Supporting Information

Visible-light-promoted phosphine-mediated synthesis of thioesters and thioalkynes from sodium arylsulfinates

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1. General Information

All reactions were carried out under an atmosphere of argon in a sealed tube. Dry DCM, DCE, THF, DMF, DMSO, Toluene, $PhCF_3$, CH_3CN were purified using a solvent-purification system that contained activated alumina and molecular sieves. Other solvents were dried and purified according to the procedure from ‘‘Purification of Laboratory Chemicals’’.

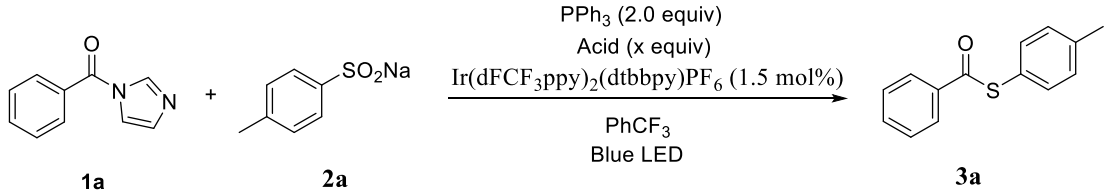
Photocatalysts were purchased from LAAjOO. Other chemicals were purchased from TCI, Adamas, and Energy chemicals, and they were used directly without further purifications. Thin-layer chromatography was carried out using NUOTAI SGF254 TLC plates. Flash chromatography was performed using NUOTAI silica gel (200-300 mesh).

^1H, ^{13}C and ^{19}FNMR spectra were collected on a Bruker AVANCE III 400MHz and 500MHz spectrometer at room temperature. ^1H NMR spectra were reported in parts per million (ppm) relative to residual $CHCl_3$ (7.26 ppm). ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.00 ppm). Coupling constants, *J*, are reported in hertz (Hz). HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI). UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a UV-2600 spectrophotometer from Shimadzu.

2. Optimization Studies

2.1 Reaction condition optimization for the preparation of thioesters

Table S1 Screening of acids.



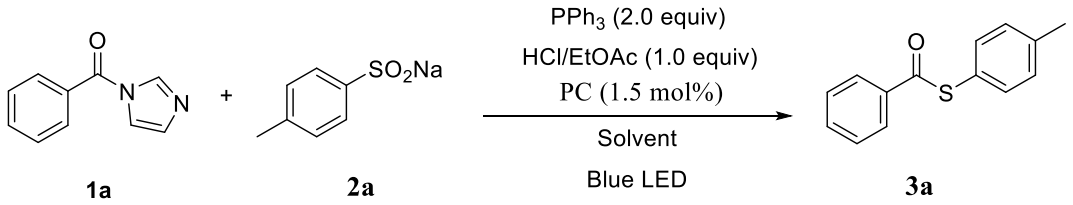
1a **2a** **3a**

Entry	Acid (x eq)	Acid	Yield %[b]
1	0	—	34
2	0.5	HCl/EtOAc	62
3	0.7	HCl/EtOAc	69
4	**1**	**HCl/EtOAc**	**70**
5	1.2	HCl/EtOAc	56

6	1	HCOOH	56
7	1	CH_3COOH	68
8[c]	—	—	43
9[c,d]	—	—	65

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), PPh_3 (0.2 mmol), HCl in EtOAc solution (x equiv), **PC** (1.5 mol %), $PhCF_3$ (1.0 mL), blue LED (λ_{max} =465 nm), 12 h. [b]NMR yields of reaction mixtures using 1,3,5-trimethylbenzene as internal standard. [c]*p*-$MePhSO_2H$ instead of *p*-$MePhSO_2Na$. [d]NaCl (0.10 mmol) was added.

Table S2 Screening of solvents and photocatalysts.



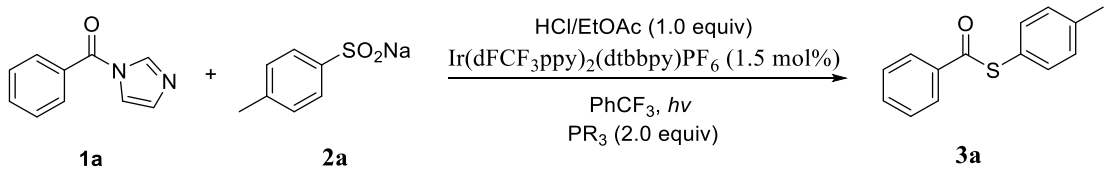
1a **2a** **3a**

Entry	**Solvent**	**Photocatalyst**	**Yield %[b]**
1	MeCN	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	56
2	DCM	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	61
3	DCE	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	53
4	DMSO	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	18
5	$PhCH_3$	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	58
6	**$PhCF_3$**	**$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$**	**70**
7	$PhCF_3$	$Ir(ppy)_3$	30
8	$PhCF_3$	$Ru(bpy)_3Cl_2$	58
9	$PhCF_3$	4CZIPN	52
10	$PhCF_3$	Mes-Arc^+-ClO_4^-	42
11	$PhCF_3$	—	40
12[c]	$PhCF_3$	—	44
13[c,d]	$PhCF_3$	—	N.R

[a]Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), PPh_3 (0.2 mmol), HCl/EtOAc (1.0 equiv), **PC** (1.5 mol %), solvent (1.0 mL), blue LED (λ_{max} =465 nm) 12 h. [b]NMR yields of reaction mixtures

using 1,3,5-trimethylbenzene as internal standard. [c]In the dark. [d]w/o HCl/EtOAc. N.R=no reaction.

Table S3 Screening of substrate ratios.



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

Entry	1a:2a	PR_3	c	Light	Yield %[b]
1	1.2:1	PPh_3	0.1 M	465 nm	70
2	1.5:1	PPh_3	0.1 M	465 nm	73
3	2:1	PPh_3	0.1 M	465 nm	80
4	1:1.2	PPh_3	0.1 M	465 nm	64
5	1:1.5	PPh_3	0.1 M	465 nm	70
6	2:1	P(4-OMe-C_6H_4)$_3$	0.1 M	465 nm	74
7	2:1	P(4-F-C_6H_4)$_3$	0.1 M	465 nm	51
8	2:1	$P(OEt)_3$	0.1 M	465 nm	50
9	2:1	PPh_3	0.2 M	465 nm	76
10	2:1	PPh_3	0.05 M	465 nm	62
11	2:1	PPh_3	0.1 M	50W CFL	78
12	2:1	PPh_3	0.1 M	380 nm	54
13[c]	**2:1**	**PPh_3**	**0.1 M**	**465 nm**	**95(89[e])**
14[d]	2:1	—	0.1 M	465 nm	trace

[a]The reaction was conducted under an argon atmosphere at 0.1 mmol scale of **2a**, 12 h. [b]NMR yields of reaction mixtures using 1,3,5-trimethylbenzene as internal standard.[c]PPh_3(3 equiv).[d]w/o PPh_3. [e]Isolated yield.

2.2 Optimization Studies of thioalkyne

Table S4 Screening of PR_3 and photocatalysts.

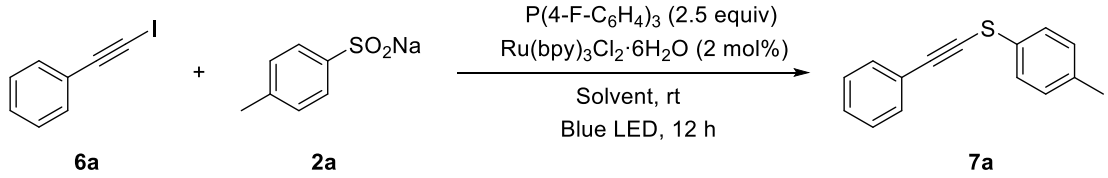
6a **2a** **7a**

Entry	PR_3	Photocatalyst	Yield %[b]

1	PPh_3	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	20
2	$P(4\text{-}F\text{-}C_6H_4)_3$	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	29
3	$P(4\text{-}OMe\text{-}C_6H_4)_3$	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	trace
4	$P(4\text{-}F\text{-}C_6H_4)_3$	$Ir(ppy)_3$	28
5	$P(4\text{-}F\text{-}C_6H_4)_3$	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	33
6	$P(4\text{-}F\text{-}C_6H_4)_3$	4CZIPN	30
7[c]	**$P(4\text{-}F\text{-}C_6H_4)_3$**	**$Ru(bpy)_3Cl_2 \cdot 6H_2O$**	**35**
8	$P(4\text{-}F\text{-}C_6H_4)_3$	—	19
9[d]	$P(4\text{-}F\text{-}C_6H_4)_3$	—	N.R

[a]Reaction conditions: **6a** (0.1 mmol), **2a** (0.15 mmol), PR_3 (0.2 mmol), **PC** (2.0 mol %), DCE (1.0 mL), under an argon atmosphere, blue LED 12 h. [b]Isolated yield. [c]$P(4\text{-}F\text{-}C_6H_4)_3$ (0.25 mmol). [d]In the dark.

Table S5 Screening of solvents and concentrations.

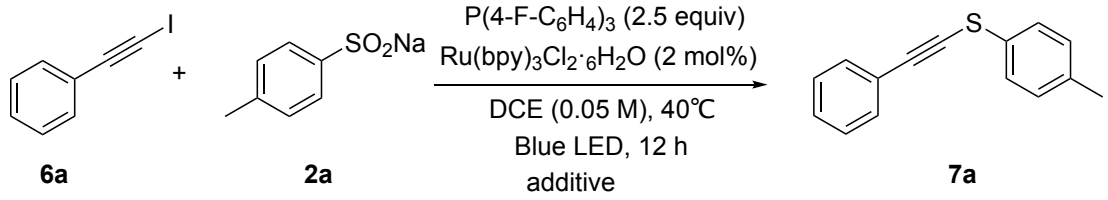


6a **2a** **7a**

Entry	Solvent	c	Yield%[b]
1	DCE	0.1 M	33
2	DCM	0.1 M	30
3	MeCN	0.1 M	17
4	$PhCF_3$	0.1 M	21
5	Et_2O	0.1 M	12
6	DMSO	0.1 M	0
7	EtOH	0.1 M	0
8	DCE	0.2 M	32
9	DCE	0.05 M	39
10[c]	**DCE**	**0.05 M**	**48**
11[d]	DCE	0.05 M	33

[a]Reaction conditions: **6a** (0.1 mmol), **2a** (0.15 mmol), **$P(4\text{-}F\text{-}C_6H_4)_3$** (0.25 mmol), **PC** (2.0 mol %), **DCE** (x mL), under an argon atmosphere, blue LED 12 h. [b]Isolated yield. [c]40℃. [d]24h.

Table S6 Screening of additives.



6a **2a** **7a**

Entry	Additive	Yield%[b]
1	H_2O (0.1 ml)	trace
2	HCl (1eq)	0
3	$(CF_3SO_2)_2Mg$ (1 eq)	0
4	K_2CO_3 (1 eq)	20
5	$LiPF_6$ (0.4 eq)	34
6	NH_4PF_6 (0.4 eq)	35
7	NBu_4I (1 eq)	40
8[c]	—	14
9[d]	—	trace

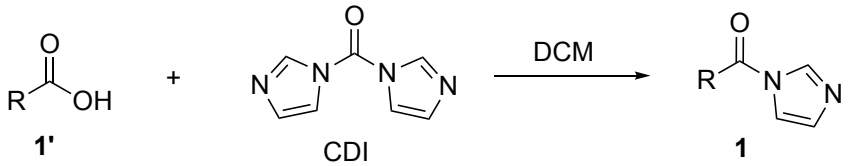
[a]Reaction conditions: **6a** (0.1 mmol), **2a** (0.15 mmol), P(4-F-C_6H_4)$_3$ (0.25 mmol), **PC** (2.0 mol %), **DCE** (1.0 mL), under an argon atmosphere, blue LED, 12 h. [b]Isolated yield. [c]380 nm. [d]under an air atmosphere.

3. General Procedures

3.1 General procedure for preparation of starting materials

Preparation of acyl imidazoles:

All the acyl imidazoles used in this work were known compounds, and were prepared from the corresponding carboxylic acids according to the literature.[1]

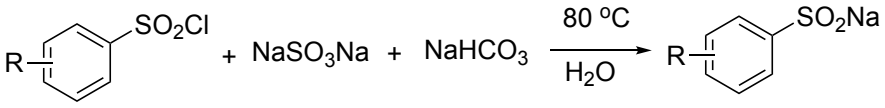


1' CDI **1**

To an oven-dried 100 mL round bottom flask equipped with a stir bar was added acid **1'** (10 mmol, 1.0 equiv) and dry DCM (30 mL), then CDI (2.43g, 15 mmol, 1.5 equiv) was added slowly under 0℃. The reaction mixture was allowed warm to room temperature and stirred overnight. Then the reaction mixture was washed vigorously 3 times with water and one time with brine. The organic layer was then dried over Na_2SO_4 and concentrated under vacuum. The resulting product **1** was used directly without further purification.

Preparation of sodium aryl sulfinates:

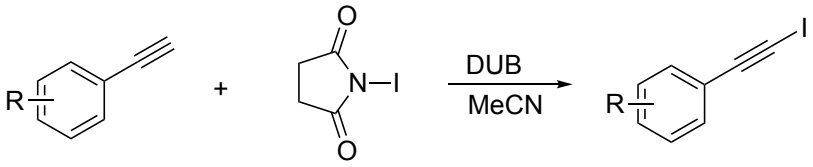
All sodium sulfinates used in this work were known compounds. Compouds **2a**-**2d**, **2g**-**2i**, **2l**, **2n**-**2p** were commercially available from chemical suppliers. Compouds **2e**, **2f**, **2j**, **2k**, **2m** were prepared according to the literature procedure.[2]



Sodium sulfite (10 mmol, 2 equiv), sodium bicarbonate (10 mmol, 2 equiv) and the corresponding aryl sulfonyl chloride (5 mmol, 1 equiv) were dissolved in distilled water (10 mL). The reaction mixture was stirred for 4 h at 80 °C. After cooling down to room temperature, water was removed in vacuo. 25 mL of ethanol was then added to this white residue and the resulting heterogeneous solution was filtered. The filtrate was concentrated under reduced pressure. The desired sodium aryl sulfinates were obtained as white crystalline powders in 78-92% yields by filtration.

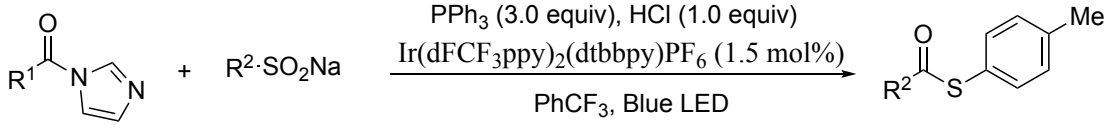
Preparation of iodoalkynes:

The iodoalkynes used in this work were all known compounds, which were prepared from the corresponding alkynes according to the literature.[3]



To a stirred solution of phenylacetylene (5.0 mmol) in MeCN (10.0 mL) was added NIS (5.5 mmol) and DBU (5.5 mmol). The mixture was stirred at room temperature for 10 min. The reaction mixture was poured into water and then extracted with Et_2O (3*20 mL). The combined organic phase was washed with saturated brine (10 mL), dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica gel, petroleum ether as eluent) to give the desired products.

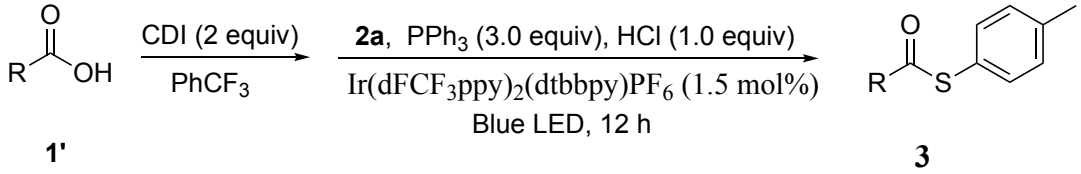
3.2 General procedure for preparation of thioesters



1 **2** **3**

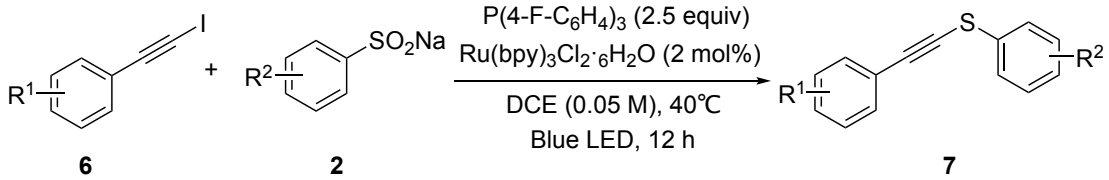
General procedure A: To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1** (0.4 mmol, 2.0 equiv), sodium sulfinate **2** (0.2 mmol, 1.0 equiv), PPh_3 (0.6 mmol, 157.4 mg, 3.0 equiv) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (0.003 mmol, 3.0 mg, 1.5 mol %) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (2.0 mL, 0.1 M) followed by HCl (2.0 M in EtOAc, 1.0 equiv). The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography to provide the desired product **3**.

Synthesis of thioesters in one-pot procedure



General procedure B: In gloves box, to a 10 mL vial equipped with a stir bar was added carboxylic acid **1'** (0.4 mmol, 2.0 equiv) and CDI (0.2 mmol, 70.5 mg, 2.0 equiv). $PhCF_3$ (2 mL) was added as solvent. The reaction mixture was stirred for 2.5 hours in the glove box at room temperature until the solution become homogenous. The resulting reaction mixture was mixed with sodium aryl sulfinate **2a** (0.2 mmol, 35.6 mg, 1.0 equiv.), PPh_3 (0.6 mmol, 157.4 mg, 3.0 equiv), HCl (2.0 M in EtOAc, 1.0 equiv) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (0.003 mmol, 3.0 mg, 1.5 mol %). The resulting mixture was sealed and take out from the gloves box. Then the mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h (distance app. 3 cm) at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography to provide the desired product.

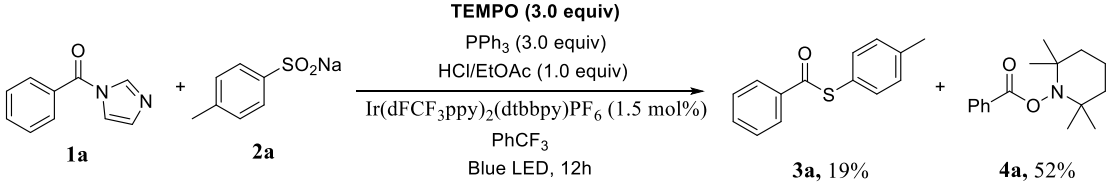
3.3 General procedure for preparation of Thioalkynes



General procedure C: To an oven-dried 10 mL vial equipped with a magnetic stir bar, iodoalkyne **6** (0.2 mmol, 1.0 equiv), sodium aryl sulfinate **2** (0.3 mmol, 1.5 equiv.), $P(4\text{-}F\text{-}C_6H_4)_3$ (0.5 mmol, 158.1 mg, 2.5 equiv) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.004 mmol, 2.5 mg, 2.0 mol %) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar, and DCE (4.0 mL, 0.05M) was added. The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at 40 ℃. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography to provide the desired product.

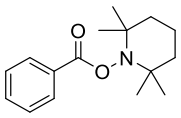
4. Mechanistic Studies

4.1 Radical trapping experiments



To an oven-dried 10 mL vial equipped with a magnetic stir bar, benzoyl imidazole **1a** (68.8 mg, 0.4 mmol), sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol), PPh_3 (156.2 mg, 0.6 mmol) , $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (3.0 mg, 0.003 mmol) and TEMPO (93.8 mg, 0.6 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (2.0 mL) followed by HCl (100 μl, 2.0 M in EtOAc). The mixture was

stirred under irradiation with blue LEDs (465 nm) for 12 h (distance app. 3 cm) at room temperature. Then the reaction mixture was concentrated in vacuo, and the desired product *S*-(p-tolyl) benzothioate **3a** was isolated by flash column chromatography on silica gel (Hexanes/DCM = 4/1) in 19% yield (8.7 mg) as a white solid. TEMPO-acyl adduct 2,2,6,6- tetramethylpiperidin-1-yl benzoate **4a** was isolated by flash column chromatography on silica gel (Hexanes/DCM = 4/1) in 52% yield (54.4 mg, yield was based **1a** used) as a white solid.

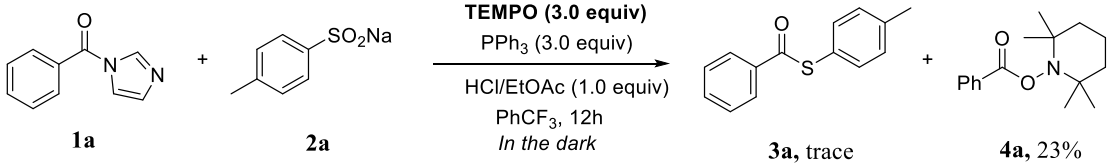


2,2,6,6-Tetramethylpiperidin-1-yl benzoate (4a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.04 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 1.84 – 1.66 (m, 3H), 1.63 – 1.55 (m, 2H), 1.51 – 1.42 (m, 1H), 1.28 (s, 6H), 1.13 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 132.9, 129.8, 129.6, 128.5, 60.4, 39.1, 32.0, 20.9, 17.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]

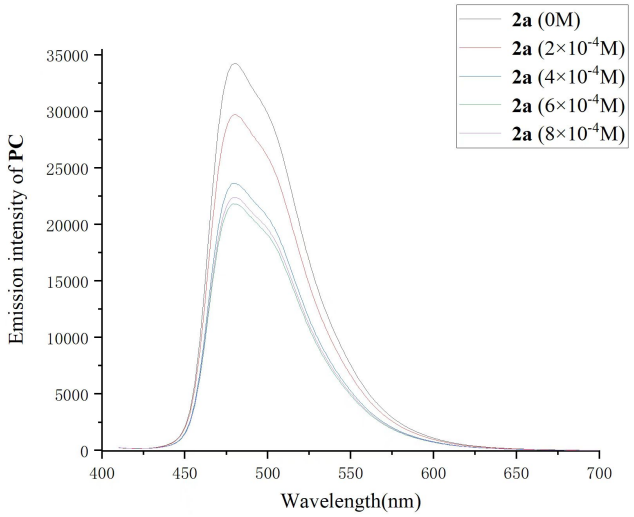


1a **2a** **3a,** trace **4a,** 23%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, benzoyl imidazole **1a** (68.8 mg, 0.4 mmol), sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol), PPh_3 (156.2 mg, 0.6 mmol) and TEMPO (93.8 mg, 0.6 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (1.0 mL) followed by HCl (100 μl, 2.0 M in EtOAc). The mixture was stirred in the dark for 12 h at room temperature. After the reaction was complete by TLC, the reaction mixture was concentrated in vacuo, The desired product *S*-(p-tolyl) benzothioate **3a** was not detected and reaction product **4a** (TEMPO-acyl adduct, 2,2,6,6- tetramethylpiperidin-1-yl benzoate) was isolated by flash column chromatography on silica gel (Hexanes/DCM = 4/1) in 23% yield (24.2 mg, yield was based **1a** used) as a white solid.

4.2 Stern-Volmer quenching experiments

For the fluorescence quenching experiments, stock solutions of **PC** [Ir(dF(CF_3)ppy)$_2$(dtbbpy)](PF_6) solutions (1×10^{-5} M), **2a** (1×10^{-4} M), PPh_3 (1×10^{-4} M), **1a** (1×10^{-4} M) were prepared in DMSO.. Samples were obtained by mixing a fixed volume of the stock solution of the photocatalyst **PC** and variable amount of the quencher in a 3 mL quartz cuvette. Before the measurements, argon gas was bubbled into the solutions for 1-2 minutes. Thereafter, the emission spectra were recorded for each sample from a wavelength of 410 nm to 700 nm, as shown in the following figures. All photocatalysts solutions were excited at 400 nm and the emission intensity was collected at 650 nm.



Figrue S1 Fluorescence quenching of **PC** with **2a**.

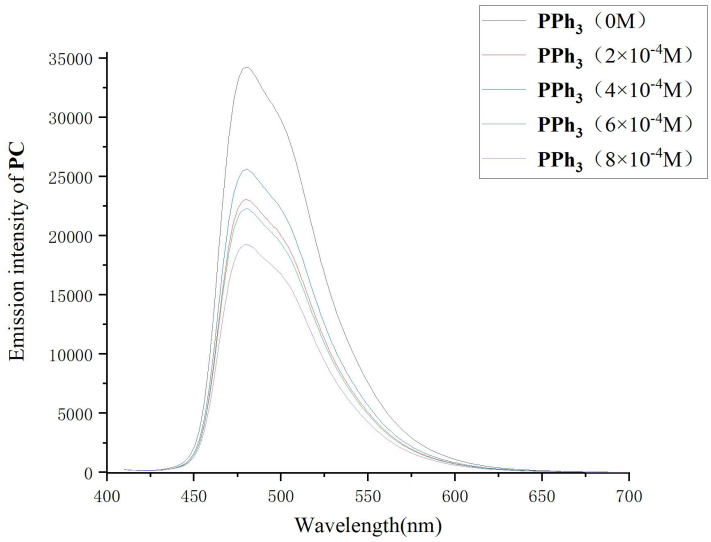


Figure S2 Fluorescence quenching of **PC** with **PPh_3**.

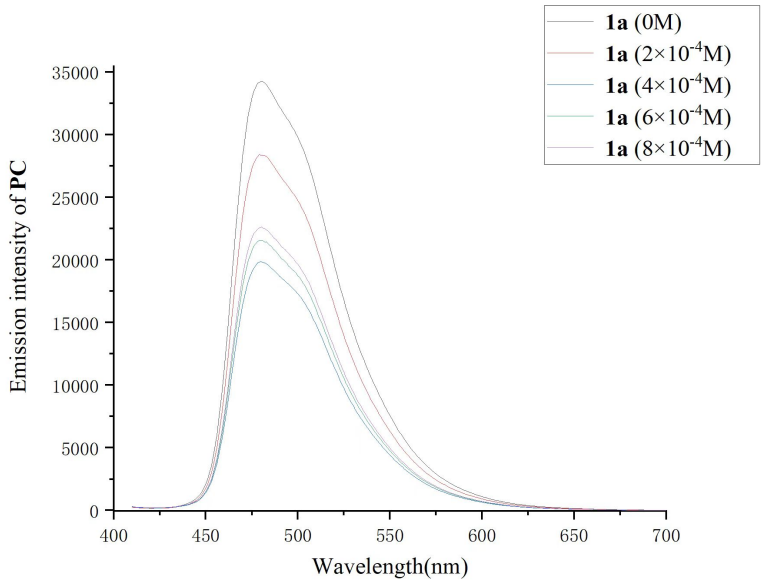


Figure S3 Fluorescence quenching of **PC** with **1a**.

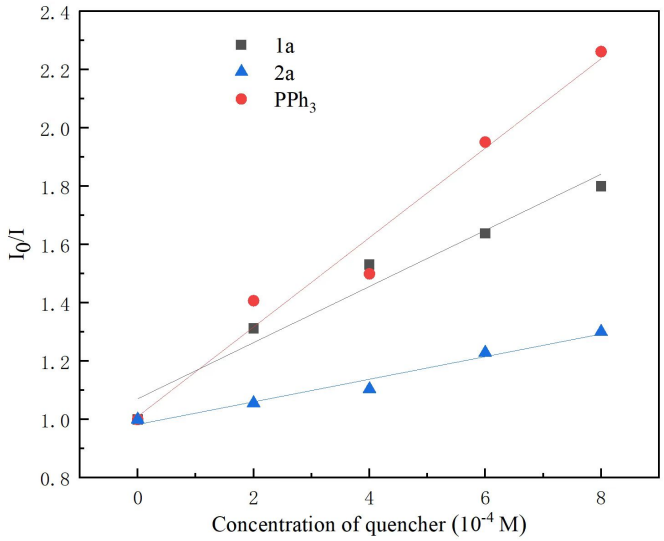
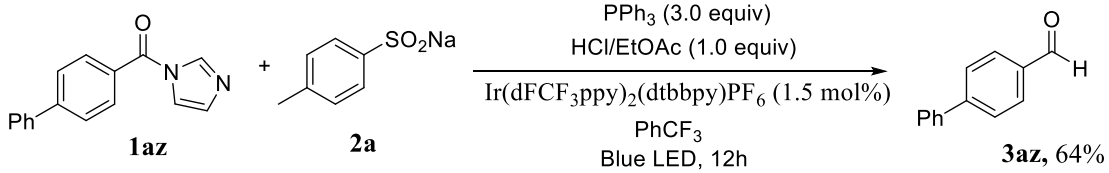


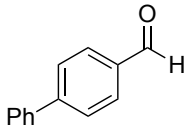
Figure S4 Stern-Volmer plots of reaction substrates.

4.3 Other mechanistic experiments



To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1az** (99.2 mg, 0.4 mmol), sodium aryl sulfinates **2a** (35.6 mg, 0.2 mmol), PPh_3 (157.2 mg, 0.6 mmol) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (3.0 mg, 0.003 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (2.0 mL,

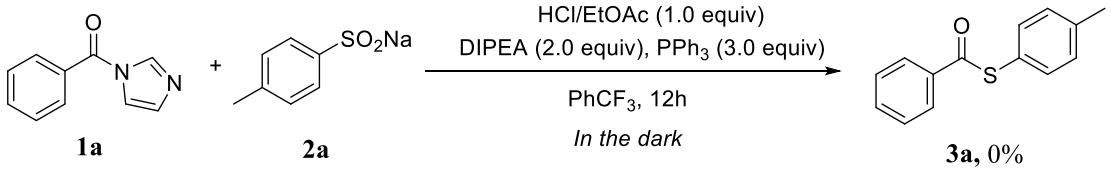
0.1 M) followed by HCl (100 μl, 2.0 M in EtOAc, 1.0 equiv). The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE/DCM = 4/1) to provide [1,1'-biphenyl]-4-carbaldehyde **3az** in 64% yield (46.4 mg, yield was based **1az** used) as a white solid.



3az

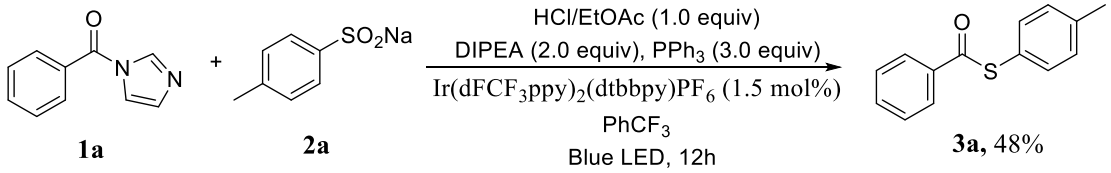
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.98 – 7.97 (m, 2H), 7.78 – 7.77 (m, 2H), 7.67 – 7.66 (m, 2H), 7.52 – 7.49 (m, 2H), 7.46 – 7.43 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 191.9, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[5]



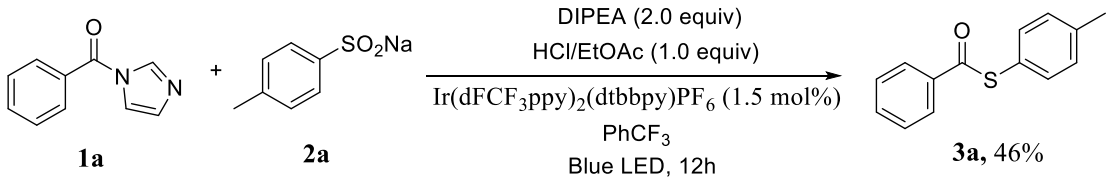
1a **2a** **3a,** 0%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (34.4 mg, 0.2 mmol), sodium aryl sulfinate **2a** (17.8 mg, 0.1 mmol), PPh_3 (78.6 mg, 0.3 mmol) and DIPEA (25.8 mg, 0.2 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (1.0 mL, 0.1 M) followed by HCl (50 μl, 1.0 M in EtOAc, 1.0 equiv). The mixture was stirred in the dark for 12 h at room temperature. After the reaction was complete by TLC, **3a** was not detected.



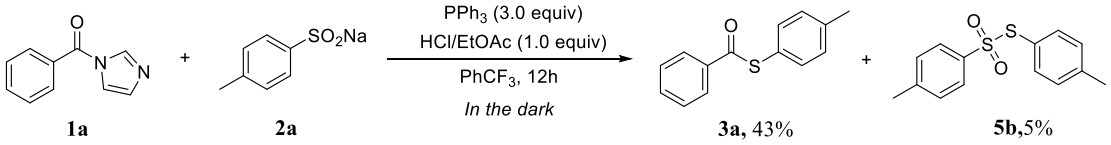
1a **2a** **3a,** 48%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (34.4 mg, 0.2 mmol), sodium aryl sulfinates **2a** (17.8 mg, 0.1 mmol), DIPEA (25.8 mg, 0.2 mmol), PPh_3 (78.6 mg, 0.3 mmol) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (1.5 mg, 0.0015 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (1.0 mL, 0.1 M) followed by HCl (50 μl, 2.0 M in EtOAc, 1.0 equiv). The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE/DCM = 4/1) to provide desired product **3a** in 48% yield (11.0 mg).



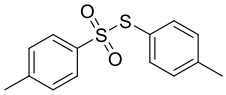
1a **2a** **3a,** 46%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (34.4 mg, 0.2 mmol), sodium aryl sulfinate **2a** (17.8 mg, 0.1 mmol), DIPEA (25.8 mg, 0.2 mmol) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (1.5 mg, 0.0015 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (1.0 mL, 0.1 M) followed by HCl (50 µl, 2.0 M in EtOAc, 1.0 equiv.). The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE/DCM = 4/1) to provide **3a** in 46% yield (10.5 mg).



1a **2a** **3a,** 43% **5b,**5%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (68.8 mg, 0.4 mmol), sodium aryl sulfinate **2a** (35.6 mg, 0.2 mmol), PPh_3 (157.2 mg, 0.6 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (2.0 mL, 0.1 M) followed by HCl (100 µl, 2.0 M in EtOAc, 1.0 equiv). The mixture was stirred in the dark for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE/DCM = 4/1) to provide desired product **3a** in 43% yield (19.6 mg) and thiosulfate **5b** as a solid in 5% yield (2.8 mg).

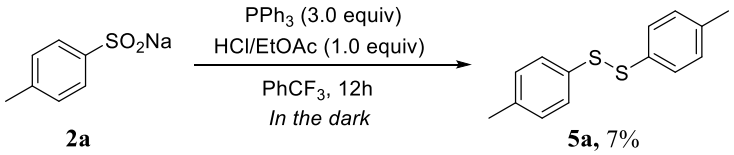


***S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (5b)**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.14 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 142.0, 140.5, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5.

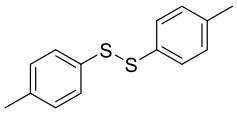
^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[6]



2a **5a,** 7%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, sodium aryl sulfinate **2a** (35.6 mg, 0.4 mmol) and PPh_3 (157.2 mg, 0.6 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (2.0 mL, 0.1

M) followed by HCl (100 μl, 2.0 M in EtOAc, 1.0 equiv). The mixture was stirred in the dark for 12 h at room temperature. Then the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE) to provide disulfide **5a** as a solid in 7% yield (3.5 mg).

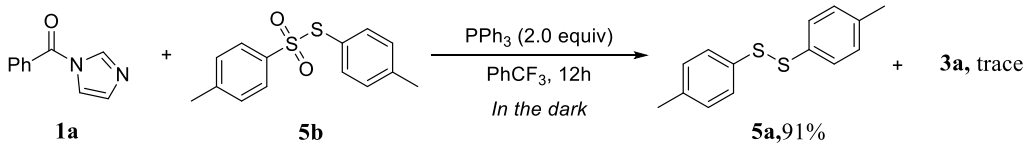


1,2-di-p-tolyldisulfane (5a)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 4H), 7.10 (d, J = 7.9 Hz, 4H), 2.32 (s, 6H).

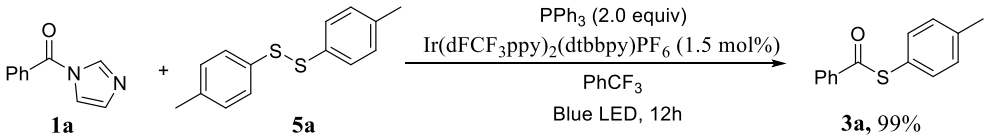
^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 133.9, 129.8, 128.6, 21.1.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[7]



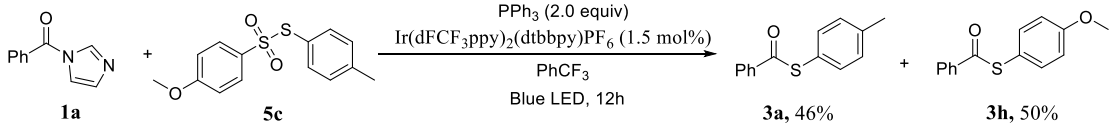
1a **5b** **5a,**91%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (34.4 mg, 0.2 mmol), thiosulfate **5b** (27.8 mg, 0.1 mmol), PPh_3 (78.6 mg, 0.3 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (2.0 mL, 0.1 M). The mixture was stirred in the dark for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE) to provide disulfide **5a** in 91% yield (22.4 mg) and the desired product **3a** could not be isolated due to the very small amout.



1a **5a** **3a,** 99%

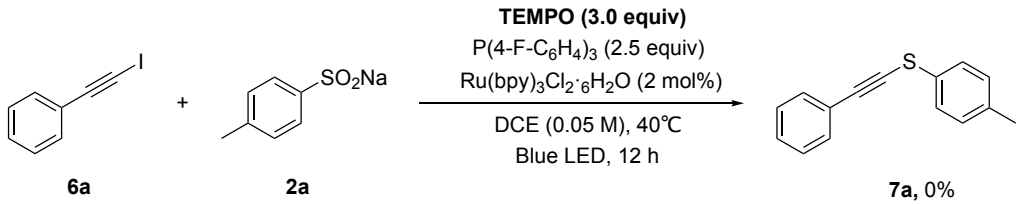
To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (34.4 mg, 0.2 mmol), disulfide **5a** (24.6 mg, 0.1 mmol), PPh_3 (52.4 mg, 0.2 mmol) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (1.5 mg, 0.0015 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous $PhCF_3$ (1.0 mL, 0.1 M). The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE/DCM = 4/1) to provide the desired product **3a** (22.8 mg) in 99% yield.



1a **5c** **3a,** 46% **3h,** 50%

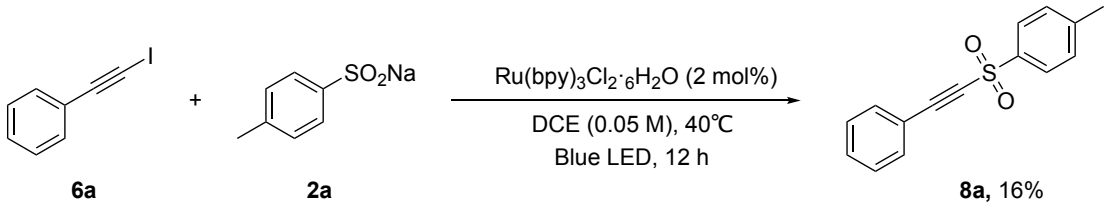
To an oven-dried 10 mL vial equipped with a magnetic stir bar, acyl imidazole **1a** (34.4 mg, 0.2 mmol), *S*-(*p*-tolyl) 4-methoxybenzenesulfonothioate **5c** (29.4 mg, 0.1 mmol,), PPh_3 (78.6 mg, 0.3 mmol) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (1.5 mg, 0.0015 mmol) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. To this vial was added anhydrous

$PhCF_3$ (1.0 mL, 0.1 M). The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at room temperature. After the reaction was complete by TLC, the solution was concentrated in vacuo, and the residue was purified by flash column chromatography (PE/DCM = 4/1) to provide corresponding thioesters **3a** in 46% yield (10.5 mg) and **3h** in 50% yield (12.2 mg).



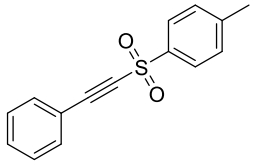
6a **2a** **7a,** 0%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, iodoalkyne **6a** (0.2 mmol, 45.6 mg, 1.0 equiv), sodium aryl sulfinate **2a** (0.3 mmol, 53.5 mg, 1.5 equiv), $P(4\text{-}F\text{-}C_6H_4)_3$ (0.5 mmol, 158.1 mg, 2.5 equiv), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.004 mmol, 2.5 mg, 2.0 mol %) and TEMPO (93.8 mg, 0.6 mmol, 3.0 equiv) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. Then DCE (4.0 mL) was added by syringe. The mixture was stirred under irradiation with blue LEDs (465 nm) for 12 h at 40 ℃. The solution was concentrated in vacuo, and the desired product **7a** was not detected.



6a **2a** **8a,** 16%

To an oven-dried 10 mL vial equipped with a magnetic stir bar, iodoalkyne **6a** (0.2 mmol, 45.6 mg, 1.0 equiv), sodium aryl sulfinate **2a** (0.3 mmol, 53.5 mg, 1.5 equiv) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.004 mmol, 2.5 mg, 2.0 mol %) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. Then DCE (4.0 mL) was added by syringe. The mixture was stirred with irradiation of blue LEDs (465 nm) for 12 h at 40 ℃. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography to provide **8a** in 16% yield (8.2 mg) as a white solid.

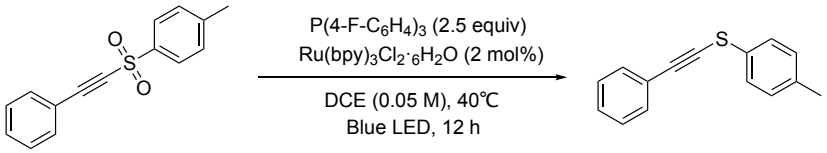


1-methyl-4-((phenylethynyl)sulfonyl)benzene（8a）

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H), 7.37 (m, 4H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 139.0, 132.7, 131.5, 130.0, 128.7, 127.5, 118.0, 93.0, 85.6, 21.8.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[8]



8a **7a**, *not detected*

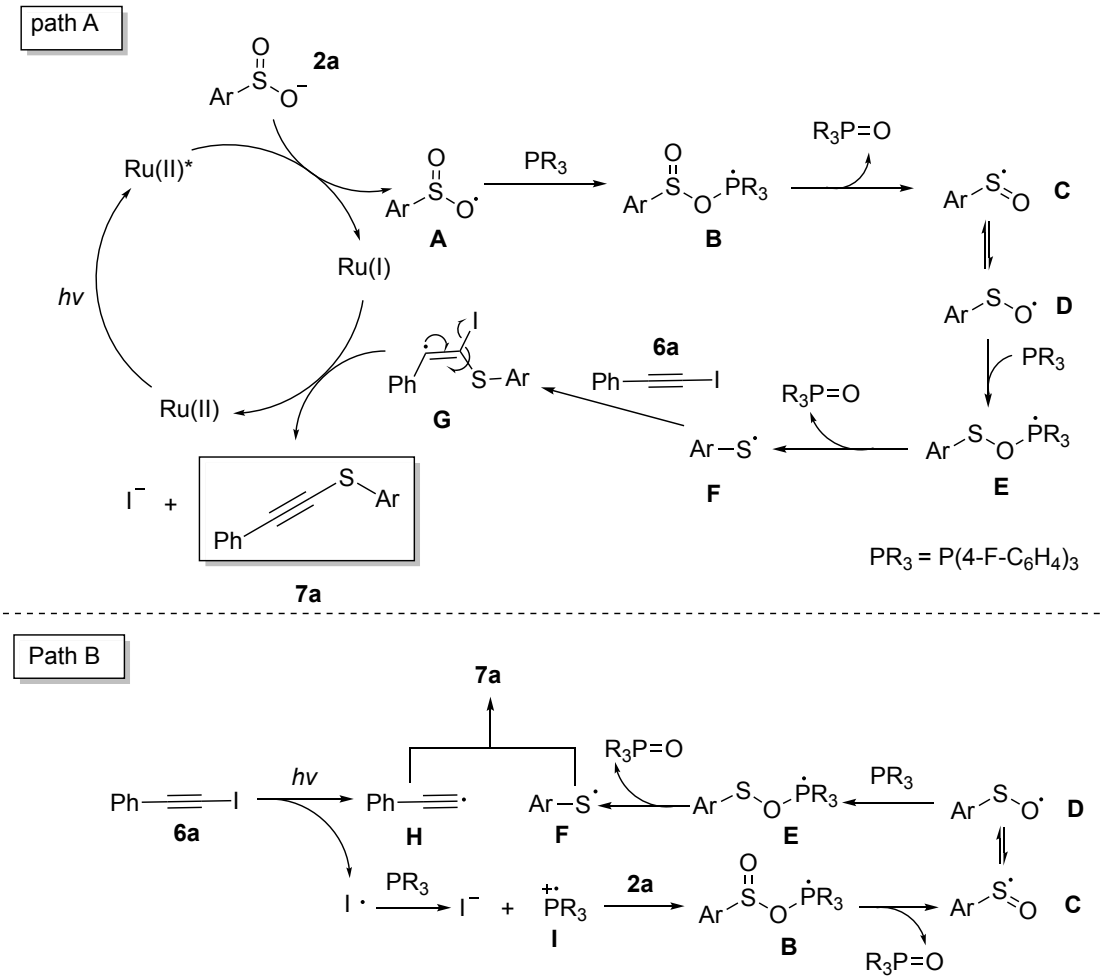
To an oven-dried 10 mL vial equipped with a magnetic stir bar, 1-methyl-4-((phenylethynyl)sulfonyl)benzene **8a** (0.1 mmol, 25.6 mg, 1.0 equiv) , $P(4\text{-F-}C_6H_4)_3$ (0.25 mmol, 79.1 mg, 2.5 equiv) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (0.002 mmol, 1.3 mg, 2.0 mol %) were added and the vial was sealed with a screw cap. The reaction vial was then purged with Ar. Then DCE (2.0 mL) was added by syringe. The mixture was stirred with irradiation of blue LEDs (465 nm) for 12 h at 40 ℃. The solution was concentrated in vacuo, and the desired product **7a** was not detected.

4.4 The tentative reaction mechanism of thioalkyne formation

Two possible pathways for the thioalkyne formation reaction were proposed as depicted in Scheme S1.

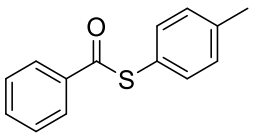
In the path A, the photocatalytic cycle may exist. The irradiation of Ru(II) photocatalyst by visible light generates the photoexcited state of Ru(II)*,[9] which undergoes single-electron transfer with sodium *p*-toluenesulfinate **2a** to form reductive Ru(I) and sulfonyl radical **A**. The latter combines with triarylphosphine to form radical intermediate **B**, affording triarylphosphine oxide and sulfoxyl radical **C** upon the β-scission of **B**. The sulfoxyl radical **C** equilibrates with the intermediate **D**, and reacts with another triarylphosphine followed by β-scission to form the thiyl radical **F**. The addition of **F** to iodoalkyne **6a** furnish the radical intermediate **G**, which is reduced by Ru(I) to deliver alkynyl sulfide **7a** and regernerate Ru(II).

In the path B, the direct excitation of **6a** enables the ensuing transformation without the photocatlyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$.[10] Specifically, the excited **6a** leads to the generation of alkynyl radical **H** and iodo radical. The latter undergoes single electron transfer with triarylphosphine, delivering the radical cation **I**. Then **I** combines with **2a** to afford **B**, which could generate thiyl radical **F** after successive deoxygenation process as in path A. Finally, the radical-radical coupling between **H** and **J** provides the target product **7a**.



Scheme S1 The possible reaction mechanism of thioalkyne formation.

5. Characterization Data of Product



***S*-(*p*-tolyl) benzothioate (3a)**

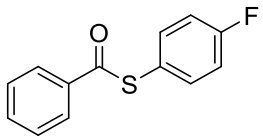
According to the general procedure **A** (0.2 mmol scale), product **3a** was isolated in 89% yield (40.6 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

Alternarively, product **3a** could be isolated in 85% yield (0.38 g) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (0.69 g, 4 mmol, 2.0 equiv), sodium 4-methylbenzenesulfinate **2a** (0.36 g, 2 mmol, 1.0 equiv), PPh_3 (6 mmol, 1.57 g, 3.0 equiv) and $Ir(dFCF_3ppy)_2(dtbby)PF_6$ (0.03 mmol, 30 mg, 1.5 mol %) in $PhCF_3$ (20 mL).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.64 – 7.58 (m, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 139.8, 136.7, 135.1, 133.6, 130.2, 128.8, 127.5, 123.8, 21.4.
^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]

Alternatively, **3a** could also be isolated in 72% yield (32.8 mg) according to the general procedure **B** (0.2 mmol scale), from benzoic acid **1a'** (48.8 mg, 0.4 mmol, 2.0 equiv), CDI (70.5 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).



***S*-(4-fluorophenyl) benzothioate (3b)**

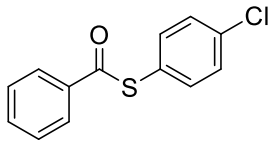
According to the general procedure **A** (0.2 mmol scale), product **3b** was isolated in 96% yield (44.6 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-fluorobenzenesulfinate 2b (36.2 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.65 – 7.59 (m, 1H), 7.53 – 7.46 (m, 4H), 7.17 (t, J = 8.6 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 163.7 (d, J_1 = 250.2 Hz), 137.2 (d, J_3 = 8.6 Hz), 136.4, 133.8, 128.8, 127.5, 122.6 (d, J_4 = 3.5 Hz), 116.6 (d, J_2 = 22.2 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –111.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



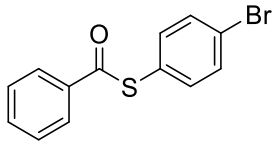
***S*-(4-chlorophenyl) benzothioate (3c)**

According to the general procedure **A** (0.2 mmol scale), product **3c** was isolated in 52% yield (25.9 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a (**68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-chlorobenzenesulfinate **2c** (39.4 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.4, 1.3 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.53 – 7.47 (m, 2H), 7.46 – 7.42 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 136.4, 136.3, 136.0, 133.9, 129.5, 128.8, 127.5, 125.9.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



***S*-(4-bromophenyl) benzothioate (3d)**

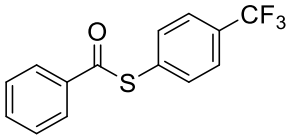
According to the general procedure **A** (0.2 mmol scale), product **3d** was isolated in 80% yield (47.1 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv)

and sodium 4-bromobenzenesulfinate **2d** (48.2 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H), 7.65 – 7.61 (m, 1H), 7.61 – 7.57 (m, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.40 – 7.36 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 136.6, 136.4, 133.9, 132.5, 128.9, 127.5, 126.5, 124.3.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[11]



***S*-(4-(trifluoromethyl)phenyl) benzothioate (3e)**

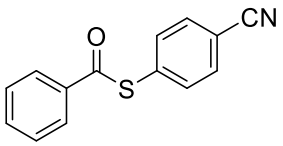
According to the general procedure **A** (0.2 mmol scale), product **3e** was isolated in 61% yield (34.6 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-(trifluoromethyl)benzenesulfinate **2e** (46.4 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.4 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.68 – 7.61 (m, 3H), 7.51 (t, J = 7.7 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.9, 136.2, 135.2, 134.1, 132.2, 131.5 (q, J_2 = 32.7 Hz), 128.9, 127.6 , 126.0 (q, J_3 = 3.7 Hz), 123.9 (q, J_1 = 272.4 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –62.8.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



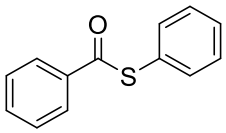
***S*-(4-cyanophenyl) benzothioate (3f)**

According to the general procedure **A** (0.2 mmol scale), product **3f** was isolated in 86% yield (40.9 mg) as a yellow solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-cyanobenzenesulfinate **2f** (37.8 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.4, 1.3 Hz, 2H), 7.74 –7.70 (m, 2H), 7.67 – 7.62 (m, 3H), 7.54 – 7.48 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 136.0, 135.3, 134.3, 134.0, 132.5, 129.0, 127.6, 118.3, 113.1.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[12]



***S*-phenyl benzothioate (3g)**

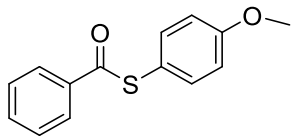
According to the general procedure **A** (0.2 mmol scale), product **3g** was isolated in 86% yield (36.9

mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium benzenesulfinate **2g** (32.8 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.4 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.56 – 7.45 (m, 7H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 136.7, 135.1, 133.7, 129.6, 129.3, 128.8, 127.5, 127.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



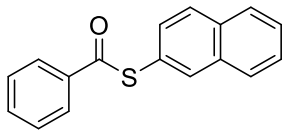
***S*-(4-methoxyphenyl) benzothioate (3h)**

According to the general procedure **A** (0.2 mmol scale), product **3h** was isolated in 49% yield (24.0 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methoxybenzenesulfinate **2h** (38.8 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 7.5 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.00 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 191.1, 160.8, 136.7 (2C), 133.6, 128.7, 127.5, 117.9, 115.0, 55.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



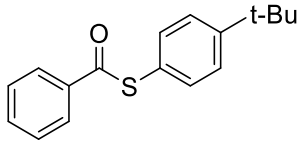
***S*-(naphthalen-2-yl) benzothioate (3i)**

According to the general procedure **A** (0.2 mmol scale), product **3i** was isolated in 69% yield (36.4 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium naphthalene-2-sulfinate **2i** (42.8 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.08 (d, J = 1.4 Hz, 2H), 7.94 (d, J = 8.5 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.66 – 7.61 (m, 1H), 7.60 – 7.49 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 136.7, 135.1, 133.8, 133.7, 133.5, 131.5, 128.9, 128.8, 128.1, 127.9, 127.6, 127.2, 126.6, 124.7.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



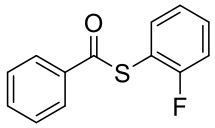
***S*-(4-(*tert*-butyl)phenyl) benzothioate (3j)**

According to the general procedure **A** (0.2 mmol scale), product **3j** was isolated in 69% yield (37.2 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-(tert-butyl)benzenesulfinate **2j** (44.0 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 2H), 7.64 – 7.58 (m, 1H), 7.53 – 7.43 (m, 6H), 1.37 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 152.8, 136.8, 134.7, 133.6, 128.7, 127.5, 126.4, 123.9, 34.8, 31.3.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



***S*-(2-fluorophenyl) benzothioate (3k)**

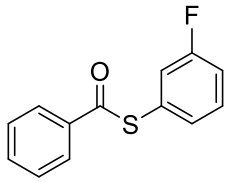
According to the general procedure **A** (0.2 mmol scale), product **3k** was isolated in 66% yield (30.6 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 2-fluorobenzenesulfinate **2k** (36.3 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 7.68 – 7.62 (m, 1H), 7.57 – 7.48 (m, 4H), 7.31 – 7.23 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 162.6 (d, J_1 = 249.8 Hz), 137.2, 136.3, 133.9, 132.3 (d, J_3 = 8.2 Hz), 128.8, 127.7, 124.7 (d, J_3 = 3.8 Hz), 116.3 (d, J_2 = 22.7 Hz), 114.9 (d, J_2 = 18.6 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ –106.1.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[13]



***S*-(3-fluorophenyl) benzothioate (3l)**

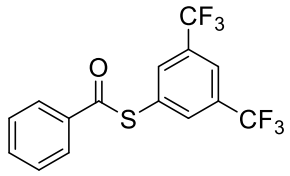
According to the general procedure **A** (0.2 mmol scale), product **3l** was isolated in 77% yield (35.8 mg) as a white solid from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 3-fluorobenzenesulfinate **2l** (36.3 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.66 – 7.59 (m, 1H), 7.50 (dd, J = 8.4, 7.2 Hz, 2H), 7.43 (td, J = 8.0, 5.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.20 – 7.13 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 162.6 (d, J_1 = 249.1 Hz), 136.4, 133.9, 130.7 (d, J_4 = 3.3 Hz), 130.4 (d, J_3 = 8.2 Hz), 129.2 (d, J_3 = 8.2 Hz), 128.9, 127.5, 122.0 (d, J_2 = 22.5 Hz), 116.7 (d, J_2 = 21.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –111.59.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[14]



***S*-(3,5-bis(trifluoromethyl)phenyl)benzothioate (3m)**

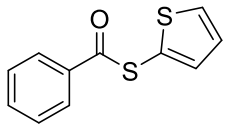
According to the general procedure **A** (0.2 mmol scale), product **3m** was isolated in 83% yield (58.4 mg) as a colorless oil from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium 3,5-bis(trifluoromethyl)benzenesulfinate **2m** (60.0 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2H), 8.01 – 7.94 (m, 3H), 7.70 – 7.63 (m, 1H), 7.56 – 7.49 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 135.7, 135.1 (d, J_3 = 3.9 Hz), 134.4, 132.4 (q, J_2 = 33.8 Hz), 130.9, 129.0, 127.7, 123.3 (p, J_3 = 3.8 Hz), 122.9 (q, J_1 = 273.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.87.

HRMS (ESI): Calcd for $C_{15}H_9F_6OS$ [M+H]: 351.0273, found: 351.0267.



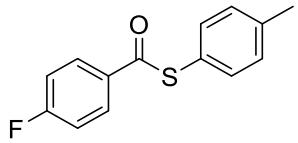
***S*-(thiophen-2-yl) benzothioate (3n)**

According to the general procedure **A** (0.2 mmol scale), product **3n** was isolated in 46% yield (20.4 mg) as a yellow oil from (1H-imidazol-1-yl)(phenyl)methanone **1a** (68.8 mg, 0.4 mmol, 2.0 equiv) and sodium thiophene-2-sulfinate **2n** (34.0 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.7 Hz, 2H), 7.68 – 7.62 (m, 2H), 7.53 (t, J = 7.7 Hz, 2H), 7.29 (dd, J = 3.7, 1.3 Hz, 1H), 7.20 (dd, J = 5.3, 3.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 136.3, 136.0, 134.0, 132.2, 128.9, 127.9, 127.6, 124.2.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



***S*-(*p*-tolyl) 4-fluorobenzothioate (3aa)**

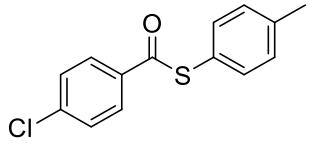
According to the general procedure **A** (0.2 mmol scale), product **3aa** was isolated in 98% yield (48.3 mg) as a white solid; (4-fluorophenyl)(1H-imidazol-1-yl)methanone **1aa** (76.0 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.19 – 7.13 (m, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 166.0 (d, J_1 = 255.2 Hz), 140.0, 135.1, 133.0 (d, J_4 = 3.0 Hz), 130.2, 130.1 (d, J_3 = 9.5 Hz), 123.5, 115.9 (d, J_2 = 22.0 Hz), 21.4.

^{19}F NMR (470 MHz, $CDCl_3$) δ –104.3.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



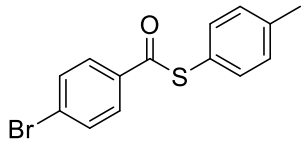
***S*-(*p*-tolyl) 4-chlorobenzothioate (3ab)**

According to the general procedure **A** (0.2 mmol scale), product **3ab** was isolated in 83% yield (43.5mg) as a white solid from (4-chlorophenyl)(1H-imidazol-1-yl)methanone **1ab** (82.4 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.48 – 7.43 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 140.03, 139.99, 135.1, 135.0, 130.2, 129.1, 128.8, 123.4, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



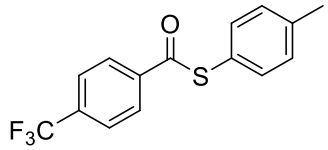
***S*-(*p*-tolyl) 4-bromobenzothioate (3ac)**

According to the general procedure **A** (0.2 mmol scale), product **3ac** was isolated in 79% yield (48.5mg) as a white solid from (4-bromophenyl)(1H-imidazol-1-yl)methanone **1ac** (99.9 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.65 – 7.60 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.7, 140.0, 135.5, 135.0, 132.0, 130.2, 128.9, 128.7, 123.3, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



***S*-(*p*-tolyl) 4-(trifluoromethyl)benzothioate (3ad)**

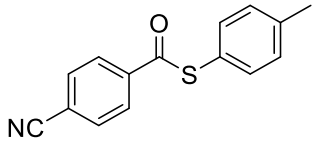
According to the general procedure **A** (0.2 mmol scale), product **3ad** was isolated in 85% yield (50.1 mg) as a white solid from (1H-imidazol-1-yl)(4-(trifluoromethyl)phenyl)methanone **1ad** (96.0 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 140.2, 139.5, 134.91, 134.86 (q, J_2 = 32.8 Hz), 130.3, 127.8, 125.8 (q, J_3 = 3.7 Hz), 123.5 (q, J_1 = 272.8 Hz), 123.0, 21.4.

^{19}F NMR (470 MHz, $CDCl_3$) δ –63.1.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[15]



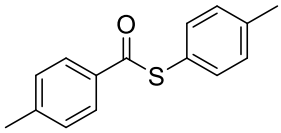
***S*-(*p*-tolyl) 4-cyanobenzothioate (3ae)**

According to the general procedure **A** (0.2 mmol scale), product **3ae** was isolated in 80% yield (40.7 mg) as a white solid from 4-(1H-imidazole-1-carbonyl)benzonitrile **1ae** (78.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 140.4, 139.8, 134.8, 132.6, 130.3, 127.9, 122.6, 117.8, 116.8, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[11]



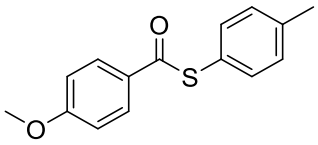
***S*-(*p*-tolyl) 4-methylbenzothioate (3af)**

According to the general procedure **A** (0.2 mmol scale), product **3af** was isolated in 90% yield (43.6 mg) as a white solid from (1H-imidazol-1-yl)(p-tolyl)methanone **1af** (74.4 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.33 – 7.28 (m, 4H), 2.46 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 144.5, 139.7, 135.1, 134.1, 130.1, 129.4, 127.6, 124.0, 21.8, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



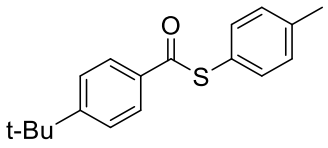
***S*-(*p*-tolyl) 4-methoxybenzothioate (3ag)**

According to the general procedure **A** (0.2 mmol scale), product **3ag** was isolated in 43% yield (22.2 mg) as a white solid from (1H-imidazol-1-yl)(4-methoxyphenyl)methanone **1ag** (80.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 163.9, 139.6, 135.1, 130.0, 129.7, 129.5, 124.0, 113.9, 55.5, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



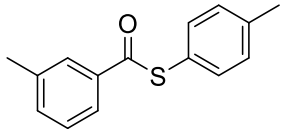
***S*-(*p*-tolyl) 4-(*tert*-butyl)benzothioate (3ah)**

According to the general procedure **A** (0.2 mmol scale), product **3ah** was isolated in 76% yield (43.2 mg) as a white solid from (4-(tert-butyl)phenyl)(1H-imidazol-1-yl)methanone **1ah** (91.2 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.53 – 7.48 (m, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 2.42 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.1, 157.4, 139.7, 135.1, 134.1, 130.1, 127.4, 125.7, 124.0, 35.2, 31.1, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[16]



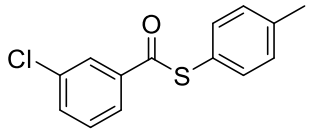
***S*-(*p*-tolyl) 3-methylbenzothioate (3ai)**

According to the general procedure **A** (0.2 mmol scale), product **3ai** was isolated in 92% yield (44.3 mg) as a colorless oil from (1H-imidazol-1-yl)(m-tolyl)methanone **1aj** (74.4 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.47 – 7.37 (m, 4H), 7.31 (d, J = 7.9 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.7, 139.8, 138.6, 136.8, 135.0, 134.4, 130.1, 128.6, 127.9, 124.7, 124.0, 21.41, 21.38.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



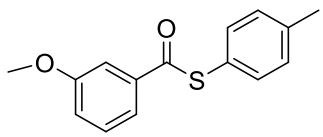
***S*-(*p*-tolyl) 3-chlorobenzothioate (3aj)**

According to the general procedure **A** (0.2 mmol scale), product **3aj** was isolated in 84% yield (44.1 mg) as a white solid from (3-chlorophenyl)(1H-imidazol-1-yl)methanone **1aj** (82.4 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (t, J = 1.9 Hz, 1H), 7.91 (dt, J = 7.8, 1.3 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.45 – 7.37 (m, 3H), 7.28 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 140.1, 138.2, 135.0, 134.9, 133.4, 130.2, 130.0, 127.5, 125.6, 123.2, 21.3.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



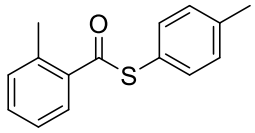
***S*-(*p*-tolyl) 3-methoxybenzothioate (3ak)**

According to the general procedure **A** (0.2 mmol scale), product **3ak** was isolated in 72% yield (36.9 mg) as a colorless oil from (1H-imidazol-1-yl)(3-methoxyphenyl)methanone **1ak** (80.8 mg, 0.4mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dt, J = 7.6, 1.2 Hz, 1H), 7.52 (dd, J = 2.7, 1.6 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.28 (d, J = 7.8 Hz, 2H), 7.17 – 7.13 (m, 1H), 3.86 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 159.8, 139.8, 138.0, 135.0, 130.1, 129.7, 123.8, 120.03, 119.97, 111.8, 55.5, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



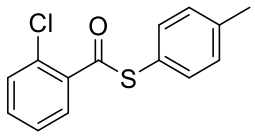
***S*-(*p*-tolyl) 2-methylbenzothioate (3al)**

According to the general procedure **A** (0.2 mmol scale), product **3al** was isolated in 79% yield (38.4 mg) as a white solid from (1H-imidazol-1-yl)(o-tolyl)methanone **1al** (74.4 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.8, 1.3 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.34 – 7.25 (m, 4H), 2.51 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.7, 139.8, 137.4, 136.9, 134.9, 132.0, 131.7, 130.1, 128.6, 125.9, 124.7, 21.4, 20.8.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



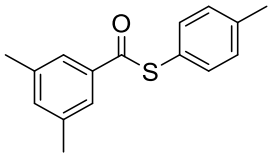
***S*-(*p*-tolyl) 2-chlorobenzothioate (3am)**

According to the general procedure **A** (0.2 mmol scale), product **3am** was isolated in 76% yield (39.9 mg) as a white solid from (2-chlorophenyl)(1H-imidazol-1-yl)methanone **1am** (82.4 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.7, 1.6 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.35 (td, J = 7.4, 1.4 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 140.1, 137.2, 134.6, 132.3, 131.1, 130.9, 130.2, 129.1, 126.7, 123.9, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



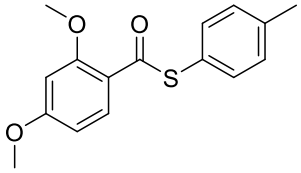
***S*-(*p*-tolyl) 3,5-dimethylbenzothioate (3an)**

According to the general procedure **A** (0.2 mmol scale), product **3an** was isolated in 57% yield (29.3 mg) as a colorless oil from (3,5-dimethylphenyl)(1H-imidazol-1-yl)methanone **1an** (80.0 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H), 7.24 (s, 1H), 2.42 (s, 3H), 2.40 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.8, 139.7, 138.5, 136.8, 135.2, 135.0, 130.1, 125.2, 124.1, 21.4, 21.3.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[15]



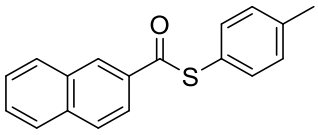
***S*-(*p*-tolyl) 2,4-dimethoxybenzothioate (3ao)**

According to the general procedure **A** (0.2 mmol scale), product **3ao** was isolated in 71% yield (40.9 mg) as a colorless oil from (2,4-dimethoxyphenyl)(1H-imidazol-1-yl)methanone **1ao** (92.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 6.54 (dd, J = 8.8, 2.3 Hz, 1H), 6.50 (d, J = 2.3 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 187.9, 164.7, 160.5, 139.3, 135.1, 132.2, 129.9, 125.6, 119.3, 105.2, 98.7, 55.8, 55.6, 21.4.

HRMS (ESI): Calcd for $C_{16}H_{17}O_3S$ [M+H]: 289.0893, found: 289.0893.



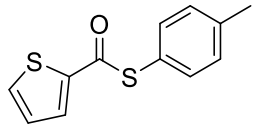
***S*-(*p*-tolyl) naphthalene-2-carbothioate (3ap)**

According to the general procedure **A** (0.2 mmol scale), product **3ap** was isolated in 37% yield (20.5 mg) as a white solid from (1H-imidazol-1-yl)(naphthalen-2-yl)methanone **1ap** (88.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

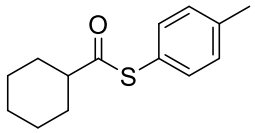
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 1.8 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.94 – 7.87 (m, 2H), 7.65 – 7.55(m, 2H), 7.48 – 7.42 (m, 2H), 7.30 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 139.9, 135.9, 135.1, 134.1, 132.5, 130.2, 129.6, 129.0, 128.63,

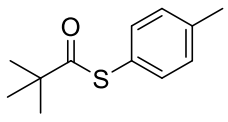
128.60, 127.9, 127.0, 123.9, 123.3, 21.4.
^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[15]



***S*-(*p*-tolyl) thiophene-2-carbothioate (3aq)**
According to the general procedure **A** (0.2 mmol scale), product **3aq** was isolated in 69% yield (32.4 mg) as a white solid from (1H-imidazol-1-yl)(thiophen-2-yl)methanone **1aq** (71.2 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 3.8, 1.2 Hz, 1H), 7.68 (dd, J = 4.9, 1.2 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.18 (dd, J = 5.0, 3.8 Hz, 1H), 2.43 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 182.5, 141.5, 140.0, 135.0, 133.1, 131.5, 130.1, 128.0, 123.4, 21.4.
^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]

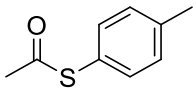


***S*-(*p*-tolyl) cyclohexanecarbothioate (3ar)**
According to the general procedure **A** (0.2 mmol scale), product **3ar** was isolated in 70% yield (32.7 mg) as a white solid from cyclohexyl(1H-imidazol-1-yl)methanone **1ar** (71.2 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.21 (d, J = 7.9 Hz, 2H), 2.60 (tt, J = 11.4, 3.6 Hz, 1H), 2.37 (s, 3H), 2.04 – 1.95 (m, 2H), 1.82 (dt, J = 13.2, 3.8 Hz, 2H), 1.72 – 1.64 (m, 1H), 1.59 – 1.46 (m, 2H), 1.38 – 1.21 (m, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 139.4, 134.6, 129.9, 124.4, 52.4, 29.6, 25.6, 25.5, 21.3.
^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[4]



***S*-(*p*-tolyl) 2,2-dimethylpropanethioate (3as)**
According to the general procedure **A** (0.2 mmol scale), product **3as** was isolated in 66% yield (27.3 mg) as a white solid from 1-(1H-imidazol-1-yl)-2,2-dimethylpropan-1-one **1as** (60.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.22 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H), 1.32 (s, 9H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 139.3, 134.9, 129.9, 124.6, 46.9, 27.5, 21.3.
^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature

data.[17]



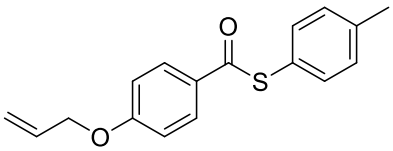
***S*-(*p*-tolyl) ethanethioate (3at)**

According to the general procedure **A** (0.2 mmol scale), product **3at** was isolated in 59% yield (19.7 mg) as colorless oil from 1-(1H-imidazol-1-yl)ethan-1-one **1at** (44.0 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 194.6, 139.7, 134.4, 130.1, 124.5, 30.1, 21.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[18]



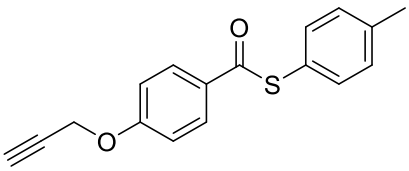
S-(p-tolyl) 4-(allyloxy)benzothioate (3au)

According to the general procedure **B** (0.2 mmol scale), product **3au** was isolated in 72% yield (34 mg) as a colorless oil from 3-(allyloxy)benzoic acid **1au'** (71.2 mg, 0.4 mmol, 2.0 equiv), CDI (64.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.5 Hz, 2H), 6.08 (ddd, J = 16.1, 10.7, 5.3 Hz, 1H), 5.47 (d, J = 17.3 Hz, 1H), 5.36 (d, J = 10.5 Hz, 1H), 4.64 (d, J = 5.3 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 162.9, 139.6, 135.1, 132.4, 130.0, 129.7 (2C), 124.1, 118.2, 114.6, 69.0, 21.4.

HRMS (ESI): Calcd for $C_{17}H_{17}O_2S$ [M+H]: 285.0944, found: 285.0942.



S-(p-tolyl) 4-(prop-2-yn-1-yloxy)benzothioate (3av)

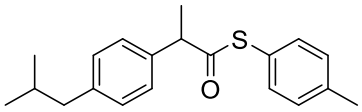
According to the general procedure **B** (0.2 mmol scale), product **3av** was isolated in 65% yield (35 mg) as a colorless oil from (1H-imidazol-1-yl)(4-(prop-2-yn-1-yloxy)phenyl)methanone **1av'** (90.4 mg, 0.4 mmol, 2.0 equiv), CDI (70.5 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.5 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 4.77 (d, J = 2.5 Hz, 2H), 2.57 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 161.7, 139.7, 135.1, 130.3, 130.1, 129.6, 124.0, 114.8, 77.7,

76.3, 56.0, 21.4.

HRMS (ESI): Calcd for $C_{17}H_{15}O_2S$ [M+H]: 283.0787, found: 283.0783.



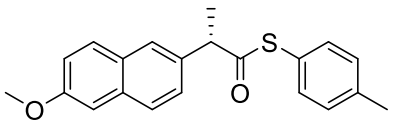
***S*-(p-tolyl) 2-(4-isobutylphenyl)propanethioate (3aw)**

According to the general procedure **B** (0.2 mmol scale), product **3aw** was isolated in 79% yield (49.1 mg) as a colorless oil from 2-(4-isobutylphenyl)propanoic acid **1aw'** (82.4 mg, 0.4 mmol, 2.0 equiv), CDI (64.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol 1.0 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 4H), 7.16 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 3.95 (q, J = 7.1 Hz, 1H), 2.46 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.86 (dp, J = 13.5, 6.8 Hz, 1H), 1.55 (d, J = 7.1 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 141.1, 139.5, 136.8, 134.4, 129.9, 129.5, 127.8, 124.6, 53.7, 45.1, 30.2, 22.5, 21.3, 18.7.

HRMS (ESI): Calcd for $C_{20}H_{25}OS$ [M+H]: 313.1622, found: 313.1621.



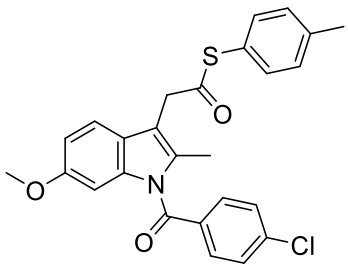
***S*-(*p*-tolyl) (*S*)-2-(6-methoxynaphthalen-2-yl)propanethioate (3ax)**

According to the general procedure **B** (0.2 mmol scale), product **3ax** was isolated in 65% yield (43.7 mg) as a white solid from (S)-2-(6-methoxynaphthalen-2-yl)propanoic acid **1ax'** (92.0 mg, 0.4 mmol, 2.0 equiv), CDI (64.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 3H), 7.46 (dd, J = 8.6, 1.8 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.20 – 7.13 (m, 4H), 4.14 (q, J = 7.1 Hz, 1H), 3.93 (s, 3H), 2.36 (s, 3H), 1.66 (d, J = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 157.8, 139.5, 134.8, 134.4, 134.0, 129.9, 129.4, 129.0, 127.3, 126.8, 126.5, 124.5, 119.1, 105.7, 55.4, 54.0, 21.3, 18.7.

HRMS (ESI): Calcd for $C_{21}H_{21}O_2S$ [M+H]: 337.1257, found: 337.1273.



***S*-(*p*-tolyl) 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl) ethanethioate (3ay)**

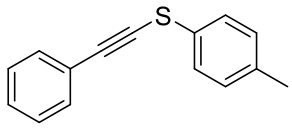
According to the general procedure **B** (0.2 mmol scale), product **3ay** was isolated in 81% yield (75.4 mg) as a yellow solid from 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)acetic acid

1ay' (142.8 mg, 0.4 mmol, 2.0 equiv), CDI (64.8 mg, 0.4 mmol, 2.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (35.6 mg, 0.2 mmol, 1.0 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.50 – 7.45 (m, 2H), 7.25 (d, J = 6.0 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.00 (d, J = 2.5 Hz, 1H), 6.91 (d, J = 9.0 Hz, 1H), 6.70 (dd, J = 9.0, 2.5 Hz, 1H), 3.94 (s, 2H), 3.85 (s, 3H), 2.44 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 168.3, 156.2, 139.8, 139.4, 136.8, 134.4, 133.8, 131.3, 130.9, 130.6, 130.1, 129.2, 124.1, 115.0, 111.96, 111.94, 101.2, 55.8, 39.1, 21.3, 13.6.

HRMS (ESI): Calcd for $C_{26}H_{23}ClNO_3S$ [M+H]: 464.1082, found: 464.1102.



(phenylethynyl)(*p*-tolyl)sulfane (7a)

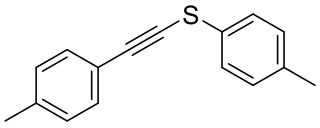
According to the general procedure **C** (0.2 mmol scale), product **7a** was isolated in 48% yield (10.8 mg) as a white solid from (iodoethynyl)benzene **6a** (45.6 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

Alternatively, product **7a** could be isolated in 51% yield (114.8 mg) from (iodoethynyl)benzene **6a** (0.46 g, 2 mmol, 1.0 equiv), sodium 4-methylbenzenesulfinate **2a** (0.53 g, 3 mmol, 1.5 equiv), P(4-F-C_6H_4)$_3$ (5 mmol, 1.58 g, 2.5 equiv) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (0.04 mmol, 25 mg, 2.0 mol %) in DCE (40 mL).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.16 (d, J = 7.9 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 131.7, 130.1, 129.2, 128.5, 128.4, 126.6, 123.1, 97.3, 76.2, 21.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[19]



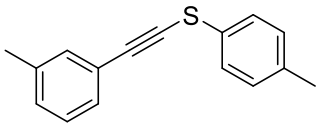
***p*-tolyl(*p*-tolylethynyl)sulfane (7b)**

According to the general procedure **A** (0.2 mmol scale), product **7b** was isolated in 49% yield (23.4 mg) as a white solid from 1-(iodoethynyl)-4-methylbenzene **6b** (48.2 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 4H), 7.16 (t, J = 8.1 Hz, 4H), 2.37 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 136.5, 131.8, 130.0, 129.5, 129.2, 126.5, 120.0, 97.5, 75.1, 21.6, 21.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[20]



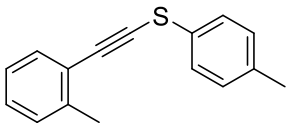
***p*-tolyl(*m*-tolylethynyl)sulfane (7c)**

According to the general procedure **A** (0.2 mmol scale), product **7c** was isolated in 43% yield (20.3 mg) as a colorless oil from 1-(iodoethynyl)-3-methylbenzene **6c** (48.2 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.16 (m, 3H), 2.35 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 136.6, 132.3, 130.0, 129.4, 129.3, 128.8, 128.3, 126.56, 122.9, 97.5, 75.7, 21.2, 21.0.

HRMS (ESI): Calcd for $C_{16}H_{15}S$ [M+H]: 239.0889, found: 239.0884.



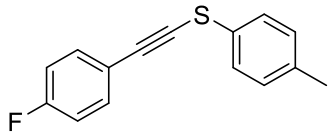
***p*-tolyl(*o*-tolylethynyl)sulfane (7d)**

According to the general procedure **A** (0.2 mmol scale), product **7d** was isolated in 65% yield (31 mg) as a white solid from 1-(iodoethynyl)-2-methylbenzene **6d** (48.2 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.44 – 7.40 (m, 2H), 7.24 (m, 2H), 7.20 – 7.15 (m, 3H), 2.49 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 140.3, 136.6, 132.0, 130.1, 129.5（2C）, 128.5, 126.5, 125.6, 122.9, 96.3, 79.6, 21.0, 20.9.

HRMS (ESI): Calcd for $C_{16}H_{15}S$ [M+H]: 239.0889, found: 239.0891.



((4-fluorophenyl)ethynyl)(*p*-tolyl)sulfane (7e)

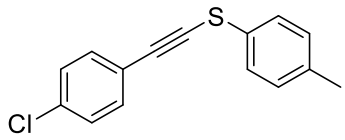
According to the general procedure **A** (0.2 mmol scale), product **7e** was isolated in 57% yield (27.4 mg) as a white solid from 1-fluoro-4-(iodoethynyl)benzene **6e** (49.2 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.09 – 7.03 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 (d, J_1 = 250.2 Hz), 136.8 , 133.8 (d, J_3= 8.4 Hz), 130.1 , 129.1 , 126.7 , 119.2 (d, J_4 = 3.6 Hz), 115.7 (d, J_2 = 22.2 Hz), 96.0 , 76.0 (d, J = 1.7 Hz), 21.0 .

^{19}F NMR (470 MHz, $CDCl_3$) δ -110.14.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[20]



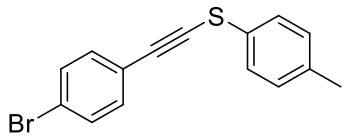
((4-chlorophenyl)ethynyl)(*p*-tolyl)sulfane (7f)

According to the general procedure **A** (0.2 mmol scale), product **7f** was isolated in 41% yield (21 mg) as a yellow solid from 1-chloro-4-(iodoethynyl)benzene **6f** (52.2 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 134.5, 132.8, 130.1, 128.8, 128.7, 126.8, 121.6, 95.9, 77.6, 21.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[20]



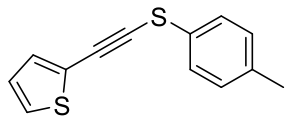
((4-bromophenyl)ethynyl)(*p*-tolyl)sulfane (7g)

According to the general procedure **A** (0.2 mmol scale), product **7g** was isolated in 50% yield (30.4 mg) as a yellow solid from 1-bromo-4-(iodoethynyl)benzene **6g** (61.0 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.36 (dd, J = 14.4, 8.4 Hz, 4H), 7.17 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 133.0, 131.7, 130.1, 128.8, 126.8, 122.7, 122.0, 96.0, 77.9, 21.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[20]



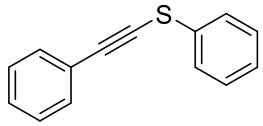
2-((*p*-tolylthio)ethynyl)thiophene (7h)

According to the general procedure **A** (0.2 mmol scale), product **7h** was isolated in 34% yield (15.7 mg) as a yellow oil from 2-(iodoethynyl)thiophene **6h** (46.8 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methylbenzenesulfinate **2a** (53.4 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.16 (d, J = 7.9 Hz, 2H), 7.01 (dd, J = 5.2, 3.7 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.7, 130.1, 129.1, 128.5, 127.1, 126.7, 123.2, 89.9, 80.7, 21.0.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[21]



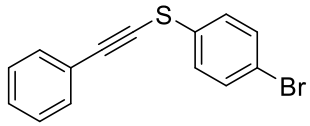
phenyl(phenylethynyl)sulfane (7i)

According to the general procedure **A** (0.2 mmol scale), product **7i** was isolated in 42% yield (17.8 mg) as a yellow oil from (iodoethynyl)benzene **6a** (45.6 mg, 0.2 mmol, 1.0 equiv) and sodium benzenesulfinate **2g** (49.2 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 5H), 7.38 – 7.33 (m, 4H), 7.26 – 7.22 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 131.8, 129.3, 128.7, 128.4, 126.5, 126.2, 122.9, 97.9, 75.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[22]



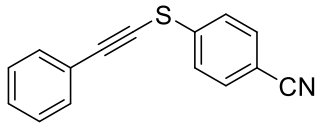
(4-bromophenyl)(phenylethynyl)sulfane (7j)

According to the general procedure **A** (0.2 mmol scale), product **7j** was isolated in 40% yield (23.3 mg) as a yellow solid from (iodoethynyl)benzene **6a** (45.6 mg, 0.2 mmol, 1.0 equiv) and sodium 4-bromobenzenesulfinate **2d** (72.6 mg, 0.3 mmol, 1.5 equiv).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 5H), 7.38 – 7.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 131.8, 129.4, 128.9, 128.5, 127.7, 122.6, 120.3, 98.6, 74.6.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[21]



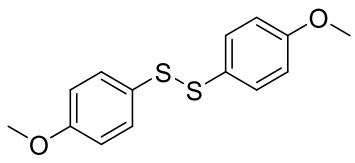
4-((phenylethynyl)thio)benzonitrile (7k)

According to the general procedure **A** (0.2 mmol scale), product **7k** was isolated in 45% yield (21.3 mg) as a colorless oil from (iodoethynyl)benzene **6a** (45.6 mg, 0.2 mmol, 1.0 equiv) and sodium 4-cyanobenzenesulfinate **2f** (56.6 mg, 0.3 mmol, 1.5 equiv)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.58 – 7.51 (m, 4H), 7.41 – 7.35 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 132.6, 132.0, 129.4, 128.6, 125.9, 122.1, 118.5, 109.8, 100.4, 72.6.

HRMS (ESI): Calcd for $C_{15}H_{10}NS$ [M+H]: 236.0528, found: 250.0523.



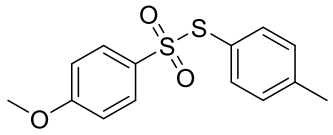
1,2-bis(4-methoxyphenyl)disulfane（5d）

According to the general procedure **A** (0.2 mmol scale), no desired product **7l** was obtained (iodoethynyl)benzene **6a** (45.6 mg, 0.2 mmol, 1.0 equiv) and sodium 4-methoxybenzenesulfinate **2h** (56.6 mg, 0.3 mmol, 1.5 equiv). Instead, **5d** was isolated in 44% yield (18.4 mg) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 6.87 – 6.80 (m, 4H), 3.80 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 132.7, 128.5, 114.6, 55.4.

^{1}H NMR and ^{13}C NMR spectra for this compound are consistent with previously reported literature data.[23]



***S*-(*p*-tolyl) 4-methoxybenzenesulfonothioate (5c)**

Was prepared according to the literature and [24] ; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.92 – 6.87 (m, 2H), 3.90 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.5, 142.0, 136.5, 135.1, 130.2, 129.9, 124.8, 113.8, 55.7, 21.5.

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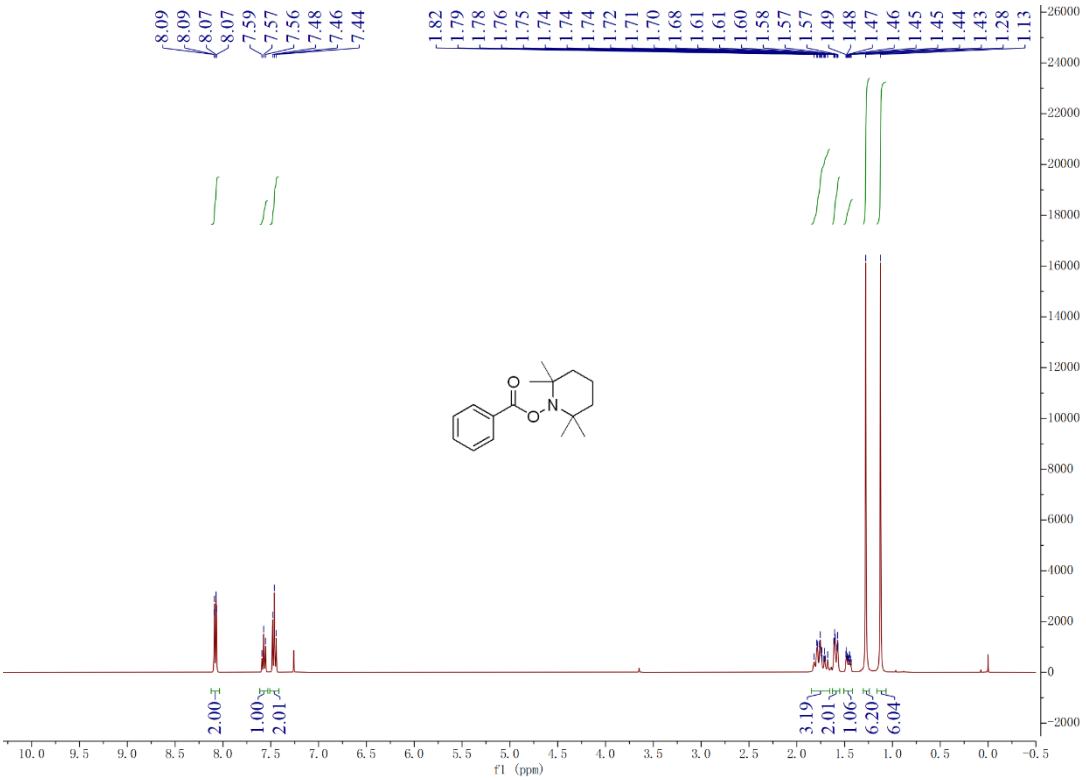
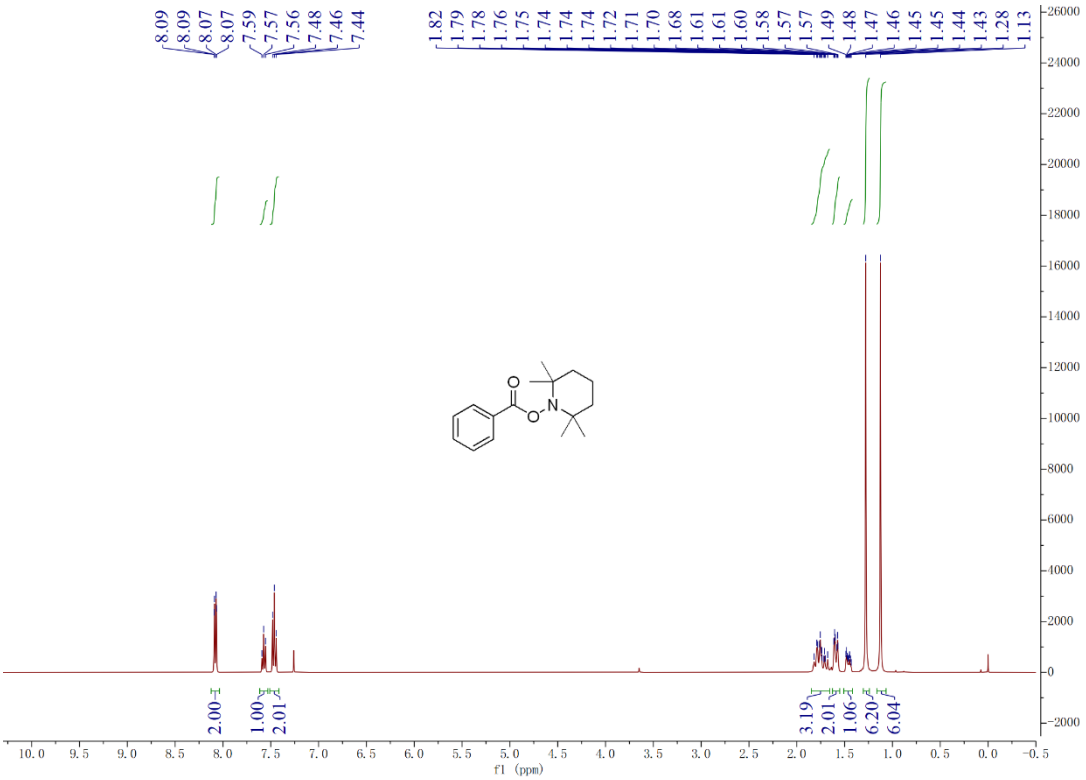
7. NMR Spectra

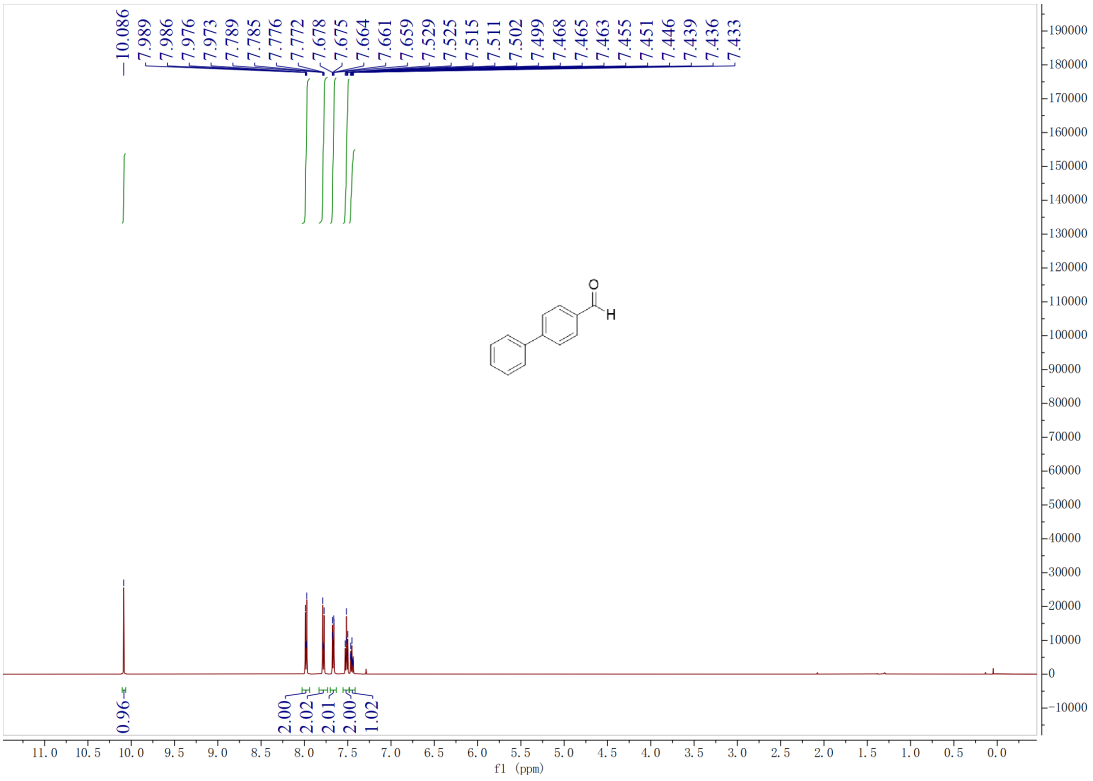
4a, ^{1}H NMR (400 MHz, $CDCl_3$)



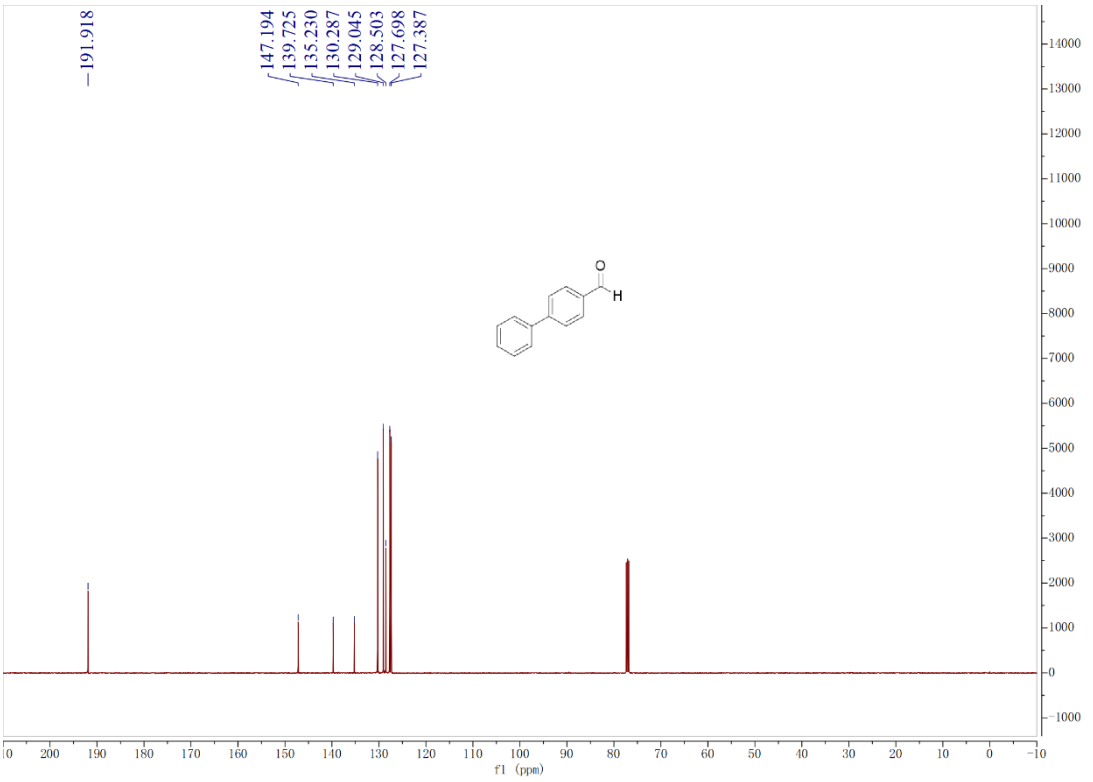
4a, ^{13}C NMR (100 MHz, $CDCl_3$)



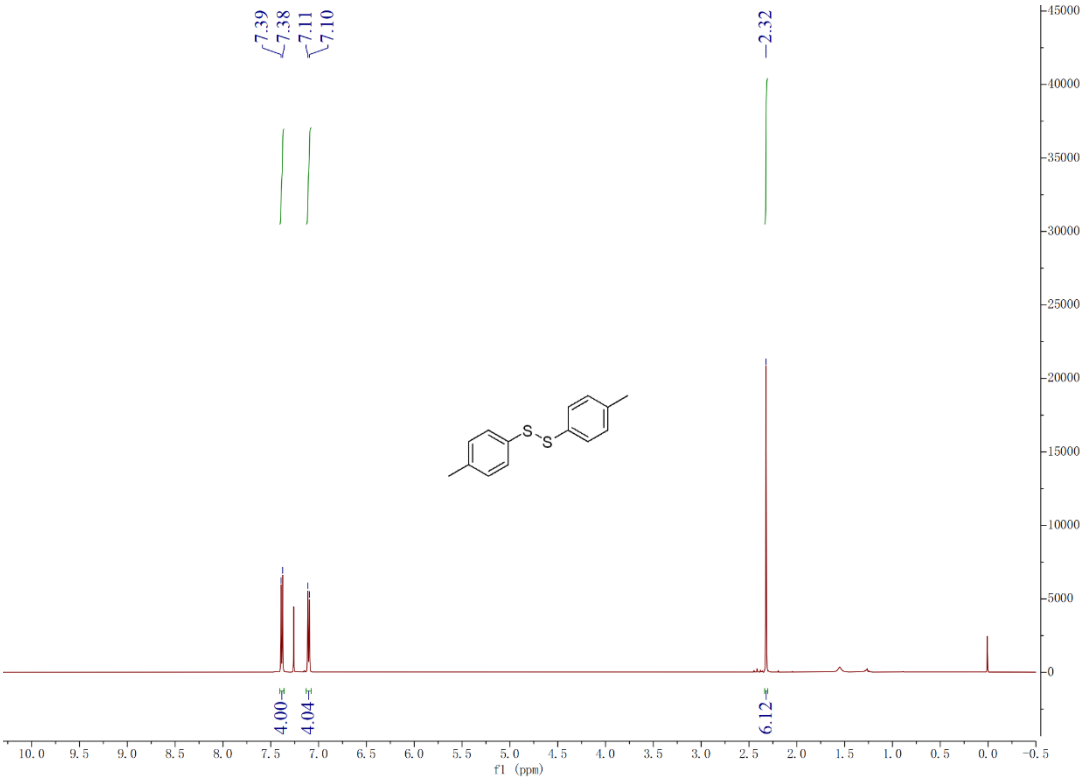
3az, ^{1}H NMR (500 MHz, $CDCl_3$)



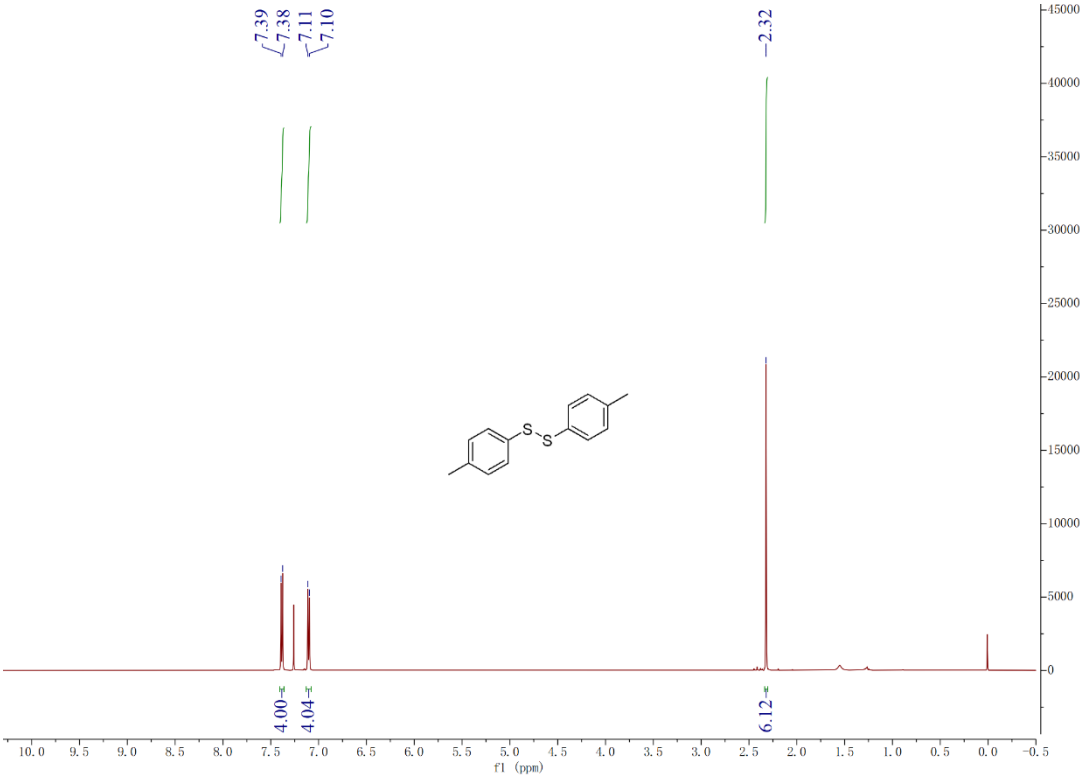
3az, ^{13}C NMR (125 MHz, $CDCl_3$)



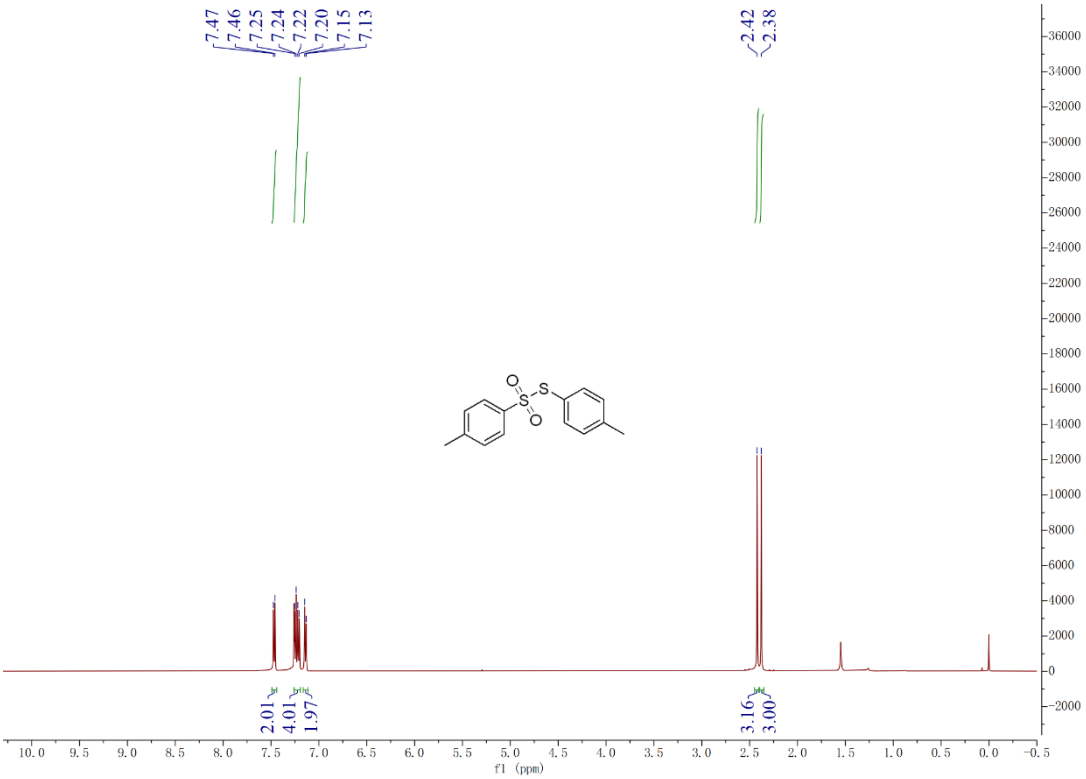
5a, ^{1}H NMR (500 MHz, $CDCl_3$)



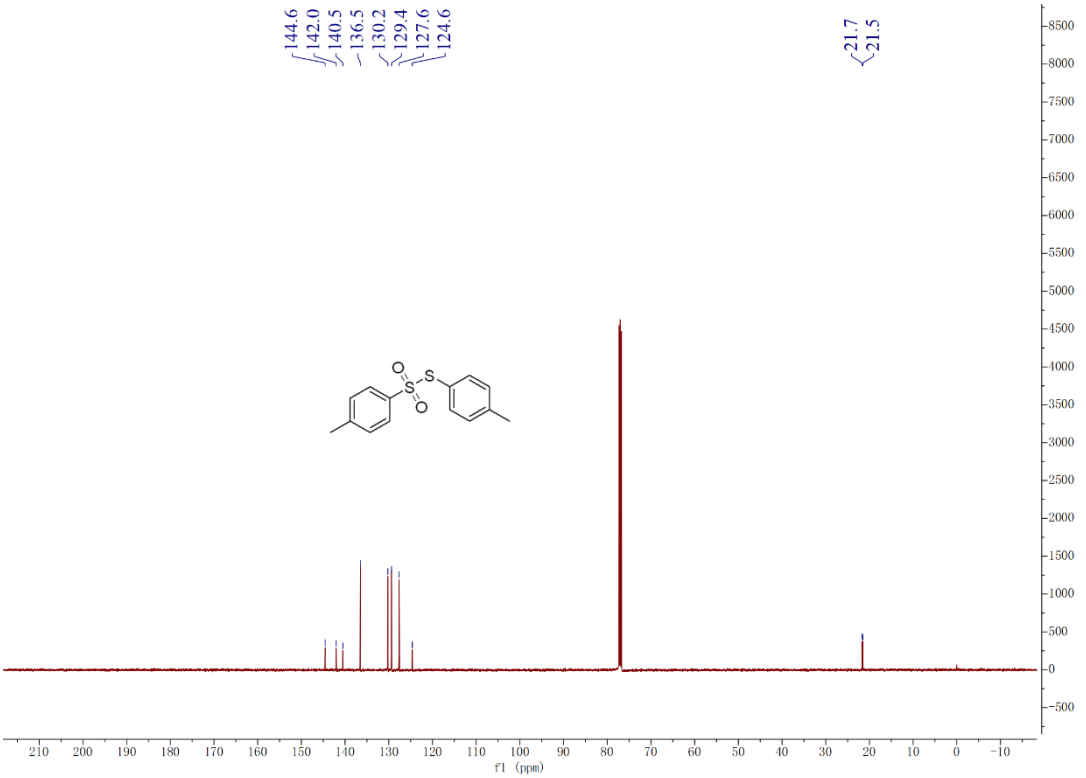
5a, ^{13}C NMR (125 MHz, $CDCl_3$)



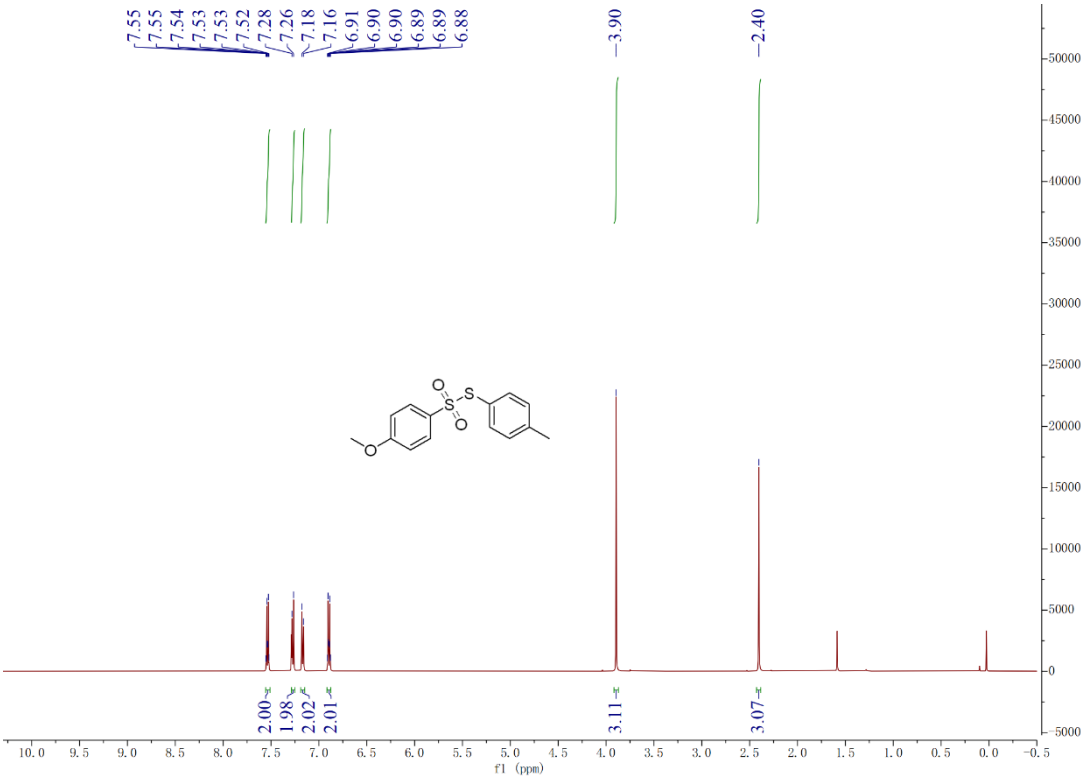
5b, ^{1}H NMR (500 MHz, $CDCl_3$)



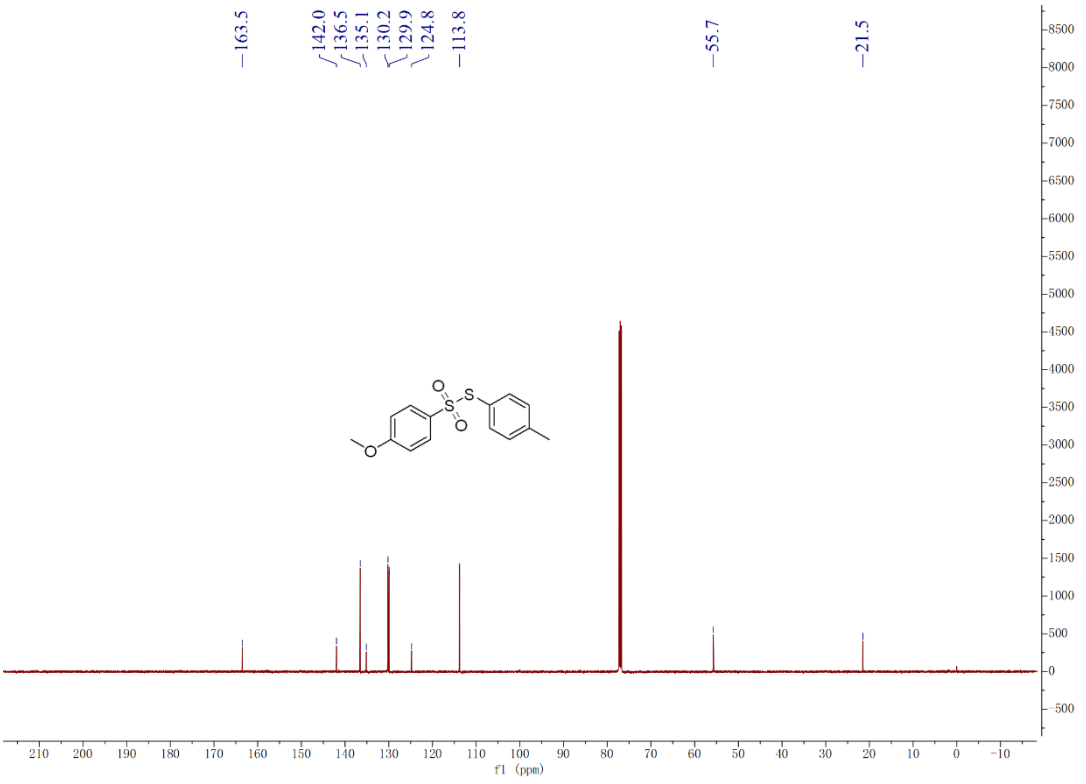
5b, ^{13}C NMR (125 MHz, $CDCl_3$)



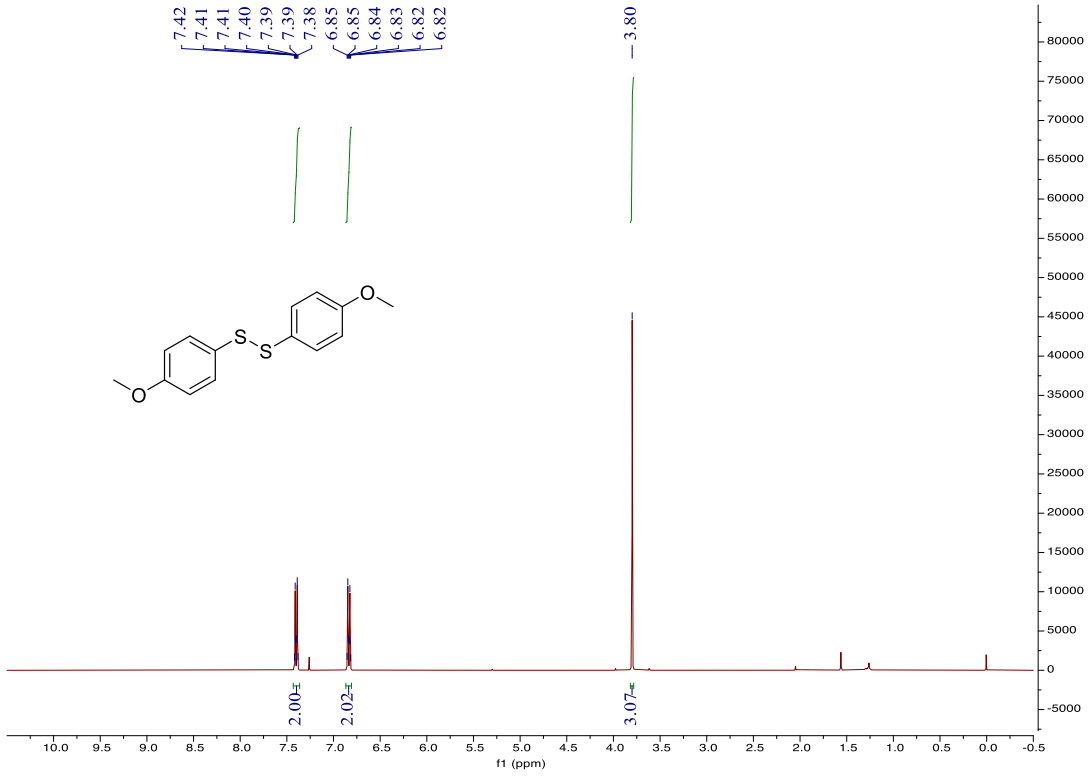
5c, ^{1}H NMR (500 MHz, $CDCl_3$)



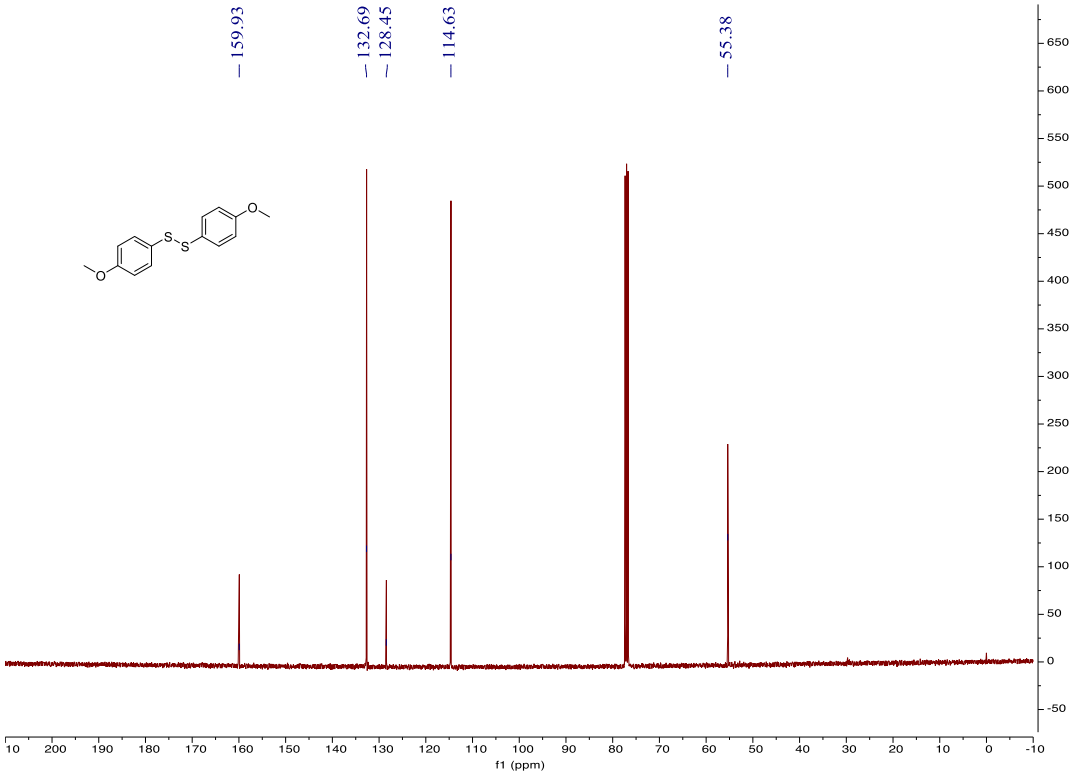
5c, ^{13}C NMR (125 MHz, $CDCl_3$)



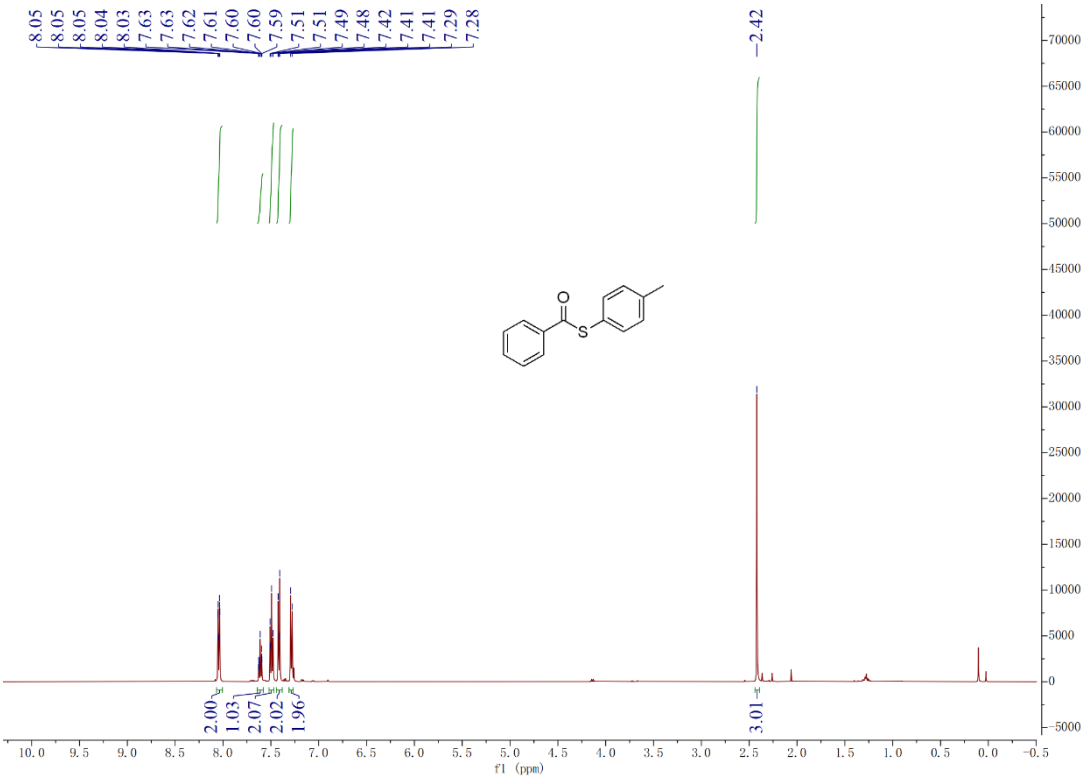
5d, ^{1}H NMR (400 MHz, $CDCl_3$)



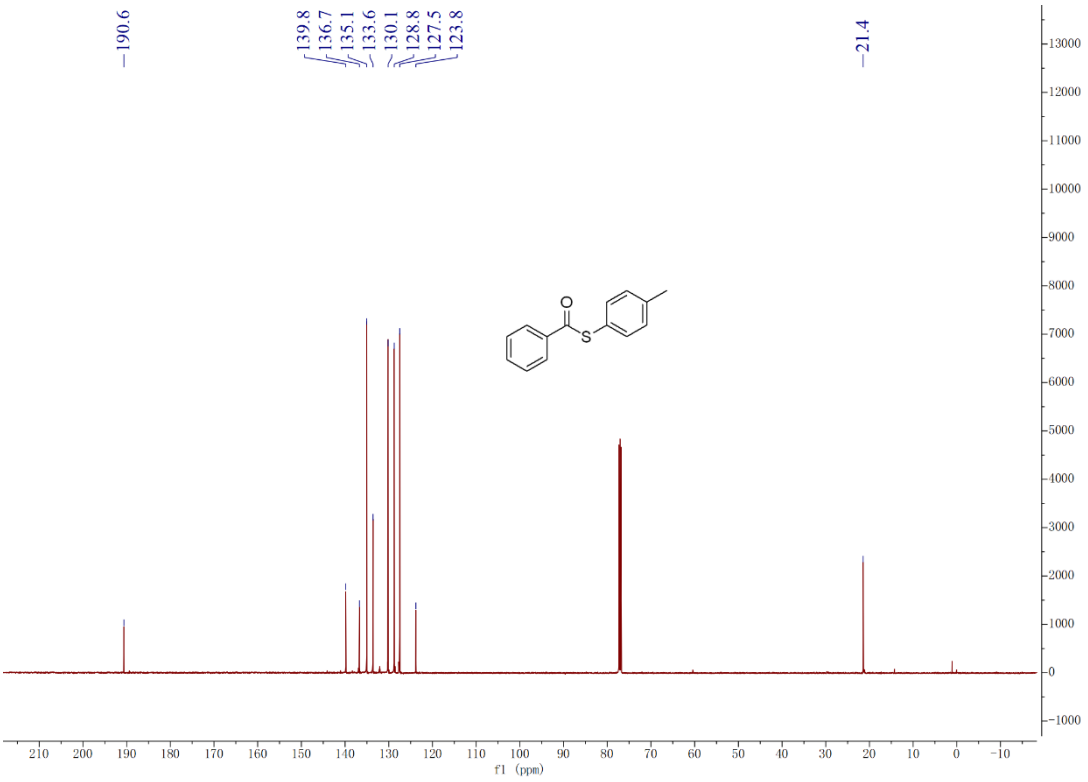
5d, ^{13}C NMR (100 MHz, $CDCl_3$)



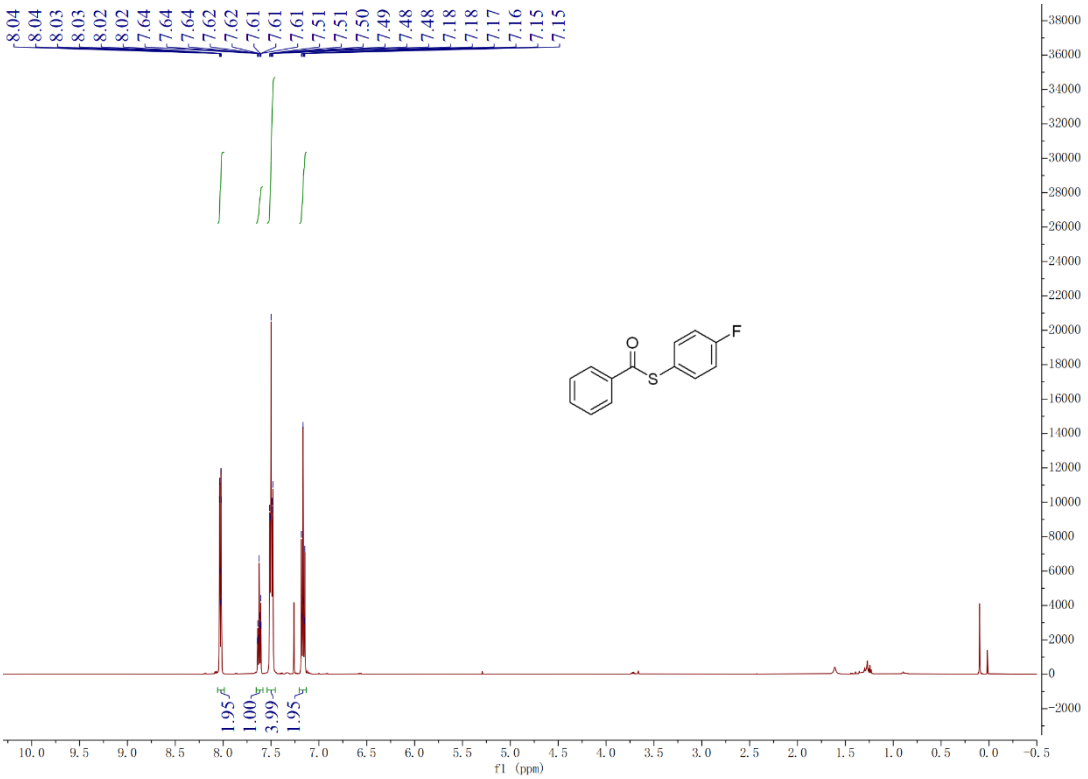
3a, ^{1}H NMR (500 MHz, $CDCl_3$)



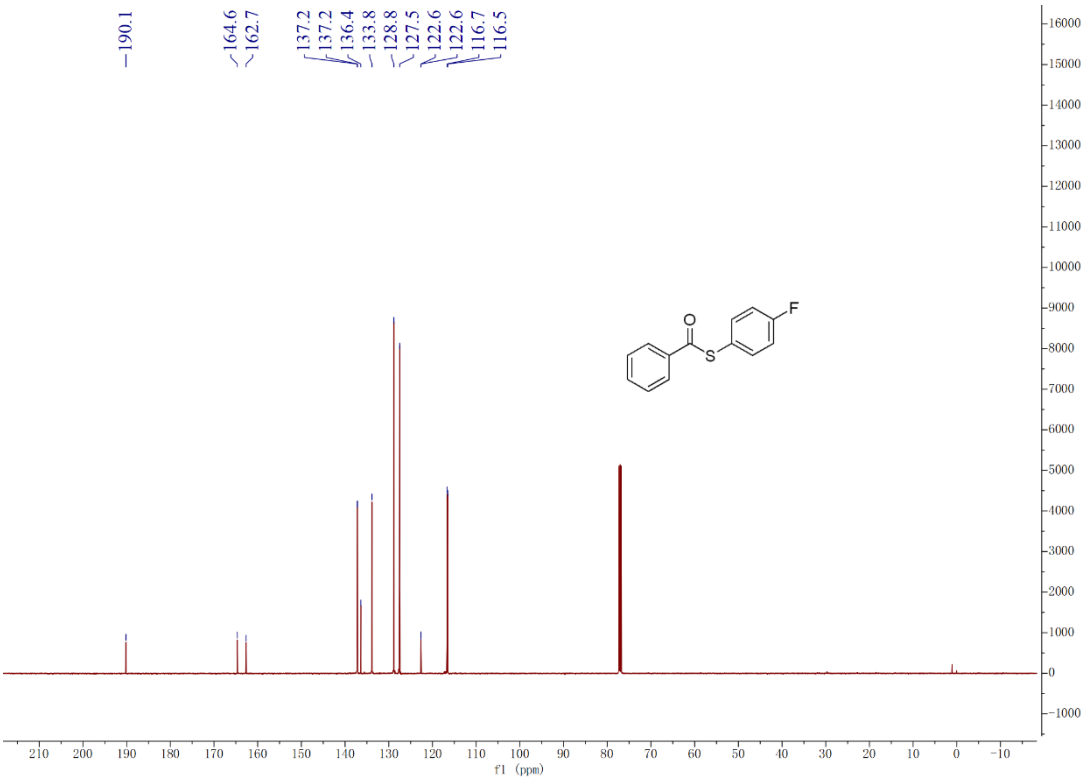
3a, ^{13}C NMR (125 MHz, $CDCl_3$)



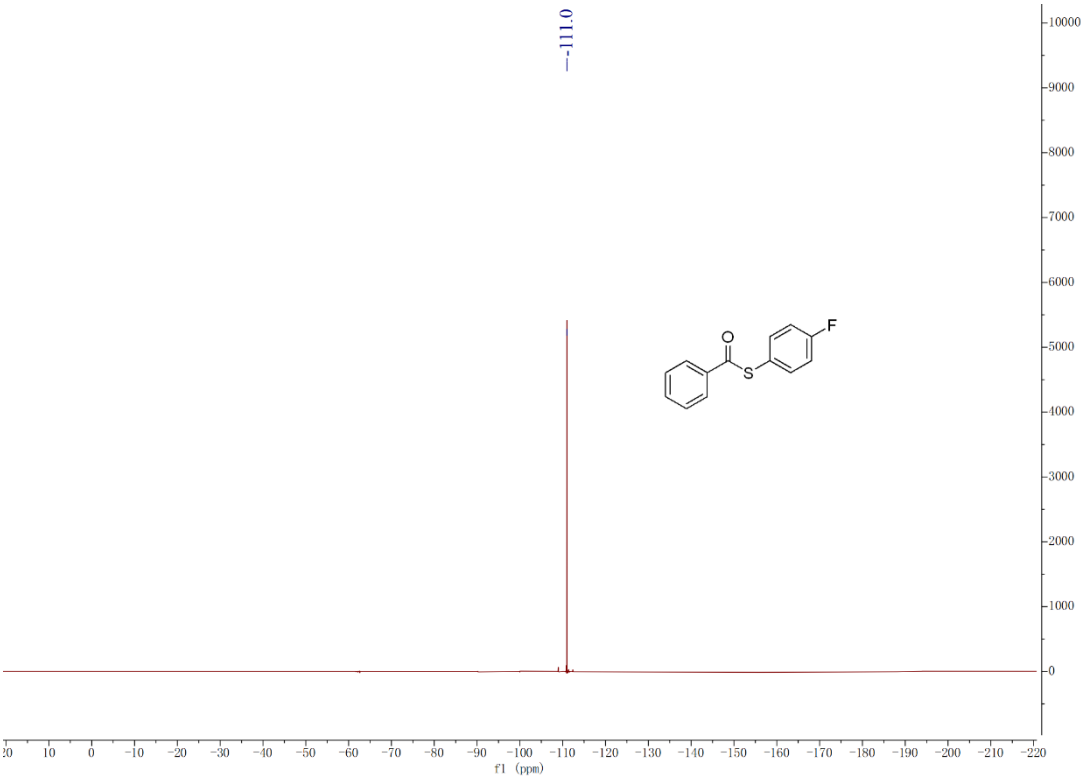
3b, ^{1}H NMR (500 MHz, $CDCl_3$)



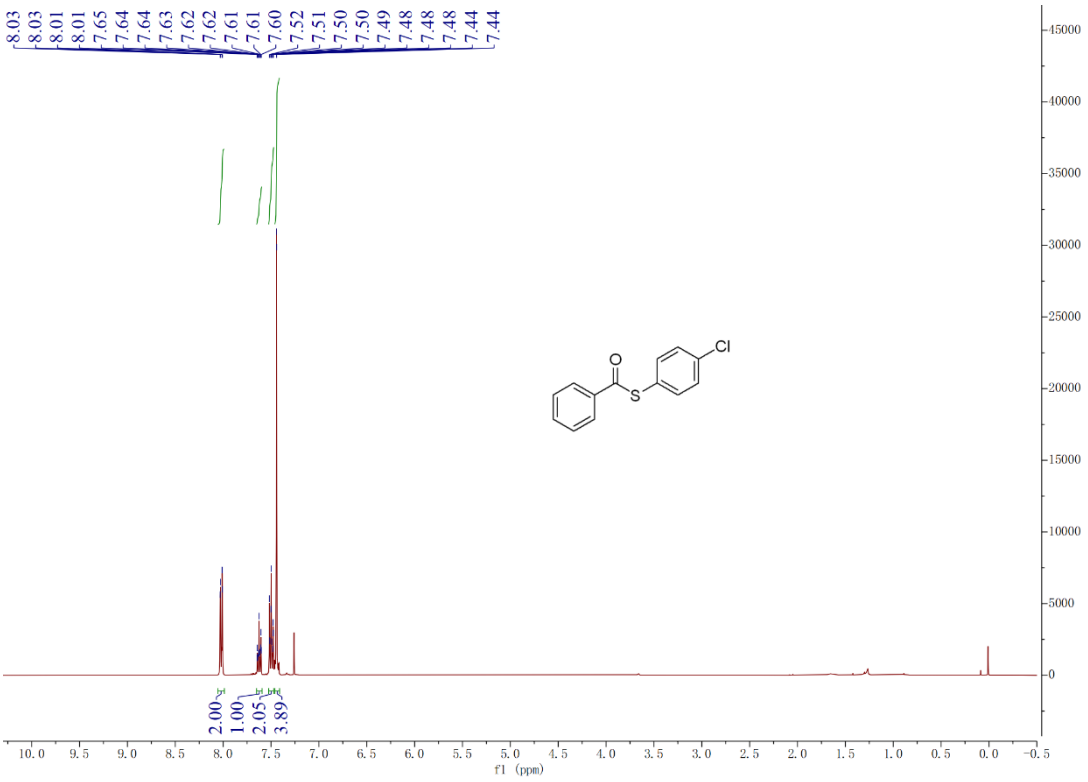
3b, ^{13}C NMR (125 MHz, $CDCl_3$)



3b, ^{19}F NMR (470 MHz, $CDCl_3$)

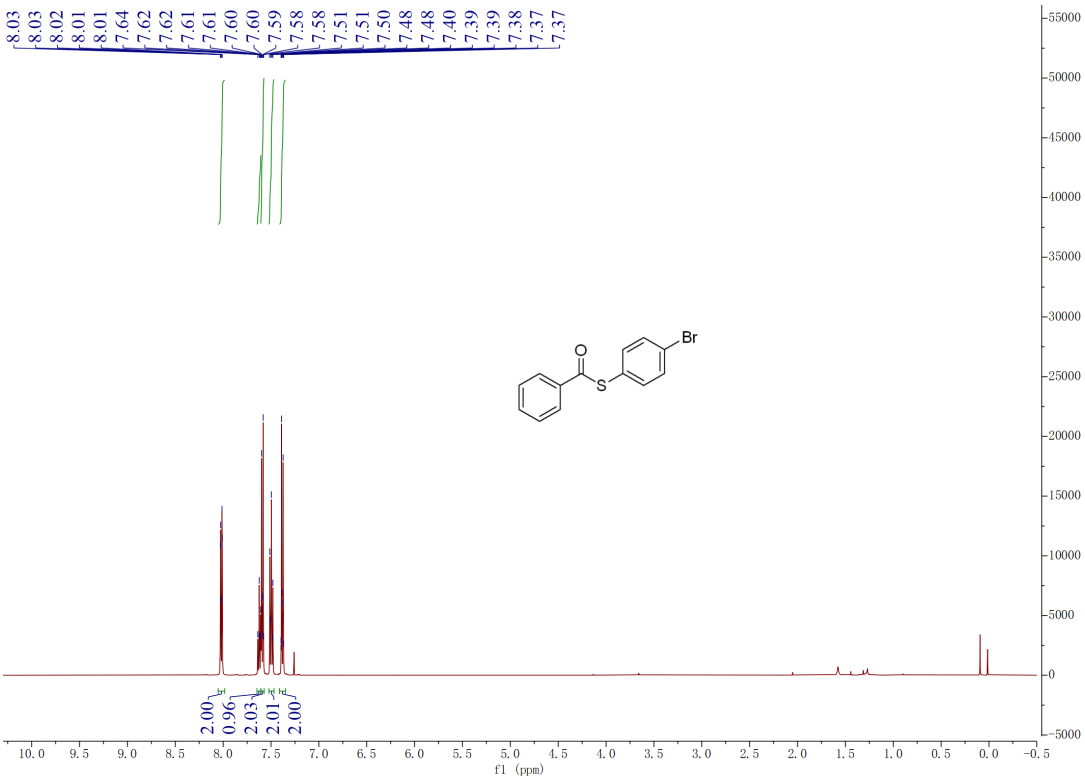


3c, ^{1}H NMR (500 MHz, $CDCl_3$)

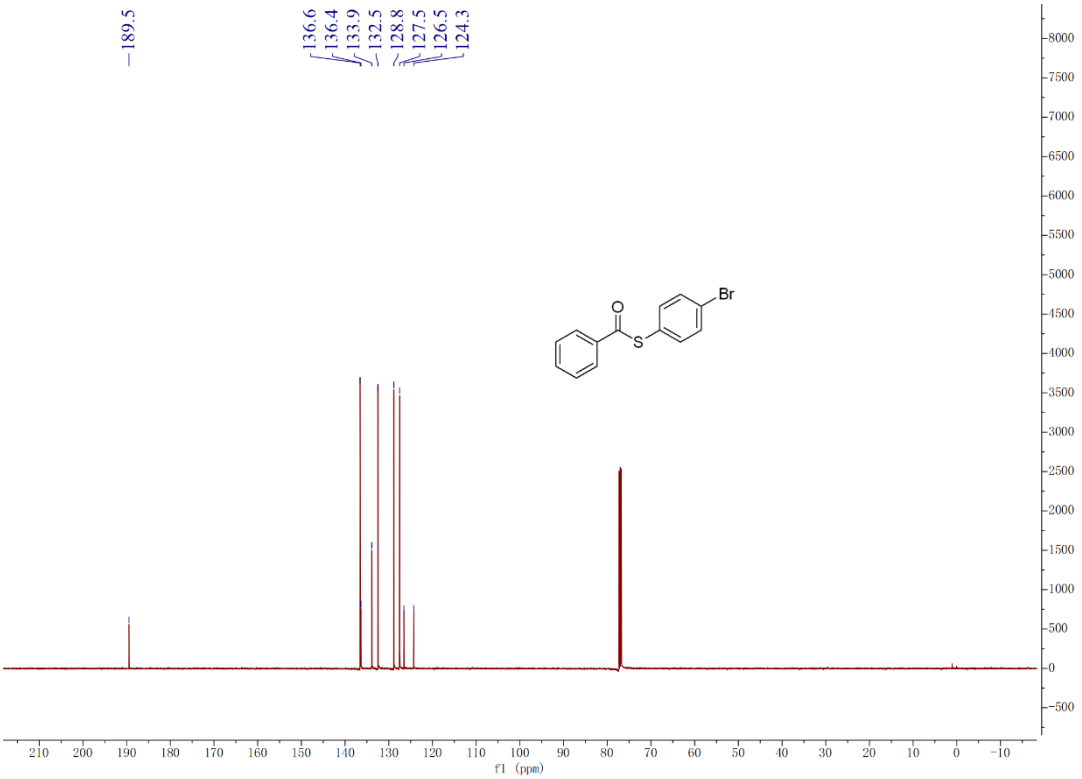


3c, ^{13}C NMR (125 MHz, $CDCl_3$)

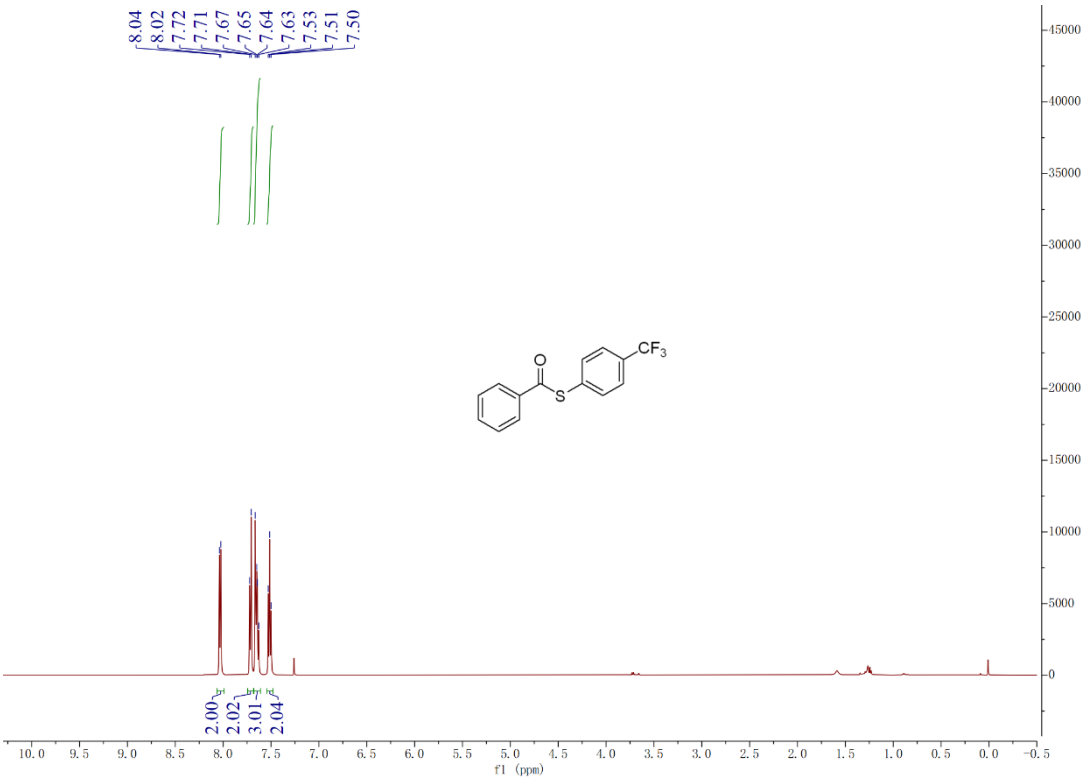
3d, ^{1}H NMR (500 MHz, $CDCl_3$)



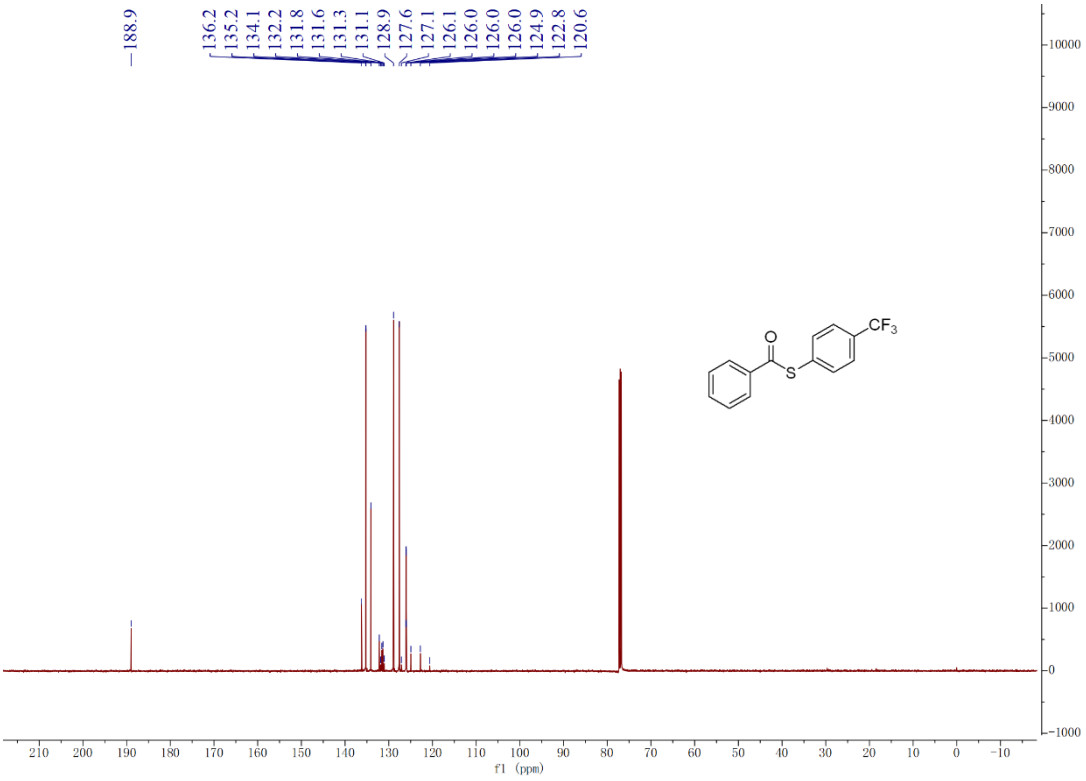
3d, ^{13}C NMR (125 MHz, $CDCl_3$)



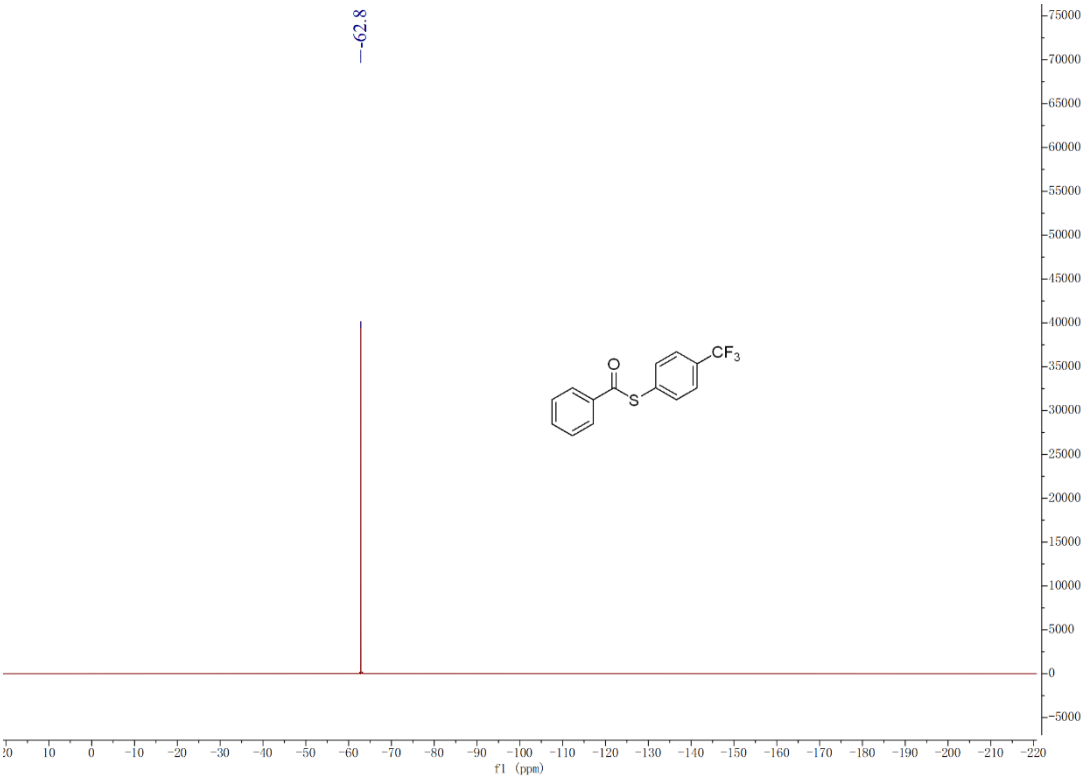
3e, ^{1}H NMR (500 MHz, $CDCl_3$)



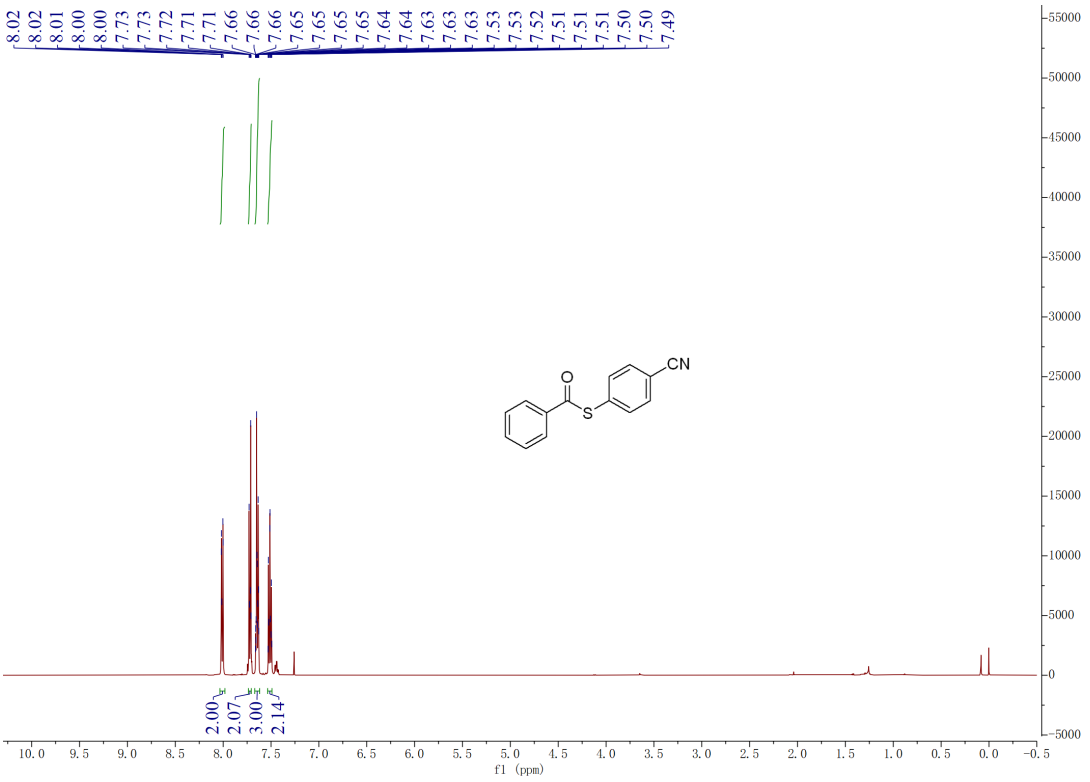
3e, ^{13}C NMR (125 MHz, $CDCl_3$)



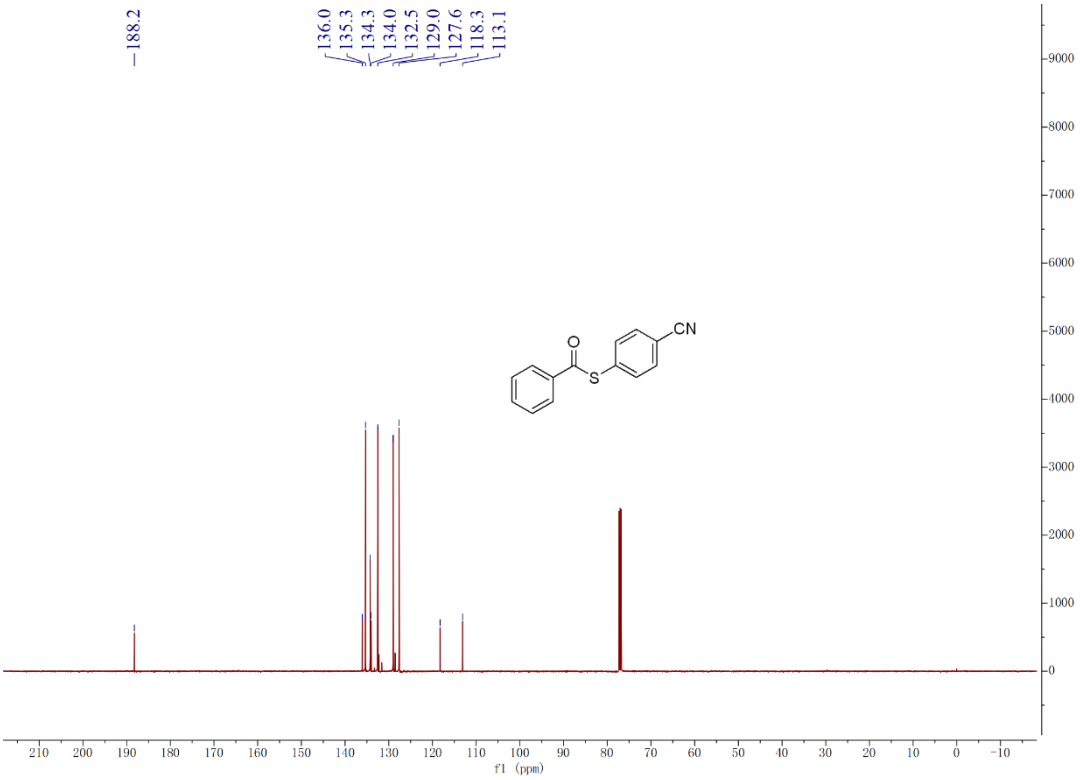
3e, ^{19}F NMR (470 MHz, $CDCl_3$)



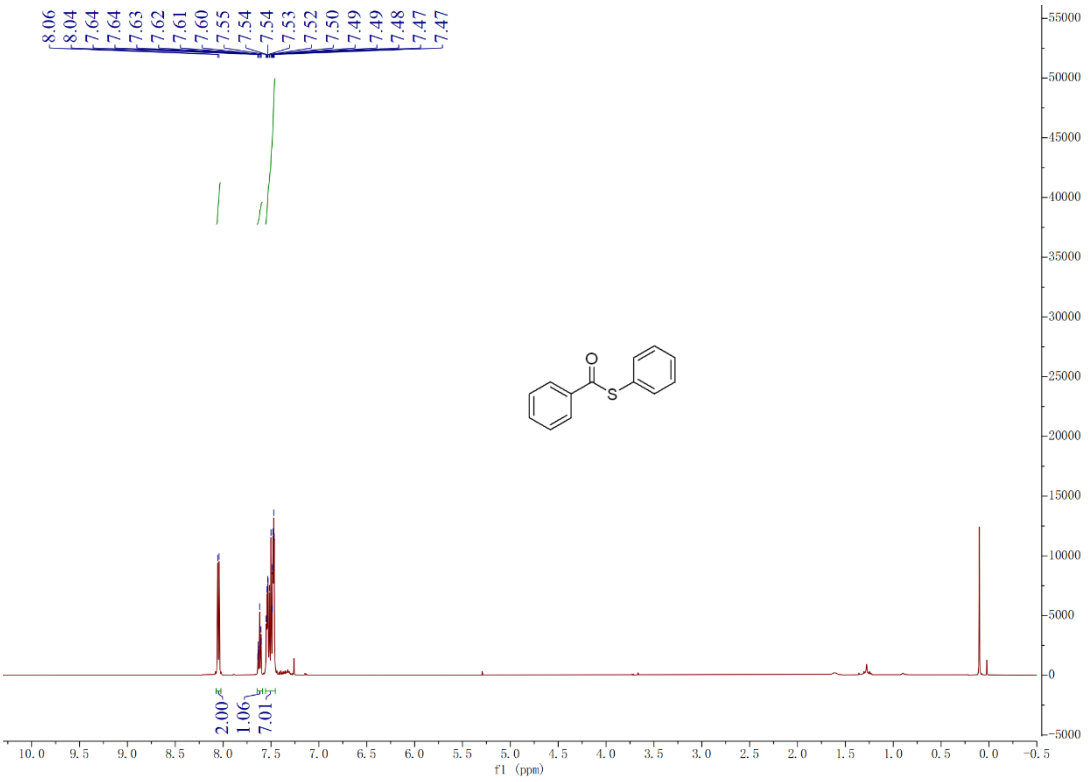
3f, ^{1}H NMR (500 MHz, $CDCl_3$)



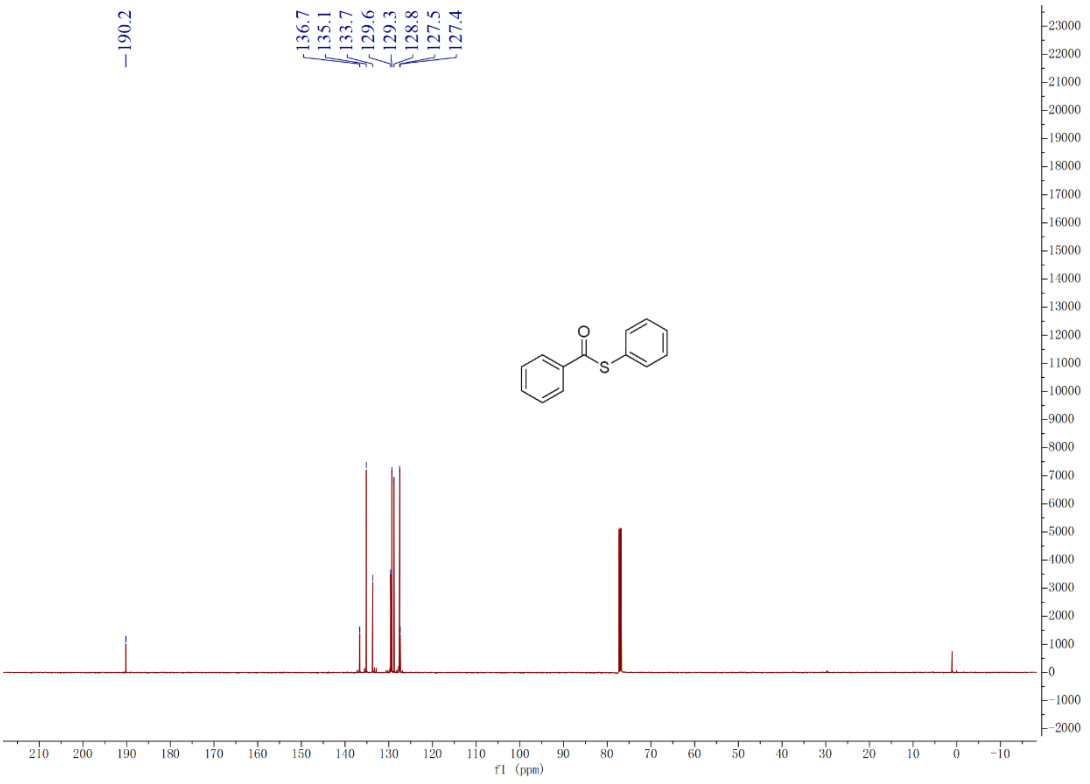
3f, ^{13}C NMR (125 MHz, $CDCl_3$)



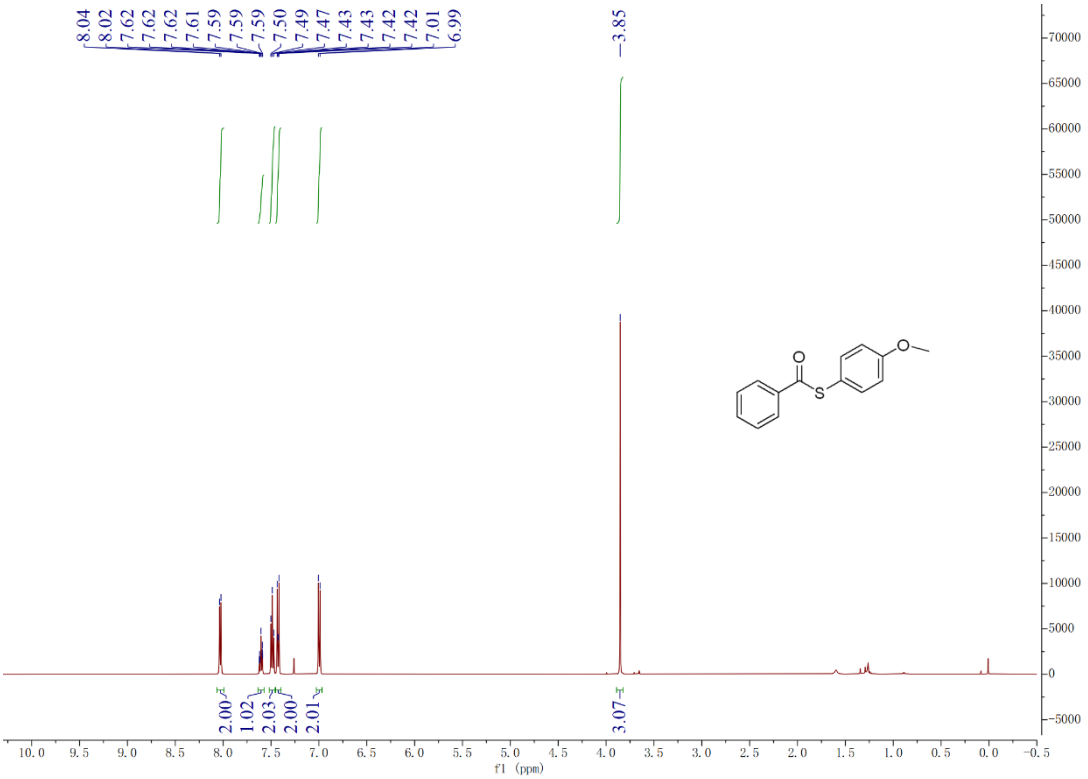
3g, ^{1}H NMR (500 MHz, $CDCl_3$)



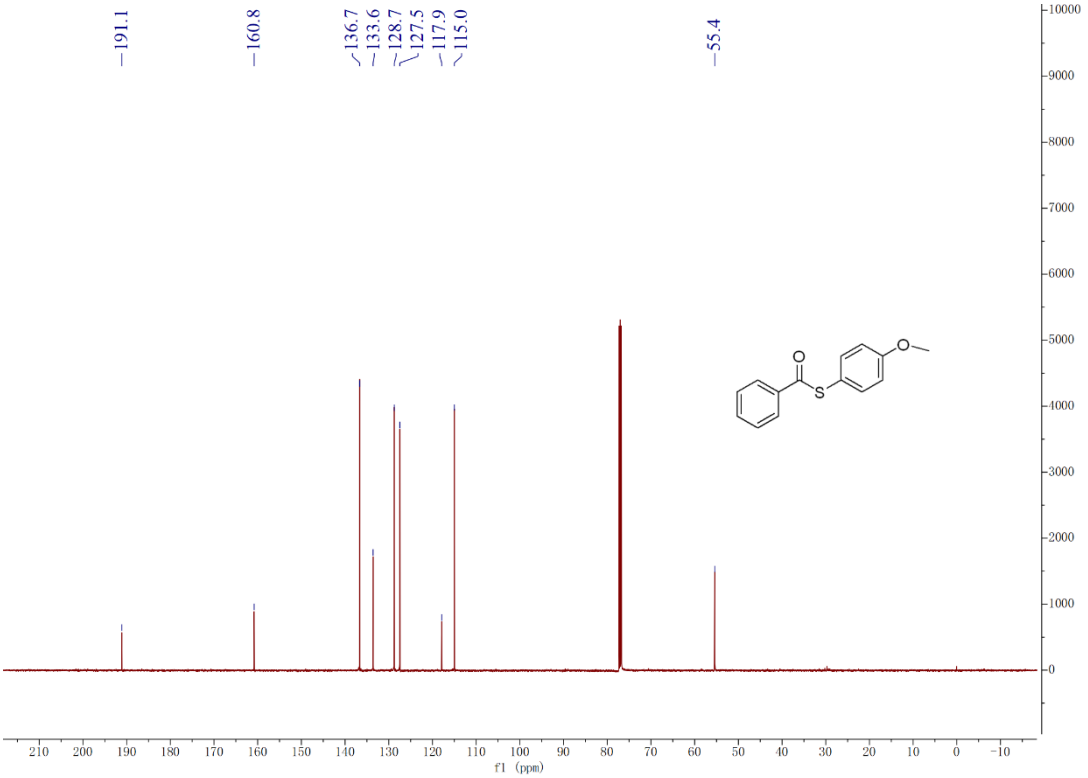
3g, ^{13}C NMR (125 MHz, $CDCl_3$)



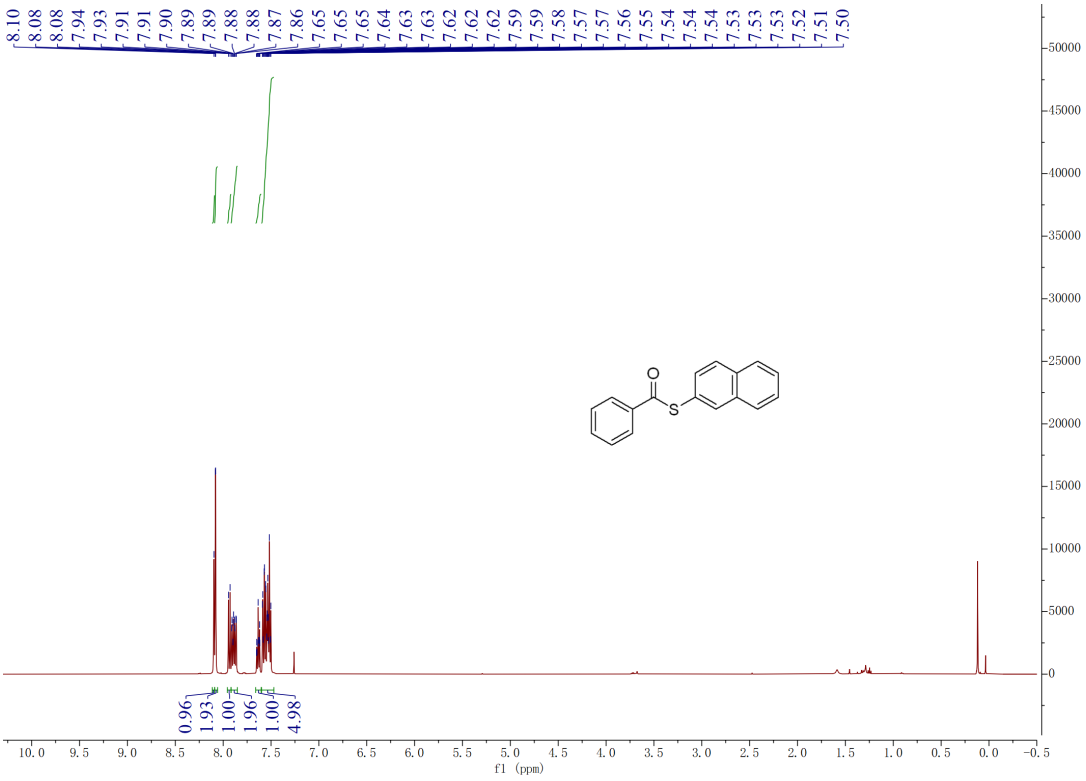
3h, ^{1}H NMR (500 MHz, $CDCl_3$)



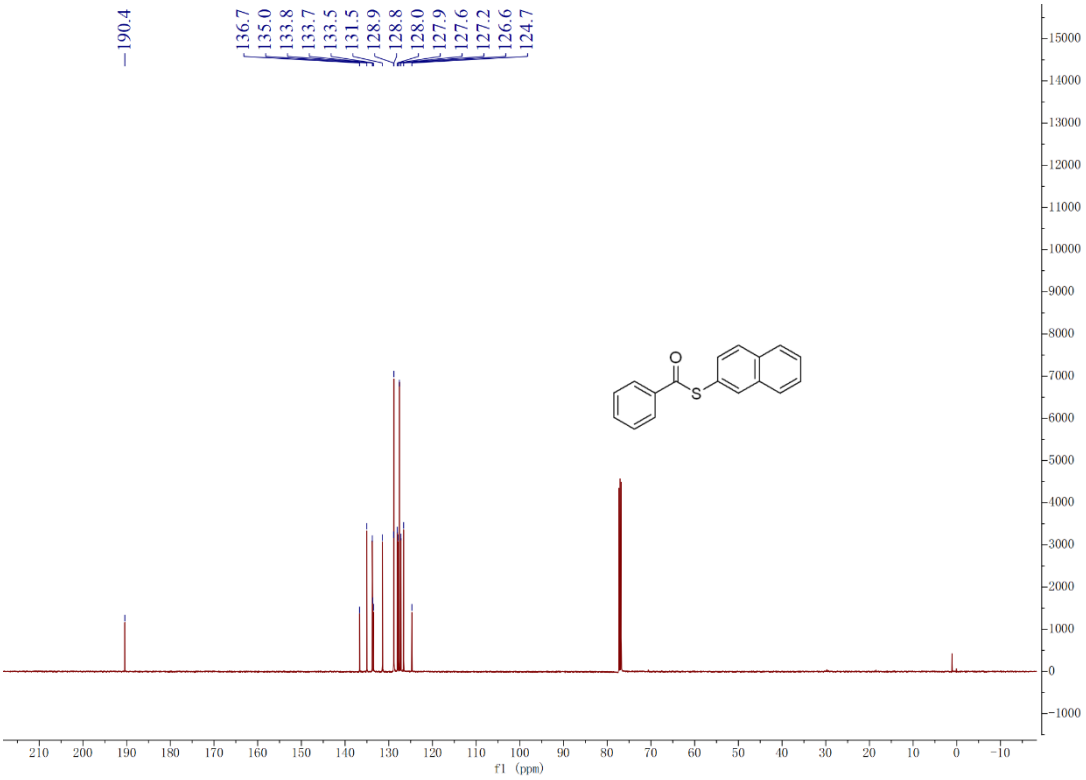
3h, ^{13}C NMR (125 MHz, $CDCl_3$)



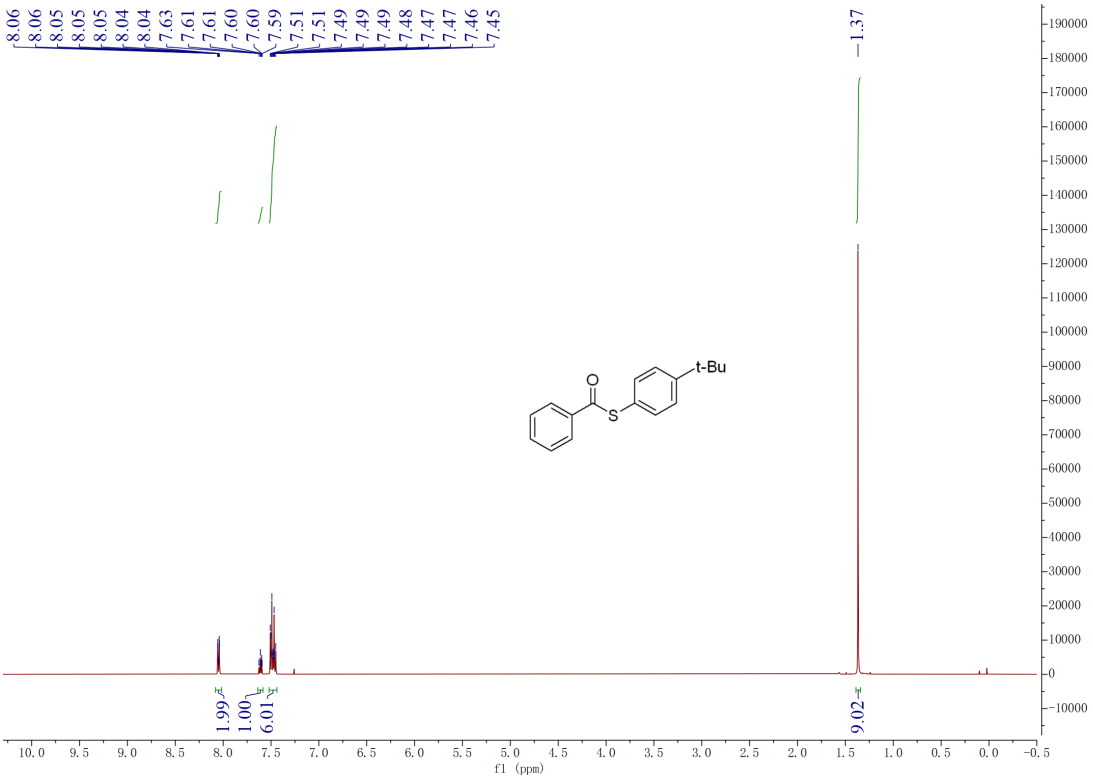
3i, ^{1}H NMR (500 MHz, $CDCl_3$)



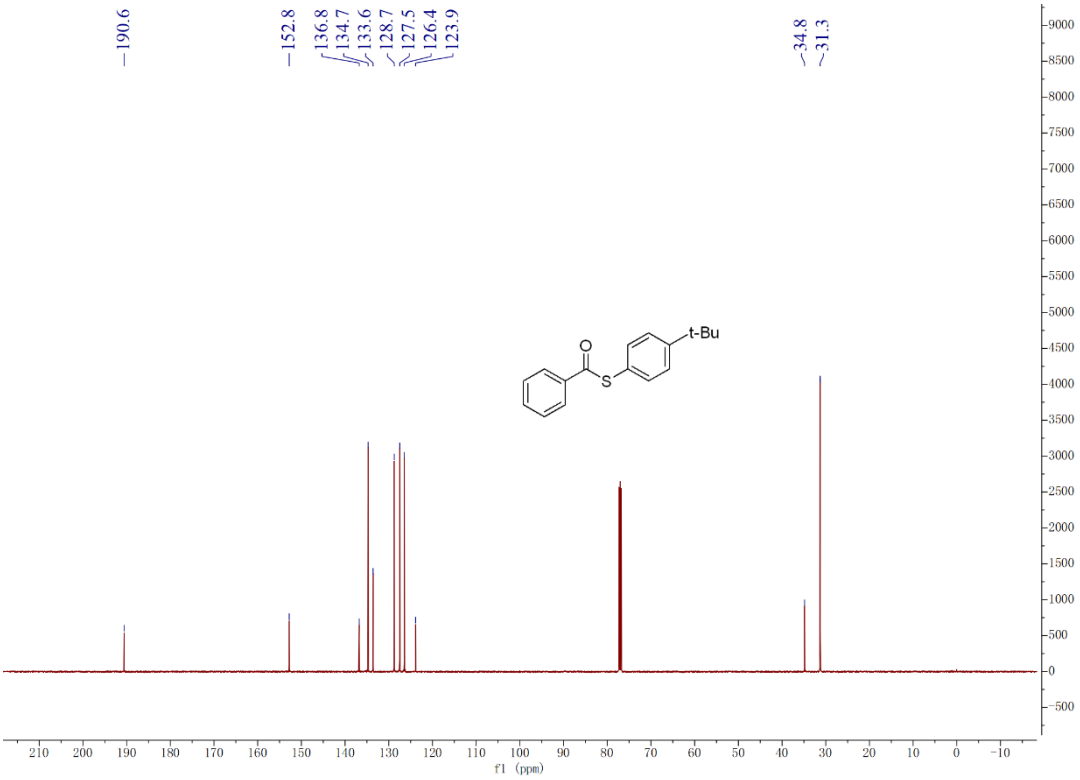
3i, ^{13}C NMR (125 MHz, $CDCl_3$)



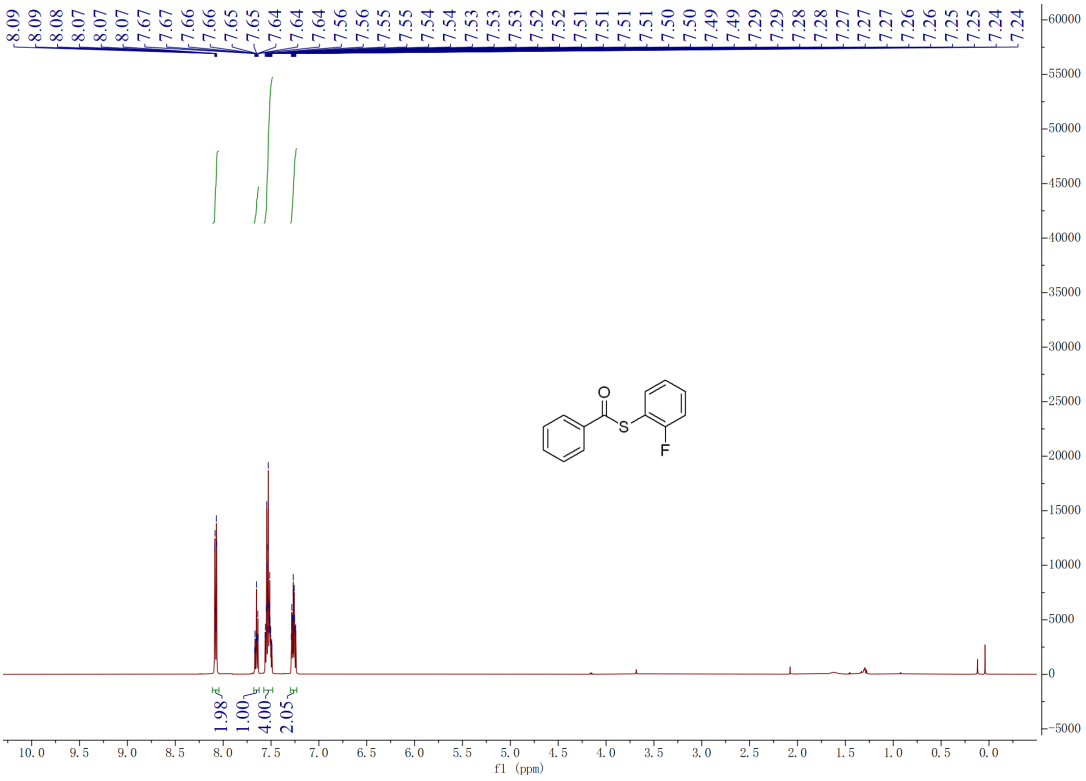
3j, ^{1}H NMR (500 MHz, $CDCl_3$)



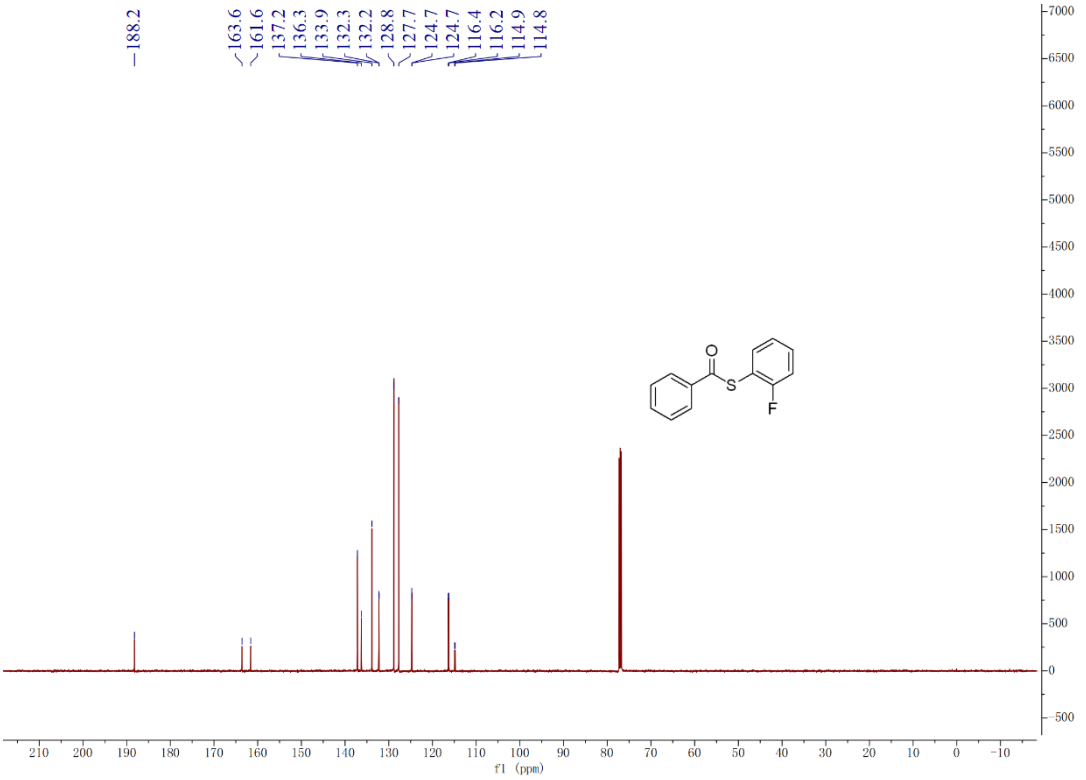
3j, ^{13}C NMR (125 MHz, $CDCl_3$)



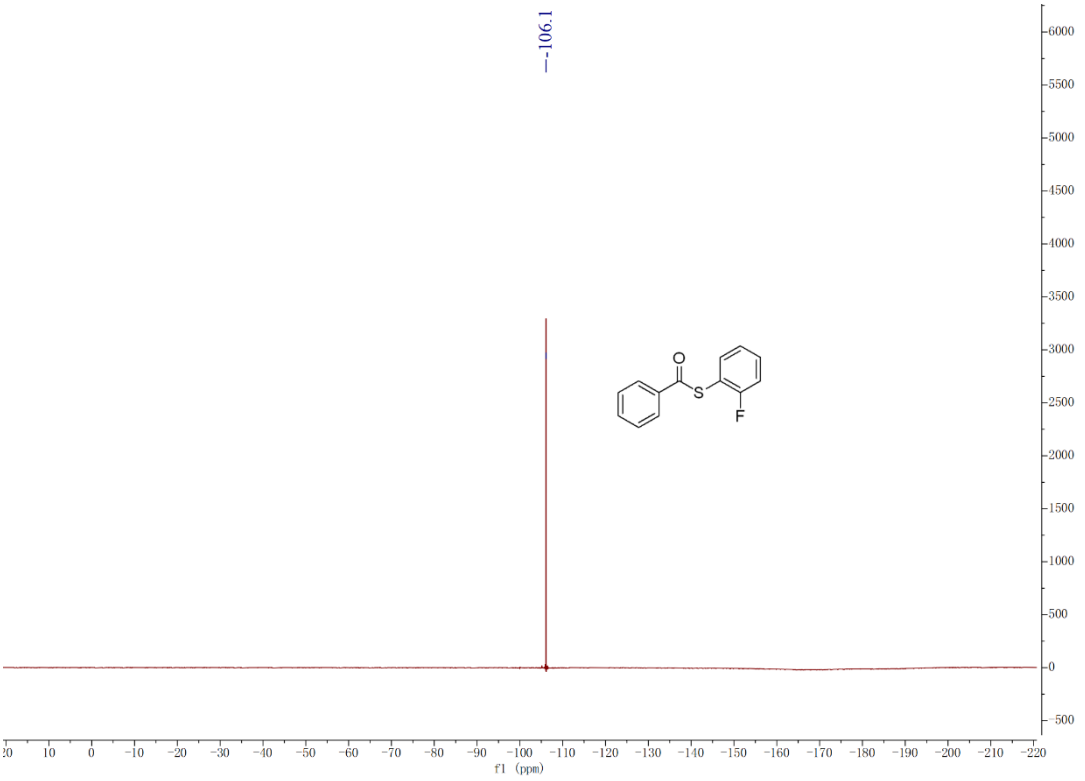
3k, ^{1}H NMR (500 MHz, $CDCl_3$)



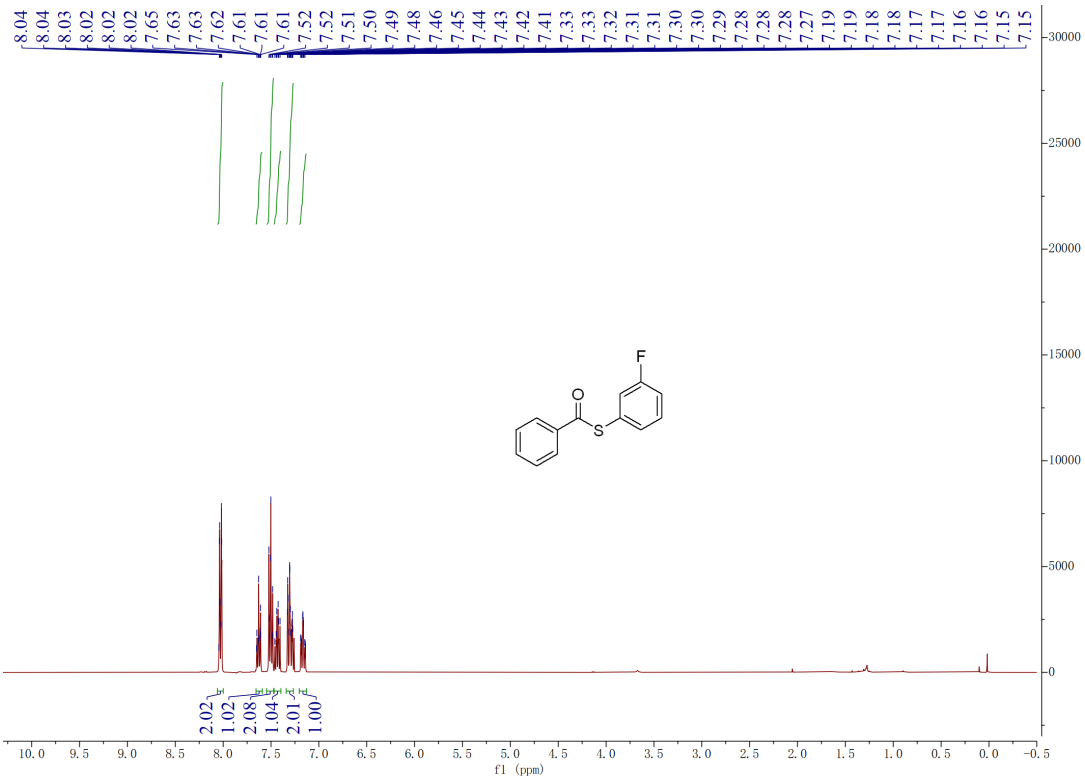
3k, ^{13}C NMR (125 MHz, $CDCl_3$)



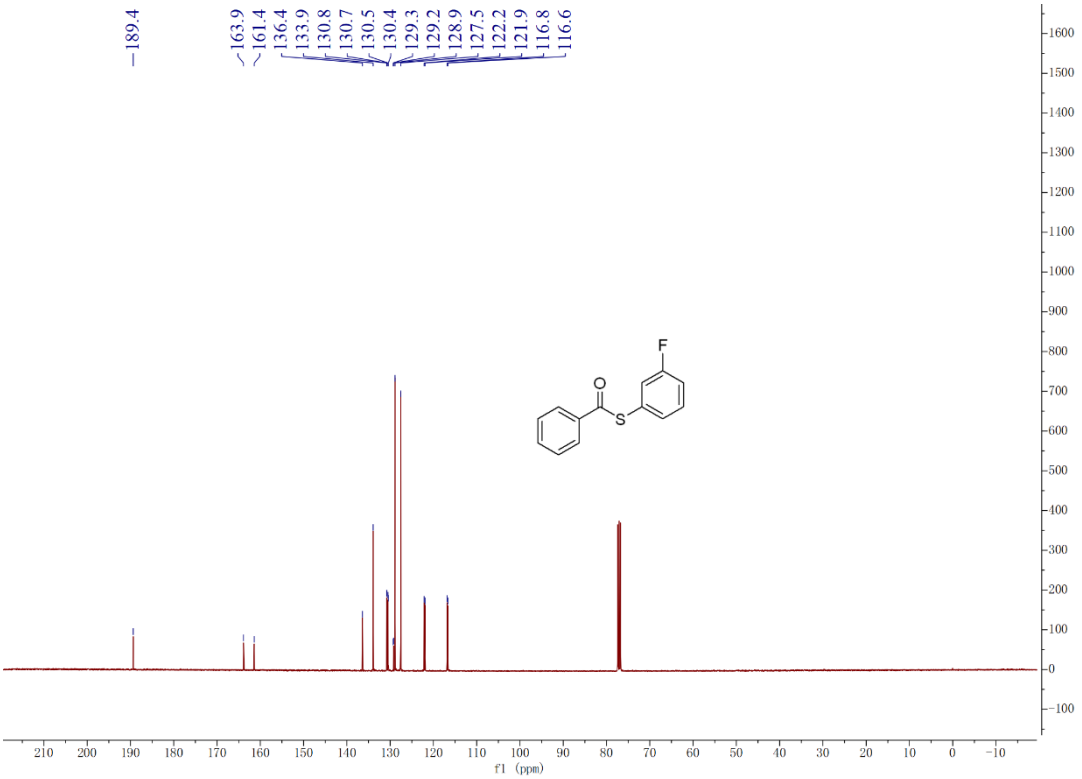
3k, ^{19}F NMR (470 MHz, $CDCl_3$)



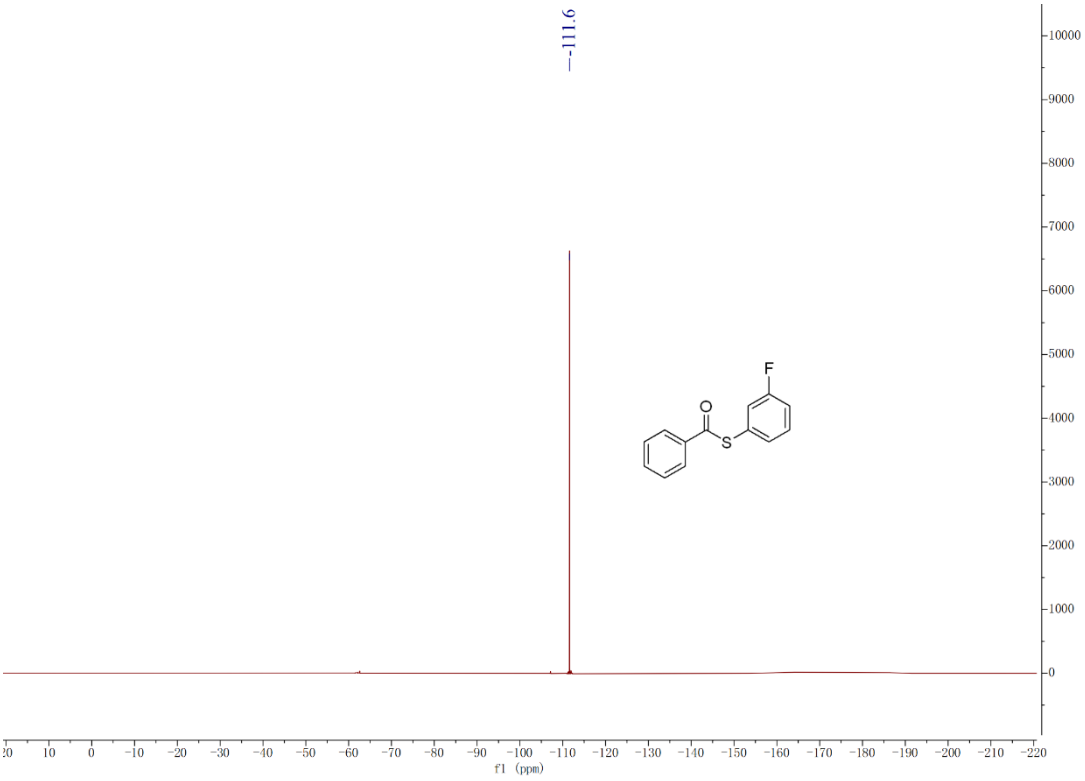
3l, ^{1}H NMR (400 MHz, $CDCl_3$)



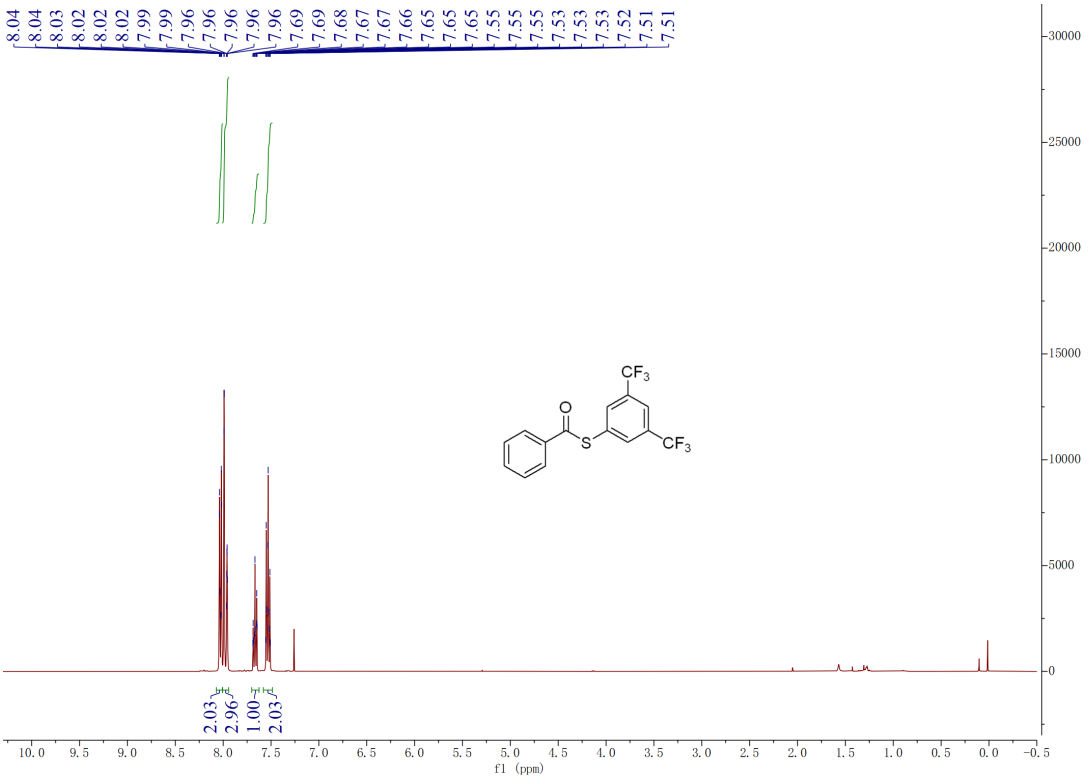
3l, ^{13}C NMR (100 MHz, $CDCl_3$)



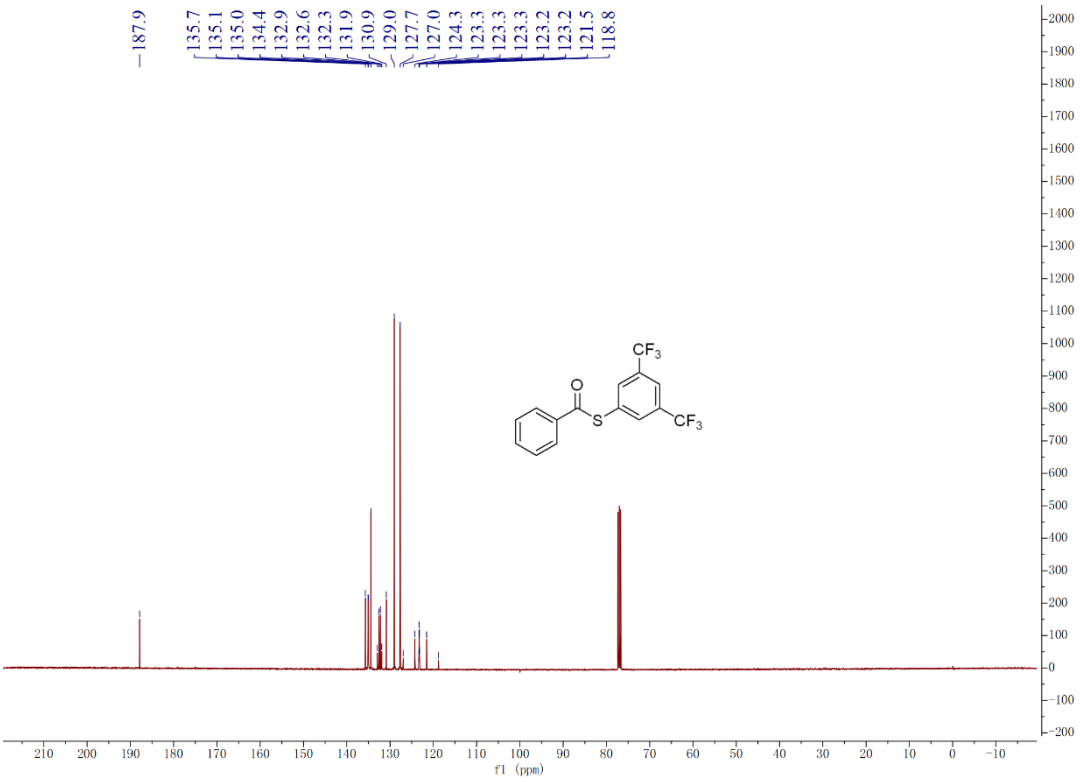
3l, ^{19}F NMR (376 MHz, $CDCl_3$)



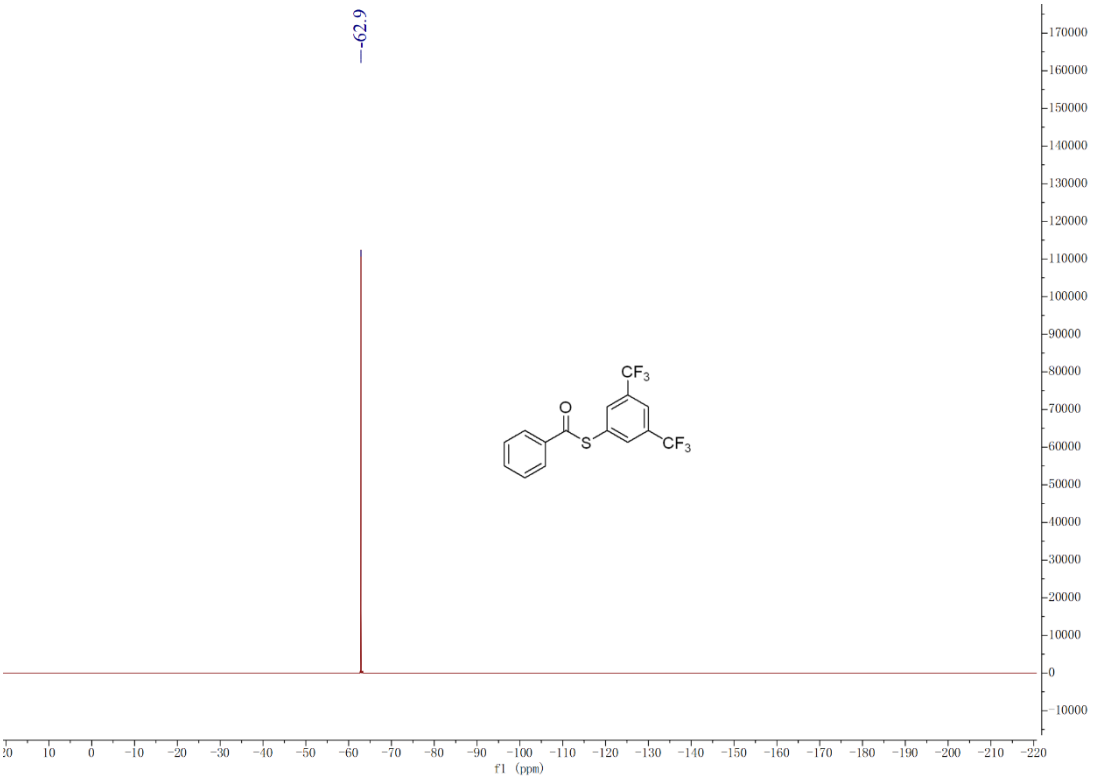
3m, ^{1}H NMR (400 MHz, $CDCl_3$)



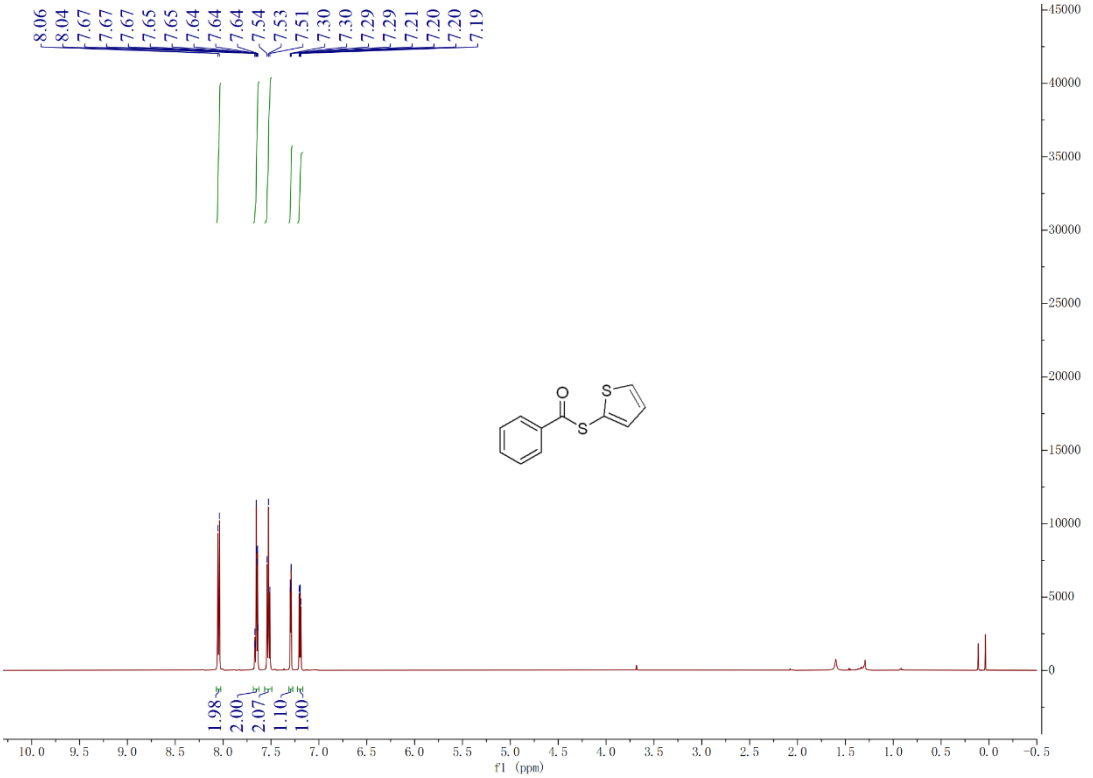
3m, ^{13}C NMR (100 MHz, $CDCl_3$)



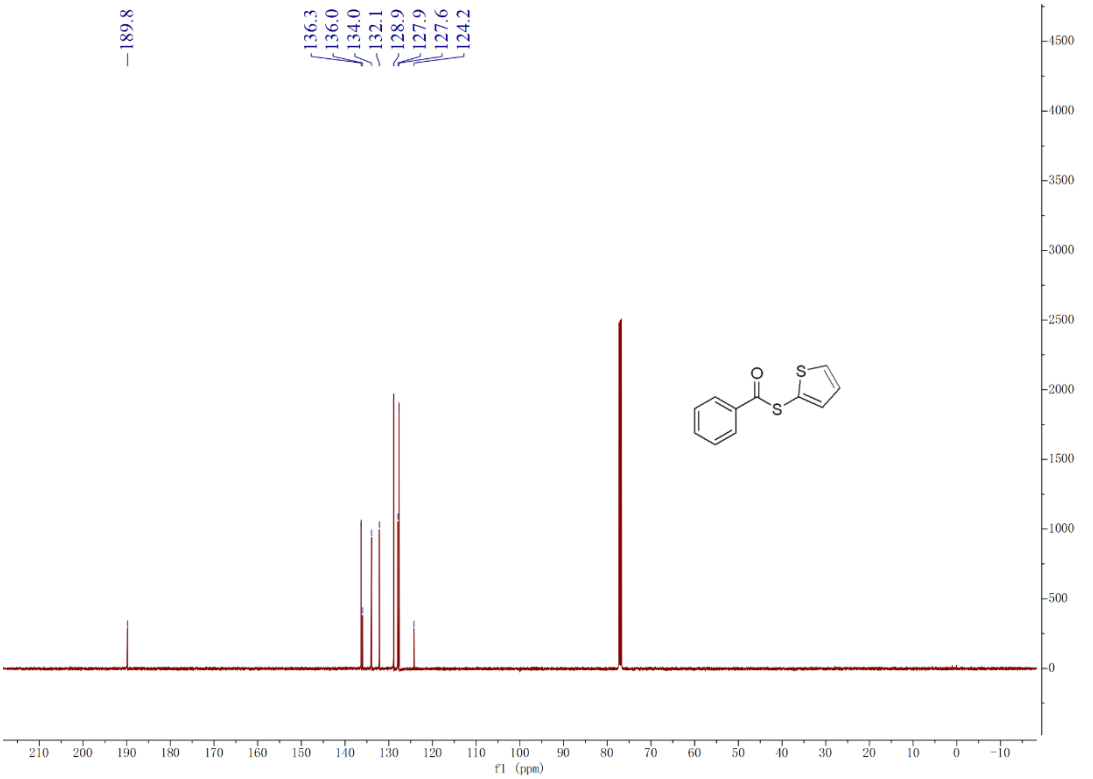
3m, ^{19}F NMR (376 MHz, $CDCl_3$)



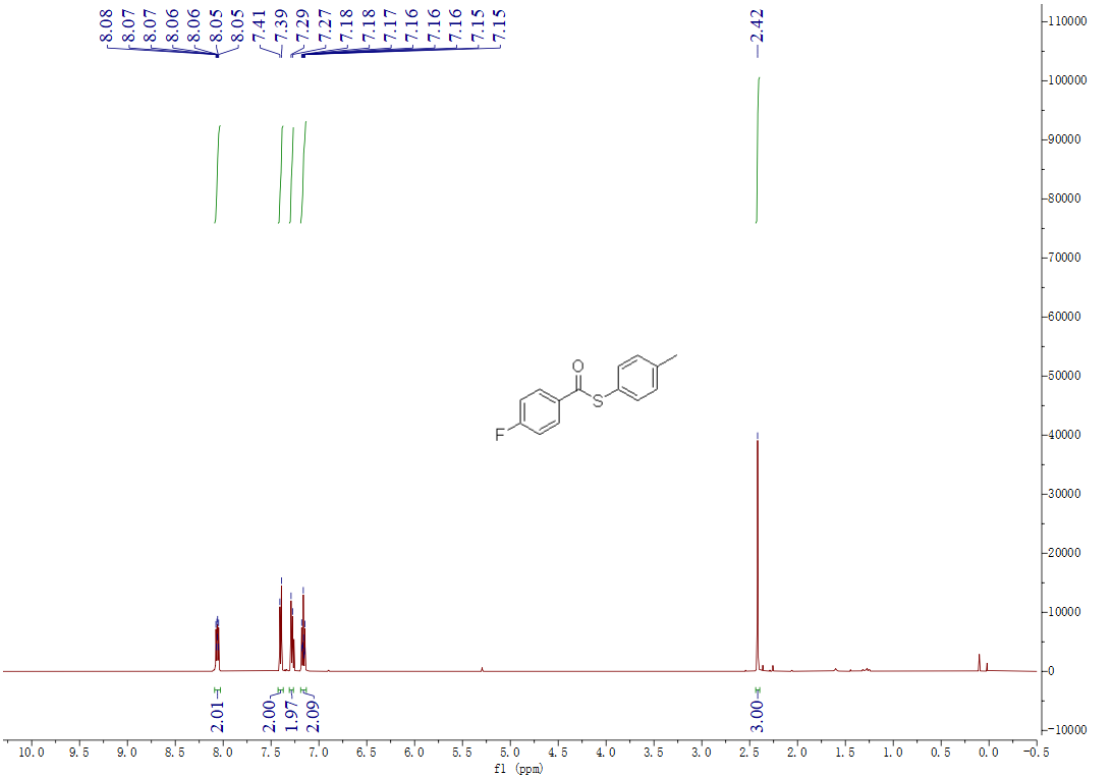
3n, ^{1}H NMR (500 MHz, $CDCl_3$),



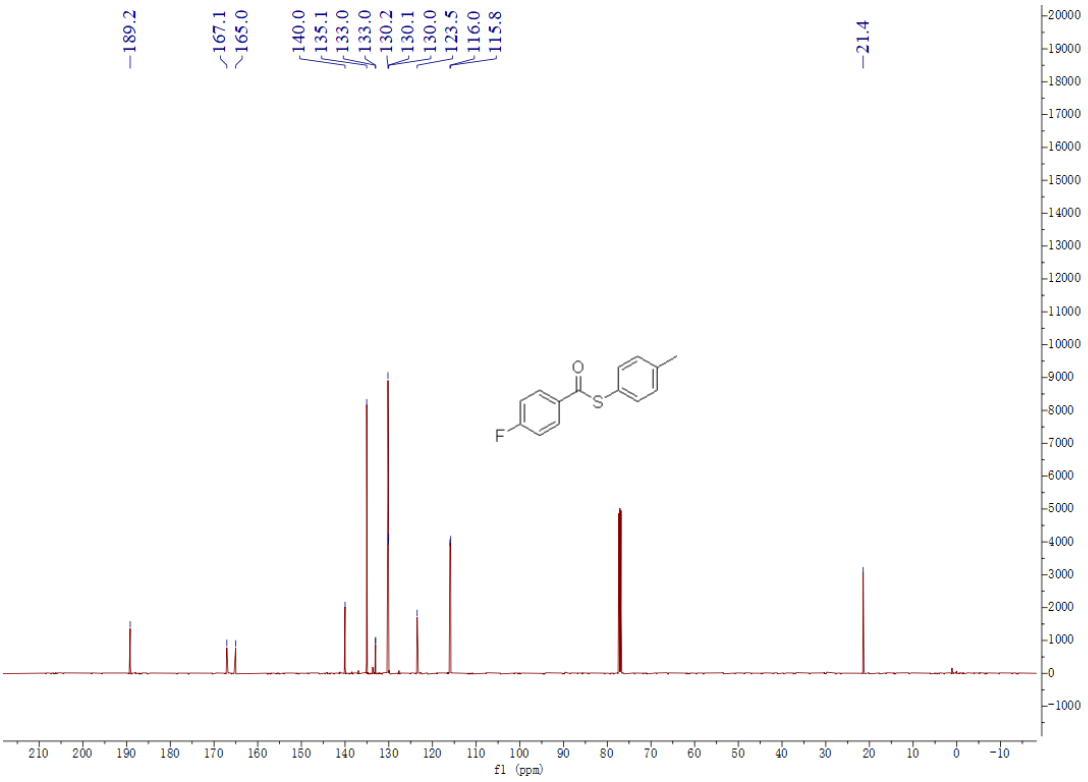
3n, ^{13}C NMR (125 MHz, $CDCl_3$)



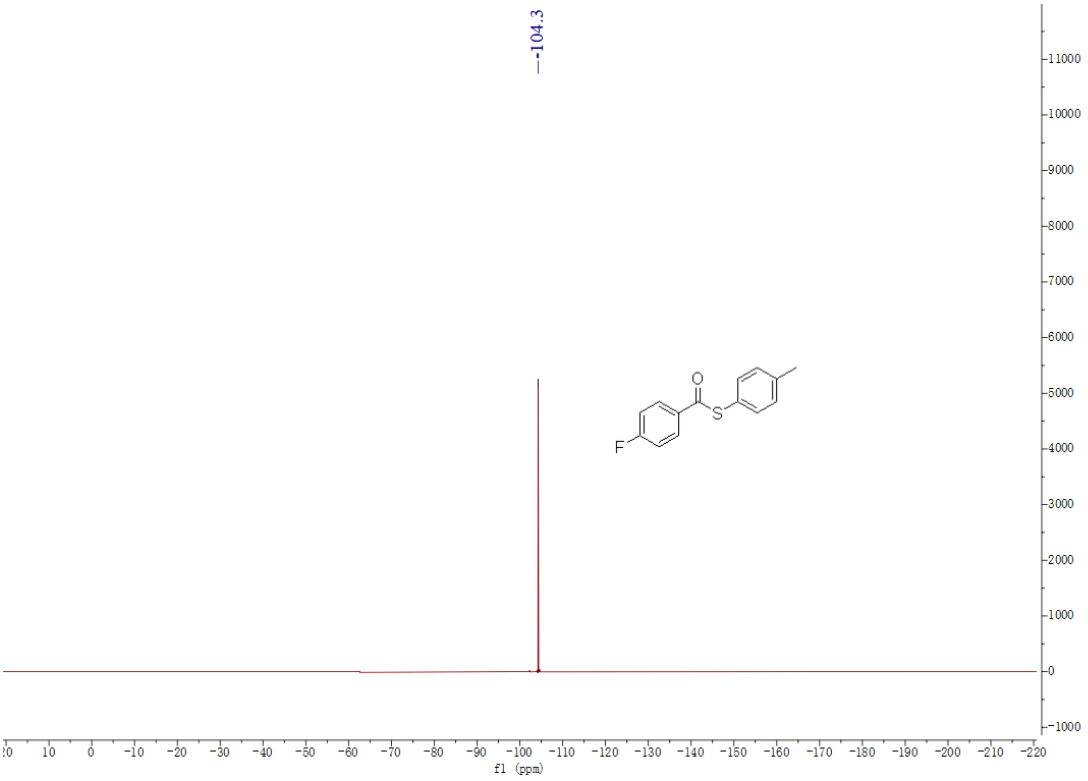
3aa, ^{1}H NMR (500 MHz, $CDCl_3$)



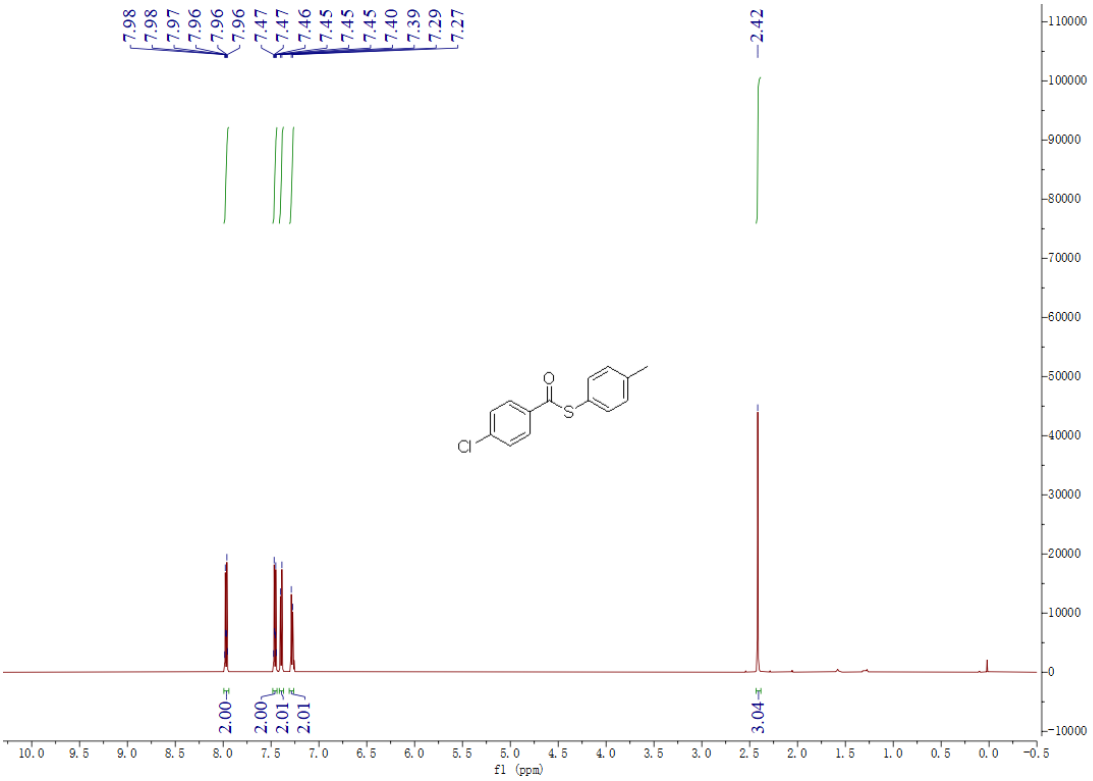
3aa, ^{13}C NMR (125 MHz, $CDCl_3$)



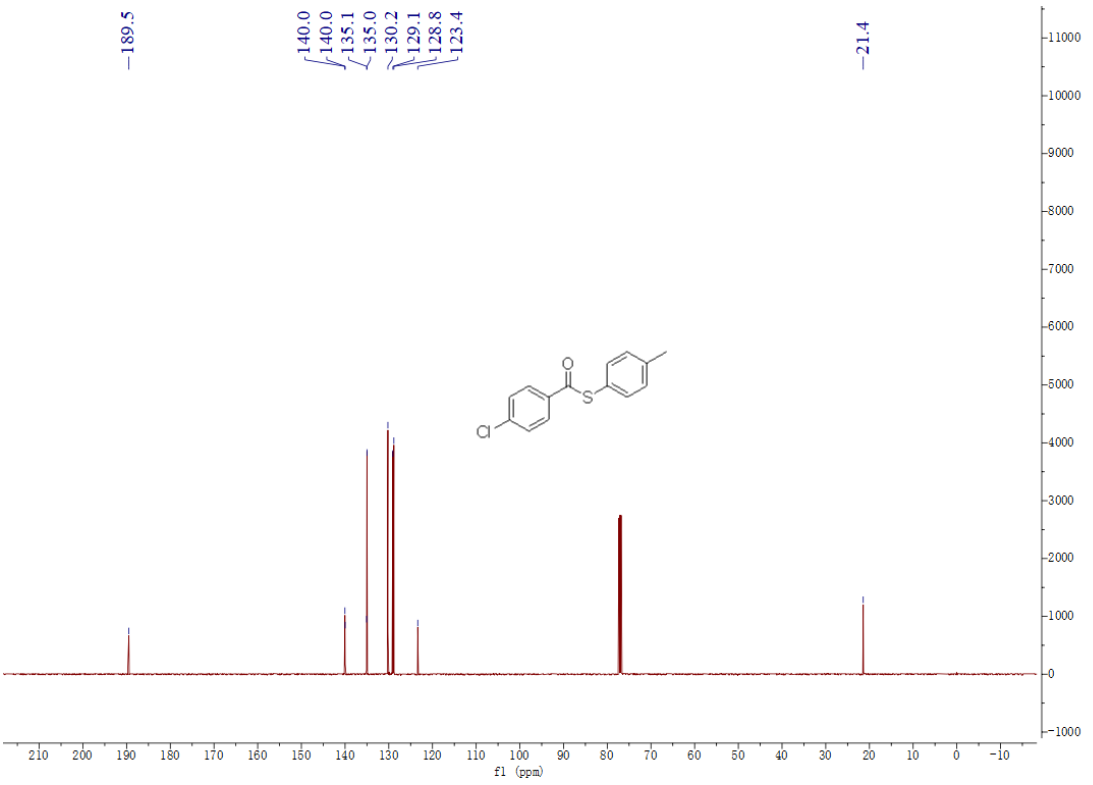
3aa, ^{19}F NMR (470 MHz, $CDCl_3$)



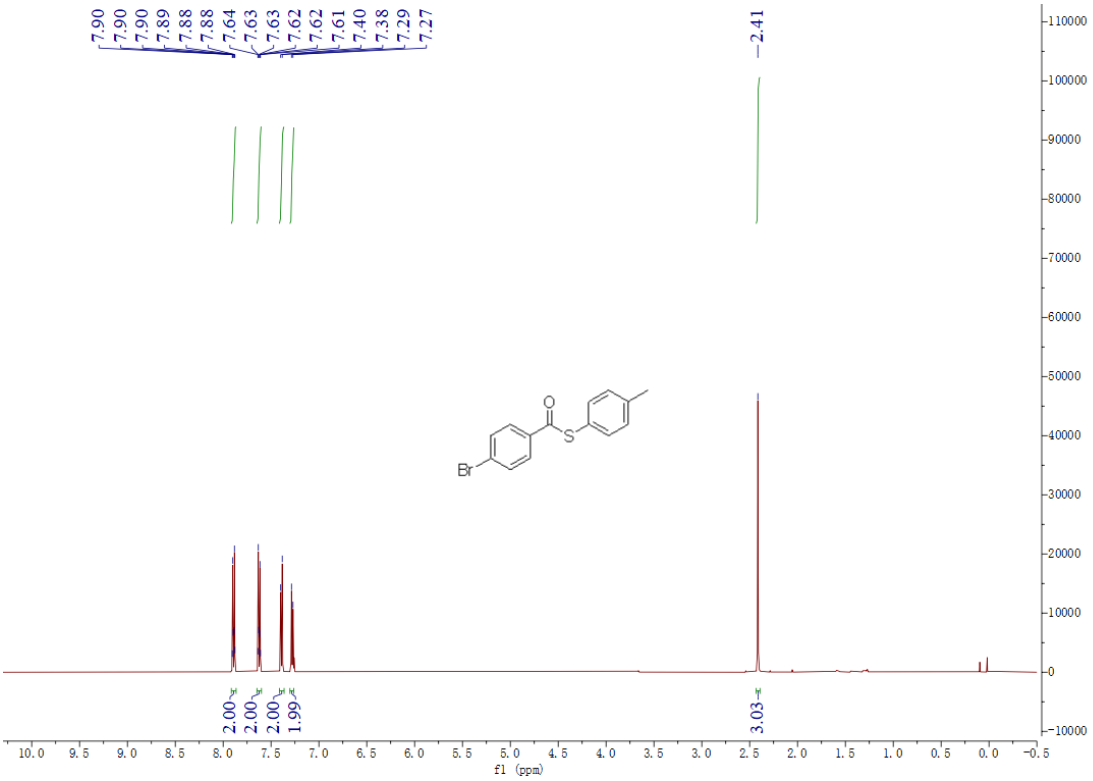
3ab, ^{1}H NMR (500 MHz, $CDCl_3$)



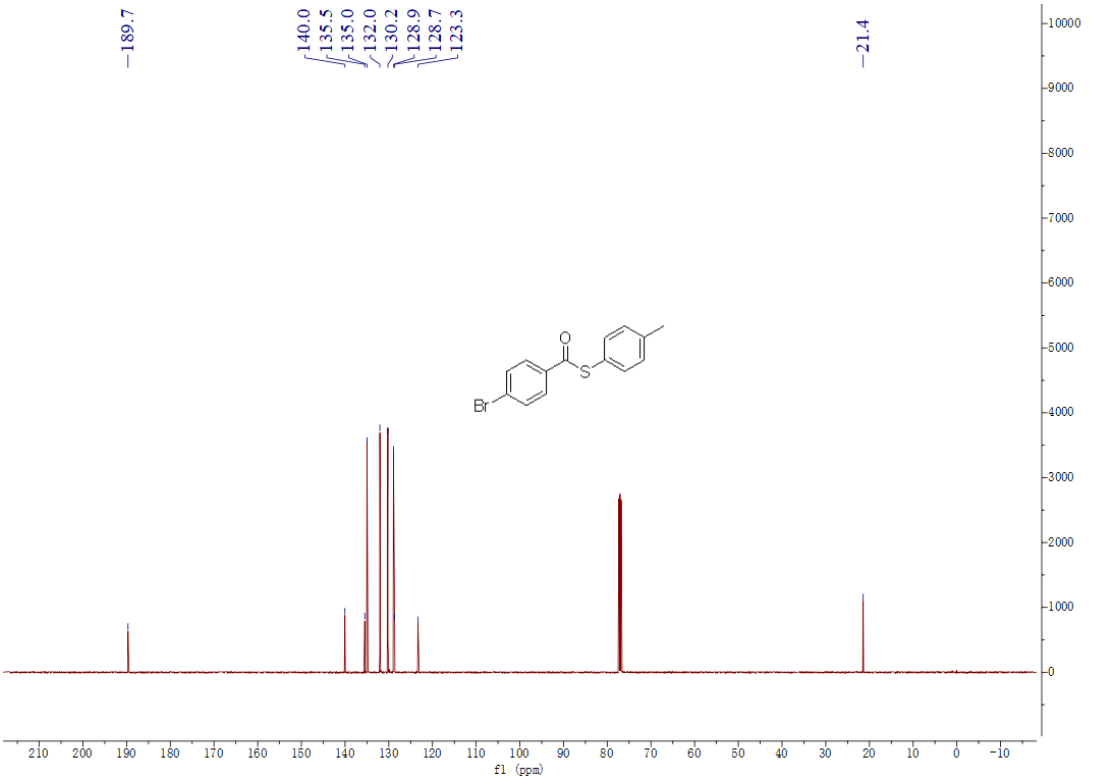
3ab, ^{13}C NMR (125 MHz, $CDCl_3$)



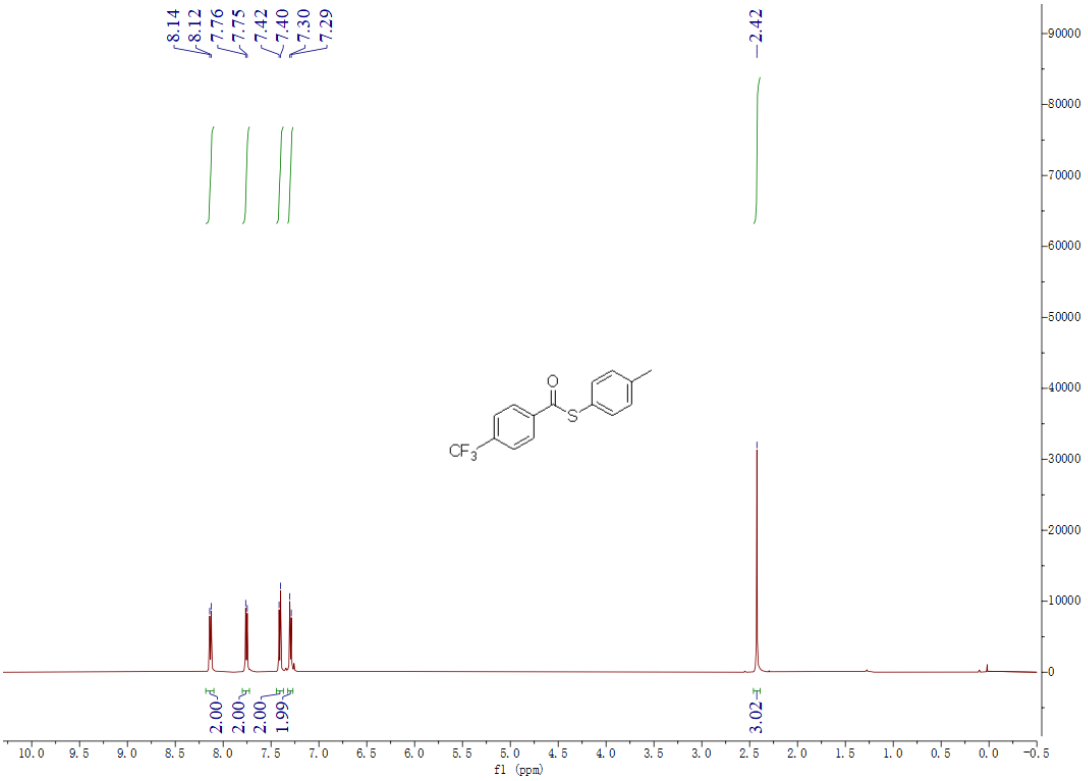
3ac, ^{1}H NMR (500 MHz, $CDCl_3$)



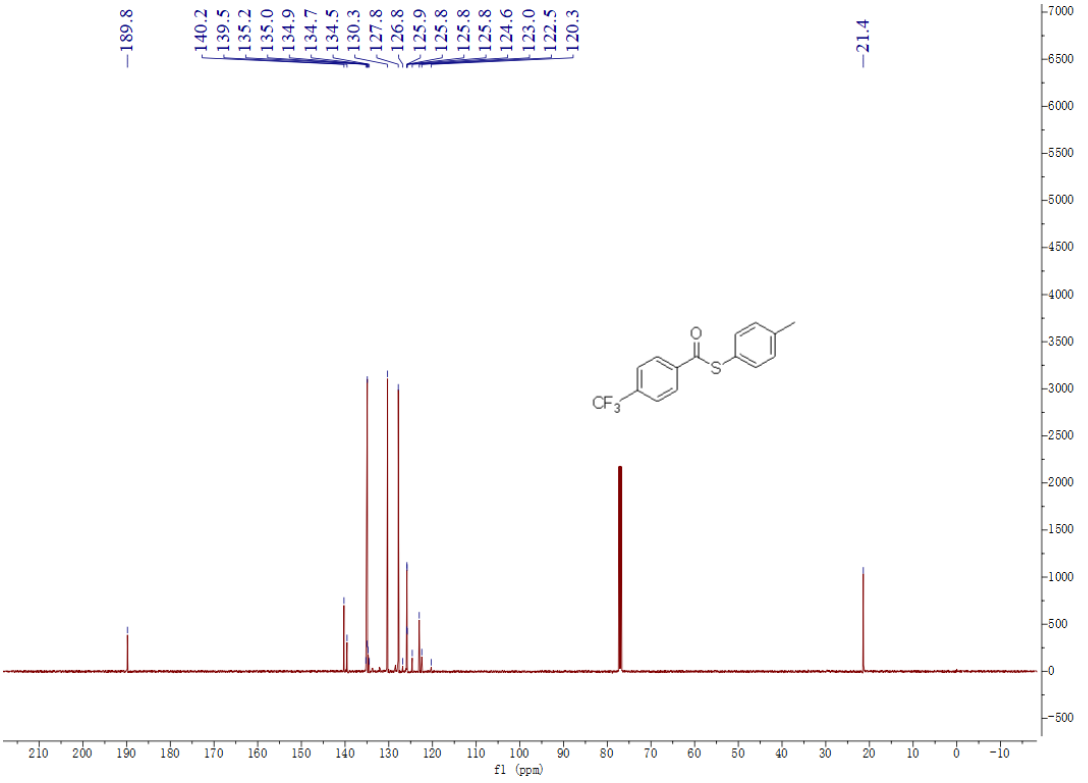
3ac, ^{13}C NMR (125 MHz, $CDCl_3$)



3ad, ^{1}H NMR (500 MHz, $CDCl_3$)

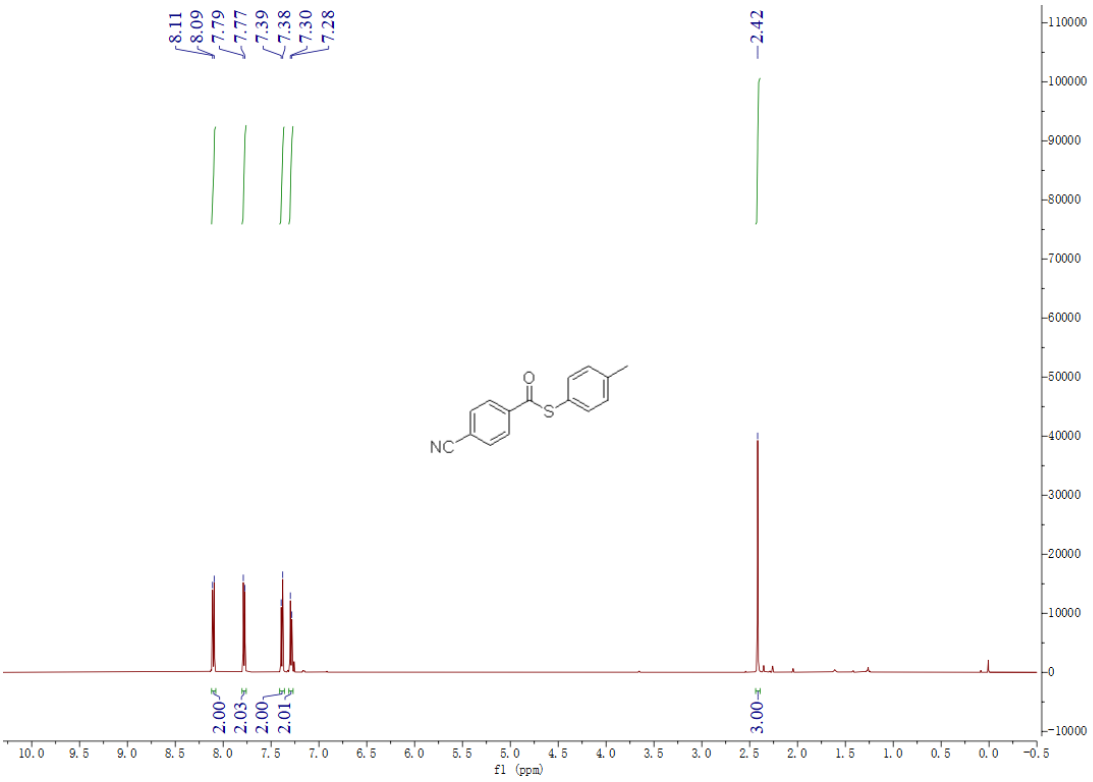


3ad, ^{13}C NMR (125 MHz, $CDCl_3$)

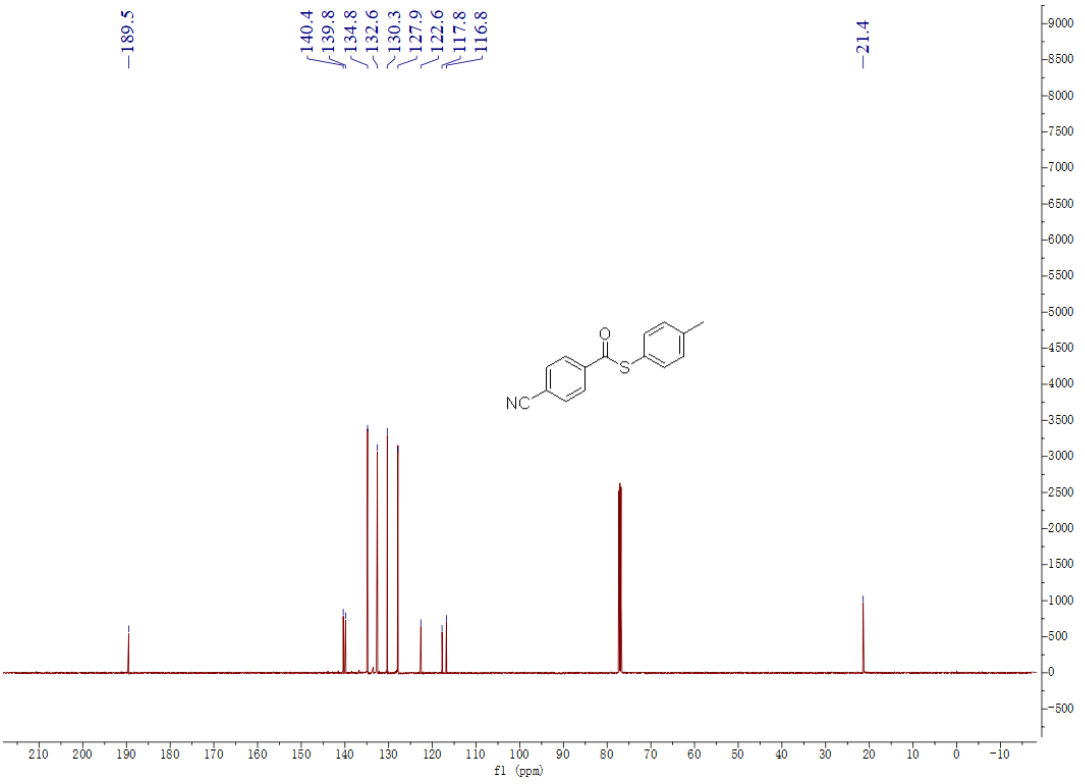


3ad, ^{19}F NMR (470 MHz, $CDCl_3$)

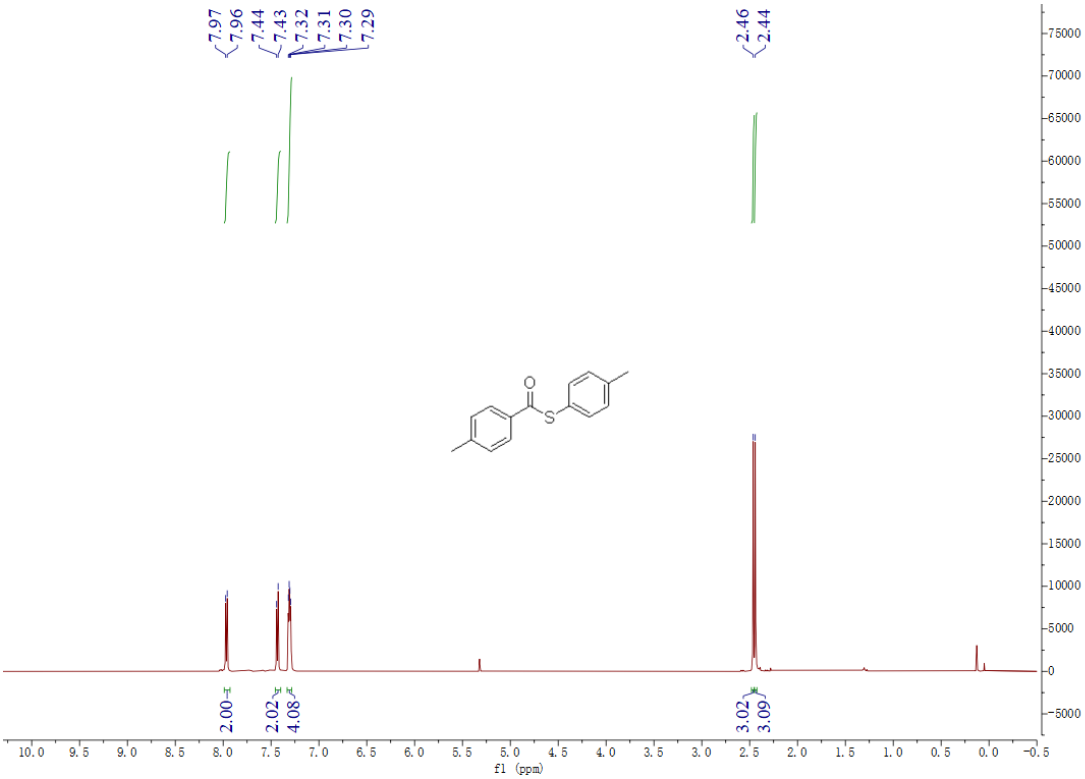
3ae, ^{1}H NMR (500 MHz, $CDCl_3$)



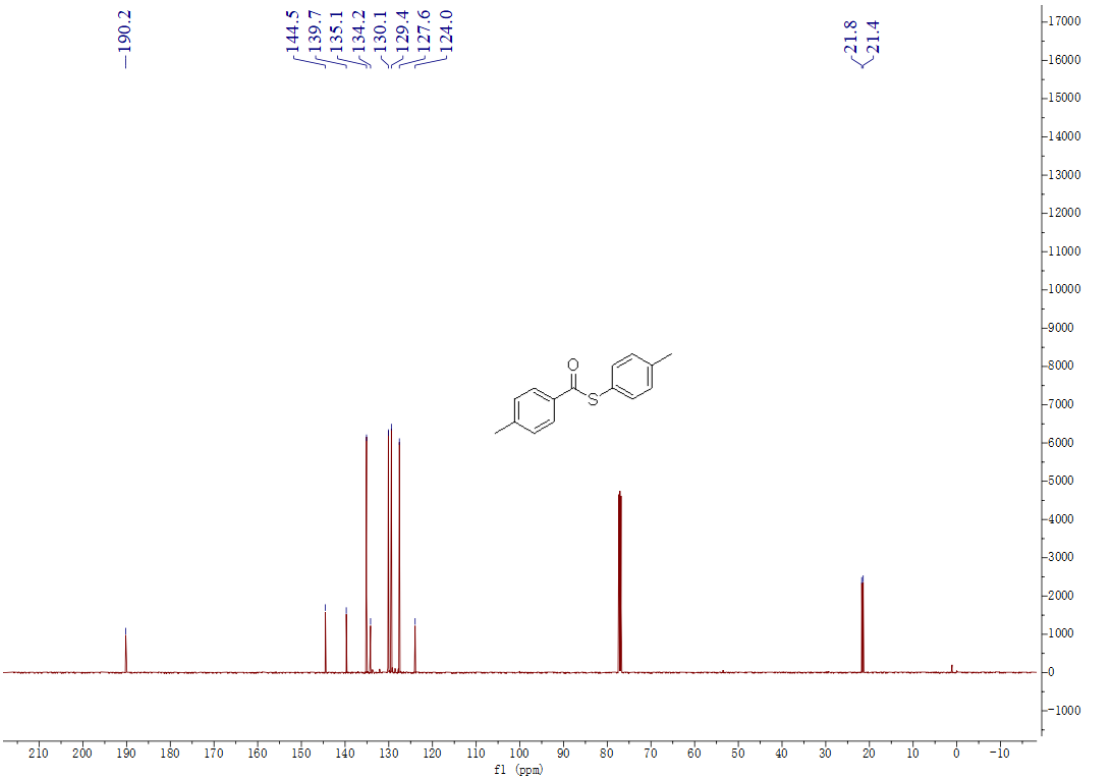
3ae, ^{13}C NMR (125 MHz, $CDCl_3$)



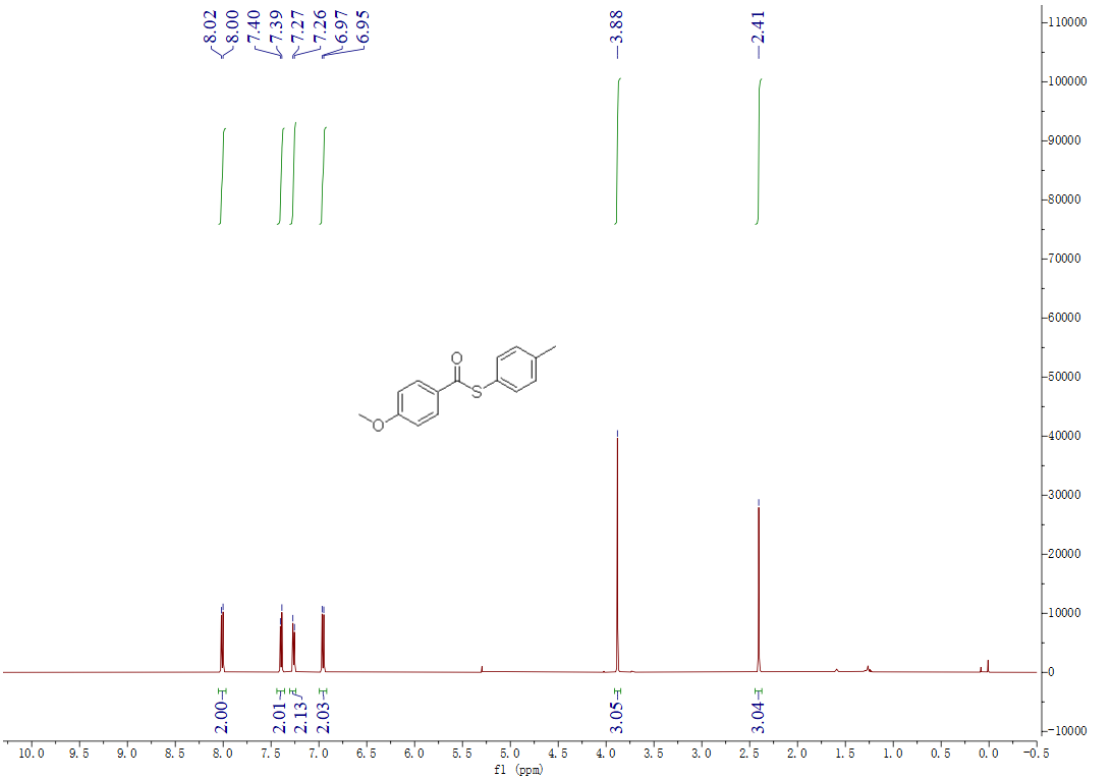
3af, ^{1}H NMR (500 MHz, $CDCl_3$)



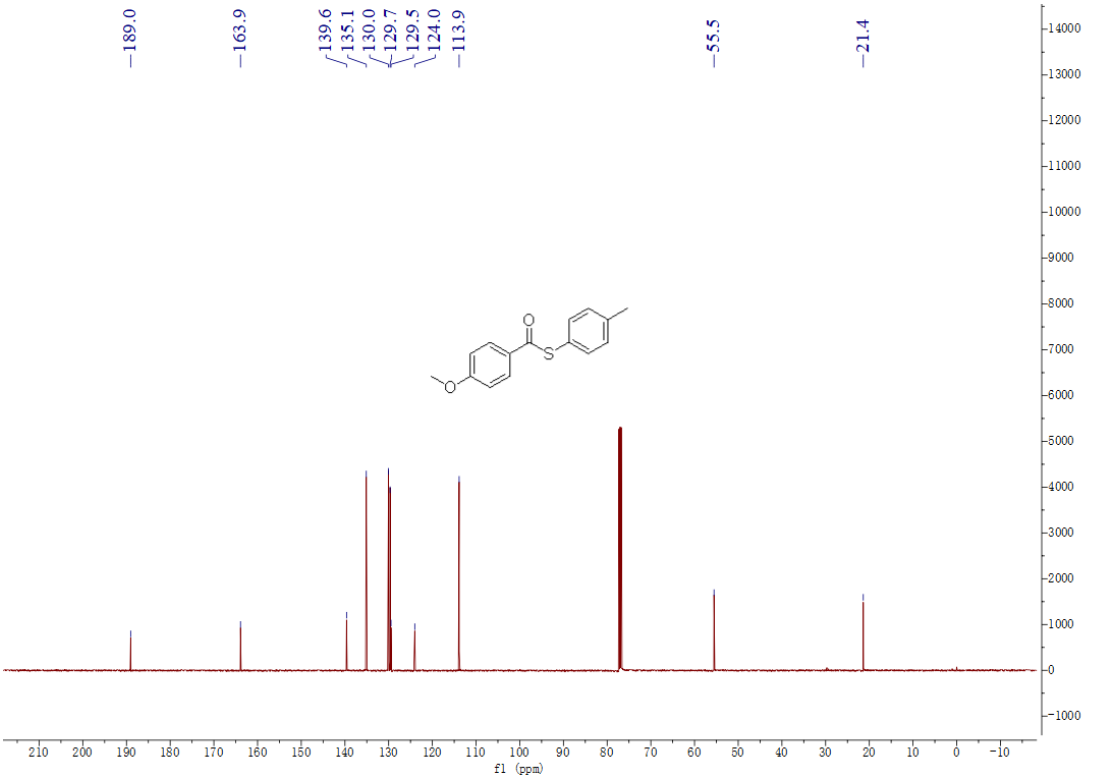
3af, ^{13}C NMR (125 MHz, $CDCl_3$)



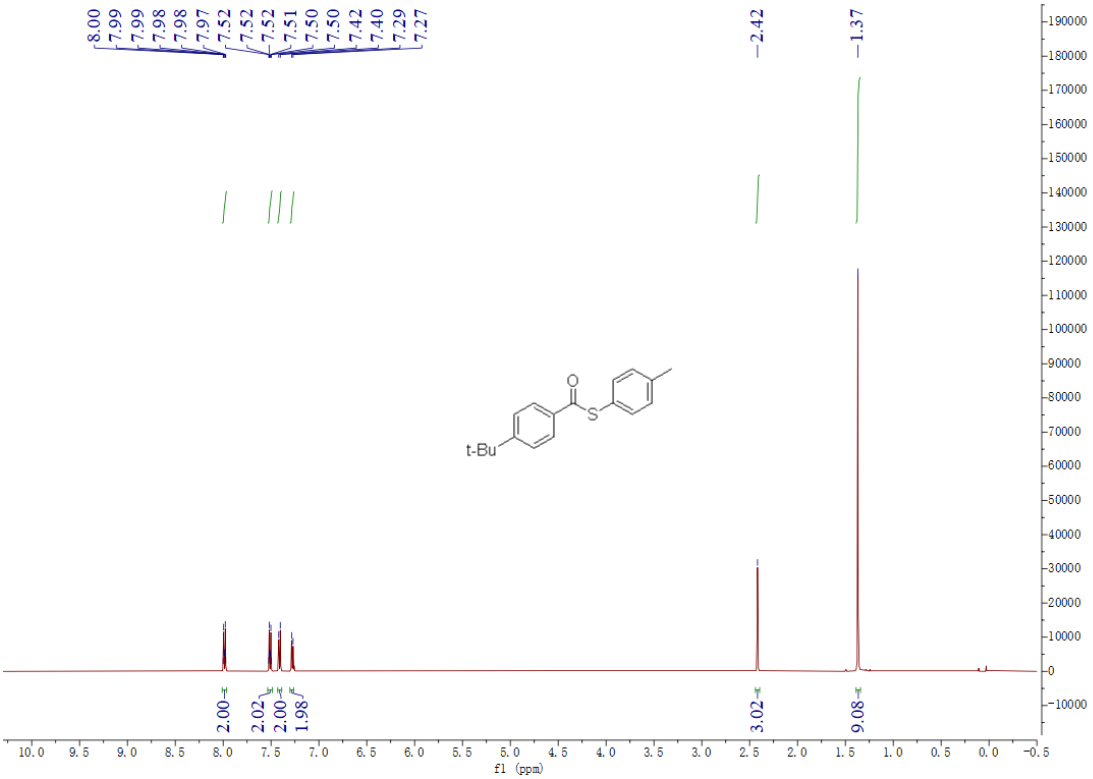
3ag, ^{1}H NMR (500 MHz, $CDCl_3$)



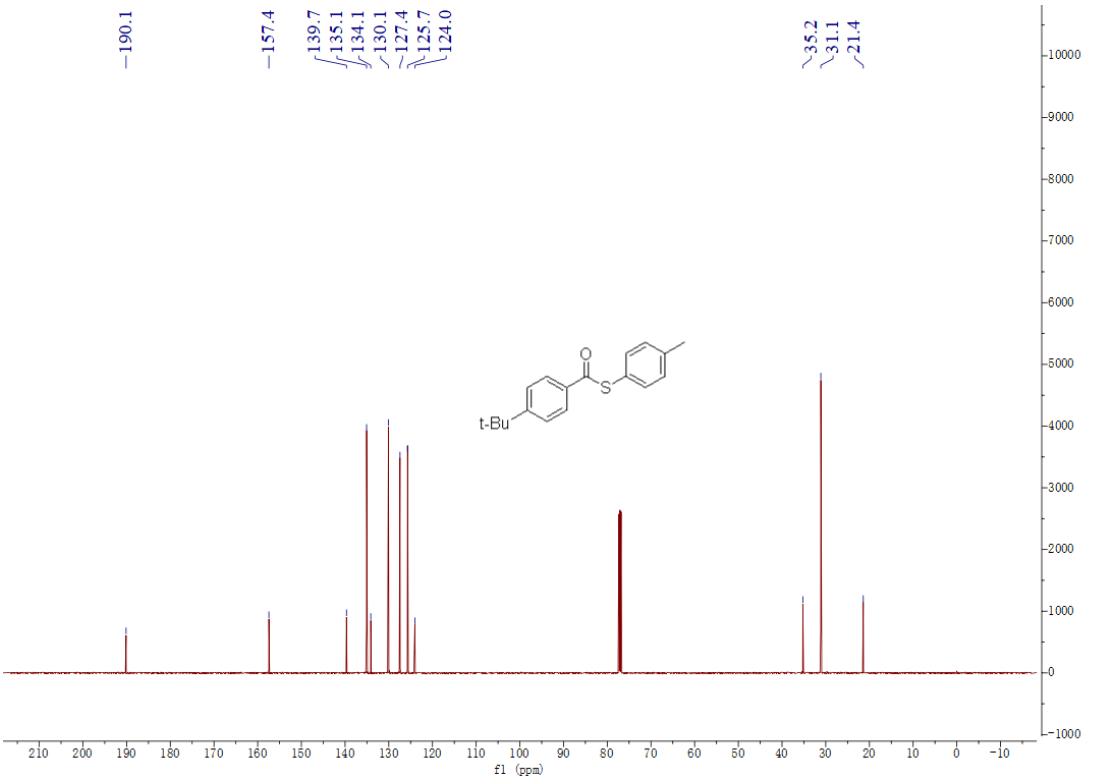
3ag, ^{13}C NMR (125 MHz, $CDCl_3$)



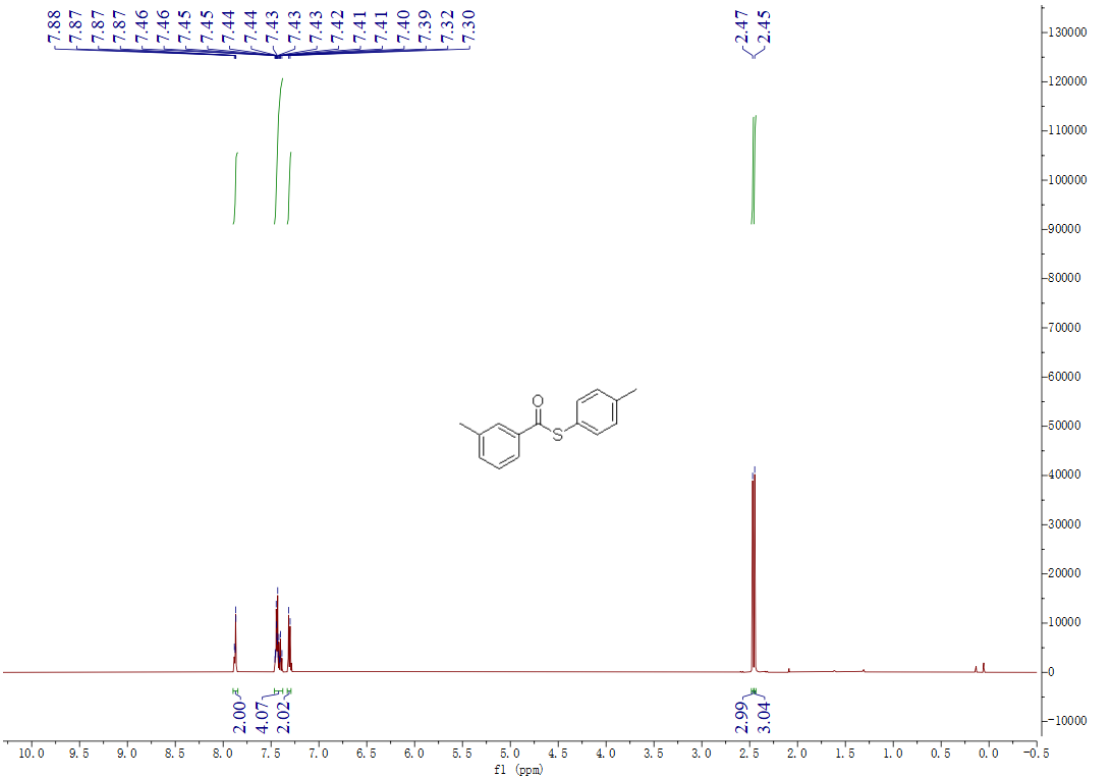
3ah, ^{1}H NMR (500 MHz, $CDCl_3$)



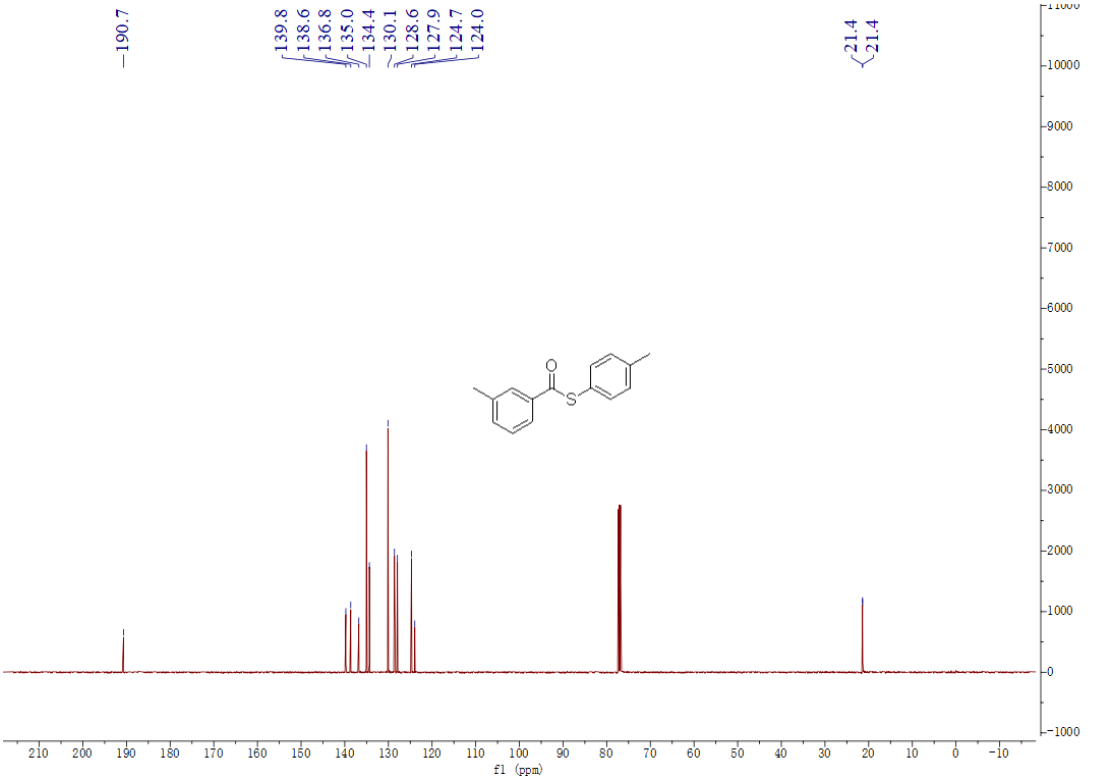
3ah, ^{13}C NMR (125 MHz, $CDCl_3$)



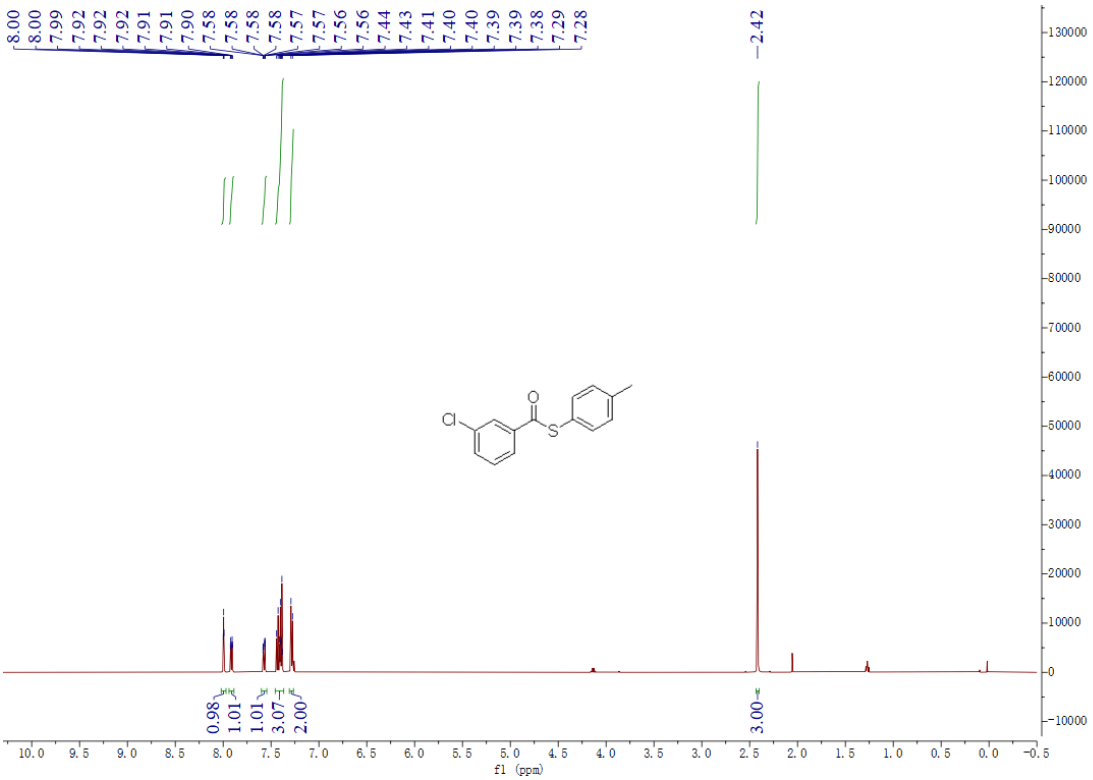
3ai, ^{1}H NMR (500 MHz, $CDCl_3$)



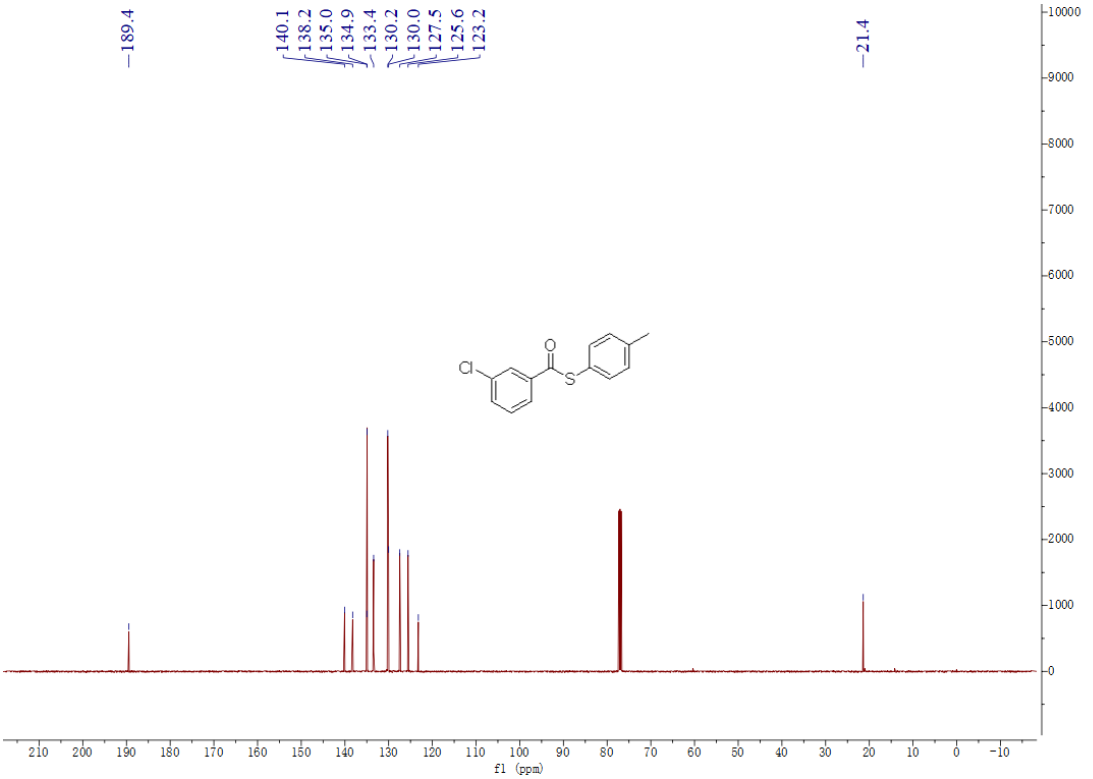
3ai, ^{13}C NMR (125 MHz, $CDCl_3$)



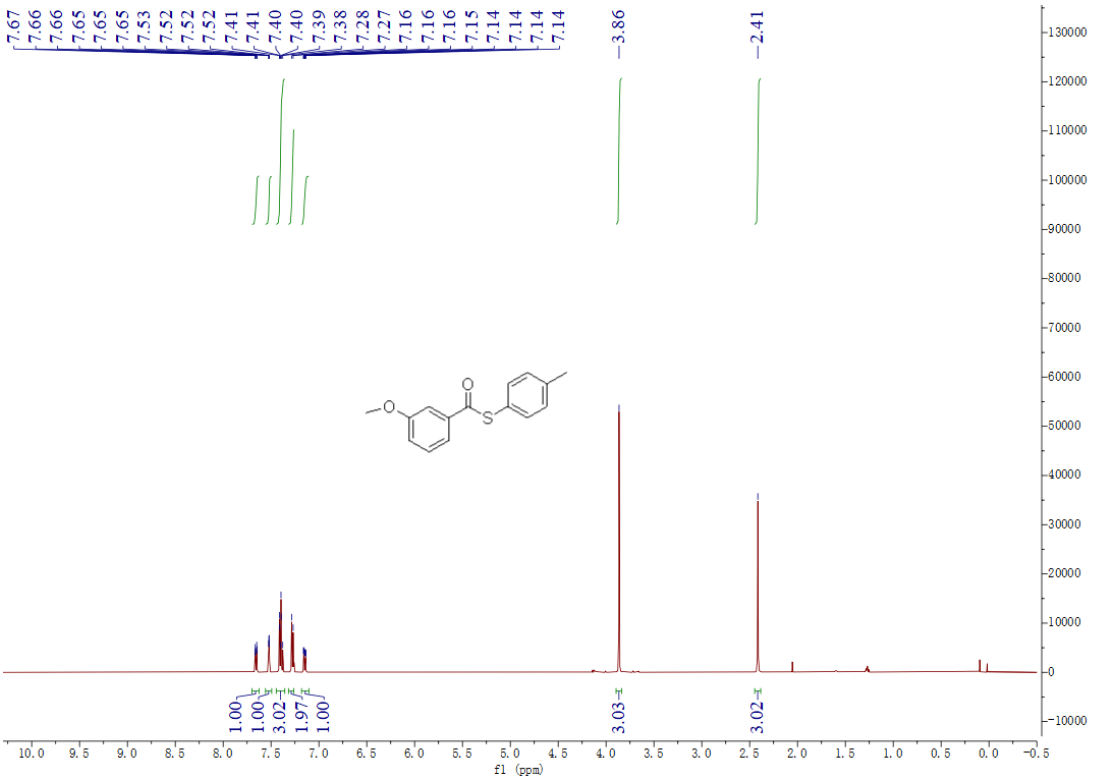
3aj, ^{1}H NMR (500 MHz, $CDCl_3$)



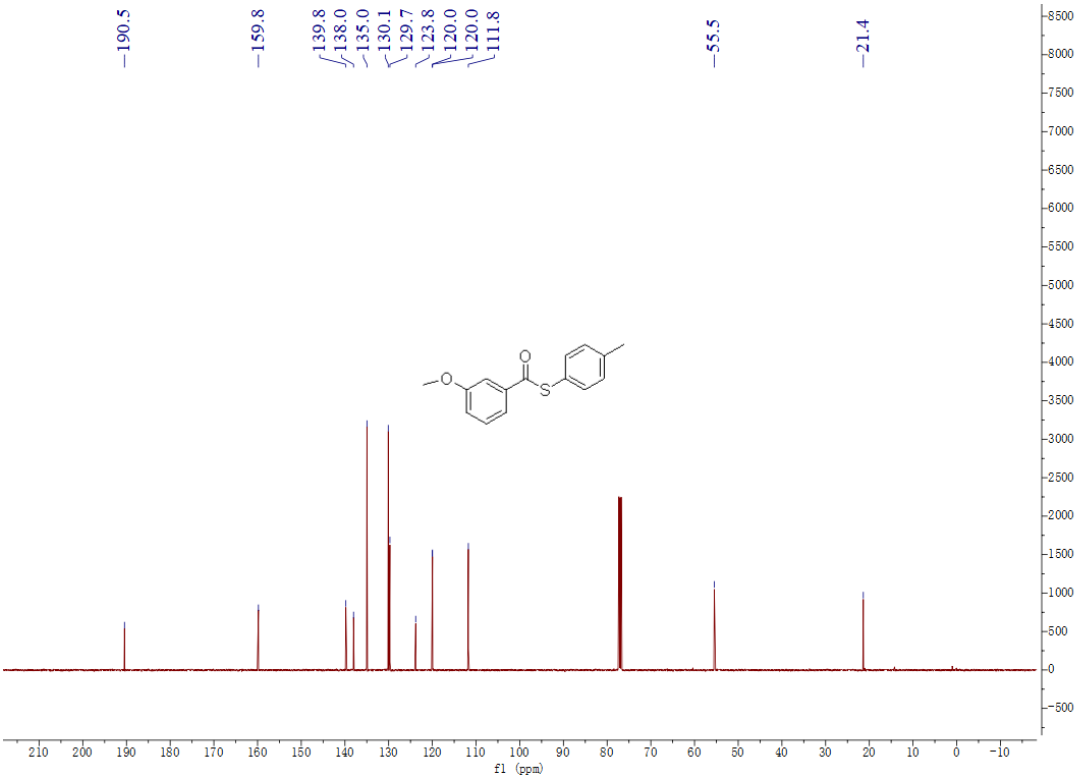
3aj, ^{13}C NMR (125 MHz, $CDCl_3$)



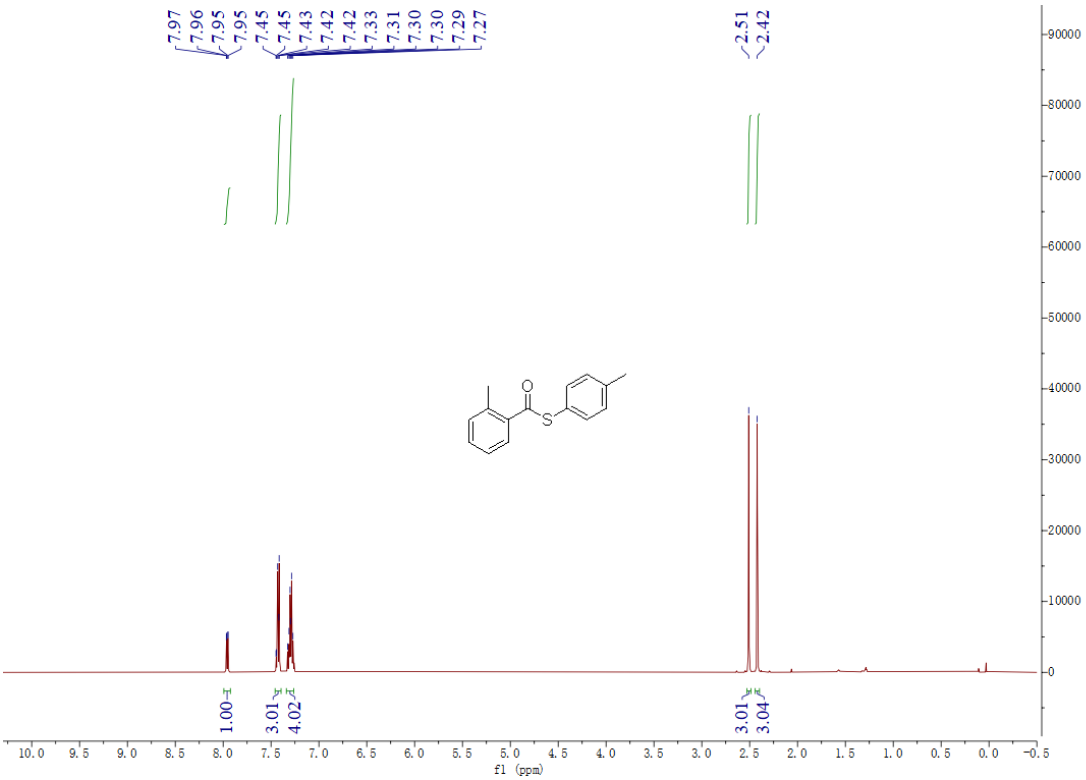
3ak, ^{1}H NMR (500 MHz, $CDCl_3$)



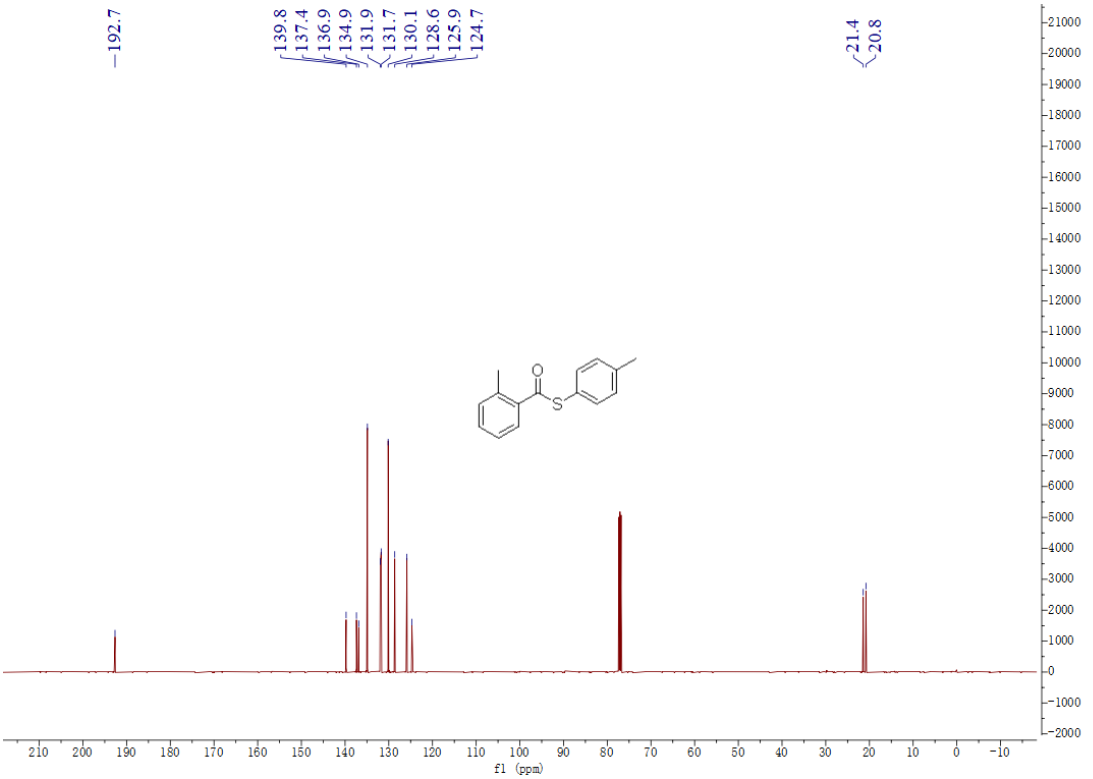
3ak, ^{13}C NMR (125 MHz, $CDCl_3$)



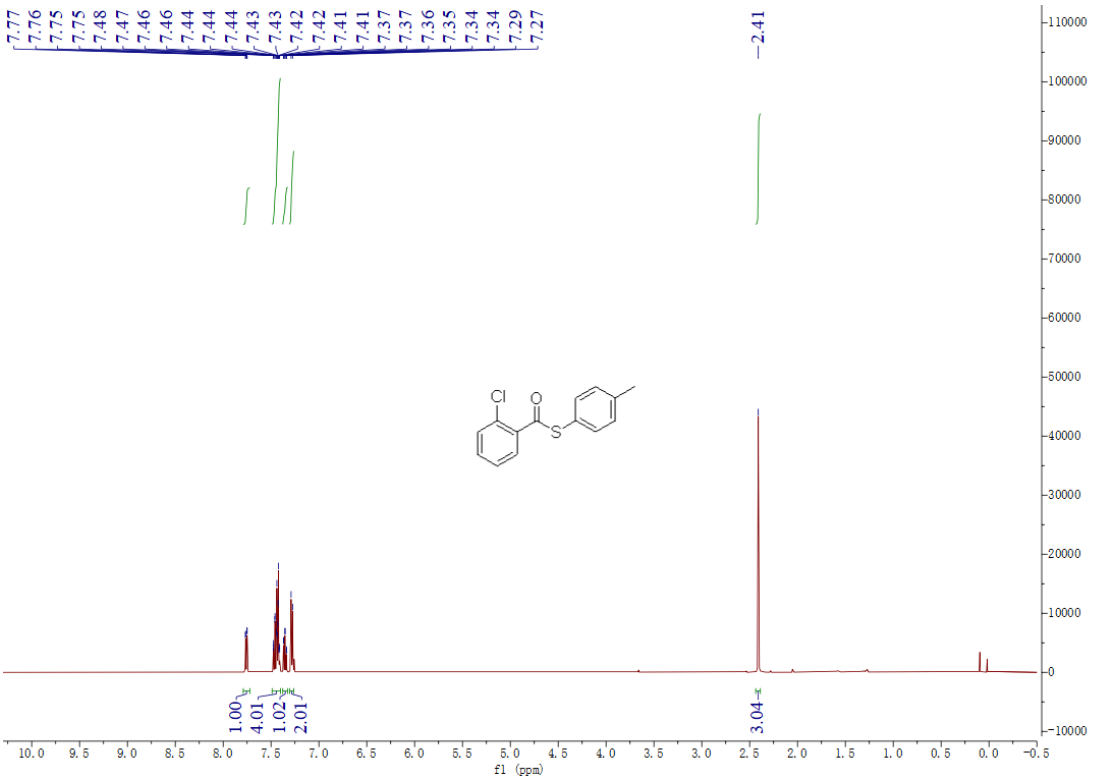
3al, ^{1}H NMR (500 MHz, $CDCl_3$)



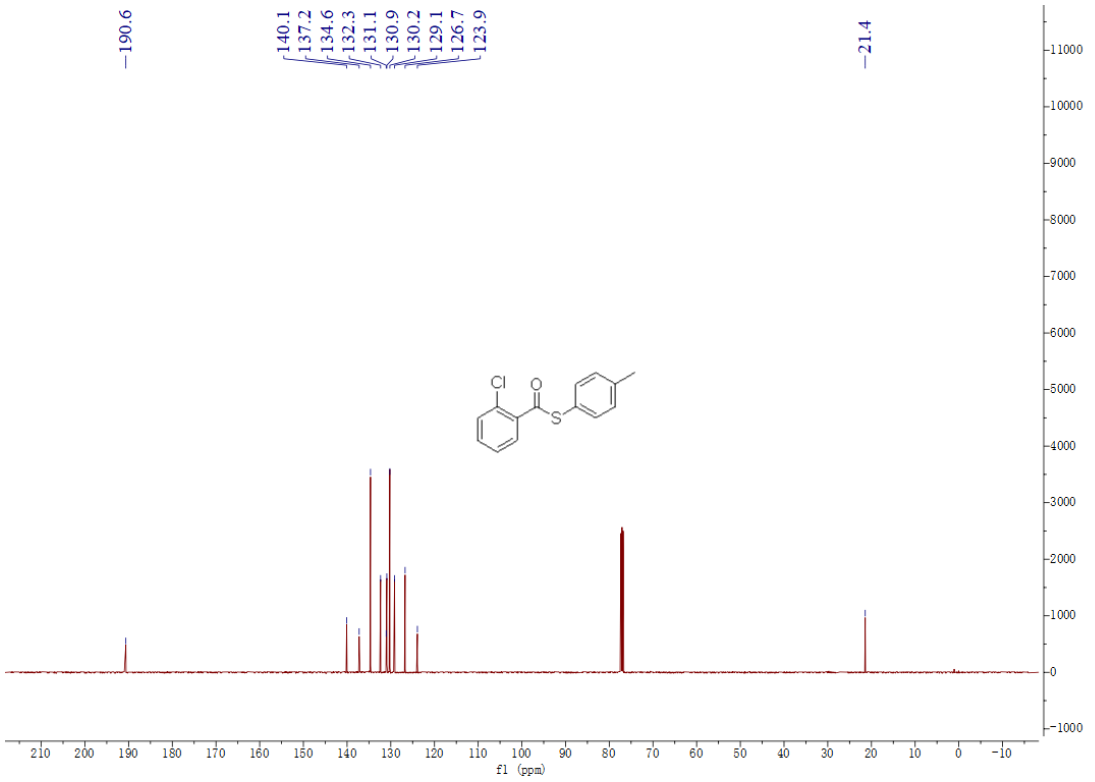
3al, ^{13}C NMR (125 MHz, $CDCl_3$)



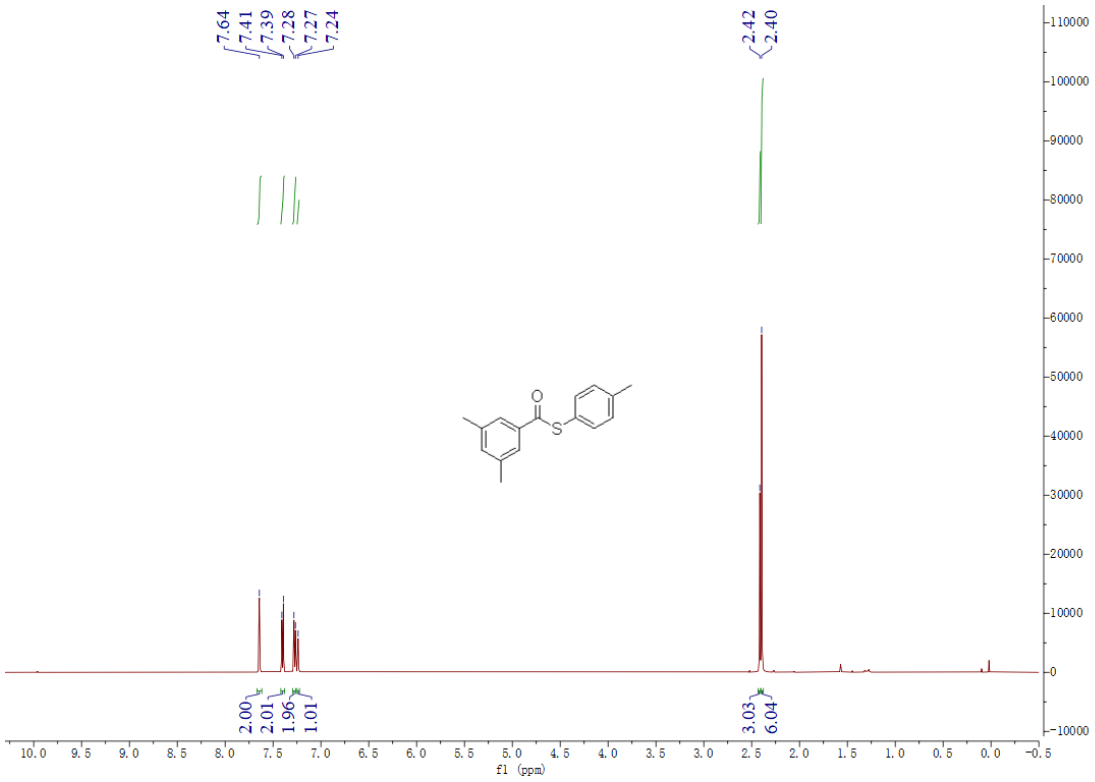
3am, ^{1}H NMR (500 MHz, $CDCl_3$)



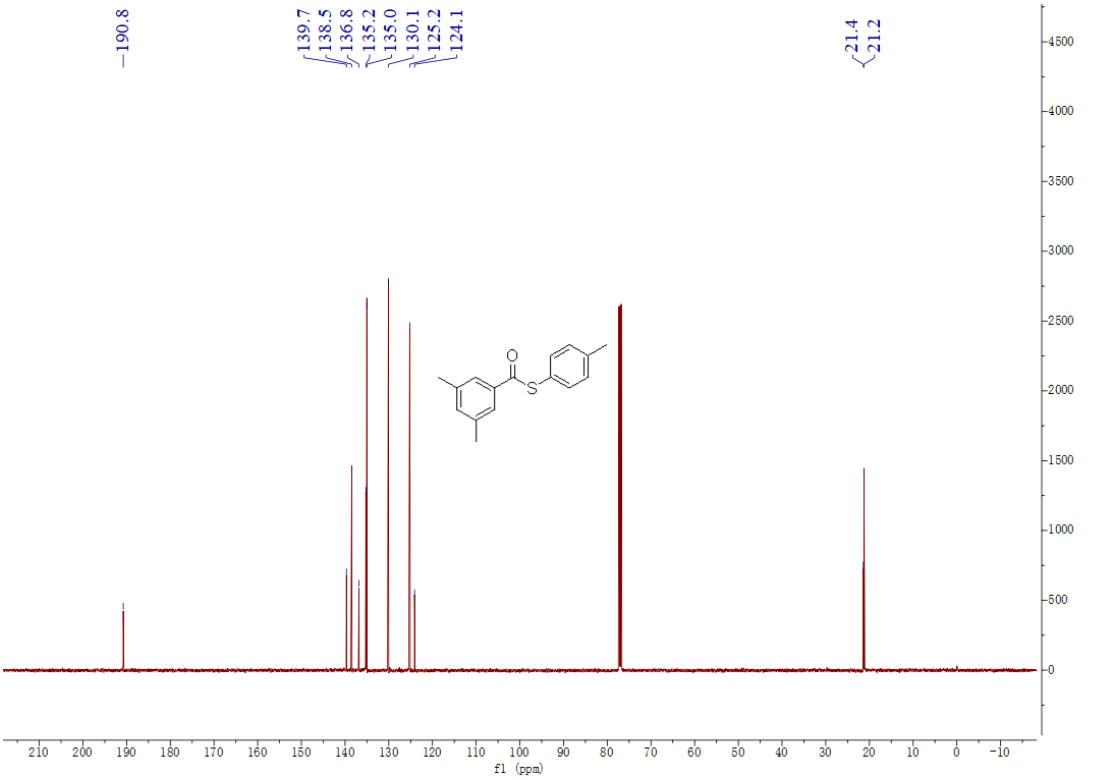
3am, ^{13}C NMR (125 MHz, $CDCl_3$)



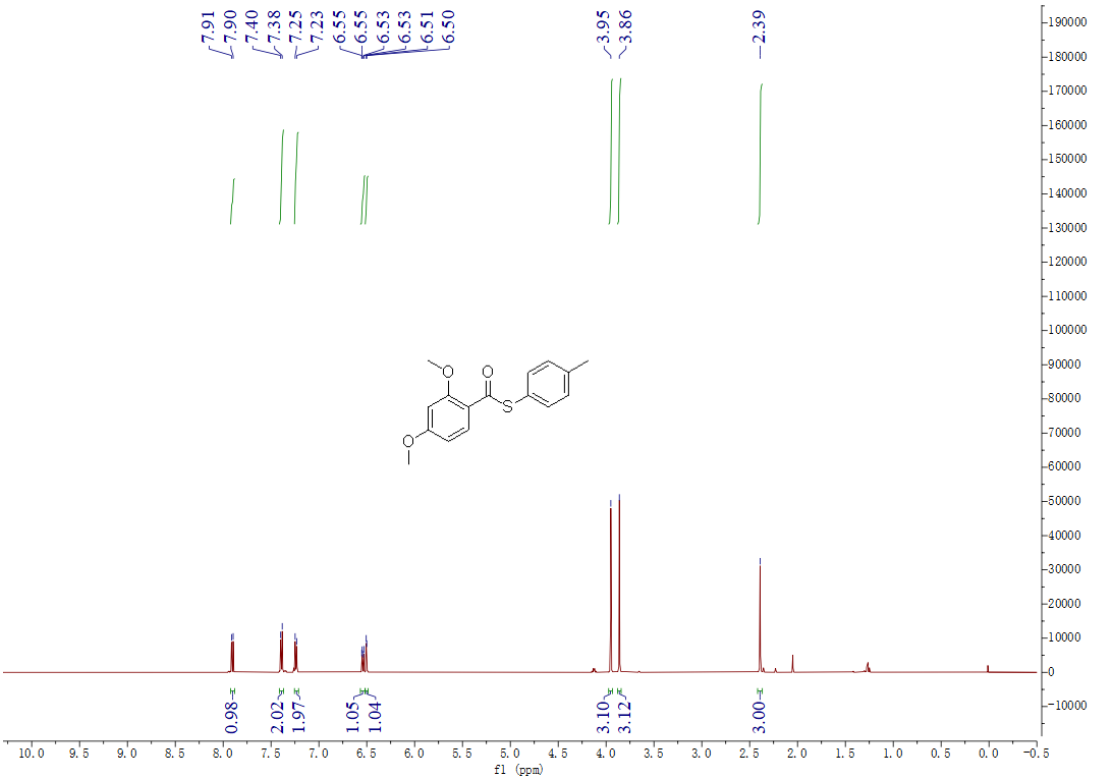
3an, ^{1}H NMR (500 MHz, $CDCl_3$)



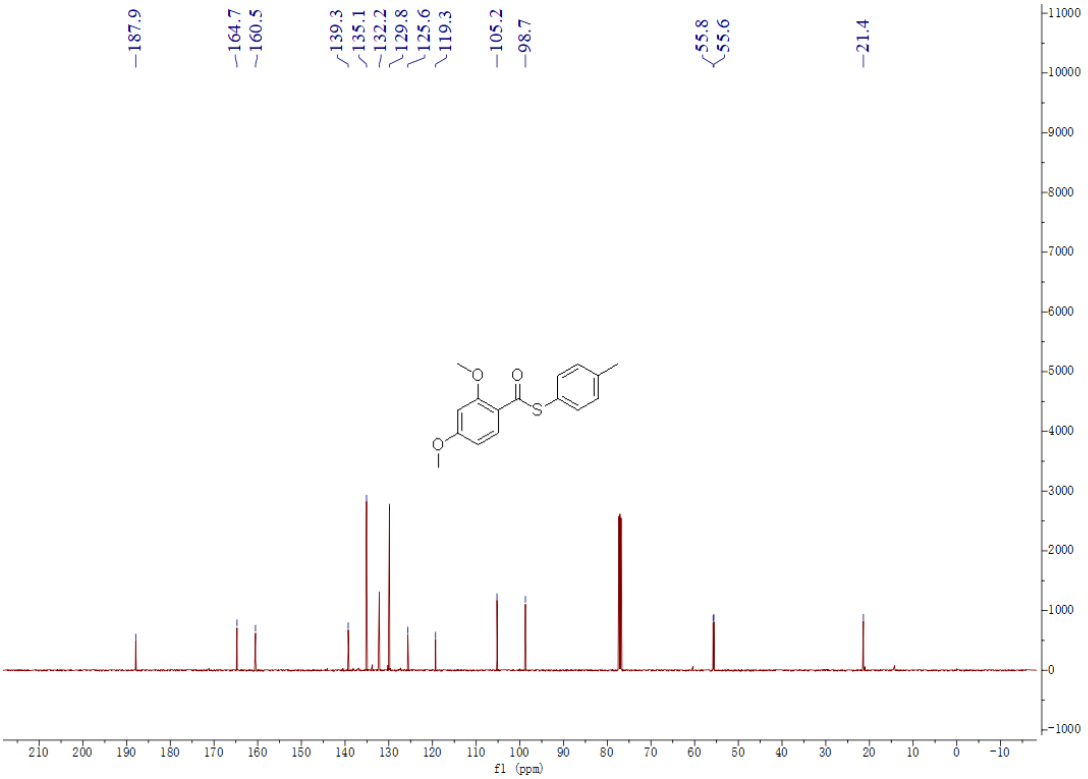
3an, ^{13}C NMR (125 MHz, $CDCl_3$)



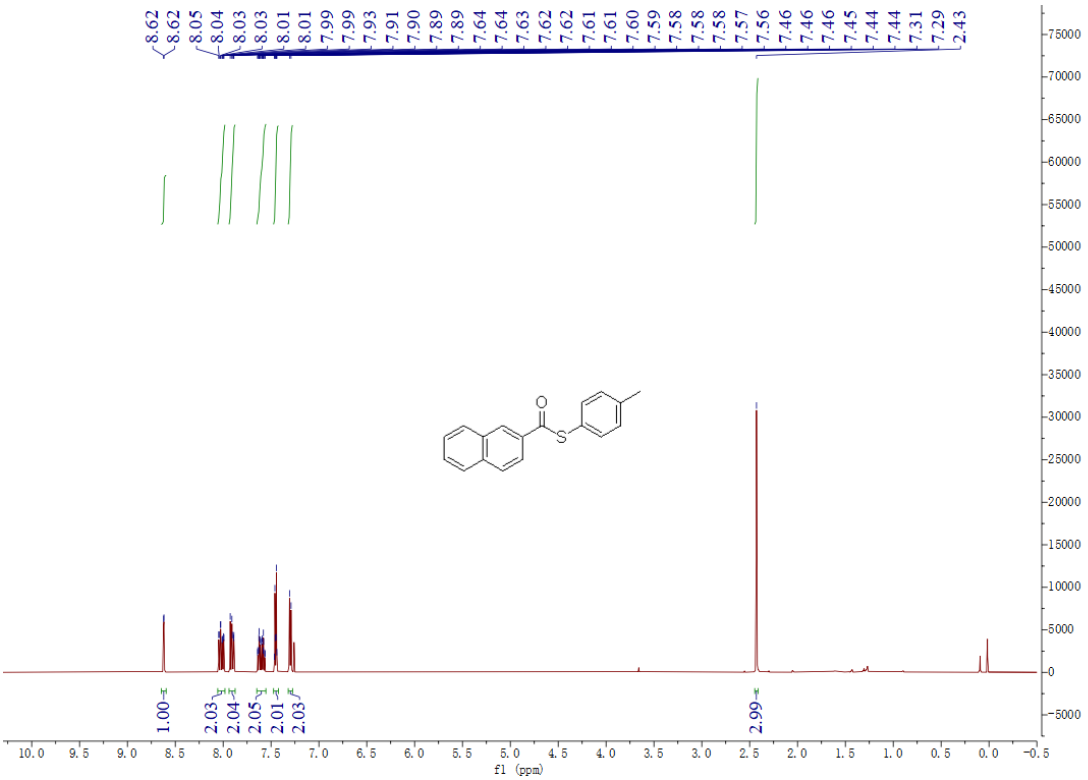
3ao, ^{1}H NMR (500 MHz, $CDCl_3$)



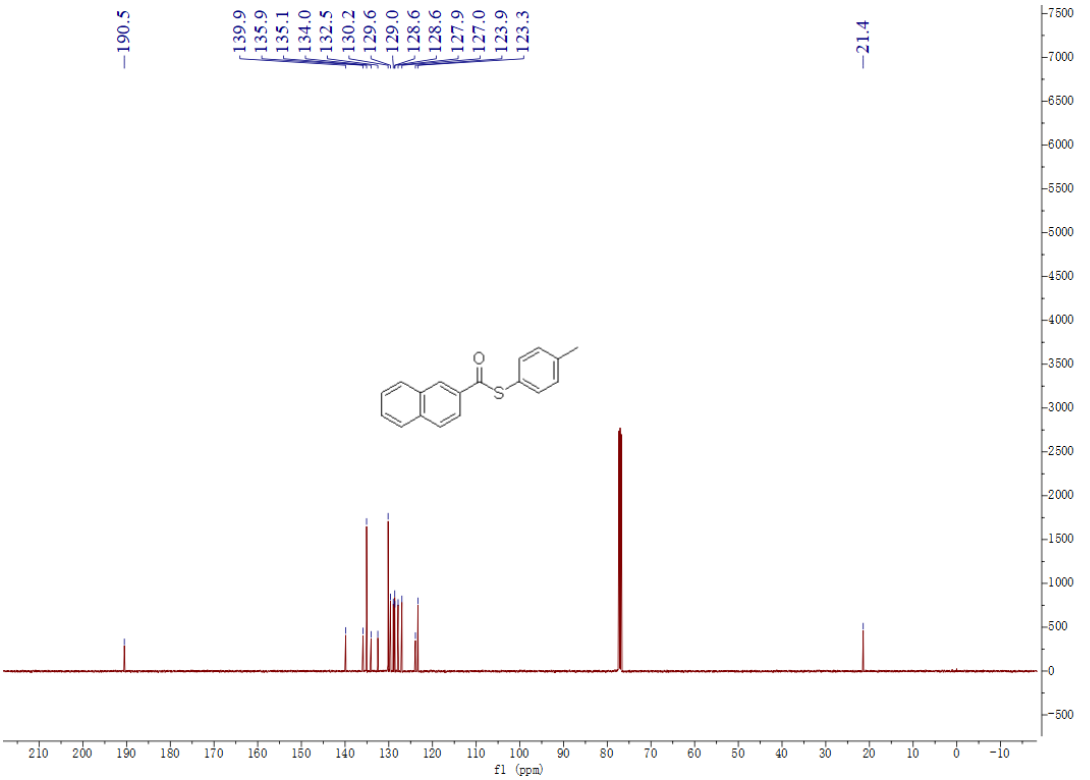
3ao, ^{13}C NMR (125 MHz, $CDCl_3$)



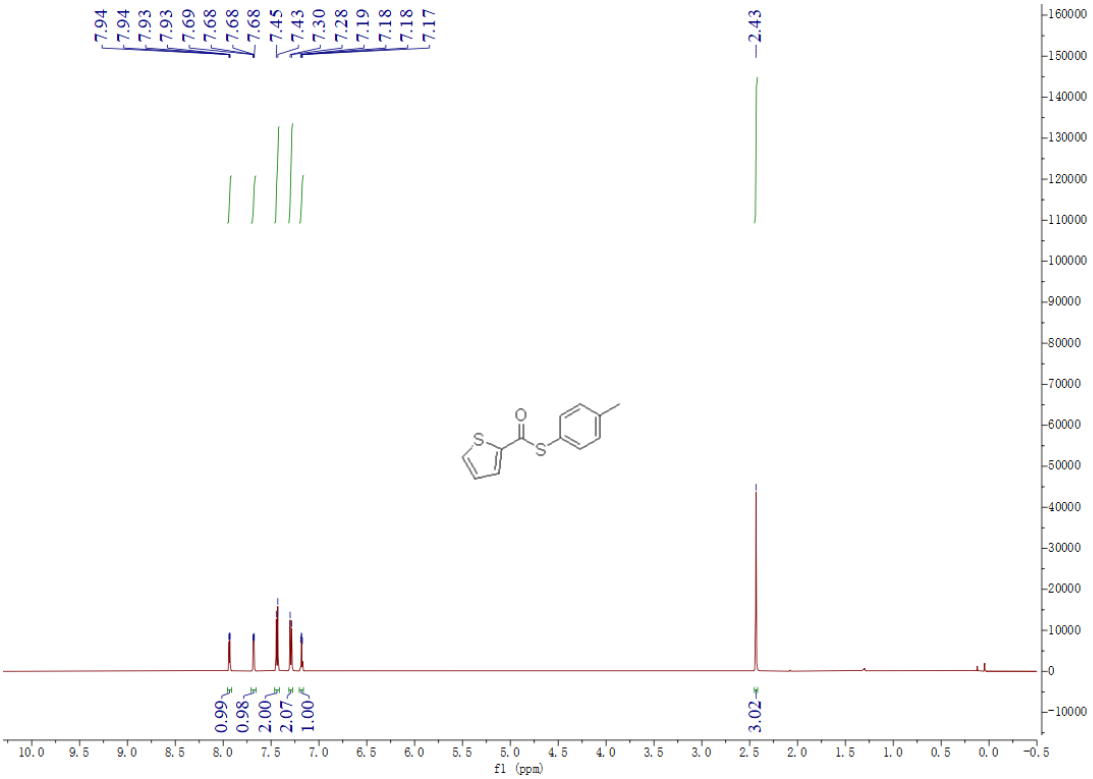
3ap, ^{1}H NMR (500 MHz, $CDCl_3$)



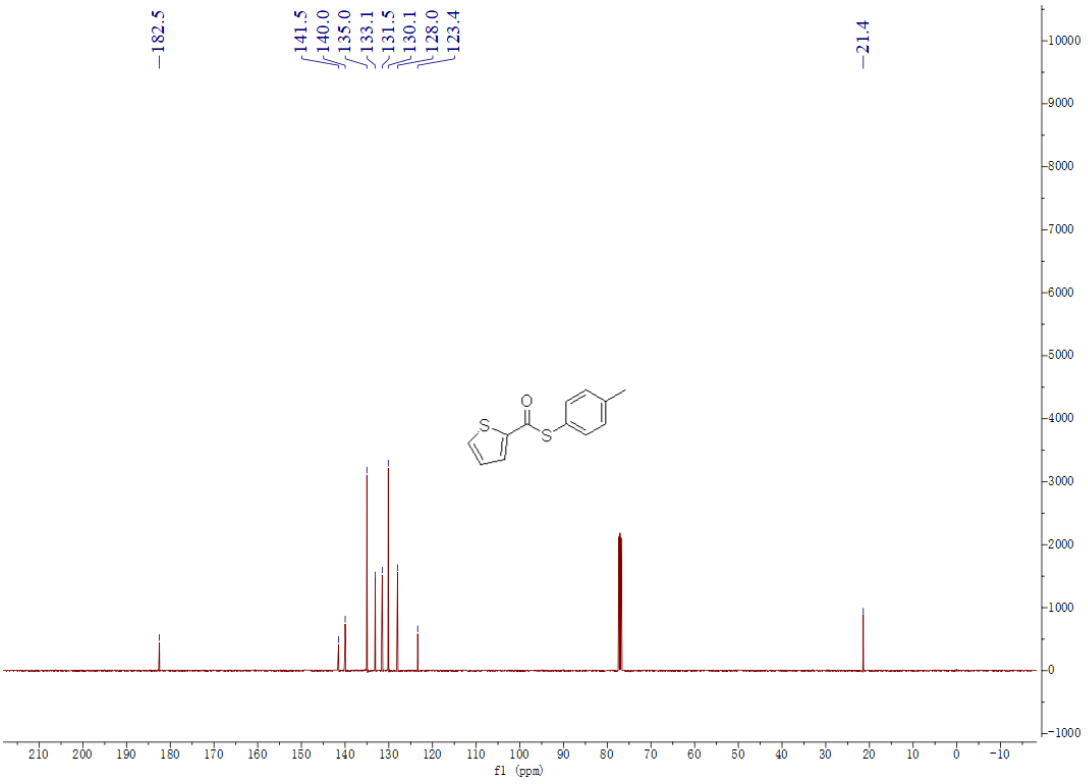
3ap, ^{13}C NMR (125 MHz, $CDCl_3$)



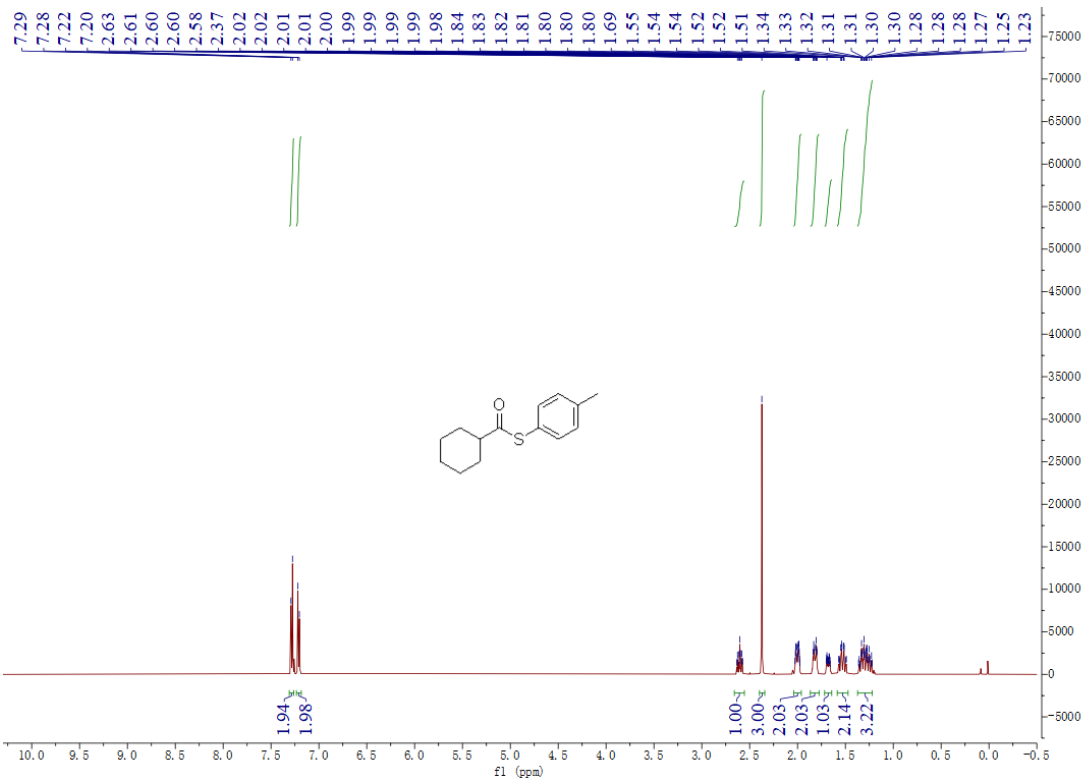
3aq, ^{1}H NMR (500 MHz, $CDCl_3$)



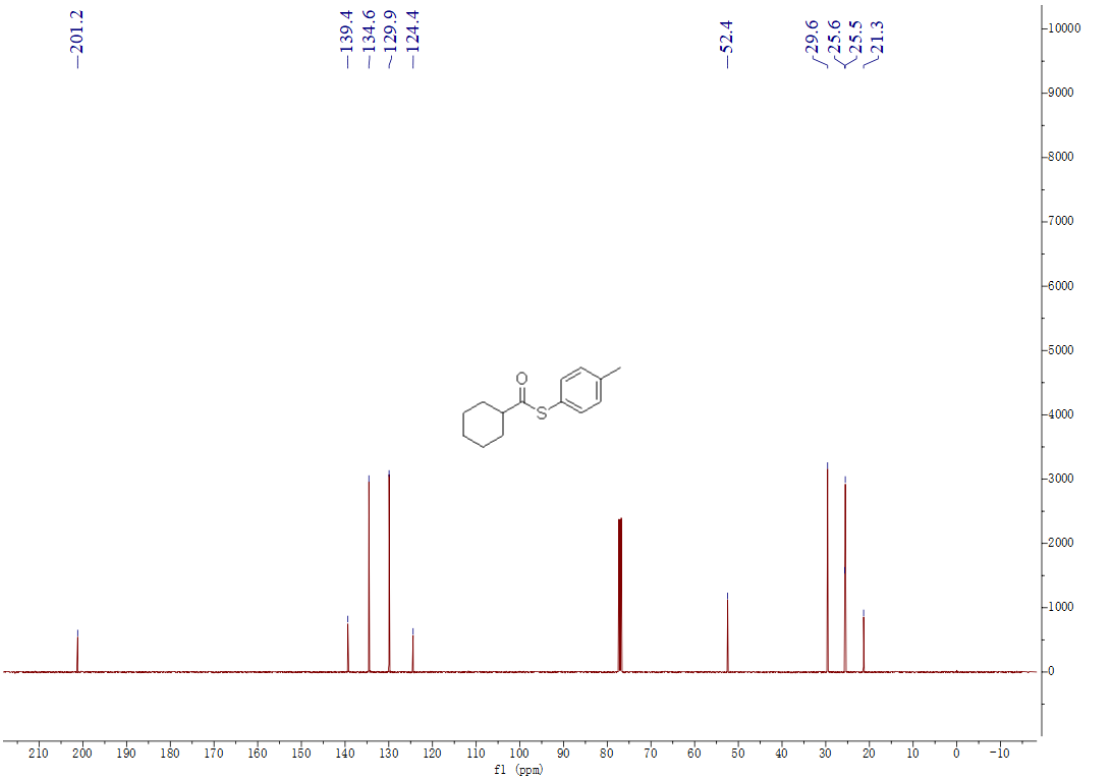
3aq, ^{13}C NMR (125 MHz, $CDCl_3$)



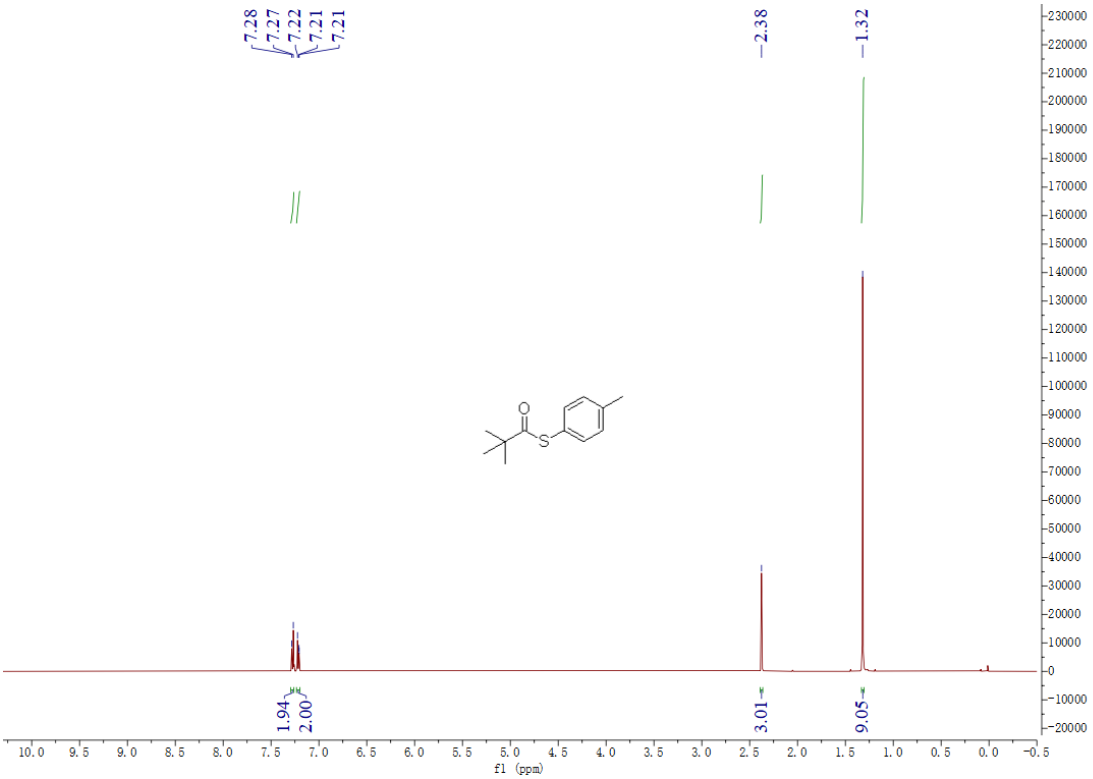
3ar, ^{1}H NMR (500 MHz, $CDCl_3$)



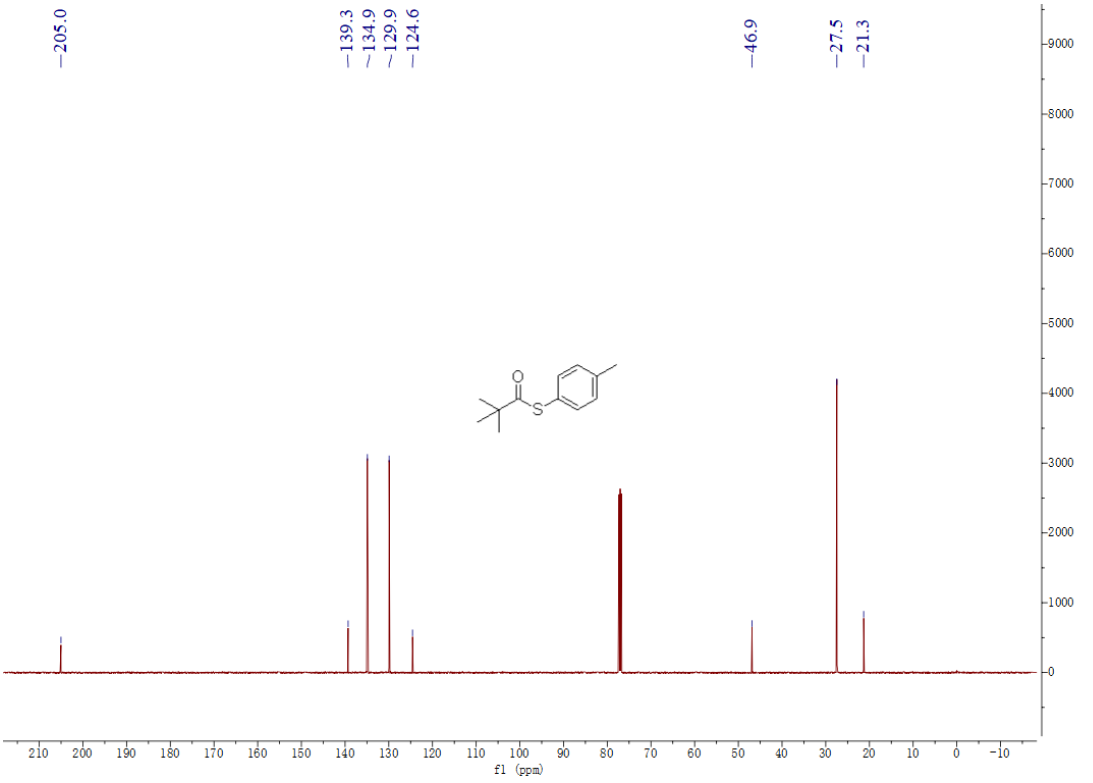
3ar, ^{13}C NMR (125 MHz, $CDCl_3$)



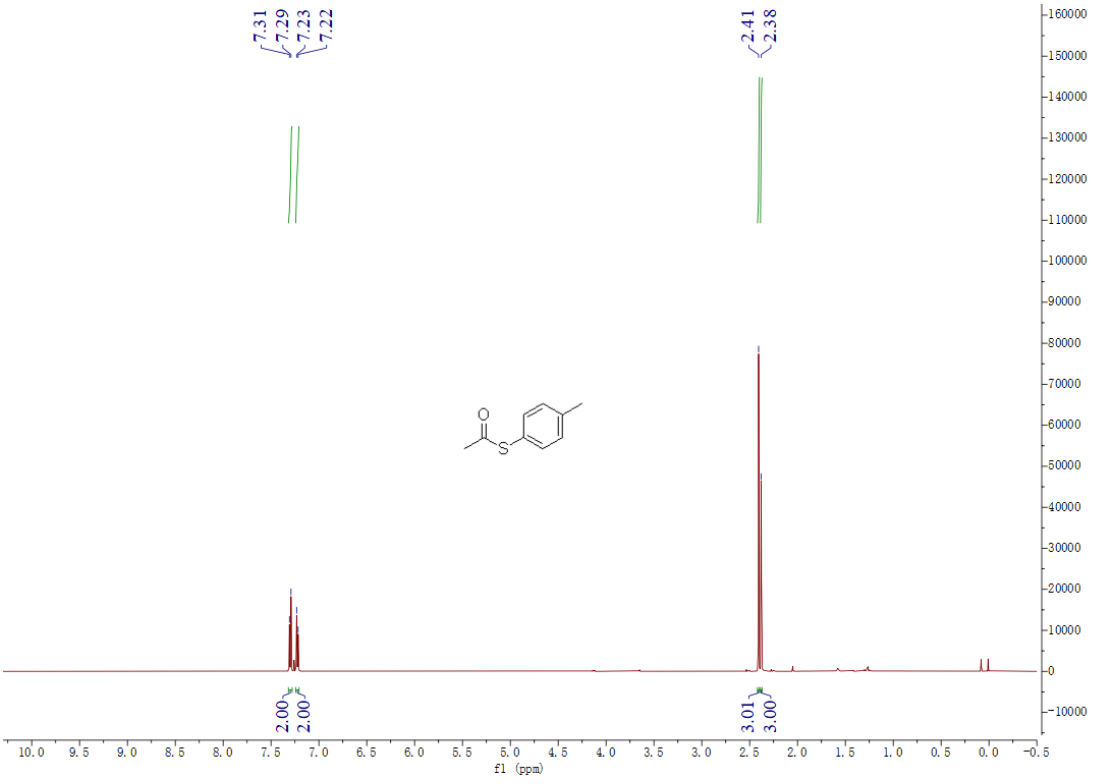
3as, ^{1}H NMR (500 MHz, $CDCl_3$)



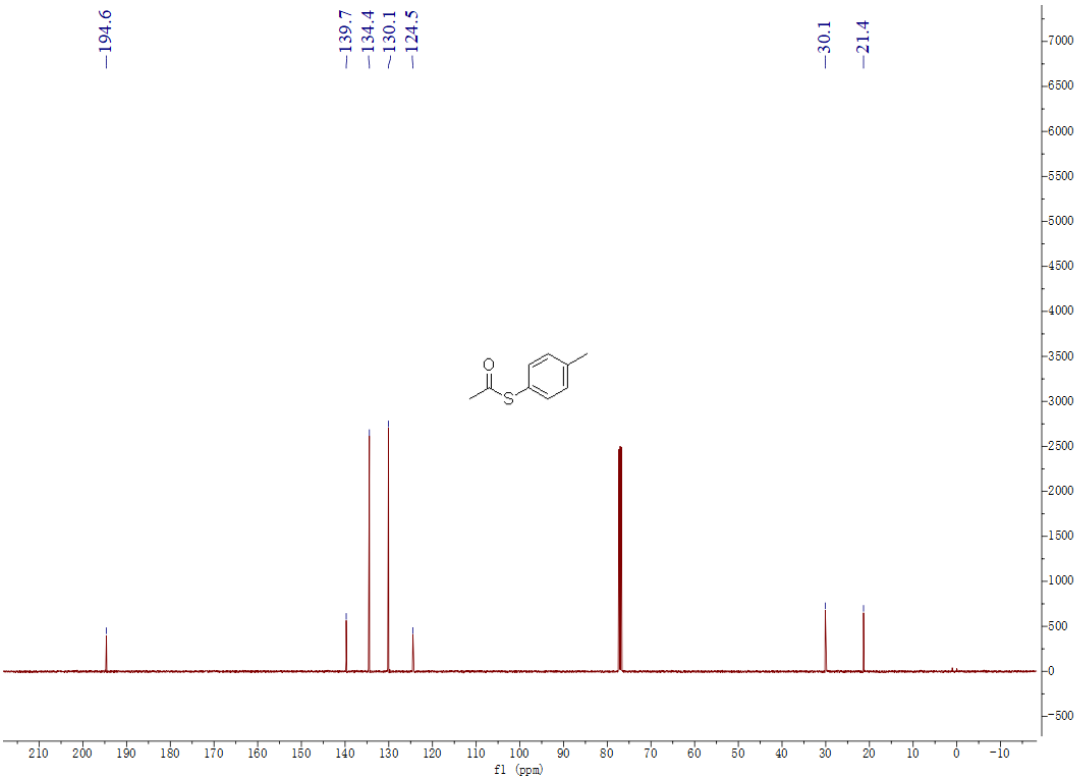
3as, ^{13}C NMR (125 MHz, $CDCl_3$)



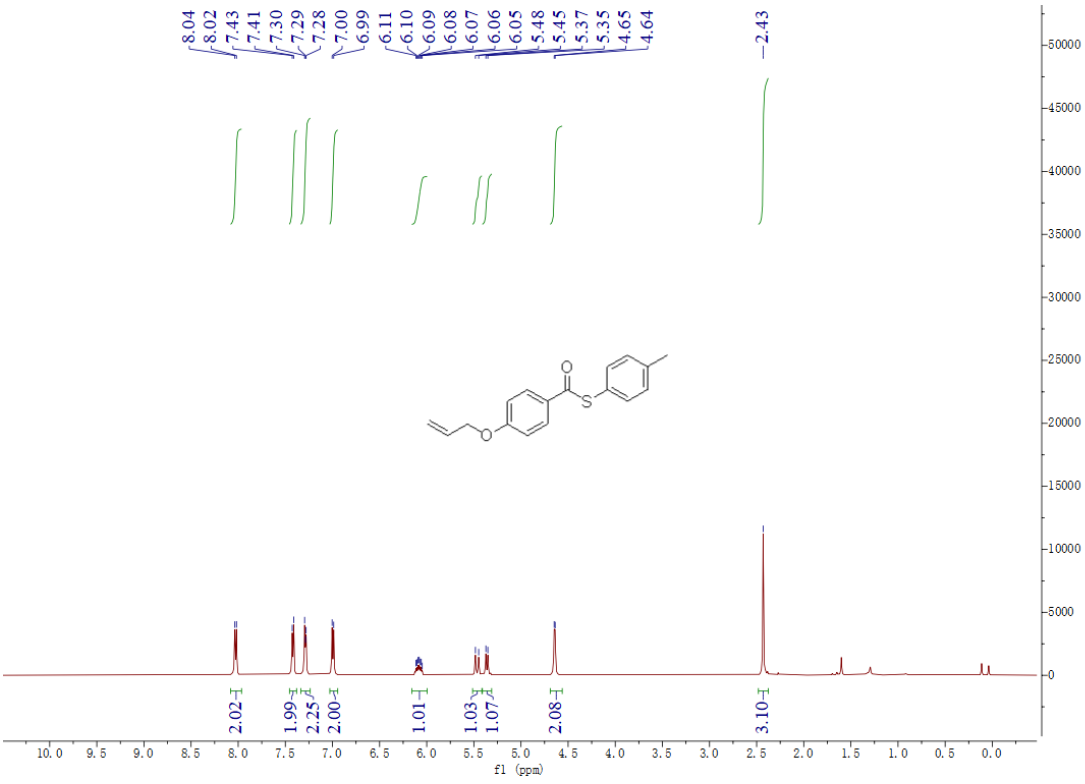
3at, ^{1}H NMR (500 MHz, $CDCl_3$)



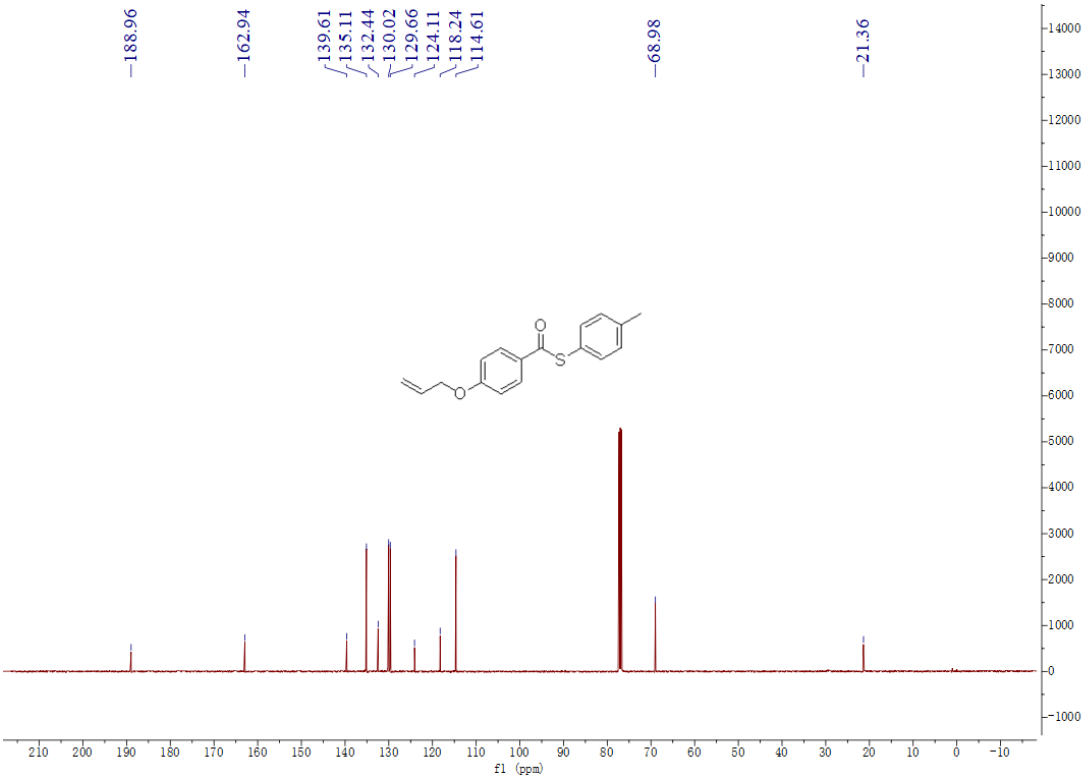
3at, ^{13}C NMR (125 MHz, $CDCl_3$)



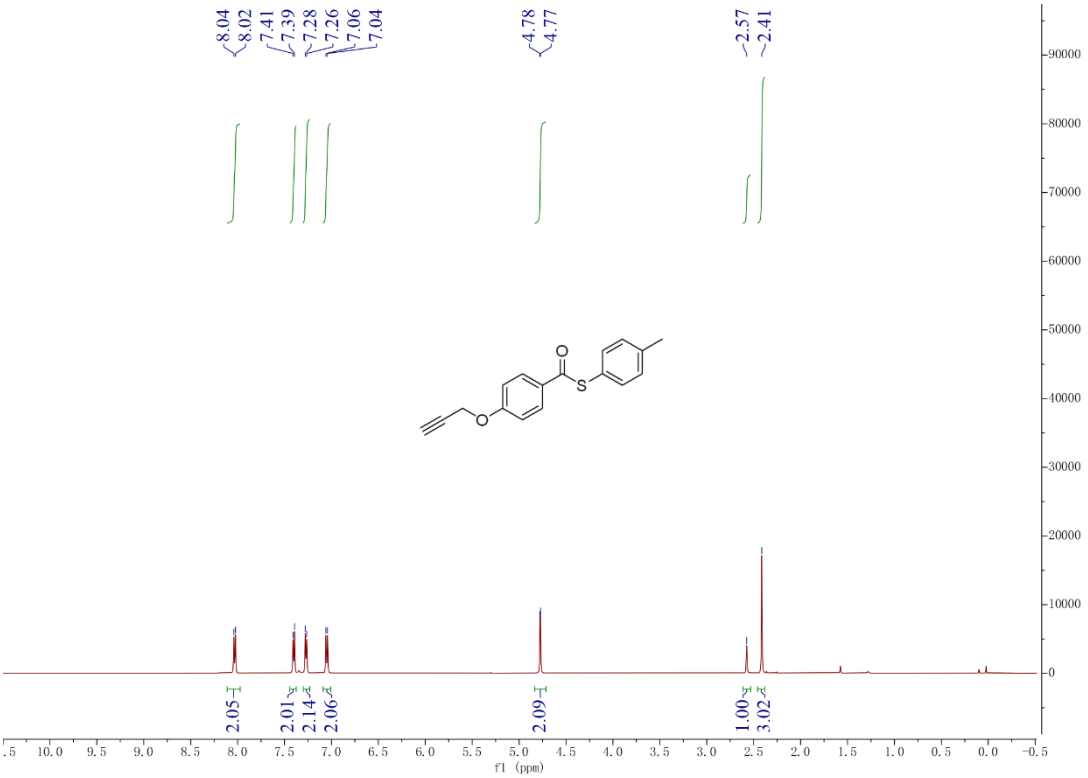
3au, ^{1}H NMR (500 MHz, $CDCl_3$)



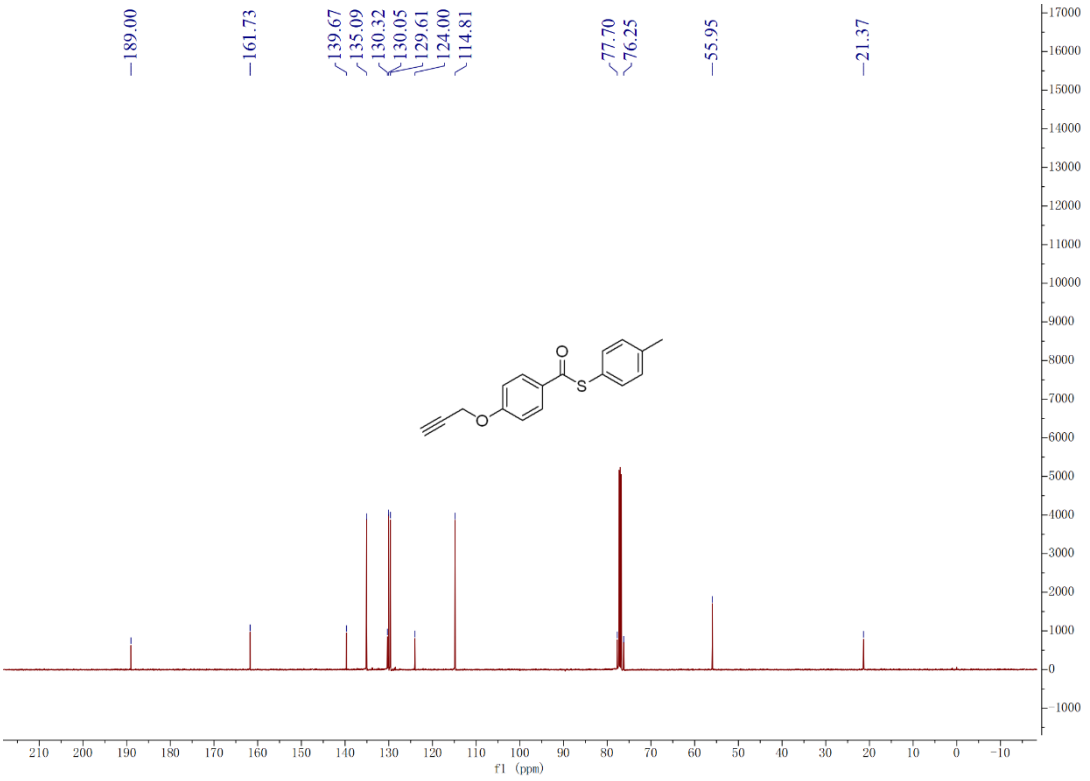
3au, ^{13}C NMR (125 MHz, $CDCl_3$)



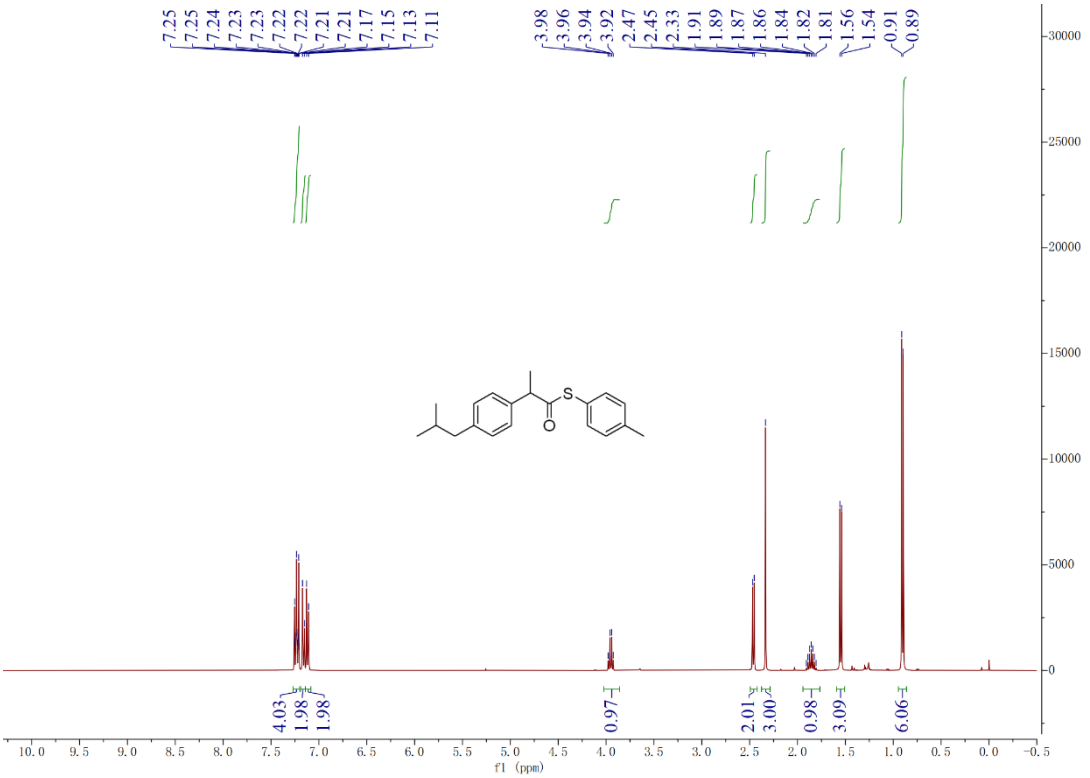
3av, ^{1}H NMR (500 MHz, $CDCl_3$)



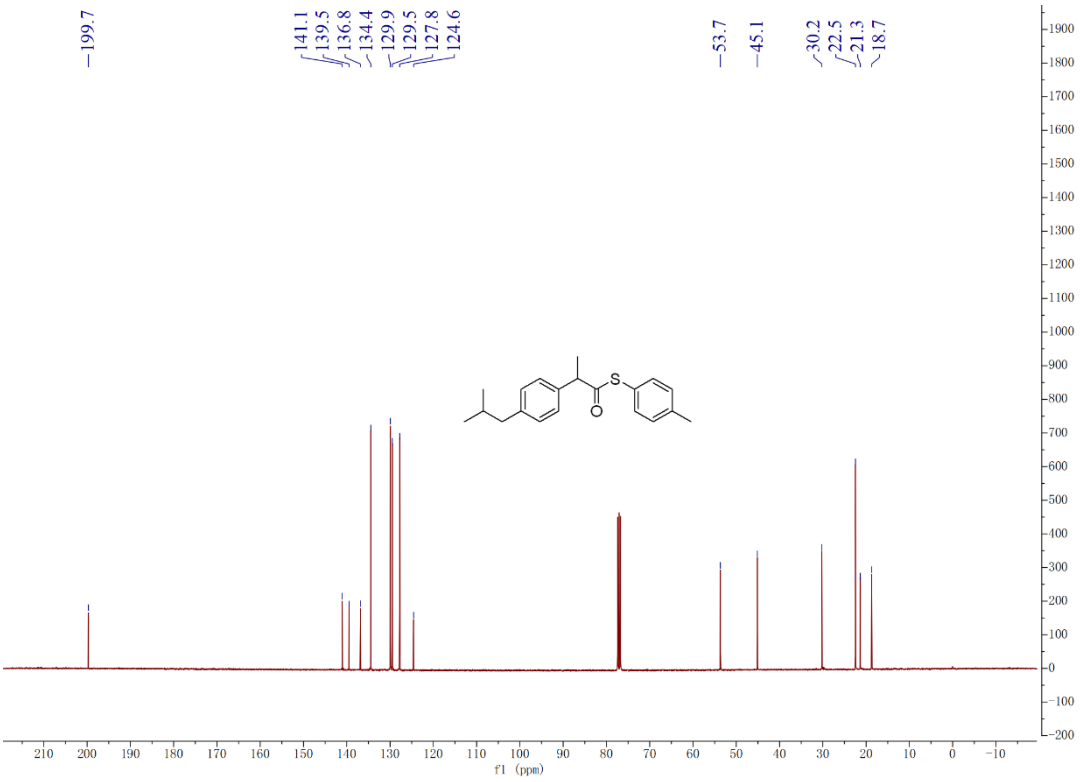
3av, ^{13}C NMR (125 MHz, $CDCl_3$)



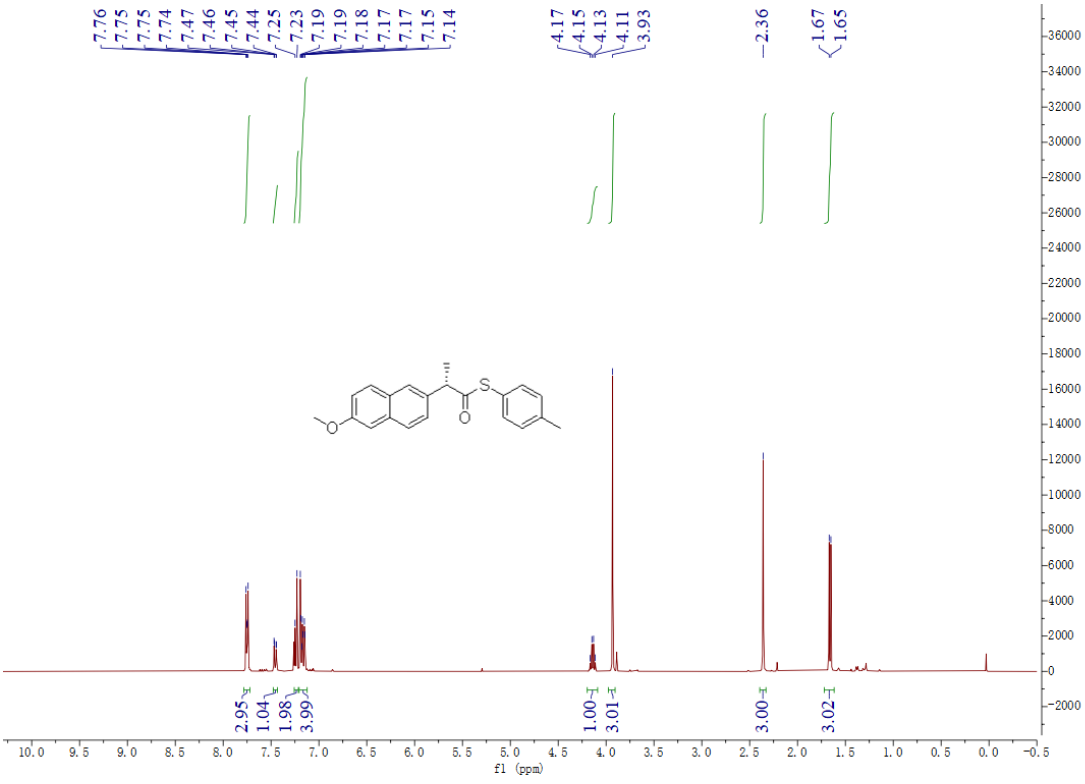
3aw, ^{1}H NMR (400 MHz, $CDCl_3$)



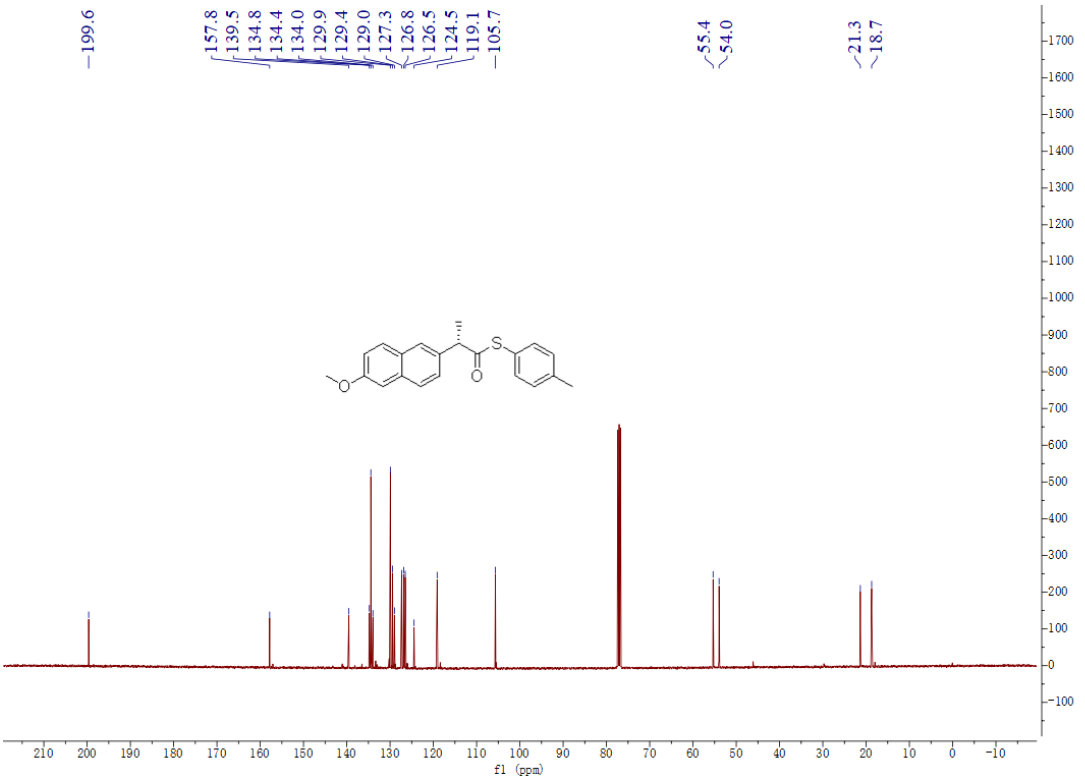
3aw, ^{13}C NMR (100 MHz, $CDCl_3$)



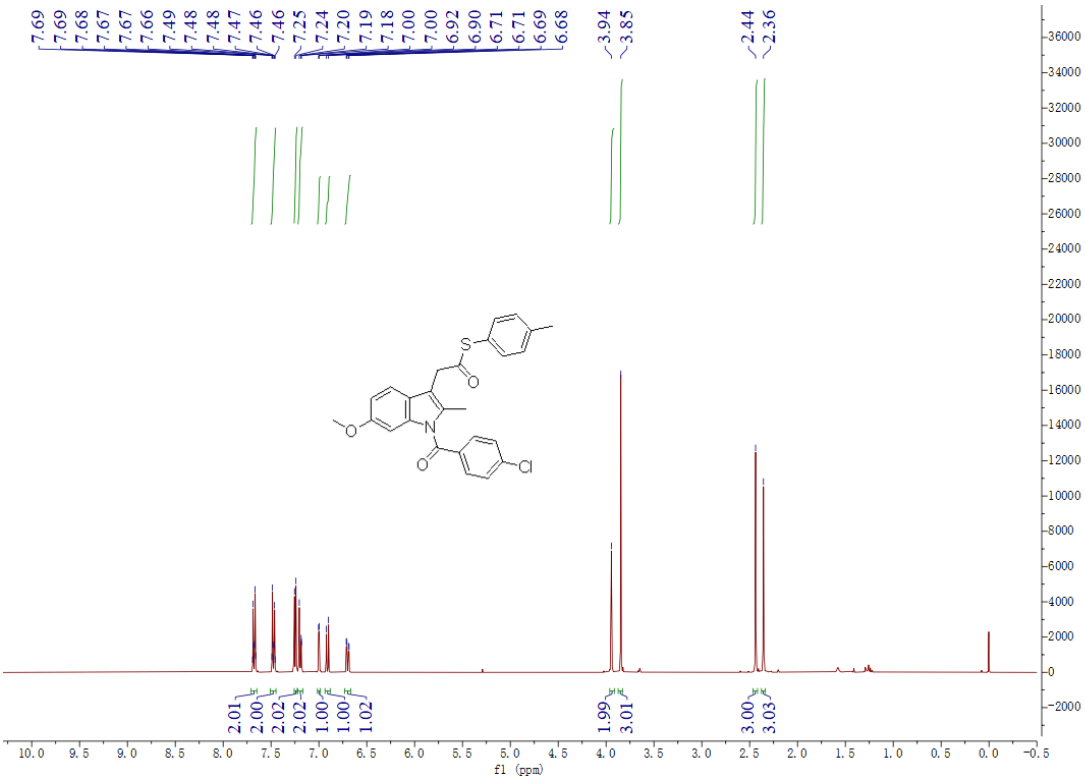
3ax, ^{1}H NMR (400 MHz, $CDCl_3$)



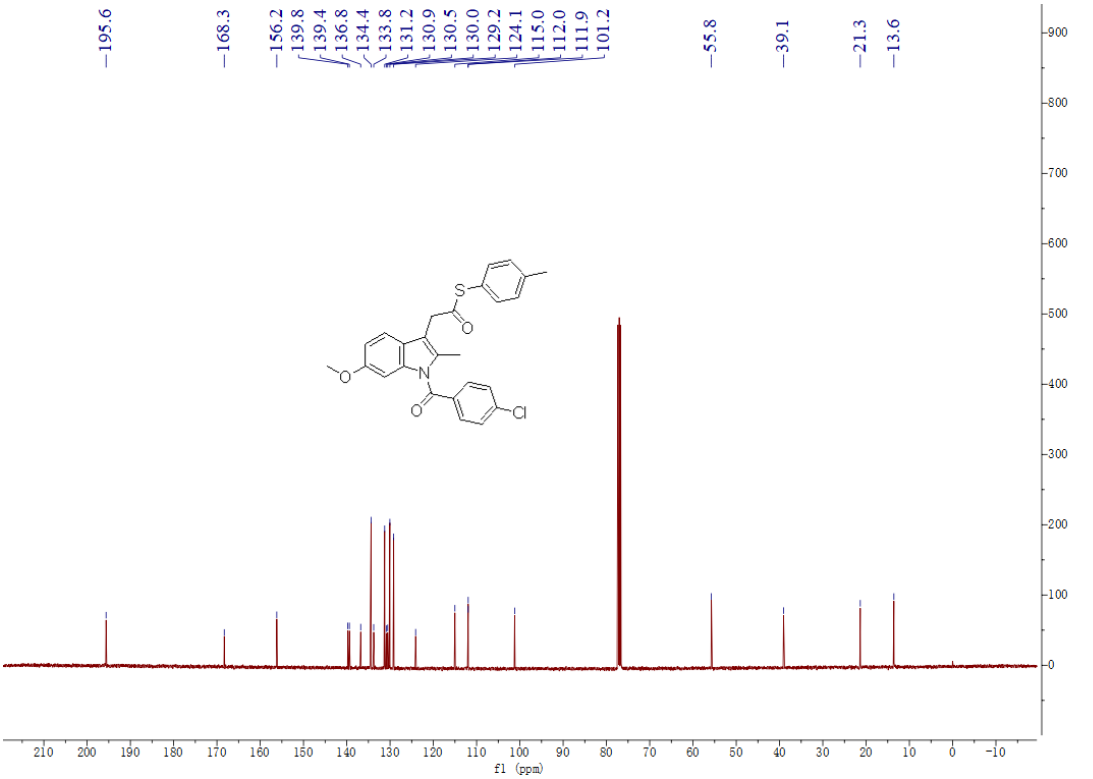
3ax, ^{13}C NMR (100 MHz, $CDCl_3$)



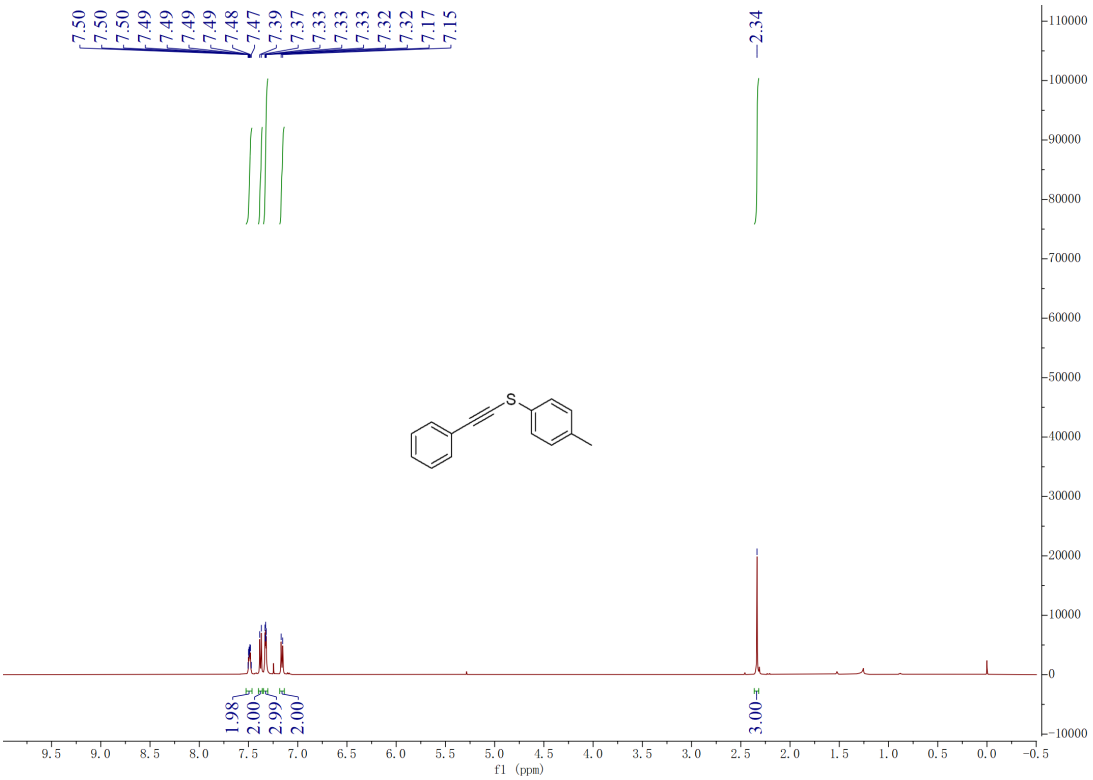
3ay, ^{1}H NMR (400 MHz, $CDCl_3$)



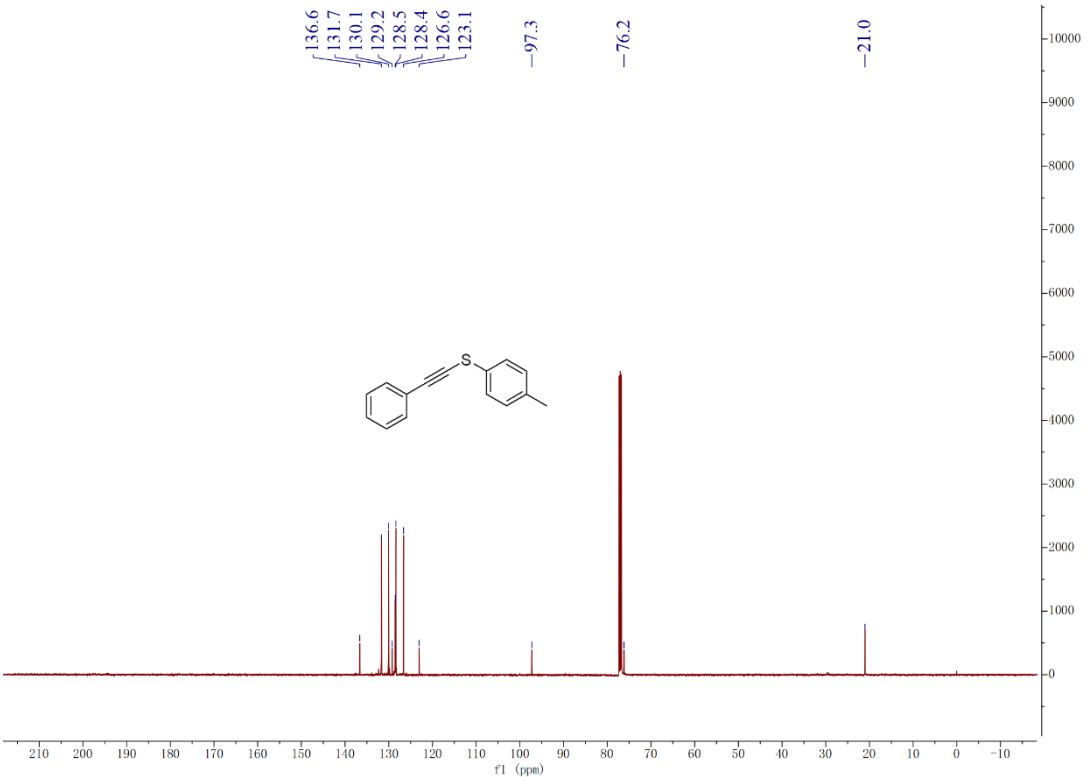
3ay, ^{13}C NMR (100 MHz, $CDCl_3$)



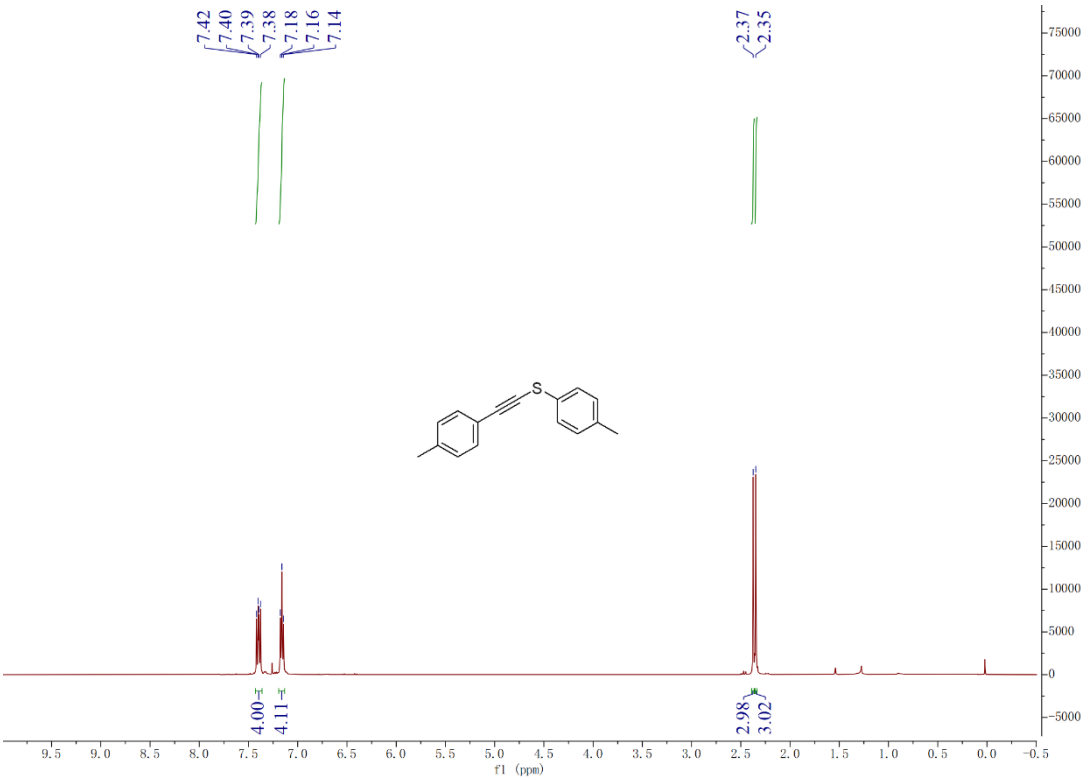
7a, ^{1}H NMR (500 MHz, $CDCl_3$)



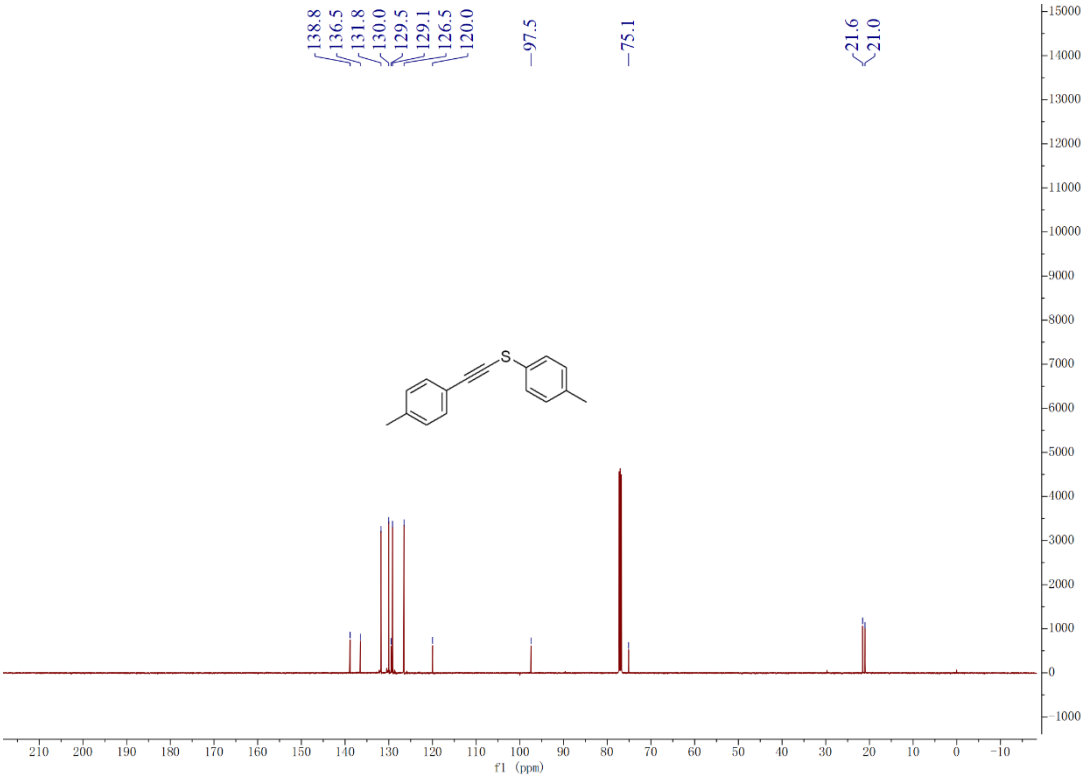
7a, ^{13}C NMR (125 MHz, $CDCl_3$)



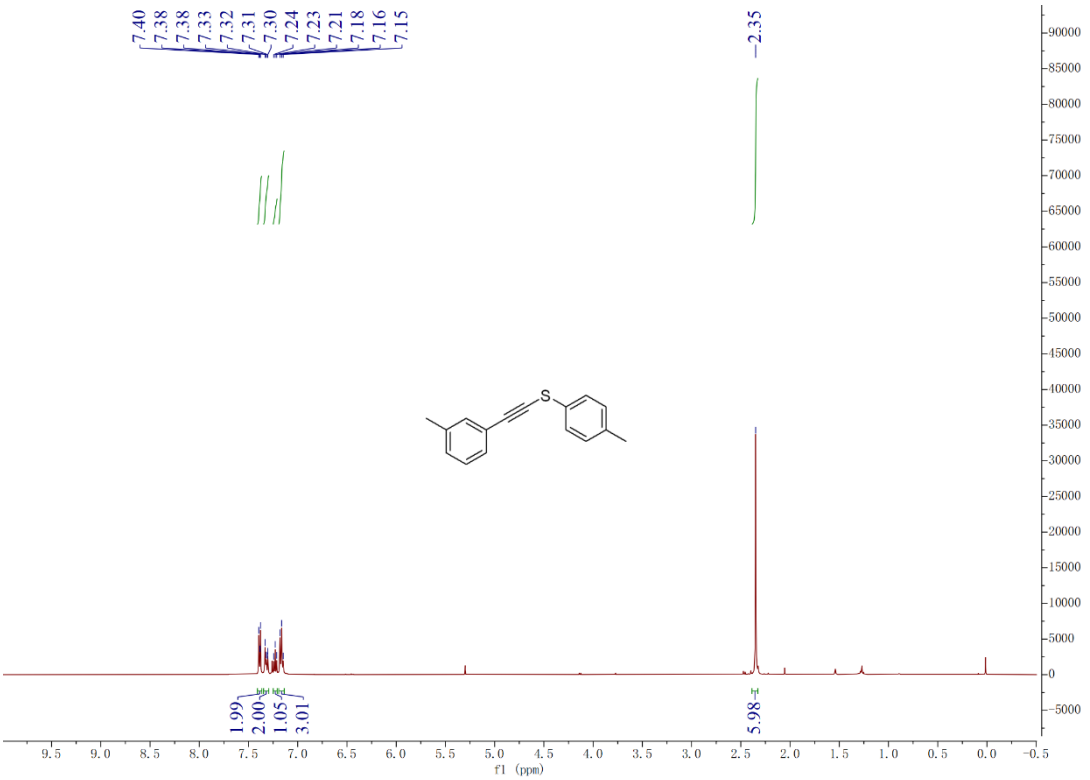
7b, ^{1}H NMR (500 MHz, $CDCl_3$)



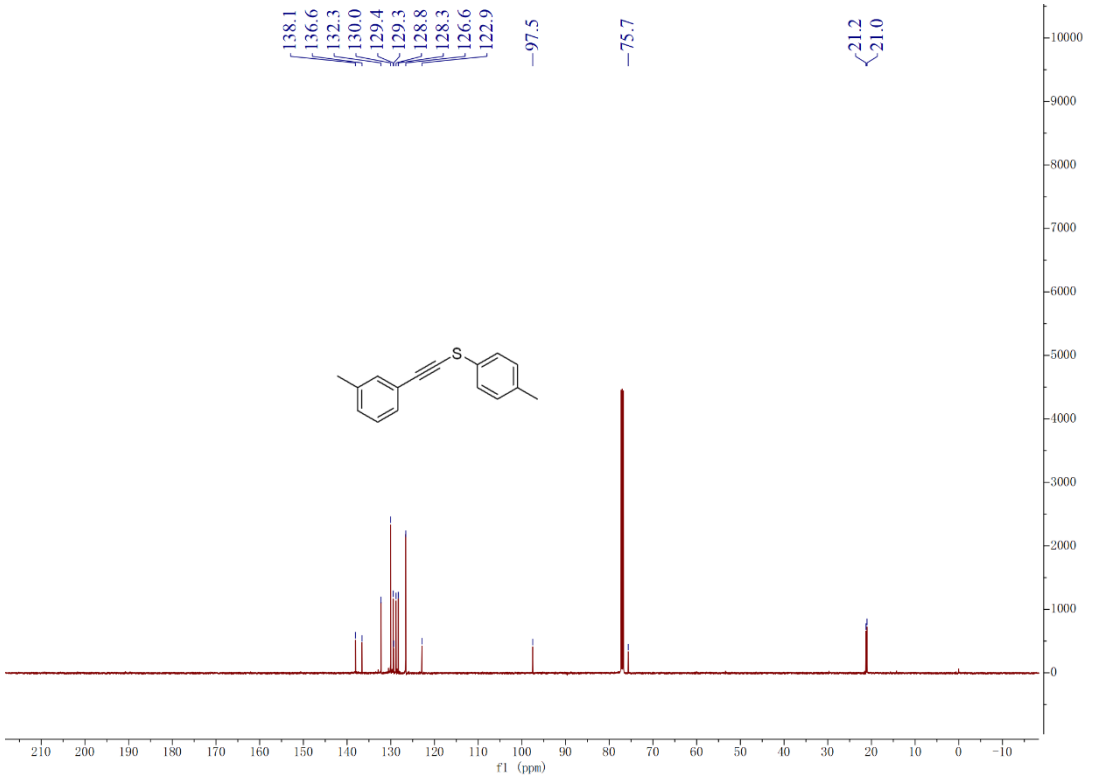
7b, ^{13}C NMR (125 MHz, $CDCl_3$)



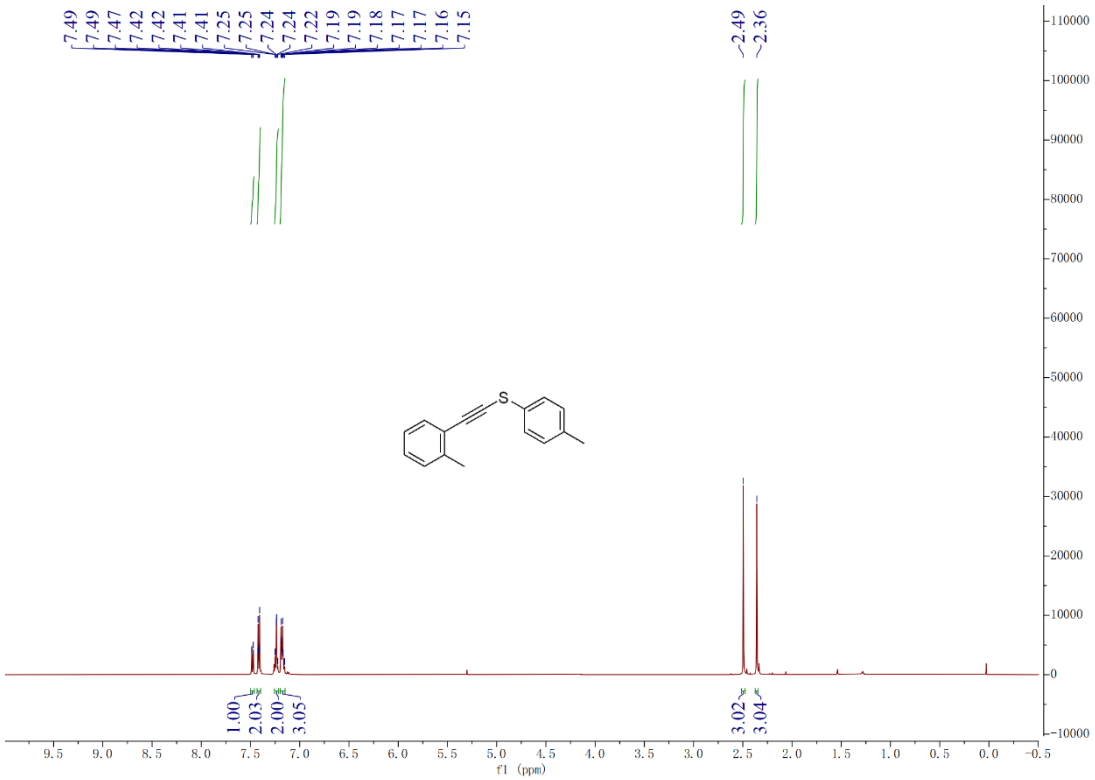
7c, ^{1}H NMR (500 MHz, $CDCl_3$)



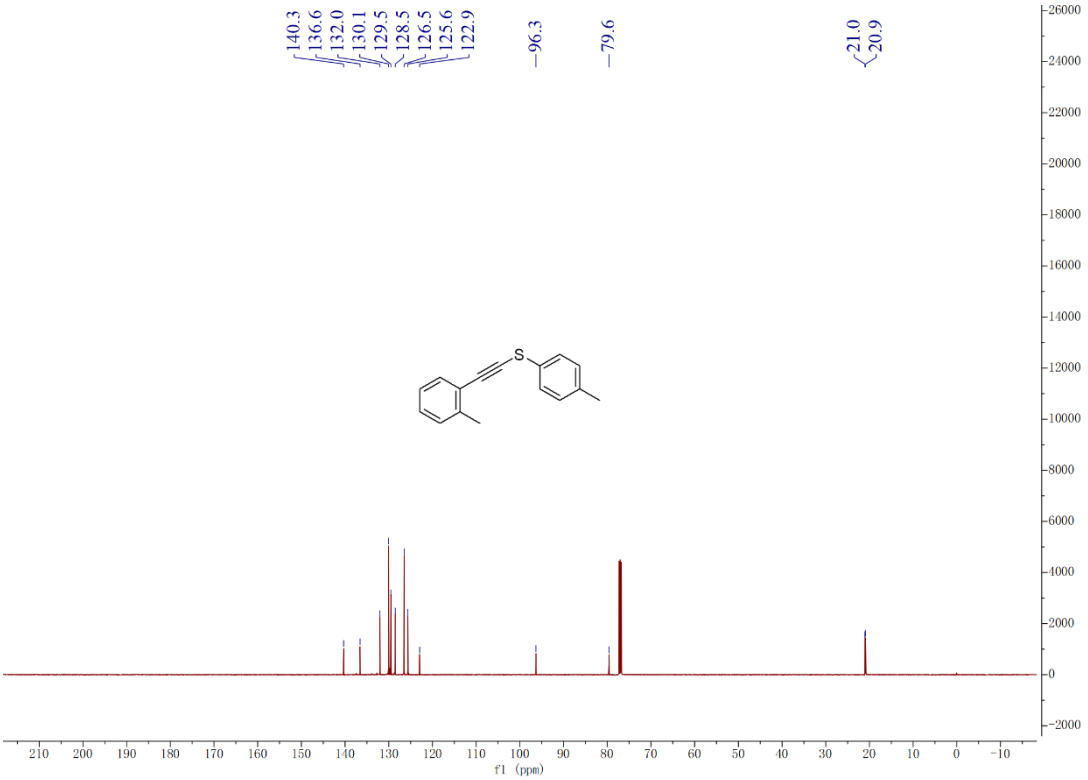
7c, ^{13}C NMR (125 MHz, $CDCl_3$)



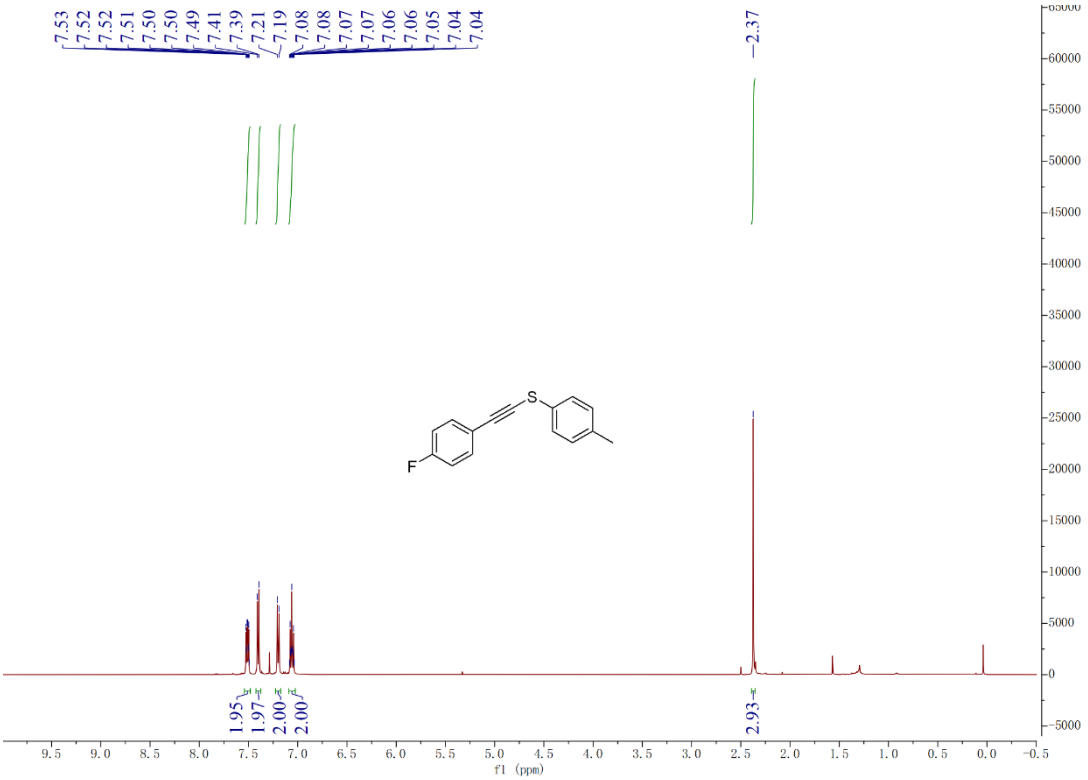
7d, ^{1}H NMR (500 MHz, $CDCl_3$)



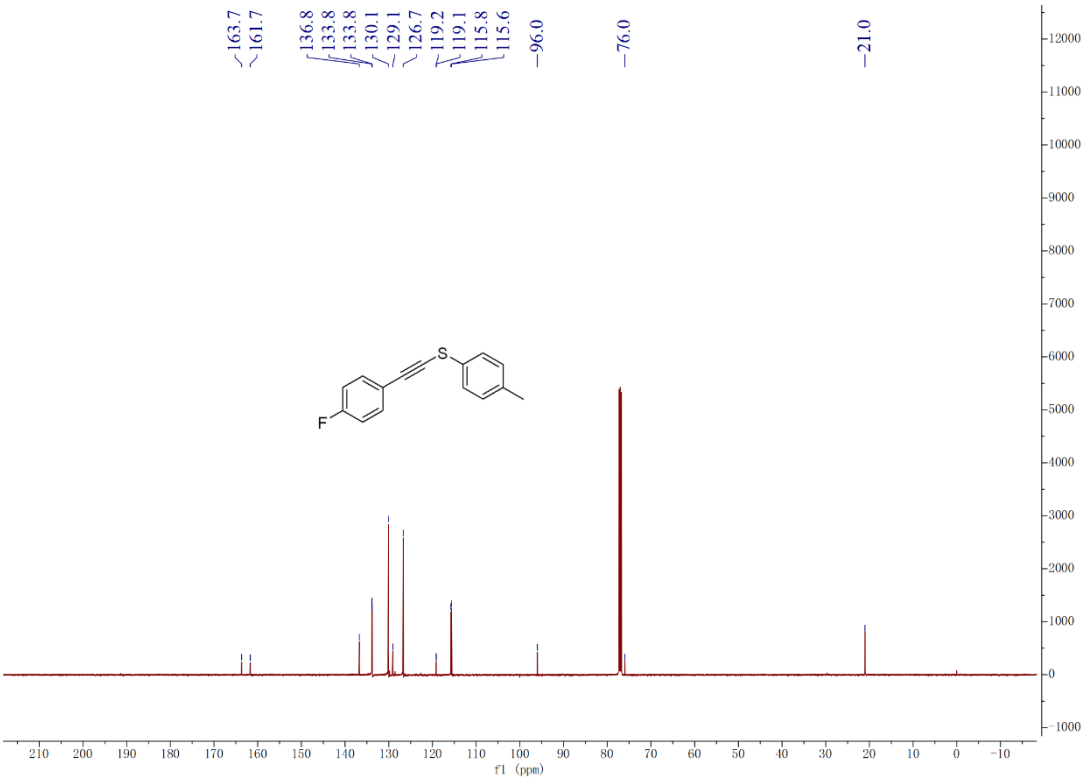
7d, ^{13}C NMR (125 MHz, $CDCl_3$)



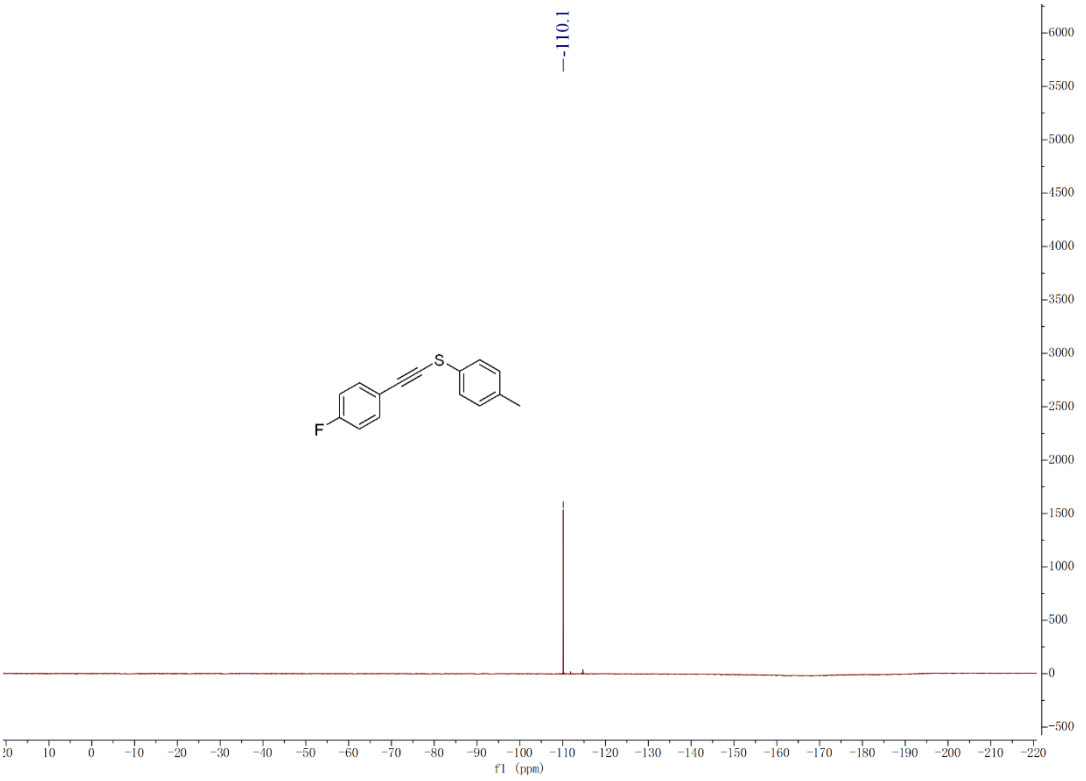
7e, ^{1}H NMR (500 MHz, $CDCl_3$)



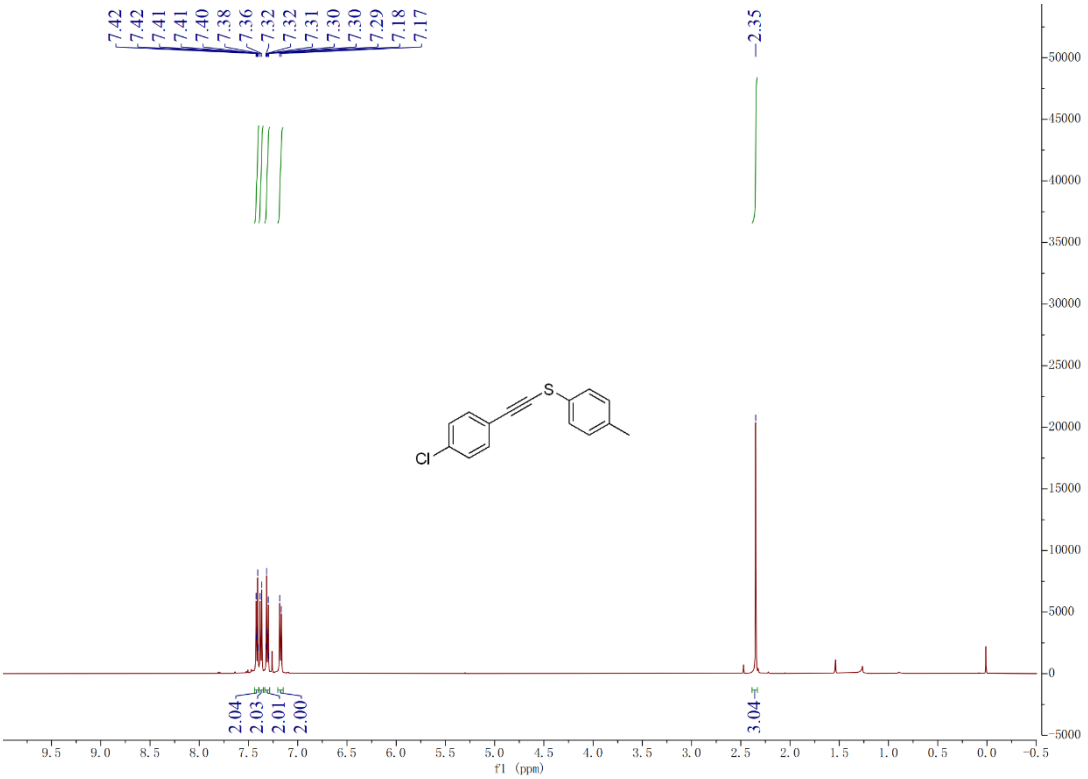
7e, ^{13}C NMR (125 MHz, $CDCl_3$)



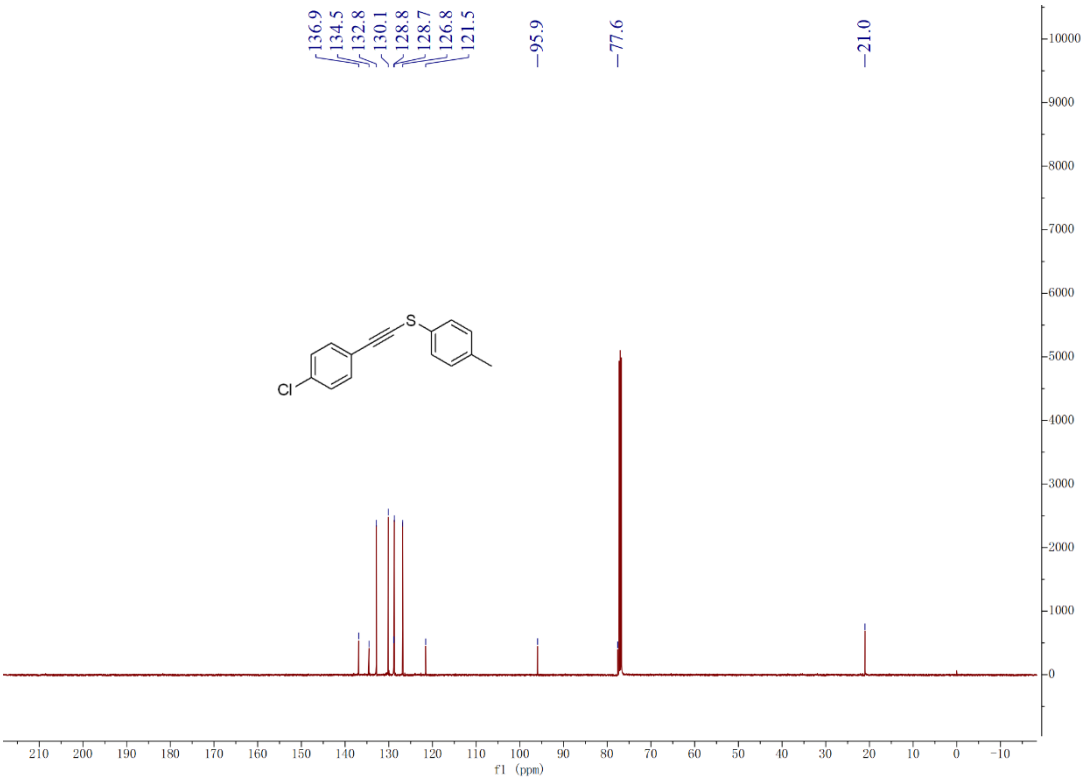
7e, ^{19}F NMR (470 MHz, $CDCl_3$)



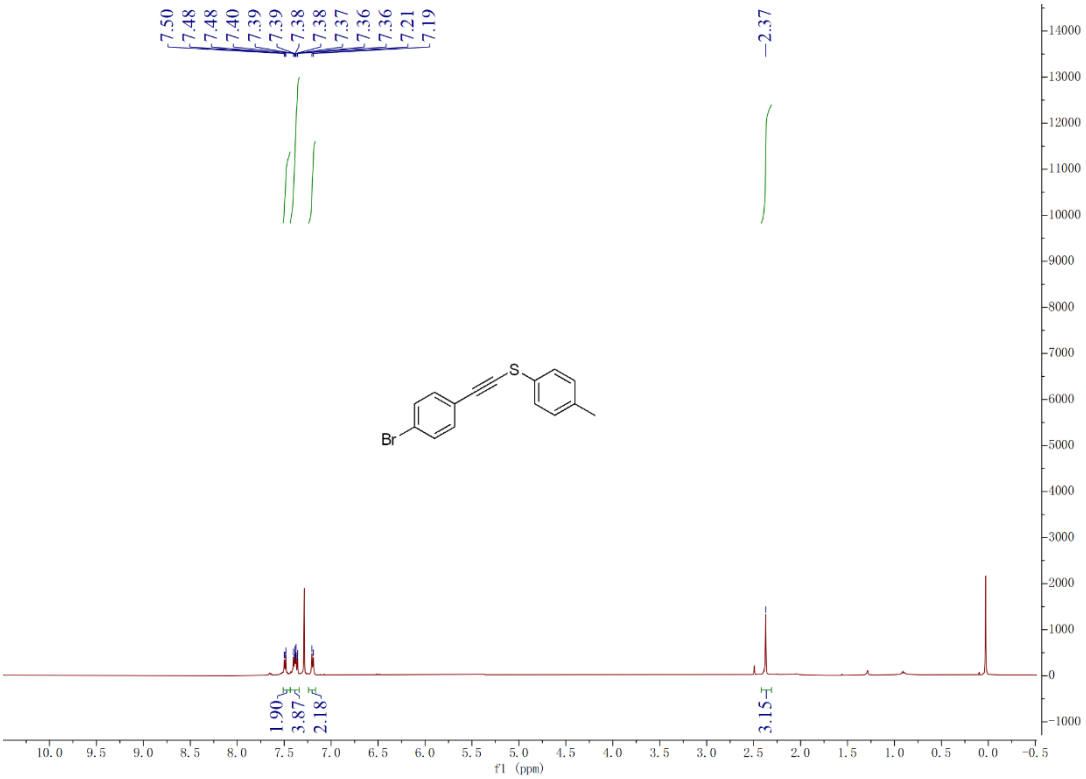
7f, ^{1}H NMR (500 MHz, $CDCl_3$)



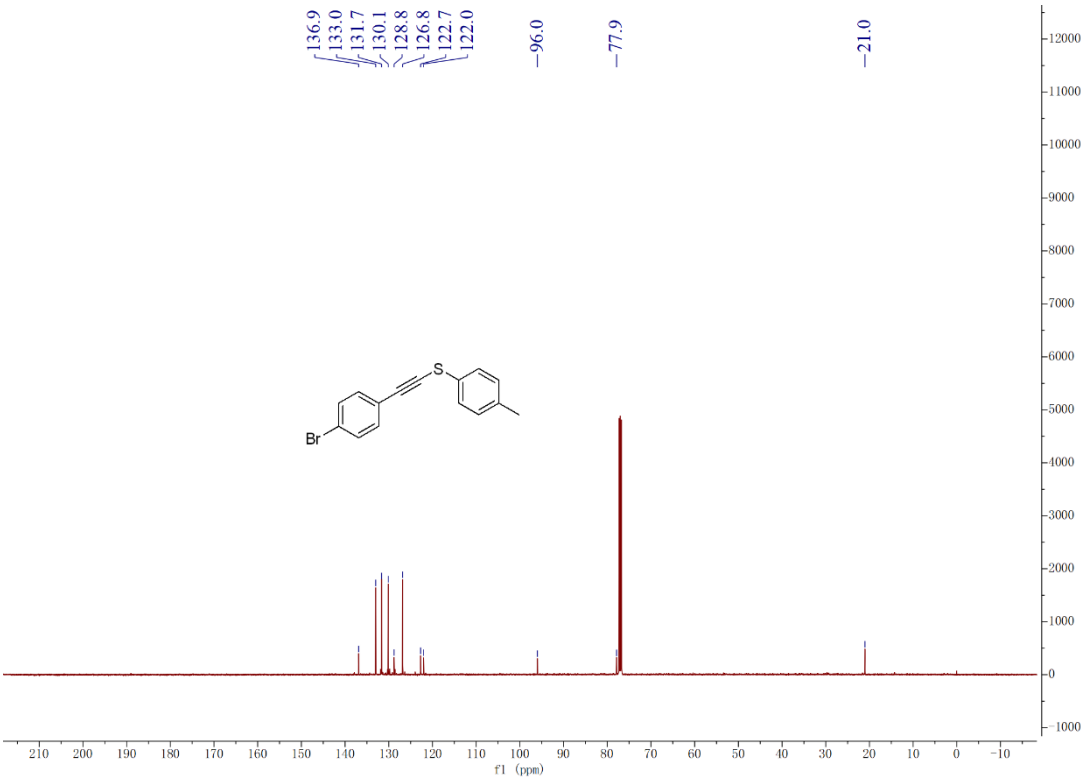
7f, ^{13}C NMR (125 MHz, $CDCl_3$)



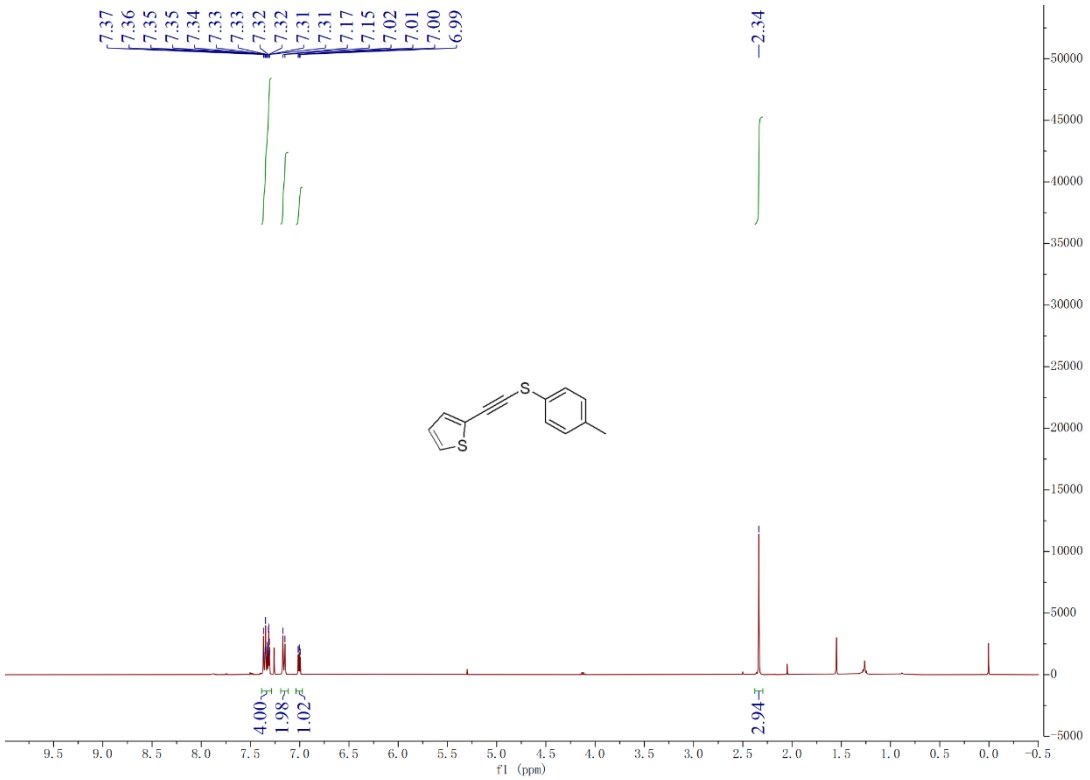
7g, ^{1}H NMR (500 MHz, $CDCl_3$)



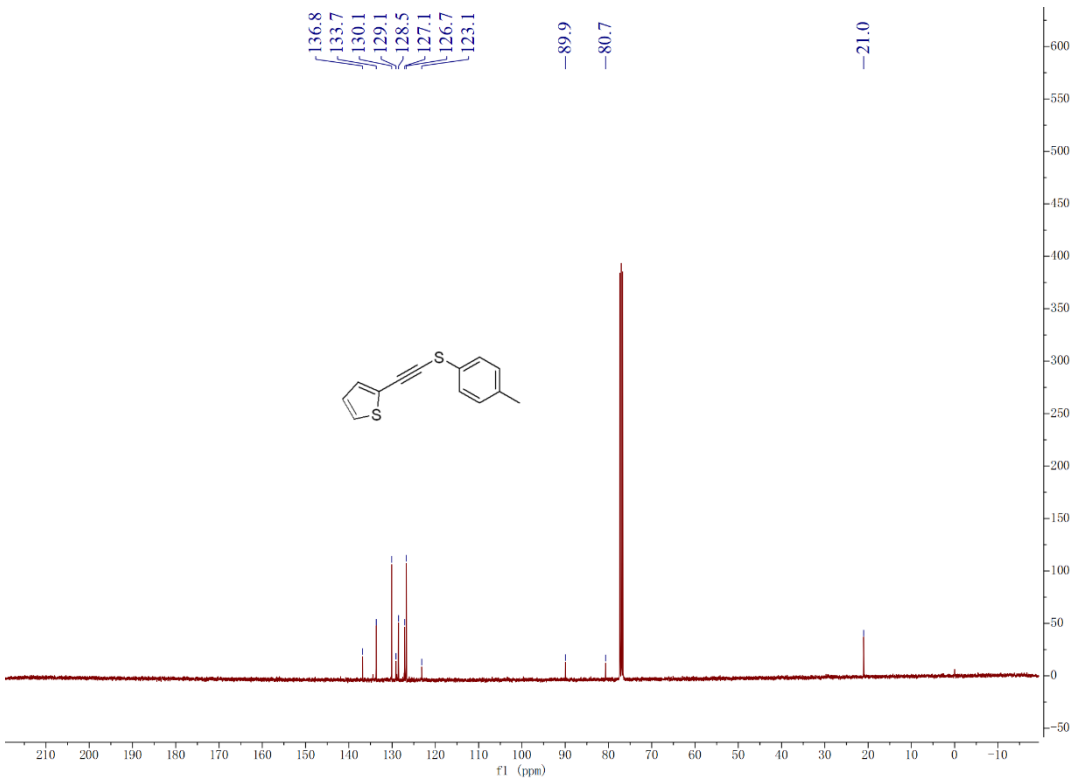
7g, ^{13}C NMR (125 MHz, $CDCl_3$)



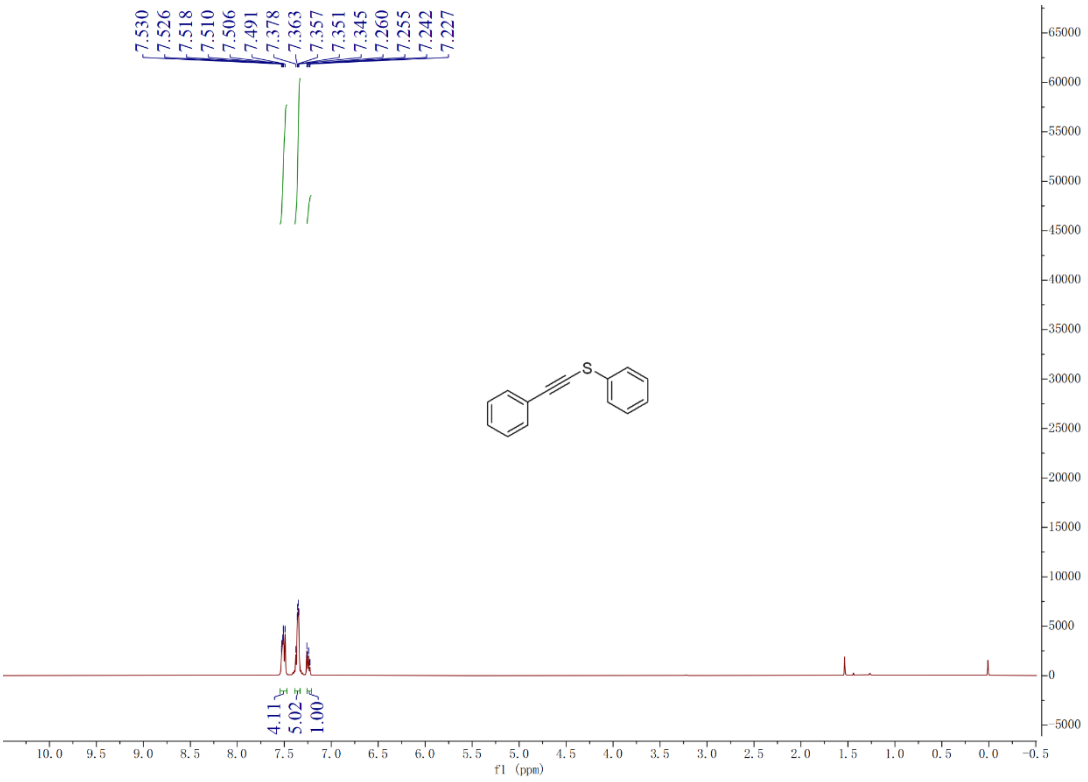
7h, ^{1}H NMR (400 MHz, $CDCl_3$)



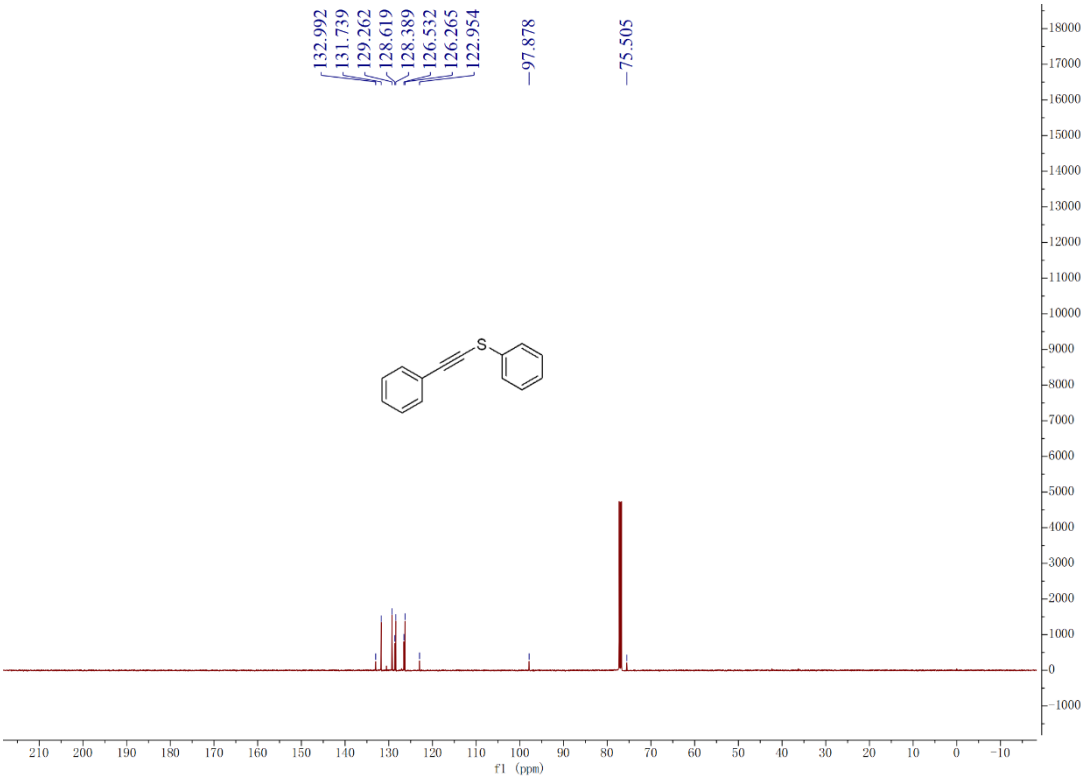
7h, ^{13}C NMR (100 MHz, $CDCl_3$)



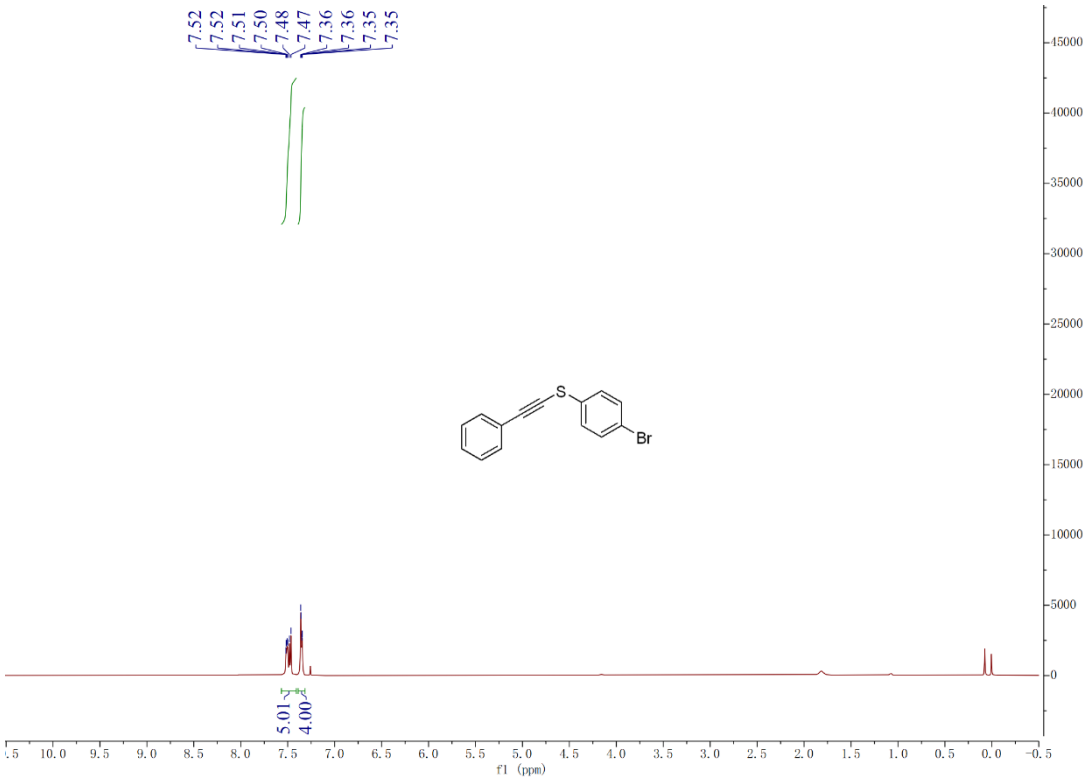
7i, ^{1}H NMR (400 MHz, $CDCl_3$)



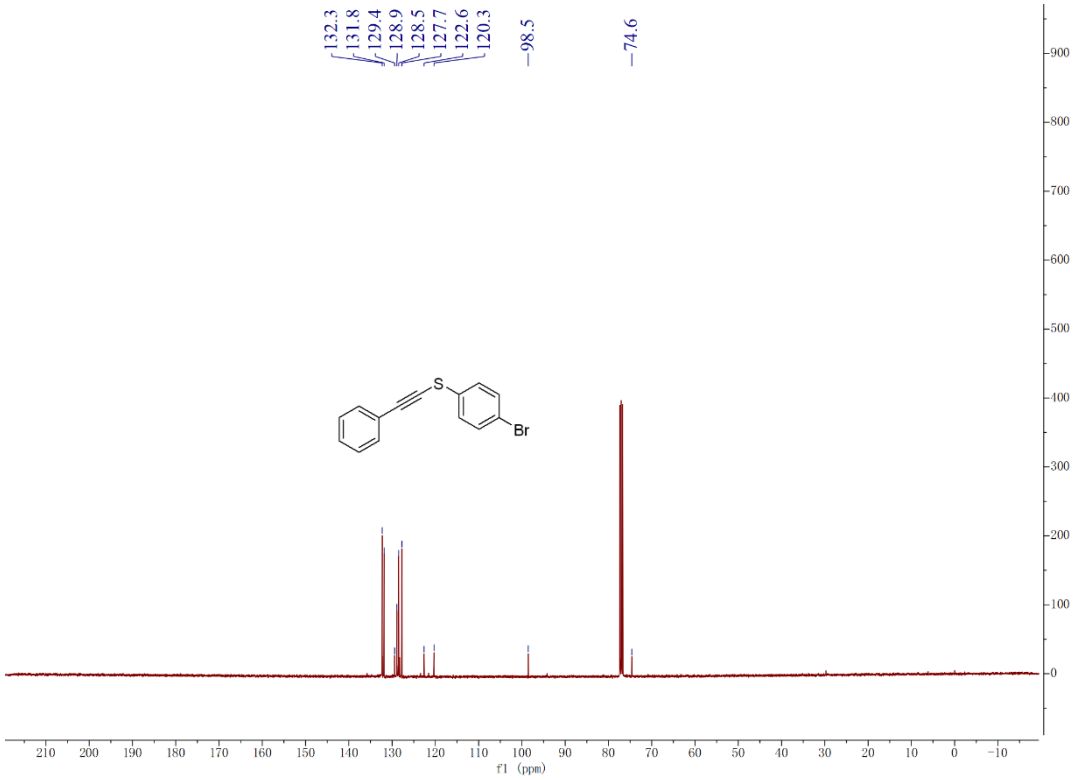
7i, ^{13}C NMR (100 MHz, $CDCl_3$)



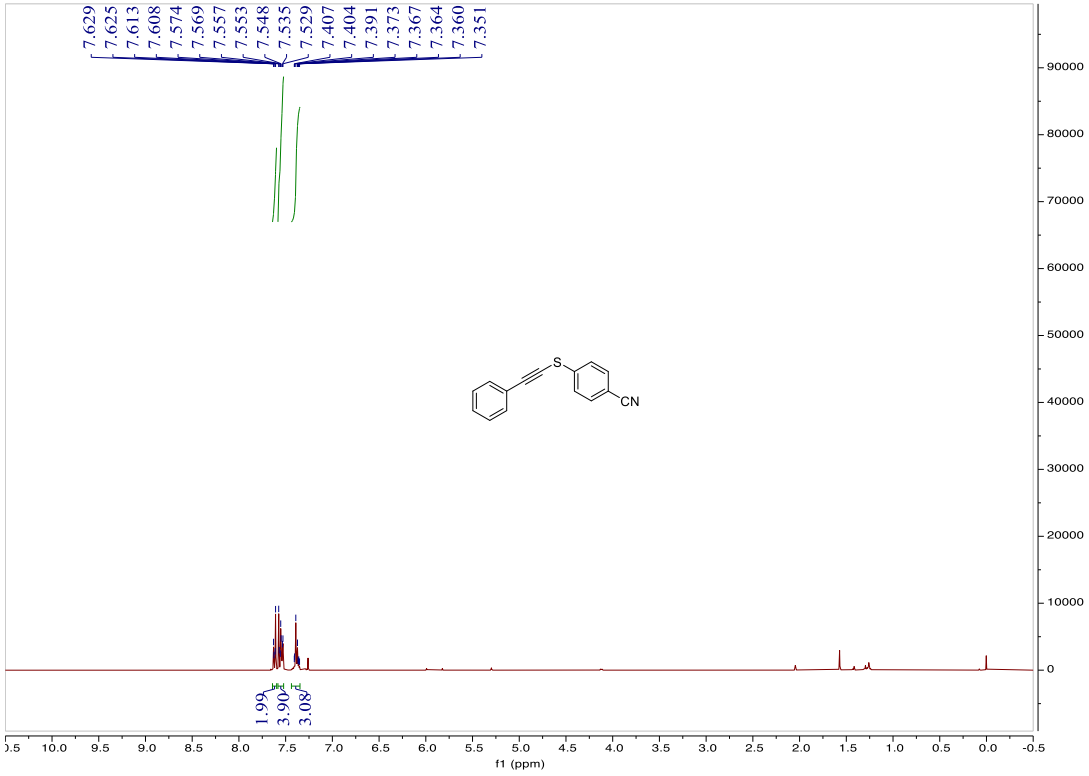
7j, ^{1}H NMR (400 MHz, $CDCl_3$)



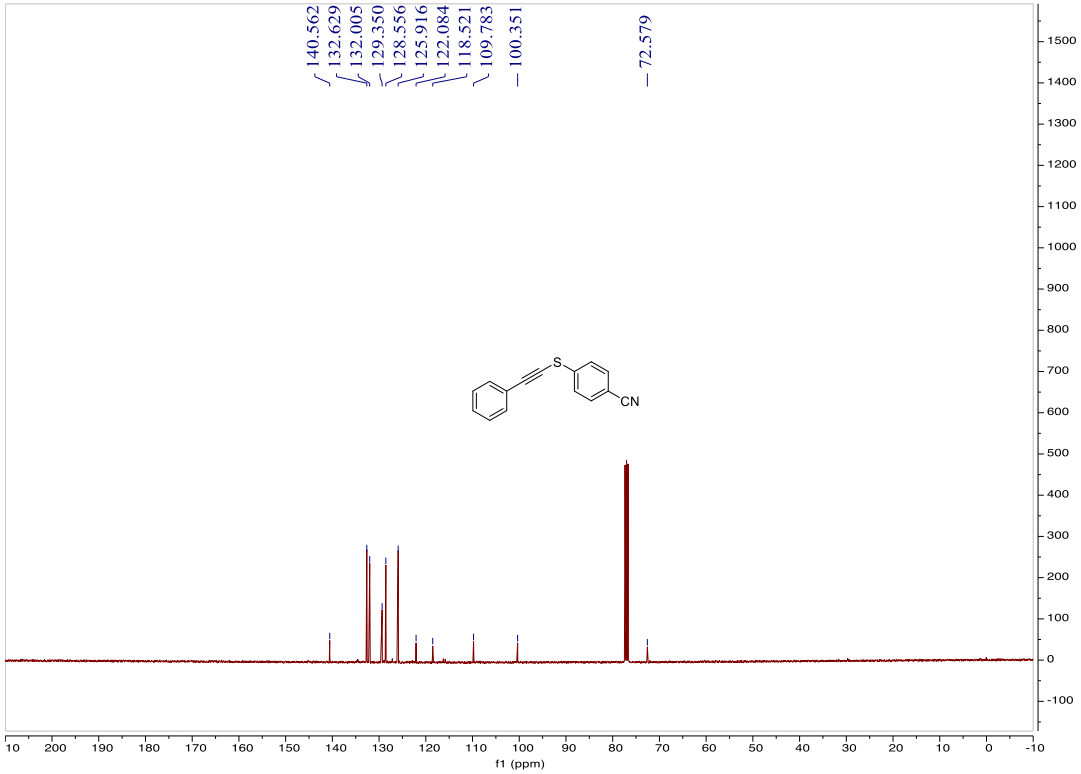
7j, ^{13}C NMR (100 MHz, $CDCl_3$)



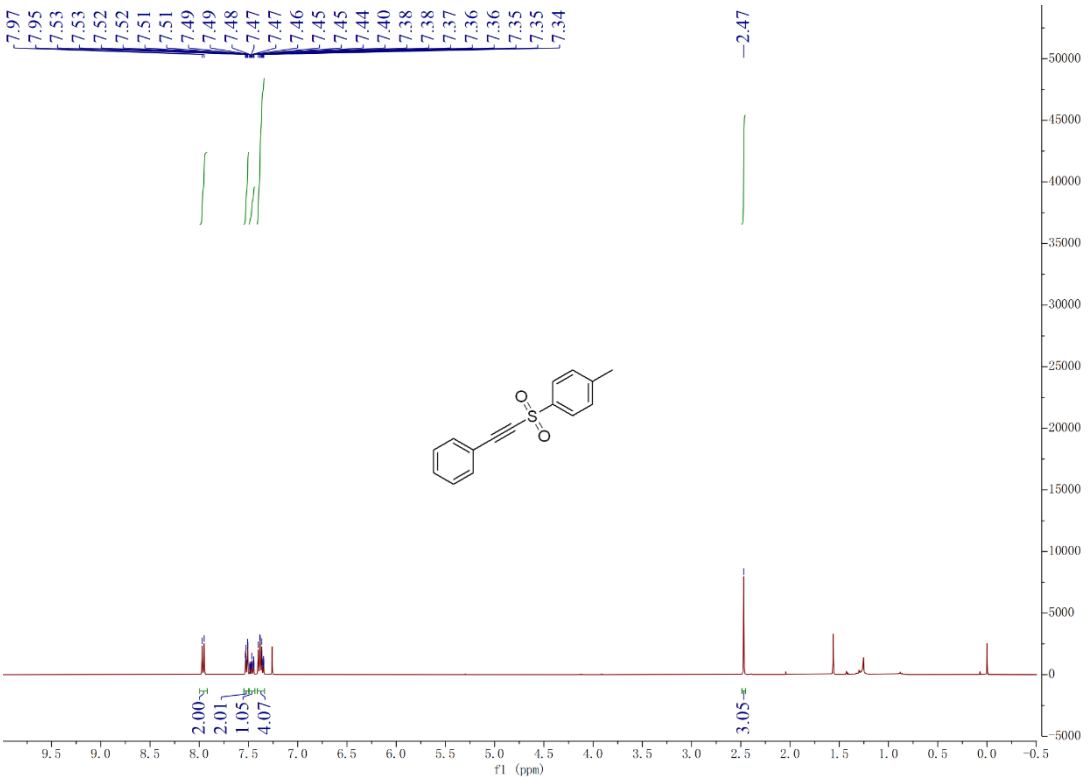
7k, ^{1}H NMR (400 MHz, $CDCl_3$)



7k, ^{13}C NMR (100 MHz, $CDCl_3$)



8a, ^{1}H NMR (400 MHz, $CDCl_3$)



8a, ^{13}C NMR (100 MHz, $CDCl_3$)