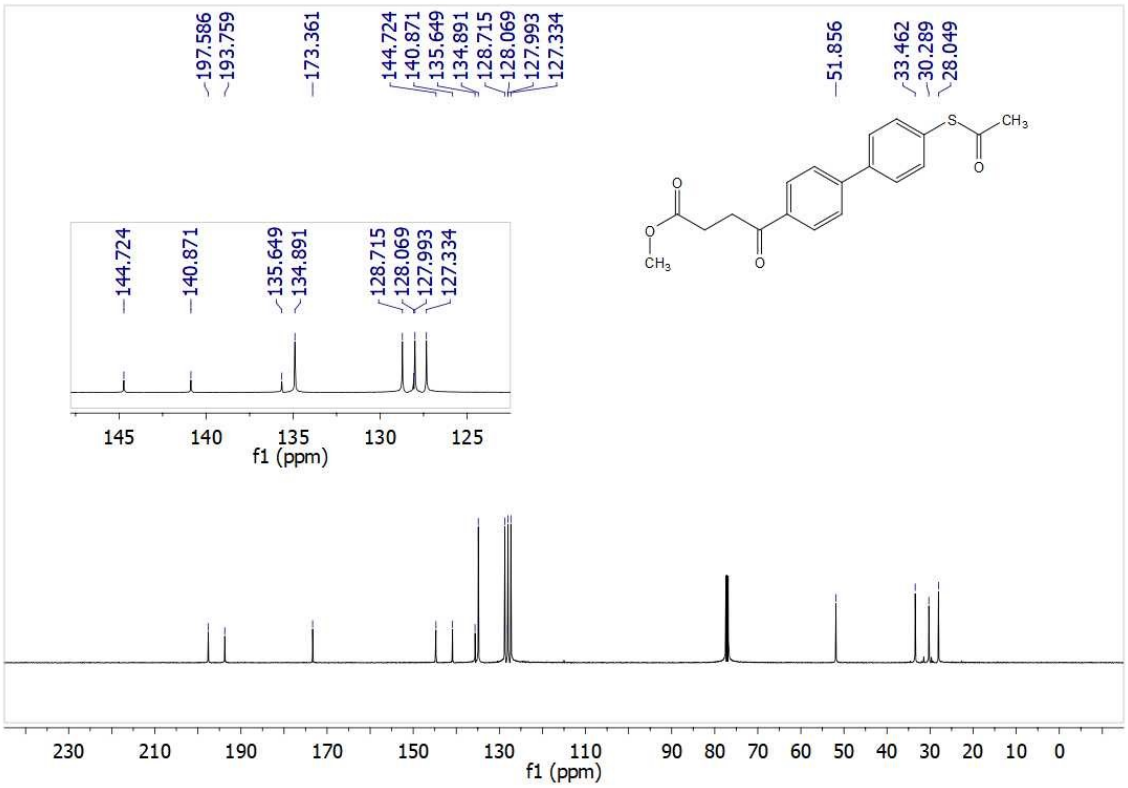
^{13}C NMR (126 MHz, $CDCl_3$) of compound **20**.



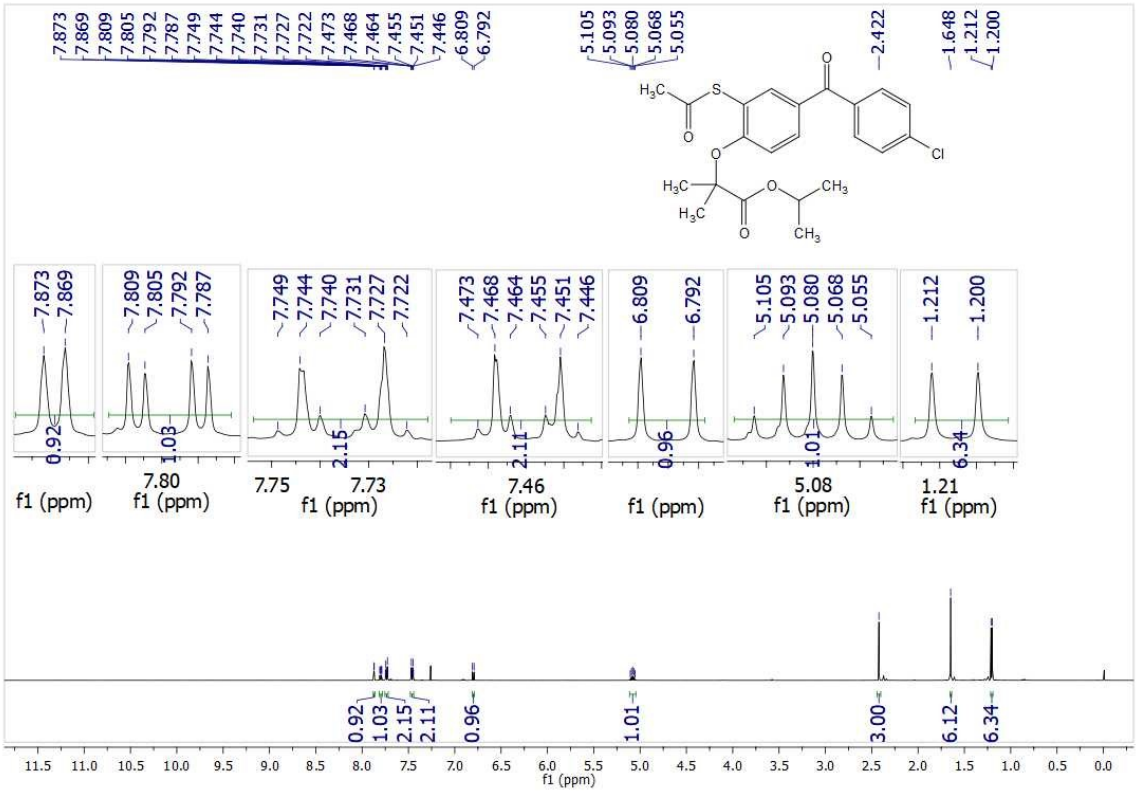
^{19}F NMR (472 MHz, $CDCl_3$) of compound **20**.



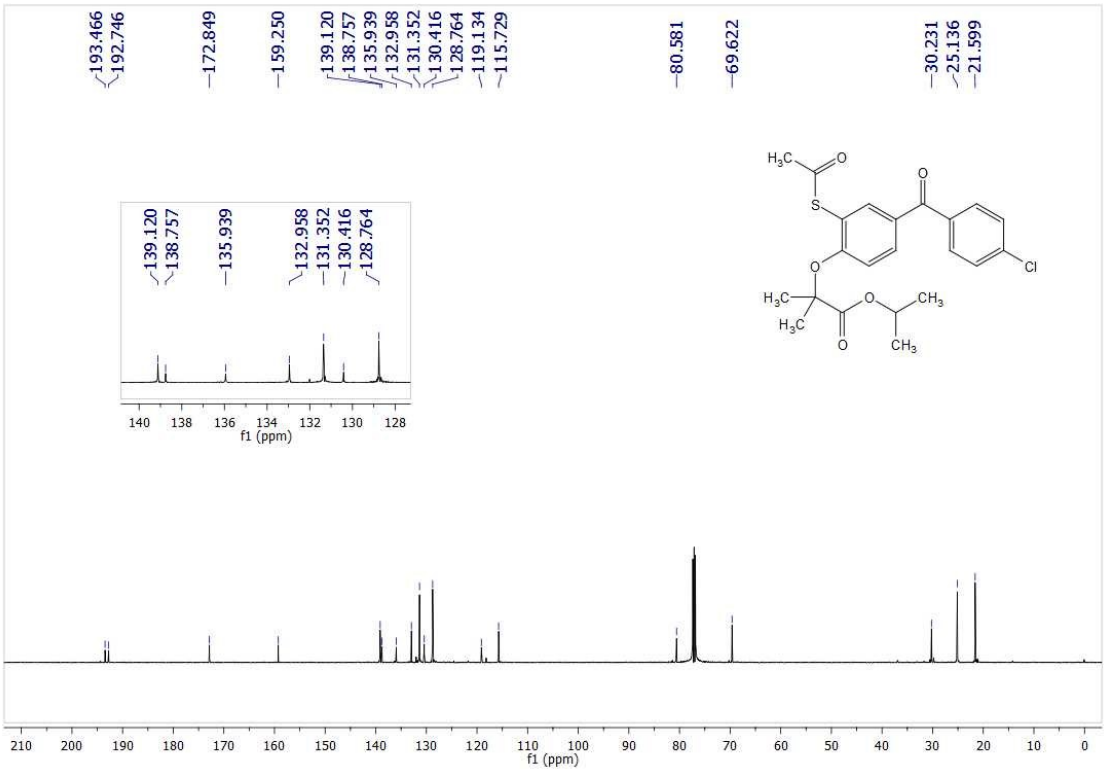
^{1}H NMR (500 MHz, $CDCl_3$) of compound **21**.



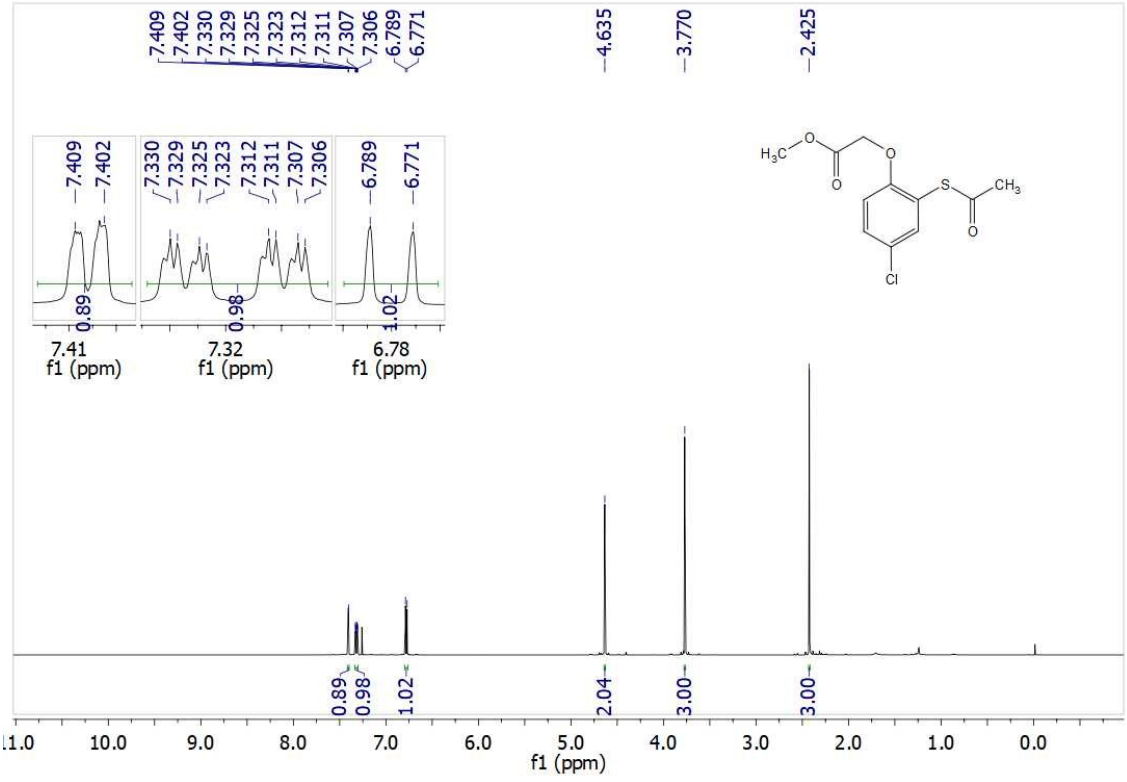
^{13}C NMR (126 MHz, $CDCl_3$) of compound **21**.



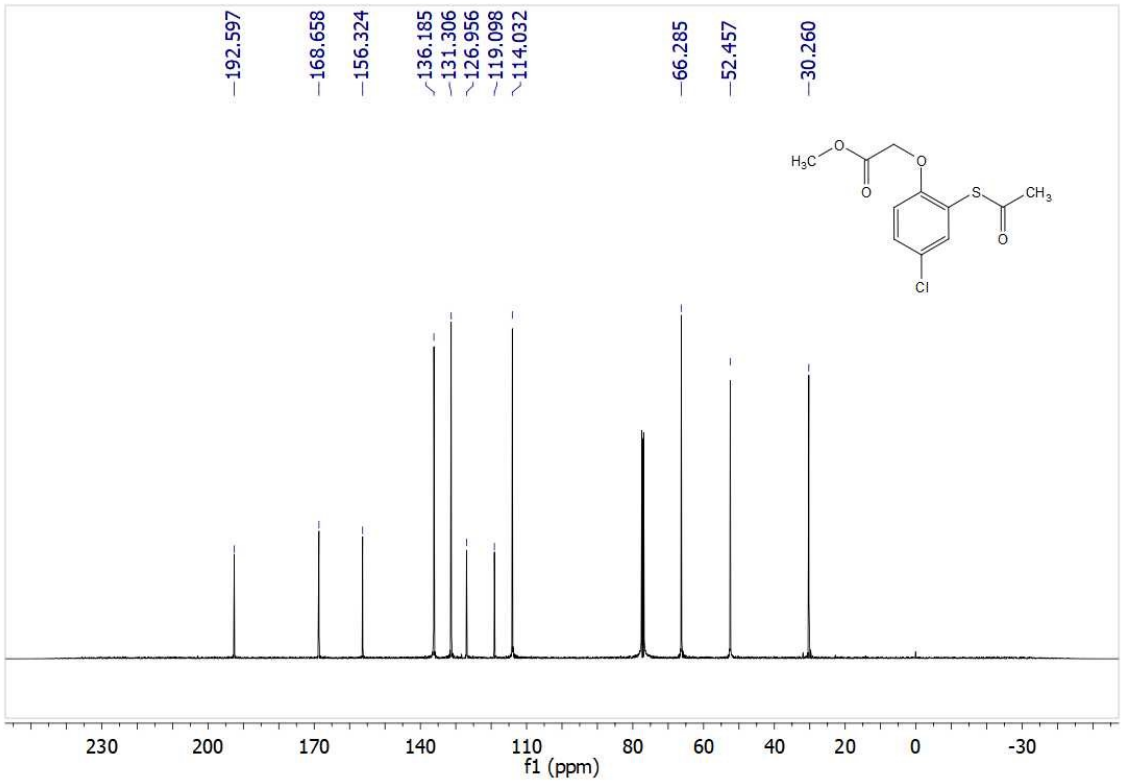
^{1}H NMR (500 MHz, $CDCl_3$) of compound **22**.



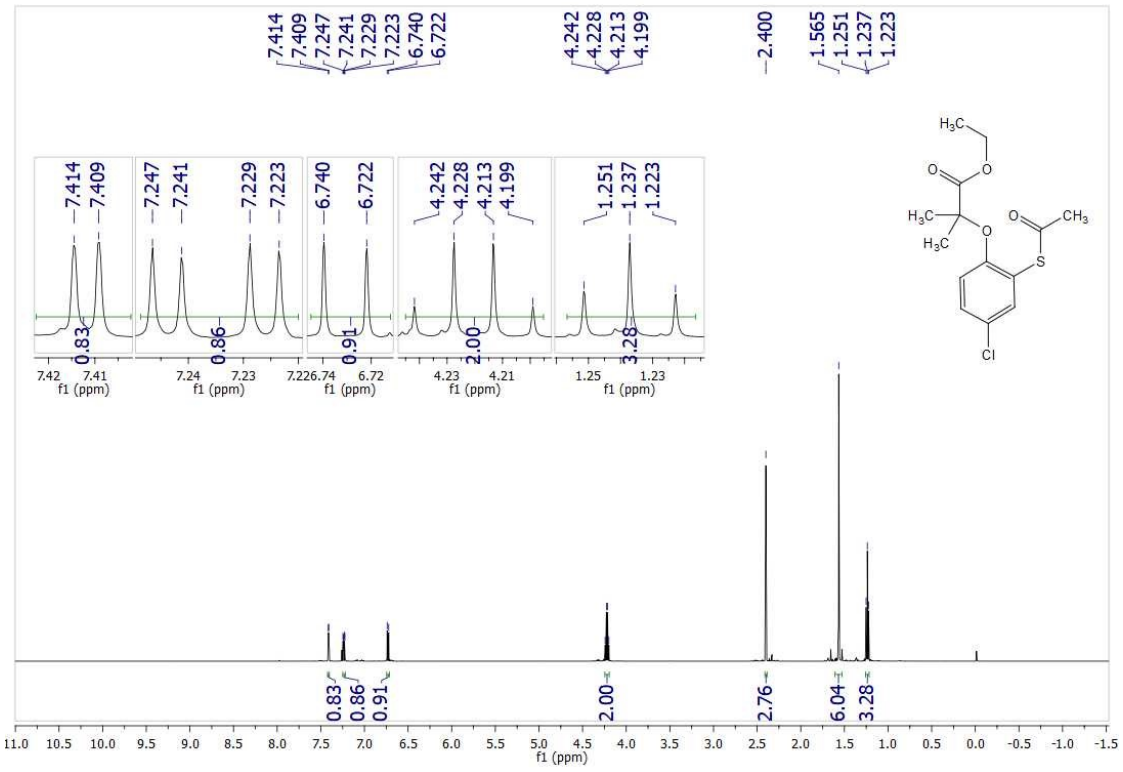
^{13}C NMR (126 MHz, $CDCl_3$) of compound **22**.



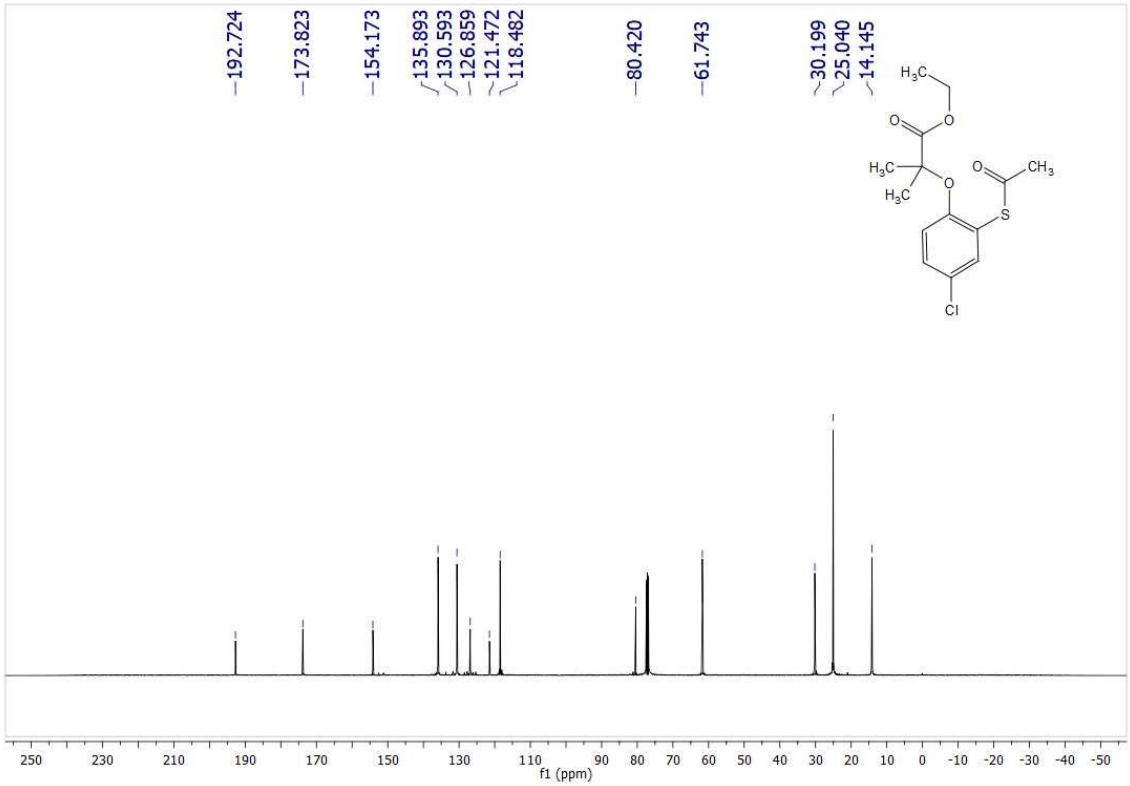
^{1}H NMR (500 MHz, $CDCl_3$) of compound **23**.



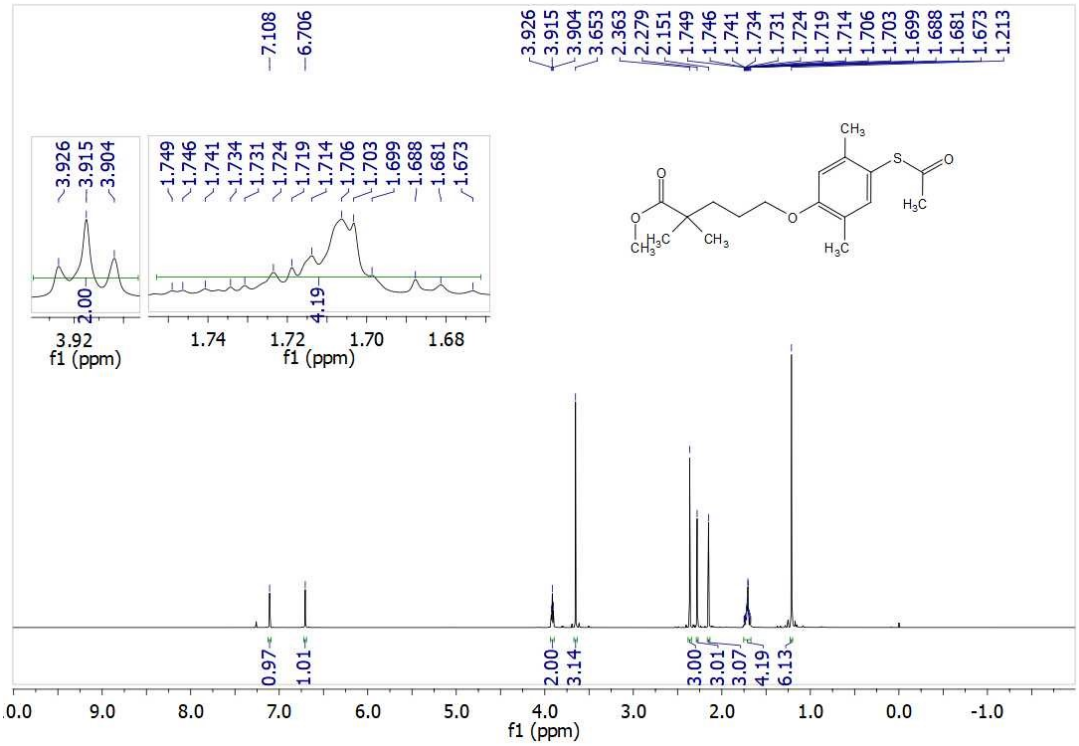
^{13}C NMR (126 MHz, $CDCl_3$) of compound **23**.



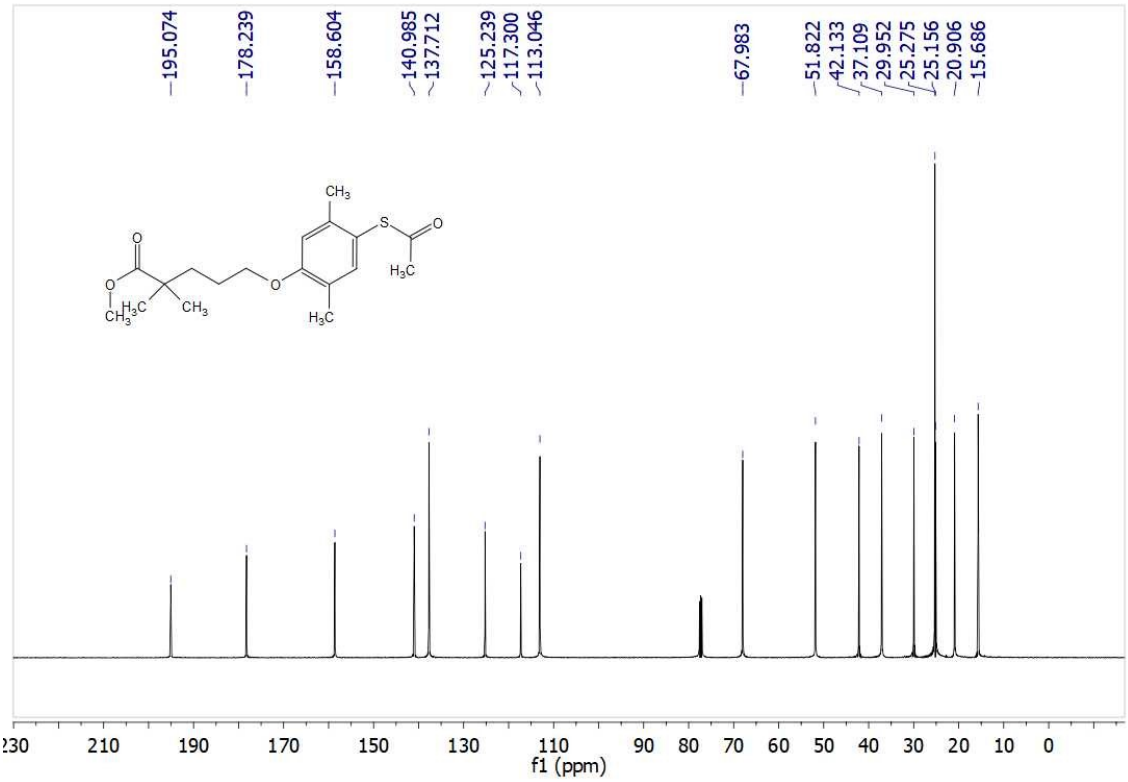
^{1}H NMR (500 MHz, $CDCl_3$) of compound **24**.



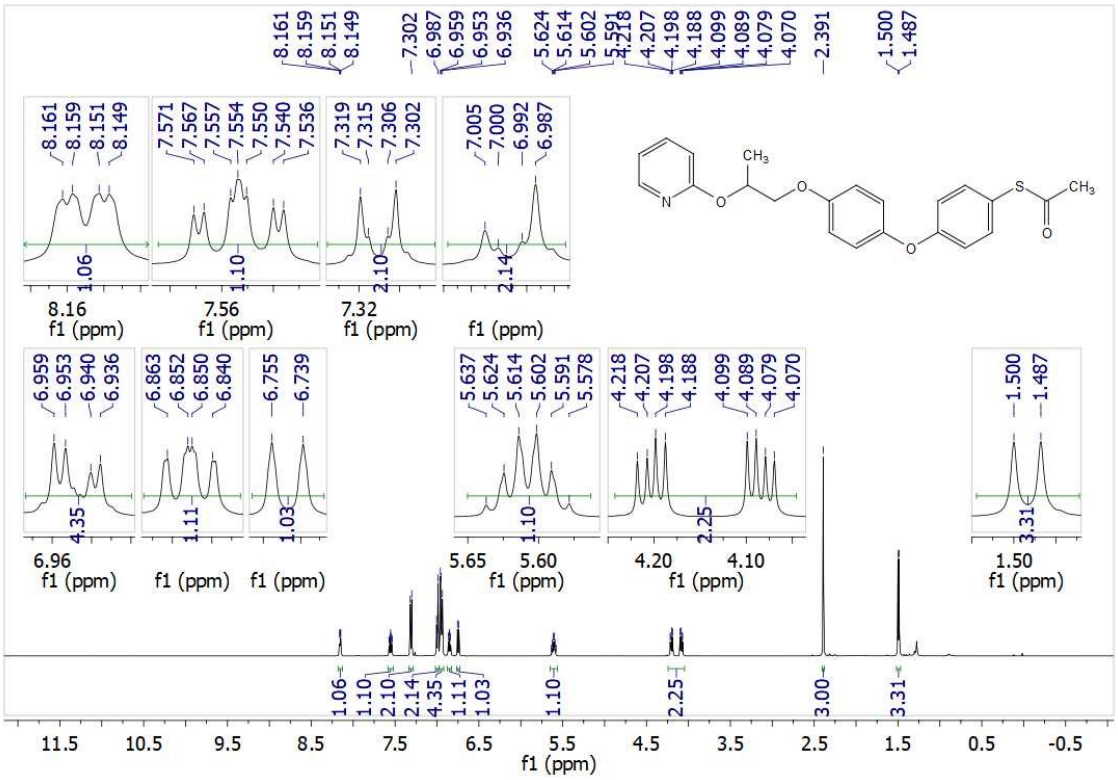
^{13}C NMR (126 MHz, $CDCl_3$) of compound **24**.



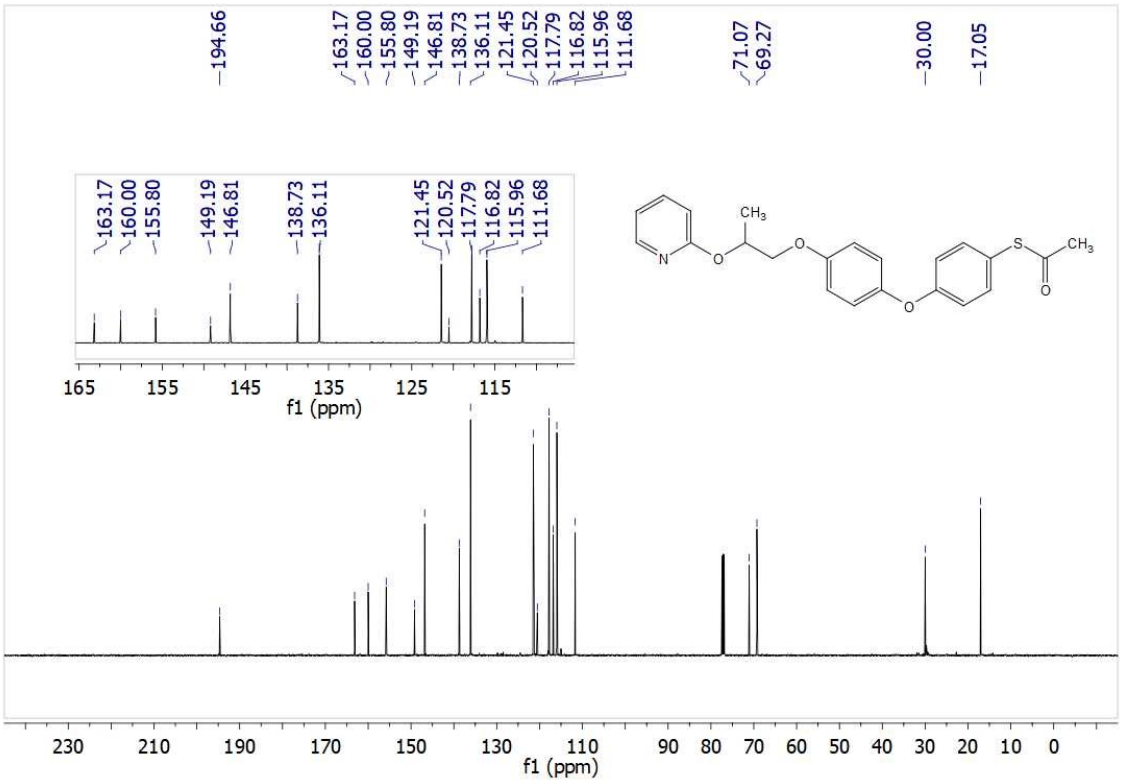
^{1}H NMR (500 MHz, $CDCl_3$) of compound **25**.



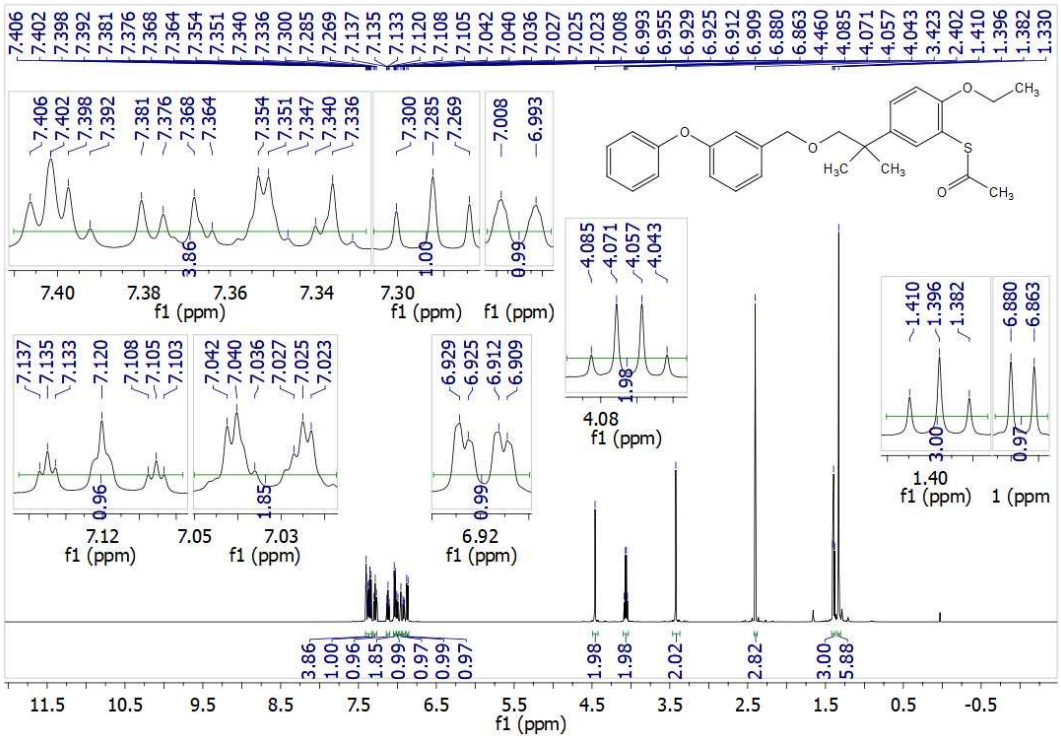
^{13}C NMR (126 MHz, $CDCl_3$) of compound **25**.



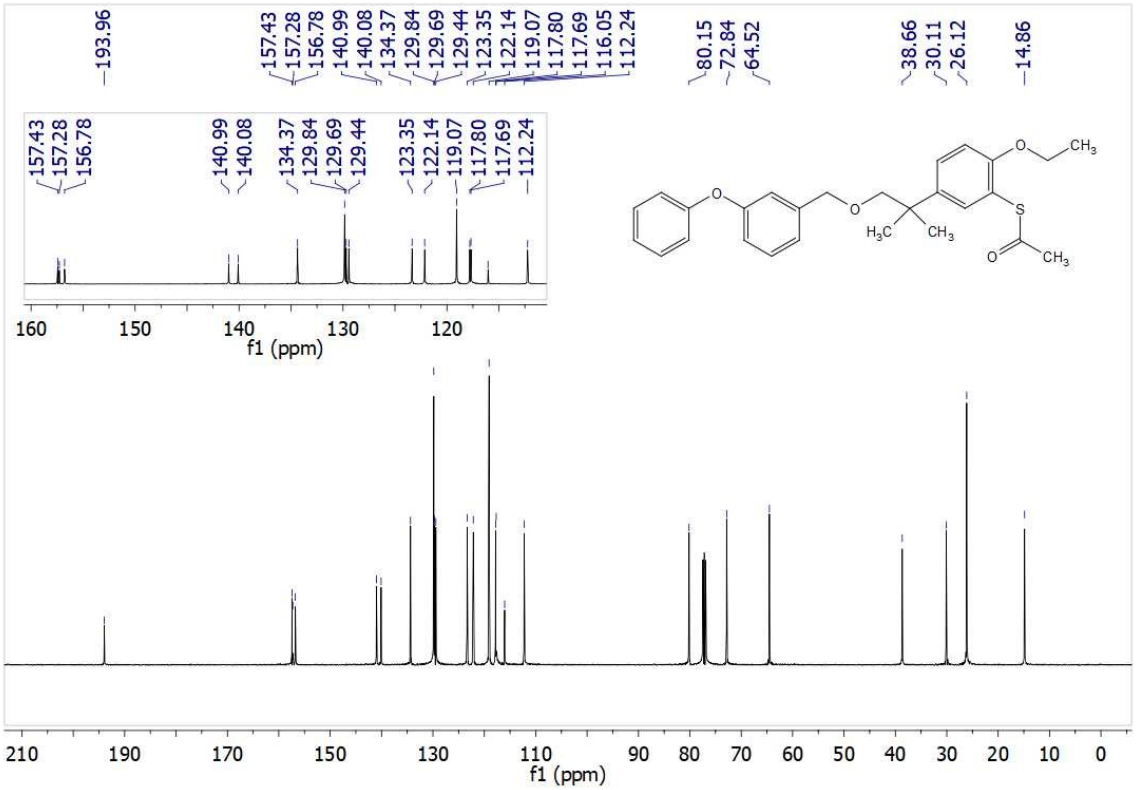
^{1}H NMR (500 MHz, $CDCl_3$) of compound **26**.



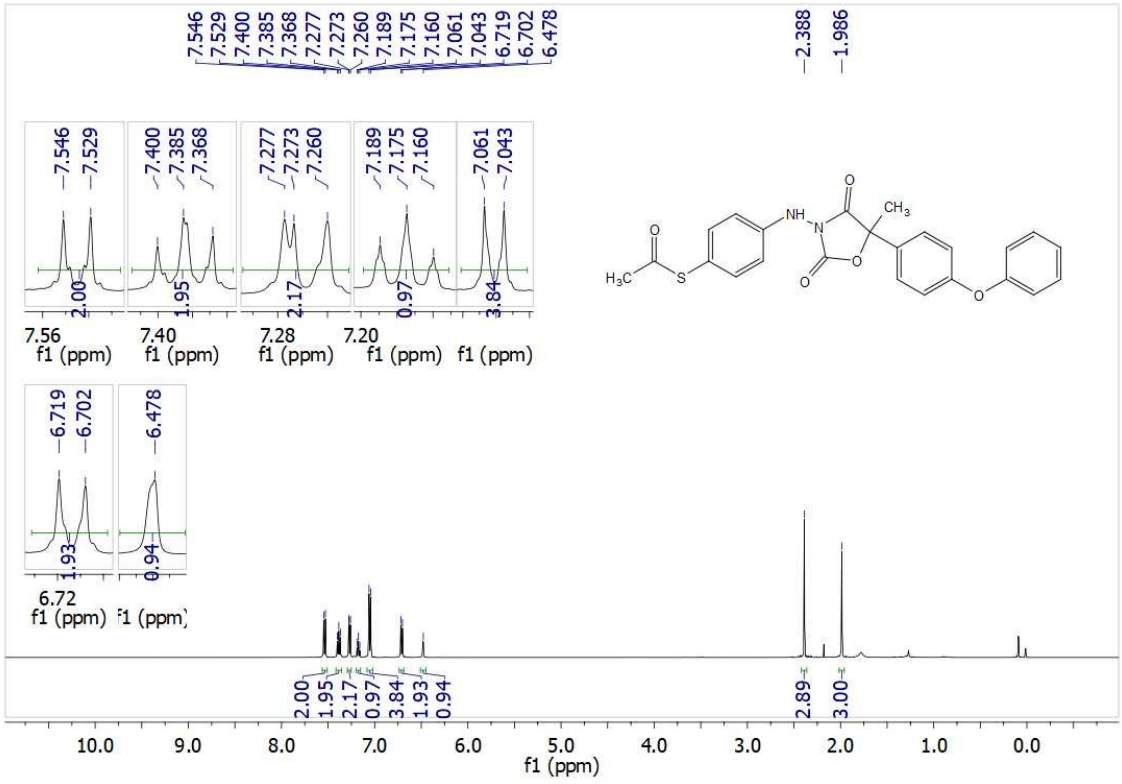
^{13}C NMR (126 MHz, $CDCl_3$) of compound **26**.



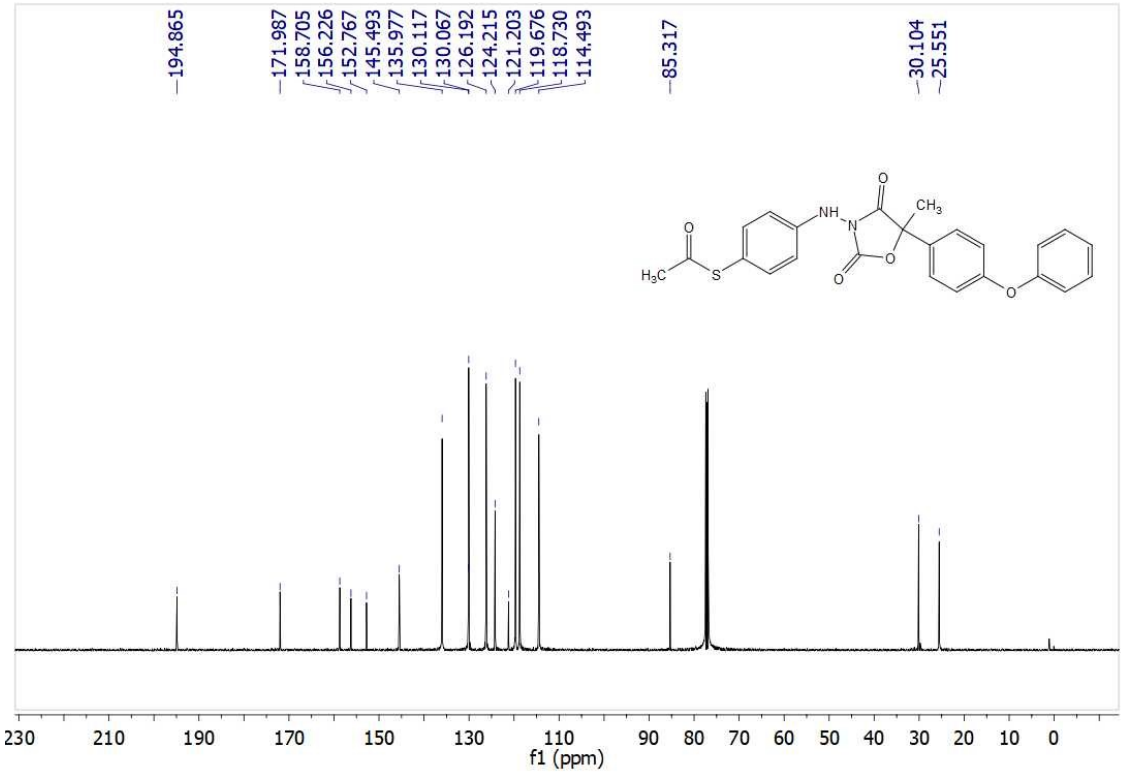
^{1}H NMR (500 MHz, $CDCl_3$) of compound **27**.



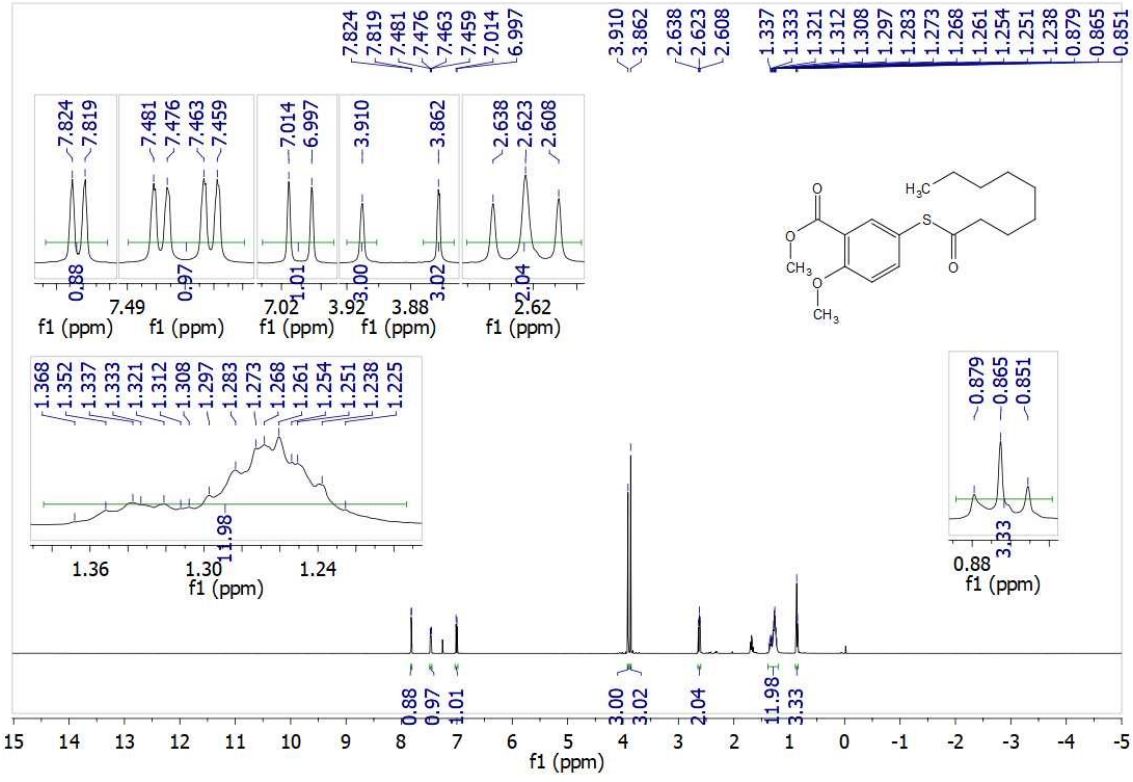
^{13}C NMR (126 MHz, $CDCl_3$) of compound **27**.



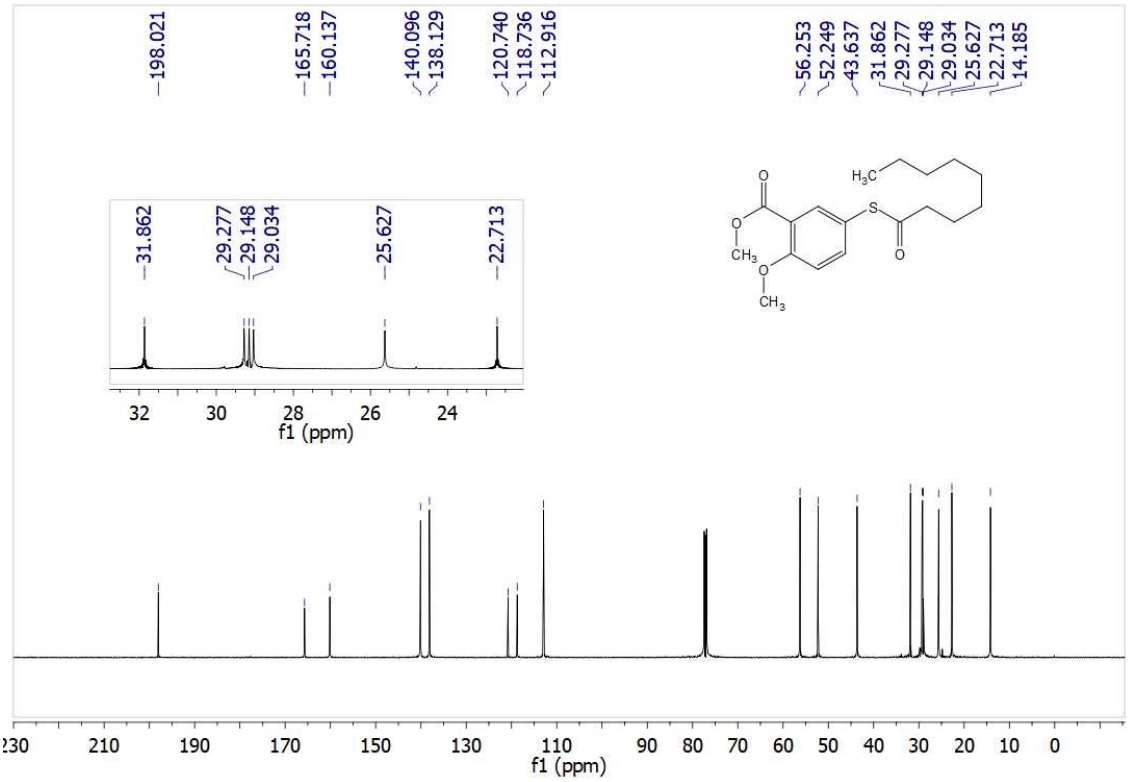
^{1}H NMR (500 MHz, $CDCl_3$) of compound **28**.



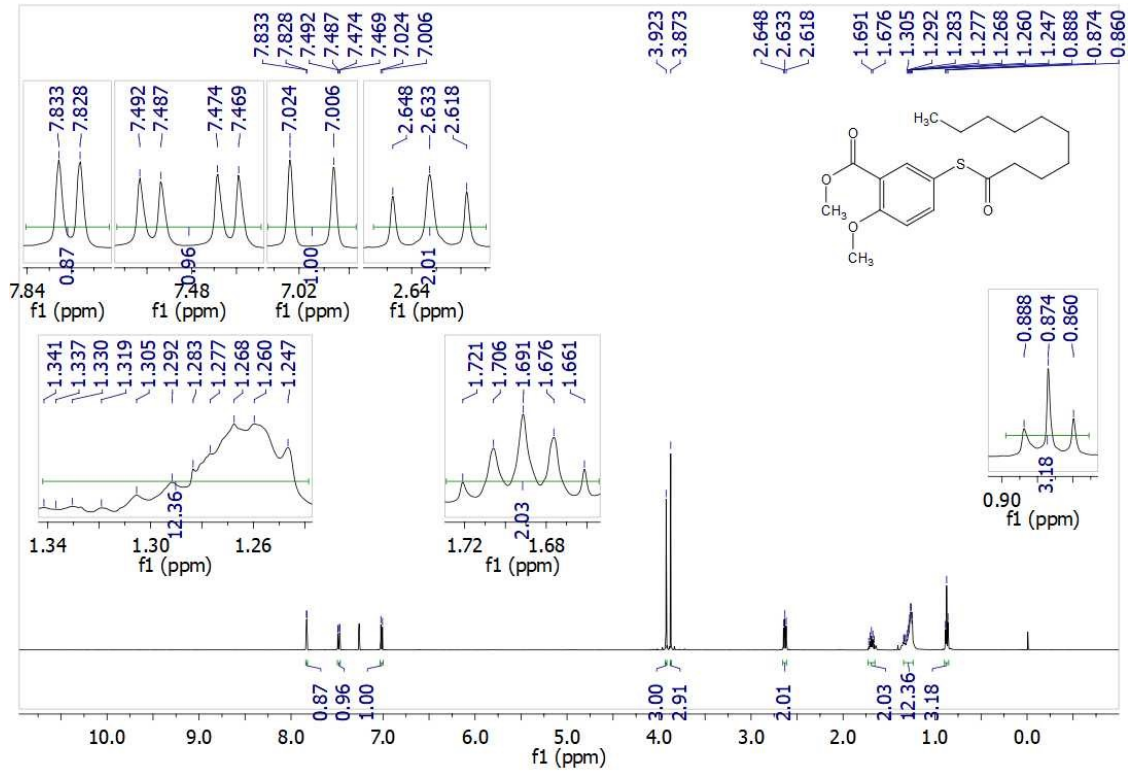
^{13}C NMR (126 MHz, $CDCl_3$) of compound **28**.



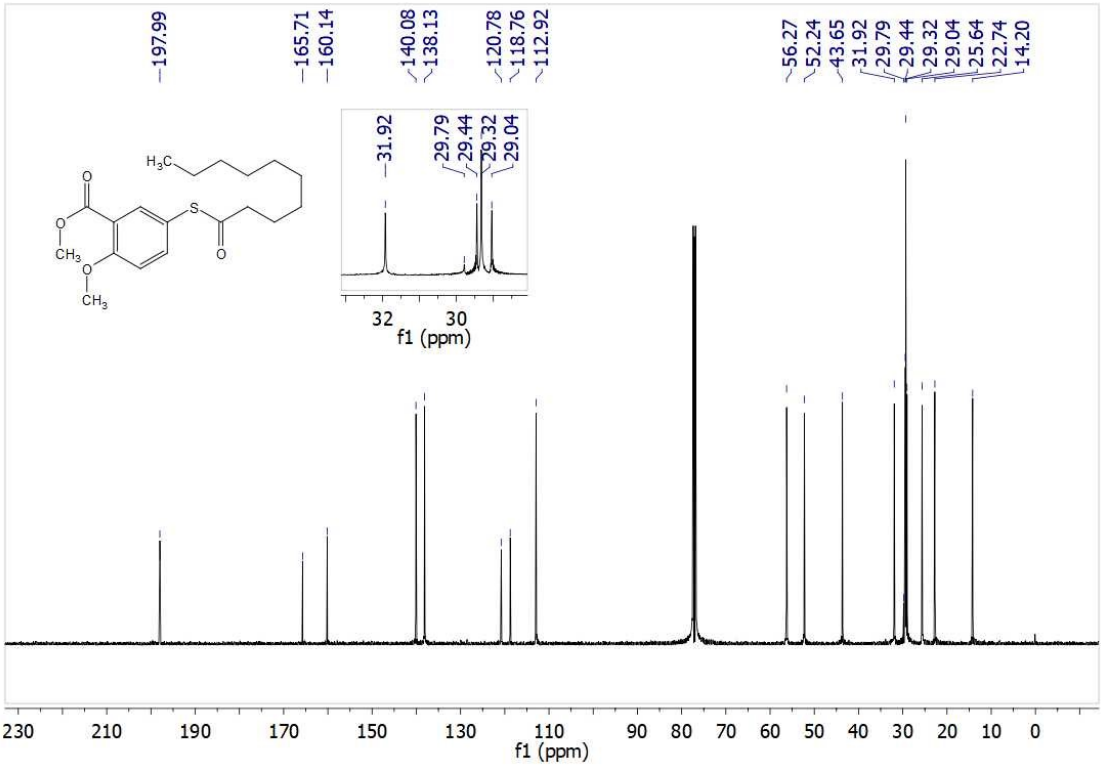
^{1}H NMR (500 MHz, $CDCl_3$) of compound **29**.



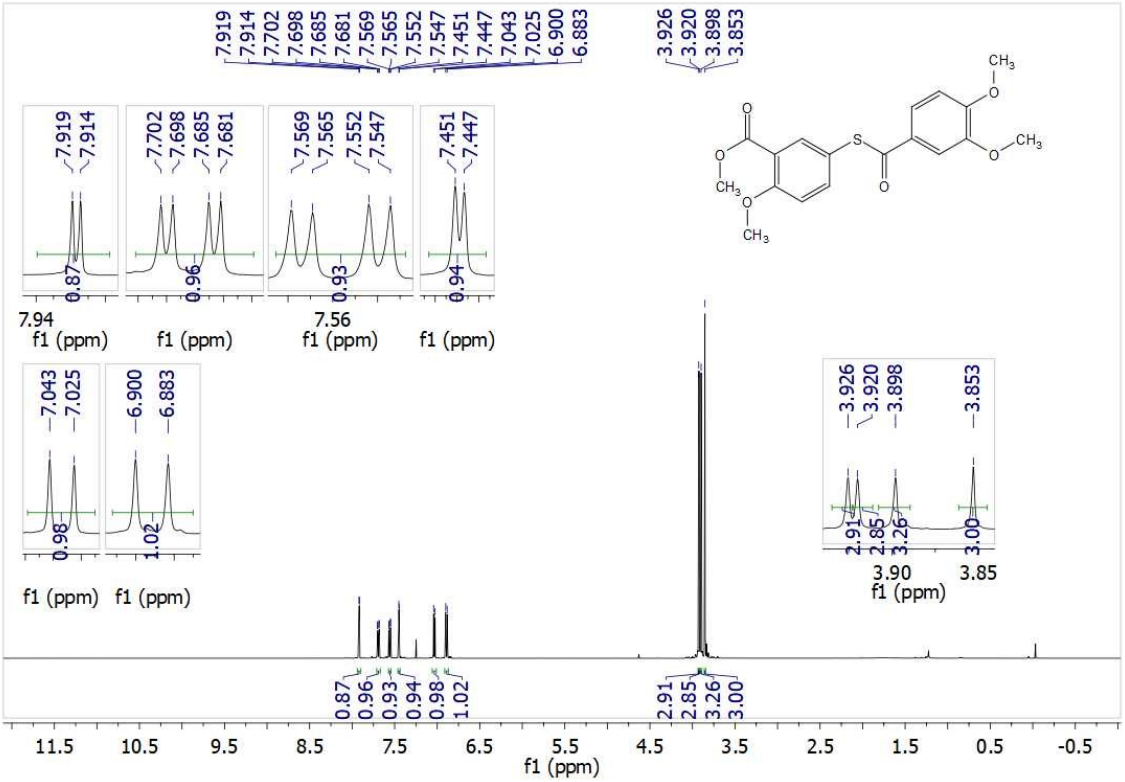
^{13}C NMR (126 MHz, $CDCl_3$) of compound **29**.



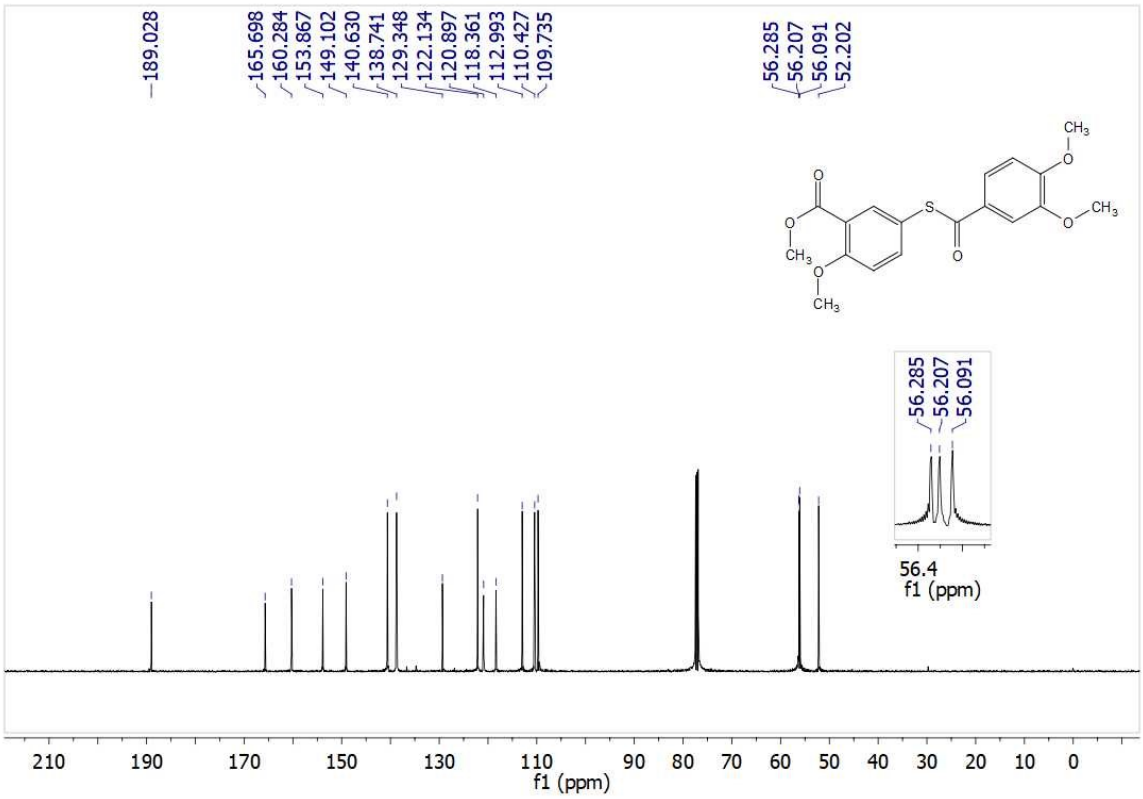
^{1}H NMR (500 MHz, $CDCl_3$) of compound **30**.



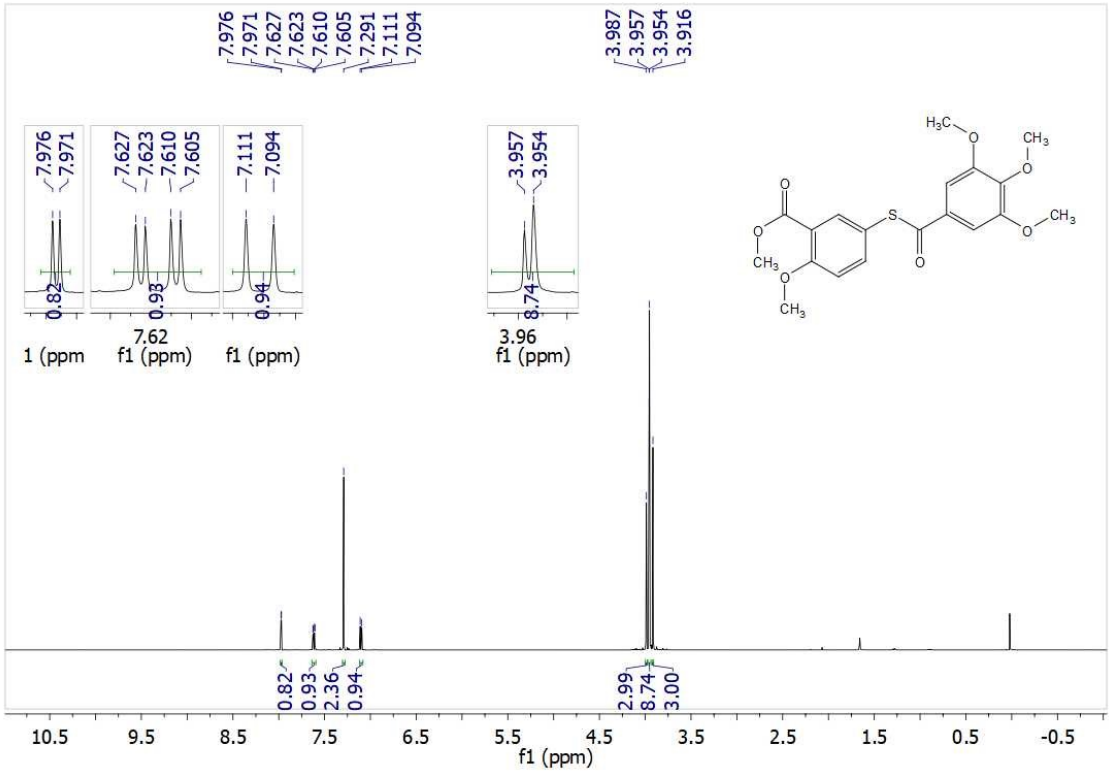
^{13}C NMR (126 MHz, $CDCl_3$) of compound **30**.



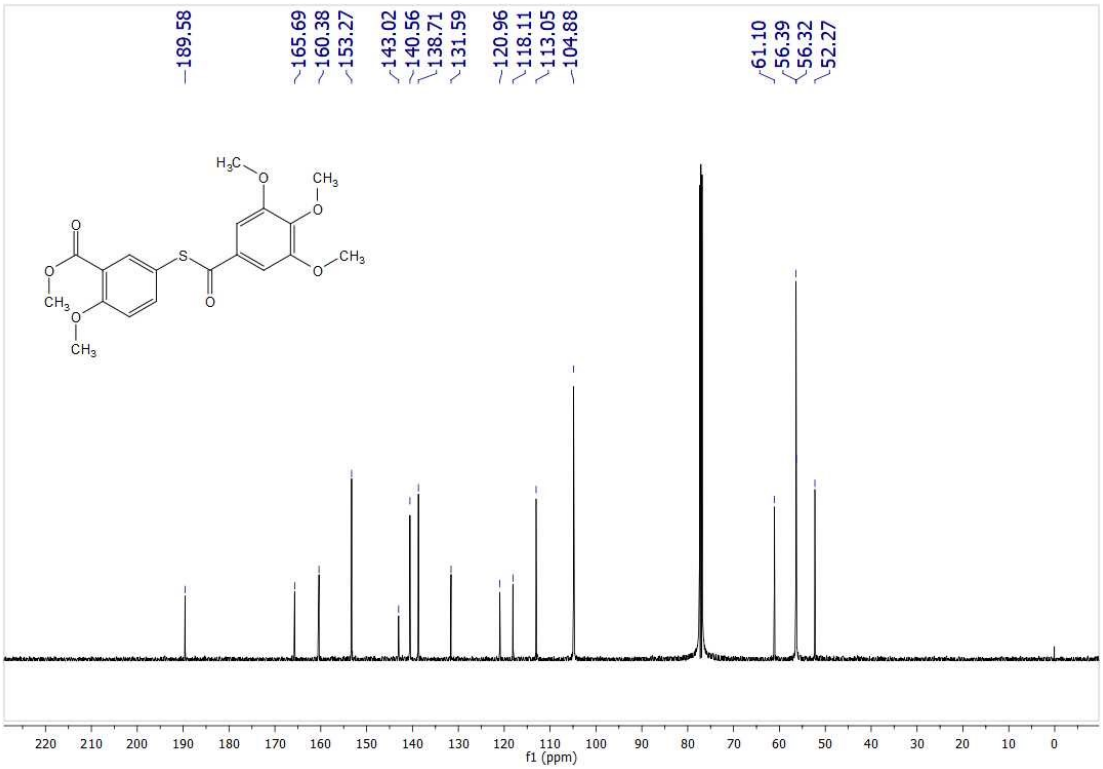
^{1}H NMR (500 MHz, $CDCl_3$) of compound **31**.



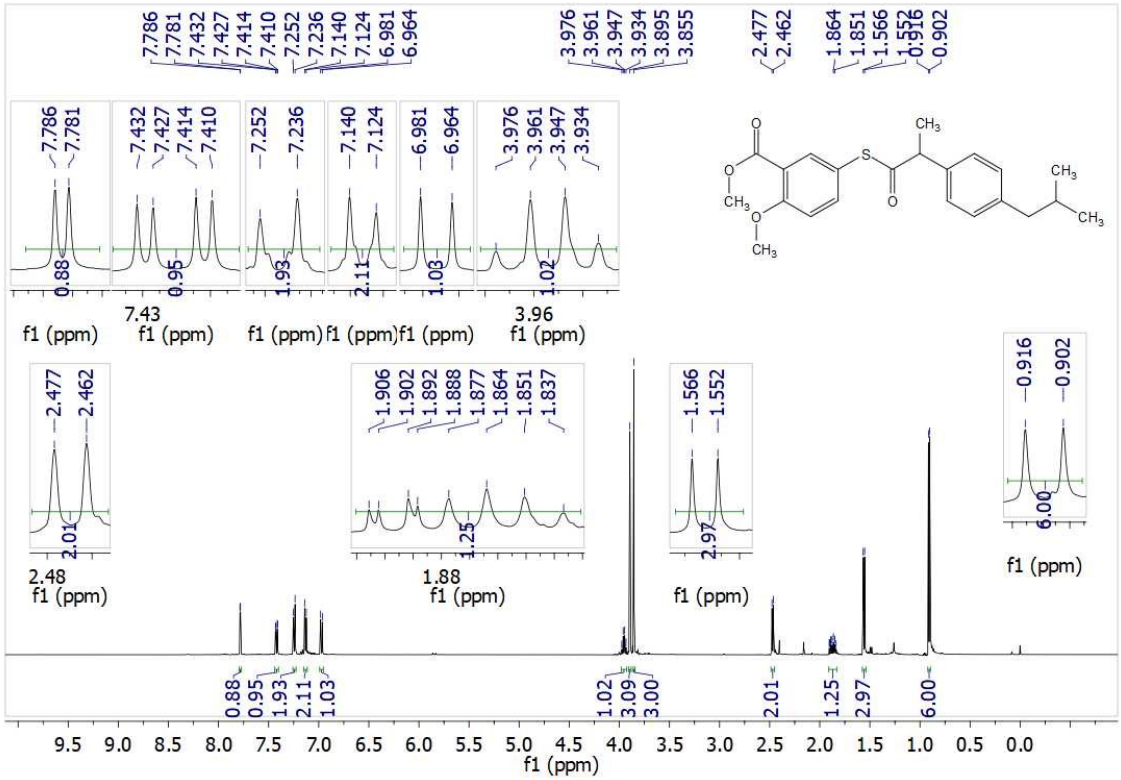
^{13}C NMR (126 MHz, $CDCl_3$) of compound **31**.



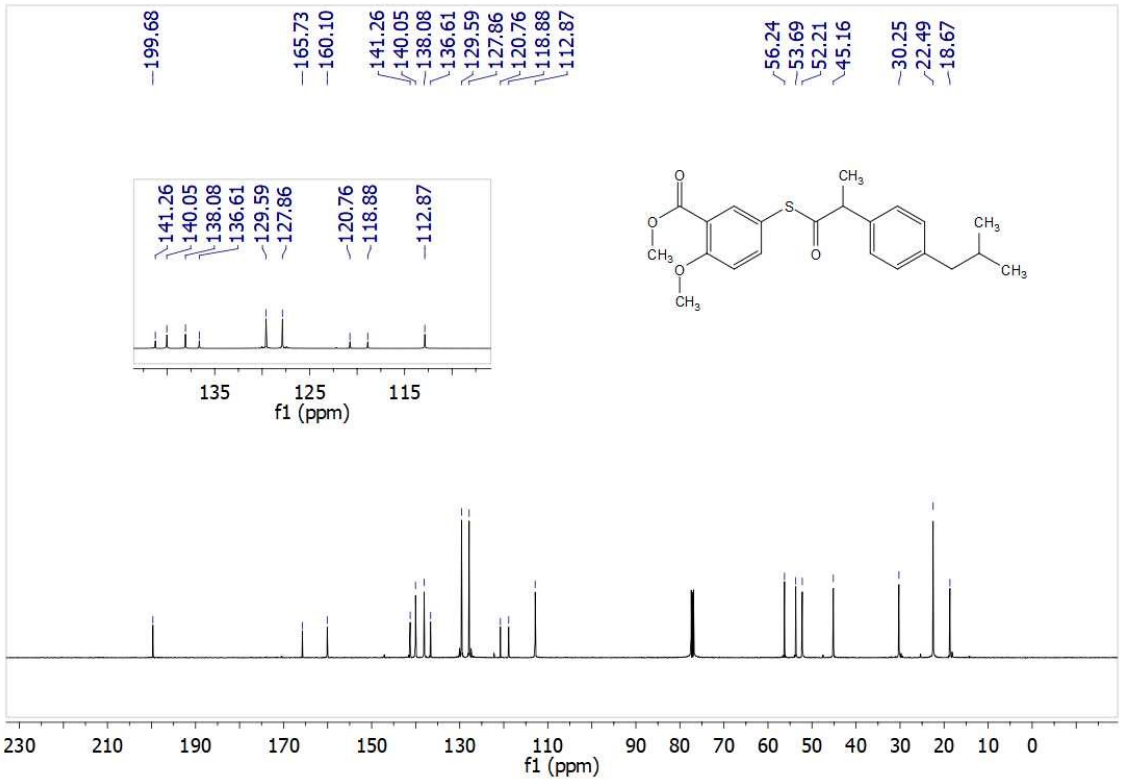
^{1}H NMR (500 MHz, $CDCl_3$) of compound **32**.



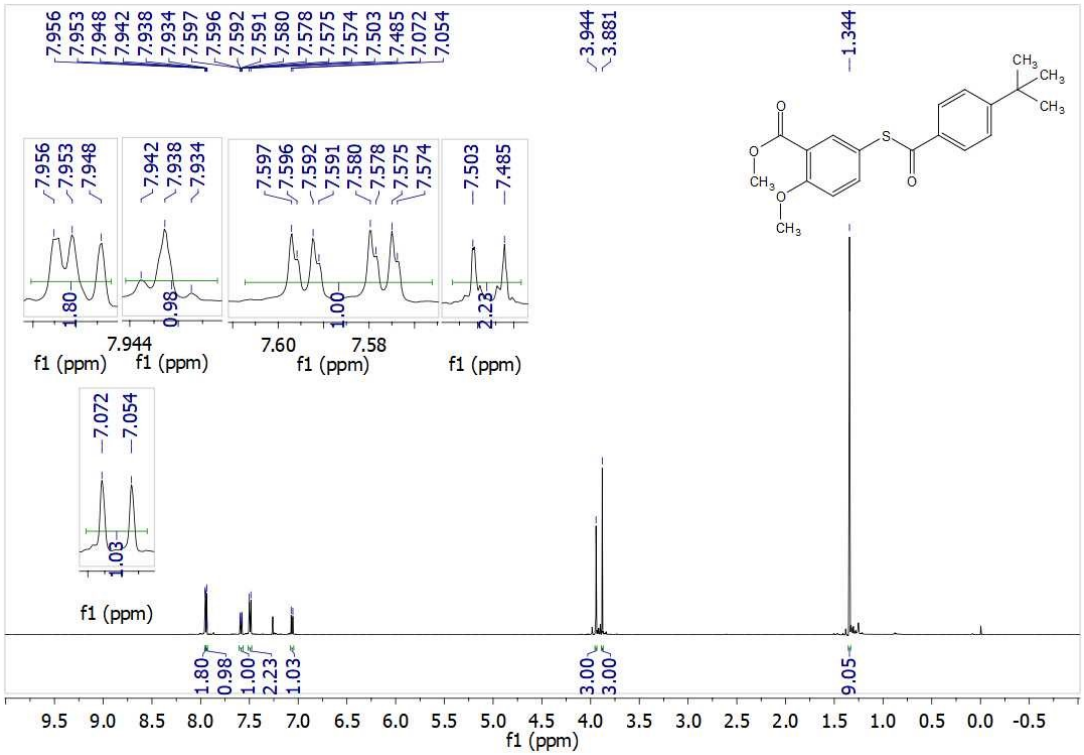
^{13}C NMR (126 MHz, $CDCl_3$) of compound **32**.



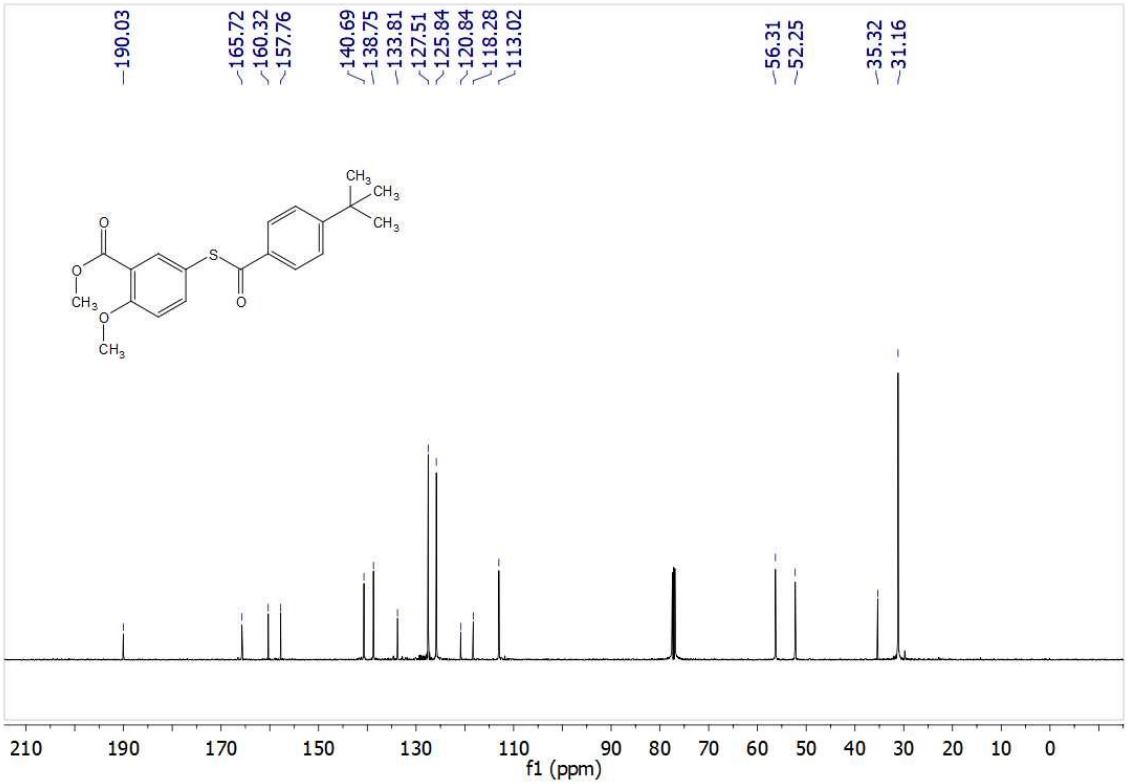
^{1}H NMR (500 MHz, $CDCl_3$) of compound **33**.



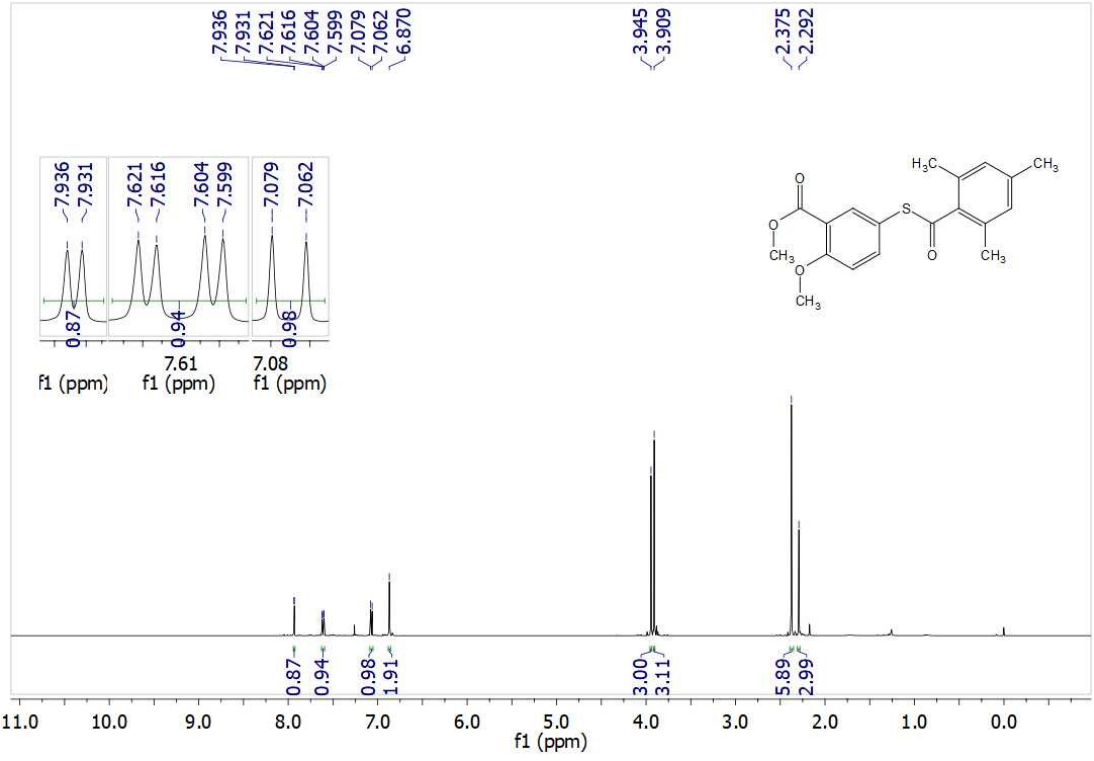
^{13}C NMR (126 MHz, $CDCl_3$) of compound **33**.



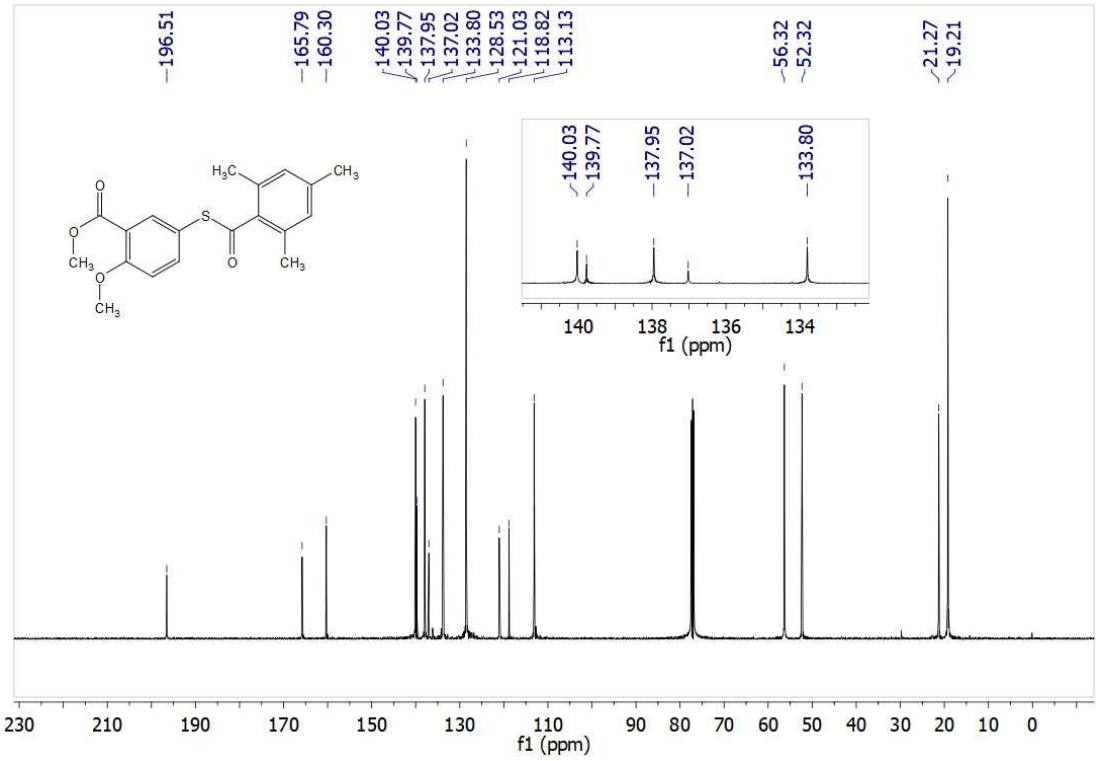
^{1}H NMR (500 MHz, $CDCl_3$) of compound **34**.



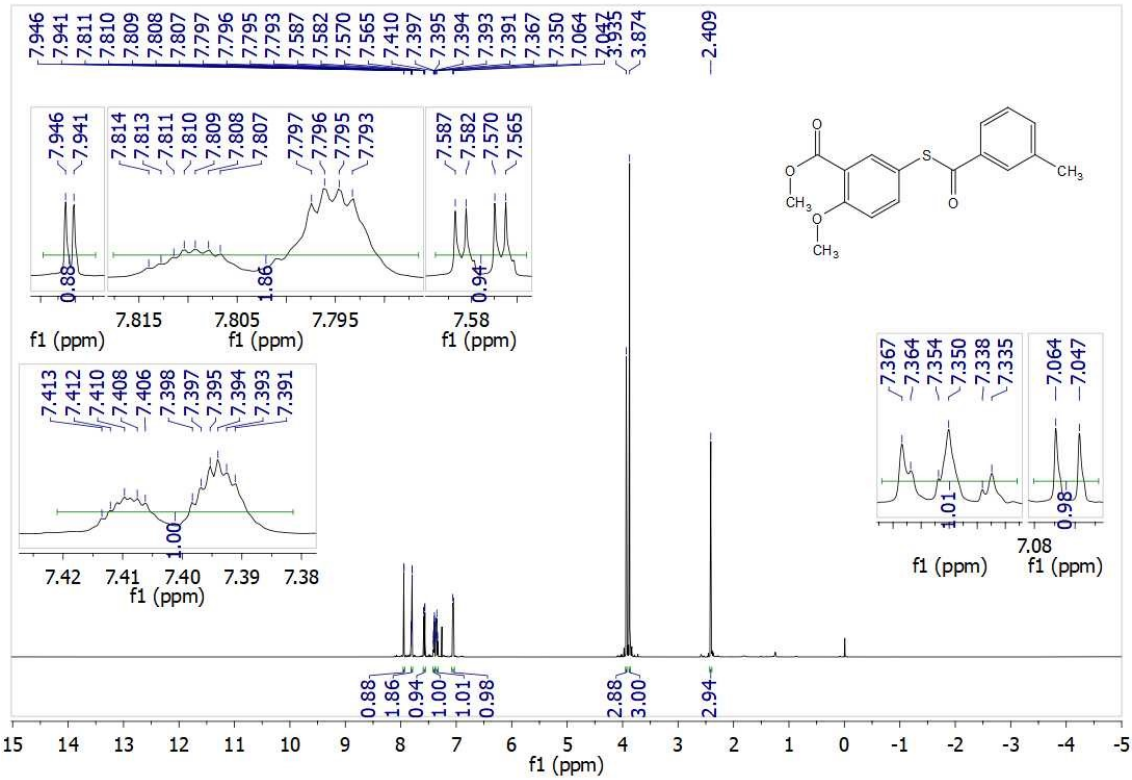
^{13}C NMR (126 MHz, $CDCl_3$) of compound **34**.



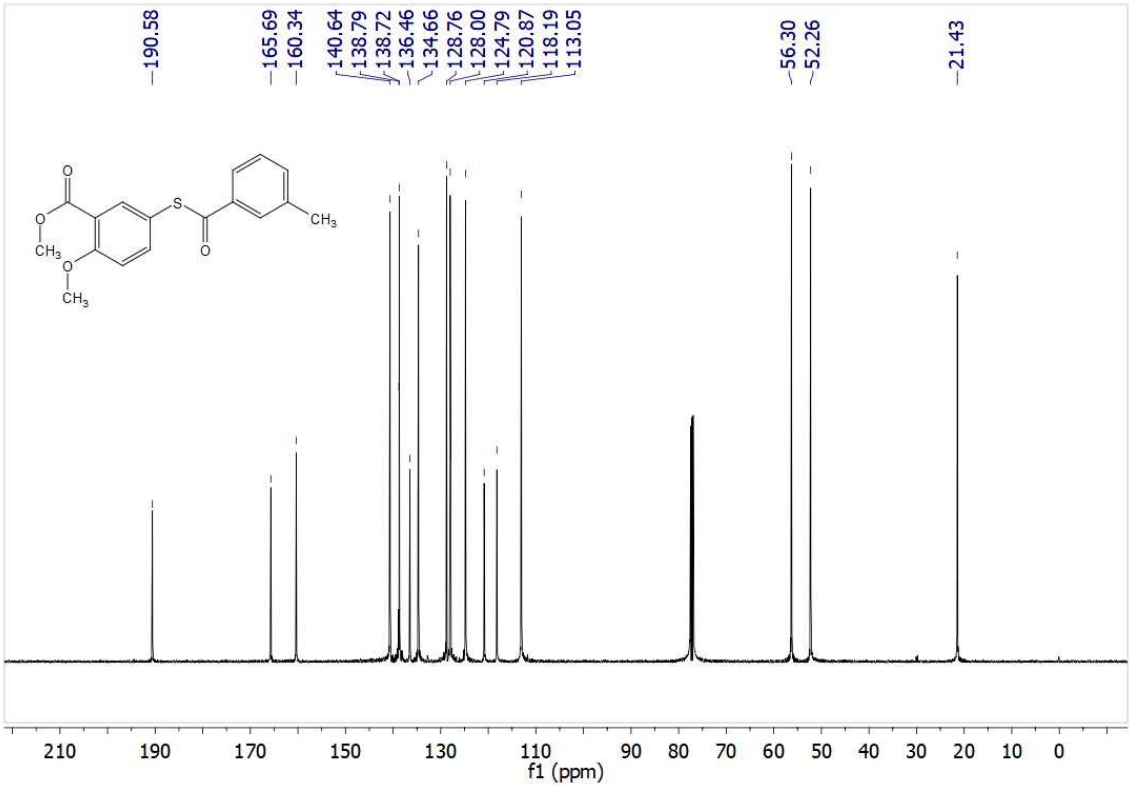
^{1}H NMR (500 MHz, $CDCl_3$) of compound **35**.



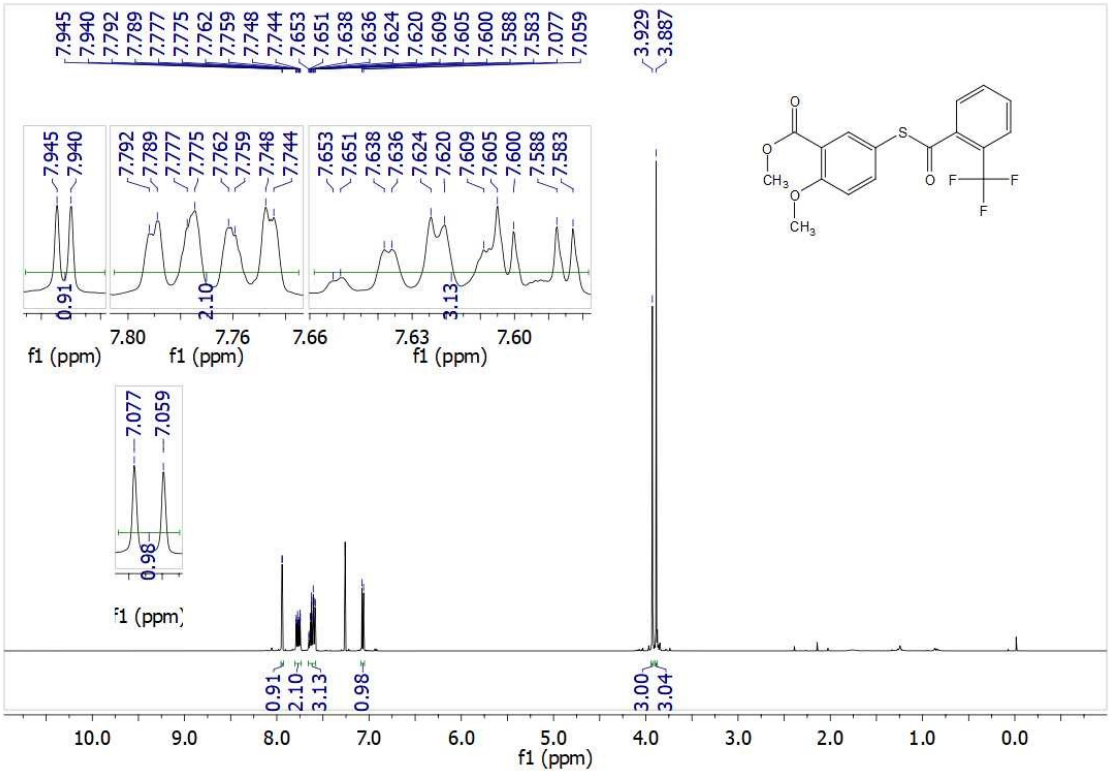
^{13}C NMR (126 MHz, $CDCl_3$) of compound **35**.



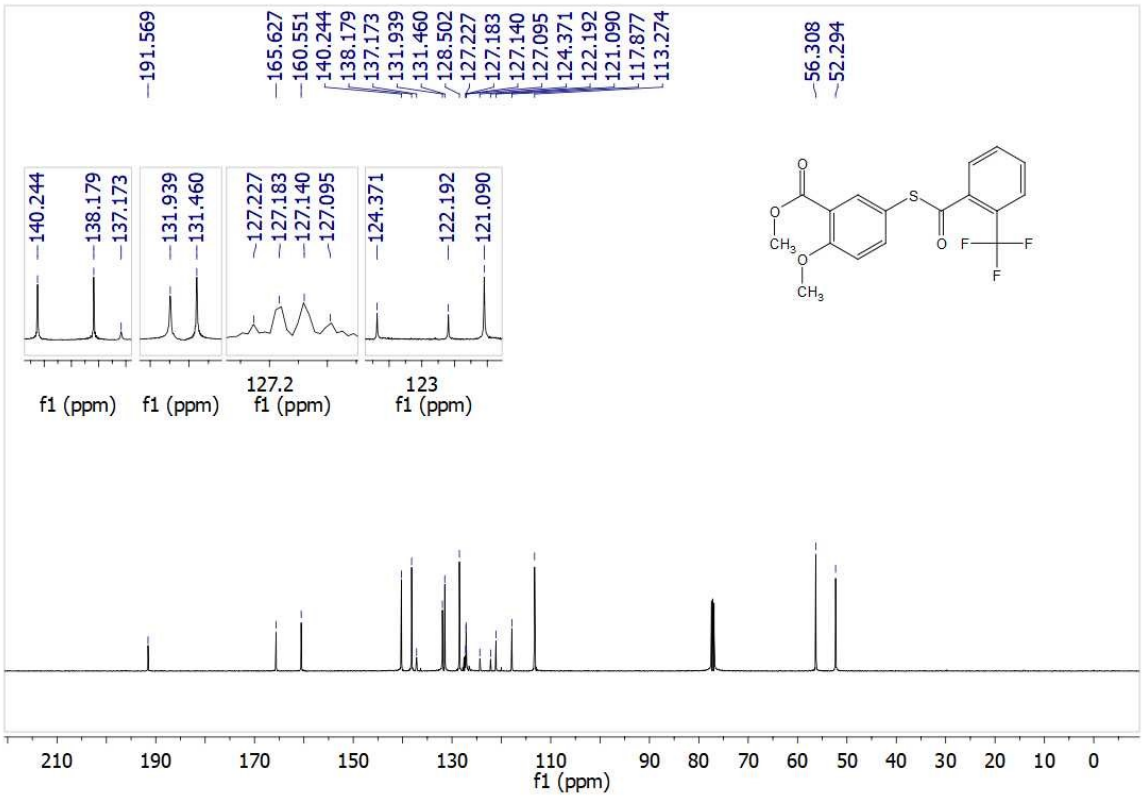
^{1}H NMR (500 MHz, $CDCl_3$) of compound **36**.



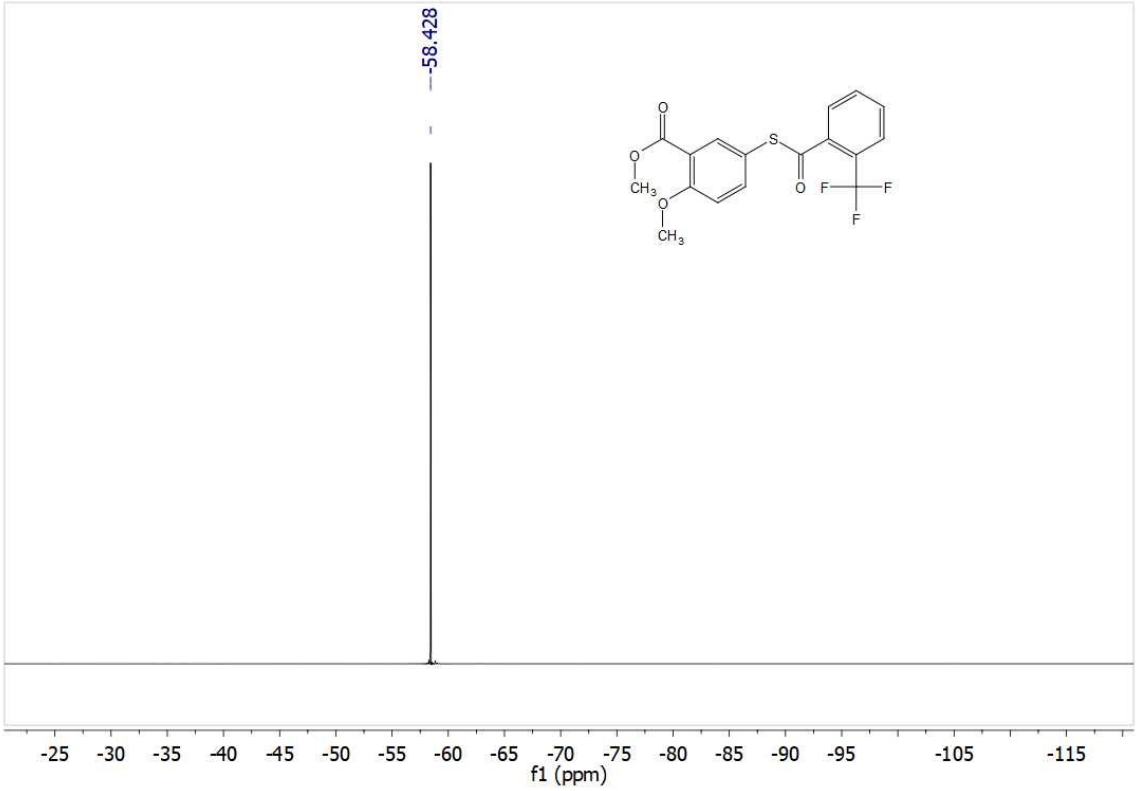
^{13}C NMR (126 MHz, $CDCl_3$) of compound **36**.



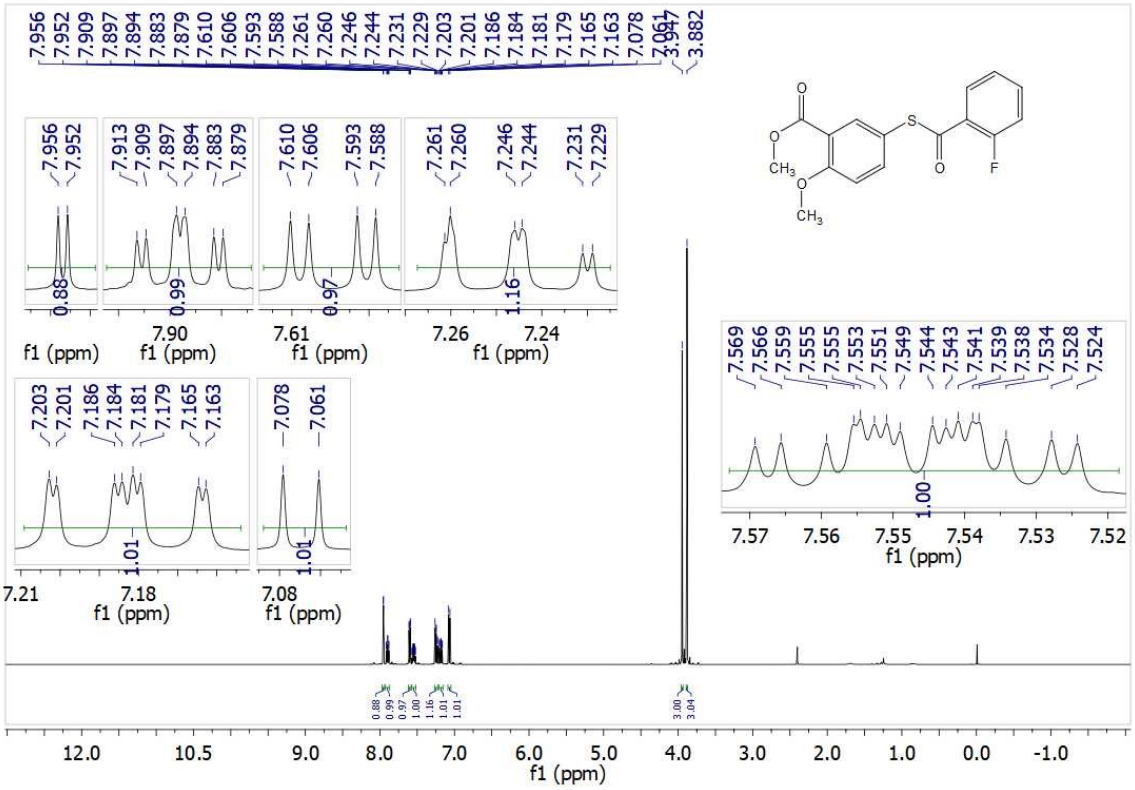
^{1}H NMR (500 MHz, $CDCl_3$) of compound **37**.



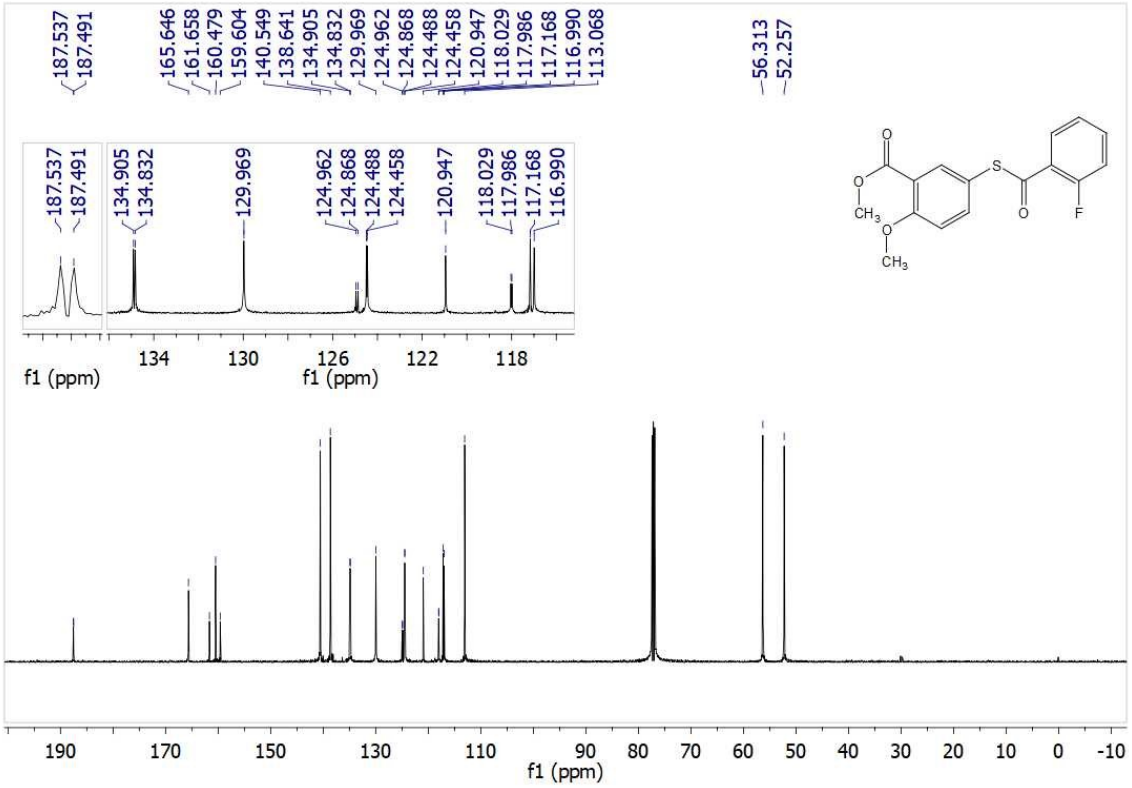
^{13}C NMR (125 MHz, $CDCl_3$) of compound **37**.



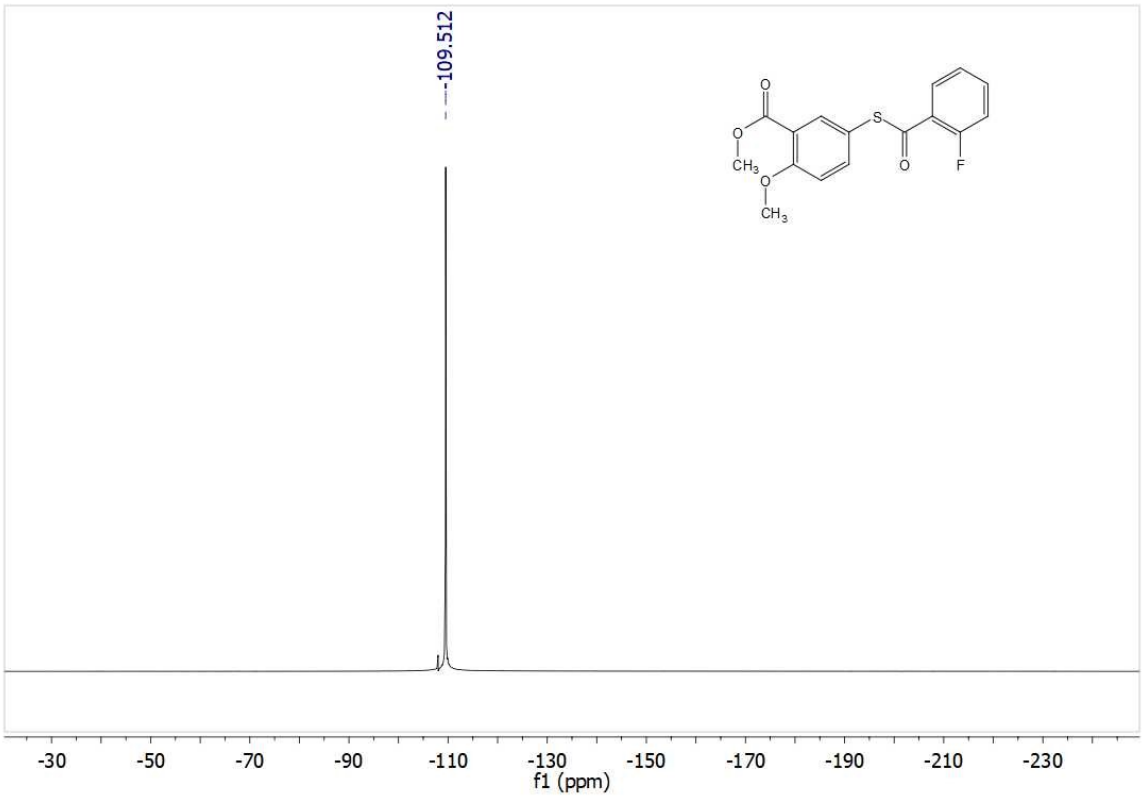
^{19}F NMR (472 MHz, $CDCl_3$) of compound **37**.



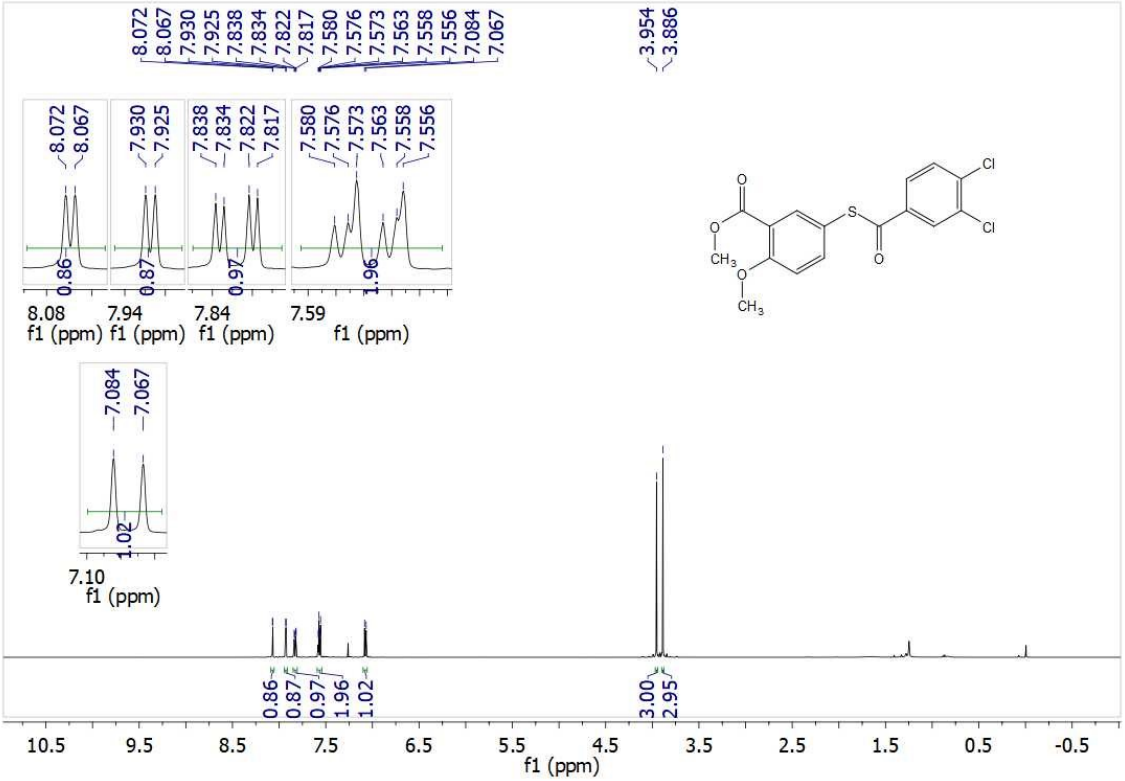
^{1}H NMR (500 MHz, $CDCl_3$) of compound **38**.



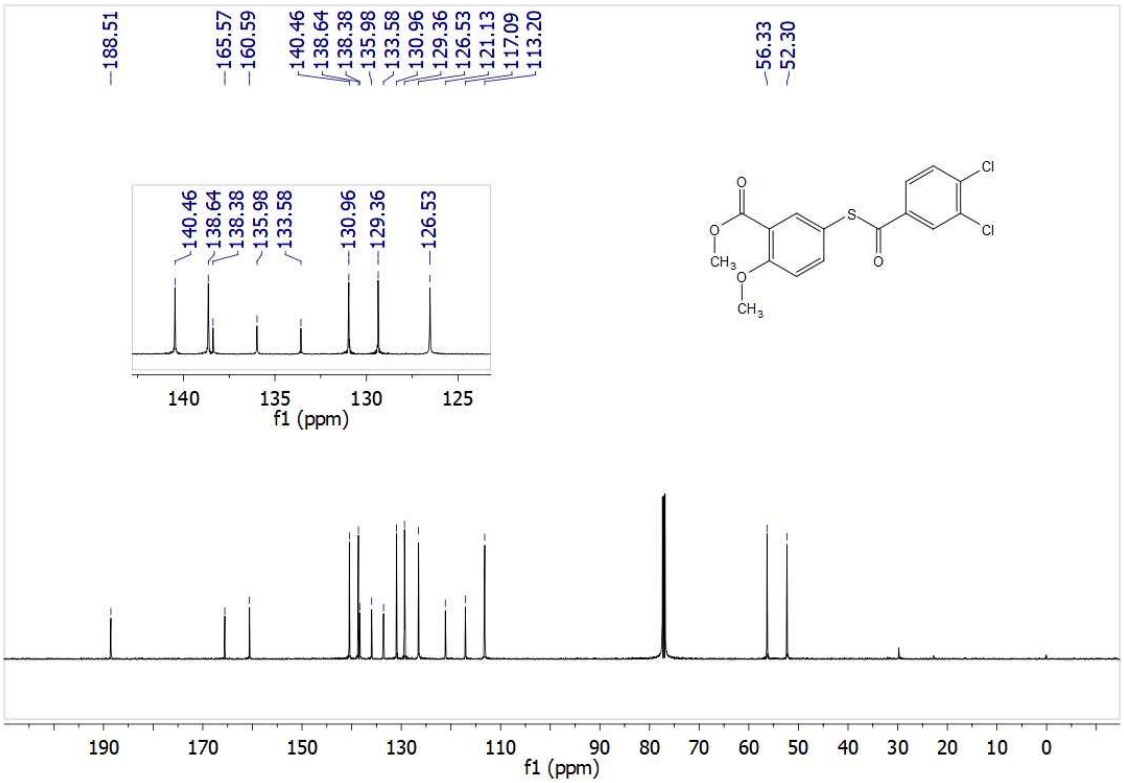
^{13}C NMR (126 MHz, $CDCl_3$) of compound **38**.



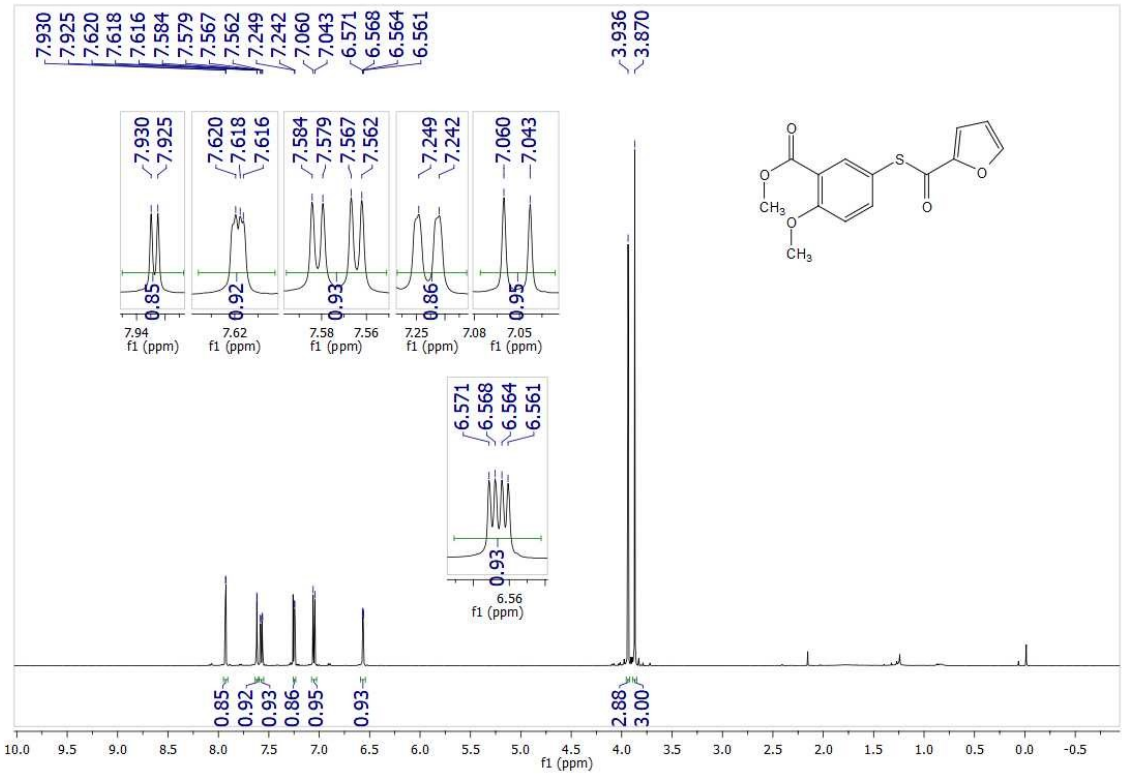
^{19}F NMR (472 MHz, $CDCl_3$) of compound **38**.



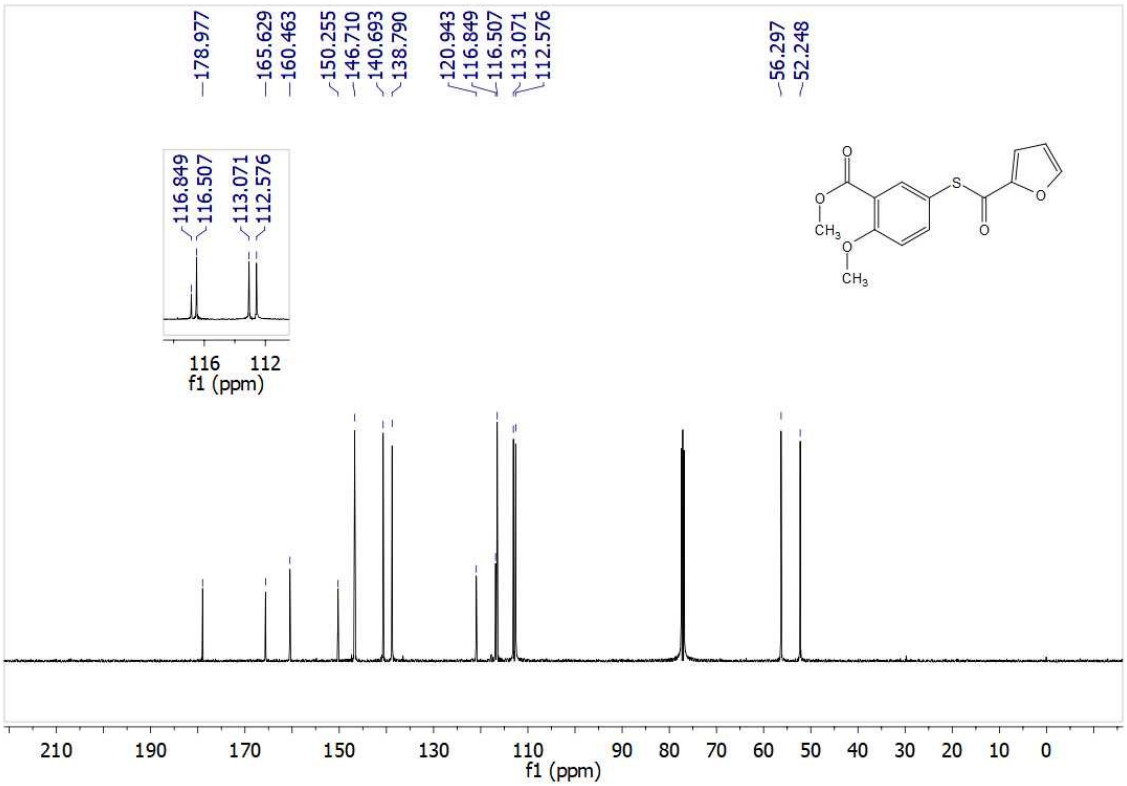
^{1}H NMR (500 MHz, $CDCl_3$) of compound **39**.



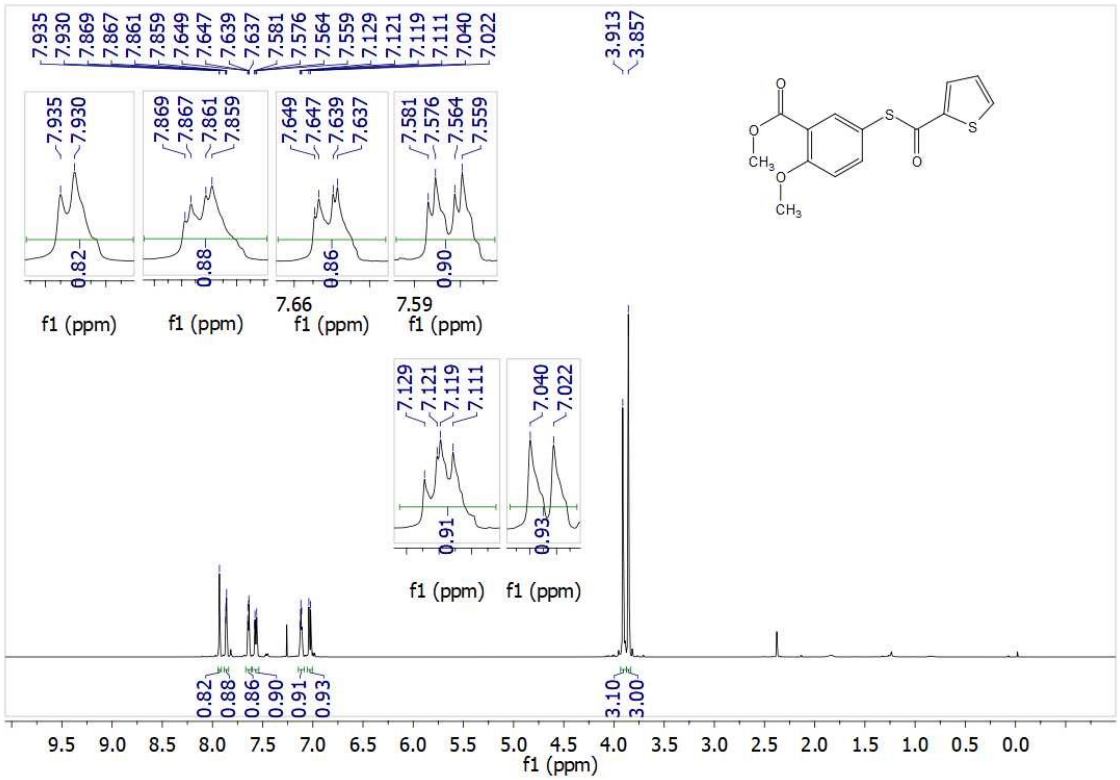
^{13}C NMR (126 MHz, $CDCl_3$) of compound **39**.



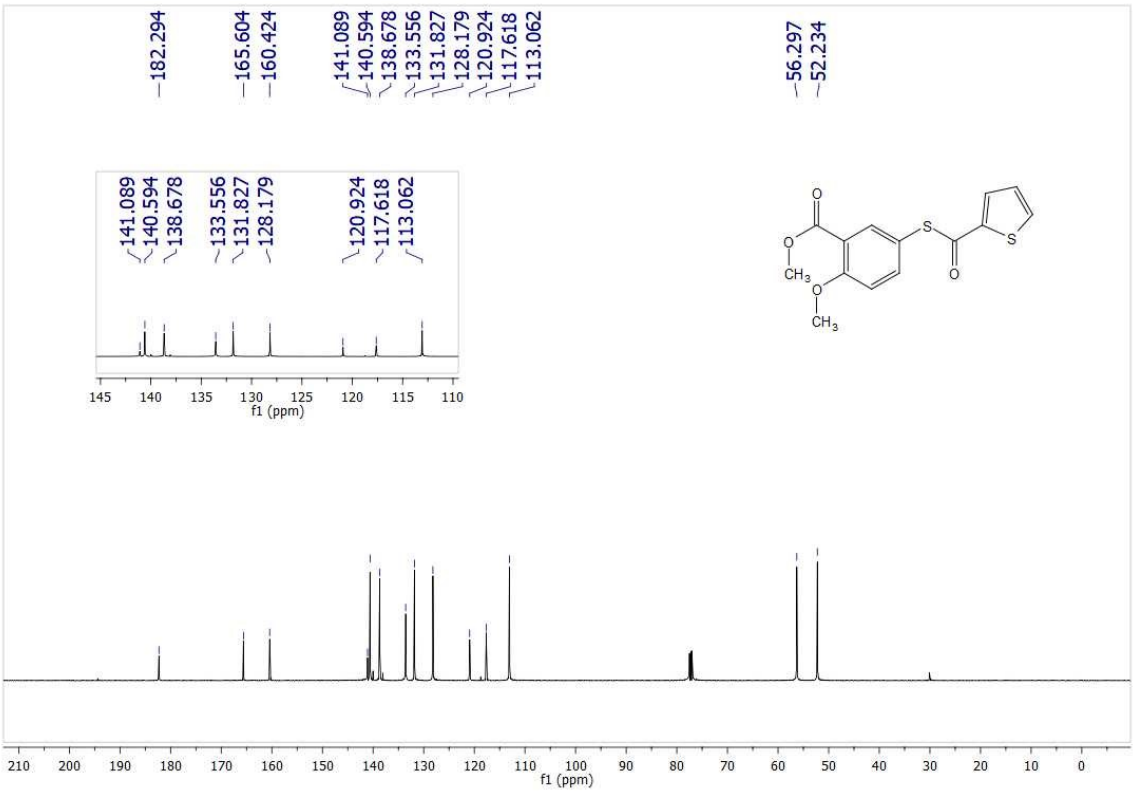
^{1}H NMR (500 MHz, $CDCl_3$) of compound **40**.



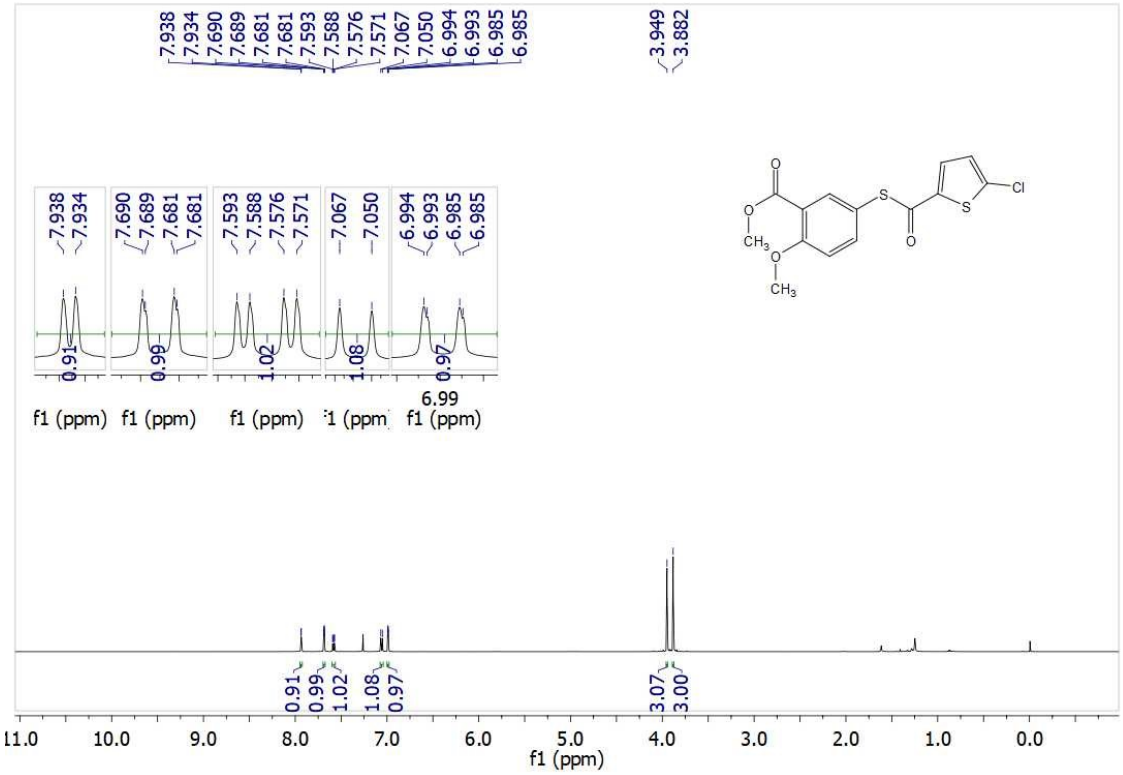
^{13}C NMR (126 MHz, $CDCl_3$) of compound **40**.



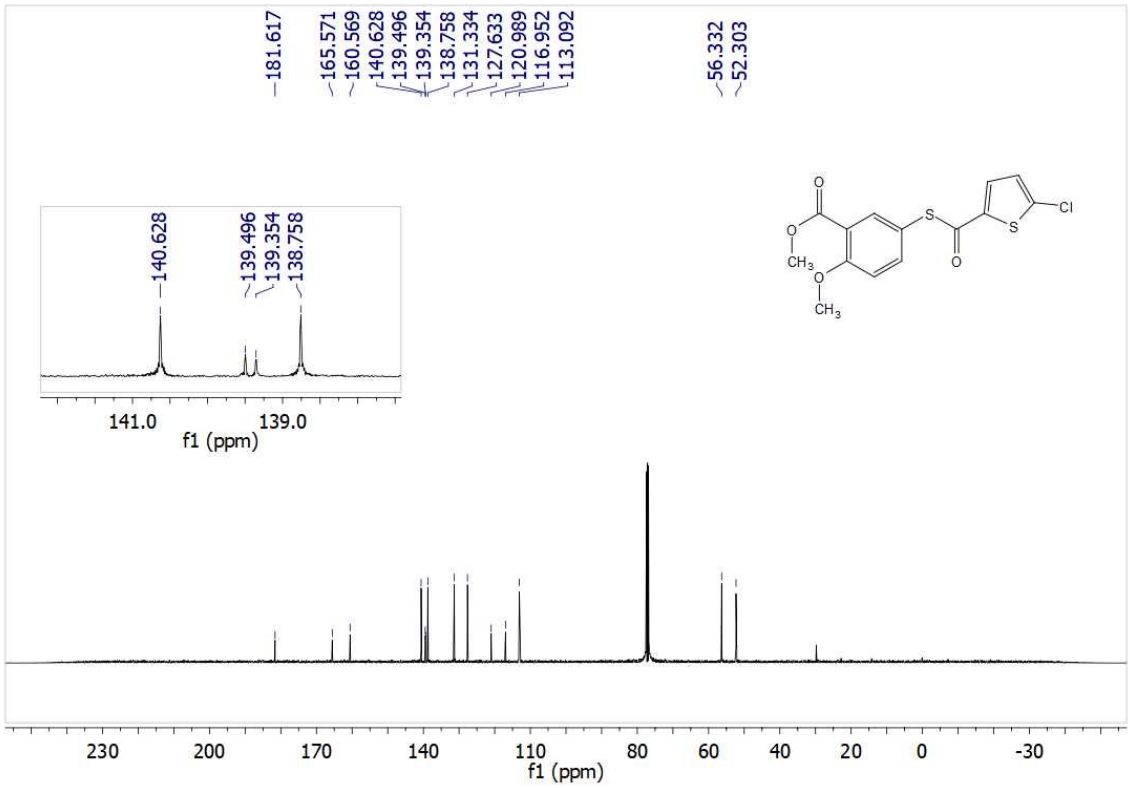
^{1}H NMR (500 MHz, $CDCl_3$) of compound **41**.



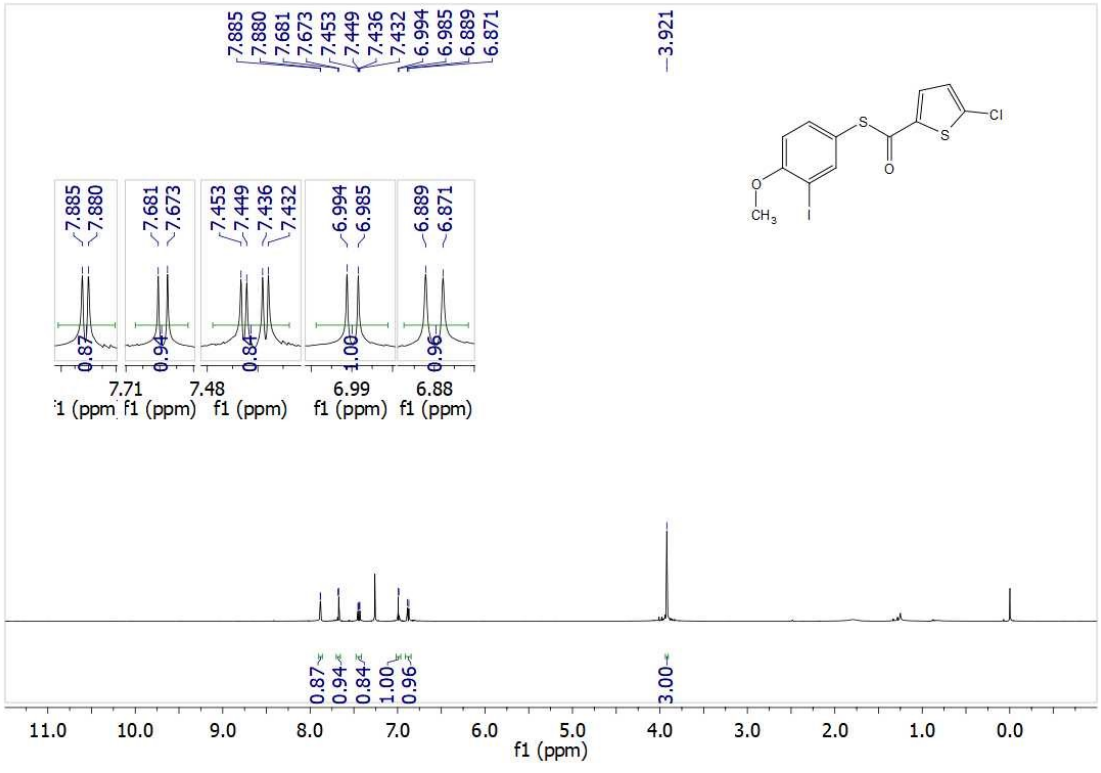
^{13}C NMR (126 MHz, $CDCl_3$) of compound **41**.



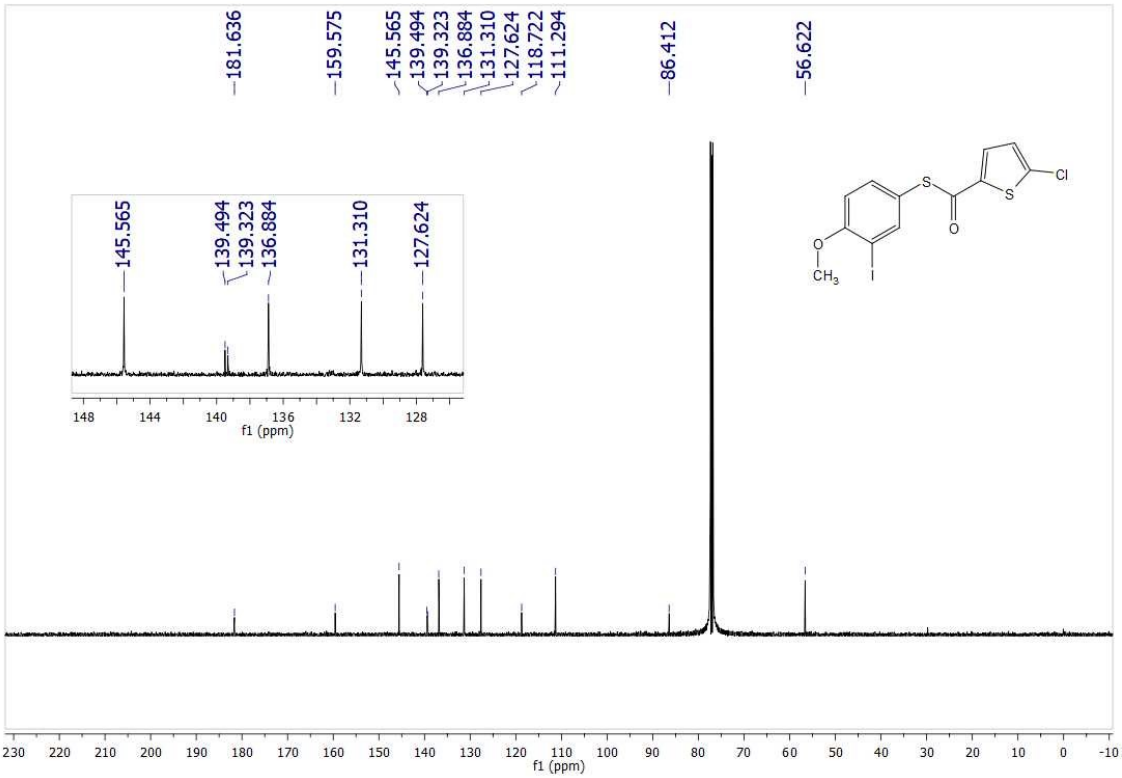
^{1}H NMR (500 MHz, $CDCl_3$) of compound **42**.



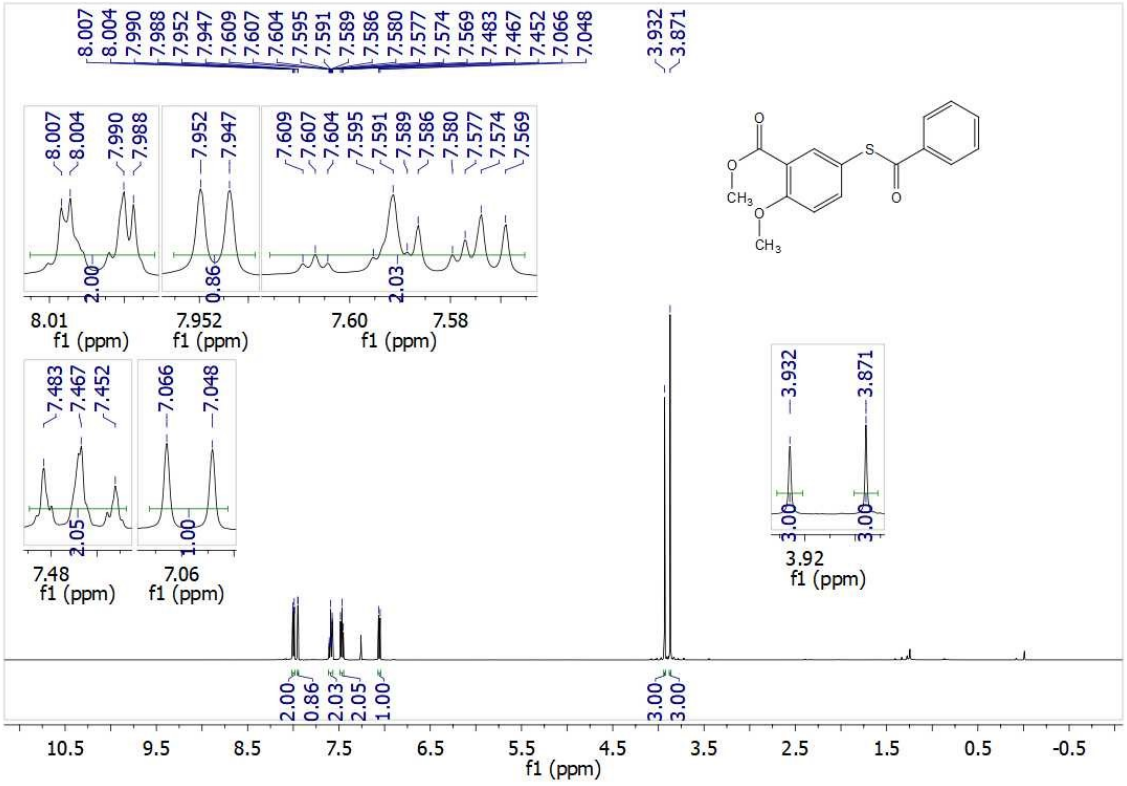
^{13}C NMR (126 MHz, $CDCl_3$) of compound **42**.



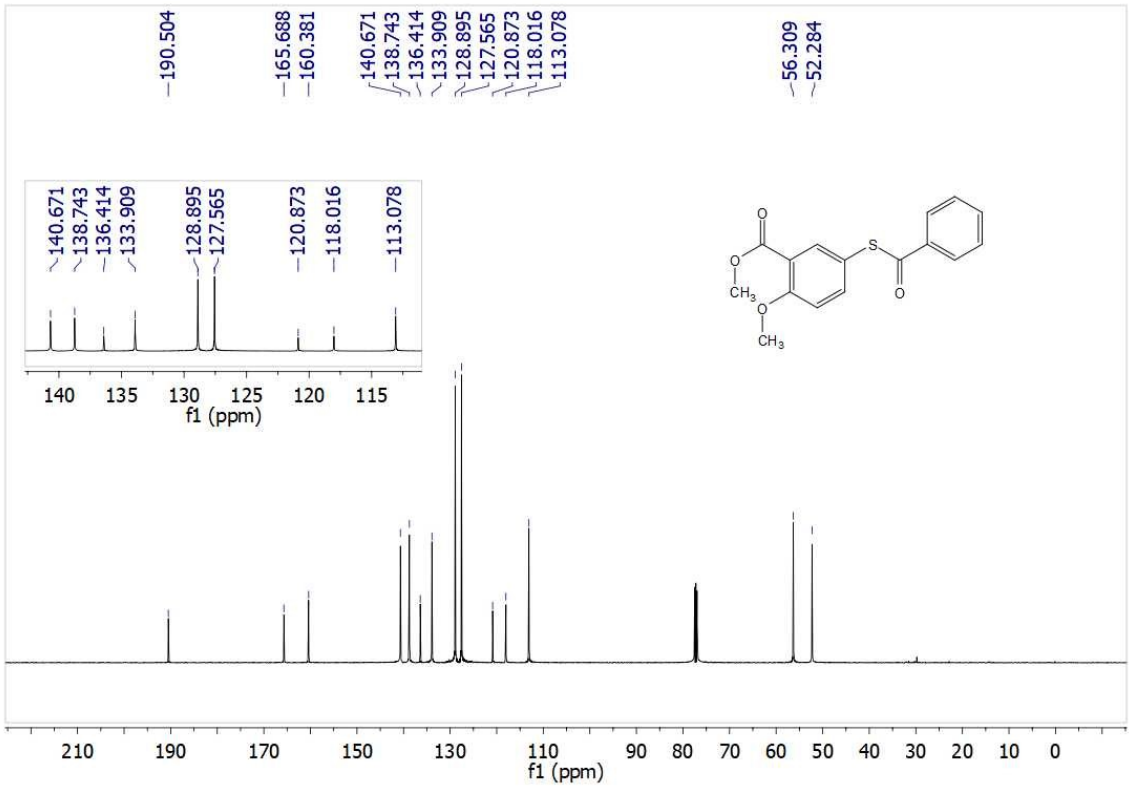
^{1}H NMR (500 MHz, $CDCl_3$) of compound **43**.



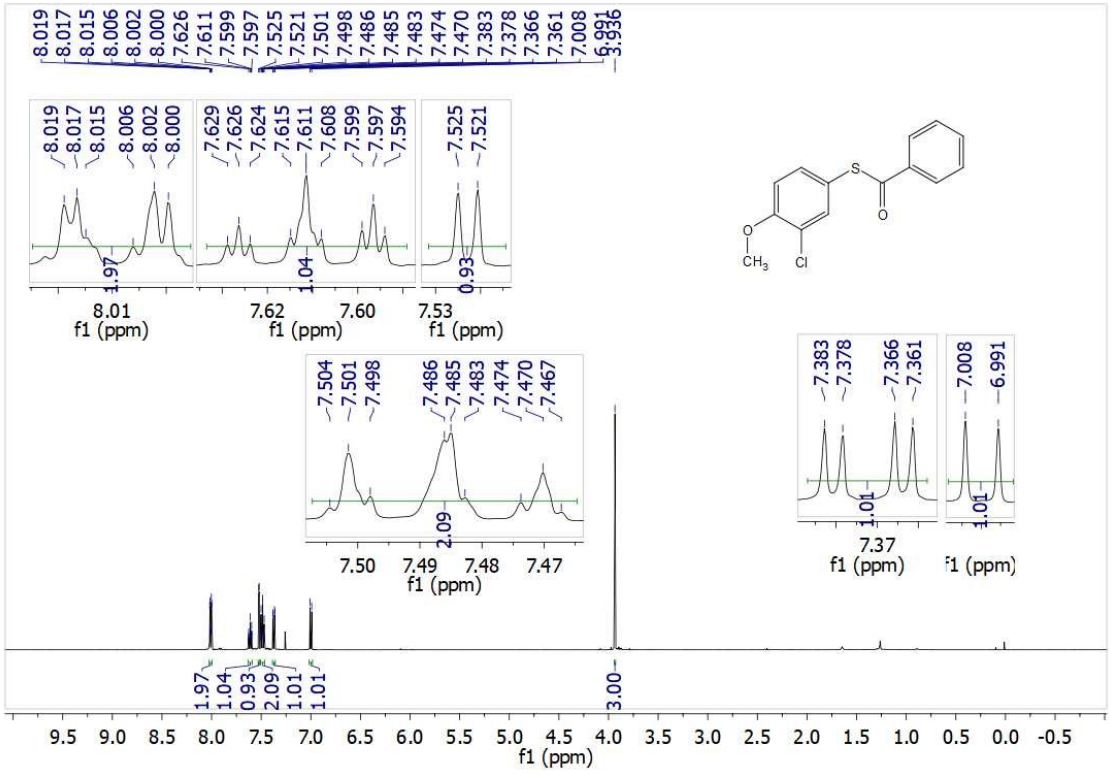
^{13}C NMR (126 MHz, $CDCl_3$) of compound **43**.



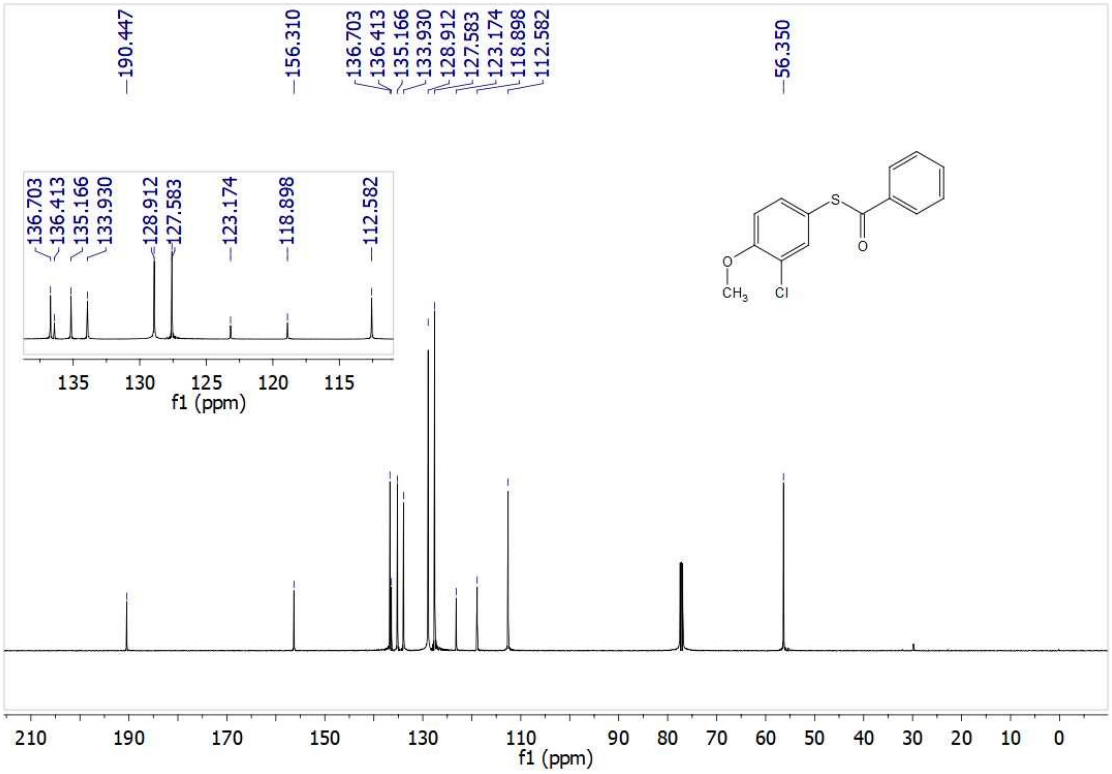
^{1}H NMR (500 MHz, $CDCl_3$) of compound **44**.



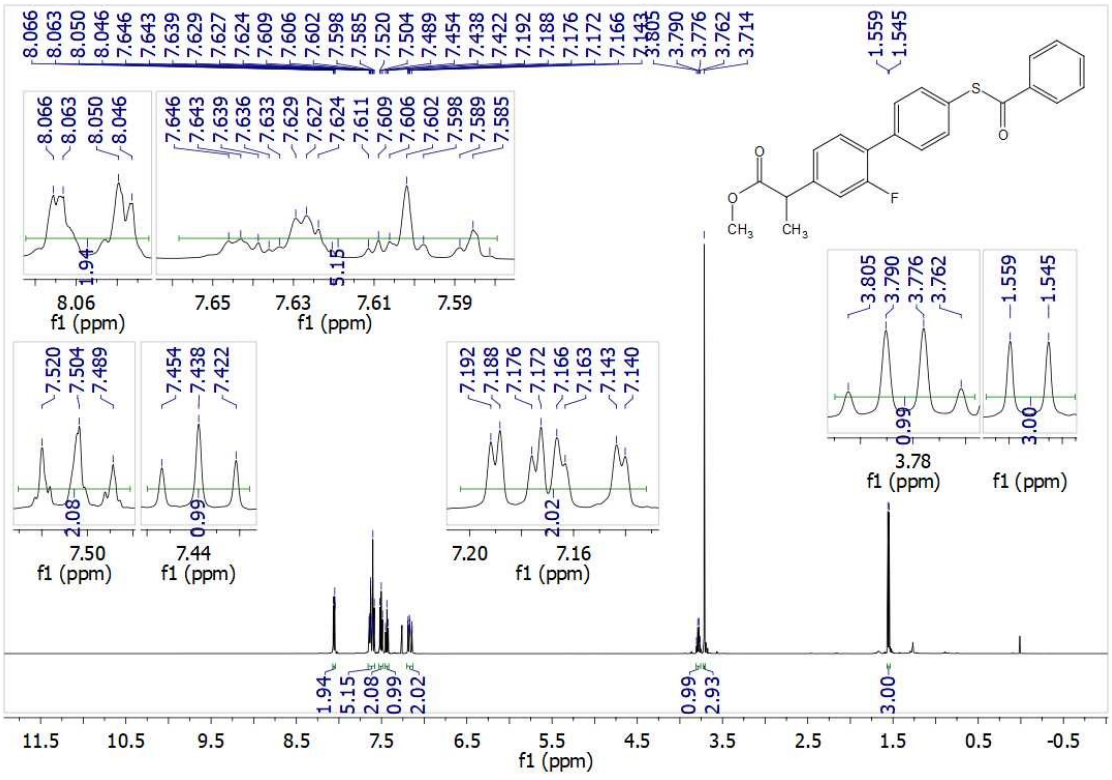
^{13}C NMR (126 MHz, $CDCl_3$) of compound **44**.



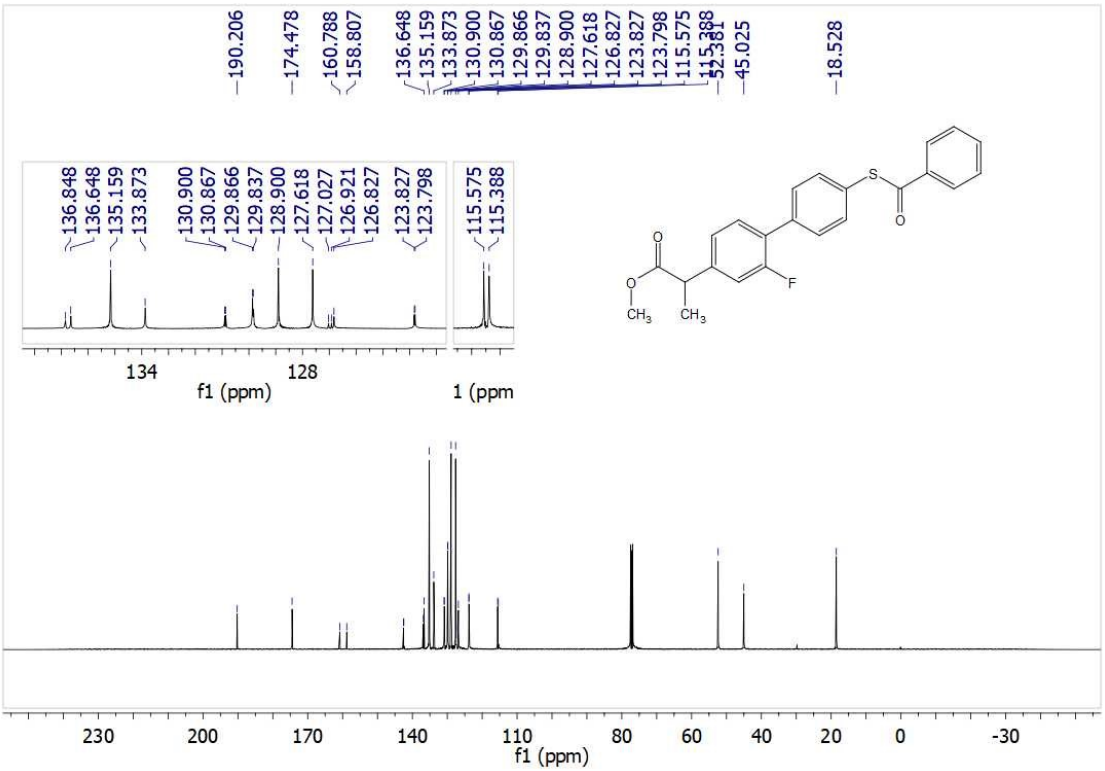
^{1}H NMR (500 MHz, $CDCl_3$) of compound **45**.



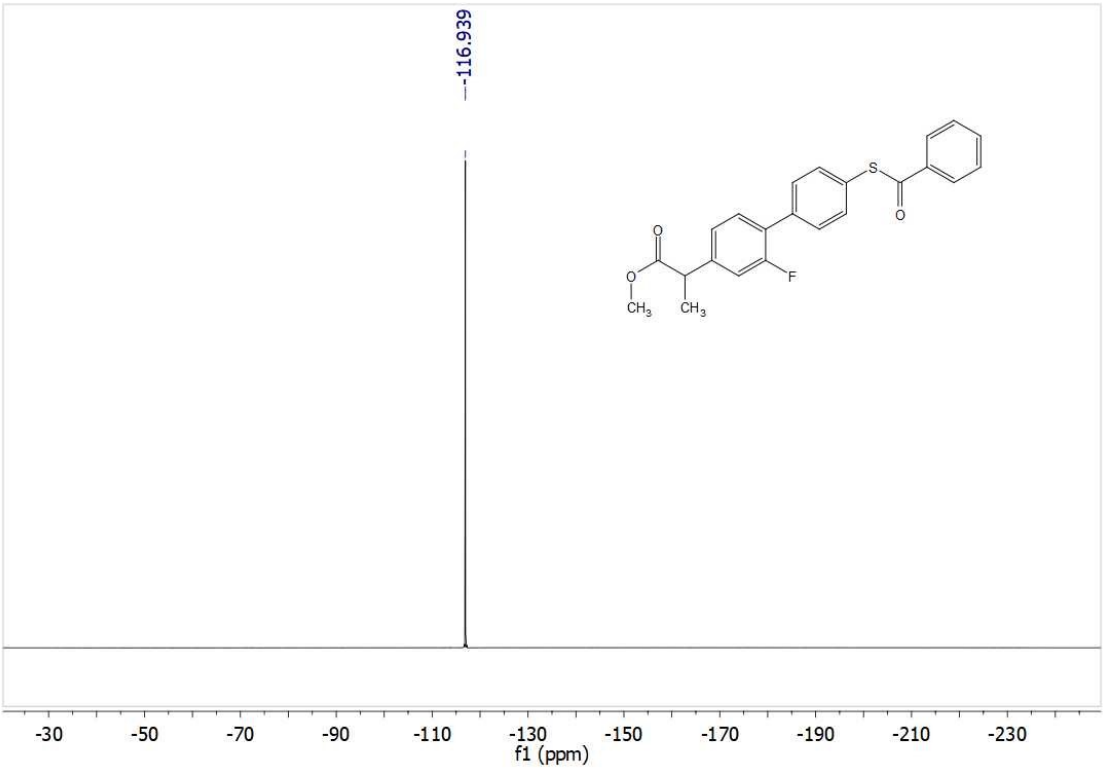
^{13}C NMR (126 MHz, $CDCl_3$) of compound **45**.



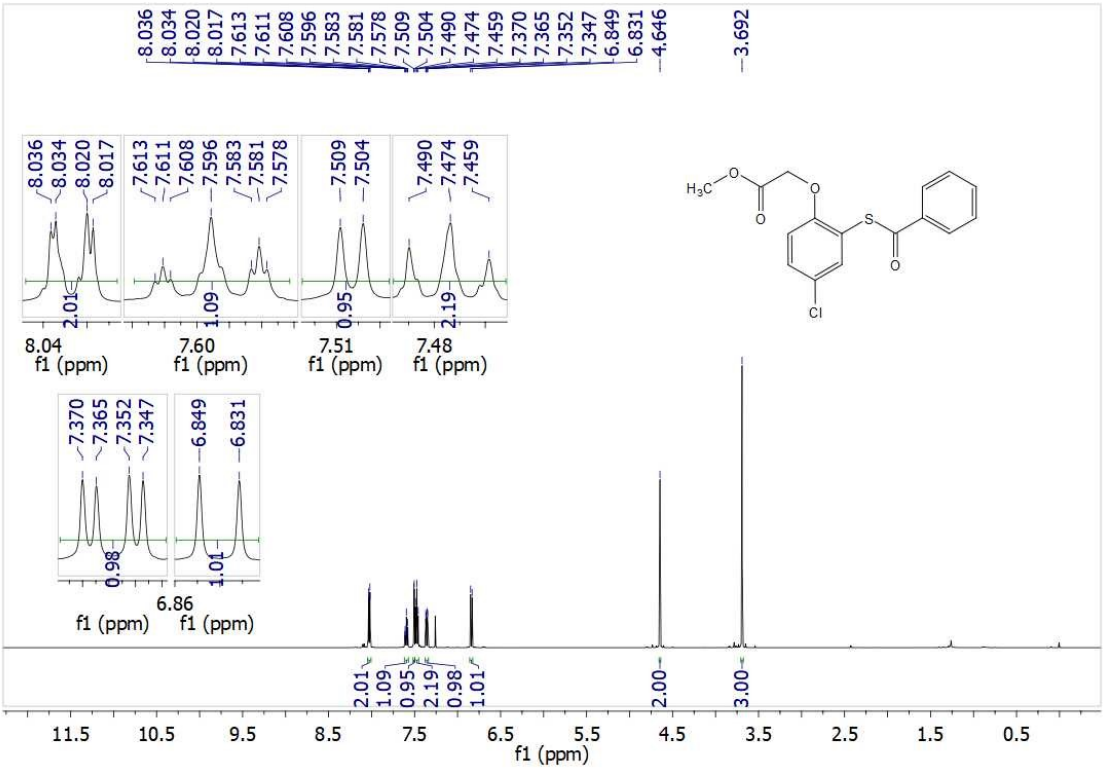
^{1}H NMR (500 MHz, $CDCl_3$) of compound **46**.



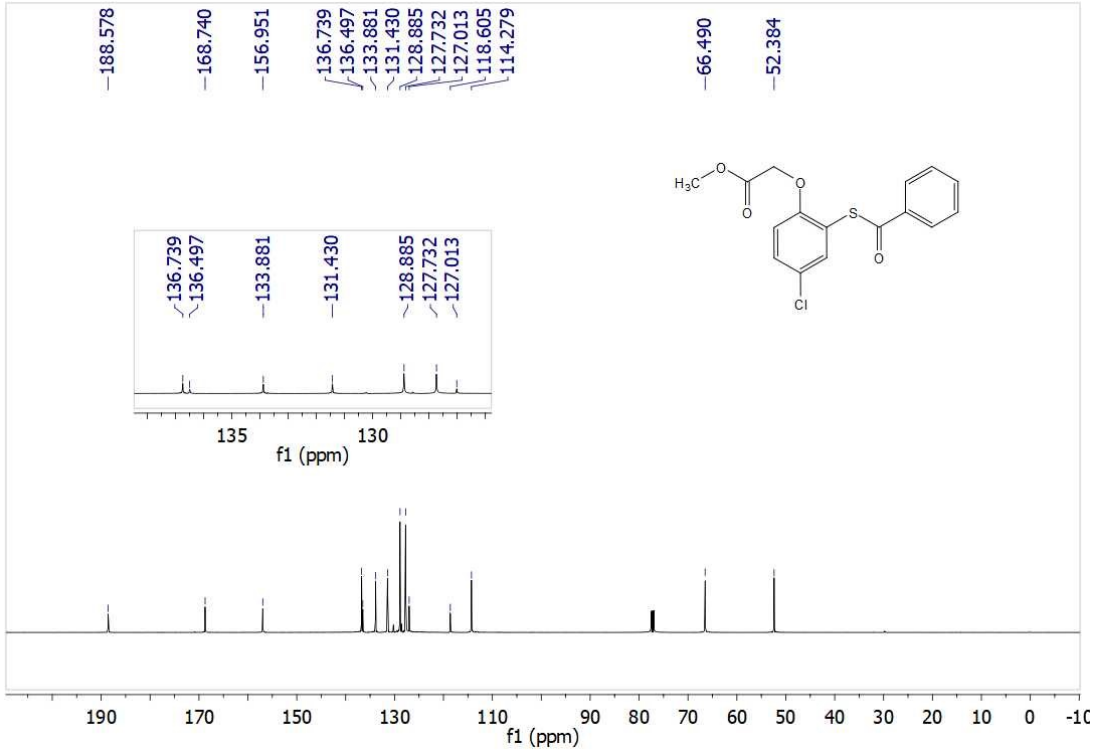
^{13}C NMR (126 MHz, $CDCl_3$) of compound **46**.



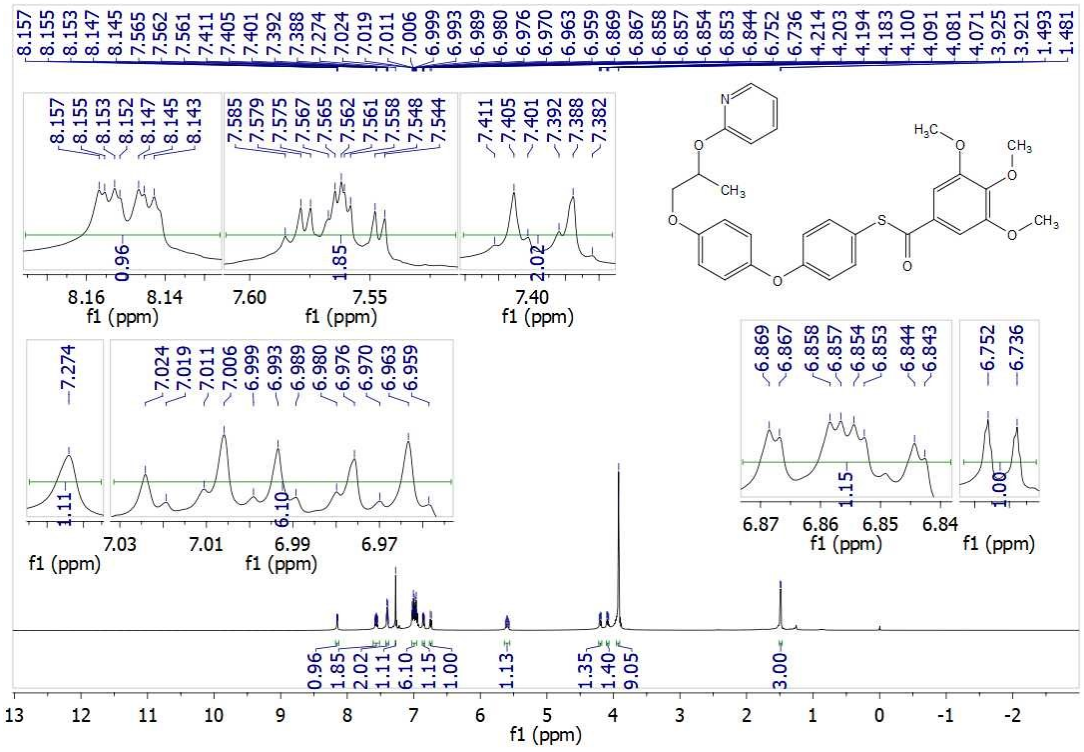
^{19}F NMR (472 MHz, $CDCl_3$) of compound **46**.



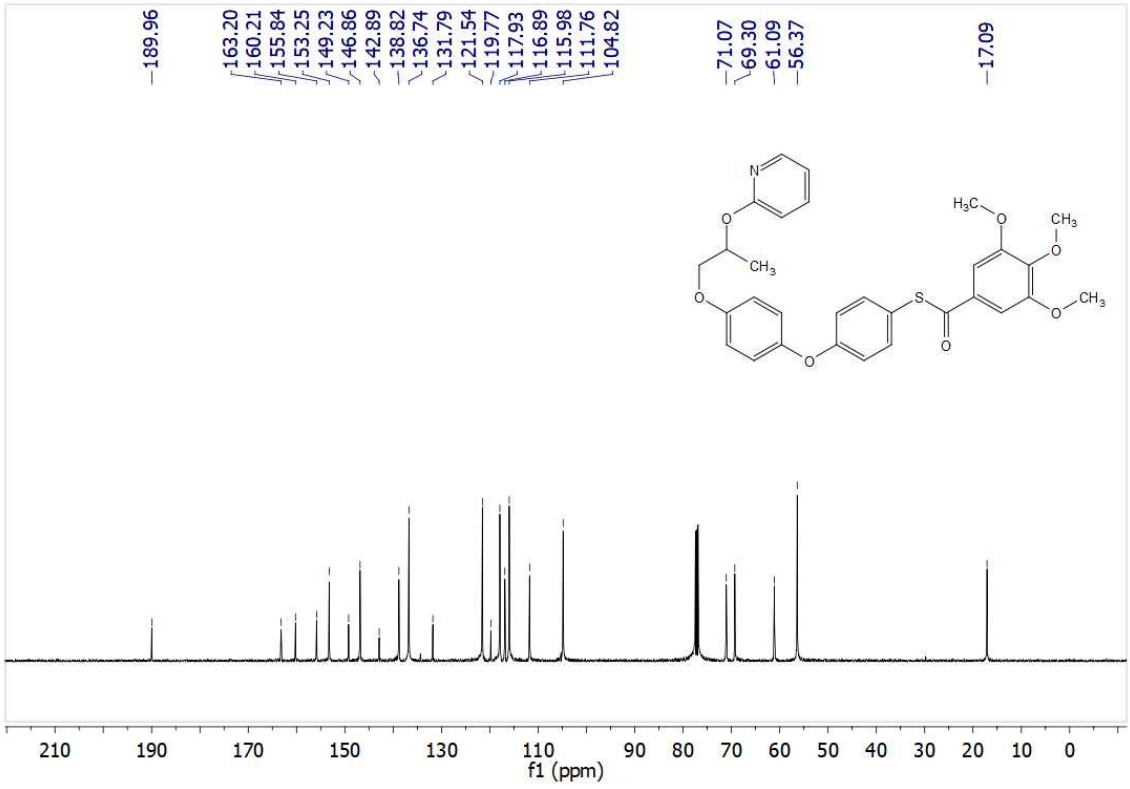
^{1}H NMR (500 MHz, $CDCl_3$) of compound **47**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **47**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **48**.



^{13}C NMR (126 MHz, $CDCl_3$) of compound **48**.

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