

**Synthetic Exploration on Electrophilic Xanthylation *via*  
Powerful *N*-xanthylphthalimides**

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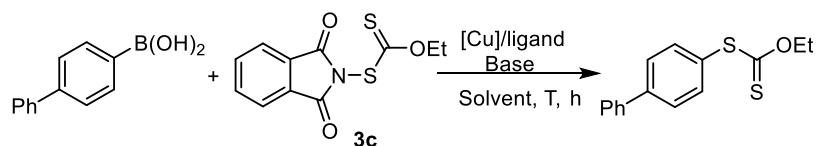
## I. General information.

All reactions were carried out under an argon atmosphere using standard Schlenk-Lines.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were acquired on 400 MHz, 101 MHz, 376 MHz on JOEL-ZETA 400 MHz or Bruker-AVANCE III-400 MHz spectrometer (400 MHz for  $^1\text{H}$ ; 101 MHz for  $^{13}\text{C}$ ; 376 MHz for  $^{19}\text{F}$ ).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts were determined relative to internal standard TMS at  $\delta$  0.0 ppm and  $^{19}\text{F}$  NMR chemical shifts were determined relative to  $\text{CFCl}_3$  as inter standard. Chemical shifts ( $\delta$ ) 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. All reactions were monitored by TLC with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F<sub>254</sub>). Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters ( $\text{cm}^{-1}$ ). Mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer or Agilent 7890B-5977A mass spectrometer. Single crystal diffraction was performed on a Bruker APEX-II CCD diffractometer.

**Materials.** All reagents were received from commercial sources unless otherwise noted. Solvents were freshly dried and degassed according to the purification handbook *Purification of Laboratory Chemicals* before using.

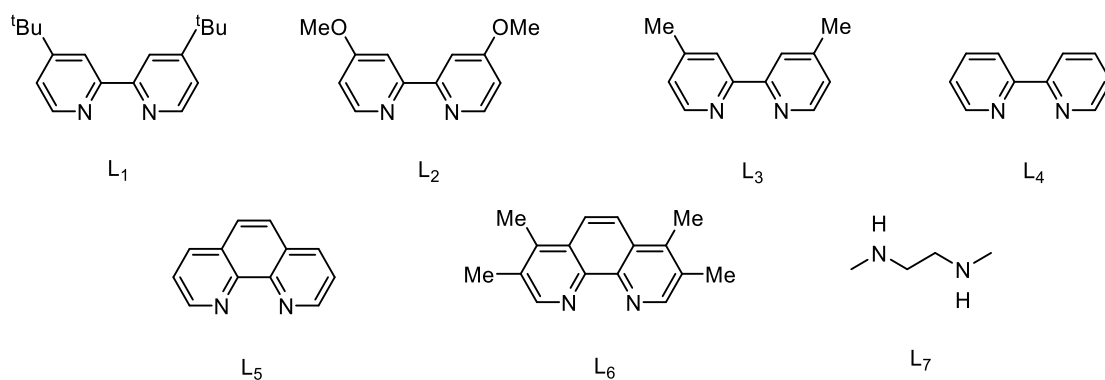
## II. Optimization of the reaction conditions

**Table S1. Optimization of conditions for reaction of aryl/vinyl boronic acids with *N*-ethylxanthylphthalimide **3c**.** *a, b*



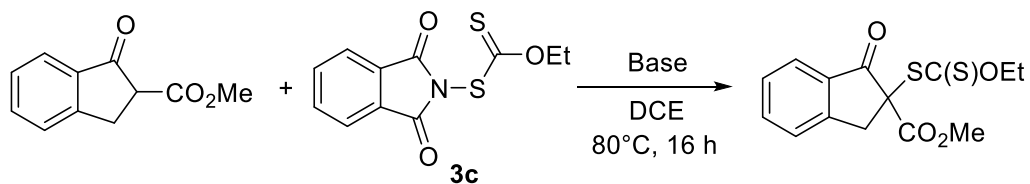
Entry	[Cu]	<b>3c</b>	Ligand	Base	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>
1	CuBr	1.05 eq.	L <sub>1</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	66
2	CuBr	1.05 eq.	L <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	77
3	CuBr	1.05 eq.	L <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	78
4	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	86
5	CuBr	1.05 eq.	L <sub>5</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	69
6	CuBr	1.05 eq.	L <sub>6</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	65
7	CuBr	1.05 eq.	L <sub>7</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	34
8	CuBr	1.05 eq.	L <sub>4</sub>	Li <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	66
9	CuBr	1.05 eq.	L <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	19
10	CuBr	1.05 eq.	L <sub>4</sub>	CS <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	18
11	CuBr	1.05 eq.	L <sub>4</sub>	K <sub>3</sub> PO <sub>4</sub>	CH <sub>3</sub> CN	60	29
12	CuBr	1.05 eq.	L <sub>4</sub>	<sup>t</sup> BuOK	CH <sub>3</sub> CN	60	24
13	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	DCM	60	70
14	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	DMF	60	NR
15	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	THF	60	68
16	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	Dioxane	60	54
17	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	Toluene	60	41
18	CuBr	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	DME	60	55
19	CuI	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	87
20	CuCl	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	80
21	CuOAc	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	77
22	CuTc	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	88
23	Cu(OAc) <sub>2</sub>	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	47

Entry	[Cu]	<b>3c</b>	Ligand	Base	Solvent	Temp. (°C)	Yield(%) <sup>b</sup>
24	CuBr <sub>2</sub>	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	69
25	CuSO <sub>4</sub>	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	89
26	CuSO <sub>4</sub> ·5H <sub>2</sub> O	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	87
27	Cu(OTf) <sub>2</sub>	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	85
28	CuCl <sub>2</sub> ·2H <sub>2</sub> O	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	67
29	CuCN	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	81
30	Cu(MeCN) <sub>4</sub> ·BF <sub>4</sub>	1.05 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	81
31	CuSO <sub>4</sub>	1.1 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	60	90
<b>32</b>	<b>CuSO<sub>4</sub></b>	<b>1.2 eq.</b>	<b>L<sub>4</sub></b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>	<b>CH<sub>3</sub>CN</b>	<b>60</b>	<b>97</b>
33	CuSO <sub>4</sub>	1.2 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	40	95
34	CuSO <sub>4</sub>	1.2 eq.	L <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	25	78



<sup>a</sup> Reaction conditions: 4-biphenylboronic acid (0.10 mmol), *N*-ethylxanthylphthalimide **3c**, [Cu] (5 mol%), ligand (5 mol%) and base (0.05 mmol, 0.5 equiv) in solvent (1.0 mL) in argon atmosphere at 60 °C for 15 h; <sup>b</sup>Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

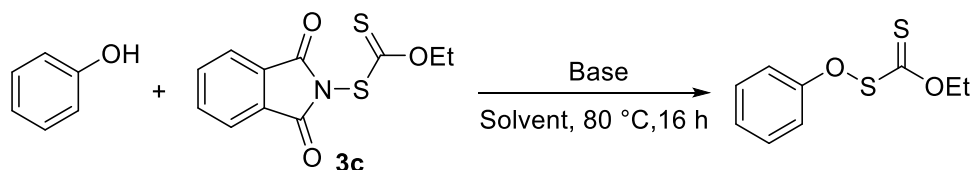
**Table S2. Optimization of conditions for reaction of  $\beta$ -ketoesters with *N*-ethylxanthylphthalimide **3c**.<sup>a, b</sup>**



Entry	Base	Yield (%) <sup>b</sup>
1	KOH	66
2	$\text{Cs}_2\text{CO}_3$	82
3	$\text{Li}_2\text{CO}_3$	2
4	$\text{Na}_2\text{CO}_3$	62
<b>5</b>	<b><math>\text{K}_2\text{CO}_3</math></b>	<b>94</b>
6	$\text{K}_3\text{PO}_4$	90
7	<i>t</i> BuOK	69

<sup>a</sup> Reaction conditions:  $\beta$ -ketoester (0.1 mmol), *N*-ethylxanthylphthalimide **3c** (0.12 mmol, 1.2 equiv), base (0.11 mmol, 1.1 equiv) in DCE (1.0 mL) in argon atmosphere at 80 °C for 16 h; <sup>b</sup>Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

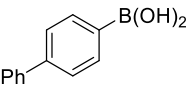
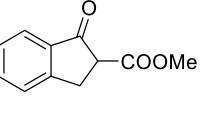
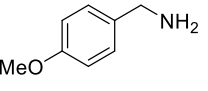
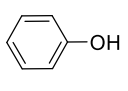
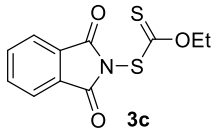
**Table S3. Optimization of conditions for reaction of phenols with *N*-ethylxanthylphthalimide **3c**.<sup>a, b</sup>**



Entry	Base	<b>3c</b> (eq.)	Solvent	Yield (%) <sup>b</sup>
1	NaH	1.1	Toluene	65
2	KOH	1.1	Toluene	57
3	Cs <sub>2</sub> CO <sub>3</sub>	1.1	Toluene	83
4	Li <sub>2</sub> CO <sub>3</sub>	1.1	Toluene	4
5	Na <sub>2</sub> CO <sub>3</sub>	1.1	Toluene	14
6	K <sub>2</sub> CO <sub>3</sub>	1.1	Toluene	56
7	<sup>t</sup> BuOK	1.1	Toluene	68
8	K <sub>3</sub> PO <sub>4</sub>	1.1	Toluene	56
9	Cs <sub>2</sub> CO <sub>3</sub>	1.2	Toluene	90
10	Cs <sub>2</sub> CO <sub>3</sub>	1.4	Toluene	92
<b>11</b>	<b>Cs<sub>2</sub>CO<sub>3</sub></b>	<b>1.4</b>	<b>DCE</b>	<b>97</b>
12	Cs <sub>2</sub> CO <sub>3</sub>	1.4	THF	53
13	Cs <sub>2</sub> CO <sub>3</sub>	1.4	DMF	Trace
14	Cs <sub>2</sub> CO <sub>3</sub>	1.4	CH <sub>3</sub> CN	Trace
15	Cs <sub>2</sub> CO <sub>3</sub>	1.4	Dioxane	60
16	Cs <sub>2</sub> CO <sub>3</sub>	1.4	DME	17

<sup>a</sup> Reaction conditions: phenols (0.1 mmol), *N*-ethylxanthylphthalimide **3c**, base (0.11 mmol, 1.1 equiv) in solvent (1.0 mL) in argon atmosphere at 80 °C for 16 h; <sup>b</sup>Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

**Table S4. Comparison of reactivity of different electrophilic reagents. <sup>q</sup>**

Substrates Electrophilic reagents				
EtO(S)CS-SC(S)OEt <b>1</b>	ND <sup>a</sup>	32% <sup>b</sup>	ND <sup>c</sup>	23% <sup>d</sup>
EtO(S)CSNa + I <sub>2</sub> <b>2</b>	ND <sup>e or f</sup>	20% <sup>g or h</sup>	ND <sup>i</sup> , 37% <sup>j</sup>	ND <sup>k or l</sup>
 <b>3c</b>	97% <sup>m</sup>	94% <sup>n</sup>	89% <sup>o</sup>	97% <sup>p</sup>

<sup>a</sup> Reaction conditions: 4-biphenylboronic acid (0.10 mmol), reagent **1** (0.12 mmol, 1.2 equiv), CuSO<sub>4</sub> (5 mol%), bpy (5 mol%) and Na<sub>2</sub>CO<sub>3</sub> (0.1 equiv) in MeCN (1.0 mL) at 60 °C for 15 h.

<sup>b</sup> Indanone methyl ester (0.10 mmol), reagent **1** (0.12 mmol, 1.2 equiv) and K<sub>2</sub>CO<sub>3</sub> (1.1 equiv) in DCE (1.0 mL) at 80 °C for 16 h.

<sup>c</sup> 4-Methoxybenzylamine (0.10 mmol) and reagent **1** (0.12 mmol, 1.2 equiv) in toluene (1.0 mL) at RT for 16 h.

<sup>d</sup> Phenol (0.10 mmol), reagent **1** (0.14 mmol, 1.4 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (1.1 equiv) in DCE (1.0 mL) at 80 °C for 16 h.

<sup>e</sup> 4-Biphenylboronic acid (0.10 mmol), reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv) in KI (20%) solution (1.0 mL) at 40 °C for 15 h.

<sup>f</sup> 4-Biphenylboronic acid (0.10 mmol), reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv), CuSO<sub>4</sub> (5 mol%), bpy (5 mol%) and Na<sub>2</sub>CO<sub>3</sub> (0.1 equiv) in MeCN (1.0 mL) at 60 °C for 15 h.

<sup>g</sup> Indanone methyl ester (0.10 mmol), reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv) in KI (20%) solution (1.0 mL) at 40 °C for 15 h.

<sup>h</sup> Indanone methyl ester (0.10 mmol), reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv) and K<sub>2</sub>CO<sub>3</sub> (1.1 equiv) in DCE (1.0 mL) at 80 °C for 16 h.

<sup>i</sup> 4-Methoxybenzylamine (0.10 mmol), reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv) in KI (20%) solution (1.0 mL) at 40 °C for 15 h.

<sup>j</sup> 4-Methoxybenzylamine (0.10 mmol) and reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv) in toluene (1.0 mL) at RT for 16 h.



<sup>k</sup> Phenol (0.10 mmol), reagent **2** (0.12 mmol EtO(S)CSNa+I<sub>2</sub>, 1.2 equiv) in KI (20%) solution (1.0 mL) at 40 °C for 15 h.

<sup>l</sup> Phenol (0.10 mmol), reagent **2** (0.14 mmol EtO(S)CSNa+I<sub>2</sub>, 1.4 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (1.1 equiv) in DCE (1.0 mL) at 80 °C for 16 h.

<sup>m</sup> 4-Biphenylboronic acid (0.10 mmol), reagent **3c** (0.12 mmol, 1.2 equiv), CuSO<sub>4</sub> (5 mol%), bpy (5 mol%) and Na<sub>2</sub>CO<sub>3</sub> (0.1 equiv) in MeCN (1.0 mL) at 60 °C for 15 h.

<sup>n</sup> Indanone methyl ester (0.10 mmol), reagent **3c** (0.12 mmol, 1.2 equiv) and K<sub>2</sub>CO<sub>3</sub> (1.1 equiv) in DCE (1.0 mL) at 80 °C for 16 h.

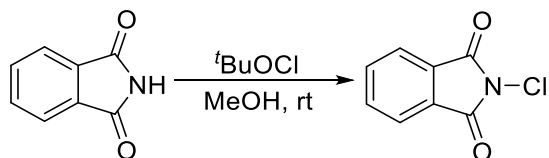
<sup>o</sup> 4-Methoxybenzylamine (0.10 mmol) and reagent **3c** (0.12 mmol, 1.2 equiv) in toluene (1.0 mL) at RT for 16 h.

<sup>p</sup> Phenol (0.10 mmol), reagent **3c** (0.14 mmol, 1.4 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (1.1 equiv) in DCE (1.0 mL) at 80 °C for 16 h.

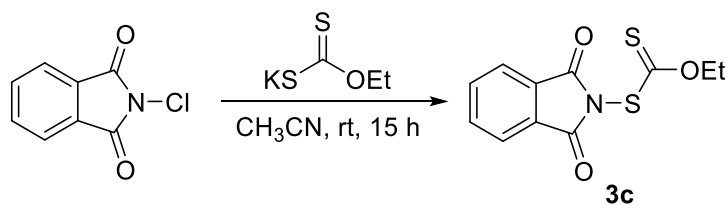
<sup>q</sup> Yields were determined by <sup>1</sup>H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

### III. General procedure

**General procedure for the preparation of *N*-ethylxanthylphthalimide **3c** and its analogues.**

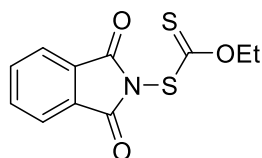


**Preparation of *N*-chlorophthalimide.**<sup>[1]</sup> To a suspension of phthalimide (7.36 g, 50.0 mmol) in  $\text{MeOH}$  (500 mL) was added  $t\text{BuOCl}$  (7.62 mL, 67.4 mmol, 1.35 equiv) quickly. The mixture was stirred for 5 min and standing for 5 min. The precipitate was filtered and dried under high vacuum to obtain a white powder (8.9 g, 98% yield). No further purification is required and can be used directly for the next step.



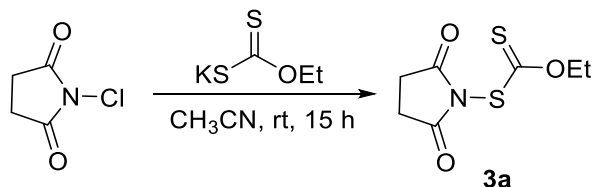
**Synthesis of *N*-ethylxanthylphthalimide **3c**.**<sup>[2]</sup> In a 1 L round-bottom flask, potassium ethyl xanthate (7.85 g, 49.0 mmol, 1.0 equiv) was suspended in  $\text{MeCN}$  (300 mL). To this suspension was added a solution of *N*-chlorophthalimide (8.9 g, 49.0 mmol, 1.0 equiv) in  $\text{MeCN}$  (300 mL) *via* constant pressure funnel over 20 min. The reaction mixture was stirred for 15 h and the suspension was concentrated in vacuo. The resultant solid was purified by flash column chromatography to afford the title compound.

**S-(1,3-Dioxoisindolin-2-yl) O-ethyl carbonodithioate **3c**.**



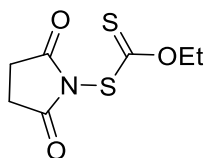
White solid (9.4 g, 72%). Mp: 115-116 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 7.82 (dd,  $J = 5.6, 3.1$  Hz, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.30 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101

MHz, CDCl<sub>3</sub>)  $\delta$  208.8, 166.2, 135.1, 132.1, 124.3, 71.4, 13.6 ppm. IR (KBr):  $\nu$  = 3006, 2990, 1749, 1726, 1469, 1276, 1262, 1039, 757, 705 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>11</sub>H<sub>9</sub>NO<sub>3</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 289.9916, found 289.9923.

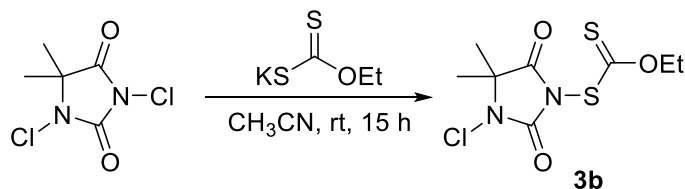


**Synthesis of reagent 3a.** According to the synthesis method of *N*-ethylxanthylphthalimide **3c**, potassium ethyl xanthate (8.0 g, 50.0 mmol, 1.0 equiv) was suspended in MeCN (300 mL). To this suspension was added a solution of *N*-chlorosuccinimide (6.68 g, 50.0 mmol, 1.0 equiv) in MeCN (200 mL) *via* constant pressure funnel over 20 min. The reaction mixture was stirred for 15 h and the suspension was concentrated in vacuo. The resultant solid was purified by flash column chromatography to afford the title compound.

***S*-(2,5-Dioxopyrrolidin-1-yl) *O*-ethyl carbonodithioate 3a.**



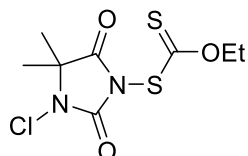
Yellow oil (1.1 g, 10%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f$  = 0.3). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.60 (q,  $J$  = 7.1 Hz, 2 H), 2.81 (s, 4 H), 1.43 (t,  $J$  = 7.1 Hz, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  184.4, 172.6, 70.7, 28.5, 13.4 ppm. IR (KBr):  $\nu$  = 3006, 2990, 1730, 1276, 1261, 765, 702 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>7</sub>H<sub>9</sub>NO<sub>3</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 241.9916, found 241.9920.



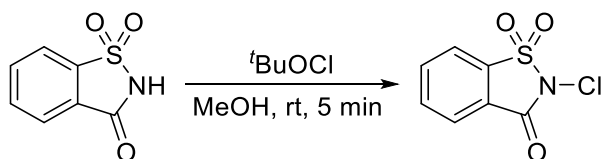
**Synthesis of reagent 3b.** According to the synthesis method of *N*-ethylxanthylphthalimide **3c**, potassium ethyl xanthate (4.0 g, 25.0 mmol, 2.5 equiv) was suspended in MeCN (300 mL). To this suspension was added a solution of 1,3-dichloro-5,5-dimethylhydantoin (1.97 g, 10.0 mmol, 1.0 equiv) in MeCN (200 mL) *via* constant

pressure funnel over 20 min. The reaction mixture was stirred for 15 h and the suspension was concentrated in vacuo. The resultant solid was purified by flash column chromatography to afford the title compound.

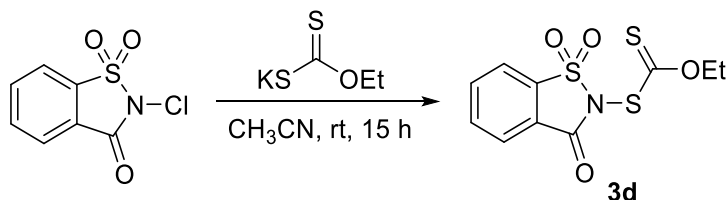
**S-(3-Chloro-4,4-dimethyl-2,5-dioximidazolidin-1-yl) O-ethylcarbonodithioate 3b.**



Yellow solid (933.1 mg, 33%). Mp: 92-93 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.4$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.62 (q,  $J = 7.1$  Hz, 2 H), 1.48 (s, 6 H), 1.45 (d,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  183.2, 172.9, 152.0, 70.1, 58.5, 25.2, 13.5 ppm. IR (KBr):  $\nu = 3006, 2990, 1737, 1276, 1262, 750, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_8\text{H}_{11}\text{ClN}_2\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 304.9792, found 304.9794.



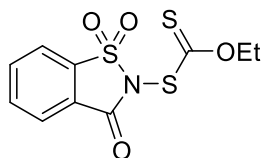
**Preparation of N-chlorosaccharin.**<sup>[1]</sup> To a suspension of saccharin (12.0 g, 65.6 mmol) in MeOH (120 mL) was added  $t\text{BuOCl}$  (10.0 mL, 88.4 mmol, 2.7 equiv) quickly. The suspension turned to clear solution and quickly a large amount of white precipitate was formed. The mixture was stirred for 5 min and standing for 5 min. The precipitate was filtered and dried under high vacuum to obtain a white powder (12.0 g, 84% yield). No further purification is required and can be used directly for the next step.



**Synthesis of reagent 3d.** According to the synthesis method of *N*-ethylxanthylphthalimide **3c**, potassium ethyl xanthate (5.16 g, 32.2 mmol, 1.0 equiv) was suspended in MeCN (300 mL). To this suspension was added a solution of *N*-chlorosaccharin (7.0 g, 32.2 mmol, 1.0 equiv) in MeCN (200 mL) *via* constant pressure

funnel over 20 min. The reaction mixture was stirred for 15 h and the suspension was concentrated in vacuo. The resultant solid was purified by flash column chromatography to afford the title compound.

***S*-(1,1-Dioxido-3-oxobenzo[*d*]isothiazol-2(3*H*)-yl) *O*-ethyl carbonodithioate 3d.**



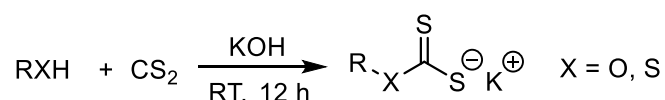
White solid (1.95 g, 20%). Mp: 100-101 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19–8.14 (m, 1 H), 7.99–7.92 (m, 2 H), 7.92–7.86 (m, 1 H), 4.73 (q,  $J = 7.1$  Hz, 2 H), 1.51 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  180.4, 156.2, 136.4, 135.0, 126.5, 125.8, 121.4, 121.3, 69.0, 13.5 ppm. IR (KBr):  $\nu = 3006, 2990, 1276, 1262, 1229, 767, 703, 675, 576, 502$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_9\text{NO}_4\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 325.9586, found 325.9589.

### Preparation of substrates.

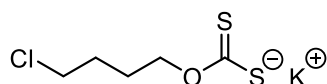
Substrates  $\beta$ -ketoesters and oxindoles were prepared according to literature methods.<sup>[3]</sup>

### I. General procedure for the synthesis of potassium thiolate<sup>[4]</sup>

Primary alcohols (1.0 equiv) were treated with KOH (1.0 equiv) and carbon disulfide (1.2 equiv) in diethyl ether. The reaction mixture was stirred at room temperature for 3-12 h. The precipitates were collected by filtration, washed with diethyl ether, and dried in vacuo to afford the title products.

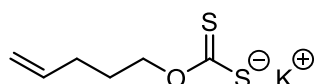


### Synthesis of potassium *O*-(4-chlorobutyl) carbonodithioate salt.



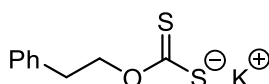
4-Chlorobutan-1-ol (2.0 mL, 20 mmol) was treated with crushed potassium hydroxide (1.0 equiv) followed by addition of carbon disulfide (1.2 equiv). The solution was stirred at room temperature for 12 h and then concentrated in vacuo to give a residue that was washed with diethyl ether and dried in vacuo to afford the title product as a white solid in 58% yield. No further purification is required and can be used directly for the next step.

### Synthesis of potassium *O*-(pent-4-en-1-yl) carbonodithioate salt.



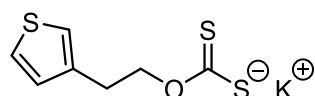
Pent-4-en-1-ol (2.1 mL, 20 mmol) was treated with crushed potassium hydroxide (1.0 equiv) followed by addition of carbon disulfide (1.2 equiv). The solution was stirred at room temperature for 12 h and then concentrated in vacuo to give a residue that was washed with diethyl ether and dried in vacuo to afford the title product as a white solid in 79% yield. No further purification is required and can be used directly for the next step.

### Synthesis of potassium *O*-phenethyl carbonodithioate salt.



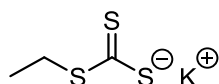
2-Phenylethanol (2.4 mL, 20 mmol) was treated with crushed potassium hydroxide (1.0 equiv) followed by addition of carbon disulfide (1.2 equiv). The solution was stirred at room temperature for 12 h and then concentrated in vacuo to give a residue that was washed with diethyl ether and dried in vacuo to afford the title product as a pale-yellow solid in 91% yield. No further purification is required and can be used directly for the next step.

**Synthesis of potassium *O*-(2-(thiophen-3-yl)ethyl) carbonodithioate salt.**



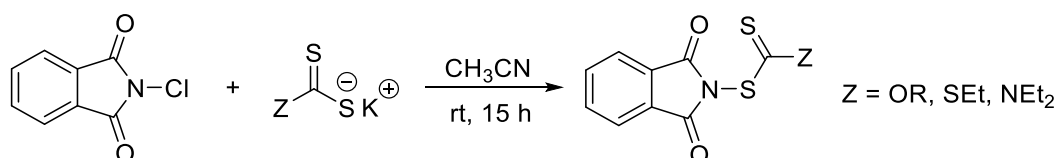
2-(Thiophen-3-yl)ethan-1-ol (2.1 mL, 18.7 mmol) was treated with crushed potassium hydroxide (1.0 equiv) followed by addition of carbon disulfide (1.2 equiv). The solution was stirred at room temperature for 12 h and then concentrated in vacuo to give a residue that was washed with diethyl ether and dried in vacuo to afford the title product as a pale-yellow solid in 30% yield. No further purification is required and can be used directly for the next step.

**Synthesis of potassium ethyl carbonotrithioate salt.**



Ethanethiol (1.48 mL, 20 mmol) was treated with freshly crushed potassium hydroxide (1.0 equiv) and carbon disulfide (1.1 equiv) in diethyl ether (15 mL). The suspension was stirred at room temperature for 3 h, and the white precipitate was collected by filtration, washed with diethyl ether and dried in vacuo to afford the desired product as a yellow solid in 93% yield. No further purification is required and can be used directly for the next step.

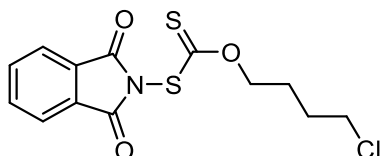
**II. General procedure for the synthesis of xanthate-derived reagents.**



According to the synthesis method of *N*-ethylxanthylphthalimide **3c**. In a 1 L round-

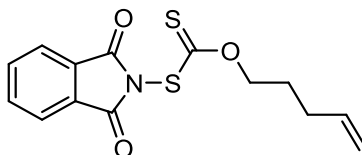
bottom flask, potassium thiolate (1.0 equiv) was suspended in MeCN. To this suspension was added a solution of *N*-chlorophthalimide (1.0 equiv) in MeCN via constant pressure funnel over 20 min. The reaction mixture was stirred for 15 h and the suspension was concentrated in vacuo. The resultant solid was purified by flash column chromatography to afford the title compounds.

***O*-(4-Chlorobutyl) *S*-(1,3-dioxoisindolin-2-yl) carbonodithioate 3ea**



Potassium *O*-(4-chlorobutyl) carbonodithioate salt (1.11 g, 4.99 mmol) reacts with *N*-chlorophthalimide (907 mg, 4.99 mmol) to afford **3ea** (1.2 g, 73% yield) as a white solid (mp: 89-90 °C) after chromatography (eluent: ethyl acetate/petroleum ether 1:5,  $R_f = 0.3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 5.6, 3.1$  Hz, 2 H), 7.84 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 4.57 (t,  $J = 6.1$  Hz, 2 H), 3.42 (t,  $J = 6.3$  Hz, 2 H), 1.88–1.79 (m, 2 H), 1.77–1.66 (m, 2 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 166.3, 135.3, 132.0, 124.5, 74.3, 44.2, 28.8, 25.6 ppm. IR (KBr):  $\nu = 3006, 2990, 1276, 1262, 1045, 747, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{13}\text{ClNO}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 351.9839, found 351.9842.

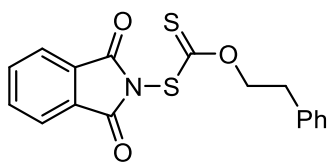
***S*-(1,3-Dioxoisindolin-2-yl) *O*-(pent-4-en-1-yl) carbonodithioate 3eb**



Potassium *O*-(pent-4-en-1-yl) carbonodithioate salt (3.0 g, 14.97 mmol) reacts with *N*-chlorophthalimide (2.72 g, 14.97 mmol) to afford **3eb** (2.3 g, 50% yield) as a white solid (mp: 44-45 °C) after chromatography (eluent: ethyl acetate/petroleum ether 1:5,  $R_f = 0.3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (dd,  $J = 5.4, 3.3$  Hz, 2 H), 7.83 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 5.73–5.50 (m, 1 H), 4.93–4.82 (m, 2 H), 4.53 (t,  $J = 6.4$  Hz, 2 H), 1.96 (q,  $J = 7.3$  Hz, 2 H), 1.78–1.69 (m, 2 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 166.3, 136.7, 135.2, 132.1, 124.5, 115.9, 74.5, 29.7, 27.3 ppm. IR (KBr):  $\nu = 3006, 2990, 1793, 1749, 1276, 1262, 1043, 745, 704$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 330.0229, found 330.0229.

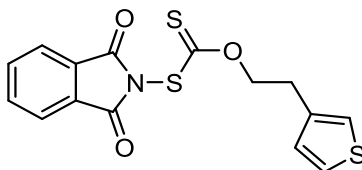


### ***S*-(1,3-Dioxoisindolin-2-yl) *O*-phenethyl carbonodithioate **3ec****



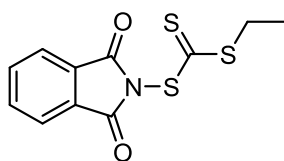
Potassium *O*-Phenethyl carbonodithioate salt (3.87 g, 16.37 mmol) reacts with *N*-chlorophthalimide (2.97 g, 16.37 mmol) to afford **3ec** (3.96 g, 70% yield) as a white solid (mp: 103-104 °C) after chromatography (eluent: ethyl acetate/petroleum ether 1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 7.84 (dd,  $J = 5.6, 3.1$  Hz, 2 H), 7.13 (d,  $J = 3.0$  Hz, 3 H), 7.03 (s, 2 H), 4.76 (t,  $J = 6.9$  Hz, 2 H), 2.98 (t,  $J = 6.9$  Hz, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 166.2, 136.5, 135.1, 132.1, 128.7, 128.6, 126.9, 124.5, 75.0, 34.5 ppm. IR (KBr):  $\nu = 3006, 2990, 1749, 1727, 1276, 1262, 1044, 745, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{17}\text{H}_{13}\text{NO}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 366.0229, found 366.0226.

### ***S*-(1,3-Dioxoisindolin-2-yl) *O*-(2-(thiophen-3-yl)ethyl) carbonodithioate **3ed****



Potassium *O*-(2-(thiophen-3-yl)ethyl) carbonodithioate salt (922.6 mg, 3.81 mmol) reacts with *N*-chlorophthalimide (691 mg, 3.81 mmol) to afford **3ed** (1.21 g, 91% yield) as a white solid (mp: 90-91 °C) after chromatography (eluent: ethyl acetate/petroleum ether 1:5,  $R_f = 0.3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 7.83 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 7.13 (dd,  $J = 5.0, 3.0$  Hz, 1 H), 6.82 (s, 1 H), 6.79 (d,  $J = 5.1$  Hz, 1 H), 4.74 (t,  $J = 6.7$  Hz, 2 H), 2.99 (t,  $J = 6.7$  Hz, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 166.2, 136.6, 135.2, 132.0, 127.9, 126.1, 124.5, 121.9, 74.4, 29.0 ppm. IR (KBr):  $\nu = 3006, 2990, 1750, 1276, 1262, 765, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{11}\text{NO}_3\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 371.9793, found 371.9794.

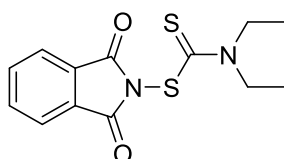
### **1,3-Dioxoisindolin-2-yl ethyl carbonotrithioate **3ee****



Potassium ethyl carbonotrithioate salt (1.76 g, 10.0 mmol) reacts with *N*-

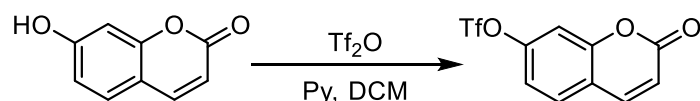
chlorophthalimide (1.82 g, 10.0 mmol) to afford **3ee** (2.23 g, 79% yield) as a yellow solid (mp: 130-131 °C) after chromatography (eluent: ethyl acetate/petroleum ether 1:5,  $R_f = 0.2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 7.86 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 3.31 (d,  $J = 14.9$  Hz, 2 H), 1.29 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  222.0, 166.1, 135.3, 131.9, 124.7, 31.1, 12.7 ppm. IR (KBr):  $\nu = 3006, 2990, 1748, 1276, 1262, 745, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_9\text{NO}_2\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 305.9688, found 305.9692.

### 1,3-Dioxoisindolin-2-yl diethylcarbamodithioate **3ef**



Sodium diethyldithiocarbamate (5.13 g, 10.0 mmol) reacts with N-chlorophthalimide (5.46 g, 10.0 mmol) to afford **3ef** (942 mg, 32% yield) as a yellow solid (mp: 109-110 °C) after chromatography (eluent: ethyl acetate/petroleum ether 1:5,  $R_f = 0.2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 5.5, 3.0$  Hz, 2 H), 7.78 (dd,  $J = 5.5, 3.1$  Hz, 2 H), 4.05 (q,  $J = 7.1$  Hz, 2 H), 3.51 (q,  $J = 7.3$  Hz, 2 H), 1.41 (t,  $J = 7.2$  Hz, 3 H), 1.23 (t,  $J = 7.3$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 165.1, 134.8, 132.2, 124.3, 48.3, 47.6, 13.9, 11.1 ppm. IR (KBr):  $\nu = 3006, 2990, 1723, 1513, 1317, 1276, 1262, 757, 676$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 317.0389, found 317.0388.

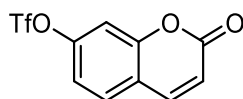
**III. (2-Oxo-2H-chromen-7-yl)boronic acid was prepared following the literature procedure:<sup>[5]</sup>**



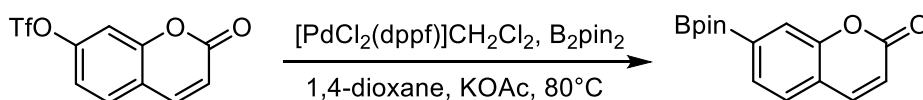
To a solution of 7-hydroxycoumarin (3.68 g, 22.72 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (80 mL), pyridine (1.84 mL, 22.72 mmol) was added at 0 °C and stirred for 30 min. To this mixture, trifluoromethanesulfonic anhydride (4.6 mL, 27.24 mmol) was added dropwise at 0 °C in argon atmosphere. The resulting mixture was allowed to warm up to room temperature and stirred for 24 h. The mixture was diluted with water (25 mL) and aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  3). The combined organic

layer was washed with brine, dried over sodium sulfate, filtered and the filtrate was concentrated to give crude compound, which was purified by silica gel column chromatography.

### 2-Oxo-2H-chromen-7-yl trifluoromethanesulfonate

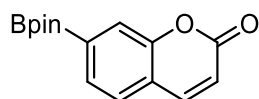


White solid (4.1 g, 61%). Mp: 67-68 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 9.7$  Hz, 1 H), 7.58 (d,  $J = 8.5$  Hz, 1 H), 7.25 (d,  $J = 2.9$  Hz, 1 H), 7.21 (dd,  $J = 8.5, 2.4$  Hz, 1 H), 6.47 (d,  $J = 9.6$  Hz, 1 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 154.7, 150.9, 142.2, 129.6, 120.3, 118.9, 117.9, 117.2, 110.6 ppm.

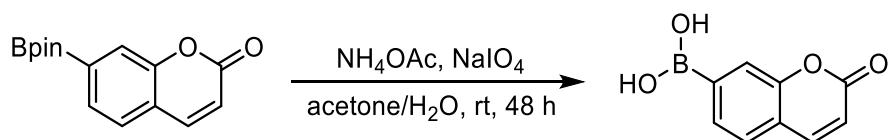


To a suspension of 2-oxo-2H-chromen-7-yl trifluoromethanesulfonate (3.81 g, 12.96 mmol), bis(pinacolato)diboron (3.96 g, 15.6 mmol) and potassium acetate (3.82 g, 38.88 mmol) in dioxane (80 mL),  $[\text{PdCl}_2(\text{dppf})]\text{CH}_2\text{Cl}_2$  (320 mg, 0.32 mmol) was added in argon atmosphere. The resulting mixture was refluxed for 12 h. Then, the reaction mixture was filtered and the filtrate was diluted with water and extracted in ethyl acetate ( $3 \times 10$  mL). The combined organic layer was washed with brine, dried by sodium sulfate and solvent was evaporated under reduced pressure. The crude compound was purified by silica gel chromatography.

### 7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-chromen-2-one

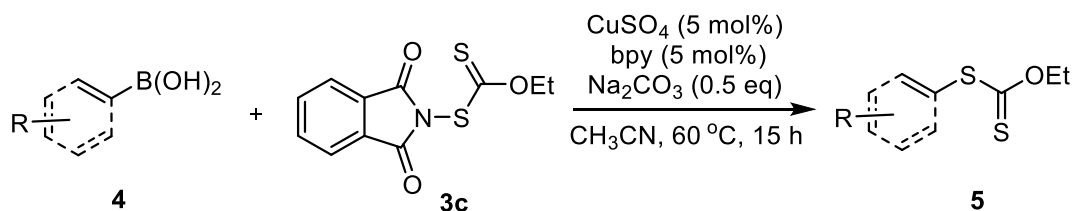


White solid (2.71 g, 77%). Mp: 170-171 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 1 H), 7.68 (d,  $J = 9.4$  Hz, 1 H), 7.65 (dd,  $J = 7.6, 1.0$  Hz, 1 H), 7.44 (d,  $J = 7.6$  Hz, 1 H), 6.42 (d,  $J = 9.5$  Hz, 1 H), 1.33 (s, 12 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 153.5, 143.3, 130.3, 130.2, 127.2, 122.9, 120.9, 117.8, 84.5, 24.9 ppm.



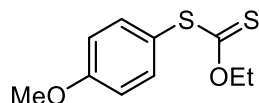
To a solution of aryl borate (2.0 g, 7.35 mmol) in acetone (60 mL) and water (30 mL) were added  $\text{NH}_4\text{OAc}$  (3.4 g, 44.1 mmol) and  $\text{NaIO}_4$  (9.43 g, 44.1 mmol). The resulting mixture was stirred at room temperature for 48 h. The reaction was filtrated through a pad of cellite and the filtrate was extracted with  $\text{Et}_2\text{O}$ . The combine organic layers were concentrated to give aryl boronic acid as a white solid (1.1 g, 76%). No further purification is required and can be used directly for the next step.

**General procedure for ethylxanthylation of aryl/vinyl boronic acids with *N*-ethylxanthylphthalimide **3c**.**



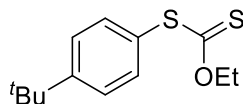
Aryl/vinyl boronic acids (0.5 mmol, 1.0 equiv), *N*-ethylxanthylphthalimide **3c** (160 mg, 0.60 mmol, 1.2 equiv),  $\text{Na}_2\text{CO}_3$  (26.5 mg, 0.25 mmol, 0.5 equiv),  $\text{CuSO}_4$  (4.0 mg, 0.025 mmol, 0.05 equiv), 2,2'-bipyridine (4.0 mg, 0.025 mmol, 0.05 equiv) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar in argon atmosphere. Then Freshly distilled  $\text{CH}_3\text{CN}$  (3.0 mL) was added to the Schlenk tube. The reaction was stirred at  $60\text{ }^\circ\text{C}$  for 15 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give ethylxanthylated arenes/alkenes.

***O*-Ethyl *S*-(4-methoxyphenyl) carbonodithioate **5aa****



Yellow oil (81.8 mg, 72%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56–7.34 (m, 2 H), 6.97–6.90 (m, 2 H), 4.60 (q,  $J = 7.2$  Hz, 2 H), 3.83 (s, 3 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 157.8, 147.1, 122.8, 114.5, 70.5, 55.6, 13.9 ppm. IR (KBr):  $\nu = 2959, 2837, 1592, 1494, 1293, 1251, 1226, 1112, 1041, 1005, 827\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 251.0171, found 251.0172.

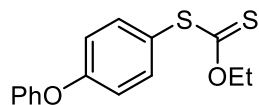
***S*-(4-(*Tert*-butyl)phenyl) *O*-ethyl carbonodithioate **5ab****



Yellow oil (111.8 mg, 88%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47–7.39 (m, 4 H), 4.61 (q,  $J = 7.1$  Hz, 2 H), 1.34 (s, 9 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.9, 153.4, 134.8, 126.9, 126.4, 70.3, 34.9, 31.3, 13.7 ppm. IR (KBr):  $\nu = 2963, 1223, 1110, 1044, 1012, 827, 764, 750, 556\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{18}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 277.0691, found

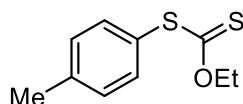
277.0693.

***O*-Ethyl *S*-(4-phenoxyphenyl) carbonodithioate 5ac**



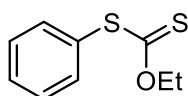
Yellow oil (114.4 mg, 79%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.48 (d,  $J = 8.7$  Hz, 2 H), 7.45–7.39 (m, 2 H), 7.22 (t,  $J = 7.4$  Hz, 1 H), 7.11 (d,  $J = 8.5$  Hz, 2 H), 7.06 (d,  $J = 8.7$  Hz, 2 H), 4.66 (q,  $J = 7.1$  Hz, 2 H), 1.39 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.9, 159.4, 156.0, 137.0, 130.1, 124.3, 123.7, 119.9, 118.7, 70.4, 13.7 ppm. IR (KBr):  $\nu = 2985, 1582, 1486, 1364, 1282, 1239, 1166, 1111, 1041, 1010, 869, 832, 798, 757, 693, 521, 497$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 313.0327, found 313.0317.

***O*-Ethyl *S*-(*p*-tolyl) carbonodithioate 5ad**



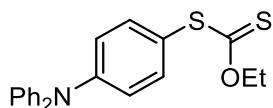
Yellow oil (82.8 mg, 78%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 7.8$  Hz, 2 H), 7.23 (d,  $J = 7.8$  Hz, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 2.39 (s, 3 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  214.1, 140.5, 135.2, 130.2, 127.0, 70.4, 21.5, 13.7 ppm. IR (KBr):  $\nu = 2983, 2923, 1275, 1260, 1225, 1112, 1041, 1017, 807, 764, 750, 510$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 235.0222, found 235.0219.

***O*-Ethyl *S*-phenyl carbonodithioate 5ae**



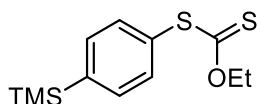
Yellow oil (63.9 mg, 64%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J = 7.3, 2.1$  Hz, 2 H), 7.47–7.39 (m, 3 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.32 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.4, 135.2, 130.3, 130.1, 129.3, 70.4, 13.7 ppm. IR (KBr):  $\nu = 3006, 2989, 1276, 1262, 1041, 750, 704$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_{10}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 221.0065, found 221.0060.

***S*-(4-(Diphenylamino)phenyl) *O*-ethyl carbonodithioate 5af**



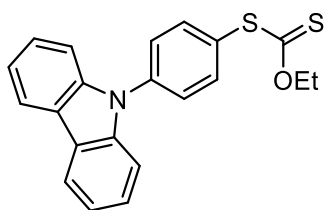
Yellow oil (141.1 mg, 77%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (t,  $J = 7.2$  Hz, 6 H), 7.17 (d,  $J = 8.7$  Hz, 4 H), 7.11 (t,  $J = 7.3$  Hz, 2 H), 7.07 (d,  $J = 7.0$  Hz, 2 H), 4.65 (q,  $J = 7.2$  Hz, 2 H), 1.39 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  214.7, 149.6, 147.1, 136.2, 129.7, 125.6, 124.2, 122.1, 121.5, 70.4, 13.9 ppm. IR (KBr):  $\nu = 3061, 3035, 2981, 2956, 2924, 2866, 1580, 1486, 1272, 1037, 822, 753, 695, 522$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{21}\text{H}_{19}\text{NOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 388.0800, found 388.0801.

***O*-Ethyl *S*-(4-(trimethylsilyl)phenyl) carbonodithioate 5ag**



Yellow oil (112.5 mg, 83%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 8.1$  Hz, 2 H), 7.48 (d,  $J = 7.9$  Hz, 2 H), 4.63 (q,  $J = 7.1$  Hz, 2 H), 1.34 (t,  $J = 7.1$  Hz, 3 H), 0.30 (s, 9 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.2, 143.1, 134.2, 134.1, 130.7, 70.4, 13.8, -1.1 ppm. IR (KBr):  $\nu = 2955, 2896, 1248, 1224, 1115, 1044, 1016, 841, 812, 757$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{12}\text{H}_{18}\text{OS}_2\text{Si}$   $[\text{M}+\text{Na}]^+$  calcd 293.0461, found 293.0455.

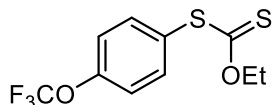
***S*-(4-(9*H*-Carbazol-9-yl)phenyl) *O*-ethyl carbonodithioate 5ah**



Pale yellow solid (140.6 mg, 77%). Mp: 44-45 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 7.8$  Hz, 2 H), 7.75 (d,  $J = 8.5$  Hz, 2 H), 7.66 (d,  $J = 8.6$  Hz, 2 H), 7.49 (d,  $J = 8.1$  Hz, 2 H), 7.45 (t,  $J = 7.6$  Hz, 2 H), 7.33 (t,  $J = 7.3$  Hz, 2 H), 4.69 (q,  $J = 7.1$  Hz, 2 H), 1.42 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.7, 140.5, 139.5, 136.8, 128.9, 127.5, 127.4, 126.3, 123.8, 120.6, 109.8, 70.7, 13.8 ppm. IR (KBr):  $\nu = 2987, 1591, 1499, 1450, 1276, 1260, 1227, 1040, 1014, 764, 749, 724$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{21}\text{H}_{17}\text{NOS}_2$   $[\text{M}+\text{Na}]^+$  calcd

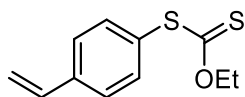
386.0644, found 386.0642.

***O*-Ethyl *S*-(4-(trifluoromethoxy)phenyl) carbonodithioate 5ai**



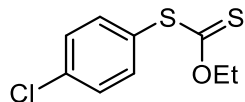
Yellow oil (123.5 mg, 87%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.6$  Hz, 2 H), 7.26 (d,  $J = 8.9$  Hz, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.32 (t,  $J = 7.1$  Hz, 3 H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.7 (s, 3 F);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.3, 150.5, 136.9, 128.7, 121.4, 120.4 (q,  $J = 262.6$  Hz), 70.6, 13.6 ppm. IR (KBr):  $\nu = 2987, 1491, 1256, 1211, 1166, 1112, 1042, 1016, 764, 750$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 304.9888, found 304.9882.

***O*-Ethyl *S*-(4-vinylphenyl) carbonodithioate 5aj**



Yellow oil (70.2 mg, 62%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 1.2$  Hz, 4 H), 6.72 (dd,  $J = 17.6, 10.9$  Hz, 1 H), 5.83 (d,  $J = 17.6$  Hz, 1 H), 5.35 (d,  $J = 11.0$  Hz, 1 H), 4.61 (q,  $J = 7.1$  Hz, 2 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.4, 139.3, 136.0, 135.4, 129.3, 127.1, 115.9, 70.5, 13.7 ppm. IR (KBr):  $\nu = 2986, 1226, 1112, 1041, 1013, 836, 750$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 247.0222, found 247.0222.

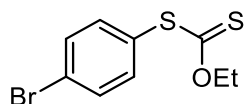
***S*-(4-Chlorophenyl) *O*-ethyl carbonodithioate 5ak**



White solid (85.3 mg, 73%). Mp: 36-37  $^\circ\text{C}$ . Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.34 (m, 4 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.5, 136.6, 136.5, 129.6, 128.7, 70.7, 13.7 ppm. IR (KBr):  $\nu = 2986, 2360, 2349, 1574, 1475, 1389, 1365, 1227, 1149, 1112, 1094, 1083, 1042, 1012, 819, 764, 749, 672, 665, 505, 441, 420$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{ClOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 254.9676, found 254.9672.

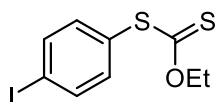
***S*-(4-Bromophenyl) *O*-ethyl carbonodithioate 5al**





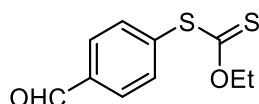
White solid (94.1 mg, 68%). Mp: 44-45 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.7$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 6.8$  Hz, 2 H), 7.35 (d,  $J = 6.8$  Hz, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.3, 136.7, 132.6, 129.3, 124.9, 70.7, 13.7 ppm. IR (KBr):  $\nu = 2986, 2349, 1567, 1473, 1386, 1363, 1275, 1226, 1149, 1111, 1068, 1041, 1008, 854, 814, 764, 750, 672, 665, 524, 495, 436, 407$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{BrOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 298.9170, found 298.9162.

**O-Ethyl S-(4-iodophenyl) carbonodithioate 5am**



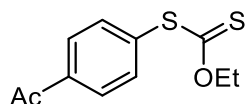
Pale yellow solid (127.4 mg, 79%). Mp: 39-40 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.7$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.3$  Hz, 2 H), 7.24 (d,  $J = 6.6$  Hz, 2 H), 4.63 (q,  $J = 7.1$  Hz, 2 H), 1.36 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.0, 138.5, 136.7, 130.0, 96.9, 70.6, 13.7 ppm. IR (KBr):  $\nu = 2988, 2359, 2349, 1471, 1381, 1276, 1260, 1228, 1111, 1040, 1004, 810, 764, 750, 672, 665, 515, 422$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{IOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 346.9032, found 346.9031.

**O-Ethyl S-(4-formylphenyl) carbonodithioate 5an**



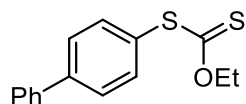
Light orange solid (92.7 mg, 82%). Mp: 36-37 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (s, 1 H), 7.90 (d,  $J = 6.7$  Hz, 2 H), 7.65 (d,  $J = 6.4$  Hz, 2 H), 4.59 (q,  $J = 7.1$  Hz, 2 H), 1.31 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.8, 191.5, 137.2, 136.9, 135.4, 130.2, 70.8, 13.7 ppm. IR (KBr):  $\nu = 2984, 2837, 2734, 1703, 1593, 1568, 1229, 1204, 1112, 1038, 1013, 836, 819, 750$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 249.0014, found 249.0012.

**S-(4-Acetylphenyl) O-ethyl carbonodithioate 5ao**



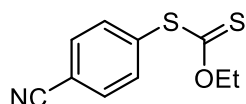
White solid (110.1 mg, 92%). Mp: 43-44 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 8.7$  Hz, 2 H), 7.56 (d,  $J = 8.6$  Hz, 2 H), 4.57 (q,  $J = 7.1$  Hz, 2 H), 2.59 (s, 3 H), 1.29 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.3, 197.4, 137.8, 135.7, 135.1, 129.0, 70.7, 26.8, 13.7 ppm. IR (KBr):  $\nu = 2983, 1686, 1591, 1395, 1358, 1259, 1227, 1112, 1039, 1013, 825, 621, 591$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 263.0171, found 263.0172.

**S-([1,1'-Biphenyl]-4-yl) O-ethyl carbonodithioate 5ap**



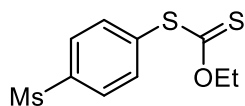
Yellow solid (126.2 mg, 92%). Mp: 60-61 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 2.0$  Hz, 1 H), 7.69–7.66 (m, 2 H), 7.65 (d,  $J = 1.5$  Hz, 1 H), 7.63–7.60 (m, 2 H), 7.53–7.48 (m, 2 H), 7.46–7.40 (m, 1 H), 4.68 (q,  $J = 7.1$  Hz, 2 H), 1.39 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.1, 142.8, 130.0, 135.5, 129.1, 129.0, 128.1, 127.9, 127.3, 70.5, 13.8 ppm. IR (KBr):  $\nu = 2987, 1478, 1275, 1260, 1225, 1111, 1041, 762, 751$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{14}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 297.0378, found 297.0377.

**S-(4-cyanophenyl) O-ethyl carbonodithioate 5aq**



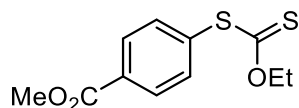
Pale yellow solid (98.1 mg, 88%). Mp: 73-74 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.6$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72–7.66 (m, 2 H), 7.64–7.57 (m, 2 H), 4.59 (q,  $J = 7.1$  Hz, 2 H), 1.32 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.2, 136.1, 135.6, 132.8, 118.2, 113.7, 70.9, 13.7 ppm. IR (KBr):  $\nu = 2990, 2227, 1264, 1113, 1033, 1014, 827, 764, 750, 550$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_9\text{NOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 246.0018, found 246.0019.

**O-Ethyl S-(4-(methylsulfonyl)phenyl) carbonodithioate 5ar**



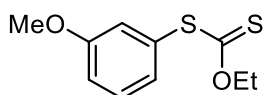
White solid (116.3 mg, 84%). Mp: 63-64 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98–7.93 (m, 2 H), 7.71–7.64 (m, 2 H), 4.59 (q,  $J = 7.2$  Hz, 2 H), 3.07 (s, 3 H), 1.31 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.2, 141.7, 137.0, 135.7, 128.1, 70.9, 44.5, 13.7 ppm. IR (KBr):  $\nu = 3749, 3648, 3566, 2987, 2925, 1313, 1234, 1154, 1039, 1014, 774, 766, 750, 538, 498$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 298.9841, found 298.9841.

**Methyl 4-((ethoxycarbonothioyl)thio)benzoate 5as**



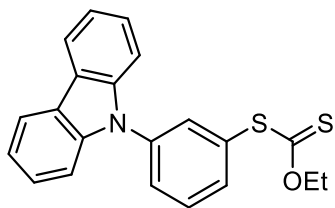
White solid (98.6 mg, 77%). Mp: 36-37 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.6$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J = 8.4$  Hz, 2 H), 7.59 (d,  $J = 8.3$  Hz, 2 H), 4.62 (q,  $J = 7.1$  Hz, 2 H), 3.95 (s, 3 H), 1.34 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.4, 166.4, 135.5, 134.9, 131.4, 130.3, 70.6, 52.5, 13.6 ppm. IR (KBr):  $\nu = 2987, 2951, 1723, 1276, 1227, 1108, 1039, 1015, 762$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 279.0120, found 279.0121.

***O*-Ethyl *S*-(3-methoxyphenyl) carbonodithioate 5at**



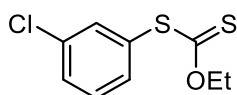
Yellow oil (84.7 mg, 74%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38–7.28 (m, 1 H), 7.09 (dd,  $J = 7.6, 1.2$  Hz, 1 H), 7.06–7.01 (m, 1 H), 6.97 (dd,  $J = 8.3, 2.6$  Hz, 1 H), 4.61 (q,  $J = 7.1$  Hz, 2 H), 3.81 (s, 3 H), 1.33 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.1, 159.9, 131.1, 130.1, 127.3, 120.1, 116.2, 70.4, 55.5, 13.7 ppm. IR (KBr):  $\nu = 2985, 2958, 2936, 2834, 1591, 1577, 1480, 1311, 1283, 1230, 1111, 1035, 765, 750, 688$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 251.0171, found 251.0169.

***S*-(3-(9*H*-Carbazol-9-yl)phenyl) *O*-ethyl carbonodithioate 5au**



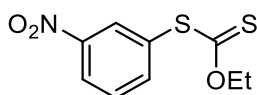
White solid (178.1 mg, 98%). Mp: 69-70 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J = 7.7$  Hz, 2 H), 7.80 (dd,  $J = 2.0$ , 0.9 Hz, 1 H), 7.72–7.65 (m, 2 H), 7.65–7.60 (m, 1 H), 7.52–7.44 (m, 4 H), 7.34 (d,  $J = 8.1$  Hz, 2 H), 4.71 (q,  $J = 7.2$  Hz, 2 H), 1.43 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.6, 140.8, 138.7, 134.2, 133.8, 132.2, 130.7, 128.7, 126.3, 123.7, 120.6, 120.5, 109.8, 70.8, 13.9 ppm. IR (KBr):  $\nu = 3056, 2983, 2956, 2929, 1588, 1493, 1475, 1450, 1388, 1360, 1335, 1227, 1111, 1038, 749, 724, 695$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{21}\text{H}_{17}\text{NOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 386.0644, found 386.0644.

***S*-(3-Chlorophenyl) *O*-ethyl carbonodithioate 5av**



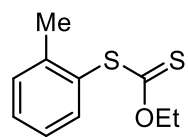
Yellow oil (105.3 mg, 90%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53–7.48 (m, 1 H), 7.43–7.38 (m, 1 H), 7.38–7.31 (m, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.8, 134.9, 134.8, 133.3, 131.9, 130.4, 130.3, 70.6, 13.7 ppm. IR (KBr):  $\nu = 2984, 1567, 1462, 1224, 1109, 1036, 996, 778, 750, 679$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{ClOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 254.9676, found 254.9681.

***O*-Ethyl *S*-(3-nitrophenyl) carbonodithioate 5aw**



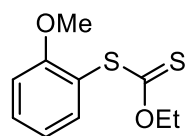
Yellow solid (99.3 mg, 82%). Mp: 43-44 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (t,  $J = 2.0$  Hz, 1 H), 8.30–8.26 (m, 1 H), 7.83–7.79 (m, 1 H), 7.62 (t,  $J = 8.0$  Hz, 1 H), 4.61 (q,  $J = 7.1$  Hz, 2 H), 1.34 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.6, 148.5, 141.0, 132.6, 130.1, 130.0, 124.9, 71.1, 13.7 ppm. IR (KBr):  $\nu = 2986, 1525, 1348, 1231, 1036, 999, 751, 732$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{NO}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 265.9916, found 265.9916.

***O*-Ethyl *S*-(*o*-tolyl) carbonodithioate 5ax**



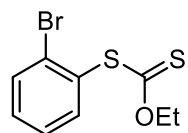
Yellow oil (92.1 mg, 87%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (dd,  $J = 7.6, 1.4$  Hz, 1 H), 7.38 (td,  $J = 7.4, 1.4$  Hz, 1 H), 7.33 (dd,  $J = 7.7, 1.8$  Hz, 1 H), 7.24 (td,  $J = 7.5, 2.0$  Hz, 1 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 2.43 (s, 3 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.0, 142.7, 136.4, 130.9, 130.8, 129.7, 126.9, 70.4, 20.8, 13.8 ppm. IR (KBr):  $\nu = 2980, 1224, 1111, 1033, 752$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 235.0222, found 235.0218.

***O*-Ethyl *S*-(2-methoxyphenyl) carbonodithioate 5ay**



Pale yellow solid (68.4 mg, 60%). Mp: 54-55 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 7.7$  Hz, 1 H), 7.42 (s, 1 H), 6.99 (dd,  $J = 7.5, 1.2$  Hz, 1 H), 6.98-6.94 (m, 1 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 3.85 (s, 3 H), 1.29 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.0, 159.6, 136.9, 132.5, 121.2, 118.5, 111.7, 70.2, 56.1, 13.7 ppm. IR (KBr):  $\nu = 2934, 1584, 1478, 1432, 1294, 1224, 1034, 752$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 251.0171, found 251.0171.

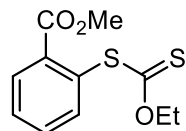
***S*-(2-Bromophenyl) *O*-ethyl carbonodithioate 5az**



Pale yellow solid (83.0 mg, 60%). Mp: 28-29 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (dd,  $J = 7.9, 1.5$  Hz, 1 H), 7.60 (dd,  $J = 7.6, 1.8$  Hz, 1 H), 7.36 (td,  $J = 7.5, 1.5$  Hz, 1 H), 7.30 (td,  $J = 7.7, 1.8$  Hz, 1 H), 4.59 (q,  $J = 7.1$  Hz, 2 H), 1.31 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.7, 137.4, 133.7, 131.9, 131.6, 130.6, 128.2, 70.6, 13.7 ppm. IR (KBr):  $\nu = 2985, 1230,$

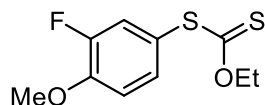
1110, 1045, 1018, 752  $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{BrOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 298.9170, found 298.9174.

**Methyl 2-((ethoxycarbonothioyl)thio)benzoate 5ba**



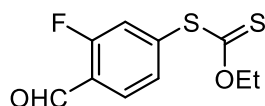
Yellow oil (75.3 mg, 59%). Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 7.2, 1.7$  Hz, 1 H), 7.57 (dd,  $J = 7.2, 1.4$  Hz, 1 H), 7.53–7.45 (m, 1 H), 4.54 (q,  $J = 7.1, 6.6$  Hz, 2 H), 3.86 (s, 3 H), 1.24 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.7, 166.8, 136.8, 134.6, 132.1, 131.0, 130.2, 130.1, 70.3, 52.6, 13.5 ppm. IR (KBr):  $\nu = 2986, 2950, 1723, 1433, 1289, 1255, 1223, 1111, 1060, 1029, 751$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 279.0120, found 279.0115.

**O-Ethyl S-(3-fluoro-4-methoxyphenyl) carbonodithioate 5bb**



Yellow oil (104.3 mg, 85%). Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.18 (m, 2 H), 6.98 (t,  $J = 8.6$  Hz, 1 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 3.92 (s, 3 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -133.4 (m, 1 F);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.6, 152.0 (d,  $J = 250.5$  Hz), 149.5 (d,  $J = 10.1$  Hz), 131.9 (d,  $J = 4.0$  Hz), 123.0 (d,  $J = 19.2$  Hz), 121.5 (d,  $J = 7.1$  Hz), 113.4 (d,  $J = 2.0$  Hz), 70.6, 56.3, 13.7 ppm. IR (KBr):  $\nu = 2988, 1505, 1274, 1230, 1041, 764, 750$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{11}\text{FO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 269.0077, found 269.0077.

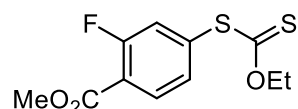
**O-Ethyl S-(3-fluoro-4-formylphenyl) carbonodithioate 5bc**



Yellow solid (88.5 mg, 72%). Mp: 47–48  $^\circ\text{C}$ . Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.35 (s, 1 H), 7.88 (t,  $J = 7.7$  Hz, 1 H), 7.44–7.31 (m, 2 H), 4.61 (q,  $J = 7.1$  Hz, 2 H), 1.34 (t,  $J = 7.1$  Hz, 3 H);  $^{19}\text{F}$  NMR (376 MHz,

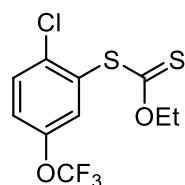
CDCl<sub>3</sub>)  $\delta$  -120.6 (m, 1 F); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  209.4, 186.5 (d,  $J$  = 6.1 Hz), 164.0 (d,  $J$  = 263.6 Hz), 139.2 (d,  $J$  = 9.1 Hz), 130.8 (d,  $J$  = 3.0 Hz), 129.1 (d,  $J$  = 2.0 Hz), 124.7 (d,  $J$  = 9.1 Hz), 122.7 (d,  $J$  = 22.2 Hz), 70.9, 13.6 ppm. IR (KBr):  $\nu$  = 2984, 2924, 2858, 2764, 1693, 1603, 1568, 1399, 1216, 1111, 1033, 901, 805, 750 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>10</sub>H<sub>9</sub>FO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 266.9920, found 266.9922.

**Methyl 4-((ethoxycarbonothioyl)thio)-2-fluorobenzoate 5bd**



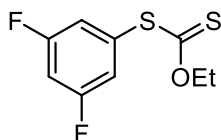
White solid (131.4 mg, 96%). Mp: 28-29 °C. Eluent: ethyl acetate/petroleum ether (1:10, R<sub>f</sub> = 0.6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (t,  $J$  = 7.8 Hz, 1 H), 7.32–7.26 (m, 2 H), 4.57 (q,  $J$  = 7.1 Hz, 2 H), 3.90 (s, 3 H), 1.30 (t,  $J$  = 7.2 Hz, 3 H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -108.0 (m, 1 F); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  209.9, 164.2 (d,  $J$  = 4.0 Hz), 161.4 (d,  $J$  = 264.2 Hz), 137.0 (d,  $J$  = 8.1 Hz), 132.6, 130.1 (d,  $J$  = 4.0 Hz), 123.2 (d,  $J$  = 24.2 Hz), 119.8 (d,  $J$  = 10.1 Hz), 70.8, 52.7, 13.6 ppm. IR (KBr):  $\nu$  = 2985, 2952, 1719, 1606, 1435, 1400, 1289, 1270, 1218, 1031, 899, 773, 686 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>11</sub>H<sub>11</sub>FO<sub>3</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 297.0026, found 297.0013.

**S-(2-Chloro-5-(trifluoromethoxy)phenyl) O-ethyl carbonodithioate 5be**



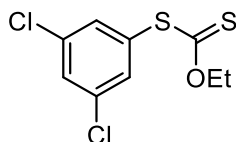
Yellow oil (104.6 mg, 66%). Eluent: ethyl acetate/petroleum ether (1:30, R<sub>f</sub> = 0.7). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d,  $J$  = 8.8 Hz, 1 H), 7.48 (dd,  $J$  = 2.9, 1.0 Hz, 1 H), 7.28–7.23 (m, 1 H), 4.60 (q,  $J$  = 7.1 Hz, 2 H), 1.31 (t,  $J$  = 7.1 Hz, 3 H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -58.1 (s, 3 F); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  208.9, 147.5, 137.6, 131.3, 131.2, 129.5, 124.2, 120.4 (q,  $J$  = 259.6 Hz), 70.9, 13.5 ppm. IR (KBr):  $\nu$  = 2986, 1457, 1257, 1217, 1172, 1047, 1030, 750 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>10</sub>H<sub>8</sub>ClF<sub>3</sub>O<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 338.9499, found 338.9506.

**S-(3,5-Difluorophenyl) O-ethyl carbonodithioate 5bf**



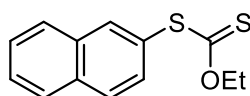
Yellow oil (85.6 mg, 73%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11–6.98 (m, 2 H), 6.92–6.86 (m, 1 H), 4.61 (q,  $J = 7.1$  Hz, 2 H), 1.35 (t,  $J = 7.1$  Hz, 3 H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.4 (m, 2 F);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.5, 164.0 (d,  $J = 20.2$  Hz), 161.5 (d,  $J = 20.2$  Hz), 133.0 (t,  $J = 10.1$  Hz), 118.1 (d,  $J = 10.1$  Hz), 117.9 (d,  $J = 10.1$  Hz), 105.8 (t,  $J = 25.3$  Hz), 70.8, 13.6 ppm. IR (KBr):  $\nu = 2989, 1606, 1592, 1430, 1259, 1123, 1040, 764, 750\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_8\text{F}_2\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 256.9877, found 256.9871.

***S*-(3,5-Dichlorophenyl) *O*-ethyl carbonodithioate 5bg**



White solid (111.4 mg, 83%). Mp: 28-29 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.9$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (t,  $J = 1.9$  Hz, 1 H), 7.39 (d,  $J = 1.9$  Hz, 2 H), 4.61 (q,  $J = 7.2$  Hz, 2 H), 1.35 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.4, 135.3, 133.2, 133.0, 130.2, 70.9, 13.7 ppm. IR (KBr):  $\nu = 2985, 1561, 1227, 1038, 858, 799, 764, 750, 667\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_8\text{Cl}_2\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 288.9286, found 288.9283.

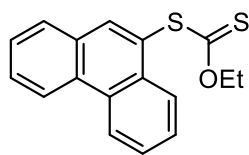
***O*-Ethyl *S*-(naphthalen-2-yl) carbonodithioate 5bh**



Pale yellow solid (101.5 mg, 82%). Mp: 45-46 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (s, 1 H), 7.87 (t,  $J = 9.8$  Hz, 3 H), 7.61–7.50 (m, 3 H), 4.64 (q,  $J = 7.1$  Hz, 2 H), 1.33 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.4, 134.9, 133.6, 133.5, 131.6, 129.0, 128.4, 128.0, 127.7, 127.6, 126.9, 70.5, 13.8 ppm. IR (KBr):  $\nu = 3055, 2984, 1585, 1501, 1441, 1364, 1225, 1147, 1133, 1111, 1041, 1002, 944, 894, 857, 813, 764, 746, 645, 519, 477, 441\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{12}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 271.0222, found 271.0216.

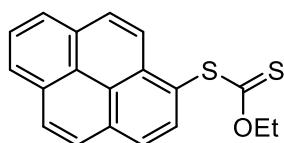


***O*-Ethyl *S*-(phenanthren-9-yl) carbonodithioate 5bi**



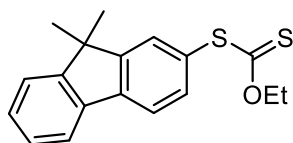
White solid (108.5 mg, 73%). Mp: 98-99 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72–8.65 (m, 2 H), 8.41–8.33 (m, 1 H), 8.10 (s, 1 H), 7.88 (dd,  $J = 8.0, 1.4$  Hz, 1 H), 7.75–7.71 (m, 1 H), 7.70–7.65 (m, 2 H), 7.65–7.60 (m, 1 H), 4.55 (q,  $J = 7.1$  Hz, 2 H), 1.14 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.6, 136.8, 131.8, 131.6, 131.4, 131.1, 129.3, 128.5, 127.4, 127.3, 127.2, 126.6, 126.5, 123.1, 122.9, 70.4, 13.6 ppm. IR (KBr):  $\nu = 2987, 1276, 1259, 1226, 1043, 763, 750, 724$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{17}\text{H}_{14}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 321.0378, found 321.0369.

***O*-Ethyl *S*-(pyren-1-yl) carbonodithioate 5bj**



Yellow solid (123.5 mg, 77%). Mp: 104-105 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J = 9.2$  Hz, 1 H), 8.21 (d,  $J = 7.3$  Hz, 2 H), 8.19–8.10 (m, 4 H), 8.03 (t,  $J = 7.3$  Hz, 2 H), 4.57 (q,  $J = 7.1$  Hz, 2 H), 1.17 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.0, 133.8, 133.3, 133.2, 131.1, 130.8, 129.1, 129.0, 127.3, 126.5, 126.2, 126.1, 125.3, 125.0, 124.8, 124.3, 124.1, 70.5, 13.7 ppm. IR (KBr):  $\nu = 3042, 2982, 2927, 1276, 1045, 1024, 845, 752, 714$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{19}\text{H}_{14}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 345.0378, found 345.0373.

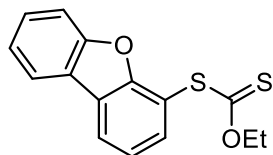
***S*-(9,9-Dimethyl-9*H*-fluoren-2-yl) *O*-ethyl carbonodithioate 5bk**



Yellow oil (134.4 mg, 85%). Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81–7.73 (m, 2 H), 7.60 (s, 1 H), 7.52–7.44 (m, 2 H), 7.41–7.34 (m, 2 H), 4.63 (q,  $J = 7.1$  Hz, 2 H), 1.53 (s, 6 H), 1.32 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  213.6, 154.6, 154.1, 141.1, 138.2, 133.8, 129.7, 128.5, 128.3,

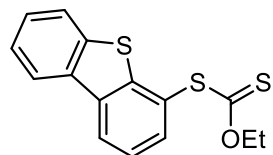
127.4, 122.9, 120.7, 120.6, 70.4, 47.2, 27.1, 13.7 ppm. IR (KBr):  $\nu = 2961, 1276, 1260, 1111, 1040, 1005, 829, 764, 750 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{18}\text{H}_{18}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 337.0691, found 337.0685.

***S*-(Dibenzo[*b,d*]furan-4-yl) *O*-ethyl carbonodithioate 5bl**



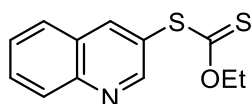
Yellow solid (133.2mg, 92%). Mp: 57-58 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (dd,  $J = 7.7, 1.3$  Hz, 1 H), 7.95 (d,  $J = 7.1$  Hz, 1 H), 7.62 (d,  $J = 8.3$  Hz, 1 H), 7.56 (dd,  $J = 7.6, 1.2$  Hz, 1 H), 7.52–7.46 (m, 1 H), 7.41–7.34 (m, 2 H), 4.59 (q,  $J = 7.1$  Hz, 2 H), 1.22 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.0, 156.4, 156.1, 133.6, 127.9, 125.3, 124.1, 123.5, 123.4, 123.3, 121.0, 113.6, 112.1, 70.6, 13.7 ppm. IR (KBr):  $\nu = 2983, 1470, 1449, 1412, 1235, 1224, 1190, 1147, 1110, 1046, 1033, 750 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 311.0171, found 311.0167.

***S*-(Dibenzo[*b,d*]thiophen-4-yl) *O*-ethyl carbonodithioate 5bm**



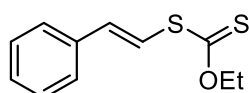
Pale yellow solid (63.4 mg, 42%). Mp: 85-86 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (dd,  $J = 7.9, 1.2$  Hz, 1 H), 8.17–8.10 (m, 1 H), 7.88–7.81 (m, 1 H), 7.62 (dd,  $J = 7.5, 1.2$  Hz, 1 H), 7.52 (t,  $J = 7.6$  Hz, 1 H), 7.50–7.44 (m, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.26 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.5, 146.5, 139.4, 136.6, 135.8, 134.1, 127.3, 125.4, 124.8, 124.1, 123.5, 123.0, 122.1, 70.7, 13.7 ppm. IR (KBr):  $\nu = 2983, 2930, 1386, 1299, 1109, 1045, 1028, 750 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{12}\text{OS}_3$   $[\text{M}+\text{Na}]^+$  calcd 326.9942, found 326.9942.

***O*-Ethyl *S*-(quinolin-3-yl) carbonodithioate 5bn**



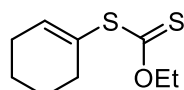
Yellow solid (54.2 mg, 43%). Mp: 45-46 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (d,  $J = 2.2$  Hz, 1 H), 8.26 (d,  $J = 1.3$  Hz, 1 H), 8.12 (d,  $J = 7.5$  Hz, 1 H), 7.82–7.74 (m, 2 H), 7.60–7.54 (m, 1 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.30 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.7, 154.8, 147.8, 142.4, 131.1, 129.6, 128.2, 128.0, 127.5, 124.3, 70.9, 13.7 ppm. IR (KBr):  $\nu = 2985, 1275, 1259, 1232, 1042, 764, 751$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{12}\text{H}_{11}\text{NOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 272.0174, found 272.0167.

**(E)-O-Ethyl S-styryl carbonodithioate 5bo**



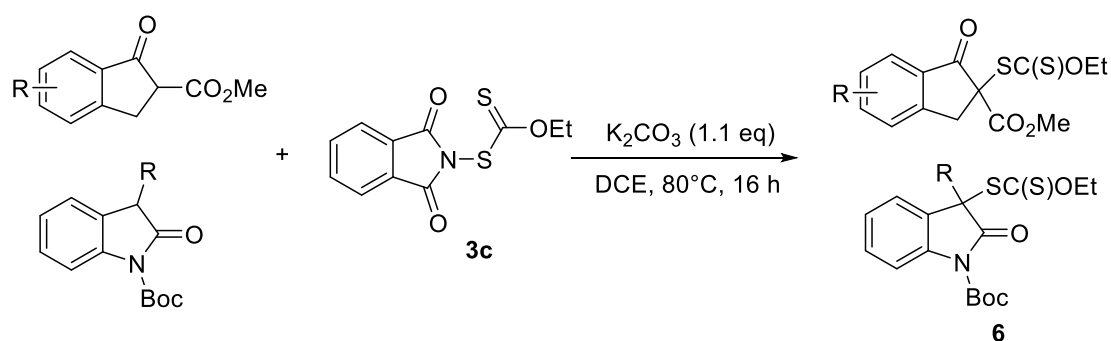
Yellow oil (103.1 mg, 92%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.46–7.40 (m, 2 H), 7.40–7.33 (m, 2 H), 7.32–7.30 (m, 1 H), 7.30–7.26 (m, 1 H), 6.76 (d,  $J = 16.1$  Hz, 1 H), 4.70 (q,  $J = 7.1$  Hz, 2 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.6, 136.0, 133.0, 128.9, 128.5, 126.7, 121.0, 70.3, 13.9 ppm. IR (KBr):  $\nu = 3030, 2986, 1225, 1112, 1046, 764, 739, 690$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 247.0222, found 247.0210.

**S-(Cyclohex-1-en-1-yl) O-ethyl carbonodithioate 5bp**



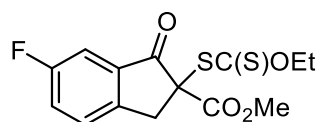
Yellow oil (64.4 mg, 64%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.23–6.19 (m, 1 H), 4.59 (q,  $J = 7.1$  Hz, 2 H), 2.37–2.30 (m, 2 H), 2.22–2.16 (m, 2 H), 1.76–1.70 (m, 2 H), 1.63–1.57 (m, 2 H), 1.39 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  214.5, 140.1, 129.9, 69.9, 31.1, 27.1, 23.6, 21.2, 13.8 ppm. IR (KBr):  $\nu = 2982, 2934, 2858, 2830, 1216, 1171, 1138, 1112, 1058, 1045, 1015, 764, 750$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_{14}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 225.0378, found 225.0370.

**General procedure for ethylxanthylation of  $\beta$ -ketoesters or oxindoles with *N*-ethylxanthylphthalimide **3c**.**



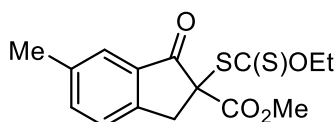
A 25 mL Schlenk tube was charged with  $\beta$ -ketoesters or oxindoles (0.5 mmol),  $K_2CO_3$  (0.55 mmol, 1.1 equiv), *N*-ethylxanthylphthalimide **3c** (0.60 mmol, 1.2 equiv) and DCE (3.0 mL) in argon atmosphere. The mixture was stirred at  $80^\circ C$  for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give ethylxanthylated  $\beta$ -ketoesters or oxindoles.

**Methyl 2-((ethoxycarbonothioyl)thio)-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **6aa****



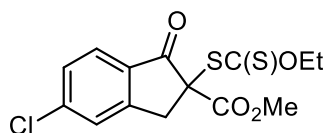
White solid (104.1 mg, 63%). Mp: 127-128  $^\circ C$ . Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.7$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.52–7.36 (m, 3 H), 4.52–4.40 (m, 2 H), 4.21 (d,  $J = 17.6$  Hz, 1 H), 3.75 (s, 3 H), 3.59 (d,  $J = 17.5$  Hz, 1 H), 1.07 (t,  $J = 7.1$  Hz, 3 H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -112.7 (m, 1 F);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  209.0, 194.4, 166.9, 162.7 (d,  $J = 251.5$  Hz), 147.8, 135.9 (d,  $J = 8.1$  Hz), 127.7 (d,  $J = 8.1$  Hz), 124.0 (d,  $J = 24.2$  Hz), 111.1 (d,  $J = 22.2$  Hz), 70.6, 68.0, 54.3, 41.0, 13.0 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 750, 703$   $cm^{-1}$ . HRMS (ESI):  $m/z$  for  $C_{14}H_{13}FO_4S_2$   $[M+Na]^+$  calcd 351.0131, found 351.0131.

**Methyl 2-((ethoxycarbonothioyl)thio)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **6ab****



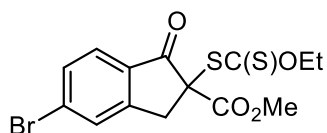
Yellow solid (155.9 mg, 96%). Mp: 118-119 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (s, 1 H), 7.48 (d,  $J = 7.8$  Hz, 1 H), 7.36 (d,  $J = 7.7$  Hz, 1 H), 4.51–4.39 (m, 2 H), 4.20 (d,  $J = 17.7$  Hz, 1 H), 3.72 (s, 3 H), 3.55 (d,  $J = 17.8$  Hz, 1 H), 2.39 (s, 3 H), 1.06 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.6, 195.2, 167.3, 149.8, 138.5, 137.6, 134.2, 125.9, 125.2, 70.5, 67.8, 54.1, 41.3, 21.2, 13.0 ppm. IR (KBr):  $\nu = 3006, 2989, 1276, 1263, 750, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{16}\text{O}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 347.0382, found 347.0383.

**Methyl 5-chloro-2-((ethoxycarbonylthio)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6ac**



Yellow solid (144.3 mg, 84%). Mp: 65-66 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 1.0$  Hz, 1 H), 7.64 (d,  $J = 8.2$  Hz, 1 H), 7.58–7.53 (m, 1 H), 4.44 (q,  $J = 7.2$  Hz, 2 H), 4.22 (d,  $J = 17.9$  Hz, 1 H), 3.73 (s, 3 H), 3.59 (d,  $J = 17.9$  Hz, 1 H), 1.07 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.0, 194.0, 166.8, 153.8, 133.0, 132.0, 131.8, 129.6, 126.4, 70.6, 67.3, 54.3, 41.1, 13.1 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 750, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{14}\text{H}_{13}\text{ClO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 366.9836, found 366.9836.

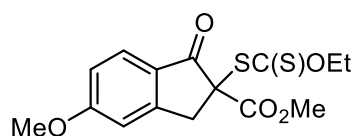
**Methyl 5-bromo-2-((ethoxycarbonylthio)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6ad**



Yellow solid (146.4 mg, 75%). Mp: 108-109 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.2$  Hz, 1 H), 7.48 (d,  $J = 0.9$  Hz, 1 H), 7.42–7.37 (m, 1 H), 4.45 (q,  $J = 7.1$  Hz, 2 H), 4.22 (d,  $J = 17.9$  Hz, 1 H), 3.73 (s, 3 H), 3.59 (d,  $J = 17.9$  Hz, 1 H), 1.07 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,

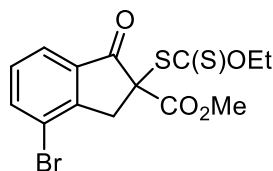
CDCl<sub>3</sub>)  $\delta$  209.0, 193.8, 166.9, 153.8, 142.9, 132.6, 129.2, 126.5, 126.4, 70.6, 67.4, 54.3, 41.2, 13.1 ppm. IR (KBr):  $\nu$  = 3006, 2989, 1275, 1263, 750, 702 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>14</sub>H<sub>13</sub>BrO<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 410.9331, found 410.9335.

**Methyl 2-((ethoxycarbonothioyl)thio)-5-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6ae**



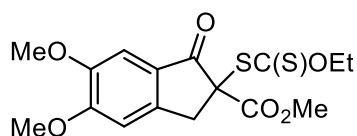
Colorless oil (150.1 mg, 88%). Eluent: ethyl acetate/petroleum ether (1:2, R<sub>f</sub> = 0.6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d,  $J$  = 8.5 Hz, 1 H), 6.98–6.87 (m, 2 H), 4.49 (q,  $J$  = 7.1 Hz, 2 H), 4.26 (d,  $J$  = 17.9 Hz, 1 H), 3.89 (s, 3 H), 3.74 (s, 3 H), 3.54 (d,  $J$  = 17.8 Hz, 1 H), 1.14 (t,  $J$  = 7.1 Hz, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  209.9, 192.9, 167.5, 166.7, 155.7, 127.2, 127.0, 116.6, 109.3, 70.4, 67.9, 56.0, 54.1, 41.6, 13.2 ppm. IR (KBr):  $\nu$  = 3006, 2989, 1275, 1263, 749, 703 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 363.0331, found 363.0331.

**Methyl 4-bromo-2-((ethoxycarbonothioyl)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6af**



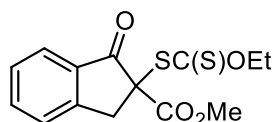
Pale yellow solid (112.3 mg, 58%). Mp: 128-129 °C. Eluent: ethyl acetate/petroleum ether (1:3, R<sub>f</sub> = 0.6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d,  $J$  = 7.8 Hz, 1 H), 7.76 (d,  $J$  = 7.6 Hz, 1 H), 7.41–7.30 (m, 1 H), 4.44 (q,  $J$  = 19.6, 7.1 Hz, 2 H), 4.16 (d,  $J$  = 18.3 Hz, 1 H), 3.75 (s, 3 H), 3.53 (d,  $J$  = 18.2 Hz, 1 H), 1.02 (t,  $J$  = 7.1 Hz, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  208.8, 194.7, 166.8, 152.0, 138.8, 136.2, 130.1, 124.1, 121.6, 70.6, 67.1, 54.3, 42.5, 12.9 ppm. IR (KBr):  $\nu$  = 3006, 2989, 1748, 1725, 1275, 1262, 1237, 1046, 999, 750, 702 cm<sup>-1</sup>. HRMS (ESI):  $m/z$  for C<sub>14</sub>H<sub>13</sub>BrO<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 410.9331, found 410.9331.

**Methyl 2-((ethoxycarbonothioyl)thio)-5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6ag**



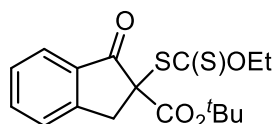
White solid (180.3 mg, 97%). Mp: 48-49 °C. Eluent: ethyl acetate/petroleum ether (1:1,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (s, 1 H), 6.88 (s, 1 H), 4.54–4.42 (m, 2 H), 4.21 (d,  $J = 18.2$  Hz, 1 H), 3.96 (s, 3 H), 3.86 (s, 3 H), 3.72 (s, 3 H), 3.48 (d,  $J = 17.4$  Hz, 1 H), 1.15 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.9, 193.2, 167.5, 156.9, 150.2, 148.5, 126.5, 107.0, 105.3, 70.4, 67.9, 56.6, 56.3, 54.1, 41.4, 13.3 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 750, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{16}\text{H}_{18}\text{O}_6\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 393.0437, found 393.0438.

**Methyl 2-((ethoxycarbonylthio)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6ah**



Yellow solid (132.3 mg, 85%). Mp: 72-73 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.9$  Hz, 1 H), 7.67 (t,  $J = 7.5$  Hz, 1 H), 7.48 (d,  $J = 7.8$  Hz, 1 H), 7.42 (t,  $J = 7.6$  Hz, 1 H), 4.51–4.37 (m, 2 H), 4.26 (d,  $J = 17.9$  Hz, 1 H), 3.73 (s, 3 H), 3.61 (d,  $J = 17.9$  Hz, 1 H), 1.02 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.4, 195.2, 167.2, 152.4, 136.3, 134.1, 128.3, 126.3, 125.4, 70.5, 67.4, 54.2, 41.6, 12.9 ppm. IR (KBr):  $\nu = 3006, 2990, 1276, 1262, 765, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 333.0226, found 333.0235.

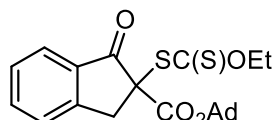
**Tert-butyl 2-((ethoxycarbonylthio)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6ai**



Yellow oil (141.1 mg, 80%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 7.7$  Hz, 1 H), 7.64 (td,  $J = 7.5, 1.2$  Hz, 1 H), 7.47 (d,  $J = 7.7$  Hz, 1 H), 7.44–7.38 (m, 1 H), 4.45–4.31 (m, 2 H), 4.10 (d,  $J = 17.6$  Hz, 1 H), 3.60 (d,  $J = 17.7$  Hz, 1 H), 1.37 (s, 9 H), 0.93 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101

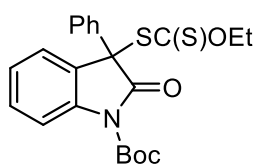
MHz, CDCl<sub>3</sub>) δ 209.9, 195.9, 165.5, 152.3, 135.8, 134.7, 128.1, 126.0, 125.1, 84.4, 70.4, 68.1, 41.6, 27.7, 12.8 ppm. IR (KBr): ν = 3006, 2989, 1716, 1276, 1263, 1149, 1046, 750, 702 cm<sup>-1</sup>. HRMS (ESI): m/z for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 375.0695, found 375.0694.

**Adamantan-1-yl 2-((ethoxycarbonothioyl)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 6aj**



Yellow oil (188.3 mg, 87%). Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 7.6 Hz, 1 H), 7.64 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.43–7.37 (m, 1 H), 4.45–4.30 (m, 2 H), 4.09 (d, *J* = 17.6 Hz, 1 H), 3.59 (d, *J* = 17.6 Hz, 1 H), 2.10 (s, 3 H), 1.99 (d, *J* = 3.1 Hz, 6 H), 1.58 (t, *J* = 3.1 Hz, 6 H), 0.92 (t, *J* = 7.1 Hz, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 210.0, 196.0, 165.1, 152.3, 135.8, 134.7, 128.1, 126.0, 125.1, 84.4, 70.3, 68.2, 41.6, 40.9, 36.0, 30.9, 12.8 ppm. IR (KBr): ν = 3006, 2989, 2914, 2854, 1716, 1276, 1262, 1232, 1042, 750, 703 cm<sup>-1</sup>. HRMS (ESI): m/z for C<sub>23</sub>H<sub>26</sub>O<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 453.1165, found 453.1166.

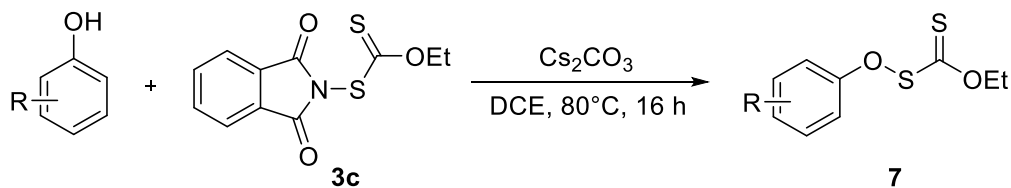
**Tert-butyl 3-((ethoxycarbonothioyl)thio)-2-oxo-3-phenylindoline-1-carboxylate 6ak**



Pale yellow solid (121.6 mg, 57%). Mp: 147-148 °C. Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 8.1 Hz, 1 H), 7.52 (dd, *J* = 7.5, 1.4 Hz, 1 H), 7.49–7.44 (m, 2 H), 7.41 (td, *J* = 7.9, 1.5 Hz, 1 H), 7.34–7.30 (m, 3 H), 7.28 (dd, *J* = 7.6, 1.1 Hz, 1 H), 4.42–4.32 (m, 1 H), 4.26–4.16 (m, 1 H), 1.61 (s, 9 H), 1.02 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 208.9, 172.3, 149.3, 140.1, 133.6, 129.7, 129.3, 129.1, 128.1, 128.0, 125.9, 124.9, 84.8, 70.5, 63.5, 28.2, 11.9 ppm. IR (KBr): ν = 3006, 2989, 1275, 1263, 750, 703 cm<sup>-1</sup>. HRMS (ESI): m/z for C<sub>22</sub>H<sub>23</sub>NO<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 452.0961, found 452.0960.

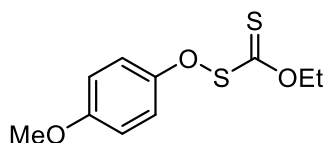


**General procedure for ethylxanthylation of phenols with *N*-ethylxanthylphthalimide **3c**.**



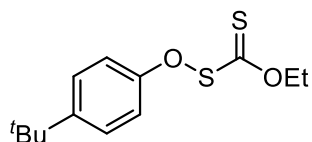
A 25 mL Shlenk tube was charged with phenols (0.5 mmol), *N*-ethylxanthylphthalimide **3c** (0.7 mmol, 1.4 equiv),  $\text{Cs}_2\text{CO}_3$  (0.55 mmol, 1.1 equiv) and DCE (3.0 mL) in argon atmosphere. The mixture was stirred at  $80^\circ\text{C}$  for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give ethylxanthylated phenols.

***O*-Ethyl *SO*-(4-methoxyphenyl) carbonothio(thioperoxoate) **7aa****



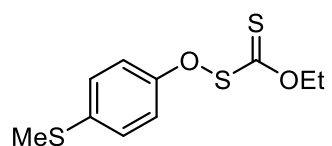
Yellow solid (103.6 mg, 85%). Mp:  $37\text{--}38^\circ\text{C}$ . Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06–6.98 (m, 2 H), 6.95–6.87 (m, 2 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 3.80 (s, 3 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 157.8, 147.1, 122.8, 114.5, 70.5, 55.6, 13.9 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 730, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 267.0120, found 267.0111.

***SO*-(4-(*Tert*-butyl)phenyl) *O*-ethyl carbonothio(thioperoxoate) **7ab****



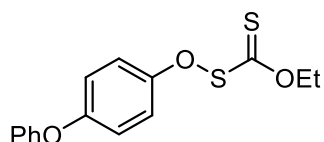
Yellow oil (120.2 mg, 89%). Eluent: ethyl acetate/petroleum ether (1:20,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46–7.37 (m, 2 H), 7.08–6.98 (m, 2 H), 4.59 (q,  $J = 7.1$  Hz, 2 H), 1.46 (t,  $J = 7.1$  Hz, 3 H), 1.33 (s, 9 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.4, 151.2, 149.4, 126.5, 121.3, 70.4, 34.7, 31.5, 13.9 ppm. IR (KBr):  $\nu = 3053, 2967, 1295, 1264, 1207, 731, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 293.0640, found 293.0646.

***O*-Ethyl *SO*-(4-(methylthio)phenyl) carbonothio(thioperoxoate) 7ac**



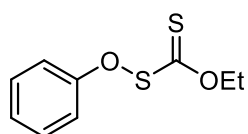
White solid (126.5 mg, 97%). Mp: 46-47 °C. Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.23 (m, 2 H), 7.08–6.98 (m, 2 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 2.48 (s, 3 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.3, 151.0, 136.8, 127.6, 122.5, 70.6, 16.2, 13.9 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 730, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 282.9892, found 282.9888.

***O*-Ethyl *SO*-(4-phenoxyphenyl) carbonothio(thioperoxoate) 7ad**



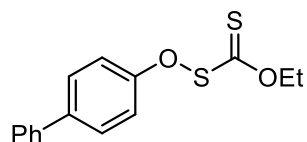
Colorless oil (123.1 mg, 80%). Eluent: ethyl acetate/petroleum ether (1:10,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39–7.32 (m, 2 H), 7.16–7.10 (m, 1 H), 7.09–7.04 (m, 3 H), 7.04–6.99 (m, 3 H), 4.62 (q, 2 H), 1.46 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 156.9, 155.6, 148.8, 130.0, 123.8, 123.3, 119.4, 119.3, 70.6, 13.9 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 731, 703, 668\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 329.0277, found 329.0270.

***O*-Ethyl *SO*-phenyl carbonothio(thioperoxoate) 7ae**



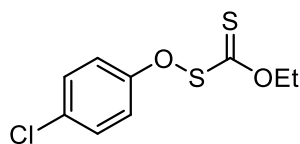
Yellow oil (96.7 mg, 90%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46–7.38 (m, 2 H), 7.33–7.26 (m, 1 H), 7.12 (d,  $J = 8.6$  Hz, 2 H), 4.60 (q,  $J = 7.1$  Hz, 2 H), 1.46 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.3, 153.5, 129.6, 126.6, 122.1, 70.5, 13.9 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 1204, 733, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_{10}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 237.0014, found 237.0033.

***SO*-([1,1'-Biphenyl]-4-yl) *O*-ethyl carbonothio(thioperoxoate) 7af**



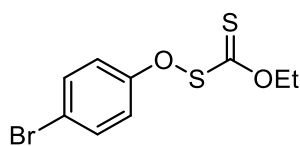
White solid (134.6 mg, 93%). Mp: 105-106 °C. Eluent: ethyl acetate/petroleum ether (1:20,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 2.0$  Hz, 1 H), 7.63 (d,  $J = 2.1$  Hz, 1 H), 7.61 (t,  $J = 1.7$  Hz, 1 H), 7.59 (t,  $J = 1.1$  Hz, 1 H), 7.48–7.43 (m, 2 H), 7.40–7.34 (m, 1 H), 7.21 (d,  $J = 2.1$  Hz, 1 H), 7.20 (d,  $J = 2.1$  Hz, 1 H), 4.63 (q,  $J = 7.1$  Hz, 2 H), 1.49 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 152.9, 140.3, 139.8, 129.0, 128.4, 127.6, 127.3, 122.4, 70.6, 13.9 ppm. IR (KBr):  $\nu = 3053, 2986, 1373, 1264, 1199, 1043, 1018, 1008, 818, 766, 731, 699$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 313.0327, found 313.0333.

***SO*-(4-Chlorophenyl) *O*-ethylcarbonothio(thioperoxoate) 7ag**



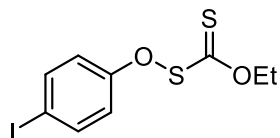
Yellow oil (115.4 mg, 93%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.34 (m, 2 H), 7.08–7.01 (m, 2 H), 4.58 (q,  $J = 7.2$  Hz, 2 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.9, 151.9, 132.1, 129.7, 123.6, 70.7, 13.8 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 730, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{ClO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 270.9625, found 270.9631.

***SO*-(4-Bromophenyl) *O*-ethyl carbonothio(thioperoxoate) 7ah**



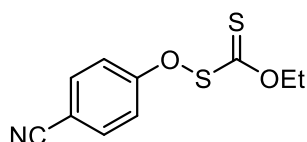
Yellow oil (138.2 mg, 94%). Eluent: ethyl acetate/petroleum ether (1:20,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57–7.46 (m, 2 H), 7.03–6.94 (m, 2 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.8, 152.4, 132.7, 124.0, 119.9, 70.7, 13.9 ppm. IR (KBr):  $\nu = 2956, 1264, 764, 730, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{BrO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 314.9120, found 314.9127.

***O*-Ethyl *SO*-(4-iodophenyl) carbonothio(thioperoxoate) 7ai**



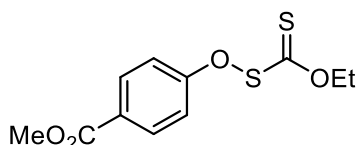
Yellow solid (162.2 mg, 95%). Mp: 34-35 °C. Eluent: ethyl acetate/petroleum ether (1:20,  $R_f = 0.7$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77–7.65 (m, 2 H), 6.92–6.80 (m, 2 H), 4.57 (q,  $J = 7.1$  Hz, 2 H), 1.45 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7, 153.2, 138.7, 124.4, 91.0, 70.7, 13.9 ppm. IR (KBr):  $\nu = 2983, 1480, 1394, 1373, 1292, 1257, 1194, 1094, 1053, 1040, 1008, 831, 810, 733, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{IO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 362.8981, found 362.8989.

***SO*-(4-Cyanophenyl) *O*-ethyl carbonothio(thioperoxoate) 7aj**



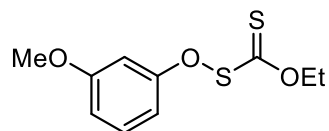
White solid (111.0 mg, 93%). Mp: 38-39 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74–7.67 (m, 2 H), 7.24–7.17 (m, 2 H), 4.57 (q,  $J = 7.2$  Hz, 2 H), 1.43 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.9, 156.2, 133.9, 123.6, 118.2, 110.7, 71.0, 13.8 ppm. IR (KBr):  $\nu = 2989, 1275, 1264, 764, 749, 730, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_9\text{NO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 261.9967, found 261.9963.

**Methyl 4-(((ethoxycarbonothioyl)thio)oxy)benzoate 7ak**



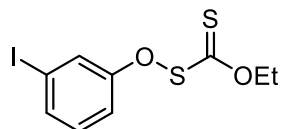
White solid (116.7 mg, 86%). Mp: 53-54 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.8$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13–8.04 (m, 2 H), 7.21–7.12 (m, 2 H), 4.57 (q,  $J = 7.1$  Hz, 2 H), 3.89 (s, 3 H), 1.44 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.3, 166.2, 156.7, 131.4, 128.5, 122.3, 70.7, 52.4, 13.8 ppm. IR (KBr):  $\nu = 3054, 2988, 1721, 1276, 1264, 1193, 1162, 1113, 1098, 1041, 1016, 731, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{O}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 295.0069, found 295.0066.

***O*-Ethyl *SO*-(3-methoxyphenyl) carbonothio(thioperoxoate) 7al**



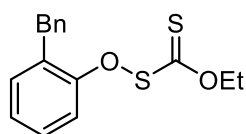
Yellow oil (104.5 mg, 86%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (t,  $J = 8.2$  Hz, 1 H), 6.85–6.81 (m, 1 H), 6.74–6.69 (m, 1 H), 6.66 (t,  $J = 2.3$  Hz, 1 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 3.79 (s, 3 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 160.6, 154.3, 120.0, 114.3, 112.3, 108.2, 70.5, 55.6, 13.9 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 1207, 1165, 1148, 1096, 1037, 732, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 267.0120, found 267.0125.

***O*-Ethyl *SO*-(3-iodophenyl) carbonothio(thioperoxoate) 7am**



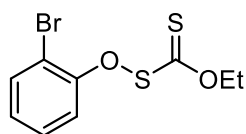
Yellow oil (162.1 mg, 95%). Eluent: ethyl acetate/petroleum ether (1:20,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63–7.60 (m, 1 H), 7.49–7.45 (m, 1 H), 7.16–7.11 (m, 1 H), 7.11–7.06 (m, 1 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 1.45 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7, 153.4, 135.8, 131.4, 130.9, 121.8, 93.5, 70.7, 13.9 ppm. IR (KBr):  $\nu = 3054, 1422, 1264, 1110, 896, 730, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{IO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 362.8981, found 362.8987.

***SO*-(2-Benzylphenyl) *O*-ethyl carbonothio(thioperoxoate) 7an**



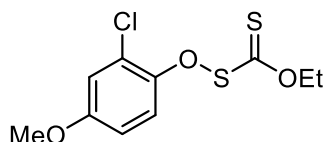
Colorless oil (140.1 mg, 92%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.29 (m, 2 H), 7.29–7.27 (m, 1 H), 7.26–7.20 (m, 4 H), 7.19 (dd,  $J = 7.6, 2.0$  Hz, 1 H), 7.10 (dd,  $J = 7.9, 1.4$  Hz, 1 H), 4.57 (q,  $J = 7.1$  Hz, 2 H), 3.94 (s, 2 H), 1.45 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.6, 151.6, 139.6, 133.6, 131.1, 129.3, 128.6, 127.7, 126.9, 126.4, 122.7, 70.5, 36.0, 13.9 ppm. IR (KBr):  $\nu = 3054, 2988, 1264, 1213, 730, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 327.0484, found 327.0488.

***SO*-(2-Bromophenyl) *O*-ethyl carbonothio(thioperoxoate) 7ao**



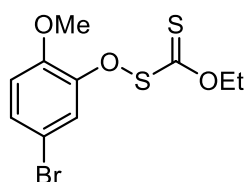
Yellow oil (131.6 mg, 90%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (dd,  $J = 8.3, 1.5$  Hz, 1 H), 7.40–7.32 (m, 1 H), 7.20–7.13 (m, 2 H), 4.62 (q,  $J = 7.1$  Hz, 2 H), 1.47 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.6, 150.5, 133.7, 128.7, 128.0, 124.3, 116.5, 71.0, 13.8 ppm. IR (KBr):  $\nu = 3054, 2988, 1399, 1375, 1299, 1263, 1194, 1059, 1030, 764, 731, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{BrO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 314.9120, found 314.9105.

***SO*-(2-Chloro-4-methoxyphenyl) *O*-ethyl carbonothio(thioperoxoate) 7ap**



Yellow oil (126.4 mg, 91%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 (d,  $J = 9.0$  Hz, 1 H), 6.98 (d,  $J = 3.0$  Hz, 1 H), 6.82 (dd,  $J = 9.0, 2.9$  Hz, 1 H), 4.60 (q,  $J = 7.2$  Hz, 2 H), 3.79 (s, 3 H), 1.46 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.4, 158.2, 143.1, 127.6, 124.4, 115.4, 113.6, 70.9, 55.9, 13.8 ppm. IR (KBr):  $\nu = 3054, 2987, 1301, 1264, 1194, 1178, 733, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{11}\text{ClO}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 300.9730, found 300.9735.

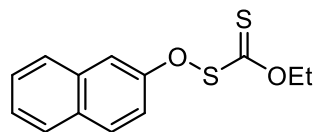
***SO*-(5-Bromo-2-methoxyphenyl) *O*-ethyl carbonothio(thioperoxoate) 7aq**



Yellow solid (141.4 mg, 87%). Mp: 92–93 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (dd,  $J = 8.8, 2.4$  Hz, 1 H), 7.21 (d,  $J = 2.4$  Hz, 1 H), 6.85 (d,  $J = 8.7$  Hz, 1 H), 4.57 (q,  $J = 7.2$  Hz, 2 H), 3.80 (s, 3 H), 1.44 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.3, 150.6, 142.6, 130.3, 126.4, 114.2, 112.0, 70.9, 56.2, 13.8 ppm. IR (KBr):  $\nu = 3054, 2987, 1374, 1298, 1264, 1195, 1178, 1136, 731, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{11}\text{BrO}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd

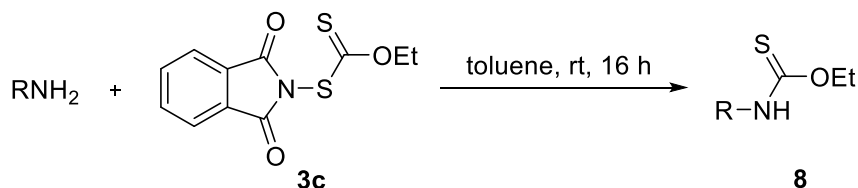
344.9225, found 344.9231.

***O*-Ethyl *SO*-(naphthalen-2-yl) carbonothio(thioperoxoate) 7ar**



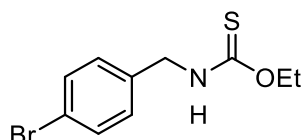
Yellow solid (89.6 mg, 68%). Mp: 60-61 °C. Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91–7.84 (m, 2 H), 7.84–7.80 (m, 1 H), 7.55 (d,  $J = 2.4$  Hz, 1 H), 7.53–7.46 (m, 2 H), 7.27 (dd,  $J = 8.9, 2.4$  Hz, 1 H), 4.63 (q,  $J = 7.1$  Hz, 2 H), 1.49 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.4, 151.0, 133.8, 131.9, 129.6, 128.0, 127.9, 126.8, 126.2, 121.5, 119.1, 70.6, 13.9 ppm. IR (KBr):  $\nu = 3055, 2987, 1372, 1294, 1276, 1263, 1199, 1165, 1123, 1094, 1041, 972, 941, 882, 858, 812, 749, 734, 703, 661$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 287.0171, found 287.0173.

**General procedure for ethylxanthylation of amines with *N*-ethylxanthylphthalimide **3c**.**



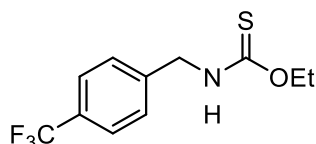
A 25 mL Shlenk tube was charged with amines (0.5 mmol), *N*-ethylxanthylphthalimide **3c** (0.6 mmol, 1.2 equiv) and toluene (3.0 mL) in argon atmosphere. The mixture was stirred at room temperature for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give the corresponding thiocarbamates, which were confirmed by NMR and GC-MS or HR(ESI)-MS.

***O*-Ethyl (4-bromobenzyl)carbamothioate **8aa****



White solid (98.3 mg, 64%, 1.9:1). Mp: 66-67 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (dd,  $J = 8.3, 1.6$  Hz, 2 H), 7.22–7.14 (m, 1.30 H, major), 7.13–7.08 (m, 0.70 H, minor), 7.02 (s, 0.34 H, minor), 6.47 (s, 0.66 H, major), 4.70 (d,  $J = 5.9$  Hz, 1.30 H, major), 4.53 (q,  $J = 7.1$  Hz, 0.70 H, minor), 4.49 (q,  $J = 7.1$  Hz, 1.30 H, major) 4.37 (d,  $J = 6.0$  Hz, 0.70 H, minor), 1.31 (td,  $J = 7.1, 3.6$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.0, 190.1, 136.1, 135.8, 132.0, 131.9, 129.6, 129.4, 121.8, 121.7, 68.3, 66.8, 48.4, 46.5, 14.3, 14.2 ppm. IR (KBr):  $\nu = 2987, 1515, 1489, 1275, 1263, 1189, 764, 749, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{12}\text{BrNOS}$   $[\text{M}+\text{Na}]^+$  calcd 295.9715, found 295.9708.

***O*-Ethyl (4-(trifluoromethyl)benzyl)carbamothioate **8ab****

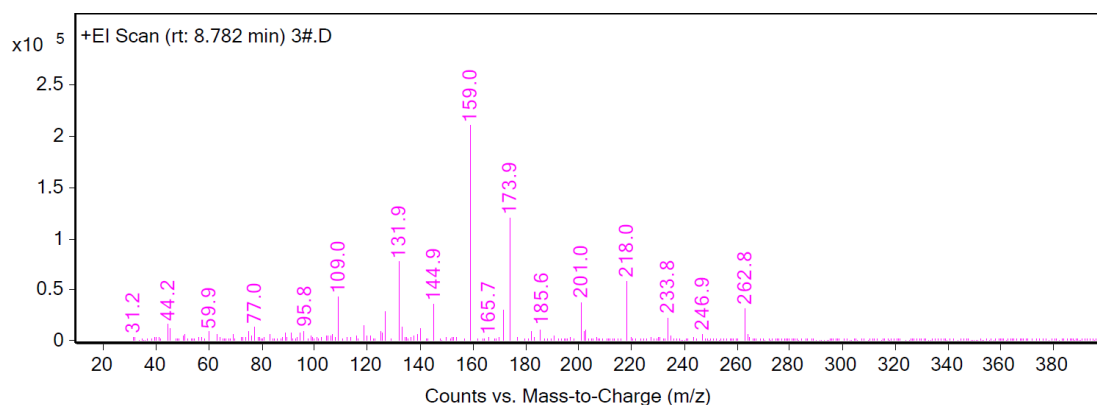


White solid (123.9 mg, 84%, 1.9:1). Mp: 39-40 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 8.0$  Hz, 2 H), 7.42 (d,  $J = 8.0$  Hz, 1.3 H, major), 7.35 (d,  $J = 8.0$  Hz, 0.7 H, minor), 7.24 (s, 0.35 H, minor), 6.57

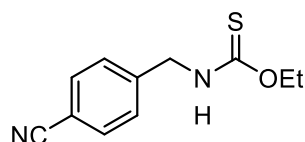


(s, 0.65 H, major), 4.82 (d,  $J = 6.0$  Hz, 1.3 H, major), 4.56–4.51 (m, 0.7 H, minor), 4.51–4.46 (m, 2 H), 1.31 (q,  $J = 7.3$  Hz, 3 H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.4 (s, 3 F);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 190.2, 141.2, 140.9, 130.9 (q,  $J = 272.7$  Hz), 128.0, 127.8, 125.9, 125.8, 125.8, 125.7, 125.7, 68.3, 67.0, 48.4, 46.6, 14.3, 14.2 ppm. IR (KBr):  $\nu = 2989, 1326, 1275, 1264, 764, 749, 731, 703$   $\text{cm}^{-1}$ . MS (EI):  $m/z$  (%) 263, 174, 159 (100). HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{F}_3\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 286.0484, found 286.0500.

GC-MS:

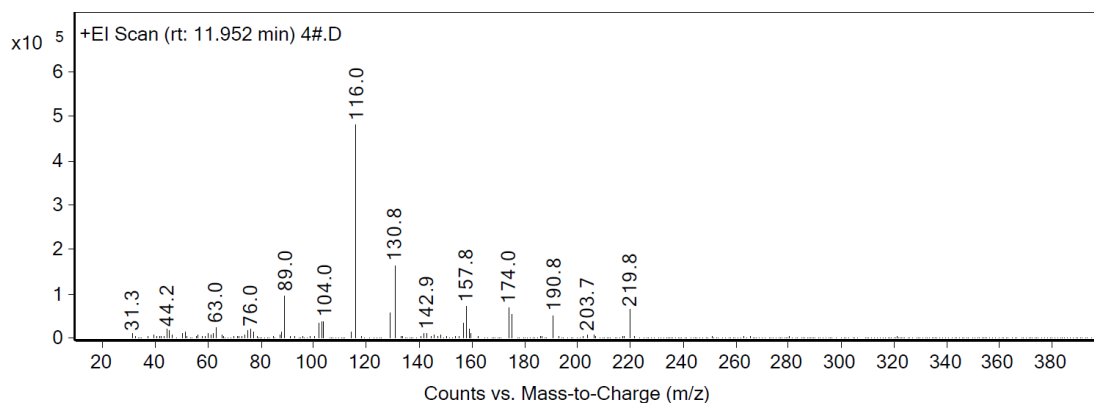


### ***O*-Ethyl (4-cyanobenzyl)carbamothioate 8ac**

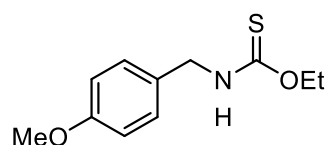


Yellow solid (90.8 mg, 72%, 2.1:1). Mp: 63–64 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67–7.56 (m, 2 H), 7.41 (d,  $J = 8.8$  Hz, 1.35 H, major), 7.35 (d,  $J = 8.4$  Hz, 0.65 H, minor), 7.22 (s, 0.33 H), 6.63 (s, 0.67 H), 4.83 (d,  $J = 6.2$  Hz, 1.35 H), 4.54–4.48 (m, 2 H), 4.47 (d,  $J = 1.4$  Hz, 0.65 H), 1.32 (t,  $J = 7.1$  Hz, 2 H), 1.28 (t,  $J = 7.1$  Hz, 1 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5, 190.3, 142.7, 142.4, 132.7, 132.6, 128.3, 128.0, 118.8, 118.6, 111.7, 111.6, 68.4, 67.1, 48.3, 46.6, 14.3, 14.2 ppm. IR (KBr):  $\nu = 2989, 1275, 1264, 764, 749, 731, 702$   $\text{cm}^{-1}$ . MS (EI):  $m/z$  (%) 220, 131, 116 (100). HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{OS}$   $[\text{M}+\text{Na}]^+$  calcd 243.0563, found 243.0550.

GC-MS:

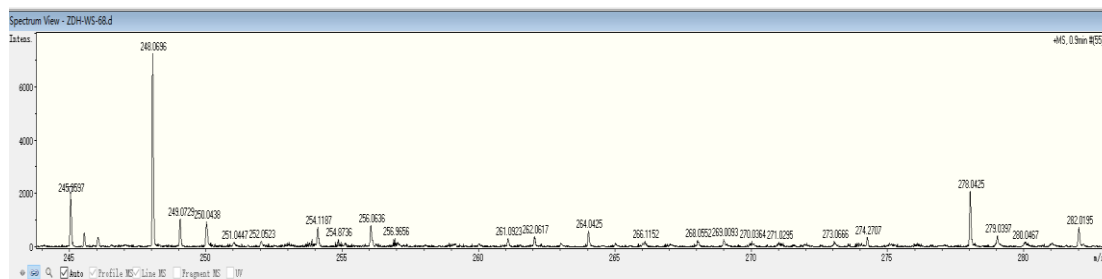


### ***O*-Ethyl (4-methoxybenzyl)carbamothioate 8ad**

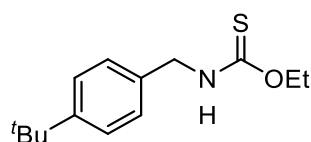


White solid (115.1 mg, 89%, 1.7:1). Mp: 41-42 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.20 (m, 1.26 H, major), 7.17–7.13 (m, 0.74 H, minor), 6.92 (s, 0.37 H, minor), 6.88–6.82 (m, 2 H), 6.43 (s, 0.63 H, major), 4.65 (d,  $J = 5.5$  Hz, 1.26 H, major), 4.54 (q,  $J = 7.1$  Hz, 0.74 H, minor), 4.48 (q,  $J = 7.1$  Hz, 1.26 H, major), 4.35 (d,  $J = 5.7$  Hz, 0.74 H, minor), 3.78 (s, 1.11 H, minor), 3.77 (s, 1.89 H, major), 1.35 (t,  $J = 7.1$  Hz, 1.11 H, minor), 1.29 (t,  $J = 7.1$  Hz, 1.89 H, major);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 189.7, 159.4, 129.5, 129.2, 129.0, 128.6, 114.2, 68.1, 66.6, 55.4, 48.8, 46.8, 14.4 ppm. IR (KBr):  $\nu = 2988, 1514, 1275, 1264, 1188, 764, 748, 731, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S}$   $[\text{M}+\text{Na}]^+$  calcd 248.0716, found 248.0696.

HR(ESI)-MS:

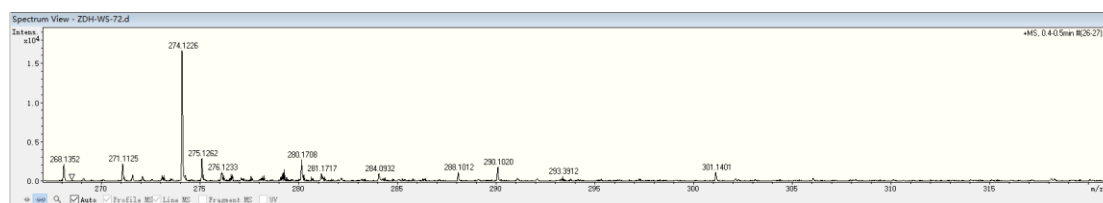


### ***O*-Ethyl (4-(*tert*-butyl)benzyl)carbamothioate 8ae**

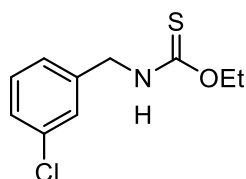


White solid (99.5 mg, 70%, 1.7:1). Mp: 31-32 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40–7.34 (m, 2 H), 7.28–7.23 (m, 1.27 H, major), 7.20–7.16 (m, 0.73 H, minor), 6.89 (s, 0.36 H, minor), 6.43 (s, 0.64 H, major), 4.70 (d,  $J = 5.5$  Hz, 1.27 H, major), 4.56 (q,  $J = 7.2$  Hz, 0.73 H, minor), 4.49 (q,  $J = 7.1$  Hz, 1.27 H, major), 4.40 (d,  $J = 5.8$  Hz, 0.73 H, minor), 1.36 (t,  $J = 7.1$  Hz, 1 H), 1.32 (s, 1 H), 1.31 (d,  $J = 1.1$  Hz, 9 H), 1.29 (s, 1 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.6, 189.8, 151.1, 151.0, 133.9, 133.6, 127.9, 127.6, 125.8, 68.1, 66.6, 49.0, 47.0, 34.7, 31.4, 14.4, 14.3 ppm. IR (KBr):  $\nu = 2988, 1275, 1264, 764, 749, 731, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{14}\text{H}_{21}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 274.1236, found 274.1226.

HR(ESI)-MS:

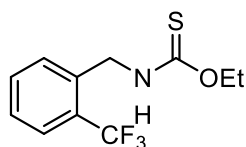


### ***O*-Ethyl (3-chlorobenzyl)carbamothioate 8af**



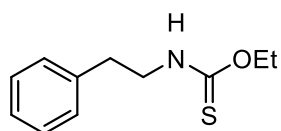
Colorless oil (85.6 mg, 65%, 1.7:1). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (s, 1 H), 7.26–7.23 (m, 2 H), 7.22 (s, 0.37 H, minor), 7.21–7.15 (m, 0.63 H, major), 7.13–7.08 (m, 0.37 H, minor), 6.55 (s, 0.63 H, major), 4.72 (d,  $J = 5.9$  Hz, 1.25 H, major), 4.55–4.45 (m, 2 H), 4.38 (d,  $J = 6.1$  Hz, 0.75 H, minor), 1.31 (td,  $J = 7.1, 2.0$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 190.0, 139.1, 138.9, 134.6, 130.1, 130.0, 128.0, 127.9, 127.8, 126.0, 125.8, 68.2, 66.9, 48.5, 46.5, 14.3, 14.2 ppm. IR (KBr):  $\nu = 2988, 1275, 1263, 764, 749, 731, 702\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{10}\text{H}_{13}\text{ClNOS}$   $[\text{M}+\text{Na}]^+$  calcd 252.0220, found 252.0213.

### ***O*-Ethyl (2-(trifluoromethyl)benzyl)carbamothioate 8ag**



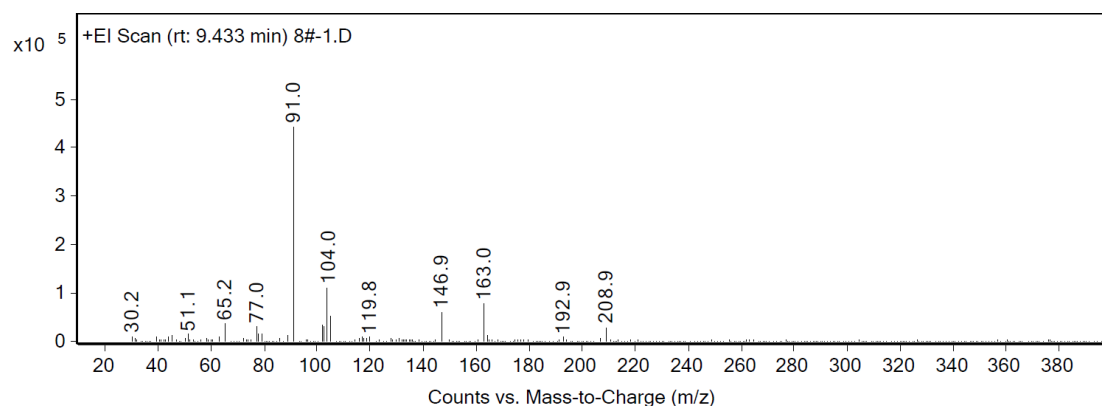
White solid (119.5 mg, 81%, 1.7:1). Mp: 34-35 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (t,  $J = 8.0$  Hz, 1.61 H, major), 7.52 (q,  $J = 6.8$  Hz, 1 H), 7.44 (d,  $J = 7.7$  Hz, 0.39 H, minor), 7.39 (t, 1 H), 7.21 (s, 0.27 H, minor), 6.56 (s, 0.63 H, major), 4.96 (d,  $J = 6.2$  Hz, 1.25 H, major), 4.62 (d,  $J = 6.3$  Hz, 0.75 H, minor), 4.56–4.44 (m, 2 H), 1.33–1.26 (m, 3 H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -59.4 (s, 1.9 F, major), -59.8 (s, 1.1 F, minor);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 190.1, 135.5, 135.4, 130.5, 129.5, 128.1, 128.0, 126.5, 126.4, 126.3, 126.2, 126.1, 126.0, 124.5 (q,  $J = 272.7$  Hz), 68.2, 66.9, 45.4, 43.5, 14.3, 14.1 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1264, 764, 749, 731, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{F}_3\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 286.0484, found 286.0484.

### ***O*-Ethyl phenethylcarbamothioate 8ah**

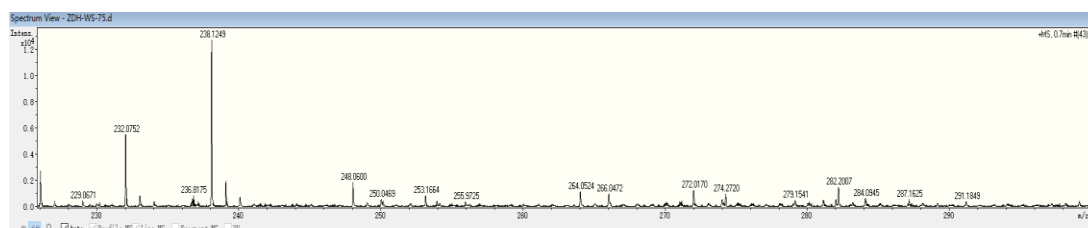


Colorless oil (97.0 mg, 80%, 1.6:1). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.28 (m, 2 H), 7.25–7.19 (m, 2 H), 7.19–7.13 (m, 1 H), 6.87 (s, 0.38 H, minor), 6.27 (s, 0.62 H, major), 4.51 (q,  $J = 7.1$  Hz, 0.77 H, minor), 4.46 (q,  $J = 7.1$  Hz, 1.23 H, major), 3.80 (q, 1.23 H, major), 3.51 (q, 0.77 H, minor), 2.91 (t,  $J = 7.1$  Hz, 1.23 H, major), 2.81 (t,  $J = 7.2$  Hz, 0.77 H, minor), 1.33 (t,  $J = 7.1$  Hz, 1.15 H, minor), 1.28 (t,  $J = 7.1$  Hz, 1.85 H, major);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.5, 190.0, 138.5, 138.1, 128.9, 128.8, 126.9, 126.8, 68.0, 66.4, 46.1, 44.4, 35.6, 34.7, 14.4, 14.3 ppm. IR (KBr):  $\nu = 3005, 2988, 1516, 1275, 1263, 749, 731, 701$   $\text{cm}^{-1}$ . MS (EI):  $m/z$  (%) 209, 104, 91 (100). HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{15}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 232.0767, found 232.0752.

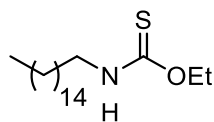
GC-MS:



HR(ESI)-MS:

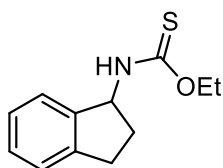


### ***O*-Ethyl hexadecylcarbamothioate 8ai**



White solid (156.6 mg, 87%, 1.3:1). Mp: 43-44 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 (s, 0.43 H, minor), 6.22 (s, 0.57 H, major), 4.52 (q,  $J = 7.1$  Hz, 0.86 H, minor), 4.44 (q,  $J = 7.1$  Hz, 1.14 H, major), 3.50 (td,  $J = 7.3, 5.6$  Hz, 1.14 H, major), 3.23 (td,  $J = 7.1, 5.8$  Hz, 0.86 H, minor), 1.60–1.44 (m, 2 H), 1.33 (t,  $J = 7.1$  Hz, 2 H), 1.28 (t,  $J = 7.1$  Hz, 6 H), 1.23 (s, 21 H), 0.85 (t,  $J = 8.0$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 190.0, 67.8, 66.2, 45.3, 43.2, 32.0, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.7, 27.0, 26.8, 22.8, 14.4, 14.3, 14.2 ppm. IR (KBr):  $\nu = 3006, 2989, 2927, 2855, 1275, 1263, 749, 731, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{19}\text{H}_{39}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 338.2488, found 338.2490.

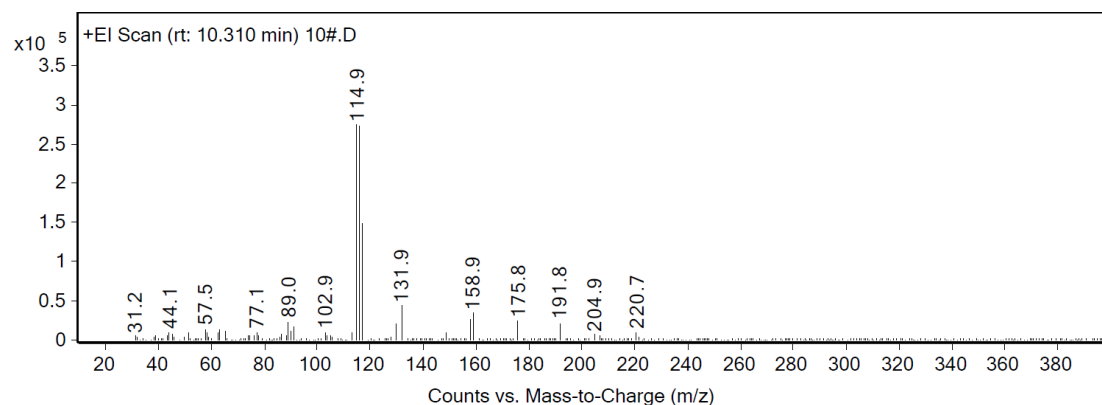
### ***O*-Ethyl (2,3-dihydro-1*H*-inden-1-yl)carbamothioate 8aj**



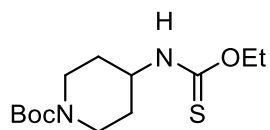
Yellow solid (95.1 mg, 75%, 1.6:1). Mp: 80-81 °C. Eluent: ethyl acetate/petroleum

ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.3$  Hz, 0.59 H, major), 7.28 (d,  $J = 8.2$  Hz, 0.41 H, minor), 7.26–7.23 (m, 2 H), 7.23–7.17 (m, 1 H), 6.87 (d,  $J = 8.0$  Hz, 0.38 H, minor), 6.44 (d,  $J = 8.1$  Hz, 0.62 H, major), 5.81 (q,  $J = 7.7$  Hz, 0.62 H, major), 5.35 (q,  $J = 7.4$  Hz, 0.38 H, minor), 4.60 (q,  $J = 7.1$  Hz, 0.77 H, minor), 4.50 (q,  $J = 7.1$  Hz, 1.23 H, major), 3.04–2.79 (m, 2 H), 2.76–2.62 (m, 0.62 H, major), 2.58–2.47 (m, 0.38 H, minor), 1.97–1.82 (m, 1 H), 1.40 (t,  $J = 7.1$  Hz, 1.14 H, minor), 1.32 (t,  $J = 7.1$  Hz, 1.86 H, major);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 189.7, 143.6, 143.3, 142.2, 141.6, 128.5, 128.4, 127.0, 126.9, 125.1, 125.0, 124.3, 124.2, 68.1, 66.5, 60.3, 58.5, 33.6, 33.4, 30.2, 30.2, 14.4, 14.3 ppm. IR (KBr):  $\nu = 3005, 2987, 1503, 1478, 1382, 1275, 1263, 1189, 749, 702, 652$   $\text{cm}^{-1}$ . MS (EI):  $m/z$  (%) 221, 132, 115 (100). HRMS (ESI):  $m/z$  for  $\text{C}_{12}\text{H}_{15}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 244.0767, found 244.0769.

GC-MS:



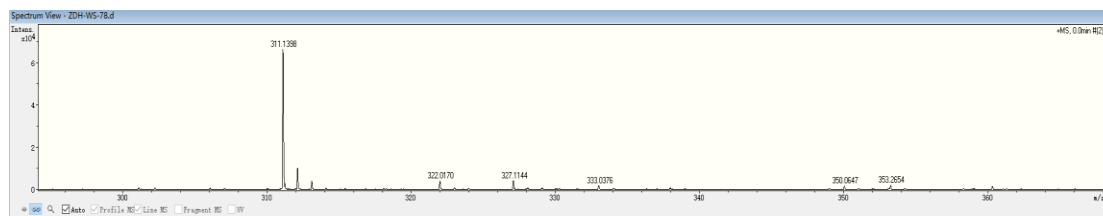
### ***Tert*-butyl 4-((ethoxycarbonothioyl)amino)piperidine-1-carboxylate **8ak****



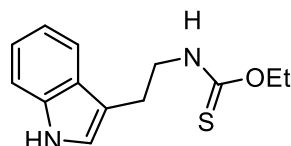
White solid (140.5 mg, 88%, 1.9:1). Mp: 147–148 °C. Eluent: ethyl acetate/petroleum ether (1:3,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.69 (d,  $J = 7.7$  Hz, 0.35 H, minor), 6.19 (d,  $J = 8.3$  Hz, 0.65 H, major), 4.53 (q,  $J = 7.2$  Hz, 0.7 H, minor), 4.43 (q,  $J = 7.1$  Hz, 1.3 H, major), 4.26–4.16 (m, 0.65 H, major), 4.01 (s, 2 H), 3.85–3.72 (m, 0.35 H, minor), 2.83 (q,  $J = 14.7, 13.9$  Hz, 2 H), 2.09–1.98 (m, 1.3 H, major), 1.92–1.82 (m, 0.7 H, minor), 1.42 (s, 9 H), 1.35 (d,  $J = 7.1$  Hz, 1.3 H, major), 1.33–1.27 (m, 3 H), 1.26 (s, 0.7 H, minor);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.5, 154.8, 154.7, 80.0, 79.8,

68.0, 66.3, 52.2, 50.6, 42.5, 31.7, 31.3, 28.5, 14.4, 14.3 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 749, 731, 703 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_3\text{S}$   $[\text{M}+\text{Na}]^+$  calcd 311.1400, found 311.1398.

HR(ESI)-MS:

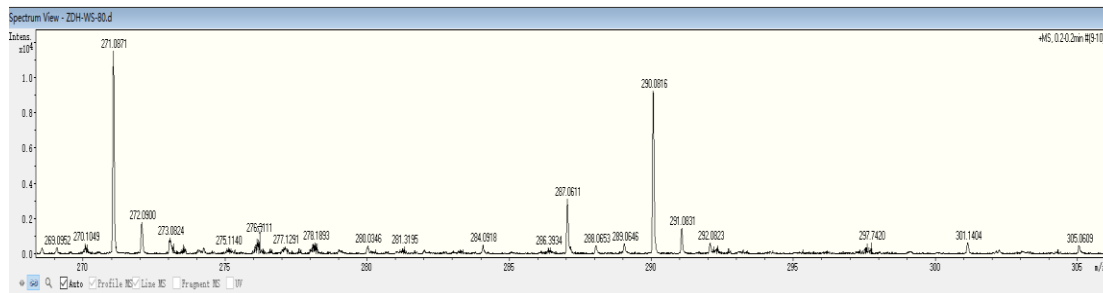


### ***O*-Ethyl (2-(1*H*-indol-3-yl)ethyl)carbamothioate 8al**

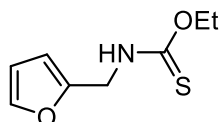


White solid (131.6 mg, 94%, 1.7:1). Mp: 63-64 °C. Eluent: ethyl acetate/petroleum ether (1:2,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1 H), 7.63 (dd,  $J = 7.9, 1.1$  Hz, 0.63 H, major), 7.56 (dd,  $J = 7.8, 1.1$  Hz, 0.37 H, minor), 7.41–7.33 (m, 1 H), 7.26–7.18 (m, 1 H), 7.16–7.11 (m, 1 H), 7.04 (d,  $J = 2.5$  Hz, 0.63 H, major), 7.01 (d,  $J = 2.3$  Hz, 0.37 H, minor), 6.66 (s, 0.37 H, minor), 6.28 (s, 0.63 H, major), 4.49 (dq,  $J = 21.4, 7.1$  Hz, 2 H),  $\delta$  3.89 (td,  $J = 6.8, 5.7$  Hz, 1.25 H, major), 3.59 (td,  $J = 6.9, 5.9$  Hz, 0.75 H, minor), 3.08 (td,  $J = 6.7, 0.9$  Hz, 1.25 H, major), 2.97 (td,  $J = 6.9, 0.9$  Hz, 0.75 H, minor), 1.32 (t,  $J = 7.1$  Hz, 1.12 H, minor), 1.27 (t,  $J = 7.1$  Hz, 1.88 H, major);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 190.0, 136.5, 127.3, 127.1, 122.4, 122.2, 119.1, 118.9, 118.6, 112.7, 112.1, 111.5, 111.4, 68.0, 66.3, 45.3, 43.2, 25.2, 24.4, 14.4, 14.3 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 749, 731, 702 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{OS}$   $[\text{M}+\text{Na}]^+$  calcd 271.0876, found 271.0871.

HR(ESI)-MS:

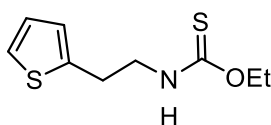


### ***O*-Ethyl (furan-2-ylmethyl)carbamothioate **8a****



Yellow oil (80.2 mg, 74%, 1.8:1). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37–7.30 (m, 1 H), 7.03 (s, 0.36 H, minor), 6.54 (s, 0.64 H, major), 6.34–6.29 (m, 1 H), 6.28 (dd,  $J = 3.2, 0.9$  Hz, 0.64 H, major), 6.19 (dd,  $J = 3.3, 0.8$  Hz, 0.36 H, minor), 4.71 (d,  $J = 5.5$  Hz, 1.28 H, major), 4.53 (q,  $J = 7.1$  Hz, 0.72 H, minor), 4.45 (q,  $J = 7.1$  Hz, 1.28 H, major), 4.40 (d,  $J = 5.7$  Hz, 0.72 H, minor), 1.34 (t,  $J = 7.1$  Hz, 1.08 H, minor), 1.28 (t,  $J = 7.1$  Hz, 1.92 H, major);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.5, 189.8, 150.0, 149.7, 142.6, 142.5, 110.6, 110.5, 108.4, 108.2, 68.1, 66.7, 42.1, 39.9, 14.3, 14.2 ppm. IR (KBr):  $\nu = 3005, 2989, 1512, 1275, 1263, 1185, 749, 731, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_8\text{H}_{11}\text{NO}_2\text{S}$   $[\text{M}+\text{Na}]^+$  calcd 208.0403, found 208.0408.

### ***O*-Ethyl (2-(thiophen-2-yl)ethyl)carbamothioate **8a****

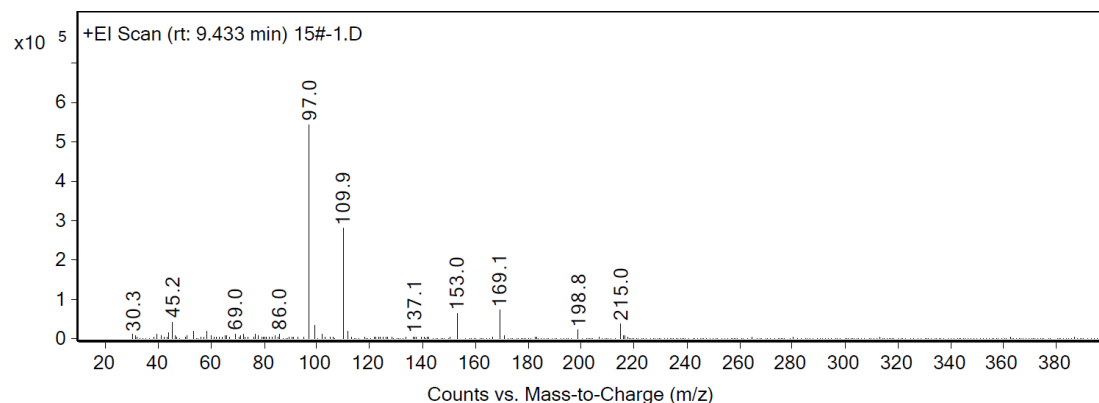


White solid (81.2 mg, 66%, 1.7:1). Mp: 30–31  $^\circ\text{C}$ . Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.17–7.12 (m, 1 H), 7.01 (s, 0.37 H, minor), 6.95–6.90 (m, 1 H), 6.86–6.80 (m, 1 H), 6.38 (s, 0.63 H, major), 4.54–4.41 (m, 2 H), 3.80 (q,  $J = 8.0$  Hz, 1.25 H, major), 3.52 (q,  $J = 8.0$  Hz, 0.75 H, minor), 3.13 (td,  $J = 6.8, 0.9$  Hz, 1.25 H, major), 3.02 (td,  $J = 7.0, 0.9$  Hz, 0.75 H, minor), 1.32 (t,  $J = 7.1$  Hz, 1.12 H, minor), 1.28 (t,  $J = 7.1$  Hz, 1.88 H, major);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.6, 190.0, 140.9, 140.3, 127.2, 127.1, 125.8, 125.6, 124.3, 124.2, 68.0, 66.5, 46.2,

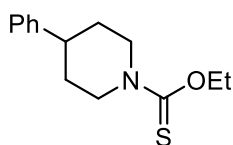


44.4, 29.7, 28.9, 14.4, 14.3 ppm. IR (KBr):  $\nu = 3005, 2988, 1514, 1275, 1263, 749, 701$   $\text{cm}^{-1}$ . MS (EI):  $m/z$  (%) 215, 110, 97 (100). HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_{13}\text{NOS}_2$   $[\text{M}+\text{Na}]^+$  calcd 238.0331, found 238.0341.

GC-MS:

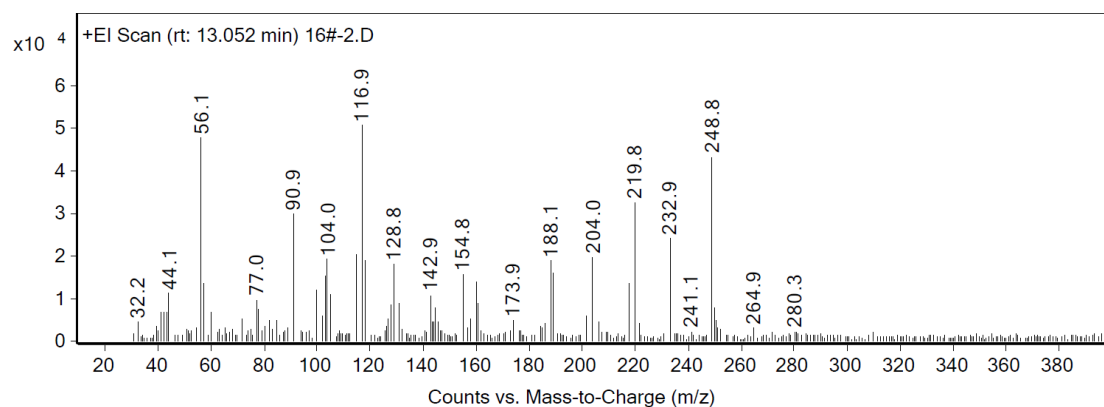


### ***O*-Ethyl 4-phenylpiperidine-1-carbothioate 8ao**

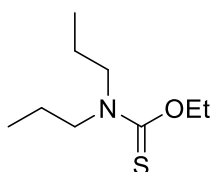


Yellow oil (99.3 mg, 71%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.27 (m, 2 H), 7.23–7.19 (m, 2 H), 7.18 (d,  $J = 1.1$  Hz, 1 H), 5.30 (d,  $J = 13.5$  Hz, 1 H), 4.73 (d,  $J = 13.1$  Hz, 1 H), 4.59–4.49 (m, 2 H), 3.09 (td,  $J = 12.9, 2.8$  Hz, 1 H), 2.92 (td,  $J = 13.1, 2.8$  Hz, 1 H), 2.82–2.72 (m, 1 H), 1.87 (d,  $J = 15.4$  Hz, 2 H), 1.83–1.70 (m, 1 H), 1.70–1.55 (m, 1 H), 1.35 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  187.2, 145.1, 128.7, 126.9, 126.7, 67.6, 50.6, 45.8, 42.8, 33.4, 32.7, 14.5 ppm. IR (KBr):  $\nu = 3005, 2988, 2940, 2864, 1493, 1443, 1276, 1263, 1218, 750, 700$   $\text{cm}^{-1}$ . MS (EI):  $m/z$  (%) 249, 220, 117 (100). HRMS (ESI):  $m/z$  for  $\text{C}_{14}\text{H}_{19}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 272.1080, found 272.1070.

GC-MS:

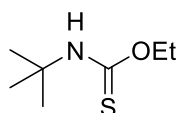


### ***O*-Ethyl dipropylcarbamothioate 8ap**



Yellow oil (100.0 mg, 91%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.47 (q,  $J = 7.1$  Hz, 2 H), 3.70–3.64 (m, 2 H), 3.38–3.31 (m, 2 H), 1.74–1.64 (m, 2 H), 1.61–1.52 (m, 2 H), 1.30 (t,  $J = 7.1$  Hz, 3 H), 0.92–0.84 (m, 6 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  187.9, 67.1, 54.9, 50.7, 21.4, 20.1, 14.4, 11.5, 11.3 ppm. IR (KBr):  $\nu = 3006, 2989, 2927, 2853, 1275, 1260, 749, 731, 700\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_{19}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 212.1080, found 212.1085.

### ***O*-Ethyl *tert*-butylcarbamothioate 8aq**



White solid (65.9 mg, 68%). Mp: 40–42 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.65 (s, 1 H), 4.55 (q,  $J = 7.1$  Hz, 2 H), 1.38 (t,  $J = 7.1$  Hz, 3 H), 1.32 (s, 9 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.4, 68.2, 54.6, 29.1, 14.3 ppm. IR (KBr):  $\nu = 3004, 2989, 2925, 2853, 1276, 1260, 750, 730, 700\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_7\text{H}_{15}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 184.0767, found 184.0774.

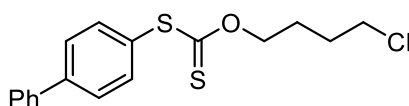
#### IV. Synthetic Applications

##### Transformation of xanthate-derived reagents.

##### General procedure I: xanthate-derived reagents react with aryl boronic acids.

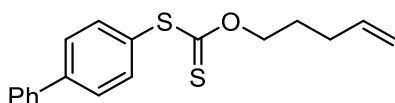
4-Biphenylboronic acid (0.5 mmol, 1.0 equiv), xanthate-derived reagents (0.60 mmol, 1.2 equiv), Na<sub>2</sub>CO<sub>3</sub> (26.5 mg, 0.25 mmol, 0.5 equiv), CuSO<sub>4</sub> (4.0 mg, 0.025 mmol, 0.05 equiv), 2,2'-bipyridine (4.0 mg, 0.025 mmol, 0.05 equiv) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar in argon atmosphere. Freshly distilled CH<sub>3</sub>CN (3.0 mL) was added. The reaction was stirred at 60 °C for 15 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give corresponding substituted biphenyl.

##### *S*-([1,1'-Biphenyl]-4-yl) *O*-(4-chlorobutyl) carbonodithioate **9aa**



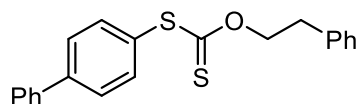
Pale yellow solid (135.6 mg, 81%). Mp: 26-27 °C. Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65 (dd, *J* = 14.4, 7.7 Hz, 4 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.40 (t, *J* = 7.3 Hz, 1 H), 4.58 (t, *J* = 6.1 Hz, 2 H), 3.44 (t, *J* = 6.4 Hz, 2 H), 1.90–1.82 (m, 2 H), 1.78–1.69 (m, 2 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 212.9, 143.1, 140.0, 135.6, 129.1, 128.7, 128.2, 128.1, 127.3, 73.4, 44.4, 29.1, 25.7 ppm. IR (KBr): ν = 3006, 2990, 1276, 1262, 1050, 1007, 765, 703 cm<sup>-1</sup>. HRMS (ESI): *m/z* for C<sub>17</sub>H<sub>17</sub>ClOS<sub>2</sub> [M+Na]<sup>+</sup> calcd 359.0302, found 359.0309.

##### *S*-([1,1'-Biphenyl]-4-yl) *O*-(pent-4-en-1-yl) carbonodithioate **9ab**



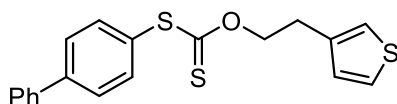
Yellow oil (113.9 mg, 72%). Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.7). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70–7.58 (m, 6 H), 7.49 (t, *J* = 7.5 Hz, 2 H), 7.41 (t, *J* = 7.3 Hz, 1 H), 5.87–5.61 (m, 1 H), 4.99 (d, *J* = 11.7 Hz, 2 H), 4.58 (t, *J* = 6.3 Hz, 2 H), 2.04 (q, *J* = 7.2 Hz, 2 H), 1.86–1.76 (m, 2 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 213.0, 143.0, 140.0, 137.2, 135.6, 129.1, 128.9, 128.1, 128.0, 127.3, 115.8, 73.7, 30.0, 27.5 ppm. IR (KBr): ν = 3006, 2990, 1476, 1276, 1262, 1047, 765, 703 cm<sup>-1</sup>. HRMS (ESI): *m/z* for C<sub>18</sub>H<sub>18</sub>OS<sub>2</sub> [M+Na]<sup>+</sup> calcd 337.0691, found 337.0682.

##### *S*-([1,1'-Biphenyl]-4-yl) *O*-phenethyl carbonodithioate **9ac**



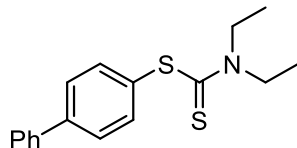
White solid (143.5 mg, 82%). Mp: 57-58 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (dd,  $J = 7.9, 3.7$  Hz, 4 H), 7.55 (dd,  $J = 13.7, 7.5$  Hz, 4 H), 7.46 (t,  $J = 7.3$  Hz, 1 H), 7.28 (d,  $J = 6.3$  Hz, 3 H), 7.08 (d,  $J = 7.8$  Hz, 2 H), 4.82 (t,  $J = 6.6$  Hz, 2 H), 3.04 (t,  $J = 6.6$  Hz, 2 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.7, 143.0, 140.1, 137.4, 135.6, 129.2, 129.1, 128.7, 128.2, 128.1, 127.4, 127.1, 126.8, 74.6, 34.6 ppm. IR (KBr):  $\nu = 3006, 2990, 1461, 1276, 1262, 757, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{21}\text{H}_{18}\text{OS}_2$   $[\text{M}+\text{Na}]^+$  calcd 373.0691, found 373.0693.

**S-([1,1'-Biphenyl]-4-yl) O-(2-(thiophen-3-yl)ethyl) carbonodithioate 9ad**



Yellow solid (140.4 mg, 79%). Mp: 50-51 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73–7.64 (m, 4 H), 7.57 (d,  $J = 8.3$  Hz, 2 H), 7.52 (t,  $J = 7.6$  Hz, 2 H), 7.45 (t,  $J = 7.3$  Hz, 1 H), 7.23 (dd,  $J = 4.9, 3.0$  Hz, 1 H), 6.84 (d,  $J = 2.3$  Hz, 1 H), 6.82 (d,  $J = 3.6$  Hz, 1 H), 4.79 (t,  $J = 6.5$  Hz, 2 H), 3.06 (t,  $J = 6.5$  Hz, 2 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.6, 141.9, 138.9, 136.4, 134.5, 128.1, 127.6, 127.2, 127.1, 127.0, 126.3, 124.7, 121.0, 72.9, 28.0 ppm. IR (KBr):  $\nu = 3006, 2990, 1462, 1276, 1262, 765, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{19}\text{H}_{16}\text{OS}_3$   $[\text{M}+\text{Na}]^+$  calcd 379.0255, found 379.0244.

**[1,1'-Biphenyl]-4-yl diethylcarbamodithioate 9ae**



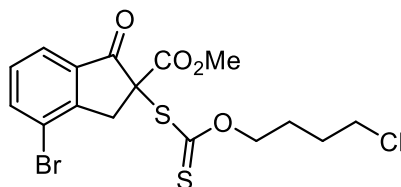
White solid (97.9 mg, 65%). Mp: 79-80 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.5$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73–7.62 (m, 4 H), 7.57 (d,  $J = 8.4$  Hz, 2 H), 7.46 (t,  $J = 7.4$  Hz, 2 H), 7.38 (t,  $J = 7.4$  Hz, 1 H), 4.05 (q,  $J = 7.1$  Hz, 2 H), 3.88 (q,  $J = 7.0$  Hz, 2 H), 1.42 (t,  $J = 7.0$  Hz, 3 H), 1.31 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 142.8, 140.3, 137.6, 130.5, 129.0, 127.9, 127.8, 127.4, 50.0, 47.5, 12.9,

11.8 ppm. IR (KBr):  $\nu = 3006, 2990, 1461, 1420, 1276, 1262, 757, 703 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{17}\text{H}_{19}\text{NS}_2 [\text{M}+\text{Na}]^+$  calcd 324.0851, found 324.0851.

**General procedure II: xanthate-derived reagents react with  $\beta$ -ketoesters.**

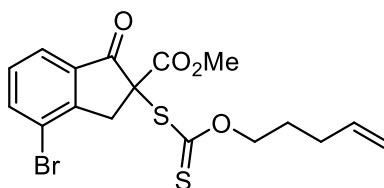
A 25 mL Schlenk tube was charged with methyl 4-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (0.5 mmol),  $\text{K}_2\text{CO}_3$  (0.55 mmol, 1.1 equiv), xanthate-derived reagents (0.60 mmol, 1.2 equiv) and DCE (3.0 mL) in argon atmosphere. The mixture was stirred at  $80^\circ\text{C}$  for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give corresponding substituted methyl 4-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate.

**Methyl 4-bromo-2-(((4-chlorobutoxy)carbonothioyl)thio)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 10aa**



White solid (179.3 mg, 79%). Mp:  $72\text{--}73^\circ\text{C}$ . Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.4$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 7.8 \text{ Hz}$ , 1 H), 7.76 (d,  $J = 7.6 \text{ Hz}$ , 1 H), 7.36 (t,  $J = 7.7 \text{ Hz}$ , 1 H), 4.50–4.39 (m, 2 H), 4.16 (d,  $J = 18.3 \text{ Hz}$ , 1 H), 3.75 (s, 3 H), 3.53 (d,  $J = 18.2 \text{ Hz}$ , 1 H), 3.46 (t,  $J = 6.4 \text{ Hz}$ , 2 H), 1.74–1.65 (m, 2 H), 1.65–1.57 (m, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.0, 194.5, 166.7, 151.8, 138.9, 136.1, 130.2, 124.2, 121.6, 73.6, 67.1, 54.4, 44.2, 42.5, 28.8, 25.3 ppm. IR (KBr):  $\nu = 3006, 2990, 1460, 1276, 1262, 765, 703 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{16}\text{H}_{16}\text{BrClO}_4\text{S}_2 [\text{M}+\text{Na}]^+$  calcd 472.9254, found 472.9253.

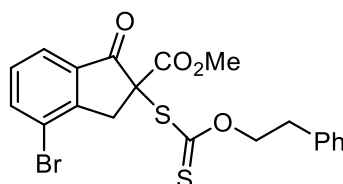
**Methyl 4-bromo-1-oxo-2-(((pent-4-en-1-yloxy)carbonothioyl)thio)-2,3-dihydro-1H-indene-2-carboxylate 10ab**



Yellow solid (206.8 mg, 96%). Mp:  $51\text{--}52^\circ\text{C}$ . Eluent: ethyl acetate/petroleum ether (1:5,

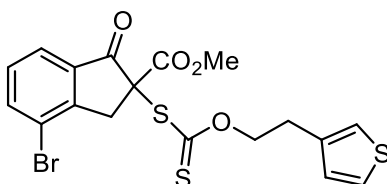
$R_f = 0.4$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 7.8$  Hz, 1 H), 7.75 (d,  $J = 7.6$  Hz, 1 H), 7.34 (t,  $J = 7.7$  Hz, 1 H), 5.79–5.58 (m, 1 H), 5.09–4.83 (m, 2 H), 4.49–4.36 (m, 2 H), 4.17 (d,  $J = 18.3$  Hz, 1 H), 3.75 (s, 3 H), 3.53 (d,  $J = 18.2$  Hz, 1 H), 1.97 (q,  $J = 8.0$ , 7.4 Hz, 2 H), 1.57–1.48 (m, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.0, 194.5, 166.8, 151.9, 138.9, 136.7, 136.1, 130.1, 124.2, 121.6, 115.9, 74.1, 67.1, 54.3, 42.5, 29.8, 26.8 ppm. IR (KBr):  $\nu = 3006, 2990, 1459, 1276, 1262, 750, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{17}\text{H}_{17}\text{BrO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 450.9644, found 450.9644.

**Methyl 4-bromo-1-oxo-2-((phenethoxycarbonothioyl)thio)-2,3-dihydro-1H-indene-2-carboxylate 10ac**



White solid (147.3 mg, 63%). Mp: 112–113 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.4$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 7.8$  Hz, 1 H), 7.74 (d,  $J = 7.5$  Hz, 1 H), 7.38–7.26 (m, 3 H), 7.24 (t,  $J = 7.2$  Hz, 1 H), 7.12 (d,  $J = 8.6$  Hz, 2 H), 4.70–4.58 (m, 2 H), 4.13 (d,  $J = 18.3$  Hz, 1 H), 3.73 (s, 3 H), 3.48 (d,  $J = 18.4$  Hz, 1 H), 2.78 (t,  $J = 7.4$  Hz, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.0, 194.6, 166.7, 152.1, 138.9, 136.3, 136.0, 130.1, 128.9, 128.8, 127.1, 124.1, 121.6, 74.3, 67.2, 54.3, 42.5, 33.9 ppm. IR (KBr):  $\nu = 3006, 2990, 1459, 1276, 1262, 765, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{20}\text{H}_{17}\text{BrO}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 486.9644, found 486.9641.

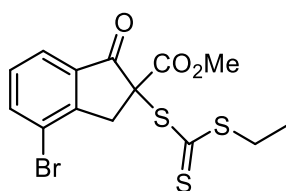
**Methyl 4-bromo-1-oxo-2-(((2-(thiophen-3-yl)ethoxy)carbonothioyl)thio)-2,3-dihydro-1H-indene-2-carboxylate 10ad**



White solid (199.9 mg, 85%). Mp: 88–89 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 7.8$  Hz, 1 H), 7.73 (d,  $J = 7.5$  Hz, 1 H), 7.33 (t,  $J = 7.7$  Hz, 1 H), 7.26 (td,  $J = 6.4, 5.6, 3.4$  Hz, 1 H), 6.97 (d,  $J = 1.8$  Hz, 1 H), 6.87 (dd,  $J = 4.9, 1.4$  Hz, 1 H), 4.71–4.60 (m, 2 H), 4.13 (d,  $J = 18.3$  Hz, 1 H),

3.73 (s, 3 H), 3.48 (d,  $J = 18.3$  Hz, 1 H), 2.82 (t,  $J = 7.1$  Hz, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.0, 194.5, 166.7, 152.0, 138.9, 136.6, 136.0, 130.1, 128.0, 126.2, 124.1, 122.0, 121.6, 73.8, 67.2, 54.3, 42.5, 28.5 ppm. IR (KBr):  $\nu = 3006, 2990, 1276, 1262, 747, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{18}\text{H}_{15}\text{BrO}_4\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 492.9208, found 492.9209.

**Methyl 4-bromo-2-(((ethylthio)carbonothioyl)thio)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 10af**

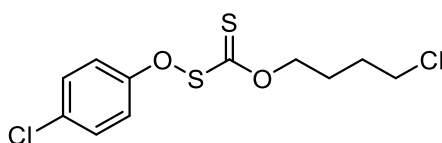


Yellow oil (67.7 mg, 33%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 7.7$  Hz, 1 H), 7.74 (d,  $J = 7.6$  Hz, 1 H), 7.33 (t,  $J = 7.7$  Hz, 1 H), 4.35 (d,  $J = 18.4$  Hz, 1 H), 3.75 (s, 3 H), 3.57 (d,  $J = 18.4$  Hz, 1 H), 3.30 (q,  $J = 7.4$  Hz, 2 H), 1.33 (t,  $J = 7.4$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  219.8, 194.4, 166.5, 152.6, 139.0, 136.0, 130.0, 124.1, 121.7, 69.0, 54.4, 41.9, 32.3, 12.9 ppm. IR (KBr):  $\nu = 3006, 2990, 1276, 1262, 745, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{14}\text{H}_{13}\text{BrO}_3\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 426.9102, found 426.9102.

**General procedure III: xanthate-derived reagents react with phenols.**

A 25 mL Shlenk tube was charged with 4-chlorophenol (0.5 mmol), xanthate-derived reagents (0.7 mmol, 1.4 equiv) and  $\text{Cs}_2\text{CO}_3$  (0.55 mmol, 1.1 equiv) and DCE (3.0 mL) in argon atmosphere. The mixture was stirred at 80 °C for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give corresponding substituted 4-chlorophenol.

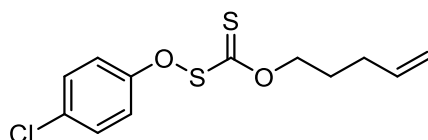
***O*-(4-Chlorobutyl) *SO*-(4-chlorophenyl) carbonothio(thioperoxoate) 11aa**



Colorless oil (129.7 mg, 83%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.34 (m, 2 H), 7.07–7.00 (m, 2 H), 4.55 (t,  $J = 6.0$  Hz,

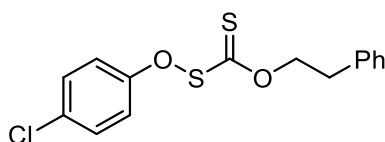
2 H), 3.60 (t,  $J = 6.0$  Hz, 2 H), 2.04–1.90 (m, 4 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.9, 151.8, 132.2, 129.8, 123.5, 73.8, 44.4, 29.0, 25.7 ppm. IR (KBr):  $\nu = 3006, 2990, 1487, 1461, 1276, 1262, 1204, 753, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{13}\text{Cl}_2\text{O}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 332.9548, found 332.9547.

***SO*-(4-Chlorophenyl) *O*-(pent-4-en-1-yl) carbonothio(thioperoxoate) 11ab**



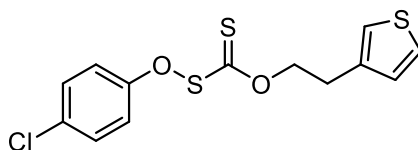
Yellow oil (140.2 mg, 97%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.9$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.31 (m, 2 H), 7.10–6.99 (m, 2 H), 5.89–5.75 (m, 1 H), 5.14–4.99 (m, 2 H), 4.52 (t,  $J = 6.6$  Hz, 2 H), 2.21 (q,  $J = 7.9, 7.5$  Hz, 2 H), 1.92 (m, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 151.8, 137.1, 132.1, 129.8, 123.6, 115.9, 74.1, 29.9, 27.4 ppm. IR (KBr):  $\nu = 3006, 2990, 1487, 1461, 1394, 1276, 1262, 1202, 765, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{12}\text{H}_{13}\text{ClO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 310.9938, found 310.9935.

***SO*-(4-Chlorophenyl) *O*-phenethyl carbonothio(thioperoxoate) 11ac**



White solid (131.4 mg, 81%). Mp: 91–92 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45–7.33 (m, 4 H), 7.29 (d,  $J = 8.3$  Hz, 3 H), 7.08–7.00 (m, 2 H), 4.76 (t,  $J = 7.1$  Hz, 2 H), 3.16 (t,  $J = 7.1$  Hz, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.8, 151.8, 137.0, 132.2, 129.8, 129.2, 128.8, 127.0, 123.6, 74.8, 34.7 ppm. IR (KBr):  $\nu = 3006, 2990, 1461, 1276, 1262, 1211, 897, 765, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{13}\text{ClO}_2\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 346.9938, found 346.9936.

***SO*-(4-Chlorophenyl) *O*-(2-(thiophen-3-yl)ethyl) carbonothio(thioperoxoate) 11ad**

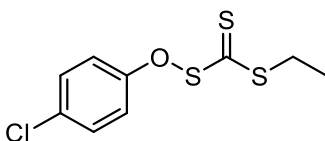


White solid (160.8 mg, 97%). Mp: 59–60 °C. Eluent: ethyl acetate/petroleum ether (1:5,



$R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.34 (m, 2 H), 7.31 (dd,  $J = 4.9, 2.9$  Hz, 1 H), 7.09 (d,  $J = 1.8$  Hz, 1 H), 7.06–7.01 (m, 2 H), 7.01 (d,  $J = 1.3$  Hz, 1 H), 4.72 (t,  $J = 6.9$  Hz, 2 H), 3.17 (t,  $J = 6.9$  Hz, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7, 151.8, 137.1, 132.2, 129.8, 128.3, 126.1, 123.5, 122.2, 74.1, 29.2 ppm. IR (KBr):  $\nu = 3006, 2990, 1487, 1461, 1276, 1262, 1205, 747, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{11}\text{ClO}_2\text{S}_3$   $[\text{M}+\text{Na}]^+$  calcd 352.9502, found 352.9496.

***SO*-(4-Chlorophenyl) *S*-ethyl carbonodithio(thioperoxoate) 11af**



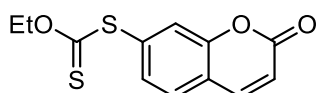
Yellow oil (88.0 mg, 66%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43–7.32 (m, 2 H), 7.07–6.98 (m, 2 H), 3.22 (q,  $J = 7.4$  Hz, 2 H), 1.41 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  214.8, 152.9, 132.1, 129.8, 123.7, 31.5, 13.2 ppm. IR (KBr):  $\nu = 3006, 2990, 1484, 1276, 1262, 1192, 1175, 1034, 1014, 897, 837, 763, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_9\text{ClOS}_3$   $[\text{M}+\text{Na}]^+$  calcd 286.9396, found 286.9390.

## Late-stage ethylxanthylation of bioactive or functional molecules.

### General procedure I: ethylxanthylation of bioactive boronic acids.

Bioactive boronic acids (0.5 mmol, 1.0 equiv), *N*-ethylxanthylphthalimide **3c** (160 mg, 0.60 mmol, 1.2 equiv), Na<sub>2</sub>CO<sub>3</sub> (26.5 mg, 0.25 mmol, 0.5 equiv), CuSO<sub>4</sub> (4.0 mg, 0.025 mmol, 0.05 equiv), 2,2'-bipyridine (4.0 mg, 0.025 mmol, 0.05 equiv) were placed into an oven-dried 25 mL Schlenk tube that was equipped with a stirring bar in argon atmosphere. Freshly distilled CH<sub>3</sub>CN (3.0 mL) was added. The reaction was stirred at 60 °C for 15 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give ethylxanthylated arenes.

### *O*-Ethyl *S*-(2-oxo-2*H*-chromen-7-yl) carbonodithioate **12aa**



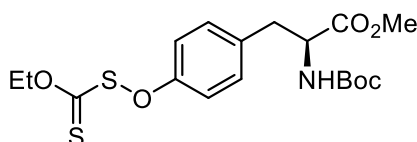
White solid (103.9 mg, 78%). Mp: 114-115 °C. Eluent: ethyl acetate/petroleum ether (1:2, R<sub>f</sub> = 0.6). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 10.2 Hz, 1 H), 7.52 (d, *J* = 8.1 Hz, 1 H), 7.49 (d, *J* = 1.6 Hz, 1 H), 7.39 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.49 (d, *J* = 9.6 Hz, 1 H), 4.62 (q, *J* = 7.1 Hz, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 210.8, 160.1, 153.9, 142.8, 134.3, 130.7, 128.3, 123.2, 119.9, 118.2, 70.9, 13.7 ppm. IR (KBr): ν = 3054, 2988, 1737, 1264, 1039, 733, 703 cm<sup>-1</sup>. HRMS (ESI): *m/z* for C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>S<sub>2</sub> [M+Na]<sup>+</sup> calcd 288.9964, found 288.9968.

### General procedure II: ethylxanthylation of bioactive phenols

A 25 mL Schlenk tube was charged with phenols (0.5 mmol), *N*-ethylxanthylphthalimide **3c** (0.7 mmol, 1.4 equiv), Cs<sub>2</sub>CO<sub>3</sub> (0.55 mmol, 1.1 equiv) and DCE (5.0 mL) in argon atmosphere. The mixture was stirred at 80 °C for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give ethylxanthylated phenols.

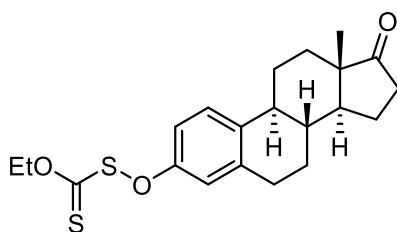
### Methyl

### (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(((ethoxycarbonothioyl)thio)oxy)phenyl)propanoate **12ab**



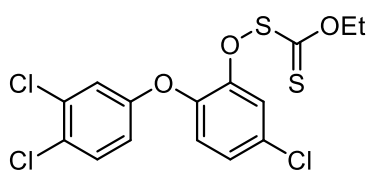
White solid (199.3 mg, 96%). Mp: 74-75 °C. Eluent: ethyl acetate/petroleum ether (1:3,  $R_f = 0.5$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (d,  $J = 8.1$  Hz, 2 H), 7.01 (d,  $J = 8.5$  Hz, 2 H), 5.03 (d,  $J = 8.4$  Hz, 1 H), 4.59 (s, 1 H), 4.56 (q,  $J = 7.1$  Hz, 2 H), 3.68 (s, 3 H), 3.20–2.91 (m, 2 H), 1.43 (t,  $J = 7.1$  Hz, 3 H), 1.39 (s, 9 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.2, 172.3, 155.1, 152.5, 134.6, 130.5, 122.1, 80.1, 70.5, 54.4, 52.4, 38.0, 28.4, 13.8 ppm. IR (KBr):  $\nu = 3054, 2986, 1743, 1712, 1505, 1439, 1370, 1264, 1215, 1194, 1165, 1102, 731, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{18}\text{H}_{25}\text{NO}_6\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 438.1016, found 438.1020.

***O*-Ethyl *SO*-((*8R,9S,13S,14S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl) carbonothio(thioperoxoate) 12ac**



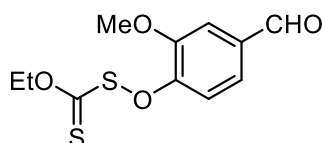
White solid (174.4 mg, 89%). Mp: 147-148 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.7$  Hz, 1 H), 6.88 (dd,  $J = 8.5, 2.7$  Hz, 1 H), 6.82 (d,  $J = 2.5$  Hz, 1 H), 4.58 (q,  $J = 7.1$  Hz, 2 H), 2.96–2.88 (m, 2 H), 2.50 (dd,  $J = 19.0, 8.4$  Hz, 1 H), 2.44–2.36 (m, 1 H), 2.30 (td,  $J = 10.6, 4.3$  Hz, 1 H), 2.20–2.10 (m, 1 H), 2.10–2.03 (m, 1 H), 2.03–1.92 (m, 2 H), 1.67–1.57 (m, 4 H), 1.55–1.48 (m, 2 H), 1.46 (d,  $J = 7.1$  Hz, 3 H), 0.90 (s, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  220.8, 195.5, 151.4, 138.3, 138.1, 126.5, 121.8, 119.1, 70.4, 50.5, 48.0, 44.3, 38.0, 35.9, 31.6, 29.5, 26.4, 25.8, 21.7, 13.9, 13.8 ppm. IR (KBr):  $\nu = 3054, 2987, 2932, 1736, 1264, 1206, 1181, 733, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{21}\text{H}_{26}\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 413.1216, found 413.1221.

***SO*-(5-Chloro-2-(3,4-dichlorophenoxy)phenyl) *O*-ethyl carbonothio(thioperoxoate) 12ad**



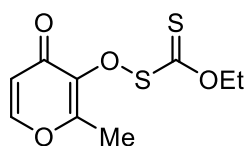
Colorless oil (194.7 mg, 95%). Eluent: ethyl acetate/petroleum ether (1:30,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 2.5$  Hz, 1 H), 7.23–7.14 (m, 3 H), 6.94 (d,  $J = 8.8$  Hz, 1 H), 6.78 (d,  $J = 8.6$  Hz, 1 H), 4.55 (q,  $J = 7.1$  Hz, 2 H), 1.42 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.8, 150.6, 147.1, 143.6, 130.6, 130.0, 128.9, 128.3, 127.7, 126.7, 124.8, 121.3, 119.7, 71.2, 13.8 ppm. IR (KBr):  $\nu = 3006, 2989, 1474, 1422, 1302, 1275, 1263, 750, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{11}\text{Cl}_3\text{O}_3\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 430.9107, found 430.9114.

***O*-Ethyl *SO*-(4-formyl-2-methoxyphenyl) carbonothio(thioperoxoate) 12ae**



Colorless oil (121.6 mg, 89%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.93 (s, 1 H), 7.53–7.43 (m, 2 H), 7.22 (d,  $J = 7.8$  Hz, 1 H), 4.56 (q,  $J = 7.2$  Hz, 2 H), 3.87 (s, 3 H), 1.43 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.8, 191.0, 152.0, 146.7, 135.7, 124.7, 123.9, 111.4, 71.0, 56.2, 13.8 ppm. IR (KBr):  $\nu = 3054, 2987, 1702, 1603, 1504, 1465, 1422, 1391, 1375, 1299, 1264, 1193, 1148, 1123, 1035, 730, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{11}\text{H}_{12}\text{O}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 295.0069, found 295.0078.

***O*-Ethyl *SO*-(2-methyl-4-oxo-4*H*-pyran-3-yl) carbonothio(thioperoxoate) 12af**

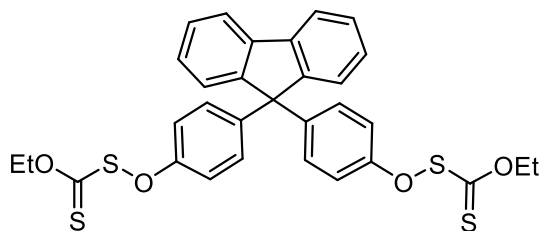


Yellow oil (117.2 mg, 95%). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.2$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 5.7$  Hz, 1 H), 6.40 (d,  $J = 5.8$  Hz, 1 H), 4.57 (t,  $J = 7.1$  Hz, 2 H), 2.24 (s, 3 H), 1.43 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 171.5, 160.2, 154.4, 140.8, 117.4, 71.4, 15.2, 13.7 ppm. IR (KBr):  $\nu = 3006, 2990, 1661, 1466, 1423, 1399, 1375, 1302, 1276, 1262, 1210, 1182, 1040, 833, 749, 702$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_9\text{H}_{10}\text{O}_4\text{S}_2$   $[\text{M}+\text{Na}]^+$  calcd 268.9913, found 268.9916.

***O*,*SO'*-((9*H*-Fluorene-9,9-diyl)bis(4,1-phenylene))**

***O*,*O'*-diethyl**

**bis(carbonothio(thioperoxoate)) 12ag**

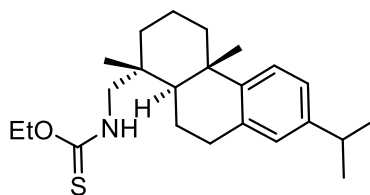


2.4 Equiv reagent **3c** was employed. White solid (228.4 mg, 77%). Mp: 153-154 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.6$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 (d,  $J = 7.6$  Hz, 2 H), 7.42 (d,  $J = 7.6$  Hz, 2 H), 7.37 (td,  $J = 7.5, 1.2$  Hz, 2 H), 7.29 (td,  $J = 7.5, 1.2$  Hz, 2 H), 7.26–7.21 (m, 4 H), 6.99–6.94 (m, 4 H), 4.56 (q,  $J = 7.1$  Hz, 4 H), 1.43 (t,  $J = 7.1$  Hz, 6 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 152.2, 150.7, 143.9, 140.2, 129.3, 128.0, 127.9, 126.3, 121.8, 120.4, 70.5, 64.7, 13.9 ppm. IR (KBr):  $\nu = 3006, 2990, 1462, 1276, 1262, 757, 703$   $\text{cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{31}\text{H}_{26}\text{O}_4\text{S}_4$   $[\text{M}+\text{Na}]^+$  calcd 613.0606, found 613.0614.

### General procedure III: ethylxanthylation of bioactive amines

A 25 mL Shlenk tube was charged with amines (0.5 mmol), *N*-ethylxanthylphthalimide **3c** (0.6 mmol, 1.2 equiv) and toluene (3.0 mL) in argon atmosphere. The mixture was stirred at room temperature for 16 h. The solvent was removed under vacuum and the residue was purified by flask column chromatography to give the corresponding thiocarbamates.

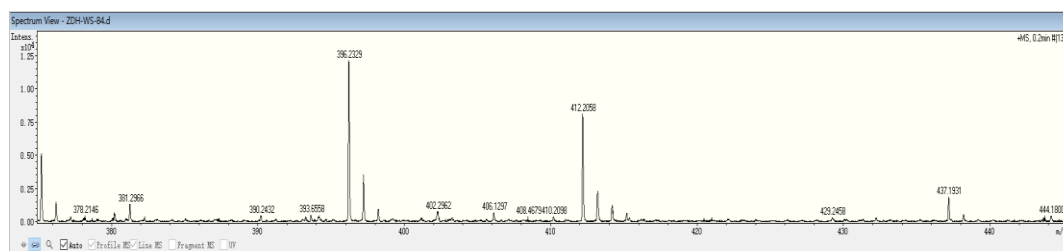
#### *O*-Ethyl (((1*R*,4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)carbamothioate **12ah**



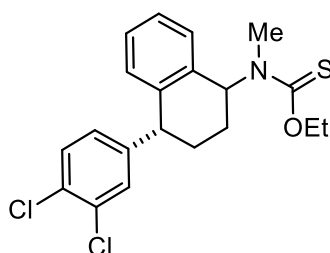
Colorless oil (101.4 mg, 50%, 1.6:1). Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.7$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 (dd,  $J = 8.2, 5.8$  Hz, 1 H), 7.02–6.97 (m, 1 H), 6.89 (dd,  $J = 10.4, 2.0$  Hz, 1 H), 6.64 (s, 0.38 H, minor), 6.22 (s, 0.62 H, major), 4.62–4.49 (m, 0.77 H, minor), 4.49–4.37 (m, 1.23 H, major), 3.57 (dd,  $J = 13.7, 6.2$  Hz, 0.5 H, minor), 3.48 (dd,  $J = 13.7, 6.4$  Hz, 0.5 H, major), 3.26–3.12 (m, 1 H), 2.96–2.76 (m, 3 H), 2.35–2.23 (m, 1 H), 1.97–1.87 (m, 1 H), 1.85–1.57 (m, 4 H), 1.50–1.41 (m, 2 H),

1.37 (t,  $J = 7.1$  Hz, 2 H), 1.29 (t,  $J = 7.1$  Hz, 2 H), 1.23 (d,  $J = 1.2$  Hz, 3 H), 1.22–1.20 (m, 6 H), 0.98 (s, 2 H), 0.93 (s, 1 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.0, 190.4, 147.1, 146.9, 145.9, 134.8, 134.4, 127.0, 126.9, 124.3, 124.2, 124.1, 124.0, 68.1, 66.4, 55.6, 53.8, 45.6, 45.4, 38.3, 38.2, 37.8, 37.7, 37.6, 36.5, 36.2, 33.5, 30.2, 25.4, 24.1, 19.2, 19.1, 19.0, 18.7, 18.6, 18.5, 14.3 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 1275, 1263\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{23}\text{H}_{35}\text{NOS}$   $[\text{M}+\text{Na}]^+$  calcd 396.2332, found 396.2329.

HR(ESI)-MS:



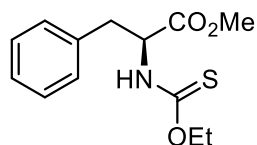
***O*-Ethyl ((4*R*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)carbamothioate 12ai**



White solid (75.9 mg, 36%, 2.3:1). Mp: 119–120 °C. Eluent: ethyl acetate/petroleum ether (1:5,  $R_f = 0.8$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (dd,  $J = 8.3, 2.5$  Hz, 1 H), 7.25–7.13 (m, 2 H), 7.12–7.04 (m, 1.3 H, major), 6.97 (d,  $J = 8.4$  Hz, 1 H), 6.83 (dd,  $J = 8.6, 1.9$  Hz, 0.7 H, minor), 6.79 (dd,  $J = 8.4, 2.3$  Hz, 0.3 H, minor), 6.58 (dd,  $J = 11.0, 6.1$  Hz, 0.7 H, major), 4.71–4.53 (m, 2 H), 4.20 (s, 1 H), 3.08 (s, 0.9 H, minor), 2.80 (s, 2.1 H, major), 2.39–2.21 (m, 1 H), 2.09–1.98 (m, 1 H), 1.97–1.84 (m, 1 H), 1.83–1.73 (m, 1 H), 1.73–1.60 (m, 1 H), 1.39 (t,  $J = 7.1$  Hz, 2.1 H, major), 1.34 (t,  $J = 7.0$  Hz, 0.9 H, minor);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.9, 189.4, 147.0, 146.8, 137.9, 137.8, 135.5, 135.4, 132.6, 132.4, 131.1, 131.0, 130.7, 130.6, 130.3, 130.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 127.2, 68.0, 67.8, 60.8, 43.0, 31.8, 30.2, 30.1, 22.4, 20.9, 14.5 ppm. IR (KBr):  $\nu = 3006, 2989, 1275, 1263, 750, 703\text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for

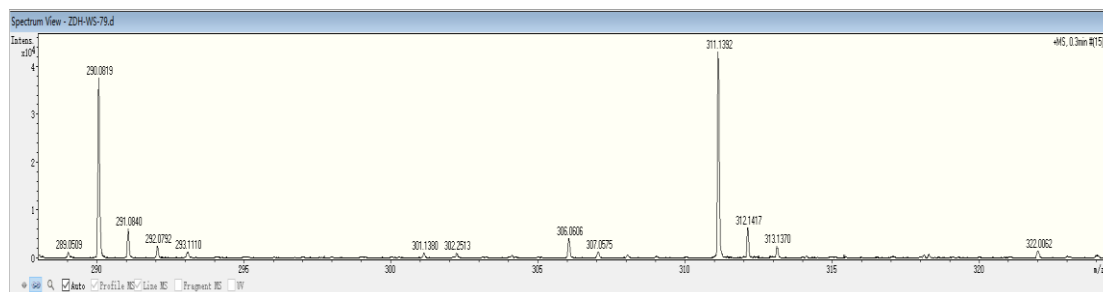
C<sub>20</sub>H<sub>21</sub>Cl<sub>2</sub>NOS [M+Na]<sup>+</sup> calcd 416.0613, found 416.0616.

### Methyl (ethoxycarbonothioyl)-*L*-phenylalaninate 12aj

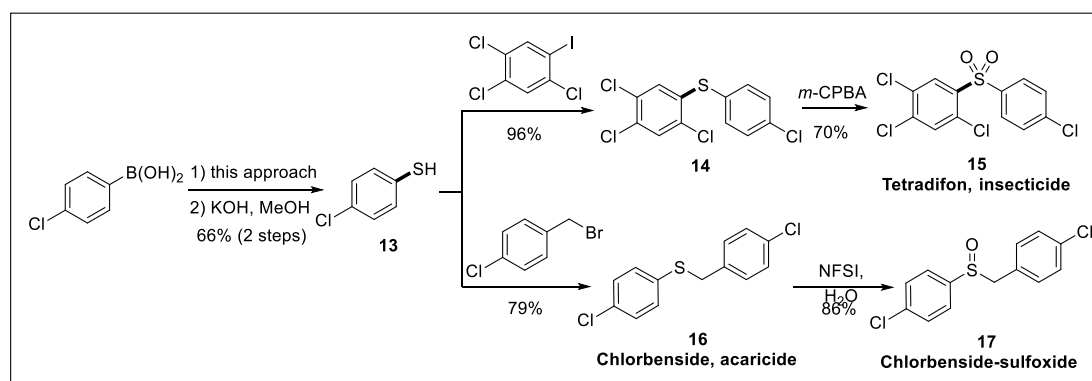


Colorless oil (87.4 mg, 58%, 3.3:1). Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.5). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32–7.21 (m, 3 H), 7.15–7.05 (m, 2 H), 6.96 (d, *J* = 7.9 Hz, 0.23 H, minor), 6.63 (d, *J* = 7.9 Hz, 0.77 H, major), 5.27–5.12 (m, 0.77 H, major), 4.83–4.66 (m, 0.23 H, minor), 4.54–4.33 (m, 2 H), 3.71 (d, *J* = 3.9 Hz, 3 H), 3.34–3.14 (m, 1.53 H, major), 3.14–2.93 (m, 0.47 H, minor), 1.30 (t, *J* = 7.1 Hz, 2.29 H, major), 1.25 (t, *J* = 7.1 Hz, 0.71 H, minor); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.1, 189.4, 171.6, 170.6, 135.6, 135.4, 129.4, 129.3, 128.9, 128.7, 127.5, 127.3, 68.1, 66.8, 58.3, 56.7, 52.6, 52.5, 38.7, 37.3, 14.3, 14.1 ppm. IR (KBr): ν = 3006, 2989, 1742, 1505, 1275, 1263, 1192, 749, 731, 702 cm<sup>-1</sup>. HRMS (ESI): *m/z* for C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub>S [M+Na]<sup>+</sup> calcd 290.0821, found 290.0819.

HR(ESI)-MS:



## Synthesis of bioactive Tetradifon and Chlorbenside-sulfoxide.

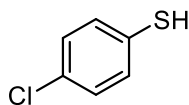


### 1) Synthesis of bioactive Tetradifon

#### A. Synthesis of **13**<sup>[6]</sup>

In argon atmosphere, *p*-chlorophenylboronic acid (15 mmol, 1.0 equiv), *N*-ethylxanthylphthalimide **3c** (18 mmol, 1.2 equiv), Na<sub>2</sub>CO<sub>3</sub> (7.5 mmol, 0.5 equiv), CuSO<sub>4</sub> (0.75 mmol, 0.05 equiv) and 2, 2'-bipyridine (0.75 mmol, 0.05 equiv) were placed in a round bottom flask, then acetonitrile (30 mL) was added and reacted at 60 °C for 15 hours. After completion of the reaction, the solvent was removed by rotary evaporation under reduced pressure, and the residue was purified by a rapid silica gel chromatography to obtain the **5ak** (2.55 g, 73%). Subsequently, **5ak** (7.32 mmol), potassium hydroxide (31.5 mmol) and ethanol (30 mL) were placed in a 100 mL Shlenk tube and refluxed overnight. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by a rapid silica gel chromatography to obtain the corresponding *p*-chlorothiophenol **13** (952.7 mg, 90%).

#### 4-Chlorobenzenethiol **13**



White solid (952.7 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (s, 4 H), 3.45 (s, 1 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 131.8, 130.9, 129.3, 129.2 ppm. The spectroscopic data were matched with those reported in the literature.<sup>[7]</sup>

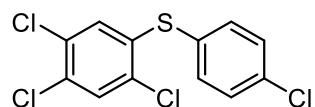
#### B. Synthesis of **14**<sup>[8]</sup>

In argon atmosphere, a mixture of CuI (60 mg, 0.30 mmol), K<sub>2</sub>CO<sub>3</sub> (1.62 g, 11.76 mmol), 1,2,4-trichloro-5-iodobenzene (1.81 g, 5.88 mmol), 4-chlorobenzenethiol (**13**) (850.4 mg, 5.88 mmol), ethylene glycol (0.66 mL, 11.76 mmol) and 2-propanol (6 mL)



were heated at 80 °C and allowed to reflux for 30 h. After cooling to room temperature, the mixture was diluted with distilled H<sub>2</sub>O and then extracted with EtOAc. The combined organic layer was washed with brine (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation under reduced pressure. The crude product was purified by a rapid silica gel chromatography.

#### (4-Chlorophenyl)(2,4,5-trichlorophenyl)sulfane **14**

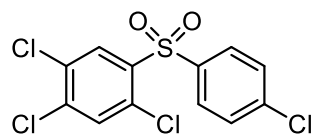


Yellow solid (1.83 g, 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (s, 1 H), 7.39 (s, 4 H), 6.94 (s, 1 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.8, 135.6, 135.0, 131.7, 131.3, 130.8, 130.2, 130.0, 129.6, 129.3 ppm. IR (KBr): ν = 3006, 2990, 1475, 1436, 1390, 1324, 1276, 1262, 761, 704, 645 cm<sup>-1</sup>. HRMS (ESI): m/z for C<sub>12</sub>H<sub>6</sub>Cl<sub>4</sub>S [M+Na]<sup>+</sup> calcd 344.8837, found 344.8839.

#### C. Synthesis of Tetradifon (**15**)<sup>[9]</sup>

In a 50 mL round bottom flask equipped with a stirrer, thermometer and condenser, (4-chlorophenyl)(2,4,5-trichlorophenyl)sulfane (324.04 mg, 1 mmol) and *m*-chloroperoxybenzoic acid (690.28 mg, 4 mol), and dichloromethane (15 mL) were added. The reaction mixture was kept at 40 °C for 12 h. The mixture was washed with deionized water until the pH was near 7, and then washed with saturated brine 1–2 times. The upper organic phase was separated, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The residue was purified by a rapid silica gel chromatography to obtain **15**.

#### 1,2,4-Trichloro-5-((4-chlorophenyl)sulfonyl)benzene **15**



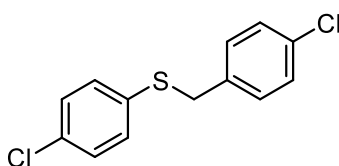
Yellow solid (250.9 mg, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.40 (s, 1 H), 7.90–7.86 (m, 2 H), 7.54 (s, 1 H), 7.52–7.48 (m, 2 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.0, 139.3, 137.8, 137.6, 133.4, 132.5, 132.2, 131.4, 130.3, 129.6 ppm. IR (KBr): ν = 3054, 2988, 1263, 732, 703, 659 cm<sup>-1</sup>. HRMS (ESI): m/z for C<sub>12</sub>H<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub>S [M+Na]<sup>+</sup> calcd 376.8735, found 376.8736.

## 2) Synthesis of bioactive Chlorbenside-sulfoxide

### A. Synthesis of **16**<sup>[10]</sup>

4-Chlorothiophenol (1.0 g, 7.5 mmol) and potassium carbonate (1.14 g, 8.25 mmol) were dissolved in 20 mL of DMF. 4-Chlorobenzyl bromide (1.54 g, 7.5 mmol) was added dropwise to reaction mixture at room temperature. The reaction mixture was stirred for 8 hours and extracted with EtOAc and brine. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography.

#### (4-Chlorobenzyl)(4-chlorophenyl)sulfane **16**

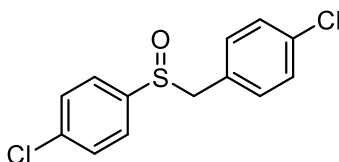


White solid (1.59 g, 79%). Mp: 55-56 °C. Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.7). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27–7.20 (m, 4 H), 7.20–7.15 (m, 4 H), 4.02 (s, 2 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.9, 134.2, 133.2, 132.9, 131.8, 130.2, 129.2, 128.8, 38.8 ppm. The spectroscopic data were matched with those reported in the literature<sup>[11]</sup>.

### B. Synthesis of Chlorbenside-sulfoxide (**17**)<sup>[12]</sup>

To a solution of (4-chlorobenzyl)(4-chlorophenyl)sulfane **16** (269.2 mg, 1.0 mmol) in H<sub>2</sub>O (2.0 mL), NFSI (315 mg, 1.0 equiv) was added at room temperature. The resulting reaction mixture was stirred for 6 h. After completion of the reaction, the resulting mixture was extracted with EtOAc (3×20 mL), and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel.

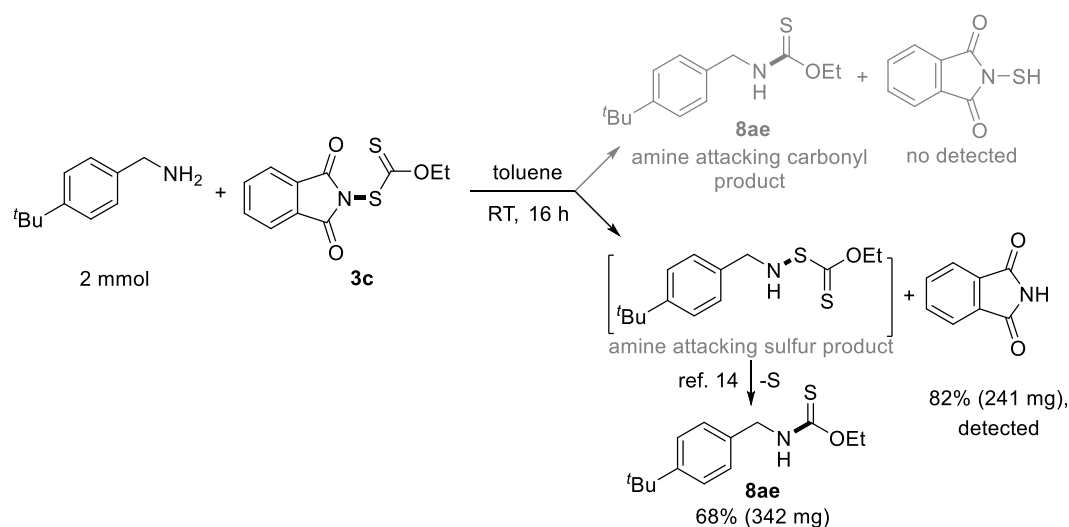
#### 1-Chloro-4-((4-chlorobenzyl)sulfinyl)benzene **17**



White solid (244.5 mg, 86%). Mp: 123-124 °C. Eluent: ethyl acetate/petroleum ether (1:5, R<sub>f</sub> = 0.7). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43–7.37 (m, 2 H), 7.30–7.24 (m, 2 H),

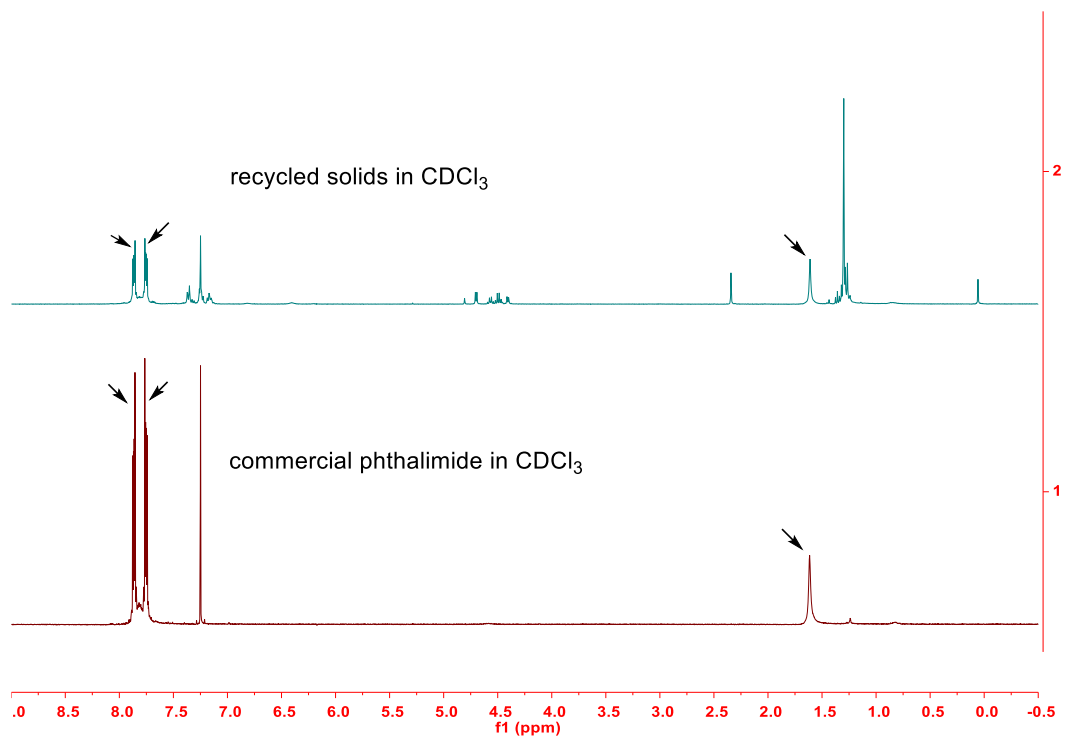
7.24–7.18 (m, 2 H), 6.90–6.84 (m, 2 H), 4.03–3.92 (m, 2 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 137.6, 134.7, 131.8, 129.4, 128.8, 127.0, 125.90, 62.3 ppm. IR (KBr):  $\nu = 3005, 2989, 1275, 1263, 749, 702 \text{ cm}^{-1}$ . HRMS (ESI):  $m/z$  for  $\text{C}_{13}\text{H}_{10}\text{C}_{12}\text{OS}$   $[\text{M}+\text{Na}]^+$  calcd 306.9722, found 306.9725.

## V. Control experiments



In order to further understand the xanthylation of alkyl amine to deliver the corresponding thiocarbamate products, control experiments were conducted. No *N*-sulfydryl phthalimide was detected by GC-MS or  $^1\text{H}$  NMR, which may exclude the possibility of amine attacking carbonyl groups. By contrast, amine attacking electrophilic sulfur and subsequent desulfurization is likely involved for this process, due to the detection of phthalimide by  $^1\text{H}$  NMR and GC-MS when the reaction is completed. This desulfurization of *N*-alkyl-*S*-(ethoxycarbonothioyl)thiohydroxylamine is also consistent with the occurrence of desulfurization phenomenon in previous literatures.<sup>[13]</sup>

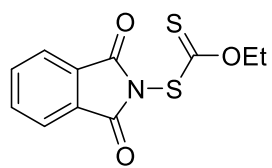
Experimental procedure: a 50 mL Shlenk tube was charged with 4-*tert*-butylbenzylamine (2.0 mmol), *N*-ethylxanthylphthalimide **3c** (2.4 mmol, 1.2 equiv) and toluene (10 mL) in argon atmosphere. The mixture was stirred at room temperature for 16 h. The residue was filtered and dried to give a recycled solid (241 mg, ~82% yield), which was proved to be phthalimide and confirmed by  $^1\text{H}$  NMR and GC-MS. ( $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.86 (q,  $J$  = 4.0 Hz, 2 H), 7.75 (q,  $J$  = 4.0 Hz, 2 H), 1.61 (s, 1 H); GC-MS (EI):  $m/z$  (%): 147 ( $\text{M}^+$ , 100)). The solvent was removed by rotary evaporation to give the corresponding thiocarbamate **8ae** (342 mg, 68% yield) by flask column chromatography.



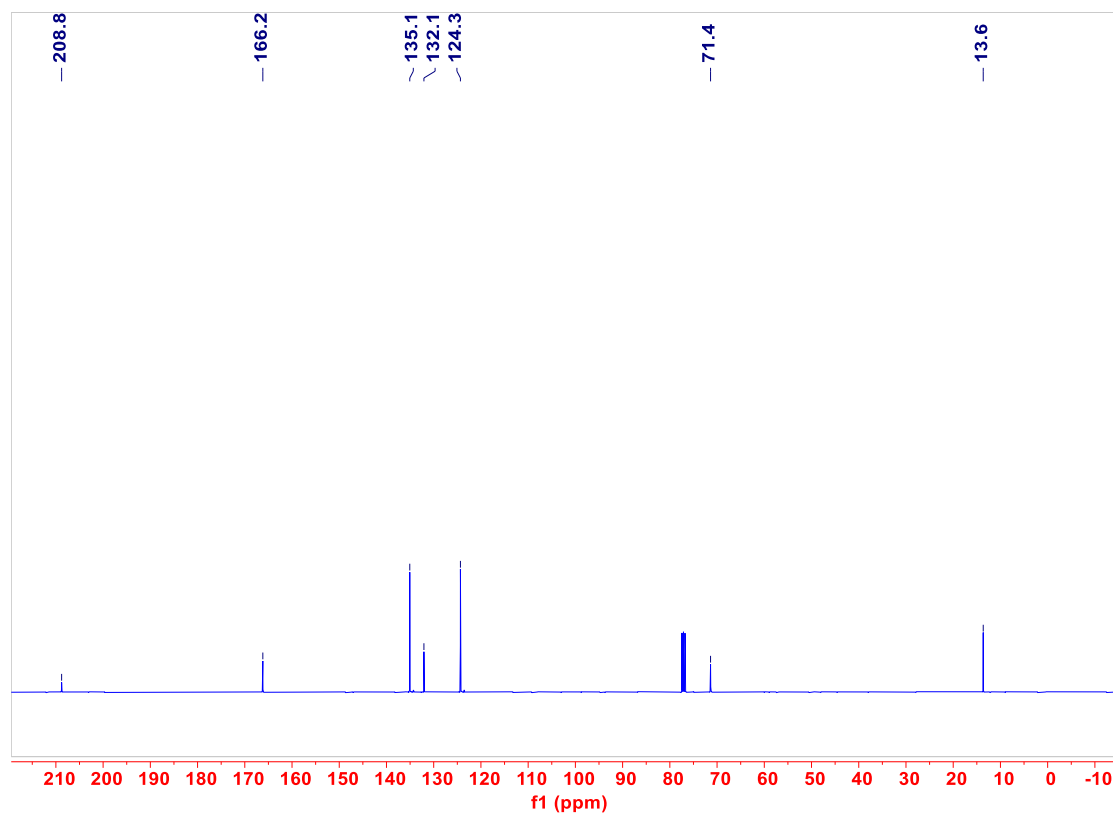
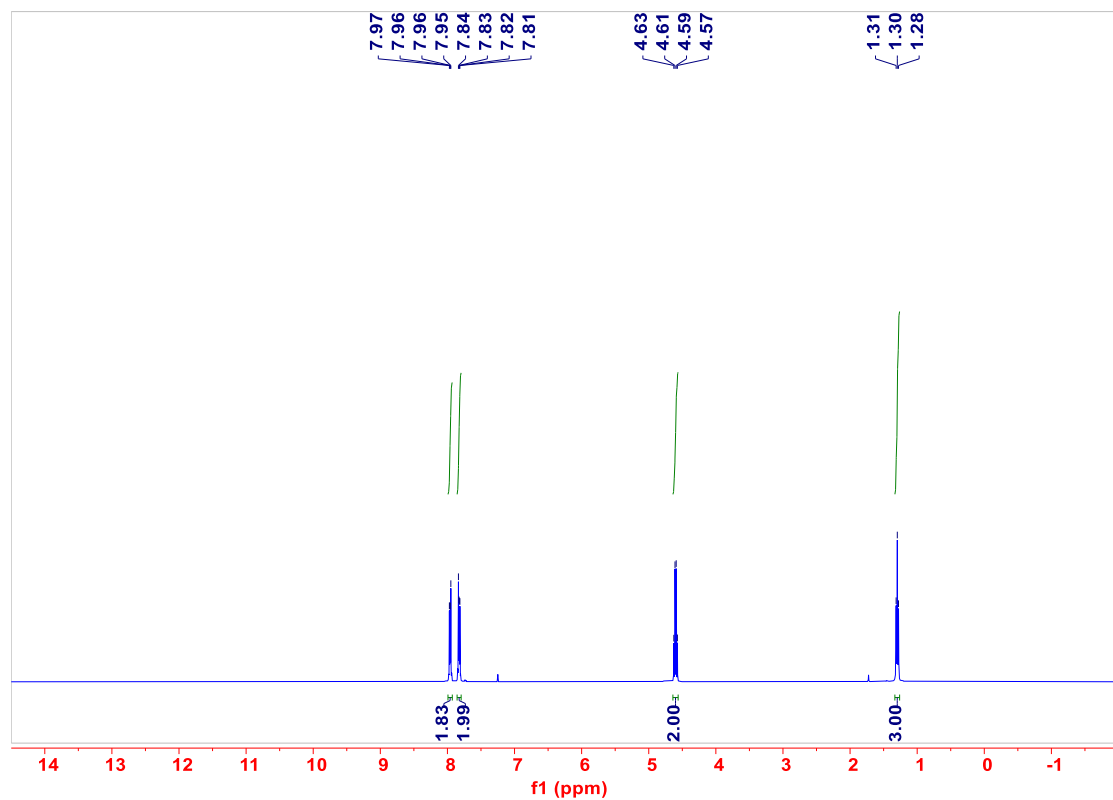
## VI. References

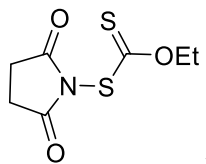
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## VII. $^1\text{H}$ , $^{19}\text{F}$ , $^{13}\text{C}$ NMR spectra of corresponding compounds

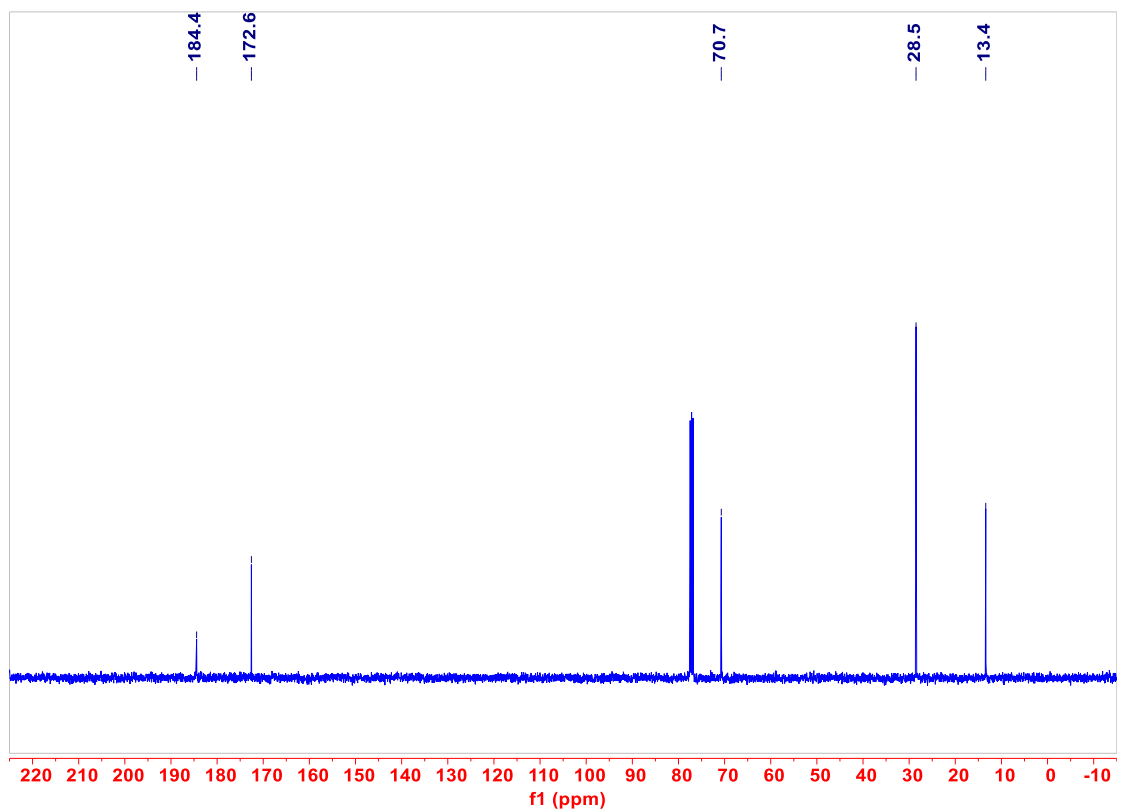
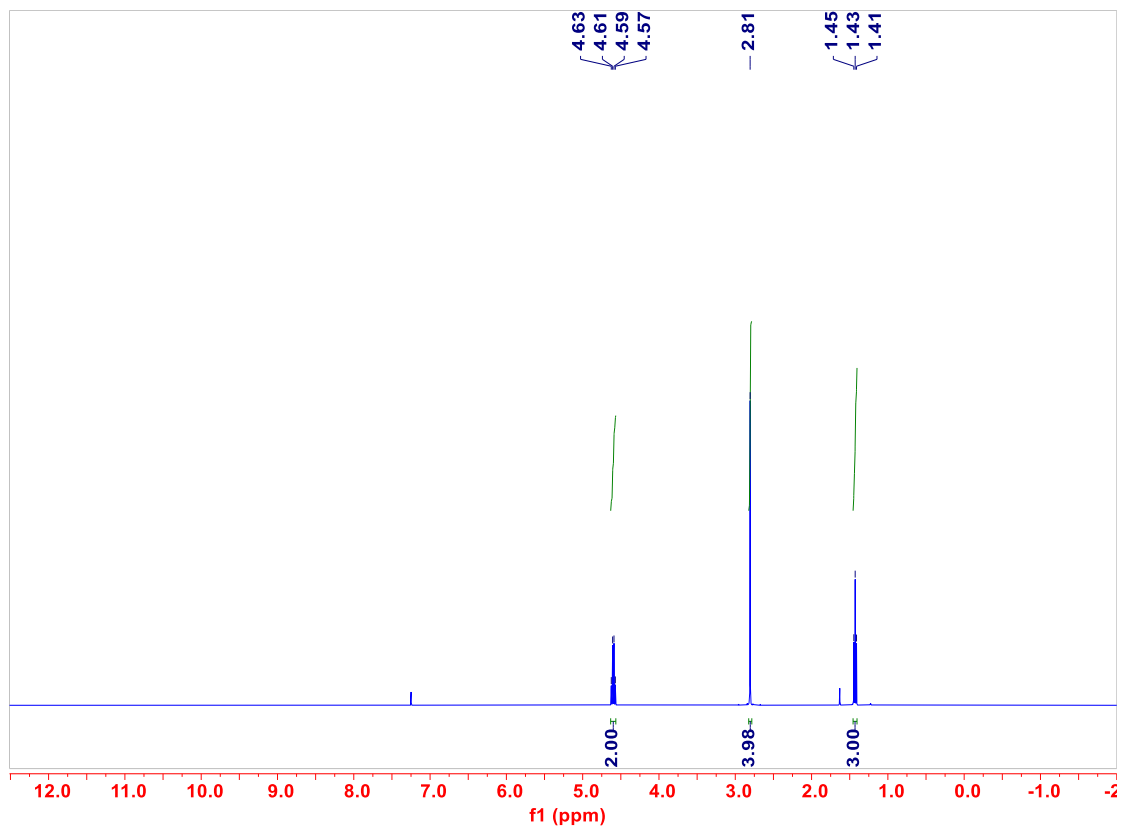


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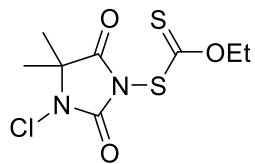




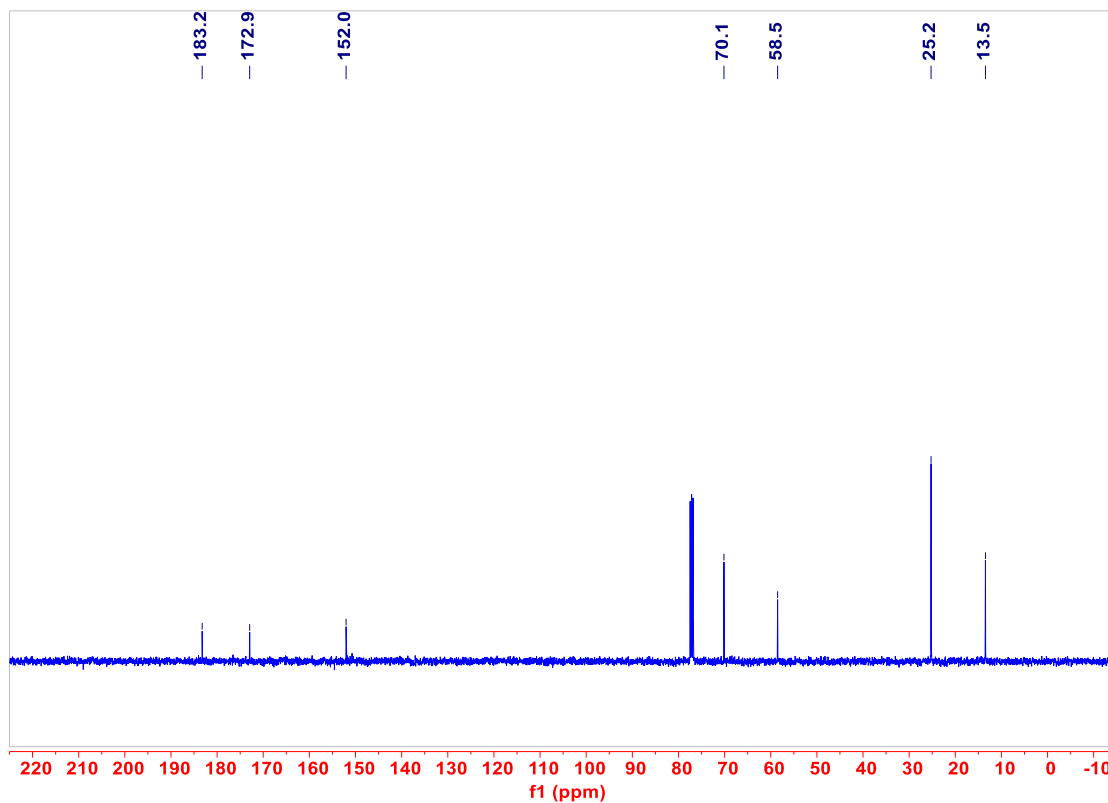
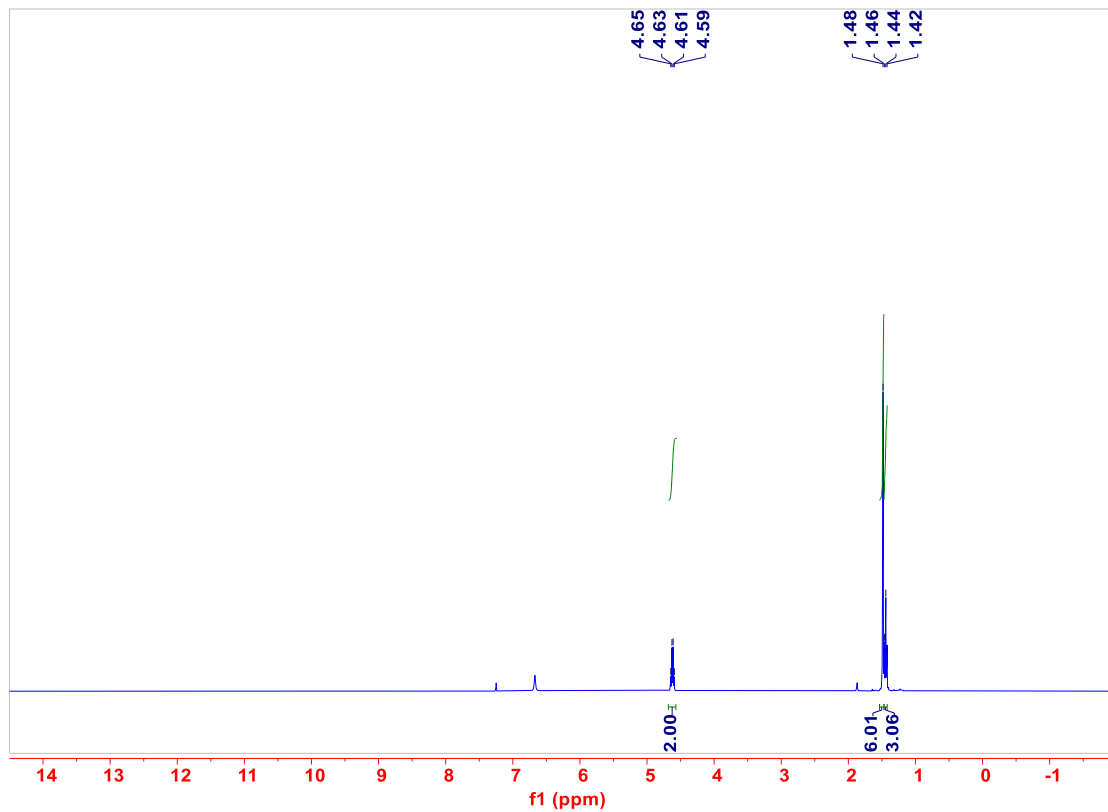
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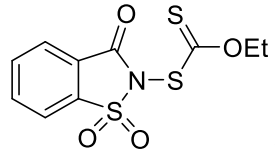




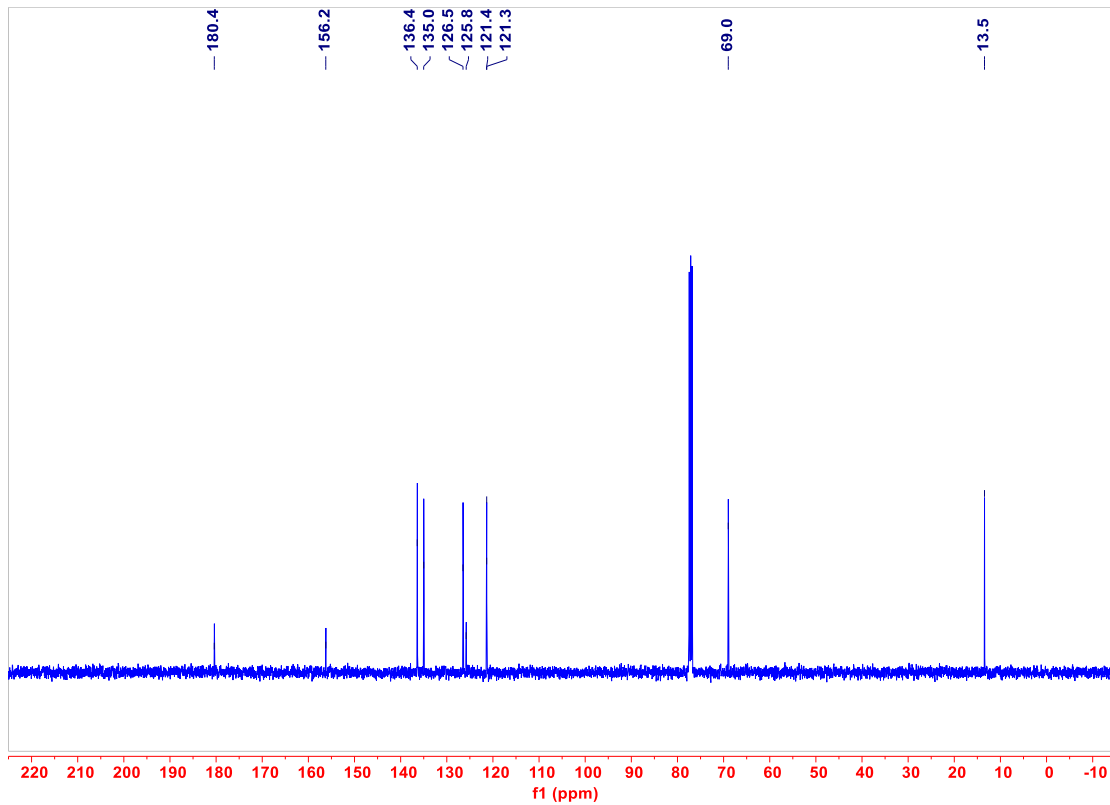
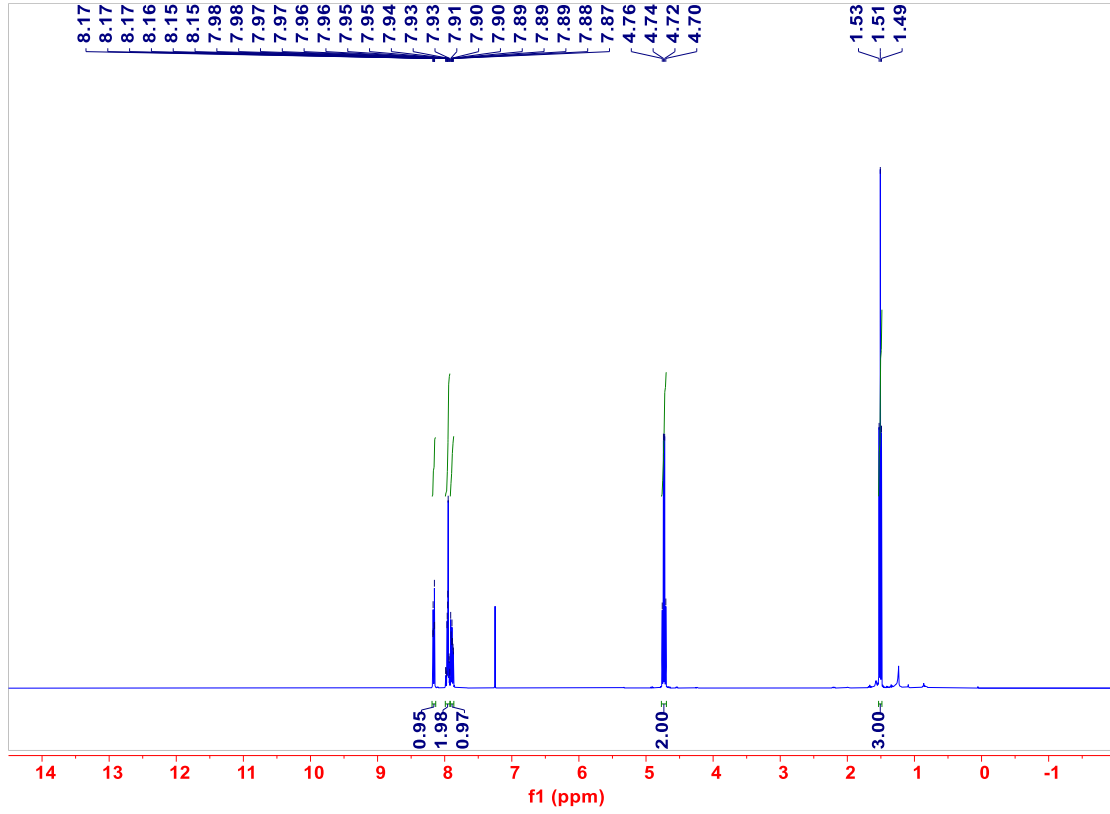


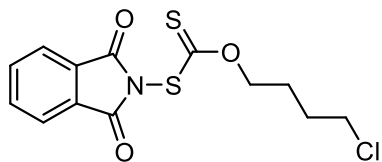
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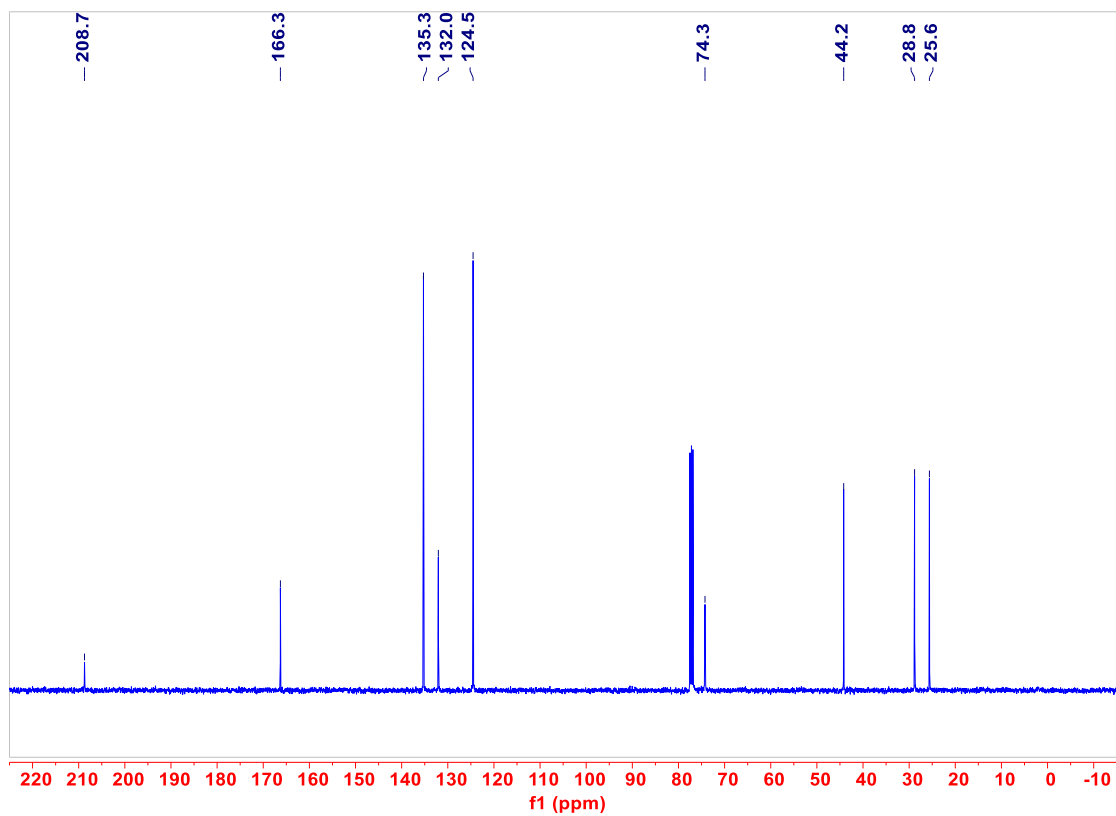
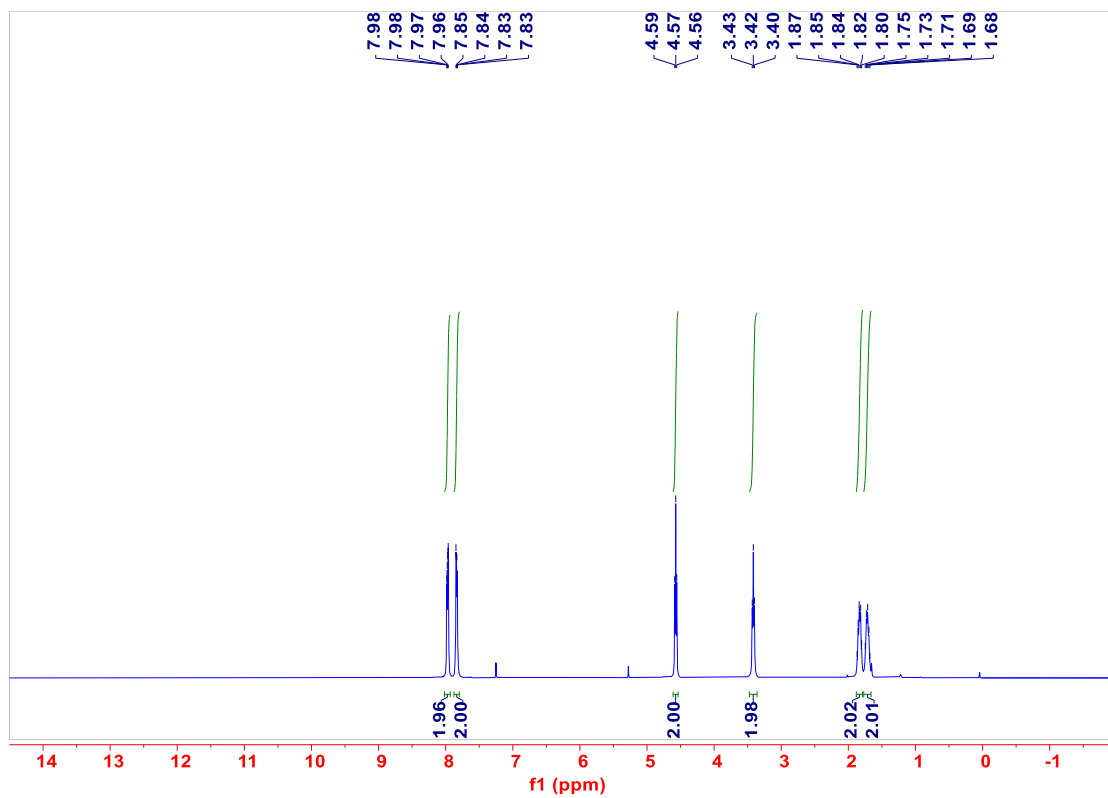


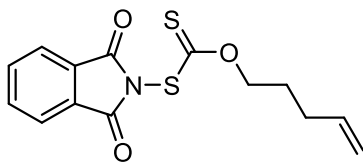
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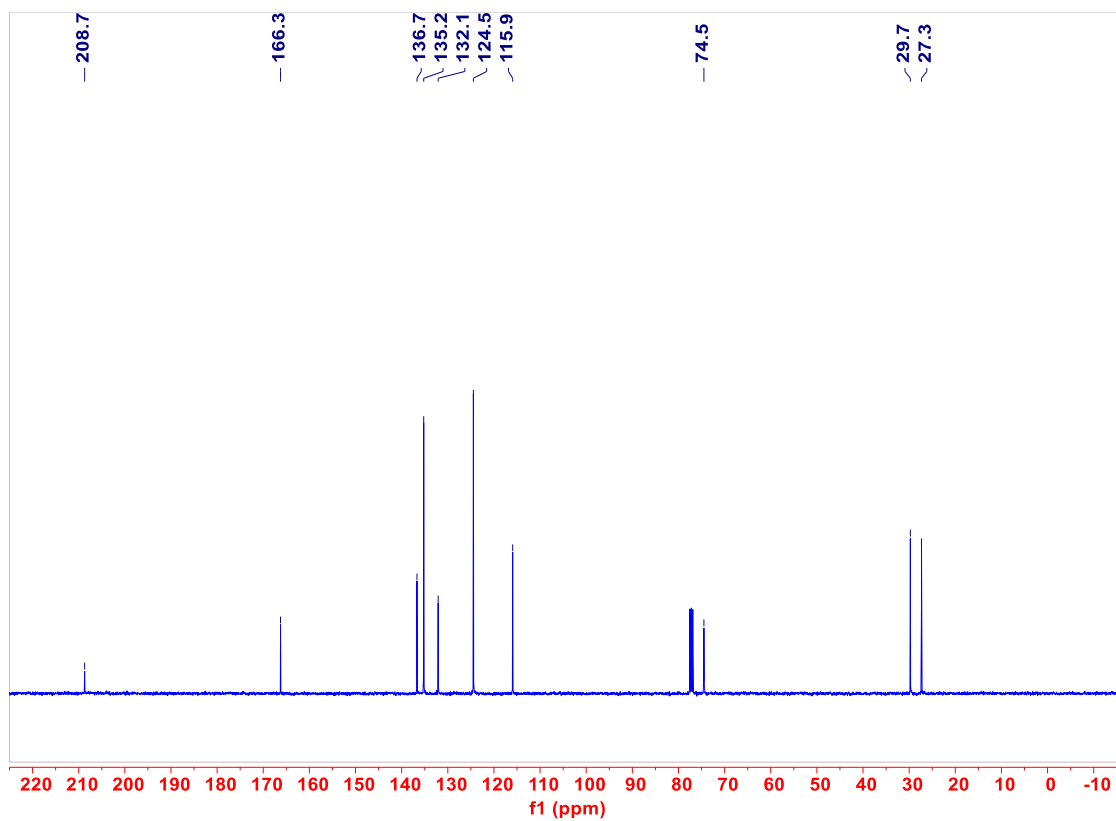
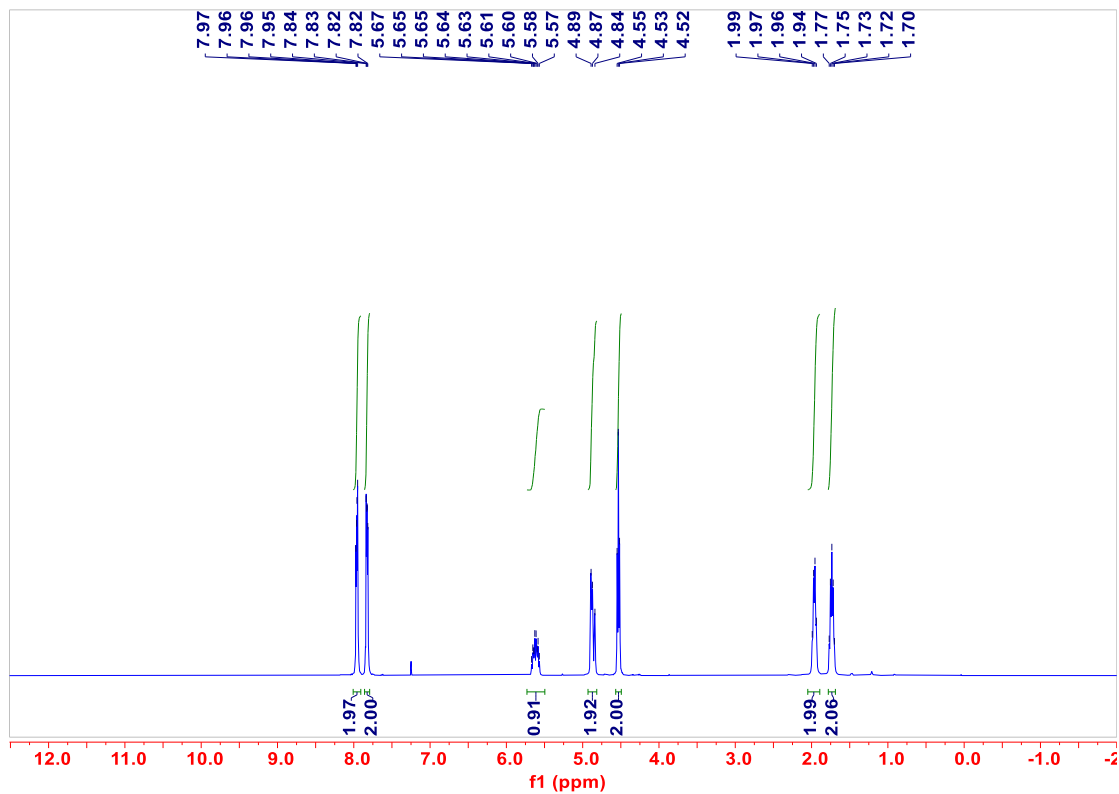


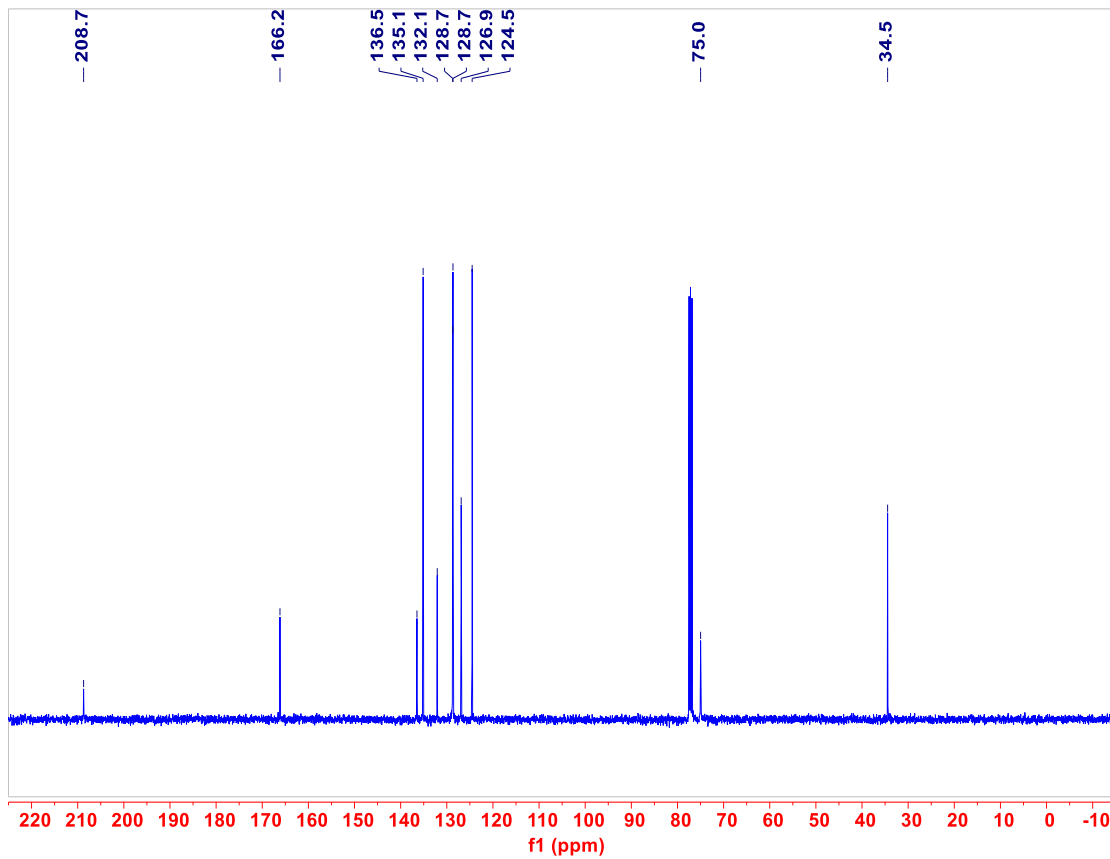
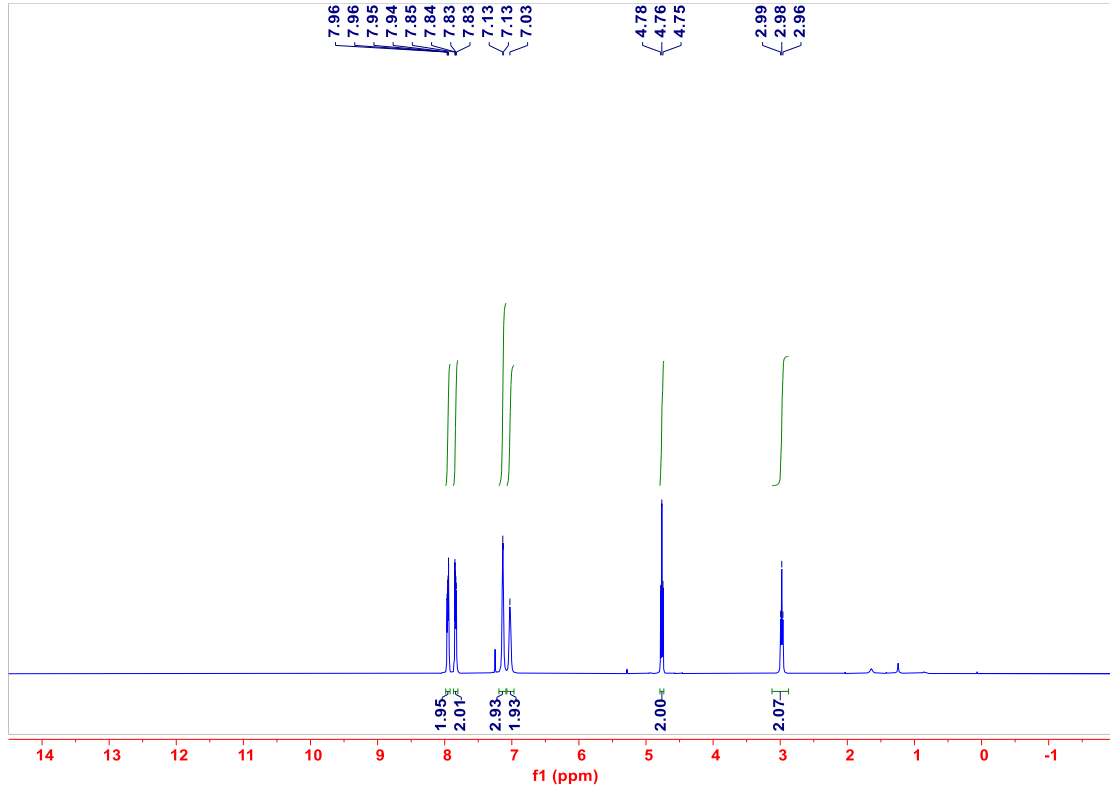
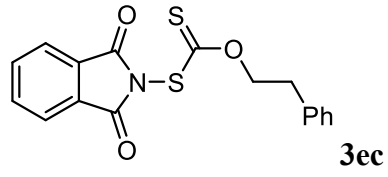
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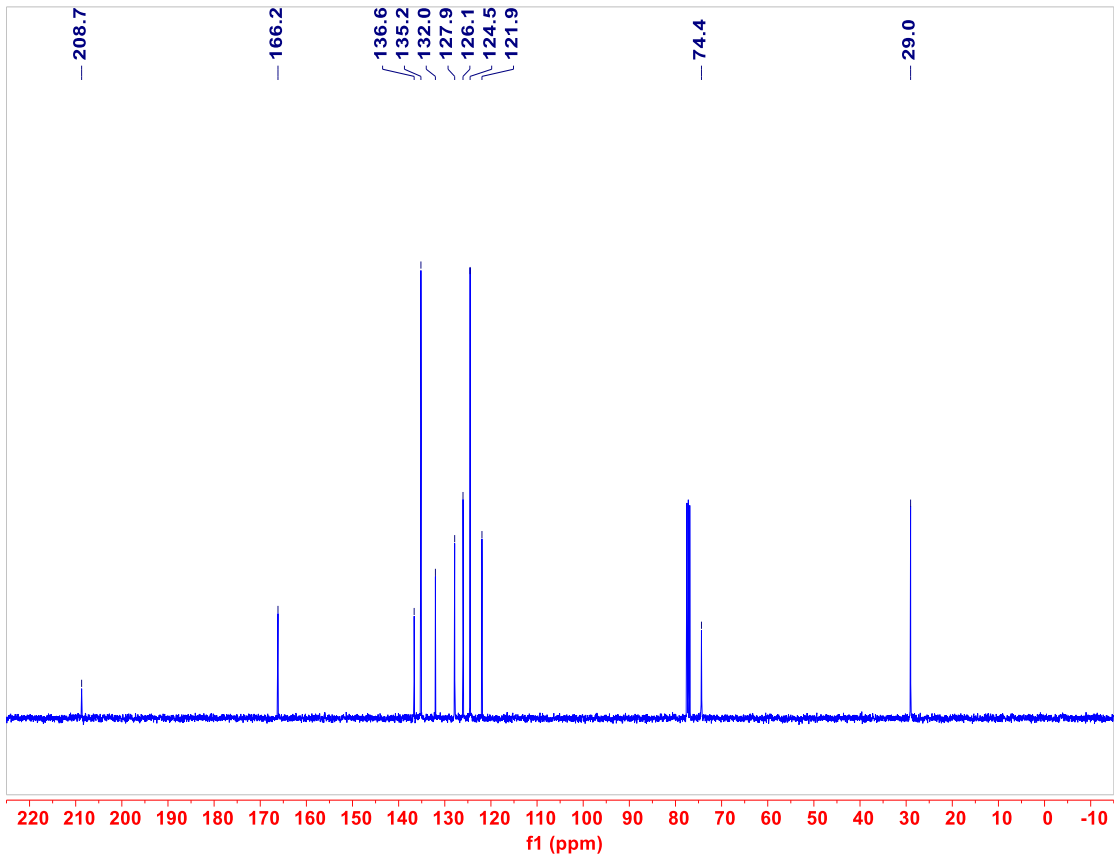
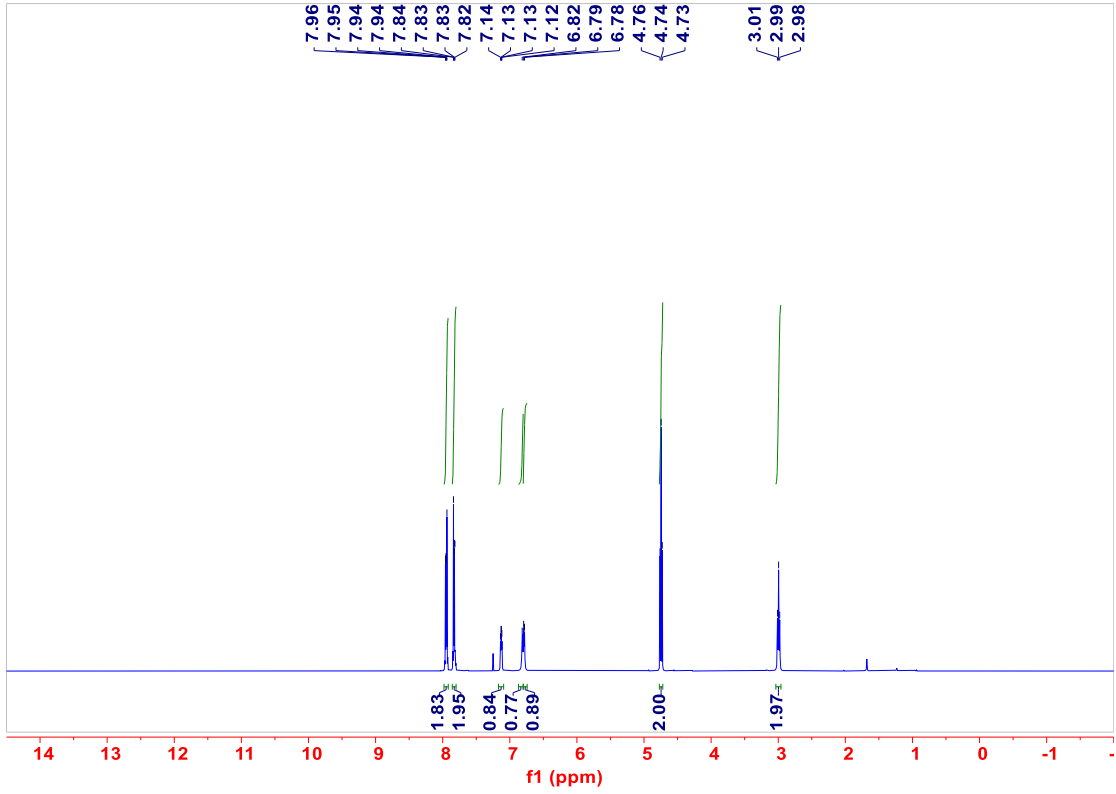
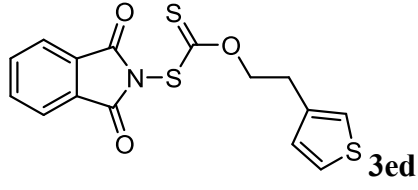


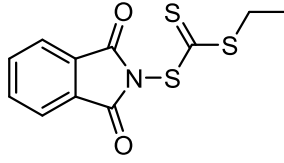


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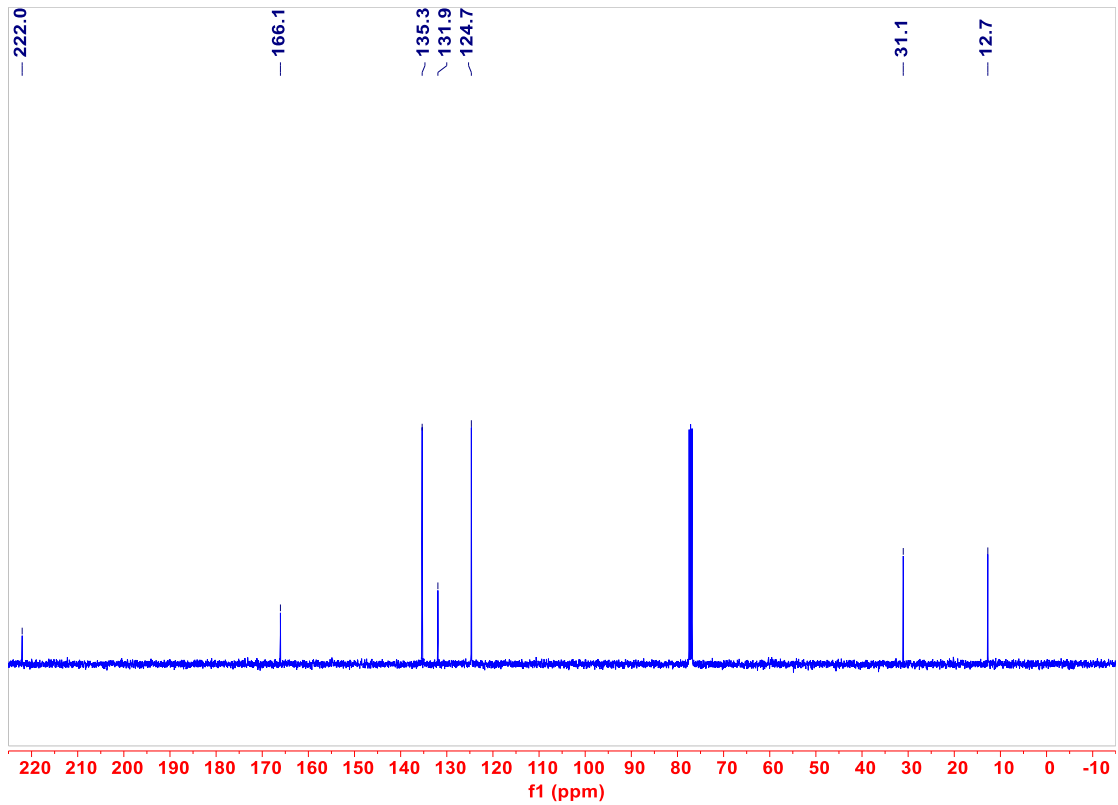
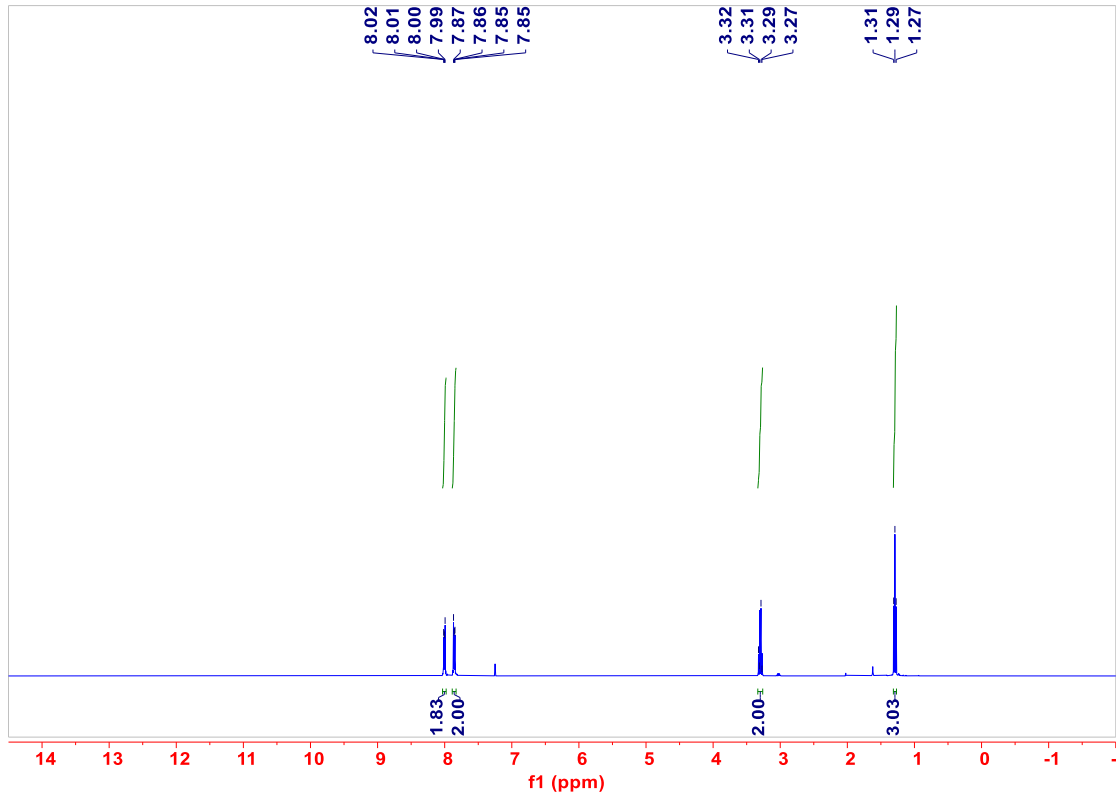


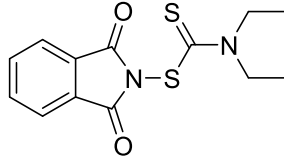




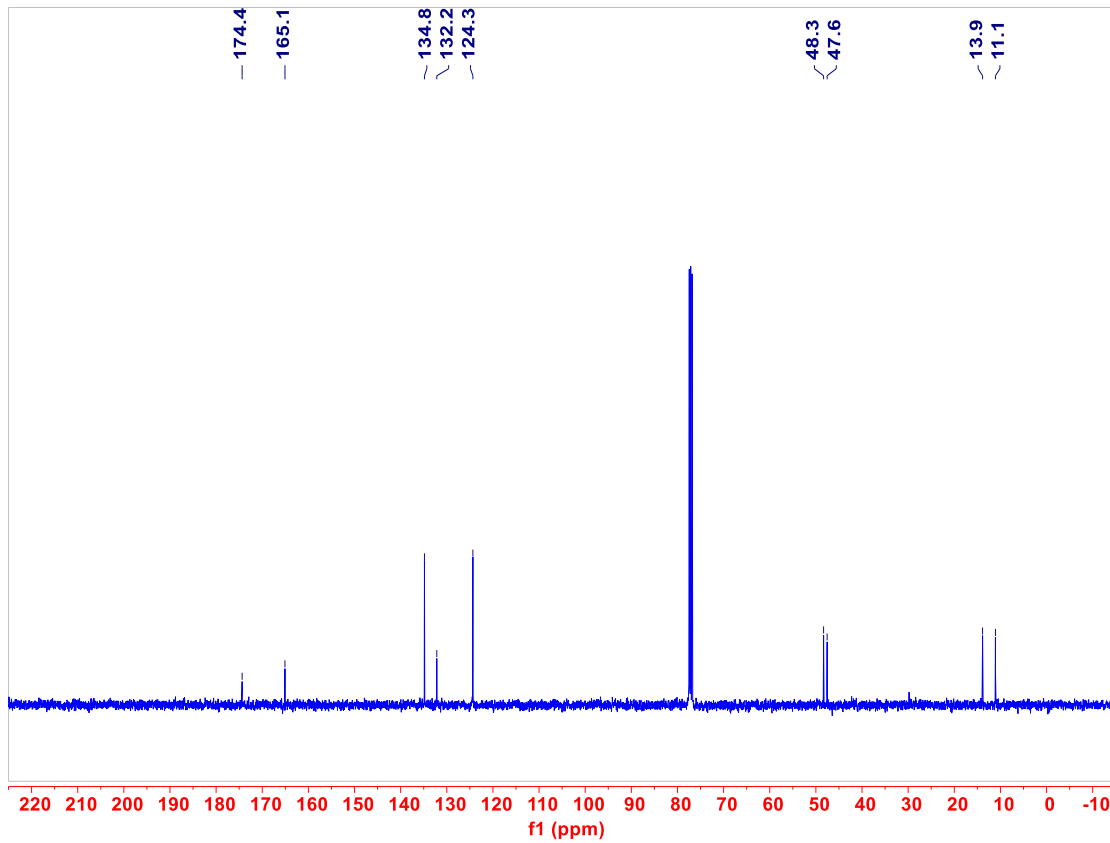
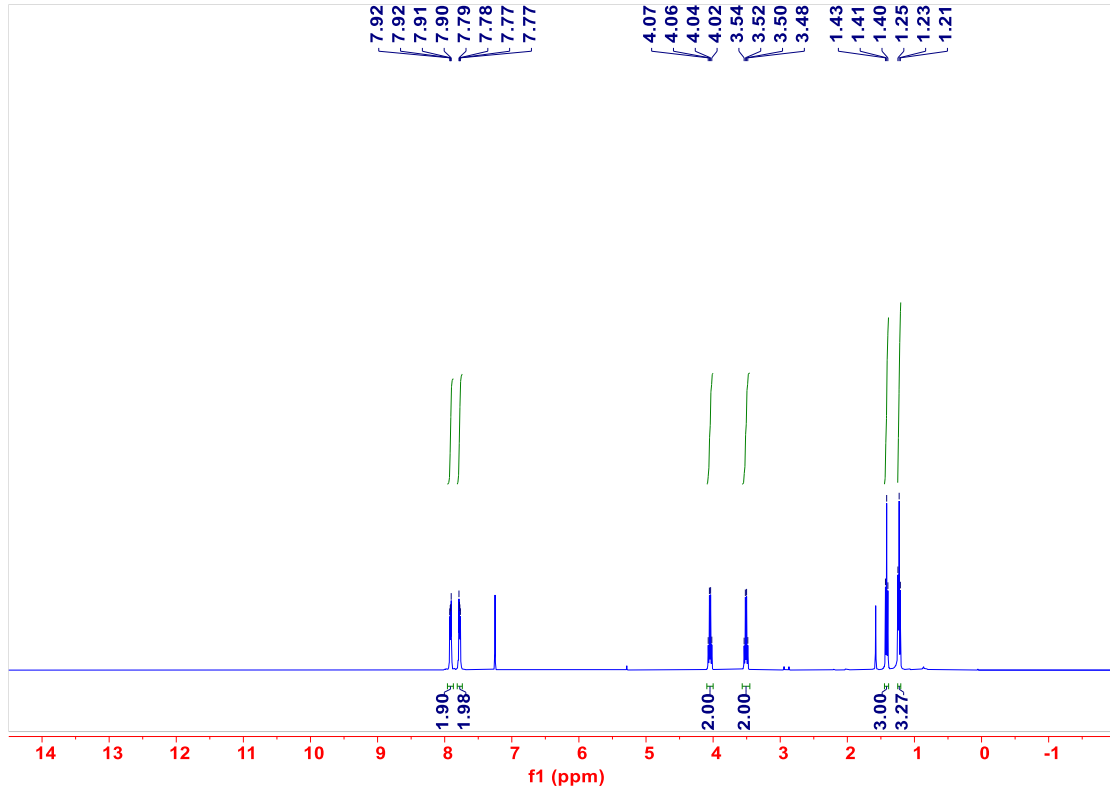


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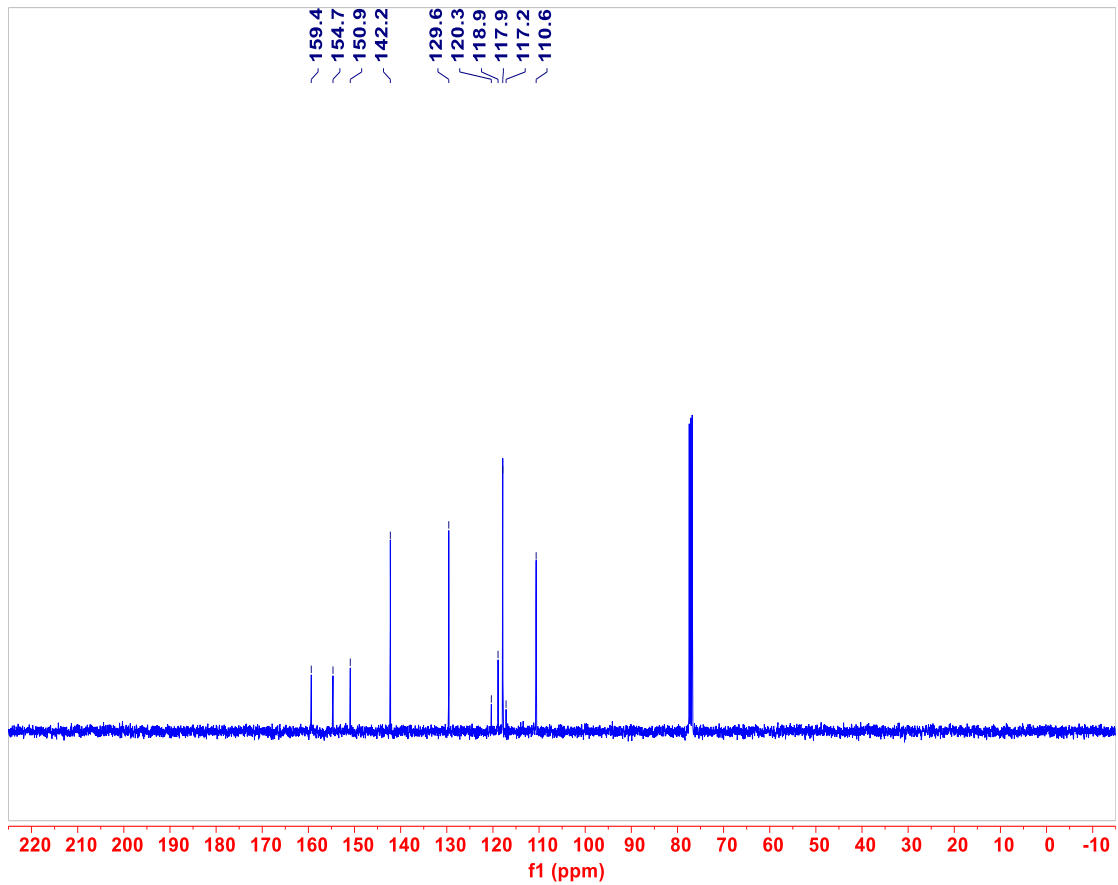
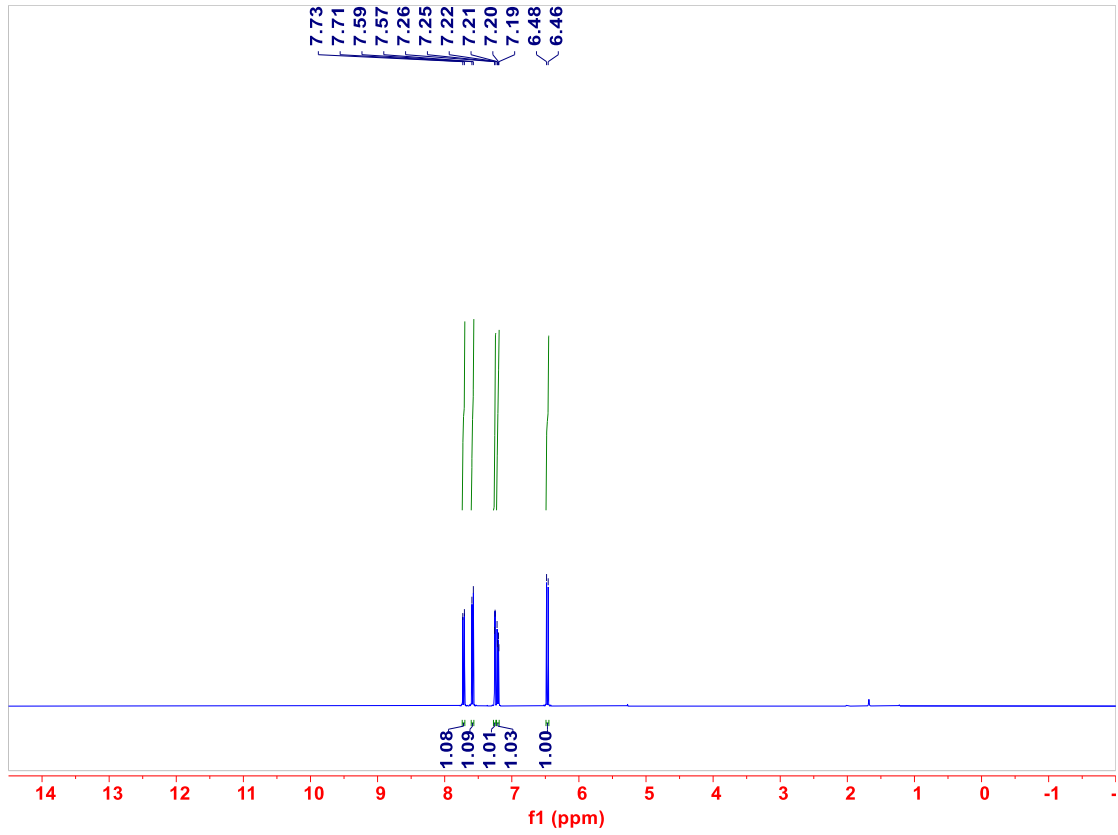
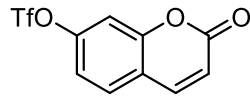


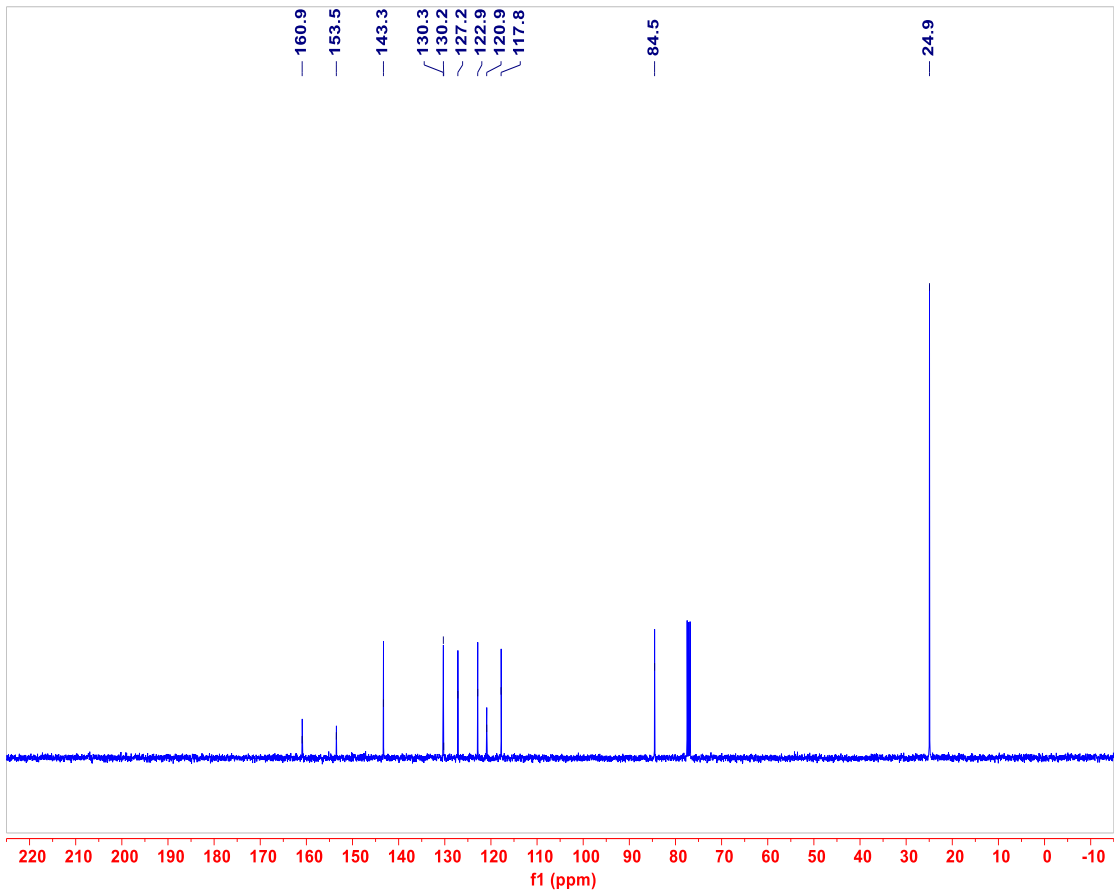
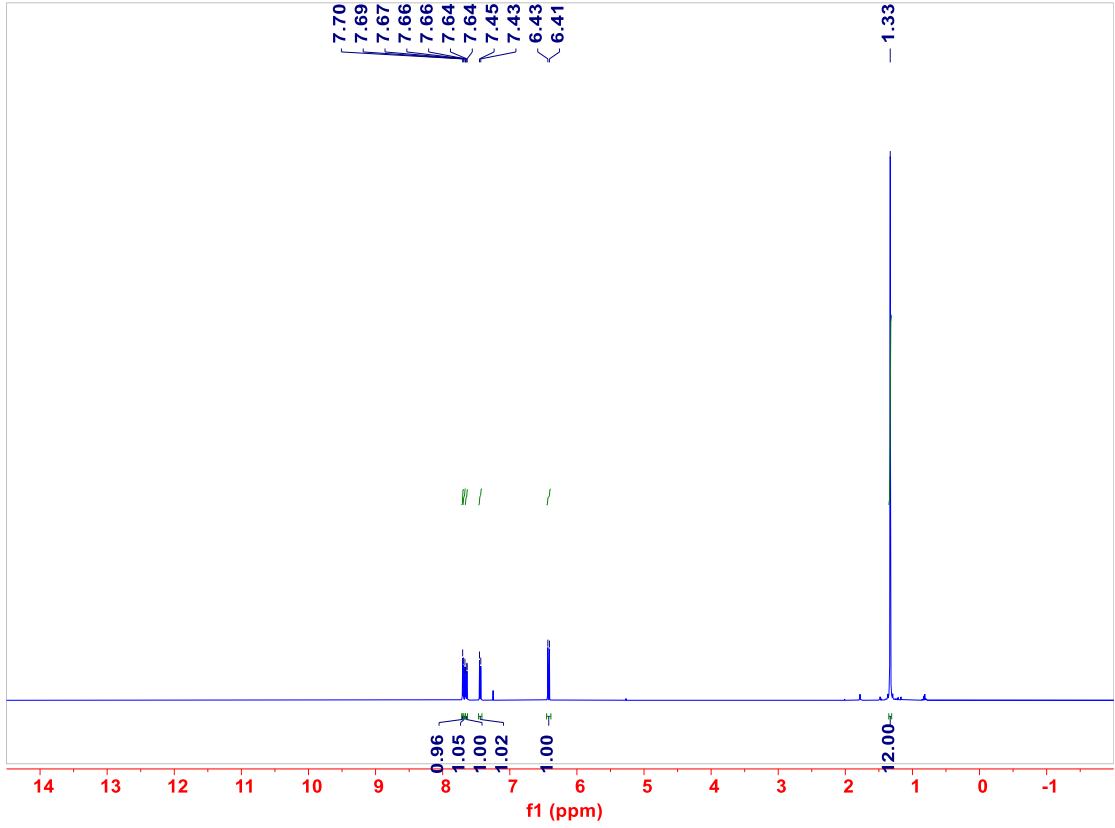
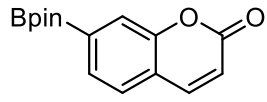


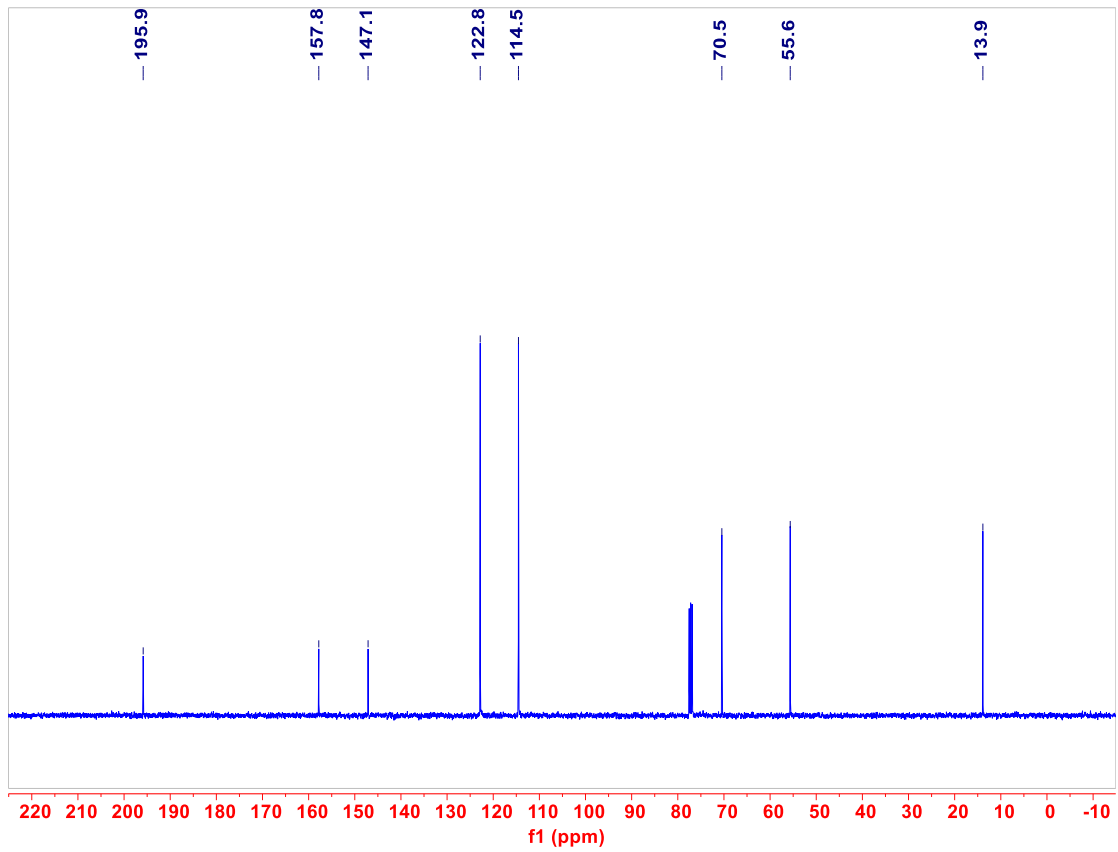
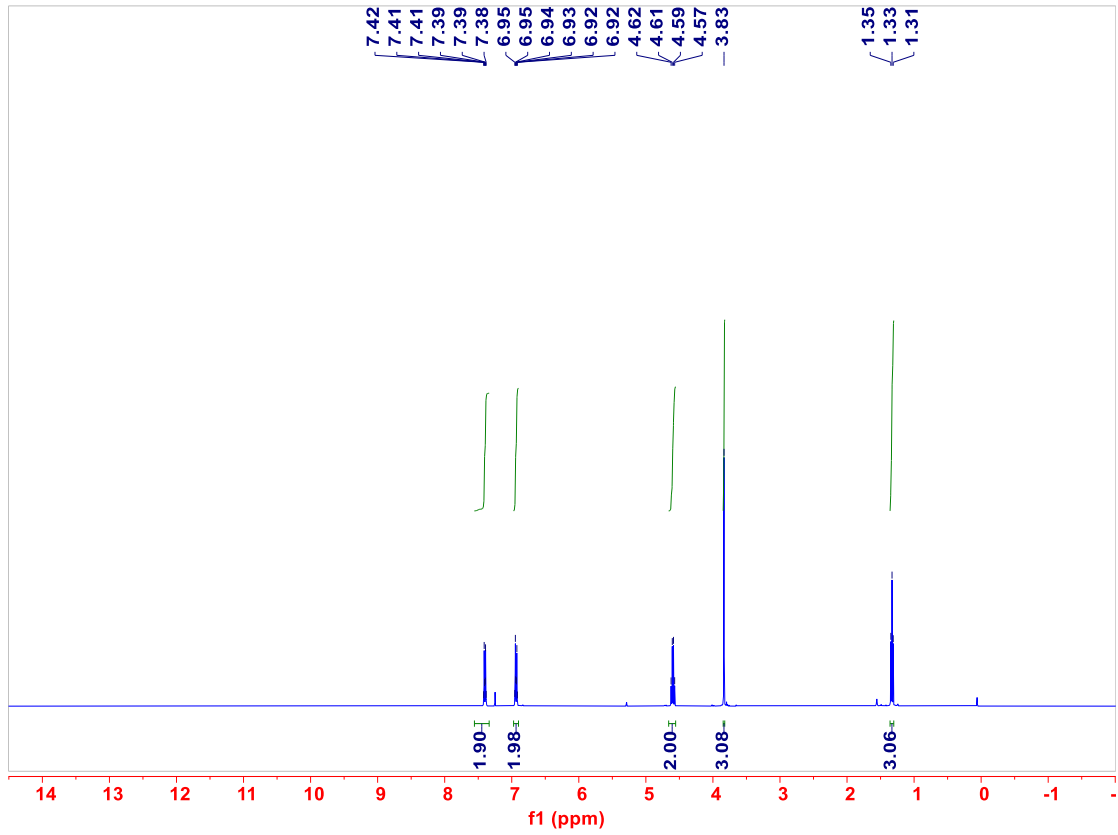
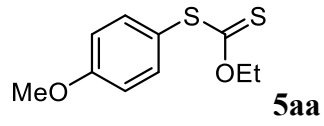
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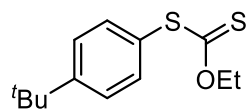




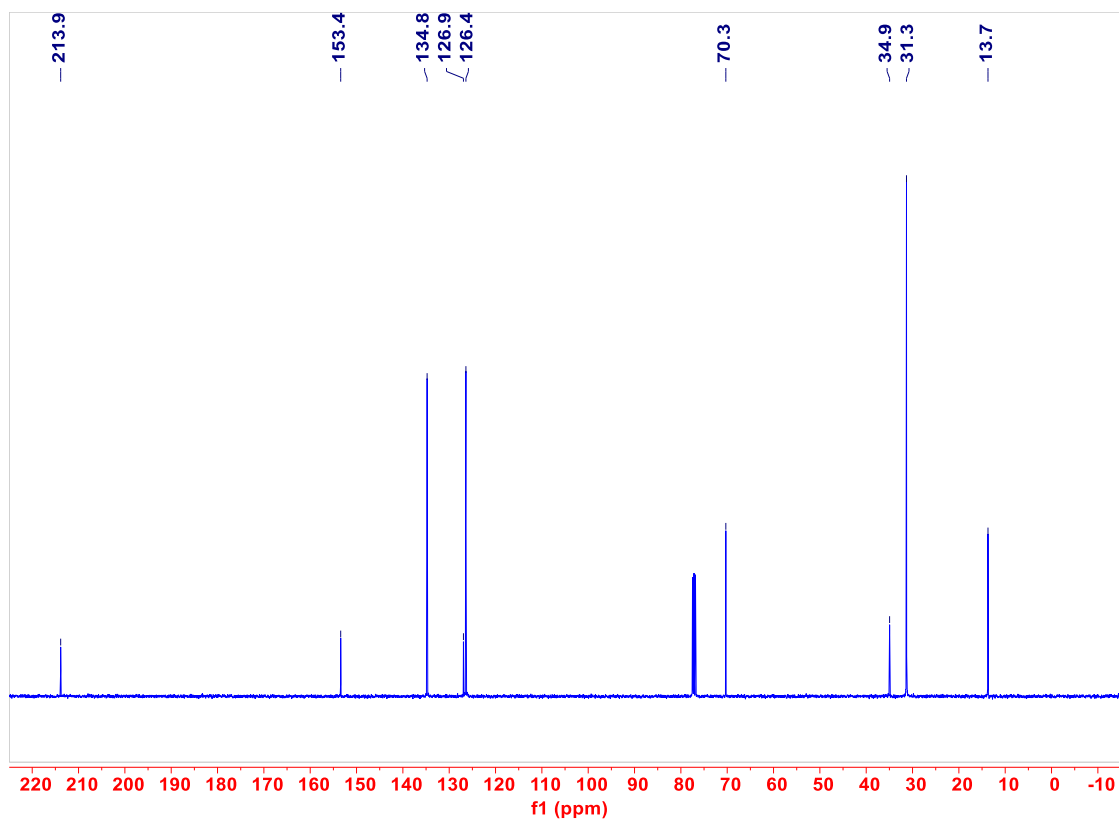
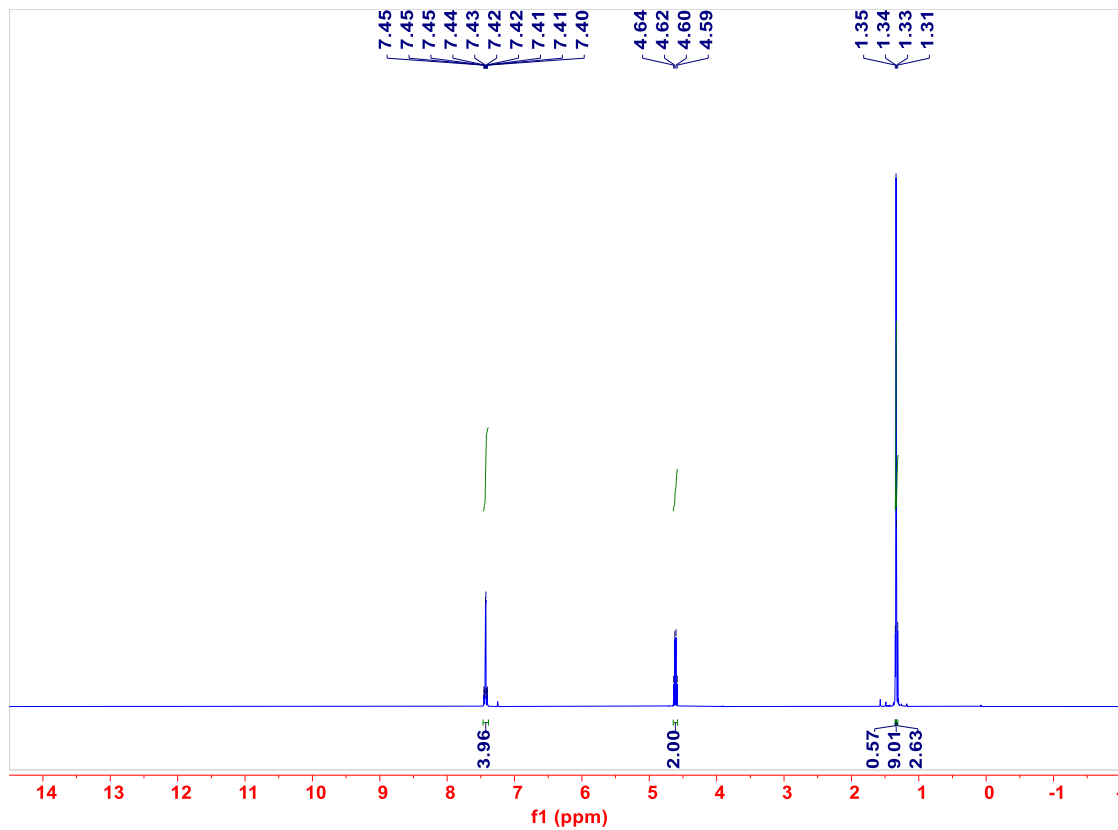


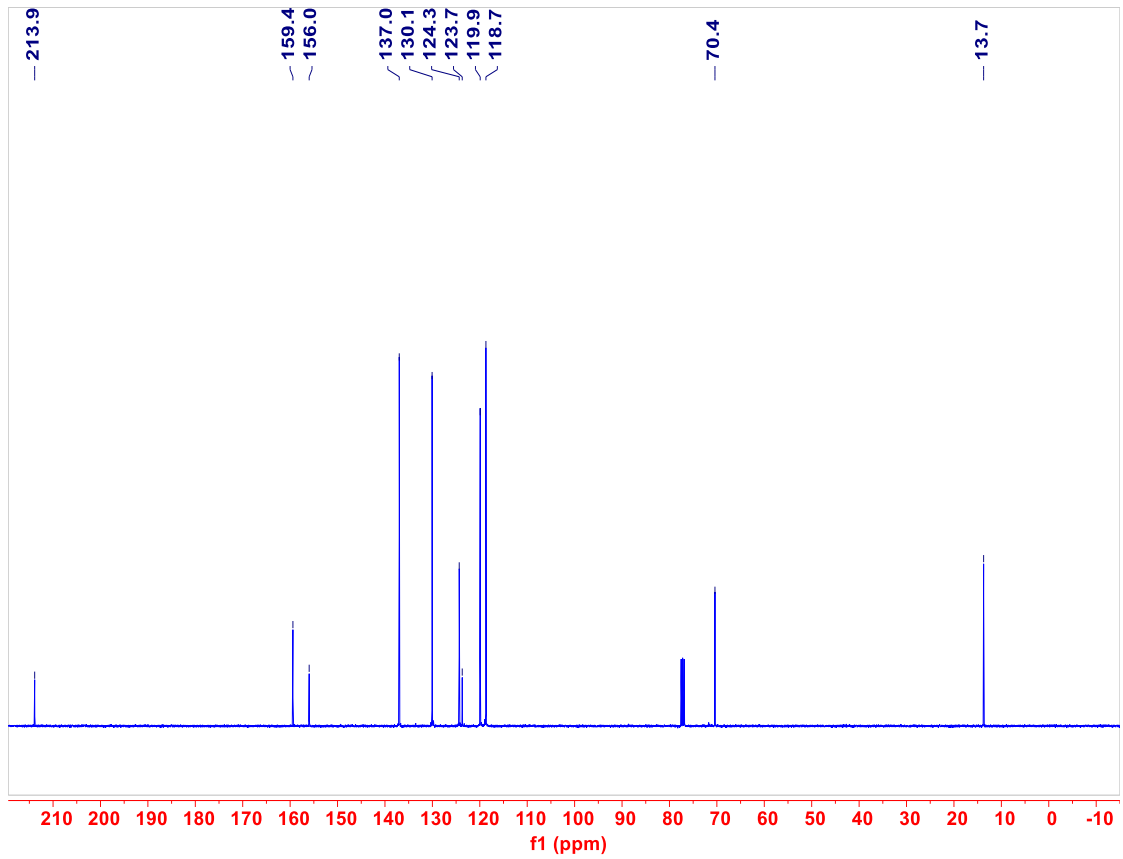
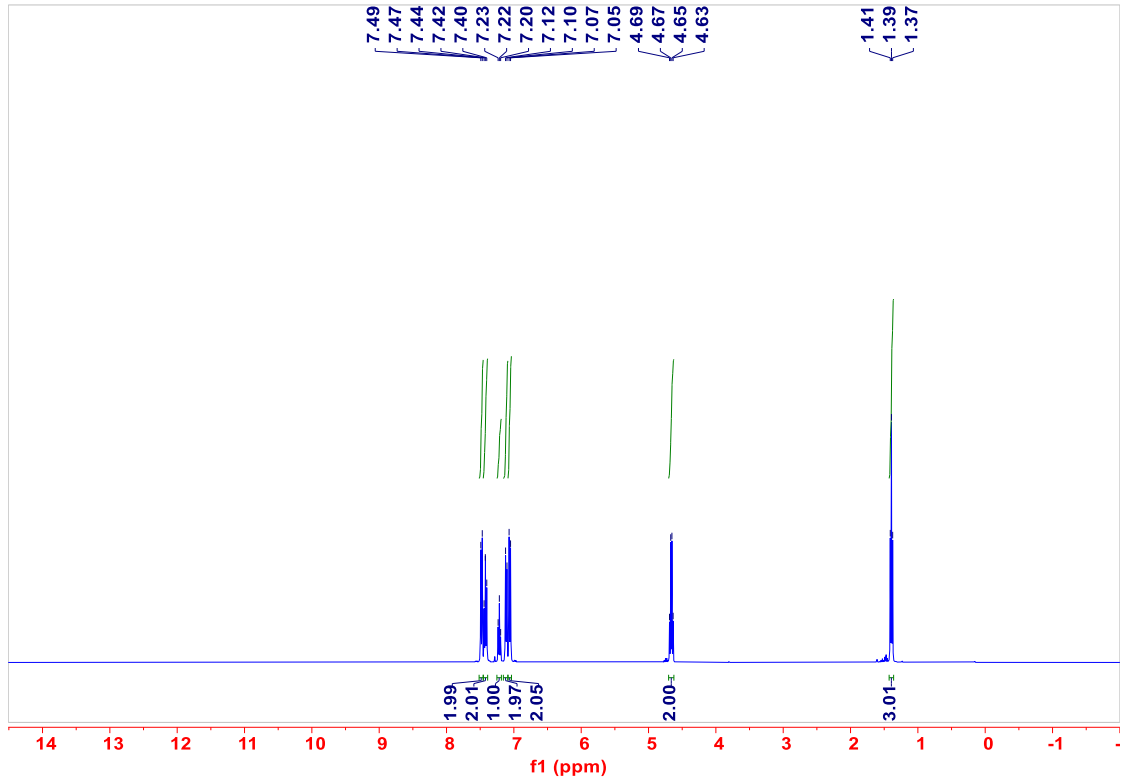
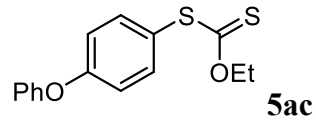


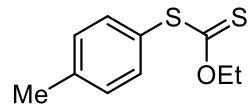




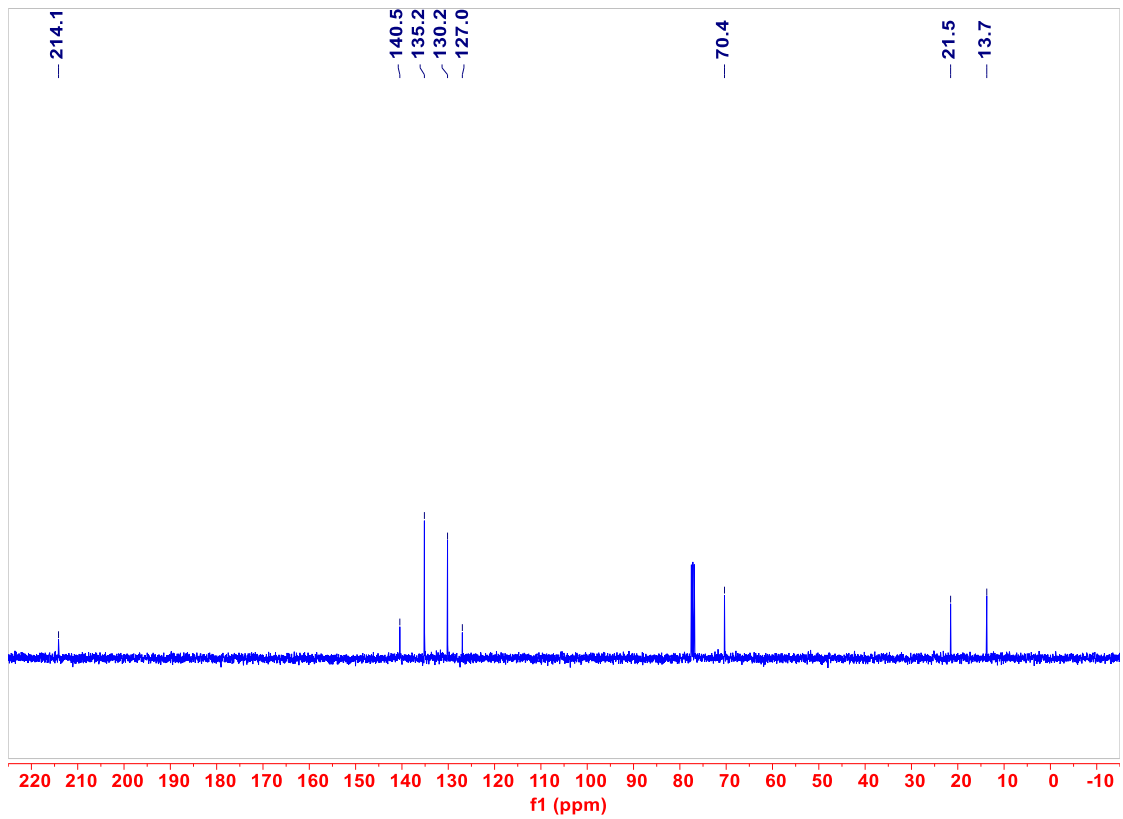
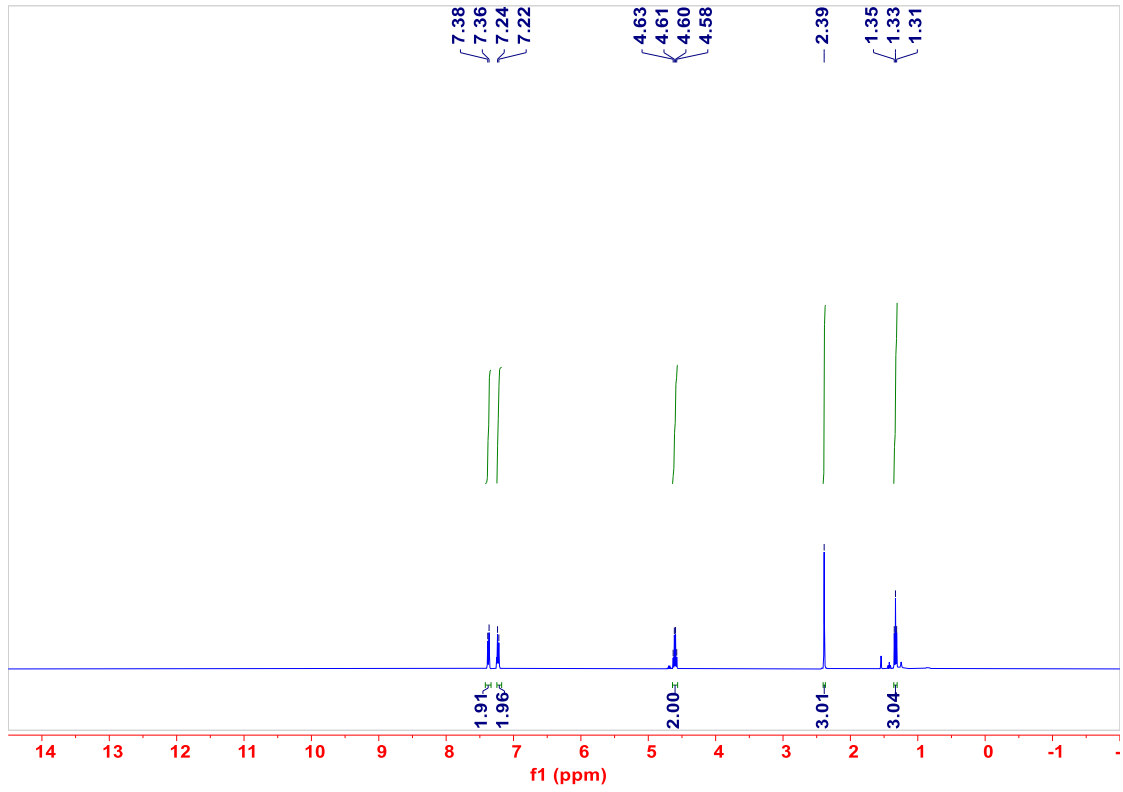
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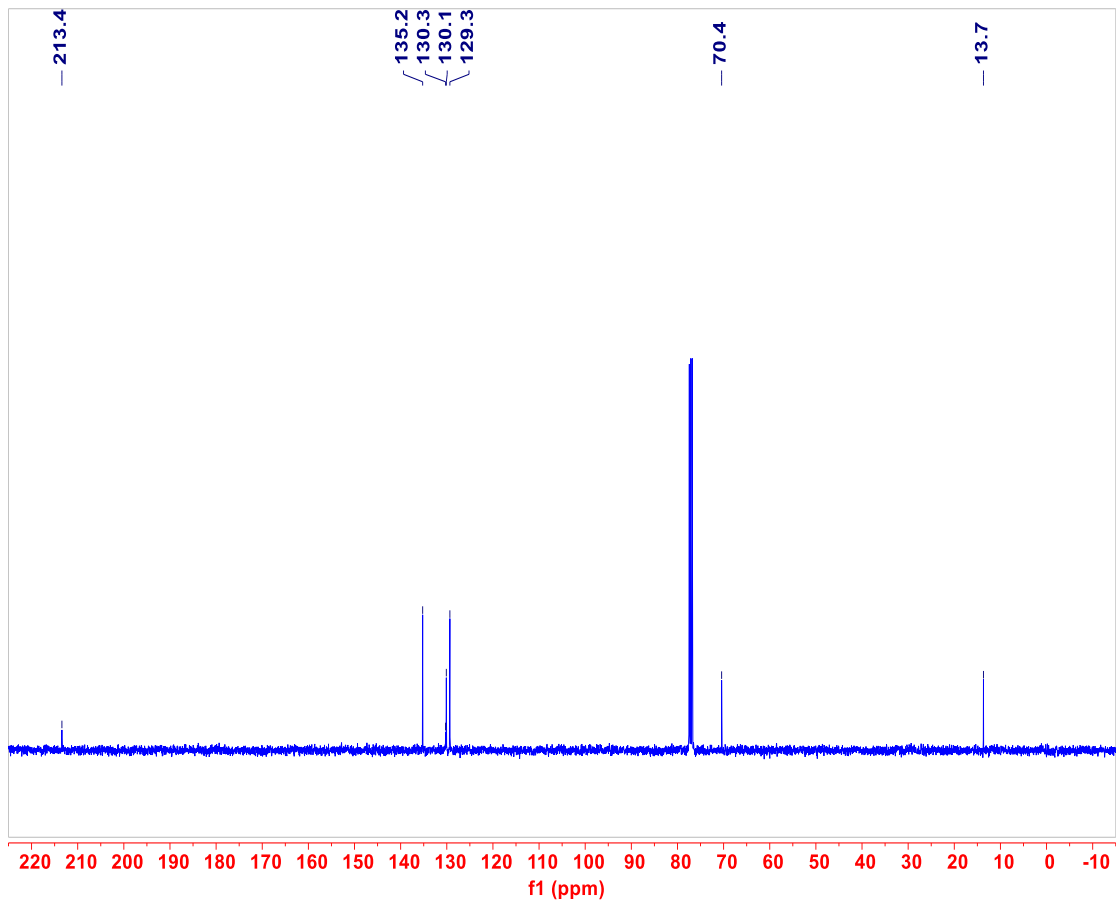
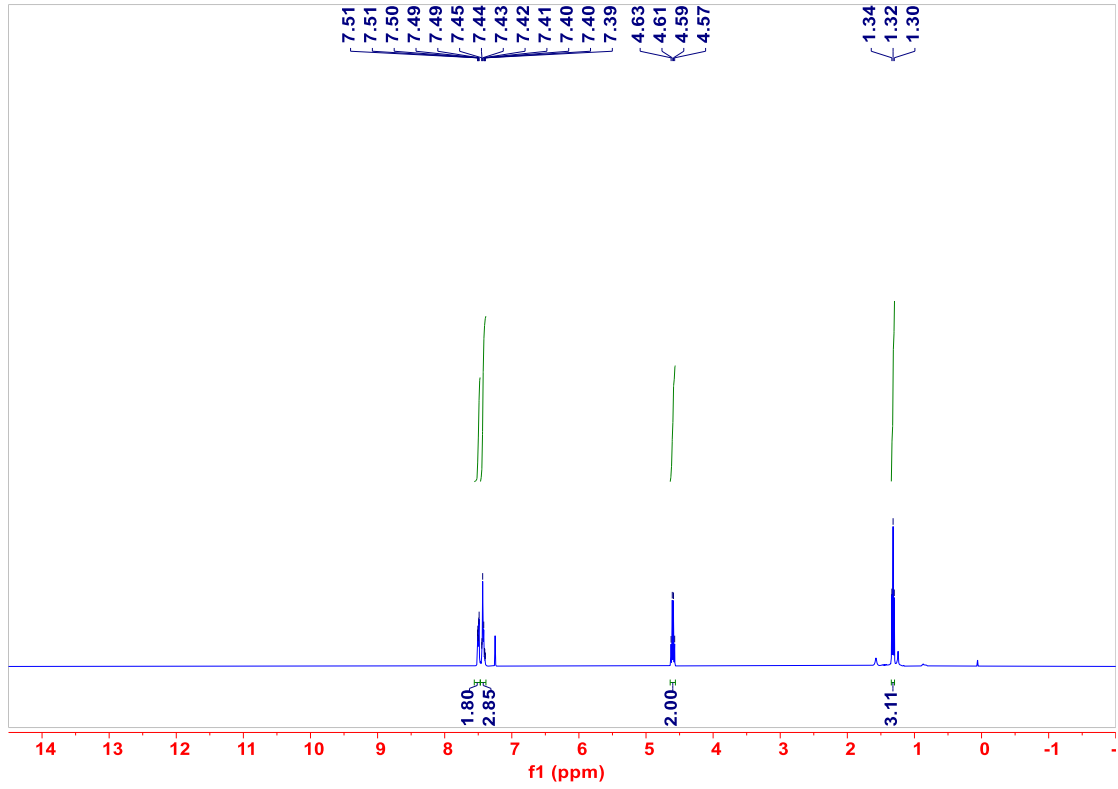
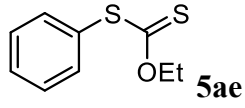


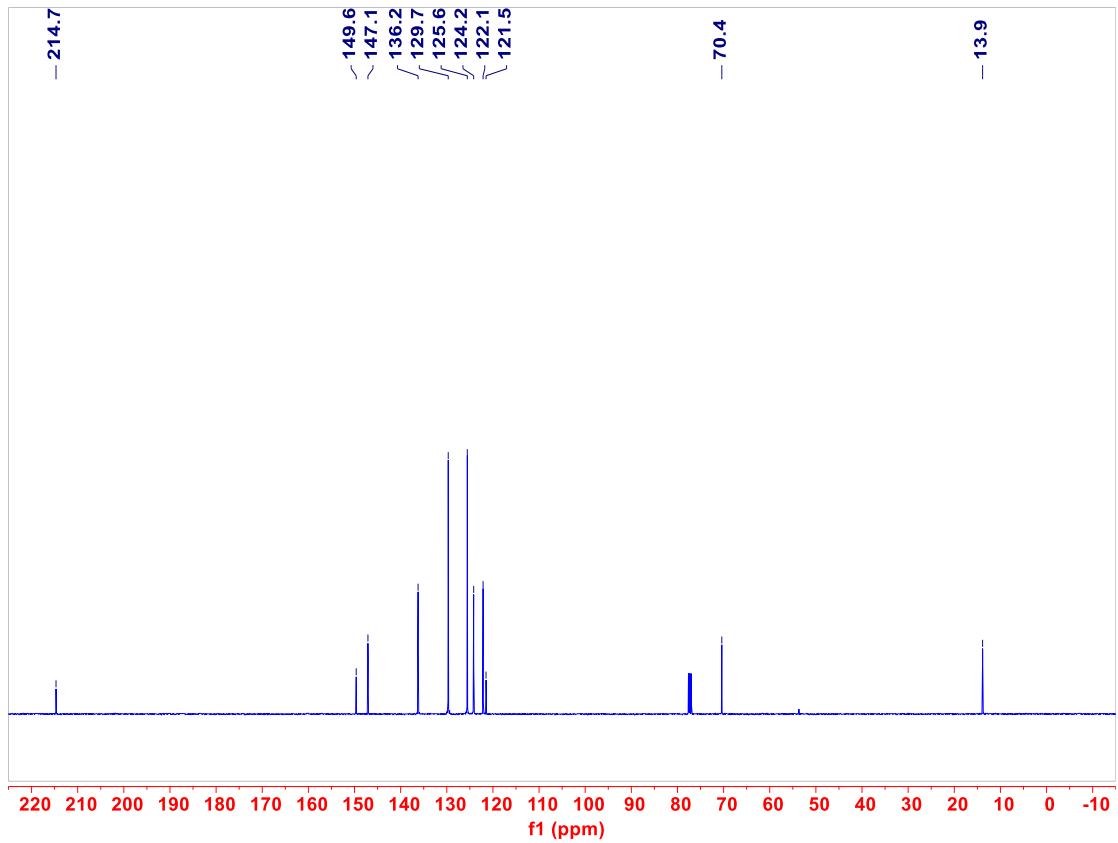
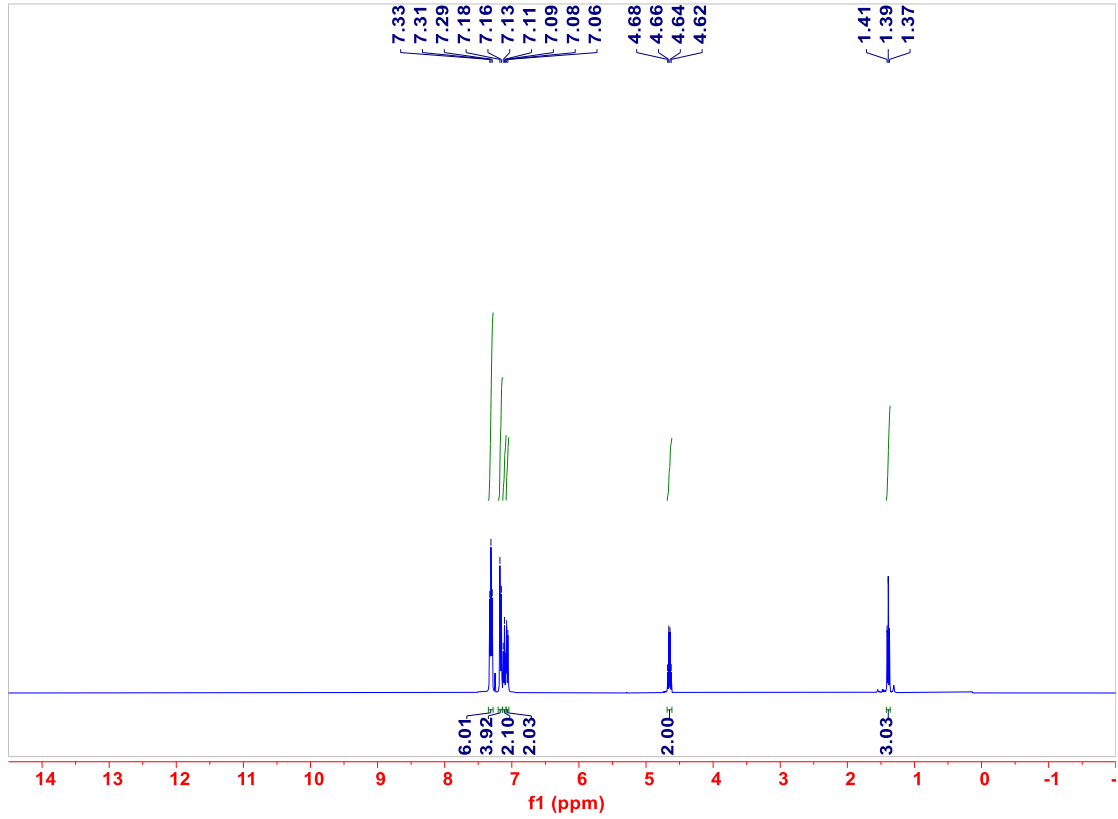
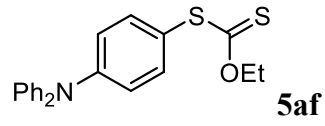




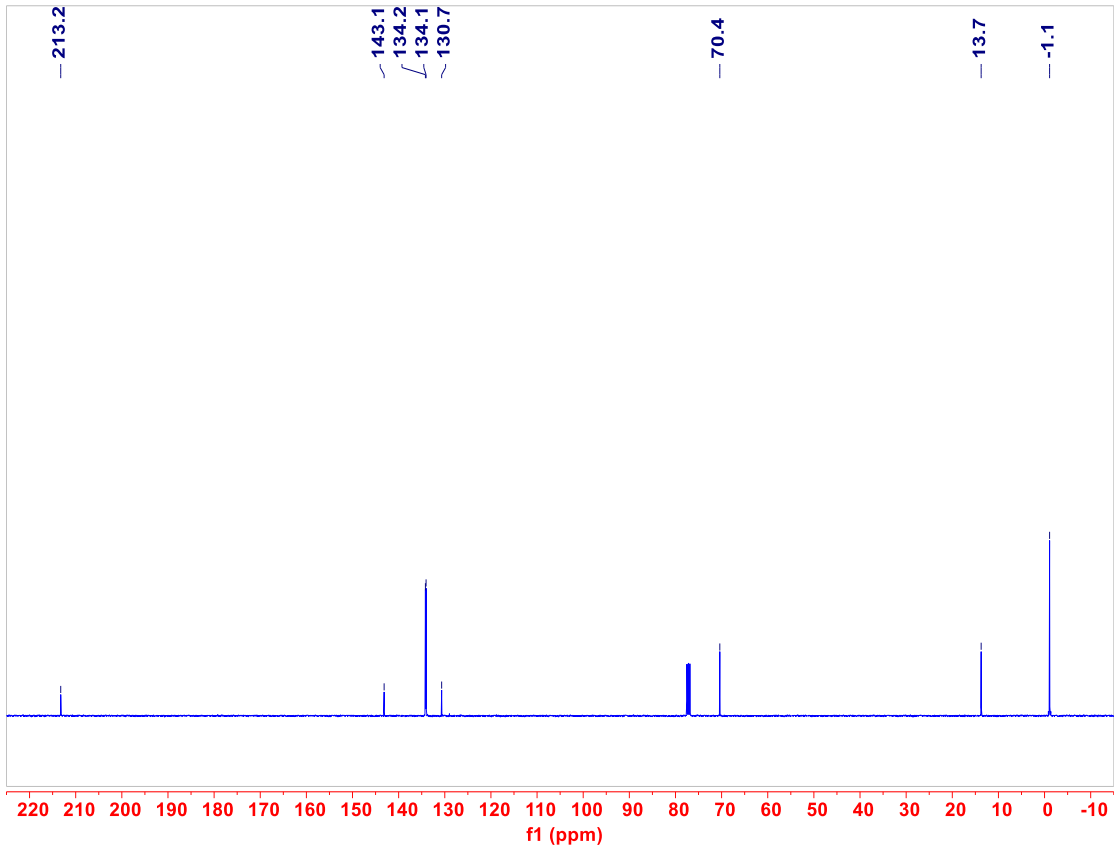
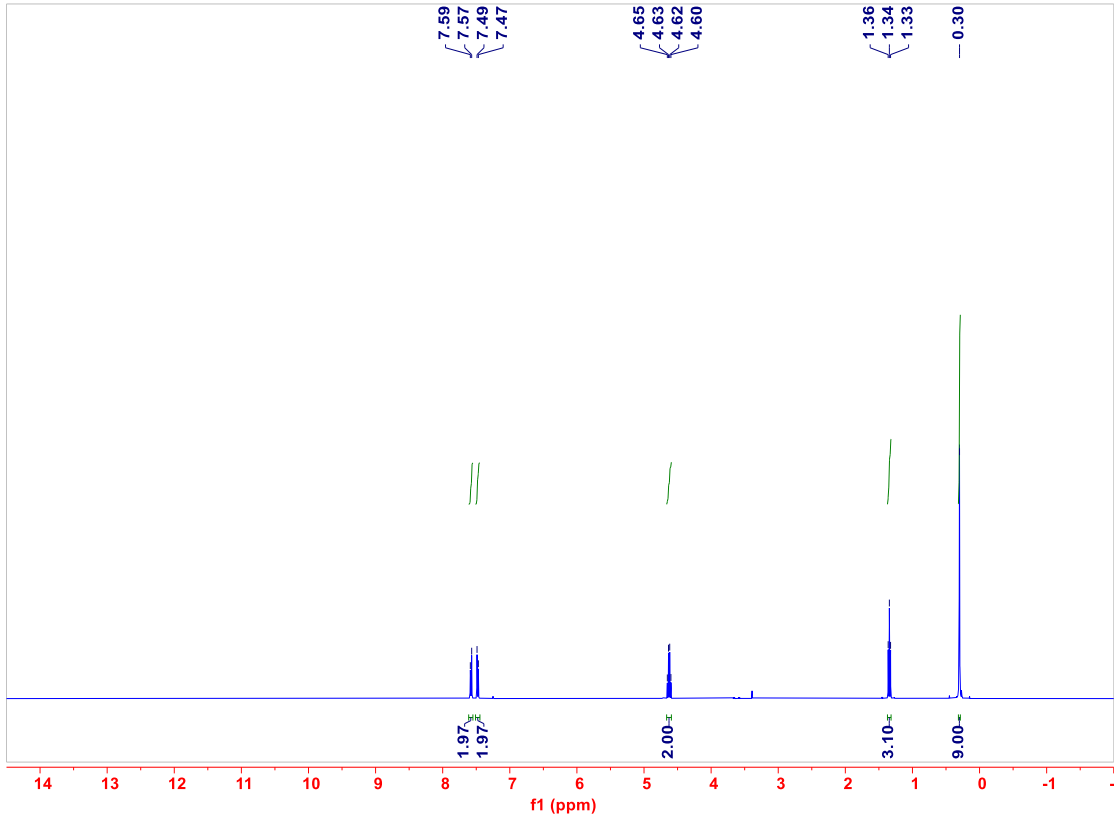
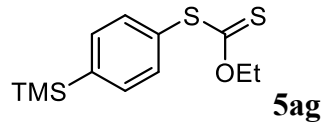
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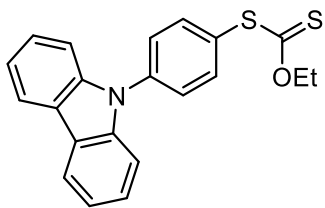




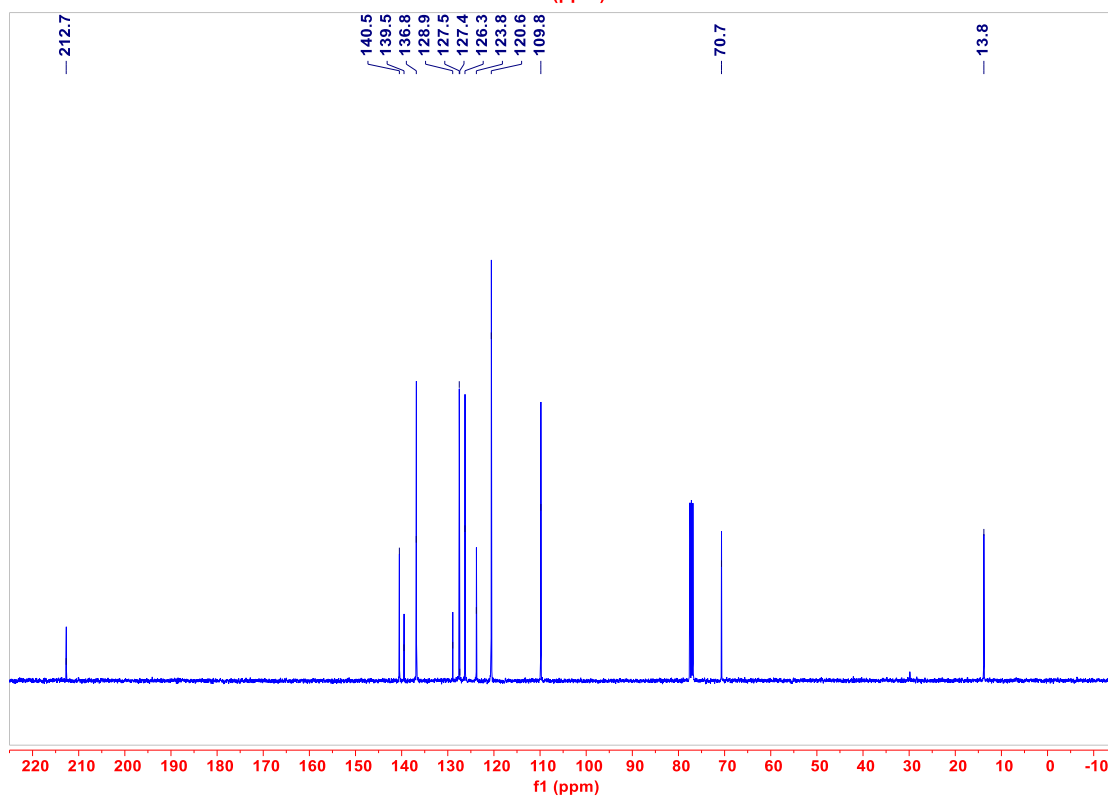
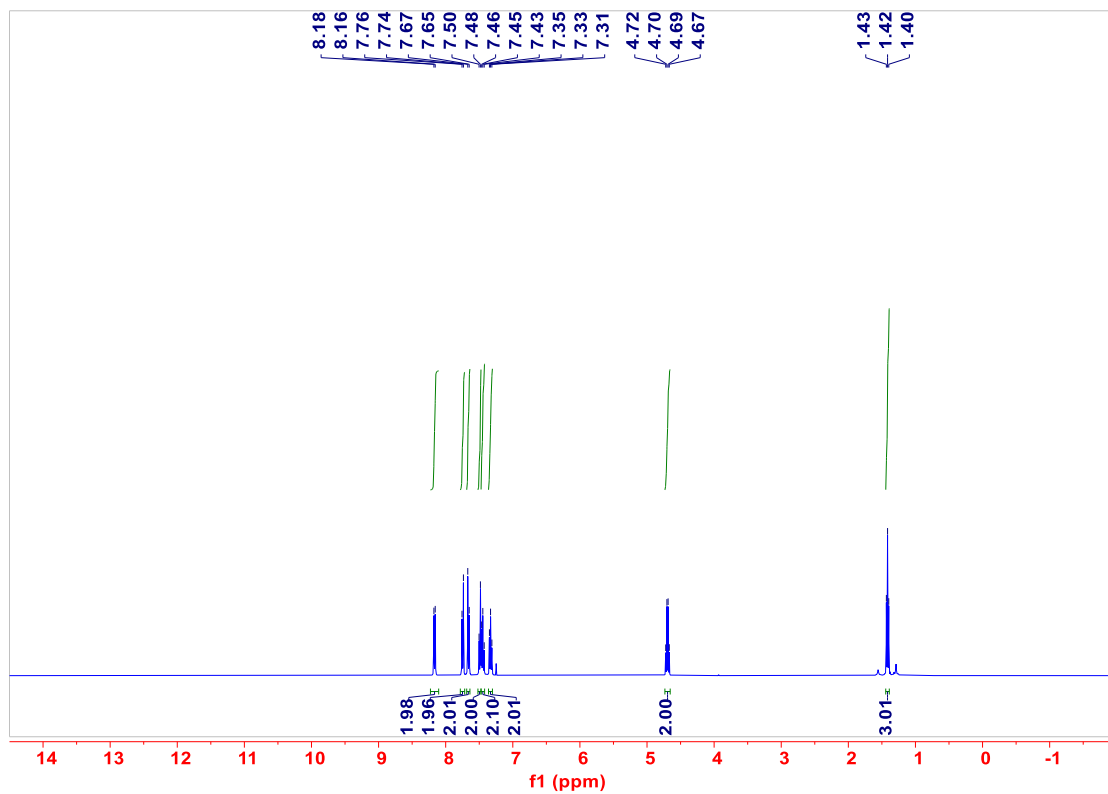


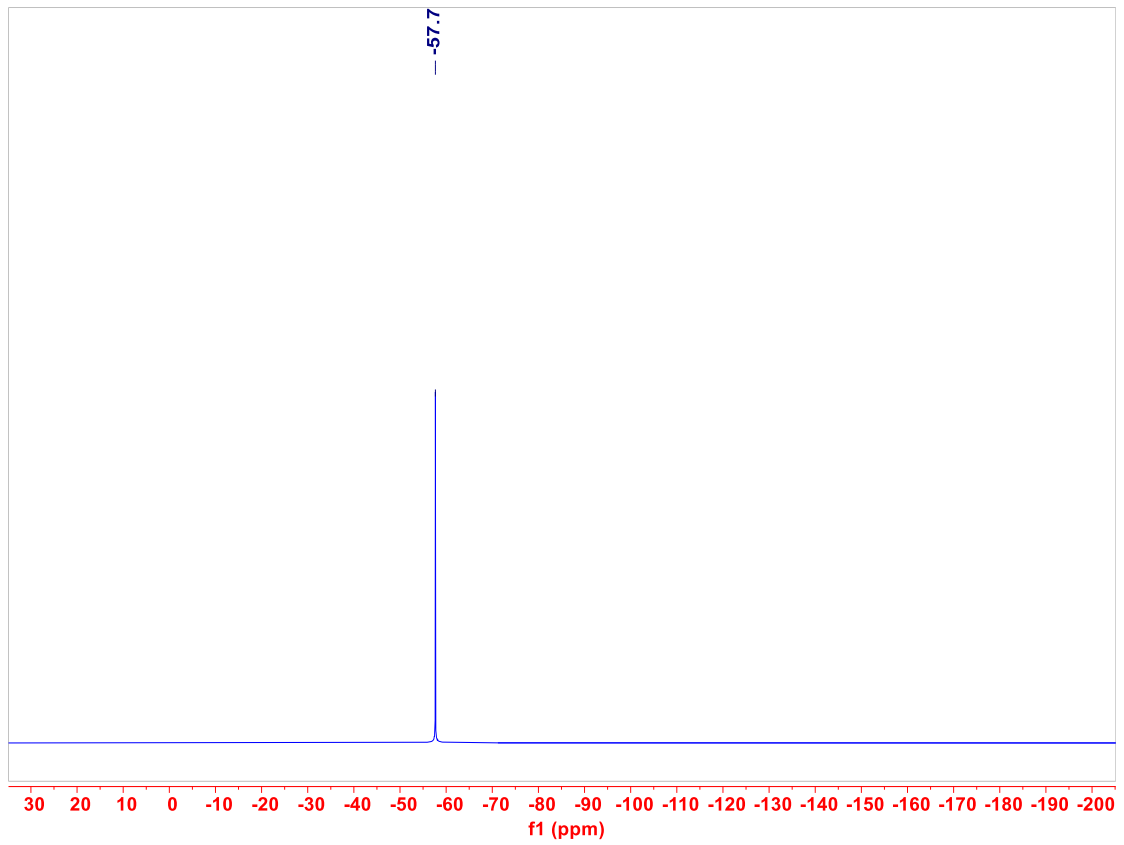
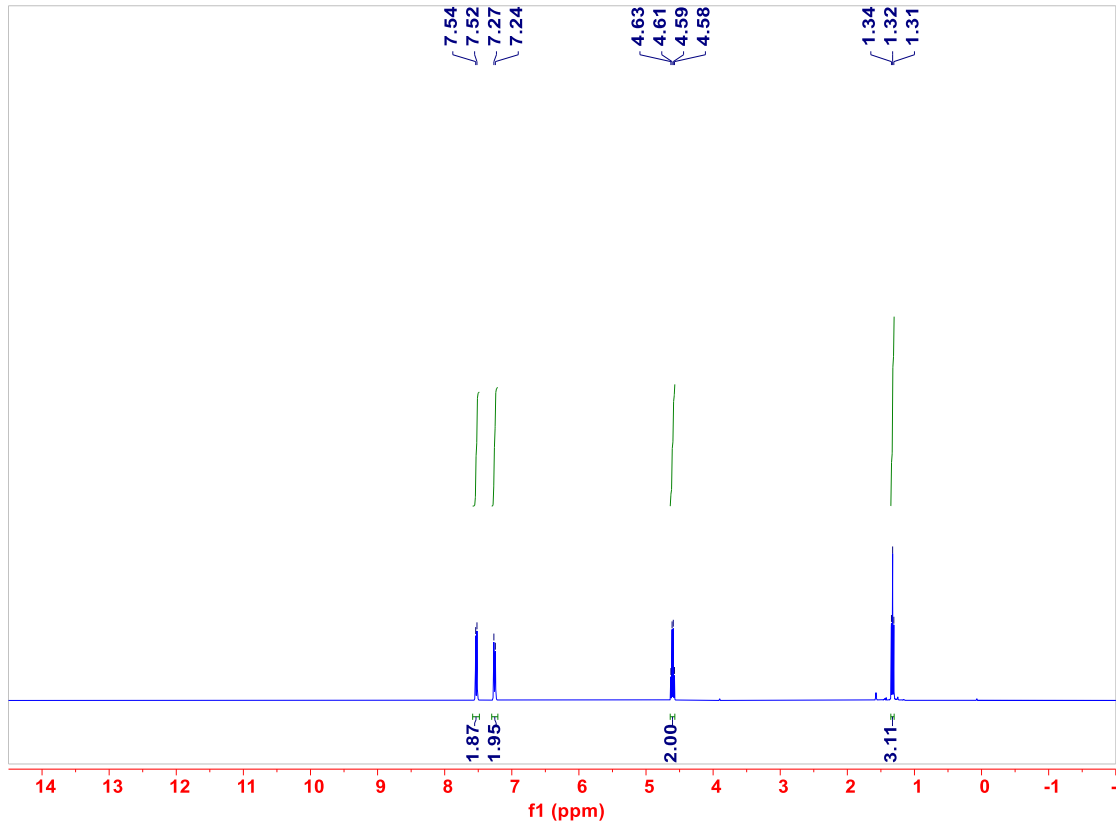
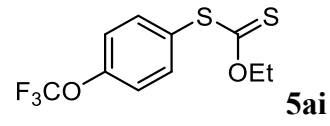


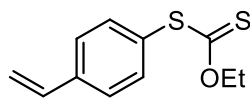
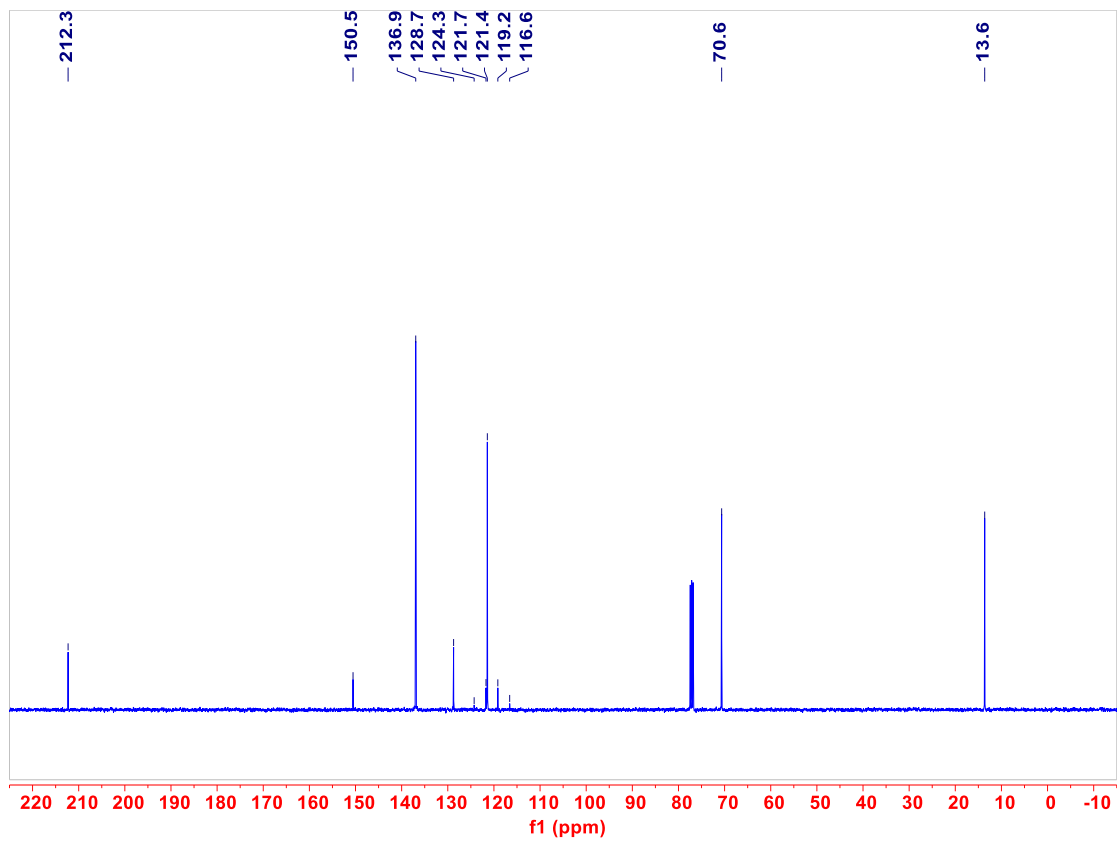




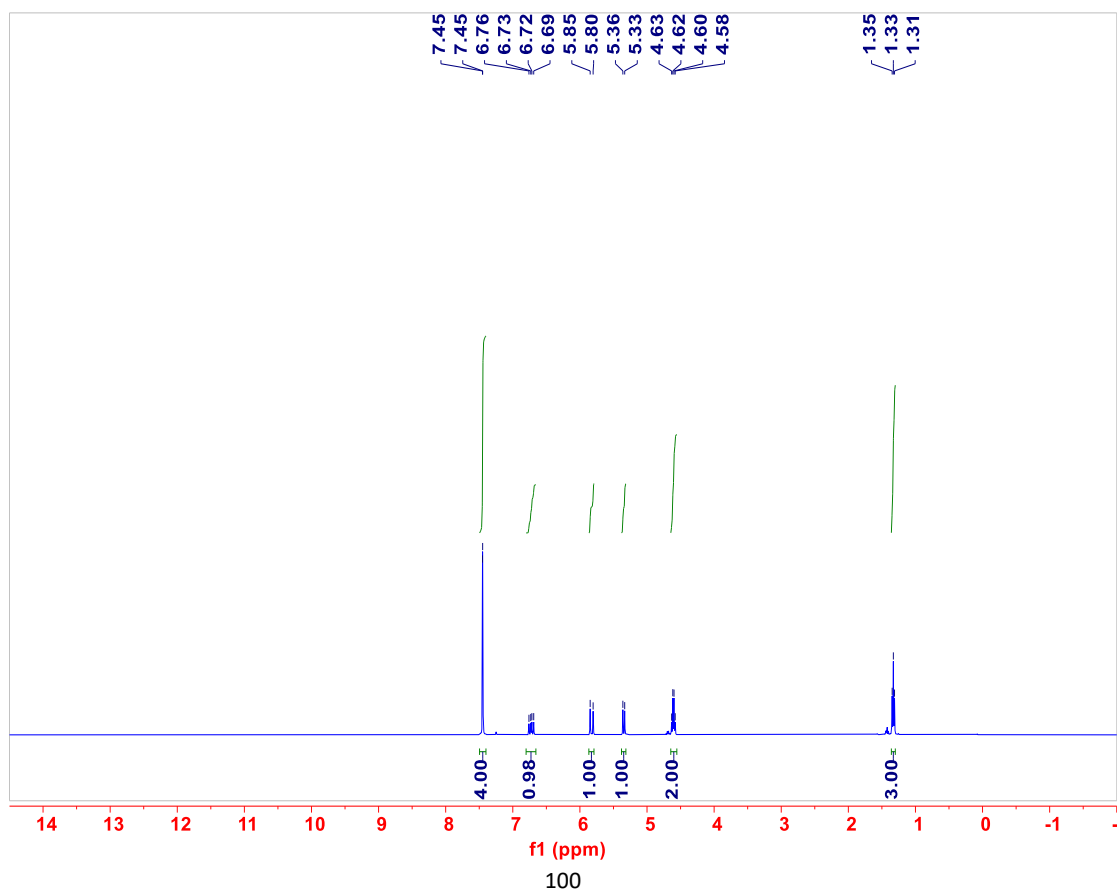
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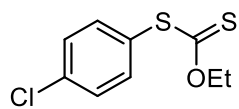
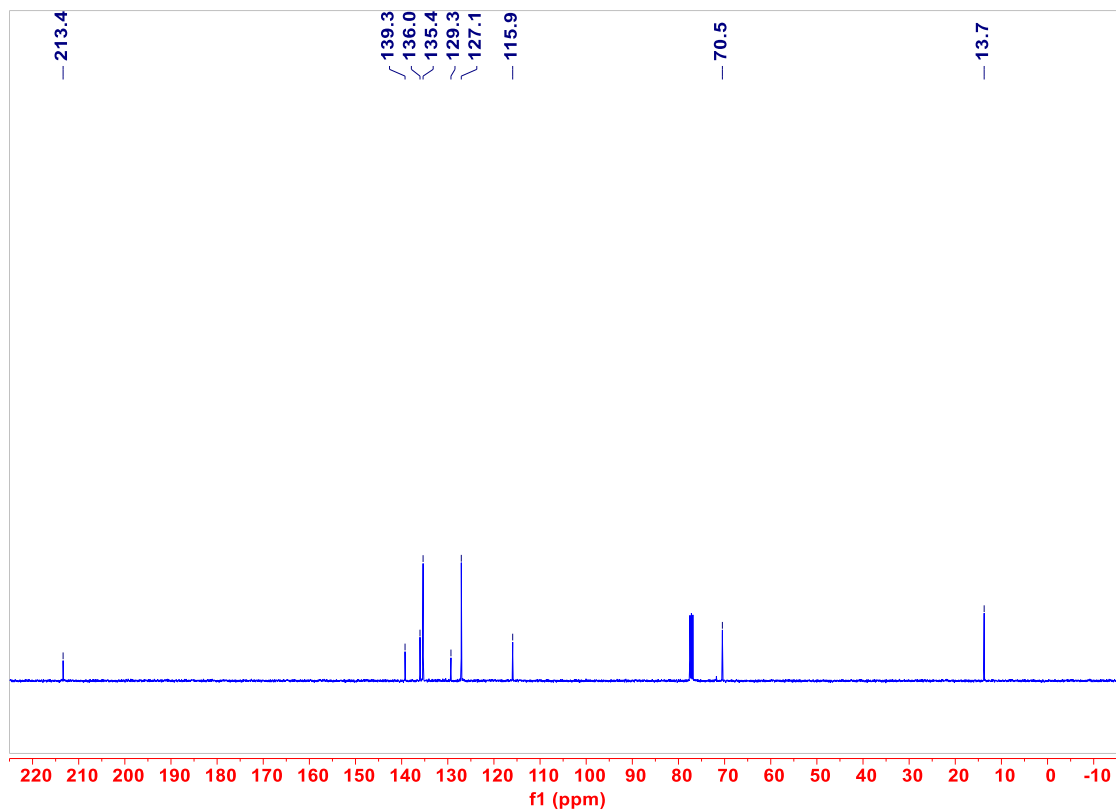




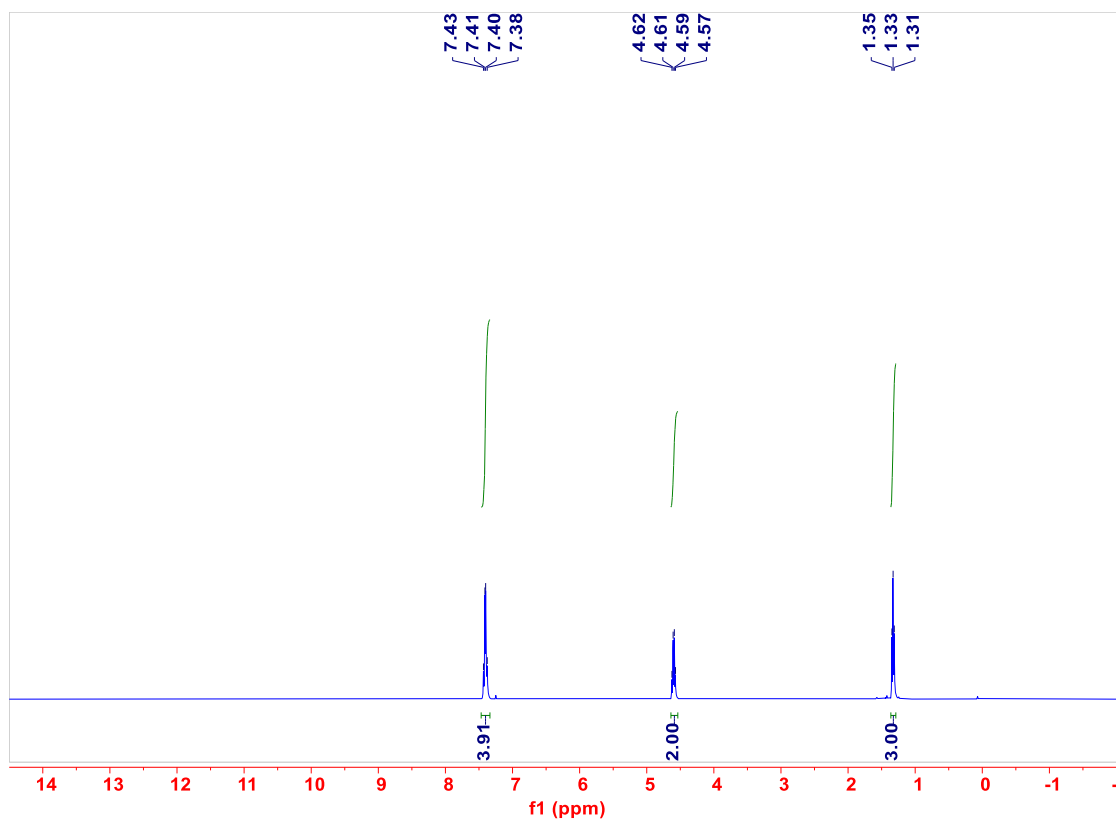


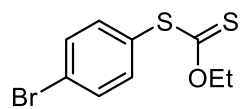
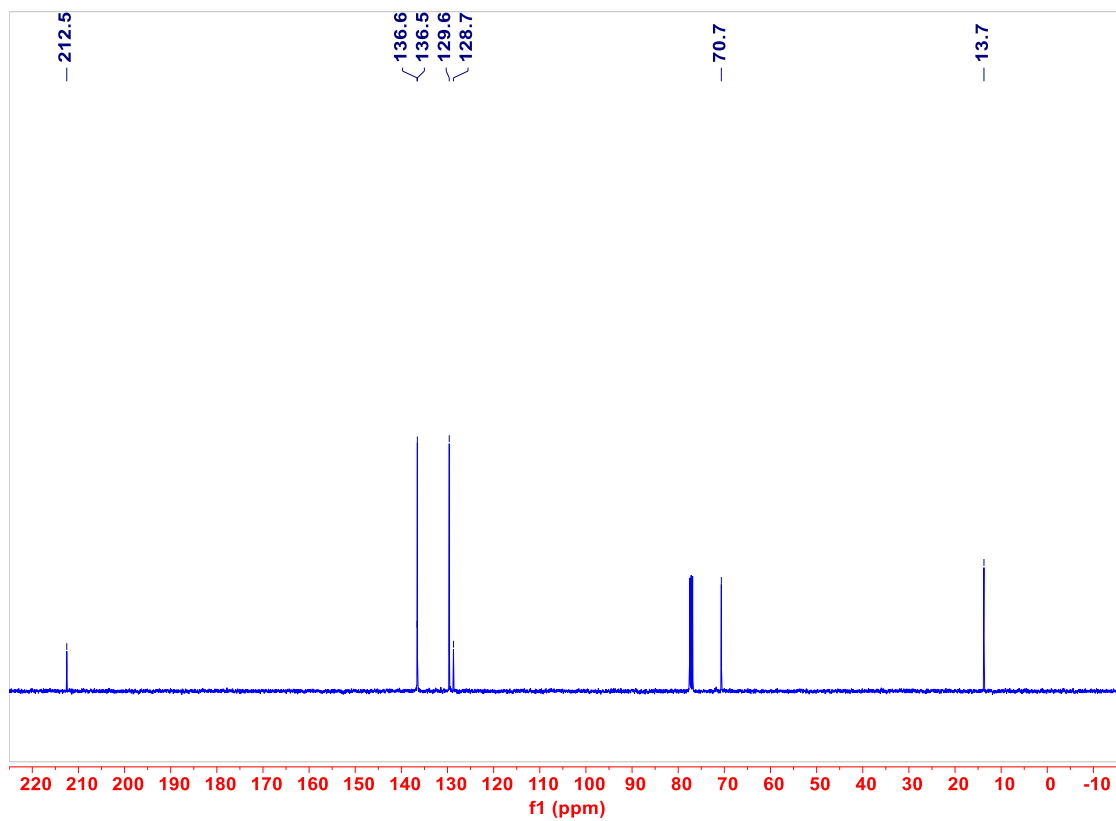
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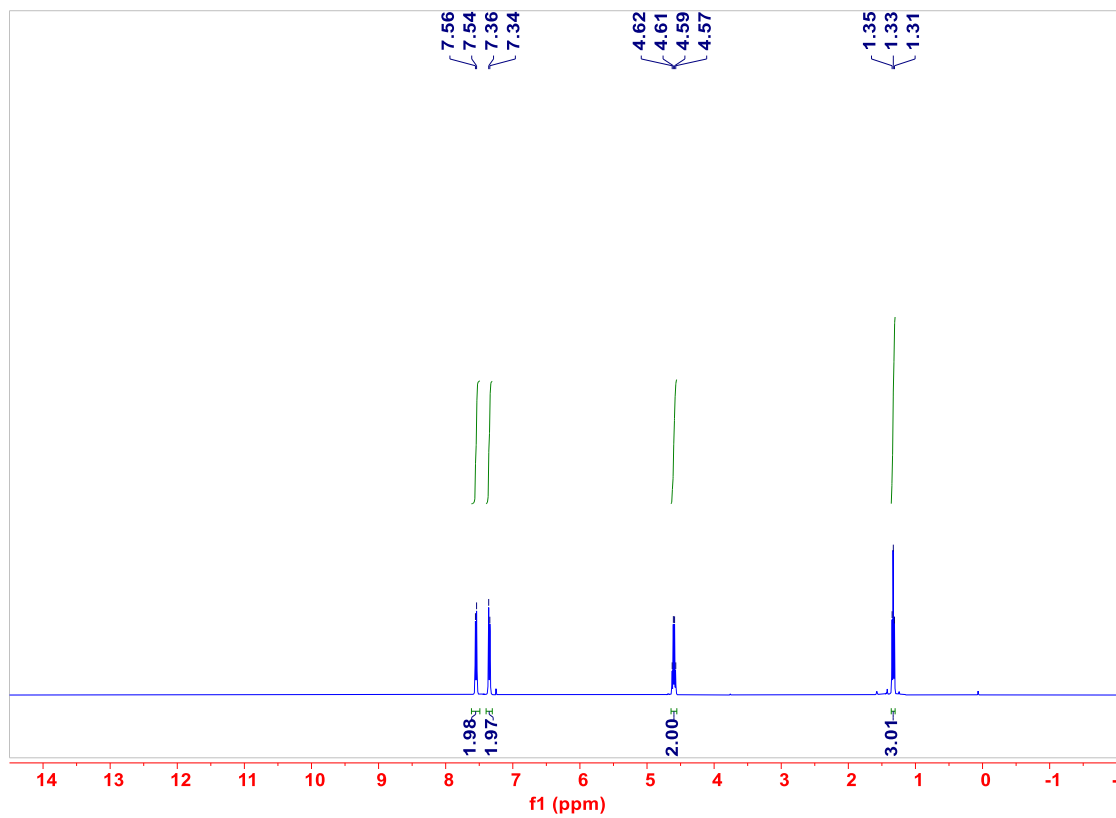


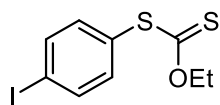
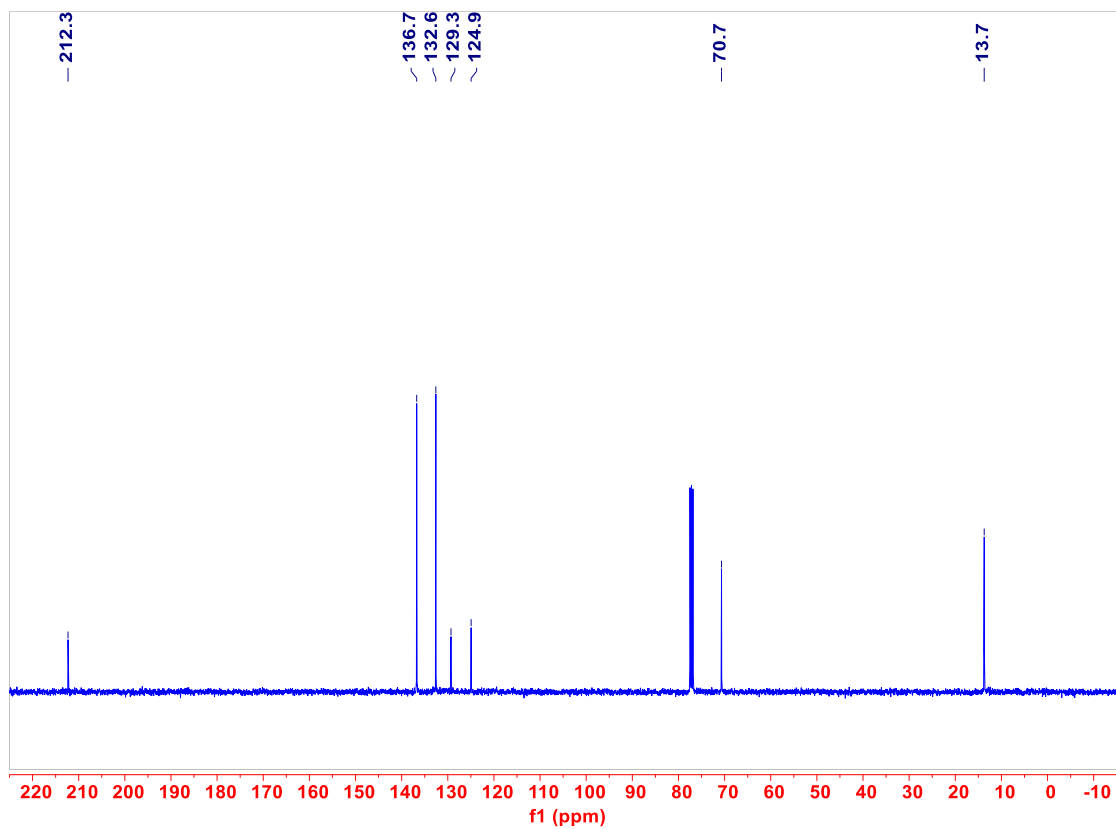
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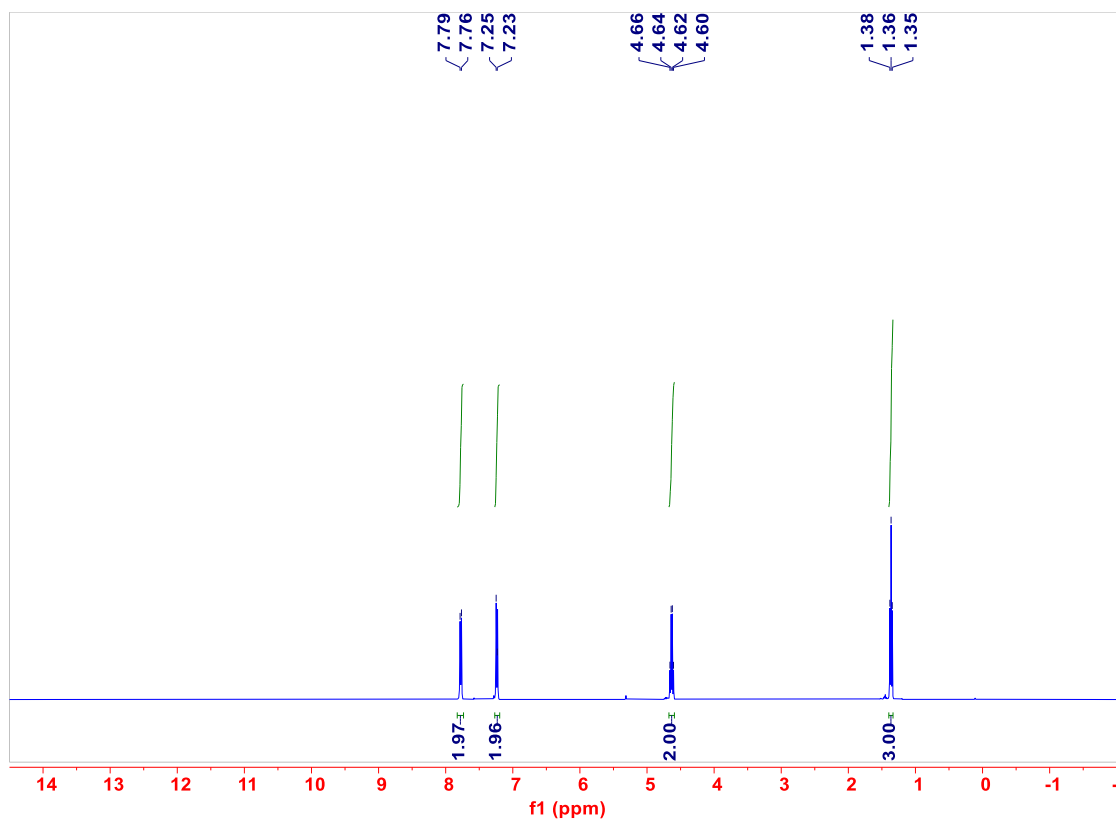


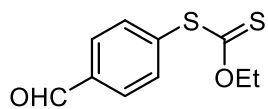
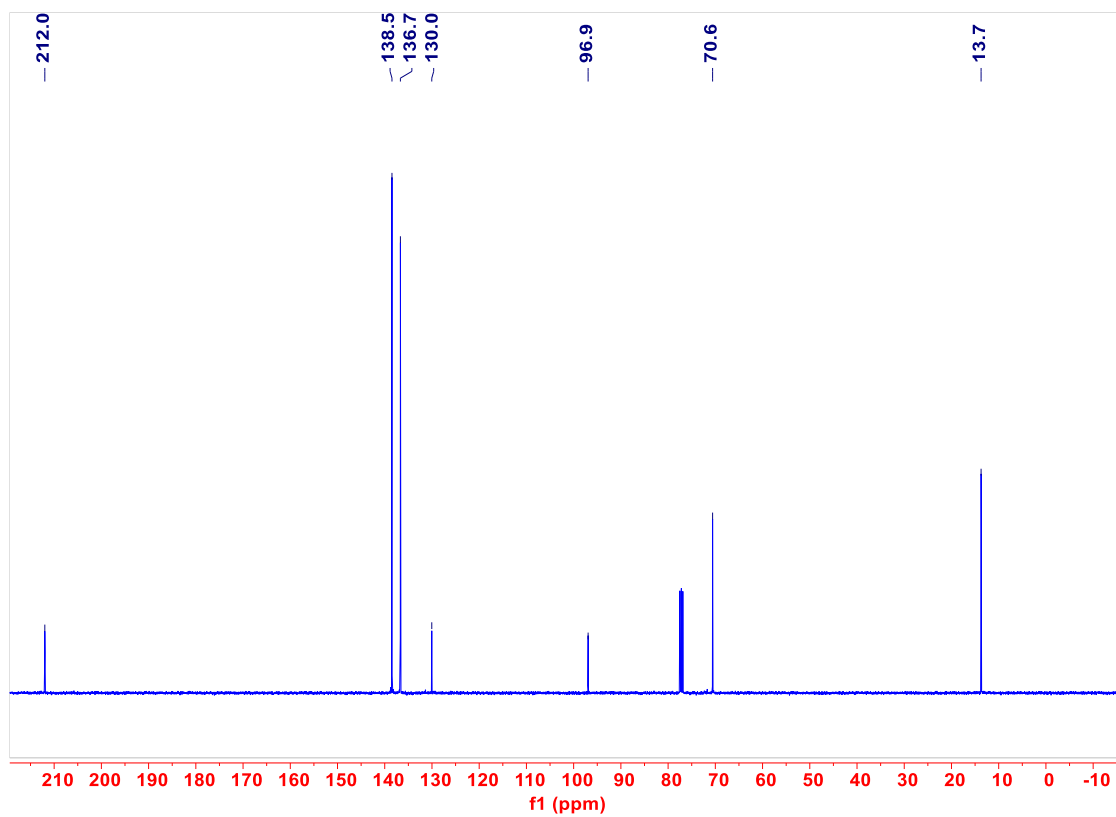
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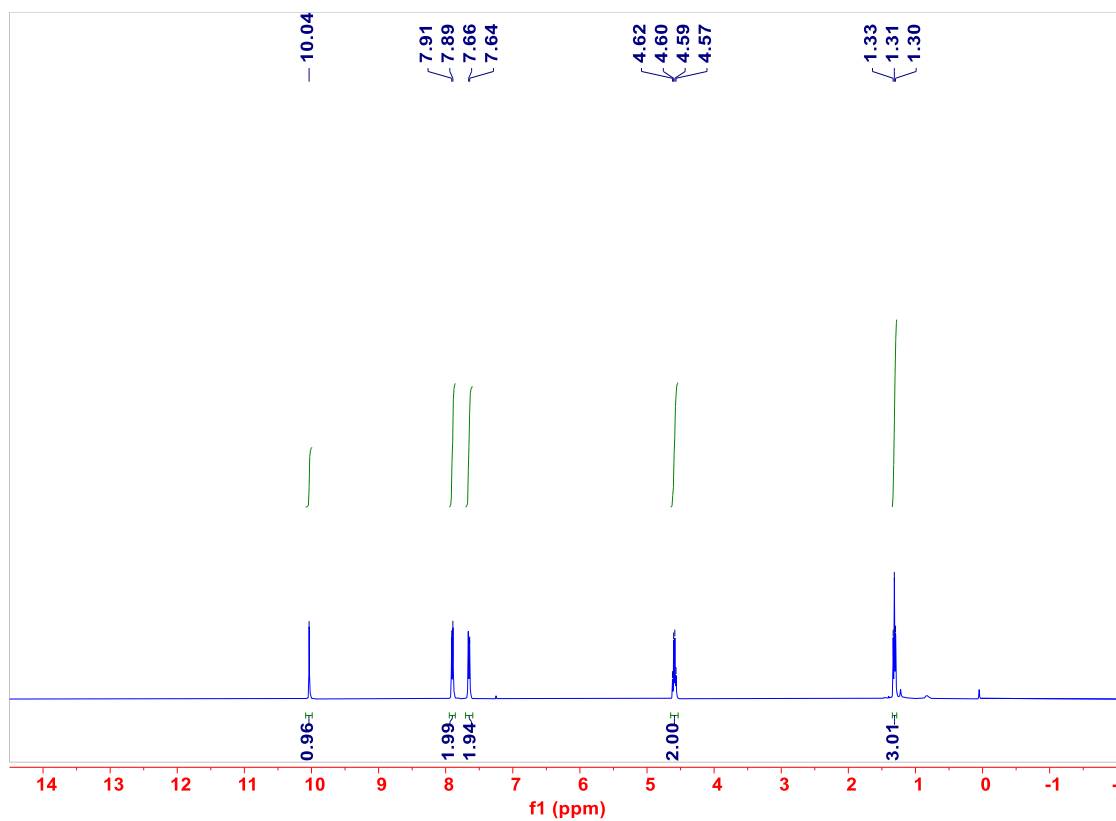


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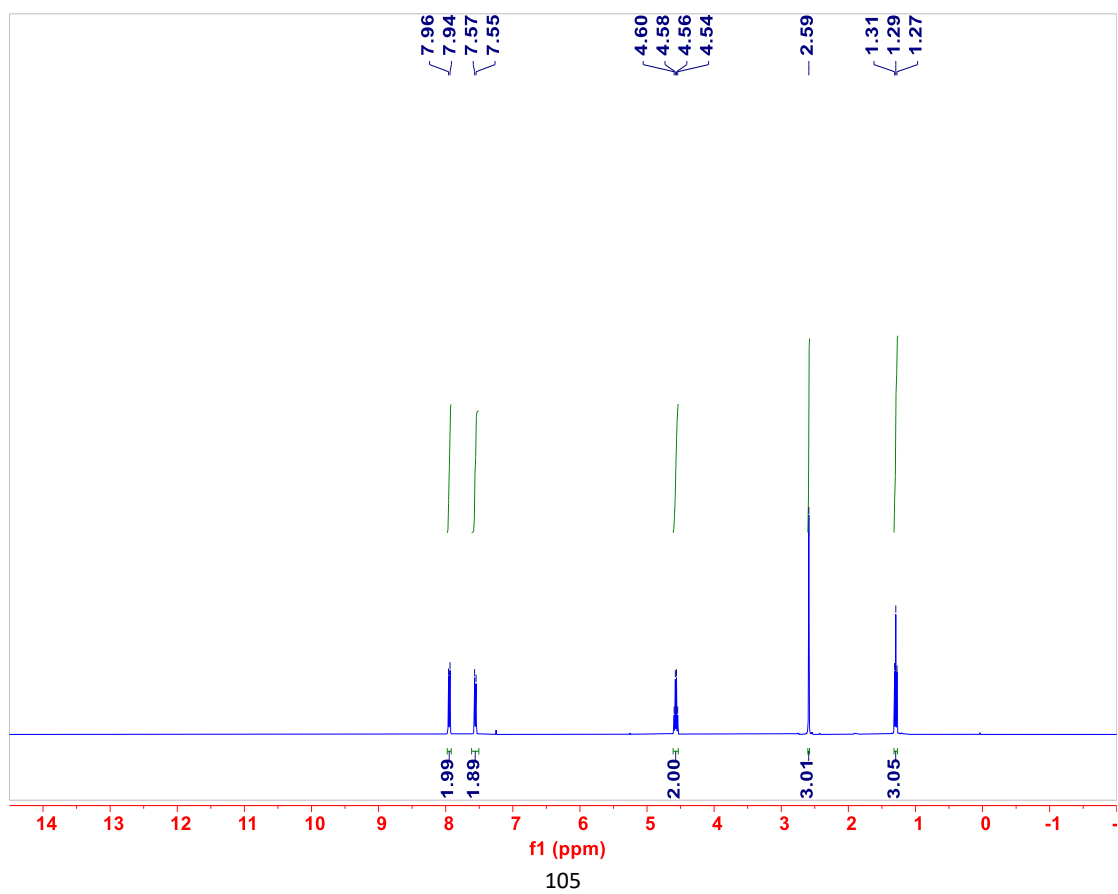
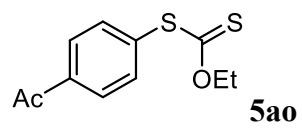
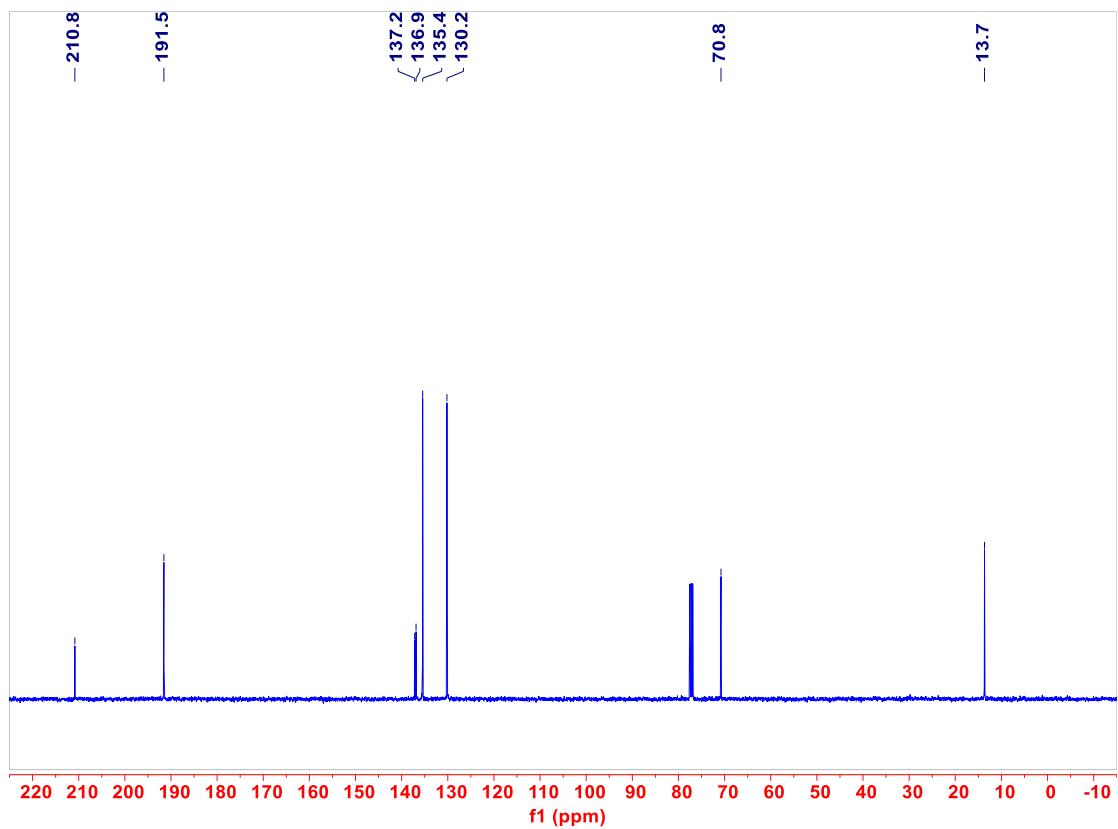


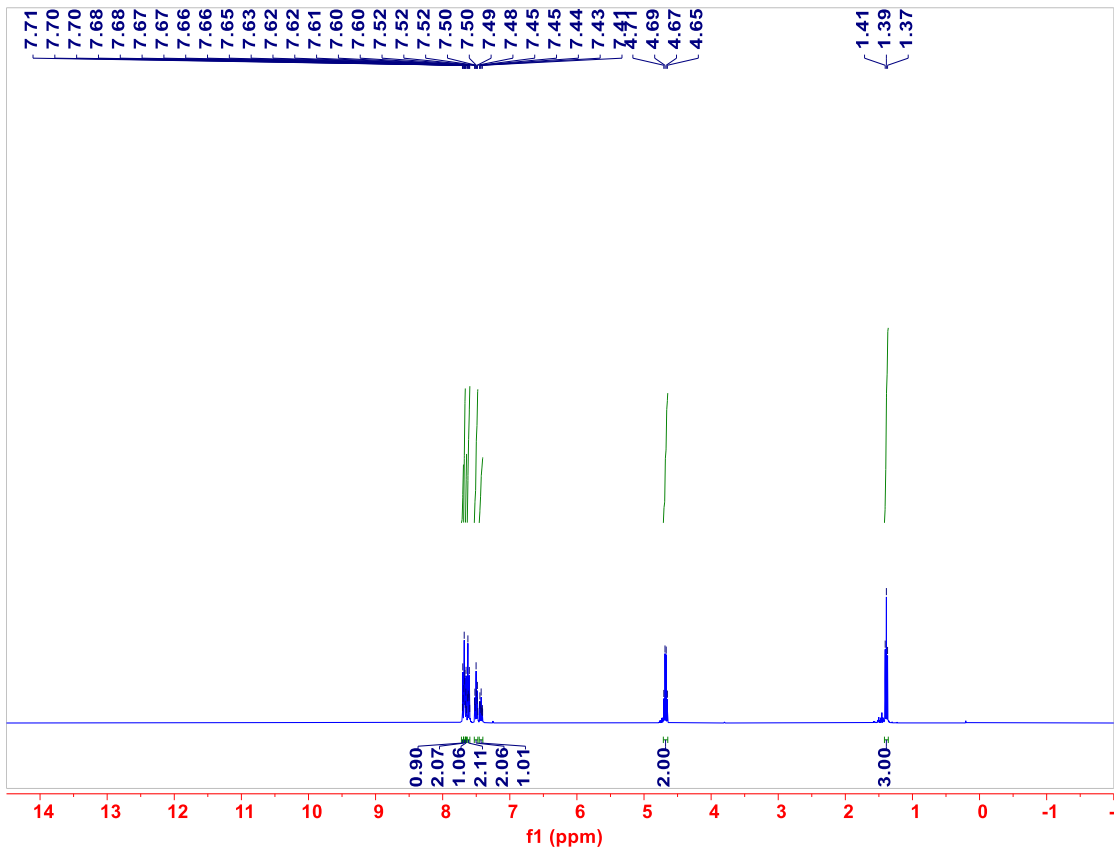
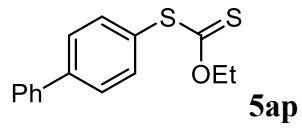
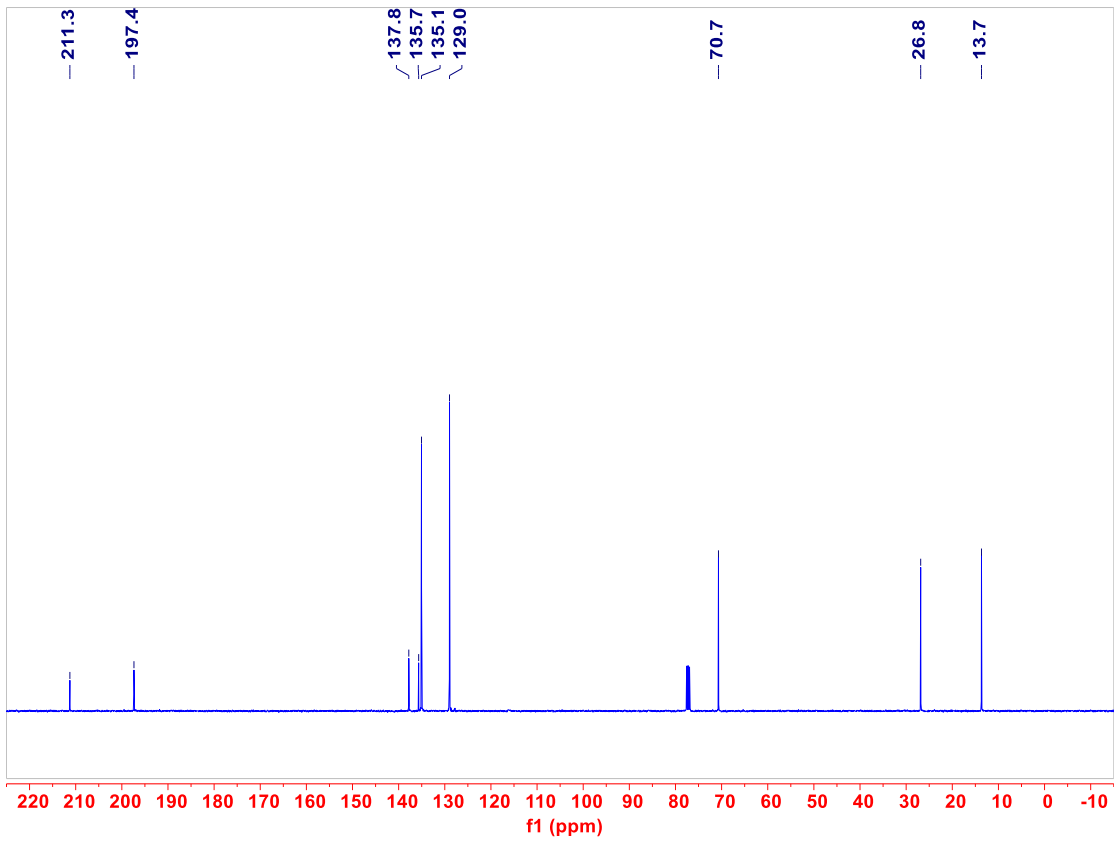


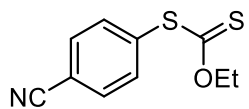
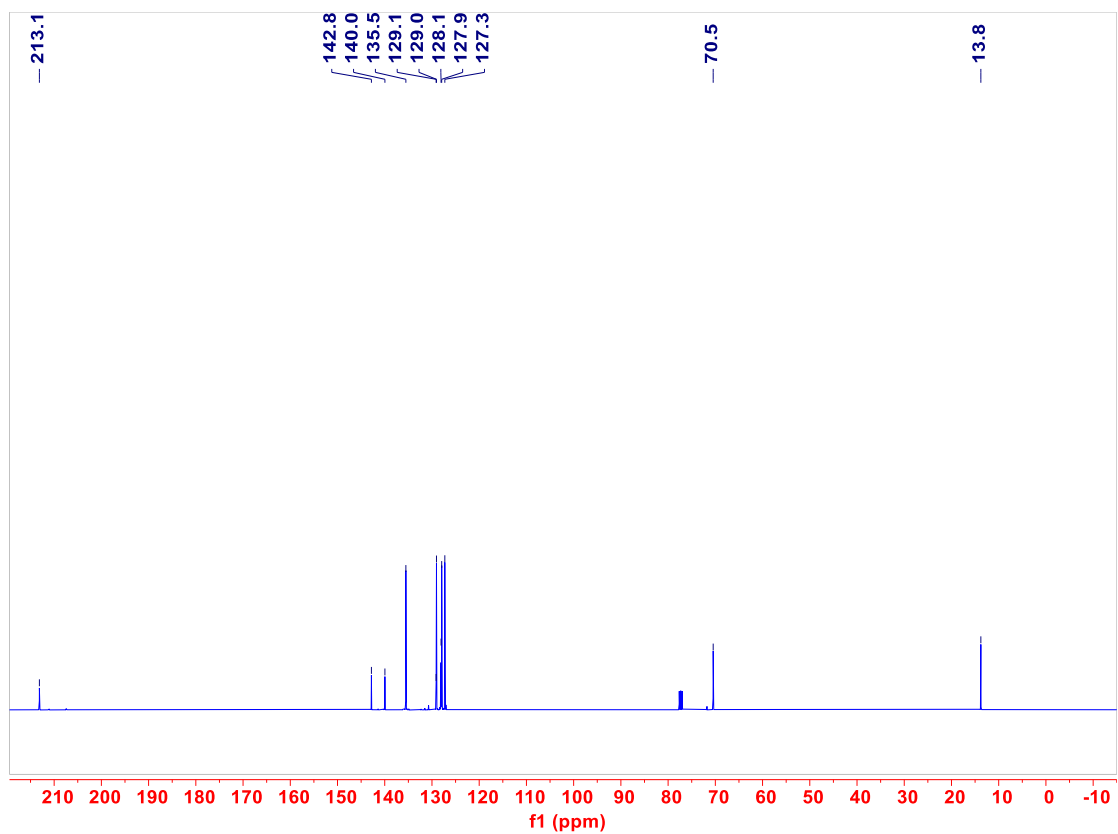
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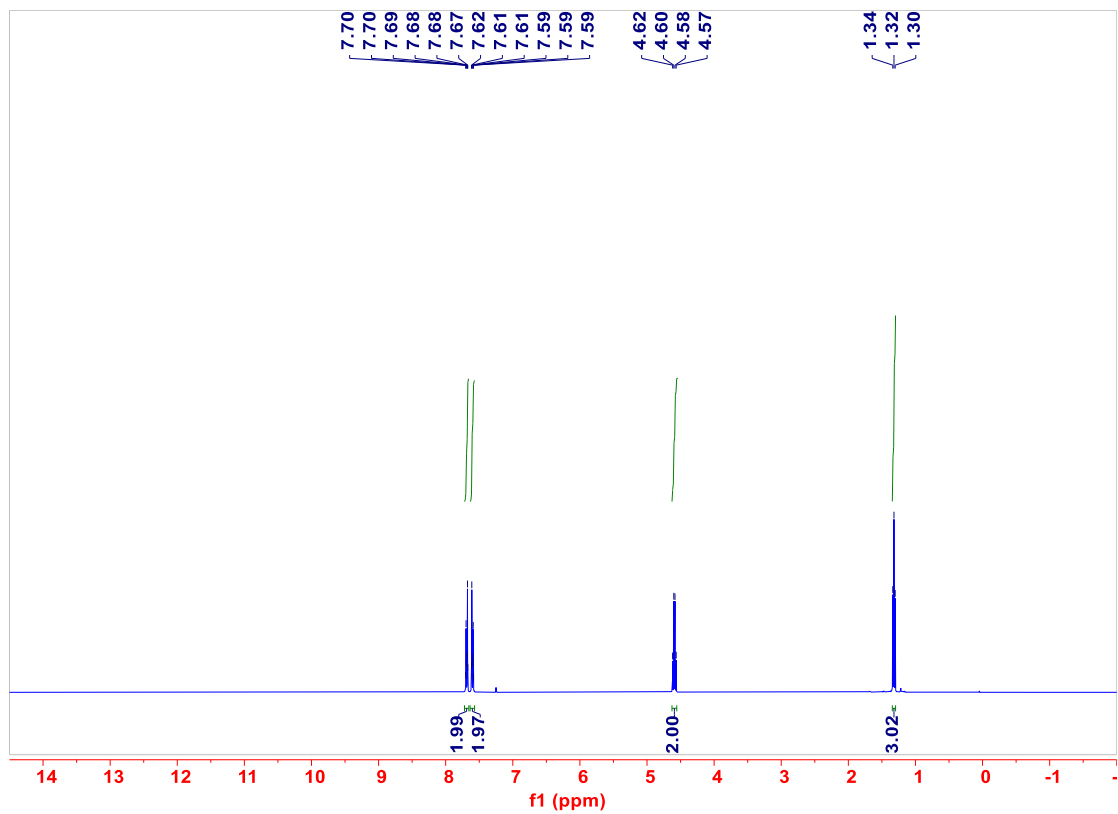


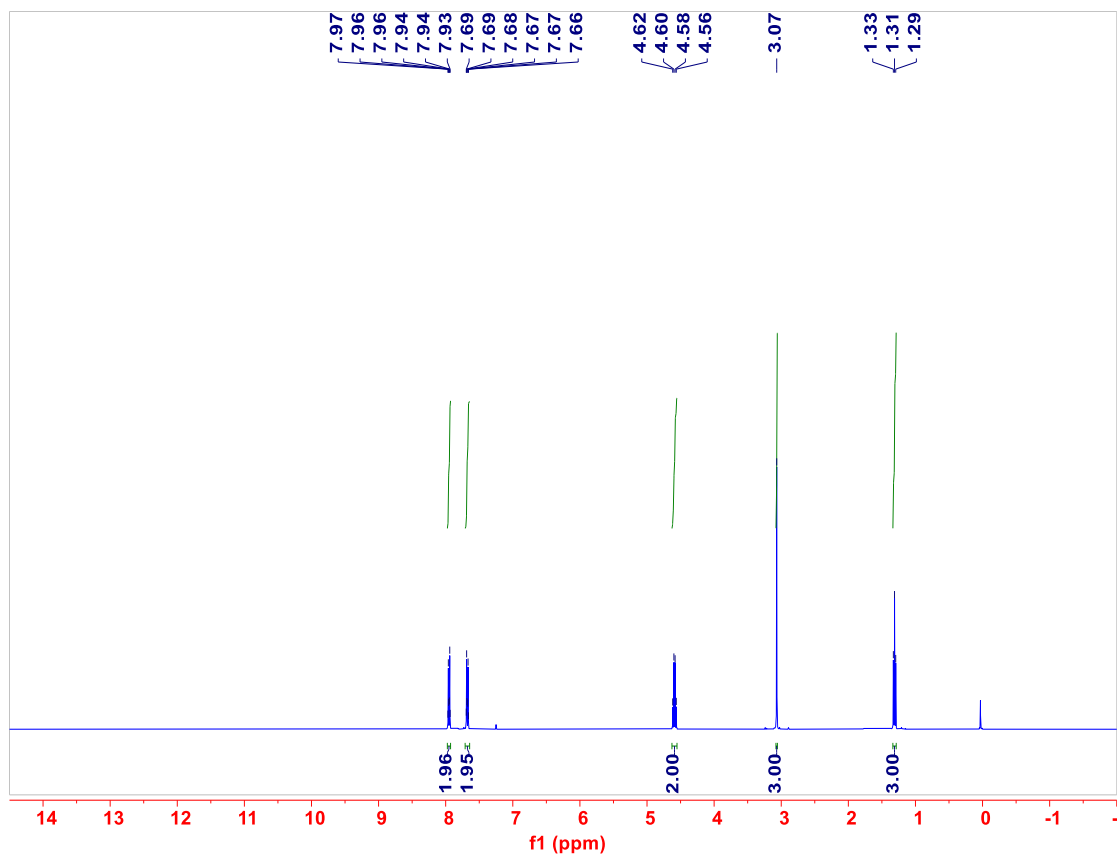
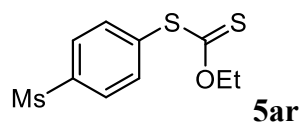
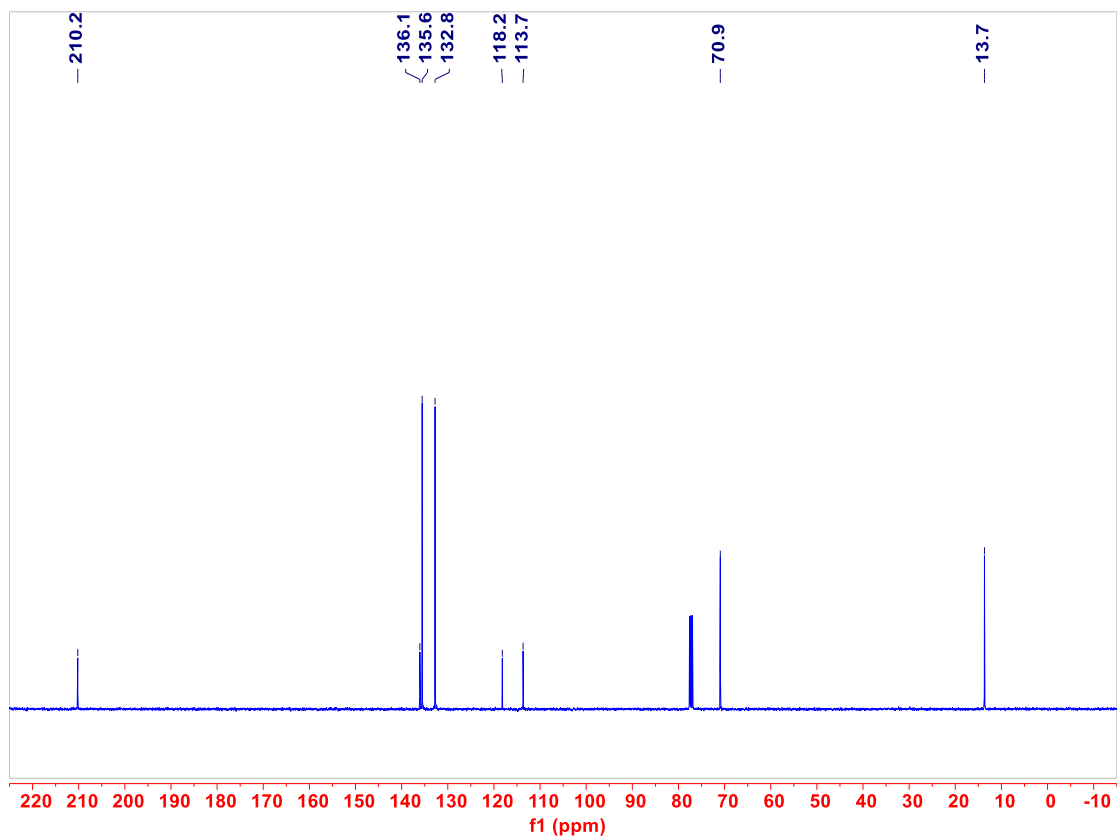


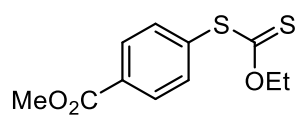
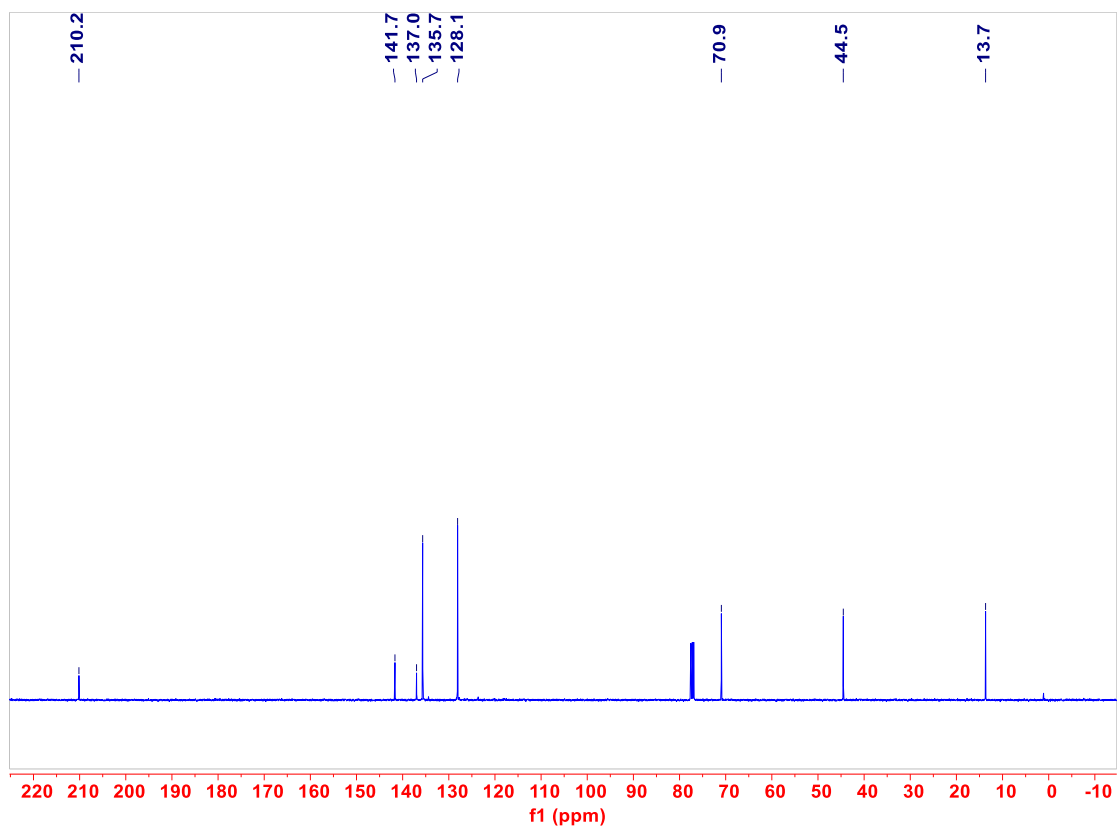




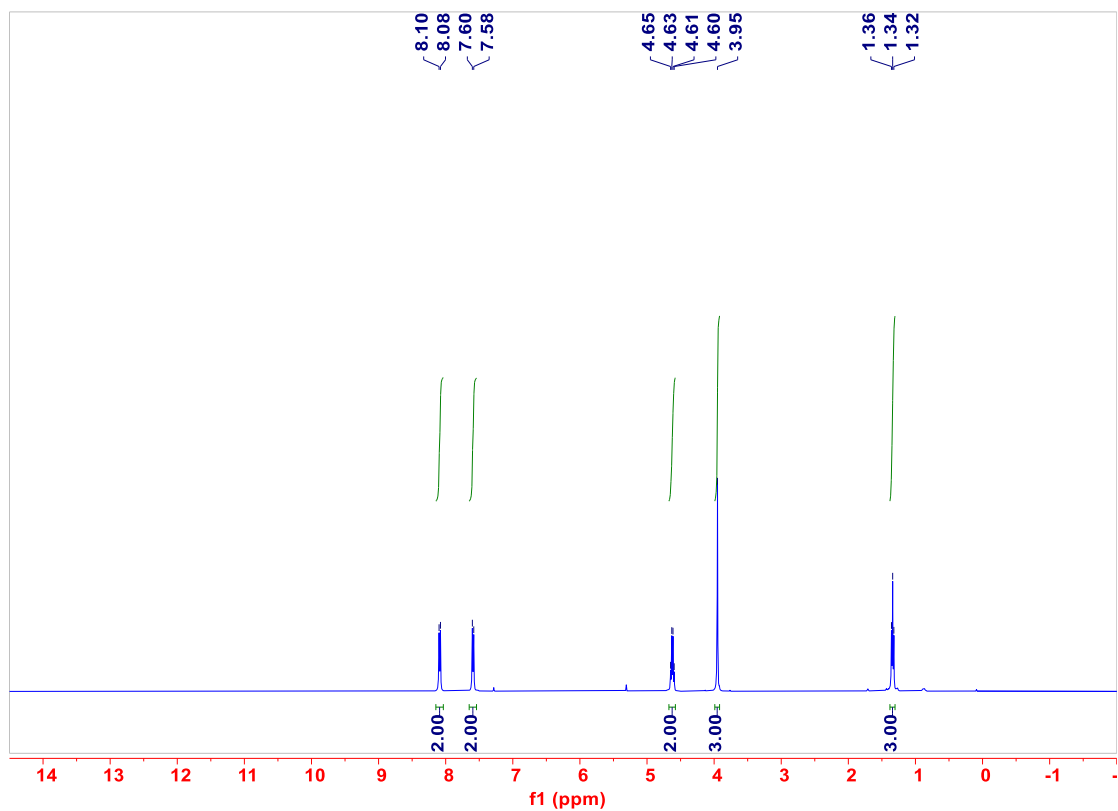
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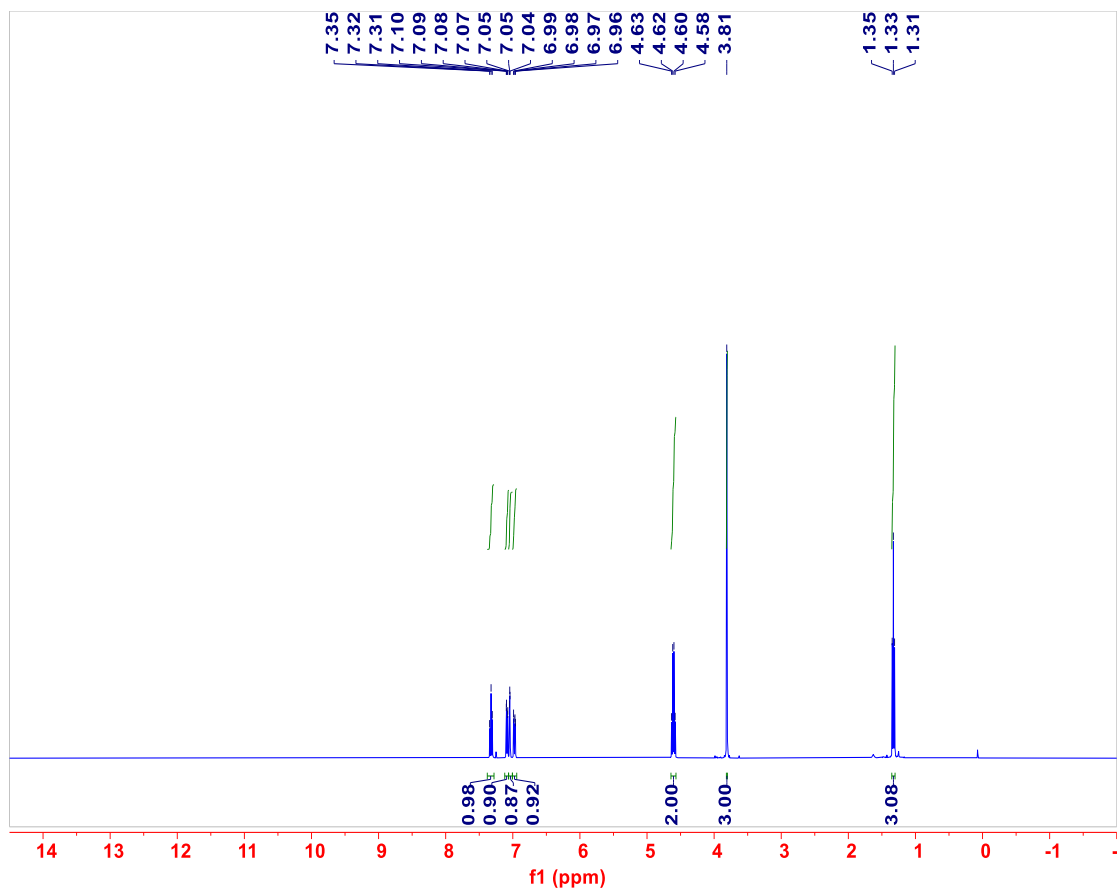
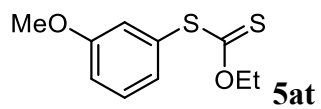
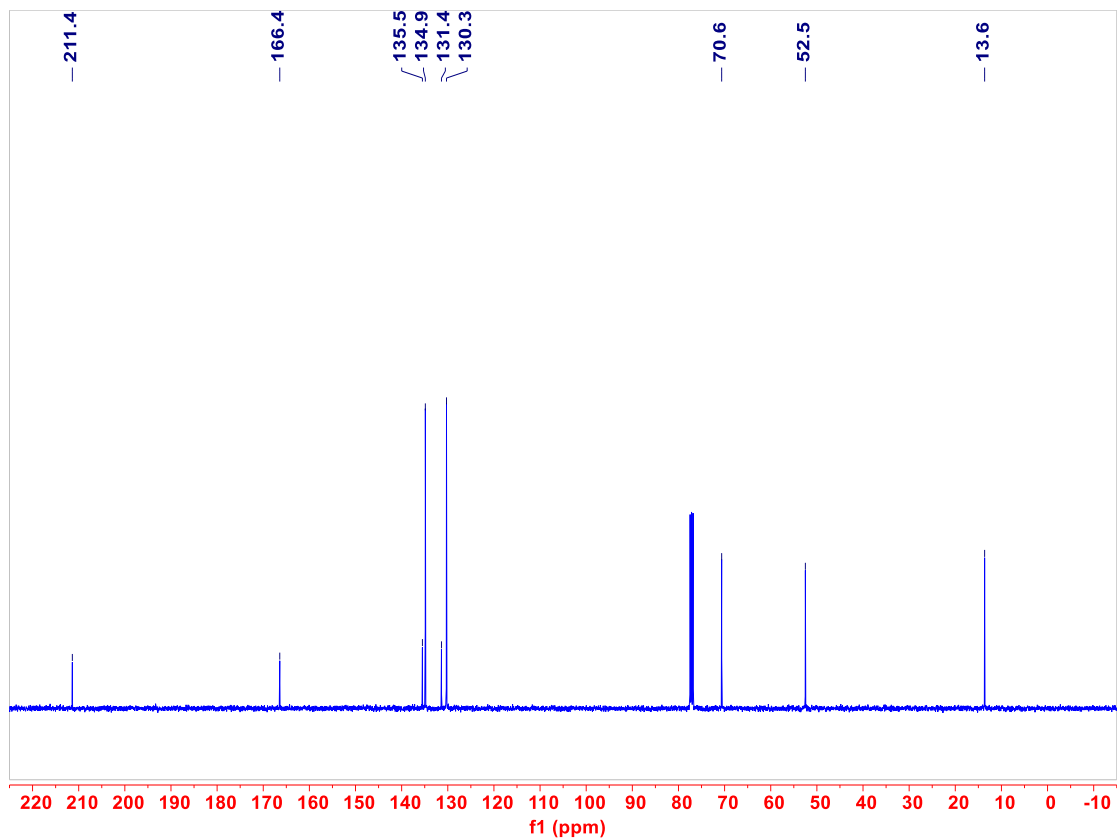


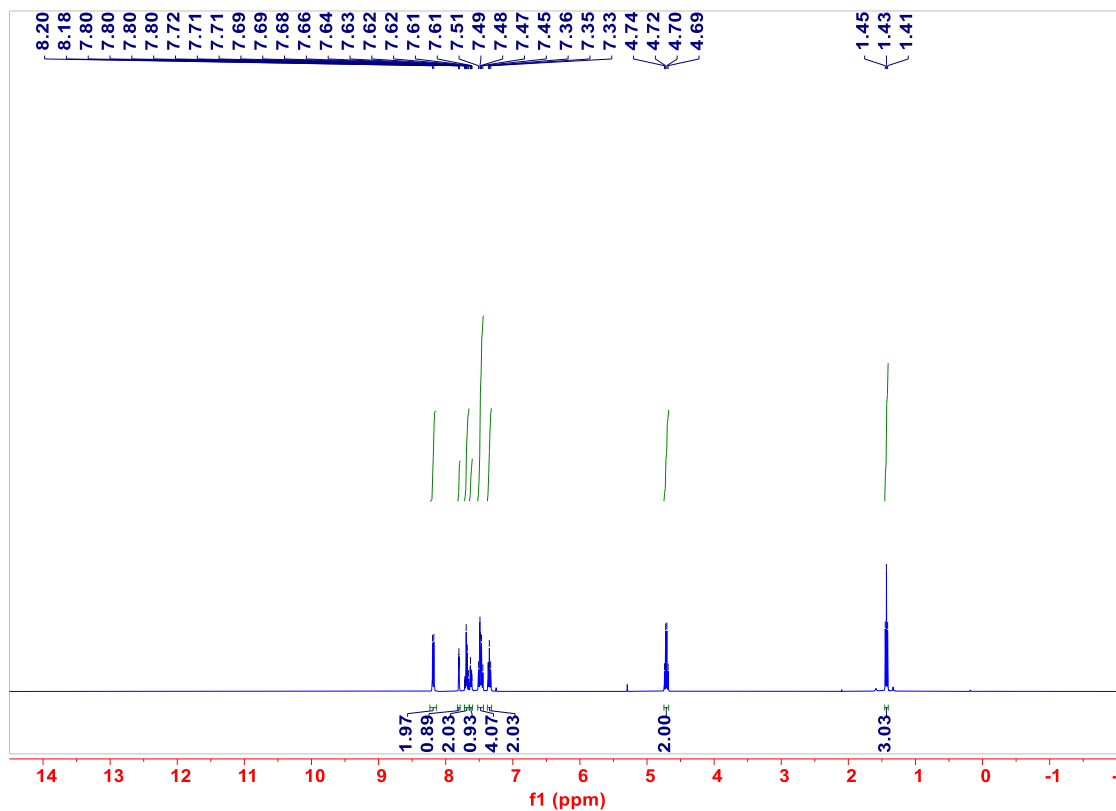
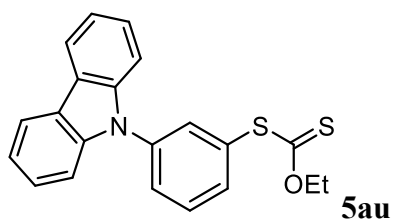
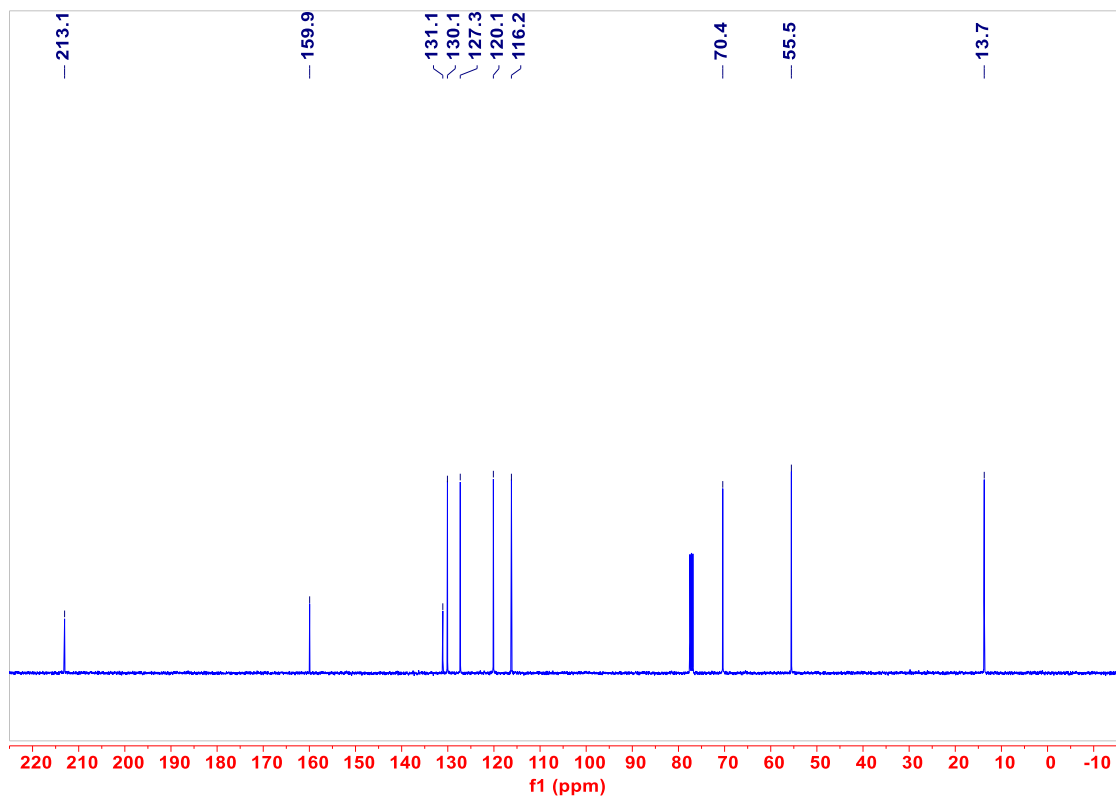


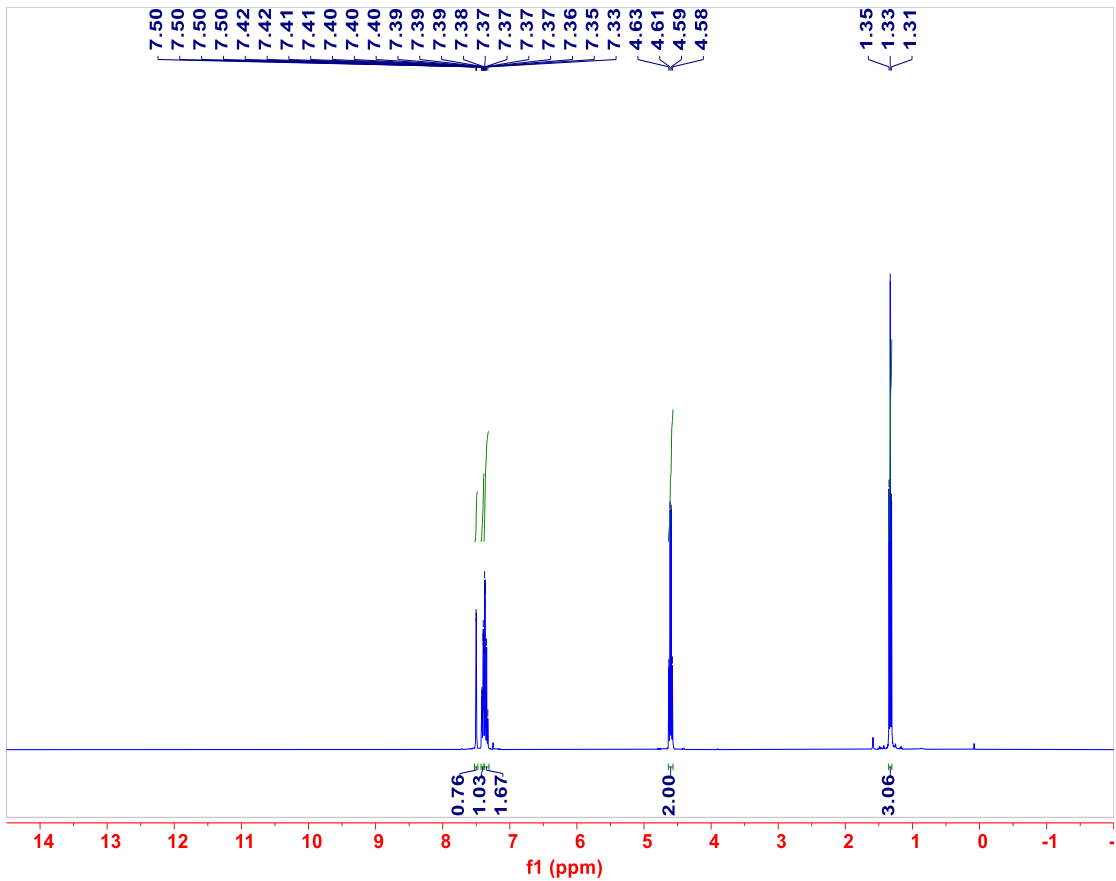
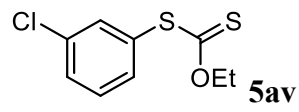
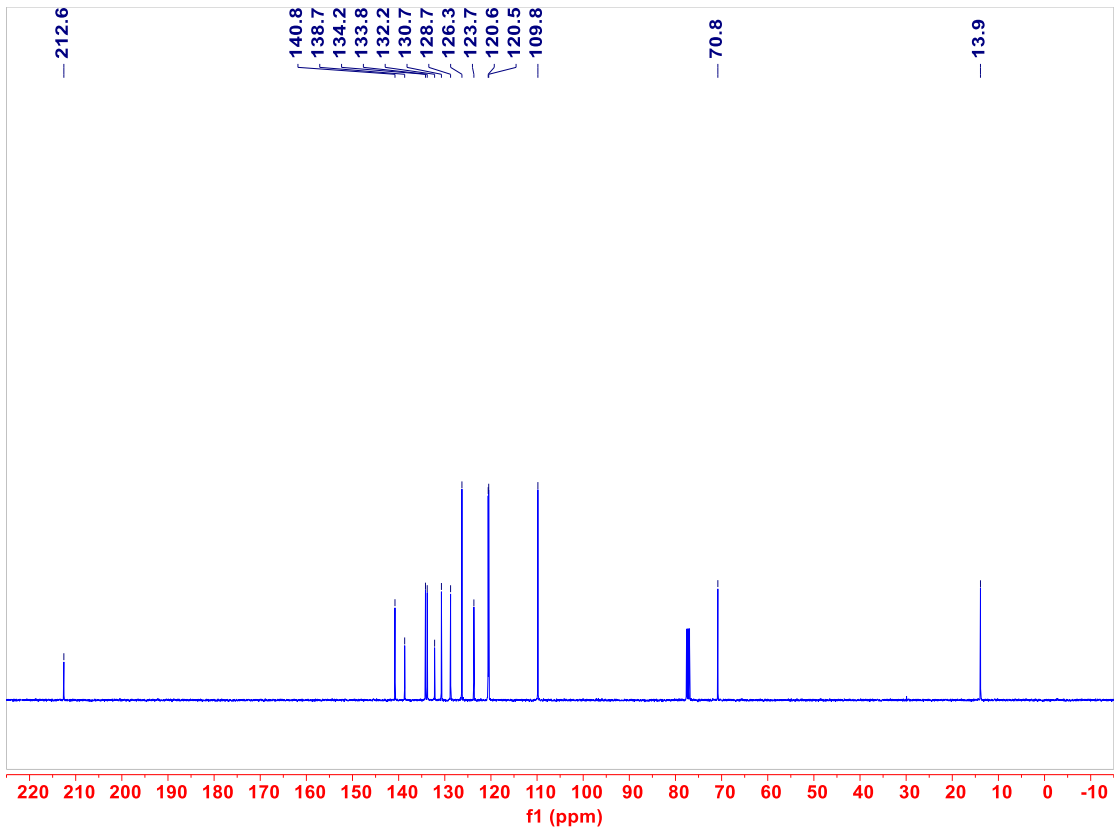


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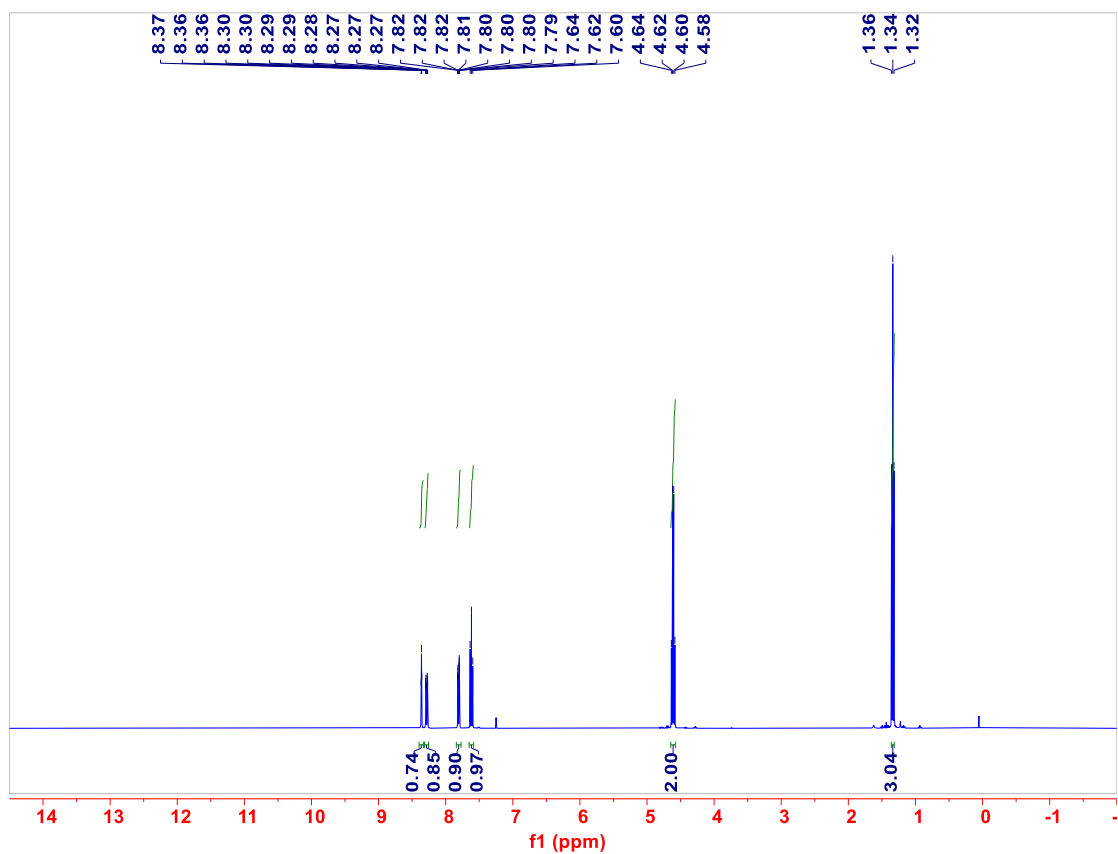
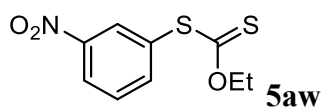
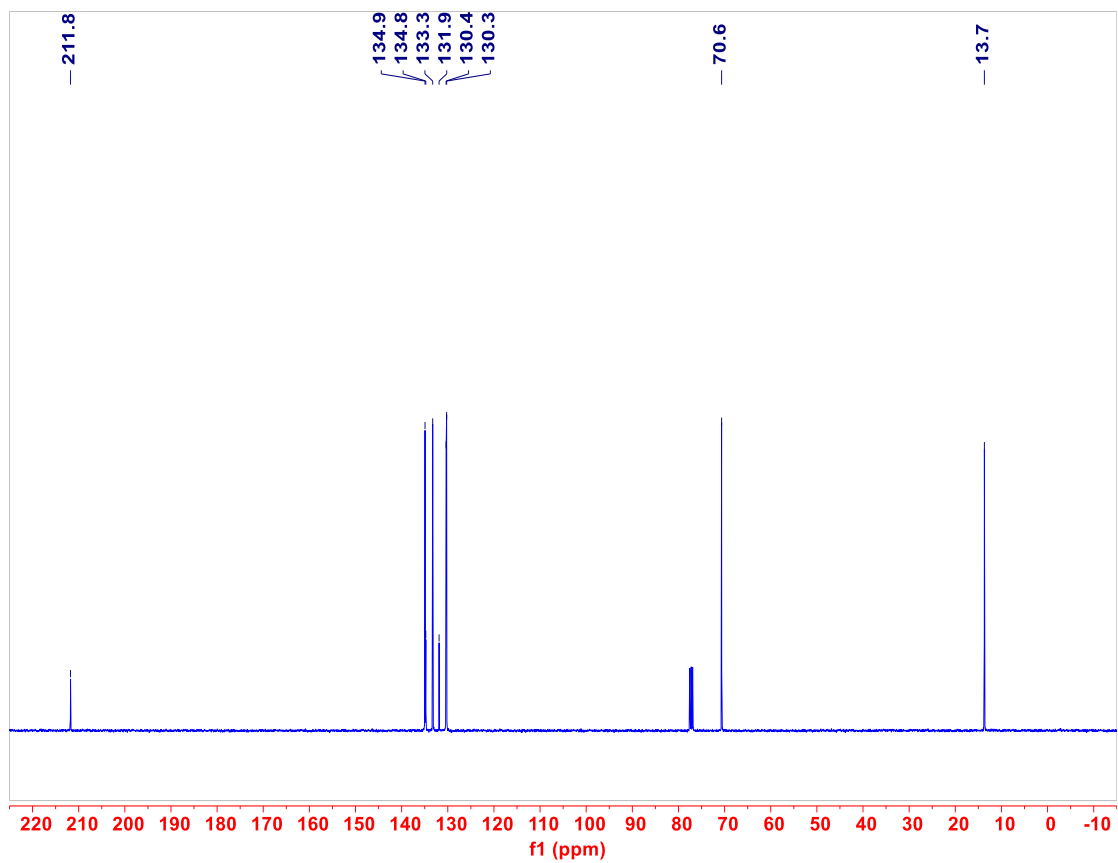


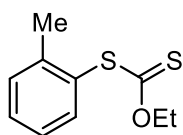
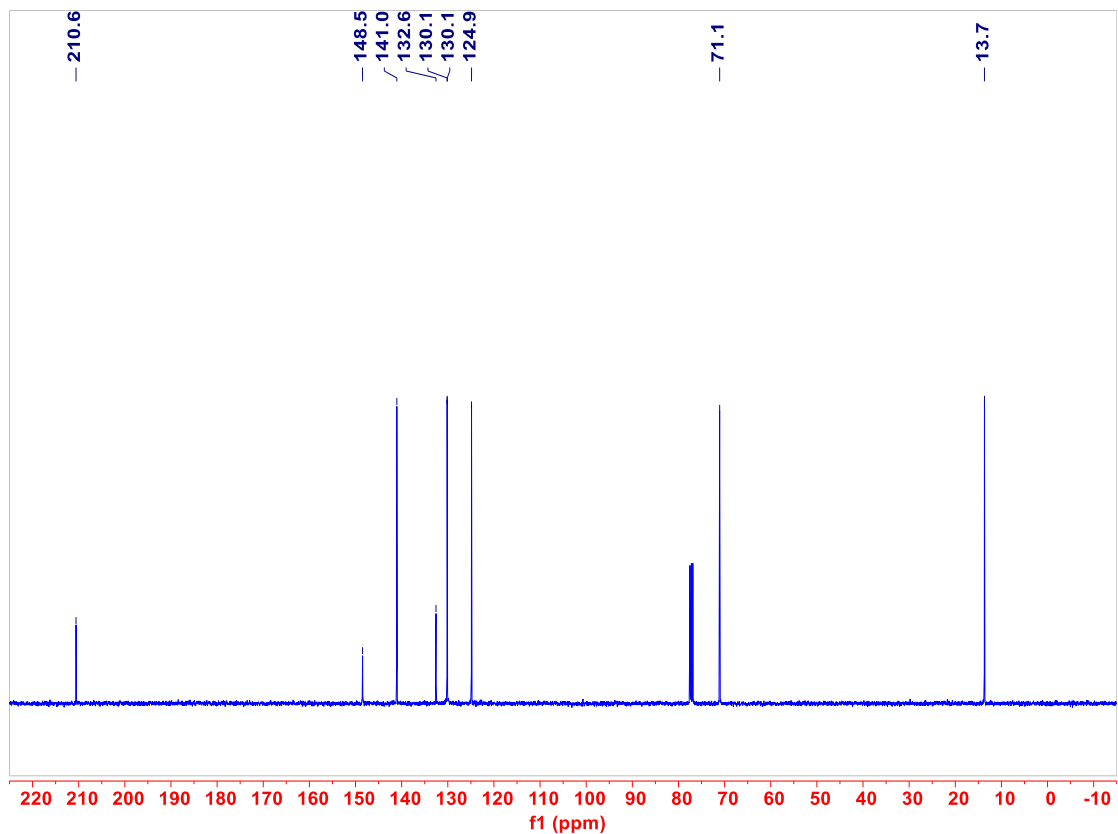




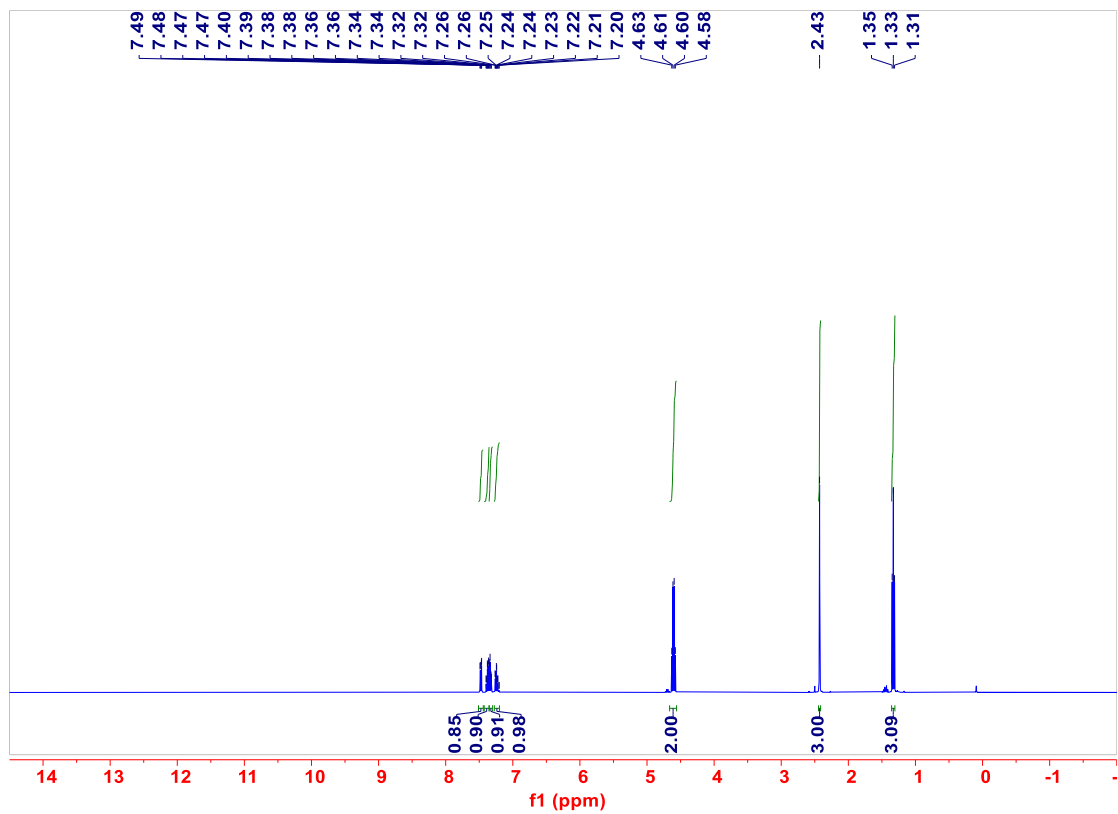


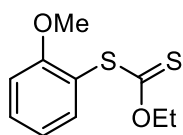
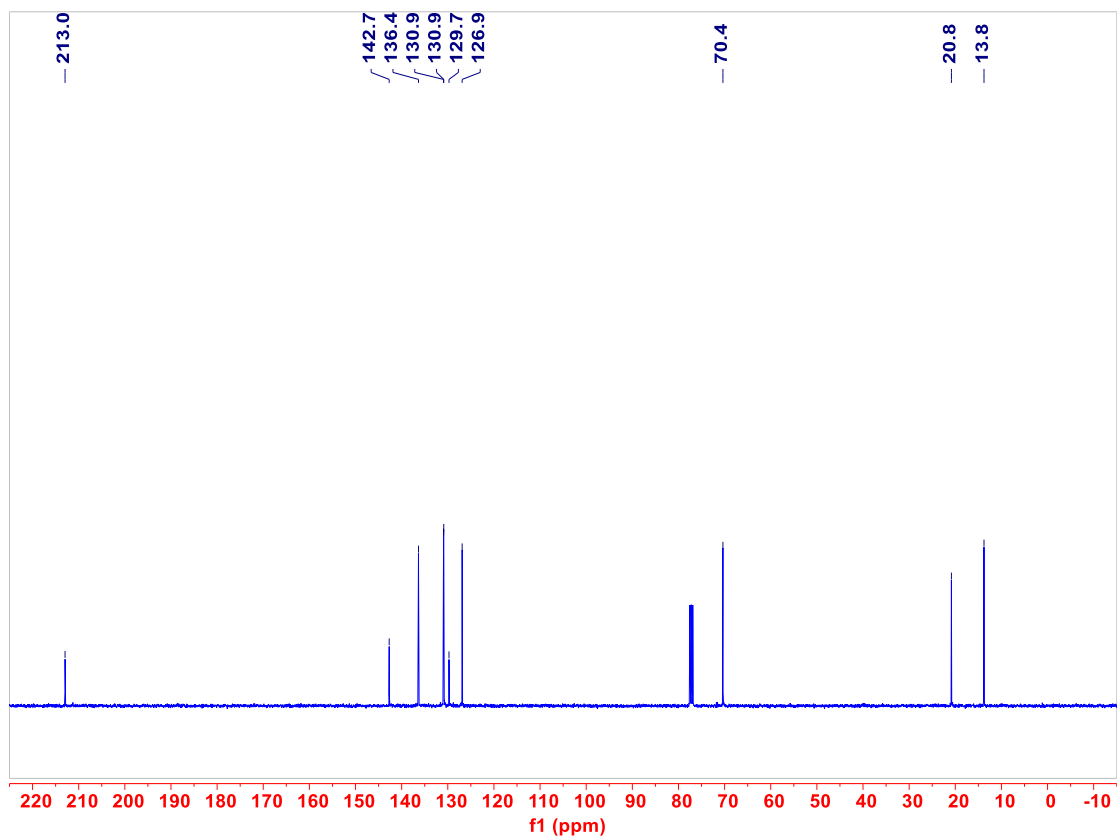




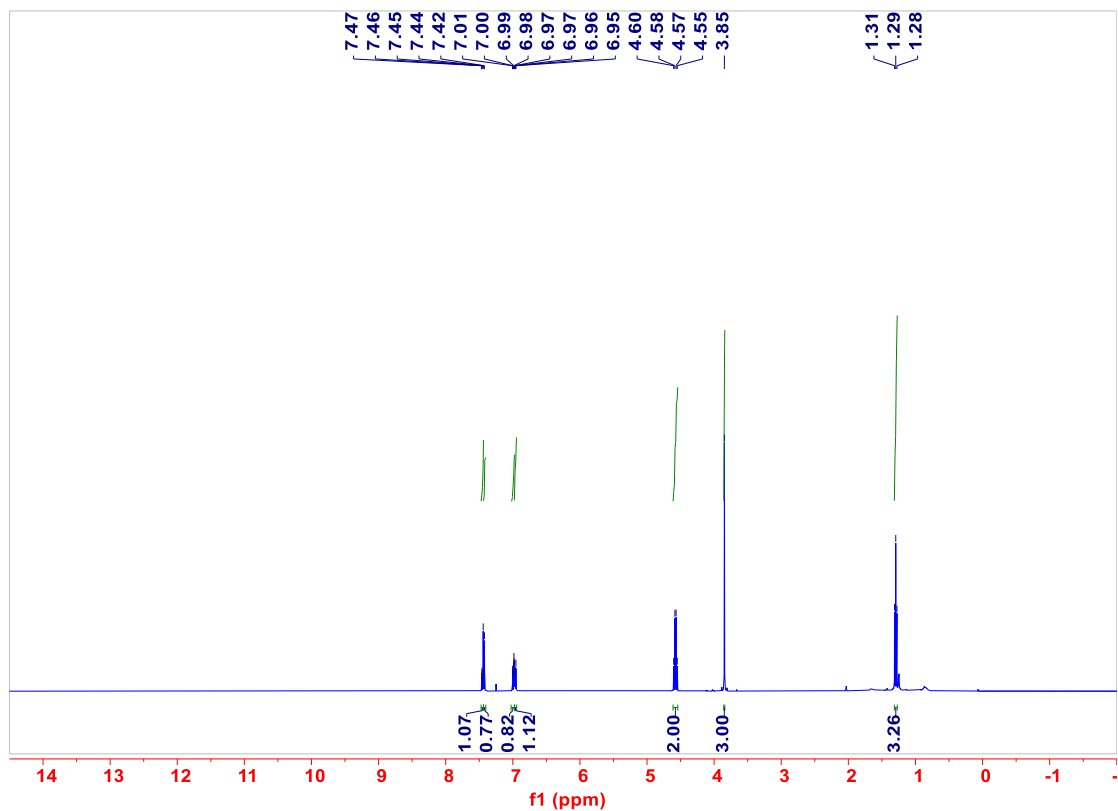


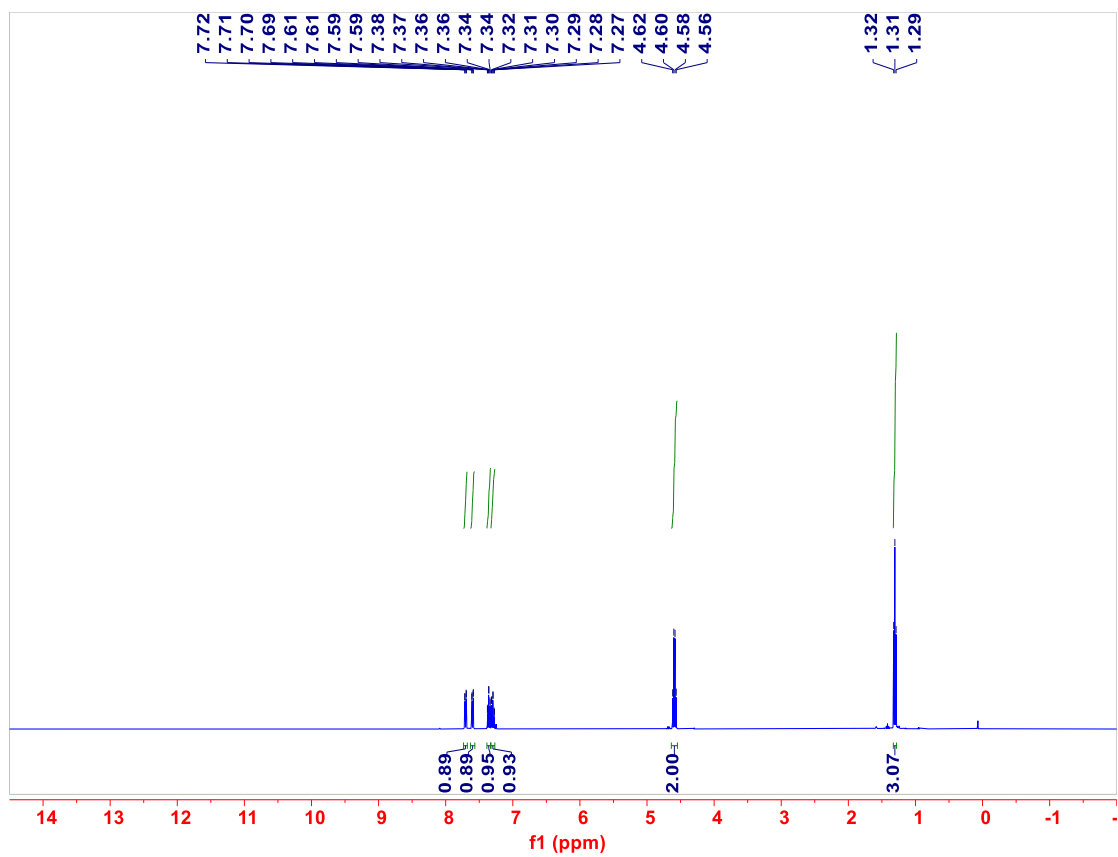
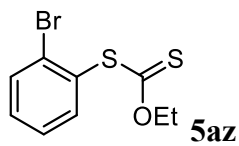
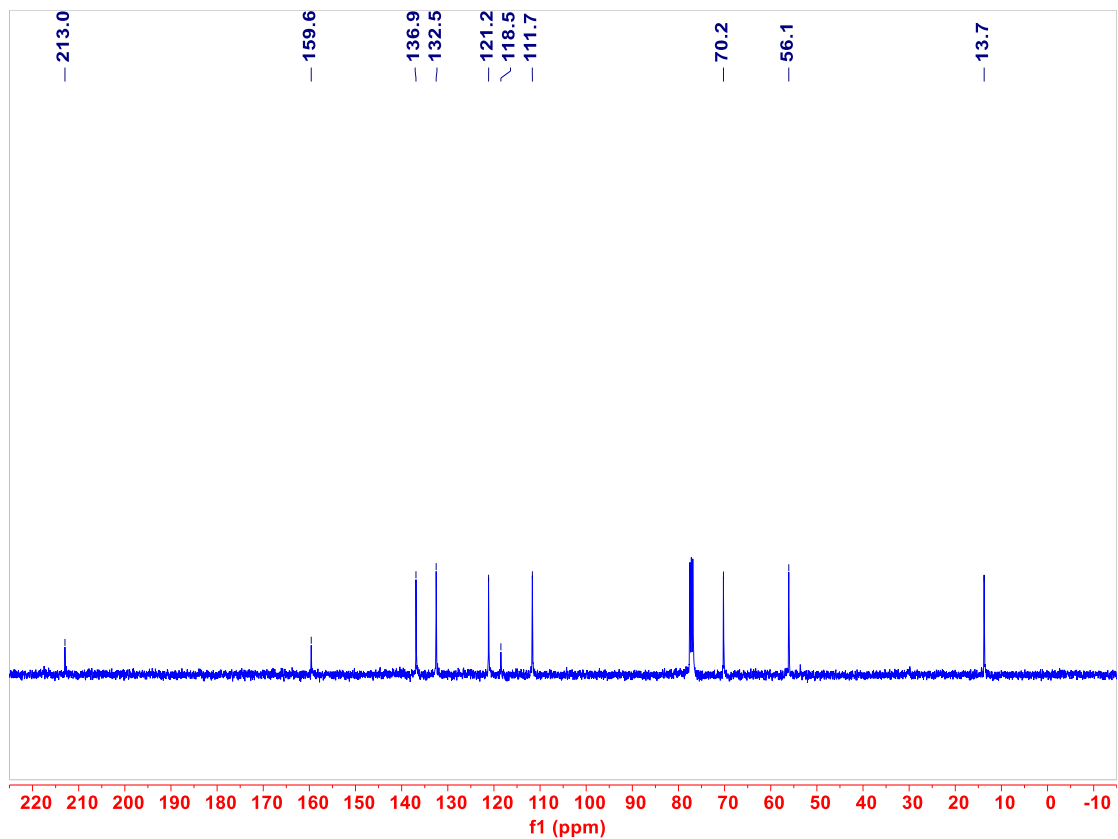
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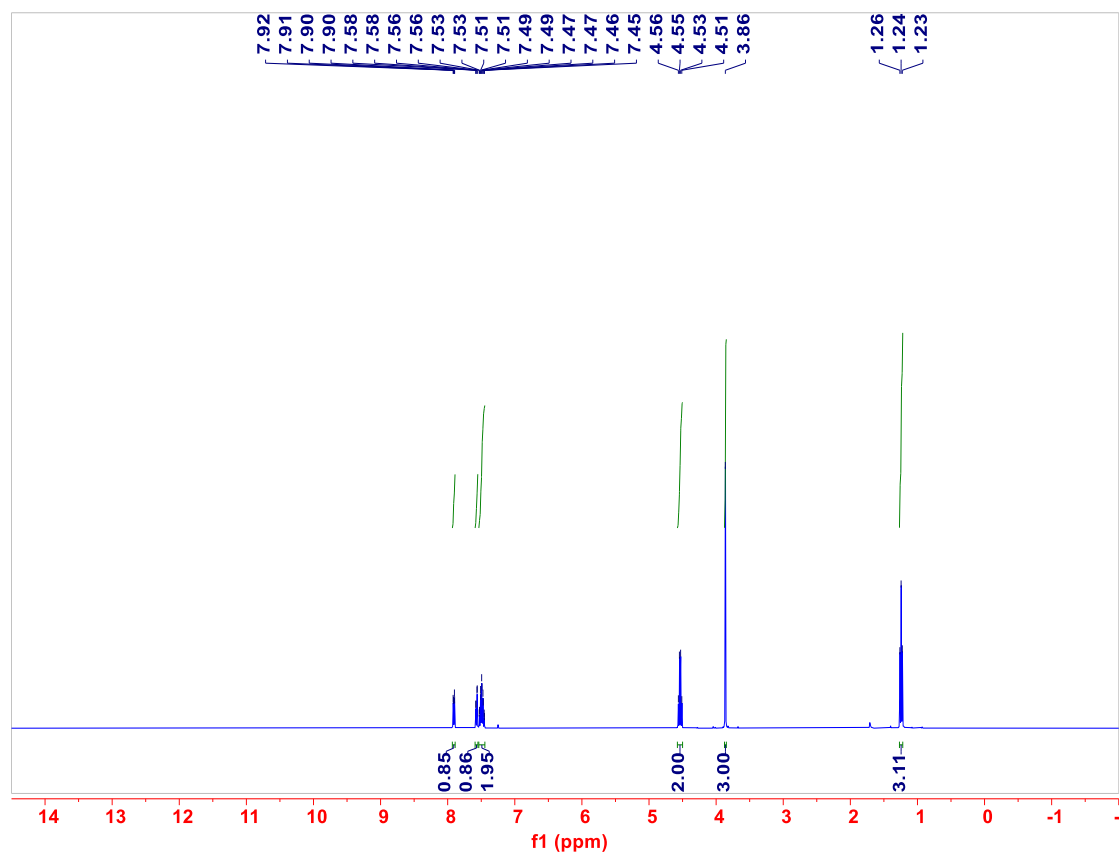
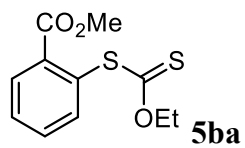
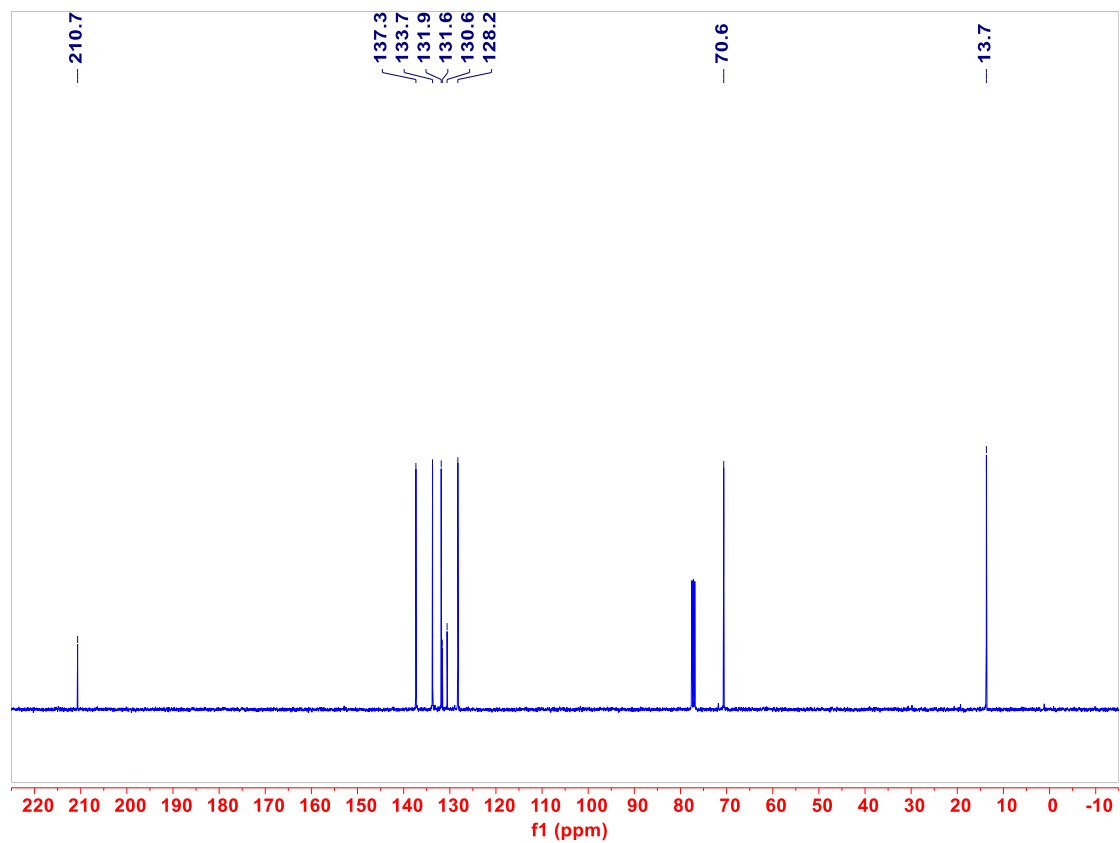


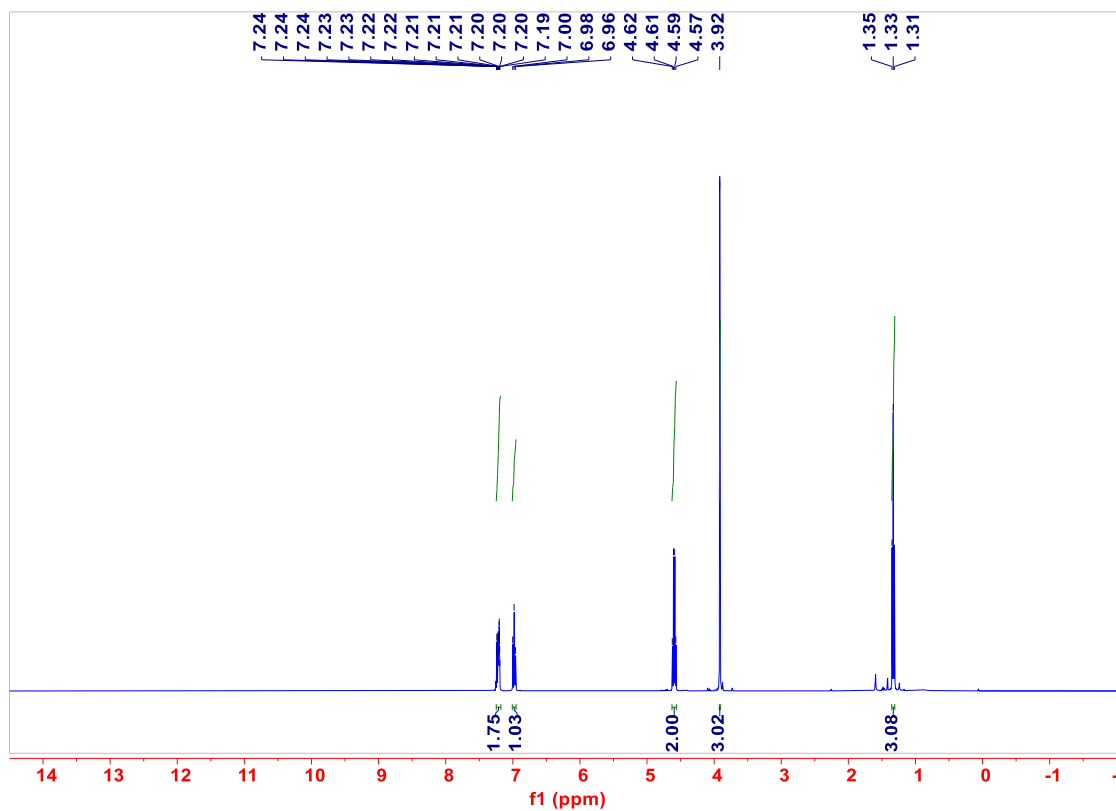
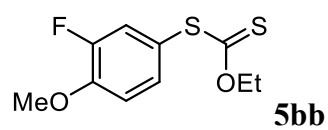
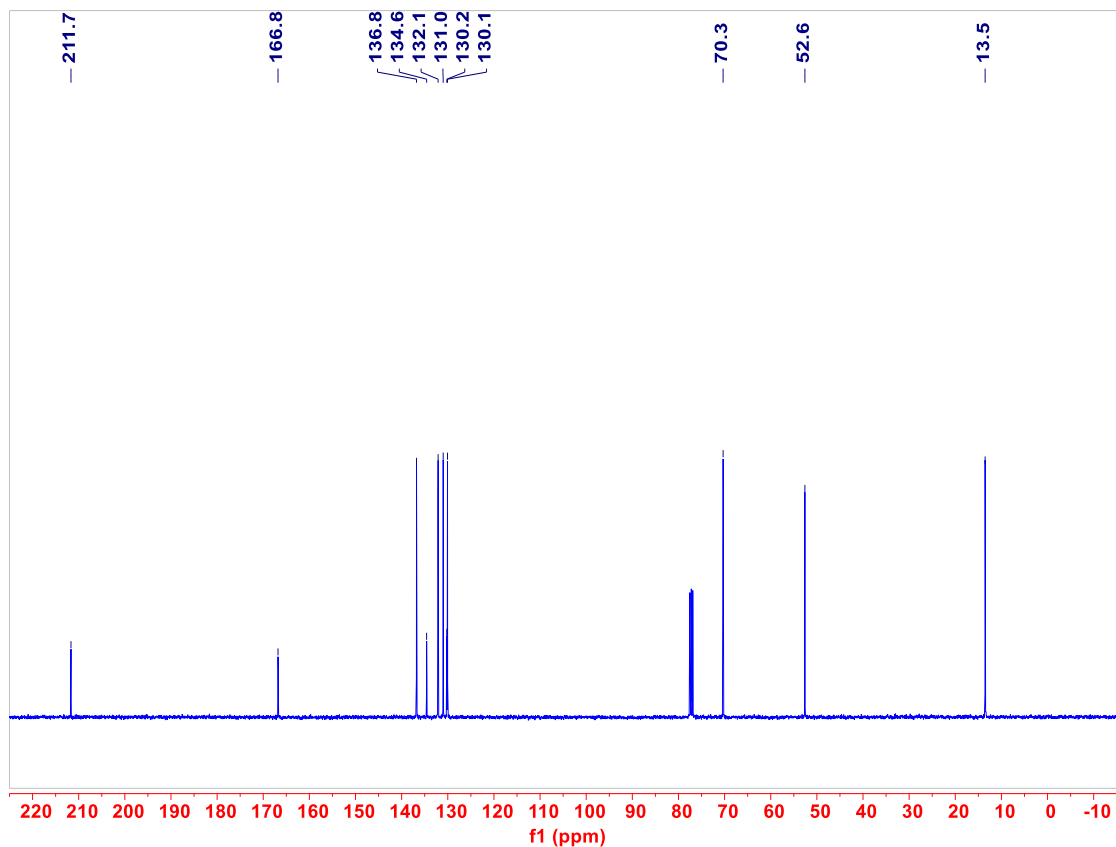


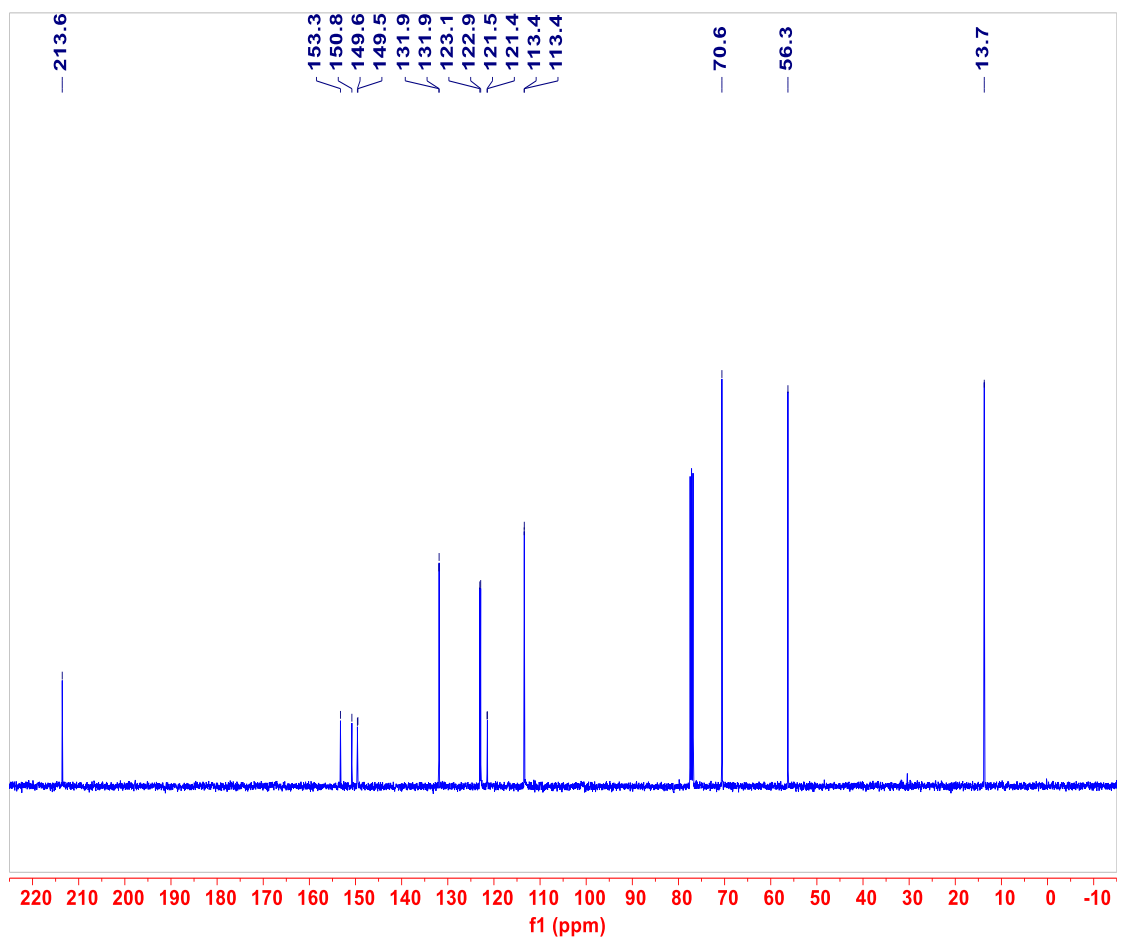
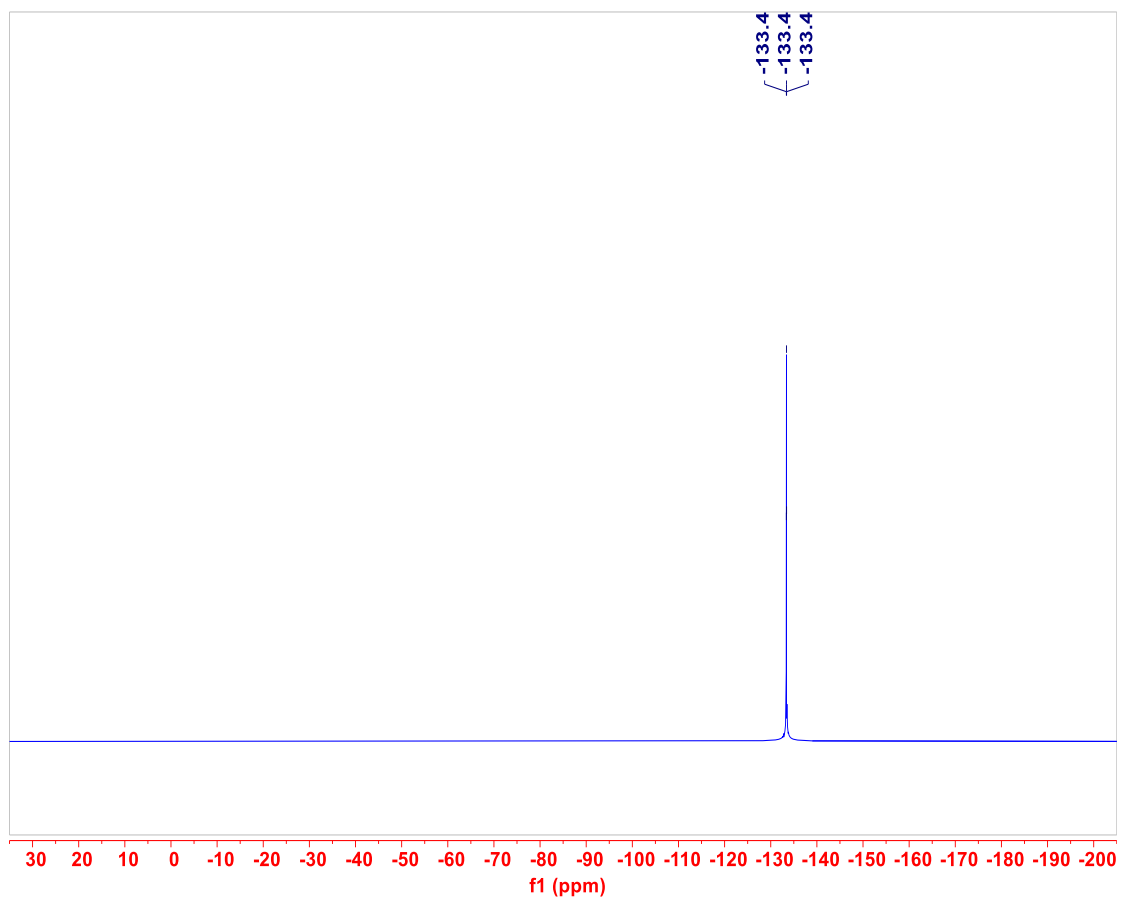
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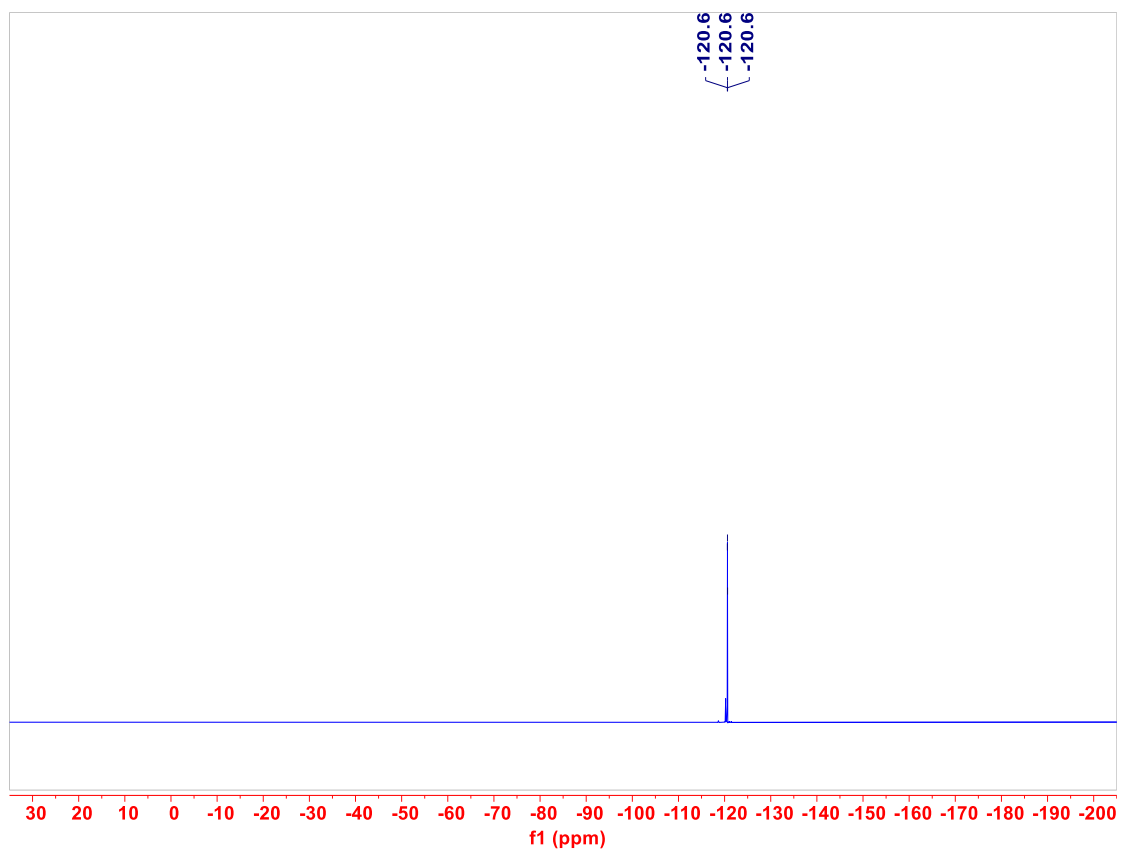
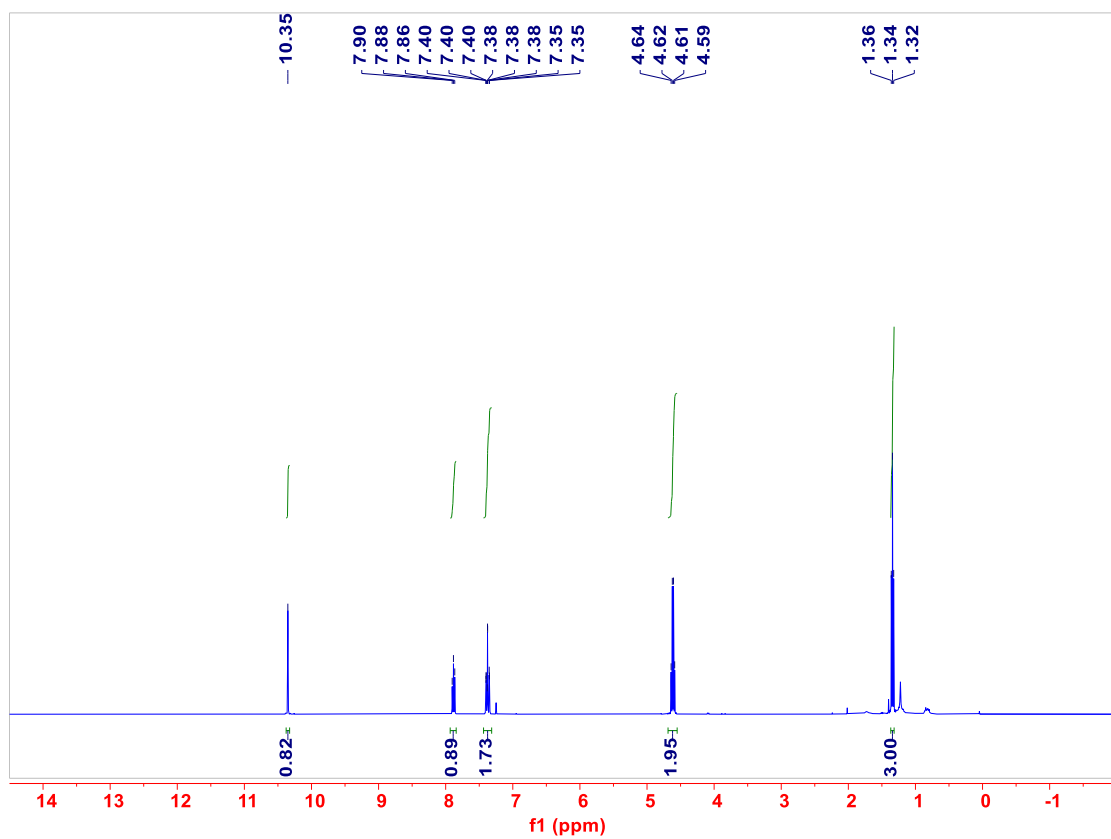
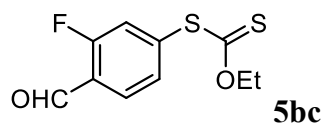




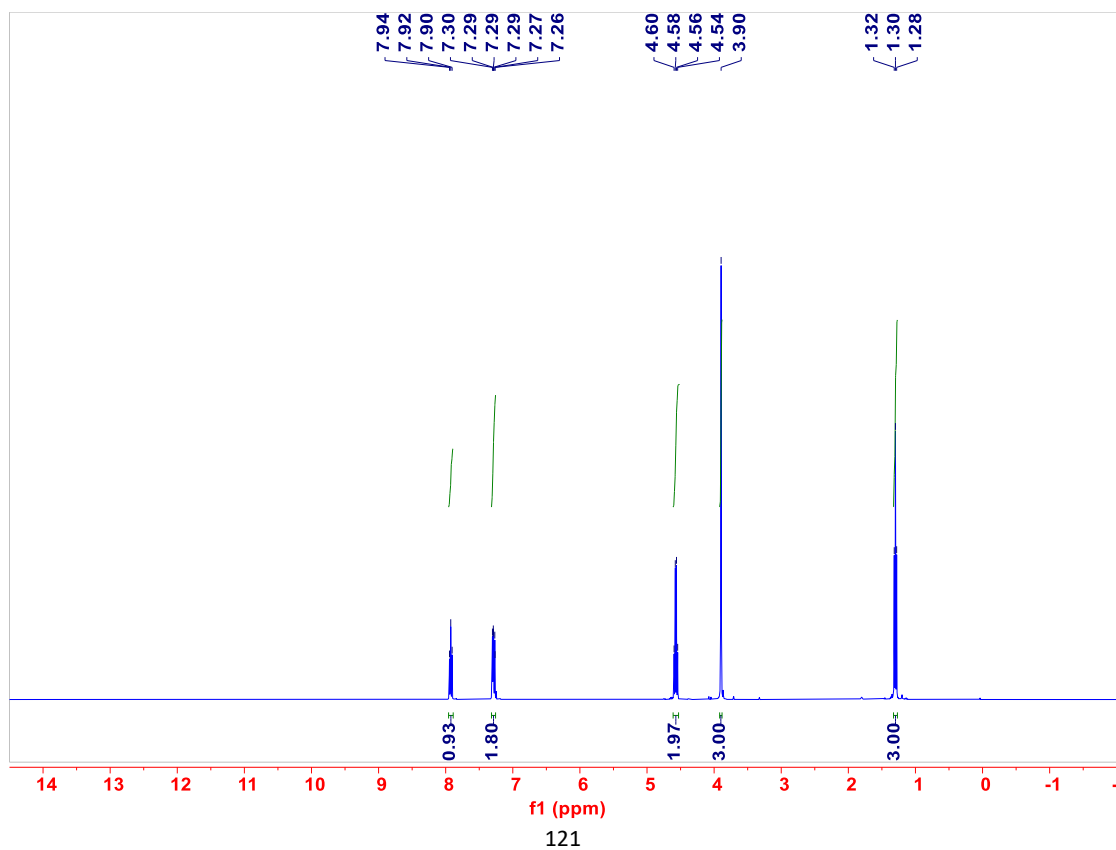
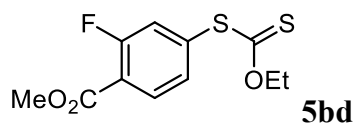
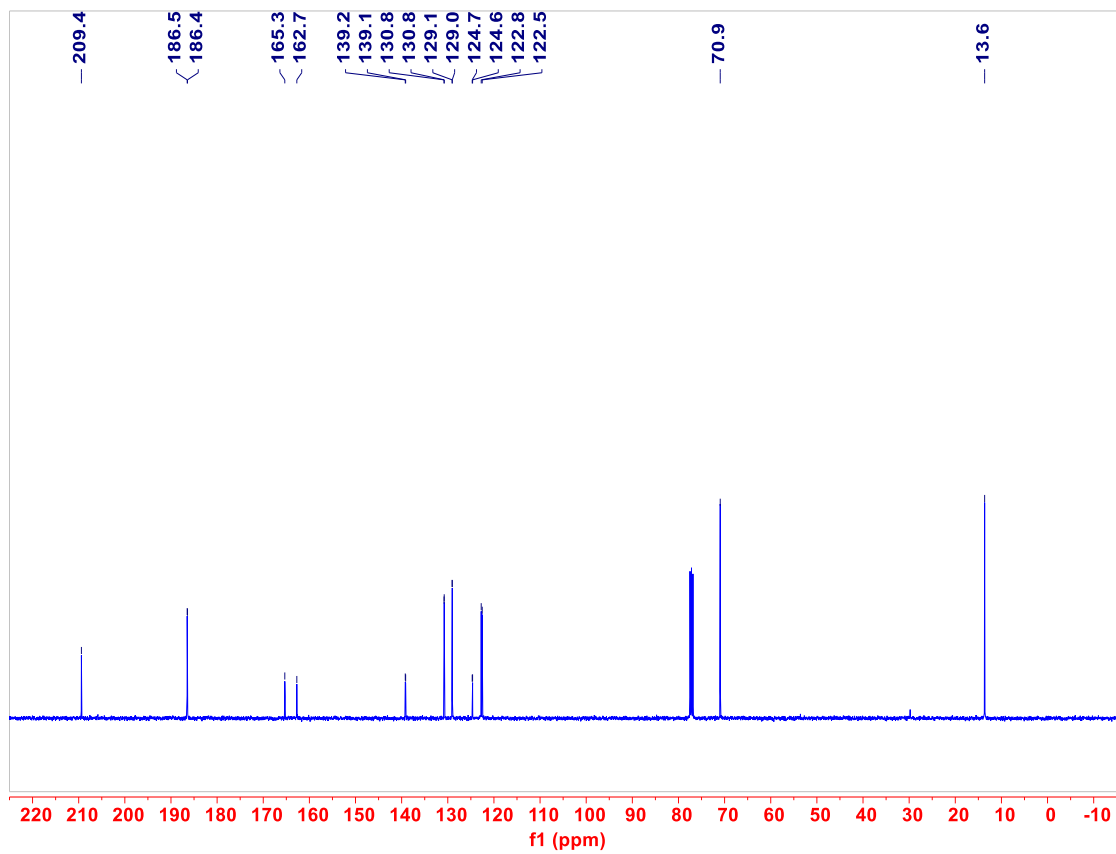


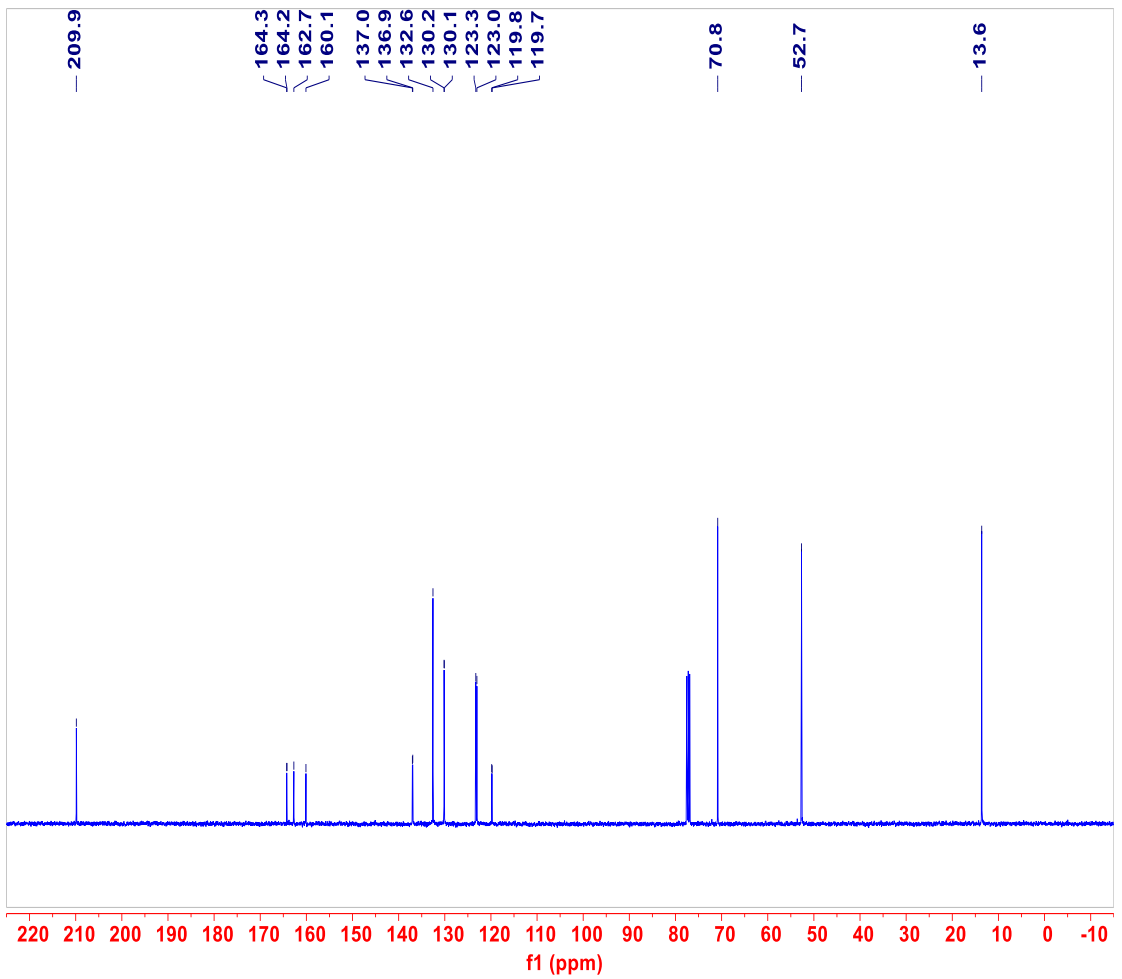
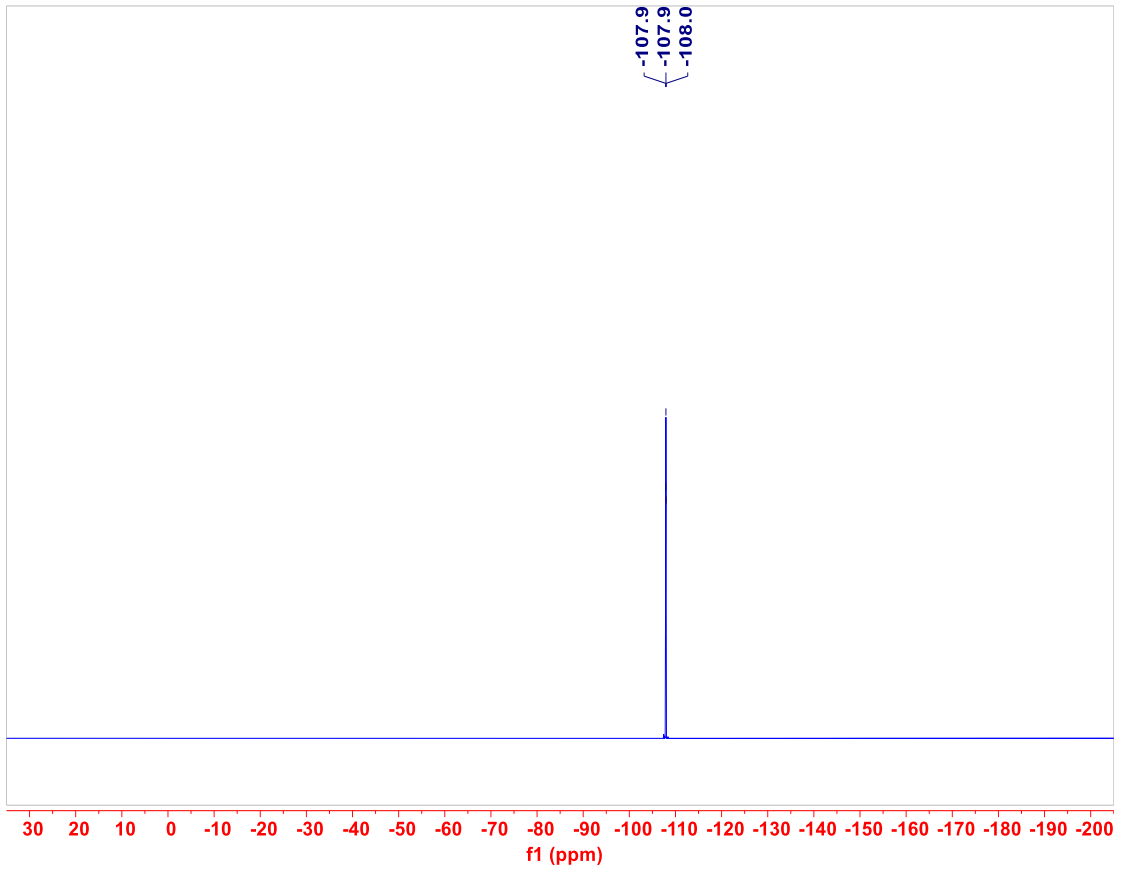


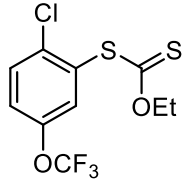




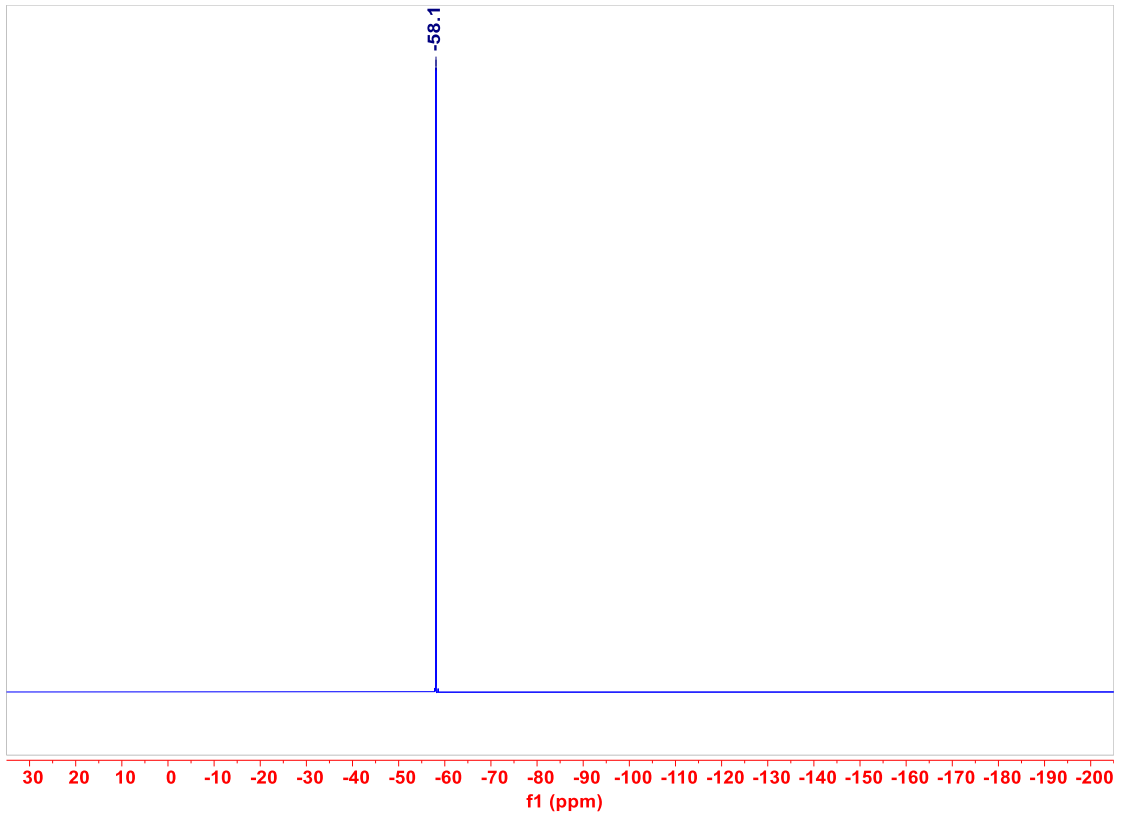
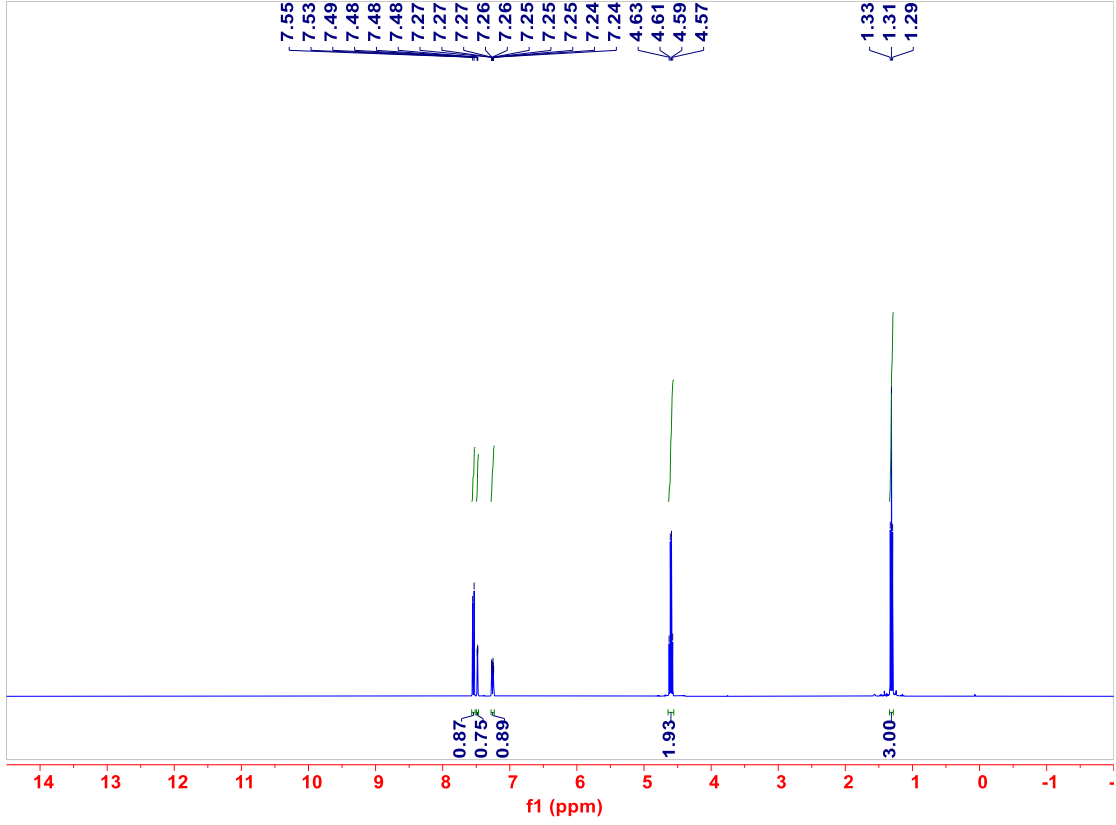


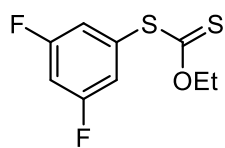
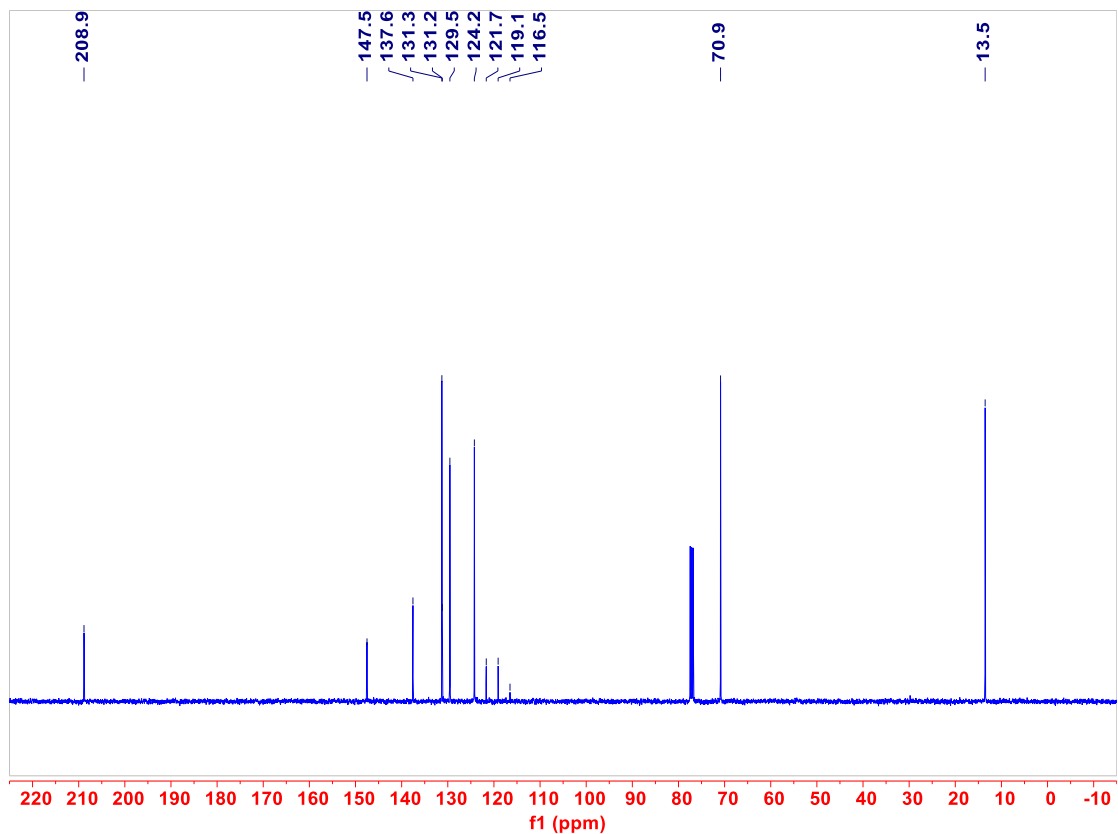




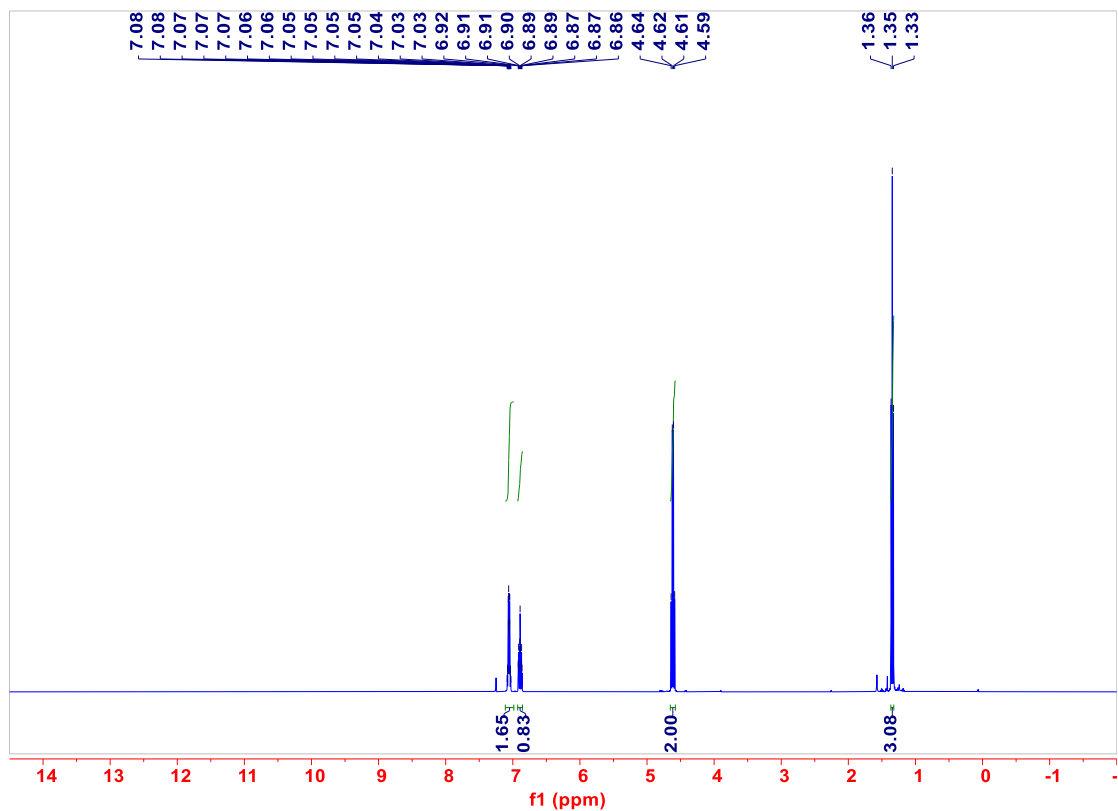


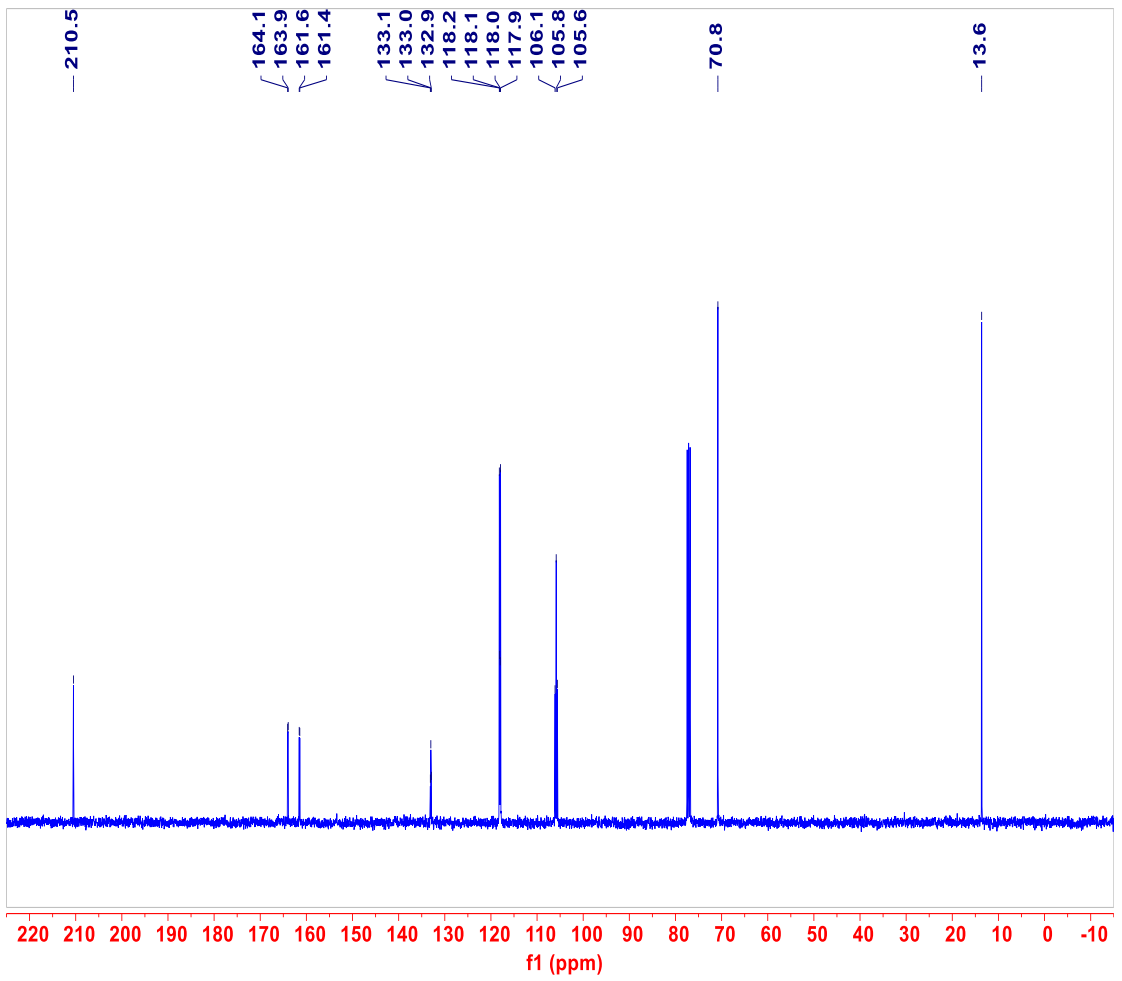
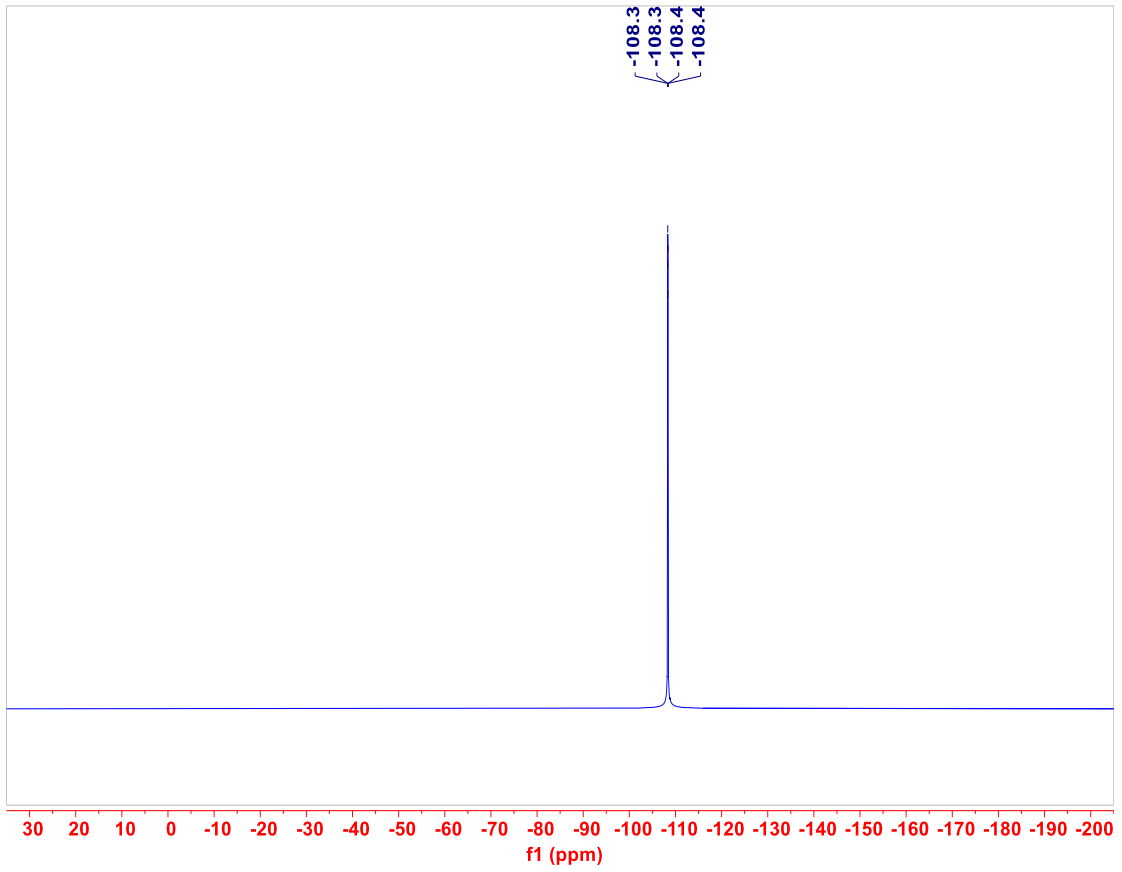
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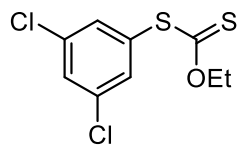




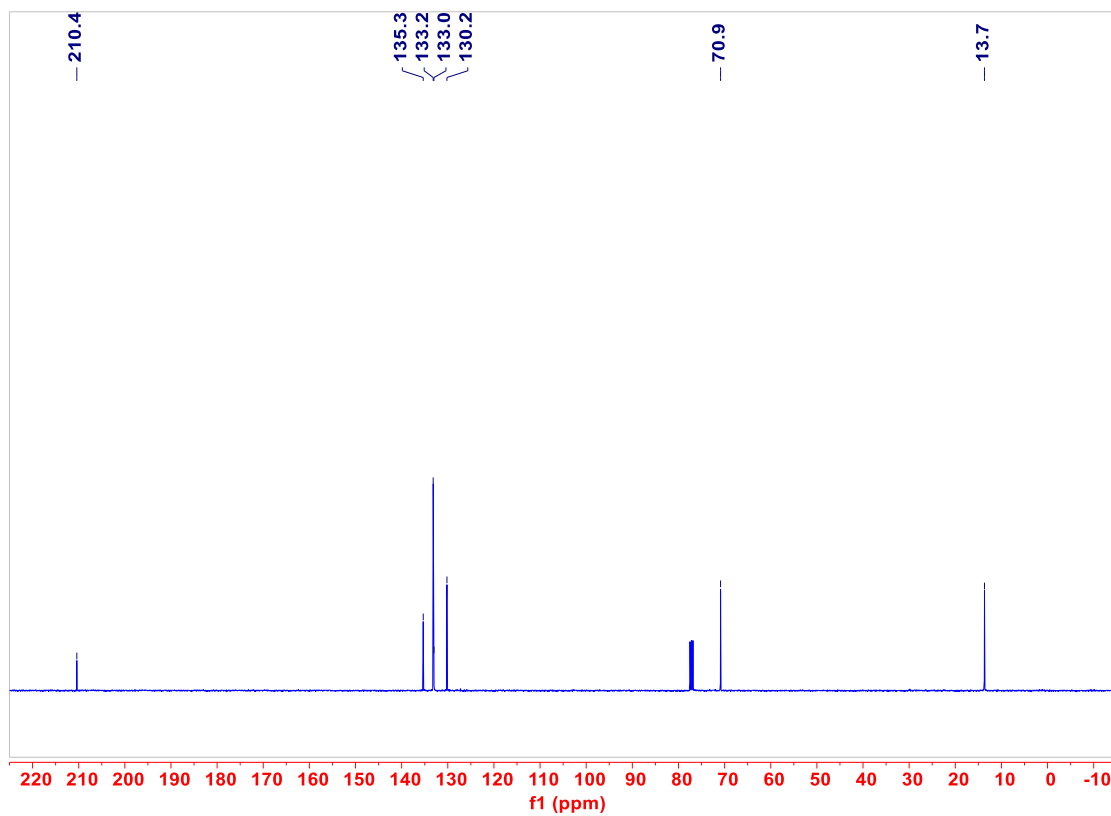
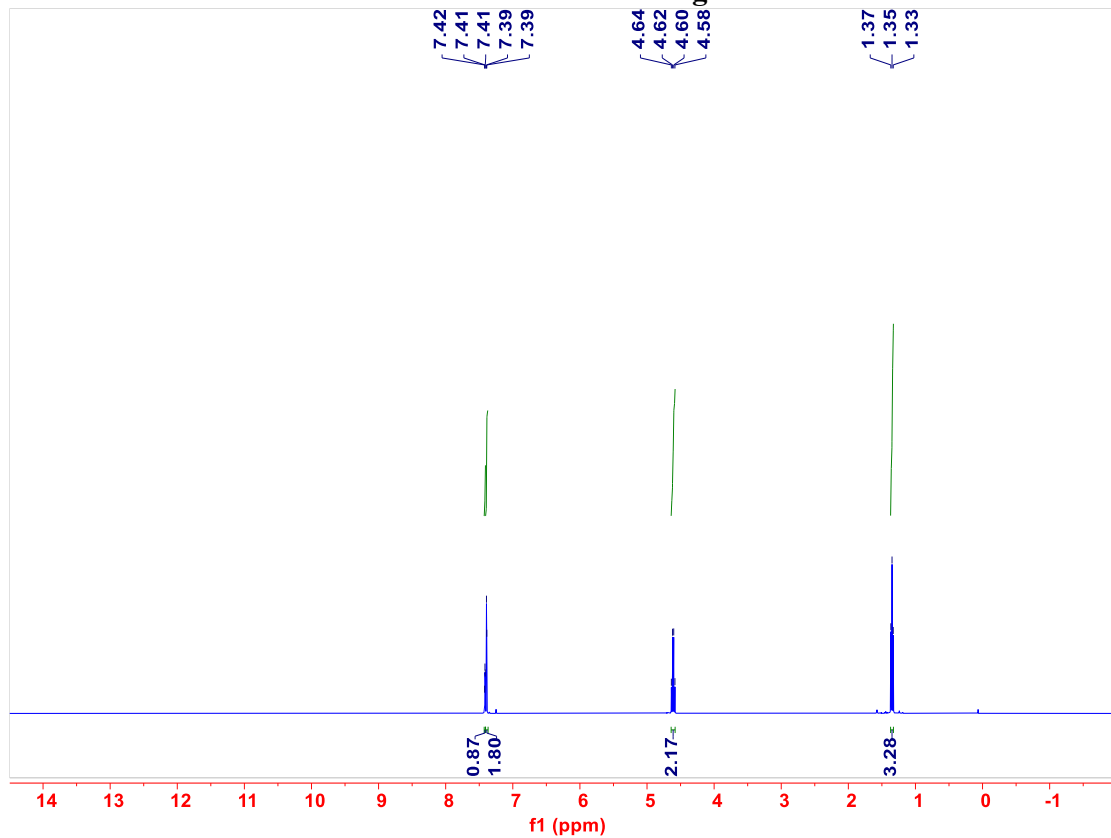
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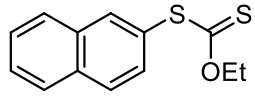




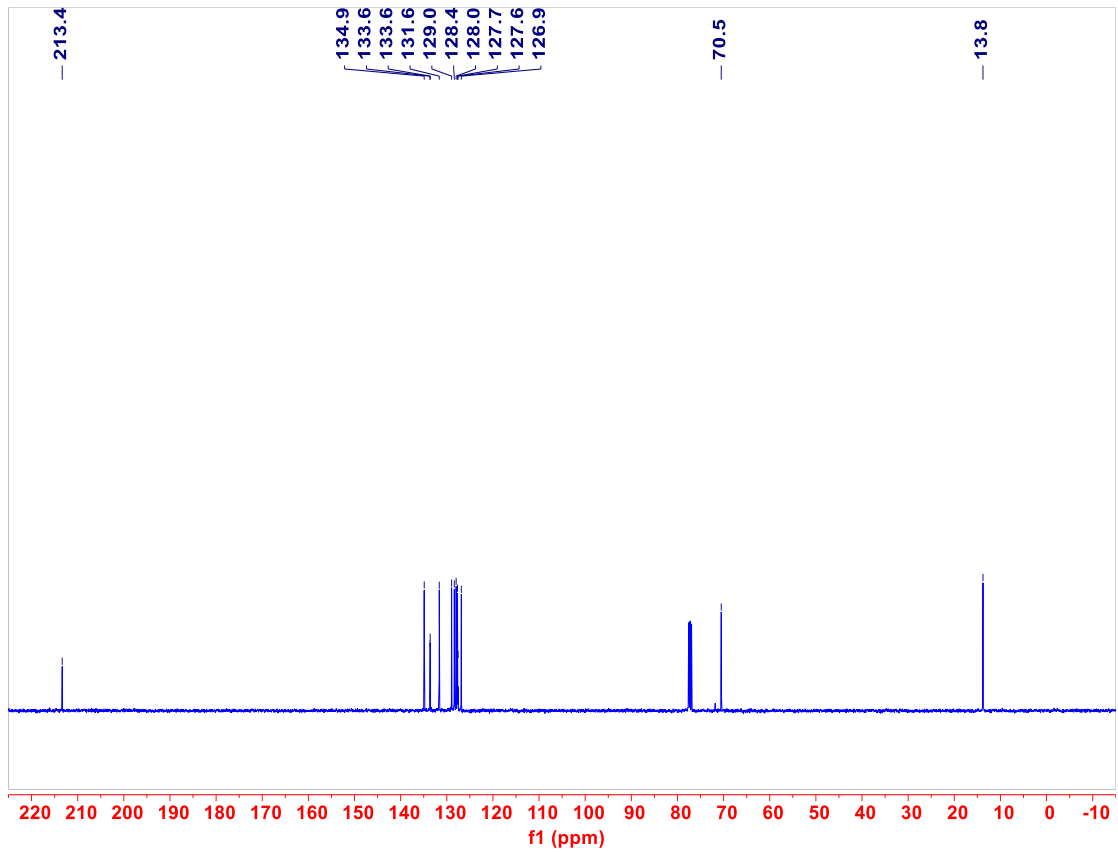
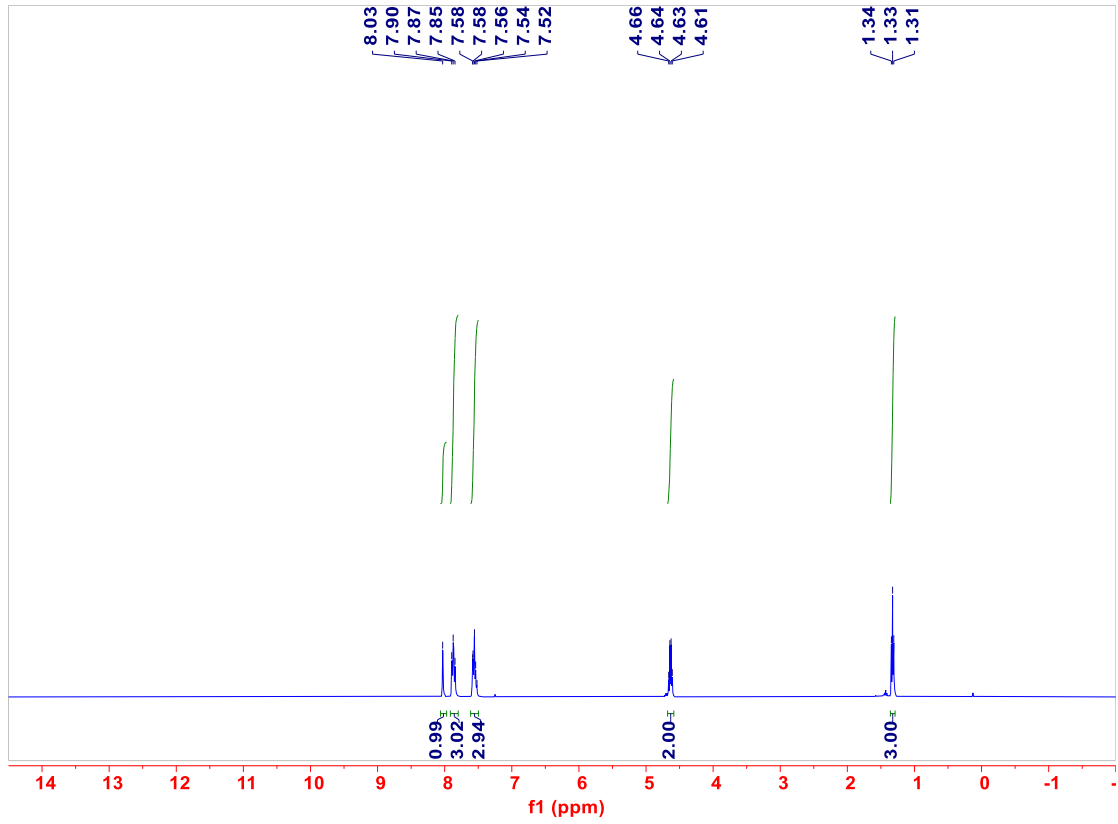


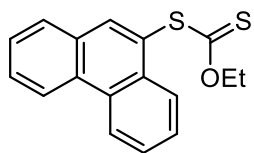
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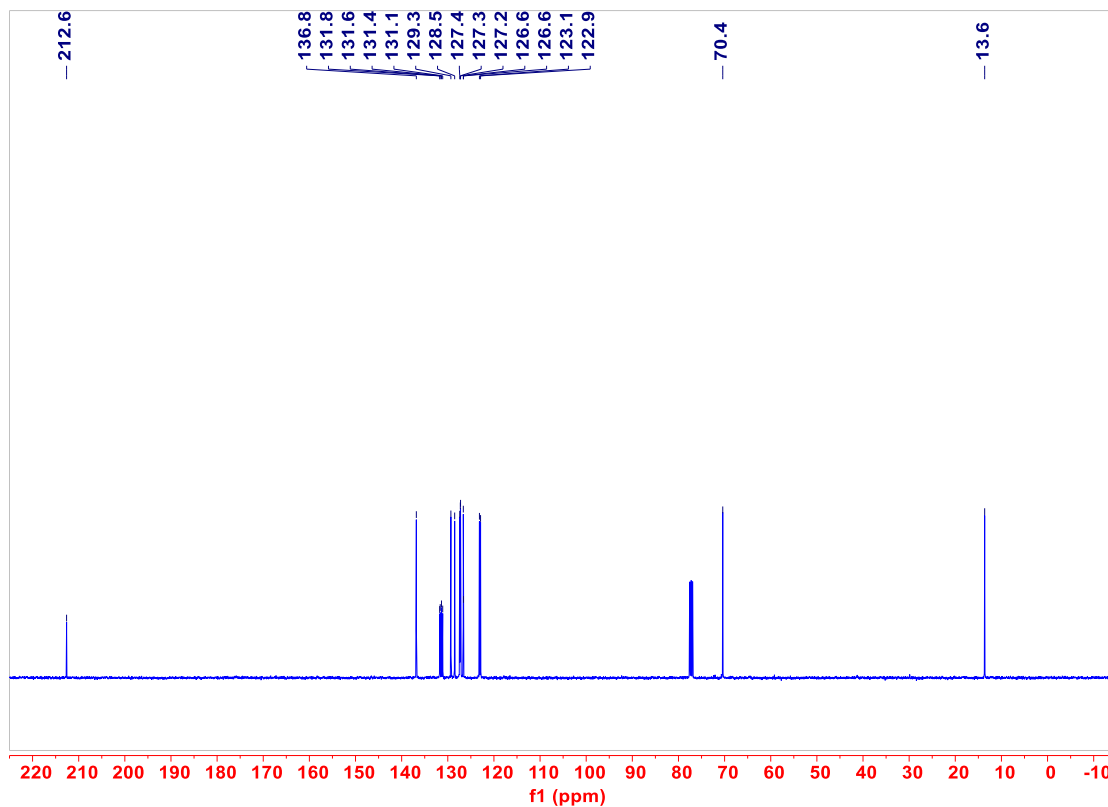
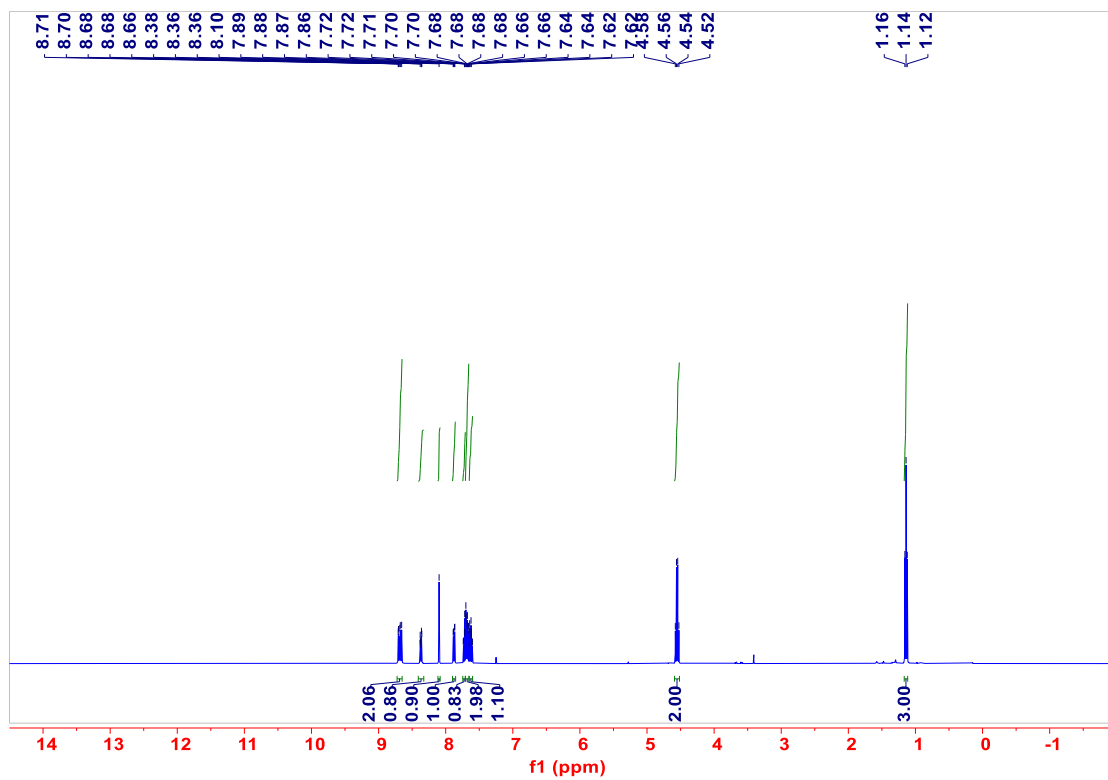


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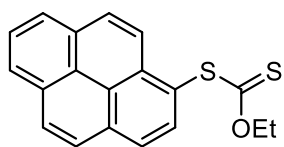




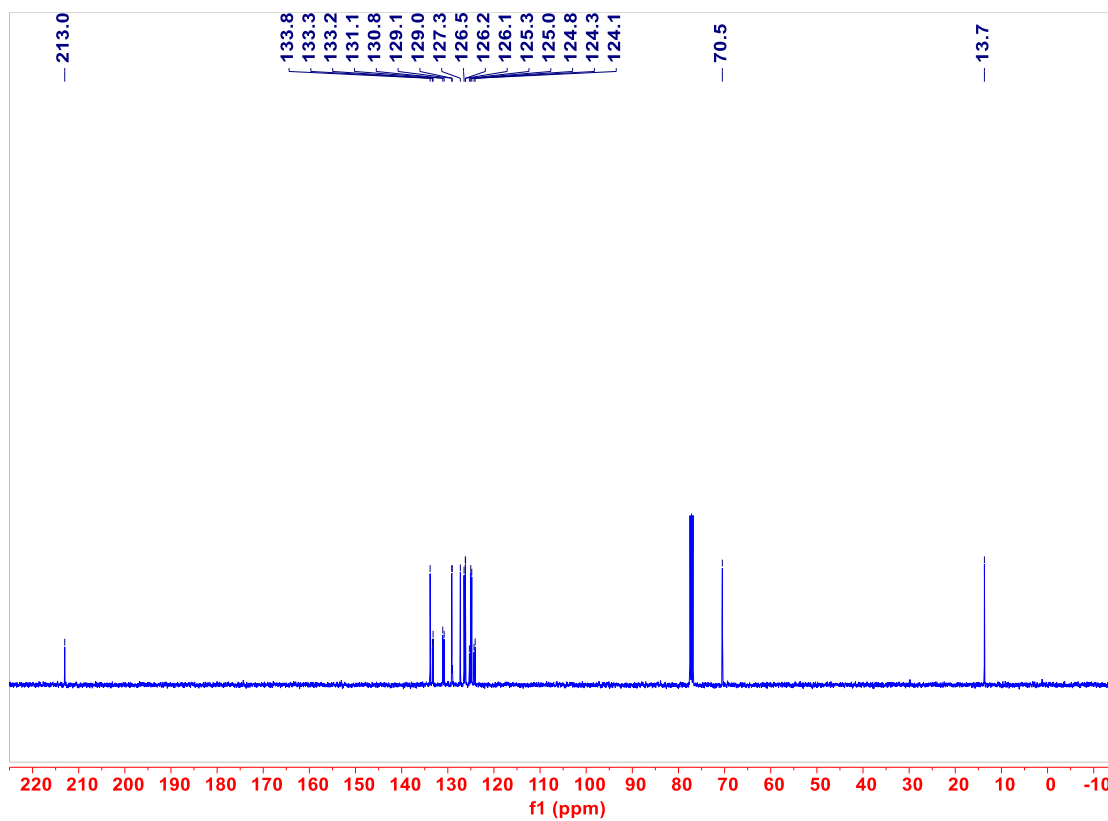
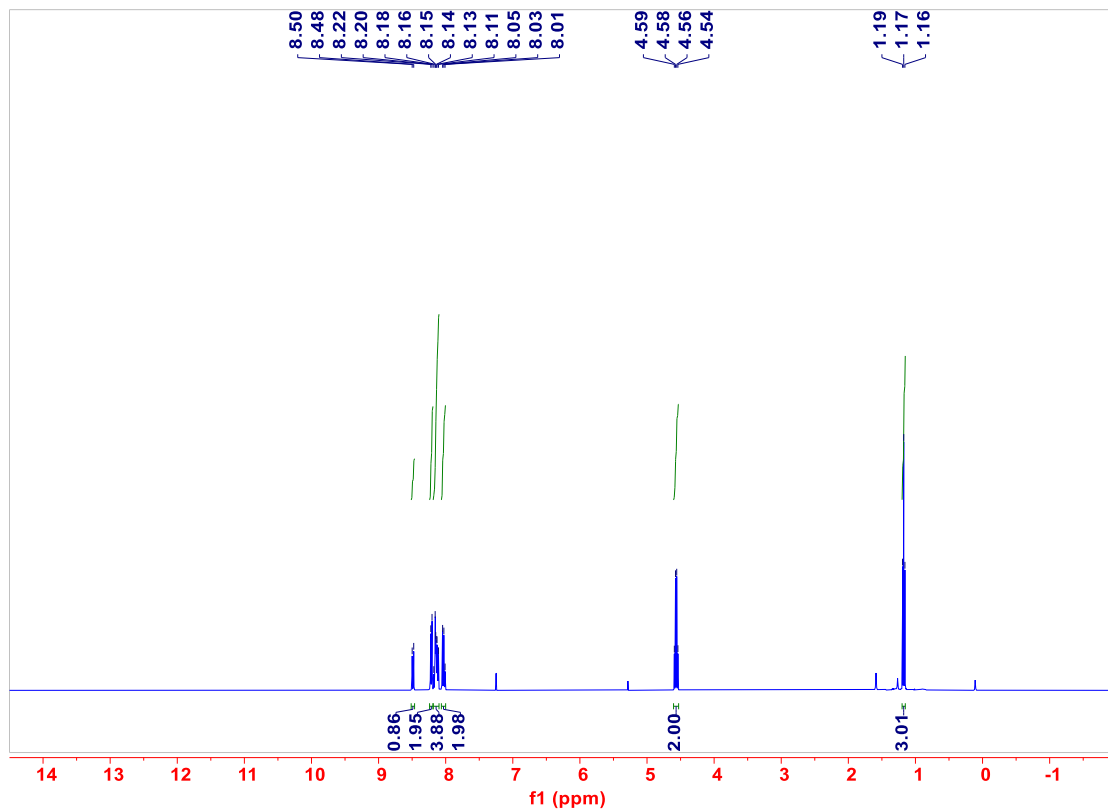
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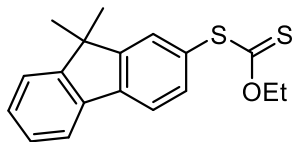




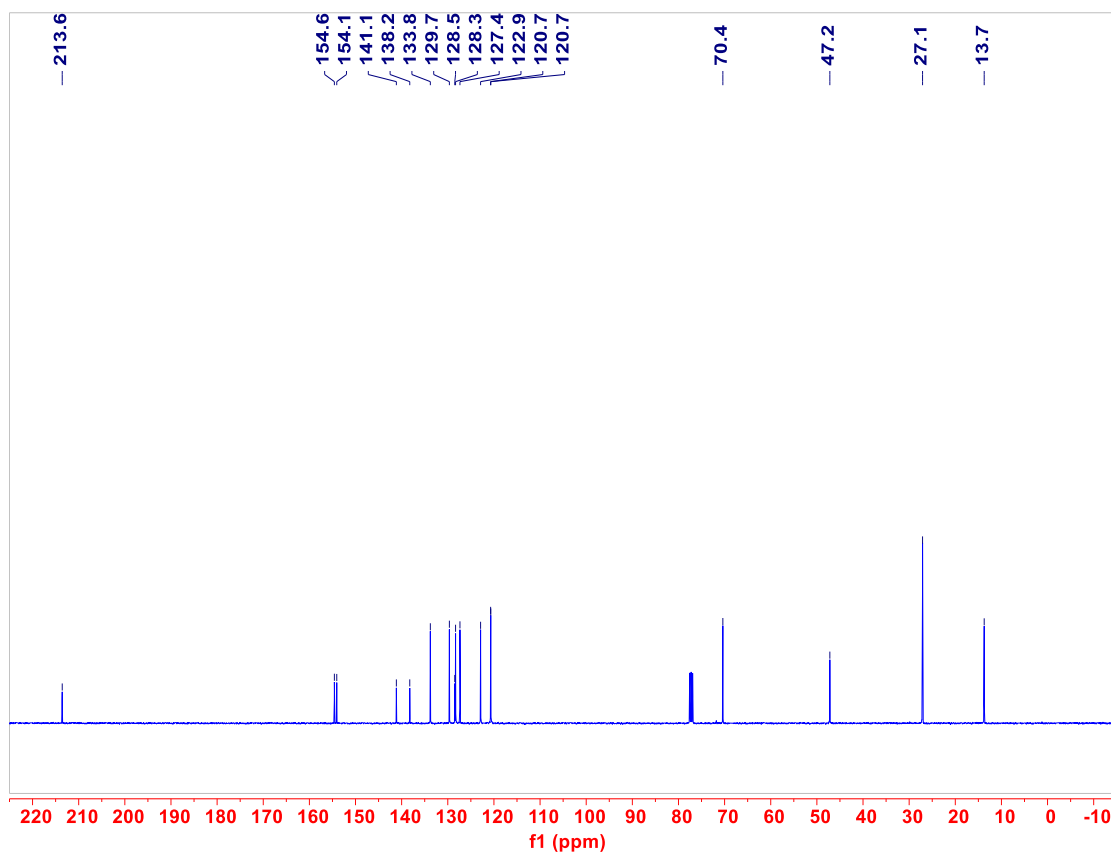
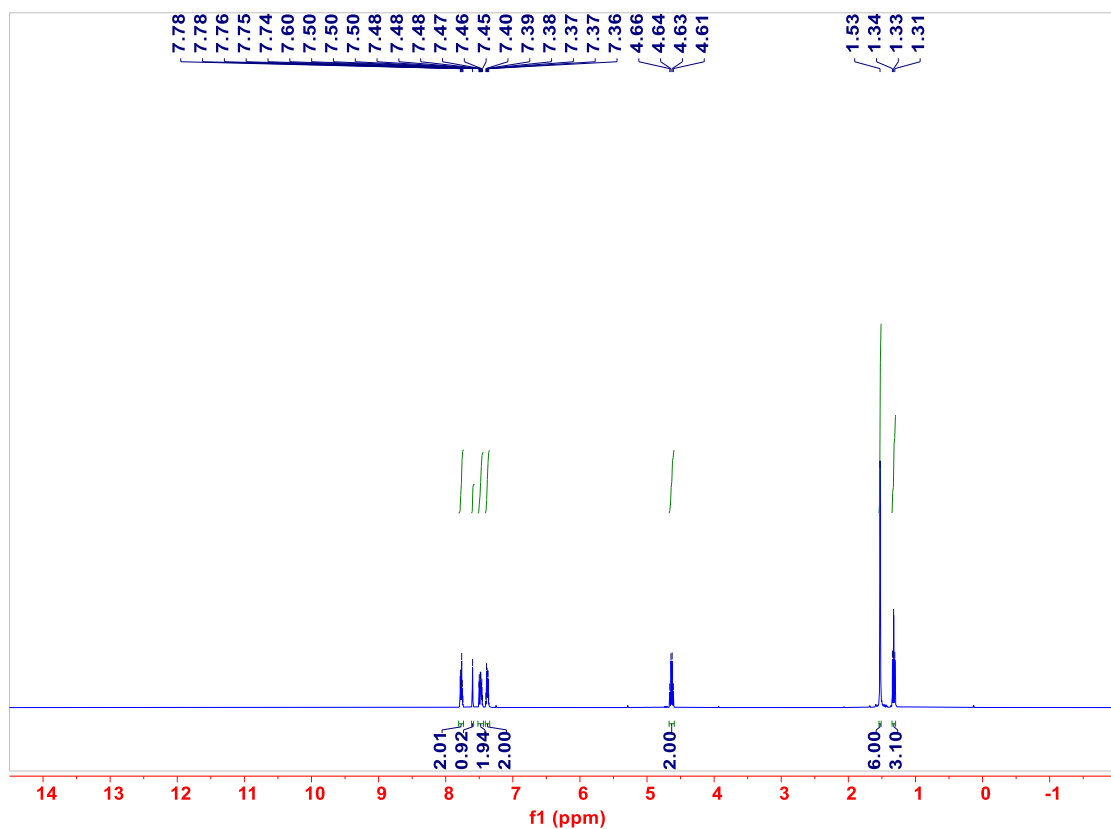


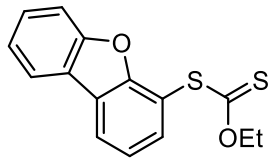
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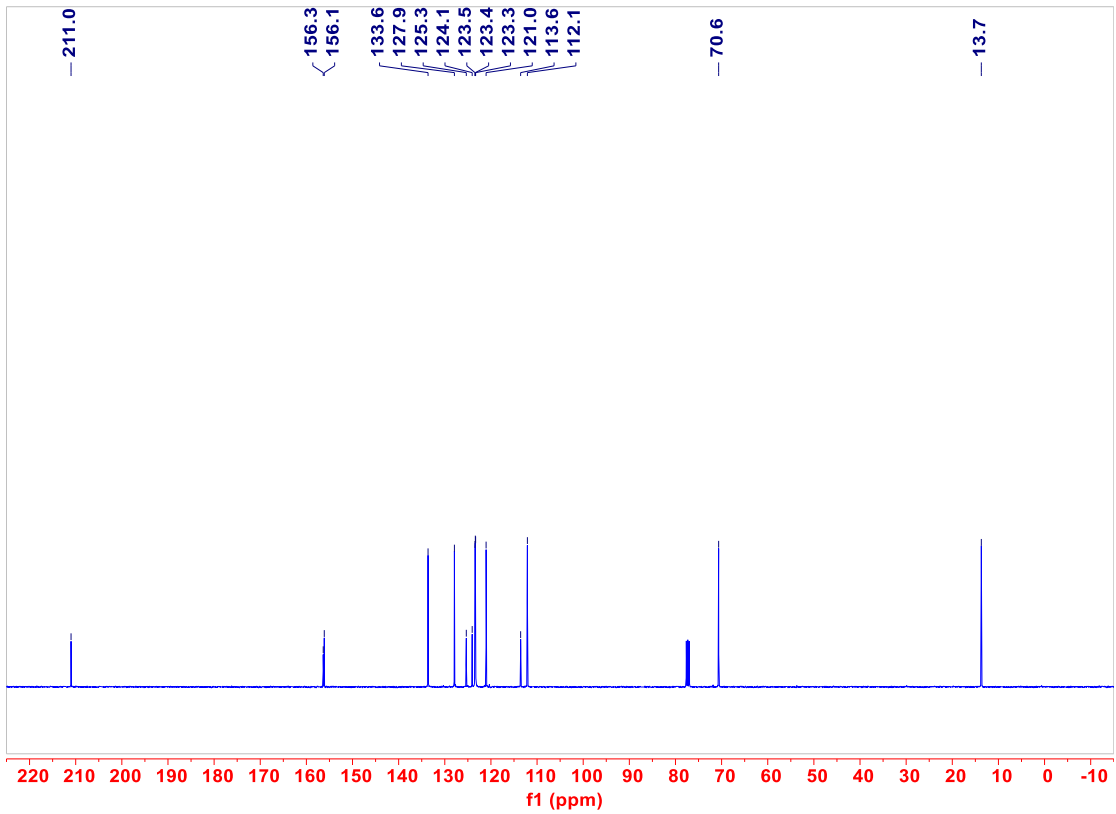
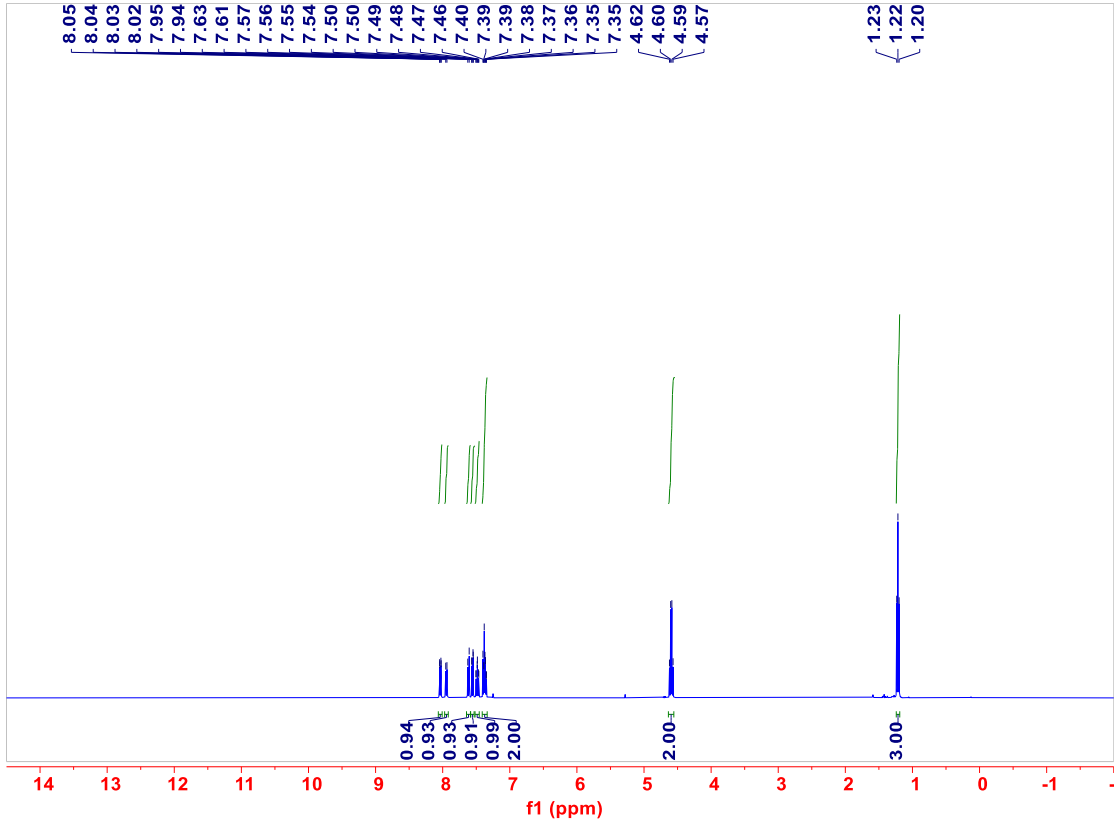


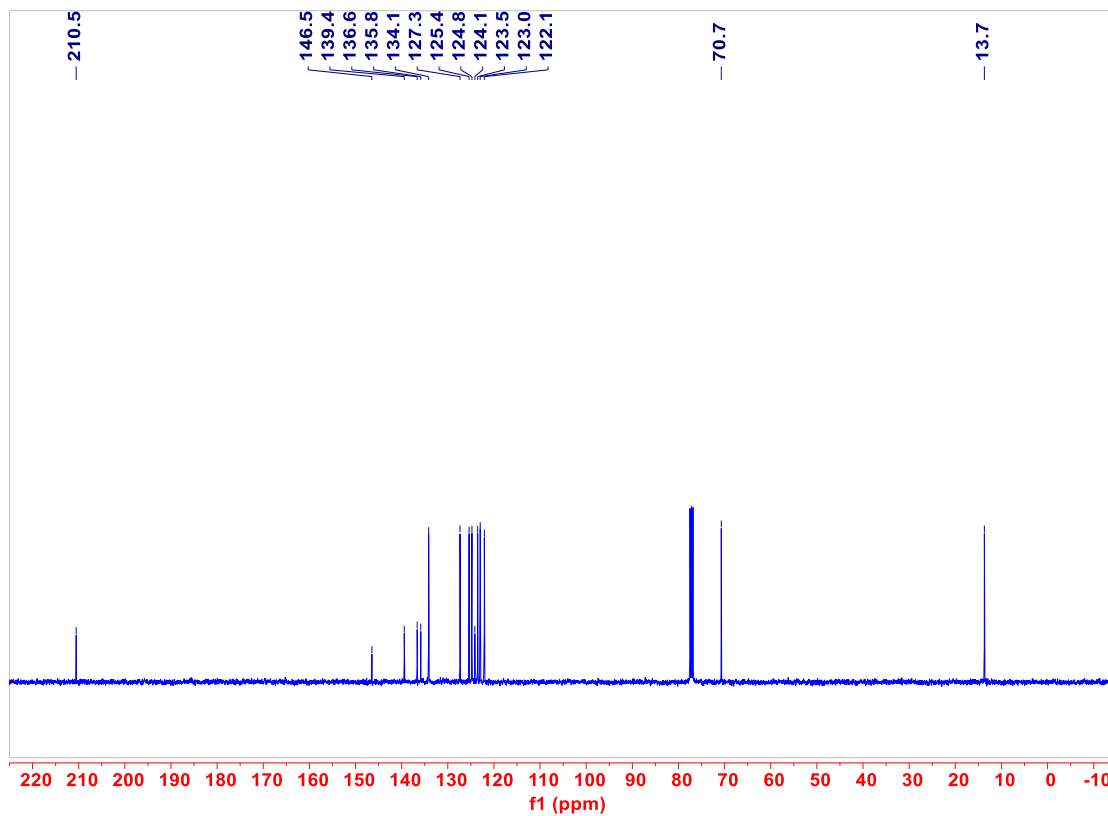
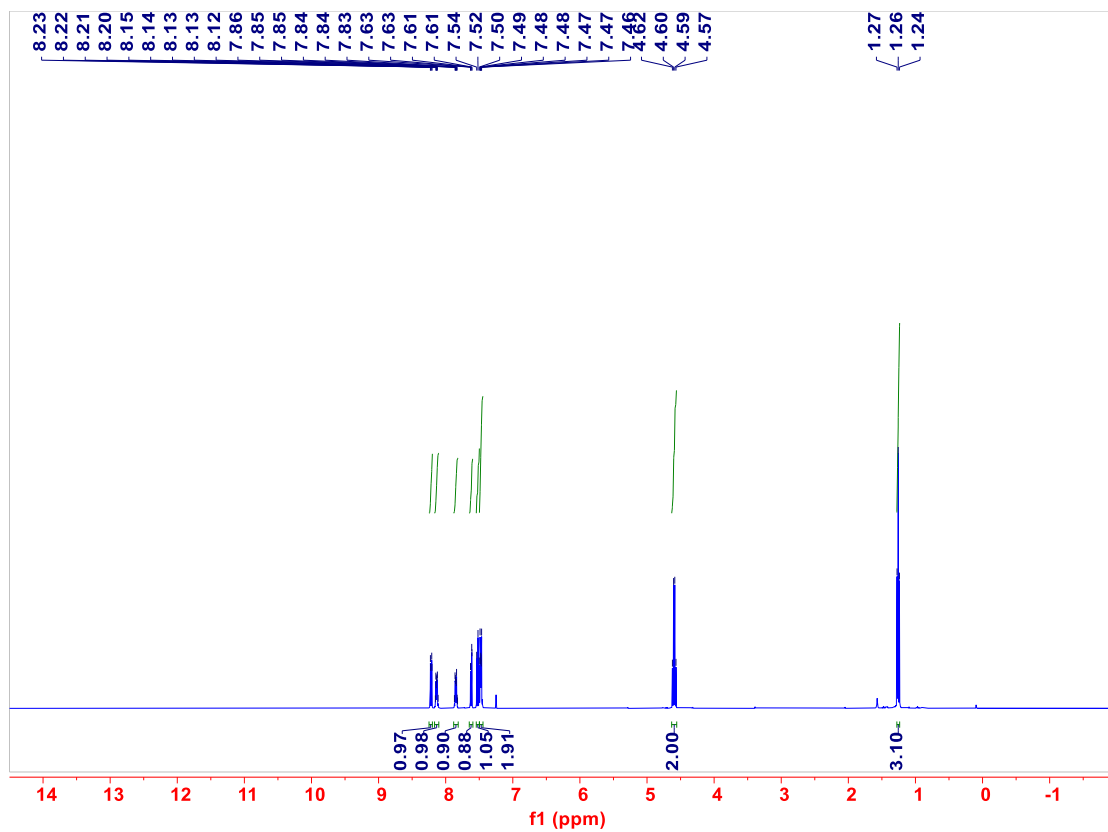
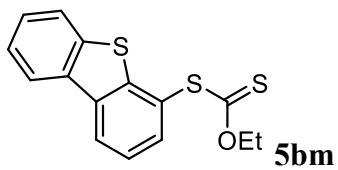
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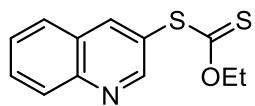




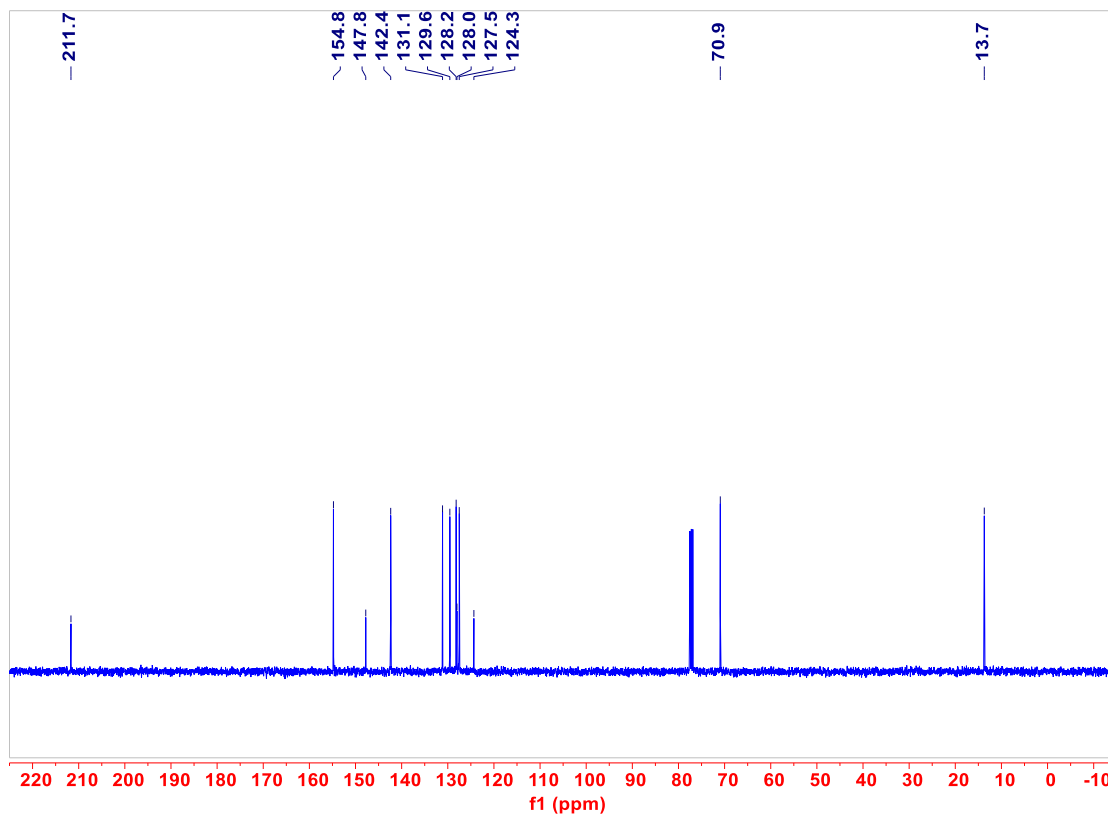
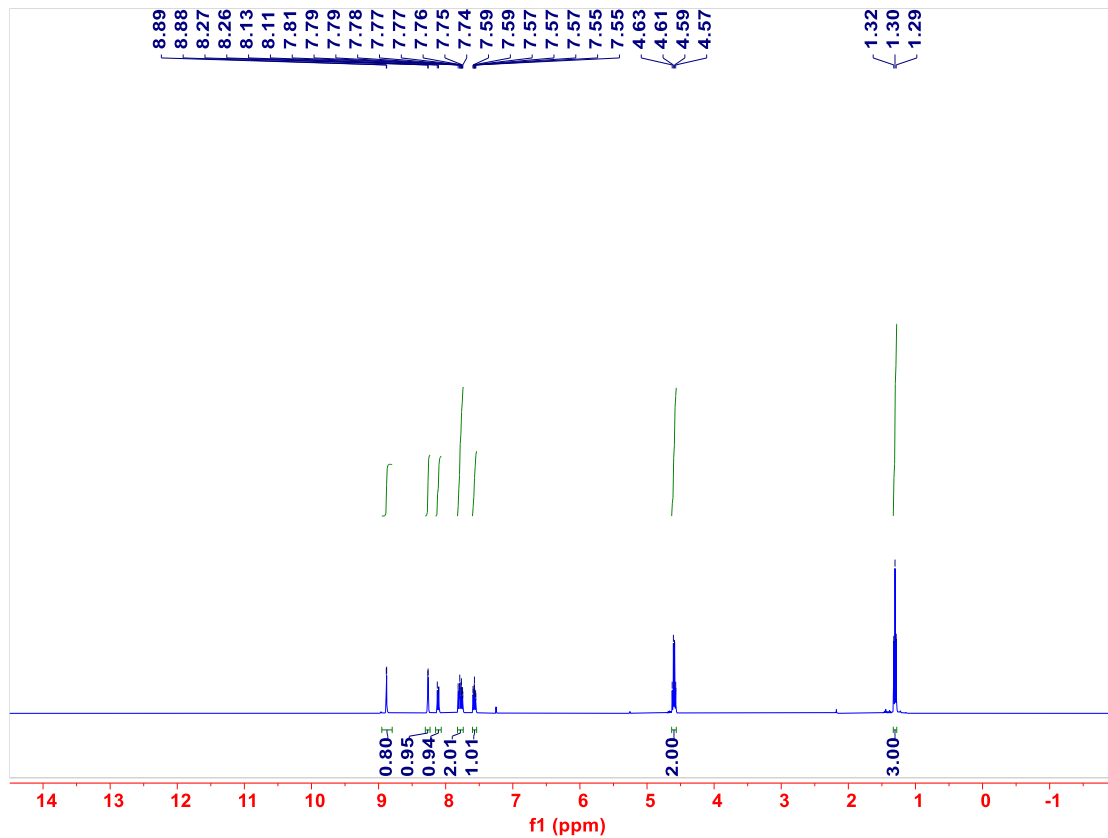
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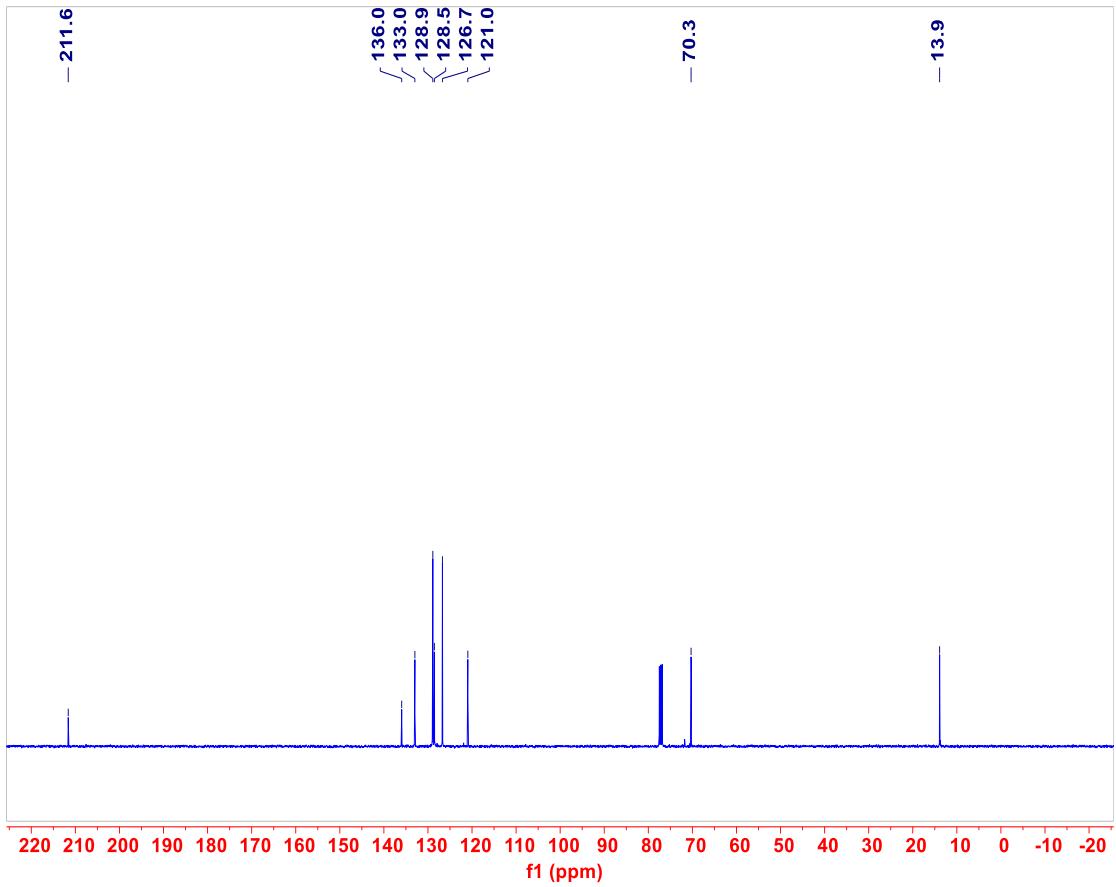
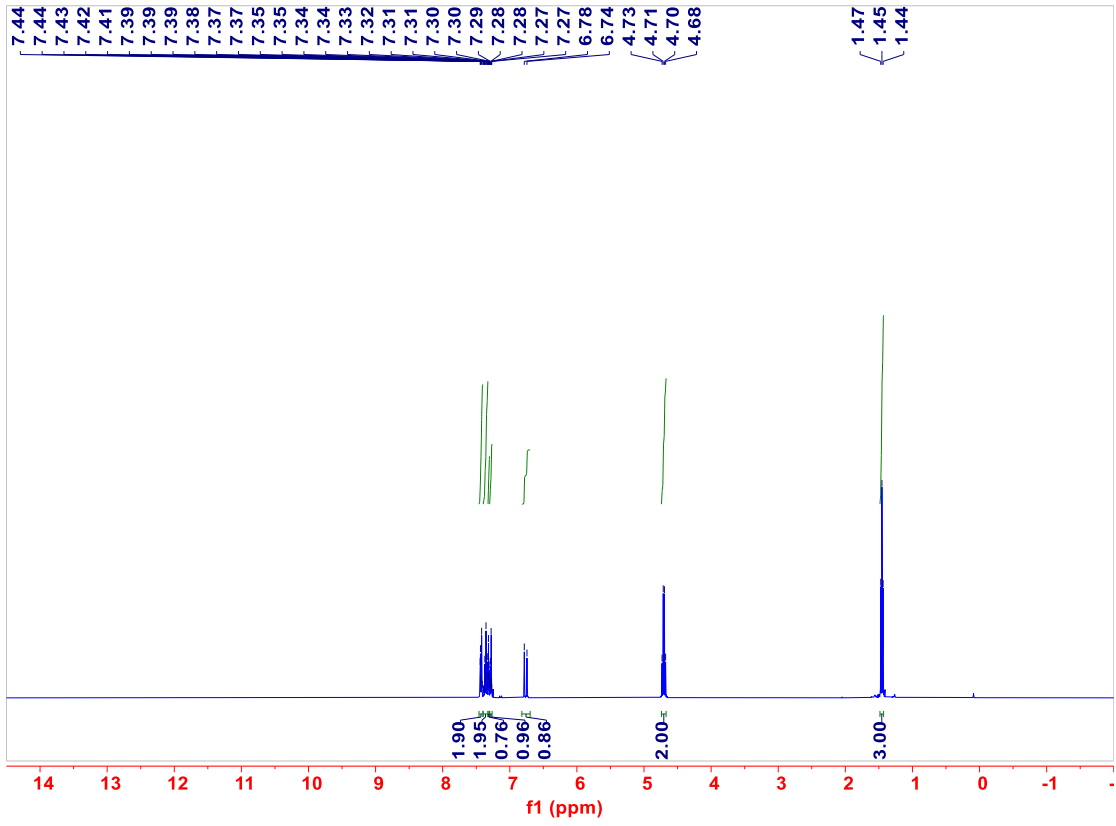
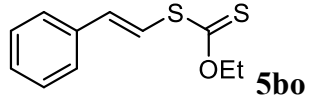


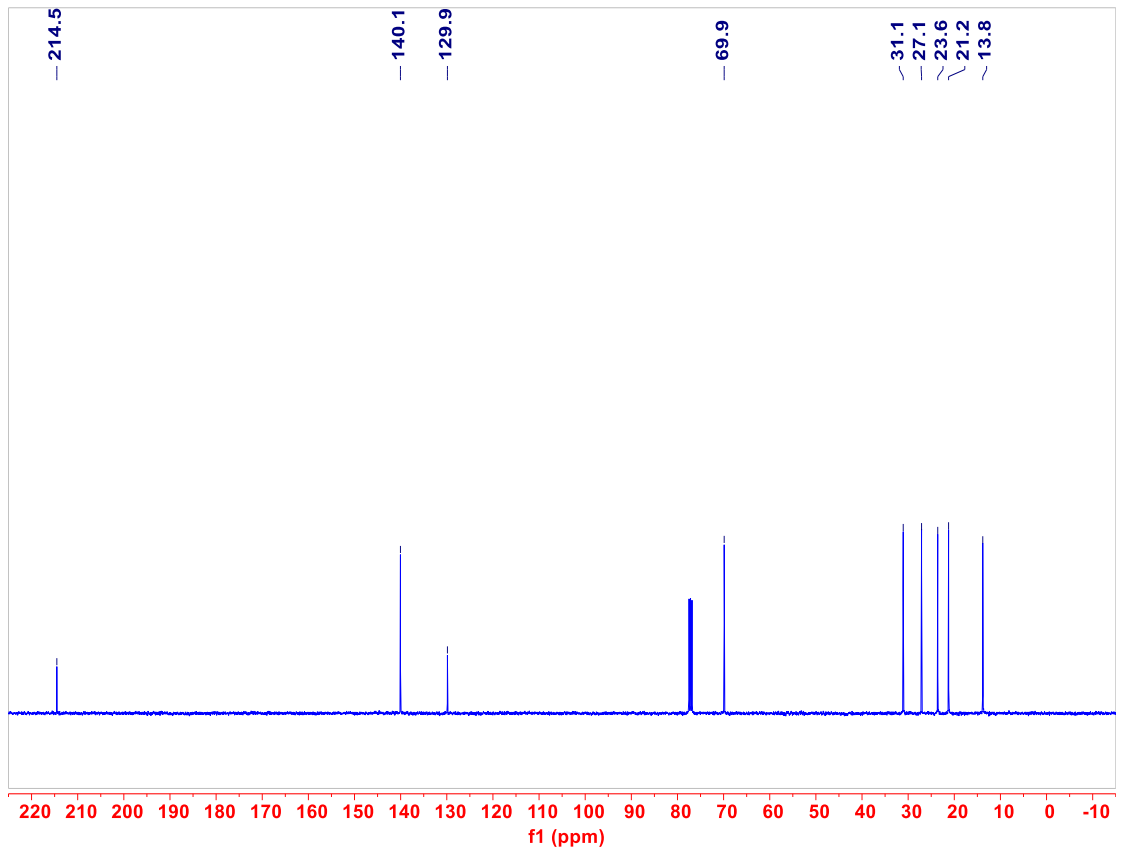
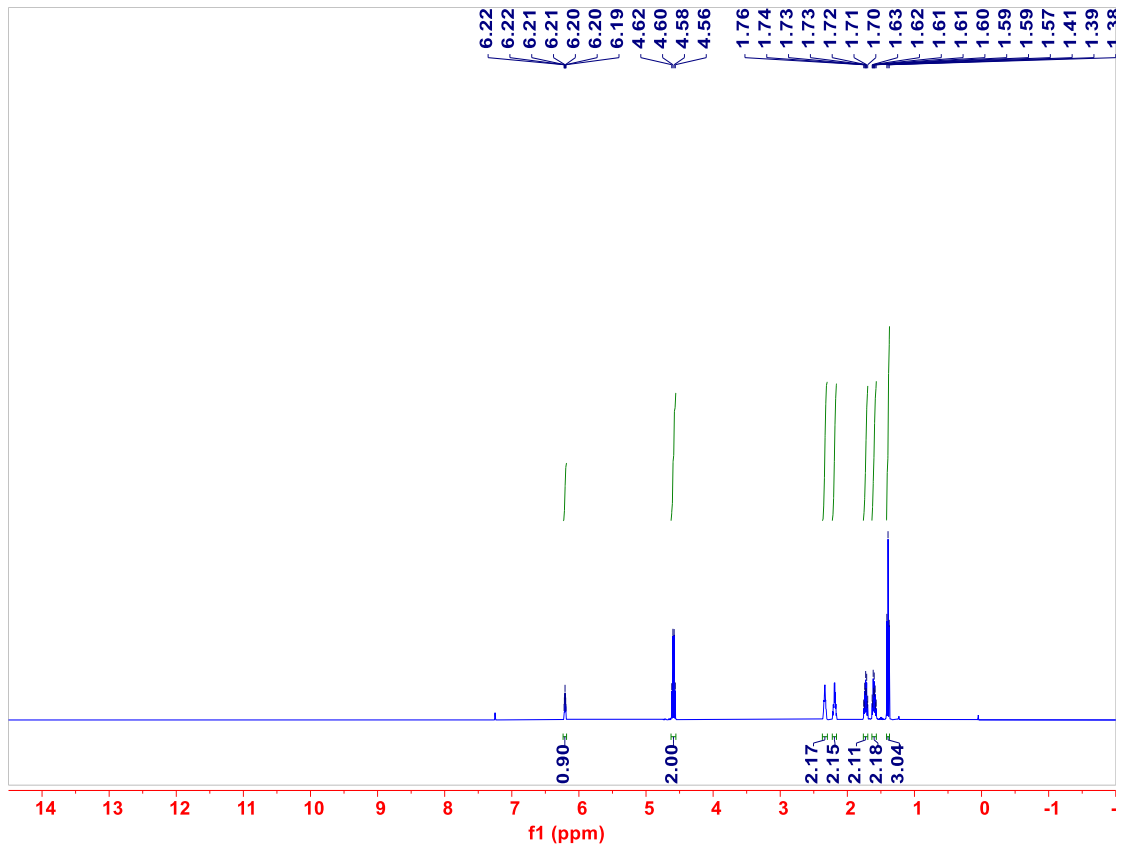
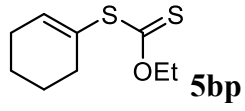


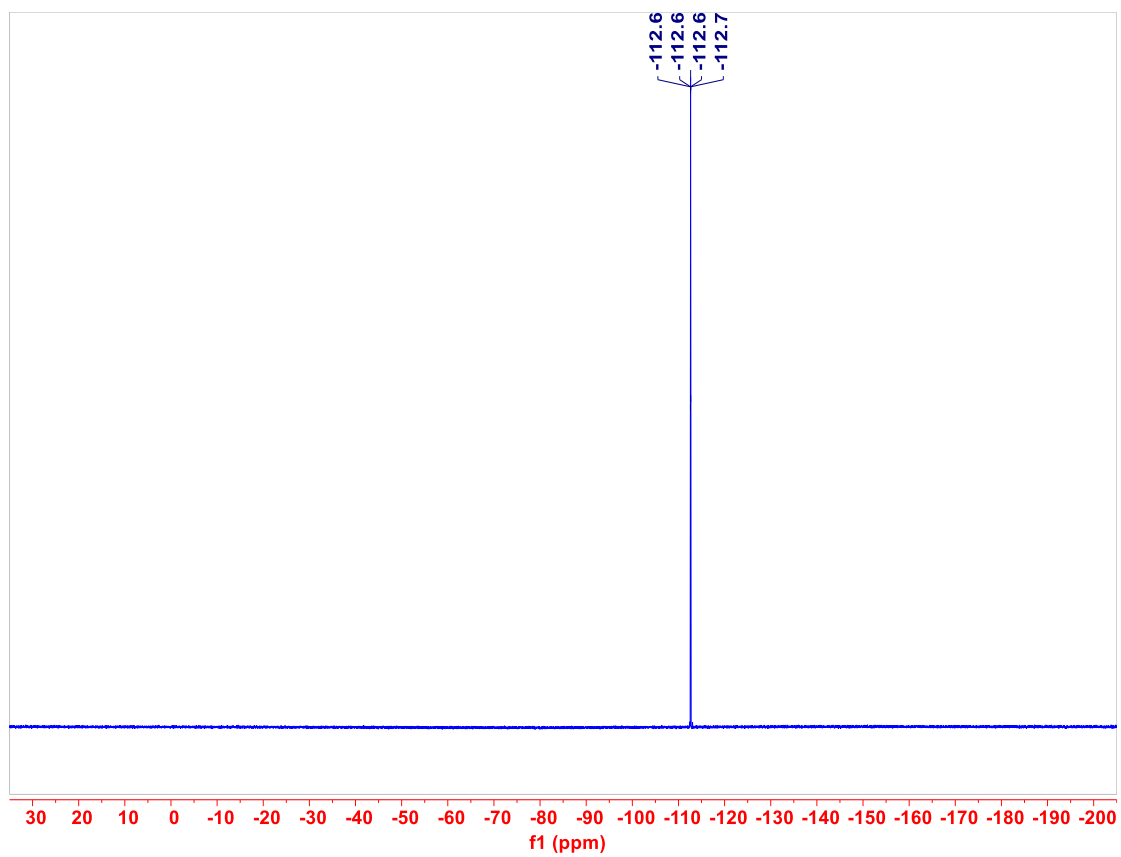
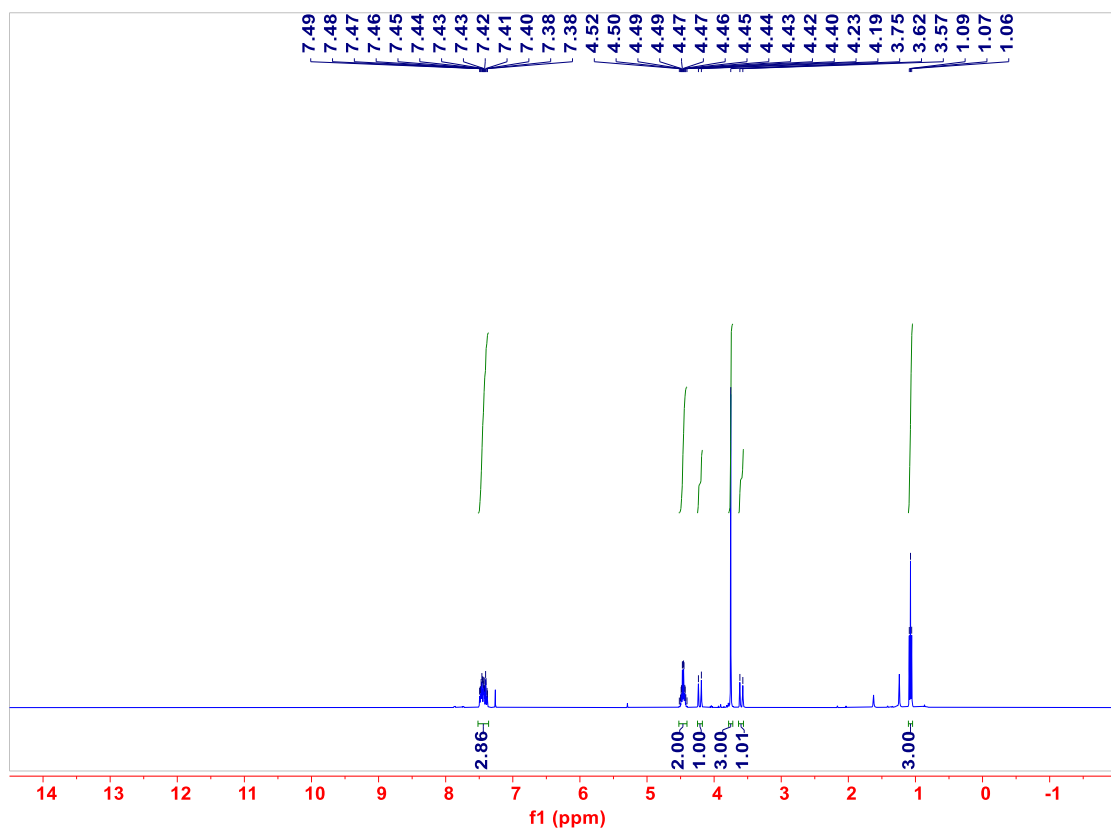
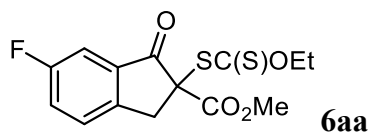


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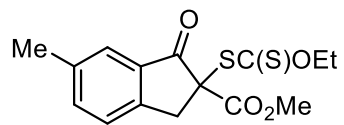
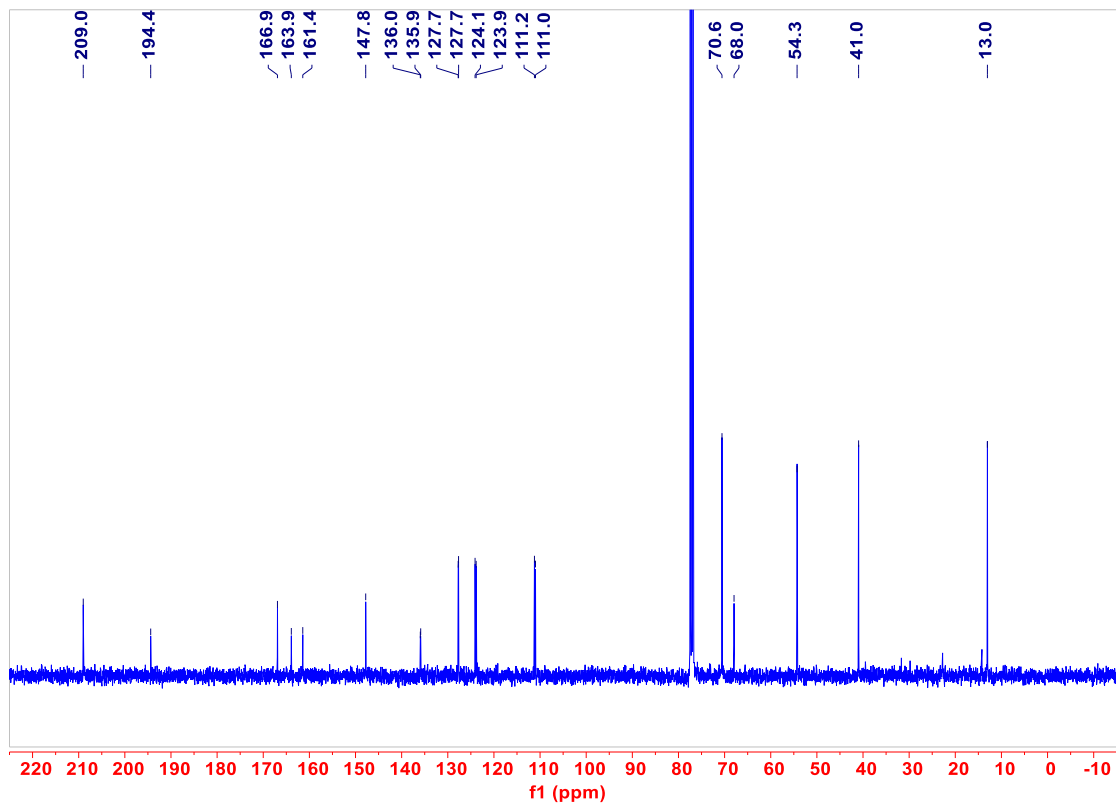




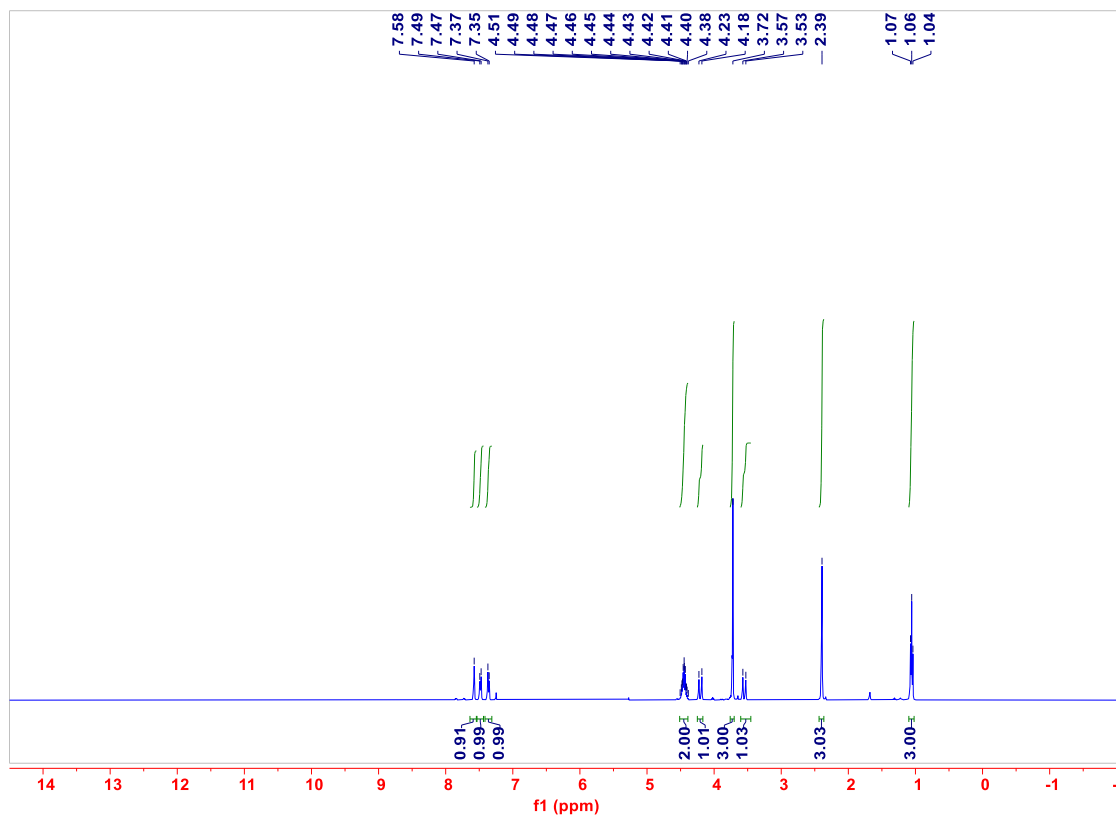


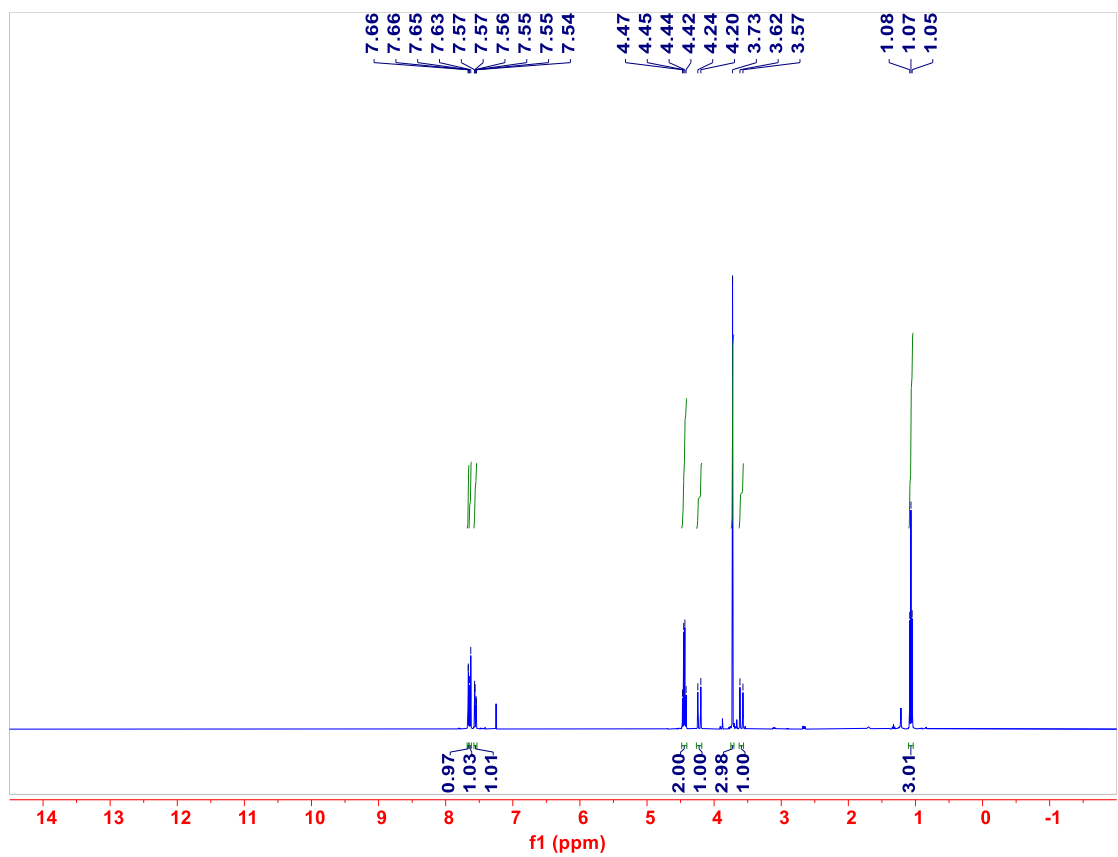
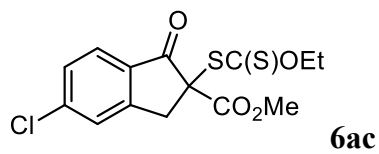
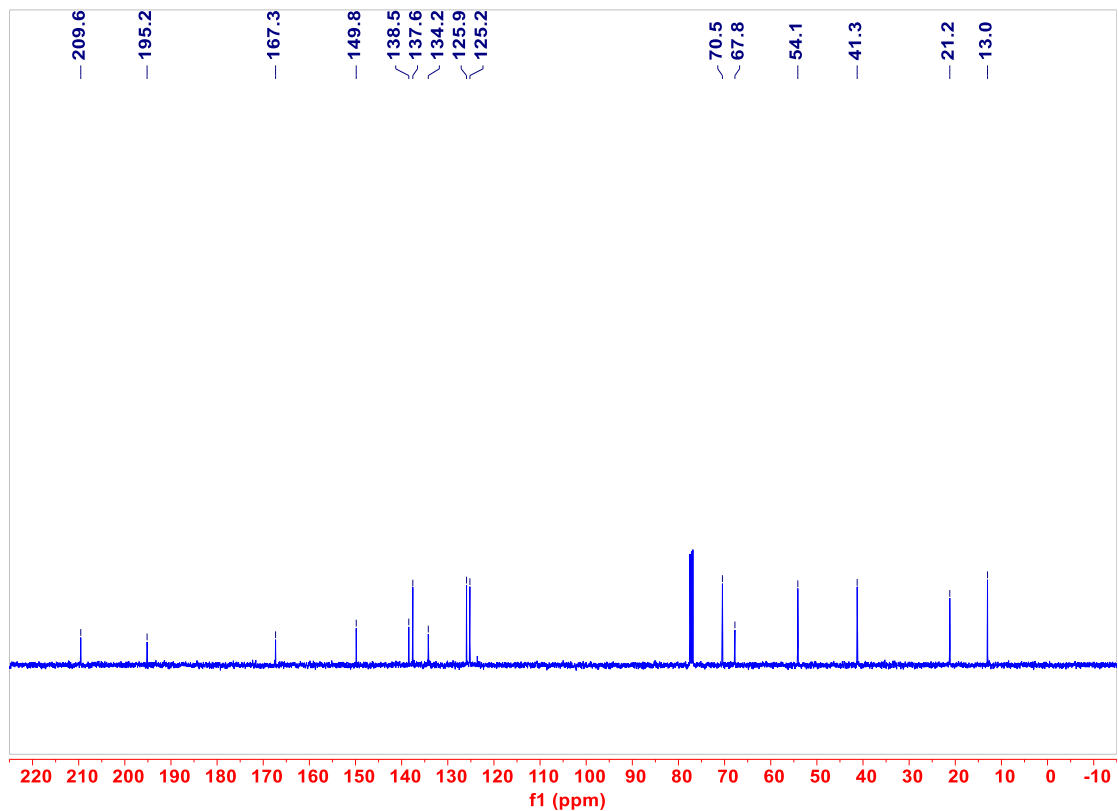


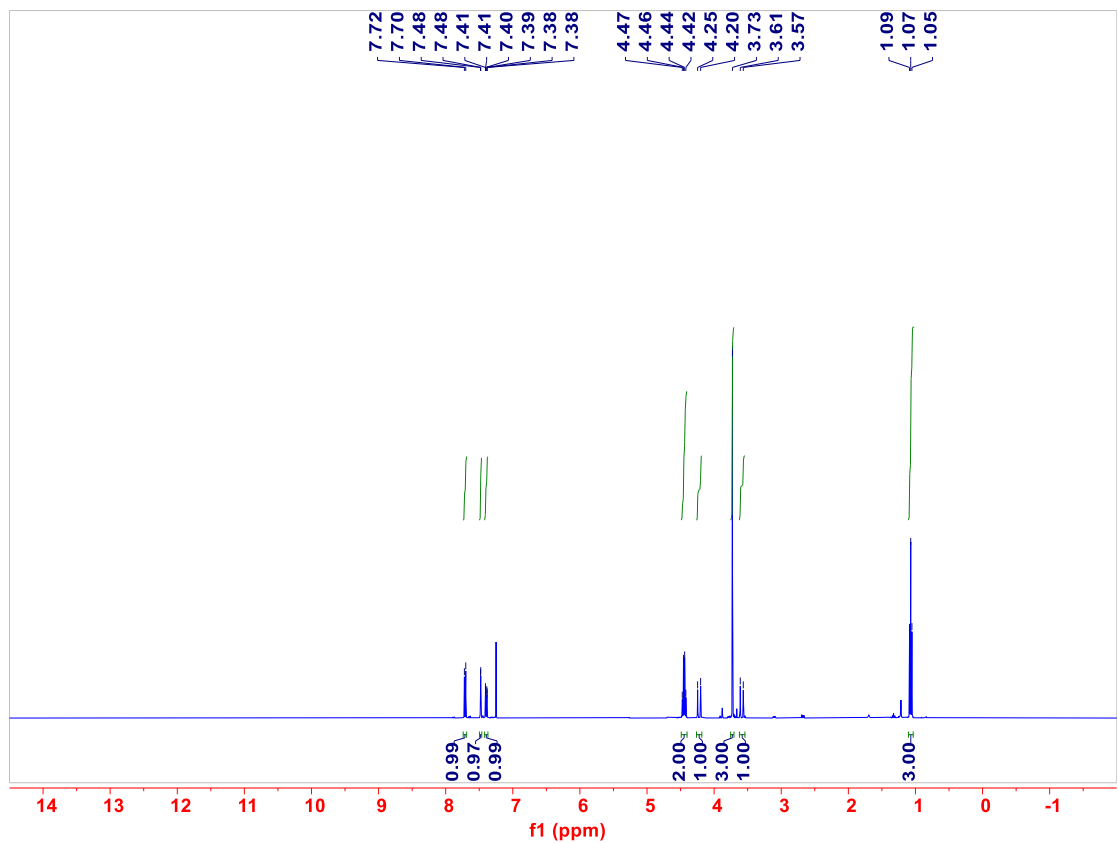
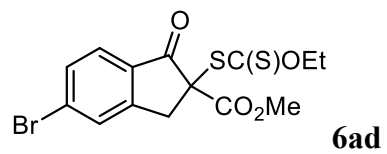
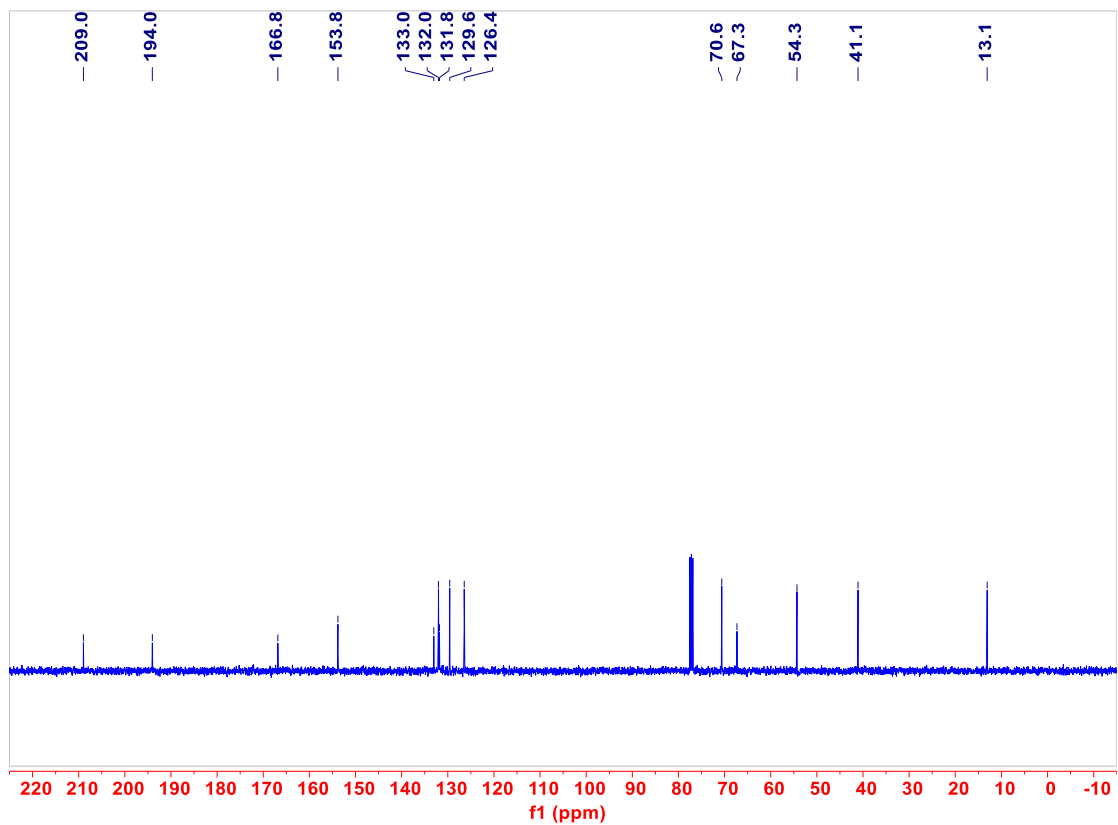


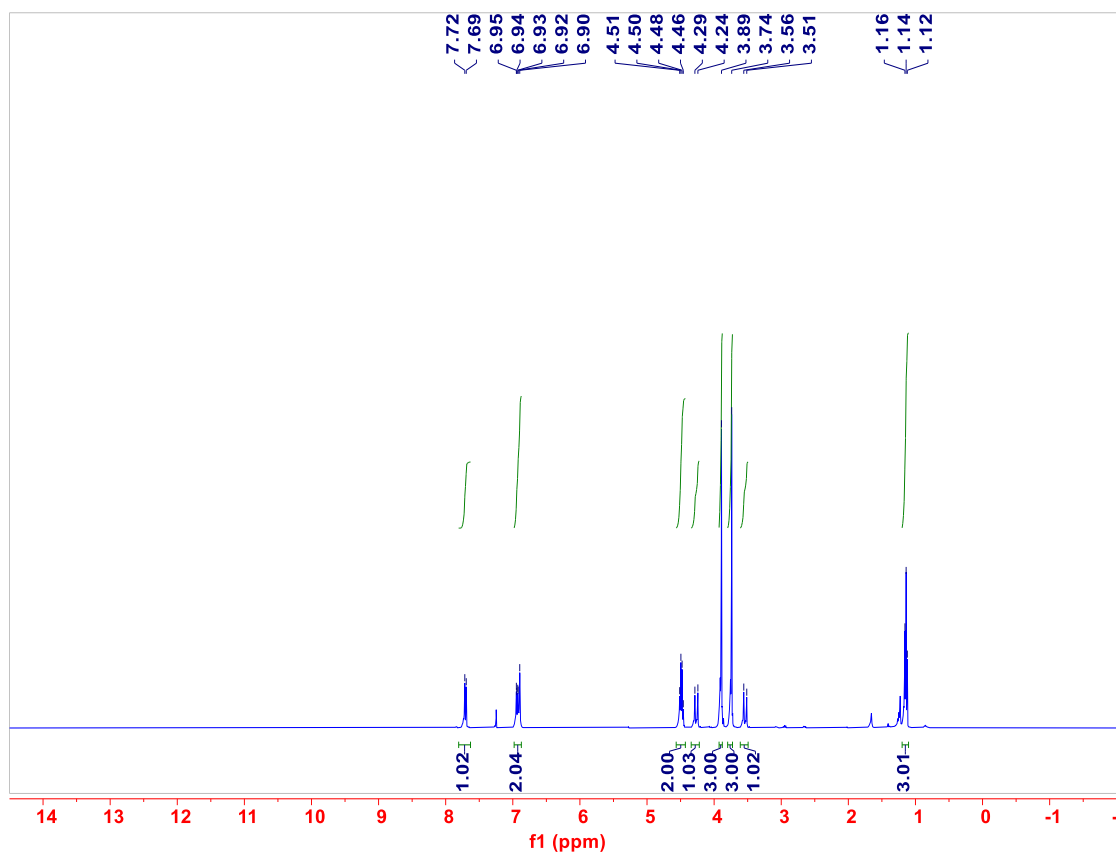
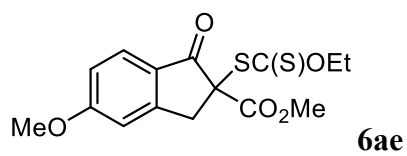
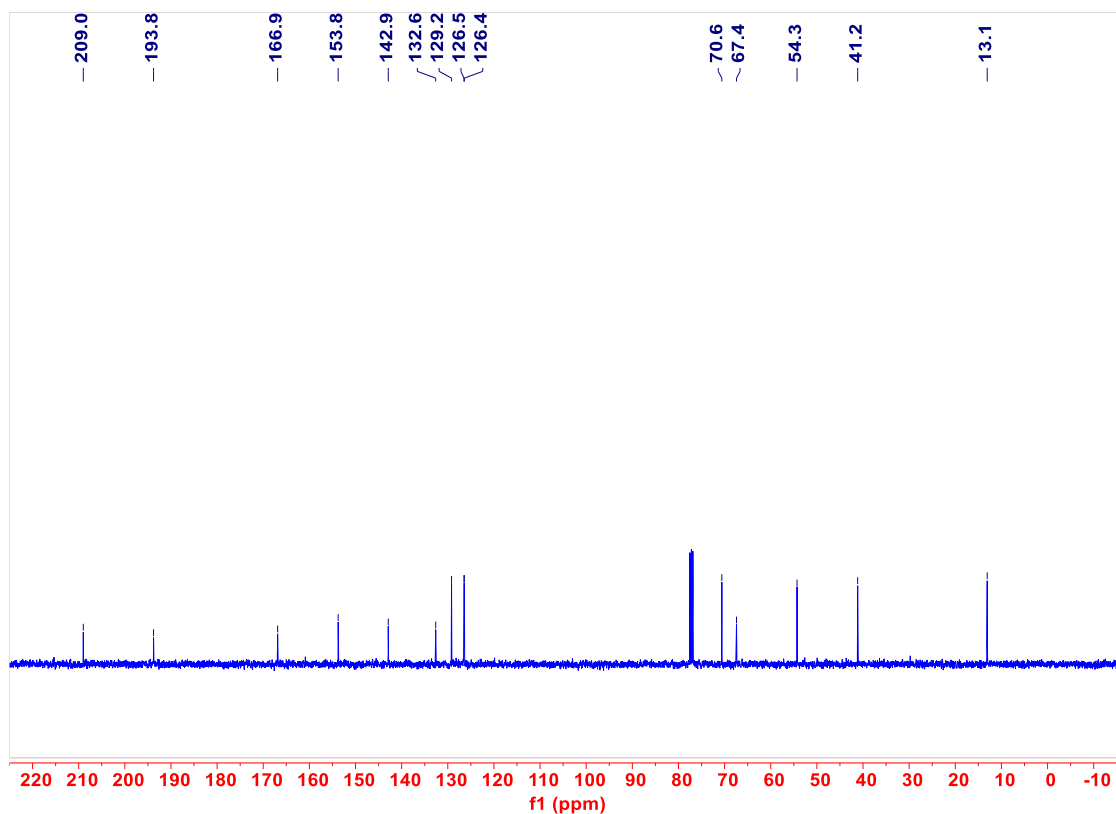


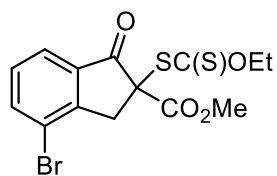
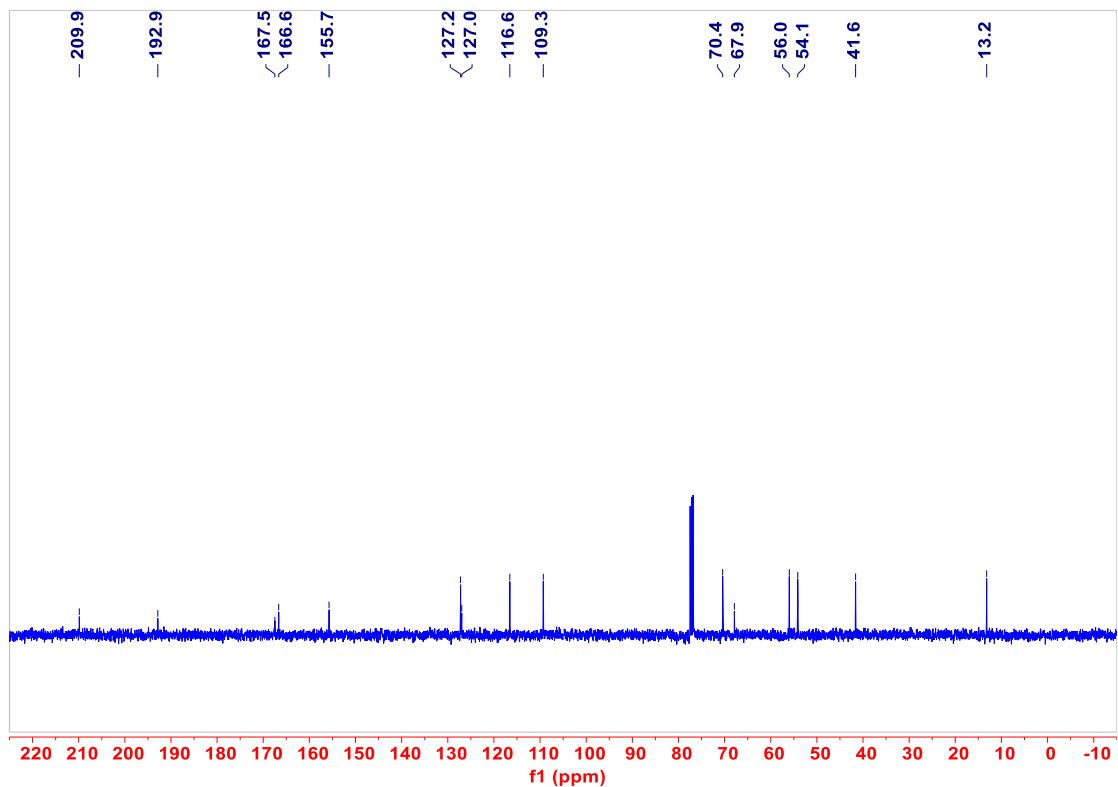
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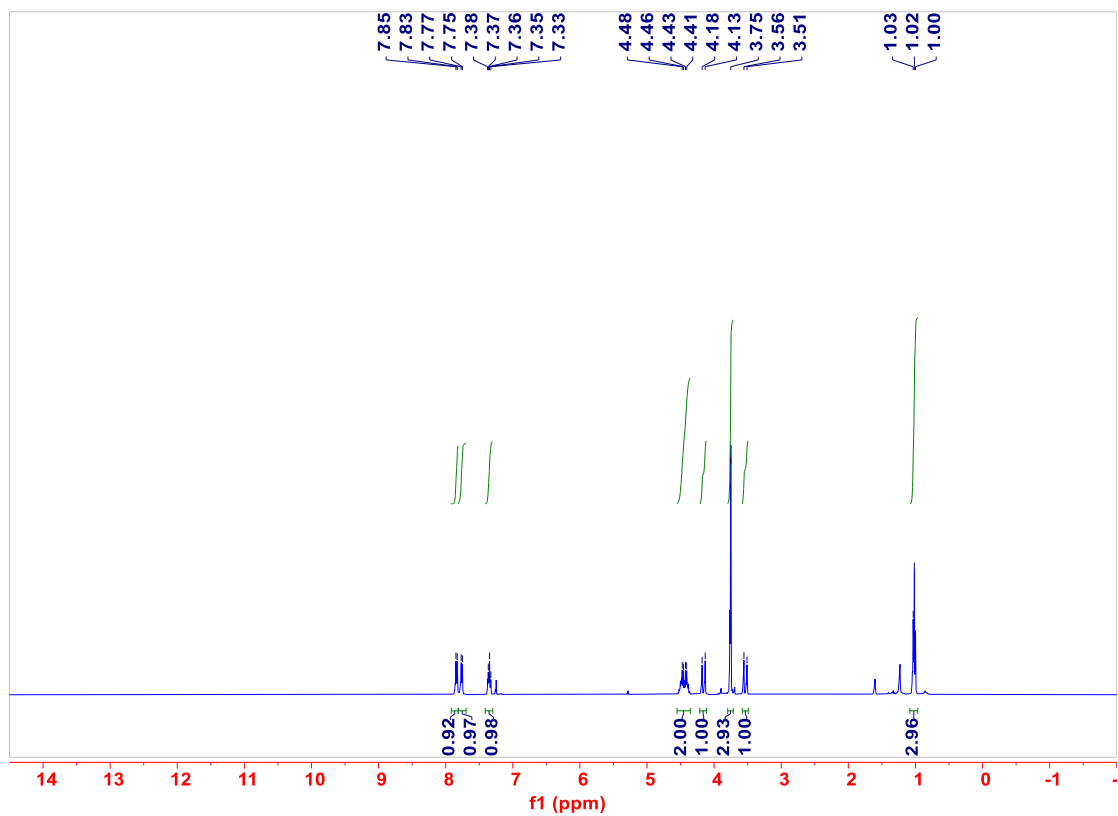


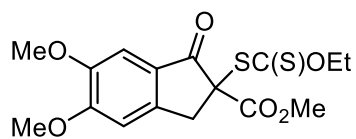
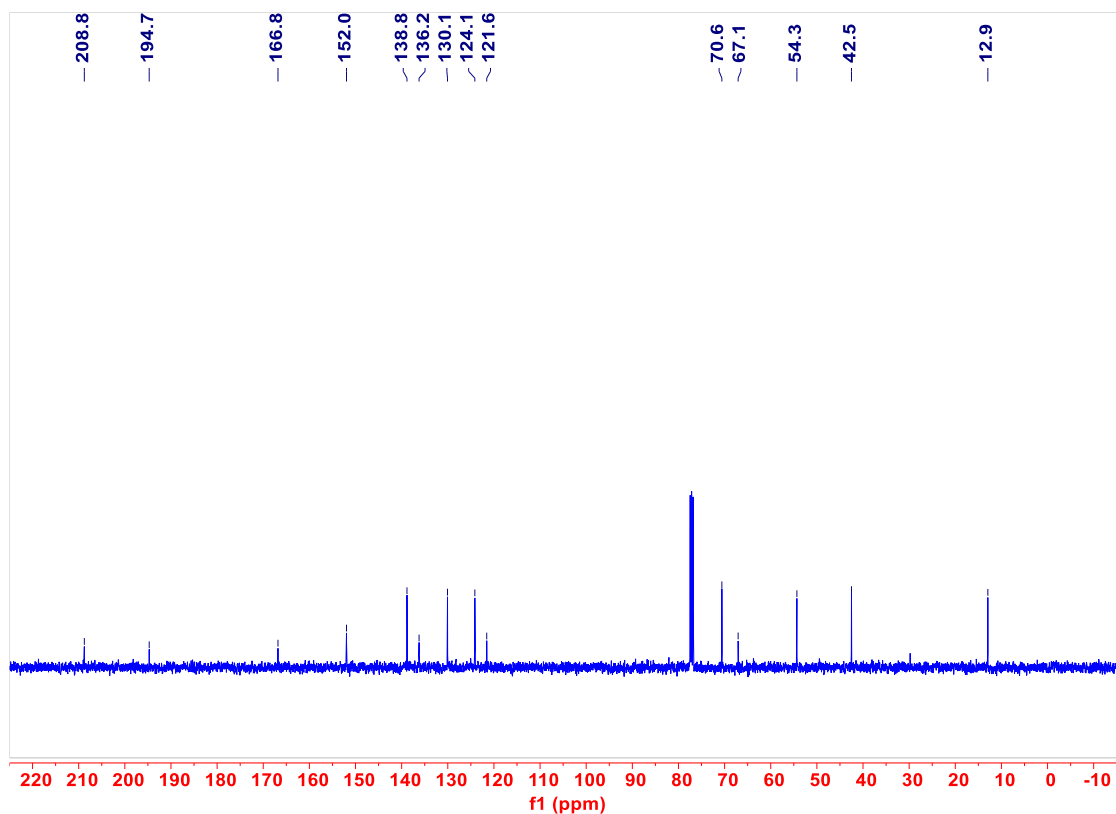




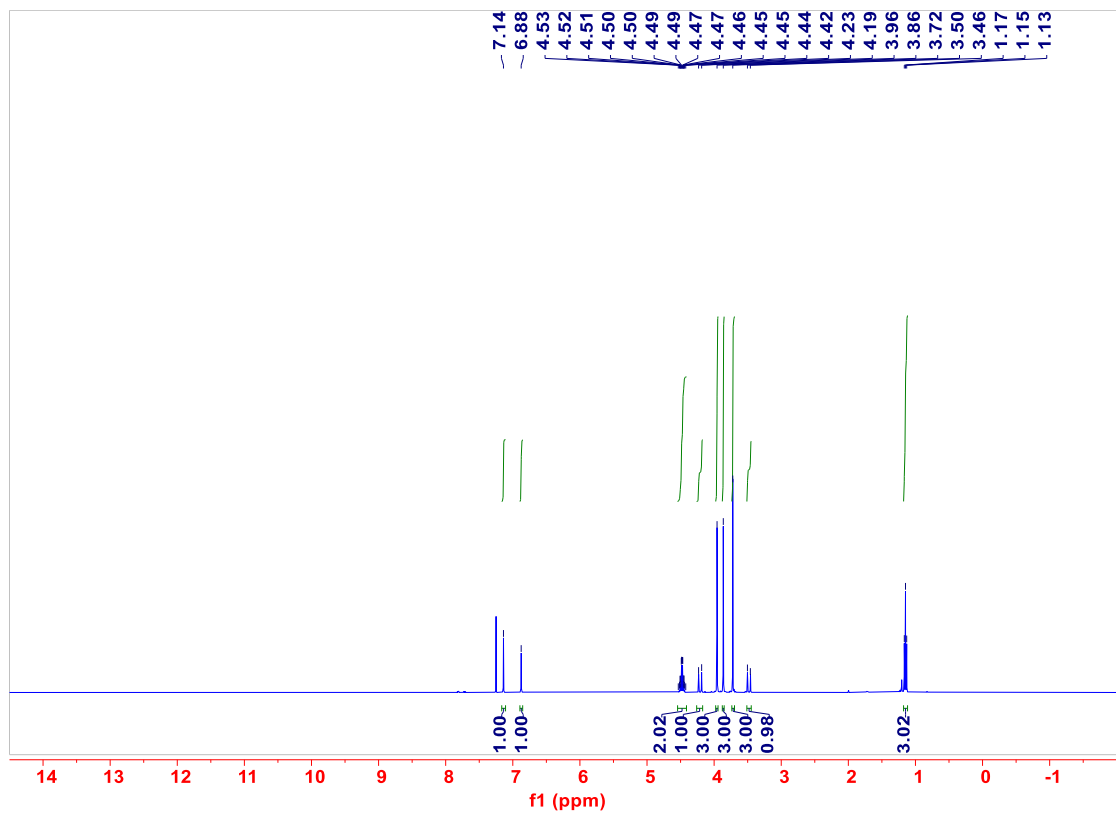


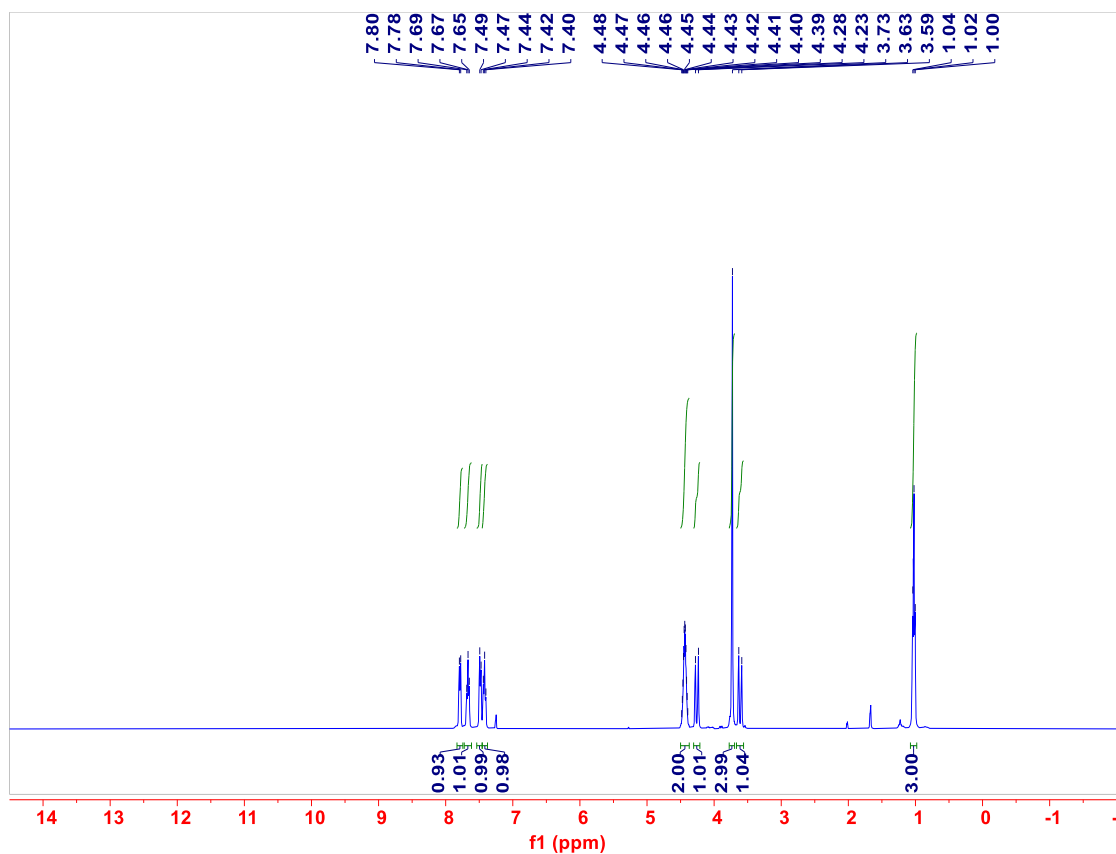
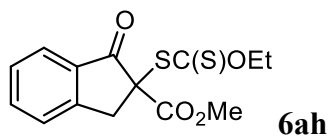
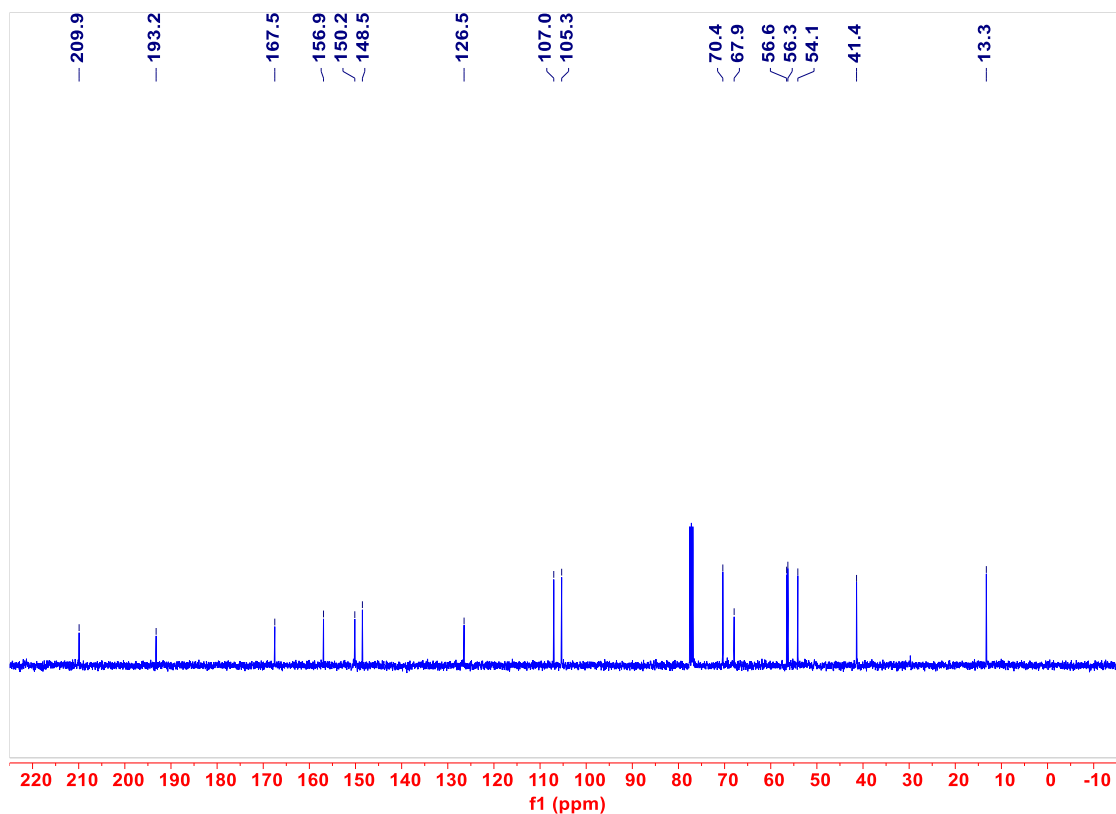
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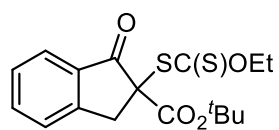
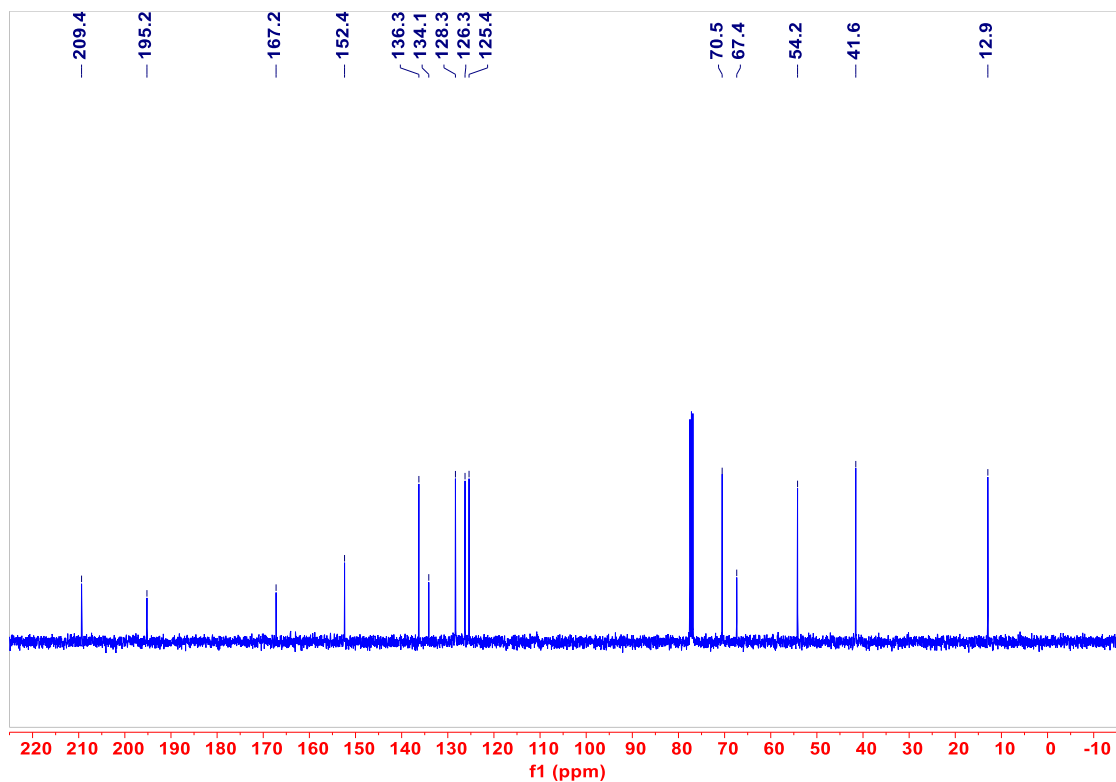




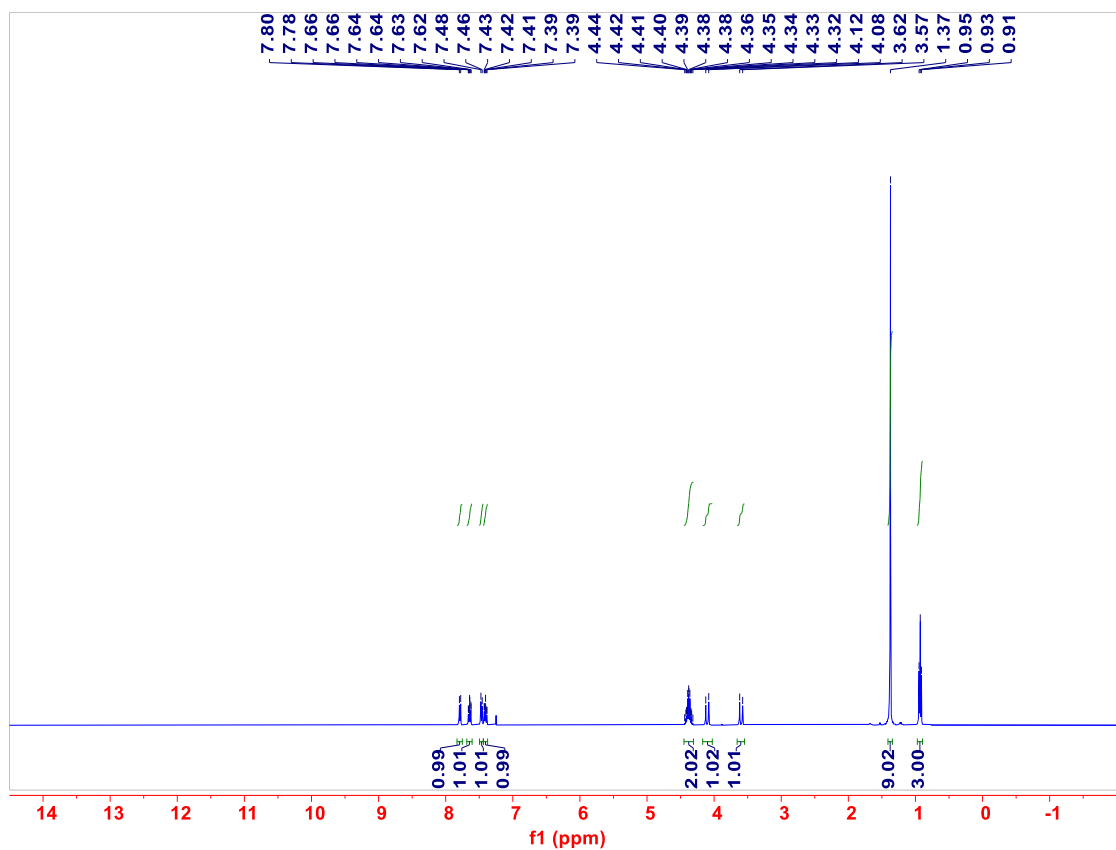
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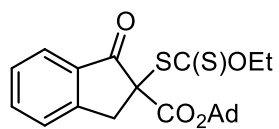
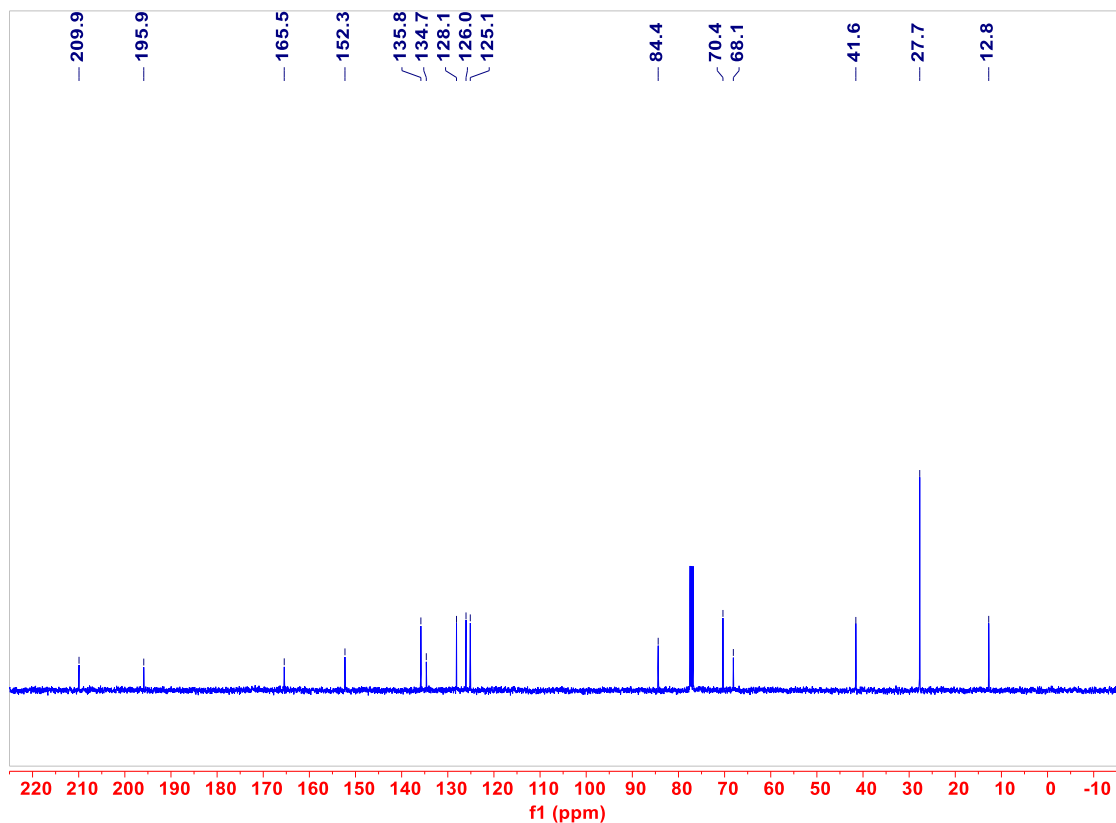




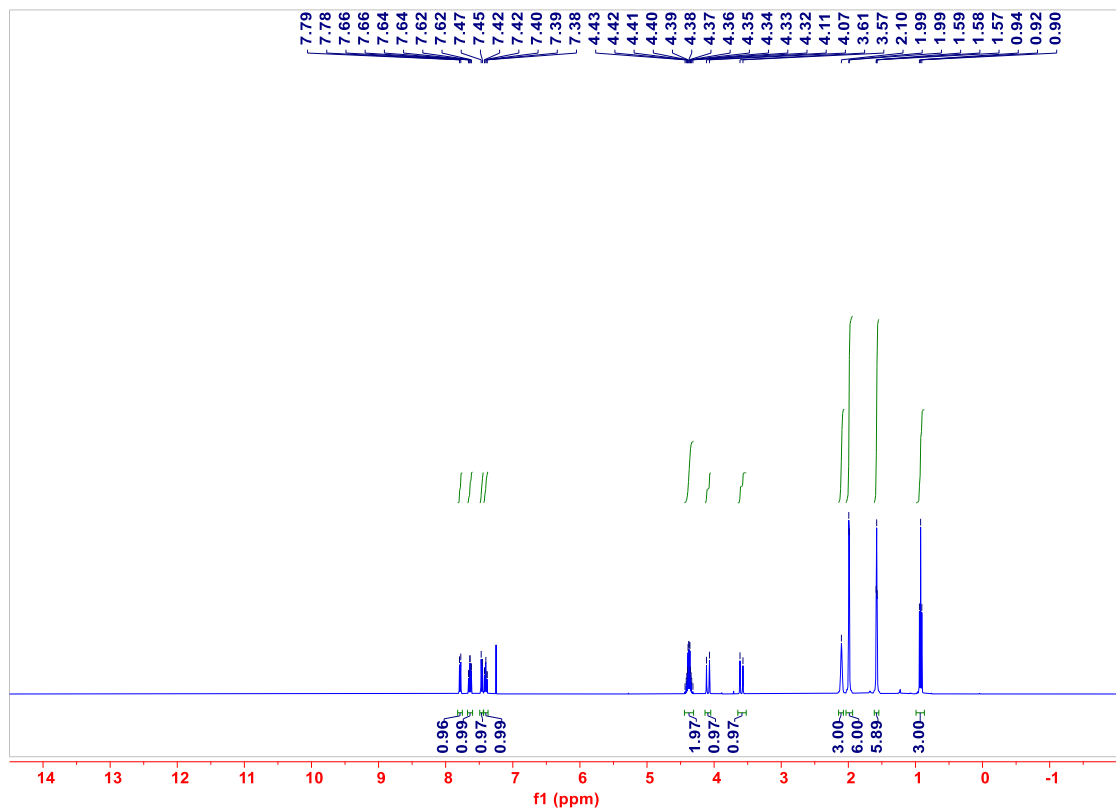
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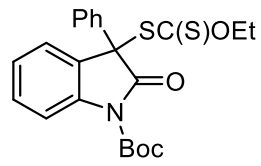
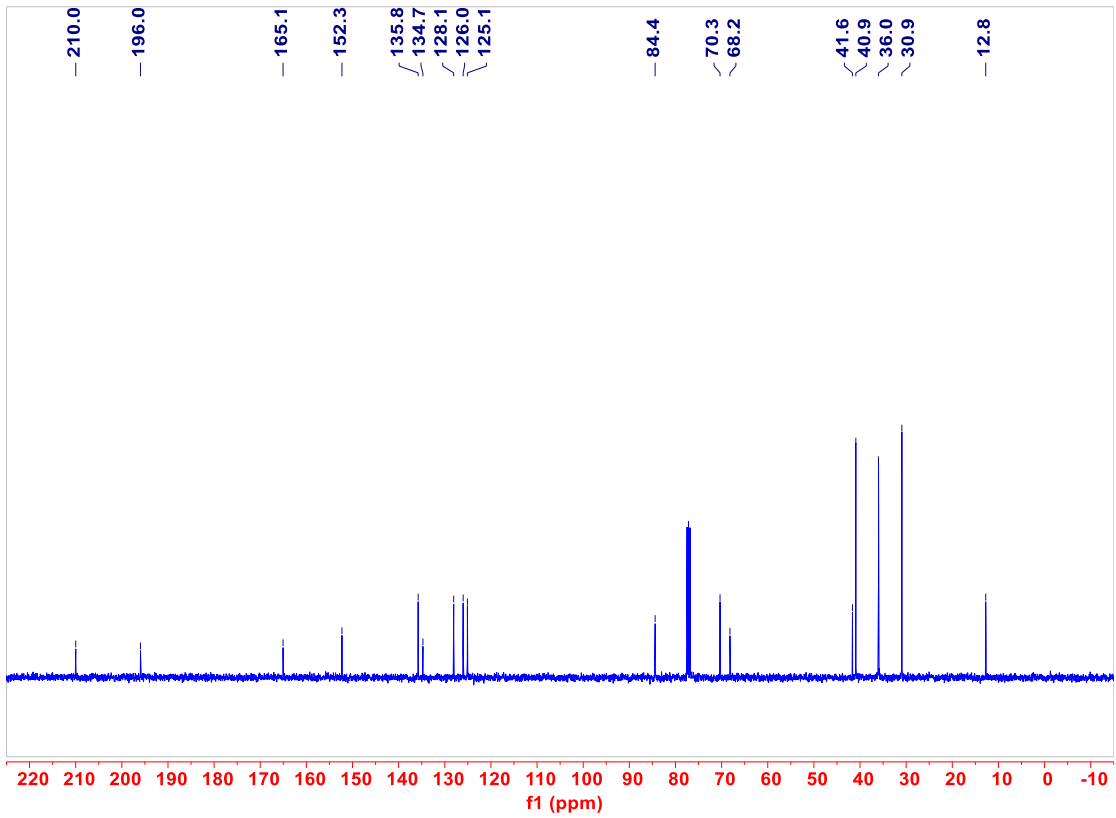




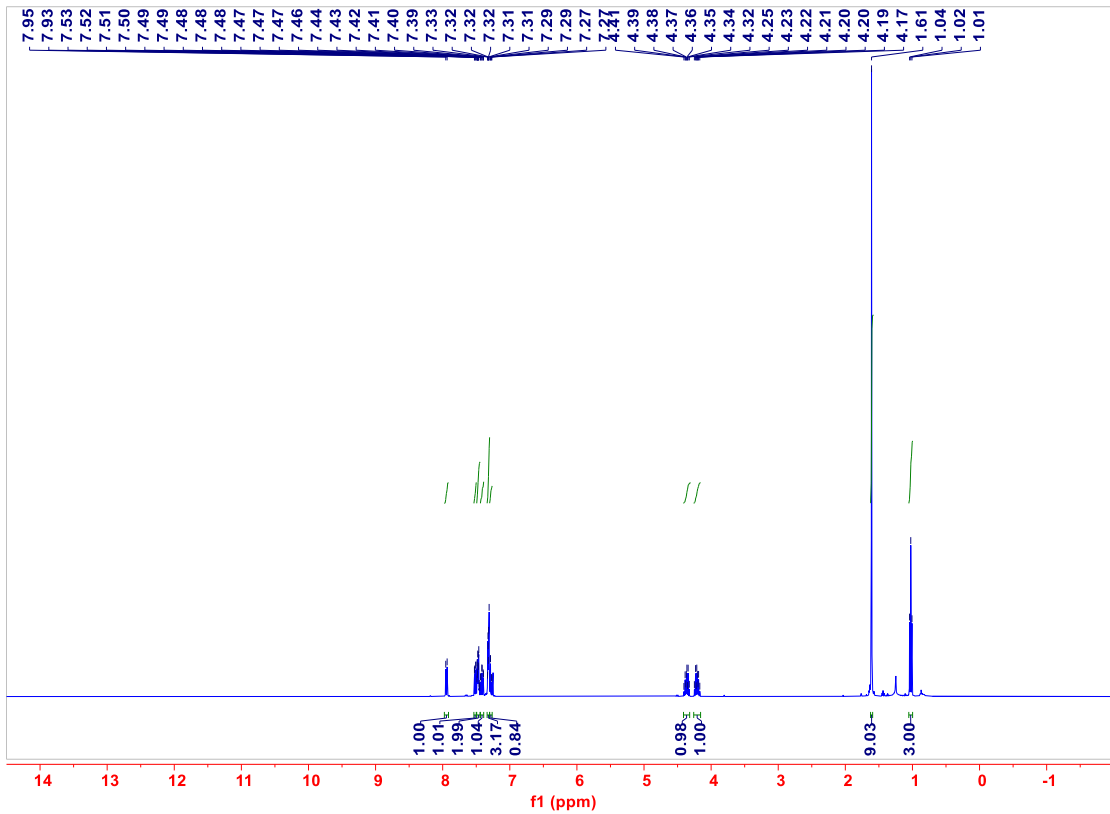


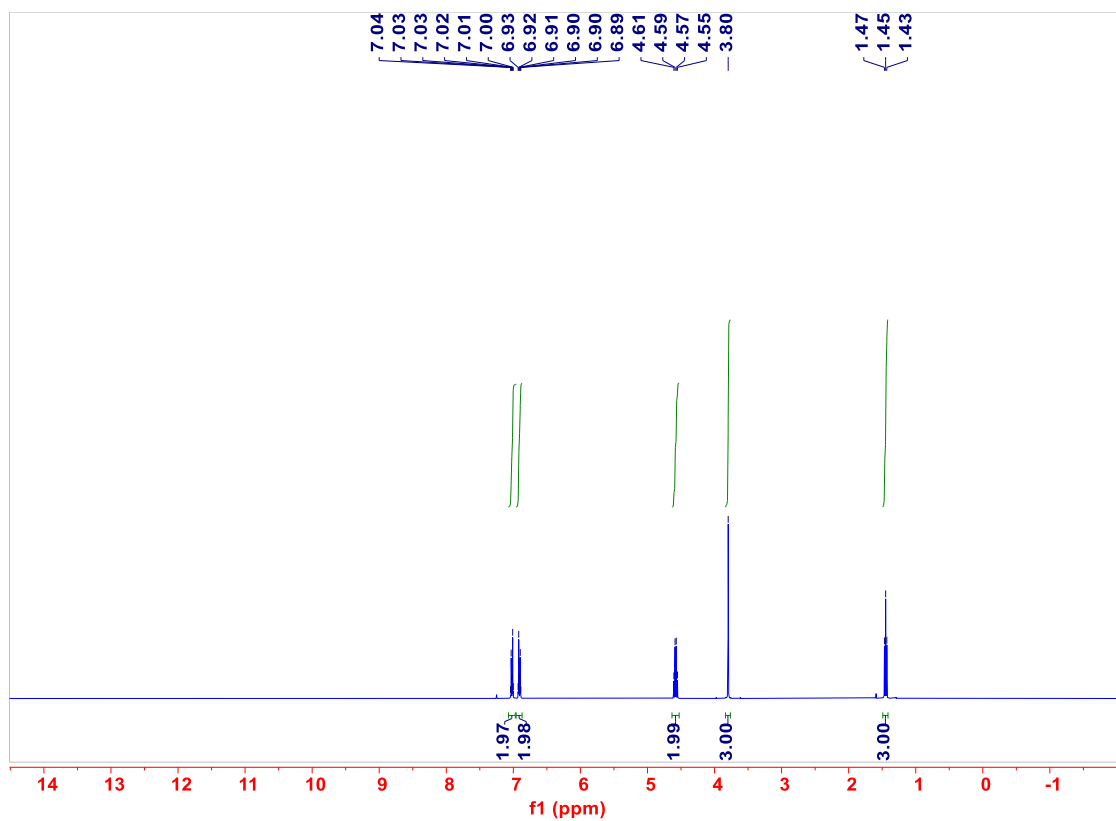
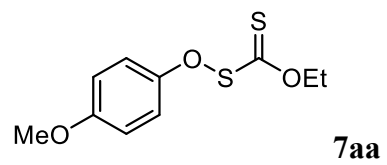
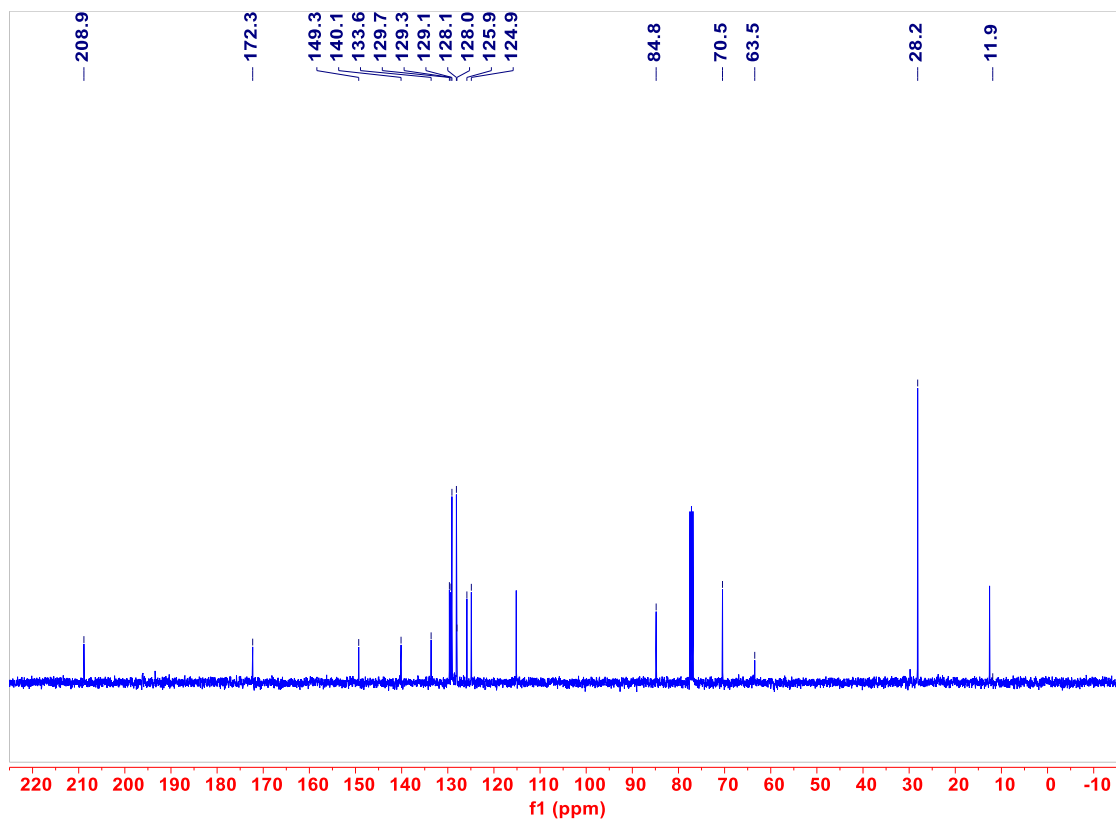
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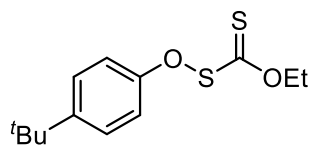
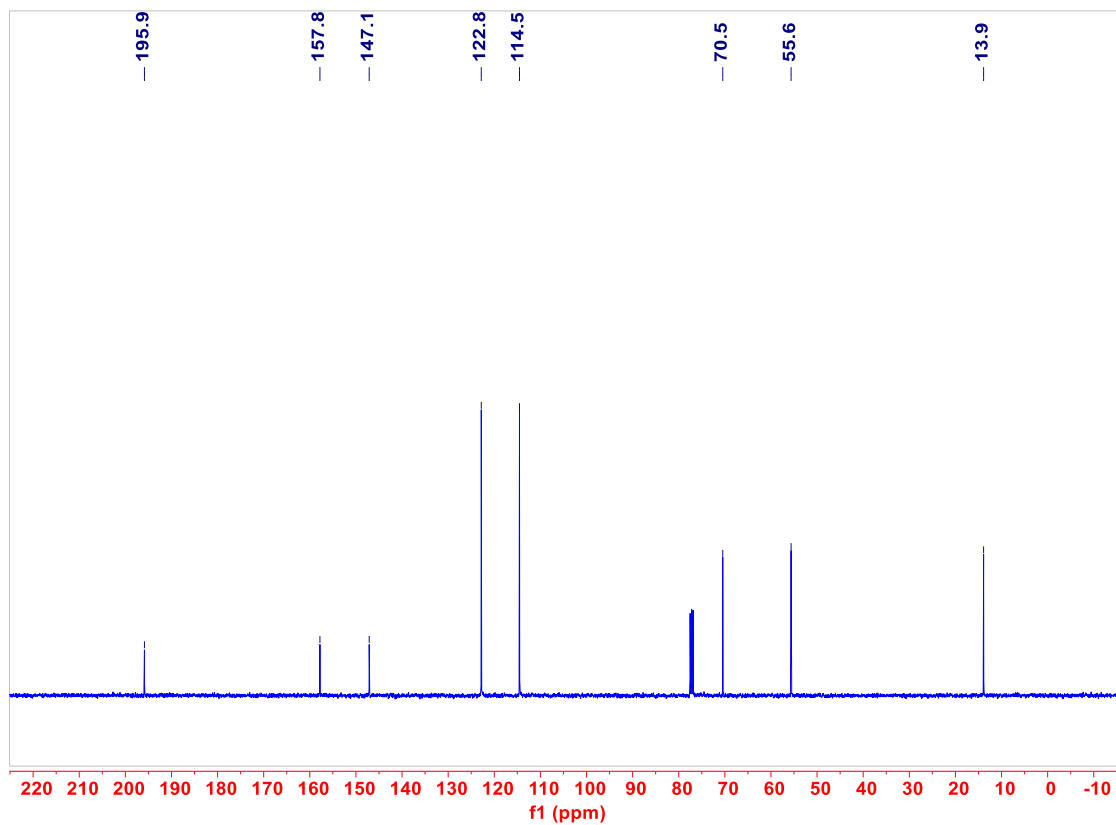




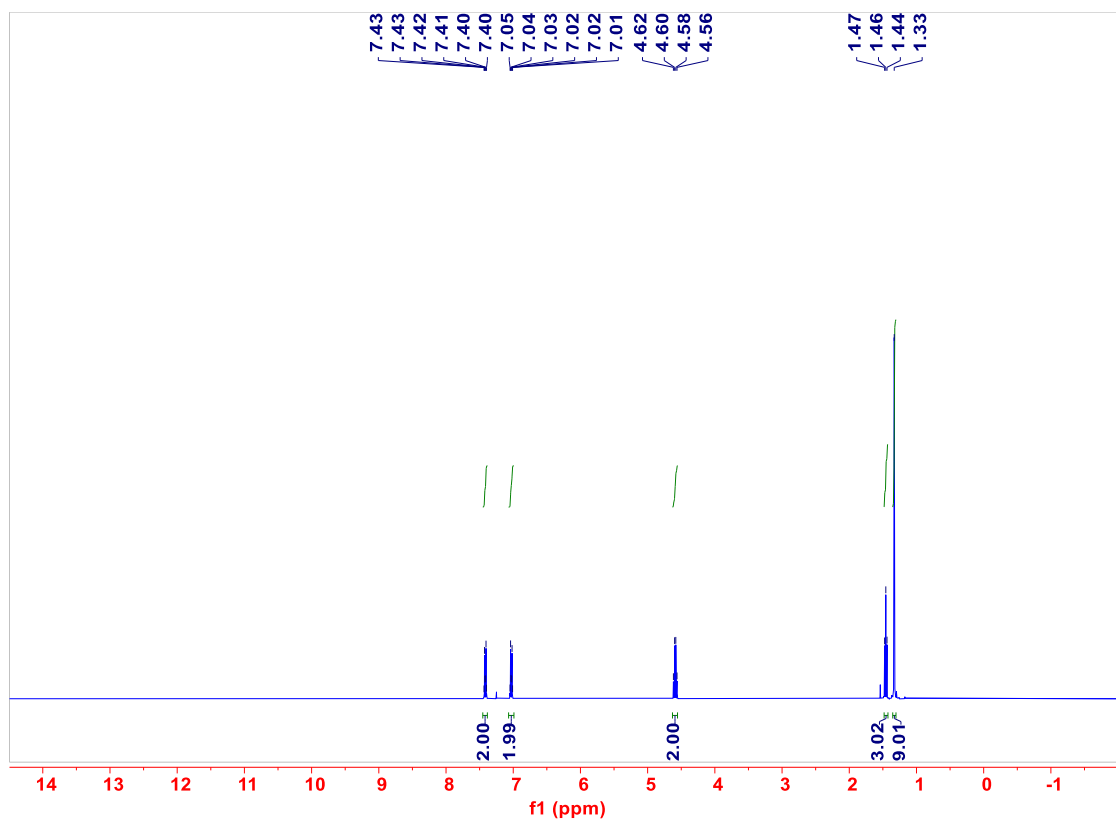
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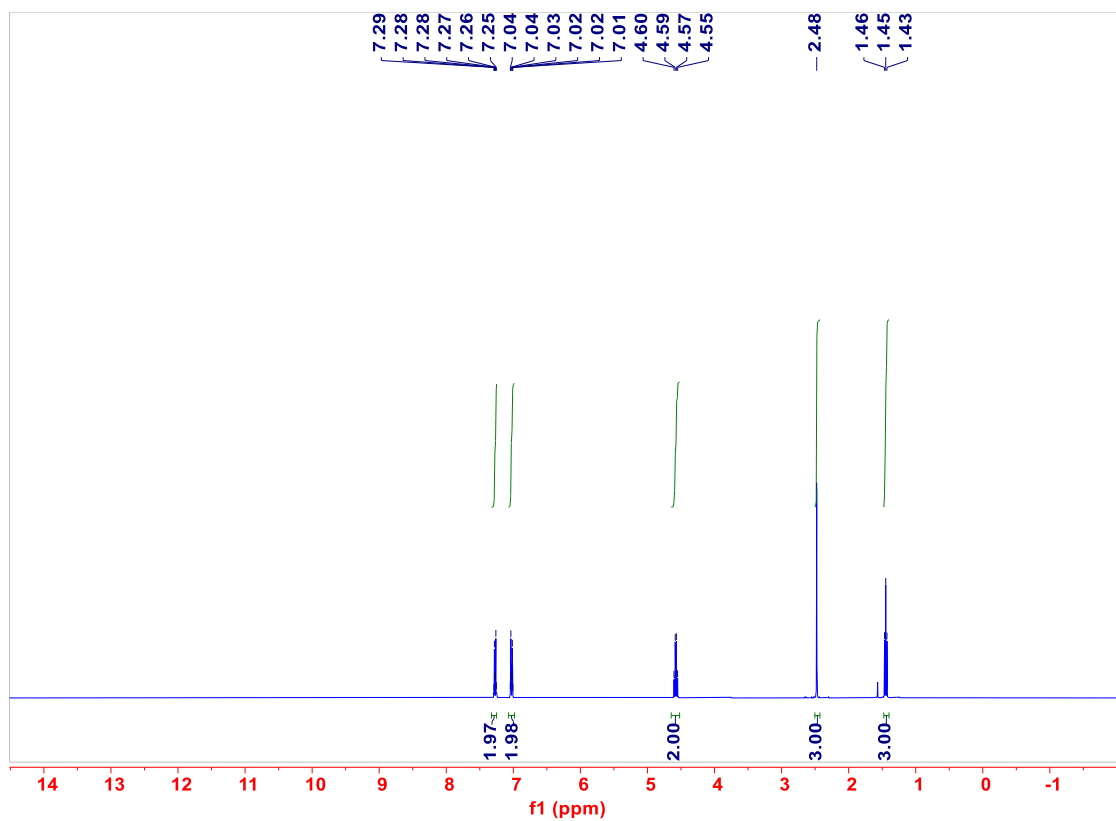
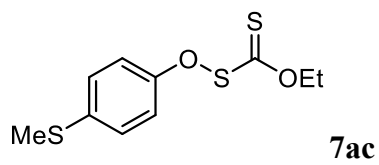
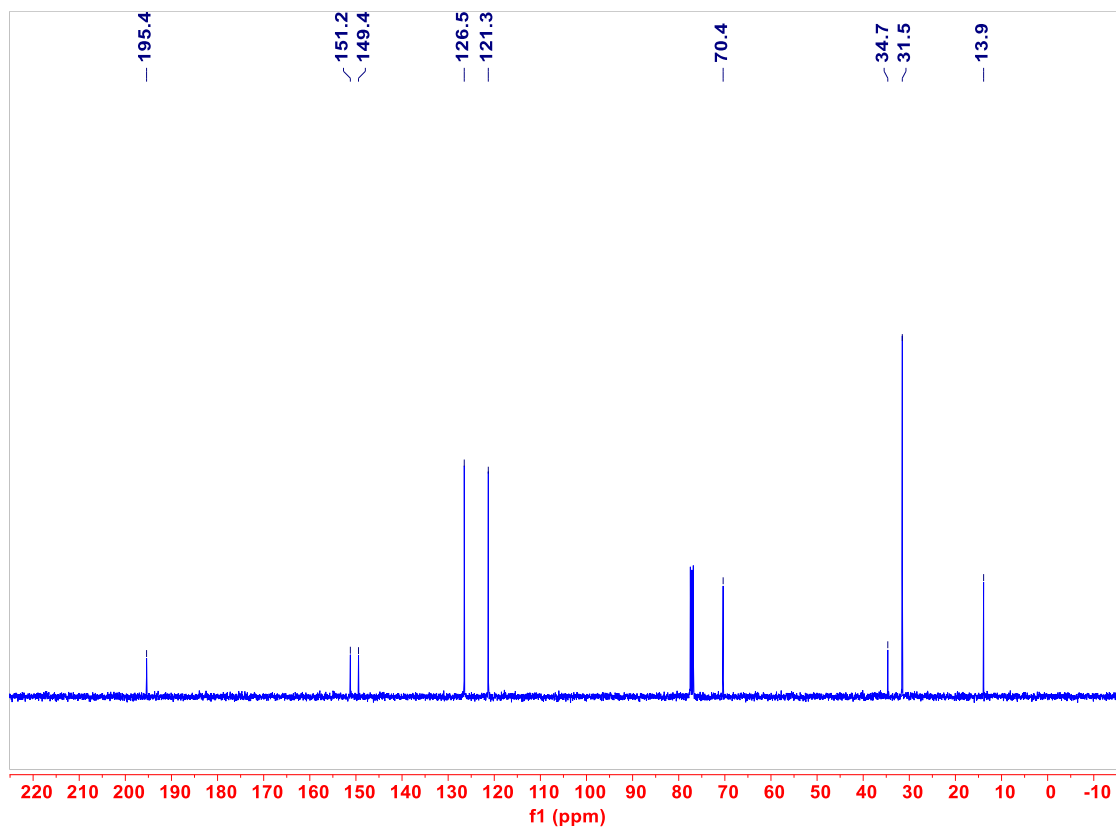


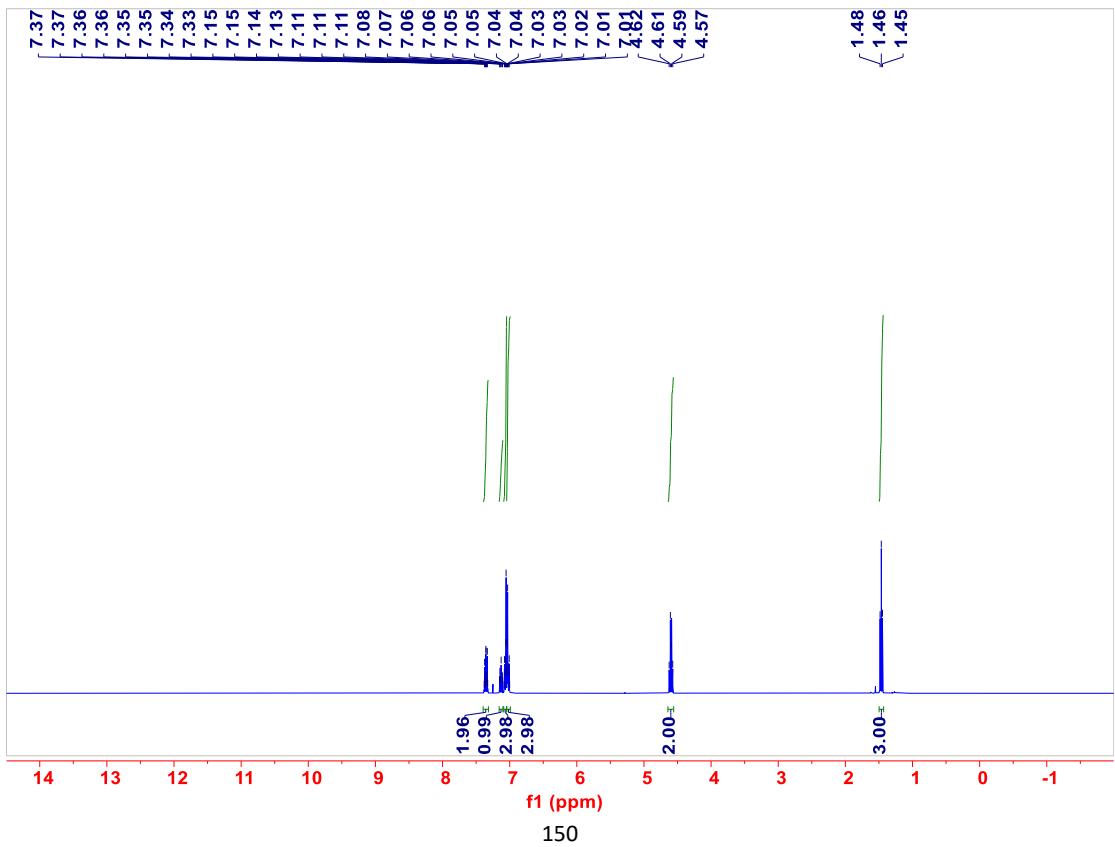
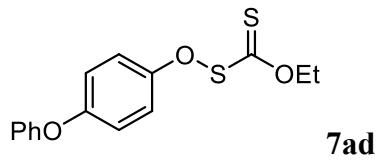
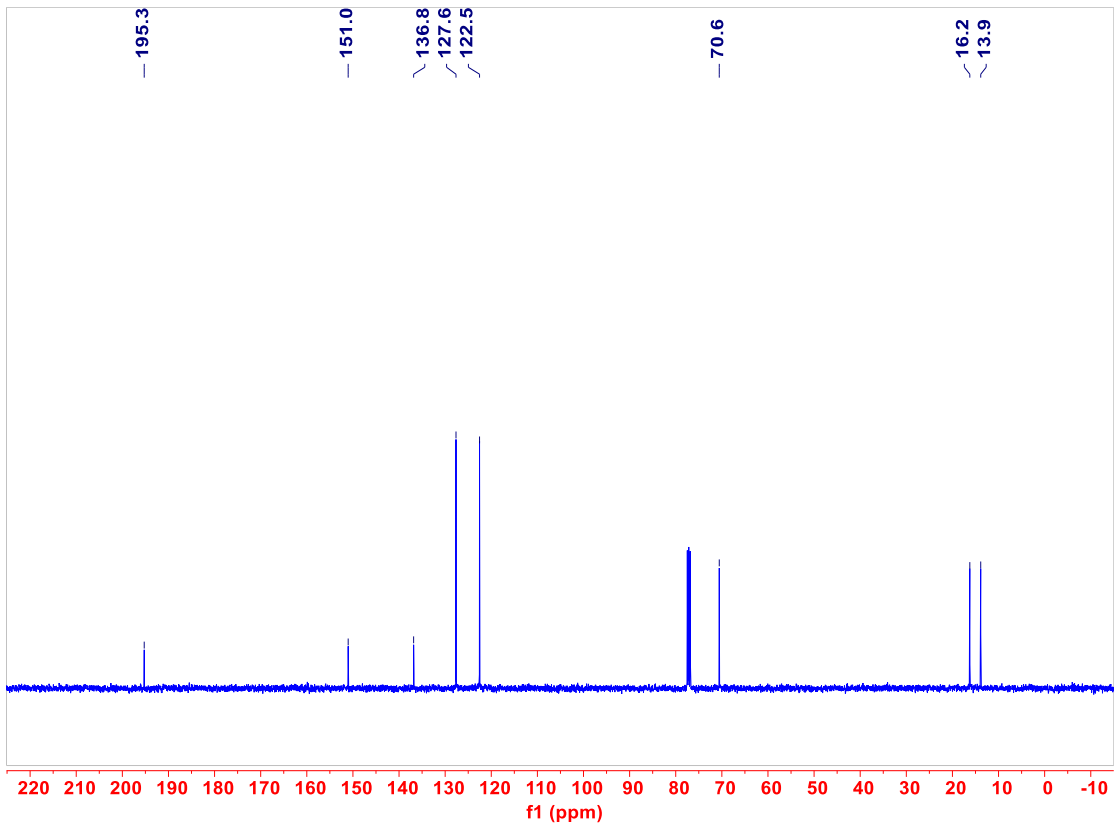


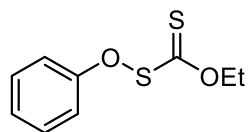
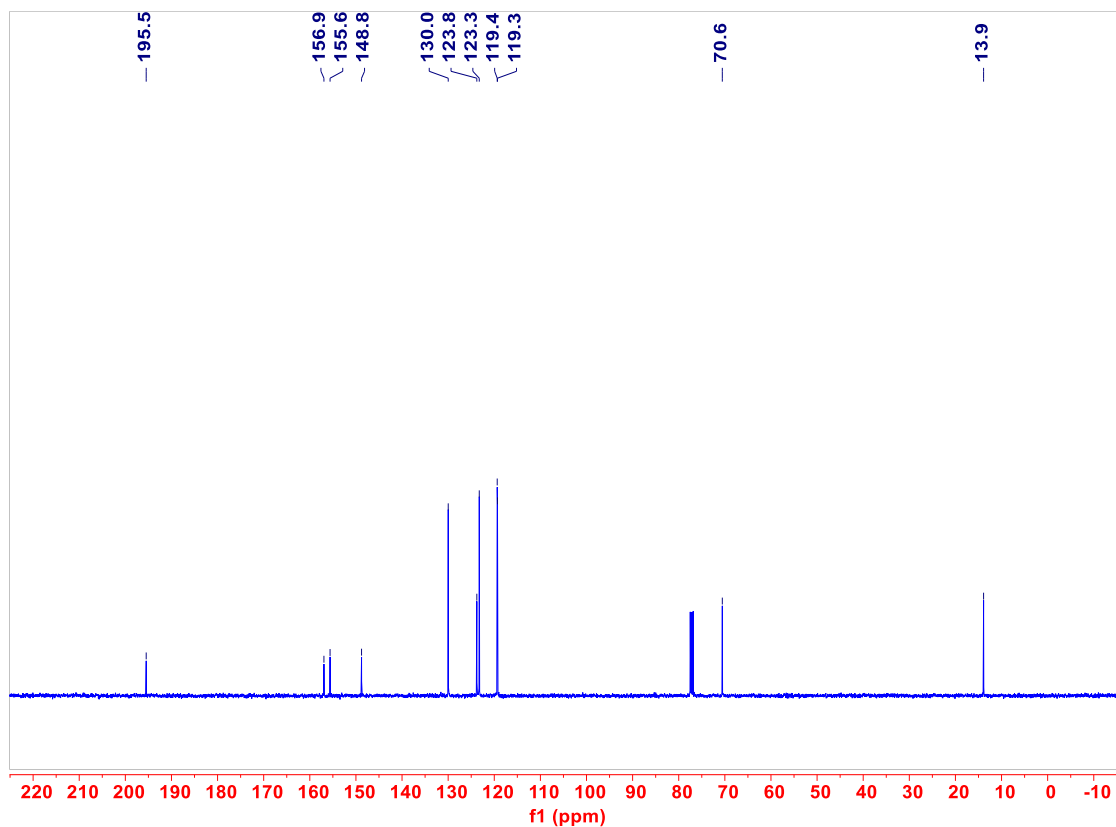


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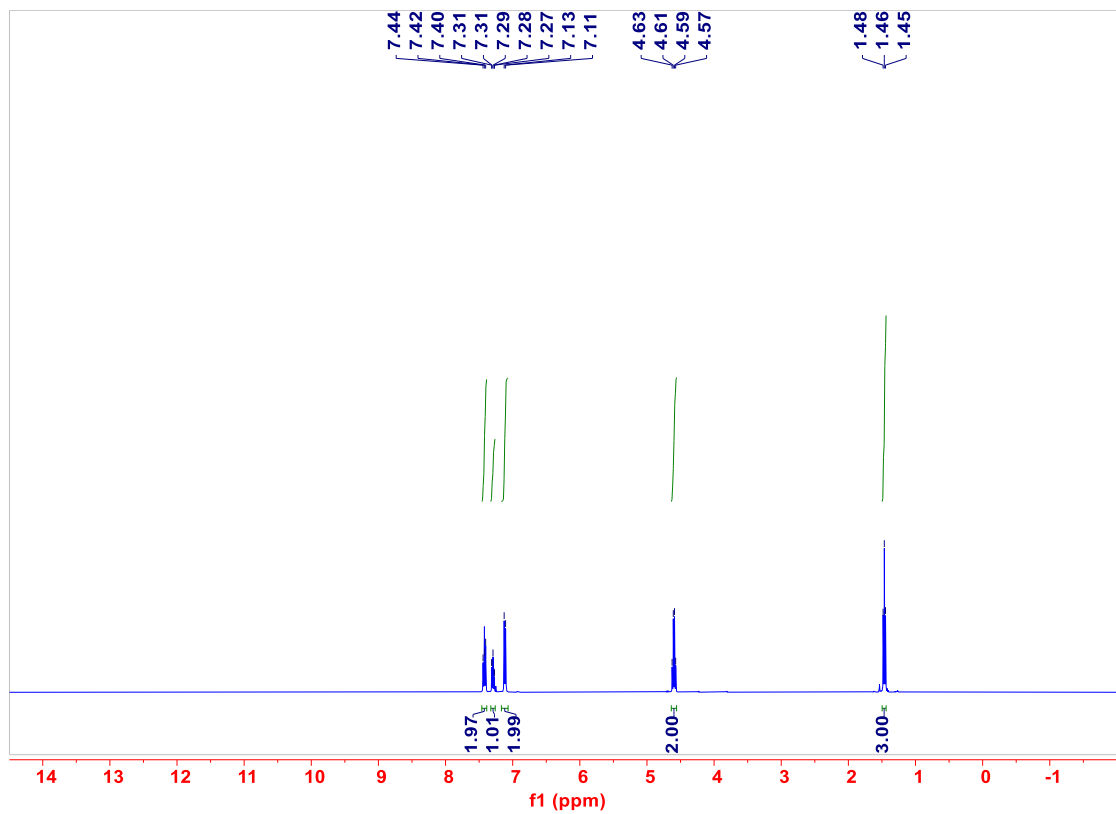


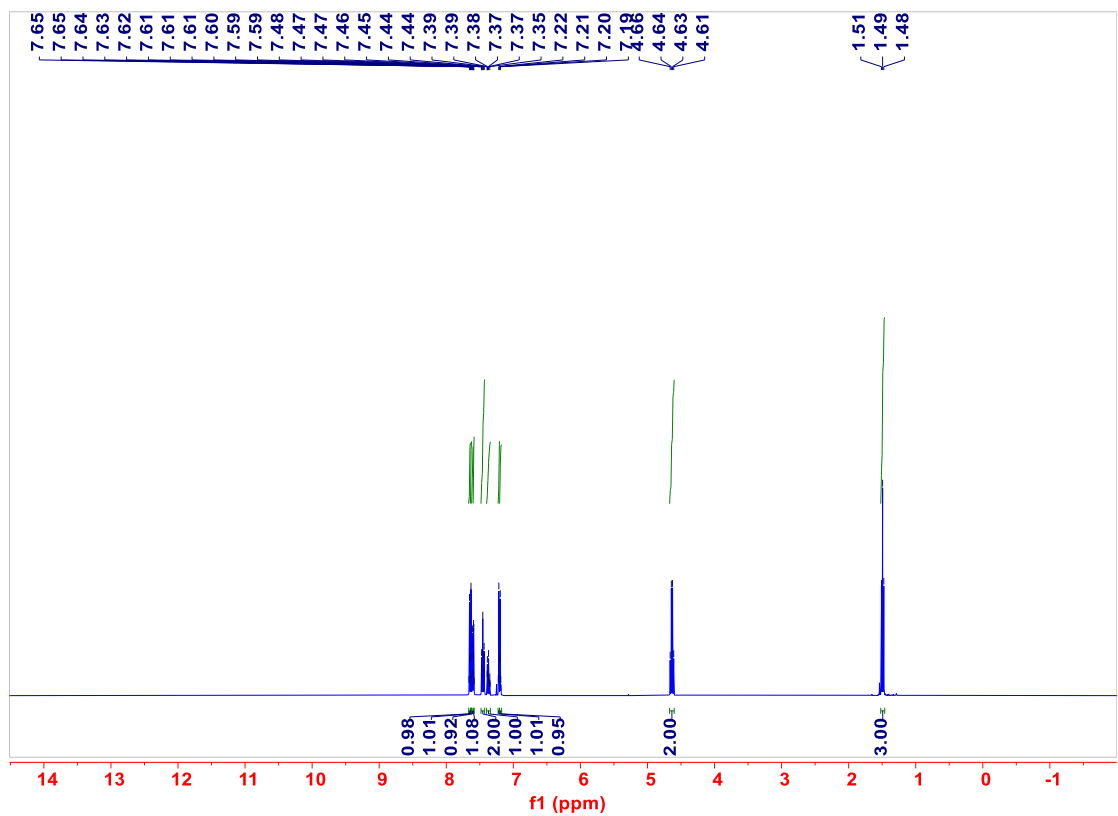
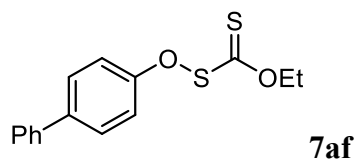
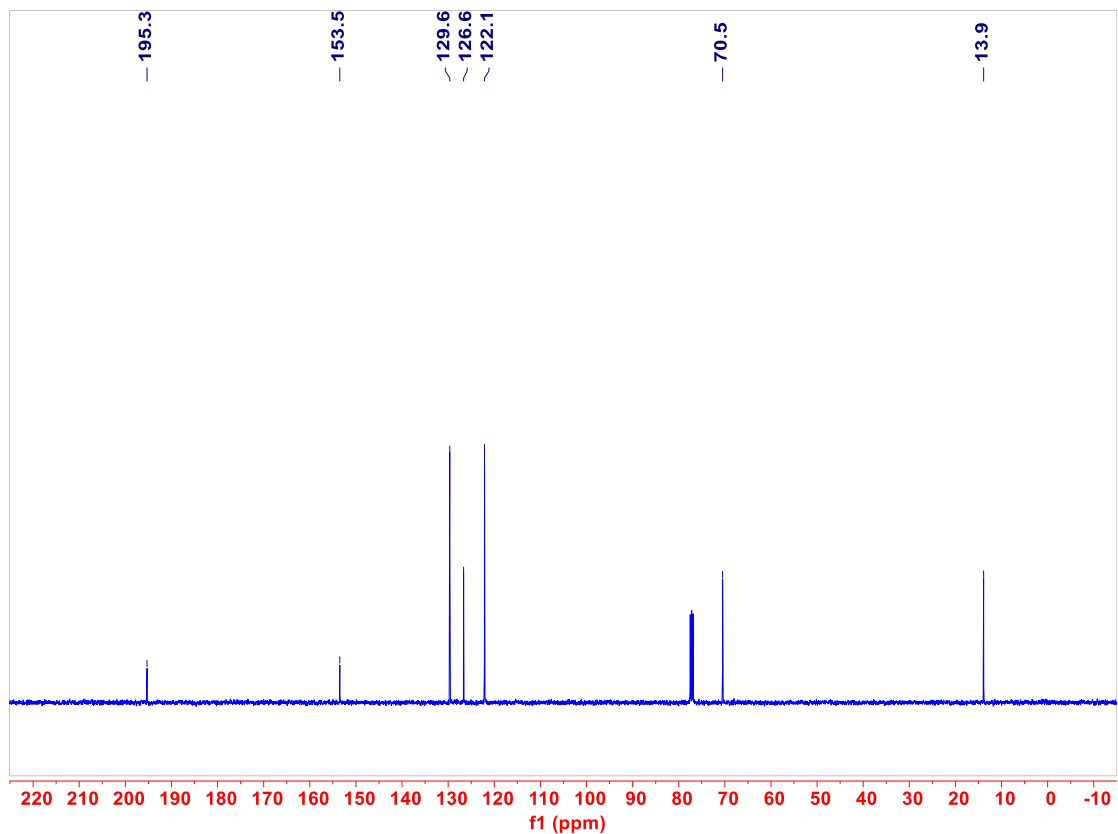




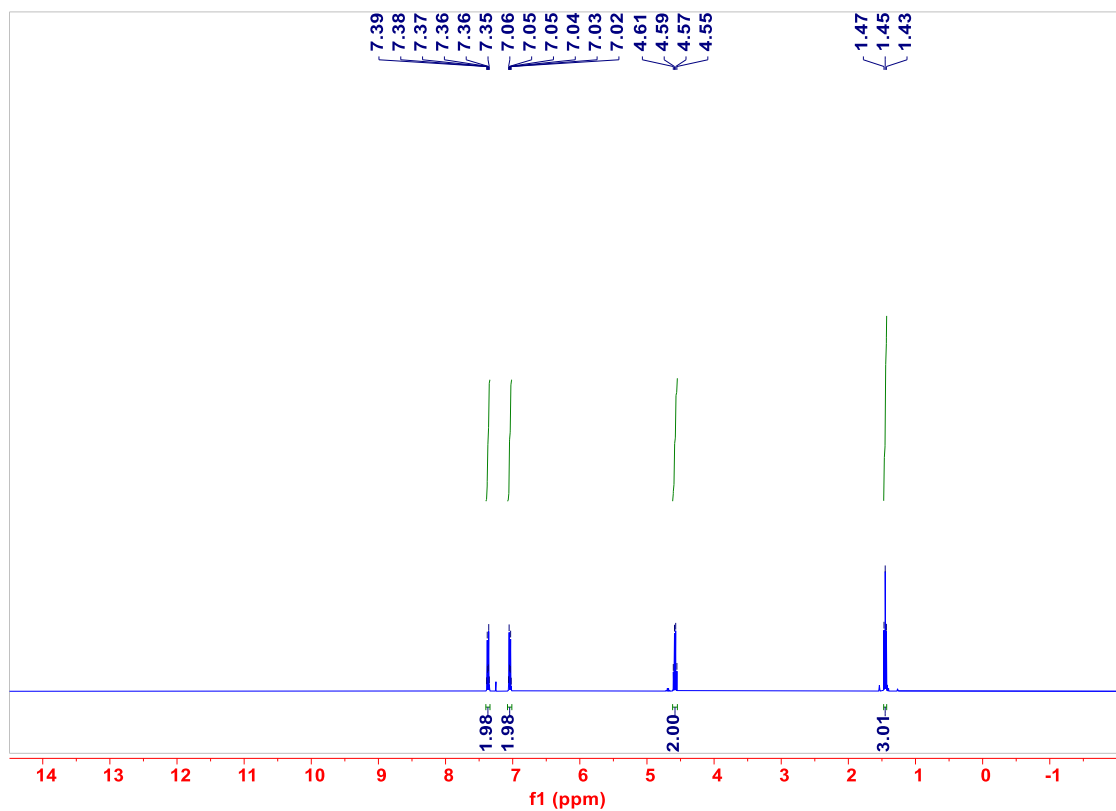
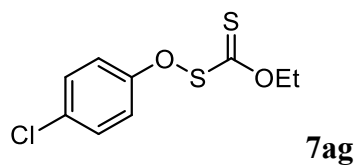
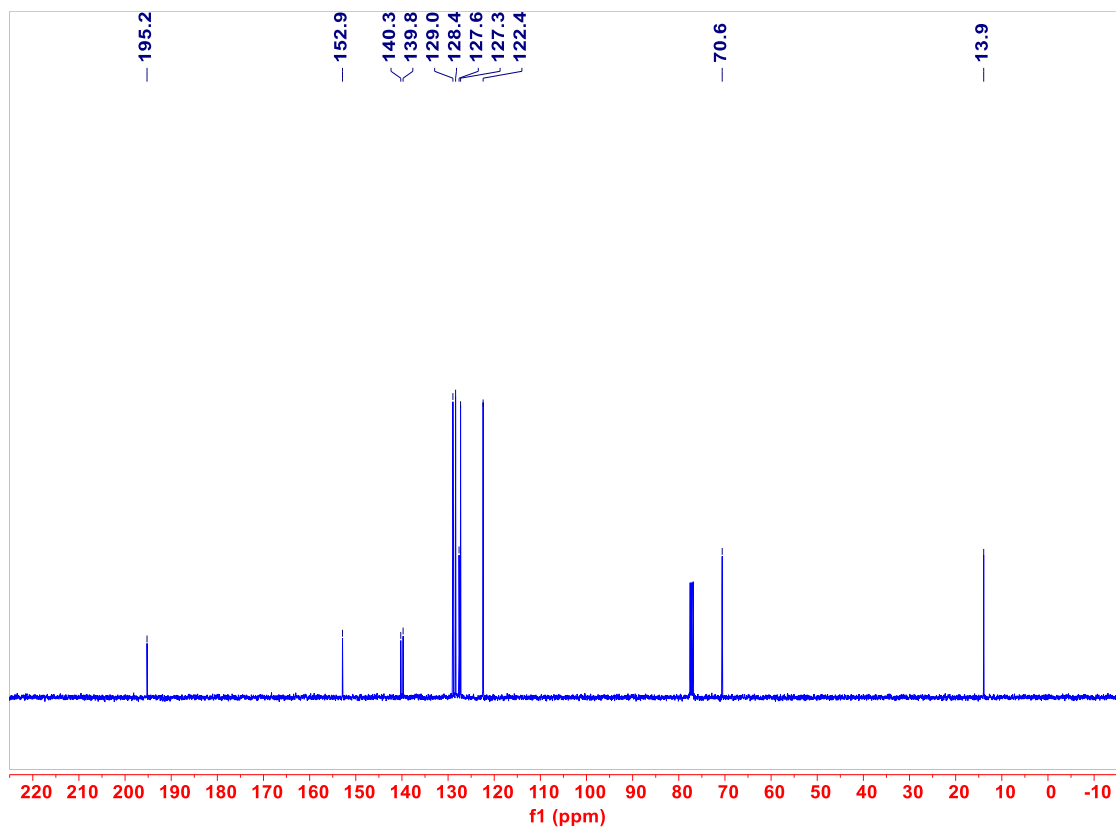


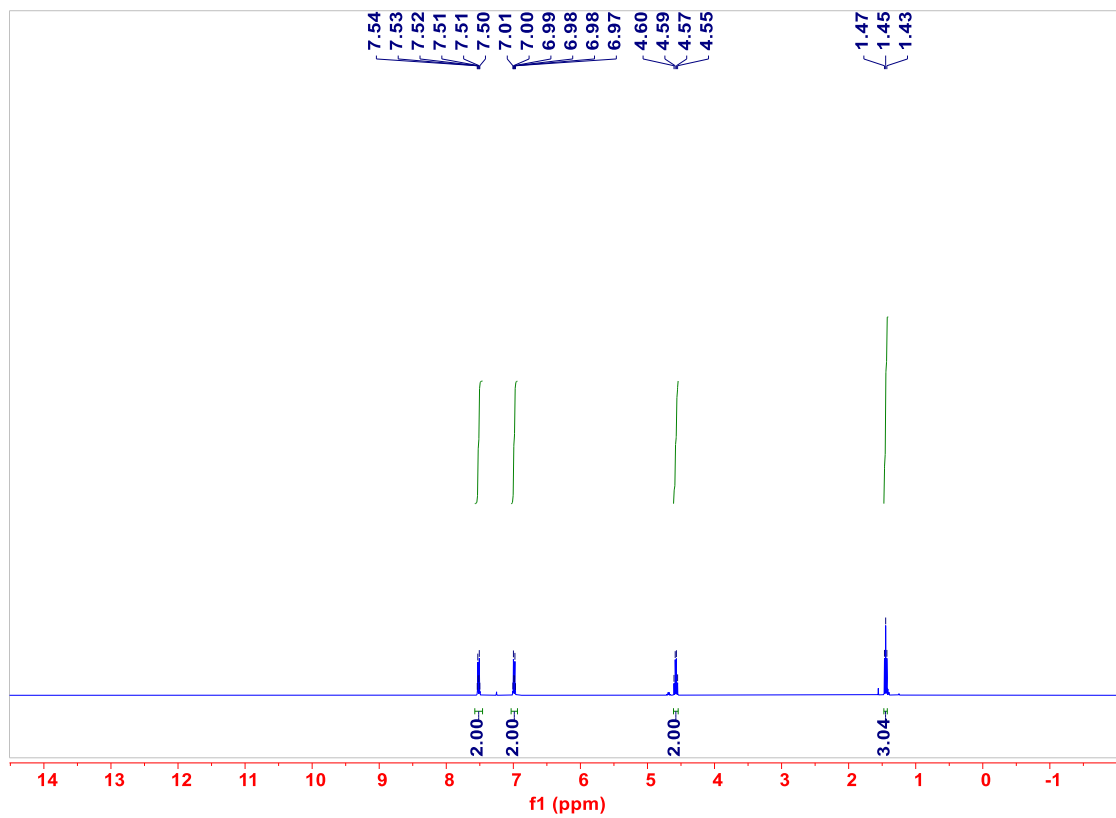
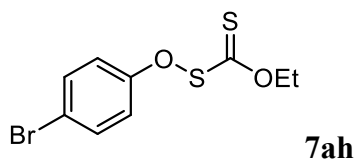
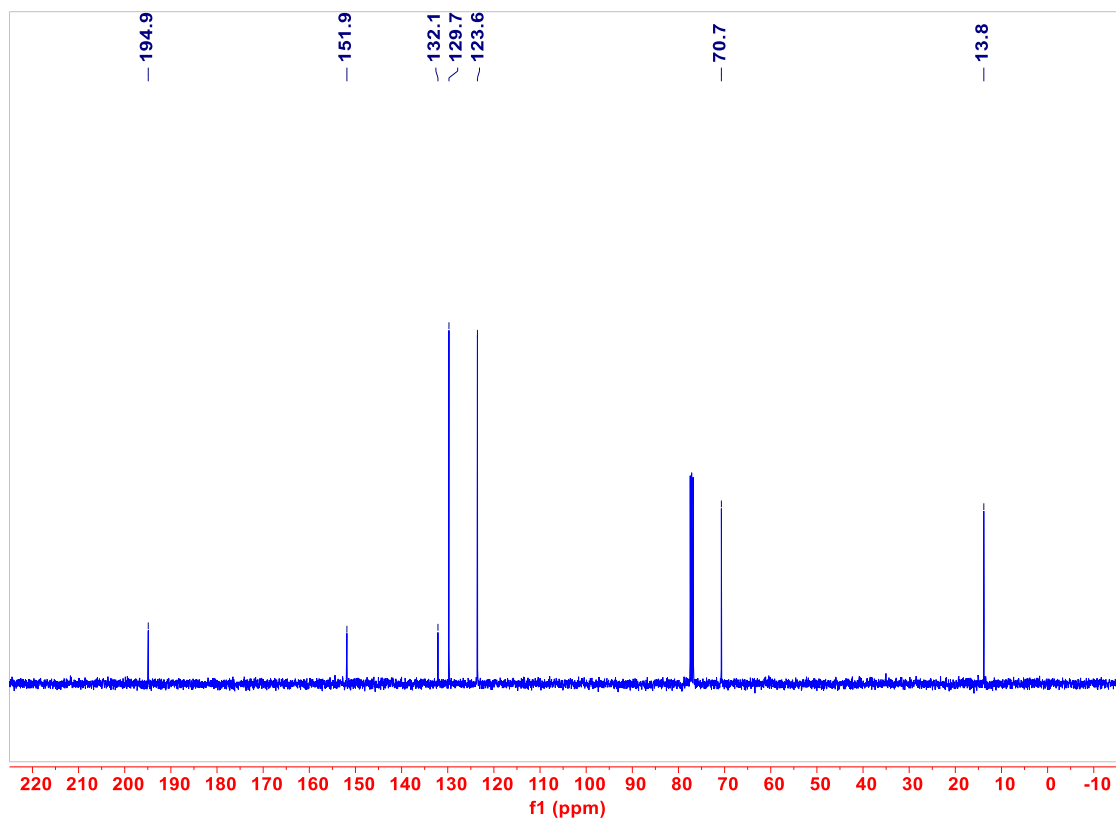
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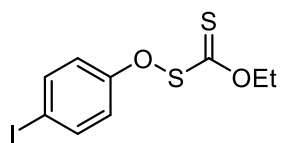
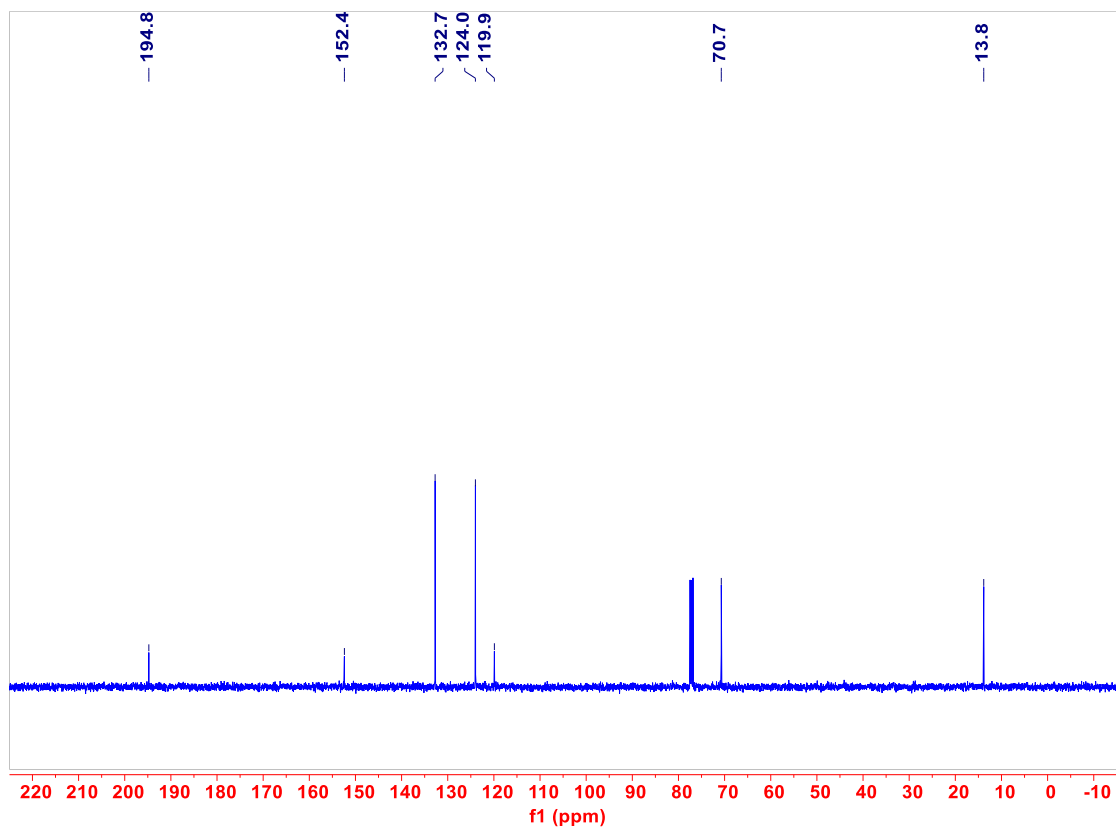




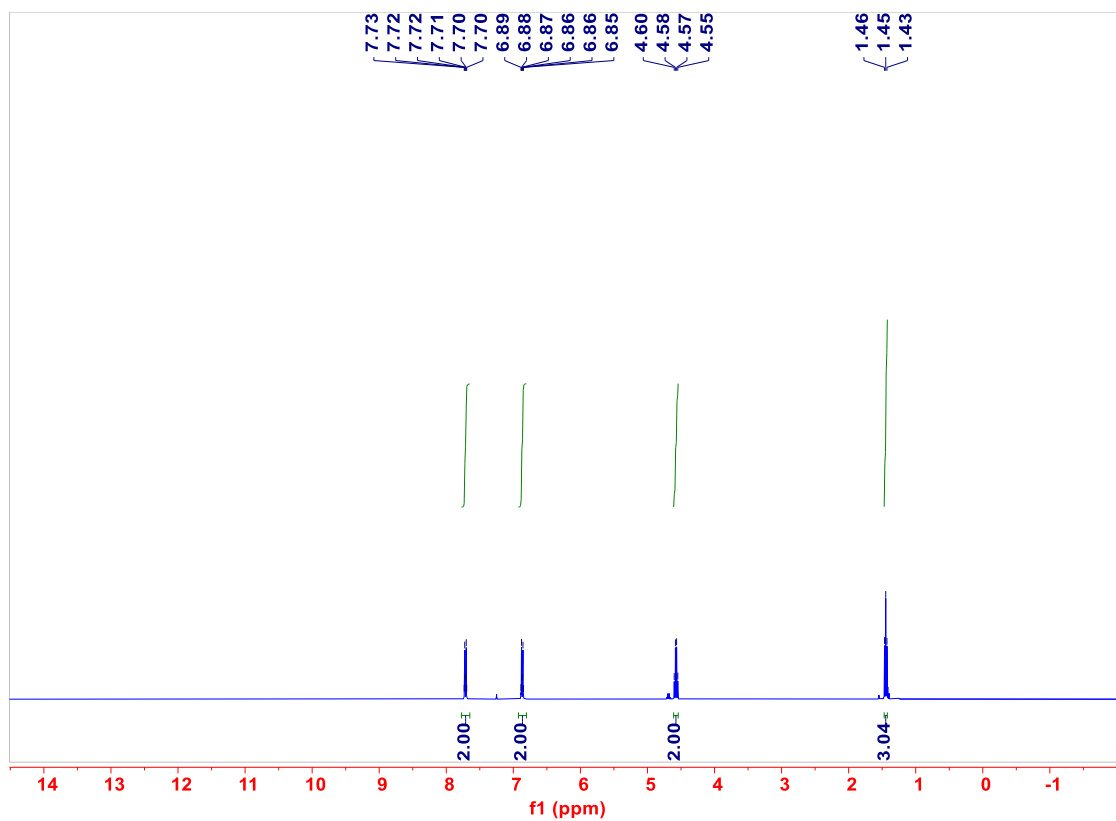


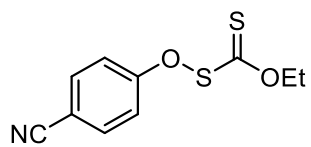
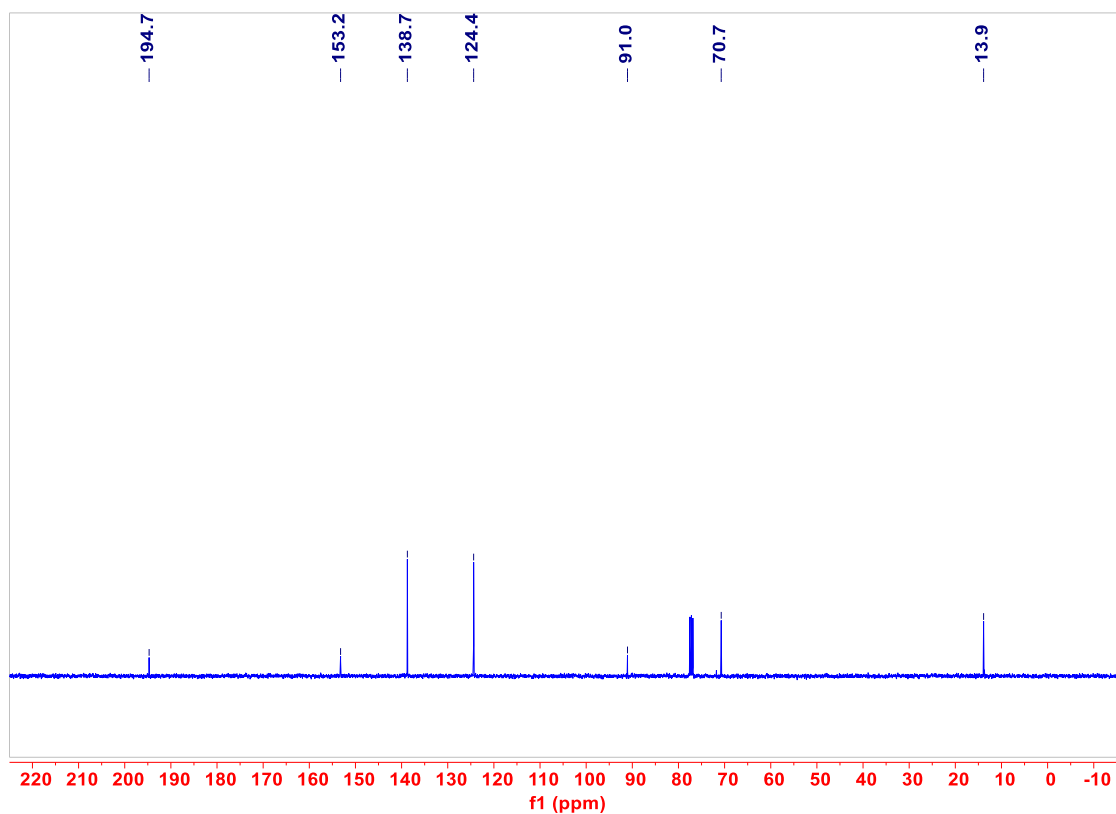




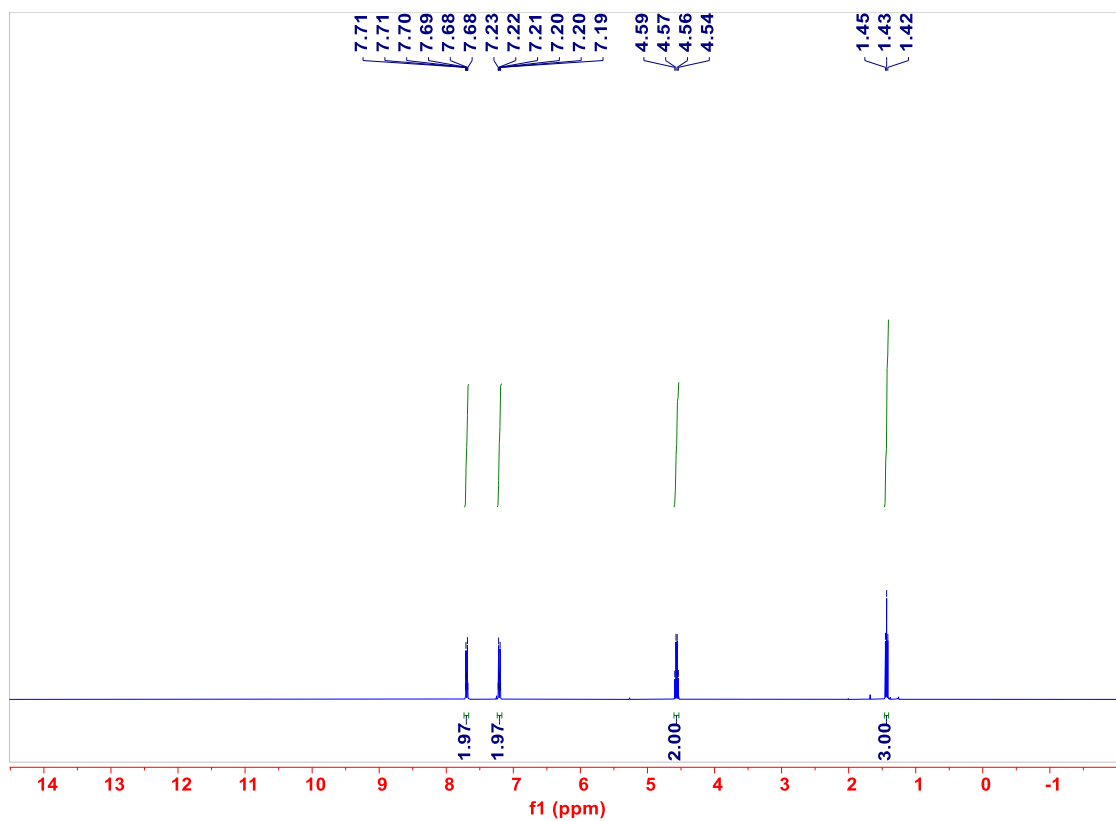


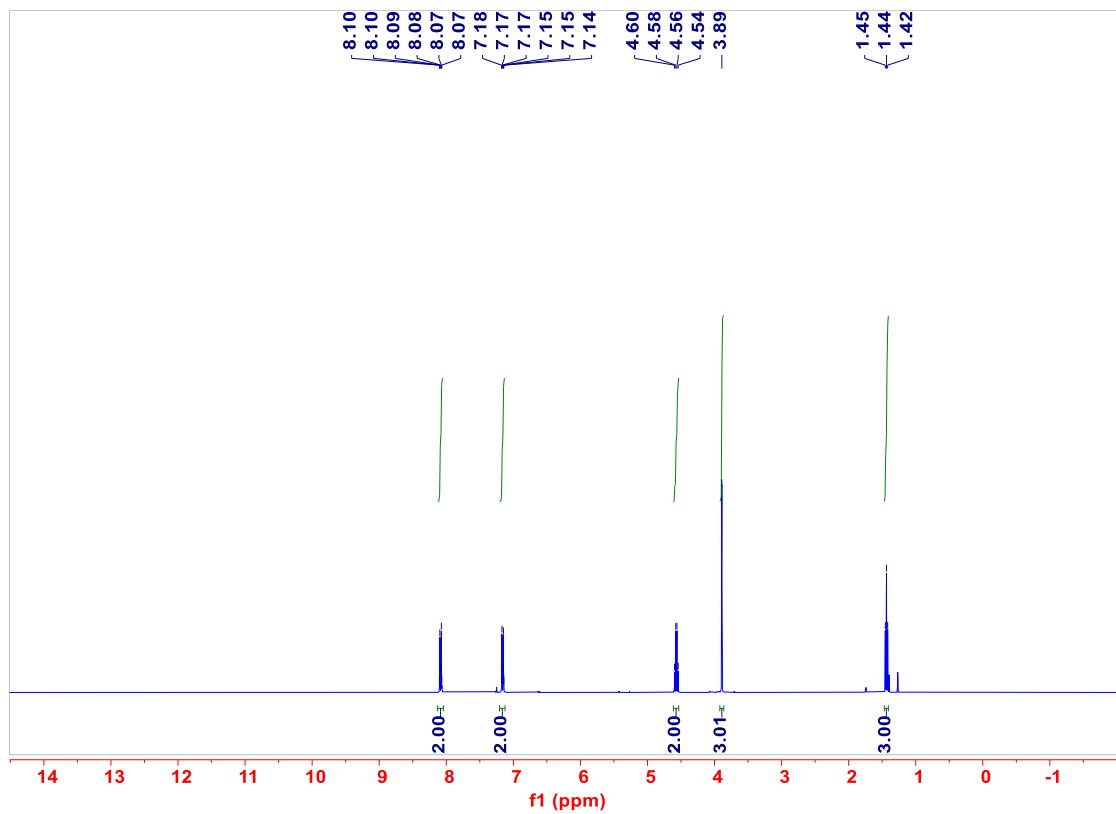
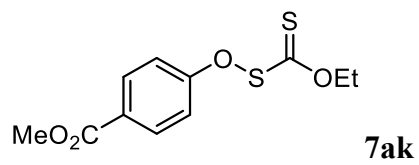
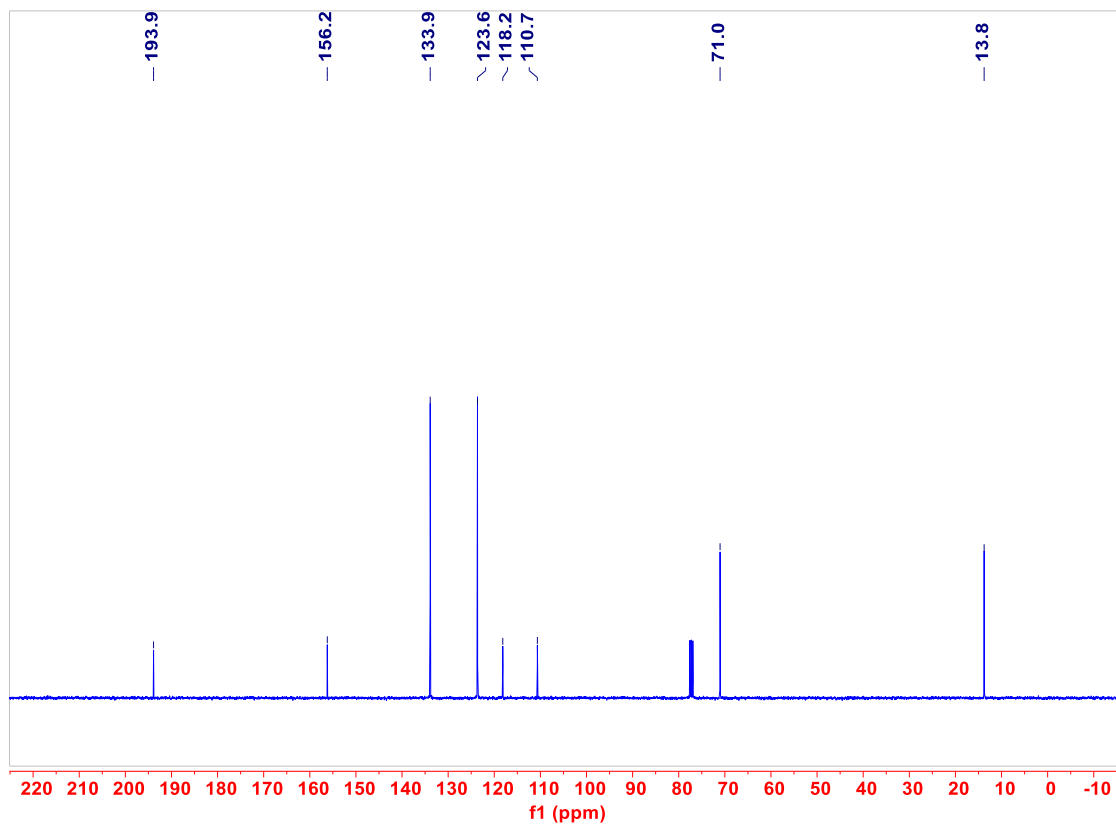
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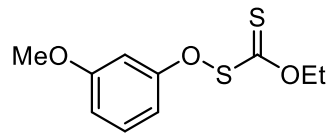
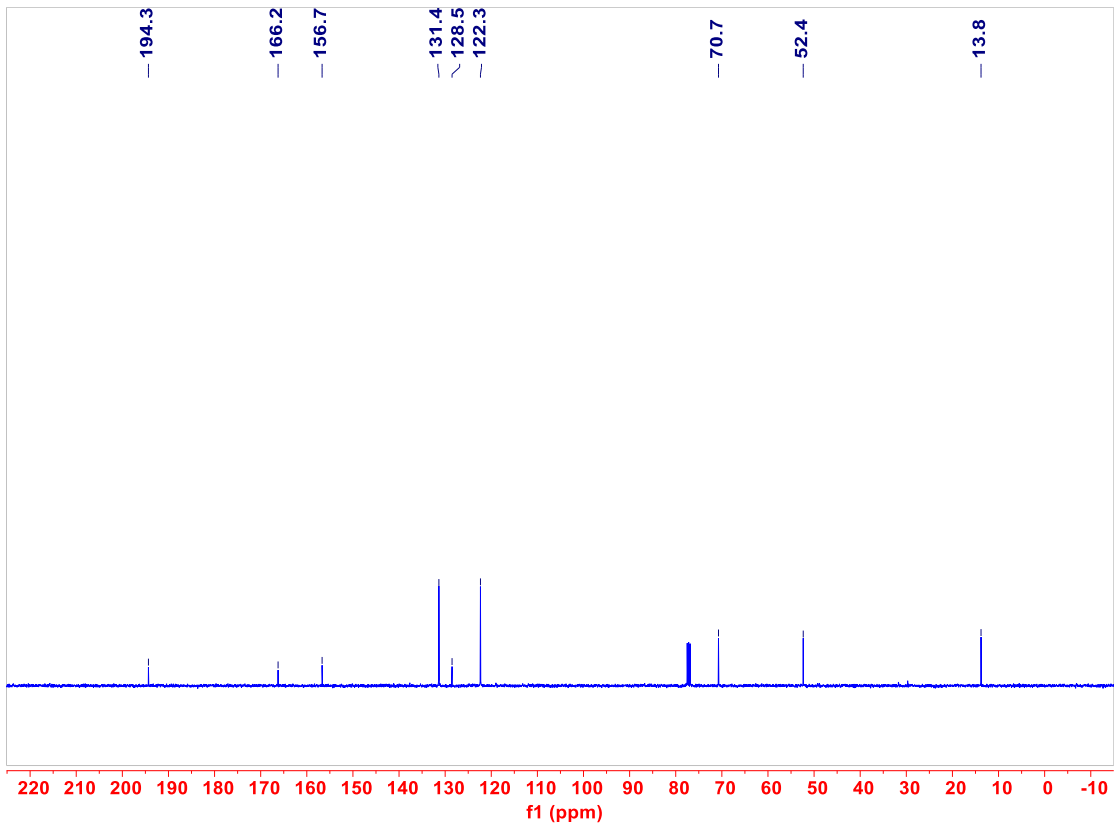




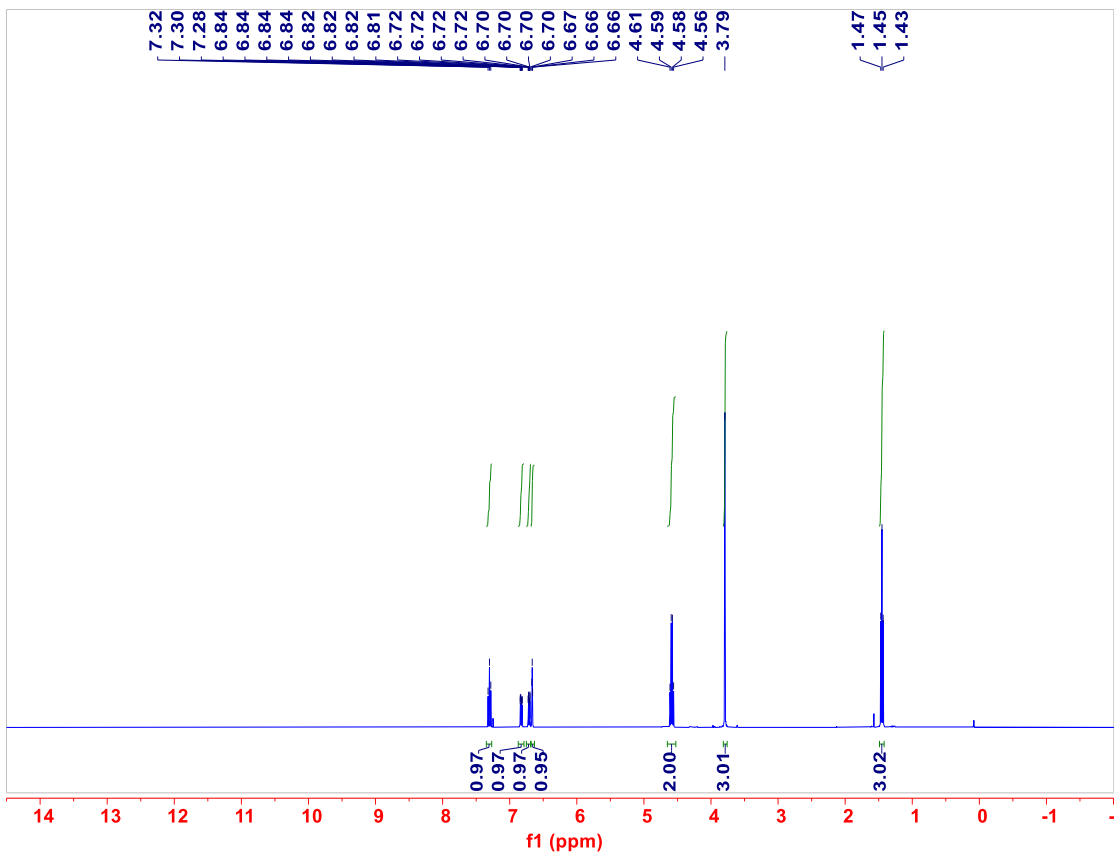
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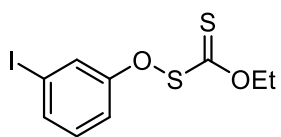
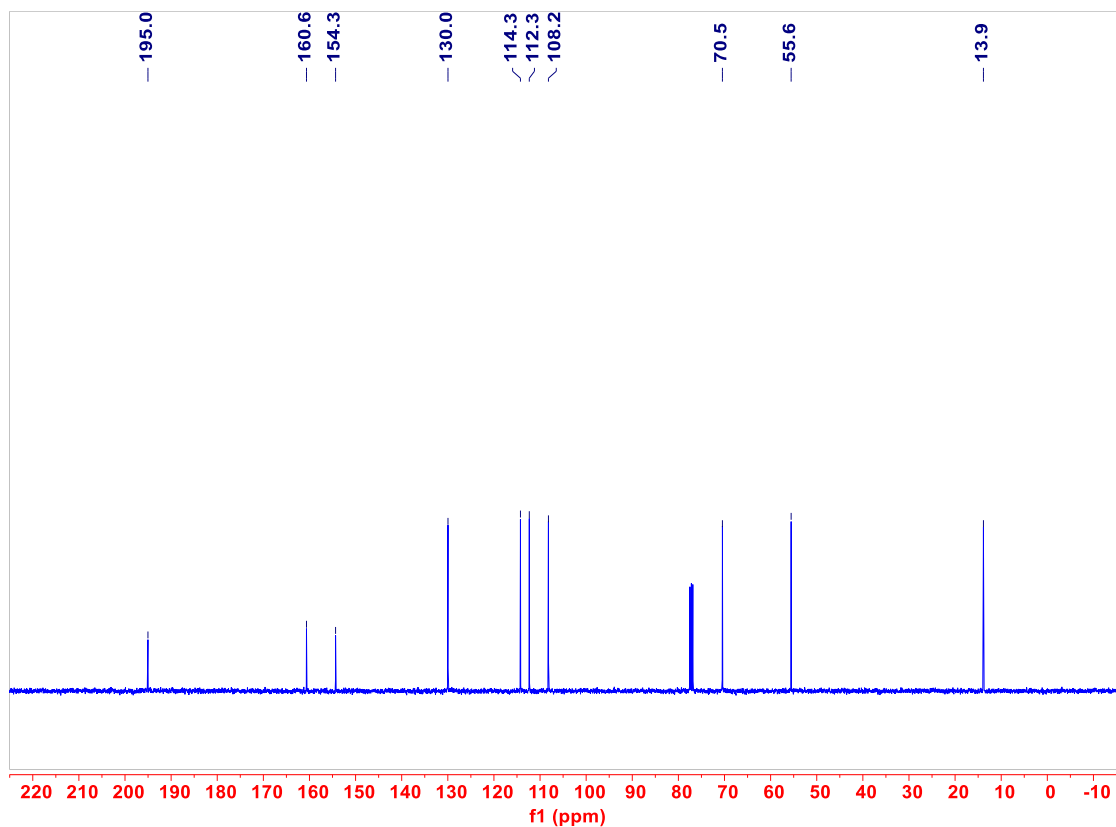




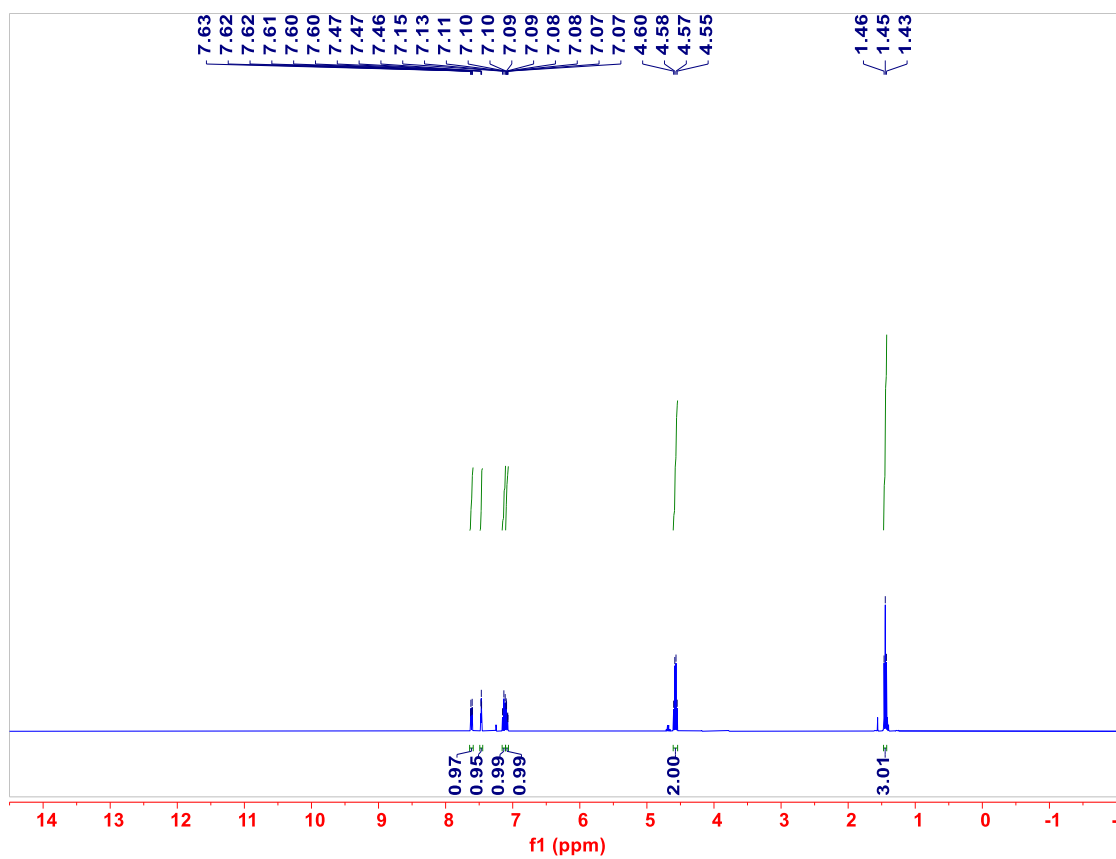


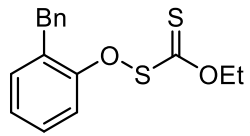
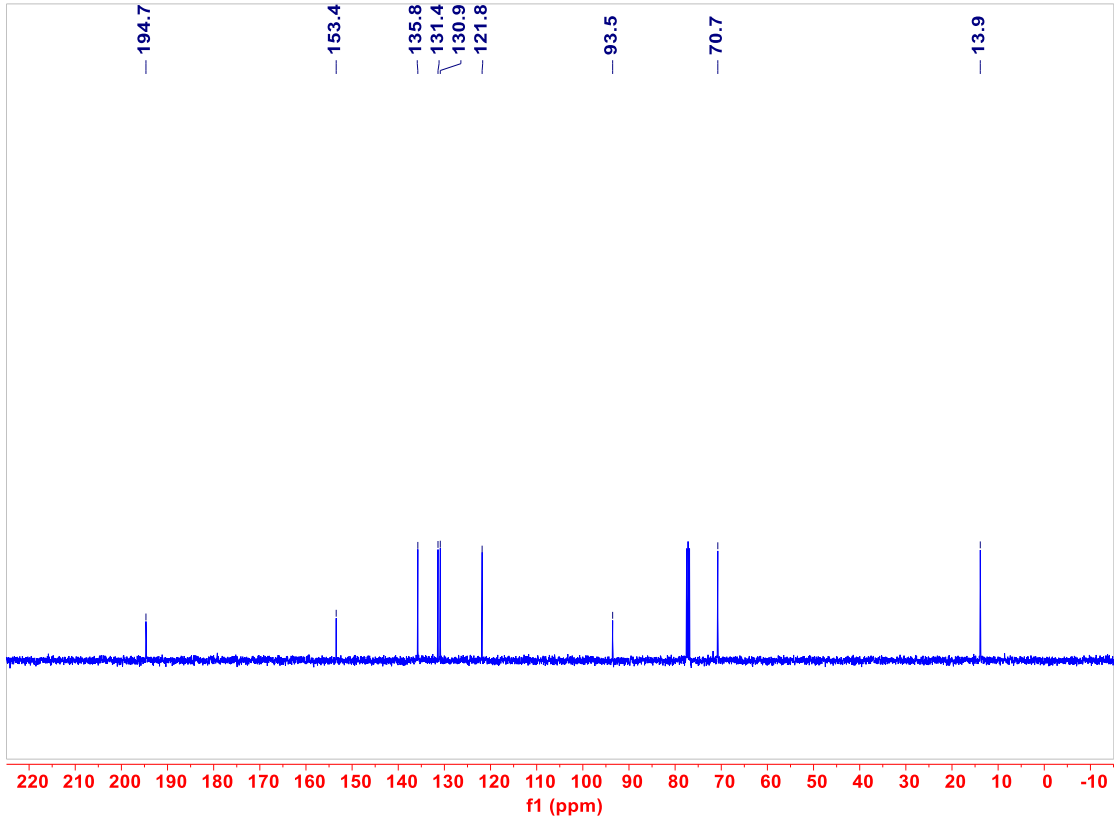
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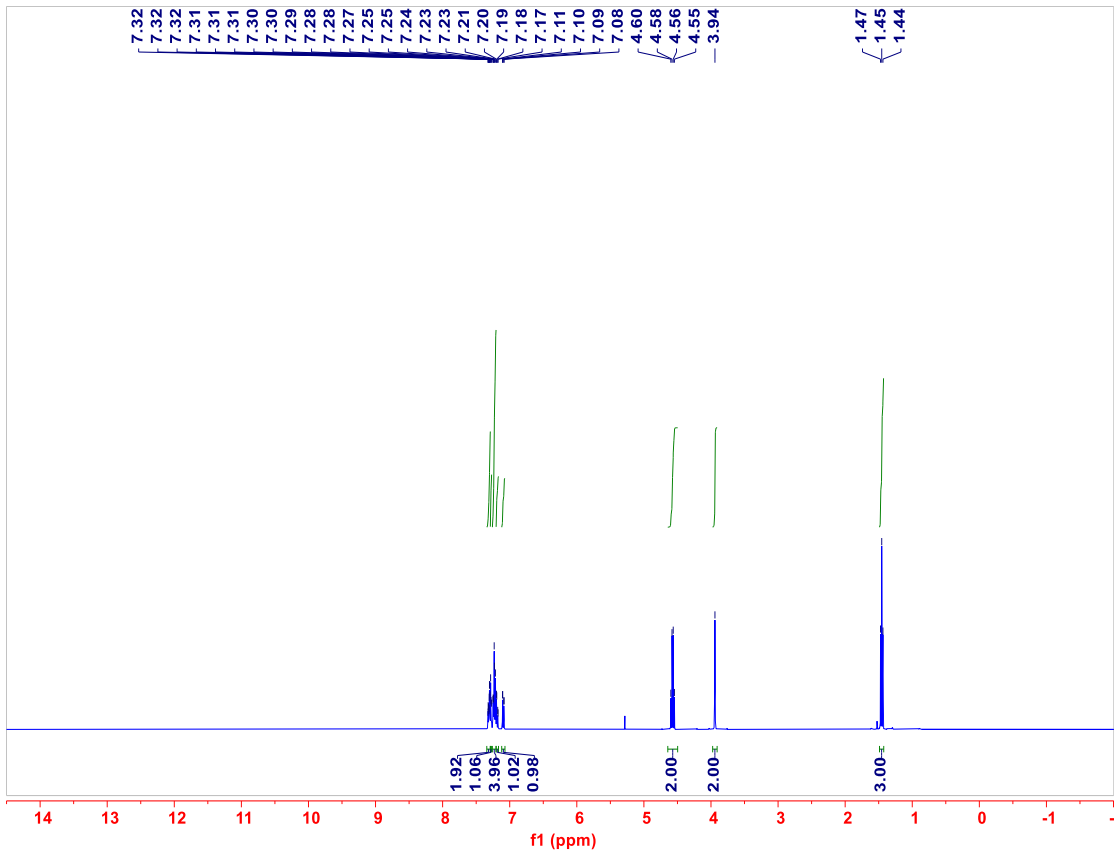


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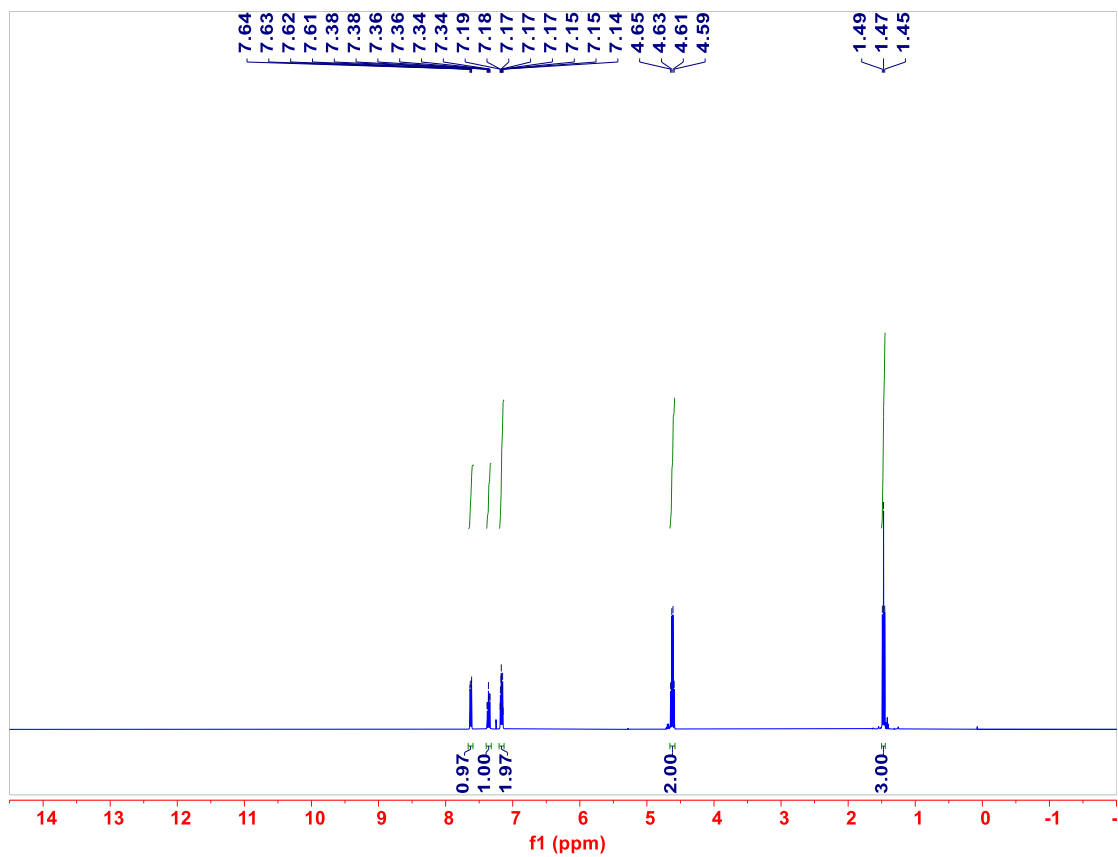
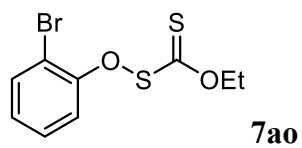
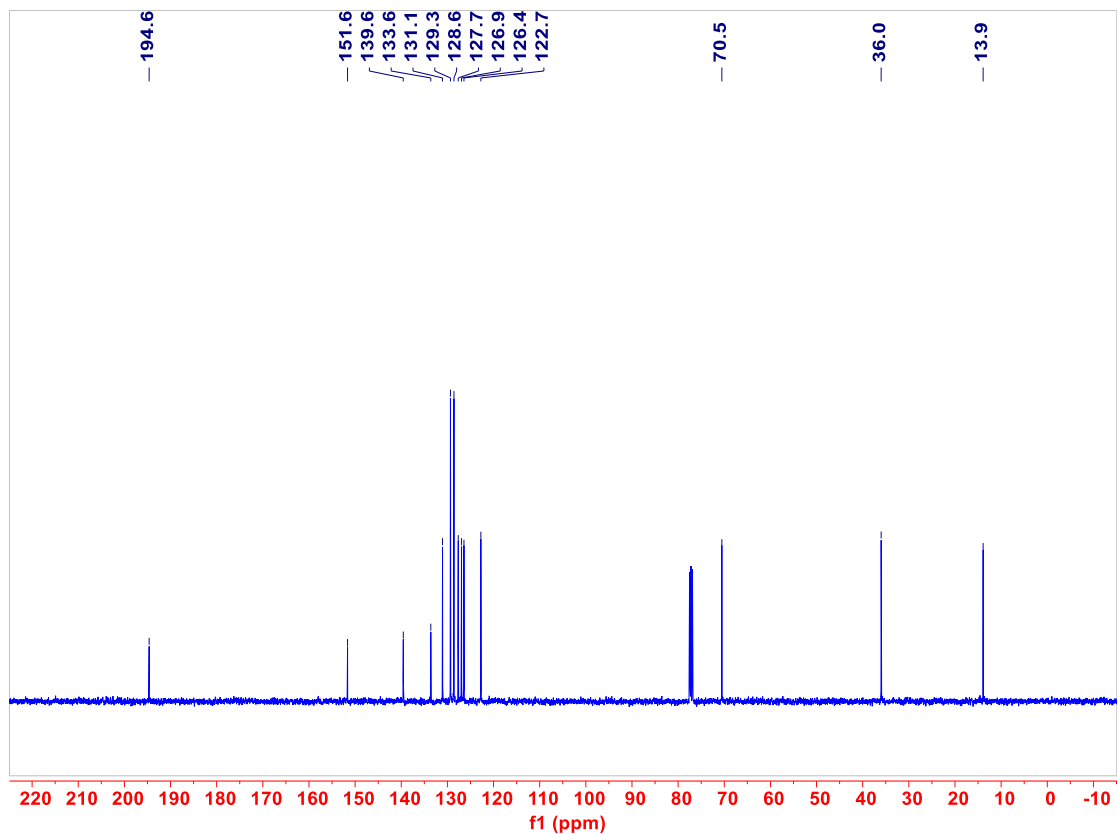


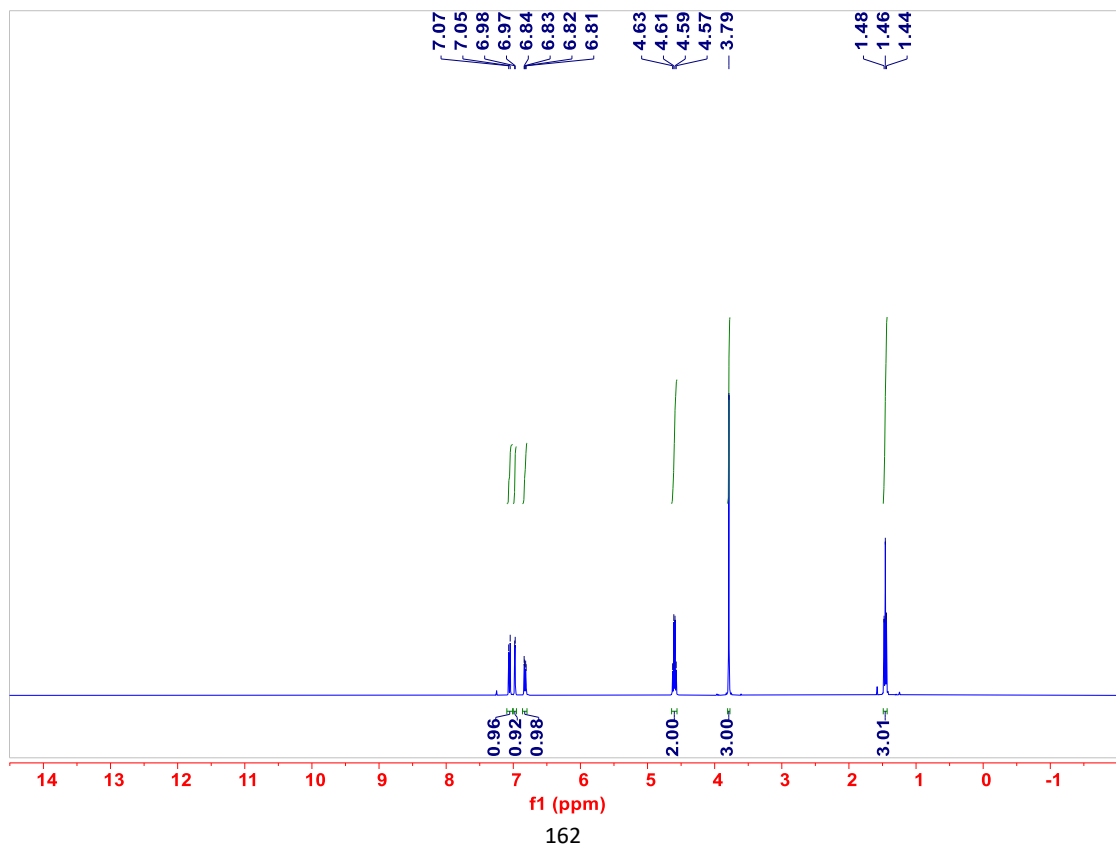
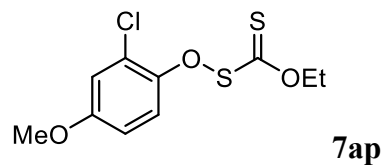
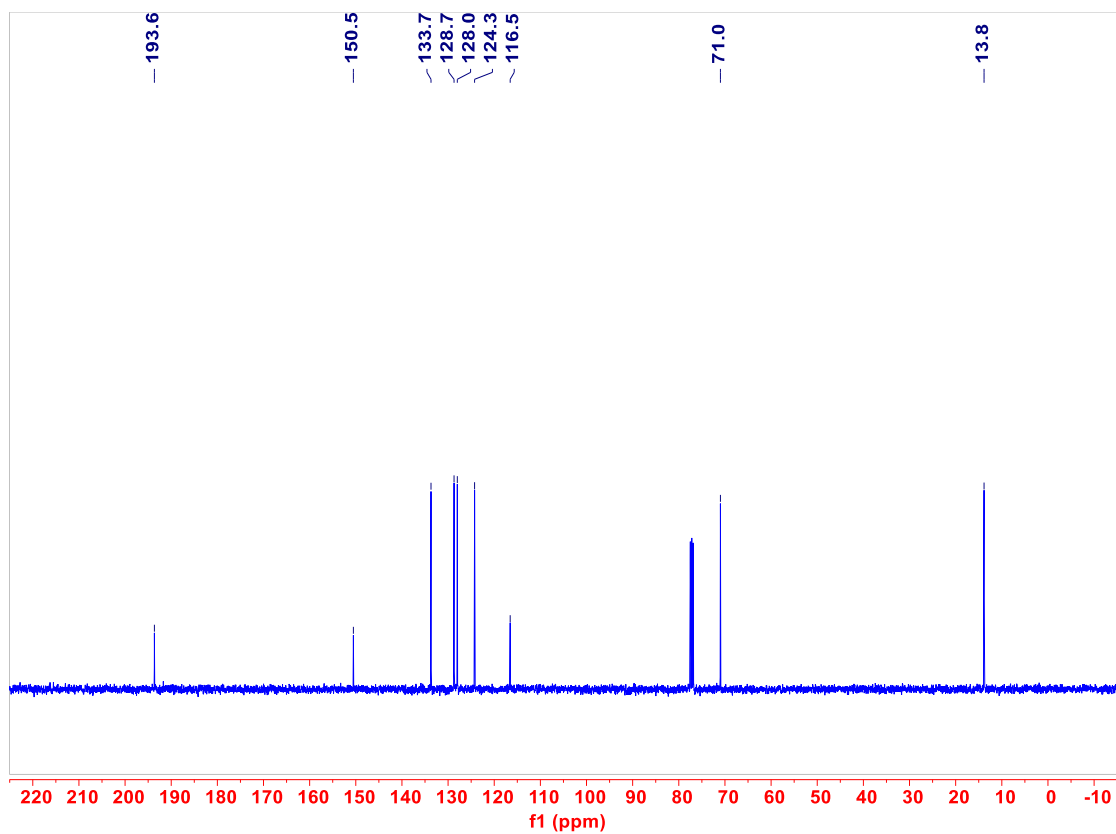


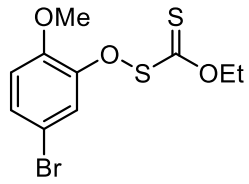
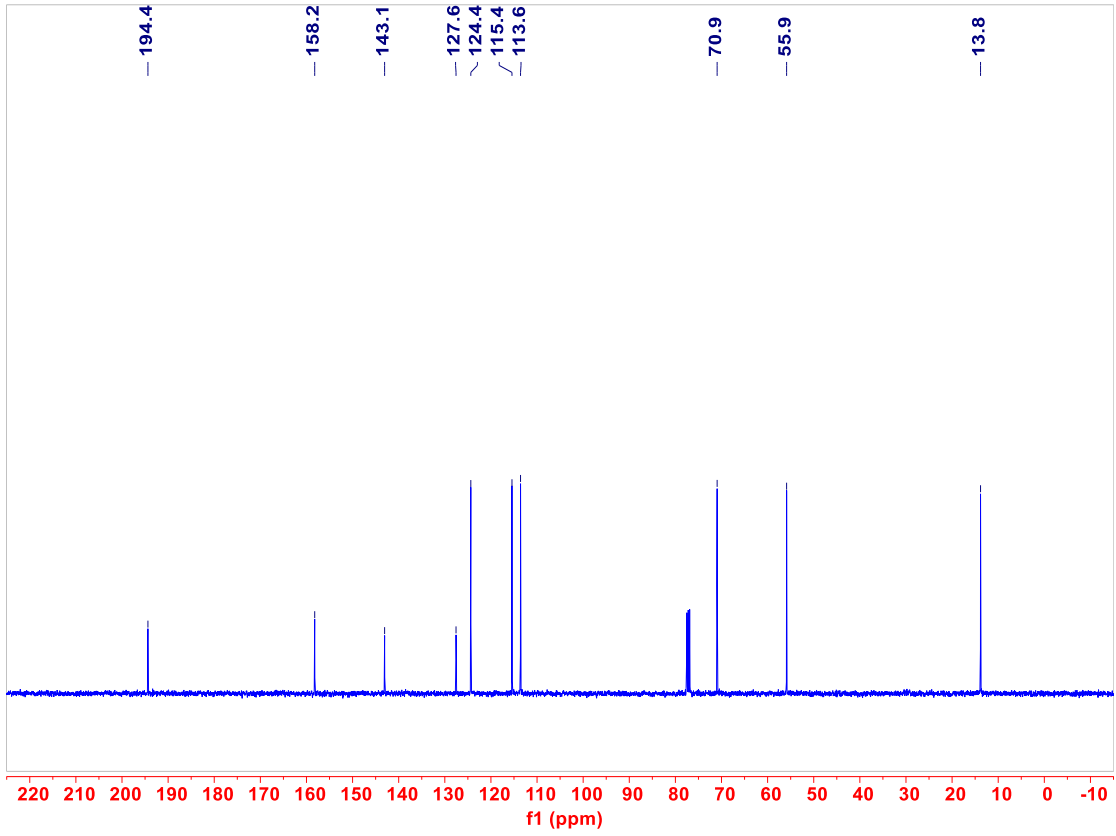
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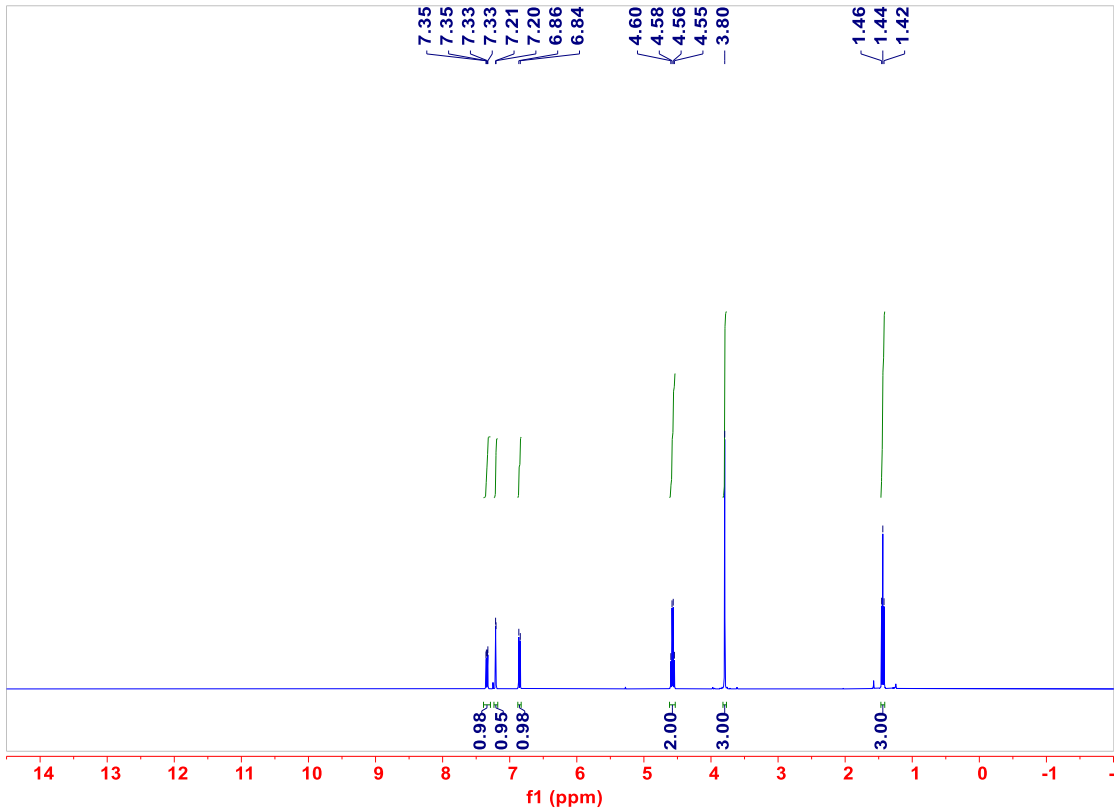


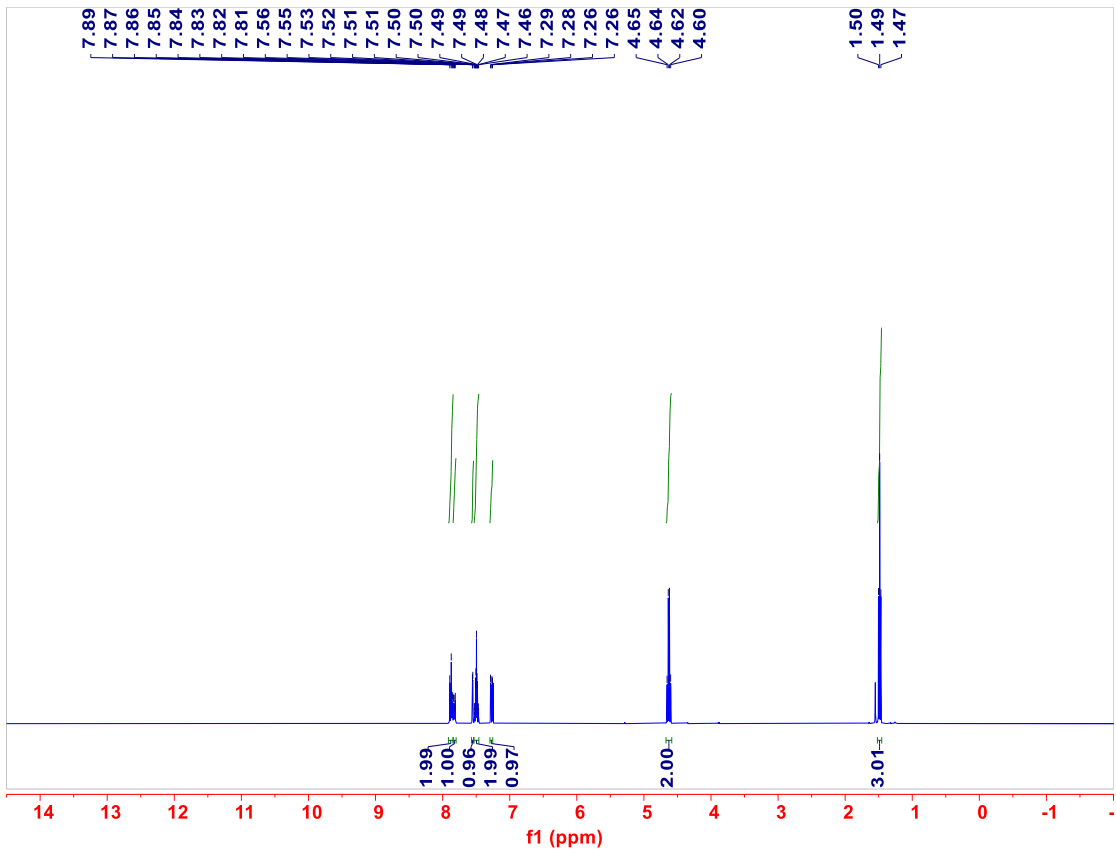
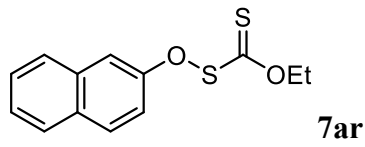
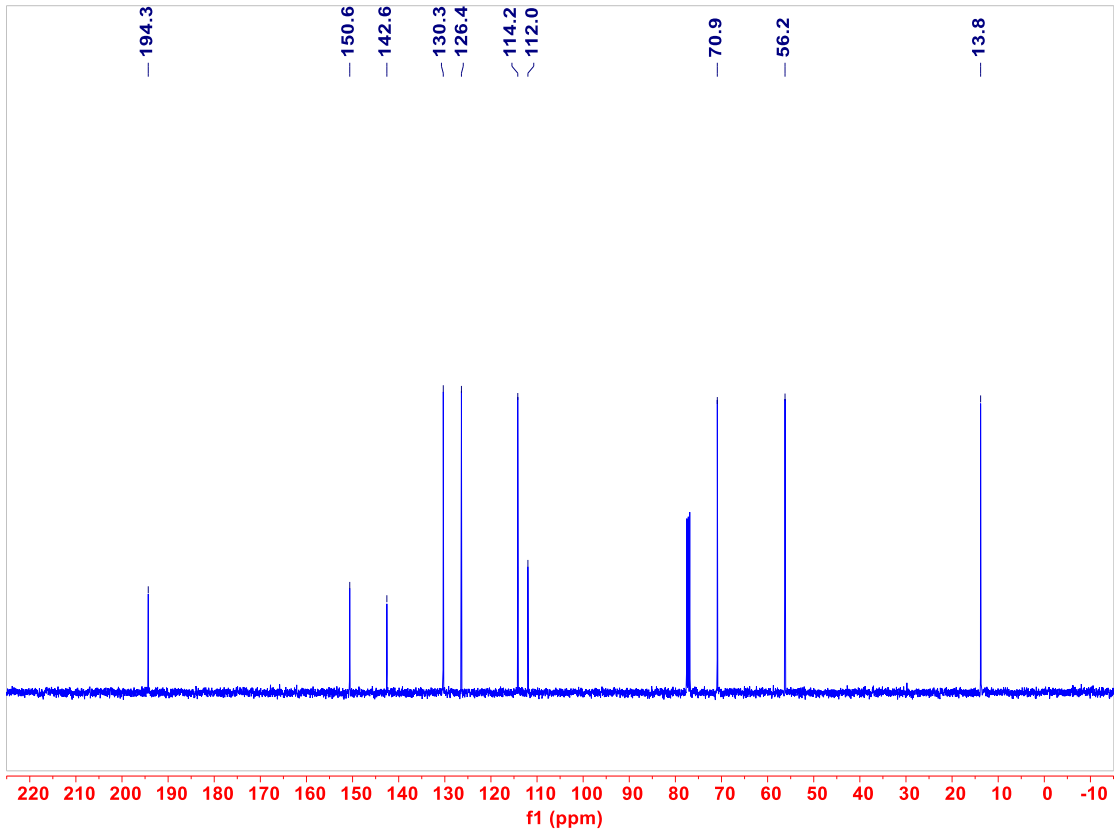


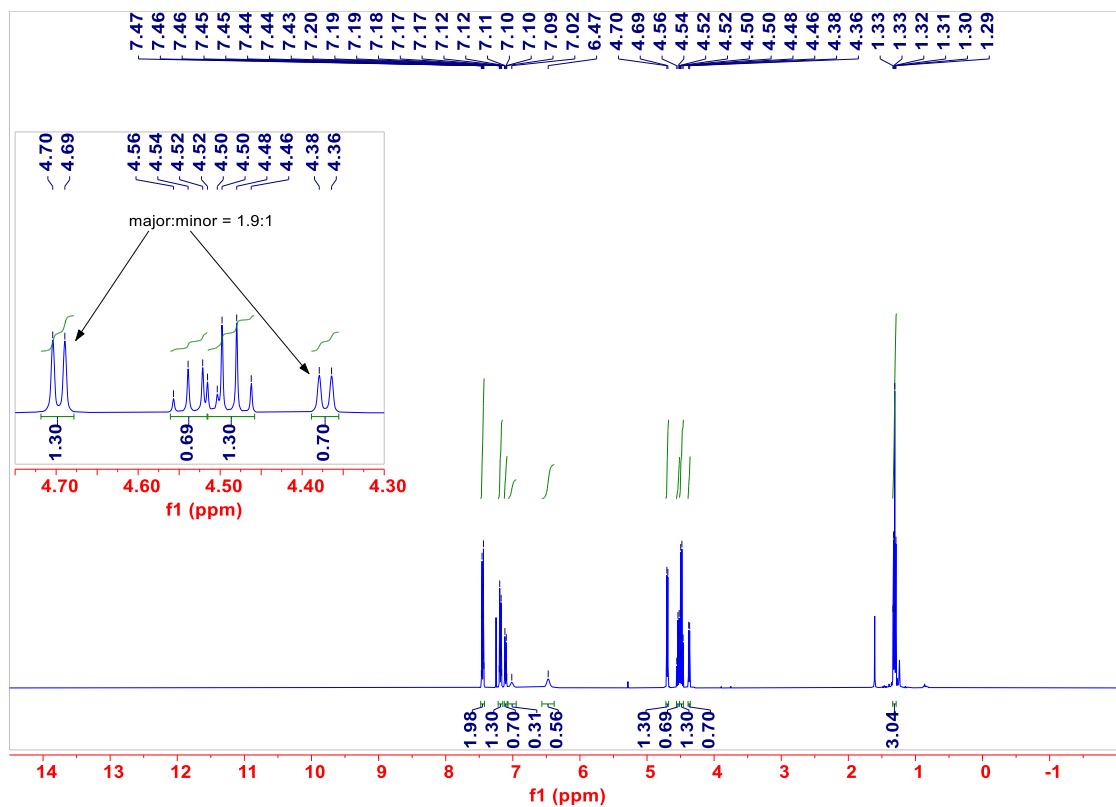
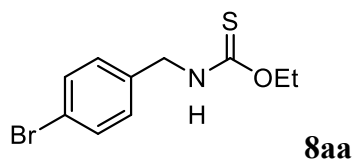
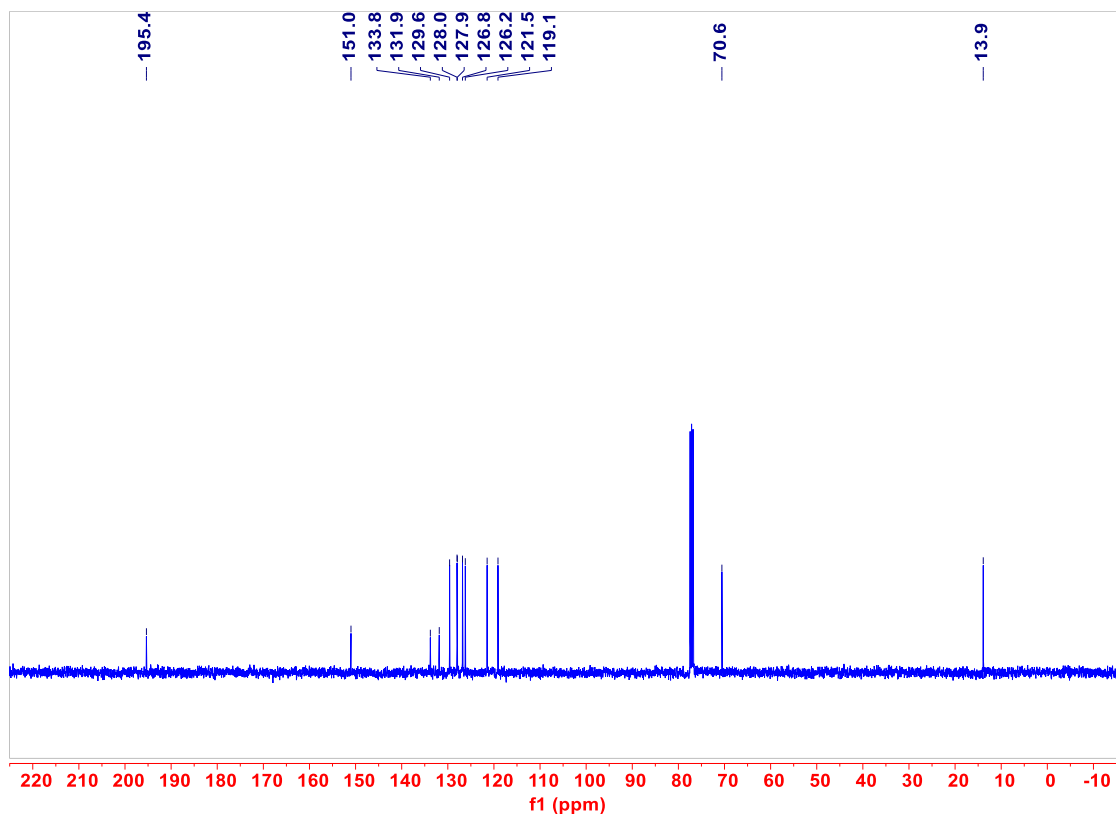


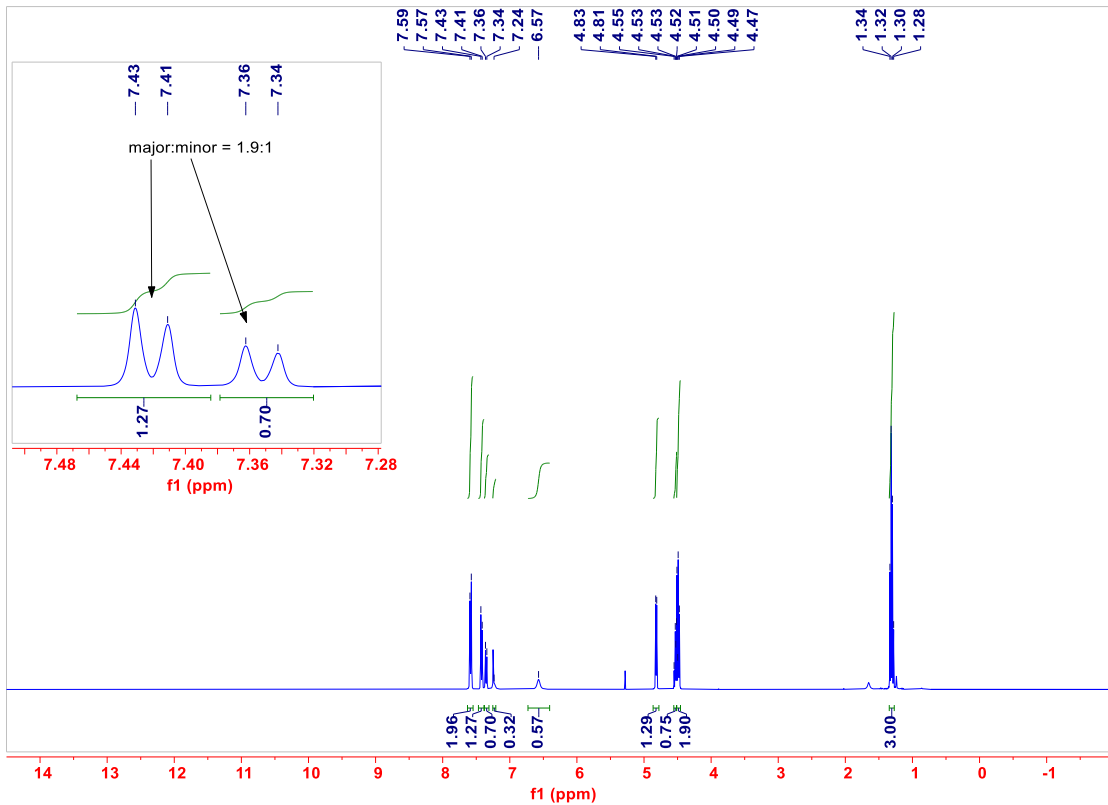
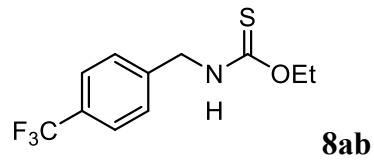
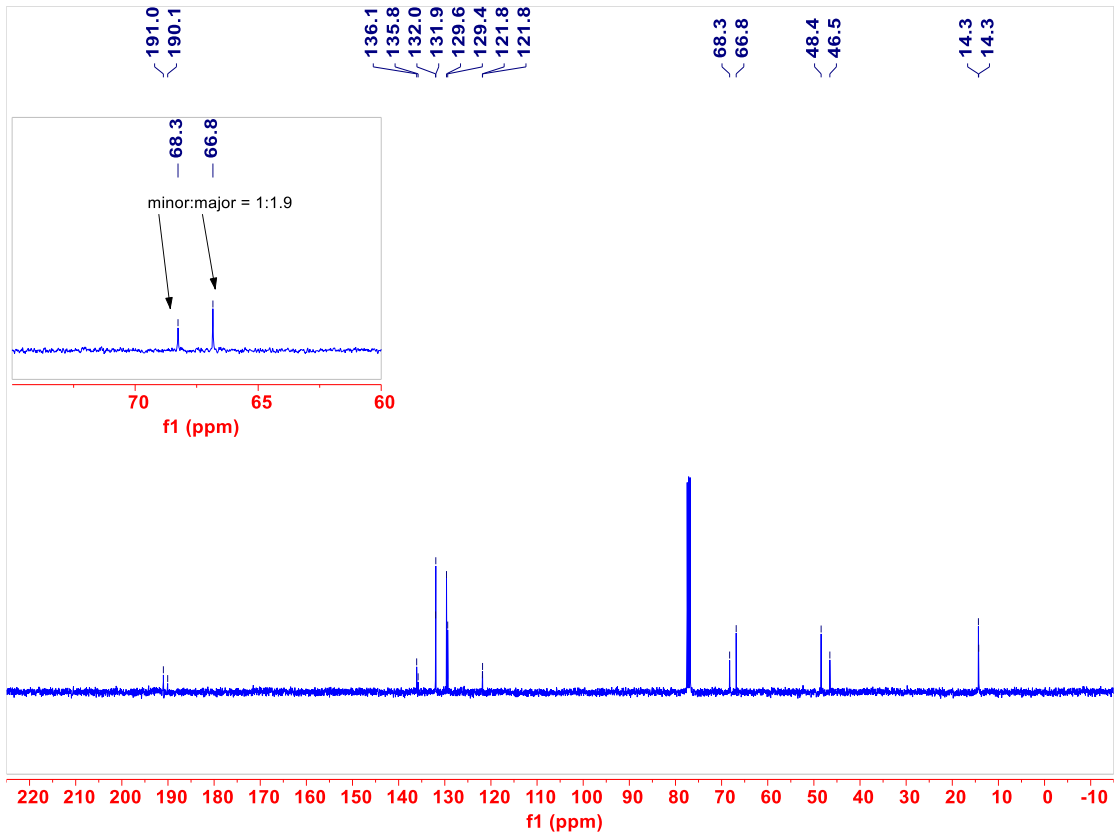


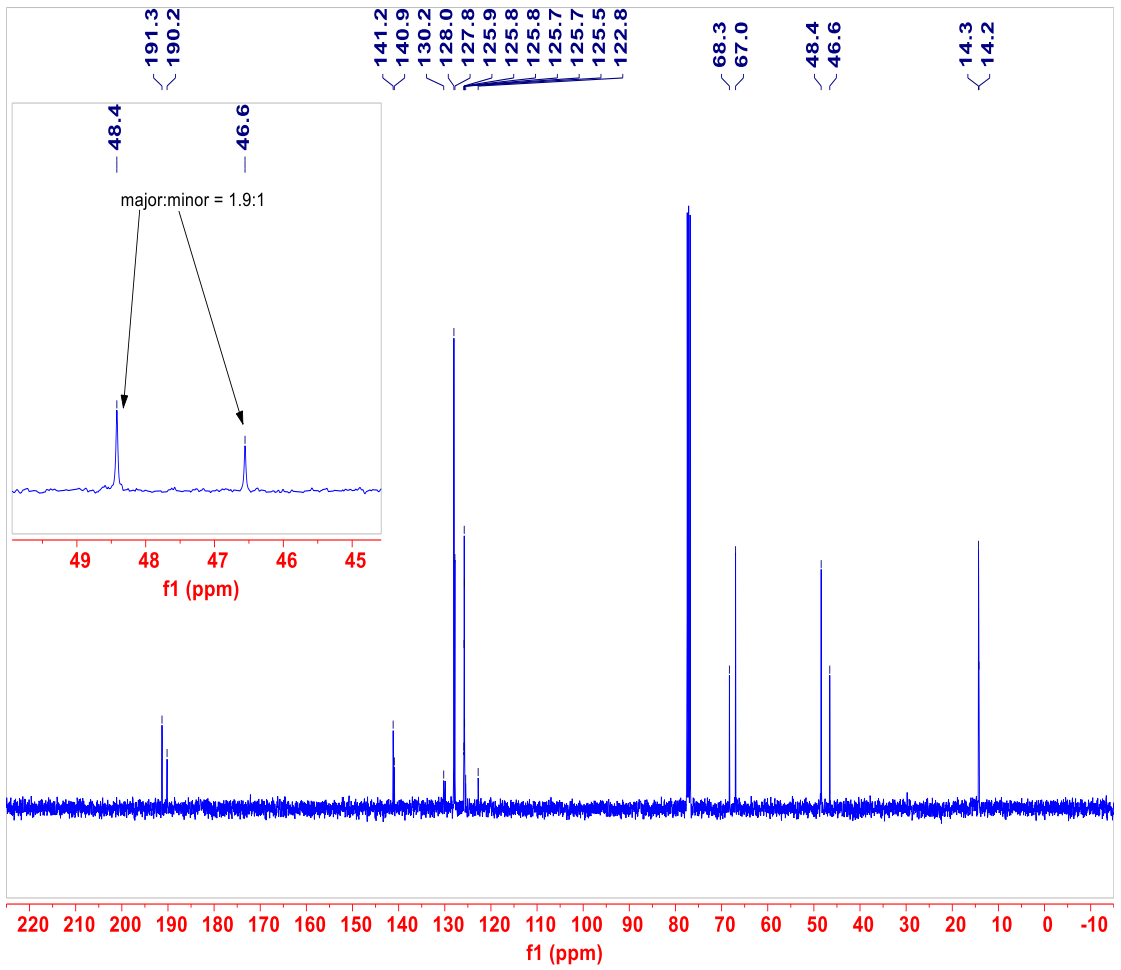
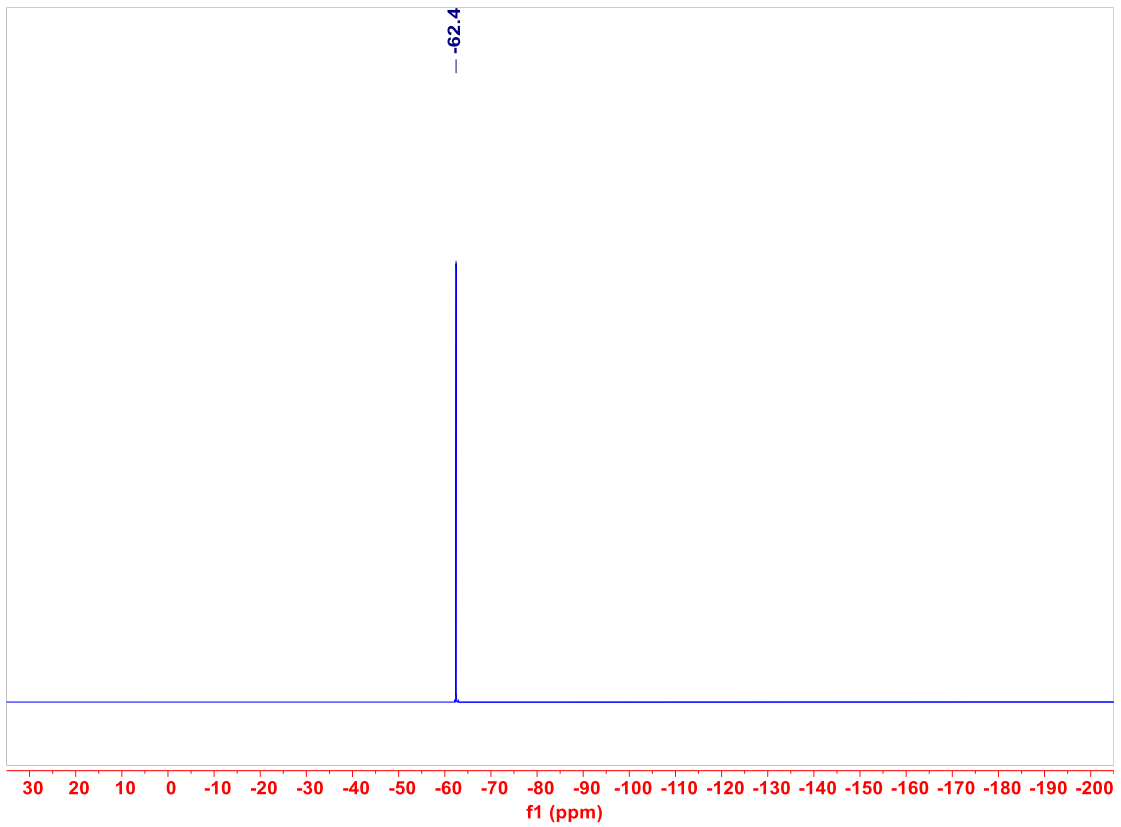
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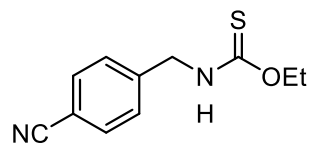




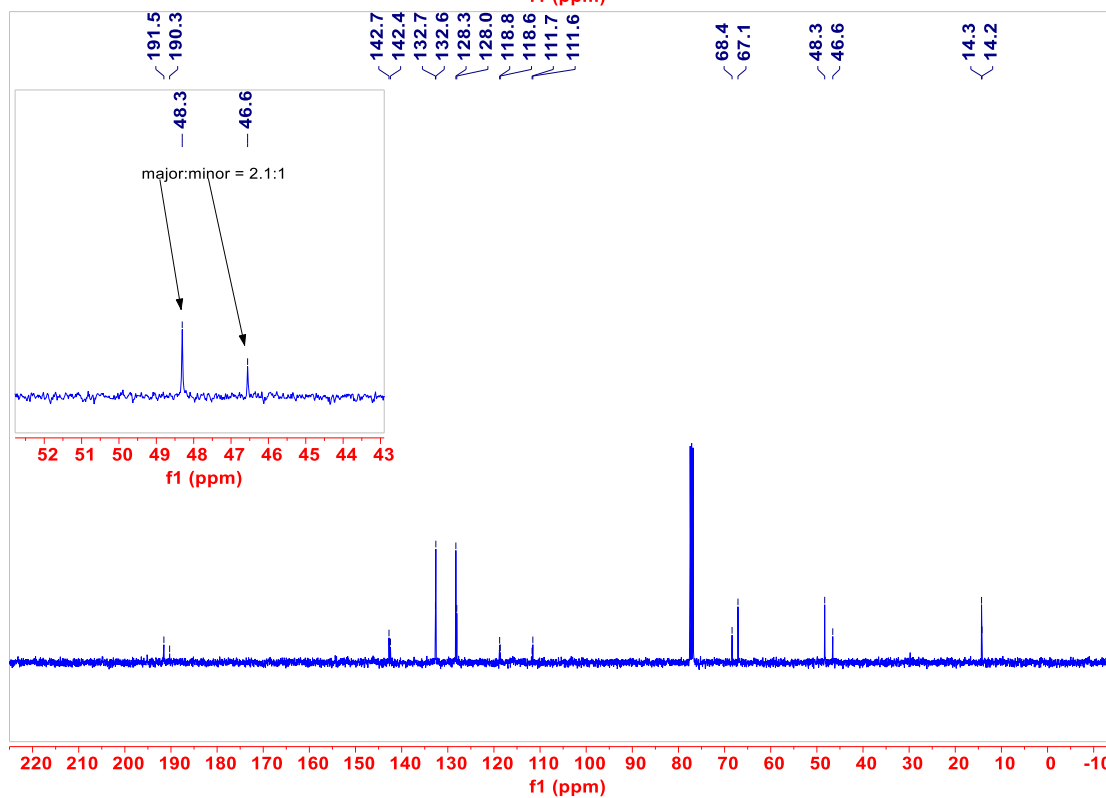
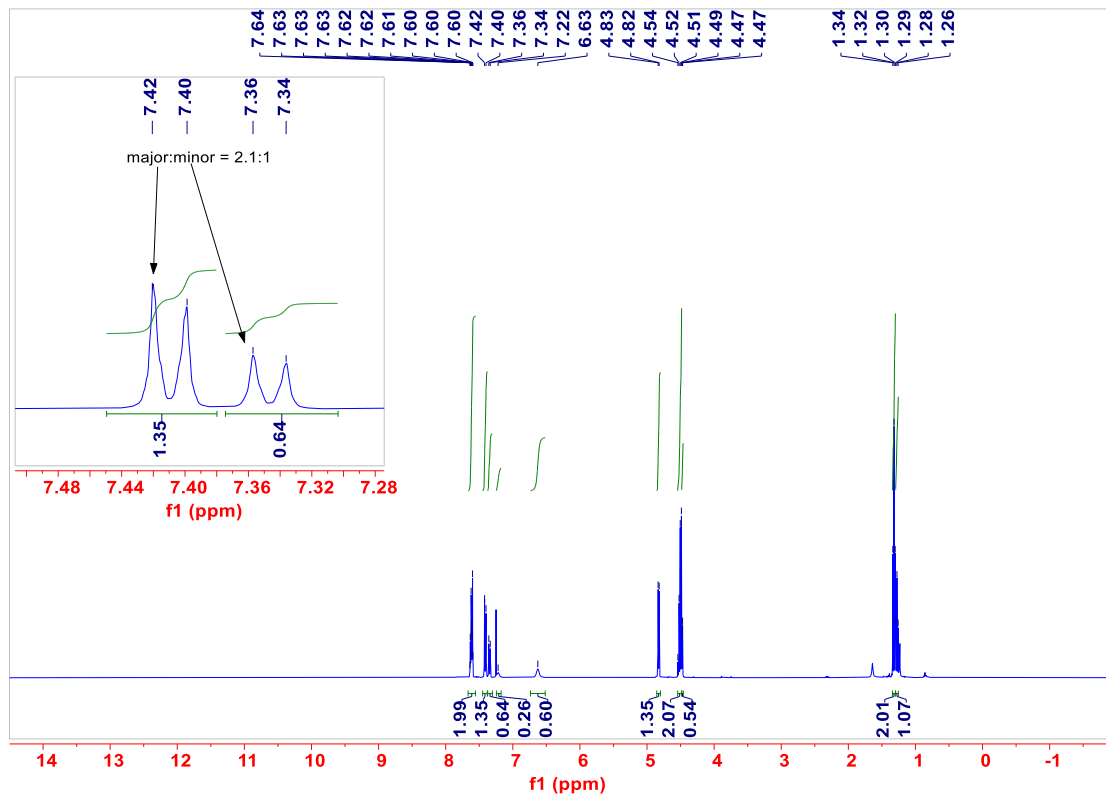




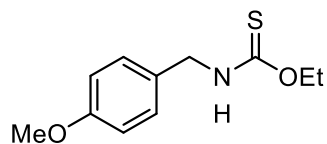




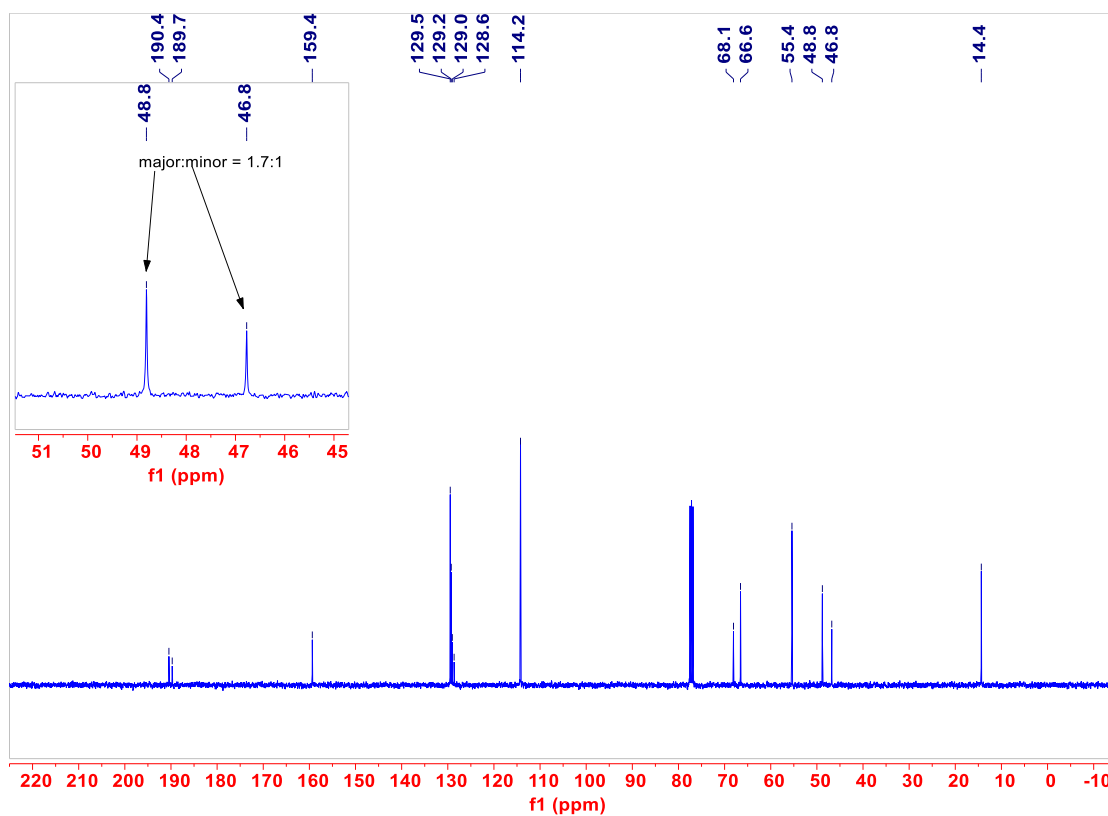
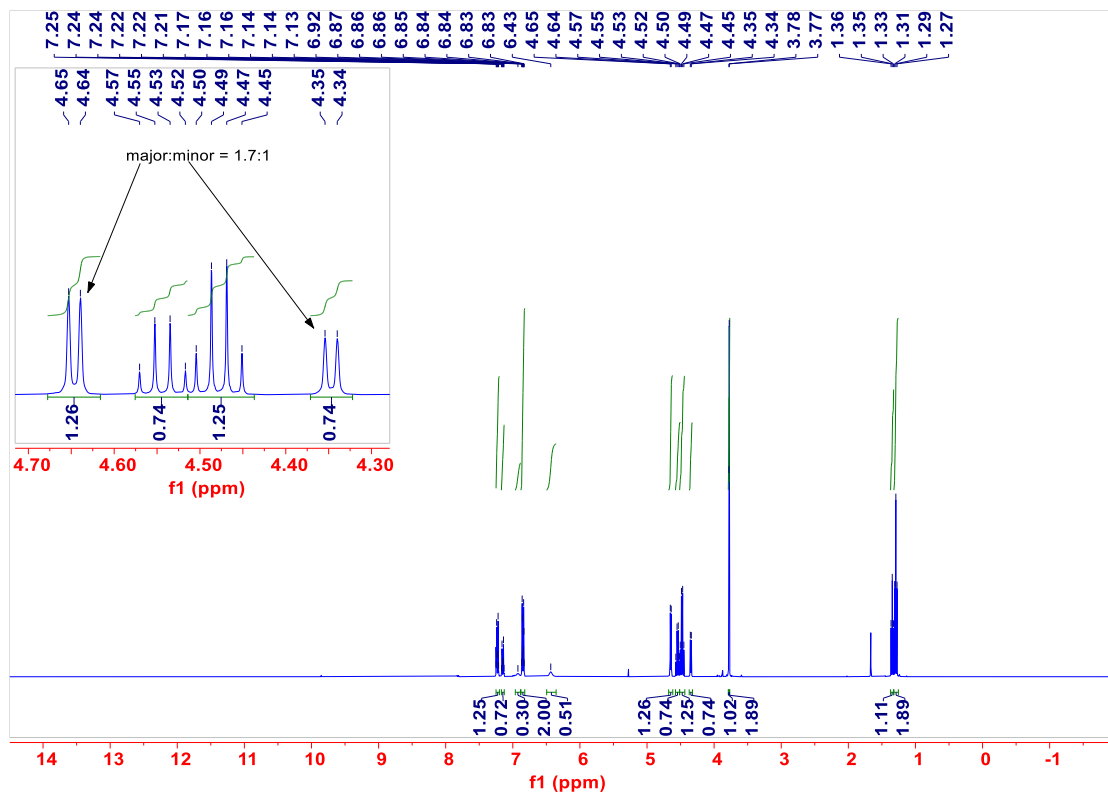
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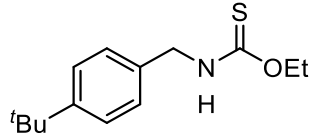




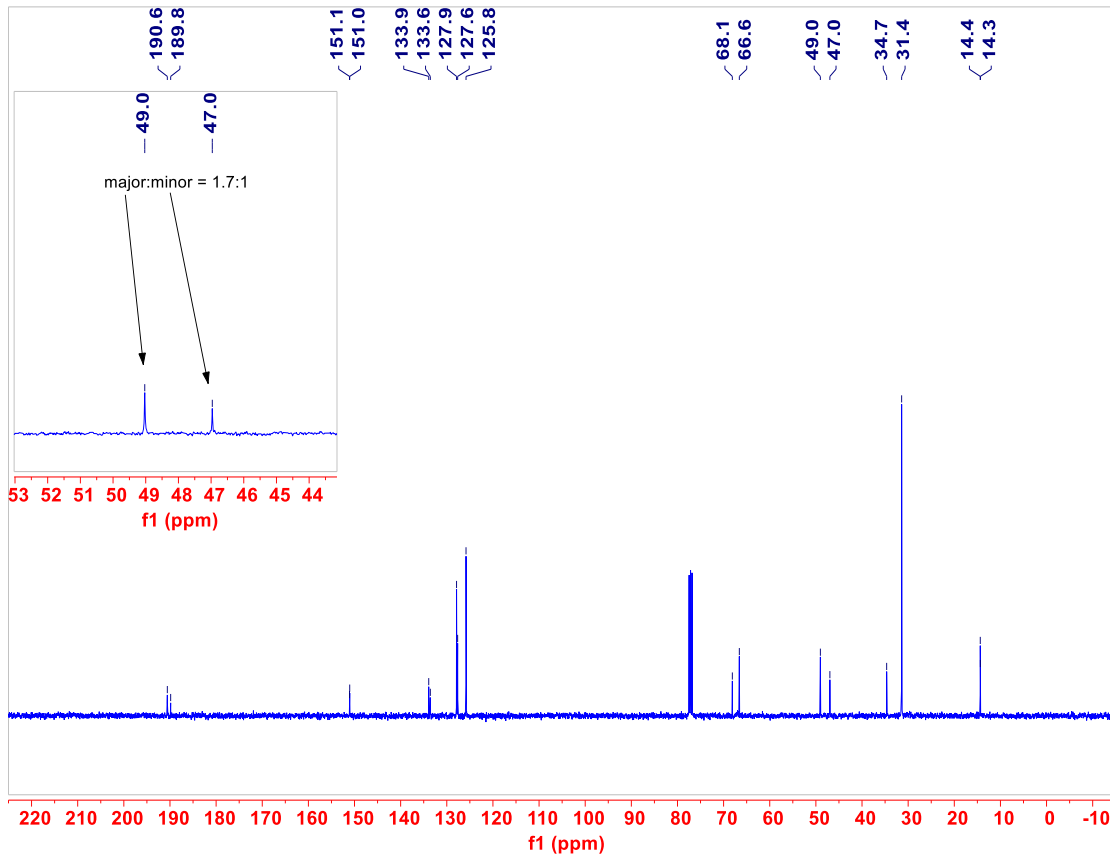
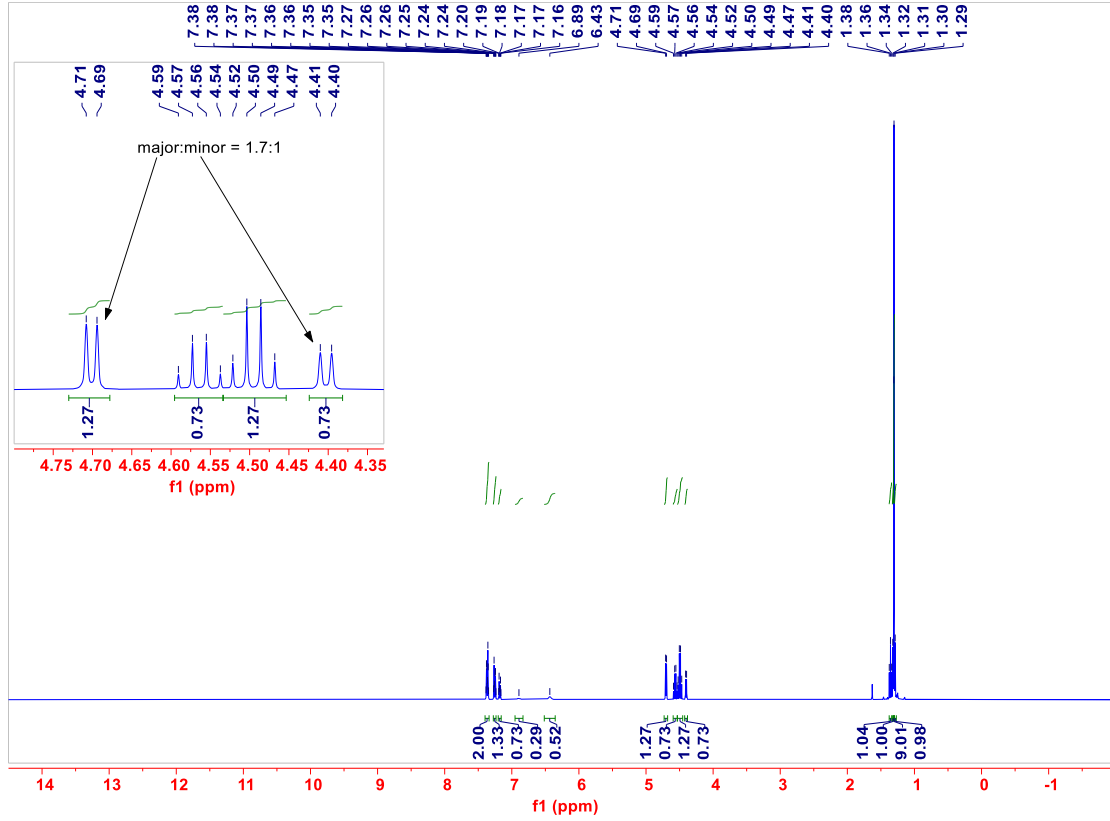


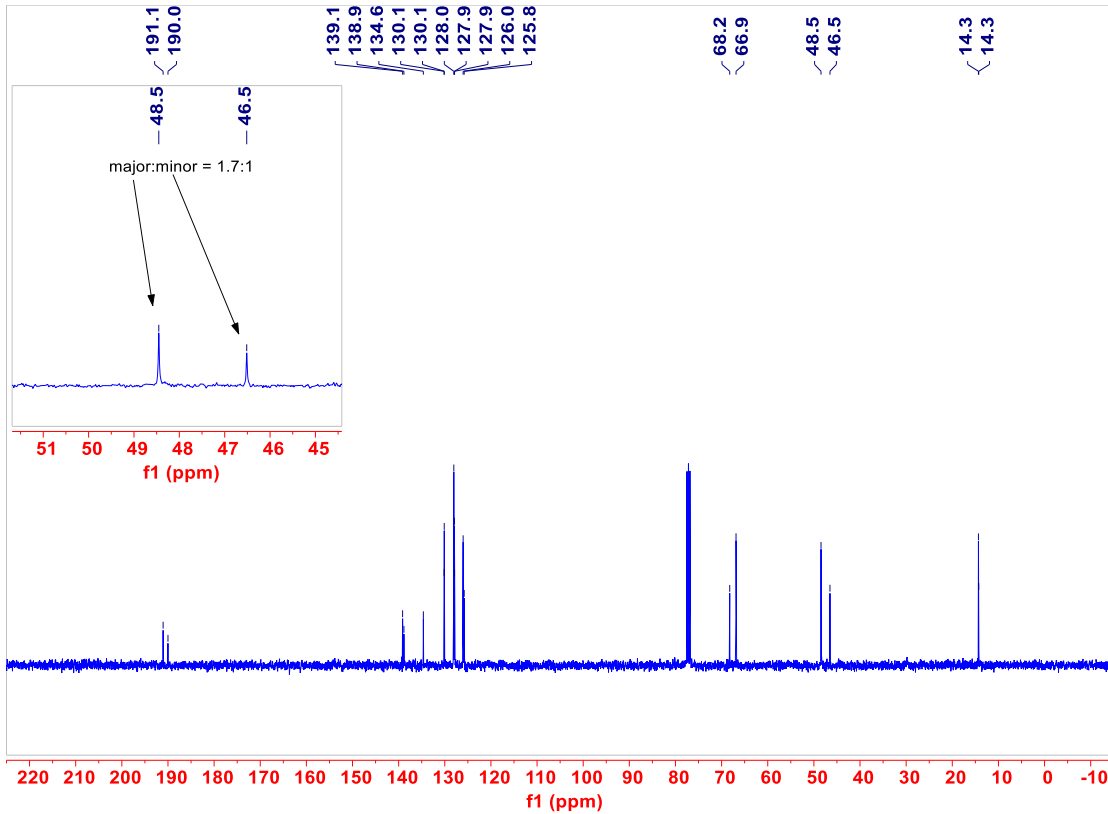
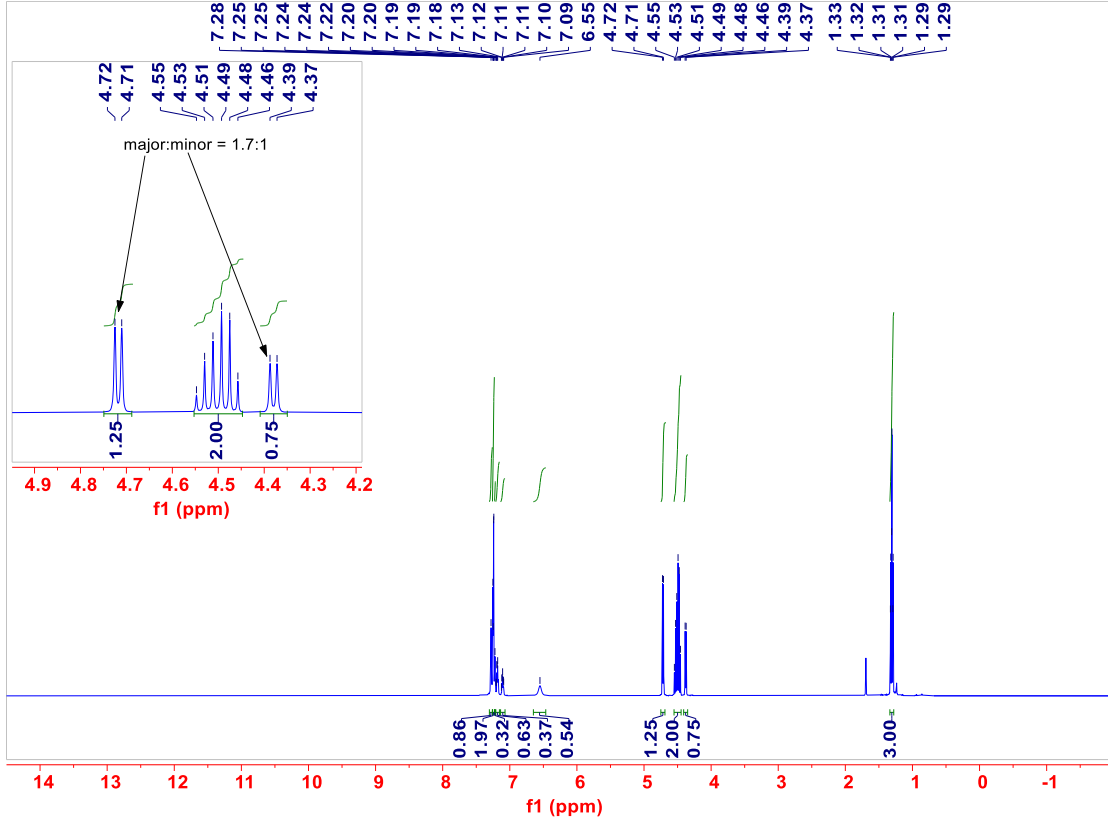
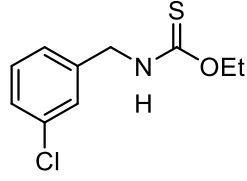
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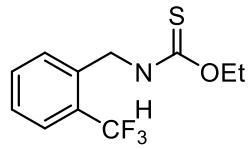




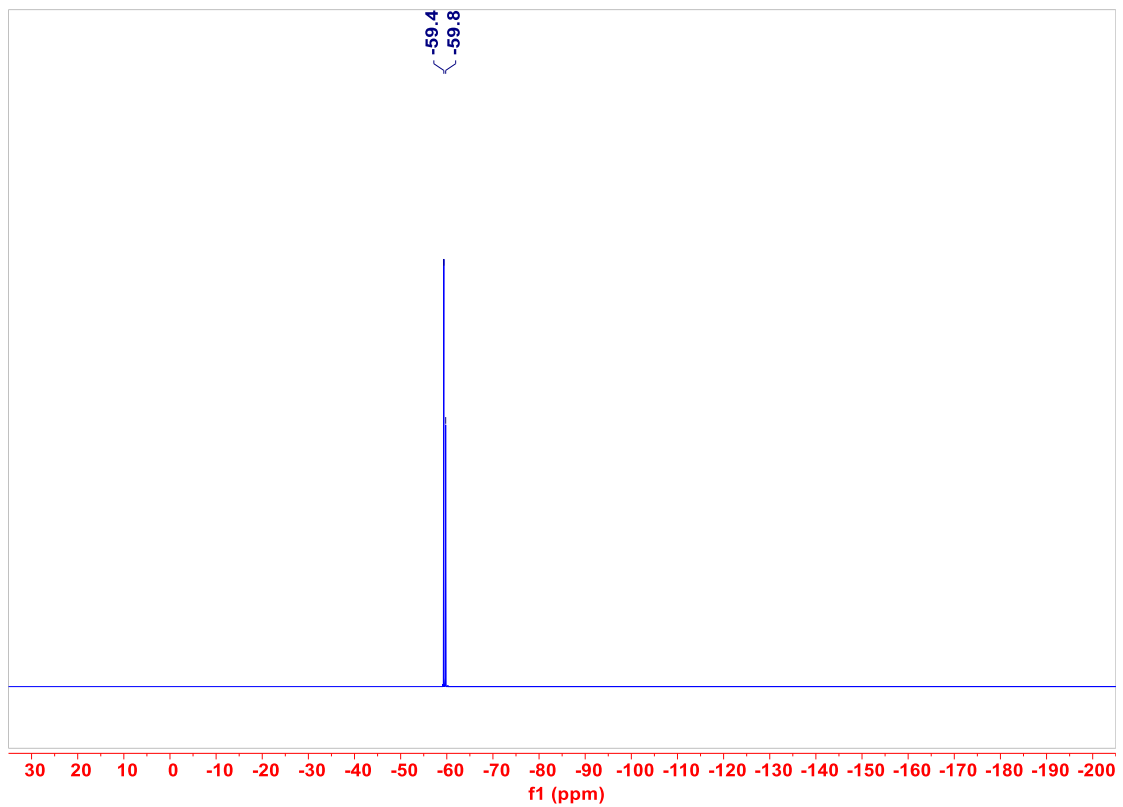
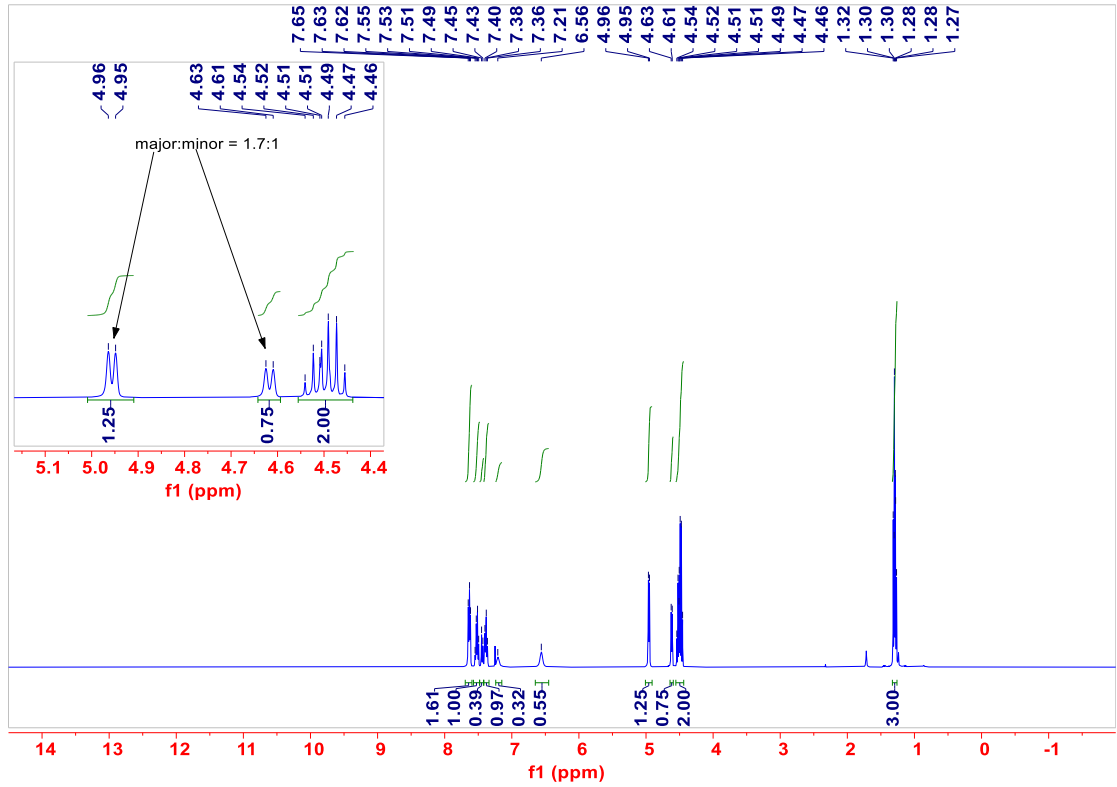
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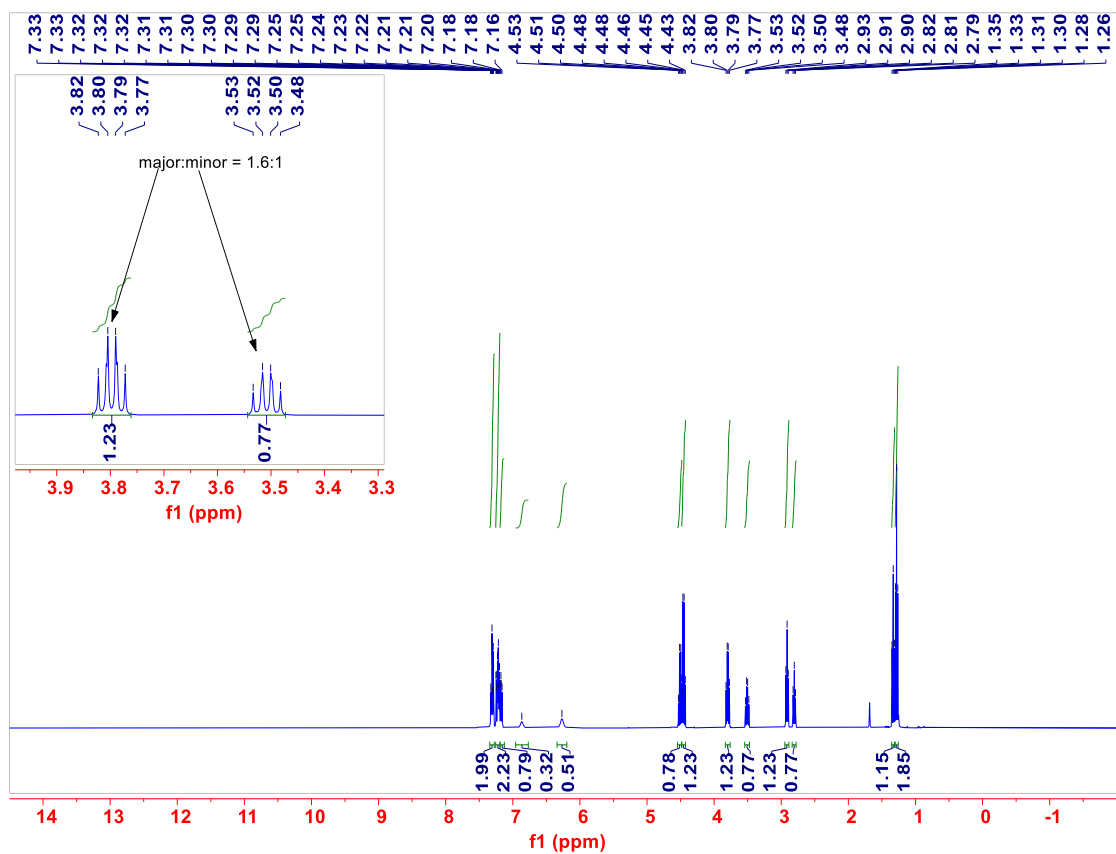
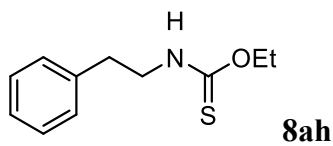
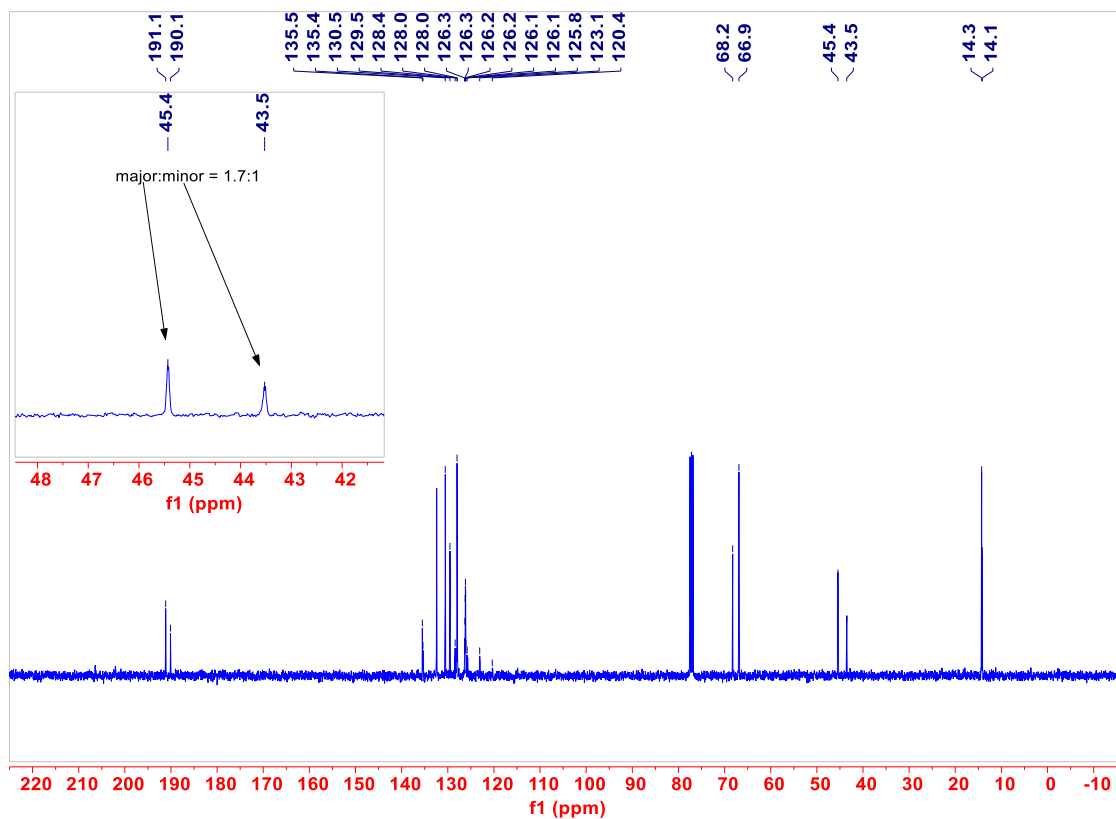


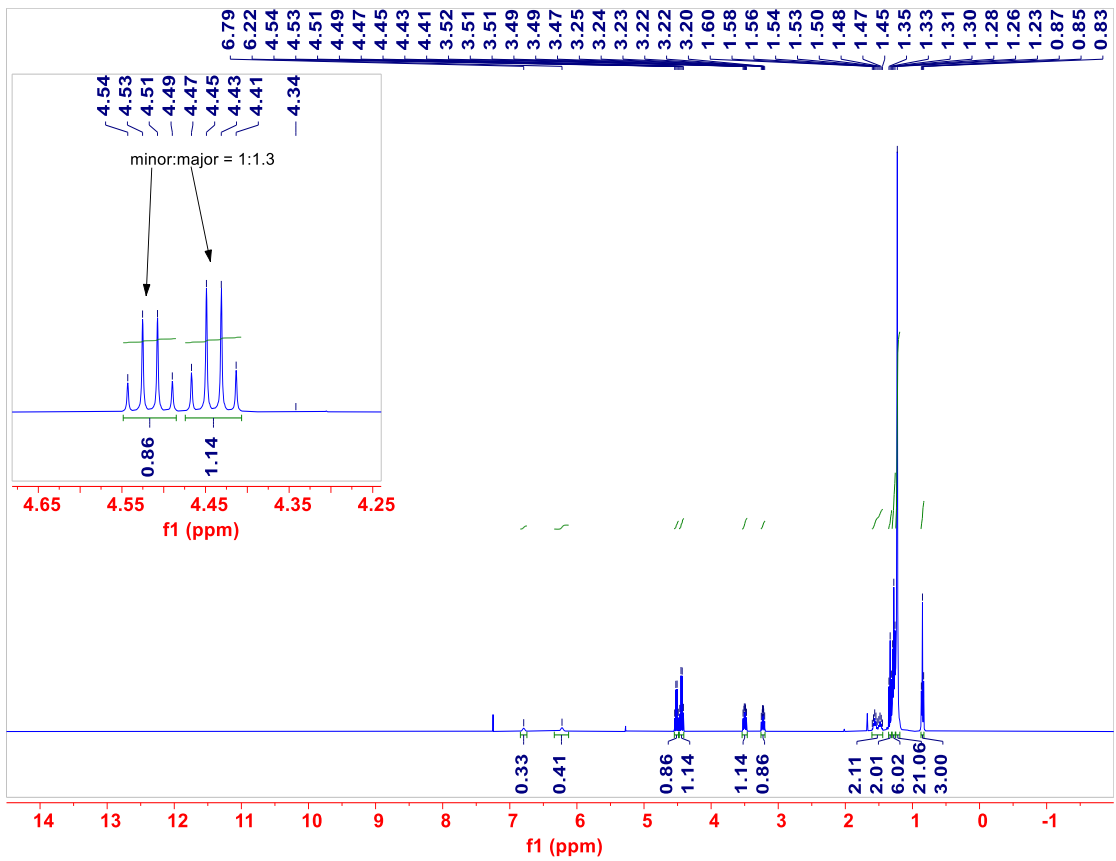
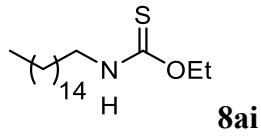
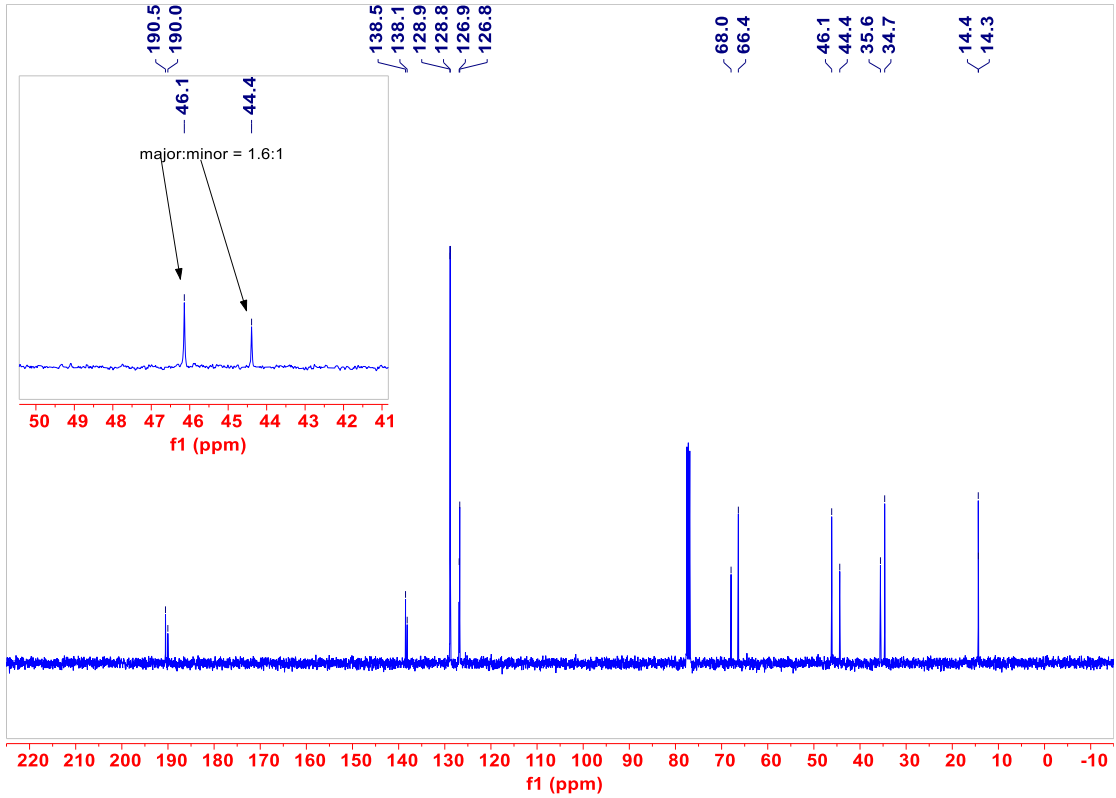


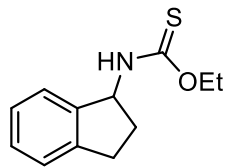
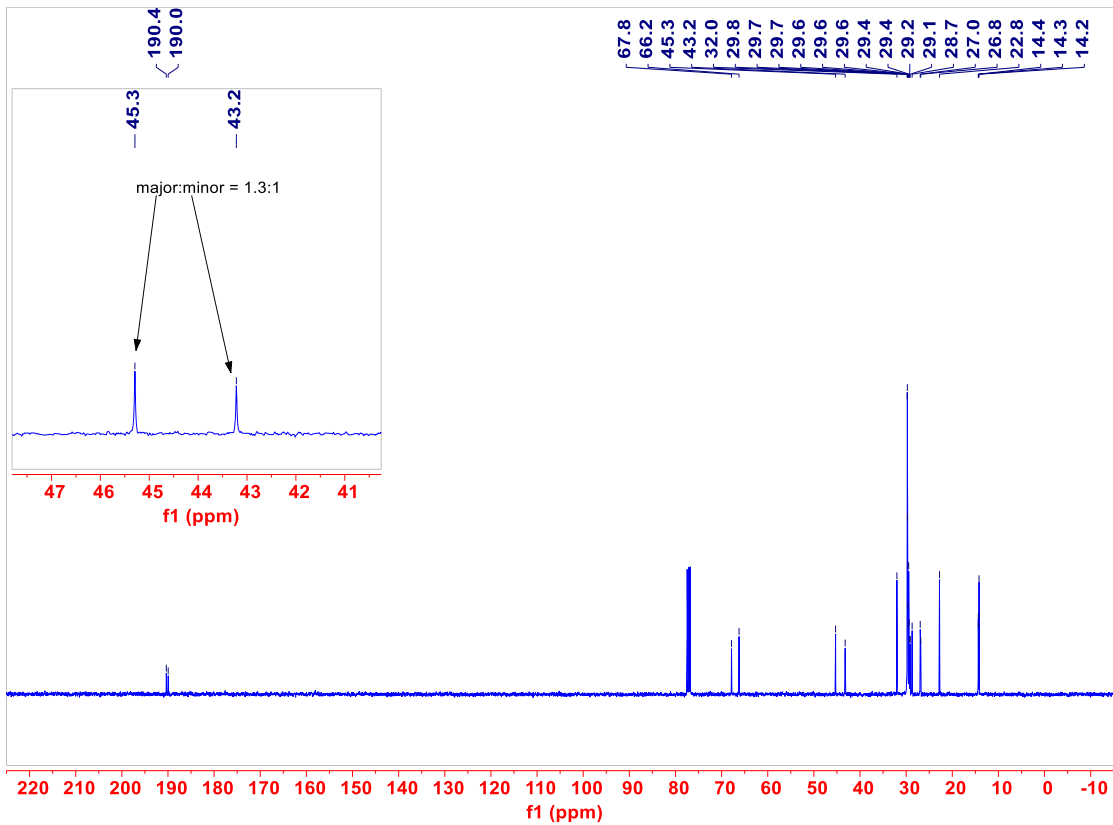


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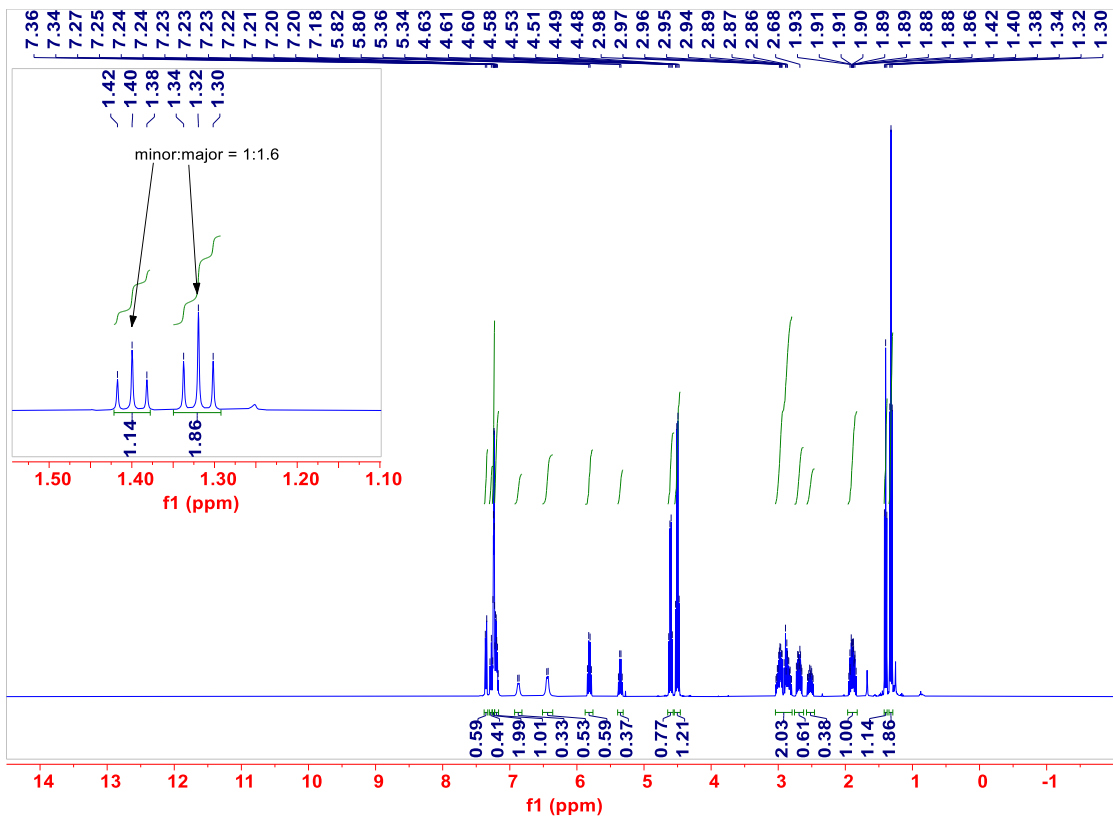


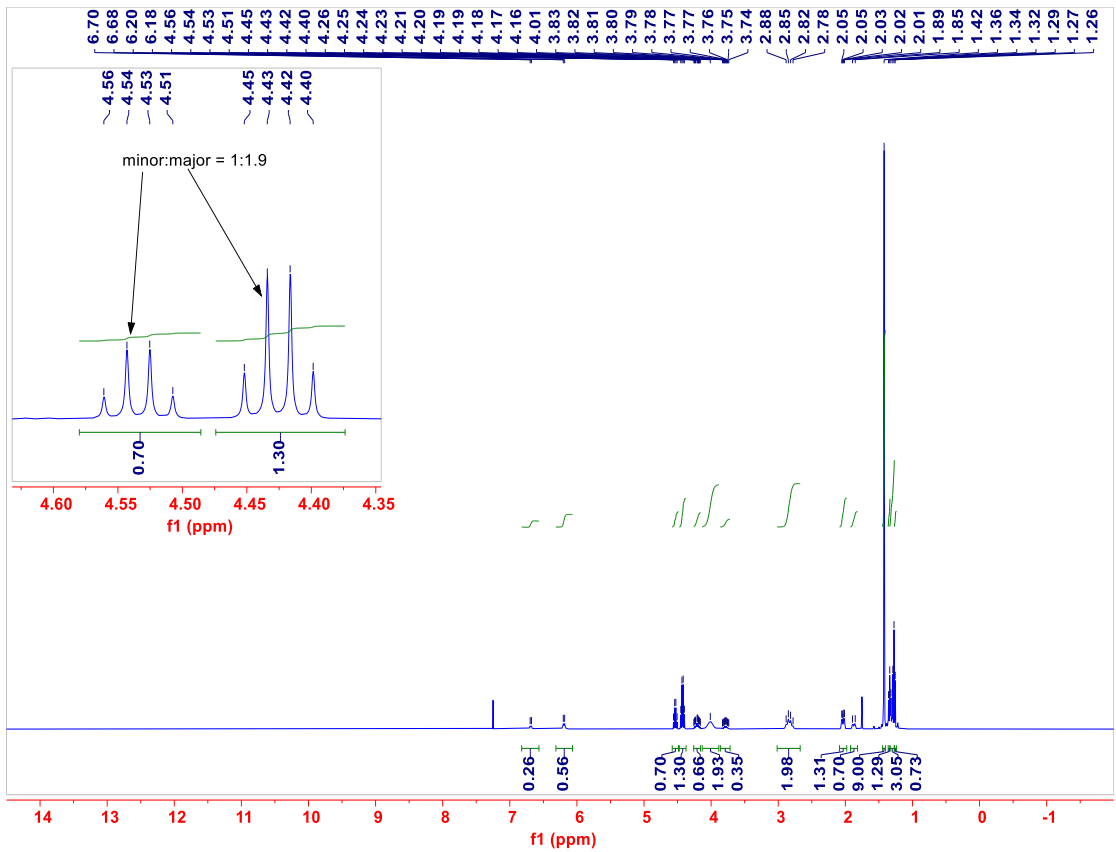
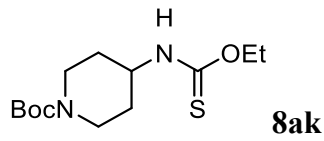
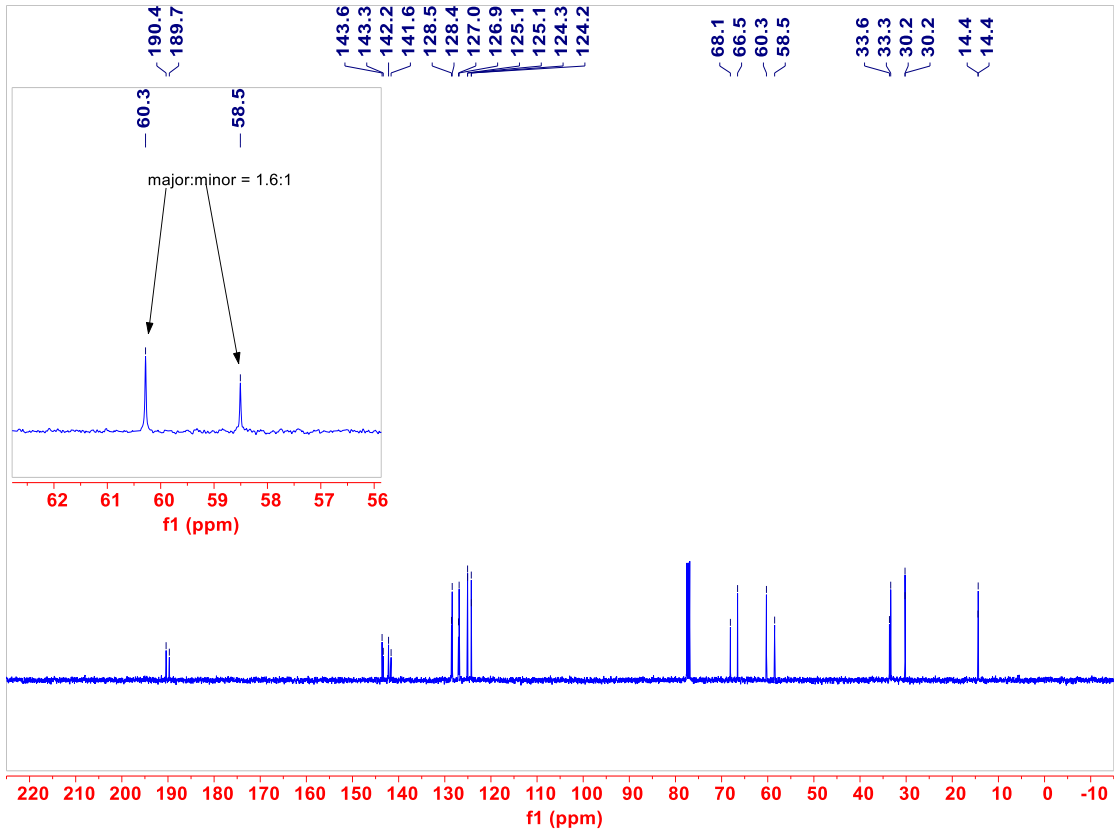




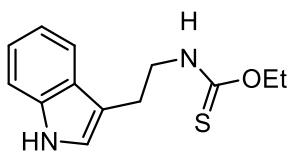
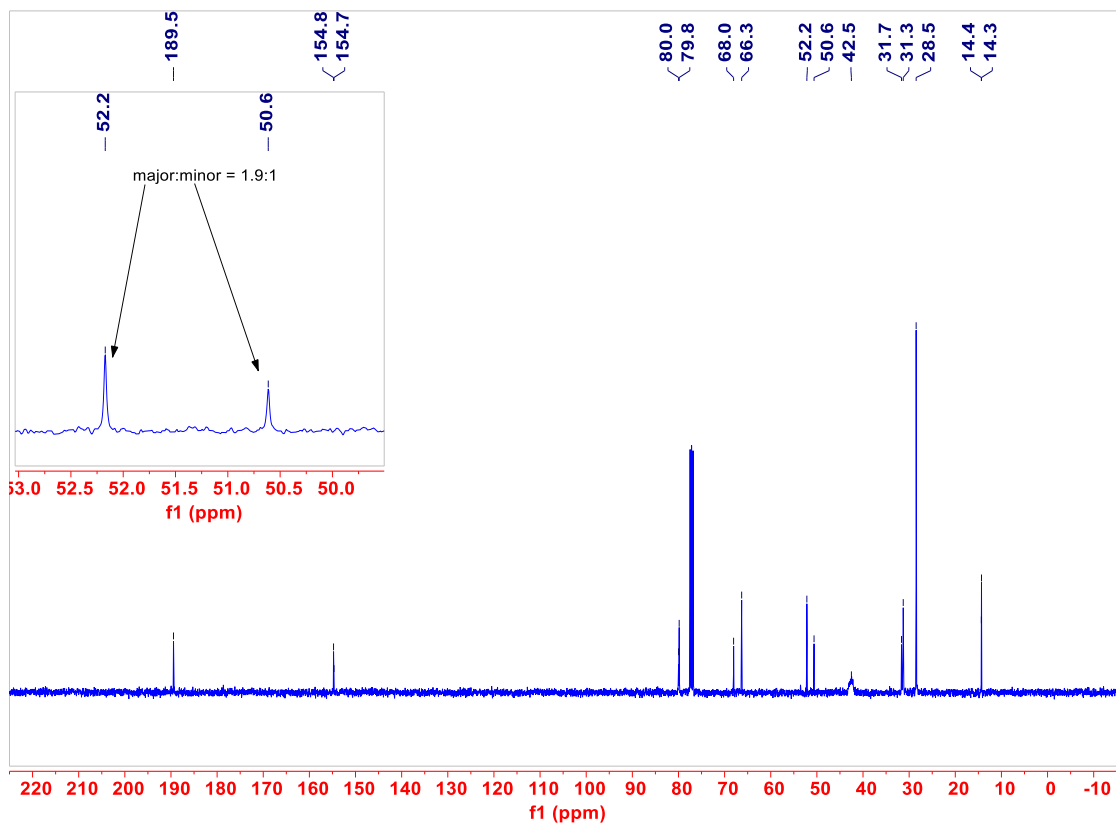


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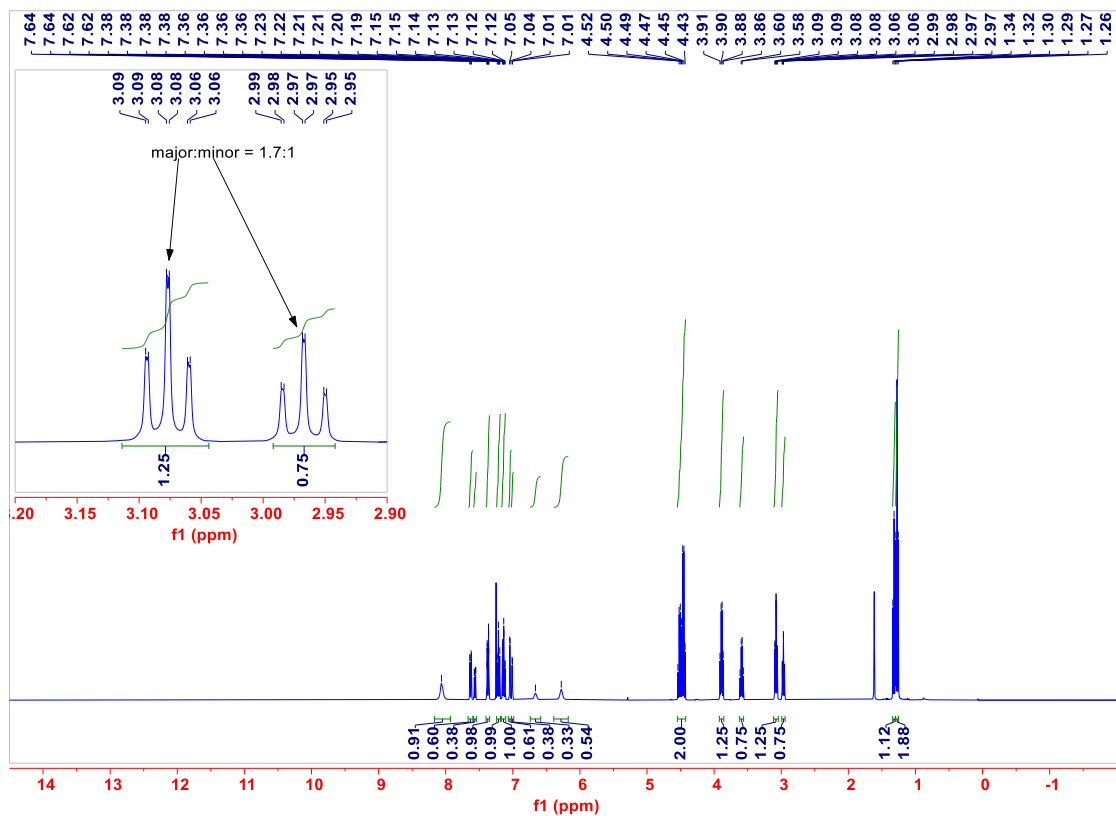


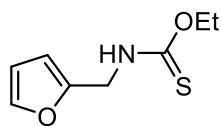
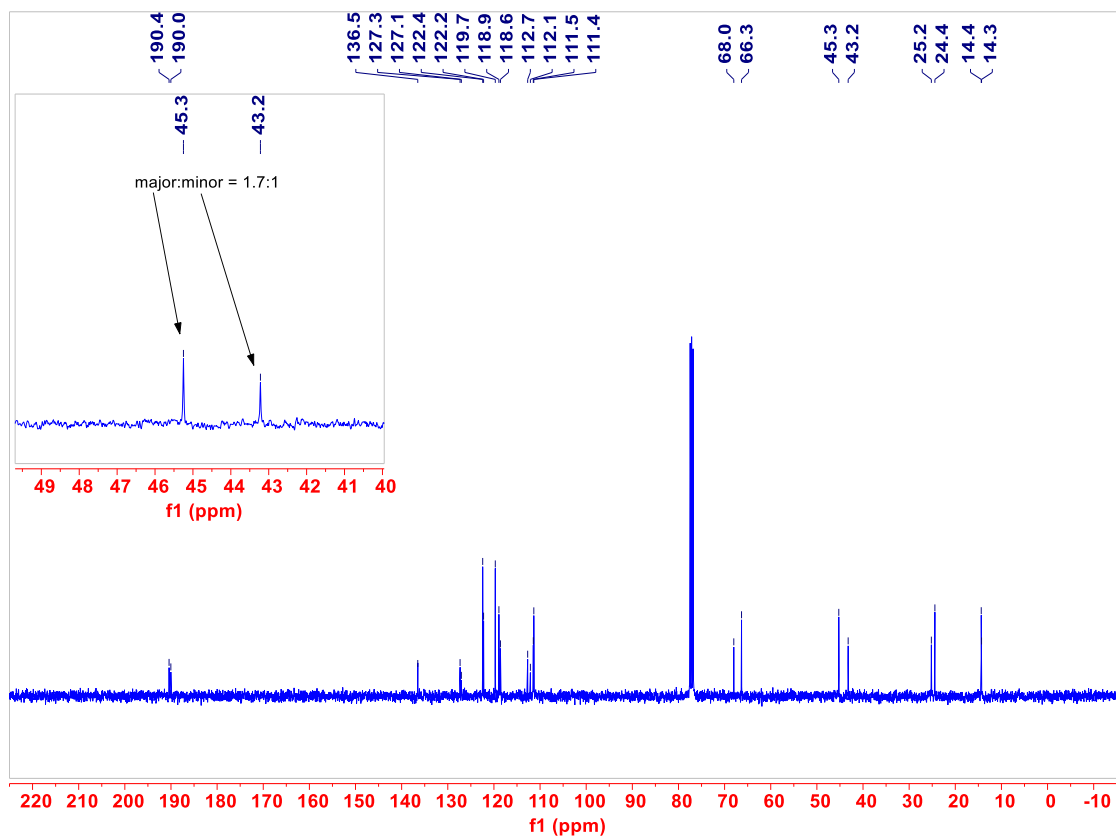




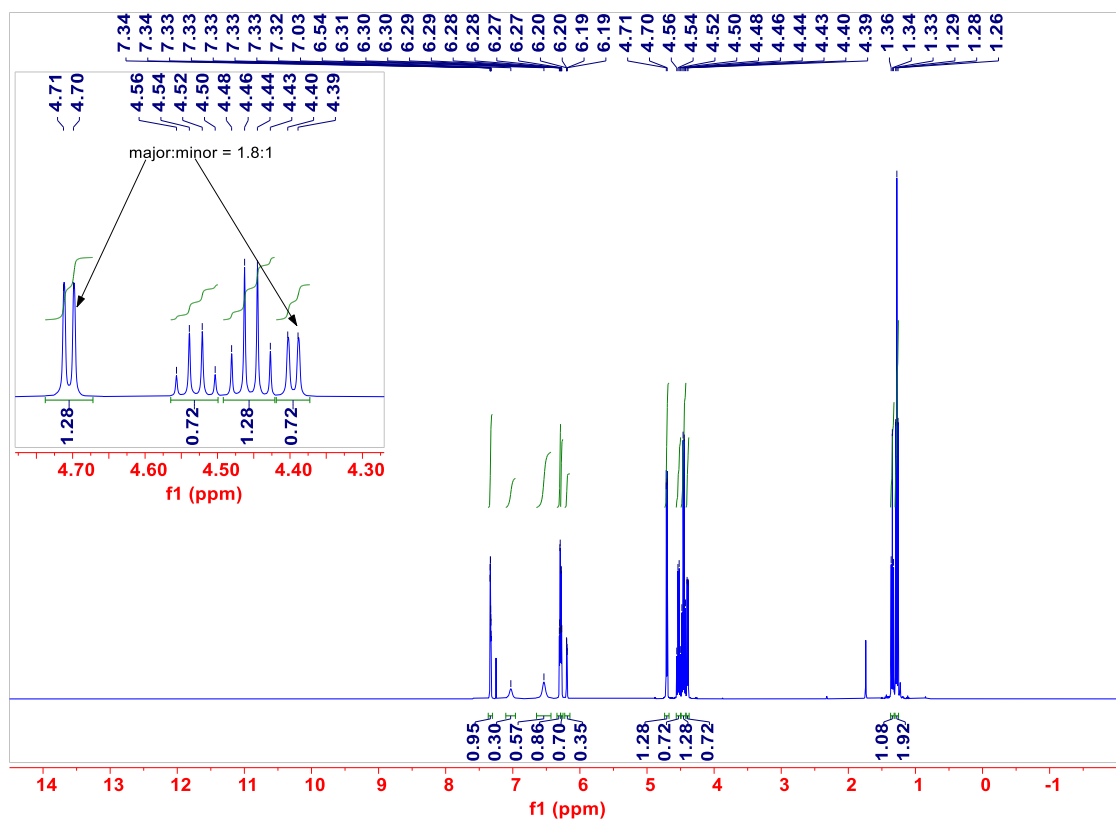


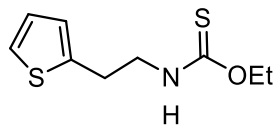
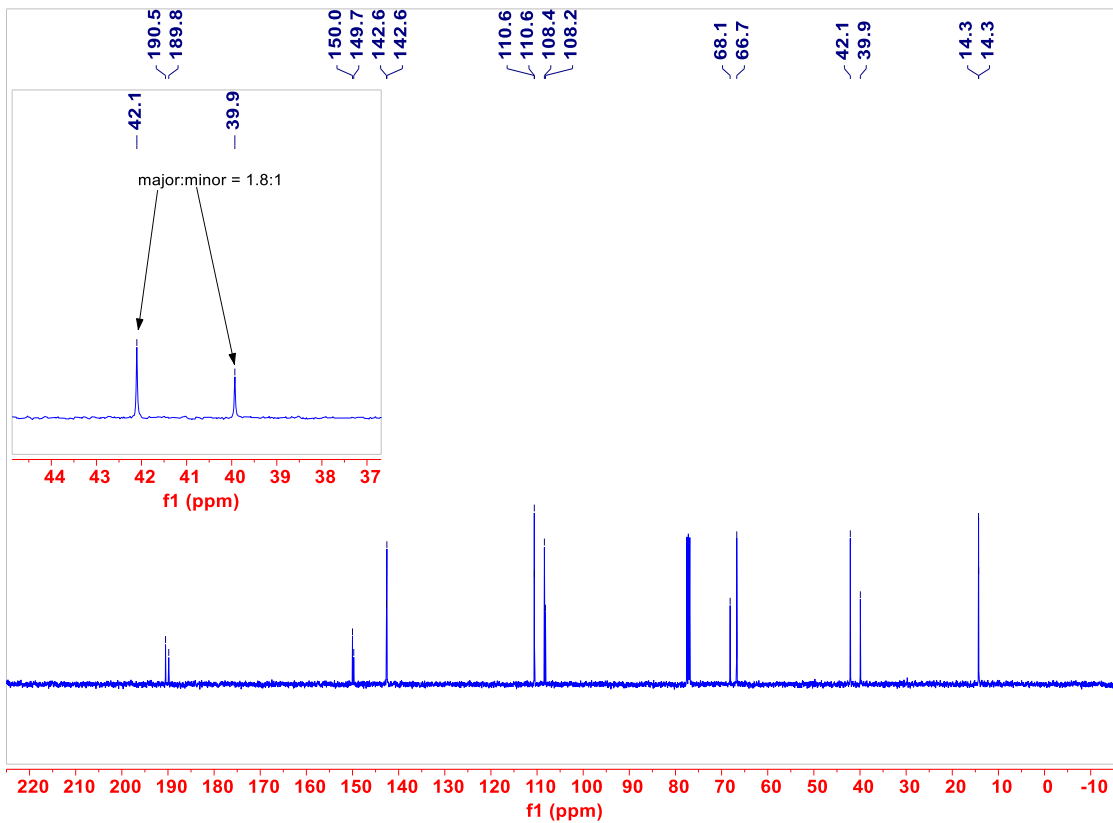
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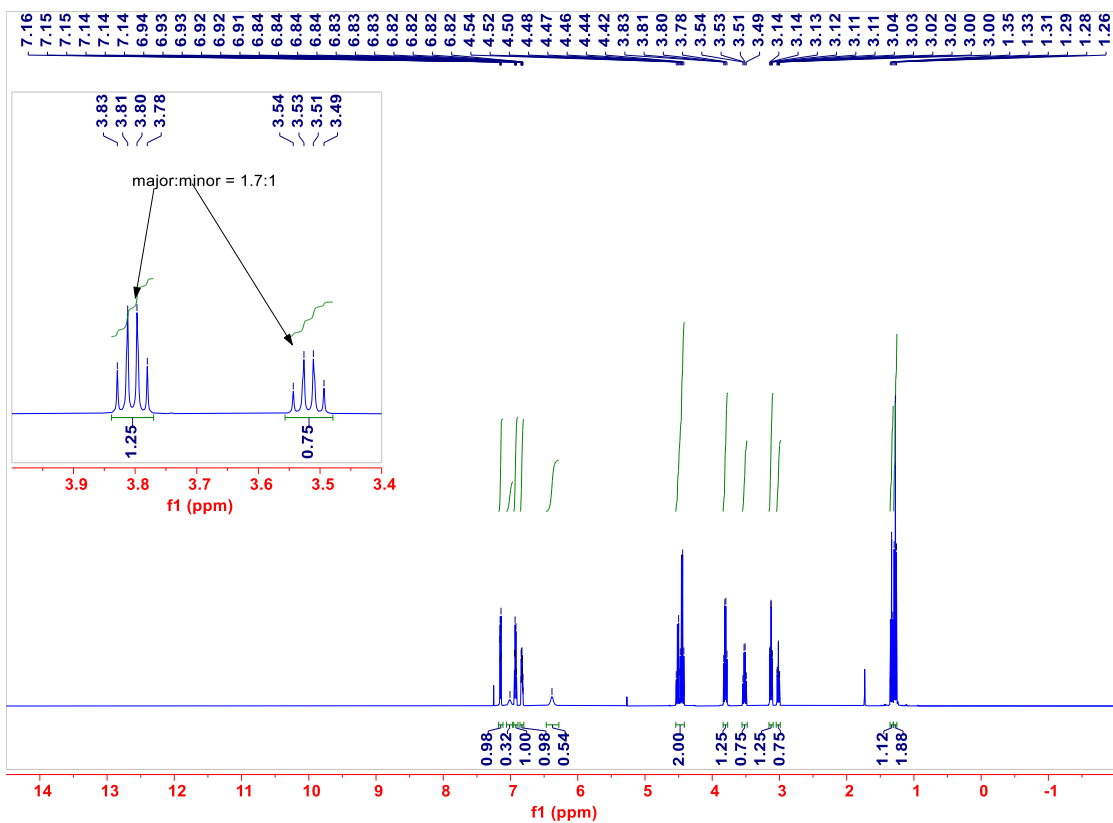


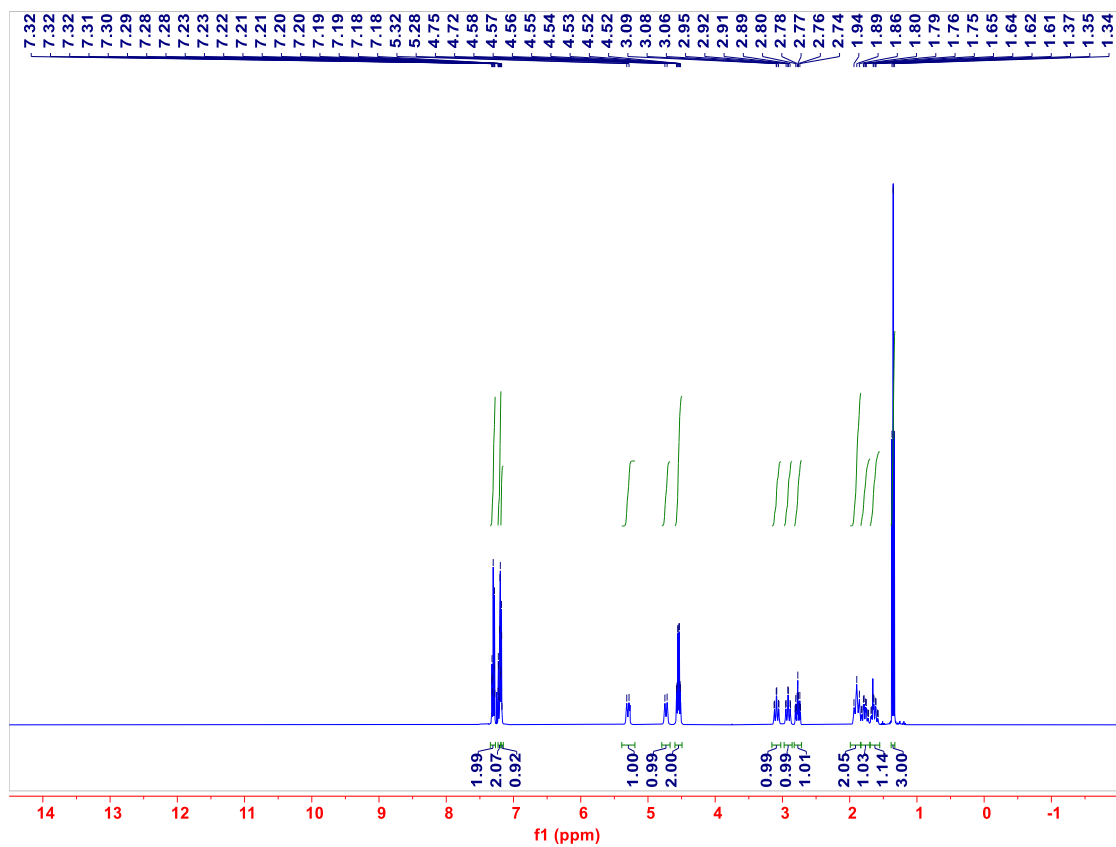
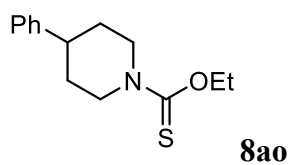
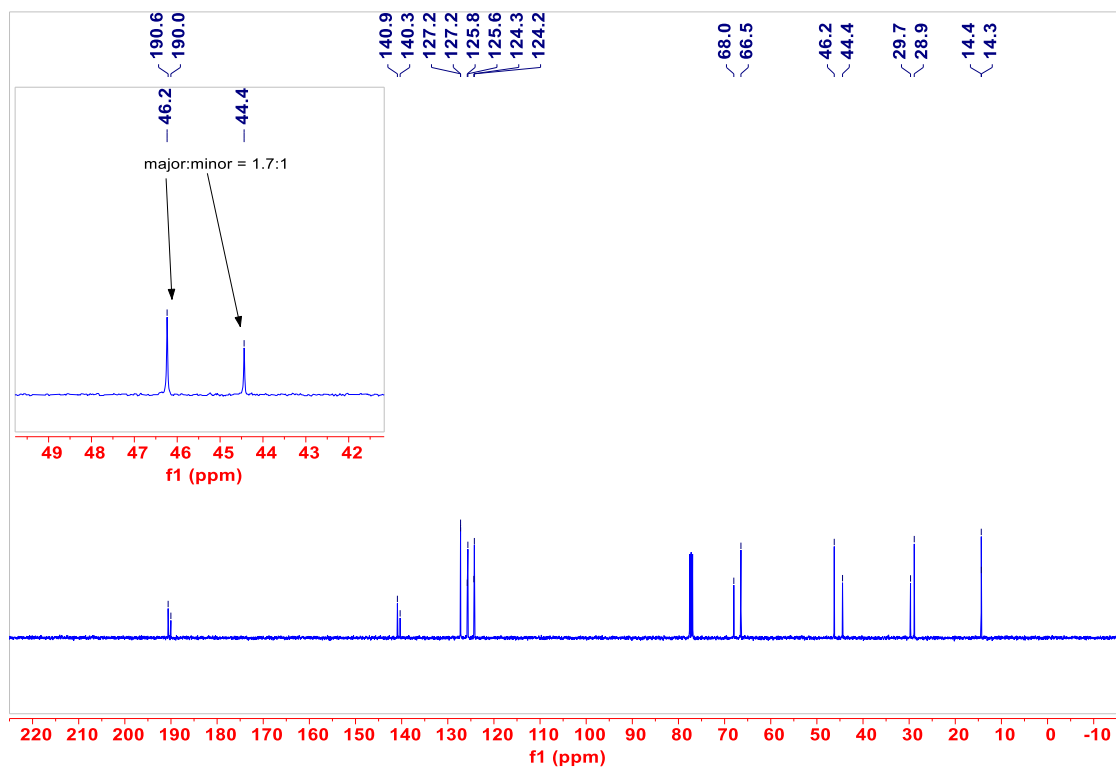
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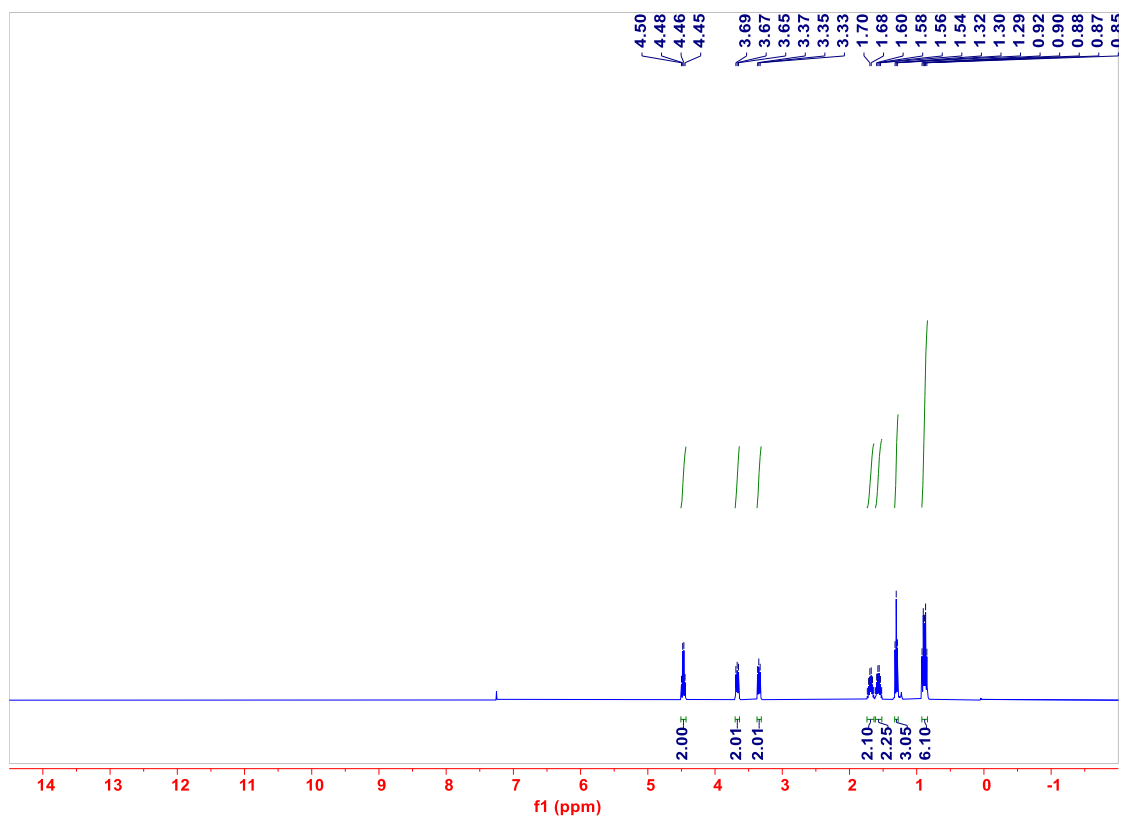
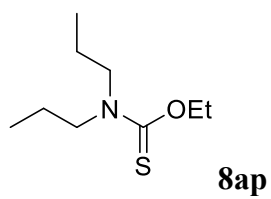
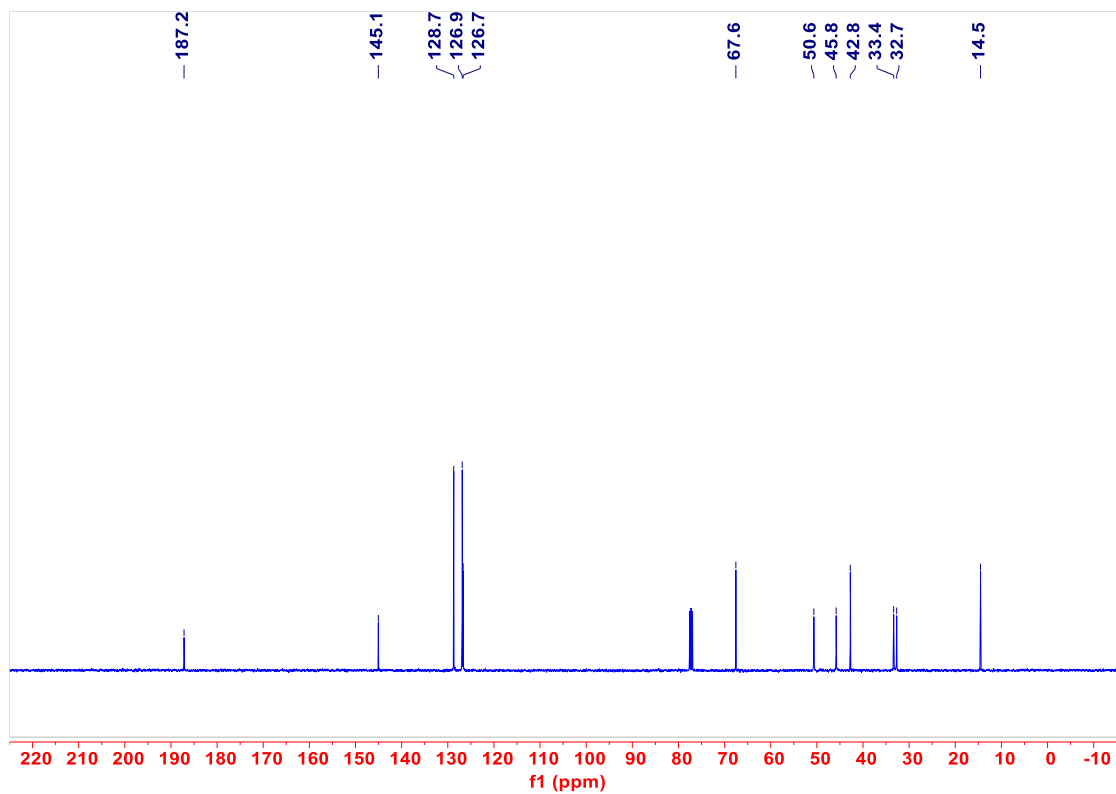


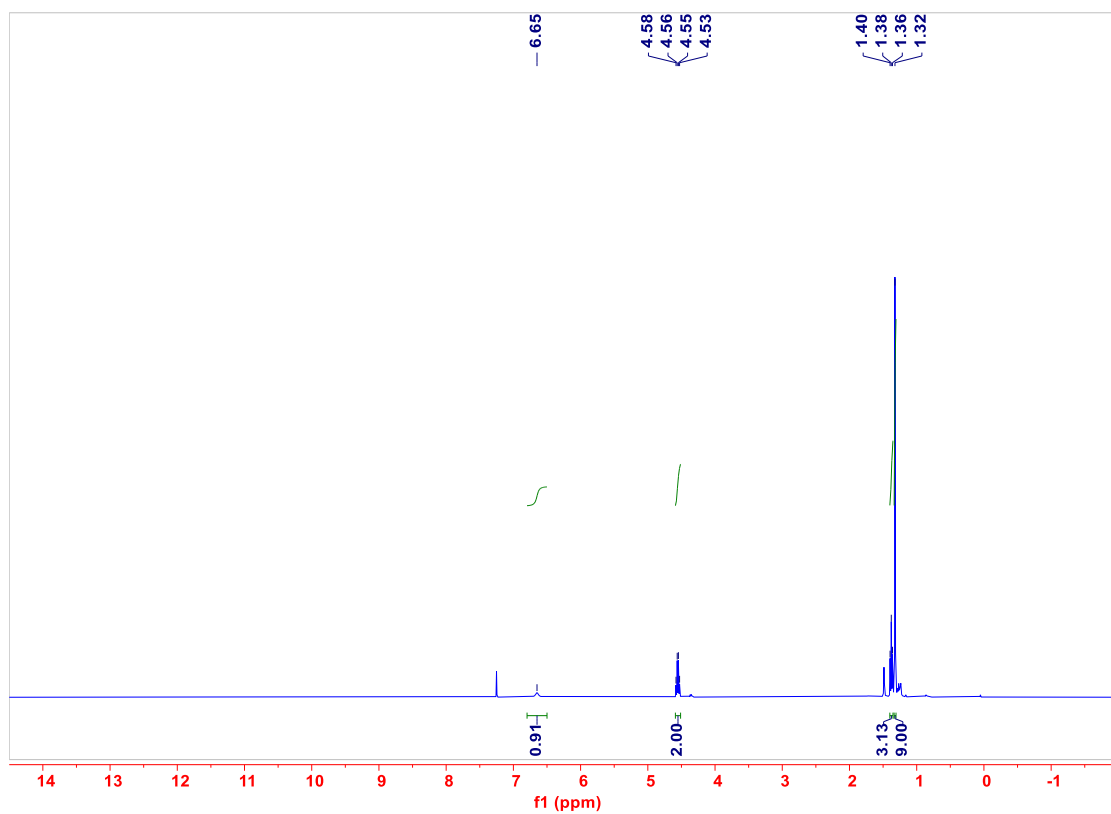
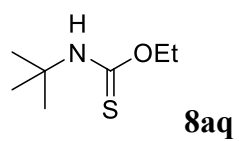
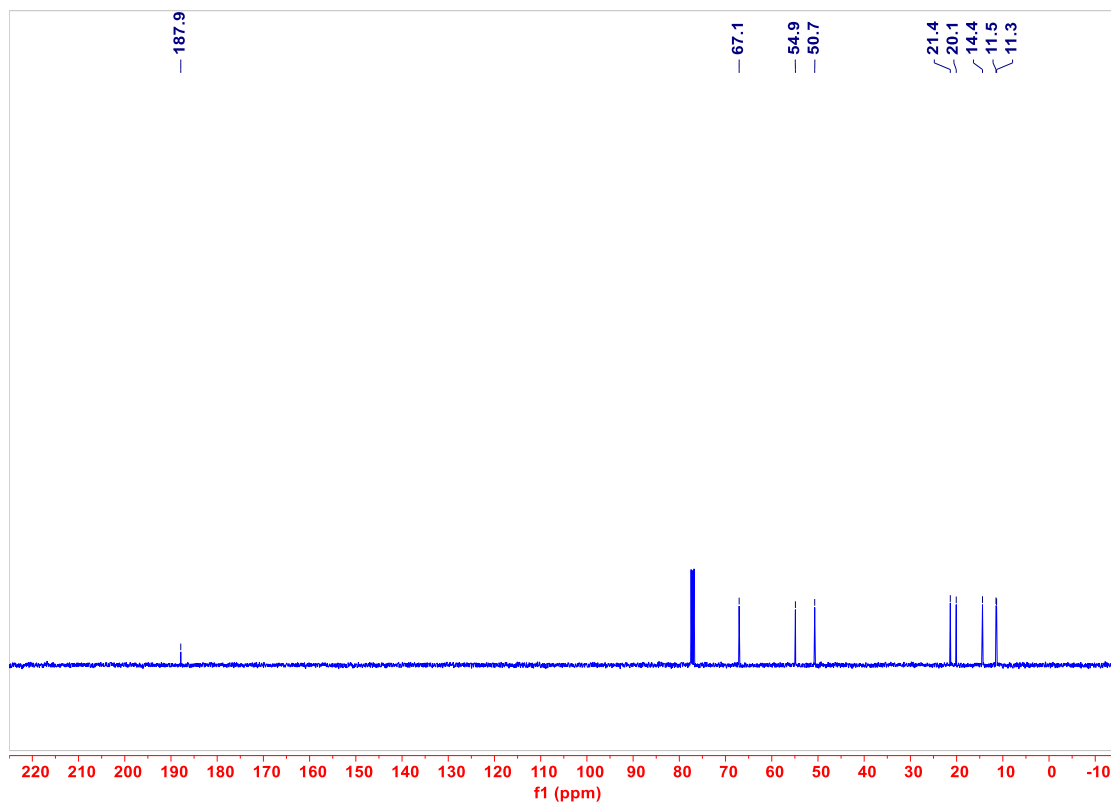


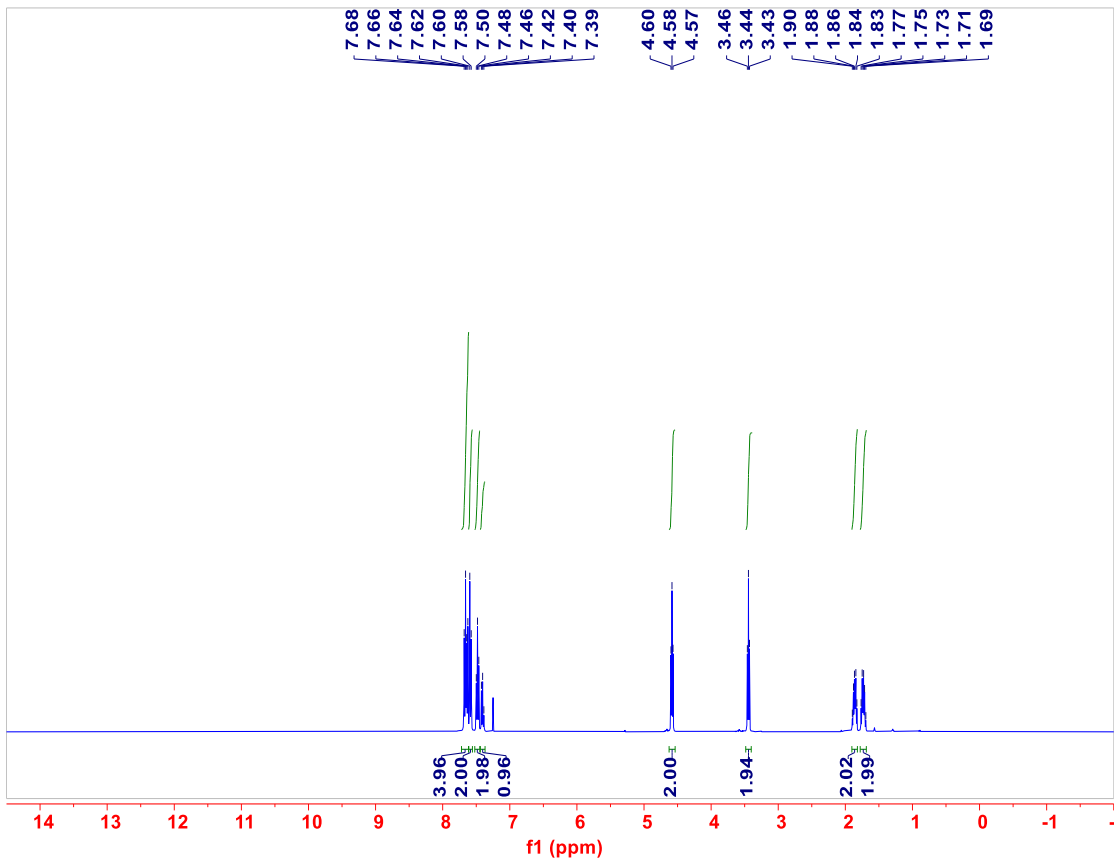
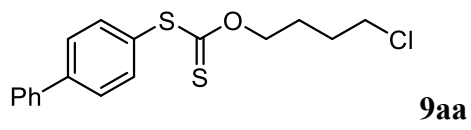
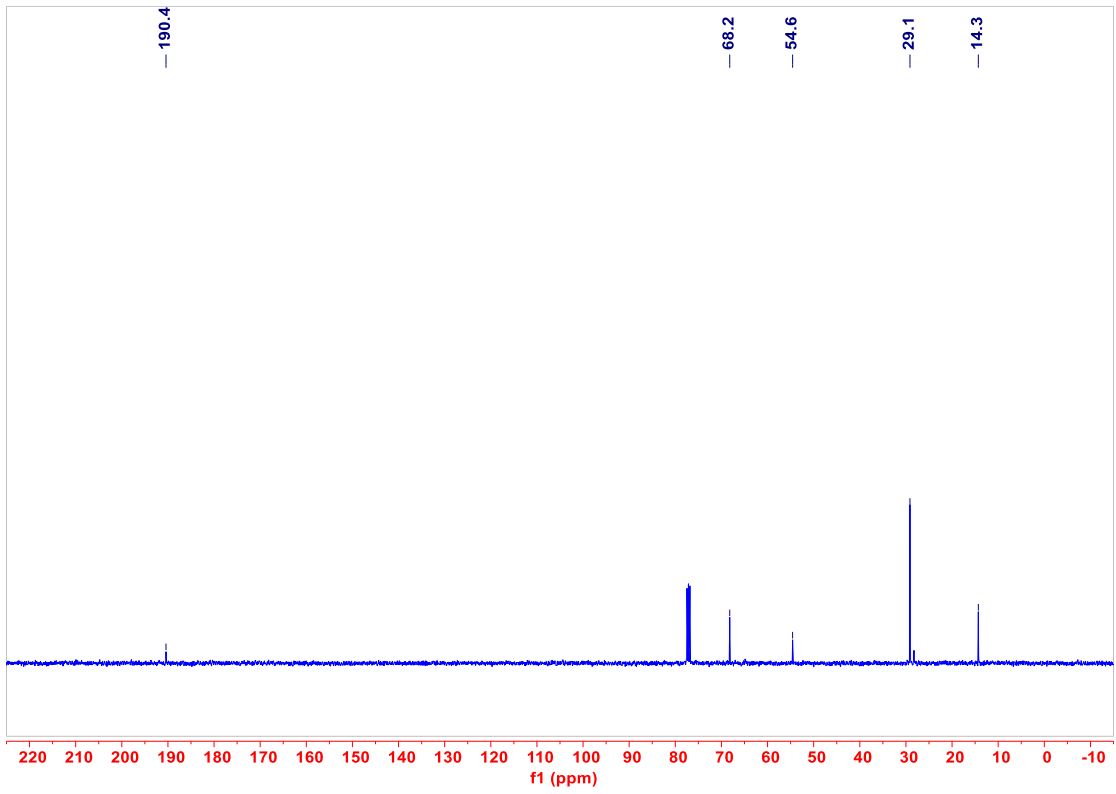
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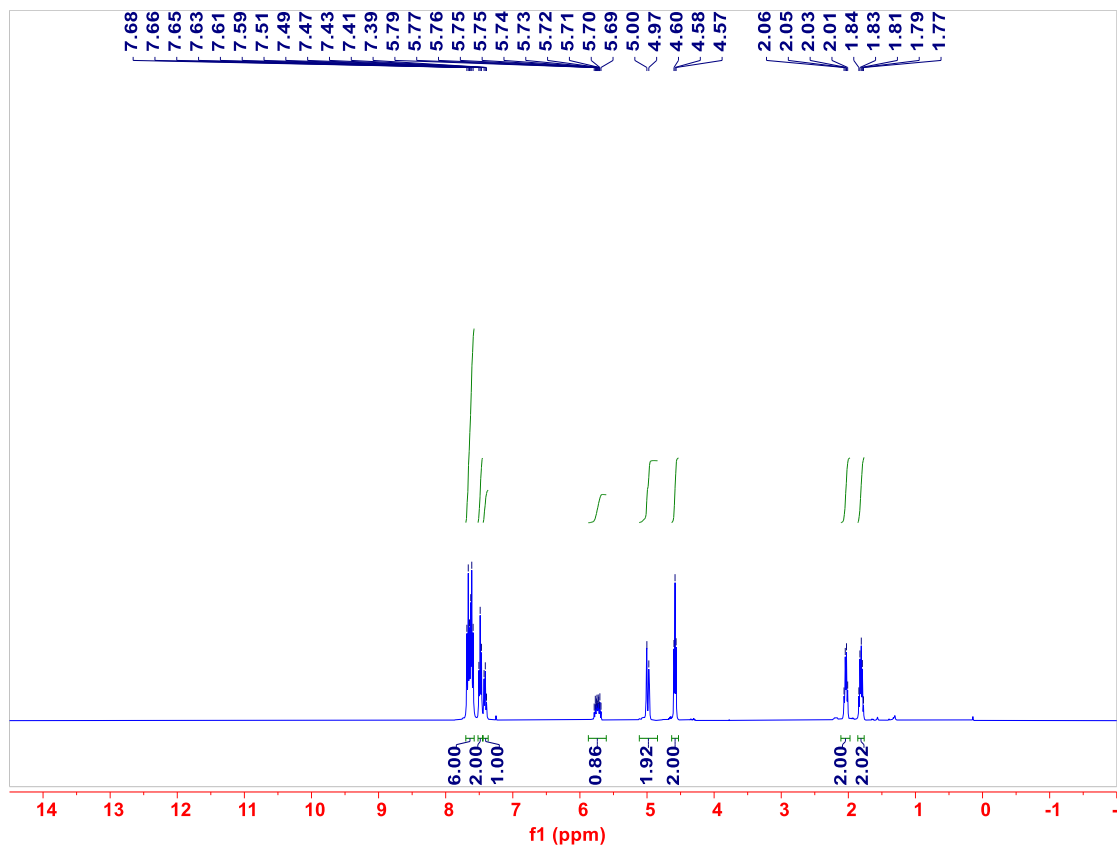
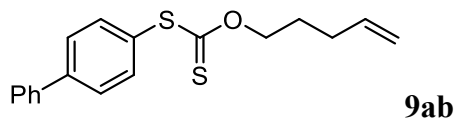
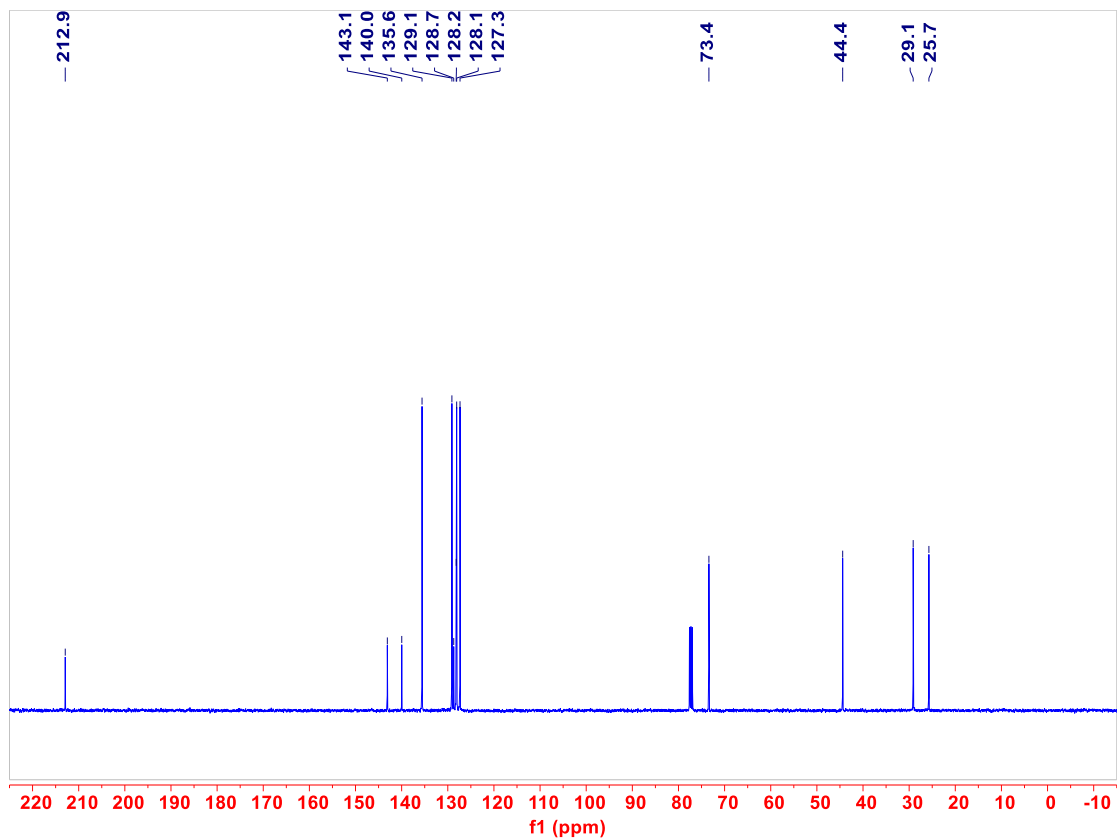




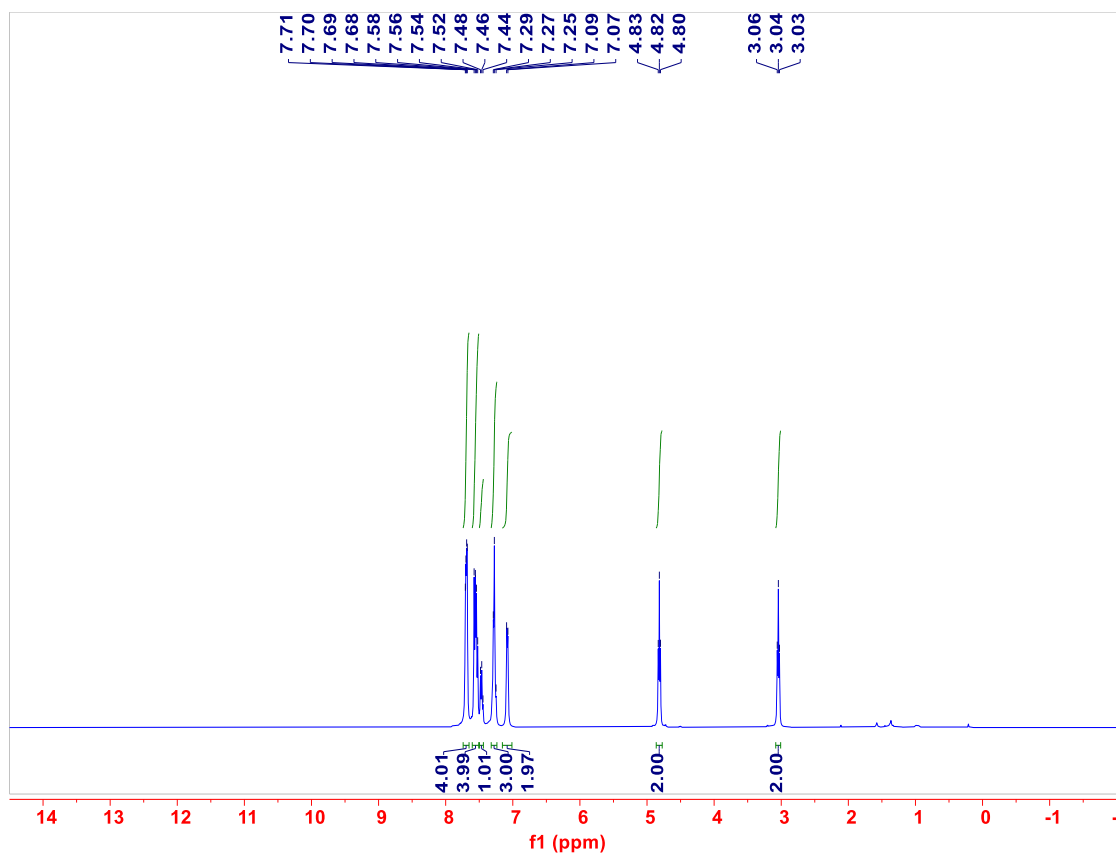
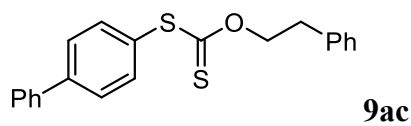
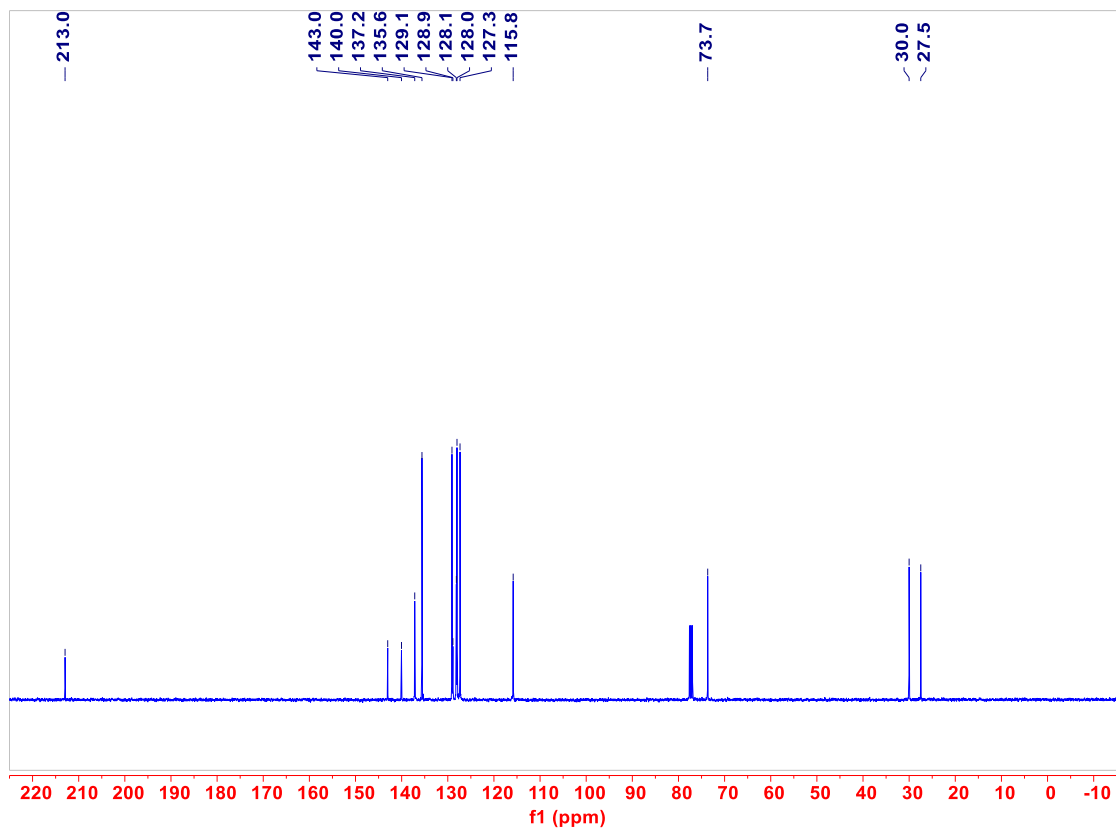


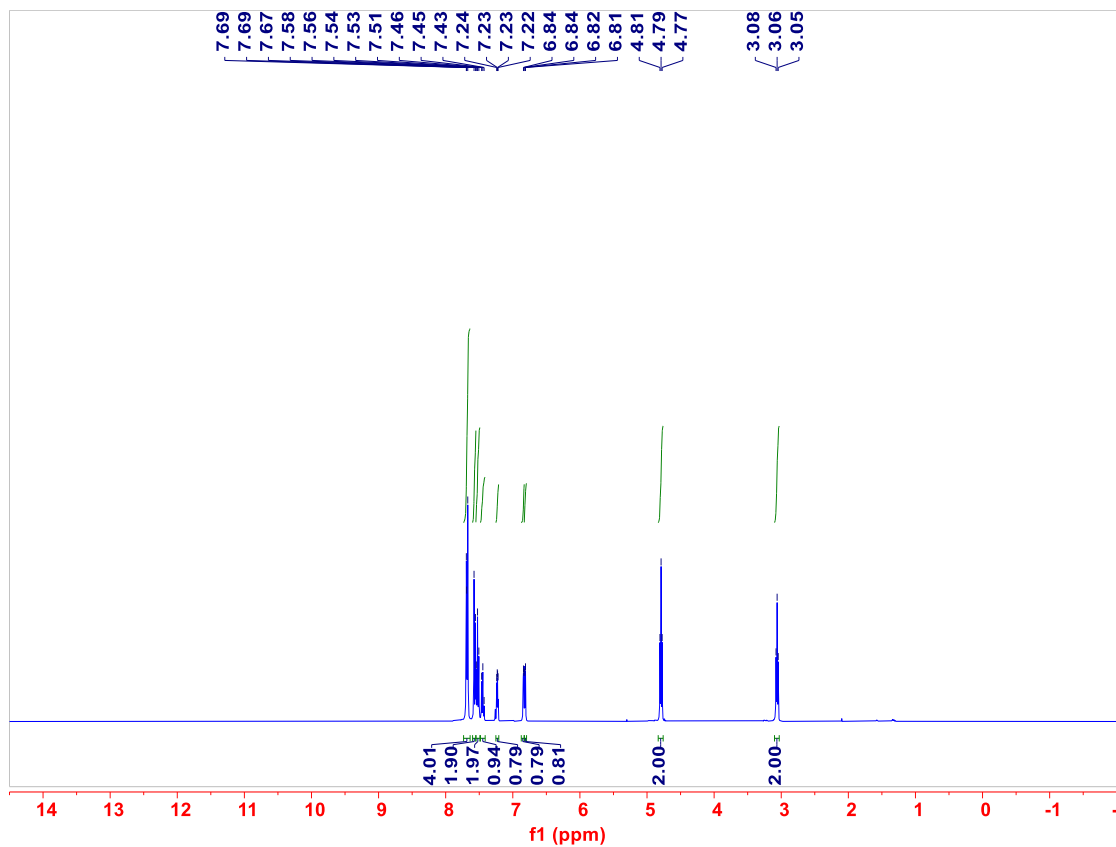
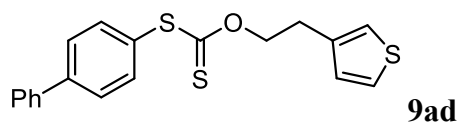
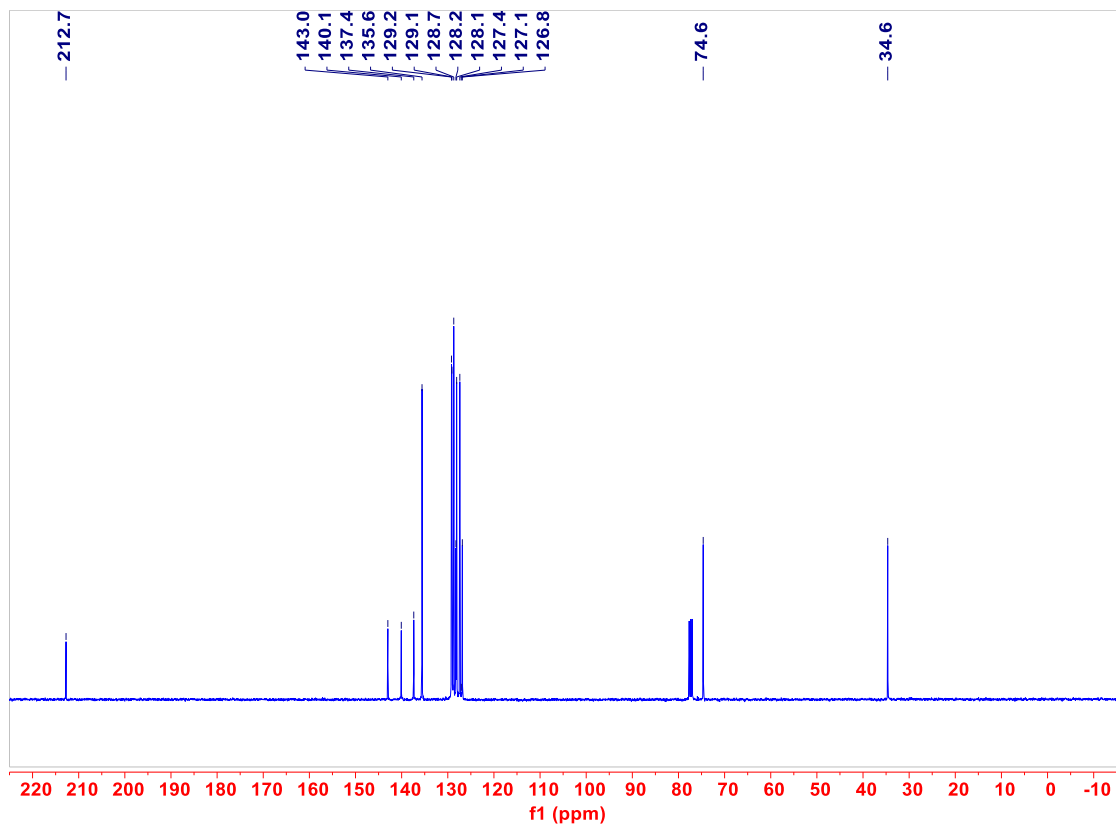


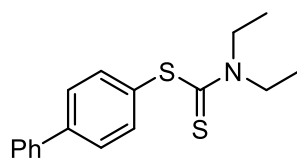
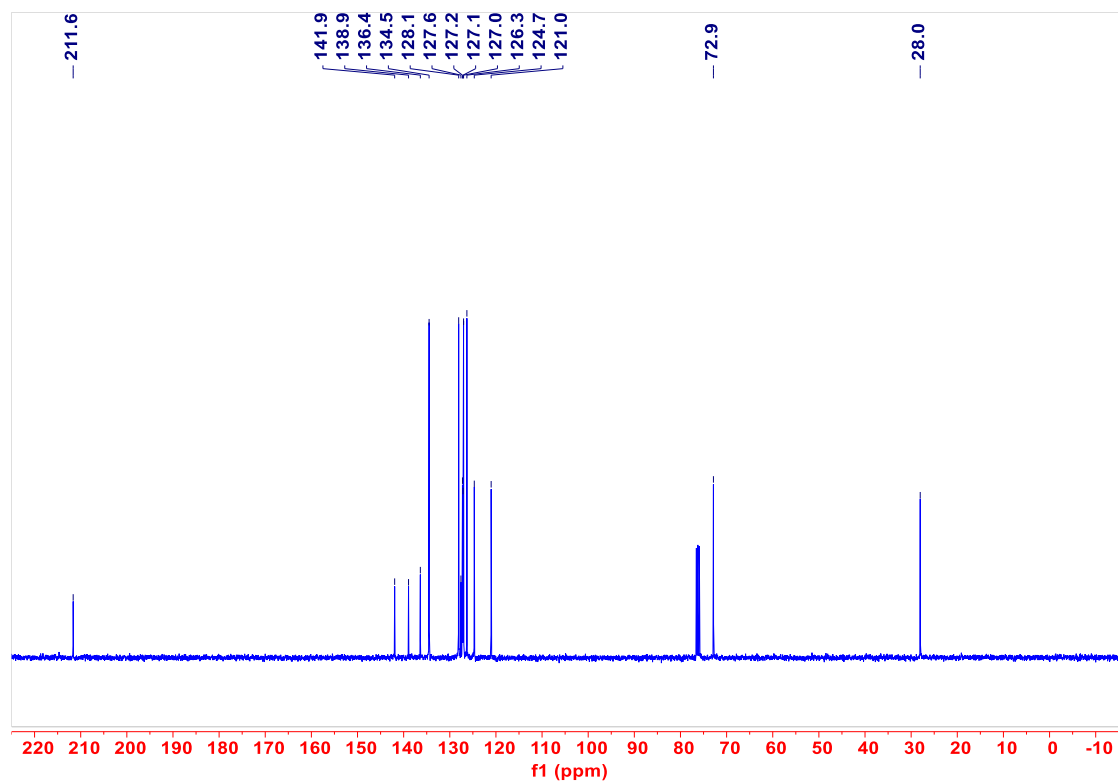




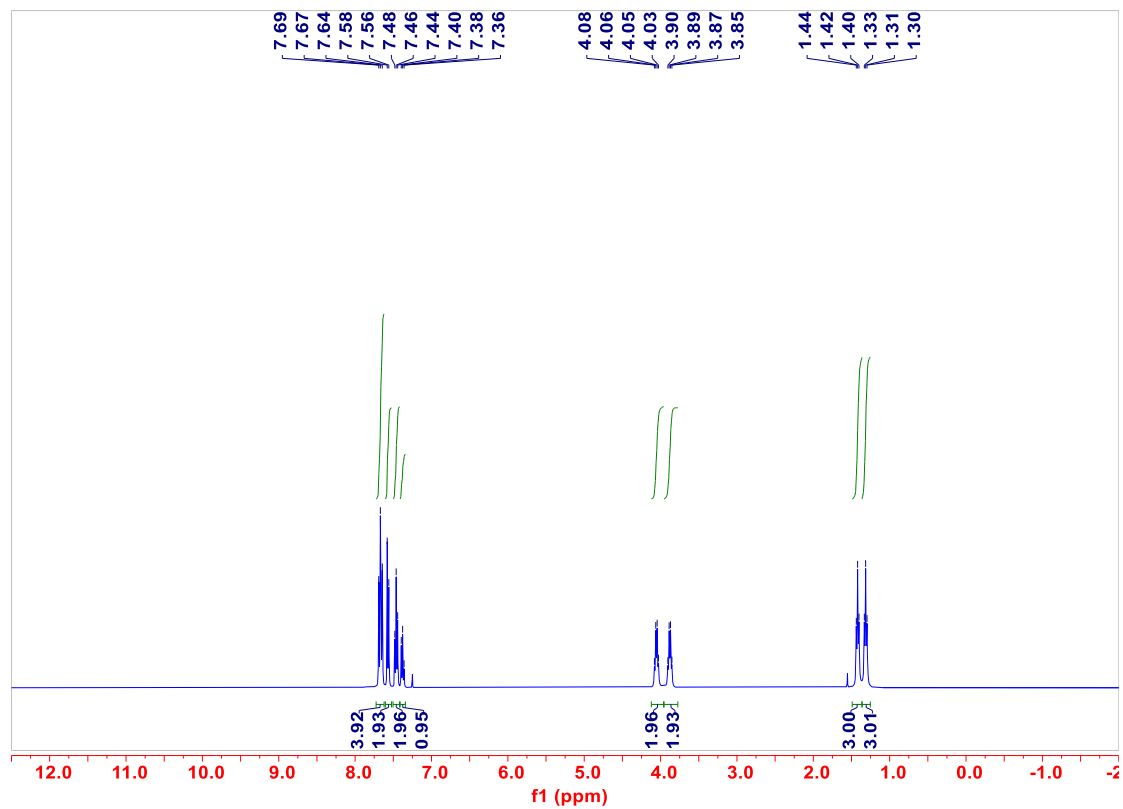


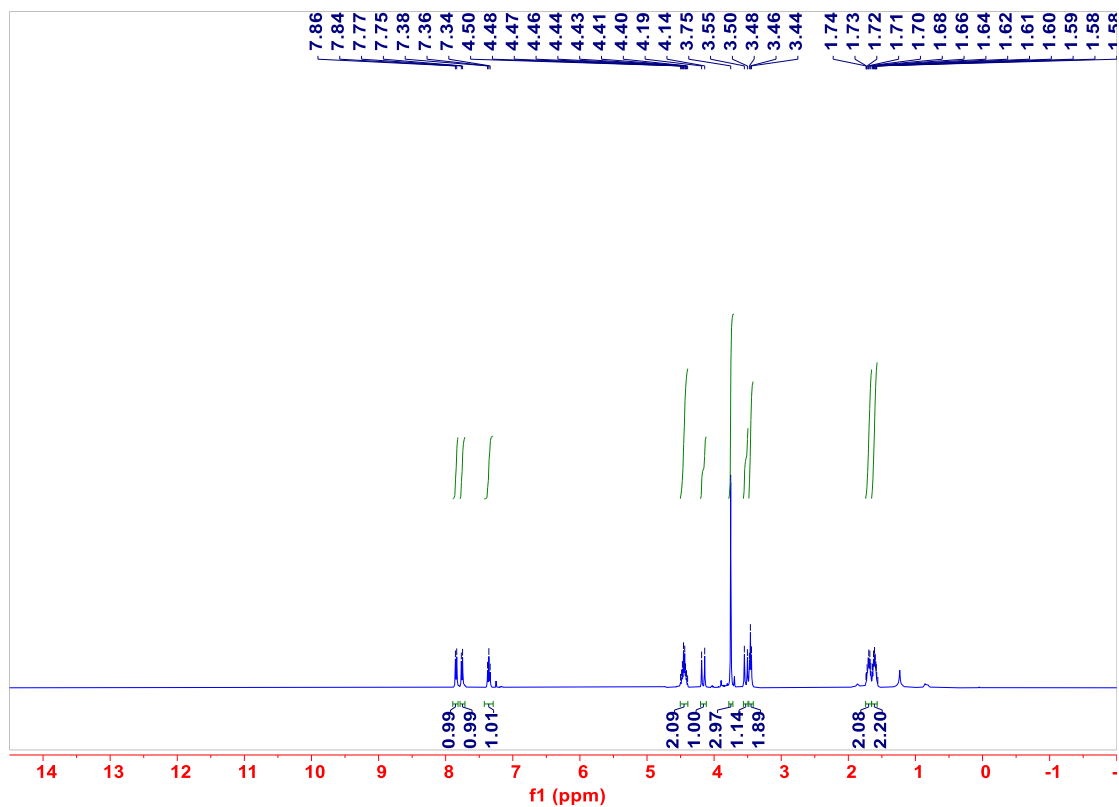
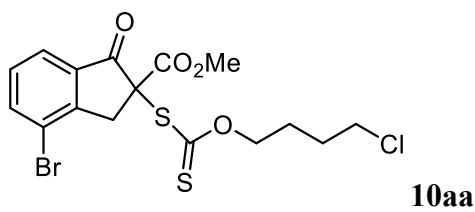
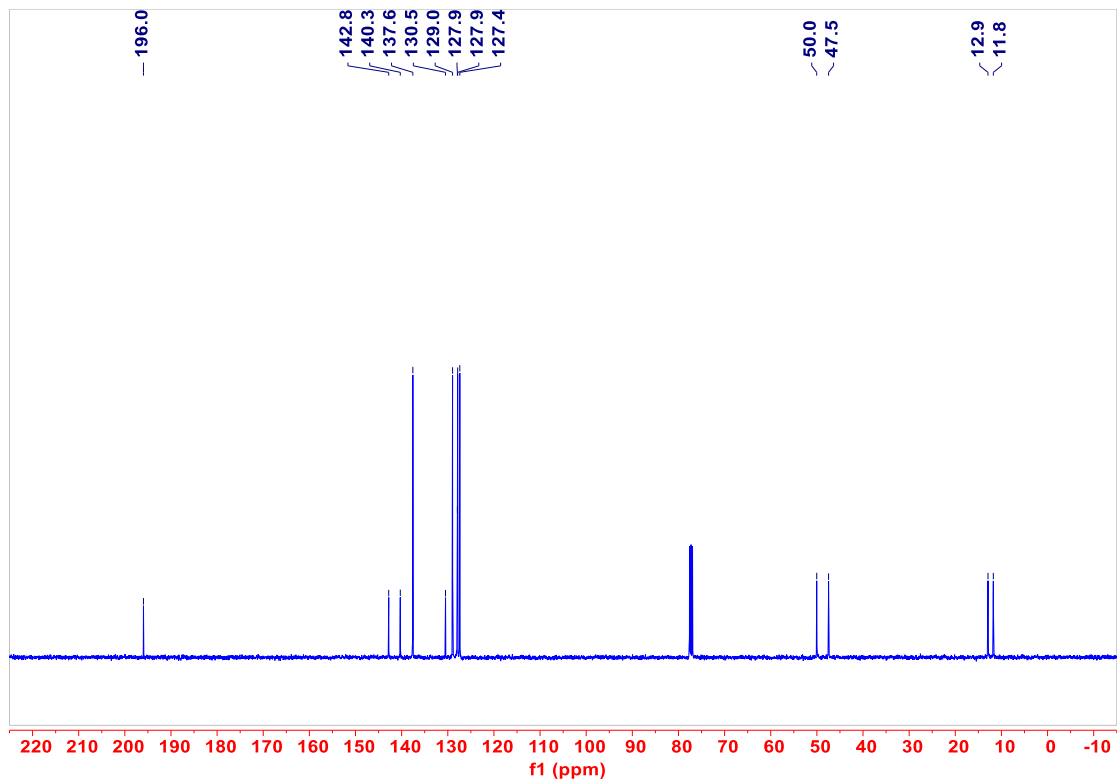


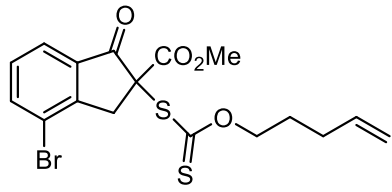
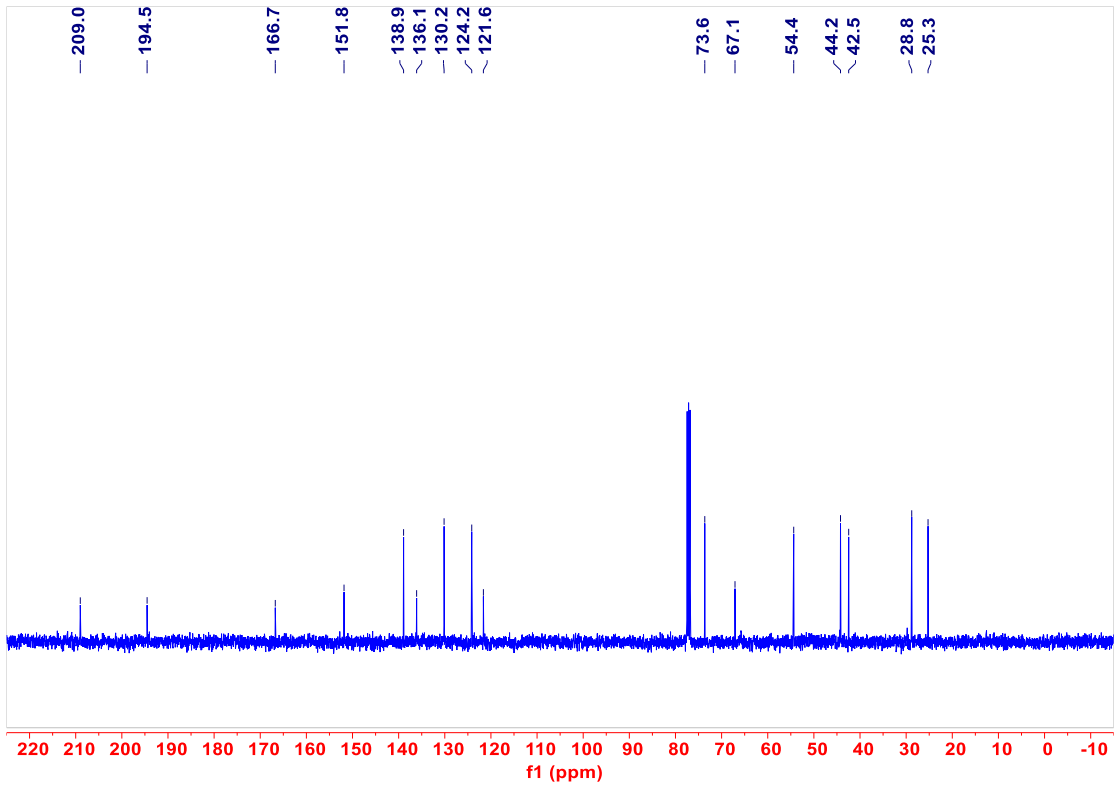




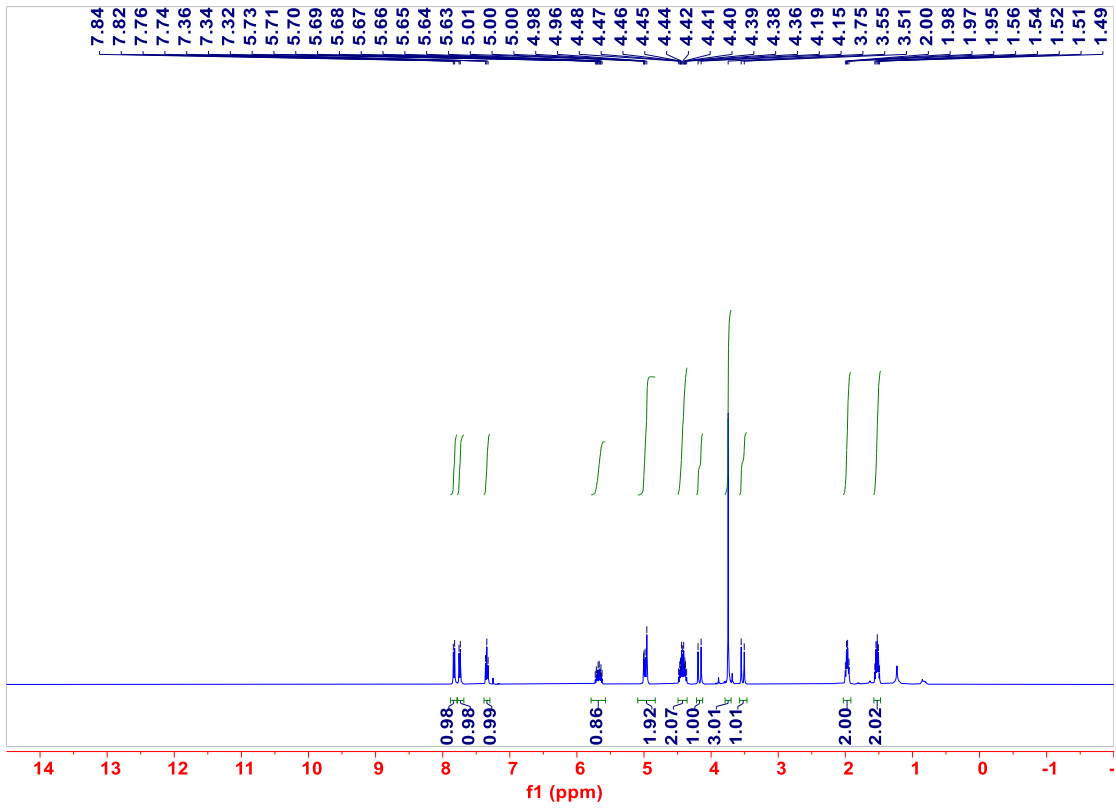
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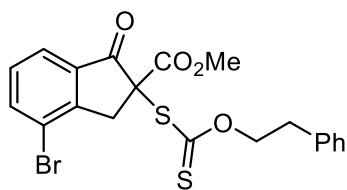
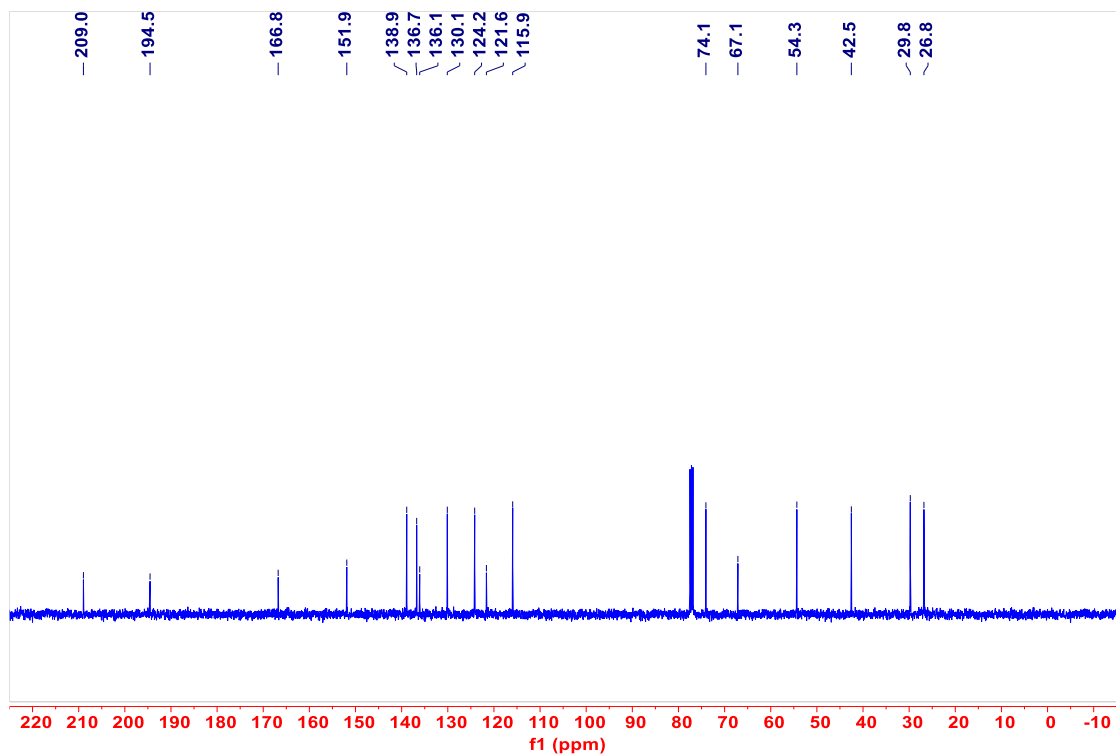




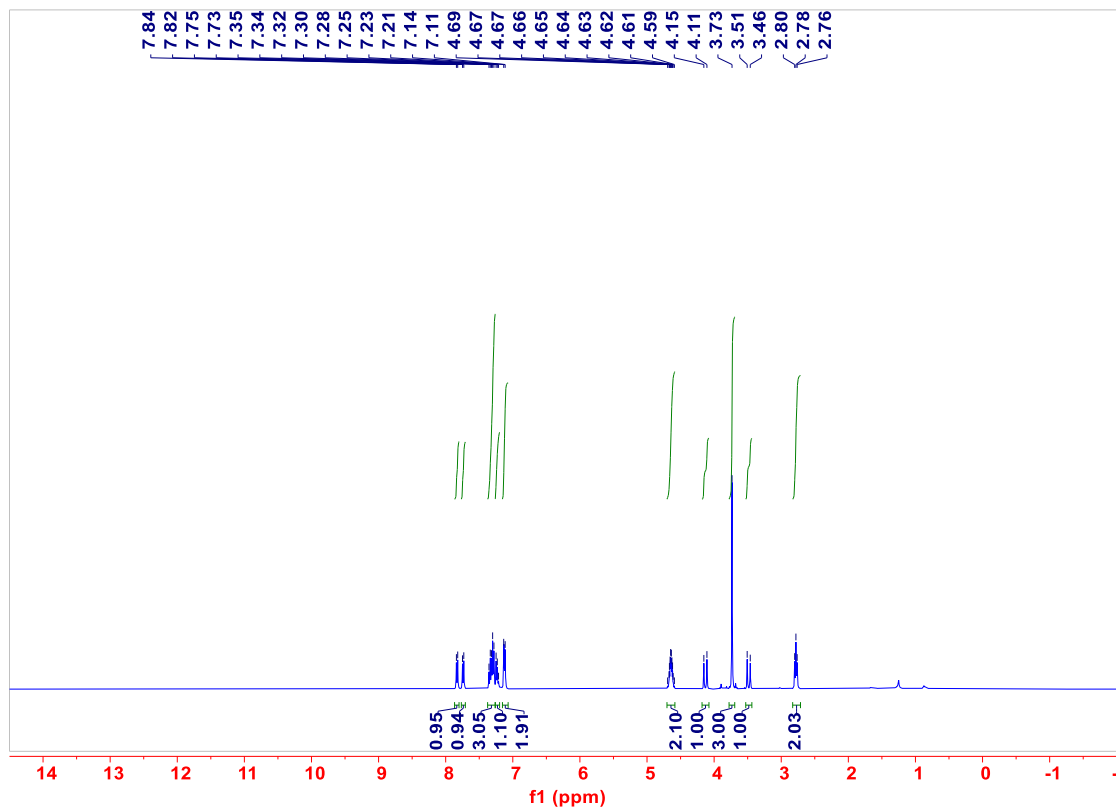


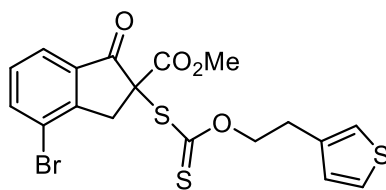
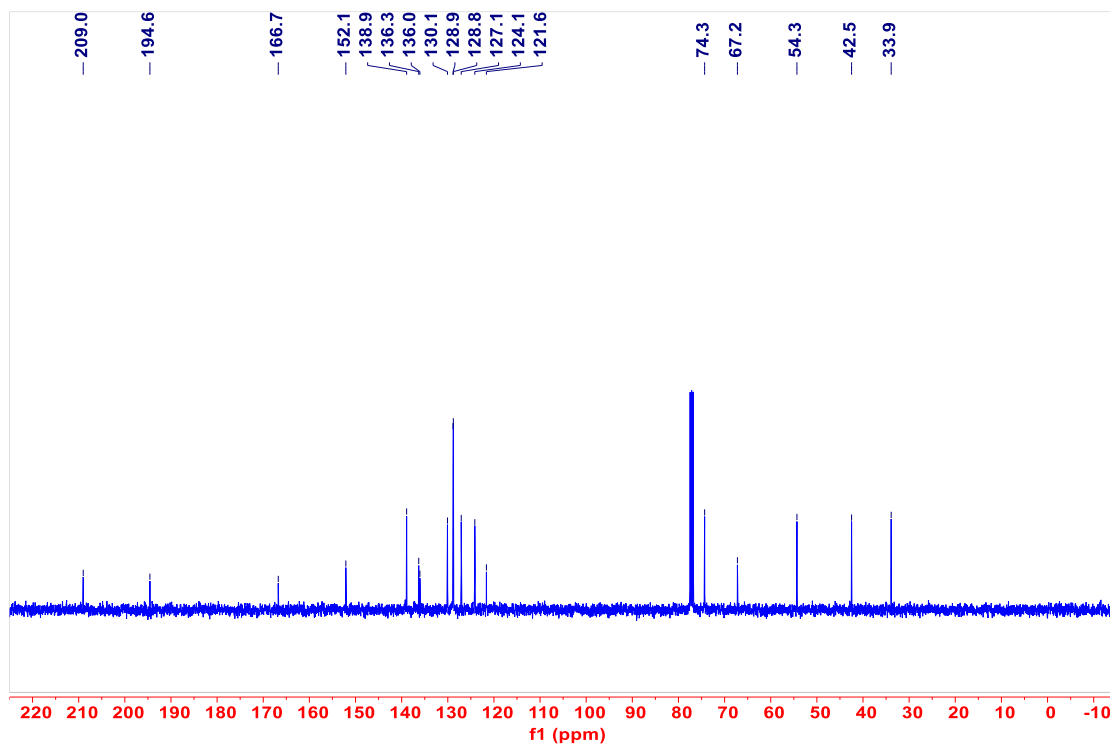
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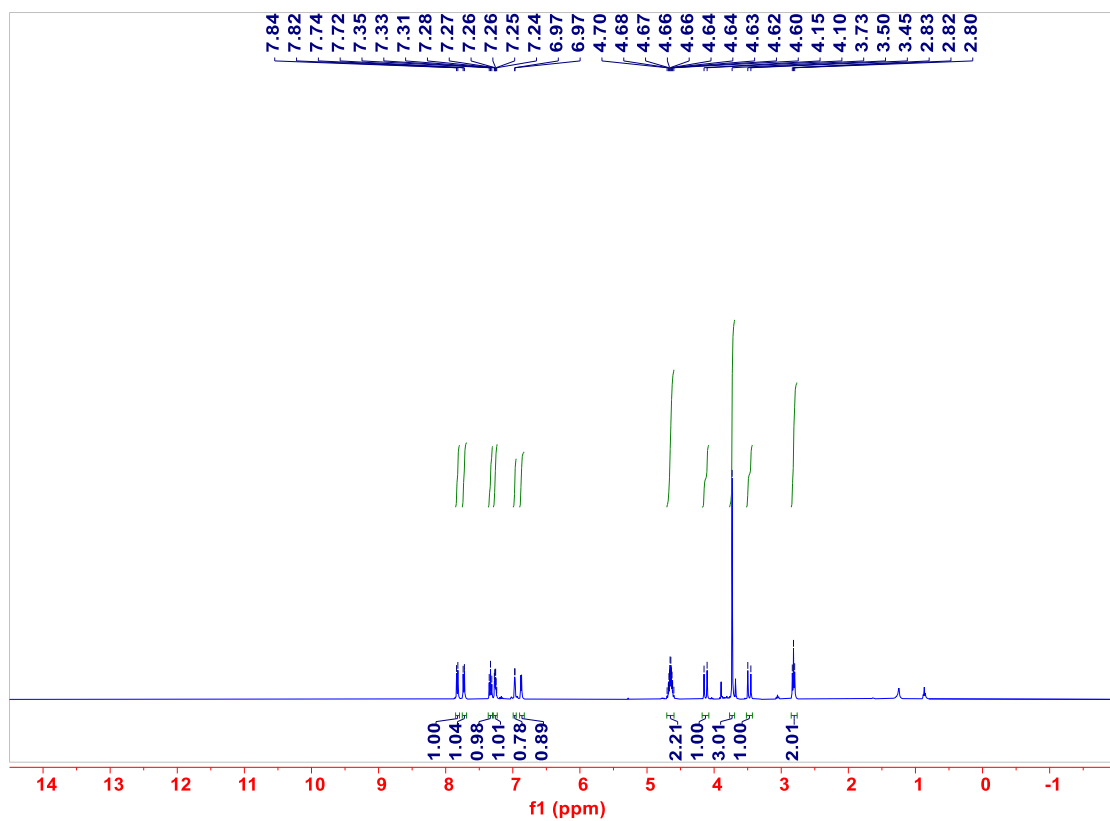


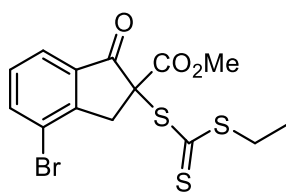
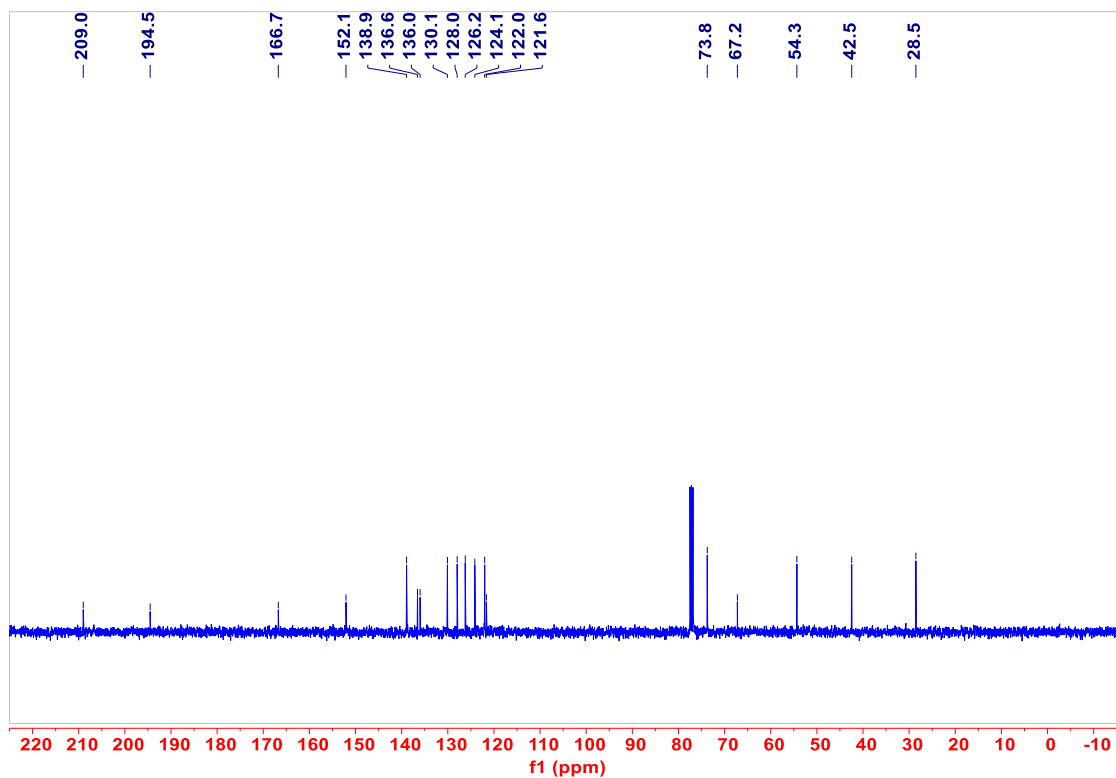
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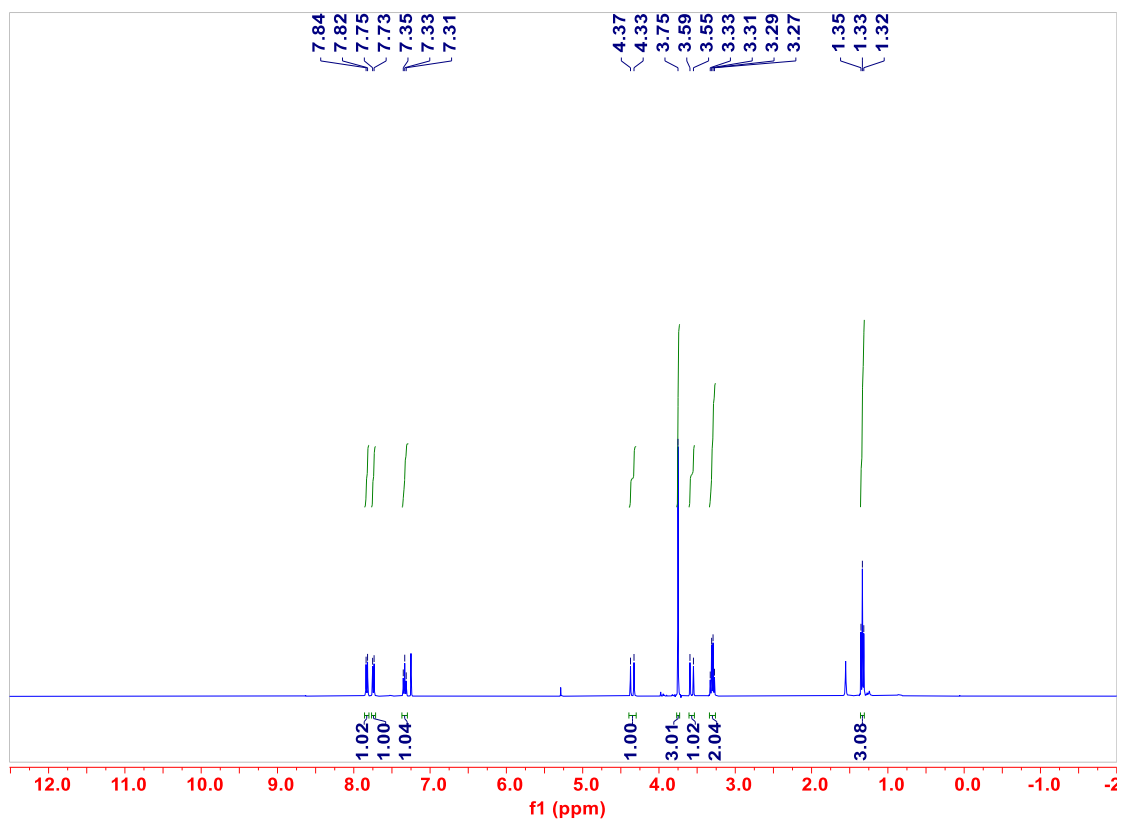


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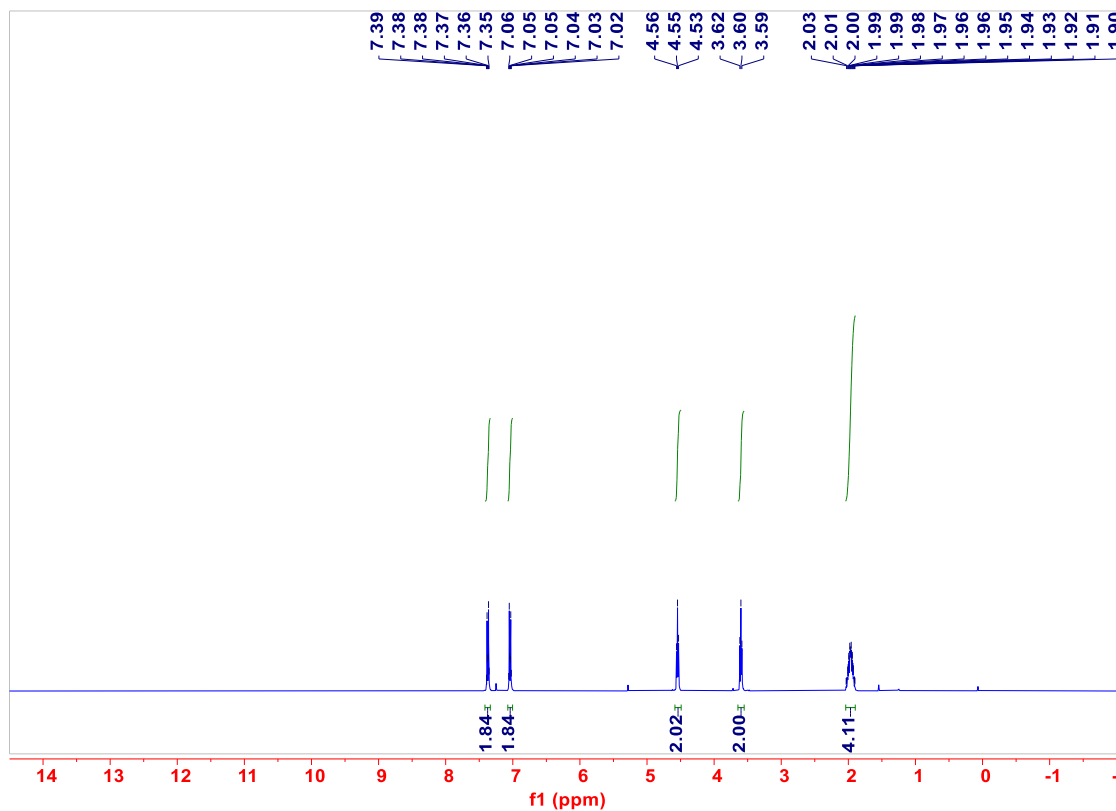
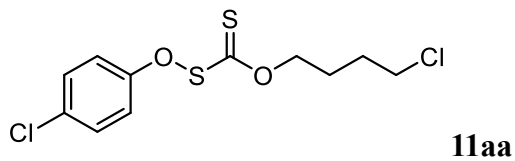
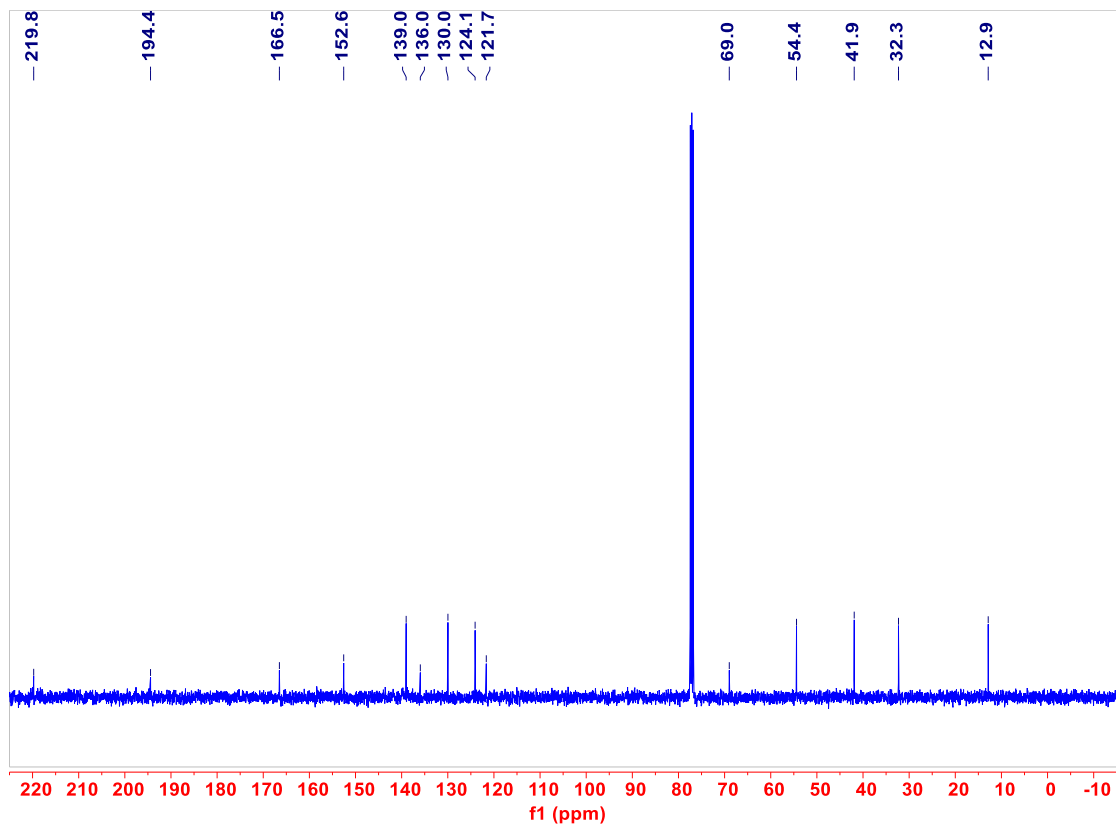


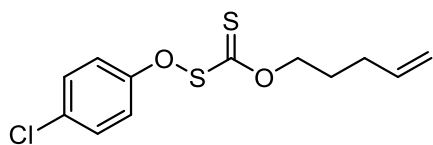
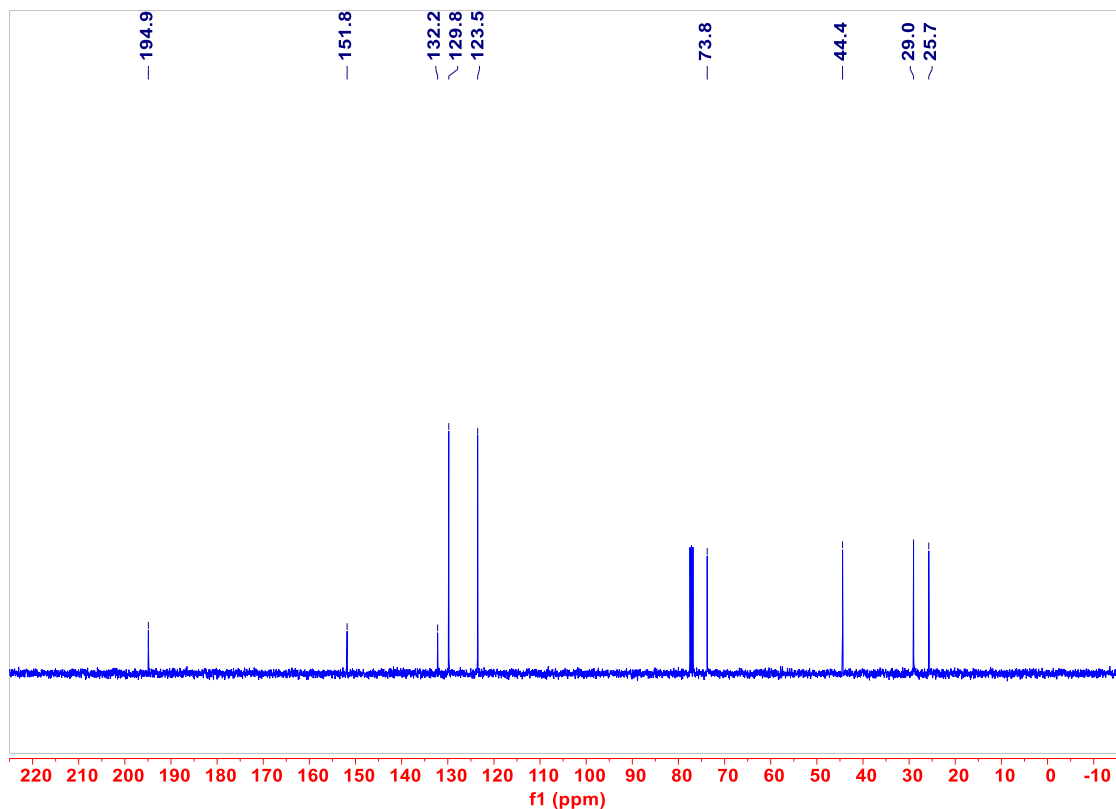


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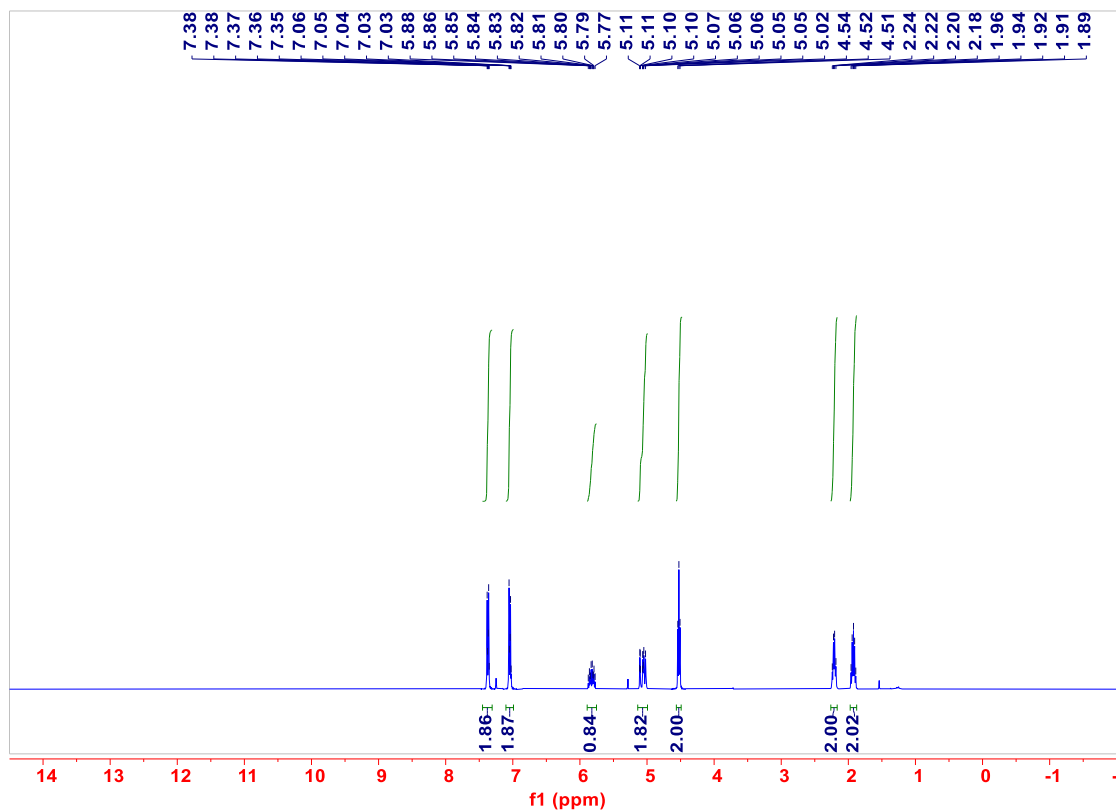


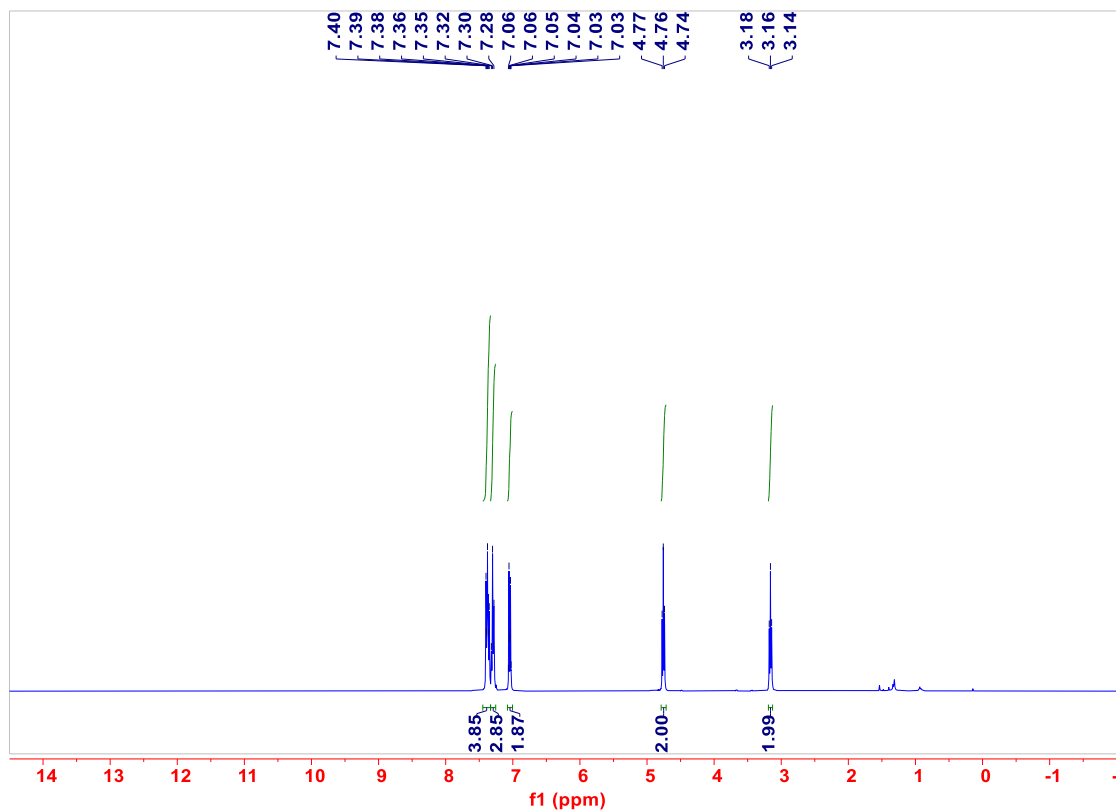
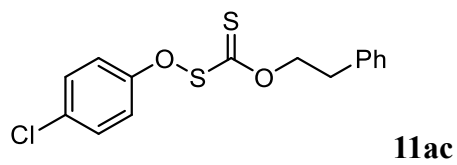
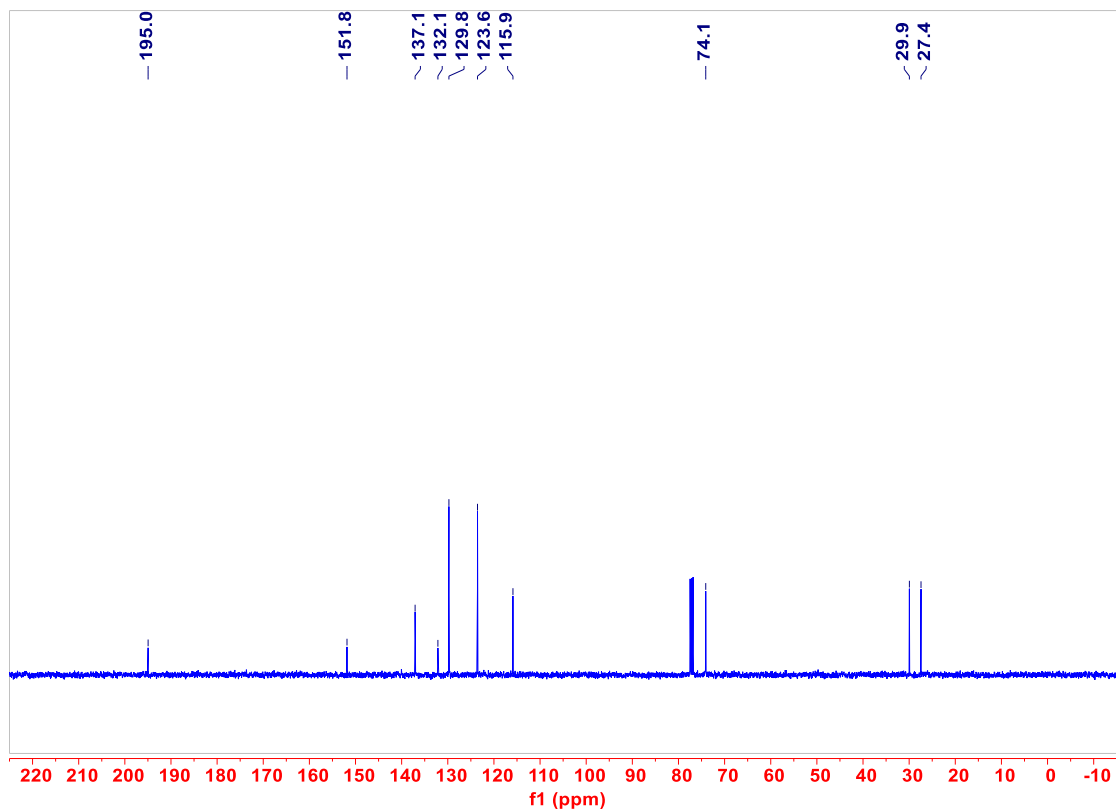


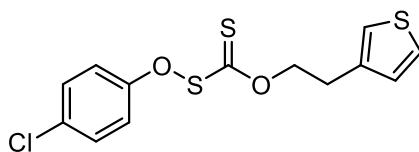
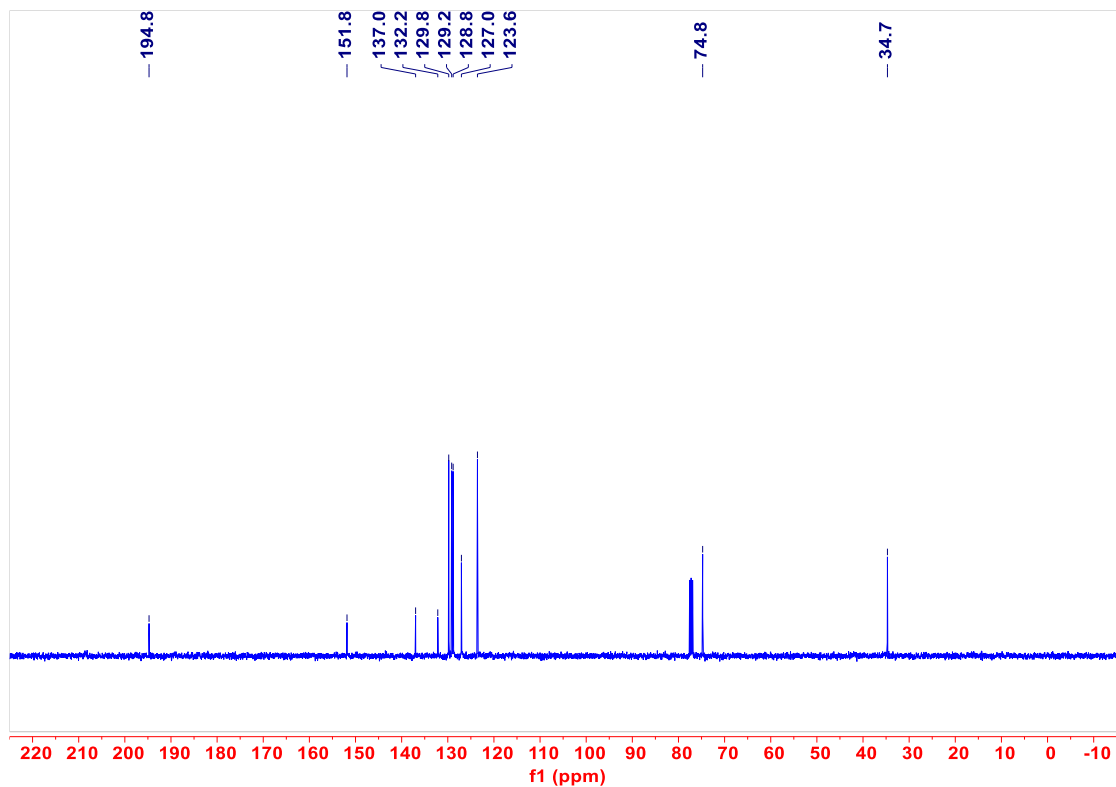




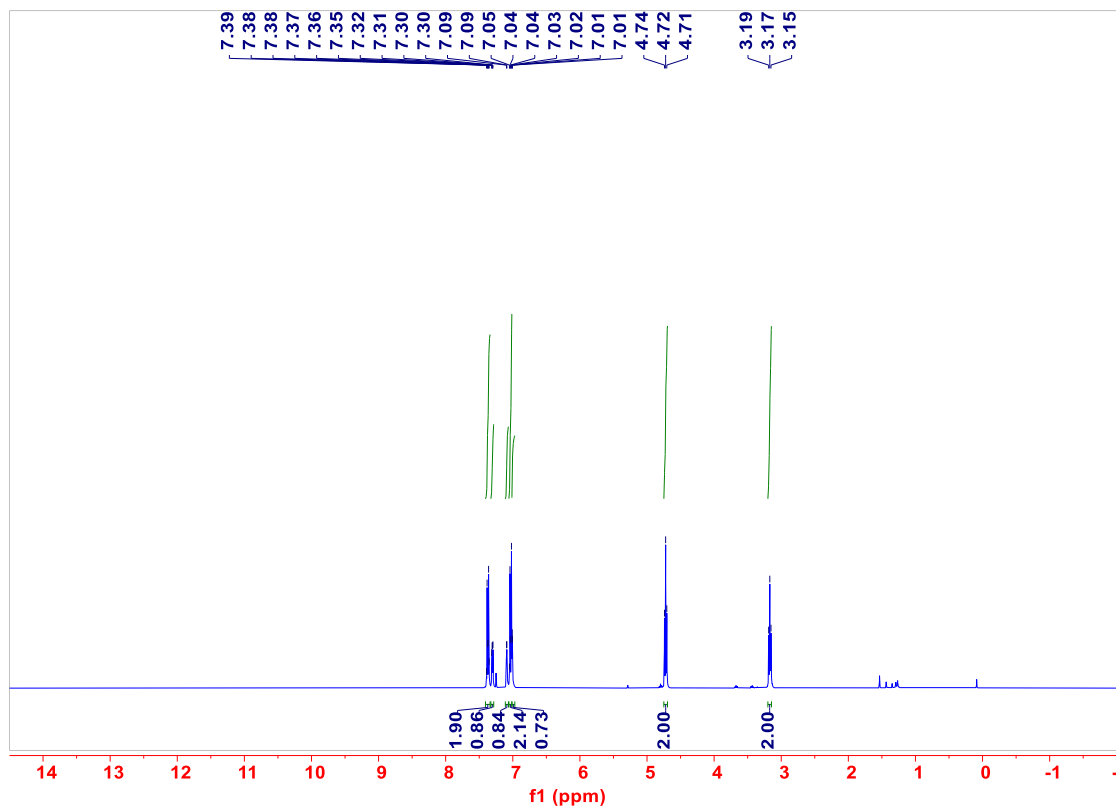
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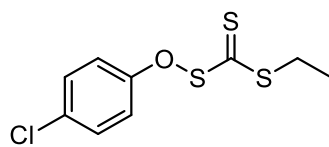
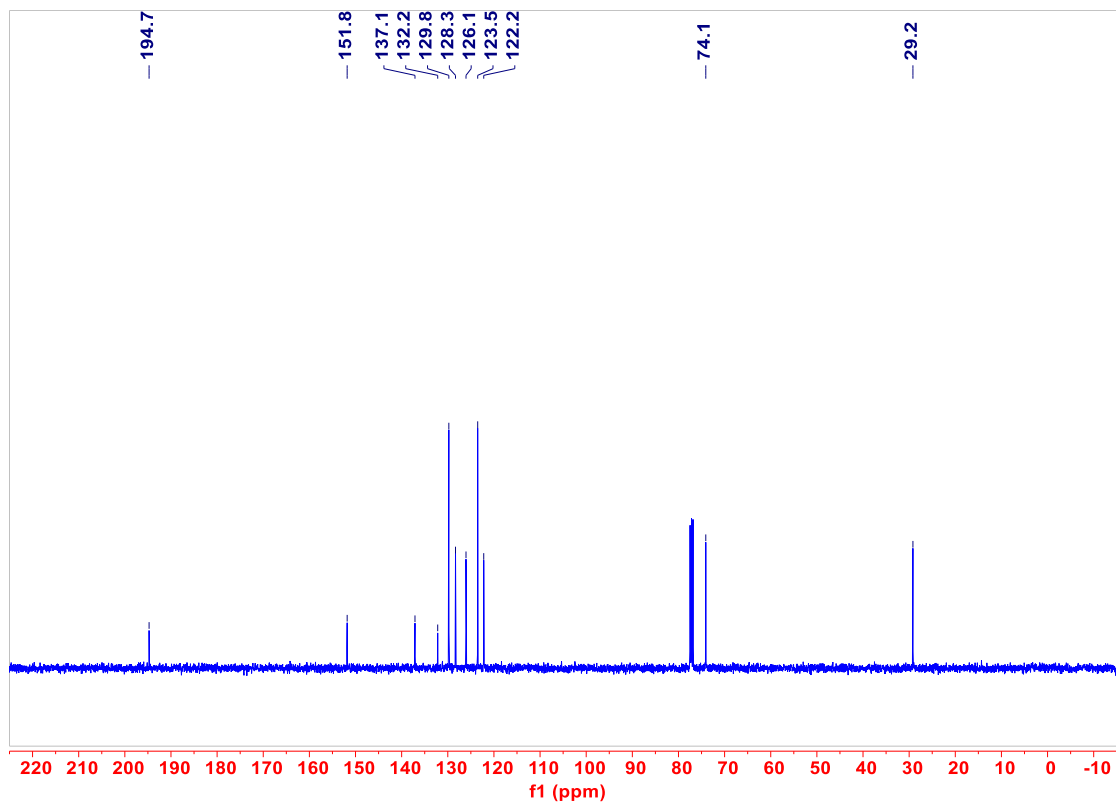




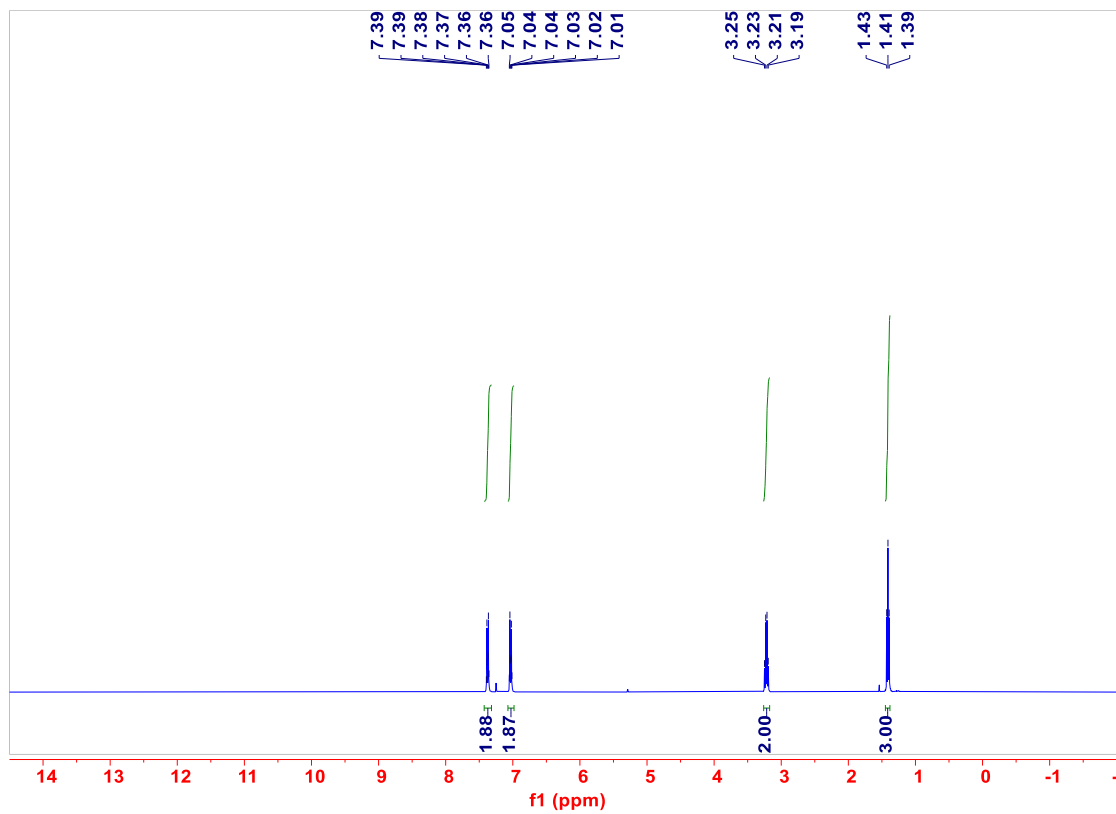


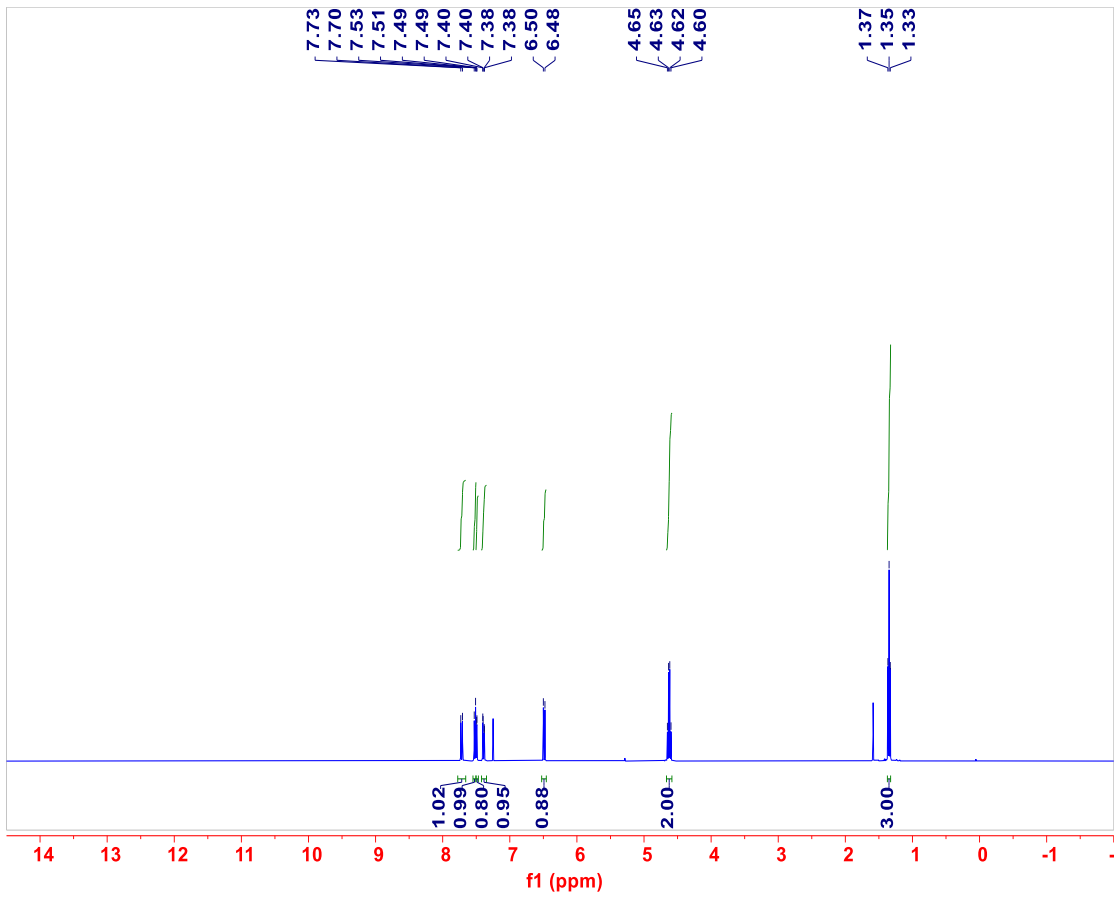
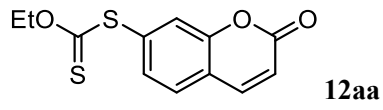
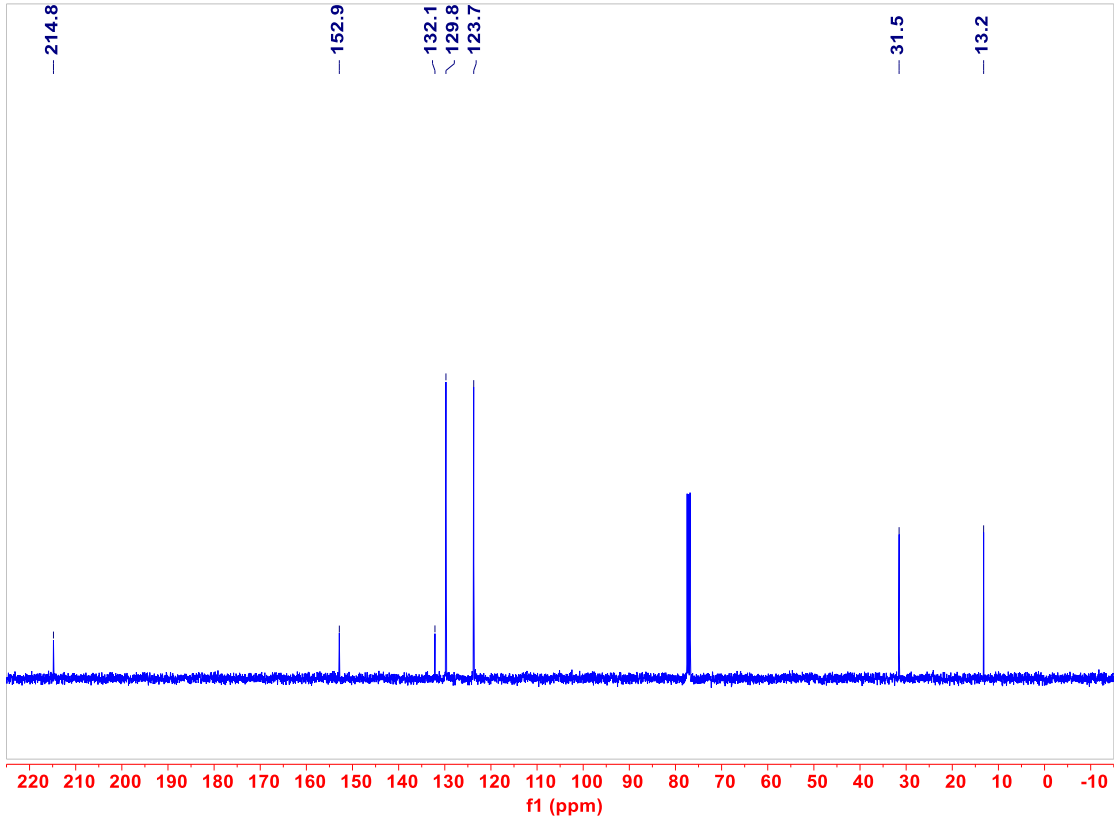
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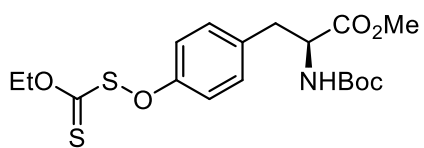
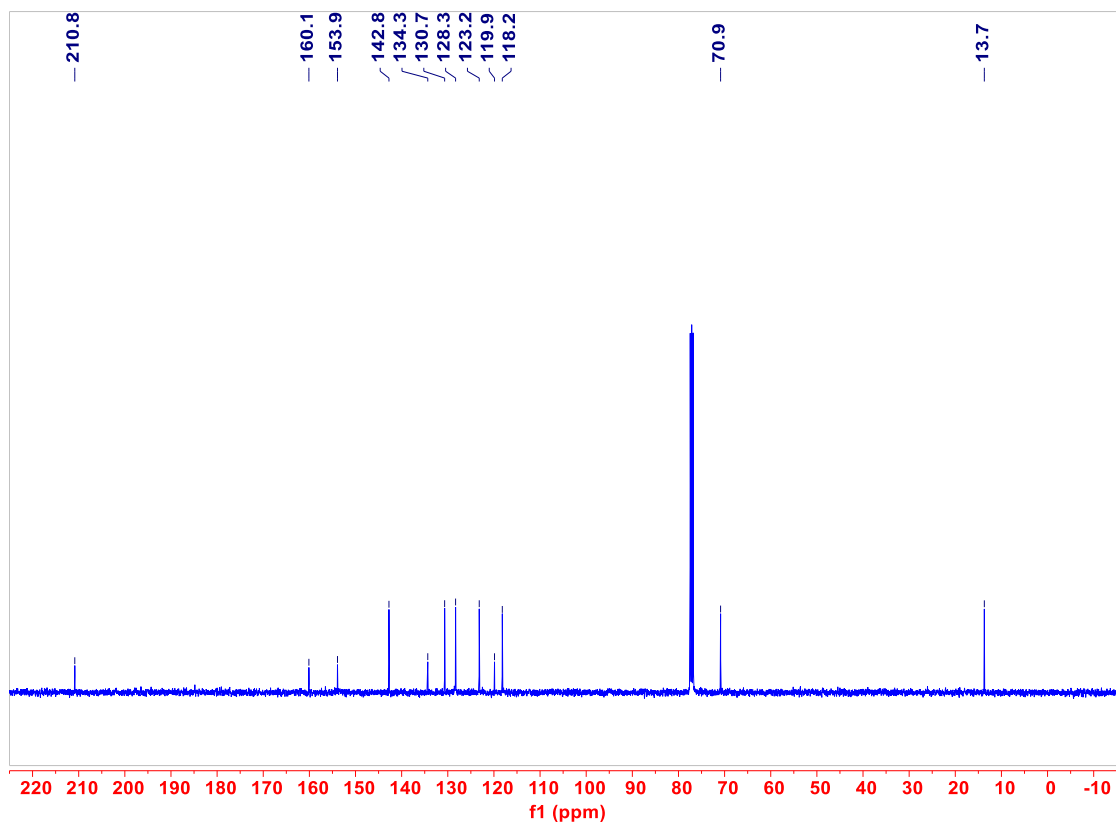




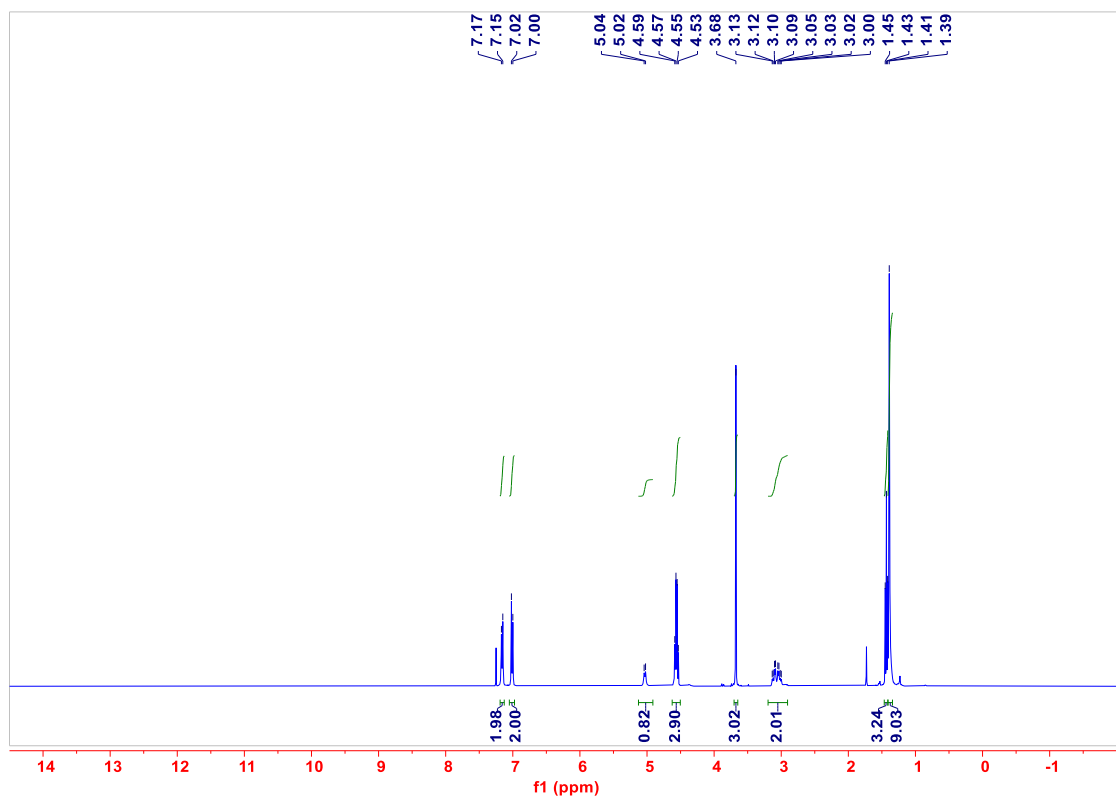
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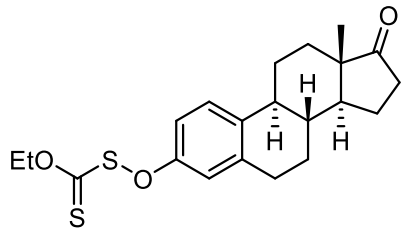
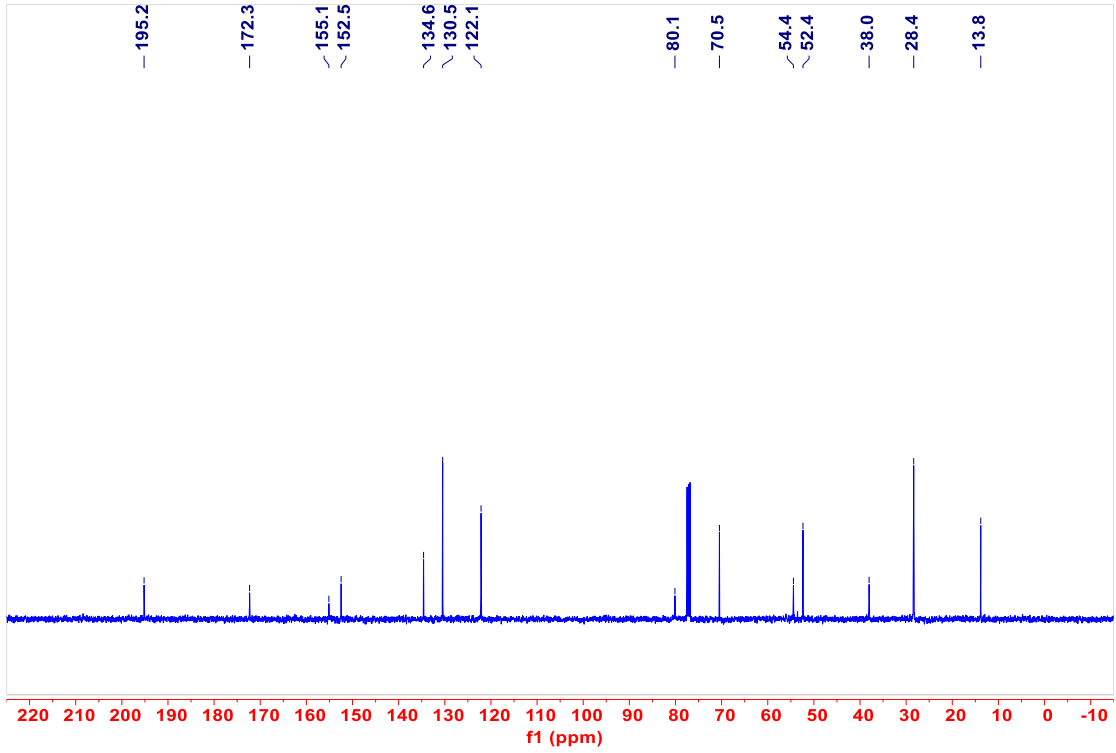




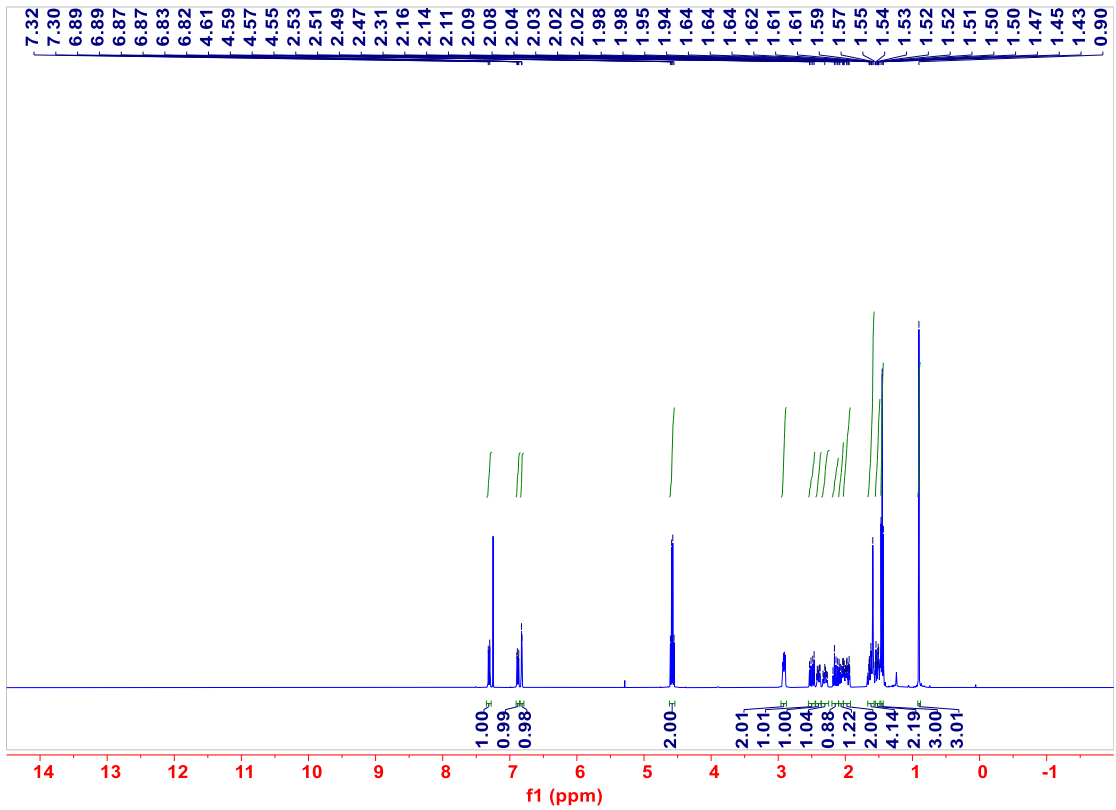


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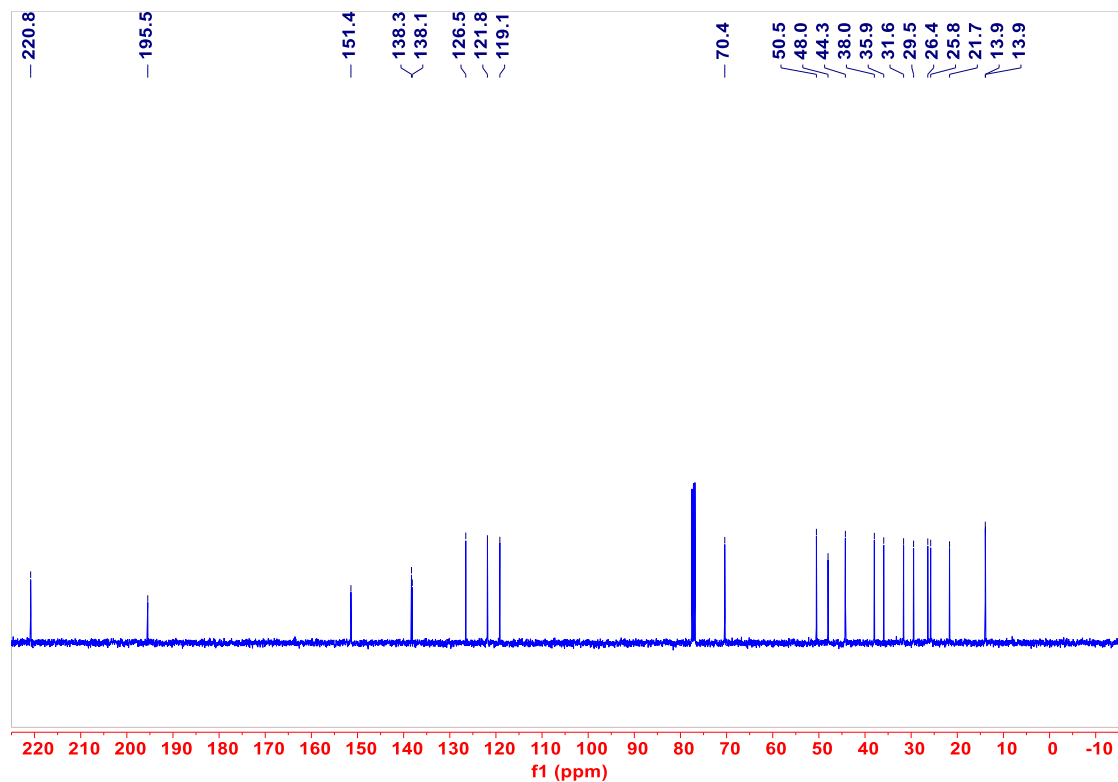




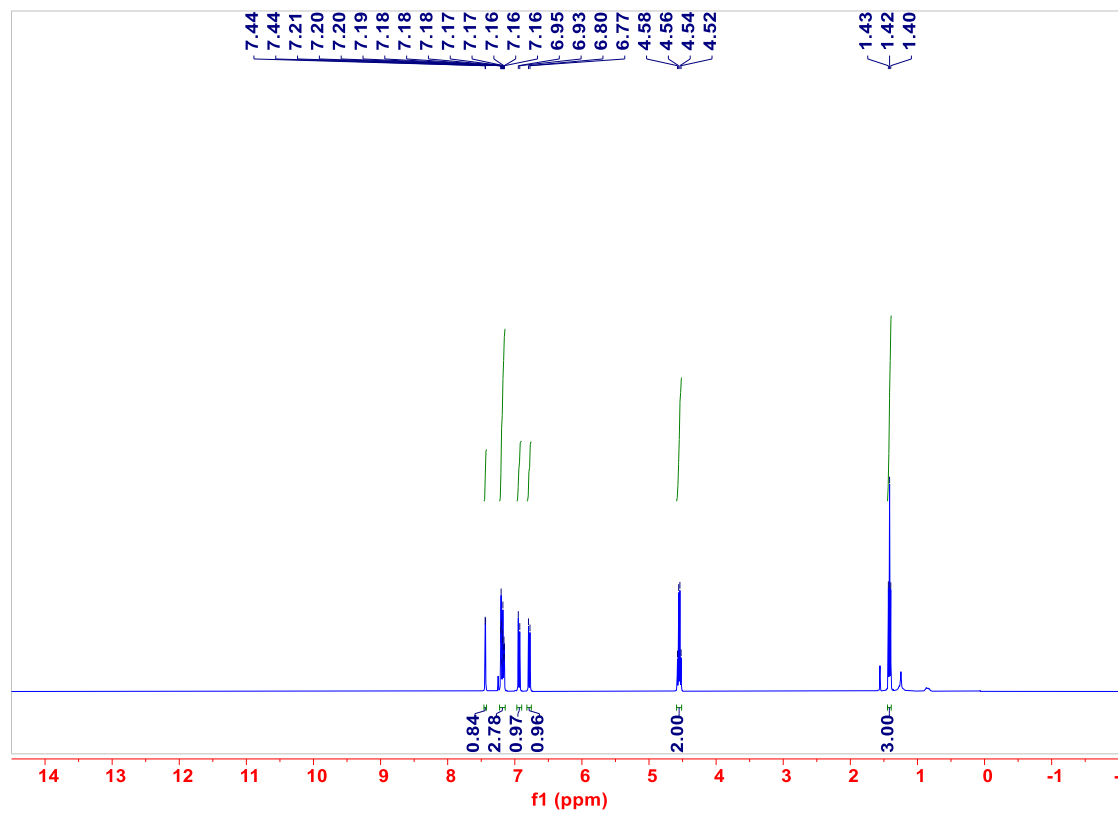
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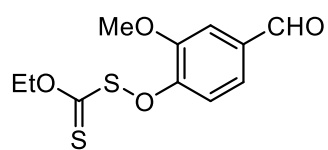
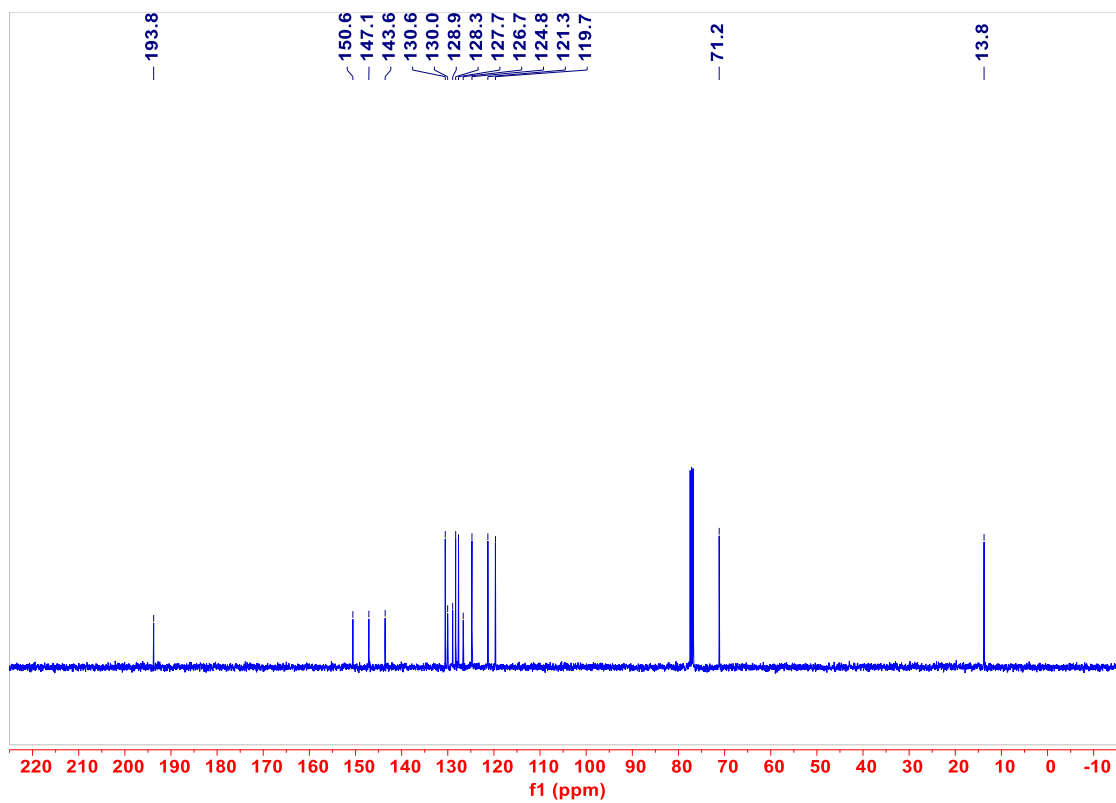




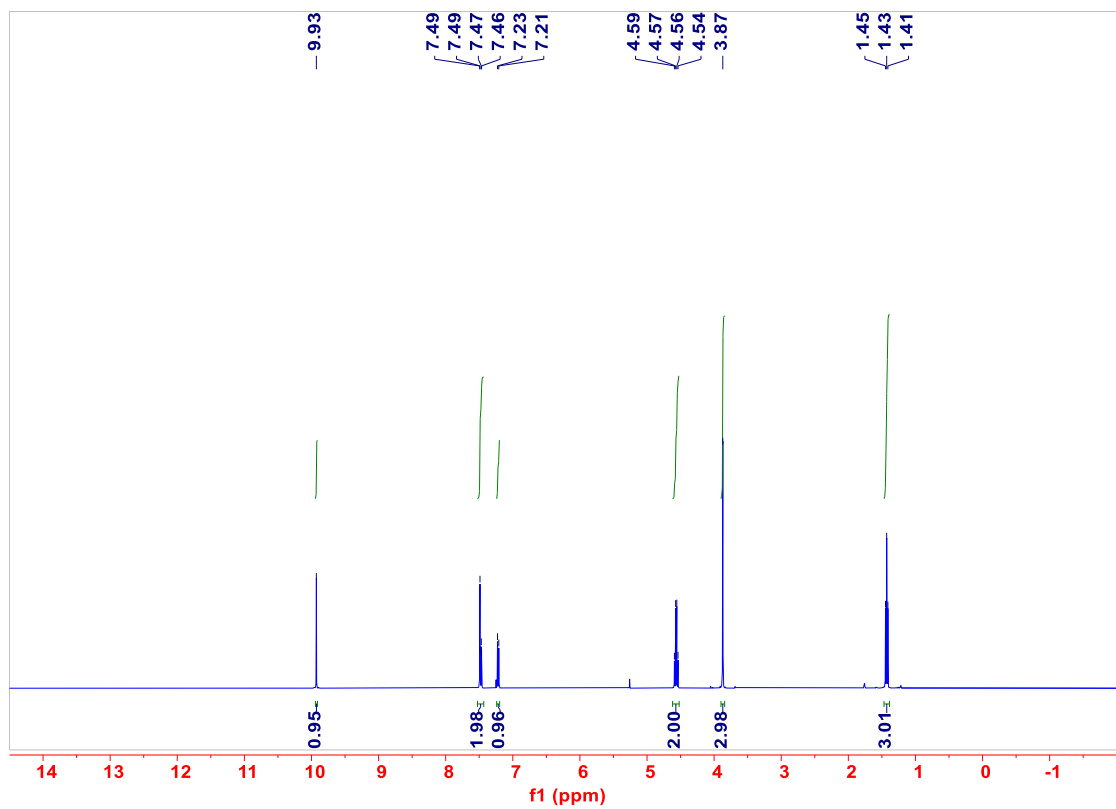


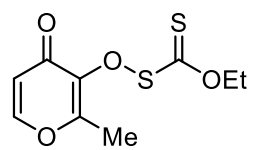
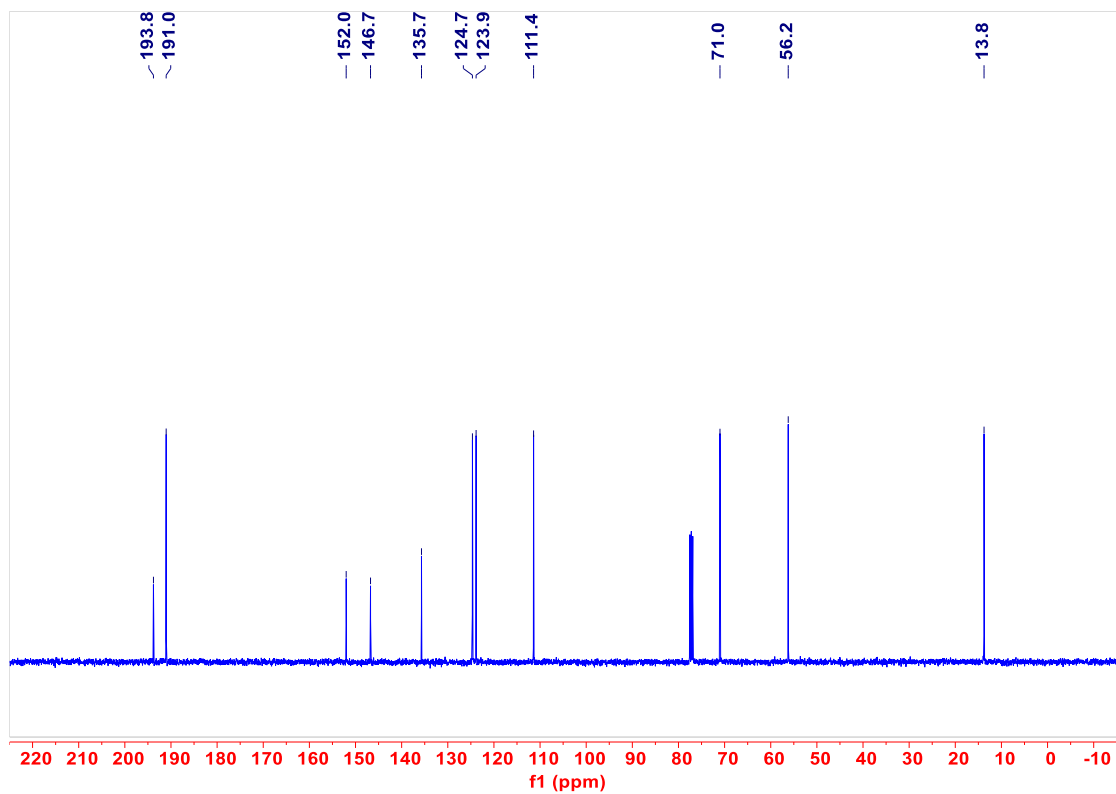
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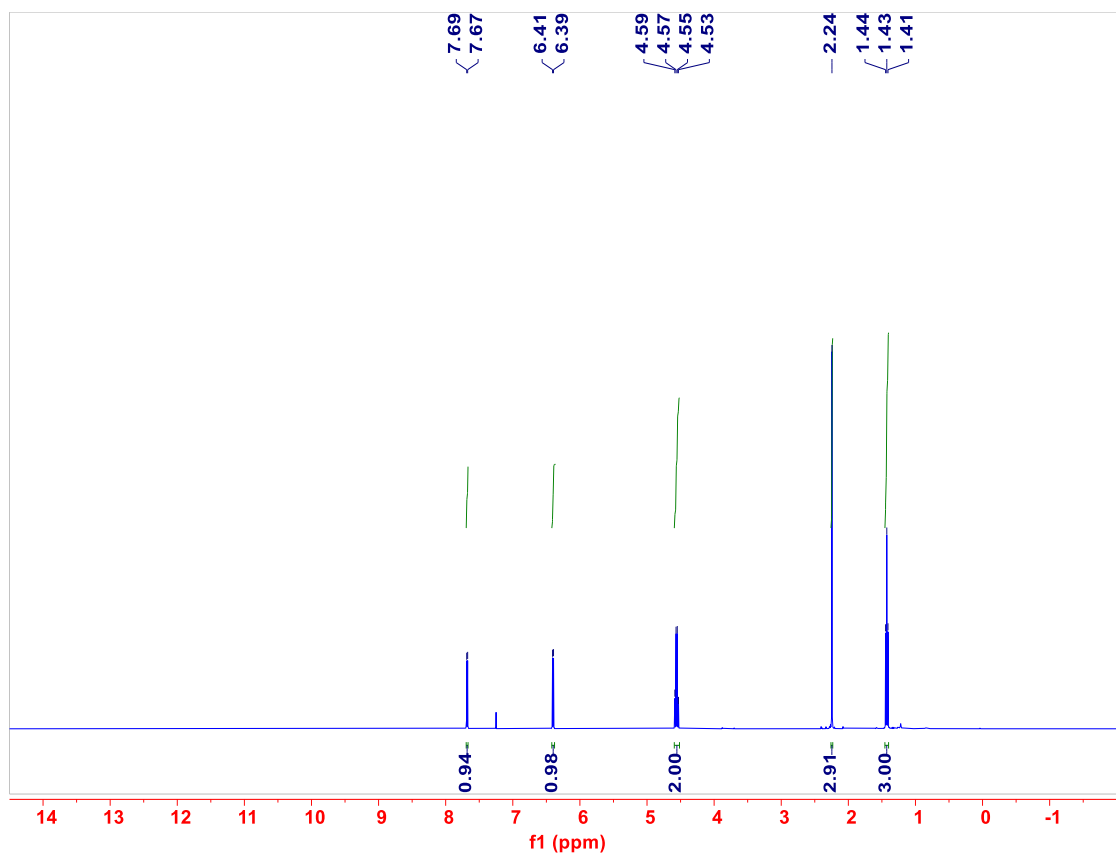


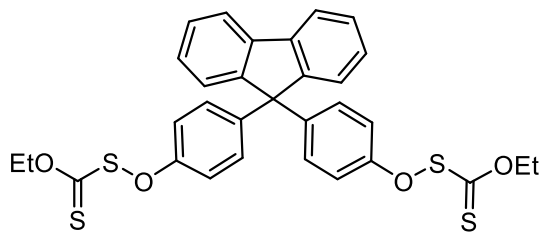
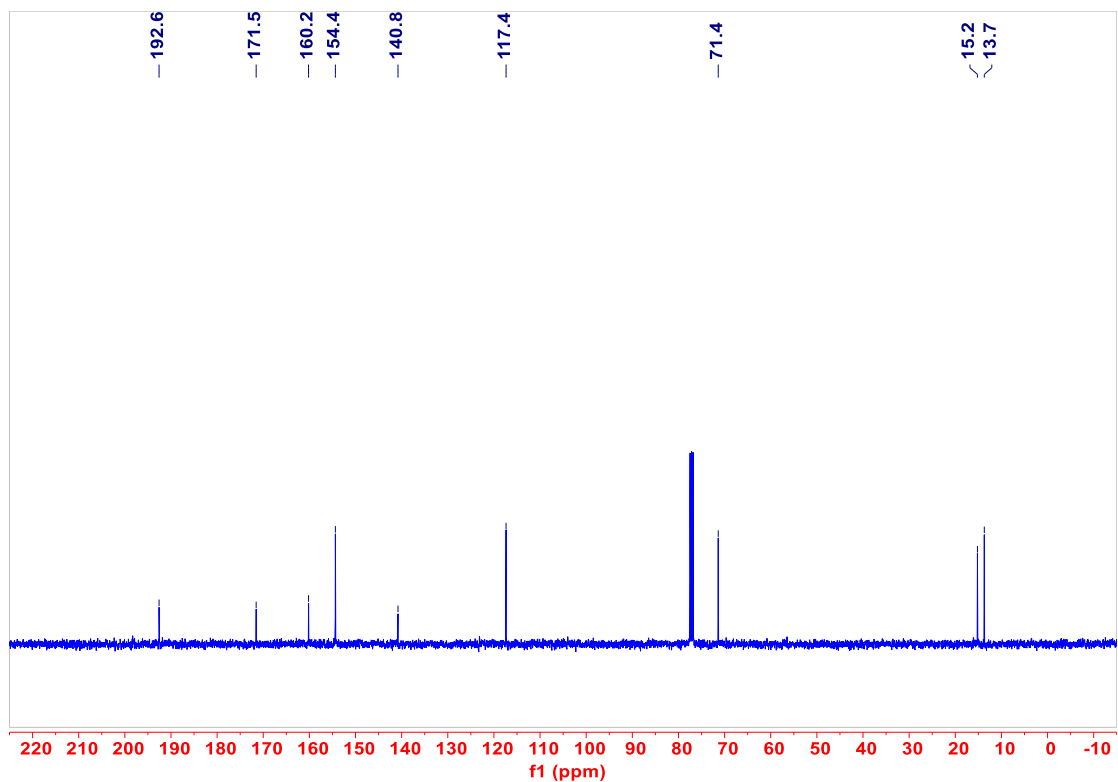
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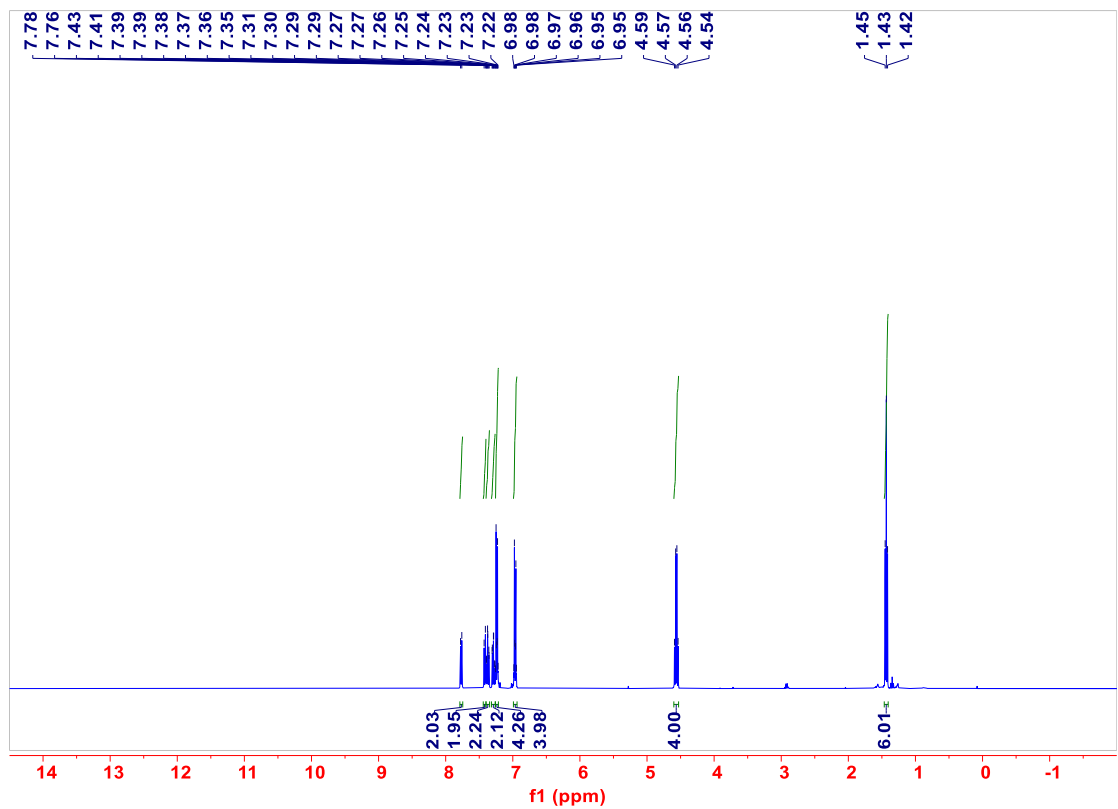


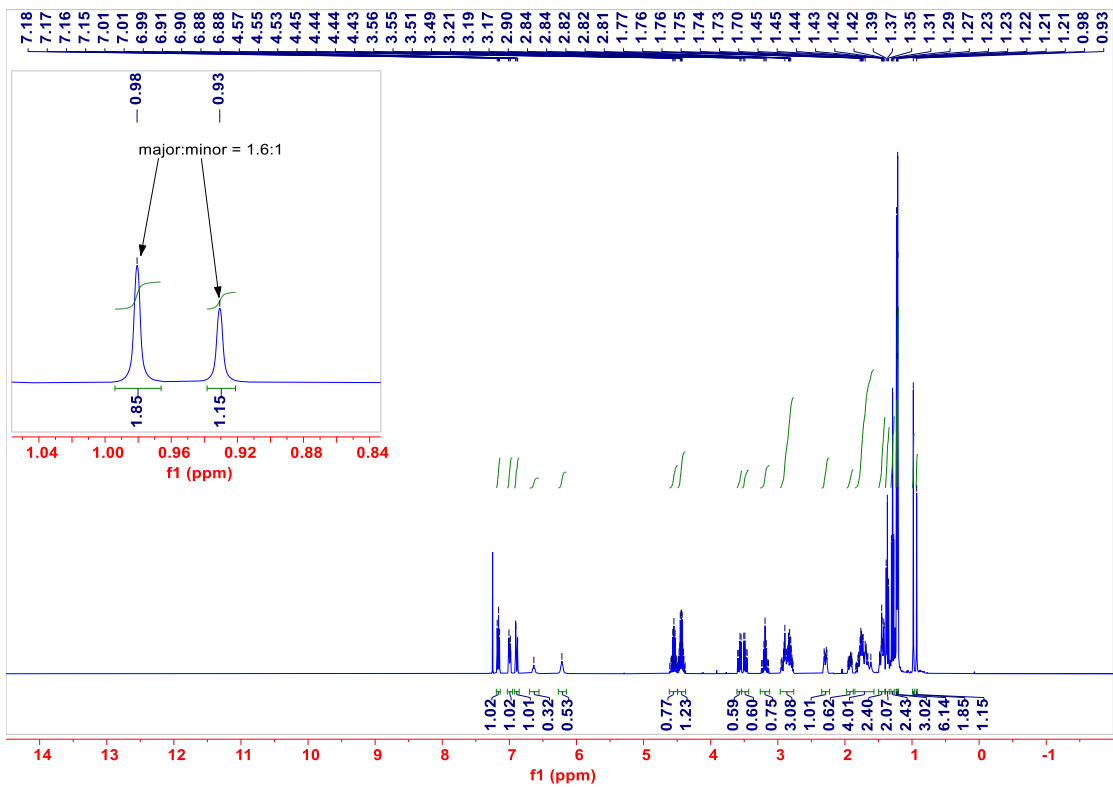
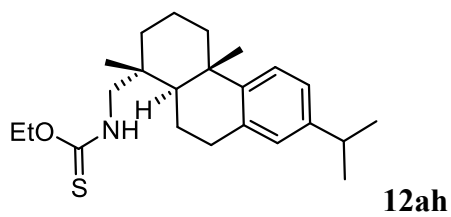
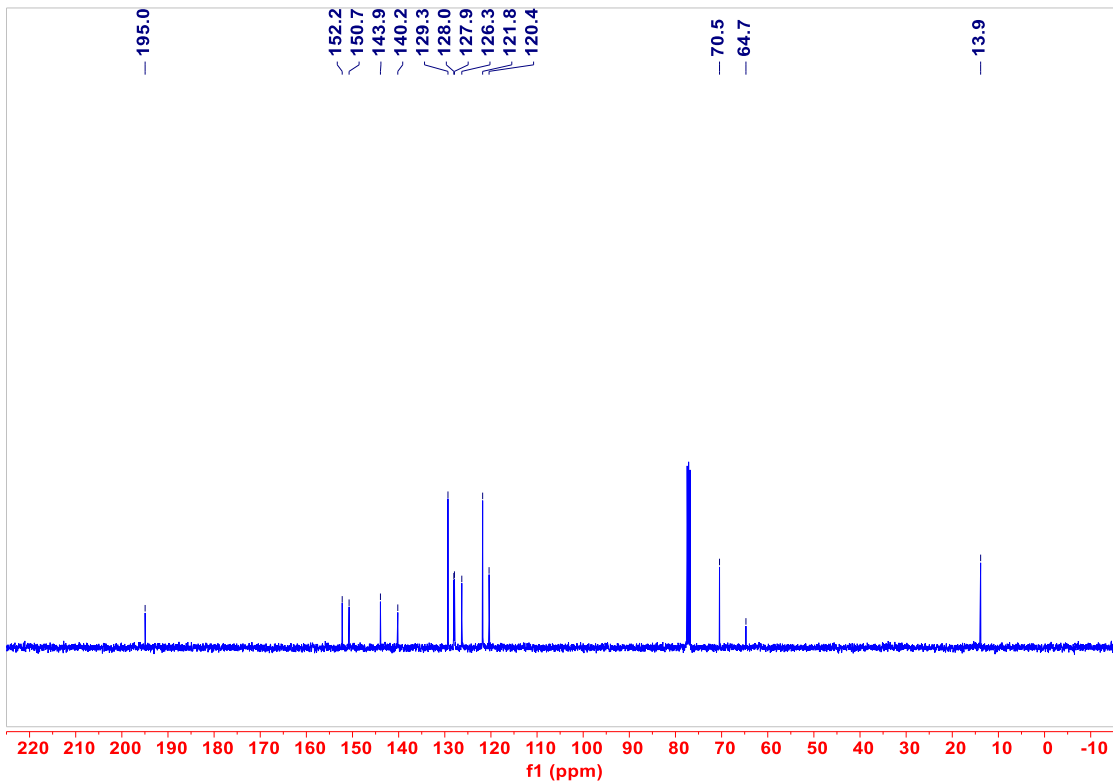
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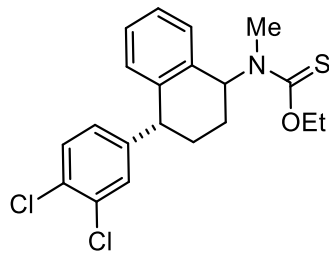
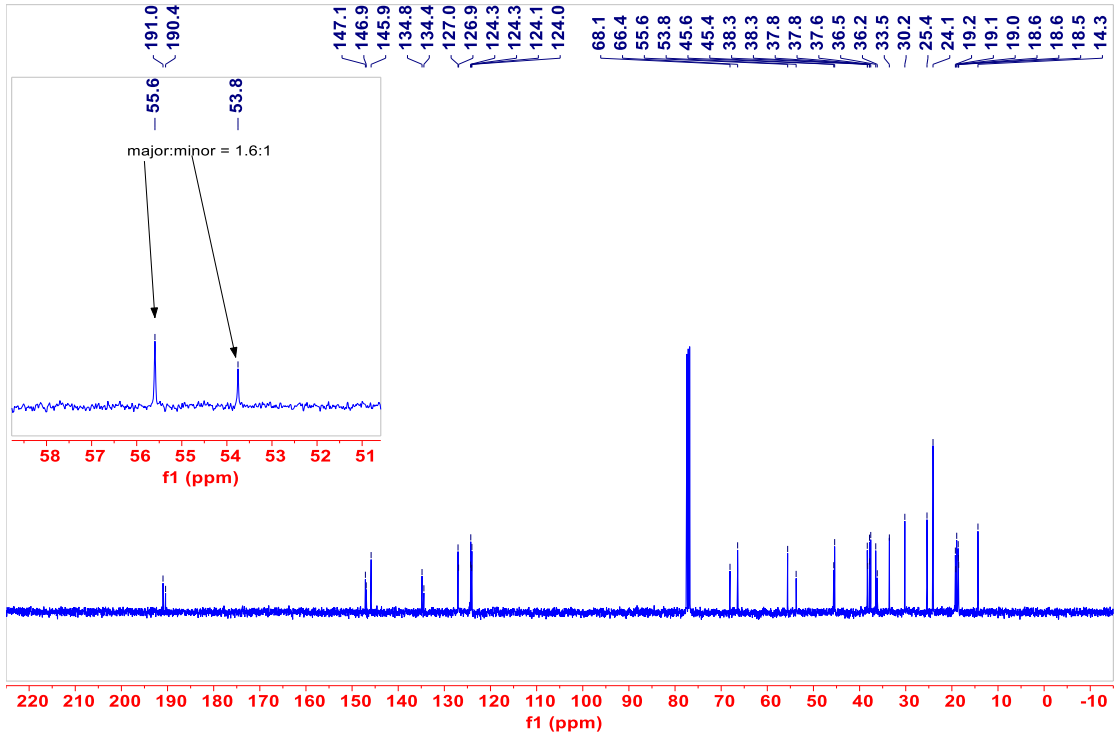




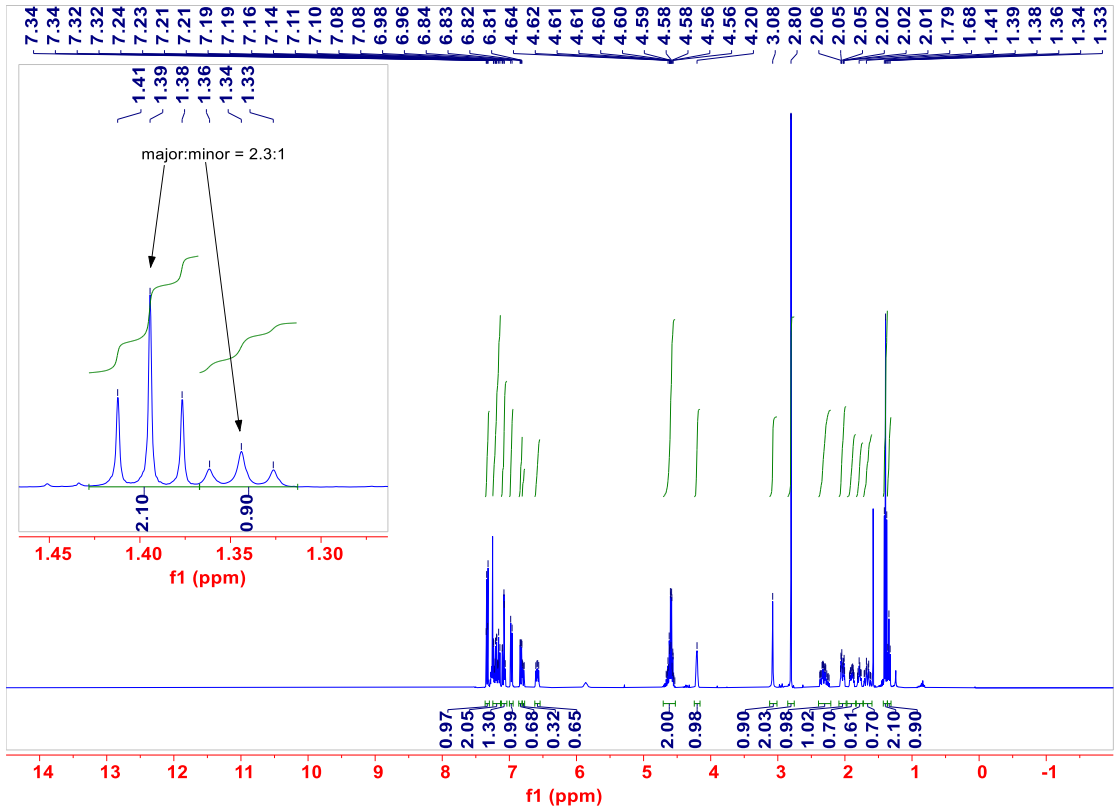
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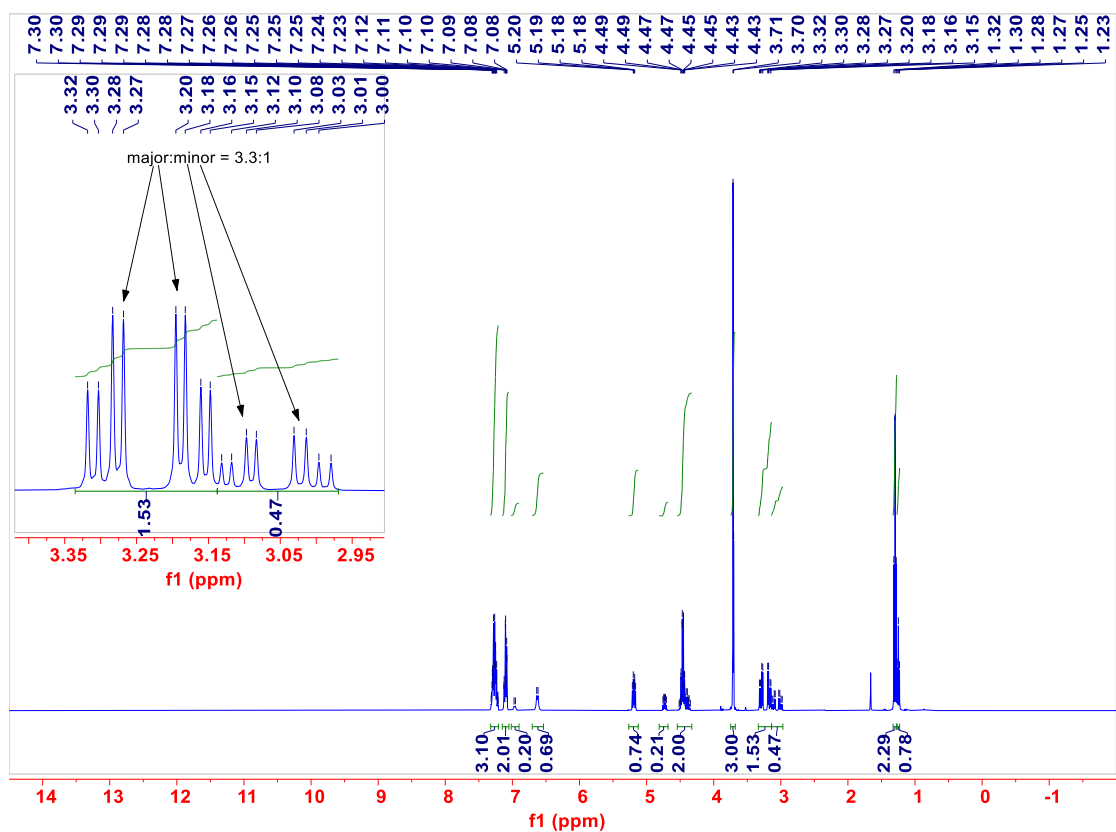
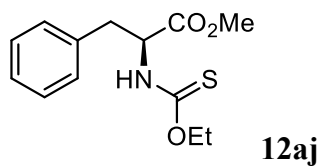
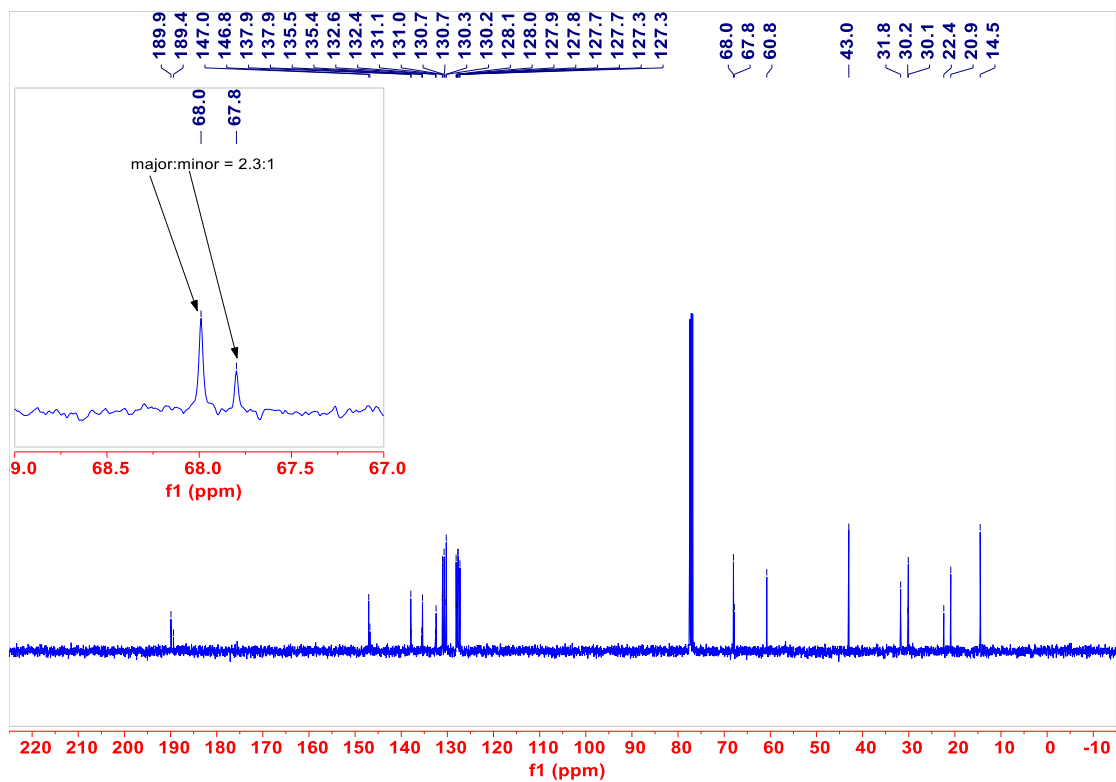


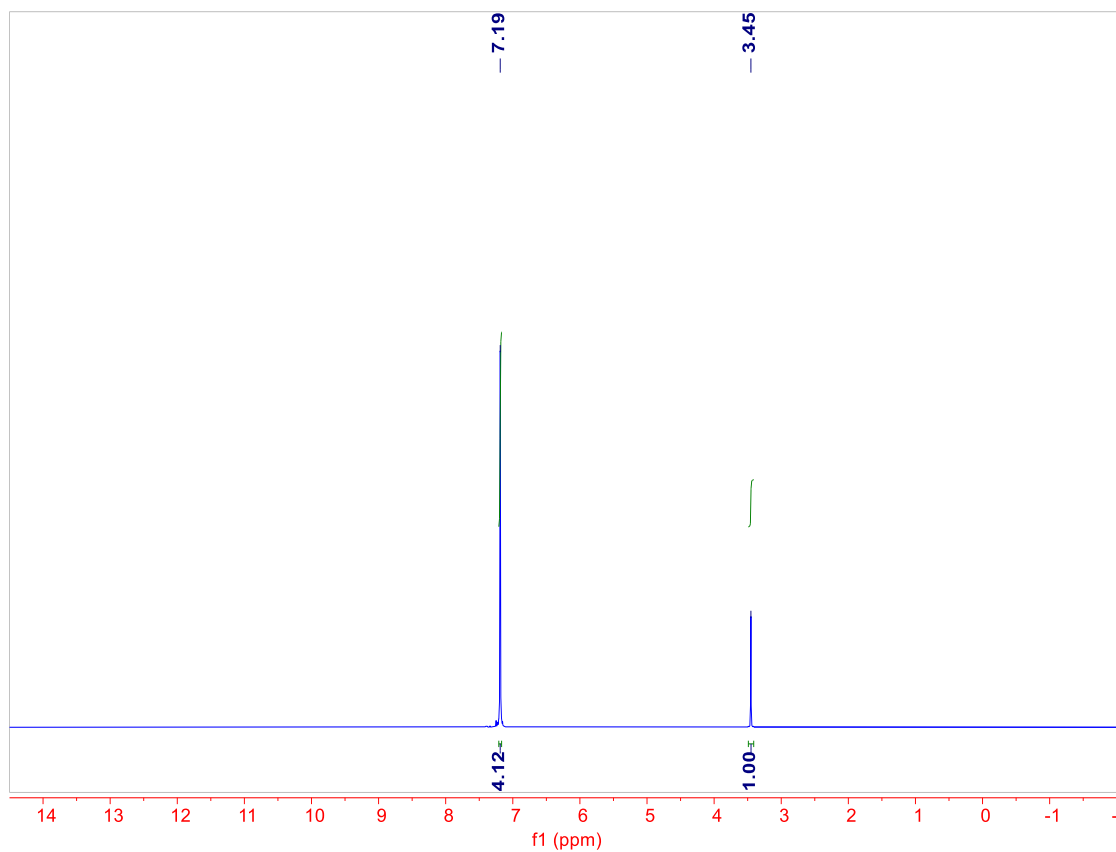
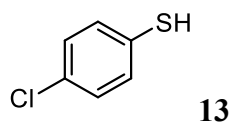
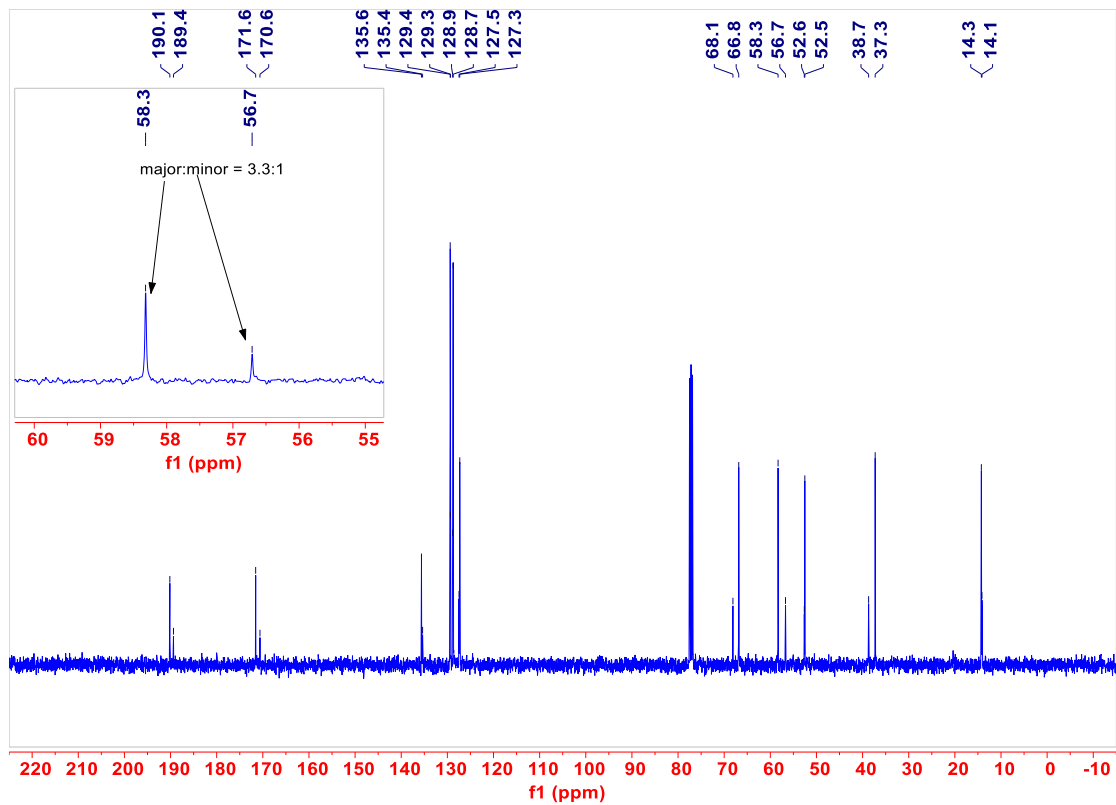




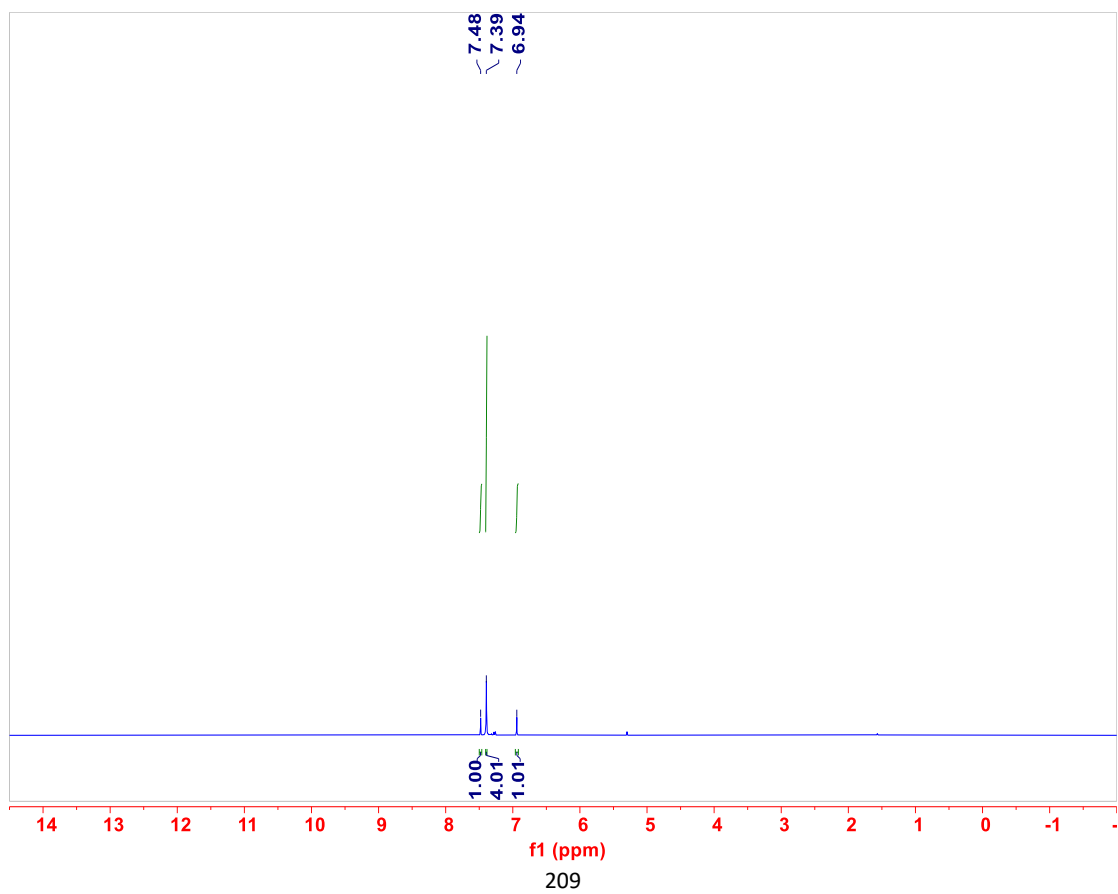
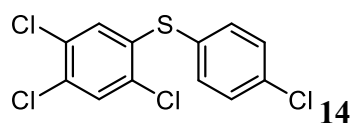
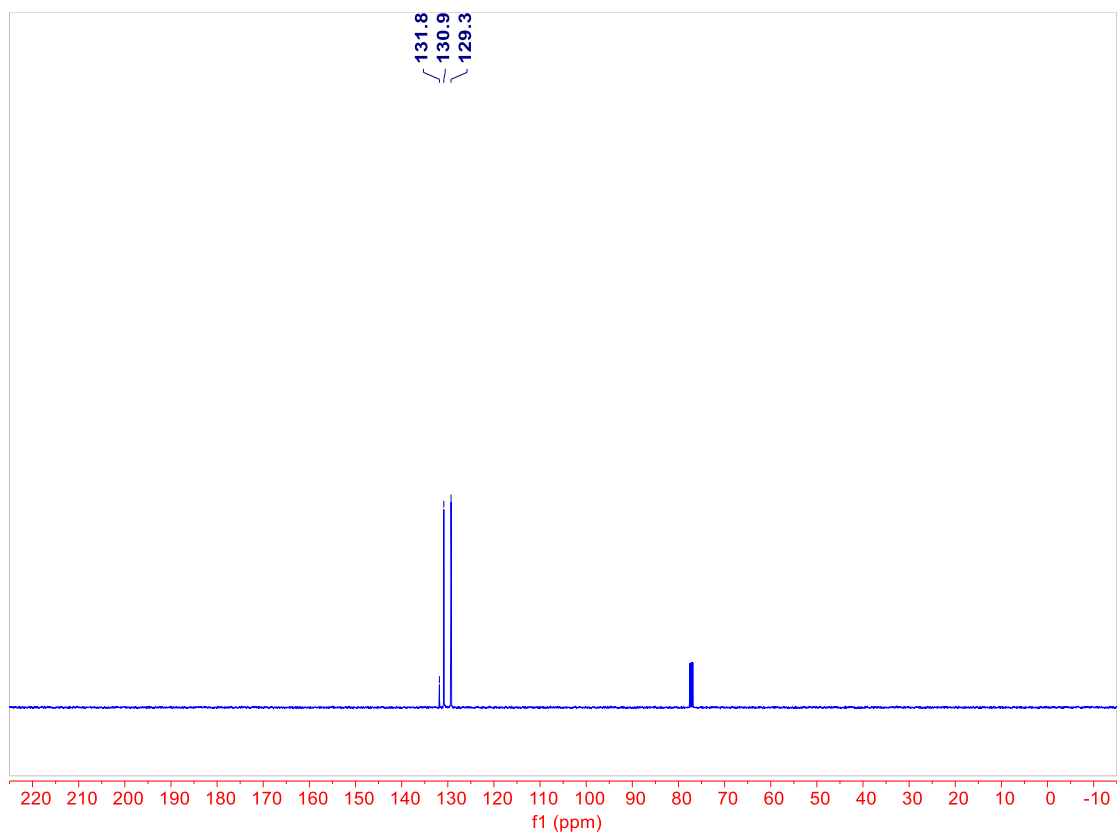
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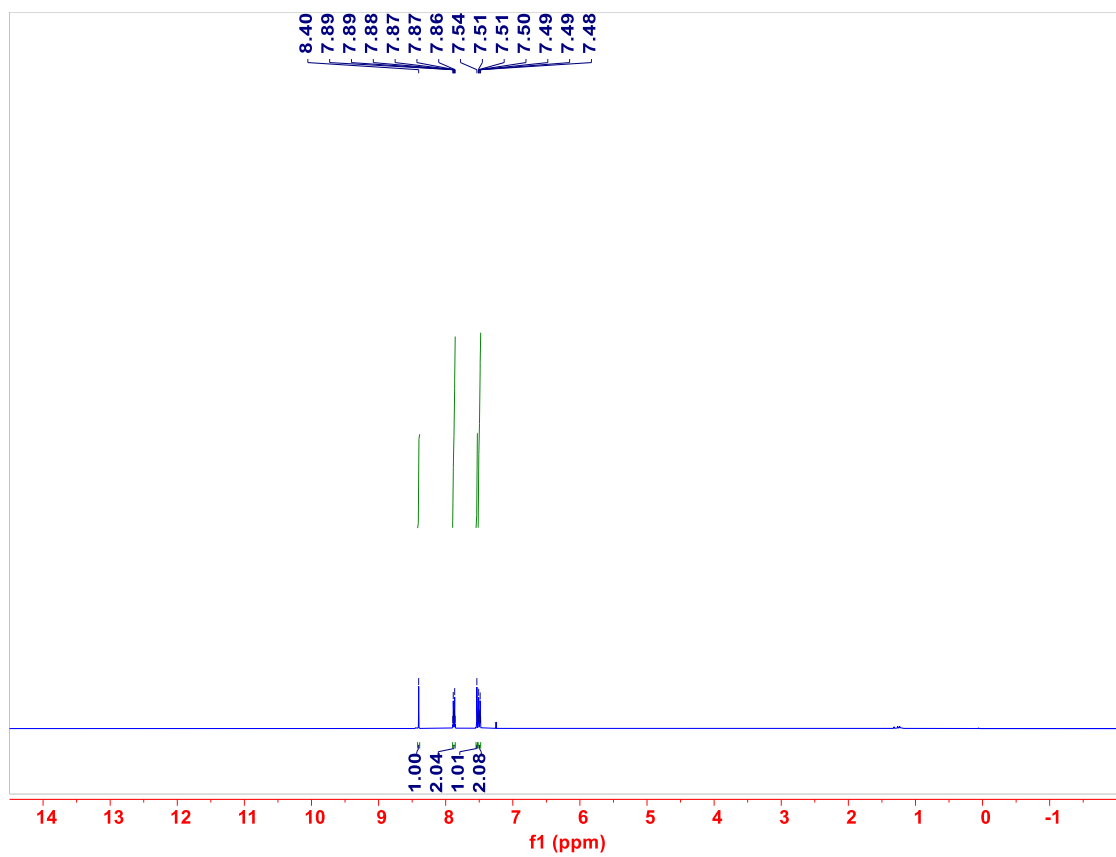
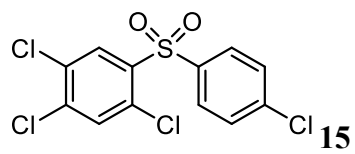
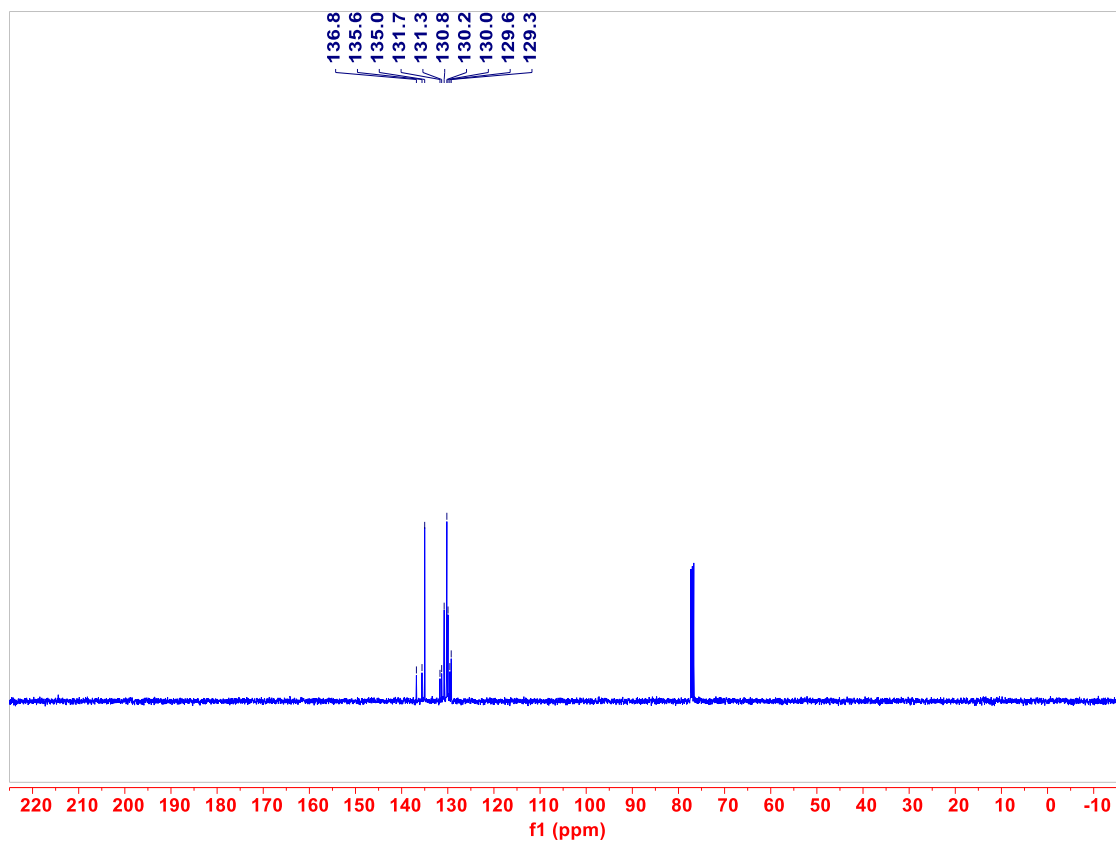


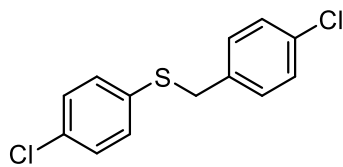
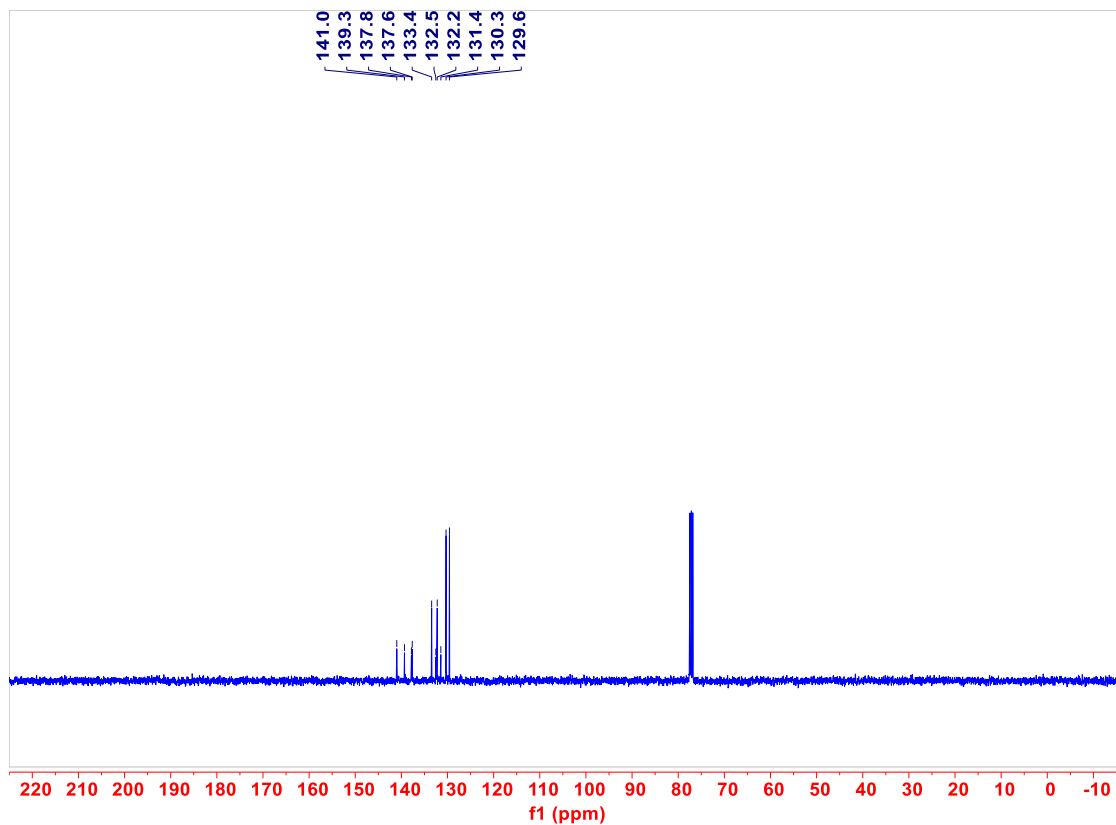




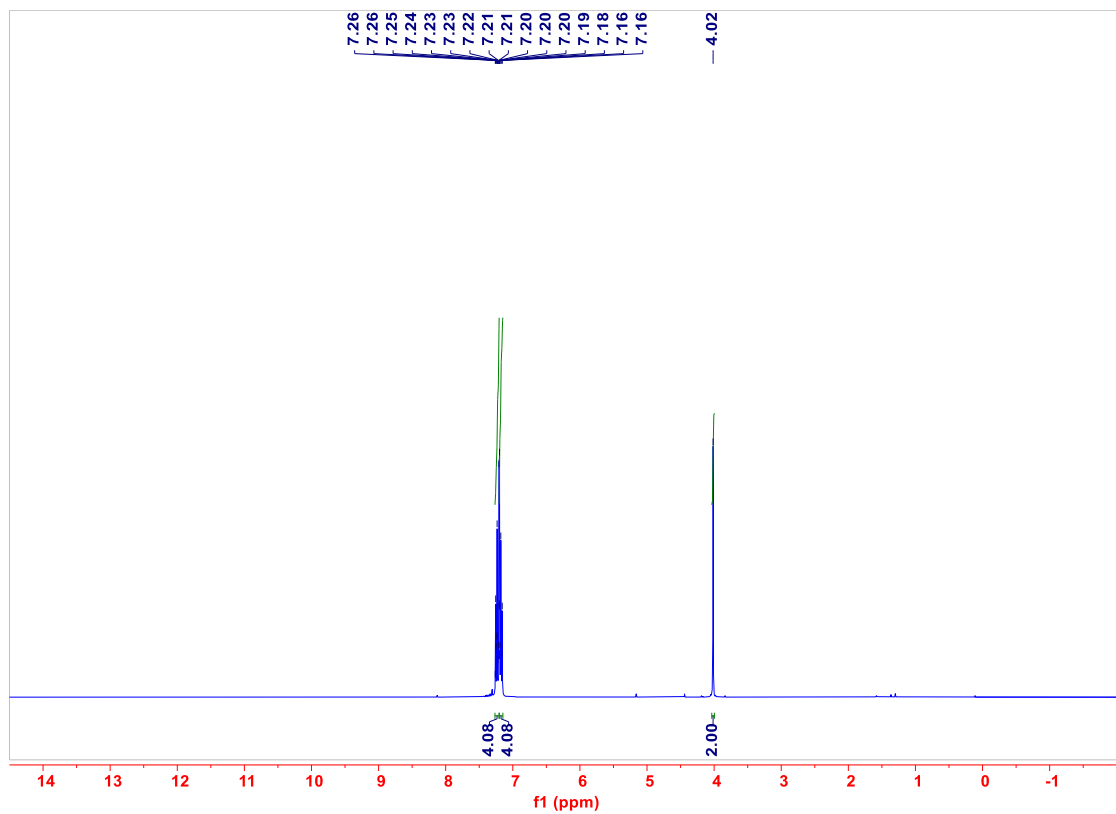


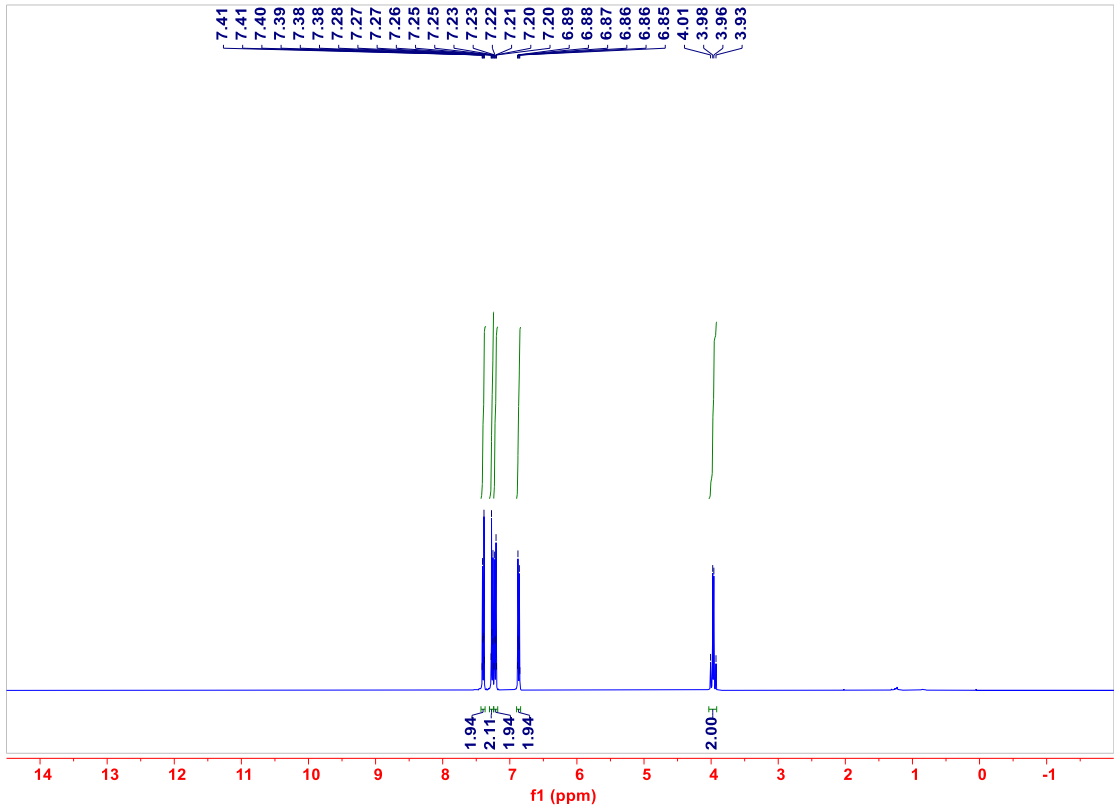
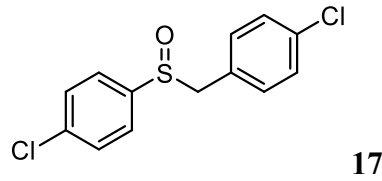
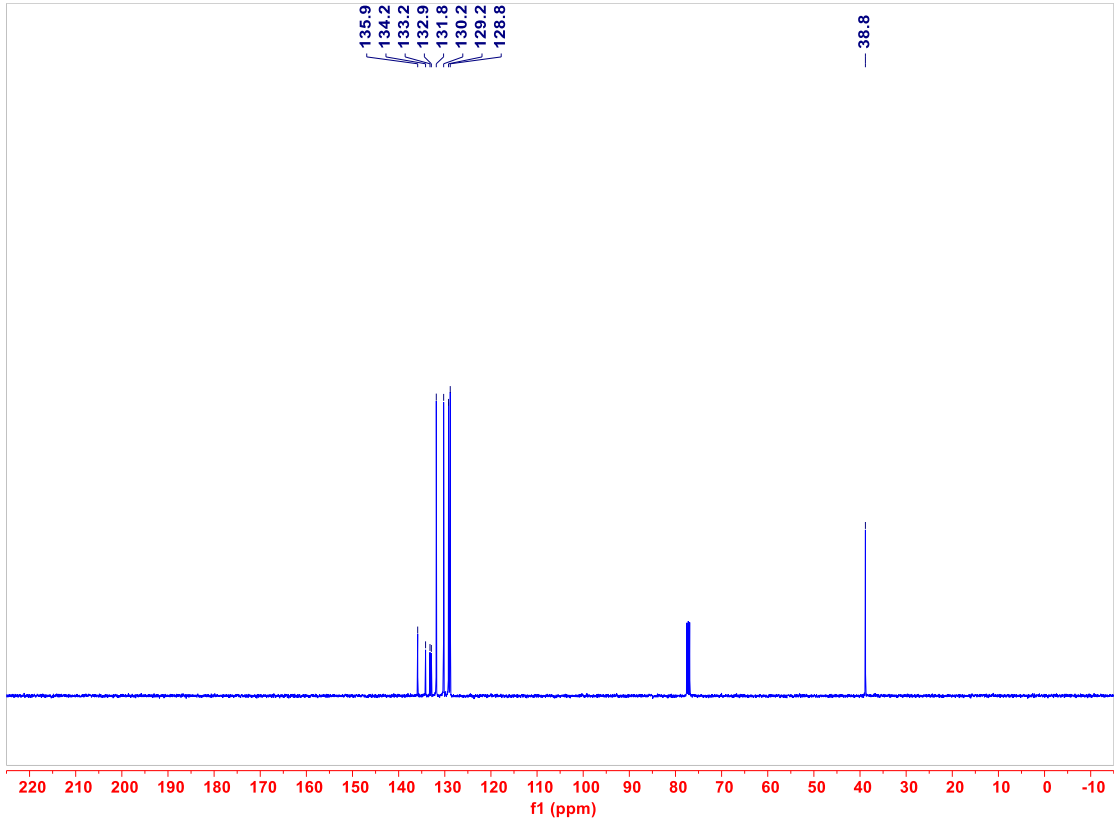


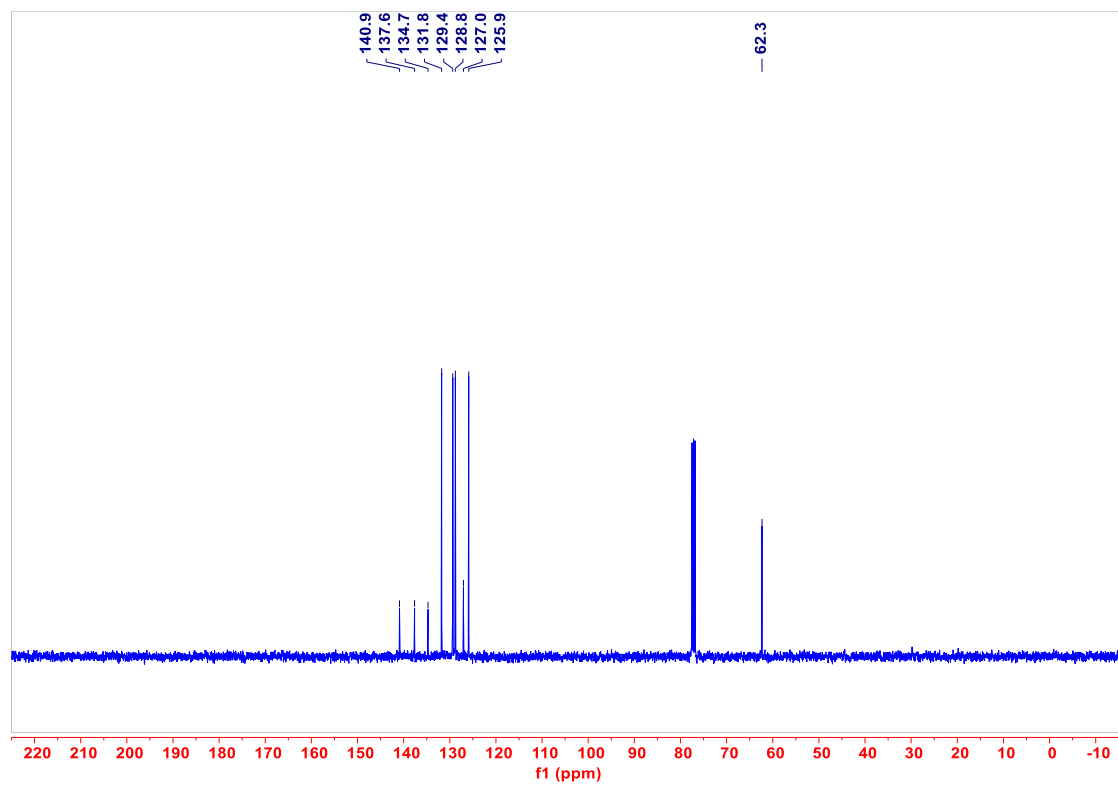




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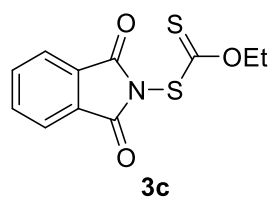
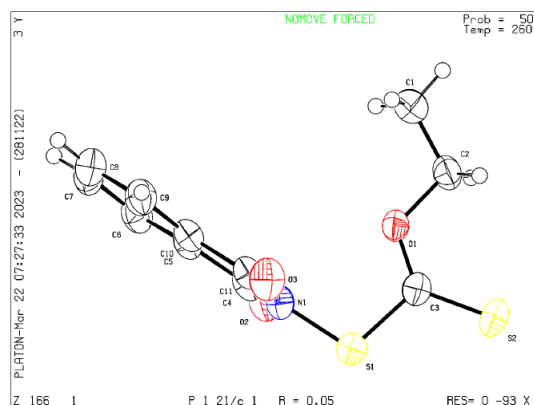






## VIII. X-ray structure of 3c

X-Ray crystallography data for **3c** (CCDC 2250745): A colorless crystal suitable for X-ray crystallography was obtained from a *n*-hexane/DCM solution at 4–8 °C under air atmosphere. The ORTEP drawing (50% probability for thermal ellipsoids) of **3c**.



**Table 1 Crystal data and structure refinement for 3c.**

Identification code	<b>3c</b>
Empirical formula	C <sub>11</sub> H <sub>9</sub> NO <sub>3</sub> S <sub>2</sub>
Formula weight	267.31
Temperature/K	260.00
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	10.3474(8)
b/Å	14.3530(10)
c/Å	8.1480(6)
α/°	90
β/°	99.271(4)
γ/°	90
Volume/Å <sup>3</sup>	1194.30(15)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.487
μ/mm <sup>-1</sup>	2.650
F(000)	552.0
Crystal size/mm <sup>3</sup>	0.2 × 0.15 × 0.12
Radiation	GaKα (λ = 1.34139)
2θ range for data collection/°	7.532 to 114.212
Index ranges	-10 ≤ h ≤ 12, -17 ≤ k ≤ 17, -10 ≤ l ≤ 9
Reflections collected	17614
Independent reflections	2442 [R <sub>int</sub> = 0.0516, R <sub>sigma</sub> = 0.0305]

Data/restraints/parameters	2442/1/155
Goodness-of-fit on F <sup>2</sup>	1.139
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0515, wR <sub>2</sub> = 0.1218
Final R indexes [all data]	R <sub>1</sub> = 0.0685, wR <sub>2</sub> = 0.1335
Largest diff. peak/hole / e Å <sup>-3</sup>	0.46/-0.51

**Table 2 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 3c.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{ij}$  tensor.**

Atom	x	y	z	U(eq)
S1	2146.4(6)	3761.1(4)	3958.8(7)	45.0(2)
S2	-651.8(6)	3787.4(4)	3861.0(8)	48.9(2)
O1	1101.8(14)	3746.8(9)	6636.4(18)	38.5(4)
O2	3640.4(15)	2114.1(11)	5800(2)	53.2(4)
O3	3756.4(17)	5308.8(10)	5953(2)	53.2(4)
N1	3449.2(17)	3720.1(11)	5489(2)	38.7(4)
C5	5113(2)	3180.1(14)	7488(3)	36.5(5)
C10	5130(2)	4151.2(14)	7575(3)	37.2(5)
C11	4070(2)	4512.6(15)	6298(3)	38.5(5)
C3	796(2)	3763.9(12)	5000(3)	35.6(5)
C4	4018(2)	2885.6(14)	6209(3)	38.4(5)
C6	6015(2)	2648.9(16)	8533(3)	46.3(5)
C9	6028(2)	4622.2(17)	8714(3)	46.5(6)
C1	617(3)	3794.6(16)	9388(3)	50.8(6)
C7	6916(2)	3123.2(19)	9682(3)	53.6(6)
C2	23(2)	3722.6(14)	7602(3)	45.5(6)
C8	6916(2)	4087.6(19)	9786(3)	54.8(6)

**Table 3 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 3c. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\dots]$ .**

Atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
S1	38.9(3)	56.2(4)	39.7(3)	0.8(2)	5.5(2)	2.6(2)
S2	36.5(3)	53.0(4)	51.8(4)	0.0(2)	-9.3(3)	1.7(2)
O1	29.1(8)	46.4(9)	39.2(8)	4.6(6)	3.2(6)	2.6(6)
O2	44.9(10)	37.3(9)	76.9(12)	-5.9(8)	8.6(8)	-4.7(7)
O3	52.0(10)	34.0(9)	72.1(11)	6.7(7)	5.6(8)	7.2(7)
N1	31.6(9)	36.8(10)	47.0(11)	2.4(7)	5.0(8)	2.1(7)
C5	31.4(11)	36.8(11)	43.6(11)	3.0(8)	12.6(9)	1.4(8)

**Table 3 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 3c. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$ .**

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C10	34.5(11)	33.6(10)	46.1(12)	1.3(9)	14.2(9)	1.4(8)
C11	34.0(11)	36.5(11)	47.3(12)	1.9(9)	12.8(9)	0.9(9)
C3	33.2(9)	29.3(10)	42.5(11)	1.5(8)	0.5(8)	2.0(8)
C4	32.0(11)	33.8(11)	52.5(13)	-0.1(9)	15.9(10)	0.1(9)
C6	39.4(13)	41.8(12)	59.4(14)	10.7(10)	13.1(11)	7.6(10)
C9	40.1(13)	44.2(13)	54.9(13)	-3.3(10)	7.0(11)	-5.3(10)
C1	47.2(14)	56.9(15)	49.8(13)	-3.7(10)	12.1(11)	3.0(11)
C7	36.7(13)	65.7(17)	57.3(15)	11.8(12)	4.3(11)	8.9(11)
C2	32.6(12)	56.0(15)	48.9(13)	11.4(10)	10.2(10)	2.0(10)
C8	39.9(13)	67.1(17)	55.5(14)	-2.0(12)	2.3(11)	-3.3(12)

**Table 4 Bond Lengths for 3c.**

Atom	Atom	Length/ $\text{\AA}$	Atom	Atom	Length/ $\text{\AA}$
S1	N1	1.6832(19)	C5	C10	1.396(3)
S1	C3	1.747(2)	C5	C4	1.472(3)
S2	C3	1.631(2)	C5	C6	1.386(3)
O1	C3	1.320(3)	C10	C11	1.479(3)
O1	C2	1.466(3)	C10	C9	1.380(3)
O2	C4	1.204(3)	C6	C7	1.388(4)
O3	C11	1.209(3)	C9	C8	1.392(3)
N1	C11	1.416(3)	C1	C2	1.490(3)
N1	C4	1.419(3)	C7	C8	1.387(4)

**Table 5 Bond Angles for 3c.**

Atom	Atom	Atom	Angle/ $^\circ$	Atom	Atom	Atom	Angle/ $^\circ$
N1	S1	C3	104.36(10)	N1	C11	C10	105.97(17)
C3	O1	C2	117.59(16)	S2	C3	S1	117.18(13)
C11	N1	S1	124.46(14)	O1	C3	S1	114.22(15)
C11	N1	C4	111.00(17)	O1	C3	S2	128.60(17)
C4	N1	S1	124.42(14)	O2	C4	N1	124.5(2)
C10	C5	C4	108.92(19)	O2	C4	C5	129.7(2)
C6	C5	C10	121.1(2)	N1	C4	C5	105.74(17)
C6	C5	C4	129.9(2)	C5	C6	C7	117.2(2)
C5	C10	C11	108.24(19)	C10	C9	C8	117.2(2)



**Table 5 Bond Angles for 3c.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	C10	C5	121.7(2)	C8	C7	C6	121.6(2)
C9	C10	C11	130.1(2)	O1	C2	C1	107.00(18)
O3	C11	N1	124.5(2)	C7	C8	C9	121.2(2)
O3	C11	C10	129.5(2)				

**Table 6 Torsion Angles for 3c.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C11	O3	-2.0(3)	C3	S1	N1	C11	-87.84(18)
S1	N1	C11	C10	178.34(14)	C3	S1	N1	C4	87.98(18)
S1	N1	C4	O2	0.6(3)	C3	O1	C2	C1	-174.93(16)
S1	N1	C4	C5	-179.62(13)	C4	N1	C11	O3	-178.30(19)
N1	S1	C3	S2	-179.23(10)	C4	N1	C11	C10	2.0(2)
N1	S1	C3	O1	0.81(16)	C4	C5	C10	C11	-2.2(2)
C5	C10	C11	O3	-179.5(2)	C4	C5	C10	C9	177.61(19)
C5	C10	C11	N1	0.2(2)	C4	C5	C6	C7	-177.2(2)
C5	C10	C9	C8	-0.3(3)	C6	C5	C10	C11	179.18(19)
C5	C6	C7	C8	0.0(3)	C6	C5	C10	C9	-1.0(3)
C10	C5	C4	O2	-176.9(2)	C6	C5	C4	O2	1.6(4)
C10	C5	C4	N1	3.4(2)	C6	C5	C4	N1	-178.2(2)
C10	C5	C6	C7	1.2(3)	C6	C7	C8	C9	-1.3(4)
C10	C9	C8	C7	1.5(3)	C9	C10	C11	O3	0.7(4)
C11	N1	C4	O2	176.9(2)	C9	C10	C11	N1	-179.6(2)
C11	N1	C4	C5	-3.3(2)	C2	O1	C3	S1	-178.40(13)
C11	C10	C9	C8	179.5(2)	C2	O1	C3	S2	1.7(2)

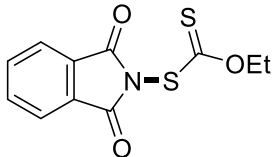
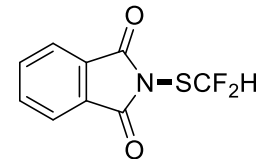
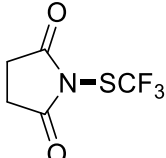
**Table 7 Hydrogen Atom Coordinates ( $\text{\AA} \times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 3c.**

Atom	x	y	z	U(eq)
H6	6017.41	2002.06	8466.23	56
H9	6038.54	5269.52	8764.58	56
H1A	1272.39	3320.56	9649.48	76
H1B	-50.57	3712.73	10068.1	76
H1C	1012.52	4397.02	9597.52	76
H7	7533.25	2785.85	10400.45	64
H2A	-463.12	3144.92	7398.39	55

**Table 7 Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for 3c.**

Atom	x	y	z	U(eq)
H2B	-571.77	4238.49	7290.27	55
H8	7521.76	4382.52	10586.16	66

**Table 8 X-ray Crystallographic Analysis of 3c and Previously Well-Known *N*-Difluoromethylthiophthalimide and *N*-Trifluoromethylthio succinimide.**

Chemical structure	Deposition number	Bond length ( $\text{\AA}$ )	Bond angle ( $^\circ$ )
	CCDC 2250745	1.683	N(1)-S(1)-C(3), 104.36
	CCDC 214330	1.681	N(1)-S(1)-C(9), 98.57
	CCDC 214110	1.676	N(1)-S(1)-C(5), 99.01