Supporting Information

Photochemical Radical Decarboxylative Disulfuration of *α*-Keto Acids and Oxamic Acids

Huangbin Sun,[a] XueTing Bin,[a] Qianfang Zhang, [a] Xiaowen Chen, [b*] Jie Tang[a*], Guofang Jiang[a*]

[a]*State Key Laboratory of Chemo/Biosensing and Chemometrics, Advanced Catalytic Engineering Research Center of the Ministry of Education, Hunan University, Changsha 410082, P. R. China.*

[b]*School of Material and Environmental Engineering, Shenzhen Polytechnic University, Shenzhen 518055, PR China.*

Table and Contents

1. General 1

2. Preparation of starting materials 1

3. General Procedure for benzo-dithioperoxoates 4

4. Screening of reaction conditions 5

4.1 Optimization of photocatalysts (Table S1) 5

4.2 Optimization of solvents (Table S2) 6

4.3 Optimization of bases (Table S3) 7

4.4 Optimization of equivalent and time (Table S4) 7

5. Mechanistic studies 8

5.1 Radical trapping experiment 8

5.2 Reaction with potassium salt of the α-oxocarboxylic acids: 8

5.3 Light on/off experiments 9

5.4 Luminescence quenching experiments 10

5.5 Electron paramagnetic resonance experiment 11

5.6 Radical clock experiment 12

6. Author Contributions 13

7. Representative significant acyl disulfides 13

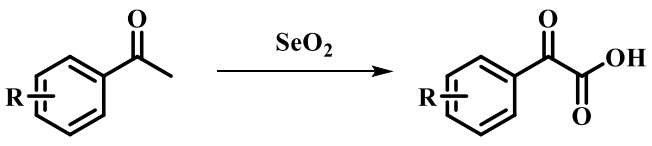
8. Spectral data of benzo-dithioperoxoates 13

9. Spectra.....37
10. Reference 88

1. General

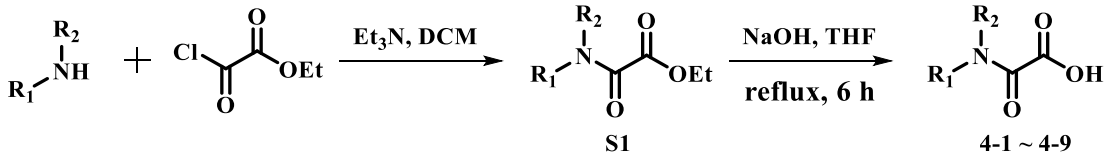
Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods (*Purification of Laboratory Chemicals*, 4th Edition, Butterworth Heinemann, W. L. F. Armarego and Douglas Dalzell Perrin). For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. Analytical thin layer chromatography (TLC) was performed using silica gel plates. ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR), ^{13}C Nuclear Magnetic Resonance (^{13}C-NMR) spectra and ^{19}F-Nuclear Magnetic Resonance (^{19}F-NMR) were recorded on Bruker 400 MHz and JEOLJNM-ECZ400S/L1 400MHz at 25 °C with $CDCl_3$ as solvent. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.06 ppm (^{13}C NMR). The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet, br = broad), coupling constant *J*(Hz), and integration. High resolution mass spectra were recorded on Thermo Oribtrap Exploris 120 and Thermo Finnigan MAT95XP. IR spectra were recorded on SHIMADZU IRSpirit-T and reported in unit of cm^{-1}. GCMS data were recorded on SHIMADZU GCMS-QP2020NX respectively. Electron paramagnetic resonance experiment was recorded on JEOL JES-FA 200. Fluorescence quenching experiment was recorded on Photon Technology International (PTl) QM40 fluorescence spectrophotometer (HORIBA).

2. Preparation of starting materials



1

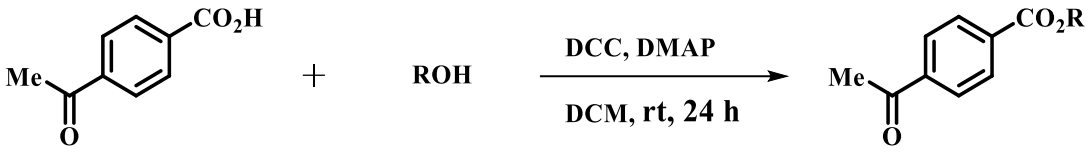
Method A: Substrate 1 were prepared according to previously reported literature procedures[1]. To a round-bottom flask equipped with a stirring bar was added the aryl methyl ketone (10.0 mmol) and selenium dioxide (SeO_2, 1.67 g, 15.0 mmol), then anhydrous pyridine (40 mL) was added quickly. The reaction was stirred and heated in an oil bath under an N_2 atmosphere to 110 ºC for 1 h, and then the bath temperature was lowered and kept at 90 ℃ for another 4 h. The reaction mixture was filtered using a Büchner funnel, and the aqueous layer was washed with EA (3 × 20.0 mL). The combined filtrate was treated with HCl (1 M) to about pH 1.5, and extracted with EA (3 × 30.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The desired products were isolated by flash chromatography on silica gel using (petroleum ether/ethyl acetate = 20: 1) to give α-keto acids 1.



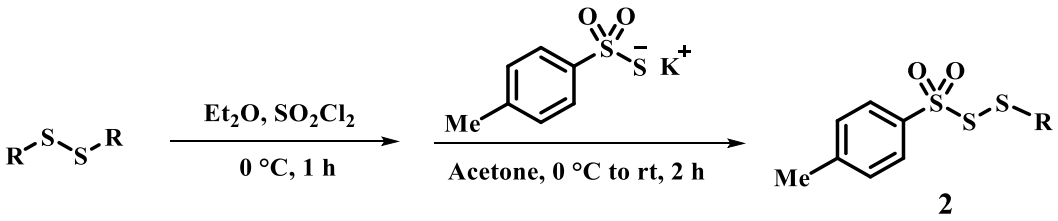
Method B: Substrate 4-1~4-9 were prepared according to previously reported literature procedures[2]. To a stirred solution of amine in dichloromethane was added triethylamine and the mixture was cooled to 0 ºC. This was followed by dropwise addition of ethyl oxalyl monochloride and the resulting reaction mixture was stirred at room temperature for 24 h. the mixture was quenched with water and extracted with dichloromethane. The combined organic layer was washed with 2N HCl solution, water and finally with brine solution. The organic layer was dried over Na_2SO_4, filtered and filtrate was concentrated under reduced pressure to afford acetylated derivatives which were used in the next step without further purification.

To a magnetically stirred solution of the above product (10 mmol) in 5 ml of THF and 5 mL of water was added 0.4 g of NaOH (10 mmol). After it was stirred for 2 h at room temperature, the mixture was acidified by adding 20 mL of 1 M HCl, and then extracted with ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and evaporated

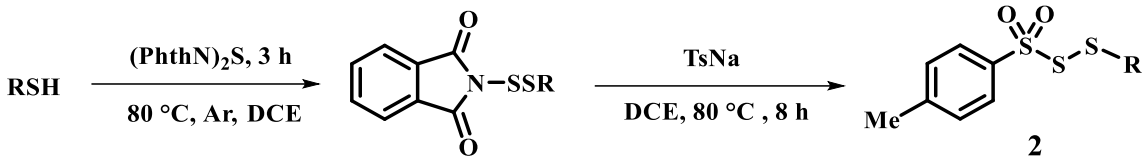
to give desired products.



Method C: Substrate 1-30 and 1-31 were prepared according to previously reported literature procedures[3]. DCC (1.2 equiv.) and DMAP (0.15 equiv.) was added to the solution of 4-acetylbenzoic acid (1.0 equiv.) in DCM (0.5 M). The reaction mixture was stirred at room temperature for 30 min, then alcohol (1.2 equiv.) was added to the reaction vessel and the resulting mixture was stirred for 12 hours. The crude mixture was filtered through a plug of celite. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to obtain desired ketone products.



Method D: Substrate 2-1~2-6 were prepared according to previously reported literature procedures[4]. In a 100 mL round-bottomed flask, disulfide (5 mmol) was first dissolved in Et_2O (20 mL). Sulfuryl chloride (5 mmol) was added to the disulfide solution dropwise at 0 °C. The reaction mixture was warmed to rt gradually and stirred for 1h. The reaction was cooled to 0 °C again and a solution of $PhSO_2SSK$ (10 mmol) in acetone (20 mL) was added dropwise. The reaction was then warmed to rt and stirred for 2 h. The mixture was diluted with water and extracted with Et_2O (30 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. The crude residue was purified by column chromatography to afford the desired disulfide products 2-1 to 2-6.



Method E: Substrate 2-7 were prepared according to previously reported literature procedures[4]. A flame-dried 25 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was sealed with a septum, degassed by alternating vacuum evacuation and argon backfilling (three times) before 2,2'-thiobis(isoindoline-1,3-dione) (1.5 equiv.) in DCE (0.3 M) was added, then thiol (1.0 equiv.) was added to the result solution in one portion. The reaction mixture was stirred at 80 ºC for 3 h. After the reaction was complete, the mixture was cooled down to room temperature and the precipitate was removed by filtration, the filtrate was concentrated with the aid of a rotary evaporator and the crude residue was directly used in the next step without further purification. A flame-dried round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was charged with crude residue obtained in previous step and TsNa (1.5 equiv) before DCE (0.1 M) was added. The reaction mixture was stirred at 80 ºC for 8 h. After the reaction was complete, the reaction mixture was cooled to room temperature and filtered through a plug of celite. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel to obtain the desired product.

3. General Procedure for benzo-dithioperoxoates

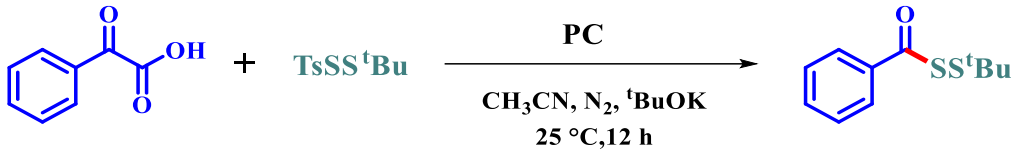
General Procedure 1 (GP1): To an oven-dried borosilicate test tube equipped with a magnetic stir bar were added Acid derivative (0.1 mmol, 1.0 equiv.), dithiosulfonate reagent (0.15 mmol, 1.5 equiv), 2 mol % photocatalyst $[Ir(dFCF_3ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 0.002 mmol) and ^{t}BuOK (22 mg, 0.2 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 2.0 mL of DCE solvent was added through the septum by a syringe and placed approximately 5 cm from the light setup. After 12 h of the reaction, 10 mL of water was

added and extracted with DCM (3 × 5 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 200−300) using hexane and EtOAc as an eluent to afford the corresponding target products.

General Procedure 2 (GP2): To an oven-dried borosilicate test tube equipped with a magnetic stir bar were added oxamic Acid (0.2 mmol, 2 equiv.), dithiosulfonate reagent (0.1 mmol, 1 equiv), 2 mol % photocatalyst Mes-Acr-PF_4 (1.3 mg, 0.002 mmol) and ^{t}BuOK (22 mg, 0.2 mmol). The reaction tube was vacuumed and backfilled with argon (3 times), and a septum was placed over the reaction tube. Next, 2 mL of DCE solvent was added through the septum by a syringe and placed approximately 5 cm from the light setup. After 12 h of the reaction, 10 mL of water was added and extracted with DCM (3 × 5 mL). The combined organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 200−300) using hexane and EtOAc as an eluent to afford the corresponding target products.

4. Screening of reaction conditions

4.1 Optimization of photocatalysts (Table S1)



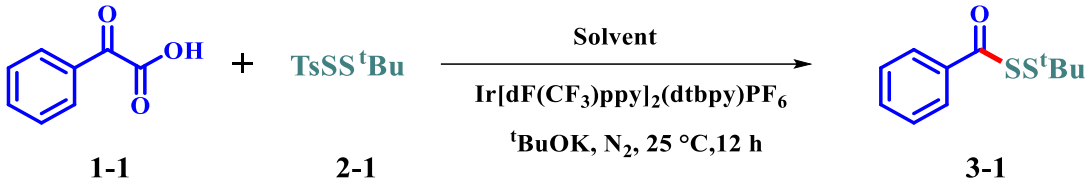
1-1 **2-1** **3-1**

Entry	Photocatalyst	Yield/%[a,b]
1	*fac*-Ir(ppy)$_3$	0
2	[Ru(bpy)$_3$]Cl$_2$ • H$_2$O	0
3	[Ru(bby)$_3$](PF$_6$)$_2$	< 5
4	Ir[(dtbbpy)(ppy)$_2$]PF$_6$	30

5	Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6	44
6	9,10-phenanthroquinone	0
7	4CzIPN	0
8	5CzBN	0
9	No photocatalyst	0
10[c]	Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6	complex
11[d]	Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6	trace

[a]Reaction conditions: 0.1 mmol 1-1, 0.15 mmol 2-1, 2 mol% PC, 0.2 mmol ^{t}BuOK and 2 mL CH_3CN under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. [b]isolated yield. [c]24 W white LEDs. [d]24 W purple LEDs.

4.2 Optimization of solvents (Table S2)

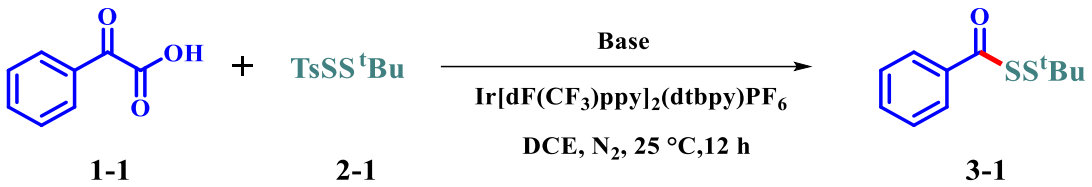


1-1 **2-1** **3-1**

Entry	Solvent	Yield/%[a,b]
1	DCM	68
2	DCE	75
3	CCl_4	complex
4	EA	< 5
5	DMSO	0
6	THF	0
7	2Me-THF	0
8	Acetone	0

[a]Reaction conditions: 0.1 mmol 1-1, 0.15 mmol 2-1, 2 mol% PC, 0.2 mmol ^{t}BuOK and 2 mL solvent under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h, [b]isolated yield.

4.3 Optimization of bases (Table S3)

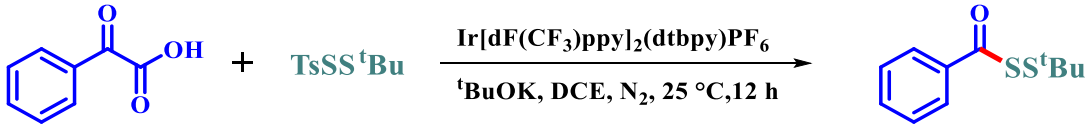


1-1 **2-1** **3-1**

Entry	Base	Yield/%[a,b]
1[c]	^{t}BuOK	53
2[d]	^{t}BuOK	58
3	^{t}BuONa	71
4	MeONa	44
5	KOH	62
6	CsF	15
7	$CsCO_3$	< 5
8	No base	0

[a]Reaction conditions: 0.1 mmol 1-1, 0.15 mmol 2-1, 2 mol% PC, 0.2 mmol base and 2 mL DCE under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h, [b]isolated yield, [c]1.0 mmol, [d]3.0 mmol.

4.4 Optimization of equivalent and time (Table S4)



1-1 **2-1(x mmol)** **3-1**

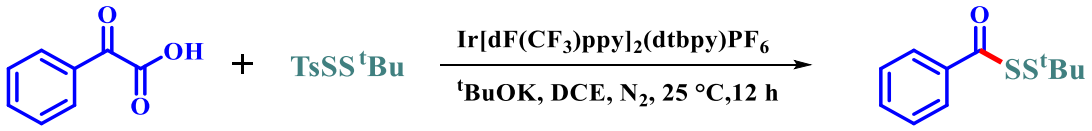
Entry	X/ eq	Yield/%[a,b]
1	1.0	72
2	1.2	75
3	1.5	88
4	1.8	83

5[c]	1.5	35
6[d]	1.5	65
7[e]	1.5	82

[a]Reaction conditions: 0.1 mmol 1-1, x eq 2-1, 2 mol% PC, 0.2 mmol base and 2 mL DCE under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h, [b]isolated yield, [c]Air, [d]6 h, [e]24h.

5. Mechanistic studies

5.1 Radical trapping experiment



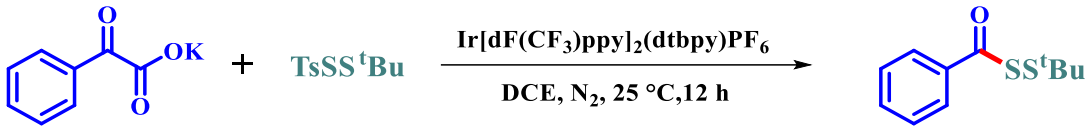
1-1 **2-1** **3-1**

Entry	Radical scavenger (5 eq)	Yield/%
1	TEMPO	0
2	BHT	0
3	1,1-diphenylethylene	< 5%

Reaction conditions: 0.1 mmol 1-1, 0.15 mmol 2-1, 2 mol% PC, 0.2 mmol ^{t}BuOK and 2 mL DCE under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h.

The above results suggest that our reaction proceeds through a radical mechanism and the TEMPO was found to be trapped as *O*-bezoylated-TEMPO. ^{1}H NMR (400 MHz, $CDCl_3$, 300K) δ: 8.12 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 1.87 – 1.69 (m, 3H), 1.66 – 1.59 (m, 2H), 1.54 – 1.49 (m, 1H), 1.31 (s, 6H), 1.16 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 165.7, 132.2, 129.1, 128.9, 127.8, 59.7, 38.4, 31.3, 20.2, 16.4. The spectral data are in accordance with literature.[5]

5.2 Reaction with potassium salt of the α-oxocarboxylic acids:

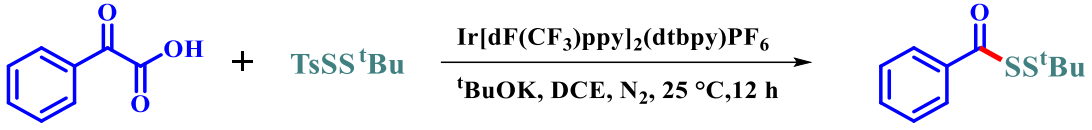


1-1' **2-1** **3-1, 75%**

To an oven-dried 10 mL reaction tube equipped with a magnetic stirring bar, 0.2 mmol of 1-1' (1 equiv.), 0.3 mmol of 2-1 (1.5 equiv.), 0.004 mmol of [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ (2 mol%), was added. The reaction tube was vacuumed and backfilled with nitrogen (3 times) and sealed with a septum. Then, 2 mL of DCE was added using a syringe and under irradiation of 24 W blue LEDs at 25 °C for 12 h. After reaction was complete, 5 mL of brine solution was added and extracted with DCM (3 x 10 mL). The combined organic layer was dried over Na_2SO_4 and solvent was evaporated under reduced pressure and purified by using column chromatography (200-300 # silica, EtOAc – Hexane = 1:50) to give the desired product in yield 75%.

The above results suggest that formation PhCOCO$_2$K from α-oxocarboxylic acid and potassium *tert*-butoxide will be one of the steps in the reaction.

5.3 Light on/off experiments



1-1 **2-1** **3-1**

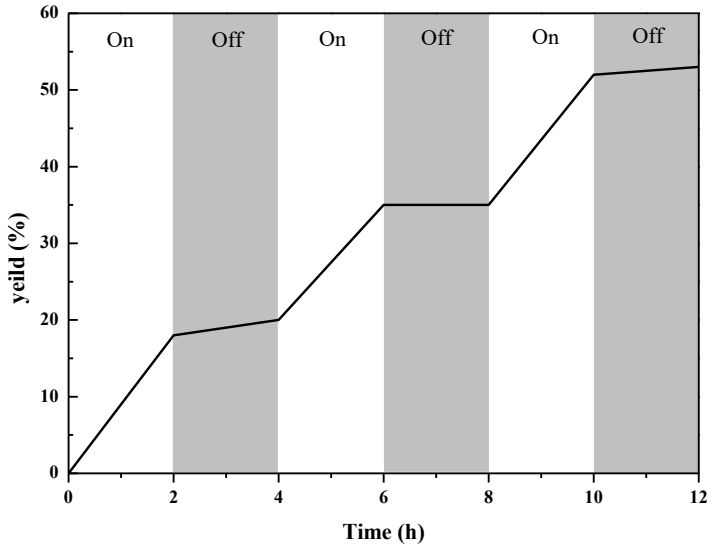


Figure S1. Light On/Off experiment

Reaction conditions: 0.1 mmol 1-1, 0.15 mmol 2-1, 2 mol% PC, 0.2 mmol ^{t}BuOK，0.1 mmol 1,4-dinnitrobenzene and 2 mL DCE under irradiation of 24 W blue LEDs with N_2 protection at 25 °C.

The light on/off experiment was performed by altering light-dark conditions (light : dark; 2 : 2 h) for up to 12 h. At the end of each light/dark session, the yield was calculated by column chromatography. The results in figure show the essential role of light, as the reaction progressed in the presence of light and stopped in the dark. **From the experiment, we conclude that continuous light supply needed for reaction and conforms that reaction does not proceed through a chain propagation mechanism.**

5.4 Luminescence quenching experiments

Luminescence quenching studies of [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ with substrate PhCOCO$_2$K (1-1'), TsSS^{t}Bu (2-1) and TsNa: To perform luminescence quenching studies of 3 μM of [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$, 4 M of 1-1', 4 M of 2-1 and 4 M of TsNa solution in acetonitrile /water (1:1) was prepared as a stock solution and all other solutions with different concentration were prepared by dilution.

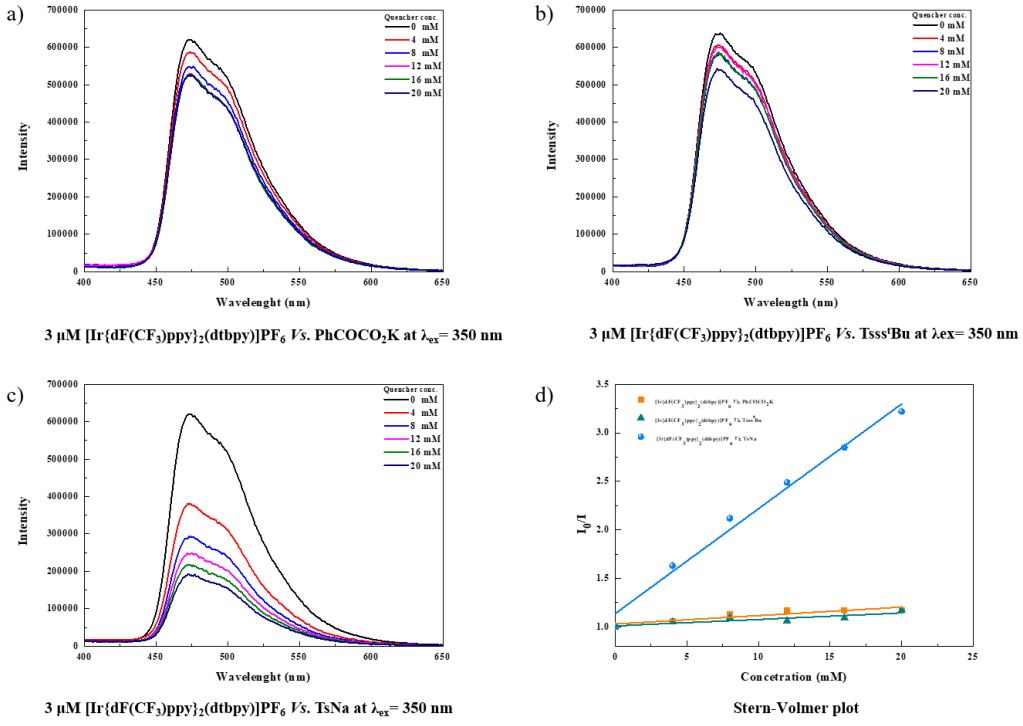


Figure S2. Luminescence quenching spectra of [Ir(dFCF$_3$ppy)$_2$(dtbpy)]PF$_6$ at λex 350 nm.

In acetonitrile/water (1:1) solution: a) 3 μM [Ir(dFCF$_3$ppy)$_2$(dtbpy)]PF$_6$ *Vs*. 1-1' at 350 nm; b) 3 μM [Ir(dFCF$_3$ppy)$_2$(dtbpy)]PF$_6$ *Vs*. 2-1 at 350 nm; c) 3 μM [Ir(dFCF$_3$ppy)$_2$(dtbpy)]PF$_6$ *Vs*. TsNa at 350 nm; d) Stern-Volmer plot of luminescence quenching of 3 μM [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ *Vs*. 1-1', 2-1 and TsNa. In the case of [Ir(dFCF$_3$ppy)$_2$(dtbbpy)]PF$_6$ as photocatalyst, as expected, no quenching was observed with respect to potassium salt of the α-oxocarboxylic acid 1-1' and dithiosulfonate reagent 2-1 shown in Figure a and b. However, quenching of the [Ir(dFCF$_3$ppy)$_2$(dtbpy)]PF$_6$ photocatalyst was observed with respect to TsNa, as shown in Figure c, as well as in Stern-Volmer plot Figure d, **By these, we can conclude that TsNa will be the main quencher in the reaction, and It follows a single electron transfer (SET) pathway mechanism.**

5.5 Electron paramagnetic resonance experiment

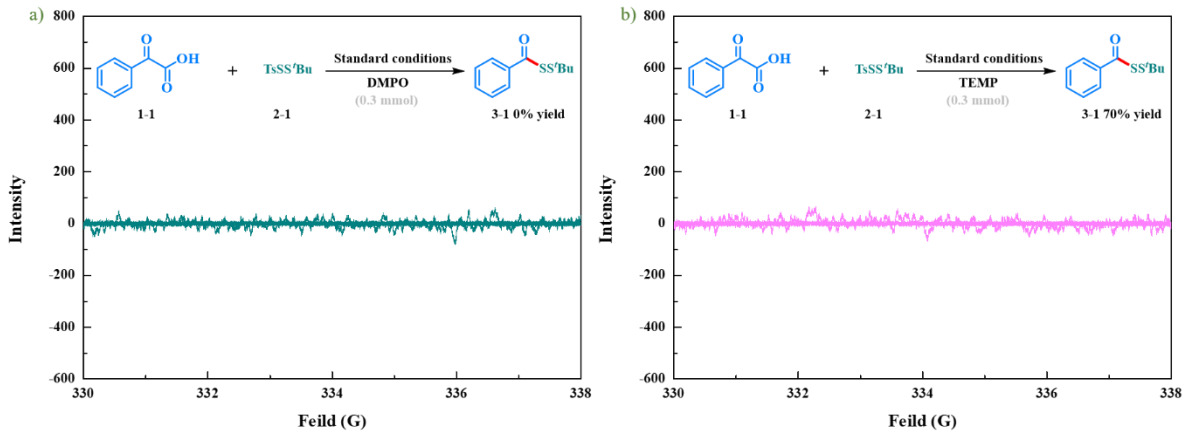


Figure S3. EPR spectra in the presence of capture.

Reaction condition: A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged with DMPO or TEMP (0.30 mmol), 1-1(0.10 mmol) 2-1 (0.15 mmol), PC (2 mol%) and ^{t}BuOK (0.4 mmol) in 2.0 mL of DCE under irradiation of 25 W blue LEDs with N_2 protection at 25 °C for 3 h.

The figure's results show that the DMPO or TEMP adduct was not detected. **Based on the experiment, it can be concluded that the presence of trace O_2 has negligible quenching effects on the excited photocatalyst.**

5.6 Radical clock experiment

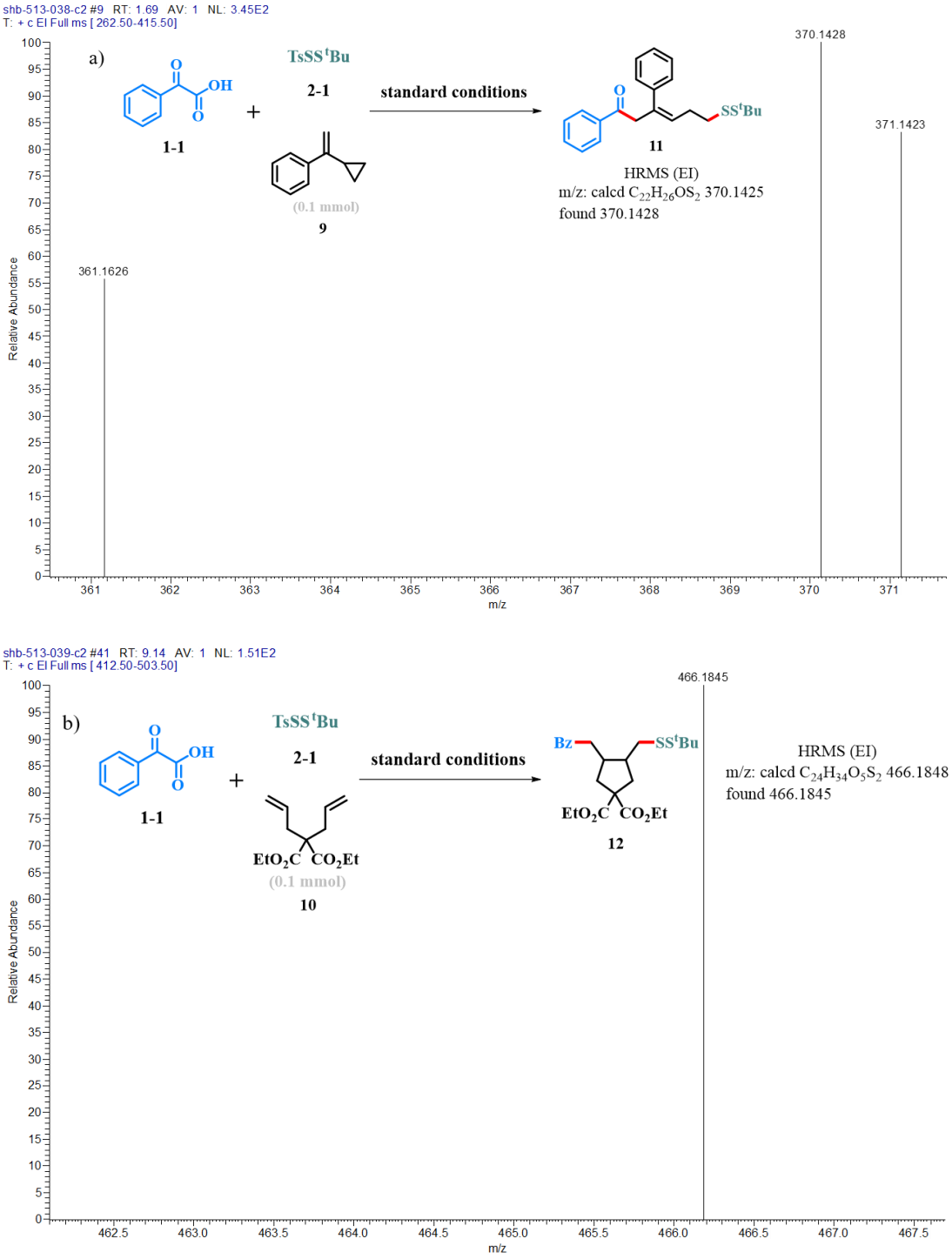


Figure S4. HRMS data of radical clock experiment.

The figure's results show that the compound 11 and 12 was detected. **For the experiment, we conclude that a radical pathway was involved.**

6. Author Contributions

H.S. discovered and developed the reaction. H.S., X. C., J.T., and G.J. conceived and designed the investigations. H.S., Z. Q. and X.B. performed the experiments. H.S., Z. Q., and G.J. wrote the manuscript.

7. Representative significant acyl disulfides

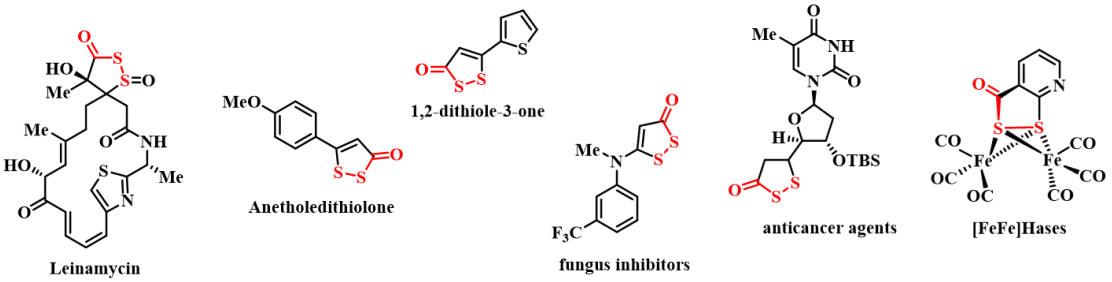
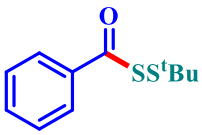
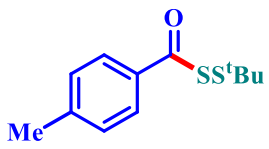


Figure S5. Representative examples of mono acyl disulfide compounds.

8. Spectral data of benzo-dithioperoxoates

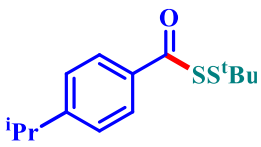


***SS*-(tert-butyl) benzo(dithioperoxoate) (3-1)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-1** as a yellow liquid (20 mg, 88%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.04 (d, *J* = 8.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.5, 136.0, 133.9, 128.9, 127.8, 49.1, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 3065, 2964, 1693, 1453, 1203, 881, 684 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{14}OS_2$ ($[M]^+$): 226.0486, mass found: 226.0484.

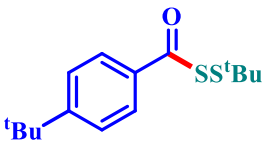


***SS*-(tert-butyl) 4-methylbenzo(dithioperoxoate) (3-2)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-(p-tolyl)acetic acid **1-2** (16 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-2** as a yellow liquid (18 mg, 75%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.96 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.9, 145.0, 133.3, 129.5, 127.9, 49.0, 29.8, 21.8. **FTIR (neat):** $\tilde{\nu}$ = 3036, 2964, 1699, 1455, 1206, 889, 623 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{16}OS_2$ ([M]$^+$): 240.0643, mass found: 240.0646.

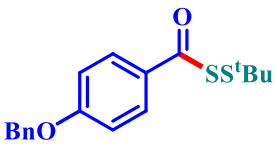
***SS*-(tert-butyl) 4-ethylbenzo(dithioperoxoate) (3-3)** was synthesized according to general procedure (**GP1**) with 2-(4-ethylphenyl)-2-oxoacetic acid **1-3** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-3** as a yellow liquid (20 mg, 79%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.96 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.35 (s, 9H), 1.26 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ:189.9, 151.1, 133.5, 128.4, 128.0, 49.0, 29.8, 29.1, 15.2. **FTIR (neat):** $\tilde{\nu}$ = 3036, 2968, 1700, 1455 1170, 896, 770 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{18}OS_2$ ([M]$^+$): 254.0799, mass found: 254.0795.



***SS*-(tert-butyl) 4-(tert-butyl)benzo(dithioperoxoate) (3-4)** was synthesized according to general procedure (**GP1**) with 2-(4-(tert-butyl)phenyl)-2-oxoacetic acid **1-4** (21 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-4** as a yellow liquid (21 mg, 75%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.98 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 1.35 (s, 9H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.8, 157.9, 133.2, 127.8, 125.8, 49.0, 35.3, 31.1, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3031, 2968, 1670, 1518, 1211, 884, 748 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{15}H_{22}OS_2$ ($[M]^+$): 282.1112, mass found: 282.1114.

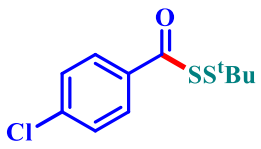


***SS*-(tert-butyl) 4-isopropylbenzo(dithioperoxoate) (3-5)** was synthesized according to general procedure (**GP1**) with 2-(4-isopropylphenyl)-2-oxoacetic acid **1-5** (19 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-5** as a yellow liquid (20 mg, 75%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.98 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.03 –2.92 (m, 1H), 1.35 (s, 9H), 1.27 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.9, 155.7, 133.7, 128.1, 127.0, 126.9, 49.0, 34.4, 29.8, 23.7. **FTIR (neat):** $\tilde{\nu}$ = 3077, 2964, 1700, 1513, 1206, 805, 731 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{14}H_{20}OS_2$ ($[M]^+$): 268.0956, mass found: 268.0960.



***SS*-(tert-butyl) 4-(benzyloxy)benzo(dithioperoxoate) (3-6)** was synthesized according to general procedure (**GP1**) with 2-(4-(benzyloxy)phenyl)-2-oxoacetic acid **1-6** (26 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 20/1) provided **3-6** as a yellow liquid (21 mg, 63%), **TLC R_f** = 0.3 (PE:EtOAc = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.03 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.30 (m, 5H), 7.03 (d, *J* = 8.9 Hz, 2H), 5.14 (s, 2H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 188.6, 163.4, 136.0, 130.1, 128.8, 128.8, 128.4, 127.5, 114.9, 70.3, 48.9, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3067, 3036, 2961, 2922, 1689, 1273, 1169, 884, 836, 738 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{18}H_{20}O_2S_2$ ($[M]^+$): 332.0905, mass found: 332.0902.

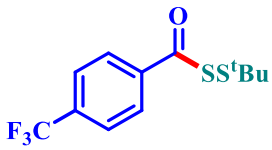
***SS*-(tert-butyl) 4-fluorobenzo(dithioperoxoate) (3-7)** was synthesized according to general procedure (**GP1**) with 2-(4-fluorophenyl)-2-oxoacetic acid **1-7** (17 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 20/1) provided **3-7** as a yellow liquid (15 mg, 61%), **TLC R_f** = 0.3 (PE:EtOAc = 50:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.07 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 1.35 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$, 300K) δ: -103.48 (s, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.0, 167.5 (d, *J* = 257.6 Hz), 165.0, 132.3 (d, *J* = 4.0 Hz), 132.3, 130.5, 130.4, 130.0 (q, *J* = 13.6 Hz), 116.2 (d, *J* = 22.2 Hz), 116.0, 49.2, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3067, 2964, 1684, 1507, 1201, 894, 619 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}FOS_2$ ($[M]^+$): 244.0392, mass found: 244.0391.



***SS*-(tert-butyl) 4-chlorobenzo(dithioperoxoate) (3-8)** was synthesized according to general procedure (**GP1**) with 2-(4-chlorophenyl)-2-oxoacetic acid **1-8** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-8** as a yellow liquid (18 mg, 69%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.98 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.5, 140.5, 134.2, 129.2, 129.2, 49.3, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2964, 1699, 1190, 889, 722 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}ClOS_2$ ($[M]^+$): 260.0096, mass found: 260.0100.

***SS*-(tert-butyl) 4-bromobenzo(dithioperoxoate) (3-9)** was synthesized according to general procedure (**GP1**) with 2-(4-bromophenyl)-2-oxoacetic acid **1-9** (23 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-9** as a yellow liquid (18 mg, 60%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.90 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.7, 134.7, 132.2, 129.2, 49.3, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 3057, 2964, 1695, 1586, 1196, 886, 707 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}BrOS_2$ ($[M]^+$): 303.9591, mass found: 303.9588.

***SS*-(tert-butyl) 4-iodobenzo(dithioperoxoate) (3-10)** was synthesized according to general procedure (**GP1**) with 2-(4-iodophenyl)-2-oxoacetic acid **1-10** (28 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-10** as a yellow liquid (25 mg, 71%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.85 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.1, 138.2, 135.2, 129.0, 101.9, 49.3, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 3051, 2958, 1695, 1518, 1200, 878, 702 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}IOS_2$ ($[M]^+$): 351.9452, mass found: 351.9451.

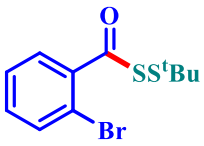


***SS*-(tert-butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) (3-11)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-(4-(trifluoromethyl)phenyl)acetic acid **1-11** (22 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-11** as a yellow liquid (20 mg, 68%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.14 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 1.37 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$, 300K) δ: -63.22 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.0, 138.7, 135.2 (q, *J* = 33.3 Hz), 128.1, 125.9 (q, *J* = 4.0 Hz), 124.8 (d, *J* = 273.7 Hz), 122.1, 49.5, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3057, 2968, 1700, 1513, 1326, 1070, 899 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{13}F_3OS_2$ ($[M]^+$): 294.0360, mass found: 294.0356.

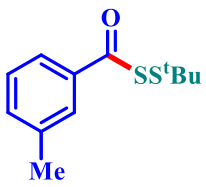
***SS*-(tert-butyl) 2-methylbenzo(dithioperoxoate) (3-12)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-(o-tolyl)acetic acid **1-12** (16 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-12** as a yellow liquid (17 mg, 71%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.86 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 192.6, 137.1, 136.2, 132.3, 131.7, 128.6, 125.9, 49.1, 29.8, 20.6. **FTIR (neat):** $\tilde{\nu}$ = 3067, 2963, 1704, 1455, 1185, 889, 764, 650 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{16}OS_2$ ([M]$^{+}$): 240.0643, mass found: 240.0644.

***SS*-(tert-butyl) 2-methoxybenzo(dithioperoxoate) (3-13)** was synthesized according to general procedure (**GP1**) with 2-(2-methoxyphenyl)-2-oxoacetic acid **1-13** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-13** as a yellow liquid (16 mg, 63%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.67 – 7.65 (m, 1H), 7.50 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.17 – 7.14 (m, 1H), 3.86 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.4, 159.9, 137.2, 129.9, 120.4, 111.9, 55.6, 49.2, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3067, 2958, 1695, 1517 1257, 1152, 779, 691 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{16}O_2S_2$ ([M]$^{+}$): 256.0592, mass found: 256.0597.

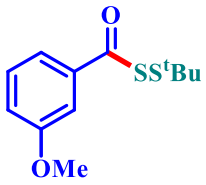
***SS*-(tert-butyl) 2-chlorobenzo(dithioperoxoate) (3-14)** was synthesized according to general procedure (**GP1**) with 2-(2-chlorophenyl)-2-oxoacetic acid **1-14** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-14** as a yellow liquid (16 mg, 62%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.35 (td, *J* = 7.3, 1.9 Hz, 1H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 191.3, 136.6, 132.6, 130.9, 129.1, 126.8, 49.6, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 3060, 2963, 1705, 1515, 1426, 1196, 882, 735 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}ClOS_2$ ($[M]^+$): 260.0096, mass found: 260.0100.



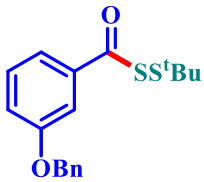
***SS*-(tert-butyl) 2-bromobenzo(dithioperoxoate) (3-15)** was synthesized according to general procedure (**GP1**) with 2-(2-bromophenyl)-2-oxoacetic acid **1-15** (23 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-15** as a yellow liquid (20 mg, 66%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.63 (ddd, *J* = 22.8, 7.5, 1.8 Hz, 2H), 7.43 – 7.33 (m, 2H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 192.1, 138.7, 134.1, 132.7, 129.1, 127.4, 118.9, 49.7, 30.0. **FTIR (neat):** $\tilde{\nu}$ = 3060, 2967, 1705, 1453, 1364, 1199, 1021, 892, 754 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}BrOS_2$ ($[M]^+$): 303.9591, mass found: 303.9588.



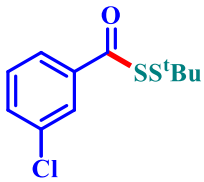
***SS*-(tert-butyl) 3-methylbenzo(dithioperoxoate) (3-16)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-(m-tolyl)acetic acid **1-16** (16 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-16** as a yellow liquid (19 mg, 79%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.84 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.39 – 7.35 (m, 1H), 2.43 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.6, 138.9, 135.9, 134.8, 128.8, 128.2, 125.1, 49.1, 29.8, 21.4. **FTIR (neat):** $\tilde{\nu}$ = 3055, 2962, 1693, 1604, 1365, 1244, 1155, 932, 779 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{16}OS_2$ ([M]$^+$): 240.0643, mass found: 240.0640.



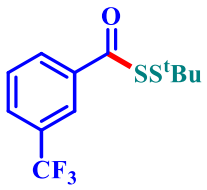
***SS*-(tert-butyl) 3-methoxybenzo(dithioperoxoate) (3-17)** was synthesized according to general procedure (**GP1**) with 2-(3-methoxyphenyl)-2-oxoacetic acid **1-17** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-17** as a yellow liquid (21 mg, 82%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.65 (d, *J* = 7.7 Hz, 1H), 7.50 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.15 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.86 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.4, 159.9, 137.2, 129.9, 120.4, 111.9, 55.5, 49.1, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3076, 2963, 2360, 1693, 1594, 1458, 1260, 1159, 1046, 781 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{16}O_2S_2$ ([M]$^+$): 256.0592, mass found: 256.0591.



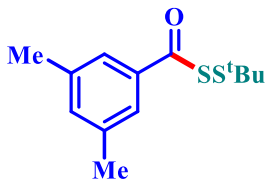
***SS*-(tert-butyl) 3-(benzyloxy)benzo(dithioperoxoate) (3-18)** was synthesized according to general procedure (**GP1**) with 2-(3-(benzyloxy)phenyl)-2-oxoacetic acid **1-18** (26 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-18** as a yellow liquid (25 mg, 76%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.67 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.61 (t, *J* = 2.1 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.33 (m, 4H), 7.22 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 5.12 (s, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.4, 159.0, 137.2, 136.3, 123.0, 128.7, 128.3, 127.7, 121.1, 120.6, 113.2, 70.3, 49.2, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 3072, 2963, 1695, 1515, 1256, 1155, 791, 694 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{18}H_{20}O_2S_2$ ($[M]^+$): 332.0905, mass found: 332.0908.



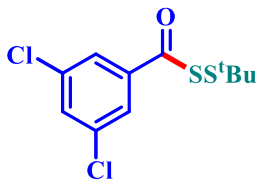
***SS*-(tert-butyl) 3-chlorobenzo(dithioperoxoate) (3-19)** was synthesized according to general procedure (**GP1**) with 2-(3-chlorophenyl)-2-oxoacetic acid **1-19** (16 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-19** as a yellow liquid (17 mg, 65%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.99 (t, *J* = 2.0 Hz, 1H), 7.92 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.6, 137.4, 135.2, 133.8, 130.2, 127.7, 125.9, 49.4, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3067, 2968, 1704, 1518, 1190, 910, 722 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{13}ClOS_2$ ($[M]^+$): 260.0096, mass found: 260.0101.



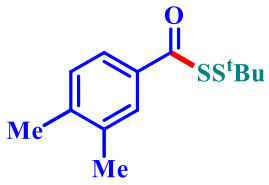
***SS*-(tert-butyl) 3-(trifluoromethyl)benzo(dithioperoxoate) (3-20)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-(3-(trifluoromethyl)phenyl)acetic acid **1-20** (22 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-20** as a yellow liquid (20 mg, 68%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.27 (s, 1H), 8.22 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.9 Hz, 1H), 1.37 (s, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$, 300K) δ: -62.83 (s, 3F). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.7, 136.5 (d, J = 158.6 Hz), 135.0,131.7 (d, J = 33.3 Hz), 131.4, 130.3 (q, J = 4.0 Hz), 129.6, 124.6 (d, J = 4.0 Hz), 124.6, 49.5, 29.9. **FTIR (neat):** $\tilde{\nu}$ = 2963, 2926, 1688, 1517, 1332, 1165, 1128, 694 cm^{-1}. **HRMS (ES):** Exact mass calculated for $C_{12}H_{13}F_3OS_2$ ($[M]^+$): 294.0360, mass found: 294.0355.



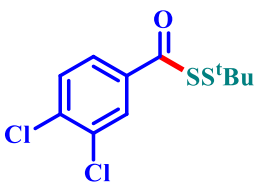
***SS*-(tert-butyl) 3,5-dimethylbenzo(dithioperoxoate) (3-21)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-(3-(trifluoromethyl)phenyl)acetic acid **1-21** (22 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-21** as a yellow liquid (21 mg, 83%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.64 (s, 2H), 7.24 (s, 1H), 2.38 (s, 6H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.6, 138.7, 135.9, 135.6, 125.5, 49.0, 29.8, 21.2. **FTIR (neat):** $\tilde{\nu}$ = 3047, 2963, 2922, 2861, 1693, 1604, 1460, 1365, 1288, 1143, 856, 759 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{18}OS_2$ ($[M]^+$): 254.0799, mass found: 254.0796.



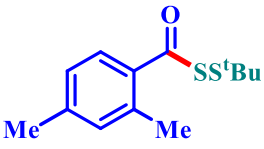
***SS*-(tert-butyl) 3,5-dichlorobenzo(dithioperoxoate) (3-22)** was synthesized according to general procedure (**GP1**) with 2-(3,5-dichlorophenyl)-2-oxoacetic acid **1-22** (22 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-22** as a yellow liquid (17 mg, 58%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.88 (d, *J* = 1.9 Hz, 2H), 7.59 (s, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 188.8, 138.3, 135.9, 133.5, 126.1, 49.7, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3035, 2967,1696, 1608, 1450, 1365, 1211, 1167, 888, 767 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{12}Cl_2OS_2$ ($[M]^+$): 293.9707, mass found: 293.9704.



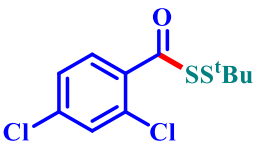
***SS*-(tert-butyl) 3,4-dimethylbenzo(dithioperoxoate) (3-23)** was synthesized according to general procedure (**GP1**) with 2-(3,4-dimethylphenyl)-2-oxoacetic acid **1-23** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-23** as a yellow liquid (19 mg, 75%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.80 (s, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 2.33 (s, 6H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.0, 143.7, 137.4, 133.7, 130.0, 128.8, 125.5, 49.0, 29.8, 20.2, 19.8. **FTIR (neat):** $\tilde{\nu}$ = 3028, 2963, 2928, 1701, 1454, 1240, 832, 799 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{18}OS_2$ ($[M]^+$): 254.0799, mass found: 254.0795.



***SS*-(tert-butyl) 3,4-dichlorobenzo(dithioperoxoate) (3-24)** was synthesized according to general procedure (**GP1**) with 2-(3,4-dichlorophenyl)-2-oxoacetic acid **1-24** (22 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-24** as a yellow liquid (15 mg, 51%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.11 (d, J = 2.1 Hz, 1H), 7.87 (dd, J = 8.4, 2.1 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 188.8, 138.6, 135.3, 133.6, 130.9, 129.5, 126.7, 49.5, 29.8. **FTIR (neat):** $\tilde{\nu}$ = 3065, 2968, 1696, 1345, 1162, 815, 666 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{12}Cl_2OS_2$ ($[M]^+$): 293.9707, mass found: 293.9710.



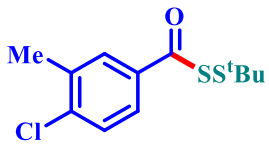
***SS*-(tert-butyl) 2,4-dimethylbenzo(dithioperoxoate) (3-25)** was synthesized according to general procedure (**GP1**) with 2-(2,4-dimethylphenyl)-2-oxoacetic acid **1-25** (18 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-25** as a yellow liquid (20 mg, 79%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.82 (d, *J* = 8.3 Hz, 1H), 7.11 – 7.07 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 191.8, 143.1, 137.5, 133.2, 132.6, 129.1, 126.5, 48.9, 29.8, 21.5, 20.7. **FTIR (neat):** $\tilde{\nu}$ = 3011, 2963, 2922, 1713, 1454, 1203, 941, 847, 625 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{18}OS_2$ ($[M]^+$): 254.0799, mass found: 226.0489.



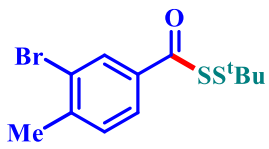
***SS*-(tert-butyl) 2,4-dichlorobenzo(dithioperoxoate) (3-26)** was synthesized according to general procedure (**GP1**) with 2-(2,4-dichlorophenyl)-2-oxoacetic acid **1-26** (22 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-26** as a yellow liquid (18 mg, 61%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.60 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.34 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.5, 138.4, 134.9, 132.1, 130.9, 130.1, 127.2, 49.7, 29.9. **FTIR (neat):** ṽ = 3063, 2963, 1713, 1515, 1458, 1369, 1196, 892 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{12}Cl_2OS_2$ ([M]$^+$): 293.9707, mass found: 293.9710.

***SS*-(tert-butyl) 2,6-dimethoxybenzo(dithioperoxoate) (3-27)**

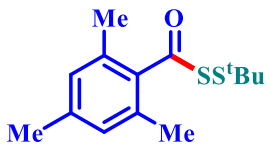
was synthesized according to general procedure (**GP1**) with 2-(2,6-dimethoxyphenyl)-2-oxoacetic acid **1-27** (21 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-27** as a yellow liquid (25 mg, 87%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.31 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 6H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 191.9, 157.0, 132.1, 116.9, 104.0, 56.0, 49.2, 29.8. **FTIR (neat):** ṽ = 3095 2963, 2846, 1709, 1592, 1475, 1256, 1111, 880, 641 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{18}O_3S_2$ ([M]$^+$): 286.0697, mass found: 268.0960.



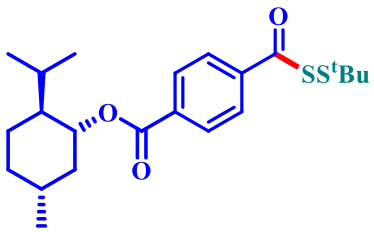
***SS*-(tert-butyl) 4-chloro-3-methylbenzo(dithioperoxoate) (3-28)** was synthesized according to general procedure (**GP1**) with 2-(4-chloro-3-methylphenyl)-2-oxoacetic acid **1-28** (20 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-28** as a yellow liquid (13 mg, 47%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.89 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 2.44 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.7, 140.6, 137.1, 134.3, 130.0, 129.6, 126.5, 49.3, 29.8, 20.2. **FTIR (neat):** $\tilde{\nu}$ = 3060, 2963, 1701, 1454, 1228, 1159, 1050, 791 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{15}ClOS_2$ ([M]$^+$): 274.0253, mass found: 274.0256.



***SS*-(tert-butyl) 3-bromo-4-methylbenzo(dithioperoxoate) (3-29)** was synthesized according to general procedure (**GP1**) with 2-(3-bromo-4-methylphenyl)-2-oxoacetic acid **1-29** (24 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-29** as a yellow liquid (22 mg, 69%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.18 (d, *J* = 1.9 Hz, 1H), 7.88 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.34 (dd, *J* = 7.9, 0.8 Hz, 1H), 2.47 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 189.0, 144.6, 135.1, 131.5, 131.1, 126.6, 125.4, 49.3, 29.8, 23.4. **FTIR (neat):** $\tilde{\nu}$ = 3064, 2963, 2324, 1693, 1515, 1187, 795 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{15}BrOS_2$ ([M]$^+$): 317.9748, mass found: 317.9745.

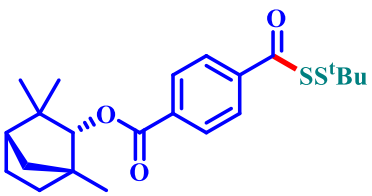


***SS*-(tert-butyl) 2,4,6-trimethylbenzo(dithioperoxoate) (3-30)** was synthesized according to general procedure (**GP1**) with 2-2-mesityl-2-oxoacetic acid **1-30** (19 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-30** as a yellow liquid (19 mg, 71%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 6.87 (s, 2H), 2.30 (s, 9H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 196.8, 140.0, 135.9, 134.1, 128.6, 49.2, 30.2, 21.2, 19.4. **FTIR (neat):** $\tilde{\nu}$ = 2967, 2918, 1729, 1454, 1138, 839, 621 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{14}H_{20}OS_2$ ($[M]^+$): 268.0956, mass found: 268.0960.

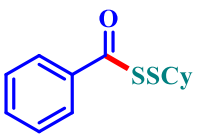


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((R)-1-(tert-butyl)-1l4-disulfanenecarbonyl)benzoate (3-31) was synthesized according to general procedure (**GP1**) with 2-(4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-2-oxoacetic acid **1-31** (33 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-21** as a yellow liquid (29 mg, 71%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.14 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H), 4.99 – 4.92 (m, 1H), 2.13 (d, J = 11.6 Hz, 1H), 1.96 – 1.89 (m, 1H), 1.77 – 1.70 (m, 2H), 1.61 – 1.52 (m, 2H), 1.37 (s, 9H), 1.16 – 1.06 (m, 2H), 0.93 (t, J = 7.0 Hz, 7H), 0.79 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.4, 165.0, 139.1, 135.4, 130.0, 127.7, 75.7, 49.4, 47.3, 40.9, 34.3, 31.5, 29.9, 26.6, 23.7, 22.1, 20.8, 16.6. **FTIR (neat):** $\tilde{\nu}$ = 2967, 2926, 1705, 1652, 1539, 1515,

1462, 795, 735 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{22}H_{32}O_3S_2$ ($[M]^+$): 408.1793, mass found: 408.1795.

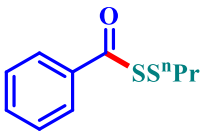


(1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-((R)-1-(tert-butyl)-1l4-disulfanenecarbonyl)benzoate (3-32) was synthesized according to general procedure (**GP1**) with 2-oxo-2-(4-((((1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl)oxy)carbonyl) phenyl)acetic acid **1-32** (33 mg, 0.10 mmol), dithiosulfonate reagent **2-1** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-32** as a yellow liquid (30 mg, 74%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.16 (d, *J* = 8.6 Hz, 2H), 8.09 (d, *J* = 8.6 Hz, 2H), 4.64 (d, *J* = 2.0 Hz, 1H), 1.94 – 1.87 (m, 1H), 1.84 – 1.74 (m, 2H), 1.69 – 1.65 (m, 1H), 1.57 – 1.48 (m, 1H), 1.37 (s, 9H), 1.29 – 1.23 (m, 2H), 1.19 (s, 3H), 1.11 (s, 3H), 0.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.3, 165.8, 139.1, 135.2, 130.0, 127.8, 87.5, 49.4, 48.7, 48.4, 41.5, 39.9, 29.9, 29.8, 26.9, 25.9, 20.3, 19.5. **FTIR (neat):** $\tilde{\nu}$ = 3064, 2963, 2878, 2339, 1721, 1280, 1114, 896, 702 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{22}H_{30}O_3S_2$ ($[M]^+$): 406.1636, mass found: 406.1639.

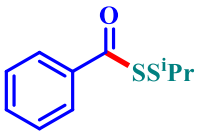


***SS*-cyclohexyl benzo(dithioperoxoate) (3-33)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-2** (45 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-33** as a yellow liquid (21 mg, 83%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400

MHz, $CDCl_3$, 300K) δ: 8.01 (d, *J* = 7.0 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 2.86 (tt, *J* = 10.9, 3.7 Hz, 1H), 2.09 – 2.01 (m, 2H), 1.84 – 1.75 (m, 2H), 1.62 – 1.58 (m, 1H), 1.46 – 1.27 (m, 4H), 1.24 – 1.17 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.9, 135.9, 134.0, 128.9, 127.8, 49.7, 32.7, 26.1, 25.5. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2930, 2853, 1689, 1515, 1200, 885, 684 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{16}OS_2$ ($[M]^+$): 252.0643, mass found: 252.0640.



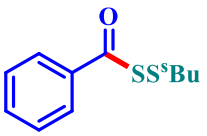
***SS*-propyl benzo(dithioperoxoate) (3-34)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-3** (39 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-34** as a yellow liquid (18 mg, 85%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.97 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 192.2, 137.3, 133.2, 128.6, 127.2, 31.0, 23.0, 13.5. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2964, 2926, 2860, 1689, 1453, 1203, 885, 680 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{10}H_{12}OS_2$ ($[M]^+$): 212.0330, mass found: 212.0332.



***SS*-butyl benzo(dithioperoxoate) (3-35)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-4** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-35** as a yellow liquid (19 mg, 84%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.97 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* =

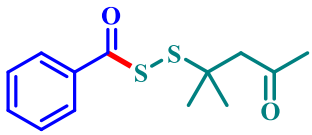
7.7 Hz, 2H), 3.08 (t, J = 7.3 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.51 – 1.41 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 192.2, 137.3, 133.3, 128.6, 127.2, 31.7, 28.8, 22.1, 13.7. **FTIR (neat):** ṽ = 3064, 2958, 2931, 2866, 1664, 1450, 1208, 912, 690 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{14}OS_2$ ($[M]^+$): 226.0486, mass found: 226.0489.

***SS*-isopropyl benzo(dithioperoxoate) (3-36)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-5** (39 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-36** as a yellow liquid (16 mg, 75%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.02 (d, J = 7.1 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 3.19 – 3.09 (m, 1H), 1.34 (s, 3H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.6, 135.9, 134.0, 128.9, 127.8, 41.6, 22.5. **FTIR (neat):** ṽ = 3062, 2964, 2930, 2874, 1665, 1450, 1207, 913, 690 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{14}OS_2$ ($[M]^+$): 212.0330, mass found: 212.0333.

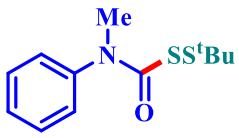


***SS*-(*sec*-butyl) benzo(dithioperoxoate) (3-37)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-6** (41 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-37** as a yellow liquid (16 mg, 71%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.01 (d, J = 7.1 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 2.95 – 2.87 (m, 1H), 1.78 – 1.67 (m, 1H), 1.61– 1.52 (m, 1H),

1.32 (d, J = 6.7 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 190.8, 135.9, 134.0, 128.9, 127.8, 48.4, 29.1, 19.9, 11.5. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2964, 2923, 1689, 1550, 1453, 1203, 885, 684 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{11}H_{14}OS_2$ ($[M]^+$): 226.0486, mass found: 226.0483.

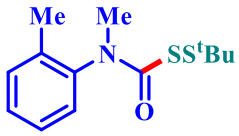


***SS*-(2-methyl-4-oxopentan-2-yl) benzo(dithioperoxoate) (3-38)** was synthesized according to general procedure (**GP1**) with 2-oxo-2-phenylacetic acid **1-1** (15 mg, 0.10 mmol), dithiosulfonate reagent **2-7** (48 mg, 1.50 mmol), PC (2.2 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 100/1) provided **3-37** as a yellow liquid (17 mg, 63%), **TLC R_f** = 0.3 (PE:EtOAc = 100:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.08 – 8.00 (m, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.45 (m, 2H), 2.77 (s, 2H), 2.16 (s, 3H), 1.47 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 206.2, 190.1, 135.7, 134.2, 129.0, 127.9, 53.4, 50.1, 32.0, 26.9. **HRMS (EI):** Exact mass calculated for $C_{13}H_{16}O_2S_2$ ($[M]^+$): 268.0592, mass found: 268.0596.

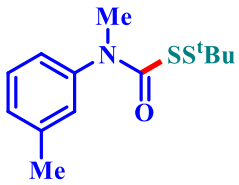


***SS-tert*-butyl methyl(phenyl)carbamo(dithioperoxoate) (5-1)** was synthesized according to general procedure (**GP2**) with 2-(methyl(phenyl)amino)-2-oxoacetic acid **4-1** (35.8 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-1** as a yellow liquid (15 mg, 59%), **TLC R_f** = 0.1 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.48 – 7.37 (m, 3H), 7.32 (d, J = 7.3 Hz, 2H), 3.37 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz,

$CDCl_3$, 300K) δ: 166.9, 141.7, 129.7, 128.9, 128.6, 48.0, 39.5, 29.7. **FTIR (neat):** ṽ = 3064, 2963, 1689, 1495, 1345, 1264, 1111, 694 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{17}NOS_2$ ($[M]^+$): 255.0752, mass found: 255.0754.

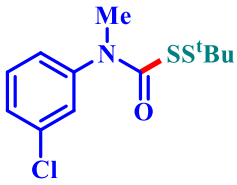


***SS-tert*-butyl methyl(o-tolyl)carbamo(dithioperoxoate) (5-2)** was synthesized according to general procedure (**GP2**) with 2-(methyl(o-tolyl)amino)-2-oxoacetic acid **4-2** (39 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-2** as a yellow liquid (17 mg, 63%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.31 – 7.12 (m, 4H), 3.21 (s, 3H), 2.23 (s, 3H), 1.20 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.8, 139.7, 137.3, 131.5, 129.6, 127.5, 47.9, 38.2, 29.6, 17.5. **FTIR (neat):** ṽ = 3027, 2964, 1689, 1459, 1342, 1269, 1096, 725 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{19}NOS_2$ ($[M]^+$): 269.0908, mass found: 269.0905.

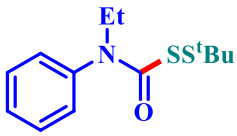


SS-*tert*-butyl methyl(m-tolyl)carbamo(dithioperoxoate) (5-3) was synthesized according to general procedure (**GP2**) with 2-(methyl(m-tolyl)amino)-2-oxoacetic acid **4-3** (39 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-3** as a yellow liquid (18 mg, 67%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.35 – 7.29 (m, 1H), 7.21 (dq, J = 7.8, 1.1 Hz, 1H), 7.13 – 7.09 (m, 2H), 3.34 (s, 3H), 2.39 (s, 3H), 1.28 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.8, 141.5, 139.8, 129.4, 129.0, 125.5, 47.9, 39.5, 29.6, 21.3. **FTIR (neat):** ṽ = 3037, 2961, 1685, 1460,

1338, 1266, 1110, 701 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{13}H_{19}NOS_2$ ($[M]^+$): 269.0908, mass found: 269.0909.

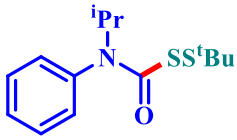


SS-*tert*-butyl (3chlorophenyl)(methyl)Carbamo (dithioperoxoate) (5-4) was synthesized according to general procedure (**GP2**) with 2-((3-chlorophenyl)(methyl)amino)-2-oxoacetic acid **4-4** (43 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-4** as a yellow liquid (15 mg, 52%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.44 – 7.37 (m, 2H), 7.34 – 7.29 (m, 1H), 7.23 (dt, *J* = 5.2, 2.2 Hz, 1H), 3.36 (s, 3H), 1.29 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.8, 142.8, 135.1, 130.6, 129.6, 129.1, 48.2, 39.4, 29.6. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2961, 1693, 1588, 1474, 1248, 1016, 694 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{12}H_{16}ClNOS_2$ ($[M]^+$): 289.0362, mass found: 289.0357.

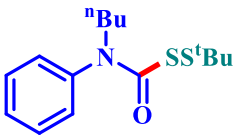


SS-*tert*-butyl ethyl(phenyl)carbamo(dithioperoxoate) (5-5) was synthesized according to general procedure (**GP2**) with 2-(ethyl(phenyl)amino)-2-oxoacetic acid **4-5** (39 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-5** as a yellow liquid (20 mg, 74%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.48 – 7.40 (m, 3H), 7.31 – 7.26 (m, 2H), 3.79 (q, *J* = 7.1 Hz, 2H), 1.27 (s, 9H), 1.15 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.2, 139.9, 129.8, 129.6, 129.0, 47.9, 46.8, 29.6, 13.2. **FTIR (neat):** $\tilde{\nu}$ = 3065, 2968, 2930, 1696, 1495, 1373, 1245, 1127, 843, 697 cm^{-}

[1]. **HRMS (EI):** Exact mass calculated for $C_{13}H_{19}NOS_2$ ($[M]^+$): 269.0908, mass found: 269.0910.

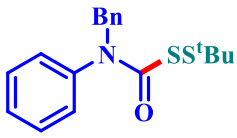


SS-*tert*-butyl isopropyl(phenyl)carbamo(dithioperoxoate) (5-6) was synthesized according to general procedure (**GP2**) with 2-(isopropyl(phenyl)amino)-2-oxoacetic acid **4-6** (41 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-6** as a yellow liquid (21 mg, 74%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.48 – 7.40 (m, 3H), 7.25 – 7.20 (m, 2H), 4.83 (hept, J = 6.8 Hz, 1H), 1.25 (s, 9H), 1.11 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.2, 136.4, 131.7, 129.4, 129.2, 50.2, 47.9, 29.6, 20.9. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2964, 1682, 1453, 1235, 1110, 697 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{14}H_{21}NOS_2$ ($[M]^+$): 283.1065, mass found: 283.1068.



SS-*tert*-butyl butyl(phenyl)carbamo(dithioperoxoate) (5-7) was synthesized according to general procedure (**GP2**) with 2-(butyl(phenyl)amino)-2-oxoacetic acid **4-7** (44 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-7** as a yellow liquid (23 mg, 77%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.43 (d, J = 6.4 Hz, 3H), 7.28 (dt, J = 7.4, 1.6 Hz, 2H), 3.74 (td, J = 7.4, 1.2 Hz, 2H), 1.52 (ddd, J = 15.3, 8.5, 6.8 Hz, 2H), 1.33 (dt, J = 15.0, 7.4 Hz, 2H), 1.26 (s, 9H), 0.89 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.5, 140.1, 129.7, 129.6, 129.0, 51.7, 47.9, 29.9,

29.6, 19.8, 13.8. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2964, 1689, 1491, 1366, 1252, 694 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{15}H_{23}NOS_2$ ($[M]^+$): 297.1221, mass found: 297.1223.



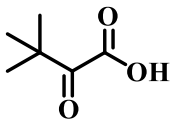
SS-*tert*-butyl benzyl(phenyl)carbamo(dithioperoxoate) (5-8) was synthesized according to general procedure (**GP2**) with 2-(benzyl(phenyl)amino)-2-oxoacetic acid **4-8** (51 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-8** as a yellow liquid (25 mg, 76%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.33 – 7.24 (m, 3H), 7.19 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.12 (dd, *J* = 7.0, 2.7 Hz, 2H), 7.04 – 6.98 (m, 2H), 4.83 (s, 2H), 1.22 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 167.2, 139.7, 136.7, 129.8, 129.5, 129.1, 128.9, 128.5, 127.7, 55.6, 48.1, 29.6. **FTIR (neat):** $\tilde{\nu}$ = 3062, 2964, 1685, 1491, 1366, 1245, 701 cm^{-1}. **HRMS (EI):** Exact mass calculated for $C_{18}H_{21}NOS_2$ ($[M]^+$): 331.1065, mass found: 331.1066.

SS-(tert-butyl) indoline-1-carbo(dithioperoxoate) (5-9) was synthesized according to general procedure (**GP2**) with 2-(indolin-1-yl)-2-oxoacetic acid **4-9** (38 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-9** as a yellow liquid (18 mg, 67%), **TLC R_f** = 0.3 (PE:EtOAc = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 8.04 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.21 – 4.13 (m, 2H), 3.24 (t, *J* = 8.4 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 163.4, 142.8, 130.9, 127.8,

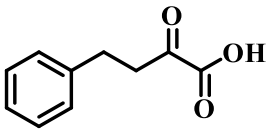
124.8, 124.1, 116.4, 48.4, 47.4, 29.7, 28.2. **FTIR (neat):** $\tilde{\nu}$ = 2962, 2857, 1690, 1481, 1372, 1277, 1089，901, 728 cm^{-1}. **HRMS (ESI):** Exact mass calculated for $C_{13}H_{17}NOS_2$ ($[M+H]^+$): 268.0830, mass found: 268.0825.

SS-(tert-butyl) 3,4-dihydroquinoline-1(2H)-carbo (dithioperoxoate) (5-10) was synthesized according to general procedure (**GP2**) with 2-(3,4-dihydroquinolin-1(2H)-yl)-2-oxoacetic acid **4-10** (41 mg, 0.20 mmol), dithiosulfonate reagent **2-1** (27.6 mg, 0.1 mmol), PC-2 (1.3 mg, 2 mol%) and ^{t}BuOK (22 mg, 0.2 mmol) in DCE (2.0 mL) under irradiation of 24 W blue LEDs with N_2 protection at 25 °C for 12 h. Purification by flash column chromatography (petroleum ether / ethyl acetate = 50/1) provided **5-10** as a yellow liquid (18 mg, 64%), **TLC R_f** = 0.6 (PE:EtOAc = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$, 300K) δ: 7.70 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.09 (m, 3H), 3.90 (t, *J* = 6.3 Hz, 2H), 2.78 (t, *J* = 6.7 Hz, 2H), 2.02 (p, *J* = 6.5 Hz, 2H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$, 300K) δ: 166.7, 137.8, 129.4, 128.8, 126.2, 125.8, 124.9, 48.2, 45.9, 29.7, 26.8, 23.8. **FTIR (neat):** $\tilde{\nu}$ = 2962, 2857, 1690, 1497, 1366, 1288, 1172, 932, 760 cm^{-1}. **HRMS (ESI):** Exact mass calculated for $C_{14}H_{19}NOS_2$ ($[M+H]^+$): 282.0986, mass found: 282.0981.

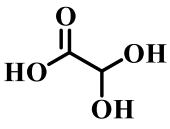
The following substrates have failed for the disulfuration reaction



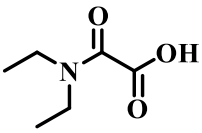
1-33



1-34



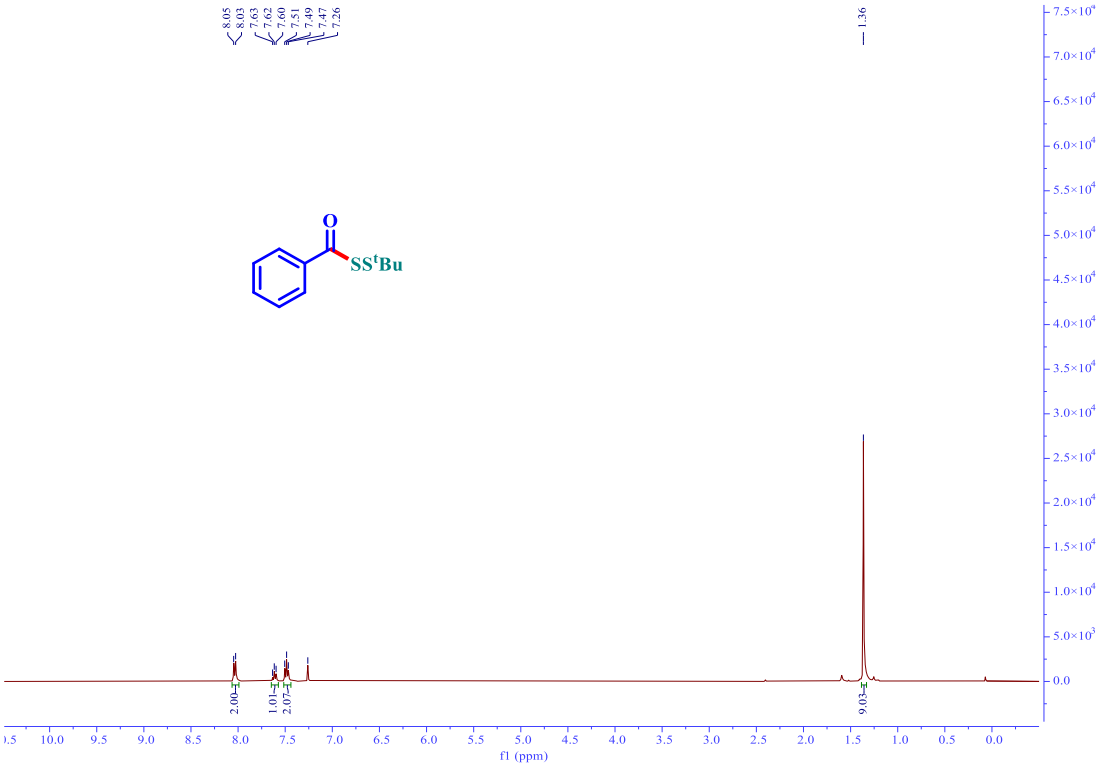
1-35



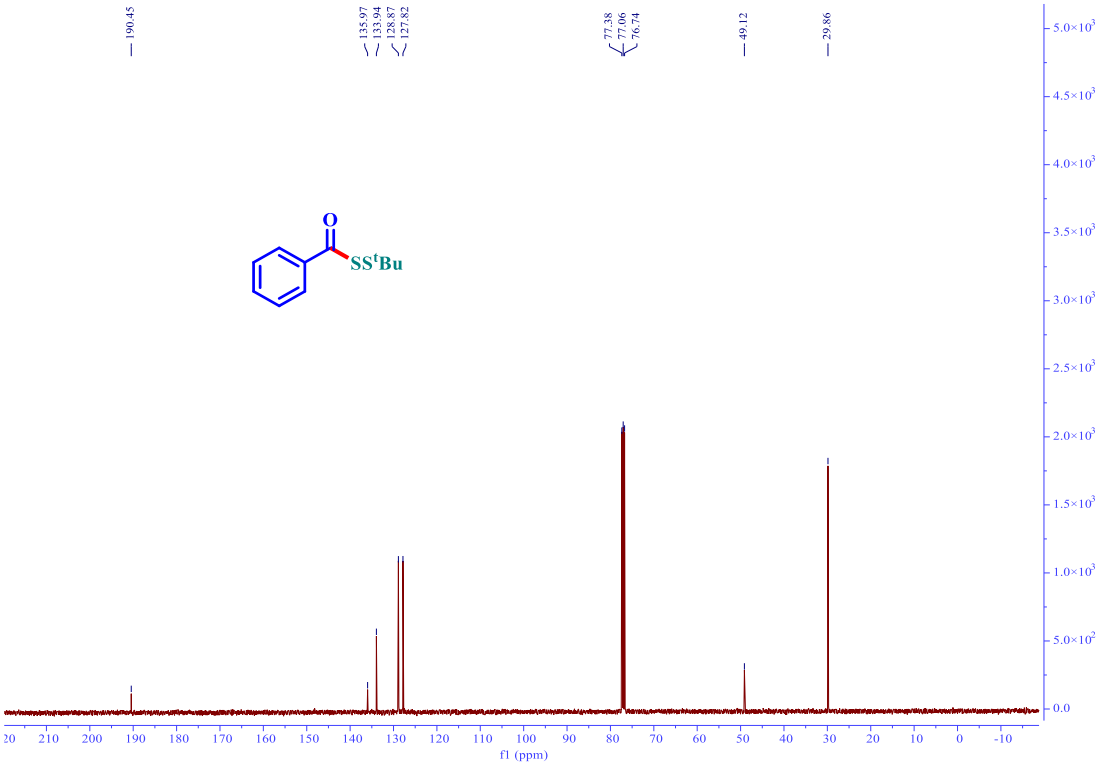
4-11

9. Spectra

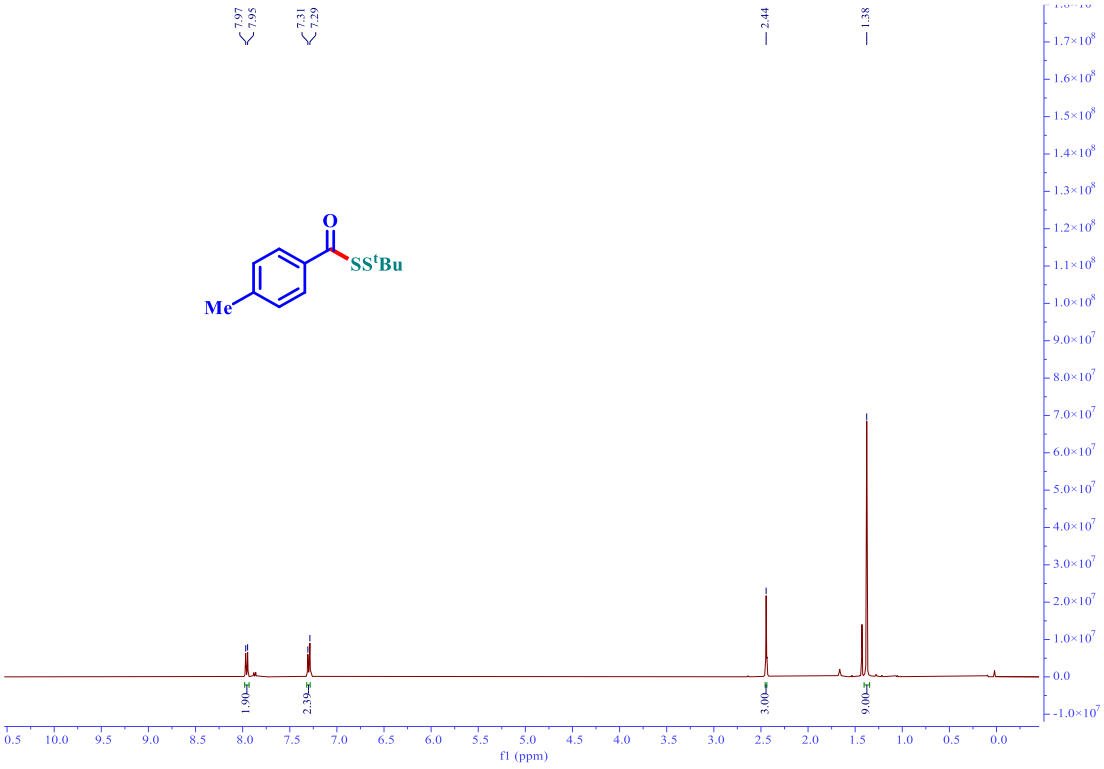
^{1}H NMR Spectrum of *SS*-(tert-butyl) benzo(dithioperoxoate) (3-1)



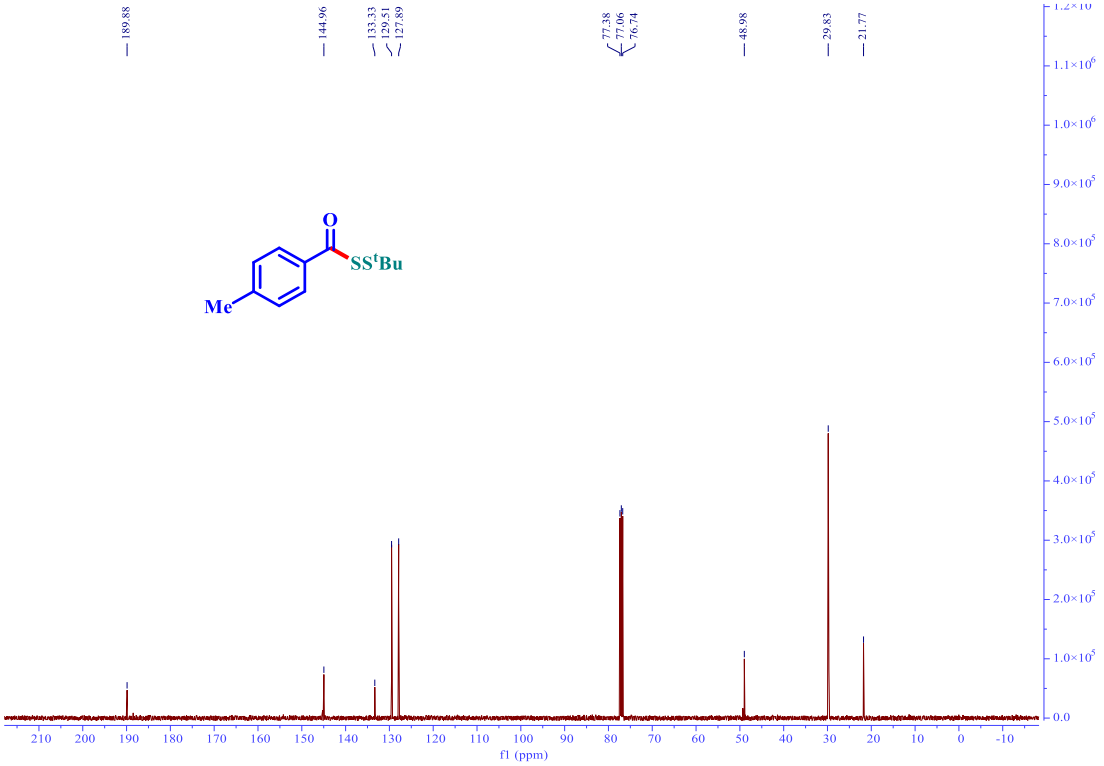
^{13}C NMR Spectrum of *SS*-(tert-butyl) benzo(dithioperoxoate) (3-1)



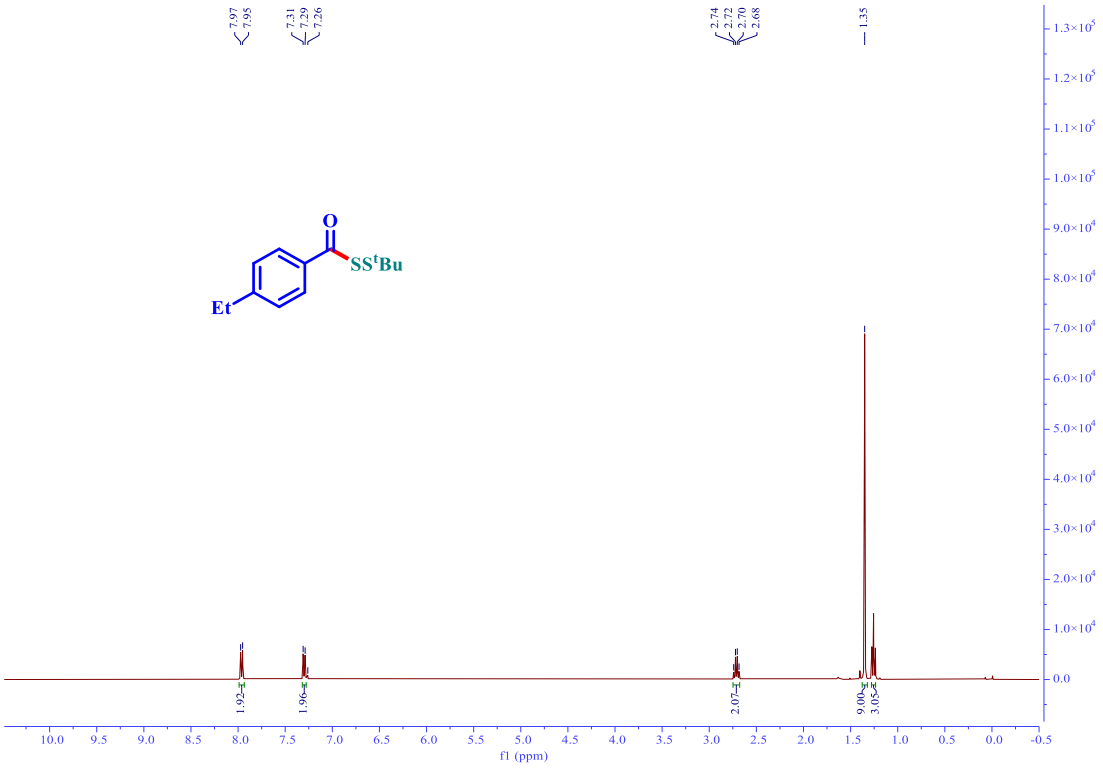
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-methylbenzo(dithioperoxoate) (3-2)



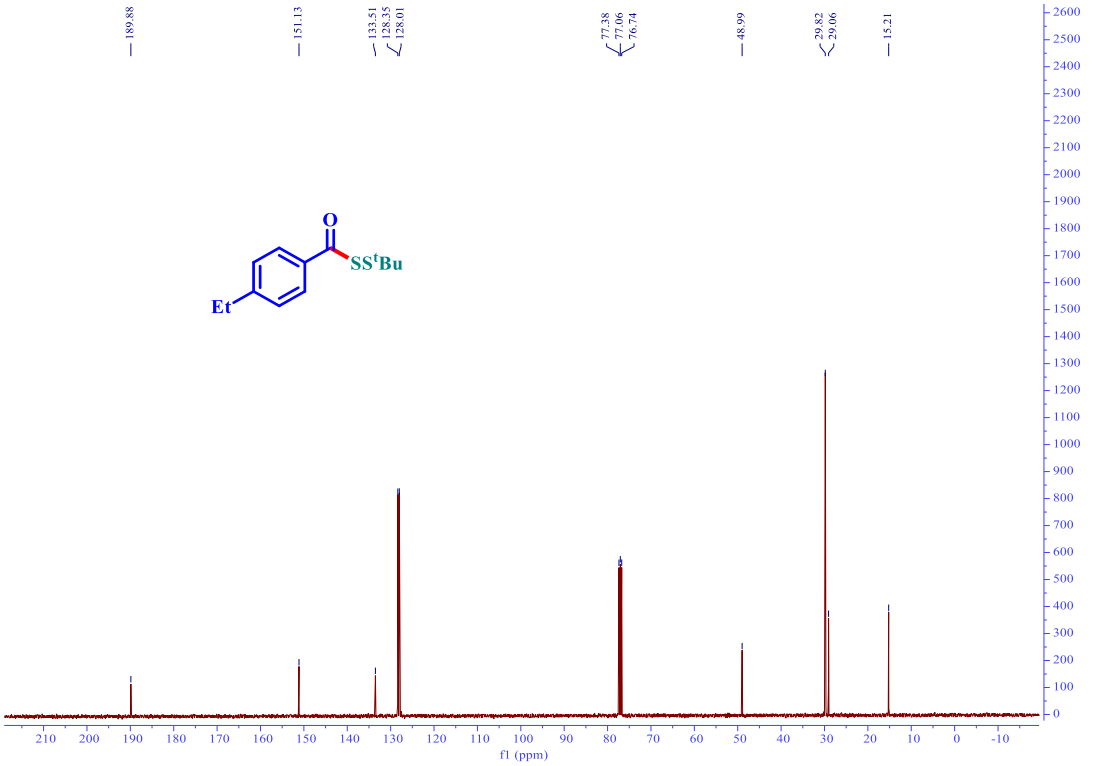
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-methylbenzo(dithioperoxoate) (3-2)



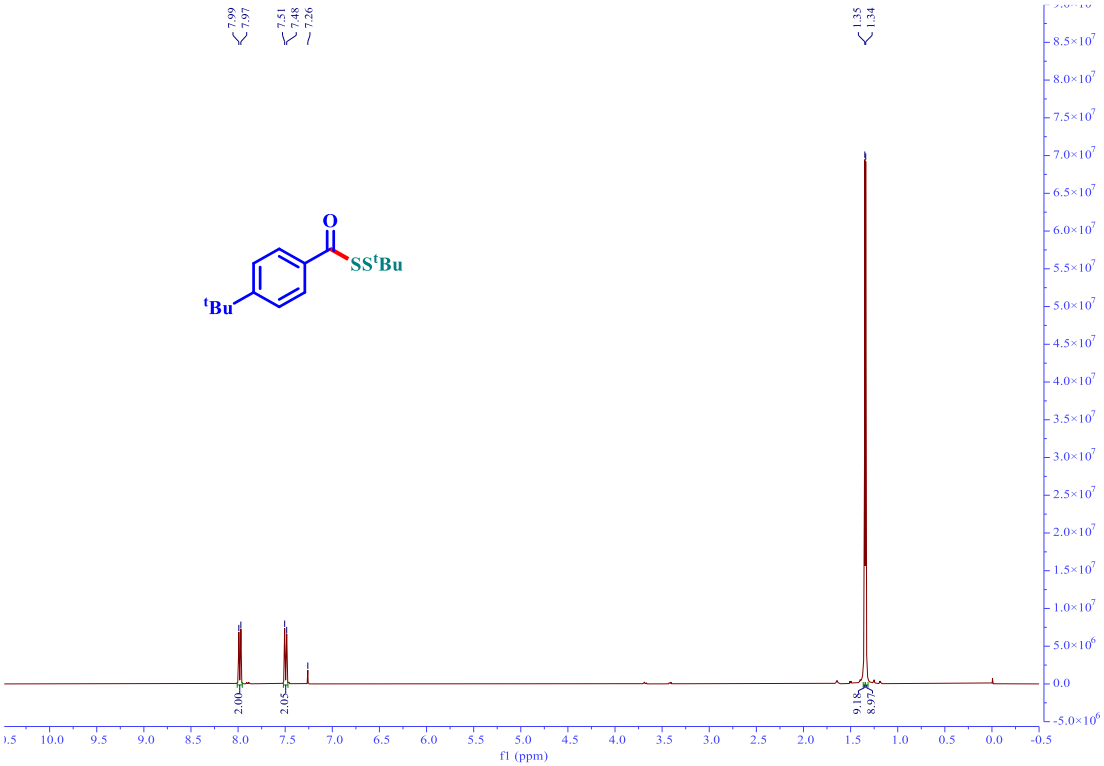
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-ethylbenzo(dithioperoxoate) (3-3)



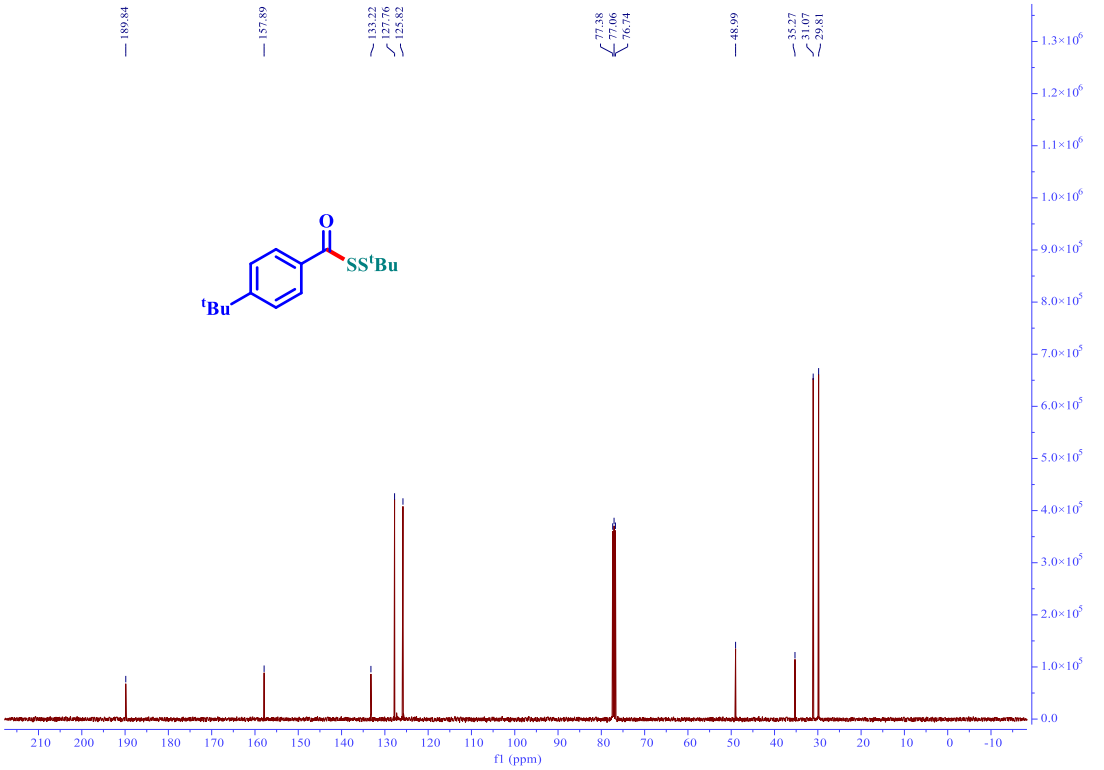
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-ethylbenzo(dithioperoxoate) (3-3)



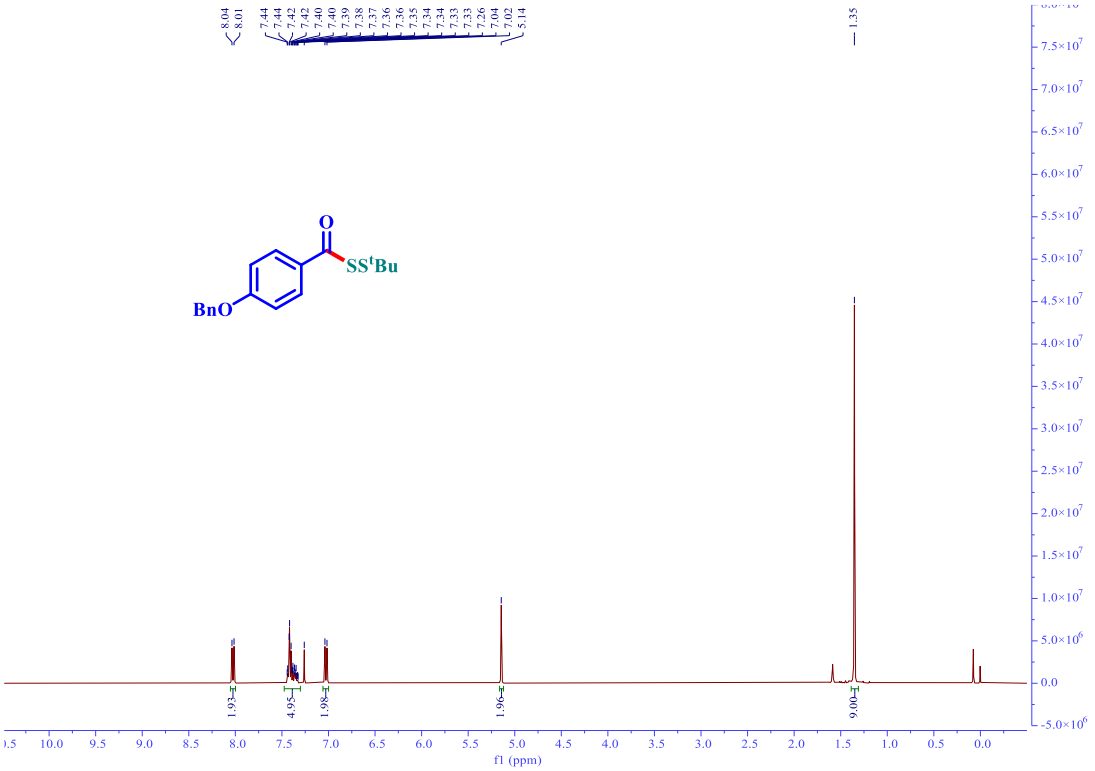
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-(tert-butyl)benzo(dithioperoxoate) (3-4)



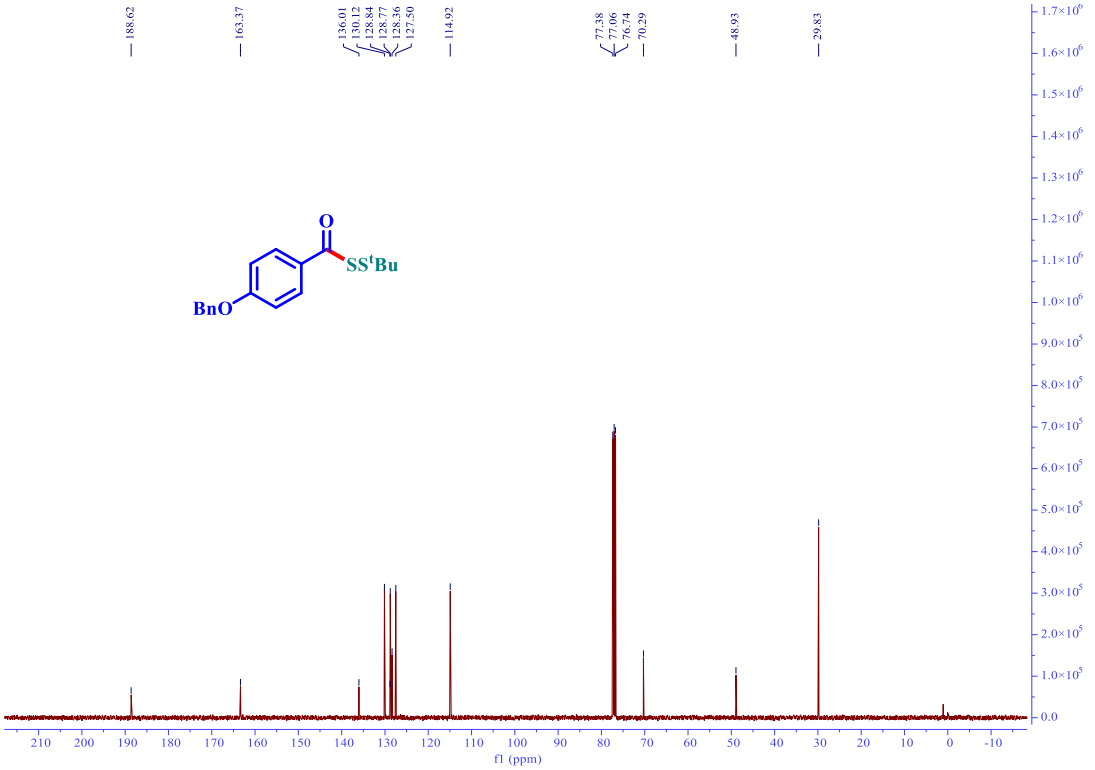
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-(tert-butyl)benzo(dithioperoxoate) (3-4)



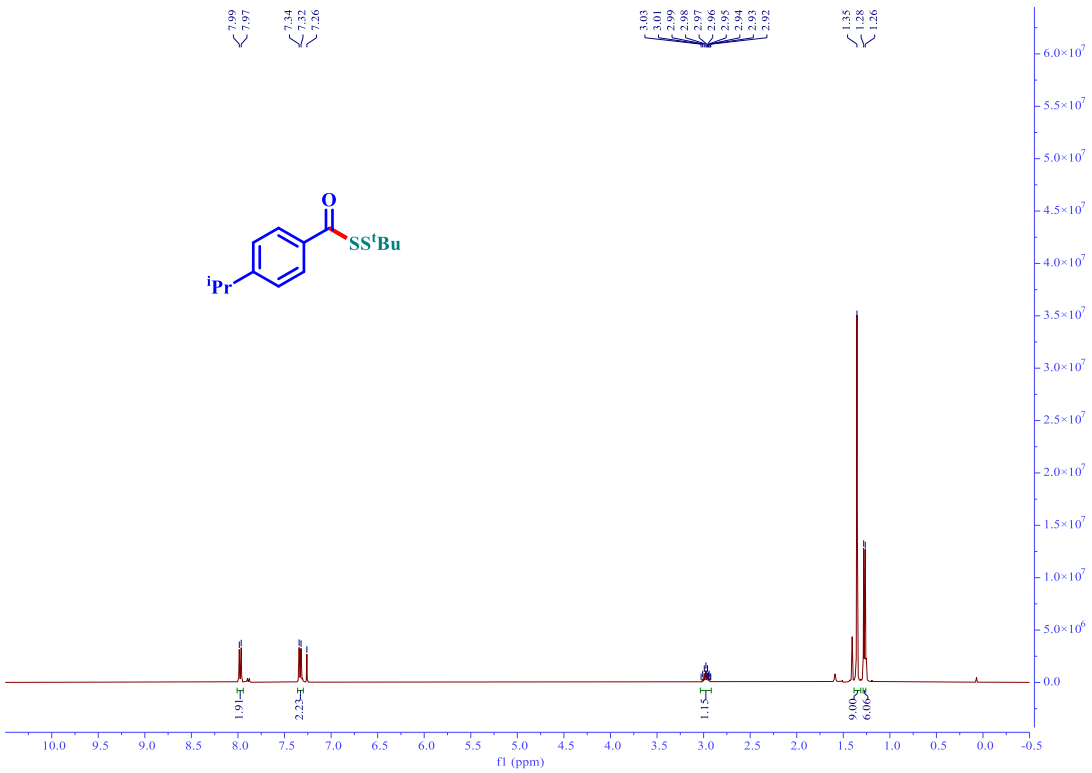
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-(benzyloxy)benzo(dithioperoxoate) (3-6)



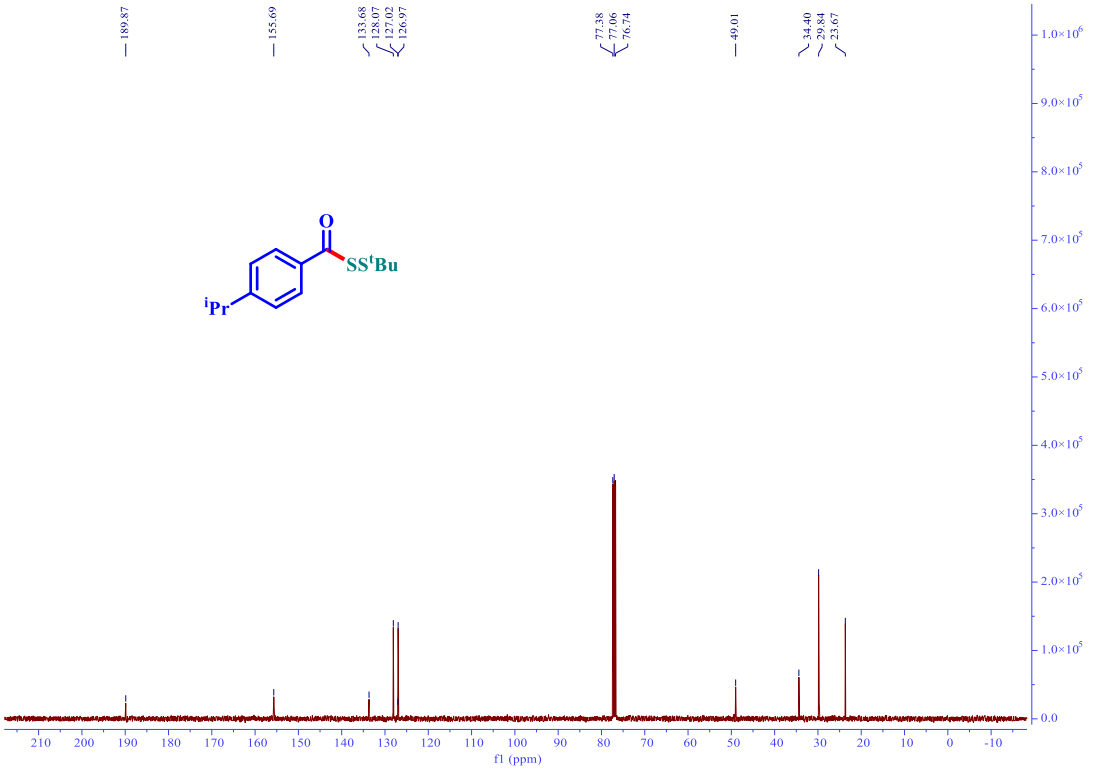
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-(benzyloxy)benzo(dithioperoxoate) (3-6)



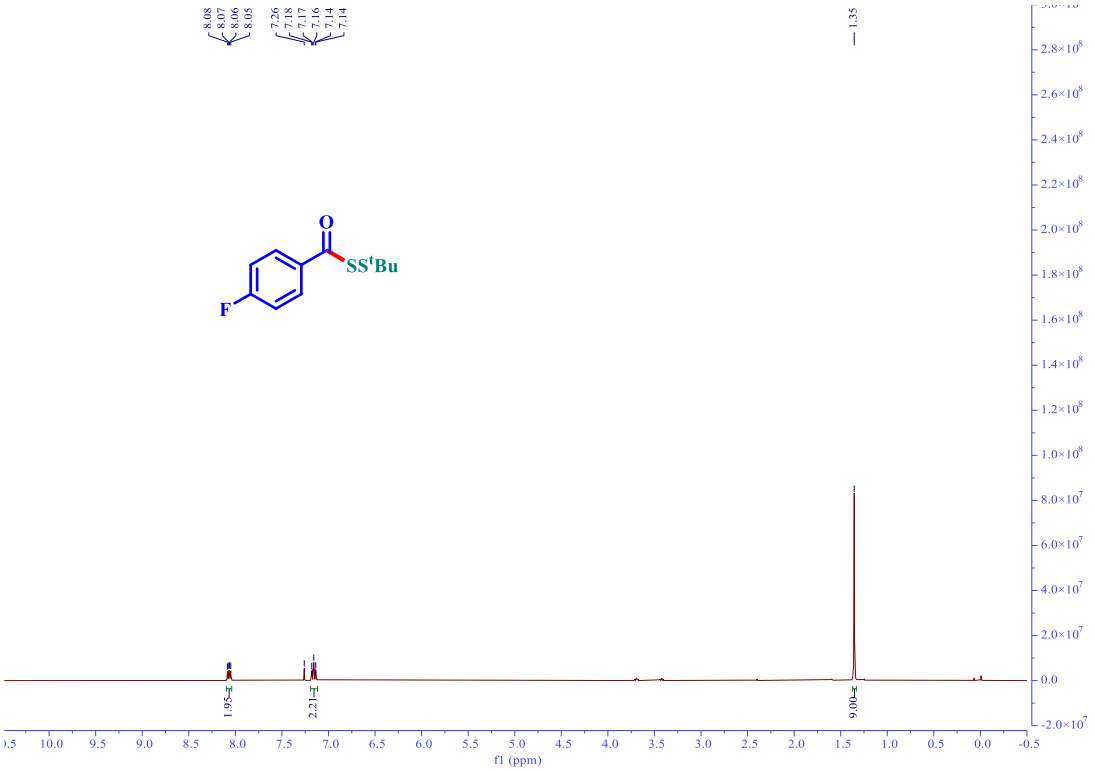
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-isopropylbenzo(dithioperoxoate) (3-5)



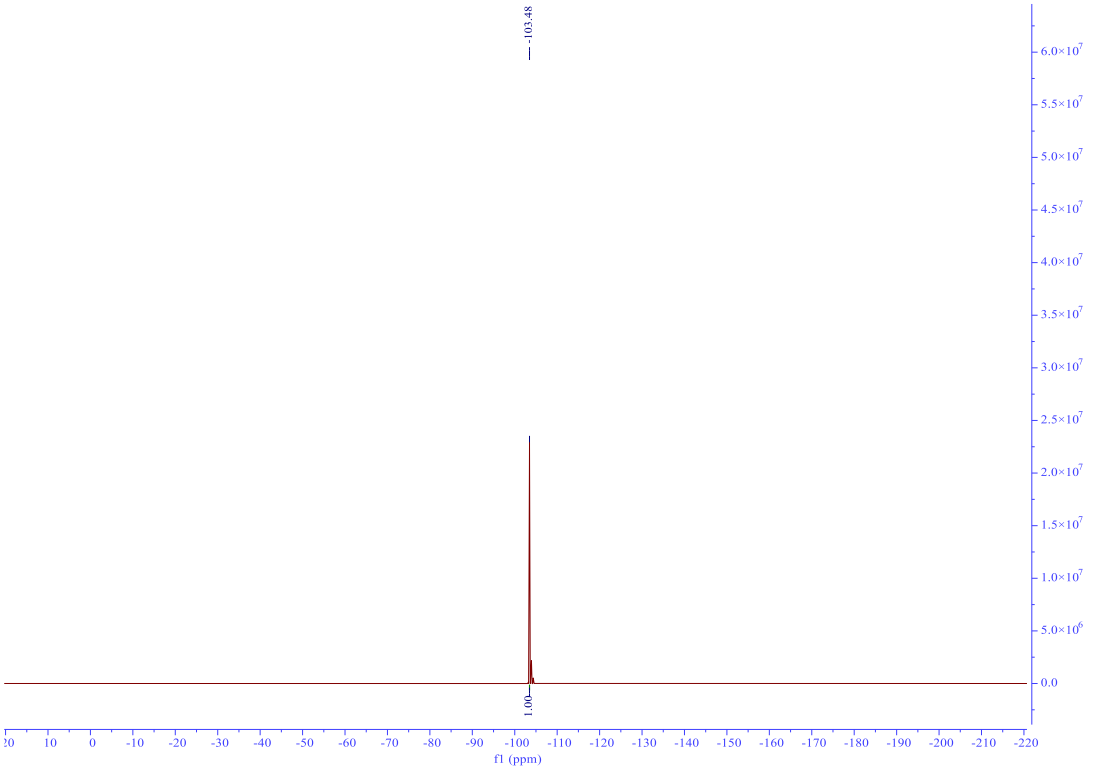
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-isopropylbenzo(dithioperoxoate) (3-5)



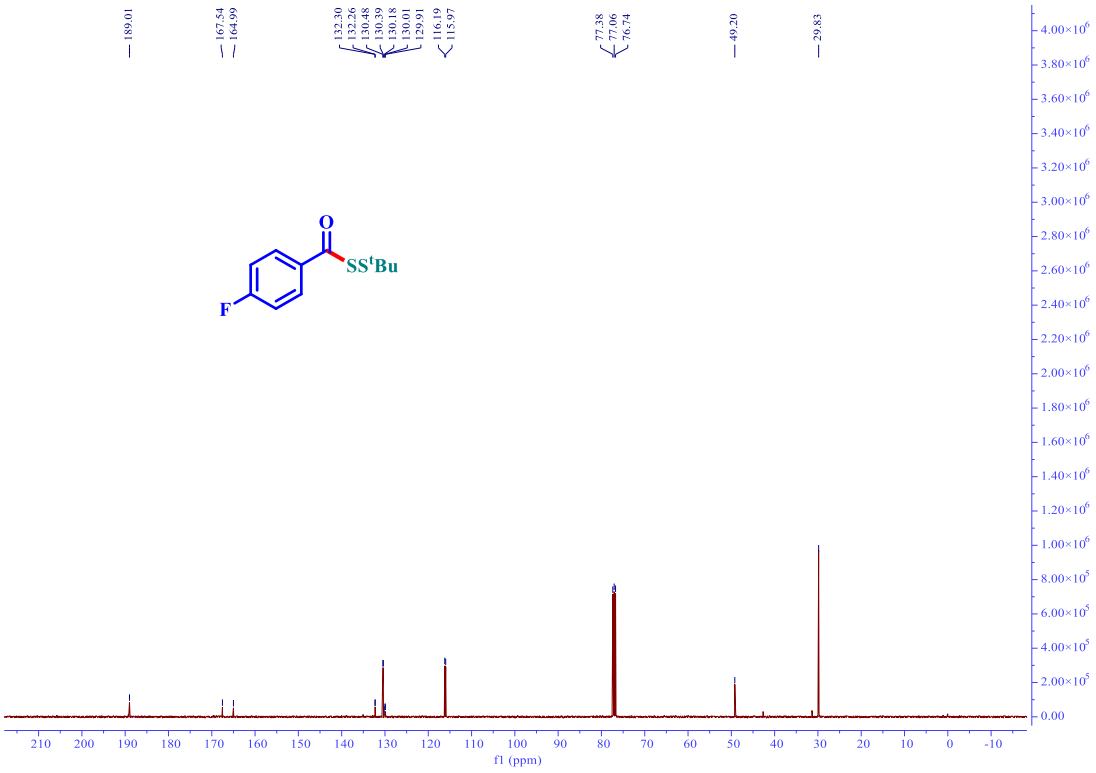
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-fluorobenzo(dithioperoxoate) (3-7)



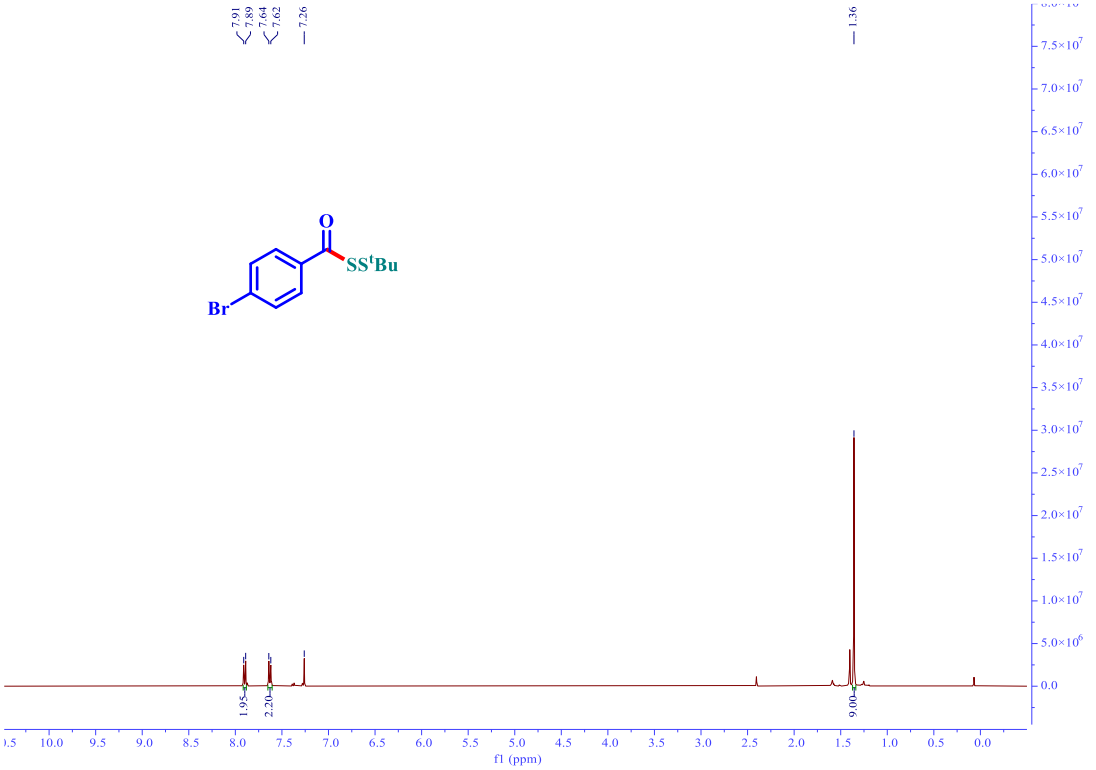
^{19}F NMR Spectrum of *SS*-(tert-butyl) 4-fluorobenzo(dithioperoxoate) (3-7)



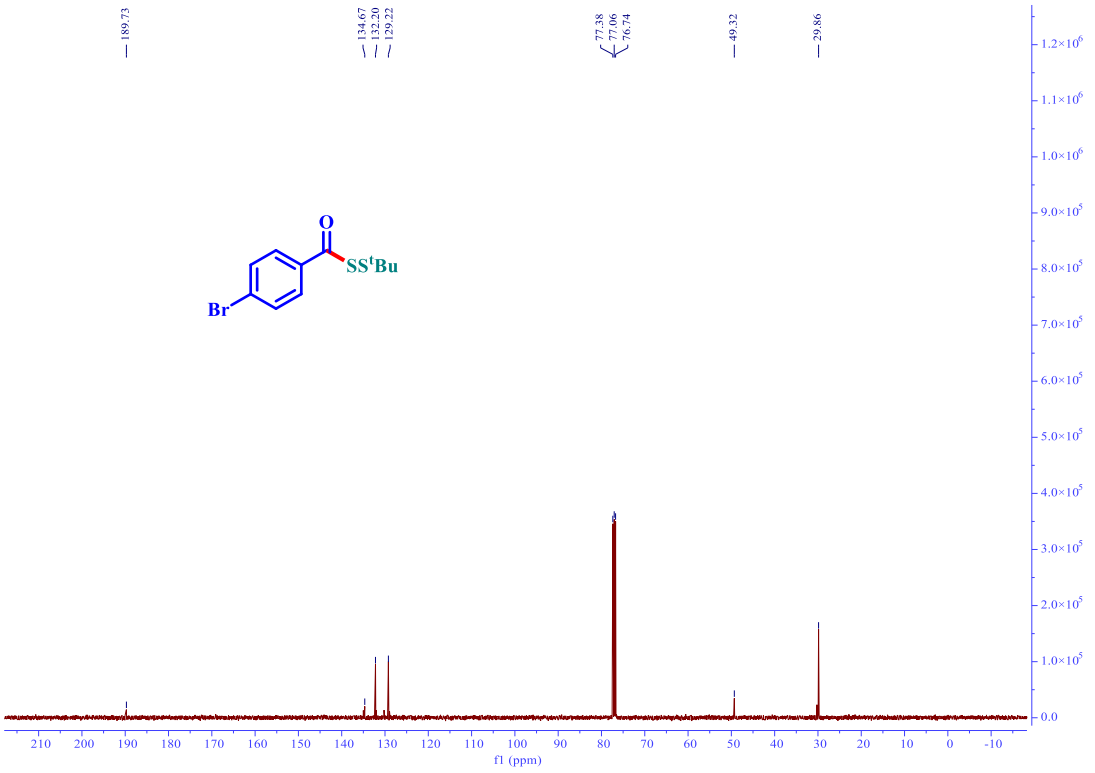
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-fluorobenzo(dithioperoxoate) (3-7)



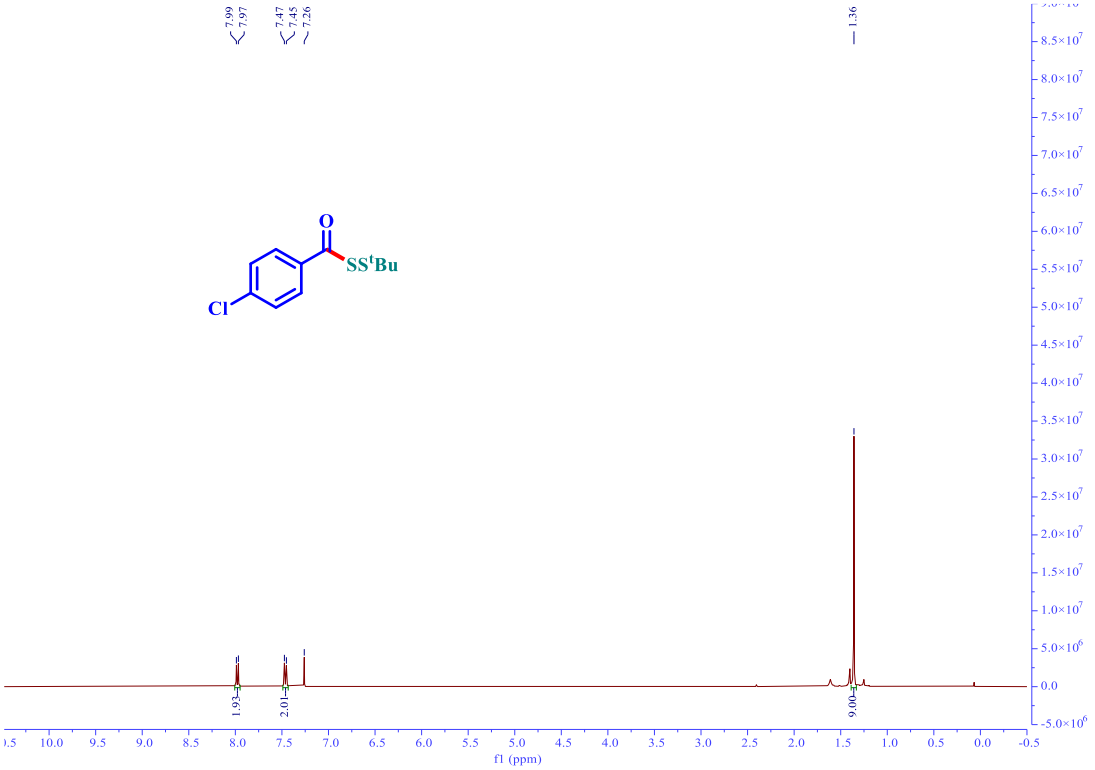
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-bromobenzo(dithioperoxoate) (3-9)



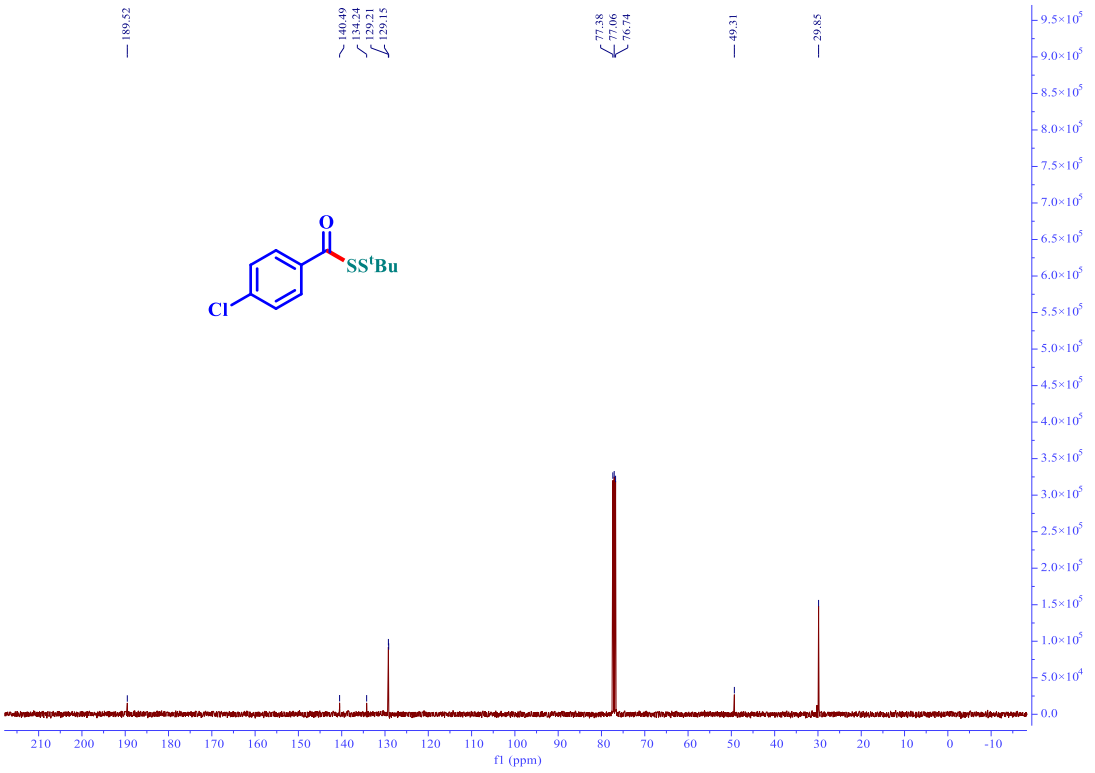
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-bromobenzo(dithioperoxoate) (3-9)



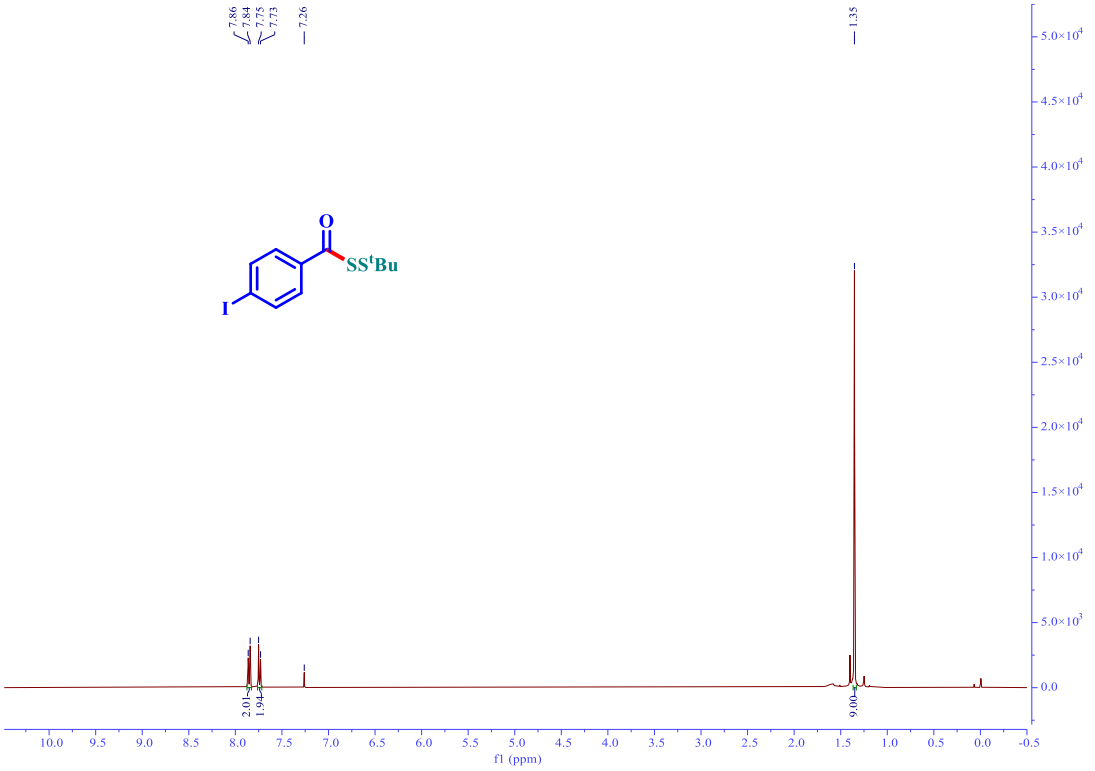
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-chlorobenzo(dithioperoxoate) (3-8)



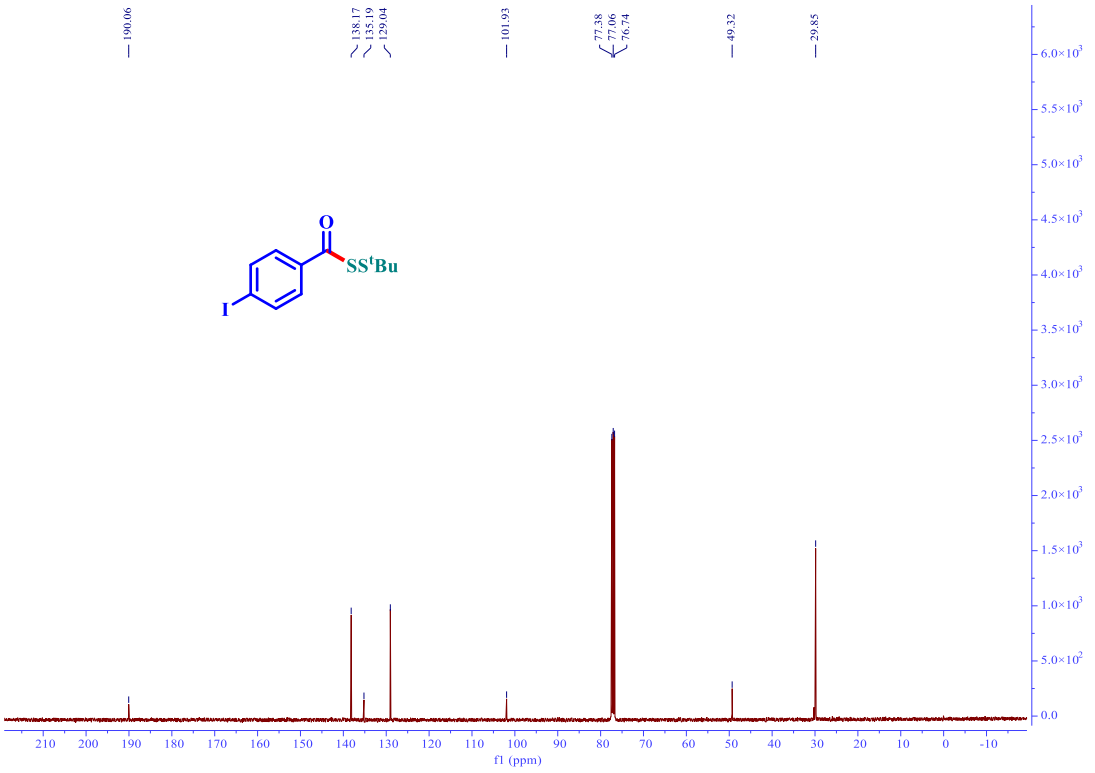
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-chlorobenzo(dithioperoxoate) (3-8)



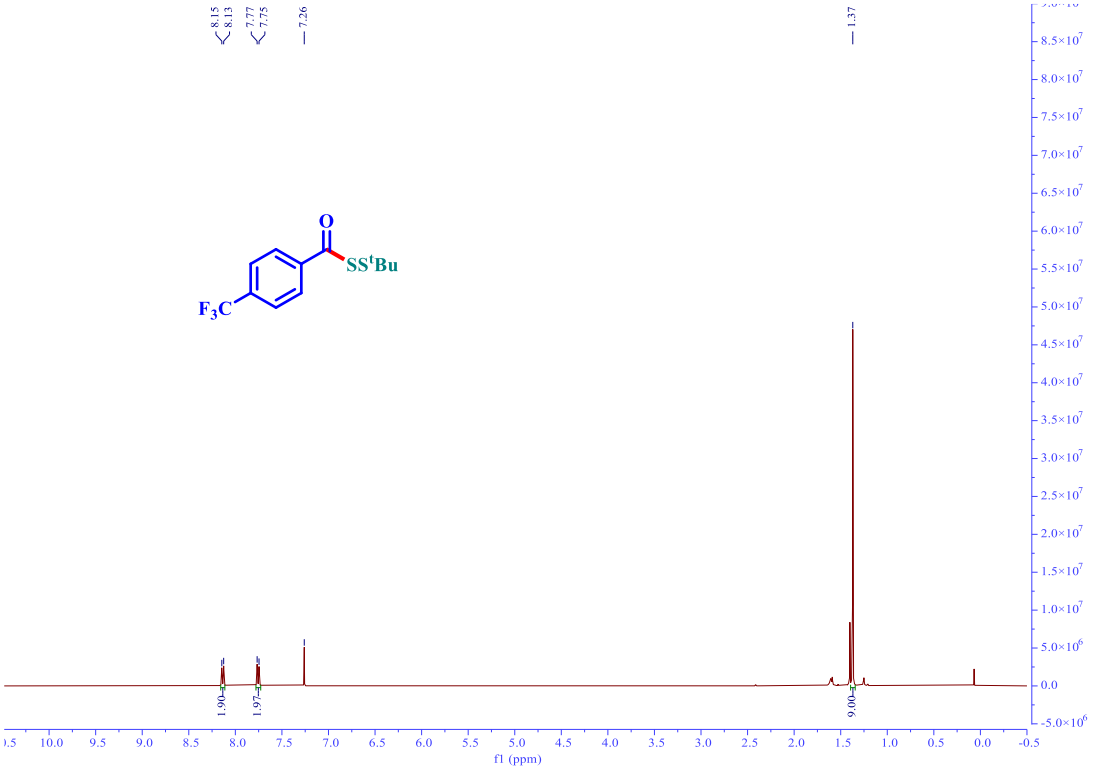
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-iodobenzo(dithioperoxoate) (3-10)



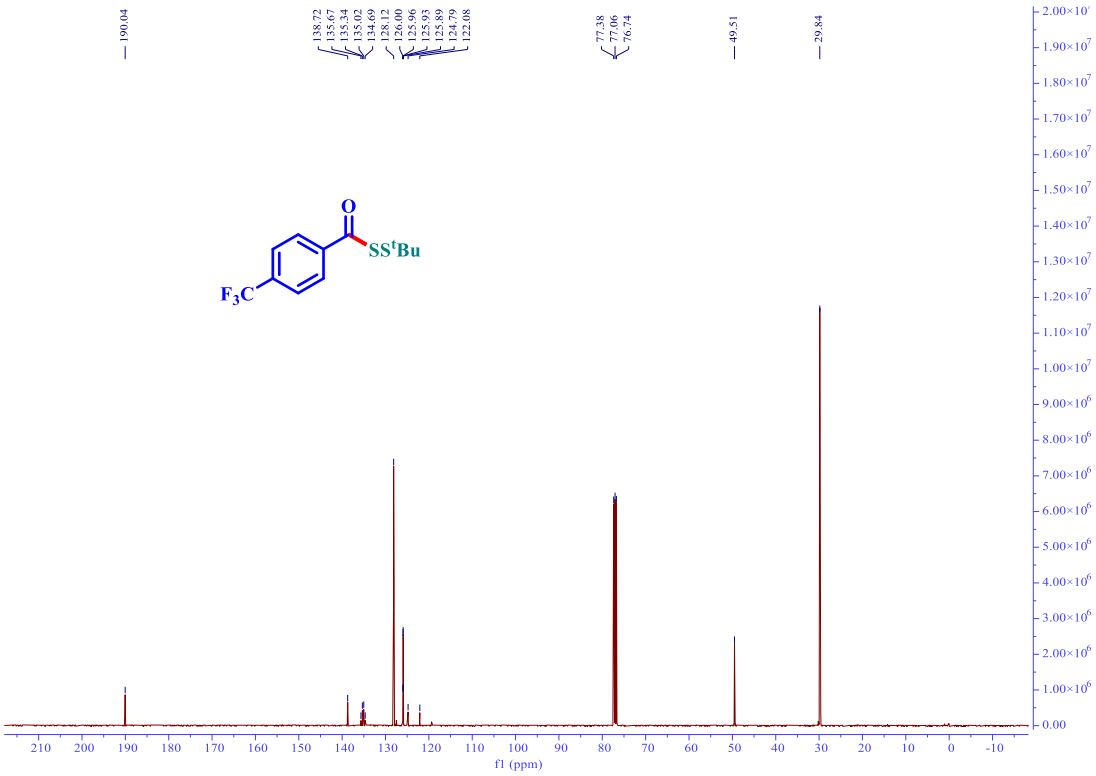
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-iodobenzo(dithioperoxoate) (3-10)



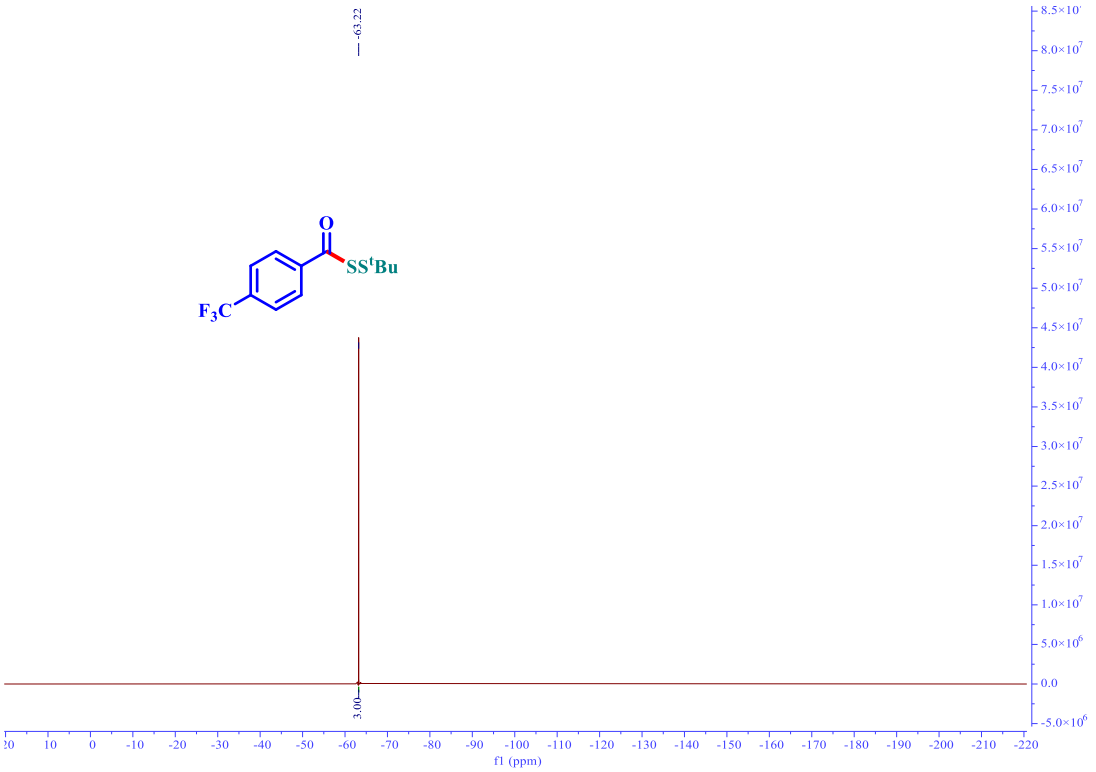
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) (3-11)



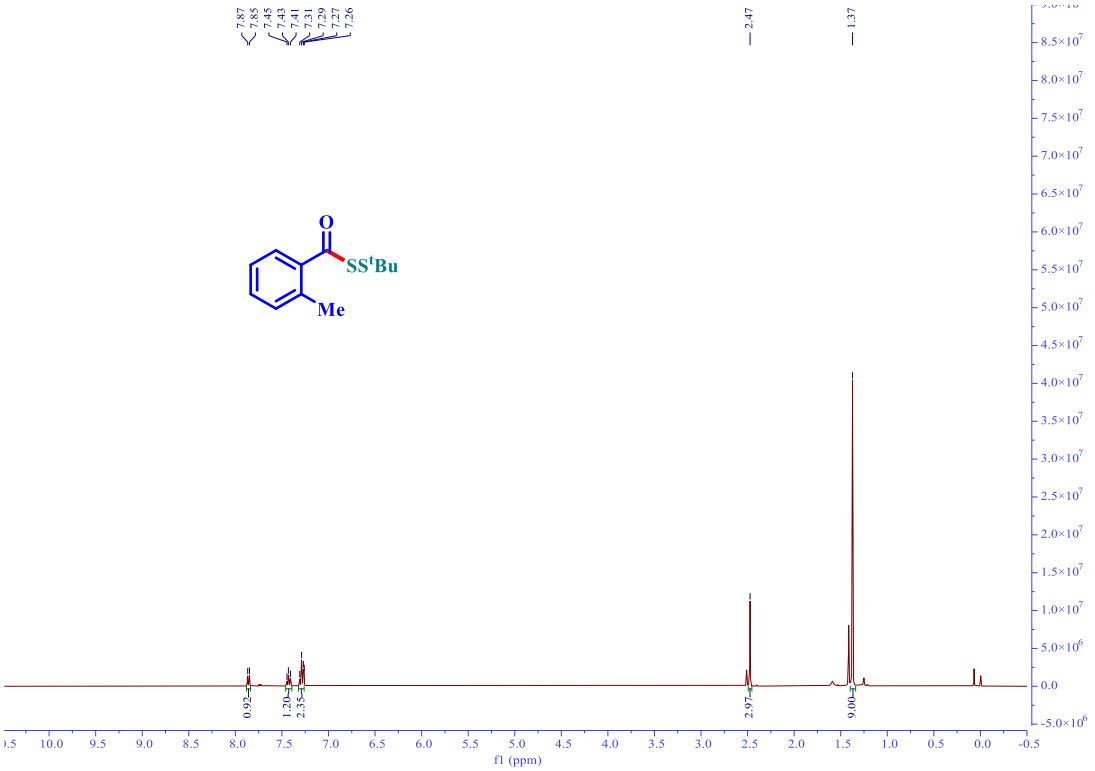
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) (3-11)



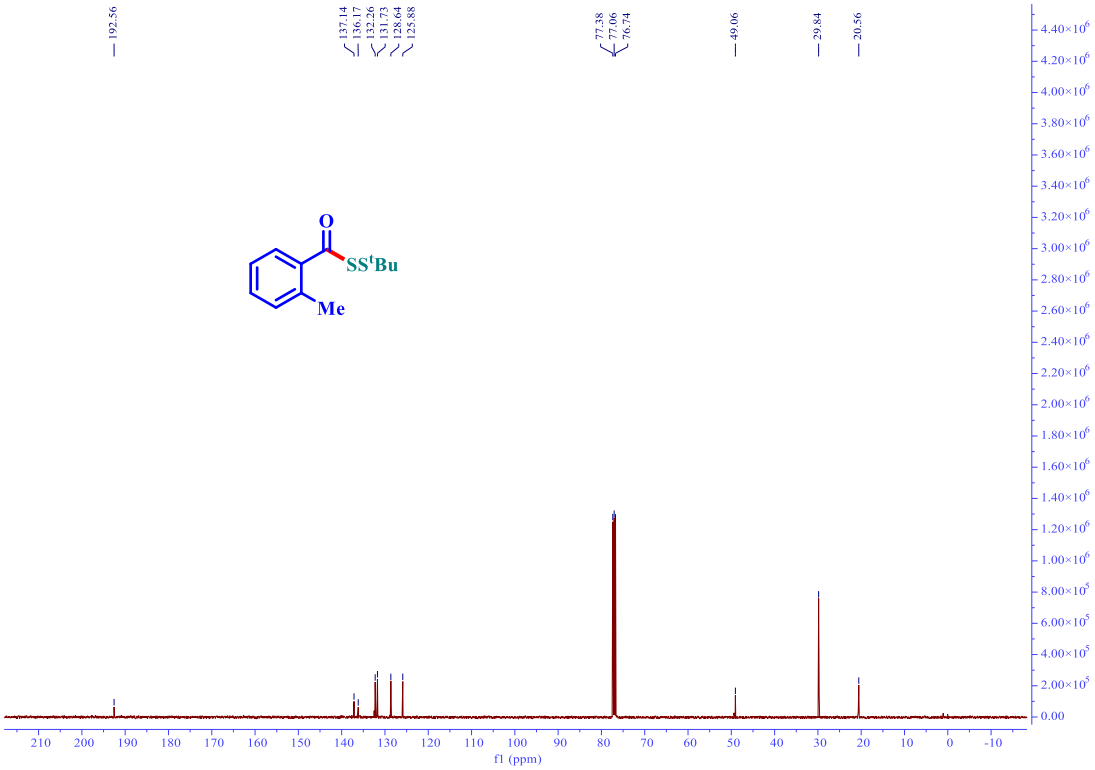
^{19}F NMR Spectrum of *SS*-(tert-butyl) 4-(trifluoromethyl)benzo(dithioperoxoate) (3-11)



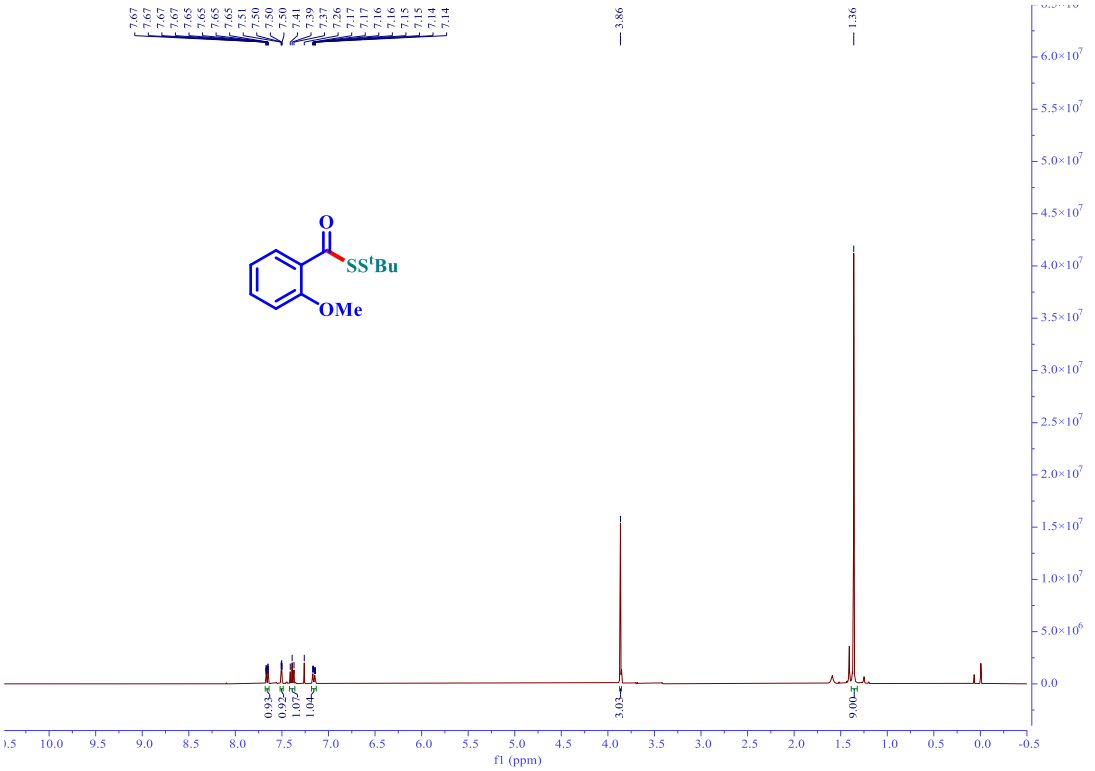
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2-methylbenzo(dithioperoxoate) (3-12)



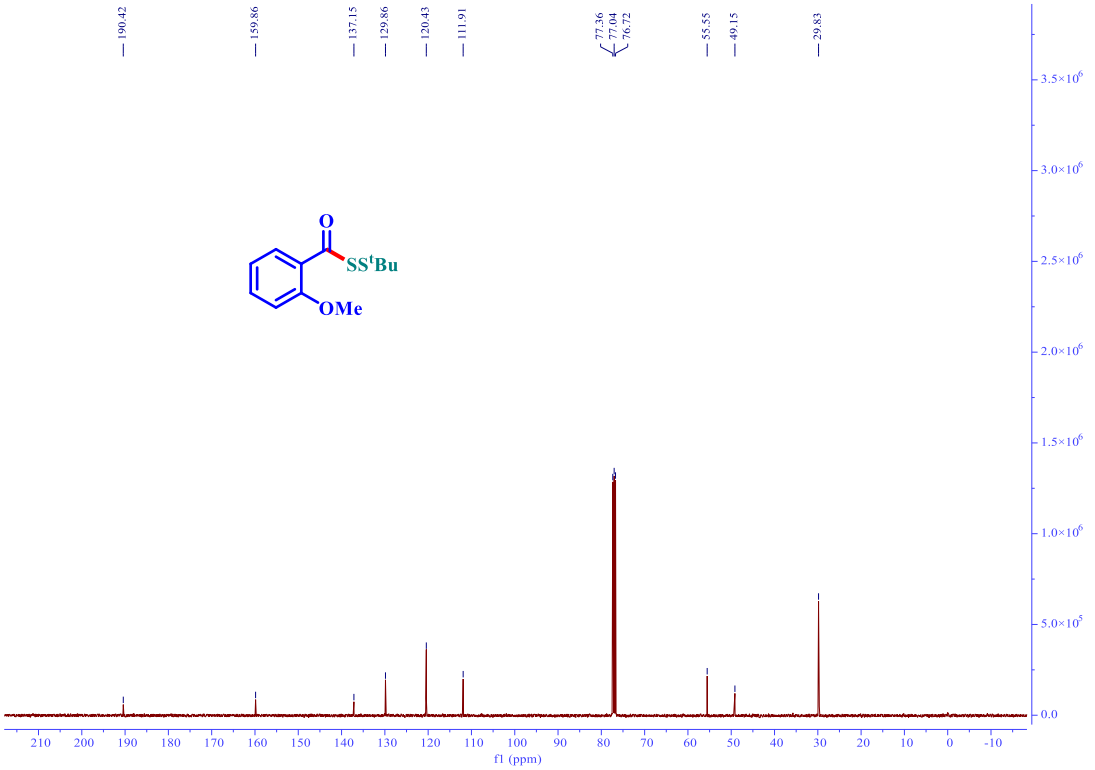
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2-methylbenzo(dithioperoxoate) (3-12)



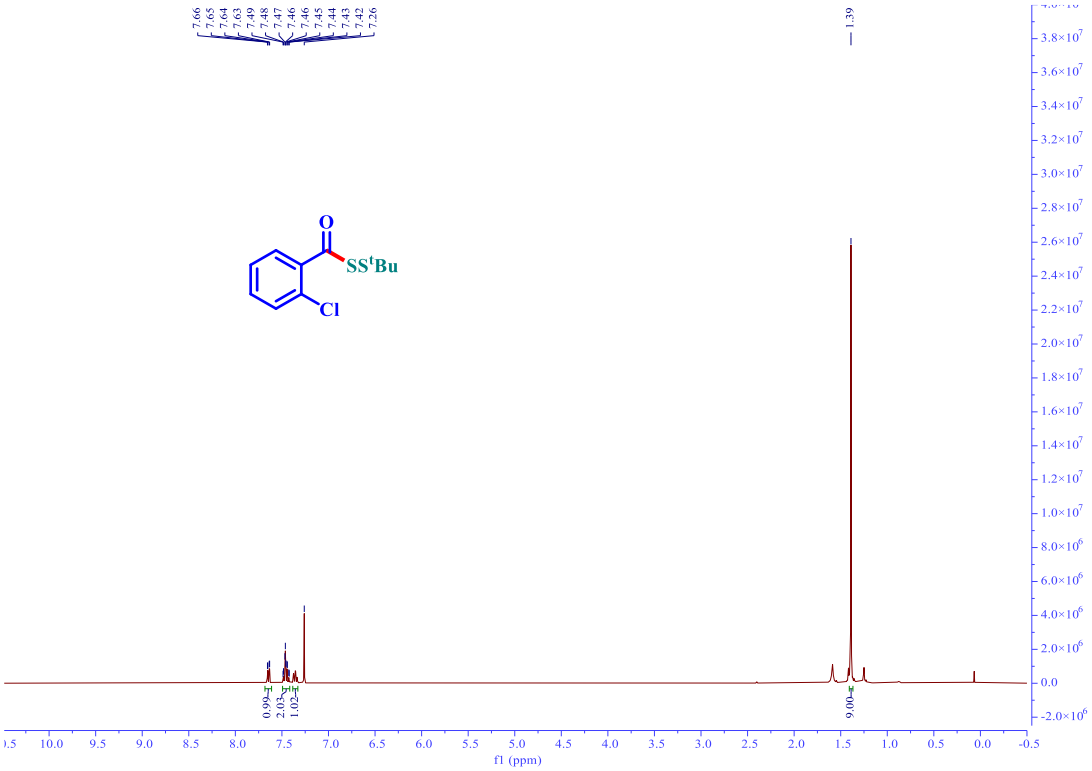
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2-methoxybenzo(dithioperoxoate) (3-13)



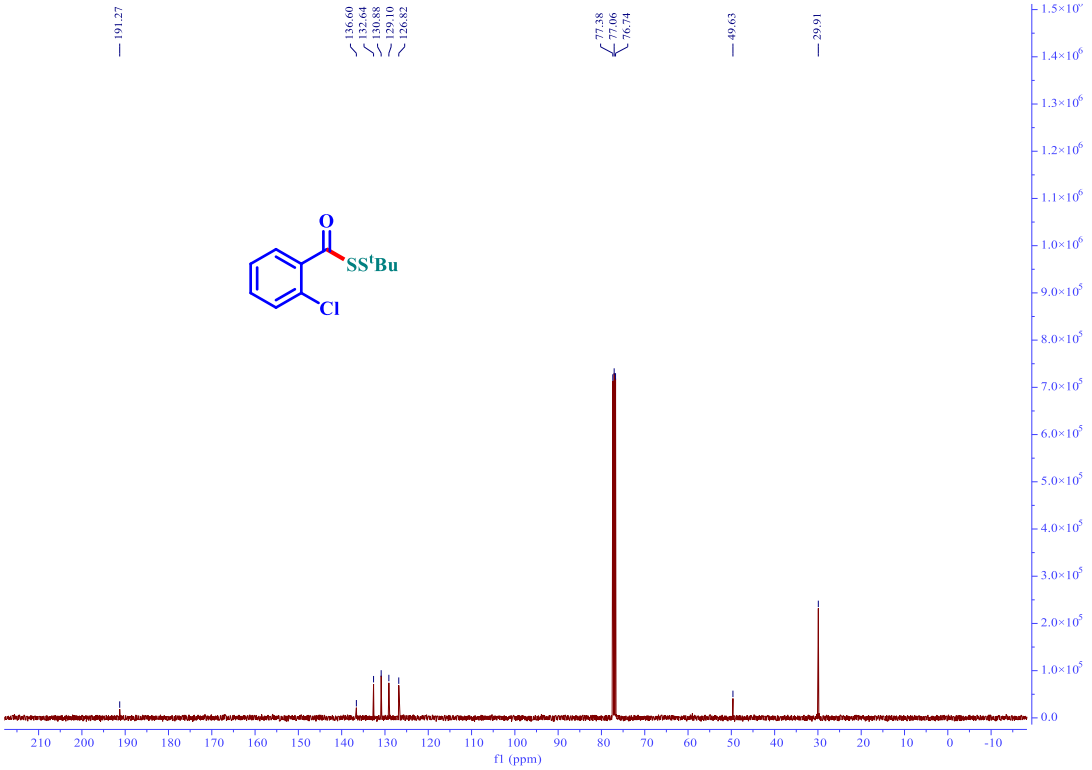
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2-methoxybenzo(dithioperoxoate) (3-13)



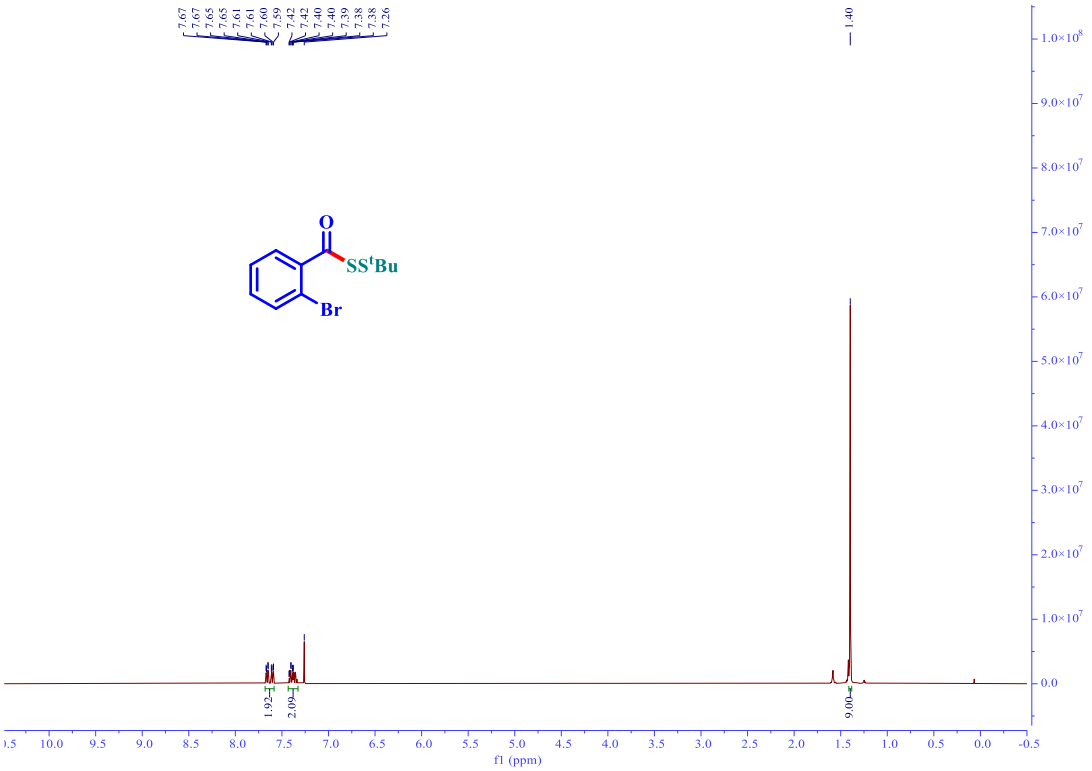
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2-chlorobenzo(dithioperoxoate) (3-14)



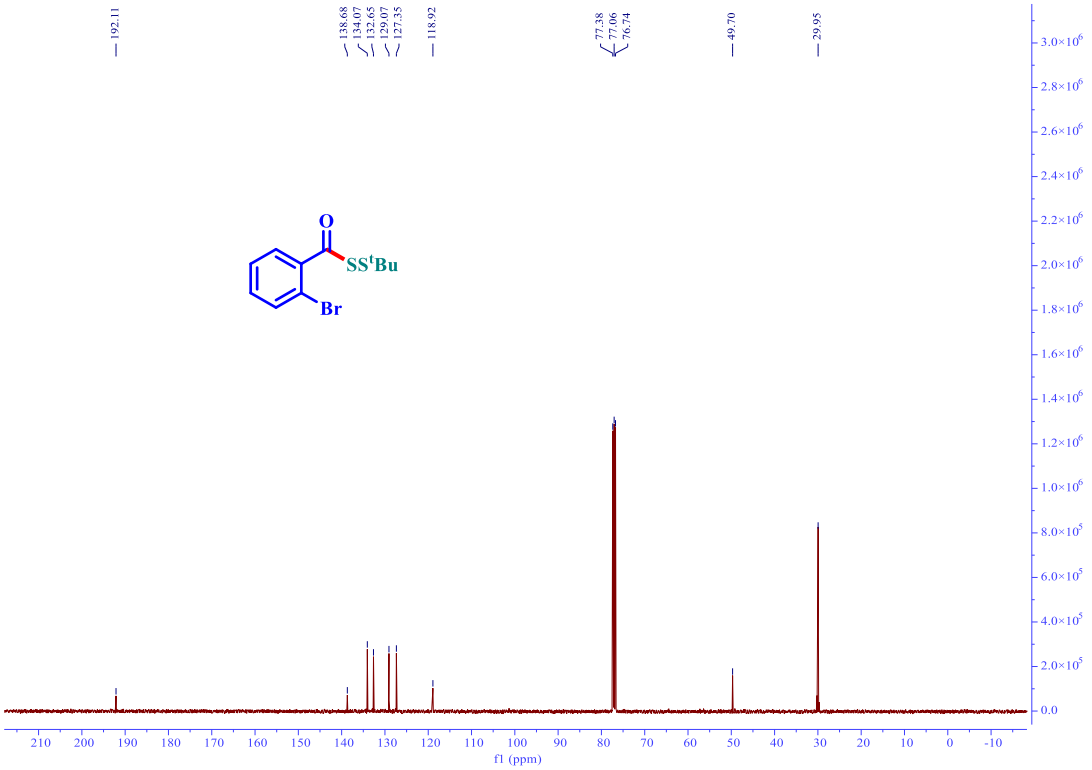
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2-chlorobenzo(dithioperoxoate) (3-14)



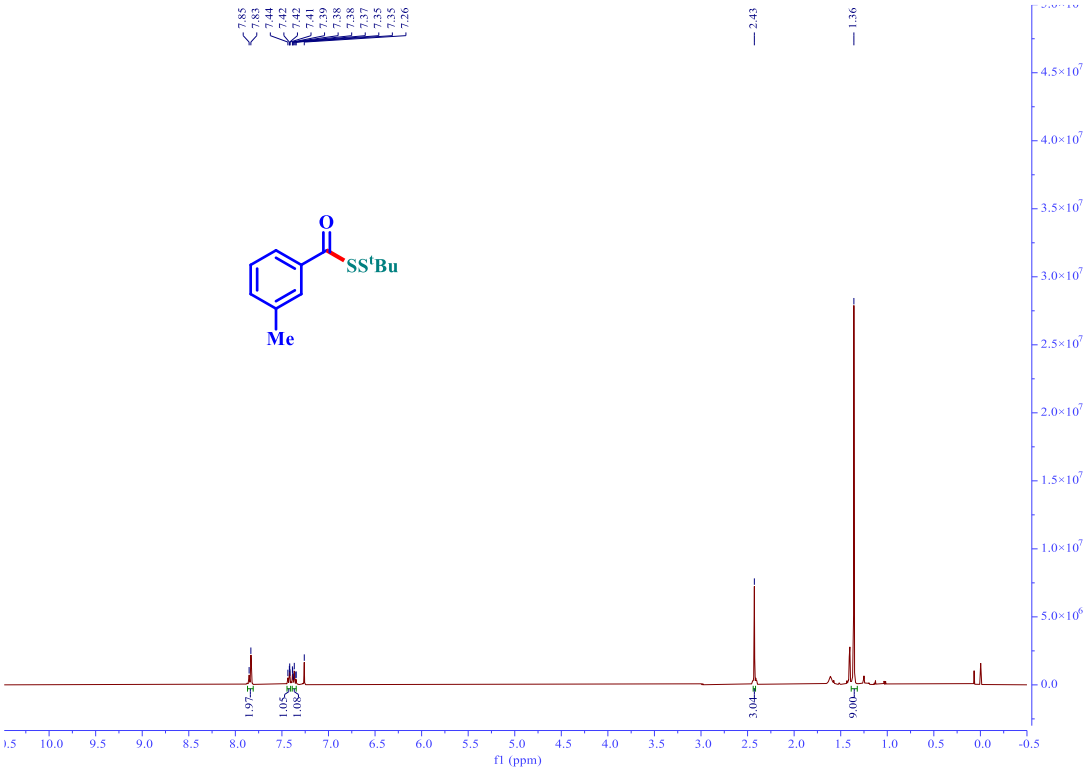
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2-bromobenzo(dithioperoxoate) (3-15)



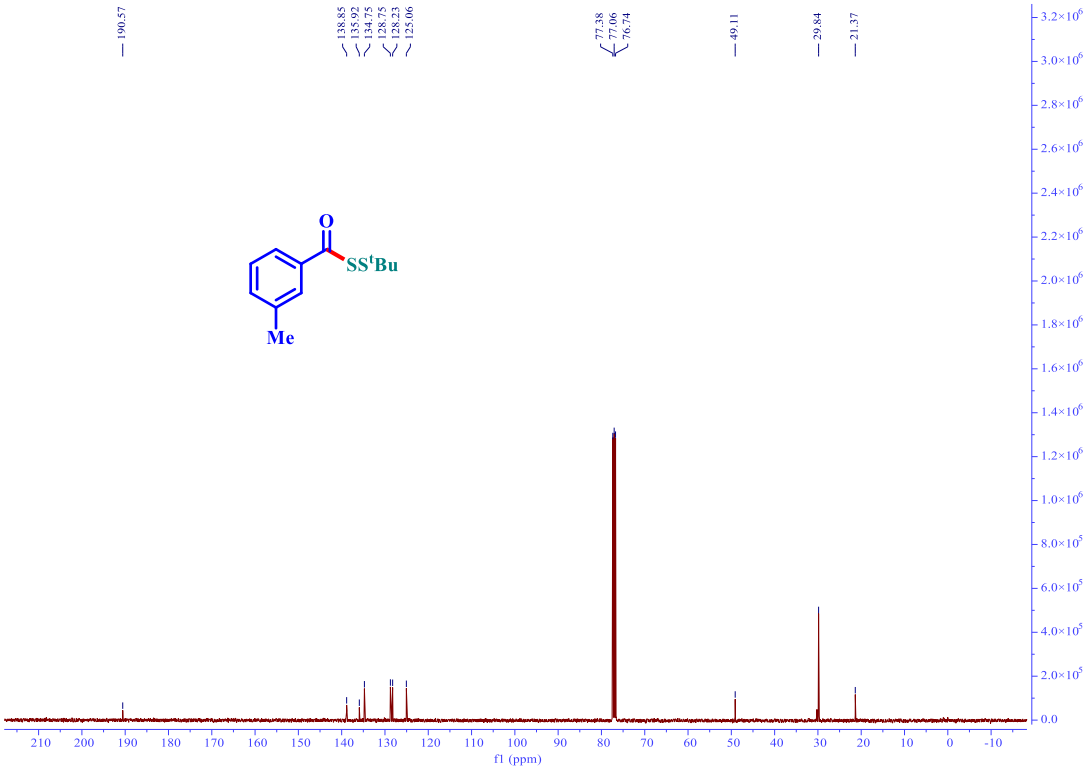
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2-bromobenzo(dithioperoxoate) (3-15)



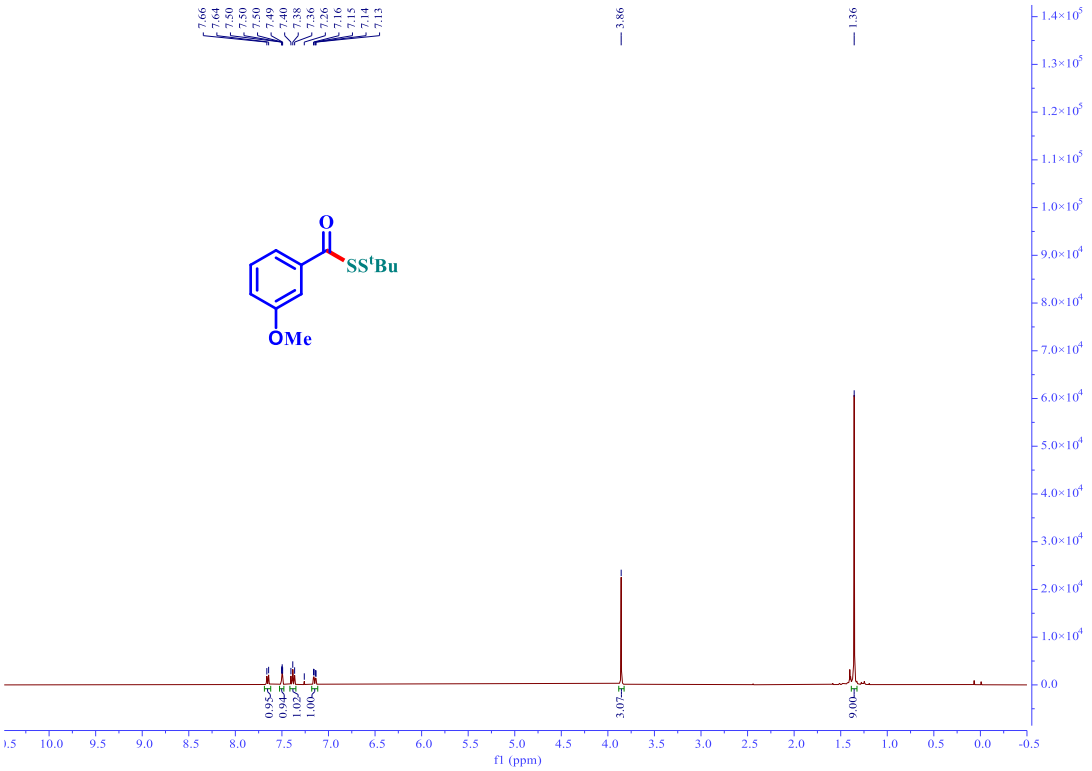
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3-methylbenzo(dithioperoxoate) (3-16)



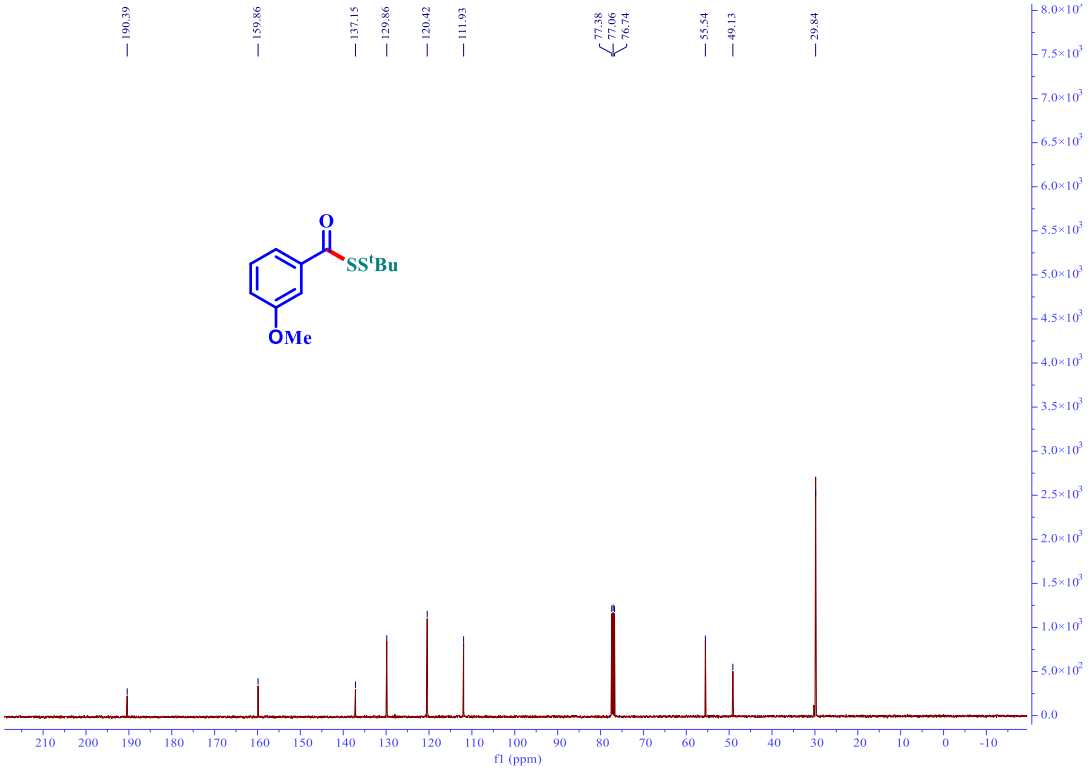
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3-methylbenzo(dithioperoxoate) (3-16)



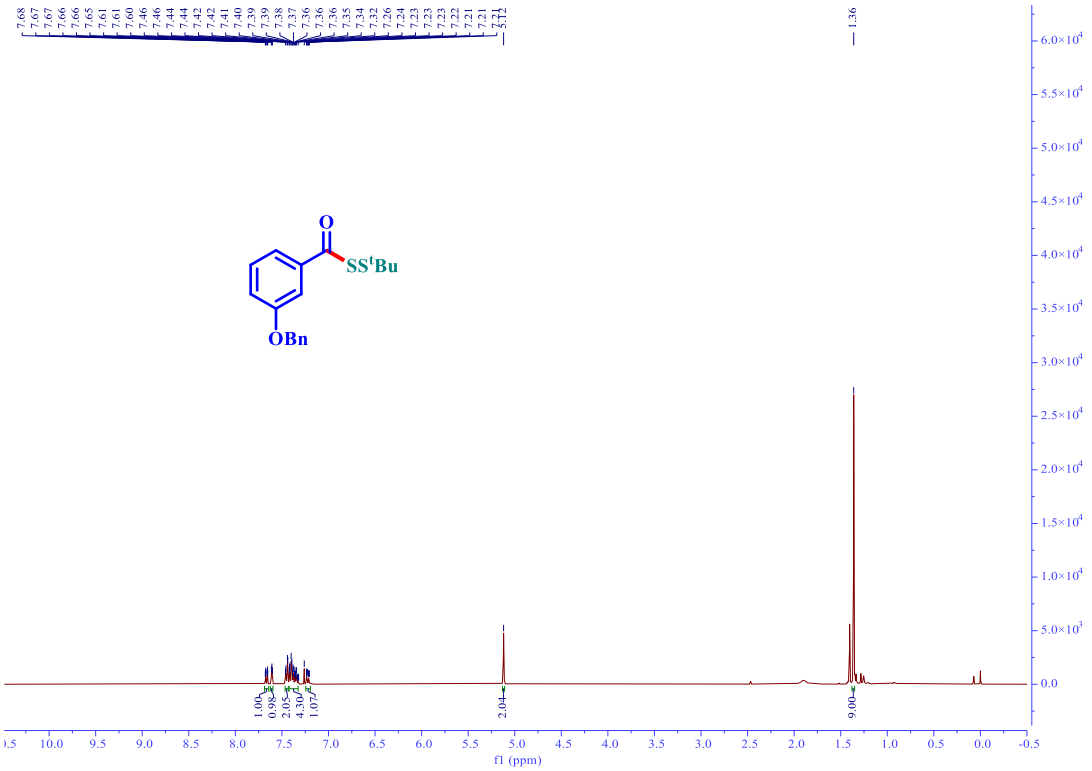
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3-methoxybenzo(dithioperoxoate) (3-17)



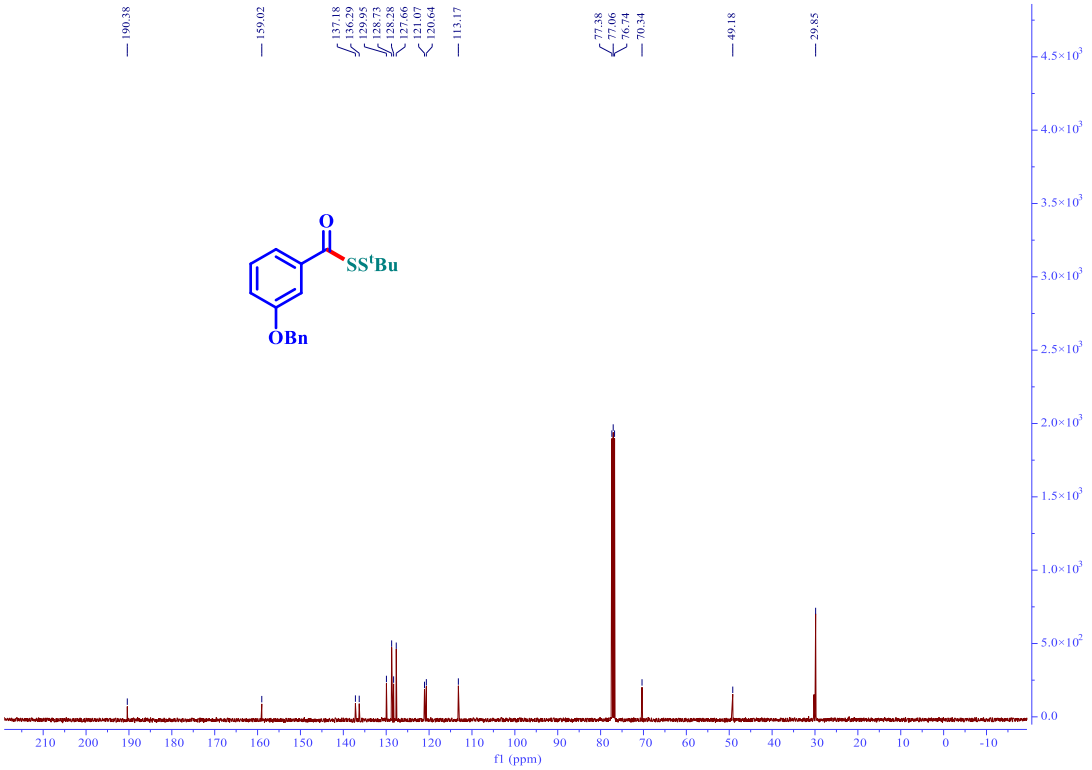
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3-methoxybenzo(dithioperoxoate) (3-17)



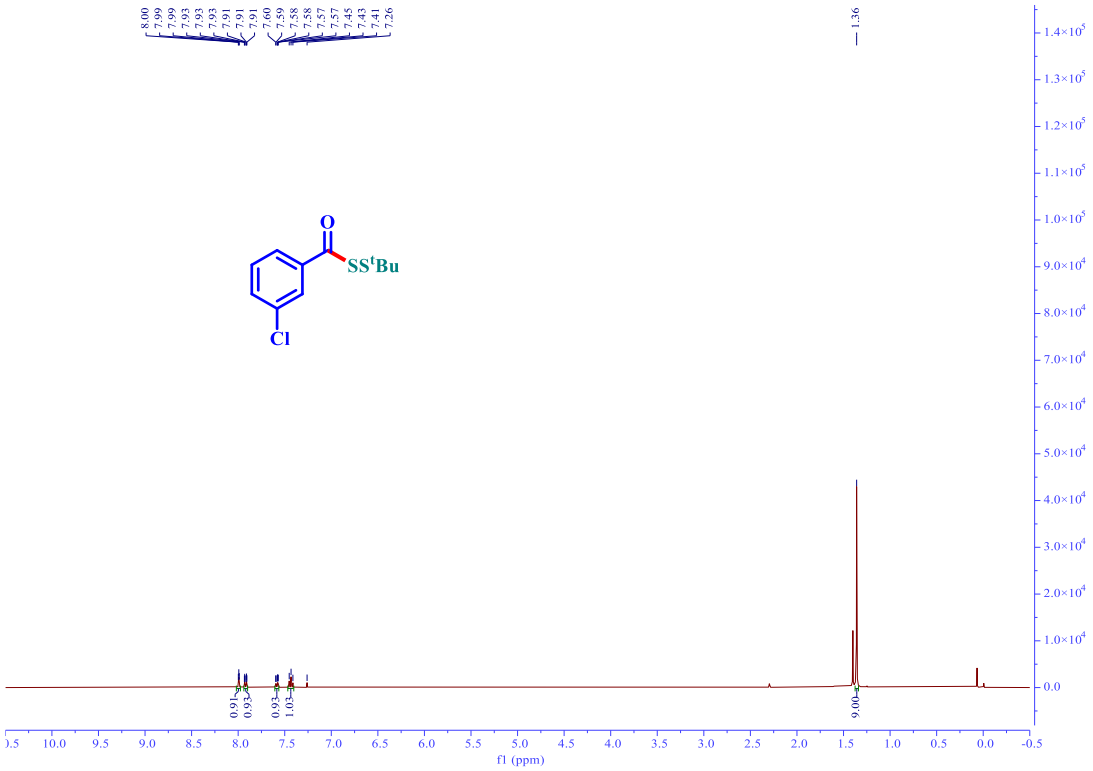
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3-(benzyloxy)benzo(dithioperoxoate) (3-18)



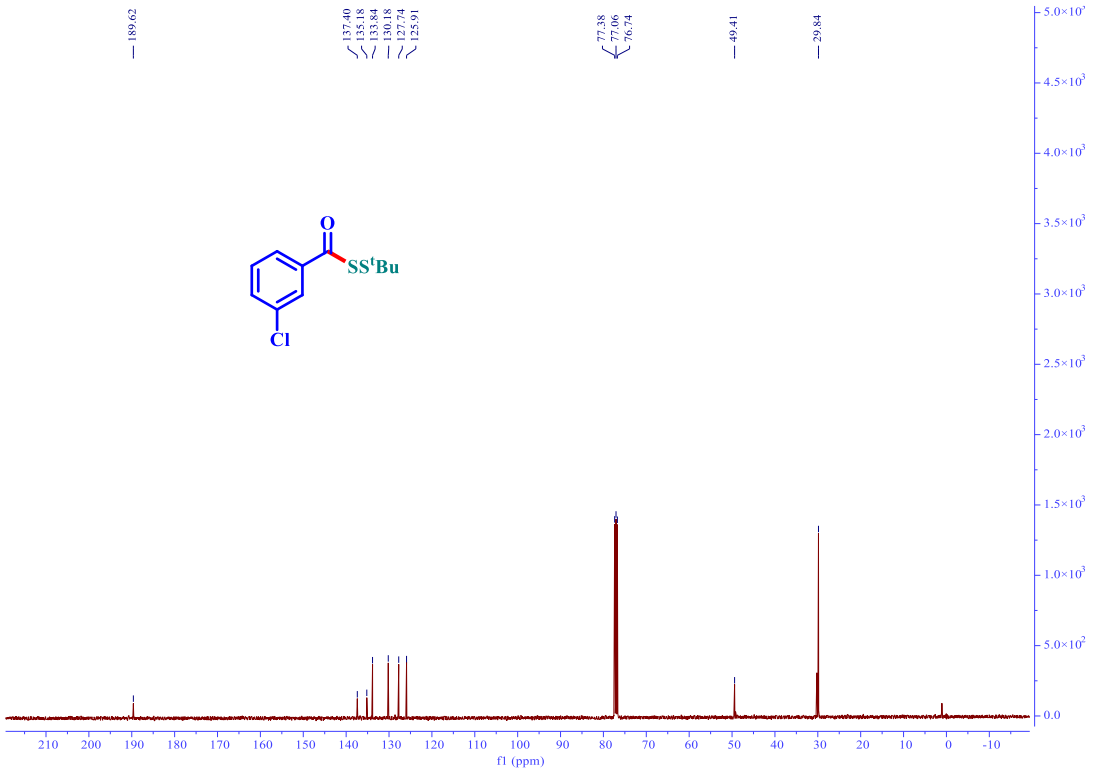
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3-(benzyloxy)benzo(dithioperoxoate) (3-18)



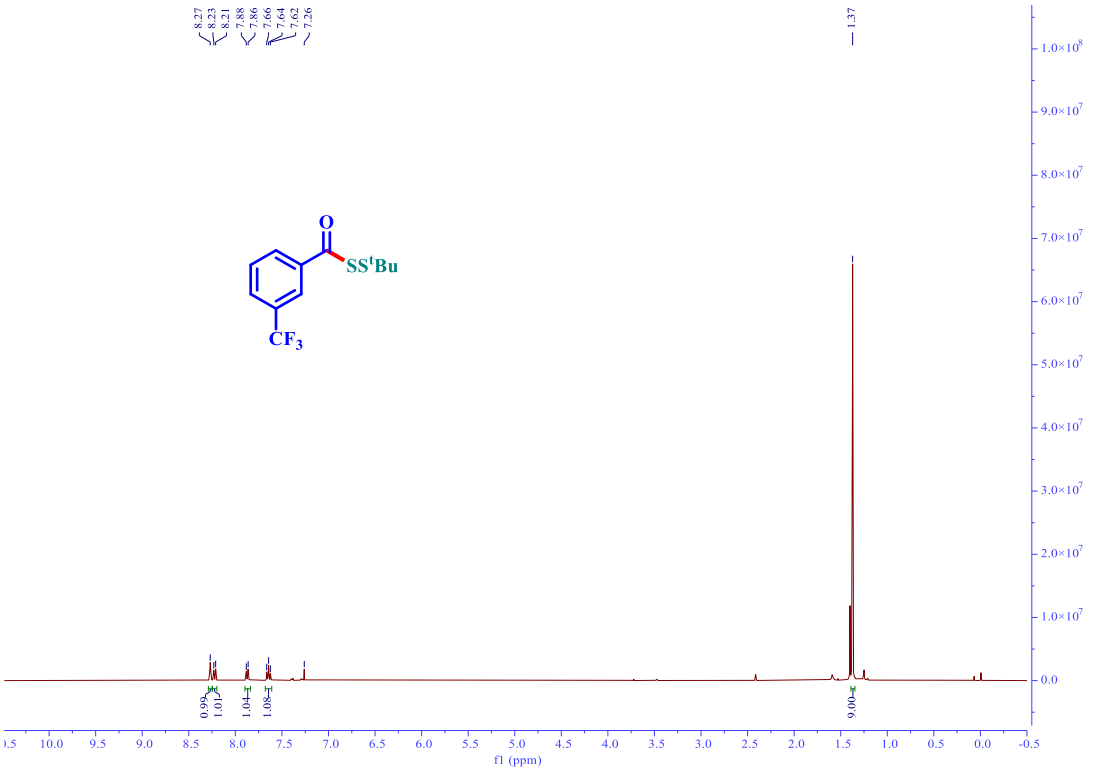
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3-chlorobenzo(dithioperoxoate) (3-19)



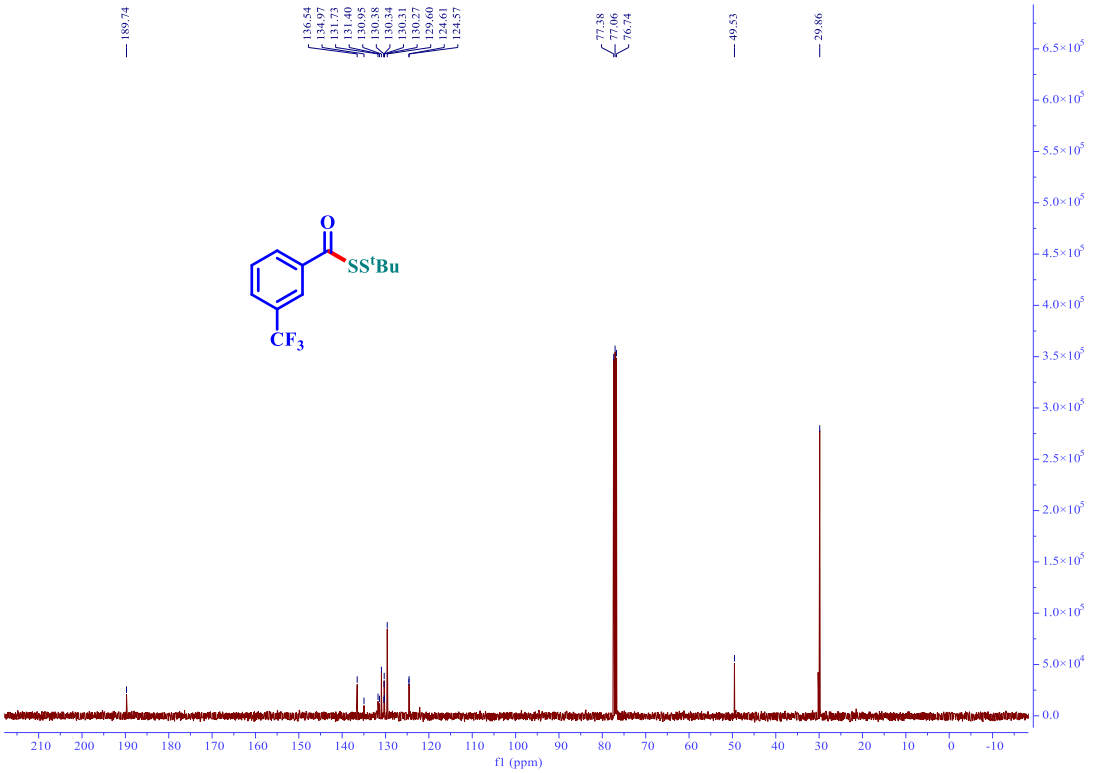
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3-chlorobenzo(dithioperoxoate) (3-19)



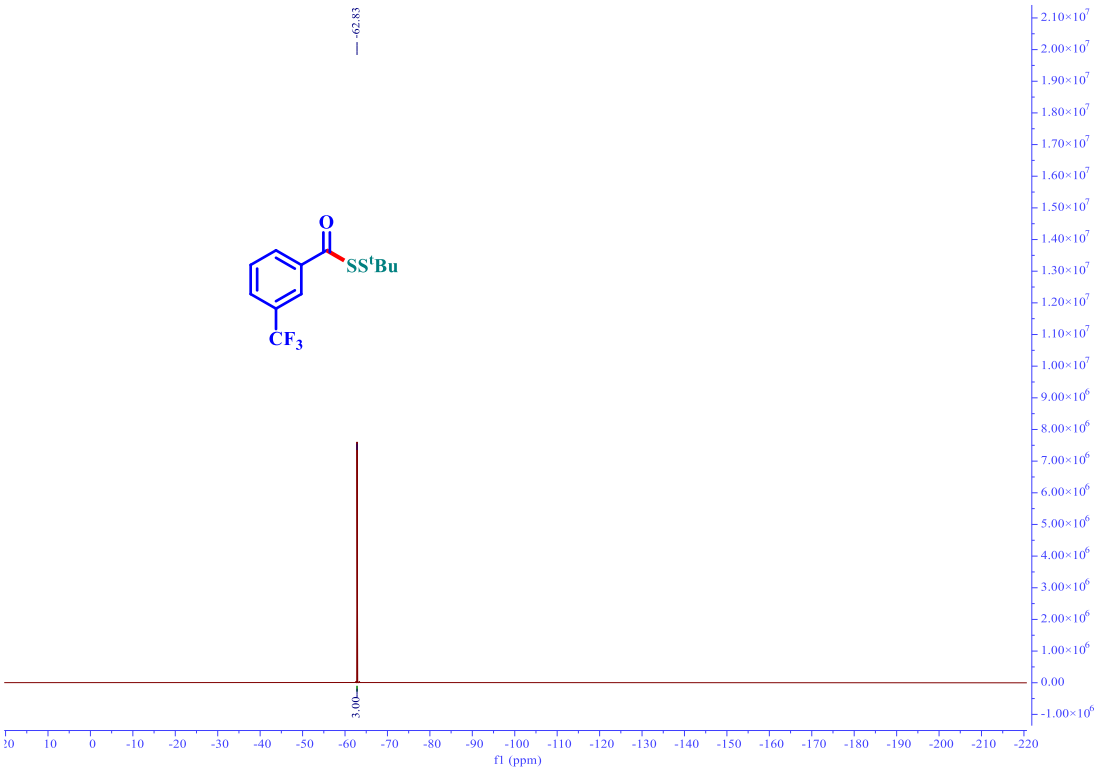
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3-(trifluoromethyl)benzo(dithioperoxoate) (3-20)



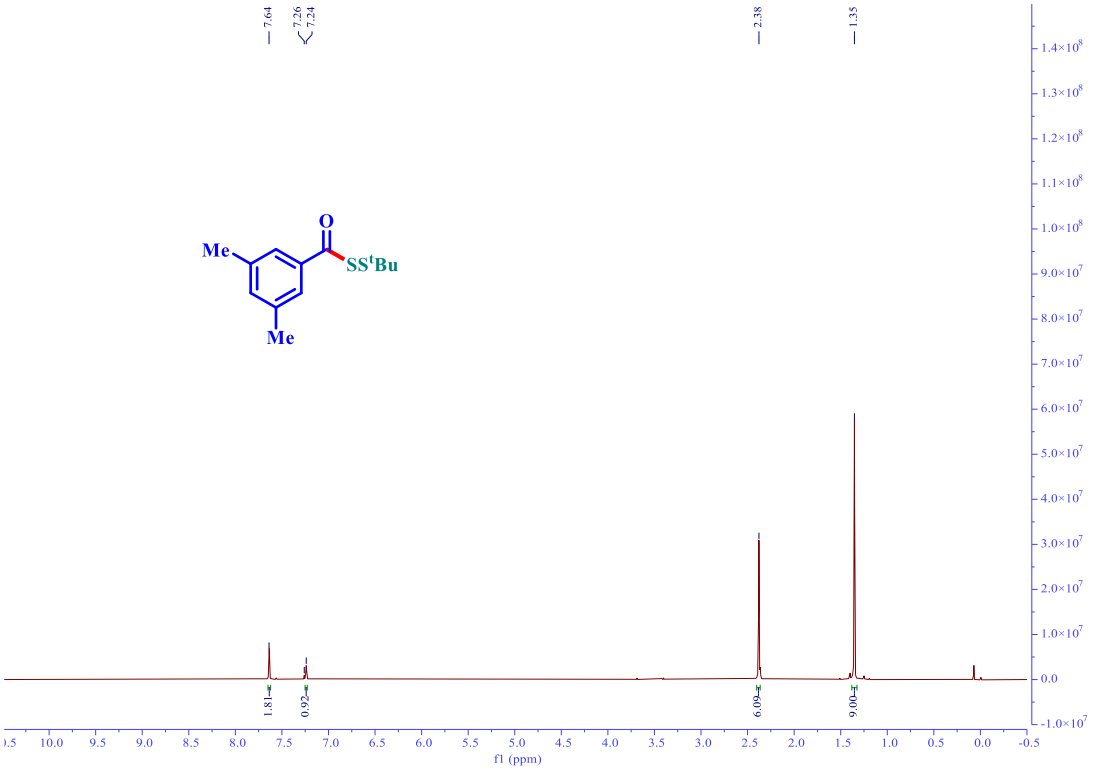
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3-(trifluoromethyl)benzo(dithioperoxoate) (3-20)



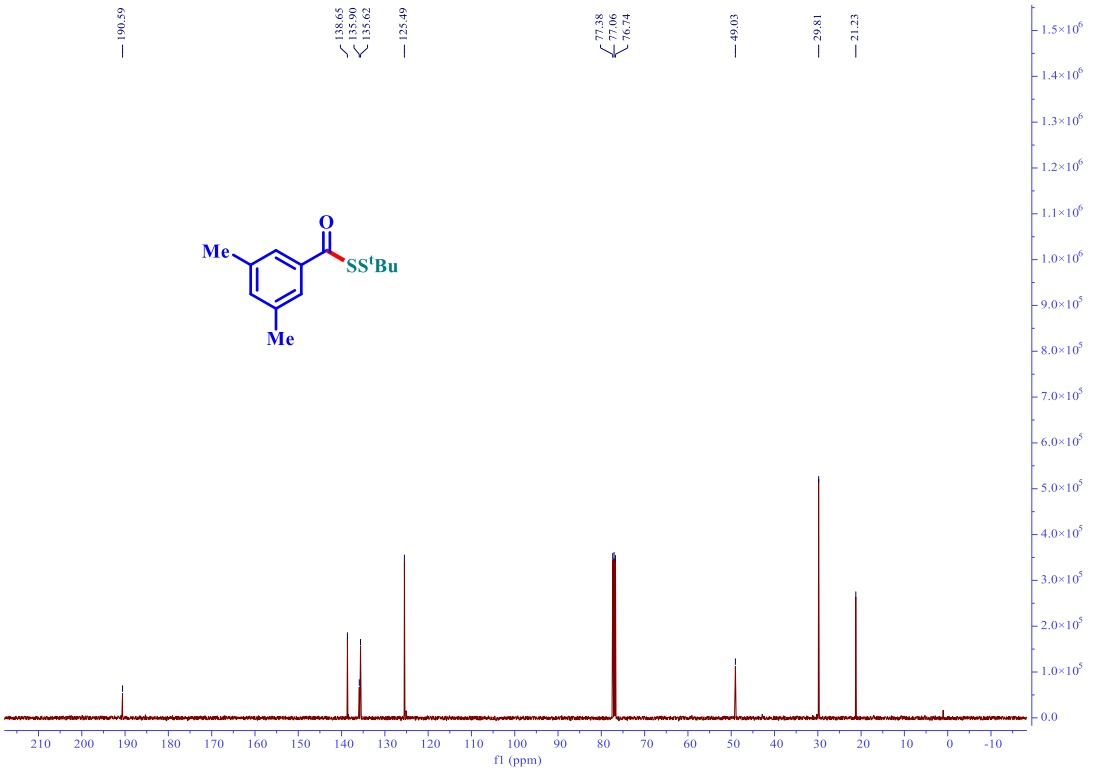
^{19}F NMR Spectrum of *SS*-(tert-butyl) 3-(trifluoromethyl)benzo(dithioperoxoate) (3-20)



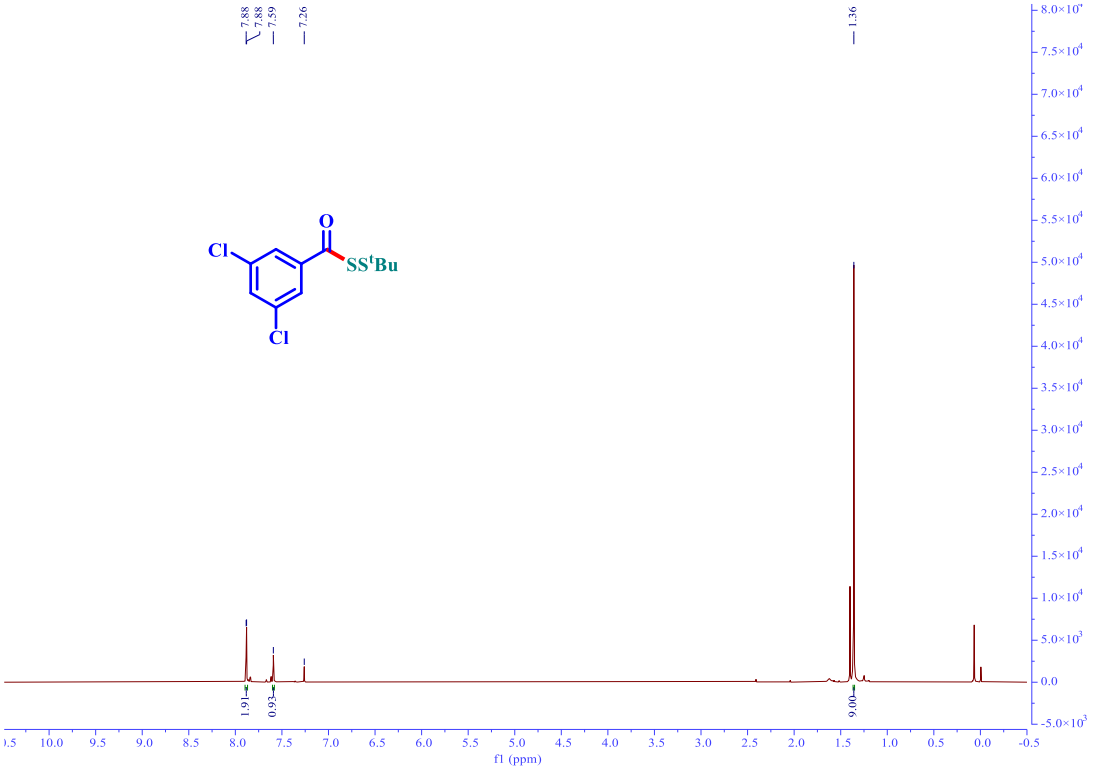
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3,5-dimethylbenzo(dithioperoxoate) (3-21)



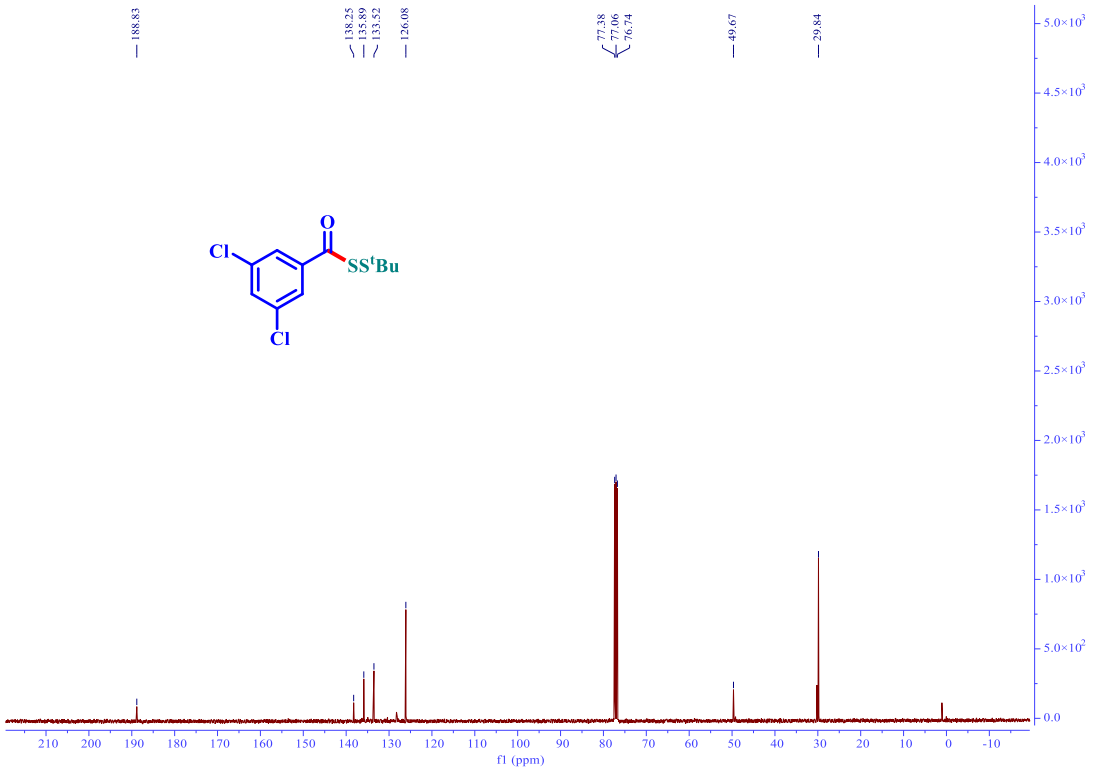
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3,5-dimethylbenzo(dithioperoxoate) (3-21)



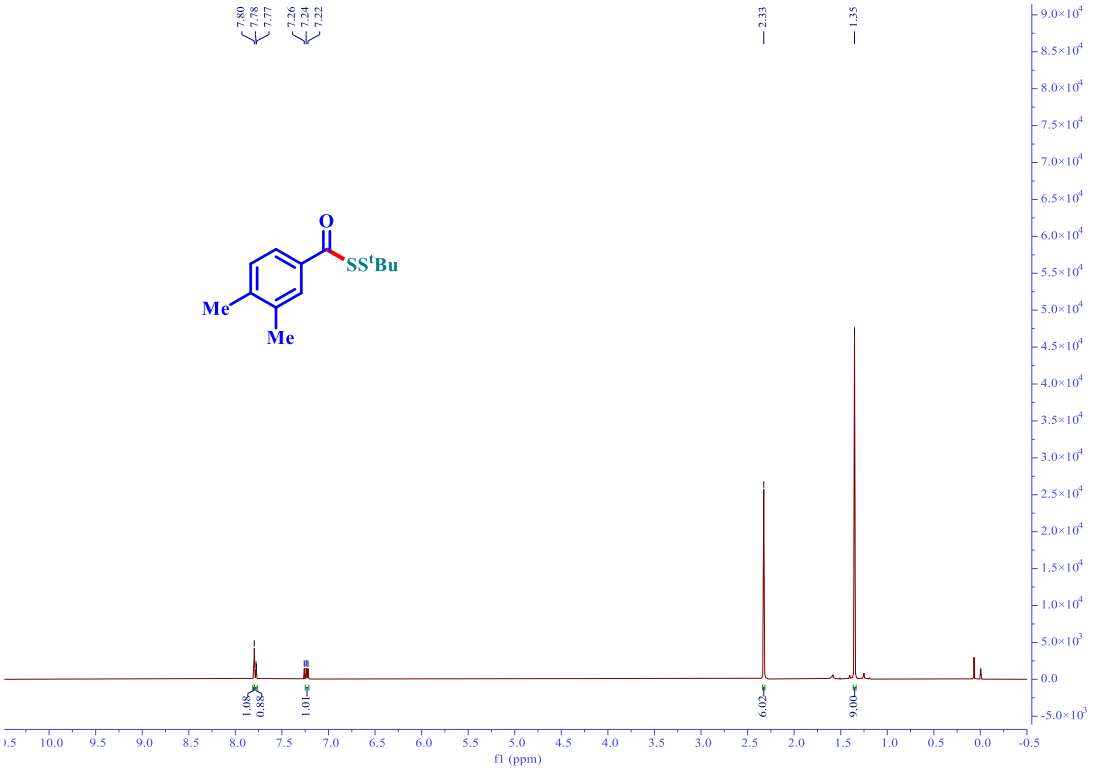
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3,5-dichlorobenzo(dithioperoxoate) (3-22)



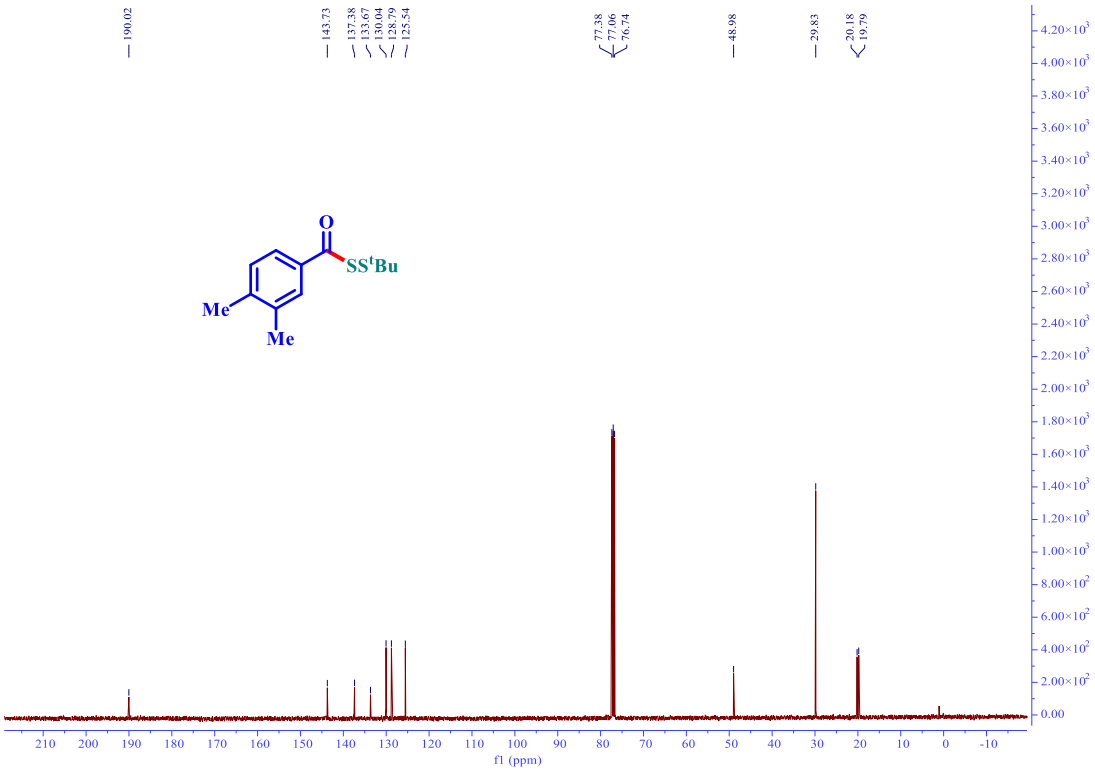
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3,5-dichlorobenzo(dithioperoxoate) (3-22)



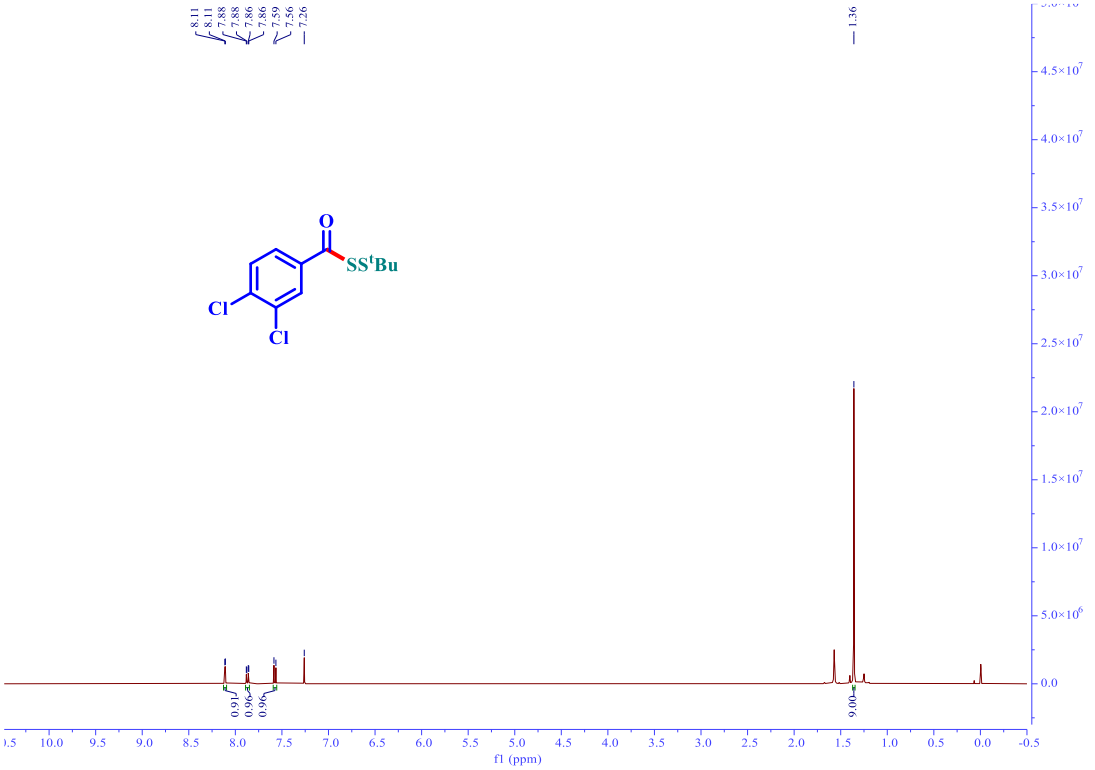
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3,4-dimethylbenzo(dithioperoxoate) (3-23)



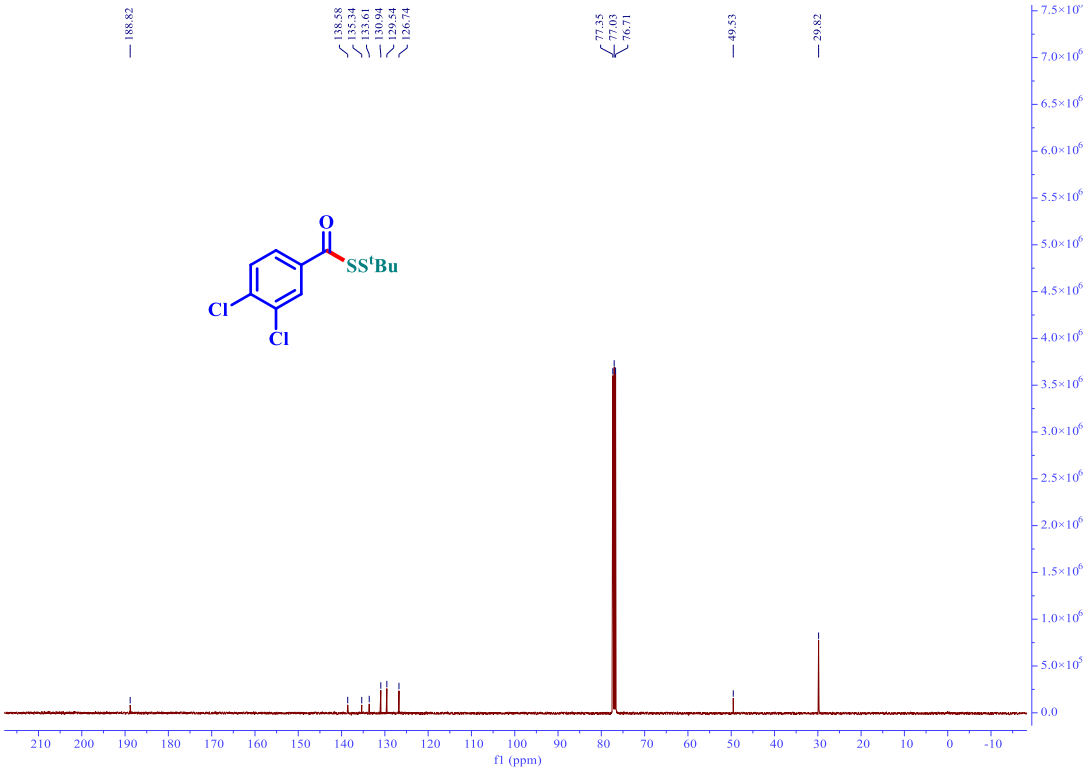
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3,4-dimethylbenzo(dithioperoxoate) (3-23)



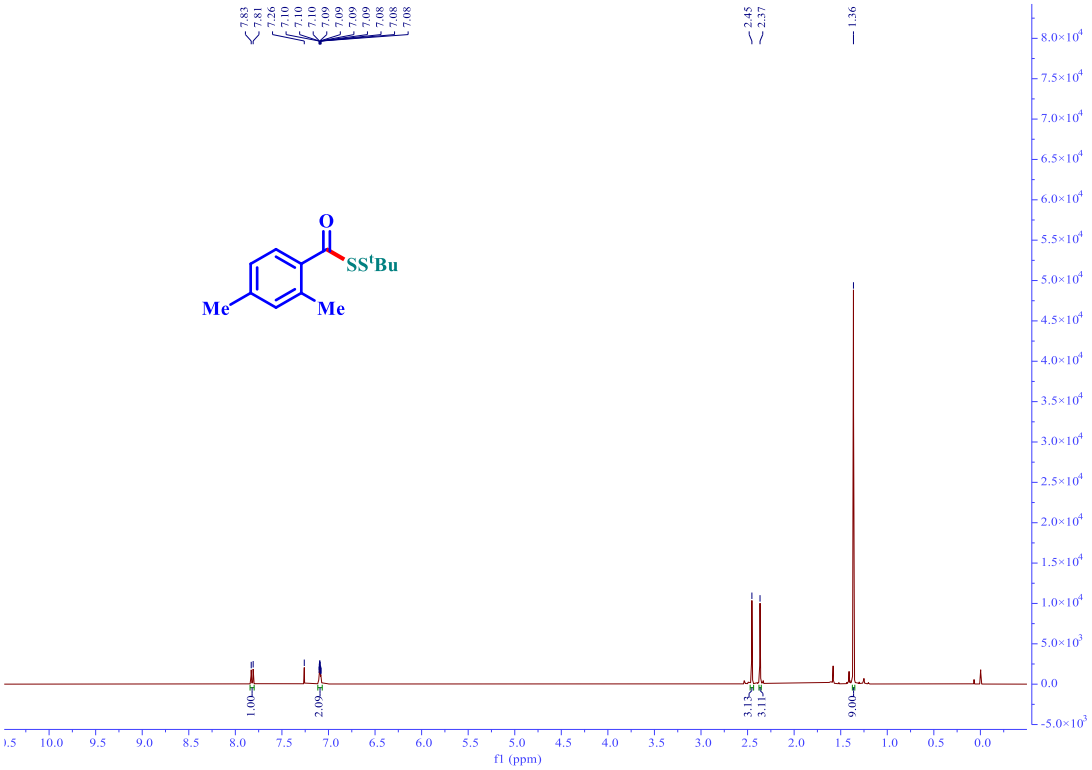
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3,4-dichlorobenzo(dithioperoxoate) (3-24)



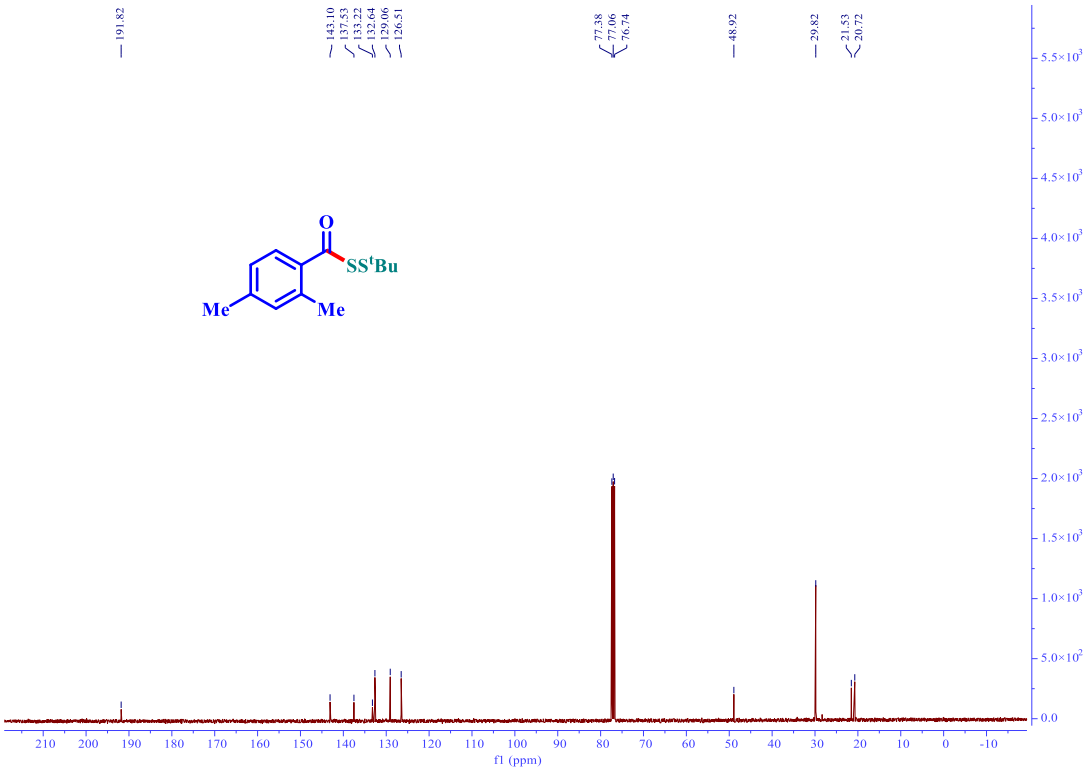
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3,4-dichlorobenzo(dithioperoxoate) (3-24)



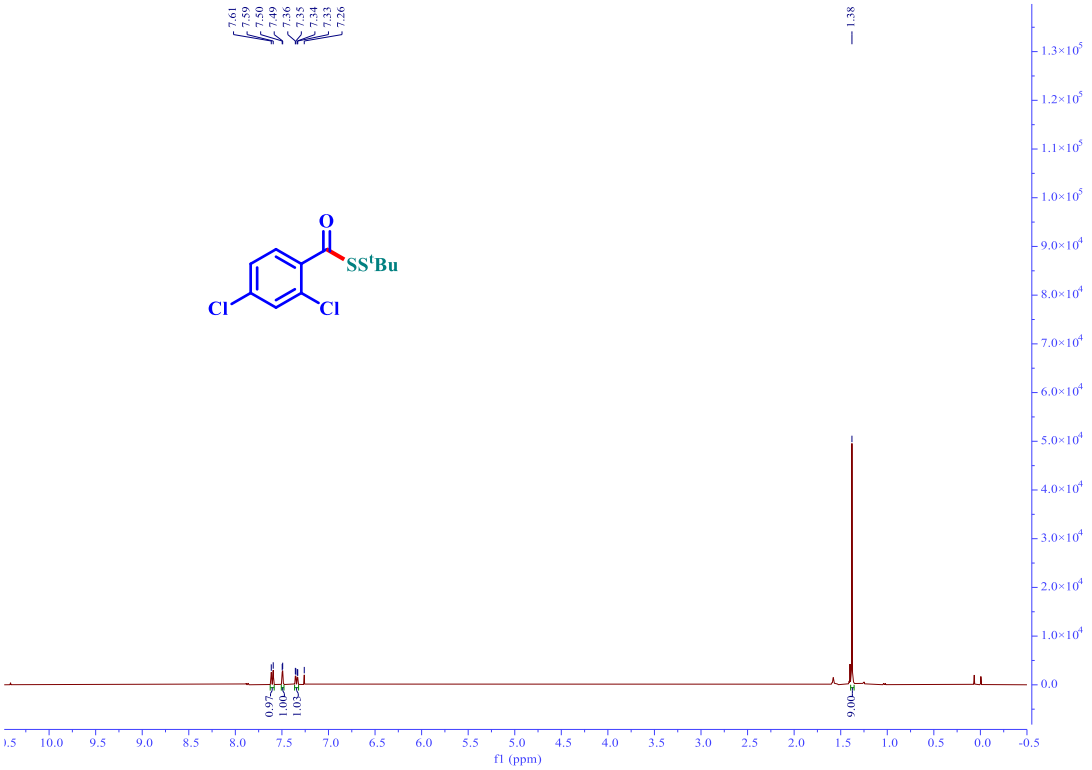
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2,4-dimethylbenzo(dithioperoxoate) (3-25)



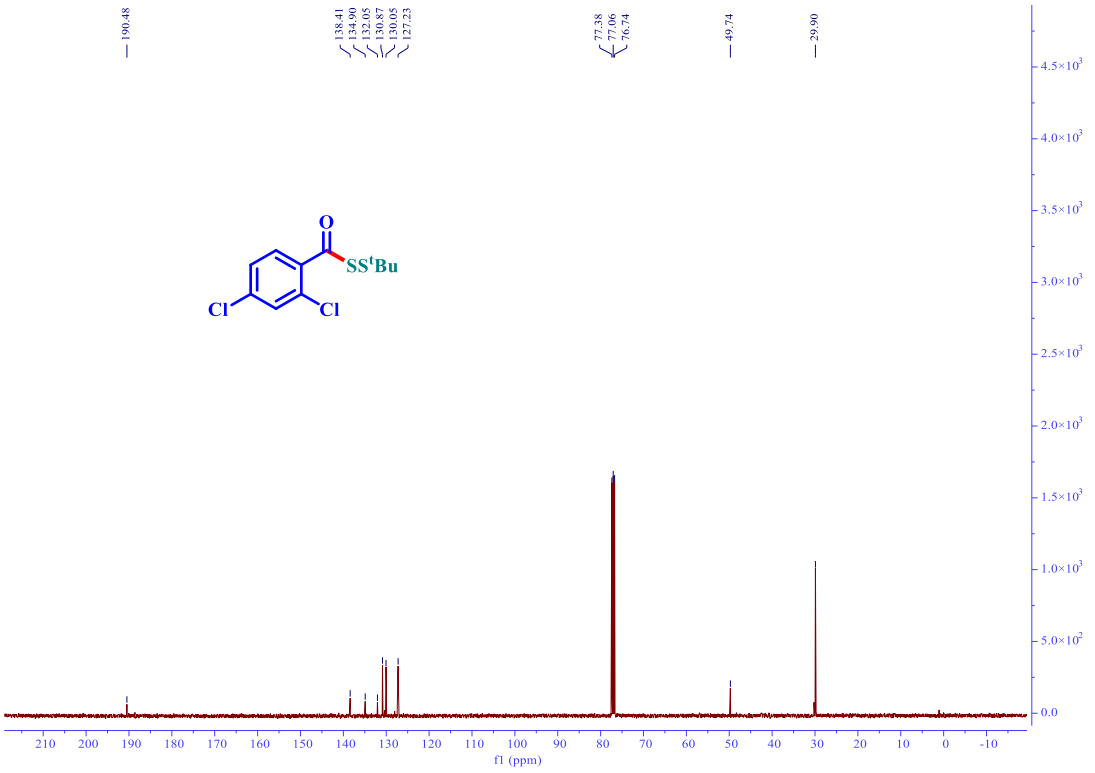
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2,4-dimethylbenzo(dithioperoxoate) (3-25)



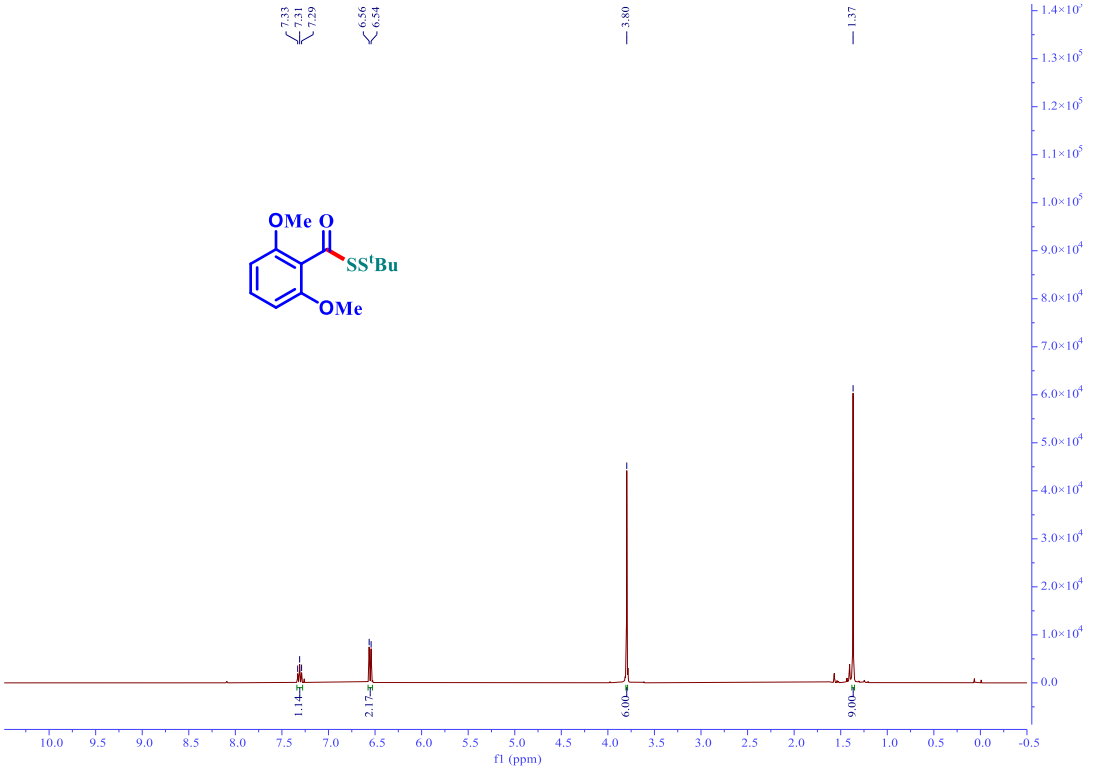
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2,4-dichlorobenzo(dithioperoxoate) (3-26)



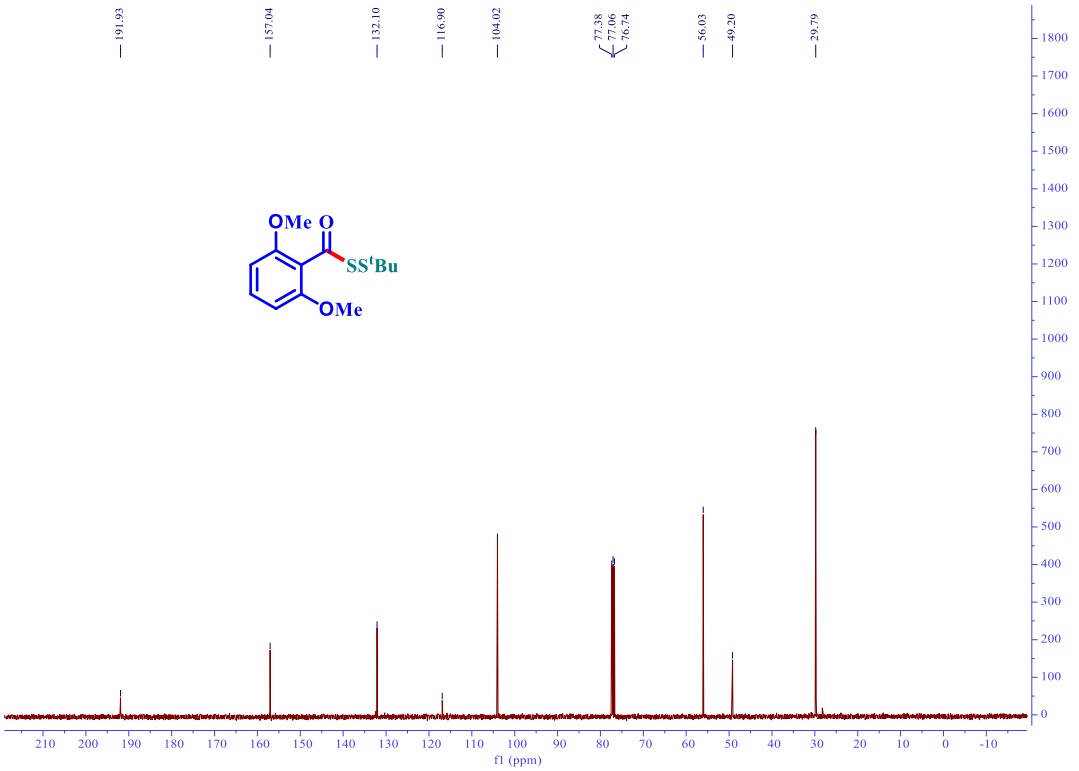
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2,4-dichlorobenzo(dithioperoxoate) (3-26)



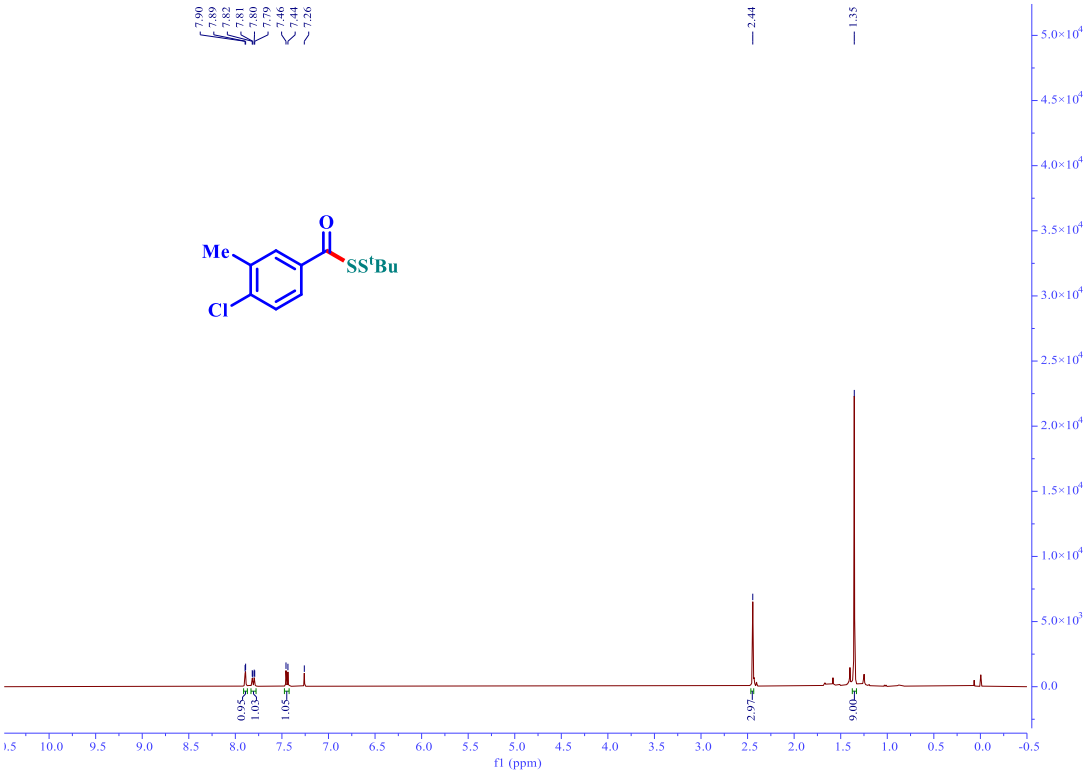
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2,6-dimethoxybenzo(dithioperoxoate) (3-27)



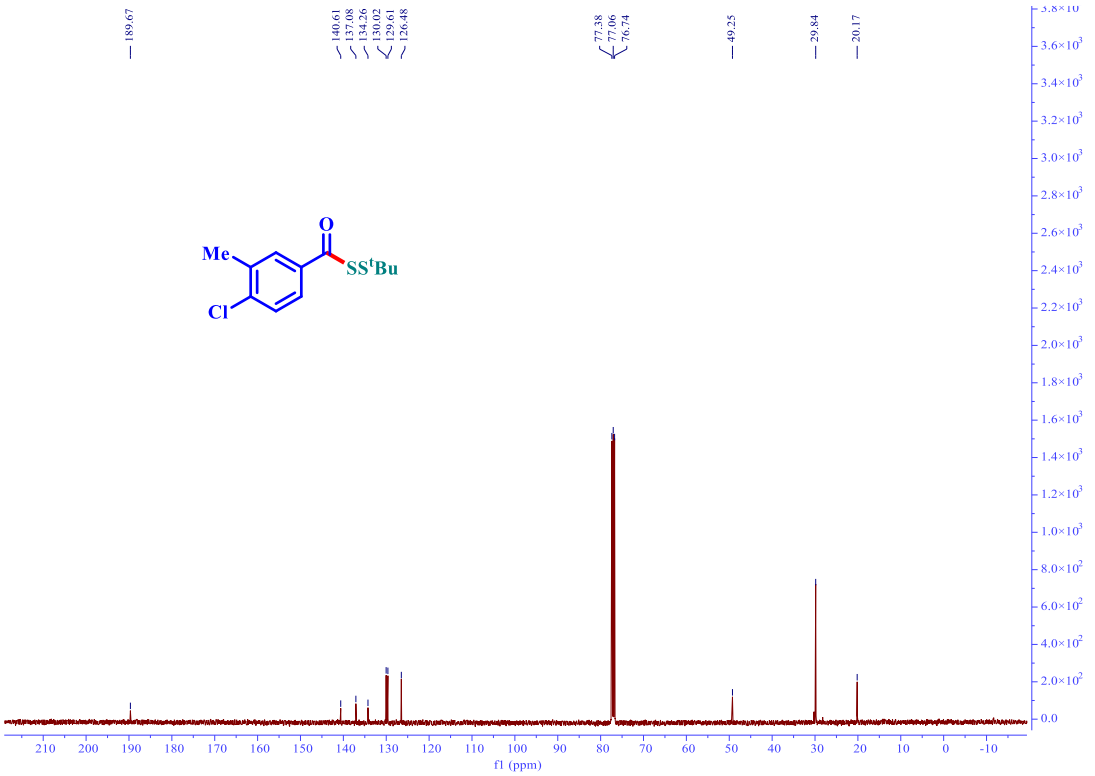
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2,6-dimethoxybenzo(dithioperoxoate) (3-27)



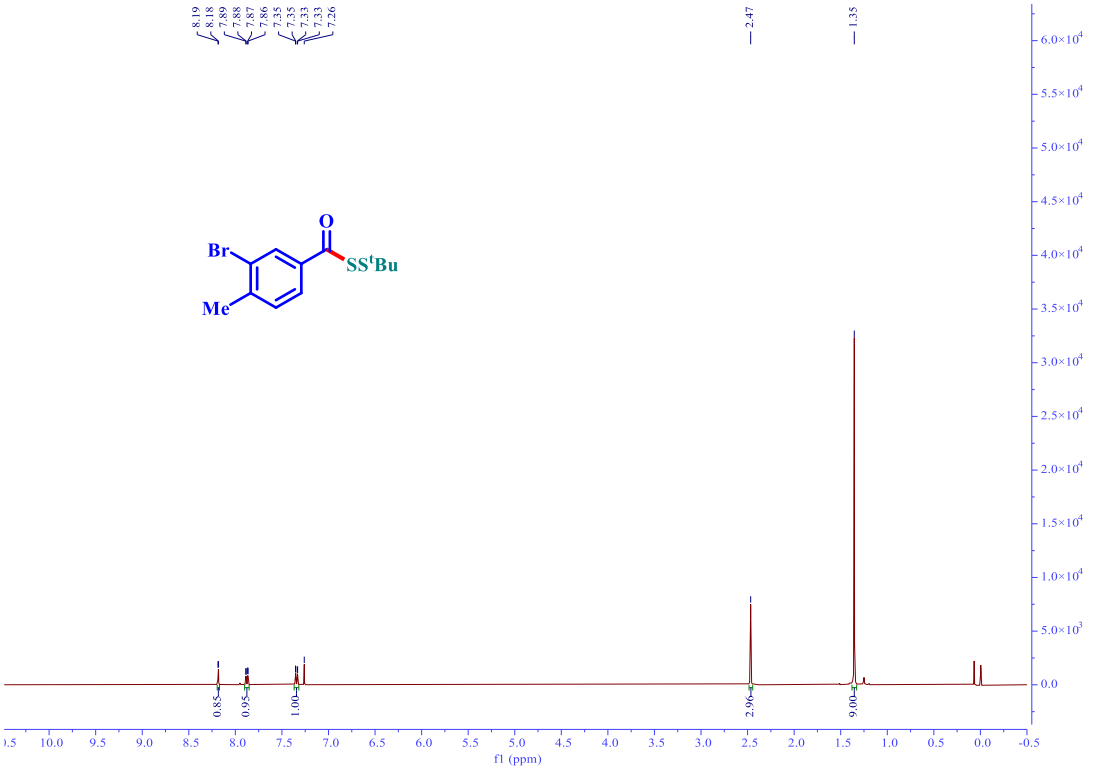
^{1}H NMR Spectrum of *SS*-(tert-butyl) 4-chloro-3-methylbenzo(dithioperoxoate) (3-28)



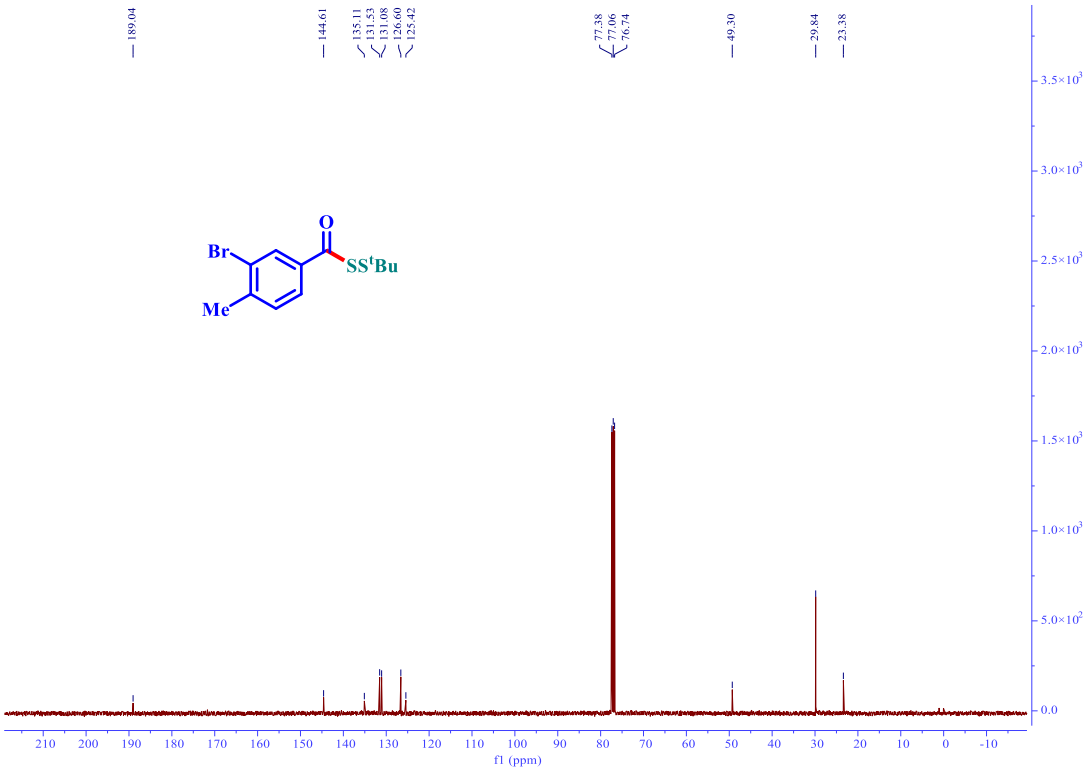
^{13}C NMR Spectrum of *SS*-(tert-butyl) 4-chloro-3-methylbenzo(dithioperoxoate) (3-28)



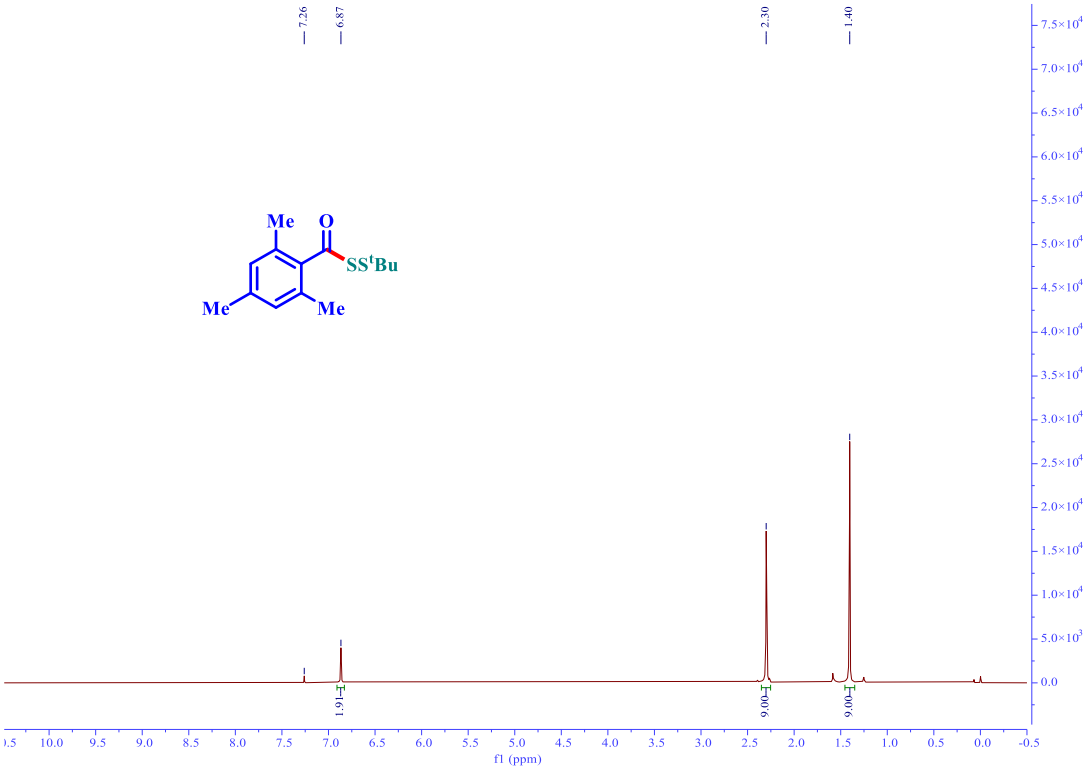
^{1}H NMR Spectrum of *SS*-(tert-butyl) 3-bromo-4-methylbenzo(dithioperoxoate) (3-29)



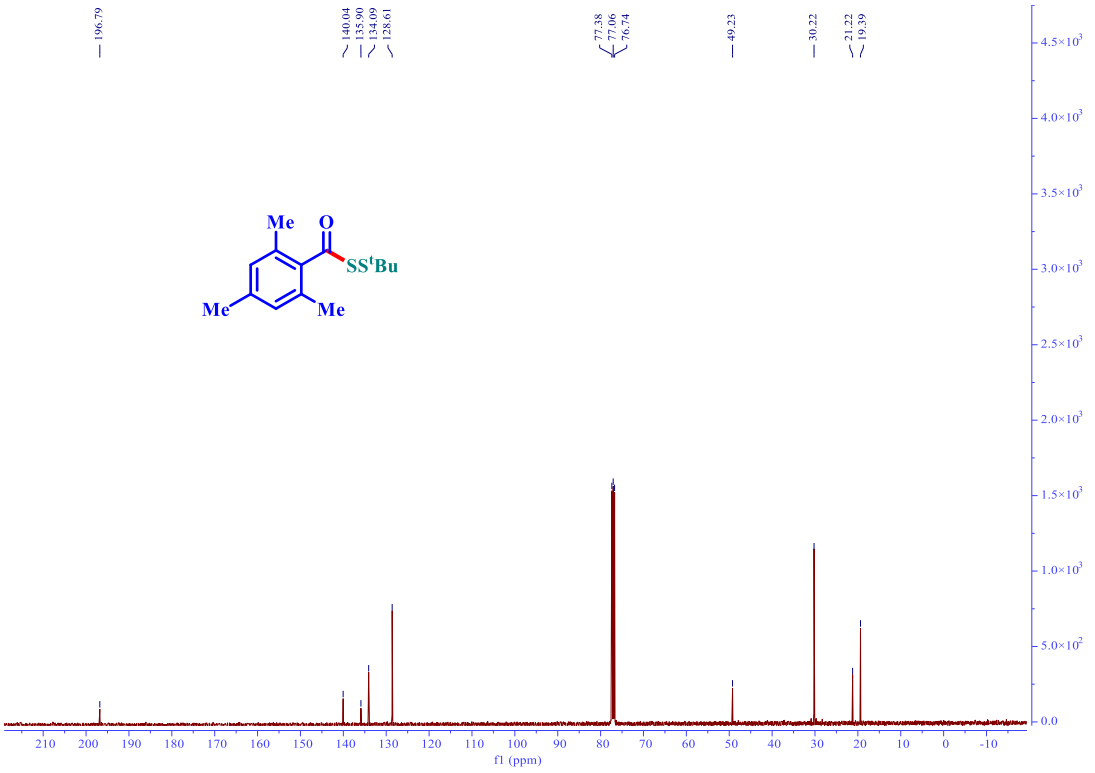
^{13}C NMR Spectrum of *SS*-(tert-butyl) 3-bromo-4-methylbenzo(dithioperoxoate) (3-29)



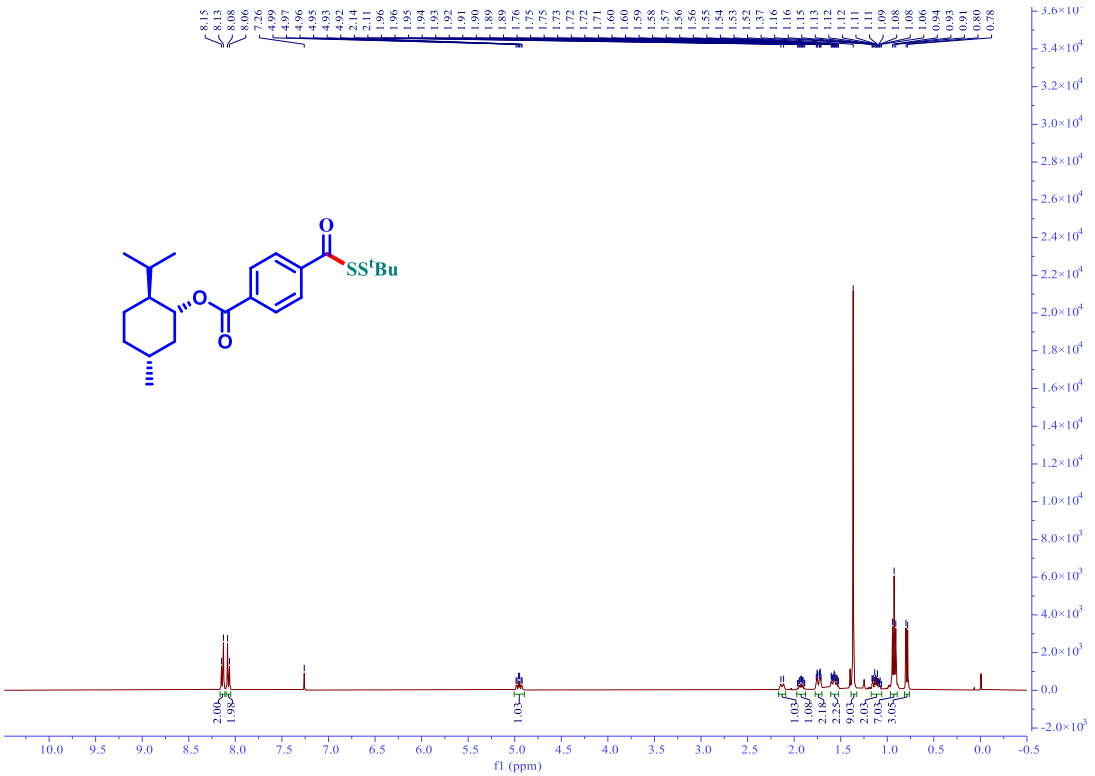
^{1}H NMR Spectrum of *SS*-(tert-butyl) 2,4,6-trimethylbenzo(dithioperoxoate) (3-30)



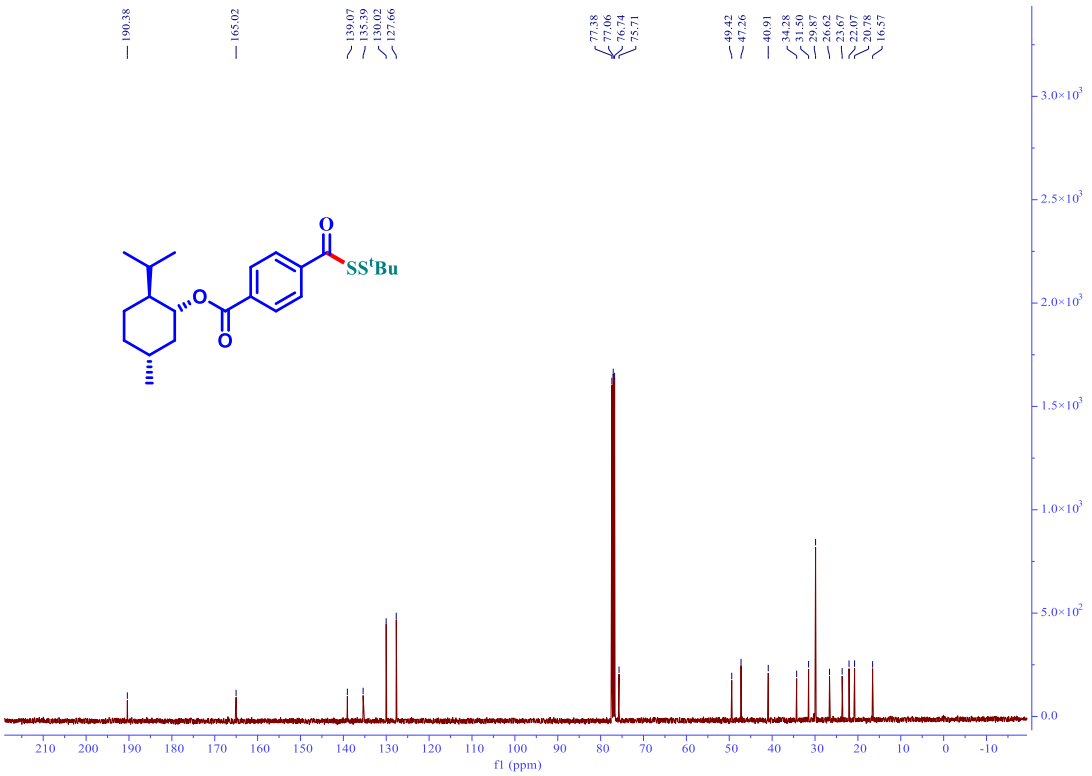
^{13}C NMR Spectrum of *SS*-(tert-butyl) 2,4,6-trimethylbenzo(dithioperoxoate) (3-30)



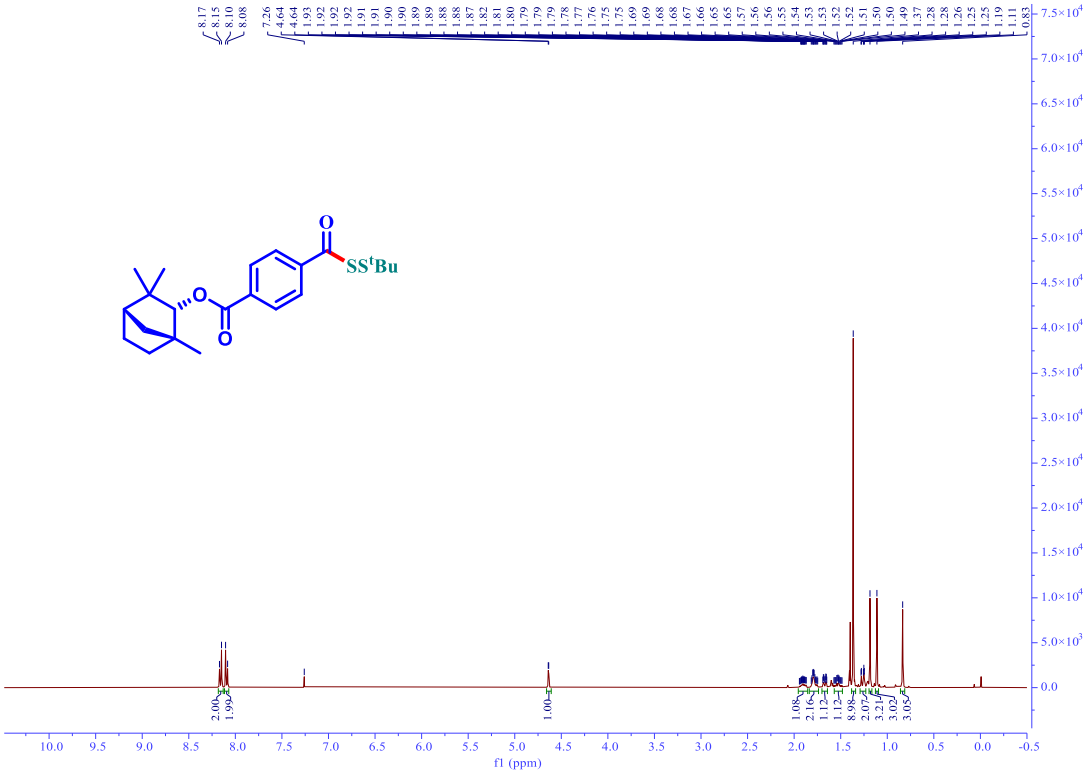
^{1}H NMR Spectrum of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((R)-1-(tert-butyl)-1l4-disulfanenecarbonyl)benzoate (3-31)



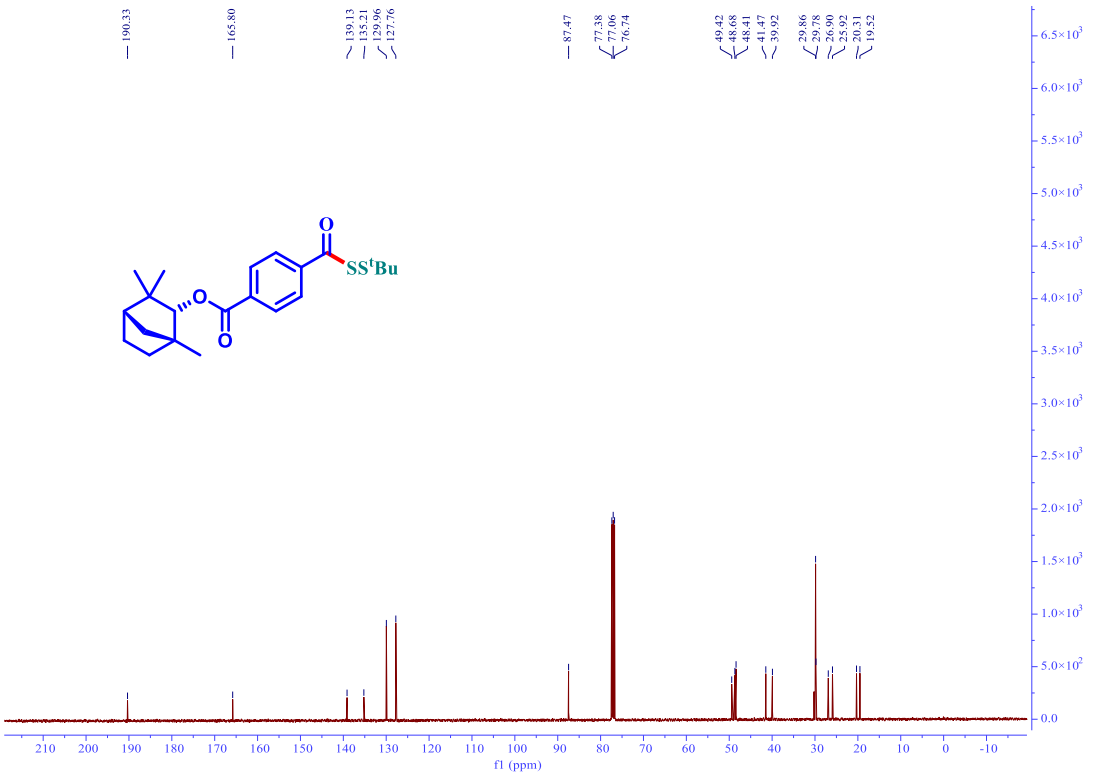
^{13}C NMR Spectrum of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((R)-1-(tert-butyl)-1l4-disulfanenecarbonyl)benzoate (3-31)



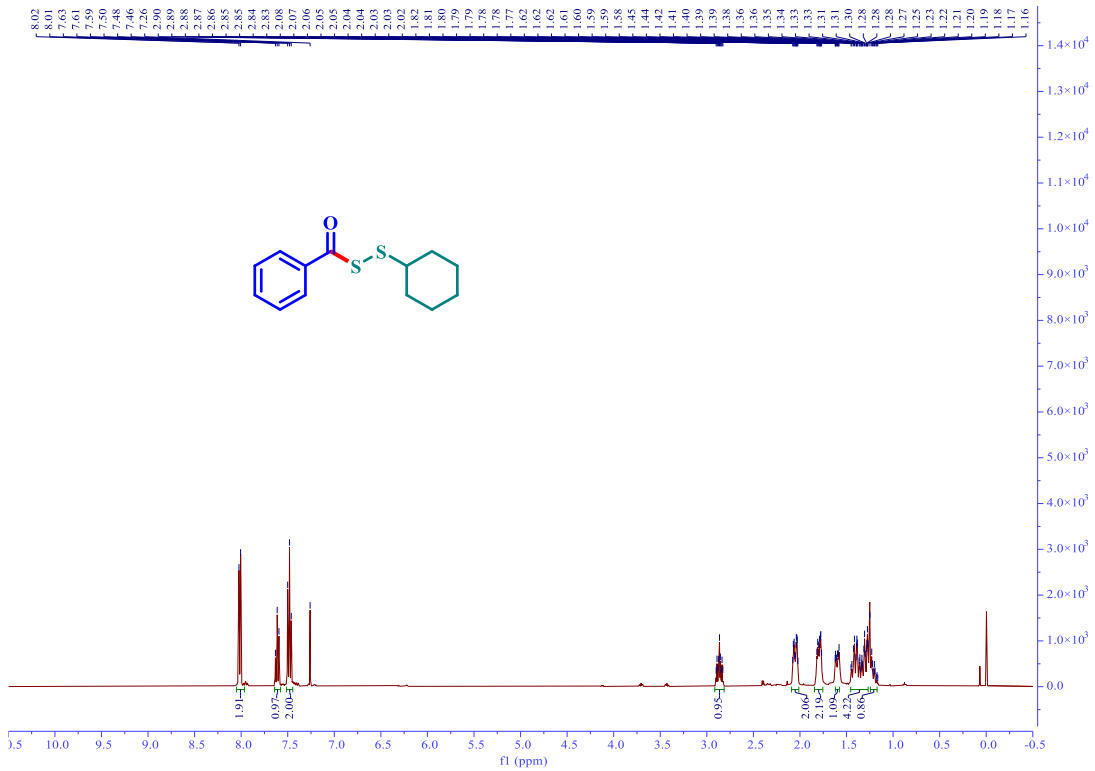
^{1}H NMR Spectrum of (1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-((R)-1-(tert-butyl)-1l4-disulfanenecarbonyl)benzoate (3-32)



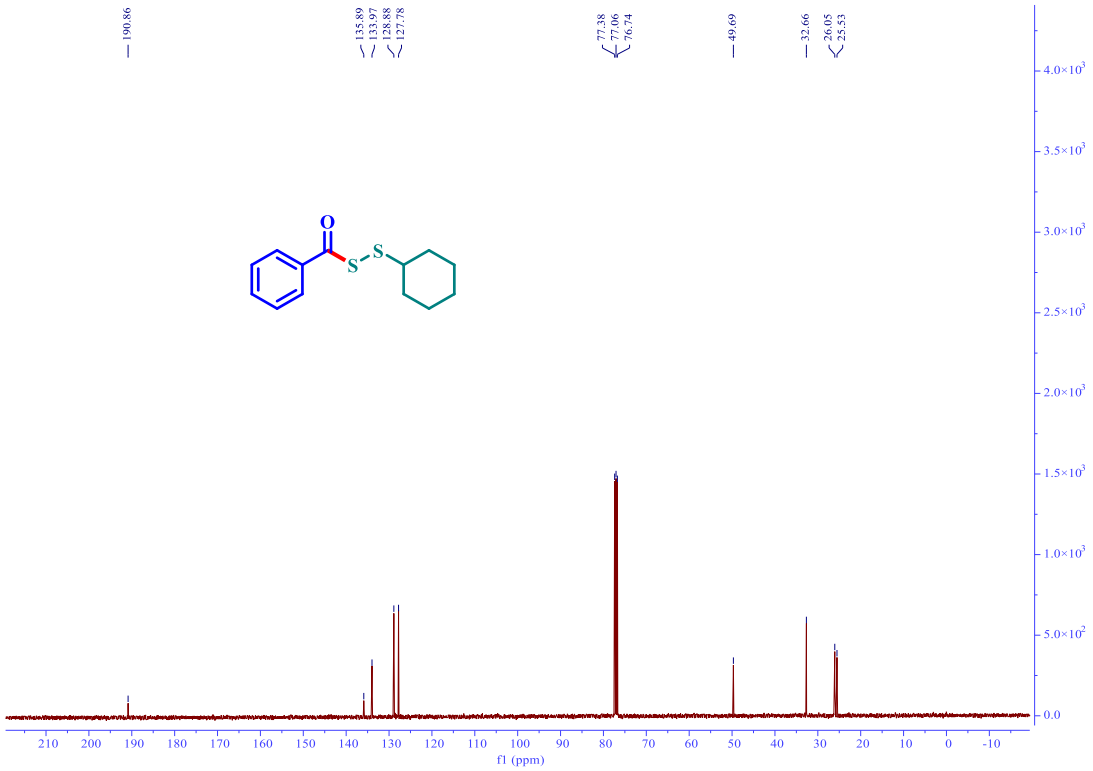
^{13}C NMR Spectrum of (1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-((R)-1-(tert-butyl)-1l4-disulfanenecarbonyl)benzoate (3-32)



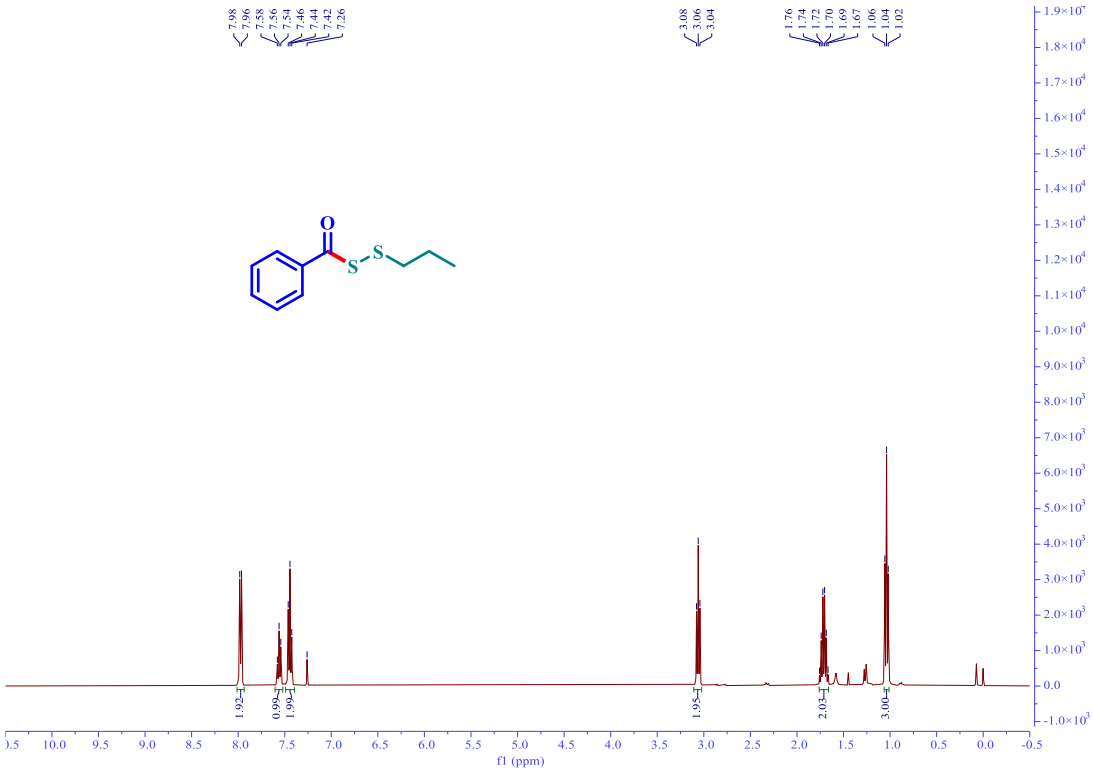
^{1}H NMR Spectrum of *SS*-cyclohexyl benzo(dithioperoxoate) (3-33)



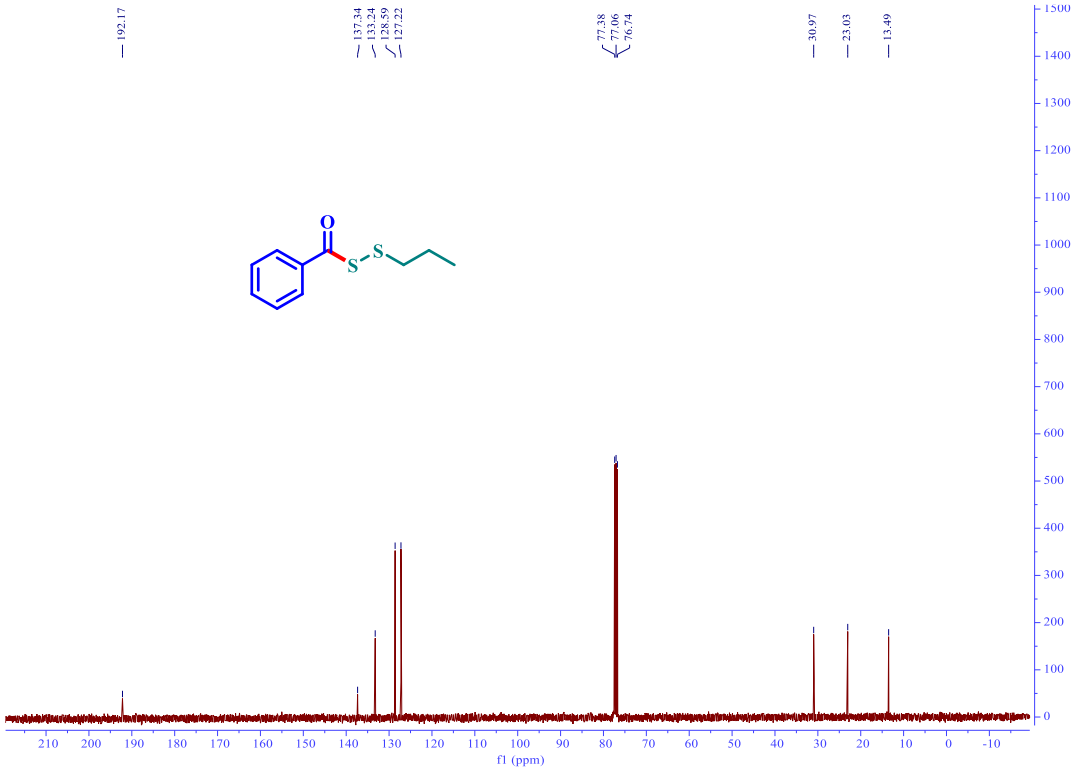
^{13}C NMR Spectrum of *SS*-cyclohexyl benzo(dithioperoxoate) (3-33)



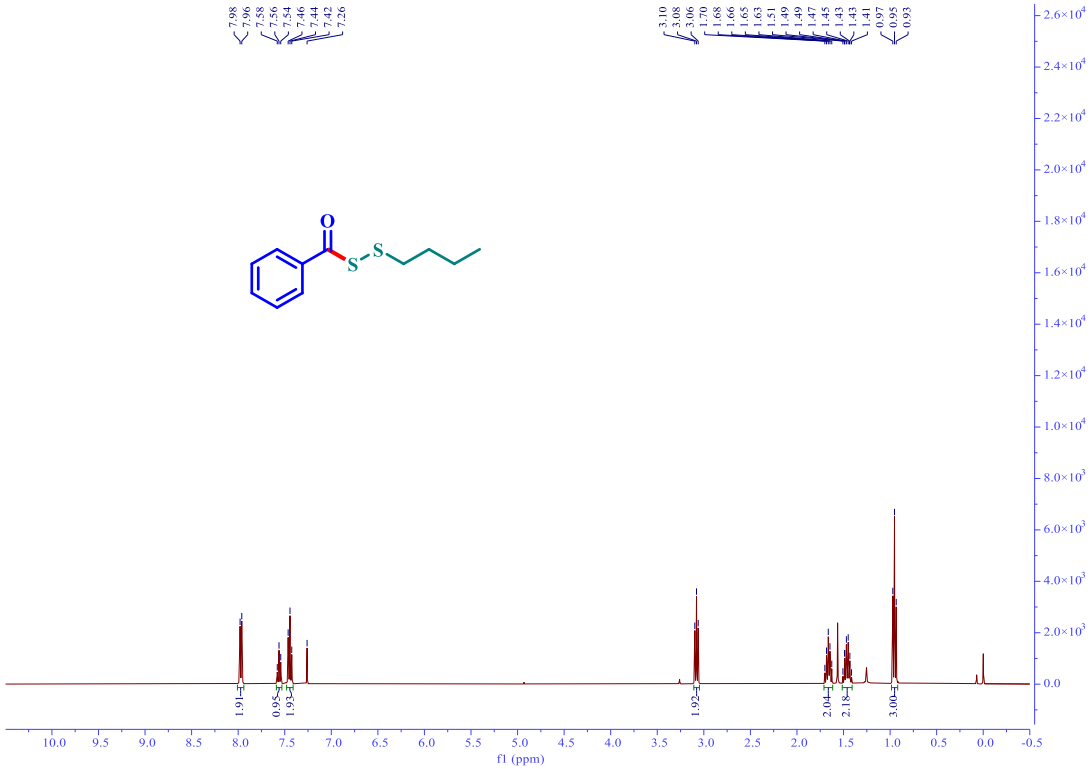
^{1}H NMR Spectrum of *SS*-propyl benzo(dithioperoxoate) (3-34)



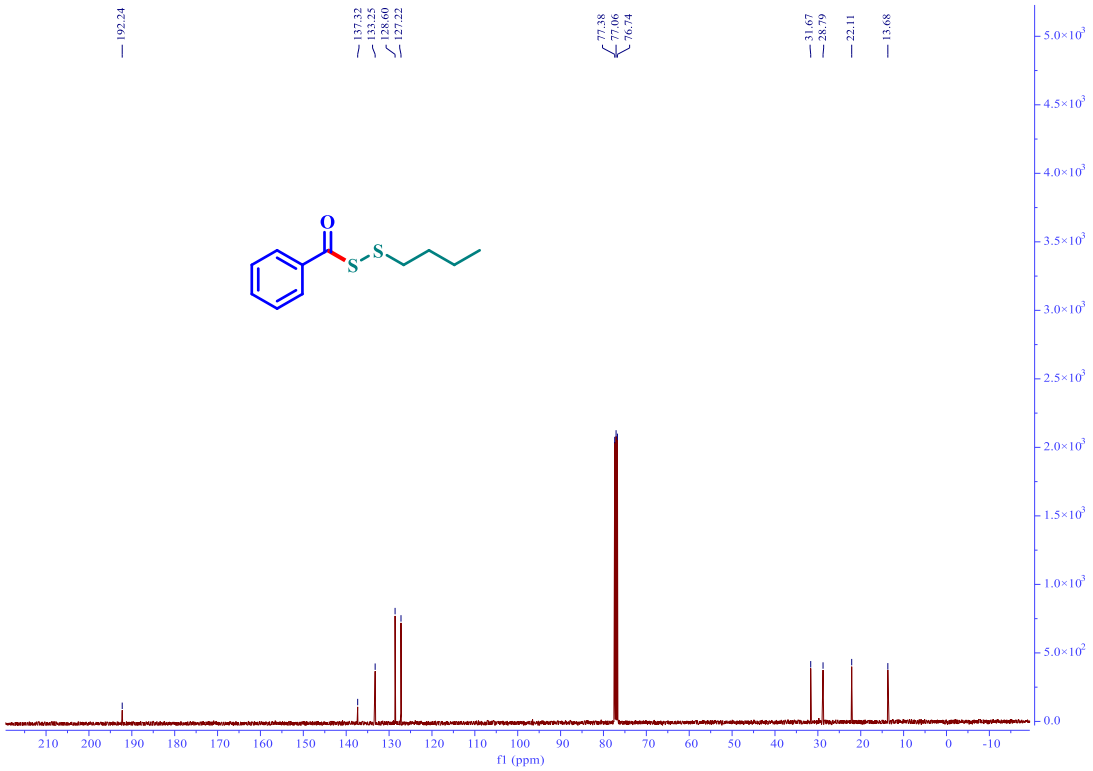
^{13}C NMR Spectrum of *SS*-propyl benzo(dithioperoxoate) (3-34)



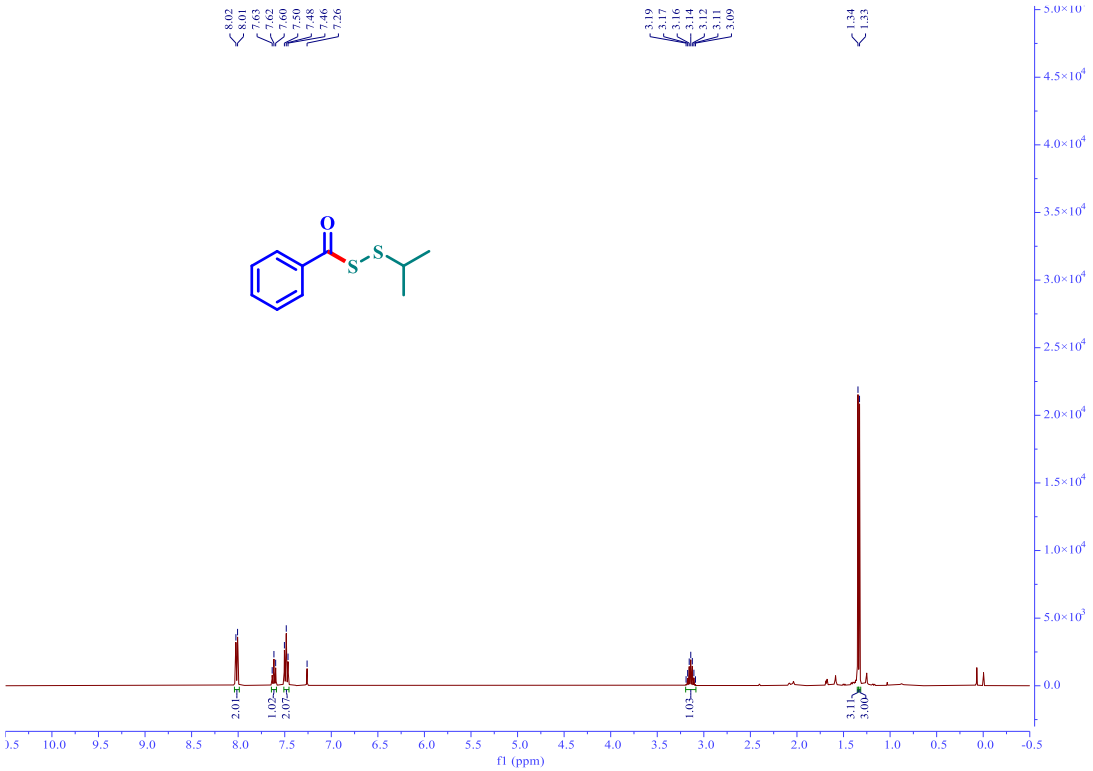
^{1}H NMR Spectrum of *SS*-butyl benzo(dithioperoxoate) (3-35)



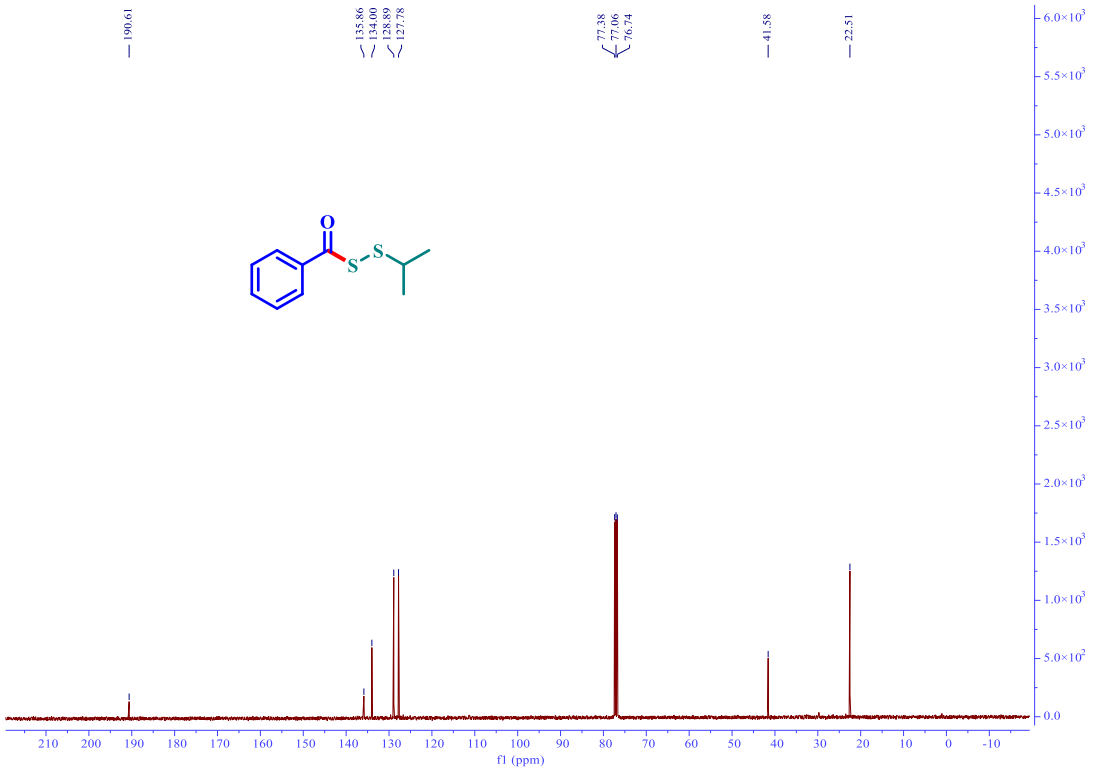
^{13}C NMR Spectrum of *SS*-butyl benzo(dithioperoxoate) (3-35)



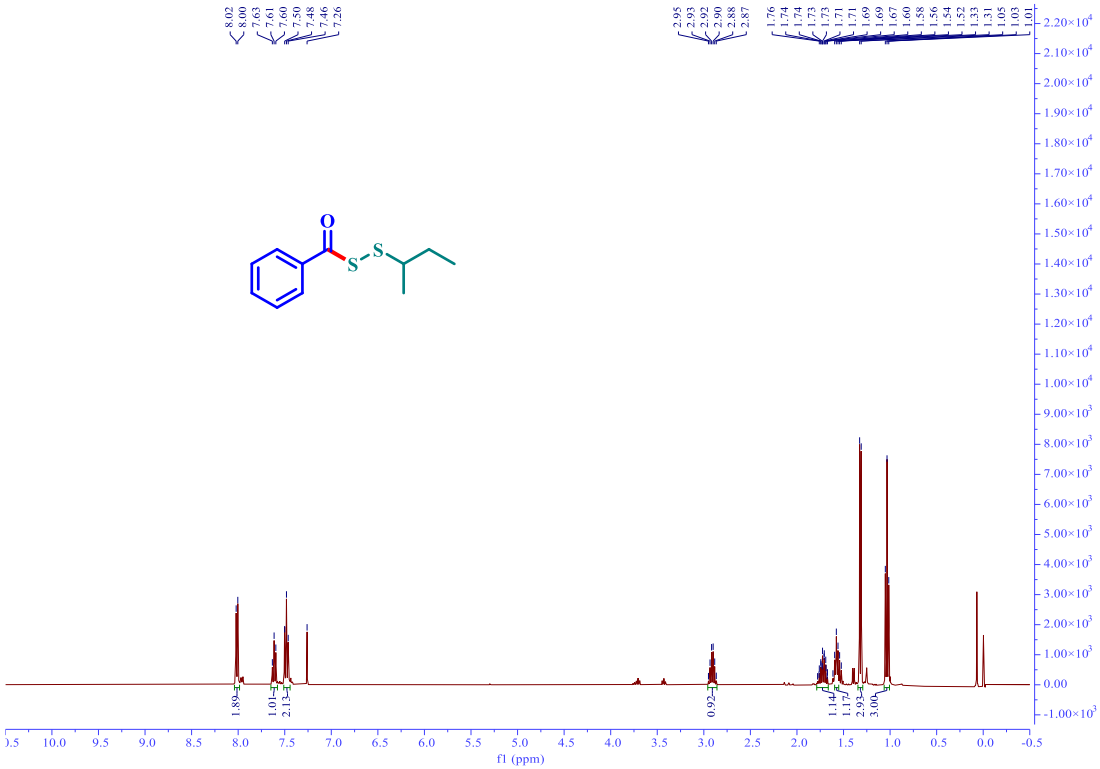
^{1}H NMR Spectrum of *SS*-isopropyl benzo(dithioperoxoate) (3-36)



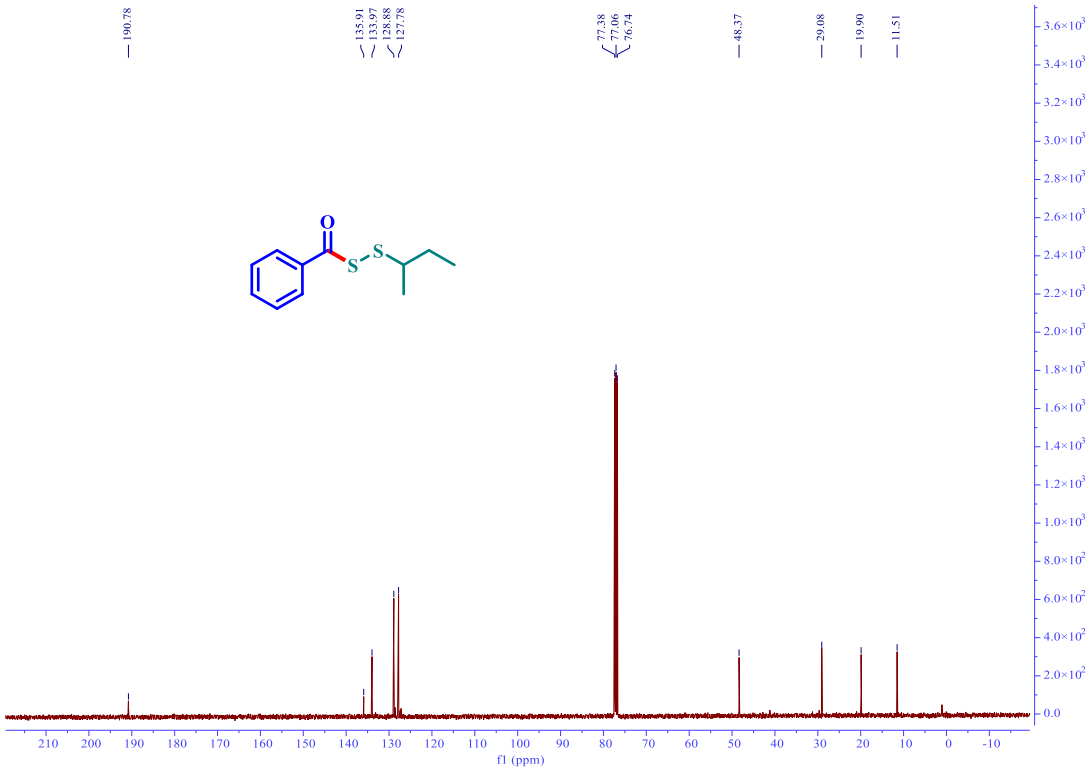
^{13}C NMR Spectrum of *SS*-isopropyl benzo(dithioperoxoate) (3-36)



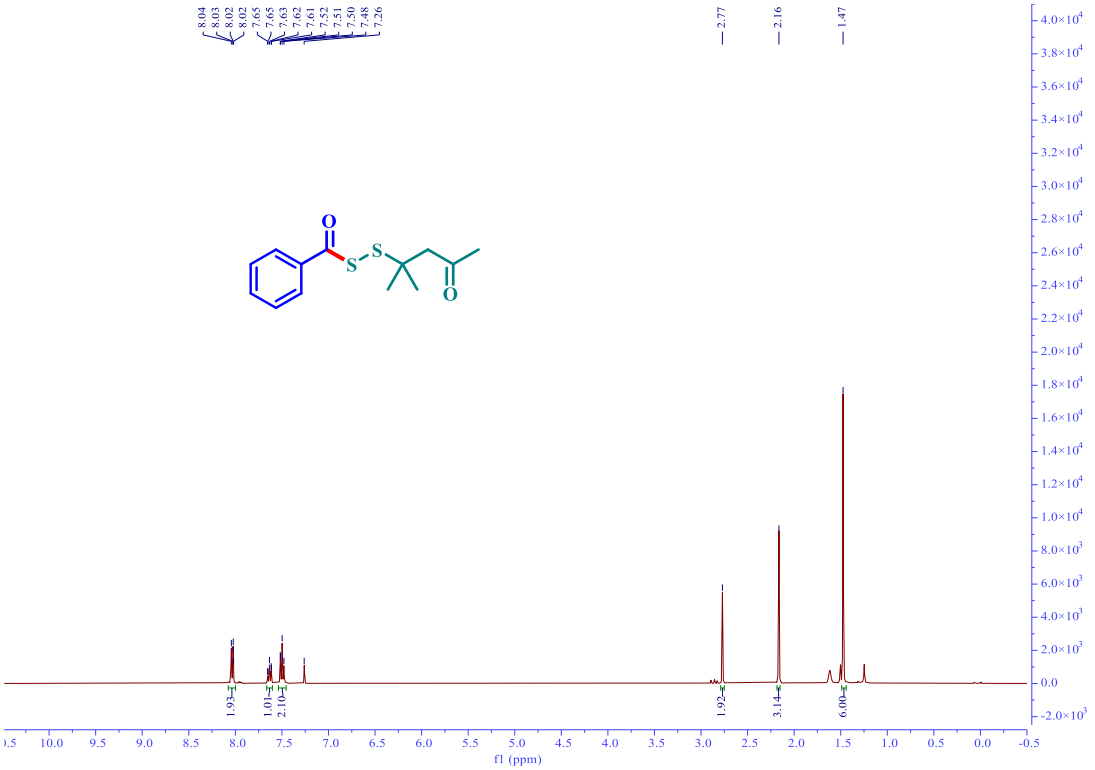
^{1}H NMR Spectrum of *SS*-(sec-butyl) benzo(dithioperoxoate) (3-37)



^{13}C NMR Spectrum of *SS*-(sec-butyl) benzo(dithioperoxoate) (3-37)

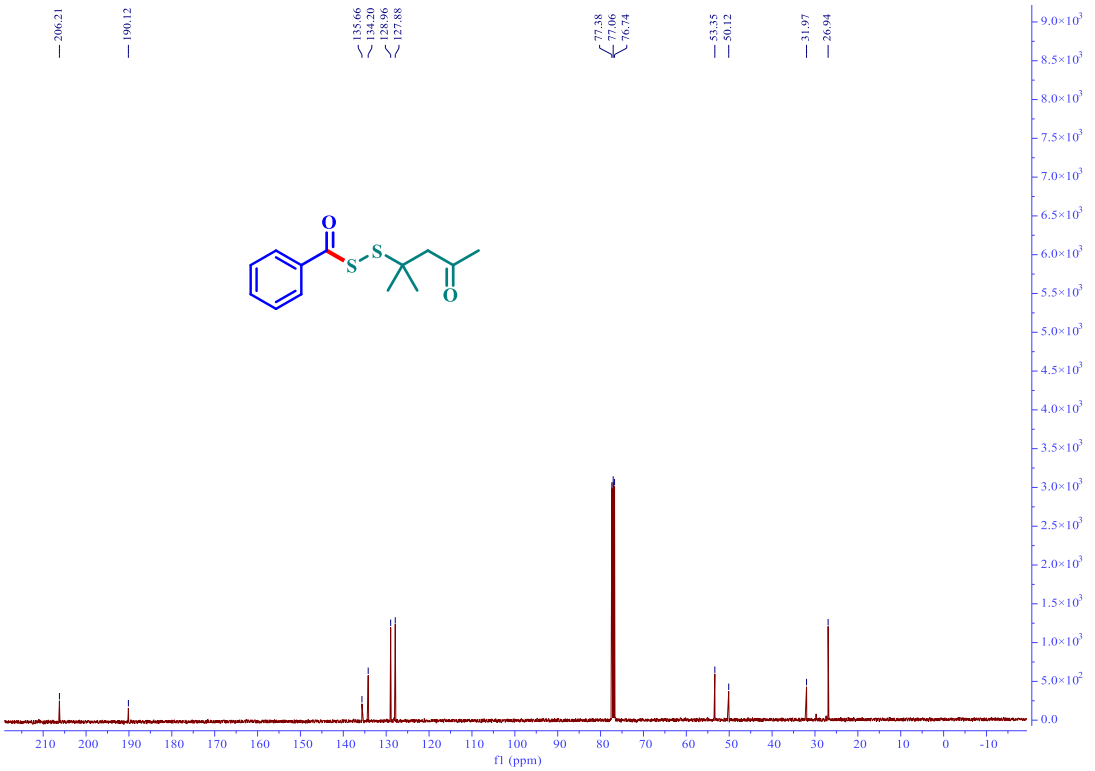


^{1}H NMR Spectrum of *SS*-(2-methyl-4-oxopentan-2-yl) benzo(dithioperoxoate) (3-38)

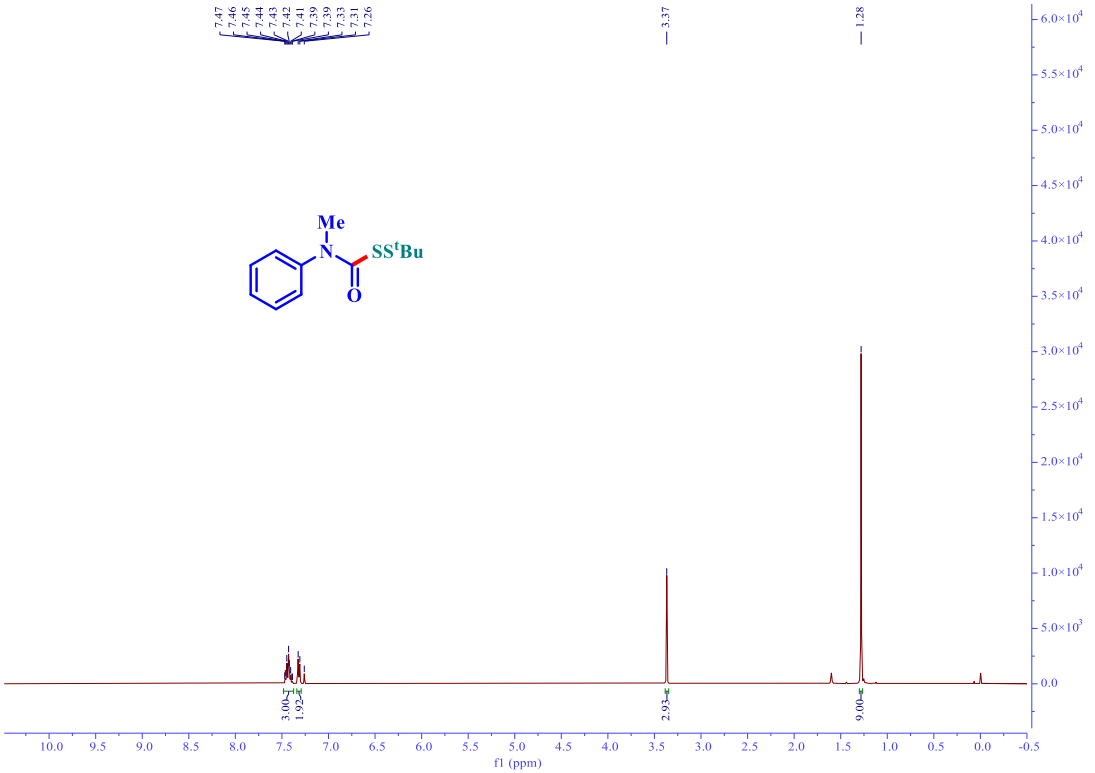


^{13}C NMR Spectrum of *SS*-(2-methyl-4-oxopentan-2-yl) benzo(dithioperoxoate) (3-

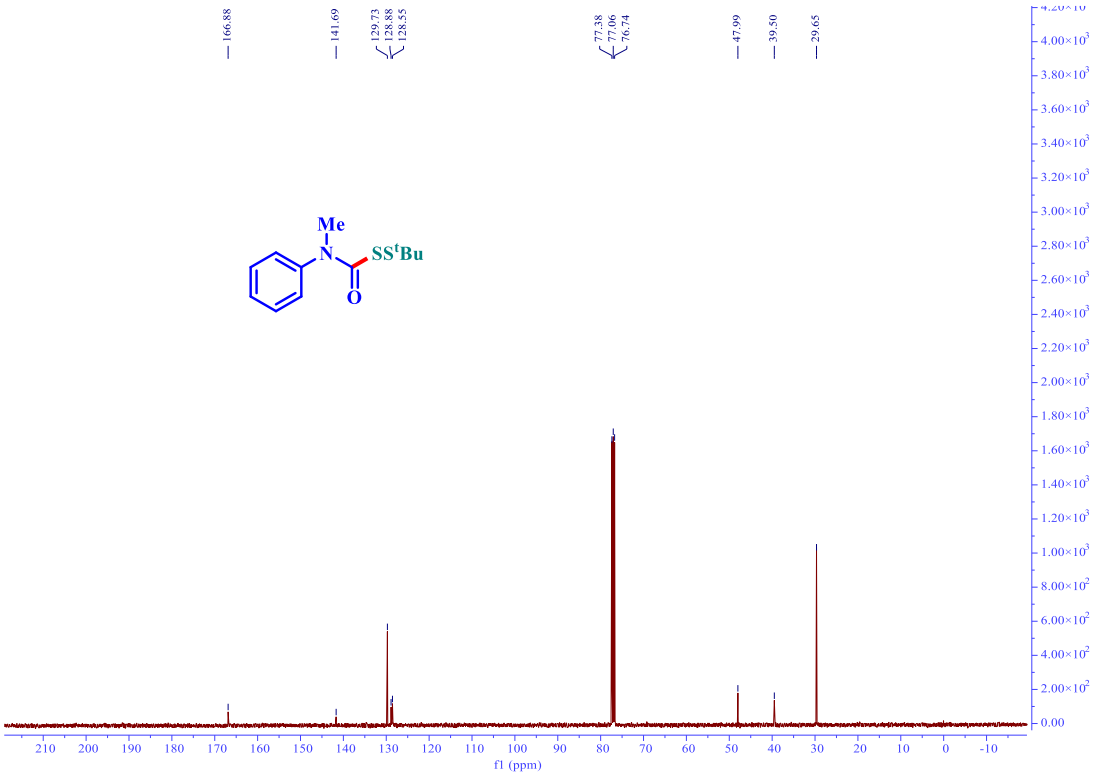
38)



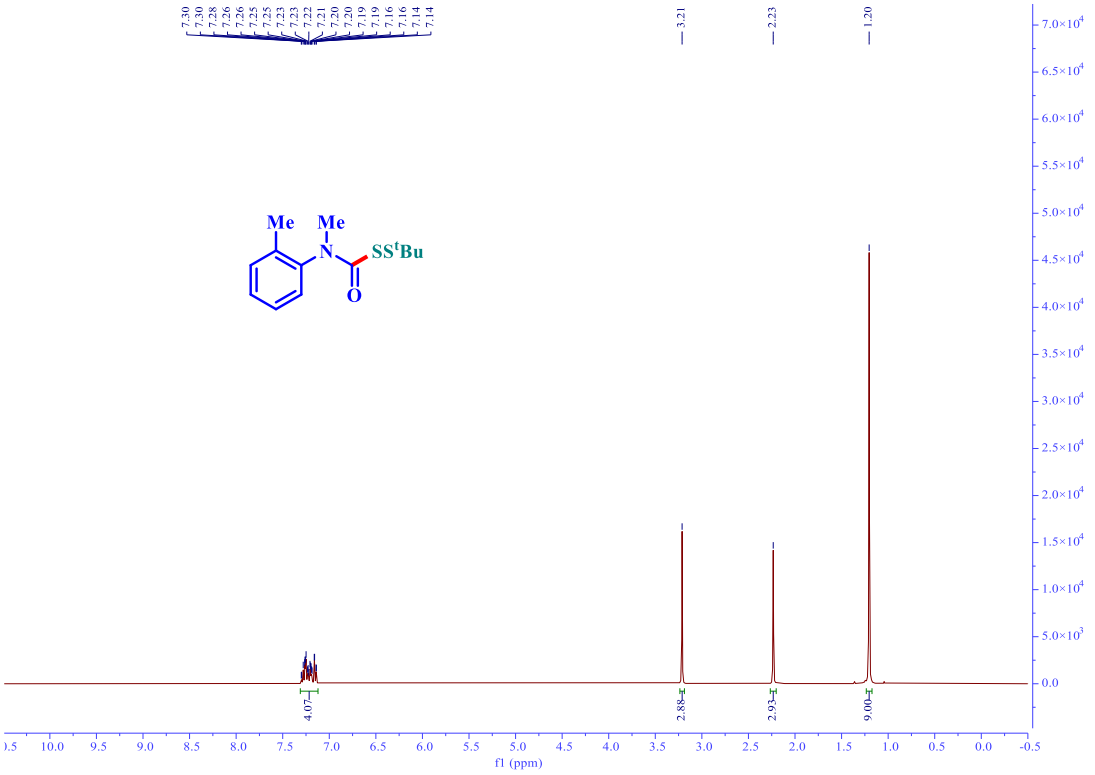
^{1}H NMR Spectrum of *SS*-tert-butyl methyl(phenyl)carbamo(dithioperoxoate (5-1)



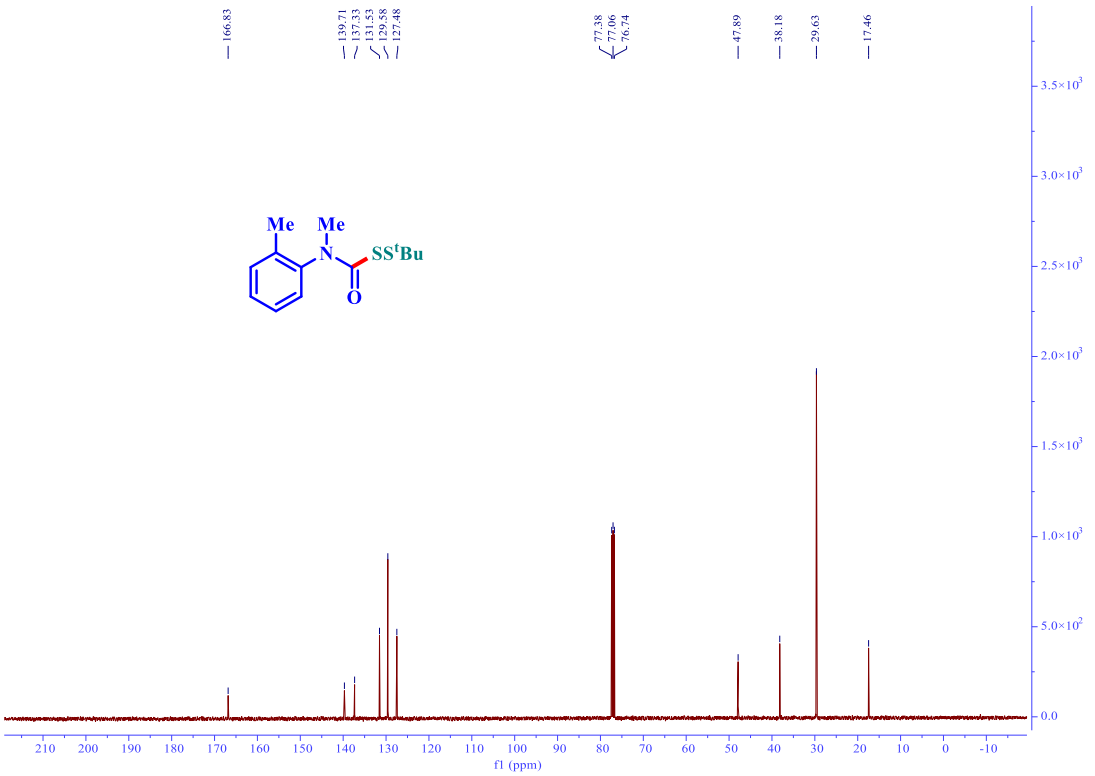
^{13}C NMR Spectrum of *SS*-tert-butyl methyl(phenyl)carbamo(dithioperoxoate (5-1)



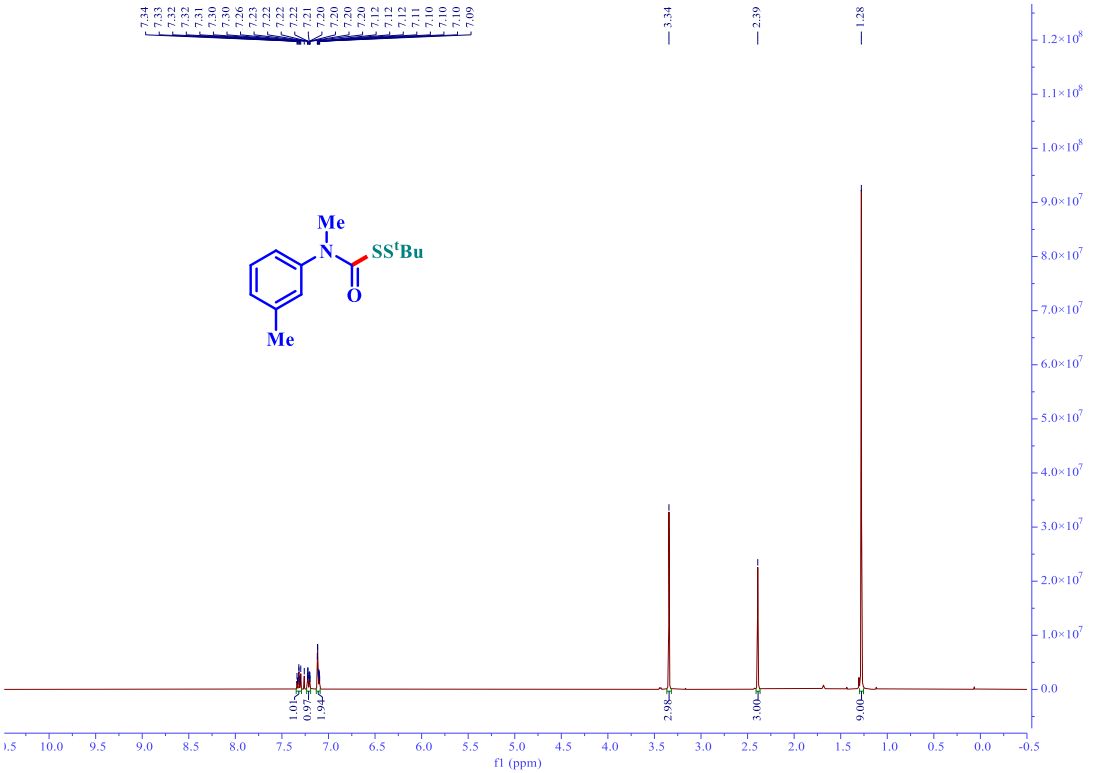
^{1}H NMR Spectrum of *SS-tert*-butyl methyl(o-tolyl)carbamo(dithioperoxoate) (5-2)



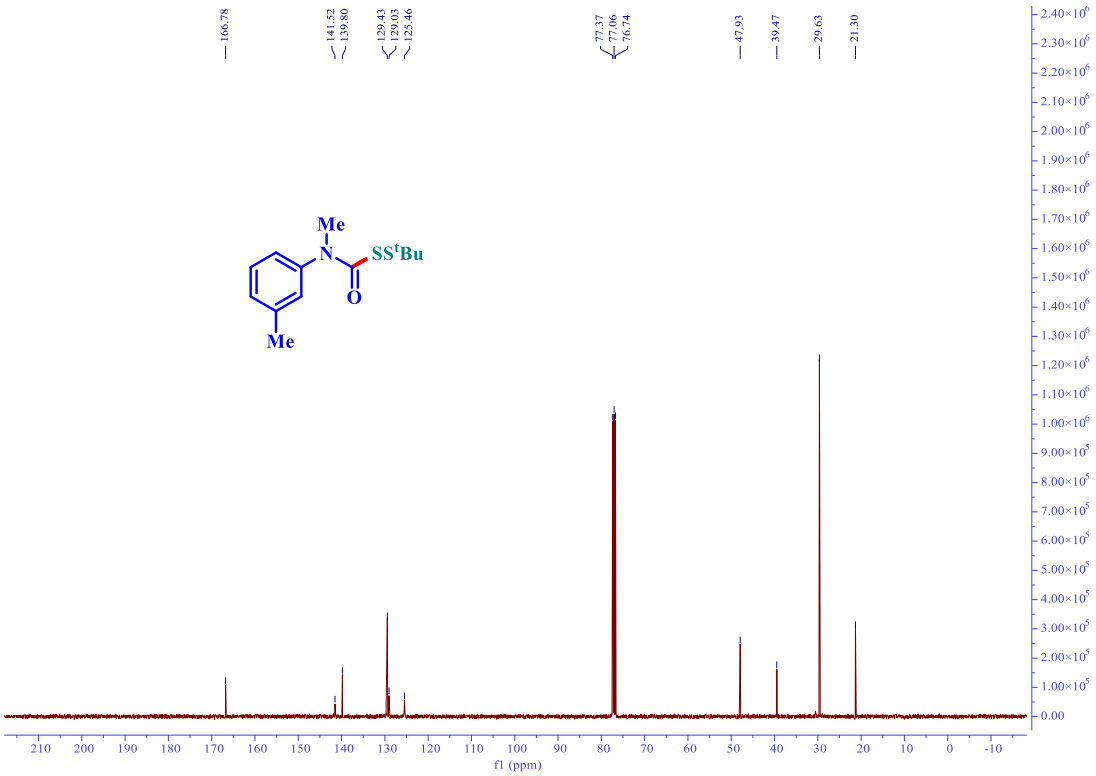
^{13}C NMR Spectrum of *SS-tert*-butyl methyl(o-tolyl)carbamo(dithioperoxoate) (5-2)



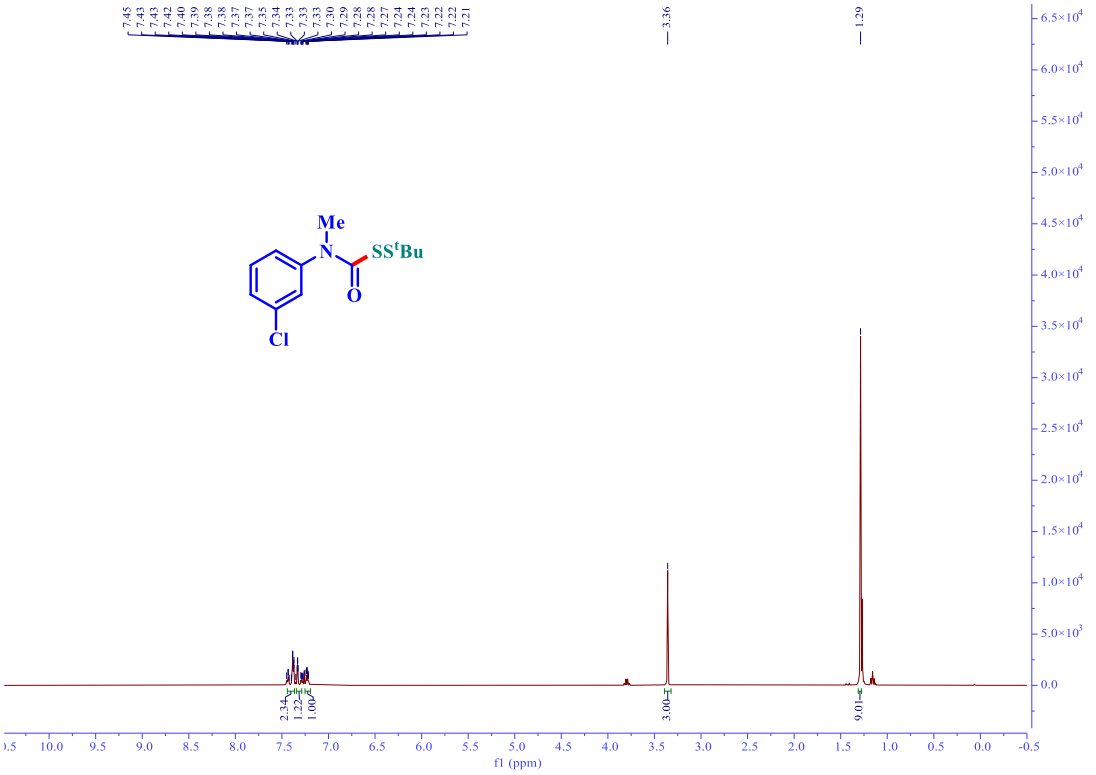
^{1}H NMR Spectrum of SS-*tert*-butyl methyl(m-tolyl)carbamo(dithioperoxoate) (5-3)



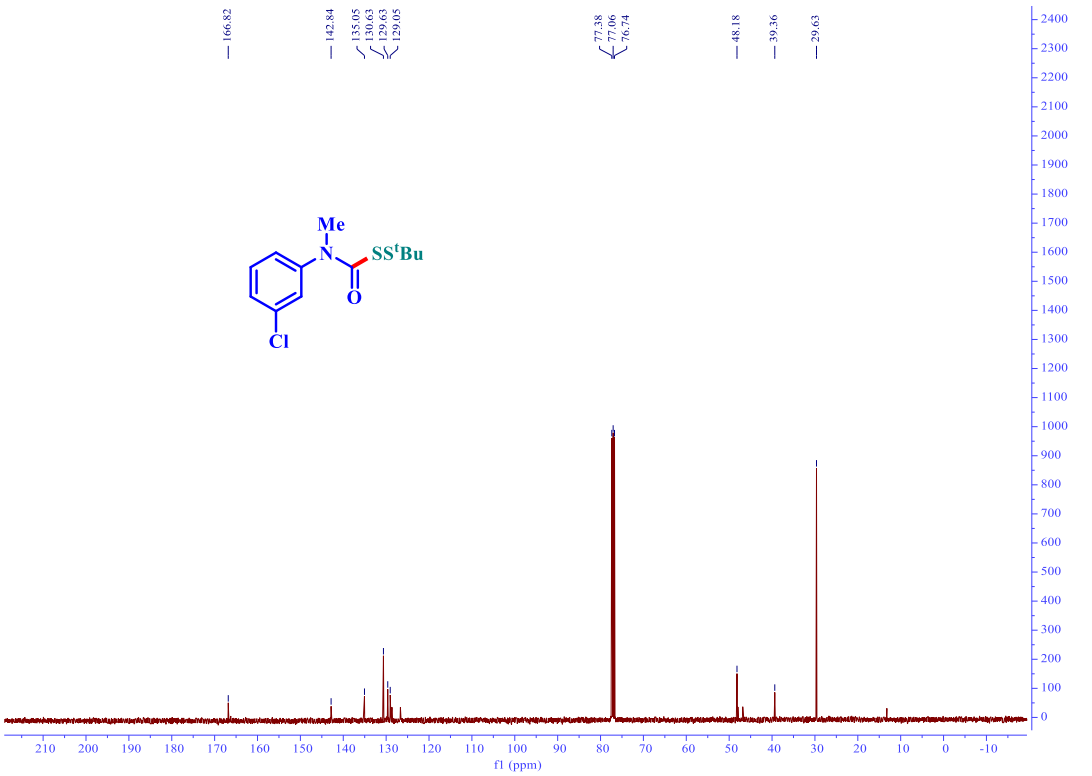
^{13}C NMR Spectrum of SS-*tert*-butyl methyl(m-tolyl)carbamo(dithioperoxoate) (5-3)



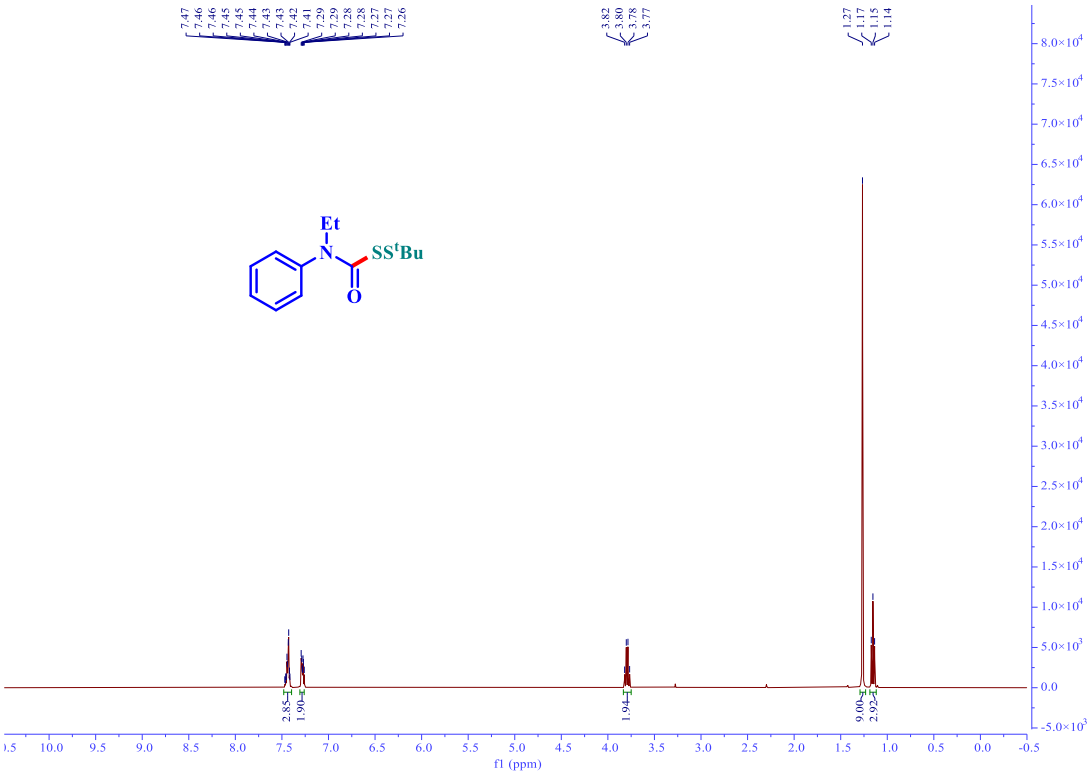
^{1}H NMR Spectrum of SS-*tert*-butyl(3chlorophenyl)(methyl)Carbamo (dithioperoxoate) (5-4)



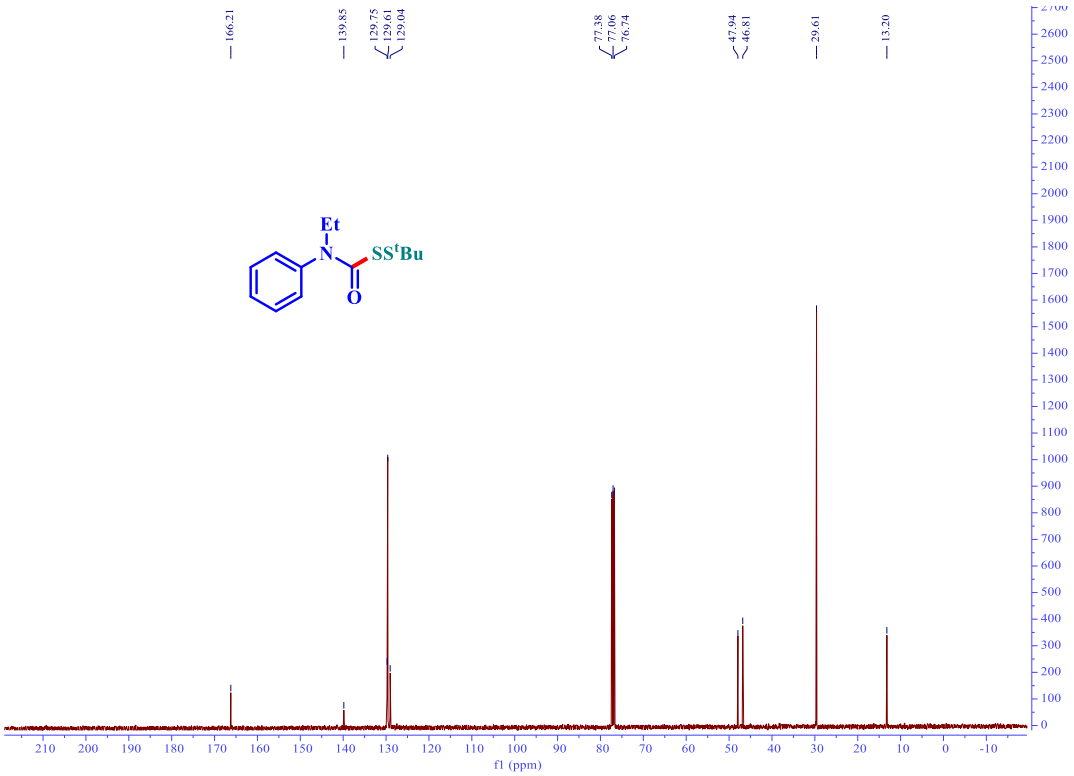
^{13}C NMR Spectrum of SS-*tert*-butyl(3chlorophenyl)(methyl)Carbamo (dithioperoxoate) (5-4)



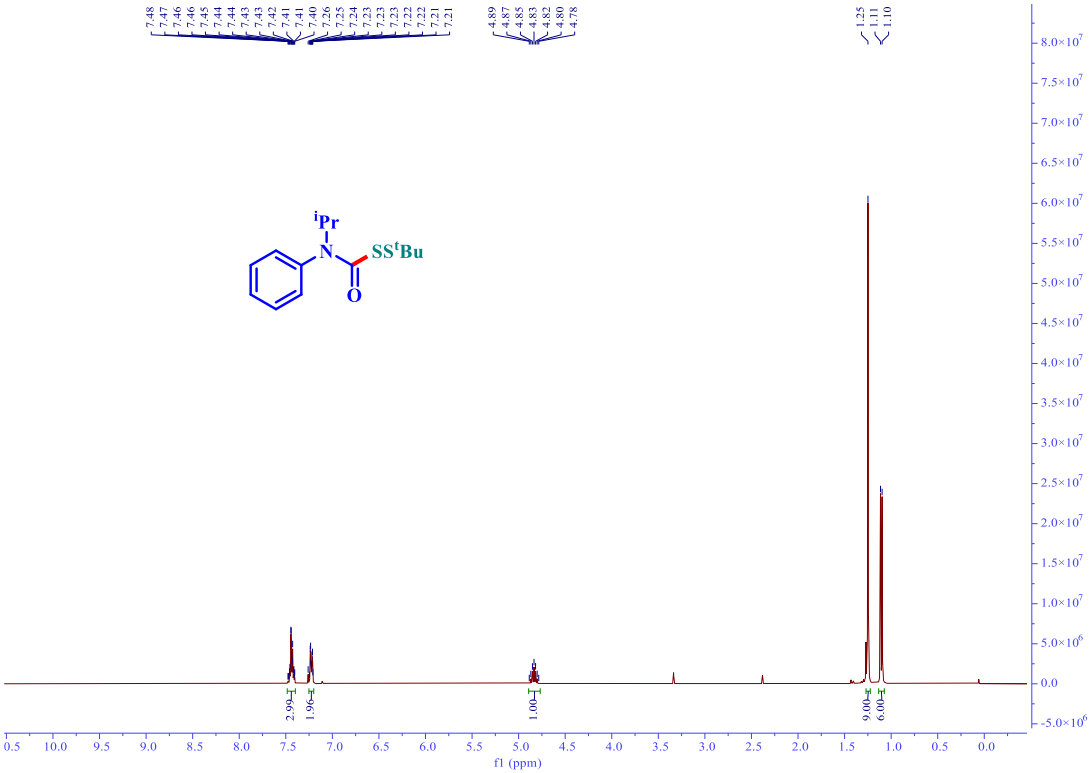
^{1}H NMR Spectrum of SS-*tert*-butylethyl(phenyl)carbamo(dithioperoxoate) (5-5)



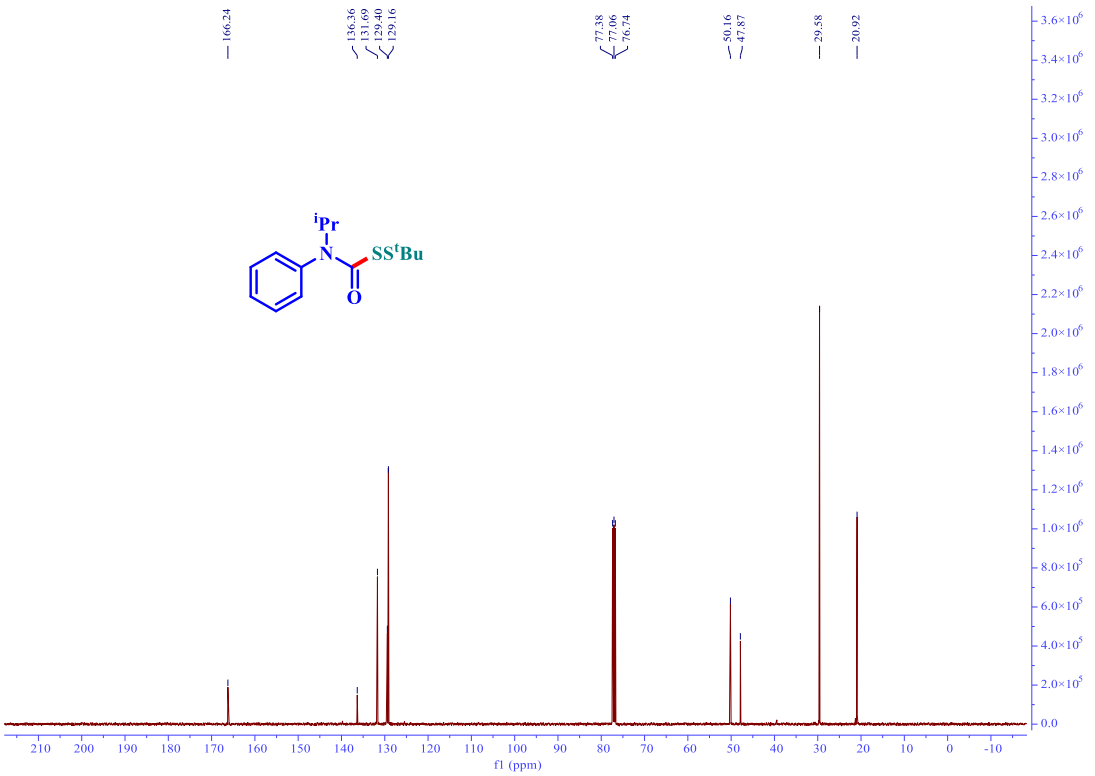
^{13}C NMR Spectrum of SS-*tert*-butylethyl(phenyl)carbamo(dithioperoxoate) (5-5)



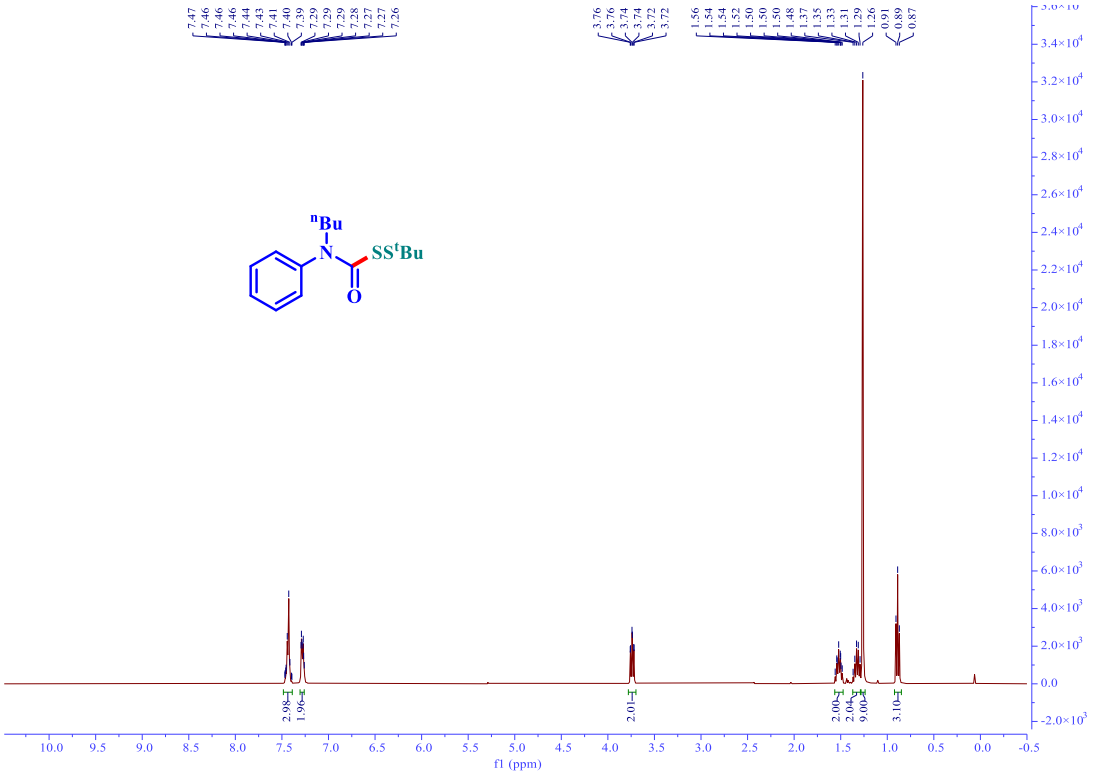
^{1}H NMR Spectrum of SS-*tert*-butyl isopropyl(phenyl)carbamo(dithioperoxoate) (5-6)



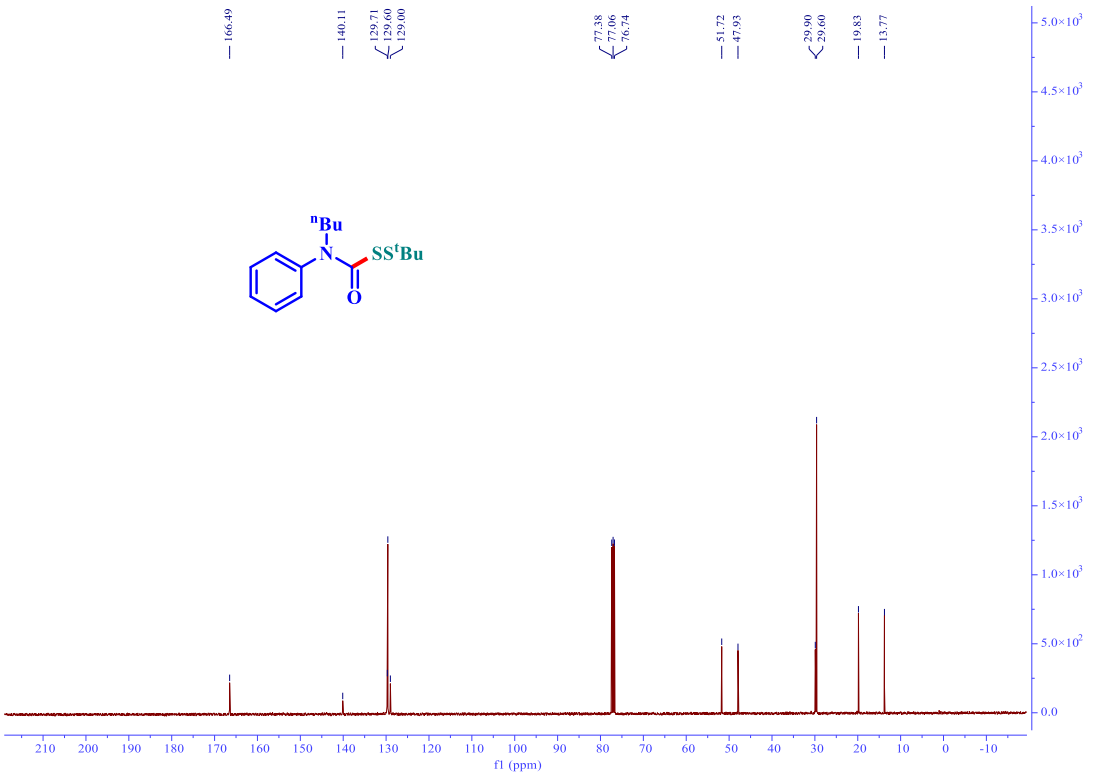
^{13}C NMR Spectrum of SS-*tert*-butyl isopropyl(phenyl)carbamo(dithioperoxoate) (5-6)



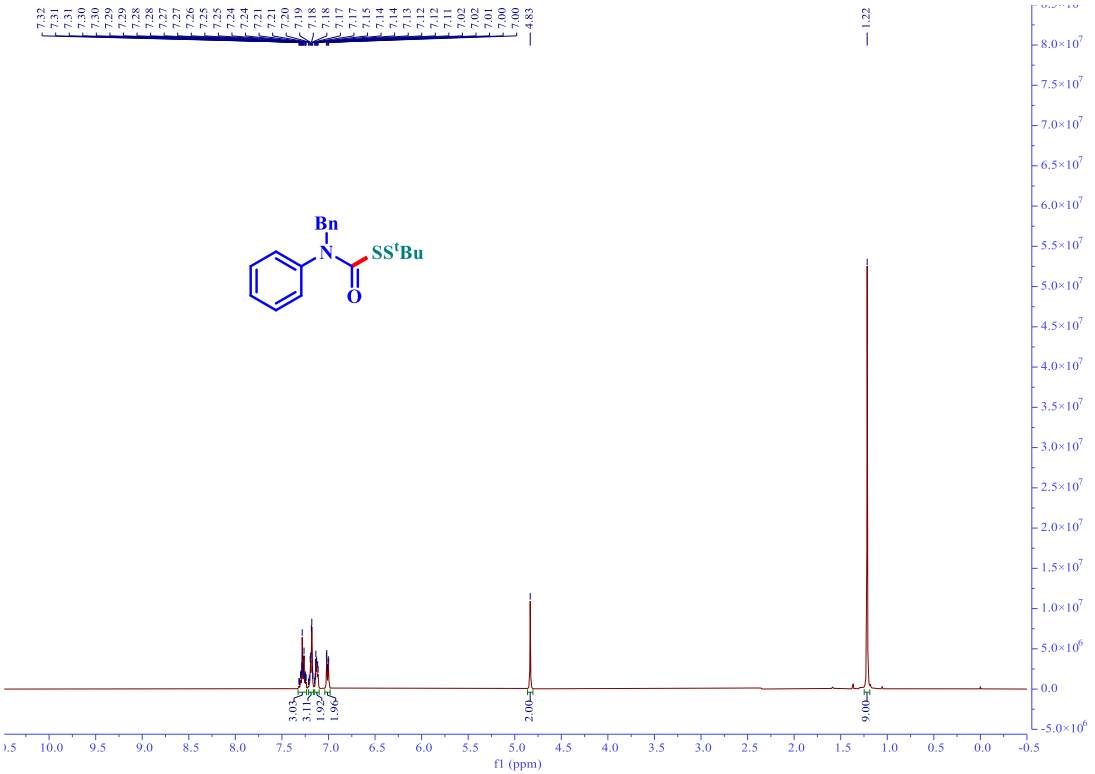
^{1}H NMR Spectrum of SS-*tert*-butyl butyl(phenyl)carbamo(dithioperoxoate) (5-7)



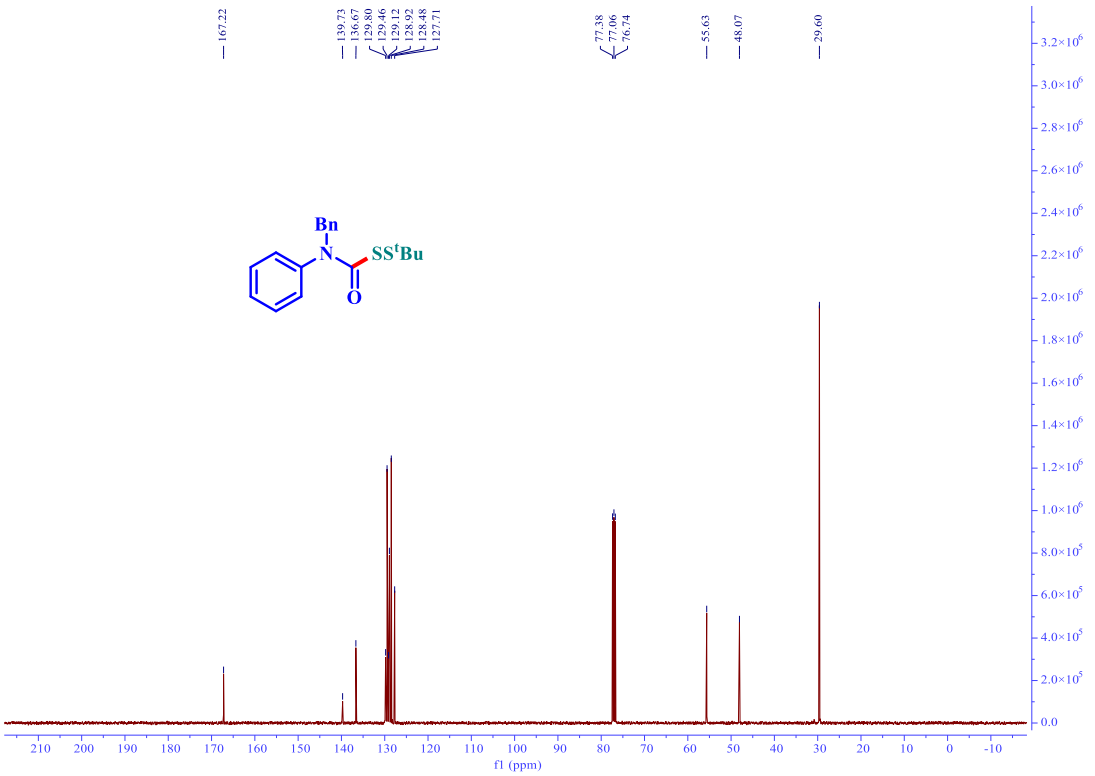
^{13}C NMR Spectrum of SS-*tert*-butyl butyl(phenyl)carbamo(dithioperoxoate) (5-7)



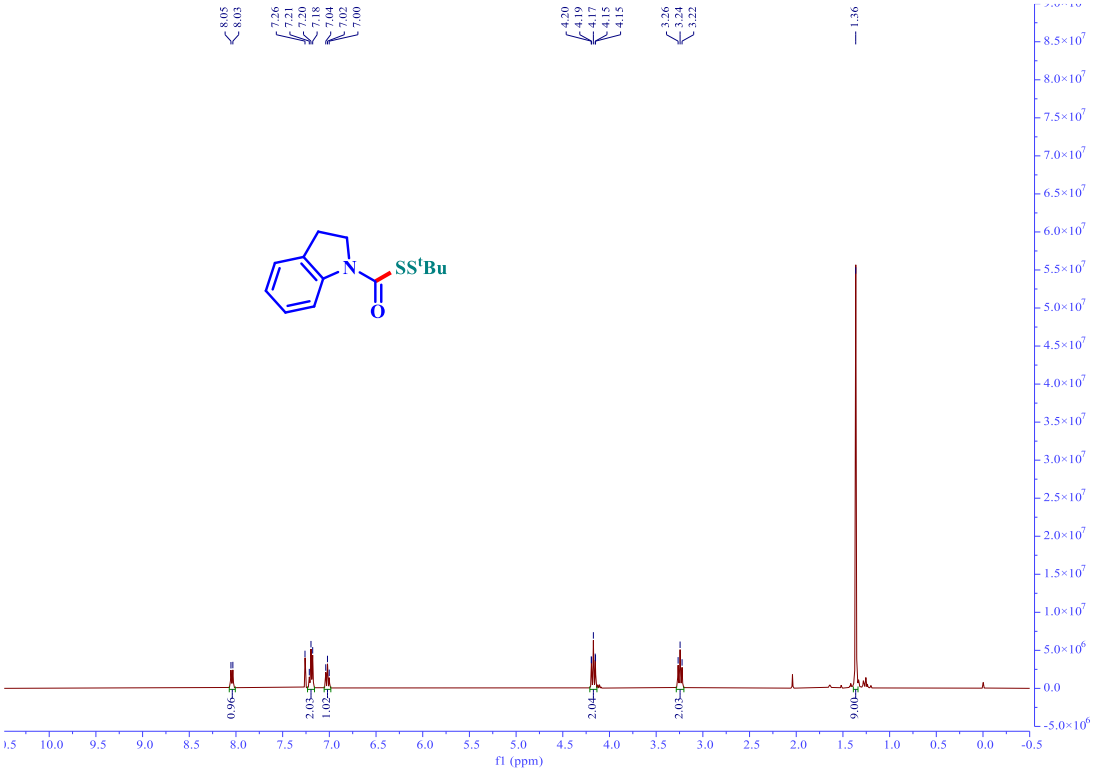
^{1}H NMR Spectrum of SS-*tert*-butyl benzyl(phenyl)carbamo(dithioperoxoate) (5-8)



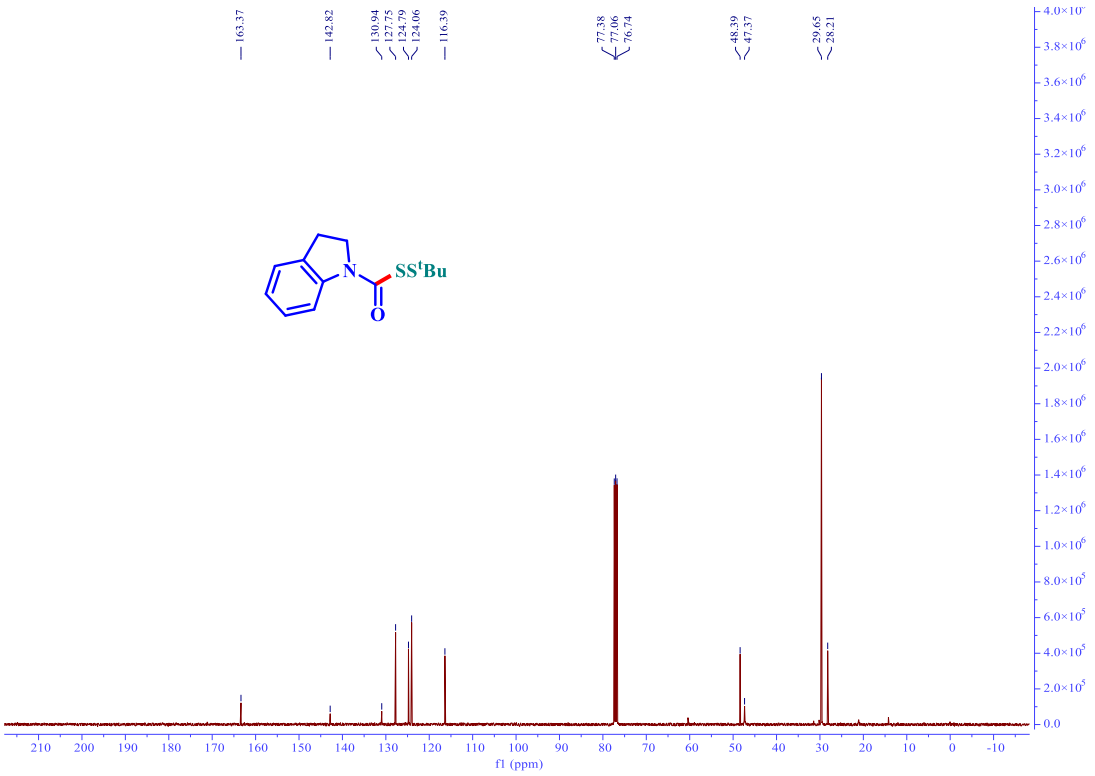
^{13}C NMR Spectrum of SS-*tert*-butyl benzyl(phenyl)carbamo(dithioperoxoate) (5-8)



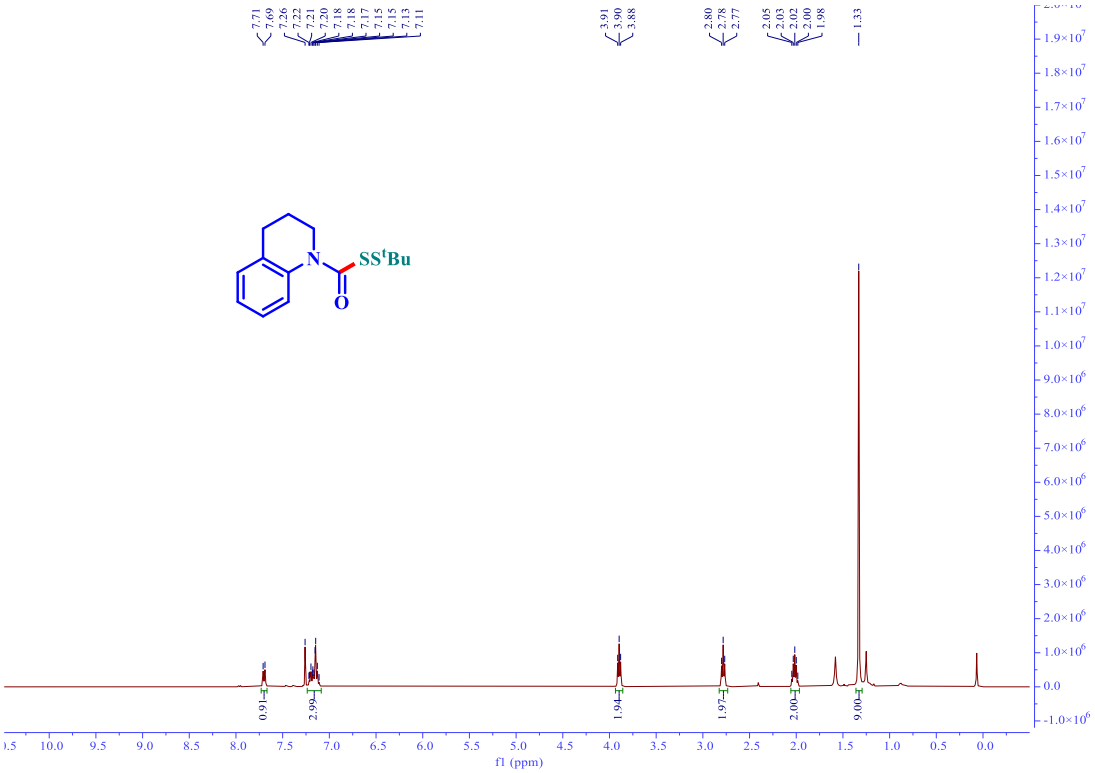
^{1}H NMR Spectrum of SS-(tert-butyl) indoline-1-carbo(dithioperoxoate) (5-9)



^{13}C NMR Spectrum of SS-(tert-butyl) indoline-1-carbo(dithioperoxoate) (5-9)

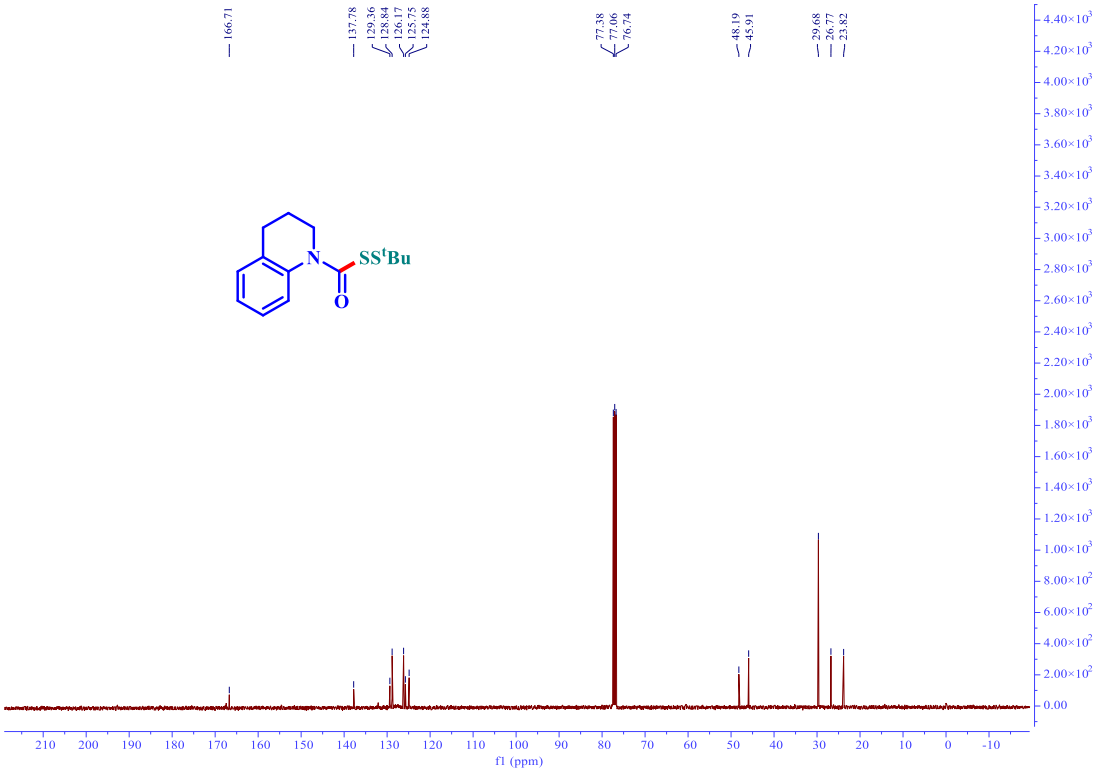


^{1}H NMR Spectrum of SS-(tert-butyl) 3,4-dihydroquinoline-1(2H)-carbo (dithioper- oxoate) (5-10)

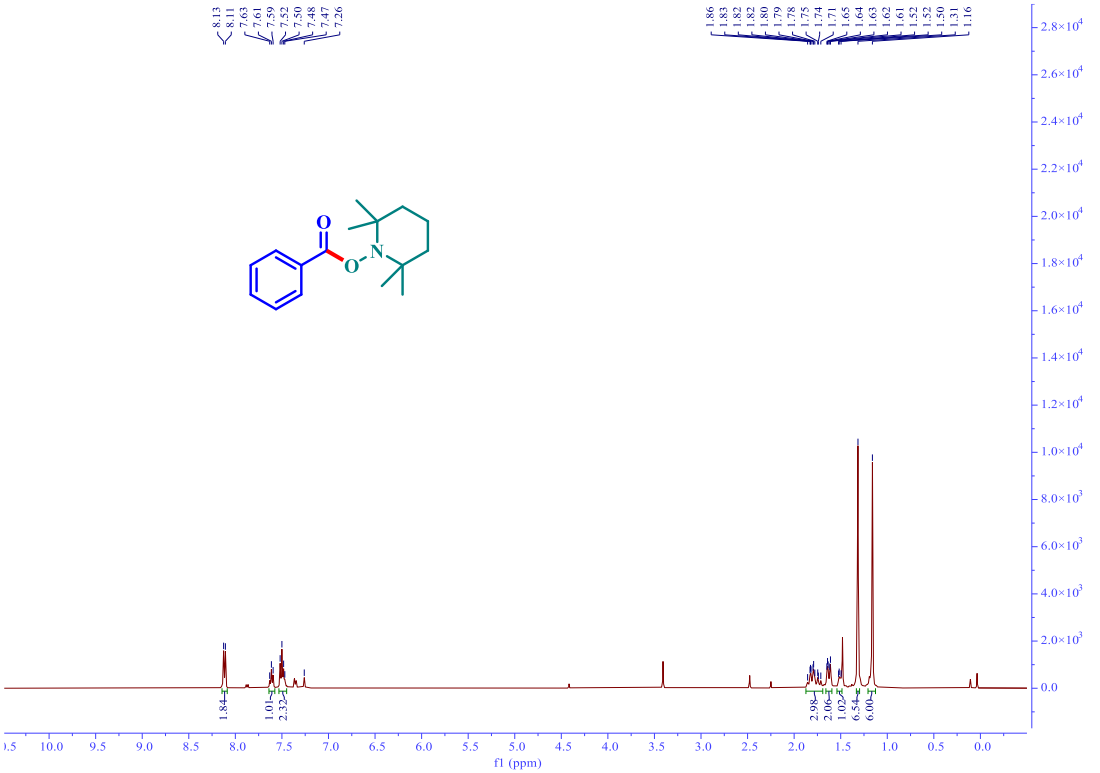


^{13}C NMR Spectrum of SS-(tert-butyl) 3,4-dihydroquinoline-1(2H)-carbo

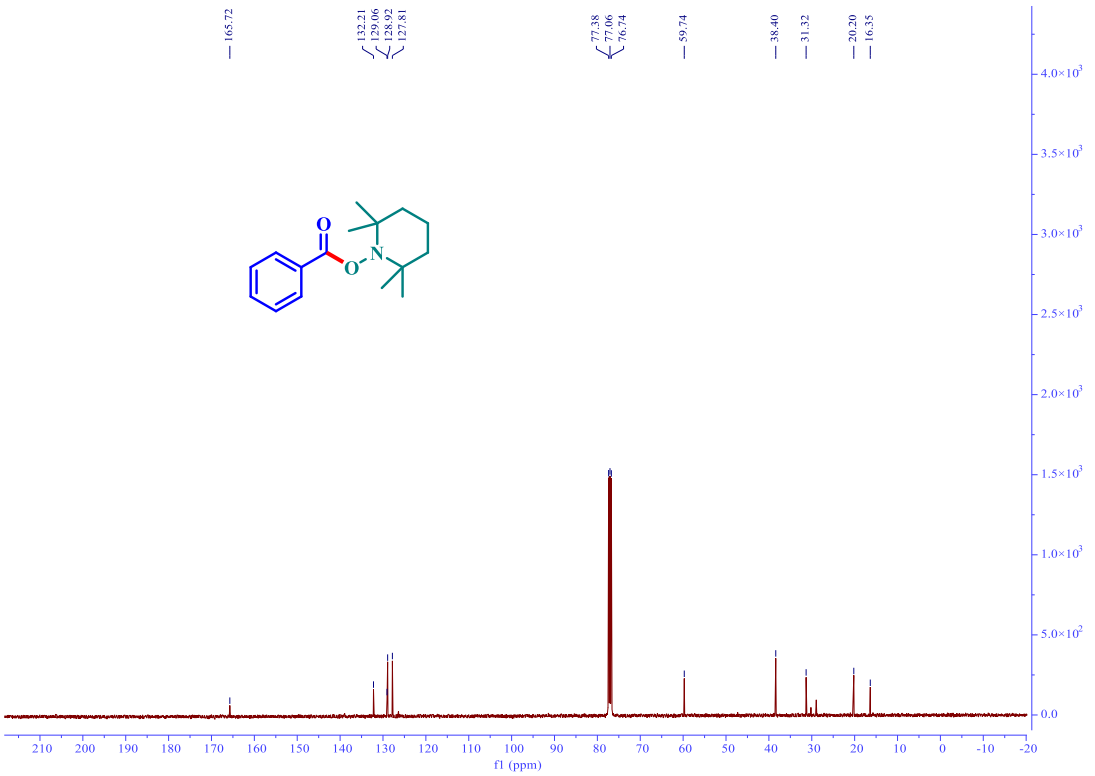
(dithioper- oxoate) (5-10)



^{1}H NMR Spectrum of *O*-bezoylated-TEMPO



^{13}C NMR Spectrum of *O*-bezoylated-TEMPO



10. Reference

[1]. (a) Xianqiang Kong, Yiyi Chen, Xiaohui Chen, Zheng-Xuan Lu, Wei Wang, Shao-Fei Ni, and Zhong-Yan Cao, *Org. Lett.,* **2022,** *24*, 2137.; (b) Xiaochen Ji, Zhonglin Yang, Xinzhuang Wu, Guo-Jun Deng and Huawen Huang, *J. Org. Chem.,* **2022**, *87*, 6, 4168.

[2]. (a)Shweta K. Gediya, Vijyesh K. Vyas, Guy J. Clarkson and Martin Wills, *Org. Lett.*, **2021**, *23*, 7803.: (b) Yu Zhang, Xinye Yang, Qizheng Yao and Dawei Ma, *Org. Lett.* **2012**, *14*, 3056.

[3]. Arnab Dey and Chandra M. R. Volla, *Org. Lett.*, **2021**, *23*, 5018.

[4]. (a) Zijun Wu and Derek A. Pratt, *Angew. Chem. Int. Ed.*, **2021**, *60*, 15598.; (b). Yue Gui, Lingqi Qiu, Yaohao Li, Hongxing Li, and Suwei Dong, *J. Am. Chem. Soc.* **2016**, 138, *14*, 4890.

[5]. Lei Bao, Zhi-Xiang Wang, and Xiang-Yu Chen, *Org. Lett.*, **2023**, *25*, 565.