Supplementary Information

For

Visible-light induced direct C(sp^3)-H bond disulfidation of saturated *N*-heterocycles through a hydrogen atom transfer (HAT) process

Junlei Wang[1, †, *], Guocheng Gao[1, †], Chengcheng Shi[2], Han Gao[3], Ji Luo[1], Guofen Wei[1], Daohai Zhang[1], Hongqing Li[1], Tonghao Yang[1, *] and Binbin Huang[4, *]

1. School of Chemical Engineering, Guizhou Minzu University, Guiyang 550000, China.

E-mail: junleiwang@gzmu.edu.cn; 1154067753@qq.com.

2. State Key Laboratory of Urban Water Resource and Environment, School of Science, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China.

3. Shanghai Spaceflight Precision Machinery Institute, Shanghai 201600, China.

4. College of Arts and Sciences & College of Education for the Future, Beijing Normal University, Zhuhai 519087, China.

E-mail: binbinhuang@bnu.edu.cn.

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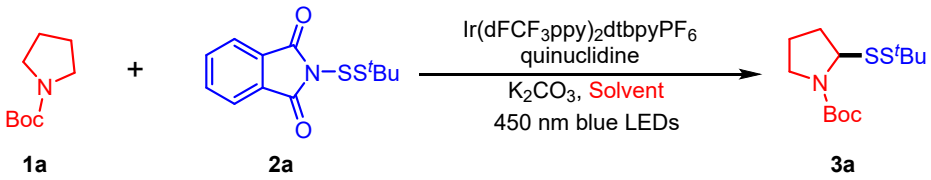
1. General Information

All of reactions were performed under an ambient temperature, magnetically stirred, and monitored by thin-layer chromatography (TLC) using Qingdao Puke Separation Materials Co., Ltd TLC plates pre-coated with 250 um thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. All of the manipulations were carried out using oven-dried glassware, including standard Schlenk techniques. All of the reagents were purchased from Alfa, Energy-Chemical or Sigma-Aldrich and used without further purification. Solvents were purified according to the method of Grubbs.[1] ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AV-400 (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz, ^{19}F NMR at 376 MHz) spectrometers using tetramethylsilane (TMS) as internal standard. ^{1}H and ^{19}F multiplicities are indicated as follows: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), quartet (q), multiplet (m), and broad resonance (br). Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). High resolution massspectra (HRMS) were collected on Bruker Esquire LC mass spectrometer using electrospray ionization. Flash column chromatography was carried out on silica gel (particle size 300-400 mesh) and eluted with petroleum/ethyl acetate.

2. Optimization of reaction conditions.

Table S1. Solvent Screening.[a,b]

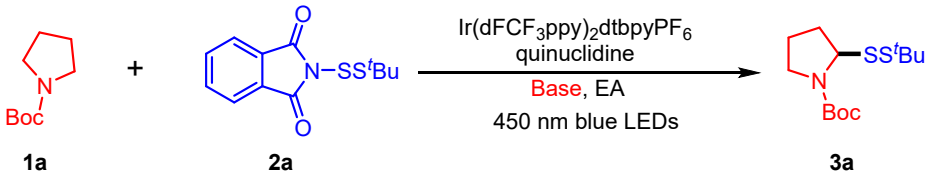


1a **2a** **3a**

Entry	Photocatalyst	Additive	Base	Solvent	Conversion(%)	Y(%)[b]
1	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	DCM	100%	12%
2	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	DCE	100%	14%
3	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	THF	100%	0
4	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	DMF	100%	23%
5	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	DMSO	100%	31%
6	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	EA	100%	46%
7	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	1,4-Dioxane	0	0
8	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	DMA	0	0
9	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	CF$_3$CH$_2$OH	0	0
10	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	CH$_3$OH	0	0
11	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	Acetone	100%	35%
12	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	PhCF$_3$	100%	33%
13	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	CHCl$_3$	100%	18%
14	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	HFIP	100%	16%
15	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	CCl$_4$	0	0
16	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	K$_2$CO$_3$	NMP	100%	0

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), quinuclidine (20 mol%), K$_2$CO$_3$ (2 equiv.), solvent (1 mL), room temperature, N$_2$ atmosphere, 2*12 W blue LEDs (450 nm), [b]isolated yields are shown.

Table S2.Base Screening.[a,b]

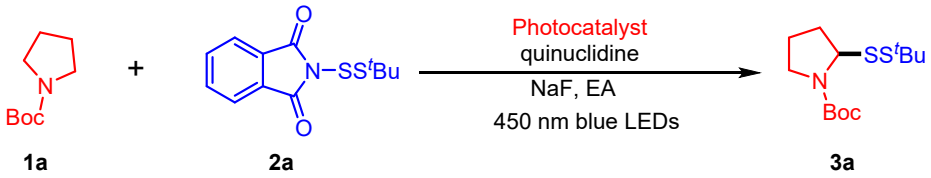


1a **2a** **3a**

Entry	Photocatalyst	Additive	Base	Solvent	Conversion(%)	Y(%)[b]
1	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	DIPEA	EA	0	0
2	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	Et_3N	EA	0	0
3	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	Na_2CO_3	EA	100%	49%
4	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	HCO_2Na	EA	100%	36%
5	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	Cs_2CO_3	EA	100%	15%
6	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	EA	100%	54%
7	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	$NaHCO_3$	EA	100%	36%
8	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaOH	EA	100%	23%
9	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	C_2H_5ONa	EA	100%	18%
10	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	DABCO	EA	100%	0
11	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	CsF	EA	100%	27%
12	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	Na_2HPO_4	EA	100%	31%
13	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	Py	EA	0	0
14	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	KF	EA	100%	50%
15	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	$(NH_4)_2CO_3$	EA	100%	29%

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), quinuclidine (20 mol%), Base (2 equiv.), EA (1 mL), room temperature, N_2 atmosphere, 2*12 W blue LEDs (450 nm), [b]isolated yields are shown.

Table S3. Photocatalyst Screening.[a,b]

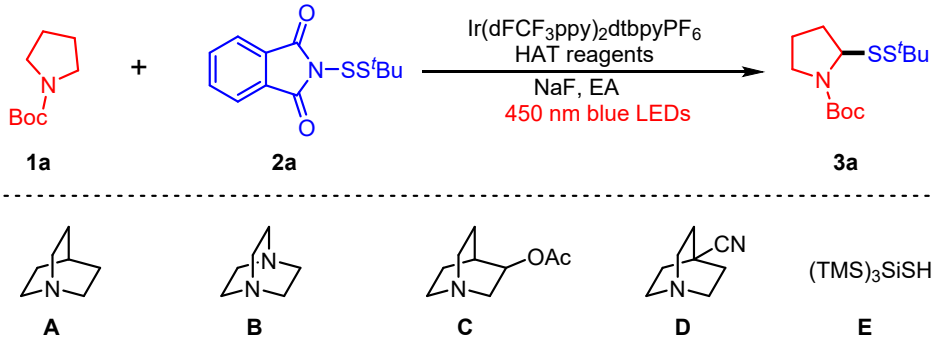


1a **2a** **3a**

Entry	Photocatalyst	Additive	Base	Solvent	Conversion(%)	Y(%)[b]
1	$Ir(dFCF_3ppy)_2bpyPF_6$	quinuclidine	NaF	EA	100%	38%
2	$Ir(dFCF_3ppy)_2dtbpyPF_6$	quinuclidine	NaF	EA	100%	54%
3	$Ir(dFppy)_2dtbpyPF_6$	quinuclidine	NaF	EA	100%	46%
4	4Cz-IPN	quinuclidine	NaF	EA	100%	38%
5	$Ir(dFppy)_2bpyPF_6$	quinuclidine	NaF	EA	100%	48%
6	*fac*-$Ir(dFppy)_3$	quinuclidine	NaF	EA	0	0
7	EosinY	quinuclidine	NaF	EA	0	0
8	$Ru(bpy)_3Cl_2$	quinuclidine	NaF	EA	0	0

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), PC (1 mol%), quinuclidine (20 mol%), NaF (2 equiv.), EA (1 mL), room temperature, N_2 atmosphere, 2*12 W blue LEDs (450 nm), [b]isolated yields are shown.

Table S4. Screening of HAT reagents.[a,b]



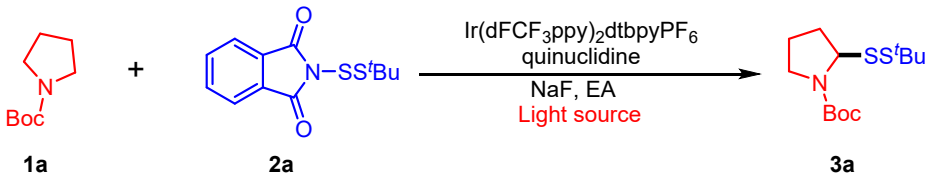
1a **2a** **3a**

A **B** **C** **D** **E**

Entry	Photocatalyst	HAT reagent	Base	Wavelength	Conversion(%)	Y(%)[b]
1	$Ir(dFCF_3ppy)_2dtbpyPF_6$	A	NaF	450nm	100%	54
2	$Ir(dFCF_3ppy)_2dtbpyPF_6$	B	NaF	450nm	100%	0
3	$Ir(dFCF_3ppy)_2dtbpyPF_6$	C	NaF	450nm	100%	trace
4	$Ir(dFCF_3ppy)_2dtbpyPF_6$	D	NaF	450nm	100%	0
5	$Ir(dFCF_3ppy)_2dtbpyPF_6$	E	NaF	450nm	100%	0
6	$Ir(dFCF_3ppy)_2dtbpyPF_6$	F	NaF	450nm	100%	0

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1 mol%), additive (2 equiv.), solvent (1 mL), room temperature, N_2 atmosphere, 450 nm blue LEDs, [b]isolated yields are shown.

Table S5. Light Screening.[a,b]

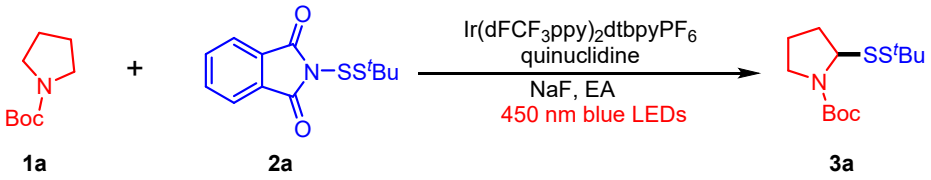


1a **2a** **3a**

Entry	Photocatalyst	Additive	Base	Wavelength	Conversion(%)	Y(%)[b]
1	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	390nm	100%	38
2	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	405nm	100%	40
3	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	425nm	100%	46
4	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	450nm	100%	54
5	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	460nm	100%	48
6	Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$	quinuclidine	NaF	490nm	100%	10

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), quinuclidine (20 mol%), NaF (2 equiv.), EA (1 mL), room temperature, N_2 atmosphere, blue LEDs (with different wavelength), [b]isolated yields are shown.

Table S6. The ratio of reaction partner Screening.[a,b]

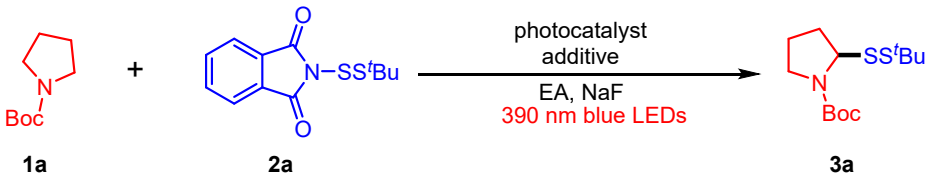


1a **2a** **3a**

Entry	The ratio of **1a**:**2a**	Additive	Base	Wavelength	Conversion(%)	Y(%)[b]
1	2:1	quinuclidine	NaF	450nm	100%	54
2	1.5:1	quinuclidine	NaF	450nm	100%	35
3	1:1.2	quinuclidine	NaF	450nm	100%	47
4	1:1.5	quinuclidine	NaF	450nm	100%	52
5	1:2	quinuclidine	NaF	450nm	100%	48

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), additive (2 equiv.), solvent (1 mL), room temperature, N_2 atmosphere, 450 nm blue LEDs, [b]isolated yields are shown.

Table S7. Screening of photocatalyst through LMCT.[a,b]

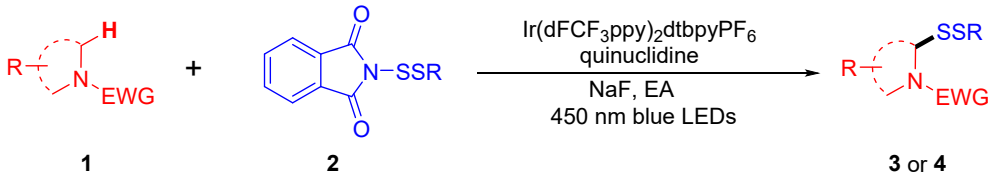


1a **2a** **3a**

Entry	Photocatalyst	Additives	Base	Wavelength	Y(%)[b]
1	$FeCl_3$	LiCl	NaF	390 nm	0
2	$Fe(acac)_3$	LiCl	NaF	390 nm	0
3	$FeBr_3$	LiCl	NaF	390 nm	0
4	$FeCl_2$	LiCl	NaF	390 nm	0
5	$CeCl_3$	LiCl	NaF	390 nm	0
6	CuCl	LiCl	NaF	390 nm	0
7	$CuCl_2$	LiCl	NaF	390 nm	0

[a]Reaction conditions: **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), photocatalyst (1 mol%), additive (2 equiv.), EA (1 mL), room temperature, N_2 atmosphere, 390 nm blue LEDs, [b]isolated yields are shown.

3. General Procedure for Disulfidation Reactions

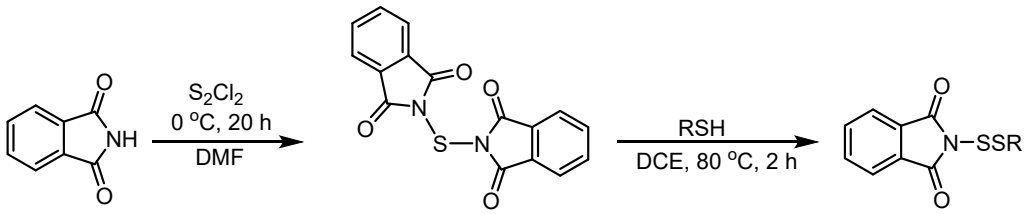


1 **2** **3** or **4**

In a 10 mL oven-dried Schlenk tube with a stirring bar**, 1** (0.1 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1.0 mmol%), quinuclidine (20 mmol%) were dissolved in Ethyl acetate (EA) (1.0 mL). The Schlenk tube was cooled to -78 °C and degassed with nitrogen for 3 times. And then, the reaction was exposed to 2 *12 W blue LEDs (450 nm) at room temperature. The reaction was stopped until the starting material completely consumed (monitored by TLC). Subsequently, the solvent was removed under vacuum and purified by flash column chromatography on silica gel with petroleum ether (PE) and ethyl acetate (EA), affording the corresponding disulfidation products.

4. General procedure for the synthesis of substrates.

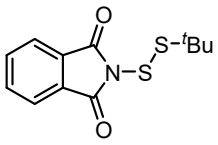
4.1 *N*-perthiophthalimide derivatives (Harpp reagents) Synthesis



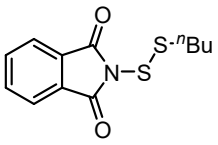
Step A: N-Perthiophthalimides was synthesized according to the previous reported literature. Phthalimide (7.36 g, 50 mmol) was dissolved in anhydrous DMF (40 mL) at 0 ℃, sulfur monochloride (4 mL, 50 mmol) was added dropwise to the reaction mixture. After that, the reaction mixture was continuously stirred at 0 ℃ for 20 h. When the starting material was completely consumed, the precipitate was filtered and washed with Et_2O, affording the corresponding *N,N'*- thiobisphthalimide as a white solid.

Step B: N,N'-Thiobisphthalimide (3.4 g, 10.5 mmol, 1.5 equiv.) was dissolved in DCM (70 mL). thiol (7 mmol, 1 equiv) was then successively added. The reaction mixture was stirred at 80 ℃ until the starting material was completely consumed. The reaction was cooled to room temperature and filtered through a plug of celite. The crude mixture was concentrated under reduced pressure and purified by column chromatography (with hexane/EtOAc or hexane/DCM as eluent), providing *N*-perthiophthalimide derivatives (Harpp reagents) **2a-2g**[1-2].

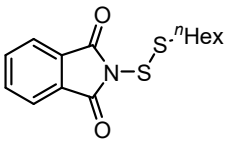
Scope of *N*-perthiophthalimide derivatives (Harpp reagents) 2a-2i.



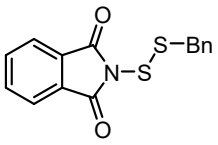
2a



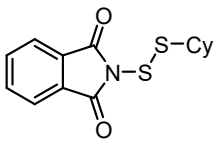
2b



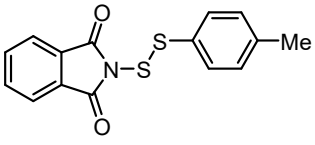
2c



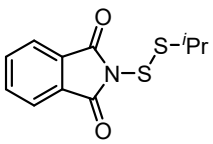
2d



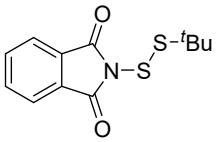
2e



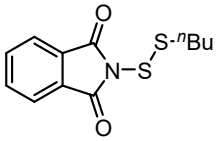
2f



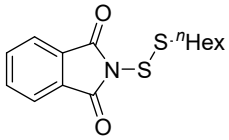
2g



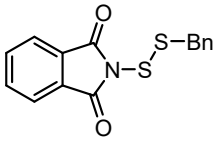
2a, white solid (85%).**^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.91 (dd, J = 5.4, 3.1 Hz, 2H), 7.77 (dd, J = 5.4, 3.1 Hz, 2H), 1.40 (s, 9H).The ^{1}H NMR was consistent with the literature report[1].



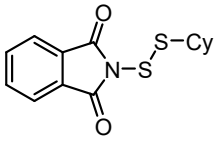
2b, white solid (80%).**^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.93 (dd, J = 5.6, 3.1 Hz, 2H), 7.79 (dd, J = 5.6, 3.1 Hz, 2H), 3.06 (t, J = 7.4 Hz, 2H), 1.77 (p, J = 7.4 Hz, 2H), 1.43 (h, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H).The ^{1}H NMR was consistent with the literature report[1].



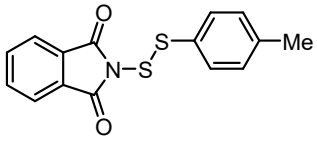
2c, colorless liquid (53%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.92 (dd, J = 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H), 1.77 (p, J = 7.4 Hz, 2H), 1.37 (q, J = 7.1 Hz, 2H), 1.28 (tt, J = 7.9, 4.1 Hz, 4H), 0.89 - 0.83 (m, 3H). The ^{1}H NMR was consistent with the literature report[2].



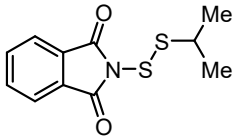
2d, white solid (75%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.88 (dd, J = 5.5, 3.1 Hz, 2H), 7.74 (dd, J = 5.5, 3.1 Hz, 2H), 7.39-7.34 (m, 2H), 7.29-7.18 (m, 3H), 4.24 (s, 2H). The ^{1}H NMR was consistent with the literature report[1].



2e, white solid (80%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.92 (dd, J = 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 3.14 (dq, J = 10.7, 6.4, 5.1 Hz, 1H), 2.16 (dt, J = 10.0, 5.1 Hz, 2H), 1.79 (h, J = 4.7 Hz, 2H), 1.66 – 1.60 (m, 1H), 1.45 – 1.31 (m, 4H), 1.26 (ddd, J = 15.5, 8.0, 3.6 Hz, 1H). The ^{1}H NMR was consistent with the literature report[1].



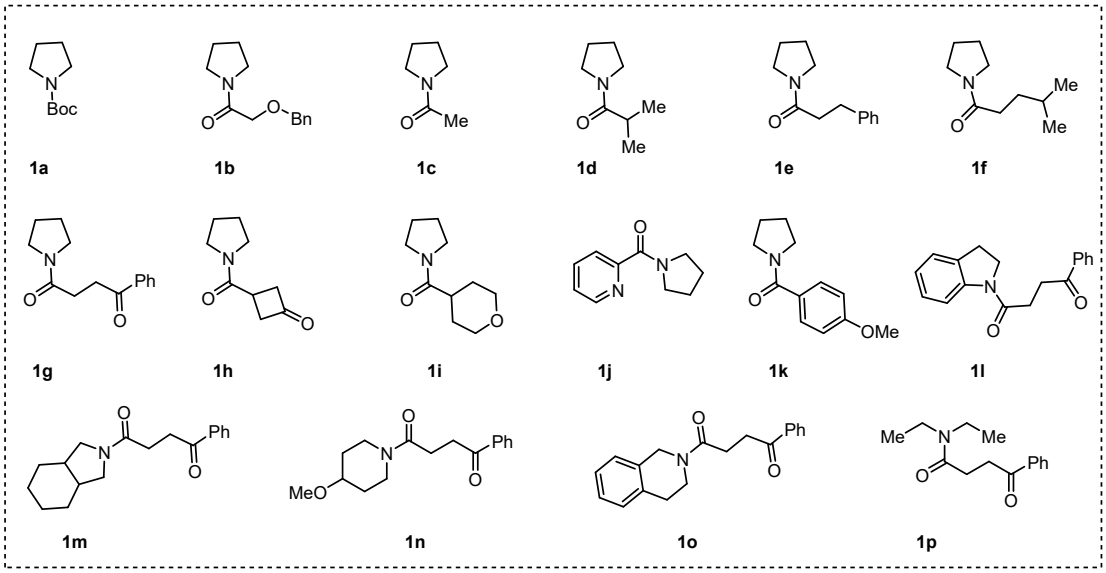
2f, white solid (80%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.89 (ddd, J = 17.8, 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.7, 3.1 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). The ^{1}H NMR was consistent with the literature report[1].



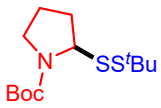
2g, white solid (64%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ_H 7.92 (dd, J = 5.5, 3.1 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 3.36 (p, J = 6.8 Hz, 1H), 1.39 (d, J = 6.8 Hz, 6H). **^{13}C NMR (400 MHz, $CDCl_3$)**: δ_C 167.9, 134.9, 132.4, 124.1, 43.2, 22.5.

4.2 Scope of amides.

General procedure for the synthesis of amides was according to our previous report.[3-5]



5. Product Characterization



3a

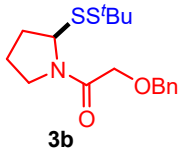
The desired product was provided according to the general procedure using **1a** (34.2 mg, 0.20 mmol, 2.0 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (30:1-10:1) to give **3a** in 54% yield, as a colorless oil, 15.7 mg.

^{1}H NMR (400 MHz,CDCl$_3$): δ_H 5.09 (d, J = 5.8 Hz, 0.38H), 4.95 (d, J = 5.1 Hz, 0.62H), 3.54-3.40 (m, 1H), 3.35-3.23 (m, 1H), 2.39-2.25 (m, 1H), 2.20 -2.04 (m, 2H), 1.91-1.81 (m, 1H), 1.51 (s, 5.7H), 1.46 (s, 3.3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, CDCl$_3$, major): δ_C 153.8, 80.7, 68.0, 47.9, 46.7, 32.6 , 30.2, 21.7.

^{13}C NMR (101 MHz, CDCl$_3$, minor): δ_C 153.8, 80.1, 68.2, 47.9, 47.0, 32.0, 28.6, 22.8.

HRMS (ESI): calcd for $C_{13}H_{26}S_2NO_2^+$, $(M+H)^+$, 292.1399, found, 292.1400.



3b

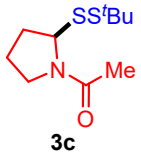
The desired product was provided according to the general procedure using **1b** (43.8 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3b** in 74% yield, as a colorless oil, 25.1 mg.

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.50-7.30 (m, 5H), 5.35 (d, J = 5.9 Hz, 0.5H), 5.05 (d, J = 4.8 Hz, 0.5H), 4.79-4.62 (m, 2H), 4.43 (q, J = 14.2 Hz, 1H), 4.13 (d, J = 14.3 Hz, 1H), 3.61 (dt, J = 18.1, 9.9 Hz, 1H), 3.42 (ddd, J = 46.0, 17.0, 9.2 Hz, 1H), 2.46-1.89 (m, 4H), 1.41 (s, 5H), 1.30 (s, 4H).

^{13}C NMR (101 MHz, CDCl$_3$, major): δ_C 168.7, 137.5, 128.6, 128.3, 128.09, 73.3, 69.5, 67.3, 48.2, 46.1, 33.2, 30.3, 20.5.

^{13}C NMR (101 MHz, CDCl$_3$, minor): δ_C 168.2, 137.5, 128.6, 128.2, 128.07, 73.6, 69.3, 67.4, 48.5, 46.6, 31.1, 30.2, 23.2.

HRMS (ESI): calcd for $C_{17}H_{26}S_2NO_2^+$, $(M+H)^+$, 340.1399, found, 340.1405.



3c

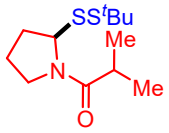
The desired product was provided according to the general procedure using **1c** (22.6 mg, 0.2 mmol, 1.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3c** in 43% yield, as a colorless oil, 10.0 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.28 (d, J = 6.0 Hz, 0.48H), 4.94 (d, J = 5.3 Hz, 0.52H), 3.60 (dd, J = 14.9, 5.3 Hz, 1H), 3.41 (ddd, J = 16.9, 13.9, 8.7 Hz, 1H), 2.55-2.27 (m, 3H), 2.24-2.14 (m, 1H), 2.12-1.86 (m, 3H), 1.38 (d, J = 11.1 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 169.9, 69.5, 48.2, 46.5, 33.1, 30.4, 23.0, 21.2.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 169.5, 67.1, 48.4, 47.9, 31.7, 30.2, 23.1, 22.8.

HRMS (ESI): calcd for $C_{10}H_{20}S_2NO^+$, $(M+H)^+$, 234.0981, found, 234.0976.



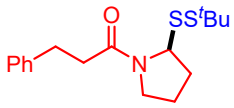
3d

The desired product was provided according to the general procedure using **1d** (28.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3d** in 40% yield, as a colorless oil, 10.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.25 (d, J = 6.0 Hz, 0.5H), 4.89 (d, J = 5.1 Hz, 0.41H), 3.63-3.46 (m, 1H), 3.42-3.23 (m, 1H), 2.53-2.23 (m, 2H), 2.09 (ddt, J = 10.2, 5.5, 3.7 Hz, 2H), 1.96-1.81 (m, 1H), 1.31 (d, J = 7.3 Hz, 9H), 1.01-0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.1, 171.5, 68.7, 67.1, 48.4, 48.3, 47.3, 46.5, 43.8, 33.1, 31.3, 30.4, 30.2, 25.8, 25.4, 23.1, 22.9, 22.9, 22.8, 21.0.

HRMS (ESI): calcd for $C_{12}H_{24}S_2NO^+$, $(M+H)^+$, 262.1294, found, 262.1299.



3e

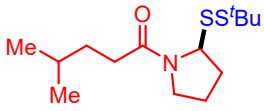
The desired product was provided according to the general procedure using **1e** (40.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3e** in 67% yield, as a colorless oil, 21.6 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83-7.67 (m, 1H), 7.22 (dd, J = 7.5, 3.4 Hz, 1H), 7.18-7.08 (m, 3H), 5.23 (d, J = 6.0 Hz, 0.52H), 4.67 (d, J = 5.7 Hz, 0.48H), 3.60-3.36 (m, 1H), 3.35-3.11 (m, 1H), 3.03 - 2.62 (m, 3H), 2.57-2.41 (m, 1H), 2.33-2.23 (m, 1H), 2.20-2.00 (m, 1H), 1.88 (qdd, J = 18.6, 12.7, 6.6 Hz, 2H), 1.33 (s, 4.75H), 1.23 (s, 4.25H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 171.2, 141.2, 134.4, 128.6, 128.6, 123.7, 68.5, 48.4, 47.2, 37.0, 32.9, 31.0, 30.2, 23.0.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 171.8, 141.3, 132.8, 128.7, 126.3, 123.7, 67.3, 48.2, 46.5, 36.8, 31.7, 31.4, 30.3, 21.0.

HRMS (ESI): calcd for $C_{17}H_{26}S_2NO^+$, $(M+H)^+$, 324.1250, found, 324.1244.



3f

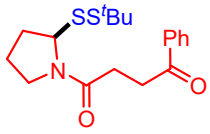
The desired product was provided according to the general procedure using **1f** (33.8 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3f** in 60% yield, as a colorless oil, 17.3 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.28 (d, J = 5.8 Hz, 0.5H), 4.96 (d, J = 4.8 Hz, 0.5H), 3.58 (t, J = 9.3 Hz, 1H), 3.49 – 3.27 (m, 1H), 2.78-2.59 (m, 0.5H), 2.52 – 2.39 (m, 1H), 2.37-2.10 (m, 3H), 2.09-1.94 (m, 1H), 1.89 (d, J = 5.8 Hz, 0.5H), 1.57 (dt, J = 22.1, 9.5 Hz, 3H), 1.37 (s, 9H), 0.92 (dd, J = 11.7, 5.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 172.9, 67.2, 48.4, 46.6, 34.1, 33.0, 32.9, 30.2, 27.9, 22.6, 22.5, 22.48.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 172.4, 68.8, 48.2, 47.2, 33.5, 33.1, 31.5, 30.4, 28.1, 23.0, 22.6, 21.0.

HRMS (ESI): calcd for $C_{14}H_{28}S_2NO^+$, $(M+H)^+$, 290.1607, found, 290.1600.



3g

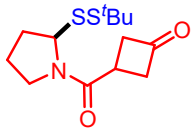
The desired product was provided according to the general procedure using **1g** (46.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3g** in 86% yield, as a colorless oil, 19.7 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.08 - 7.93 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (td, J = 7.7, 2.1 Hz, 2H), 5.29 (d, J = 6.0 Hz, 0.56H), 5.17 (d, J = 5.4 Hz, 0.44H), 3.71-3.39 (m, 3H), 3.28 (ddt, J = 18.1, 15.5, 6.0 Hz, 1H), 3.15-2.95 (m, 1H), 2.86-2.57 (m, 1H), 2.52-.18 (m, 2H), 2.17-1.86 (m, 2H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 198.9, 170.8, 136.8, 133.3, 128.7, 128.2, 67.3, 48.3, 47.3, 33.5, 31.4, 30.19, 28.7, 23.0.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 199.10, 171.4, 136.93, 133.2, 128.7, 128.2, 68.8, 48.2, 46.7, 33.9, 33.1, 30.4, 29.0, 21.1.

HRMS (ESI): calcd for $C_{18}H_{26}S_2NO_2^+$, $(M+H)^+$, 352.1399, found, 352.1393.

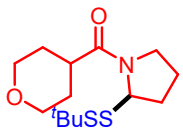


3h

The desired product was provided according to the general procedure using **1h** (33.4 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3h** in 45% yield, as a colorless oil, 12.9 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.34 (d, J = 6.0 Hz, 0.54H), 5.04 (d, J = 5.8 Hz, 0.46H), 3.75-3.60 (m, 2H), 3.59-3.16 (m, 5H), 2.56-1.87 (m, 4H), 1.41 (s, 4H), 1.38 (s, 5H).
^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 203.8, 172.5, 67.5, 51.4, 50.7, 48.3, 47.1, 33.3, 30.2, 27.2, 23.0.
^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 204.3, 171.6, 69.0, 52.6, 51.3, 48.5, 47.1, 31.4, 30.4, 27.1, 21.2.

HRMS (ESI): calcd for $C_{13}H_{21}S_2NaNO_2^+$, $(M+Na)^+$, 310.0906, found, 310.0910.

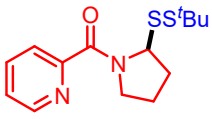


3i

The desired product was provided according to the general procedure using **1i** (36.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3i** in 54% yield, as a colorless oil, 16.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.32 (d, J = 5.5 Hz, 0.5H), 5.01 (d, J = 5.0 Hz, 0.5H), 4.05 (t, J = 14.5 Hz, 2H), 3.71-3.56 (m, 1H), 3.52-3.37 (m, 3H), 2.82 (dddd, J = 201.9, 14.8, 7.7, 3.5 Hz, 1H), 2.48 -2.30 (m, 1H), 2.23 (ddd, J = 18.7, 12.7, 7.0 Hz, 1H), 2.14-1.96 (m, 2H), 1.88 (ddd, J = 29.3, 17.5, 8.9 Hz, 3H), 1.64 (dd, J = 37.8, 13.5 Hz, 1H), 1.41-1.35 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 174.2, 68.7, 67.43, 67.2, 48.3, 46.7, 40.4, 33.3, 30.4, 29.4, 28.3, 20.95.
^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 173.3, 67.5, 67.4, 66.98, 48.3, 46.8, 40.1, 30.97, 30.1, 29.6, 29.1, 23.1.

HRMS (ESI): calcd for $C_{14}H_{16}S_2NO_2^+$, $(M+H)^+$, 304.1399, found, 304.1401.



3j

The desired product was provided according to the general procedure using **1j** (35.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3j** in 77% yield, as a colorless oil, 22.8 mg.

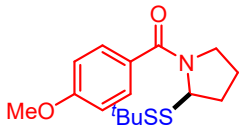
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.56 (dd, J = 12.9, 4.6 Hz, 1H), 8.02-7.70 (m, 2H), 7.35 (dt, J = 12.4, 6.3 Hz, 1H), 6.09 (d, J = 5.5 Hz, 0.64H), 5.53 (d, J = 5.3 Hz, 0.36H), 4.15-3.81 (m, 1H),

3.79-3.61 (m, 1H), 2.47-2.10 (m, 3H), 2.05-1.88 (m, 1H), 1.41 (d, J = 4.1 Hz, 3.2H), 1.05 (d, J = 4.1 Hz, 5.8H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 167.0, 154.4, 147.98, 137.1, 125.08, 125.02, 67.9, 47.6, 47.03, 32.39, 29.89, 20.72.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 166.5, 153.7, 148.00, 136.9, 125.1, 124.6, 68.4, 49.6, 48.32, 31.03, 30.2, 23.9.

HRMS (ESI): calcd for $C_{14}H_{21}S_2NO_2^+$, $(M+H)^+$,297.1090, found, 297.1091.



3k

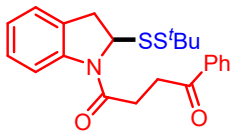
The desired product was provided according to the general procedure using **1k** (41.0 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3k** in 72% yield, as a colorless oil, 23.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.55 (d, J = 7.1 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 5.62 (s, 0.54H), 4.98 (s, 0.46H), 3.82 (s, 3H), 3.56 (m,2H), 2.25 (m, 3H), 1.92 (m, 1H), 1.54-1.25 (s, 5.6H), 1.06 (s, 3.4H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 170.8, 136.4, 129.9, 128.4, 127.1, 69.3, 49.5, 48.23, 48.0, 32.1, 29.8, 20.9.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 170.1, 136.9, 136.4, 128.4, 127.5, 66.6, 49.48, 48.2, 46.0, 31.3, 30.1, 23.9.

HRMS (ESI): calcd for $C_{16}H_{24}S_2NO_2^+$, $(M+H)^+$, 326.1243, found, 326.1236.



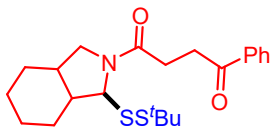
3l

The desired product was provided according to the general procedure using **1l** (55.8 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3l** in 33% yield, as a colorless oil, 13.2 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.19 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 1.7 Hz, 2H), 7.62-7.54 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.39 (d, J = 7.5 Hz, 1H), 7.30-7.23 (m, 1H), 7.06 (t, J = 7.5 Hz, 1H), 4.62 (dd, J = 7.5, 3.3 Hz, 1H), 4.46 (t, J = 5.4 Hz, 2H), 3.56 (dt, J = 18.6, 6.9 Hz, 1H), 3.38 (dt, J = 12.4, 6.4 Hz, 1H), 2.94 (dd, J = 6.1, 4.7 Hz, 2H), 1.38 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 198.8, 170.2, 143.1, 136.8, 133.3, 130.0, 129.9, 128.7, 128.3, 125.3, 123.95, 117.4, 69.9, 55.4, 50.8, 48.5, 33.3, 30.2.

HRMS (ESI): calcd for $C_{22}H_{26}S_2NO_2^+$, $(M+H)^+$,400.1399, found, 400.1390.



3m

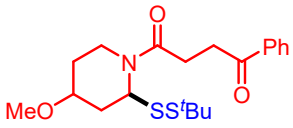
The desired product was provided according to the general procedure using **1m** (57.0 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3m** in 54% yield, as a colorless oil, 21.9 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.13-7.86 (m, 2H), 7.65-7.53 (m, 1H), 7.47 (dd, J = 10.2, 4.9 Hz, 2H), 4.93 (s, 0.54 H), 4.80 (s, 0.45H), 3.62-3.21 (m, 4H), 3.14-2.96 (m, 1H), 2.92-2.58 (m, 2H), 2.45 (ddd, J = 21.9, 11.0, 5.4 Hz, 1H), 1.75 (d, J = 14.1 Hz, 1H), 1.58 (dd, J = 24.5, 9.6 Hz, 3H), 1.38 (s, 10H), 1.23 (ddd, J = 34.7, 17.7, 8.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, major): 198.8, 171.5, 136.7, 133.1, 128.6, 128.1, 72.99, 48.2, 48.1, 43.3, 33.8, 33.5, 30.3, 28.5, 27.0, 24.4, 24.3, 20.8.

^{13}C NMR (101 MHz, $CDCl_3$, minor): 198.9, 172.2, 136.8, 133.0, 128.6, 128.1, 74.8, 48.8, 47.9, 44.9, 33.8, 31.8, 30.1, 28.7, 27.1, 24.5, 24.20, 20.6.

HRMS (ESI): calcd for $C_{22}H_{32}S_2NO_2^+$, $(M+H)^+$, 406.1869, found, 406.1864.



3n

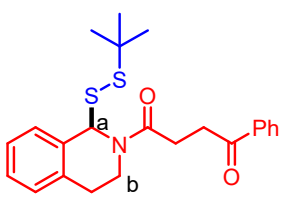
The desired product was provided according to the general procedure using **1n** (55.0 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3n** in 60% yield, as a colorless oil, 23.7 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.03 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 6.18 (d, J = 4.3 Hz, 0.58H), 5.58 (s, 0.42H), 4.27 (dd, J = 271.3, 13.7 Hz, 1H), 3.80-3.60 (m, 1H), 3.55-3.07 (m, 6H), 2.91 (dddd, J = 23.0, 16.7, 16.1, 9.2 Hz, 2H), 2.57 (ddd, J = 13.6, 8.7, 6.8 Hz, 1H), 2.15 (t, J = 11.6 Hz, 1H), 1.38 (s, 3.3H), 1.35 (s, 5.7H).

^{13}C NMR (101 MHz, $CDCl_3$, major): 198.85, 171.0, 136.9, 133.2, 128.7, 128.2, 73.10, 59.7, 56.0, 48.3, 39.6, 34.0, 33.9, 31.7, 30.1, 27.8.

^{13}C NMR (101 MHz, $CDCl_3$, minor): 198.98, 171.0, 136.9, 133.2, 128.7, 128.2, 73.3, 65.1, 56.0, 48.4, 36.1, 35.2, 33.8, 31.1, 30.2, 27.5.

HRMS (ESI): calcd for $C_{20}H_{30}S_2NO_3^+$, $(M+H)^+$, 396.1662, found, 396.1671.



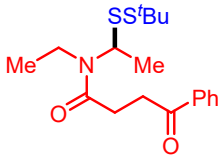
3o

The desired product was provided according to the general procedure using **1o** (58.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3o** in 60% yield, as a colorless oil, 24.8 mg, **a**:**b** = 1.17:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97-7.91 (m, 2H), 7.50-7.44 (m, 1H), 7.38 (dd, J = 10.0, 5.2 Hz, 2H), 7.34-7.20 (m, 1H), 7.19-7.11 (m, 2H), 7.06 (t, J = 4.5 Hz, 1H), 6.86 (s, 0.31H), 6.29 (s, 0.23H), 4.50 (ddd, J = 5.7, 5.2, 2.7 Hz, 0.23H), 4.06-4.00 (m, 0.23H), 3.92- 3.82 (m, 1H), 3.53-3.23 (m, 3H), 3.21-2.56 (m, 4H), 1.33-1.23 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.1, 199.0, 198.9, 198.8, 176.0, 171.2, 171.0, 165.9, 140.4, 136.9, 136.9, 136.9, 135.5, 134.3, 133.5, 133.2, 133.2, 133.1, 133.0, 132.0, 129.6, 129.3, 129.2, 128.9, 128.7, 128.6, 128.3, 128.3, 128.2, 128.2, 128.2, 127.4, 126.4, 126.3, 67.6, 66.1, 62.4, 61.8, 49.5, 49.1, 48.5, 48.2, 42.2, 39.3, 35.6, 33.96, 33.9, 33.9, 33.7, 31.4, 30.2, 30.1, 30.0, 29.9, 28.7, 28.3, 28.1, 28.0, 27.96, 27.7.

HRMS (ESI): calcd for $C_{23}H_{28}S_2NO_2^+$, $(M+H)^+$, 414.1556, found, 414.1550.



3p

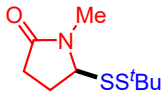
The desired product was provided according to the general procedure using **1p** (46.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3p** in 72% yield, as a colorless oil, 25.5 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.05-7.96 (m, 2H), 7.59-7.51 (m, 1H), 7.48-7.41 (m, 2H), 6.00 (q, J = 7.0 Hz, 0.64H), 5.32 (q, J = 6.9 Hz, 0.36H), 3.57-3.22 (m, 4H), 3.13-2.83 (m, 2H), 1.60 (d, J = 6.9 Hz, 1H), 1.47 (d, J = 7.0 Hz, 1H), 1.39-1.29 (m, 11H), 1.17 (t, J = 7.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 199.10, 172.8, 136.90, 133.2, 128.66, 128.2, 60.2, 47.9, 34.2, 30.1, 30.02, 27.7, 20.2, 16.4.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 199.2, 171.4, 136.93, 133.2,128.68, 128.2, 64.6, 48.0, 37.6, 34.0, 30.08, 27.9, 19.2, 14.7.

HRMS (ESI): calcd for $C_{18}H_{28}S_2NO_2^+$, $(M+H)^+$, 354.1556, found, 354.1549.

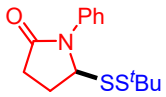


3q

The desired product was provided according to the general procedure using **1q** (0.5mL) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3p** in 52% yield, as a colorless oil, 11.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.55-4.44 (m, 1H), 2.87 (s, 3H), 2.46 (qdd, J = 12.9, 9.8, 6.7 Hz, 2H), 2.35-2.19 (m, 2H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.4, 74.4, 47.7, 30.0, 29.95, 29.4, 28.4, 26.7.
HRMS (ESI): calcd for $C_9H_{17}S_2NNaO^+$, $(M+Na)^+$, 242.0644, found, 242.0653.

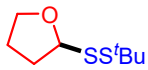


3r

The desired product was provided according to the general procedure using **1p** (32.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2a** (23.4mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3p** in 39% yield, as a colorless oil, 11.0 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 (d, J = 7.7 Hz, 2H), 7.41 (t, J = 7.9 Hz, 2H), 7.29-7.21 (m, 1H), 5.17 (dd, J = 6.4, 2.1 Hz, 1H), 2.87 (dt, J = 16.1, 8.8 Hz, 1H), 2.67-2.42 (m, 3H), 1.27 (s, 9H).

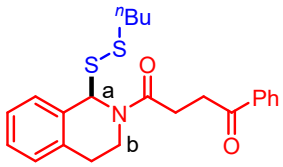
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 174.1, 137.4, 129.2, 126.4, 123.8, 72.6, 48.1, 30.4, 30.1, 27.1.
HRMS (ESI): calcd for $C_{14}H_{20}S_2NO^+$, $(M+H)^+$, 282.0981, found, 282.0976.



3s

The desired product was provided according to the general procedure using **1s** (0.5 ml) and Harpp reagents **2a** (23.4 mg, 0.1 mmol, 1.0 eq.) with EA (0.5 ml) as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **3s** in 27% yield, as a colorless oil, 5.2 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 5.27 (dd, J = 7.1, 3.2 Hz, 1H), 4.02 -3.85 (m, 2H), 2.37-2.19 (m, 1H), 2.09-1.96 (m, 2H), 1.95-1.78 (m, 1H), 1.35 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 91.3, 67.8, 47.4, 32.6, 30.2, 24.8.
HRMS (ESI): calcd for $C_8H_{17}S_2O^+$, $(M+H)^+$, 193.0715, found, 193.0724.



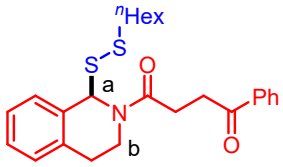
4a

The desired product was provided according to the general procedure using **1o** (58.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2b** (26.7mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4a** in 60% yield, as a colorless oil, 24.8 mg, **a**:**b** = 1.35:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.01 (t, J = 6.6 Hz, 2H), 7.56 (t, J = 7.1 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.32-7.08 (m, 4H), 6.91 (s, 0.29H), 6.40 (s, 0.28H), 4.81-4.31 (m, 0.43H), 4.13-3.82 (m, 1H), 3.65 -3.26 (m, 3H), 3.08-2.79 (m, 4H), 2.70-2.53 (m, 1H), 1.77-1.56 (m, 2H), 1.49-1.32 (m, 2H), 0.90 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C199.1, 199.05, 198.98, 198.8, 171.4, 171.2, 171.1, 170.7, 137.0, 136.9, 136.9, 135.3, 134.5, 134.5, 134.3, 134.2, 133.9, 133.5, 133.2, 133.2, 133.2, 133.1, 132.8, 132.3, 132.3, 131.9, 129.7, 129.4, 129.3, 129.2, 128.9, 128.8, 128.8, 128.7, 128.5, 128.4, 128.3, 128.23, 128.22, 127.9, 127.8, 127.5, 127.5, 126.7, 126.6, 126.5, 126.45, 126.4, 66.3, 62.0, 60.6, 57.5, 39.7, 39.3, 39.1, 39.0, 38.6, 35.6, 34.0, 33.96, 33.9, 33.8, 33.7, 33.6, 32.1, 31.6, 31.2, 31.0, 28.9, 28.8, 28.3, 28.2, 28.0, 27.9, 27.7, 27.6, 22.1, 21.8, 21.7, 13.9, 13.8, 13.79, 13.76, 13.7.

HRMS (ESI): calcd for $C_{23}H_{28}S_2NO_2^+$, $(M+H)^+$, 414.1556, found, 414.1563.



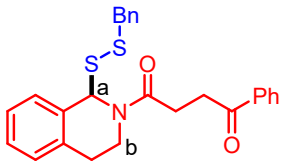
4b

The desired product was provided according to the general procedure using **1o** (58.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2c** (29.5mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4b** in 50% yield, as a colorless oil, 22.1 mg, **a**:**b** = 1.04:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.01 (t, J = 6.3 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.34-7.01 (m, 4H), 6.91 (s, 0.29H), 6.40 (s, 0.22H), 4.55 (dt, J = 27.1, 20.7 Hz, 0.49H), 4.09-3.93 (m, 1H), 3.90-3.24 (m, 3H), 3.20-2.85 (m, 4H), 2.83-2.41 (m, 2H), 1.80-1.58 (m, 2H), 1.44-1.22 (m, 6H), 0.94-0.79 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 199.1, 199.04, 199.02, 198.95, 171.15, 171.13, 171.1, 170.7, 136.93, 136.90, 136.9, 135.4, 135.3, 134.5, 134.2, 133.9, 133.22, 133.20, 132.9, 132.3, 131.98, 129.3, 129.2, 129.0, 128.9, 128.8, 128.8, 128.7, 128.68, 128.5, 128.4, 128.3, 128.24, 128.23, 128.21, 127.9, 127.8, 127.78, 127.5, 126.7, 126.6, 126.5, 126.45, 126.4, 66.3, 66.1, 60.6, 57.5, 39.7, 39.5, 39.3, 39.3, 39.2, 38.7, 35.65, 34.0, 33.9, 33.8, 33.8, 33.7, 31.9, 31.6, 31.6, 31.5, 31.45, 30.0, 29.2, 29.1, 28.95, 28.9, 28.8, 28.75, 28.4, 28.3, 28.25, 28.2, 28.0, 27.7, 27.6, 22.7, 22.66, 22.64, 22.61, 14.2, 14.14, 14.12.

HRMS (ESI): calcd for $C_{19}H_{19}S_2NO_2^+$, $(M+H)^+$, 357.0852, found, 357.0849.



4c

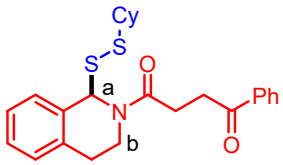
The desired product was provided according to the general procedure using **1o** (58.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2d** (30.1mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4c** in 56% yield, as a colorless oil, 25.0 mg, **a**:**b** = 1.17:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (d, J = 7.6 Hz, 2H), 7.60-7.53 (m, 1H), 7.48 (dd, J = 11.6, 4.9 Hz, 2H), 7.43-7.25 (m, 5H), 7.18 (dddd, J = 11.4, 8.9, 7.0, 4.1 Hz, 4H), 6.98 (s, 0.29H), 6.21 (s, 0.25H), 4.58-4.48 (m, 0.3H), 4.20-4.15 (m, 0.16H), 4.14-3.80 (m, 3H), 3.56-3.21 (m, 3H), 3.19-2.58 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 199.0, 199.0, 198.9, 198.8, 171.4, 171.3, 171.2, 170.8,

140.4, 139.0, 137.0, 136.93, 136.90, 136.8, 136.8, 135.4, 134.2, 134.1, 134.0, 133.5, 133.3, 133.2, 133.2, 133.17, 133.1, 132.7, 131.9, 129.7, 129.6, 129.58, 129.56, 129.52, 129.25, 129.24, 128.94, 128.9, 128.85, 128.82, 128.76, 128.70, 128.69, 128.66, 128.58, 128.44, 128.31, 128.25, 128.24, 128.21, 128.0, 127.86, 127.84, 127.8, 127.6, 127.5, 127.46, 127.4, 126.9, 126.7, 126.45, 126.4, 66.6, 60.6, 58.3, 44.2, 44.0, 39.3, 38.8, 36.6, 36.0, 35.8, 33.96, 33.90, 33.88, 33.7, 33.6, 28.8, 28.7, 28.3, 28.10, 28.0, 27.9, 27.68, 27.6.

HRMS (ESI): calcd for $C_{26}H_{26}S_2NO_2^+$, $(M+H)^+$, 448.1399, found, 448.1400.



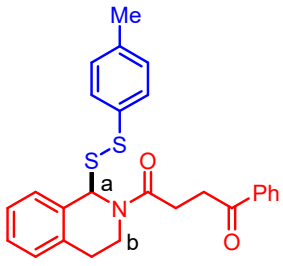
4d

The desired product was provided according to the general procedure using **1o** (58.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2e** (29.3mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4d** in 66% yield, as a colorless oil, 29.0 mg, , **a**:**b** = 1.04:1.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.02 (d, J = 7.4 Hz, 2H), 7.56 (dd, J = 10.8, 3.8 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.34-7.11 (m, 4H), 6.88 (s, 0.32H), 6.36 (s, 0.23H), 4.56-4.49 (m, 0.28H), 4.10 (dd, J = 12.0, 5.9 Hz, 0.27H), 3.94 (dddd, J = 18.0, 13.3, 11.4, 5.3 Hz, 1H), 3.54-3.28 (m, 3H), 3.13-2.54 (m, 5H), 2.17-1.84 (m, 2H), 1.67 (m, 3H), 1.42-1.18 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 199.0, 198.96, 198.9, 198.8, 176.0, 171.1, 171.06, 170.4, 140.4, 136.94, 136.90, 136.89, 136.85, 135.4, 135.3, 135.1, 134.7, 134.4, 134.2, 133.9, 133.5, 133.23, 133.20, 133.18, 133.13, 132.9, 132.1, 129.7, 129.4, 129.2, 129.2, 128.9, 128.8, 128.75, 128.7, 128.6, 128.58, 128.3, 128.26, 128.2, 128.18, 127.9, 127.4, 127.4, 126.5, 126.4, 126.3, 66.5, 61.1, 56.5, 49.6, 49.2, 43.7, 42.2, 39.3, 38.6, 35.7, 34.8, 34.0, 33.9, 33.8, 33.78, 33.7, 33.6, 33.5, 32.8, 32.7, 32.7, 32.4, 28.9, 28.7, 28.3, 28.1, 28.1, 27.9, 27.7, 27.6, 26.1, 26.1, 25.97, 25.95, 25.8, 25.7.

HRMS (ESI): calcd for $C_{25}H_{30}S_2NO_2^+$, $(M+H)^+$, 440.1712, found, 440.1721.



4e

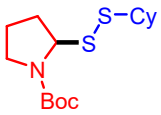
The desired product was provided according to the general procedure using **1o** (58.6 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2f** (30.1mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4e** in 51% yield, as a colorless oil, 22.8 mg, **a**:**b** = 1:1.5.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.07-7.97 (m, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.51-7.43 (m, 3H), 7.39 (d, J = 8.1 Hz, 1H), 7.26-7.19 (m, 2H), 7.18-7.06 (m, 4H), 6.59 (s, 0.09H), 6.40 (s, 0.31H), 4.46-

4.32 (m, 0.31H), 4.16-4.07 (m, 0.29H), 4.03-3.71 (m, 1H), 3.66-3.35 (m, 2H), 3.29-2.93 (m, 3H), 2.92-2.72 (m, 2H), 2.31 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 199.1, 198.9, 198.8, 177.6, 176.1, 175.8, 171.1, 171.1, 140.4, 137.7, 137.5, 136.9, 135.5, 135.2, 134.4, 134.4, 133.7, 133.5, 133.3, 133.2, 132.2, 131.7, 131.7, 131.0, 130.2, 130.0, 129.7, 129.4, 129.4, 129.4, 128.9, 128.8, 128.7, 128.7, 128.6, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 127.7, 127.5, 126.6, 126.5, 123.7, 65.9, 62.5, 42.3, 39.3, 35.5, 33.96, 33.8, 33.7, 28.8, 28.3, 27.97, 27.9, 27.7, 21.2, 21.2.

HRMS (ESI): calcd for $C_{26}H_{26}S_2NO_2^+$, $(M+H)^+$, 448.1399, found, 448.1391.



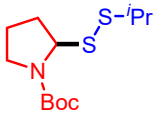
4f

The desired product was provided according to the general procedure using **1a** (34.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2e** (29.3mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4f** in 39% yield, as a colorless oil, 12.4 mg.

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 5.12 (s, 0.41H), 4.95 (s, 0.49H), 3.47 (d, J = 5.7 Hz, 1H), 3.40-3.24 (m, 1H), 3.08-2.62 (m, 1H), 2.32 (m, 1H), 2.04 (ddd, J = 27.0, 13.0, 2.3 Hz, 4H), 1.94-1.84 (m, 1H), 1.79 (s, 2H), 1.63 (s, 1H), 1.52 (s, 4.95H), 1.49 (s, 4.05H), 1.41-1.18 (m, 5H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 153.8, 153.2, 80.5, 79.7, 67.95, 67.9, 50.3, 49.7, 46.8, 46.6, 33.2, 32.9, 32.8, 32.7, 28.6, 28.5, 26.2, 25.8, 25.7, 22.0.

HRMS (ESI): calcd for $C_{15}H_{28}S_2NO_2^+$, $(M+H)^+$, 318.1556, found, 318.1547.



4g

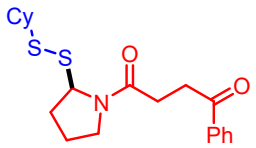
The desired product was provided according to the general procedure using **1a** (34.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2g** (25.3mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4g** in 41% yield, as a colorless oil, 11.4 mg.

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 5.09 (d, J = 5.2 Hz, 0.47H), 4.94 (d, J = 5.2 Hz, 0.53H), 3.50-3.39 (m, 1H), 3.36-3.27 (m, 1H), 3.18-2.91 (m, 1H), 2.27 (dd, J = 17.9, 13.5 Hz, 1H), 2.18-2.07 (m, 2H), 1.94-1.84 (m, 1H), 1.49 (s, 5H), 1.46 (s, 4H), 1.36-1.24 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$, major): δ_C 153.7, 80.1, 67.9, 46.8, 41.4, 33.1, 28.5, 22.8, 22.0.

^{13}C NMR (101 MHz, CDCl$_3$, minor): δ_C 153.8, 80.1, 67.7, 46.5, 41.2, 32.4, 28.5, 23.0, 22.5.

HRMS (ESI): calcd for $C_{12}H_{24}S_2NO_2^+$, $(M+H)^+$, 278.1243, found, 278.1244.



4h

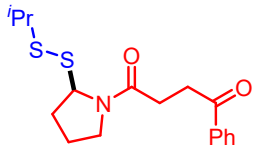
The desired product was provided according to the general procedure using **1g** (46.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2e** (29.3mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4h** in 70% yield, as a colorless oil, 26.4 mg.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.03-7.95 (m, 2H), 7.60-7.51 (m, 1H), 7.45 (td, J = 7.7, 1.7 Hz, 2H), 5.31 (d, J = 6.1 Hz, 0.56H), 5.15 (d, J = 5.7 Hz, 0.48H), 3.73-3.40 (m, 3H), 3.26 (qd, J = 11.8, 6.0 Hz, 1H), 3.10-2.93 (m, 1H), 2.85-2.58 (m, 2H), 2.44-2.20 (m, 2H), 2.18 -1.90 (m, 4H), 1.83- 1.73 (m, 2H), 1.66-1.52 (m, 1H), 1.41-1.20 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 199.1, 171.4, 136.9, 133.3, 128.7, 128.2, 66.7, 49.9, 46.5, 33.9, 33.5, 33.1, 32.8, 31.5, 29.0, 26.1, 25.7, 23.2.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 199.0, 170.7, 136.8, 133.2, 128.7, 128.2, 68.7, 49.8, 47.1, 33.6, 33.2, 33.1, 32.7, 32.7, 28.7, 26.2, 25.8, 21.3.

HRMS (ESI): calcd for $C_{20}H_{28}S_2NO_2^+$, $(M+H)^+$, 378.1556, found, 378.1560.



4i

The desired product was provided according to the general procedure using **1g** (46.2 mg, 0.2 mmol, 2.00 eq.) and Harpp reagents **2g** (25.3mg, 0.1 mmol, 1.0 eq.) with EA as the solvent. The crude was purified by by flash column chromatography with PE/EA (10:1-5:1) to give **4i** in 82% yield, as a colorless oil, 27.6 mg.

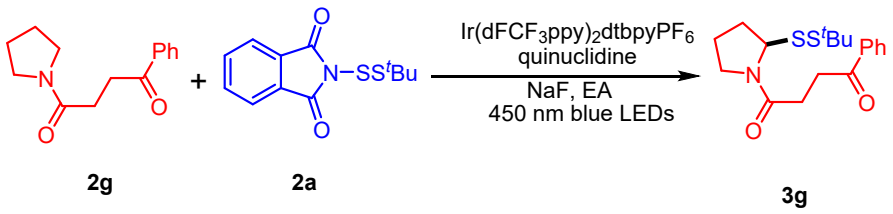
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.06-7.94 (m, 2H), 7.63-7.51 (m, 1H), 7.45 (td, J = 7.6, 1.7 Hz, 2H), 5.31 (d, J = 6.1 Hz, 0.58H), 5.18 (d, J = 5.7 Hz, 0.42H), 3.71-3.42 (m, 3H), 3.34-3.19 (m, 1H), 3.11-2.95 (m, 2H), 2.88-2.61 (m, 1H), 2.43-2.23 (m, 2H), 2.21-1.89 (m, 2H), 1.40-1.25 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, major): δ_C 199.0, 170.7, 136.8, 133.3, 128.7, 128.2, 68.6, 46.5, 41.6, 33.90, 33.5, 28.9, 22.9, 22.9, 22.6.

^{13}C NMR (101 MHz, $CDCl_3$, minor): δ_C 199.1, 171.4, 136.9, 133.2, 128.7, 128.2, 66.9, 47.1, 41.5, 33.7, 31.8, 28.7, 23.2, 22.8, 21.3.

HRMS (ESI): calcd for $C_{17}H_{24}S_2NO_2^+$, $(M+H)^+$, 338.1243, found, 338.1249.

6. Gram Scale Reaction.



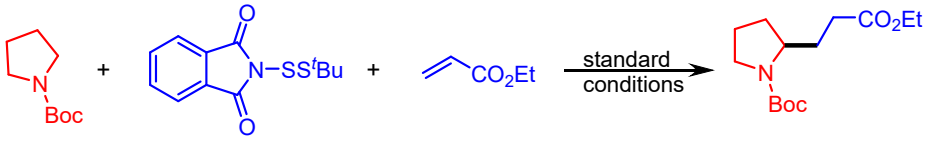
2g **2a** **3g**

In a sealed tube**, 2a** (1.4 g, 3.0 mmol), **2g** (0.7g, 6.0 mmol), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), quinuclidine (20 mol%), NaF (6.0 mmol), were dissolved in EA (10.0 mL). The open flask was caped and degassed with nitrogen for three times at -78 ^{o}C. Subsequently, the reaction mixture was irradiated with 2*12 W blue LEDs at room temperature until **2a** was completely consumed (monitored by TLC). The solvent was removed under vacuum when the reaction finished. Finally, the residue was purified by flash column chromatography on silica gel with PE and EA, affording the desired product **3g** in 62% yield.

7. Mechanistic Studies

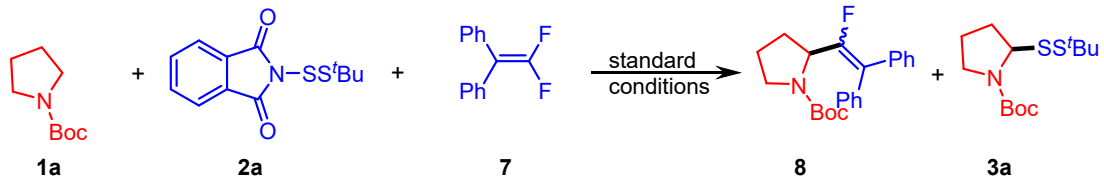
a) Radical trapping experiment

In a oven-dried sealed tube, **1a** (0.2 mmol), **2a** (0.1 mmol), **5** (0.2 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1 mol%), quinuclidine (20 mol%), NaF (0.2 mmol) were dissolved in EA (1.0 mL). The flask was caped and degassed with N_2 for three times at -78 °C. Subsequently, the reaction system was moved to 2 *12 W blue LEDs (450 nm) at room temperature (Monitored by TLC). 12 h later, there was no radical addition product **6** was detected in the reaction system.

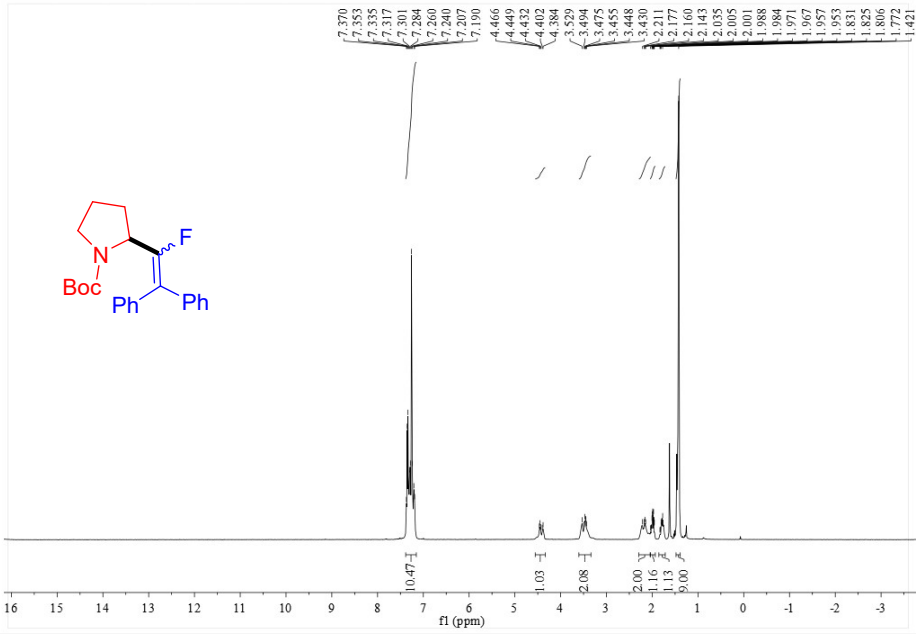


1a **2a** **5** **6**

In a oven-dried sealed tube, **1a** (0.2 mmol), **2a** (0.1 mmol), **7** (0.2 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1 mol%), quinuclidine (20 mol%), NaF (0.2 mmol) were dissolved in EA (1.0 mL). The flask was caped and degassed with N_2 for three times at -78 °C. Subsequently, the reaction system was moved to 2 *12 W blue LEDs (450 nm) at room temperature (Monitored by TLC). The reaction solvent was removed under vacuum when the starting material was completely consumed, the residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate as the fluent, providing the desired product **3a** and **8** in 53% and 14% yield, respectively. The ^{1}H NMR of **8** was consistent with the previous literature[6]. White solid .^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39-7.15 (m, 10H), 4.56-4.34 (m, 1H), 3.60-3.34 (m, 2H), 2.17 (dd, J = 17.0, 10.2 Hz, 2H), 1.98 (ddd, J = 12.4, 6.1, 1.7 Hz, 1H), 1.85-1.71 (m, 1H), 1.42 (s, 9H).

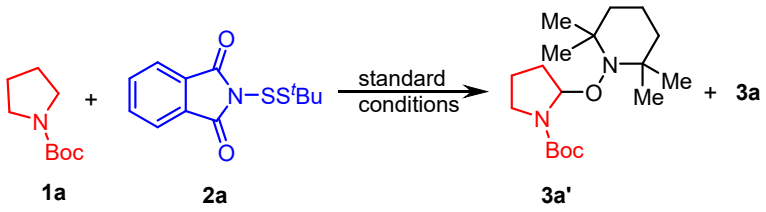


1a **2a** **7** **8** **3a**



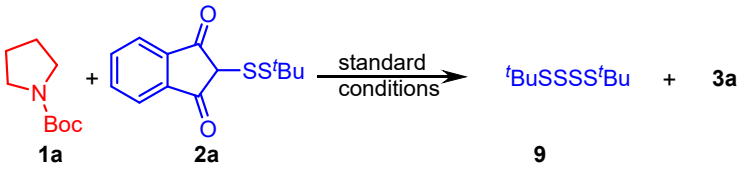
b) Radical inhibition experiment

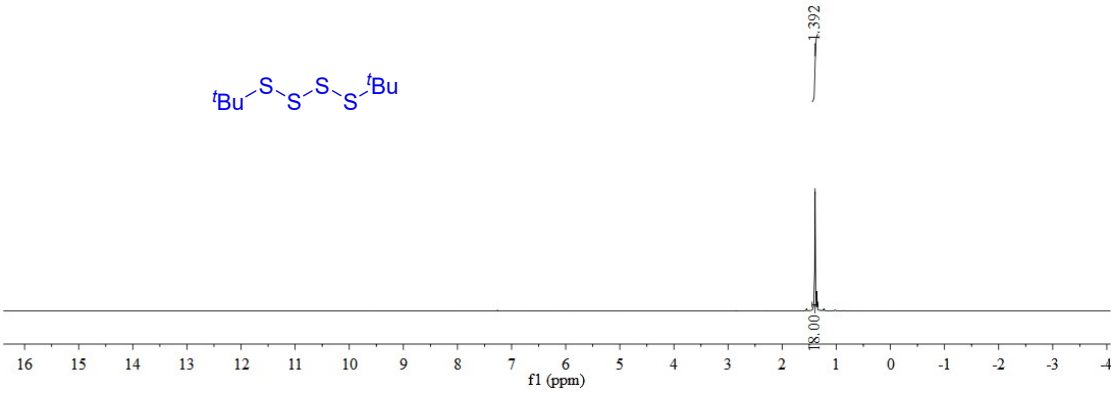
In a dried sealed tube, **1a** (0.2 mmol), **2a** (0.1 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1 mol%), quinuclidine (20 mol%), NaF (0.2 mmol),TEMPO (0.2 mmol) were dissolved in EA (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. The reaction system was placed to 2 *12 W blue LEDs (450 nm) at room temperature. 12 hours later, the reaction was detected with GC-MS, there was no desired product **3a** was founded, further studies indicate that **3a'** was also not isolated in the reaction mixture. The results indicate that the transformation is a radical intermediate involved by single electron transfer.



c) Determination the intermediate of the reaction

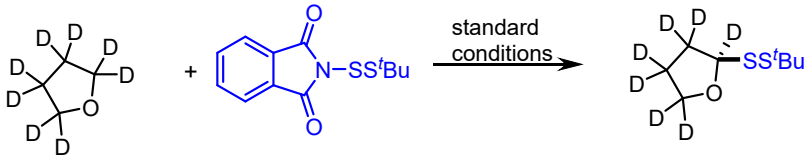
In a dried sealed tube, 1**a** (0.2 mmol),**2a** (0.1 mmol), $Ir(dFCF_3ppy)_2dtbpyPF_6$ (1 mol%), quinuclidine (20 mol%), NaF (0.2 mmol) were dissolved in EA (1.0 mL). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. And then, the reaction system was placed to 2 *12 W blue LEDs (450 nm) at rt. The reaction was stopped until the starting material completely consumed. The reaction solvent was removed under vacuum and purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate, affording **3a** and tert-butyl tetrasulfide **9** in 54% and 11% yields, respectively. The ^1H NMR of **9** was consistent with the previous literature[7-8]. ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.39 (s, 18H).



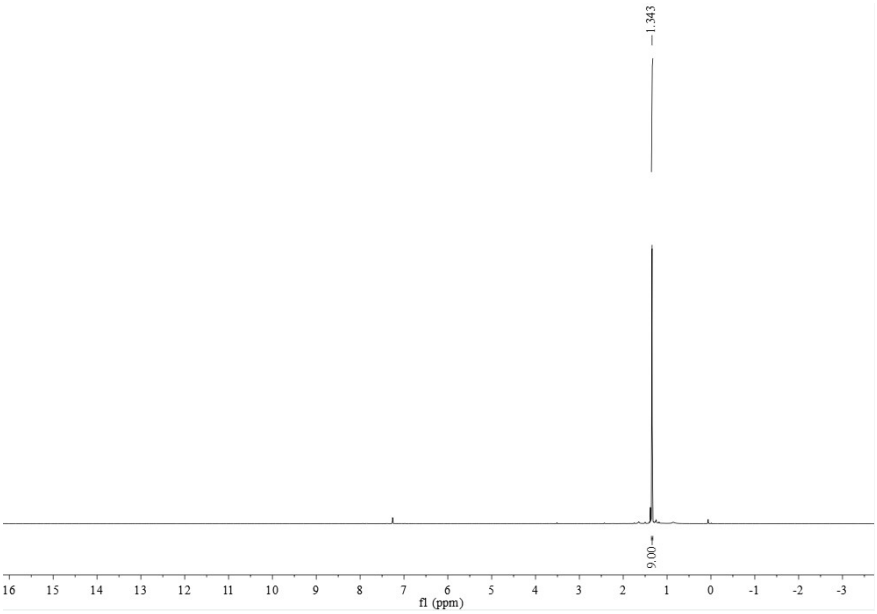


d) Reaction to confirm KIE

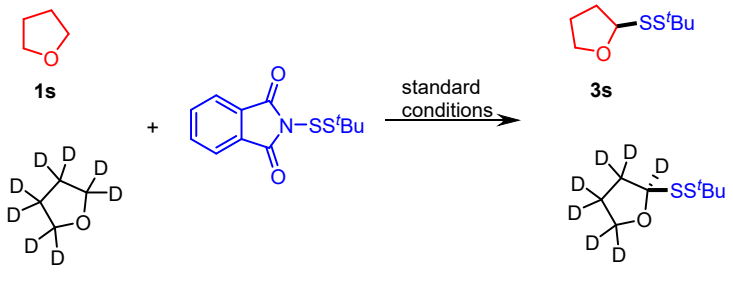
In a dried sealed tube, **2a** (0.1 mmol), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), quinuclidine (20 mol%), NaF (0.2 mmol) were dissolved in EA (0.5 mL) and **d$_8$-1s** (0.5 ml). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. And then, the reaction system was placed to 2 *12 W blue LEDs (450 nm) at rt. The reaction was stopped until the starting material completely consumed. The reaction solvent was removed under vacuum and purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate, affording **d$_7$-3s** in 29% yield.



d$_8$-1s **2a** **d$_7$-3s**

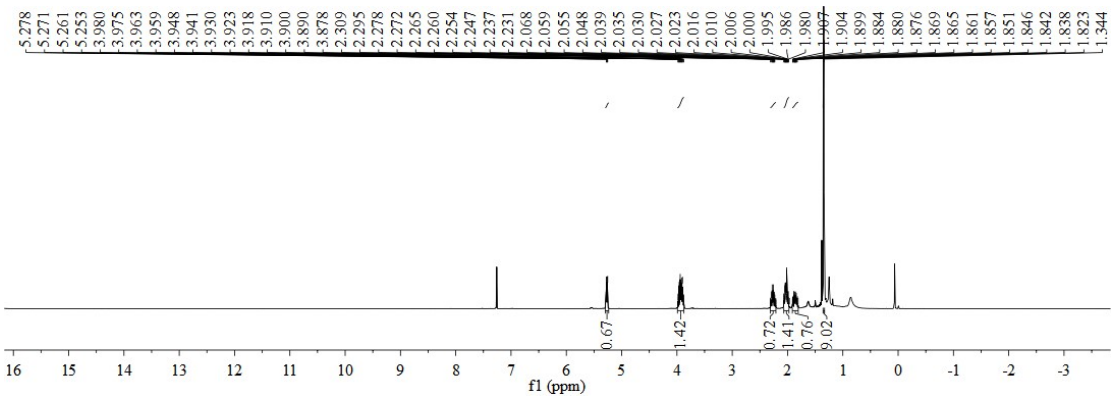


In a dried sealed tube, **2a** (0.1 mmol), Ir(dFCF$_3$ppy)$_2$dtbpyPF$_6$ (1 mol%), quinuclidine (20 mol%), NaF (0.2 mmol) were dissolved in EA (0.5 mL), **d$_8$-1s** (0.25 ml) and THF (0.25 ml). The flask was caped and degassed oxygen with nitrogen for three times at -78 °C. And then, the reaction system was placed to 2 *12 W blue LEDs (450 nm) at rt. The reaction was stopped until the starting material completely consumed. The reaction solvent was removed under vacuum and purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate, affording **d$_7$-3s** and **3s** in 28% yield, the KIE was calculated as 2.03, which indicate the hydrogen atom abstraction was the critical step.



1s **3s**

d$_8$-1s **2a** **d$_7$-3s**



e) Emission Quenching Experiments (Stern-Volmer Studies)

To evaluate the role of quinuclidine in this transformation, the Stern-Volmer fluorescence quenching experiments were conducted (Fig S1, Fig S2). The samples were prepared mixing the quinuclidine (2.5×10^{-3} M) with the required amount of $Ir(dFCF_3ppy)_2dtbpyPF_6$ in a total volume of 1 mL of EA in a 10 × 10 mm light path quartz fluorescence cuvette under an argon atmosphere. The excitation wavelength was fixed at 420 nm, the emission light was acquired from 400 nm to 700 nm.

1) Fluorescence Quenching of $Ir(dFCF_3ppy)_2dtbpyPF_6$ by quinuclidine

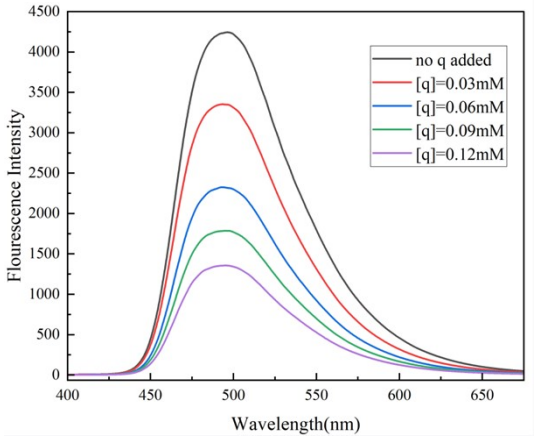


Figure S1. Fluorescence spectra of a solution of photocatalyst $Ir(dFCF_3ppy)_2dtbpyPF_6$ in EA containing 0.0 mM 0.03 mM, 0.06 mM, 0.09 mM, 0.12 mM of quinuclidine.

2) Fluorescence Quenching of $Ir(dFCF_3ppy)_2dtbpyPF_6$ by *N*-perthiophthalimide derivative **2a**

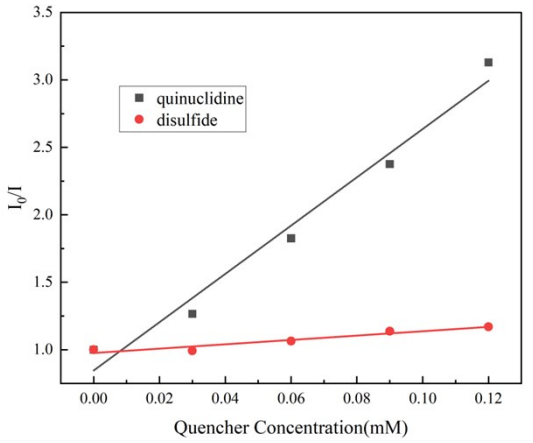


Figure S2. Fluorescence spectra of a solution of photocatalyst $Ir(dFCF_3ppy)_2dtbpyPF_6$ in EA containing 0.0 mM 0.03 mM, 0.06 mM, 0.09 mM, 0.12 mM of **2a**.

8. Reference

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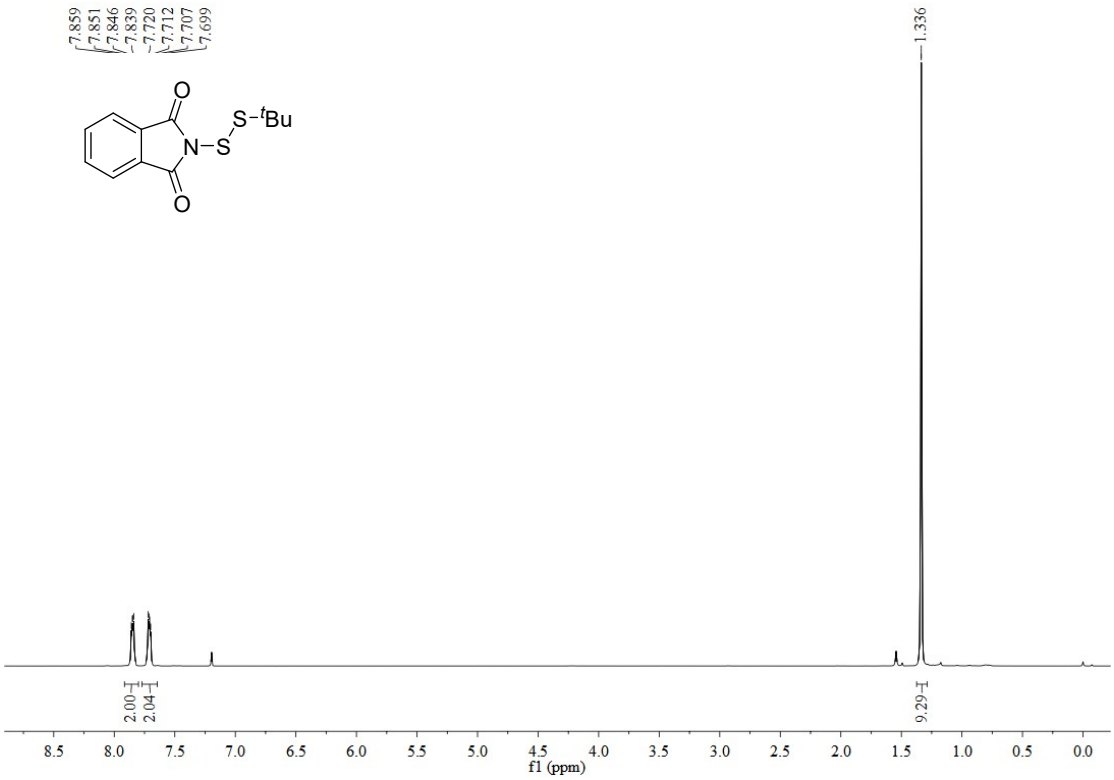
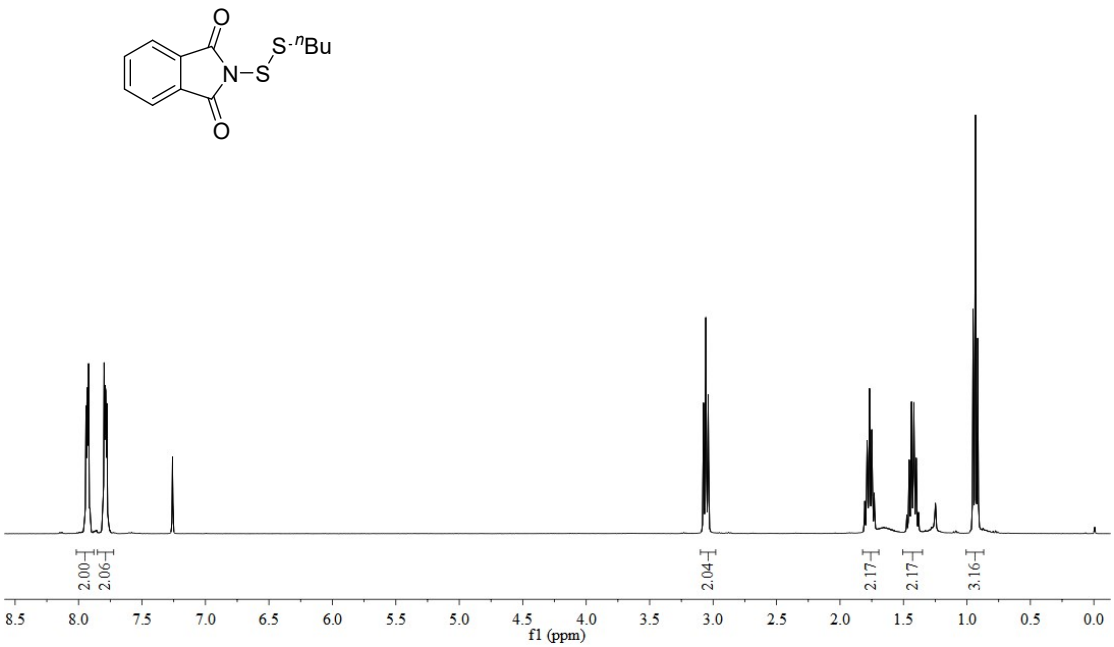
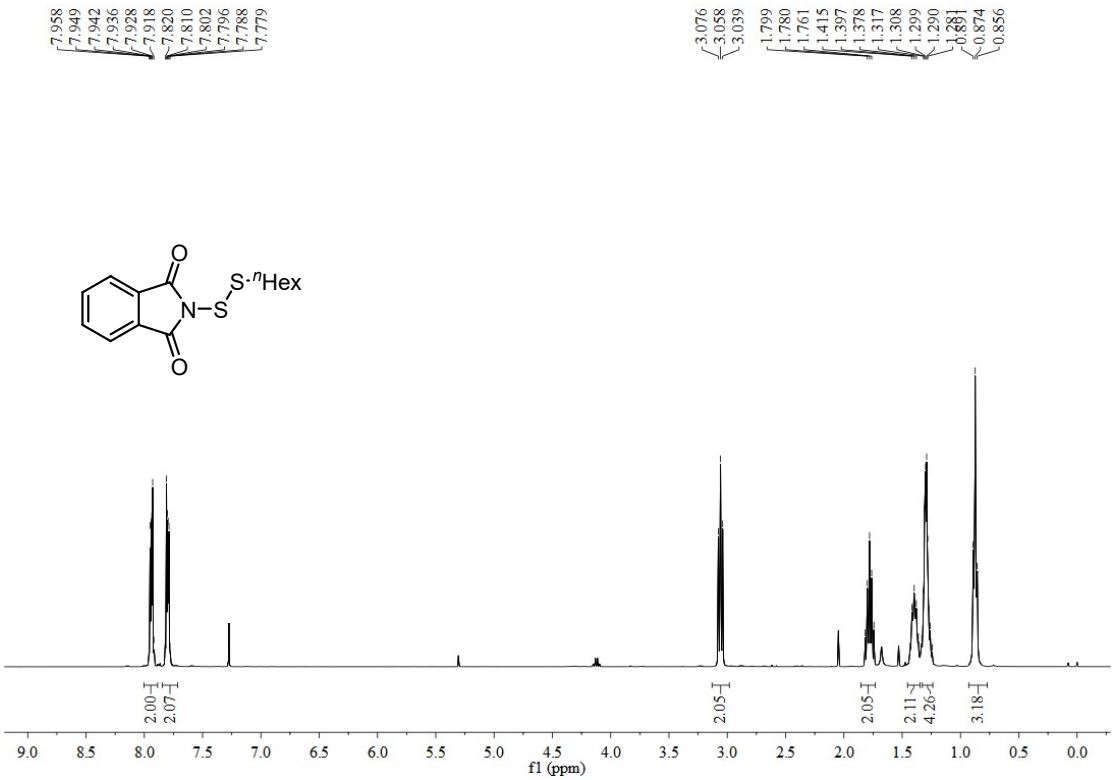
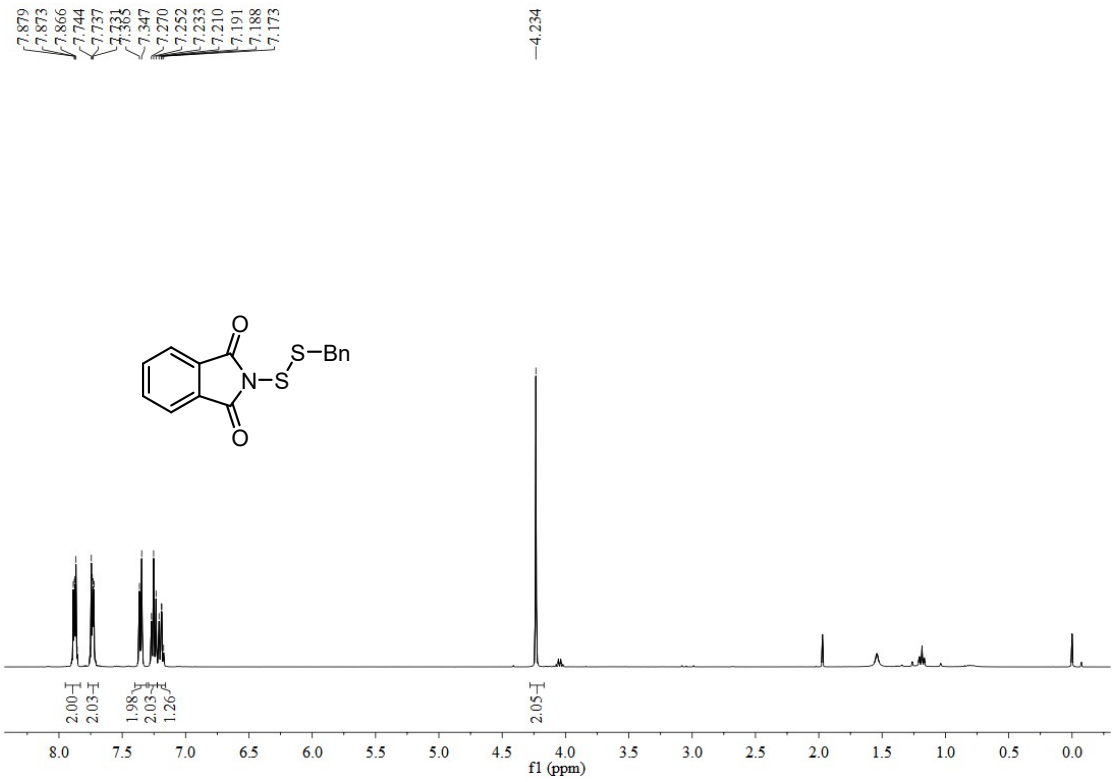
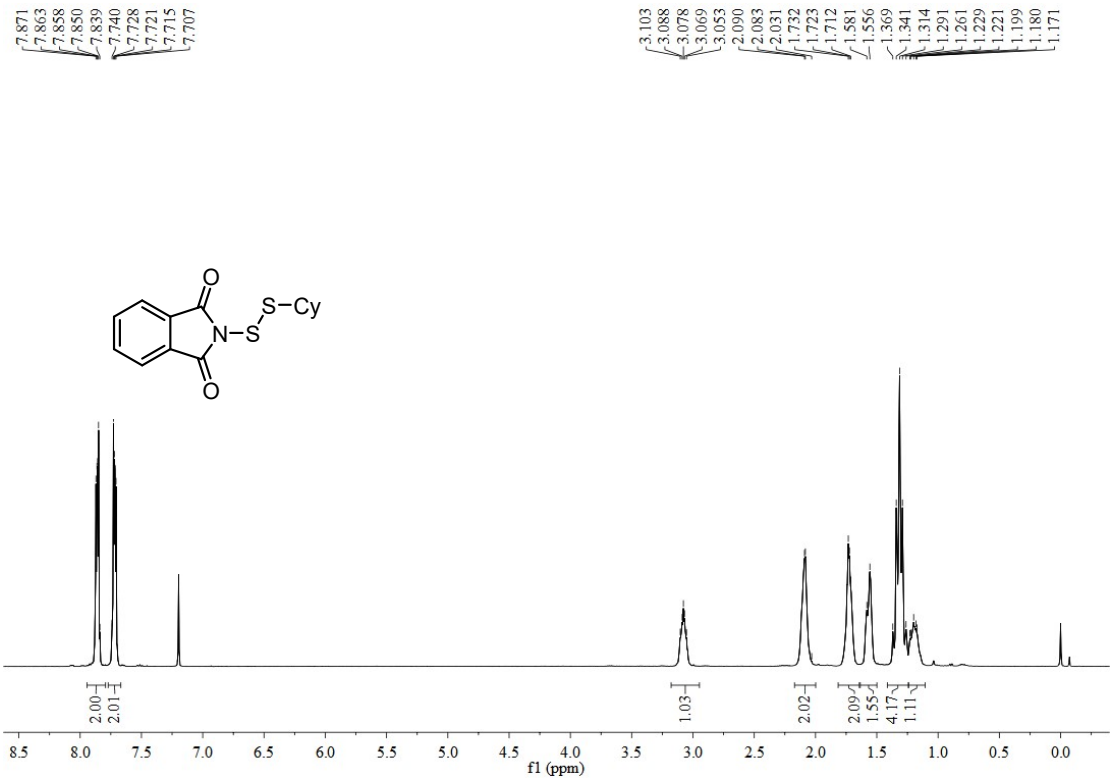
9. Spectra of Substrates and Products

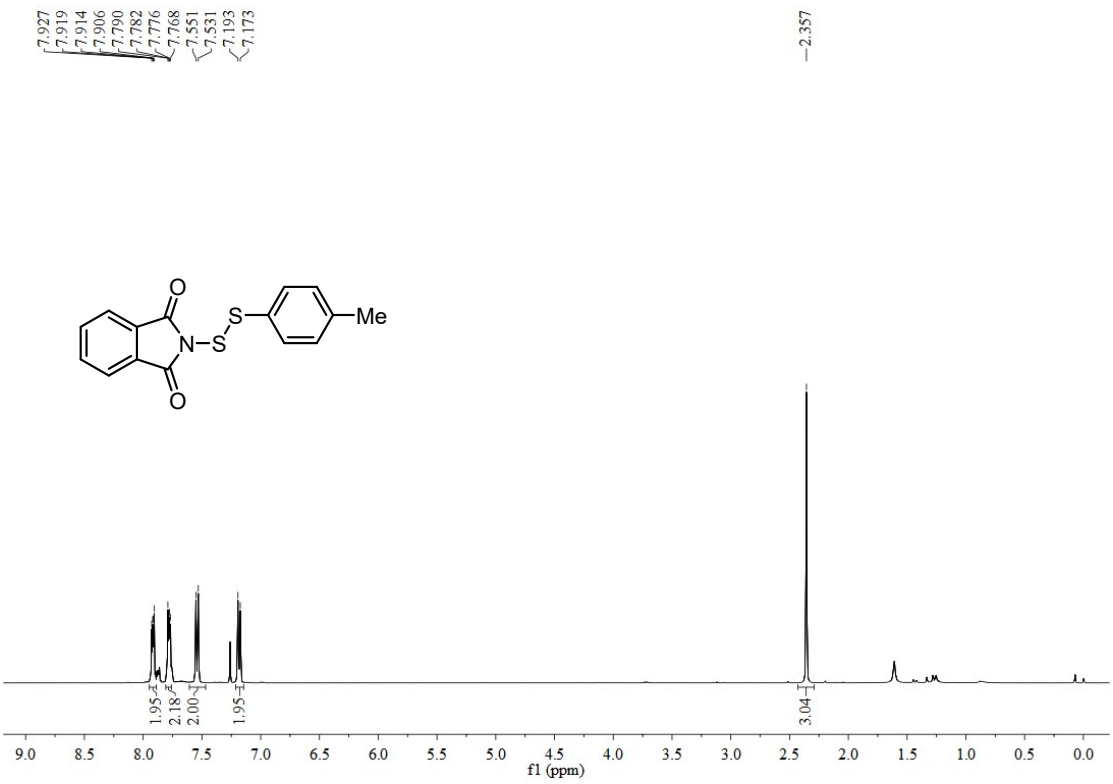

7.859
7.851
7.846
7.839
7.720
7.712
7.707
7.699
1.336
O
N–S
S-tBu
O
2.00
2.04
9.29
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

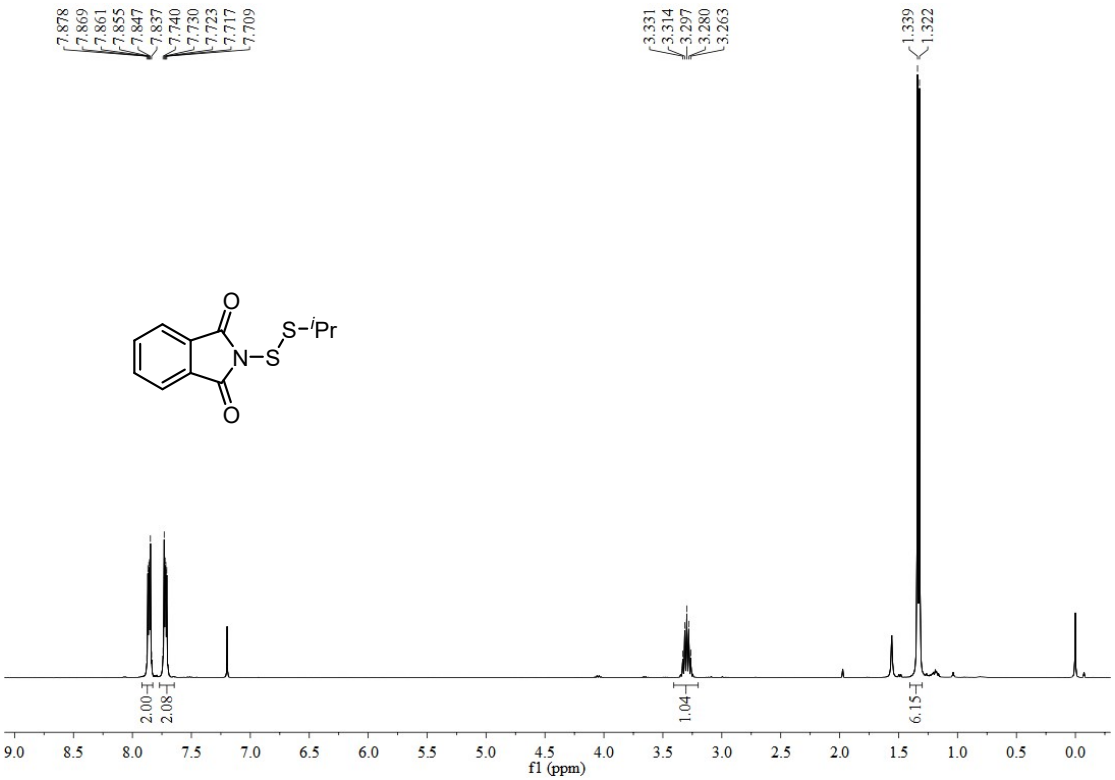

O
N–S
S-nBu
O
2.00
2.06
2.04
2.17
2.17
3.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

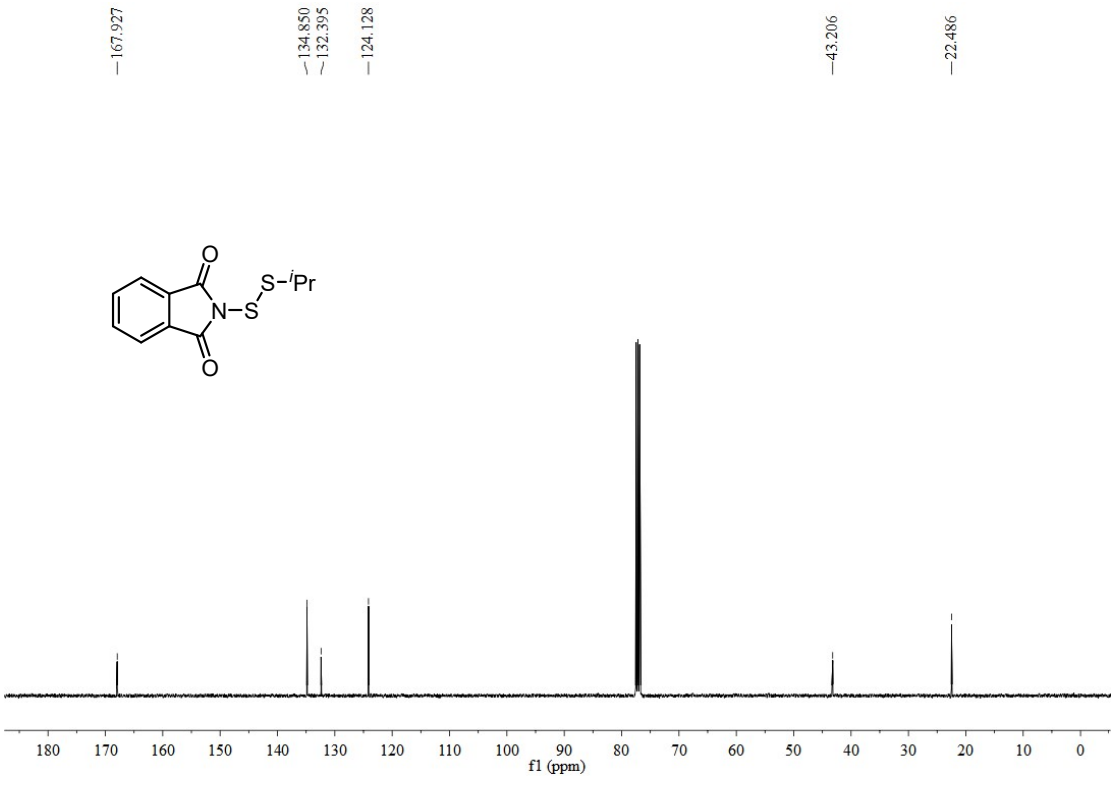

7.958
7.949
7.942
7.936
7.928
7.918
7.820
7.810
7.802
7.796
7.788
7.779
3.076
3.058
3.039
1.799
1.780
1.761
1.415
1.397
1.378
1.317
1.308
1.299
1.290
1.281
0.891
0.874
0.856
O
N–S
S·nHex
O
2.00
2.07
2.05
2.05
2.11
4.26
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.879
7.873
7.866
7.744
7.737
7.731
7.385
7.347
7.270
7.252
7.233
7.210
7.191
7.188
7.173
4.234
O
N–S
S–Bn
O
2.00
2.03
1.98
2.03
1.26
2.05
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
f1 (ppm)

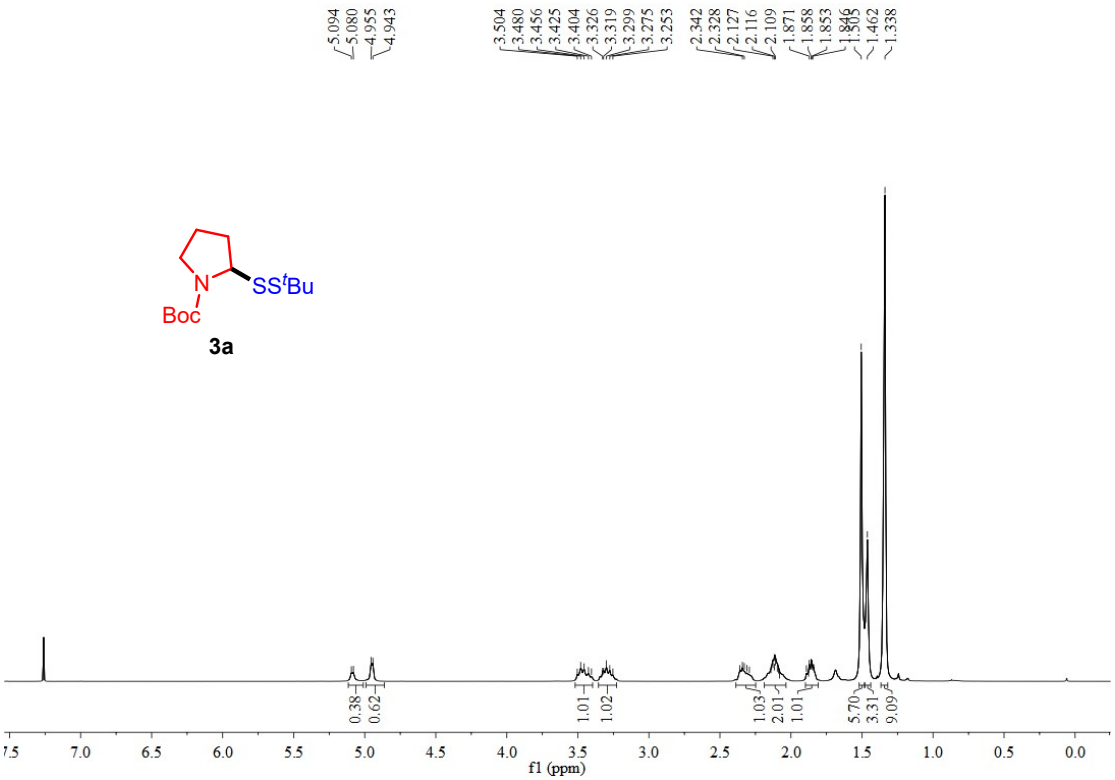

7.871
7.863
7.858
7.850
7.839
7.740
7.728
7.721
7.715
7.707
3.103
3.088
3.078
3.069
3.053
2.090
2.083
2.031
1.732
1.723
1.712
1.581
1.556
1.369
1.341
1.314
1.291
1.261
1.229
1.221
1.199
1.180
1.171
O
N–S
S–Cy
O
2.00
2.01
1.03
2.02
2.09
1.55
4.17
1.11
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

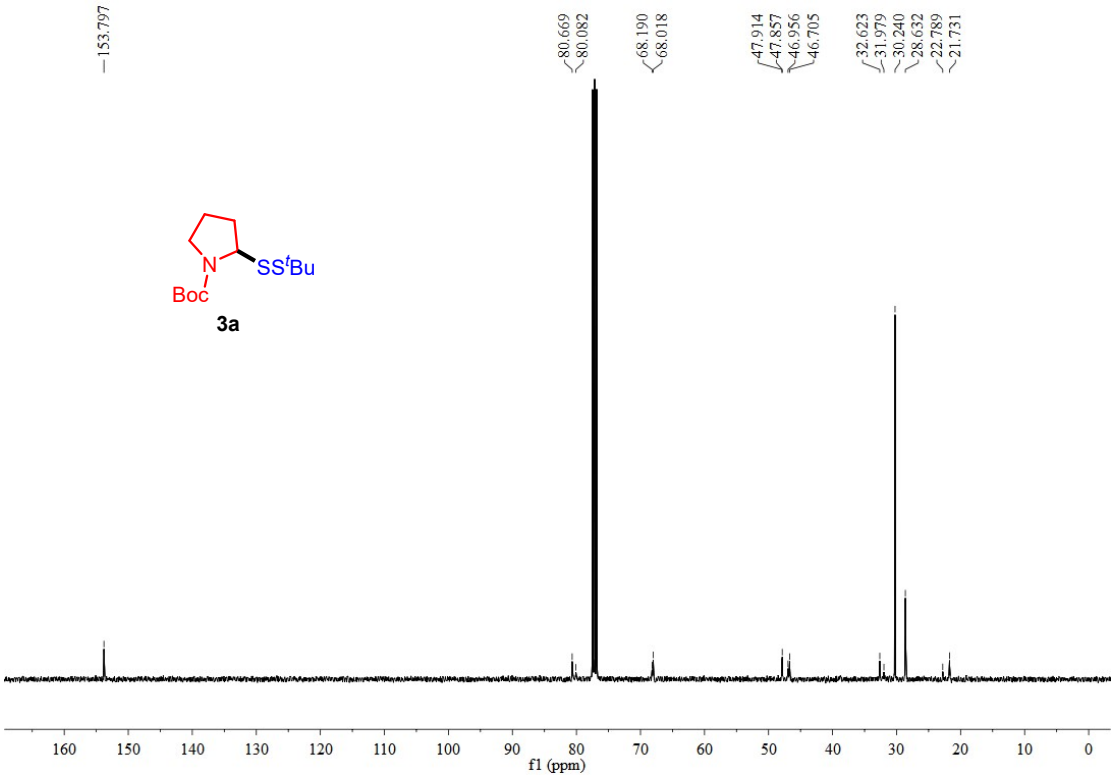

7.927
7.919
7.914
7.906
7.790
7.782
7.776
7.768
7.551
7.531
7.193
7.173
2.357
O
N–S
S
Me
O
1.95
2.18
2.00
1.95
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.878
7.869
7.861
7.855
7.847
7.837
7.740
7.730
7.723
7.717
7.709
3.331
3.314
3.297
3.280
3.263
1.339
1.322
O
N–S
S–iPr
O
2.00
2.08
1.04
6.15
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
f1 (ppm)

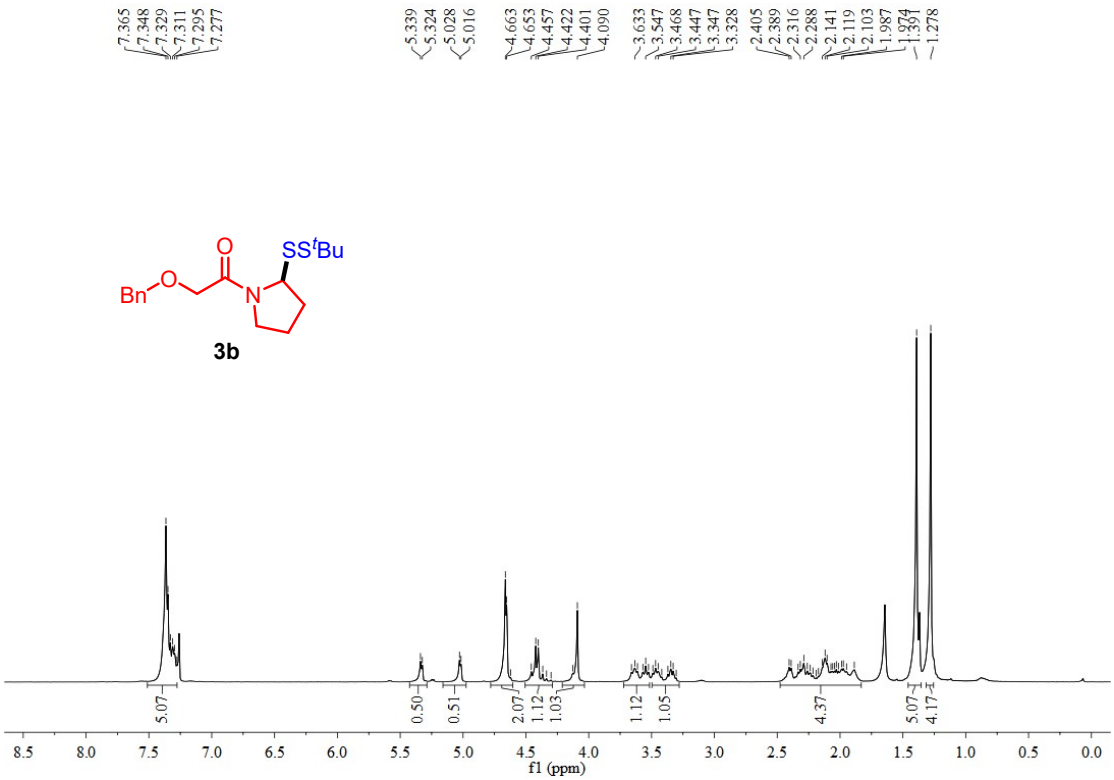

167.927
134.850
132.395
124.128
43.206
22.486
O
N–S
S–iPr
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

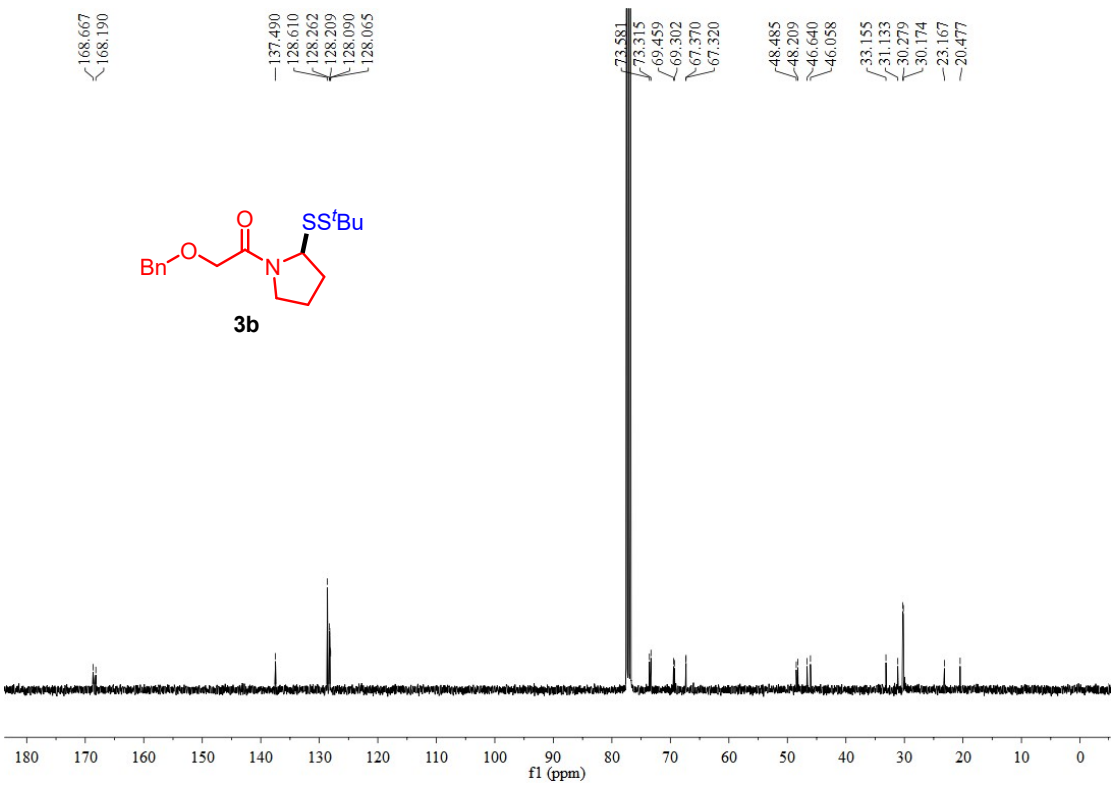
3a, $^{1}H+^{13}C$


5.094
5.080
4.955
4.943
3.504
3.480
3.456
3.425
3.404
3.326
3.319
3.299
3.275
3.253
2.342
2.328
2.127
2.116
2.109
1.871
1.858
1.853
1.505
1.462
1.338
N
SS^{t}Bu
Boc
3a
0.38
0.62
1.01
1.02
1.03
2.01
1.01
5.70
3.31
9.09
f1 (ppm)

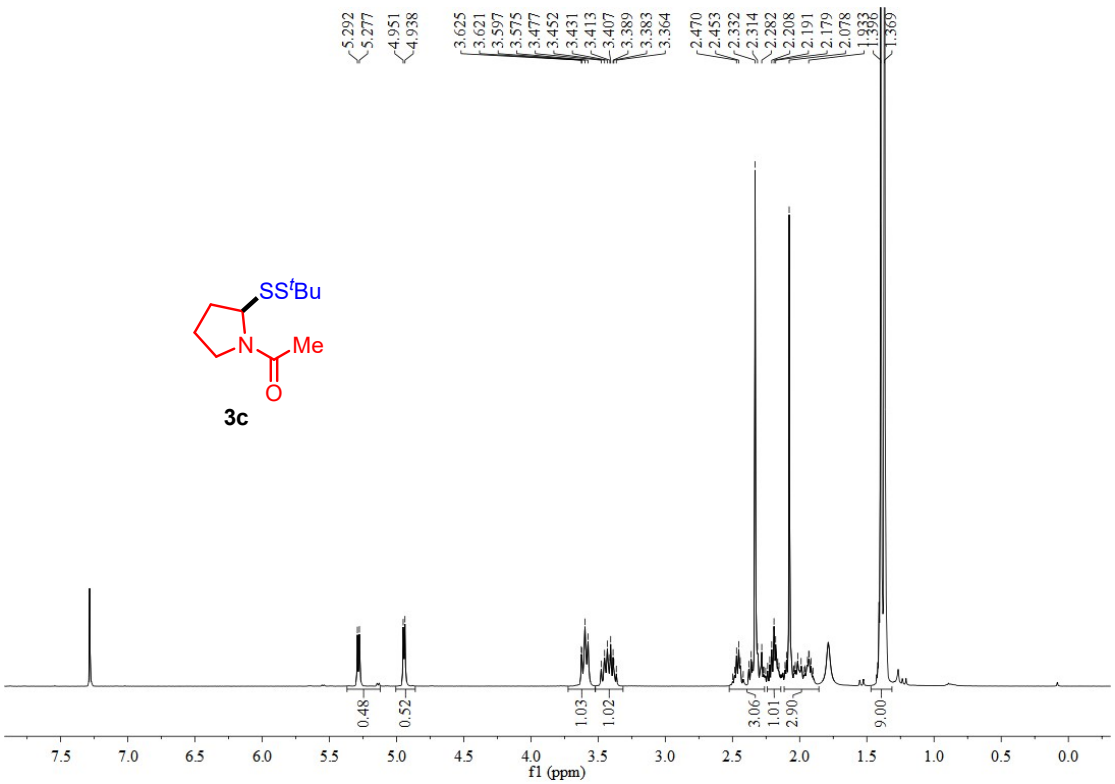

153.797
80.669
80.082
68.190
68.018
47.914
47.857
46.956
46.705
32.623
31.979
30.240
28.632
22.789
21.731
N
SS^{t}Bu
Boc
3a
f1 (ppm)

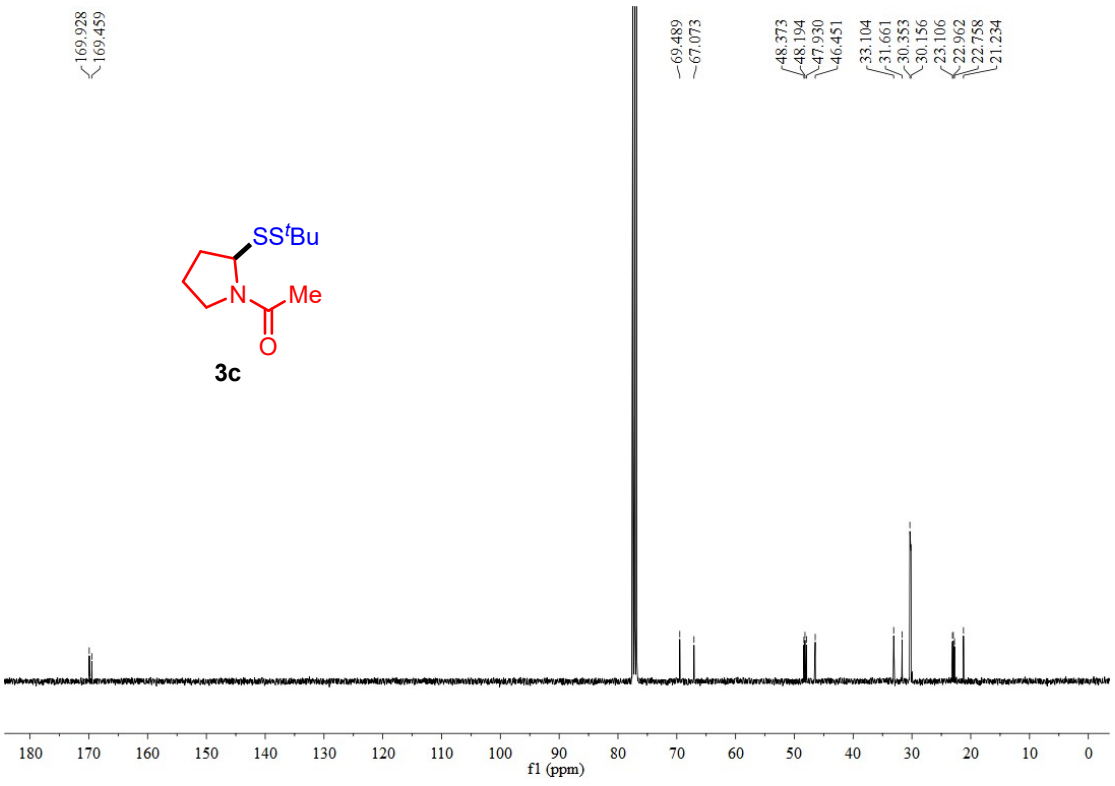
3b, $^{1}H+^{13}C$


7.365
7.348
7.329
7.311
7.295
7.277
5.339
5.324
5.028
5.016
4.663
4.653
4.457
4.422
4.401
4.090
3.633
3.547
3.468
3.447
3.347
3.328
2.405
2.389
2.316
2.288
2.141
2.119
2.103
1.987
1.974
1.391
1.278
O
SS^{t}Bu
Bn
O
N
3b
5.07
0.50
0.51
2.07
1.12
1.03
1.12
1.05
4.37
5.07
4.17
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
f1 (ppm)

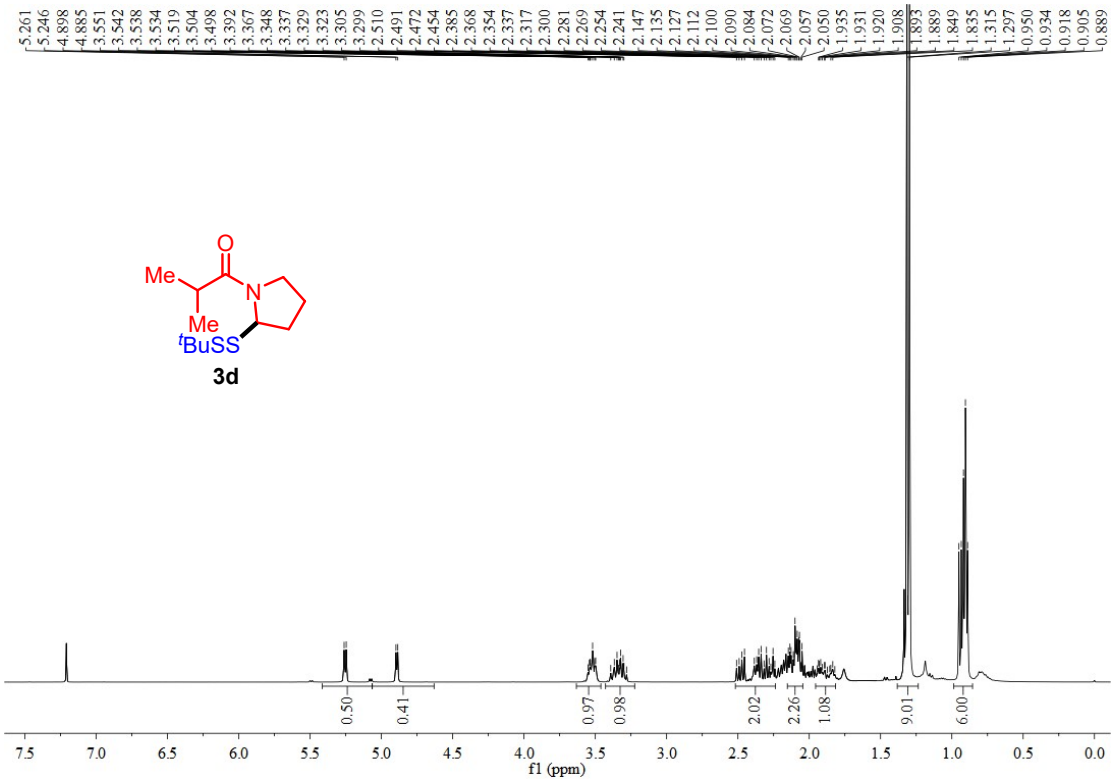

168.667
168.190
137.490
128.610
128.262
128.209
128.090
128.065
73.581
73.315
69.459
69.302
67.370
67.320
48.485
48.209
46.640
46.058
33.155
31.133
30.279
30.174
23.167
20.477
O
SS^{t}Bu
Bn
O
N
3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

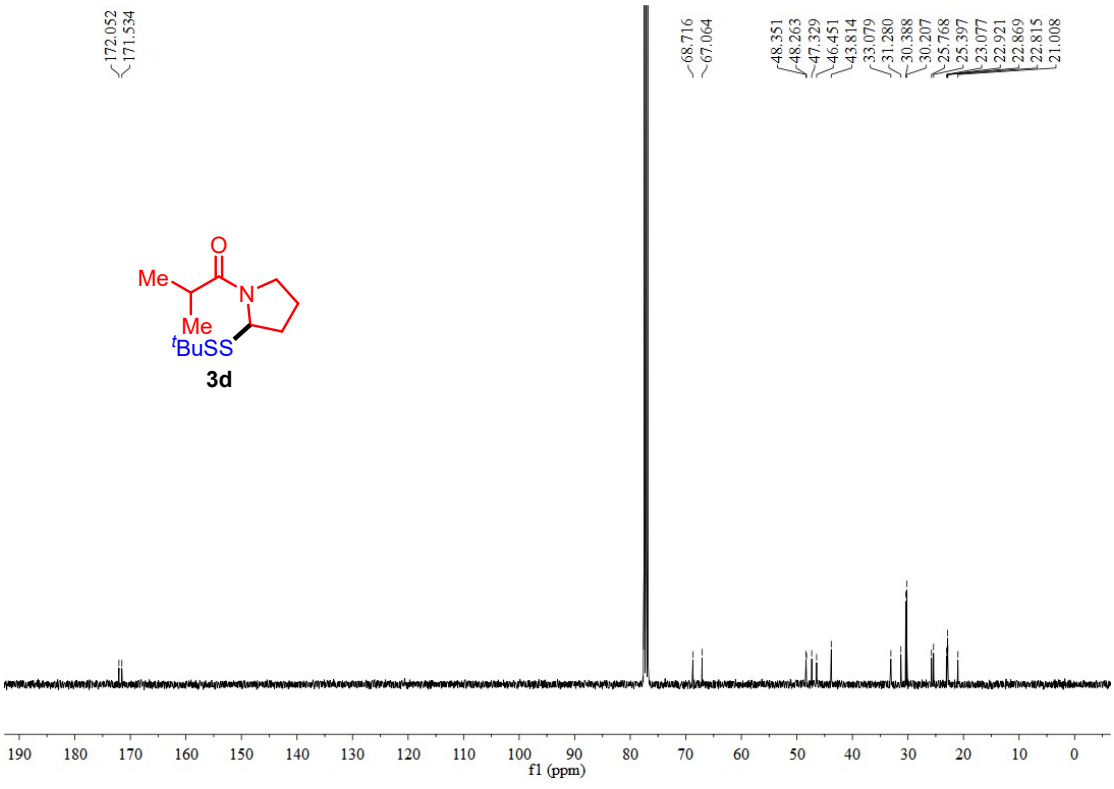
3c, $^{1}H+^{13}C$


5.292
5.277
4.951
4.938
3.625
3.621
3.597
3.575
3.477
3.452
3.431
3.413
3.407
3.389
3.383
3.364
2.470
2.453
2.332
2.314
2.282
2.208
2.191
2.179
2.078
1.933
1.396
1.369
SStBu
N
Me
O
3c
0.48
0.52
1.03
1.02
3.06
1.01
2.90
9.00
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
f1 (ppm)

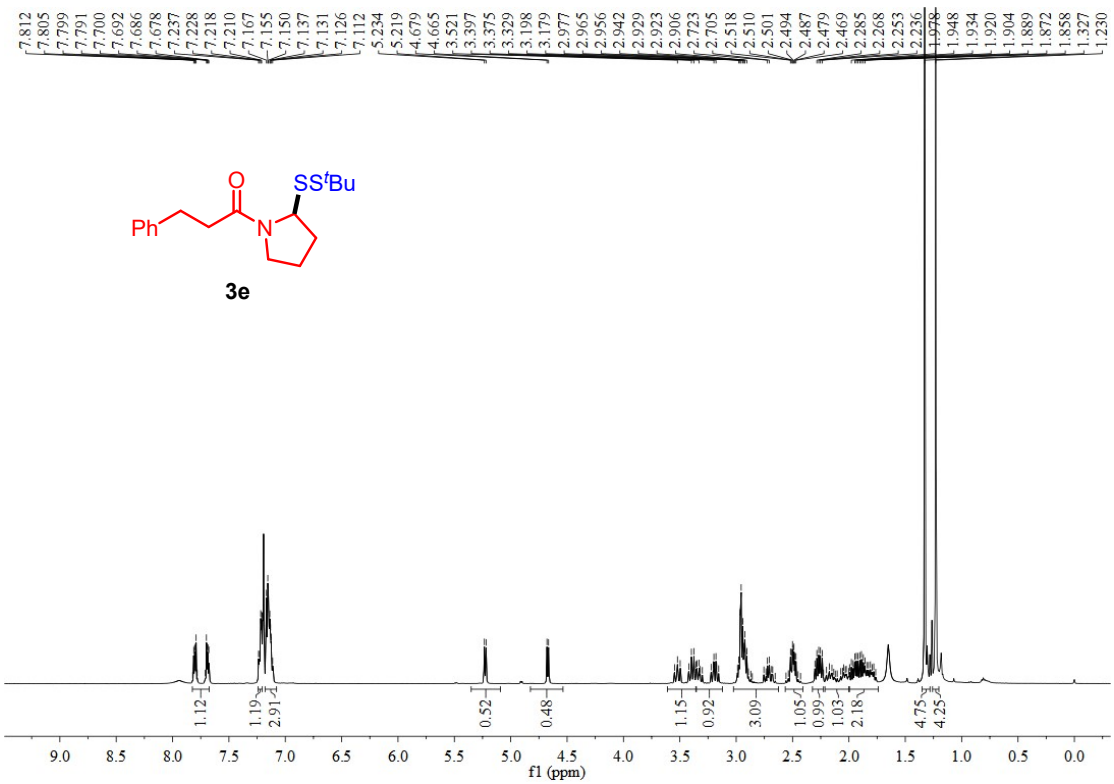

169.928
169.459
69.489
67.073
48.373
48.194
47.930
46.451
33.104
31.661
30.353
30.156
23.106
22.962
22.758
21.234
SStBu
N
Me
O
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

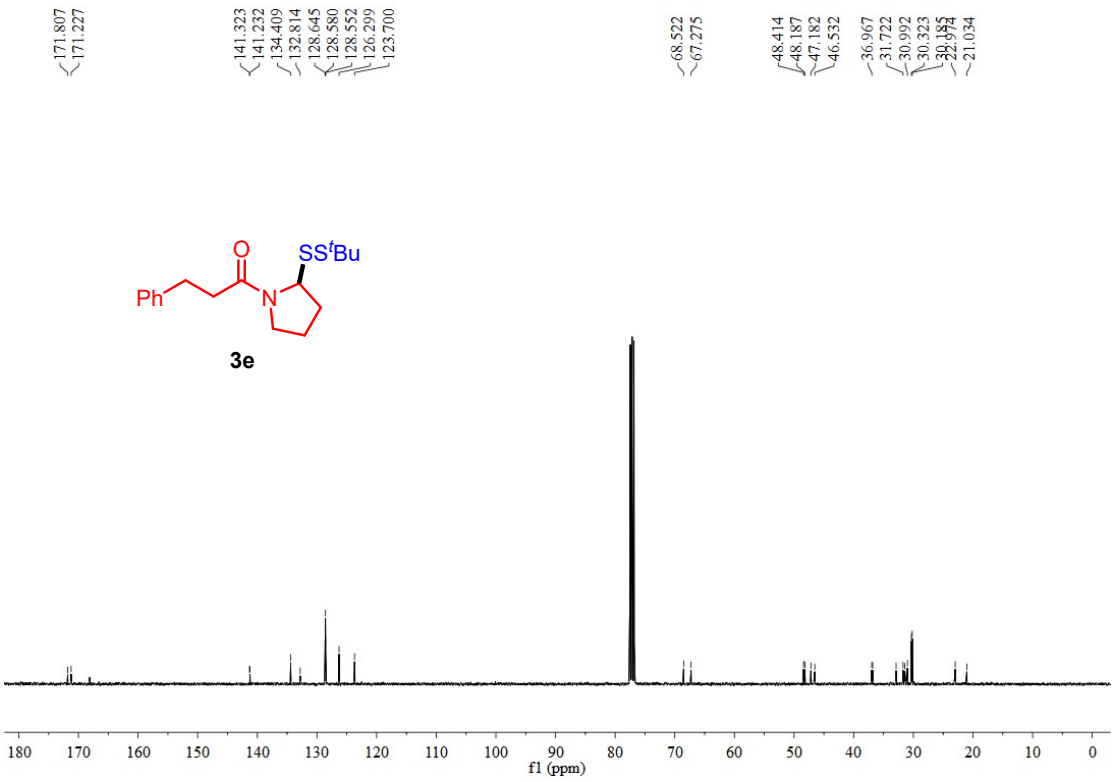
3d, $^{1}H+^{13}C$


5.261
5.246
4.898
4.885
3.551
3.542
3.538
3.534
3.519
3.504
3.498
3.392
3.367
3.348
3.337
3.329
3.323
3.305
3.299
2.510
2.491
2.472
2.454
2.385
2.368
2.354
2.337
2.317
2.300
2.281
2.269
2.254
2.241
2.147
2.135
2.127
2.112
2.100
2.090
2.084
2.072
2.069
2.057
2.050
1.935
1.931
1.920
1.908
1.893
1.889
1.849
1.835
1.315
1.297
0.950
0.934
0.918
0.905
0.889
O
Me
N
Me
tBuSS
3d
0.50
0.41
0.97
0.98
2.02
2.26
1.08
9.01
6.00
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
f1 (ppm)

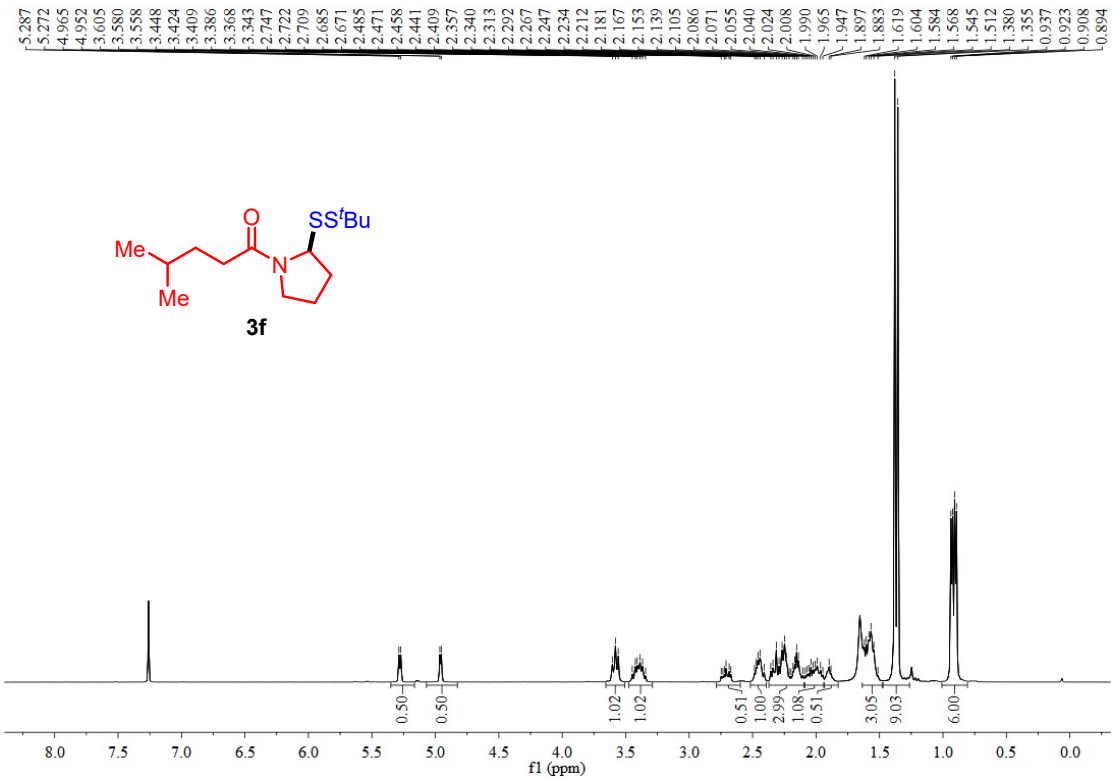

172.052
171.534
68.716
67.064
48.351
48.263
47.329
46.451
43.814
33.079
31.280
30.388
30.207
25.768
25.397
23.077
22.921
22.869
22.815
21.008
O
Me
N
Me
tBuSS
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

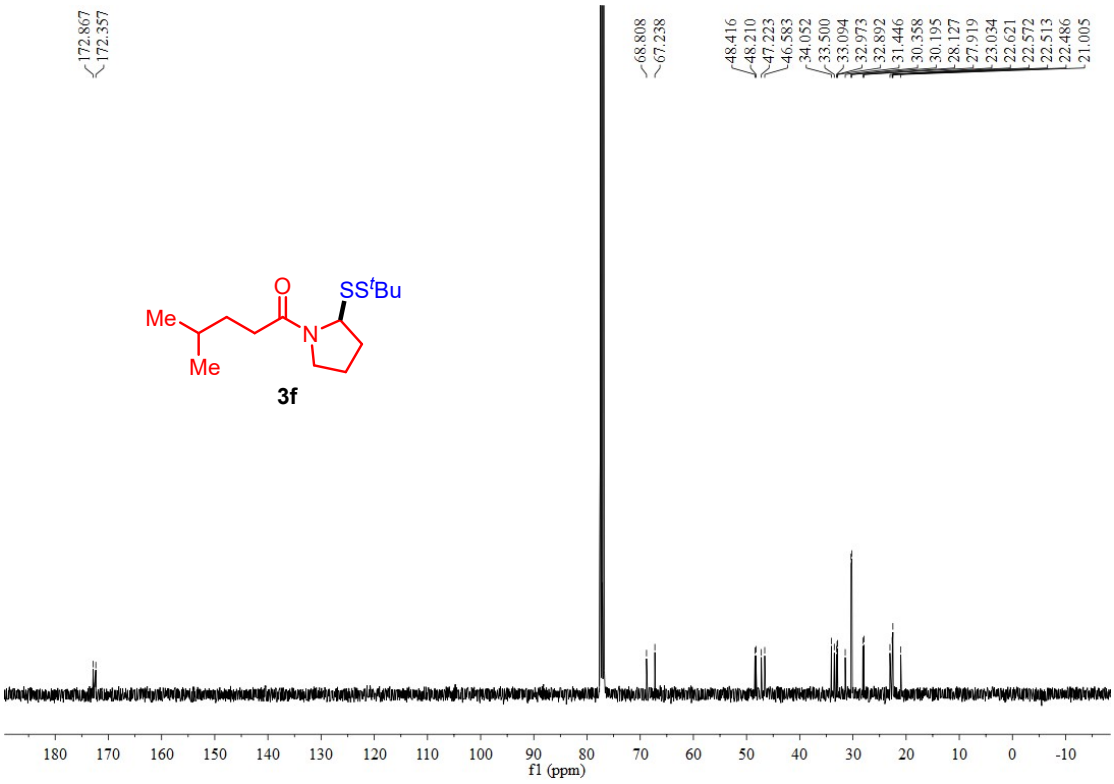
3e, $^{1}H+^{13}C$


7.812
7.805
7.799
7.791
7.700
7.692
7.686
7.678
7.237
7.228
7.218
7.210
7.167
7.155
7.150
7.137
7.131
7.126
7.112
5.234
5.219
4.679
4.665
3.521
3.397
3.375
3.329
3.198
3.179
2.977
2.965
2.956
2.942
2.929
2.923
2.906
2.723
2.705
2.518
2.510
2.501
2.494
2.487
2.479
2.469
2.285
2.268
2.253
2.236
1.978
1.948
1.934
1.920
1.904
1.889
1.872
1.858
1.327
1.230
O
SS^{t}Bu
Ph
N
3e
1.12
1.19
2.91
0.52
0.48
1.15
0.92
3.09
1.05
0.99
1.03
2.18
4.75
4.25
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
f1 (ppm)

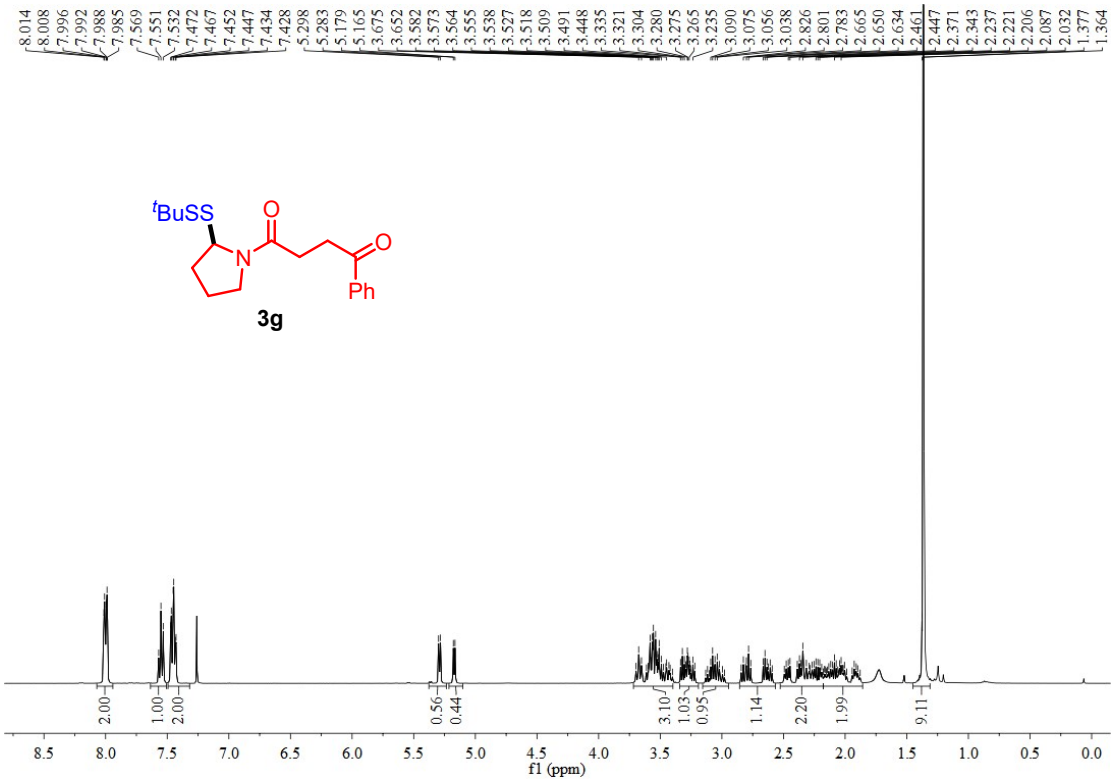

171.807
171.227
141.323
141.232
134.409
132.814
128.645
128.580
128.552
126.299
123.700
68.522
67.275
48.414
48.187
47.182
46.532
36.967
31.722
30.992
30.323
21.034
O
SS^{t}Bu
Ph
N
3e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

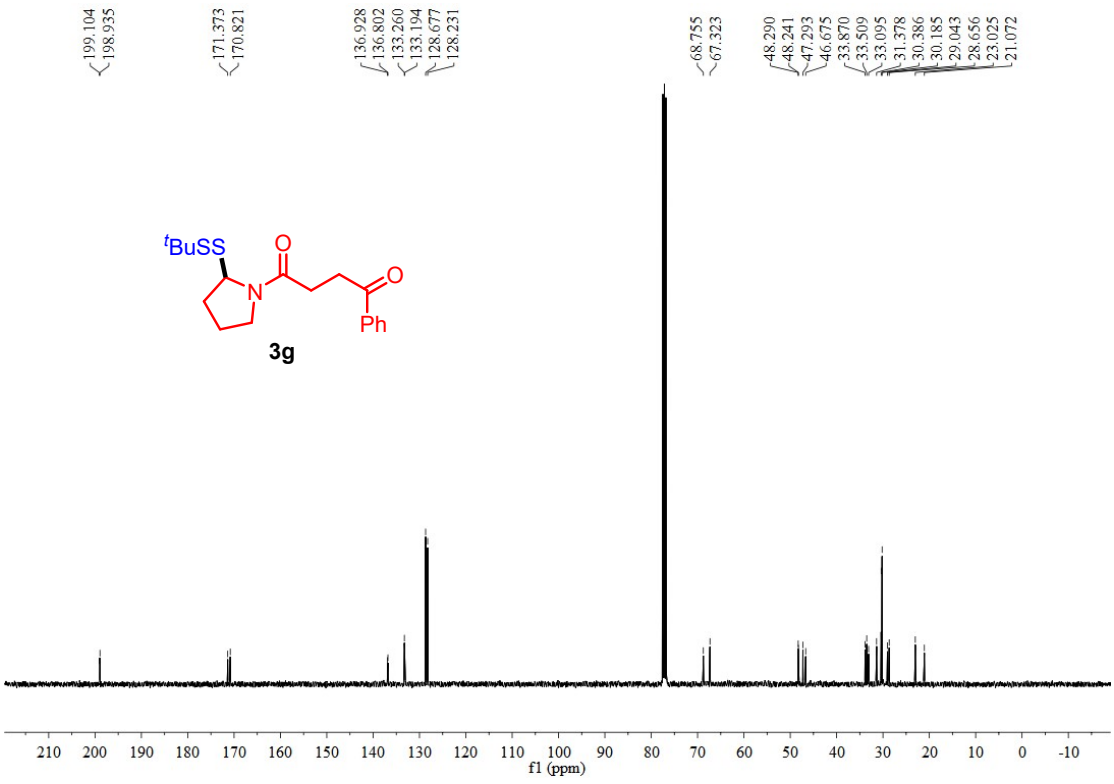
3f, $^{1}H+^{13}C$


5.287
5.272
4.965
4.952
3.605
3.580
3.558
3.448
3.424
3.409
3.386
3.368
3.343
2.747
2.722
2.709
2.685
2.671
2.485
2.471
2.458
2.441
2.409
2.357
2.340
2.313
2.292
2.267
2.247
2.234
2.212
2.181
2.167
2.153
2.139
2.105
2.086
2.071
2.055
2.040
2.024
2.008
1.990
1.965
1.947
1.897
1.883
1.619
1.604
1.584
1.568
1.545
1.512
1.380
1.355
0.937
0.923
0.908
0.894
Me
Me
O
N
SS^{t}Bu
3f
0.50
0.50
1.02
1.02
0.51
1.00
2.99
1.08
0.51
3.05
9.03
6.00
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
f1 (ppm)

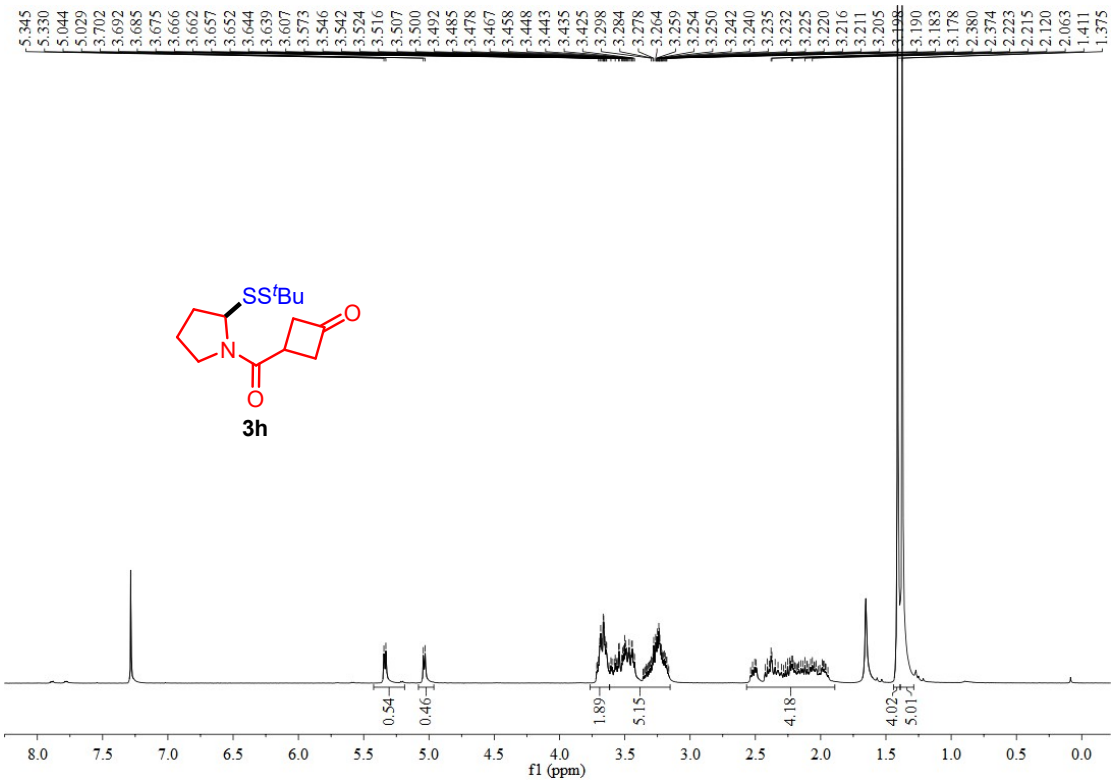

172.867
172.357
68.808
67.238
48.416
48.210
47.223
46.583
34.052
33.500
33.094
32.973
32.892
31.446
30.358
30.195
28.127
27.919
23.034
22.621
22.572
22.513
22.486
21.005
Me
Me
O
N
SS^{t}Bu
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

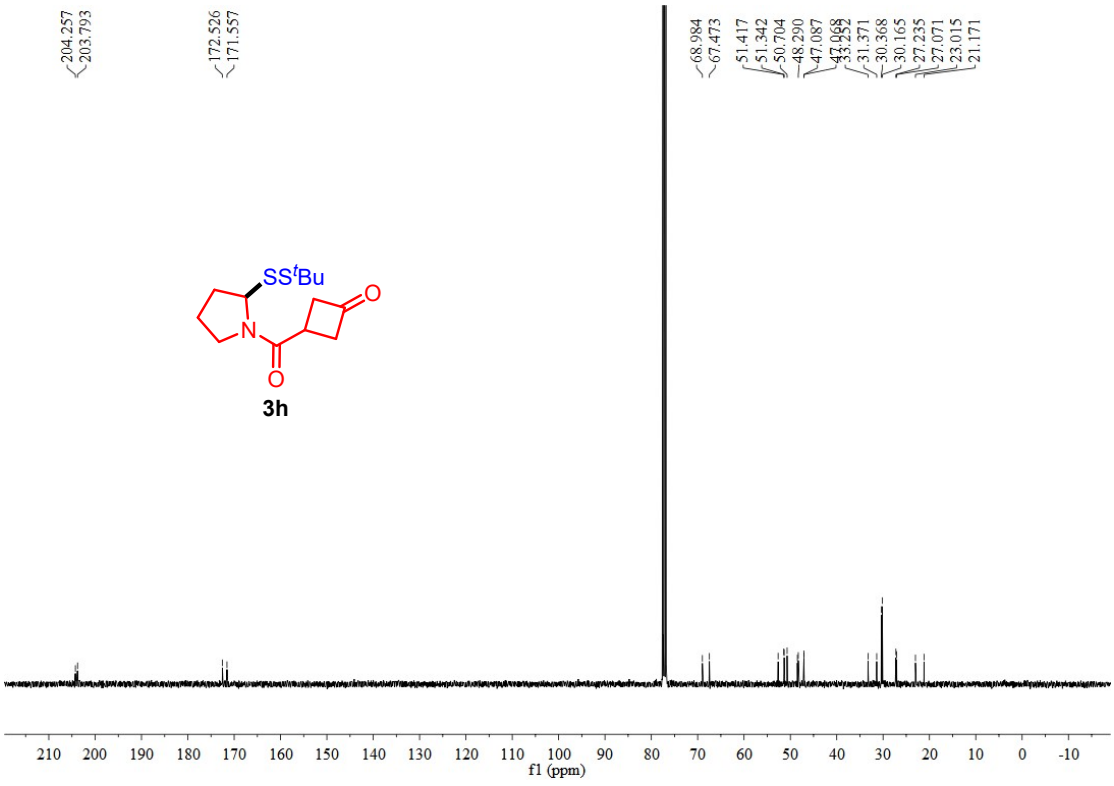
3g, $^{1}H+^{13}C$


8.014
8.008
7.996
7.992
7.988
7.985
7.569
7.551
7.532
7.472
7.467
7.452
7.447
7.434
7.428
5.298
5.283
5.179
5.165
3.675
3.652
3.582
3.573
3.564
3.555
3.538
3.527
3.518
3.509
3.491
3.448
3.335
3.321
3.304
3.280
3.275
3.265
3.235
3.090
3.075
3.056
3.038
2.826
2.801
2.783
2.665
2.650
2.634
2.461
2.447
2.371
2.343
2.237
2.221
2.206
2.087
2.032
1.377
1.364
tBuSS
O
N
O
Ph
3g
2.00
1.00
2.00
0.56
0.44
3.10
1.03
0.95
1.14
2.20
1.99
9.11
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
f1 (ppm)

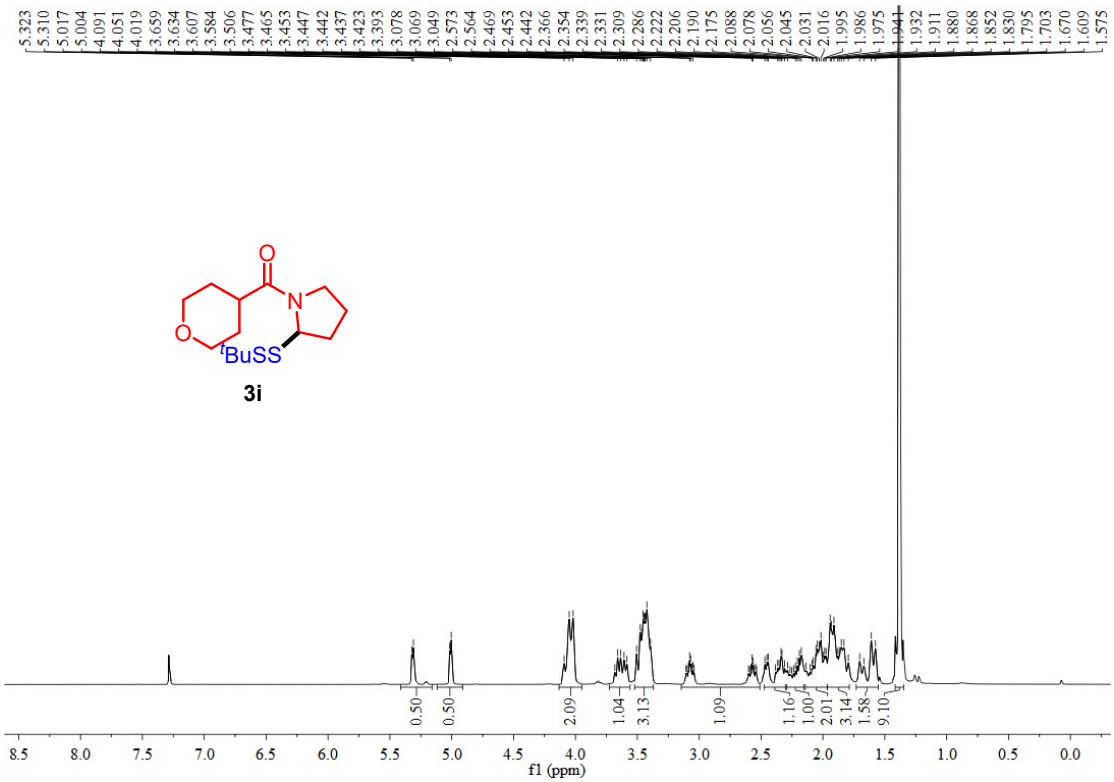

199.104
198.935
171.373
170.821
136.928
136.802
133.260
133.194
128.677
128.231
68.755
67.323
48.290
48.241
47.293
46.675
33.870
33.509
33.095
31.378
30.386
30.185
29.043
28.656
23.025
21.072
tBuSS
O
N
O
Ph
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

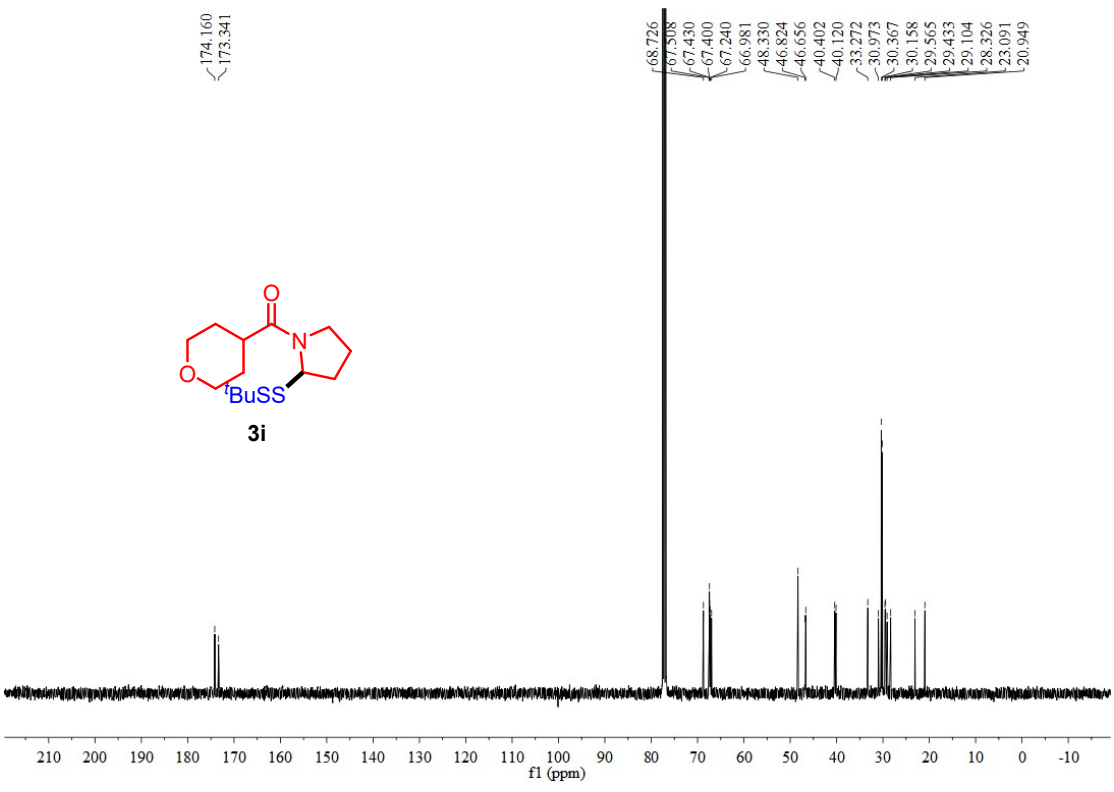
3h, $^{1}H+^{13}C$


5.345
5.330
5.044
5.029
3.702
3.692
3.685
3.675
3.666
3.662
3.657
3.652
3.644
3.639
3.607
3.573
3.546
3.542
3.524
3.516
3.507
3.500
3.492
3.485
3.478
3.467
3.458
3.448
3.443
3.435
3.425
3.298
3.284
3.278
3.264
3.259
3.254
3.250
3.242
3.240
3.235
3.232
3.225
3.220
3.216
3.211
3.205
3.198
3.190
3.183
3.178
2.380
2.374
2.223
2.215
2.120
2.063
1.411
1.375
SS^{t}Bu
N
O
O
3h
0.54
0.46
1.89
5.15
4.18
4.02
5.01
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
f1 (ppm)

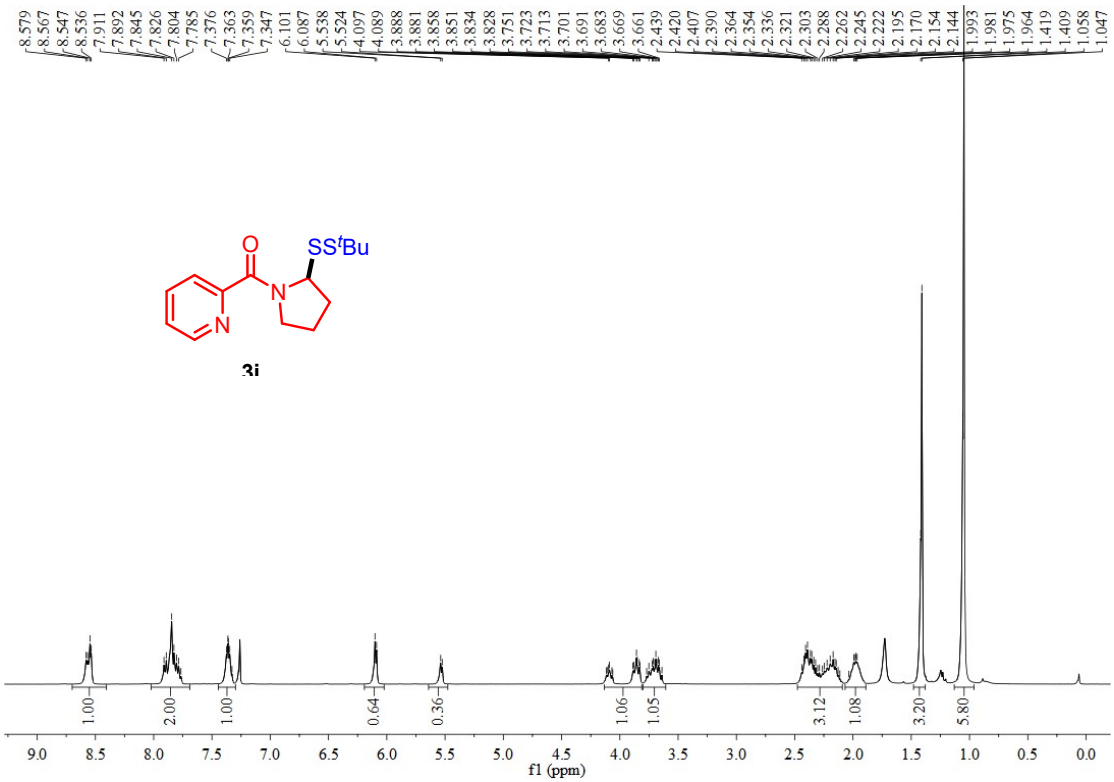

204.257
203.793
172.526
171.557
68.984
67.473
51.417
51.342
50.704
48.290
47.087
47.068
33.252
31.371
30.368
30.165
27.235
27.071
23.015
21.171
SS^{t}Bu
N
O
O
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3i, $^{1}H+^{13}C$

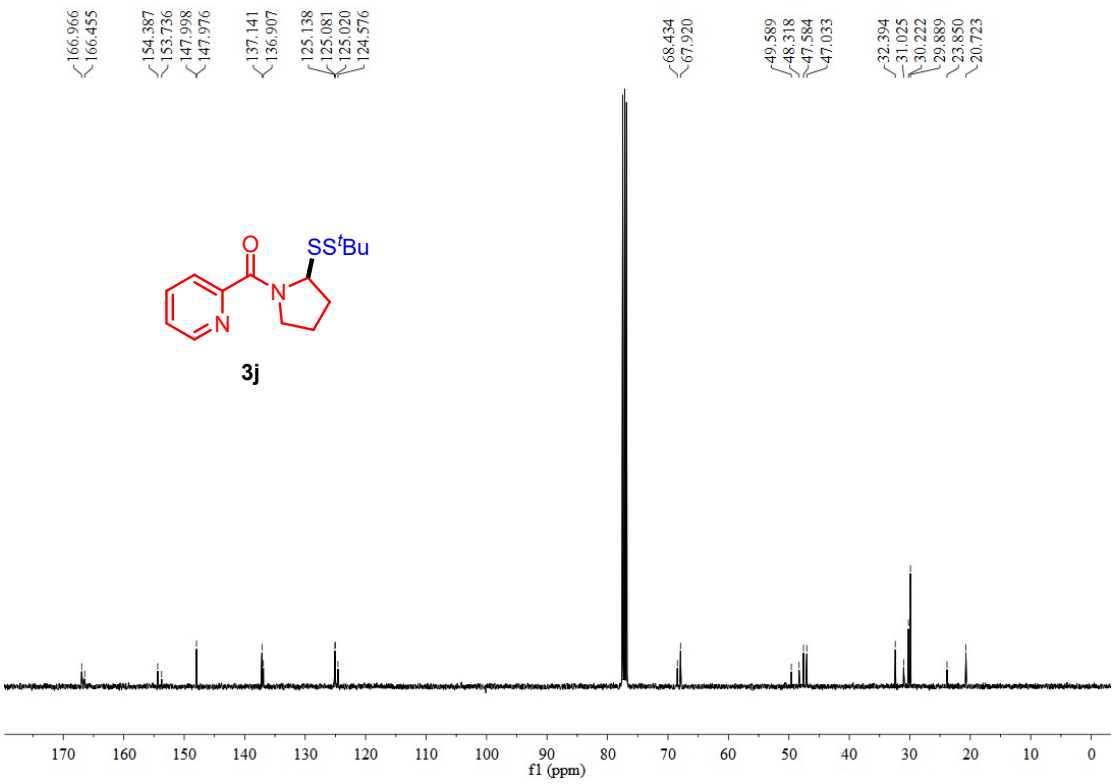

5.323
5.310
5.017
5.004
4.091
4.051
4.019
3.659
3.634
3.607
3.584
3.506
3.477
3.465
3.453
3.447
3.442
3.437
3.423
3.393
3.078
3.069
3.049
2.573
2.564
2.469
2.453
2.442
2.366
2.354
2.339
2.331
2.309
2.286
2.222
2.206
2.190
2.175
2.088
2.078
2.056
2.045
2.031
2.016
1.995
1.986
1.975
1.941
1.932
1.911
1.880
1.868
1.852
1.830
1.795
1.703
1.670
1.609
1.575
O
N
O
tBuSS
3i
0.50
0.50
2.09
1.04
3.13
1.09
1.16
1.00
2.01
3.14
1.58
9.10
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
f1 (ppm)


174.160
173.341
68.726
67.508
67.430
67.400
67.240
66.981
48.330
46.824
46.656
40.402
40.120
33.272
30.973
30.367
30.158
29.565
29.433
29.104
28.326
23.091
20.949
O
N
O
tBuSS
3i
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)

3j, $^{1}H+^{13}C$

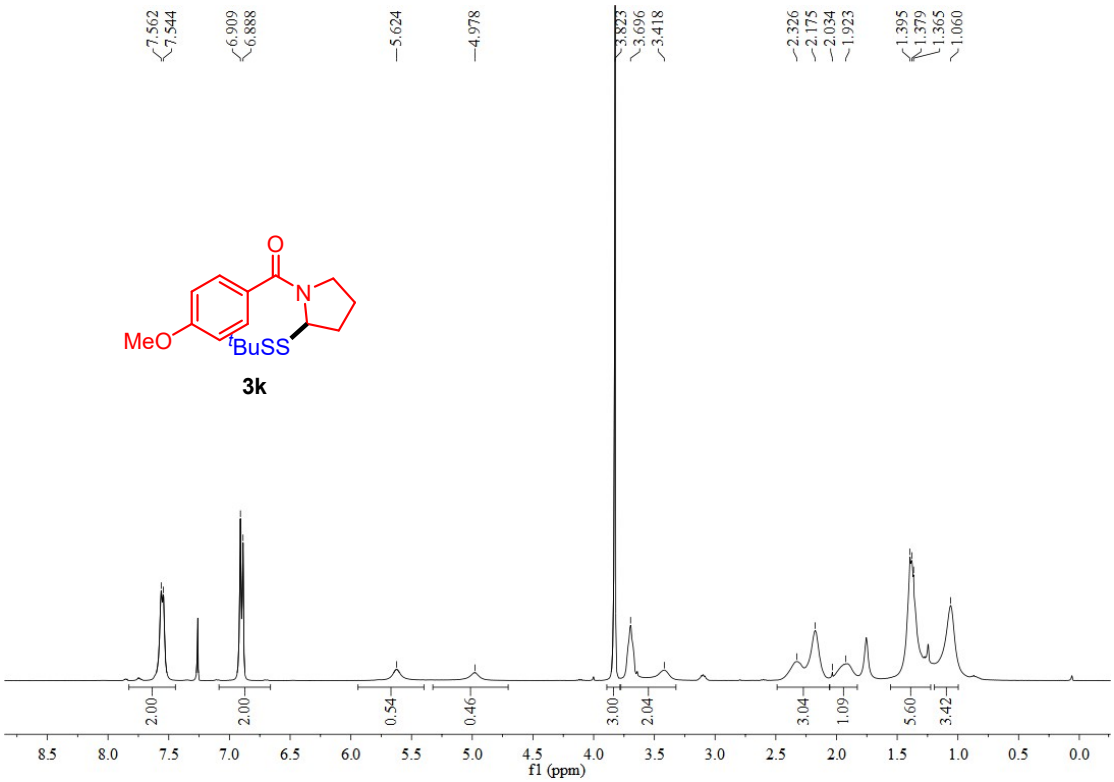


3i

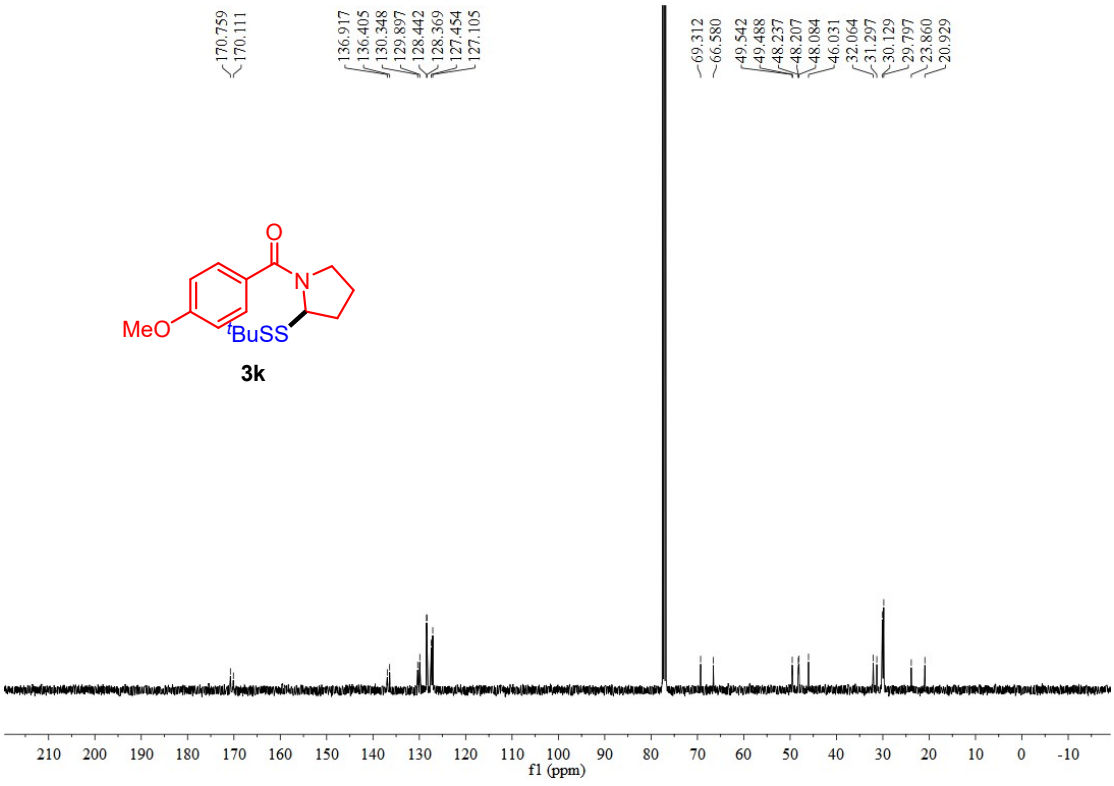


3j

3k, $^{1}H+^{13}C$

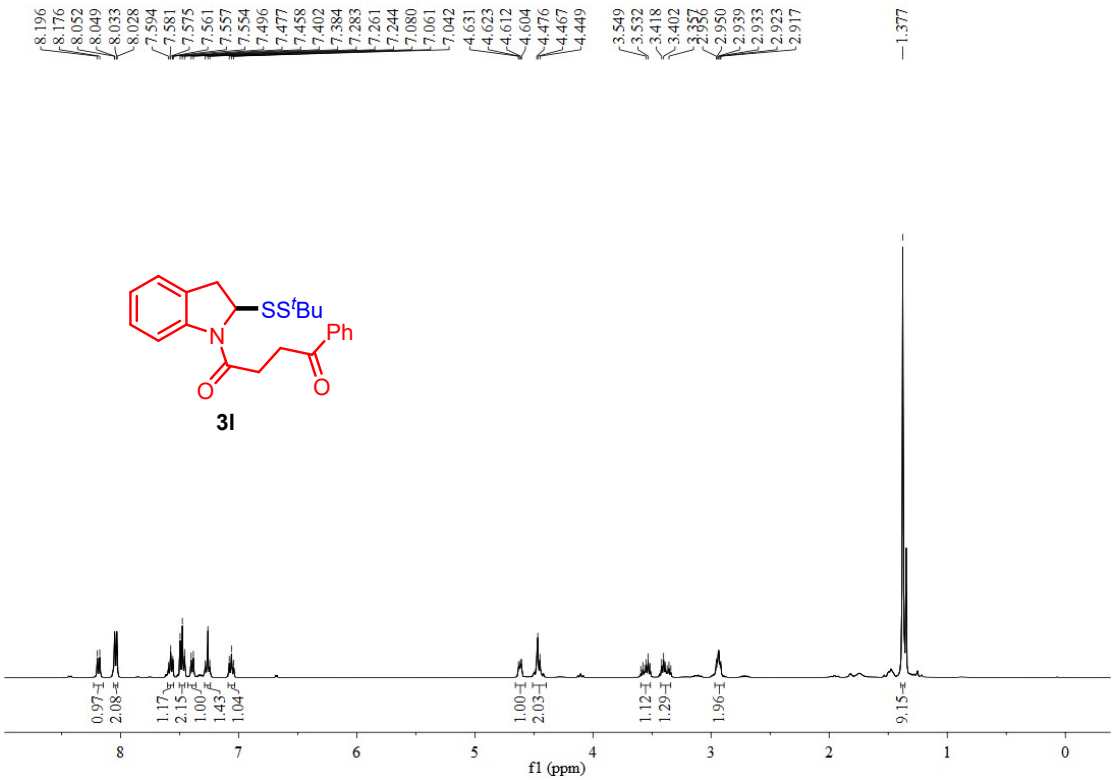


3k

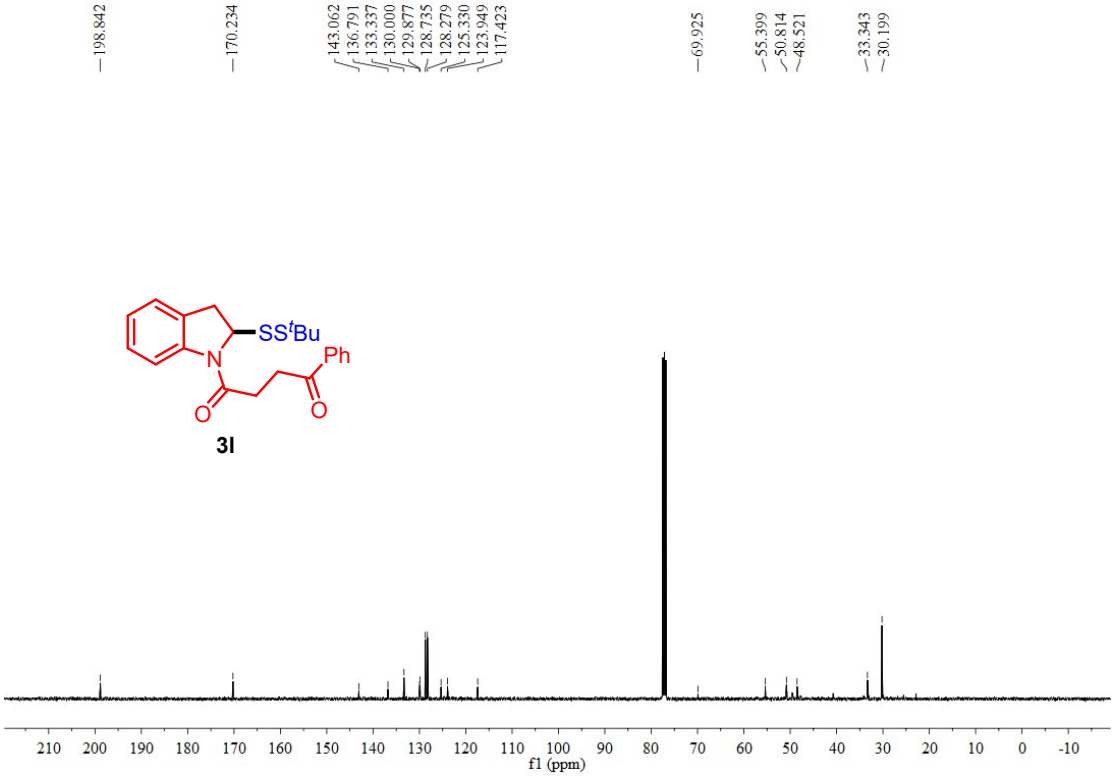


3k

3l, $^{1}H+^{13}C$

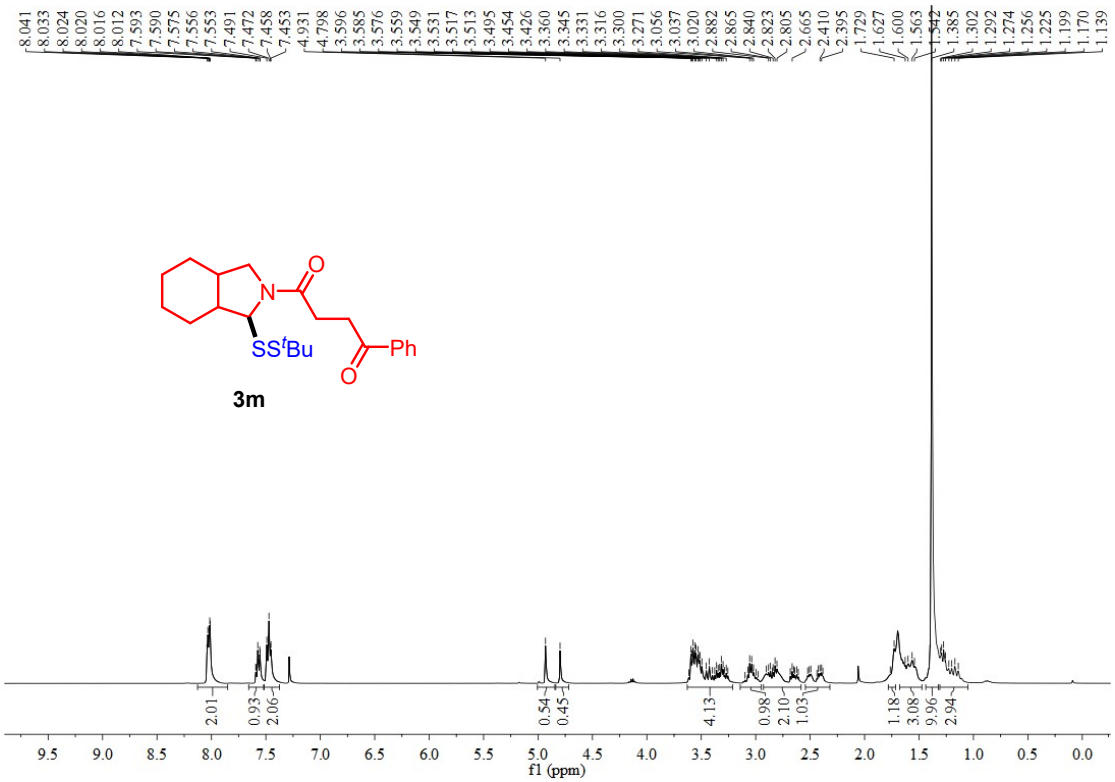


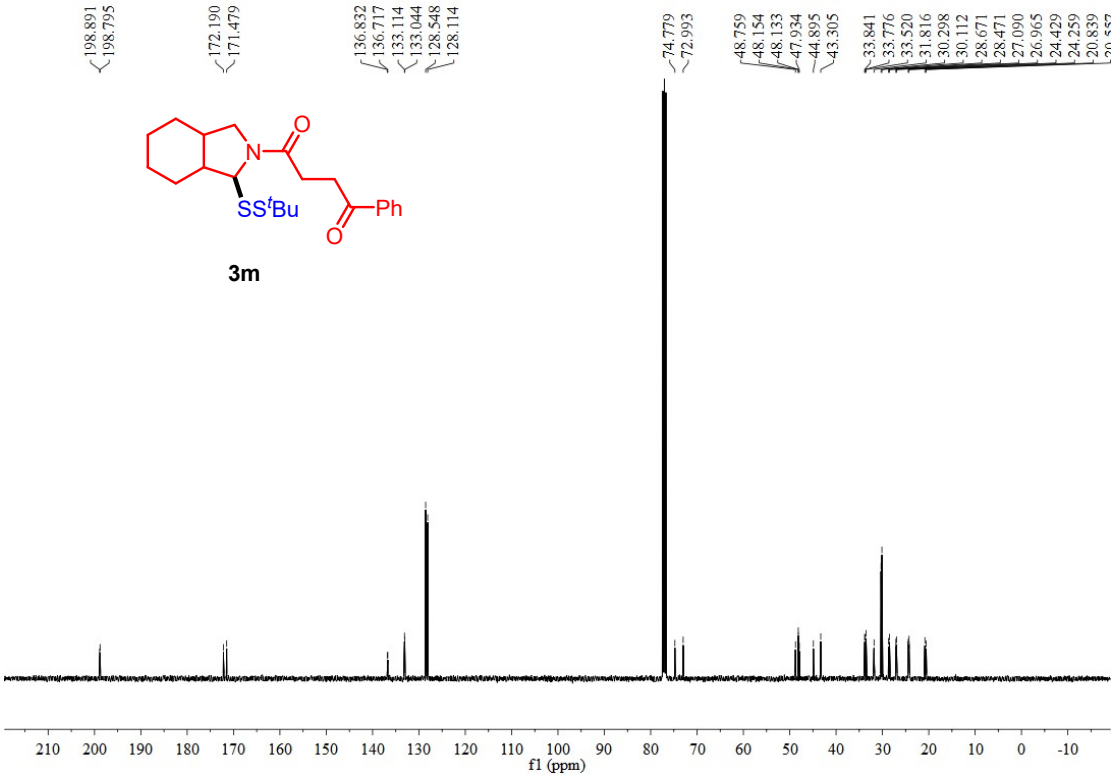
3l



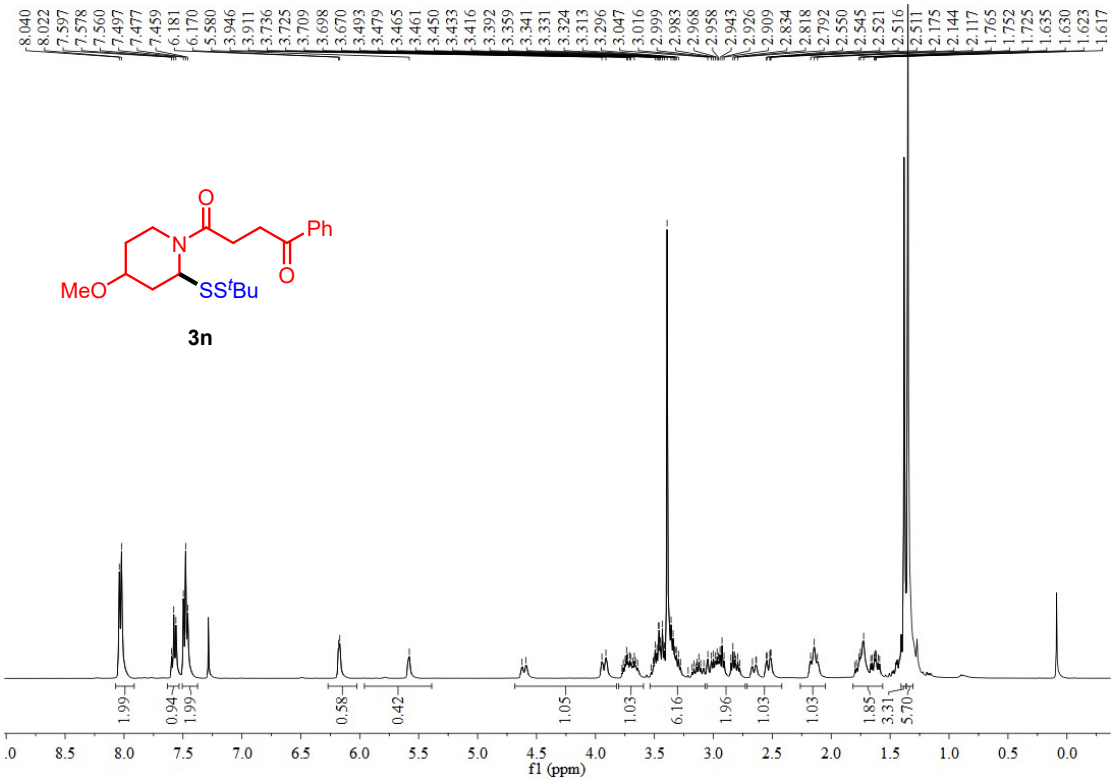
3l

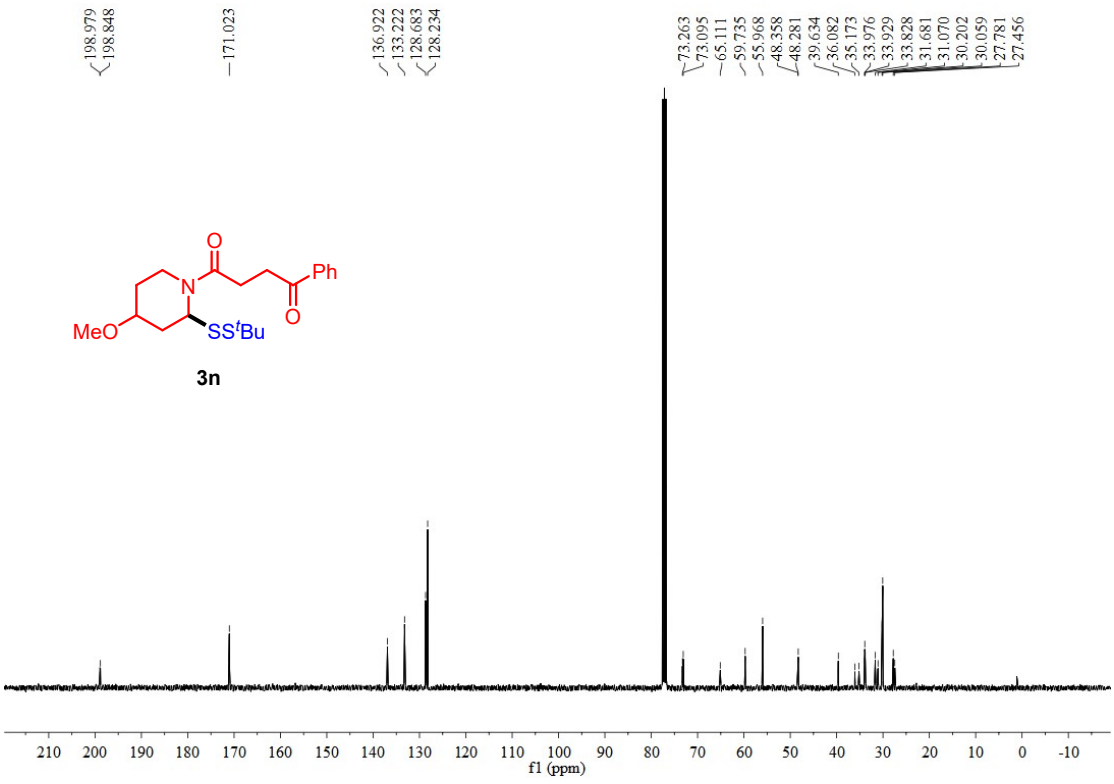
3m, $^{1}H+^{13}C$


8.041
8.033
8.024
8.020
8.016
8.012
7.593
7.590
7.575
7.556
7.553
7.491
7.472
7.458
7.453
4.931
4.798
3.596
3.585
3.576
3.559
3.549
3.531
3.517
3.513
3.495
3.454
3.426
3.360
3.345
3.331
3.316
3.300
3.271
3.056
3.037
3.020
2.882
2.865
2.840
2.823
2.805
2.665
2.410
2.395
1.729
1.627
1.600
1.563
1.542
1.385
1.302
1.292
1.274
1.256
1.225
1.199
1.170
1.139
N
O
SS^{t}Bu
Ph
O
3m
2.01
0.93
2.06
0.54
0.45
4.13
0.98
2.10
1.03
1.18
3.08
9.96
2.94
f1 (ppm)

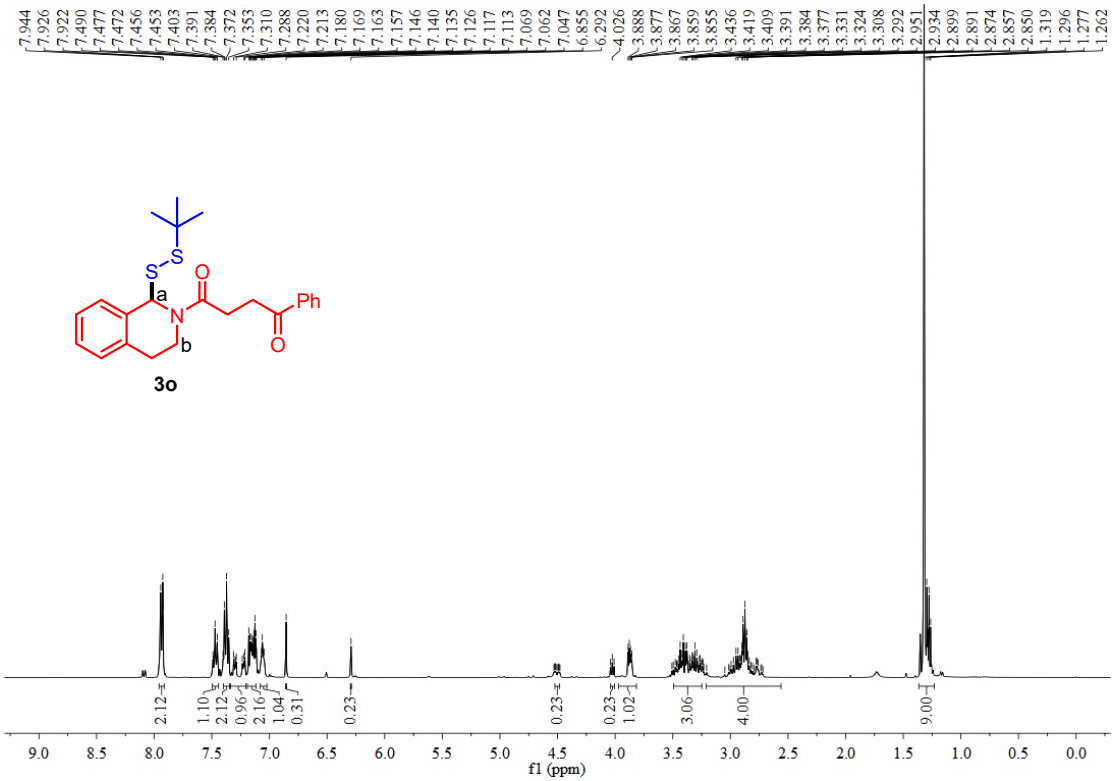

198.891
198.795
172.190
171.479
136.832
136.717
133.114
133.044
128.548
128.114
74.779
72.993
48.759
48.154
48.133
47.934
44.895
43.305
33.841
33.776
33.520
31.816
30.298
30.112
28.671
28.471
27.090
26.965
24.429
24.259
20.839
N
O
SS^{t}Bu
Ph
O
3m
f1 (ppm)

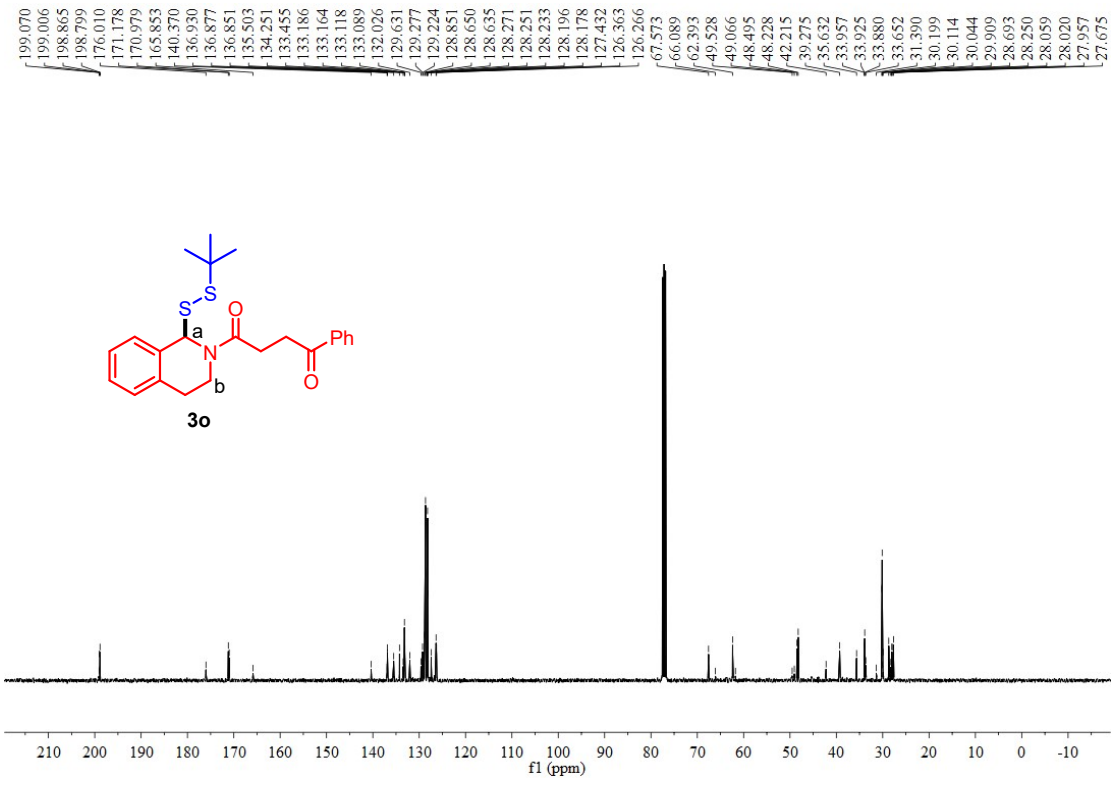
3n, $^{1}H+^{13}C$


8.040
8.022
7.597
7.578
7.560
7.497
7.477
7.459
6.181
6.170
5.580
3.946
3.911
3.736
3.725
3.709
3.698
3.670
3.493
3.479
3.465
3.461
3.450
3.433
3.416
3.392
3.359
3.341
3.331
3.324
3.313
3.296
3.047
3.016
2.999
2.983
2.968
2.958
2.943
2.926
2.909
2.834
2.818
2.792
2.550
2.545
2.521
2.516
2.511
2.175
2.144
2.117
1.765
1.752
1.725
1.635
1.630
1.623
1.617
O
N
Ph
O
MeO
SS^{t}Bu
3n
1.99
0.94
1.99
0.58
0.42
1.05
1.03
6.16
1.96
1.03
1.03
1.85
3.31
5.70
f1 (ppm)

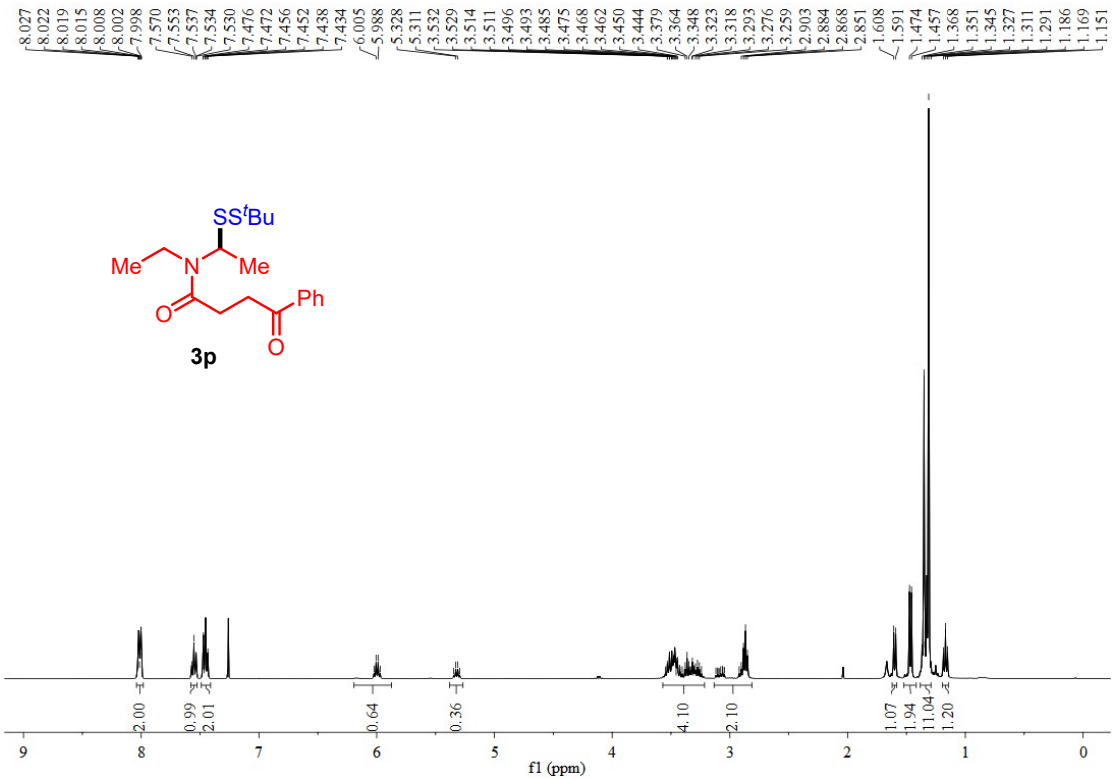

198.979
198.848
171.023
136.922
133.222
128.683
128.234
73.263
73.095
65.111
59.735
55.968
48.358
48.281
39.634
36.082
35.173
33.976
33.929
33.828
31.681
31.070
30.202
30.059
27.781
27.456
O
N
Ph
O
MeO
SS^{t}Bu
3n
f1 (ppm)

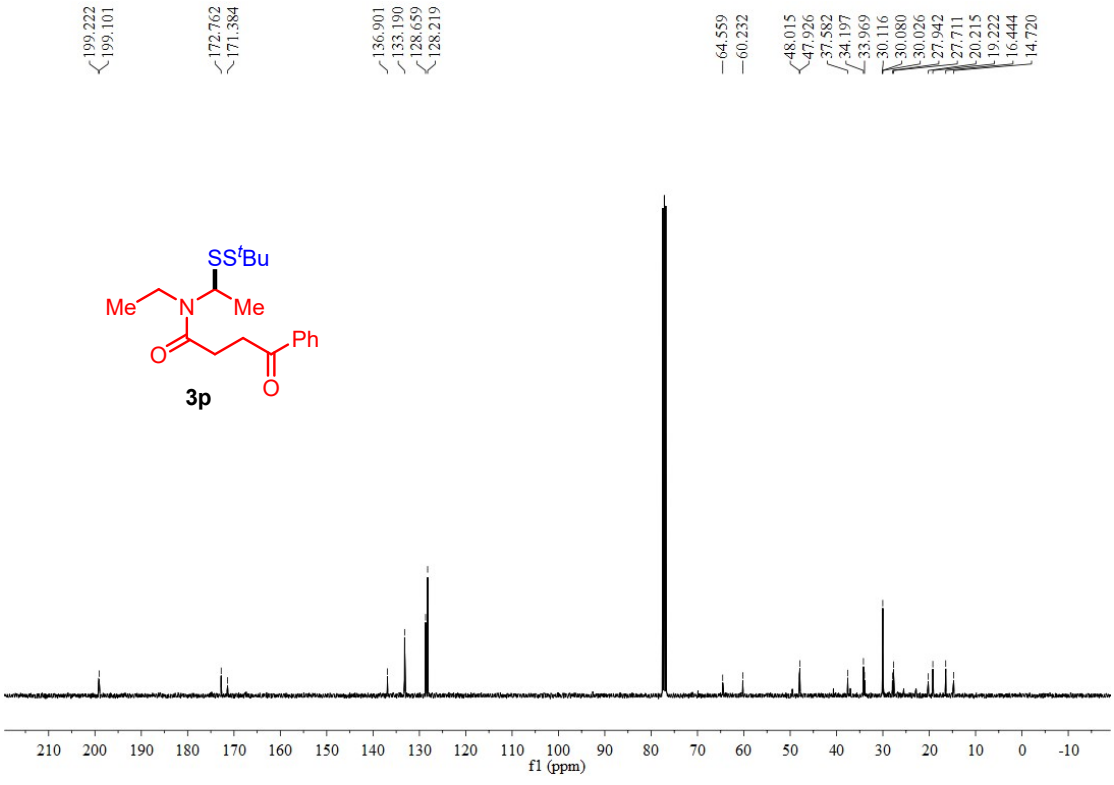
3o, $^{1}H+^{13}C$


7.944
7.926
7.922
7.490
7.477
7.472
7.456
7.453
7.403
7.391
7.384
7.372
7.353
7.310
7.288
7.220
7.213
7.180
7.169
7.163
7.157
7.146
7.140
7.135
7.126
7.117
7.113
7.069
7.062
7.047
6.855
6.292
4.026
3.888
3.877
3.867
3.859
3.855
3.436
3.419
3.409
3.391
3.384
3.377
3.331
3.324
3.308
3.292
2.951
2.934
2.899
2.891
2.874
2.857
2.850
1.319
1.296
1.277
1.262
S
S
a
N
b
O
Ph
O
3o
2.12
1.10
2.12
0.96
2.16
1.04
0.31
0.23
0.23
0.23
1.02
3.06
4.00
9.00
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
f1 (ppm)

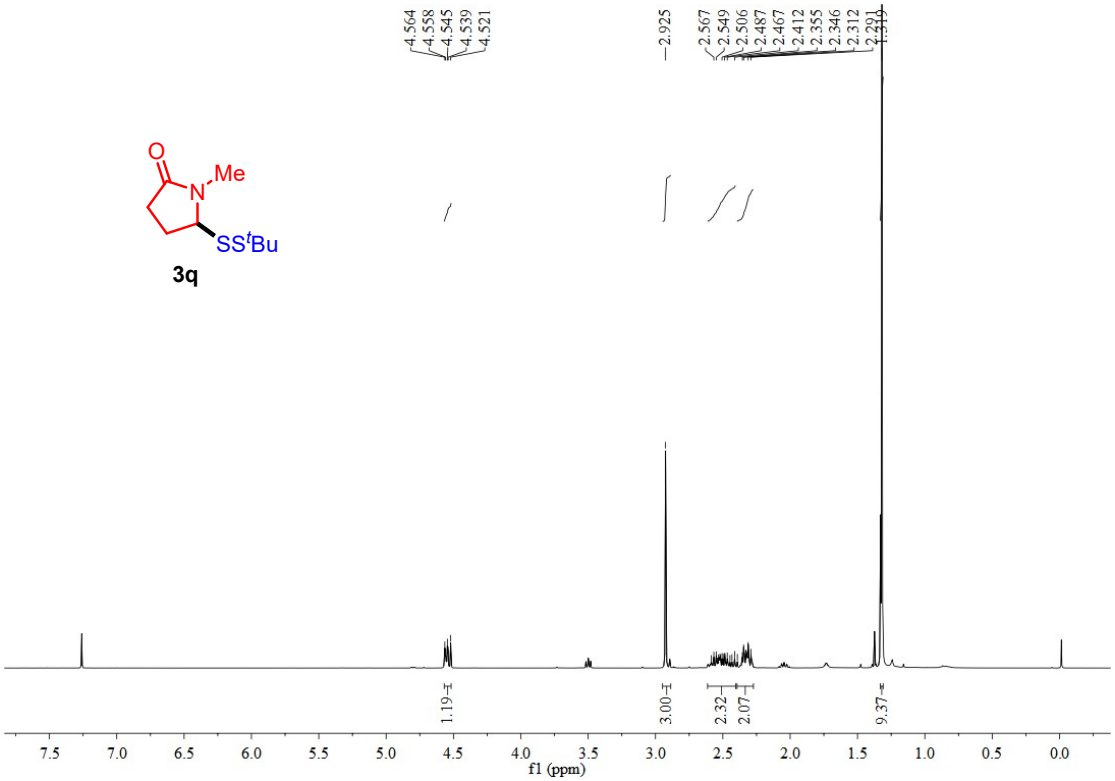

199.070
199.006
198.865
198.799
176.010
171.178
170.979
165.853
140.370
136.930
136.877
136.851
135.503
134.251
133.455
133.186
133.164
133.118
133.089
132.026
129.631
129.277
129.224
128.851
128.650
128.635
128.271
128.251
128.233
128.196
128.178
127.432
126.363
126.266
67.573
66.089
62.393
49.528
49.066
48.495
48.228
42.215
39.275
35.632
33.957
33.925
33.880
33.652
31.390
30.199
30.114
30.044
29.909
28.693
28.250
28.059
28.020
27.957
27.675
S
S
a
N
b
O
Ph
O
3o
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)

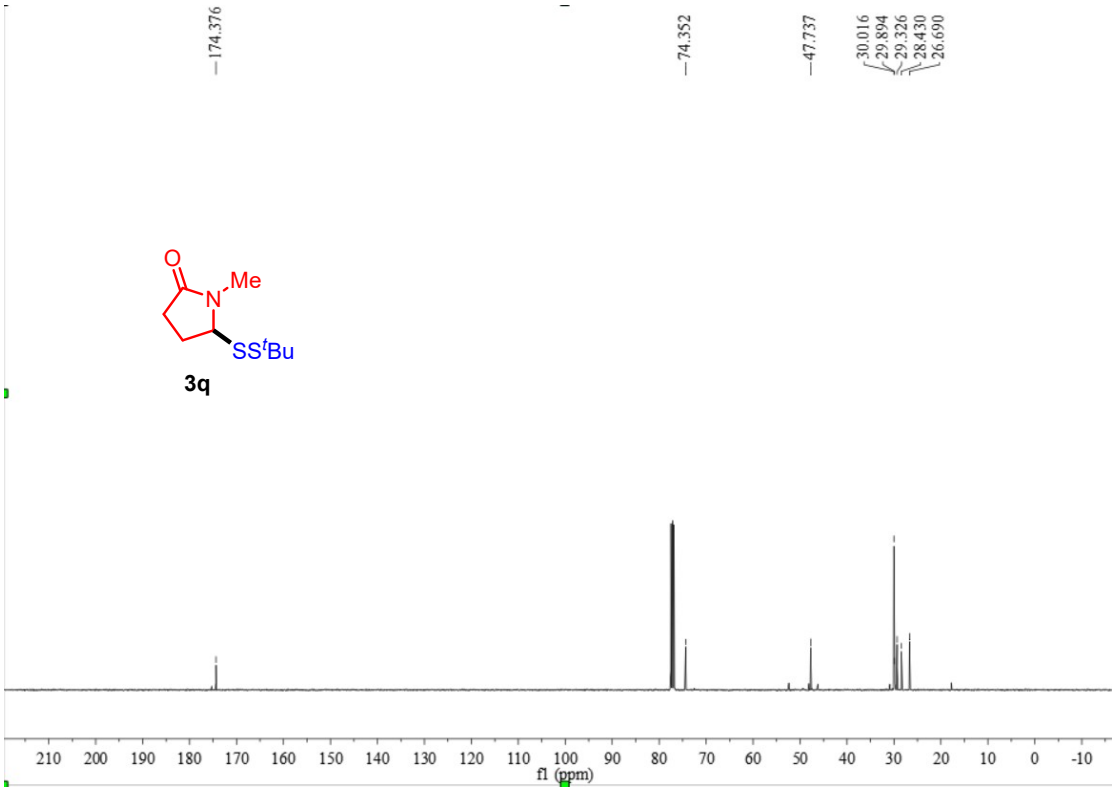
3p, $^{1}H+^{13}C$


8.027
8.022
8.019
8.015
8.008
8.002
7.998
7.570
7.553
7.537
7.534
7.530
7.476
7.472
7.456
7.452
7.438
7.434
6.005
5.988
5.328
5.311
5.332
5.529
3.514
3.511
3.496
3.493
3.485
3.475
3.468
3.462
3.450
3.444
3.379
3.364
3.348
3.323
3.318
3.293
3.276
3.259
2.903
2.884
2.868
2.851
1.608
1.591
1.474
1.457
1.368
1.351
1.345
1.327
1.311
1.291
1.186
1.169
1.151
SS^{t}Bu
Me
N
Me
Ph
O
O
3p
2.00
0.99
2.01
0.64
0.36
4.10
2.10
1.07
1.94
11.04
1.20
f1 (ppm)

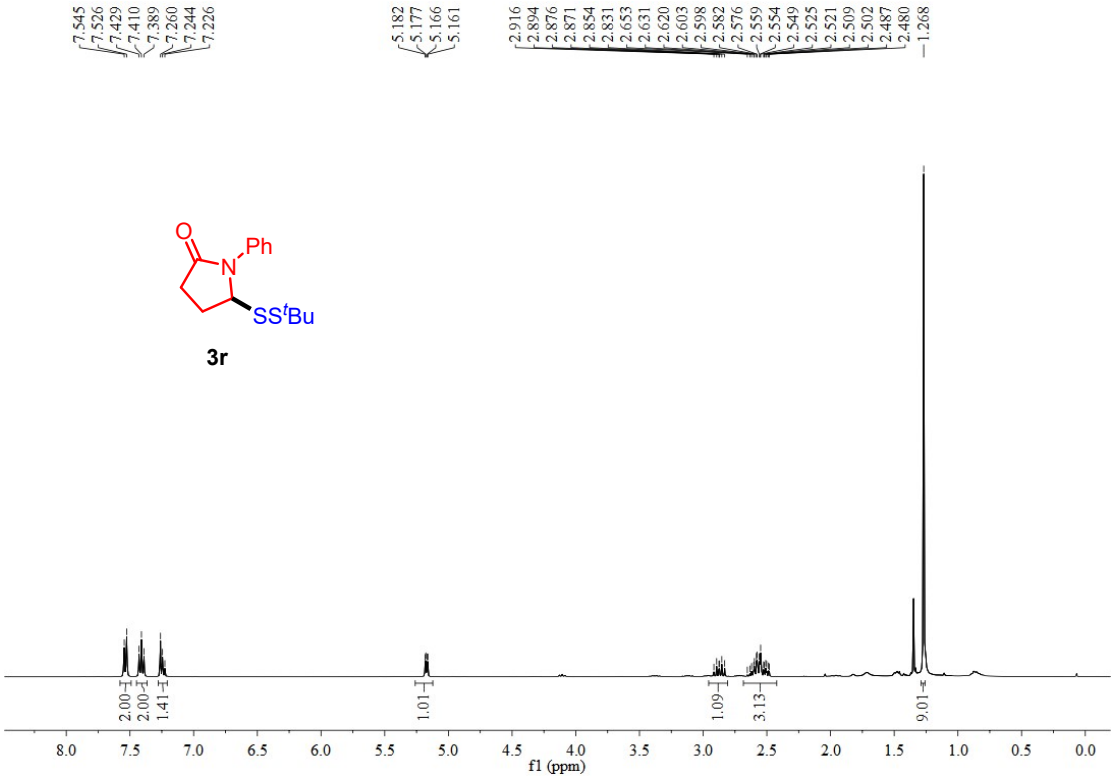

199.222
199.101
172.762
171.384
136.901
133.190
128.659
128.219
64.559
60.232
48.015
47.926
37.582
34.197
33.969
30.116
30.080
30.026
27.942
27.711
20.215
19.222
16.444
14.720
SS^{t}Bu
Me
N
Me
Ph
O
O
3p
f1 (ppm)

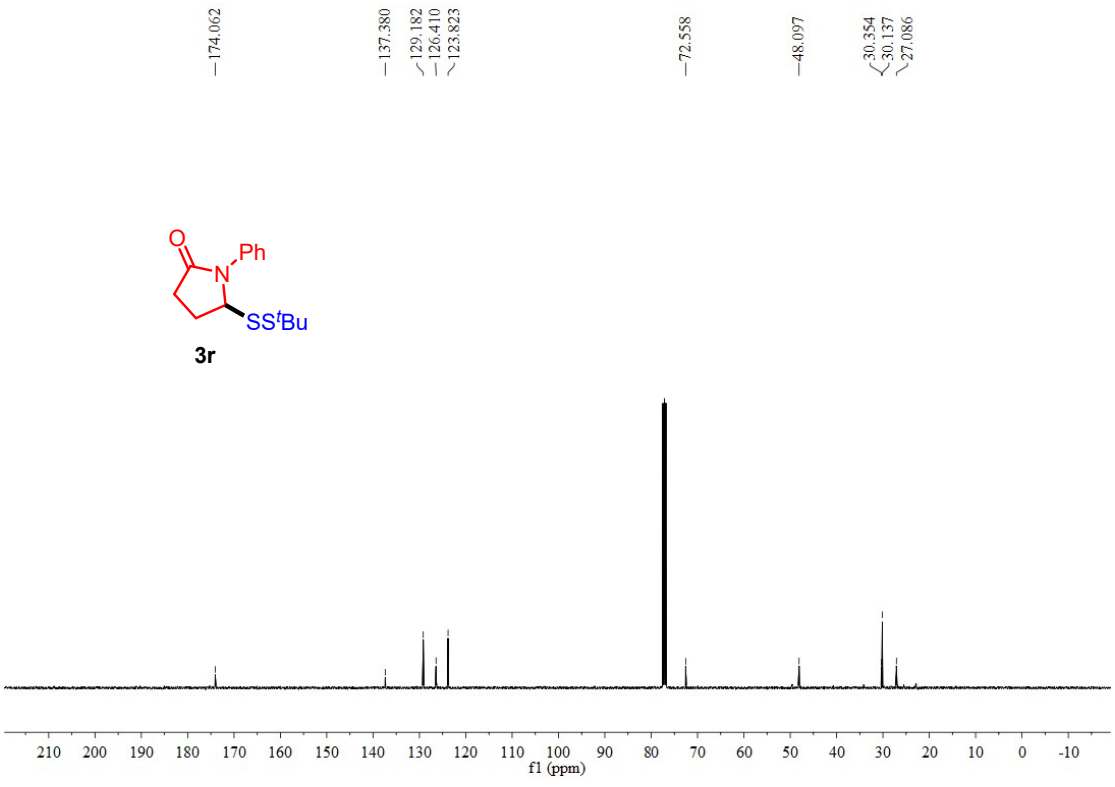
3q, $^{1}H+^{13}C$


4.564
4.558
4.545
4.539
4.521
2.925
2.567
2.549
2.506
2.487
2.467
2.412
2.355
2.346
2.312
2.291
1.319
O
N
Me
SS^{t}Bu
3q
1.19
3.00
2.32
2.07
9.37
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
f1 (ppm)

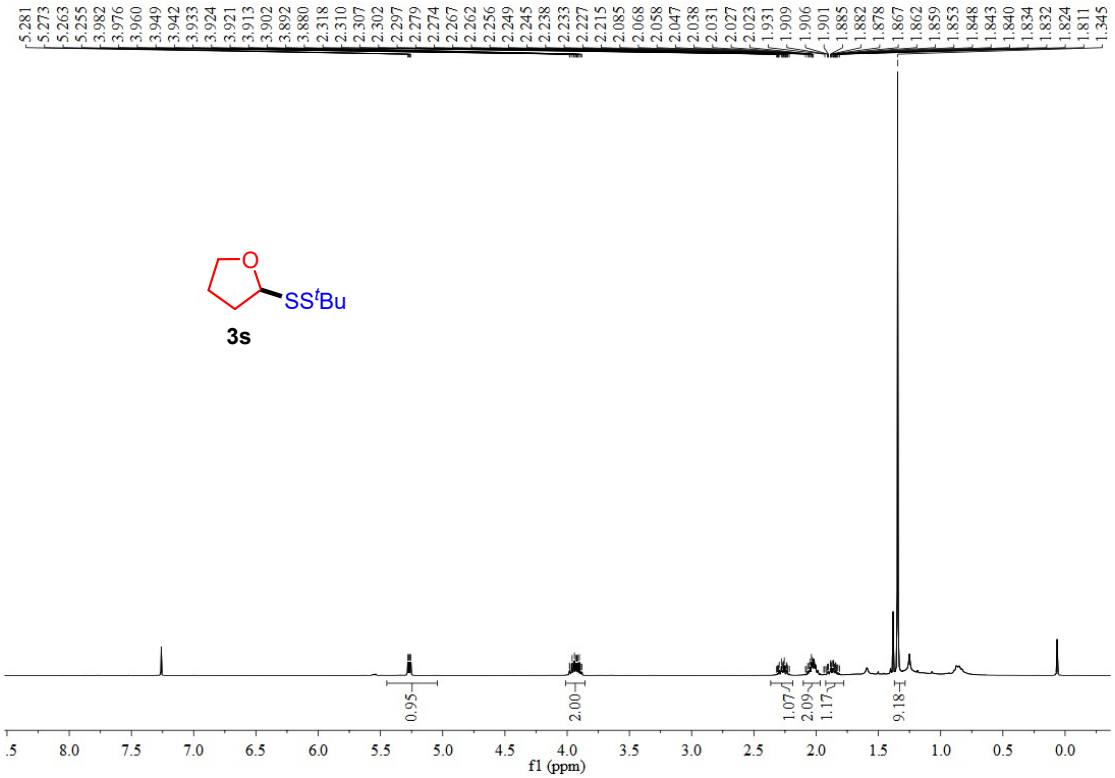

174.376
74.352
47.737
30.016
29.894
29.326
28.430
26.690
O
N
Me
SS^{t}Bu
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

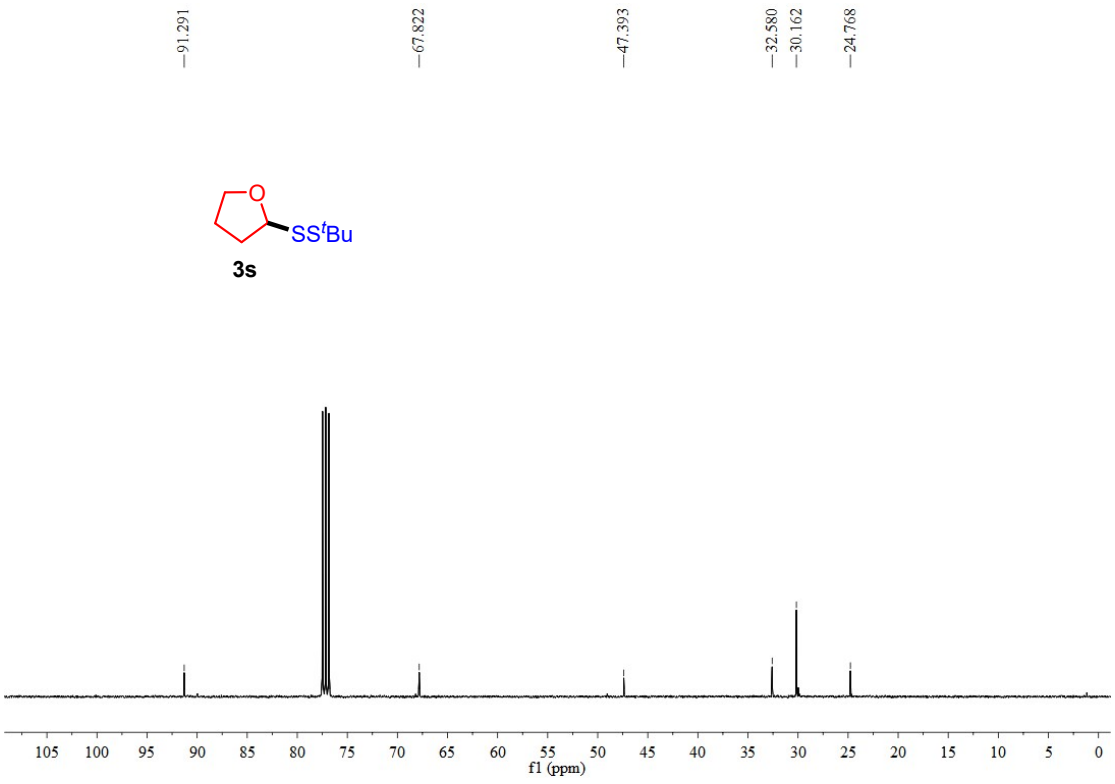
3r, $^{1}H+^{13}C$


7.545
7.526
7.429
7.410
7.389
7.260
7.244
7.226
5.182
5.177
5.166
5.161
2.916
2.894
2.876
2.871
2.854
2.831
2.653
2.631
2.620
2.603
2.598
2.582
2.576
2.559
2.554
2.549
2.525
2.521
2.509
2.502
2.487
2.480
1.268
Ph
N
O
SS^{t}Bu
3r
2.00
2.00
1.41
1.01
1.09
3.13
9.01
f1 (ppm)

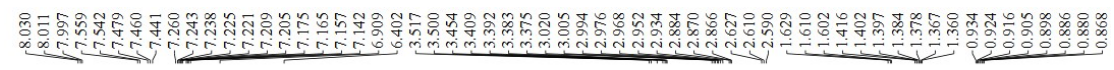

174.062
137.380
129.182
126.410
123.823
72.558
48.097
30.354
30.137
27.086
Ph
N
O
SS^{t}Bu
3r
f1 (ppm)

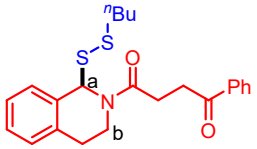
3s, $^{1}H+^{13}C$


5.281
5.273
5.263
5.255
3.982
3.976
3.960
3.949
3.942
3.933
3.924
3.921
3.913
3.902
3.892
3.880
2.318
2.310
2.307
2.302
2.297
2.279
2.274
2.267
2.262
2.256
2.249
2.245
2.238
2.233
2.227
2.215
2.085
2.068
2.058
2.047
2.038
2.031
2.027
2.023
1.931
1.909
1.906
1.901
1.885
1.882
1.878
1.867
1.862
1.859
1.853
1.848
1.843
1.840
1.834
1.832
1.824
1.811
1.345
SS^{t}Bu
3s
0.95
2.00
1.07
2.09
1.17
9.18
f1 (ppm)

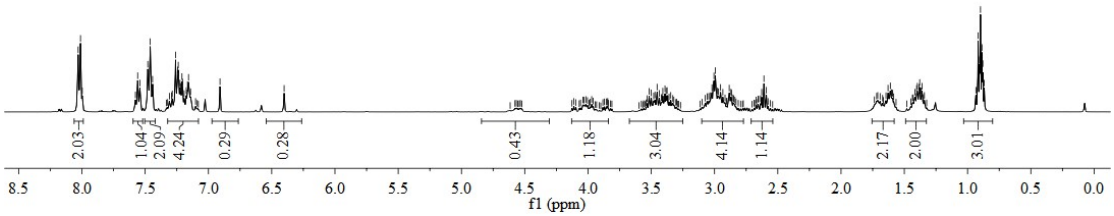

91.291
67.822
47.393
32.580
30.162
24.768
SS^{t}Bu
3s
f1 (ppm)

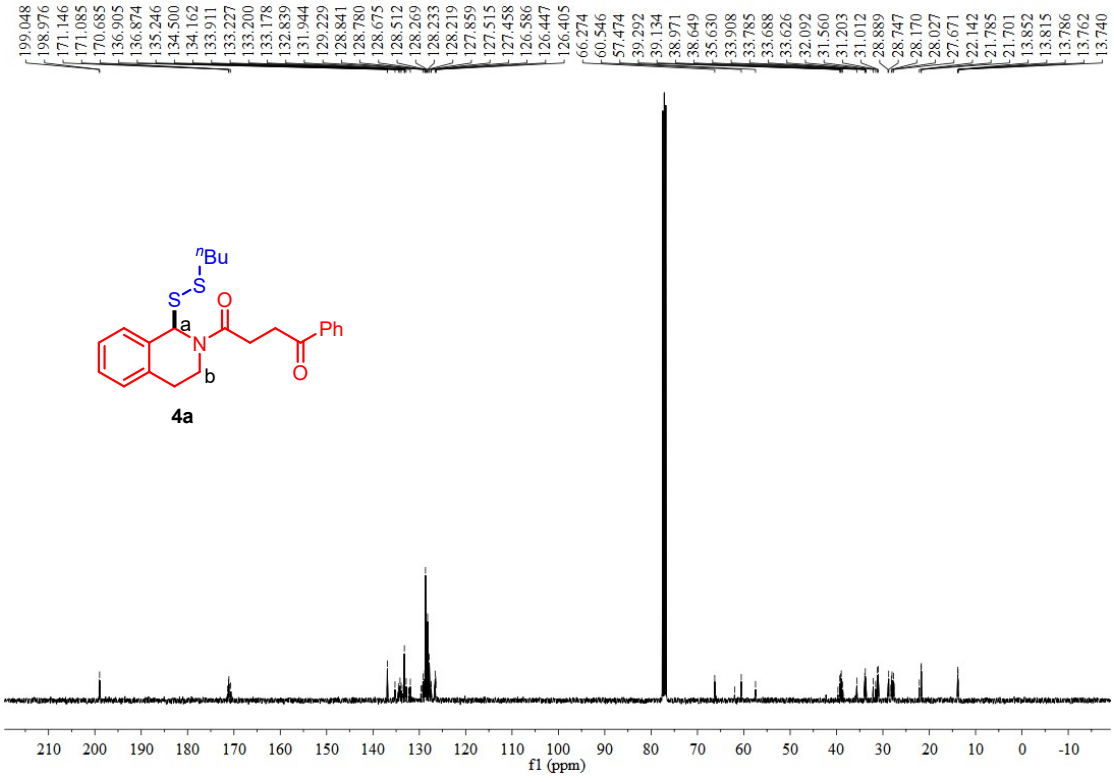
4a, $^{1}H+^{13}C$





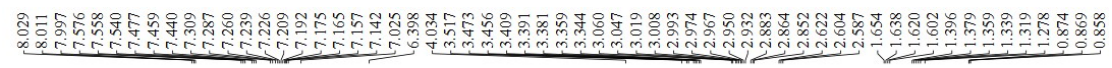
4a

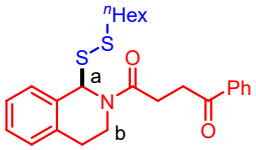




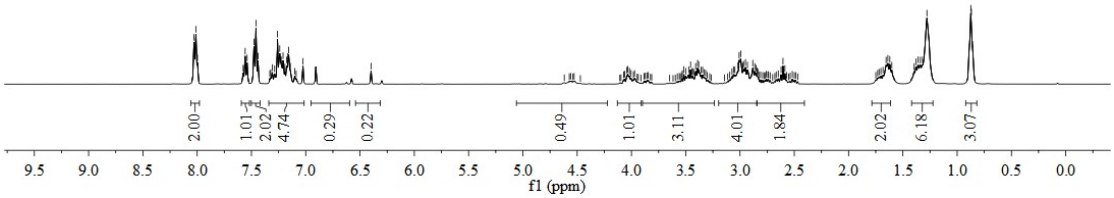
4a

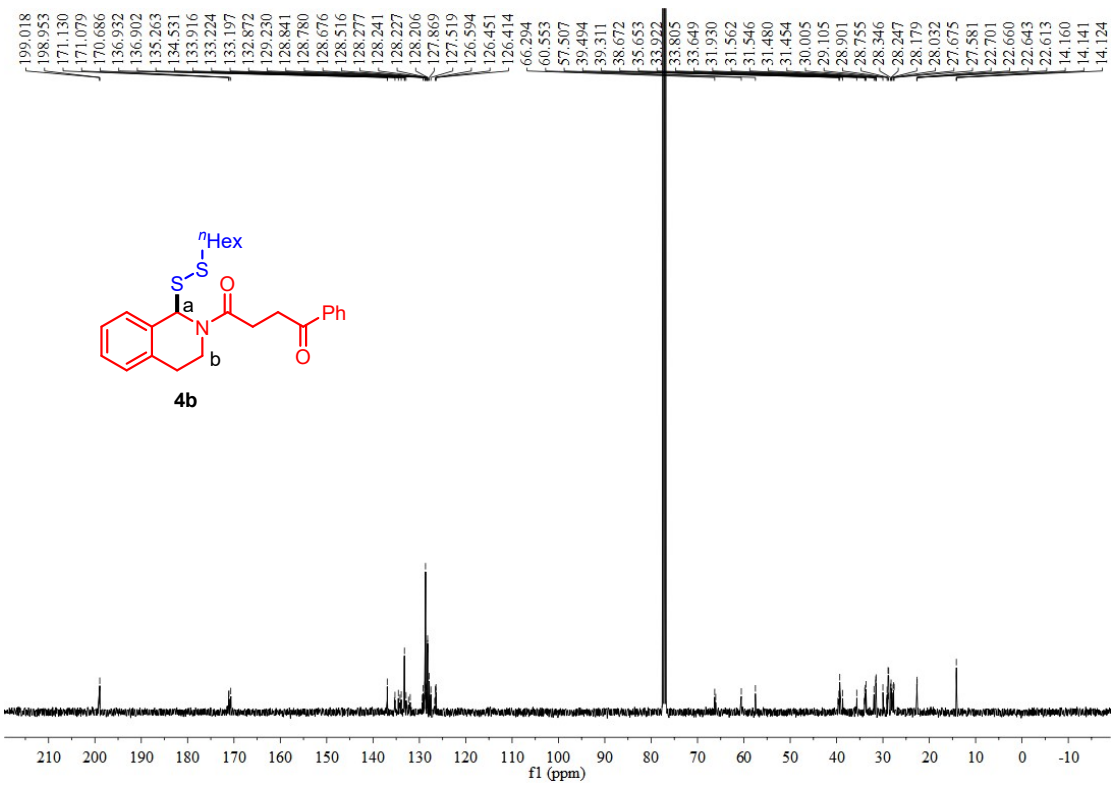
4b, $^{1}H+^{13}C$





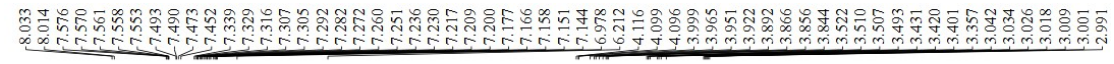
4b

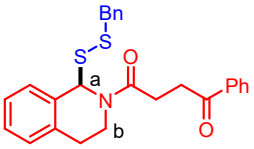




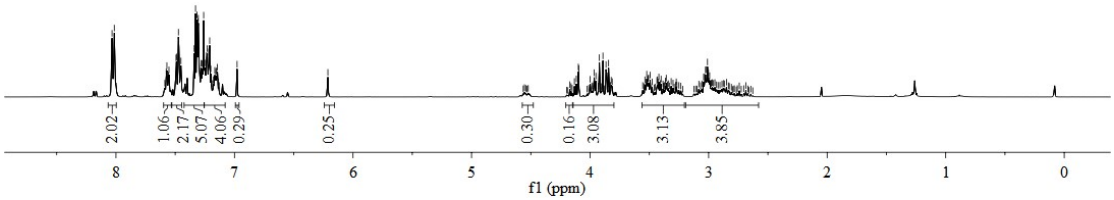
4b

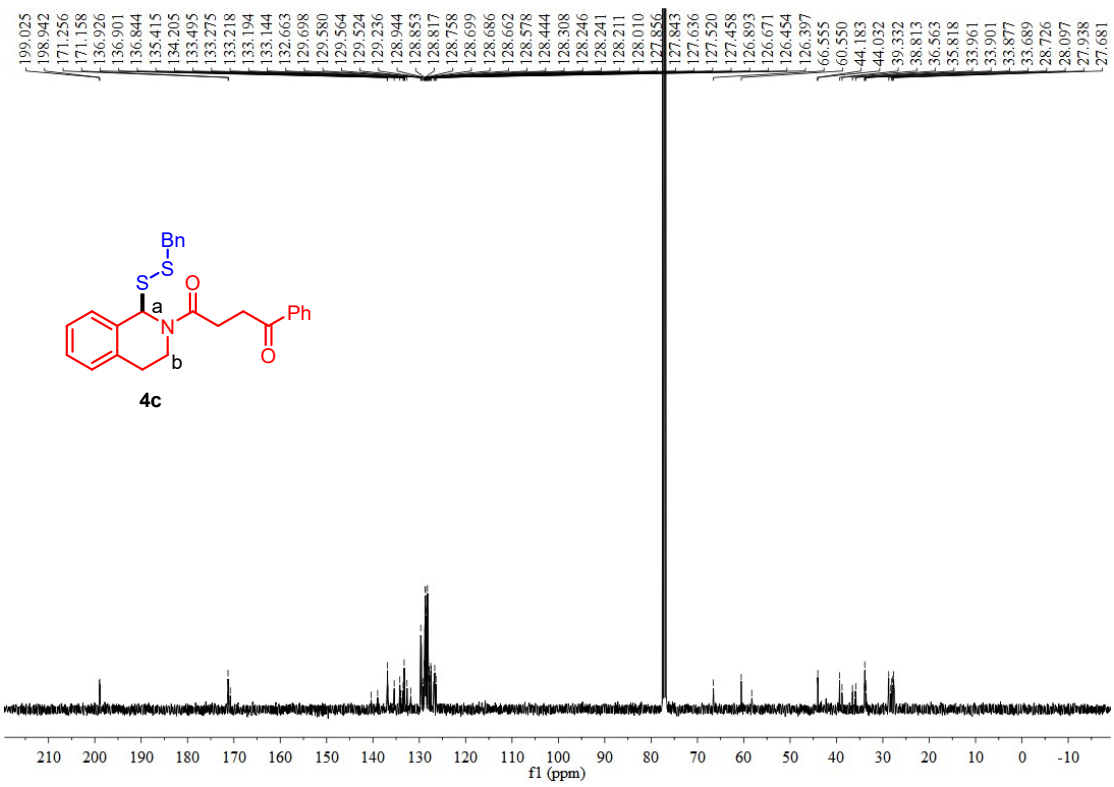
4c, $^{1}H+^{13}C$





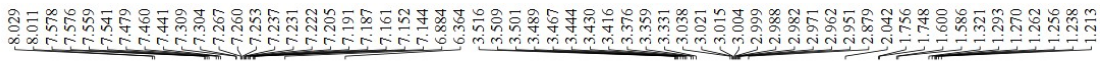
4c

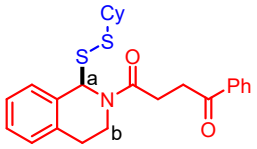




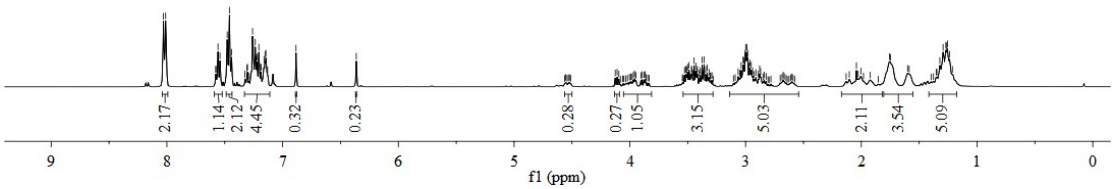
4c

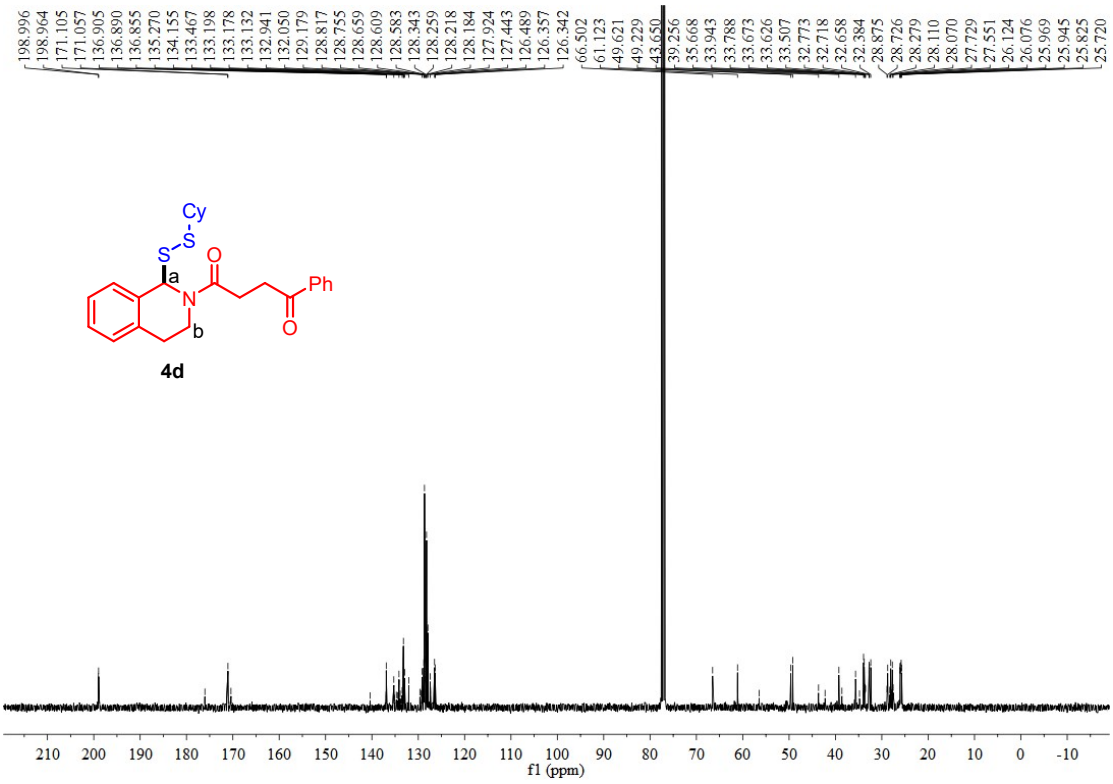
4d, $^{1}H+^{13}C$





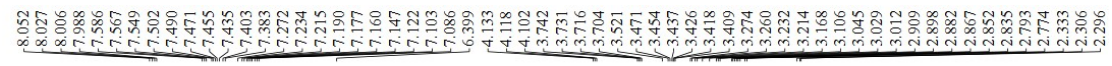
4d

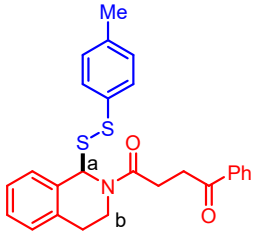




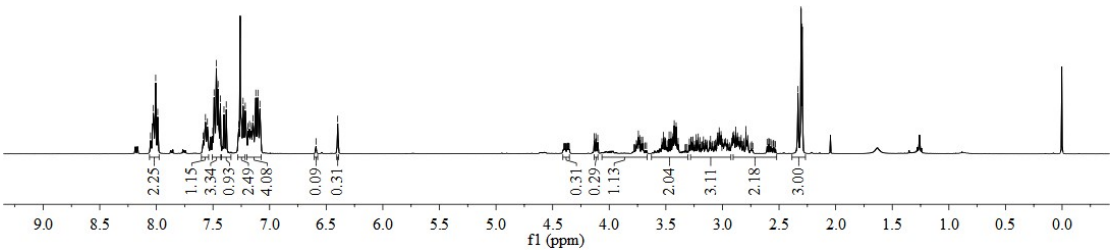
4d

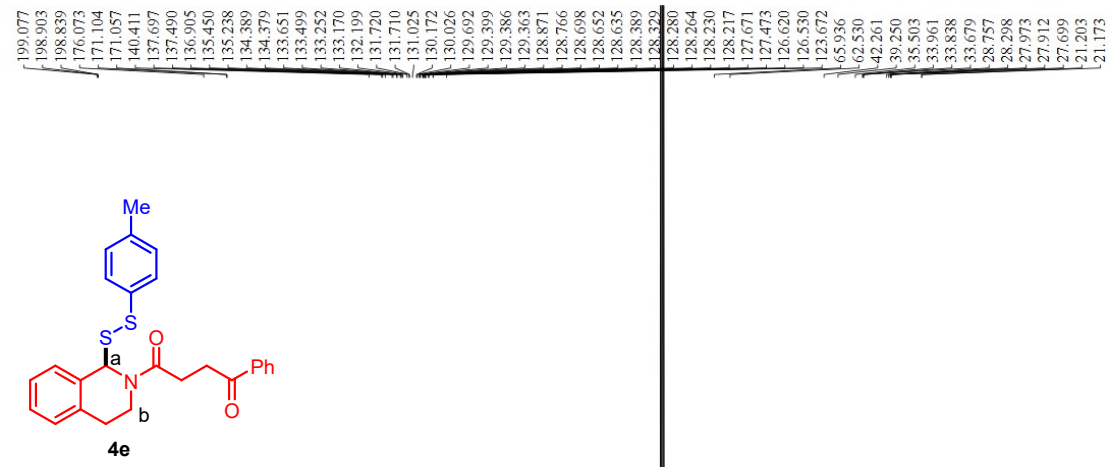
4e, $^{1}H+^{13}C$



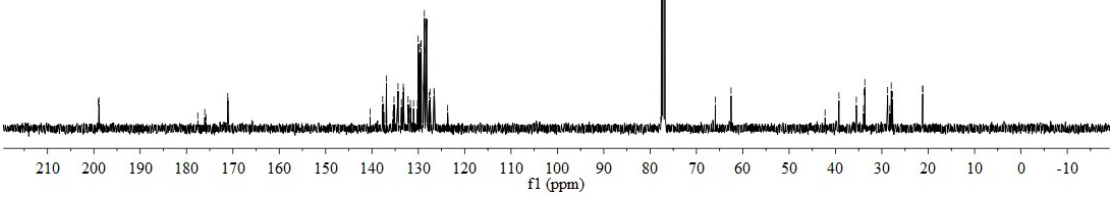


4e

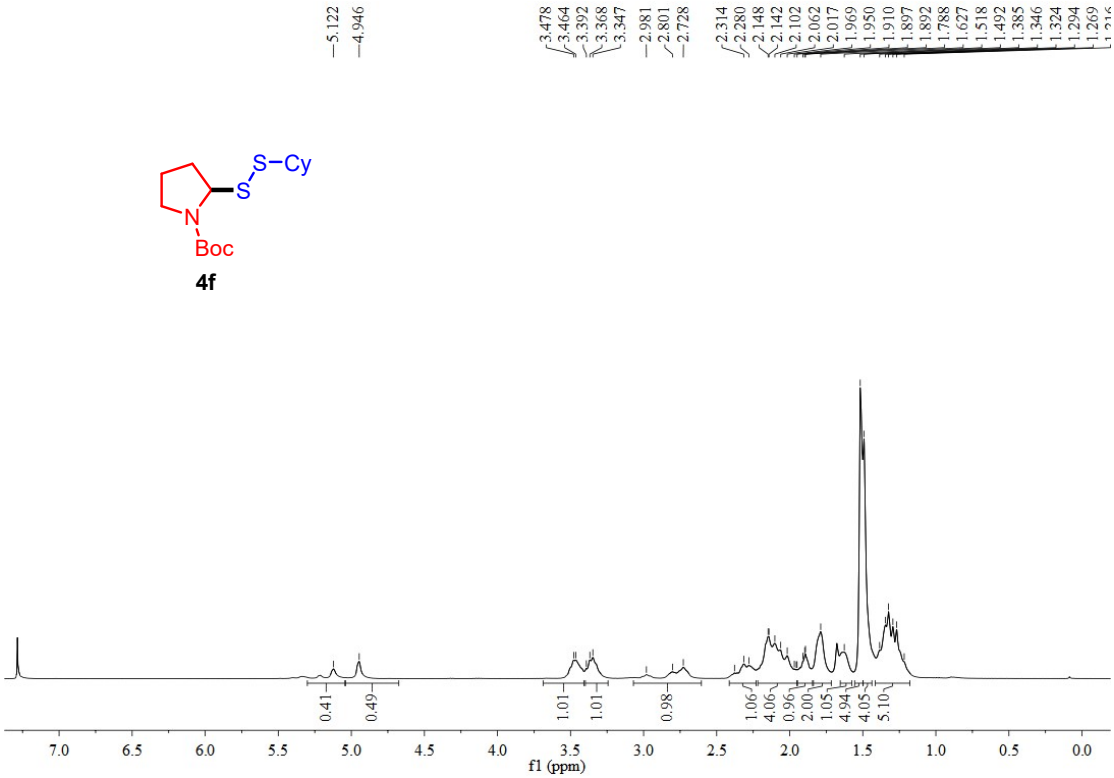


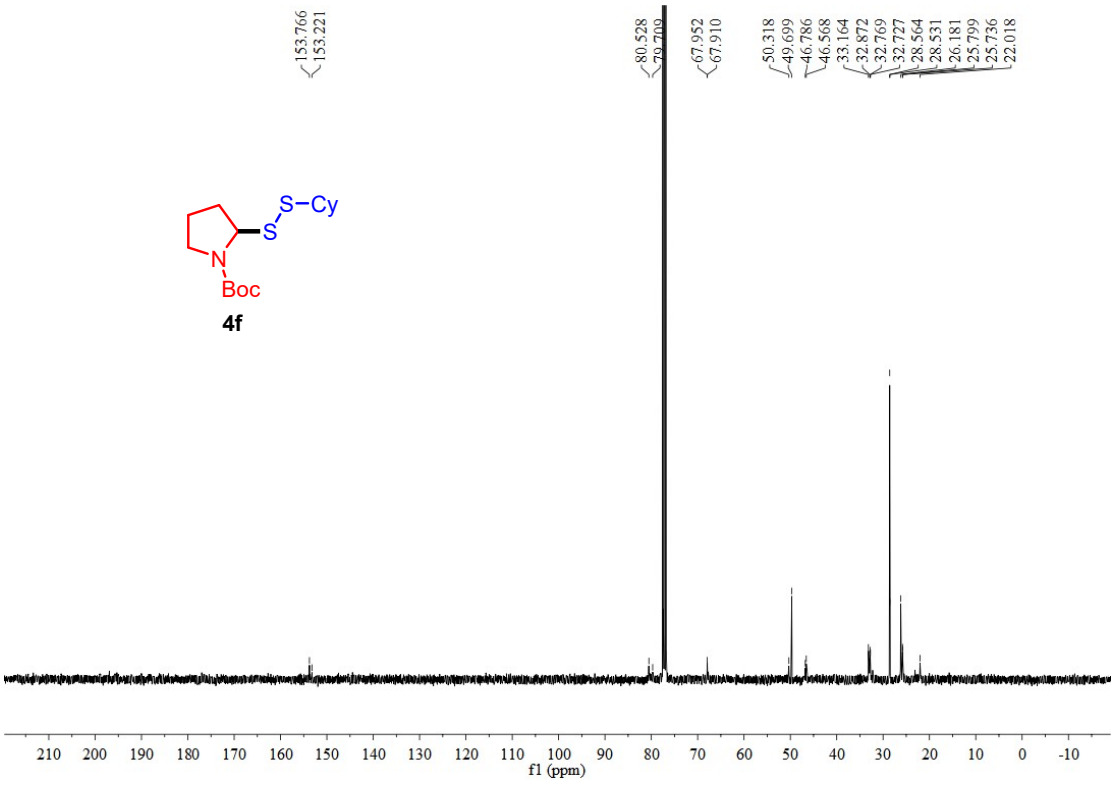


4e

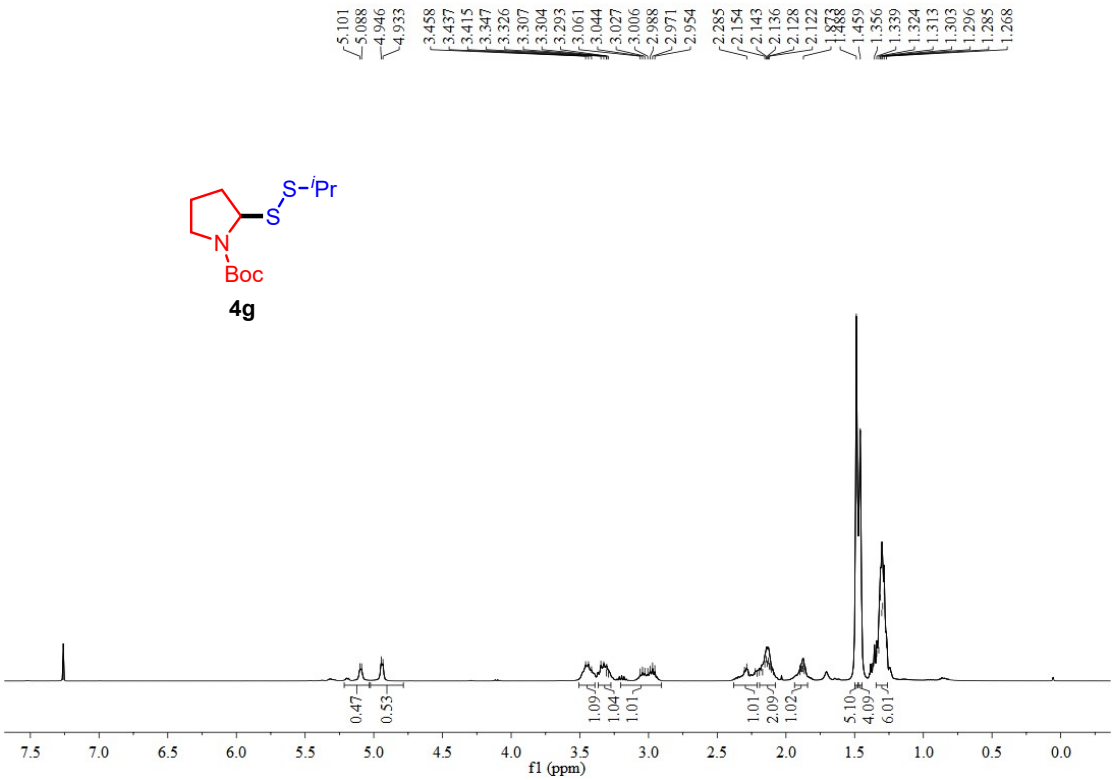


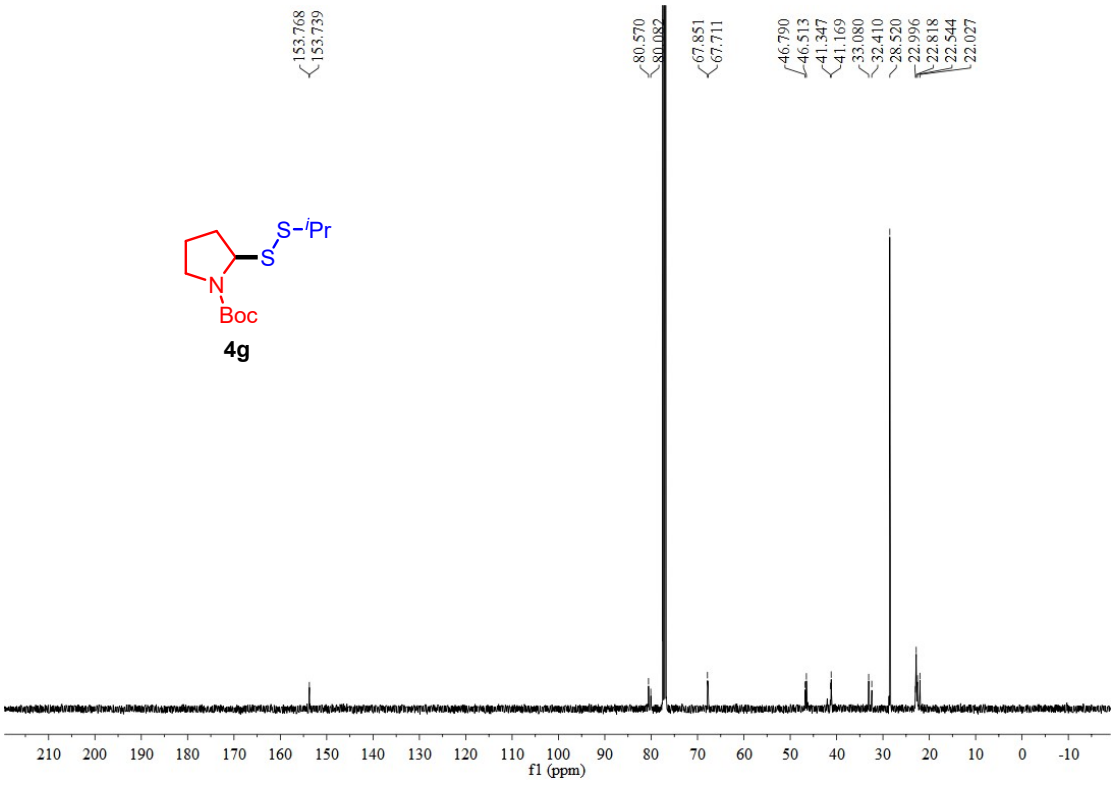
4f, $^{1}H+^{13}C$


5.122
4.946
3.478
3.464
3.392
3.368
3.347
2.981
2.801
2.728
2.314
2.280
2.148
2.142
2.102
2.062
2.017
1.969
1.950
1.910
1.897
1.892
1.788
1.627
1.518
1.492
1.385
1.346
1.324
1.294
1.269
S–Cy
S
N
Boc
4f
0.41
0.49
1.01
1.01
0.98
1.06
4.06
0.96
2.00
1.05
4.94
4.05
5.10
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
f1 (ppm)

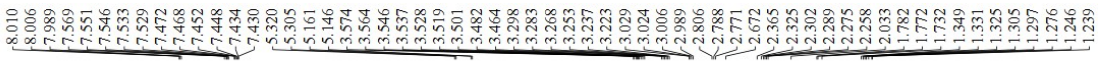

153.766
153.221
80.528
79.709
67.952
67.910
50.318
49.699
46.786
46.568
33.164
32.872
32.769
32.727
28.564
28.531
26.181
25.799
25.736
22.018
S–Cy
S
N
Boc
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

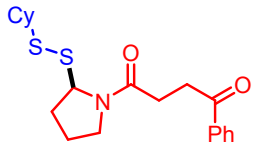
4g, $^{1}H+^{13}C$


5.101
5.088
4.946
4.933
3.458
3.437
3.415
3.347
3.326
3.307
3.304
3.293
3.061
3.044
3.027
3.006
2.988
2.971
2.954
2.285
2.154
2.143
2.136
2.128
2.122
1.488
1.459
1.356
1.339
1.324
1.313
1.303
1.296
1.285
1.268
S-iPr
S
N
Boc
4g
0.47
0.53
1.09
1.04
1.01
1.01
2.09
1.02
5.10
4.09
6.01
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
f1 (ppm)

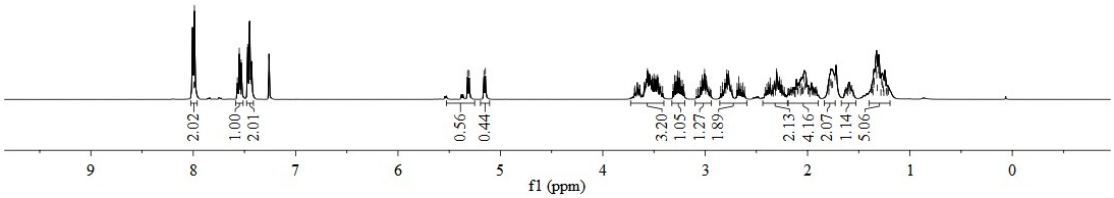

153.768
153.739
80.570
80.082
67.851
67.711
46.790
46.513
41.347
41.169
33.080
32.410
28.520
22.996
22.818
22.544
22.027
S-iPr
S
N
Boc
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

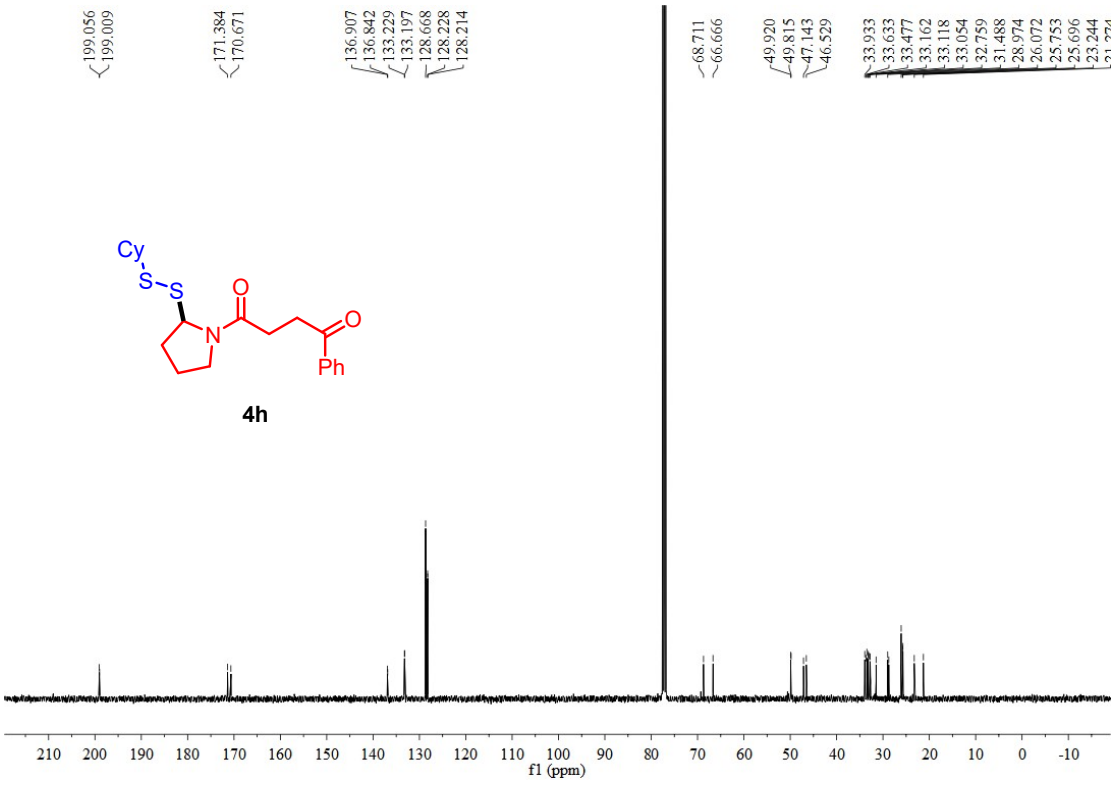
4h, $^{1}H+^{13}C$





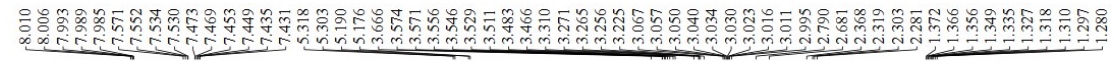
4h

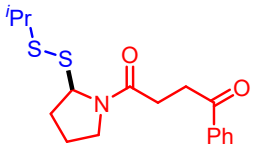




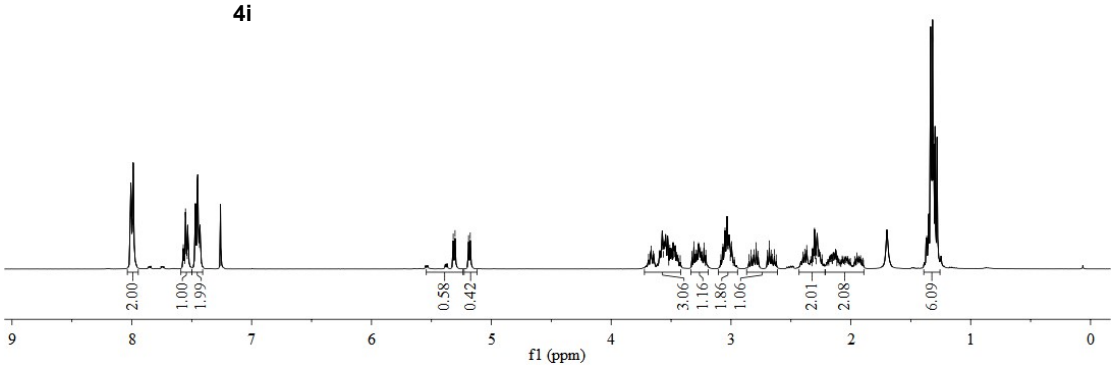
4h

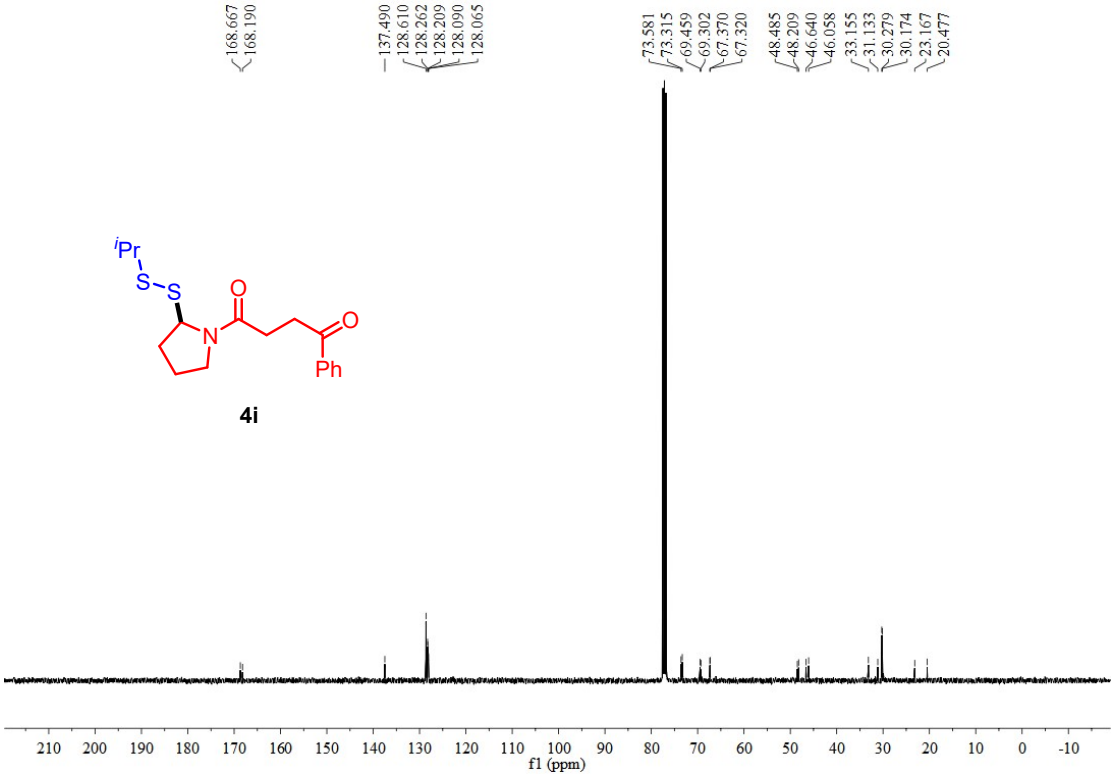
4i, $^{1}H+^{13}C$





4i





4i