Supporting Information for

Rhodium-Catalyzed Carbonylative Coupling of Alkyl Halides with Thiols: A Radical Process Faster than Easier Nucleophilic Substitution

Han-Jun Ai,[1] Jabor Rabeah,[1] Angelika Brückner,[1] and Xiao-Feng Wu[1,2]*

[1]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, Rostock, 18059

[2]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning, 116023

*Corresponding Author(s): Xiao-Feng Wu: Xiao-Feng.Wu@catalysis.de

Table of Contents

1. General Remarks

Reagents and solvents: Unless otherwise noted, the chemicals were commercially available from *Sigma-Aldrich, TCI* or *Alfa Aesar* and were used without further purification. Dioxane was bought from *Alfa Aesar*, HPLC grade, 99% min, packaged under argon in resealable ChemSeal bottles.

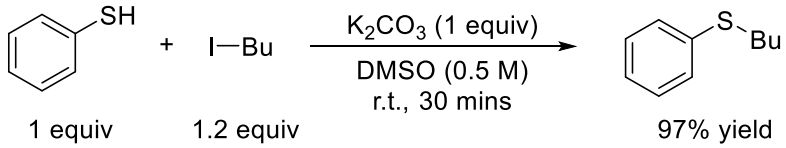
Purification: The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck). Gradient flash chromatography was conducted eluting with PE/EA, PE refers to pentane and EA refers to ethyl acetate, they were listed as volume/volume ratios.

Data collection: GC-yields were calculated using hexadecane as internal standard. GC analysis was performed on an Agilent HP-7890A instrument with FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas.

High resolution mass spectra (HRMS) were recorded on Agilent 6210. NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^1H NMR) and 77.00 ppm (^{13}C NMR). All measurements were carried out at room temperature unless otherwise stated.

Electron paramagnetic resonance (EPR) spectra were recorded on an X-band Bruker EMX CW-micro spectrometer (9.3 GHz) with a microwave power of 6.9 mW and modulation frequency of 100 kHz and modulation amplitude up to 5 G. For monitoring the EPR spectra at different temperatures, the EPR spectrometer was connected to a temperature controller and a liquid N_2 cryostat. Effective g values were calculated using the equation $h\nu = gB_0\beta$ with h = Planck's constant, ν = frequency, B_0 = resonance field and β= Bohr magneton.

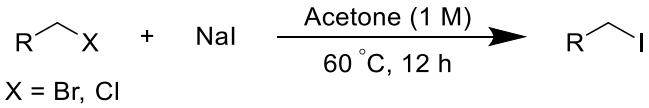
2. Procedure and Result of the S_N Reaction



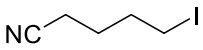
Room temperature under air, K_2CO_3 (0.5 mmol, 1 equiv) was transferred into an 8-mL vial with a 1.0 cm stir bar. Then added DMSO (1 mL) with syringe, 1-iodobutane (68 μL, 0.6 mmol, 1.2 equiv) and thiophenol (51 μL, 0.5 mmol, 1 equiv) with micro syringe. The vial was then capped, and the mixture was stirred at r.t. for 30 mins. Then, 10 μL of hexadecane was added to the vial. Then a proper amount of solution was taken for GC analysis.

3. Synthesis of the Substrates

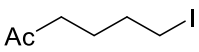
3.1 General Procedure A: Iodination of chlorides and bromides by Finkelstein reaction



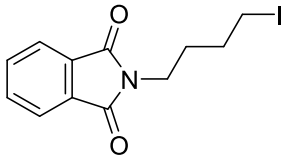
In a sealed tube, to a 1 M solution of the corresponding alkyl-X (X = Br or Cl) (1 equiv) in acetone was added NaI (3 equiv). The mixture was stirred at 60 °C for 12 h. After the reaction was completed, the reaction mixture was quenched with saturated $Na_2S_2O_3$ solution, extracted with EA (3x), The organic layer was dried over $MgSO_4$, filtered and concentrated. Then the solvent was evaporated under vacuum. The crude product was purified by column chromatography. Iodides indicated below were obtained following this procedure.



5-Iodopentanenitrile. The product was obtained using 5-bromopentanenitrile (350 μL, 3 mmol) as the starting alkyl halide. The compound was purified by column chromatography (pentane/EA = 5/1) and was obtained as a light tellow oil in 95% yield (595 mg). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.22 (t, *J* = 6.6 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 2.08 - 1.89 (m, 2H), 1.89 - 1.71 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 119.0, 31.7, 26.0, 16.1, 4.5.

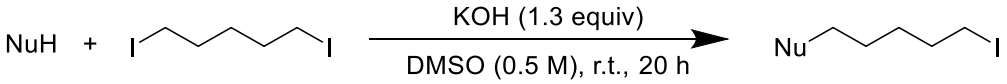


6-Iodohexan-2-one. The product was obtained using 6-chlorohexan-2-one (396 μL, 3 mmol) as the starting alkyl halide. The compound was purified by column chromatography (pentane/EA = 5/1) and was obtained as a brown oil in 97% yield (657 mg). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 3.19 (t, *J* = 6.8 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 2.15 (s, 3H), 1.83 (m, 2H), 1.80 - 1.59 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 207.9, 42.1, 32.5, 29.7, 24.3, 6.1.

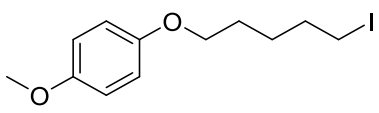


2-(4-Iodobutyl)isoindoline-1,3-dione. The product was obtained using 2-(4-bromobutyl)isoindoline-1,3-dione (846 mg, 3 mmol) as the starting alkyl halide. The compound was purified by column chromatography (pentane/EA = 5/1) and was obtained as a white solid in 93% yield (784 mg). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.87 - 7.83 (m, 2H), 7.77 - 7.69 (m, 2H), 3.72 (t, *J* = 6.7 Hz, 2H), 3.21 (t, 2H), 1.96 - 1.73 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 168.3, 133.9, 132.0, 123.2, 36.7, 30.5, 29.5, 5.5.

3.2 General Procedure B: Alkylation of phenols, benzyl alcohol and indoles with diiodoalkanes

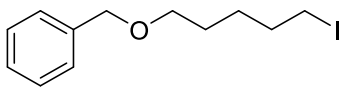


In a sealed tube, to a 0.5 M solution of the corresponding NuH (phenols, benzyl alcohol or indoles) (1 equiv) in DMSO was added KOH (1.3 equiv). The solution was stirred for 15 min before the addition of alkyl iodides (3 equiv). The mixture was stirred at r.t. for 20 h. After the reaction was completed, the reaction mixture was quenched H_2O, extracted with EA (3x), The organic layer was dried over $MgSO_4$, filtered and concentrated. Then the solvent was evaporated under vacuum. The crude product was purified by column chromatography. Iodides indicated below were obtained following this procedure.

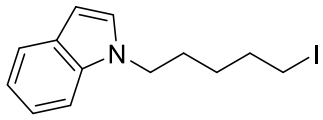


1-((5-Iodopentyl)oxy)-4-methoxybenzene. The product was obtained using 4-methoxyphenol (372 mg, 3 mmol) and 1,5-diiodopentane (1.3 mL, 9 mmol). The compound was purified by column chromatography (pentane/EA = 20/1) and was obtained as a light-yellow oil in 52% yield (500 mg). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.82 (m, 4H), 3.90 (t, *J* = 6.3 Hz, 2H), 3.75 (s, 3H), 3.20 (t, *J* = 7.0 Hz, 2H), 1.97 - 1.69 (m, 4H), 1.65 - 1.48 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.7,

153.1, 115.4, 114.6, 68.2, 55.7, 33.2, 28.3, 27.1, 6.6.

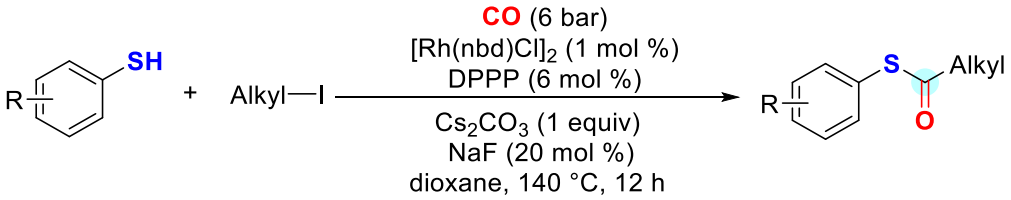


(((5-Iodopentyl)oxy)methyl)benzene. The product was obtained using benzyl alcohol (310 μL, 3 mmol) and 1,5-diiodopentane (1.3 mL, 9 mmol). The compound was purified by column chromatography (pentane/EA = 100/1) and was obtained as a colorless oil in 35% yield (318 mg). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.37 - 7.21 (m, 5H), 4.49 (s, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 1.91 - 1.76 (m, 2H), 1.71 - 1.56 (m, 2H), 1.56 - 1.40 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 138.4, 128.3, 127.6, 127.5, 72.9, 69.9, 33.3, 28.6, 27.2, 6.9.



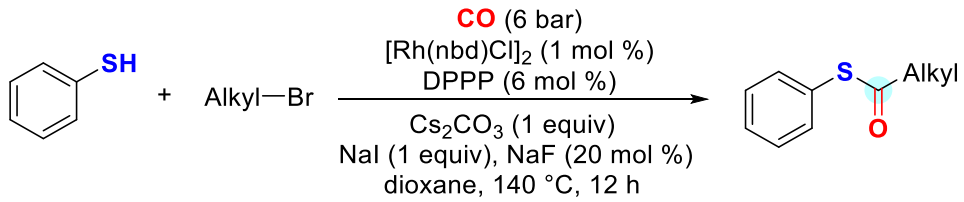
1-(5-Iodopentyl)-1*H*-indole. The product was obtained using indole (351.5 mg, 3 mmol) and 1,5-diiodopentane (1.3 mL, 9 mmol). The compound was purified by column chromatography (pentane/EA = 50/1) and was obtained as a yellow oil in 45% yield (422 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 6.9 Hz, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 6.47 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.06 (t, *J* = 7.0 Hz, 2H), 3.08 (t, *J* = 7.0 Hz, 2H), 1.91 - 1.64 (m, 4H), 1.43 - 1.30 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.8, 128.5, 127.6, 121.3, 120.9, 119.2, 109.2, 101.0, 46.0, 32.9, 29.1, 27.8, 6.4.

4. General Procedure of Carbonylative Coupling of Thiophenols and Alkyl Iodides



An oven-dried vial (4 mL) containing a stirring bar was charged with $[Rh(nbd)Cl]_2$ (0.005 mmol, 2.3 mg, 0.01 equiv), DPPP (0.03 mmol, 12.4 mg, 0.06 equiv), thiophenols (0.5 mmol, 1 equiv, if it is soild), iodoalkane (1 mmol, 2 equiv, if it is solid). Then the vial was introduced into the glovebox, where Cs_2CO_3 (0.5 mmol, 162.9 mg, 1 equiv) and NaF (0.1 mmol, 4.2 mg, 0.2 equiv) were subsequently added. The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and taken out from the glovebox. Then, thiophenols (0.5 mmol, 1 equiv, if it is liquid), iodoalkane (1 mmol, 2 equiv, if it is liquid) and dioxane (1.5 mL) were added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 6 bar of CO was adjusted at ambient temperature. (NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood). Then, the mixture was stirred for 12 h at 140 ℃. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. The product was purified by column chromatography on silica gel (pentane/EA) to deliver the desired product.

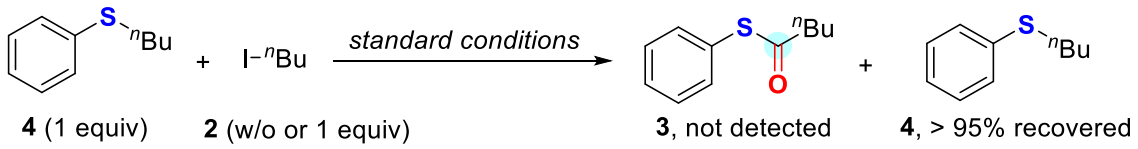
5. General Procedure of Carbonylative Coupling of Thiophenol and Alkyl Bromides



An oven-dried vial (4 mL) containing a stirring bar was charged with $[Rh(nbd)Cl]_2$ (0.005 mmol, 2.3 mg, 0.01 equiv), DPPP (0.03 mmol, 12.4 mg, 0.06 equiv), NaI (0.1 mmol, 75 mg, 0.2 equiv), bromoalkane (1 mmol, 2 equiv, if it is solid). Then the vial was introduced into the glovebox, where Cs_2CO_3 (0.5 mmol, 162.9 mg, 1 equiv) and NaF (0.1 mmol, 4.2 mg, 0.2 equiv) were subsequently added. The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and taken out from the glovebox. Then, thiophenol (0.5 mmol, 51 μL, 1 equiv), bromoalkane (1 mmol, 2 equiv, if it is liquid) and dioxane (1.5 mL) were added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 6 bar of CO was adjusted at ambient temperature. (NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood). Then, the mixture was stirred for 12 h at 140 °C. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. The product was purified by column chromatography on silica gel (pentane/EA) to deliver the desired product.

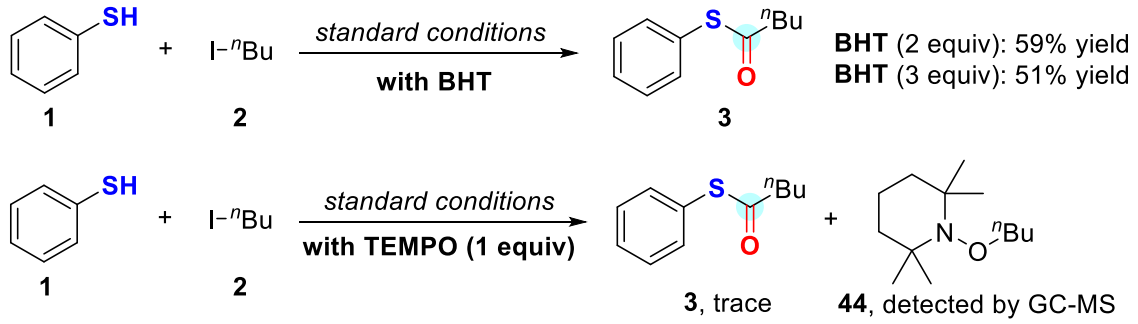
6. Procedure and Result of the Mechanistic Studies

6.1 Carbonylation of thioether 4



An oven-dried vial (4 mL) containing a stirring bar was charged with $[Rh(nbd)Cl]_2$ (0.002 mmol, 0.92 mg, 0.01 equiv), DPPP (0.012 mmol, 5 mg, 0.06 equiv). Then the vial was introduced into the glovebox, where Cs_2CO_3 (0.2 mmol, 65.2 mg, 1 equiv) and NaF (0.04 mmol, 1.7 mg, 0.2 equiv) were subsequently added. The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and taken out from the glovebox. Then, phenol butyl sulfide (0.2 mmol, 33mg, 1 equiv), iodobutane (without or 0.2 mmol, 23 μL, 1 equiv) and dioxane (0.6 mL) were added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 6 bar of CO was adjusted at ambient temperature. (NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood). Then, the mixture was stirred for 12 h at 140 °C. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. Then, 10 μL of hexadecane was added to the vial. Then a proper amount of solution was taken for GC analysis. The result is shown above.

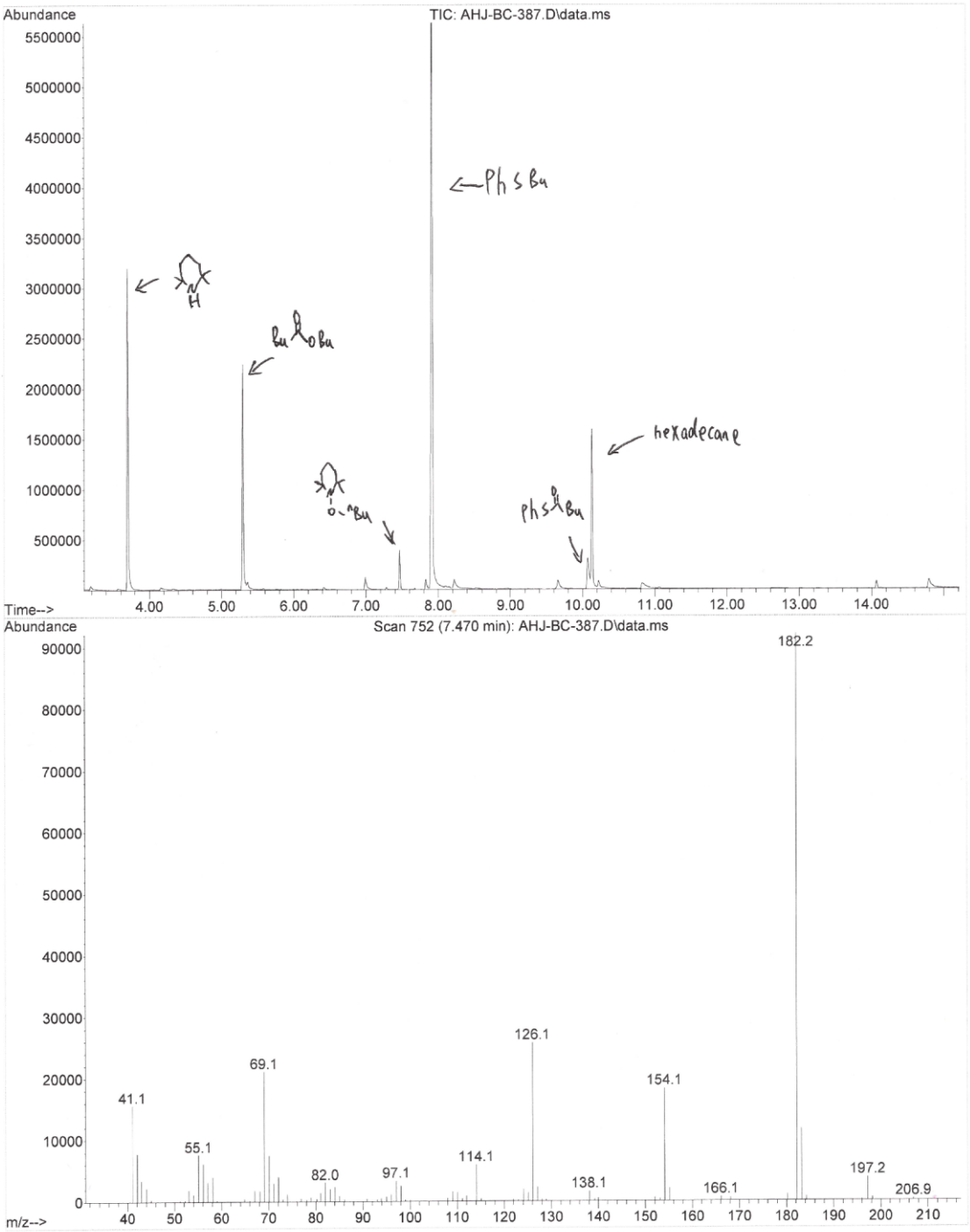
6.2 Radical inhibition & trapping experiments



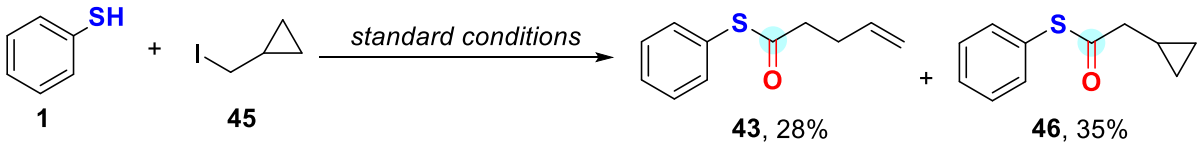
An oven-dried vial (4 mL) containing a stirring bar was charged with $[Rh(nbd)Cl]_2$ (0.005 mmol, 2.3 mg, 0.01 equiv), DPPP (0.03 mmol, 12.4 mg, 0.06 equiv) and BHT (0.5 mmol **or** 1 mmol), **or** TEMPO (0.5 mmol). Then the vial was introduced into the glovebox, where Cs_2CO_3 (0.5 mmol, 162.9 mg, 1 equiv) and NaF (0.1 mmol, 4.2 mg, 0.2 equiv) were subsequently added. The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and

phenolic cap and taken out from the glovebox. Then, thiophenol (0.5 mmol, 51 μL, 1 equiv), iodobutane (1 mmol, 114 μL, 2 equiv) and dioxane (1.5 mL) were added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 6 bar of CO was adjusted at ambient temperature. (NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood). Then, the mixture was stirred for 12 h at 140 °C. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. Then, 10 μL of hexadecane was added to the vial. Then a proper amount of solution was taken for GC and GC-MS analysis (GC-MS analysis of TEMPO-added reaction, see it below). The result is shown above.

```
File       :D:\MassHunter\GCMS\1\data\202008\AHJ-BC-387.D
Operator   :
Acquired   : 05 Aug 2020  19:48     using AcqMethod SK-Q30.M
Instrument :    GCMS
Sample Name: AHJ-BC-387
Misc Info  :
Vial Number: 1
```

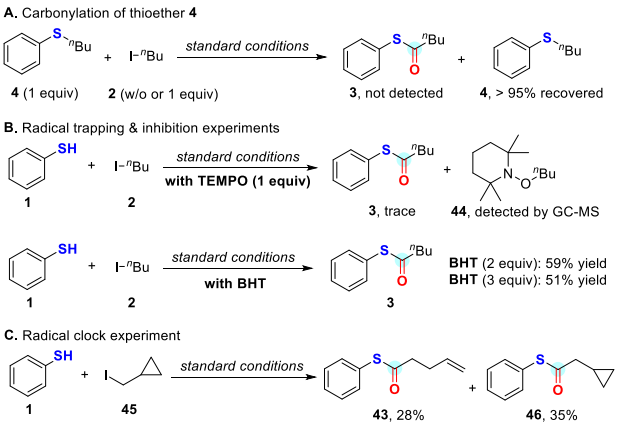


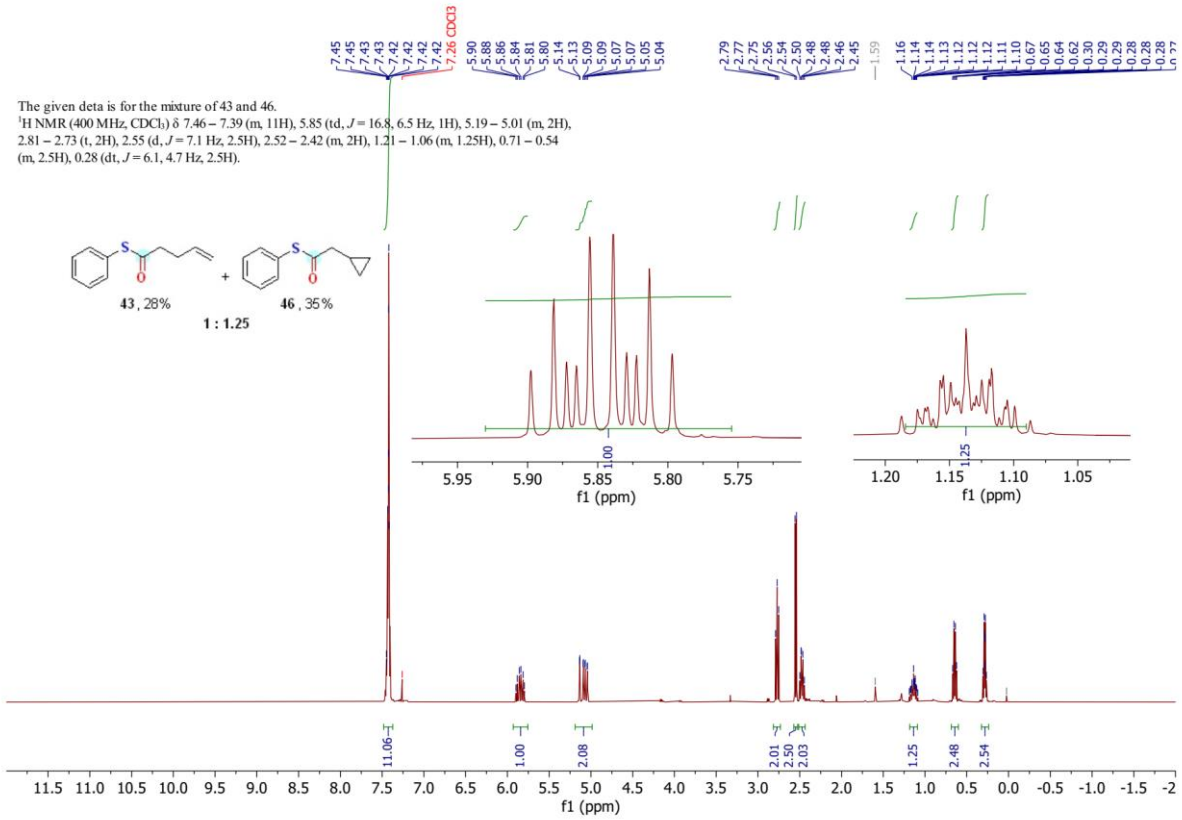
6.3 Radical clock experiment

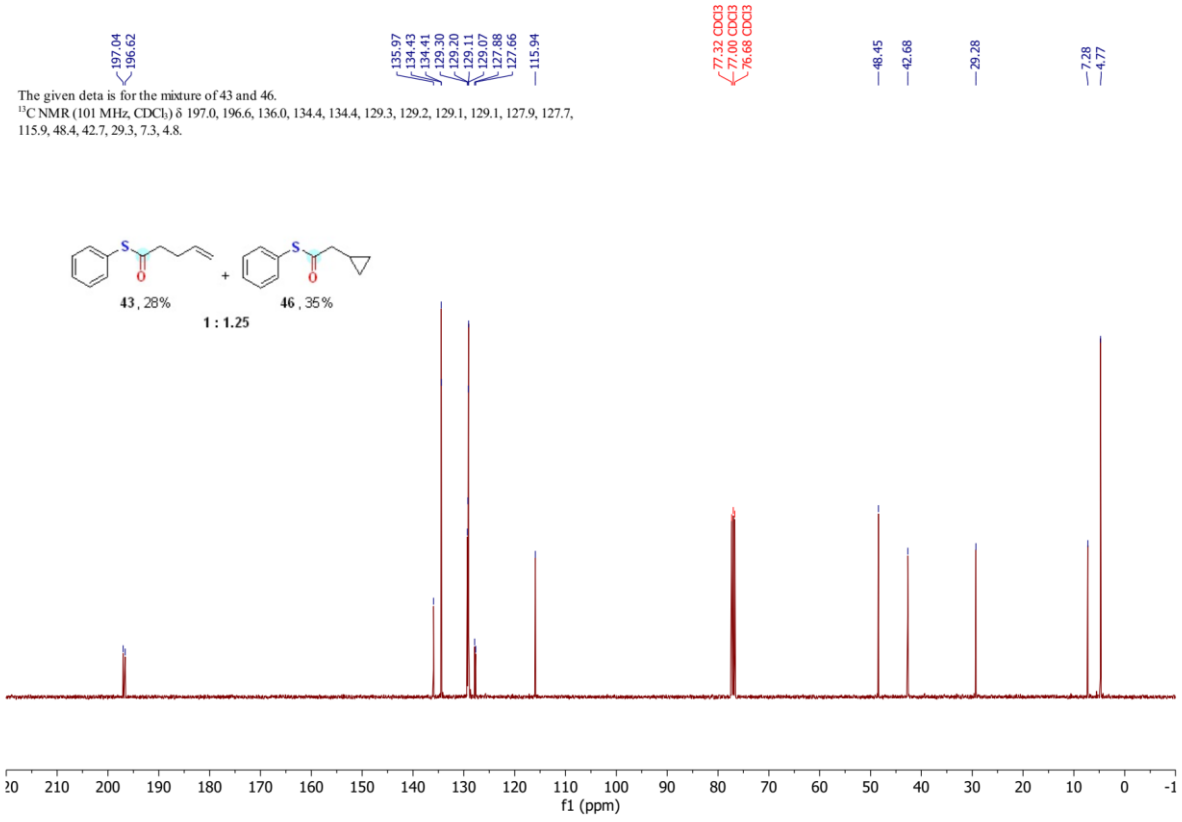


An oven-dried vial (4 mL) containing a stirring bar was charged with $[Rh(nbd)Cl]_2$ (0.005 mmol, 2.3 mg, 0.01 equiv), DPPP (0.03 mmol, 12.4 mg, 0.06 equiv). Then the vial was introduced into the glovebox, where Cs_2CO_3 (0.5 mmol, 162.9 mg, 1 equiv) and NaF (0.1 mmol, 4.2 mg, 0.2 equiv) were subsequently added. The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and taken out from the glovebox. Then, thiophenol (0.5 mmol, 51 μL, 1 equiv), iodomethylcyclopropane (1 mmol, 93 μL, 2 equiv) and dioxane (1.5 mL) were added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 6 bar of CO was adjusted at ambient temperature. (NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood). Then, the mixture was stirred for 12 h at 140 °C. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. The crude product was purified by column chromatography on silica gel (pentane/EA) to deliver the desired product. Then the products analyzed by NMR (see it below), the result is shown above.

Preliminary Mechanistic Studies.

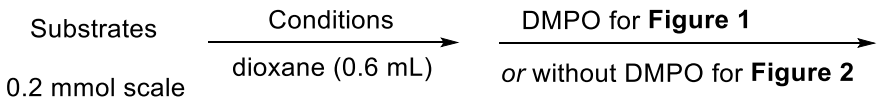



The given deta is for the mixture of 43 and 46.
¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.39 (m, 11H), 5.85 (td, J = 16.8, 6.5 Hz, 1H), 5.19 – 5.01 (m, 2H), 2.81 – 2.73 (t, 2H), 2.55 (d, J = 7.1 Hz, 2.5H), 2.52 – 2.42 (m, 2H), 1.21 – 1.06 (m, 1.25H), 0.71 – 0.54 (m, 2.5H), 0.28 (dt, J = 6.1, 4.7 Hz, 2.5H).
43 , 28%
46 , 35%
1 : 1.25
f1 (ppm)


The given deta is for the mixture of 43 and 46.
¹³C NMR (101 MHz, CDCl₃) δ 197.0, 196.6, 136.0, 134.4, 134.4, 129.3, 129.2, 129.1, 129.1, 127.9, 127.7, 115.9, 48.4, 42.7, 29.3, 7.3, 4.8.
43 , 28%
46 , 35%
1 : 1.25
f1 (ppm)

6.4 The EPR experiments

6.4.1 General procedure for EPR studies:



An oven-dried vial (4 mL) containing a stirring bar was charged *with **or** without (according to the experiments)* $[Rh(nbd)Cl]_2$ (0.002 mmol, 0.9 mg, 0.01 equiv) and DPPP (0.012 mmol, 5 mg, 0.06 equiv). Then the vial was introduced into the glovebox, where Cs_2CO_3 (0.2 mmol, 65.2 mg, 1 equiv) and NaF (0.04 mmol, 1.7 mg, 0.2 equiv) were subsequently added. The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and taken out from the glovebox.

*For experiments in **Figure 1***: then, thiophenol (*with **or** without, according to the experiments.* 0.2 mmol, 21 μL, 1 equiv), iodobutane (*with **or** without, according to the experiments.* 0.4 mmol, 46 μL, 2 equiv) and dioxane (0.6 mL) were added by syringe. The solution sample was transformed into the EPR tube. Then, DMPO (15 μL) was added into the tube and analyzed by EPR.

*For experiments in **Figure 2***: then, dioxane (0.6 mL) were added by syringe to solid mixture in a vial. The solution sample was transformed into the EPR tube under Ar. Thiophenol (0.2 mmol, 21 μL, 1 equiv) ***or*** iodobutane (0.4 mmol, 46 μL, 2 equiv) was then added into the tube and analyzed by EPR.

6.4.2 The data of the simulation.

The EPR spectra were simulated using *Easyspin* program.
Program data:

```
Clear;
[B,spc] = textread('DMPO1.txt'); % DMPO1 experimental spectrum
Exp.mwFreq = 9.330;
Exp.Range = [322 342];

%for DMPO-H
Sys1.g =[2.0066];
Sys1.Nucs = '14N,1H';
Sys1.n=[1 2];
Sys1.A_N = mt2mhz([14.68 ]/10); % G --> MHz
Sys1.A_H = mt2mhz([18.59]/10);
Sys1.A = [Sys1.A_N, Sys1.A_H];
Sys1.lwpp=[0.07792 0.07984];
Sys1.weight=0.50942;
```

```
% For DMPO-nBu
Sys2.g=[2.0066];
Sys2.Nucs='14N,1H';
Sys2.n=[1,1];
Sys2.A_N=mt2mhz([14.58]/10);
Sys2.A_H=mt2mhz([18.92]/10);
Sys2.A=[Sys2.A_N,Sys2.A_H];
Sys2.lwpp=[0.08006 0.08006];
Sys2.weight=0.15353;

Vary1.lwpp=[0.006 0.0006];
Vary1.A=[1 1];
Vary1.weight=0.4;
Vary1.g=0.001;
Vary2.lwpp=[0.01 0.01];
Vary2.weight=.4;
Vary2.A=[1 1];
FitOpt.Method='simplex fcn';
FitOpt.Scaling='lsq0';
esfit('garlic',spc,{Sys1,Sys2},{Vary1,Vary2},Exp,[],FitOpt);
```

6.4.3 Figure S1

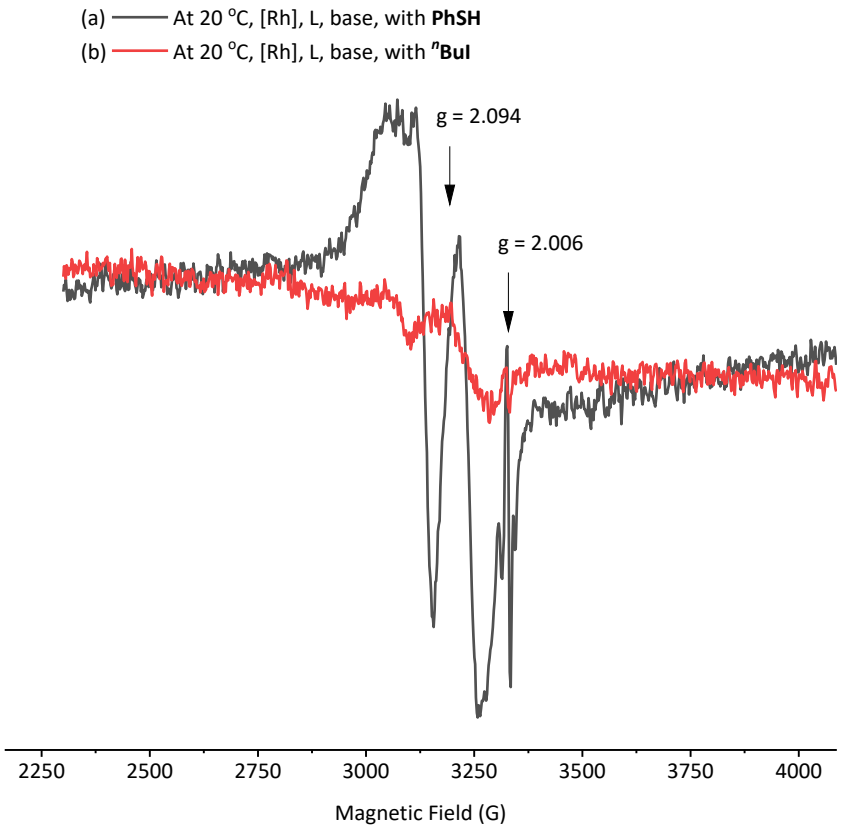
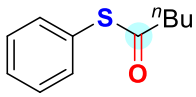


Figure S1. EPR spectra in dioxane under Ar at 20 °C of (a) $[Rh(nbd)Cl]_2$, DPPP, Cs_2CO_3, and PhSH; (b) $[Rh(nbd)Cl]_2$, DPPP, Cs_2CO_3, and ^{n}BuI.

7. Procedure and Characterization of the Products

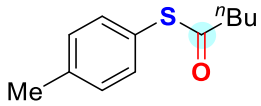


***S*-Phenyl pentanethioate (3).** Prepared according to general procedure using thiophenol (51 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (73.7 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 - 7.37 (m, 5H), 2.67 (t, *J* = 8 Hz, 2H), 1.72 (m, 2H), 1.41 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 134.4, 129.2, 129.1, 127.9, 43.4, 27.6, 22.1, 13.7.

HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{14}OSNa^+$ ([M+Na]$^+$) 217.0662, found 217.0666.

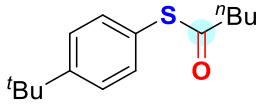


***S*-(*p*-Tolyl) pentanethioate (5).** Prepared according to general procedure using *p*-toluenethiol (62.1 mg, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (75.6 mg, 73% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 2.71 - 2.60 (t, 2H), 2.38 (s, 3H), 1.79 - 1.63 (m, 2H), 1.41 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.9, 139.4, 134.4, 129.9, 124.4, 43.3, 27.6, 22.1, 21.2, 13.7.

HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{17}OS^+$ ([M+H]$^+$) 209.1000, found 209.1005.

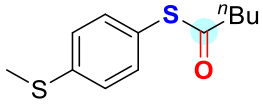


***S*-(4-(*tert*-Butyl)phenyl) pentanethioate (6).** Prepared according to general procedure on a 0.2 mmol scale using 4-(*tert*-butyl)benzenethiol (35 μL, 0.2 mmol) and iodobutane (46 μL, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (41 mg, 82% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 2.71 - 2.60 (t, 2H), 1.79 - 1.63 (m, 2H), 1.42 (m, 2H), 1.34 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 152.4, 134.1, 126.2, 124.5, 43.3, 34.7, 31.2, 27.6, 22.1, 13.7.

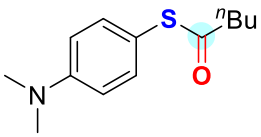
HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_{23}OS^+$ ([M+H]$^+$) 251.1469, found 251.1467.



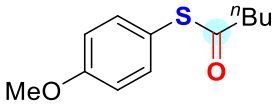
***S*-(4-(Methylthio)phenyl) pentanethioate (7).** Prepared according to general procedure using 4-(methylthio)benzenethiol (66 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a light-yellow oil (84.1 mg, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.20 (m, 4H), 2.70 - 2.59 (t, 2H), 2.49 (s, 3H), 1.77 - 1.60 (m, 2H), 1.53 - 1.30 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

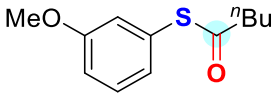
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 140.8, 134.7, 126.6, 123.8, 43.4, 27.6, 22.1, 15.3, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{17}OS_2^+$ ([M+H]$^+$) 241.0721, found 241.0717.



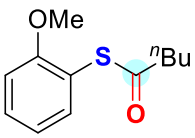
***S*-(4-(Dimethylamino)phenyl) pentanethioate (8).** Prepared according to general procedure using 4-(dimethylamino)benzenethiol (76.6 mg, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the titl e compound as a colorless oil (59.3 mg, 50% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 - 7.17 (m, 2H), 6.76 - 6.68 (m, 2H), 2.98 (s, 6H), 2.68 - 2. 54 (t, 2H), 1.68 (m, 2H), 1.39 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 151.0, 135.7, 112.6, 112.2, 42.9, 40.2, 27.7, 22.1, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{20}NOS^+$ ([M+H]$^+$) 238.1265, found 238.1266.



***S*-(4-Methoxyphenyl) pentanethioate (9).** Prepared according to general procedure using 4-methoxybenzenethiol (62 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude produc t was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a c olorless oil (84 mg, 75% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 2.69 - 2.58 (t, 2H), 1.77 - 1.61 (m, 2H), 1.49 - 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 160.5, 136.0, 118.6, 114.7, 55.2, 43.1, 27.6, 22.1, 13.6.
HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{17}O_2S^+$ ([M+H]$^+$) 225.0949, found 225.0954.

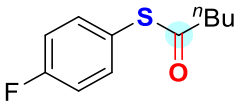


***S*-(3-Methoxyphenyl) pentanethioate (10).** Prepared according to general procedure using 3-methoxybenzenethiol (62 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude produc t was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a c olorless oil (78.4 mg, 70% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.26 (m, 1H), 7.05 - 6.89 (m, 3H), 3.81 (s, 3H), 2.71 - 2. 60 (t, 2H), 1.80 - 1.62 (m, 2H), 1.52 - 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 159.8, 129.9, 128.9, 126.6, 119.5, 115.4, 55.3, 43.4, 27. 6, 22.1, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{17}OS^+$ ([M+H]$^+$) 225.0949, found 225.0955.

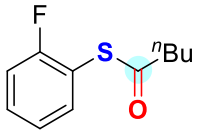


***S*-(2-Methoxyphenyl) pentanethioate (11).** Prepared according to general procedure using 2-methoxybenzenethiol (61 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude produc t was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a c olorless oil (67.2 mg, 60% yield).

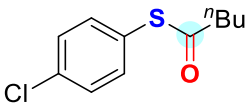
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 - 7.36 (m, 2H), 7.04 - 6.91 (m, 2H), 3.84 (s, 3H), 2.72 - 2.61 (t, 2H), 1.79 - 1.63 (m, 2H), 1.41 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 159.1, 136.6, 131.4, 121.0, 116.1, 111.4, 55.9, 43.2, 27.6, 22.0, 13.6.
HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{16}O_2SNa^+$ ([M+Na]$^+$) 247.0769, found 247.0771.



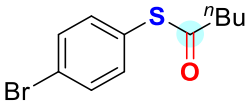
***S*-(4-Fluorophenyl) pentanethioate (12).** Prepared according to general procedure using 4-fluorobenzenethiol (54 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (82 mg, 77% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.10 (m, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 1.77 - 1.64 (m, 2H), 1.49 - 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 163.34 (d, *J* = 249.9 Hz), 136.46 (d, *J* = 8.6 Hz), 123.22 (d, *J* = 3.4 Hz), 116.31 (d, *J* = 22.0 Hz), 43.3, 27.5, 22.0, 13.6.
^{19}F NMR (282 MHz, $CDCl_3$) δ -111.37.
HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{14}FOS^+$ ([M+H]$^+$) 213.0749, found 213.0750.



***S*-(2-Fluorophenyl) pentanethioate (13).** Prepared according to general procedure using 2-fluorobenzenethiol (54 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (55.6 mg, 53% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 - 7.36 (m, 1H), 7.24 - 7.11 (m, 2H), 1.80 - 1.64 (m, 2H), 1.50 - 1.32 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 162.05 (d, *J* = 249.3 Hz), 136.6, 131.91 (d, *J* = 8.1 Hz), 124.55 (d, *J* = 3.9 Hz), 116.12 (d, *J* = 22.7 Hz), 115.35 (d, *J* = 18.7 Hz), 43.3, 27.5, 22.0, 13.6.
^{19}F NMR (282 MHz, $CDCl_3$) δ -106.67.
HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{14}FOS^+$ ([M+H]$^+$) 213.0749, found 213.0753.



***S*-(4-Chlorophenyl) pentanethioate (14).** Prepared according to general procedure using 4-chlorobenzenethiol (72.3 mg, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (51.3 mg, 45% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 - 7.26 (m, 4H), 2.79 - 2.53 (t, 2H), 1.80 - 1.61 (m, 2H), 1.54 - 1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 135.7, 129.4, 126.4, 43.5, 27.6, 22.1, 13.7.

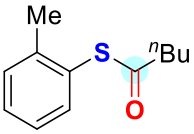


***S*-(4-Bromophenyl) pentanethioate (15).** Prepared according to general procedure using 4-br omobenzenethiol (94.5 mg, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a c olorless oil (72 mg, 53% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 2.63 - 2.52 (m, 2H), 1.69 - 1.53 (m, 2H), 1.41 - 1.22 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 135.8, 132.3, 127.0, 123.8, 43.4, 27.5, 22.0, 13.6.

HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{14}BrOS^+$ ([M+H]$^+$) 272.9949, found 272.9951.

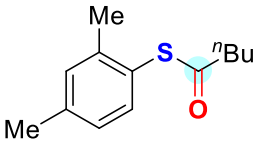


***S*-(*o*-Tolyl) pentanethioate (16).** Prepared according to general procedure using 2-methylben zenethiol (59 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purifie d by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (80.1 mg, 77% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.23 (m, 1H), 7.22 (m, 2H), 7.20 - 7.06 (m, 1H), 2.63 - 2.52 (t, 2H), 2.26 (s, 3H), 1.70 - 1.54 (m, 2H), 1.32 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 141.9, 135.9, 130.6, 129.9, 127.4, 126.5, 43.4, 27.7, 22. 1, 20.7, 13.7.

HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{17}OS^+$ ([M+H]$^+$) 209.1000, found 209.1002.

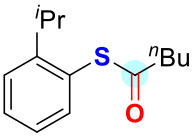


***S*-(2,4-Dimethylphenyl) pentanethioate (17).** Prepared according to general procedure using 2,4-dimethylbenzenethiol (68 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude pr oduct was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (88.8 mg, 80% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.8 Hz, 1H), 7.16 (s, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 2.68 (t, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.81 - 1.60 (m, 2H), 1.55 - 1.32 (m, 2H), 0.97 (t, *J* = 7. 3 Hz, 3H).

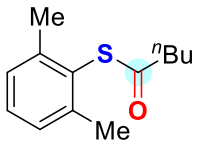
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 141.6, 140.0, 135.7, 131.5, 127.3, 124.0, 43.2, 27.7, 22. 1, 21.1, 20.5, 13.6.

HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{19}OS^+$ ([M+H]$^+$) 223.1156, found 223.1156.

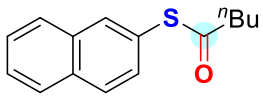


***S*-(2-Isopropylphenyl) pentanethioate (18).** Prepared according to general procedure using 2 -isopropylbenzenethiol (76 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude prod uct was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound a s a colorless oil (75.5 mg, 64% yield).

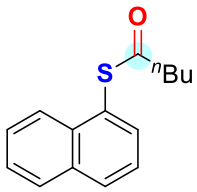
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 - 7.31 (m, 3H), 7.25 - 7.14 (m, 1H), 3.32 (hept, *J* = 6.9 Hz, 1H), 2.73 - 2.60 (t, 2H), 1.79 - 1.62 (m, 2H), 1.50 - 1.30 (m, 2H), 1.21 (s, 3H), 1.18 (s, 3H), 0.93 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 151.7, 136.5, 130.3, 126.3, 126.2, 126.1, 43.4, 31.1, 27.7, 23.5, 22.1, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{14}H_{21}OS^+$ ([M+H]$^+$) 237.1313, found 237.1316.



***S*-(2,6-Dimethylphenyl) pentanethioate (19).** Prepared according to general procedure using 2,6-dimethylbenzenethiol (67 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (63 mg, 57% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.20 (m, 1H), 7.19 - 7.13 (m, 2H), 2.72 - 2.64 (t, 2H), 2.37 (s, 6H), 1.73 (m, 2H), 1.43 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 142.6, 129.7, 128.2, 127.3, 43.5, 27.9, 22.1, 21.7, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{19}OS^+$ ([M+H]$^+$) 223.1156, found 223.1158.

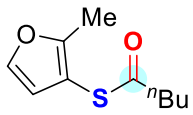


***S*-(Naphthalen-2-yl) pentanethioate (20).** Prepared according to general procedure using naphthalene-2-thiol (72.1 mg, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (85.4 mg, 70% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 - 7.91 (m, 1H), 7.91 - 7.78 (m, 3H), 7.58 - 7.47 (m, 2H), 7.45 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.76 - 2.65 (t, 2H), 1.81 - 1.64 (m, 2H), 1.52 - 1.34 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 134.3, 133.5, 133.3, 131.0, 128.7, 127.9, 127.8, 127.1, 126.5, 125.3, 43.5, 27.7, 22.1, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_{16}OSNa^+$ ([M+Na]$^+$) 267.0819, found 267.0823.



***S*-(Naphthalen-1-yl) pentanethioate (21).** Prepared according to general procedure using naphthalene-1-thiol (69 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (84.2 mg, 69% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.5 Hz, 1H), 7.93 (dd, *J* = 21.1, 8.1 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.56 (m, 3H), 2.81 - 2.73 (t, 2H), 1.78 (m, 2H), 1.47 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 135.0, 134.2, 134.1, 130.8, 128.6, 127.1, 126.3, 125.5, 125.4, 125.2, 43.5, 27.7, 22.1, 13.7.

HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_{17}OS^+$ ([M+H]$^+$) 245.1000, found 245.0999.

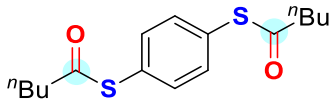


***S*-(2-Methylfuran-3-yl) pentanethioate (22).** Prepared according to general procedure using 2-methylfuran-3-thiol (50 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (64 mg, 65% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.0 Hz, 1H), 6.31 (d, *J* = 2.0 Hz, 1H), 2.67 - 2.56 (t, 2H), 2.25 (s, 3H), 1.76 - 1.59 (m, 2H), 1.49 - 1.28 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 156.0, 140.9, 114.8, 104.3, 42.9, 27.5, 22.1, 13.6, 11.8.

HRMS (ESI-TOF): *m/z* calcd. for $C_{10}H_{14}O_2SNa^+$ ([M+Na]$^+$) 221.0612, found 221.0616.

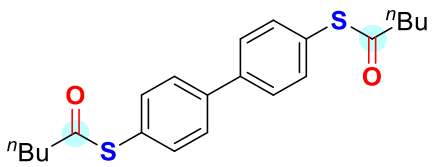


***S,S'*-(1,4-Phenylene) dipentanethioate (23).** Prepared according to general procedure using benzene-1,4-dithiol (35.6 mg, 0.25 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (62 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 4H), 2.70 - 2.62 (t, 4H), 1.70 (m, 4H), 1.40 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 134.7, 129.5, 43.5, 27.6, 22.1, 13.7.

HRMS (ESI-TOF): *m/z* calcd. for $C_{16}H_{23}O_2S_2^+$ ([M+H]$^+$) 311.1139, found 311.1143.

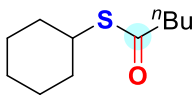


***S,S'*-([1,1'-Biphenyl]-4,4'-diyl) dipentanethioate (24).** Prepared according to general procedure using [1,1'-biphenyl]-4,4'-dithiol (54.6 mg, 0.25 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless solid (59 mg, 62% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 2.69 (t, 2H), 1.81 - 1.65 (m, 2H), 1.51 - 1.31 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 141.2, 134.8, 127.9, 127.4, 43.5, 27.6, 22.1, 13.7.

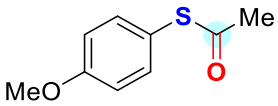
HRMS (ESI-TOF): *m/z* calcd. for $C_{22}H_{27}O_2S_2^+$ ([M+H]$^+$) 387.1452, found 387.1455.



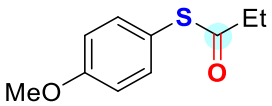
***S*-Cyclohexyl pentanethioate (25).** Prepared according to general procedure using cyclohexanethiol (62 μL, 0.5 mmol) and iodobutane (114 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (75 mg, 75% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 - 3.36 (m, 1H), 2.50 (t, 2H), 1.99 - 1.83 (m, 2H), 1.76 - 1.55 (m, 5H), 1.49 - 1.26 (m, 7H), 0.91 (t, *J* = 7.3 Hz, 3H).

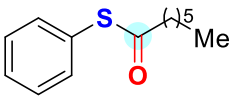
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 43.9, 42.1, 33.1, 27.7, 25.9, 25.5, 22.1, 13.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{21}OS^+$ ([M+H]$^+$) 201.1313, found 201.1310.



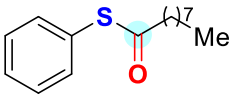
***S*-(4-Methoxyphenyl) ethanethioate (26).** Prepared according to general procedure using 4-methoxybenzenethiol (62 μL, 0.5 mmol) and iodomethane (62 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (75 mg, 82% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 2.39 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 160.6, 136.0, 118.6, 114.8, 55.3, 29.8.
HRMS (ESI-TOF): *m/z* calcd. for $C_9H_{11}O_2S^+$ ([M+H]$^+$) 183.0479, found 183.0481.



***S*-(4-Methoxyphenyl) ethanethioate (27).** Prepared according to general procedure using 4-methoxybenzenethiol (62 μL, 0.5 mmol) and iodoethane (80 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (78 mg, 80% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 160.5, 136.1, 118.5, 114.8, 55.3, 36.8, 9.6.
HRMS (ESI-TOF): *m/z* calcd. for $C_{10}H_{13}O_2S^+$ ([M+H]$^+$) 197.0636, found 197.0638.

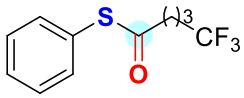


***S*-Phenyl heptanethioate (28).** Prepared according to general procedure using thiophenol (51 μL, 0.5 mmol) and iodohexane (148 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (91.1 mg, 82% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.37 (m, 5H), 2.74 - 2.62 (t, 2H), 1.72 (p, *J* = 7.5 Hz, 2H), 1.43 - 1.26 (m, 6H), 0.95 - 0.87 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 134.4, 129.2, 129.1, 127.9, 43.7, 31.4, 28.6, 25.5, 22.4, 14.0.
HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{19}OS^+$ ([M+H]$^+$) 223.1156, found 223.1151.

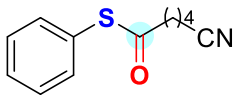


***S*-Phenyl nonanethioate (29).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and iodooctane (72 μL, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a light-yellow oil (40 mg, 80% yield).

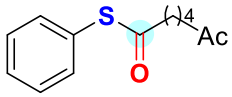
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 5H), 2.71 - 2.60 (m, 2H), 1.72 (p, *J* = 7.3 Hz, 2 H), 1.42 - 1.24 (m, 10H), 0.98 - 0.79 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 134.5, 129.3, 129.1, 128.0, 43.7, 31.8, 29.2, 29.1, 28.9, 25.6, 22.6, 14.1.
HRMS (ESI-TOF): *m/z* calcd. for $C_{15}H_{23}OS^+$ ($[M+H]^+$) 251.1469, found 251.1467.



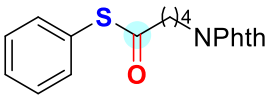
***S*-Phenyl 5,5,5-trifluoropentanethioate (30).** Prepared according to general procedure using thiophenol (51 μL, 0.5 mmol) and 1,1,1-trifluoro-4-iodobutane (129 μL, 1 mmol). The crude p roduct was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compoun d as a colorless oil (74.4 mg, 60% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.41 (m, 5H), 2.77 (t, *J* = 7.2 Hz, 2H), 2.26 - 2.12 (m, 2 H), 2.03 - 1.93 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 134.4, 129.5, 129.2, 127.23, 126.74 (q, *J* = 275.3 Hz), 4 1.7, 32.68 (q, *J* = 29.0 Hz), 17.78 (q, *J* = 3.2 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -66.28.
HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{12}F_3OS^+$ ($[M+H]^+$) 249.0561, found 249.0564.



***S*-Phenyl 5-cyanopentanethioate (31).** Prepared according to general procedure on a 0.2 mm ol scale using thiophenol (21 μL, 0.2 mmol) and 5-iodopentanenitrile (83.4 mg, 0.4 mmol). Th e crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title c ompound as a colorless oil (25.5 mg, 60% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 - 7.32 (m, 5H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.37 (t, *J* = 6.9 H z, 2H), 1.95 - 1.79 (m, 2H), 1.82 - 1.66 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 134.4, 129.5, 129.2, 127.3, 119.2, 42.3, 24.6, 24.3, 16.9.
HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{13}NOSNa^+$ ($[M+Na]^+$) 242.0615, found 242.0609.



***S*-Phenyl 6-oxoheptanethioate (32).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and 6-iodohexan-2-one (90.4 mg, 0.4 mmol). The cr ude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title comp ound as a colorless oil (33.4 mg, 71% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 - 7.35 (m, 5H), 2.67 (t, *J* = 7.1 Hz, 2H), 2.45 (t, 2H), 2.13 (s, 3H), 1.83 - 1.51 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4, 197.2, 134.5, 129.4, 129.2, 127.7, 43.3, 43.2, 29.9, 24.9, 23.0.
HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{16}O_2SNa^+$ ($[M+Na]^+$) 259.0768, found 259.0770.

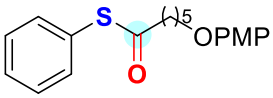


***S*-Phenyl 5-(1,3-dioxoisoindolin-2-yl)pentanethioate (33).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and 2-(4-iodobutyl)isoindoline-1,3-dione (131.6 mg, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a white solid (43.3 mg, 64% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 - 7.79 (m, 2H), 7.75 - 7.66 (m, 2H), 7.45 - 7.34 (m, 5H), 3.78 - 3.65 (t, 2H), 2.78 - 2.64 (t, 2H), 1.85 - 1.68 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 168.3, 134.4, 133.9, 132.0, 129.3, 129.1, 127.6, 123.2, 42.8, 37.3, 27.7, 22.6.

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{17}NO_3S^+$ ([M+Na]$^+$) 362.0826, found 362.0823.

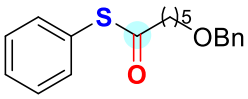


***S*-Phenyl 6-(4-methoxyphenoxy)hexanethioate (34).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and 1-((5-iodopentyl)oxy)-4-methoxybenzene (128 mg, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (59 mg, 89% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 - 7.36 (m, 5H), 6.87 - 6.80 (m, 4H), 3.92 (t, *J* = 6.3 Hz, 2H), 3.77 (s, 3H), 2.70 (t, 2H), 1.88 - 1.72 (m, 4H), 1.65 - 1.48 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 153.7, 153.1, 134.4, 129.3, 129.1, 127.8, 115.4, 114.6, 68.2, 55.7, 43.5, 29.0, 25.5, 25.3.

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{22}O_3SNa^+$ ([M+Na]$^+$) 353.1187, found 353.1187.

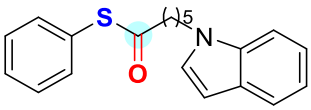


***S*-Phenyl 6-(benzyloxy)hexanethioate (35).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and (((5-iodopentyl)oxy)methyl)benzene (121.6 mg, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (43.5 mg, 69% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 5H), 7.33 (m, 5H), 4.50 (s, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 2.71 - 2.60 (t, 2H), 1.81 - 1.54 (m, 4H), 1.54 - 1.34 (m, 2H).

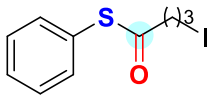
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 138.5, 134.4, 129.3, 129.1, 128.3, 127.6, 127.5, 72.9, 70.0, 43.6, 29.4, 25.6, 25.3.

HRMS (ESI-TOF): *m/z* calcd. for $C_{19}H_{22}O_2SNa^+$ ([M+Na]$^+$) 337.1238, found 337.1236.

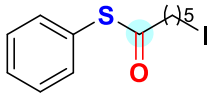


***S*-Phenyl 6-(1*H*-indol-1-yl)hexanethioate (36).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and 1-(5-iodopentyl)-1*H*-indole (125 mg, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (35 mg, 54% yield).

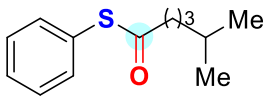
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (ddd, *J* = 7.9, 1.3, 0.8 Hz, 1H), 7.40 - 7.37 (m, 5H), 7.36 - 7.28 (m, 1H), 7.25 - 7.14 (m, 1H), 7.14 - 7.03 (m, 2H), 6.48 (dd, *J* = 3.1, 0.9 Hz, 1H), 4.10 (t, *J* = 7.0 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.84 (m, 2H), 1.79 - 1.63 (m, 2H), 1.38 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 135.9, 134.4, 129.3, 129.1, 128.6, 127.7, 127.7, 121.4, 120.9, 119.2, 109.3, 101.0, 46.0, 43.3, 29.9, 26.2, 25.0.
HRMS (ESI-TOF): *m/z* calcd. for $C_{20}H_{22}NOS^+$ ($[M+H]^+$) 324.1422, found 324.1430.



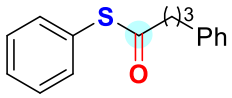
S-phenyl 4-iodobutanethioate (37). Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and 1,3-diiodopropane (46 μL, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (36 mg, 59% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 - 7.39 (m, 5H), 3.25 (t, *J* = 6.7 Hz, 2H), 2.81 (t, *J* = 7.1 Hz, 2H), 2.28 - 2.14 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 134.5, 129.5, 129.2, 127.4, 43.9, 28.8, 4.9.
HRMS (ESI-TOF): *m/z* calcd. for $C_{10}H_{12}IOS^+$ ($[M+H]^+$) 306.9653, found 306.9655.



***S*-Phenyl 6-iodohexanethioate (38).** Prepared according to general procedure on a 0.2 mmol scale using thiophenol (21 μL, 0.2 mmol) and 1,5-diiodopentane (60 μL, 0.4 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (41 mg, 59% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 5H), 3.19 (t, *J* = 7.0 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.90 - 1.80 (m, 2H), 1.79 - 1.66 (m, 2H), 1.54 - 1.43 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.2, 134.5, 129.4, 129.2, 127.7, 43.3, 33.0, 29.7, 24.4, 6.4.
HRMS (ESI-TOF): *m/z* calcd. for $C_{12}H_{16}IOS^+$ ($[M+H]^+$) 334.9966, found 334.9972.

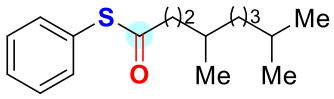


***S*-Phenyl 5-methylhexanethioate (39).** Prepared according to general procedure using thiophenol (51 μL, 0.5 mmol) and 1-bromo-4-methylpentane (146 μL, 1 mmol). The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (68.8 mg, 62% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.36 (m, 5H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.81 - 1.65 (m, 2H), 1.57 (m, 1H), 1.33 - 1.19 (m, 2H), 0.92 (s, 3H), 0.90 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 134.4, 129.2, 129.1, 127.9, 43.9, 38.1, 27.7, 23.4, 22.4.
HRMS (ESI-TOF): *m/z* calcd. for $C_{13}H_{19}OS^+$ ($[M+H]^+$) 223.1156, found 223.1152.

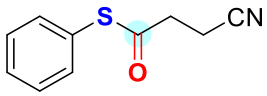


***S*-Phenyl 4-phenylbutanethioate (40).** Prepared according to general procedure using thiophenol (51 μL, 0.5 mmol) and (3-bromopropyl)benzene (152 μL, 1 mmol). The crude product w

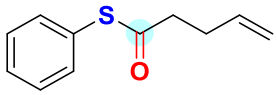
as purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a co lorless oil (87.1 mg, 68% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 5H), 7.36 - 7.25 (m, 2H), 7.26 - 7.15 (m, 3H), 2.69 (m, 4H), 2.13 - 1.97 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 141.1, 134.5, 129.3, 129.2, 128.5, 128.4, 127.8, 126.1, 4 2.9, 34.9, 27.0.
HRMS (ESI-TOF): *m/z* calcd. for $C_{16}H_{16}OS^+$ ([M+Na]$^+$) 279.0819, found 279.0819.



***S*-Phenyl 4,8-dimethylnonanethioate (41).** Prepared according to general procedure using thi ophenol (51 μL, 0.5 mmol) and 1-bromo-3,7-dimethyloctane (207 μL, 1 mmol). The crude pro duct was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (65 mg, 50% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 - 7.36 (m, 5H), 2.67 (m, 2H), 1.85 - 1.67 (m, 1H), 1.63 - 1.45 (m, 3H), 1.38 - 1.23 (m, 3H), 1.22 - 1.08 (m, 3H), 0.90 (m, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7, 134.4, 129.2, 129.1, 127.9, 41.5, 39.2, 36.8, 32.5, 32.3, 27.9, 24.6, 22.7, 22.6, 19.3.
HRMS (ESI-TOF): *m/z* calcd. for $C_{17}H_{27}OS^+$ ([M+H]$^+$) 279.1783, found 279.1780.

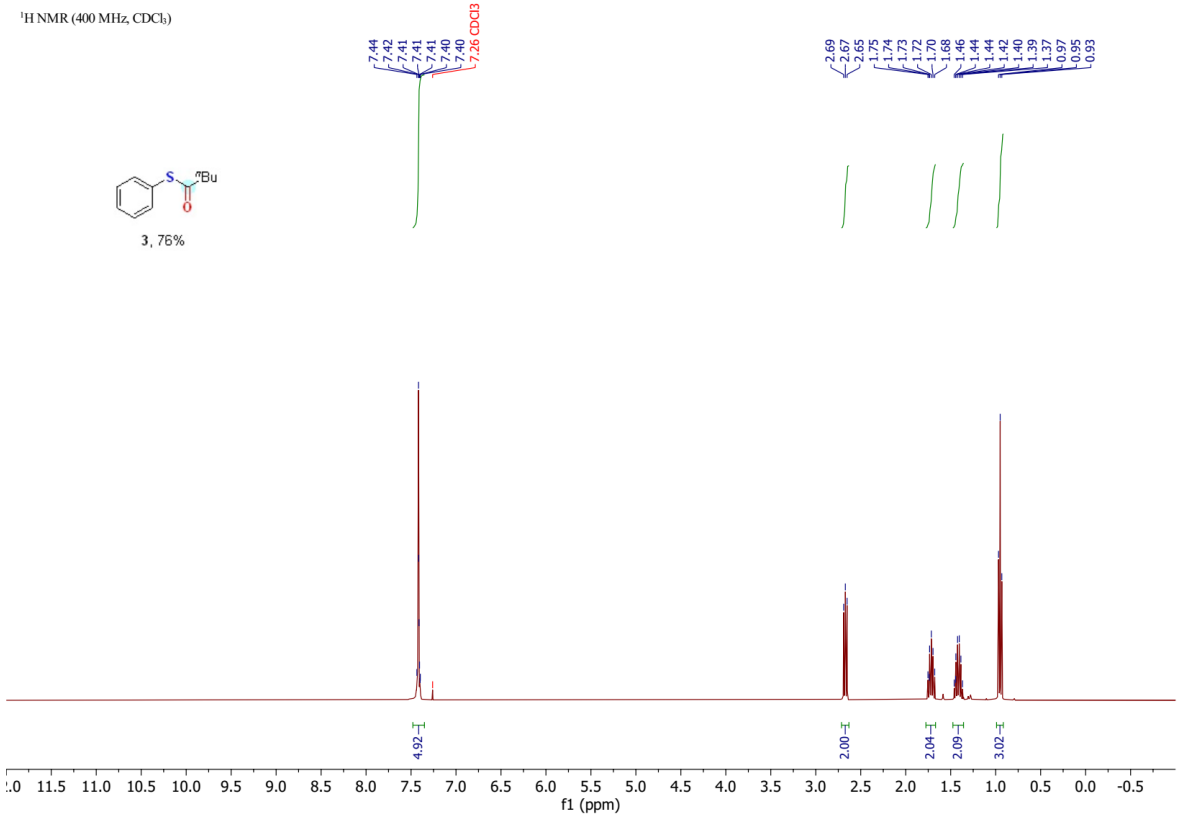


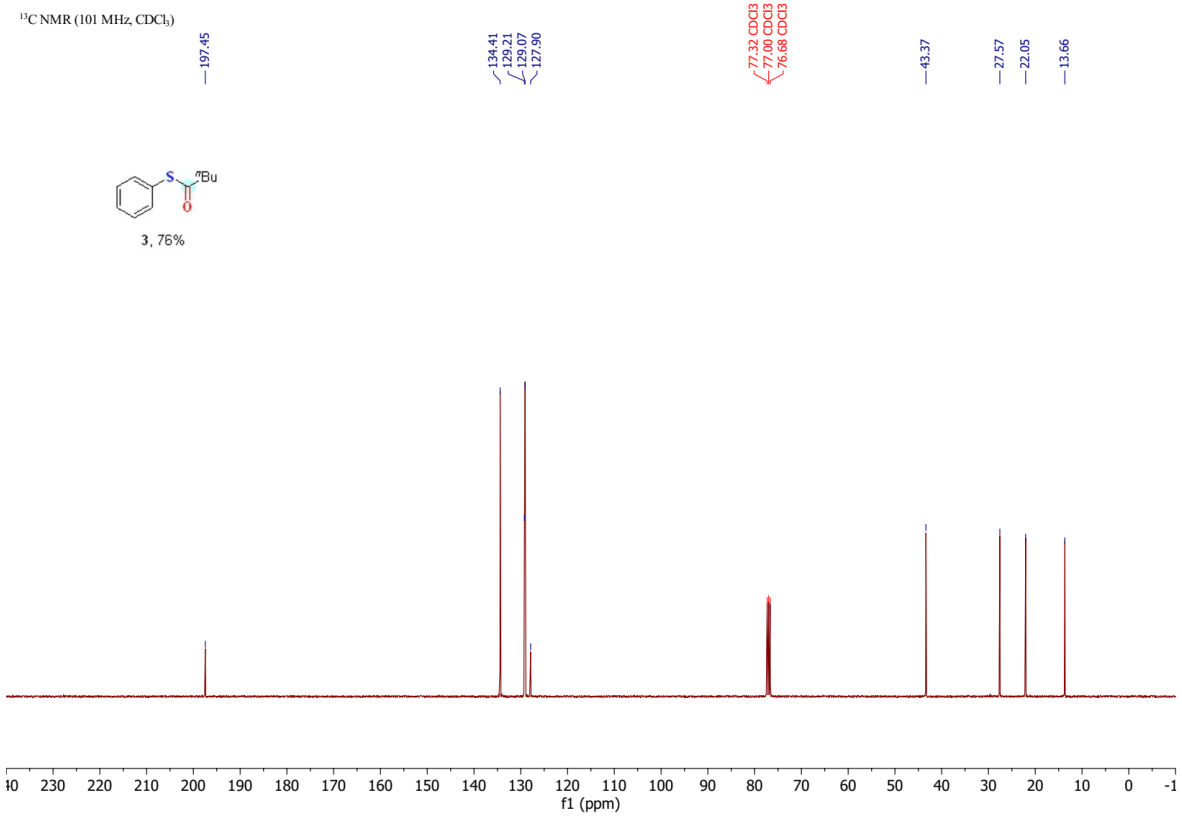
***S*-Phenyl 3-cyanopropanethioate (42).** Prepared according to general procedure using thioph enol (51 μL, 0.5 mmol) and 3-bromopropanenitrile (83 μL, 1 mmol). The crude product was p urified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorle ss oil (40 mg, 44% yield).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 - 7.37 (m, 5H), 3.00 (t, 2H), 2.68 (t, *J* = 7.3 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 134.5, 129.9, 129.4, 126.3, 118.0, 38.2, 12.7.
HRMS (ESI-TOF): *m/z* calcd. for $C_{10}H_{10}NOS^+$ ([M+H]$^+$) 192.0483, found 192.0482.

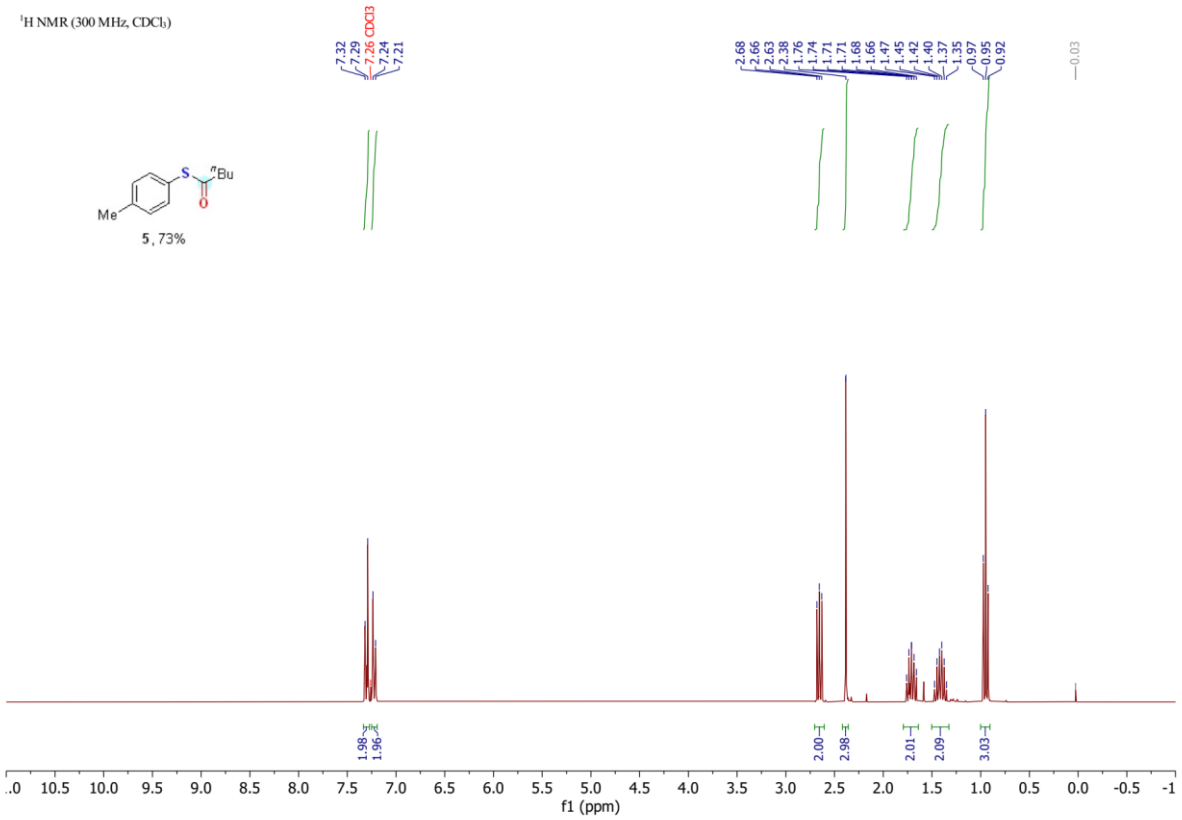


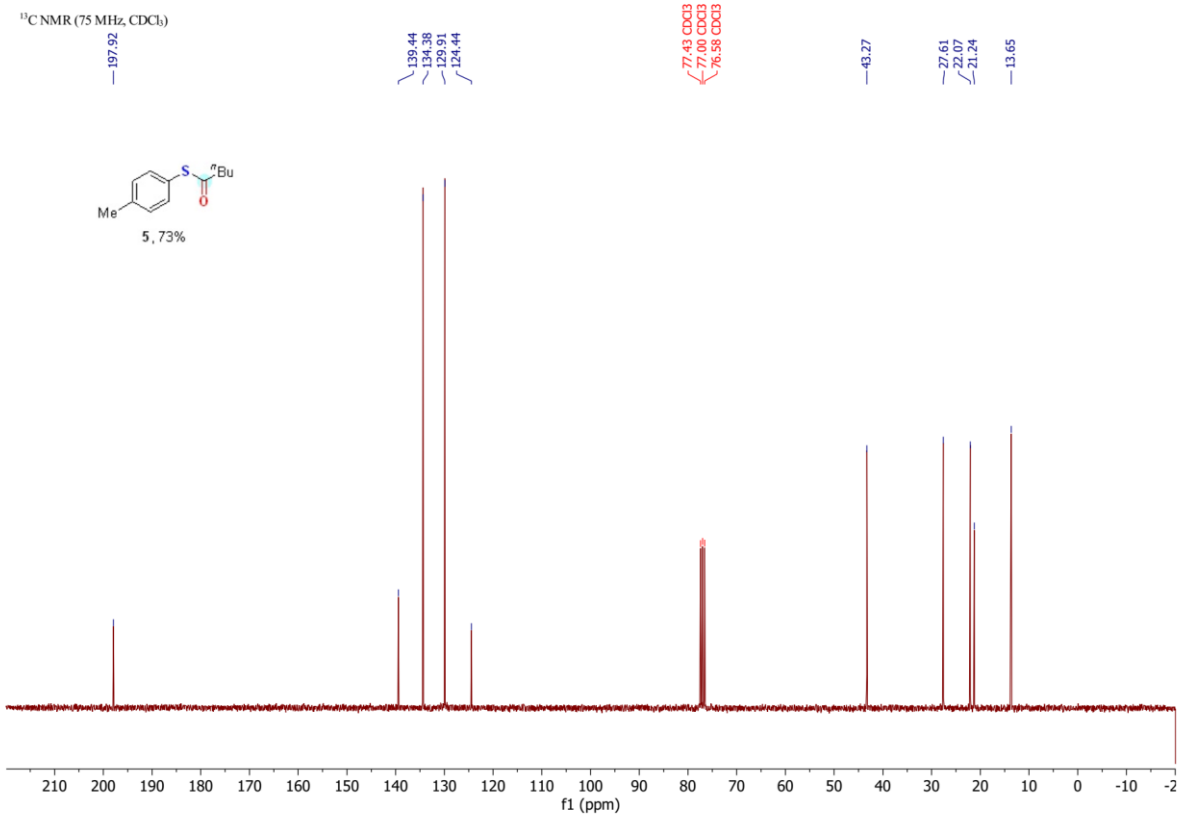
***S*-Phenyl pent-4-enethioate (43).** Prepared according to general procedure using thiophenol (51 μL, 0.5 mmol) and 4-bromobut-1-ene (102 μL, 1 mmol). The crude product was purified b y silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (5 3.8 mg, 56% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.38 (m, 5H), 5.92 - 5.77 (m, 1H), 5.16 - 5.01 (m, 2H), 2.77 (t, 2H), 2.52 - 2.42 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 136.0, 134.4, 129.3, 129.1, 127.7, 116.0, 42.7, 29.3.
HRMS (ESI-TOF): *m/z* calcd. for $C_{11}H_{13}OS^+$ ([M+H]$^+$) 193.0687, found 193.0685.

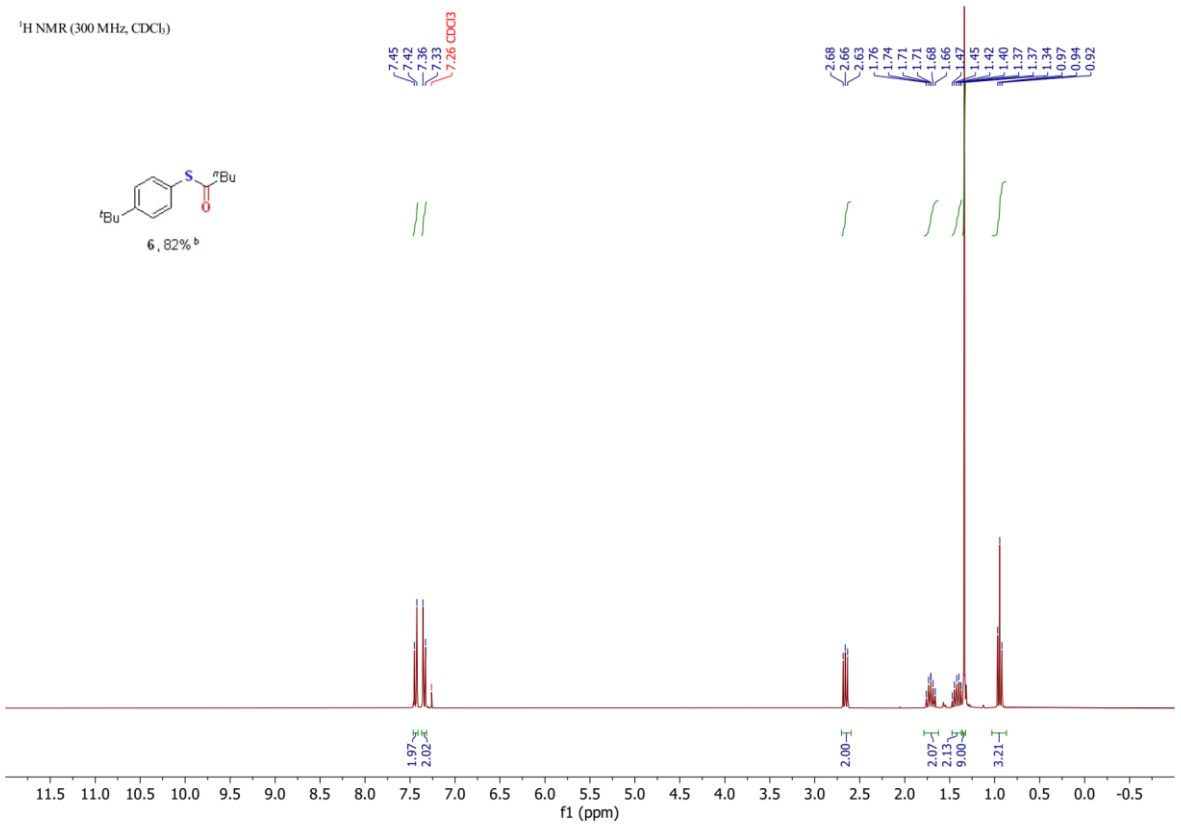
8. Spectral Date of the Products

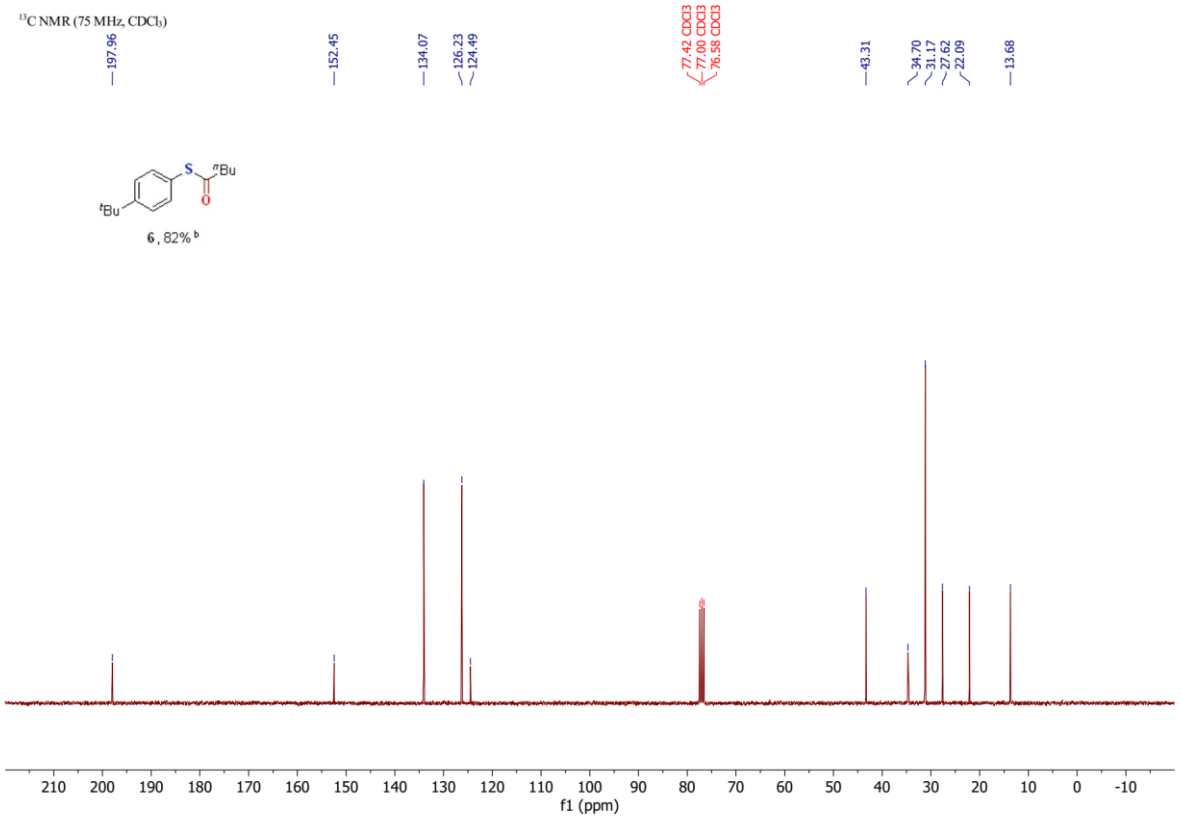


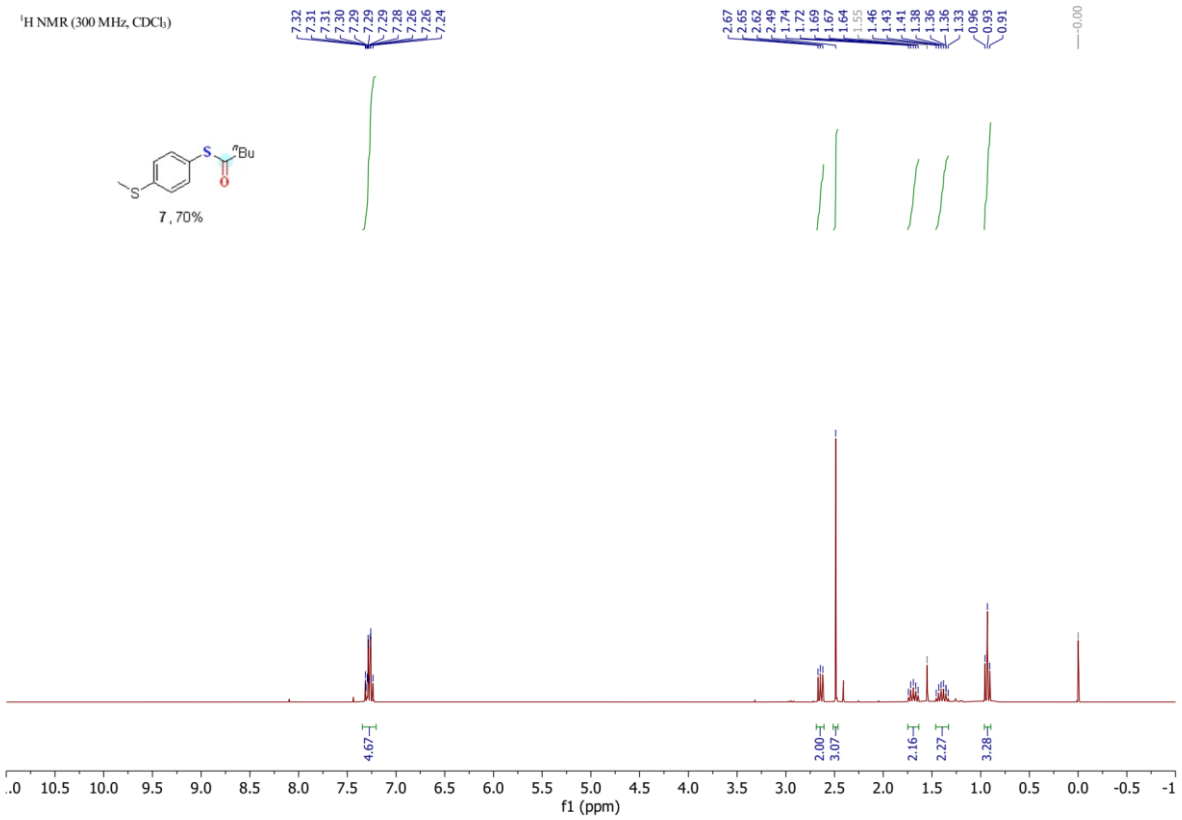


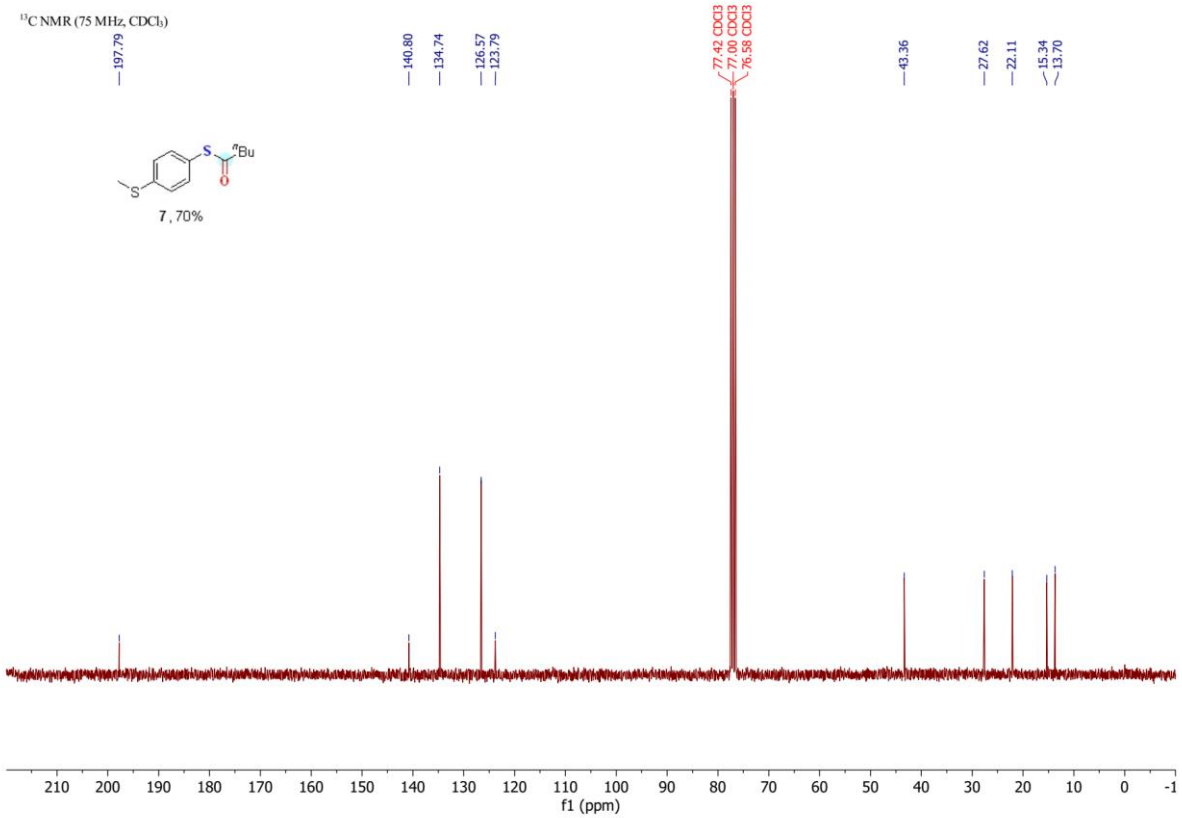

^{1}H NMR (300 MHz, CDCl$_3$)
7.32
7.29
7.26 CDCl3
7.24
7.21
2.68
2.66
2.63
2.38
1.76
1.74
1.71
1.71
1.68
1.66
1.47
1.45
1.42
1.40
1.37
1.35
0.97
0.95
0.92
0.03
Me
S
O
nBu
5, 73%
1.98
1.96
2.00
2.98
2.01
2.09
3.03
f1 (ppm)

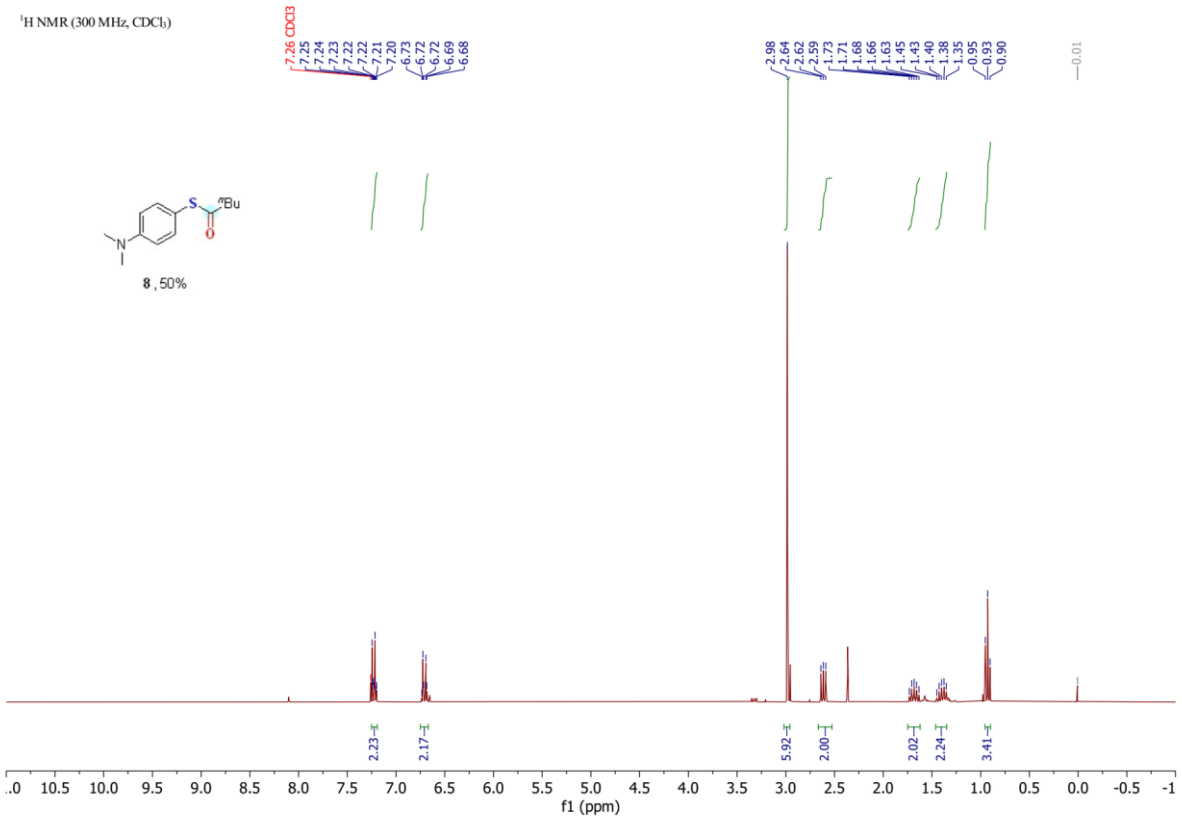

^{13}C NMR (75 MHz, CDCl$_3$)
197.92
139.44
134.38
129.91
124.44
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
43.27
27.61
22.07
21.24
13.65
Me
S
O
nBu
5, 73%
f1 (ppm)

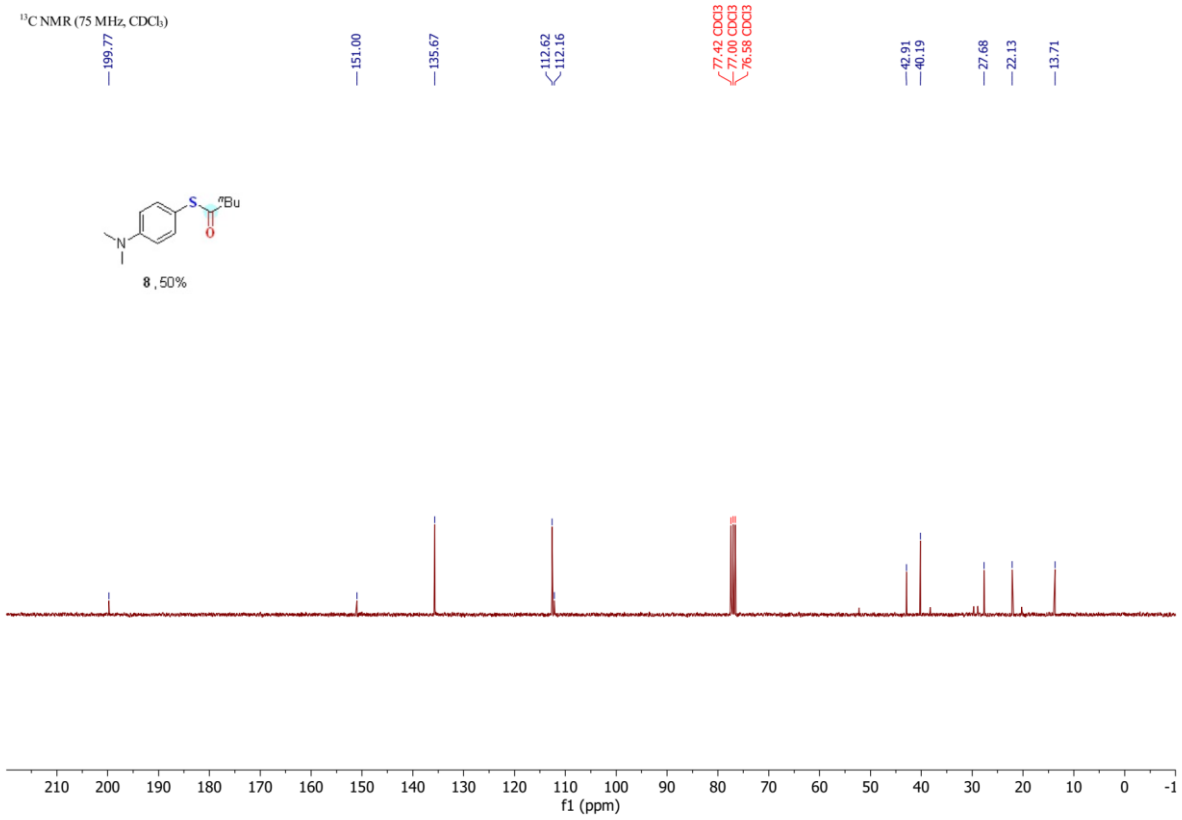

^{1}H NMR (300 MHz, CDCl$_3$)
7.45
7.42
7.36
7.33
7.26 CDCl3
2.68
2.66
2.63
1.76
1.74
1.71
1.71
1.68
1.66
1.47
1.45
1.42
1.40
1.37
1.37
1.34
0.97
0.94
0.92
S
nBu
tBu
O
6, 82% b
1.97
2.02
2.00
2.07
2.13
9.00
3.21
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

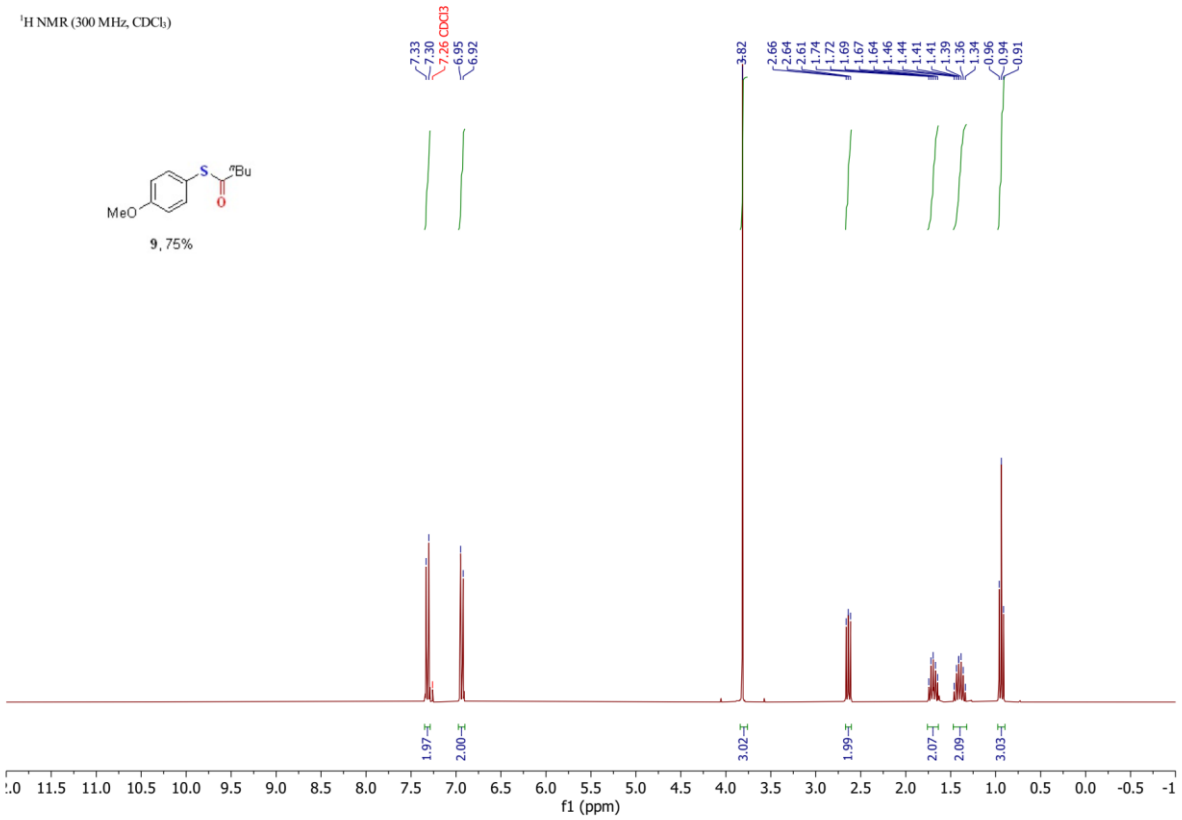

^{13}C NMR (75 MHz, CDCl$_3$)
197.96
152.45
134.07
126.23
124.49
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.31
34.70
31.17
27.62
22.09
13.68
S
nBu
tBu
O
6, 82% b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

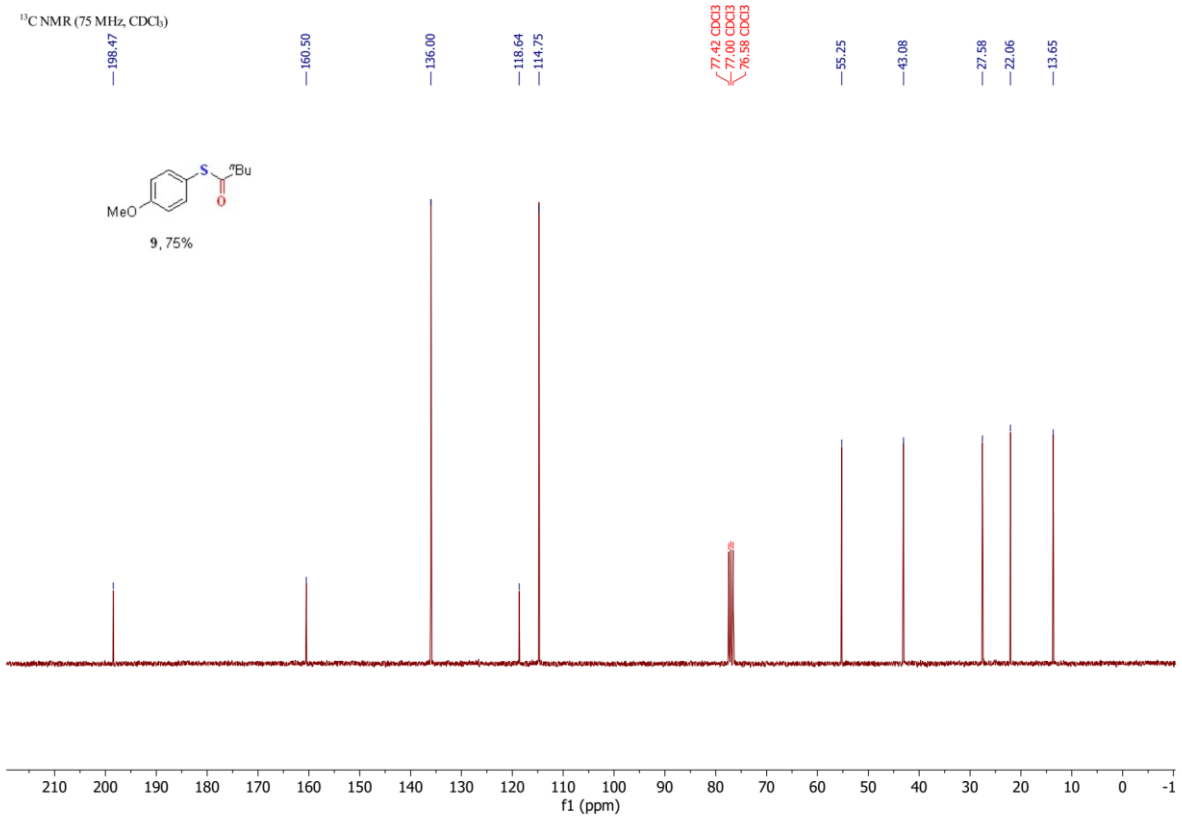

^{1}H NMR (300 MHz, CDCl$_3$)
7.32
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.26
7.26
7.24
2.67
2.65
2.62
2.49
1.74
1.72
1.69
1.67
1.64
1.55
1.46
1.43
1.41
1.38
1.36
1.36
1.33
0.96
0.93
0.91
0.00
7, 70%
4.67
2.00
3.07
2.16
2.27
3.28
f1 (ppm)

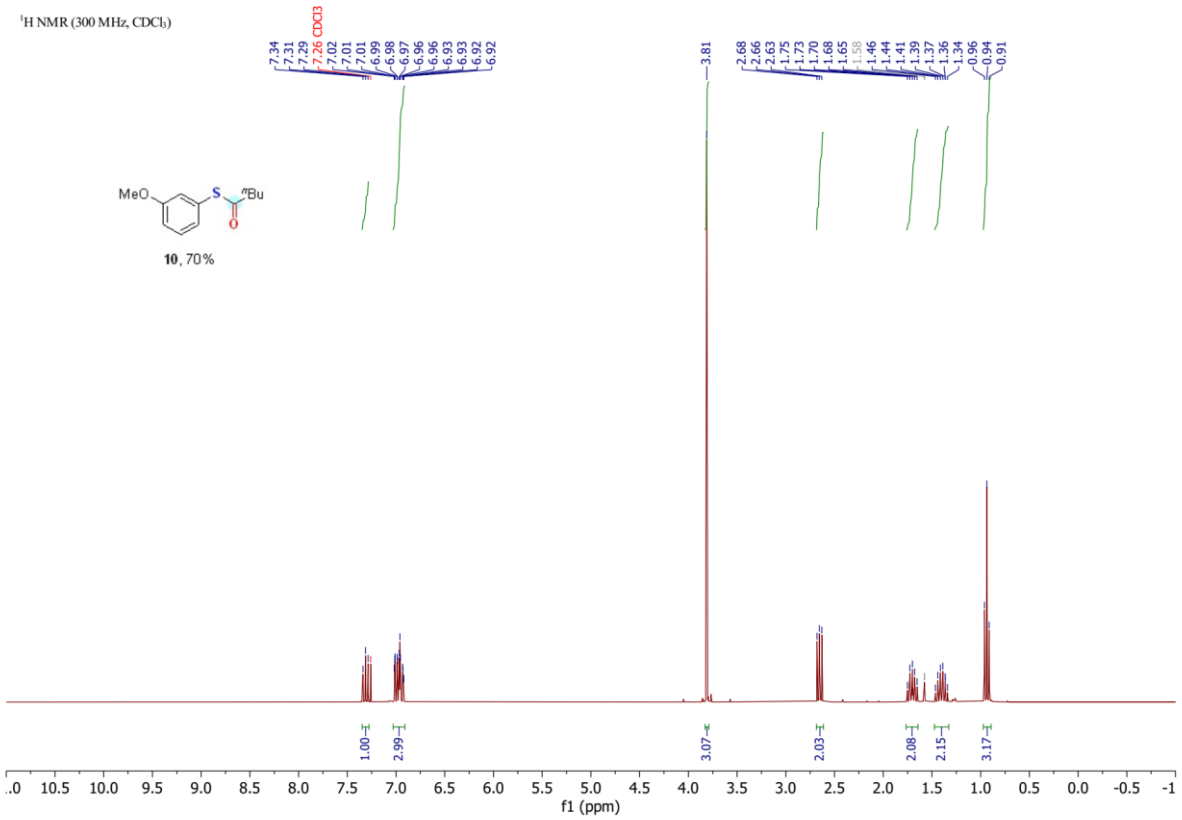

^{13}C NMR (75 MHz, CDCl$_3$)
197.79
140.80
134.74
126.57
123.79
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.36
27.62
22.11
15.34
13.70
7, 70%
f1 (ppm)

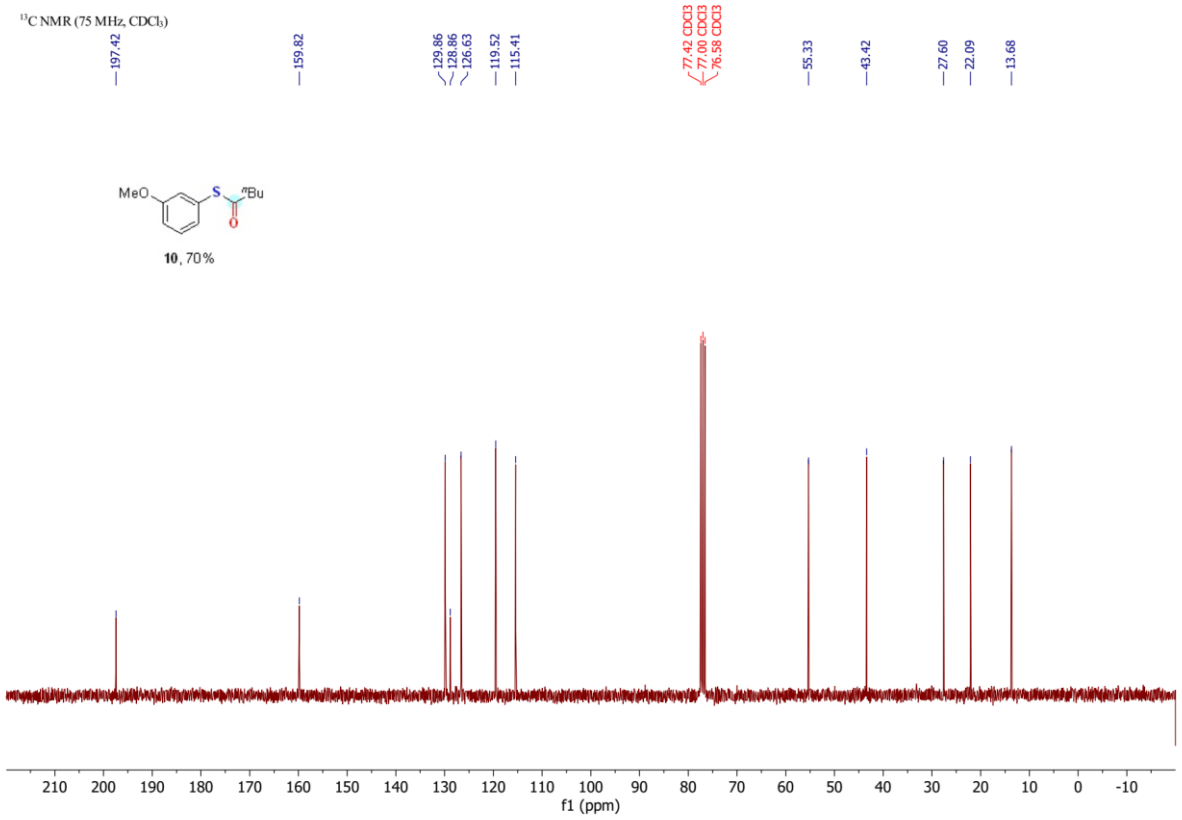

^{1}H NMR (300 MHz, CDCl$_3$)
7.26 CDCl3
7.25
7.24
7.23
7.22
7.22
7.21
7.20
6.73
6.72
6.72
6.69
6.68
2.98
2.64
2.62
2.59
1.73
1.71
1.68
1.66
1.63
1.45
1.43
1.40
1.38
1.35
0.95
0.93
0.90
0.01
nBu
8 , 50%
2.23
2.17
5.92
2.00
2.02
2.24
3.41
f1 (ppm)

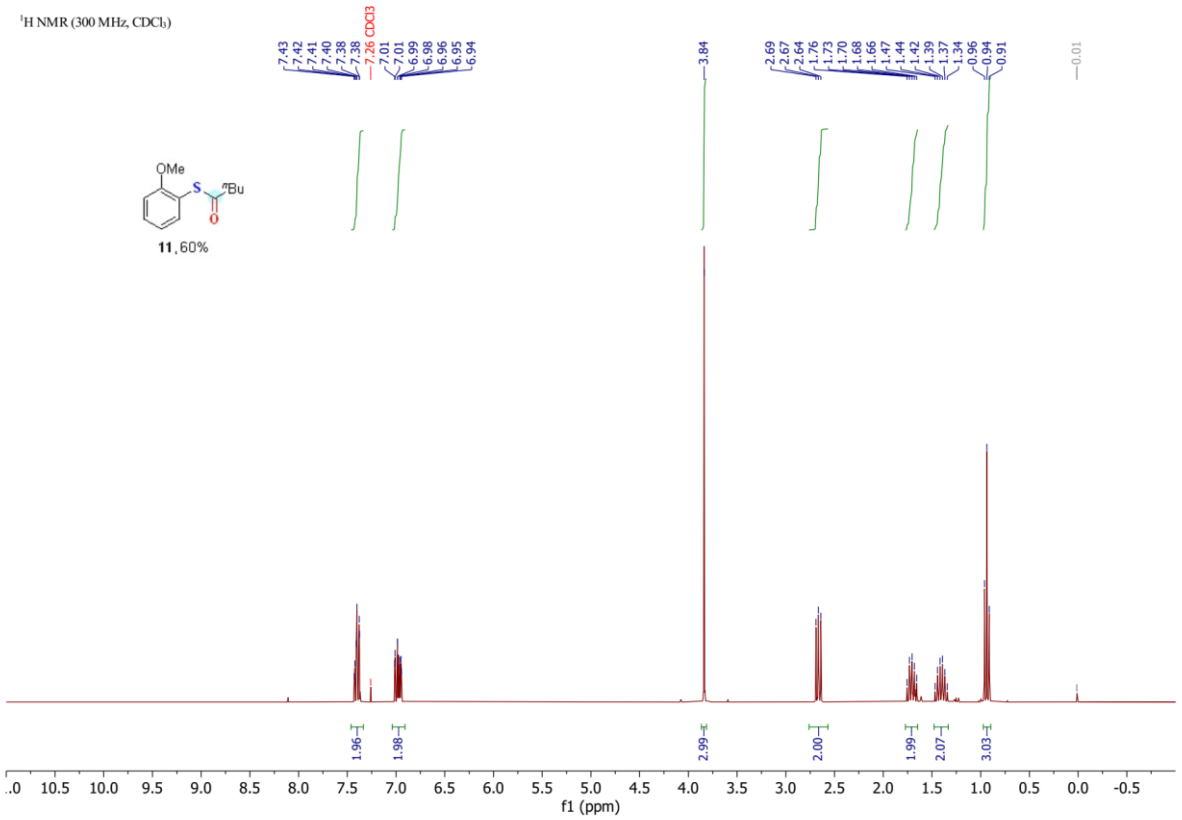

^{13}C NMR (75 MHz, CDCl$_3$)
199.77
151.00
135.67
112.62
112.16
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
42.91
40.19
27.68
22.13
13.71
nBu
8 , 50%
f1 (ppm)

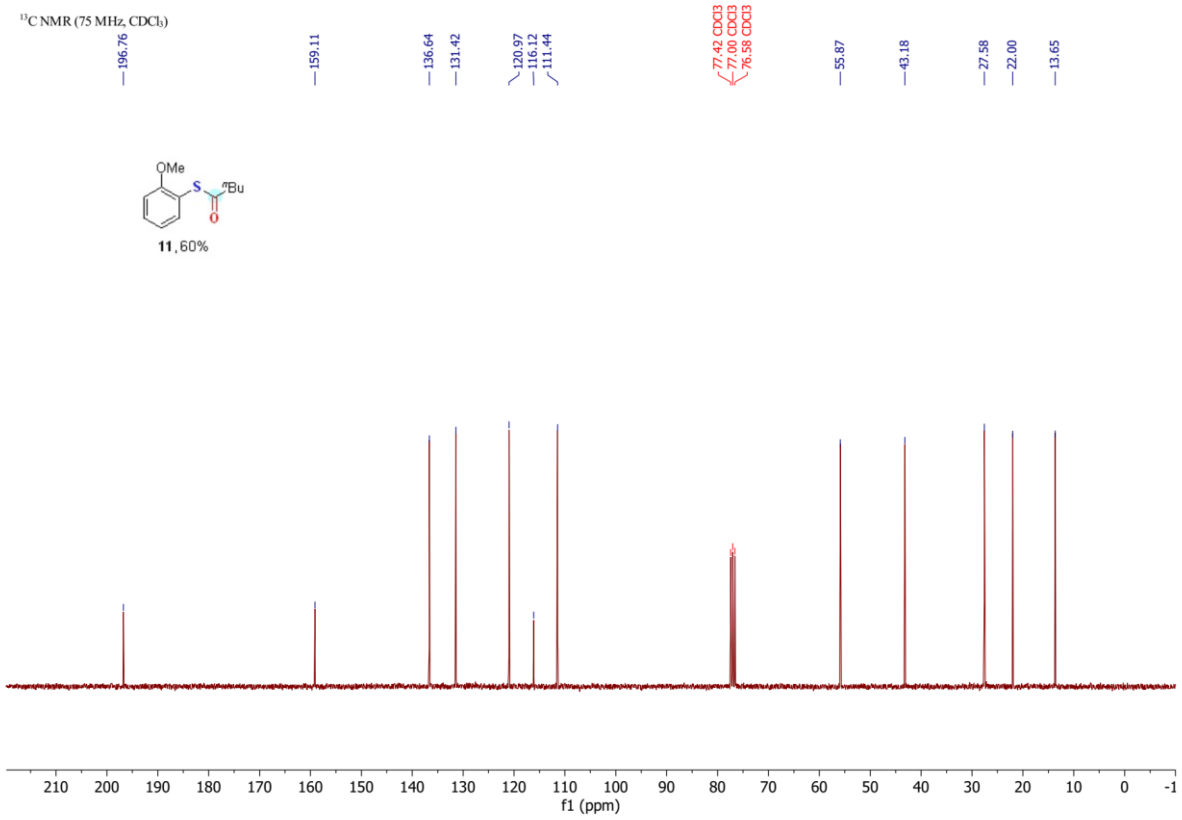

¹H NMR (300 MHz, CDCl₃)
7.33
7.30
7.26 CDCl3
6.95
6.92
3.82
2.66
2.64
2.61
1.74
1.72
1.69
1.67
1.64
1.46
1.44
1.41
1.41
1.39
1.36
1.34
0.96
0.94
0.91
MeO
S
nBu
O
9, 75%
1.97
2.00
3.02
1.99
2.07
2.09
3.03
f1 (ppm)


¹³C NMR (75 MHz, CDCl₃)
198.47
160.50
136.00
118.64
114.75
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.25
43.08
27.58
22.06
13.65
MeO
S
nBu
O
9, 75%
f1 (ppm)

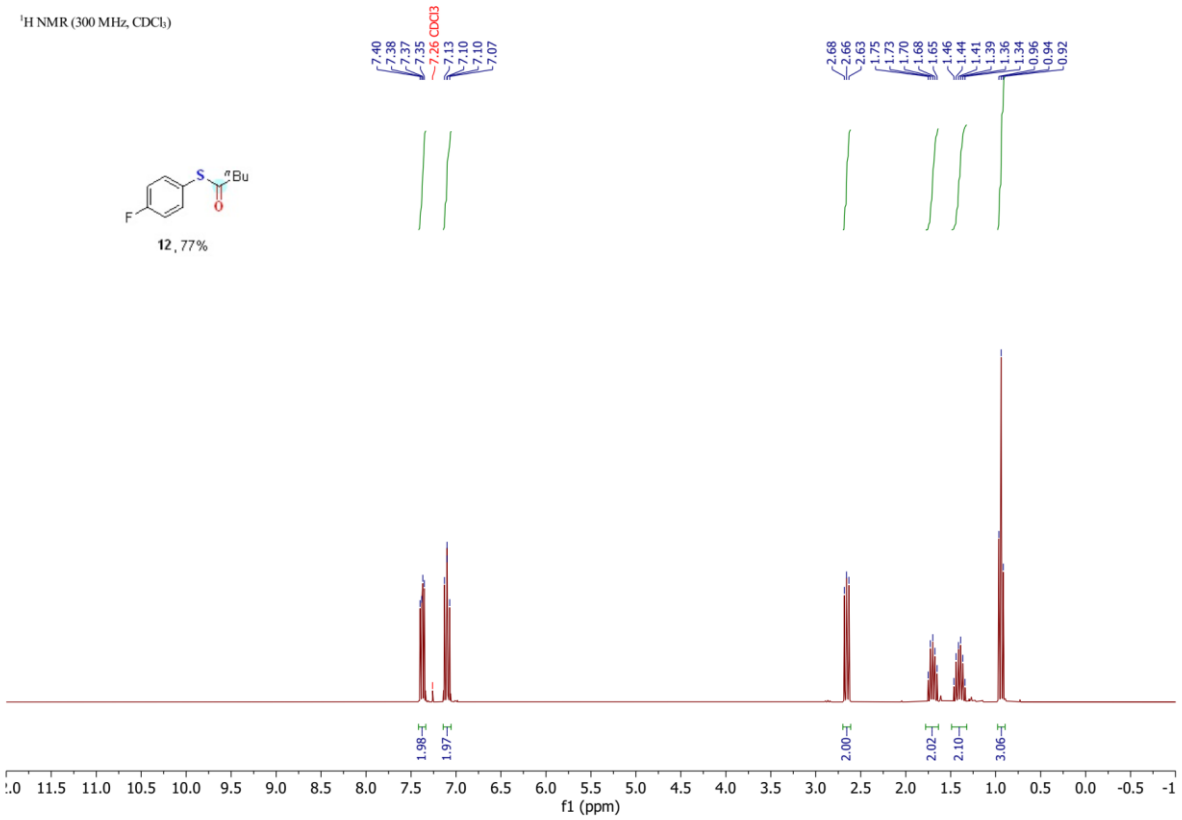

^{1}H NMR (300 MHz, CDCl$_3$)
7.34
7.31
7.29
7.26 CDCl3
7.02
7.01
7.01
6.99
6.98
6.97
6.96
6.96
6.93
6.93
6.92
6.92
3.81
2.68
2.66
2.63
1.75
1.73
1.70
1.68
1.65
1.58
1.46
1.44
1.41
1.39
1.37
1.36
1.34
0.96
0.94
0.91
MeO
S
nBu
O
10, 70%
1.00
2.99
3.07
2.03
2.08
2.15
3.17
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
197.42
159.82
129.86
128.86
126.63
119.52
115.41
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.33
43.42
27.60
22.09
13.68
MeO
S
nBu
O
10, 70%
f1 (ppm)


^{1}H NMR (300 MHz, CDCl$_3$)
7.43
7.42
7.41
7.40
7.38
7.38
7.26 CDCl3
7.01
7.01
6.99
6.98
6.96
6.95
6.94
3.84
2.69
2.67
2.64
1.76
1.73
1.70
1.68
1.66
1.47
1.44
1.42
1.39
1.37
1.34
0.96
0.94
0.91
0.01
OMe
S
nBu
O
11, 60%
1.96
1.98
2.99
2.00
1.99
2.07
3.03
f1 (ppm)

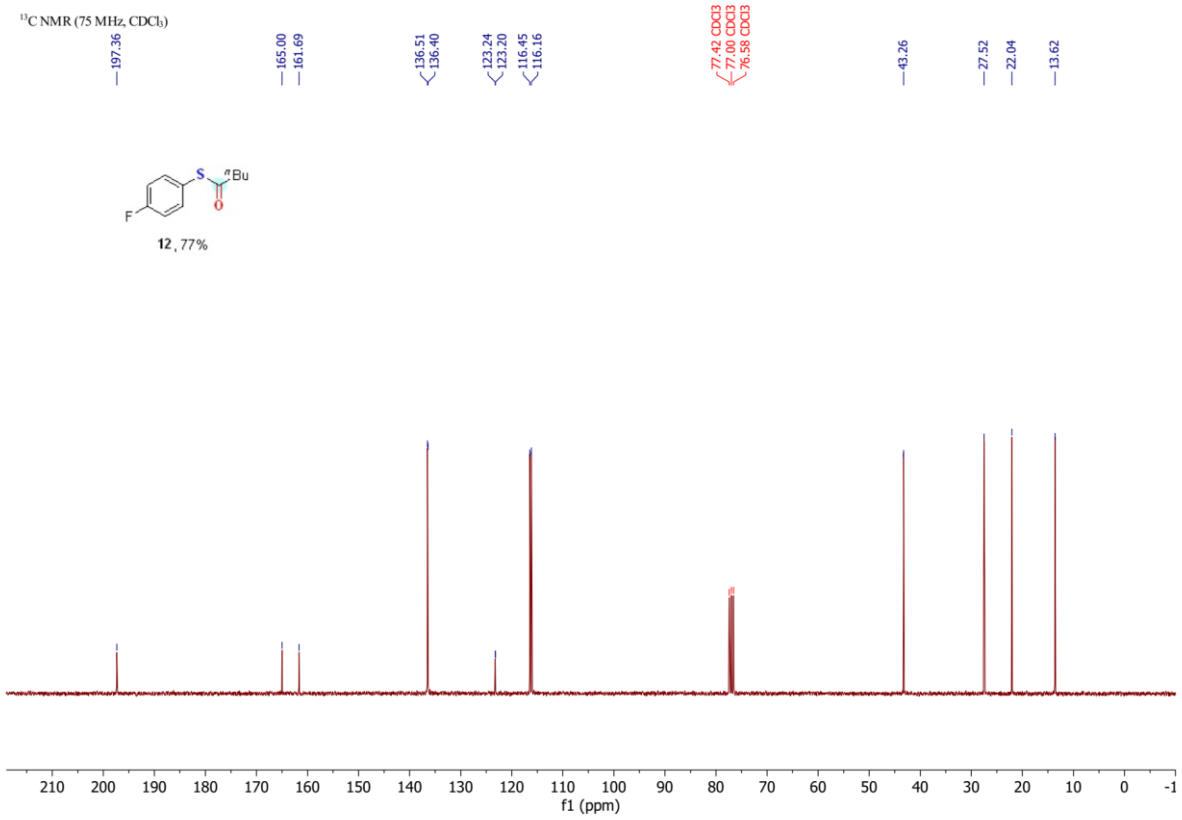

^{13}C NMR (75 MHz, CDCl$_3$)
196.76
159.11
136.64
131.42
120.97
116.12
111.44
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.87
43.18
27.58
22.00
13.65
OMe
S
nBu
O
11, 60%
f1 (ppm)

^{1}H NMR (300 MHz, $CDCl_3$)



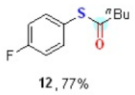
12, 77%

^{13}C NMR (75 MHz, $CDCl_3$)



12, 77%

^{19}F NMR (282 MHz, $CDCl_3$)

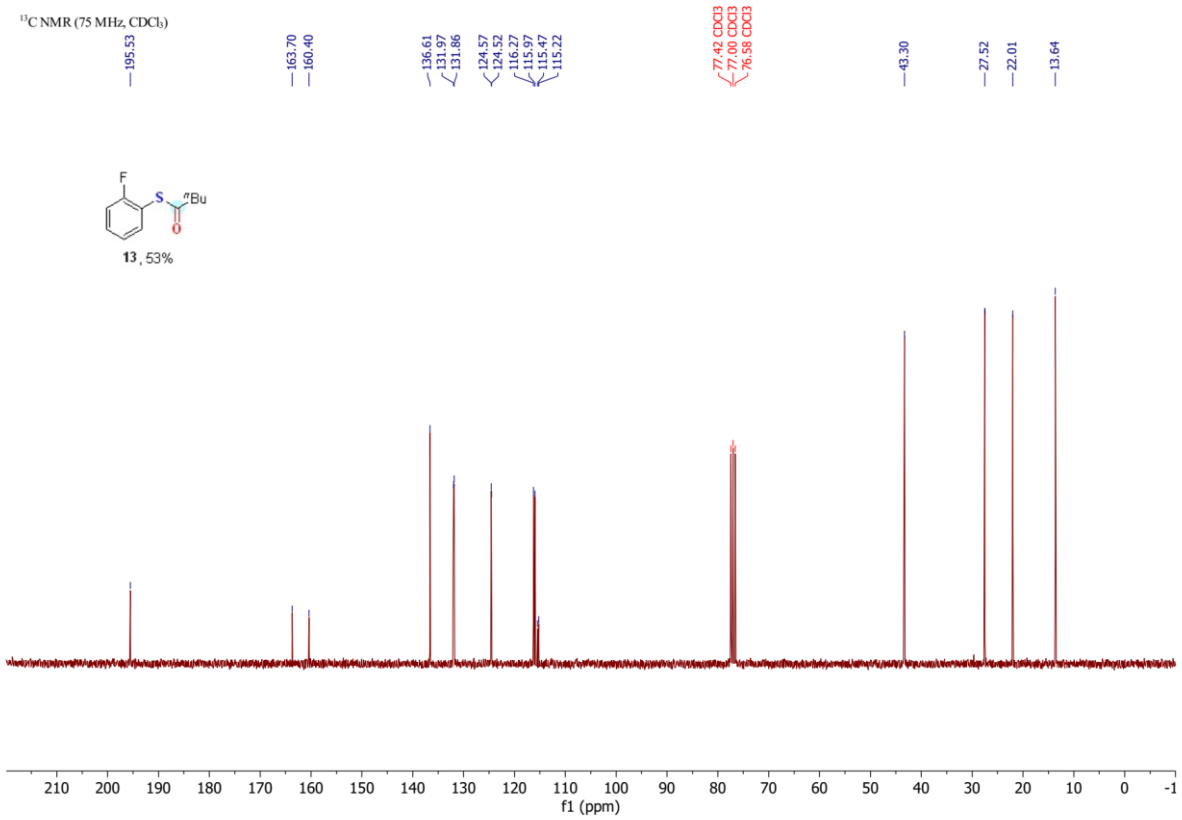


12, 77%

^{1}H NMR (300 MHz, $CDCl_3$)

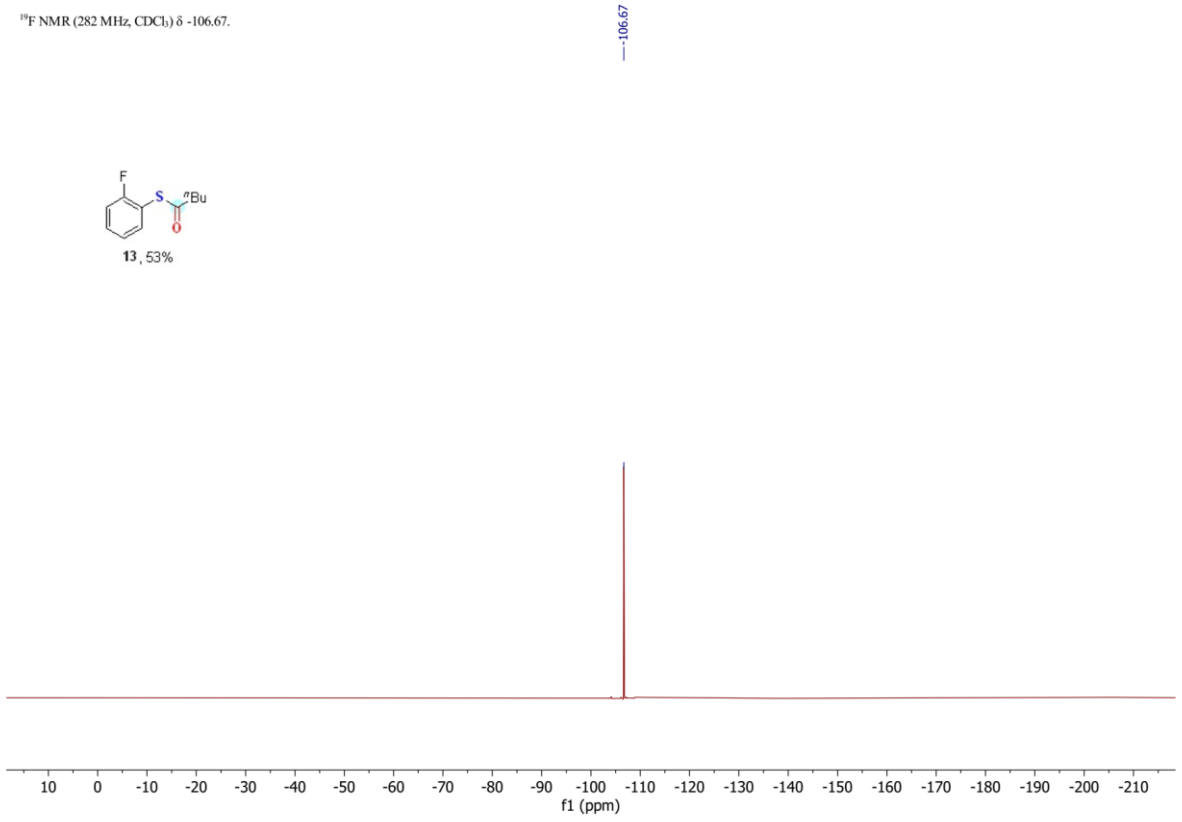
13, 53%

^{13}C NMR (75 MHz, $CDCl_3$)



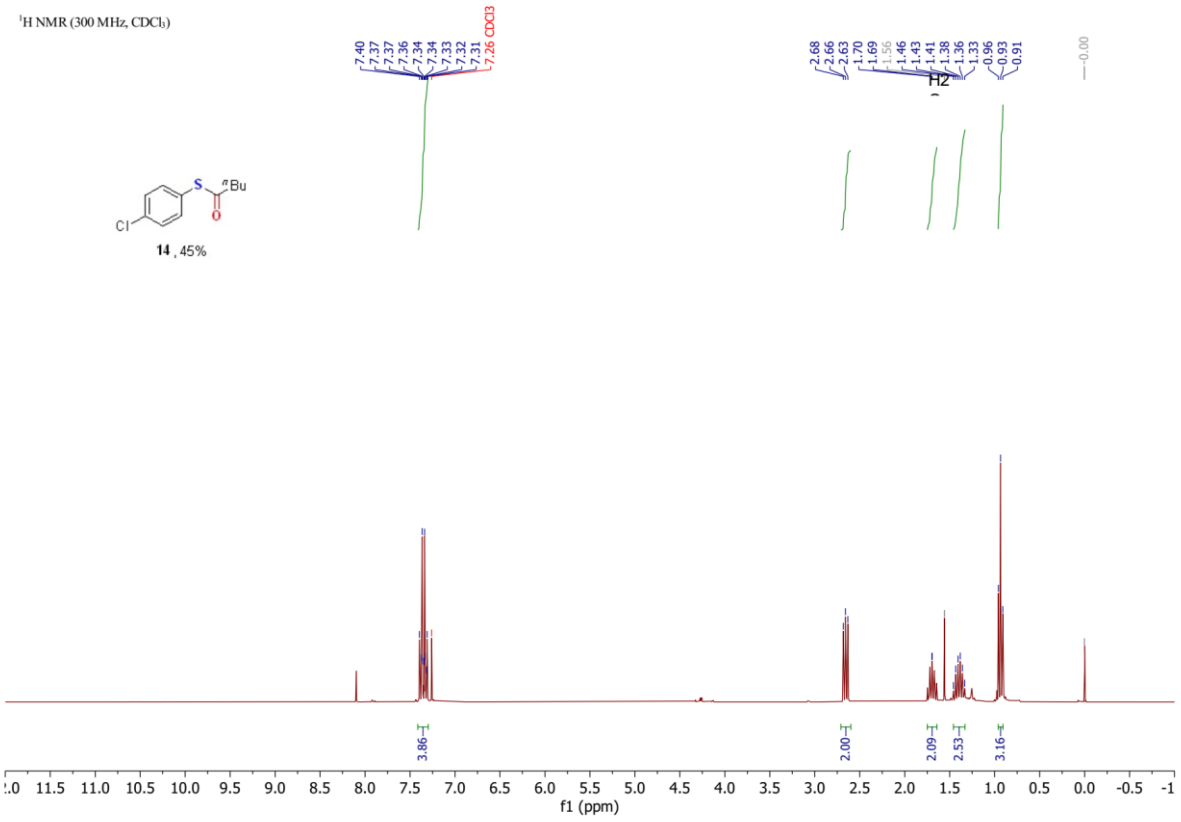
13, 53%

^{19}F NMR (282 MHz, $CDCl_3$) δ -106.67.



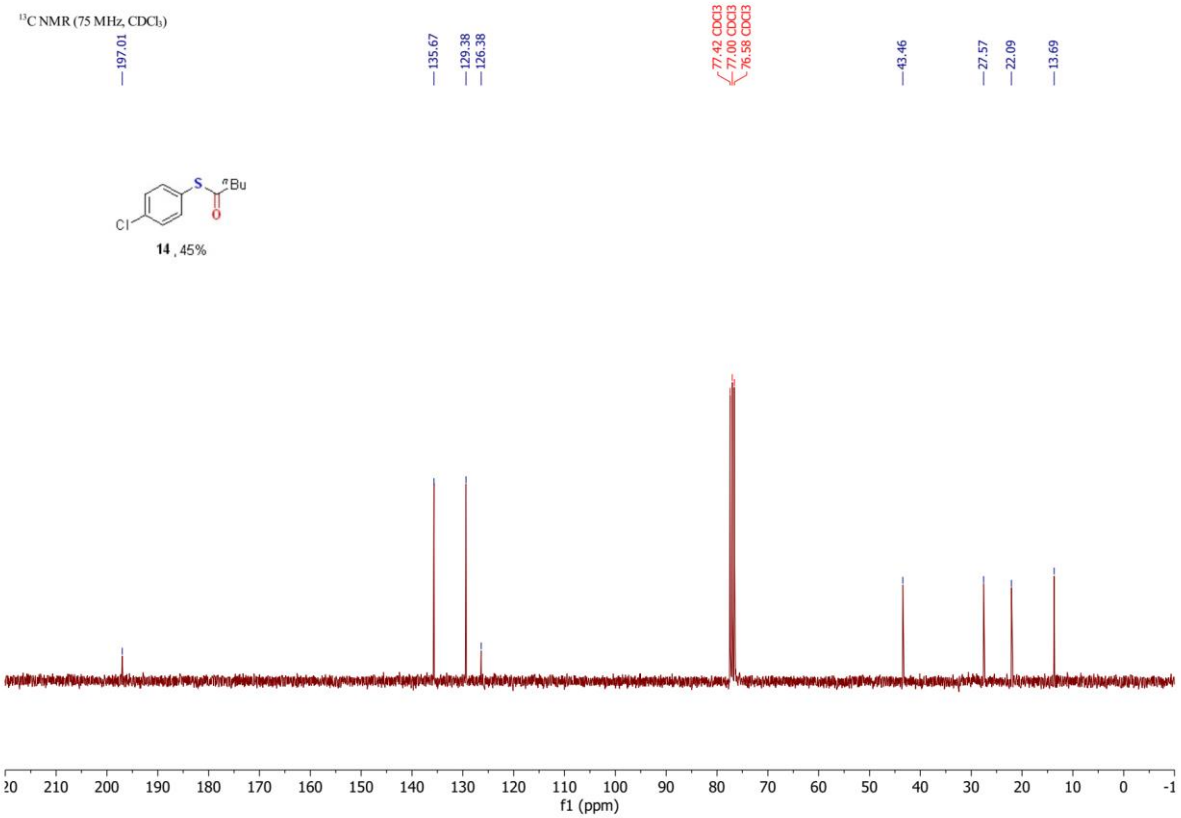
13, 53%

^{1}H NMR (300 MHz, $CDCl_3$)



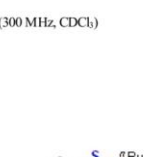
14 , 45%

^{13}C NMR (75 MHz, $CDCl_3$)



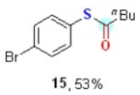
14 , 45%

^{1}H NMR (300 MHz, $CDCl_3$)

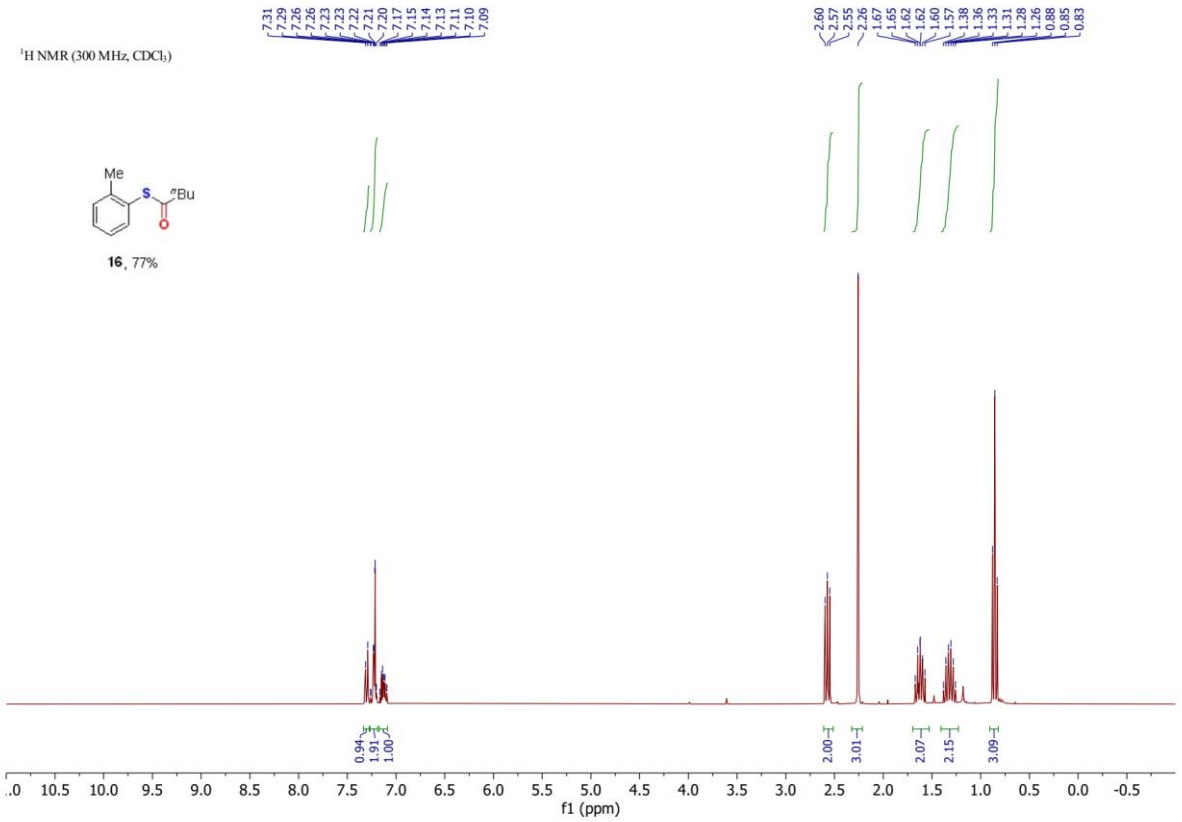


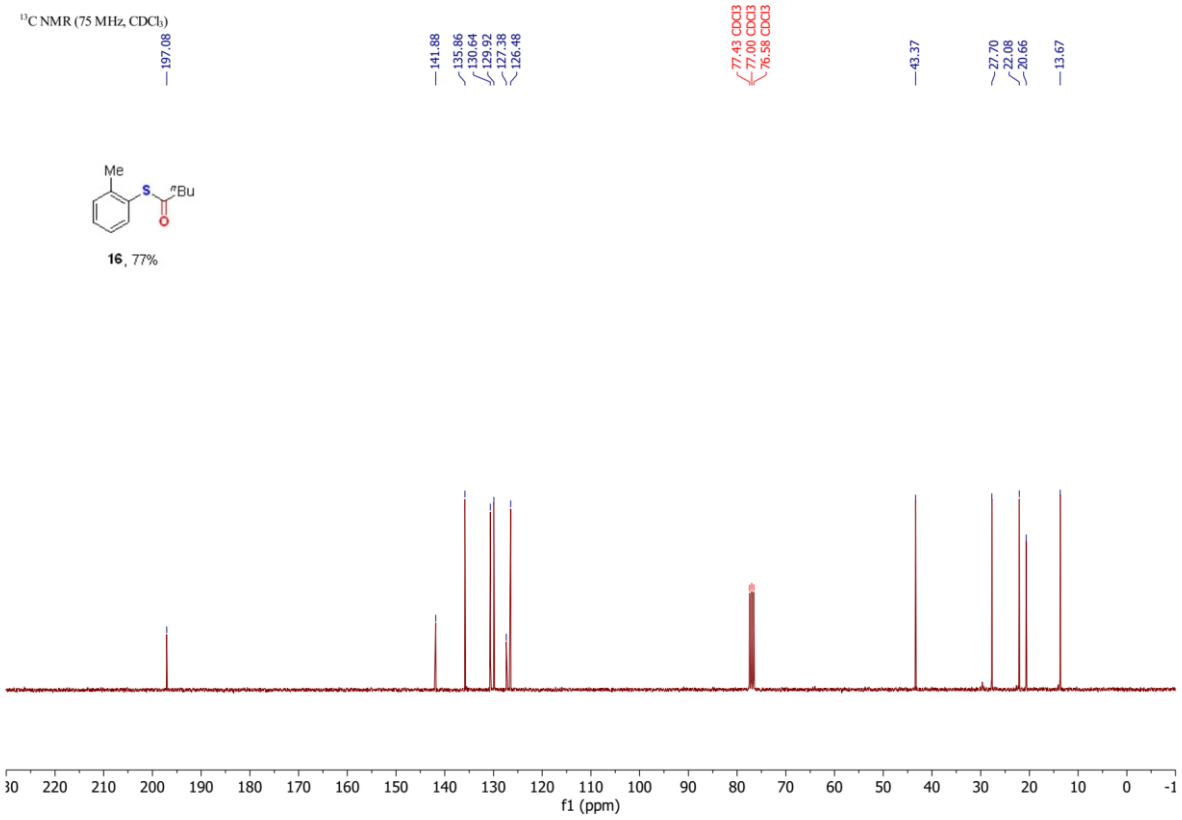
15, 53%

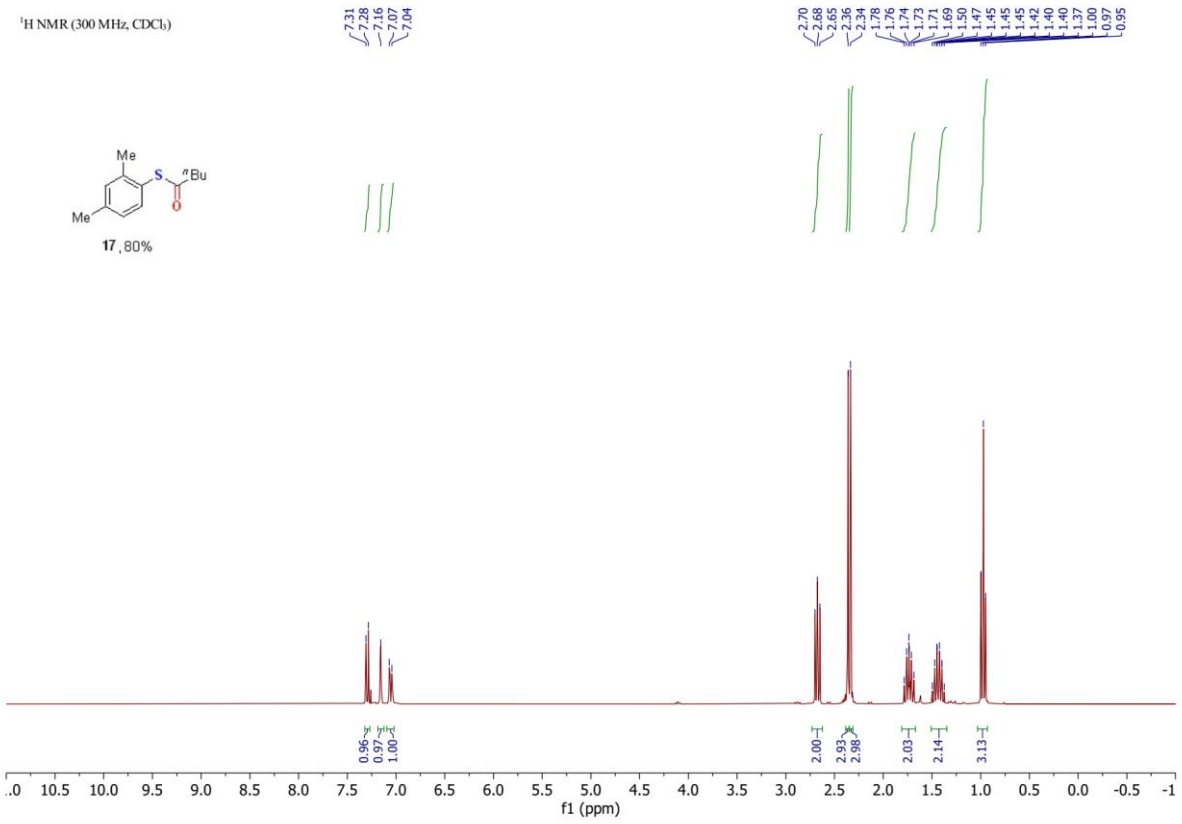
^{13}C NMR (75 MHz, $CDCl_3$)

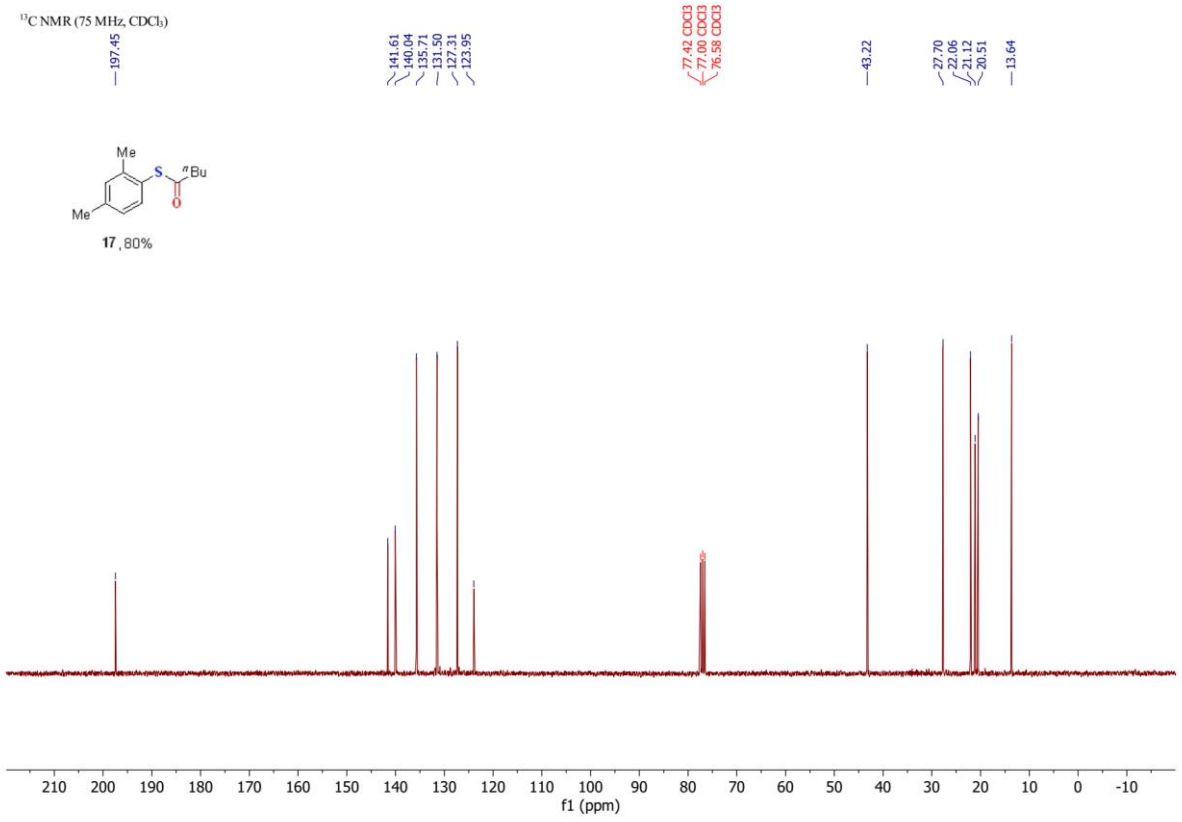


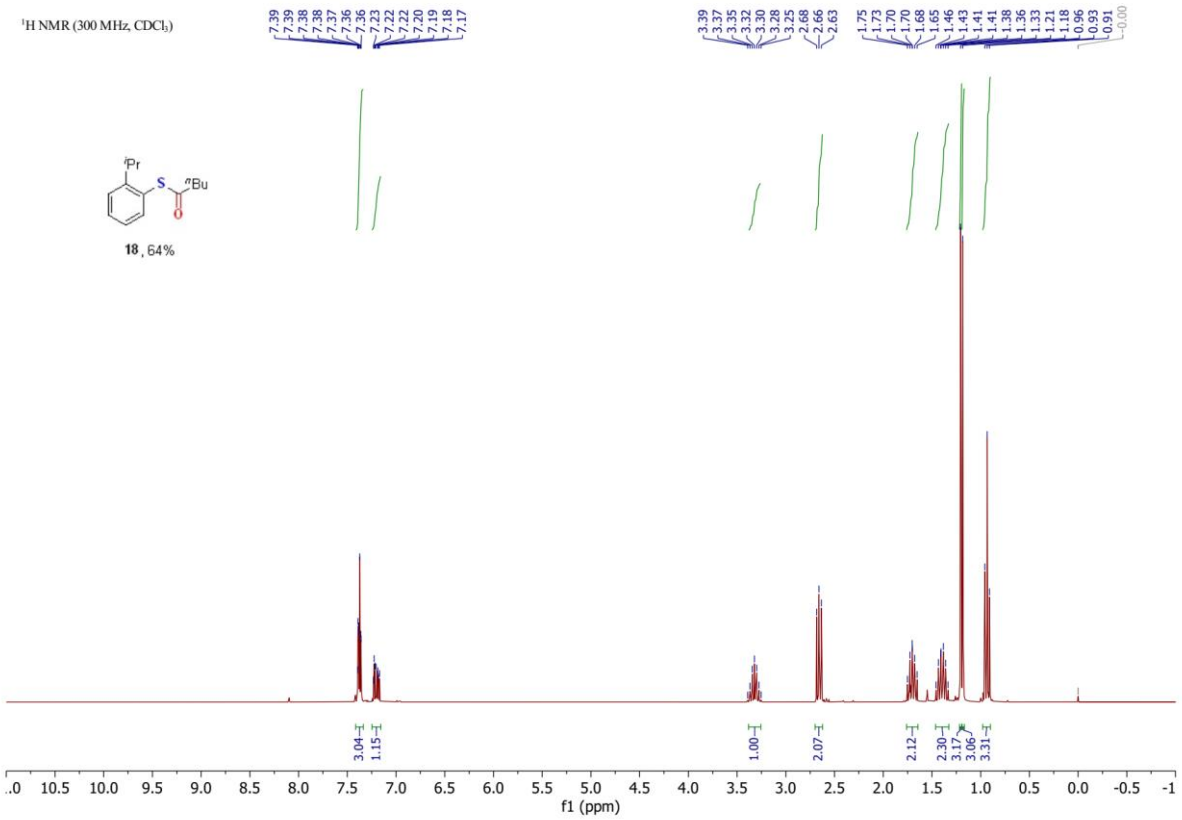
15, 53%

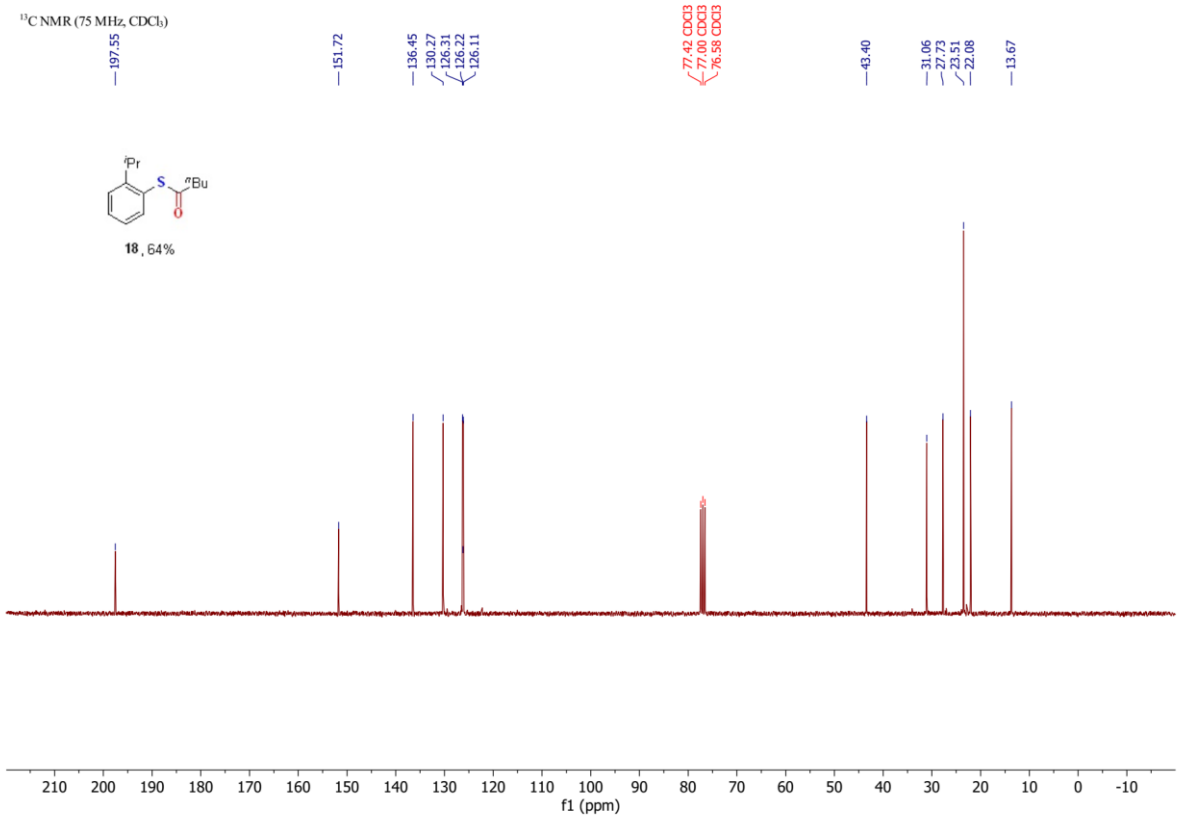

^{1}H NMR (300 MHz, CDCl$_3$)
7.31
7.29
7.26
7.26
7.23
7.23
7.22
7.21
7.20
7.17
7.15
7.14
7.13
7.11
7.10
7.09
2.60
2.57
2.55
2.26
1.67
1.65
1.62
1.62
1.60
1.57
1.38
1.36
1.33
1.31
1.28
1.26
0.88
0.85
0.83
Me
S
nBu
O
16, 77%
0.94
1.91
1.00
2.00
3.01
2.07
2.15
3.09
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
197.08
141.88
135.86
130.64
129.92
127.38
126.48
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
43.37
27.70
22.08
20.66
13.67
Me
S
nBu
O
16, 77%
f1 (ppm)

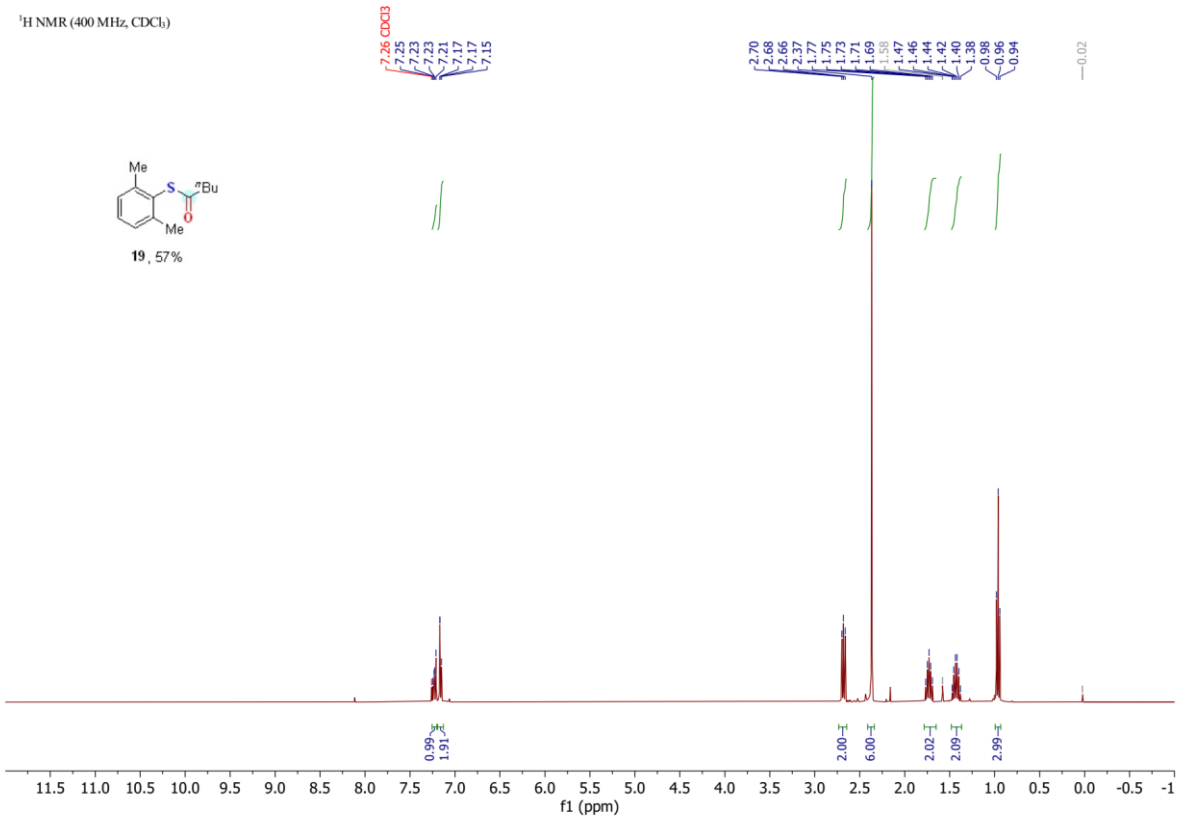

1H NMR (300 MHz, CDCl3)
7.31
7.28
7.16
7.07
7.04
2.70
2.68
2.65
2.36
2.34
1.78
1.76
1.74
1.73
1.71
1.69
1.50
1.47
1.45
1.45
1.45
1.42
1.40
1.40
1.37
1.00
0.97
0.95
Me
S
nBu
O
Me
17, 80%
0.96
0.97
1.00
2.00
2.93
2.98
2.03
2.14
3.13
f1 (ppm)


13C NMR (75 MHz, CDCl3)
197.45
141.61
140.04
135.71
131.50
127.31
123.95
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.22
27.70
22.06
21.12
20.51
13.64
Me
S
nBu
O
Me
17, 80%
f1 (ppm)


^{1}H NMR (300 MHz, CDCl$_3$)
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.23
7.22
7.22
7.20
7.19
7.18
7.17
3.39
3.37
3.35
3.32
3.30
3.28
3.25
2.68
2.66
2.63
1.75
1.73
1.70
1.70
1.68
1.65
1.46
1.43
1.41
1.41
1.38
1.36
1.33
1.21
1.18
0.96
0.93
0.91
0.00
iPr
S
nBu
O
18, 64%
3.04
1.15
1.00
2.07
2.12
2.30
3.17
3.06
3.31
f1 (ppm)

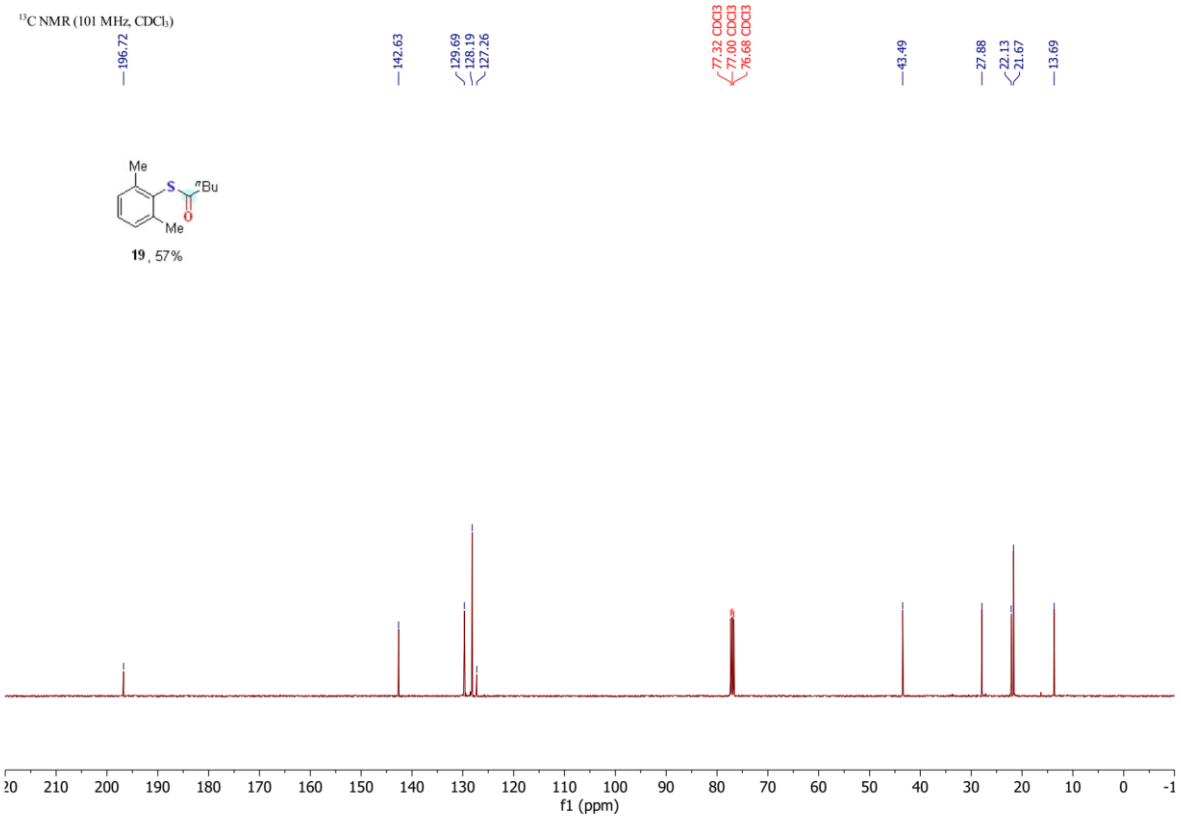

^{13}C NMR (75 MHz, CDCl$_3$)
197.55
151.72
136.45
130.27
126.31
126.22
126.11
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.40
31.06
27.73
23.51
22.08
13.67
iPr
S
nBu
O
18, 64%
f1 (ppm)

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

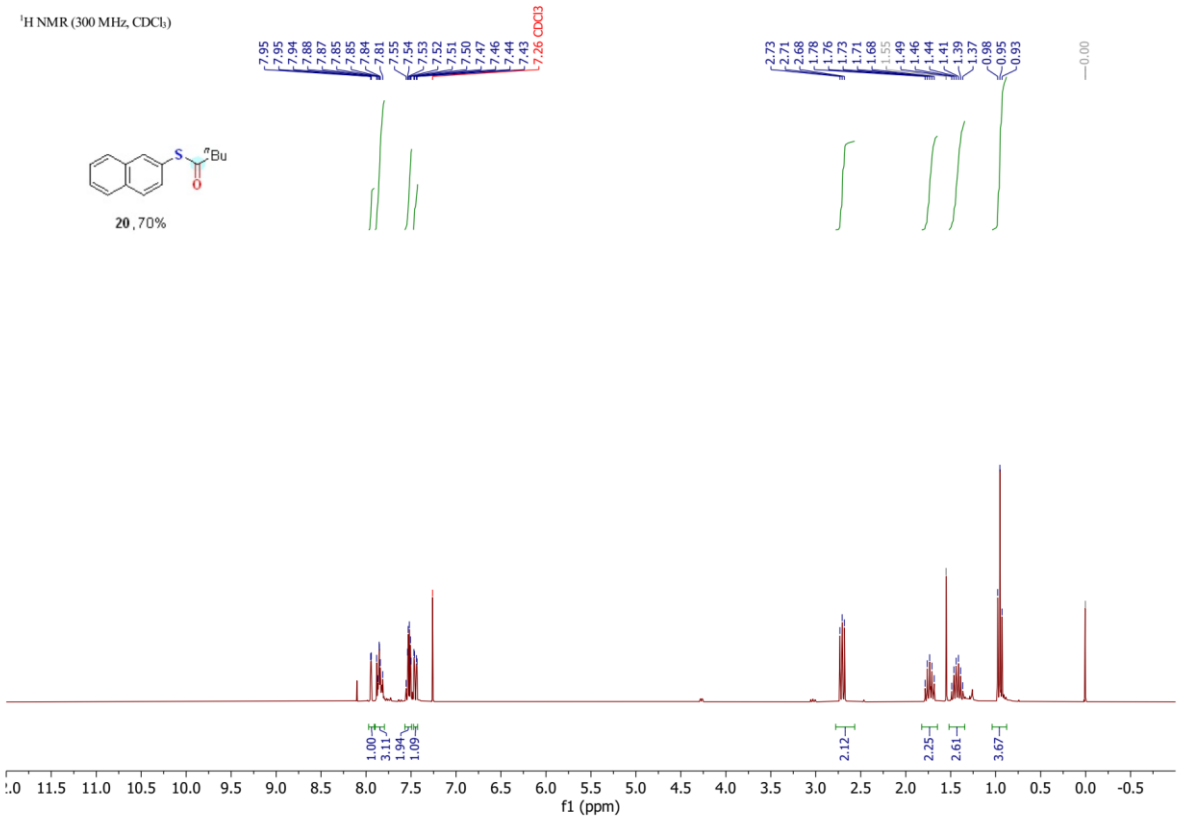


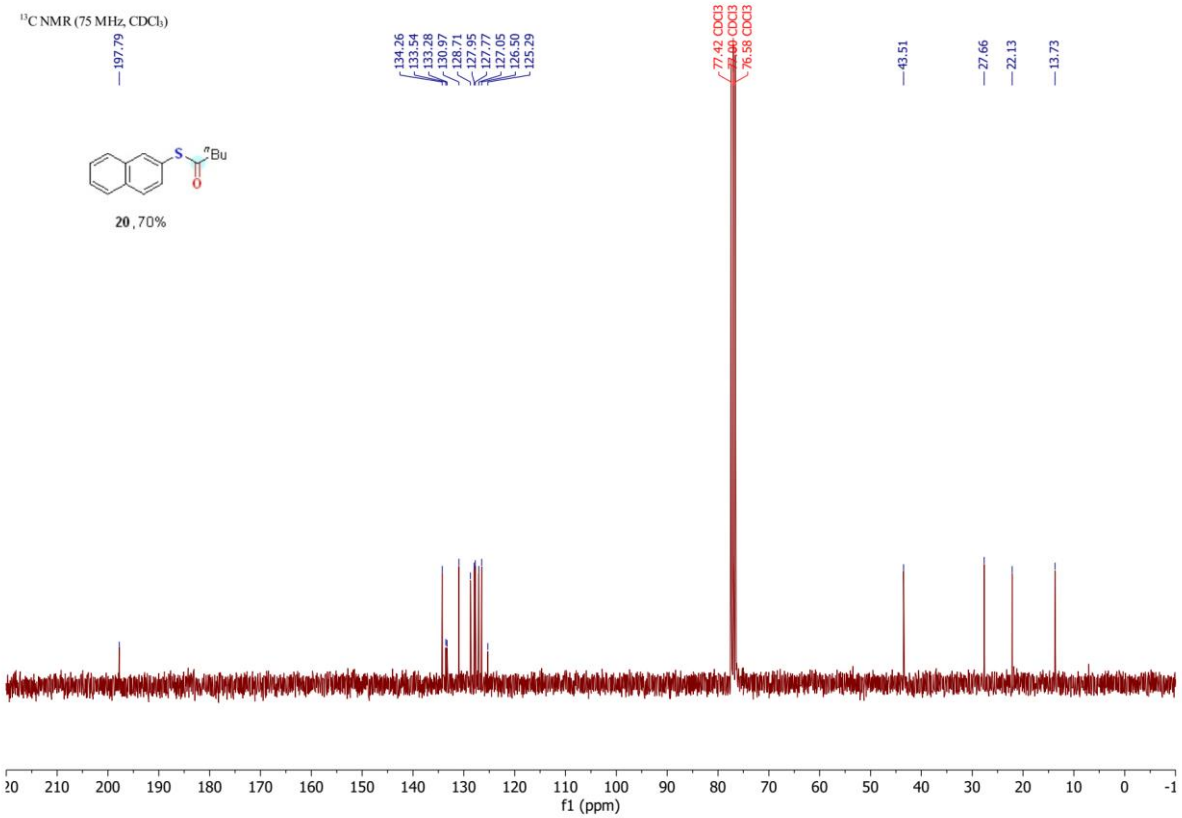
19, 57%

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

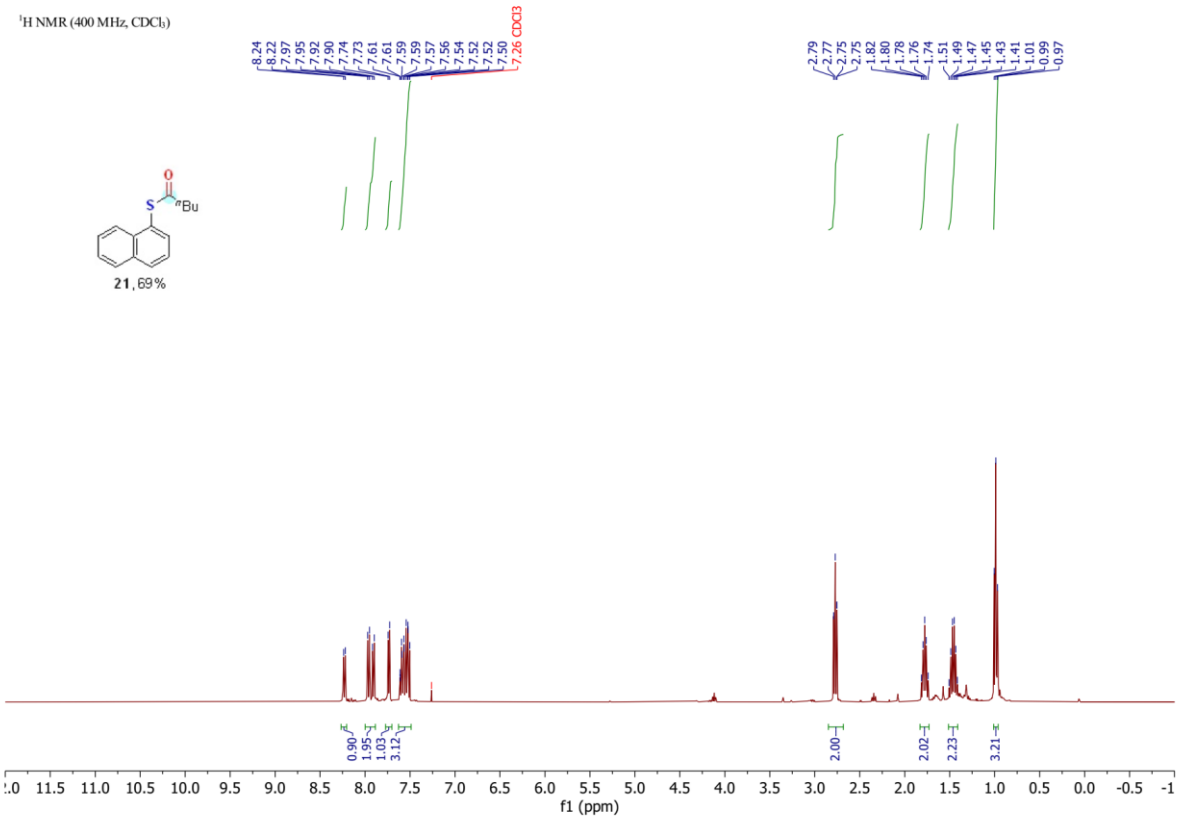


19, 57%


^{1}H NMR (300 MHz, CDCl$_3$)
7.95
7.95
7.94
7.88
7.87
7.85
7.85
7.84
7.81
7.55
7.54
7.53
7.52
7.51
7.50
7.47
7.46
7.44
7.43
7.26 CDCl3
2.73
2.71
2.68
1.78
1.76
1.73
1.71
1.68
1.55
1.49
1.46
1.44
1.41
1.39
1.37
0.98
0.95
0.93
0.00
S
nBu
O
20, 70%
1.00
3.11
1.94
1.09
2.12
2.25
2.61
3.67
f1 (ppm)

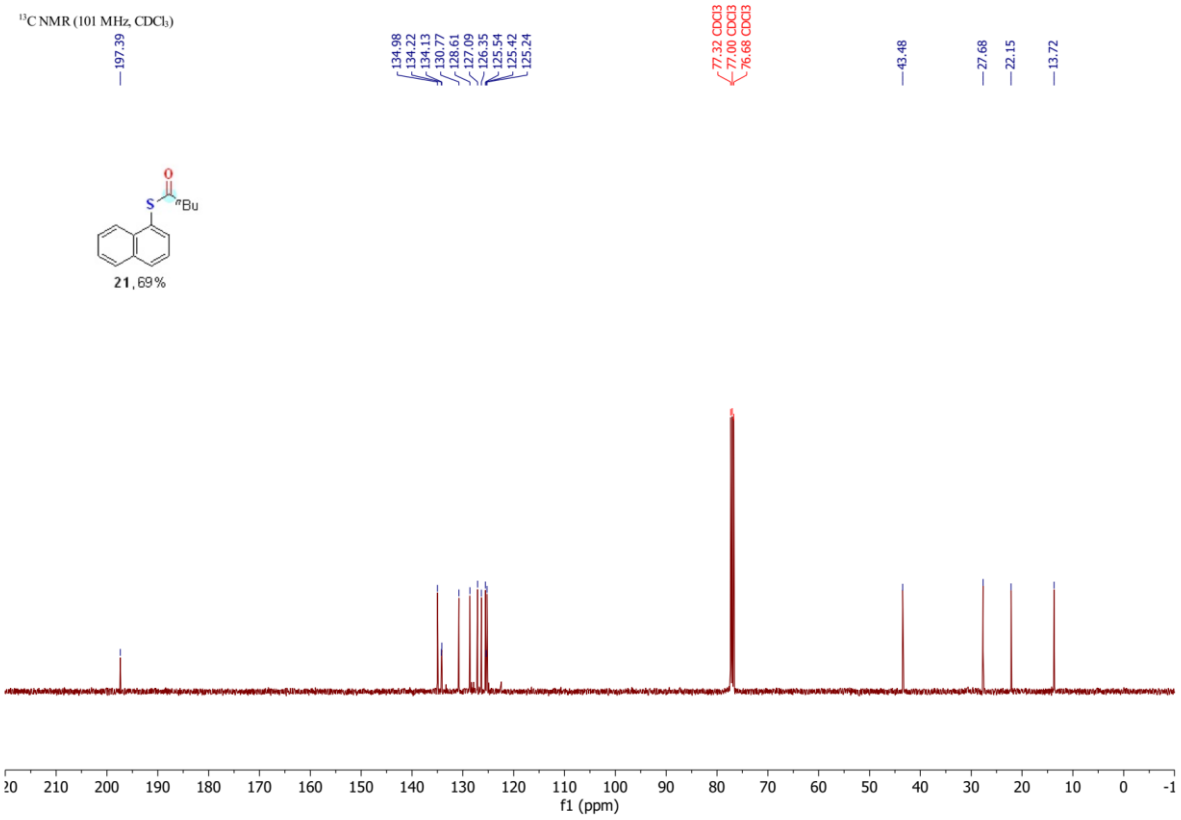

^{13}C NMR (75 MHz, CDCl$_3$)
197.79
134.26
133.54
133.28
130.97
128.71
127.95
127.77
127.05
126.50
125.29
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.51
27.66
22.13
13.73
S
nBu
O
20, 70%
f1 (ppm)

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

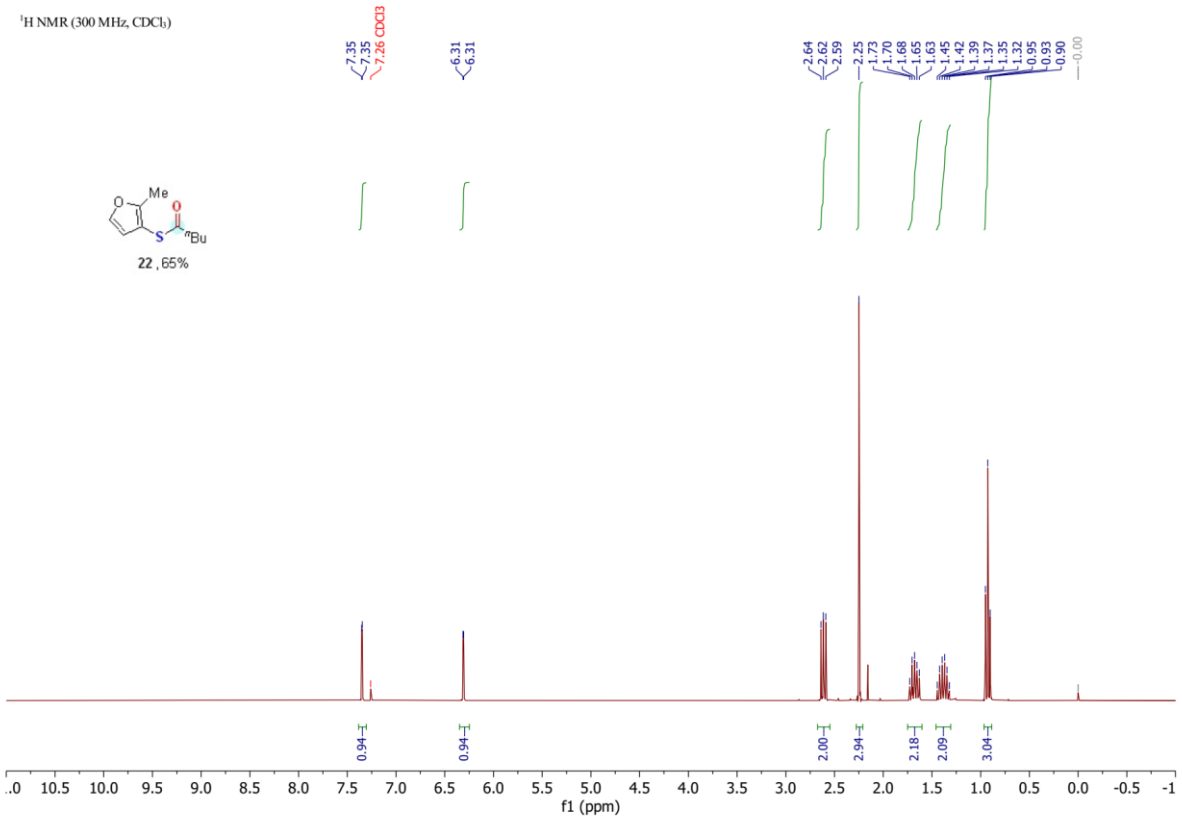


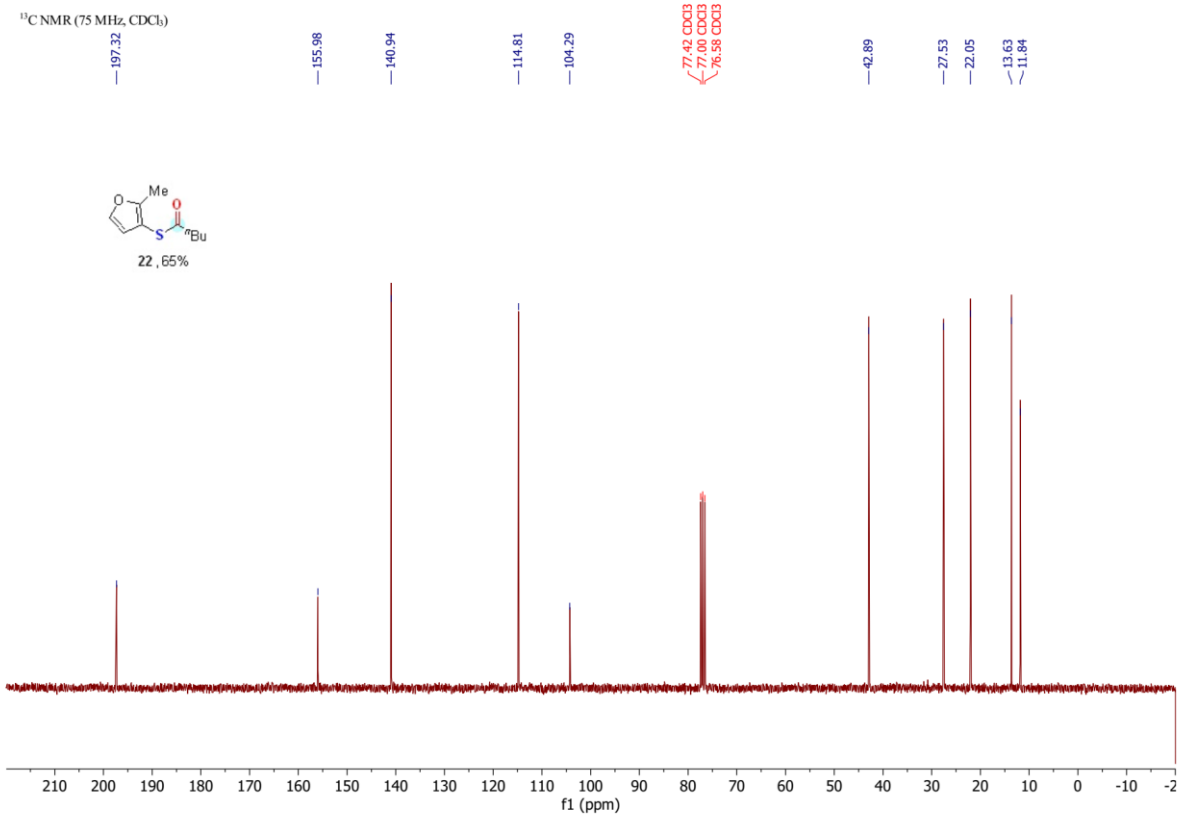
21, 69%

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

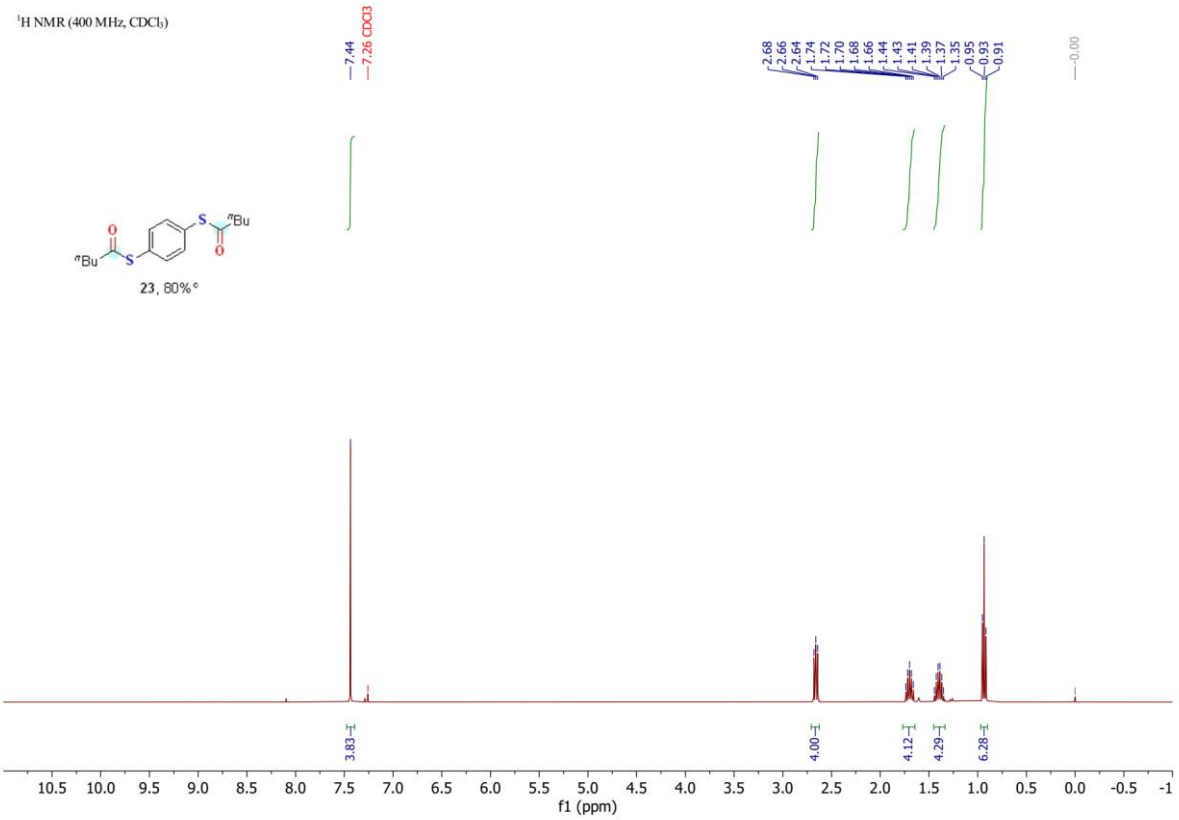


21, 69%


^{1}H NMR (300 MHz, CDCl$_3$)
7.35
7.35
7.26 CDCl3
6.31
6.31
2.64
2.62
2.59
2.25
1.73
1.70
1.68
1.65
1.63
1.45
1.42
1.39
1.37
1.35
1.32
0.95
0.93
0.90
0.00
Me
O
S
nBu
22 , 65%
0.94
0.94
2.00
2.94
2.18
2.09
3.04
f1 (ppm)

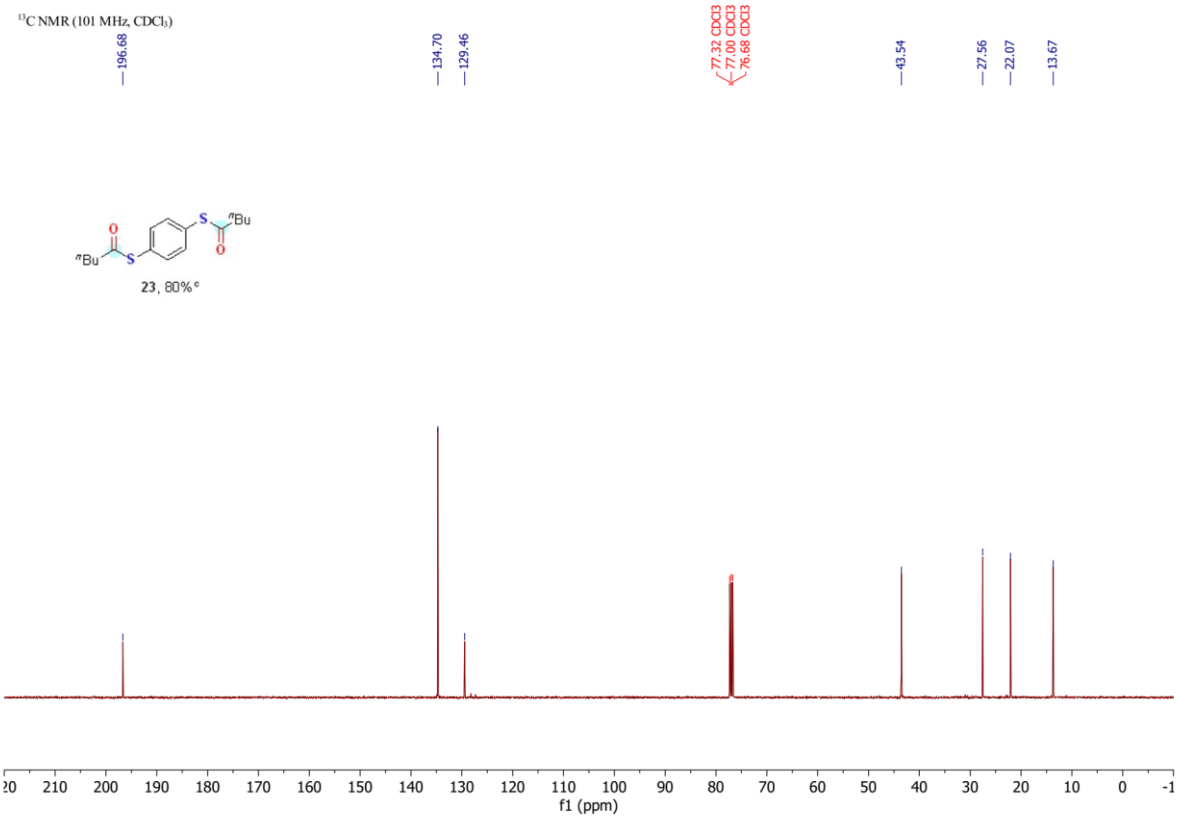

^{13}C NMR (75 MHz, CDCl$_3$)
197.32
155.98
140.94
114.81
104.29
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
42.89
27.53
22.05
13.63
11.84
Me
O
S
nBu
22 , 65%
f1 (ppm)

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

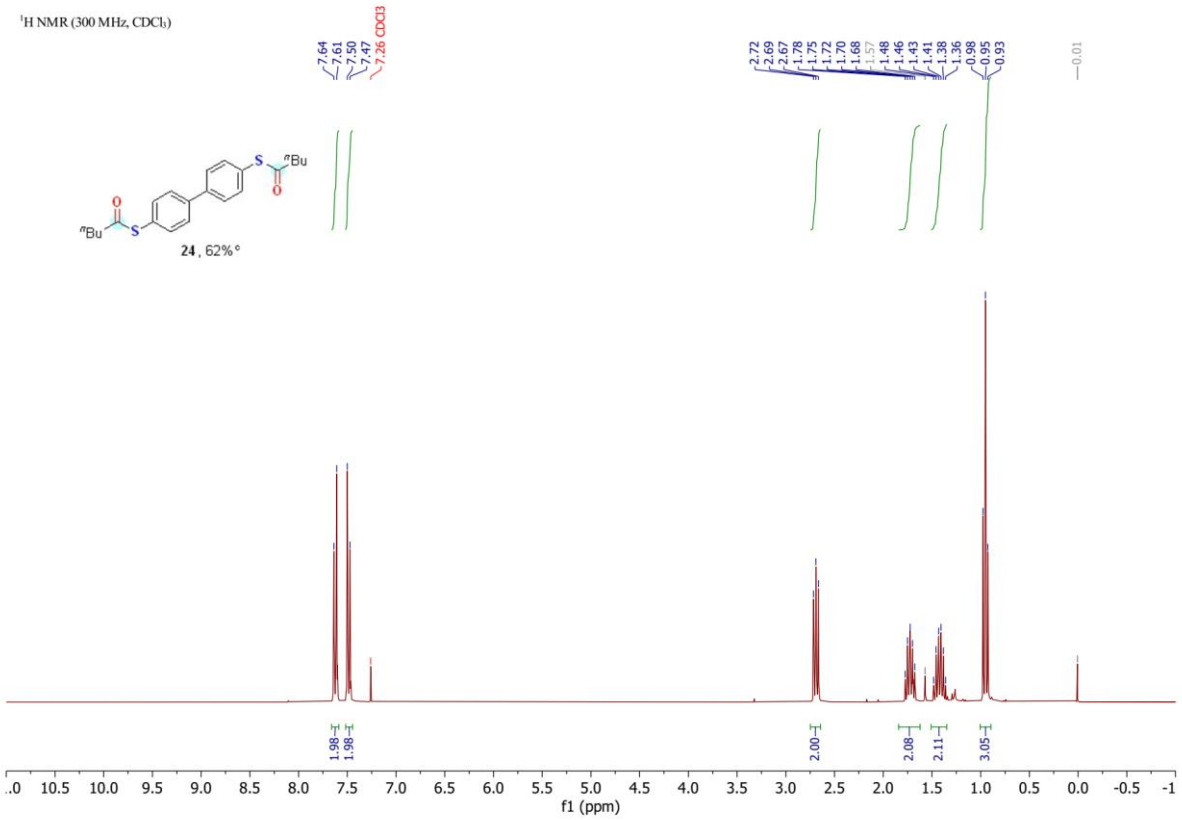


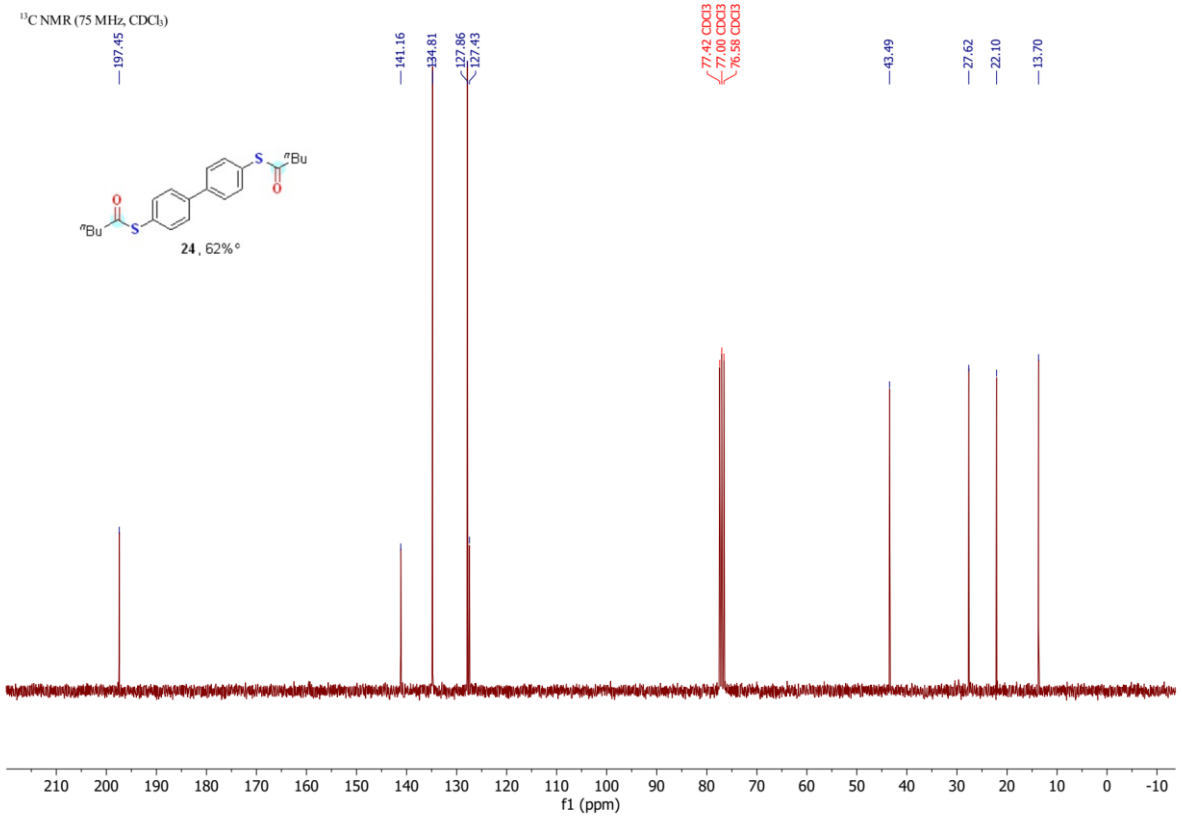
23, 80%[c]

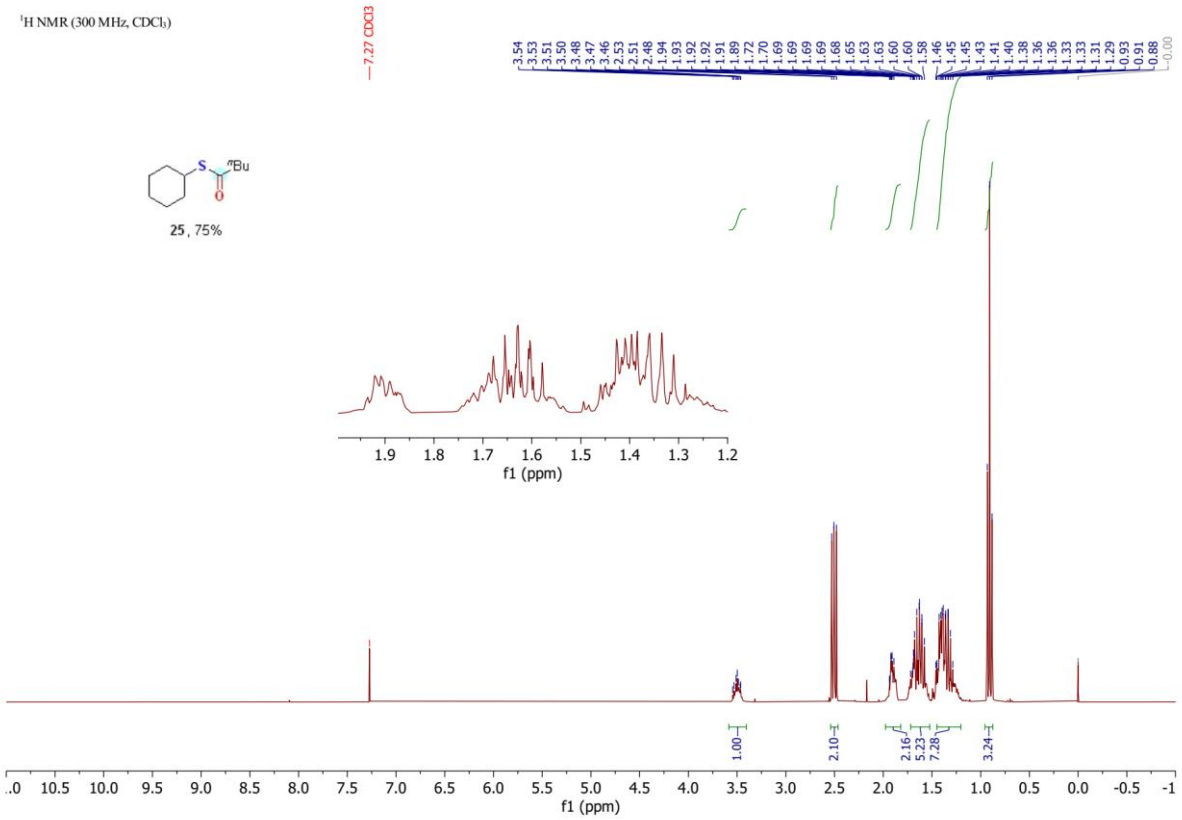
^{13}C NMR (101 MHz, $CDCl_3$)

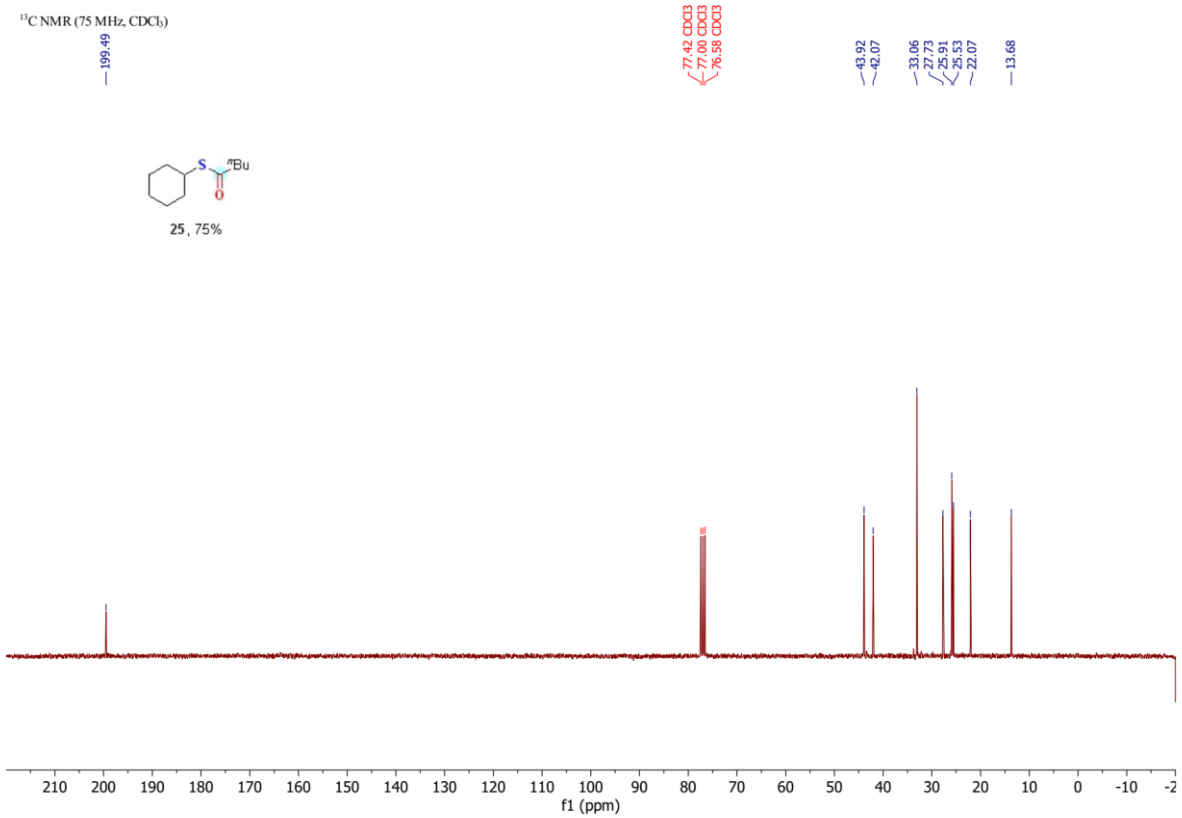


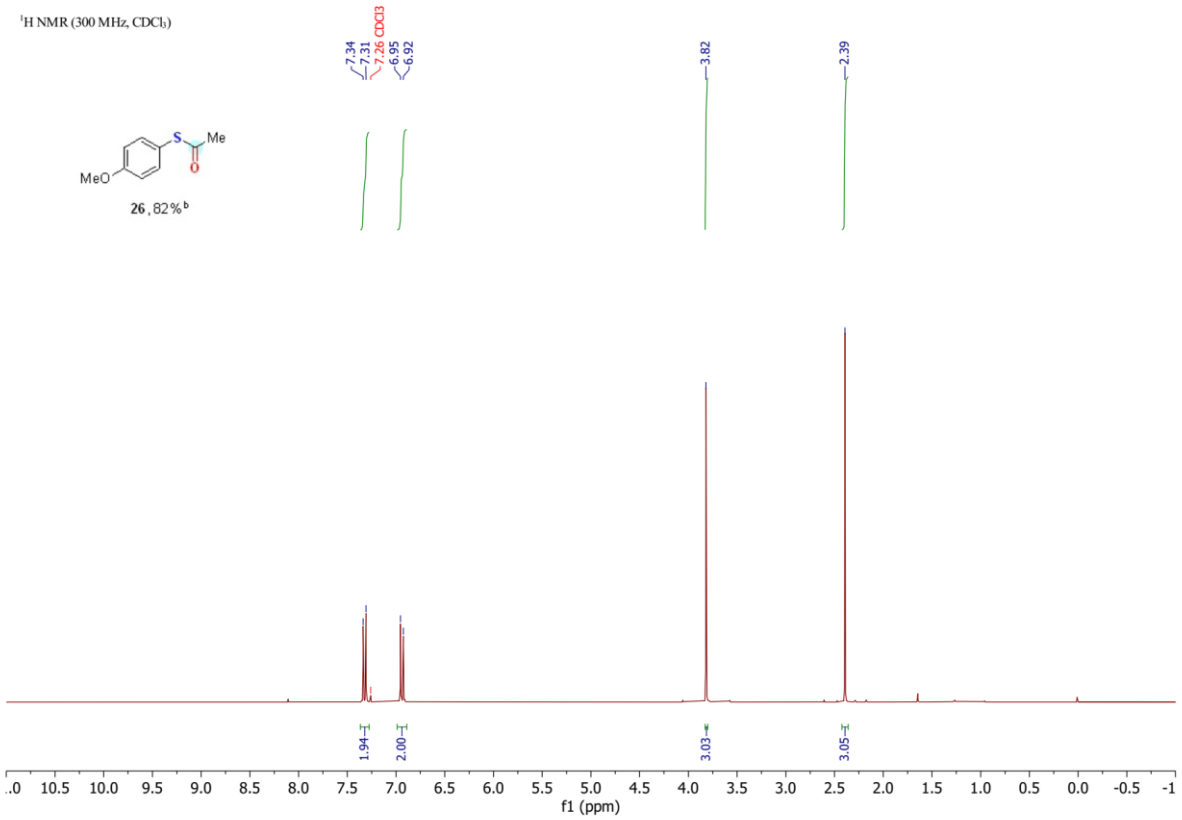
23, 80%[c]

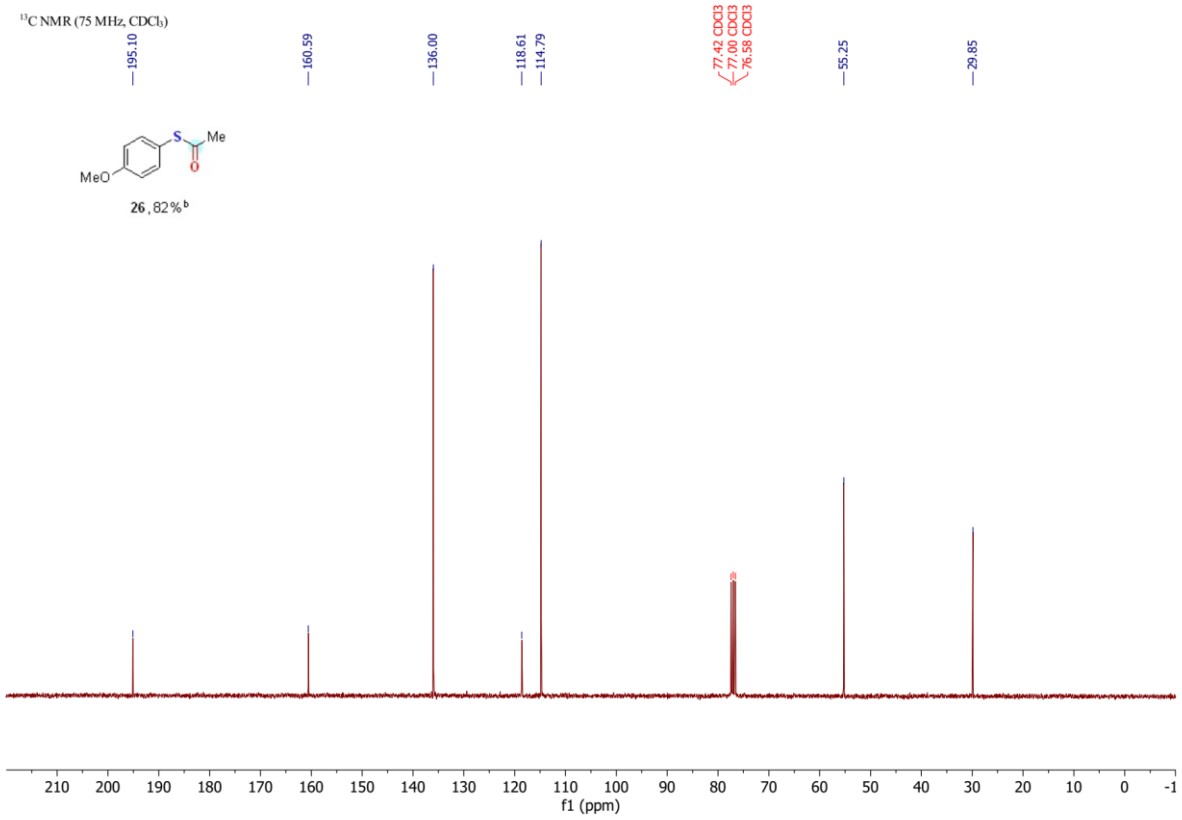

^{1}H NMR (300 MHz, CDCl$_3$)
7.64
7.61
7.50
7.47
7.26 CDCl3
2.72
2.69
2.67
1.78
1.75
1.72
1.70
1.68
1.57
1.48
1.46
1.43
1.41
1.38
1.36
0.98
0.95
0.93
0.01
nBu
S
O
nBu
24, 62%°
1.98
1.98
2.00
2.08
2.11
3.05
f1 (ppm)

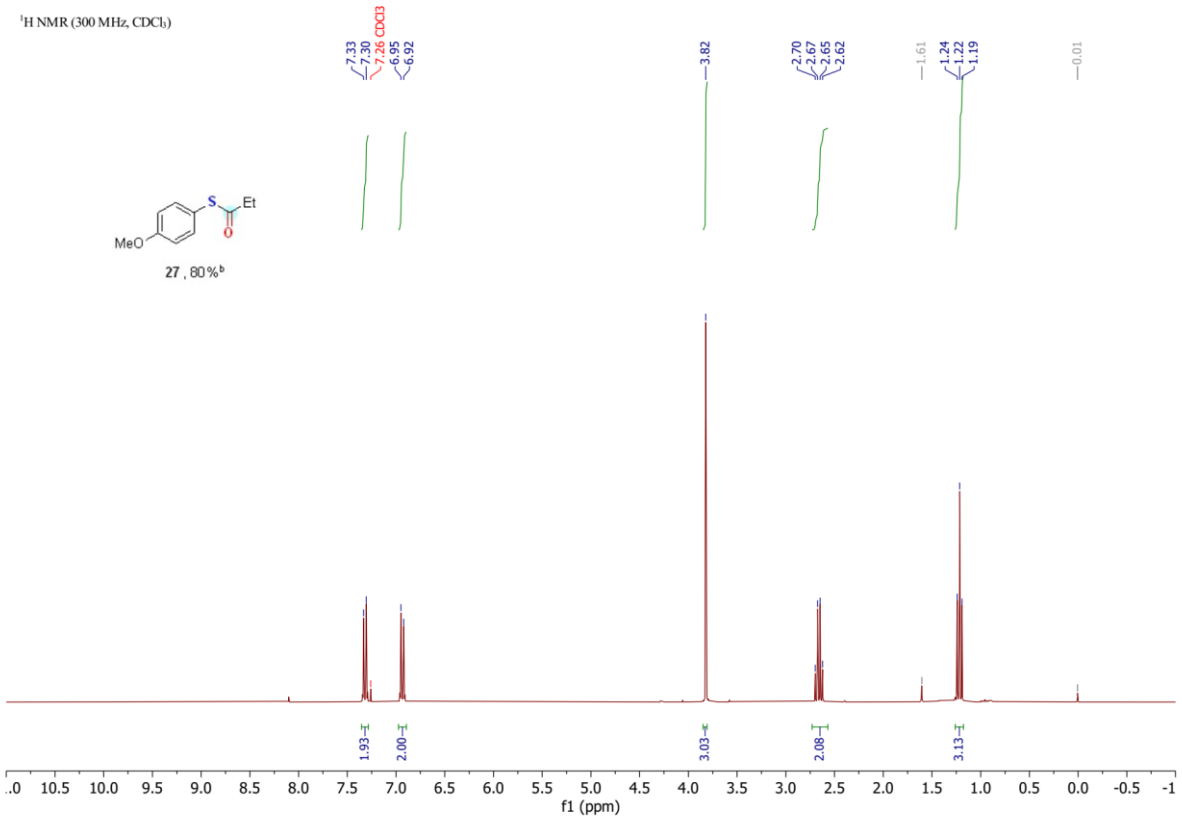

^{13}C NMR (75 MHz, CDCl$_3$)
197.45
141.16
134.81
127.86
127.43
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.49
27.62
22.10
13.70
nBu
S
O
nBu
24, 62%°
f1 (ppm)

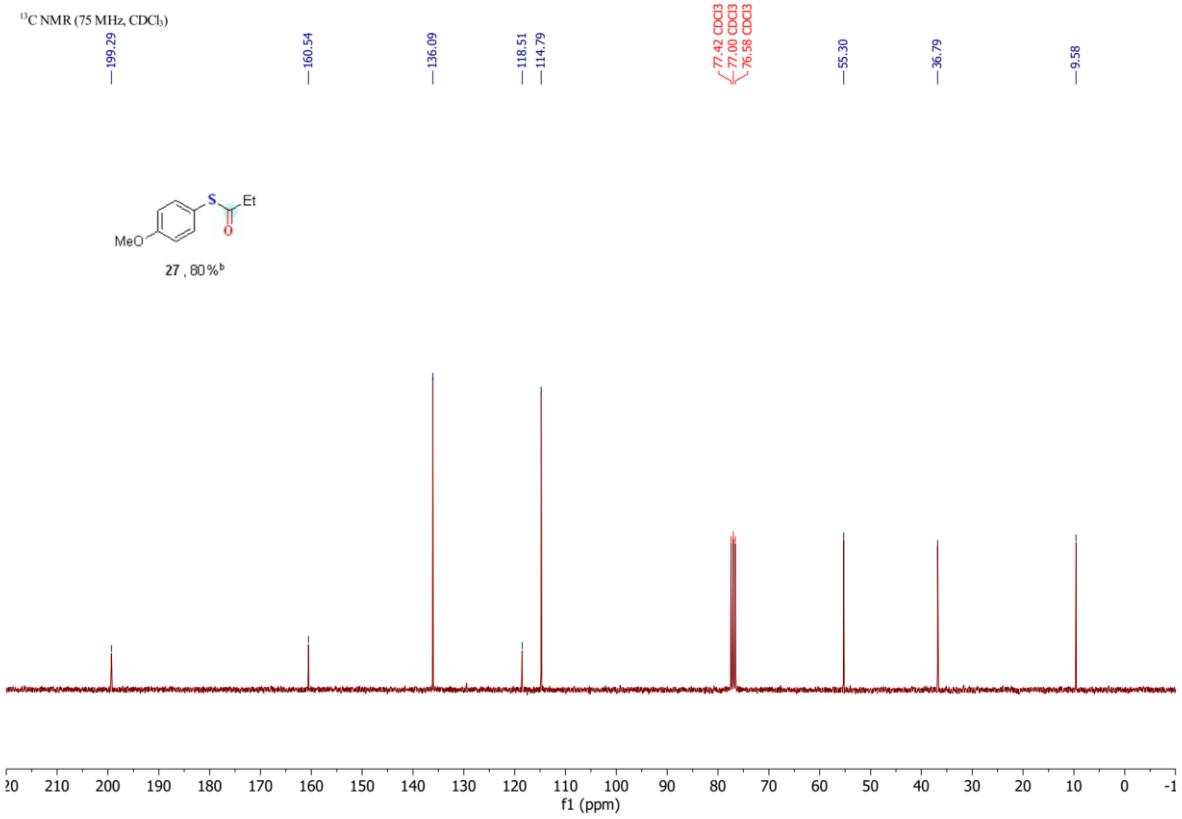

^{1}H NMR (300 MHz, CDCl$_3$)
7.27 CDCl3
nBu
25, 75%
f1 (ppm)

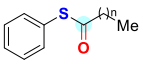

^{13}C NMR (75 MHz, CDCl$_3$)
199.49
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
43.92
42.07
33.06
27.73
25.91
25.53
22.07
13.68
nBu
25, 75%
f1 (ppm)


¹H NMR (300 MHz, CDCl₃)
7.34
7.31
7.26 CDCl3
6.95
6.92
3.82
2.39
MeO
S
Me
O
26, 82%ᵇ
1.94
2.00
3.03
3.05
f1 (ppm)


¹³C NMR (75 MHz, CDCl₃)
195.10
160.59
136.00
118.61
114.79
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.25
29.85
MeO
S
Me
O
26, 82%ᵇ
f1 (ppm)

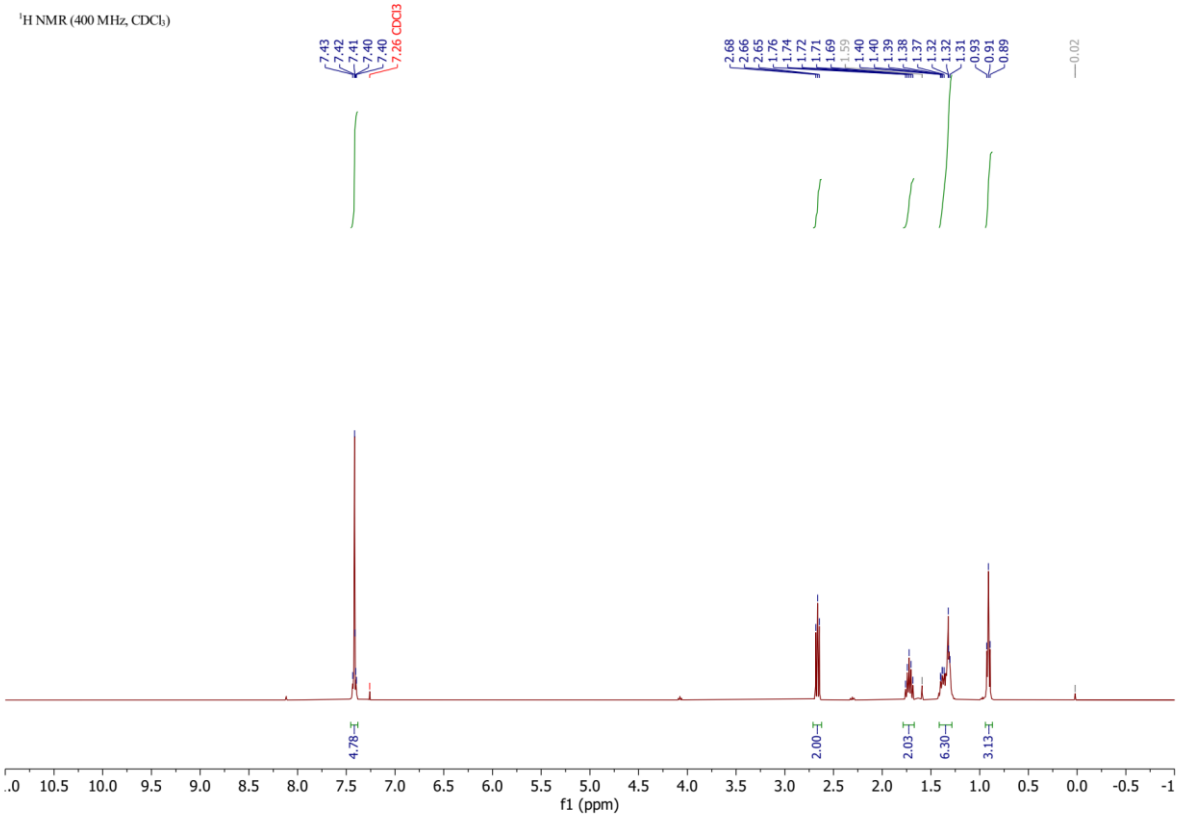

¹H NMR (300 MHz, CDCl₃)
7.33
7.30
7.26 CDCl3
6.95
6.92
3.82
2.70
2.67
2.65
2.62
1.61
1.24
1.22
1.19
0.01
MeO
S
Et
O
27 , 80 %b
1.93
2.00
3.03
2.08
3.13
f1 (ppm)


¹³C NMR (75 MHz, CDCl₃)
199.29
160.54
136.09
118.51
114.79
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
55.30
36.79
9.58
MeO
S
Et
O
27 , 80 %b
f1 (ppm)

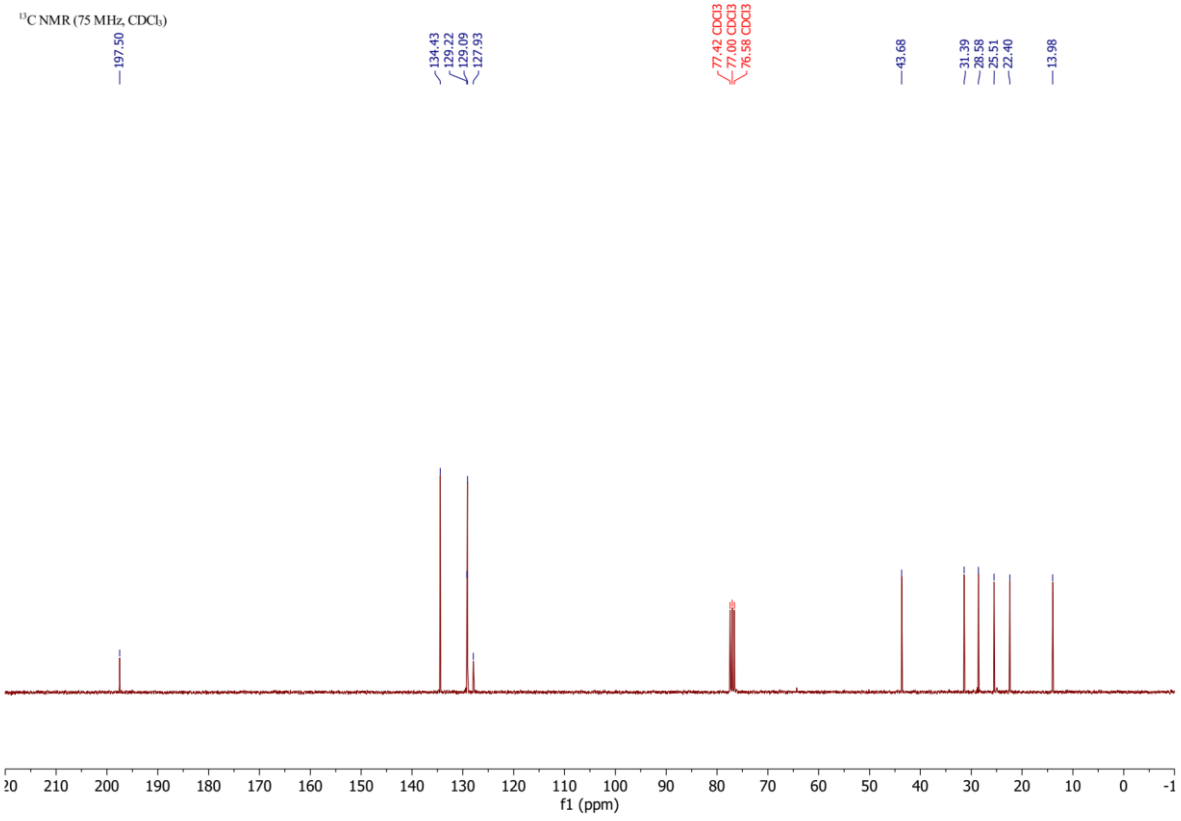


28, n = 5

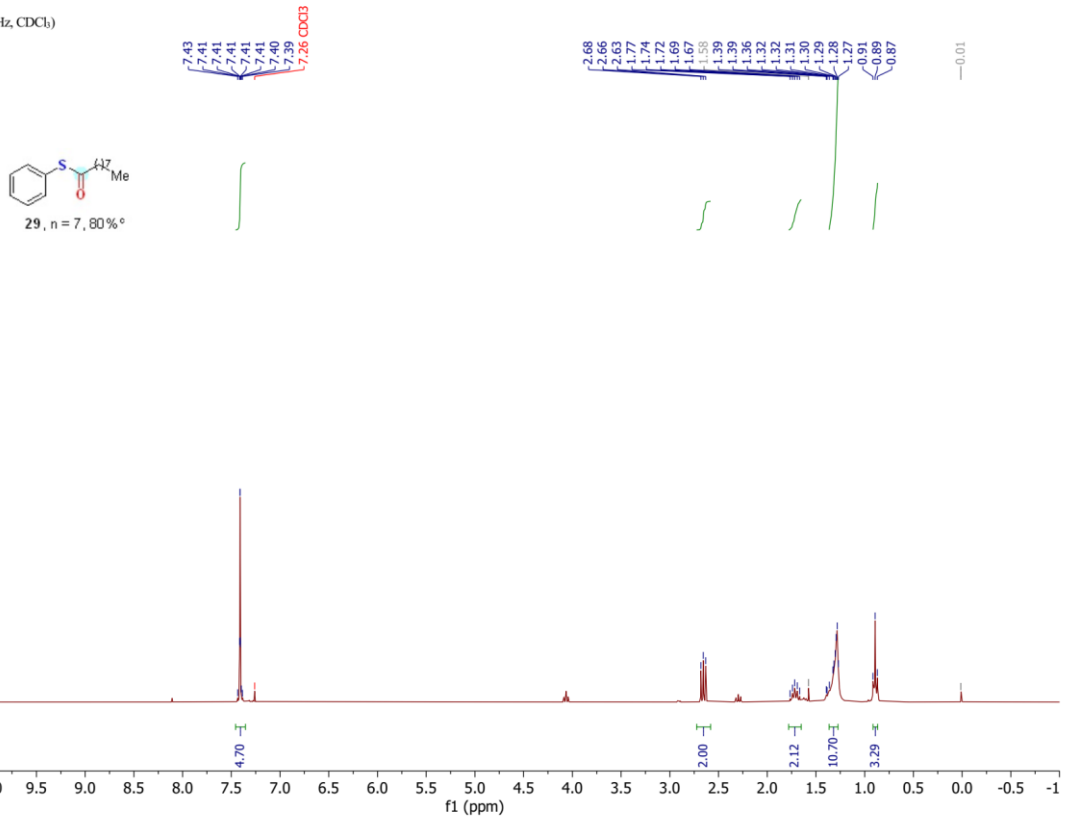
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

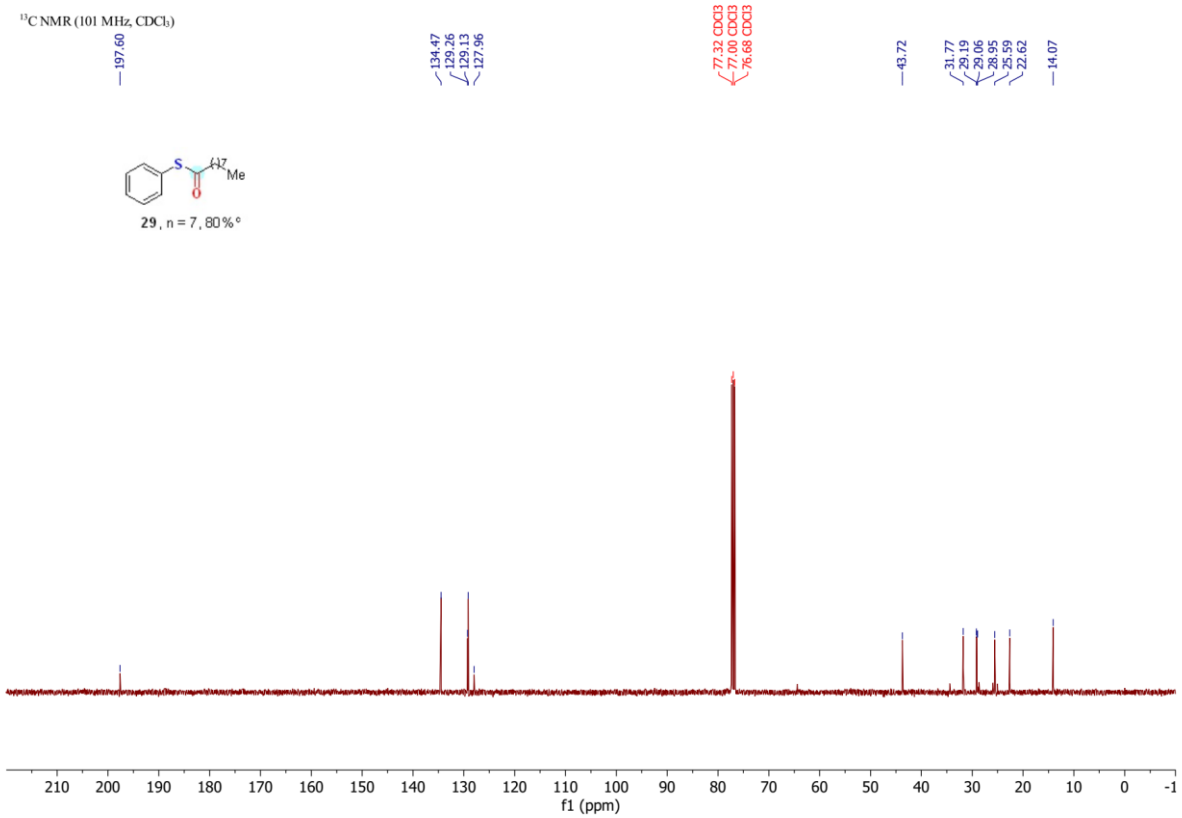


^{1}H NMR (300 MHz, $CDCl_3$)

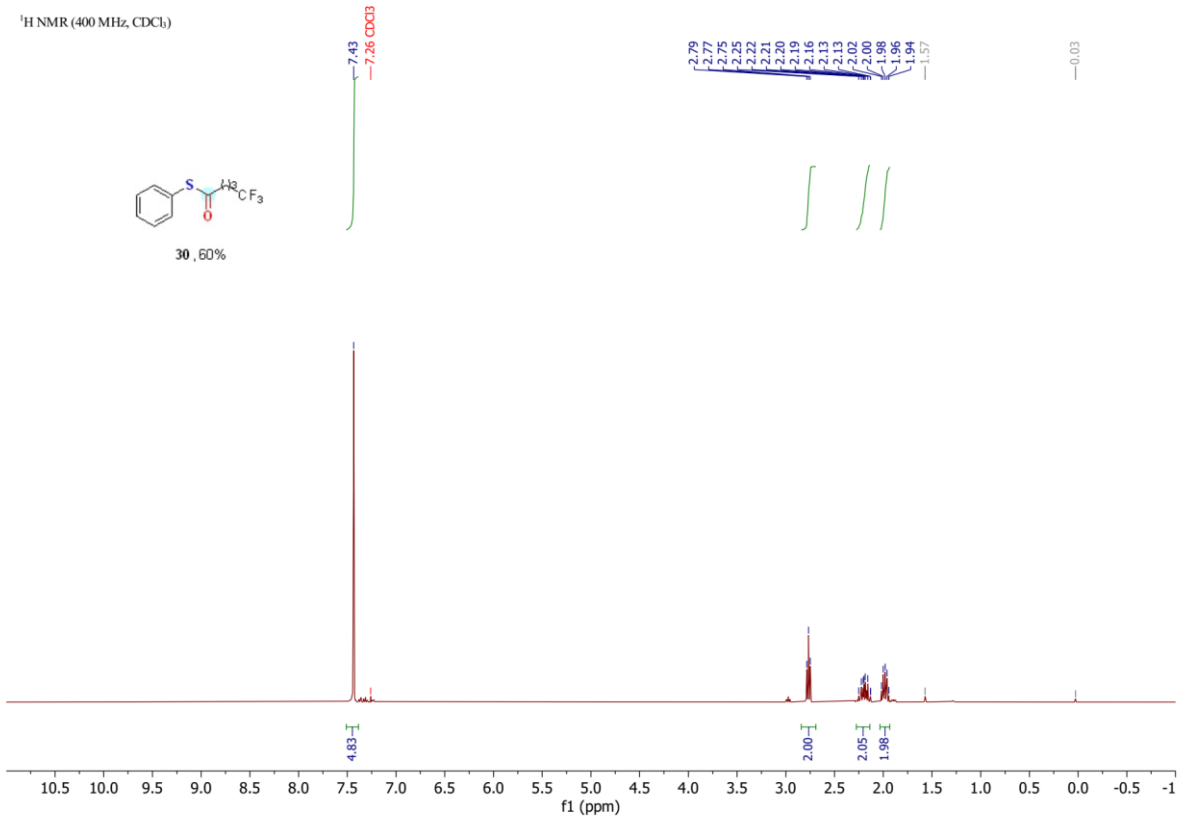


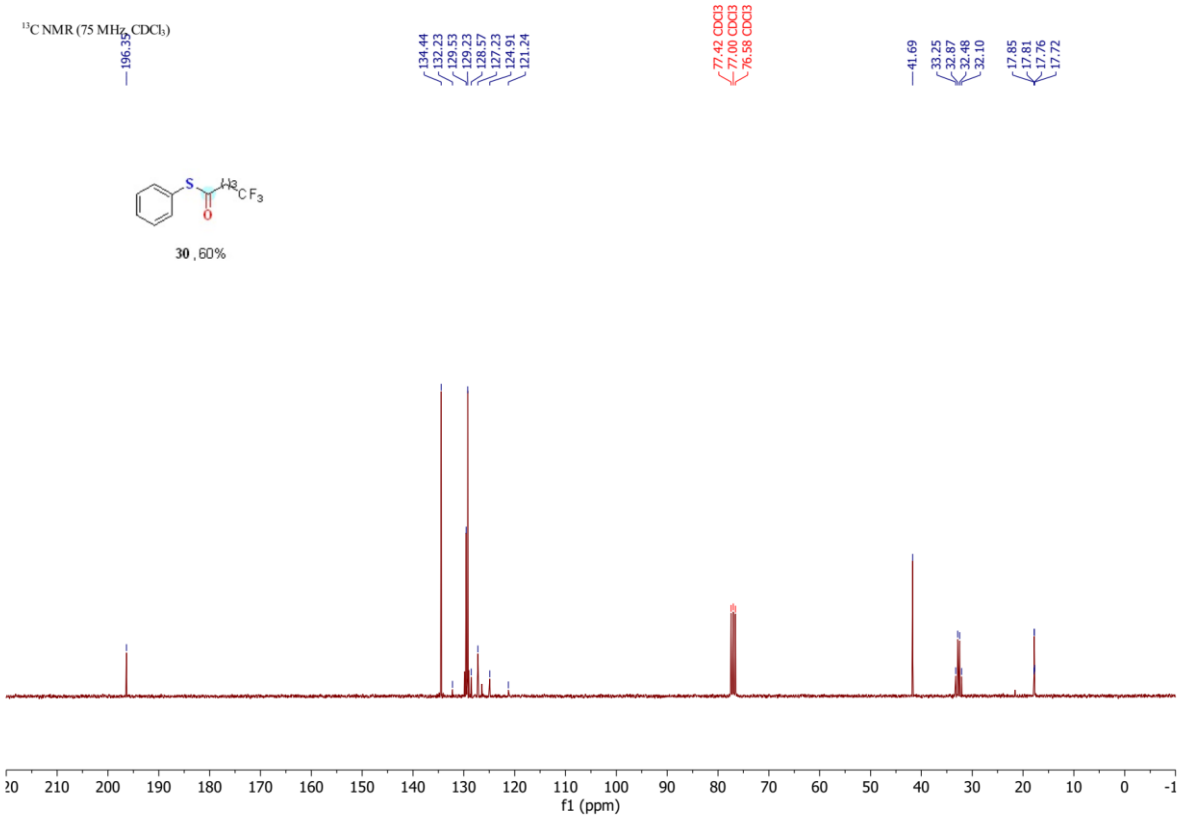
29, n = 7, 80%°

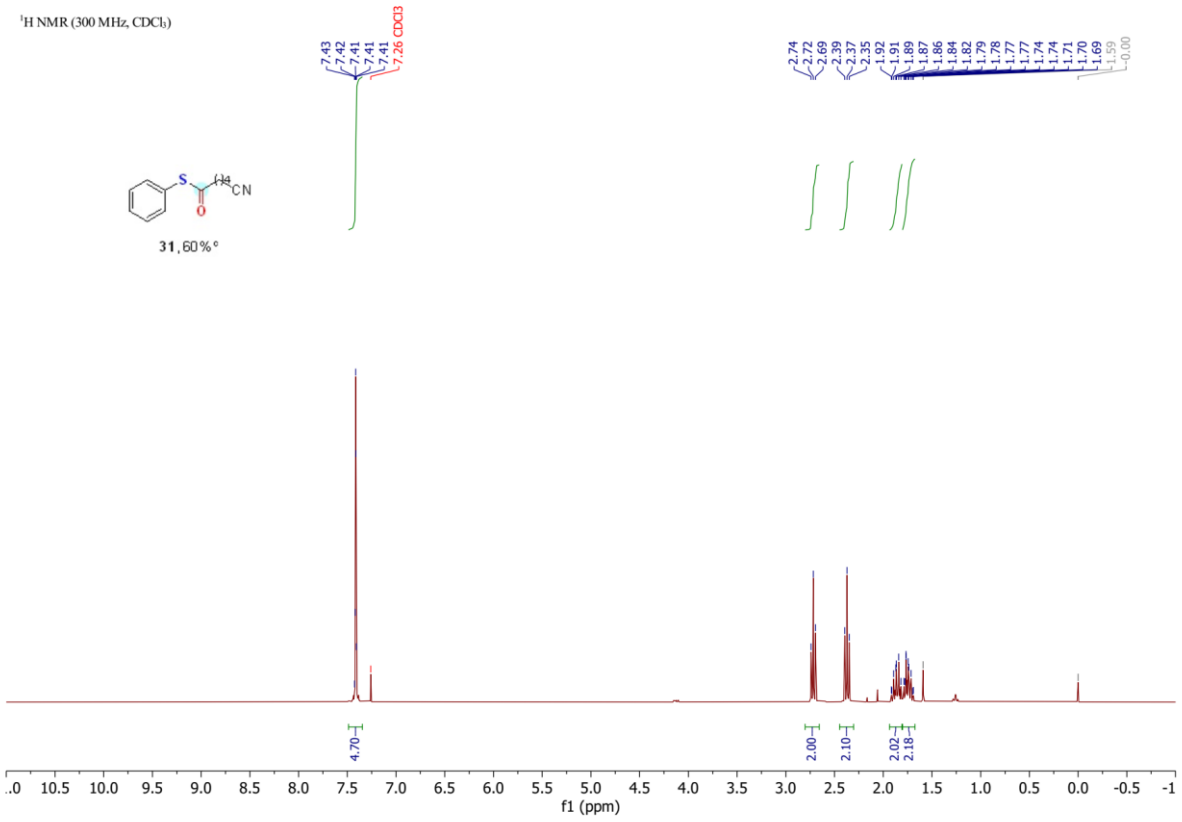
^{13}C NMR (101 MHz, $CDCl_3$)

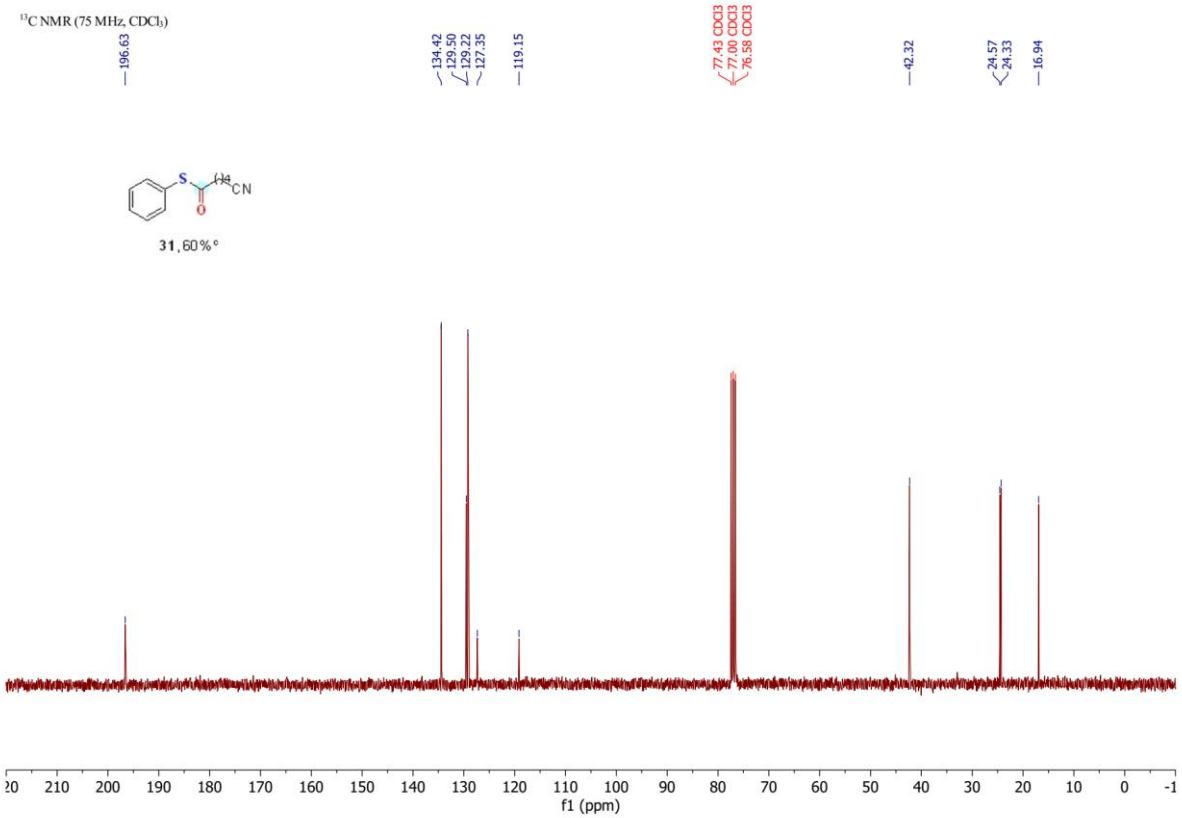


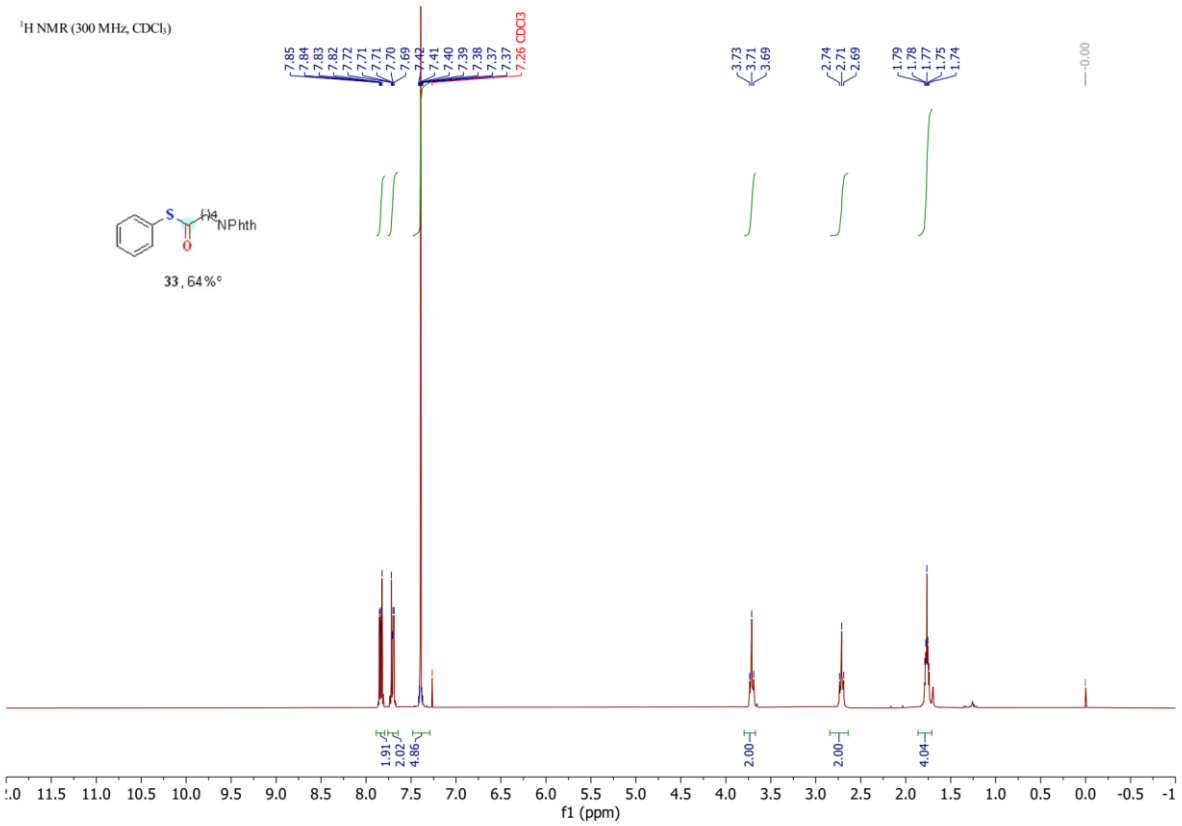
29, n = 7, 80%°

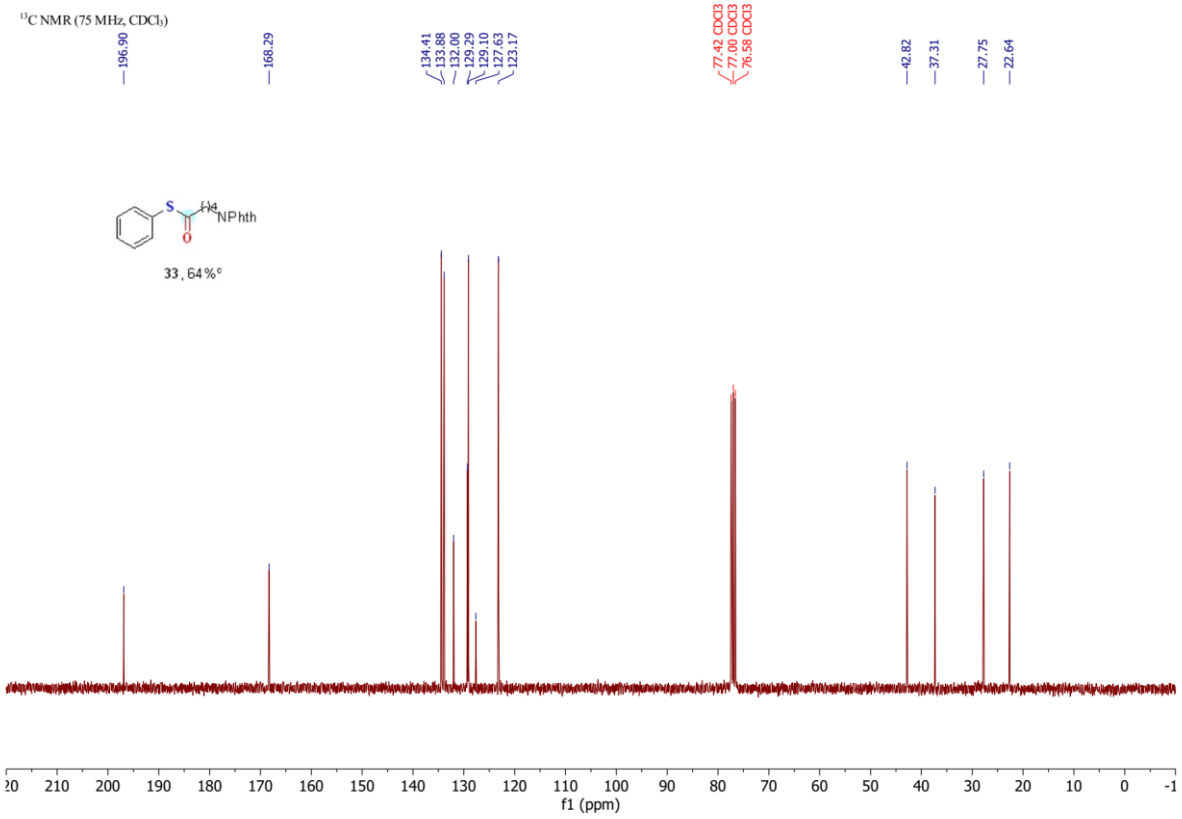

1H NMR (400 MHz, CDCl3)
7.43
7.26 CDCl3
2.79
2.77
2.75
2.25
2.22
2.21
2.20
2.19
2.16
2.13
2.13
2.02
2.00
1.98
1.96
1.94
1.57
0.03
S
O
CF3
30 , 60%
4.83
2.00
2.05
1.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

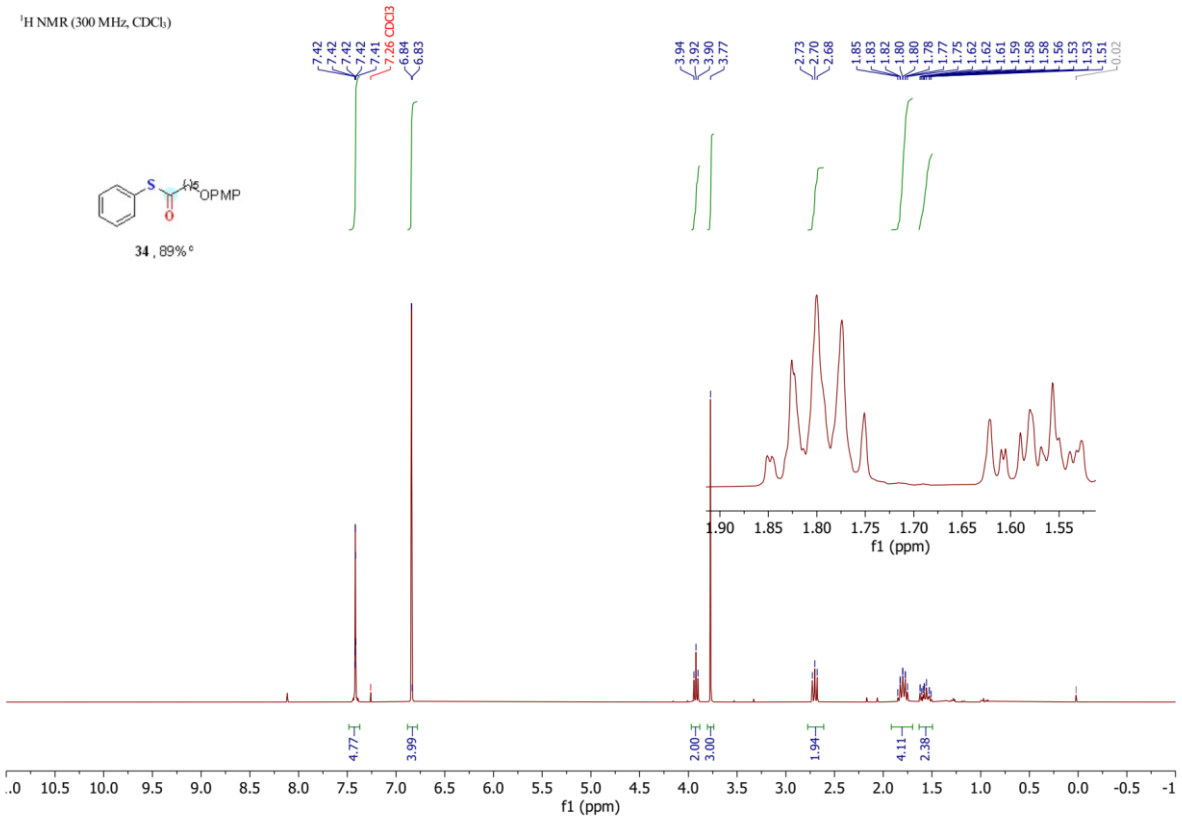

13C NMR (75 MHz, CDCl3)
196.39
134.44
132.23
129.53
129.23
128.57
127.23
124.91
121.24
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
41.69
33.25
32.87
32.48
32.10
17.85
17.81
17.76
17.72
S
O
CF3
30 , 60%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

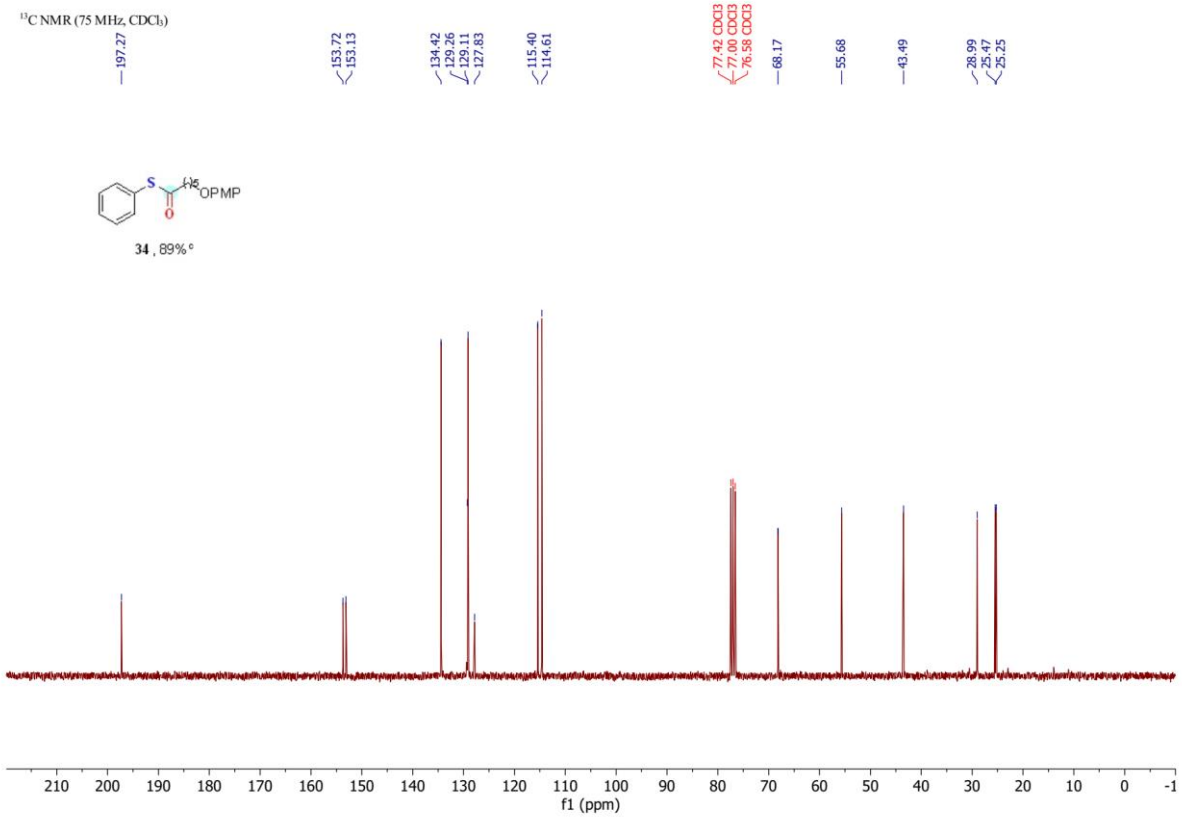

^{1}H NMR (300 MHz, CDCl$_3$)
7.43
7.42
7.41
7.41
7.41
7.26 CDCl3
2.74
2.72
2.69
2.39
2.37
2.35
1.92
1.91
1.89
1.87
1.86
1.84
1.82
1.79
1.78
1.77
1.77
1.74
1.74
1.71
1.70
1.69
1.59
0.00
S
O
CN
31, 60%
4.70
2.00
2.10
2.02
2.18
f1 (ppm)

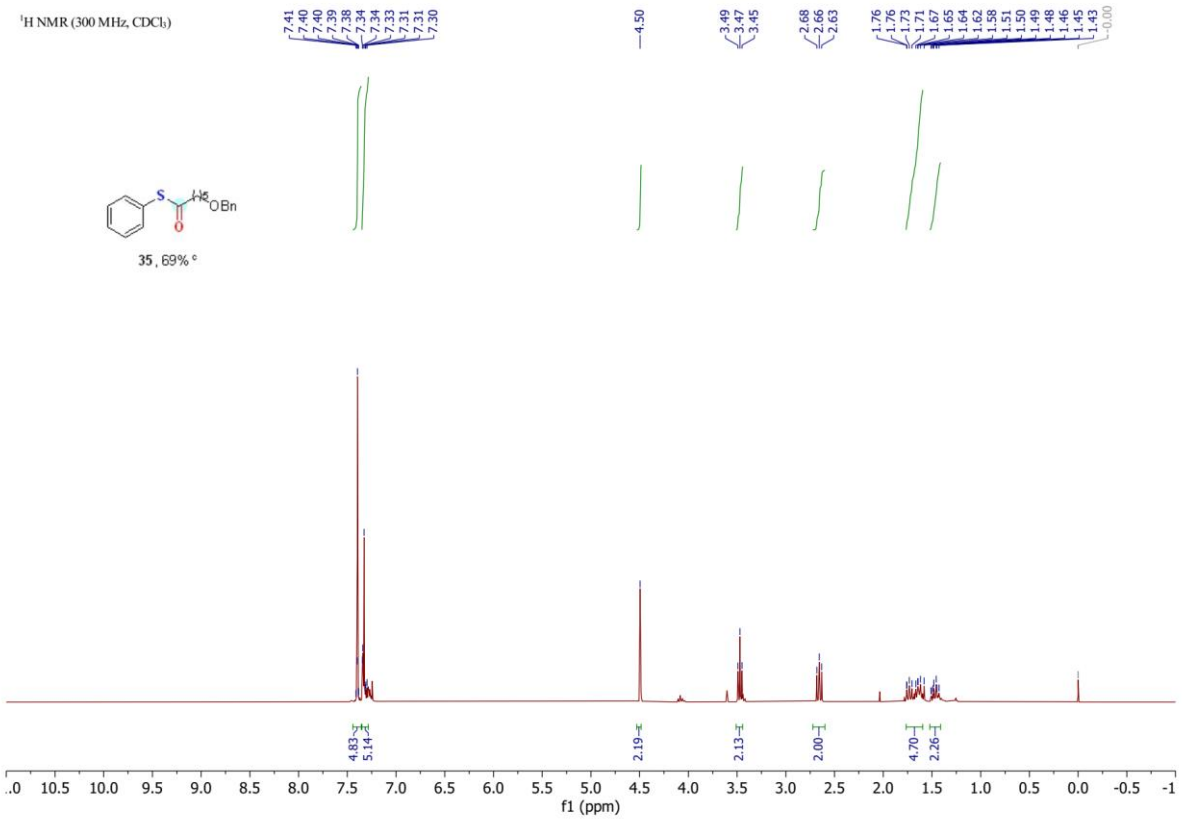

^{13}C NMR (75 MHz, CDCl$_3$)
196.63
134.42
129.50
129.22
127.35
119.15
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
42.32
24.57
24.33
16.94
S
O
CN
31, 60%
f1 (ppm)

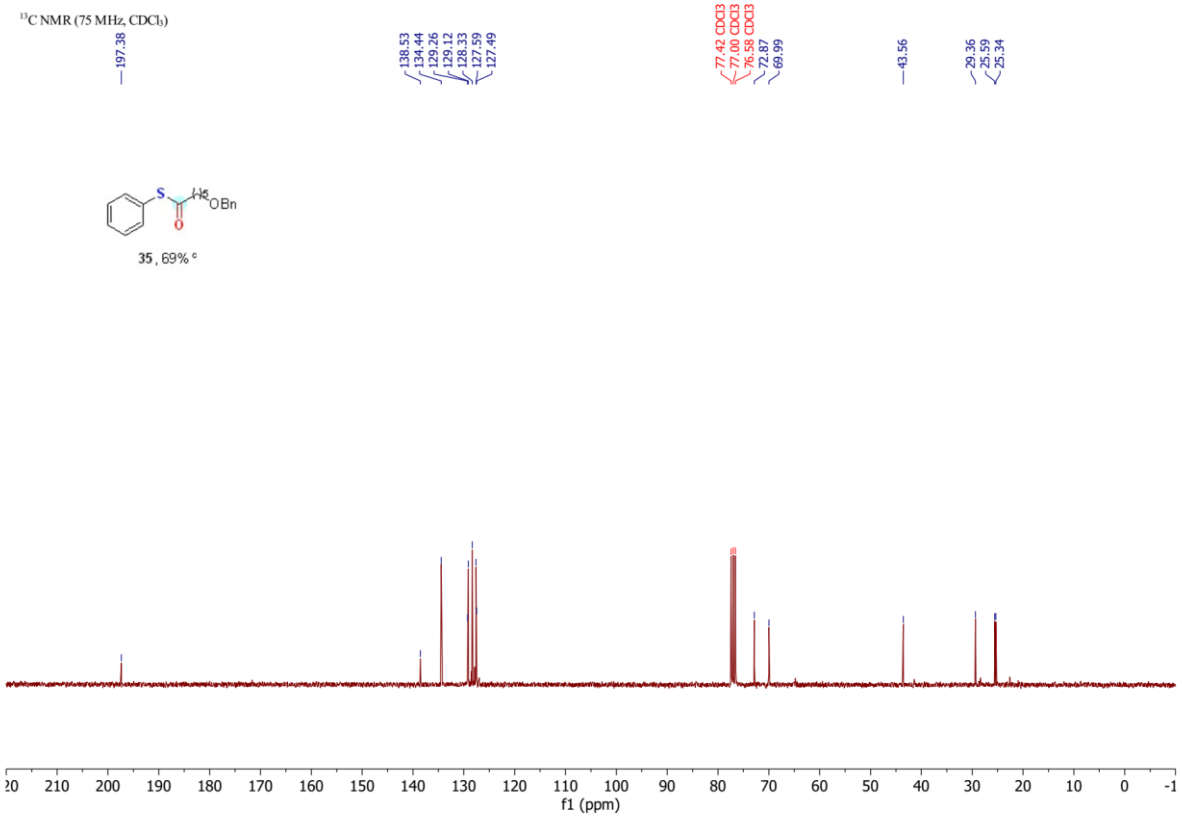

^{1}H NMR (300 MHz, CDCl$_3$)
7.85
7.84
7.83
7.82
7.72
7.71
7.71
7.70
7.69
7.42
7.41
7.40
7.39
7.38
7.37
7.37
7.26 CDCl3
3.73
3.71
3.69
2.74
2.71
2.69
1.79
1.78
1.77
1.75
1.74
0.00
NPhth
33, 64%°
1.91
2.02
4.86
2.00
2.00
4.04
f1 (ppm)

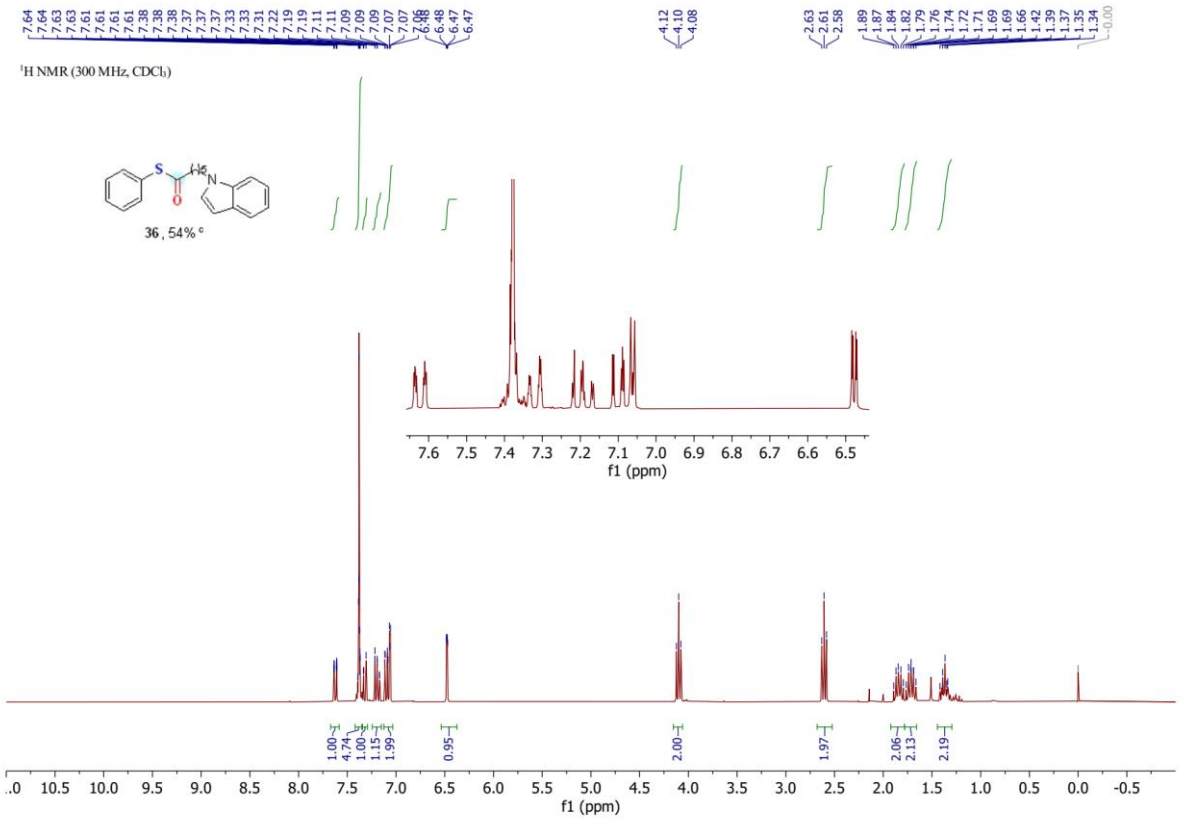

^{13}C NMR (75 MHz, CDCl$_3$)
196.90
168.29
134.41
133.88
132.00
129.29
129.10
127.63
123.17
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
42.82
37.31
27.75
22.64
NPhth
33, 64%°
f1 (ppm)

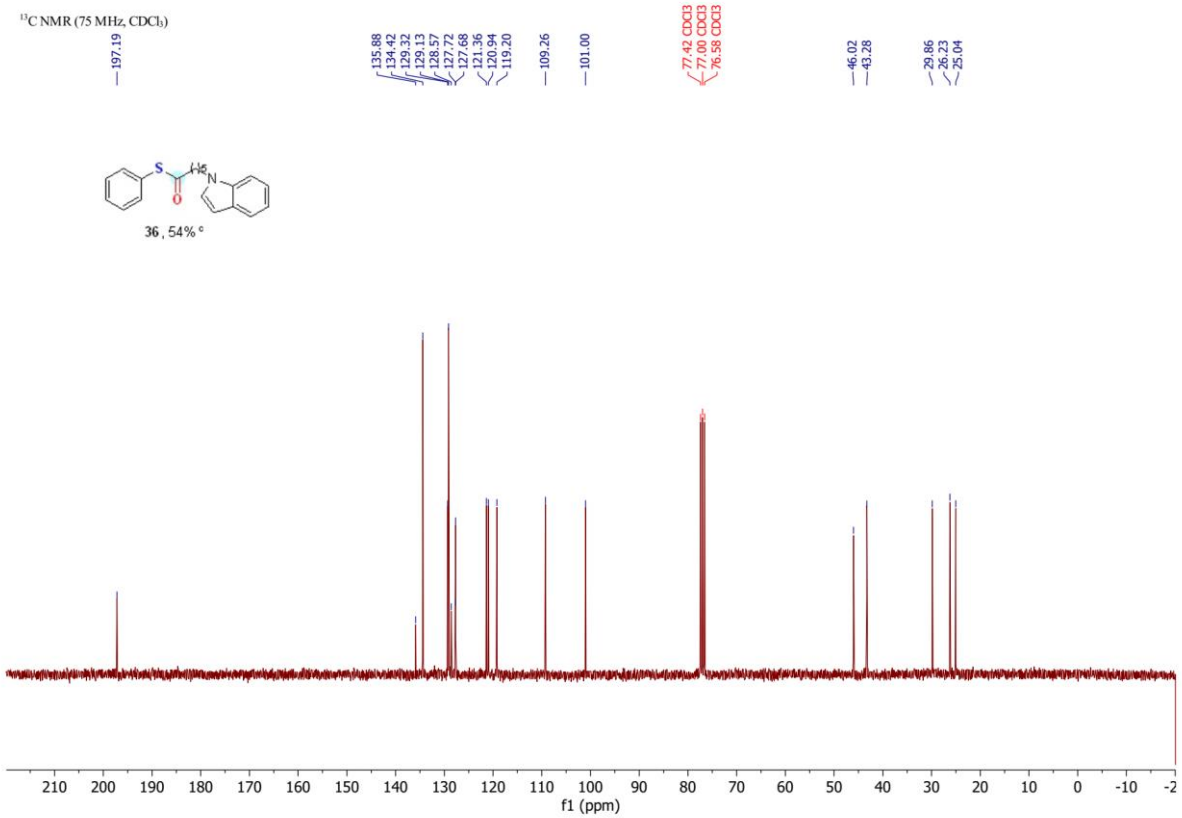

1H NMR (300 MHz, CDCl3)
7.42
7.42
7.42
7.42
7.41
7.26 CDCl3
6.84
6.83
3.94
3.92
3.90
3.77
2.73
2.70
2.68
1.85
1.83
1.82
1.80
1.80
1.78
1.77
1.75
1.62
1.62
1.61
1.59
1.58
1.58
1.56
1.53
1.53
1.51
0.02
OPMP
34 , 89% °
1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55
f1 (ppm)
4.77
3.99
2.00
3.00
1.94
4.11
2.38
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

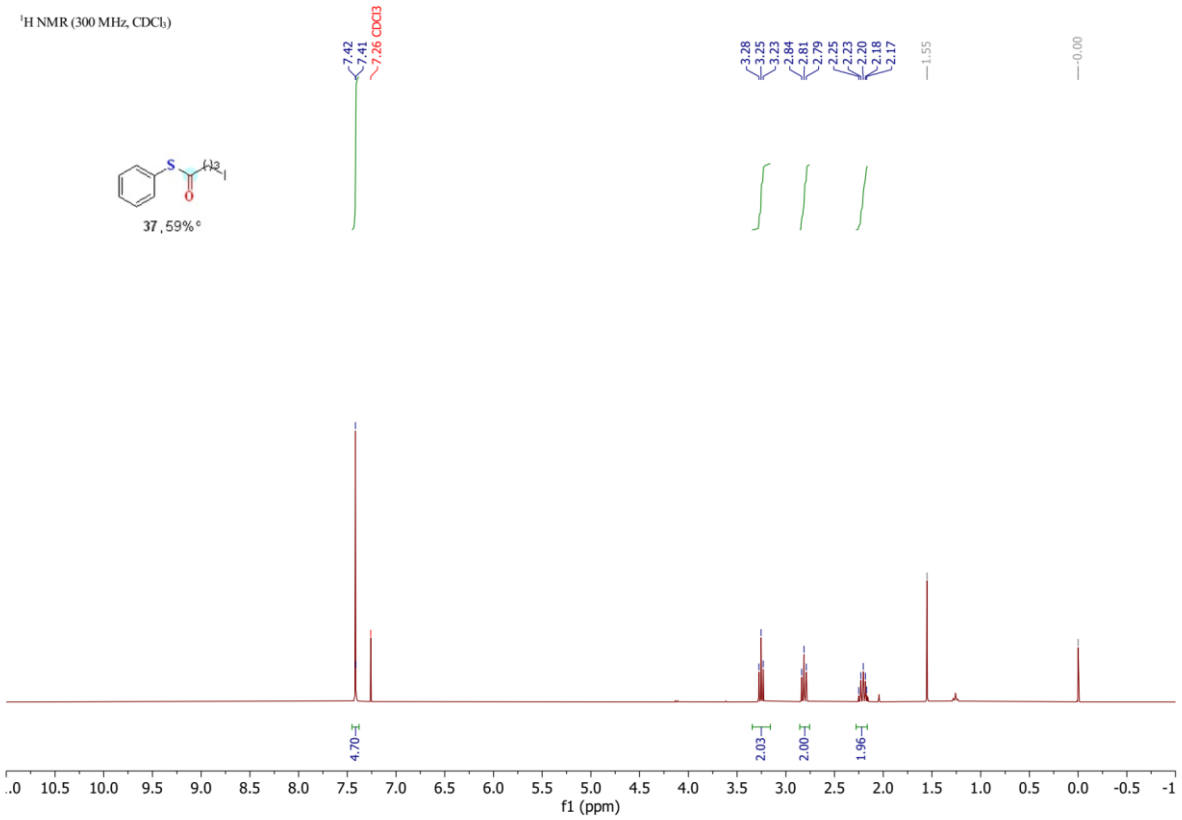

13C NMR (75 MHz, CDCl3)
197.27
153.72
153.13
134.42
129.26
129.11
127.83
115.40
114.61
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
68.17
55.68
43.49
28.99
25.47
25.25
OPMP
34 , 89% °
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

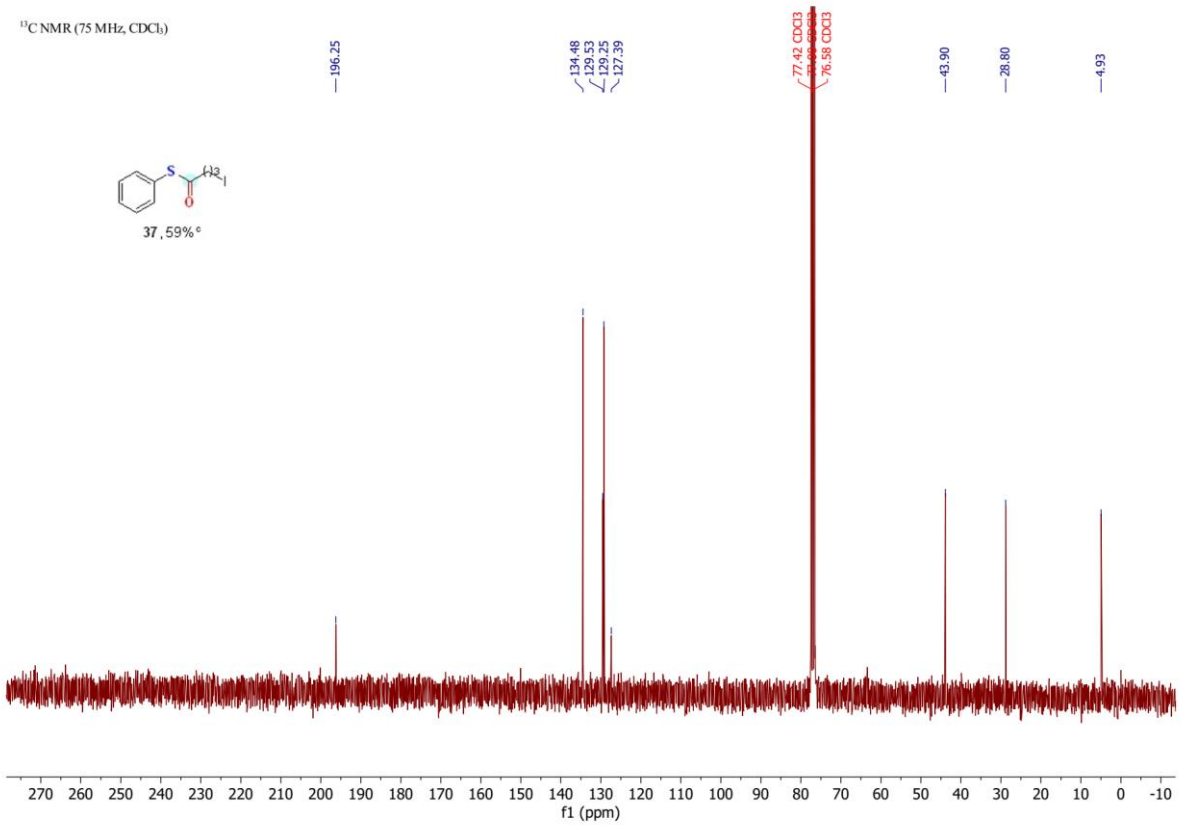

¹H NMR (300 MHz, CDCl₃)
7.41
7.40
7.40
7.39
7.38
7.34
7.34
7.33
7.31
7.31
7.30
4.50
3.49
3.47
3.45
2.68
2.66
2.63
1.76
1.76
1.73
1.71
1.67
1.65
1.64
1.62
1.58
1.51
1.50
1.49
1.48
1.46
1.45
1.43
0.00
OBn
35, 69% c
4.83
5.14
2.19
2.13
2.00
4.70
2.26
f1 (ppm)

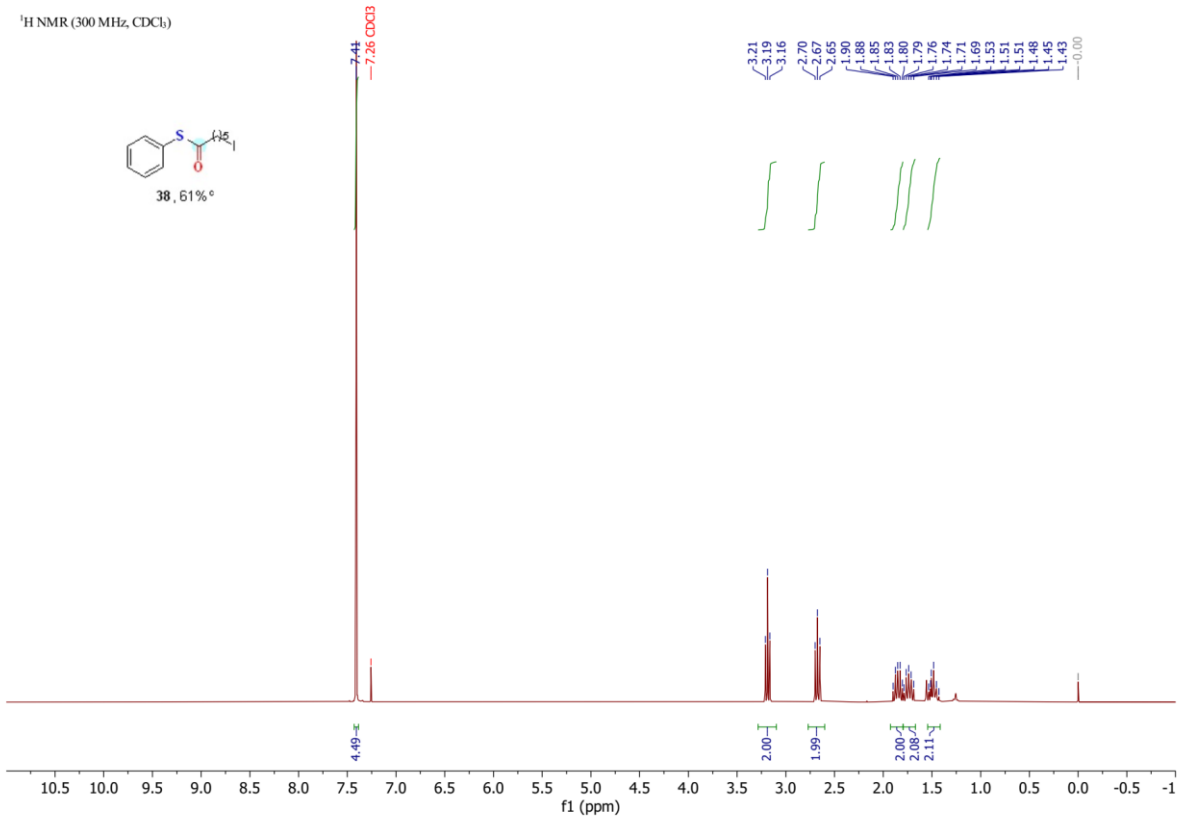

¹³C NMR (75 MHz, CDCl₃)
197.38
138.53
134.44
129.26
129.12
128.33
127.59
127.49
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
72.87
69.99
43.56
29.36
25.59
25.34
OBn
35, 69% c
f1 (ppm)

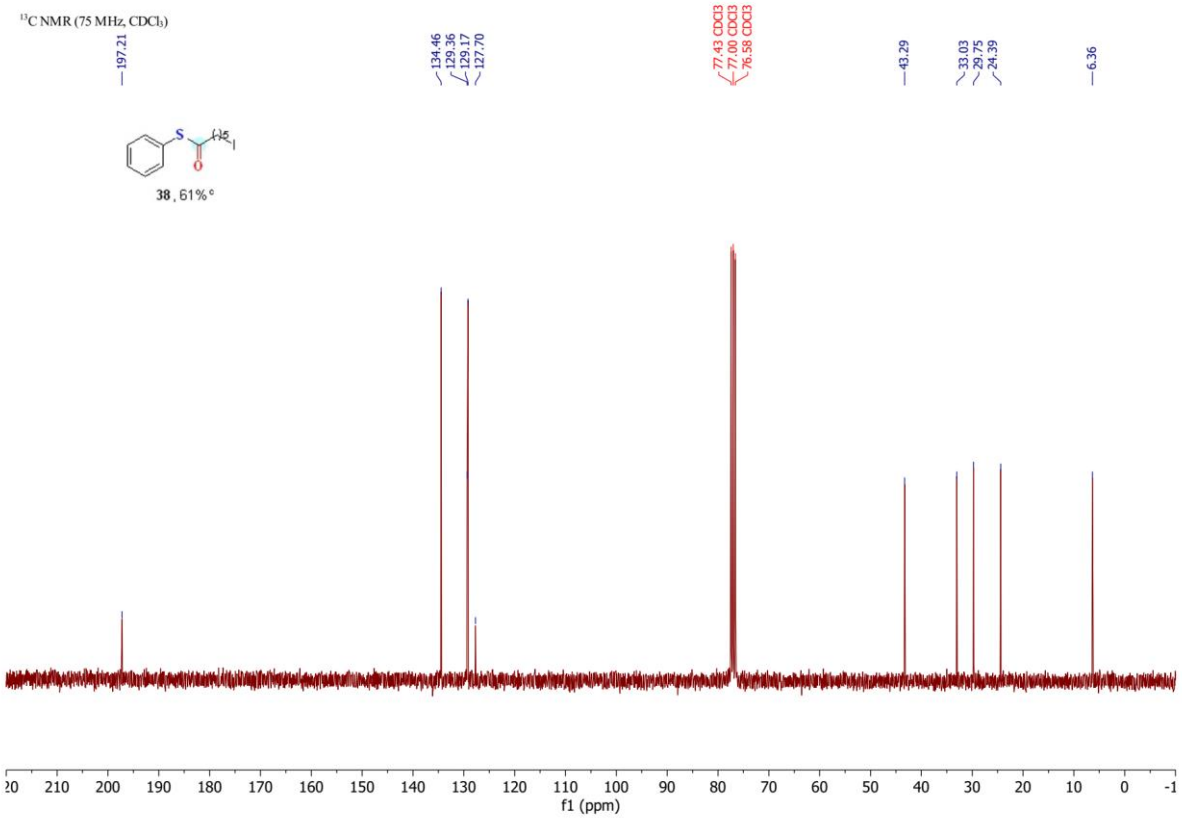

^{1}H NMR (300 MHz, CDCl$_3$)
36 , 54% ^{c}
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
36 , 54% ^{c}
f1 (ppm)

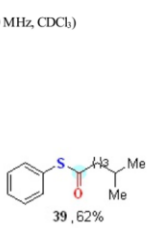

^{1}H NMR (300 MHz, CDCl$_3$)
7.42
7.41
7.26 CDCl3
3.28
3.25
3.23
2.84
2.81
2.79
2.25
2.23
2.20
2.18
2.17
1.55
0.00
37, 59%
4.70
2.03
2.00
1.96
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
196.25
134.48
129.53
129.25
127.39
77.42 CDCl3
76.58 CDCl3
43.90
28.80
4.93
37, 59%
f1 (ppm)


^{1}H NMR (300 MHz, CDCl$_3$)
7.44
7.26 CDCl3
3.21
3.19
3.16
2.70
2.67
2.65
1.90
1.88
1.85
1.83
1.80
1.79
1.76
1.74
1.71
1.69
1.53
1.51
1.51
1.48
1.45
1.43
0.00
38, 61%
4.49
2.00
1.99
2.00
2.08
2.11
f1 (ppm)

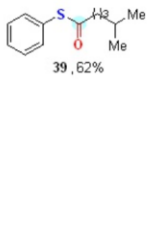

^{13}C NMR (75 MHz, CDCl$_3$)
197.21
134.46
129.36
129.17
127.70
77.43 CDCl3
77.00 CDCl3
76.58 CDCl3
43.29
33.03
29.75
24.39
6.36
38, 61%
f1 (ppm)

^{1}H NMR (300 MHz, $CDCl_3$)

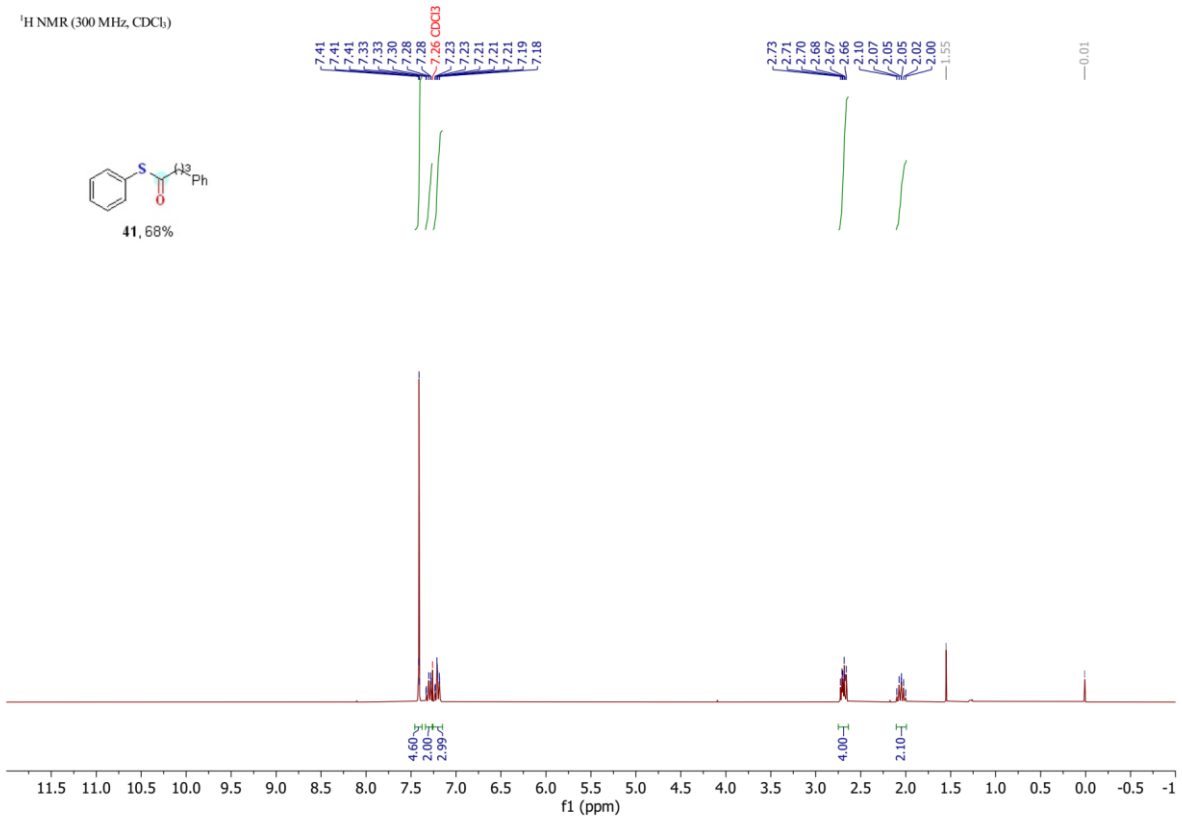


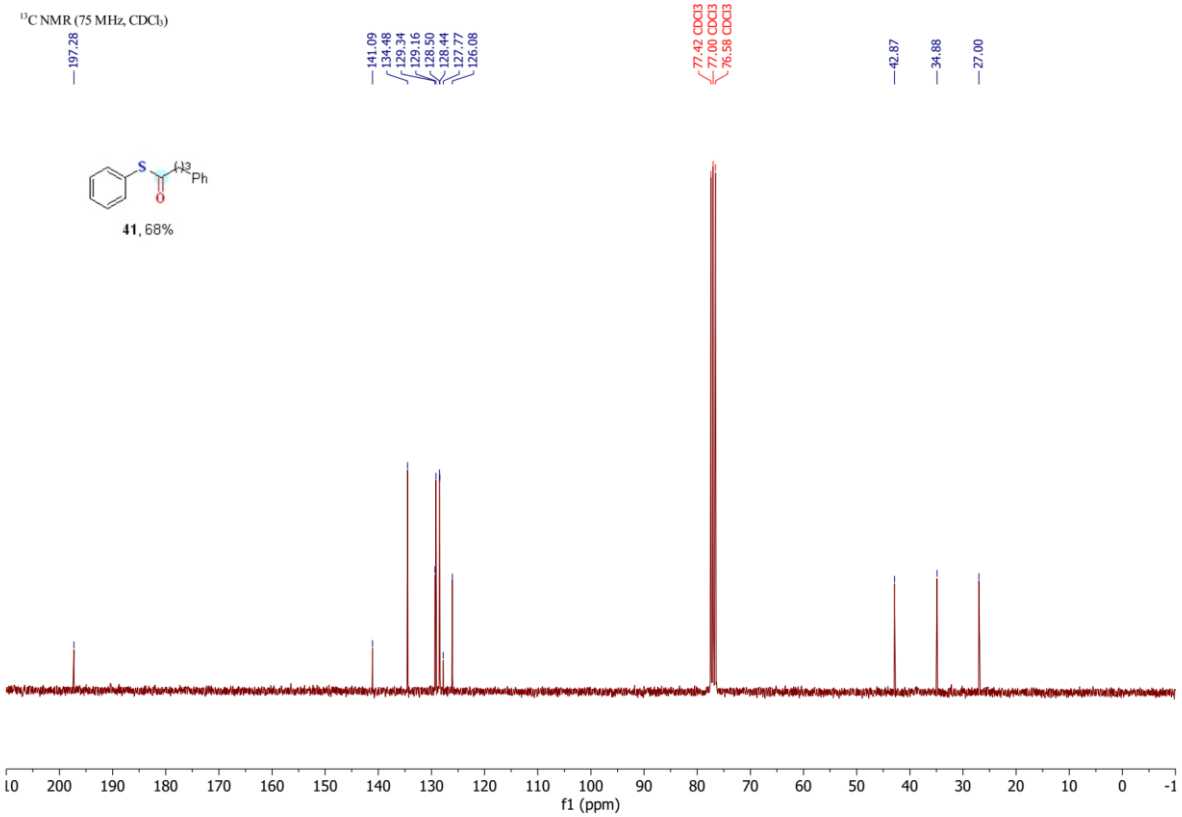
39, 62%

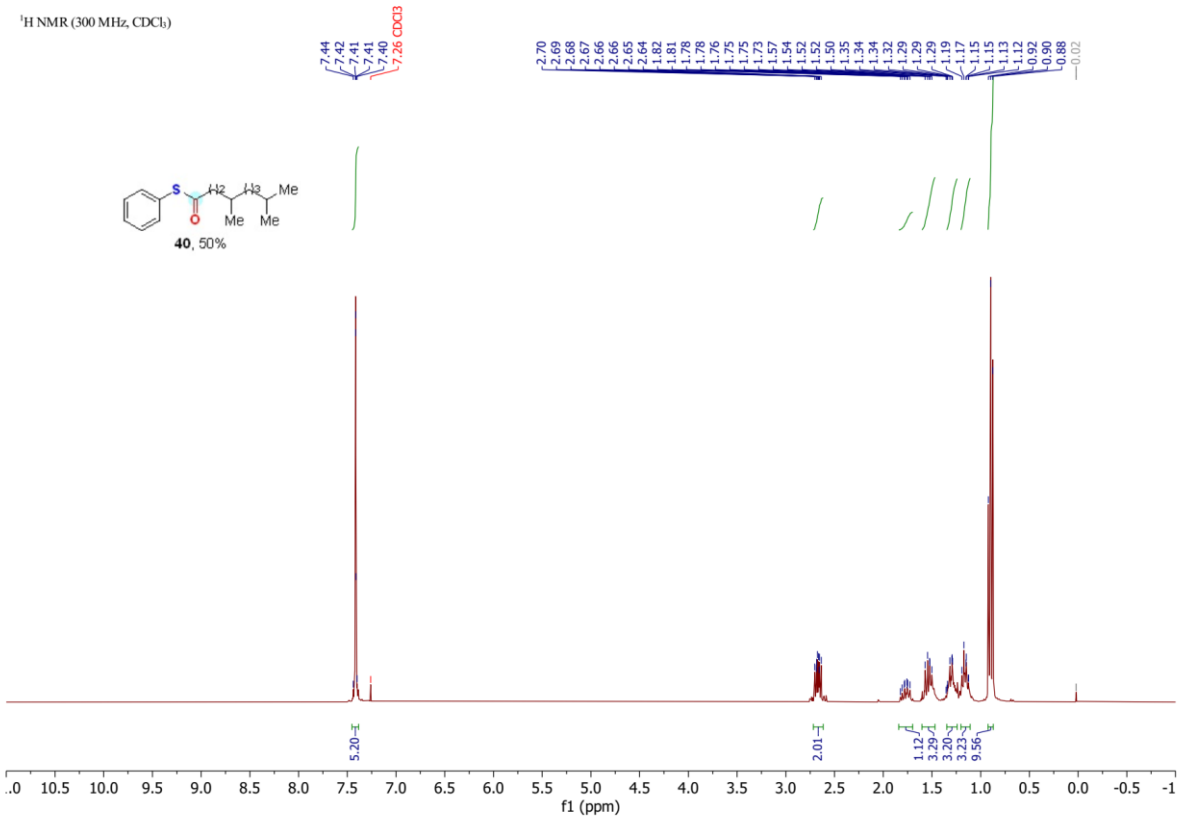
^{13}C NMR (75 MHz, $CDCl_3$)

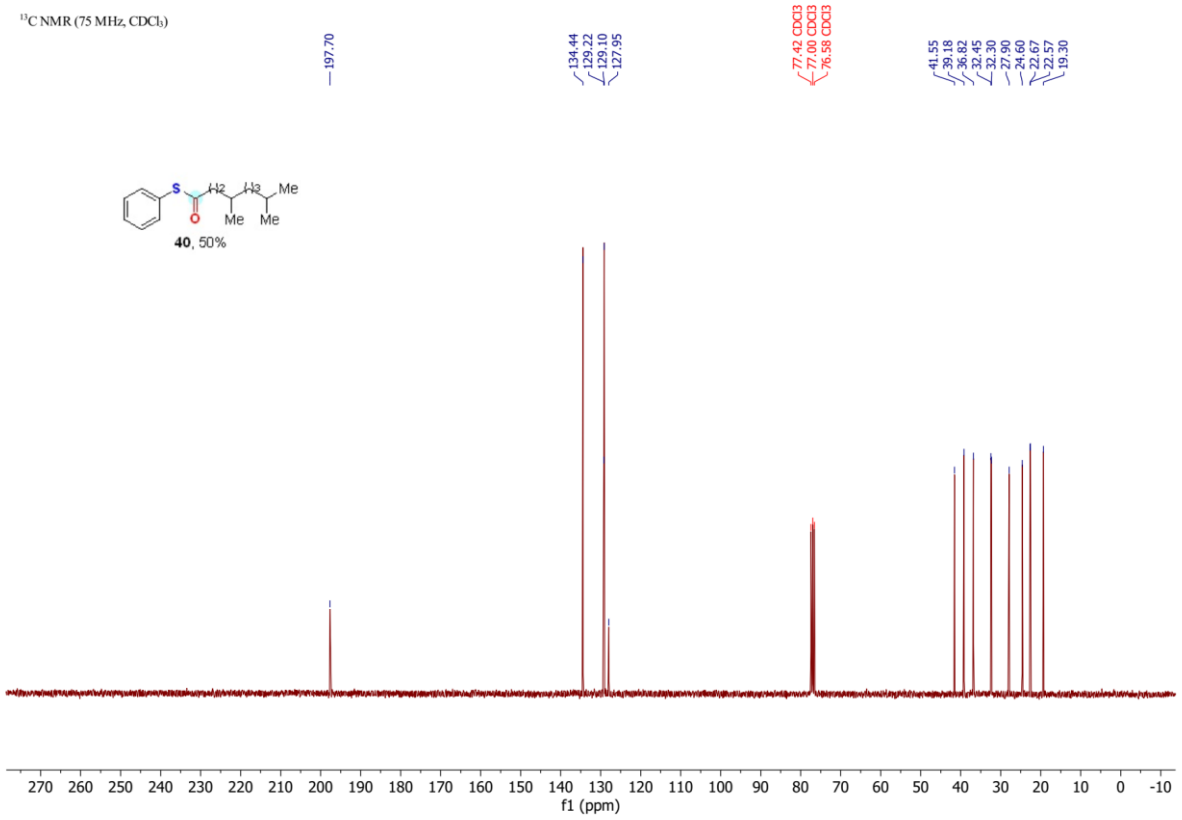


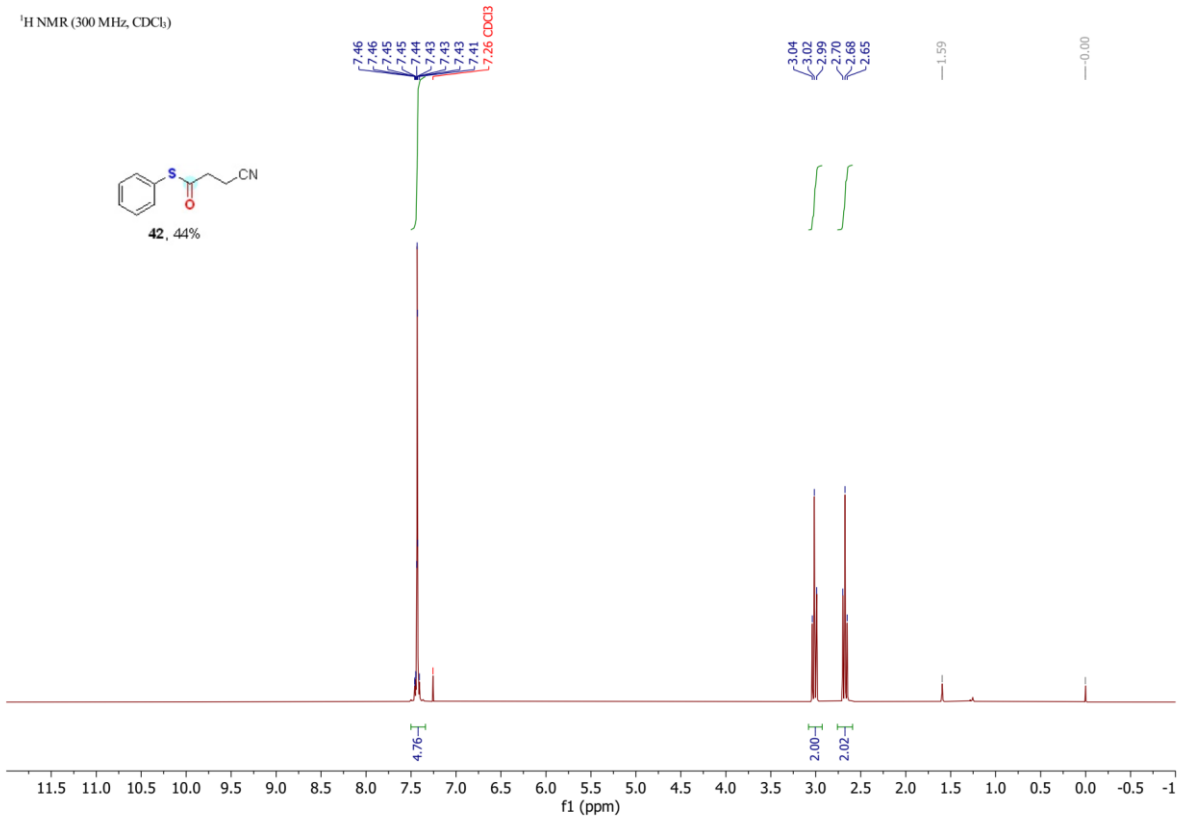
39, 62%

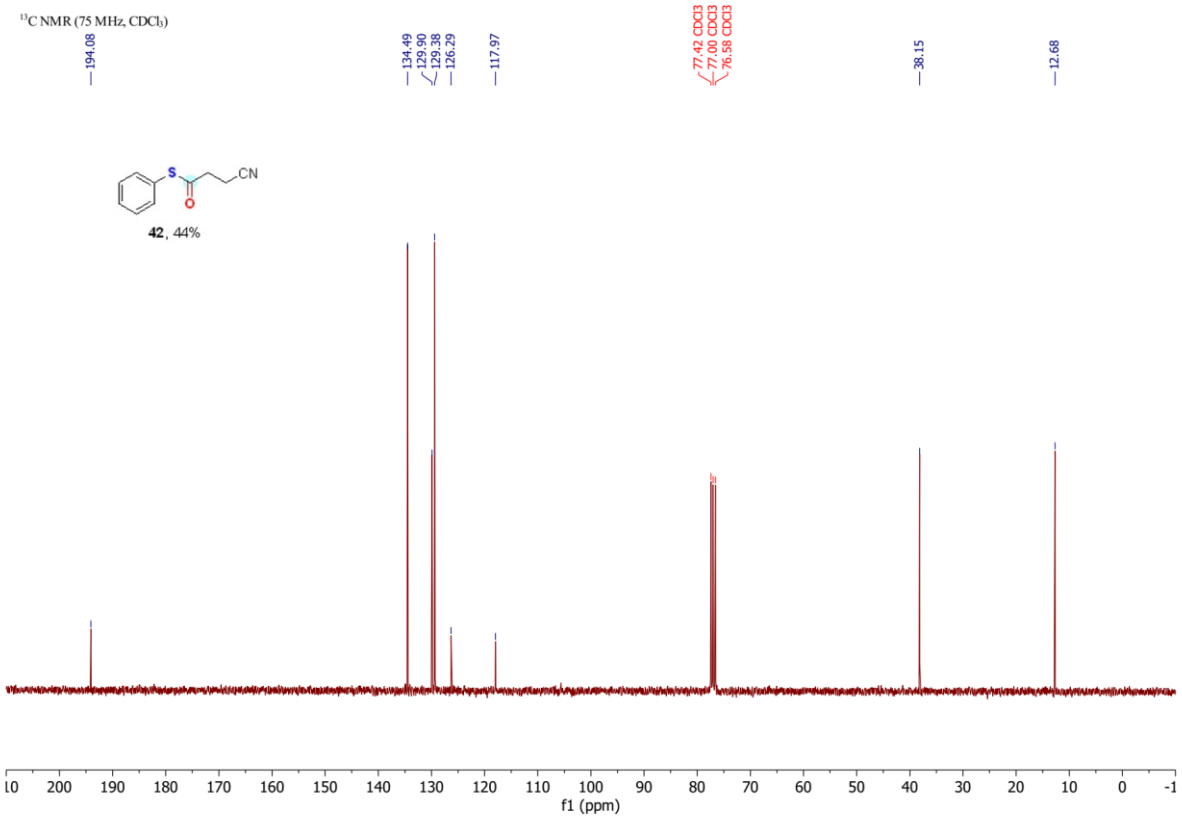

^{1}H NMR (300 MHz, CDCl$_3$)
7.41
7.41
7.41
7.33
7.30
7.28
7.26 CDCl3
7.23
7.23
7.21
7.21
7.21
7.19
7.18
2.73
2.71
2.70
2.68
2.67
2.66
2.10
2.07
2.05
2.05
2.02
2.00
1.55
0.01
Ph
41, 68%
4.60
2.00
2.99
4.00
2.10
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

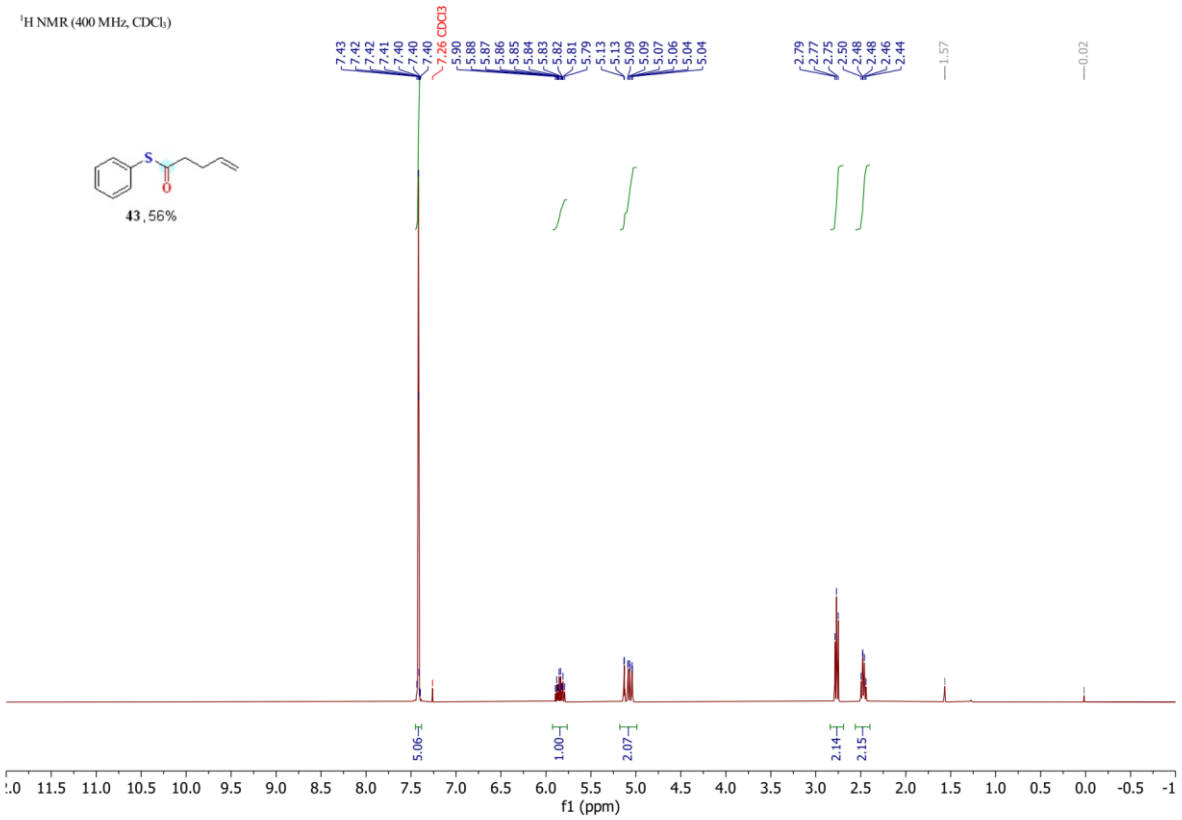

^{13}C NMR (75 MHz, CDCl$_3$)
197.28
141.09
134.48
129.34
129.16
128.50
128.44
127.77
126.08
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
42.87
34.88
27.00
Ph
41, 68%
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

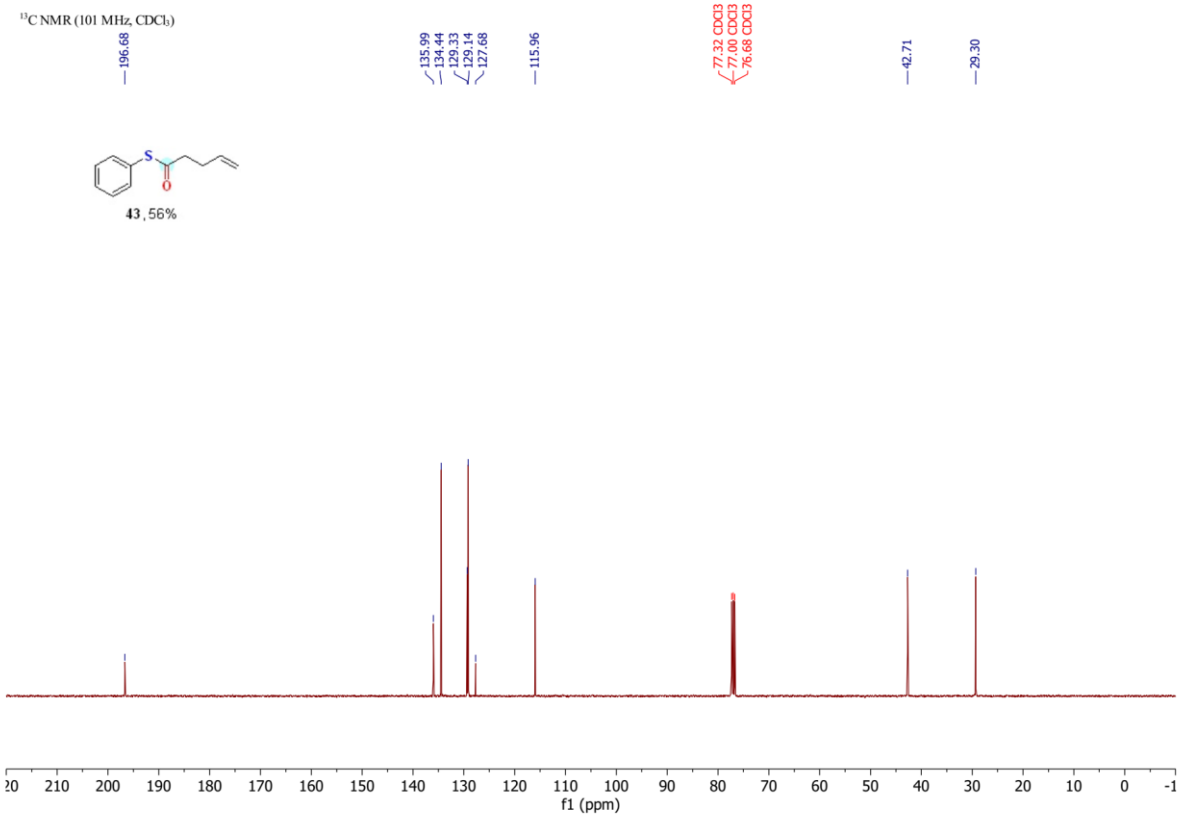

^{1}H NMR (300 MHz, CDCl$_3$)
7.44
7.42
7.41
7.41
7.40
7.26 CDCl3
2.70
2.69
2.68
2.67
2.66
2.66
2.65
2.64
1.82
1.81
1.78
1.78
1.76
1.75
1.75
1.73
1.57
1.54
1.52
1.52
1.50
1.35
1.34
1.34
1.32
1.29
1.29
1.29
1.19
1.17
1.15
1.15
1.13
1.12
0.92
0.90
0.88
0.02
Me
Me
Me
40, 50%
5.20
2.01
1.12
3.29
3.20
3.23
9.56
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
197.70
134.44
129.22
129.10
127.95
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
41.55
39.18
36.82
32.45
32.30
27.90
24.60
22.67
22.57
19.30
Me
Me
Me
40, 50%
f1 (ppm)


^{1}H NMR (300 MHz, CDCl$_3$)
7.46
7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.41
7.26 CDCl3
3.04
3.02
2.99
2.70
2.68
2.65
1.59
0.00
S
CN
O
42, 44%
4.76
2.00
2.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


^{13}C NMR (75 MHz, CDCl$_3$)
194.08
134.49
129.90
129.38
126.29
117.97
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
38.15
12.68
S
CN
O
42, 44%
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


^{1}H NMR (400 MHz, CDCl$_3$)
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.26 CDCl3
5.90
5.88
5.87
5.86
5.85
5.84
5.83
5.82
5.81
5.79
5.13
5.09
5.09
5.07
5.06
5.04
5.04
2.79
2.77
2.75
2.50
2.48
2.48
2.46
2.44
1.57
0.02
43, 56%
5.06
1.00
2.07
2.14
2.15
f1 (ppm)


^{13}C NMR (101 MHz, CDCl$_3$)
196.68
135.99
134.44
129.33
129.14
127.68
115.96
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
42.71
29.30
43, 56%
f1 (ppm)