Supporting Information

Visible light/copper catalysis enabled alkylation of silyl enol ethers with arylsulfonium salts

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I. General considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. The starting materials were synthesized according to literature procedures. Flash chromatography was performed on silica gel (200~300 mesh). ^{1}H and ^{13}C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in $CDCl_3$. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR).

High resolution mass spectrometry (HRMS) were measured on an UPLC-Q/TOF Xevo G2-XS (Waters, MA, USA) with an ESI source. UV-visible spectroscopy was recorded on a UV-2600 UV-Vis spectrophotometer. The fluorescence emission intensities of reaction solution was recorded on a RF-6000 Fluorescence spectrophotometer. The power density of the incident light was recorded on CEL-FZ-A radiometer. The reactor was 3.0 cm from a 20W blue LED. Cyclic voltammetry was performed on a CorrTest Instruments electrochemical workstation model CS150M.

The spectrum of our lamp and the visible-light irradiation instrument

All reactions have been studied in borosilicate glass vessels irradiated by a blue light LED manufactured by Xuzhou Ai Jia Electronic Technology Co., Ltd. without using filters.

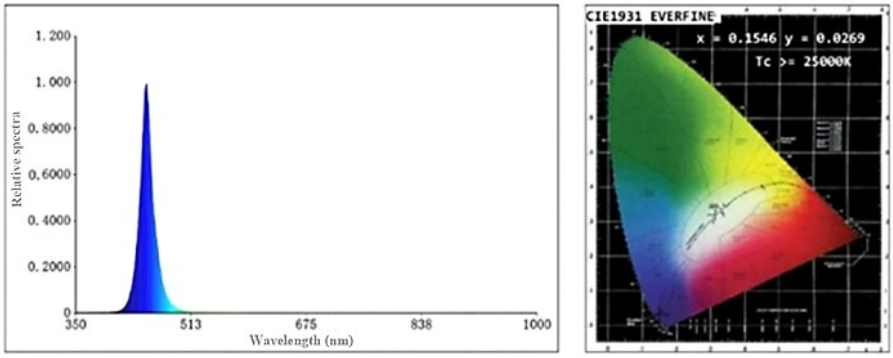


Figure S1. The spectrum of our lamp (blue LED)

Figure S2. The blue light LED

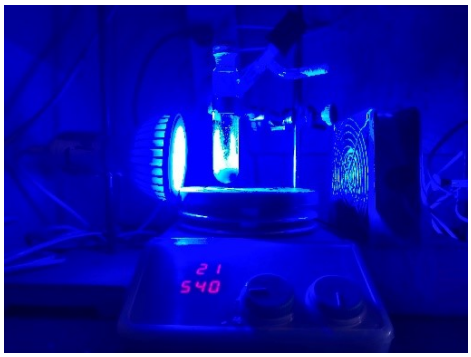
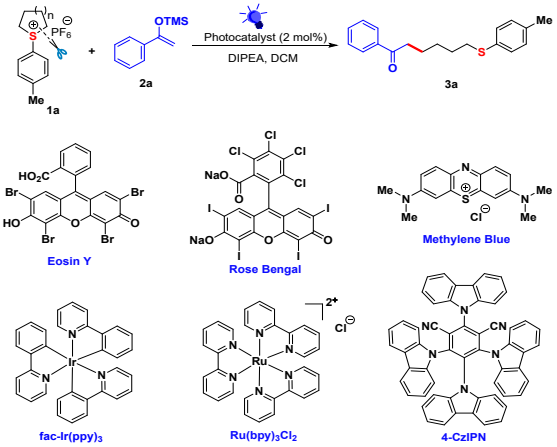


Figure S3. Photograph of the reaction setup

II. Optimization of Reaction Condition:

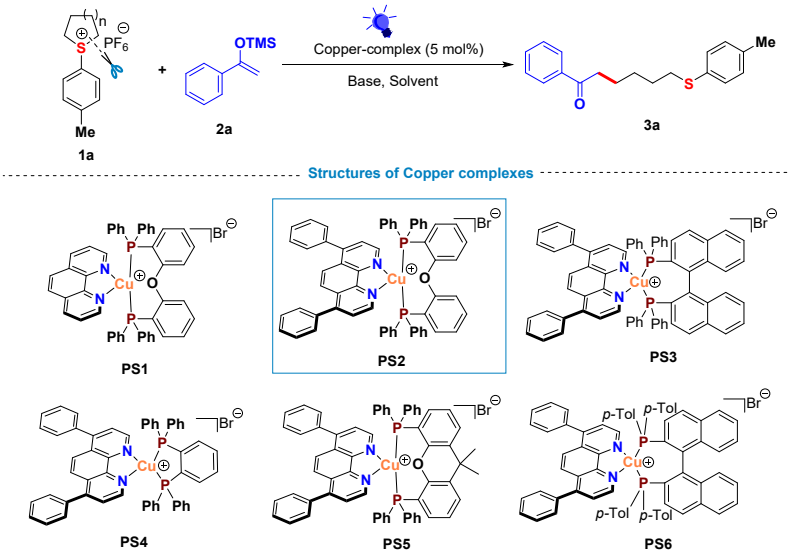
Table S1. Optimization of other Photocatalysts [a]



Entry	Photocatalyst	Solvent	Base	Yield of **3a** (%)[b]
1	EY	DCM	DIPEA	38
2	RB	DCM	DIPEA	Trace
3	MB	DCM	DIPEA	40
4	fac-Ir(ppy)$_3$	DCM	DIPEA	56
5	Ru(bpy)$_3$Cl$_2$	DCM	DIPEA	49
6	4-CzIPN	DCM	DIPEA	70

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Photocatalyst (2 mol%), DIPEA (0.4 mmol) and DCM (2 mL) at room temperature under irradiation with a 20 W blue LED (455 nm) for 24 h under nitrogen atmosphere. DIPEA = N,N-diisopropylethylamine. [b] Isolated yield.

Table S2. Optimization of Reaction Conditions [a]

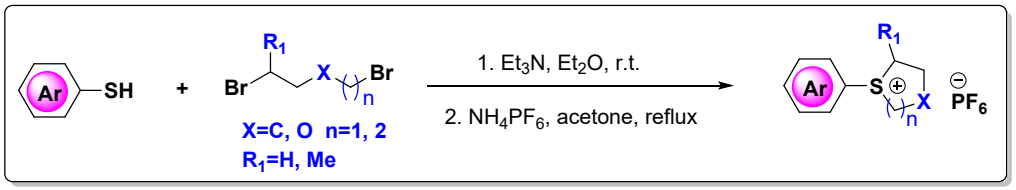


Entry	Copper-complex	Solvent	Base	Yield of **3a** (%)[b]
1	PS1	DCM	DIPEA	49
2	**PS2**	**DCM**	**DIPEA**	**85**
3	PS3	DCM	DIPEA	70
4	PS4	DCM	DIPEA	Trace
5	PS5	DCM	DIPEA	53
6	PS6	DCM	DIPEA	67
7	None	DCM	DIPEA	N.R.
8	PS2	DCM	Et_3N	53
9	PS2	DCM	*t*-BuOK	32
10	PS2	DCM	Na_2CO_3	Trace
11	PS2	DCM	K_3PO_4	30
12	PS2	DCM	None	Trace
13	PS2	DMSO	DIPEA	69
14	PS2	DMF	DIPEA	47
15	PS2	NMP	DIPEA	50
16	PS2	CH_3CN	DIPEA	Trace
17	PS2	DCM	DIPEA	N.R[c].

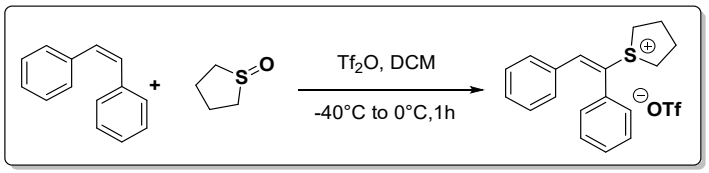
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), Cu (I) photosensitizer (5 mol%), base (0.4 mmol) and solvent (2 mL) at room temperature under irradiation with a 20 W blue LED (455 nm) for 24 h under nitrogen atmosphere. DIPEA = N,N-diisopropylethylamine. [b] Isolated yield. [c] In the dark. N.R. = no reaction.

III. Experimental procedures

1. General method for sulfonium salt synthesis[1, 2]:

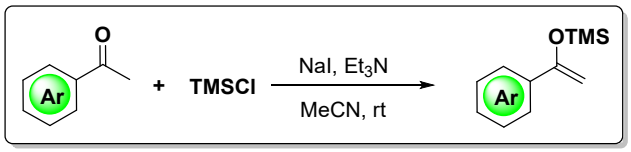


General procedure: Triethylamine (3.9 mL, 27.23 mmol, 1.5 equiv.) was slowly added to a 50 mL round-bottom flask containing thiophenol (2.25 g, 18.15 mmol, 1.0 equiv.), dibromide (4.3 mL, 36.3 mmol, 2.0 equiv.) and Et_2O (20 mL). The reaction mixture was stirred until the substrate was completely consumed which monitored by TLC. Then use 1.2 M HCl (15 mL) and EA (3 × 15 mL) to treat the reaction solution, and wash with saturated $NaHCO_3$ solution. The organic layer was dried (Na_2SO_4), later the crude material was dissolved in acetone (20 mL) after the solvents were evaporated, and add NH_4PF_6 (4.44 g, 27.23 mmol) to the solution. Reflux and stir until the substrate was completely consumed which monitored by TLC, then the reaction mixture was filtered through glass bush funnel and the filtrate was concentrated to 10 mL under reduced pressure. After that add Et_2O (20 mL) to precipitate white or beige solid, the resulting solid was filtered and washed with water (30 mL) and ethanol (30 mL). Finally, the product was dried under vacuum and obtained in 10-70% yield.



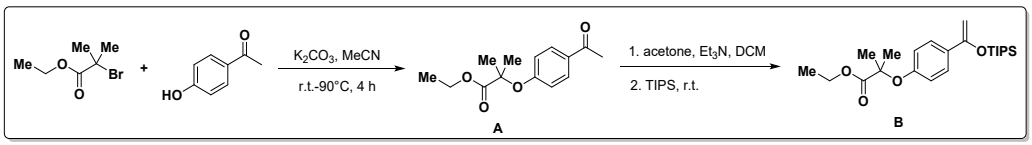
General procedure: Tetramethylene sulfoxide (0.49 mL, 5.5 mmol) and anhydrous DCM (25 mL) were added to a 100 mL round bottom flask at -40 ˚ C. The Tf_2O (0.93 mL, 5.5 mmol) was added dropwise under argon, then diphenylethylene (5.0 mmol) was added gradually. The reaction mixture was stirred at -40 ˚ C for 15 min before warming to 0 ˚ C. Upon completion monitored by the TLC, the solvent was removed under reduced pressure. The resulted crude product was dissolved in a small amount of anhydrous DCM, which was slowly dropped into anhydrous ether (100 mL) to precipitate out the vinyl sulfonium salts solid. The pure product was obtained by recrystallisation (CH_2Cl_2/Et_2O); yield 85%.

2. General method for silyl enol ethers[3]:



General procedure: Unless otherwise noted in the experimental procedures, the silyl enol ethers were prepared from the corresponding ketones according to procedures described in the literature. To an oven-dried round bottom flask was added ketone (5.0 mmol, 1.0 equiv.) and anhydroussodium iodide (899 mg, 6.0 mmol, 1.2 equiv.). The reaction vessel was evacuated and backfilled with N_2 (×3), then anhydrous MeCN (7.5 mL, 1.5 mL/mmol) was added. The resulting solution was stirred at rt for 30 min, and then added Et_3N (1.0 mL, 7.5 mmol, 1.5 equiv.), followed by chlorotrimethylsilane (0.76 mL, 6.0 mmol, 1.2 equiv.). The reaction mixture was stirred for 16 h at room temperature, then cooled to 0 °C and quenched with a mixture of Et_2O (20 mL) and saturated NH_4Cl(aq.) solution (20 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic extract was sequentially washed with ice-water (20 mL) and saturated NH_4Cl(aq.) solution (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was distilled under reduced pressure to provide pure silyl enol ethers.

3. Synthesis of natural product 3x[4, 5]:

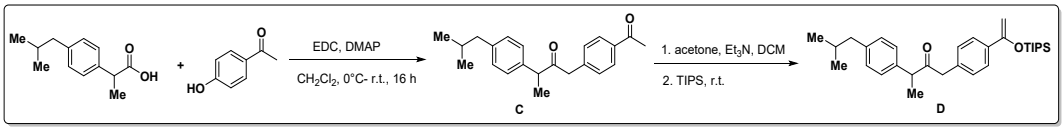


General procedure: Charge an oven dried 50 mL round bottom flask with 4-hydroxy acetophenone (1.0 equiv.), substituted bromoester (1.1 equiv.) and acetonitrile (25 mL). Add K_2CO_3 (10.0 equiv.) and heat the reaction mixture to 90 °C for 4 h. Evaporate the acetonitrile in vacuo. Purify the residue by silica gel column chromatography (20% EtoAc/Hexane) to obtain the desired ketone **A**.

To a 50 mL round-bottom flask equipped with a stirring bar was added a solution of **A** (5.0 mmol) in dichloromethane (15 mL) and triethylamine (0.91 g, 9.0 mmol). The reaction mixture was stirred at room temperature for 40 min before triisopropylsilyl triflate (1.84 g, 6.0 mmol) was added slowly. Then the resulting mixture was stirred at

room temperature for several minutes. Once the reaction was complete (reaction monitored by TLC), the reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) and diluted with dichloromethane (15 mL). The organic layer was washed twice with a cooled saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography over on basic alumina (pH 9.0-9.5) eluting with petroleum ether to afford the desired silyl enol ether **B**.

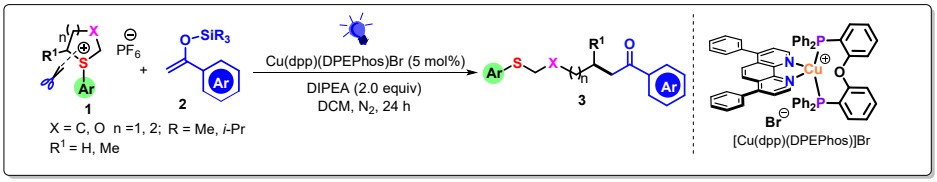
4. Synthesis of natural product 3ab[6]:



General procedure: EDC (2.5 equiv.) and DMAP (0.5 equiv.) were added sequentially to an ice-cold solution of the 4'-hydroxy acetophenone (1.0 equiv.) and corresponding acid (2.5 equiv.) in CH_2Cl_2 (0.1 M). After 30 min, the ice-water cooling bath was removed, and the resulting suspension was stirred vigorously at room temperature for 16 h. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (*n*-hexane/EtOAc) afforded the desired ketone **C**.

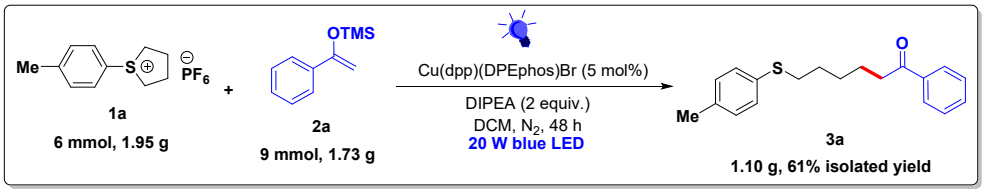
To a 50 mL round-bottom flask equipped with a stirring bar was added a solution of **C** (5.0 mmol) in dichloromethane (15 mL) and triethylamine (0.91 g, 9.0 mmol). The reaction mixture was stirred at room temperature for 40 min before triisopropylsilyl triflate (1.84 g, 6.0 mmol) was added slowly. Then the resulting mixture was stirred at room temperature for several minutes. Once the reaction was complete (reaction monitored by TLC), the reaction was quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL) and diluted with dichloromethane (15 mL). The organic layer was washed twice with a cooled saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography over on basic alumina (pH 9.0-9.5) eluting with petroleum ether to afford the desired silyl enol ether **D**.

5. General method for sulfonium salts with *O*-silyl enol ethers:



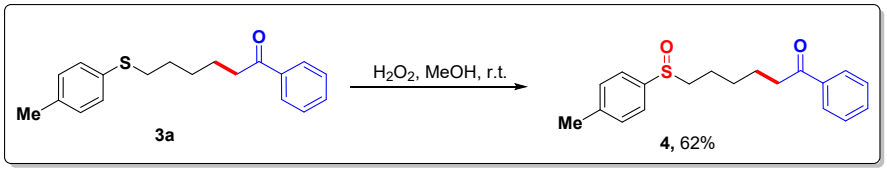
General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salts **1** (0.2 mmol), *O*-silyl enol ethers **2** (0.3 mmol), DIPEA (0.4 mmol) and Cu[(dpp)(DPEphos)]Br (5 mol%) in degassed DCM (2.0 mL). The tube was evacuated and backfilled with nitrogen (three times), Then the mixture was stirred and irradiated by the one 20W blue LEDs at room temperature for 24 h. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products.

6. Synthesis of 3a on a gram scale



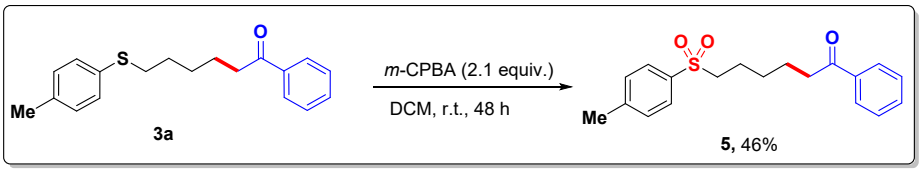
General procedure: A 200 mL Schlenk tube equipped with a magnetic stirring bar was charged with **1a** (6 mmol) and **2a** (9 mmol), Cu(dpp)(DPEphos)Br (5 mol%) and DIPEA (12 mmol). The tube was evacuated and backfilled with nitrogen (three times), 100 mL of degassed DCM was added by syringe under a nitrogen atmosphere. The solution was stirred at room temperature with the irradiation of two 20 W blue LEDs lights for 48 h. After completion of the reaction (TLC). The solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether as eluent to provide the desired products **3a** in 61% yield, 1.04g.

7. Product derivatization[7]



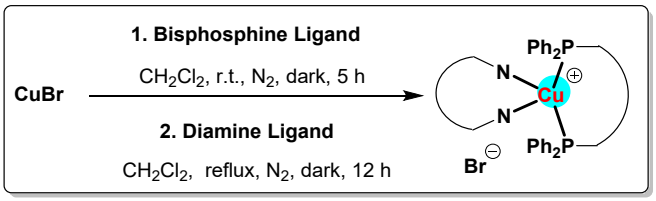
General procedure: To a stirred solution of the sulfide **3a** (0.060 g, 0.2mmol, 1 equiv.) in 1mL methanol was added H_2O_2 (30% in water, 0.06 mL, 0.8mmol, 4.0 equiv.) at room temperature. The reaction was stirred for 48 h and then concentrated in vacuo in

ice bath. The crude product was further purified by silica gel flash chromatography (PE: EA=5:1 as the eluent) to give Phenyl(4-(*p*-tolylsulfinyl)butyl)selane **4** (62% yield) as a yellow oil. (Note: The temperature of water bath during solvent evaporation should be controlled under 10 ˚C.)



General procedure: 3a (0.060 g, 0.2 mmol, 1 equiv.), *m*-CPBA (0.1081 g, 0.42 mmol, 2.1 equiv.), and DCM (3 mL) were added to an oven-dried test tube equipped with a magnetic stirring bar. Then, the reaction tube was sealed with an air balloon (atmospheric pressure) and stirred at the desired temperature for 48 h. After the reaction was completed, the reaction solution was extracted by EtOAc (3 × 2 mL). The organic solvent was removed in vacuo, and the residue was purified by flash column chromatography (PE:EA, v/v = 10:1) on silica gel to give **5** in 46% yield.

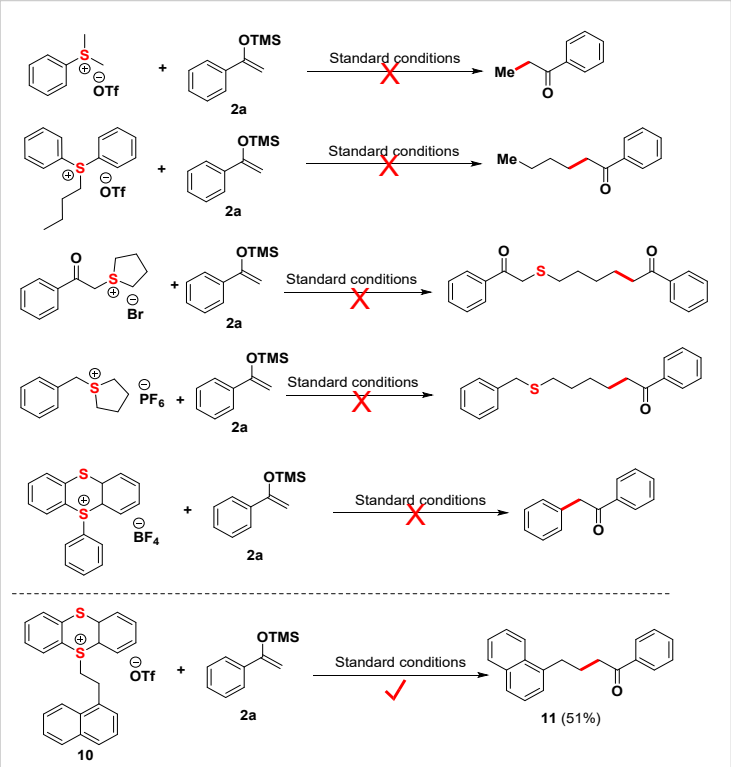
8. Synthesis of Cu-photocatalyzed[8]



General procedure: To a solution of CuBr (0.0495 g, 0.5 mmol, 1.0 equiv.) in dry dichloromethane (80 mL) was added the corresponding phosphine (0.52 mmol, 1.05 equiv.) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 hours. A solution of the corresponding amine (0.52 mmol, 1.05 equiv.) in dry dichloromethane (3 mL) was then added dropwise under a nitrogen atmosphere and the resulting reaction mixture was heated to reflux for another 12 hours. The reaction mixture was then allowed to cool to room temperature. Then the resulting filtrate was concentrated under reduced pressure to one tenth of the original volume and *n*-hexane was added to precipitate the product. It was filtered and washed with *n*-hexane. The resulting solid was further purified by recrystallization in a DCM/n-hexane mixture at 4 ˚C. The yellow precipitate was collected by filtration and dried under

vacuum to give the desired copper complex catalyst as a yellow solid.

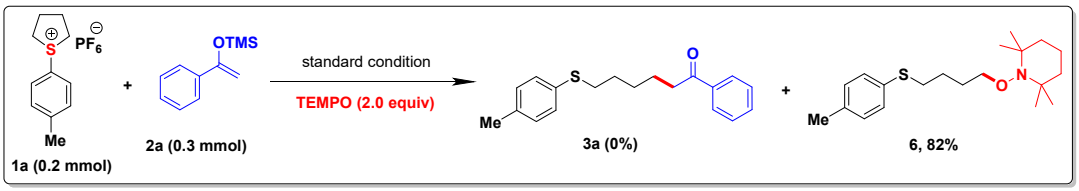
9. Investigation of other sulfonium salts



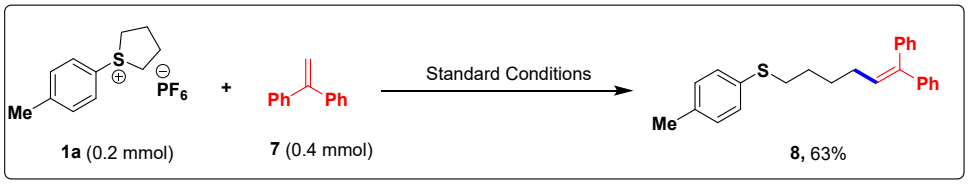
General procedure: To a 25 mL Schlenk tube equipped with a magnetic stir bar, added sulfonium salts (0.2 mmol), *O*-silyl enol ethers **2a** (0.3 mmol), DIPEA (0.4 mmol) and Cu(dpp)(DPEphos)Br (5 mol%) in degassed DCM (2.0 mL). The tube was evacuated and backfilled with nitrogen (three times), Then the mixture was stirred and irradiated by the one 20W blue LEDs at room temperature for 24 h. Monitored by TLC, when the reaction was completed. It is a pity that the above eight alkyl sulfonium salts cannot obtain ideal products under current conditions. But the thianthrenium salt **10** can obtain ideal product **11** in 51% yield under current conditions.

IV. Mechanistic studies

1. Radical capturing reaction



General procedure: Reaction conditions: a mixture of **1a** (0.20 mmol), **2a** (0.30 mmol), Cu[(dpp)(DPEphos)]Br (5 mol %), DIPEA (0.4 mmol) and 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO, 0.40 mmol) in degassed DCM (2 mL) irradiated with a 20W blue LED (455 nm) for 24 hours at room temperature under a N_2 atmosphere. The radical trapping experiments were conducted with **1a** and **2a** under the standard conditions with a trapping agent 2, 2, 6, 6-tetramethyl-1-piperidinyloxy to capture the radical intermediate expected in our system, and the products were purified by column chromatography (eluent petroleum ether) to afford the product **6** in 82% yield.



General procedure: A mixture of **1a** (0.2 mmol), Cu[(dpp)(DPEphos)]Br (5 mol%), DIPEA (0.4 mmol) and 1, 1-diphenylethylene **7** (0.4 mmol) in DCM (2 mL) irradiated with a 20W blue LED for 24 hours at room temperature under a N_2 atmosphere. The radical trapping experiments were conducted with **1a** under the standard conditions with a trapping agent 1,1-diphenylethylene to capture the radical intermediate expected in our system, and the products were purified by column chromatography (eluent petroleum ether) to afford the product **8** in 63% yield.

2. Calculation of apparent quantum efficiency (A. Q. E) ：

The photon flux of the light source was determined by an optical power meter to be 170.60 mW (average of three experiments).

$$E_{photon} = \frac{hc}{\lambda_{inc\ (455\ nm)}} = \frac{6.63 \times 10^{-34} J{\cdot}S \times 3 \times 10^{8} m{\cdot}x{\cdot}s^{-1}}{455 \times 10^{-9} m} = 4.37 \times 10^{-19} J$$

$$E_{total} = PSt = 170.60 \times 10^{-3}\ W{\cdot}cm^{-2} \times 4.75\ cm^{2} \times 2.0 \times 3600\ s = 5.83 \times 10^{3} J$$

$$\text{Number of incident photons} = \frac{E_{total}}{E_{photon}} = 1.34 \times 10^{22} = 22.26\ mmol$$

$$\text{A. Q. Y (\%)} = \frac{Number\ of\ product}{Number\ of\ incident\ photons} = \frac{0.026\ mmol}{22.26\ mmol} = 0.12\% < 1$$

Where h (J·s) is Planck's constant, c ($m \cdot s^{-1}$) is the speed of light and λ_{inc} (m) is the wavelength of the incident light. P ($W \cdot cm^{-2}$) is the power density of the incident light, S (cm^2) is the irradiation area and t (s) is the photoreaction time. The A.Q.E(%) result indicated that our reaction not involved radical chain pathway.

3. Effect of Visible Light Irradiation

Experimental procedure

A standard reaction mixtures in 25 mL schlenk tube were equipped with a magnetic stir bar, added Sulfonium salt **1a** (0.20 mmol), *O*-silyl enol ether **2a** (0.30 mmol), DIPEA (0.40 mmol) and Cu[(dpp)(DPEphos)]Br (5 mol %) in degassed DCM (2.0 mL). The tube was evacuated twice and backfilled with nitrogen. Then the mixture was stirred and irradiated by one 20W blue LEDs at room temperature. At each time point, one reaction system was suspended, which was then purified with chromatography column on silica gel (petroleum ether:EtOAc=80:1) to give the corresponding products **3a**. The yield of **3a** was measured by weight of the product.

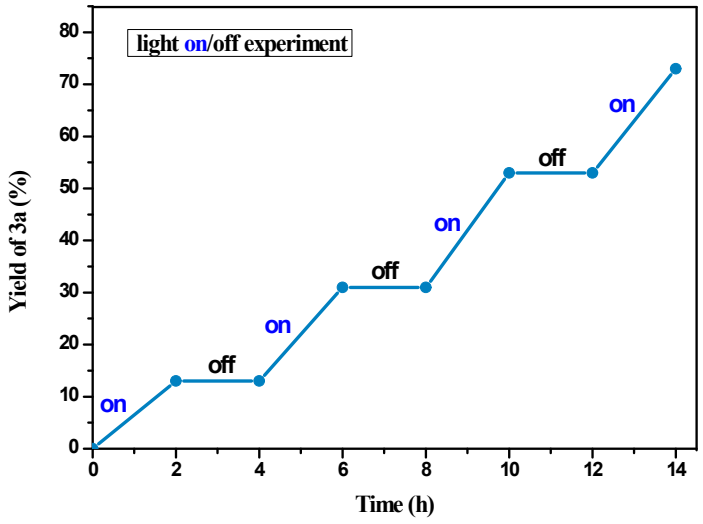


Figure S4. Light on/ off experiment

4. Fluorescence quenching experiments:

The fluorescence emission intensities were recorded on a RF-6000 spectrofluorimeter. The excitation wavelength was fixed at 455 nm. The samples were prepared by the in-situ-formed [Cu(dpp)(DPEphos)]Br (5×10^{-4} mol/L) and different amount of quencher in DCM in a light path quartz fluorescence cuvette. The concentration of quencher is 5×10^{-4} mol/L in DCM. For each quenching experiment, 0.01 ml of quencher solution was titrated to a mixed solution of copper complex (0.005 mL, in a total volume = 3.0 mL). Then the emission intensity was collected and the results were presented in Figure S5 or Figure S6.

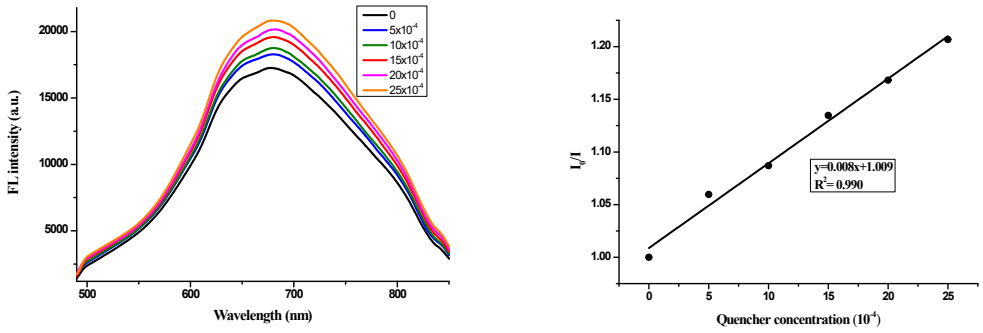


Figure S5. The emission quenching of in situ generated [Cu(dpp)(DPEphos)]Br in DCM by various concentrations of quencher **1a**.

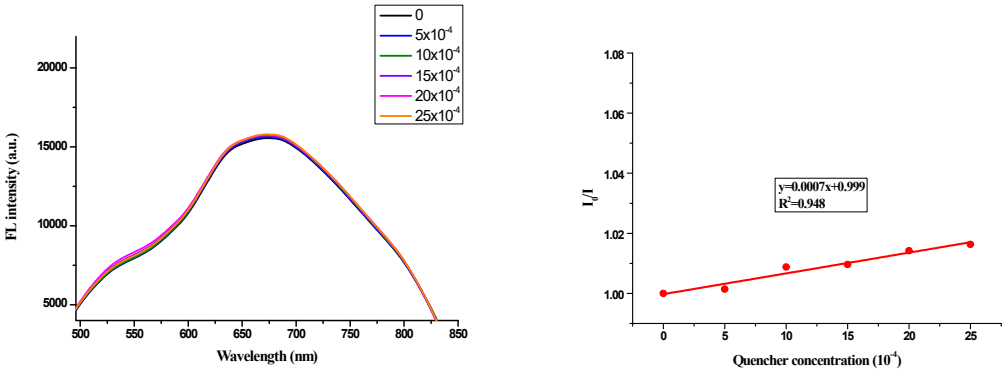


Figure S6. The emission quenching of in situ generated [Cu(dpp)(DPEphos)]Br in DCM by various concentrations of quencher **2a**.

5. UV–vis absorption experiment:

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-visible spectrophotometer. The sample was prepared by mixing copper catalysts ($C=5.0\times10^{-4}$ M), Sulfonium salt **1a**, *O*-silyl enol ether **2a** ($C=5.0\times10^{-4}$ M) ($C=5.0\times10^{-4}$ M) in DCM.

The absorption was collected and the result was listed in Figure S7.

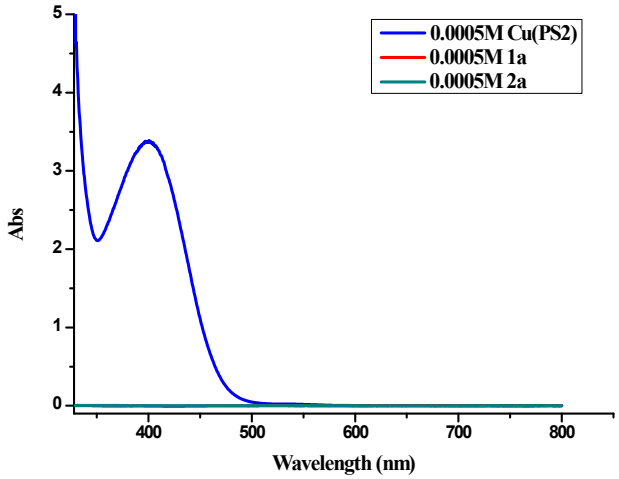


Figure S7. UV–vis absorption spectra

6. Normalized absorption and emission sprectra for [Cu(dpp)(DPEphos)]Br

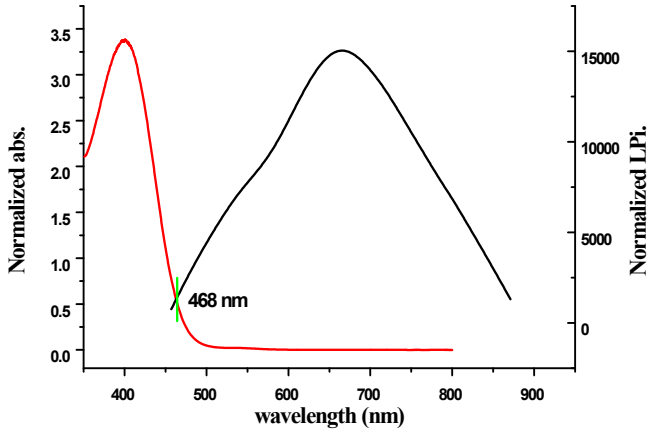


Figure S8. Normalized absorption (red line) and emission spectra (photoluminescence intensity (PLi), black line) for [Cu(dpp)(DPEphos)]Br.

7. Cyclic Voltammetry Experiments

Cyclic Voltammetry was performed on a CorrTest Instruments Electrochemical Workstation model CS150M. A solution of the sample in DCM (0.005 M) was tested with 0.2 M Bu_4NPF_6 as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and $Hg/Hg_2Cl_2/KCl$ as reference electrode. The cyclic voltammetry scans were done one time at a scan rate of 100 mVs^{-1}.

Reductive potential of Sulfonium salt 1a

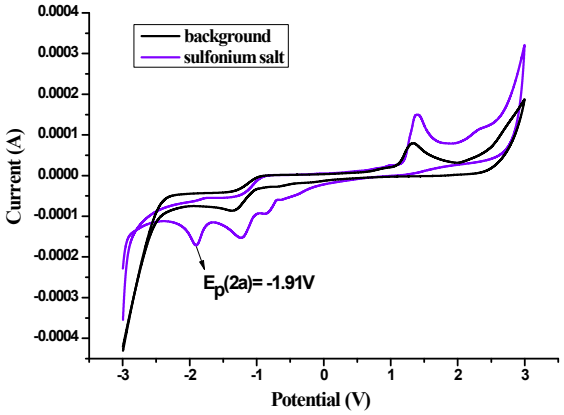


Figure S9. CV spectra of sulfonium salt **1a** in DCM (0.005 M) was tested with 0.2 M Bu_4NPF_6 as the supporting electrolyte.

Ep (**1*a***) = – 1.91 *V* (*vs*. SCE)

Reductive potential of [Cu(dpp)(DPEphos)]Br

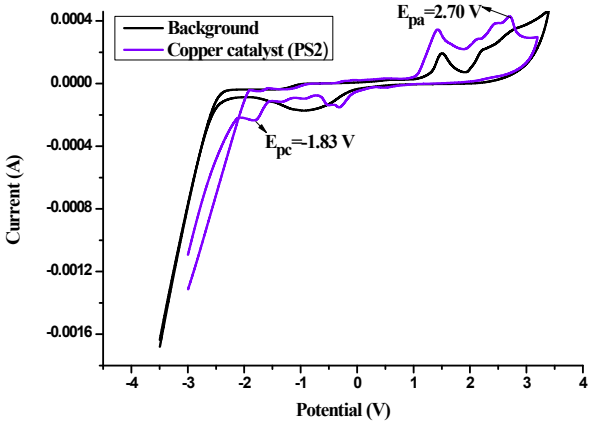


Figure S10. CV spectra of [Cu(dpp)(DPEphos)]Br in DCM (0.005 M) was tested with 0.2 M Bu_4NPF_6 as the supporting electrolyte.

Note: According to previous literature[9, 10], the value obtained from the intersection of the normalized absorption and emission spectra of [Cu(dpp)(DPEphos)]Br was used to calculated Triplet energy E_T.

$$E_T = h\nu = h \times \frac{c}{\lambda} = \frac{1240}{468} = 2.650 \text{ eV}$$

h (Planck constant) = 6.62607015×10^{-34} J·s = $4.1356676969 \times10^{-15}$ eV·s

c (velocity of light) = 3×10^8 m/s

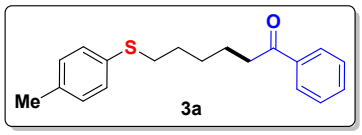
$E_{1/2}$[Cu(II) /Cu(I) [Cu(dpp)(DPEphos)][Br] = (2.70-1.83)/2= 0.435 *V* (*vs*. SCE)

$E^* = E_{1/2}$[Cu(II) /Cu(I) [Cu(dpp)(DPEphos)][Br] - E_T= 0.435-2.650= -2.215 V ($vs.$ SCE)

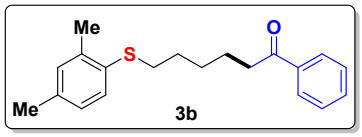
The reduction potential of Sulfonium salt (**1a**) to be $Ep^{0/-1} = -1.91\ V$ ($vs.$ SCE). This result suggests that Sulfonium salt (**1a**) can reach with [Cu(dpp)(DPEphos)]Br through a single electron transfer (SET) process under visible light irradiation.

V. Characterization of products

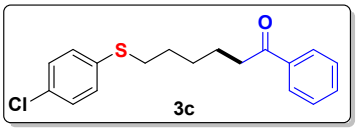
Characterization data of compounds



1-Phenyl-6-(*p*-tolylthio)hexan-1-one (3a). Eluent petroleum ether/ethyl acetate (80:1). Yellow solid, 51 mg, 86% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.75 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.68 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.55 – 1.48 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.4, 137.2, 136.1, 133.1, 132.9, 130.1, 129.8, 128.7, 128.2, 38.5, 34.4, 29.2, 28.5, 23.9, 21.1. HRMS calcd for $C_{19}H_{23}OS^+$ $[M+H]^+$: 299.1470; found 299.1473.

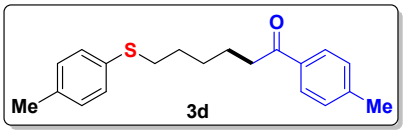


6-((2,4-Dimethylphenyl)thio)-1-phenylhexan-1-one (3b). Eluent petroleum ether/ethyl acetate (80:1). White solid, 52 mg, 83% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.98 – 7.91 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.00 (s, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.36 (s, 3H), 2.29 (s, 3H), 1.76 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.69 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.57 – 1.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.4, 138.2, 137.2, 135.9, 133.08, 132.3, 131.2, 129.3, 128.7, 128.2, 127.2, 38.5, 33.6, 29.1, 28.7, 23.9, 21.0, 20.5. HRMS calcd for $C_{20}H_{25}OS^+$ $[M+H]^+$: 313.1626; found 313.1626.

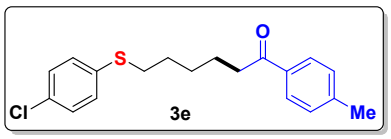


6-((4-Chlorophenyl)thio)-1-phenylhexan-1-one (3c). Eluent petroleum ether/ethyl acetate (80:1). Colorless oil, 48 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.20

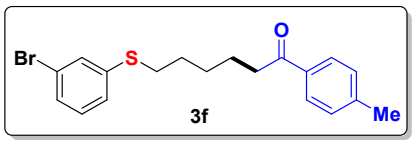
(m, 4H), 2.96 (t, J = 7.3 Hz, 2H), 2.91 (t, J = 7.3 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.68 (dt, J = 14.9, 7.5 Hz, 2H), 1.51 (dt, J = 15.2, 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 137.1, 135.4, 133.1, 131.9, 130.5, 129.1, 128.7, 128.1, 38.4, 33.8, 28.9, 28.5, 23.8. HRMS calcd for $C_{18}H_{20}ClOS^+$ $[M+H]^+$: 319.0923; found 319.0928.



1-(*p*-Tolyl)-6-(*p*-tolylthio)hexan-1-one (3d). Eluent petroleum ether/ethyl acetate (80:1). White solid, 53 mg, 85% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.88 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 4H), 7.12 (d, J = 7.9 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 2.44 (s, 3H), 2.34 (s, 3H), 1.77 (dt, J = 15.0, 7.4 Hz, 2H), 1.71 (dt, J = 14.9, 7.6 Hz, 2H), 1.58 – 1.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.9, 143.8, 136.0, 134.6, 132.9, 130.0, 129.7, 129.3, 128.2, 38.3, 34.3, 29.2, 28.5, 23.9, 21.7, 21.1. HRMS calcd for $C_{20}H_{25}OS^+$ $[M+H]^+$: 313.1626; found 313.1627.

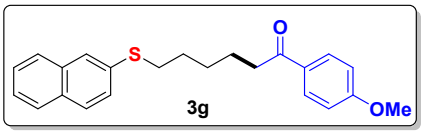


6-((4-Chlorophenyl)thio)-1-(*p*-tolyl)hexan-1-one (3e). Eluent petroleum ether/ethyl acetate (70:1). White solid, 47 mg, 71% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.84 (d, J = 8.1 Hz, 2H), 7.28 – 7.19 (m, 6H), 2.93 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.3 Hz, 2H), 2.41 (s, 3H), 1.74 (dt, J = 15.0, 7.4 Hz, 2H), 1.67 (dt, J = 14.9, 7.4 Hz, 2H), 1.55 – 1.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.9, 143.9, 135.5, 134.7, 131.9, 130.5, 129.4, 129.1, 128.28, 38.3, 33.9, 29.0, 28.5, 23.9, 21.8. HRMS calcd for $C_{19}H_{22}ClOS^+$ $[M+H]^+$: 333.1080; found 333.1082.

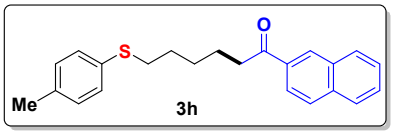


6-((3-Bromophenyl)thio)-1-(*p*-tolyl)hexan-1-one (3f). Eluent petroleum ether/ethyl acetate (70:1). Yellow solid, 55 mg, 73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.88 (d, J = 7.9 Hz, 2H), 7.46 (s, 1H), 7.31 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.25 (d, J

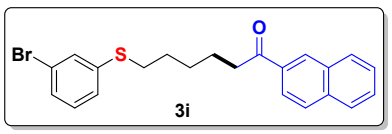
= 7.7 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 2.99 – 2.95 (m, 4H), 2.44 (s, 3H), 1.80 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.73 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.55 (dt, *J* = 15.0, 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.9, 143.9, 139.6, 134.7, 131.1, 130.2, 129.4, 128.8, 128.3, 127.2, 122.9, 38.3, 33.3, 28.9, 28.6, 23.9, 21.8. HRMS calcd for $C_{19}H_{22}BrOS^+$ $[M+H]^+$: 377.0575; found 377.0567.



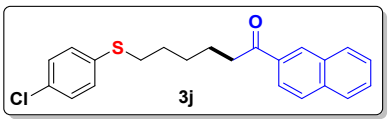
1-(4-Methoxyphenyl)-6-(naphthalen-2-ylthio)hexan-1-one (3g). Eluent petroleum ether/ethyl acetate (70:1). White solid, 60 mg, 82% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 3H), 7.47 – 7.40 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 1.79 – 1.72 (m, 4H), 1.57 – 1.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.0, 163.5, 134.5, 133.9, 131.8, 130.4, 130.3, 128.4, 127.8, 127.4, 127.1, 126.7, 126.6, 125.6, 113.8, 55.6, 38.1, 33.5, 29.1, 28.7, 24.1. HRMS calcd for $C_{23}H_{25}O_2S^+$ $[M+H]^+$: 365.1575; found 365.1573.



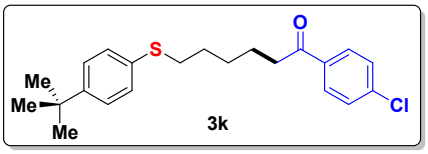
1-(Naphthalen-2-yl)-6-(*p*-tolylthio)hexan-1-one (3h). Eluent petroleum ether/ethyl acetate (70:1). White solid, 56 mg, 80% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.46 (s, 1H), 8.02 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 7.9 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.30 (s, 3H), 1.81 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.70 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.57 – 1.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.3, 136.1, 135.7, 134.5, 132.9, 132.7, 130.1, 129.8, 129.7, 128.6, 128.5, 127.9, 126.9, 124.0, 38.6, 34.4, 29.2, 28.6, 24.1, 21.1. HRMS calcd for $C_{23}H_{25}OS^+$ $[M+H]^+$: 349.1626; found 349.1635.



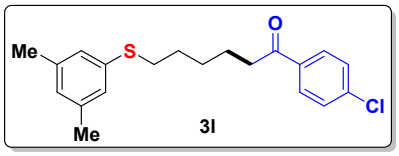
6-((3-Bromophenyl)thio)-1-(naphthalen-2-yl)hexan-1-one (3i). Eluent petroleum ether/ethyl acetate (70:1). Yellow solid, 65 mg, 79% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.46 (s, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.89 (t, J = 8.5 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.44 (s, 1H), 7.28 (s, 1H), 7.22 (d, J = 7.8 Hz, 1H), 7.12 (t, J = 7.9 Hz, 1H), 3.11 (t, J = 7.3 Hz, 2H), 2.95 (t, J = 7.3 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.78 – 1.69 (m, 2H), 1.59 – 1.54 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 139.6, 135.7, 134.5, 132.7, 131.1, 130.3, 129.8, 129.7, 128.8, 128.6, 128.5, 127.9, 127.2, 126.9, 124.0, 122.9, 38.5, 33.4, 28.9, 28.6, 24.0. HRMS calcd for $C_{22}H_{22}BrOS^+$ $[M+H]^+$: 413.0575; found 413.0583.



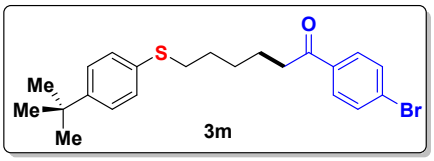
6-((4-Chlorophenyl)thio)-1-(naphthalen-2-yl)hexan-1-one (3j). Eluent petroleum ether/ethyl acetate (70:1). White solid, 57 mg, 77% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.45 (s, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 8.2 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.26 – 7.20 (m, 4H), 3.10 (t, J = 7.3 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 1.86 – 1.82 (dt, J = 15.1, 7.4 Hz, 2H), 1.71 (dt, J = 14.8, 7.4 Hz, 2H), 1.59 – 1.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 135.7, 135.5, 134.5, 132.7, 131.9, 130.6, 129.7, 129.7, 129.1, 128.6, 128.5, 127.9, 126.9, 124.0, 38.5, 33.9, 29.0, 28.6, 24.0. HRMS calcd for $C_{22}H_{22}ClOS^+$ $[M+H]^+$: 369.1080; found 369.1073.



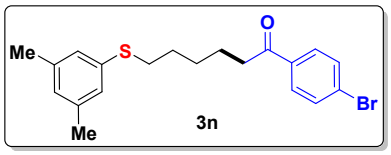
6-((4-(*tert*-Butyl)phenyl)thio)-1-(4-chlorophenyl)hexan-1-one (3k). Eluent petroleum ether/ethyl acetate (70:1). Colorless oil, 54 mg, 72% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.80 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 (t, J = 4.2 Hz, 2H), 2.95 – 2.91 (m, 2H), 2.91 – 2.88 (m, 2H), 1.74 (dt, J = 12.4, 6.0 Hz, 2H), 1.68 (dt, J = 14.8, 7.4 Hz, 2H), 1.51 (dt, J = 15.2, 7.5 Hz, 2H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.3, 149.3, 135.9, 133.2, 132.0, 129.7, 129.5, 128.2, 126.1, 38.5, 34.6, 34.1, 31.4, 29.2, 28.5, 23.8. HRMS calcd for $C_{22}H_{28}ClOS^+$ $[M+H]^+$: 375.1549; found 375.1558.



1-(4-Chlorophenyl)-6-((3,5-dimethylphenyl)thio)hexan-1-one (3l). Eluent petroleum ether/ethyl acetate (70:1). Yellow solid, 51 mg, 74% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 6.94 (s, 2H), 6.79 (s, 1H), 2.95 – 2.91 (m, 2H), 2.92 – 2.89 (m, 2H), 2.27 (s, 6H), 1.75 (dt, *J* = 12.5, 6.1 Hz, 2H), 1.69 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.52 (dt, *J* = 15.1, 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.1, 139.5, 138.6, 136.4, 135.5, 129.6, 129.0, 127.9, 126.9, 38.5, 33.6, 29.1, 28.5, 23.8, 21.4. HRMS calcd for $C_{20}H_{24}ClOS^+$ $[M+H]^+$: 347.1236; found 347.1243.

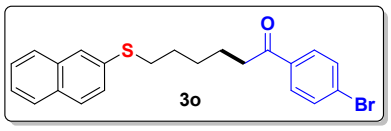


1-(4-Bromophenyl)-6-((4-(*tert*-butyl)phenyl)thio)hexan-1-one (3m). Eluent petroleum ether/ethyl acetate (70:1). Colorless oil, 59 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 (t, *J* = 4.2 Hz, 2H), 2.95 – 2.91 (m, 2H), 2.91 – 2.88 (m, 2H), 1.74 (dt, *J* = 12.4, 6.0 Hz, 2H), 1.68 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.51 (dt, *J* = 15.2, 7.5 Hz, 2H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.3, 149.3, 135.9, 133.2, 132.0, 129.7, 129.5, 128.2, 126.1, 38.5, 34.6, 34.1, 31.4, 29.2, 28.5, 23.8. HRMS calcd for $C_{22}H_{28}BrOS^+$ $[M+H]^+$: 419.1044; found 419.1054.

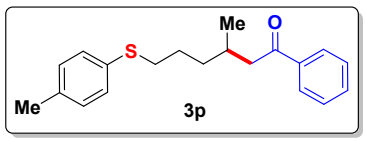


1-(4-Bromophenyl)-6-((3,5-dimethylphenyl)thio)hexan-1-one (3n). Eluent petroleum ether/ethyl acetate (70:1). Yellow solid, 59 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 6.94 (s, 2H), 6.79 (s, 1H), 2.95 – 2.91 (m, 2H), 2.92 – 2.89 (m, 2H), 2.27 (s, 6H), 1.75 (dt, *J* = 12.5, 6.1 Hz, 2H), 1.69 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.52 (dt, *J* = 15.1, 7.5 Hz, 2H). ^{13}C NMR

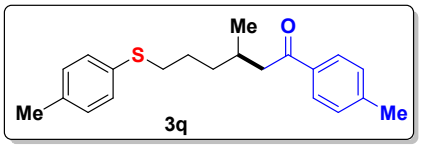
($CDCl_3$, 125 MHz, ppm) δ 199.3, 138.6, 136.3, 135.9, 132.0, 129.7, 128.2, 127.9, 126.9, 38.5, 33.6, 29.1, 28.5, 23.8, 21.4. HRMS calcd for $C_{20}H_{24}BrOS^+$ $[M+H]^+$: 391.0731; found 391.0737.



1-(4-Bromophenyl)-6-(naphthalen-2-ylthio)hexan-1-one (3o). Eluent petroleum ether/ethyl acetate (70:1). Yellow solid, 57 mg, 69% yield. ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.81 – 7.76 (m, 3H), 7.75 – 7.71 (m, 3H), 7.58 (d, J = 8.5 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.44 – 7.40 (m, 2H), 3.04 (t, J = 7.2 Hz, 2H), 2.92 (t, J = 7.2 Hz, 2H), 1.79 – 1.72 (m, 4H), 1.55 – 1.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.2, 135.8, 134.4, 133.9, 132.0, 131.8, 129.7, 128.5, 128.2, 127.9, 127.5, 127.2, 126.9, 126.7, 125.7, 38.4, 33.5, 29.0, 28.5, 23.8. HRMS calcd for $C_{22}H_{22}BrOS^+$ $[M+H]^+$: 413.0575; found 413.0575.

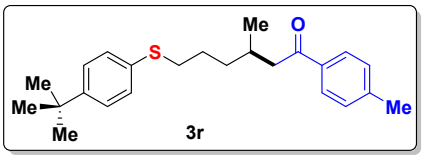


3-Methyl-1-phenyl-6-(*p*-tolylthio)hexan-1-one (3p). Eluent petroleum ether/ethyl acetate (90:1). Yellow oil, 46 mg, 74% yield. ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.93 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.08 (d, J = 7.8 Hz, 2H), 2.97 – 2.87 (m, 2H), 2.83 – 2.74 (m, 2H), 2.31 (s, 3H), 2.21 – 2.15 (m, 1H), 1.69 – 1.59 (m, 2H), 1.55 – 1.51 (m, 1H), 1.42 – 1.32 (m, 1H), 0.95 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 137.5, 136.1, 133.0, 132.9, 130.1, 129.8, 128.7, 128.2, 45.9, 36.2, 34.7, 29.5, 26.9, 21.1, 20.1. HRMS calcd for $C_{20}H_{25}OS^+$ $[M+H]^+$: 313.1626; found 313.1629.

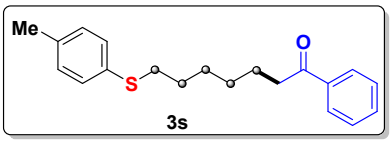


3-Methyl-1-(*p*-tolyl)-6-(*p*-tolylthio)hexan-1-one (3q). Eluent petroleum ether/ethyl acetate (80:1). White solid, 45 mg, 68% yield. ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.95

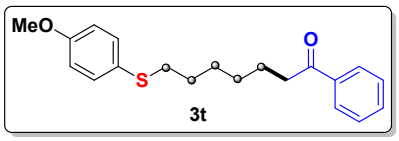
(t, J = 7.9 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.09 (d, J = 7.9 Hz, 2H), 2.92 – 2.85 (m, 2H), 2.78 (dd, J = 16.0, 7.8 Hz, 1H), 2.32 (s, 3H), 2.22 – 2.16 (m, 1H), 1.76 – 1.66 (m, 2H), 1.57 – 1.50 (m, 1H), 1.43 – 1.35 (m, 1H), 0.96 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 137.5, 136.1, 133.0, 132.9, 130.1, 129.8, 128.7, 128.2, 45.9, 36.2, 34.7, 29.5, 26.9, 21.1, 20.1. HRMS calcd for $C_{21}H_{27}OS^+$ $[M+H]^+$: 327.1783; found 327.1784.



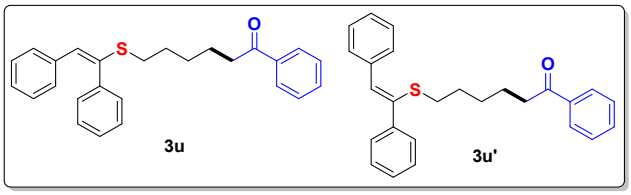
6-((4-(*tert*-Butyl)phenyl)thio)-3-methyl-1-(*p*-tolyl)hexan-1-one (3r). Eluent petroleum ether/ethyl acetate (80:1). Yellow solid, 46 mg, 63% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.78 – 7.71 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.27 (m, 4H), 2.92 – 2.87 (m, 2H), 2.77 (dd, J = 16.0, 7.8 Hz, 1H), 2.41 (s, 3H), 2.22 – 2.16 (m, 1H), 1.77 – 1.67 (m, 2H), 1.55 – 1.53 (m, 2H), 1.30 (s, 9H), 1.29 – 1.25 (m, 2H), 0.95 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.4, 149.3, 138.5, 133.8, 132.4, 129.6, 128.7, 128.6, 126.0, 125.4, 45.9, 36.3, 34.6, 34.5, 31.4, 29.5, 26.9, 21.5, 20.1. HRMS calcd for $C_{24}H_{33}OS^+$ $[M+H]^+$: 369.2252; found 369.2259.



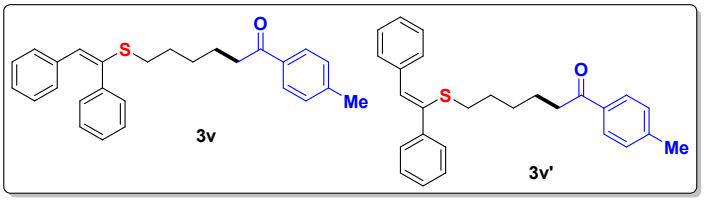
1-Phenyl-7-(*p*-tolylthio)heptan-1-one (3s). Eluent petroleum ether/ethyl acetate (80:1). White solid, 44 mg, 71% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.95 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.24 (t, J = 7.0 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 2.96 (t, J = 7.3 Hz, 2H), 2.88 (t, J = 7.4 Hz, 2H), 2.31 (s, 3H), 1.77 – 1.70 (m, 2H), 1.63 (dt, J = 14.9, 7.5 Hz, 2H), 1.47 (dt, J = 14.3, 6.9 Hz, 2H), 1.40 (dt, J = 15.0, 7.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.5, 137.2, 136.0, 133.1, 133.1, 129.9, 129.8, 128.7, 128.2, 38.6, 34.4, 29.2, 29.0, 28.7, 24.3, 21.1. HRMS calcd for $C_{20}H_{25}OS^+$ $[M+H]^+$: 313.1626; found 313.1631.



7-((4-Methoxyphenyl)thio)-1-phenylheptan-1-one (3t). Eluent petroleum ether/ethyl acetate (80:1). White solid, 45 mg, 69% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.3 Hz, 2H), 1.76 – 1.69 (m, 2H), 1.59 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.45 (dt, *J* = 14.4, 6.9 Hz, 2H), 1.37 (dt, *J* = 14.2, 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.5, 158.9, 137.2, 133.1, 133.0, 128.7, 128.2, 126.9, 114.6, 55.4, 38.6, 35.9, 29.3, 28.9, 28.6, 24.3. HRMS calcd for $C_{20}H_{25}O_2S^+$ $[M+H]^+$: 329.1575; found 329.1573.

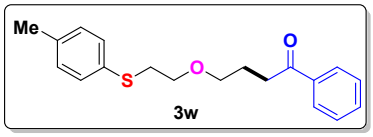


Compound 3u and 3u'. Eluent petroleum ether/ethyl acetate (60:1). Yellow solid, 48 mg, 62% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.98 – 7.93 (m, 2H), 7.92 – 7.88 (m, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.59 – 7.54 (m, 4H), 7.47 – 7.44 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 4H), 7.35 – 7.26 (m, 8H), 7.09 – 7.06 (m, 2H), 6.95 – 6.90 (m, 2H), 6.81 (s, 1H), 6.75 (s, 1H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.54 (t, *J* = 7.3 Hz, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 1.71 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.60 (t, *J* = 8.1 Hz, 4H), 1.45 (dt, *J* = 15.1, 7.3 Hz, 4H), 1.33 – 1.29 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.3, 141.2, 138.3, 138.2, 137.8, 137.2, 137.1, 136.9, 133.1, 133.1, 132.3, 129.7, 129.7, 129.0, 128.8, 128.7, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.3, 127.0, 126.6, 38.5, 38.4, 32.7, 31.8, 29.7, 29.1, 28.5, 28.3, 23.9, 23.8. HRMS calcd for $C_{26}H_{27}OS^+$ $[M+H]^+$: 387.1783; found 387.1785.

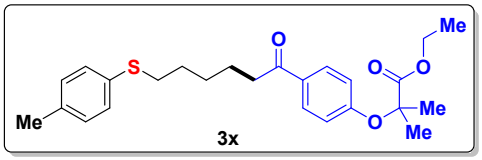


Compound 3v and 3v'. Eluent petroleum ether/ethyl acetate (60:1). Yellow oil, 46 mg,

58% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.39 – 7.35 (m, 4H), 7.33 – 7.31 (m, 4H), 7.29 – 7.27 (m, 2H), 7.26 – 7.24 (m, 2H), 7.24 – 7.22 (m, 4H), 7.08 – 7.05 (m, 2H), 6.93 – 6.91 (m, 2H), 6.80 (s, 1H), 6.74 (s, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 7.3 Hz, 2H), 2.42 (d, *J* = 7.5 Hz, 2H), 2.40 (s, 6H), 1.68 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.64 – 1.57 (m, 4H), 1.48 – 1.43 (m, 4H), 1.29 (dt, *J* = 9.3, 2.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.0, 143.8, 141.3, 138.4, 138.2, 137.8, 137.3, 136.9, 134.7, 132.3, 129.8, 129.7, 129.4, 129.4, 129.0, 128.8, 128.5, 128.5, 128.3, 128.2, 128.1, 128.0, 127.3, 127.1, 126.6, 38.4, 38.3, 32.7, 31.8, 29.9, 29.7, 29.2, 28.6, 28.3, 24.0, 23.9, 21.8. HRMS calcd for $C_{27}H_{29}OS^+$ $[M+H]^+$: 401.1939; found 401.1930.

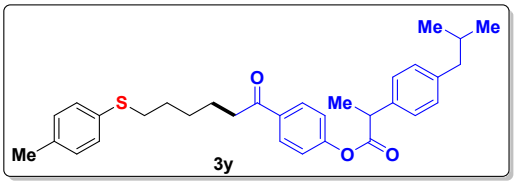


1-Phenyl-4-(2-(*p*-tolylthio)ethoxy)butan-1-one (3w). Eluent petroleum ether/ethyl acetate (60:1). White solid, 33 mg, 52% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.52 (t, *J* = 6.1 Hz, 2H), 3.07 (t, *J* = 5.6 Hz, 2H), 3.04 (t, *J* = 5.3 Hz, 2H), 2.30 (s, 3H), 2.05 – 1.97 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 137.2, 136.5, 133.1, 130.4, 129.8, 128.7, 128.2, 70.1, 69.6, 35.2, 34.1, 24.4, 21.1. HRMS calcd for $C_{19}H_{23}O_2S^+$ $[M+H]^+$: 315.1419; found 315.1419.

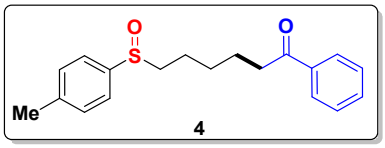


Ethyl 2-methyl-2-(4-(6-(*p*-tolylthio)hexanoyl)phenoxy)propanoate (3x). Eluent petroleum ether/ethyl acetate (40:1). Colorless oil, 61 mg, 71% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.3 Hz, 4H), 2.31 (s, 3H), 1.75 – 1.70 (m, 2H), 1.69 – 1.67 (m, 2H), 1.65 (s, 6H), 1.49 (dt, *J* = 15.0,

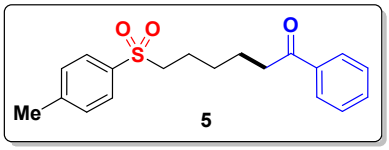
7.4 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 198.9, 173.9, 159.8, 136.1, 132.9, 130.3, 130.1, 130.0, 129.8, 117.5, 79.5, 61.8, 38.2, 34.4, 29.2, 28.6, 25.5, 24.1, 21.1, 14.2. HRMS calcd for $C_{25}H_{33}O_4S^+$ $[M+H]^+$: 429.2100; found 429.2109.



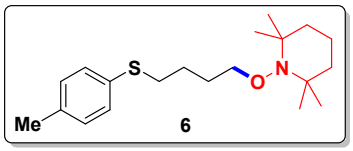
4-(6-(*p*-Tolylthio)hexanoyl)phenyl 2-(4-isobutylphenyl)propanoate (3y). Eluent petroleum ether/ethyl acetate (40:1). Yellow oil, 68 mg, 68% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.93 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.12 – 7.04 (m, 5H), 3.95 (q, J = 7.1 Hz, 1H), 2.90 (dt, J = 12.2, 7.3 Hz, 4H), 2.48 (d, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.90 – 1.84 (m, 1H), 1.76 – 1.71 (m, 2H), 1.69 – 1.64 (m, 2H), 1.61 (d, J = 7.2 Hz, 3H), 1.53 – 1.46 (m, 2H), 0.92 (s, 3H), 0.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.1, 172.9, 154.6, 141.2, 137.0, 136.1, 134.6, 132.9, 130.1, 129.8, 129.7, 129.7, 127.3, 121.7, 45.5, 45.2, 38.4, 34.4, 30.3, 29.2, 28.5, 23.9, 22.5, 21.1, 18.6. HRMS calcd for $C_{32}H_{39}O_3S^+$ $[M+H]^+$: 503.2620; found 503.2621.



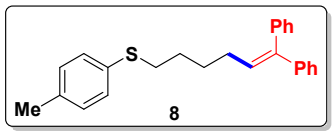
1-Phenyl-6-(*p*-tolylsulfinyl)hexan-1-one (4). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 39 mg, 62% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.92 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.50 (d, J = 7.9 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 2.95 (t, J = 7.2 Hz, 2H), 2.80 (t, J = 6.2 Hz, 2H), 2.40 (s, 3H), 1.83 – 1.70 (m, 3H), 1.65 (dt, J = 14.5, 6.6 Hz, 1H), 1.57 – 1.44 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.0, 141.6, 140.7, 137.1, 133.1, 130.1, 128.7, 128.1, 124.2, 57.1, 38.2, 28.4, 23.8, 22.2, 21.5. HRMS calcd for $C_{19}H_{23}O_2S^+$ $[M+H]^+$: 315.1419; found 315.1417.



1-Phenyl-6-tosylhexan-1-one (5). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 30 mg, 46% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.91 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 7.1 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 3.08 (t, J = 8.2 Hz, 2H), 2.94 (t, J = 6.8 Hz, 2H), 2.44 (s, 3H), 1.76 (dt, J = 15.3, 7.6 Hz, 2H), 1.70 (dt, J = 14.6, 7.1 Hz, 2H), 1.49 – 1.41 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 199.8, 144.7, 137.0, 136.4, 133.2, 130.0, 128.7, 128.2, 128.1, 56.3, 38.0, 28.0, 23.6, 22.8, 21.7. HRMS calcd for $C_{19}H_{23}O_3S^+$ $[M+H]^+$: 331.1368; found 331.1367.

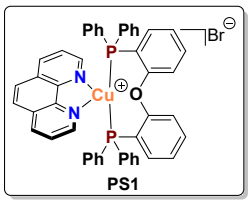


2,2,6,6-Tetramethyl-1-(4-(*p*-tolylthio)butoxy)piperidine (6). Eluent petroleum ether. White solid, 55 mg, 82% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.30 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 3.77 (t, J = 6.2 Hz, 2H), 2.94 (t, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.75 (dt, J = 14.5, 7.2 Hz, 2H), 1.69 (dt, J = 13.3, 6.2 Hz, 2H), 1.59 – 1.54 (m, 1H), 1.50 – 1.46 (m, 4H), 1.35 (d, J = 12.0 Hz, 1H), 1.16 (s, 6H), 1.11 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 136.1, 133.1, 130.2, 129.7, 76.3, 59.8, 39.7, 34.8, 33.2, 28.1, 26.5, 21.1, 20.3, 17.3. HRMS calcd for $C_{20}H_{34}NOS^+$ $[M+H]^+$: 336.2361; found 336.2360.



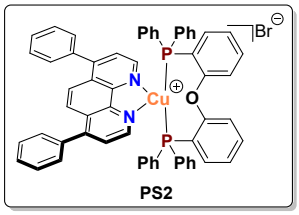
(6,6-Diphenylhex-5-en-1-yl)(*p*-tolyl)sulfane (8). Eluent petroleum ether. White solid, 45 mg, 63% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.38 (t, J = 7.4 Hz, 2H), 7.35 – 7.25 (m, 4H), 7.25 – 7.21 (m, 4H), 7.18 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.07 (t, J = 7.4 Hz, 1H), 2.84 (t, J = 6.9 Hz, 2H), 2.34 (s, 3H), 2.15 (q, J = 7.1 Hz, 2H), 1.66 – 1.57 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 142.8, 142.1, 140.3, 136.1,

132.9, 130.1, 130.0, 129.7, 129.6, 128.3, 128.2, 127.3, 127.0, 126.9, 34.3, 29.3, 29.0, 28.8, 21.1. HRMS calcd for $C_{25}H_{27}S^+$ $[M+H]^+$: 359.1833; found 359.1834.



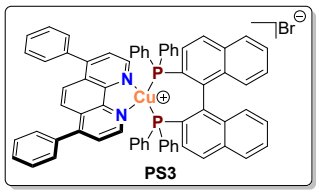
PS1

[Cu(Phen)(DPEphos)]Br (PS1). Yellow solid, 259 mg, 60% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.66 (s, 2H), 8.60 (d, *J* = 7.8 Hz, 2H), 8.09 (s, 2H), 7.76 – 7.67 (m, 2H), 7.30 – 7.26 (m, 2H), 7.20 (d, *J* = 6.2 Hz, 4H), 7.07 – 7.01 (m, 10H), 6.97 – 6.91 (m, 10H), 6.74 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 158.4, 158.4, 158.3, 149.4, 143.2, 137.8, 134.2, 132.9, 132.9, 132.8, 132.1, 130.8, 130.6, 130.5, 130.1, 129.6, 128.7, 128.7, 128.7, 127.5, 125.2, 123.9, 123.8, 123.7, 120.4. HRMS calcd for $C_{48}H_{36}CuN_2OP_2^+$ $[M]^+$: 781.1593; found 781.1589.



PS2

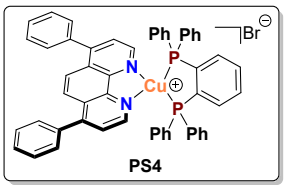
[Cu(dpp)(DPEphos)]Br (PS2). Yellow solid, 320 mg, 63% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.39 (s, 2H), 8.06 (s, 2H), 7.75 (s, 2H), 7.63 – 7.55 (m, 15H), 7.41 – 7.36 (m, 13H), 7.28 – 7.26 (m, 13H), 7.06 – 7.04 (m, 5H), 6.93 (s, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 158.3, 158.3, 158.3, 149.8, 148.9, 143.8, 135.9, 134.1, 132.9, 132.8, 132.8, 132.2, 130.7, 130.6, 130.5, 130.0, 129.4, 129.0, 128.7, 128.6, 128.6, 127.1, 125.2, 125.1, 124.8, 123.7, 123.6, 123.5, 120.4. HRMS calcd for $C_{60}H_{44}CuN_2OP_2^+$ $[M]^+$: 933.2219; found 933.2214.



PS3

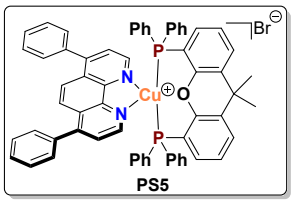
[Cu(dpp)(BINAP)]Br (PS3). Yellow solid, 368 mg, 67% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 9.05 (s, 2H), 8.13 (s, 2H), 7.95 (s, 2H), 7.59 (s, 10H), 7.35 – 7.23 (m, 16H), 7.11 (s, 8H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.79 (s, 2H), 6.65 (s, 4H). ^{13}C NMR

($CDCl_3$, 125 MHz, ppm) δ 150.5, 150.2 144.2, 139.3, 136.0, 134.2, 133.7, 133.2, 132.9, 132.1, 131.4, 130.6, 129.7, 129.2, 128.1, 127.6, 127.3, 126.9, 126.6, 125.5, 125.2. HRMS calcd for $C_{68}H_{48}CuN_2P_2^+$ $[M]^+$: 1017.2583; found 1017.2587.



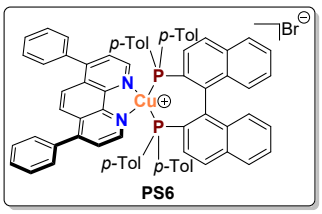
PS4

[Cu(dpp)(DPPBz)]Br (PS4). Yellow solid, 272 mg, 59% yield. ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.37 (s, 2H), 8.04 (s, 2H), 7.73 (s, 2H), 7.64 – 7.59 (m, 3H), 7.53 (s, 9H), 7.40 – 7.37 (m, 3H), 7.35 – 7.32 (m, 8H), 7.25 – 7.22 (m, 9H), 7.04 – 7.01 (m, 1H), 6.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 150.4, 149.5, 144.4, 141.2, 135.9, 134.9, 134.0, 132.7, 132.7, 132.6, 132.4, 132.1, 131.9, 131.8, 131.7, 130.4, 130.2, 129.6, 129.2, 129.1, 128.9, 127.6, 125.3, 125.1. HRMS calcd for $C_{54}H_{40}CuN_2P_2^+$ $[M]^+$: 841.1957; found 841.1954.



PS5

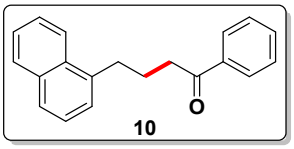
[Cu(dpp)(Xantphos)]Br (PS5). Yellow solid, 343 mg, 65% yield. ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.51 (s, 2H), 7.95 (s, 2H), 7.69 – 7.58 (m, 4H), 7.57 – 7.44 (m, 10H), 7.21 (t, J = 7.3 Hz, 4H), 7.15 (t, J = 7.5 Hz, 2H), 7.05 (t, J = 7.0 Hz, 9H), 6.95 (s, 7H), 6.65 (s, 2H), 1.74 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 154.9, 154.9, 154.8, 150.0, 148.6, 143.9, 135.9, 133.9, 132.7, 131.4, 131.2, 131.1, 131.1, 129.9, 129.5, 129.1, 128.7, 128.6, 128.6, 127.4, 127.3, 125.3, 125.2, 124.9, 119.6, 119.5, 119.4, 36.1, 28.3. HRMS calcd for $C_{63}H_{48}CuN_2OP_2^+$ $[M]^+$: 973.2532; found 973.2529.



PS6

[Cu(dpp)(*Tol*-BINAP)]Br (PS6). Yellow solid, 352 mg, 61% yield. ^1H NMR ($CDCl_3$, 500 MHz, ppm) δ 9.09 (s, 2H), 8.14 (s, 2H), 7.94 (s, 2H), 7.74 (s, 2H), 7.59 (s, 13H),

7.35 (s, 4H), 7.13 (d, J = 41.2 Hz, 6H), 6.95 (s, 8H), 6.87 (d, J = 7.0 Hz, 2H), 6.38 (s, 4H), 2.20 (s, 6H), 1.94 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 150.3, 149.8, 144.0, 140.8, 139.5, 139.0, 135.8, 133.9, 133.5, 133.0, 132.5, 132.1, 131.9, 131.9, 129.7, 129.7, 129.6, 129.5, 129.1, 128.8, 128.1, 127.9, 127.5, 127.2, 126.9, 126.4, 126.3, 126.3, 125.4, 125.1, 21.1, 20.9. HRMS calcd for $C_{72}H_{56}CuN_2P_2^+$ $[M]^+$: 1073.3209; found 1073.3215.



10

4-(Naphthalen-1-yl)-1-phenylbutan-1-one. Eluent petroleum ether. Yellow solid, 28 mg, 51% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 8.13 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 7.7 Hz, 2H), 7.86 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.49 – 7.42 (m, 3H), 7.40 (t, J = 7.5 Hz, 1H), 7.34 (d, J = 6.8 Hz, 1H), 3.19 (t, J = 7.6 Hz, 2H), 3.08 (t, J = 7.0 Hz, 2H), 2.27 – 2.18 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 200.2, 138.1, 137.3, 134.1, 133.1, 132.1, 128.9, 128.7, 128.2, 126.9, 126.3, 126.0, 125.7, 124.1, 38.2, 32.6, 25.2. HRMS calcd for $C_{20}H_{19}O^+$ $[M+H]^+$: 275.1436; found 275.1441.

VI. References

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VII. X-ray Crystallography Data of 3d.

Crystal preparation of compound 3d.

Compound **3d** (25 mg) was dissolved in 4 mL of CH_2Cl_2/Et_2O (v_1/v_2 = 1:3), and it was crystallized to give crystal as colorless prisms after the solvent was slowly volatilized in 3 days at room temperature (~ 25 °C).

All diffraction data were obtained on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo Kα radiation. X-ray crystallographic data for **3d** is available as Figure S11. X-ray crystallographic data in CIF format are available from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/).

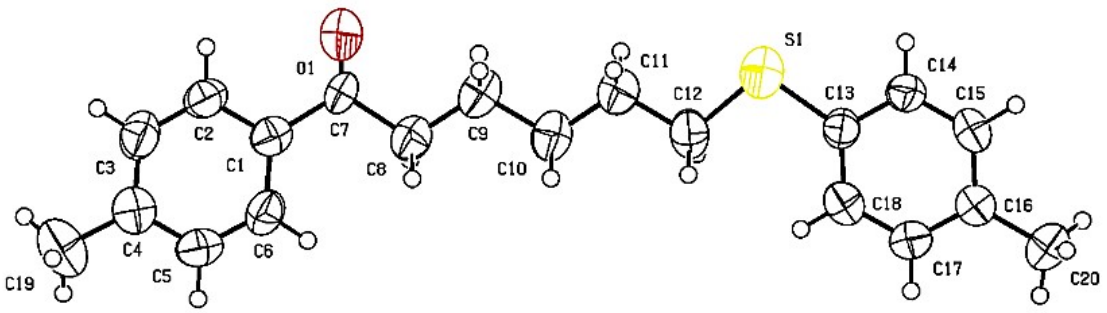


Figure S11. X-ray crystallography of **3d**.

Table 1. Crystal data and structure refinement for **3d**.

CCDC number	2242756
Identification code	230215d
Empirical formula	C20 H24 O S
Formula weight	312.45
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 20.6821(17) A alpha = 90 deg.
	b = 14.2922(12) A beta = 92.440(2) deg.
	c = 5.8697(4) A gamma = 90 deg.
Volume	1733.5(2) A^3
Z, Calculated density	4, 1.197 Mg/m^3
Absorption coefficient	0.187 mm^-1
F(000)	672

Crystal size	0.35 x 0.30 x 0.04 mm
Theta range for data collection	2.43 to 25.02 deg.
Limiting indices	-24<=h<=17, -17<=k<=16, -5<=l<=6
Reflections collected / unique	8197 / 3025 [R(int) = 0.1345]
Completeness to theta = 25.02	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9926 and 0.9375
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3025 / 0 / 199
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0792, wR2 = 0.1191
R indices (all data)	R1 = 0.2016, wR2 = 0.1424
Largest diff. peak and hole	0.238 and -0.198 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3d**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	7869(2)	4084(3)	10550(6)	93(1)
S(1)	4233(1)	4201(1)	7363(2)	93(1)
C(1)	8570(2)	3814(3)	7832(7)	53(1)
C(2)	9116(2)	4098(3)	9123(6)	62(1)
C(3)	9725(2)	4033(3)	8289(8)	71(1)
C(4)	9835(2)	3663(3)	6194(9)	66(1)
C(5)	9295(2)	3389(3)	4915(7)	64(1)
C(6)	8688(2)	3457(3)	5687(7)	64(1)
C(7)	7919(2)	3858(3)	8863(7)	48(1)
C(8)	7343(2)	3545(3)	7332(6)	64(1)
C(9)	6708(2)	3813(3)	8254(7)	66(1)
C(10)	6115(2)	3548(3)	6775(7)	69(1)
C(11)	5497(2)	3900(3)	7622(6)	70(1)
C(12)	4912(2)	3706(3)	6105(6)	69(1)
C(13)	3587(2)	3975(3)	5395(7)	53(1)
C(14)	2994(2)	4265(3)	6024(6)	56(1)
C(15)	2447(2)	4127(3)	4633(7)	60(1)

C(16)	2479(2)	3667(3)	2567(7)	51(1)
C(17)	3072(2)	3389(3)	1951(7)	58(1)
C(18)	3623(2)	3520(3)	3330(7)	60(1)
C(19)	10498(2)	3605(3)	5362(8)	98(2)
C(20)	1885(2)	3503(3)	1045(6)	74(1)

Table 3. Bond lengths [A] and angles [deg] for **3d**.

O(1)-C(7)	1.051(4)
S(1)-C(13)	1.759(4)
S(1)-C(12)	1.763(4)
C(1)-C(6)	1.389(5)
C(1)-C(2)	1.393(5)
C(1)-C(7)	1.501(5)
C(2)-C(3)	1.373(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.367(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(5)
C(4)-C(19)	1.476(5)
C(5)-C(6)	1.357(5)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.528(5)
C(8)-C(9)	1.491(4)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.520(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.480(5)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.497(4)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9700

C(12)-H(12B)	0.9700
C(13)-C(14)	1.359(4)
C(13)-C(18)	1.381(5)
C(14)-C(15)	1.380(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.383(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.353(5)
C(16)-C(20)	1.506(5)
C(17)-C(18)	1.383(4)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(13)-S(1)-C(12)	104.4(2)
C(6)-C(1)-C(2)	115.6(4)
C(6)-C(1)-C(7)	125.1(4)
C(2)-C(1)-C(7)	119.3(4)
C(3)-C(2)-C(1)	121.3(4)
C(3)-C(2)-H(2)	119.3
C(1)-C(2)-H(2)	119.3
C(4)-C(3)-C(2)	122.6(4)
C(4)-C(3)-H(3)	118.7
C(2)-C(3)-H(3)	118.7
C(3)-C(4)-C(5)	116.0(4)
C(3)-C(4)-C(19)	120.9(5)
C(5)-C(4)-C(19)	123.1(5)
C(6)-C(5)-C(4)	122.6(4)
C(6)-C(5)-H(5)	118.7
C(4)-C(5)-H(5)	118.7
C(5)-C(6)-C(1)	121.9(4)
C(5)-C(6)-H(6)	119.0
C(1)-C(6)-H(6)	119.0
O(1)-C(7)-C(1)	121.3(4)

O(1)-C(7)-C(8)	122.5(5)
C(1)-C(7)-C(8)	116.2(4)
C(9)-C(8)-C(7)	112.8(3)
C(9)-C(8)-H(8A)	109.0
C(7)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8B)	109.0
C(7)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
C(8)-C(9)-C(10)	115.5(3)
C(8)-C(9)-H(9A)	108.4
C(10)-C(9)-H(9A)	108.4
C(8)-C(9)-H(9B)	108.4
C(10)-C(9)-H(9B)	108.4
H(9A)-C(9)-H(9B)	107.5
C(11)-C(10)-C(9)	114.3(3)
C(11)-C(10)-H(10A)	108.7
C(9)-C(10)-H(10A)	108.7
C(11)-C(10)-H(10B)	108.7
C(9)-C(10)-H(10B)	108.7
H(10A)-C(10)-H(10B)	107.6
C(10)-C(11)-C(12)	115.2(3)
C(10)-C(11)-H(11A)	108.5
C(12)-C(11)-H(11A)	108.5
C(10)-C(11)-H(11B)	108.5
C(12)-C(11)-H(11B)	108.5
H(11A)-C(11)-H(11B)	107.5
C(11)-C(12)-S(1)	108.4(3)
C(11)-C(12)-H(12A)	110.0
S(1)-C(12)-H(12A)	110.0
C(11)-C(12)-H(12B)	110.0
S(1)-C(12)-H(12B)	110.0
H(12A)-C(12)-H(12B)	108.4
C(14)-C(13)-C(18)	117.8(4)
C(14)-C(13)-S(1)	115.7(3)
C(18)-C(13)-S(1)	126.5(3)
C(13)-C(14)-C(15)	121.4(4)
C(13)-C(14)-H(14)	119.3
C(15)-C(14)-H(14)	119.3

C(14)-C(15)-C(16)	121.2(4)
C(14)-C(15)-H(15)	119.4
C(16)-C(15)-H(15)	119.4
C(17)-C(16)-C(15)	116.8(4)
C(17)-C(16)-C(20)	121.4(4)
C(15)-C(16)-C(20)	121.7(4)
C(16)-C(17)-C(18)	122.6(4)
C(16)-C(17)-H(17)	118.7
C(18)-C(17)-H(17)	118.7
C(13)-C(18)-C(17)	120.2(4)
C(13)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
C(4)-C(19)-H(19A)	109.5
C(4)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(4)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(16)-C(20)-H(20A)	109.5
C(16)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(16)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 230215d. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2hka*b*U12]

	U11	U22	U33	U23	U13	U12
O(1)	62(2)	126(3)	90(2)	-6(2)	-5(2)	9(2)
S(1)	66(1)	124(1)	90(1)	-4(1)	-4(1)	-2(1)
C(1)	63(3)	45(3)	52(3)	1(2)	-5(2)	7(2)
C(2)	68(3)	66(4)	52(3)	-8(2)	-7(3)	3(3)
C(3)	57(3)	70(4)	85(3)	-11(3)	-12(3)	-1(3)

C(4)	66(4)	58(4)	74(3)	5(3)	3(3)	2(3)
C(5)	79(4)	63(4)	50(3)	-6(2)	-2(3)	5(3)
C(6)	55(3)	74(4)	62(3)	4(3)	-13(3)	2(2)
C(7)	42(3)	47(3)	53(3)	4(2)	-14(3)	-2(2)
C(8)	60(3)	64(4)	66(3)	0(2)	-9(2)	2(2)
C(9)	67(3)	55(3)	74(3)	3(2)	-17(3)	-4(3)
C(10)	59(3)	62(4)	84(3)	1(2)	-8(3)	-4(2)
C(11)	61(3)	80(4)	68(3)	1(3)	-6(3)	3(3)
C(12)	50(3)	79(4)	79(3)	7(3)	2(3)	1(2)
C(13)	46(3)	61(3)	52(3)	4(2)	0(2)	-2(2)
C(14)	54(3)	65(4)	48(2)	-3(2)	5(2)	-6(2)
C(15)	47(3)	64(4)	69(3)	-1(3)	12(2)	4(2)
C(16)	55(3)	43(3)	56(3)	5(2)	5(2)	-1(2)
C(17)	63(3)	60(3)	49(3)	-2(2)	1(3)	-1(3)
C(18)	55(3)	60(4)	65(3)	5(2)	10(3)	5(2)
C(19)	80(4)	99(5)	118(4)	12(3)	28(3)	13(3)
C(20)	68(3)	80(4)	71(3)	-2(2)	-13(3)	-7(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3d**.

	x	y	z	U(eq)
H(2)	9067	4337	10580	75
H(3)	10075	4249	9185	85
H(5)	9349	3147	3465	77
H(6)	8340	3259	4753	77
H(8A)	7379	3822	5835	76
H(8B)	7358	2870	7156	76
H(9A)	6705	4485	8482	79
H(9B)	6673	3521	9736	79
H(10A)	6167	3789	5249	82
H(10B)	6093	2871	6670	82
H(11A)	5534	4571	7836	83
H(11B)	5432	3623	9102	83
H(12A)	4853	3036	5927	83

H(12B)	4966	3977	4611	83
H(14)	2956	4563	7421	67
H(15)	2050	4346	5095	72
H(17)	3110	3098	546	69
H(18)	4020	3300	2865	72
H(19A)	10520	3103	4280	147
H(19B)	10798	3488	6623	147
H(19C)	10606	4184	4642	147
H(20A)	1989	3084	-165	110
H(20B)	1737	4088	410	110
H(20C)	1551	3232	1920	110

Table 6. Torsion angles [deg] for **3d**.

C(6)-C(1)-C(2)-C(3)	0.7(6)
C(7)-C(1)-C(2)-C(3)	177.1(4)
C(1)-C(2)-C(3)-C(4)	-2.1(7)
C(2)-C(3)-C(4)-C(5)	2.4(7)
C(2)-C(3)-C(4)-C(19)	-179.9(4)
C(3)-C(4)-C(5)-C(6)	-1.5(7)
C(19)-C(4)-C(5)-C(6)	-179.1(4)
C(4)-C(5)-C(6)-C(1)	0.2(7)
C(2)-C(1)-C(6)-C(5)	0.2(6)
C(7)-C(1)-C(6)-C(5)	-176.0(4)
C(6)-C(1)-C(7)-O(1)	174.8(5)
C(2)-C(1)-C(7)-O(1)	-1.3(7)
C(6)-C(1)-C(7)-C(8)	-4.6(6)
C(2)-C(1)-C(7)-C(8)	179.3(4)
O(1)-C(7)-C(8)-C(9)	14.0(7)
C(1)-C(7)-C(8)-C(9)	-166.6(3)
C(7)-C(8)-C(9)-C(10)	178.2(3)
C(8)-C(9)-C(10)-C(11)	-174.5(4)
C(9)-C(10)-C(11)-C(12)	175.8(3)
C(10)-C(11)-C(12)-S(1)	-178.6(3)
C(13)-S(1)-C(12)-C(11)	177.6(3)
C(12)-S(1)-C(13)-C(14)	177.7(3)

C(12)-S(1)-C(13)-C(18)	-0.7(4)
C(18)-C(13)-C(14)-C(15)	-1.2(6)
S(1)-C(13)-C(14)-C(15)	-179.8(3)
C(13)-C(14)-C(15)-C(16)	1.5(6)
C(14)-C(15)-C(16)-C(17)	-2.0(6)
C(14)-C(15)-C(16)-C(20)	179.4(3)
C(15)-C(16)-C(17)-C(18)	2.3(6)
C(20)-C(16)-C(17)-C(18)	-179.1(3)
C(14)-C(13)-C(18)-C(17)	1.4(6)
S(1)-C(13)-C(18)-C(17)	179.8(3)
C(16)-C(17)-C(18)-C(13)	-2.0(6)

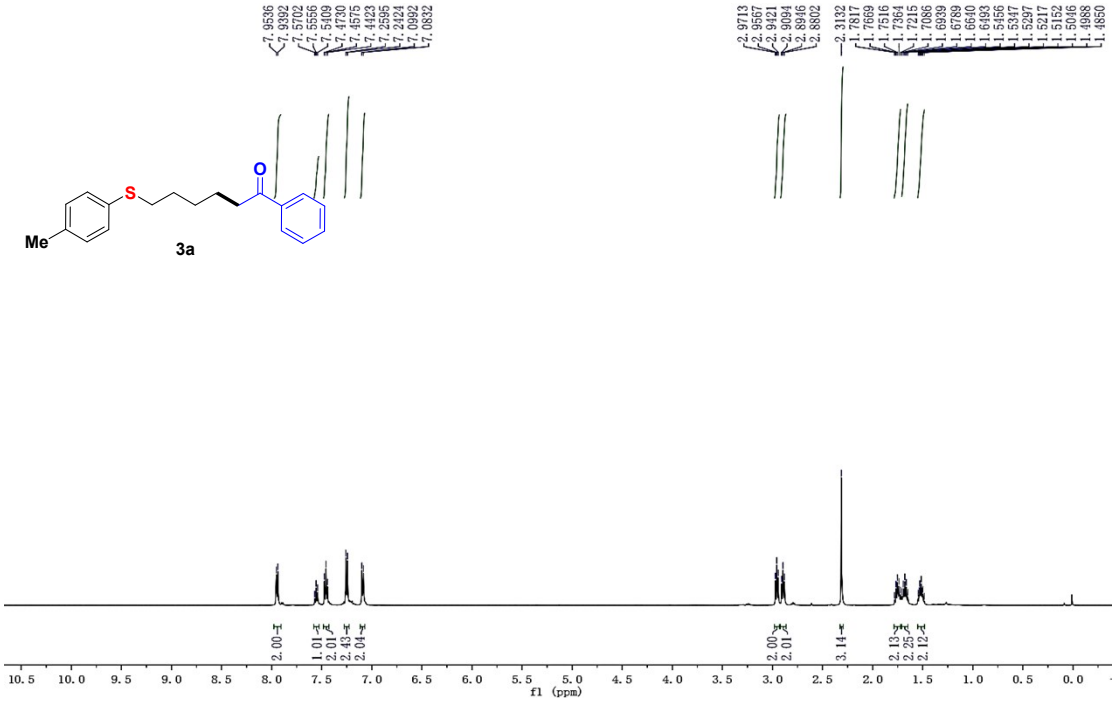
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3d** [A and deg.].

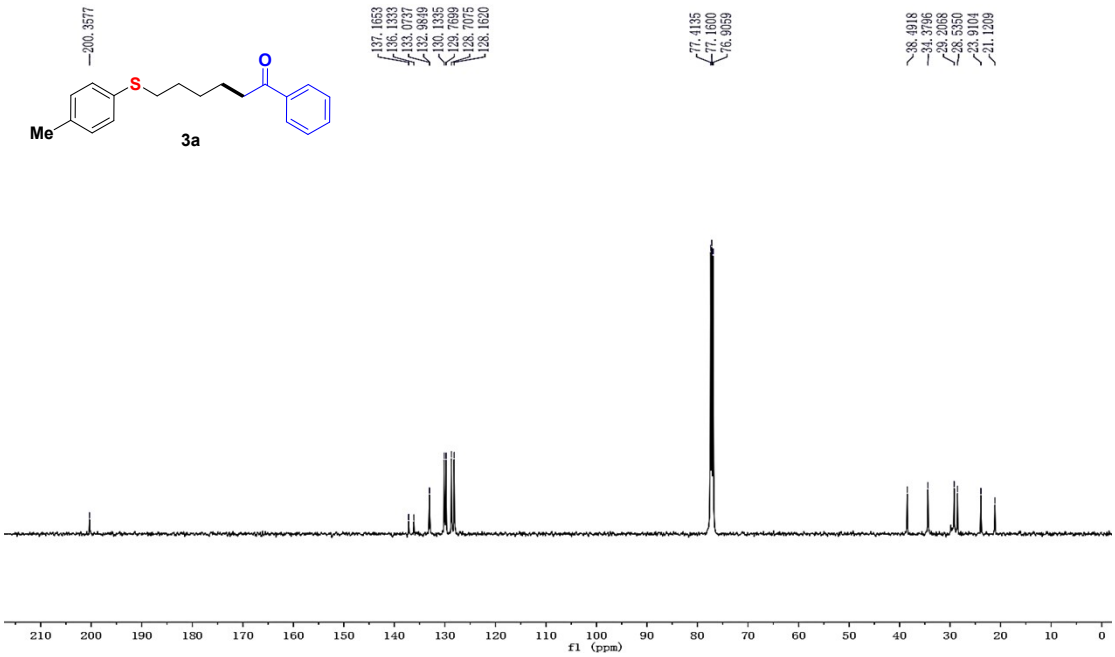
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

VIII. NMR spectra and HRMS of the products

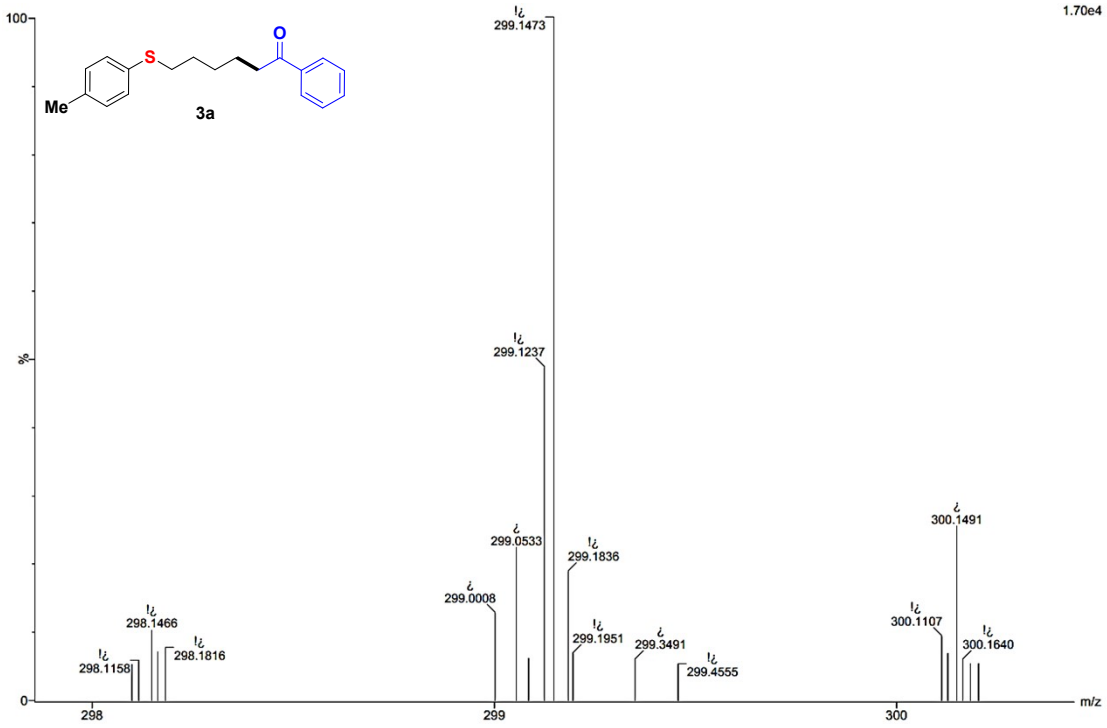
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3a**



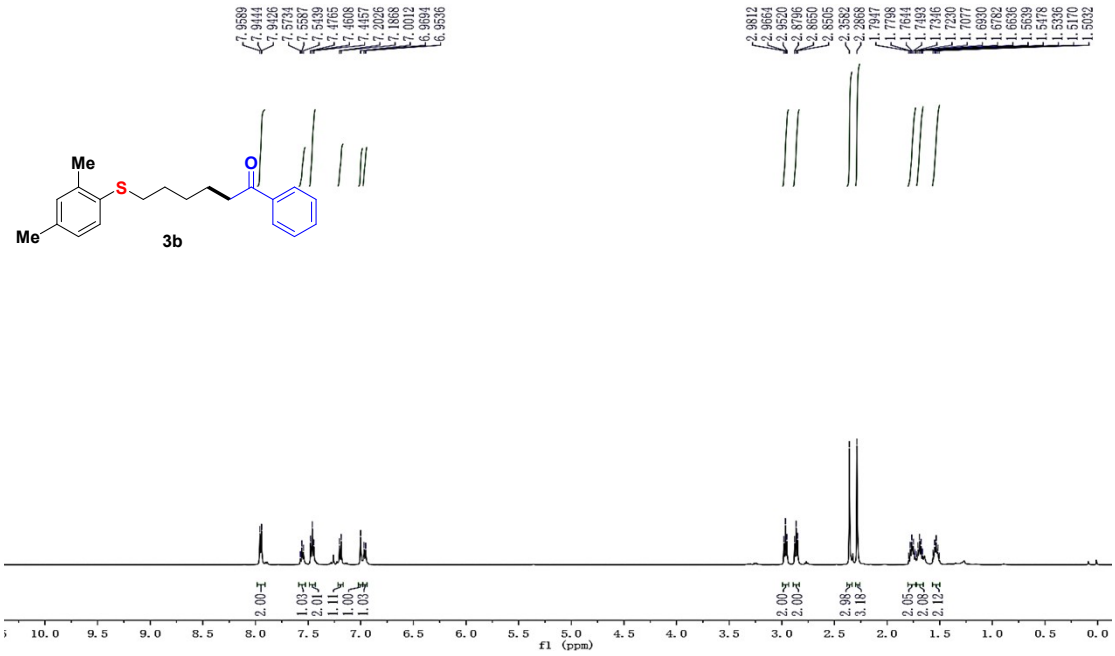
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3a**



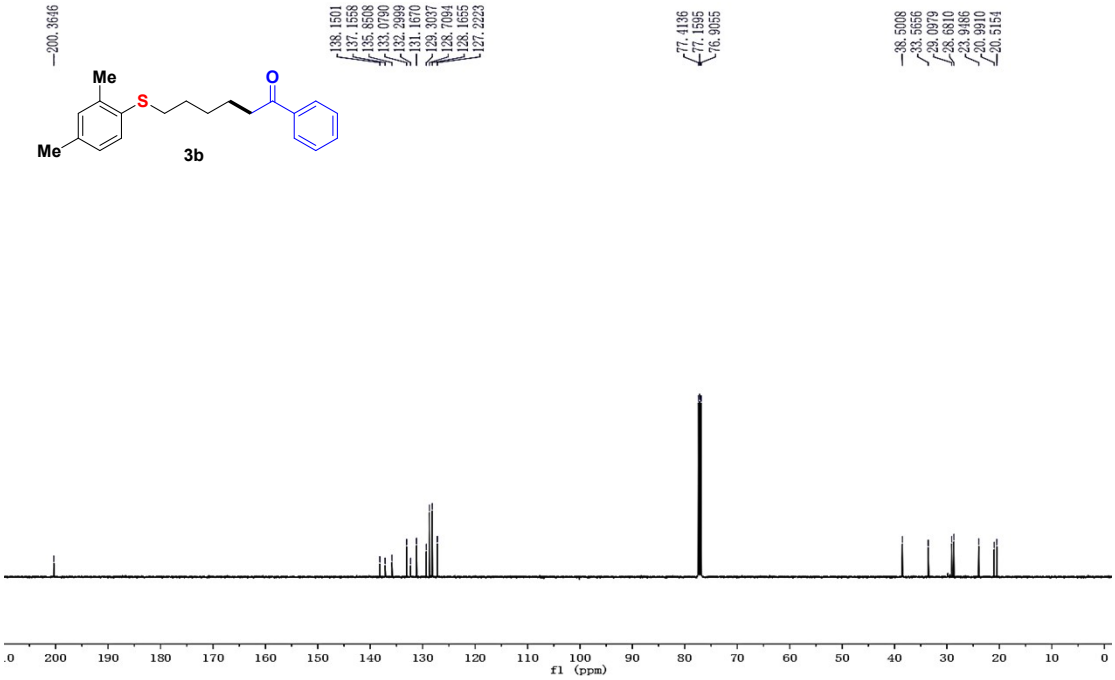
HRMS of **3a**


100
%
0
1.70e4
Me
S
O
3a
299.1473
299.1237
299.0533
299.1836
299.0008
299.1951
299.3491
299.4555
298.1466
298.1158
298.1816
300.1491
300.1107
300.1640
298
299
300
m/z

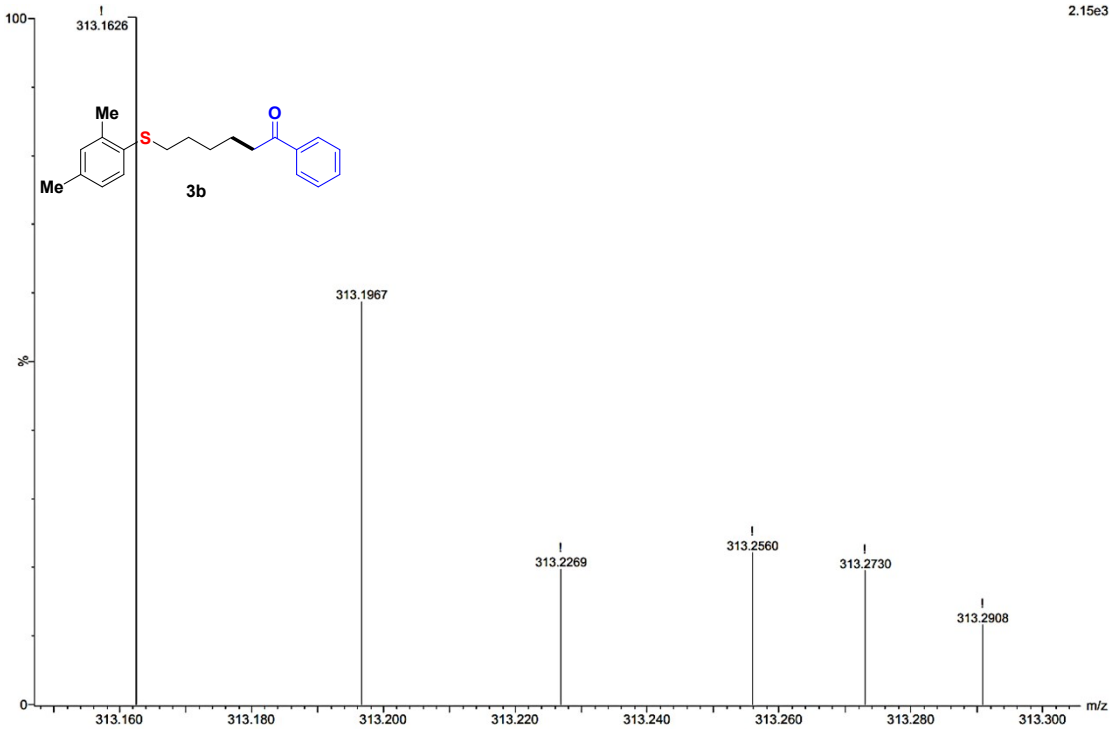
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3b**



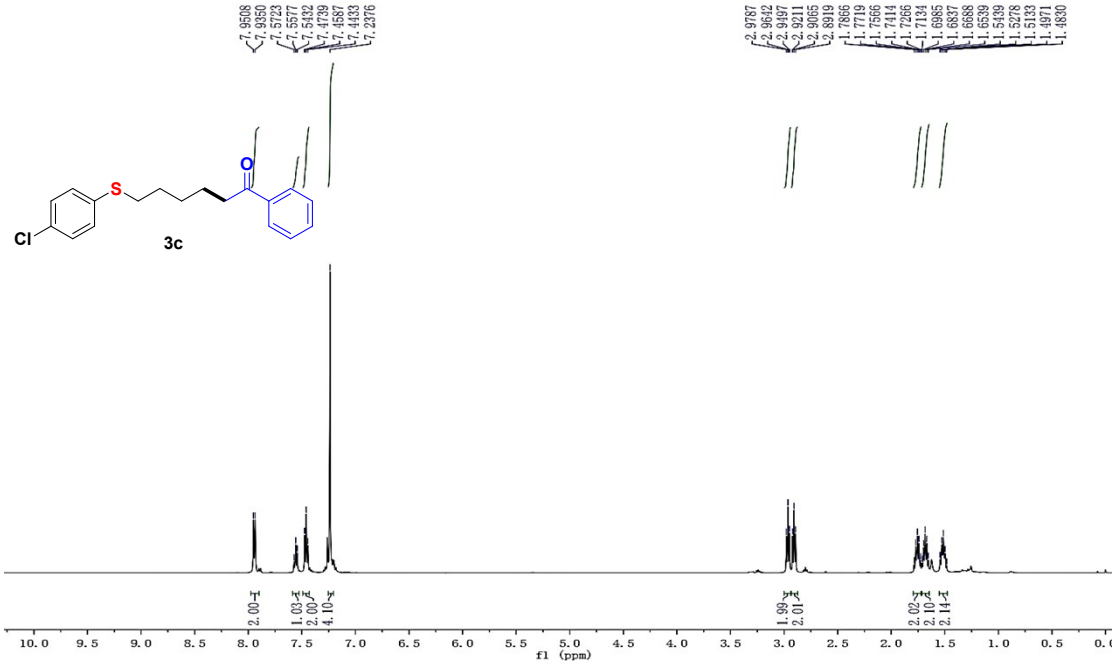
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3b**



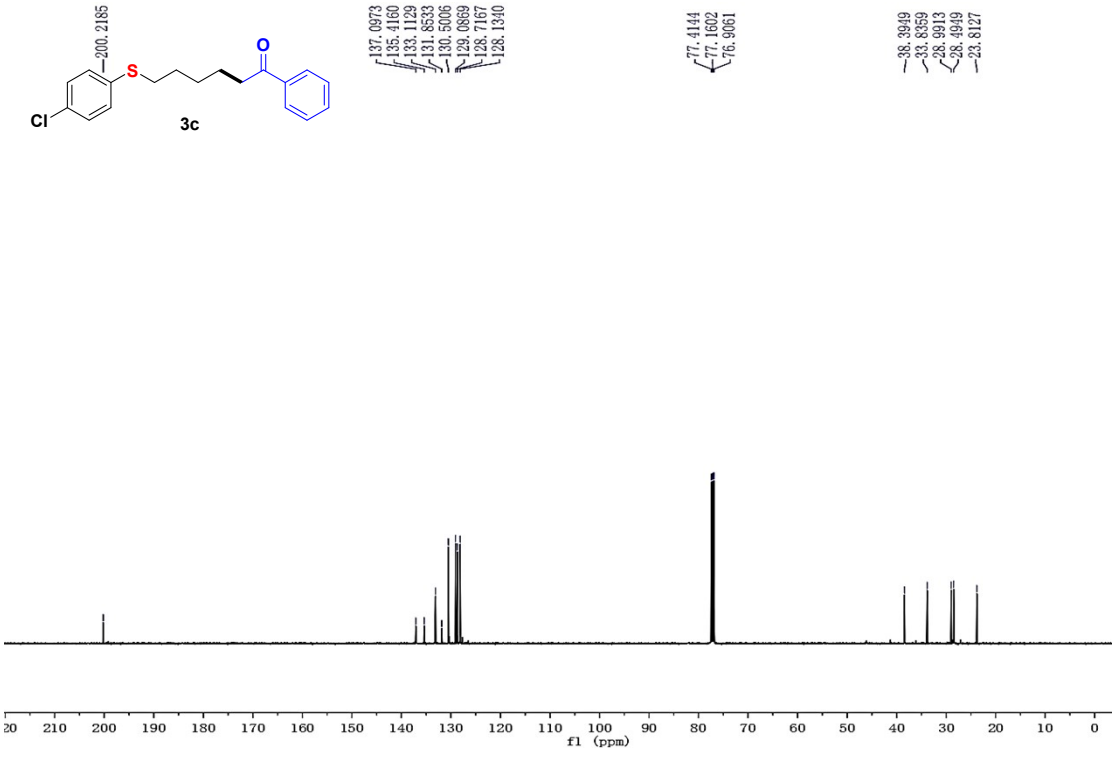
HRMS of **3b**


2.15e3
100
313.1626
Me
S
O
Me
3b
313.1967
%
313.2269
313.2560
313.2730
313.2908
0
313.160
313.180
313.200
313.220
313.240
313.260
313.280
313.300
m/z

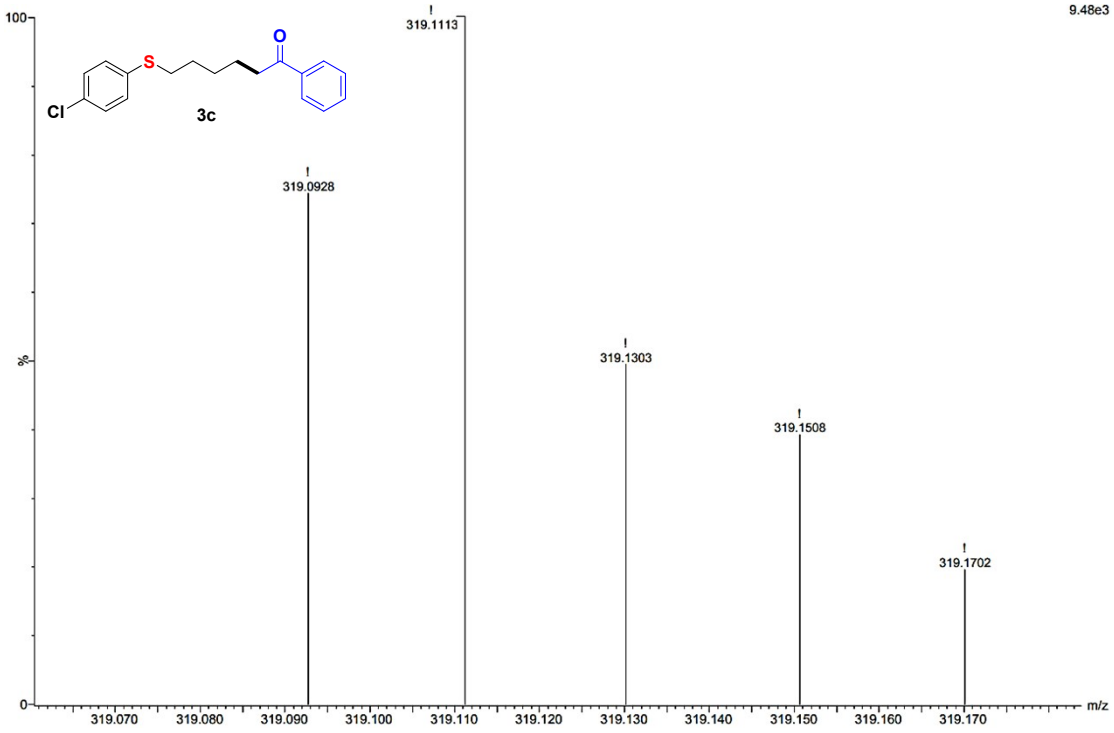
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3c**



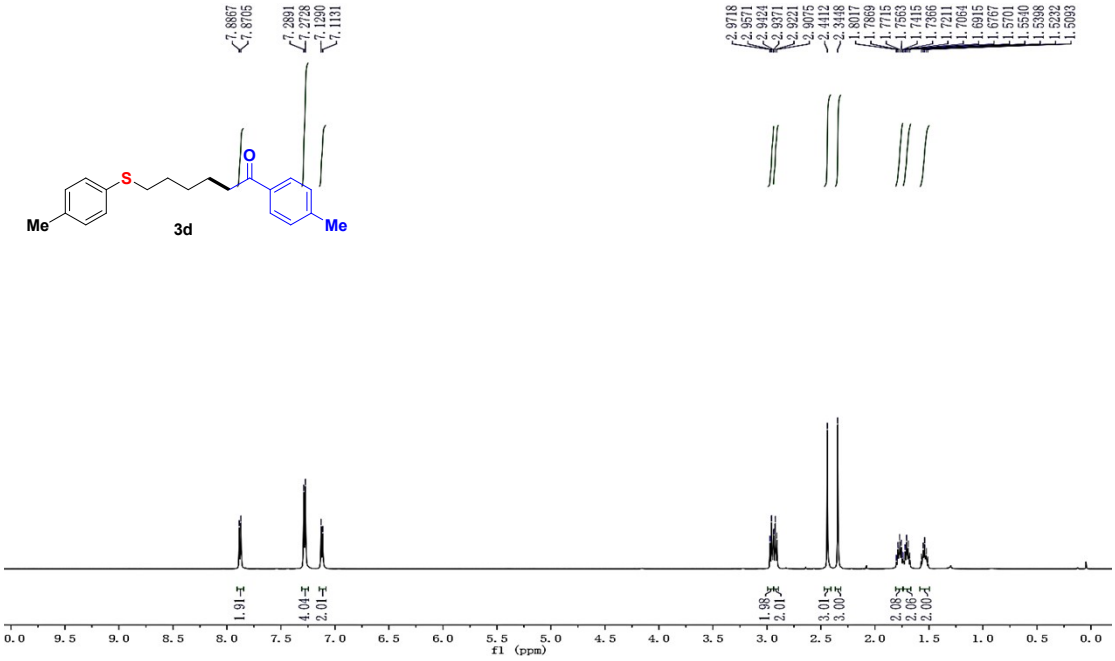
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3c**



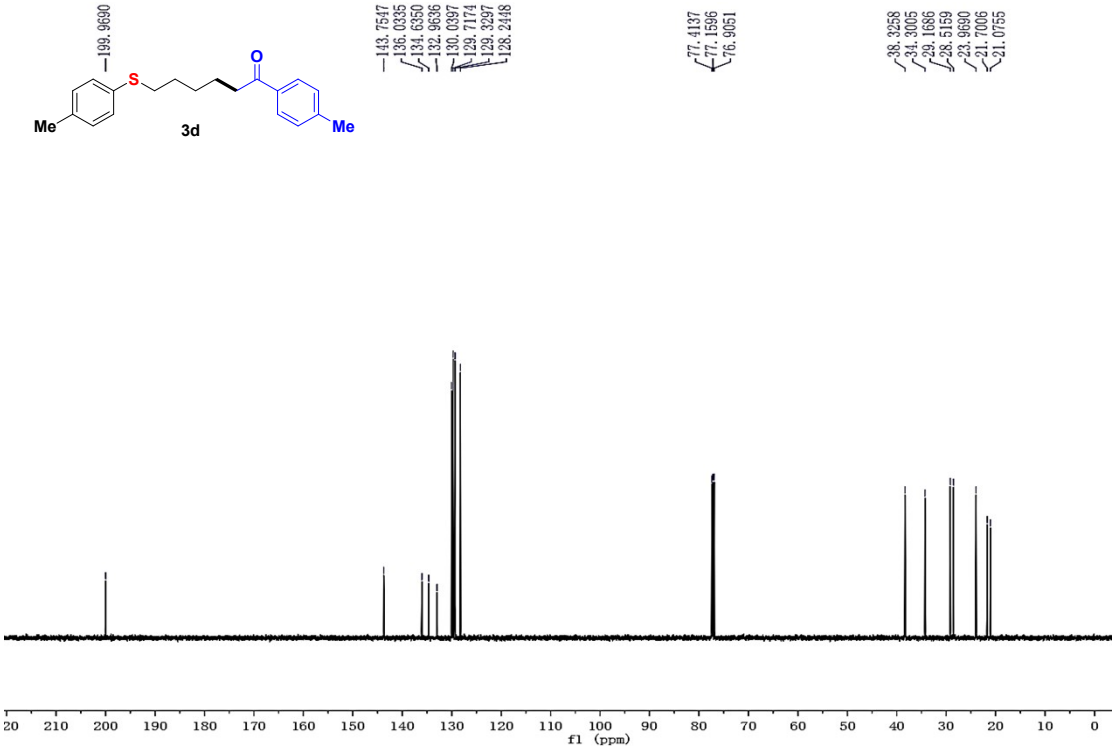
HRMS of **3c**


100
%
0
9.48e3
319.1113
319.0928
319.1303
319.1508
319.1702
m/z
319.070
319.080
319.090
319.100
319.110
319.120
319.130
319.140
319.150
319.160
319.170
O
S
Cl
3c

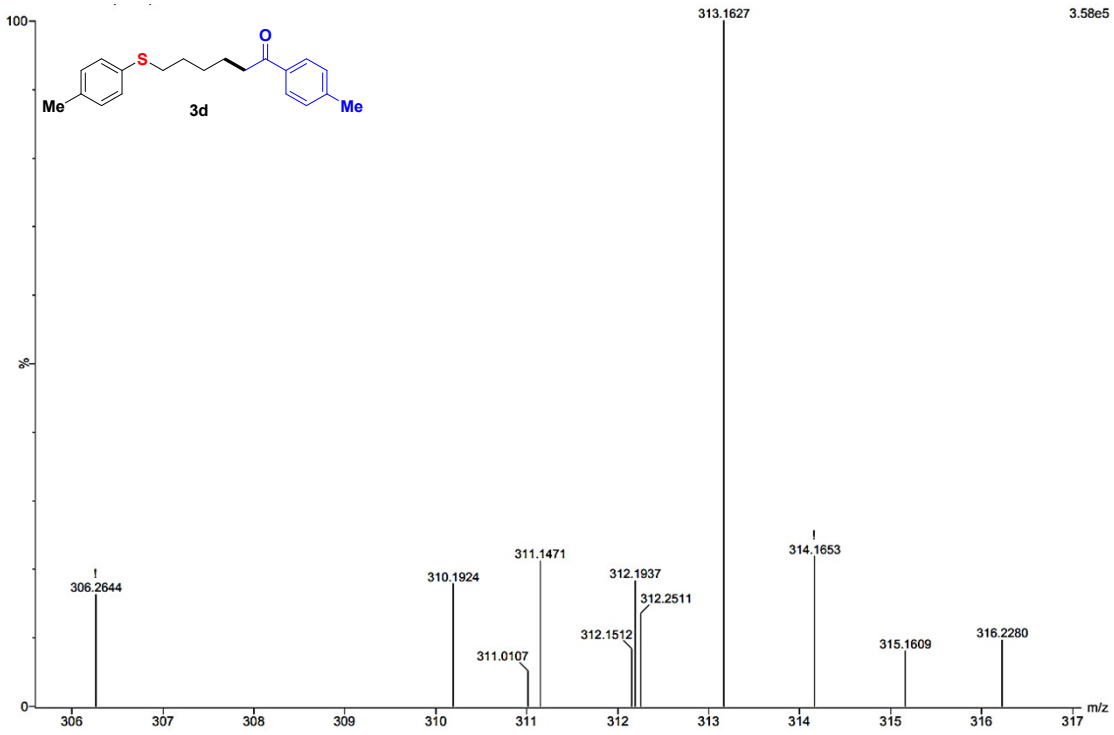
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3d**



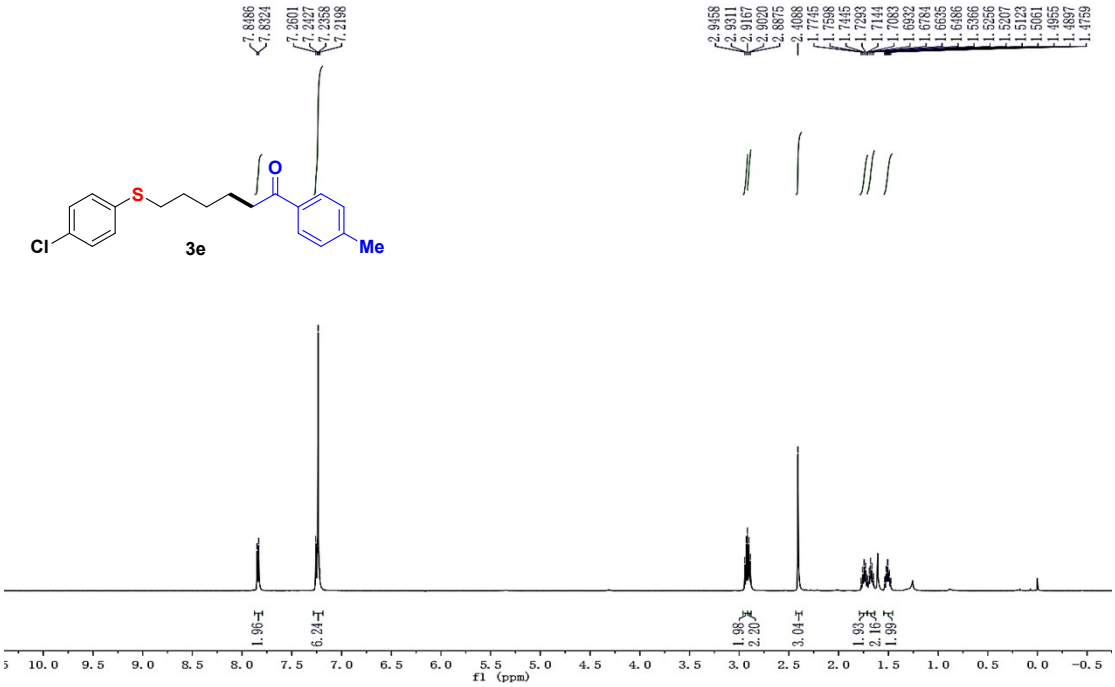
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3d**



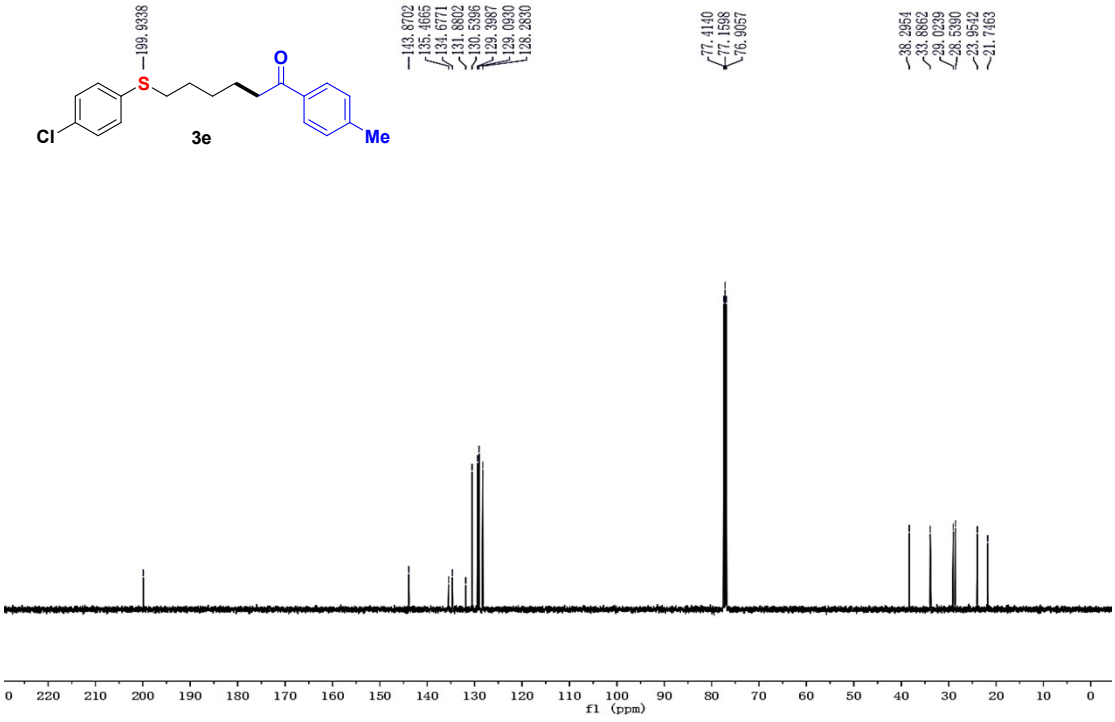
HRMS of **3d**


100
%
0
313.1627
3.58e5
306.2644
310.1924
311.1471
311.0107
312.1512
312.1937
312.2511
314.1653
315.1609
316.2280
306
307
308
309
310
311
312
313
314
315
316
317
m/z
O
S
Me
Me
3d

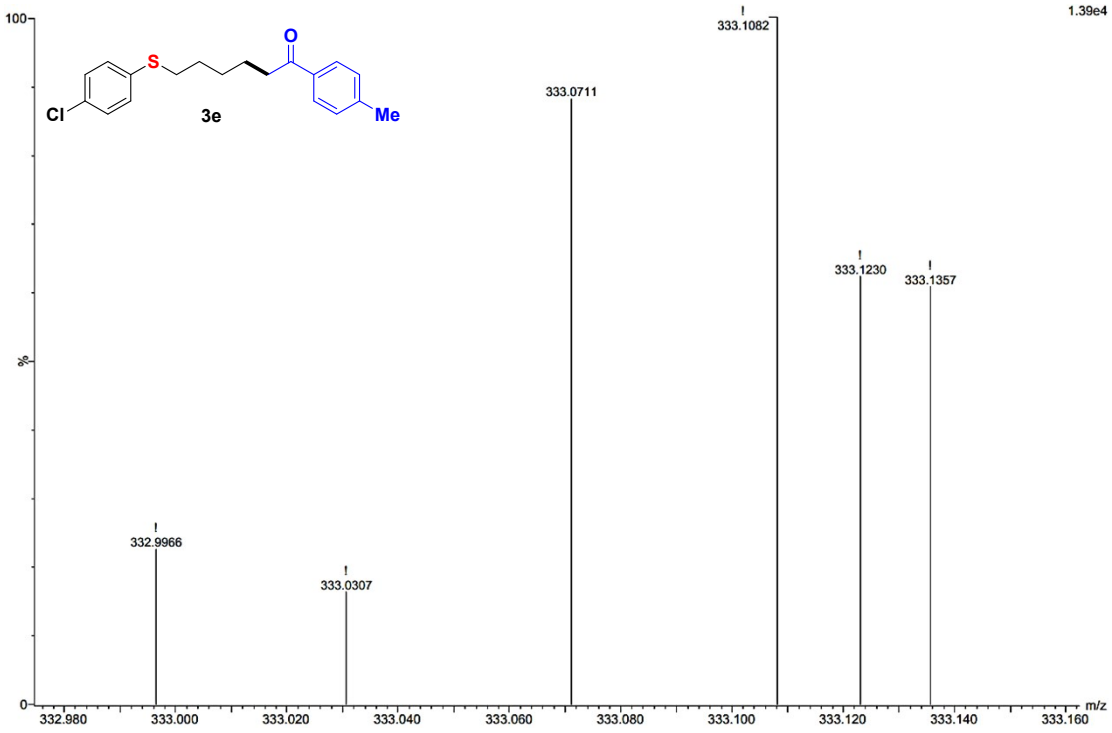
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3e**



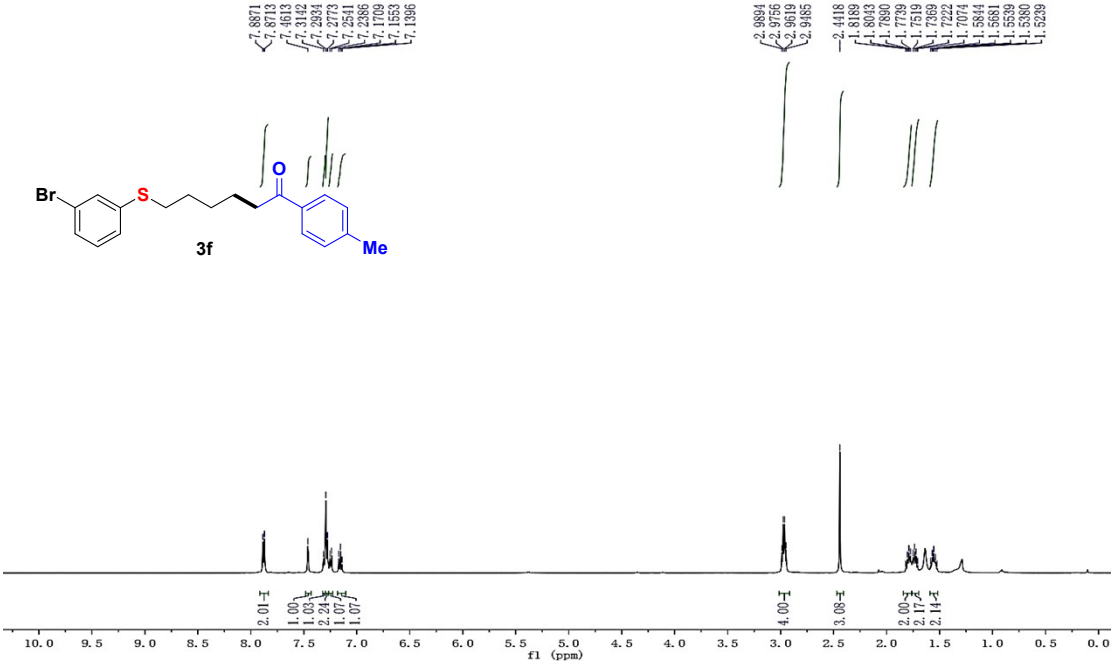
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3e**



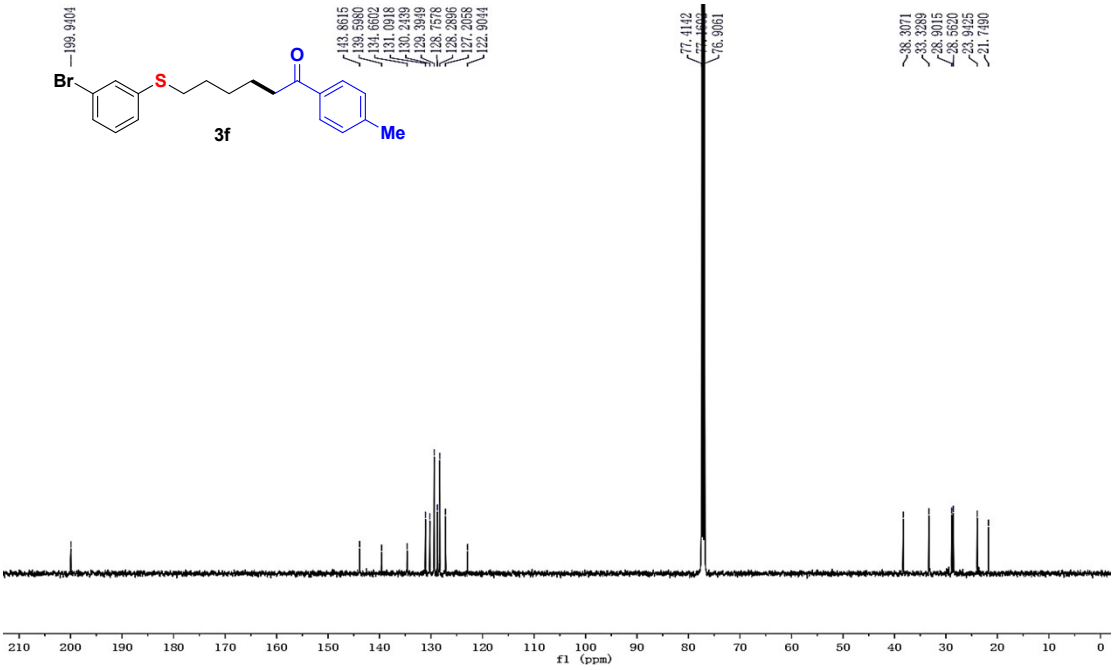
HRMS of **3e**


100
%
0
1.39e4
S
O
Cl
Me
3e
333.1082
333.0711
333.1230
333.1357
332.9966
333.0307
m/z
332.980
333.000
333.020
333.040
333.060
333.080
333.100
333.120
333.140
333.160

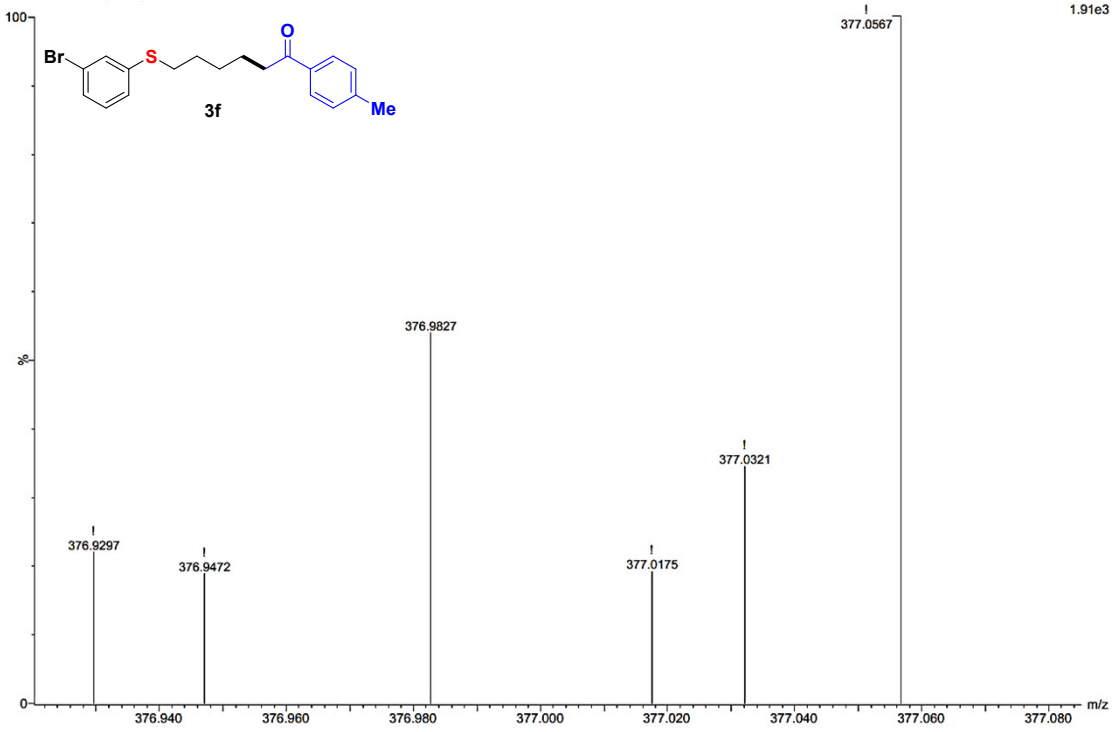
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3f**



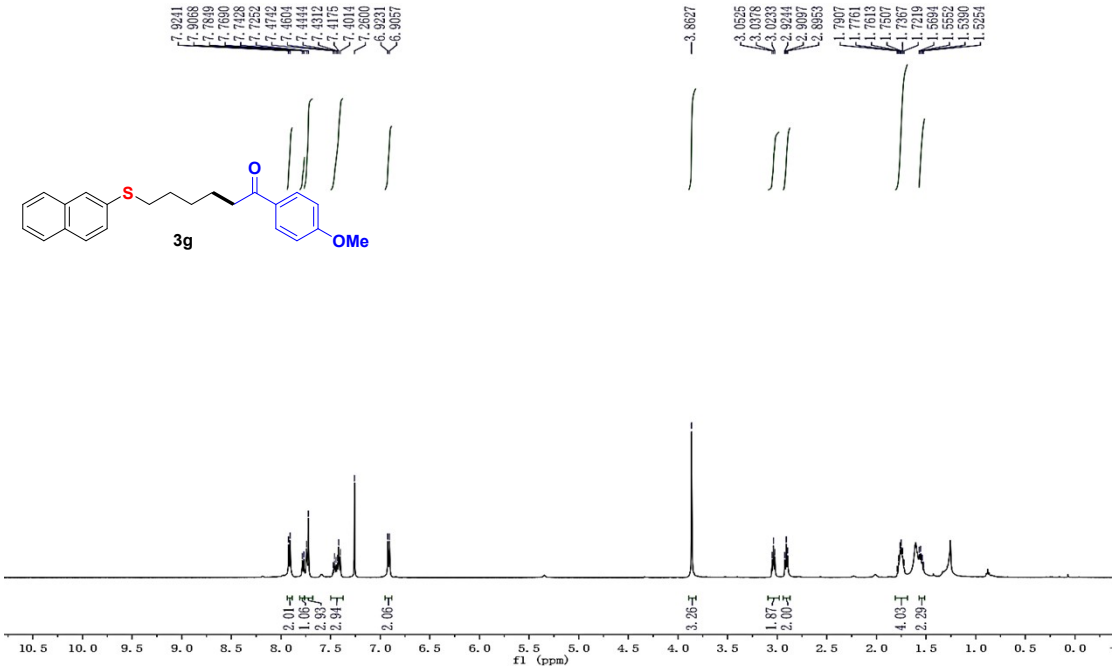
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3f**



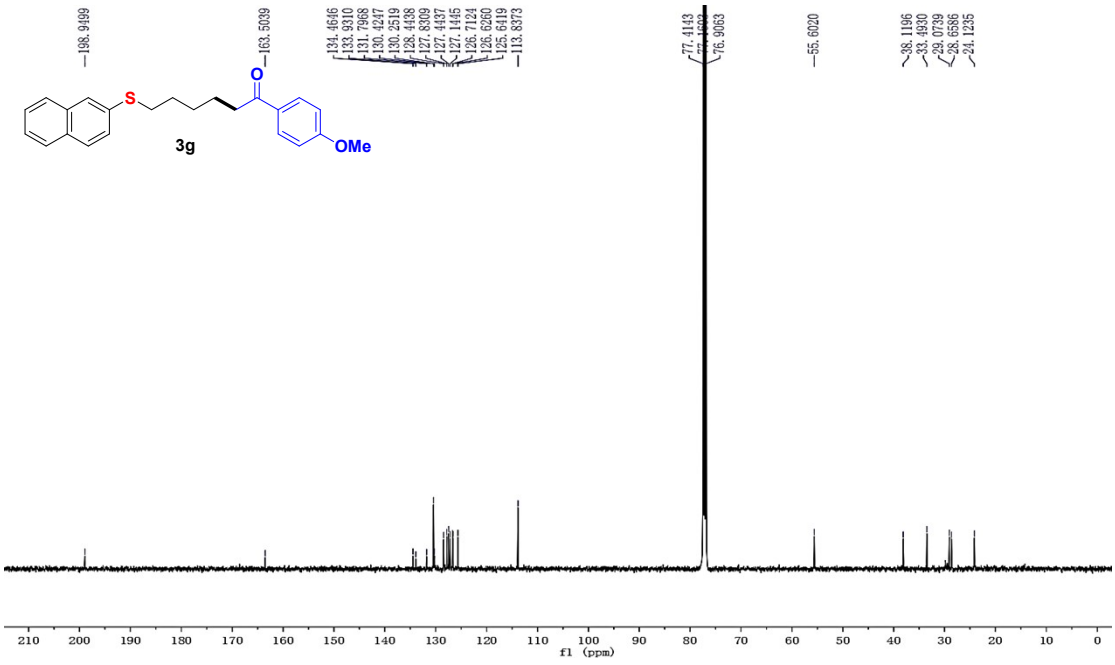
HRMS of **3f**


100
%
0
Br
S
O
Me
3f
1.91e3
377.0567
376.9827
377.0321
376.9297
376.9472
377.0175
376.940
376.960
376.980
377.000
377.020
377.040
377.060
377.080
m/z

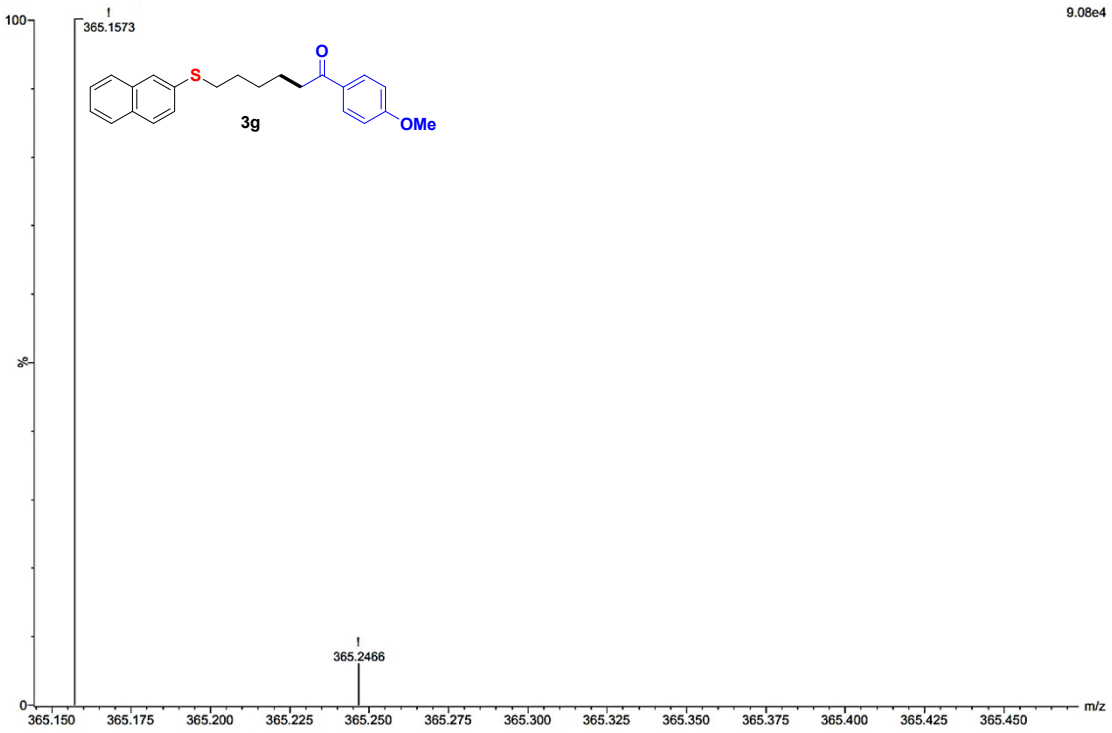
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3g**



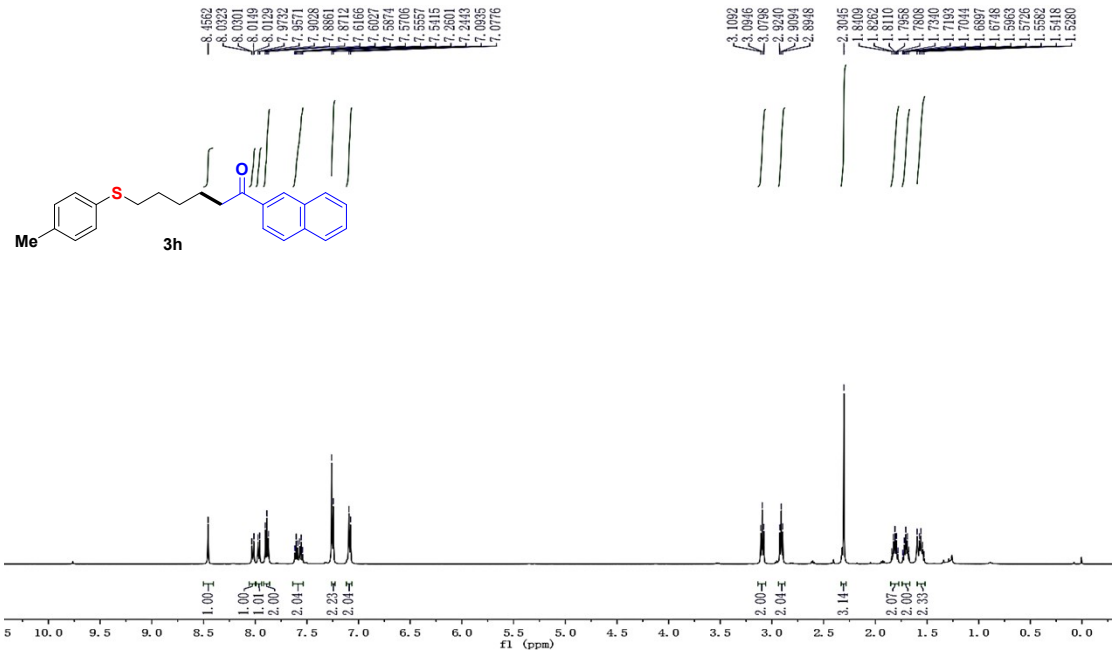
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3g**



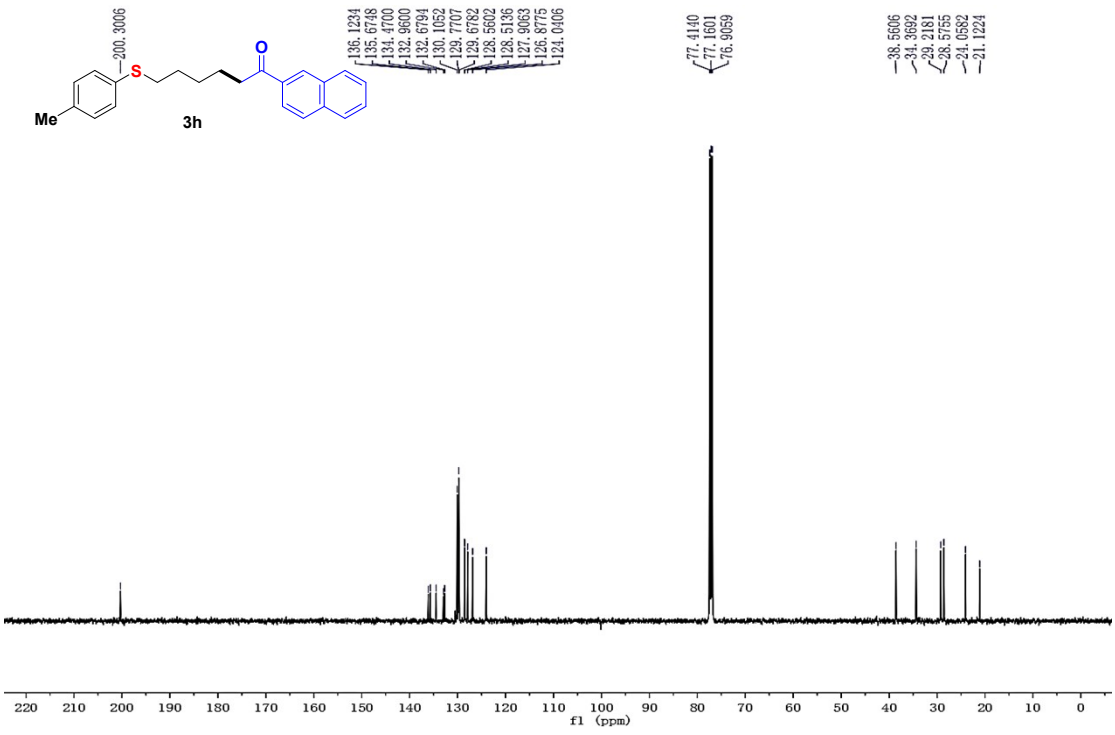
HRMS of **3g**


9.08e4
100
%
0
365.1573
365.2466
S
O
OMe
3g
m/z
365.150
365.175
365.200
365.225
365.250
365.275
365.300
365.325
365.350
365.375
365.400
365.425
365.450

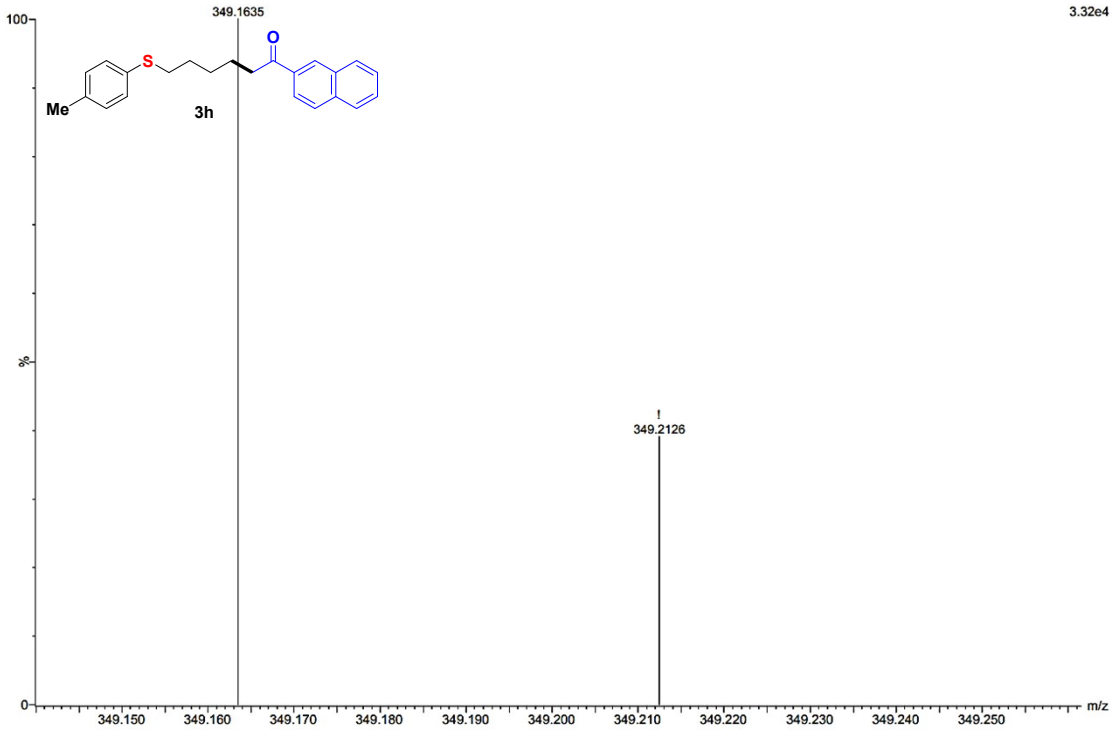
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3h**



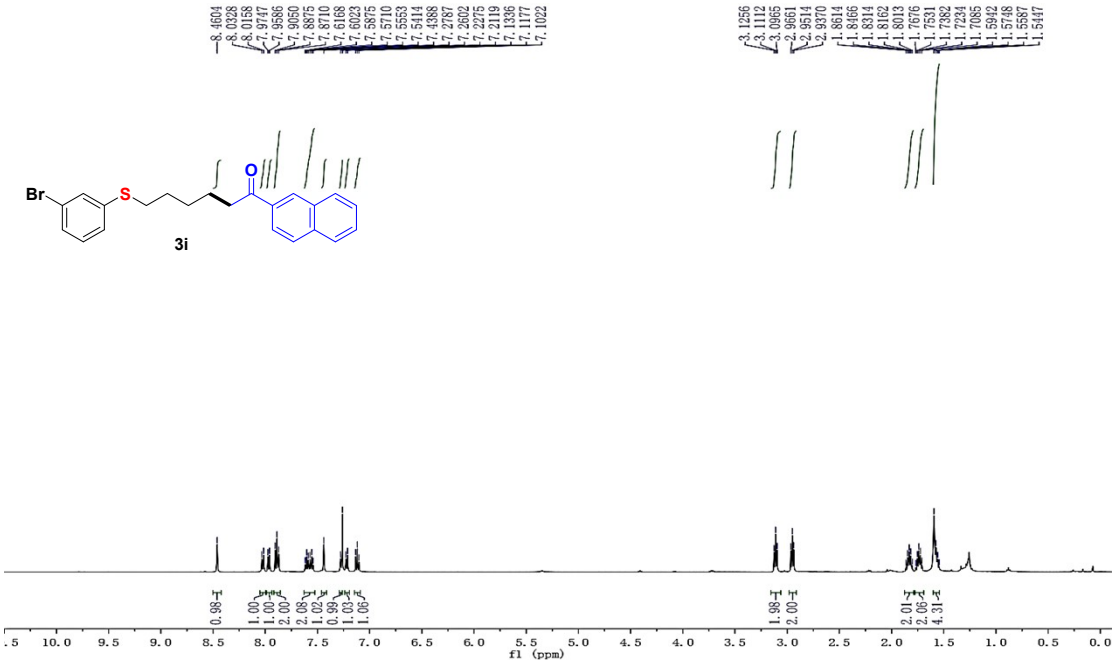
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3h**



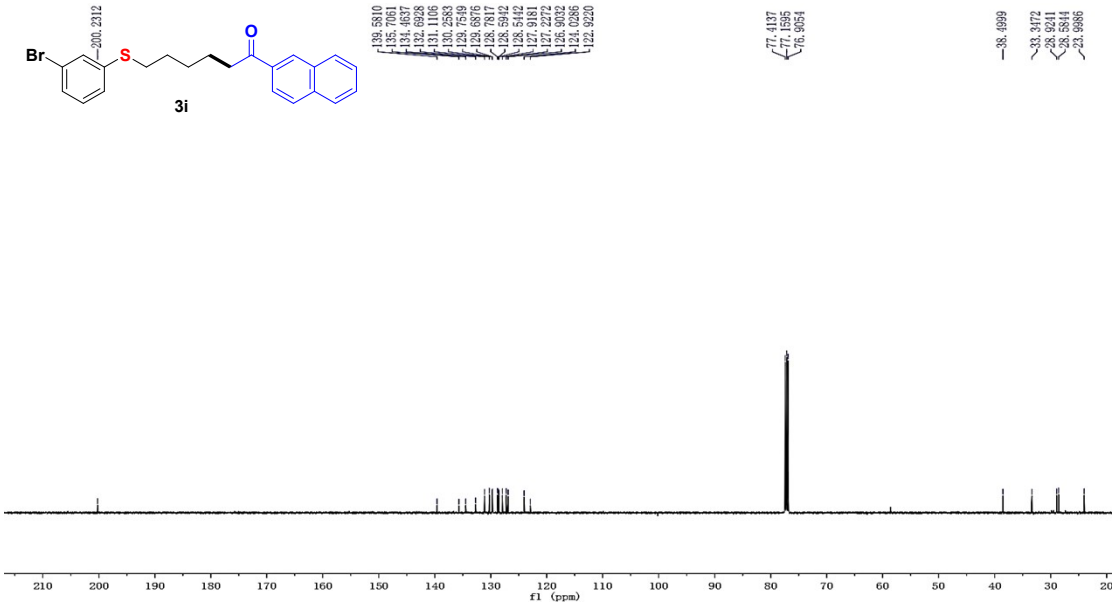
HRMS of **3h**


349.1635
3.32e4
100
%
0
S
O
Me
3h
!
349.2126
349.150
349.160
349.170
349.180
349.190
349.200
349.210
349.220
349.230
349.240
349.250
m/z

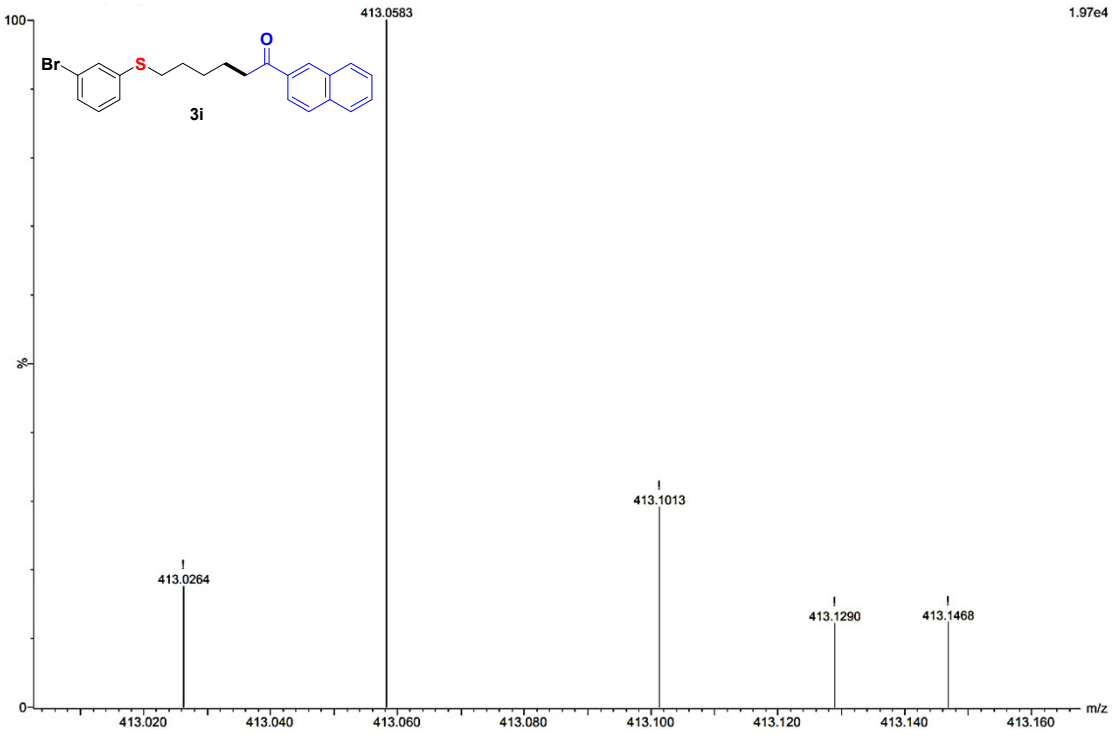
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3i**



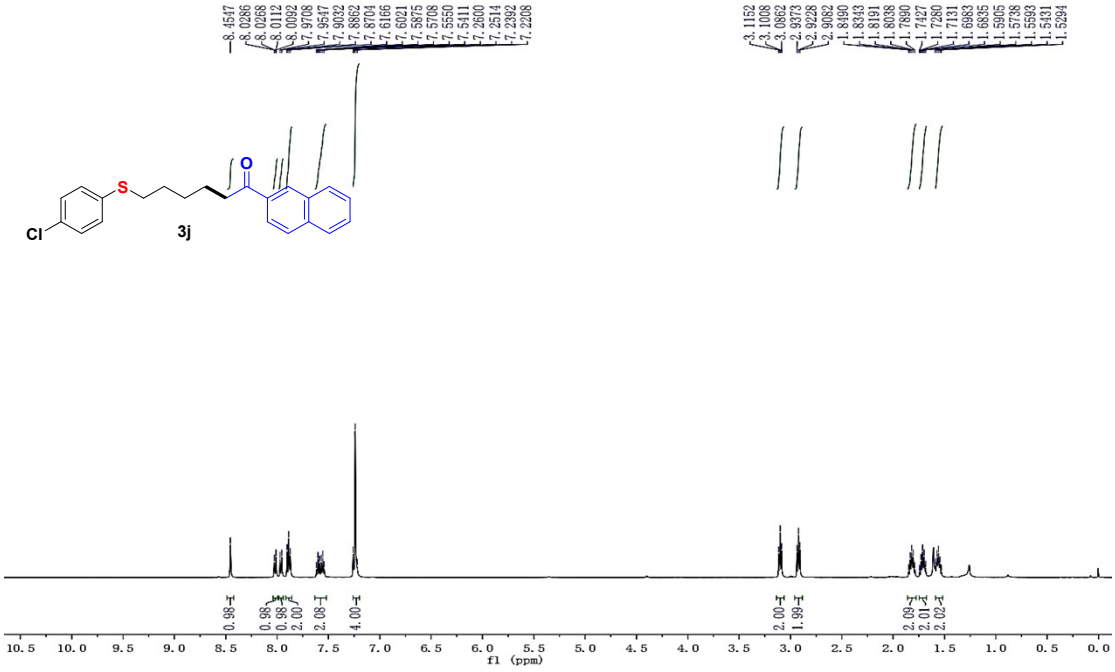
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3i**



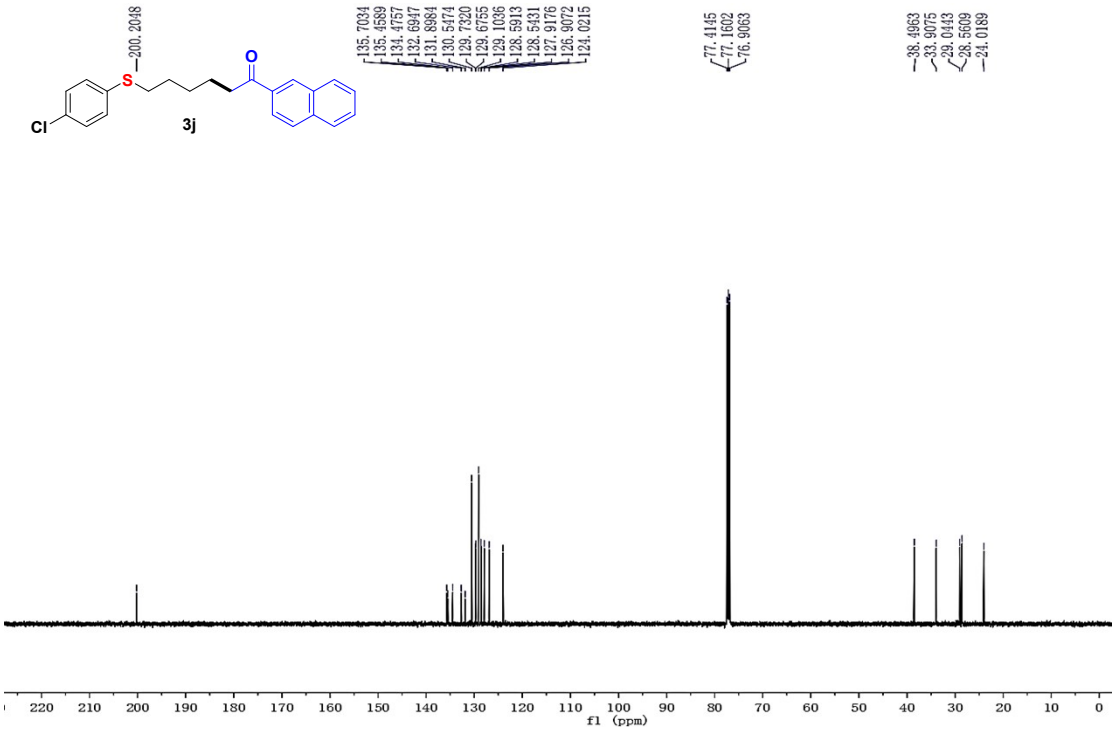
HRMS of **3i**


413.0583
1.97e4
100
Br
S
O
3i
%
413.1013
413.0264
413.1290
413.1468
0
m/z
413.020
413.040
413.060
413.080
413.100
413.120
413.140
413.160

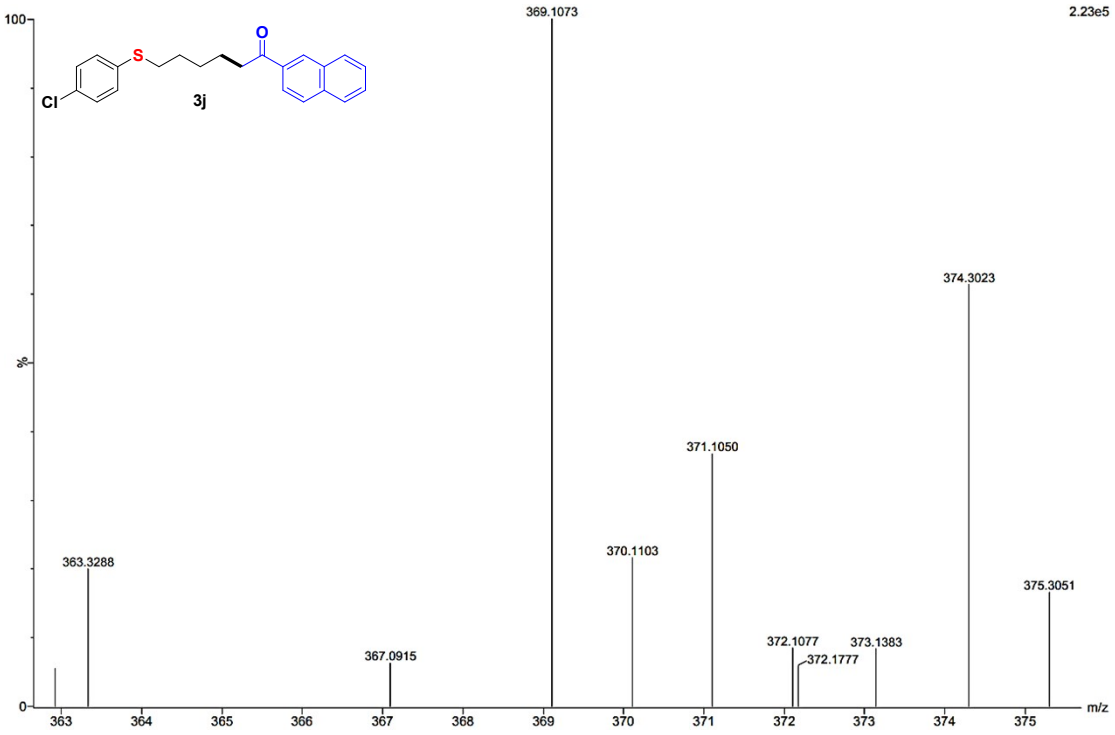
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3j**



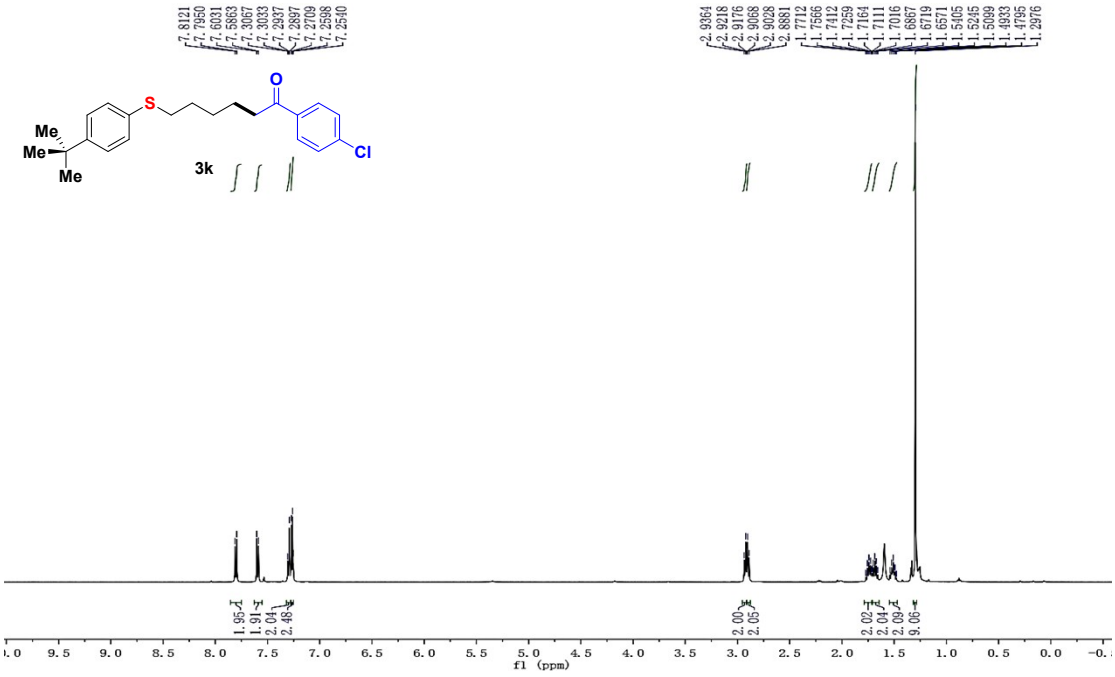
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3j**



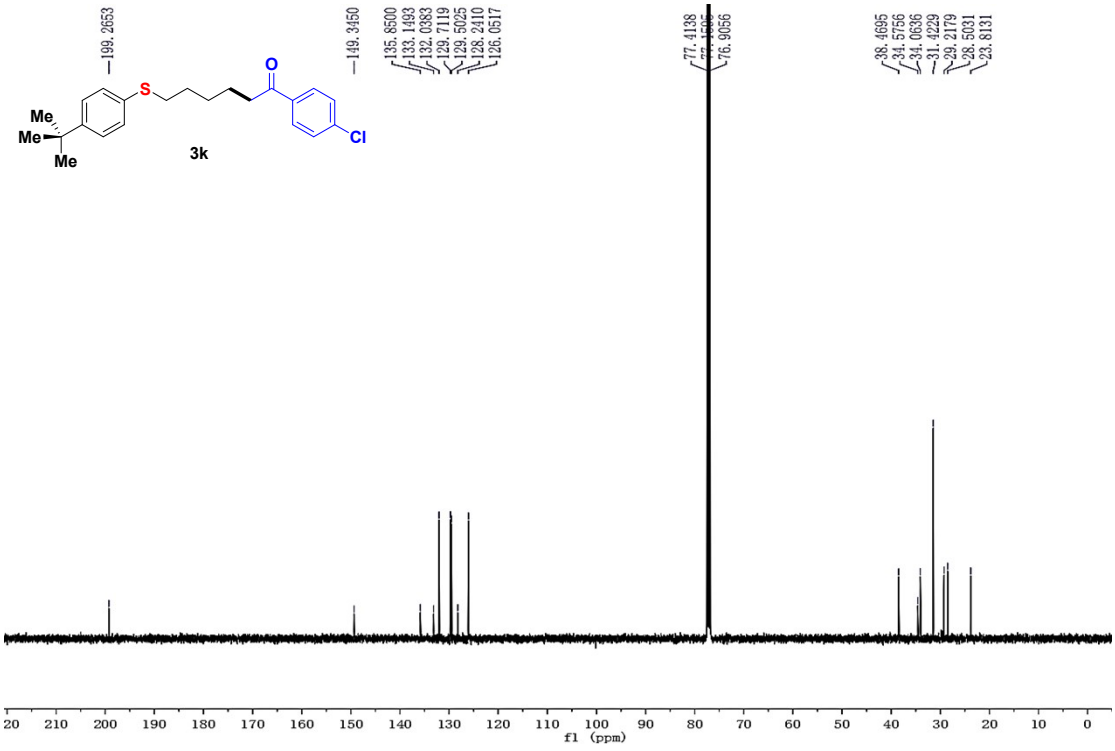
HRMS of **3j**


100
%
0
Cl
S
O
3j
369.1073
2.23e5
374.3023
371.1050
370.1103
363.3288
375.3051
372.1077
373.1383
372.1777
367.0915
363
364
365
366
367
368
369
370
371
372
373
374
375
m/z

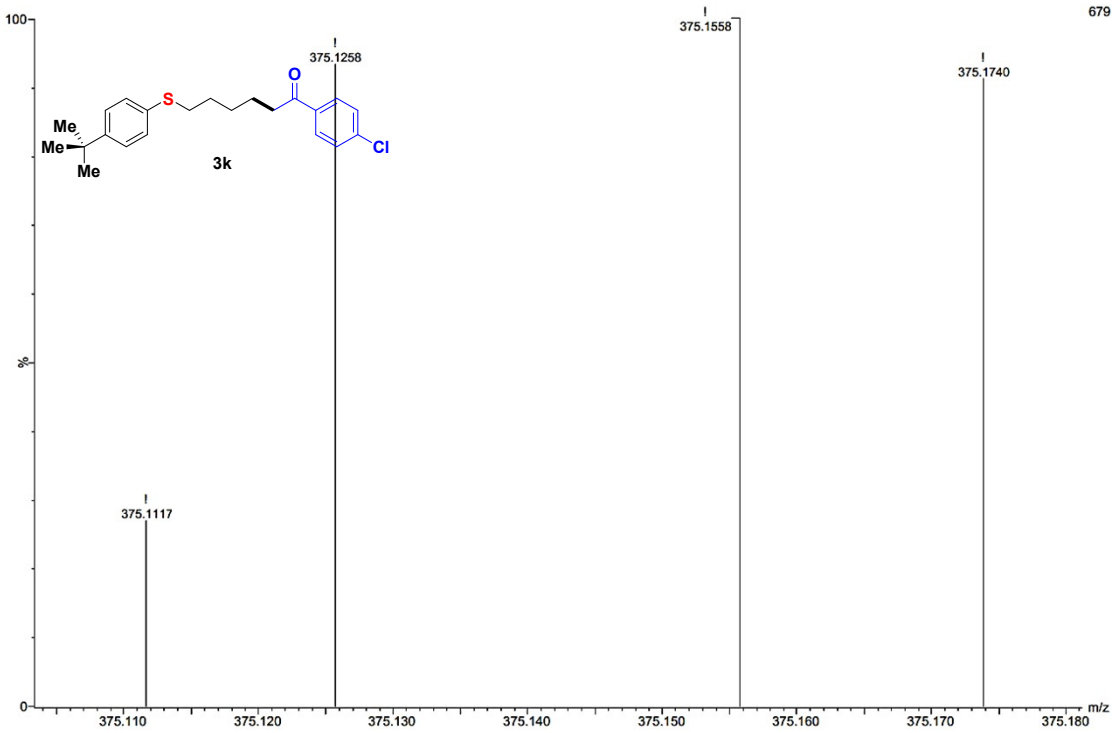
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3k**



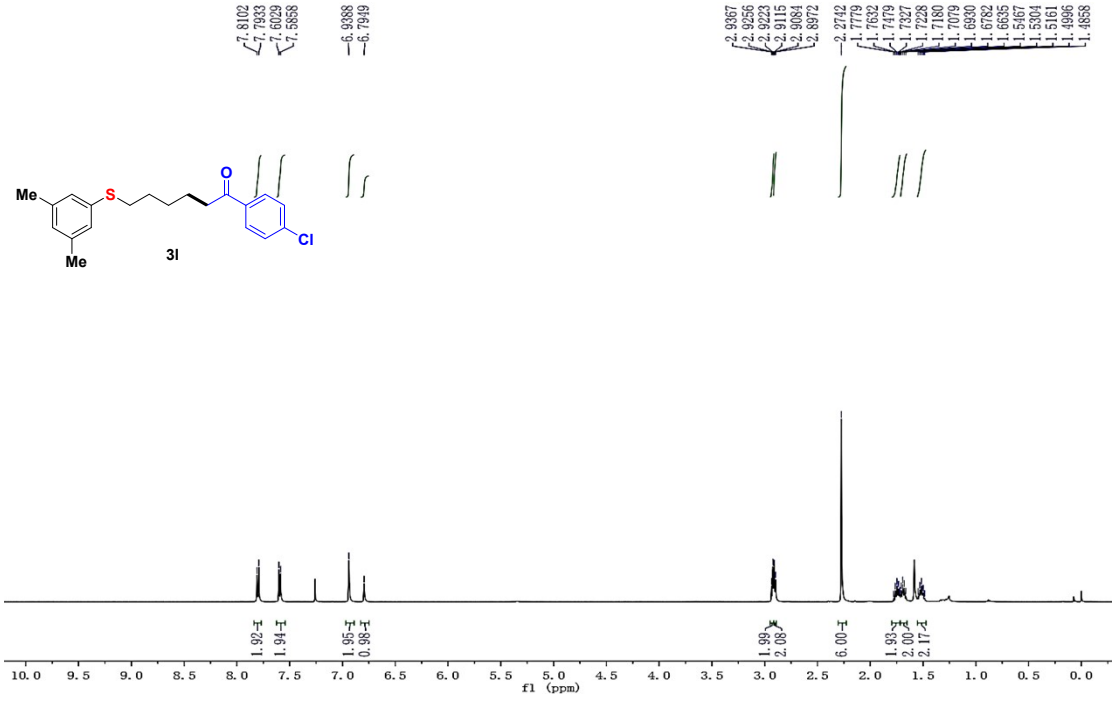
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3k**



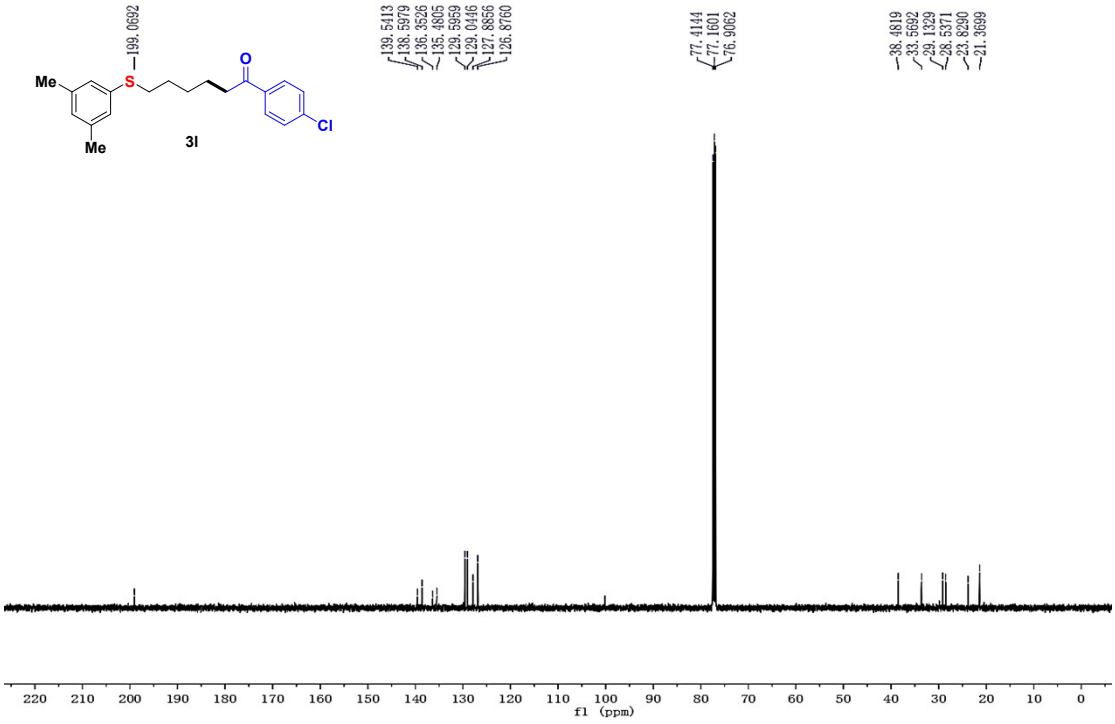
HRMS of **3k**


100
%
0
375.1258
375.1558
375.1740
375.1117
679
S
O
Cl
Me
Me
Me
3k
375.110
375.120
375.130
375.140
375.150
375.160
375.170
375.180
m/z

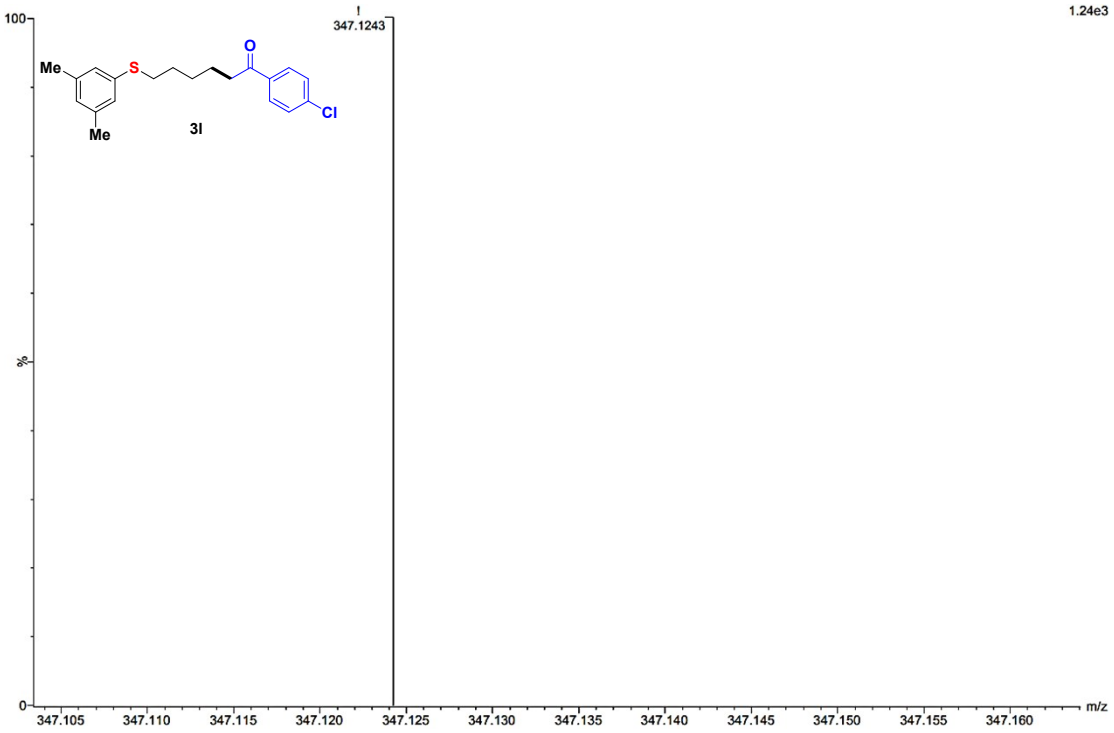
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3l**



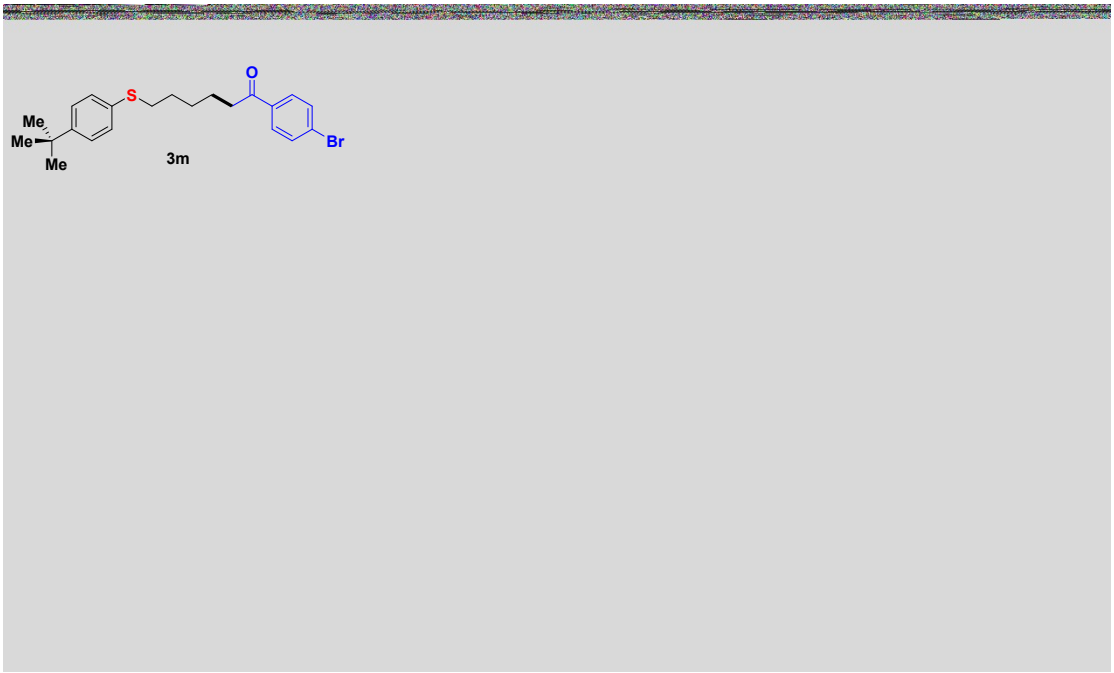
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3l**



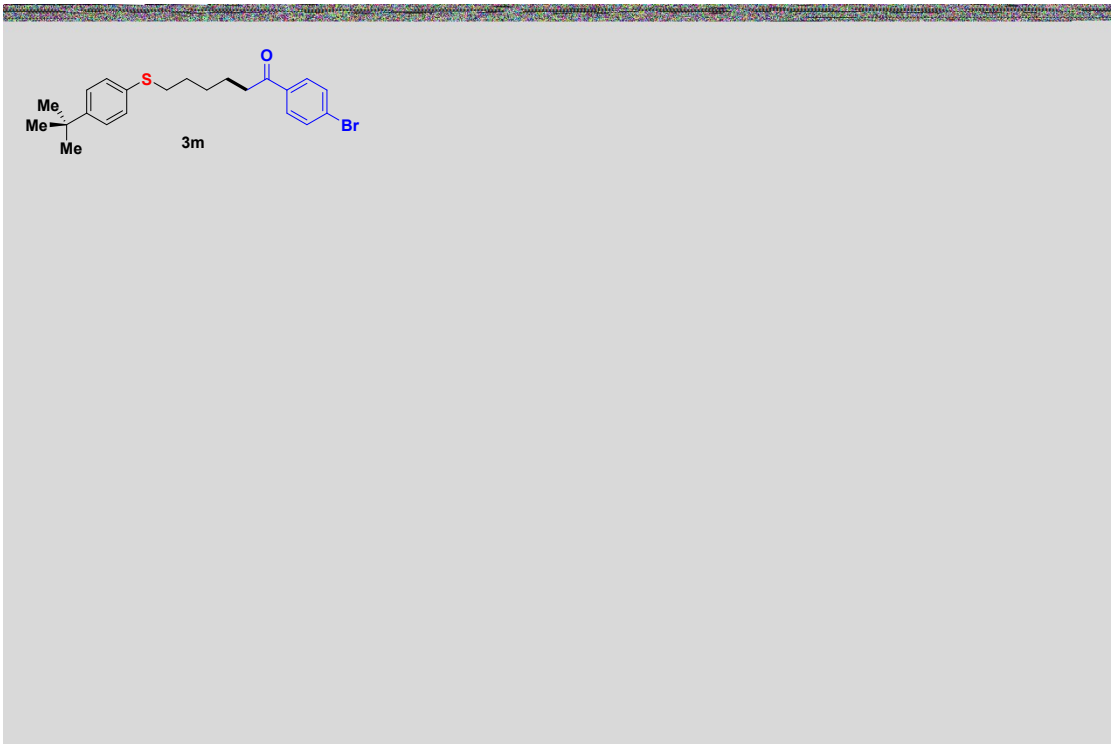
HRMS of **3l**


100
%
0
347.1243
1.24e3
Me
S
O
Cl
Me
3l
347.105
347.110
347.115
347.120
347.125
347.130
347.135
347.140
347.145
347.150
347.155
347.160
m/z

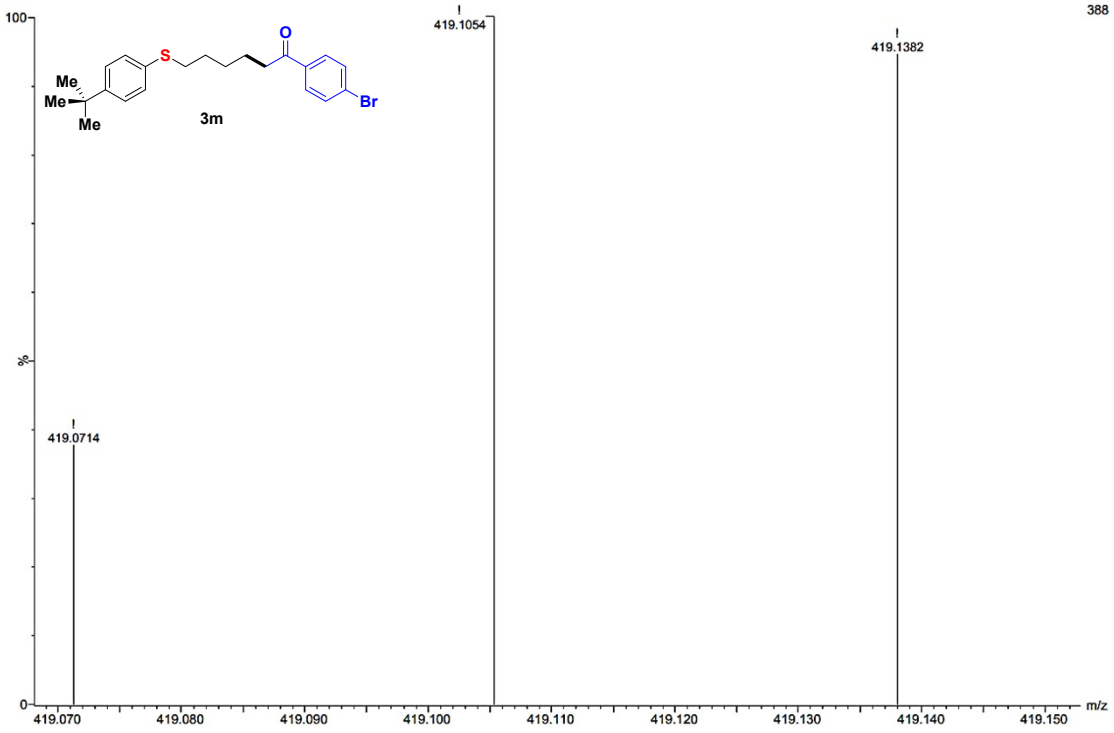
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3m**



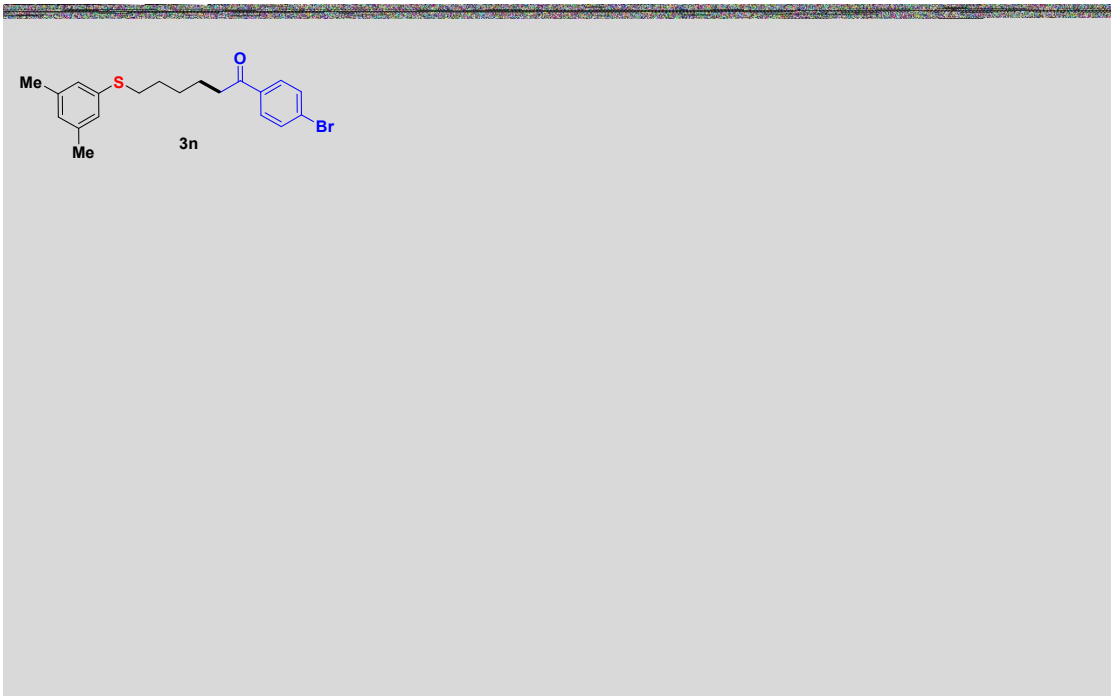
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3m**



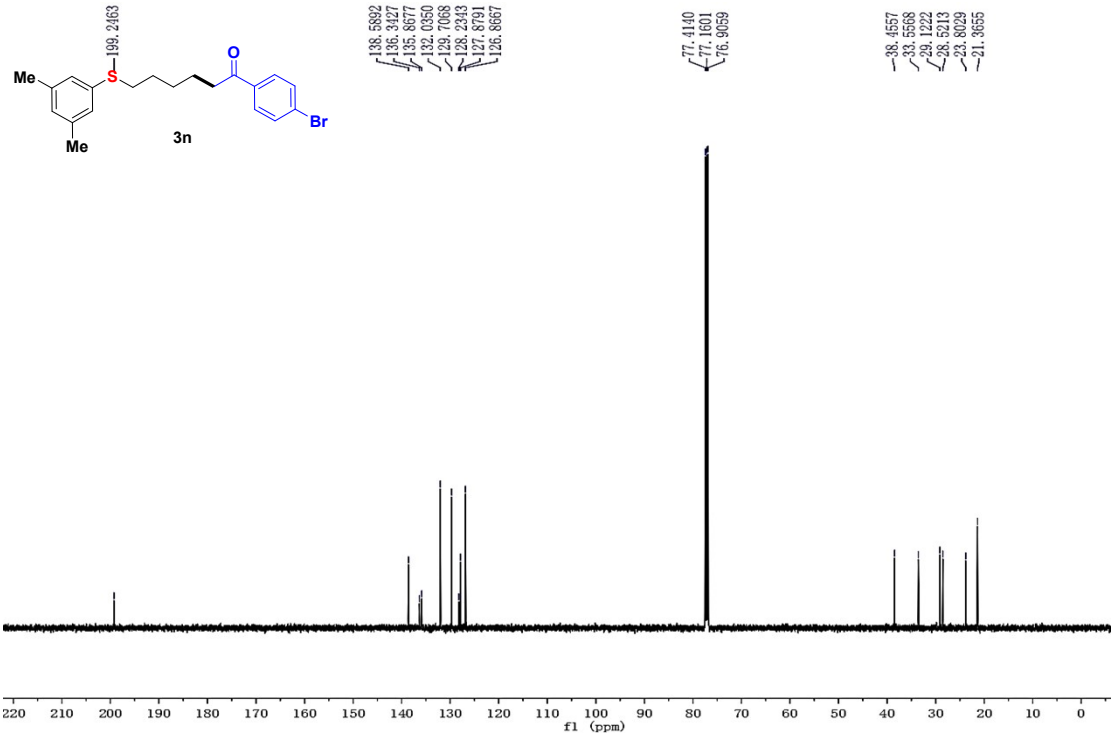
HRMS of **3m**


100
%
0
388
419.1054
419.1382
419.0714
419.070
419.080
419.090
419.100
419.110
419.120
419.130
419.140
419.150
m/z
Me
Me
Me
S
O
Br
3m

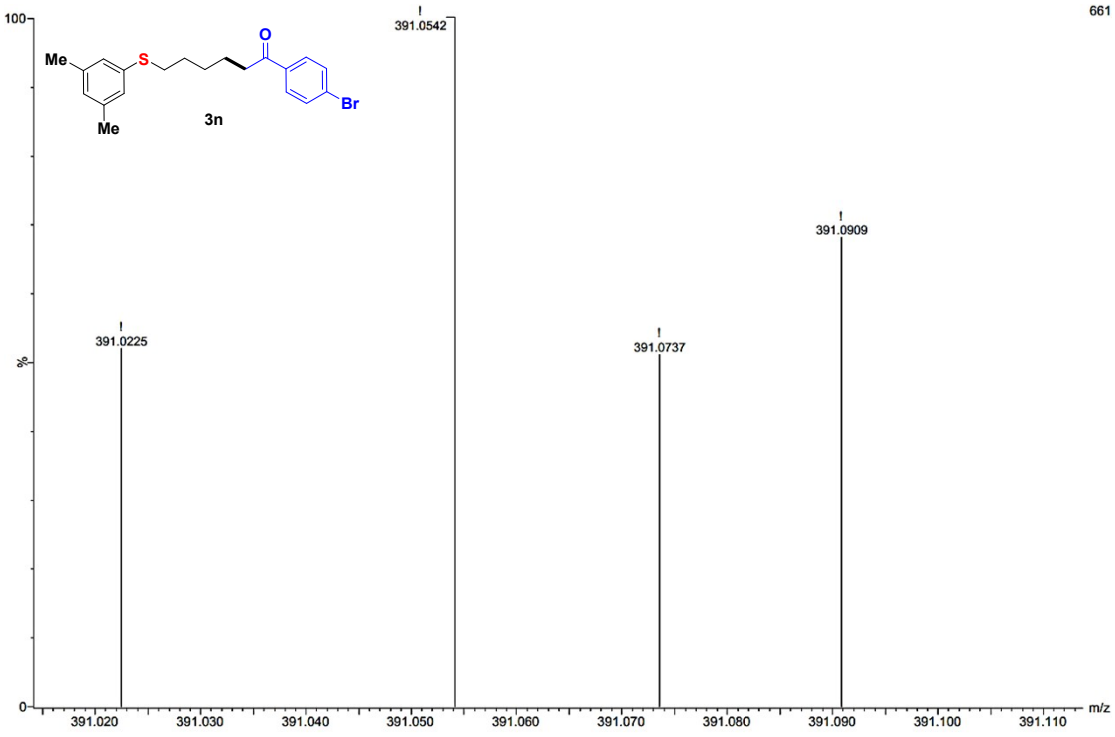
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3n**



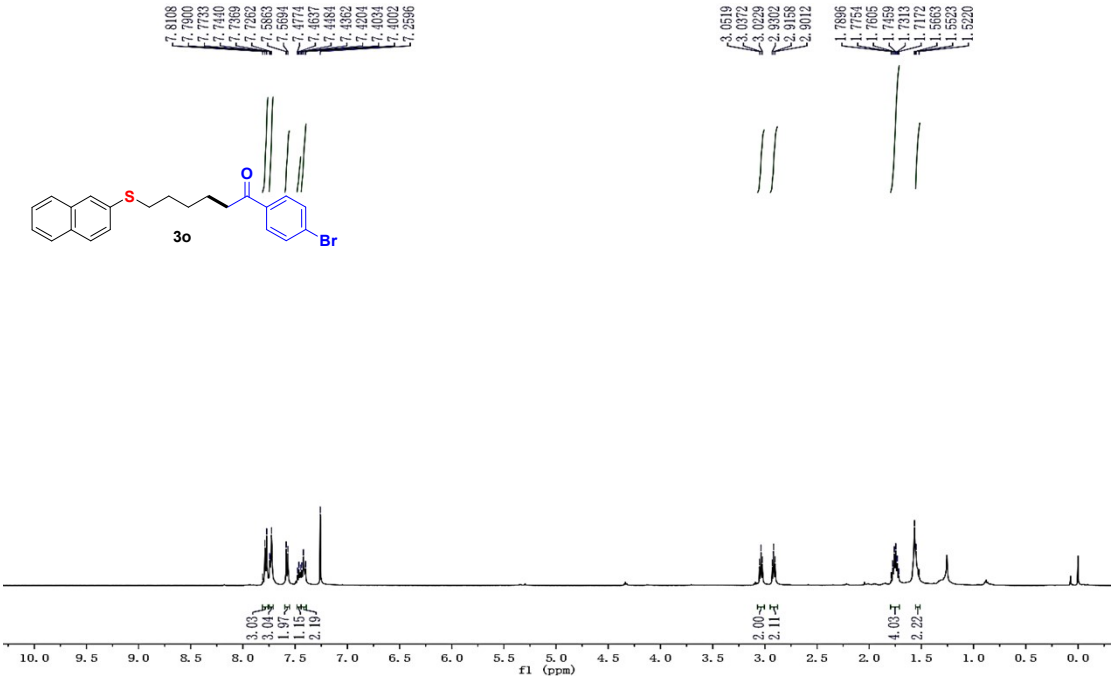
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3n**



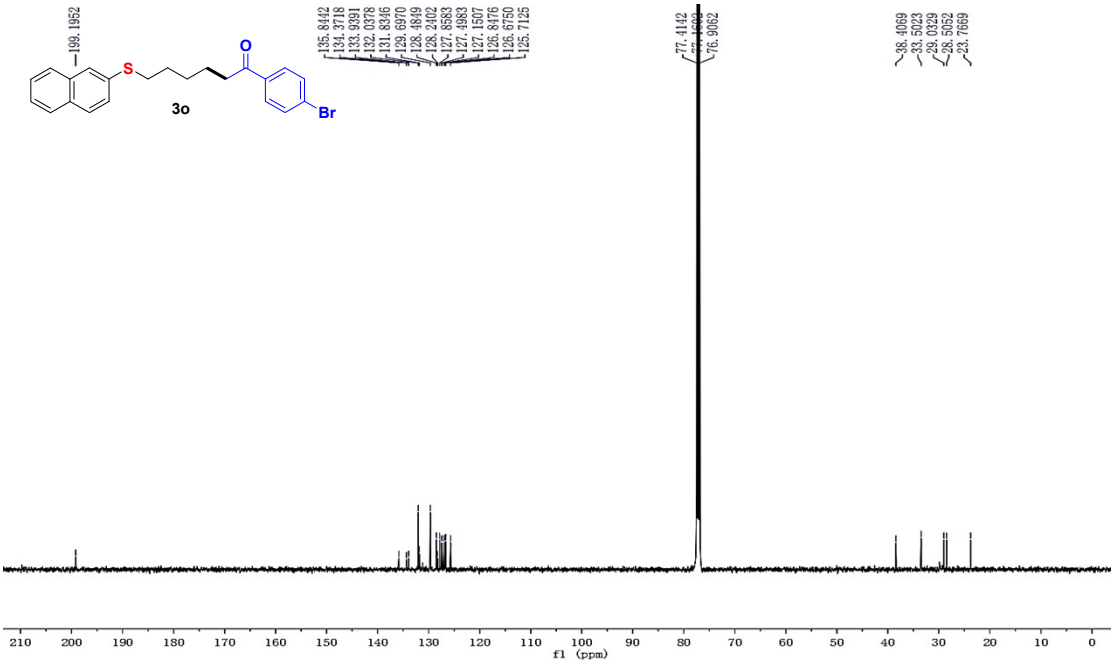
HRMS of **3n**


100
%
0
661
391.0542
391.0909
391.0225
391.0737
391.020
391.030
391.040
391.050
391.060
391.070
391.080
391.090
391.100
391.110
m/z
Me
S
O
Br
Me
3n

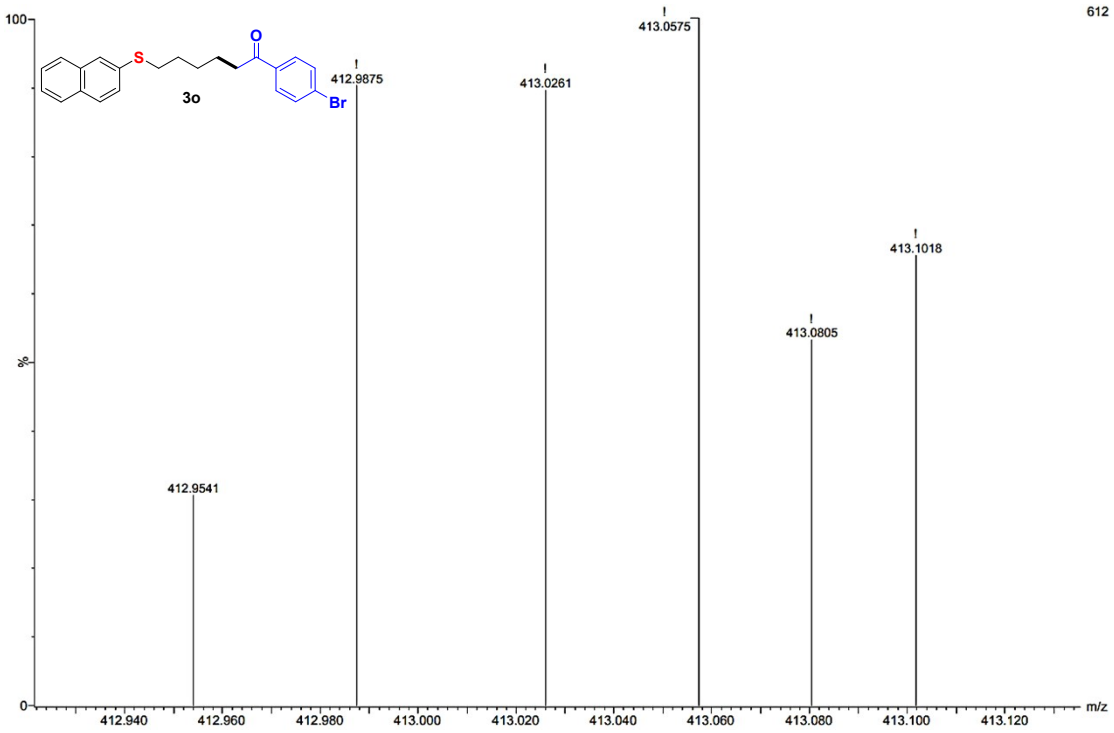
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3o**



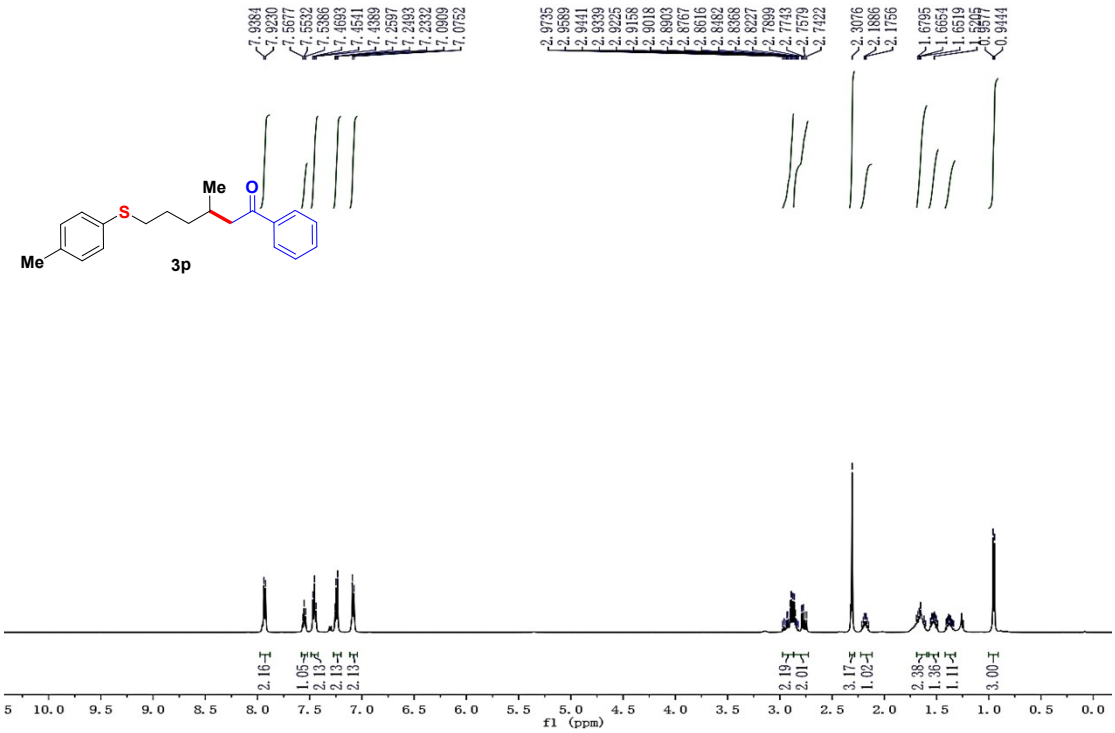
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3o**



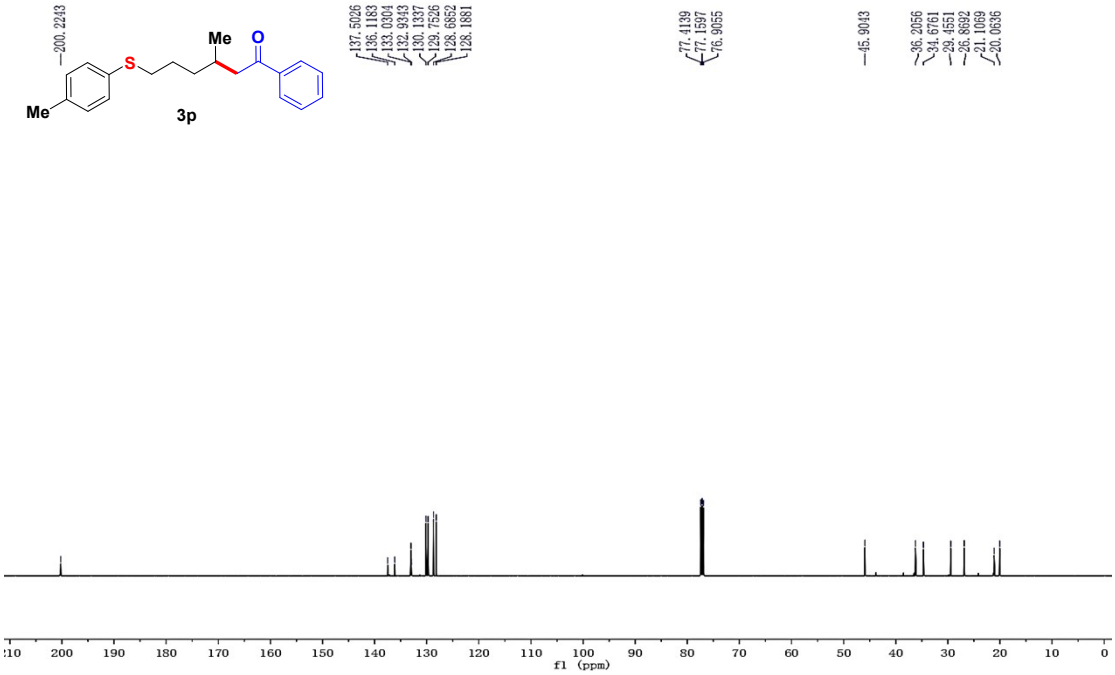
HRMS of **3o**


100
%
0
612
S
O
Br
3o
412.9875
413.0261
413.0575
413.0805
413.1018
412.9541
412.940
412.960
412.980
413.000
413.020
413.040
413.060
413.080
413.100
413.120
m/z

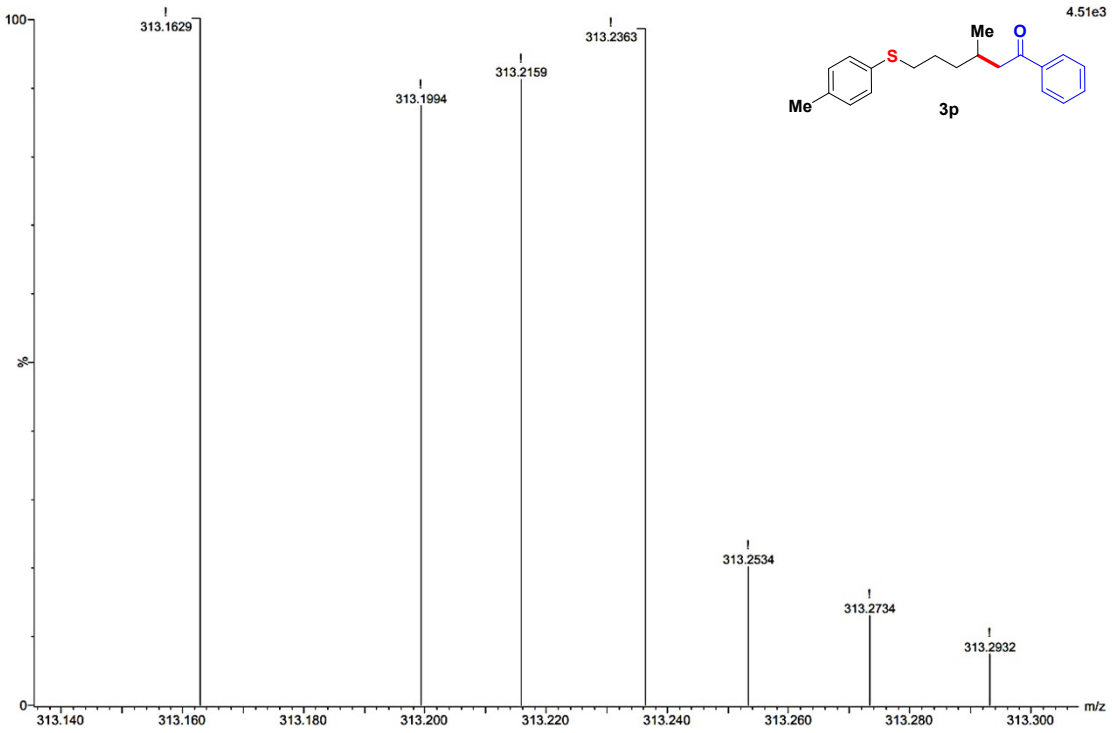
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3p**



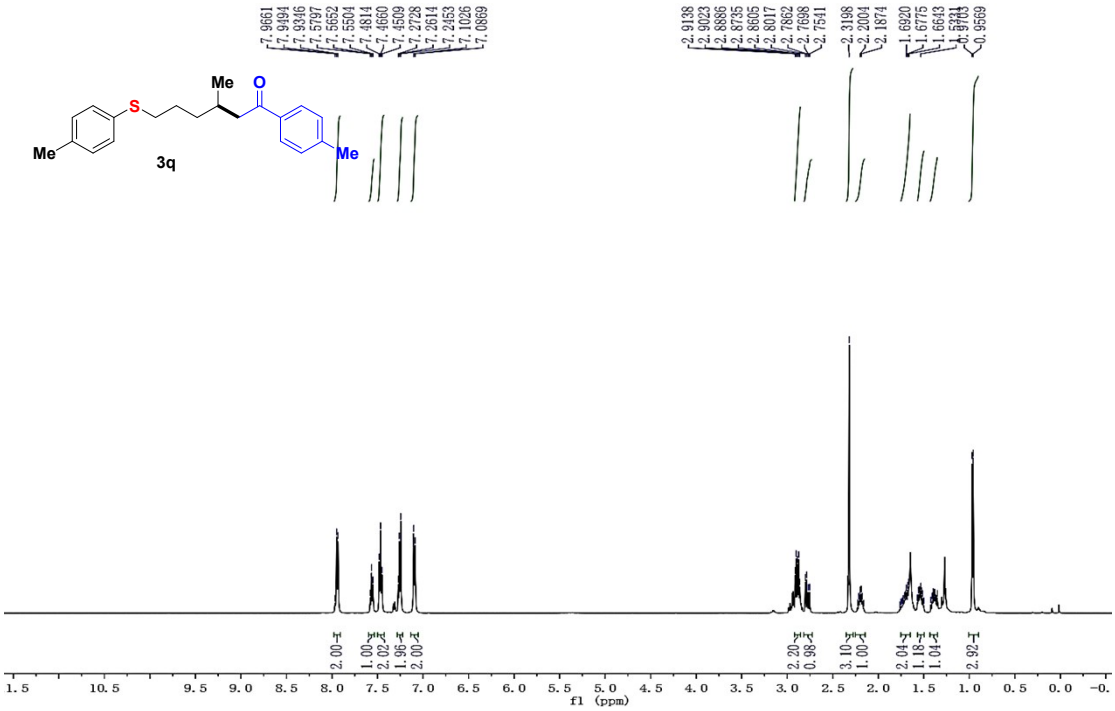
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3p**



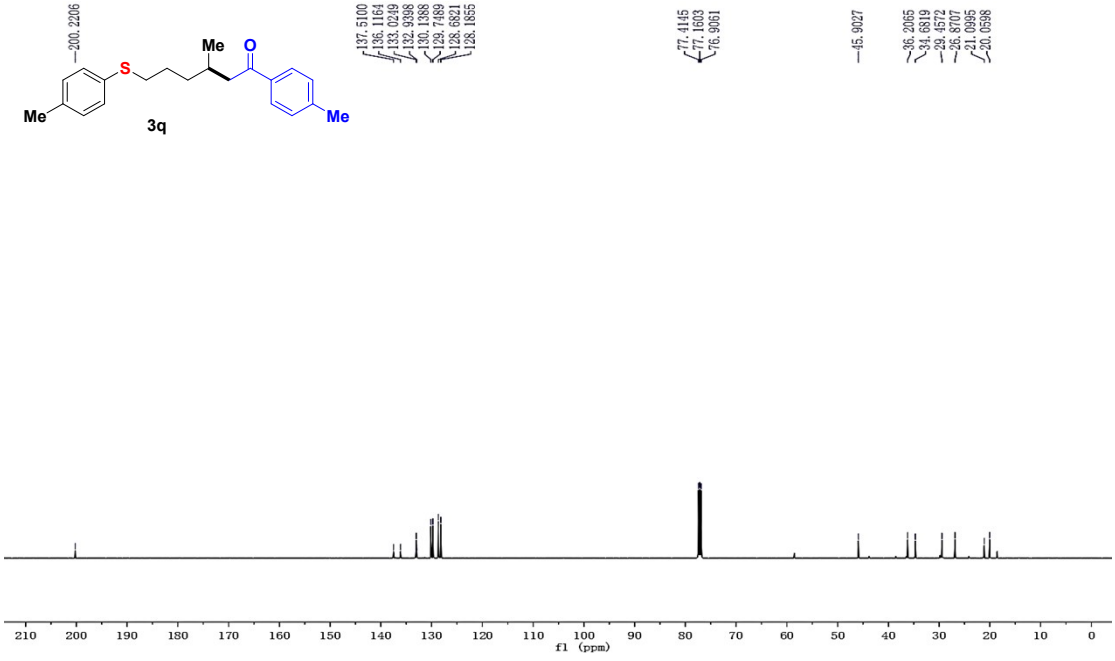
HRMS of **3p**


4.51e3
100
%
0
313.1629
313.1994
313.2159
313.2363
313.2534
313.2734
313.2932
313.140
313.160
313.180
313.200
313.220
313.240
313.260
313.280
313.300
m/z
Me
O
S
Me
3p

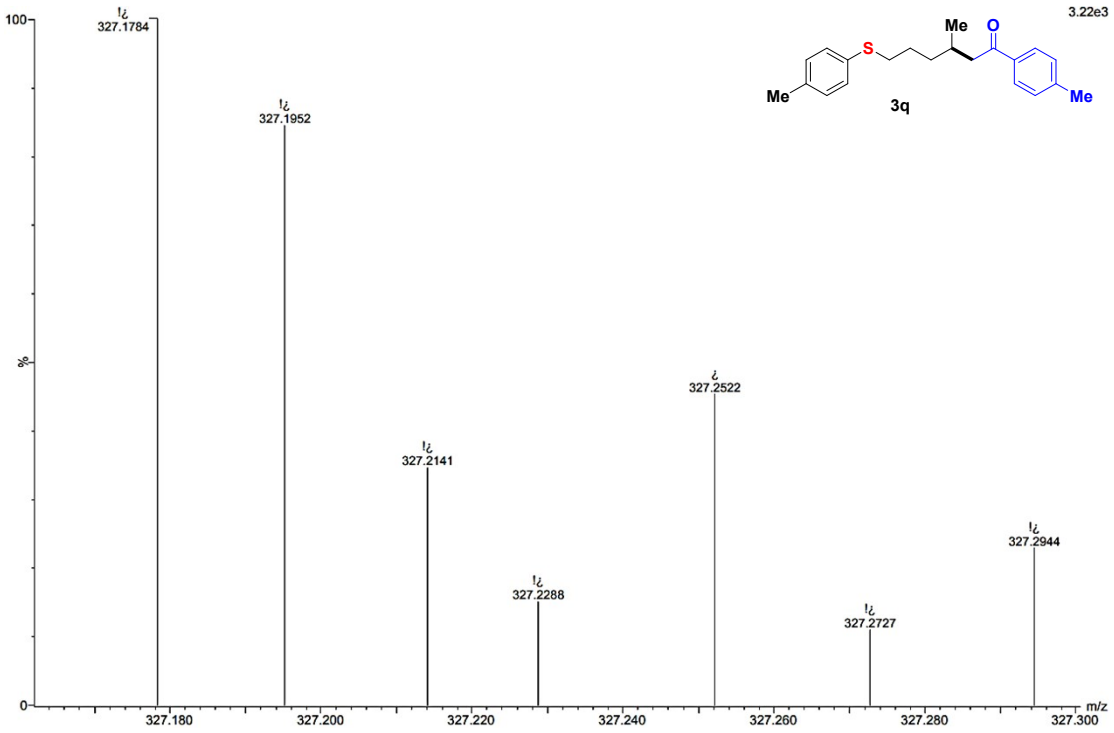
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3q**



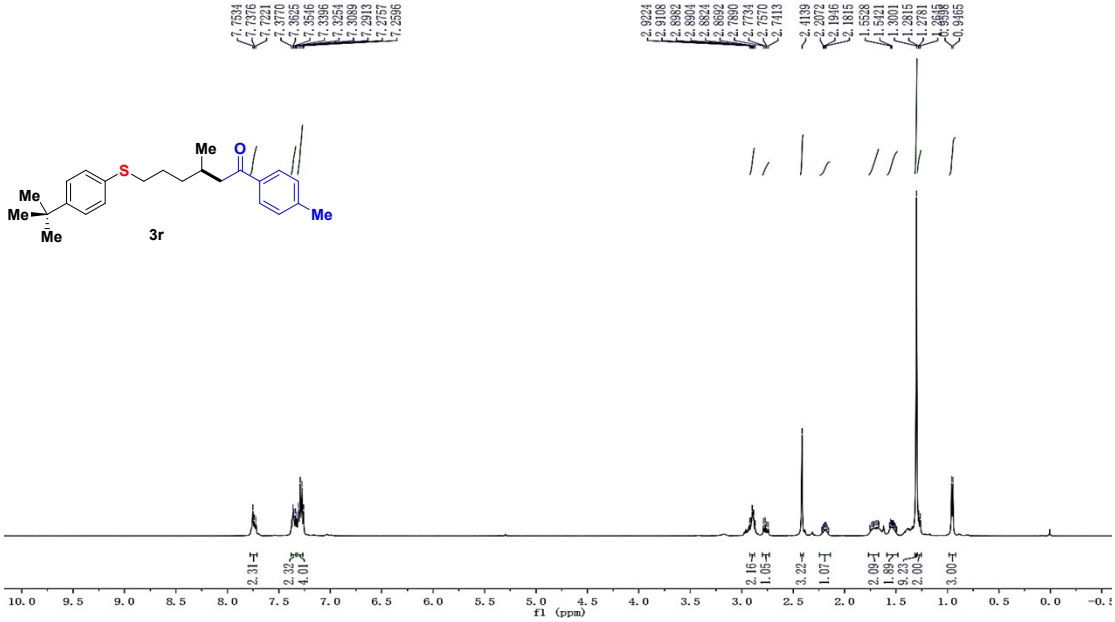
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3q**



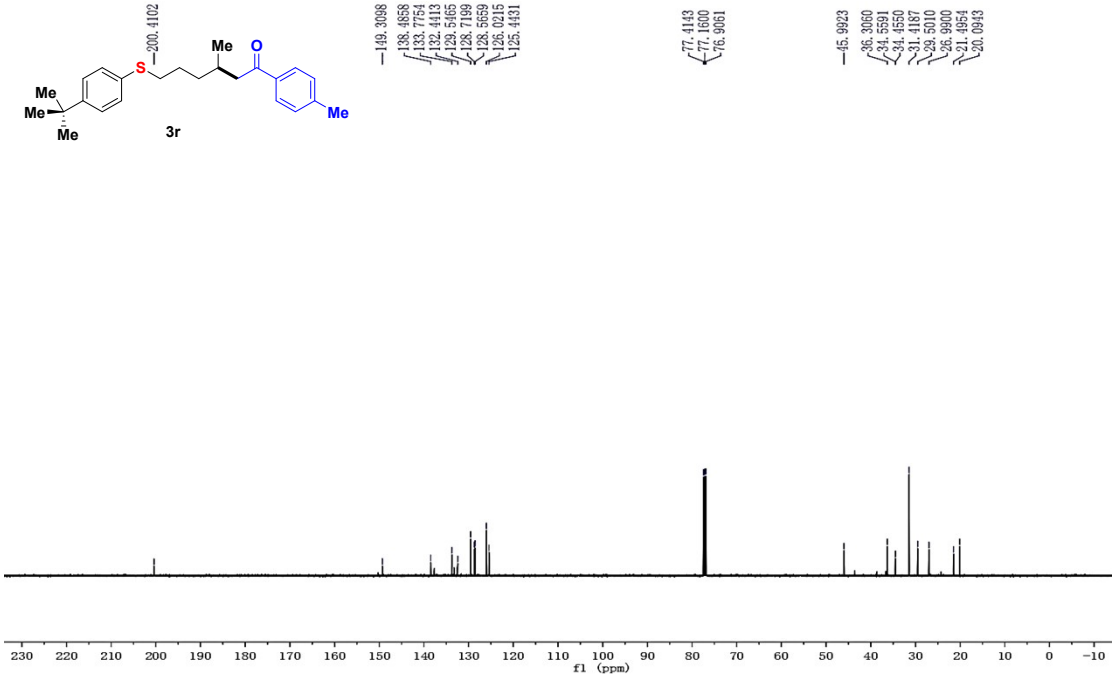
HRMS of **3q**


100
%
0
327.1784
327.1952
327.2141
327.2288
327.2522
327.2727
327.2944
327.180
327.200
327.220
327.240
327.260
327.280
327.300
m/z
3.22e3
Me
O
S
Me
Me
3q

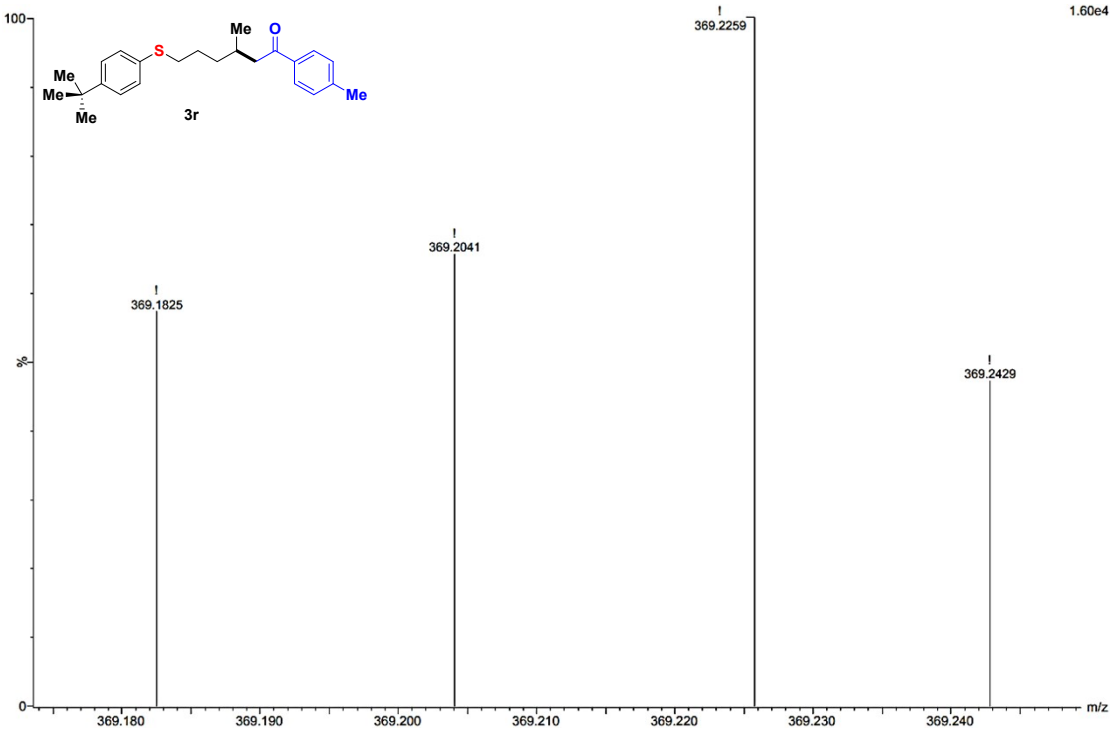
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3r**



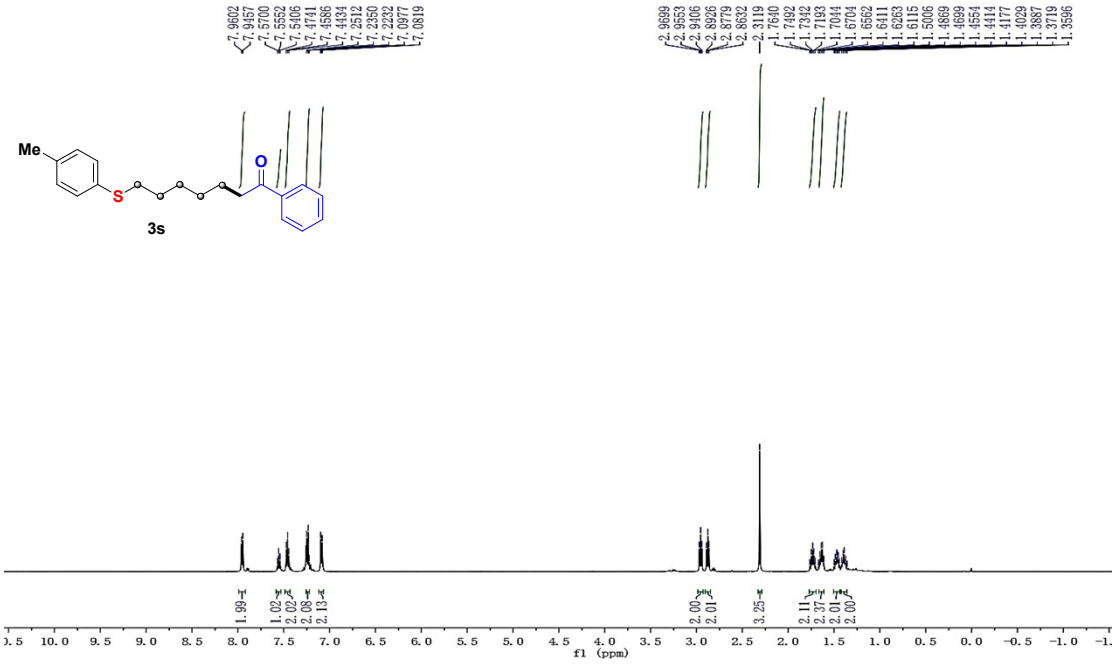
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3r**



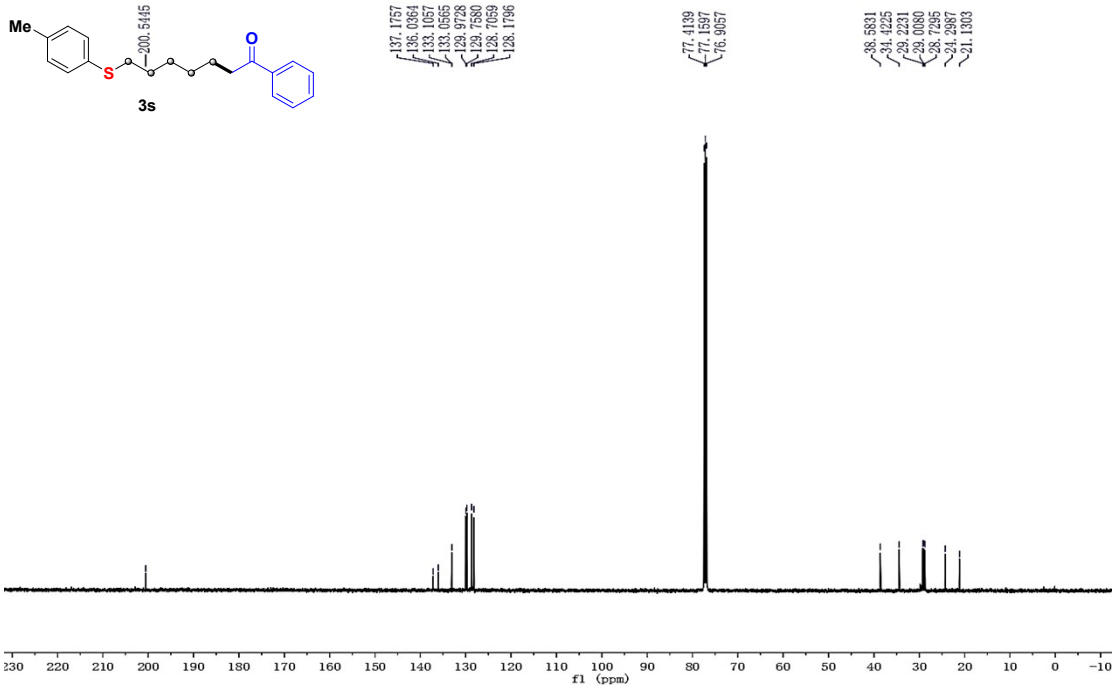
HRMS of **3r**


100
%
0
1.60e4
369.2259
369.2041
369.1825
369.2429
369.180
369.190
369.200
369.210
369.220
369.230
369.240
m/z
Me
Me
Me
S
Me
O
Me
3r

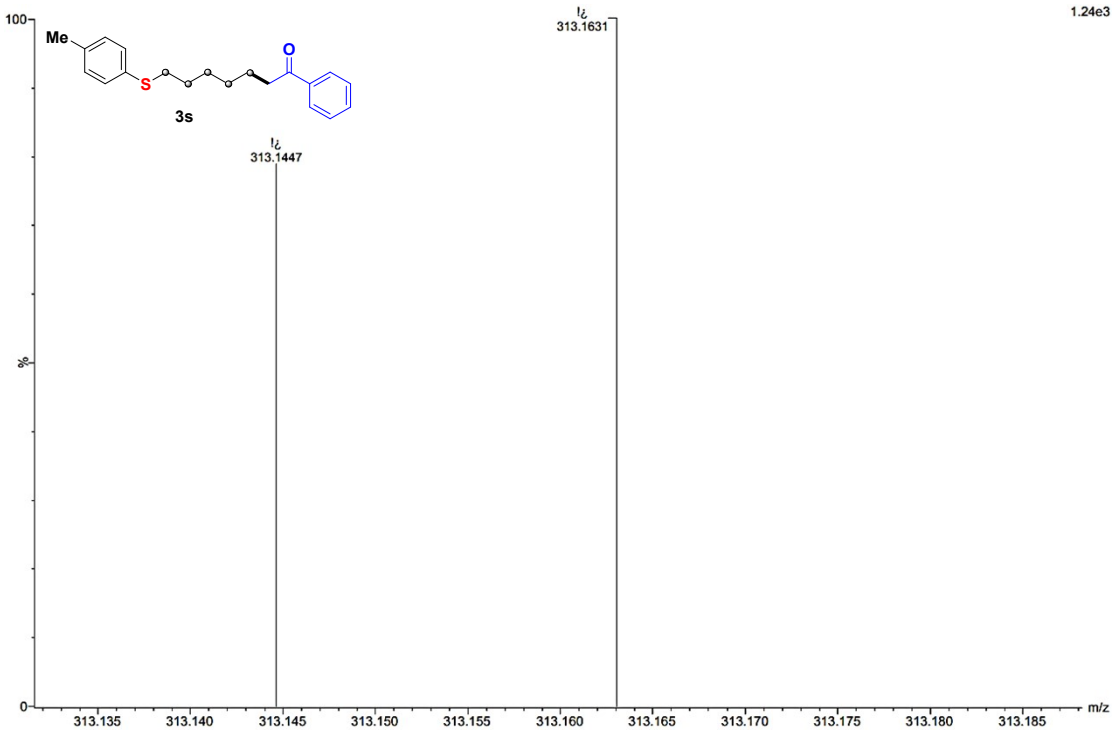
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3s**



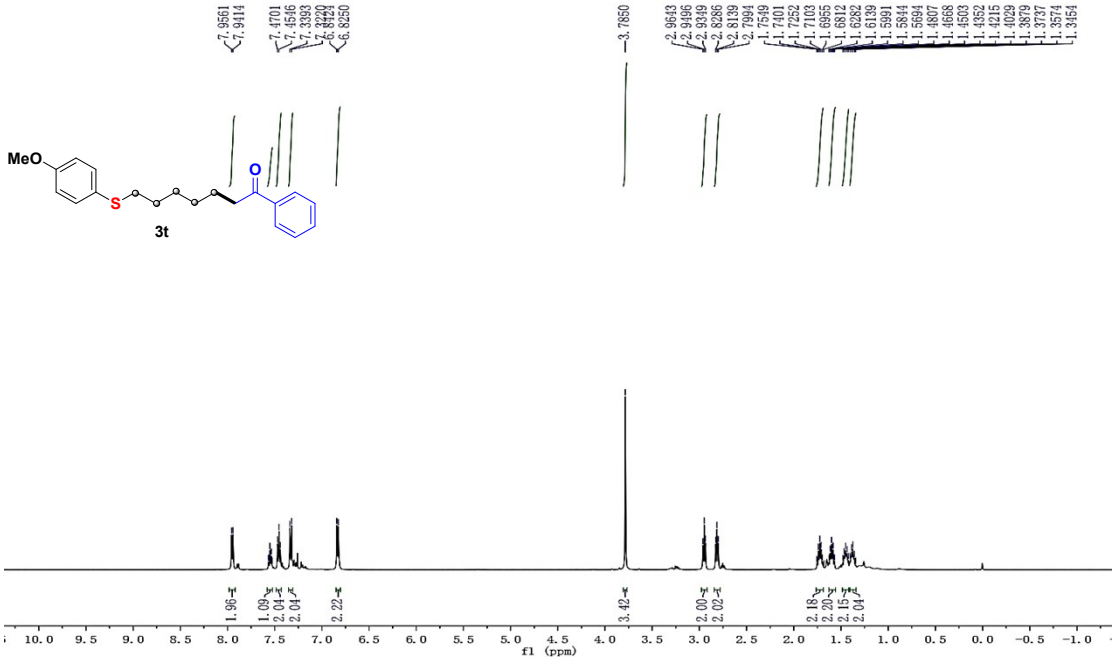
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3s**



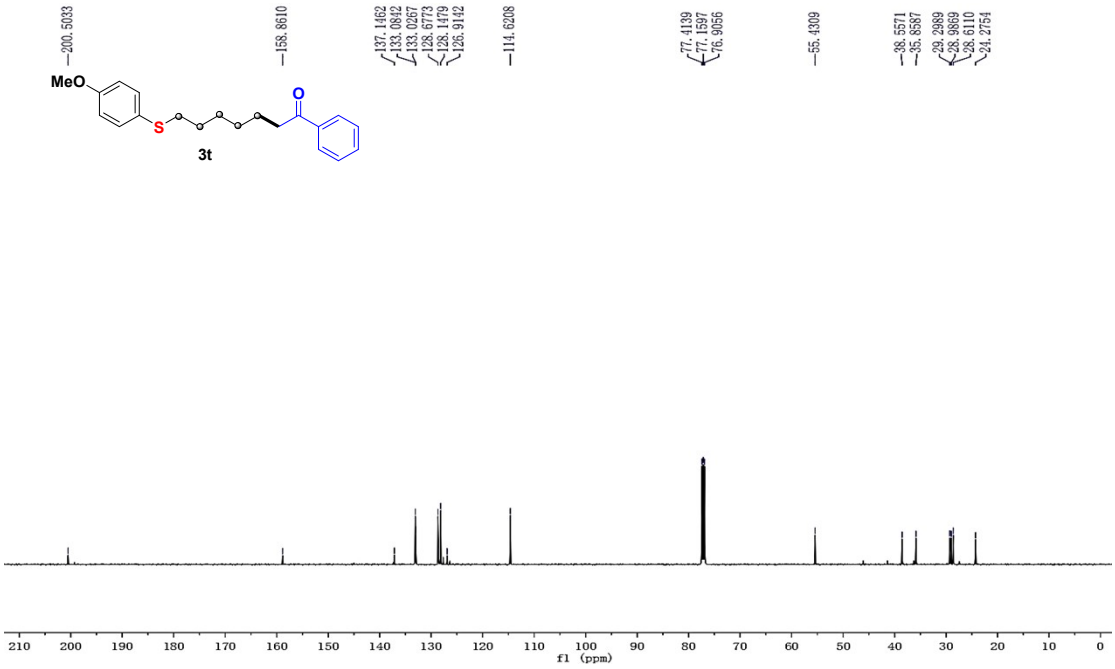
HRMS of **3s**


100
%
0
Me
S
O
3s
313.1447
313.1631
1.24e3
313.135
313.140
313.145
313.150
313.155
313.160
313.165
313.170
313.175
313.180
313.185
m/z

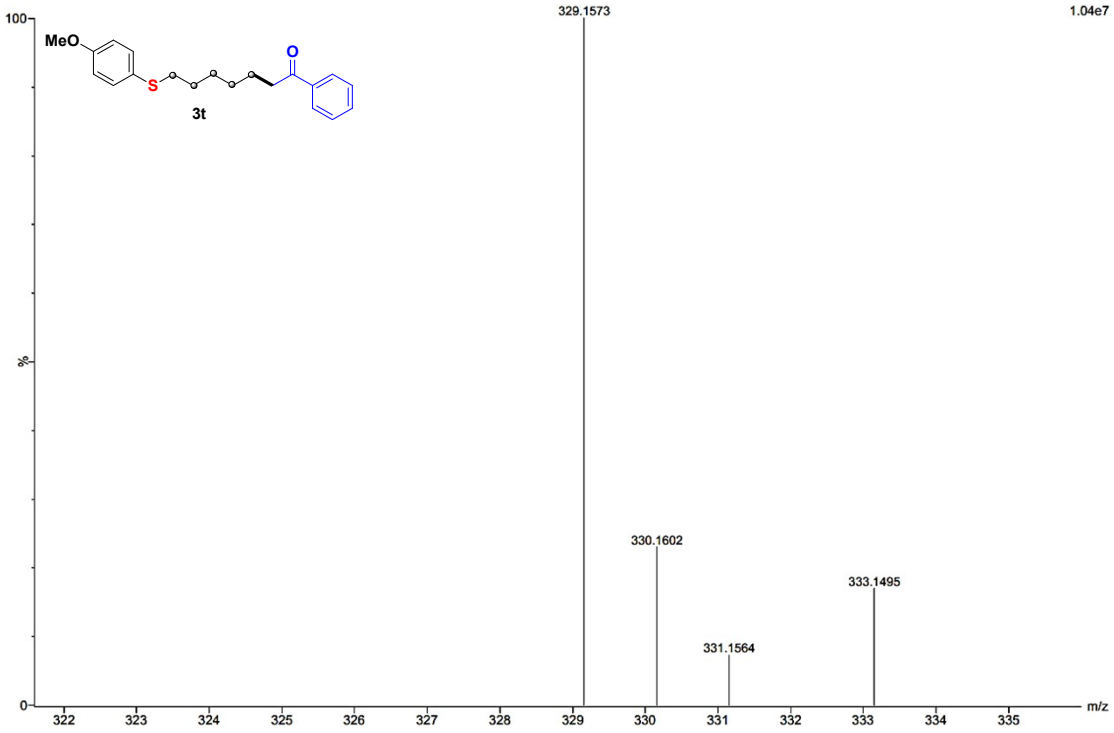
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3t**



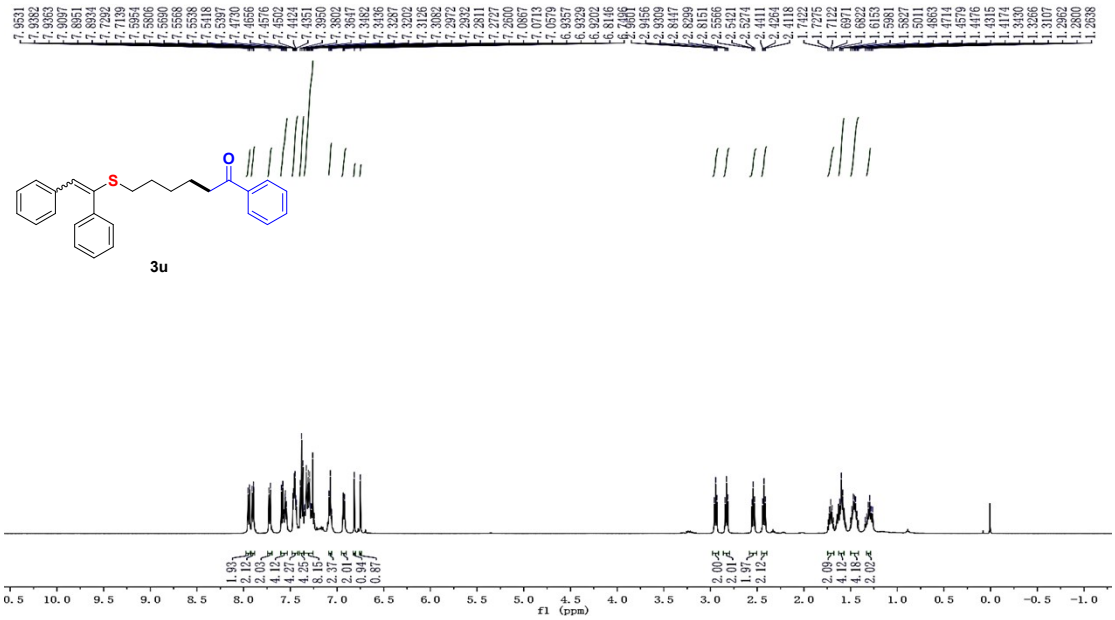
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3t**



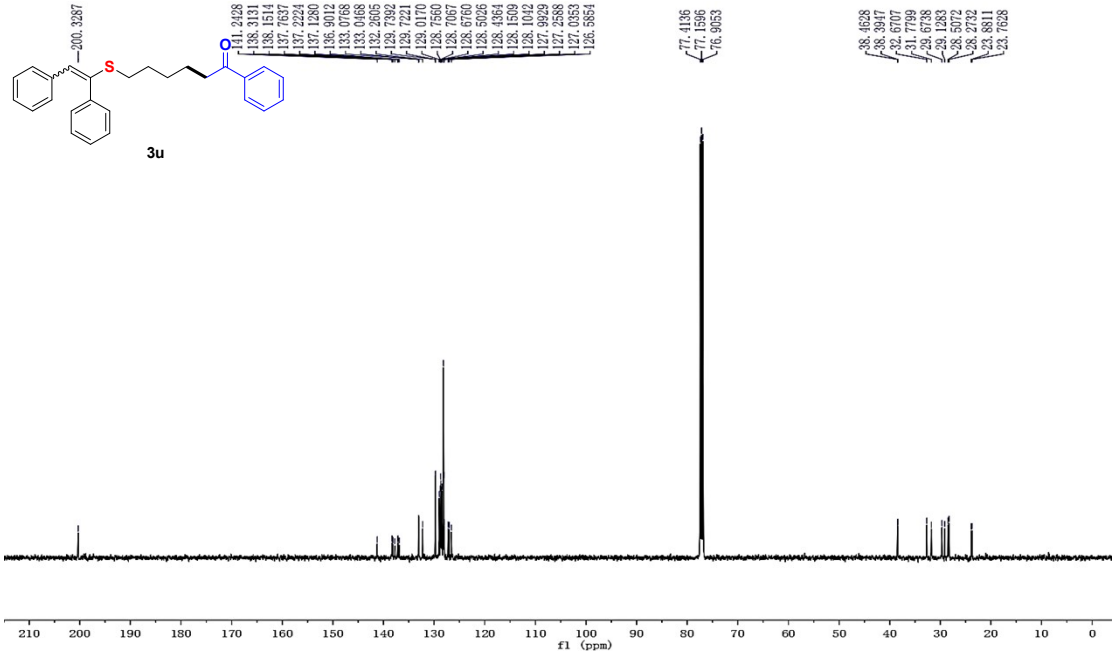
HRMS of **3t**


100
%
0
MeO
S
O
3t
329.1573
1.04e7
330.1602
331.1564
333.1495
322
323
324
325
326
327
328
329
330
331
332
333
334
335
m/z

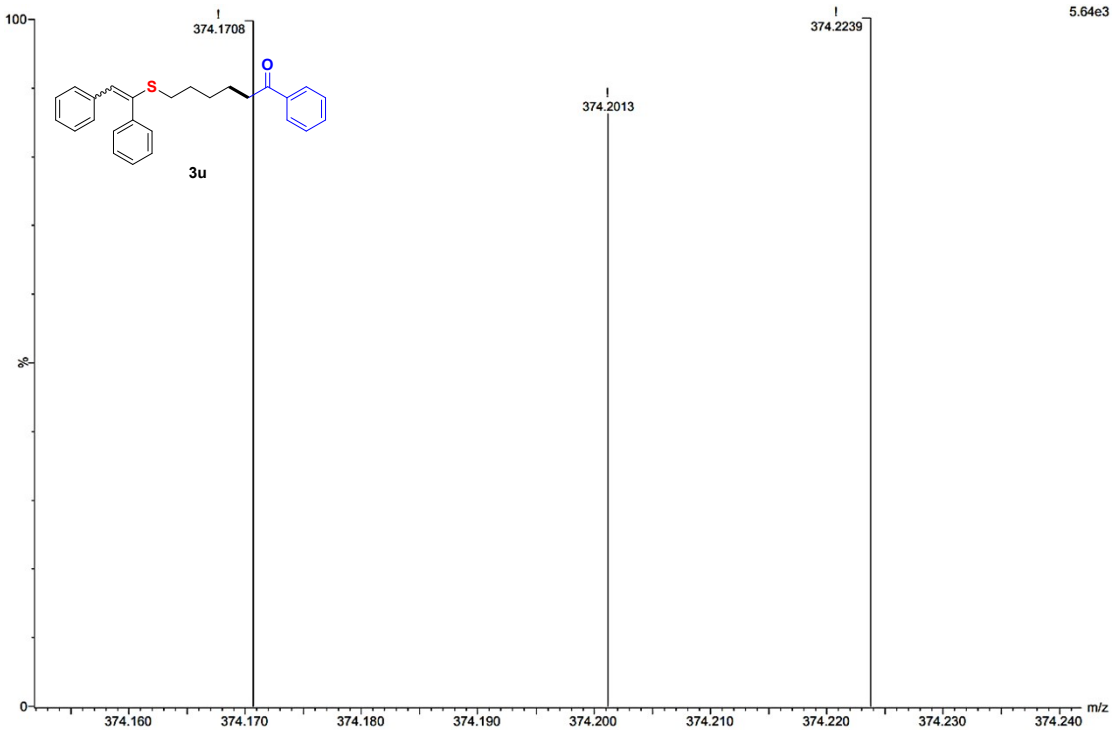
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3u**



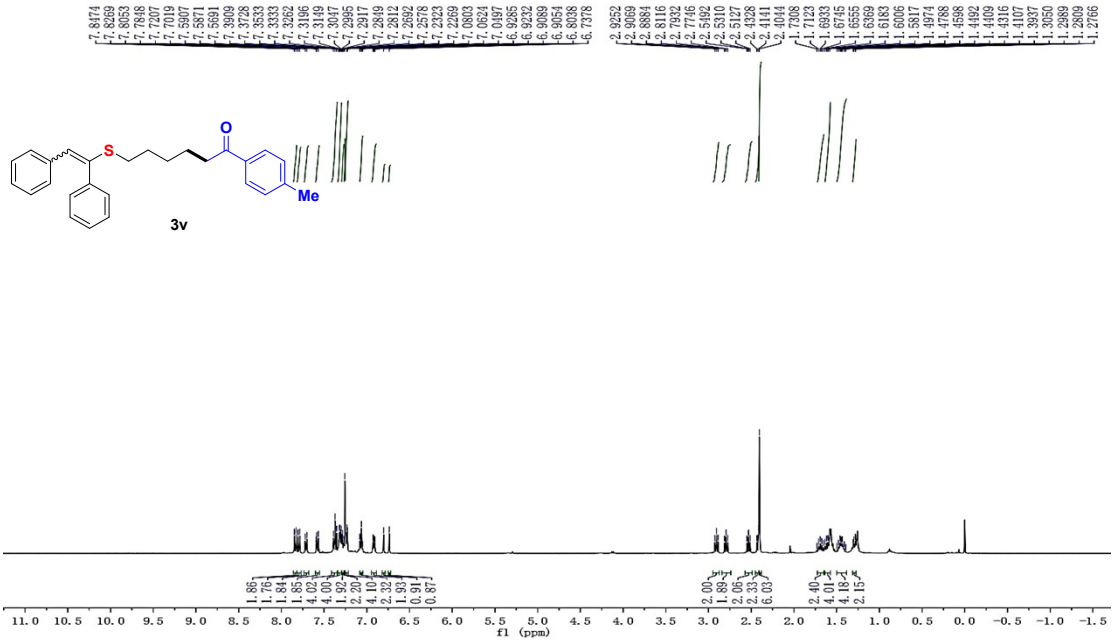
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3u**



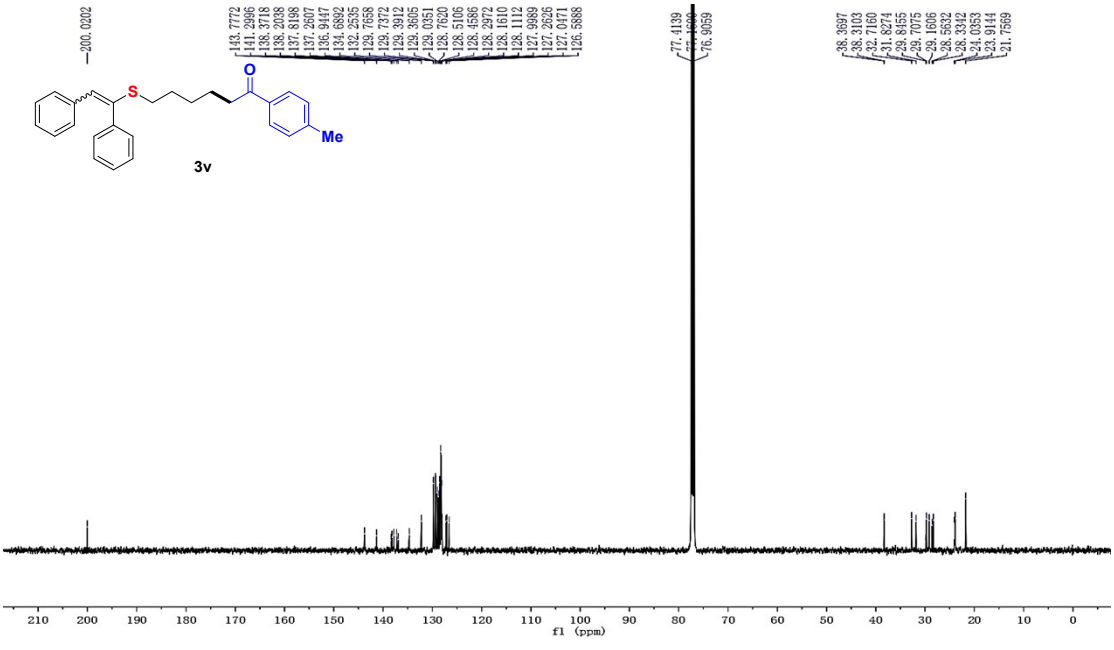
HRMS of **3u**


374.1708
374.2239
5.64e3
374.2013
100
%
0
S
O
3u
374.160
374.170
374.180
374.190
374.200
374.210
374.220
374.230
374.240
m/z

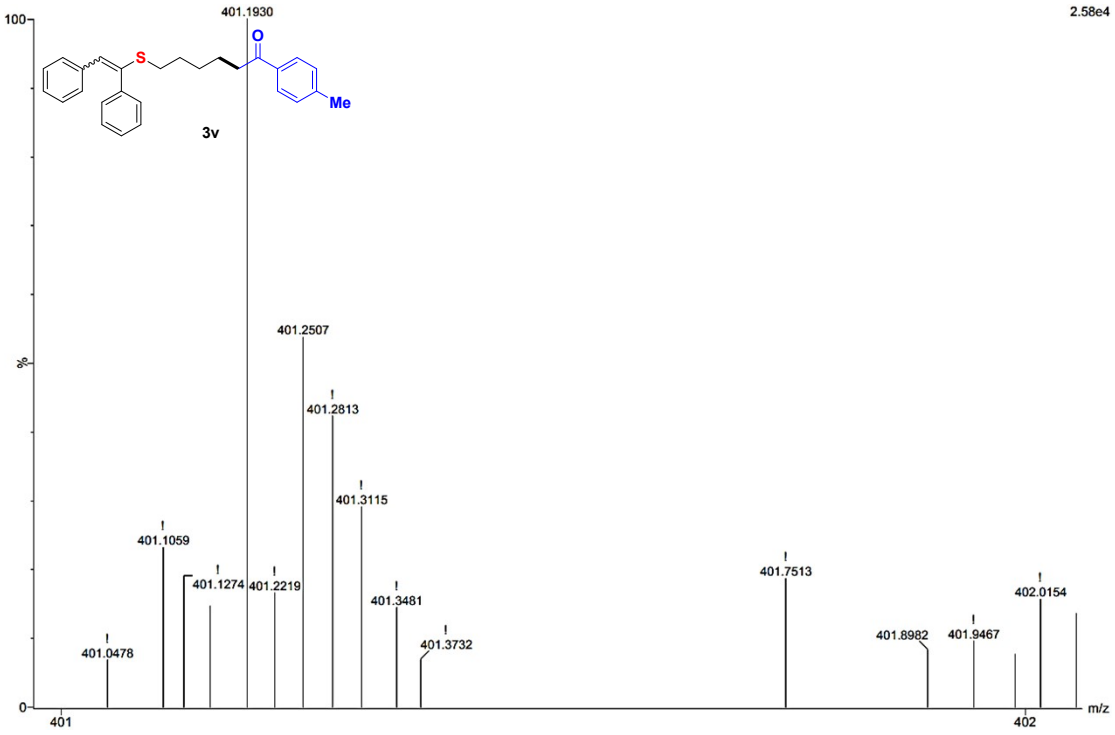
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3v**



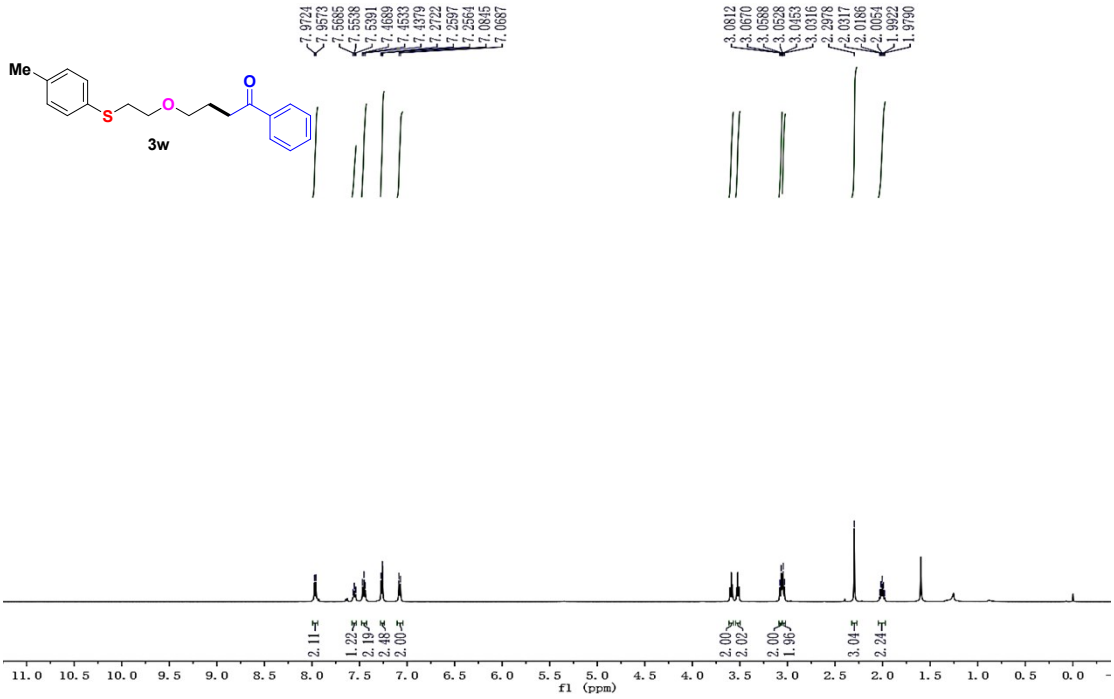
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3v**



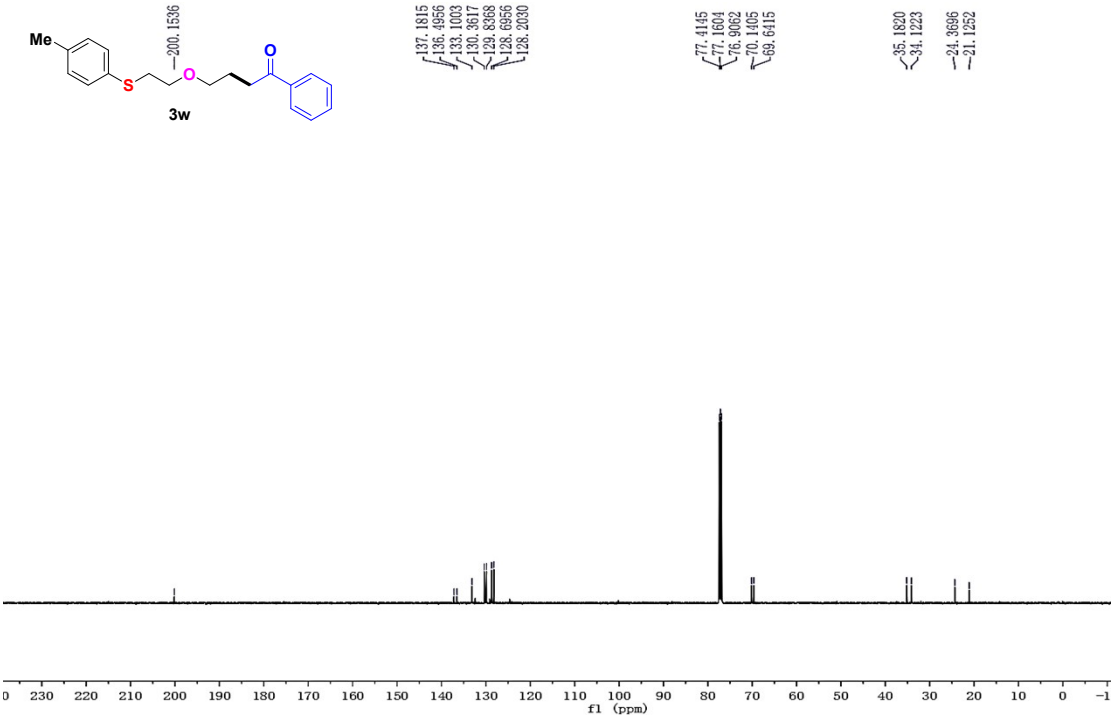
HRMS of **3v**


401.1930
2.58e4
100
%
0
401
402
m/z
S
O
Me
3v
401.2507
401.2813
401.3115
401.1059
401.1274
401.2219
401.3481
401.3732
401.0478
401.7513
401.8982
401.9467
402.0154

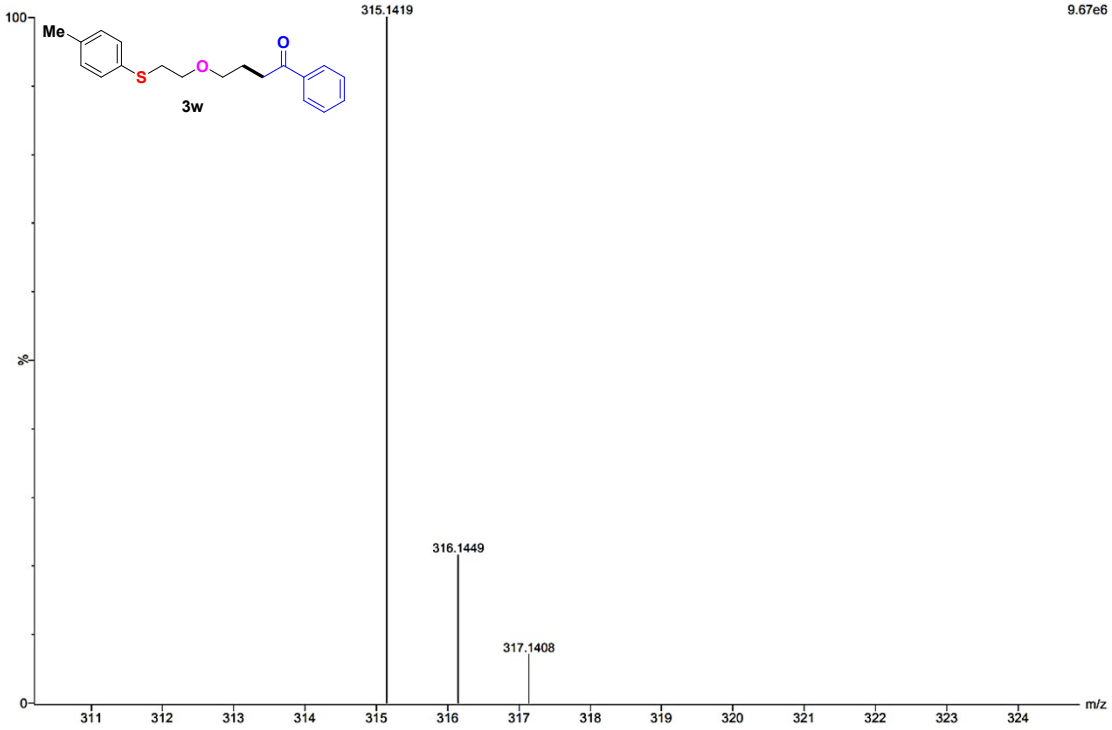
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3w**



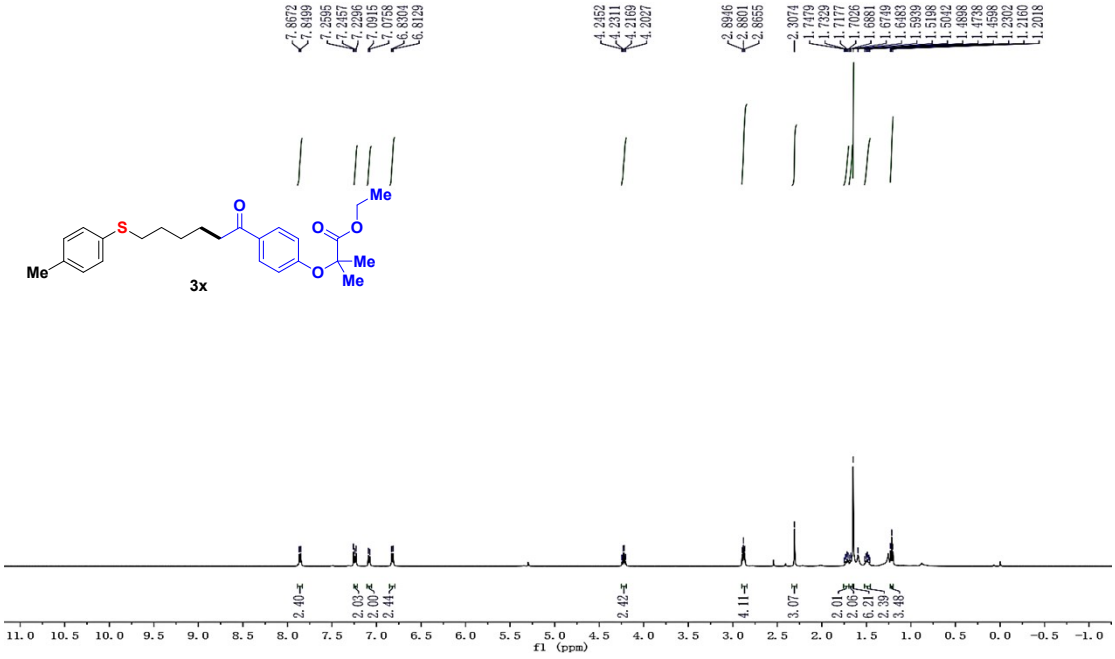
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3w**



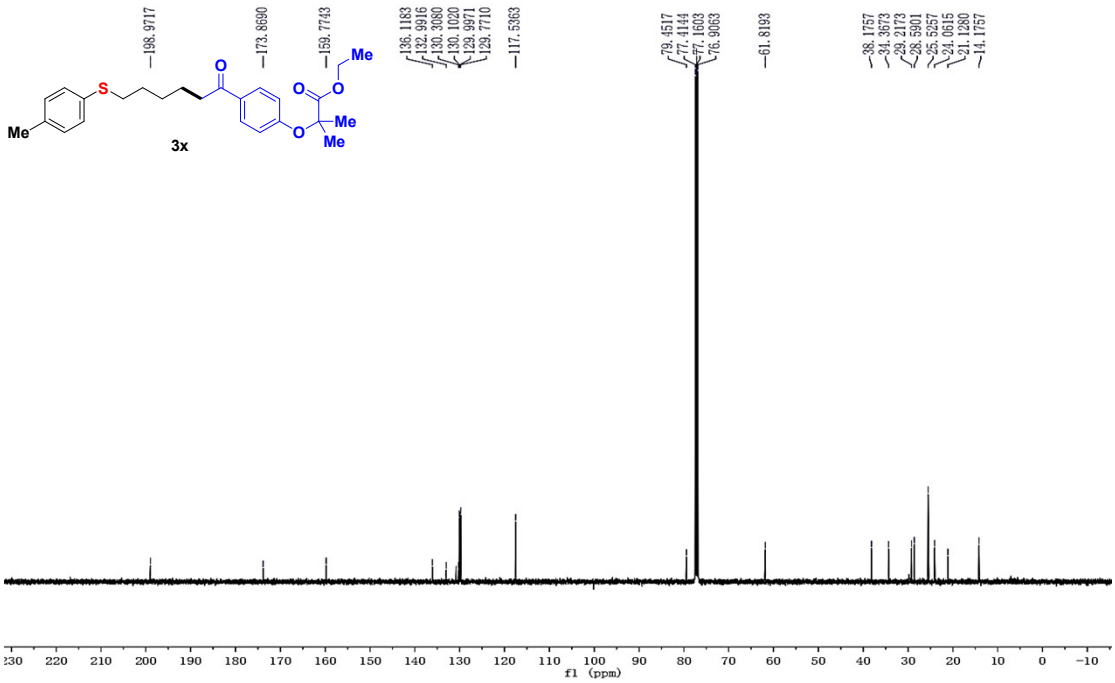
HRMS of **3w**


315.1419
9.67e6
100
%
0
Me
S
O
O
3w
316.1449
317.1408
311
312
313
314
315
316
317
318
319
320
321
322
323
324
m/z

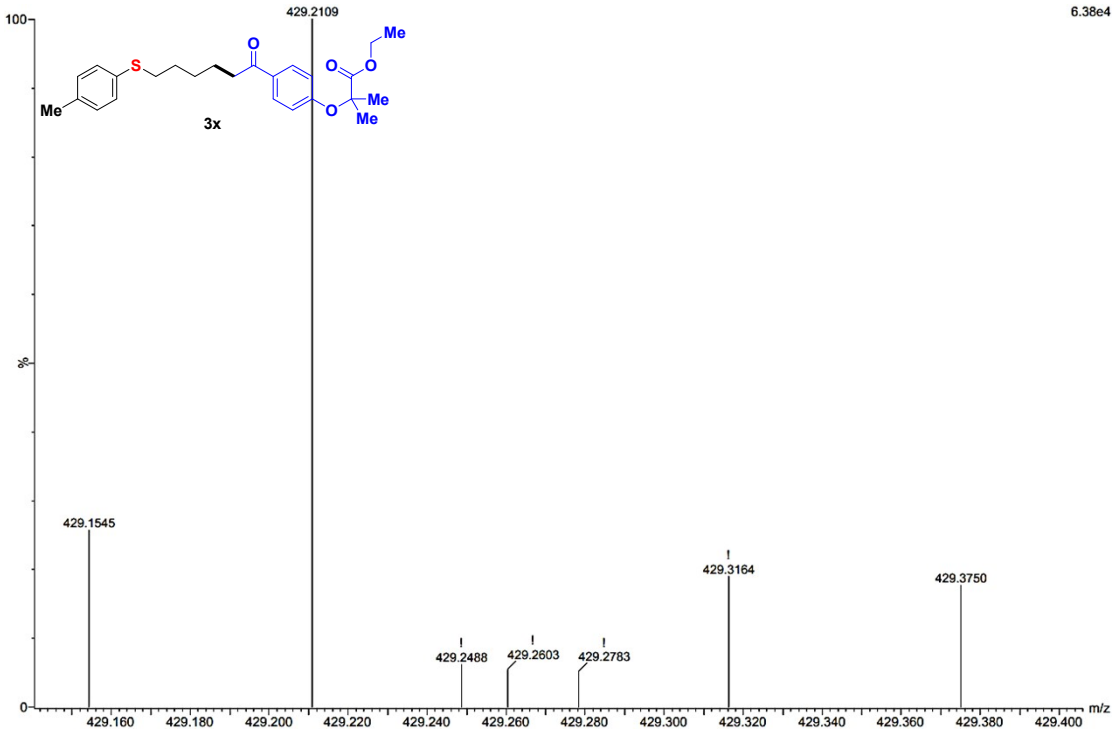
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3x**



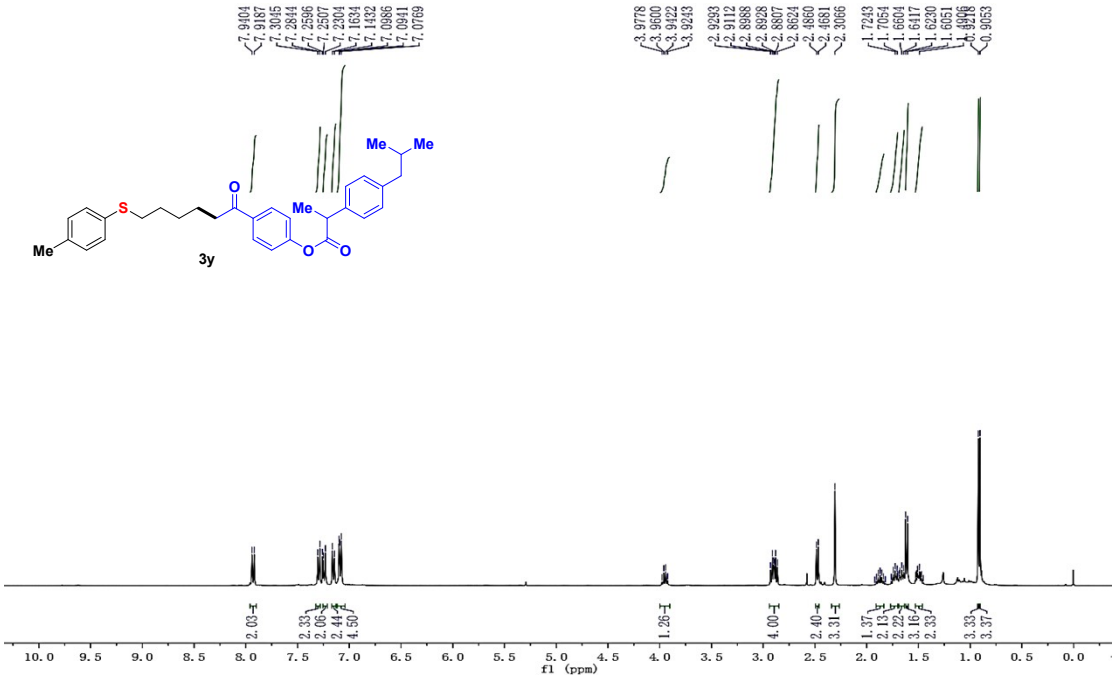
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3x**



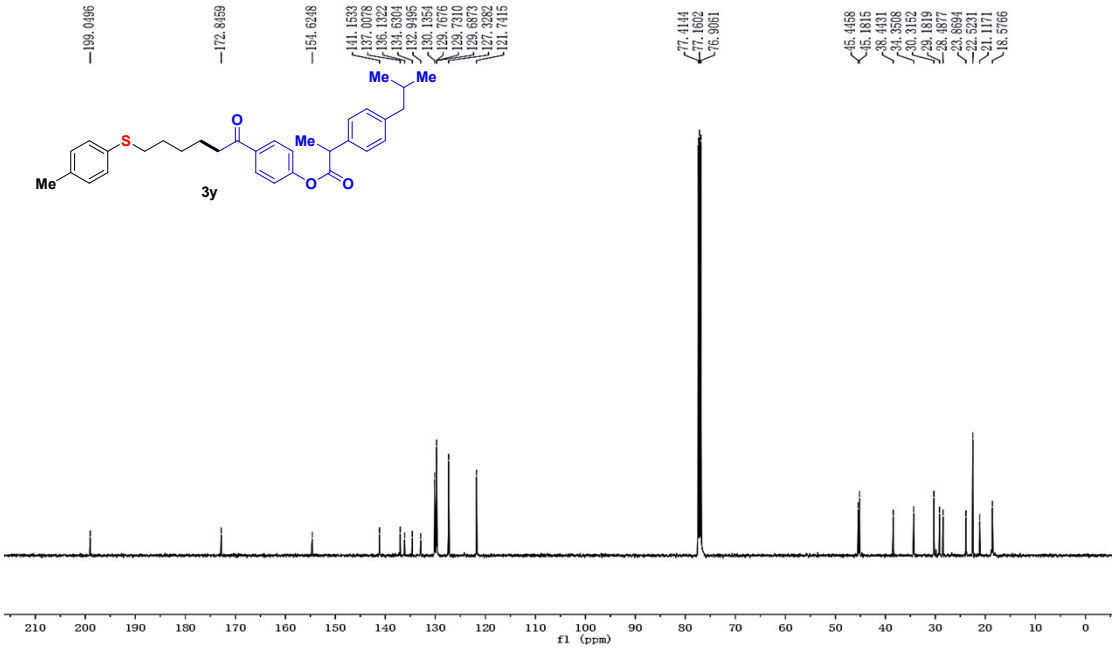
HRMS of **3x**


429.2109
6.38e4
100
%
0
Me
S
O
O
O
O
Me
Me
3x
429.1545
429.2488
429.2603
429.2783
429.3164
429.3750
429.160
429.180
429.200
429.220
429.240
429.260
429.280
429.300
429.320
429.340
429.360
429.380
429.400
m/z

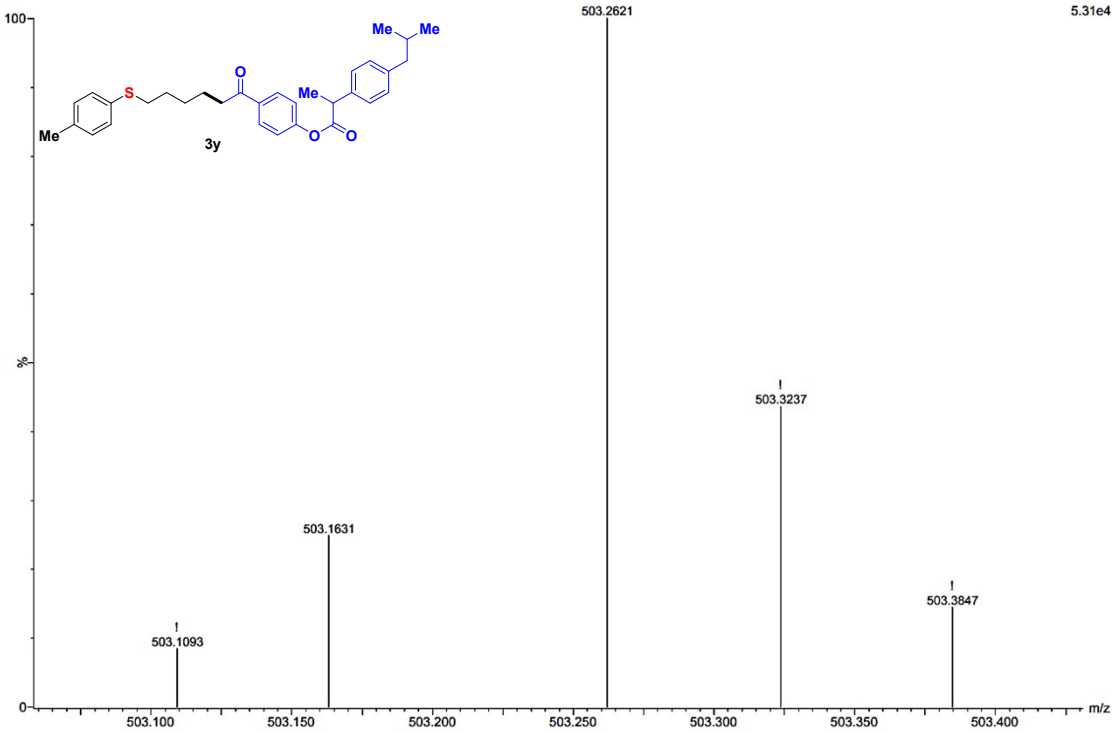
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3y**



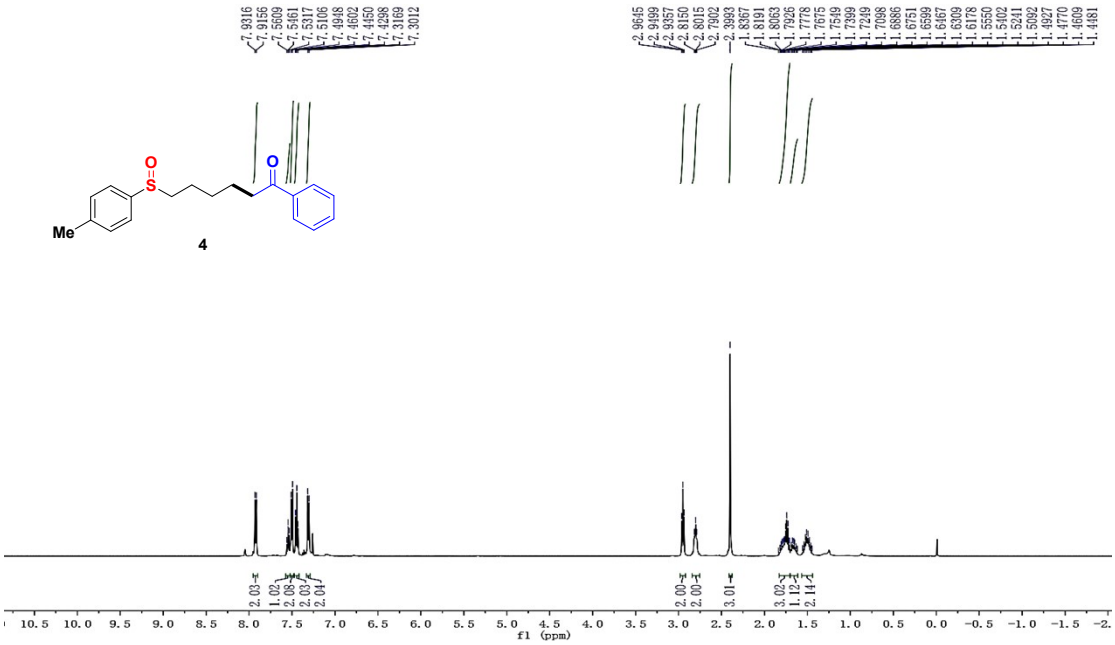
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3y**



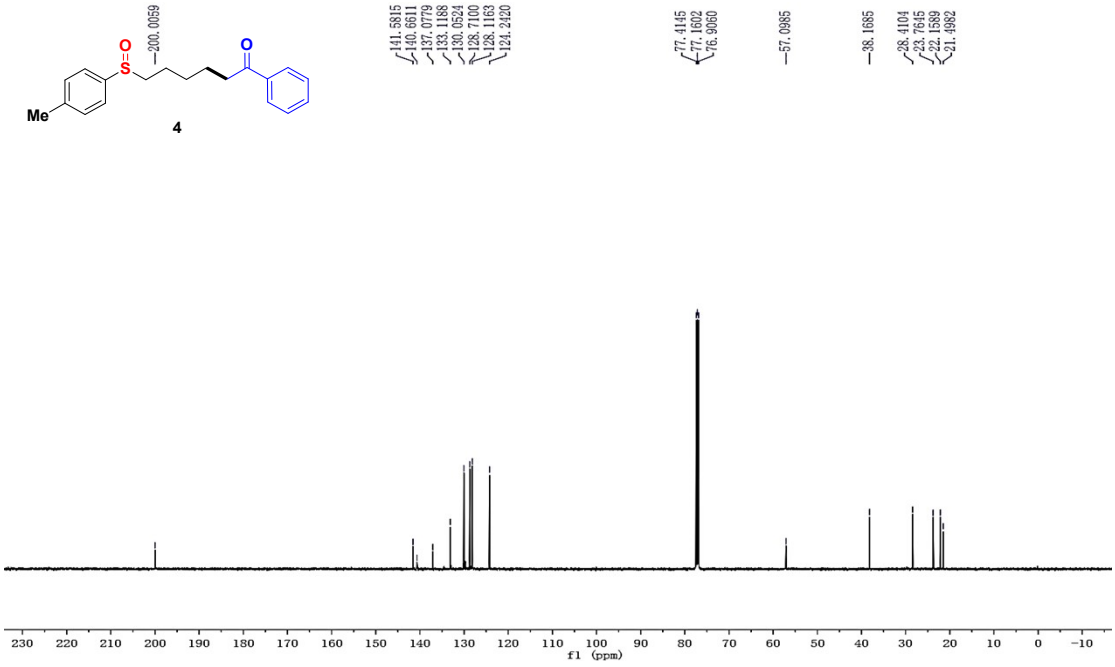
HRMS of **3y**


503.2621
5.31e4
100
%
0
503.3237
503.1631
503.3847
503.1093
503.100
503.150
503.200
503.250
503.300
503.350
503.400
m/z
Me
Me
Me
S
O
O
O
Me
3y

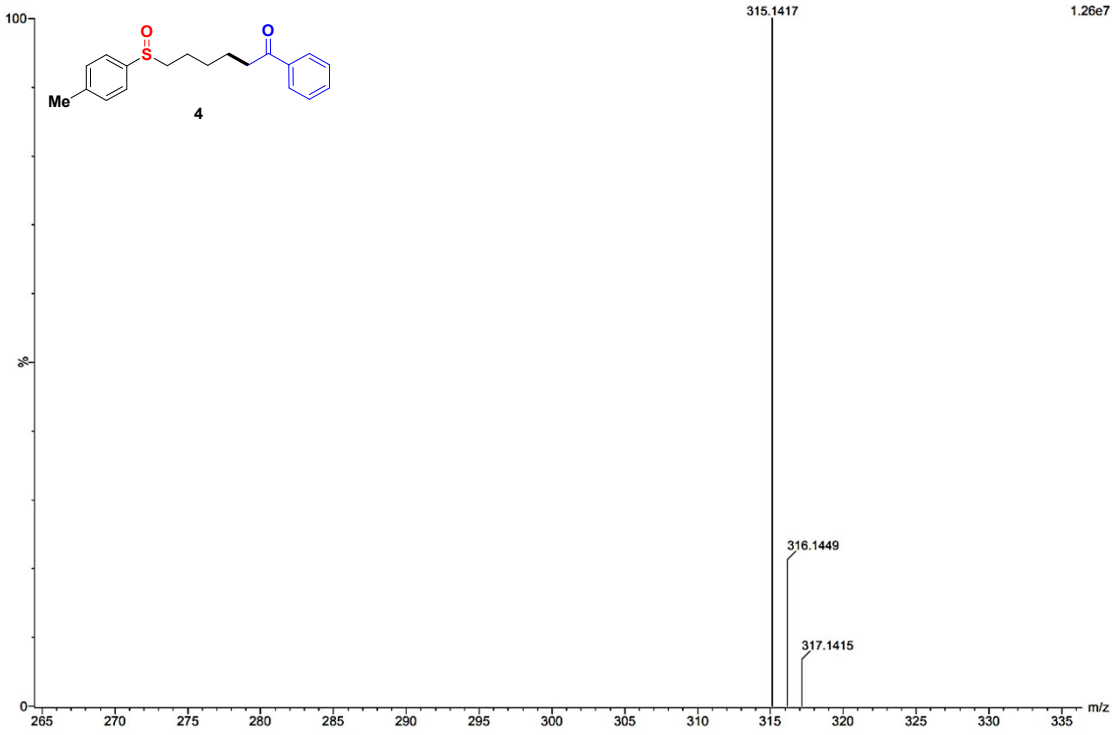
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4**



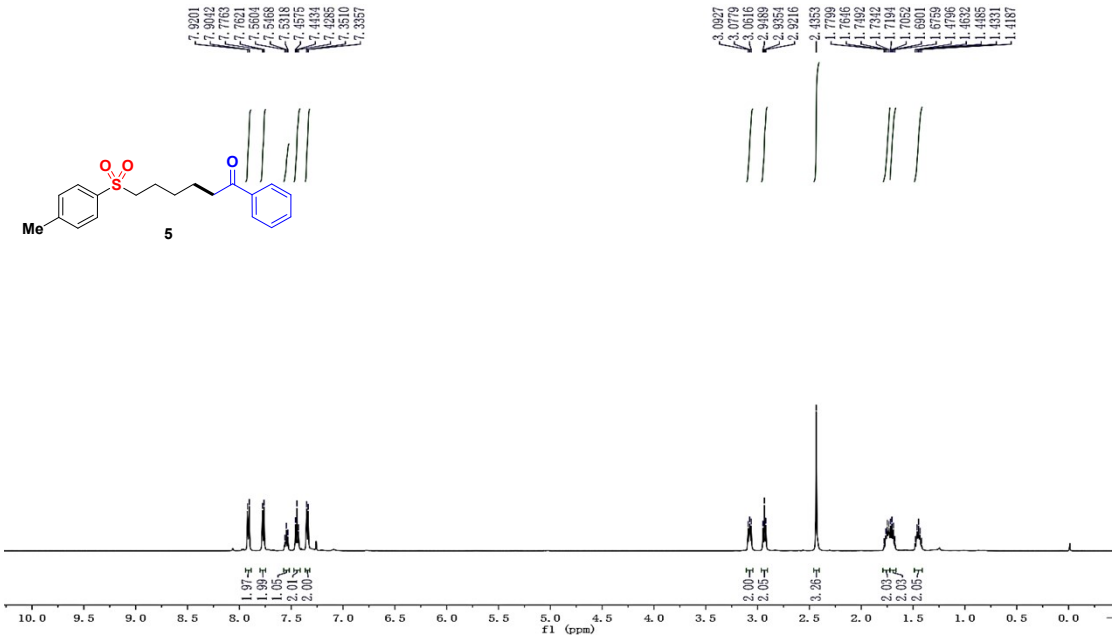
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **4**



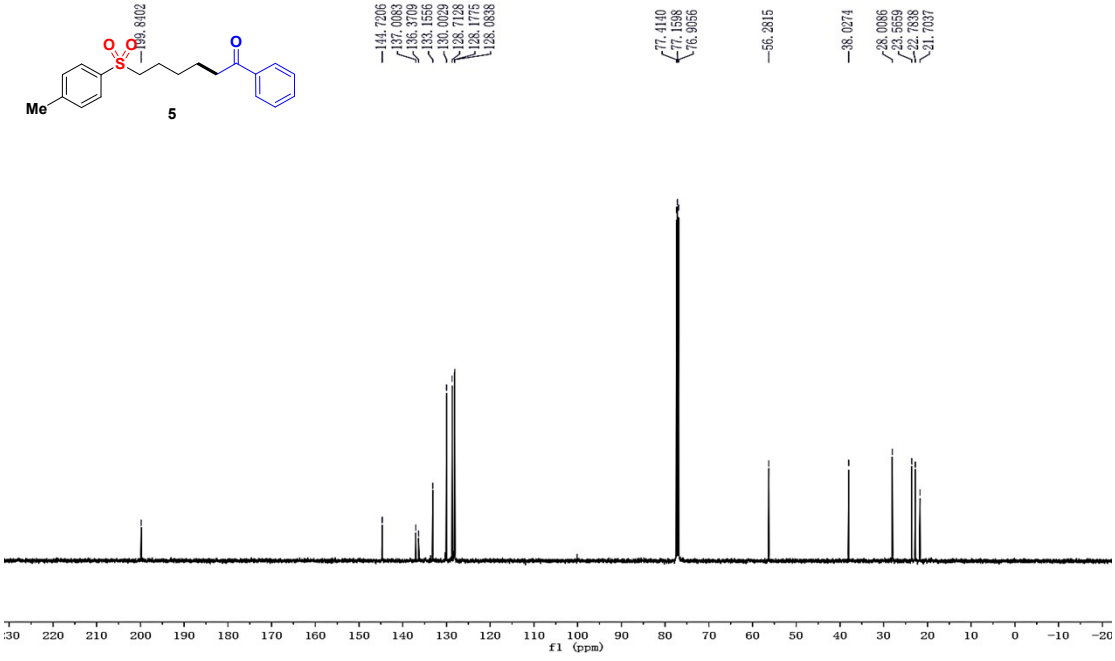
HRMS of **4**


100
%
0
Me
O
S
O
4
315.1417
1.26e7
316.1449
317.1415
265
270
275
280
285
290
295
300
305
310
315
320
325
330
335
m/z

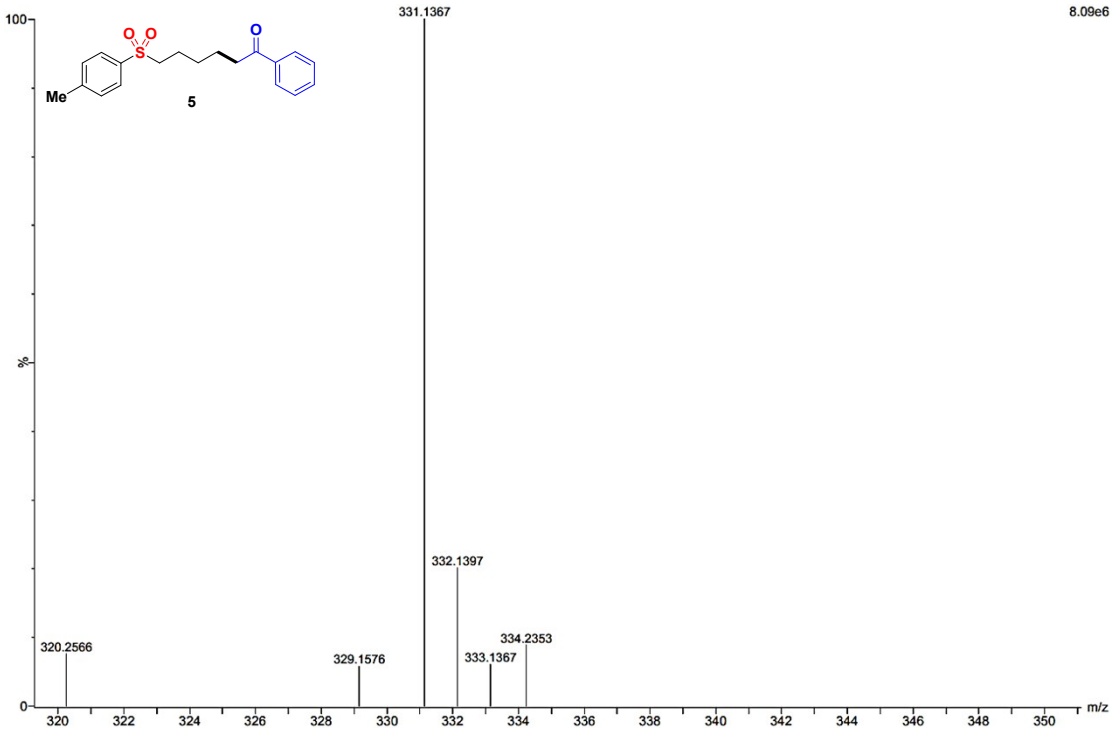
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5**



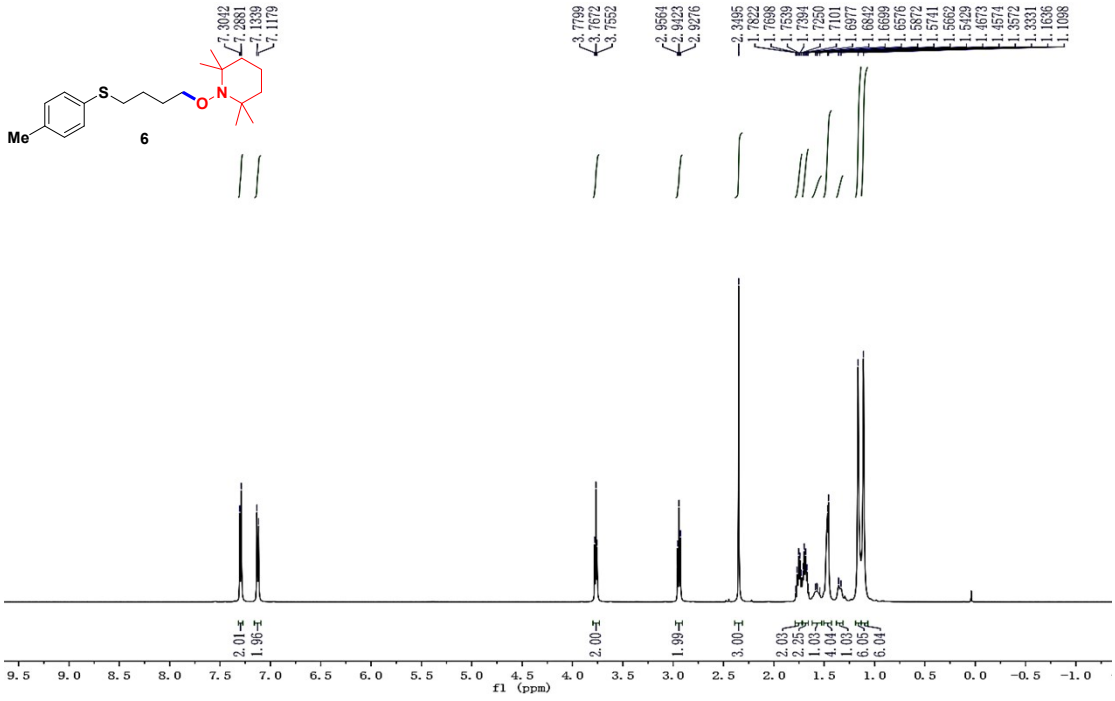
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **5**



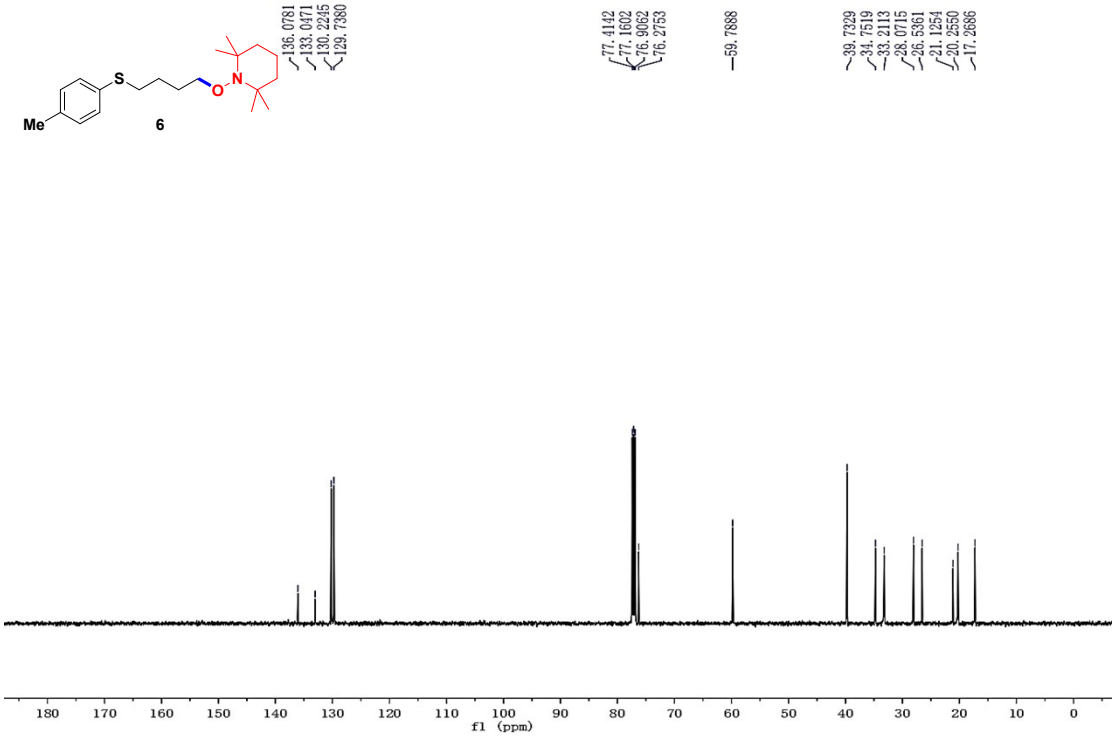
HRMS of **5**


100
%
0
Me
5
331.1367
8.09e6
332.1397
320.2566
329.1576
334.2353
333.1367
320
322
324
326
328
330
332
334
336
338
340
342
344
346
348
350
m/z

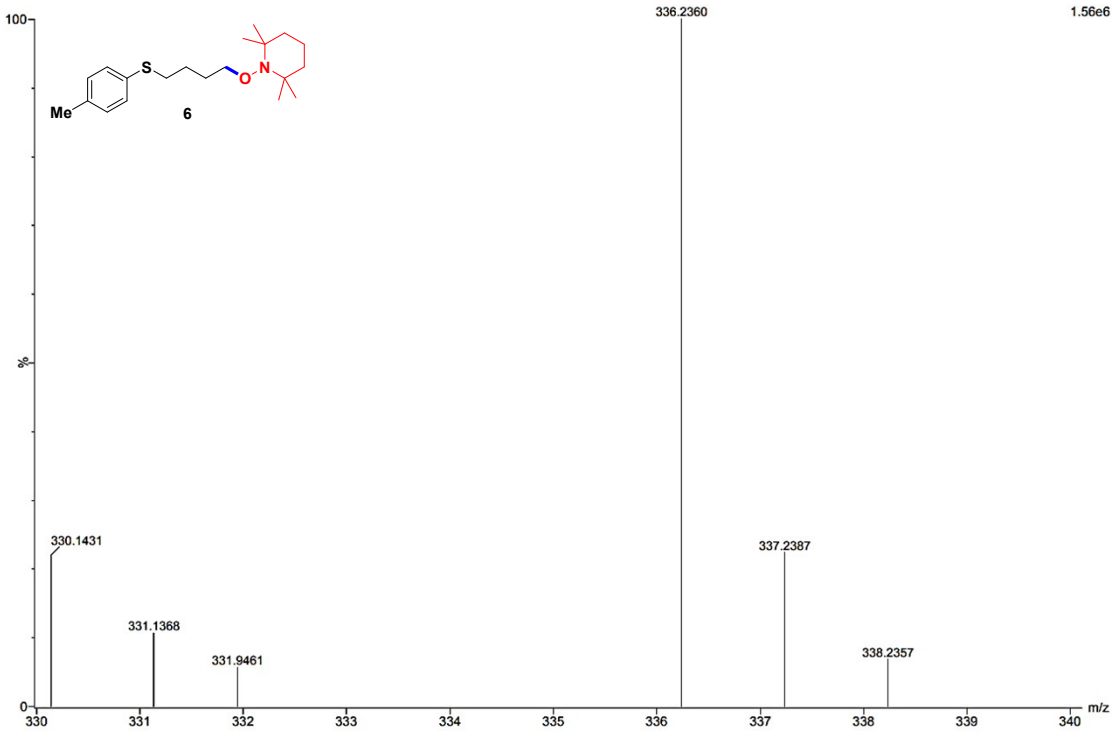
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6**



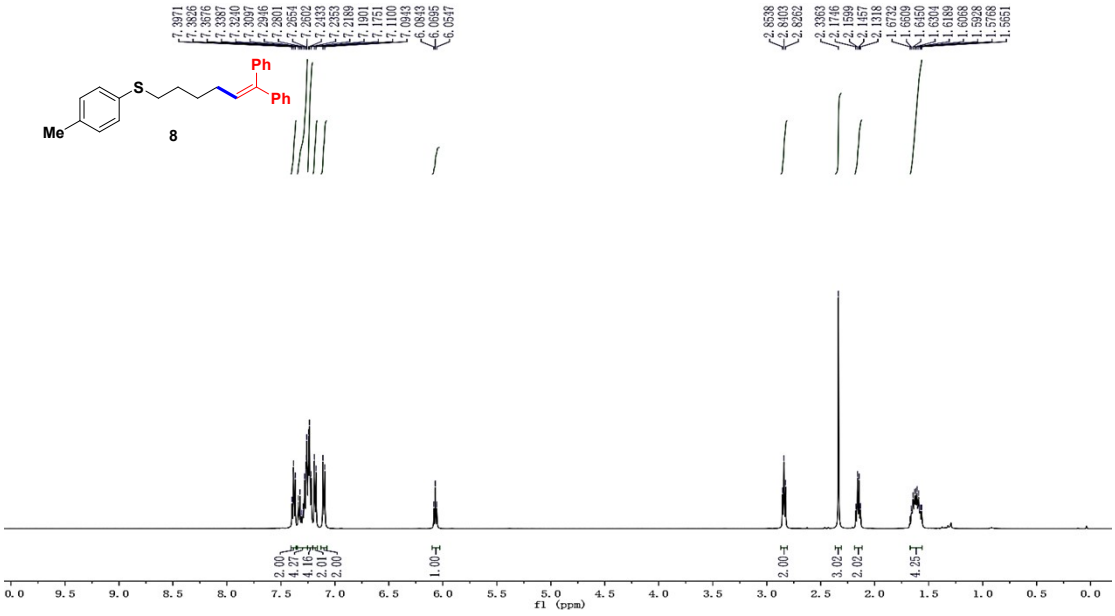
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **6**



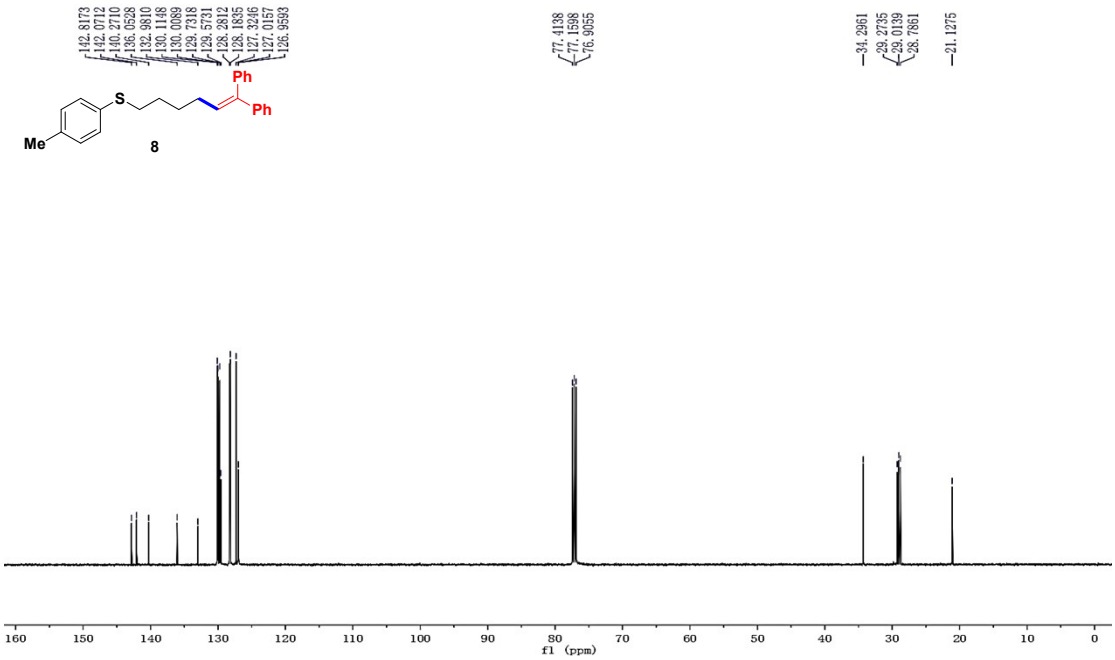
HRMS of **6**


100
%
0
Me
S
O
N
6
336.2360
1.56e6
330.1431
331.1368
331.9461
337.2387
338.2357
m/z
330
331
332
333
334
335
336
337
338
339
340

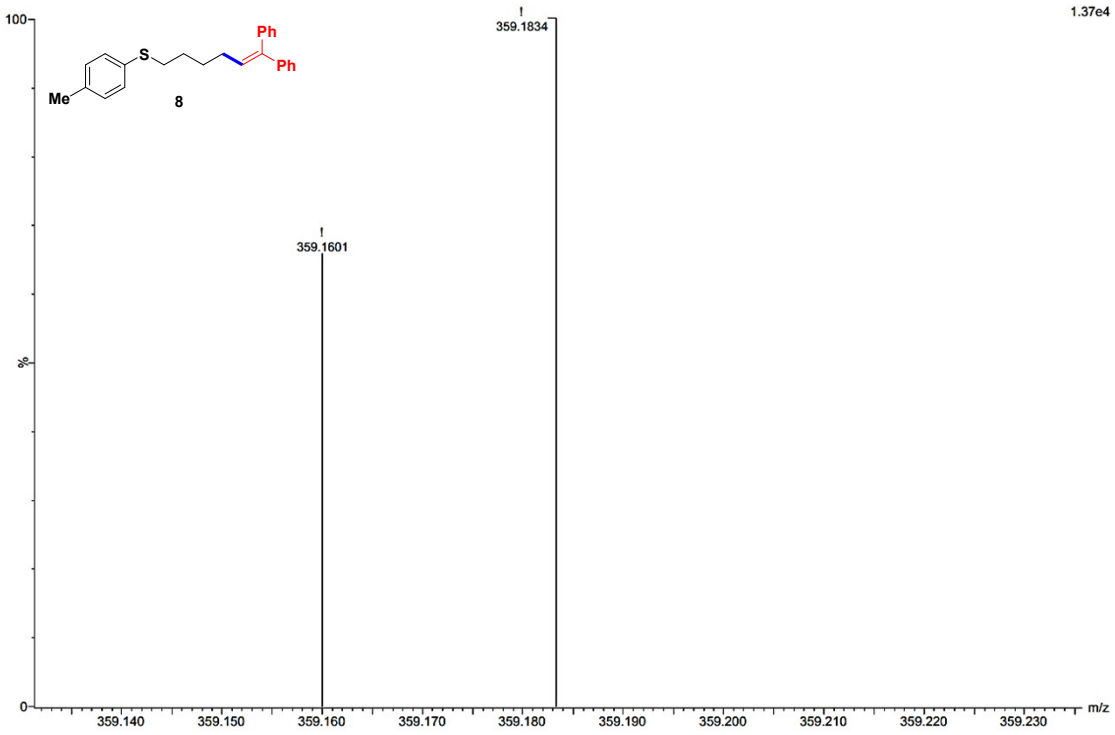
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **8**



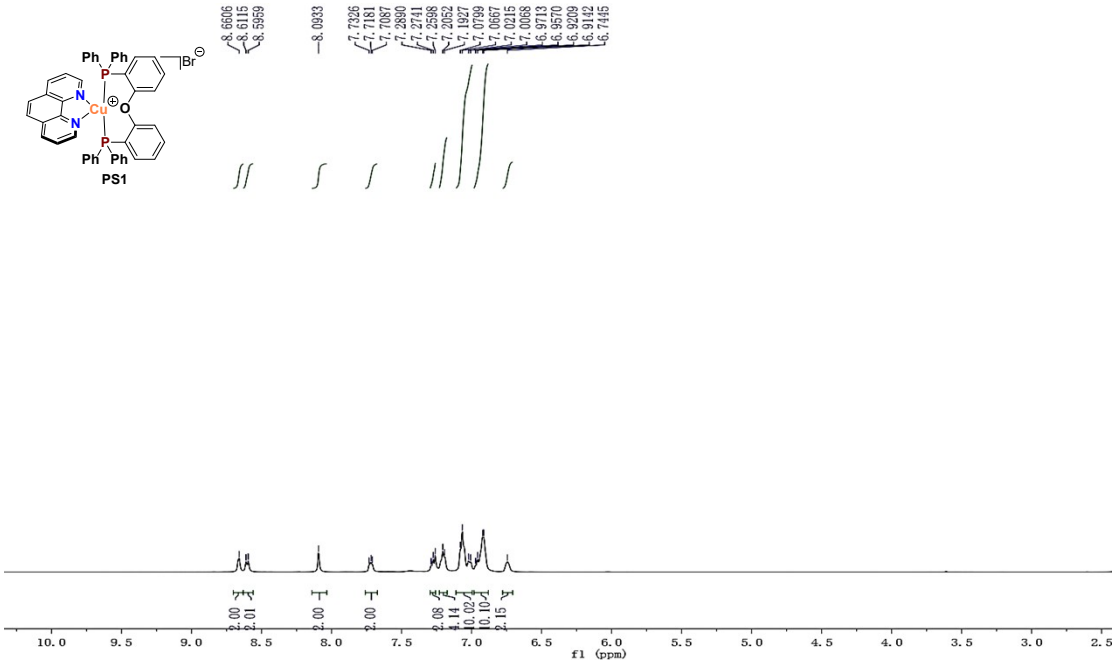
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **8**



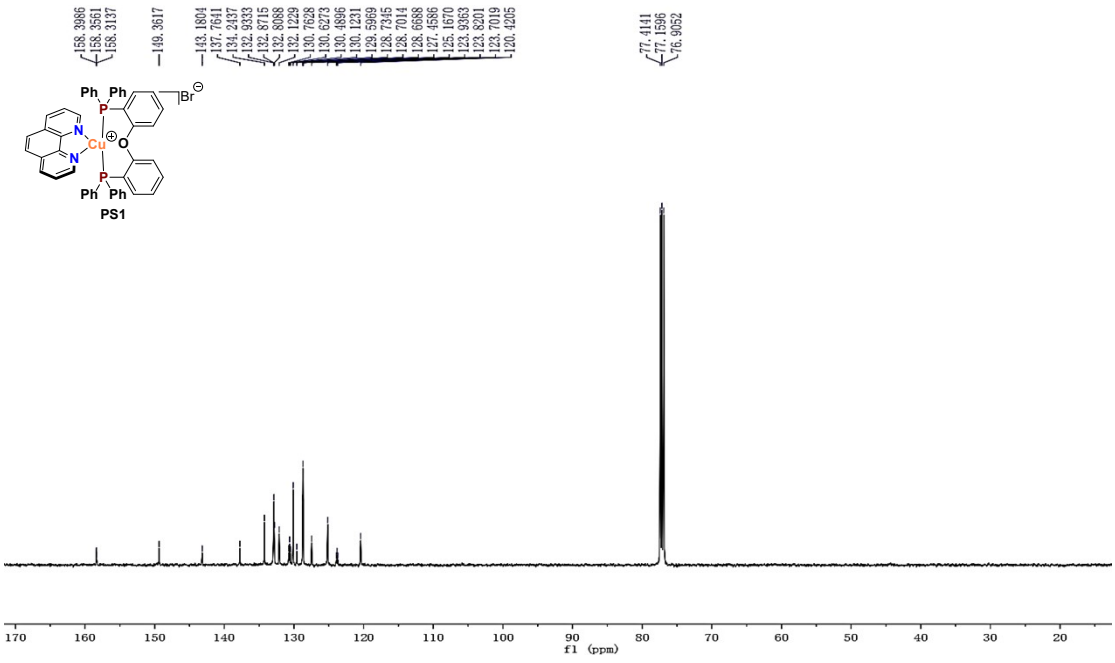
HRMS of **8**


100
%
0
Me
S
Ph
Ph
8
359.1834
359.1601
1.37e4
359.140
359.150
359.160
359.170
359.180
359.190
359.200
359.210
359.220
359.230
m/z

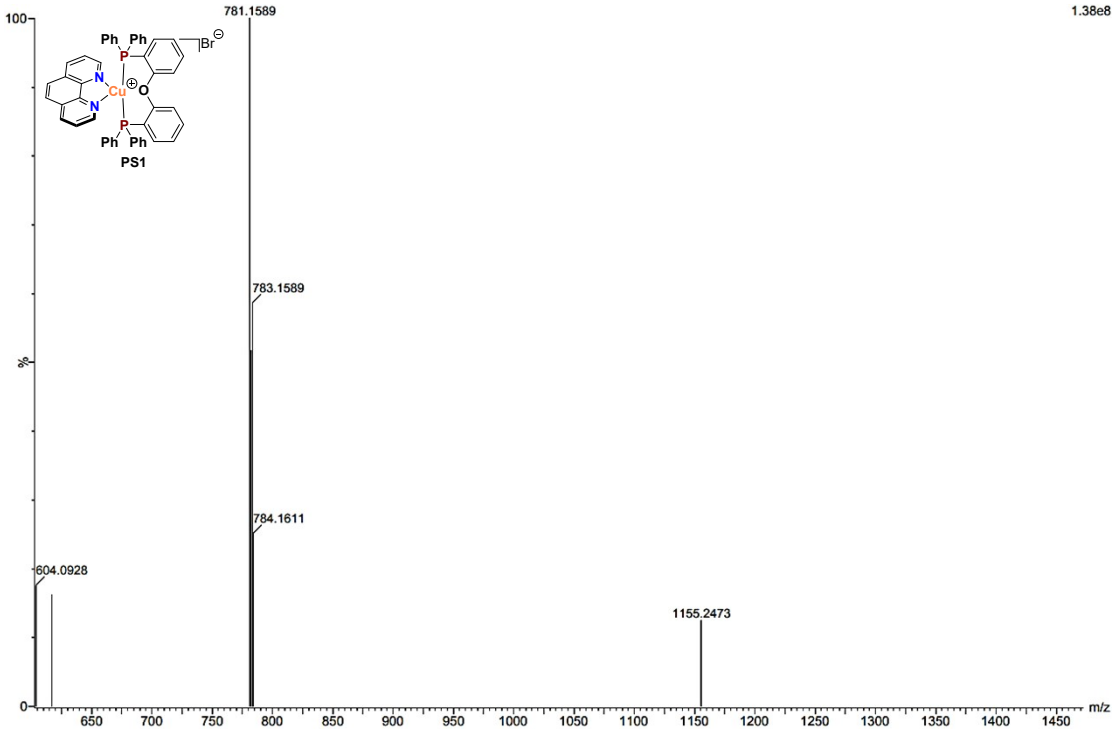
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of copper catalyst **PS1**



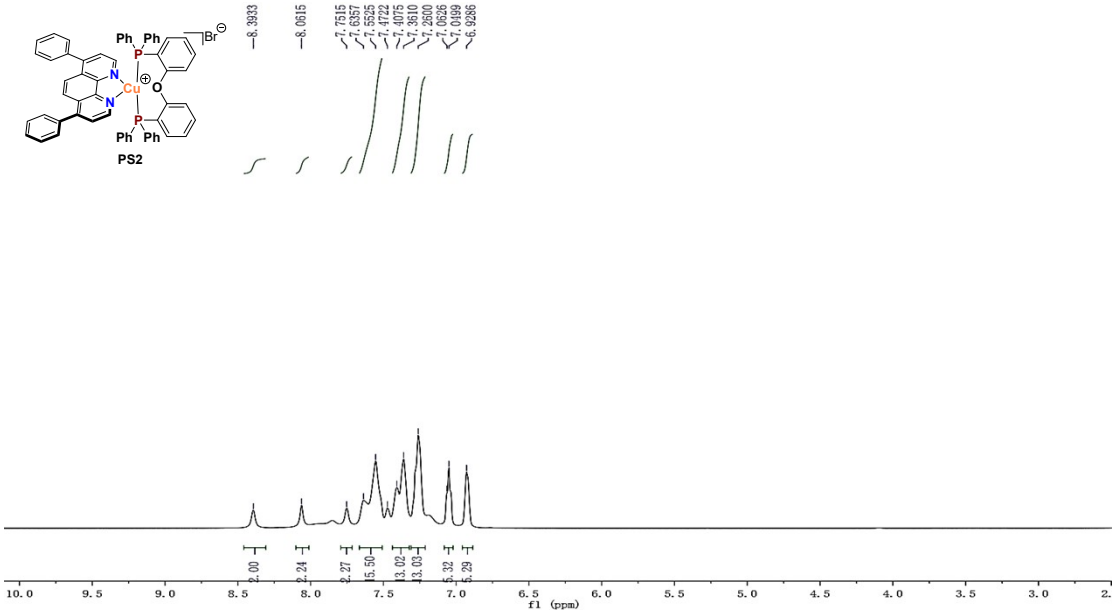
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of copper catalyst **PS1**



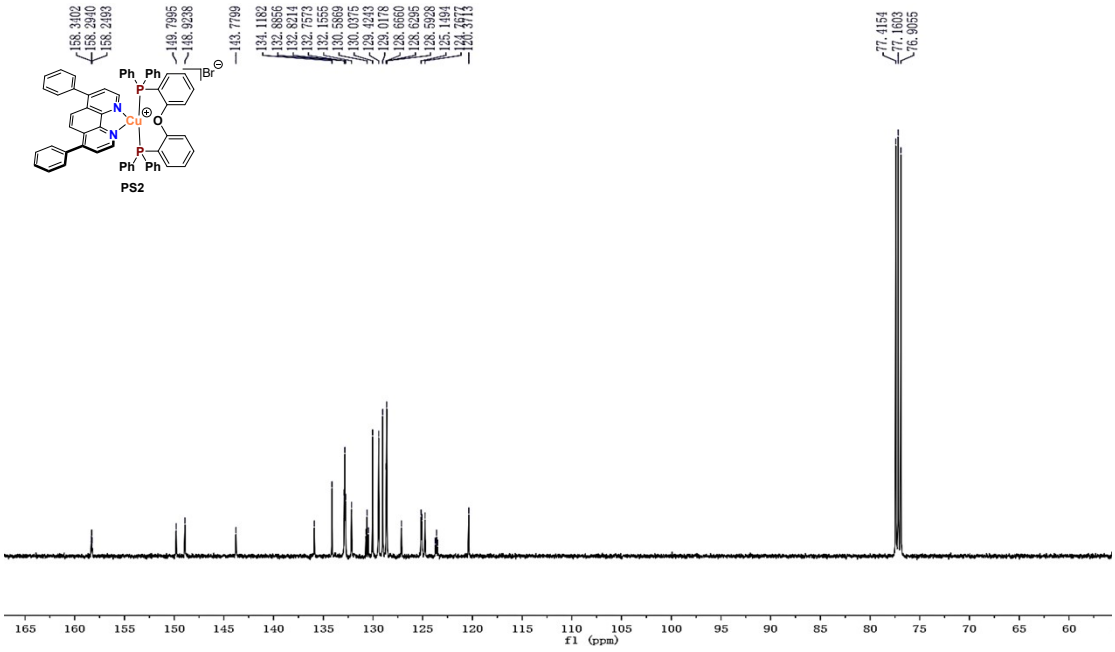
HRMS of **PS1**


781.1589
1.38e8
783.1589
784.1611
604.0928
1155.2473
100
%
0
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
1450
m/z
PS1

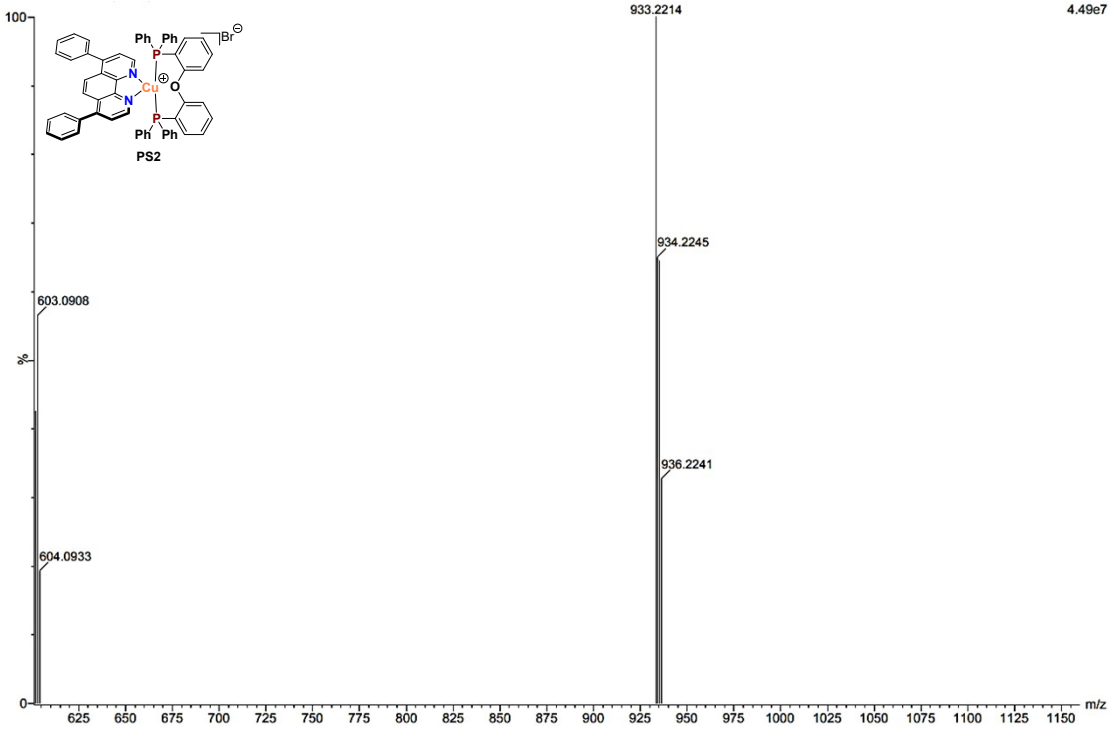
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of copper catalyst **PS2**



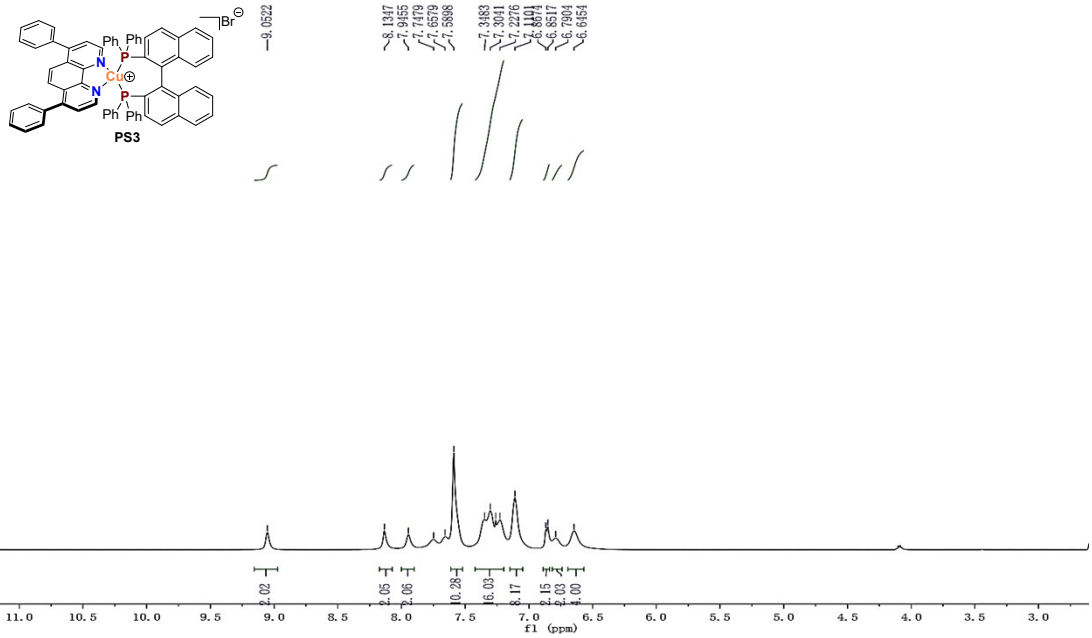
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of copper catalyst **PS2**



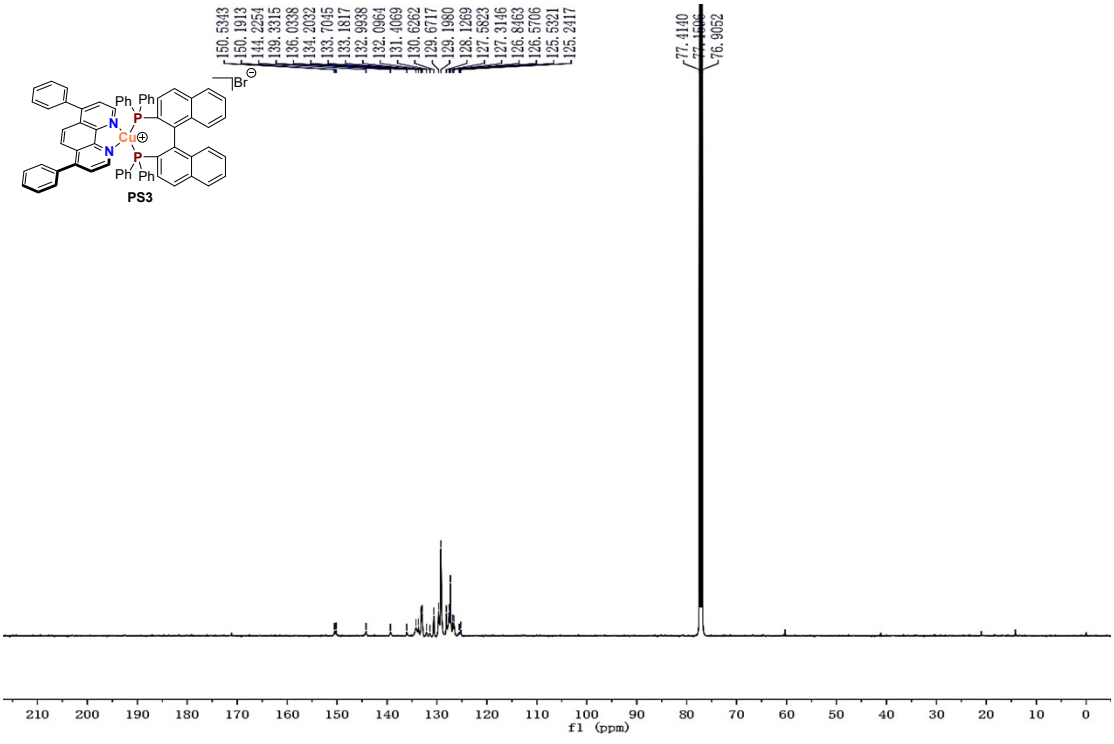
HRMS of **PS2**


100
%
0
933.2214
4.49e7
934.2245
936.2241
603.0908
604.0933
625 650 675 700 725 750 775 800 825 850 875 900 925 950 975 1000 1025 1050 1075 1100 1125 1150
m/z
Ph Ph
P
N
Cu
O
N
P
Ph Ph
Br
PS2

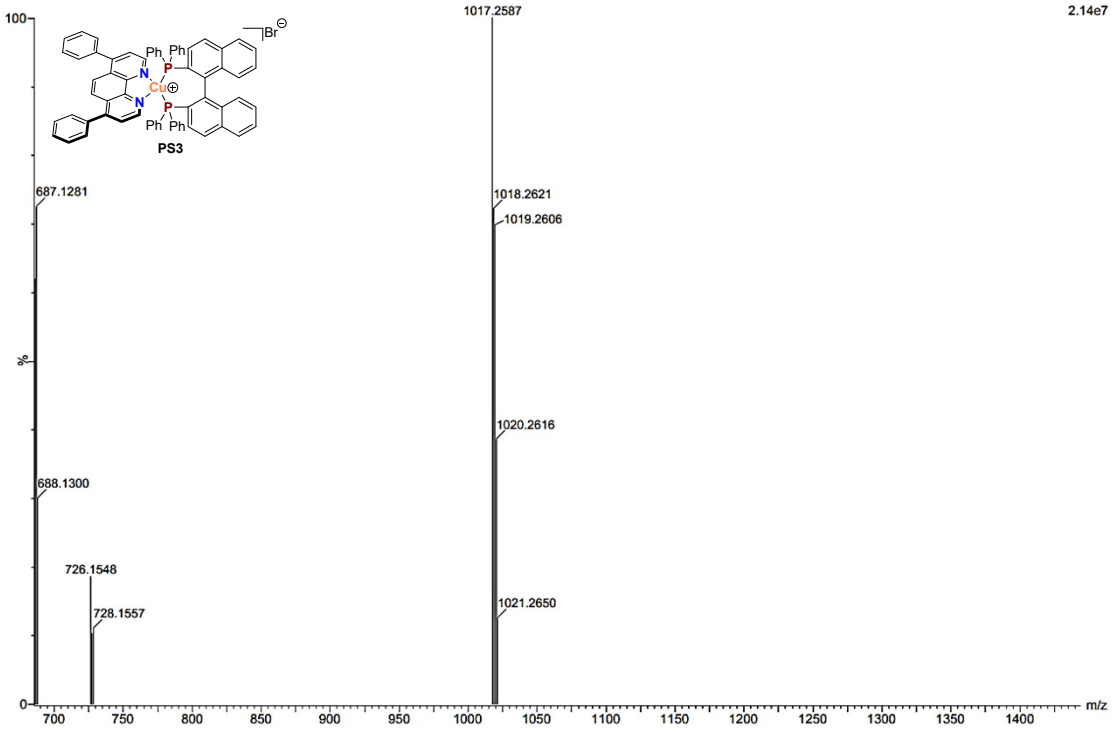
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of copper catalyst **PS3**



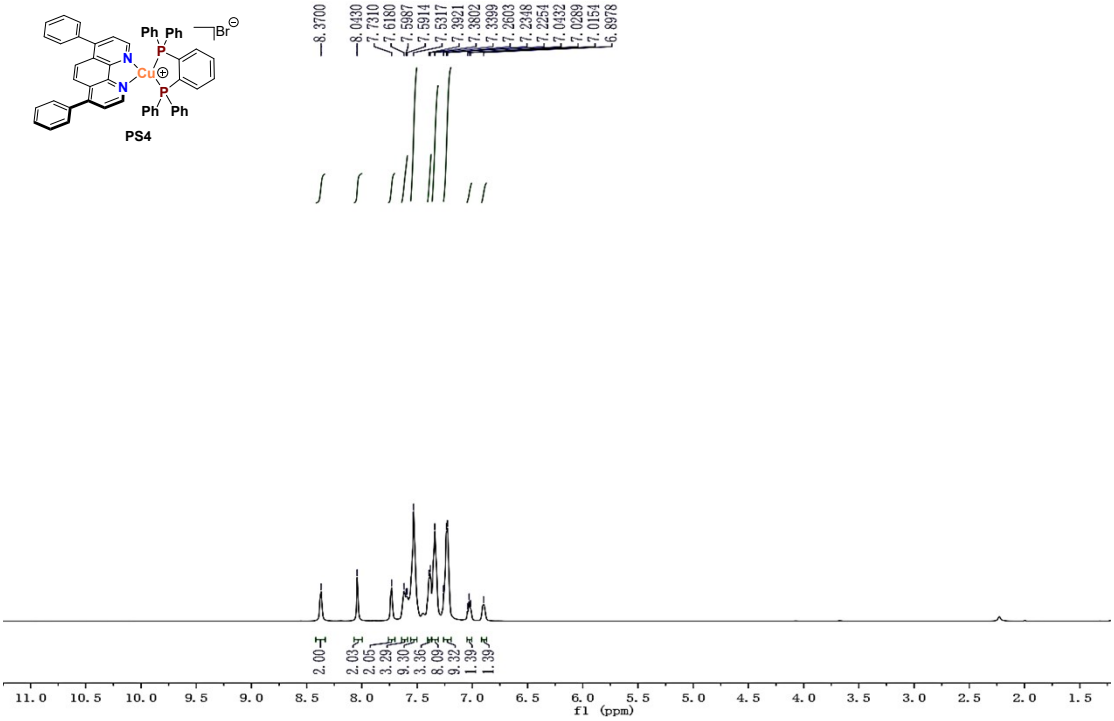
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **PS3**



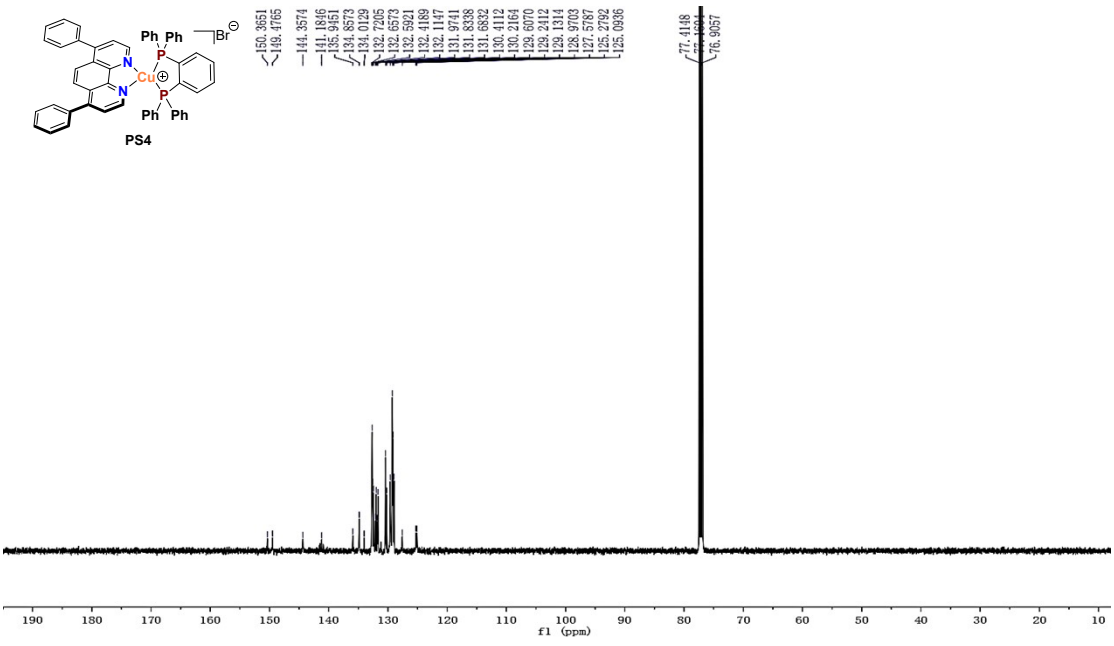
HRMS of **PS3**


100
%
0
1017.2587
2.14e7
687.1281
1018.2621
1019.2606
1020.2616
688.1300
726.1548
728.1557
1021.2650
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
m/z
PS3

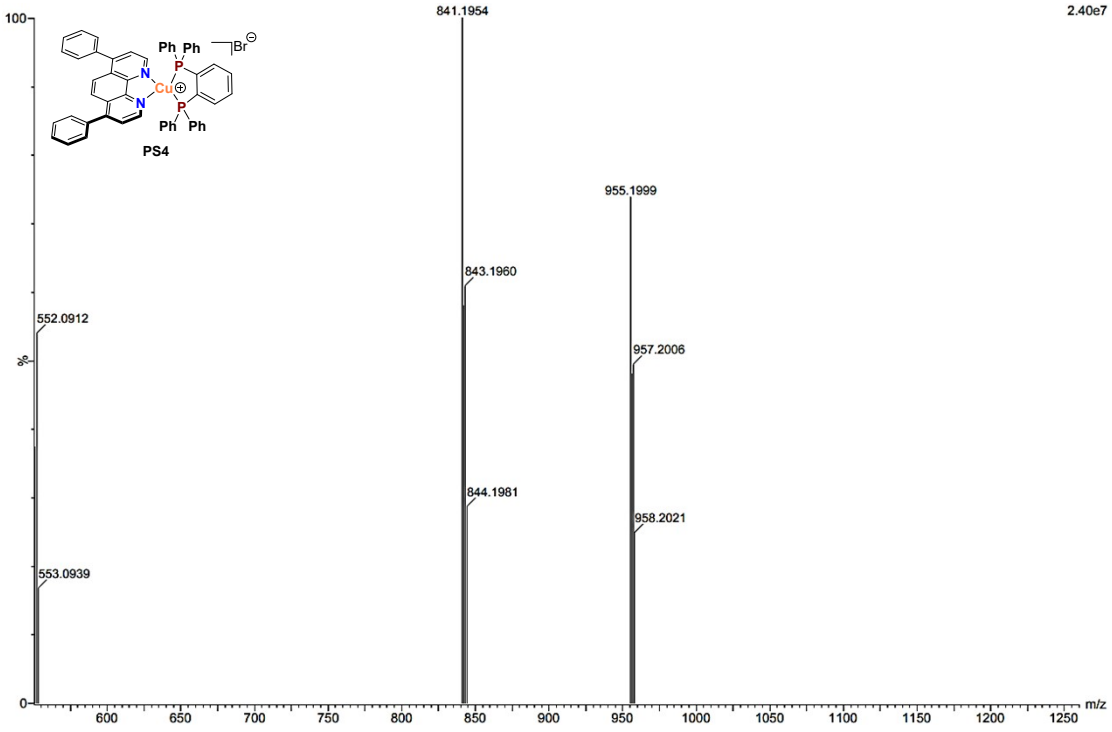
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of copper catalyst **PS4**



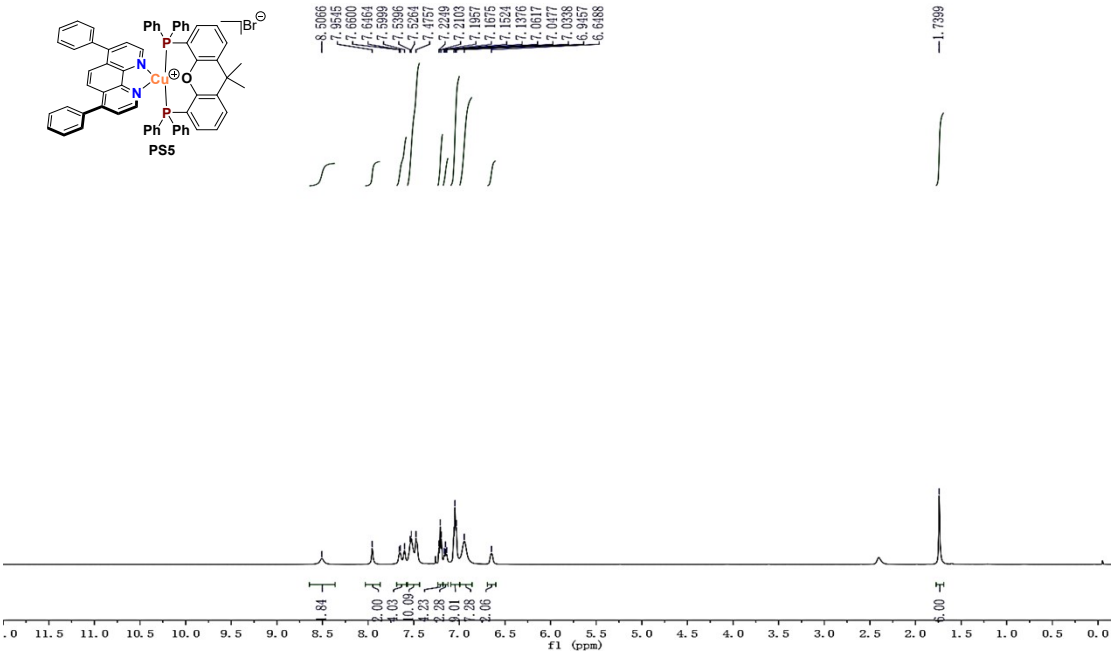
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of copper catalyst **PS4**



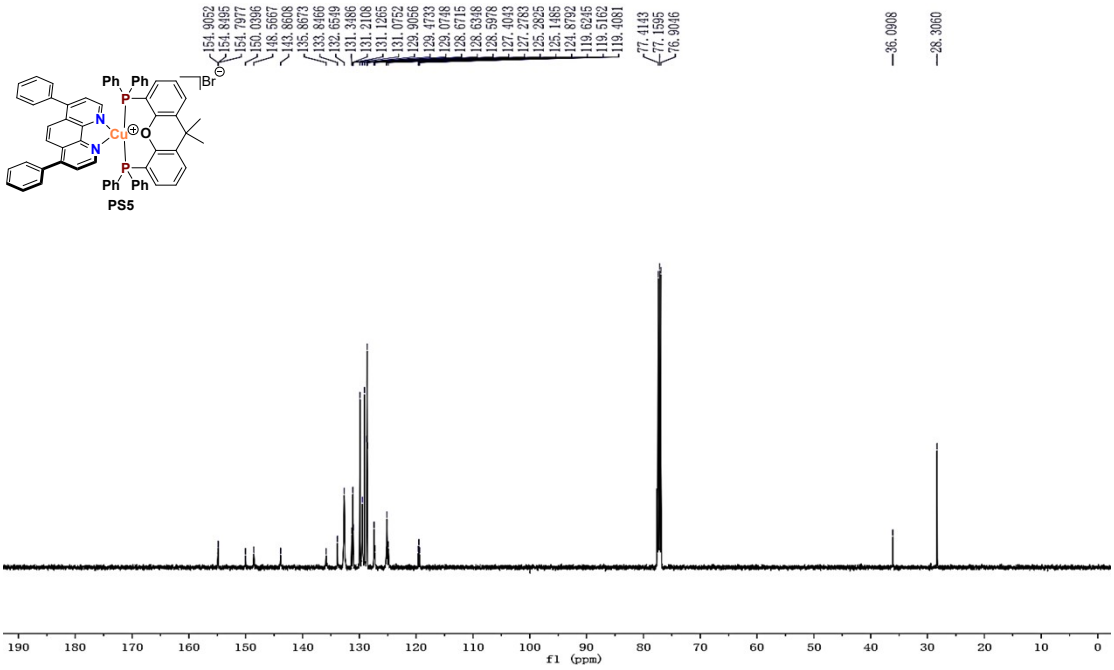
HRMS of **PS4**


841.1954
2.40e7
100
Ph Ph
P
N
Cu
N
P
Ph Ph
Br
PS4
955.1999
843.1960
552.0912
%
957.2006
844.1981
958.2021
553.0939
0
600
650
700
750
800
850
900
950
1000
1050
1100
1150
1200
1250
m/z

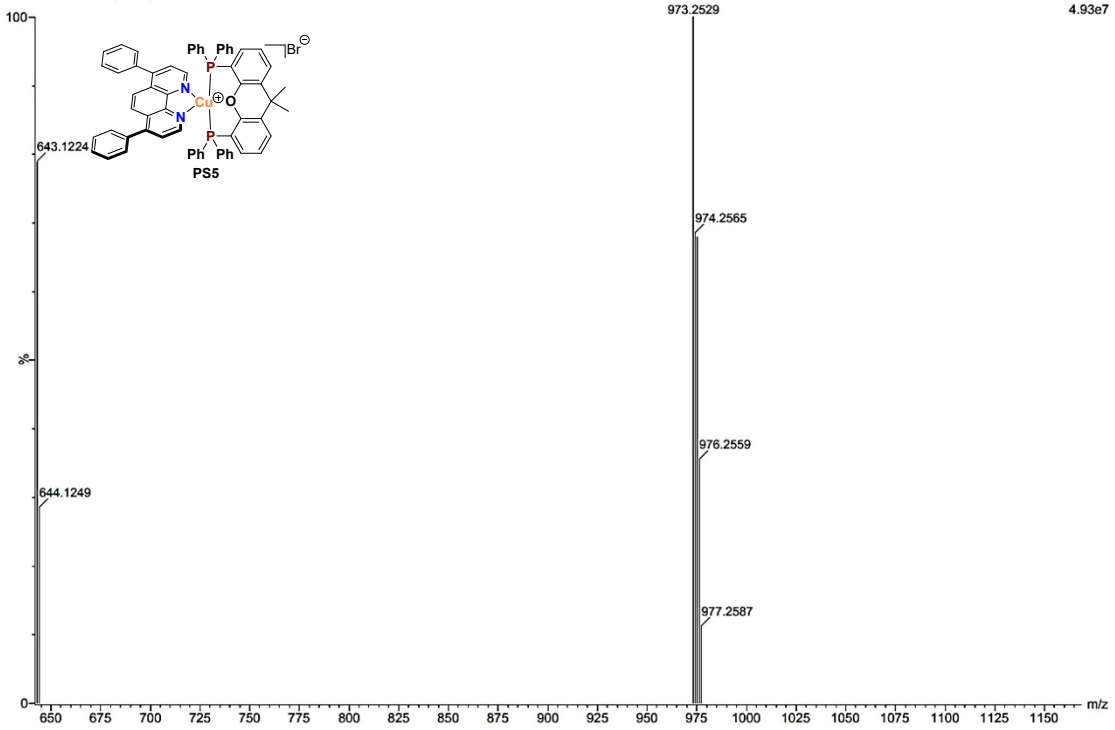
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of copper catalyst **PS5**



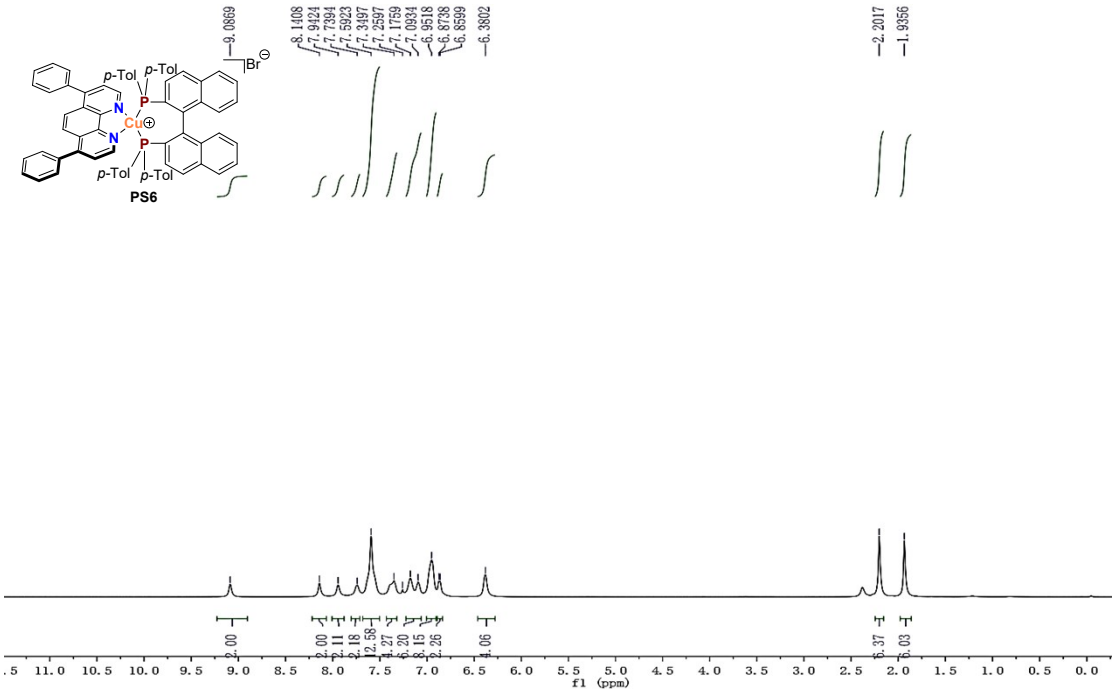
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of copper catalyst **PS5**



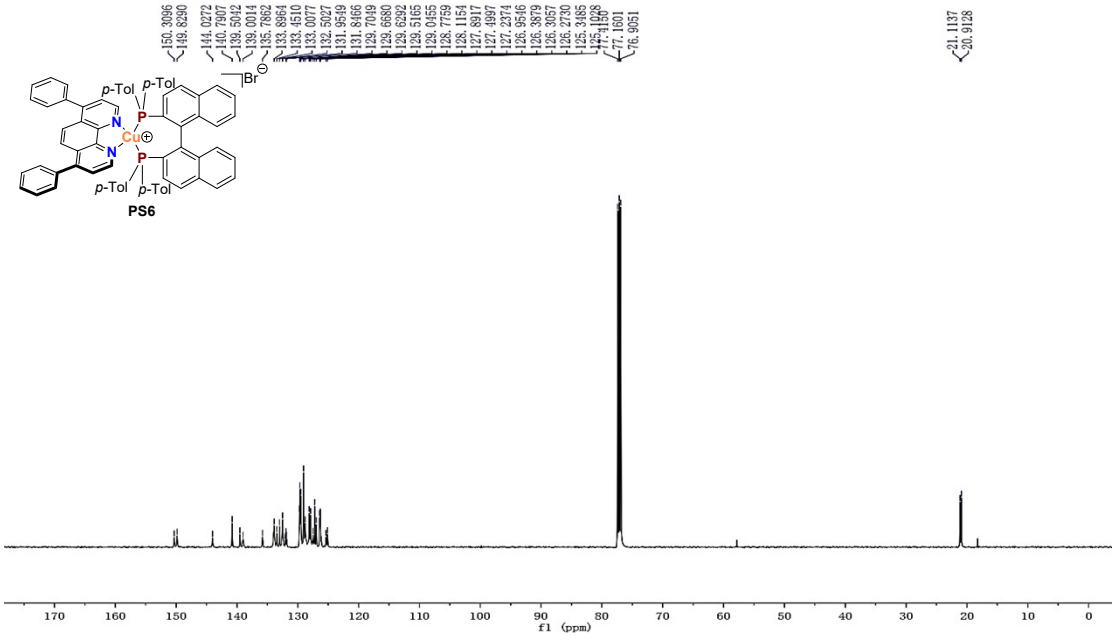
HRMS of **PS5**


973.2529
4.93e7
643.1224
644.1249
974.2565
976.2559
977.2587
PS5
%
m/z

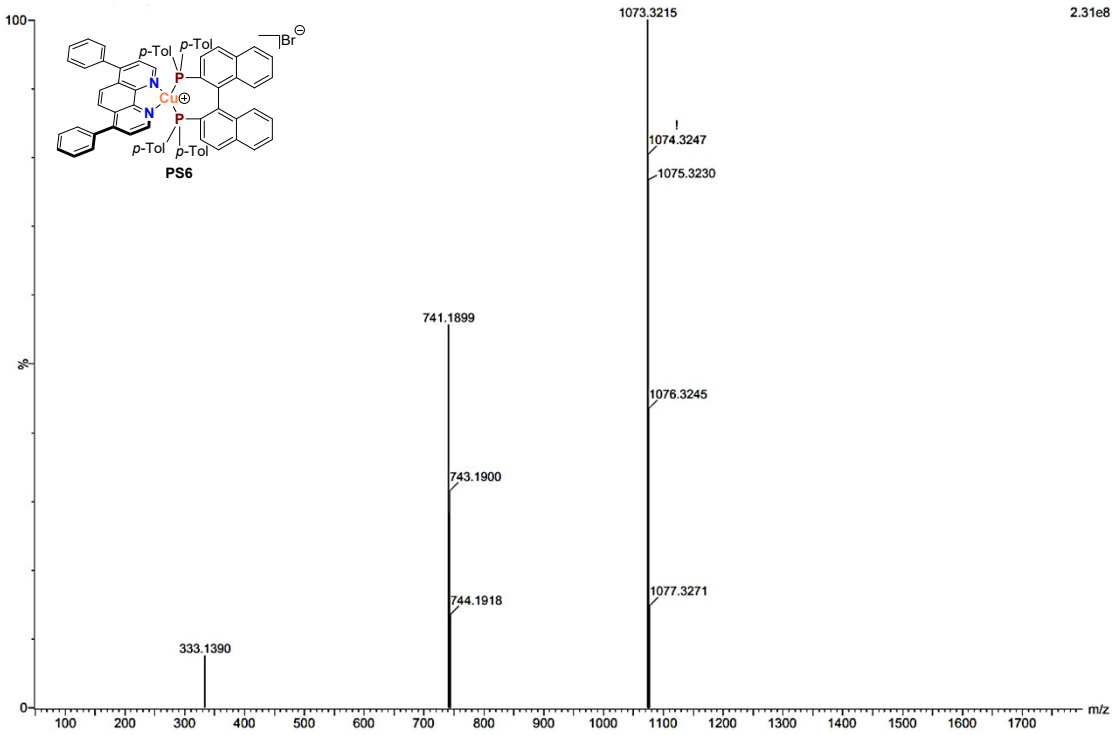
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of copper catalyst **PS6**



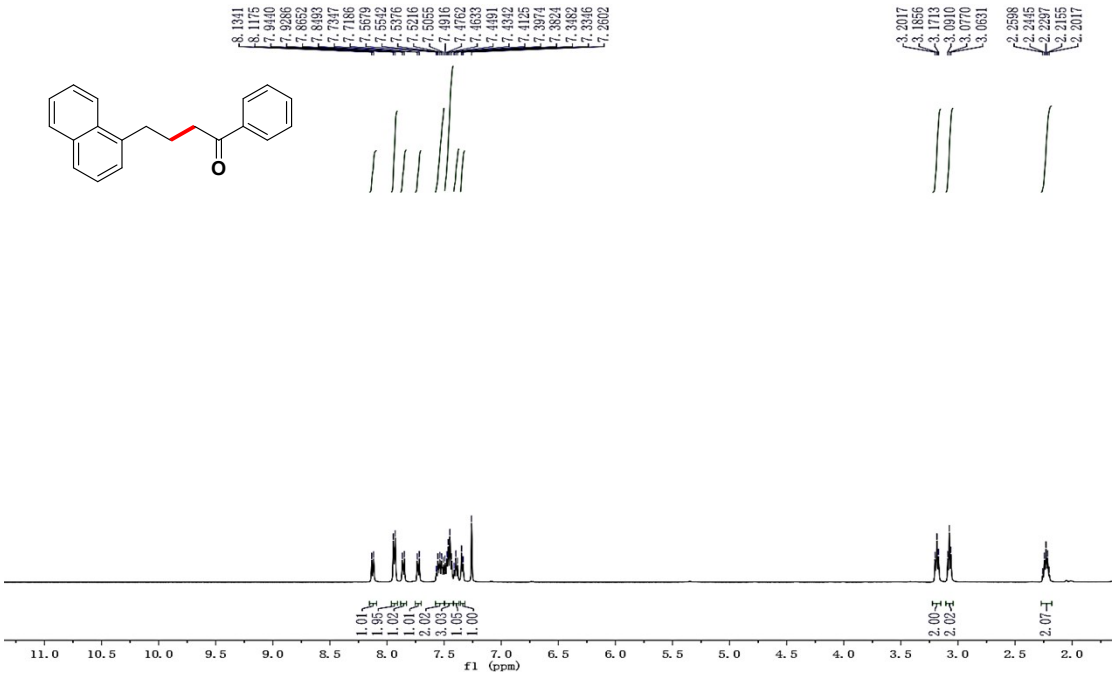
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of copper catalyst **PS6**



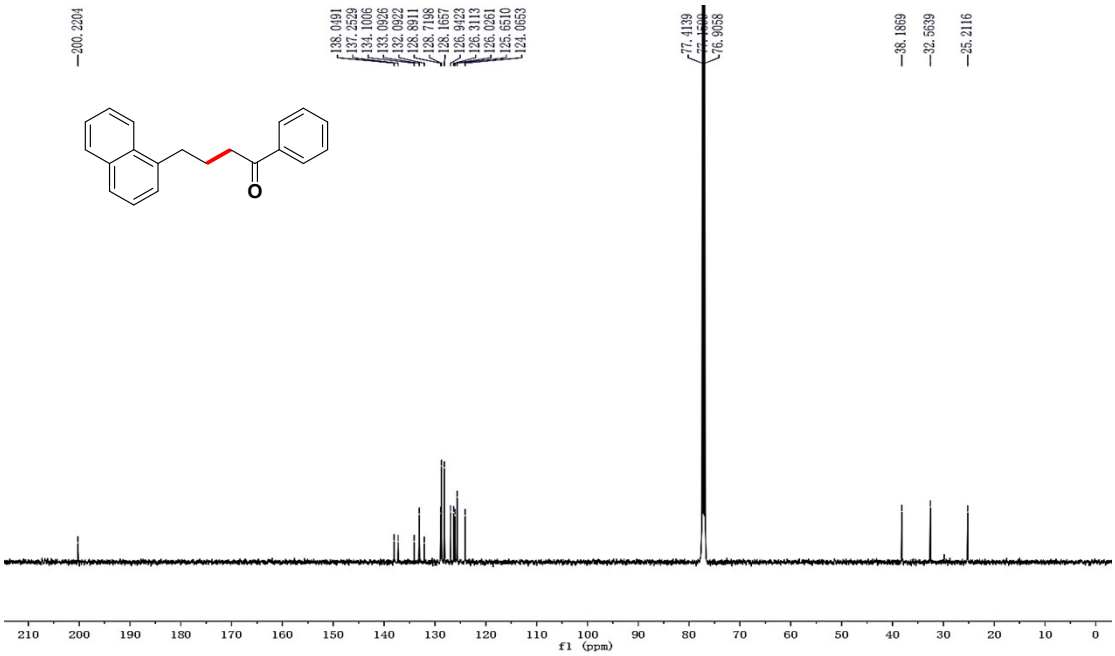
HRMS of **PS6**


PS6
1073.3215
2.31e8
1074.3247
1075.3230
741.1899
1076.3245
743.1900
744.1918
1077.3271
333.1390
%
m/z

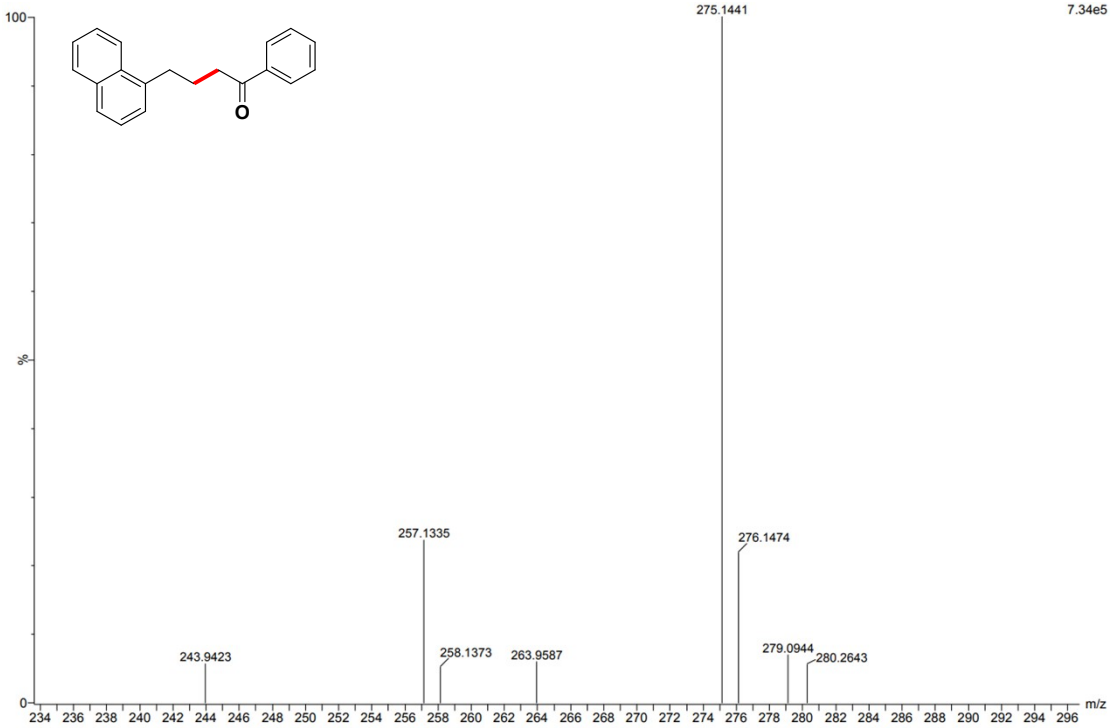
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **11**



^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **11**



HRMS of compound **11**



HRMS of intermediate **9** in reaction mechanism

HRMS calcd for $C_{11}H_{28}NSi^+$ $[M]^+$: 202.1986; found: 202.1990