Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Thioesters by Electrochemical Three-Component Reaction Involving Elemental Sulfur

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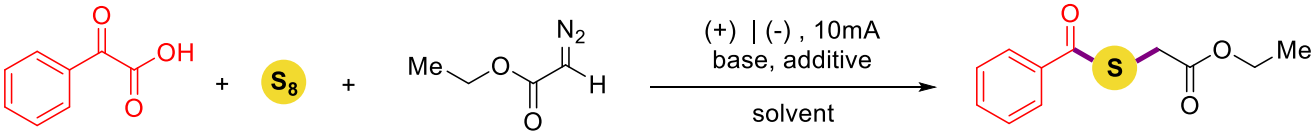
1 General information

Unless otherwise noted, all commercially available reagents and solvents were used without further additional purification. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60 μm). The instrument for electrolysis was dual display potentiostat (HY3005ET). The electrode all bought from Shanghai Yueci Electronic Technology Co.,Ltd. Cyclic voltammograms were obtained on a CHI 605E potentiostat. ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance spectra (NMR) were obtained on Bruker Avance II 400 MHz, Bruker Avance III 500 MHz and Bruker Avance NEO 600M recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (J) in hertz (Hz). High resolution mass spectra (HRMS) were performed by an Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer.

2 Optimization of supplementary reaction conditions

Table S1. Optimization of supplementary reaction conditions for the synthesis of **3a**[a].



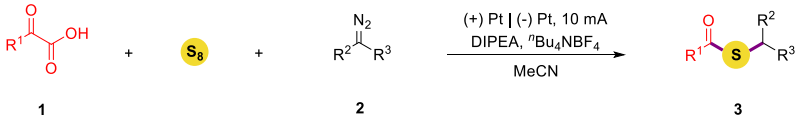
1a, 1.5 equiv 0.3 equiv **2a**, 1.0 equiv **3a**

Entry	(+)	(-)	Base	Additive	Solvent	Yield[b]/%
1	Graphite rod	Graphite rod	DIPEA	$^{n}Bu_4NBF_4$	MeCN	42
2	Graphite rod	Ni plate	DIPEA	$^{n}Bu_4NBF_4$	MeCN	60
3	Graphite rod	Cu plate	DIPEA	$^{n}Bu_4NBF_4$	MeCN	51
4	Graphite rod	Ti plate	DIPEA	$^{n}Bu_4NBF_4$	MeCN	48
5	Pt plate	Graphite rod	DIPEA	$^{n}Bu_4NBF_4$	MeCN	62
6	Pt plate	Cu plate	DIPEA	$^{n}Bu_4NBF_4$	MeCN	42
7	Pt plate	Ti plate	DIPEA	$^{n}Bu_4NBF_4$	MeCN	45
8	Pt plate	Pt plate	PMDETA	$^{n}Bu_4NBF_4$	MeCN	31
9	Pt plate	Pt plate	DMAP	$^{n}Bu_4NBF_4$	MeCN	20
10	Pt plate	Pt plate	DBU	$^{n}Bu_4NBF_4$	MeCN	trace
11	Pt plate	Pt plate	DABCO	$^{n}Bu_4NBF_4$	MeCN	49
12	Pt plate	Pt plate	KOH	$^{n}Bu_4NBF_4$	MeCN	trace
13	Pt plate	Pt plate	Cs_2CO_3	$^{n}Bu_4NBF_4$	MeCN	n.r.
14	Pt plate	Pt plate	DIPEA	LiOAc	MeCN	trace
15	Pt plate	Pt plate	DIPEA	KI	MeCN	trace
16	Pt plate	Pt plate	DIPEA	$^{n}Bu_4NBF_4$	DMF	26
17	Pt plate	Pt plate	DIPEA	$^{n}Bu_4NBF_4$	DMSO	n.r.
18	Pt plate	Pt plate	DIPEA	$^{n}Bu_4NBF_4$	THF	n.r.

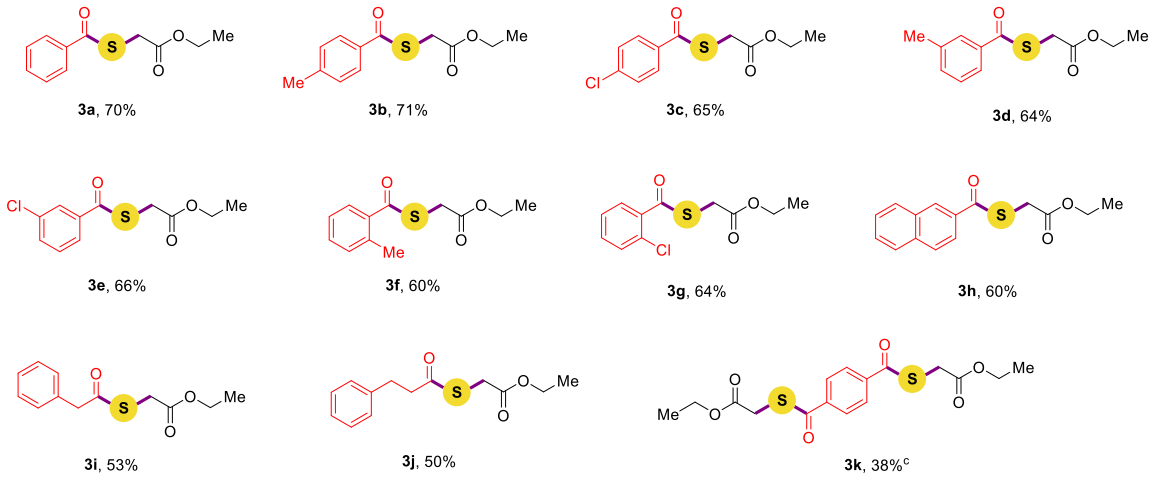
[a] Standard reaction conditions: **1a** (0.9 mmol), **2a** (0.6 mmol), $\mathbf{S_8}$ (0.3 equiv, 0.18 mmol), Additive (0.5 mmol), Base (0.9 mmol), Solvent (6 ml), I = 10 mA, 50 ℃, N_2, 12 h. [b] Isolated yield. n.r.: no reaction occurred.

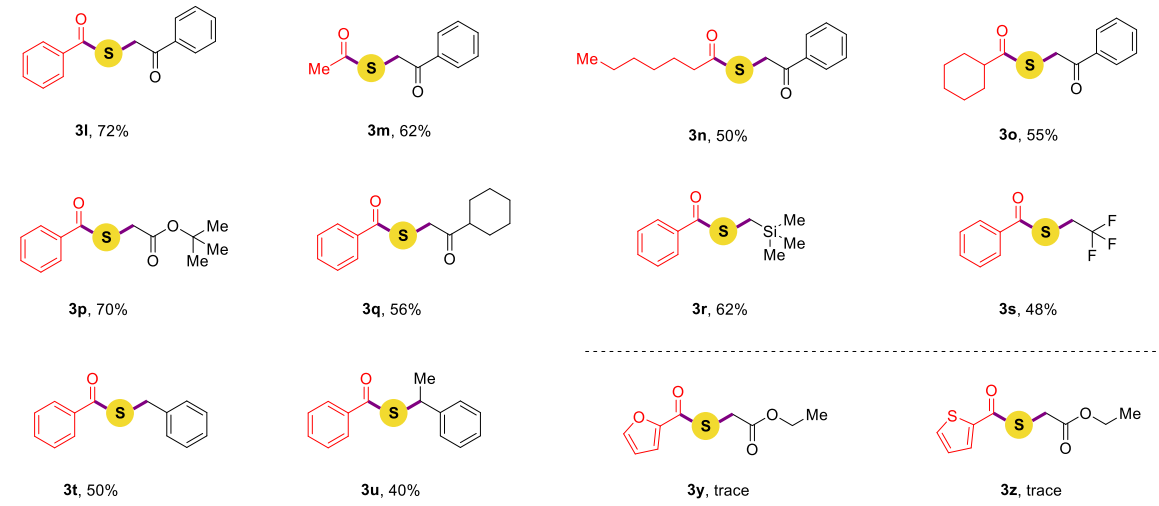
3 Substrate scope of three-component reaction

Table S2. Substrate scope of three-component reaction[a,b]



1 + S_8 + 2 → 3





[a] Standard reaction conditions: undivided cell, Pt plate (15×15×0.3 mm) anode and cathode, **1** (0.9 mmol), **2** (0.6 mmol), $\mathbf{S_8}$ (0.3 equiv, 0.18 mmol), $^{n}Bu_4NBF_4$ (0.5 mmol), DIPEA (0.9 mmol), MeCN (6 mL), constant current = 10 mA, 50 ℃. [b] Isolated yield. n.r.: no reaction. [c] Di-*α*-ketoacid **1k** (0.45 mmol) was used, partial decomposition of **3k** was observed during electrochemical process.

4 Details of device

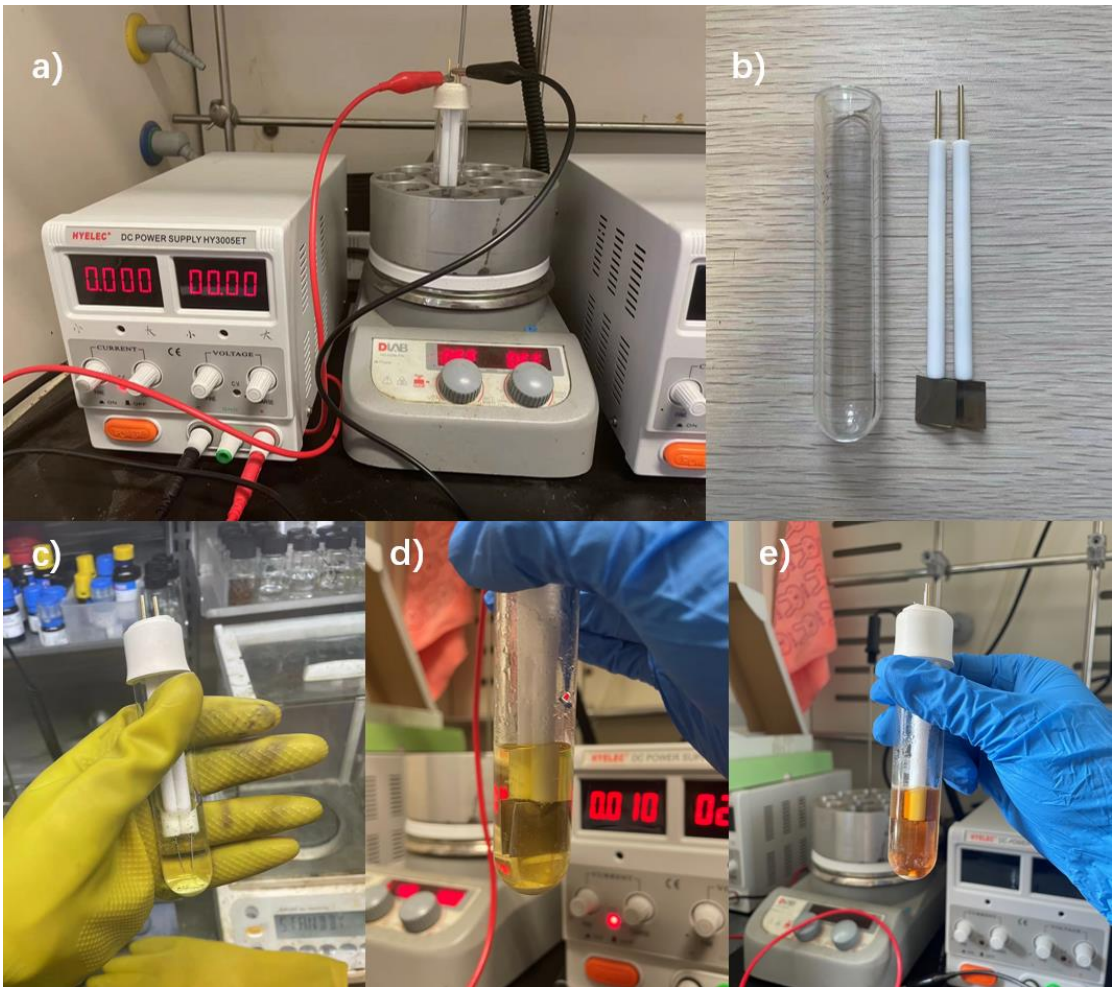
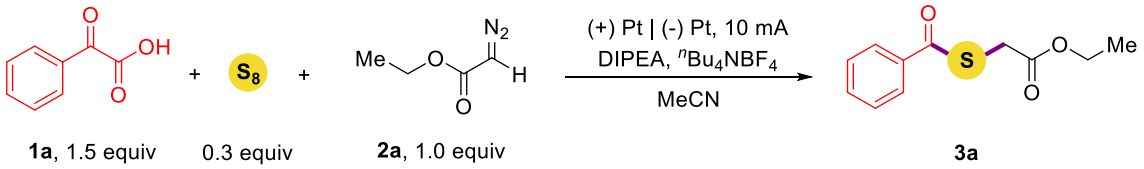


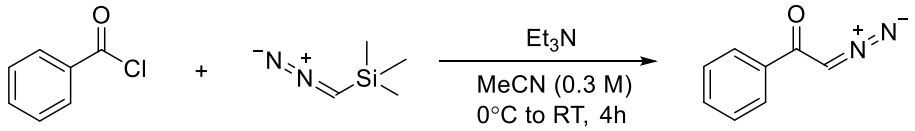
Figure S1. (a): electrolysis device; (b): reaction vial and Pt plates; (c): the image of the vial before starting the reaction; (d): the image of the vial reacting for 6 h; (e): the image of the end of reaction.

5 Representative procedures for the synthesis of products

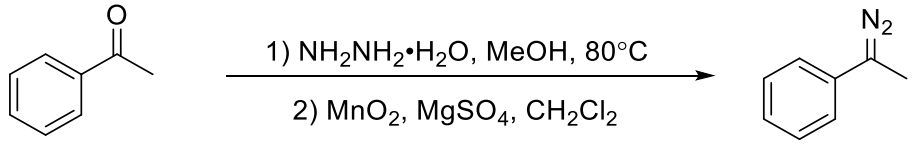


1a, 1.5 equiv 0.3 equiv **2a**, 1.0 equiv **3a**

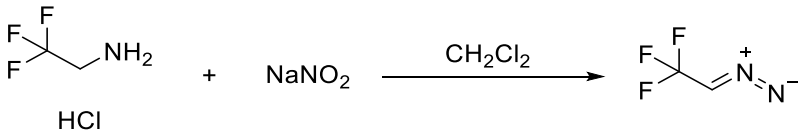
In an oven-dried quartz tube equipped with a stir bar, $^{n}Bu_4NBF_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **1a** (1.5 equiv, 0.9 mmol), $\mathbf{S_8}$ (0.3 equiv, 0.18 mmol), **2a** (1.0 equiv, 0.6 mmol), DIPEA (1.5 equiv, 0.9 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃. The reaction mixture was concentrated in vacuum. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 12:1 to 8:1) to give the pure product **3a** as a yellow liquid.



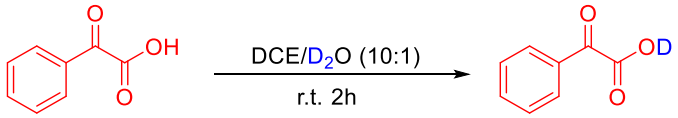
To (trimethylsilyl)diazomethane (1.2 equiv.) and triethylamine (1.0 equiv.) was dissolved in MeCN at 0 ℃. To this mixture the corresponding benzoyl chloride was added dropwise under Ar. The reaction mixture was allowed to warm to room temperature and stirred for 4 hours or until the full consumption of the benzoyl chloride. The solvent was evaporated and Na_2CO_3 (sat. aq.) was added before extracting with Et_2O. Dry the combined organic part and concentrate. The crude was purified by flash chromatography using PE/EtOAc (10:1).[S1]



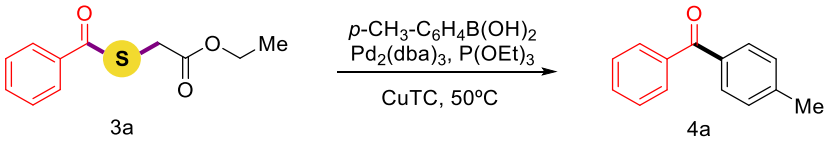
To a solution of acetophenone (20.0 mmol, 1.0 equiv) in methanol (20 mL) was added hydrazine hydrate (2.9 mL, 60.0 mmol, 3.0 equiv) and the mixture was stirred at 80 ℃ for 3 h in a sealed vial. The solvent was removed under reduced pressure and the crude residue diluted with water (25 mL) and CH_2Cl_2 (25 mL). The mixture was separated and the aqueous layer extracted with CH_2Cl_2 (3×25 mL) and the combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to provide the desired hydrazone. The crude hydrazone was used for the generation of corresponding diazo compound without further purification. Activated manganese dioxide (690 mg, 8.0 mmol) was added to a cold solution (0 ℃) of hydrazone (2.0 mmol) and $MgSO_4$ (361 mg, 3.0 mmol) in CH_2Cl_2 (5 mL), at which point the mixture turned deep red immediately. The reaction mixture was stirred for 2 h at 0 ℃ and 1 h at room temperature, and then filtered off through cotton to provide the aryldiazoalkanes as a clear, deep red solution. The solution of compound was used without further purification.[S2]



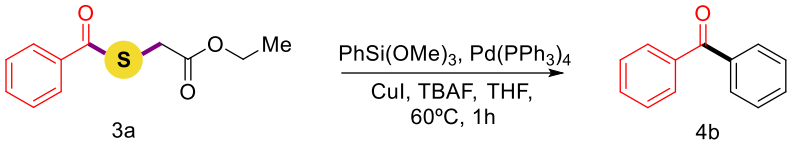
$CF_3CH_2NH_2$ ·HCl (13.55 g, 100 mmol) and $NaNO_2$ (7.59 g, 110 mmol) were added to a 500 mL round bottom flask equipped with a stir bar, and the flask was sealed with a septum and purged with argon three times. Degassed toluene (200 mL) was added, and the reaction mixture was cooled to 0 ℃ upon stirring under Ar for 30 min. Degassed H_2O (20 mL) was added under Ar. The solution was stirred for 2 h at 0 ℃, then for an additional 30 min at 10 ℃ under Ar. The aqueous layer was frozen in the freezer overnight. The organic layer was then transferred using a Teflon needle to a flame-dried round bottom flask and dried (K_2CO_3, 10 g) for 1 h. The concentration of the yellow solution of CF_3CHN_2 was analyzed by ^{19}F NMR using trifluorotoluene as an internal standard.[S3]



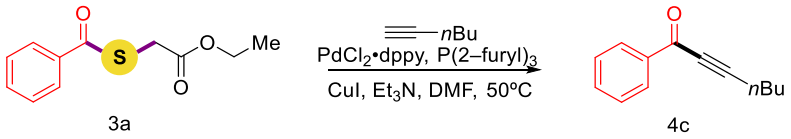
To the 20 mL-Schlenk tube, the carboxylic acid (0.4 mmol) was dissoved in 2 mL DCE, and then 0.2 mL D_2O was added and stirred at rt for 2 h. And the deuterated acids were directly used via syringe about 1 mL (0.2 mmol) to the reaction Schlenk tube and removed the solvent by vaccum.[S4]



3a (1 equiv, 0.1 mmol), *p*-CH_3-$C_6H_4B(OH)_2$ (10 equiv), CuTC (1.5 equiv), $Pd_2(dba)_3$ (2.5 mol%) and triethylphosphite (20 mol%) were added in 2 mL THF under N_2 atmosphere. The mixture was stirred at 50 ℃ for 24 h and then was concentrated in vacuo. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 16:1 to 10:1) to give the pure product **4a** as a white solid.[S5]

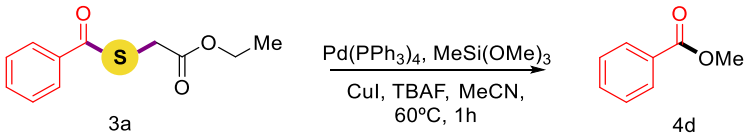


3a (1 equiv, 0.1 mmol), $PhSi(OMe)_3$ (1.1 equiv), $Pd(PPh_3)_4$ (10 mol%), TBAF (1 equiv) and CuI (1 equiv) were added in 2 mL THF under N_2 atmosphere. The mixture was stirred at room temperature and then was concentrated in vacuo. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 16:1 to 10:1) to give the pure product **4b** as a white solid.[S6]



3a (1 equiv, 0.1 mmol), $PdCl_2$ dppf (20 mol%), $P(2\text{-furyl})_3$ (20 mol%), CuI (1.2 equiv), Et_3N (2 equiv)and hexyne (2 equiv) were added in 2 mL DMF under N_2 atmosphere. The mixture was stirred at room temperature 3h and then was

concentrated in vacuo. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 16:1 to 10:1) to give the pure product **4c** as a white solid.[S6]

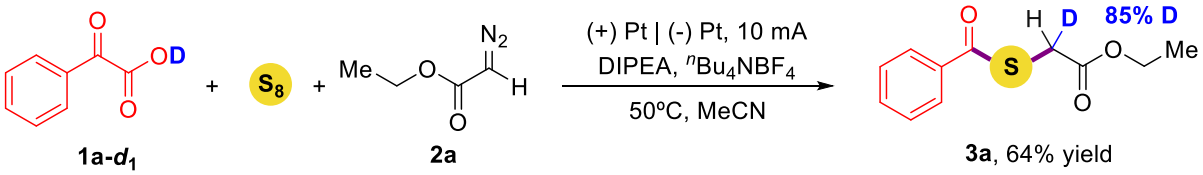


3a (1 equiv, 0.1 mmol), $PhSi(OMe)_3$ (1.5 equiv), $Pd(PPh_3)_4$ (10 mol%), TBAF (1 equiv) and CuI (1 equiv)were added in 2 mL MeCN under N_2 atmosphere. The mixture was stirred at room temperature and then was concentrated in vacuo. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 16:1 to 10:1) to give the pure product **4d** as a white solid.[S6]

6 Mechanistic investigations

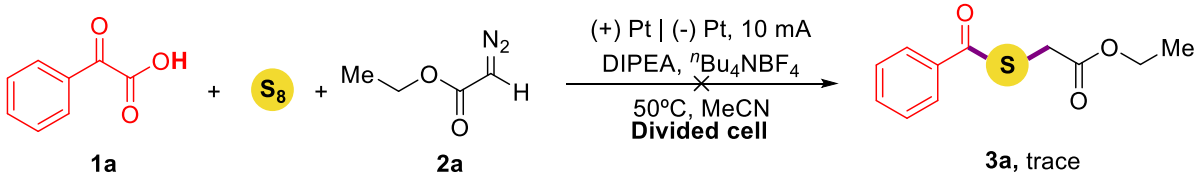
To clarify the reaction mechanisms, a variety of experiments were conducted in Figure S2 and Figure S4. Deuterium labelling experiments indicated that the proton from α-keto acid can be transferred to thioester efficiently (Figure S2a). Only trace amount of **3a** could be observed when using a divided cell as the reaction vessel, implying that cathodic reduction of the intermediate could be an important step in the synthesis of thioesters (Figure S2b). Product **3a** was not detected when 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as radical scavenger was added to the system (Figure S2c, equation (1)). 1,4-diphenylbuta-1,3-diyne was utilized to detect whether the presence of trisulfur radical anion [S7,S8]. Product **5a** was not obtained and an abundant amount of 1,4-diphenylbuta-1,3-diyne was left, which may exclude the formation of trisulfur radical anion by two electrons transfer process in electrochemical environment (Figure S2c, equation (2)). When only **1a** was used as the reactant, the acyl radical coupled product **5b** was isolated in 26% yield. This result indirectly showed that α-keto acids can provide acyl radicals by anodic oxidation process (Figure S2c, equation (3)). When α-keto acid and S_8 were used as substrates without diazoalkane, benzoic dithioperoxyanhydride (**5c**) was isolated in 35% yield, which was from the radical dimerization and confirmed the existence of carbonyl thiyl radical in this transformation (Figure S2c, equation (4)). Under the electrochemical conditions, **5c** could not further react with diazo compound **2a** to afford desired product **3a**, which suggested that **5c** were not involved in such electrochemical reaction (Figure S2c, equation (5)). Next, the cyclic voltammetry (CV) experiments were carried out to gain more insights about this electrochemical mechanism (Figure S4). Two oxidation peaks of benzoylformic acid (**1a**) (the red line) were observed at 0.87 V and 1.22 V respectively. The CV of ethyl diazoacetate (**2a**) (the blue line) showed one oxidation peak at 2.50 V. These results demonstrated that the oxidation of benzoylformic acid occurred preferentially during the reaction process (Figure S4 in Supporting information).

a) Deuterium labeling experiment



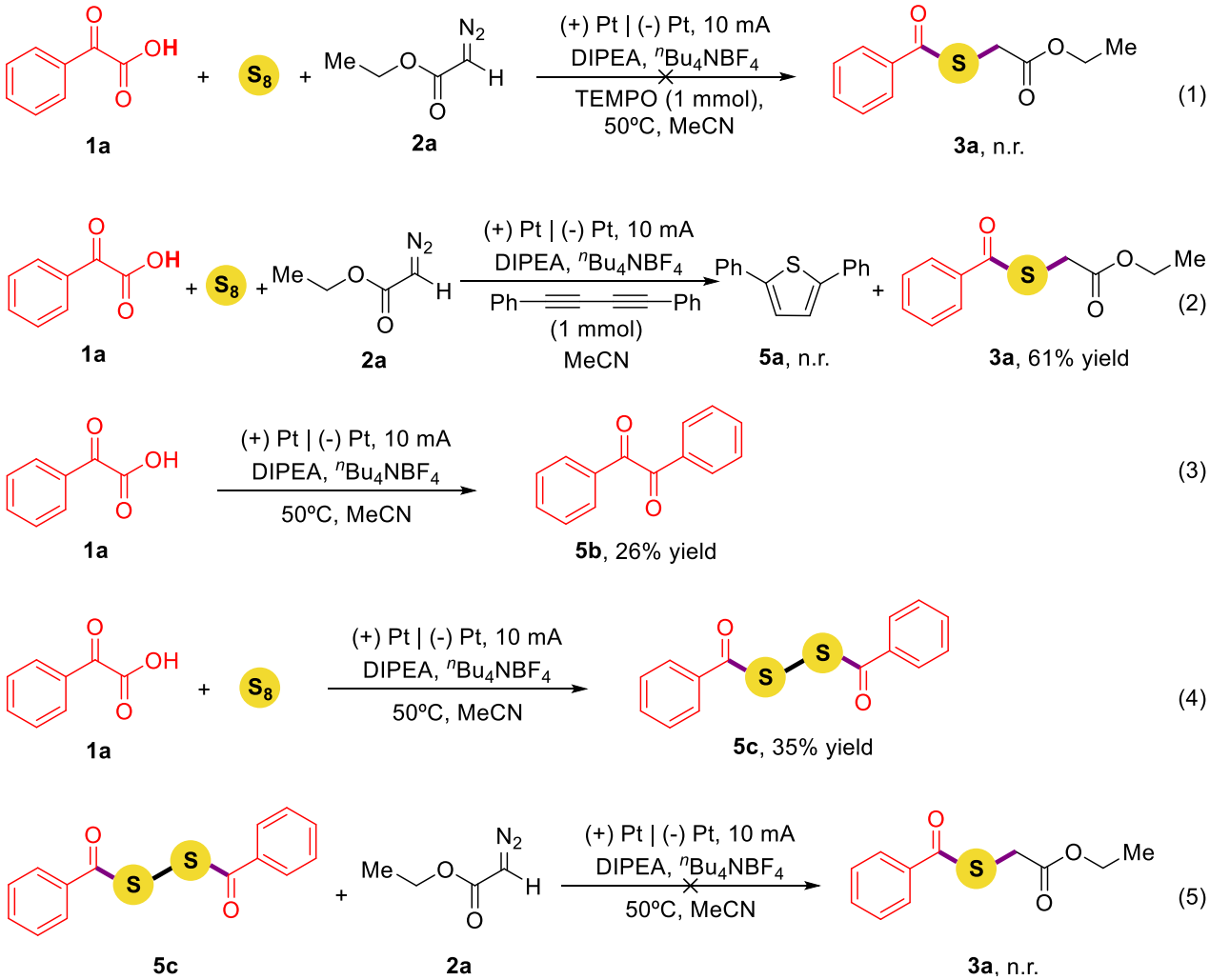
1a-d_1 **2a** **3a**, 64% yield

b) Divided cell experiment



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

c) Control experiments



1a **2a** **5a**, n.r. **3a**, 61% yield

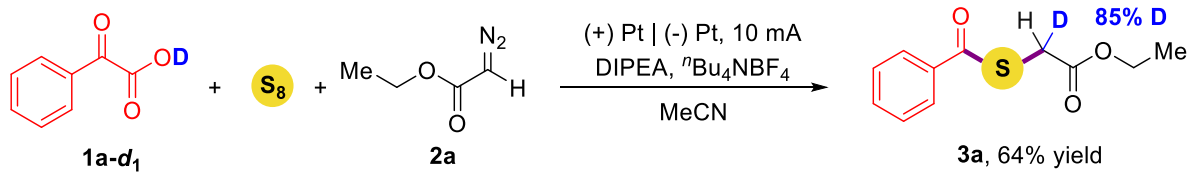
1a **5b**, 26% yield

1a **5c**, 35% yield

5c **2a** **3a**, n.r.

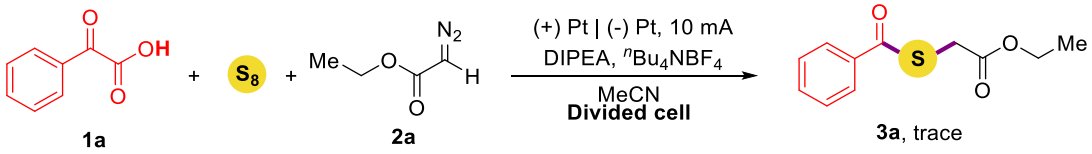
Figure S2. Mechanistic investigation for the synthesis of thioesters by electrochemical activation of elemental sulfur.

6.1 Procedures for the deuterium labeling experiment



In an oven-dried quartz tube equipped with a stir bar, ^{n}Bu$_4$NBF$_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **1a-d_1** (1.5 equiv, 0.9 mmol), **S_8** (0.3 equiv, 0.18 mmol), **2a** (1.0 equiv, 0.6 mmol), DIPEA (1.5 equiv, 0.9 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃. The reaction mixture was concentrated in vacuum. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 12:1 to 8:1) to give the pure product **3a** as a yellow liquid. The ratio of deuteration was determined by ^{1}H NMR spectra.

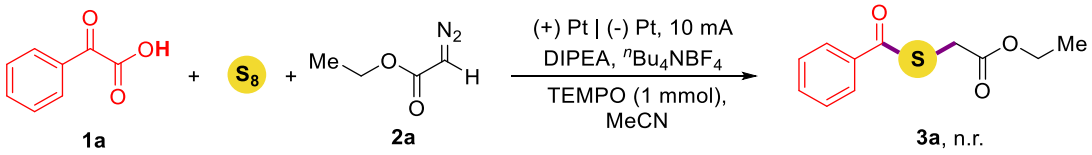
6.2 Procedures for the divided cell experiment



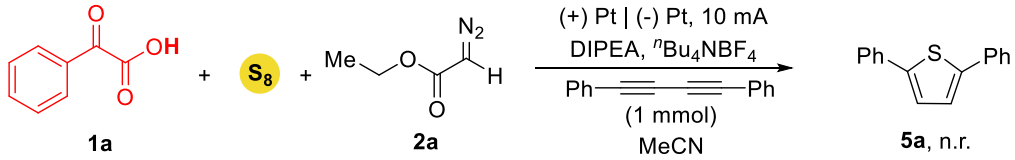
In an oven-dried divided electrolysis cell equipped with a stir bar. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 3.0 cm. Under nitrogen atmosphere, ^{n}Bu$_4$NBF$_4$ (0.5 mmol), **1a** (1.5 equiv, 0.9 mmol), **S_8** (0.3 equiv, 0.18 mmol), **2a** (1.0 equiv, 0.6 mmol), DIPEA (1.5 equiv, 0.9 mmol), MeCN (6.0 mL) were addeded to the anode cell, ^{n}Bu$_4$NBF$_4$ (0.5 mmol), MeCN (6.0 mL) were addeded to the cathode cell. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃.

Figure S3. Divided cell device

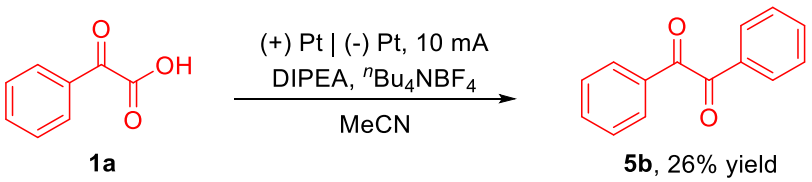
6.3 Procedures for the control experiments



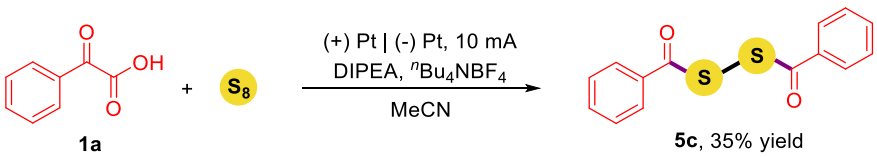
In an oven-dried quartz tube equipped with a stir bar, $^{n}Bu_4NBF_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **1a** (1.5 equiv, 0.9 mmol), $\mathbf{S_8}$ (0.3 equiv, 0.18 mmol), **2a** (1.0 equiv, 0.6 mmol), DIPEA (1.5 equiv, 0.9 mmol), TEMPO (1 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃. **3a** was not detected by ^{1}H NMR spectra.



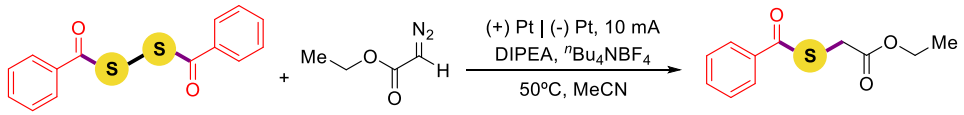
In an oven-dried quartz tube equipped with a stir bar, $^{n}Bu_4NBF_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **1a** (1.5 equiv, 0.9 mmol), $\mathbf{S_8}$ (0.3 equiv, 0.18 mmol), **2a** (1.0 equiv, 0.6 mmol), 1,4-diphenylbuta-1,3-diyne (1 mmol), DIPEA (1.5 equiv, 0.9 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃. The reaction mixture was concentrated in vacuum. **5a** was not detected by ^{1}H NMR spectra.



In an oven-dried quartz tube equipped with a stir bar, $^{n}Bu_4NBF_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **1a** (1.5 equiv, 0.9 mmol), DIPEA (1.5 equiv, 0.9 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃. The reaction mixture was concentrated in vacuum. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 12:1 to 8:1) to give the pure product **5b** as a colorless liquid.



In an oven-dried quartz tube equipped with a stir bar, $^{n}Bu_4NBF_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **1a** (1.5 equiv, 0.9 mmol), $\mathbf{S_8}$ (0.3 equiv, 0.18 mmol), DIPEA (1.5 equiv, 0.9 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 12 h at 50 ℃. The mixture was purified with flash column chromatography (petroleum ether:ethyl acetate 12:1 to 8:1) to give the pure product **5c** as a colorless soild.



5c **2a** **3a**, n.r.

In an oven-dried quartz tube equipped with a stir bar, $^{n}Bu_4NBF_4$ (0.5 mmol) was added. The bottle was equipped with platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the anode and platinum plate (1.5 cm × 1.5 cm × 0.3 mm) as the cathode. The distance between two electrodes is 0.5 cm. Under nitrogen atmosphere, **5c** (1.5 equiv, 0.9 mmol), **2a** (1.0 equiv, 0.6 mmol), DIPEA (1.5 equiv, 0.9 mmol) and MeCN (6.0 mL) were addeded respectively into the tube. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 4 h at 50 ℃. **3a** was not detected.

6.4 Cyclic voltammetry (CV) experiments

Cyclic voltammetry was performed in a three-electrode system at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode is a platinum plate. The reference was Ag/AgCl electrode submerged in saturated aqueous KCl solution,and separated from reaction by a salt bridge. The scan rate was 0.01 V/s.

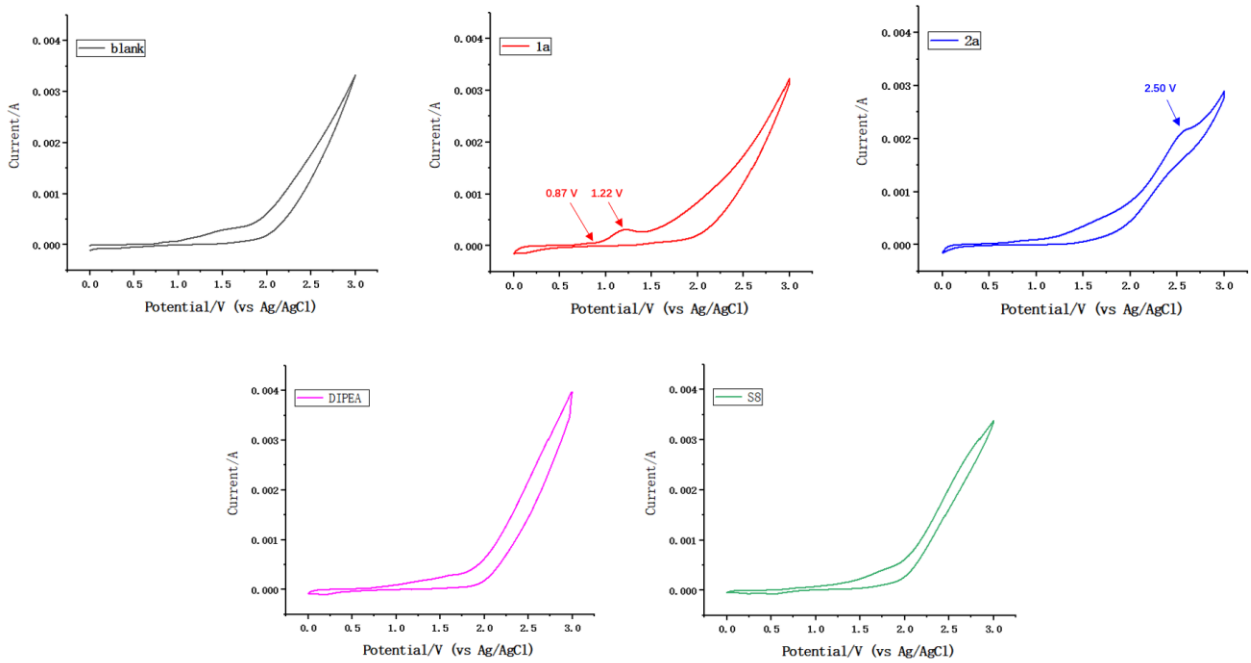


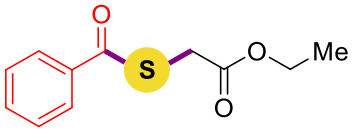
Figure S4. The cyclic voltammogram (CV) experiments. $^{n}Bu_4NBF_4$ (0.4 mmol), **1a** (0.2 mmol), **2a** (0.2 mmol), DIPEA (0.2 mmol), $\mathbf{S_8}$ (0.2 mmol), in MeCN (24 mL).

6.5 Faradaic efficiency[S9]

m = 0.42 mmol, n = 1, F = 96485 C*mol^{-1}, I = 10 mA, t = 12 h.

$$\eta = \frac{m*n*F}{I*t} * 100\% = 9.38\%$$

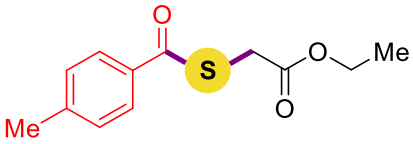
7 Characterization data of synthesized compound



3a

ethyl 2-(benzoylthio)acetate (3a) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (94 mg, 70% yield).

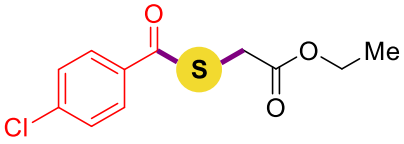
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.88 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).
Compound **3a** is known compound, and the proton spectrum is fully consistent with literature reported.[S10]



3b

ethyl 2-((4-methylbenzoyl)thio)acetate (3b) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (100 mg, 71% yield).

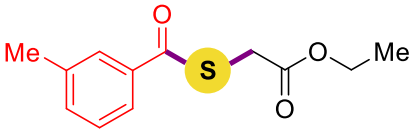
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 4.31 – 4.15 (m, 2H), 3.87 (s, 2H), 2.41 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.61, 168.89, 144.73, 133.72, 129.38, 127.50, 61.84, 31.37, 21.69, 14.12.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_3SNa$, 261.0558; found, 261.0561.



3c

ethyl 2-((4-chlorobenzoyl)thio)acetate (3c) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (100 mg, 65% yield).

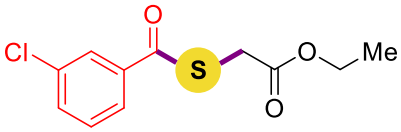
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).
Compound **3c** is known compound, and the proton spectrum is fully consistent with literature reported.[S10]



3d

ethyl 2-((3-methylbenzoyl)thio)acetate (3d) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (91 mg, 64% yield).

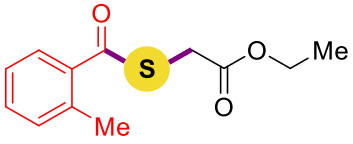
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.19 (dd, *J* = 7.0, 3.3 Hz, 1H), 4.03 – 3.91 (m, 2H), 2.46 (m, *J* = 16.0, 11.4, 7.3 Hz, 1H), 2.24 – 2.11 (m, 1H), 2.11 – 1.92 (m, 2H), 1.33 (s, 9H).
Compound **3d** is known compound, and the proton spectrum is fully consistent with literature reported.[S10]



3e

ethyl 2-((3-chlorobenzoyl)thio)acetate (3e) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (102 mg, 66% yield).

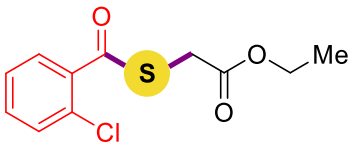
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 6.19 (dd, *J* = 7.0, 3.2 Hz, 1H), 4.04 – 3.93 (m, 2H), 2.53 – 2.35 (m, 1H), 2.16 (m, *J* = 16.7, 8.3, 4.4 Hz, 1H), 2.10 – 1.95 (m, 2H).
^{13}C NMR (101 MHz, CDCl3) δ 190.94, 137.89, 136.48, 128.72, 101.29, 83.89, 68.53, 32.81, 24.66.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_3SClNa$, 281.0020; found, 281.0015.



3f

***S*-(tetrahydrofuran-2-yl) 4-chlorobenzothioate (3f)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (85 mg, 60% yield).

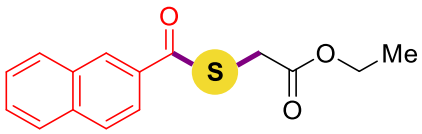
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.41 (m, *J* = 10.8, 4.2 Hz, 1H), 7.26 (m, *J* = 11.1, 7.9 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 2H), 2.49 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.10, 168.85, 137.28, 136.49, 132.10, 131.68, 128.62, 125.88, 77.35, 77.04, 76.72, 61.85, 32.00, 20.62, 14.13.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_3SNa$, 261.0560; found, 261.0561.



3g

ethyl 2-((2-chlorobenzoyl)thio)acetate (3g) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (93 mg, 64% yield).

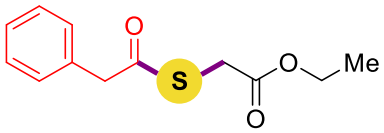
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.92, 168.34, 136.42, 132.70, 131.14, 131.01, 129.49, 126.80, 61.98, 32.28, 14.11.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{11}O_3SClNa$, 281.0013; found, 281.0015.



3h

ethyl 2-((2-naphthoyl)thio)acetate (3h) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (98 mg, 60% yield).

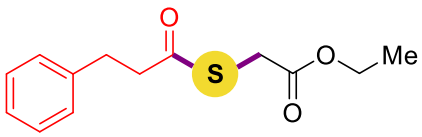
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.95 (m, *J* = 12.9, 8.4 Hz, 2H), 7.90 – 7.79 (m, 2H), 7.56 (m, *J* = 14.8, 7.0 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.98, 168.83, 135.93, 133.52, 132.41, 129.61, 129.05, 128.72, 128.64, 127.84, 127.05, 123.09, 61.93, 31.59, 14.16.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{14}NO_3SNa$, 297.0563; found, 297.0561.



3i

ethyl 2-((2-phenylacetyl)thio)acetate (3i) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (75 mg, 53% yield).

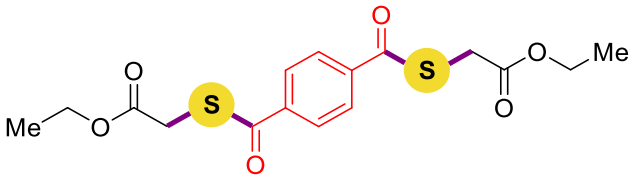
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.13 (m, 5H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 3.67 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.64, 168.55, 133.01, 129.66, 128.75, 127.63, 61.84, 50.02, 31.66, 14.05.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}O_3SNa$, 261.0556; found, 261.0561.



3j

ethyl 2-((3-phenylpropanoyl)thio)acetate (3j) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (75 mg, 50% yield).

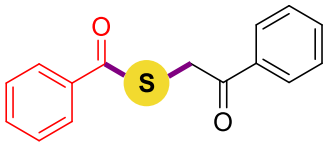
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, *J* = 13.5, 6.1 Hz, 2H), 7.20 (m, *J* = 12.7, 7.1 Hz, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 2H), 3.08 – 2.96 (m, 2H), 2.92 (m, *J* = 11.5, 4.8 Hz, 2H), 1.29 – 1.26 (t, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.56, 168.66, 139.79, 128.58, 128.28, 126.44, 61.84, 45.10, 31.31, 31.24, 14.09.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{13}H_{16}O_3SNa$, 275.0723; found, 275.0718.



3k

diethyl 2,2'-(terephthaloylbis(sulfanediyl))diacetate (3k) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (84 mg, 38% yield).

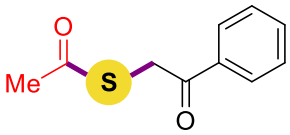
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 4H), 4.24 (q, *J* = 7.1 Hz, 4H), 3.91 (s, 4H), 1.31 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.43, 168.35, 139.97, 127.74, 62.07, 31.66, 14.12.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{16}H_{18}O_6S_2Na$, 393.0444; found, 393.0442.



3l

S-(2-oxo-2-phenylethyl) benzothioate (3l) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (110 mg, 72% yield).

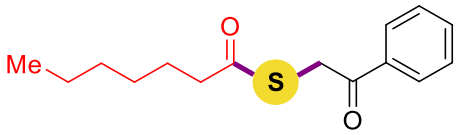
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06, 8.04, 8.01, 7.99, 7.62, 7.60, 7.59, 7.57, 7.52, 7.50, 7.48, 7.46, 7.44, 4.59.
Compound **3l** is known compound, and the proton spectrum is fully consistent with literature reported.[S11]



3m

S-(2-oxo-2-phenylethyl) ethanethioate (3m) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (72 mg, 62% yield).

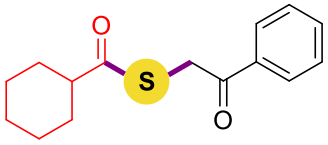
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 4.40 (s, 2H), 2.41 (s, 3H).
Compound **3m** is known compound, and the proton spectrum is fully consistent with literature reported.[S12]



3n

S-(2-oxo-2-phenylethyl) heptanethioate (3n) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 20:1 to 16:1) to afford the product as a colorless oil (79 mg, 50% yield).

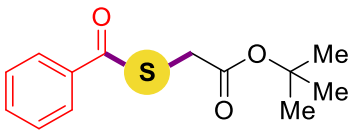
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.39 (s, 2H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.63 (m, 2H), 1.35 – 1.27 (m, 6H), 0.88 (t, *J* = 6.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.04, 193.54, 135.61, 133.69, 128.77, 128.52, 43.79, 36.25, 31.39, 28.57, 25.54, 22.42, 14.00.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{20}O_2SNa$, 287.1082; found, 287.1082.



3o

S-(2-oxo-2-phenylethyl) cyclohexanecarbothioate (3o) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 20:1 to 16:1) to afford the product as a colorless oil (86 mg, 55% yield).

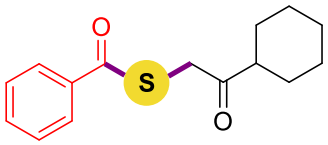
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.37 (s, 2H), 2.69 – 2.49 (m, 1H), 1.96 (d, *J* = 12.6 Hz, 2H), 1.89 – 1.74 (m, 2H), 1.68 (m, *J* = 13.7, 7.2 Hz, 1H), 1.56 – 1.41 (m, 2H), 1.32 – 1.26 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.40, 193.73, 135.69, 133.61, 128.73, 128.50, 52.41, 35.93, 29.47, 25.58, 25.43.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{19}O_2S$, 263.1100; found, 263.1106.



3p

tert-butyl 2-(benzoylthio)acetate (3p) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (105 mg, 60% yield).

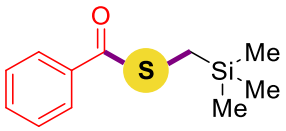
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 6.5 Hz, 1H), 7.45 (t, *J* = 6.8 Hz, 2H), 3.81 (s, 2H), 1.48 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.29, 167.78, 136.38, 133.68, 128.69, 127.39, 82.34, 32.61, 27.96.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{13}H_{16}O_3SNa$, 275.0722; found, 275.0718.



3q

***S*-(tetrahydrofuran-2-yl) heptanethioate (3q)** Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (88 mg, 56% yield).

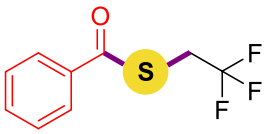
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.25 (m, 1H), 4.09 – 3.88 (m, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.30 (m, *J* = 19.8, 12.4, 6.9 Hz, 1H), 2.17 – 1.97 (m, 2H), 1.97 – 1.84 (m, 1H), 1.79 – 1.63 (m, 2H), 1.29 (s, 6H), 0.88 (t, *J* = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.89, 89.39, 67.87, 42.52, 32.37, 31.36, 28.59, 25.45, 24.35, 22.40, 13.97.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{15}H_{18}O_2SNa$, 285.0921; found, 285.0925.



3r

S-((trimethylsilyl)methyl) benzothioate (3r) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (74 mg, 62% yield).

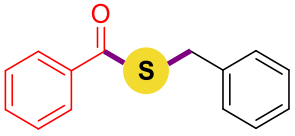
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 2.28 (s, 2H), 0.15 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.11, 137.26, 133.06, 128.54, 127.13, 13.69, -1.74.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{11}H_{17}OSiS$, 225.0770; found, 225.0769.



3s

S-(2,2,2-trifluoroethyl) benzothioate (3s) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a colorless oil (63 mg, 48% yield).

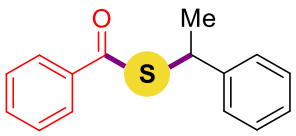
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 3.80 (q, *J* = 9.8 Hz, 2H).
^{19}F NMR (565 MHz, $CDCl_3$) δ -66.22.
Compound **3s** is known compound, and the proton spectrum is fully consistent with literature reported.[S13]



3t

S-benzyl benzothioate (3t) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (68 mg, 50% yield).

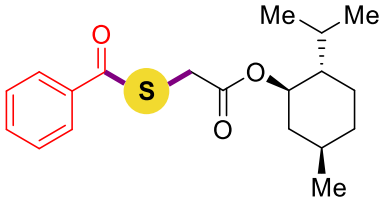
^{1}H NMR (400 MHz, $CDCl_3$). δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 5.4 Hz, 1H), 4.32 (s, 2H).
Compound **3t** is known compound, and the proton spectrum is fully consistent with literature reported.[S14]



3u

S-(1-phenylethyl) benzothioate (3u) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 12:1 to 8:1) to afford the product as a colorless oil (58 mg, 40% yield).

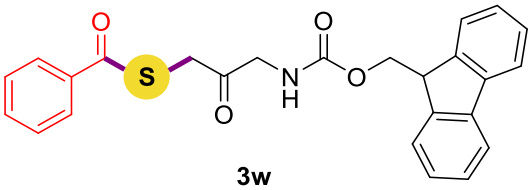
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27 (s, 1H), 4.96 (q, *J* = 7.1 Hz, 1H), 1.76 (d, *J* = 7.1 Hz, 3H).
Compound **3u** is known compound, and the proton spectrum is fully consistent with literature reported.[S14]



3v

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(benzoylthio)acetate (3v) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a violet oil (106 mg, 50% yield).

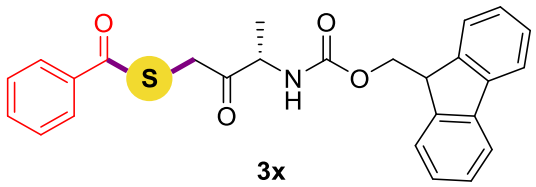
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 9.9 Hz, 2H), 7.60 (t, *J* = 16.9, 9.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.74 (m, *J* = 10.9, 4.4 Hz, 1H), 3.87 (s, 2H), 2.15 – 1.99 (m, 1H), 1.91 (m, *J* = 13.9, 7.0, 2.8 Hz, 1H), 1.66 (m, *J* = 19.6, 9.8 Hz, 3H), 1.58 – 1.38 (m, 2H), 1.09 – 0.99 (m, 2H), 0.95 – 0.88 (m, 6H), 0.76 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.07, 168.29, 136.35, 133.71, 128.71, 127.40, 76.07, 46.99, 40.66, 34.20, 31.75, 31.41, 26.22, 23.43, 21.98, 20.73, 16.29.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for $C_{19}H_{26}O_3SNa$, 357.1506; found, 357.1500.



3w

S-(3-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-oxopropyl) benzothioate (3w) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 4:1 to 1:1) to afford the product as a white soild (108 mg, 42% yield).

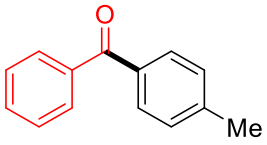
^{1}H NMR (400 MHz, $CDCl_3$). δ 7.99 – 7.93 (m, 2H), 7.75 (d, J = 7.5 Hz, 2H), 7.62 – 7.57 (m, 3H), 7.47 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 5.51 (s, 1H), 4.40 (d, J = 7.0 Hz, 2H), 4.33 (d, J = 4.9 Hz, 2H), 4.22 (t, J = 7.0 Hz, 1H), 3.90 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$). δ 199.97, 190.37, 156.16, 143.81, 141.33, 135.82, 134.11, 128.84, 127.73, 127.54, 127.10, 125.10, 119.99, 67.23, 50.03, 47.16, 36.17.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for, 454.1083; found, 454.1090.



3x

(S)-S-(3-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-2-oxobutyl) benzothioate (3x) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 4:1 to 1:1) to afford the product as a white soild (109 mg, 41% yield).

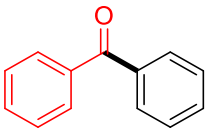
^{1}H NMR (400 MHz, $CDCl_3$). δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.57 (m, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (td, *J* = 7.4, 1.0 Hz, 2H), 5.53 (d, *J* = 6.7 Hz, 1H), 4.61 (dd, *J* = 14.1, 6.9 Hz, 1H), 4.42 (dt, *J* = 17.4, 10.5 Hz, 2H), 4.22 (t, *J* = 6.7 Hz, 1H), 4.01 (q, *J* = 16.6 Hz, 2H), 1.49 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$). δ 203.06, 190.31, 155.70, 143.79, 141.35, 136.01, 133.94, 128.77, 127.74, 127.51, 127.10, 125.04, 120.00, 66.96, 55.14, 47.25, 36.12, 17.77.
HRMS (ESI-TOF, *m/z*): $[M+Na]^+$ calcd for, 468.1240; found, 468.1249.



4a

4-Methylbenzophenone (4a) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (14 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.75 – 7.69 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H).
Compound **4a** is known compound, and the proton spectrum is fully consistent with literature reported.[S15]

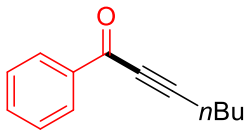


4b

Benzophenone (4b) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (13 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.70 – 7.66 (m, 2H), 7.65 – 7.58 (m, 3H), 7.52 – 7.46 (m, 2H).

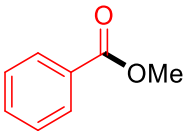
Compound **4b** is known compound, and the proton spectrum is fully consistent with literature reported.[S15]



4c

1-phenylhept-2-yn-1-one (4c) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 8:1) to afford the product as a colorless oil (14 mg, 73% yield).

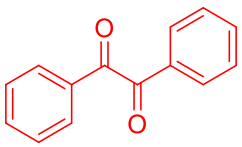
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 7.1 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.76 – 1.61 (m, 2H), 1.51 (dd, *J* = 14.2, 7.1 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 3H).
Compound **4c** is known compound, and the proton spectrum is fully consistent with literature reported.[S16]



4d

methyl benzoate (4d) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a colorless oil (9 mg, 68% yield).

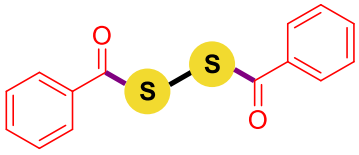
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.93 (m, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 3.91 (s, 3H).
Compound **4d** is known compound, and the proton spectrum is fully consistent with literature reported.[S17]



5b

Benzil (5b) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 14:1 to 8:1) to afford the product as a white solid (24 mg, 26% yield).

^{1}H NMR (400 MHz, $CDCl_3$).δ 8.06 – 7.92 (m, 2H), 7.66 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.58 – 7.43 (m, 2H).
Compound **5b** is known compound, and the proton spectrum is fully consistent with literature reported.[S18]



5c

Benzoic dithioperoxyanhydride (5c) Purified via flash column chromatography on silica gel (from petroleum ether:ethyl acetate 16:1 to 10:1) to afford the product as a white solid (43 mg, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H).

Compound **5c** is known compound, and the proton spectrum is fully consistent with literature reported.[S15]

8 Reference

(S1) H. Yang, Z. P. Bao, L. C. Wang, X. F. Wu, *Org. Lett.* **2023**, *25*, 1963-1968.

(S2) J.-S. Poh, D. N. Tran, C. Battilocchio, J. M. Hawkins, S. V. Ley, *Angew. Chem. Int. Ed.* **2015**, *54*, 7920.

(S3) O. A. Argintaru, D. Ryu, I. Aron, G. A. Molander, *Angew. Chem. Int. Ed.* **2013**, *52*, 13656-13660.

(S4) P. Ji, Y. Zhang, Y. Dong, H. Huang, Y. Wei, W. Wang, *Org. Lett.* **2020**, *22*, 1557-1562.

(S5) M. A. Maverick, M. Gaillard, J.-J. Vasseur, F. Debart, M. Smietana, *Eur. J. Org. Chem.* **2022**, e202101061.

(S6) Z. Qiao, X. Jiang, *Org. Lett.* **2016**, *18*, 1550-1553.

(S7) S. Murakami, T. Nanjo, Y. Takemoto, *Org. Lett.* **2021**, *23*, 7650-7655.

(S8) J. Fährmann, G. Hilt, *Chem. Eur. J.* **2021**, *27*, 11141-11149.

(S9) C. Jiang, S. J. A. Moniz, A. Wang, T. Zhang, J. Tang, *Chem. Soc. Rev.* **2017**, *46*, 4645-4660.

(S10) C.-L. Yi, Y.-T. Huang, C.-F. Lee, *Green. Chem.* **2013**, *15*, 2476-2484.

(S11) T. Aoyama, T. Takido, M. Kodomari, *Synth. Commun.* **2003**, *33*, 3817-3824.

(S12) A. A. Heredia, S. M. Soria-Castro, L. M. Bouchet, G. Oksdath-Mansilla, C. A. Barrionuevo, D. A. Caminos, F. R. Bisogno, J. E. Arguello, A. B. Penenory, *Org. Biomol. Chem.* **2014**, *12*, 6516-6526.

(S13) S. Huang, Z. Xia, K. Lu, H. Lu, C. H. Tung, Z. Xu, *Chin. J. Chem.* **2020**, *38*, 1625-1628.

(S14) T. Xu, T. Cao, M. Yang, R. Xu, X. Nie, S. Liao, *Org. Lett.* **2020**, *22*, 3692-3696.

(S15) G. Liu, N. Zheng, X. Duan, X. Sun, W. Song, *Green. Chem.* **2023**, *25*, 5035-5040.

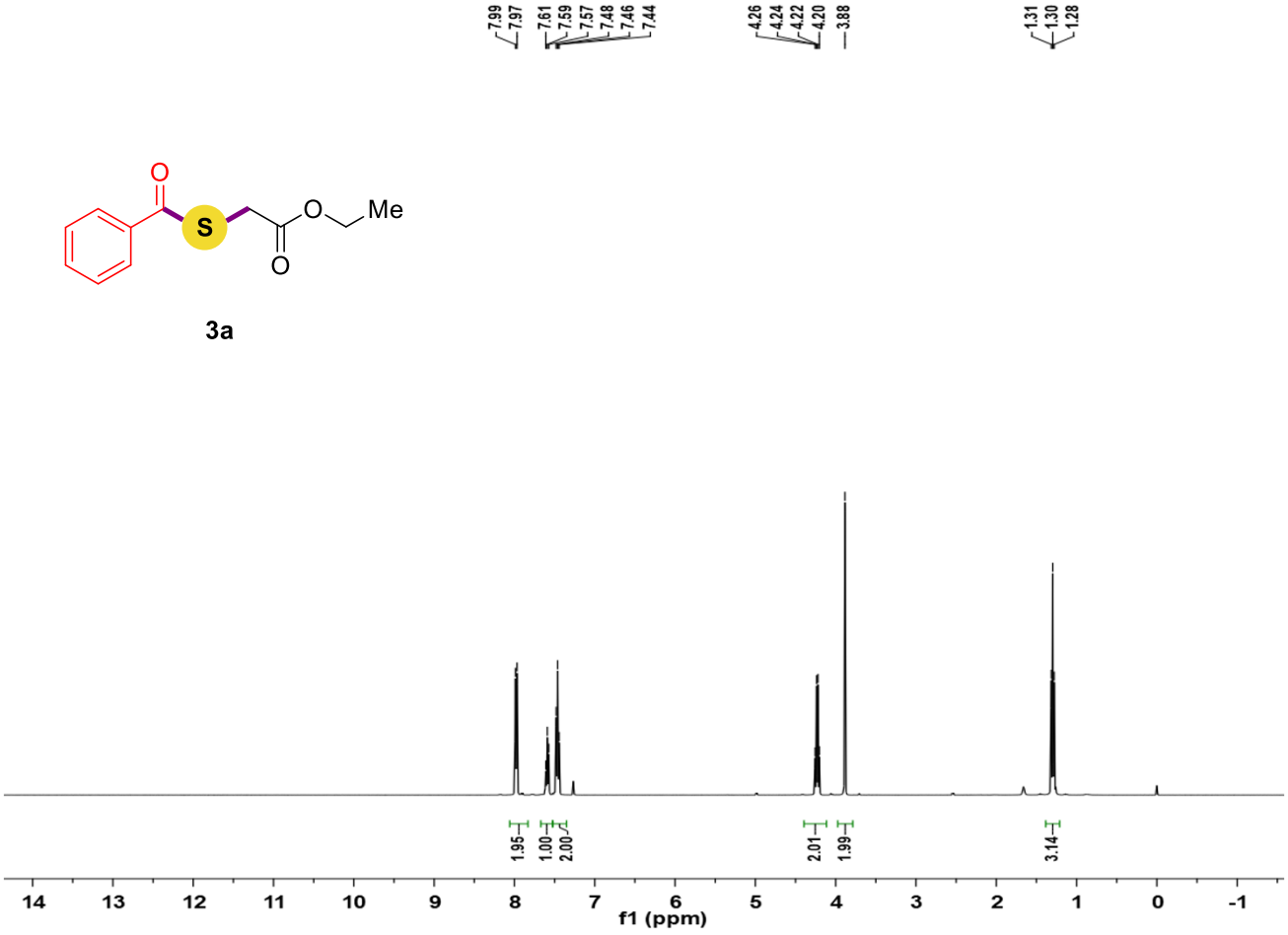
(S16) S. Yang, X. Zhu, S. Zhou, S. Wang, Z. Feng, Y. Wei, H. Miao, L. Guo, F. Wang, G. Zhang, X. Gu, X. Mu, *Sci. China Chem.* **2014**, *57*, 1090-1097.

(S17) M. Majek, A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.* **2015**, *54*, 2270-2274.

(S18) B. Xu, J.-P. Lumb, B. A. Arndtsen, *Angew. Chem. Int. Ed.* **2015**, *54*, 4208-4211.

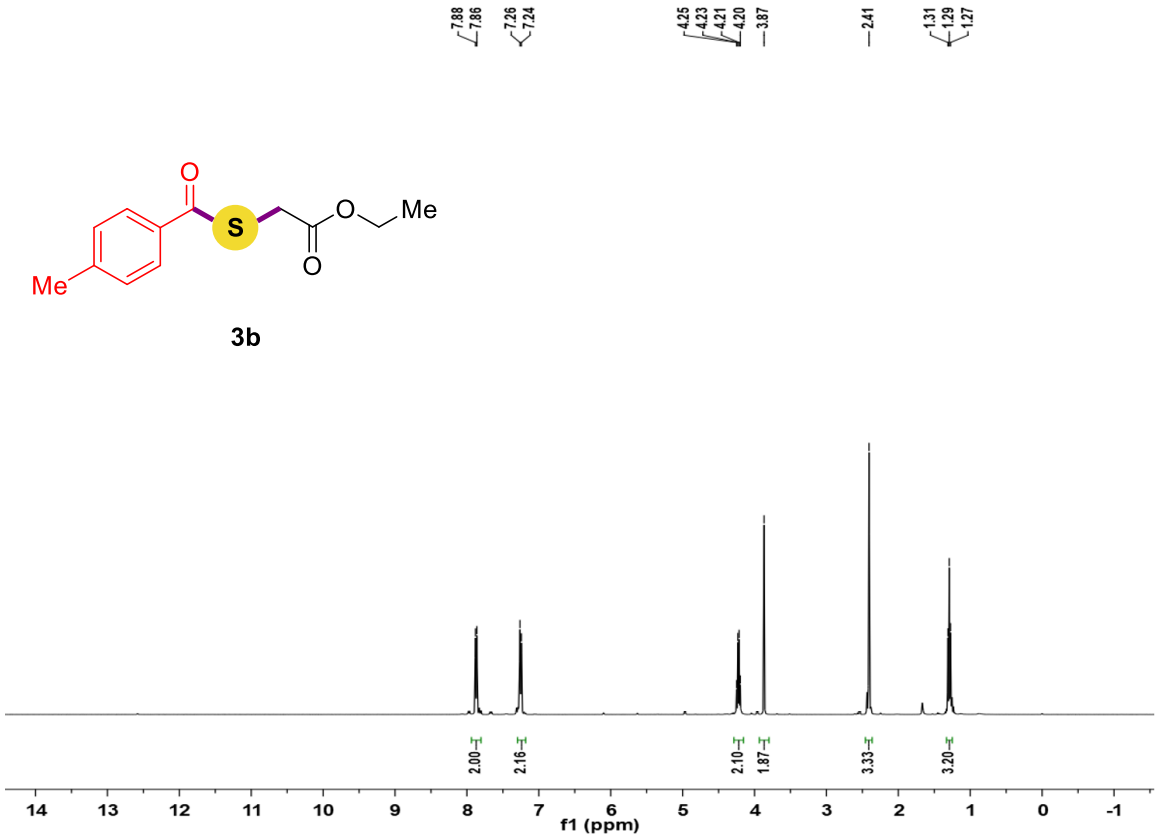
9 NMR spectra

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

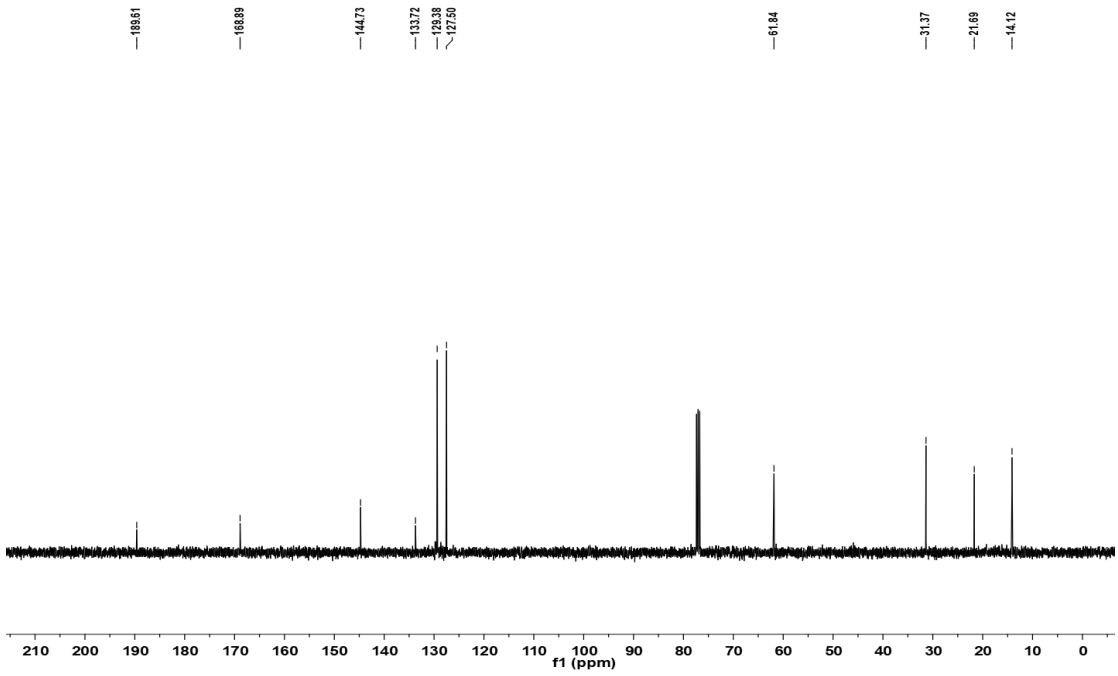


3a

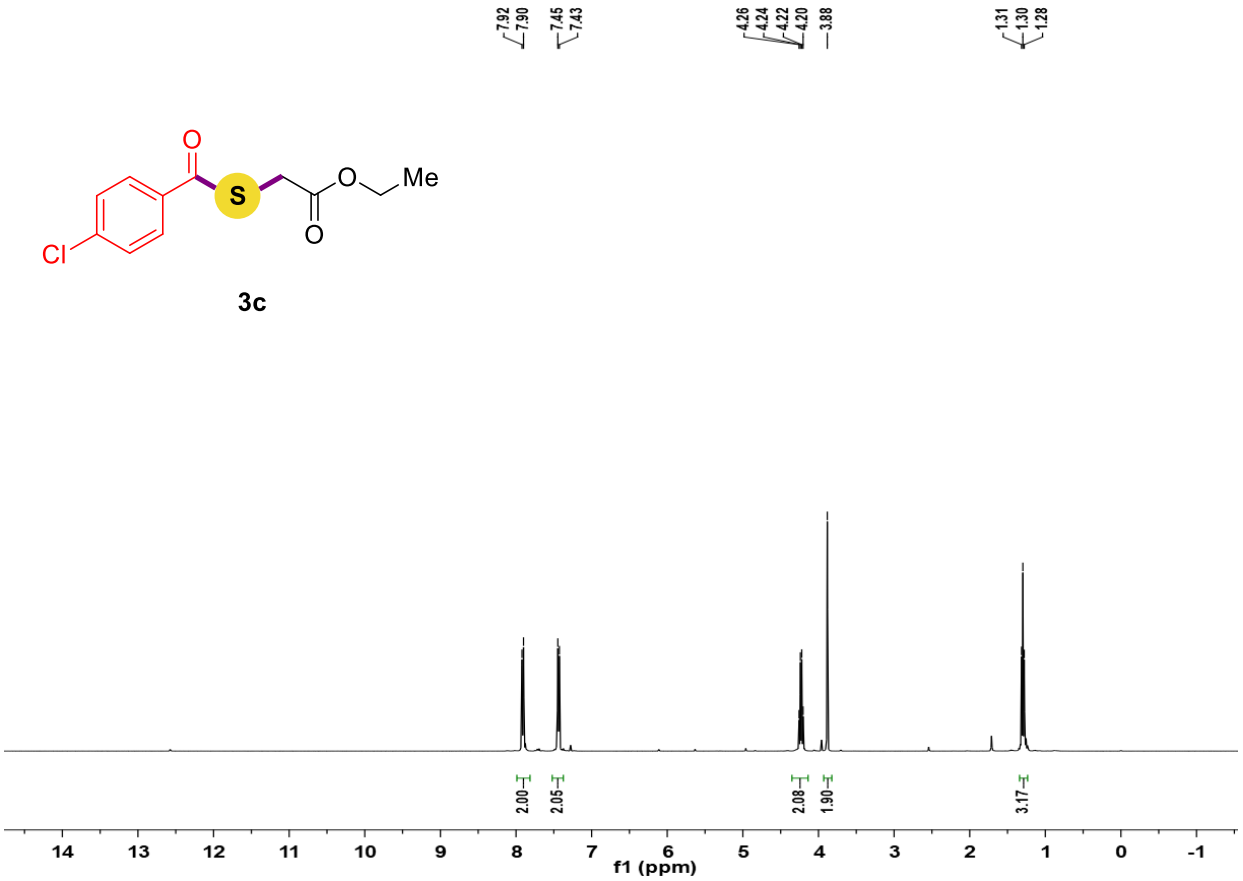
^{1}H NMR (400 MHz, $CDCl_3$) of 3b



^{13}C NMR (101 MHz, $CDCl_3$) of 3b

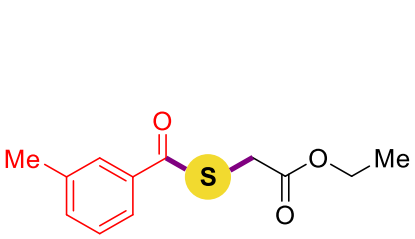


^{1}H NMR (400 MHz, $CDCl_3$) of 3c



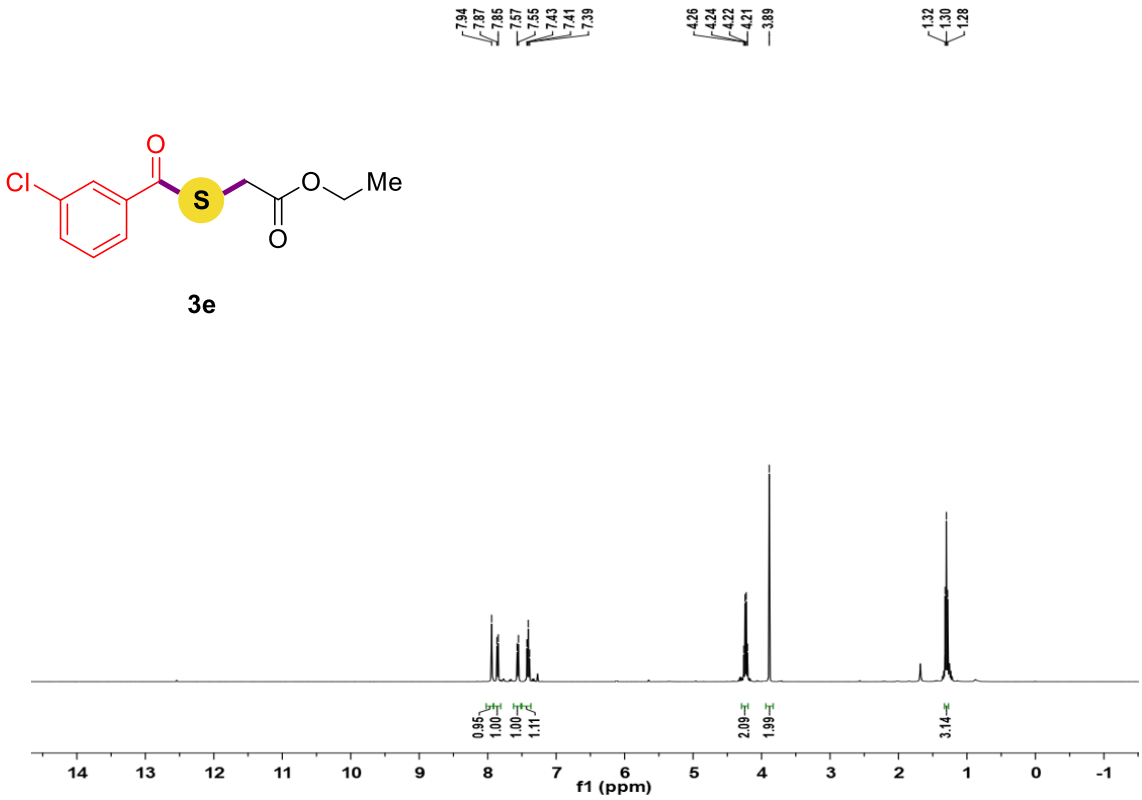
3c

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



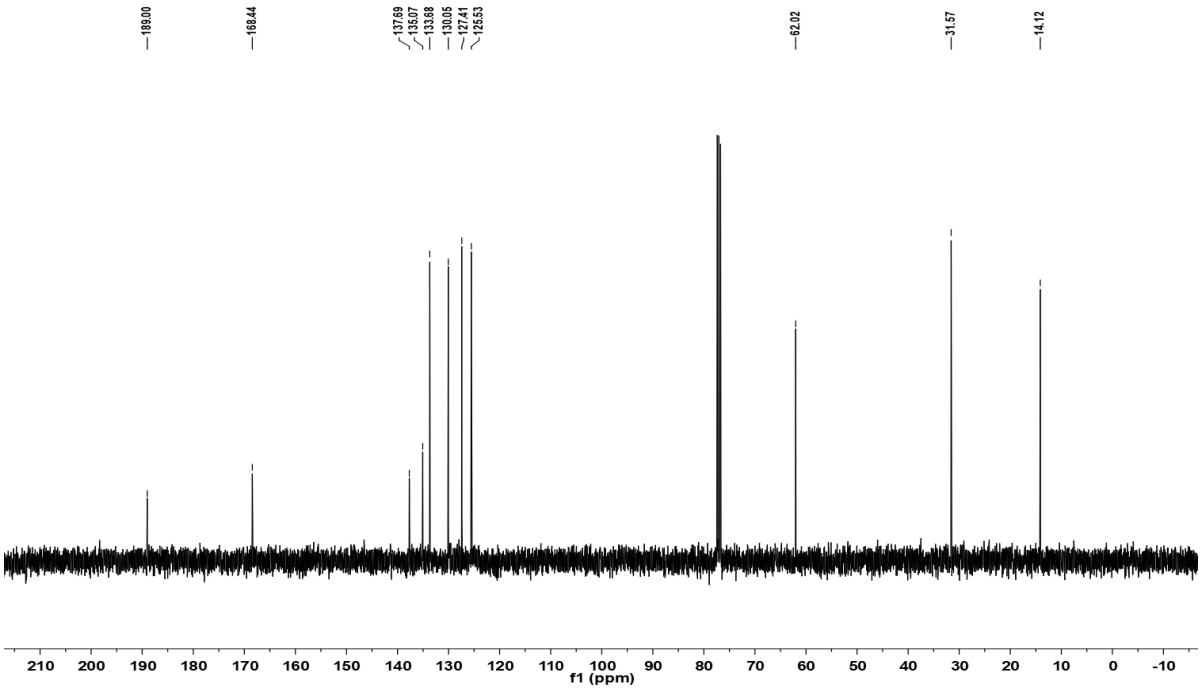
3d

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

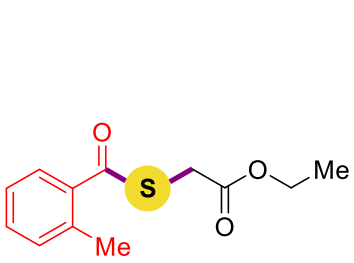


3e

^{13}C NMR (101 MHz, $CDCl_3$) of 3e

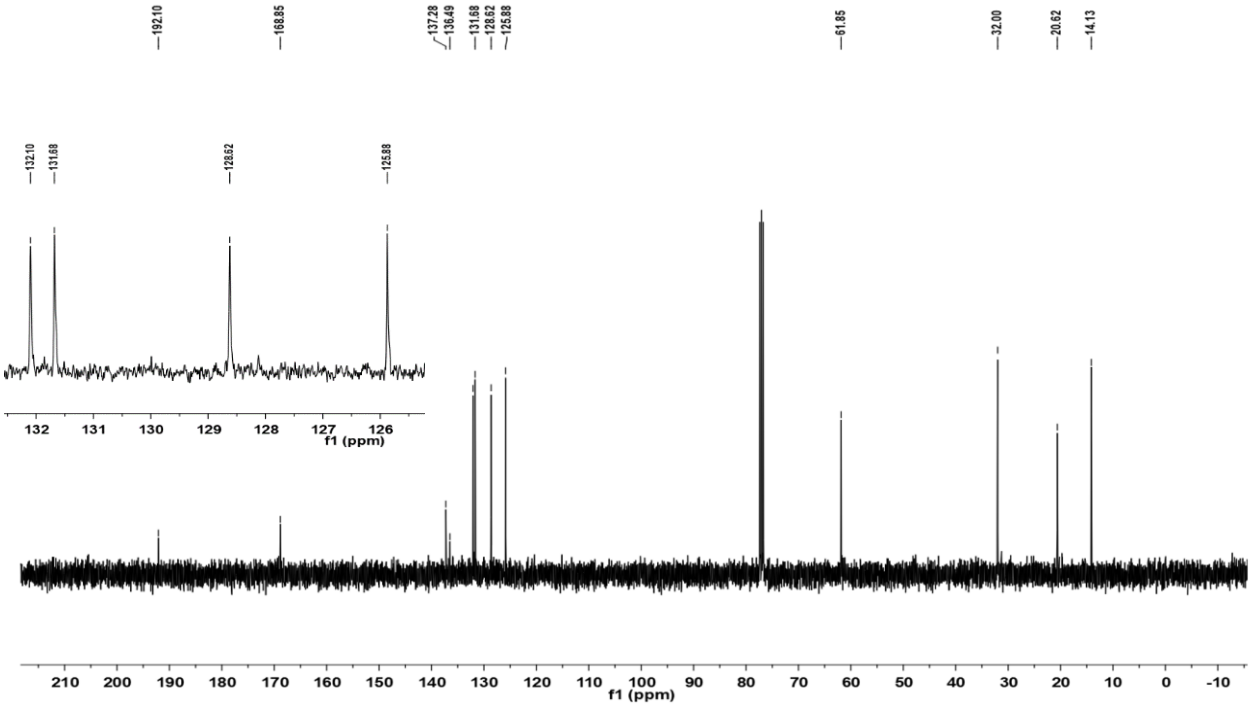


^{1}H NMR (400 MHz, $CDCl_3$) of 3f

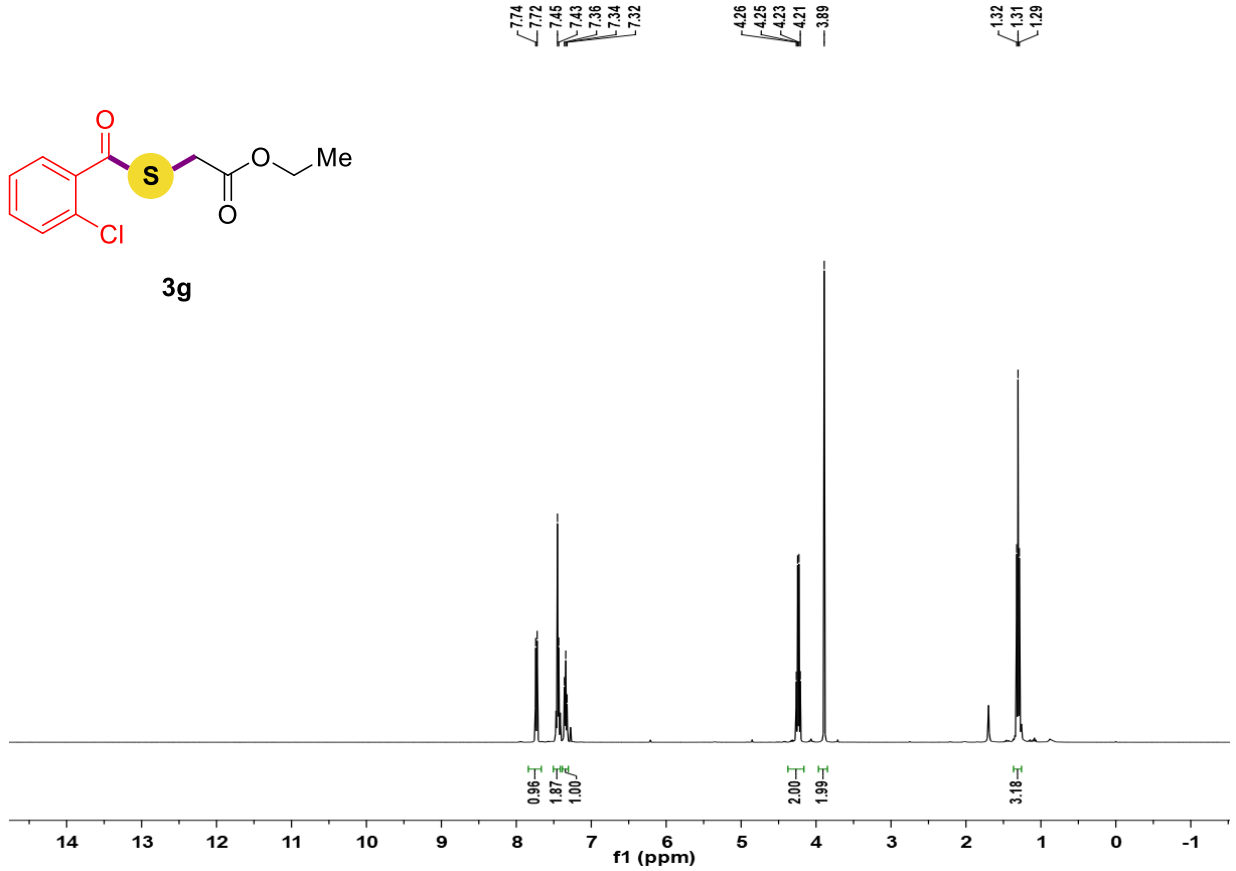


3f

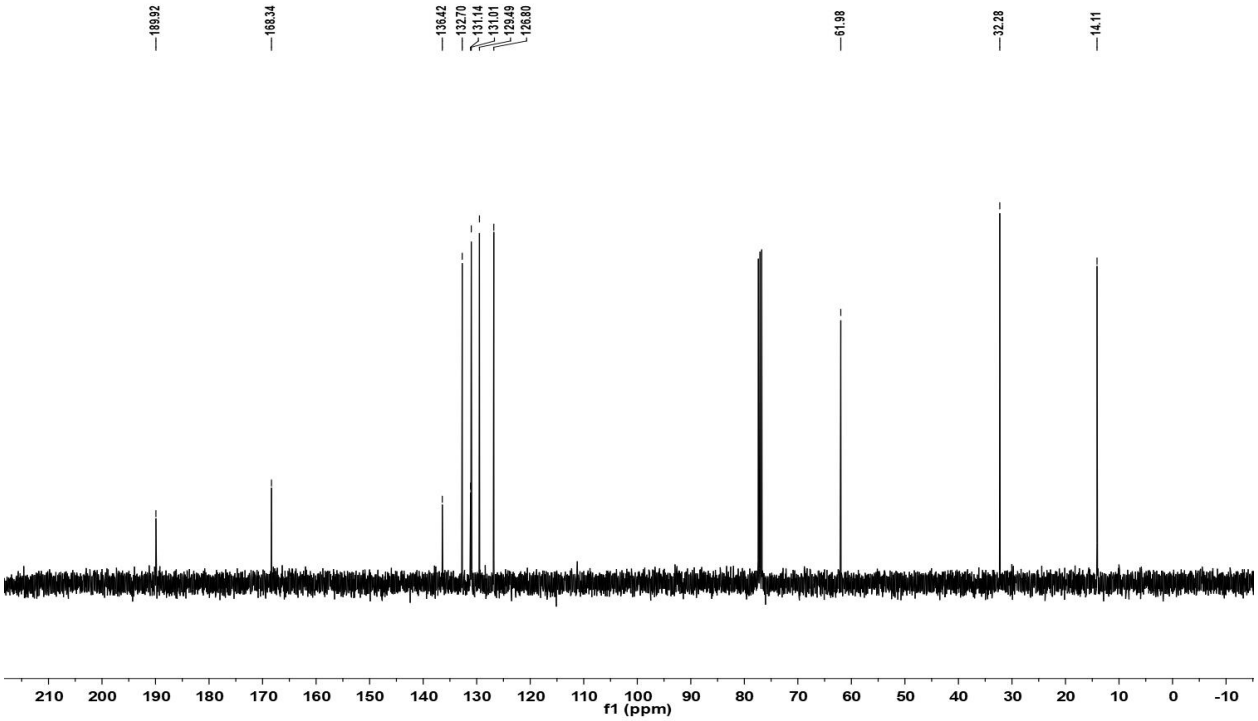
^{13}C NMR (101 MHz, $CDCl_3$) of 3f



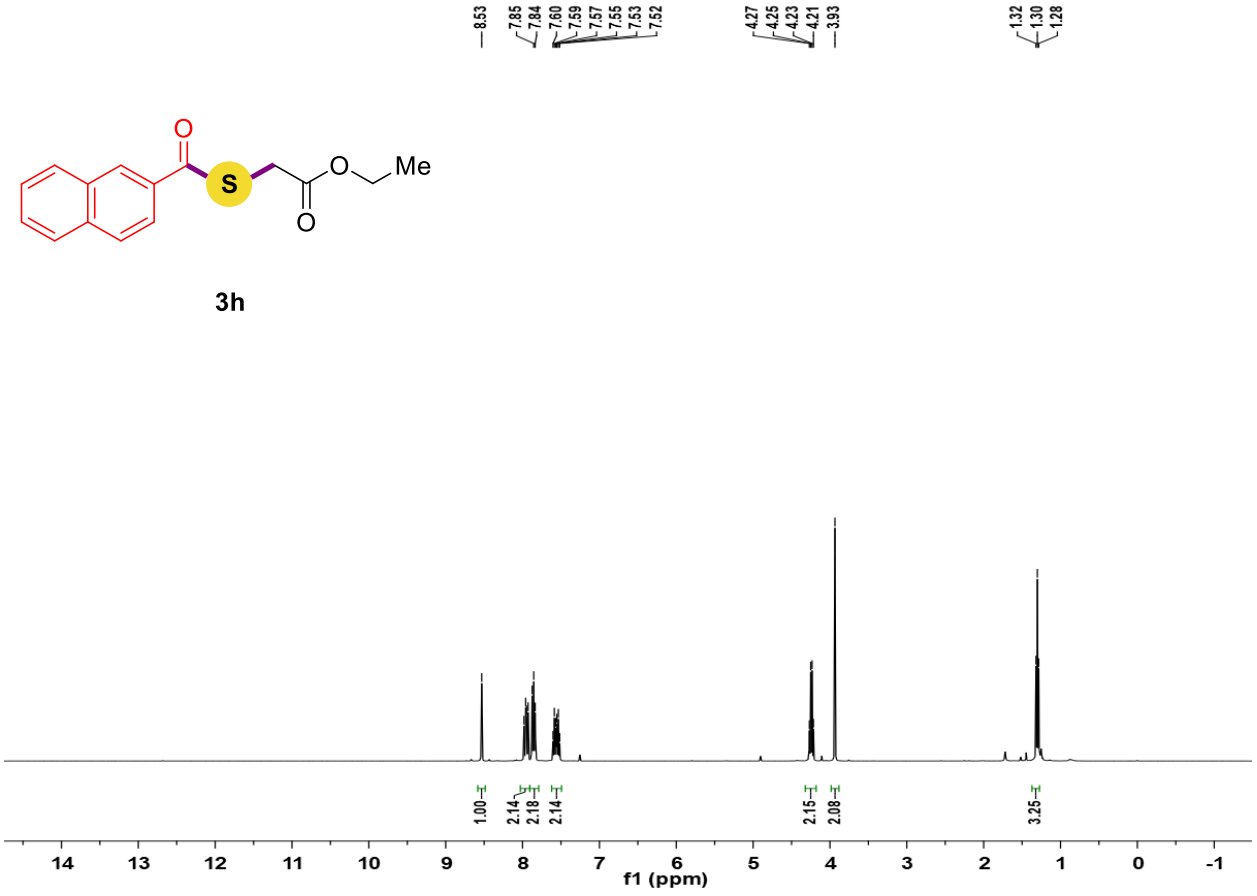
^{1}H NMR (400 MHz, $CDCl_3$) of 3g



^{13}C NMR (101 MHz, $CDCl_3$) of 3g

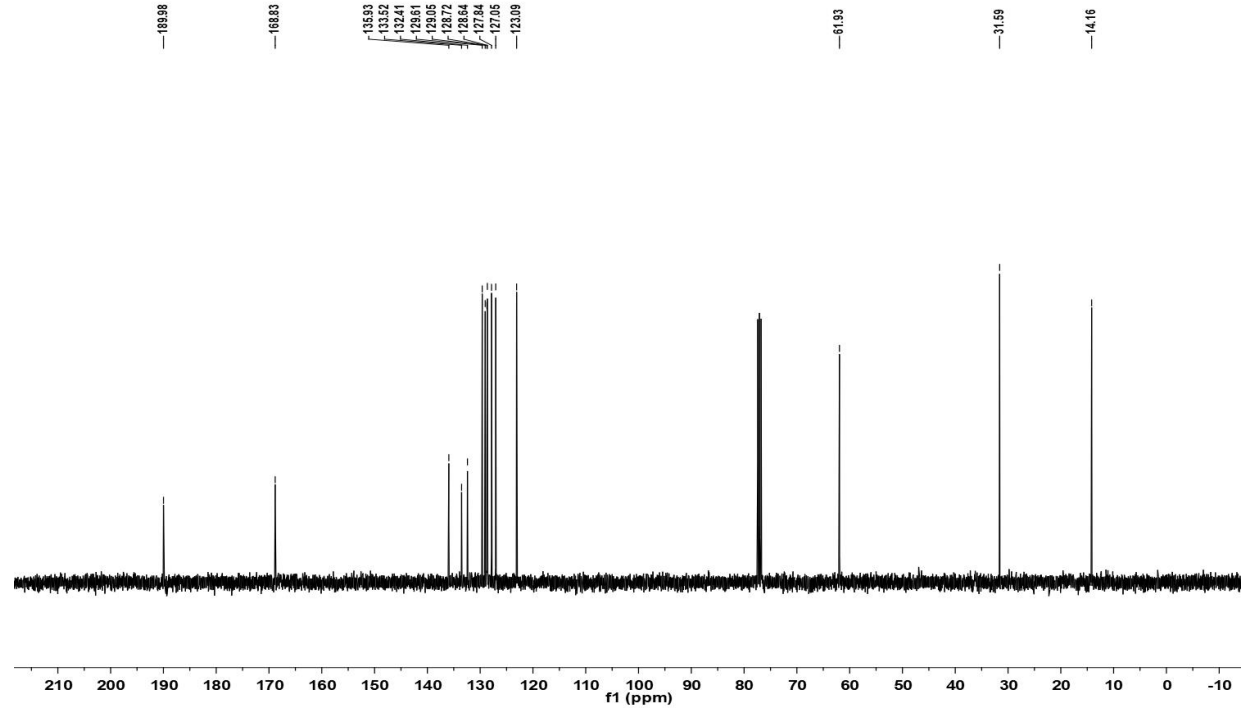


^{1}H NMR (400 MHz, $CDCl_3$) of 3h

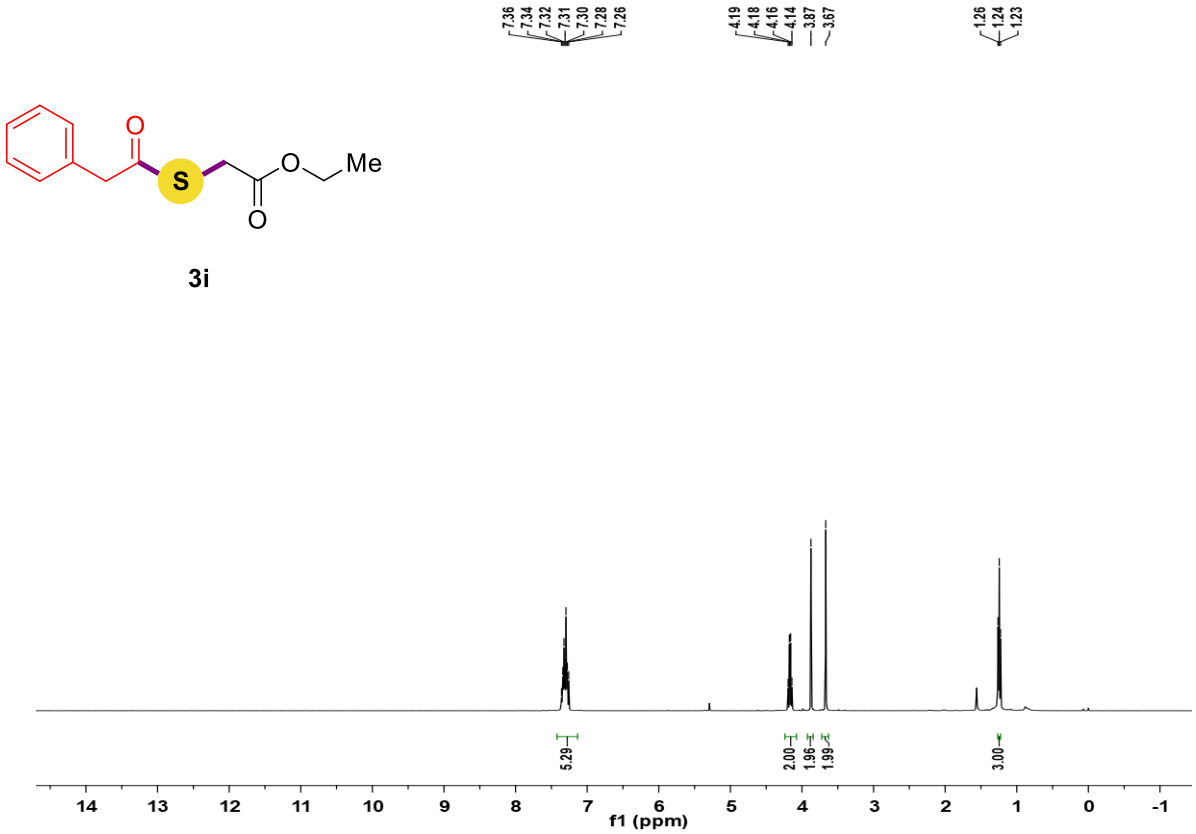


3h

^{13}C NMR (101 MHz, $CDCl_3$) of 3h

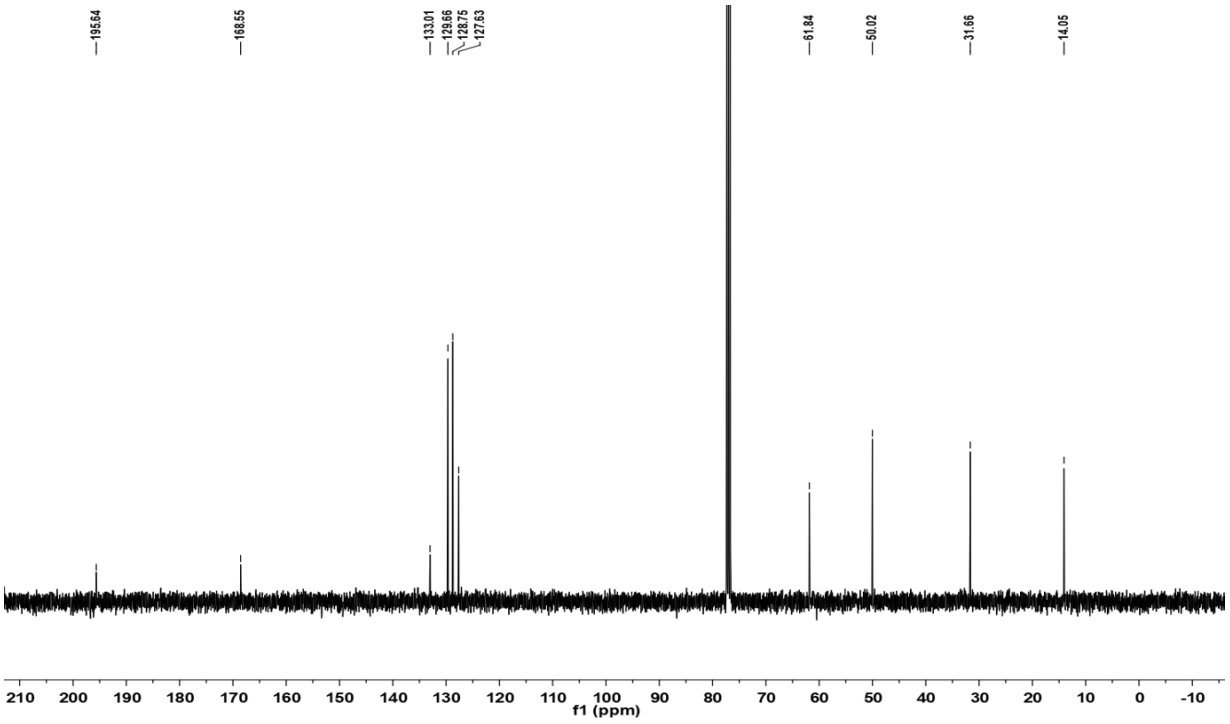


^{1}H NMR (400 MHz, $CDCl_3$) of 3i

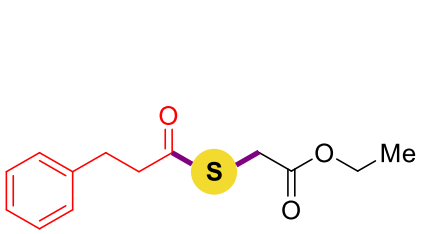


3i

^{13}C NMR (101 MHz, $CDCl_3$) of 3i

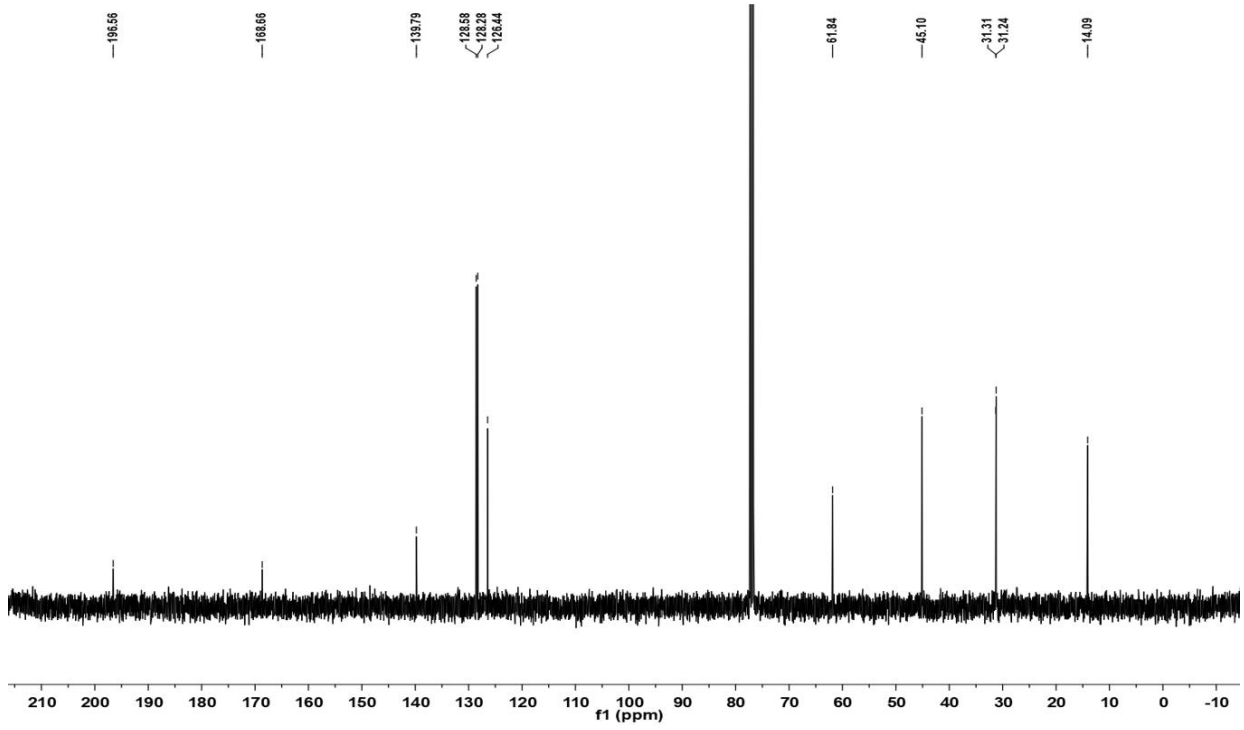


^{1}H NMR (400 MHz, $CDCl_3$) of 3j

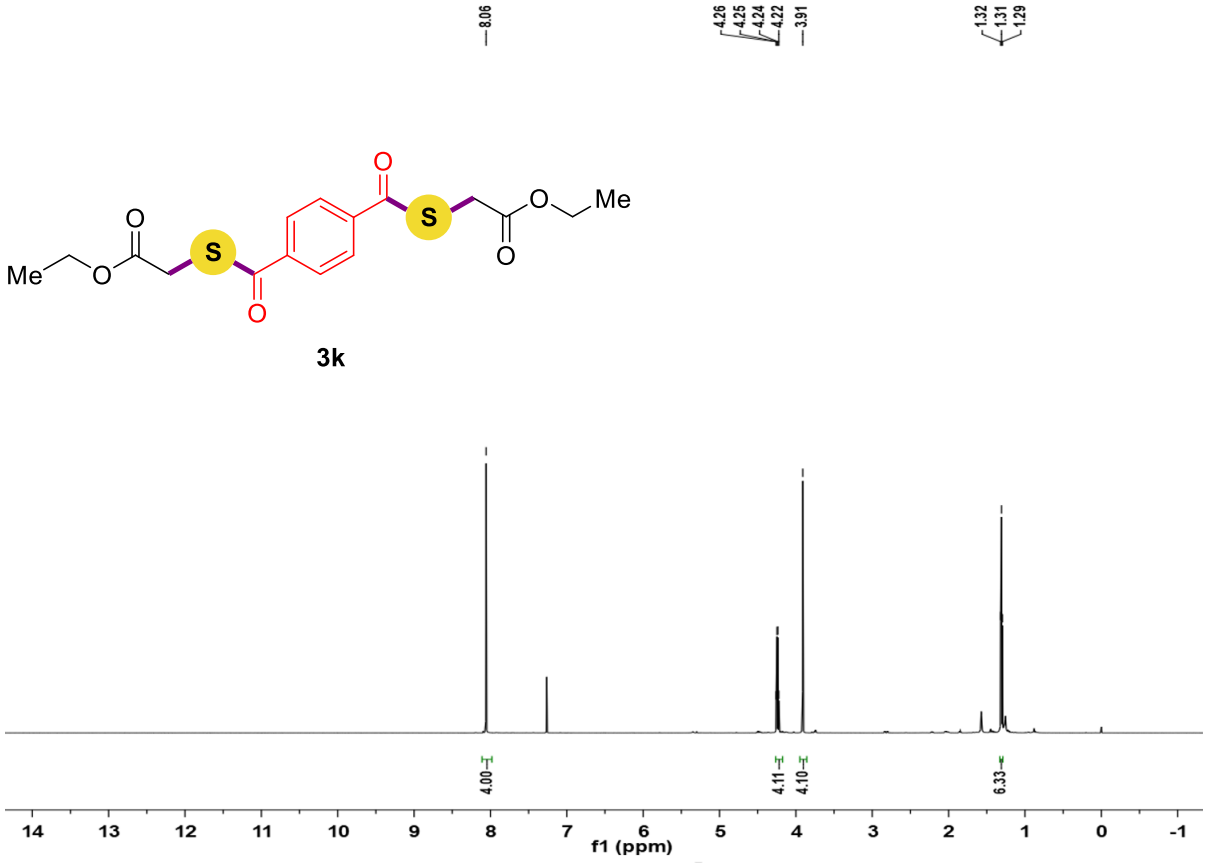


3j

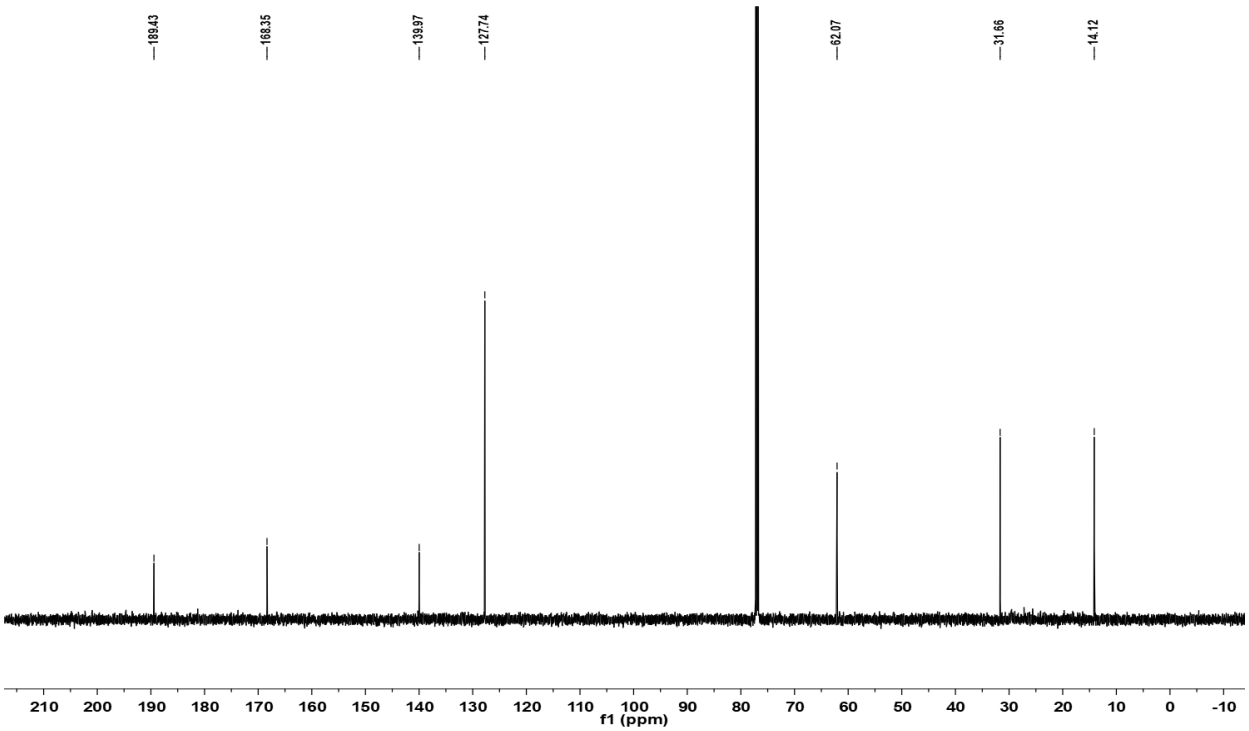
^{13}C NMR (101 MHz, $CDCl_3$) of 3j



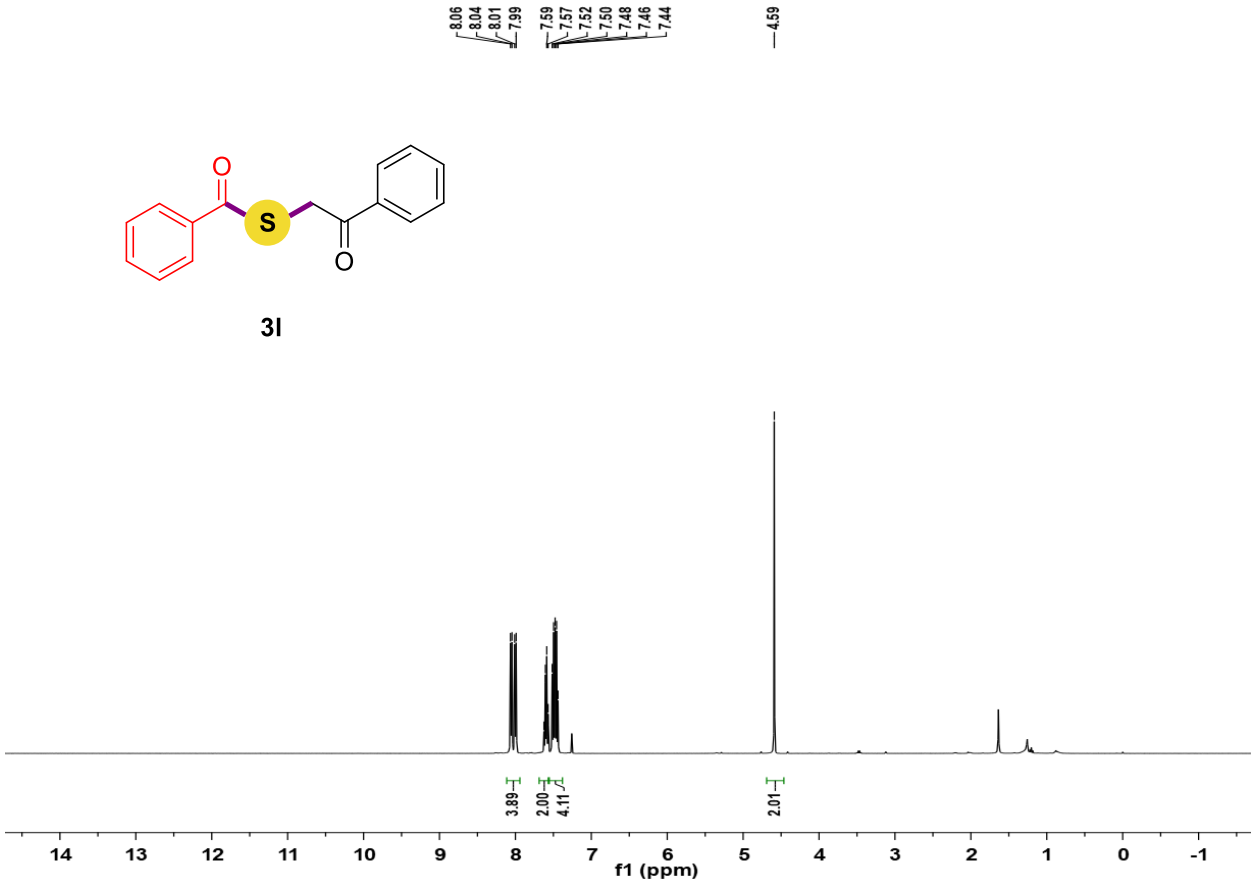
^{1}H NMR (400 MHz, $CDCl_3$) of 3k



^{13}C NMR (101 MHz, $CDCl_3$) of 3k

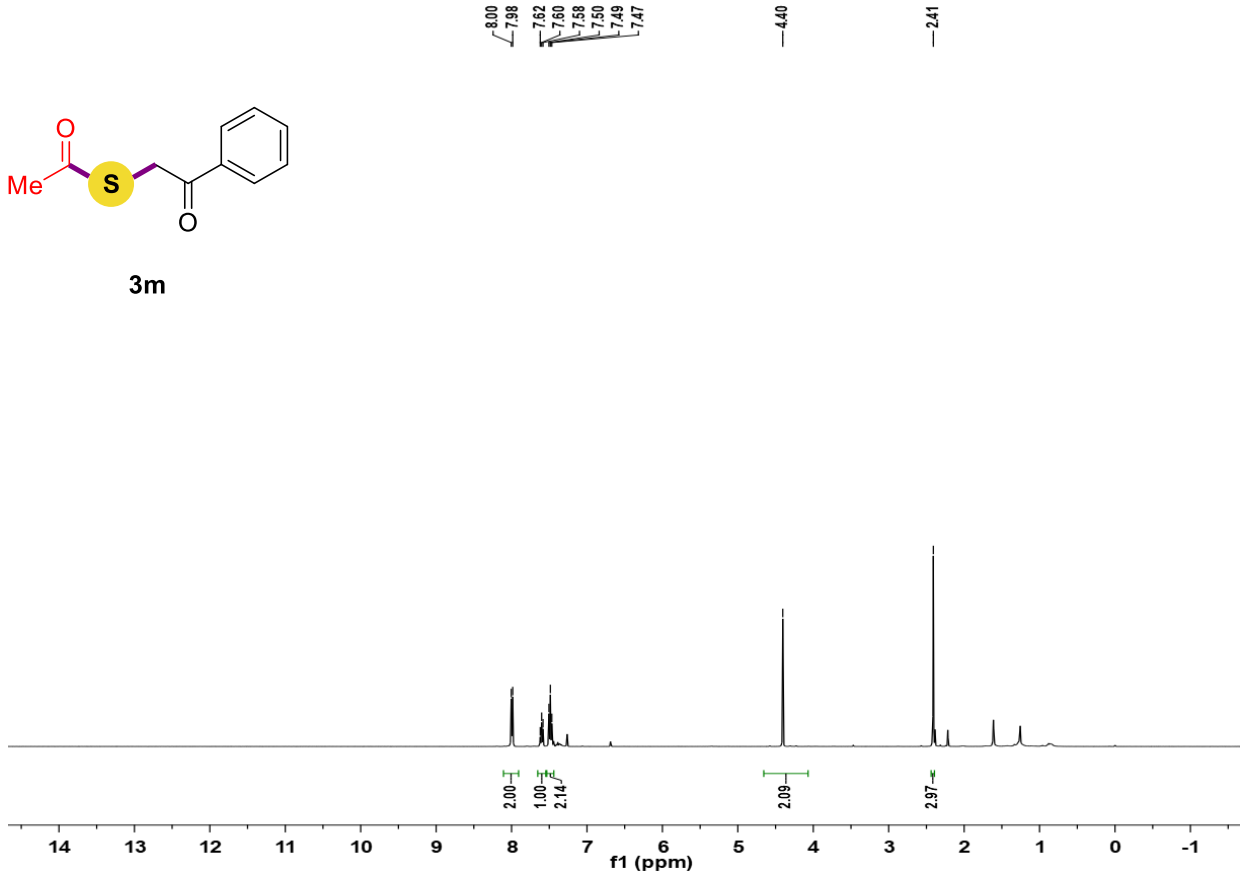


^{1}H NMR (400 MHz, $CDCl_3$) of 3l



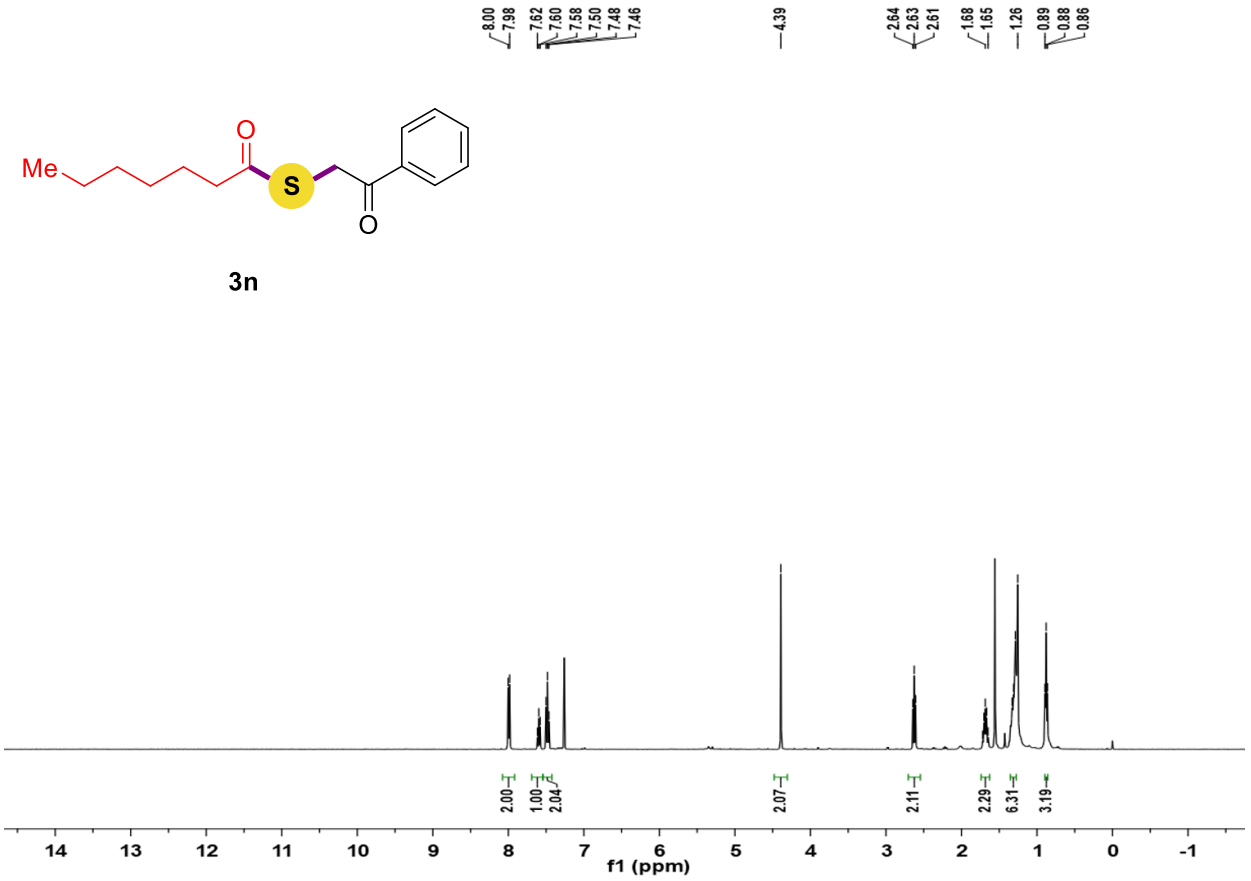
3l

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



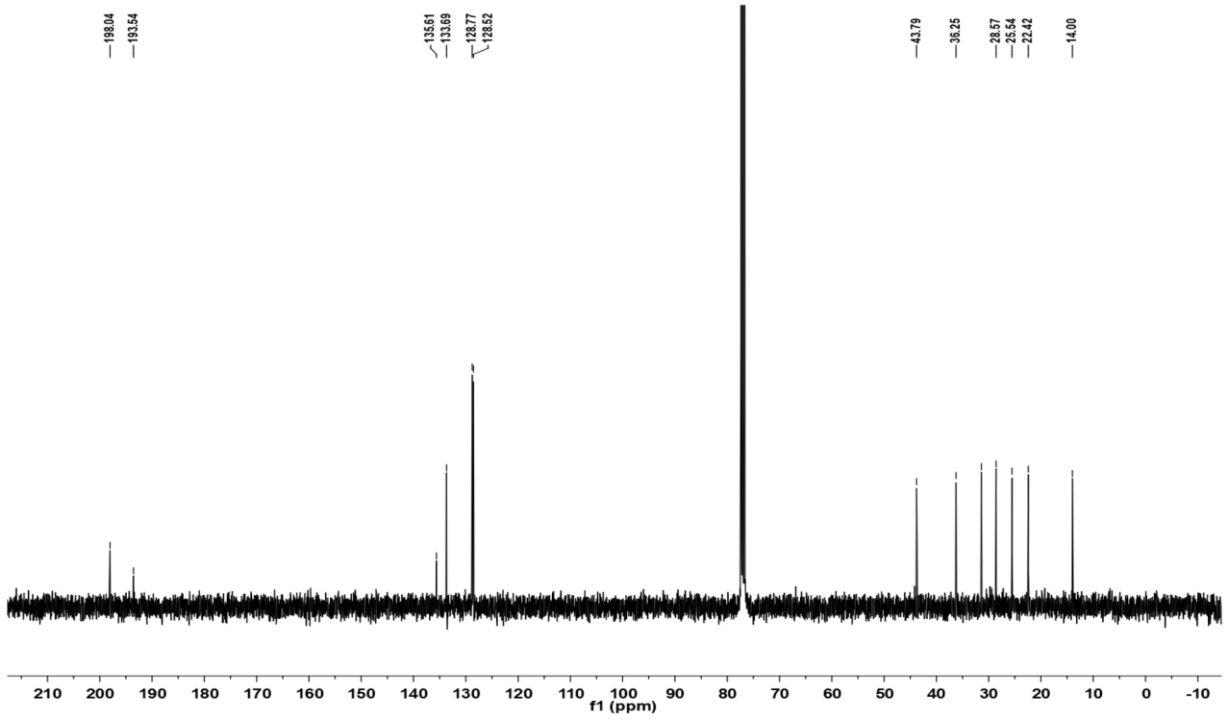
3m

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

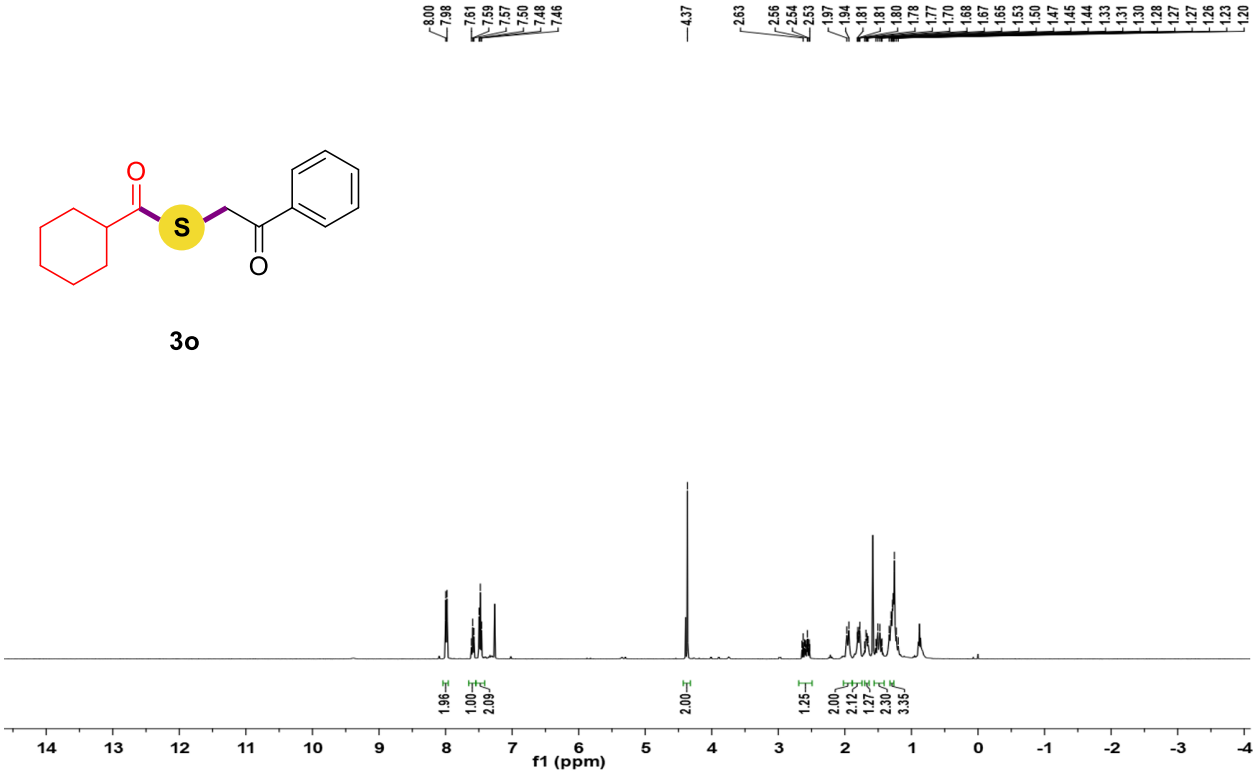


3n

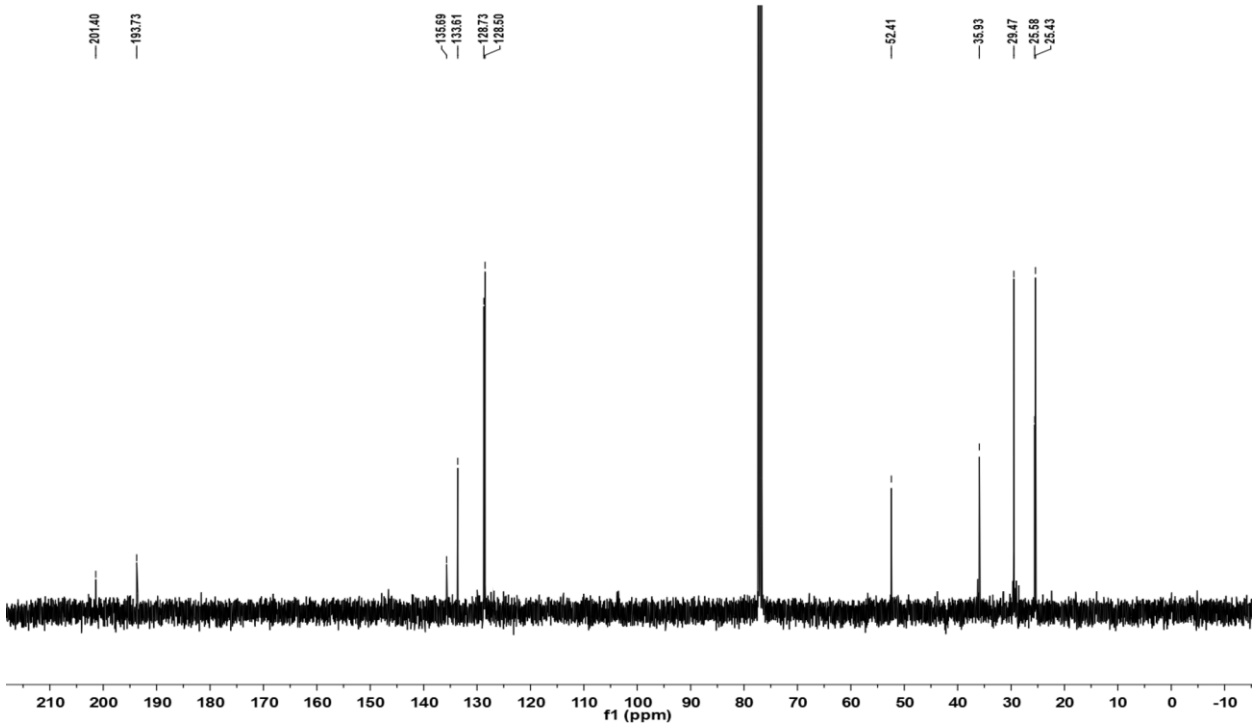
^{13}C NMR (101 MHz, $CDCl_3$) of 3n



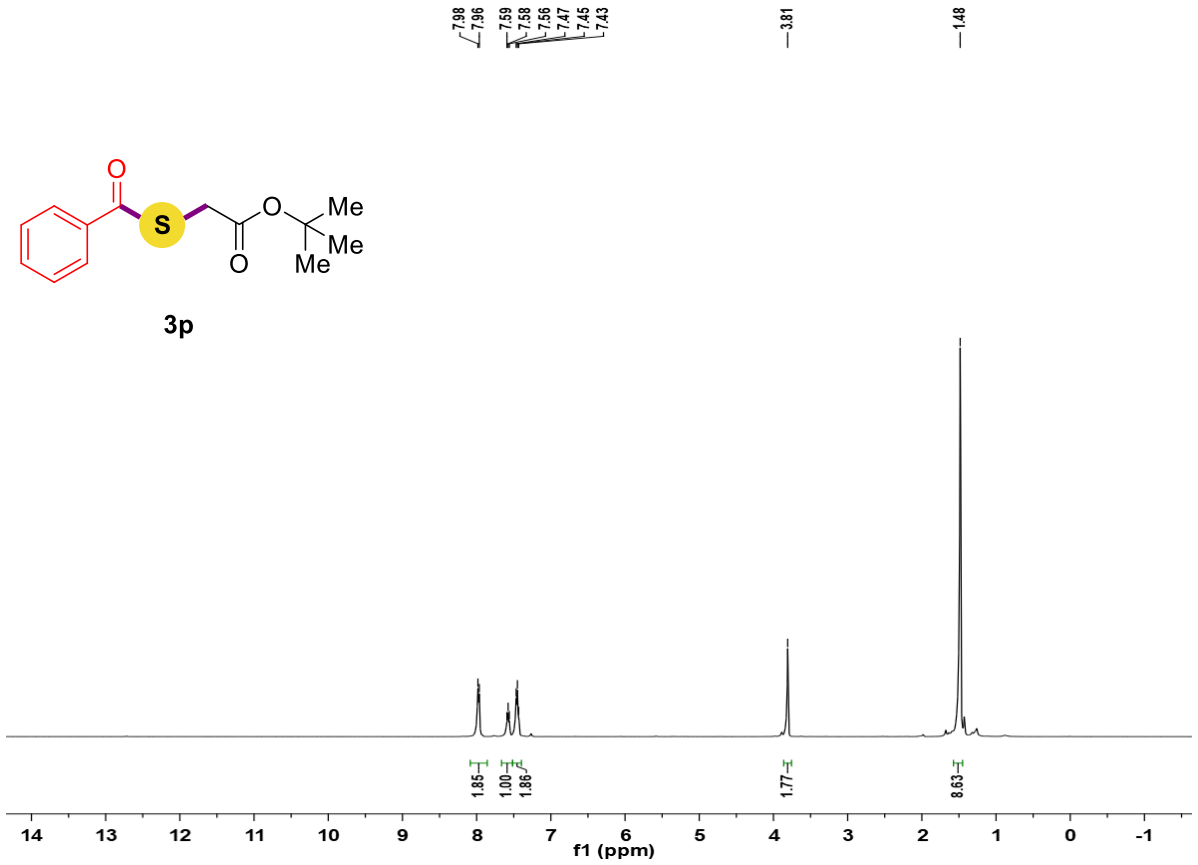
^{1}H NMR (400 MHz, $CDCl_3$) of 3o



^{13}C NMR (101 MHz, $CDCl_3$) of 3o

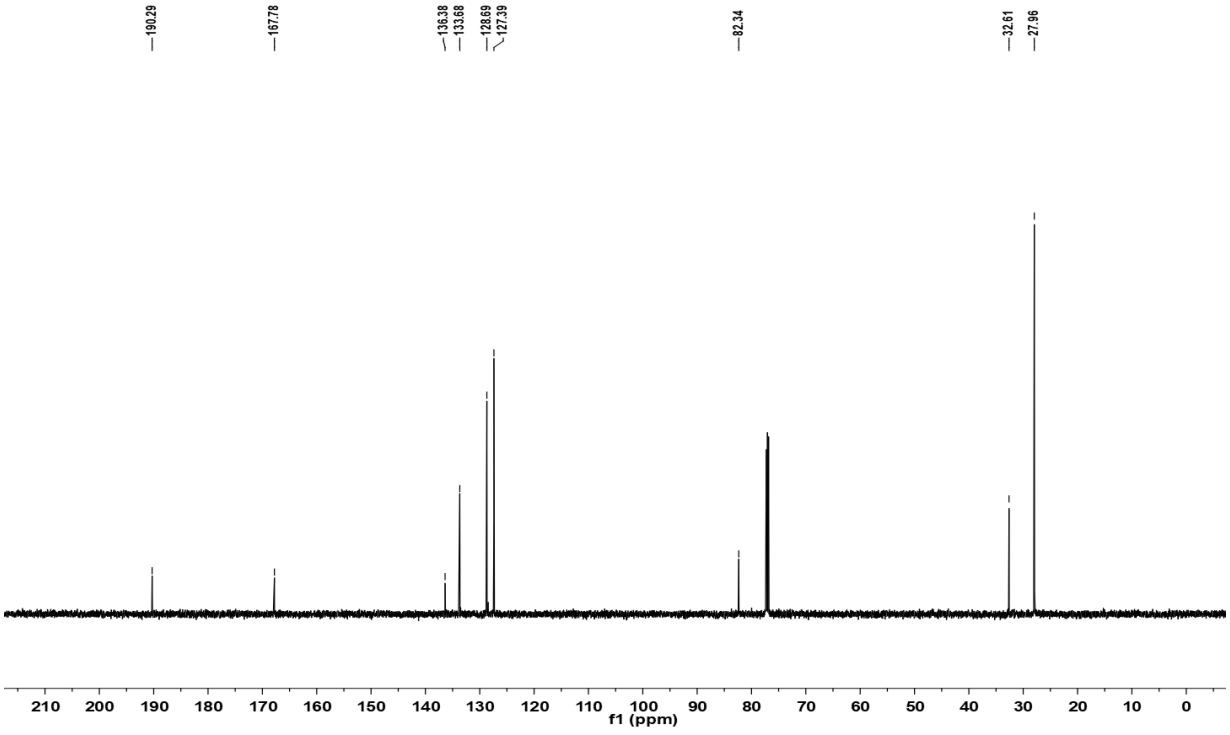


^{1}H NMR (400 MHz, $CDCl_3$) of 3p

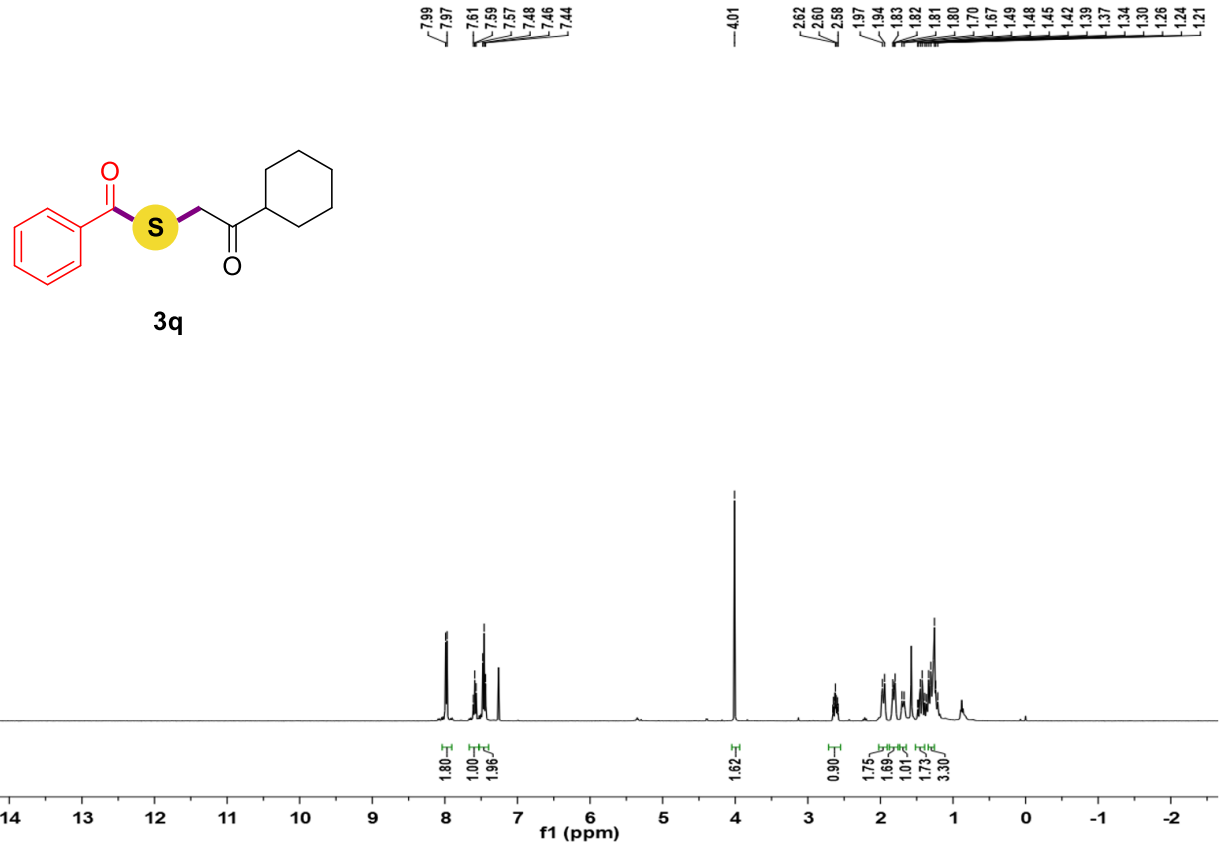


3p

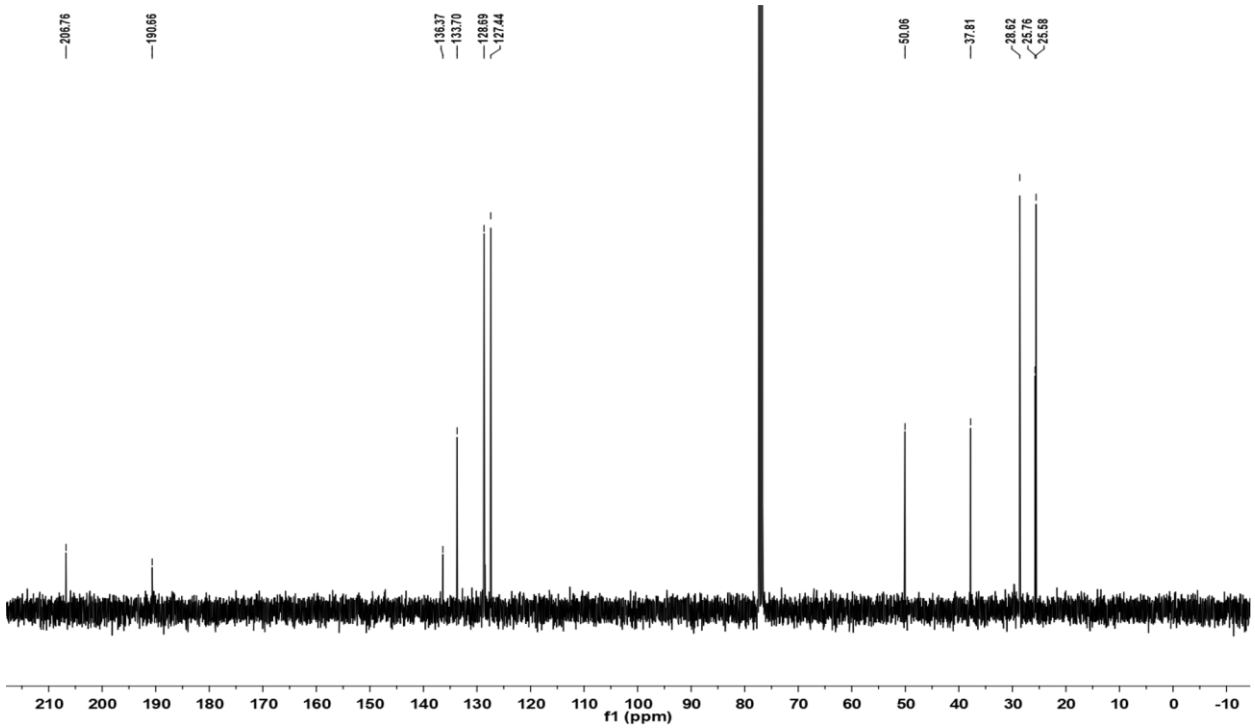
^{13}C NMR (101 MHz, $CDCl_3$) of 3p



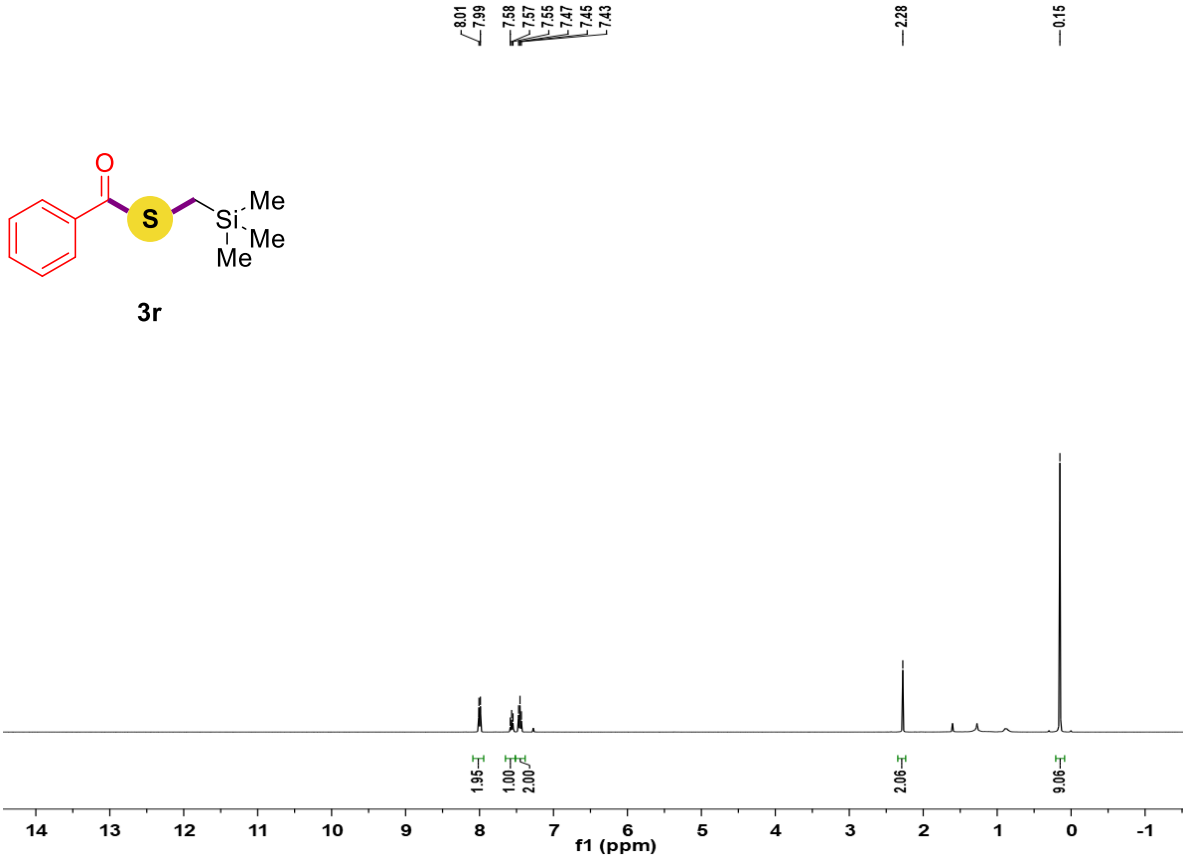
^{1}H NMR (400 MHz, $CDCl_3$) of 3q



^{13}C NMR (101 MHz, $CDCl_3$) of 3q

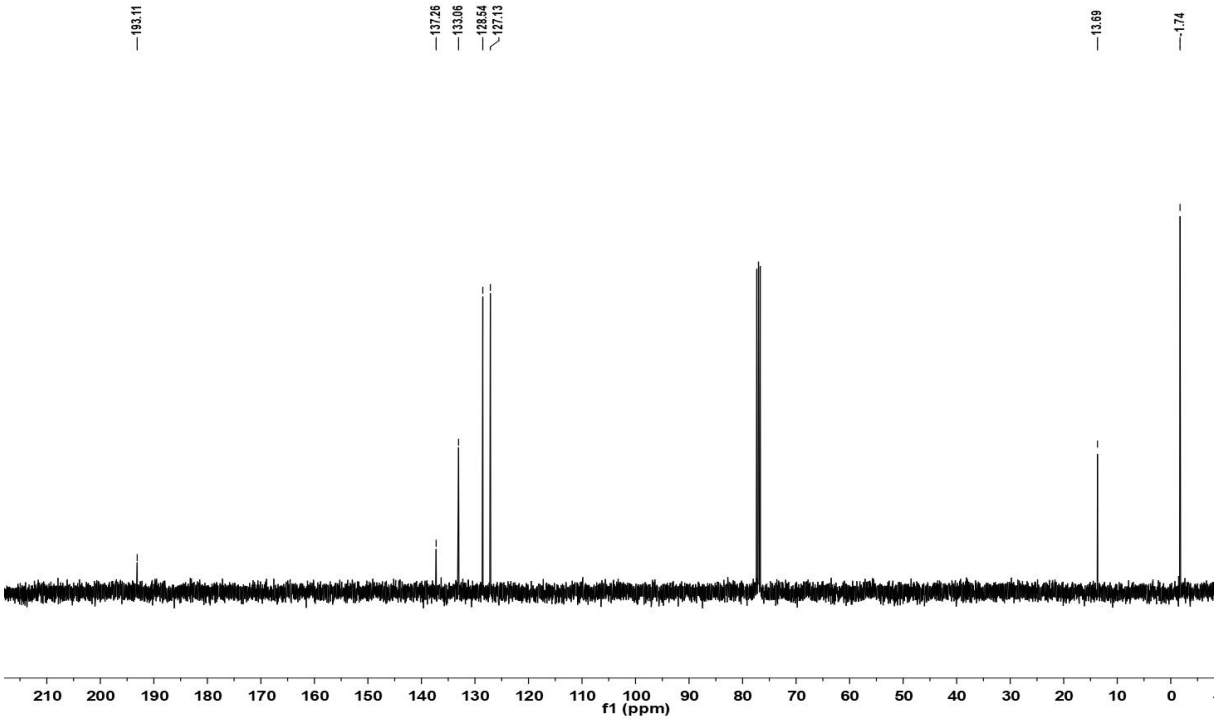


^{1}H NMR (400 MHz, $CDCl_3$) of 3r

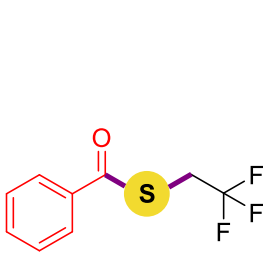


3r

^{13}C NMR (101 MHz, $CDCl_3$) of 3r

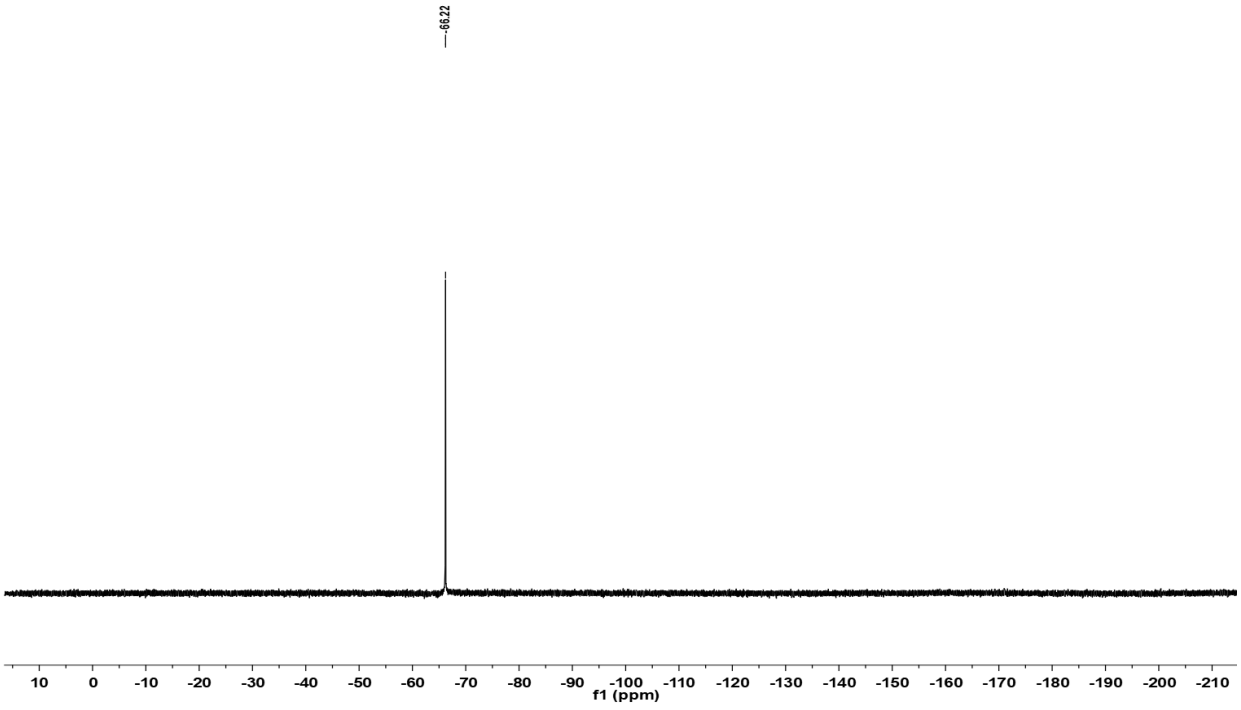


^{1}H NMR (400 MHz, $CDCl_3$) of 3s

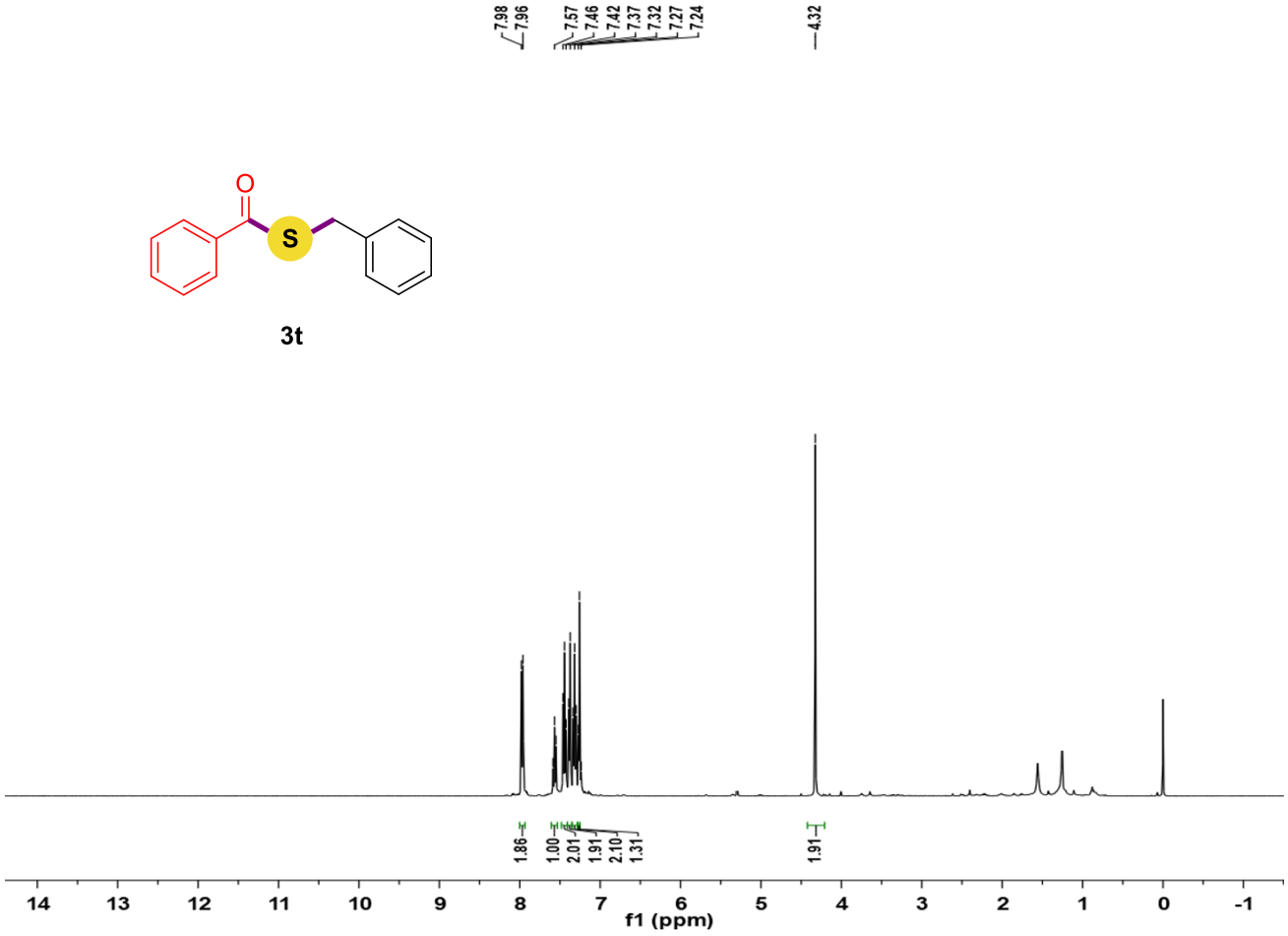


3s

^{19}F NMR (101 MHz, $CDCl_3$) of 3s

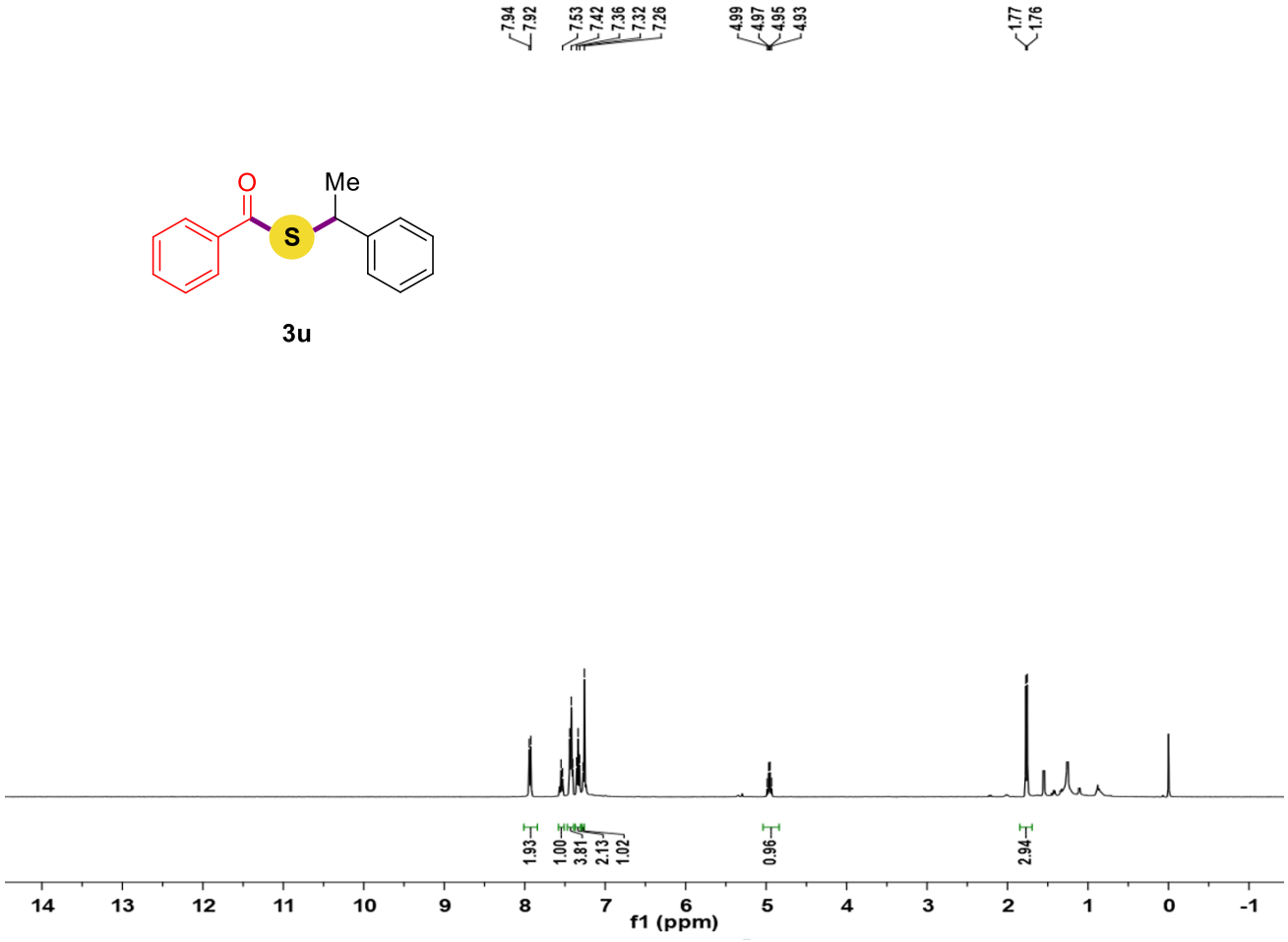


^{1}H NMR (400 MHz, $CDCl_3$) of 3t



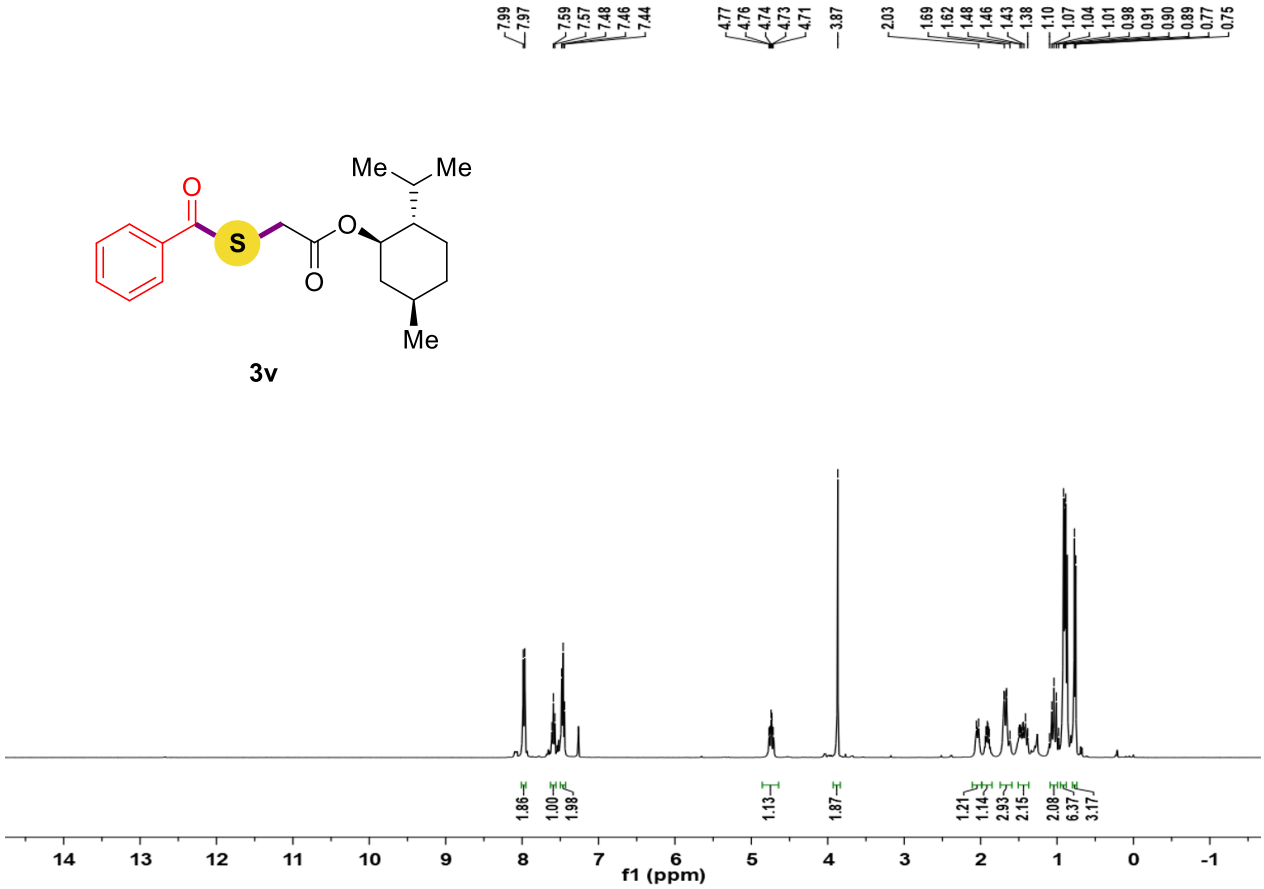
3t

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



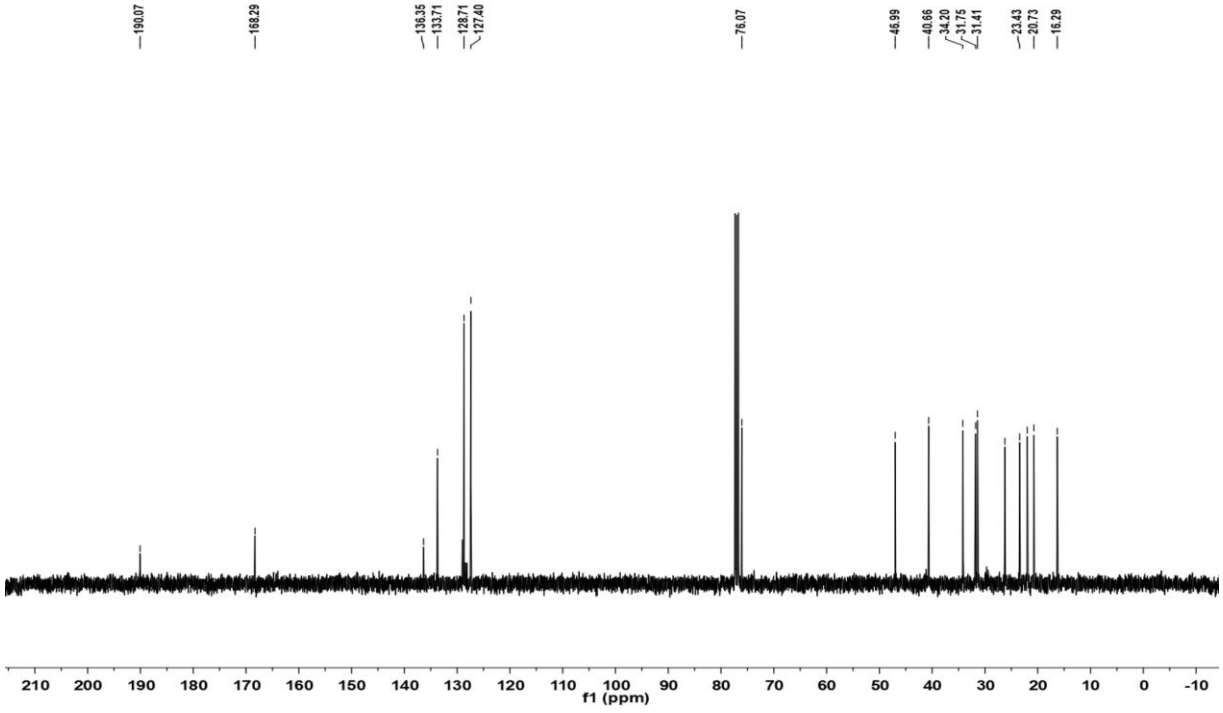
3u

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

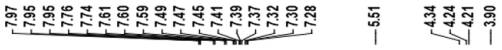


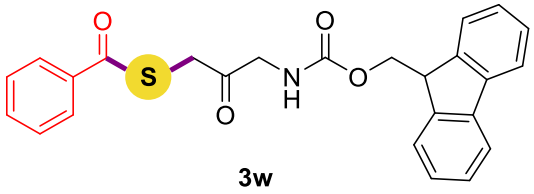
3v

^{13}C NMR (101 MHz, $CDCl_3$) of 3v

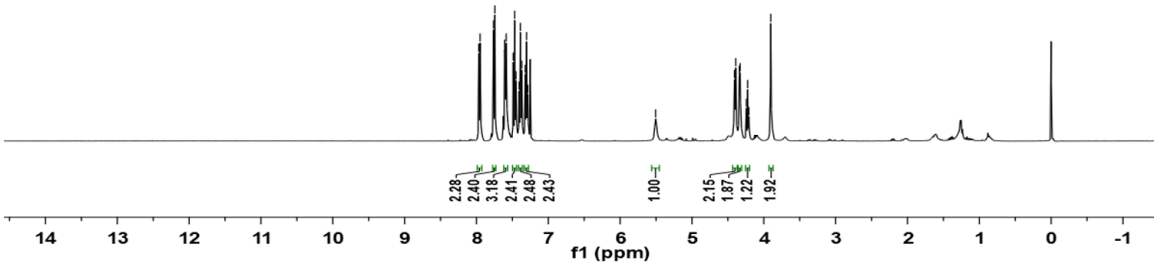


^{1}H NMR (400 MHz, $CDCl_3$) of 3w

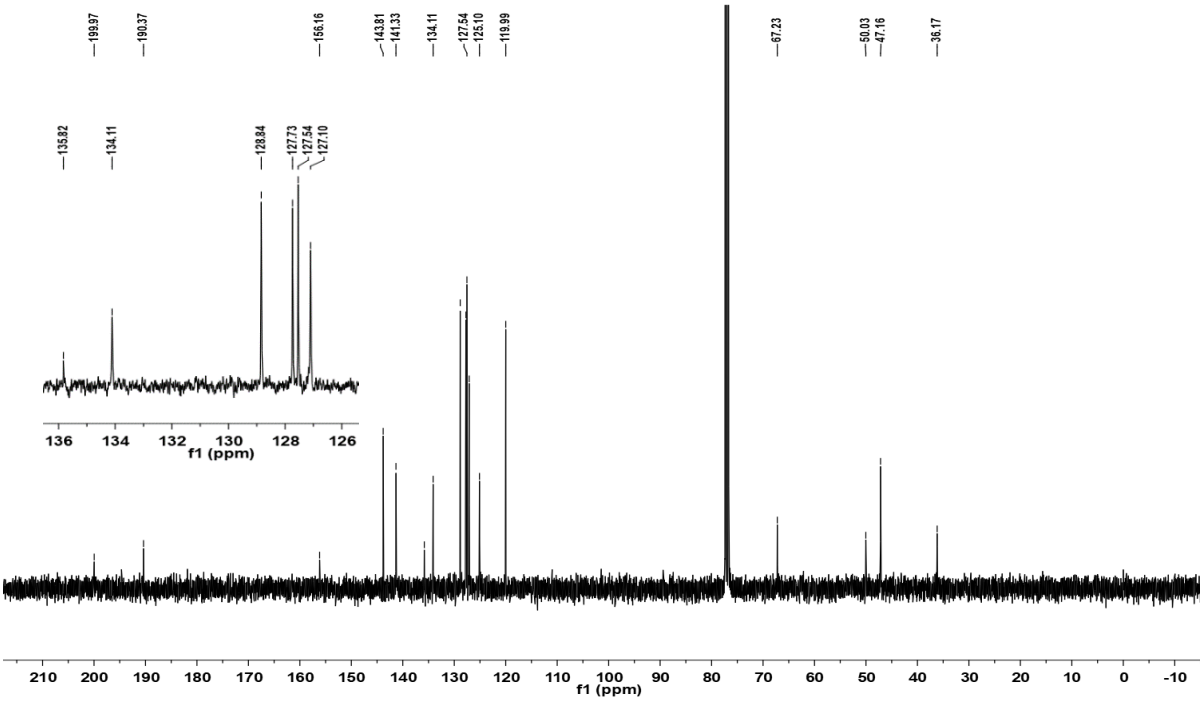




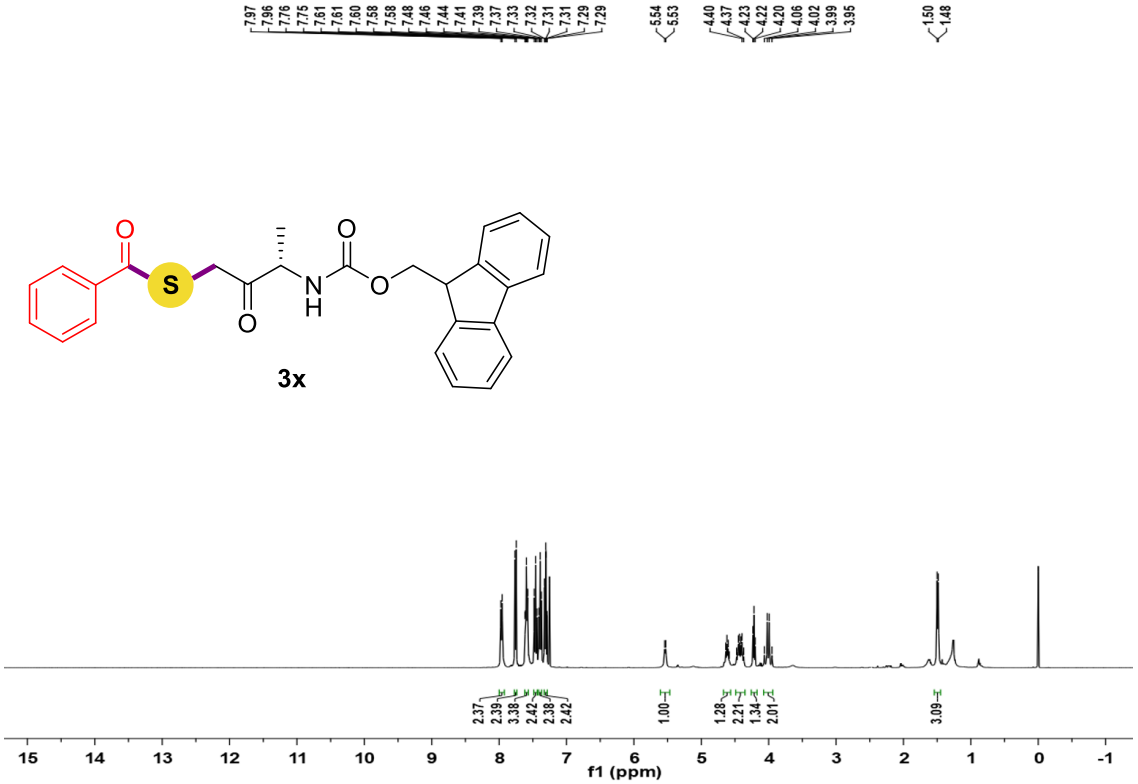
3w



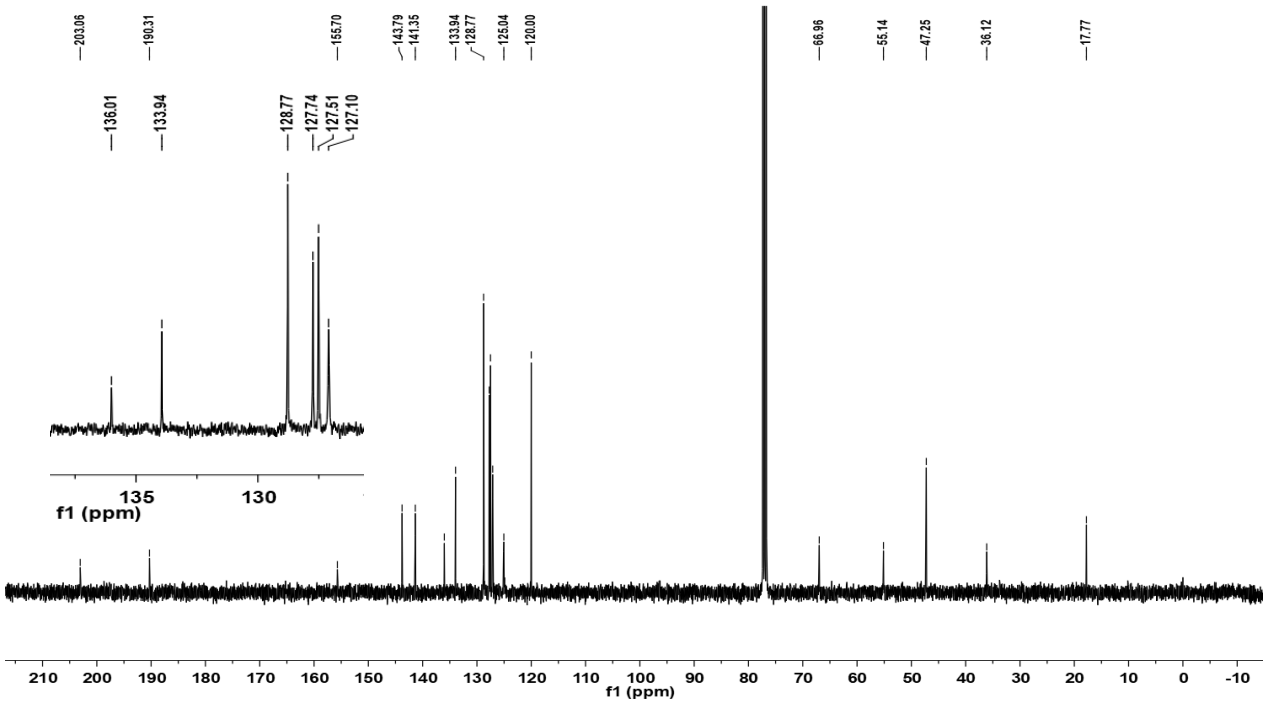
^{13}C NMR (101 MHz, $CDCl_3$) of 3w



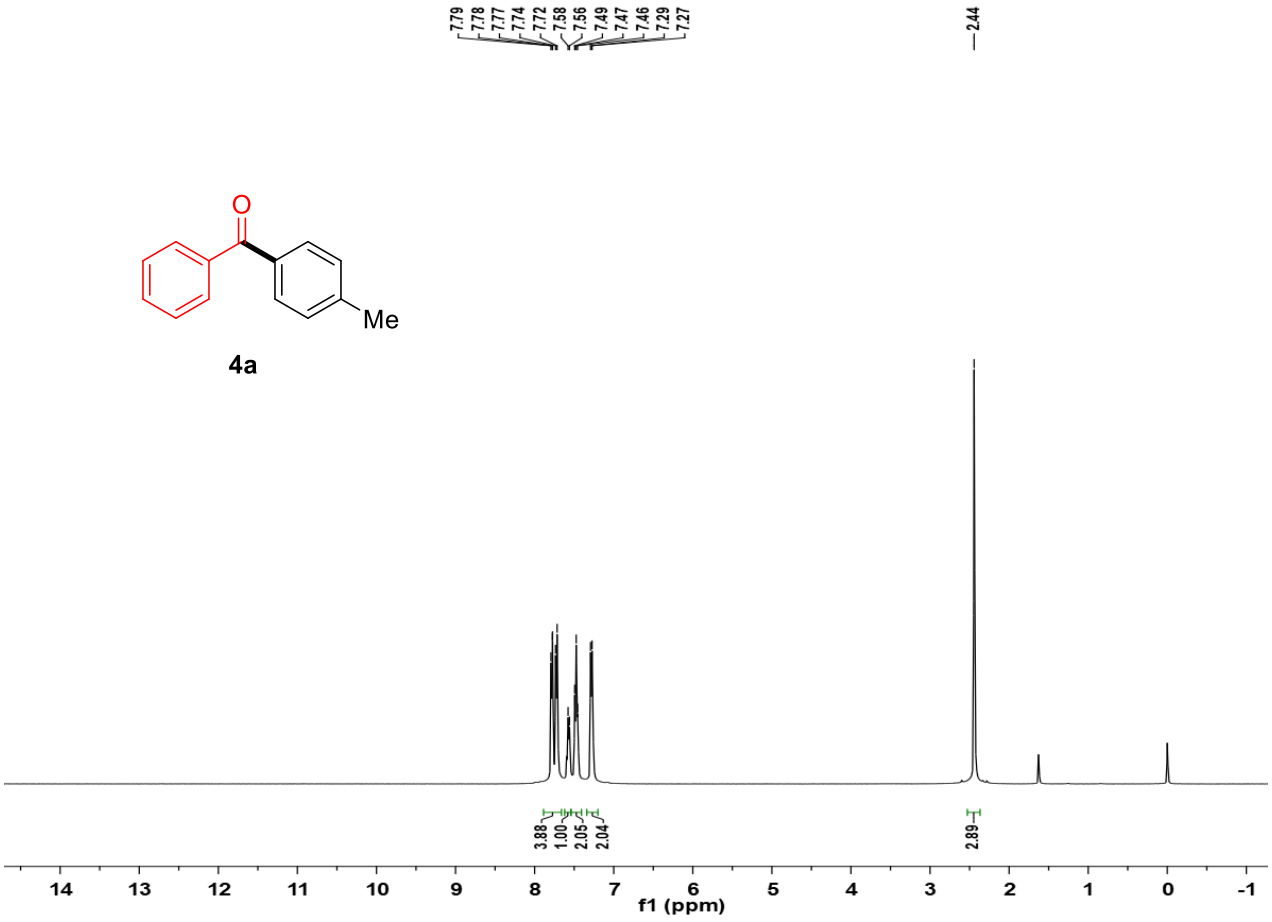
^{1}H NMR (400 MHz, $CDCl_3$) of 3x



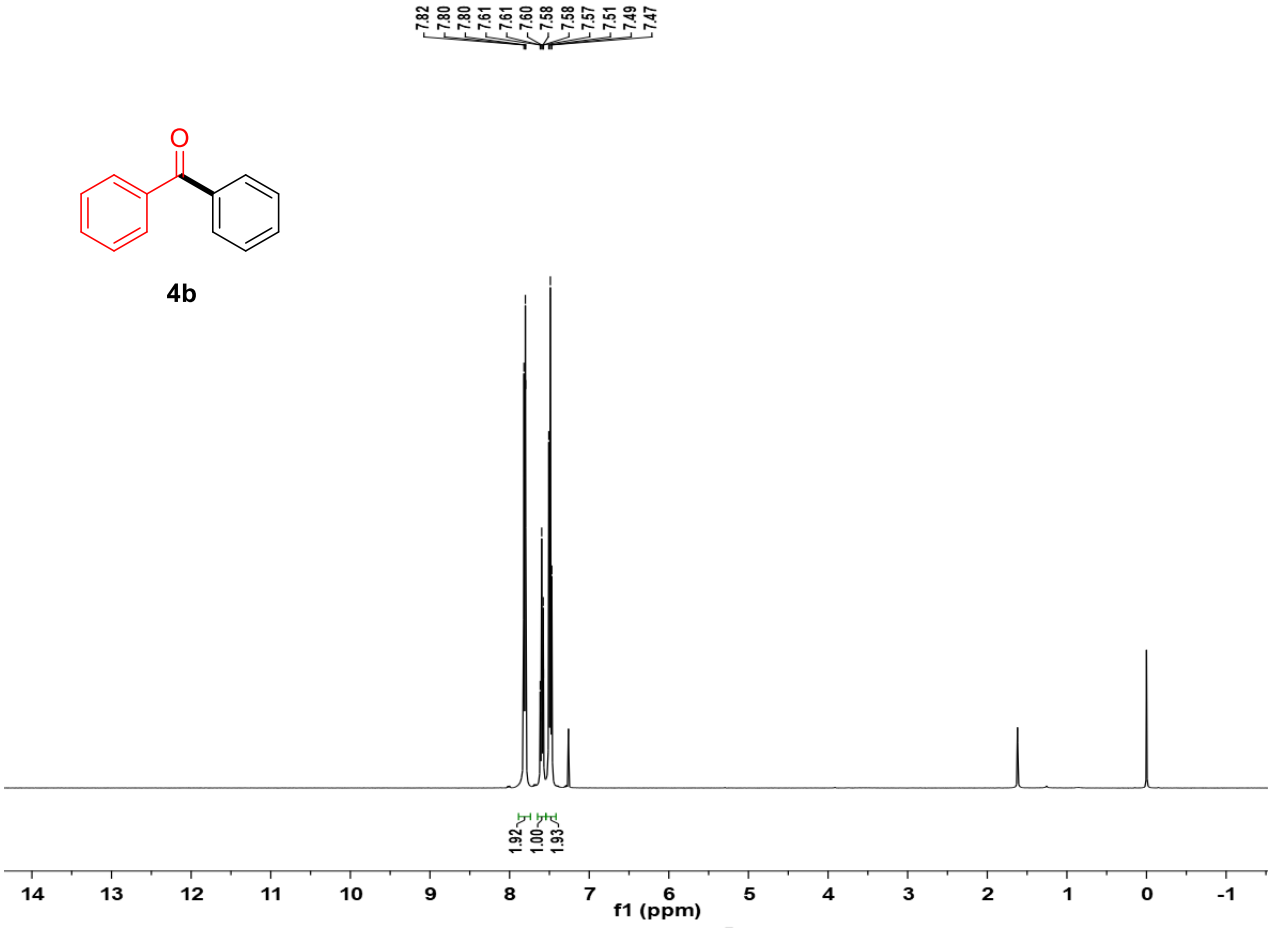
^{13}C NMR (101 MHz, $CDCl_3$) of 3x



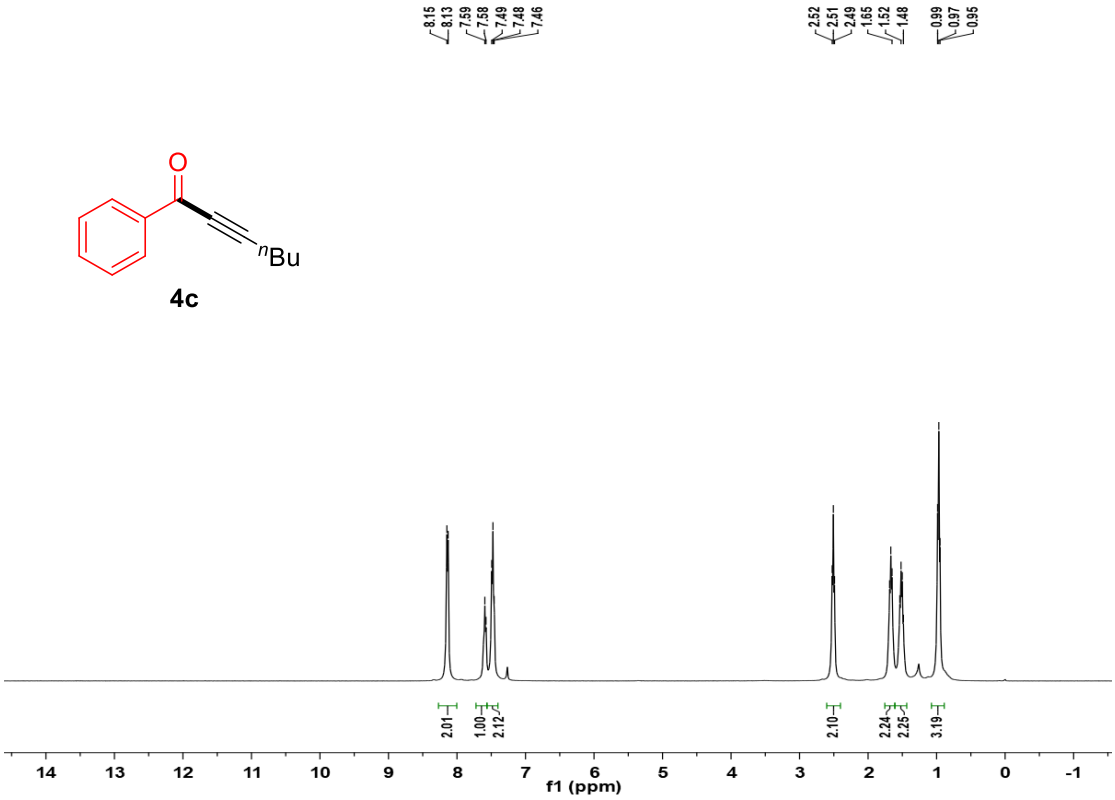
^{1}H NMR (400 MHz, $CDCl_3$) of 4a



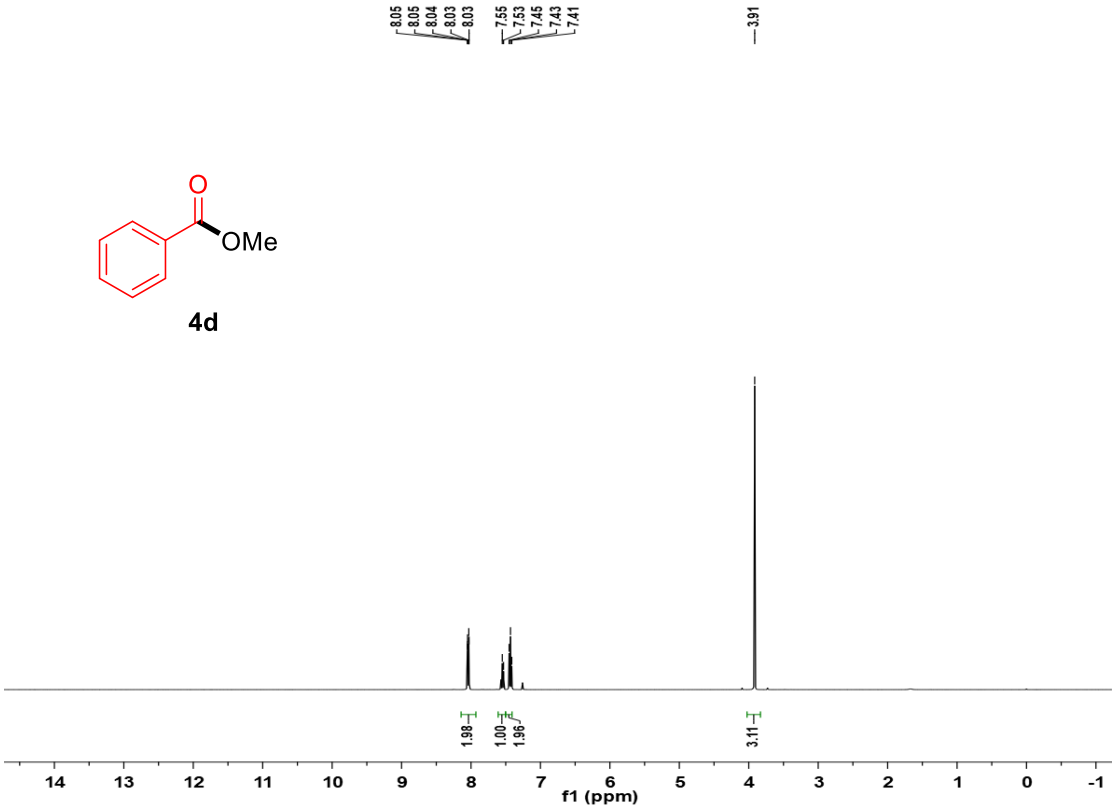
^{1}H NMR (400 MHz, $CDCl_3$) of 4b



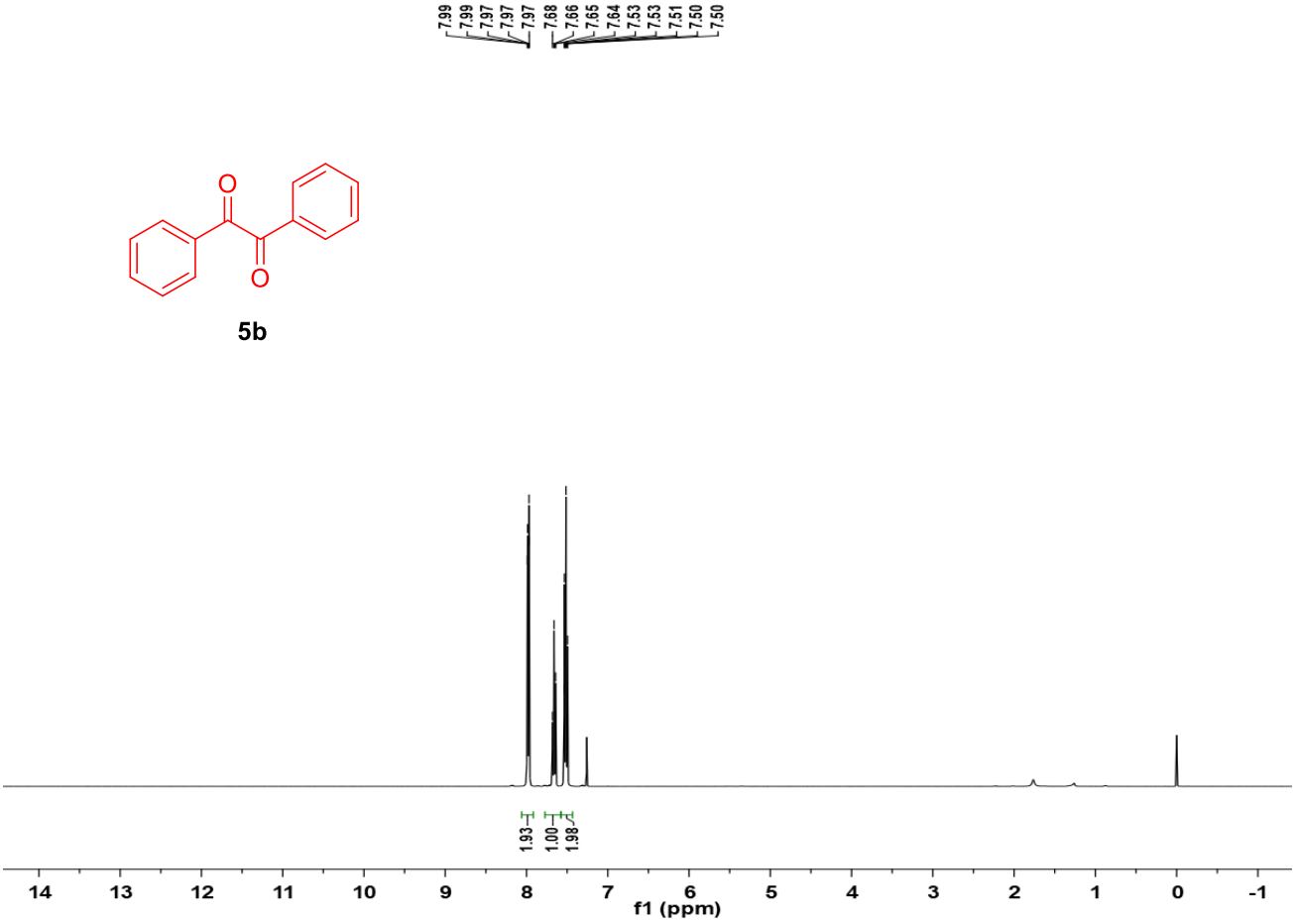
^{1}H NMR (400 MHz, $CDCl_3$) of 4c



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



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



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