Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

N-(Acetoxy)phthalimide motif as a visible-light pro-photosensitizer in photoredox decarboxylative arylthiation

Yunhe Jin, Haijun Yang and Hua Fu*

Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China. Email: fuhua@mail.tsinghua.edu.cn

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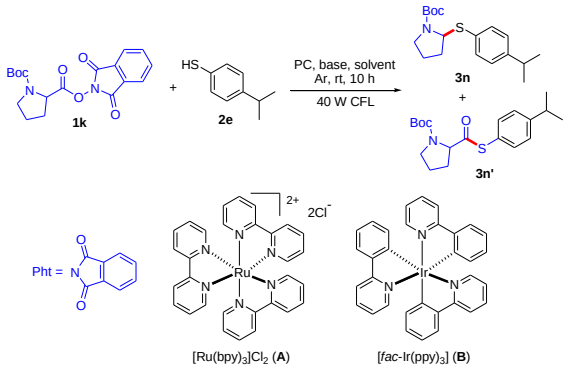
1. General Information

Commercial reagents, aryl thiols and *N*,*N*-Dimethylformamide (DMF) were purchased from J&K Chemical and Beijing Ouhe Technology, and they were used directly without further purification. Organic solutions were concentrated under reduced pressure on a Heidolph rotary evaporator using an alcohol-ice bath. Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh). Thin layer chromatography (TLC) was performed on Shandong Jiangyou 0.2 mm silica gel plates. Visualization of the developed chromatogram was performed by fluorescence quenching, *p*-anisaldehyde, potassium permanganate, or ceric ammonium molybdate stain. ^{1}H and ^{13}C NMR spectra were recorded on JEOL 300 MHz, 400 MHz (100 MHz) and 600 MHz (150 MHz) instruments, and are internally referenced to TMS and residual portion solvent signals (note: TMS referenced at 0.00 ppm; $CDCl_3$ referenced at 7.26 and 77.0 ppm respectively; DMSO-d_6 referenced at 2.54 and 40.4 ppm respectively; Because the probe for $CDCl_3$ on the 400 MHz instrument was slightly polluted, there was a needless signal at 168.2 ppm in ^{13}C spectra). ^{15}N NMR spectra were recorded on JEOL 600 (60.8 MHz) instrument by using $Me^{15}NO_2$ (0.0 ppm) as the external standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, h = heptet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (*J* Hz). Data for ^{13}C and ^{15}N are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. Melting points were recorded on a Beijing Tech X-4 melting point apparatus. High resolution mass spectra were obtained on LCMS-IT/TOF (SHIMADZU, Japan) with electrospray ionization method.

2. Optimization of Conditions

Table S1 Optimization of conditions for visible-light photoredox decarboxylative arylthiation[a]



entry	PC	base	solvent	yield of **3n** (%)[b]	yield of **3n'** (%)[b]
1	A	Cs_2CO_3	DMF	90	trace
2	B	Cs_2CO_3	DMF	58	trace
3	-	Cs_2CO_3	DMF	93 (91[c])	trace
4	-	K_2CO_3	DMF	89	trace
5	-	Na_2CO_3	DMF	85	7
6	-	$NaHCO_3$	DMF	70	22
7	-	DIPEA	DMF	13	63
8		Cs_2CO_3	DMSO	91	trace
9		Cs_2CO_3	MeCN	35	38
10		Cs_2CO_3	DCE	trace	31
11[d]		Cs_2CO_3	DMF	61	15
12[e]		Cs_2CO_3	DMF	0	82
13[f]		Cs_2CO_3	DMF	92	trace

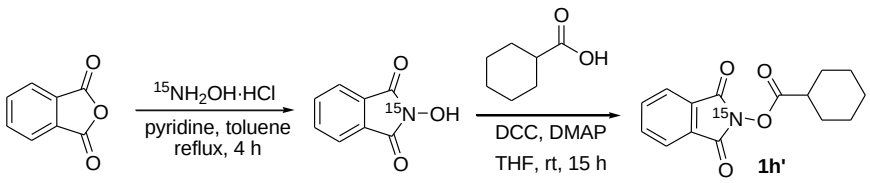
[a] Reaction conditions: under Ar atmosphere and irradiation of visible light, *N*-Boc-Pro-OPht (**1k**) (0.15 mmol), 4-isopropylbenzenethiol (**2e**) (0.18 mmol), photocatalyst (PC) (1.5 μmol), base (0.225 mmol), solvent (1.5 mL), temperature (rt, ~25 °C), time (10 h) in a sealed Schlenk tube. [b] Conversion yields were determined by ^{1}H NMR using trichloroethylene as the internal standard. [c] Isolated yield. [d] 4-Isopropylbenzenethiol (**2e**) (0.3 mmol). [e] No light. [f] 3 W blue LED was used as the light source for 20 h. PC = photocatalyst. DIPEA = diisopropylethylamine. DCE = 1,2-dichloroethane. CFL = compact fluorescent light.

First, coupling of *N*-Pro-OH with *N*-hydroxyphthalimide (PhtOH) in the presence of coupling agent (*N*,*N'*-dicyclohexylcarbodiimide (DCC)) led to corresponding active esters, *N*-Boc-Pro-OPht (Pht = phthalimide) (**1k**). Next, coupling of **1k** with 4-isopropylbenzenethiol (**2e**) was selected as the model to optimize conditions of visible-light photoredox catalysis including photocatalysts, bases and solvents. As shown in Table 1, two common transition-metal photocatalysts, $[Ru(bpy)_3]Cl_2$ and [*fac*-Ir(ppy)$_3$], were tested using 1.5 equiv of Cs_2CO_3 as the base and DMF as the solvent under Ar atmosphere and irradiation of visible light with 40 W compact

fluorescent light (CFL) (entries 1 and 2), and $[Ru(bpy)_3]Cl_2$ provided the target product (**3n**) in 90% conversion yield (determination by ^1H NMR using trichloroethylene as the internal standard) together with trace amount of substituted product (**3n'**) (entry 1). However, [*fac*-Ir(ppy)$_3$] afforded a weak result (entry 2). Interestingly, the reaction gave target product **3n** in 93% conversion (91% isolated yield) in the absence of photocatalyst (entry 3). We also attempted K_2CO_3, Na_2CO_3 and $NaHCO_3$ as the bases (entries 4-6), and the results exhibited that Cs_2CO_3 was optimal (compare entries 3, 4-6). **3n'** became the major product when diisopropylethylamine (DIPEA) was used as the base (entry 7). Effect of solvents was investigated, and we found that DMF was a suitable solvent (compare entries 3, 8-10). When amount of 4-isopropylbenzenethiol (**2e**) increased from 1.2 equivalents to 2.0 equivalents (relative to amount of **1k**), yield of **3n** decreased with that of **3n'** increasing (entry 11). Only substituted product **3n'** was observed without irradiation of visible light (entry 12). When 3 W blue LED was used as the light source for 20 h, **3n** was observed in 92% conversion (entry 13).

3. Experimental Procedures

(1) Synthesis of ^{15}N-Labeled *c*-Hex-COOPht (1h')



Synthesis of ^{15}N-hydroxyphthalimide. Synthesis of ^{15}N-hydroxyphthalimide was performed according to the previous reference.[1] A flask fitted with a Dean-Stark trap was charged with ^{15}N-hydroxylamine hydrochloride (1.5 mmol, 0.104 g) and toluene (5 mL). To the suspension were added phthalic anhydride (1.56 mmol, 0.23 g) and pyridine (1.5 mmol, 120 μL). The solution was stirred and heated to reflux. After 4 h, the resulting solution was allowed to cool to room temperature and concentrated by rotary evaporation until precipitation occurred. The precipitated crop was collected and washed with Et_2O (15 mL) and cold water (15 mL). The washed solids were combined and dried in a vacuum desiccator to afford ^{15}N-hydroxyphthalimide as a light yellow solid, yield 0.115 g (47%).

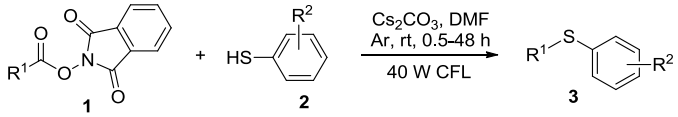
Synthesis of ^{15}N-Labeled *c*-Hex-COOPht (1h'). Synthesis of ^{15}N-labeled *c*-Hex-COOPht (**1h'**) was performed according to the previous reference.[2] DCC (0.24 mmol, 49.4 mg) was added to a solution of cyclohexanecarboxylic acid (0.2 mmol, 25.6 mg), ^{15}N-hydroxyphthalimide (0.22 mmol, 36.1 mg) and DMAP (0.02 mmol, 2.4 mg) in THF (2 mL). The mixture was stirred at room temperature for 15 h, and the resulting solution was filtered. The filtrate was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel (PE/CH_2Cl_2 = 1:1) to provide ^{15}N-labeled *c*-Hex-COOPht (**1h'**) as a white solid, yield 38.9 mg (71%).

References

(1) Lane, A.; Arumugam, S.; Lorkiewicz, P.; Higashi, R.; Laulhé, S.; Nantz, M.; Moseley, H.; Fan, T. *Magn. Reson. Chem.* **2015**, 53, 337–343.

(2) Kachkovskyi, G.; Faderl, C.; Reiser, O. *Adv. Synth. Catal.* **2013**, 355, 2240-2248.

(2) General procedure for synthesis of compounds 3a-ah



RCO-OPht (**1**) (0.15 mmol), aryl thiol (**2**) (0.18 mmol) and Cs_2CO_3 (0.225 mmol, 73.3 mg) were added to a 25-mL Schlenk tube with DMF (1.5 mL), and the tube was evacuated and back-filled with argon for three cycles. The tube was sealed, and then irradiated with a 40 W fluorescent lamp (approximately 2 cm away from the light source). After the complete conversion of the substrates (monitored by TLC), the reaction mixture was diluted with 20 mL of EtOAc, and the solution was filtered by flash chromatography. The filtrate was evaporated by rotary evaporator, and the residue was purified by silica gel column chromatography to give the desired product (**3**).

4. Mechanism Investigations

a. The UV-visible absorption spectra of aryl thiols and disulfides

The UV-visible absorption spectra of 4-(trifluoromethyl)thiophenol (TFTP) (**2l**) and 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (BTFPD) were determined in the absence or presence of Cs_2CO_3, and no new absorption peak was observed beyond 400 nm (Figure S1-I,II), which implied that neither aryl thiols nor disulfides could be the visible light photosensitizers in the reactions. Unexpectedly, a new absorption band at 340 nm was observed, and one possible reason is that small amount of by-product from homolysis of BTFPD appeared in the presence of Cs_2CO_3 under irradiation of UV.

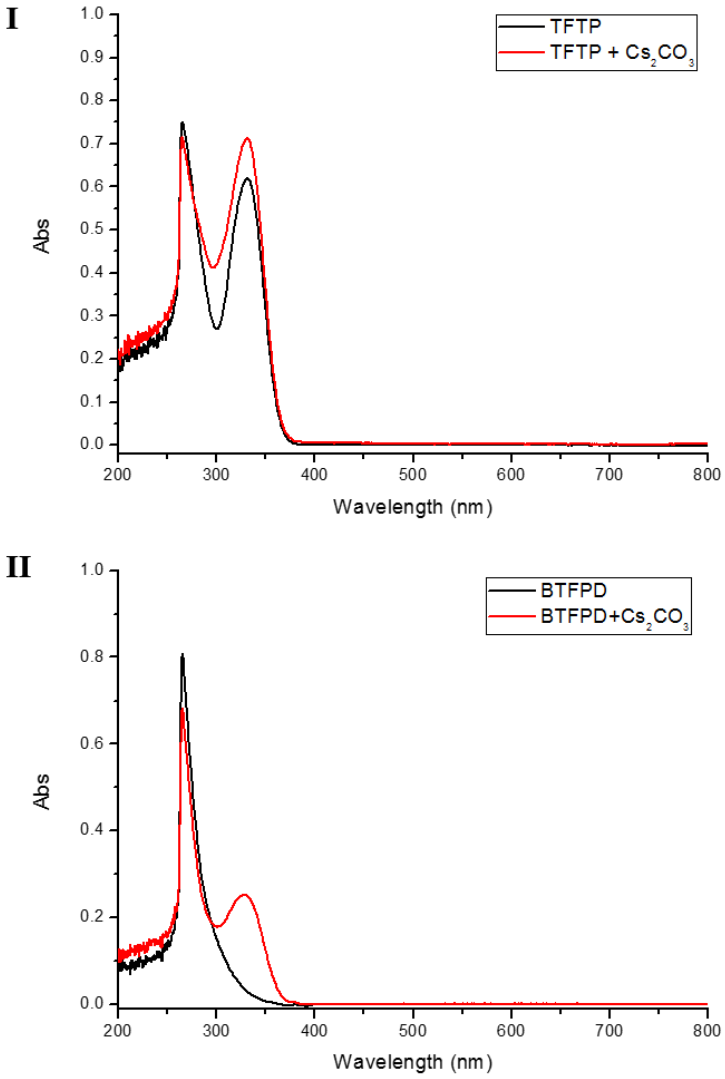


Figure S1. (I) the UV-visible absorption spectra of 4-(trifluoromethyl)thiophenol (TFTP) in the absence or presence of Cs_2CO_3. (II) The UV-visible absorption spectra of 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (BTFPD) in the absence or presence of Cs_2CO_3.

b. Investigation on treatment of cyclopentanecarboxylic acid active ester (*c*-Pen-COOPht) with 4-cyanobenzyl bromide by HRESI-MS

Cyclopentanecarboxylic acid active ester (*c*-Pen-COOPht (**1g**)) (0.1 mmol), 4-cyanobenzyl bromide (0.3 mmol) and Cs_2CO_3 (0.2 mmol) were added to a 5-mL flask with DMF (1 mL), and the mixture was stirred overnight at room temperature. The resulting solution was centrifuged, and the solid was removed. The remained solution was diluted with CH_3CN (1 mL), and then performed a mass spectral analysis with high resolution electrospray ionization mass spectrometer. Mass spectral peaks at m/z 391.1299 (Figure S2) and 508.1867 (Figure S3) corresponding to **B-2** and **B-3** in Scheme S1 were observed. According to the results and UV-visible absorption spectrum of *c*-Pen-COOPht (**1g**) in the presence of Cs_2CO_3 (Line **1g**+Cs_2CO_3 in Figure 1a in text), treatment of *c*-Pen-COOPht with 4-cyanobenzyl bromide can undergo the following process: Tautomerization of **1g** in the presence of base (Cs_2CO_3) gives **Ig**, and reaction of **Ig** with 4-cyanobenzyl bromide affords **B-1**. Hydrolysis of **B-1** leds to **B-2**, and further coupling of **B-2** with 4-cyanobenzyl bromide provides **B-3** (see Scheme S1). Therefore, the experiment showed that tautomerization of *c*-Pen-COOPht (**1g**) via n-π electron delocalization could be reasonable.

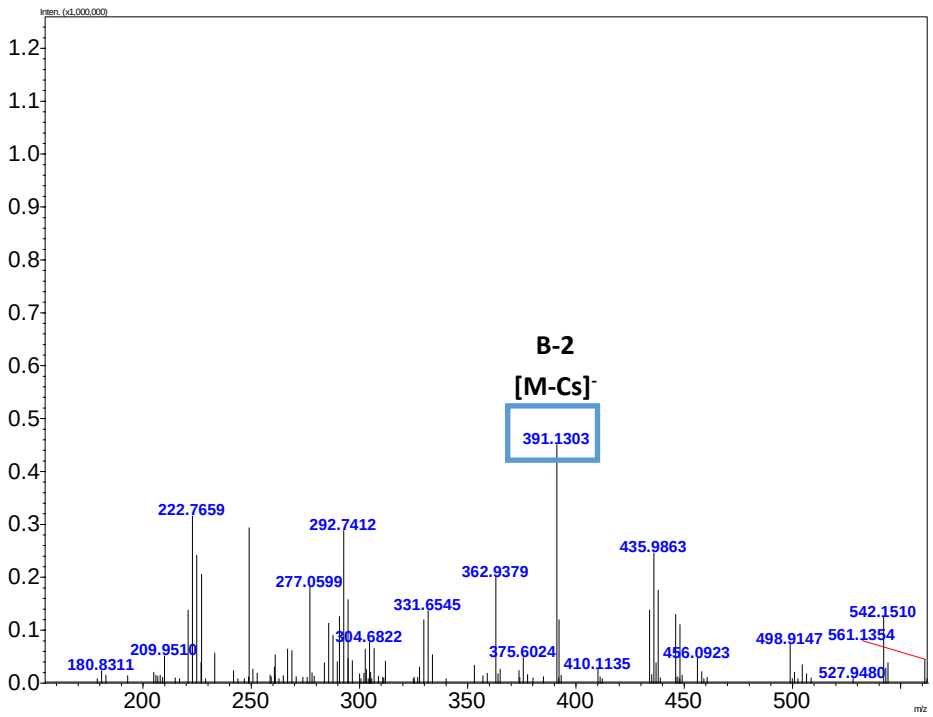


Figure S2. Negtive ion mass spectrum of products from reaction of *c*-Pen-COOPht (**1g**) with 4-cyanobenzyl bromide.

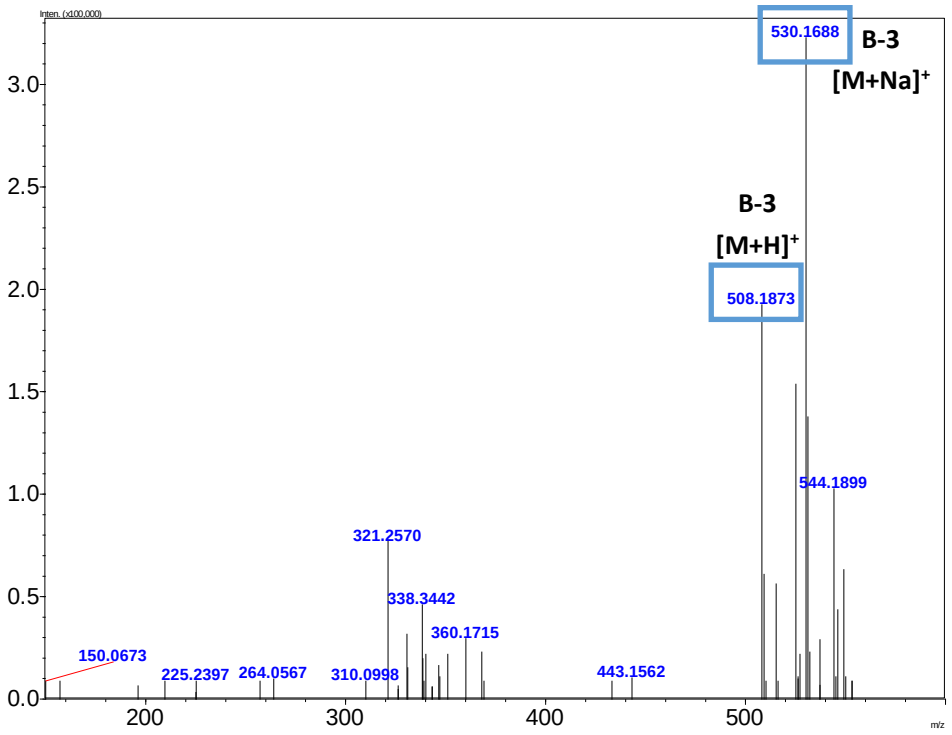
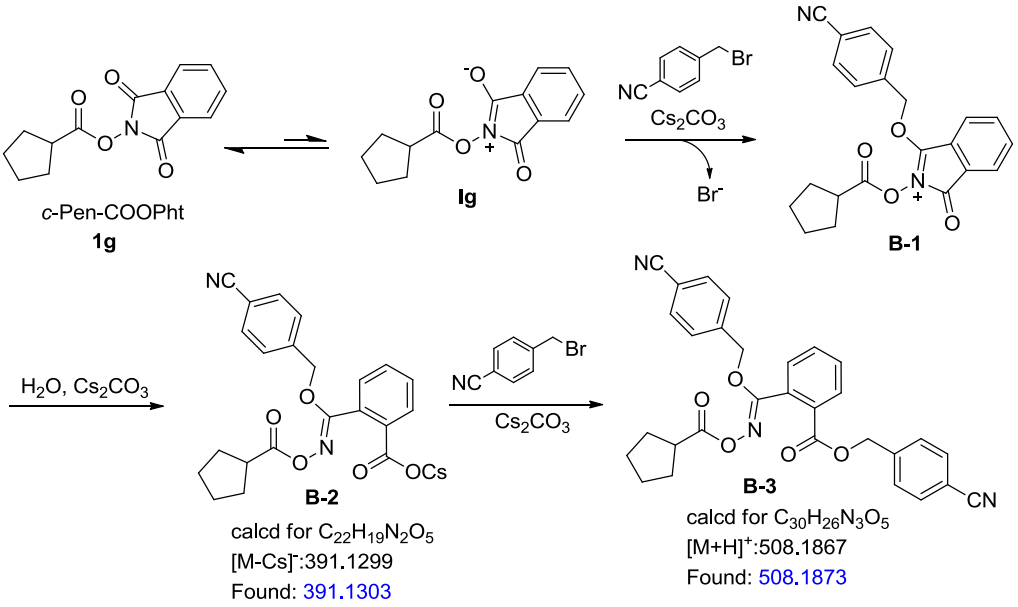


Figure S3. Positive ion mass spectrum of products from reaction of *c*-Pen-COOPht (**1g**) with 4-cyanobenzyl bromide.



Scheme S1. Treatment of *c*-Pen-COOPht (**1g**) with 4-cyanobenzyl bromide.

c. The radical-trapping experiments

Treatment of *c*-Pen-COOPht (**1g**) and methyl 4-mercaptobenzoate in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT) was investigated, and only trace amount of **3g** was found. HRESI-MS showed that intermediate **B-4** occurred in the former reaction. The results displayed that free-radical intermediates were involved in the reactions (Figure S4, Scheme S2).

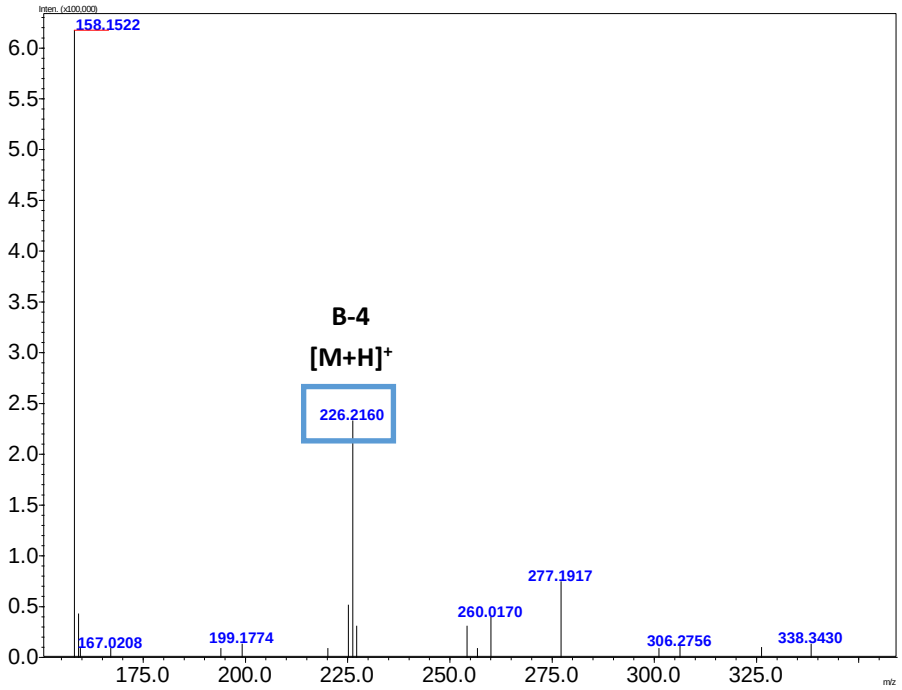
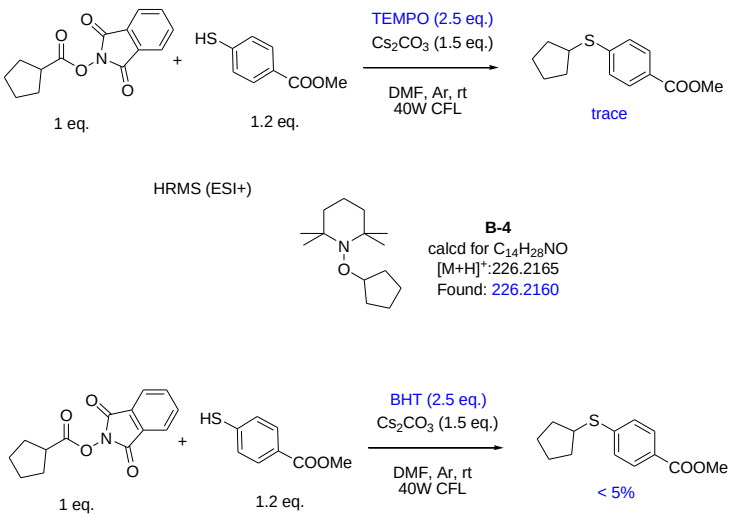


Figure S4. Positive ion mass spectrum of products from reaction of *c*-Pen-COOPht (**1g**), methyl 4-mercaptobenzoate and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).



Scheme S2. Treatment of *c*-Pen-COOPht (**1g**) and methyl 4-mercaptobenzoate in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylated hydroxytoluene (BHT).

d. Stern-Volmer fluorescence quenching experiments

Firstly, we investigated the emission and excitation spectrums of the active esters in the absence or presence of bases. A 1.0 mM solution of cyclopentanecarboxylic acid active ester (*c*-Pen-COOPht (**1g**)) in DMF in the presence of Cs_2CO_3 (1.5 mM) was chosen as the model. To avoid the effect of UV absorption of 4-(trifluoromethyl)thiophenol (TFTP) and 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (BTFPD), the emission spectra were obtained under irradiation of 375 nm exciting light (Figure S5). Meanwhile, the fluorescence excitation spectra were obtained with the detection wavelength of 429 nm (emission maximum of **IIg***) (Figure S6). The results exhibited that the active esters can absorb a part of visible light and launch fluorescence in the presence of base. The quantum yield of **Ig** in Scheme S1 was 10.3% using 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) as the reference (Table S2).

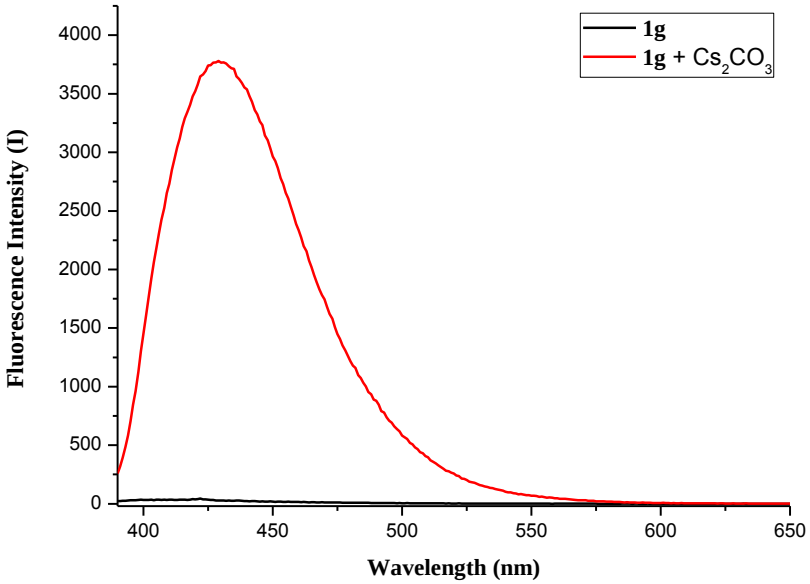


Figure S5. The fluorescence emission spectra of *c*-Pen-COOPht (**1g**) in the absence or presence of Cs_2CO_3 excited at 375 nm.

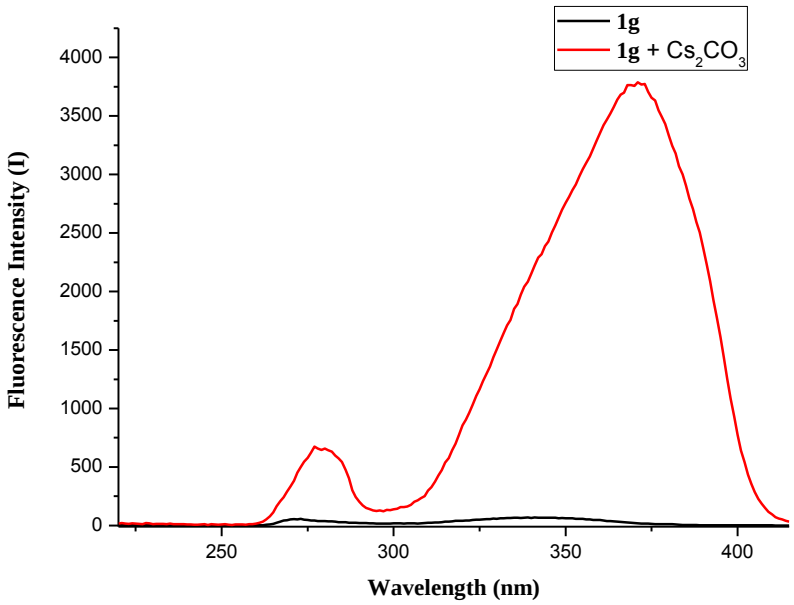
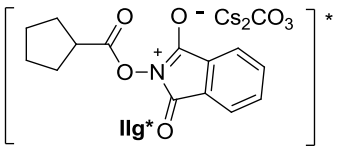


Figure S6. The fluorescence excitation spectra of *c*-Pen-COOPht (**1g**) in the absence or presence of Cs_2CO_3 with the detection wavelength of 429 nm.

Table S2. Measurement of the Quantum Yield of **IIg*** in Scheme S1 Using 1,4-Bis(5-phenyloxazol-2-yl)benzene (POPOP) as the Reference. (φ = quantum yield, I = fluorescence intensity, A = absorbance, T = transmissvity)



substrate	transmissvity (T) (350 nm)	fluorescence intensity (I) (402 nm)	quantum yield (φ)
POPOP (**p**)	0.789	5158	0.885 (Ref.3)
I	0.860	382	φ_I

$$\varphi_I = \varphi_p \times \frac{I_I}{I_p} \times \frac{A_p}{A_I} = \varphi_p \times \frac{I_I}{I_p} \times \frac{\log(1/T_p)}{\log(1/T_I)} = 10.3\ \%$$

Next, we conducted the fluorescence quenching experiments. In a typical experiment, 1.0 mL solution of *c*-Pen-COOPht (**1g**) (1.0 mM) in DMF in the presence of Cs_2CO_3 (1.5 mM) was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, 0.1 M solution of the quencher was added to the cuvette by microliters and the emission of the sample was collected. The solutions were excited at λ= 375 nm (to avoid the effects of UV absorption of TFTP and BTFPD) and the emission intensity at 429 nm (emission maximum of **IIg***) was observed (Figure S7-9). Stern–Volmer fluorescence quenching experiments demonstrated that the emission intensity of **IIg*** diminished in the presence of TFTP, presumably signifying an electron transferring from TFTP to **IIg***.

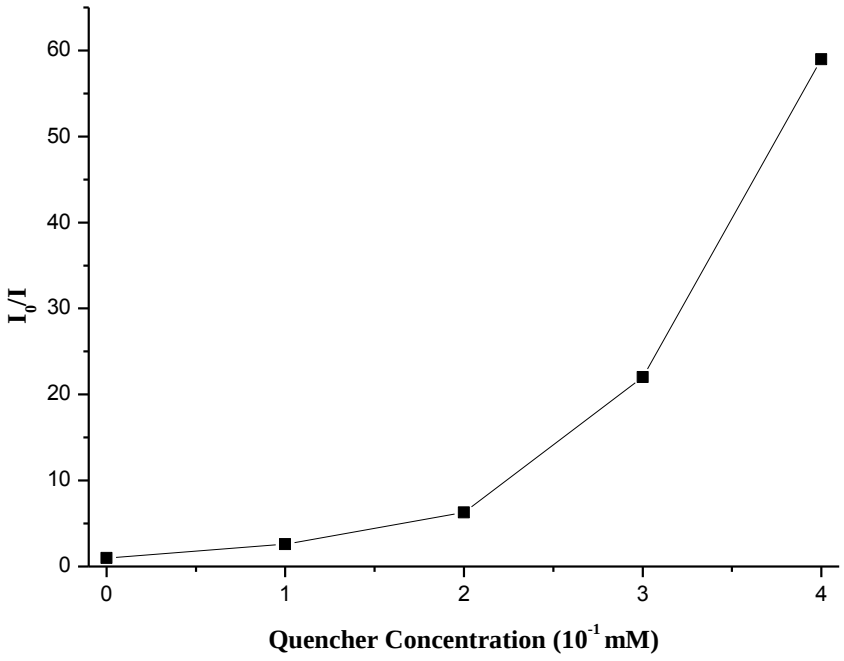


Figure S7. IIg* emission quenching by 4-(trifluoromethyl)thiophenol (TFTP). Non-linear quenching is observed.

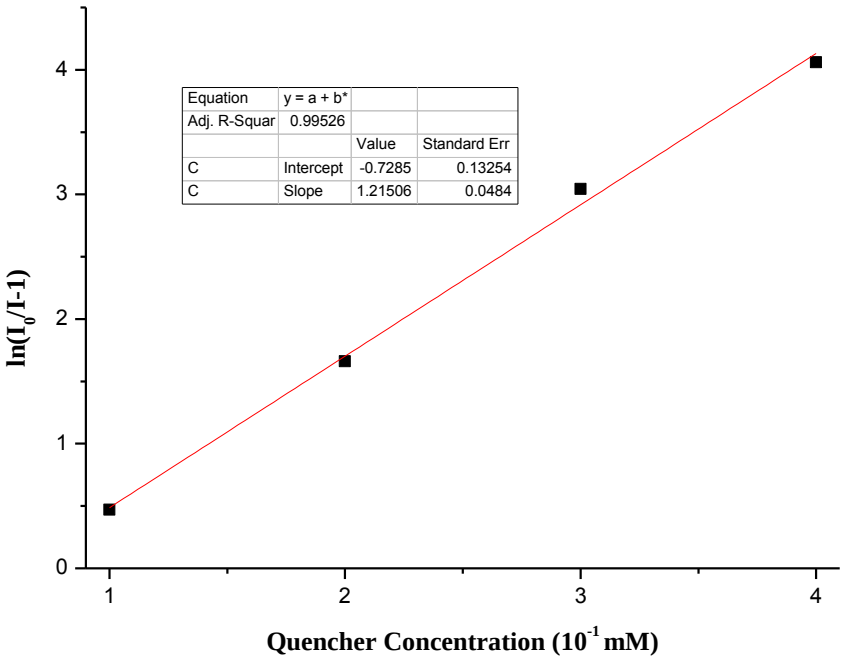


Figure S8. Log plot of emission quenching of **IIg*** by 4-(trifluoromethyl)thiophenol (TFTP). Linear correlation represents exponential trend in emission quenching.

As highlighted in Figure S7, we observe non-linear quenching of **IIg*** in the presence of TFTP. The diminished intensity of **IIg*** emission is attributed to several factors. Firstly, nucleophilic substitution could occur in the solution. Besides that, the reactive hydrogen of TFTP may affect the PH of the solution. Taking into consideration these effects, we suggest that the trend observed in Figure S8 is due to the additive effects of non-linear emission quenching by TFTP and some other factors although we cannot rule out all factors that may influence the emission intensity.

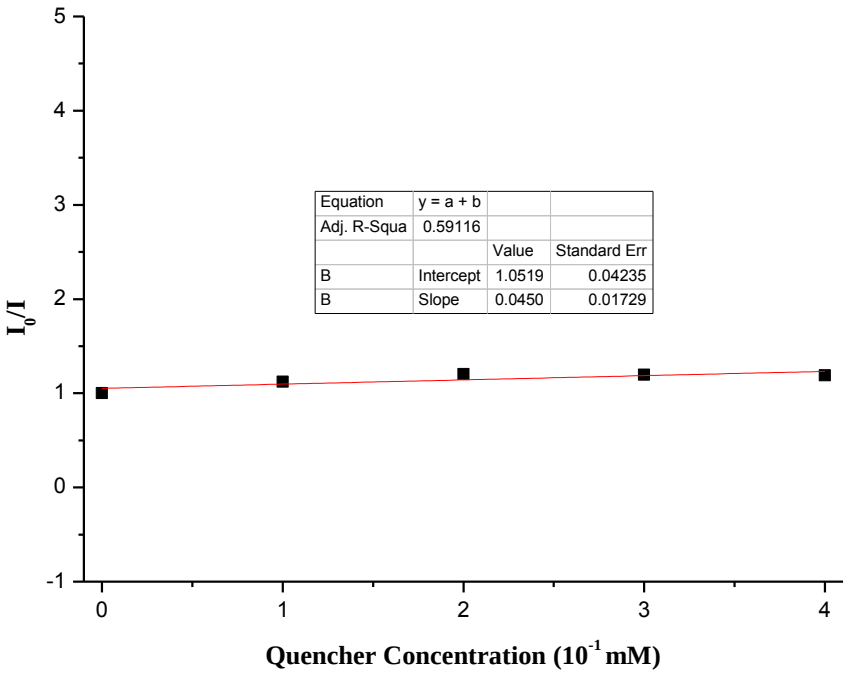
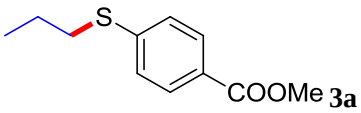


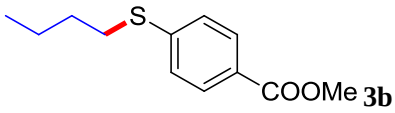
Figure S9. IIg* emission quenching in the presence of 1,2-bis(4-(trifluoromethyl)phenyl)disulfane (BTFPD). No quenching was observed.

5. Characterization of the Products



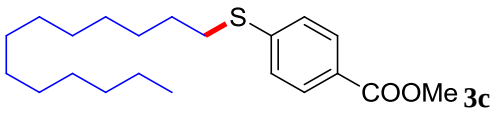
3a

Methyl 4-(propylthio)benzoate (3a). Eluent: PE/EtOAc (25:1). Yield 21.0 mg (67%). White solid, mp 45-47 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 1.73 (sext, *J* = 7.6 Hz, 2H), 1.05 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 144.5, 130.0, 126.6, 126.4, 52.1, 34.1, 22.2, 13.6. HRMS (ESI$^+$): Calcd for $C_{11}H_{15}O_2S$, $[M+H]^+$ m/z 211.0787. Found 211.0784.



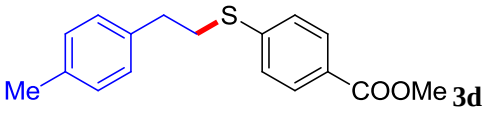
3b

Methyl 4-(butylthio)benzoate (3b). Eluent: PE/EtOAc (25:1). Yield 22.9 mg (68%). Colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H), 2.98 (t, *J* = 7.6 Hz, 2H), 1.68 (quint, *J* = 7.6 Hz, 2H), 1.48 (sext, *J* = 7.6 Hz, 2H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 144.6, 130.0, 126.6, 126.3, 52.1, 31.8, 30.9, 22.1, 13.7. HRMS (ESI$^+$): Calcd for $C_{12}H_{17}O_2S$, $[M+H]^+$ m/z 225.0944. Found 225.0940.



3c

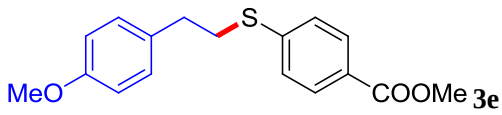
Methyl 4-(tridecylthio)benzoate (3c). Eluent: PE/EtOAc (25:1). Yield 37.7 mg (72%). White solid, mp 74-75 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 2.97 (t, *J* = 7.6 Hz, 2H), 1.69 (quint, *J* = 7.6 Hz, 2H), 1.51-1.37 (m, 2H), 1.36-1.18 (m, 18H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 144.6, 130.0, 126.6, 126.3, 52.1, 32.1, 32.0, 29.76, 29.75, 29.73, 29.65, 29.57, 29.4, 29.2, 29.0, 28.8, 22.8, 14.2. HRMS (ESI$^+$): Calcd for $C_{21}H_{35}O_2S$, $[M+H]^+$ m/z 351.2352. Found 351.2351.



3d

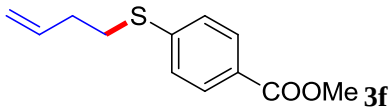
Methyl 4-((4-methylphenethyl)thio)benzoate (3d). Eluent: PE/EtOAc (25:1). Yield 28.5 mg (66%). White solid, mp 75-76 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.15-7.07 (m, 4H), 3.89 (s, 3H), 3.20 (t, *J* = 7.9 Hz, 2H), 2.92 (t, *J* = 7.9 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 144.0, 136.8, 136.3, 130.1, 129.4, 128.5, 126.8,

126.6, 52.2, 34.8, 33.8, 21.2. HRMS (ESI$^+$): Calcd for $C_{17}H_{19}O_2S$, $[M+H]^+$ m/z 287.1100. Found 287.1098.



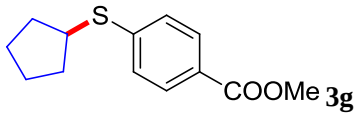
3e

Methyl 4-((4-methoxyphenethyl)thio)benzoate (3e). Eluent: PE/EtOAc (15:1). Yield 31.6 mg (70%). White solid, mp 57-58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 3H), 3.19 (t, *J* = 7.8 Hz, 2H), 2.91 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 158.4, 144.0, 131.9, 130.0, 129.6, 126.9, 126.6, 114.1, 55.4, 52.1, 34.4, 34.0. HRMS (ESI$^+$): Calcd for $C_{17}H_{18}NaO_3S$, $[M+Na]^+$ m/z 325.0869. Found 325.0872.



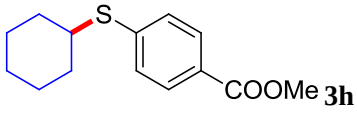
3f

Methyl 4-(but-3-en-1-ylthio)benzoate (3f). Eluent: PE/EtOAc (25:1). Yield 14.8 mg (44%). Colorless oil. ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 5.91-5.81 (m, 1H), 5.12 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 3.84 (s, 3H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.38 (q, *J* = 6.9 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 166.4, 144.5, 136.8, 130.1, 126.7, 126.4, 117.1, 52.6, 32.8, 30.5. HRMS (ESI$^+$): Calcd for $C_{12}H_{15}O_2S$, $[M+H]^+$ m/z 223.0787. Found 223.0784.



3g

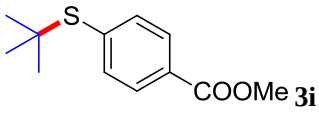
Methyl 4-(cyclopentylthio)benzoate (3g). Eluent: PE/EtOAc (25:1). Yield 32.8 mg (93%). White solid, mp 37-38 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 3.71 (quint, *J* = 6.2 Hz, 1H), 2.18-2.09 (m, 2H), 1.83-1.74 (m, 2H), 1.68-1.60 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 145.2, 129.9, 127.0, 126.5, 52.1, 44.2, 33.5, 25.0. HRMS (ESI$^+$): Calcd for $C_{13}H_{17}O_2S$, $[M+H]^+$ m/z 237.0944. Found 237.0945.



3h

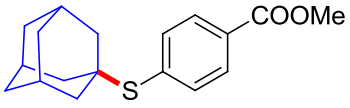
Methyl 4-(cyclohexylthio)benzoate (3h). Eluent: PE/EtOAc (25:1). Yield 33.6 mg (89%). White solid, mp 69-70 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 3.34-3.23 (m, 1H), 2.09-1.96 (m, 2H), 1.84-1.72 (m, 2H), 1.68-1.59 (m, 1H),

1.48-1.23 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 143.1, 129.9, 128.5, 127.1, 52.1, 45.1, 33.2, 26.0, 25.8. HRMS (ESI^+): Calcd for $C_{14}H_{19}O_2S$, $[M+H]^+$ m/z 251.1100. Found 251.1103.



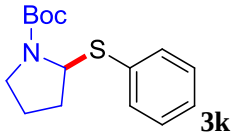
3i

Methyl 4-(*tert*-butylthio)benzoate (3i). Eluent: PE/EtOAc (25:1). Yield 30.4 mg (90%). White solid, mp 62-63 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 3.92 (s, 3H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 139.0, 136.9, 130.1, 129.5, 52.3, 46.8, 31.1. HRMS (ESI^+): Calcd for $C_{12}H_{17}O_2S$, $[M+H]^+$ m/z 225.0944. Found 225.0943.



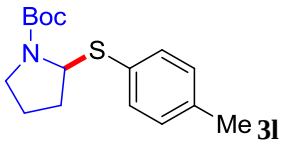
3j

Methyl 4-(adamantan-1-ylthio)benzoate (3j). Eluent: PE/EtOAc (25:1). Yield 41.5 mg (91%). White solid, mp 129-130 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 3.92 (s, 3H), 2.04-1.99 (m, 3H), 1.85-1.78 (m, 6H), 1.67-1.56 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 137.3, 137.0, 130.1, 129.3, 52.3, 49.0, 43.8, 36.1, 30.1. HRMS (ESI^+): Calcd for $C_{18}H_{23}O_2S$, $[M+H]^+$ m/z 303.1413. Found 303.1414.



3k

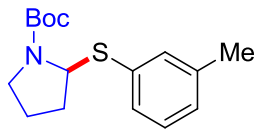
***tert*-Butyl 2-(phenylthio)pyrrolidine-1-carboxylate (3k).** Eluent: PE/EtOAc (15:1). Yield 38.8 mg (93%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58-7.42 (m, 2H), 7.35-7.22 (m, 3H), 5.44-5.24 (m, 1H), 3.51-3.23 (m, 2H), 2.21-1.82 (m, 4H), 1.53-1.24 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 134.7, 134.4, 134.1, 129.0, 128.0, 127.8, 80.1, 80.0, 67.1, 66.8, 46.3, 45.6, 34.0, 33.3, 28.5, 28.3, 23.1, 22.3. HRMS (ESI^+): Calcd for $C_{15}H_{21}NNaO_2S$, $[M+Na]^+$ m/z 302.1185. Found 302.1186.



3l

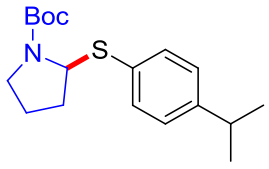
***tert*-Butyl 2-(p-tolylthio)pyrrolidine-1-carboxylate (3l).** Eluent: PE/EtOAc (15:1). Yield 36.7 mg (83%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of

rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47-7.33 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 5.36-5.17 (m, 1H), 3.49-3.22 (m, 2H), 2.33 (s, 3H), 2.20-1.81 (m, 4H), 1.49-1.30 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 138.2, 138.0, 135.1, 134.9, 130.3, 129.7, 80.1, 79.9, 67.1, 66.9, 46.3, 45.6, 33.8, 33.1, 28.5, 28.3, 23.1, 22.3, 21.2. HRMS (ESI$^+$): Calcd for $C_{16}H_{23}NNaO_2S$, $[M+Na]^+$ m/z 316.1342. Found 316.1338.



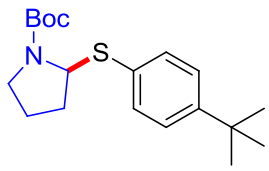
3m

***tert*-Butyl 2-(m-tolylthio)pyrrolidine-1-carboxylate (3m).** Eluent: PE/EtOAc (15:1). Yield 37.7 mg (86%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.25 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12-7.05 (m, 1H), 5.41-5.23 (m, 1H), 3.51-3.22 (m, 2H), 2.32 (s, 3H), 2.20-1.83 (m, 4H), 1.52-1.31 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 138.7, 135.2, 134.9, 133.9, 131.6, 131.3, 128.8, 80.1, 67.2, 66.8, 46.4, 45.6, 34.0, 33.3, 28.5, 28.3, 23.0, 22.3, 21.3. HRMS (ESI$^+$): Calcd for $C_{16}H_{23}NNaO_2S$, $[M+Na]^+$ m/z 316.1342. Found 316.1348.



3n

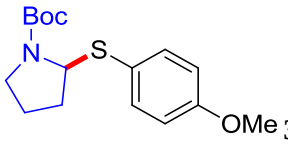
***tert*-Butyl 2-((4-isopropylphenyl)thio)pyrrolidine-1-carboxylate (3n).** Eluent: PE/EtOAc (15:1). Yield 44.0 mg (91%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.33 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 5.40-5.22 (m, 1H), 3.51-3.22 (m, 2H), 2.89 (h, *J* = 6.9 Hz, 1H), 2.20-1.82 (m, 4H), 1.50-1.27 (m, 9H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 149.1, 135.2, 134.9, 130.7, 127.2, 80.0, 67.1, 66.8, 46.3, 45.5, 33.9, 33.1, 28.5, 28.3, 24.0, 23.0, 22.3. HRMS (ESI$^+$): Calcd for $C_{18}H_{27}NNaO_2S$, $[M+Na]^+$ m/z 344.1655. Found 344.1654.



3o

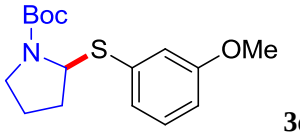
***tert*-Butyl 2-((4-(*tert*-butyl)phenyl)thio)pyrrolidine-1-carboxylate (3o).** Eluent: PE/EtOAc

(15:1). Yield 39.4 mg (78%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.38 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.41-5.23 (m, 1H), 3.52-3.22 (m, 2H), 2.20-1.83 (m, 4H), 1.51-1.23 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.7, 151.4, 134.8, 134.6, 130.4, 126.0, 80.0, 67.1, 66.7, 46.2, 45.5, 34.7, 33.9, 33.2, 31.3, 28.5, 28.3, 23.1, 22.3. HRMS (ESI$^+$): Calcd for $C_{19}H_{29}NNaO_2S$, $[M+Na]^+$ m/z 358.1811. Found 358.1809.



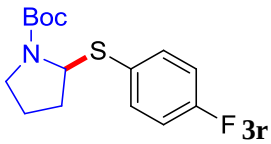
3p

***tert*-Butyl 2-((4-methoxyphenyl)thio)pyrrolidine-1-carboxylate (3p).** Eluent: PE/EtOAc (5:1). Yield 36.8 mg (79%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.37 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.29-5.11 (m, 1H), 3.80 (s, 3H), 3.48-3.22 (m, 2H), 2.19-1.71 (m, 4H), 1.54-1.28 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.1, 160.0, 153.7, 137.2, 132.7, 124.3, 114.7, 114.6, 80.0, 79.8, 67.1, 55.4, 46.3, 45.6, 33.6, 33.0, 28.5, 28.3, 23.1, 22.3. HRMS (ESI$^+$): Calcd for $C_{16}H_{23}NNaO_3S$, $[M+Na]^+$ m/z 332.1291. Found 332.1291.



3q

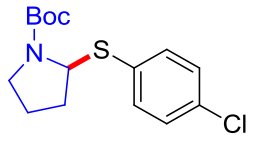
***tert*-Butyl 2-((3-methoxyphenyl)thio)pyrrolidine-1-carboxylate (3q).** Eluent: PE/EtOAc (5:1). Yield 39.0 mg (84%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (t, *J* = 8.0 Hz, 1H), 7.14-6.98 (m, 2H), 6.87-6.78 (m, 1H), 5.47-5.25 (m, 1H), 3.80 (s, 3H), 3.52-3.23 (m, 2H), 2.23-1.82 (m, 4H), 1.54-1.28 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.7, 153.6, 135.4, 129.7, 126.6, 126.2, 119.5, 119.0, 113.9, 80.1, 67.1, 66.7, 55.4, 46.4, 45.6, 34.1, 33.3, 28.5, 28.3, 23.1, 22.3. HRMS (ESI$^+$): Calcd for $C_{16}H_{23}NNaO_3S$, $[M+Na]^+$ m/z 332.1291. Found 332.1291.



3r

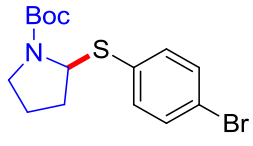
***tert*-Butyl 2-((4-fluorophenyl)thio)pyrrolidine-1-carboxylate (3r).** Eluent: PE/EtOAc (15:1). Yield 36.3 mg (81%). White solid, mp 56-57 °C. The product gives two sets of NMR signals,

owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.57-7.41 (m, 2H), 7.08-6.95 (m, 2H), 5.39-5.18 (m, 1H), 3.50-3.25 (m, 2H), 2.20-1.85 (m, 4H), 1.51-1.26 (m, 9H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 163.1 (d, *J* = 247.1 Hz), 153.7, 137.3 (d, *J* = 8.7 Hz), 137.1 (d, *J* = 247.1 Hz), 129.0, 116.1 (d, *J* = 21.7 Hz), 115.9 (d, *J* = 21.7 Hz), 80.2, 80.0, 67.3, 67.2, 46.3, 45.6, 33.7, 33.1, 28.4, 28.3, 23.2, 22.3. HRMS (ESI$^+$): Calcd for $C_{15}H_{20}NNaO_2SF$, $[M+Na]^+$ m/z 320.1091. Found 320.1088.



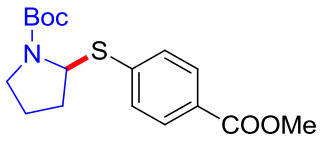
3s

***tert*-Butyl 2-((4-chlorophenyl)thio)pyrrolidine-1-carboxylate (3s).** Eluent: PE/EtOAc (15:1). Yield 40.6 mg (86%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52-7.33 (m, 2H), 7.32-7.18 (m, 2H), 5.43-5.18 (m, 1H), 3.54-3.22 (m, 2H), 2.23-1.82 (m, 4H), 1.53-1.26 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 136.0, 135.8, 132.6, 129.4, 129.3, 129.1, 80.3, 80.1, 67.3, 67.1, 46.3, 45.6, 33.9, 33.3, 28.4, 28.3, 23.2, 22.3. HRMS (ESI$^+$): Calcd for $C_{15}H_{20}NNaO_2SCl$, $[M+Na]^+$ m/z 336.0795. Found 336.0795.



3t

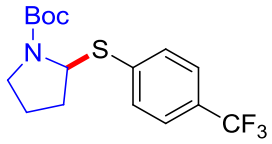
***tert*-Butyl 2-((4-bromophenyl)thio)pyrrolidine-1-carboxylate (3t).** Eluent: PE/EtOAc (15:1). Yield 50.4 mg (94%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.29 (m, 4H), 5.43-5.20 (m, 1H), 3.53-3.22 (m, 2H), 2.23-1.83 (m, 4H), 1.54-1.22 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.6, 136.2, 135.9, 133.3, 132.1, 132.0, 80.3, 80.1, 67.2, 67.0, 46.3, 45.6, 34.0, 33.3, 28.4, 28.3, 23.2, 22.3. HRMS (ESI$^+$): Calcd for $C_{15}H_{20}NNaO_2SBr$, $[M+Na]^+$ m/z 382.0270. Found 382.0263.



3u

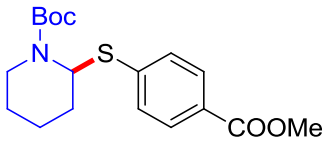
***tert*-Butyl 2-((4-(methoxycarbonyl)phenyl)thio)pyrrolidine-1-carboxylate (3u).** Eluent: PE/EtOAc (5:1). Yield 48.0 mg (95%). Colorless oil. The product gives two sets of NMR signals,

owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.00-7.89 (m, 2H), 7.54-7.43 (m, 2H), 5.57-5.35 (m, 1H), 3.90 (s, 3H), 3.55-3.24 (m, 2H), 2.30-1.82 (m, 4H), 1.53-1.27 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 153.5, 141.7, 131.9, 131.4, 130.0, 80.5, 80.3, 66.8, 66.3, 52.2, 46.3, 45.7, 34.5, 33.6, 28.4, 28.3, 23.2, 22.3. HRMS (ESI$^+$): Calcd for $C_{17}H_{23}NNaO_4S$, $[M+Na]^+$ m/z 360.1240. Found 360.1238.



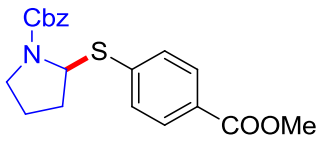
3v

***tert*-Butyl 2-((4-(trifluoromethyl)phenyl)thio)pyrrolidine-1-carboxylate (3v).** Eluent: PE/EtOAc (15:1). Yield 47.8 mg (92%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.46 (m, 4H), 5.60-5.32 (m, 1H), 3.57-3.23 (m, 2H), 2.30-1.85 (m, 4H), 1.54-1.21 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.5, 139.8, 133.1 (*J* = 41.2 Hz), 125.7, 124.7 (*J* = 388.2 Hz), 80.4, 80.3, 67.1, 66.7, 46.2, 45.7, 34.3, 33.5, 28.4, 28.2, 23.2, 22.3. HRMS (ESI$^+$): Calcd for $C_{16}H_{20}NNaO_2SF_3$, $[M+Na]^+$ m/z 370.1059. Found 370.1060.



3w

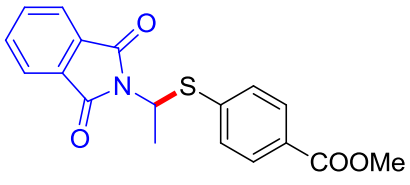
***tert*-Butyl 2-((4-(methoxycarbonyl)phenyl)thio)piperidine-1-carboxylate (3w).** Eluent: PE/EtOAc (15:1). Yield 48.6 mg (92%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR (DMSO-*d*6, 400 MHz) δ 7.99-7.78 (m, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 6.20-5.84 (m, 1H), 3.99-3.73 (m, 4H), 3.21-3.00 (m, 1H), 2.02-1.81 (m, 2H), 1.79-1.60 (m, 3H), 1.45-1.01 (m, 10H). ^{13}C NMR (DMSO-*d*6, 100 MHz) δ 166.3, 153.4, 141.1, 132.8, 131.5, 130.0, 80.1, 64.0, 61.3, 52.6, 38.8, 31.8, 30.9, 28.1, 25.2, 19.9. HRMS (ESI$^+$): Calcd for $C_{18}H_{25}NNaO_4S$, $[M+Na]^+$ m/z 374.1397. Found 374.1398.



3x

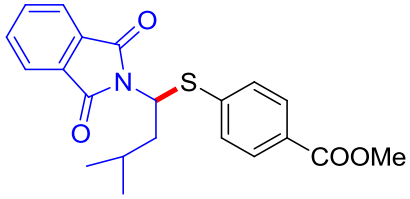
Benzyl 2-((4-(methoxycarbonyl)phenyl)thio)pyrrolidine-1-carboxylate (3x). Eluent: PE/EtOAc (5:1). Yield 48.2 mg (87%). Colorless oil. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.10-7.78 (m,

2H), 7.65-7.12 (m, 7H), 5.63-5.42 (m, 1H), 5.28-4.82 (m, 2H), 3.90 (s, 3H), 3.64-3.36 (m, 2H), 2.40-1.87 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 166.7, 154.2, 154.1, 141.4, 141.0, 136.5, 136.3, 132.1, 131.4, 130.0, 128.6, 128.5, 128.2, 128.1, 128.0, 67.4, 67.2, 66.9, 66.6, 52.2, 46.3, 46.2, 34.6, 33.8, 23.3, 22.4. HRMS (ESI$^+$): Calcd for $C_{20}H_{21}NNaO_4S$, $[M+Na]^+$ m/z 394.1084. Found 394.1085.



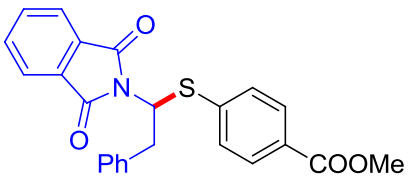
3y

Methyl 4-((1-(1,3-dioxoisoindolin-2-yl)ethyl)thio)benzoate (3y). Eluent: PE/EtOAc (5:1). Yield 43.2 mg (84%). White solid, mp 97-98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.83-7.75 (m, 2H), 7.74-7.66 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.93 (q, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 1.95 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.0, 166.6, 140.2, 134.4, 131.6, 130.6, 130.2, 128.9, 123.6, 52.9, 52.2, 20.2. HRMS (ESI$^+$): Calcd for $C_{18}H_{15}NNaO_4S$, $[M+Na]^+$ m/z 364.0614. Found 364.0607.



3z

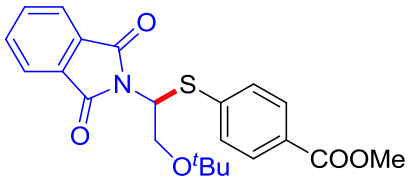
Methyl 4-((1-(1,3-dioxoisoindolin-2-yl)-3-methylbutyl)thio)benzoate (3z). Eluent: PE/EtOAc (5:1). Yield 46.4 mg (81%). Colorless gum. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.83-7.77 (m, 2H), 7.74-7.68 (m, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 5.84 (dd, J_1 = 6.2 Hz, J_2 = 9.6 Hz, 1H), 3.87 (s, 3H), 2.45-2.37 (m, 1H), 2.07-1.98 (m, 1H), 1.70-1.58 (m, 1H), 1.02-0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.2, 166.6, 140.4, 134.4, 131.5, 130.4, 130.2, 128.7, 123.6, 55.9, 52.2, 41.8, 25.9, 22.6, 21.8. HRMS (ESI$^+$): Calcd for $C_{21}H_{21}NNaO_4S$, $[M+Na]^+$ m/z 406.1084. Found 406.1083.



3aa

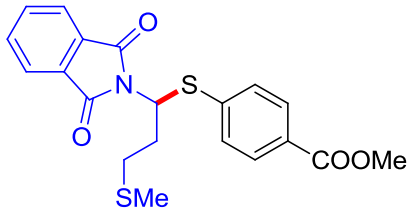
Methyl 4-((1-(1,3-dioxoisoindolin-2-yl)-2-phenylethyl)thio)benzoate (3aa). Eluent: PE/EtOAc (5:1). Yield 43.3 mg (69%). Colorless gum. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.87 (d, *J* = 6.5 Hz,

2H), 7.77-7.62 (m, 4H), 7.43 (d, J = 6.5 Hz, 2H), 7.25-7.12 (m, 5H), 5.97 (dd, J_1 = 6.2 Hz, J_2 = 10.3 Hz, 1H), 3.86 (s, 3H), 3.72 (dd, J_1 = 10.6 Hz, J_2 = 12.4 Hz, 1H), 3.54 (dd, J_1 = 6.2 Hz, J_2 = 14.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.1, 166.6, 140.1, 136.5, 134.3, 131.3, 130.6, 130.2, 129.1, 128.9, 128.7, 127.3, 123.6, 58.2, 52.2, 39.3. HRMS (ESI$^+$): Calcd for $C_{24}H_{19}NNaO_4S$, $[M+Na]^+$ m/z 440.0927. Found 440.0928.



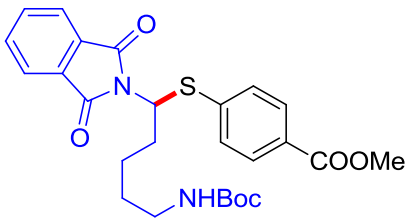
3ab

Methyl 4-((2-(*tert*-butoxy)-1-(1,3-dioxoisoindolin-2-yl)ethyl)thio)benzoate (3ab). Eluent: PE/EtOAc (5:1). Yield 49.7 mg (80%). Colorless gum. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (d, J = 8.2 Hz, 2H), 7.88-7.81 (m, 2H), 7.78-7.69 (m, 2H), 7.51 (d, J = 7.9 Hz, 2H), 5.79 (dd, J_1 = 6.2 Hz, J_2 = 9.3 Hz, 1H), 4.16 (t, J = 9.6 Hz, 1H), 3.94-3.82 (m, 4H), 1.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.3, 166.6, 140.6, 134.3, 131.7, 130.2, 129.9, 128.7, 123.6, 74.1, 61.6, 57.4, 52.2, 27.5. HRMS (ESI$^+$): Calcd for $C_{22}H_{23}NNaO_5S$, $[M+Na]^+$ m/z 436.1189. Found 436.1187.



3ac

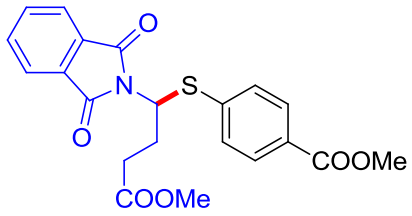
Methyl 4-((1-(1,3-dioxoisoindolin-2-yl)-3-(methylthio)propyl)thio)benzoate (3ac). Eluent: PE/EtOAc (5:1). Yield 47.8 mg (79%). Colorless gum. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.89 (d, J = 8.2 Hz, 2H), 7.85-7.78 (m, 2H), 7.76-7.68 (m, 2H), 7.49 (d, J = 8.2 Hz, 2H), 5.95 (t, J = 7.6 Hz, 1H), 3.88 (s, 3H), 2.67-2.54 (m, 4H), 2.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.1, 166.6, 140.0, 134.5, 131.5, 130.6, 130.2, 128.9, 123.7, 56.3, 52.2, 32.4, 31.2, 15.5. HRMS (ESI$^+$): Calcd for $C_{20}H_{19}NNaO_4S_2$, $[M+Na]^+$ m/z 424.0648. Found 424.0648.



3ad

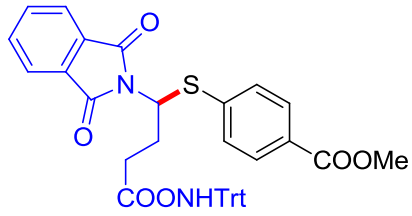
Methyl 4-((5-((tert-butoxycarbonyl)amino)-1-(1,3-dioxoisoindolin-2-yl)pentyl)thio)benzoate

(3ad). Eluent: PE/EtOAc (2:1). Yield 61.9 mg (83%). Colorless gum. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.83-7.77 (m, 2H), 7.75-7.69 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 5.72 (dd, J_1 = 6.9 Hz, J_2 = 8.9 Hz, 1H), 4.69-4.58 (m, 1H), 3.88 (s, 3H), 3.16-3.00 (m, 2H), 2.48-2.20 (m, 2H), 1.60-1.31 (m, 13H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.2, 166.6, 156.0, 140.3, 134.4, 131.4, 130.4, 130.2, 128.8, 123.6, 79.1, 57.3, 52.2, 40.2, 33.0, 29.4, 28.4, 24.2. HRMS (ESI$^+$): Calcd for $C_{26}H_{30}N_2NaO_6S$, $[M+Na]^+$ m/z 521.1717. Found 521.1719.



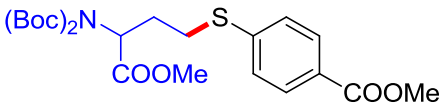
3ae

Methyl 4-((1-(1,3-dioxoisoindolin-2-yl)-4-methoxy-4-oxobutyl)thio)benzoate (3ae). Eluent: PE/EtOAc (5:1). Yield 54.1 mg (87%). Colorless gum. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.85-7.79 (m, 2H), 7.77-7.71 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 5.81 (t, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 3.64 (s, 3H), 2.73-2.60 (m, 2H), 2.49 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.4, 167.0, 166.5, 140.0, 134.5, 131.4, 130.5, 130.2, 128.9, 123.7, 56.7, 52.2, 51.9, 31.2, 28.8. HRMS (ESI$^+$): Calcd for $C_{21}H_{19}NNaO_6S$, $[M+Na]^+$ m/z 436.0825. Found 436.0828.



3af

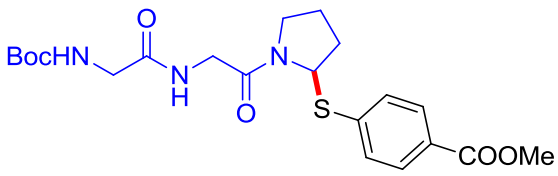
Methyl 4-((1-(1,3-dioxoisoindolin-2-yl)-4-oxo-4-((tritylamino)oxy)butyl)thio)benzoate (3af). Eluent: PE/EtOAc (2:1). Yield 77.7 mg (81%). White solid, mp 98-100 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.79-7.73 (m, 2H), 7.71-7.64 (m, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32-7.10 (m, 15H), 6.72-6.65 (m, 1H), 5.87 (t, *J* = 7.7 Hz, 1H), 3.84 (s, 3H), 2.72-2.56 (m, 2H), 2.50-2.38 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 167.1, 166.6, 144.7, 140.2, 134.5, 131.5, 130.3, 130.2, 128.8, 128.1, 127.2, 123.7, 70.8, 57.1, 52.3, 34.4, 29.2. HRMS (ESI$^+$): Calcd for $C_{39}H_{32}N_2NaO_5S$, $[M+Na]^+$ m/z 663.1924. Found 663.1923.



3ag

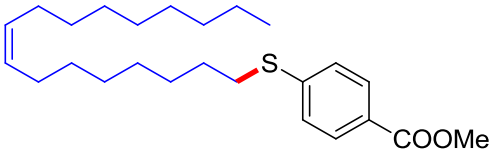
Methyl 4-((3-(diBoc-amino)-4-methoxy-4-oxobutyl)thio)benzoate (3ag). Eluent: PE/EtOAc

(5:1). Yield 41.5 mg (57%). Colorless oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.07 (dd, J_1 = 5.8 Hz, J_2 = 8.2 Hz, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.57-2.50 (m, 1H), 2.25-2.17 (m, 1H), 1.49 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.8, 166.8, 152.0, 143.4, 130.1, 127.0, 126.7, 83.6, 57.1, 52.4, 52.1, 29.9, 29.1, 28.0. HRMS (ESI$^+$): Calcd for $C_{23}H_{33}NNaO_8S$, $[M+Na]^+$ m/z 506.1819. Found 506.1818.



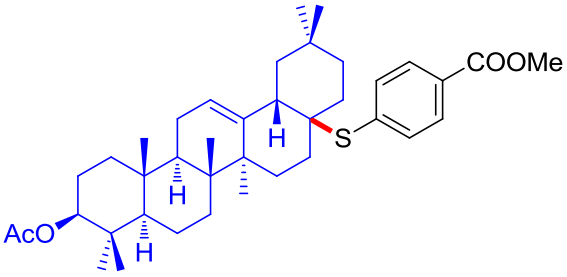
3ah

Methyl 4-((1-(2-(2-((tert-butoxycarbonyl)amino)acetamido)acetyl)pyrrolidin-2-yl)thio)benzo-ate (3ah). Eluent: DCM/MeOH (25:1). Yield 49.3 mg (73%). Colorless gum. The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.01-7.92 (m, 2H), 7.54-7.44 (m, 2H), 7.12 (br, 1H), 5.71-5.32 (m, 2H), 4.36-3.95 (m, 2H), 3.94-3.74 (m, 5H), 3.65-3.38 (m, 2H), 2.34-1.93 (m, 4H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 167.6, 166.8, 166.7, 166.5, 156.0, 140.9, 139.3, 132.0, 131.2, 130.4, 130.1, 129.5, 128.8, 80.2, 65.2, 52.4, 52.3, 46.5, 45.7, 44.1, 42.2, 42.0, 34.5, 33.1, 28.4, 23.4, 21.0. HRMS (ESI$^+$): Calcd for $C_{21}H_{29}N_3NaO_6S$, $[M+Na]^+$ m/z 474.1699. Found 474.1694.



3ai

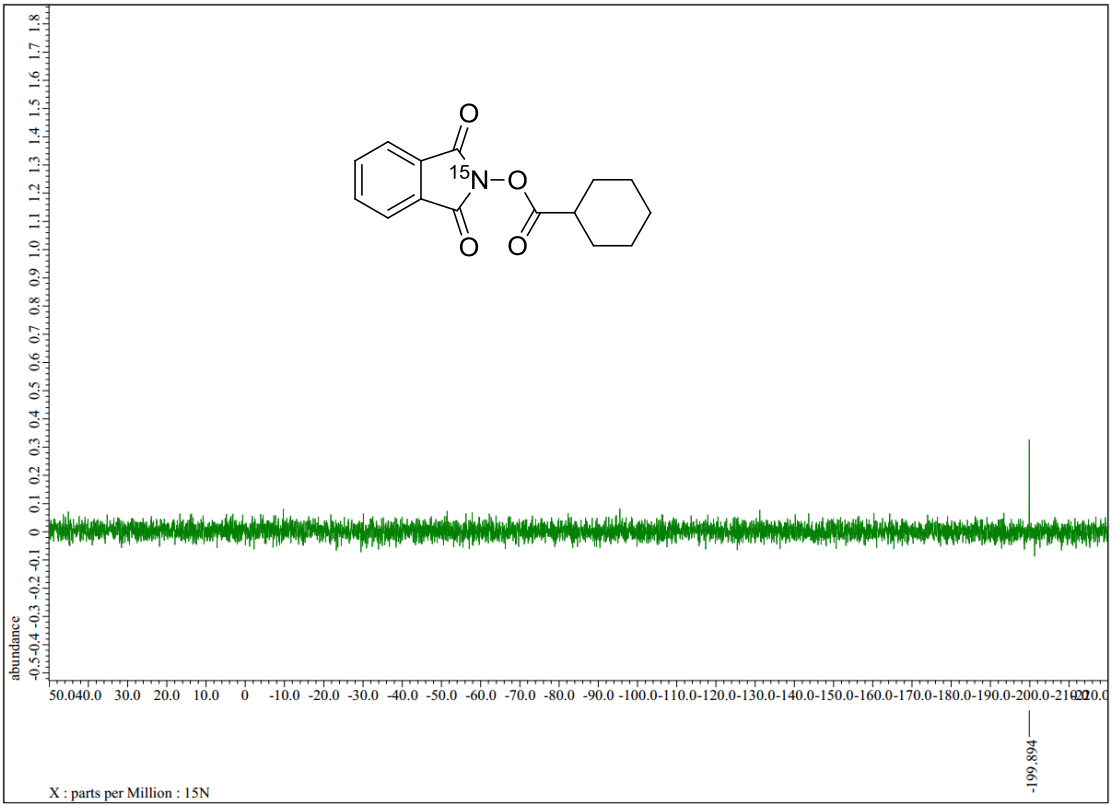
(Z)-methyl 4-(heptadec-8-en-1-ylthio)benzoate (3ai). Eluent: PE/EtOAc (25:1). Yield 38.4 mg (63%). White solid, mp 50-51 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 5.40-5.31 (m, 2H), 3.89 (s, 3H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.04-1.89 (m, 4H), 1.69 (quint, *J* = 7.3 Hz, 2H), 1.50-1.19 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 144.6, 130.6, 130.3, 130.0, 126.6, 126.4, 52.1, 32.7, 32.6, 32.2, 32.0, 29.9, 29.8, 29.4, 29.3, 29.1, 29.0, 28.8, 27.4, 27.3, 22.8, 14.2. HRMS (ESI$^+$): Calcd for $C_{25}H_{41}O_2S$, $[M+H]^+$ m/z 405.2822. Found 405.2830.

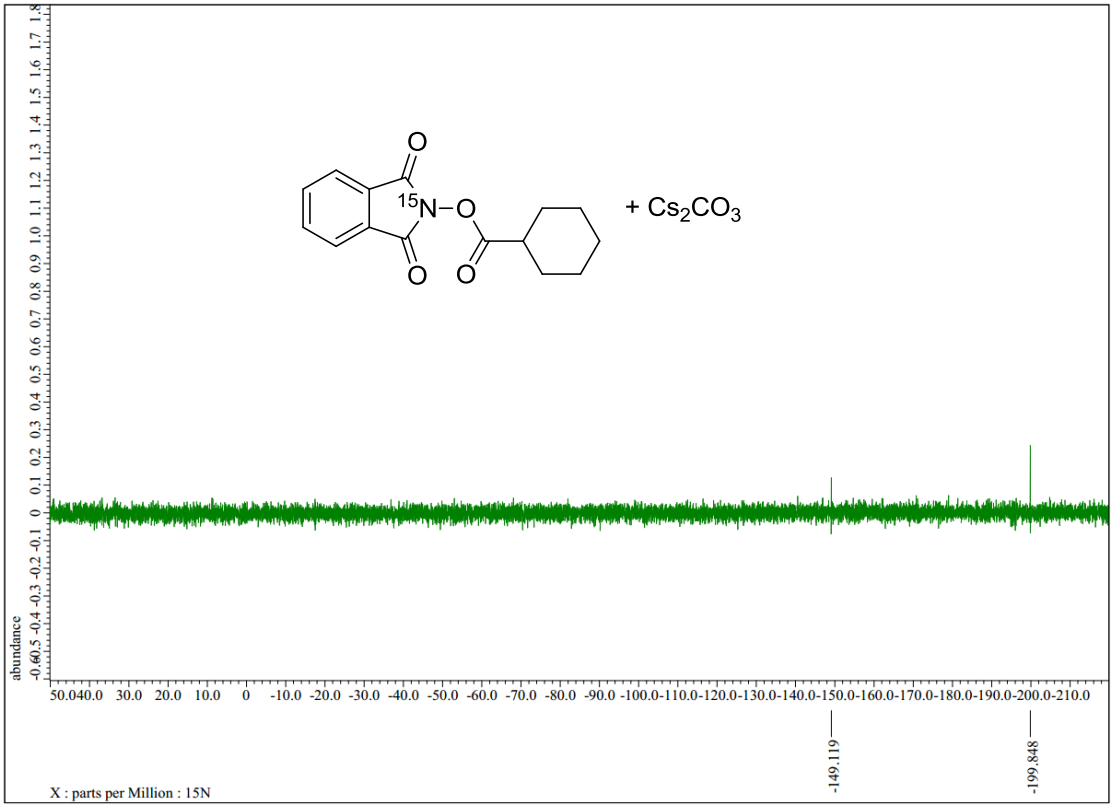


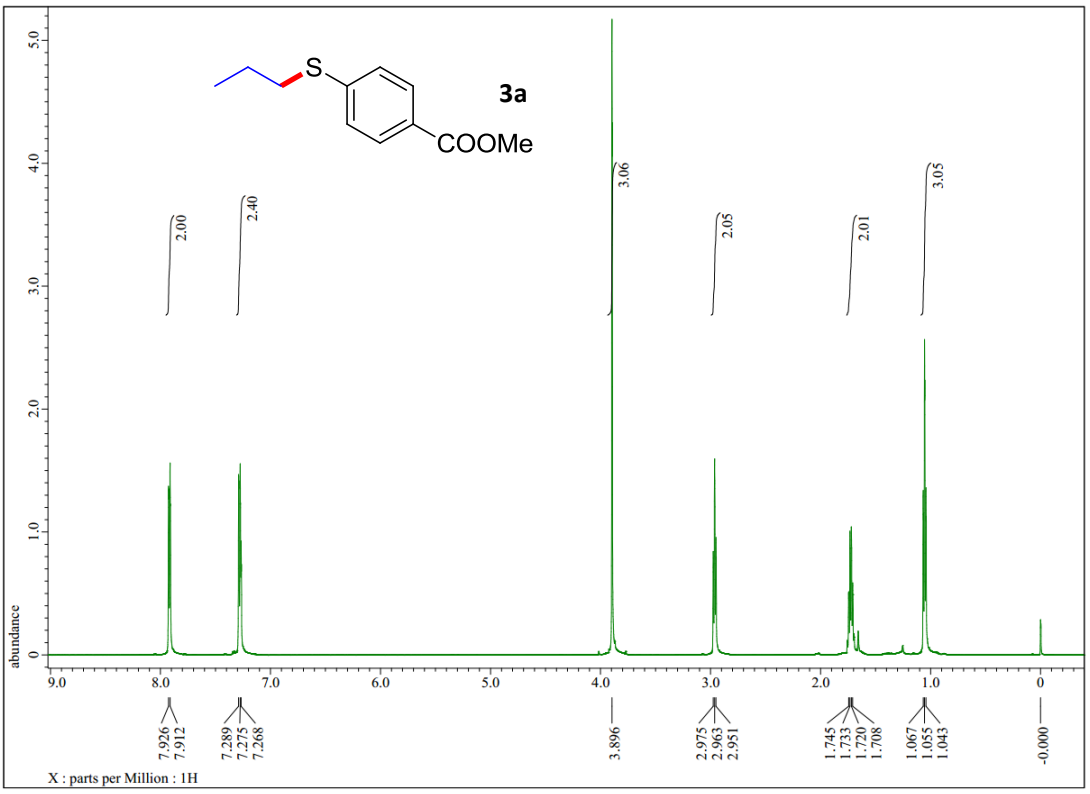
3aj

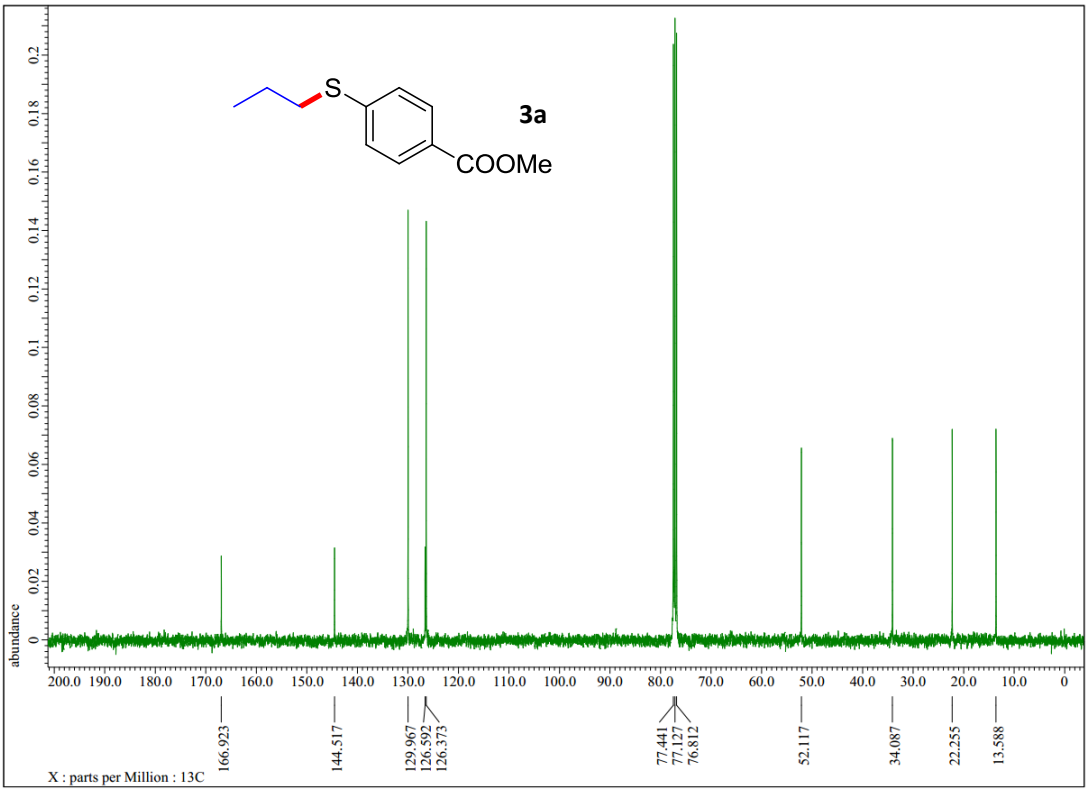
methyl 4-(((6aS,6bR,8aR,10S,12aR,12bR,14bS)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicen-4a-yl)thio)benzoate (3aj). Eluent: PE/DCM/EtOAc (20:10:1). Yield 51.0 mg (55%). White solid, mp 263-265 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 5.25 (t, *J* = 3.4 Hz, 1H), 4.52 (t, *J* = 8.0 Hz, 1H), 3.91 (s, 3H), 2.41-2.27 (m, 2H), 2.23-2.12 (m, 1H), 2.10-1.84 (m, 6H), 1.79-1.38 (m, 10H), 1.33-0.97 (m, 15H), 0.94-0.80 (m, 10H), 0.72 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 166.9, 143.6, 139.1, 137.0, 129.9, 129.4, 122.9, 81.0, 56.2, 55.4, 52.3, 47.8, 47.7, 45.6, 41.7, 40.1, 38.3, 37.8, 37.1, 36.4, 35.6, 33.0, 32.9, 30.8, 28.2, 27.0, 26.2, 25.5, 23.7, 23.6, 23.4, 21.4, 18.4, 17.7, 16.8, 15.6. HRMS (ESI^+): Calcd for $C_{39}H_{57}O_4S$, $[M+H]^+$ m/z 621.3972. Found 621.3956.

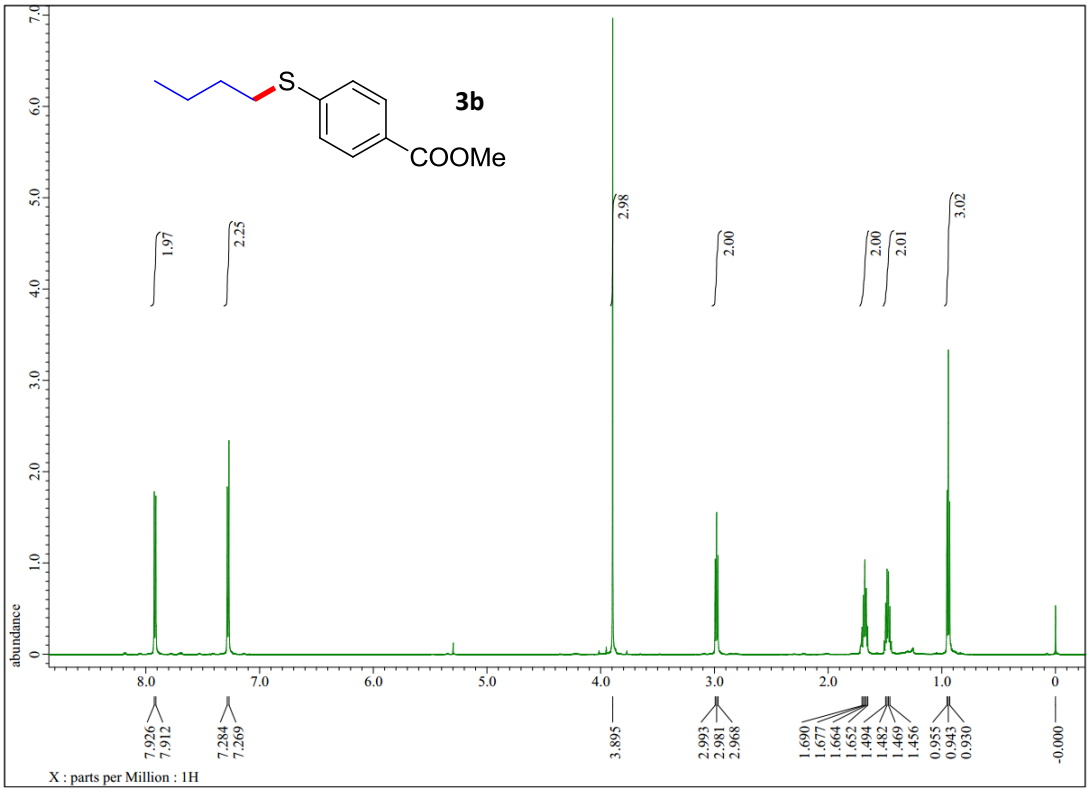
6. NMR Spectra of the Products

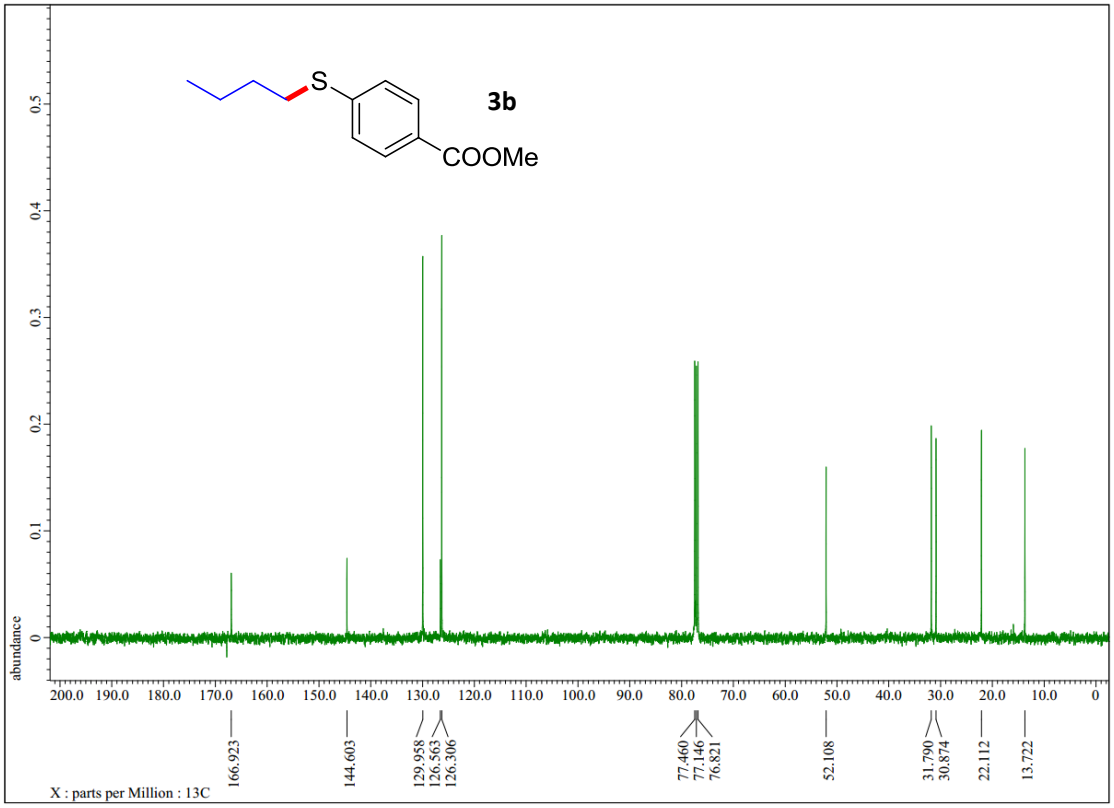


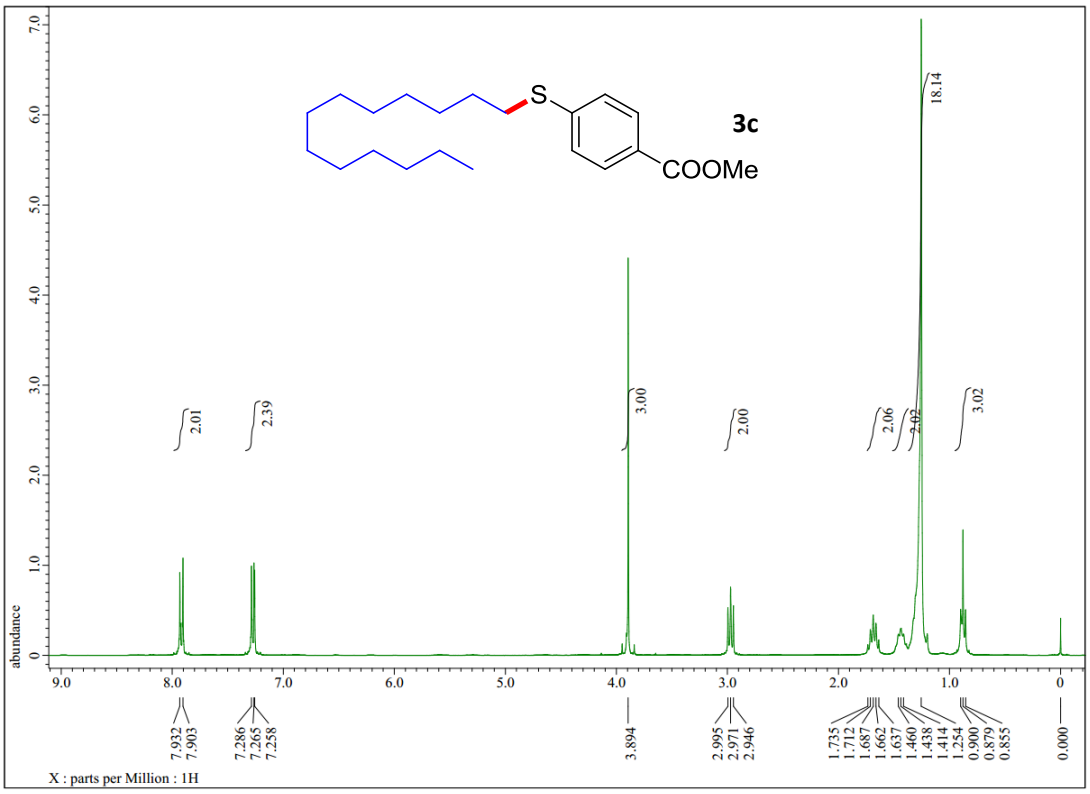


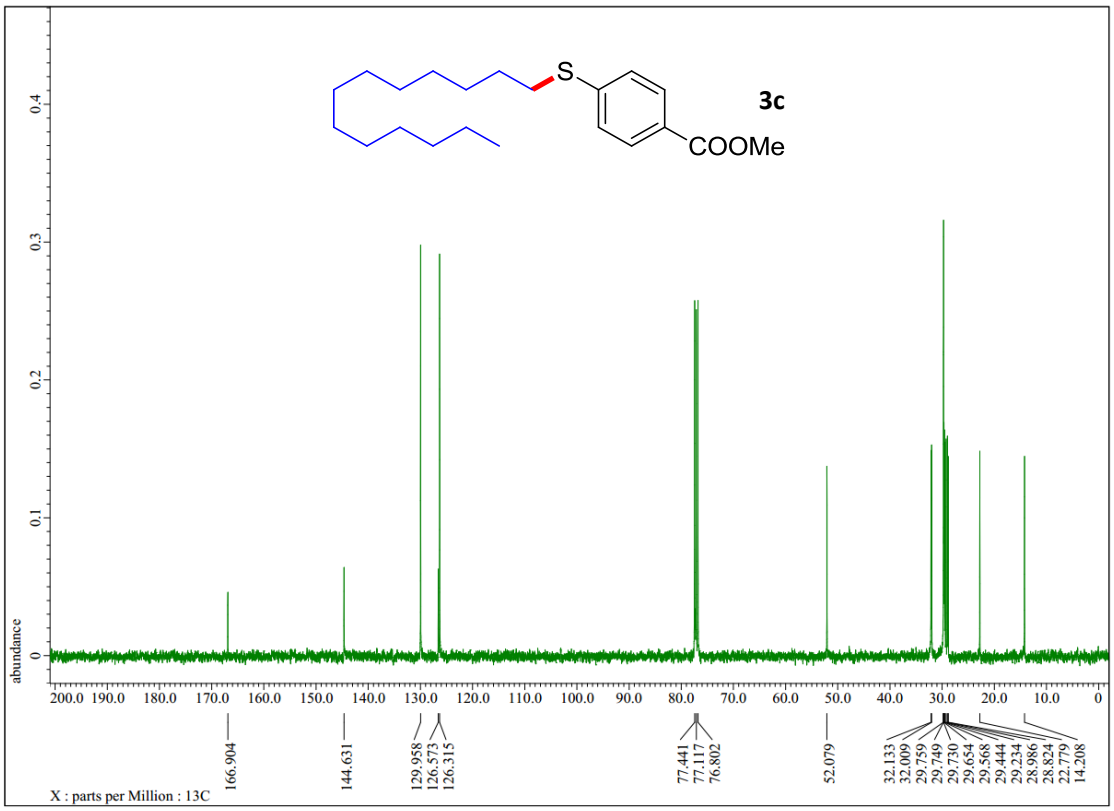

3a
COOMe
S
2.00
2.40
3.06
2.05
2.01
3.05
abundance
X : parts per Million : 1H
7.926
7.912
7.289
7.275
7.268
3.896
2.975
2.963
2.951
1.745
1.733
1.720
1.708
1.067
1.055
1.043
-0.000

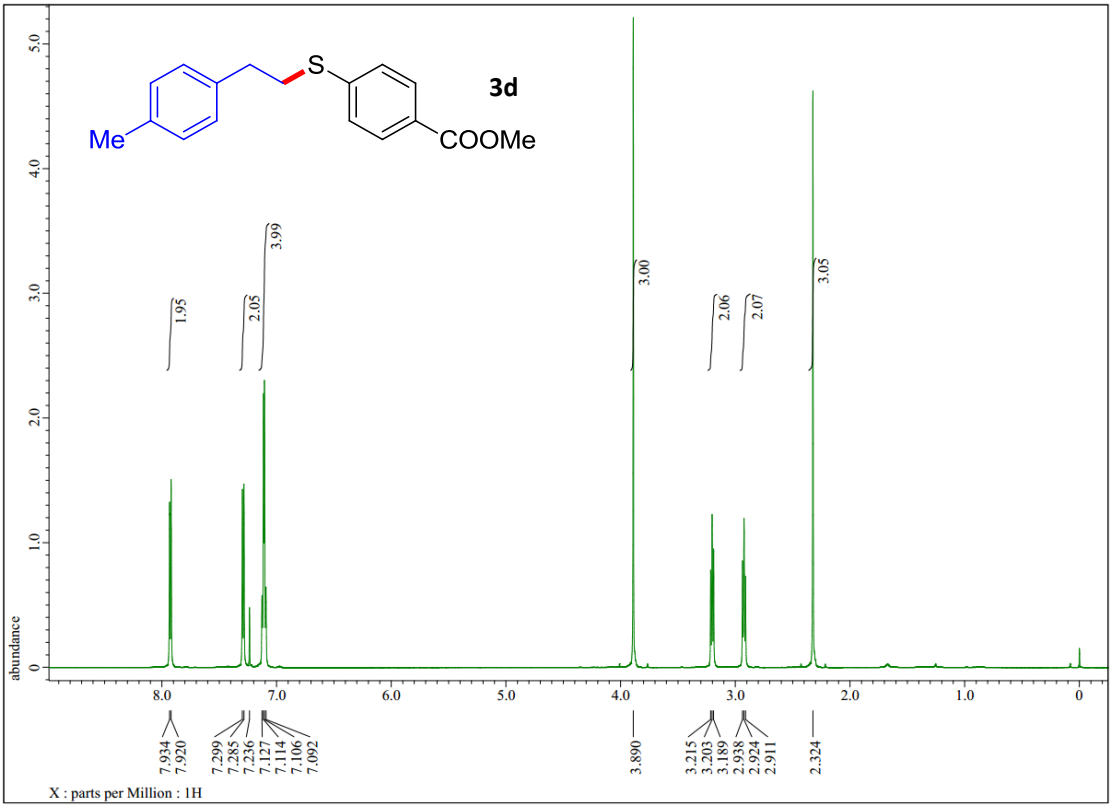

3a
COOMe
S
abundance
X : parts per Million : 13C
166.923
144.517
129.967
126.592
126.373
77.441
77.127
76.812
52.117
34.087
22.255
13.588

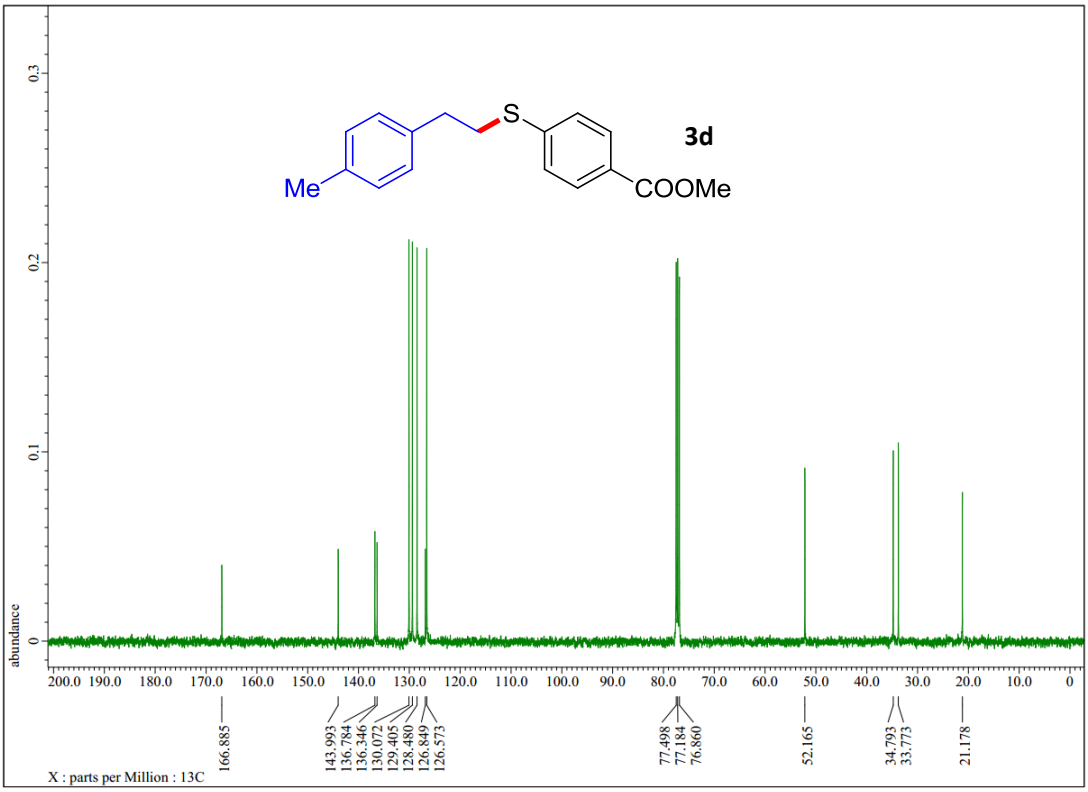

3b
COOMe
abundance
X : parts per Million : 1H

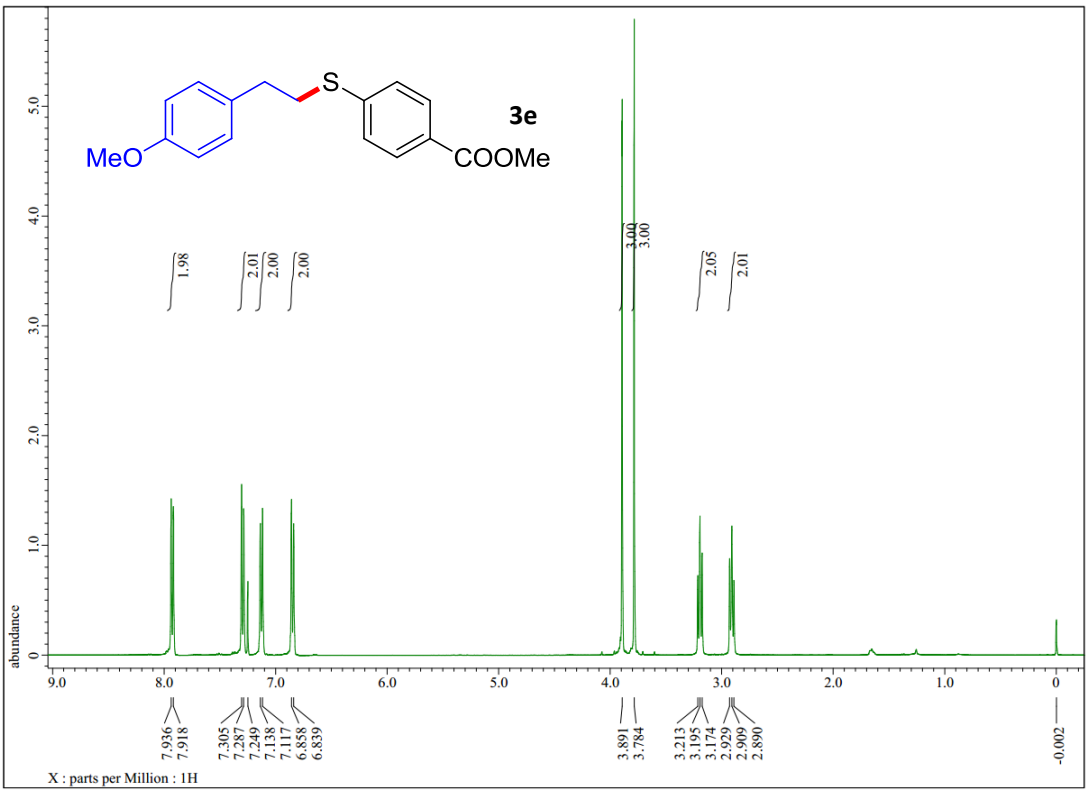

3b
COOMe
abundance
X : parts per Million : 13C

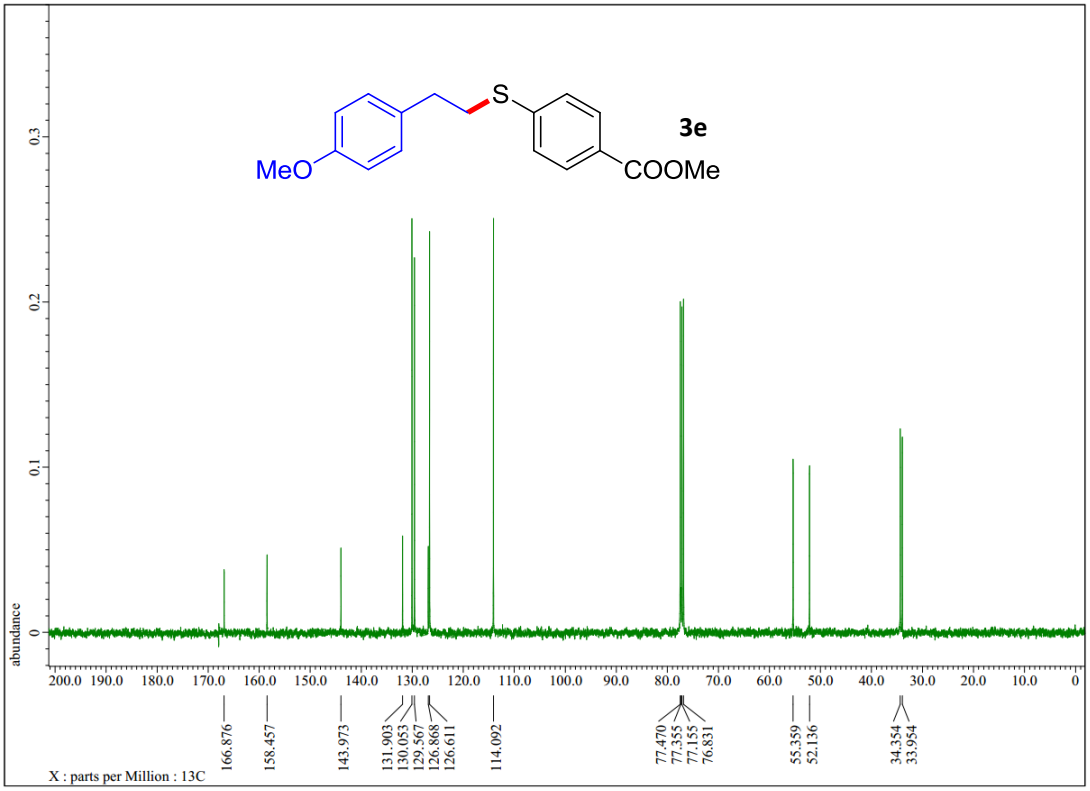

3c
S
COOMe
abundance
X : parts per Million : 1H
2.01
2.39
3.00
2.00
2.06
2.02
18.14
3.02
7.932
7.903
7.286
7.265
7.258
3.894
2.995
2.971
2.946
1.735
1.712
1.687
1.662
1.637
1.460
1.438
1.414
1.254
0.900
0.879
0.855
0.000

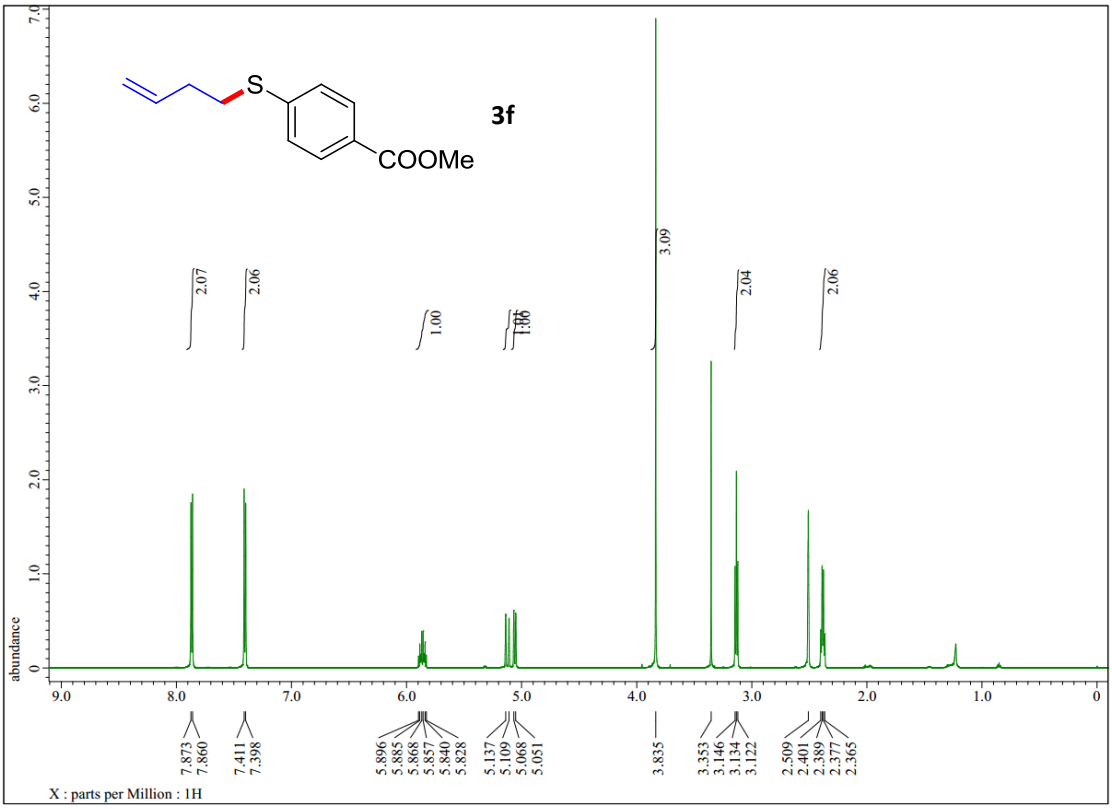

3c
S
COOMe
abundance
X : parts per Million : 13C
166.904
144.631
129.958
126.573
126.315
77.441
77.117
76.802
52.079
32.133
32.009
29.759
29.749
29.730
29.654
29.568
29.444
29.234
28.986
28.824
22.779
14.208

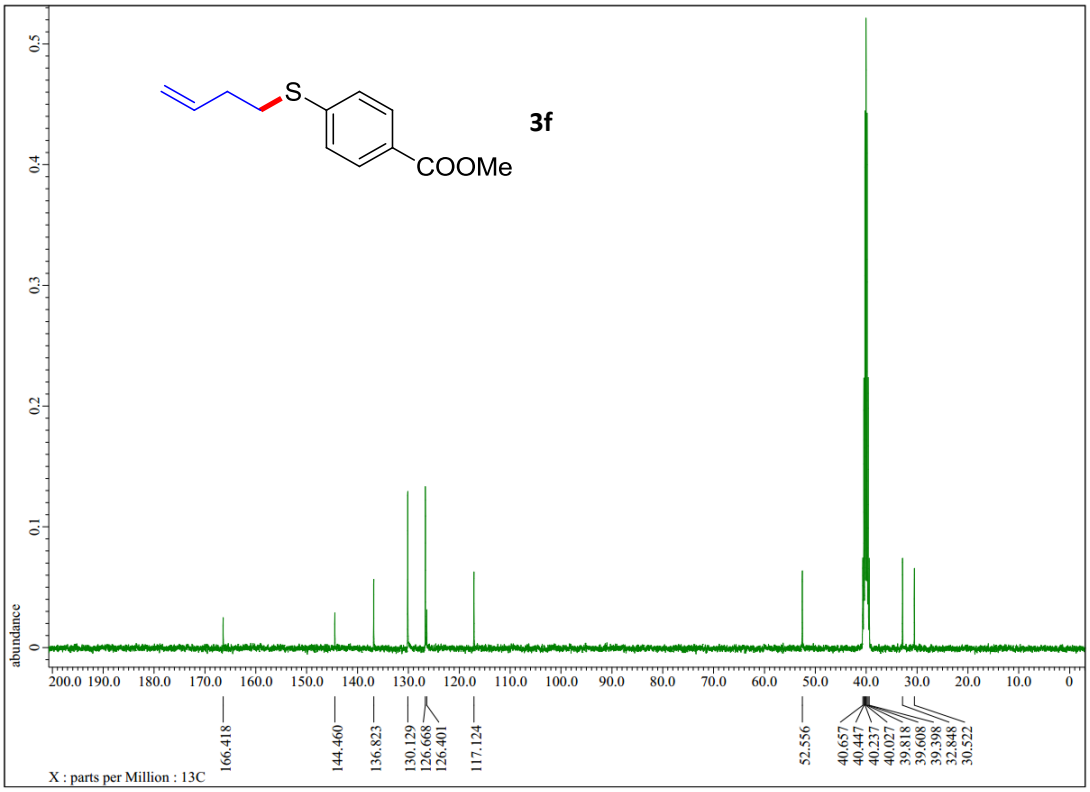

3d
Me
S
COOMe
abundance
1.95
2.05
3.99
3.00
2.06
2.07
3.05
7.934
7.920
7.299
7.285
7.236
7.127
7.114
7.106
7.092
3.890
3.215
3.203
3.189
2.938
2.924
2.911
2.324
X : parts per Million : 1H

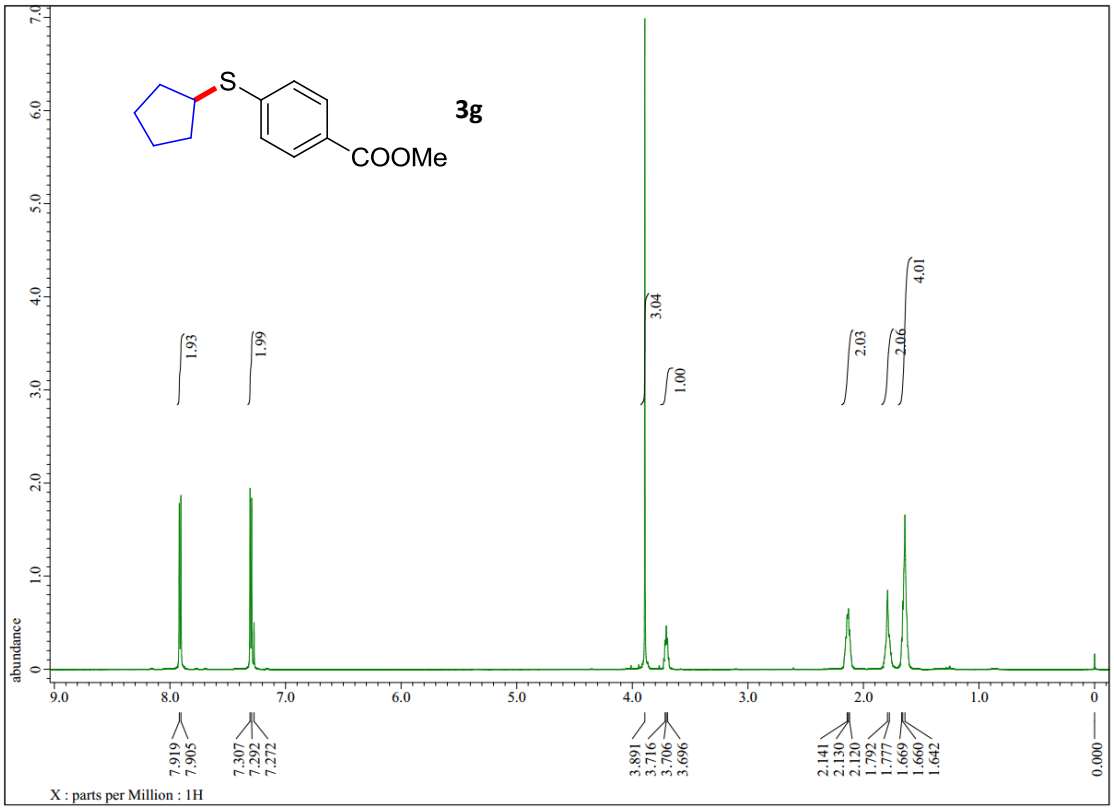

3d
Me
S
COOMe
abundance
166.885
143.993
136.784
136.346
130.072
129.405
128.480
126.849
126.573
77.498
77.184
76.860
52.165
34.793
33.773
21.178
X : parts per Million : 13C

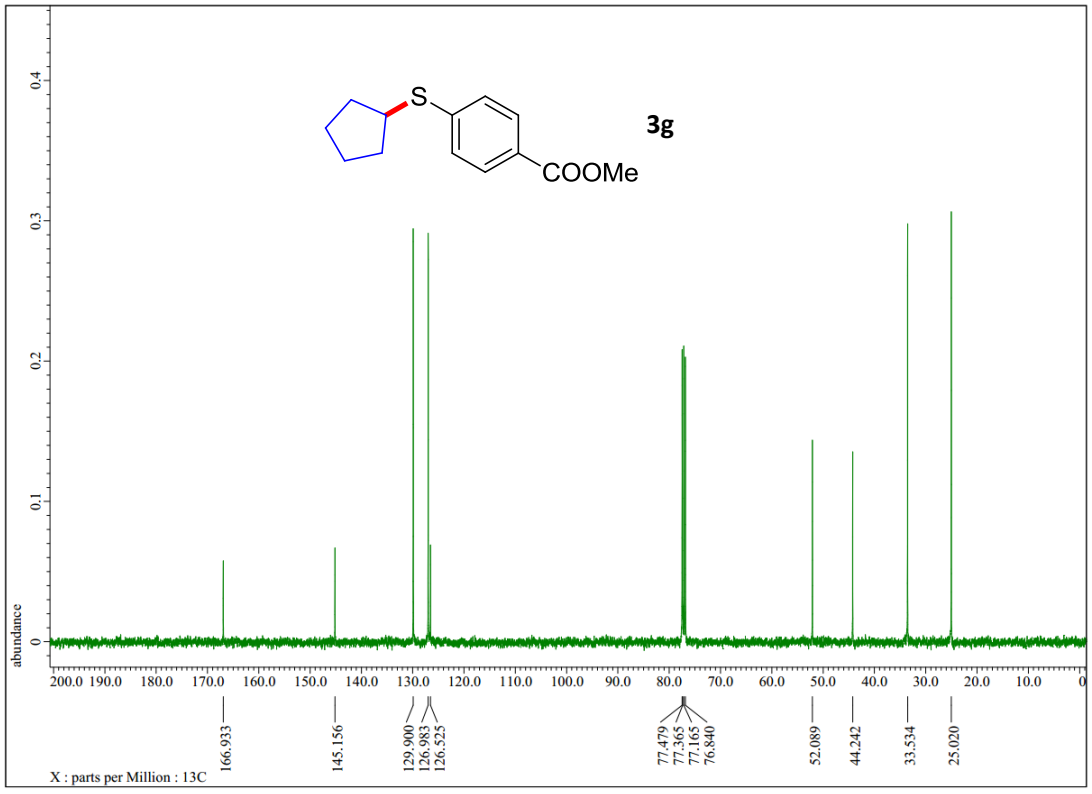

3e
MeO
COOMe
abundance
X : parts per Million : 1H

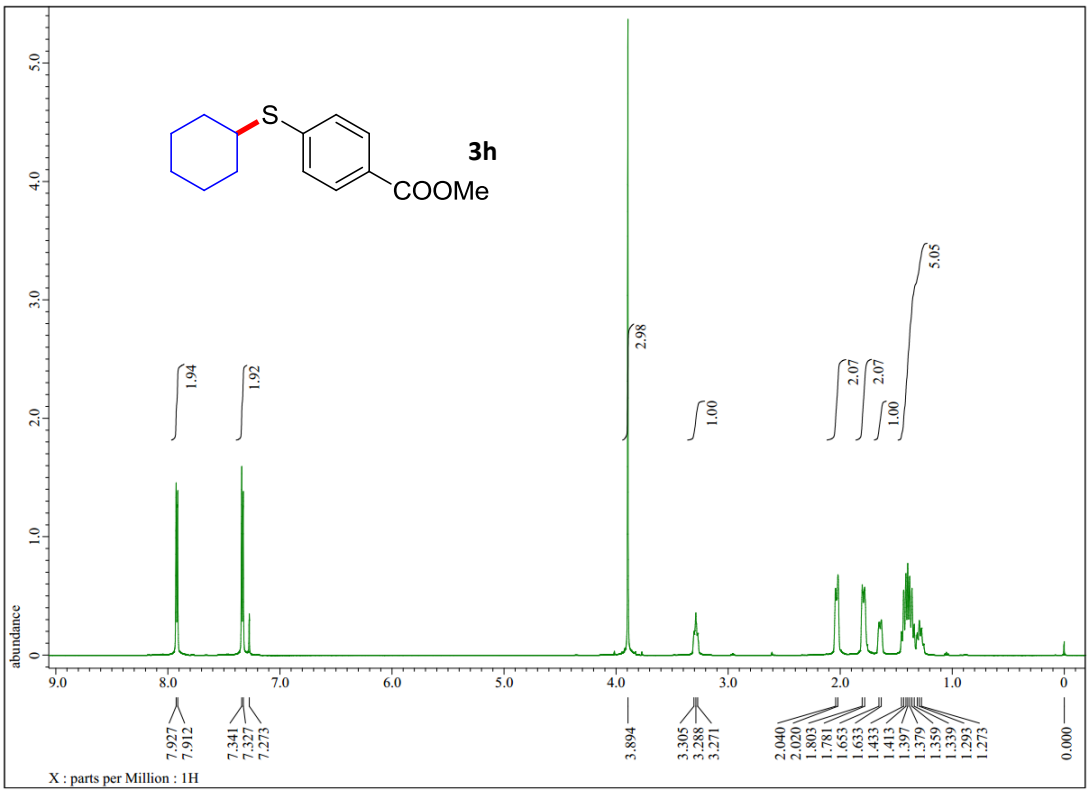

3e
MeO
COOMe
abundance
X : parts per Million : 13C

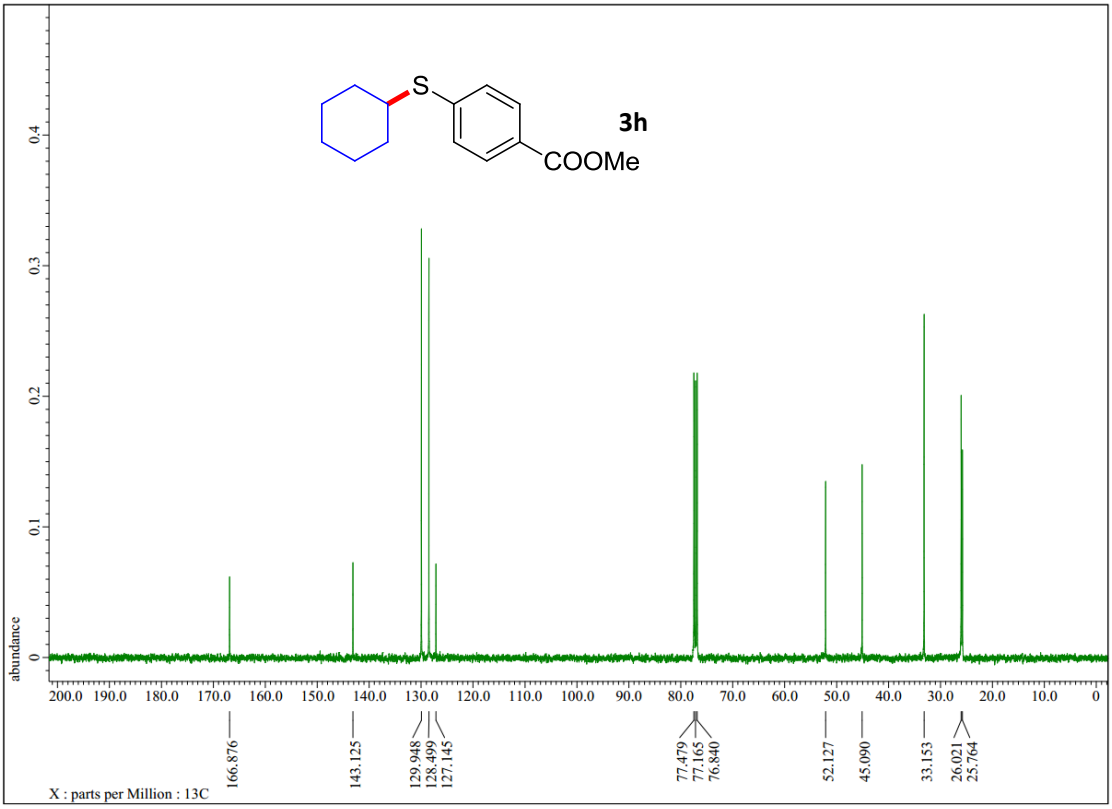

3f
S
COOMe
abundance
X : parts per Million : 1H

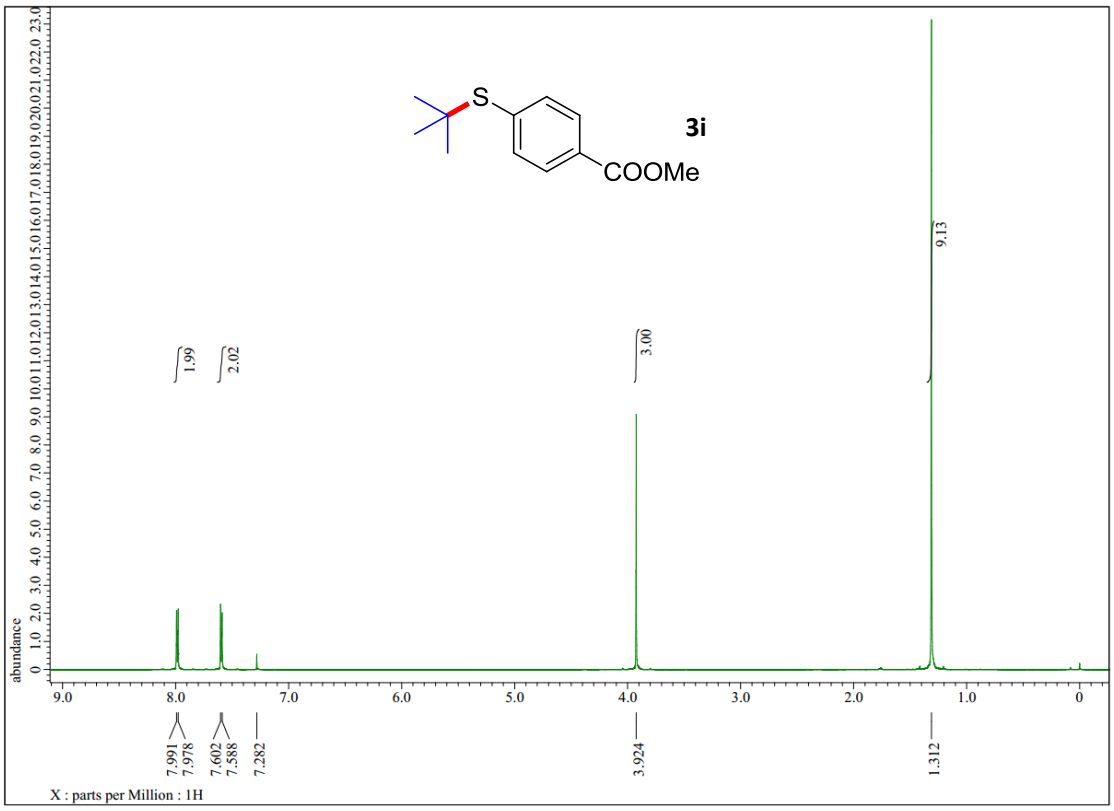

3f
S
COOMe
abundance
X : parts per Million : 13C

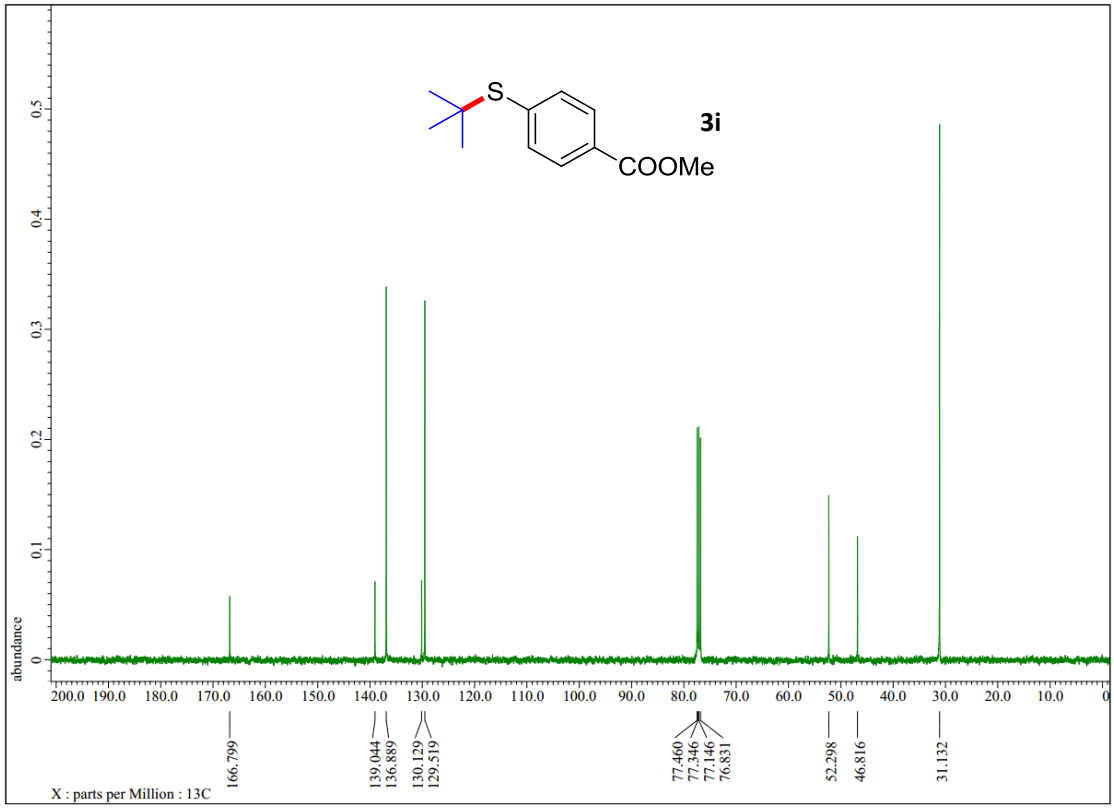

3g
S
COOMe
abundance
1.93
1.99
3.04
1.00
2.03
2.06
4.01
7.919
7.905
7.307
7.292
7.272
3.891
3.716
3.706
3.696
2.141
2.130
2.120
1.792
1.777
1.669
1.660
1.642
0.000
X : parts per Million : 1H

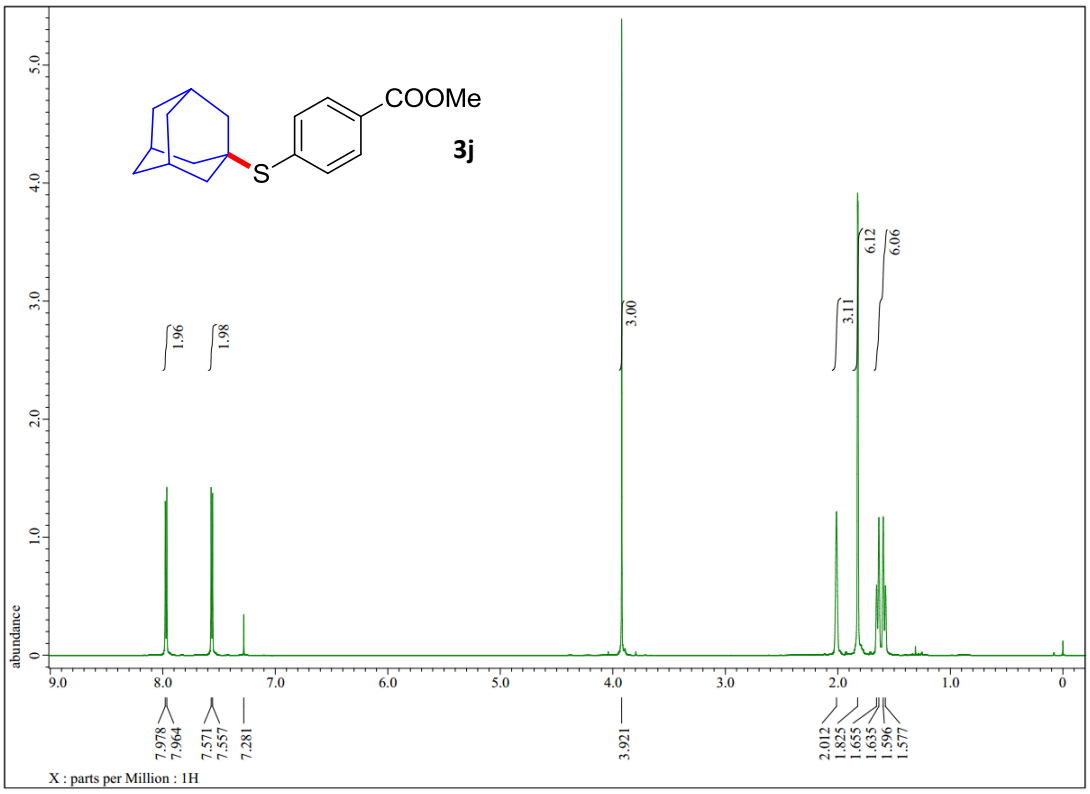

3g
S
COOMe
abundance
166.933
145.156
129.900
126.983
126.525
77.479
77.365
77.165
76.840
52.089
44.242
33.534
25.020
X : parts per Million : 13C

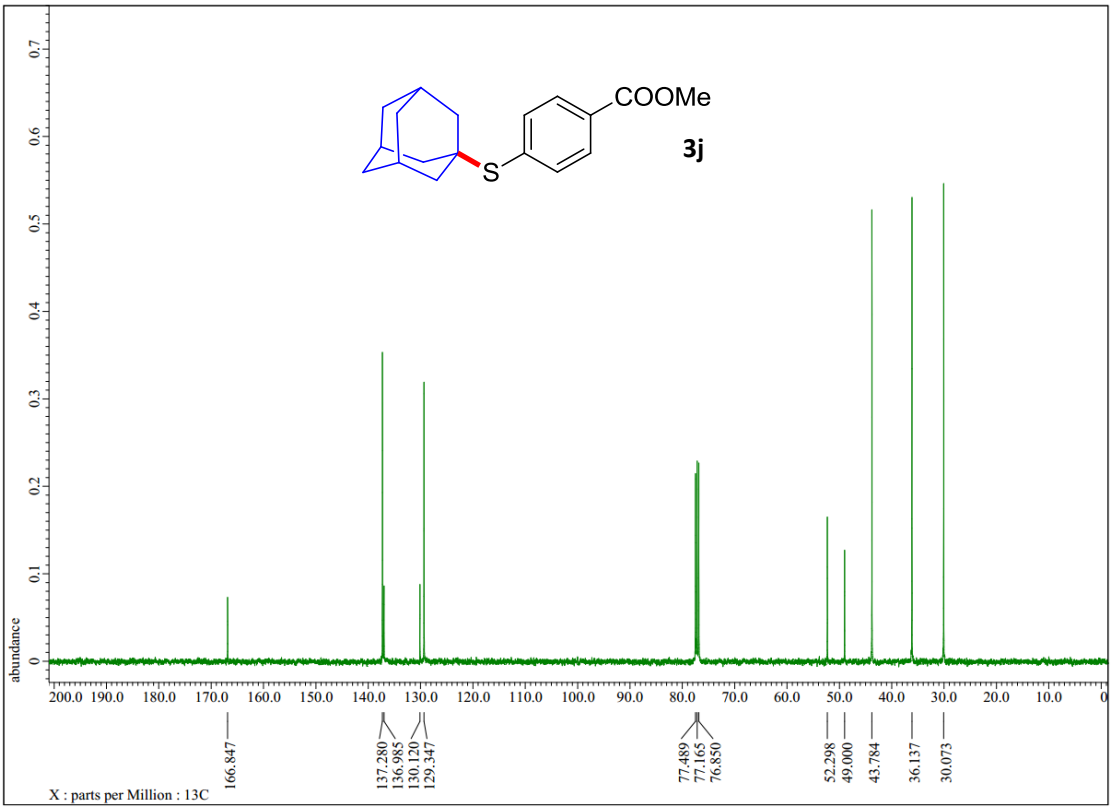

3h
COOMe
abundance
X : parts per Million : 1H

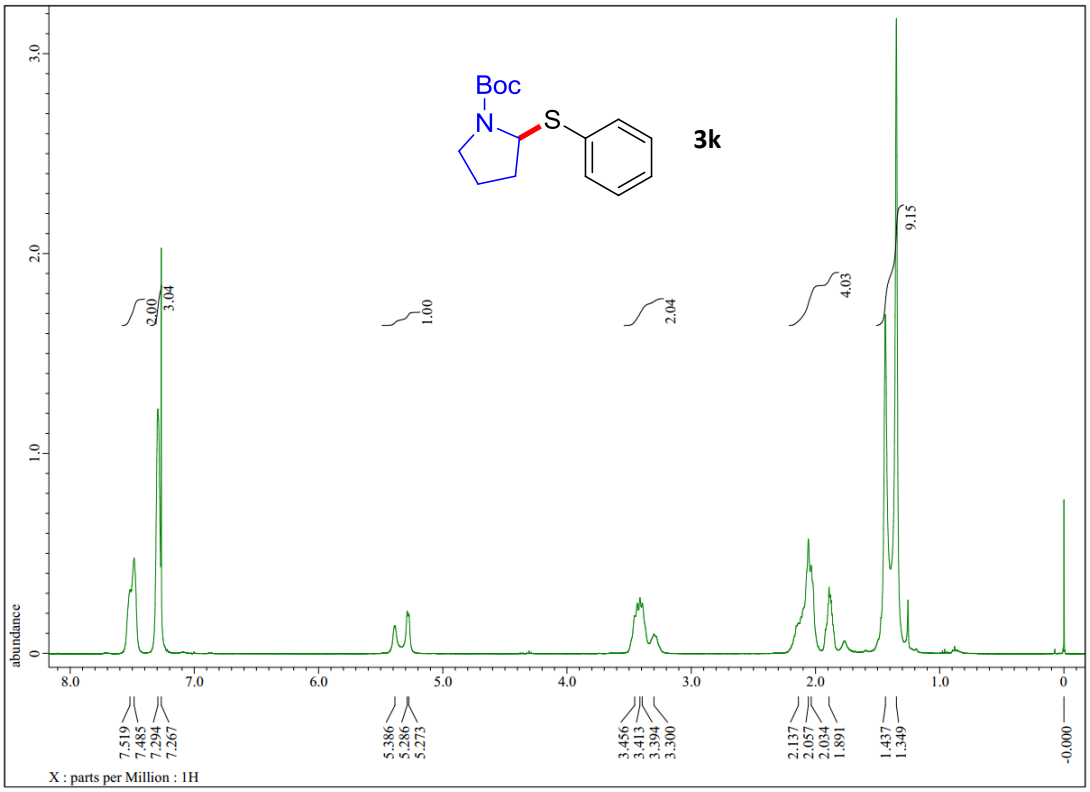

3h
COOMe
abundance
X : parts per Million : 13C

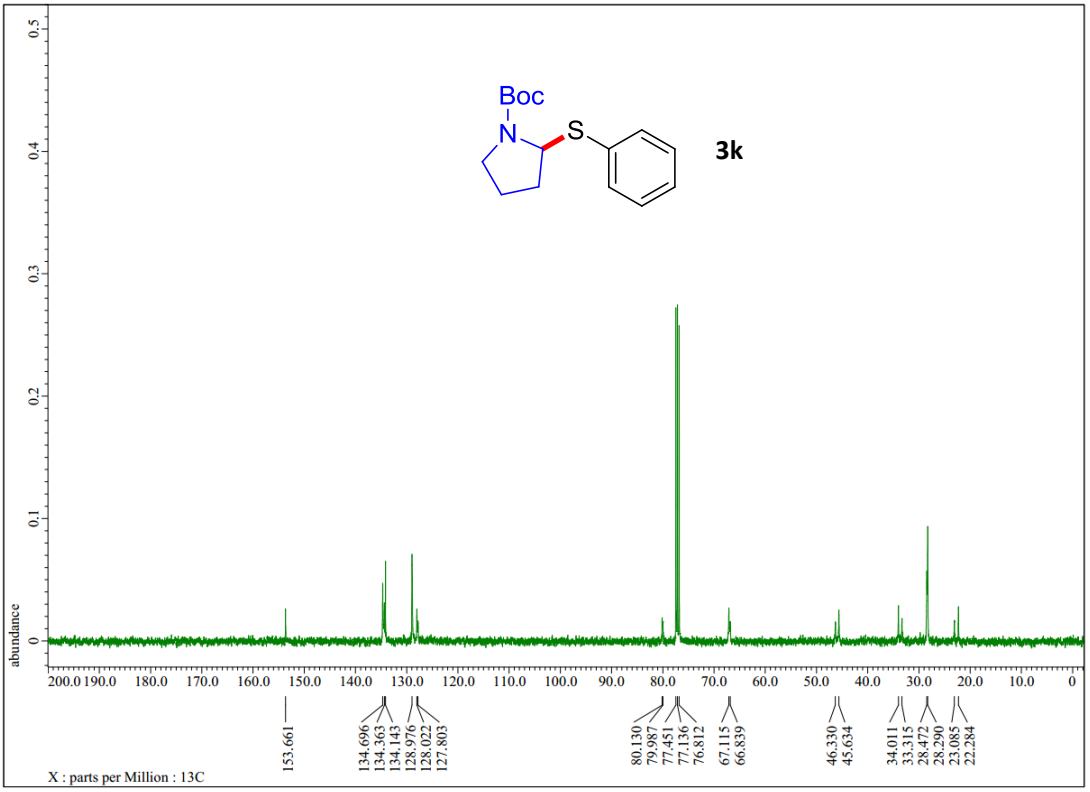

3i
COOMe
S
1.99
2.02
3.00
9.13
abundance
7.991
7.978
7.602
7.588
7.282
3.924
1.312
X : parts per Million : 1H

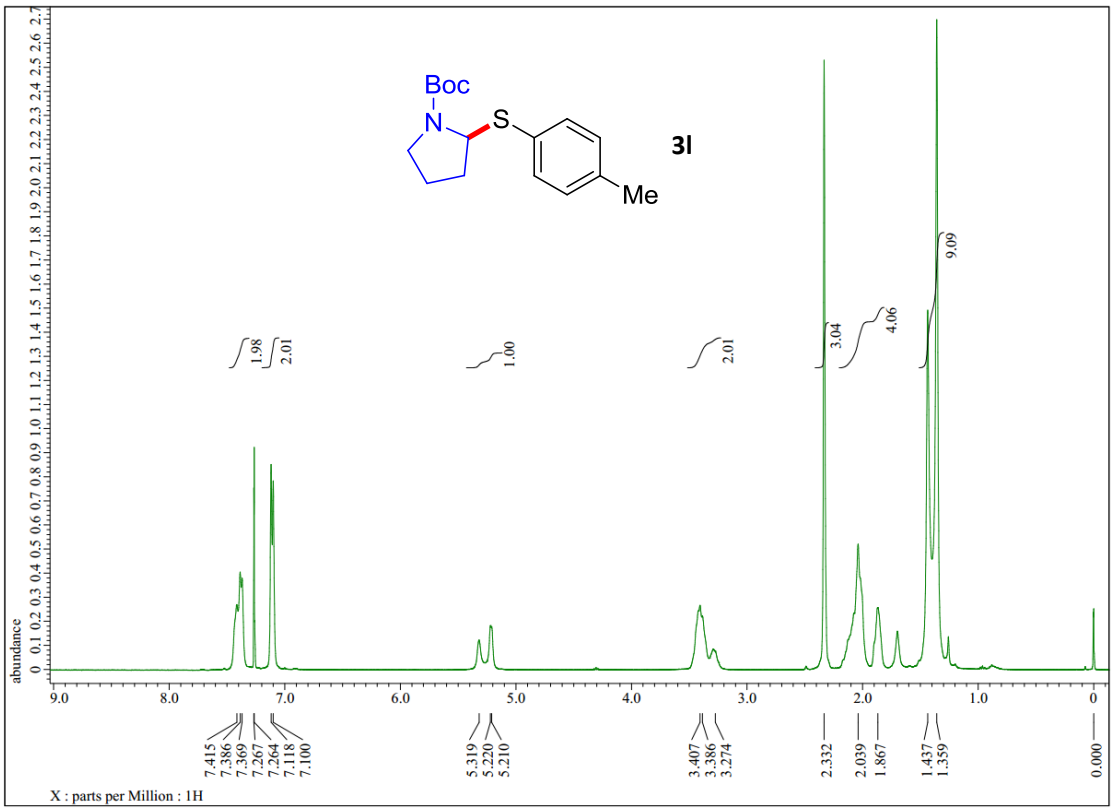

3i
COOMe
S
abundance
166.799
139.044
136.889
130.129
129.519
77.460
77.346
77.146
76.831
52.298
46.816
31.132
X : parts per Million : 13C

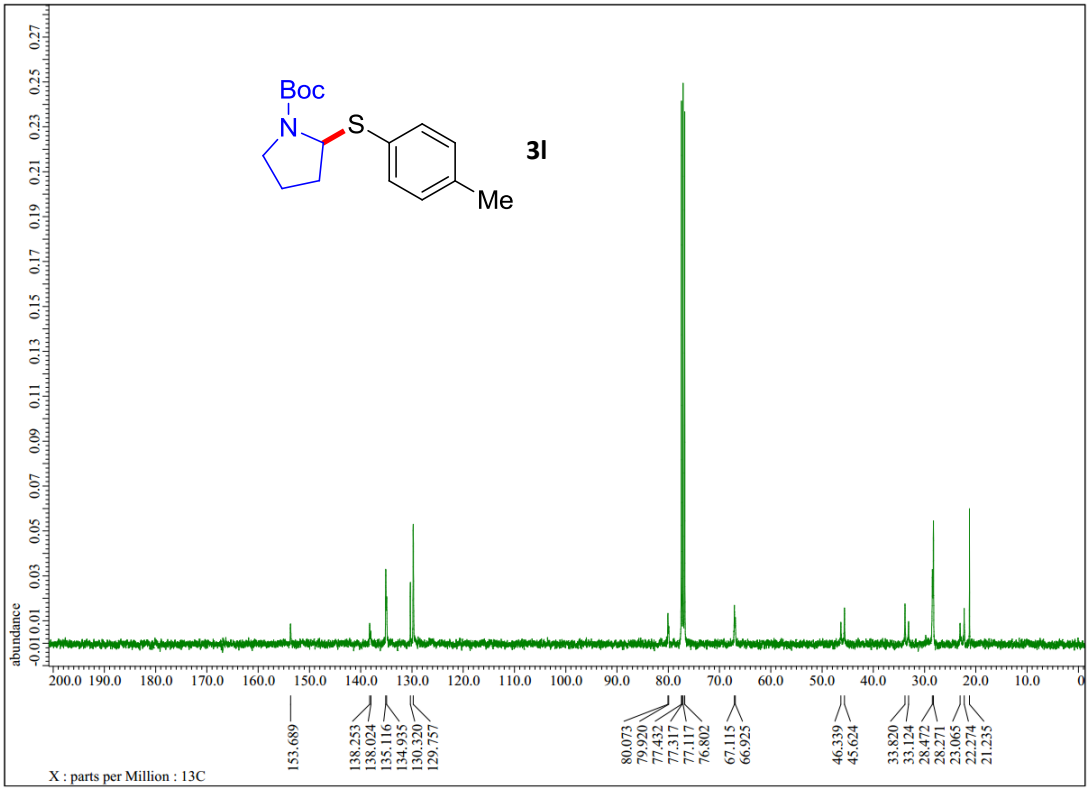

COOMe
3j
S
1.96
1.98
3.00
3.11
6.12
6.06
abundance
7.978
7.964
7.571
7.557
7.281
3.921
2.012
1.825
1.655
1.635
1.596
1.577
X : parts per Million : 1H

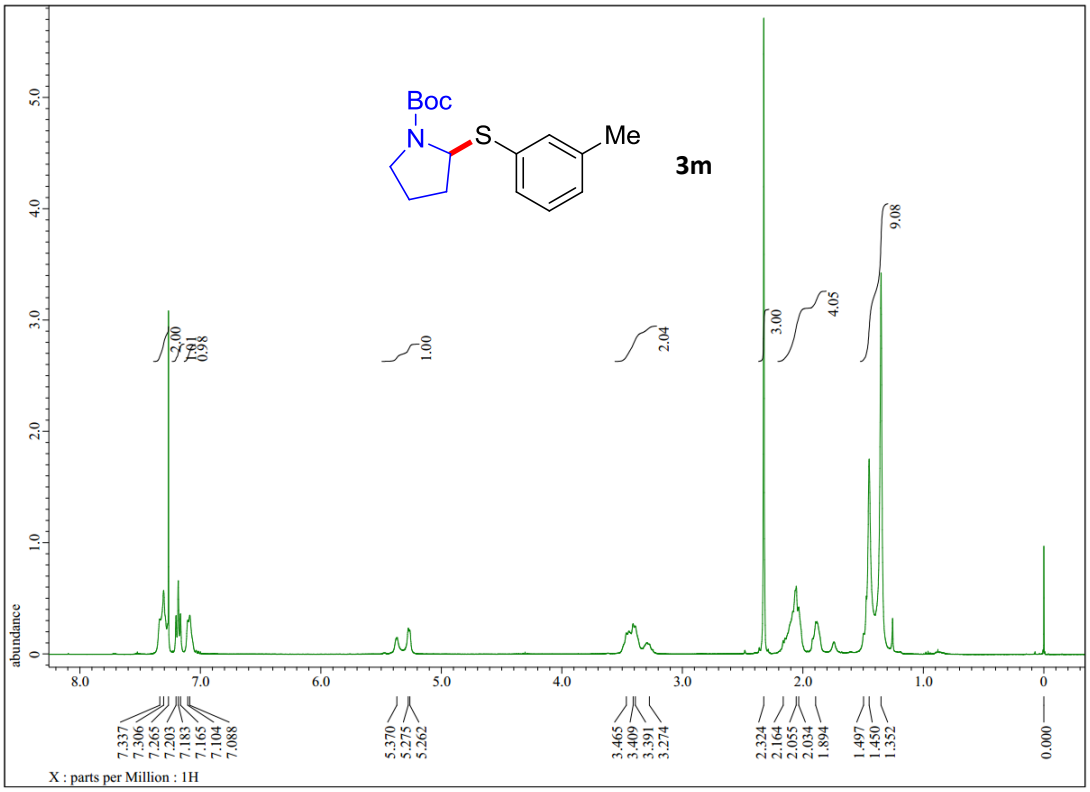

COOMe
3j
S
abundance
166.847
137.280
136.985
130.120
129.347
77.489
77.165
76.850
52.298
49.000
43.784
36.137
30.073
X : parts per Million : 13C

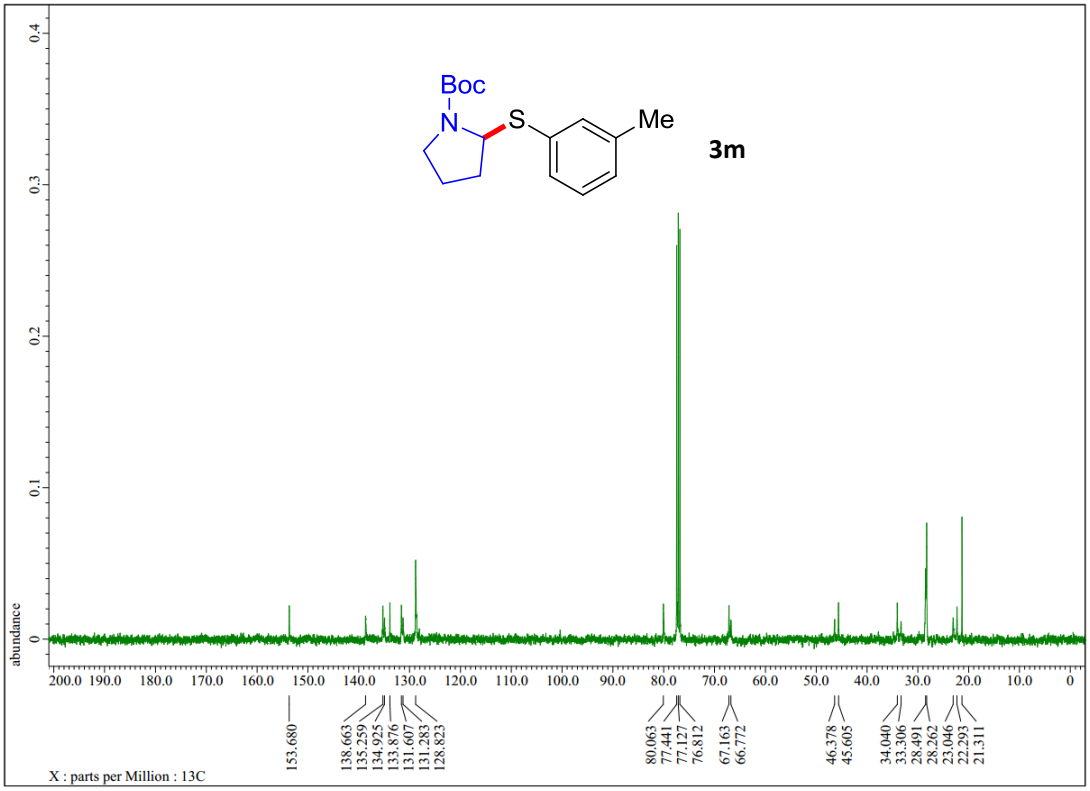

Boc
N
S
3k
abundance
X : parts per Million : 1H
2.00
3.04
1.00
2.04
4.03
9.15
7.519
7.485
7.294
7.267
5.386
5.286
5.273
3.456
3.413
3.394
3.300
2.137
2.057
2.034
1.891
1.437
1.349
-0.000

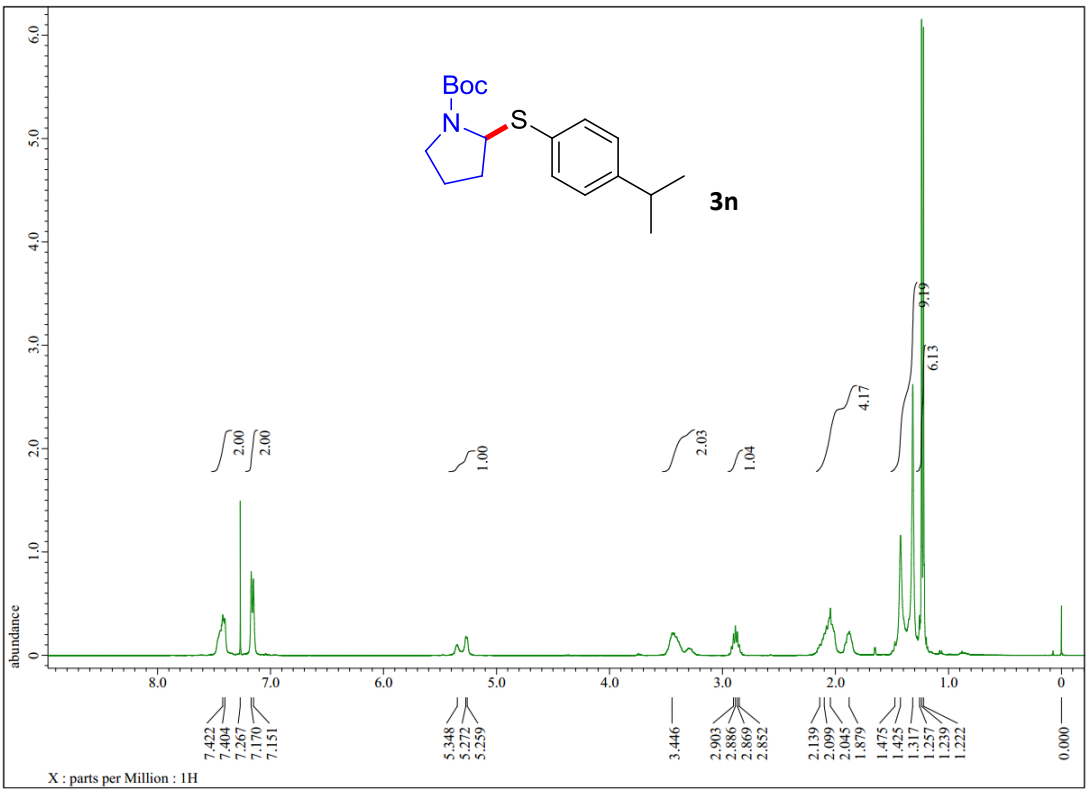

Boc
N
S
3k
abundance
X : parts per Million : 13C
153.661
134.696
134.363
134.143
128.976
128.022
127.803
80.130
79.987
77.451
77.136
76.812
67.115
66.839
46.330
45.634
34.011
33.315
28.472
28.290
23.085
22.284

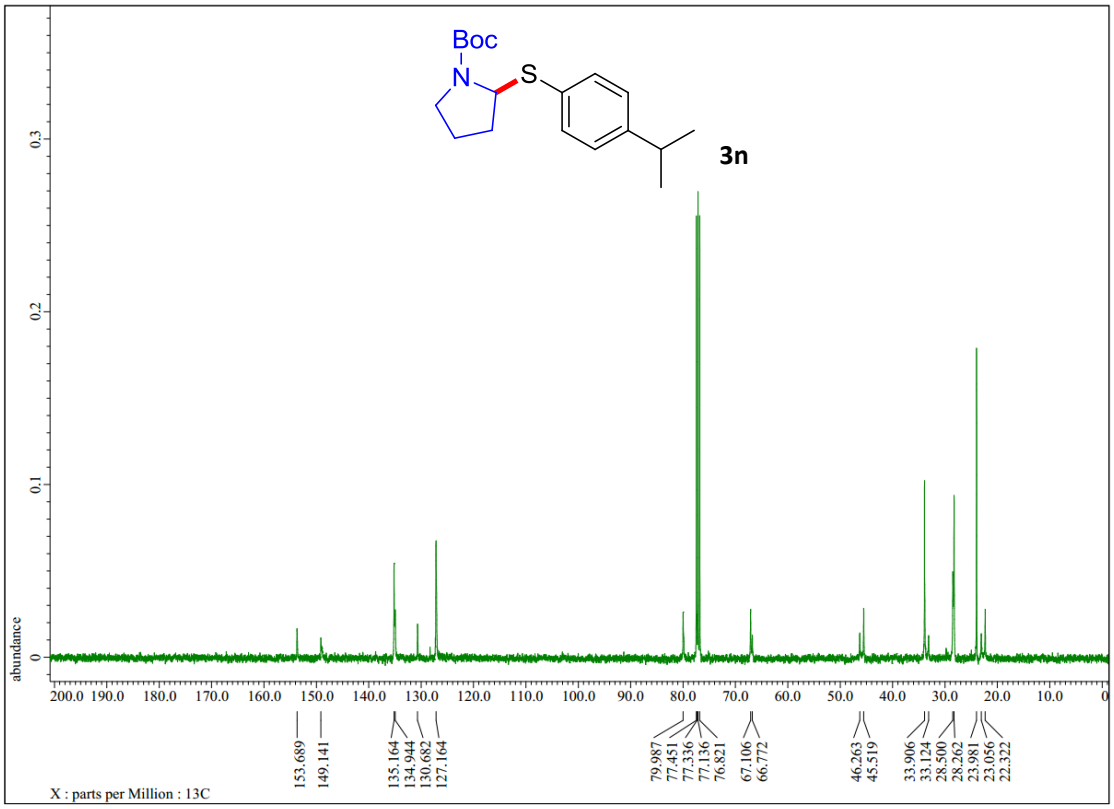

Boc
N
S
Me
3l
abundance
1.98
2.01
1.00
2.01
3.04
4.06
9.09
7.415
7.386
7.369
7.267
7.264
7.118
7.100
5.319
5.220
5.210
3.407
3.386
3.274
2.332
2.039
1.867
1.437
1.359
0.000
X : parts per Million : 1H

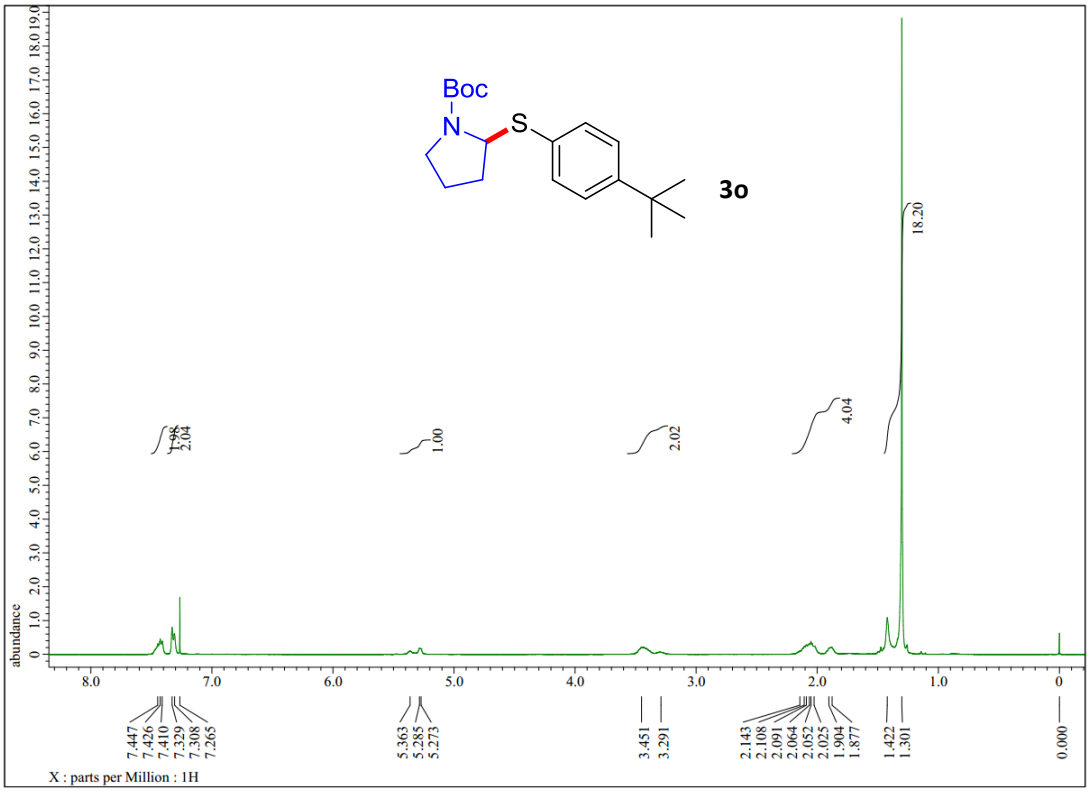

Boc
N
S
Me
3l
abundance
153.689
138.253
138.024
135.116
134.935
130.320
129.757
80.073
79.920
77.432
77.317
77.117
76.802
67.115
66.925
46.339
45.624
33.820
33.124
28.472
28.271
23.065
22.274
21.235
X : parts per Million : 13C

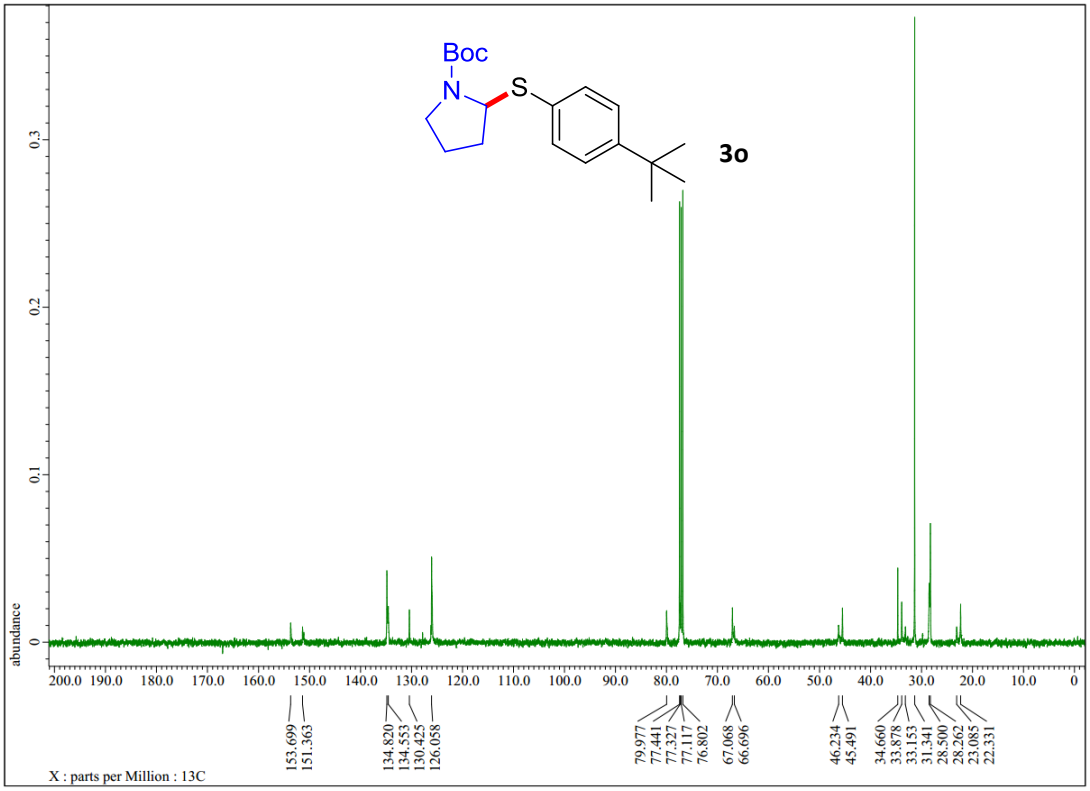

Boc
N
S
Me
3m
abundance
X : parts per Million : 1H

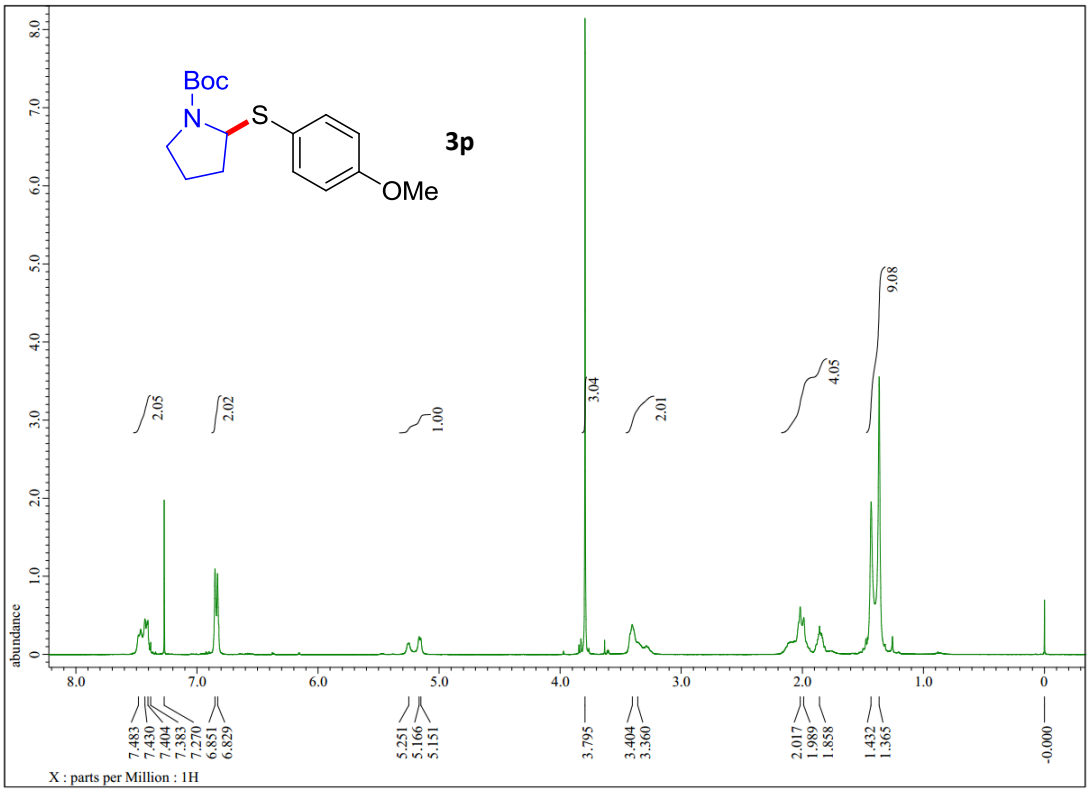

Boc
N
S
Me
3m
abundance
X : parts per Million : 13C

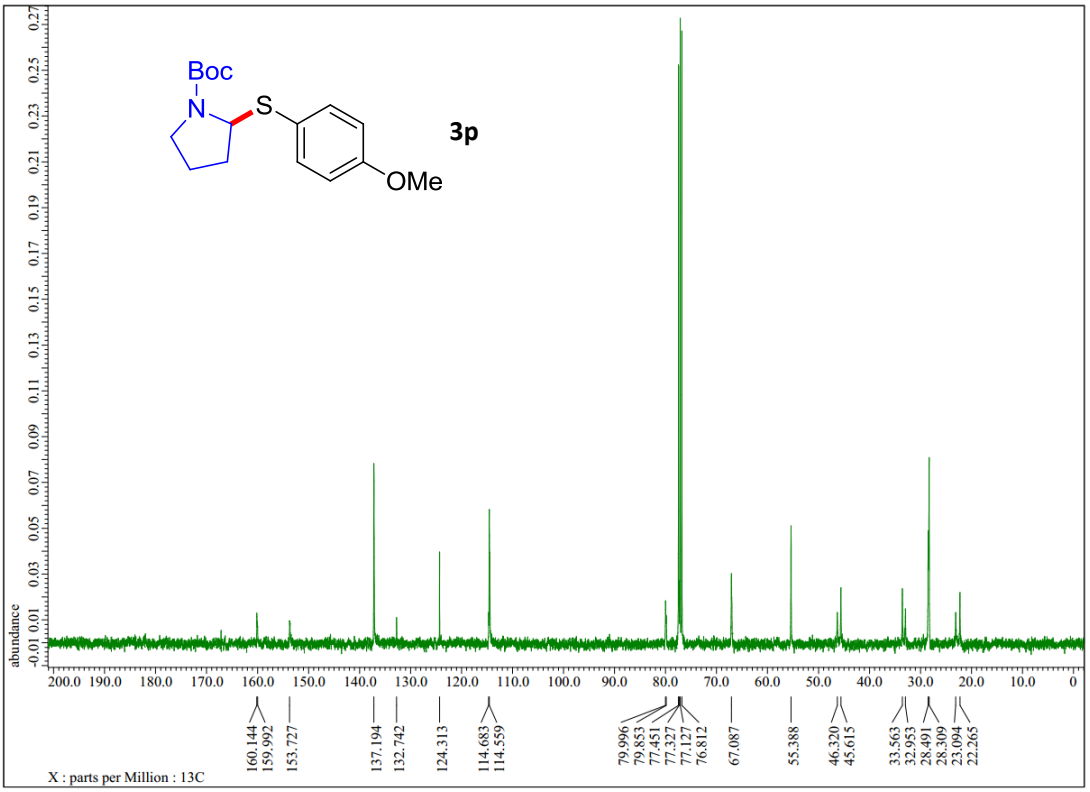

Boc
N
S
3n
abundance
X : parts per Million : 1H
2.00
2.00
1.00
2.03
1.04
4.17
6.13
9.19
7.422
7.404
7.267
7.170
7.151
5.348
5.272
5.259
3.446
2.903
2.886
2.869
2.852
2.139
2.099
2.045
1.879
1.475
1.425
1.317
1.257
1.239
1.222
0.000

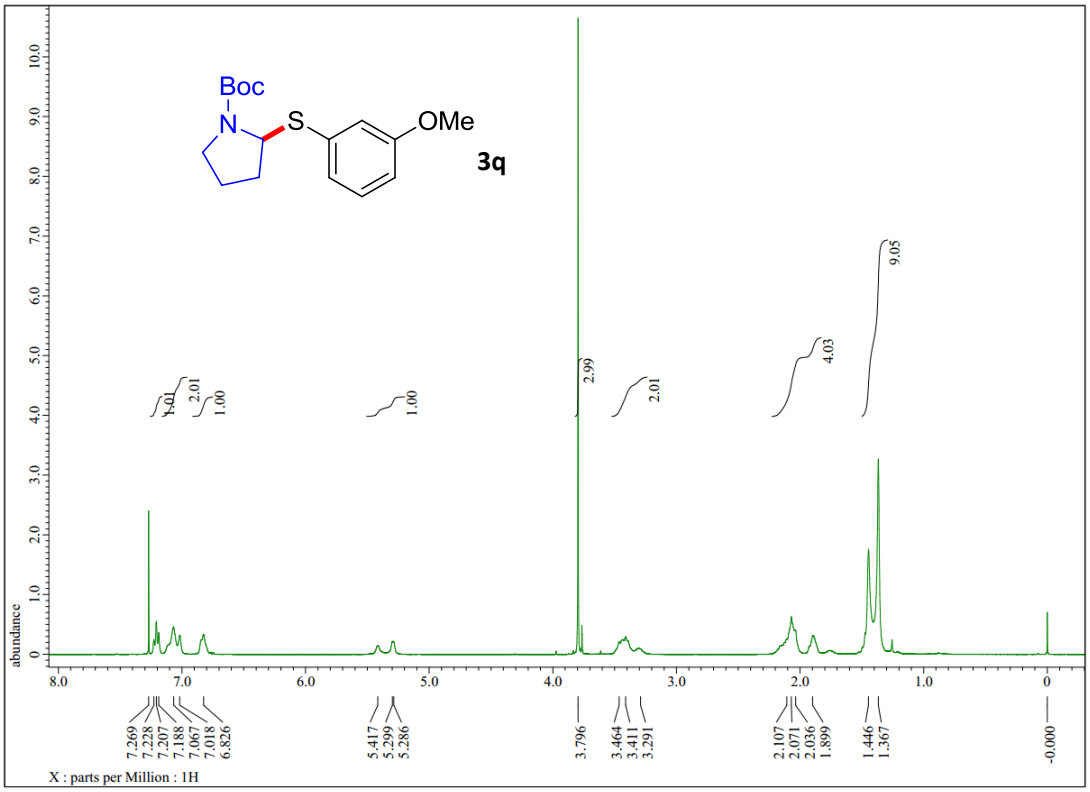

Boc
N
S
3n
abundance
X : parts per Million : 13C
153.689
149.141
135.164
134.944
130.682
127.164
79.987
77.451
77.336
77.136
76.821
67.106
66.772
46.263
45.519
33.906
33.124
28.500
28.262
23.981
23.056
22.322


Boc
N
S
3o
18.20
4.04
2.02
1.00
1.98
2.04
abundance
X : parts per Million : 1H


Boc
N
S
3o
abundance
X : parts per Million : 13C


Boc
N
S
OMe
3p
abundance
X : parts per Million : 1H


Boc
N
S
OMe
3p
abundance
X : parts per Million : 13C


Boc
N
S
OMe
3q
abundance
X : parts per Million : 1H
7.269
7.228
7.207
7.188
7.067
7.018
6.826
5.417
5.299
5.286
3.796
3.464
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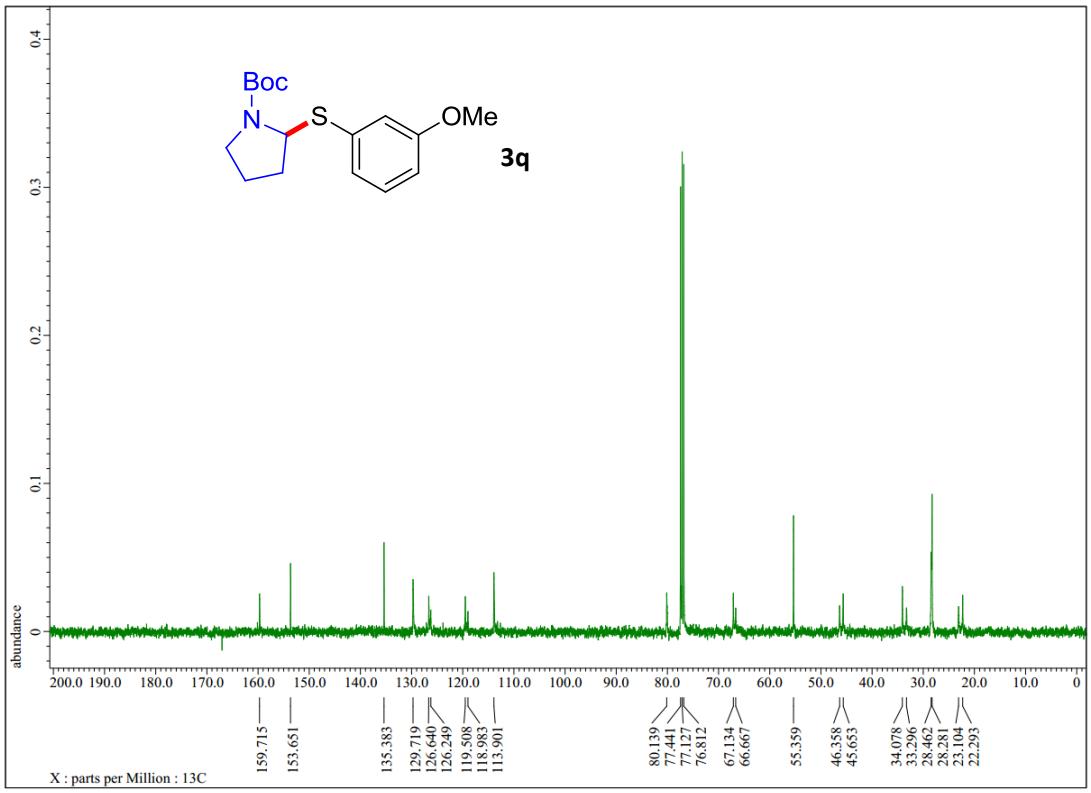
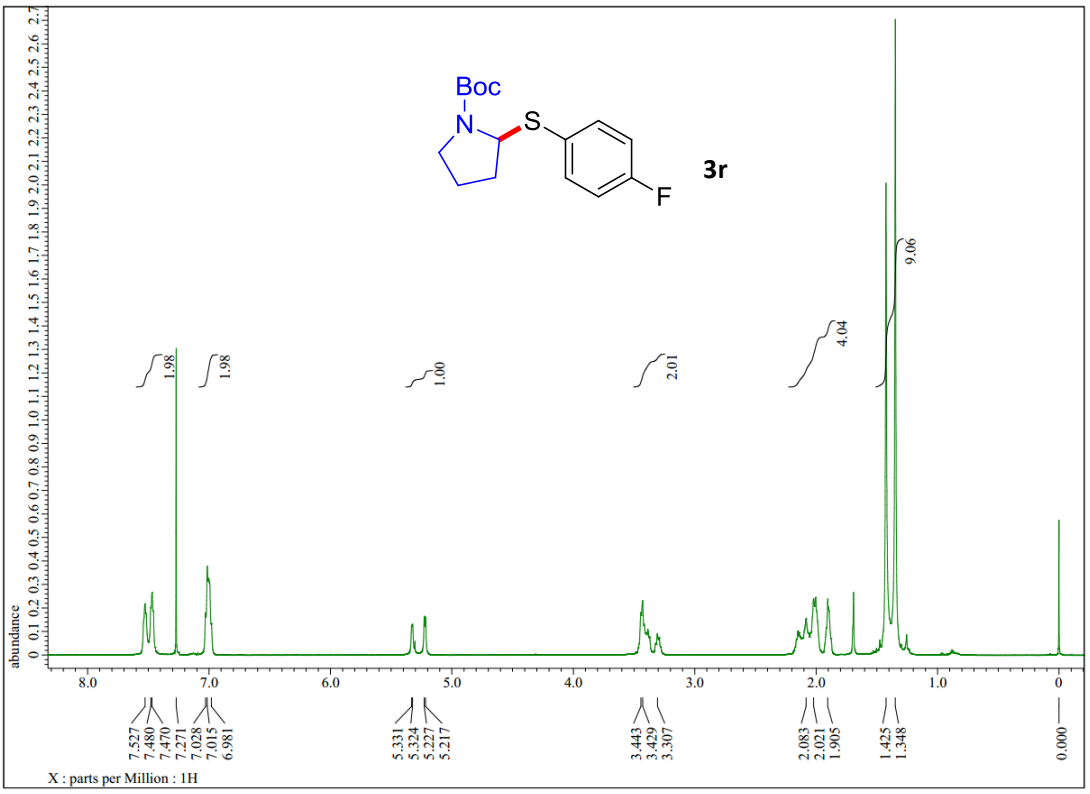
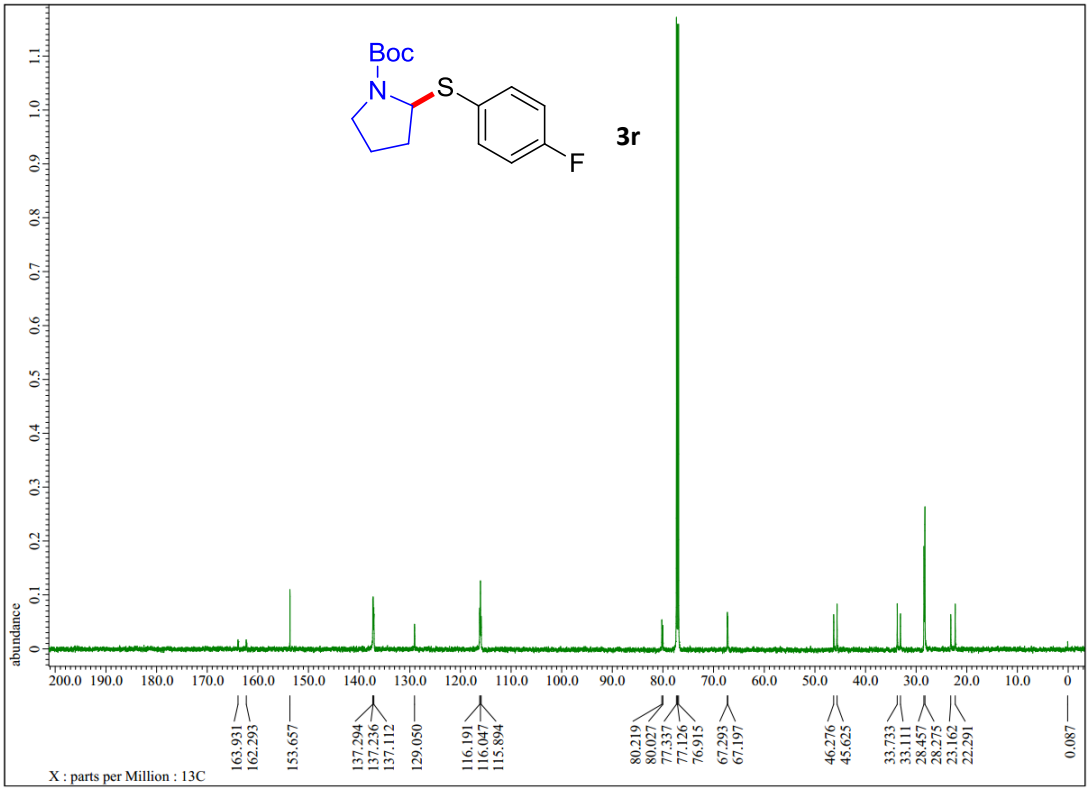
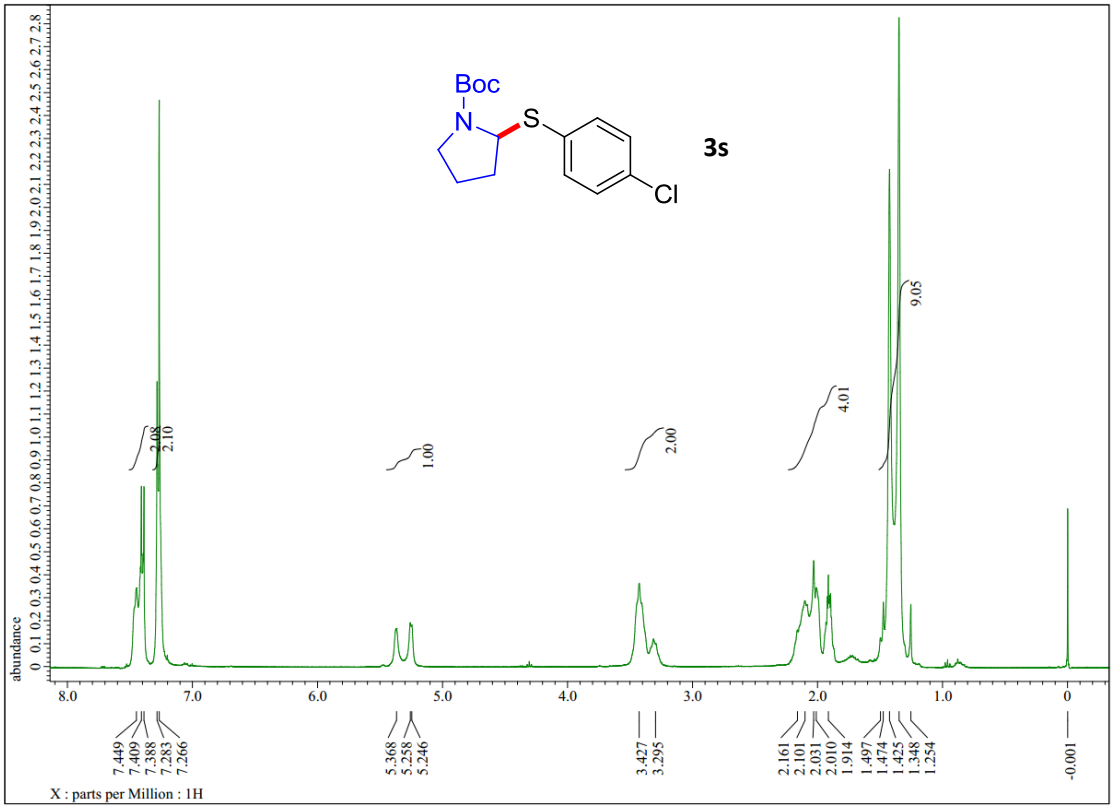
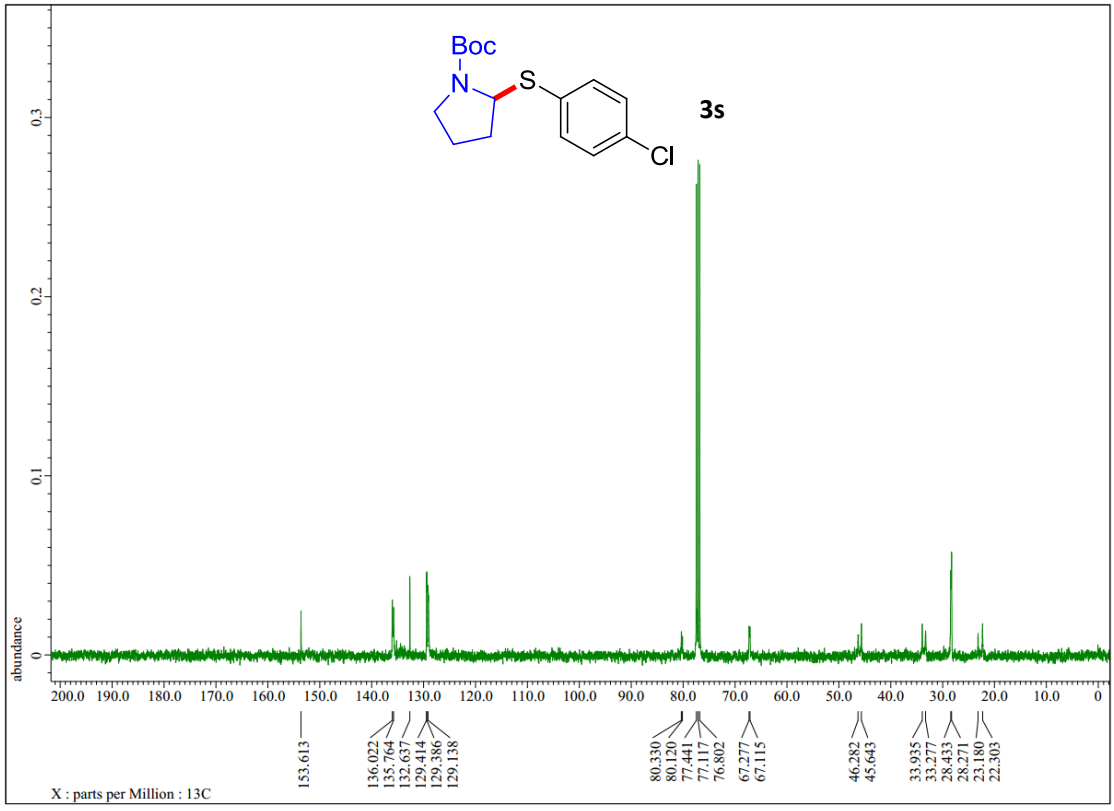
2.071
2.036
1.899
1.446
1.367
-0.000

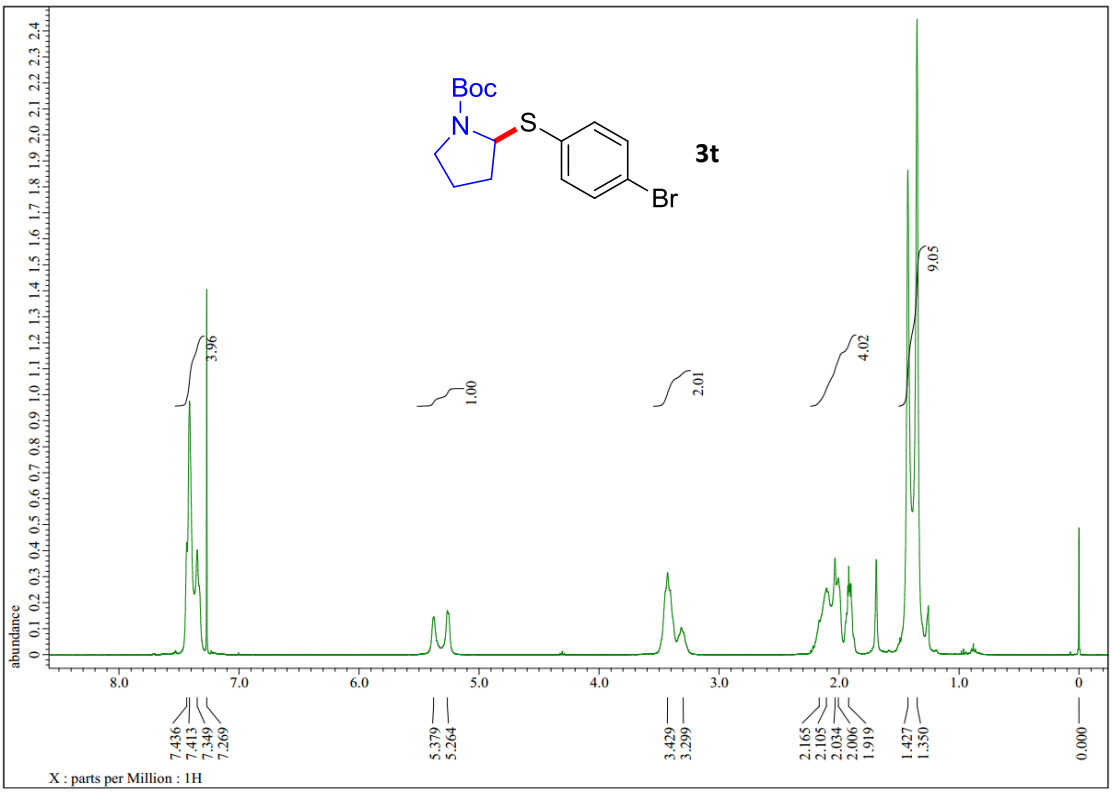

Boc
N
S
OMe
3q
abundance
X : parts per Million : 13C
159.715
153.651
135.383
129.719
126.640
126.249
119.508
118.983
113.901
80.139
77.441
77.127
76.812
67.134
66.667
55.359
46.358
45.653
34.078
33.296
28.462
28.281
23.104
22.293

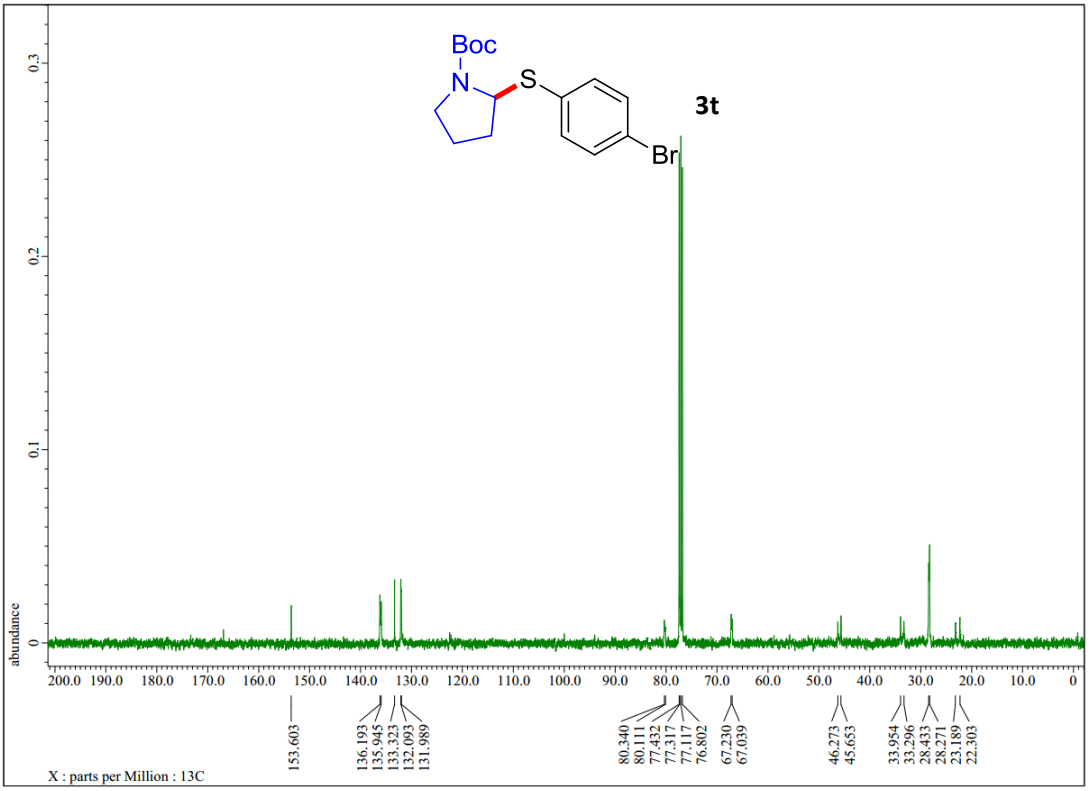

Boc
N
S
F
3r
abundance
1.98
1.98
1.00
2.01
4.04
9.06
7.527
7.480
7.470
7.271
7.028
7.015
6.981
5.331
5.324
5.227
5.217
3.443
3.429
3.307
2.083
2.021
1.905
1.425
1.348
0.000
X : parts per Million : 1H

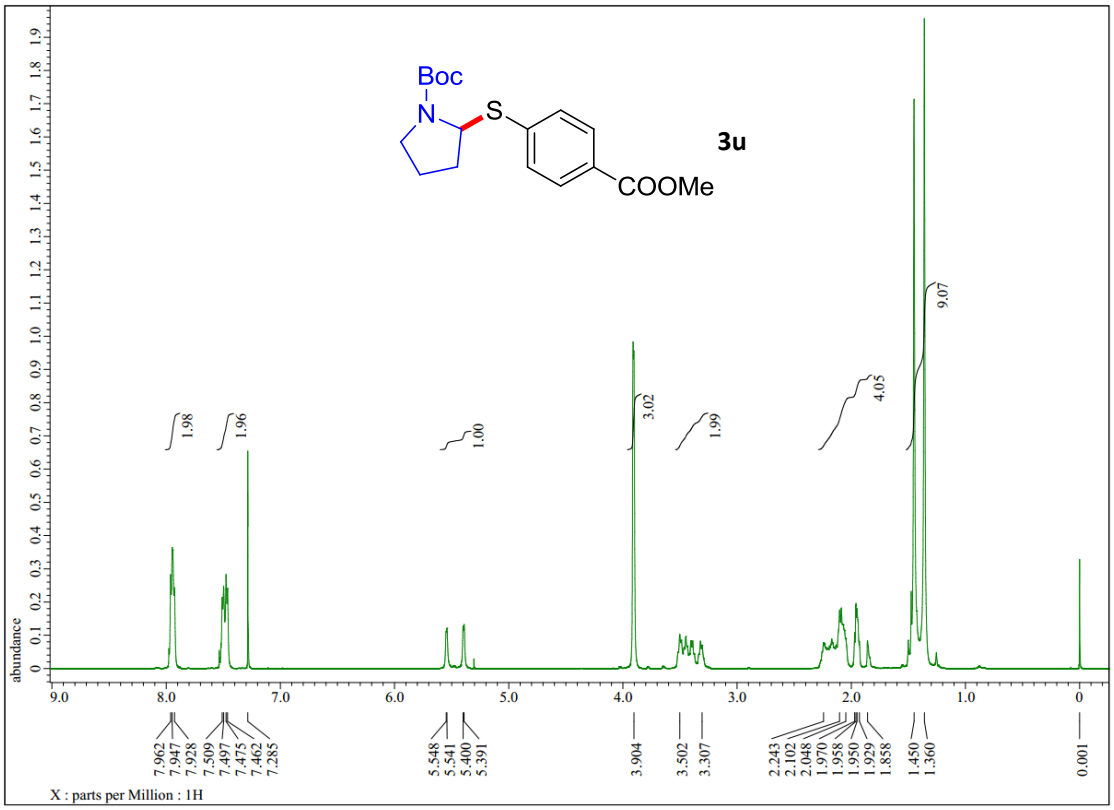

Boc
N
S
F
3r
abundance
163.931
162.293
153.657
137.294
137.236
137.112
129.050
116.191
116.047
115.894
80.219
80.027
77.337
77.126
76.915
67.293
67.197
46.276
45.625
33.733
33.111
28.457
28.275
23.162
22.291
0.087
X : parts per Million : 13C

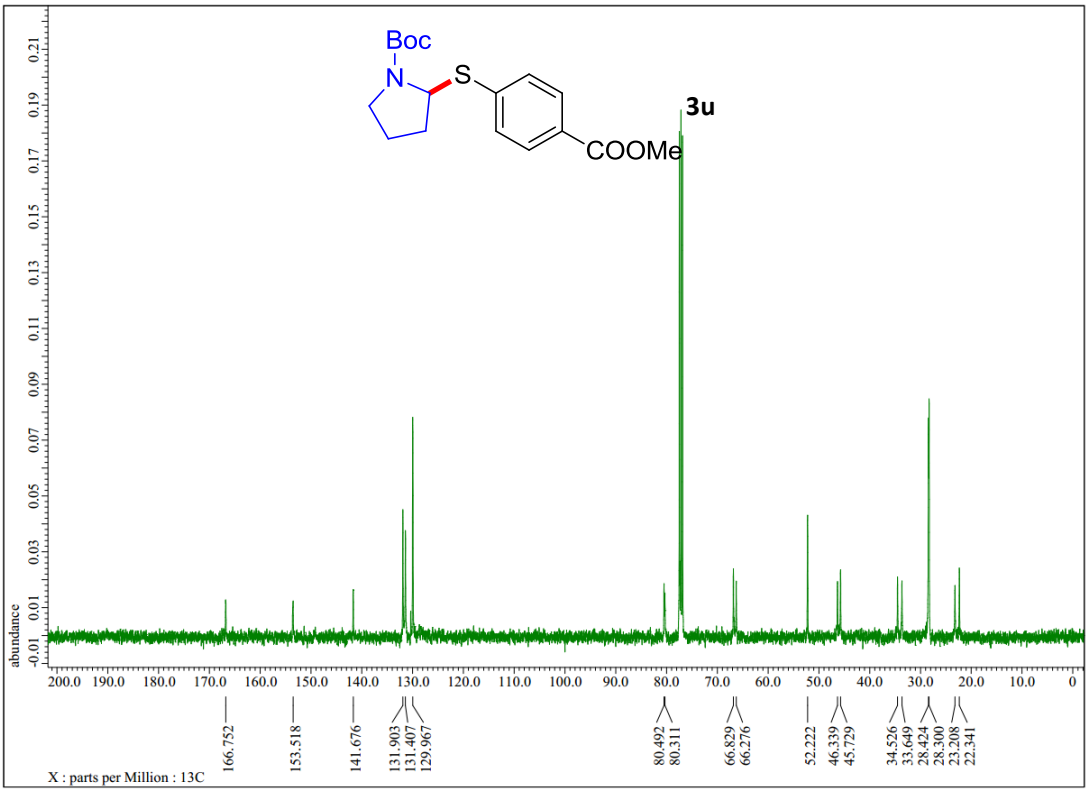

Boc
N
S
Cl
3s
abundance
X : parts per Million : 1H
7.449
7.409
7.388
7.283
7.266
5.368
5.258
5.246
3.427
3.295
2.161
2.101
2.031
2.010
1.914
1.497
1.474
1.425
1.348
1.254
-0.001
2.08
2.10
1.00
2.00
4.01
9.05

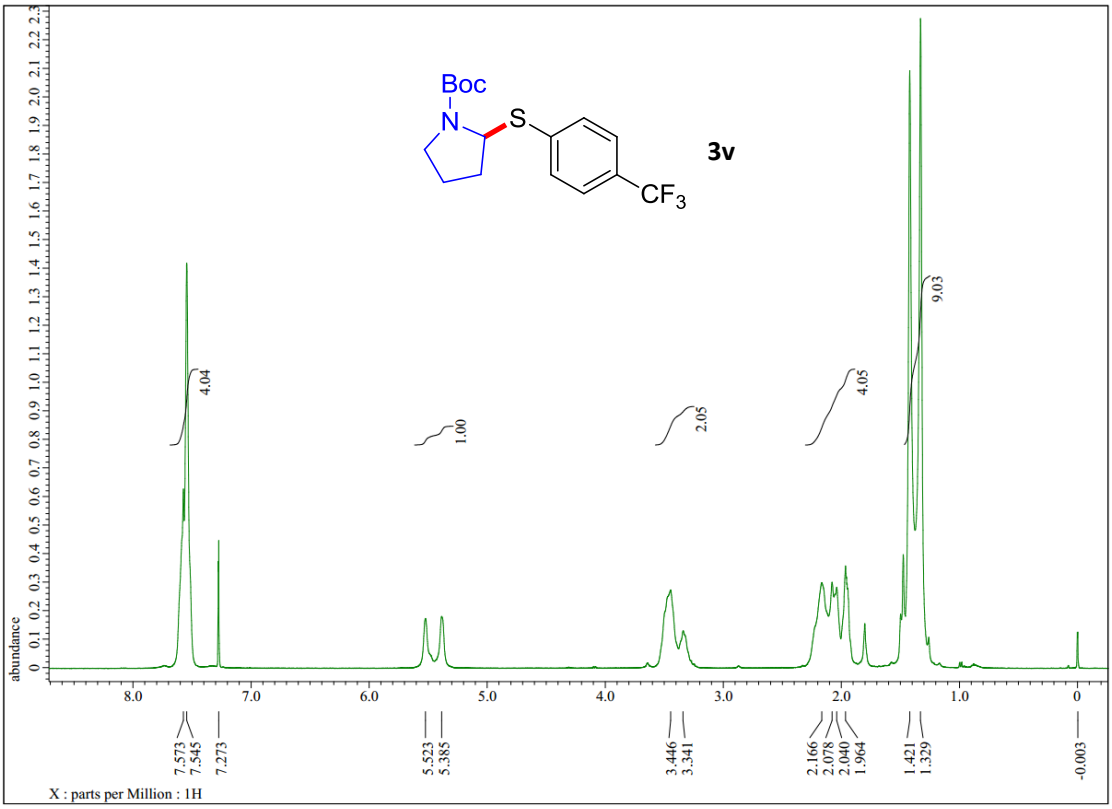

Boc
N
S
Cl
3s
abundance
X : parts per Million : 13C
153.613
136.022
135.764
132.637
129.414
129.386
129.138
80.330
80.120
77.441
77.117
76.802
67.277
67.115
46.282
45.643
33.935
33.277
28.433
28.271
23.180
22.303

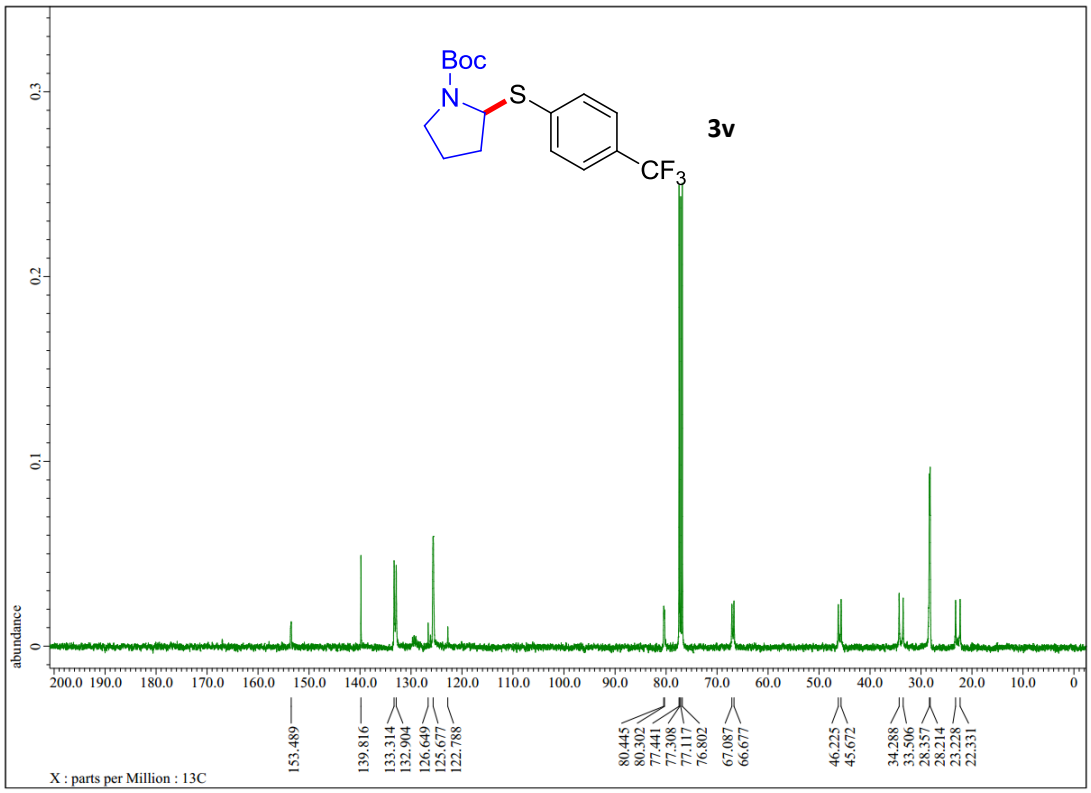

Boc
N
S
Br
3t
abundance
3.96
1.00
2.01
4.02
9.05
7.436
7.413
7.349
7.269
5.379
5.264
3.429
3.299
2.165
2.105
2.034
2.006
1.919
1.427
1.350
0.000
X : parts per Million : 1H

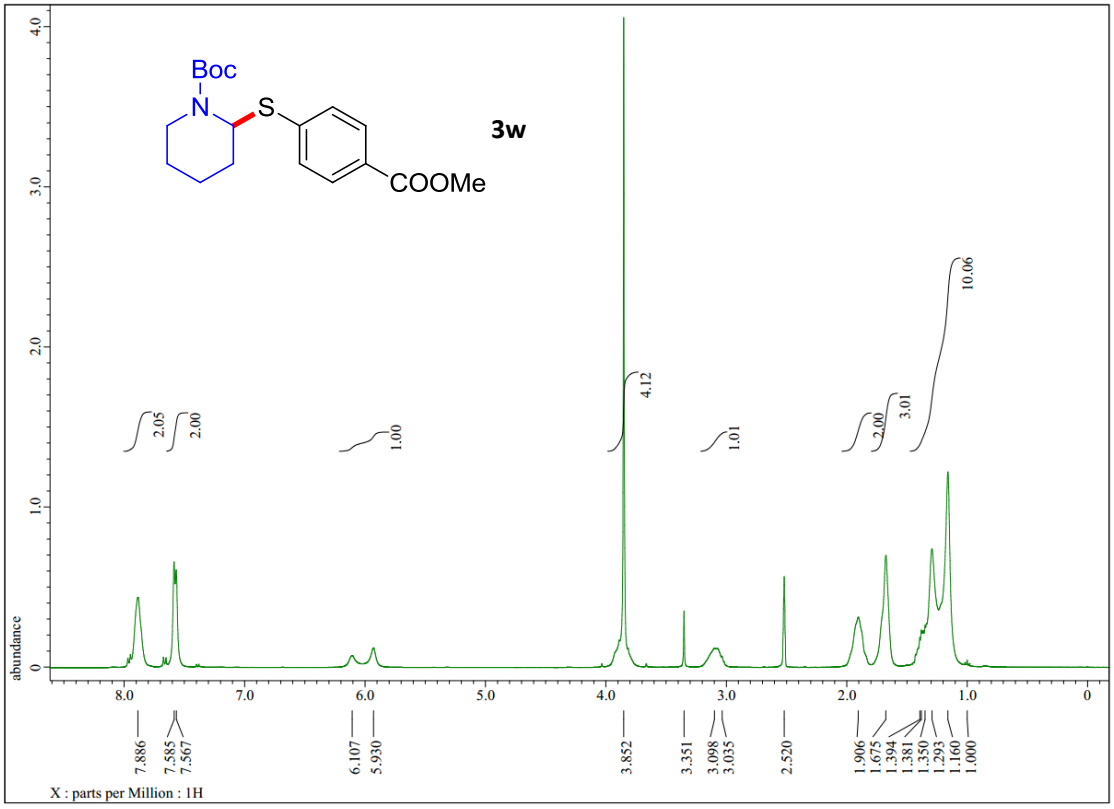

Boc
N
S
Br
3t
abundance
153.603
136.193
135.945
133.323
132.093
131.989
80.340
80.111
77.432
77.317
77.117
76.802
67.230
67.039
46.273
45.653
33.954
33.296
28.433
28.271
23.189
22.303
X : parts per Million : 13C

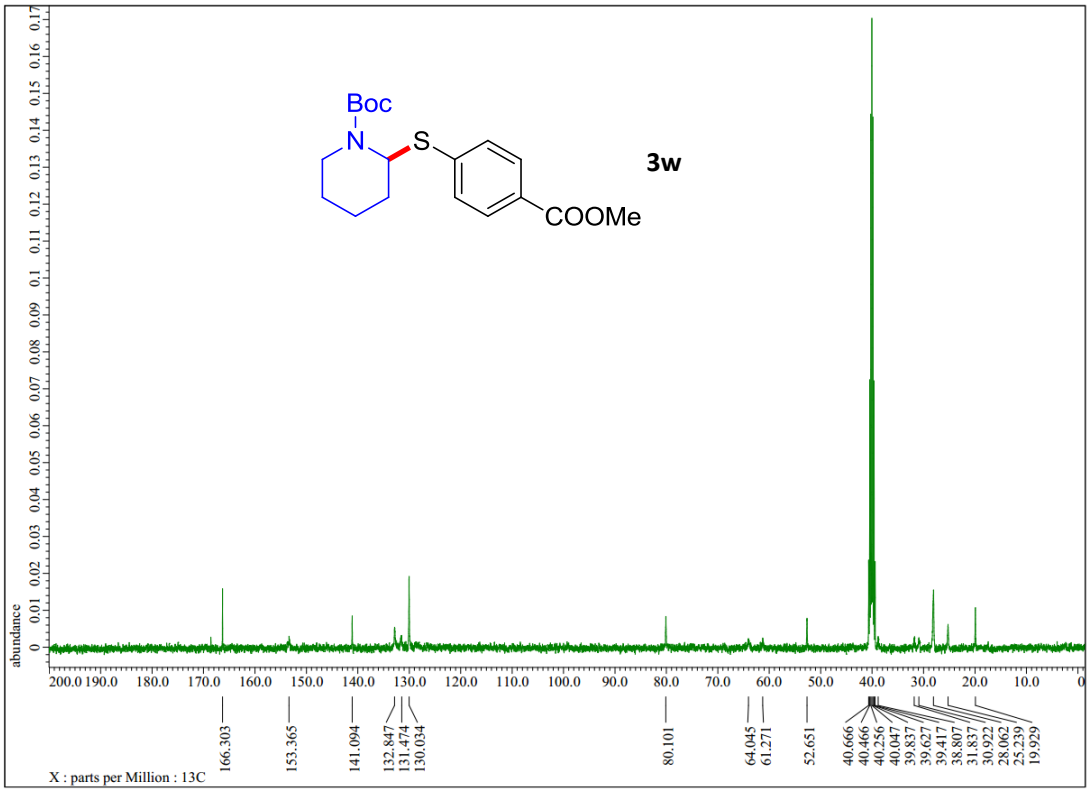

Boc
N
S
COOMe
3u
abundance
X : parts per Million : 1H

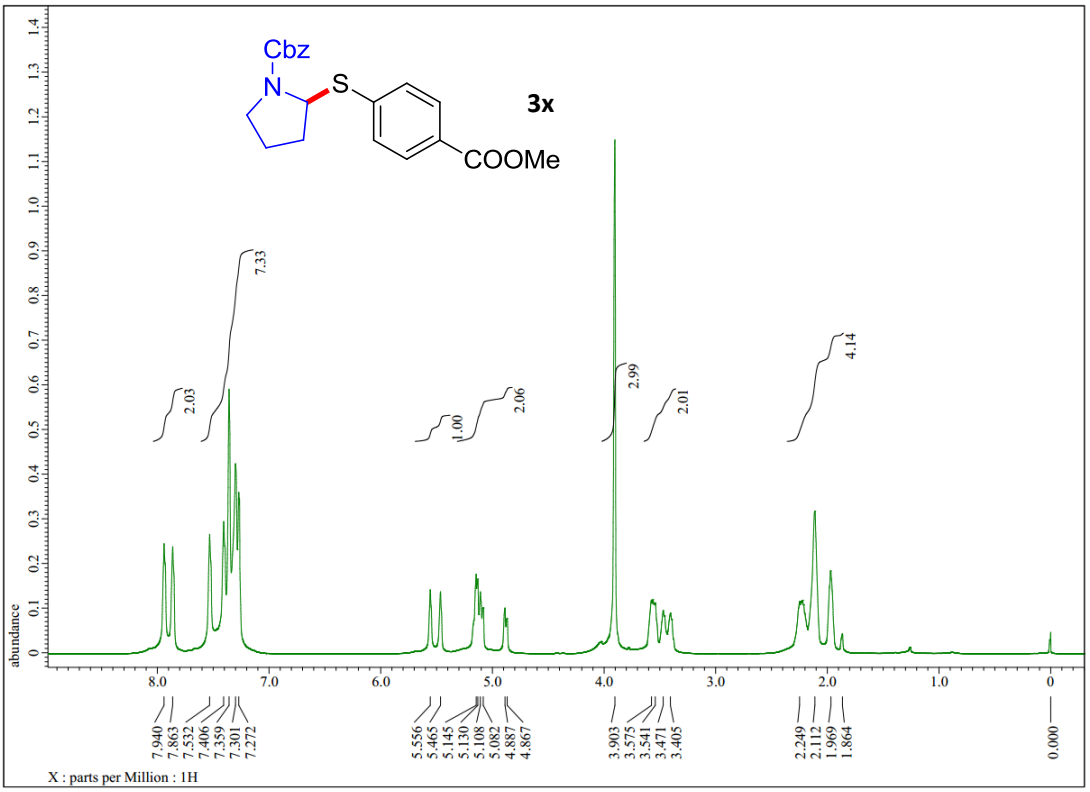

Boc
N
S
COOMe
3u
abundance
X : parts per Million : 13C

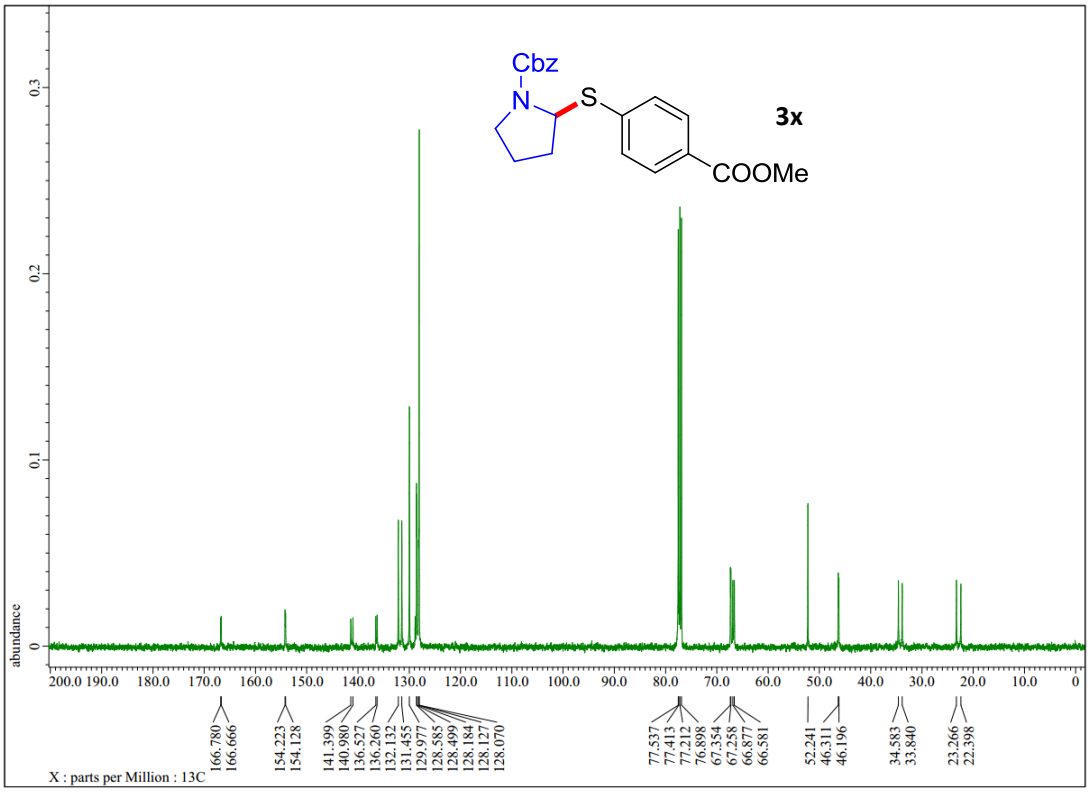

Boc
N
S
CF3
3v
4.04
1.00
2.05
4.05
9.03
abundance
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.573
7.545
7.273
5.523
5.385
3.446
3.341
2.166
2.078
2.040
1.964
1.421
1.329
-0.003
X : parts per Million : 1H

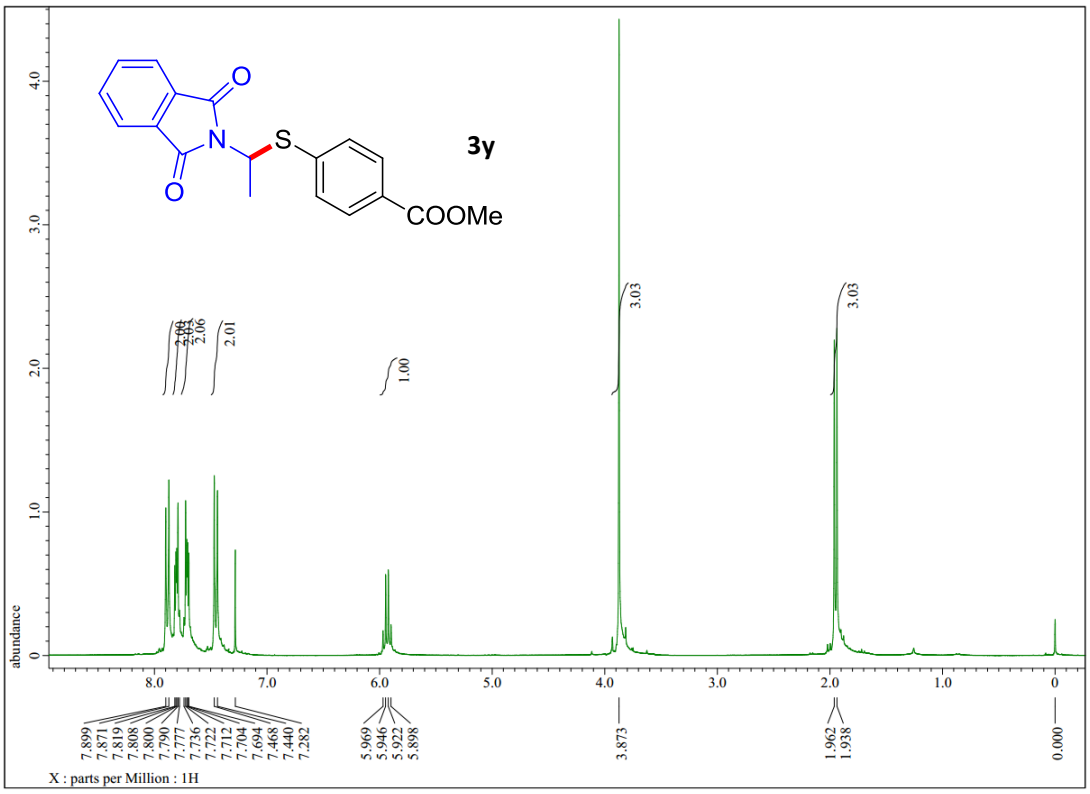

Boc
N
S
CF3
3v
abundance
0.3
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
153.489
139.816
133.314
132.904
126.649
125.677
122.788
80.445
80.302
77.441
77.308
77.117
76.802
67.087
66.677
46.225
45.672
34.288
33.506
28.357
28.214
23.228
22.331
X : parts per Million : 13C

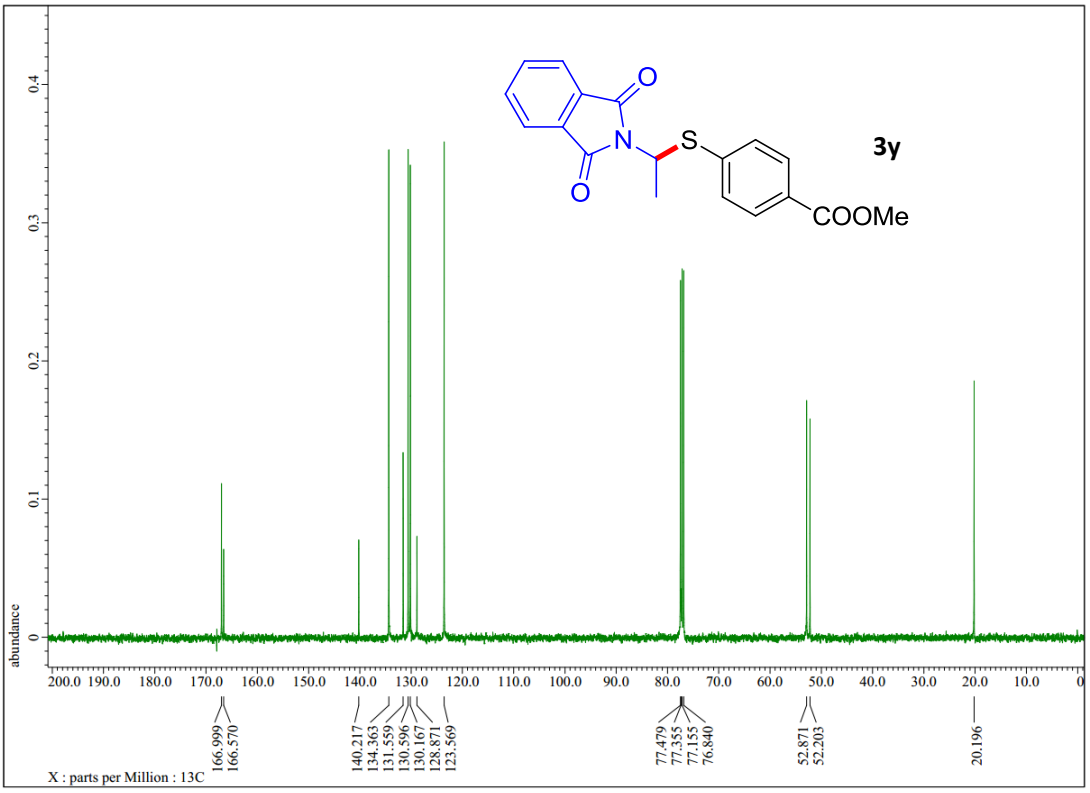

Boc
N
S
COOMe
3w
abundance
X : parts per Million : 1H

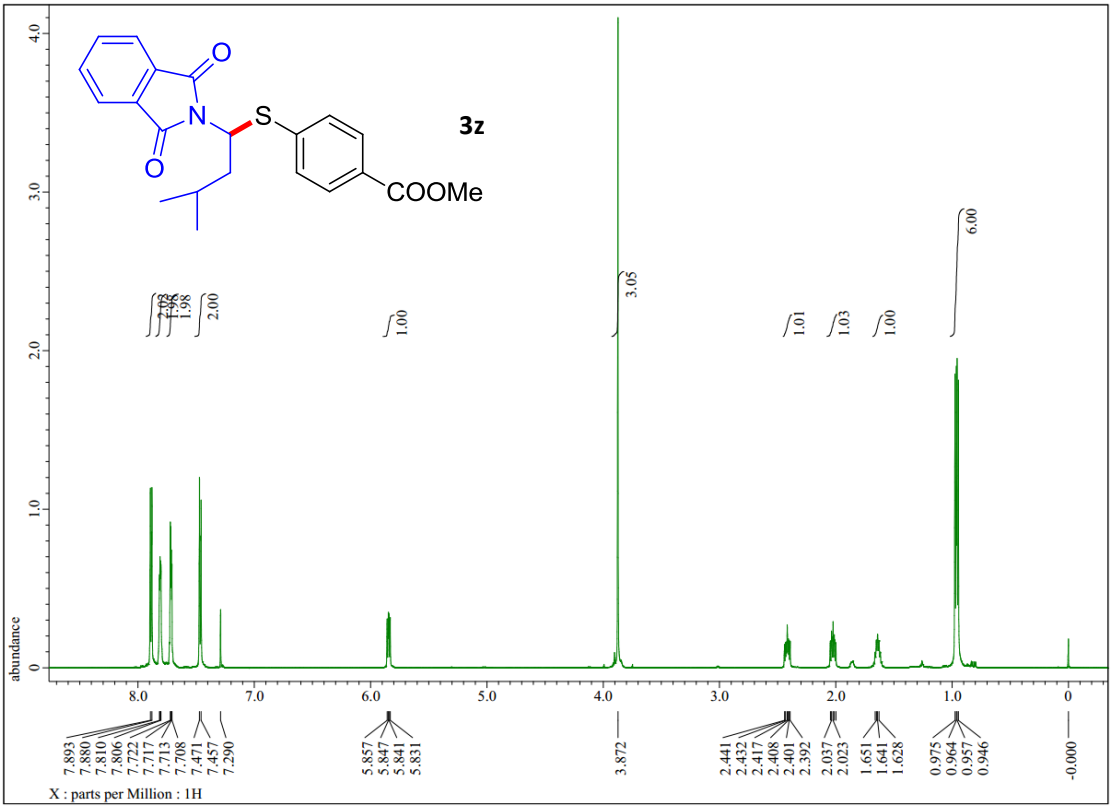

Boc
N
S
COOMe
3w
abundance
X : parts per Million : 13C

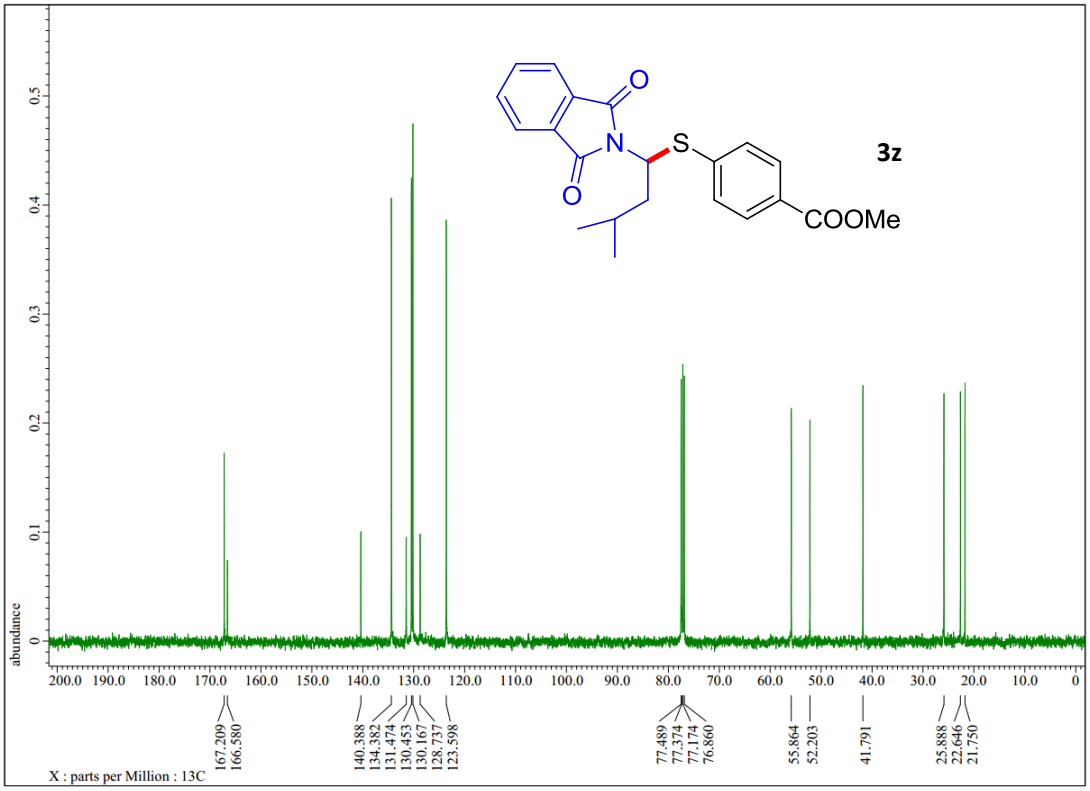

Cbz
N
S
COOMe
3x
7.33
2.03
1.00
2.06
2.99
2.01
4.14
abundance
X : parts per Million : 1H

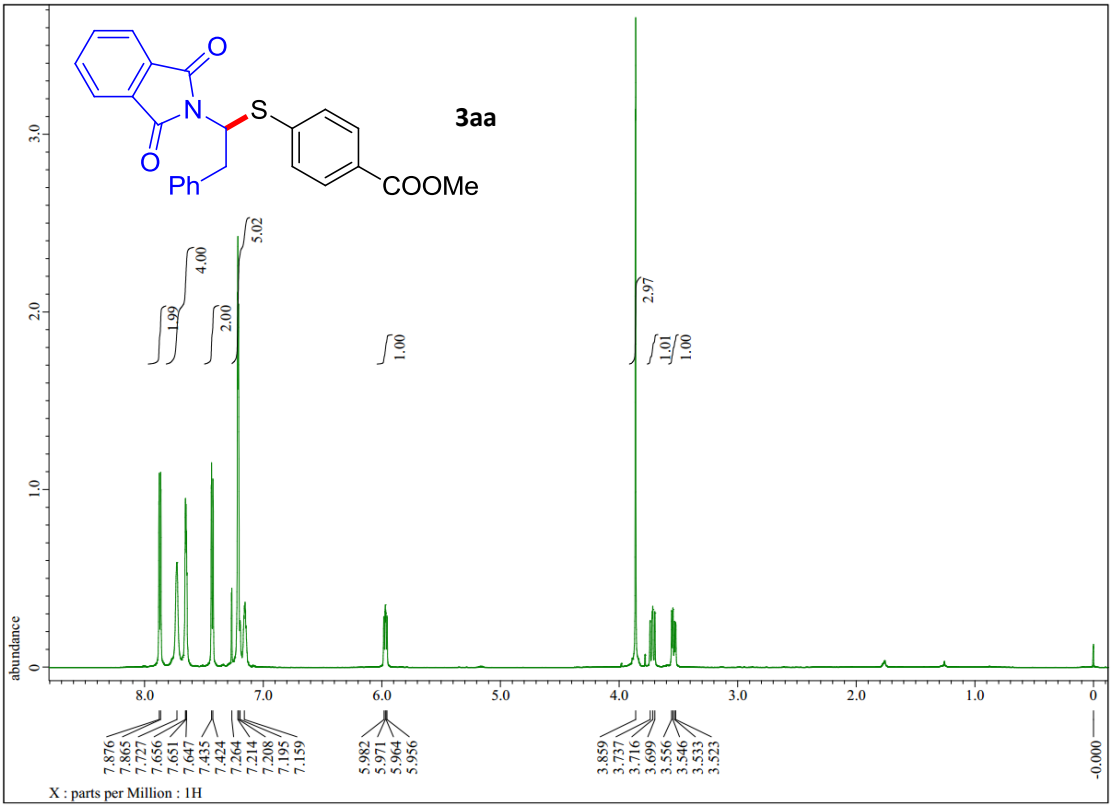

Cbz
N
S
COOMe
3x
abundance
X : parts per Million : 13C

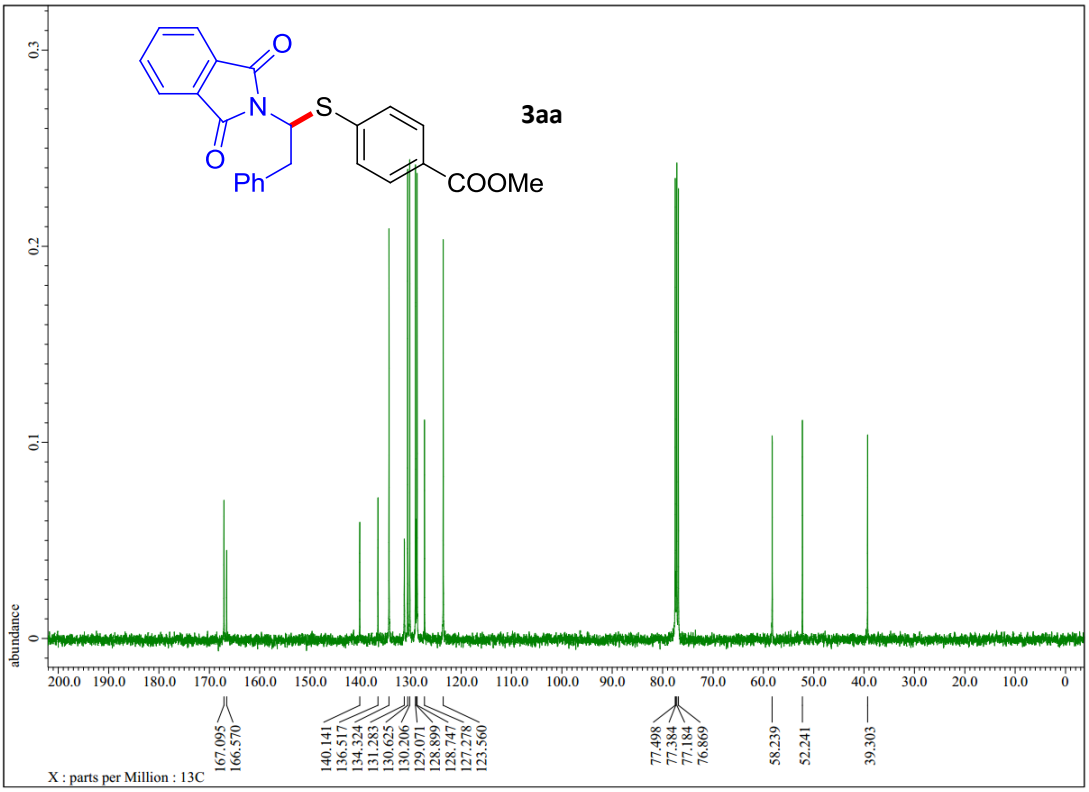

3y
COOMe
abundance
X : parts per Million : 1H

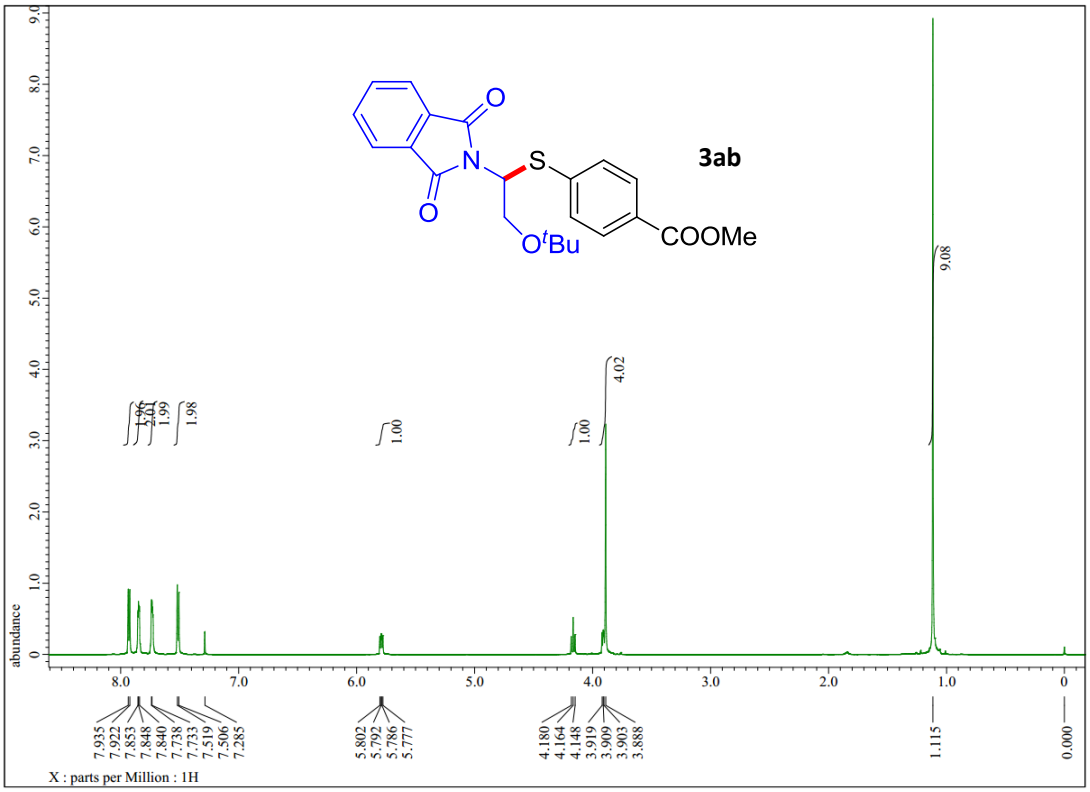

3y
COOMe
abundance
X : parts per Million : 13C

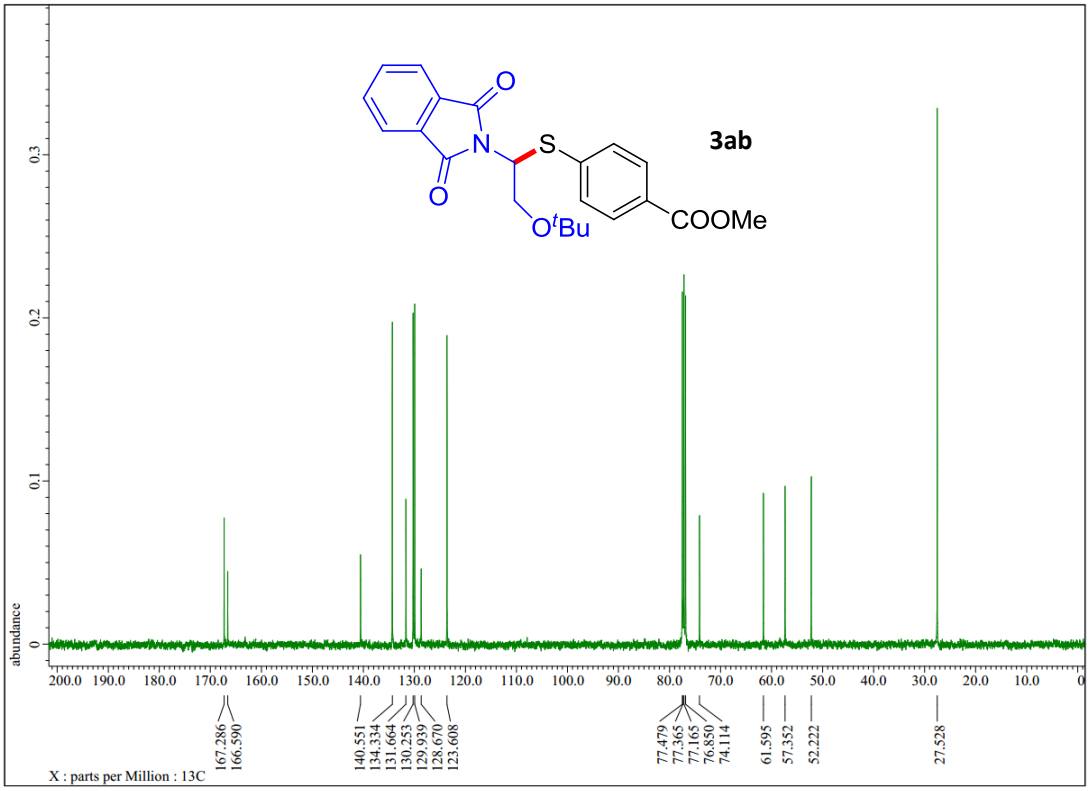

3z
COOMe
abundance
X : parts per Million : 1H

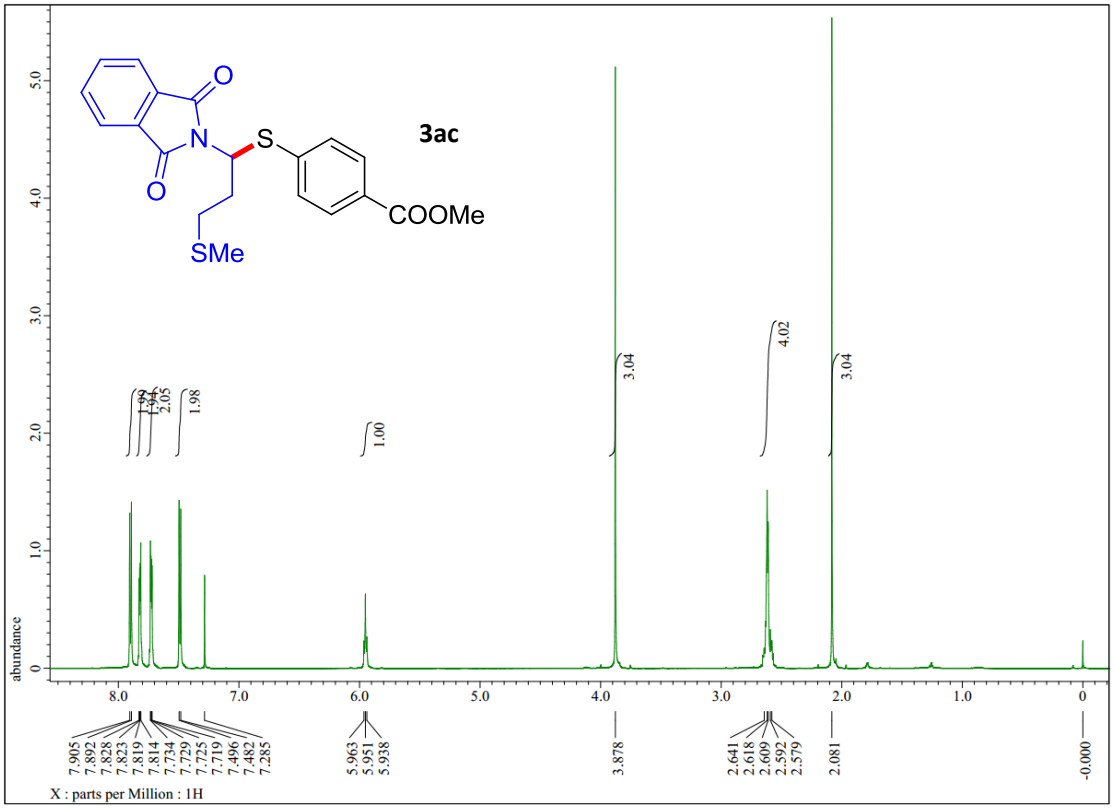

3z
COOMe
abundance
X : parts per Million : 13C

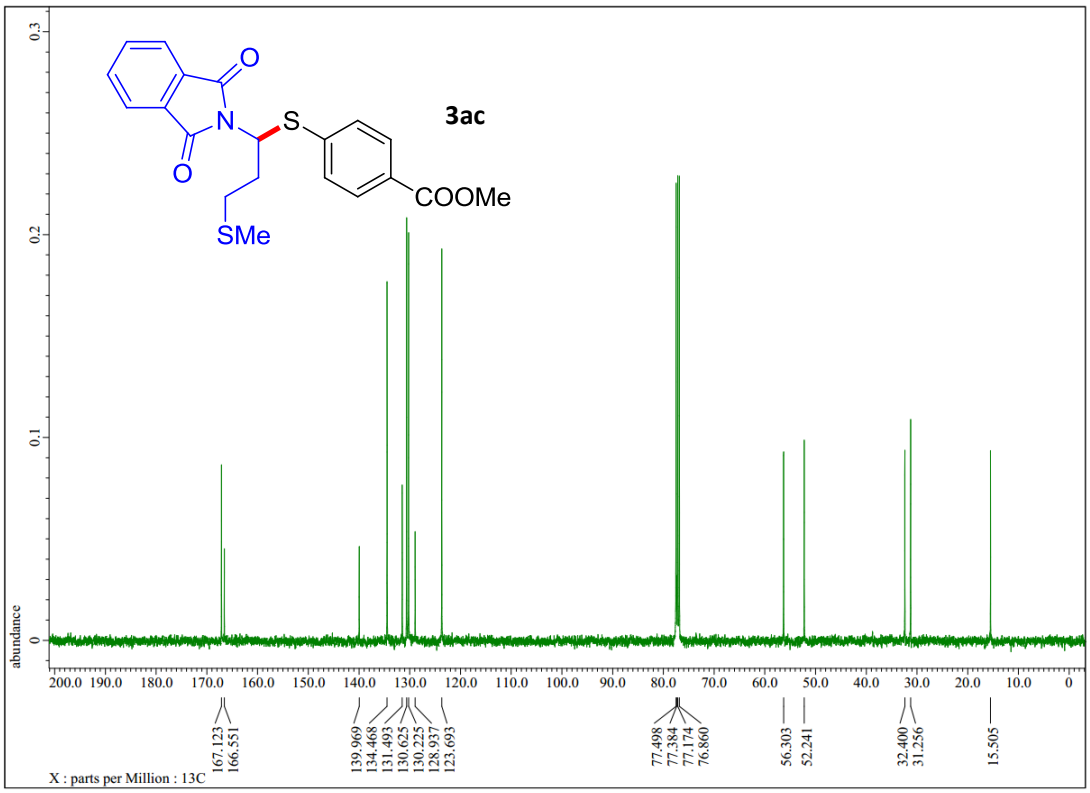

3aa
O
N
S
O
Ph
COOMe
abundance
X : parts per Million : 1H
7.876
7.865
7.727
7.656
7.651
7.647
7.435
7.424
7.264
7.214
7.208
7.195
7.159
5.982
5.971
5.964
5.956
3.859
3.737
3.716
3.699
3.556
3.546
3.533
3.523
-0.000

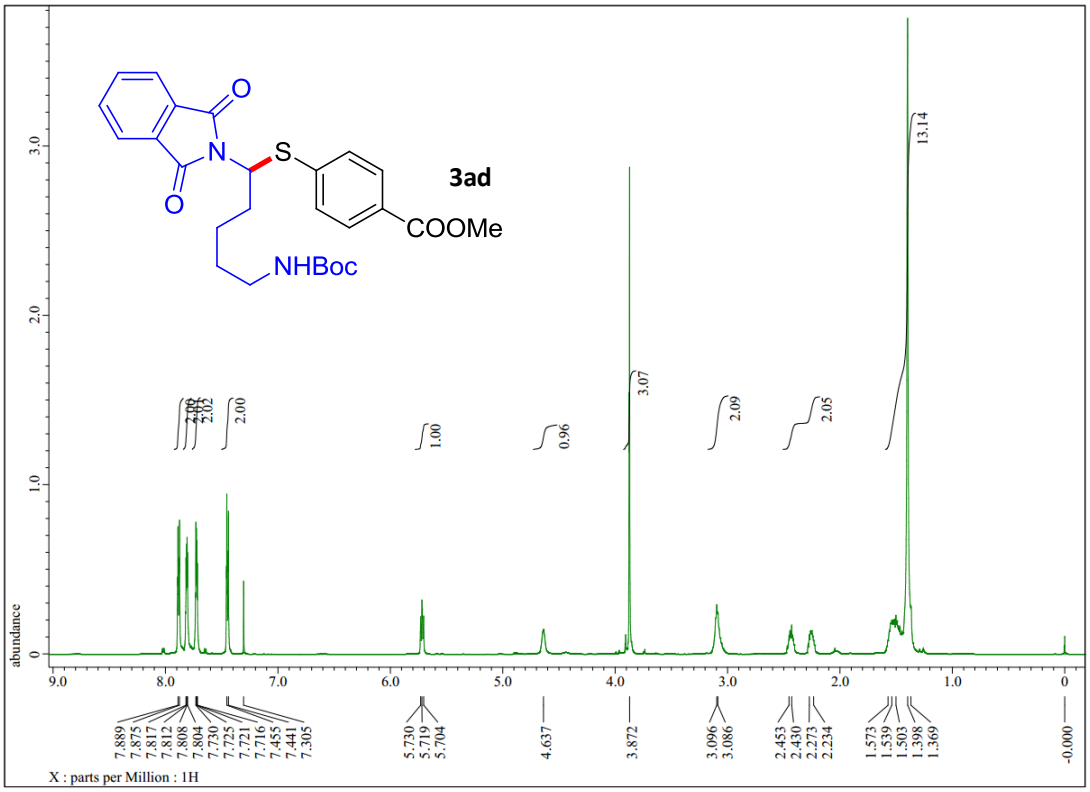

3aa
O
N
S
O
Ph
COOMe
abundance
X : parts per Million : 13C
167.095
166.570
140.141
136.517
134.324
131.283
130.625
130.206
129.071
128.899
128.747
127.278
123.560
77.498
77.384
77.184
76.869
58.239
52.241
39.303

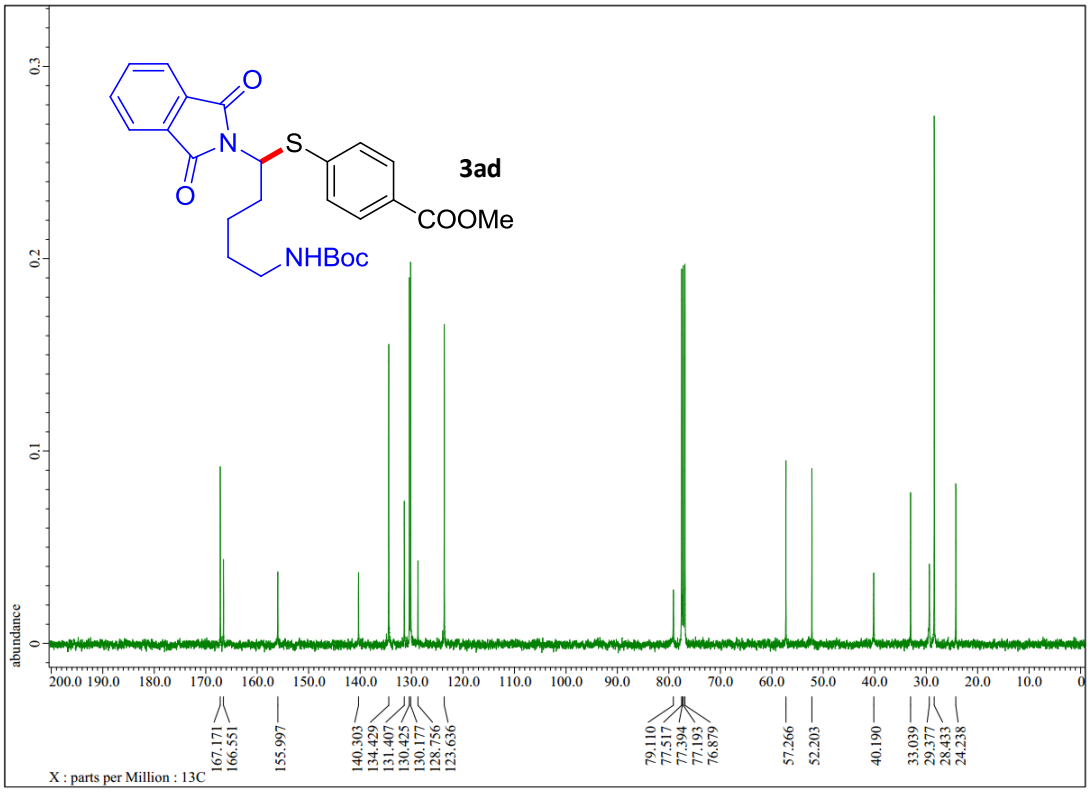

3ab
COOMe
O
N
S
O
O
O^{t}Bu
abundance
9.08
4.02
1.98
1.99
1.00
1.00
7.935
7.922
7.853
7.848
7.840
7.738
7.733
7.519
7.506
7.285
5.802
5.792
5.786
5.777
4.180
4.164
4.148
3.919
3.909
3.903
3.888
1.115
0.000
X : parts per Million : 1H

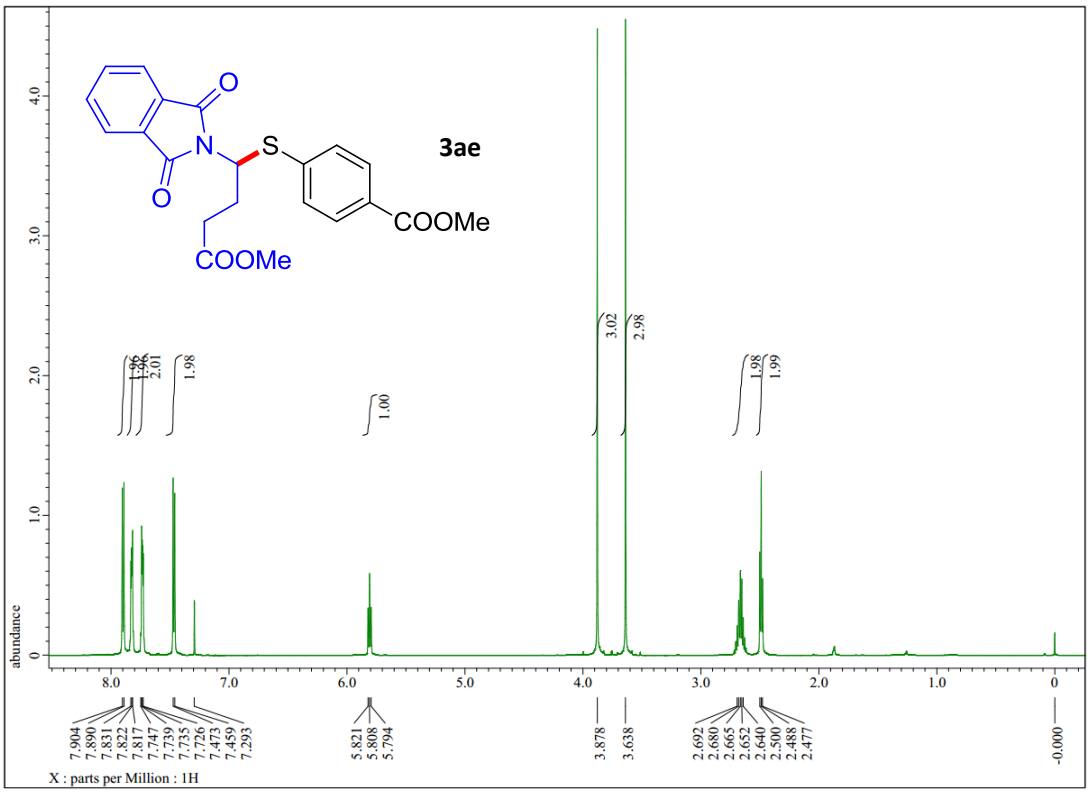

3ab
COOMe
O
N
S
O
O
O^{t}Bu
abundance
167.286
166.590
140.551
134.334
131.664
130.253
129.939
128.670
123.608
77.479
77.365
77.165
76.850
74.114
61.595
57.352
52.222
27.528
X : parts per Million : 13C

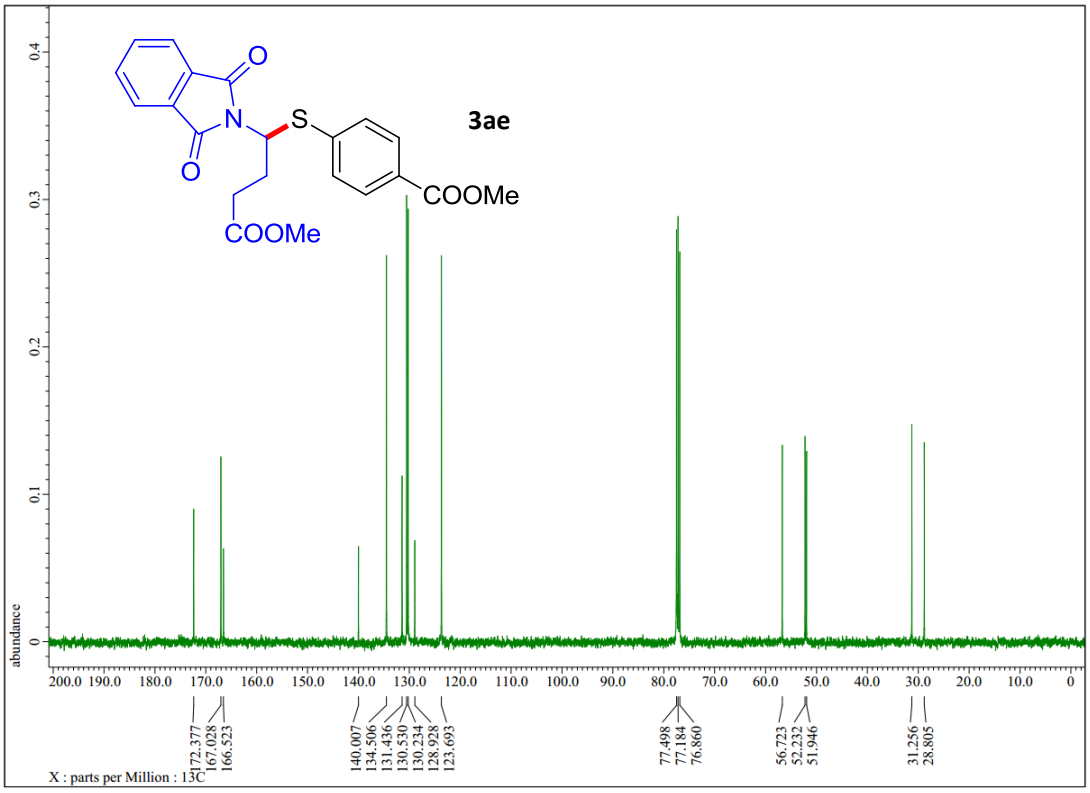

3ac
O
N
O
S
COOMe
SMe
abundance
X : parts per Million : 1H
7.905
7.892
7.828
7.823
7.819
7.814
7.734
7.729
7.725
7.719
7.496
7.482
7.285
5.963
5.951
5.938
3.878
2.641
2.618
2.609
2.592
2.579
2.081
-0.000

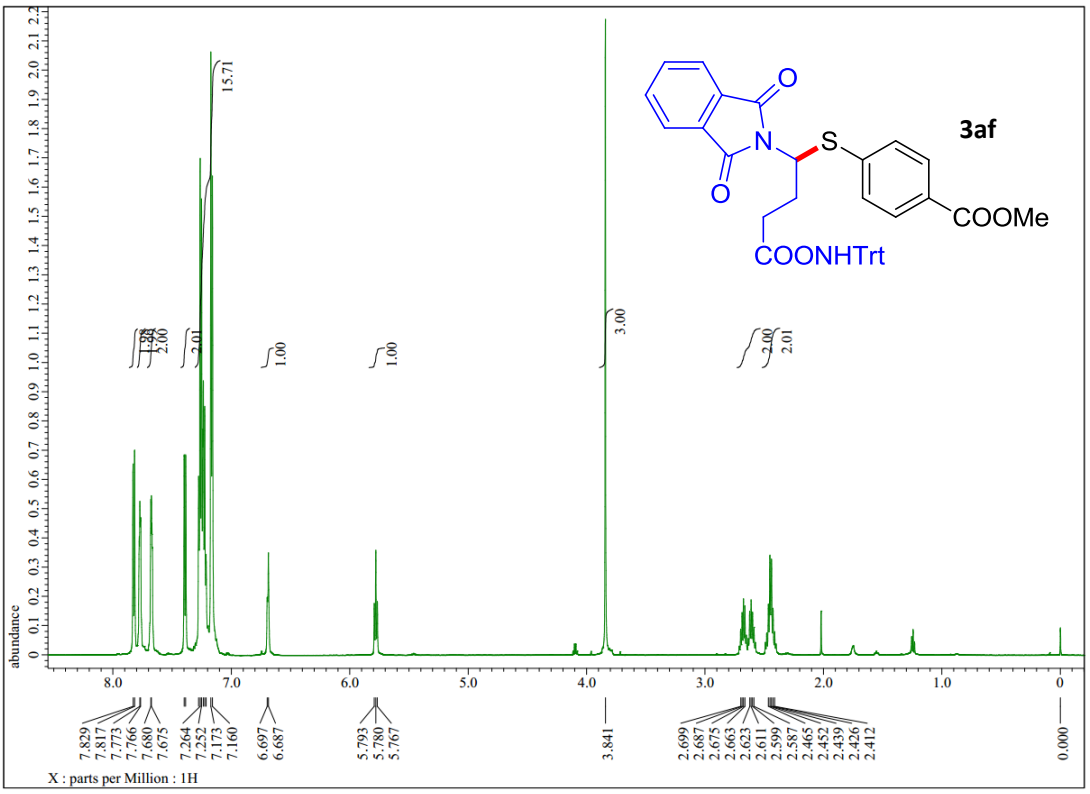

3ac
O
N
O
S
COOMe
SMe
abundance
X : parts per Million : 13C
167.123
166.551
139.969
134.468
131.493
130.625
130.225
128.937
123.693
77.498
77.384
77.174
76.860
56.303
52.241
32.400
31.256
15.505

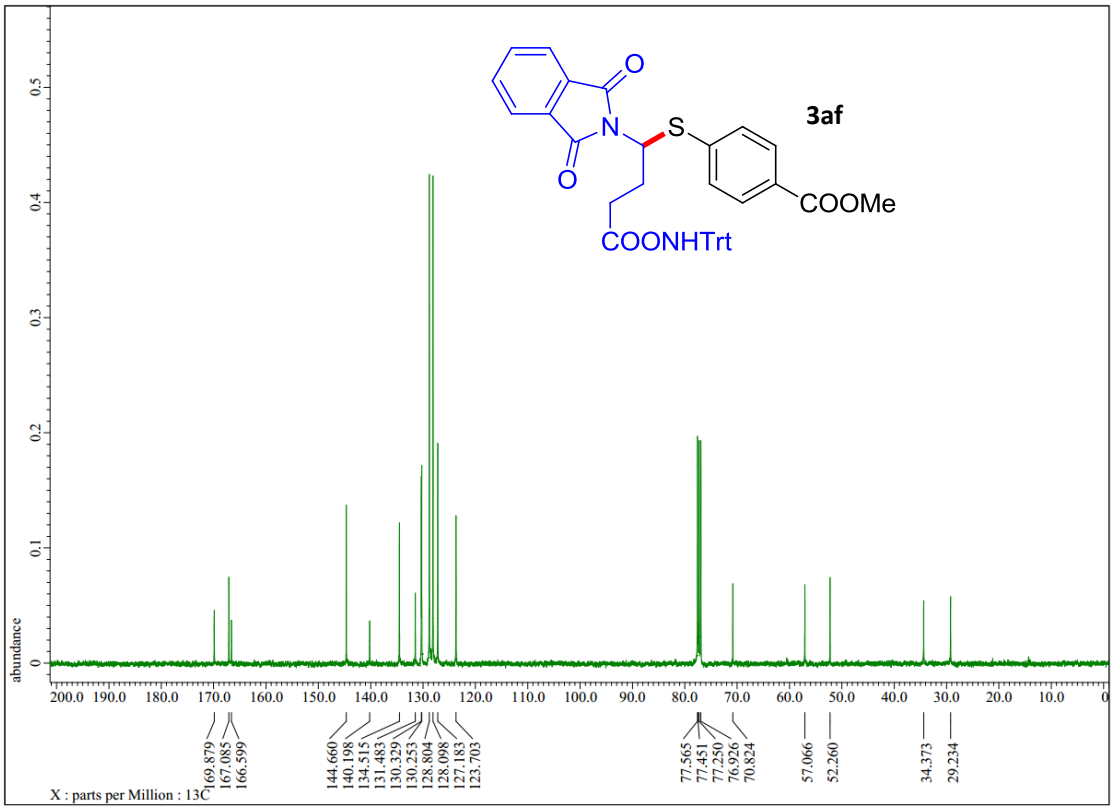

3ad
COOMe
NHBoc
abundance
X : parts per Million : 1H

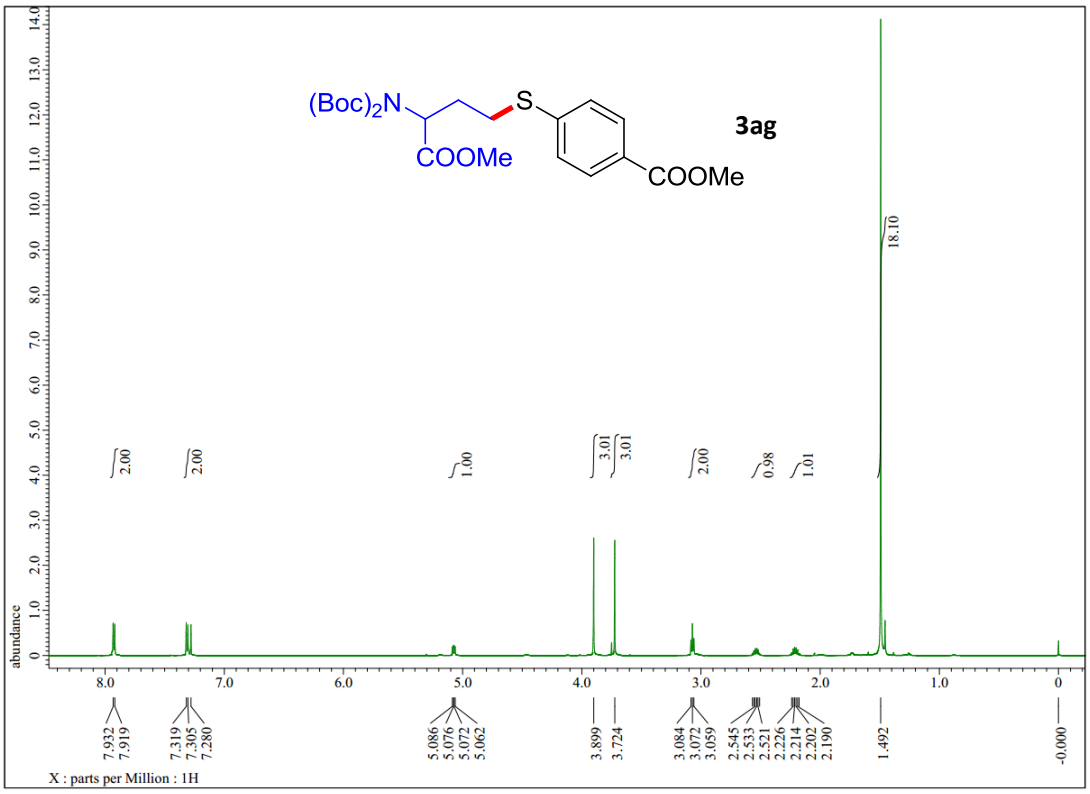

3ad
COOMe
NHBoc
abundance
X : parts per Million : 13C

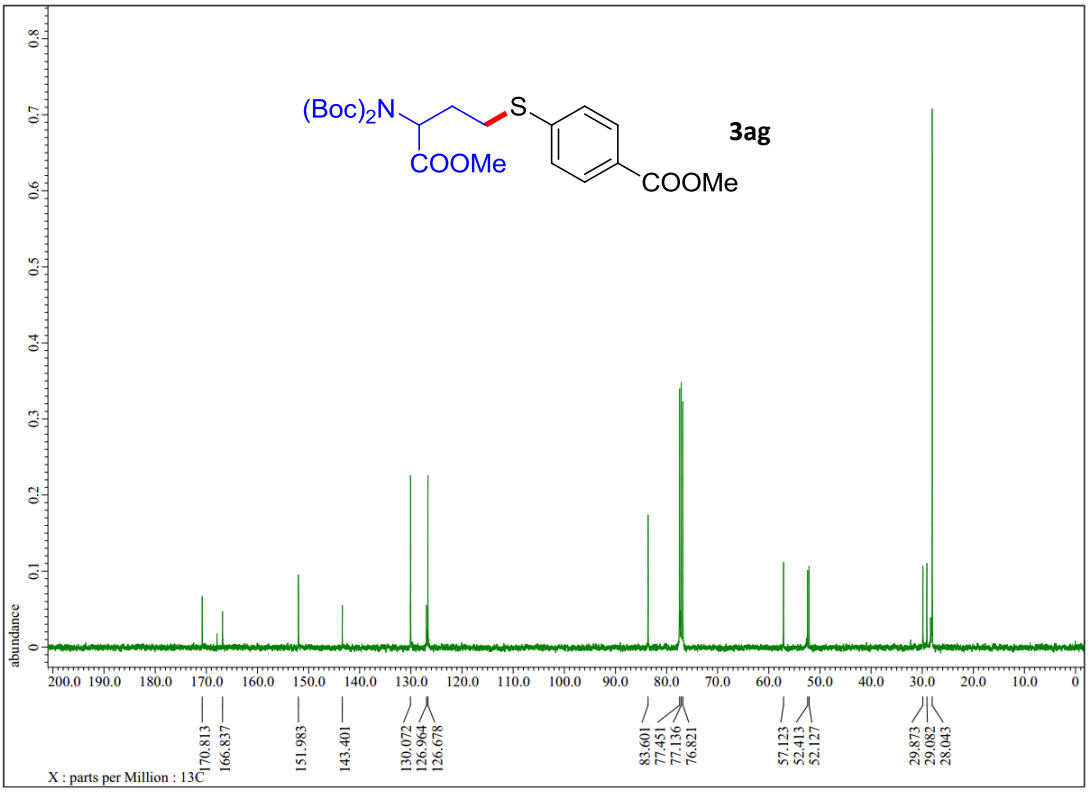

3ae
COOMe
COOMe
abundance
X : parts per Million : 1H

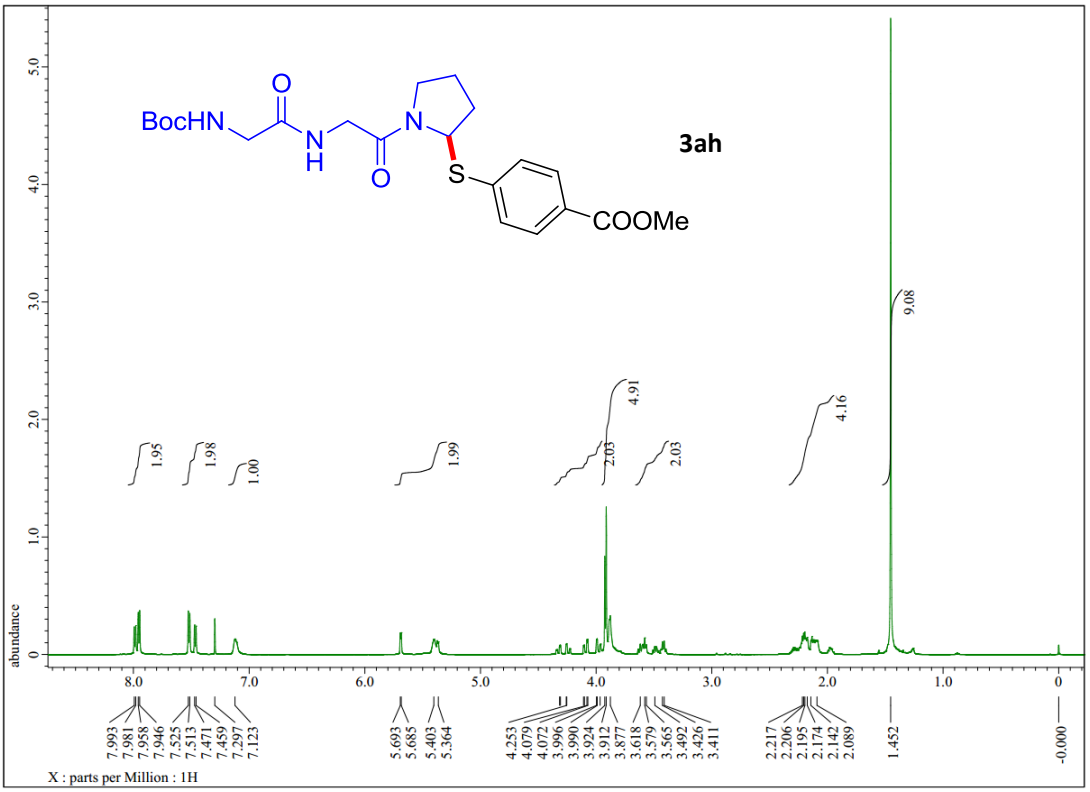

3ae
COOMe
COOMe
abundance
X : parts per Million : 13C

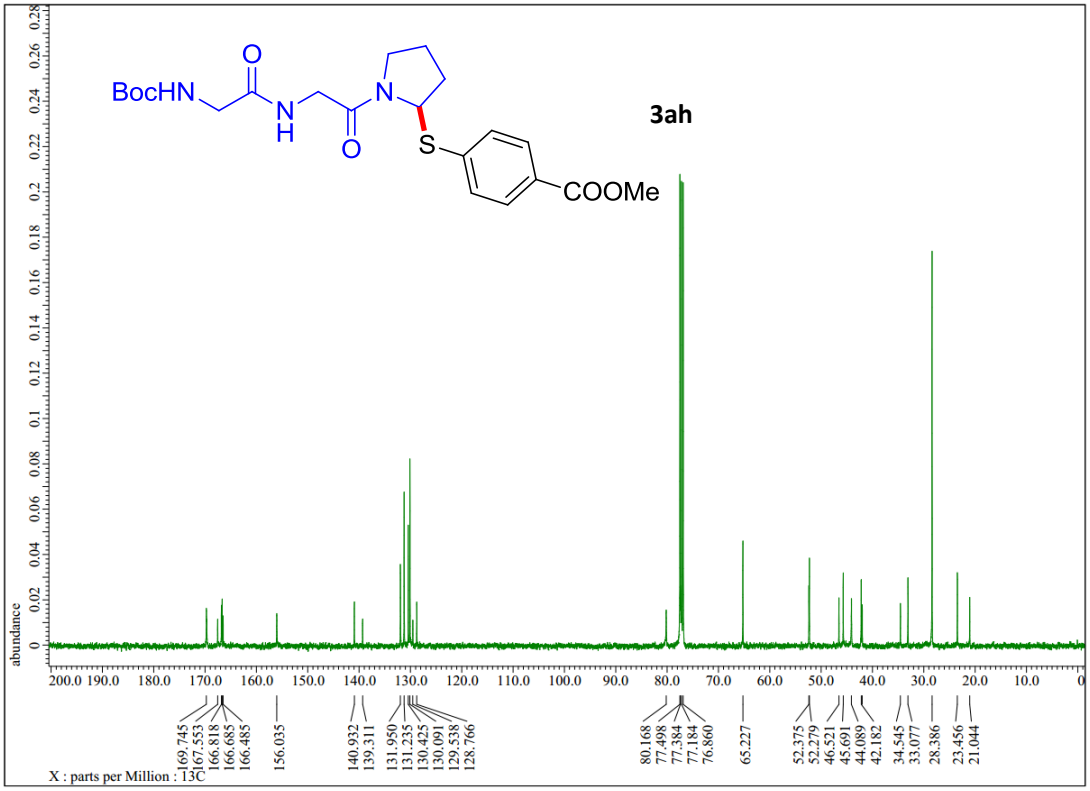

3af
COOMe
COONHTrt
abundance
X : parts per Million : 1H

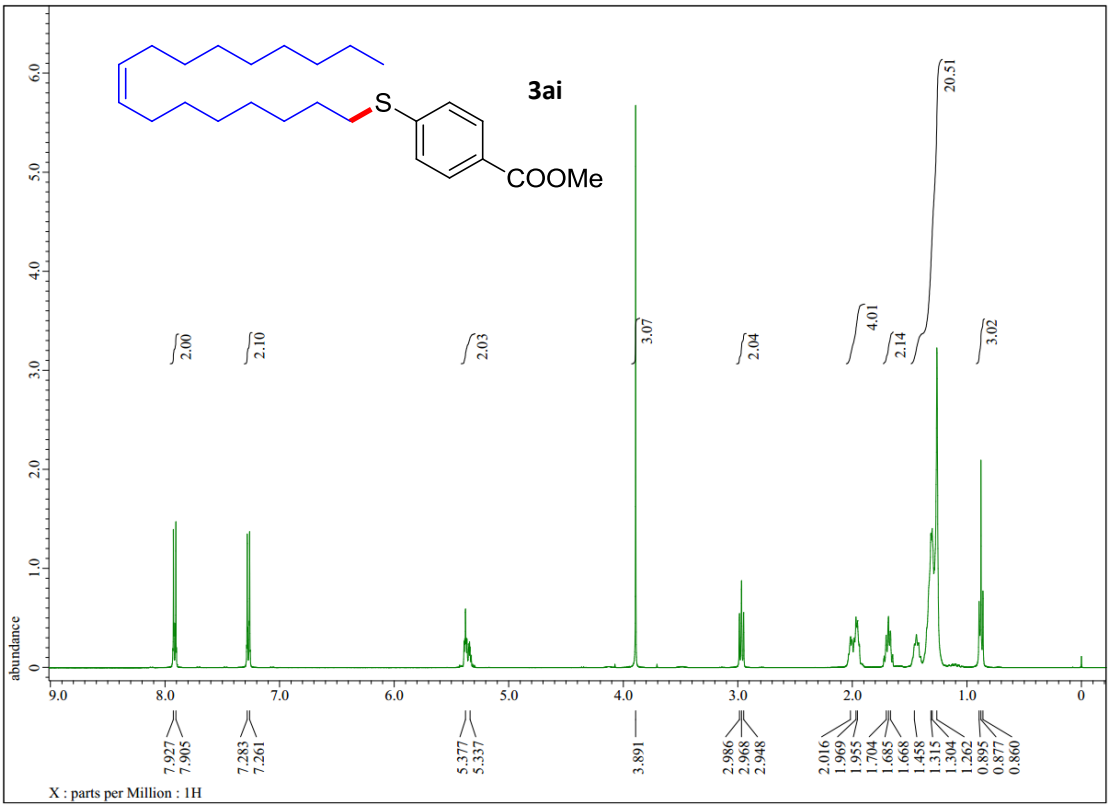

3af
COOMe
COONHTrt
abundance
X : parts per Million : 13C

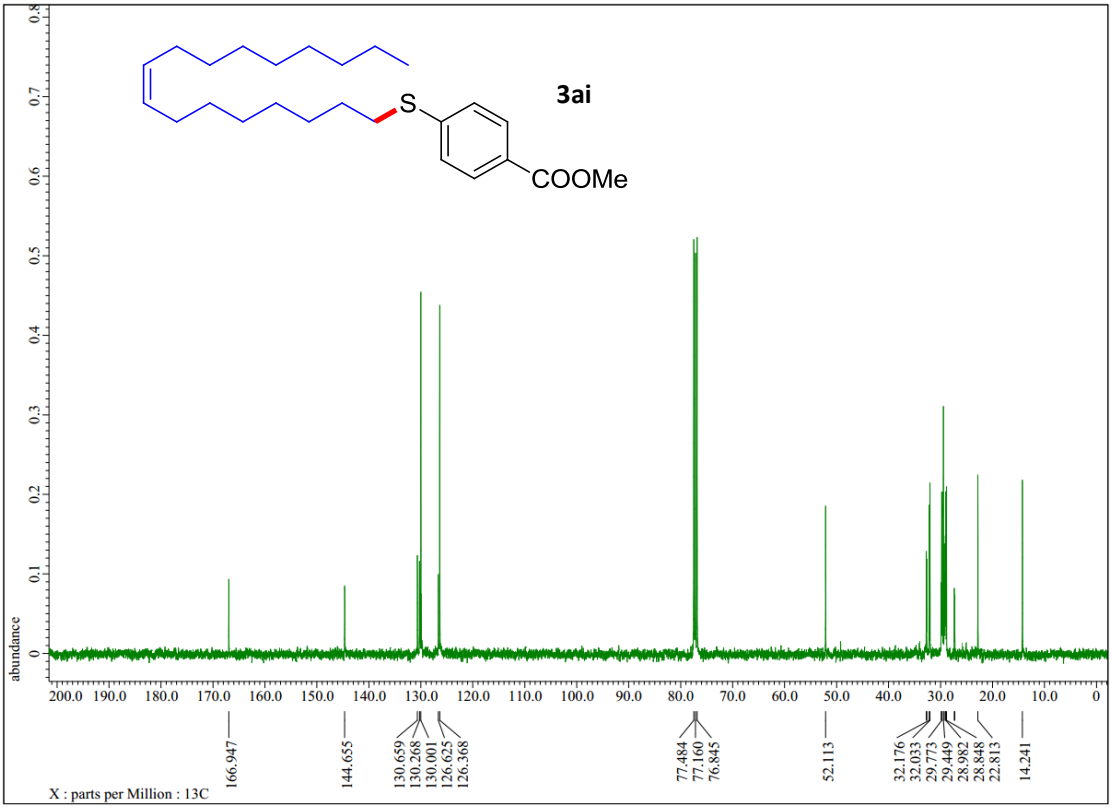

(Boc)2N
COOMe
S
COOMe
3ag
abundance
X : parts per Million : 1H


(Boc)2N
COOMe
S
COOMe
3ag
abundance
X : parts per Million : 13C


BocHN
O
N
H
O
N
S
COOMe
3ah
abundance
X : parts per Million : 1H


BocHN
O
N
H
O
N
S
COOMe
3ah
abundance
X : parts per Million : 13C


3ai
S
COOMe
abundance
X : parts per Million : 1H
2.00
2.10
2.03
3.07
2.04
4.01
2.14
20.51
3.02
7.927
7.905
7.283
7.261
5.377
5.337
3.891
2.986
2.968
2.948
2.016
1.969
1.955
1.704
1.685
1.668
1.458
1.315
1.304
1.262
0.895
0.877
0.860


3ai
S
COOMe
abundance
X : parts per Million : 13C
166.947
144.655
130.659
130.268
130.001
126.625
126.368
77.484
77.160
76.845
52.113
32.176
32.033
29.773
29.449
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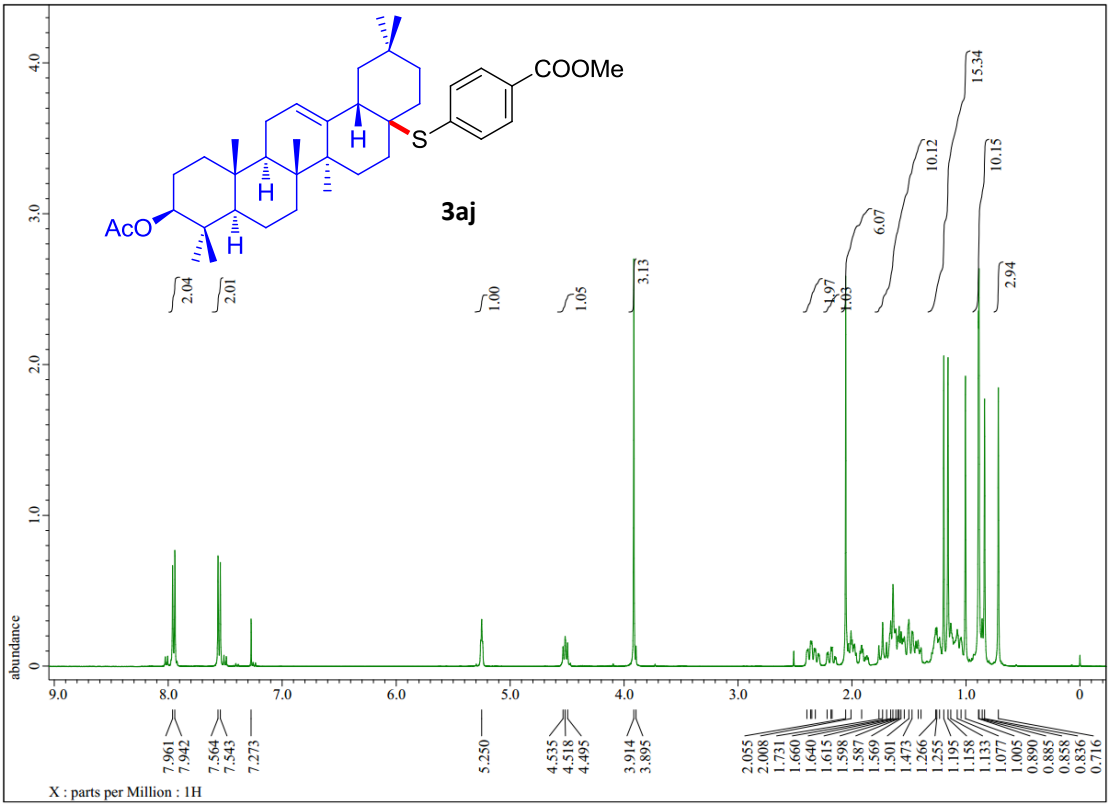
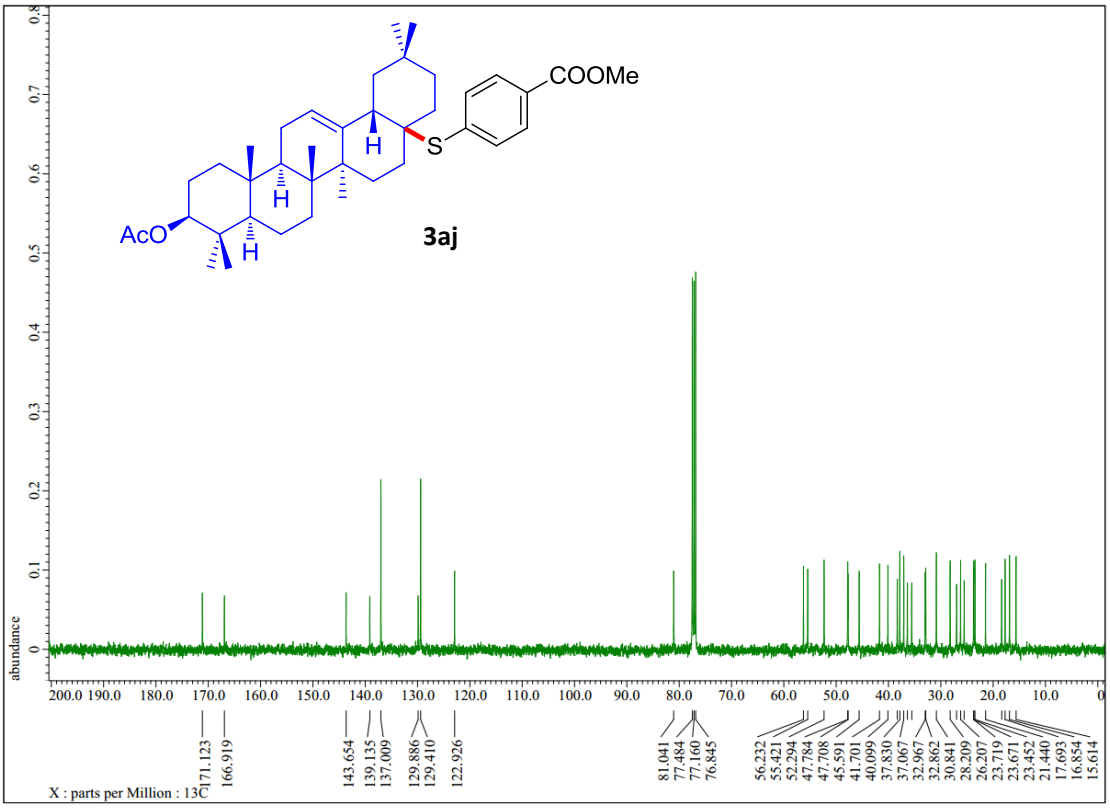
28.848
22.813
14.241


COOMe
S
H
H
H
AcO
3aj
abundance
X : parts per Million : 1H


COOMe
S
H
H
H
AcO
3aj
abundance
X : parts per Million : 13C