Supporting Information

Visible-light Induced Decarboxylative Coupling of Redox-Active Esters with Disulfides to Construct C-S Bonds

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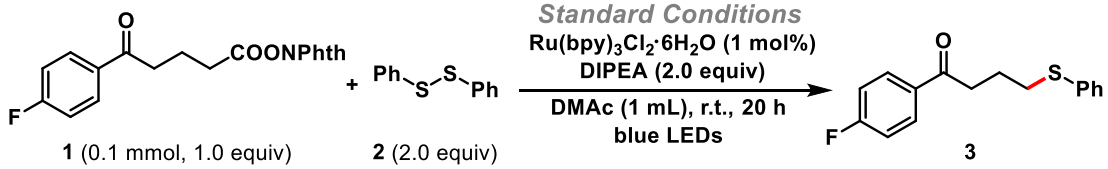
1. General information

NMR spectra were obtained on the 300 (or 400) MHz spectrometer using $CDCl_3$ as deuterated solvents, with proton, carbon and fluorine resonances at 400 MHz, 100 MHz and 376 MHz, respectively. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relatived to $CFCl_3$ as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ^{19}F NMR using fluorobenzene (^{19}F NMR δ: -114.0 ppm) as an internal standard before working up the reaction. HRMS (ESI) data were tested on a Thermo Scientific LTQ Orbitrap XL. Unless otherwise noted, solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using. Flash column chromatography was carried out using 300-400 mesh silica gel.

2. Reaction Optimization

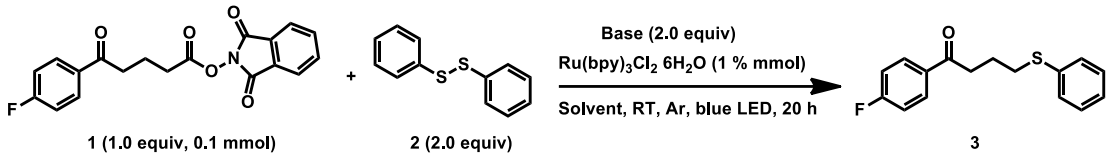
Table S1. Optimization of Parameters for the Photoinduced C-S bond Formation[a]



Entry	Variations from standard conditions	Yield of **3**[a]
1	none	> 99%
2	1.0 equiv of **2**	37%
3	DCM instead of DMAc	n.d.
4	CH_3CN instead of DMAc	35%
5	THF instead of DMAc	n.d.
6	NEt_3 instead of DIPEA	60%
7	$HNEt_2$ instead of DIPEA	n.d.
8	Cs_2CO_3 instead of DIPEA	n.d.
9	under air atmosphere	7%
10	without photocatalyst	n.d.
11	without DIPEA	n.d.
12	without light	n.d.

[a]Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. n.d. = not detected.

Table S2. Exploring the effect of different reaction conditions[a]



Entry	Solvent	Base	Atmosphere	Yield (%) [a]
1	DCM	DIPEA	Ar	n.d.
2	CH_3CN	DIPEA	Ar	35
3	DMF	DIPEA	Ar	67
4	EtOAc	DIPEA	Ar	n.d.
5	DMAc	DIPEA	Ar	>99 (96)
6	THF	DIPEA	Ar	n.d.
7	DMSO	DIPEA	Ar	9
8	DMAc	NEt_3	Ar	60
9	DMAc	$HNEt_3$	Ar	n.d.
10	DMAc	Cs_2CO_3	Ar	n.d.
11	DMAc	DIPEA	Air	7
12[b]	DMAc	DIPEA	Ar	n.d.
13[c]	DMAc	DIPEA	Ar	n.d.
14[d]	DMAc	DIPEA	Ar	n.d.
15[e]	DMAc	DIPEA	Ar	36
16[e,f]	DMAc	DIPEA	Ar	n.d.
17[e,g]	DMAc	DIPEA	Ar	n.d.

[a] Reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), $Ru(bpy)_3Cl_2$ $6H_2O$ (1 mol %), DIPEA (0.1 mmol) in DMAc (1 mL), Blue LED, RT, Ar, 20 h. Yields were determined by ^{19}F NMR spectroscopy using fluorobenzene as an internal standard. Isolated yield is shown in parentheses. [b] Without photocatalyst. [c] Without DIPEA. [d] Under dark. [e] Time = 30 min. [f] $Ru(bpy)_3Cl_2$ $6H_2O$ (10 mol %). [g] $Ru(bpy)_3Cl_2$ $6H_2O$ (100 mol %).

3. General Procedure

3.1 General procedure for the synthesis of NHPI esters of α-amino acids[1-4].

A round-bottom flask equipped with a Tefloncoated magnetic stir bar was added α-amino acid (1.0 equiv), nucleophie (N-hydroxyphthalimide, 1.5 equiv) and DMAP (0.1 equiv). Then DIC (1.1 equiv) and dichloromethane (0.1 - 0.2 M) were added, and the mixture was stirred vigorously for 12 hours under Ar atmosphere. The solvent was removed under reduced pressure, and the expectant esters were purified by column chromatography.

3.2 General procedure for the synthesis of NHPI esters of carboxylic acids[5].

A round-bottom flask equipped with a Tefloncoated magnetic stir bar was added carboxylic acid (1.0 equiv), nucleophie (N-hydroxyphthalimide, 1.2 equiv) and DMAP (0.1 equiv). Then DIC (1.2 equiv) and dichloromethane (0.1 - 0.2 M) were added, and the mixture was stirred vigorously for 4 - 12 hours under Ar atmosphere. The solvent was removed under reduced pressure, and the expectant esters were purified by column chromatography.

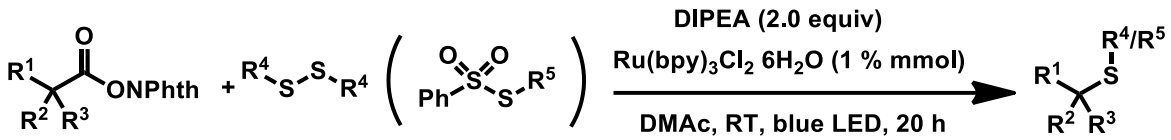
3.3 General procedure for the synthesis of diaryl disulfides[5].

A round-bottom flask equipped with a Tefloncoated magnetic stir bar was added thiophenol (1.0 equiv), NaI (0.2 equiv) and acetonitrile (0.3 M). After $FeCl_3$ (0.3 equiv) was added, the mixture was stirred vigorously for 4 hours under air atmosphere. Then the solvent was removed under reduced pressure, and the expectant phenyl disulfides were purified by column chromatography.

3.4 General procedure for the synthesis of $PhSO_2SAr$[6].

A round-bottom flask equipped with a Tefloncoated magnetic stir bar was added disulphide (1.0 equiv), $PhSO_2Na$ (4.0 equiv) and NBS (2.0 equiv) in acetonitrile (0.1 M). After stirred for 12 hours under air atmosphere, the solvent was removed under reduced pressure, and the expectant phenyl disulfides were purified by column chromatography.

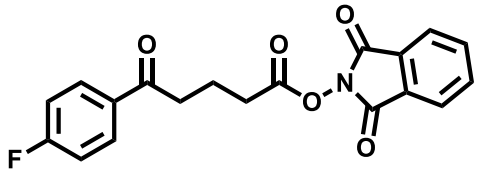
3.5 General procedure for the decarboxylative coupling with aryl disulfides and $PhSO_2SAr$.



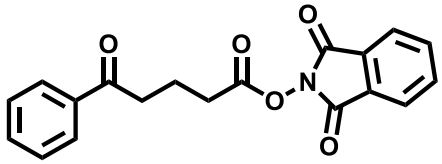
To an oven-dried Shrek tube equippied with a magnetic stir bar was added the actived ester (0.2 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (1.5 mg, 0.002 mmol), DIPEA (N,N-Diisopropylethylamine, 25.8 mg, 0.2 mmol), disulfide (0.4 mmol) or $PhSO_2SAr$ (0.4 mmol) and freshly-distilled DMAc (1 mL) under Ar atmosphere at room temperature. Then the tube was irradiated with a blue LEDs at room temperature for 20 hours. After reaction completed, the mixture was extracted with ethyl acetate (3× 15 mL) and dried over Na_2SO_4. After removal of the ethyl acetate under reduced pressure with a rotary evaporator, the crude product was purified by column chromatography on silica gel to give the desired product.

4. Characterization data

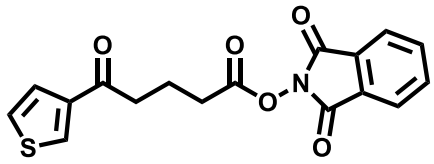
4.1 Characterization data for esters



1,3-dioxoisoindolin-2-yl 5-(4-fluorophenyl)-5-oxopentanoate[7] **(s1):** Obtained as a white solid in 78% yield (686 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.07 (dd, J = 8.7, 5.5 Hz, 2H), 7.93 (dd, J = 5.3, 3.3 Hz, 2H), 7.83 (dd, J = 5.3, 3.3 Hz, 2H), 7.17 (t, J = 8.6 Hz, 2H), 3.20 (t, J = 7.1 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H), 2.26 (p, J = 7.0 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -105.09 (ddd, J = 13.8, 8.5, 5.5 Hz).

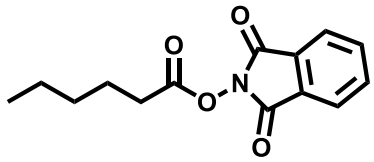


1,3-dioxoisoindolin-2-yl 5-oxo-5-phenylpentanoate[7] **(s2):** Obtained as a white solid in 67% yield (453 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.99 (d, J = 7.3 Hz, 2H), 7.92 – 7.84 (m, 2H), 7.79 (d, J = 2.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.3 Hz, 2H), 3.19 (t, J = 7.0 Hz, 2H), 2.83 (t, J = 6.9 Hz, 2H), 2.24 (p, J = 6.8 Hz, 2H).

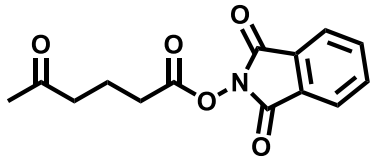


1,3-dioxoisoindolin-2-yl-5-oxo-5-(thiophen-3-yl)pentanoate (s3): Obtained as a white solid in 83% yield (284 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.88 (dd, J = 5.3, 3.1 Hz, 2H), 7.83 – 7.74 (m, 3H), 7.64 (d, J = 4.4 Hz, 1H), 7.13 (t, J = 4.3 Hz, 1H), 3.12 (t, J = 7.1 Hz, 2H), 2.81 (t, J = 6.9 Hz, 2H), 2.22 (p, J = 7.0 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 191.9, 169.3, 162.0, 144.0, 134.8, 133.9, 132.3, 128.9, 128.3, 124.0, 37.3,

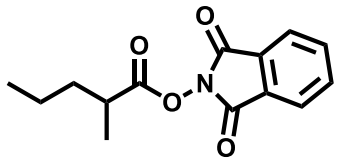
30.2, 19.5. **HRMS** (ESI): calcd for $C_{17}H_{13}NO_5SNa$ $(M+Na)^+$ 366.0407, found 366.0409.



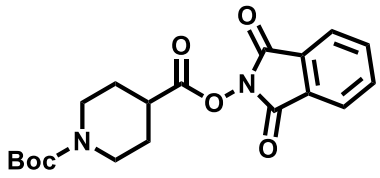
1,3-dioxoisoindolin-2-yl-hexanoate[8] **(s4):** Obtained as a white solid in 72% yield (188 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.89 (dd, J = 5.4, 3.1 Hz, 2H), 7.79 (dd, J = 5.5, 3.1 Hz, 2H), 2.66 (t, J = 7.5 Hz, 2H), 1.79 (p, J = 7.5 Hz, 2H), 1.48 – 1.33 (m, 6H), 0.93 (t, J = 7.0 Hz, 3H).



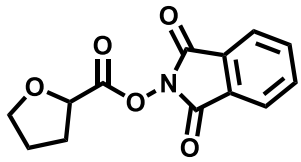
1,3-dioxoisoindolin-2-yl-5-oxohexanoate[9] **(s5):** Obtained as a white solid in 92% yield (507 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.85 (dd, J = 5.5, 3.2 Hz, 2H), 7.76 (dd, J = 5.4, 3.2 Hz, 2H), 2.69 (t, J = 7.1 Hz, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.15 (s, 3H), 2.01 (p, J = 7.0 Hz, 2H).



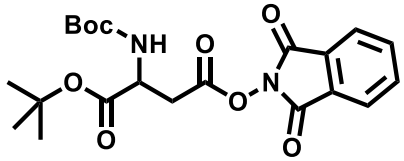
1,3-dioxoisoindolin-2-yl-2-methylpentanoate[10] **(s6):** Obtained as a white solid in 80% yield (210 mg) by silica gel flash column chromatography eluted with PE:EA = 5 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.87 (td, J = 5.2, 2.0 Hz, 2H), 7.78 (dd, J = 5.5, 3.1 Hz, 2H), 2.84 (h, J = 7.0 Hz, 1H), 1.82 (ddd, J = 15.3, 13.8, 7.6 Hz, 1H), 1.62 – 1.53 (m, 1H), 1.52 – 1.45 (m, 2H), 1.35 (d, J = 7.0 Hz, 3H), 1.19 (dd, J = 12.6, 7.0 Hz, 1H), 0.97 (t, J = 7.2 Hz, 3H).



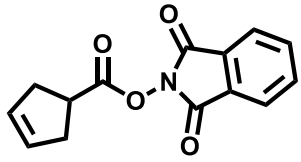
1-(tert-butyl)-4-(1,3-dioxoisoindolin-2-yl)-piperidine-1,4-dicarboxylate[11] **(s7):** Obtained as a white solid in 56% yield (211 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.91 (dd, J = 5.2, 3.1 Hz, 2H), 7.86 – 7.79 (m, 2H), 4.06 (d, J = 11.1 Hz, 2H), 3.15 – 2.85 (m, 3H), 2.09 (d, J = 12.1 Hz, 2H), 1.87 (td, J = 14.0, 3.8 Hz, 2H), 1.48 (s, 9H).



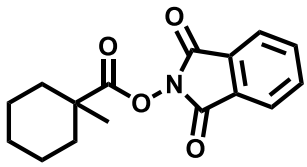
1,3-dioxoisoindolin-2-yl-tetrahydrofuran-2-carboxylate[12] **(s8):** Obtained as a white solid in 70% yield (365 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.89 (dd, J = 5.3, 3.1 Hz, 2H), 7.80 (dd, J = 5.4, 3.1 Hz, 2H), 4.88 (dd, J = 8.2, 5.3 Hz, 1H), 4.04 (dq, J = 21.6, 7.7 Hz, 2H), 2.42 (tq, J = 14.2, 6.8, 5.9 Hz, 2H), 2.07 (ddp, J = 19.6, 12.6, 6.6, 6.2 Hz, 2H).



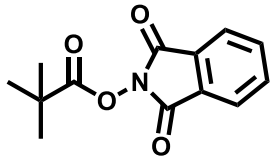
1-(*tert*-butyl)-4-(1,3-dioxoisoindolin-2-yl)-(*tert*-butoxycarbonyl)aspartate[9] **(s9):** Obtained as a white solid in 46% yield (401 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.87 (dd, J = 5.3, 3.2 Hz, 2H), 7.78 (dd, J = 5.4, 3.2 Hz, 2H), 5.51 (d, J = 7.7 Hz, 1H), 4.62 – 4.48 (m, 1H), 3.26 (qd, J = 17.2, 4.4 Hz, 2H), 1.47 (s, 9H), 1.45 (s, 9H).



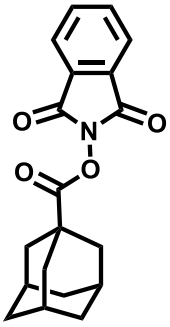
1,3-dioxoisoindolin-2-yl-cyclopent-3-ene-1-carboxylate[13] **(s10):** Obtained as a white solid in 86% yield (442 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.89 (dd, J = 5.4, 3.2 Hz, 2H), 7.79 (dd, J = 5.4, 3.2 Hz, 2H), 5.72 (s, 2H), 3.49 (p, J = 8.2, 7.3 Hz, 1H), 2.87 (d, J = 7.8 Hz, 4H).



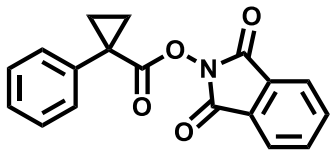
1,3-dioxoisoindolin-2-yl-1-methylcyclohexane-1-carboxylate[14] **(s11):** Obtained as a white solid in 95% yield (548 mg) by silica gel flash column chromatography eluted with PE:EA = 5 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.87 (dt, J = 7.4, 3.8 Hz, 2H), 7.77 (dd, J = 5.4, 3.1 Hz, 2H), 1.71 – 1.53 (m, 6H), 1.42 (s, 3H), 1.40 – 1.24 (m, 4H).



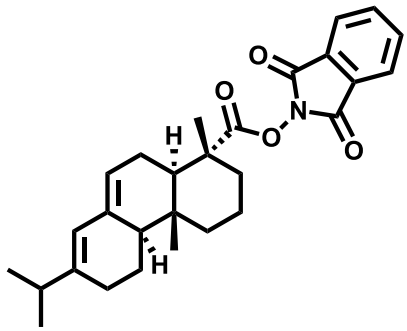
1,3-dioxoisoindolin-2-yl-pivalate[9] **(s12):** Obtained as a white solid in 90% yield (447 mg) by silica gel flash column chromatography eluted with PE:EA = 5 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.84 (dd, J = 5.4, 3.1 Hz, 2H), 7.75 (dd, J = 5.4, 3.2 Hz, 2H), 1.41 (s, 6H).



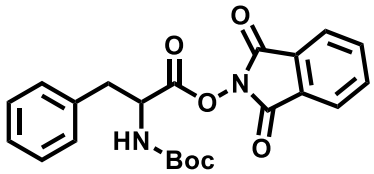
1,3-dioxoisoindolin-2-yl-(3*r*,5*r*,7*r*)-adamantane-1-carboxylate[12] **(s13):** Obtained as a white solid in 80% yield (2.62 g) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.90 (dd, J = 5.2, 3.2 Hz, 2H), 7.80 (dd, J = 5.3, 3.2 Hz, 2H), 2.16 (s, 9H), 1.80 (s, 6H).



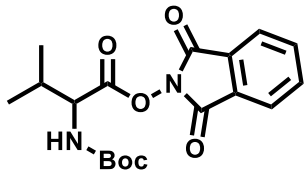
1,3-dioxoisoindolin-2-yl-1-phenylcyclopropane-1-carboxylate[10] **(s14):** Obtained as a white solid in 39% yield (243 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.85 (dt, J = 7.2, 3.7 Hz, 2H), 7.76 (dd, J = 5.5, 3.1 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.40 – 7.28 (m, 3H), 1.91 (q, J = 4.3 Hz, 2H), 1.49 (q, J = 4.3 Hz, 2H).



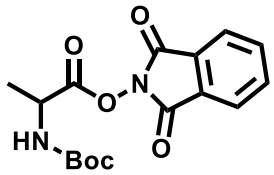
1,3-dioxoisoindolin-2-yl-(1*R*,4a*R*,4b*R*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a, 4b,5,6,10,10a-decahydrophenanthrene-1-carboxylate[15] **(s15):** Obtained as a white solid in 26% yield (260 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.86 (dd, J = 5.5, 3.0 Hz, 2H), 7.77 (dd, J = 5.4, 3.2 Hz, 2H), 5.83 – 5.72 (m, 1H), 5.50 – 5.30 (m, 1H), 2.25 (dd, J = 15.6, 11.0 Hz, 3H), 2.12 – 1.88 (m, 5H), 1.88 – 1.77 (m, 1H), 1.73 – 1.62 (m, 2H), 1.44 (d, J = 7.0 Hz, 3H), 1.22 (dd, J = 13.8, 6.9 Hz, 4H), 1.01 (dd, J = 6.7, 2.9 Hz, 6H), 0.88 (s, 3H).



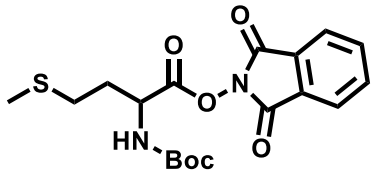
1,3-dioxoisoindolin-2-yl-(*tert*-butoxycarbonyl)phenylalaninate[9] **(s16):** Obtained as a white solid in 62% yield (256 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.93 (dd, J = 5.5, 3.1 Hz, 2H), 7.83 (dd, J = 5.4, 3.1 Hz, 2H), 7.43 – 7.30 (m, 5H), 5.19 – 4.56 (m, 2H), 3.33 (ddt, J = 20.1, 14.2, 5.8 Hz, 2H), 1.45 (s, 9H).



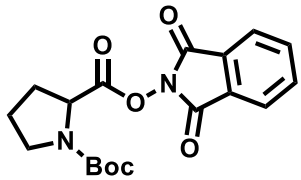
1,3-dioxoisoindolin-2-yl-(*tert*-butoxycarbonyl)valinate[4] **(s17):** Obtained as a white solid in 69% yield (251 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.98 – 7.84 (m, 2H), 7.81 (dd, J = 5.3, 3.0 Hz, 2H), 5.36 – 4.58 (m, 2H), 2.71 (s, 2H), 2.17 (s, 6H), 1.48 (s, 9H).



1,3-dioxoisoindolin-2-yl-(*tert*-butoxycarbonyl)alaninate[4] **(s18):** Obtained as a white solid in 62% yield (207 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.90 (dd, J = 5.4, 3.1 Hz, 2H), 7.80 (dd, J = 5.4, 3.2 Hz, 2H), 5.26 – 4.31 (m, 2H), 1.63 (d, J = 7.2 Hz, 3H), 1.48 (s, 9H).

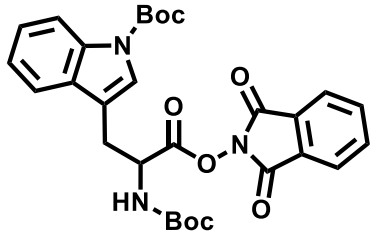


1,3-dioxoisoindolin-2-yl-(*tert*-butoxycarbonyl)methioninate[12] **(s19):** Obtained as a white solid in 61% yield (239 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.95 – 7.89 (m, 2H), 7.88 – 7.80 (m, 2H), 5.39 – 4.61 (m, 2H), 2.81 – 2.64 (m, 2H), 2.41 – 2.09 (m, 5H), 1.49 (s, 9H).

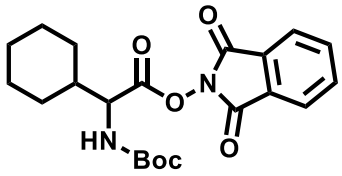


1-(tert-butyl)-2-(1,3-dioxoisoindolin-2-yl)-pyrrolidine-1,2-dicarboxylate[4] **(s20):** Obtained as a white solid in 66% yield (237 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.02 –

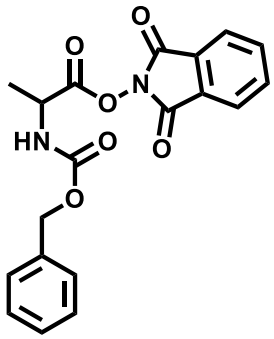
7.66 (m, 4H), 4.76 – 4.44 (m, 2H), 3.83 – 3.38 (m, 2H), 2.58 – 2.29 (m, 2H), 2.23 – 1.86 (m, 2H), 1.51 (s, 9H).



1,3-dioxoisoindolin-2-yl-(*tert*-butoxycarbonyl)tryptophanate[16] **(s21):** Obtained as a white solid in 11% yield (59 mg) by silica gel flash column chromatography eluted with PE:EA = 1 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.93 (dd, J = 5.0, 3.2 Hz, 2H), 7.88 – 7.80 (m, 2H), 7.66 (d, J = 8.1 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.26 – 7.14 (m, 2H), 5.21 – 4.69 (m, 2H), 3.66 – 3.43 (m, 2H), 1.61 (s, 9H), 1.46 (s, 9H).

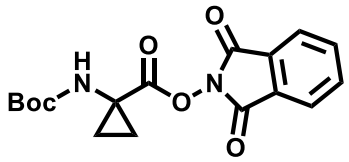


1,3-dioxoisoindolin-2-yl-2-((*tert*-butoxycarbonyl)amino)-2-cyclohexylacetate[4] **(s22):** Obtained as a white solid in 83% yield (334 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.93 – 7.74 (m, 4H), 5.14 – 4.29 (m, 2H), 2.04 – 1.92 (m, 1H), 1.89 – 1.77 (m, 4H), 1.75 – 1.64 (m, 1H), 1.48 (s, 9H), 1.26 (dq, J = 23.6, 12.0, 11.5 Hz, 5H).

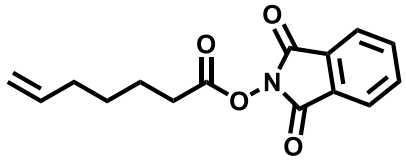


1,3-dioxoisoindolin-2-yl-((benzyloxy)carbonyl)alaninate[10] **(s23):** Obtained as a white solid in 24% yield (88 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.85 (ddd, J = 29.2, 5.4, 3.2

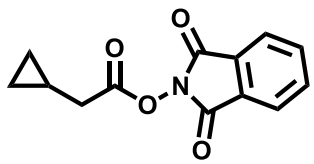
Hz, 4H), 7.36 (s, 5H), 5.37 (d, J = 7.4 Hz, 1H), 5.25 – 5.07 (m, 2H), 4.94 – 4.78 (m, 1H), 1.66 (d, J = 7.1 Hz, 3H).



1,3-dioxoisoindolin-2-yl-1-((tert-butoxycarbonyl)amino)cyclopropane-1-carboxylate[17] **(s24):** Obtained as a white solid in 29% yield (99 mg) by silica gel flash column chromatography eluted with PE:EA = 2 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (dd, J = 5.2, 3.1 Hz, 2H), 7.83 – 7.73 (m, 2H), 5.39 – 4.99 (m, 1H), 1.90 – 1.73 (m, 2H), 1.50 (d, J = 27.3 Hz, 9H), 1.33 – 1.21 (m, 2H).

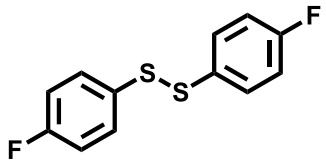


1,3-dioxoisoindolin-2-yl-hept-6-enoate[10] **(s25):** Obtained as a white solid in 79% yield (217 mg) by silica gel flash column chromatography eluted with PE:EA = 5 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (dd, J = 5.4, 3.1 Hz, 2H), 7.79 (td, J = 5.1, 1.9 Hz, 2H), 5.81 (ddt, J = 17.0, 10.1, 6.7 Hz, 1H), 5.09 – 4.92 (m, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.80 (dt, J = 15.3, 7.4 Hz, 2H), 1.60 – 1.50 (m, 2H).

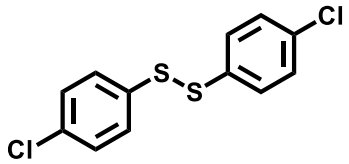


1,3-dioxoisoindolin-2-yl-2-cyclopropylacetate[18] **(s26):** Obtained as a white solid in 82% yield (200 mg) by silica gel flash column chromatography eluted with PE:EA = 5 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (td, J = 5.2, 2.0 Hz, 2H), 7.80 (td, J = 5.3, 2.1 Hz, 2H), 2.59 (d, J = 7.1 Hz, 2H), 1.24 – 1.12 (m, 1H), 0.71 – 0.63 (m, 2H), 0.32 (q, J = 5.0 Hz, 2H).

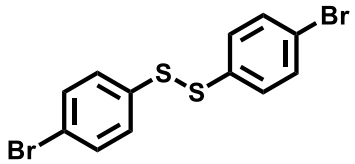
4.2 Characterization data for diaryl disulfides



1,2-bis(4-fluorophenyl)disulfane[19] **(s27):** Obtained as a yellow oil in 94% yield (120 mg) by silica gel flash column chromatography eluted with PE:EA = 30 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.52 – 7.36 (m, 4H), 7.01 (t, *J* = 8.4 Hz, 4H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -113.86 (tt, *J* = 8.8, 5.1 Hz, 2F).

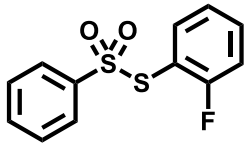


1,2-bis(4-chlorophenyl)disulfane[19] **(s28):** Obtained as a yellow solid in 80% yield (920 mg) by silica gel flash column chromatography eluted with PE:EA = 30 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.43 – 7.38 (m, 4H), 7.31 – 7.25 (m, 4H).

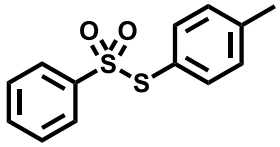


1,2-bis(4-bromophenyl)disulfane[20] **(s29):** Obtained as a yellow solid in 85% yield (1.27 g) by silica gel flash column chromatography eluted with PE:EA = 30 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.46 – 7.40 (m, 4H), 7.36 – 7.31 (m, 4H).

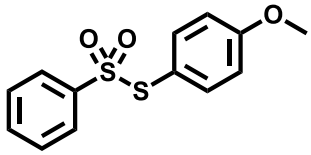
4.3 Characterization data for $PhSO_2SAr$



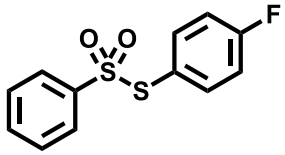
S-(2-fluorophenyl)-benzenesulfonothioate[21] **(s30):** Obtained as a colourless oil in 86% yield (461 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.65 – 7.58 (m, 3H), 7.53 – 7.41 (m, 4H), 7.18 (td, *J* = 7.7, 1.1 Hz, 1H), 7.05 (td, *J* = 8.7, 1.2 Hz, 1H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.10 (ddd, *J* = 8.9, 6.8, 5.1 Hz, 1F).



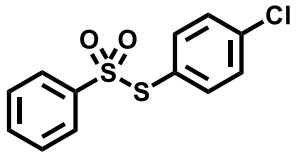
S-(*p*-tolyl)-benzenesulfonothioate[21] **(s31):** Obtained as a yellow solid in 85% yield (897 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.60 – 7.54 (m, 3H), 7.45 – 7.38 (m, 2H), 7.24 – 7.19 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H).



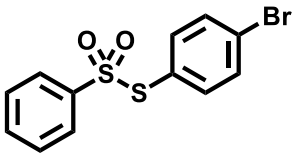
S-(4-methoxyphenyl)-benzenesulfonothioate[22] **(s32):** Obtained as a yellow solid in 84% yield (945 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.65 – 7.54 (m, 3H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.30 – 7.21 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H).



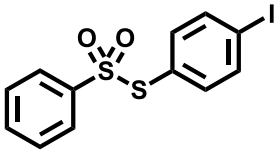
S-(4-fluorophenyl)-benzenesulfonothioate[21] **(s33):** Obtained as a colourless oil in 80% yield (429 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.62 – 7.55 (m, 3H), 7.48 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.03 (ddt, *J* = 8.7, 6.7, 2.6 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ-107.16 (tt, *J* = 8.2, 5.1 Hz, 1F).



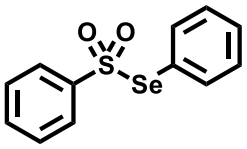
S-(4-chlorophenyl)-benzenesulfonothioate[21] **(s34):** Obtained as a colourless oil in 77% yield (439 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.63 – 7.57 (m, 3H), 7.48 – 7.42 (m, 2H), 7.34 – 7.26 (m, 4H).



S-(4-bromophenyl)-benzenesulfonothioate[22] **(s35):** Obtained as a yellow solid in 23% yield (299 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.62 – 7.52 (m, 3H), 7.51 – 7.38 (m, 2H), 7.23 – 7.18 (m, 4H).

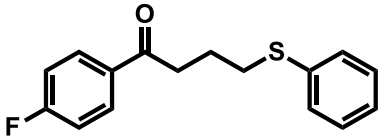


S-(4-iodophenyl)-benzenesulfonothioate (s36): Obtained as a yellow solid in 42% yield (633 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.71 – 7.65 (m, 2H), 7.64 – 7.56 (m, 3H), 7.46 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.10 – 7.04 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 142.9, 138.8, 137.9, 133.9, 129.0, 127.7, 127.6. **HRMS** (ESI): calc'd for $C_{12}H_9IO_2S_2Na^+$ $(M+Na)^+$ 398.8981, found 399.0163.



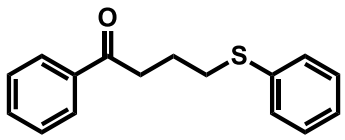
Se-phenylbenzenesulfonoselenoate[23] **(s37):** Obtained as a brown solid in 11% yield (131 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.50 (ddd, *J* = 20.1, 12.1, 7.5 Hz, 6H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H).

4.4 Characterization data for product

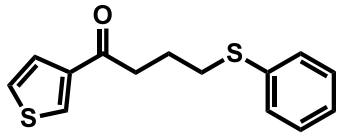


1-(4-fluorophenyl)-4-(phenylthio)butan-1-one (3): Obtained as a yellow oil in 92% yield (50 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.00 – 7.92 (m, 2H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 6.5 Hz, 2H), 7.21 – 7.07 (m, 3H), 3.12 (t, *J* = 7.0 Hz, 2H), 3.04 (t, *J* = 6.9

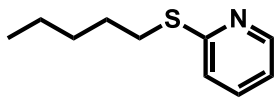
Hz, 2H), 2.09 (p, *J* = 6.9 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -102.21 – -107.99 (m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 197.8, 165.7 (d, *J* = 254.6 Hz), 136.0, 133.2 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.3 Hz), 129.2, 129.0, 126.0, 115.7 (d, *J* = 21.8 Hz), 36.8, 33.1, 23.4. **HRMS** (ESI): calc'd for $C_{16}H_{16}FOS^+$ $(M+H)^+$ 275.0900, found 275.0885.



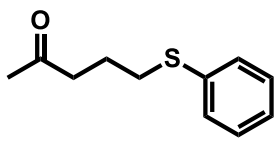
1-phenyl-4-(phenylthio)butan-1-one[24] **(4):** Obtained as a yellow oil in 81% yield (42 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.13 (p, *J* = 7.0 Hz, 2H).



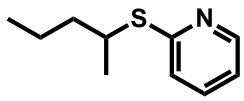
4-(phenylthio)-1-(thiophen-3-yl)butan-1-one[24] **(5):** Obtained as a yellow oil in 68% yield (36 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.73 – 7.71 (m, 1H), 7.65 (d, *J* = 4.9 Hz, 1H), 7.38 (dt, *J* = 8.2, 1.7 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 – 7.12 (m, 1H), 3.10 (t, *J* = 7.1 Hz, 2H), 3.06 (t, *J* = 7.0 Hz, 2H), 2.12 (p, *J* = 7.0 Hz, 2H).



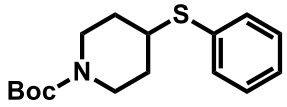
2-(pentylthio)pyridine[25] **(6):** Obtained as a yellow liquid in 84% yield (31 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.45 – 8.42 (m, 1H), 7.51 – 7.44 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 6.97 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 3.21 – 3.14 (m, 2H), 1.73 (dt, *J* = 15.0, 7.3 Hz, 2H), 1.50 – 1.31 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 159.6, 149.4, 135.8, 122.1, 119.1, 31.1, 30.1, 29.0, 22.3, 14.0.



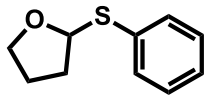
5-(phenylthio)pentan-2-one[26] **(7):** Obtained as a yellow oil in 92% yield (36 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.1 Hz, 1H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H), 2.14 (s, 3H), 1.93 (p, *J* = 7.0 Hz, 2H).



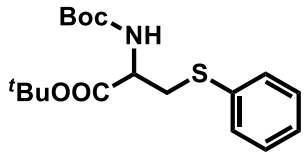
2-(pentan-2-ylthio)pyridine (8): Obtained as a yellow oil in 75% yield (27 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.46 – 8.41 (m, 1H), 7.47 (td, *J* = 7.7, 1.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.97 (ddd, *J* = 7.3, 4.9, 1.0 Hz, 1H), 3.99 – 3.88 (m, 1H), 1.76 – 1.56 (m, 2H), 1.55 – 1.44 (m, 2H), 1.41 (d, *J* = 6.8 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 159.6, 149.5, 135.8, 122.9, 119.2, 39.6, 38.8, 21.4, 20.3, 14.0. **HRMS** (ESI): calc'd for $C_{10}H_{16}NS^+$ $(M+H)^+$ 182.0998, found 182.0968.



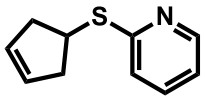
***tert*-butyl-4-(phenylthio)piperidine-1-carboxylate**[27] **(9):** Obtained as a yellow oil in 87% yield (51mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 6.6 Hz, 2H), 7.35 – 7.21 (m, 3H), 3.97 (d, *J* = 11.6 Hz, 2H), 3.20 (td, *J* = 10.2, 5.1 Hz, 1H), 2.91 (t, *J* = 11.3 Hz, 2H), 2.02 – 1.83 (m, 2H), 1.60 – 1.49 (m, 2H), 1.44 (s, 9H).



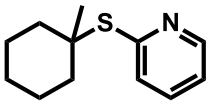
2-(phenylthio)tetrahydrofuran[28] **(10):** Obtained as a yellow solid in 70% yield (25 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.1 Hz, 2H), 7.30 (dt, *J* = 14.7, 7.1 Hz, 3H), 5.68 (dd, *J* = 7.0, 3.6 Hz, 1H), 4.11 – 3.95 (m, 2H), 2.39 (ddd, *J* = 11.5, 8.6, 5.3 Hz, 1H), 2.17 – 1.79 (m, 3H).



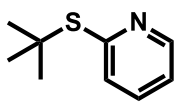
***tert*-butyl-2-((*tert*-butoxycarbonyl)amino)-3-(phenylthio)propanoate (11):** Obtained as a yellow oil in 82% yield (58 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.25 – 7.17 (m, 1H), 5.40 – 4.13 (m, 2H), 3.51 – 3.26 (m, 2H), 1.46 (s, 9H), 1.42 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 169.6, 161.4, 155.0, 135.7, 130.2, 129.0, 126.6, 82.6, 79.8, 54.1, 37.1. **HRMS** (ESI): calc'd for $C_{18}H_{28}NO_4S^+$ $(M+H)^+$ 354.1739, found 354.1740.



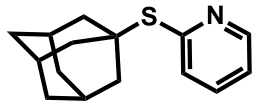
2-(cyclopent-3-en-1-ylthio)pyridine (12): Obtained as a white oil in 89% yield (32 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.45 (d, *J* = 4.2 Hz, 1H), 7.54 – 7.44 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.03 – 6.95 (m, 1H), 5.79 (s, 2H), 4.39 (tt, *J* = 8.4, 5.1 Hz, 1H), 3.02 (dd, *J* = 15.2, 8.2 Hz, 2H), 2.46 (dd, *J* = 15.1, 4.7 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 160.1, 149.6, 135.8, 129.4, 122.2, 119.2, 40.4, 40.3. **HRMS** (ESI): calc'd for $C_{10}H_{12}NS^+$ $(M+H)^+$ 178.0690, found 178.0682.



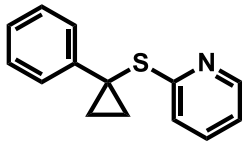
2-((1-methylcyclohexyl)thio)pyridine (13): Obtained as a yellow oil in 96% yield (40 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.52 (d, *J* = 4.5 Hz, 1H), 7.52 (td, *J* = 7.6, 1.6 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.2, 5.0 Hz, 1H), 2.03 (dd, *J* = 12.9, 6.1 Hz, 2H), 1.75 (ddt, *J* = 15.5, 12.5, 4.9 Hz, 2H), 1.64 – 1.54 (m, 4H), 1.52 (s, 3H), 1.42 – 1.26 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 158.1, 149.5, 135.9, 128.2, 120.9, 52.3, 38.6, 28.9, 25.9, 22.6. **HRMS** (ESI): calc'd for $C_{12}H_{18}NS^+$ $(M+H)^+$ 208.1160, found 208.1151.



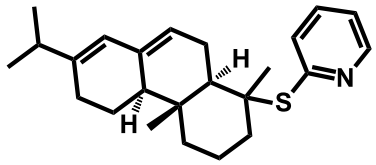
2-(*tert*-butylthio)pyridine[29] **(14):** Obtained as a yellow solid in 59% yield (20 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.57 – 8.51 (m, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.06 (m, 1H), 1.53 (s, 9H).



2-((3s,5s,7s)-adamantan-1-ylthio)pyridine[29] **(15):** Obtained as a white solid in 89% yield (44 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 3.9 Hz, 1H), 7.54 (td, *J* = 7.8, 1.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.09 (m, 1H), 2.08 (brs, 9H), 1.69 (brs, 6H).

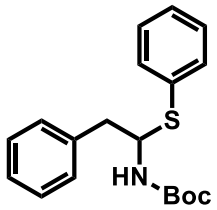


2-((1-phenylcyclopropyl)thio)pyridine (16): Obtained as a yellow oil in 64% yield (29 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.43 (ddd, *J* = 4.8, 1.7, 0.8 Hz, 1H), 7.51 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.46 (td, *J* = 7.9, 1.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 2H), 6.97 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1H), 1.63 – 1.50 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 161.2, 149.5, 142.6, 136.3, 128.4, 126.7, 126.3, 121.2, 119.4, 26.7, 19.8. **HRMS** (ESI): calc'd for $C_{14}H_{14}NS^+$ $(M+H)^+$ 228.0841, found 228.0822.

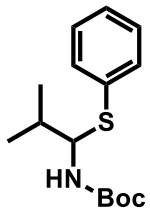


2-(((4aR,4bR,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthren-1-yl)thio)pyridine[30] **(17):** Obtained as a yellow oil in 32% yield (24mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.54 (d, *J* = 3.6 Hz, 1H), 7.61 – 7.49 (m, 1H), 7.40 (dd, *J* = 21.4, 7.8 Hz, 1H), 7.18 – 7.07 (m, 1H), 5.80 (s, 1H), 5.50 – 5.44 (m, 1H), 2.70 (d, *J*

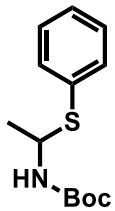
= 17.6 Hz, 1H), 2.21 (td, *J* = 12.6, 11.5, 5.9 Hz, 3H), 2.14 – 2.02 (m, 4H), 1.95 – 1.76 (m, 3H), 1.63 – 1.53 (m, 2H), 1.50 (s, 3H), 1.25 (t, *J* = 8.0 Hz, 2H), 1.03 (dd, *J* = 6.7, 2.4 Hz, 6H), 0.87 (s, 3H).



***tert*-butyl-(2-phenyl-1-(phenylthio)ethyl)carbamate (18):** Obtained as a yellow oil in 89% yield (58 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 5.8 Hz, 2H), 7.38 – 7.24 (m, 8H), 5.57 – 4.53 (m, 2H), 3.20 – 3.02 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 154.3, 136.6, 133.2, 132.8, 129.5, 128.9, 128.4, 127.7, 126.9, 80.0, 59.5, 42.2, 28.2. **HRMS** (ESI): calc'd for $C_{19}H_{23}NO_2SNa^+$ $(M+Na)^+$ 352.1347, found 352.1342.

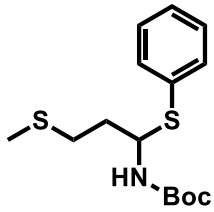


***tert*-butyl-(2-methyl-1-(phenylthio)propyl)carbamate**[31] **(19):** Obtained as a pale yellow solid in 97% yield (55 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 6.7 Hz, 2H), 7.35 – 7.24 (m, 3H), 5.17 – 4.52 (m, 2H), 2.05 (dt, *J* = 12.0, 6.2 Hz, 1H), 1.34 (s, 9H), 1.08 (d, *J* = 4.6 Hz, 6H).

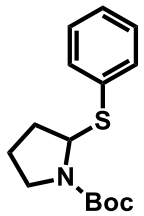


***tert*-butyl-(1-(phenylthio)ethyl)carbamate (20):** Obtained as a yellow oil in 86% yield (44 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.53 – 7.47 (m, 2H), 7.37 – 7.30 (m, 3H), 5.41 –

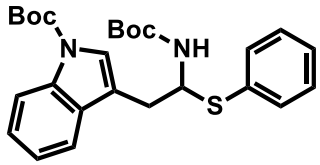
4.46 (m, 2H), 1.50 (d, J = 6.8 Hz, 3H), 1.36 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 154.2, 133.8, 132.6, 128.9, 127.8, 79.9, 54.6, 28.2, 22.6. **HRMS** (**ESI):** calc'd for $C_{13}H_{20}NO_2S^+$ $(M+H)^+$ 254.1209, found 254.1022.



***tert*-butyl-(3-(methylthio)-1-(phenylthio)propyl)carbamate (21):** Obtained as a yellow solid in 88% yield (35 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.53 – 7.47 (m, 2H), 7.39 – 7.31 (m, 3H), 5.33 – 4.49 (m, 2H), 2.66 (t, J = 6.6 Hz, 3H), 2.13 (s, 2H), 2.10 – 1.91 (m, 2H), 1.37 (s, 9H).**^{13}C NMR (**75 MHz, $CDCl_3$) δ: 154.5, 133.8, 132.2, 129.0, 128.0, 80.1, 58.2, 35.6, 30.7, 28.2, 15.6. **HRMS** (ESI): calc'd for $C_{15}H_{24}NO_2S_2^+$ $(M+H)^+$ 314.1243, found 314.1235.

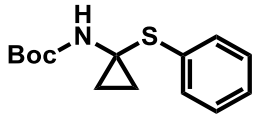


***tert*-butyl-2-(phenylthio)pyrrolidine-1-carboxylate**[32] **(22):** Obtained as a yellow oil in 91% yield (51 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.49 (brs, 2H), 7.30 (brs, 3H), 5.43 – 5.24 (m, 1H), 3.52 – 3.23 (m, 2H), 2.18 – 1.83 (m, 4H), 1.52 – 1.30 (m, 9H).

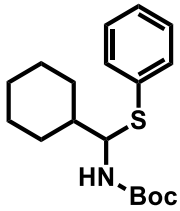


***tert*-butyl-3-(2-((tert-butoxycarbonyl)amino)-2-(phenylthio)ethyl)-1H-indole-1-carboxylate (23):** Obtained as a yellow oil in 62% yield (58 mg) by silica gel flash column chromatography eluted with PE:EA = 3 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.18 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 25.8, 7.0 Hz, 4H), 7.33 (dt, J = 13.1, 6.9 Hz,

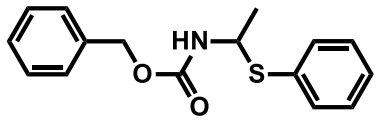
5H), 5.64 – 4.58 (m, 2H), 3.30 – 3.10 (m, 2H), 1.70 (s, 9H), 1.35 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 154.4, 149.7, 135.4, 133.2, 132.8, 130.5, 129.0, 127.7, 124.5, 124.3, 122.6, 119.0, 115.7, 115.3, 83.6, 80.0, 58.6, 31.9, 28.2. **HRMS** (ESI): calc'd for $C_{26}H_{33}N_2O_4S^+$ $(M+H)^+$ 469.2161, found 469.2151.



***tert*-butyl-(1-(phenylthio)cyclopropyl)carbamate (24):** Obtained as a yellow solid in 48% yield (26 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 6.9 Hz, 2H), 7.41 – 7.27 (m, 3H), 5.30 (s, 1H), 1.45 (s, 9H), 1.35 – 1.26 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 154.6, 134.9, 131.5, 129.0, 127.3, 80.1, 39.3 (d, *J* = 8.2 Hz), 28.3, 18.3. **HRMS** (ESI): calc'd for $C_{14}H_{20}NO_2S^+$ $(M+H)^+$ 266.1215, found 266.1203.

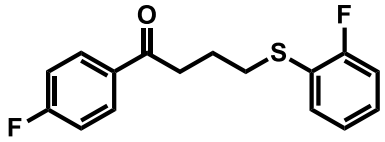


***tert*-butyl-(cyclohexyl(phenylthio)methyl)carbamate (25):** Obtained as a pale yellow solid in 91% yield (59 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 6.8 Hz, 2H), 7.34 – 7.22 (m, 3H), 5.16 – 4.53 (m, 2H), 1.91 (d, *J* = 10.6 Hz, 2H), 1.80 (d, *J* = 9.1 Hz, 2H), 1.74 – 1.61 (m, 2H), 1.33 (s, 9H), 1.29 – 1.11 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 154.9, 133.5, 132.7, 128.8, 127.2, 79.7, 64.2, 43.6, 30.0, 28.8, 28.2, 26.2, 26.0 (d, *J* = 1.1 Hz). **HRMS** (ESI): calc'd for $C_{18}H_{28}NO_2S^+$ $(M+H)^+$ 322.1841, found 344.1660.

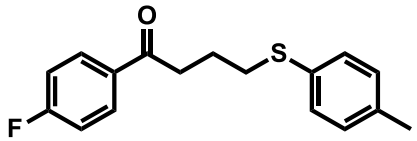


benzyl-(1-(phenylthio)ethyl)carbamate **(26):** Obtained as a yellow oil in 61% yield (35 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.48 – 7.43 (m, 2H), 7.36 – 7.22 (m, 8H), 5.34 – 5.21 (m, 1H), 5.11 – 4.94 (m, 3H), 1.49 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ:

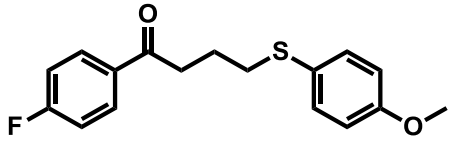
154.9, 136.2, 133.8, 132.3, 129.0, 128.5, 128.2, 128.1, 66.8, 55.2, 22.5. **HRMS** (ESI): calc'd for $C_{16}H_{17}NO_2SNa^+$ $(M+Na)^+$ 310.0878, found 310.0877.



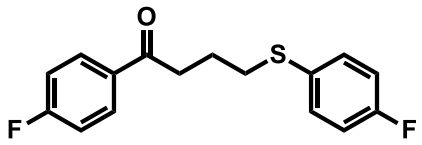
1-(4-fluorophenyl)-4-((2-fluorophenyl)thio)butan-1-one (27): Obtained as a yellow oil in 89% yield (52 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.00 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.47 – 7.39 (m, 1H), 7.29 – 7.19 (m, 1H), 7.18 – 7.02 (m, 4H), 3.15 (t, *J* = 7.0 Hz, 2H), 3.05 (t, *J* = 6.9 Hz, 2H), 2.07 (p, *J* = 6.9 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -105.19 (ddd, *J* = 13.8, 8.4, 5.5 Hz), -109.51 (ddd, *J* = 9.4, 7.6, 5.5 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 197.7, 165.7 (d, *J* = 254.6 Hz), 161.5 (d, *J* = 245.0 Hz), 133.2 (d, *J* = 3.1 Hz), 132.1 (d, *J* = 1.8 Hz), 130.7 (d, *J* = 9.3 Hz), 128.4 (d, *J* = 7.9 Hz), 124.5 (d, *J* = 3.7 Hz), 122.7 (d, *J* = 17.5 Hz), 115.7 (d, *J* = 21.8 Hz), 36.7, 32.8 (d, *J* = 2.3 Hz), 23.4. **HRMS** (ESI): calc'd for $C_{16}H_{14}F_2OSNa^+$ $(M+Na)^+$ 315.0631, found 315.0623.



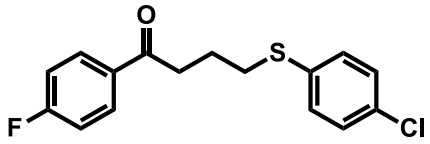
1-(4-fluorophenyl)-4-(p-tolylthio)butan-1-one (28): Obtained as a yellow oil in 45% yield (26 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.96 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.04 (m, 4H), 3.10 (t, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 2.05 (p, *J* = 6.9 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -105.31 (ddd, *J* = 13.7, 8.4, 5.5 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 197.9, 165.7 (d, *J* = 254.5 Hz), 136.3, 133.3 (d, *J* = 3.1 Hz), 132.1, 130.7 (d, *J* = 9.3 Hz), 130.2, 129.8, 115.7 (d, *J* = 21.8 Hz), 36.8, 33.8, 23.4, 21.0. **HRMS** (ESI): calc'd for $C_{17}H_{17}FOSNa^+$ $(M+Na)^+$ 311.0882, found 311.0873.



1-(4-fluorophenyl)-4-((4-methoxyphenyl)thio)butan-1-one (29): Obtained as a yellow oil in 38% yield (23 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.99 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 6.9 Hz, 2H), 2.03 (p, *J* = 6.9 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -105.32 (ddd, *J* = 13.7, 8.4, 5.4 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 197.9, 165.7 (d, *J* = 254.7 Hz), 158.9, 133.3 (d, *J* = 5.1 Hz), 130.7 (d, *J* = 9.3 Hz), 126.0, 115.7 (d, *J* = 21.9 Hz), 114.6, 55.3, 36.8, 35.2, 23.5. **HRMS** (ESI): calc'd for $C_{17}H_{18}FO_2S^+$ $(M+H)^+$ 305.1012, found 305.1010.

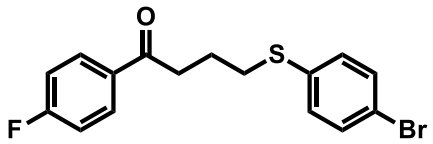


phenyl(1,1,1-trifluoroundecan-3-yl)sulfane (30): Obtained as a yellow oil in 69% yield (40 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.99 (ddd, *J* = 8.9, 5.2, 2.5 Hz, 1H), 7.37 (ddt, *J* = 8.4, 5.3, 2.6 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.04 – 6.97 (m, 1H), 3.12 (t, *J* = 7.0 Hz, 1H), 3.00 (t, *J* = 7.0 Hz, 1H), 2.07 (p, *J* = 7.0 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.15 (tt, *J* = 8.4, 5.4 Hz), -115.55 (tt, *J* = 8.6, 5.2 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 197.7, 165.8 (d, *J* = 254.8 Hz), 161.8 (d, *J* = 246.2 Hz), 133.2 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 8.0 Hz), 130.8 (d, *J* = 3.5 Hz), 130.6 (d, *J* = 9.3 Hz), 116.1 (d, *J* = 21.8 Hz), 115.7 (d, *J* = 21.9 Hz), 36.7, 34.4, 23.4. **HRMS** (ESI): calcd for $C_{16}H_{15}F_2OS^+$ $(M+H)^+$ 293.0806, found 293.0795.

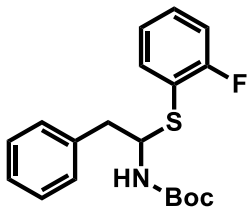


4-((4-chlorophenyl)thio)-1-(4-fluorophenyl)butan-1-one (31): Obtained as a pale yellow solid in 98% yield (65 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.02 – 7.96 (m, 2H), 7.32 – 7.24 (m, 4H), 7.15 (ddt, *J* = 8.6, 6.9, 2.5 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.09 (p, *J* = 7.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.07 (tt, *J* =

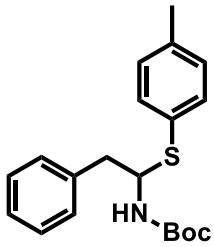
8.5, 5.4 Hz). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 197.6, 165.8 (d, *J* = 254.8 Hz), 134.6, 133.2 (d, *J* = 3.0 Hz), 132.0, 130.6 (d, *J* = 9.3 Hz), 130.5, 129.1, 115.7 (d, *J* = 21.9 Hz), 36.7, 33.3, 23.3. **HRMS** (ESI): calcd for $C_{16}H_{15}FClOS^+$ $(M+H)^+$ 309.0511, found 309.0503.



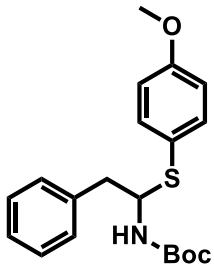
4-((4-bromophenyl)thio)-1-(4-fluorophenyl)butan-1-one (32): Obtained as a pale yellow solid in 92% yield (65 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.01 – 7.95 (m, 2H), 7.40 (dq, *J* = 8.5, 2.0, 1.4 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.18 – 7.10 (m, 2H), 3.12 (t, *J* = 6.9 Hz, 2H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.10 (p, *J* = 7.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.04 (ddd, *J* = 14.1, 8.5, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 197.6, 165.8 (d, *J* = 254.9 Hz), 135.4, 133.2 (d, *J* = 3.0 Hz), 132.0, 130.7, 130.6 (d, *J* = 8.7 Hz), 119.8, 115.7 (d, *J* = 21.9 Hz), 36.7, 33.1, 23.2. **HRMS** (ESI): calcd for $C_{16}H_{15}BrFOS^+$ $(M+H)^+$ 353.0006, found 352.9996.



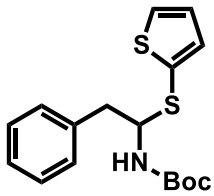
***tert*-butyl-(1-((2-fluorophenyl)thio)-2-phenylethyl)carbamate (33):** Obtained as a white solid in 94% yield (65 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.50 (t, *J* = 7.3 Hz, 1H), 7.42 – 7.19 (m, 6H), 7.10 (t, *J* = 7.7 Hz, 2H), 5.60 – 4.55 (m, 2H), 3.25 – 2.90 (m, 2H), 1.29 (s, 9H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -106.94 – -107.07 (m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 194.7, 162.8 (d, *J* = 245.4 Hz), 154.3, 136.4 (d, *J* = 3.4 Hz), 130.3 (d, *J* = 8.2 Hz), 129.5, 128.5, 127.0, 124.5 (d, *J* = 3.5 Hz), 119.7 (d, *J* = 18.3 Hz), 115.8 (d, *J* = 23.5 Hz), 79.9, 59.2, 42.1, 28.1. **HRMS** (ESI): calc'd for $C_{19}H_{22}FNO_2SNa^+$ $(M+Na)^+$ 370.1253, found 370.1251.



***tert*-butyl-(2-phenyl-1-(p-tolylthio)ethyl)carbamate (34):** Obtained as a white solid in 83% yield (57 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.24 (m, 5H), 7.14 (d, *J* = 7.6 Hz, 2H), 5.51 – 4.46 (m, 2H), 3.21 – 2.86 (m, 2H), 2.35 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 154.3, 136.8, 134.0, 129.7, 129.5, 129.0, 128.4, 126.9, 125.2, 79.9, 59.8, 42.2, 28.2, 21.2. **HRMS (ESI):** calc'd for $C_{20}H_{25}NO_2SNa^+$ $(M+Na)^+$ 366.1504, found 366.1503.

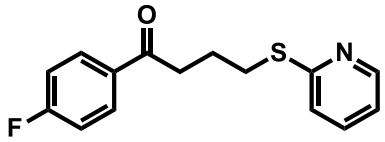


***tert*-butyl-(1-((4-methoxyphenyl)thio)-2-phenylethyl)carbamate (35):** Obtained as a yellow solid in 70% yield (50 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (dt, *J* = 19.4, 6.9 Hz, 3H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.44 – 4.51 (m, 2H), 3.81 (s, 3H), 3.16 – 2.95 (m, 2H), 1.32 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 160.0, 154.3, 136.8, 136.6, 129.5, 128.4, 126.8, 122.9, 114.5, 79.8, 60.3, 55.3, 42.0, 28.2. **HRMS** (ESI): calc'd for $C_{20}H_{25}NO_3SNa^+$ $(M+Na)^+$ 382.1447, found 382.1431.

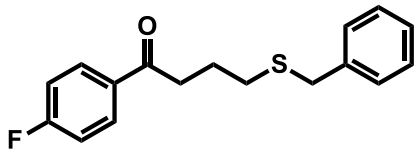


***tert*-butyl-(2-phenyl-1-(thiophen-2-ylthio)ethyl)carbamate (36):** Obtained as a yellow solid in 36% yield (24 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.64 – 7.57 (m, 1H), 7.42 – 7.30 (m, 3H), 7.21 (d, *J* = 6.9 Hz, 2H), 7.16 (s, 2H), 5.04 – 4.46 (m, 2H), 3.28 – 2.93

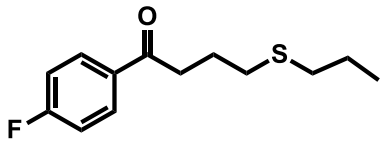
(m, 2H), 1.46 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 165.2, 135.9, 135.3, 132.0, 129.4, 128.8, 127.9, 127.3, 124.2, 80.7, 60.7, 38.2, 28.3.



1-(4-fluorophenyl)-4-(pyridin-2-ylthio)butan-1-one (37): Obtained as a yellow oil in 77% yield (40 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.37 – 8.34 (m, 1H), 8.01 – 7.96 (m, 2H), 7.47 (td, *J* = 7.9, 1.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.96 (ddd, *J* = 7.3, 4.9, 0.9 Hz, 1H), 3.30 (t, *J* = 6.9 Hz, 2H), 3.14 (t, *J* = 7.1 Hz, 2H), 2.18 (p, *J* = 7.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.45 (tt, *J* = 8.5, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 197.9, 165.7 (d, *J* = 254.5 Hz), 158.8, 149.4, 135.9, 133.3 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.3 Hz), 122.3, 119.4, 115.6 (d, *J* = 21.8 Hz), 37.1, 29.4, 23.9. **HRMS** (ESI): calc'd for $C_{15}H_{15}FNOS^+$ $(M+H)^+$ 276.0858, found 276.0848.

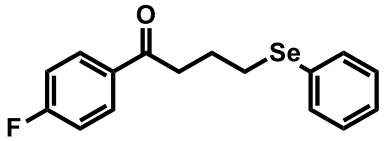


4-(benzylthio)-1-(4-fluorophenyl)butan-1-one (38): Obtained as a pale yellow solid in 24% yield (14 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 7.99 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.40 – 7.22 (m, 5H), 7.15 (t, *J* = 8.5 Hz, 2H), 3.74 (s, 2H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 2.03 (p, *J* = 6.9 Hz, 2H). **^{19}F NMR** (282 MHz, $CDCl_3$) δ: -105.39 (ddd, *J* = 13.6, 8.4, 5.5 Hz). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 197.9, 165.7 (d, *J* = 254.7 Hz), 138.4, 133.3 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.3 Hz), 128.7 (d, *J* = 26.3 Hz), 127.0, 115.7 (d, *J* = 21.9 Hz), 37.0, 36.1, 30.8, 23.3. **HRMS** (ESI): calc'd for $C_{17}H_{17}FOSNa^+$ $(M+Na)^+$ 311.0882, found 311.0873.

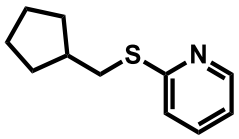


1-(4-fluorophenyl)-4-(propylthio)butan-1-one (39): Obtained as a pale yellow solid in 31% yield (15 mg) by silica gel flash column chromatography eluted with PE:EA =

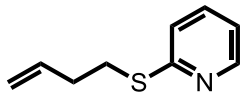
10 : 1 v/v. **^{1}H NMR** (300 MHz, $CDCl_3$) δ: 8.02 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.05 (p, *J* = 7.0 Hz, 2H), 1.63 (h, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).**^{19}F NMR** (282 MHz, $CDCl_3$) δ: -105.34 – -105.50 (m). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 198.1, 165.7 (d, *J* = 254.4 Hz), 133.4 (d, *J* = 3.1 Hz), 130.7 (d, *J* = 9.3 Hz), 115.7 (d, *J* = 21.8 Hz), 37.0, 34.0, 31.5, 23.7, 22.9, 13.5. **HRMS** (ESI): calc'd for $C_{13}H_{18}FOS^+$ $(M+H)^+$ 241.1062, found 241.1055.



1-(4-fluorophenyl)-4-(phenylselanyl)butan-1-one (41): Obtained as a colorless liquid in 11% yield (7 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.98 (ddd, *J* = 8.9, 5.2, 2.5 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.31 – 7.24 (m, 4H), 7.17 – 7.10 (m, 2H), 3.12 (t, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.16 (p, *J* = 7.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.31 (tt, *J* = 8.2, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 197.8, 165.7 (d, *J* = 254.6 Hz), 136.5, 133.3 (d, *J* = 2.9 Hz), 132.6, 130.6 (d, *J* = 9.2 Hz), 129.1, 126.9, 115.7 (d, *J* = 21.9 Hz), 37.9, 27.4, 24.4. **HRMS** (ESI): calcd for $C_{16}H_{16}F_3OSe^+$ $(M+H)^+$ 323.0345, found 323.0338.

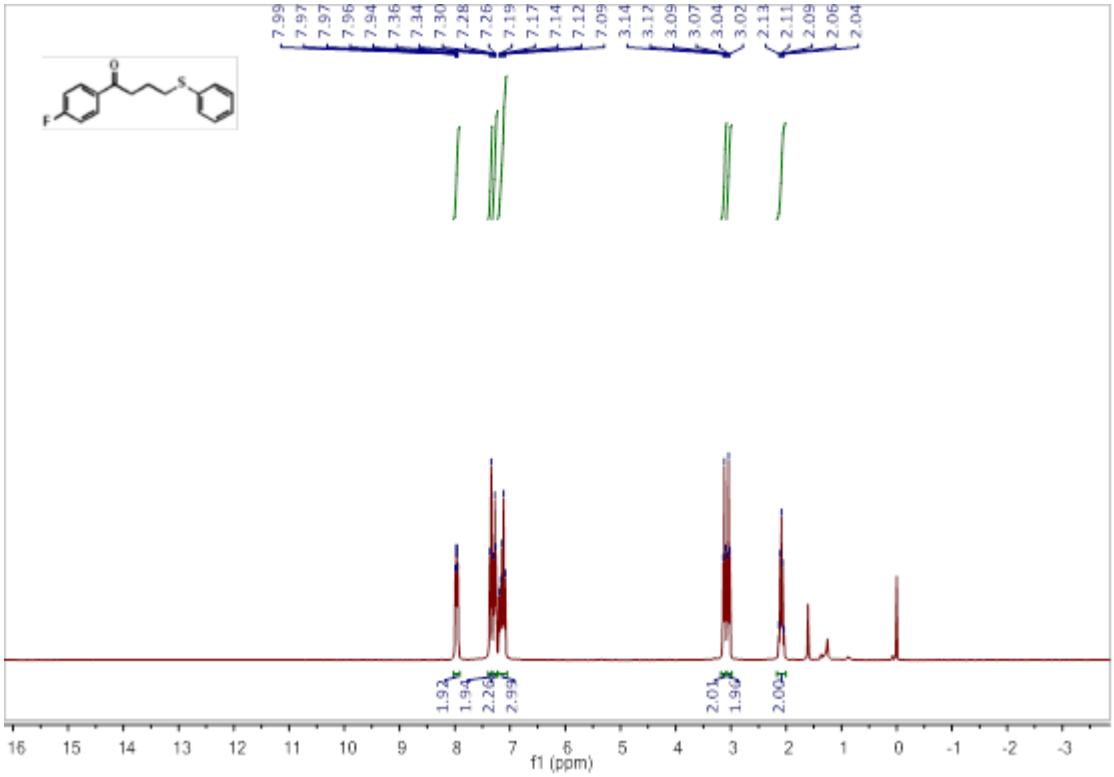


2-((cyclopentylmethyl)thio)pyridine (43): Obtained as a yellow oil in 27% yield (11 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.46 – 8.41 (m, 1H), 7.48 (td, *J* = 7.8, 1.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.98 (ddd, *J* = 7.3, 5.0, 1.0 Hz, 1H), 3.21 (d, *J* = 7.3 Hz, 2H), 2.28 – 2.17 (m, 1H), 1.93 – 1.83 (m, 2H), 1.79 – 1.63 (m, 2H), 1.60 – 1.52 (m, 2H), 1.40 – 1.32 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 159.9, 149.4, 135.8, 122.1, 119.1, 39.5, 36.0, 32.4, 31.0, 29.7, 25.3. **HRMS** (ESI): calcd for $C_{11}H_{16}NS^+$ $(M+H)^+$ 194.0998, found 194.0977.

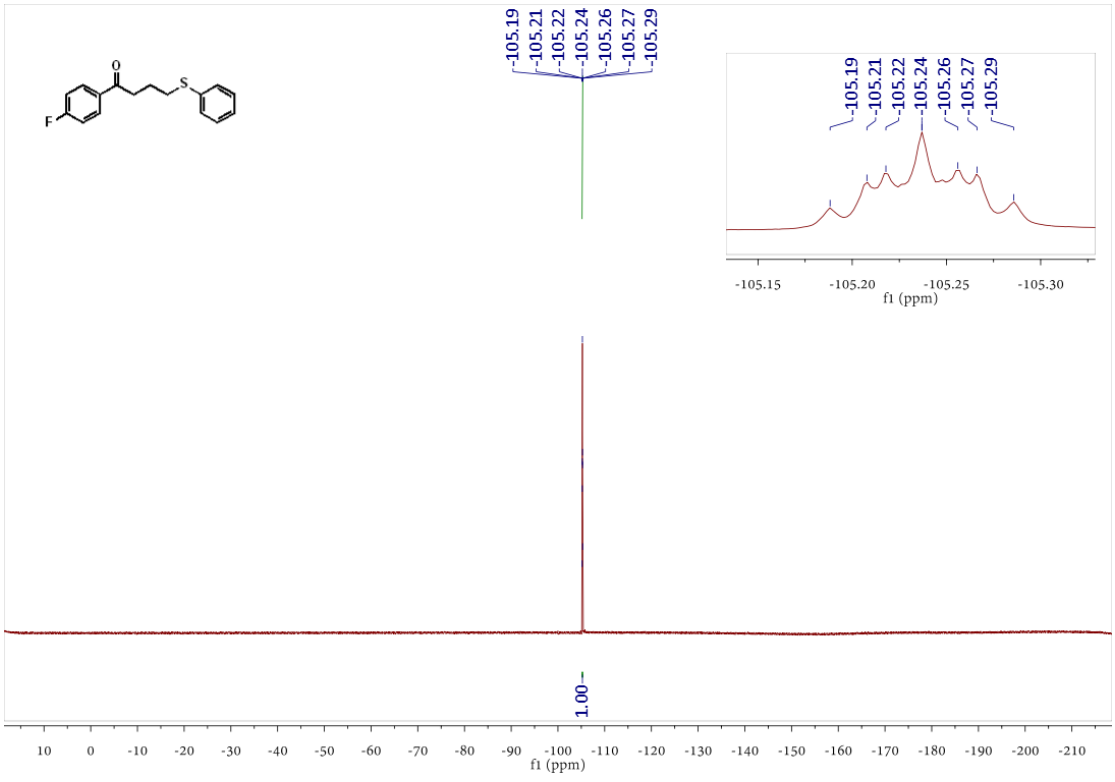


2-(but-3-en-1-ylthio)pyridine[33] **(45):** Obtained as a yellow oil in 63% yield (21 mg) by silica gel flash column chromatography eluted with PE:EA = 10 : 1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.46 – 8.42 (m, 1H), 7.48 (td, *J* = 7.9, 1.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.98 (ddd, *J* = 7.3, 4.9, 0.9 Hz, 1H), 5.91 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.14 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.08 (dd, *J* = 10.2, 1.5 Hz, 1H), 3.26 (t, *J* = 7.4 Hz, 2H), 2.49 (q, *J* = 7.0 Hz, 2H).

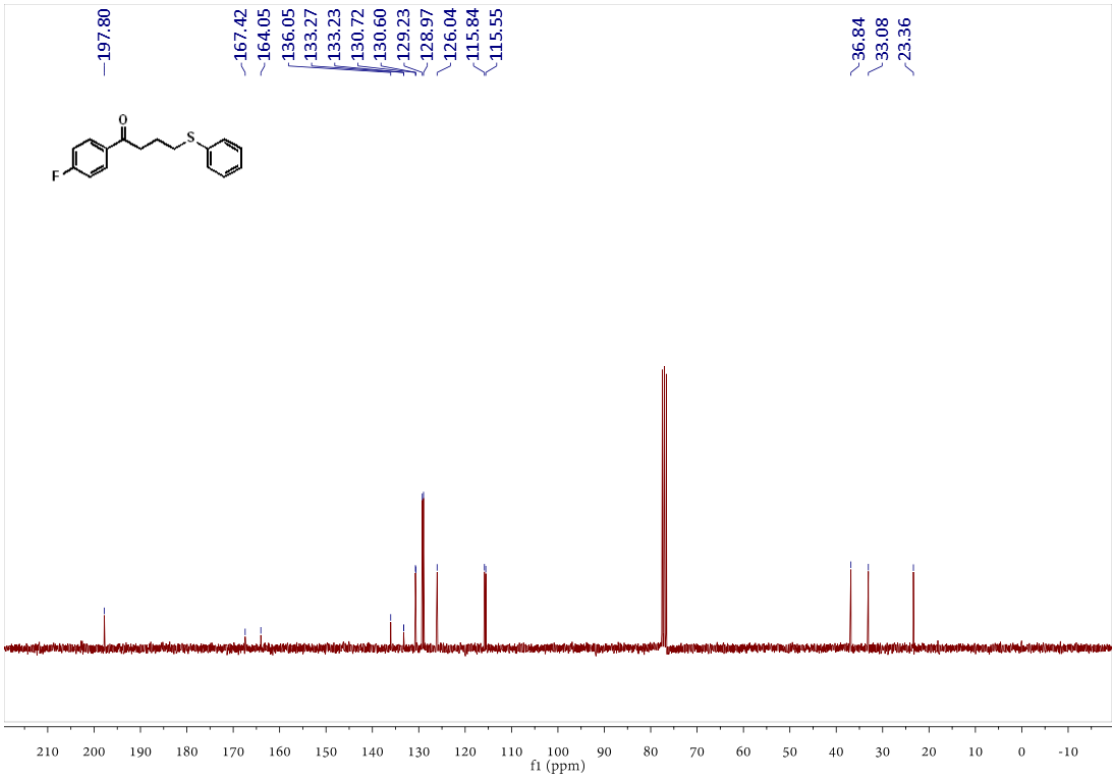
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-(phenylthio)butan-1-one (3)



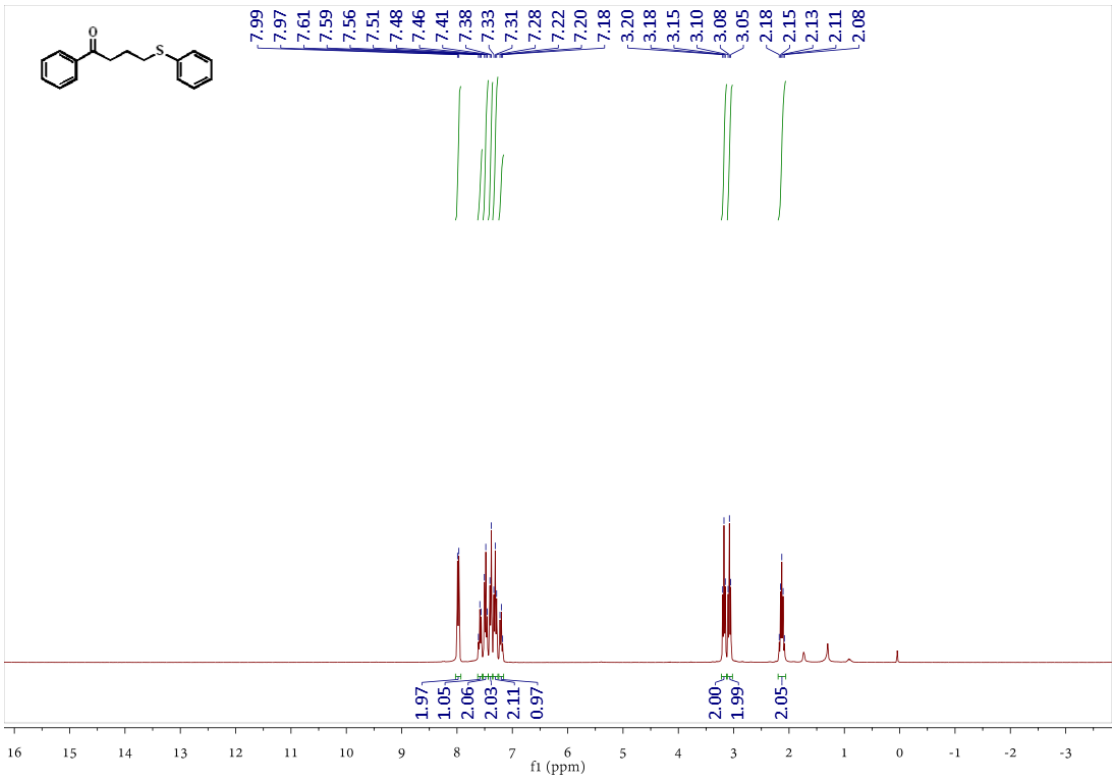
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-(phenylthio)butan-1-one (3)



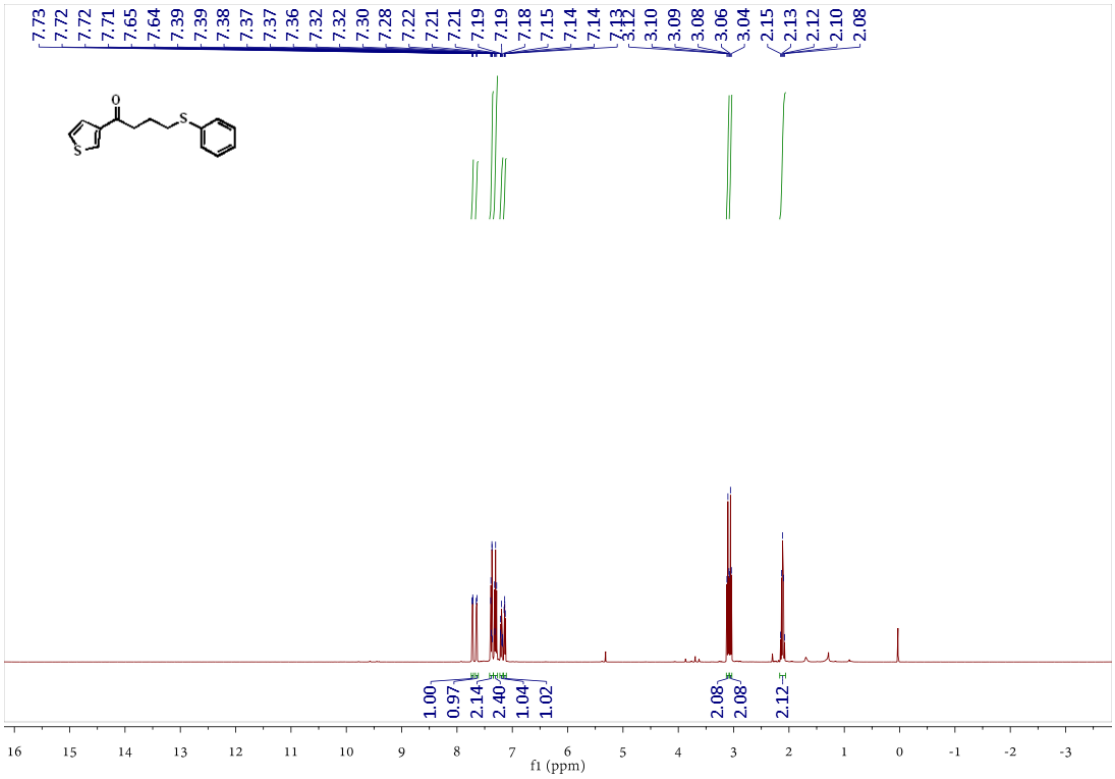
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-(phenylthio)butan-1-one (3)



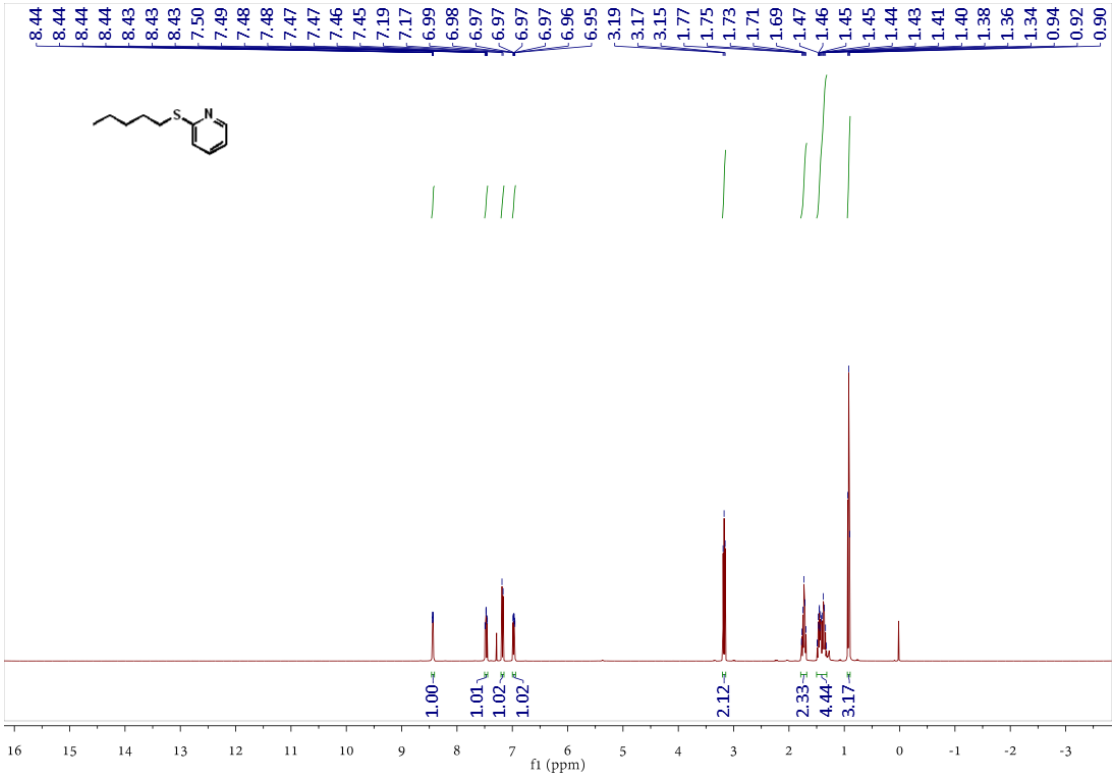
^{1}H NMR spectrum of 1-phenyl-4-(phenylthio)butan-1-one (4)



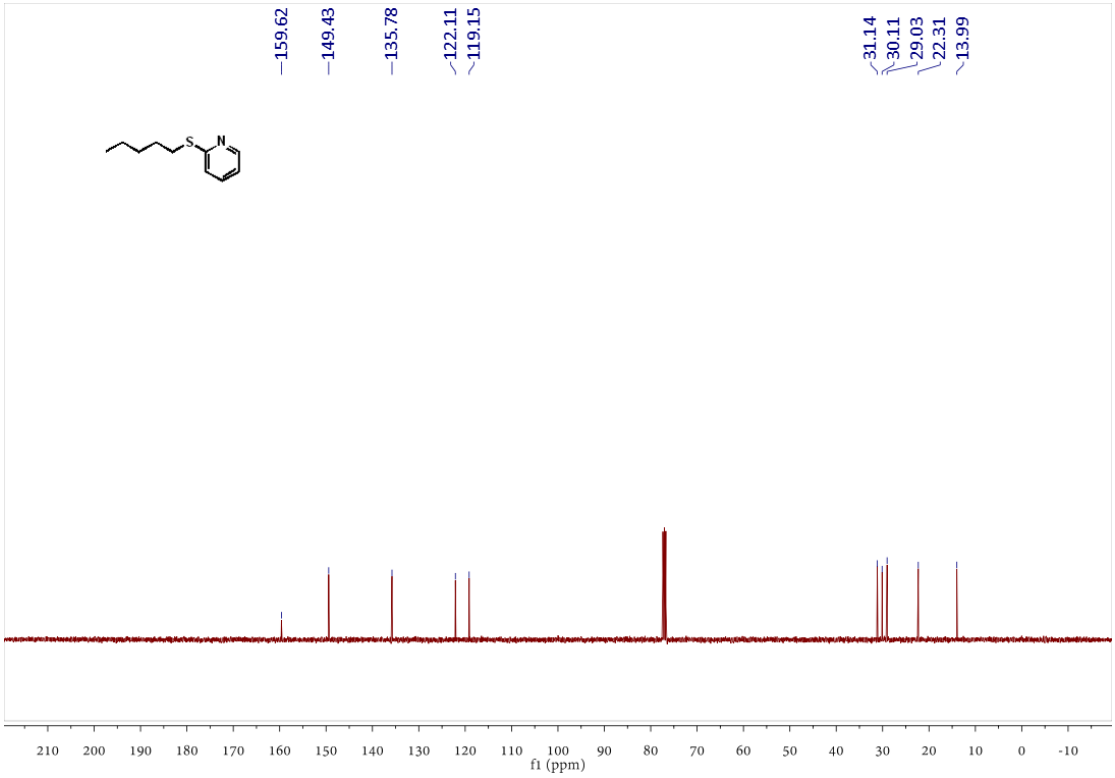
^{1}H NMR spectrum of 4-(phenylthio)-1-(thiophen-3-yl)butan-1-one (5)



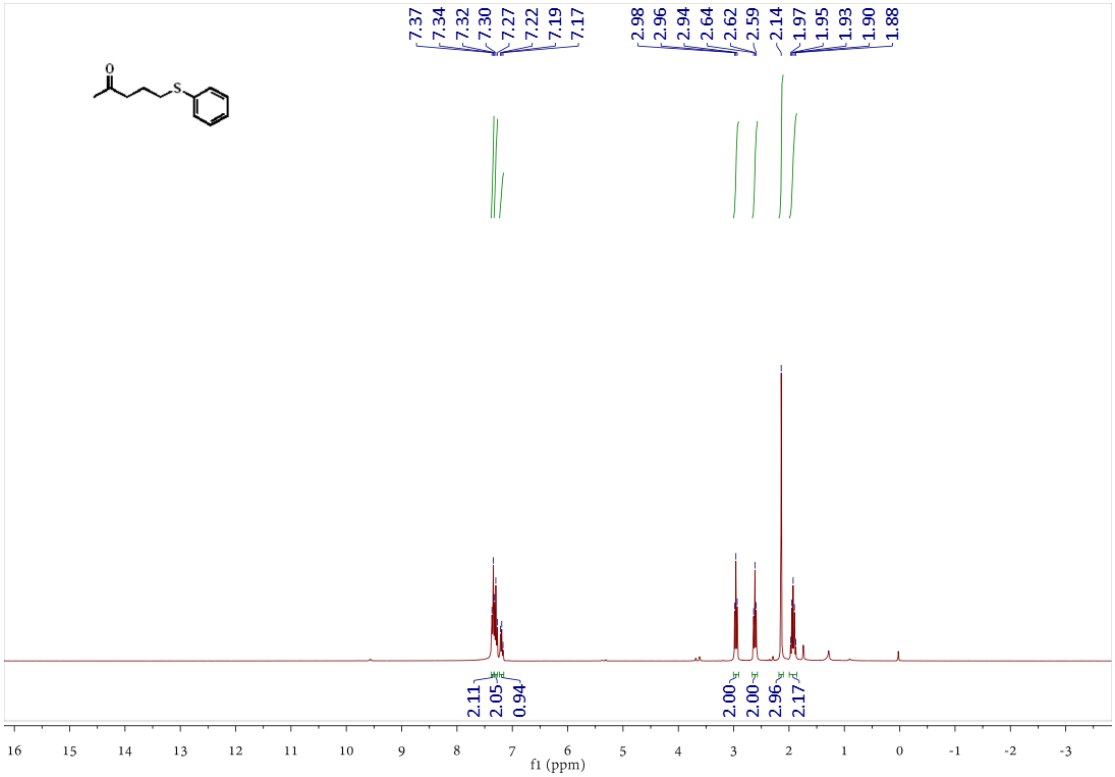
^{1}H NMR spectrum of 2-(pentylthio)pyridine (6)



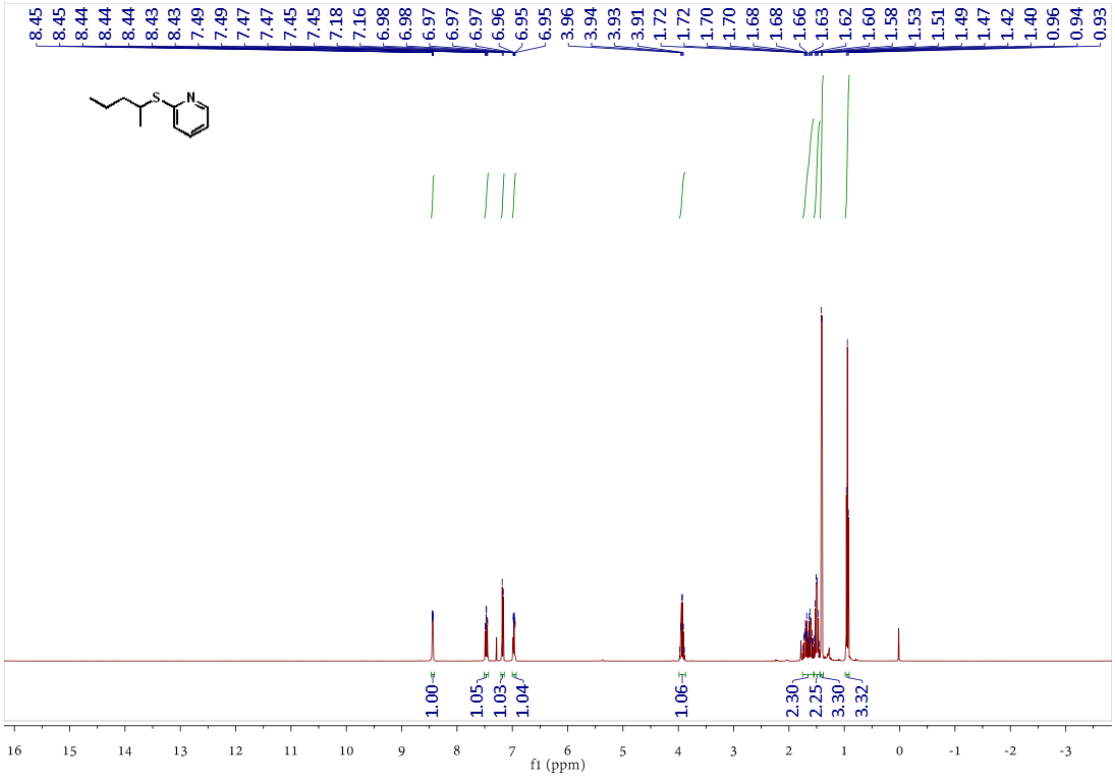
^{13}C NMR spectrum of 2-(pentylthio)pyridine (6)



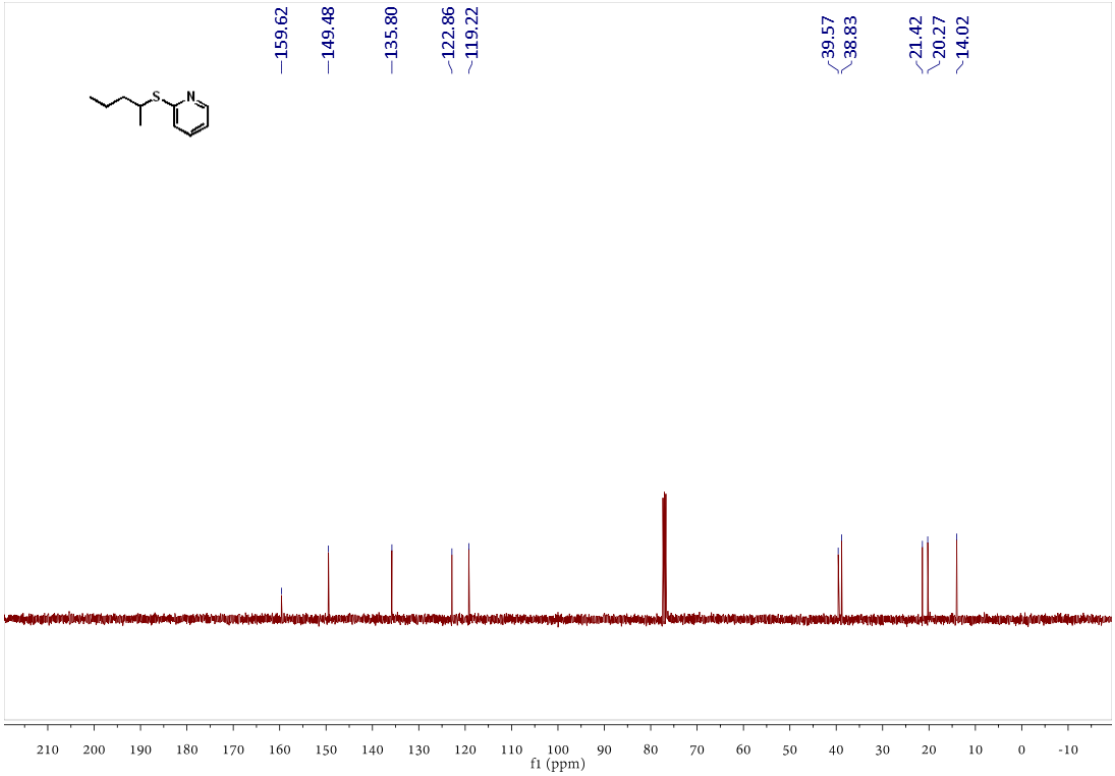
^{1}H NMR spectrum of 5-(phenylthio)pentan-2-one (7)



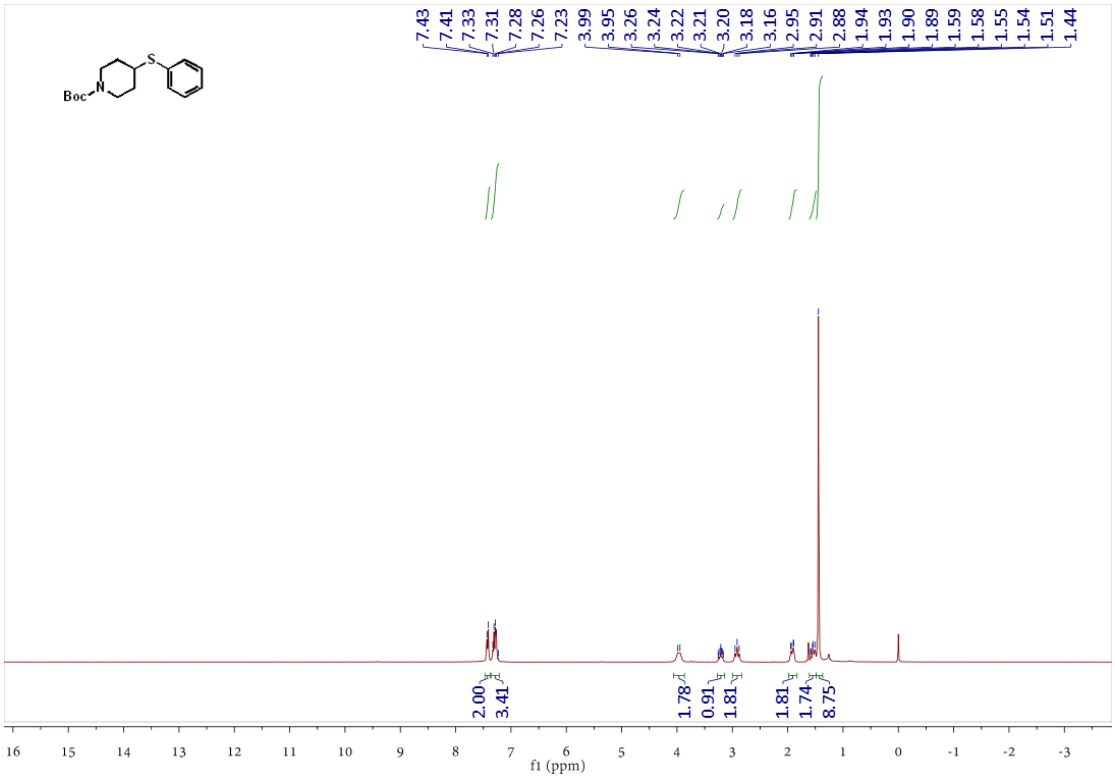
^{1}H NMR spectrum of 2-(pentan-2-ylthio)pyridine (8)



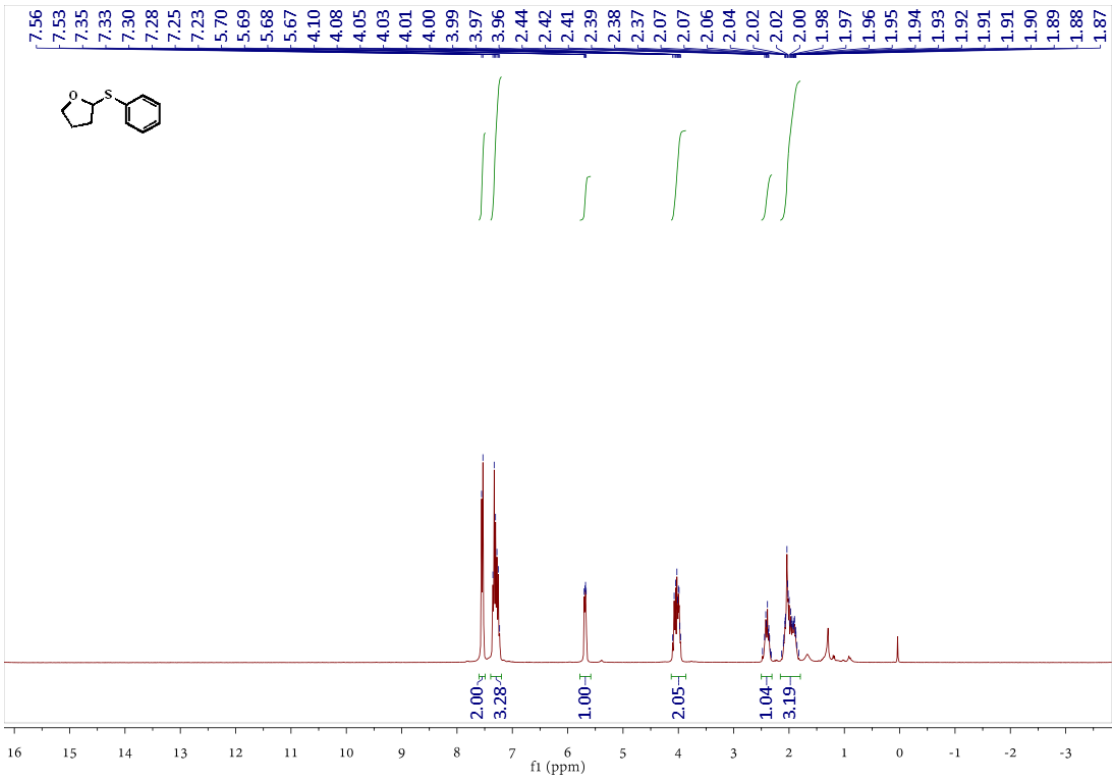
^{13}C NMR spectrum of 2-(pentan-2-ylthio)pyridine (8)



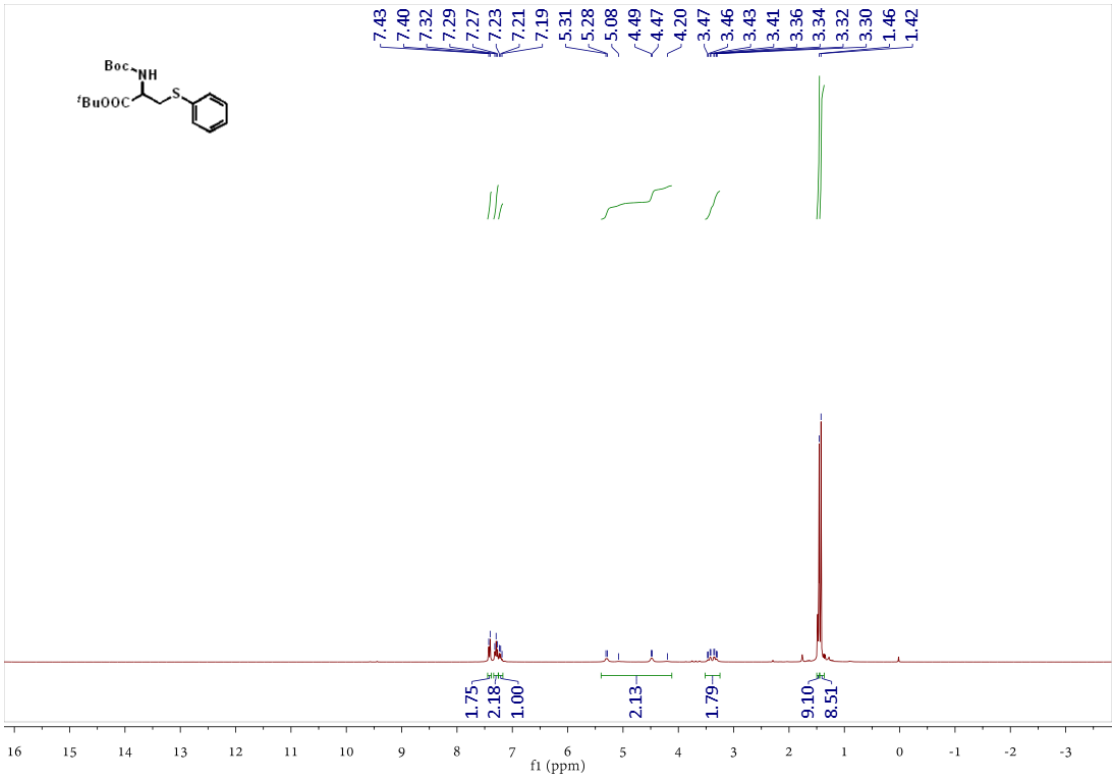
^{1}H NMR spectrum of *tert*-butyl-4-(phenylthio)piperidine-1-carboxylate (9)



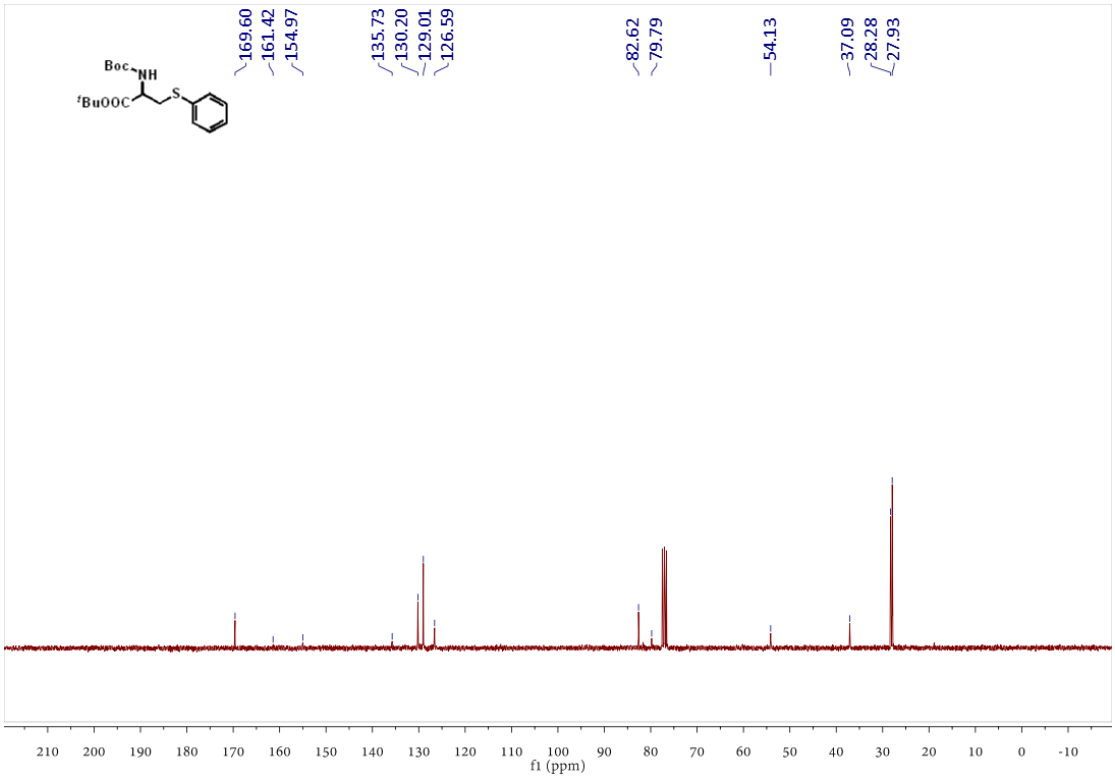
^{1}H NMR spectrum of 2-(phenylthio)tetrahydrofuran (10)



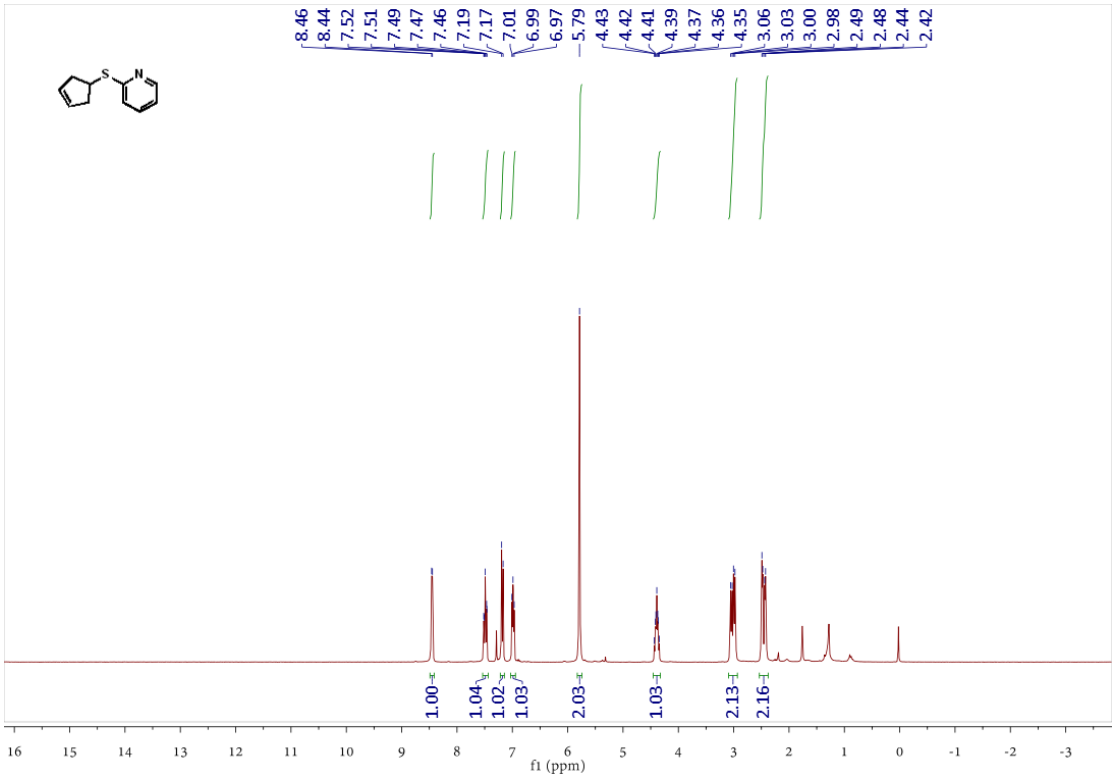
^{1}H NMR spectrum of
***tert*-butyl-2-((*tert*-butoxycarbonyl)amino)-3-(phenylthio)propanoate (11)**



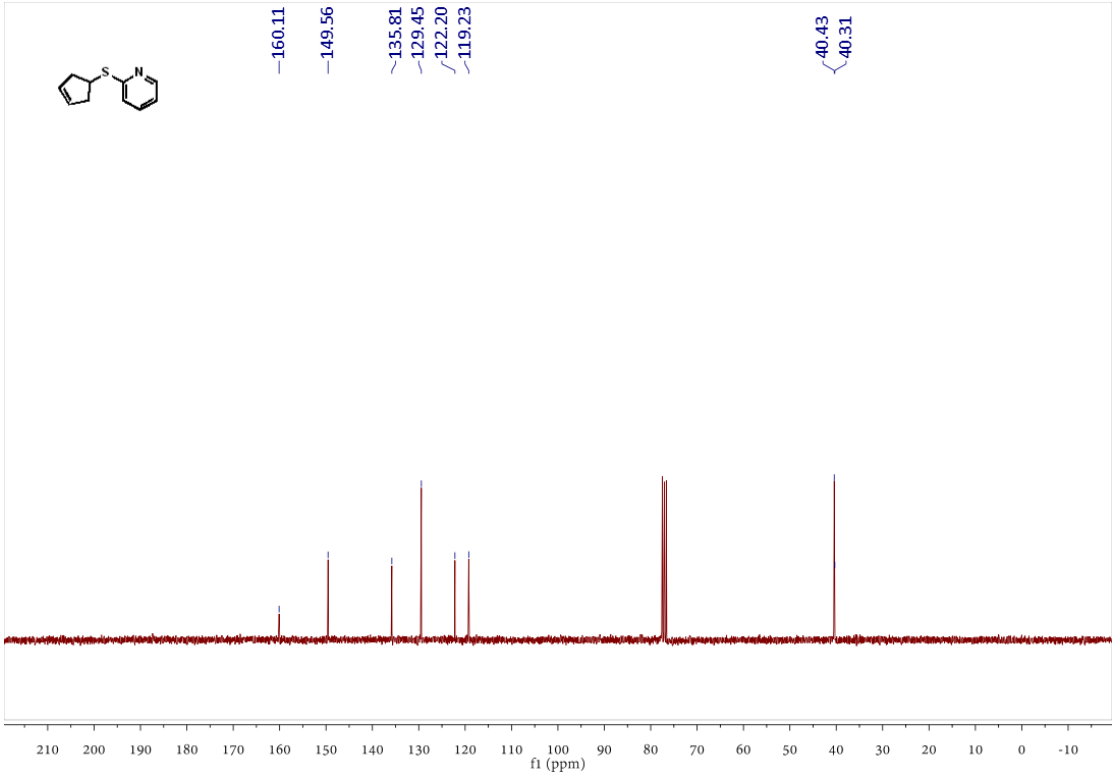
^{13}C NMR spectrum of
***tert*-butyl-2-((*tert*-butoxycarbonyl)amino)-3-(phenylthio)propanoate (11)**



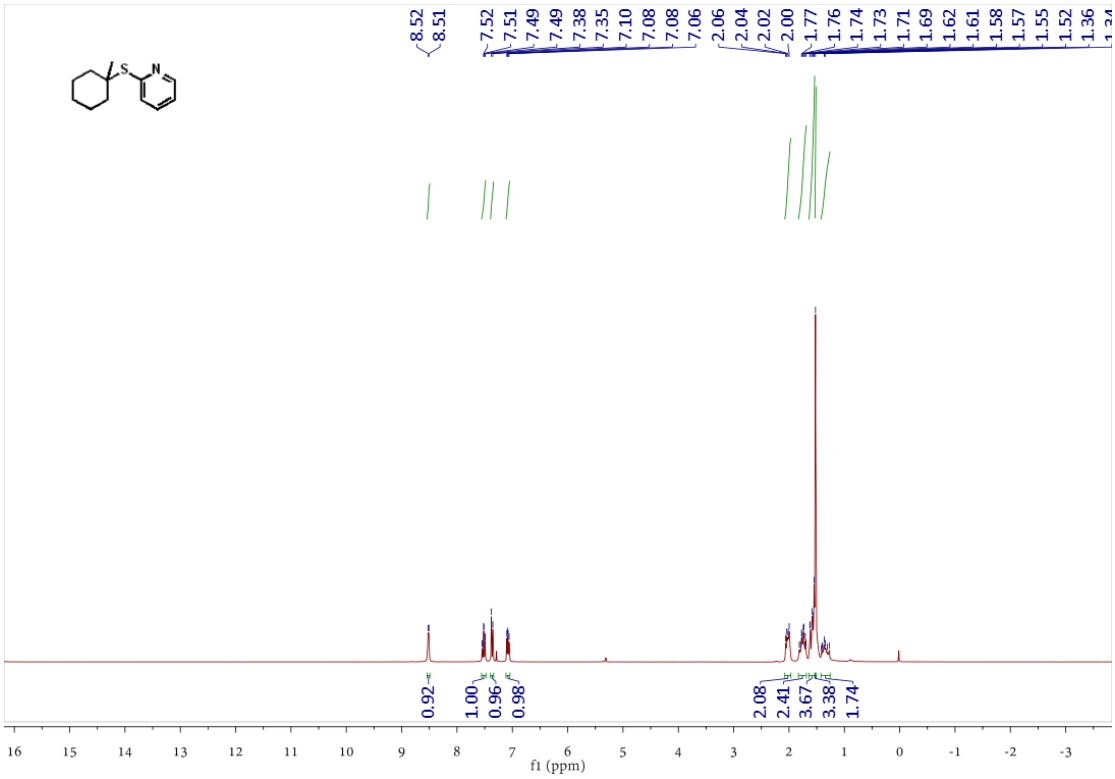
^{1}H NMR spectrum of 2-(cyclopent-3-en-1-ylthio)pyridine (12)



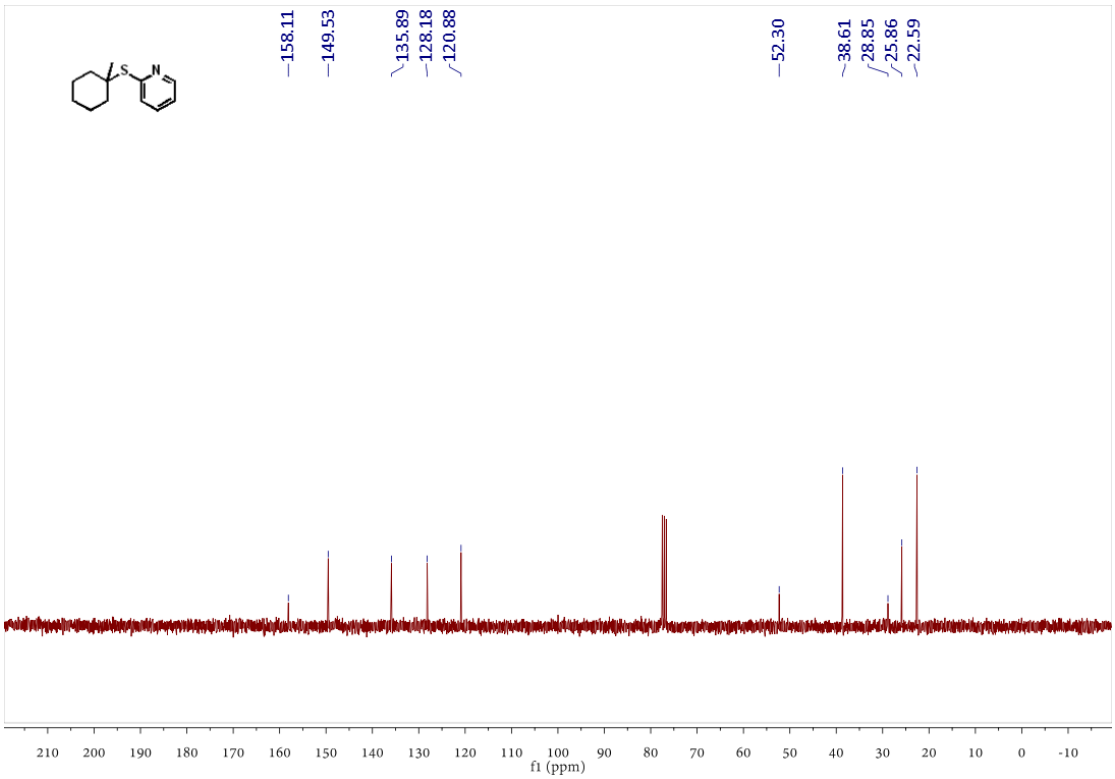
^{13}C NMR spectrum of 2-(cyclopent-3-en-1-ylthio)pyridine (12)



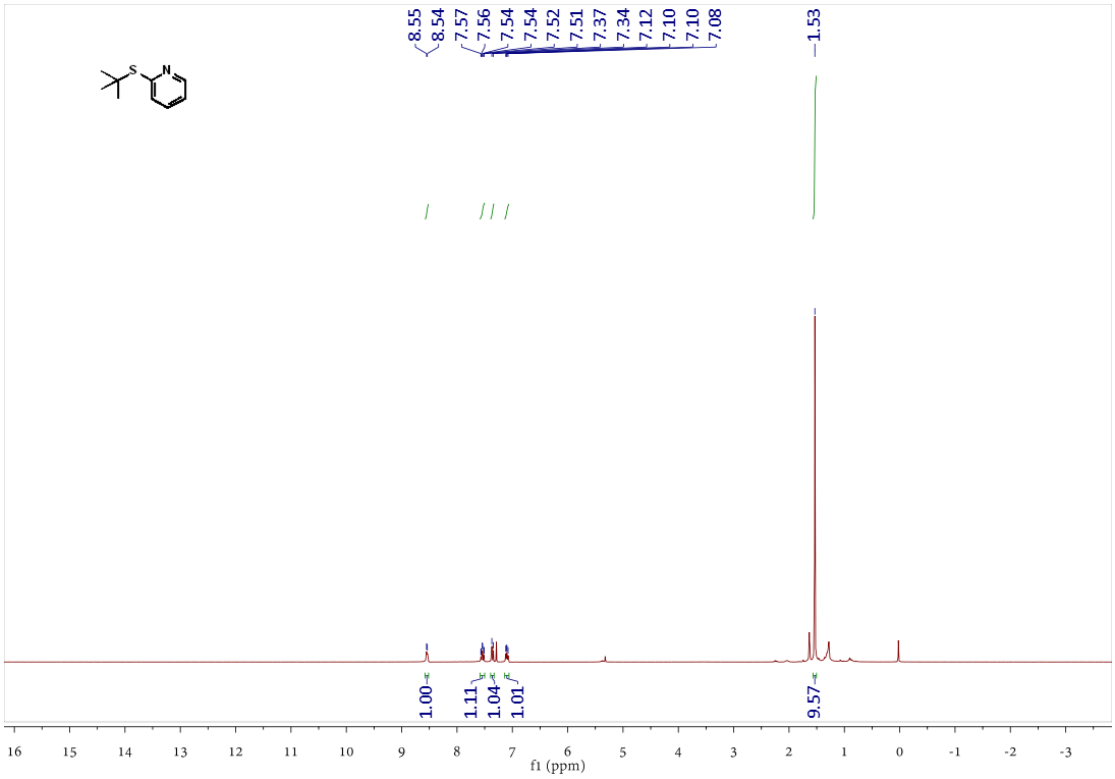
^{1}H NMR spectrum of 2-((1-methylcyclohexyl)thio)pyridine (13)



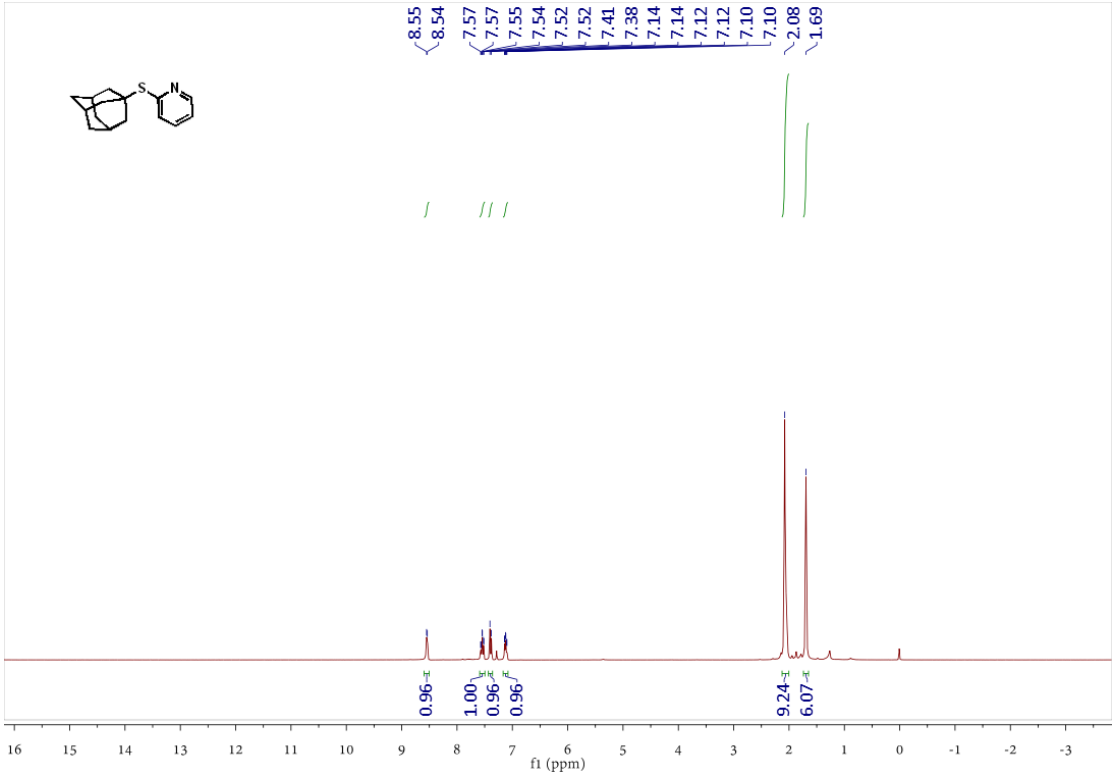
^{13}C NMR spectrum of 2-((1-methylcyclohexyl)thio)pyridine (13)



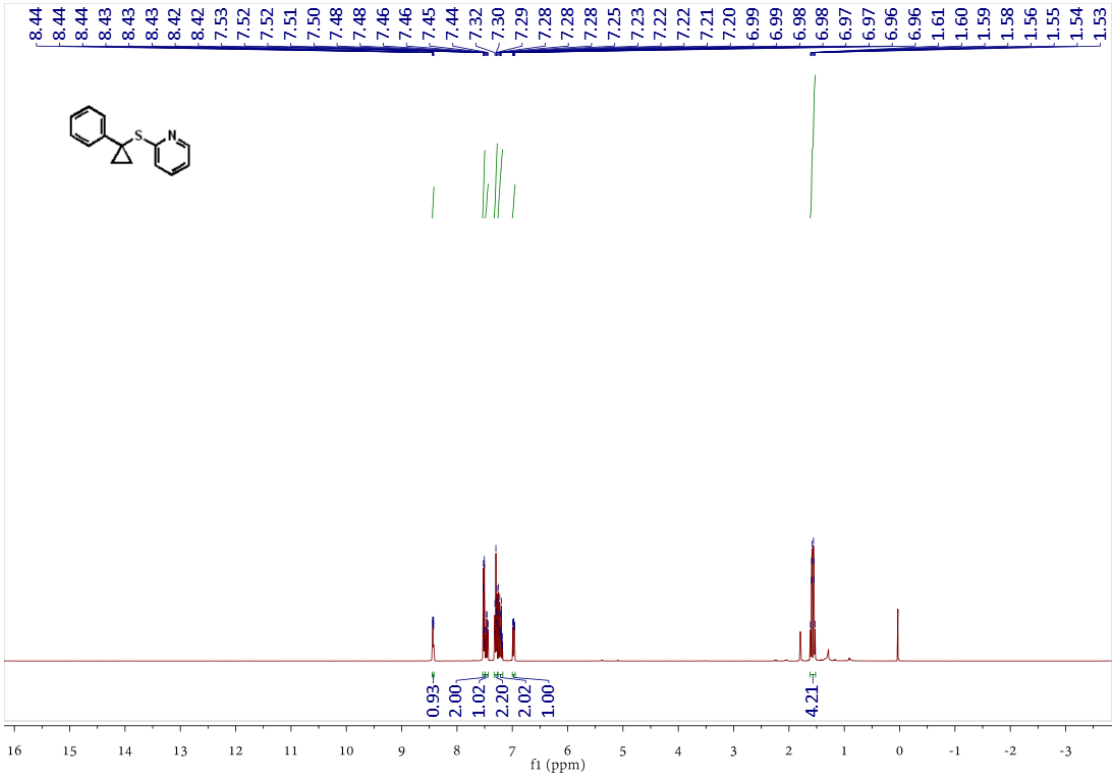
^{1}H NMR spectrum of 2-(*tert*-butylthio)pyridine (14)



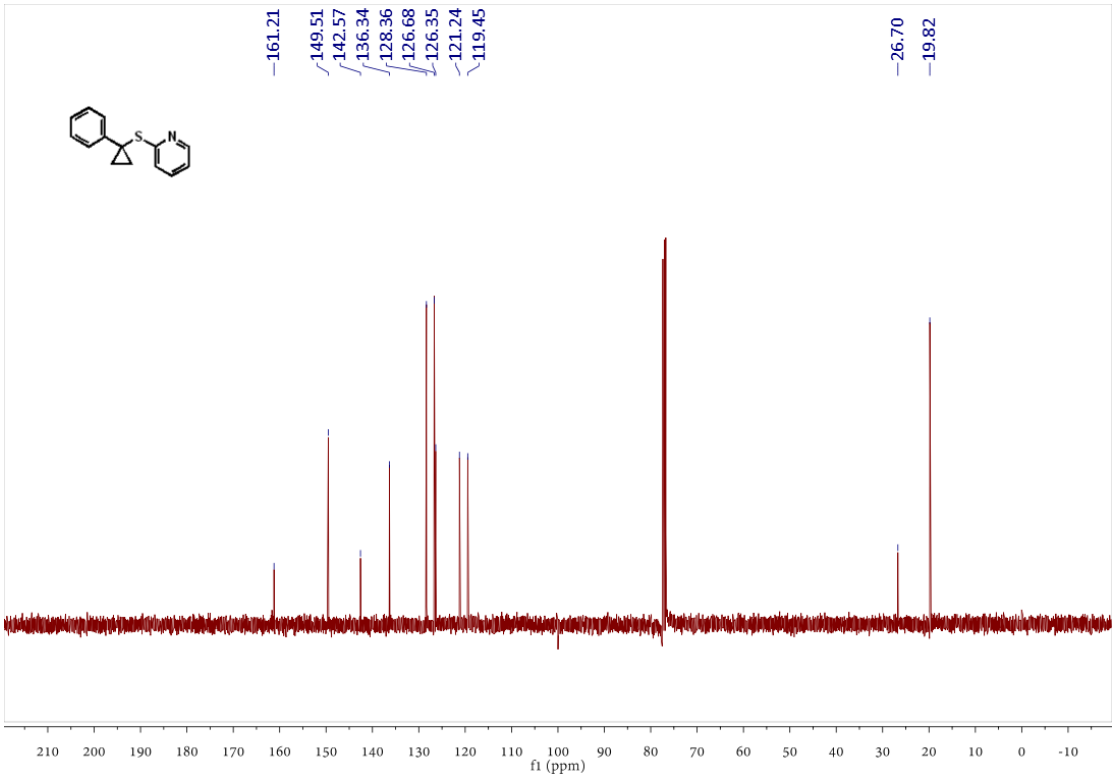
^{1}H NMR spectrum of 2-((3s,5s,7s)-adamantan-1-ylthio)pyridine (15)



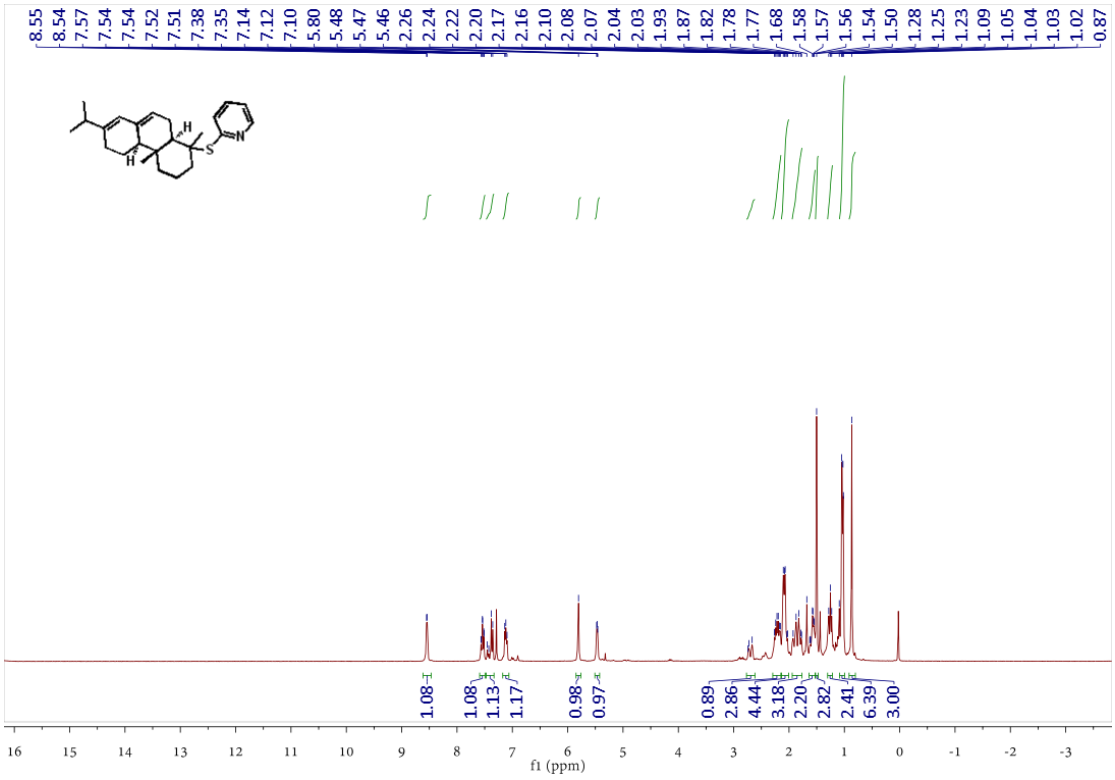
^{1}H NMR spectrum of 2-((1-phenylcyclopropyl)thio)pyridine (16)



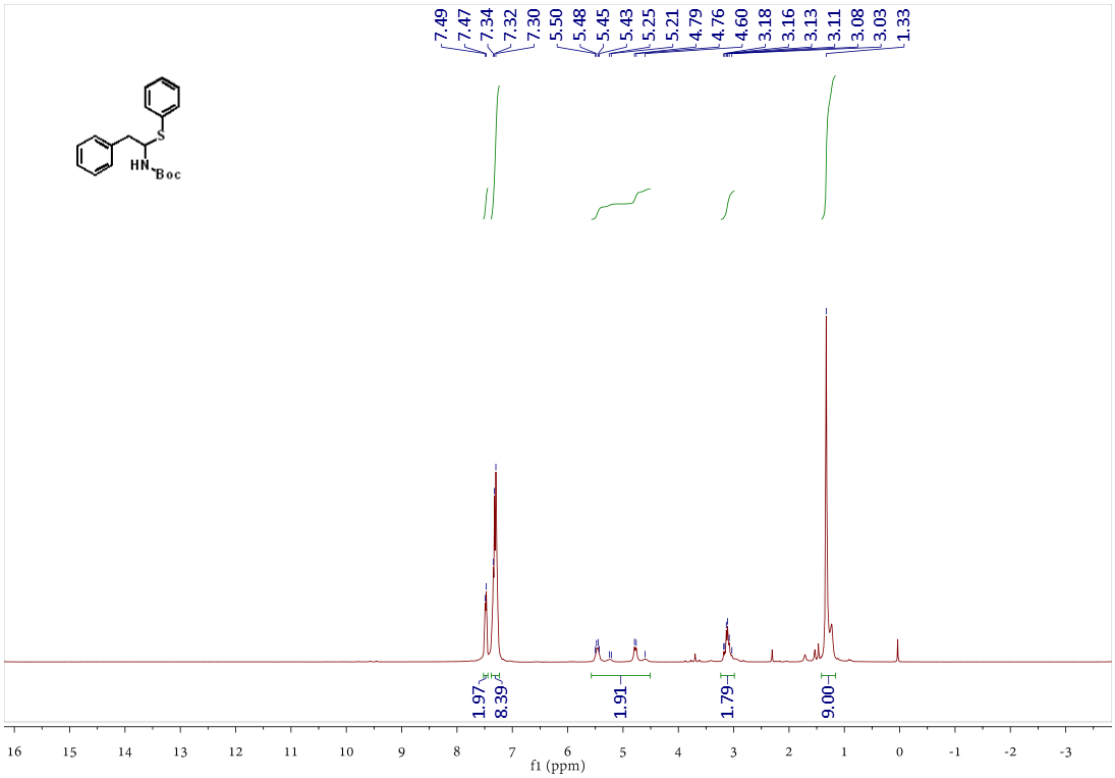
^{13}C NMR spectrum of 2-((1-phenylcyclopropyl)thio)pyridine (16)



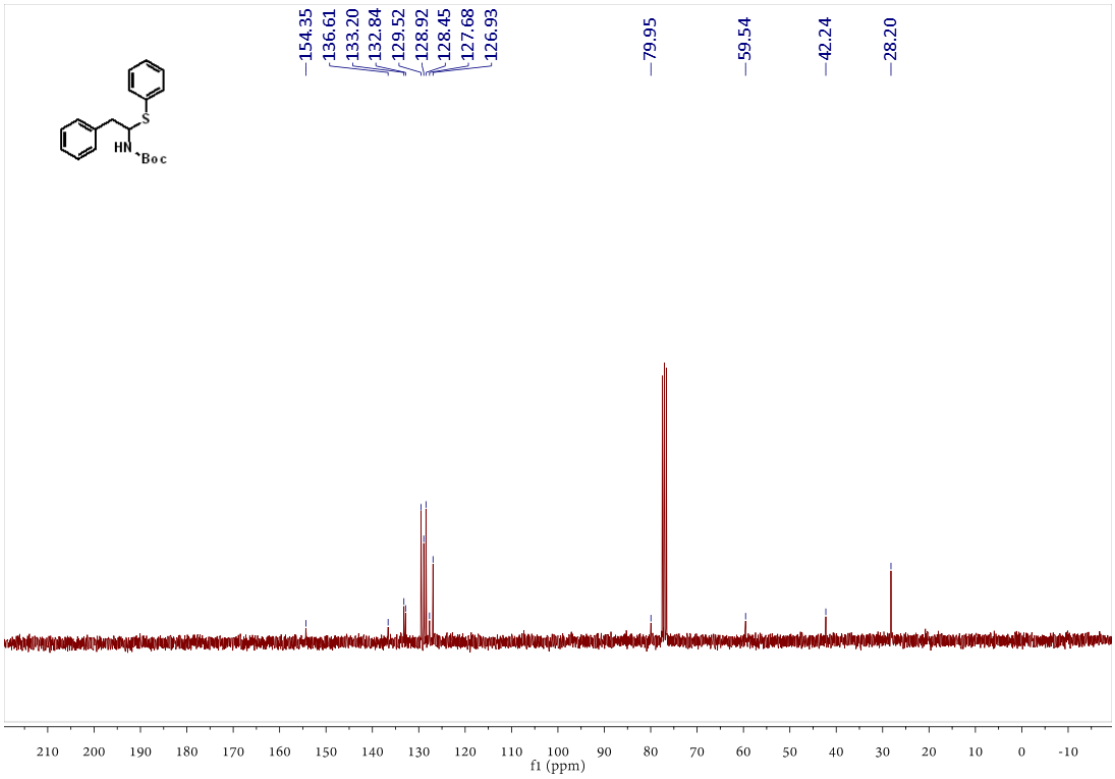
^{1}H NMR spectrum of 2-(((4aR,4bR,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthren-1-yl)thio)pyridine (17)



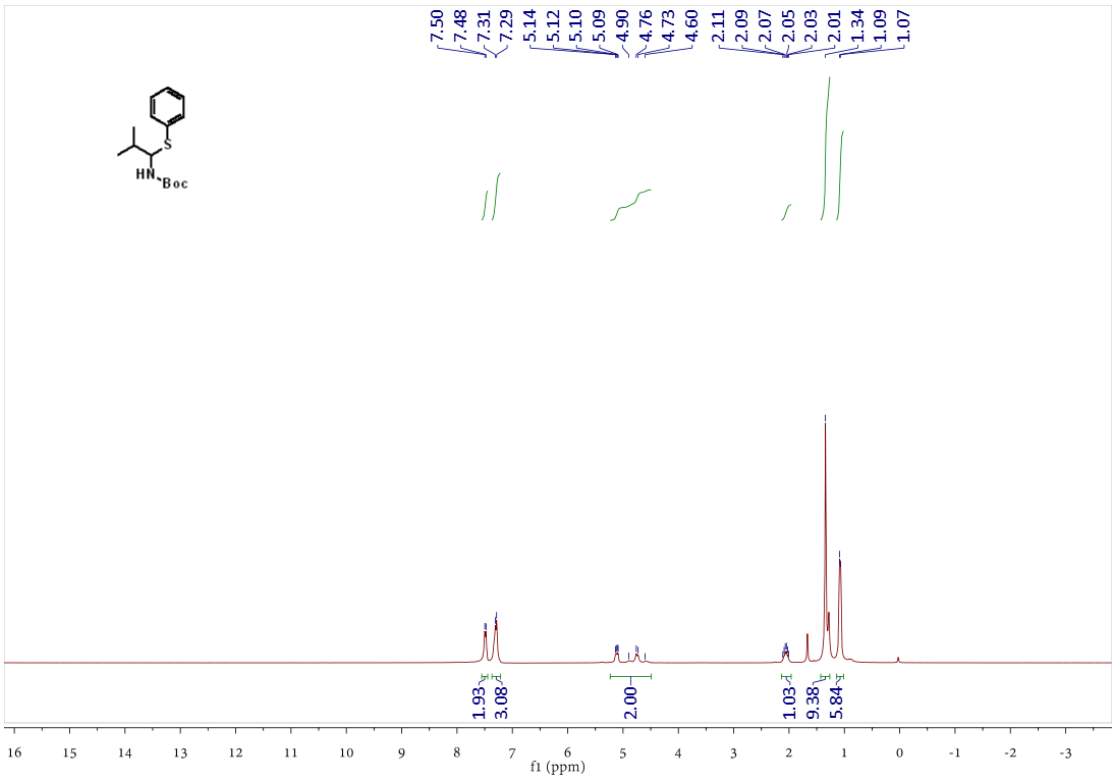
^{1}H NMR spectrum of *tert*-butyl-(2-phenyl-1-(phenylthio)ethyl)carbamate (18)



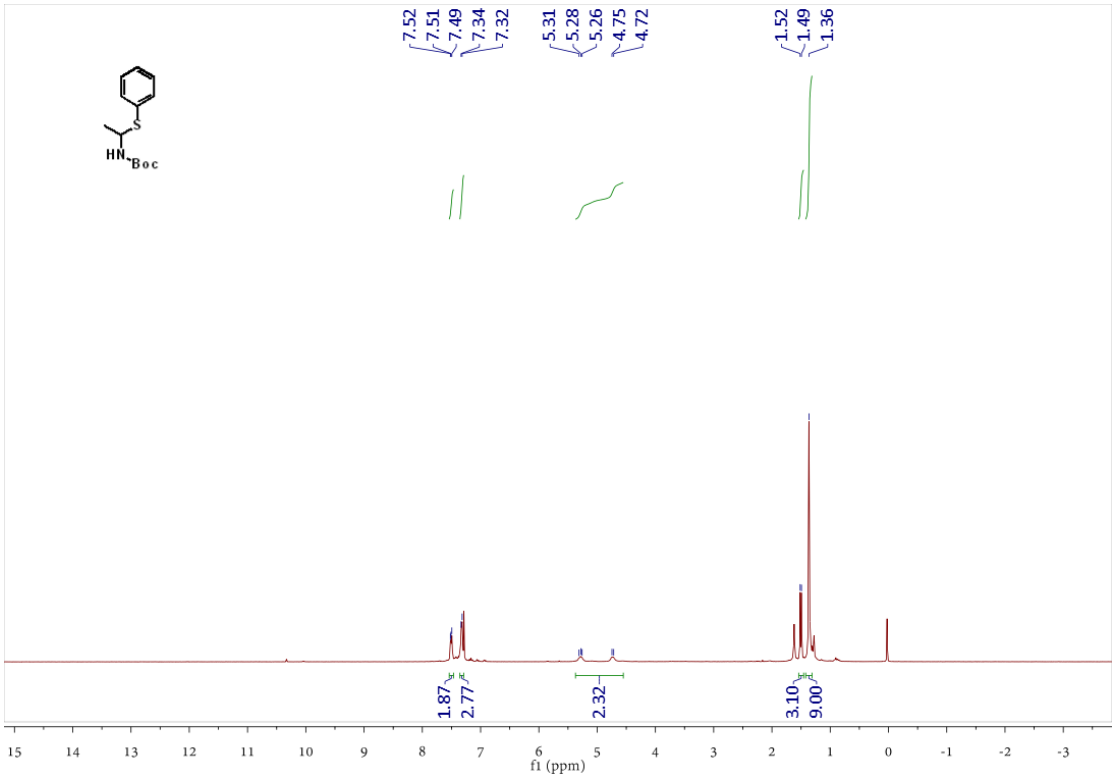
^{13}C NMR spectrum of *tert*-butyl-(2-phenyl-1-(phenylthio)ethyl)carbamate (18)



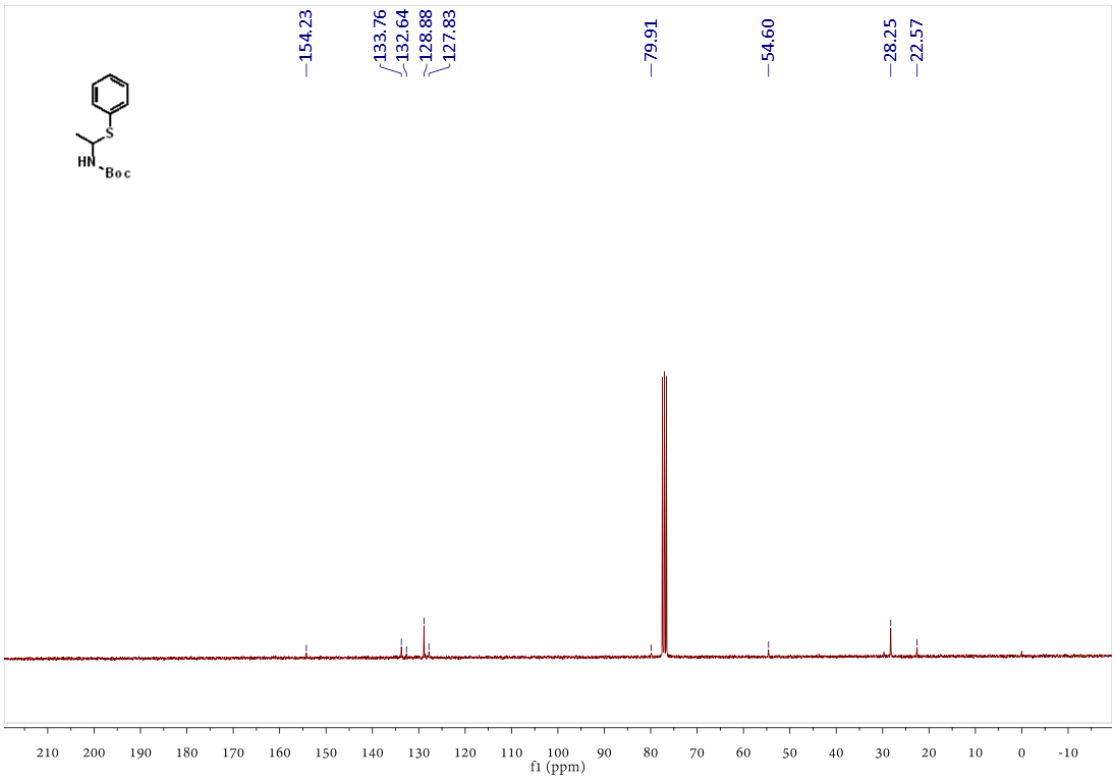
^{1}H NMR spectrum of *tert*-butyl (2-methyl-1-(phenylthio)propyl)carbamate (19)



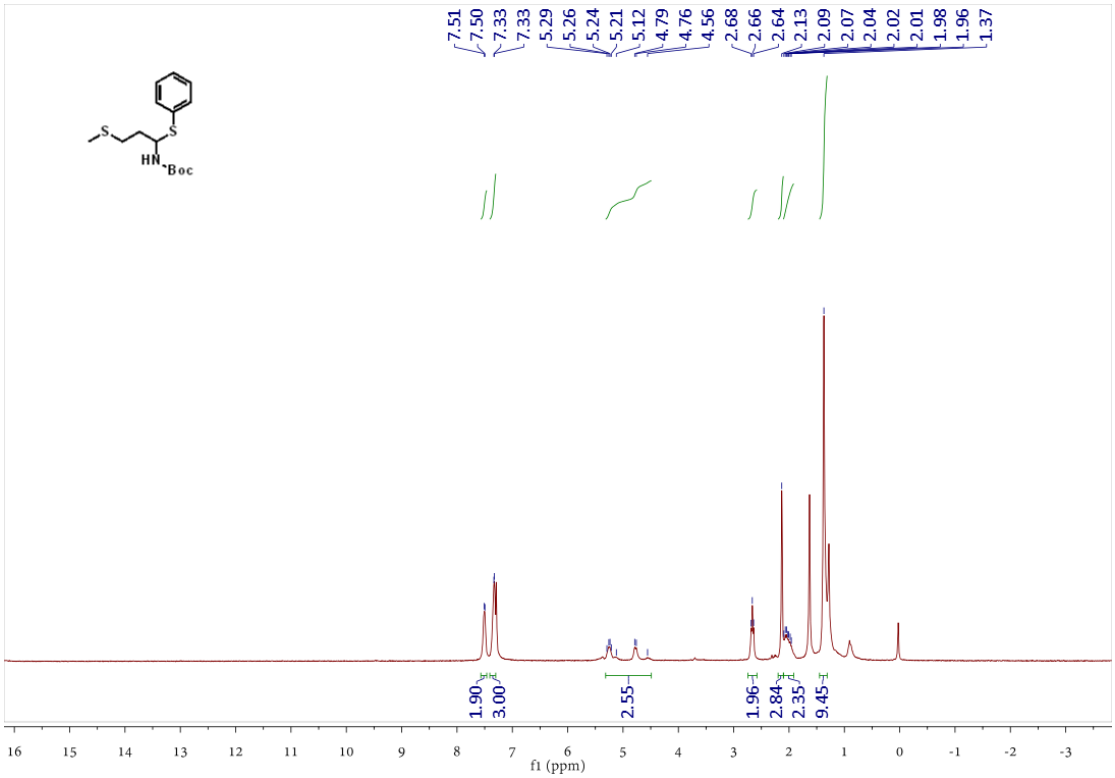
^{1}H NMR spectrum of *tert*-butyl-(1-(phenylthio)ethyl)carbamate (20)



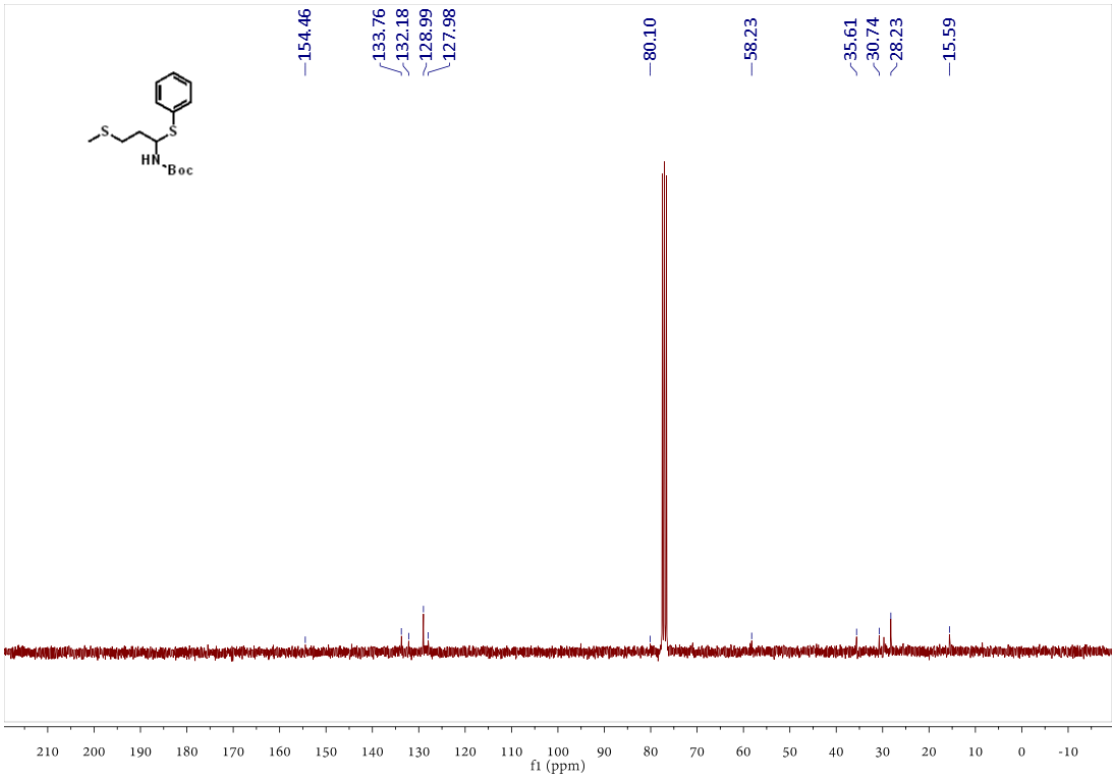
^{13}C NMR spectrum of *tert*-butyl-(1-(phenylthio)ethyl)carbamate (20)



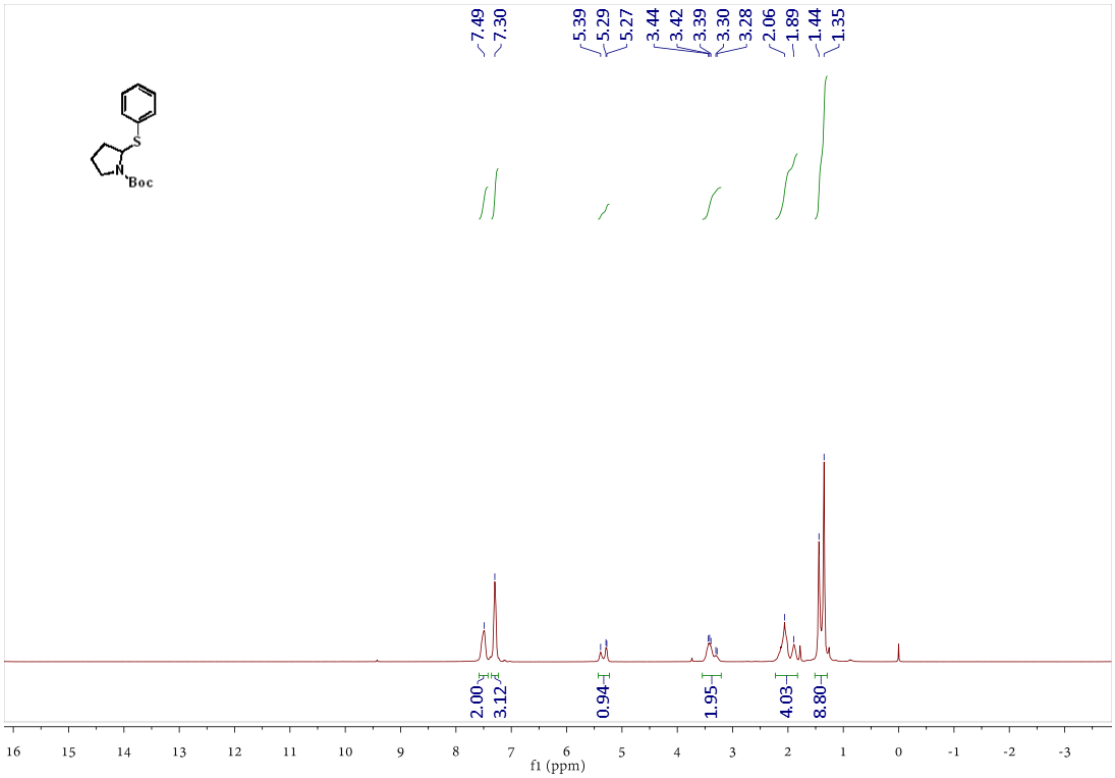
^{1}H NMR spectrum of *tert*-butyl-(3-(methylthio)-1-(phenylthio)propyl)carbamate (21)



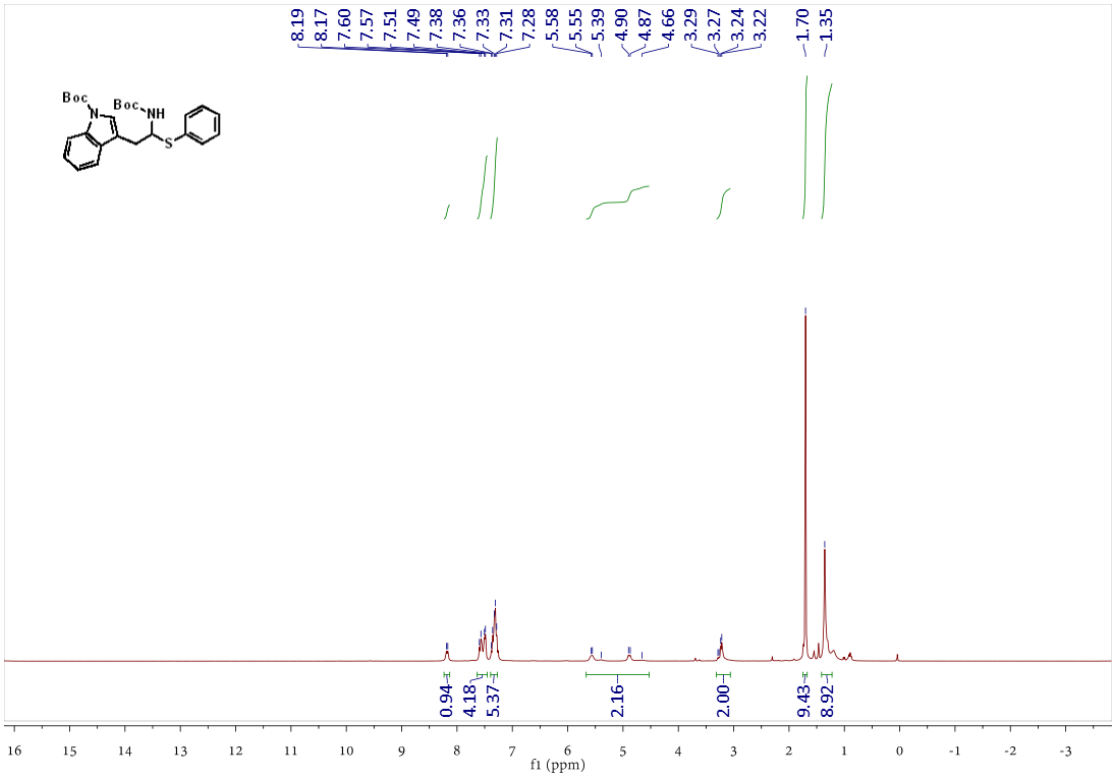
^{13}C NMR spectrum of *tert*-butyl-(3-(methylthio)-1-(phenylthio)propyl)carbamate (21)



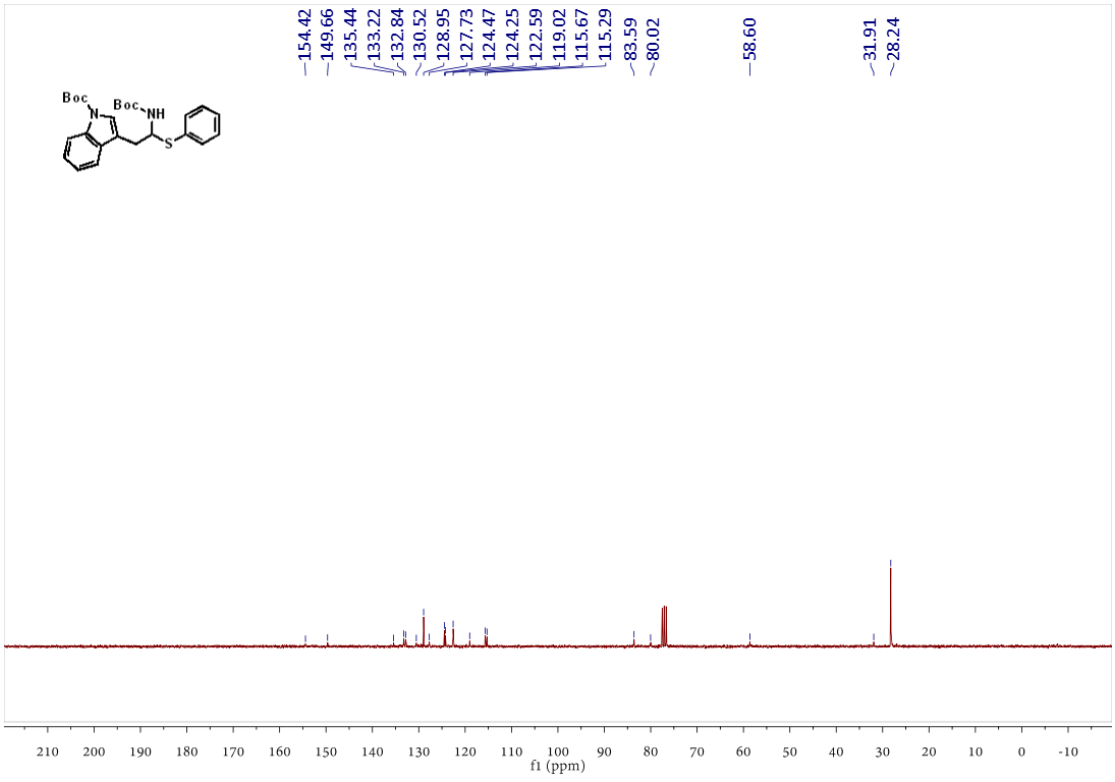
^{1}H NMR spectrum of *tert*-butyl-2-(phenylthio)pyrrolidine-1-carboxylate (22)



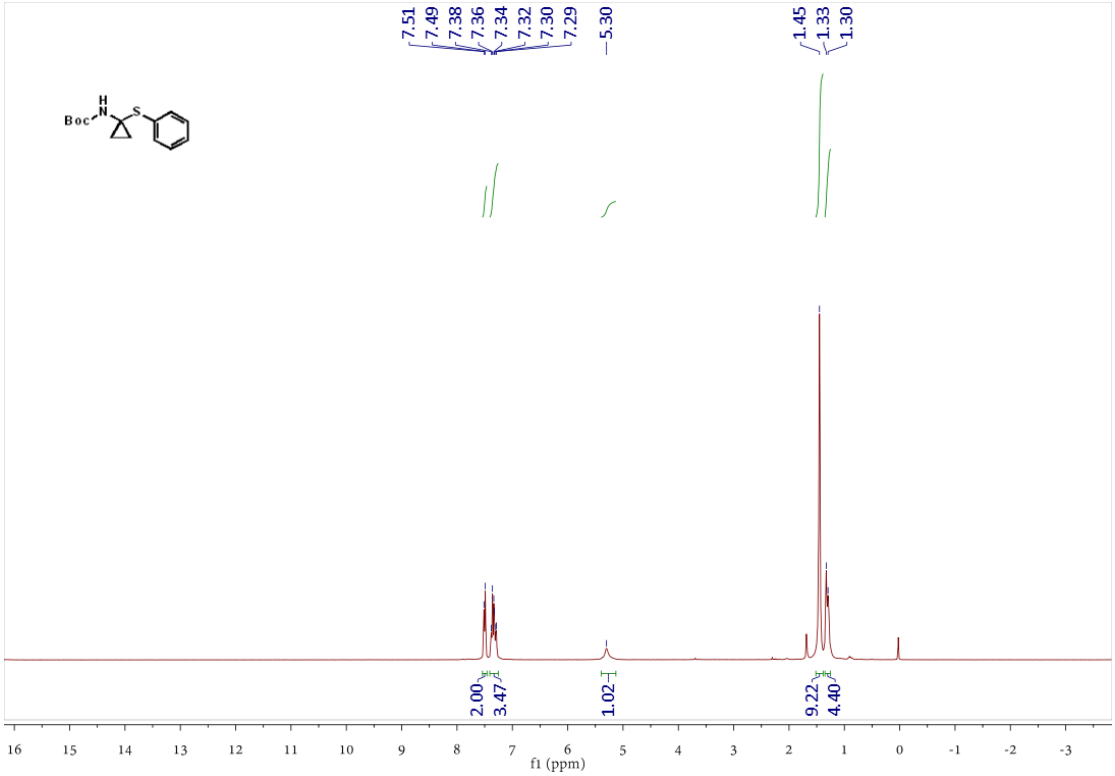
^{1}H NMR spectrum of *tert*-butyl-3-(2-((tert-butoxycarbonyl)amino)-2-(phenylthio)ethyl)-1H-indole-1-carboxylate (23)



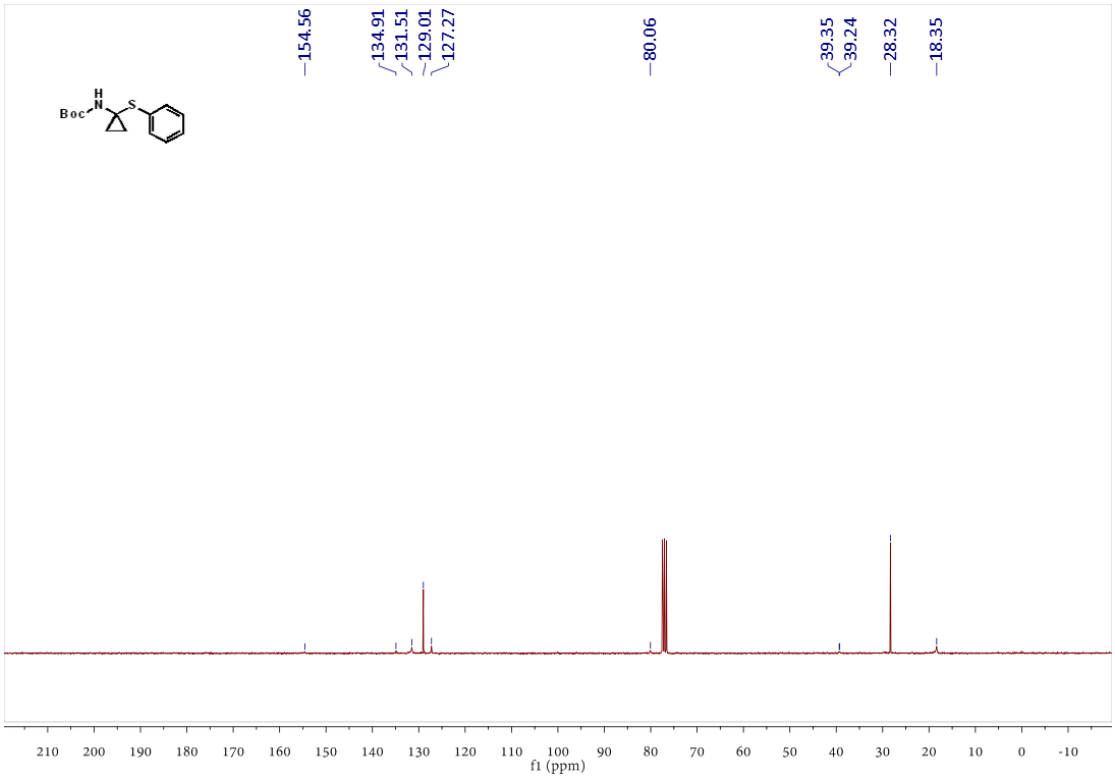
^{13}C NMR spectrum of *tert*-butyl-3-(2-((tert-butoxycarbonyl)amino)-2-(phenylthio)ethyl)-1H-indole-1-carboxylate (23)



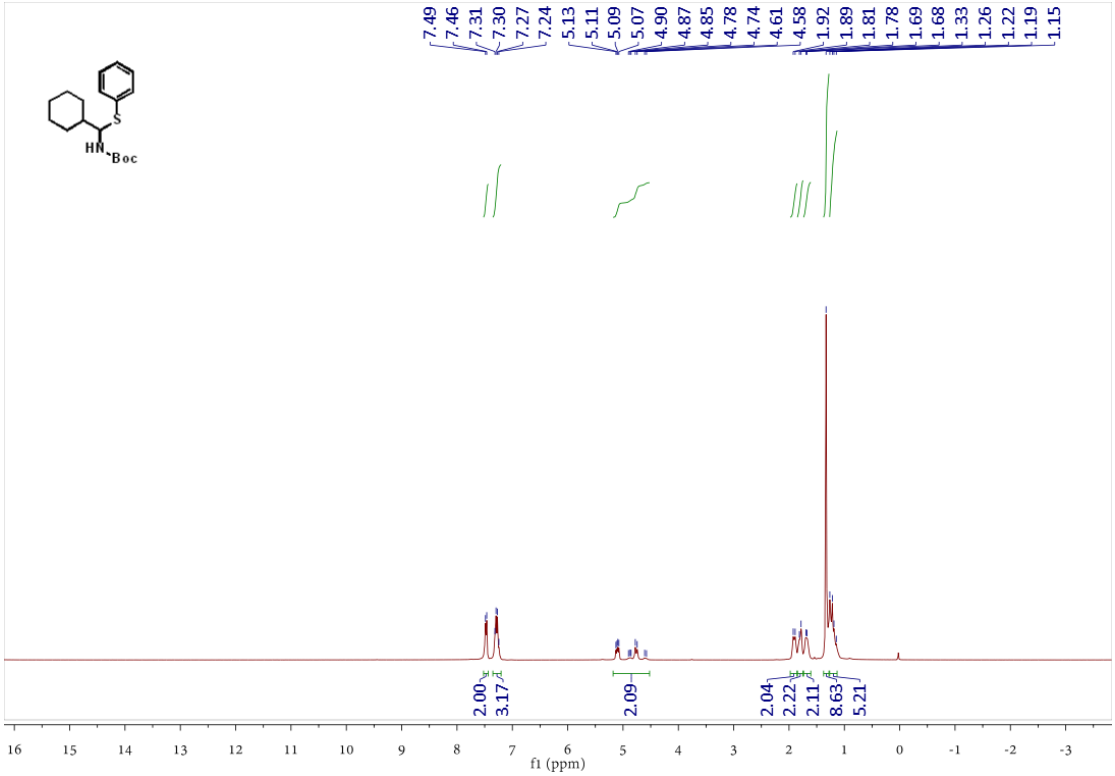
^{1}H NMR spectrum of *tert*-butyl-(1-(phenylthio)cyclopropyl)carbamate (24)



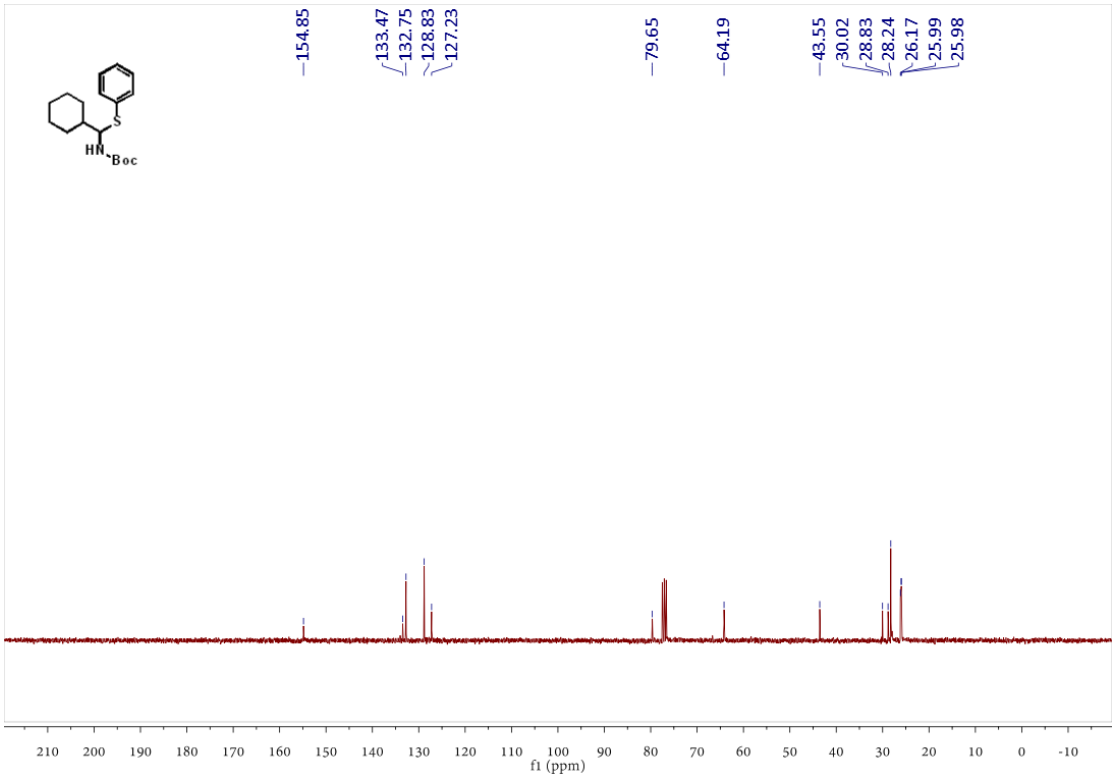
^{13}C NMR spectrum of *tert*-butyl-(1-(phenylthio)cyclopropyl)carbamate (24)



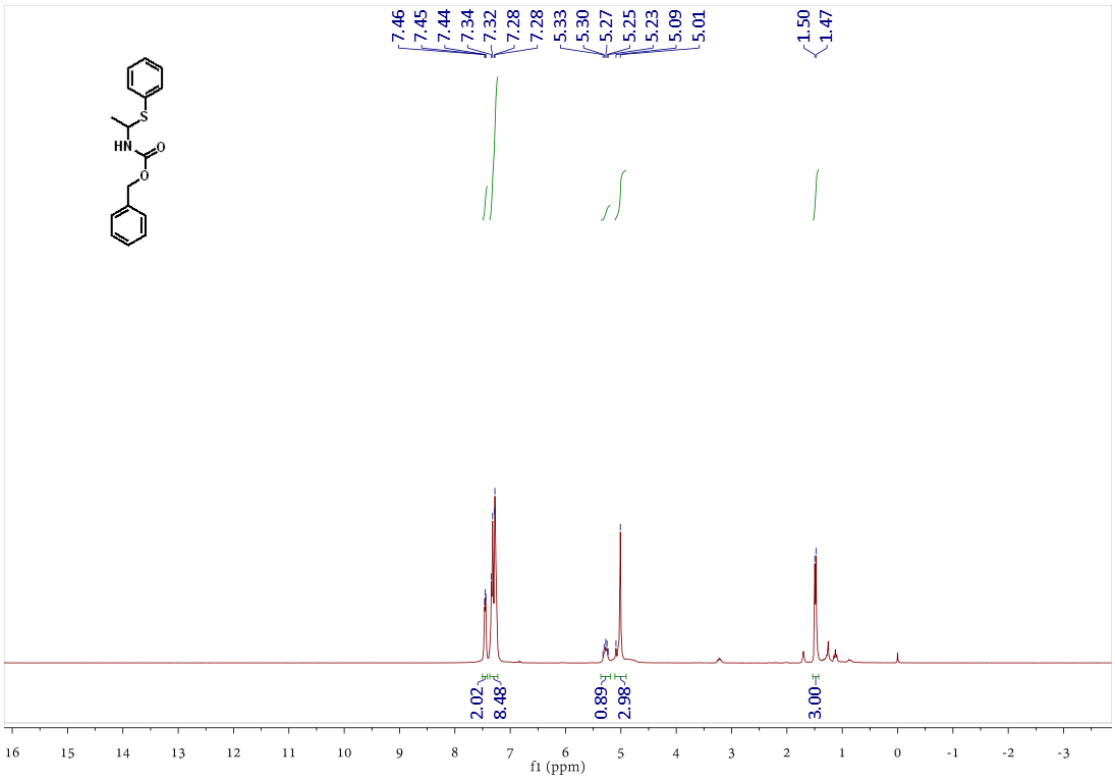
^{1}H NMR spectrum of *tert*-butyl-(cyclohexyl(phenylthio)methyl)carbamate (25)



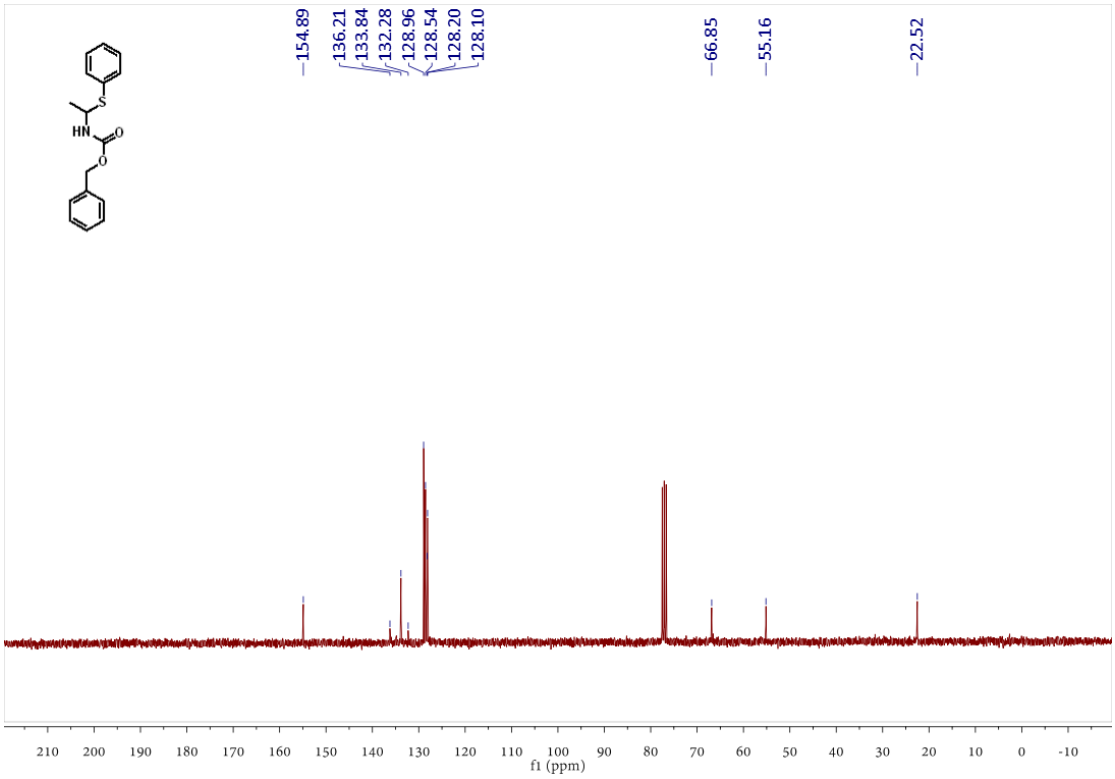
^{13}C NMR spectrum of *tert*-butyl-(cyclohexyl(phenylthio)methyl)carbamate (25)



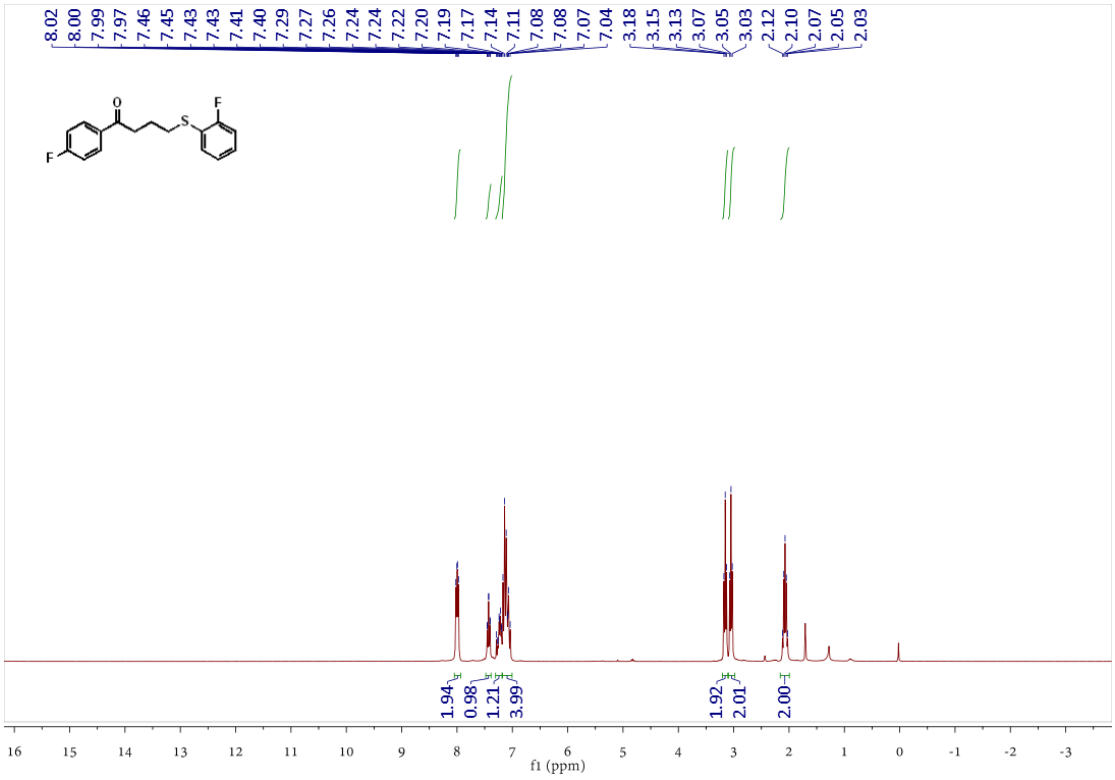
^{1}H NMR spectrum of benzyl-(1-(phenylthio)ethyl)carbamate (26)



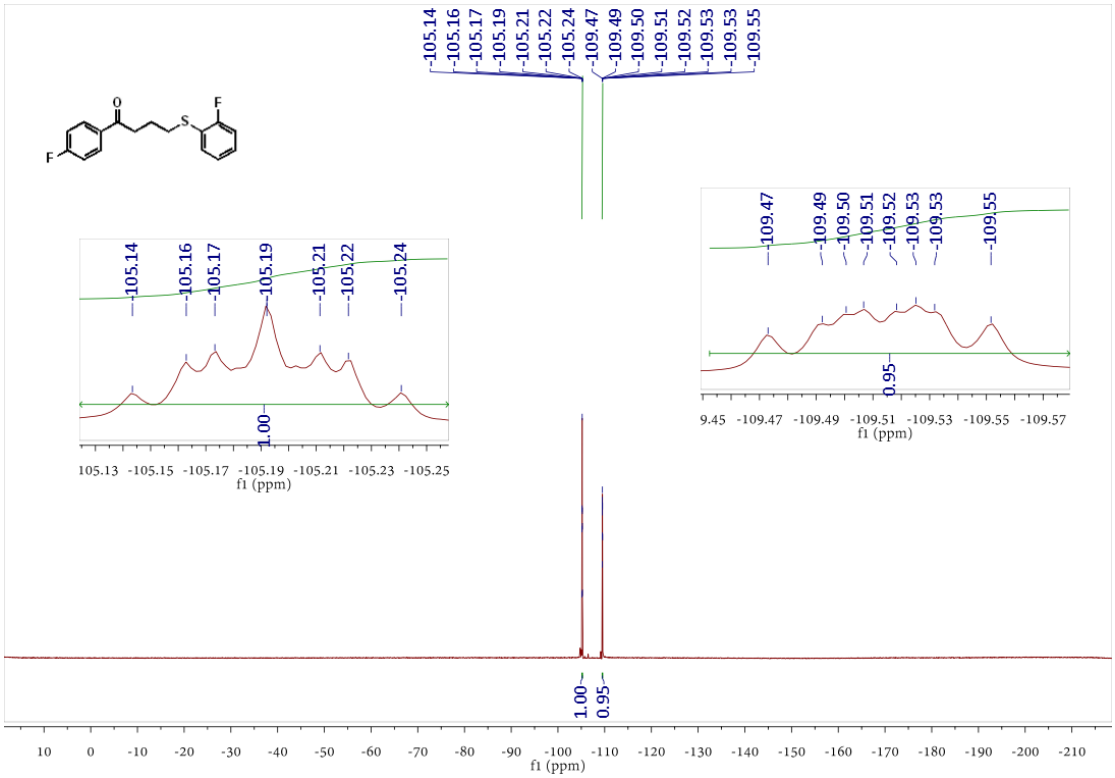
^{13}C NMR spectrum of benzyl-(1-(phenylthio)ethyl)carbamate (26)



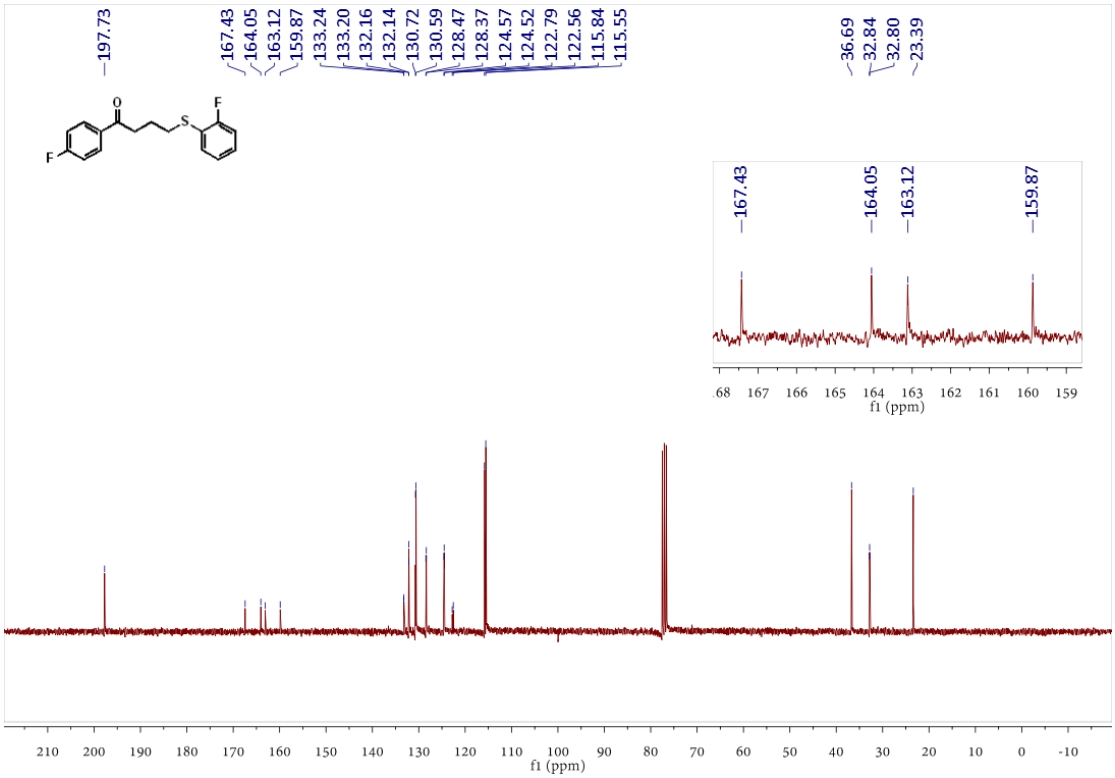
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-((2-fluorophenyl)thio)butan-1-one (27)



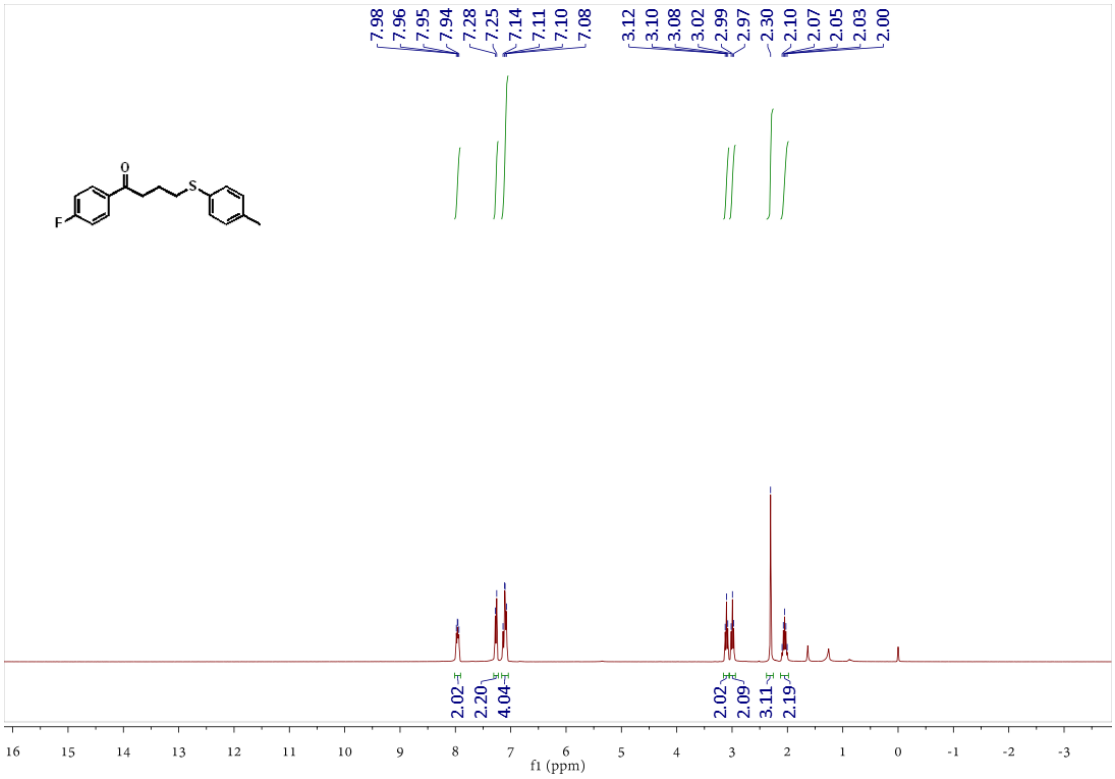
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-((2-fluorophenyl)thio)butan-1-one (27)



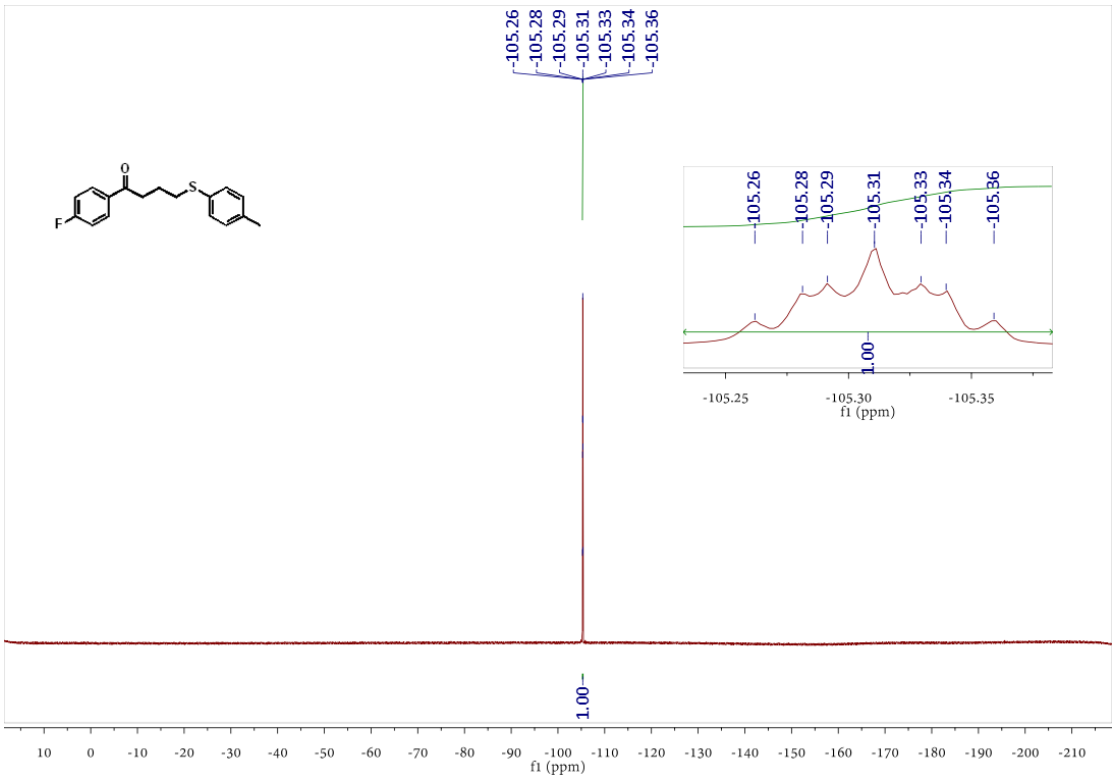
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-((2-fluorophenyl)thio)butan-1-one (27)



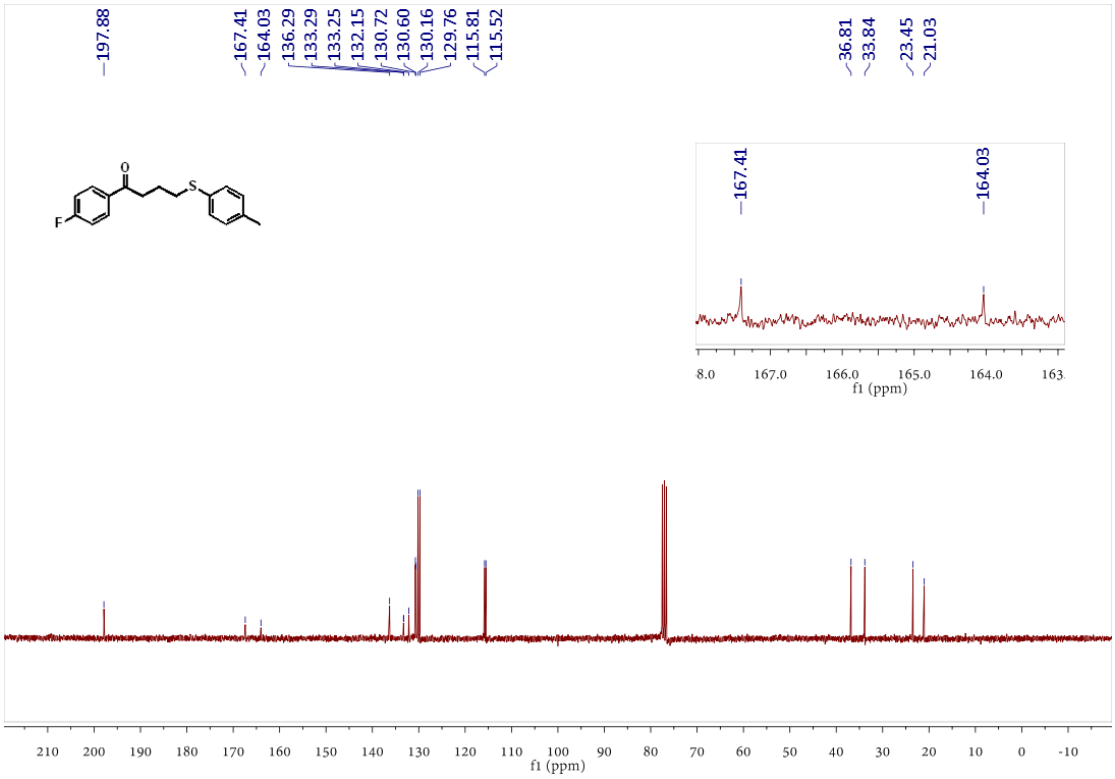
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-(p-tolylthio)butan-1-one (28)



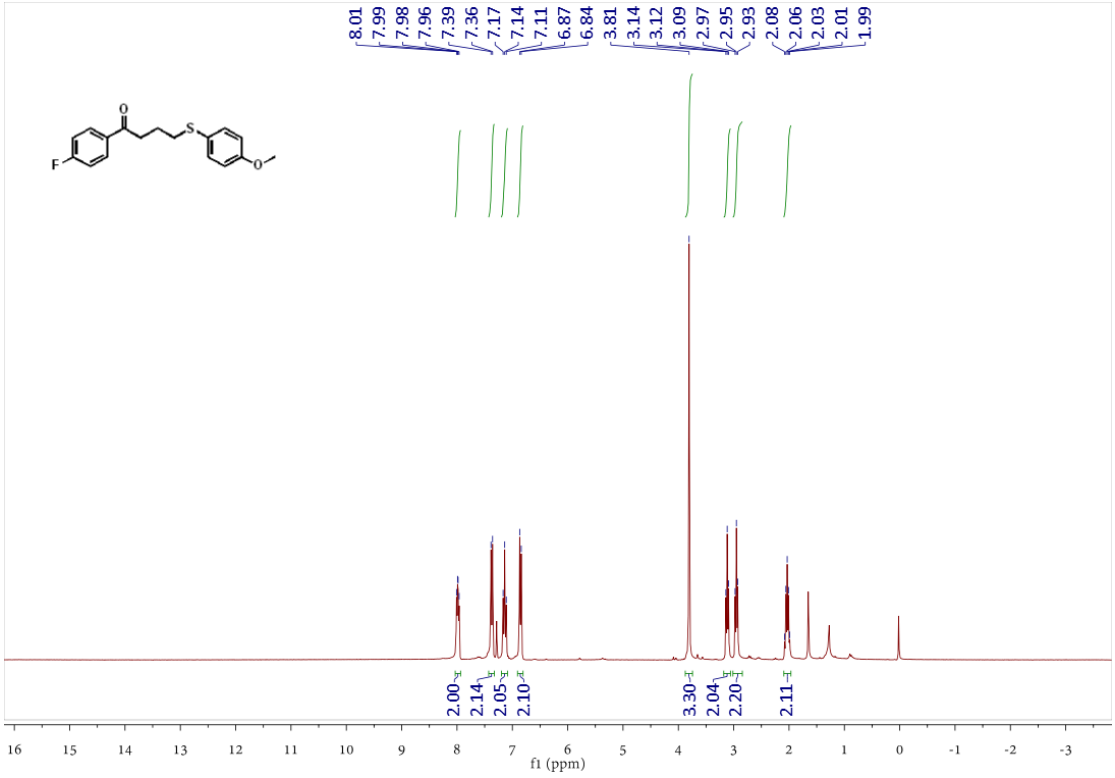
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-(p-tolylthio)butan-1-one (28)



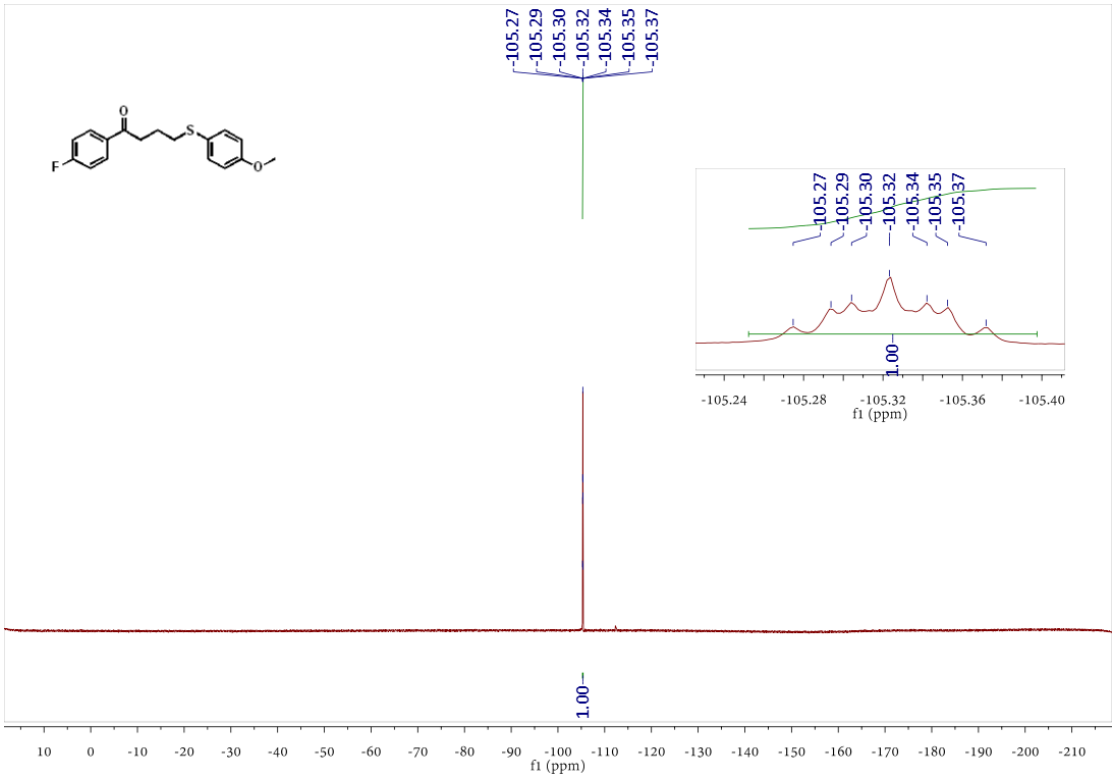
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-(p-tolylthio)butan-1-one (28)



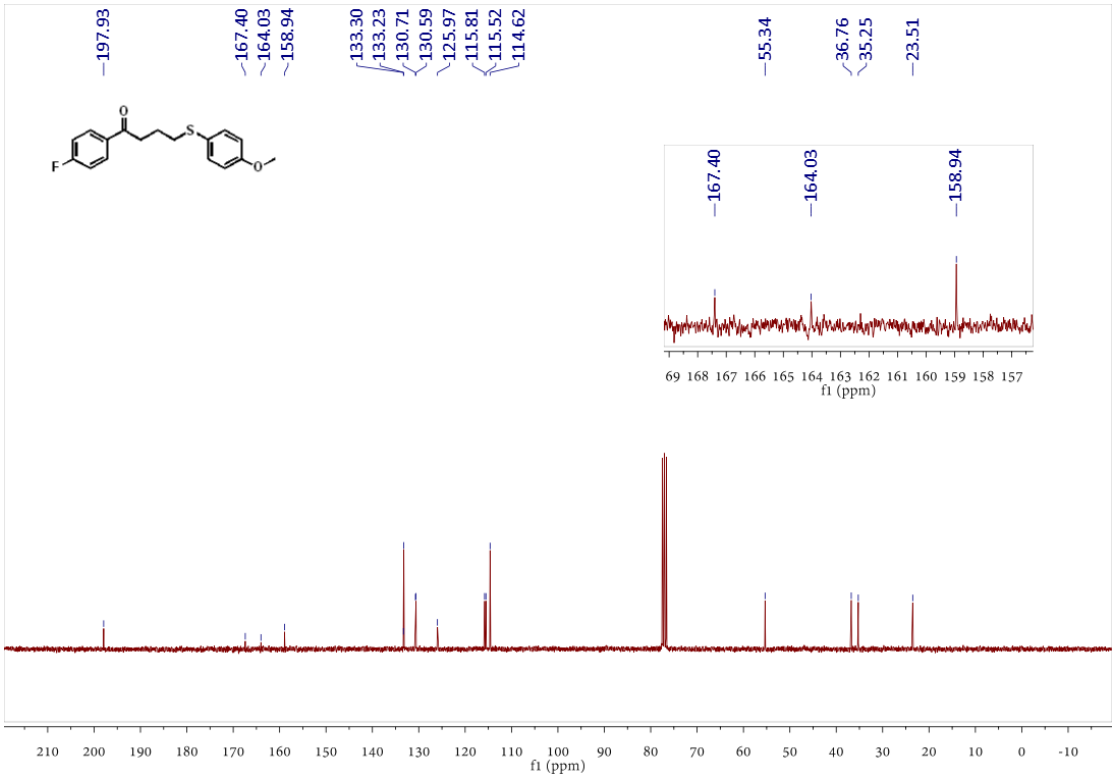
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-((4-methoxyphenyl)thio)butan-1-one (29)



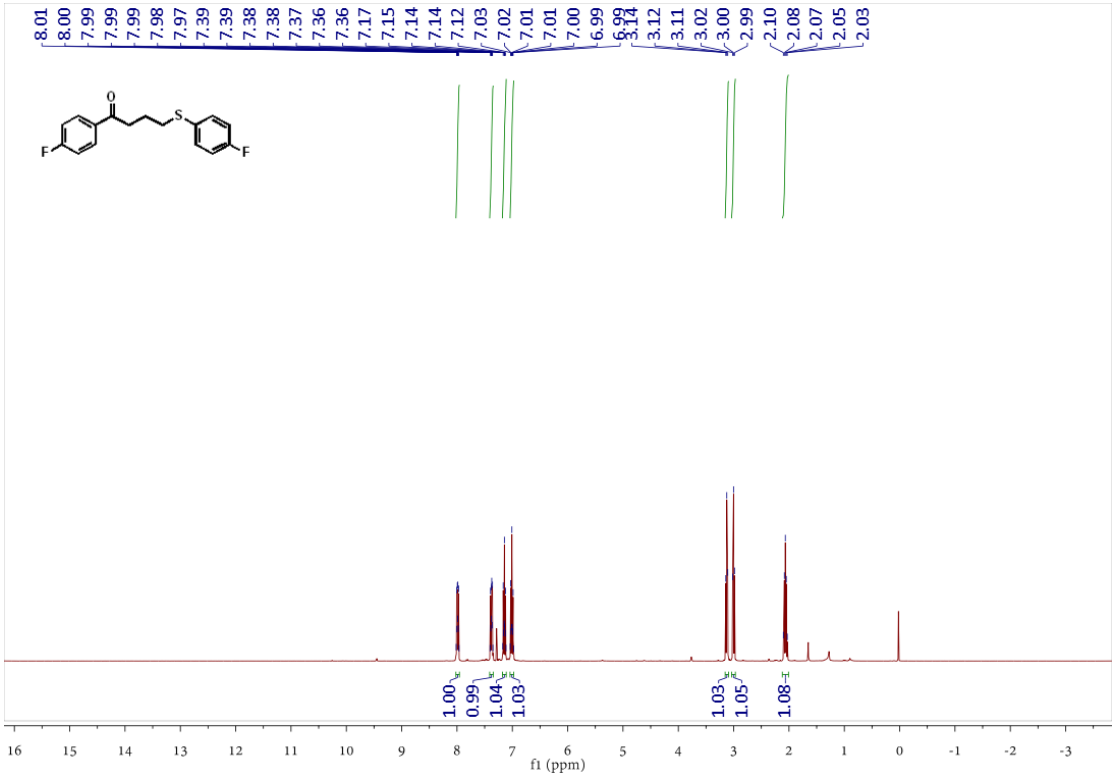
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-((4-methoxyphenyl)thio)butan-1-one (29)



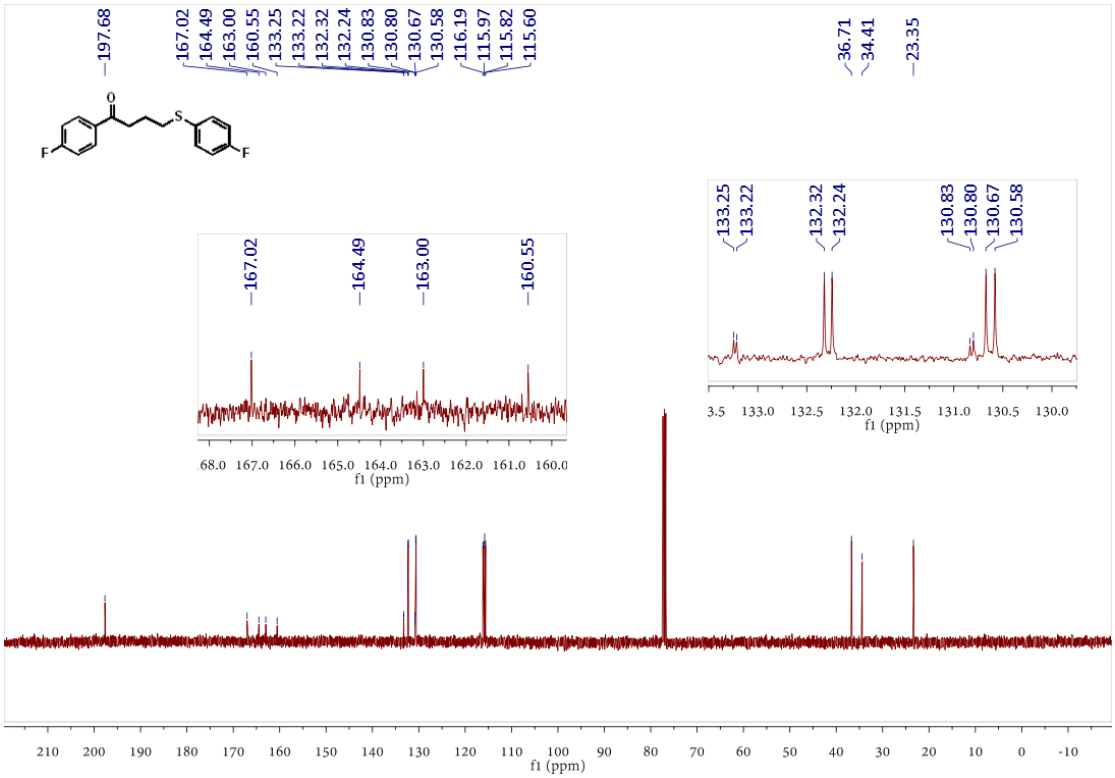
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-((4-methoxyphenyl)thio)butan-1-one (29)



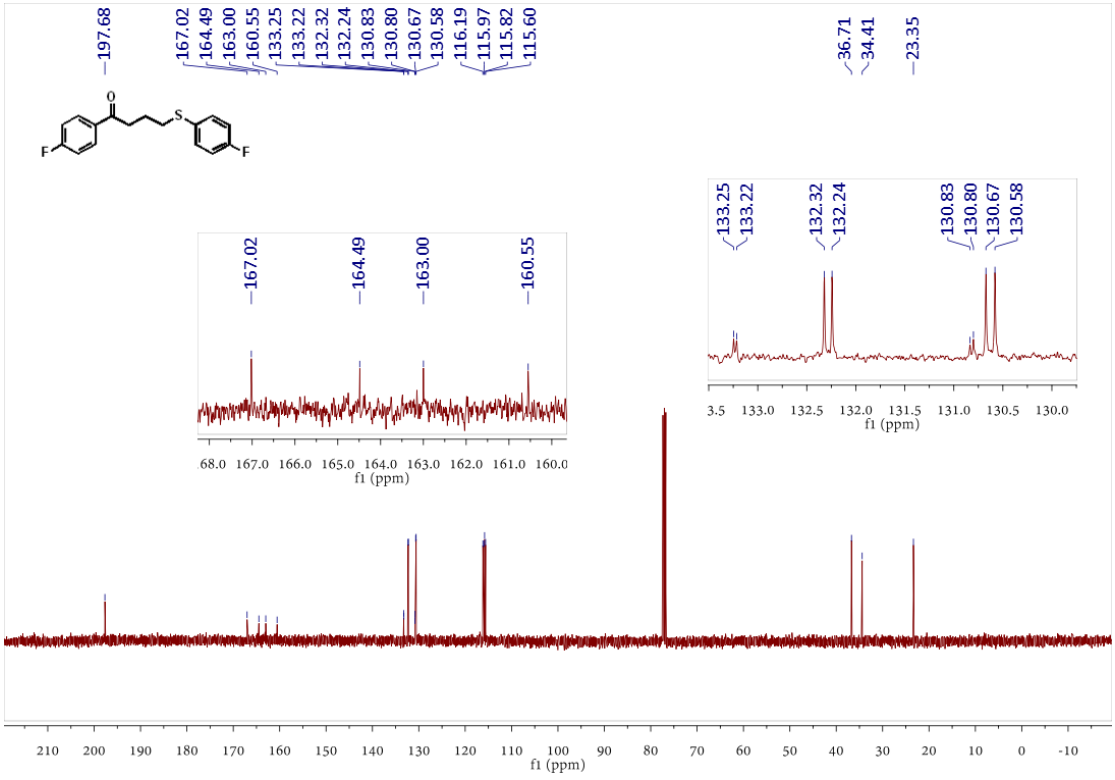
^{1}H NMR spectrum of phenyl(1,1,1-trifluoroundecan-3-yl)sulfane (30)



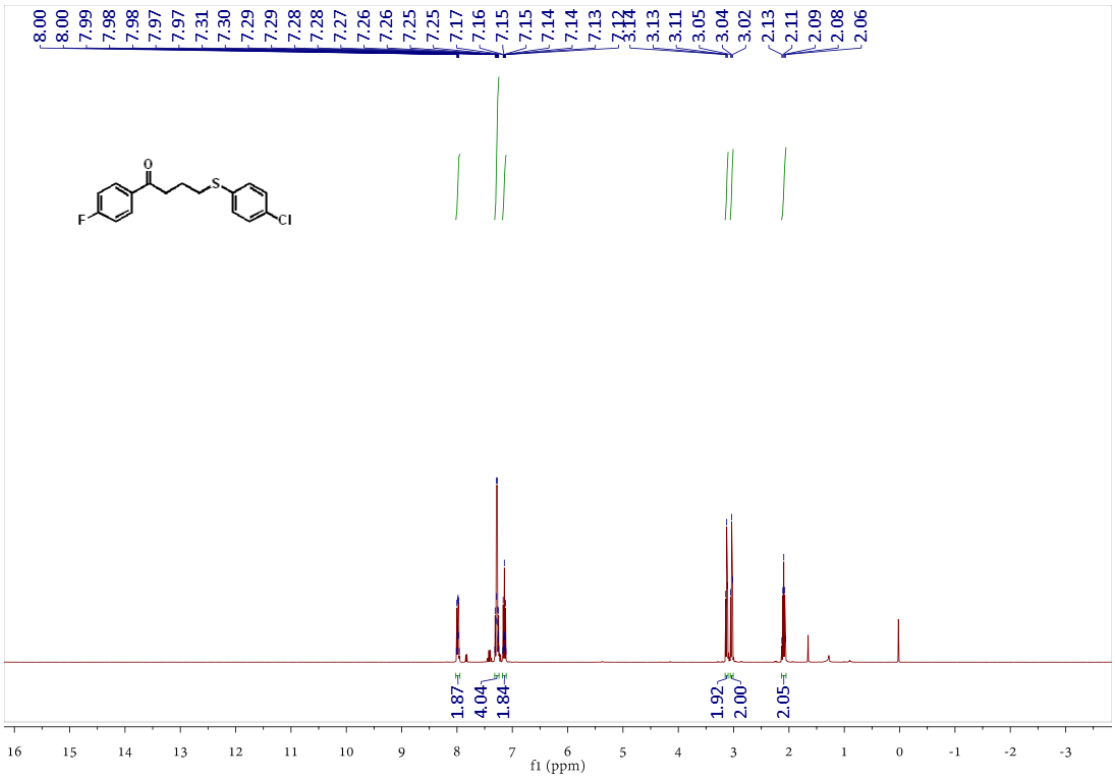
^{19}F NMR spectrum of phenyl(1,1,1-trifluoroundecan-3-yl)sulfane (30)



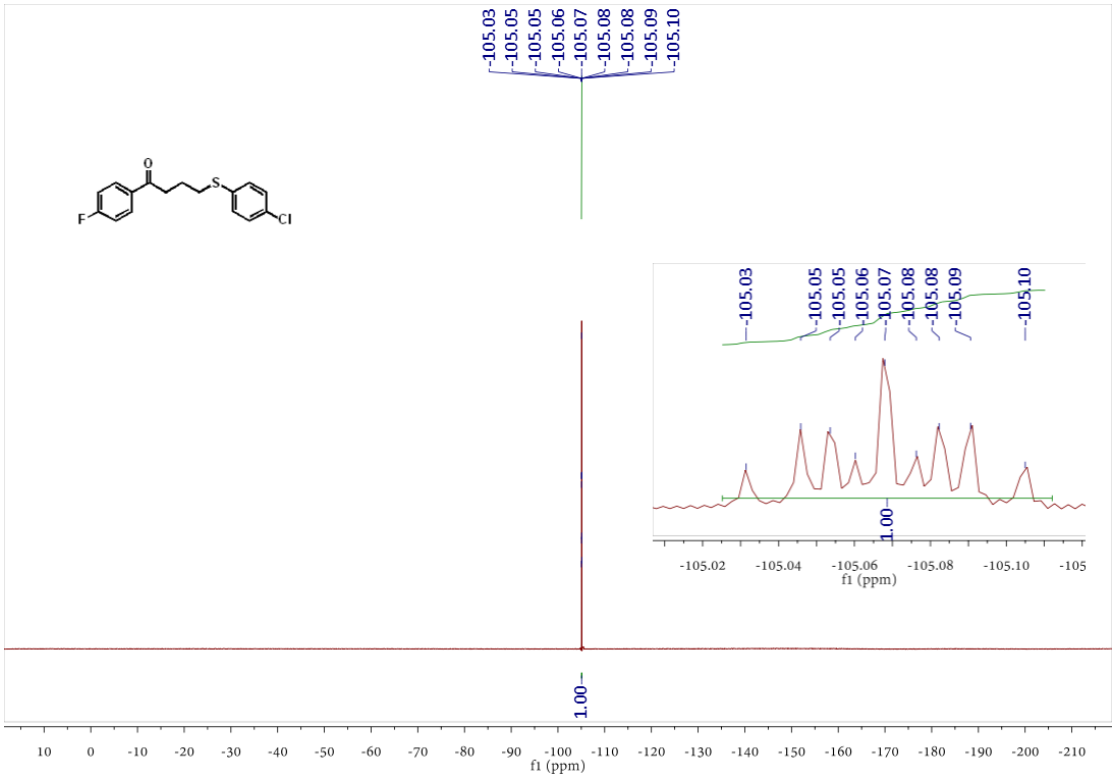
^{13}C NMR spectrum of phenyl(1,1,1-trifluoroundecan-3-yl)sulfane (30)



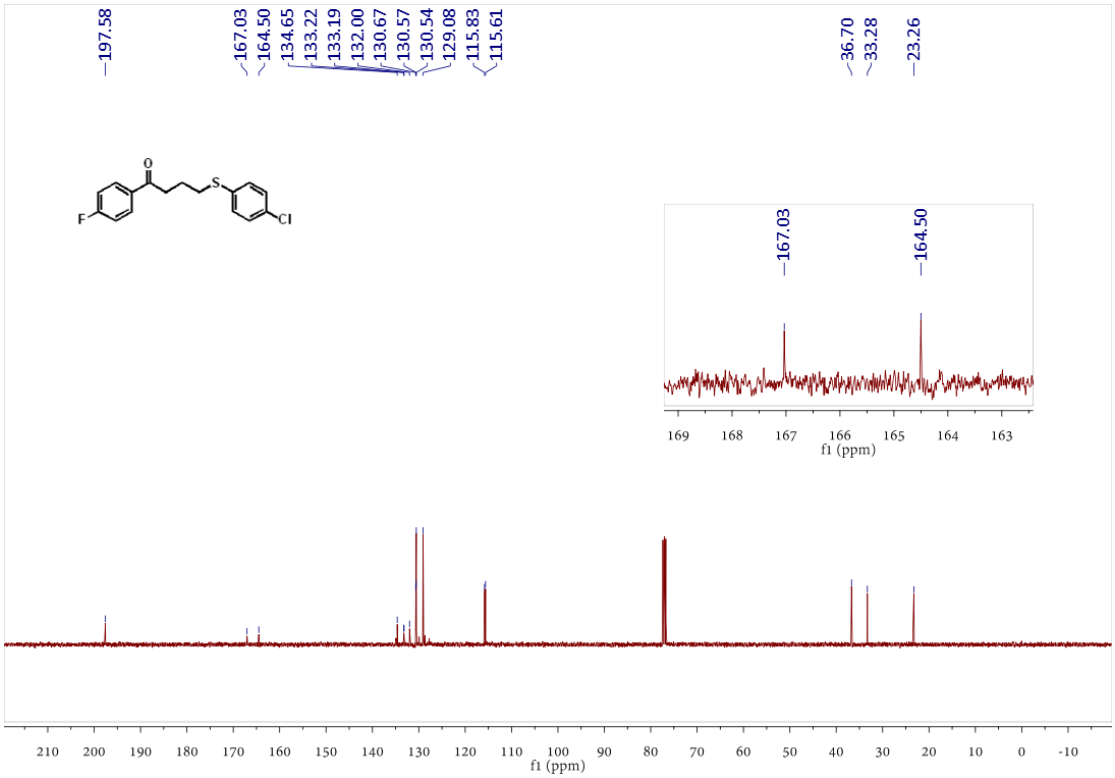
^{1}H NMR spectrum of 4-((4-chlorophenyl)thio)-1-(4-fluorophenyl)butan-1-one (31)



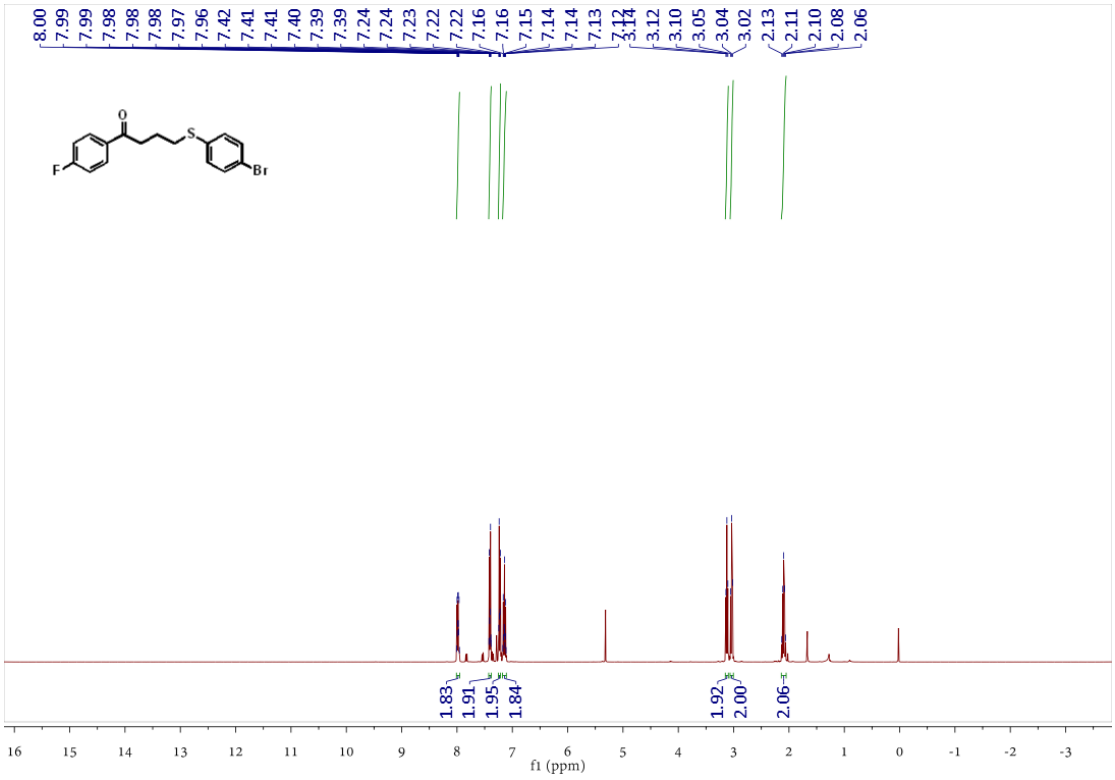
^{19}F NMR spectrum of 4-((4-chlorophenyl)thio)-1-(4-fluorophenyl)butan-1-one (31)



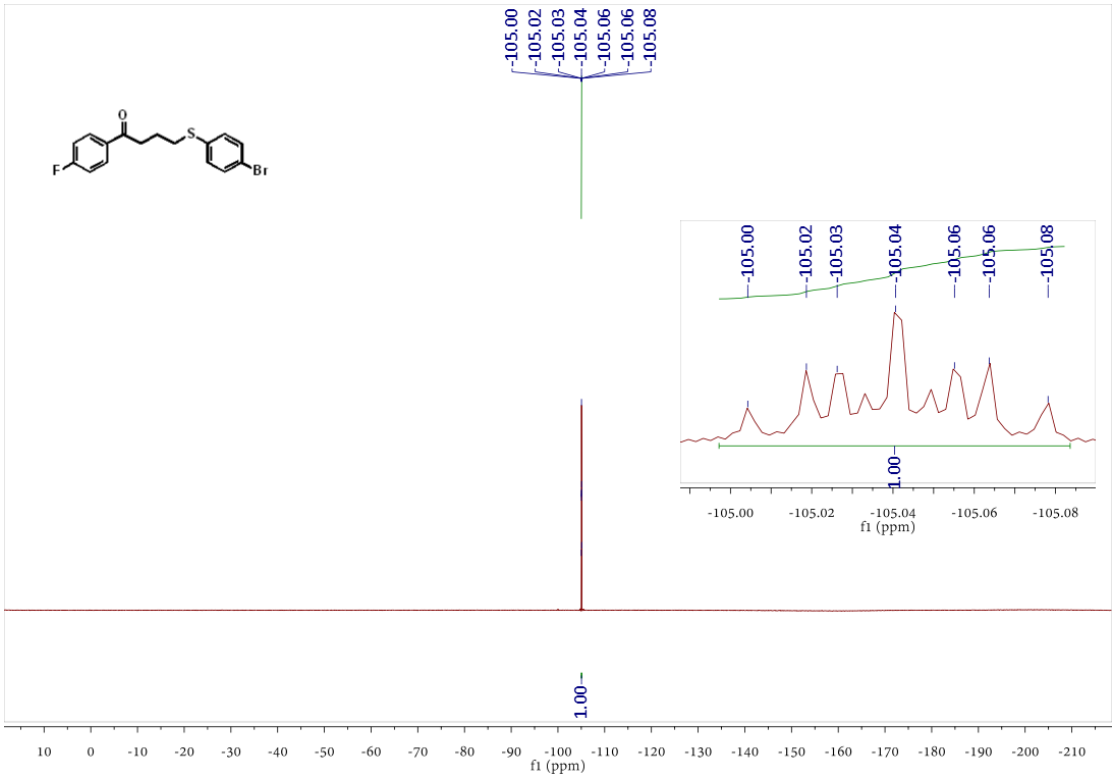
^{13}C NMR spectrum of 4-((4-chlorophenyl)thio)-1-(4-fluorophenyl)butan-1-one (31)



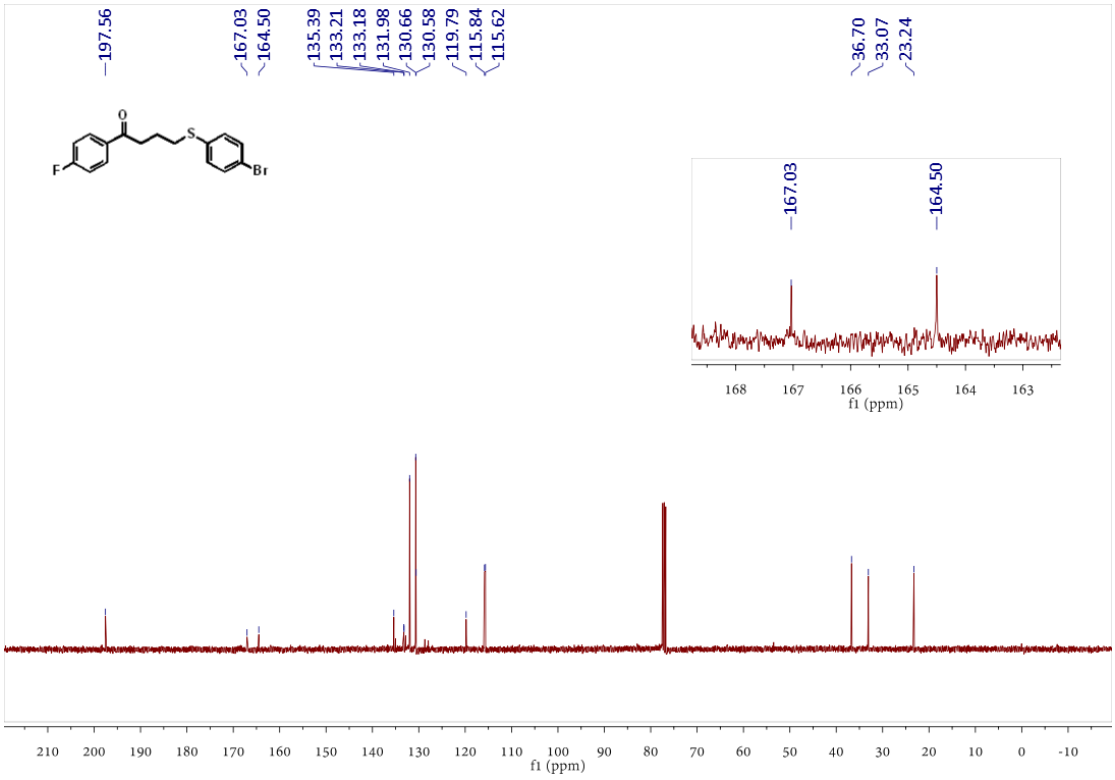
^{1}H NMR spectrum of 4-((4-bromophenyl)thio)-1-(4-fluorophenyl)butan-1-one (32)



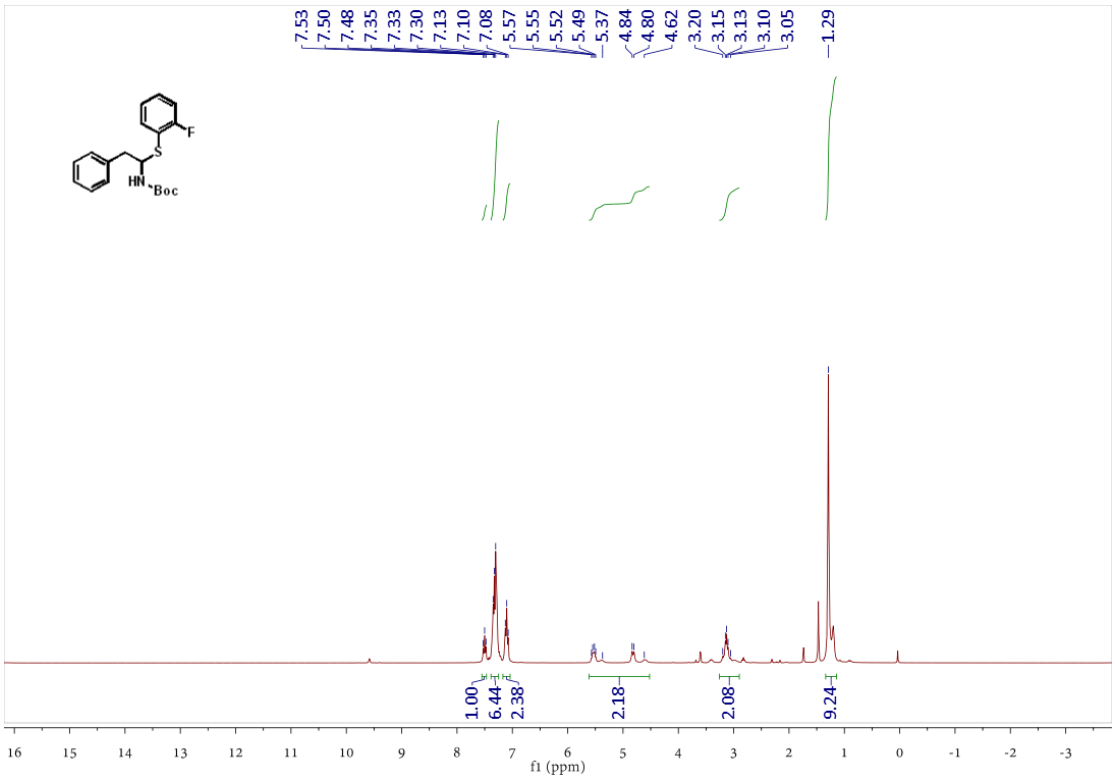
^{19}F NMR spectrum of 4-((4-bromophenyl)thio)-1-(4-fluorophenyl)butan-1-one (32)



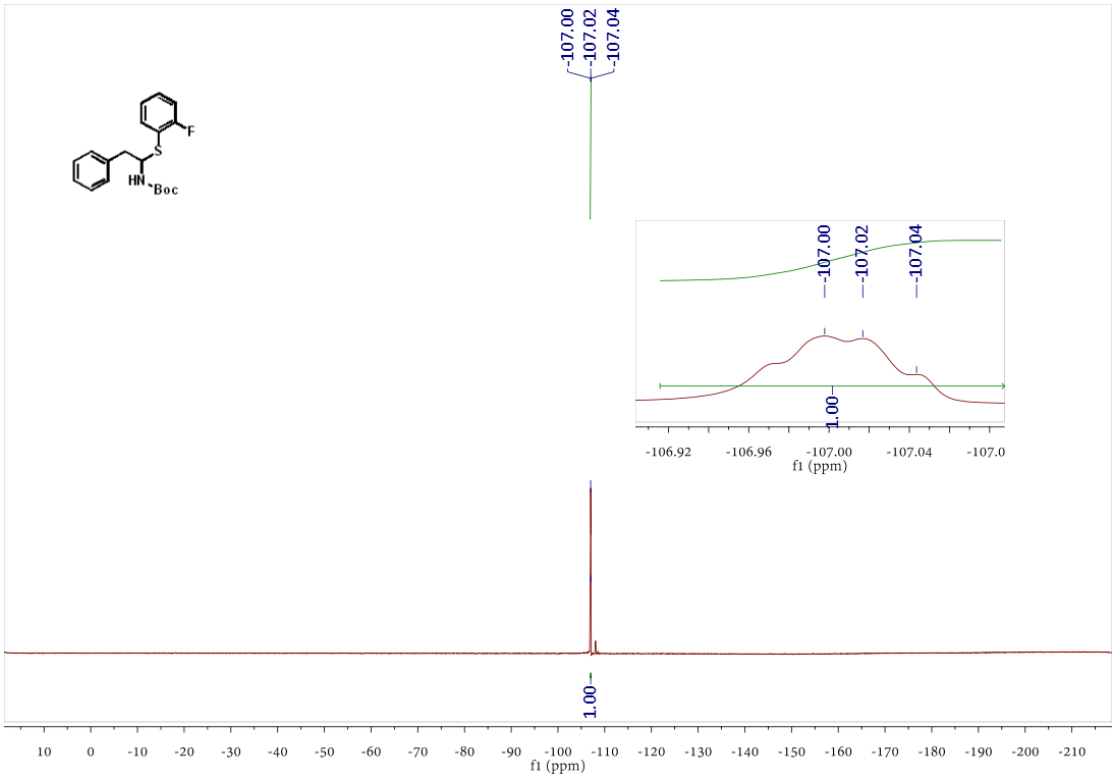
^{13}C NMR spectrum of 4-((4-bromophenyl)thio)-1-(4-fluorophenyl)butan-1-one (32)



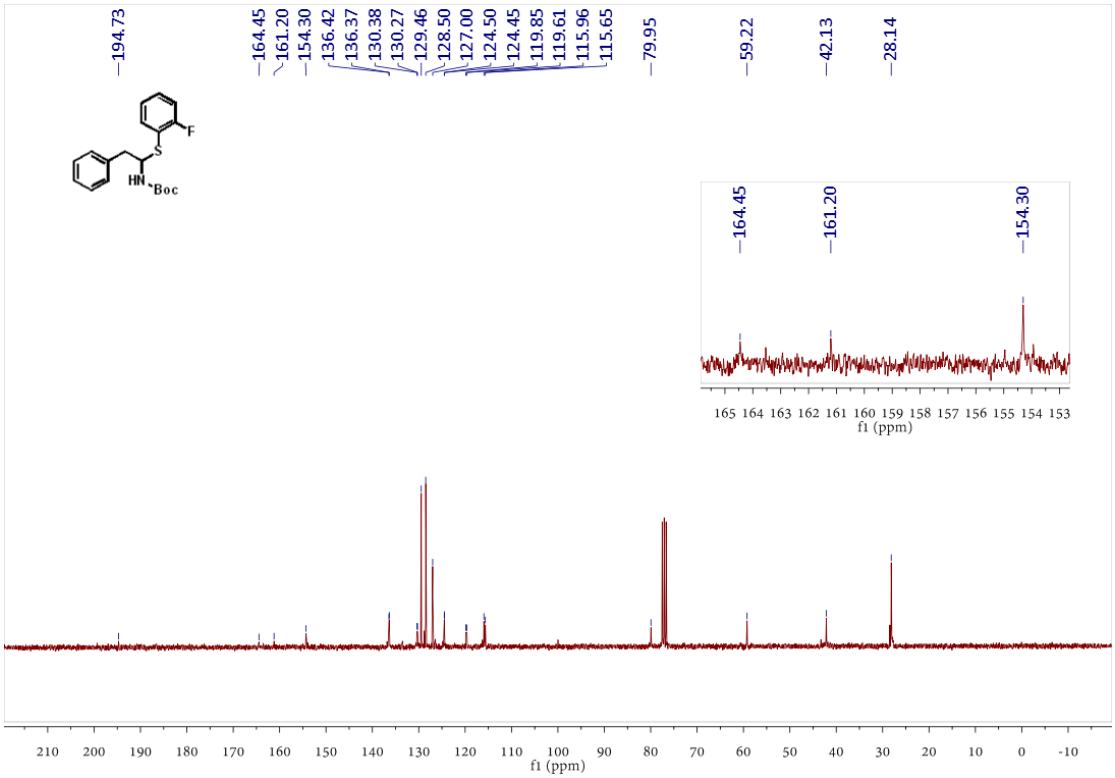
^{1}H NMR spectrum of *tert*-butyl-(1-((2-fluorophenyl)thio)-2-phenylethyl)carbamate (33)



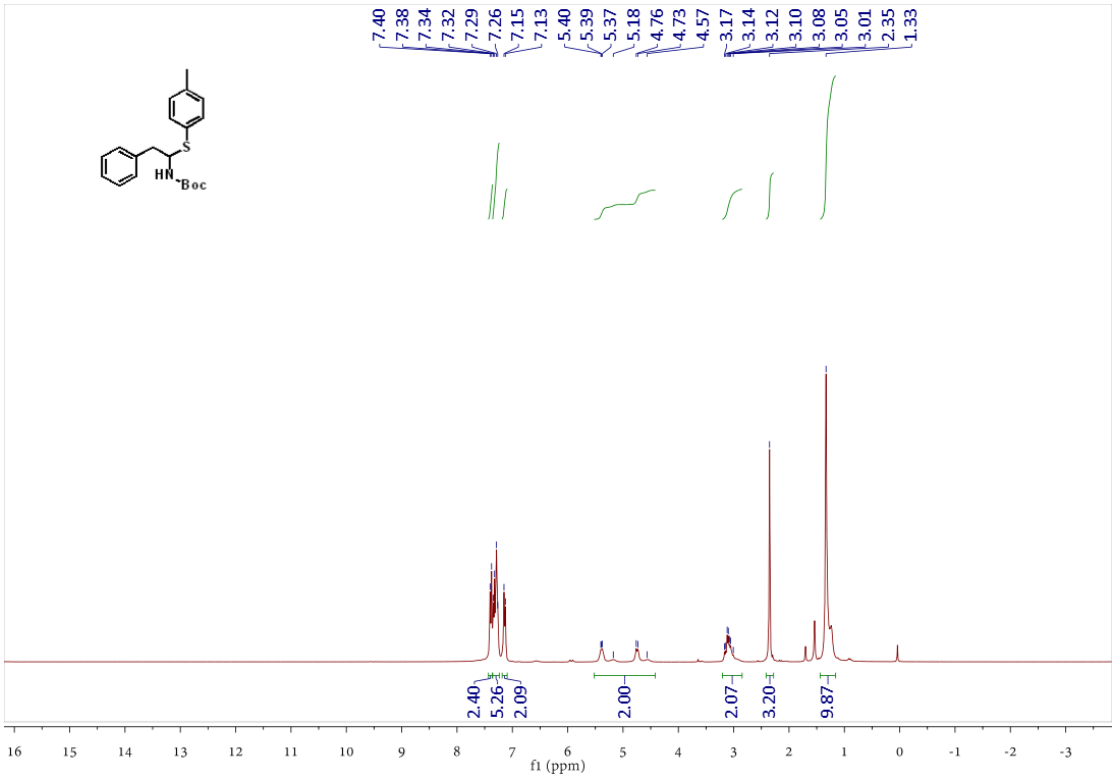
^{19}F NMR spectrum of
***tert*-butyl-(1-((2-fluorophenyl)thio)-2-phenylethyl)carbamate (33)**



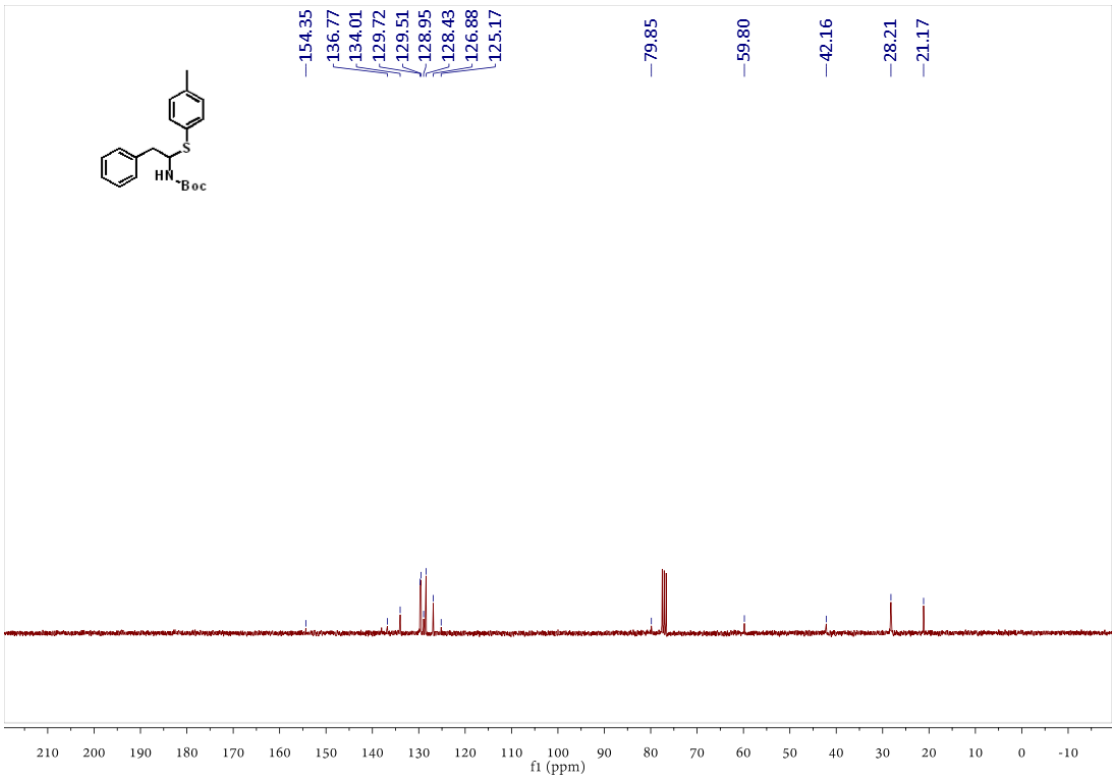
^{13}C NMR spectrum of
***tert*-butyl-(1-((2-fluorophenyl)thio)-2-phenylethyl)carbamate (33)**



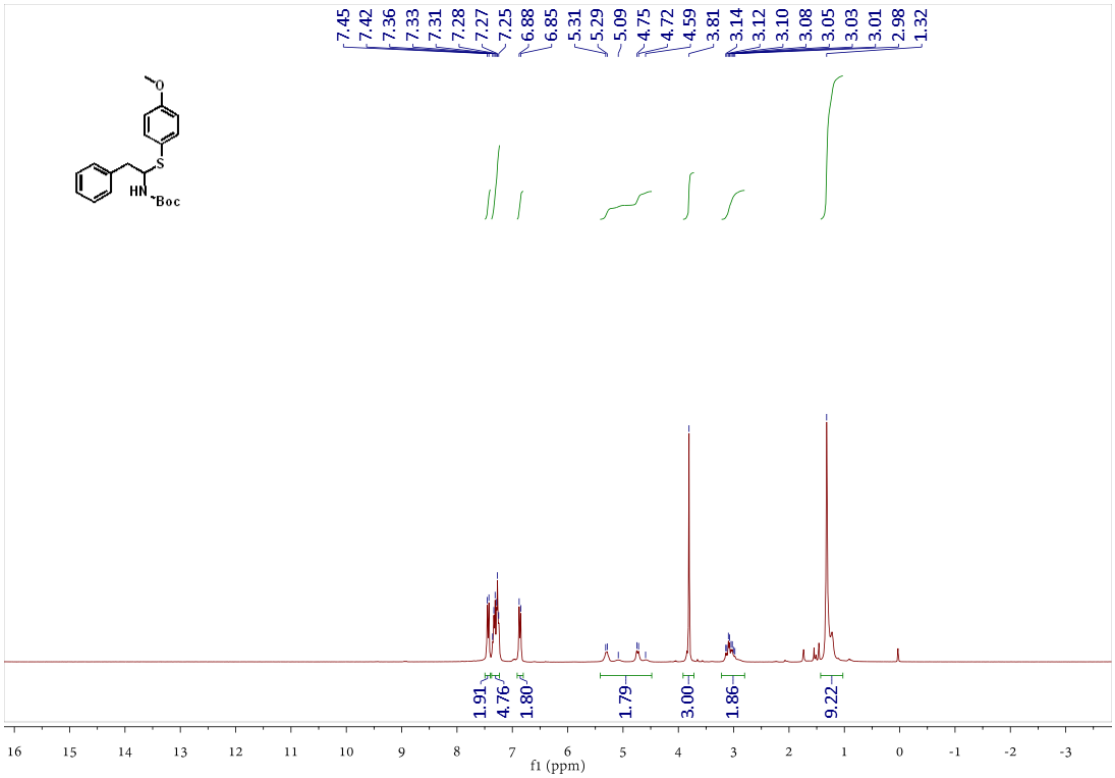
^{1}H NMR spectrum of *tert*-butyl-(2-phenyl-1-(p-tolylthio)ethyl)carbamate (34)



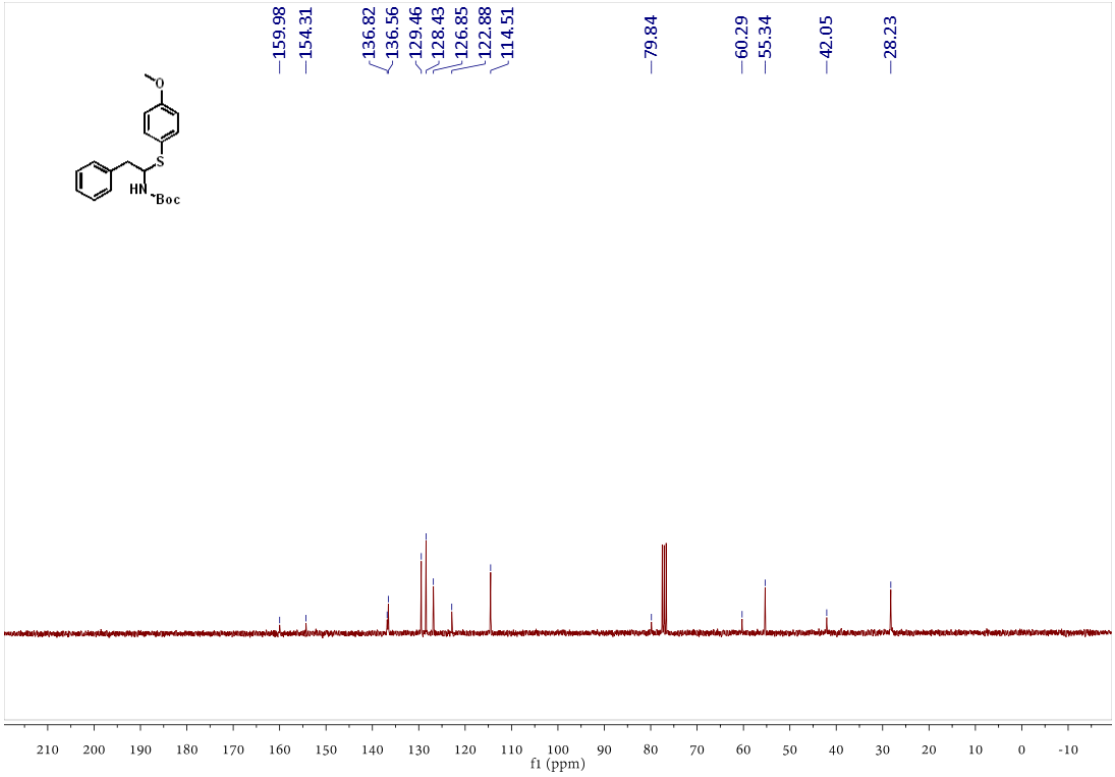
^{13}C NMR spectrum of *tert*-butyl-(2-phenyl-1-(p-tolylthio)ethyl)carbamate (34)



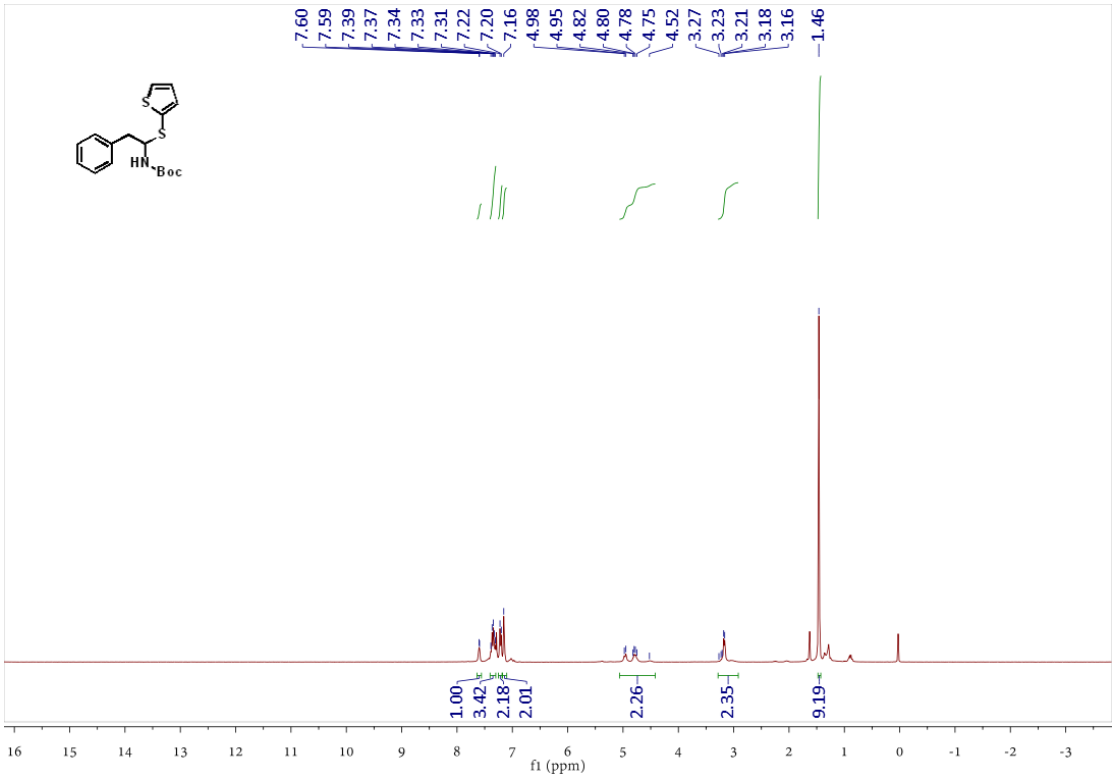
^{1}H NMR spectrum of
***tert*-butyl-(1-((4-methoxyphenyl)thio)-2-phenylethyl)carbamate (35)**



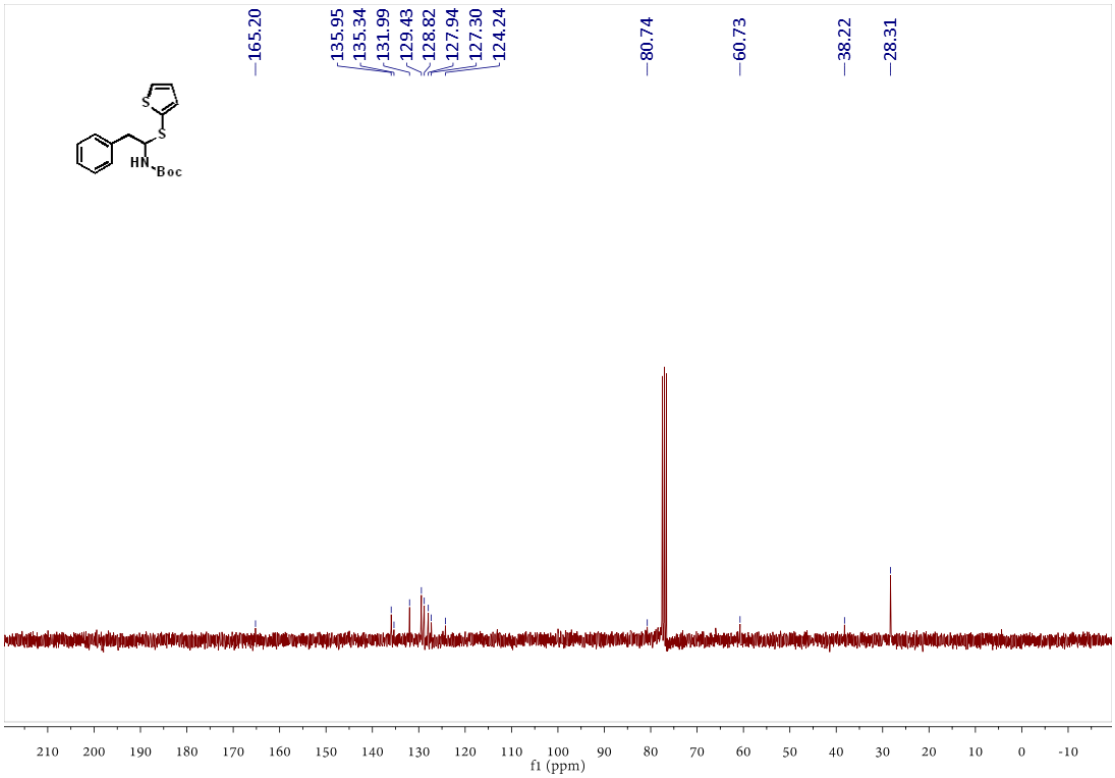
^{13}C NMR spectrum of
***tert*-butyl-(1-((4-methoxyphenyl)thio)-2-phenylethyl)carbamate (35)**



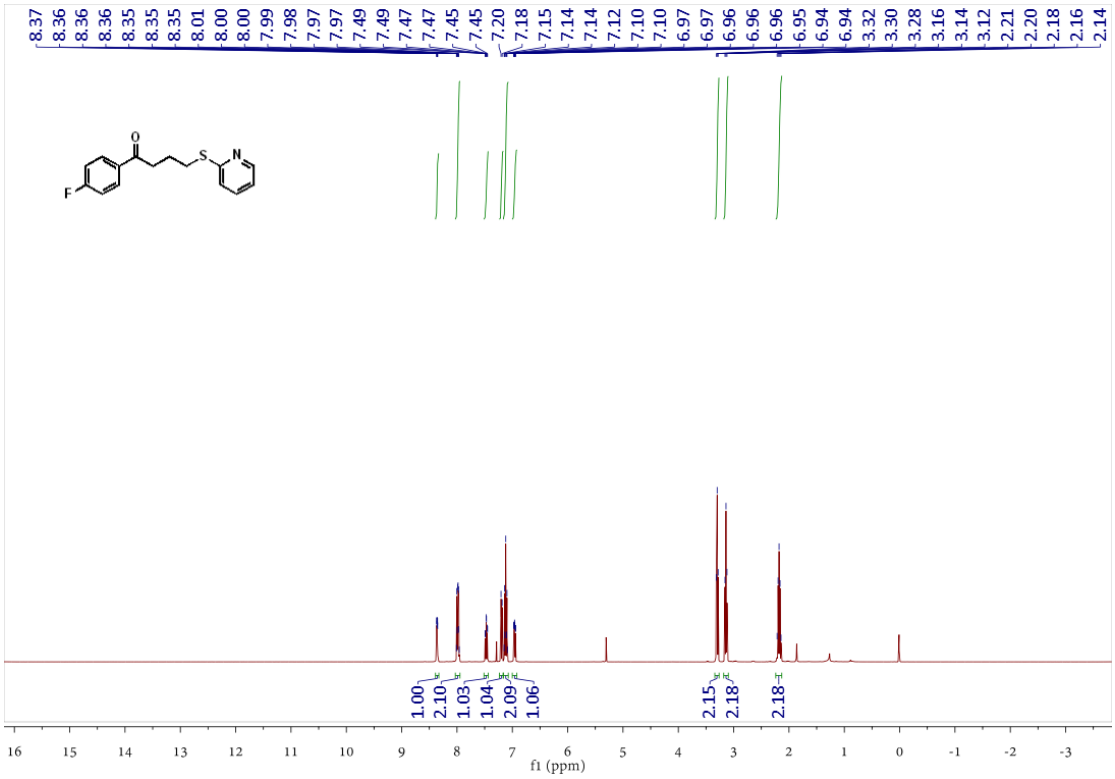
^{1}H NMR spectrum of *tert*-butyl-(2-phenyl-1-(thiophen-2-ylthio)ethyl)carbamate (36)



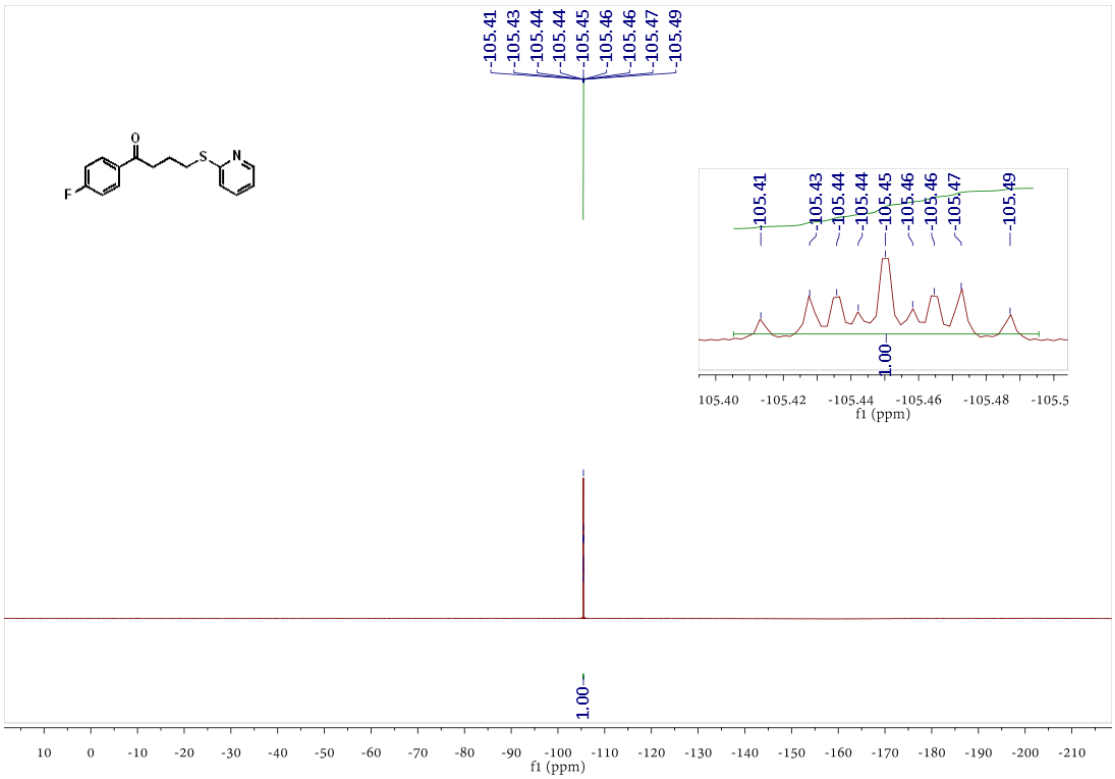
^{13}C NMR spectrum of *tert*-butyl-(2-phenyl-1-(thiophen-2-ylthio)ethyl)carbamate (36)



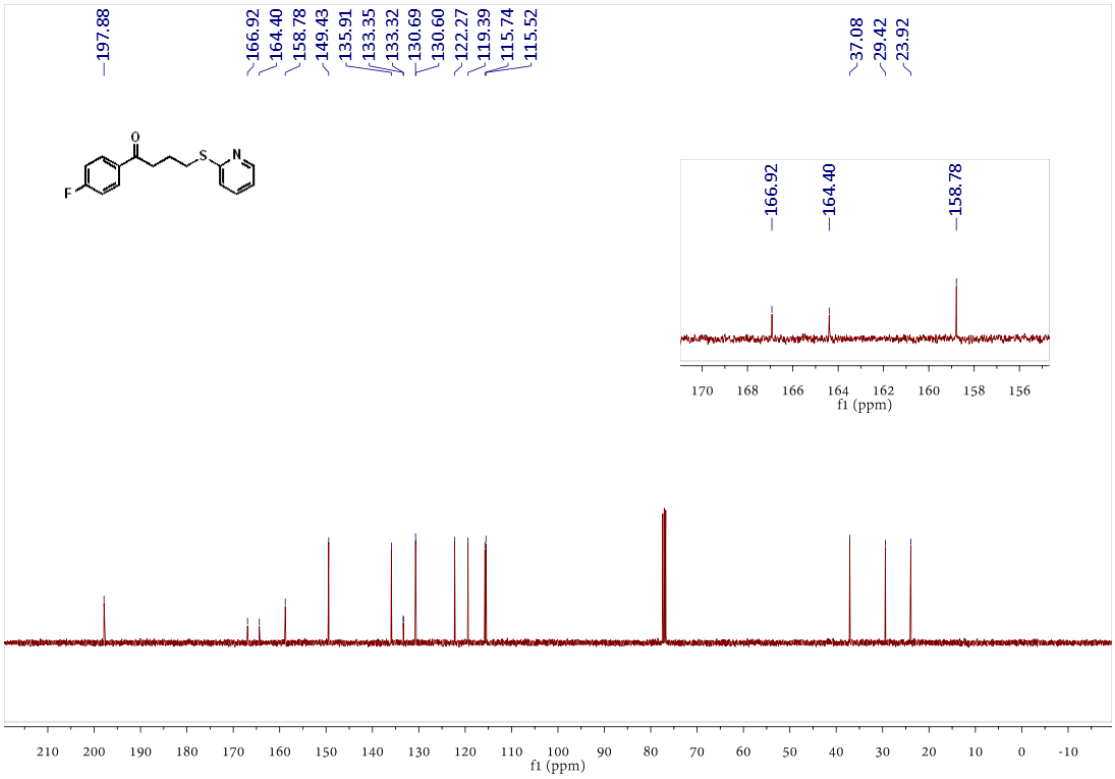
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-(pyridin-2-ylthio)butan-1-one (37)



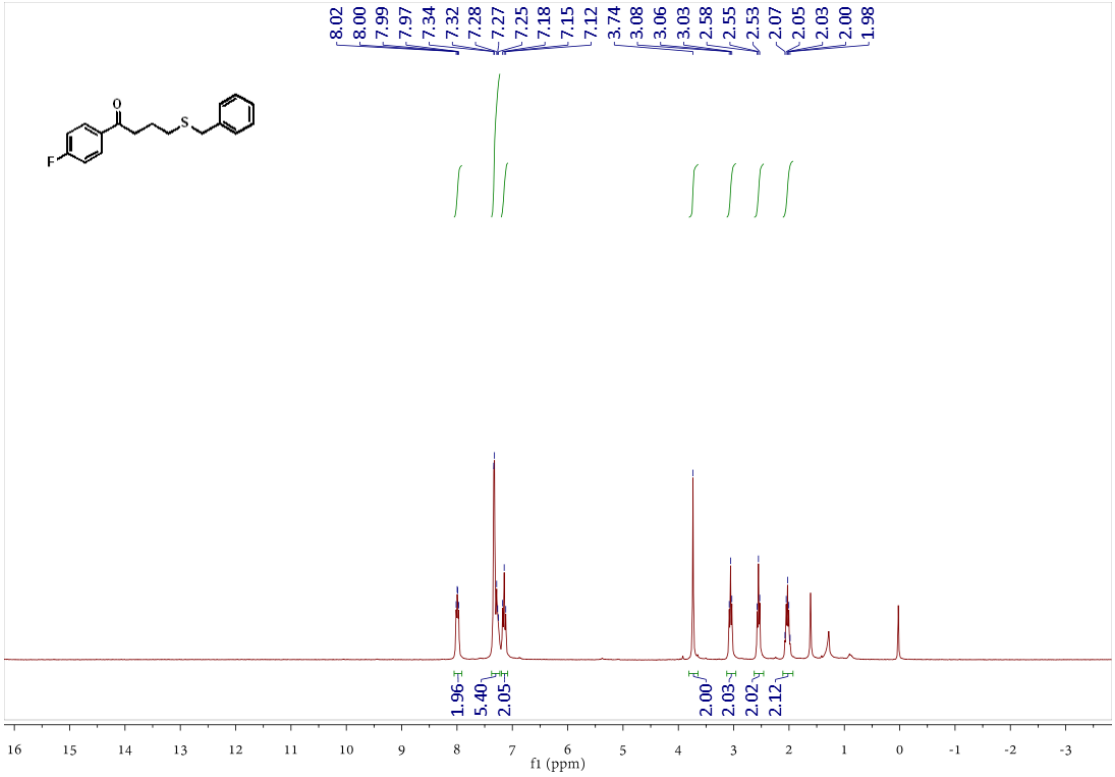
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-(pyridin-2-ylthio)butan-1-one (37)



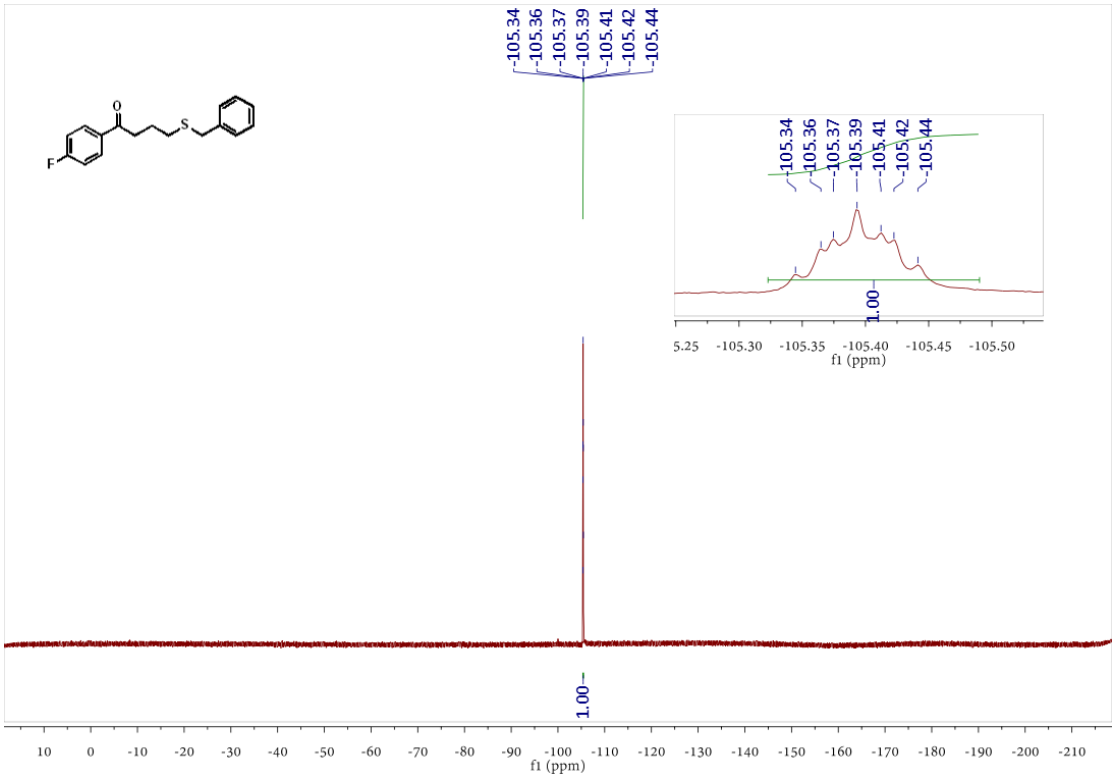
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-(pyridin-2-ylthio)butan-1-one (37)



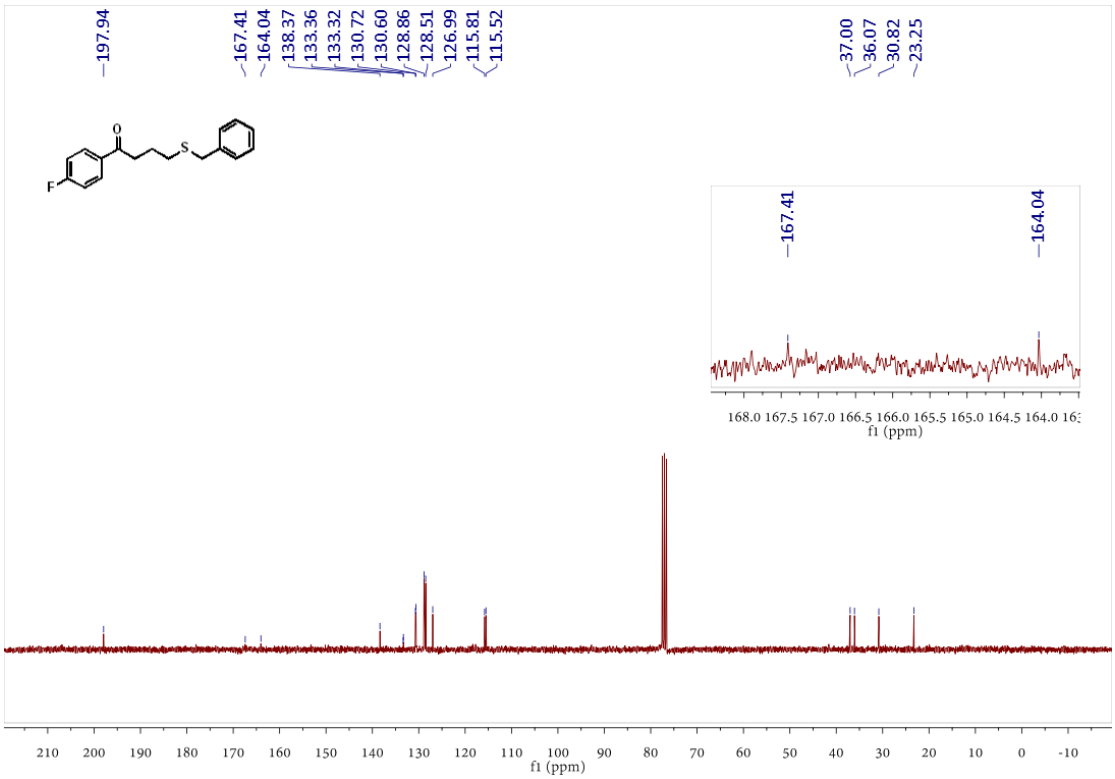
^{1}H NMR spectrum of 4-(benzylthio)-1-(4-fluorophenyl)butan-1-one (38)



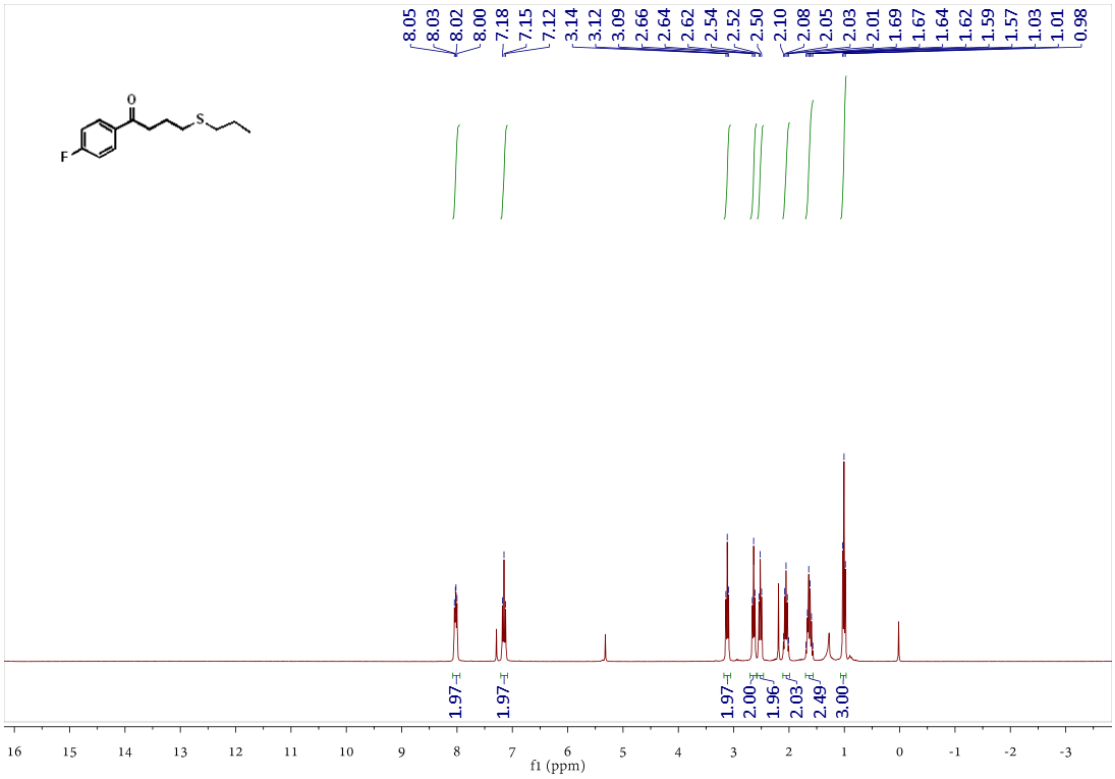
^{19}F NMR spectrum of 4-(benzylthio)-1-(4-fluorophenyl)butan-1-one (38)



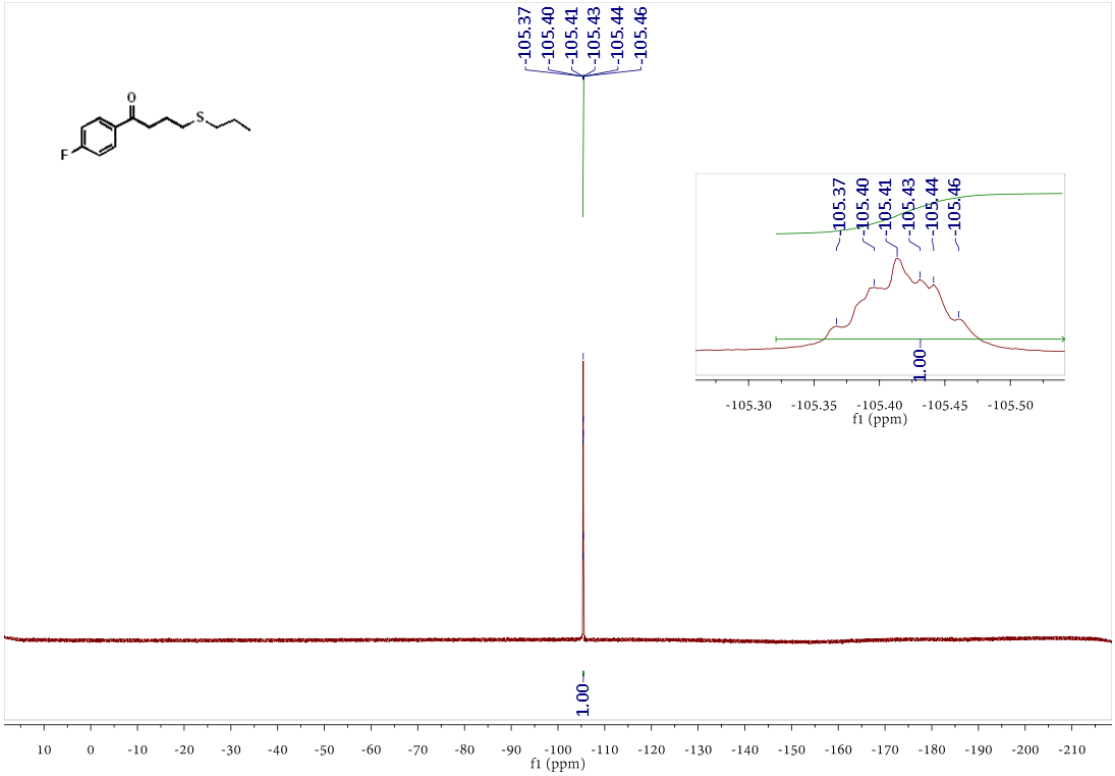
^{13}C NMR spectrum of 4-(benzylthio)-1-(4-fluorophenyl)butan-1-one (38)



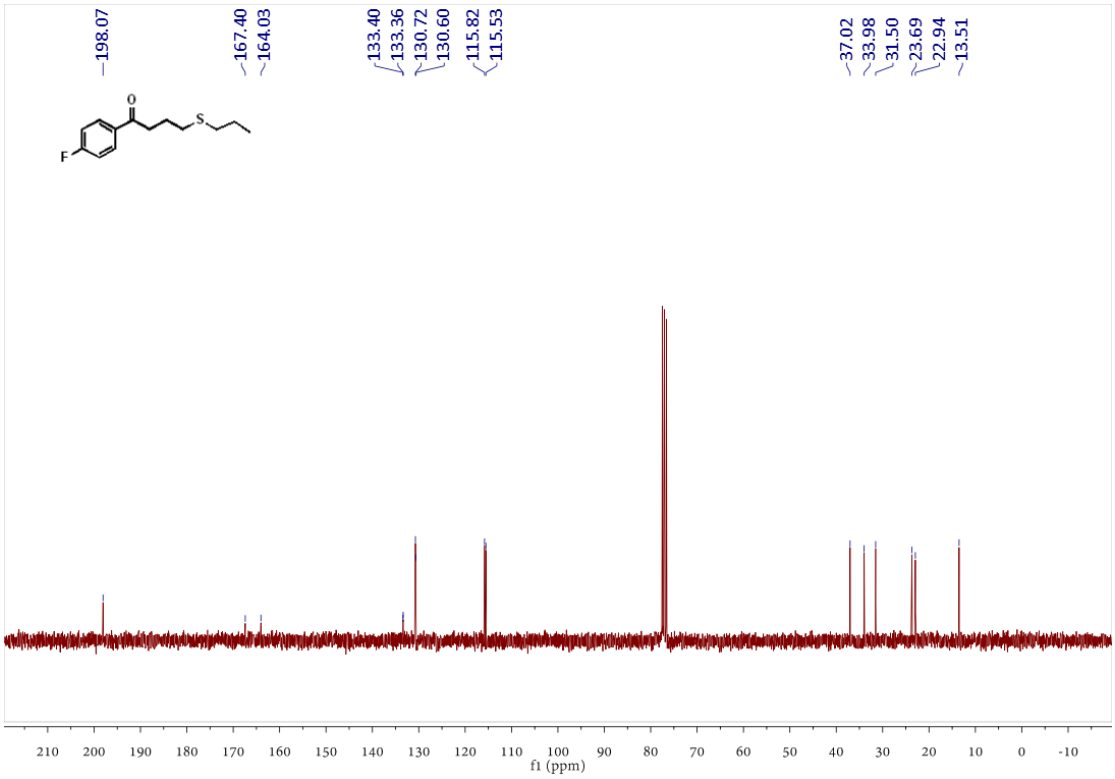
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-(propylthio)butan-1-one (39)



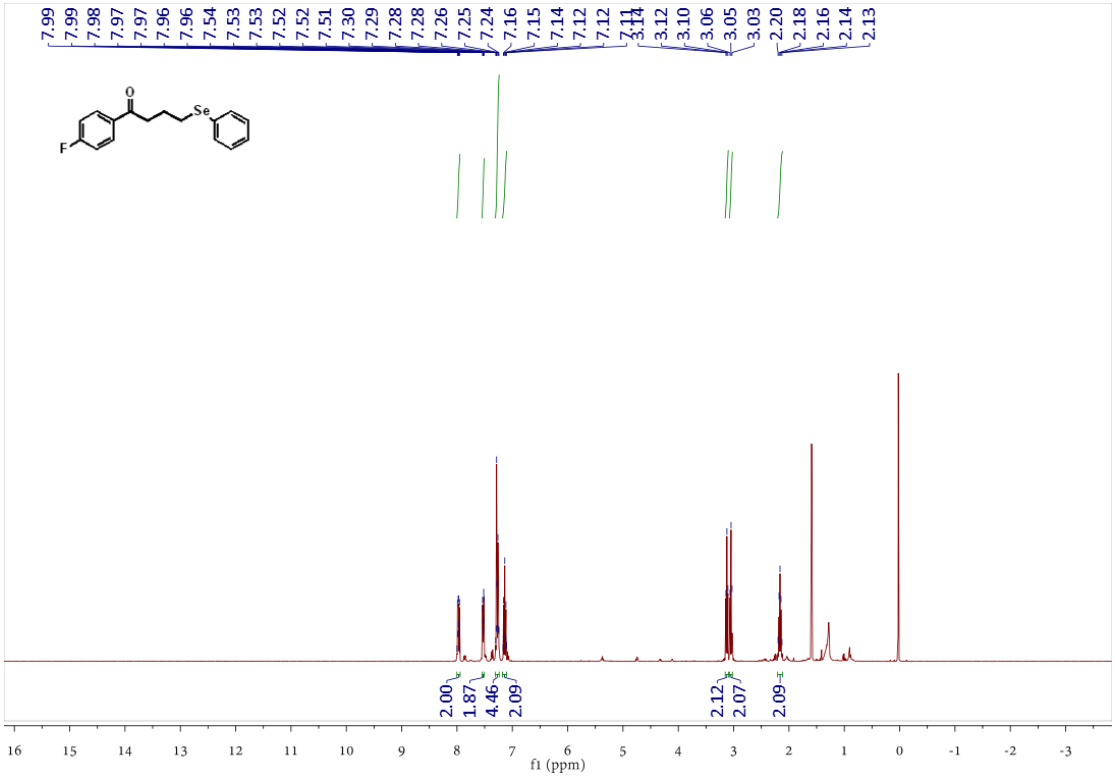
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-(propylthio)butan-1-one (39)



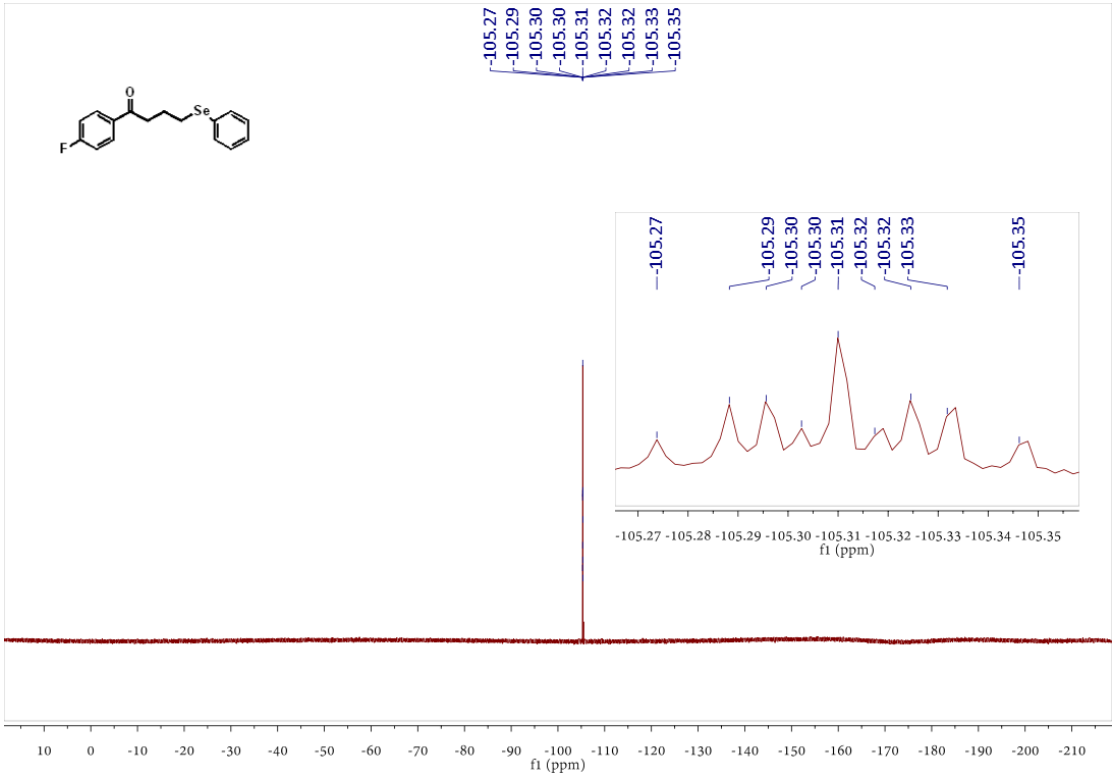
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-(propylthio)butan-1-one (39)



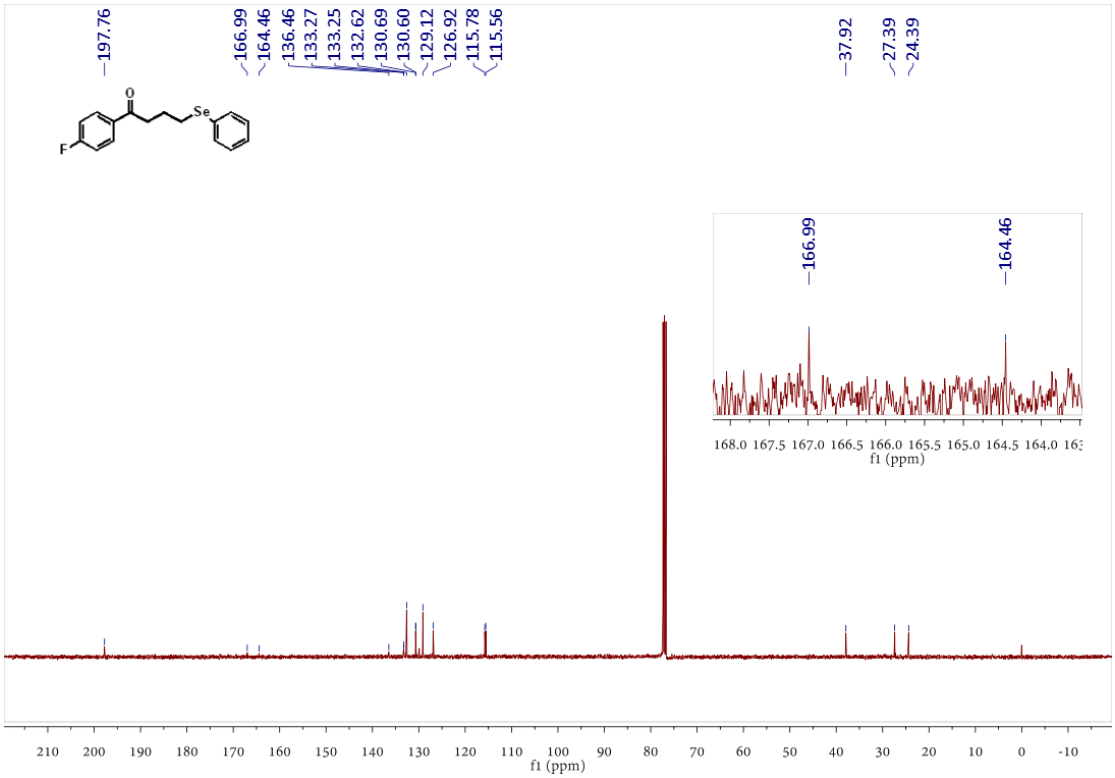
^{1}H NMR spectrum of 1-(4-fluorophenyl)-4-(phenylselanyl)butan-1-one (41)



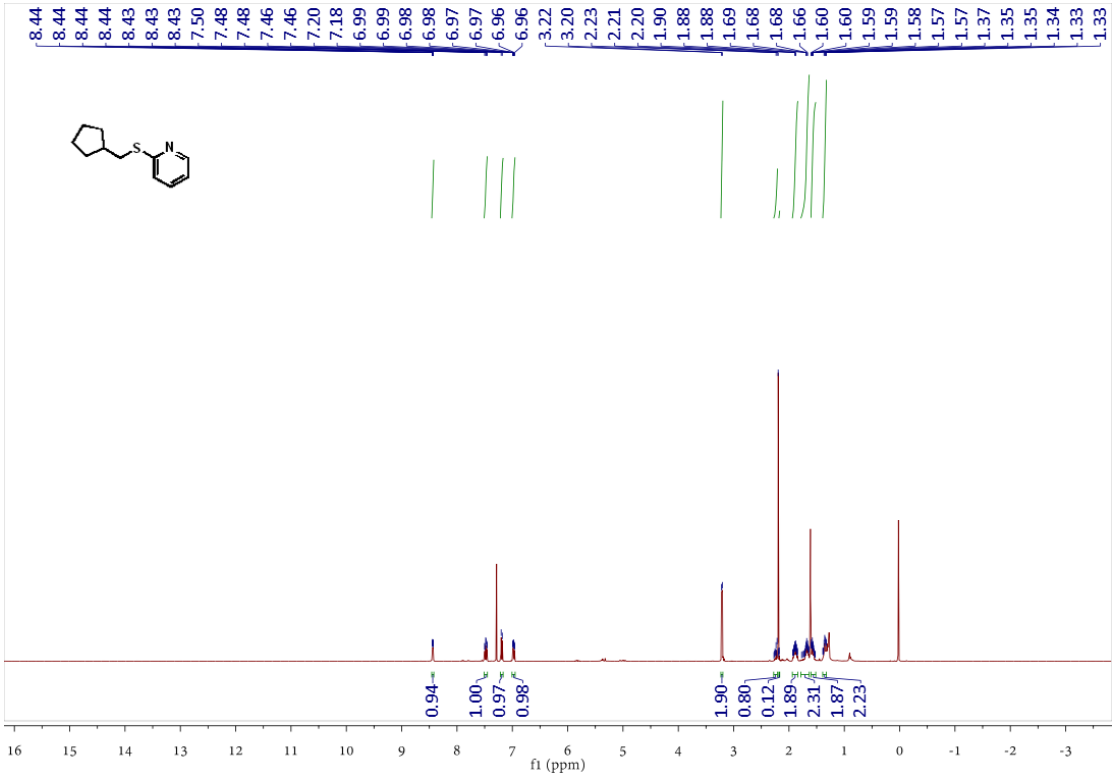
^{19}F NMR spectrum of 1-(4-fluorophenyl)-4-(phenylselanyl)butan-1-one (41)



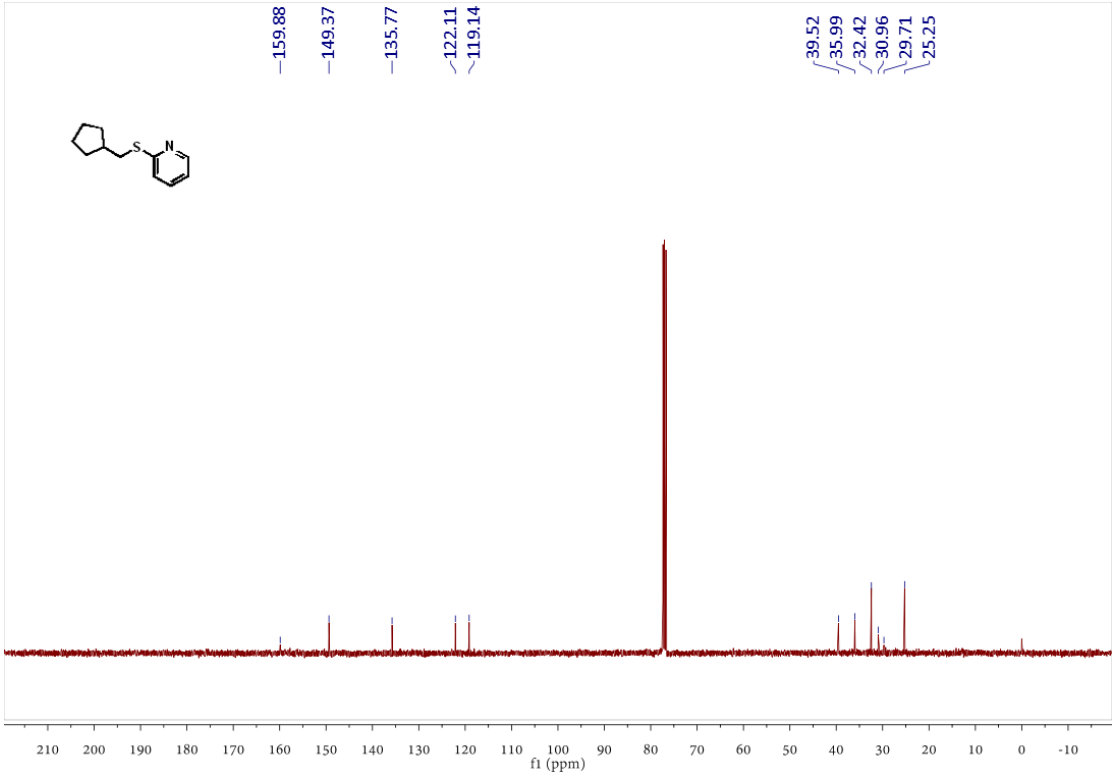
^{13}C NMR spectrum of 1-(4-fluorophenyl)-4-(phenylselanyl)butan-1-one (41)



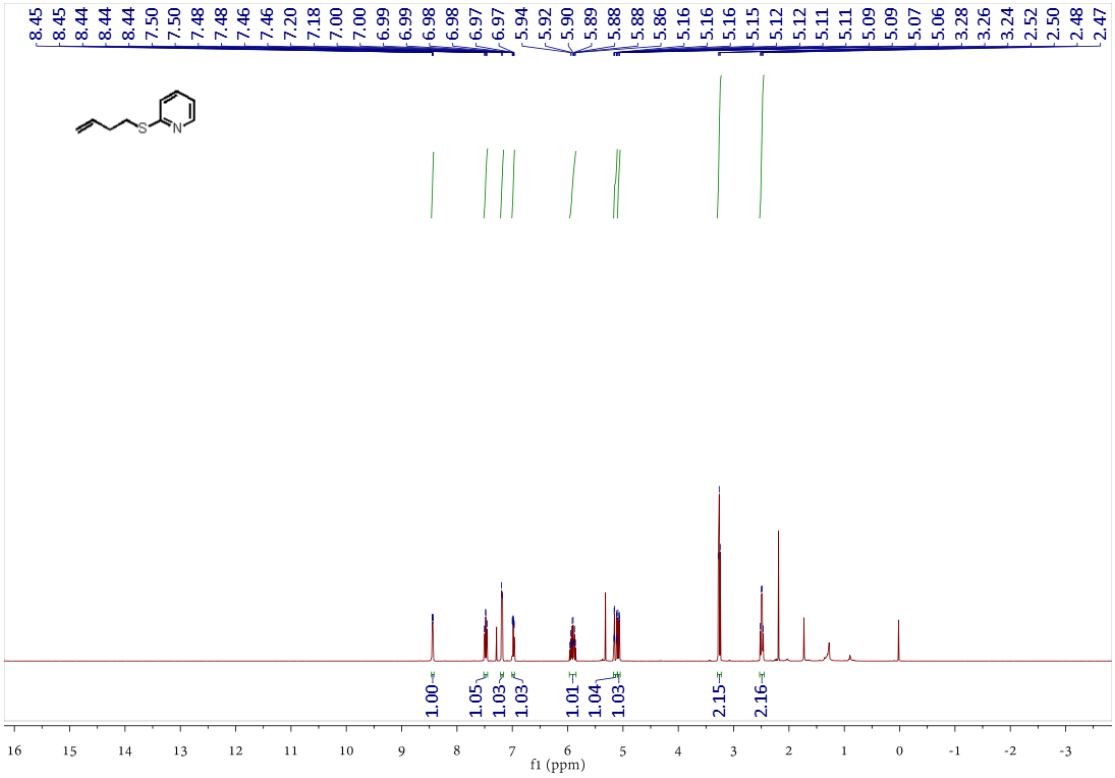
^{1}H NMR spectrum of 2-((cyclopentylmethyl)thio)pyridine (43)



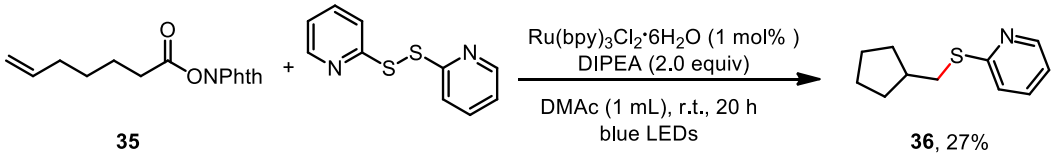
^{13}C NMR spectrum of 2-((cyclopentylmethyl)thio)pyridine (43)



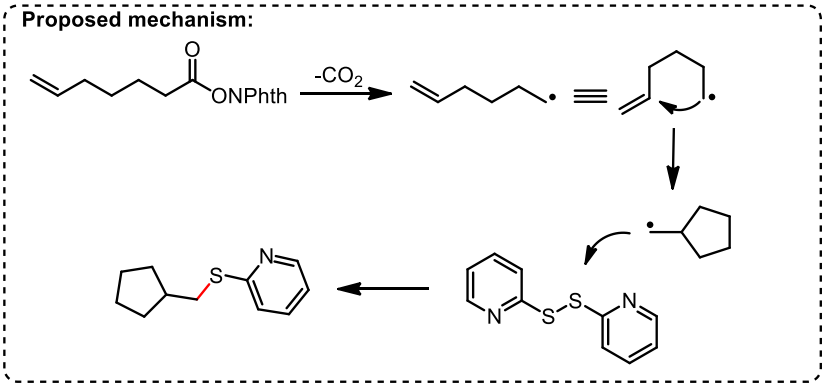
^{1}H NMR spectrum of 2-(but-3-en-1-ylthio)pyridine (45)

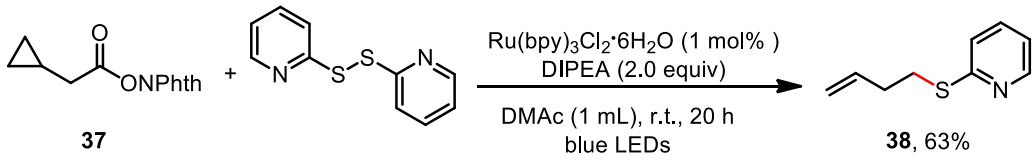


5. Proposed mechanism of control experiments

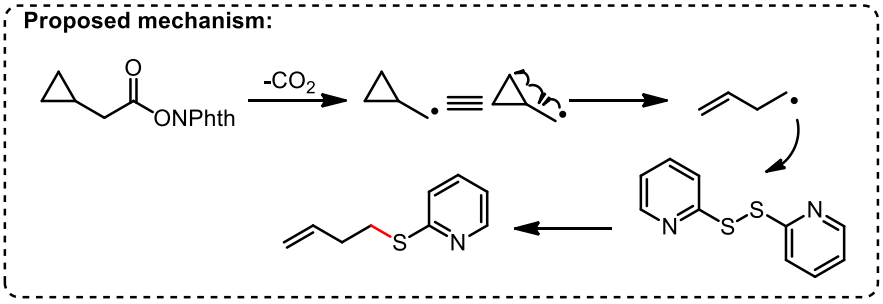


35 **36**, 27%





37 **38**, 63%



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