

## Supporting Information

# An Ambient Temperature Newman-Kwart Rearrangement Mediated by Organic Photoredox Catalysis

Andrew J. Perkowski, Cole L. Cruz, and David A. Nicewicz\*

*Department of Chemistry, University of North Carolina at Chapel Hill, New Venable Laboratories, Chapel Hill, NC 27599-3290, USA*

*E-mail: nicewicz@unc.edu*

### Table of Contents

I.	General Information.....	S2
II.	Synthesis and Characterization of Catalyst and Substrates.....	S3-S10
III.	Methods for Cation Radical Accelerated Newman-Kwart Rearrangement and Analytical Data for Rearranged Products.....	S11-S16
IV.	Large Scale Flow Synthesis of <i>S</i> -(2,4,6-trimethylphenyl) dimethylcarbamothioate.....	S17
V.	Additional Kinetic Data.....	S18
VI.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra.....	S19-S64
VII.	References.....	S65

## I. General Information

**Methods and Materials:** Proton and carbon magnetic resonance spectra ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) were recorded on a Bruker AVANCE III 600 CryoProbe ( $^1\text{H}$  NMR at 400 MHz, 600 MHz and  $^{13}\text{C}$  NMR at 100, 150 MHz) spectrometer with solvent resonance as the internal standard ( $^1\text{H}$  NMR:  $\text{CDCl}_3$  at 7.26 ppm;  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  at 77.0 ppm).  $^1\text{H}$  NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet, br = broad singlet, bm = broad multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. High Resolution Mass Spectra (HRMS) were obtained using a Thermo LTqFT mass spectrometer with electrospray ionization in positive or negative mode. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63  $\mu\text{m}$ ) purchased from Silicycle. All solvents were dried by passage over activated alumina columns immediately prior to use unless otherwise noted. Irradiation of photochemical reactions was carried out using three 15W PAR38 blue LED floodlamp purchased from EagleLight (Carlsbad, CA) with an output centered at a wavelength of approximately 450 nm. The reactions were carried out in 2 dram borosilicate glass vials (purchased from Fisher Scientific, catalogue # 03-339-22D) sealed with polypropylene caps equipped with Teflon coated septa (purchased through VWR international, Microliter Product # 15-0060K), or in 16mm x 150mm glass culture tubes sealed with rubber septa if reaction volume was greater than 7 mL. All reagents were purchased from Sigma-Aldrich, Fisher Scientific, or TCI corporation and were used without additional purification unless otherwise noted.

### Reaction Monitoring using *in situ* IR Spectroscopy

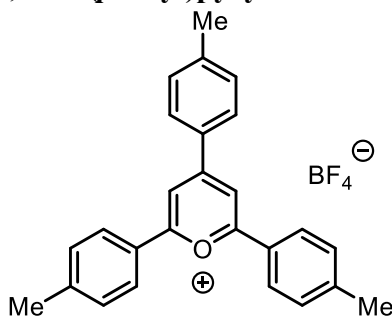
In-situ monitoring of the reaction was performed using a Mettler-Toledo ReactIR<sup>TM</sup> 15 instrument equipped with a 6.3 mm AgX Sicamp Fiber Conduit. Plots were generated from absorbance at  $1670\text{ cm}^{-1}$  (corresponding to  $\pi_{\text{C-O}}$  stretching frequency of the rearranged product) over the course of the reaction. The reactions were setup in flame dried Schlenk tubes and irradiated with two 15W PAR38 blue LED floodlamps purchased from EagleLight (Carlsbad, CA).

### Measurement of Redox Potentials via Cyclic Voltammetry

Electrochemical potentials were obtained by collecting cyclic voltammograms with a Pine WaveNow Potentiostat. Samples were prepared with 0.05 mmol of substrate in 5 mL of 0.1 M tetra-*n*-butylammonium hexafluorophosphate in dry, degassed acetonitrile. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction; the glassy carbon electrode was polished between each scan. Data was analyzed using MATLAB by subtracting a background current prior to identifying the maximum current ( $C_p$ ) and determining the potential ( $E_{p/2}$ ) at half this value ( $C_{p/2}$ ). The obtained value was referenced to Ag|AgCl and converted to SCE by subtracting 0.03 V.

## II. Synthesis and Characterization of Catalyst and Substrates

### Preparation of 2,4,6-Tri(*p*-tolyl)pyrylium Tetrafluoroborate Salt



2,4,6-tri(*p*-tolyl)pyrylium tetrafluoroborate  
**1**

2,4,6-Tri(*p*-tolyl)pyrylium tetrafluoroborate (**1**) was synthesized according to literature procedures in an isolated yield of 2.5 g (31% yield relative to starting *p*-tolualdehyde). The product was recrystallized from hot acetic acid. Residual acetic acid was removed by taking up the resulting crystals in a minimum amount of dichloromethane (~200 mL), and precipitating the material from diethyl ether (~800 mL). The resulting precipitate was collected via filtration and dried under high vacuum. The analytical data matched that reported in the literature.<sup>1</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.43 (s, 2H), 8.27 – 8.22 (m, 4H), 8.22 – 8.16 (m, 2H), 7.55 – 7.48 (m, 4H), 7.23 – 7.17 (m, 2H), 2.48 (s, 6H), 2.15 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 169.40, 164.46, 147.10, 147.09, 131.13, 131.01, 130.04, 129.09, 128.42, 125.76, 112.77, 22.03, 21.72.

### Synthesis of *O*-aryl dimethylcarbamothioate substrates

#### Method A (adapted from literature procedure<sup>2</sup>)

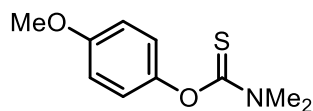
A 100 mL round-bottom flask was equipped with a Teflon coated stir bar and flame dried and allowed to cool under N<sub>2</sub> atmosphere. The flask was then charged with dimethylthiocarbamoyl chloride (1.5 equiv) and anhydrous dimethylformamide (DMF) to create a 0.75 M solution of the chloride. The phenol and 1,4 Diazabicyclo[2.2.2]-octane (DABCO, 1.5 equiv) were added sequentially and the solution was sealed, placed under an atmosphere of N<sub>2</sub> and allowed to stir at ambient temperature for 16 hours. Then, the flask was placed in a 0 °C bath and the resulting suspension was diluted with 25 mL water. Workup and purification was then achieved in one of two ways.

- I) If addition of water resulted in formation of a precipitate, the precipitate could be collected *via* vacuum filtration and washed with water affording the crude phenyl-*O*-dimethyl carbamothioate. The crude product could be recrystallized from either ethanol (EtOH) or EtOH/water solvent systems to afford the pure carbamothioate product.
- II) If addition of water did not result in formation of a precipitate, then the solution was transferred to a separatory funnel and extracted with ethyl acetate (3x). The

combined organics were then washed 4-5 times with a saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The resulting residue was then purified by column chromatography using a hexanes/ethyl acetate eluent. In some cases, residual phenol starting material co-eluted with the product carbamothioate. The phenol could be removed by dissolving the sample in Et<sub>2</sub>O and washing (3x) with a 0.3 M NaOH solution. The organic layer could then be concentrated under reduced pressure to afford the pure carbamothioate.

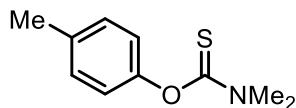
**Method B** (adapted from literature procedure<sup>3</sup>)

A clean, dry, 100 mL round-bottom flask (rbf) equipped with a teflon coated stir bar was purged with nitrogen and then charged with 1.06 g (26.4 mmol, 1.2 equiv.) of sodium hydride (60% dispersion in mineral oil). A syringe was then used to wash the sodium hydride with petroleum ether (20 to 30 mL of petroleum ether in four to six portions) to remove the mineral oil. Then, 10 mL of anhydrous DMF was added to the rbf via syringe under positive nitrogen pressure and allowed to stir. Then, the relevant phenol (22 mmol, 1.0 equiv.), dissolved in 12 mL of anhydrous DMF, was added dropwise to the sodium hydride suspension. Addition was carried out slowly over the course of 3 to 5 minutes. After addition was complete, 3.26 g (26.4 mmol, 1.2 equiv.) of dimethylthiocarbamoyl chloride was added in a single portion. The rbf was then heated in an oil bath to 80 °C with stirring for one to three hours. The rbf was allowed to cool to room temperature, and then transferred to a 1 L separatory funnel containing 200 mL of diethyl ether. The rbf was rinsed with approximately 50 mL of diethyl ether and 50 mL of deionized water. The organic layer was then washed with three 100 mL portions of water, followed by four 50 mL portions of water. The diethyl ether was transferred to a 500 mL Erlenmeyer flask and dried using anhydrous magnesium sulfate, filtered via filter paper, and the solvent removed under reduced pressure, giving either a yellow oil or, sometimes, a yellowish-white solid. All oils were purified by flash chromatography using hexanes/ethyl acetate as eluent. Some solids were amenable to purification via recrystallization from ethanol or ethanol/water, though most were also purified via flash chromatography.



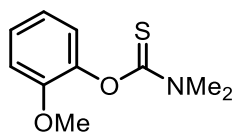
Analytical data for **O-(4-methoxyphenyl) dimethylcarbamothioate (2a)**: Synthesized by **Method B** from 4-methoxyphenol. Purified via recrystallization from 19:1 hexanes/diethyl ether to give 12.6 g (60% yield) of a white crystalline solid. Analytical data were in agreement with previous literature reports.<sup>4</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.01 – 6.94 (m, 2H), 6.93 – 6.87 (m, 2H), 3.81 (s, 3H), 3.46 (s, 3H), 3.34 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 188.5, 157.4, 147.7, 123.6, 114.3, 55.7, 43.6, 38.8



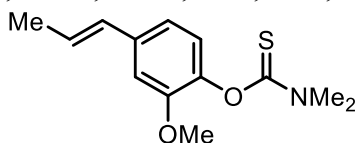
**O-(4-methylphenyl) dimethylcarbamothioate (2b):** Synthesized by **Method A** from 4-methylphenol (p-Cresol) in 31% yield. Analytical data were in agreement with previous literature reports.<sup>4</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.21 – 7.16 (m, 2H), 6.97 – 6.92 (m, 2H), 3.46 (s, 3H), 3.34 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 188.2, 151.9, 135.7, 129.9, 122.5, 43.4, 38.8, 21.1



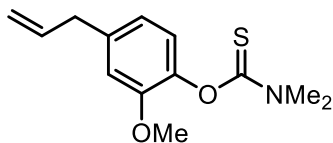
**O-(2-methoxyphenyl) dimethylcarbamothioate (2d):** Synthesized by **Method A** from 2-Methoxyphenol (Guaiacol) in 43% yield. Analytical data were in agreement with previous literature reports.<sup>5</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.23 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.00 – 6.95 (m, 2H), 3.83 (s, 3H), 3.47 (s, 3H), 3.36 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 188.0, 151.7, 143.0, 127.1, 124.2, 120.7, 112.7, 56.1, 43.5, 38.9



**O-(2-methoxy-4-propenylphenyl) dimethylcarbamothioate (2e):** Synthesized by **Method A** from (E)-2-methoxy-4-(prop-1-en-1-yl)phenol (Isoeugenol) in 74% yield. Isolated as a >19:1 mix of *E* : *Z* isomers. NMR shifts are reported for the *E* isomer unless otherwise noted.

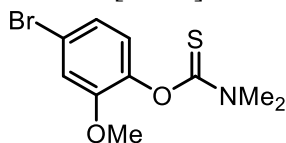
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 6.98 – 6.88 (m, 3H), 6.37 (dq, *J* = 15.6, 1.7 Hz, 1H), 6.19 (dq, *J* = 15.7, 6.6 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 3H), 3.35 (s, 3H), 1.87 (dd, *J* = 6.6, 1.7 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 188.1, 151.5, 141.8, 137.1, 130.7, 129.6 (*Z*), 127.1 (*Z*), 126.1, 123.9, 123.7 (*Z*), 121.2 (*Z*), 118.3, 113.3 (*Z*), 109.9, 56.0, 43.5, 38.9, 18.6; IR (thin film): 2936, 1598, 1536, 1506, 1464, 1394, 1289, 1263, 1205, 1134, 1033 cm<sup>-1</sup>; HRMS (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 252.1058; found: 252.1051



**O-(4-allyl-2-methoxyphenyl) dimethylcarbamothioate (2f):** Synthesized by **Method A** from 4-allyl-2-methoxyphenol (Eugenol) in 63% yield.

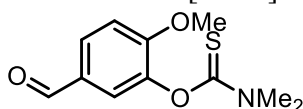
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 6.95 (d, *J* = 8.6 Hz, 1H), 6.79 (d, *J* = 6.7 Hz, 2H), 6.03 – 5.93 (m, 1H), 5.14 – 5.07 (m, 2H), 3.81 (s, 3H), 3.46 (s, 3H), 3.40 (d, *J* = 6.7 Hz, 2H), 3.35 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 188.1, 151.3, 141.2, 139.0, 137.1, 123.7, 120.6, 116.3, 113.0,

56.0, 43.5, 40.2, 38.8; **IR** (thin film): 2937, 1638, 1603, 1508, 1463, 1394, 1288, 1204, 1133, 1033  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 252.1058; found: 252.1050



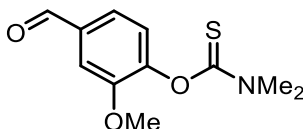
**O-(4-bromo-2-methoxyphenyl) dimethylcarbamothioate (2g)**: Synthesized by **Method A** from 4-bromo-2-methoxyphenol in 47% yield.

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.09 (d,  $J = 7.1$  Hz, 2H), 6.93 – 6.88 (m, 1H), 3.82 (s, 3H), 3.45 (s, 3H), 3.34 (s, 3H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.4, 152.3, 142.1, 125.4, 123.6, 119.6, 116.2, 56.3, 43.6, 38.9; **IR** (thin film): 2939, 1540, 1495, 1395, 1287, 1259, 1200, 1175, 1119, 1024, 863  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 289.9850; found: 289.9843



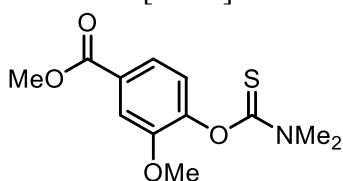
**O-(3-formyl-2-methoxyphenyl) dimethylcarbamothioate (2h)**: Synthesized by **Method A** from 3-hydroxy-4-methoxybenzaldehyde (Isovanillin) in 75% yield.

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.88 (s, 1H), 7.79 (d,  $J = 8.4$  Hz, 1H), 7.57 (s, 1H), 7.08 (d,  $J = 8.3$  Hz, 1H), 3.91 (s, 3H), 3.46 (s, 3H), 3.37 (s, 3H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.3, 187.2, 156.9, 143.3, 130.0, 129.8, 125.0, 112.3, 56.4, 43.6, 38.9; **IR** (thin film): 2939, 1687, 1605, 1509, 1438, 1395, 1287, 1195, 1132, 1008  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 240.0694; found: 240.0687



**O-(4-formyl-2-methoxyphenyl) dimethylcarbamothioate (2i)**: Synthesized by **Method A** from 4-hydroxy-3-methoxybenzaldehyde (Vanillin) in 76% yield.

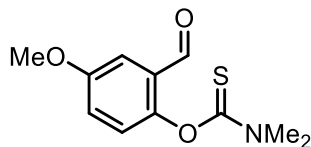
**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.96 (s, 1H), 7.51 (m, 2H), 7.23 (d,  $J = 8.4$  Hz, 1H), 3.90 (s, 3H), 3.47 (s, 3H), 3.38 (s, 3H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.2, 186.9, 152.5, 147.8, 135.2, 124.8, 124.7, 111.0, 56.2, 43.5, 39.0; **IR** (thin film): 1690, 1536, 1506, 1377, 1288, 1205, 1158, 1024  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 240.0694; found: 240.0688



**methyl 4-((dimethylcarbamothioyl)oxy)-3-methoxybenzoate (2j)**: Synthesized by **Method A** from methyl 4-hydroxy-3-methoxybenzoate (methyl vanillate) in 34% yield.

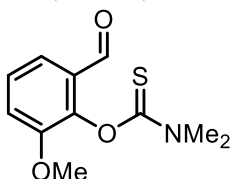
**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (d,  $J = 8.2$  Hz, 1H), 7.66 (s, 1H), 7.10 (d,  $J = 8.2$  Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.46 (s, 3H), 3.37 (s, 3H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.1, 166.5, 151.6, 146.6, 128.8, 124.1, 122.5, 113.7, 56.2, 52.4, 43.5, 38.9; **IR** (thin film): 2748,

1720, 1604, 1536, 1507, 1433, 1396, 1291, 1244, 1201, 1175, 1120, 1030  $\text{cm}^{-1}$ ; **HRMS (+ESI)**:  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 270.0800; found: 270.0794



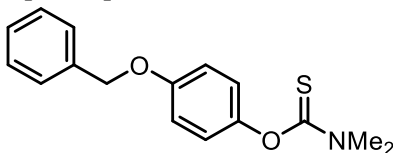
**O-(2-formyl-4-methoxyphenyl) dimethylcarbamothioate (2k)**: Synthesized by **Method A**, with heating at 60 °C, from 2-hydroxy-5-methoxybenzaldehyde in 35% yield. Analytical data were in agreement with previous literature reports.<sup>6</sup>

**<sup>1</sup>H NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.02 (s, 1H), 7.38 (d,  $J = 3.2$  Hz, 1H), 7.17 (dd,  $J = 8.9, 3.2$  Hz, 1H), 7.04 (d,  $J = 8.9$  Hz, 1H), 3.86 (s, 3H), 3.47 (s, 3H), 3.42 (s, 3H); **<sup>13</sup>C NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.3, 187.9, 157.7, 149.7, 129.6, 125.5, 122.1, 111.4, 55.9, 43.6, 39.0



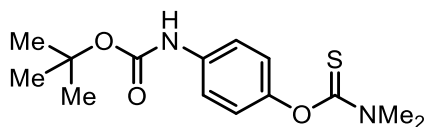
**O-(2-formyl-6-methoxyphenyl) dimethylcarbamothioate (2l)**: Synthesized by **Method A**, with heating at 60 °C, from 2-hydroxy-3-methoxybenzaldehyde in 35% yield. Analytical data were in agreement with previous literature reports.<sup>6</sup>

**<sup>1</sup>H NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.09 (d,  $J = 0.7$  Hz, 1H), 7.50 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.34 (td,  $J = 8.0, 0.7$  Hz, 1H), 7.21 (dd,  $J = 8.2, 1.5$  Hz, 1H), 3.87 (s, 3H), 3.48 (s, 3H), 3.43 (s, 3H); **<sup>13</sup>C NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.97, 188.95, 187.3, 152.1, 145.1, 130.4, 126.8, 120.1, 117.9, 56.5, 43.7, 39.1 **IR** (thin film): 1697, 1584, 1541, 1483, 1394, 1274, 1250, 1179, 1116  $\text{cm}^{-1}$ ; **HRMS (+ESI)**:  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 240.0694; found: 240.0685



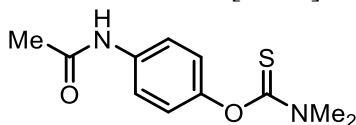
**O-(4-benzyloxyphenyl) dimethylcarbamothioate (2m)**: Synthesized by **Method A** from 4-(Benzyloxy)phenol in 67% yield.

**<sup>1</sup>H NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.33 (t,  $J = 7.3$  Hz, 1H), 6.98 (s, 2H), 5.05 (s, 1H), 3.46 (s, 2H), 3.34 (s, 2H); **<sup>13</sup>C NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.4, 156.6, 147.9, 136.9, 128.7, 128.1, 127.7, 123.6, 115.1, 70.4, 43.6, 38.8; **IR** (thin film): 2936, 2360, 1534, 1502, 1393, 1287, 1195, 1132, 1008  $\text{cm}^{-1}$ ; **LRMS (+ESI)**:  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 288.1058; found: 288.1049



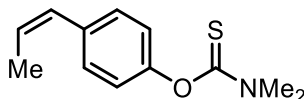
**tert-butyl(4-((dimethylcarbamothioyl)oxy)phenyl)carbamate (2n)**: Synthesized by **Method B** from tert-butyl (4-hydroxyphenyl)carbamate. Purified by recrystallization from ethanol/water (~9:1) to give 2.52 g (84% yield) of a white crystalline solid.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.38 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.47 (s, 1H), 3.45 (s, 3H), 3.33 (s, 3H), 1.51 (s, 9H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 170.5, 135.9, 134.5, 129.3, 129.0, 71.5, 41.8, 21.3, 21.0, 19.4; **IR** (thin film): 2360, 1642, 1529, 1393, 1287, 1204, 1159, 1053 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 297.1273; found: 297.1266



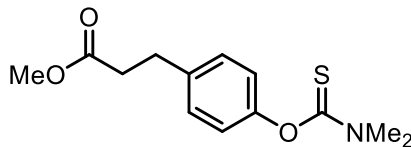
***O*-(4-acetamidophenyl) dimethylcarbamothioate (2o)**: Synthesized by **Method A** from *N*-(4-hydroxyphenyl)acetamide (Acetaminophen) in 62% yield.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.21 (br, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.45 (s, 3H), 3.34 (s, 3H), 2.17 (s, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): 188.0, 168.3, 150.2, 135.8, 123.2, 120.7, 43.4, 38.9, 24.7; **IR** (thin film): 1667, 1536, 1504, 1395, 1286, 1201 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 239.0854; found: 239.0848



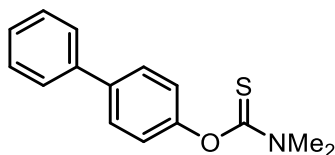
***O*-(4-propenylphenyl) dimethylcarbamothioate (2p)**: Synthesized by **Method A** from 4-(prop-1-en-1-yl)phenol as a 9 : 1 mixture of *Z* : *E* isomers. 4-(prop-1-en-1-yl)phenol was prepared according to a published literature procedure. The analytical data matched that reported in the literature.<sup>7</sup>

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.32 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.41 (d, *J* = 11.6 Hz, 1H), 5.90 – 5.72 (m, 1H), 3.46 (s, 2H), 3.35 (s, 2H), 1.91 (d, *J* = 7.2 Hz, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 187.9, 187.8, 152.8, 152.4, 135.9, 135.4, 130.2, 129.8, 129.6, 129.4, 129.1, 127.0, 126.5, 126.0, 122.8, 122.4, 43.3, 38.84, 18.6, 14.7; **IR** (thin film): 2938, 1643, 1531, 1504, 1393, 1286, 1208, 1168, 1130, 1014, 845 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 222.0952; found: 222.0946



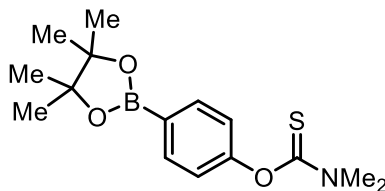
**methyl 3-(4-((dimethylcarbamothioyl)oxy)phenyl)propanoate (2q)**: Synthesized by **Method A** with heating at 60 °C from methyl 3-(4-hydroxyphenyl)propanoate in 76% yield. 3-(4-hydroxyphenyl)propanoate was prepared according to a published literature procedure. The analytical data matched that reported in the literature.<sup>8</sup>

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.22 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 2H), 3.45 (s, 2H), 3.33 (s, 2H), 2.96 (t, *J* = 7.9 Hz, 1H), 2.81 – 2.61 (m, 1H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 187.9, 173.4, 152.5, 138.2, 129.1, 122.8, 51.8, 43.4, 38.8, 35.6, 30.5; **IR** (thin film): 2938, 1737, 1537, 1506, 1395, 1288, 1213, 1170, 1017 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 268.1007; found: 268.0998



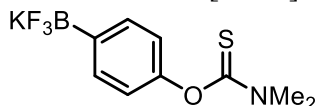
**O-([1,1'-biphenyl]-4-yl) dimethylcarbamothioate (2r):** Synthesized by **Method A** from 4-phenylphenol in 73% yield.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64 – 7.54 (m, 4H), 7.43 (dd,  $J = 8.4, 7.1$  Hz, 2H), 7.37 – 7.31 (m, 1H), 7.16 – 7.12 (m, 2H), 3.48 (d,  $J = 1.1$  Hz, 3H), 3.37 (d,  $J = 1.0$  Hz, 3H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.8, 153.5, 140.4, 139.0, 128.8, 127.4, 127.4, 127.2, 123.1, 43.4, 38.9; **IR** (thin film): 1646, 1509, 1484, 1394, 1287, 1209, 1132, 1007, 765  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 258.0952; found: 258.0944



**O-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) dimethylcarbamothioate (2w):** Synthesized by **Method B** from 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol in a 43% yield.

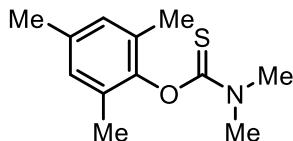
$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 – 7.82 (m, 2H), 7.10 – 7.04 (m, 2H), 3.45 (s, 3H), 3.35 (s, 3H), 1.33 (s, 12H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.61, 156.46, 135.98, 122.19, 83.87, 43.25, 38.78, 24.88; **IR** (thin film): 2977, 1600, 1536, 1397, 1358, 1323, 1286, 1206, 1141, 1085, 1016  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 308.1492; found: 308.1482



**O-(4-(trifluoro- $\lambda^4$ -boranyl)phenyl) dimethylcarbamothioate, potassium salt (2s):**

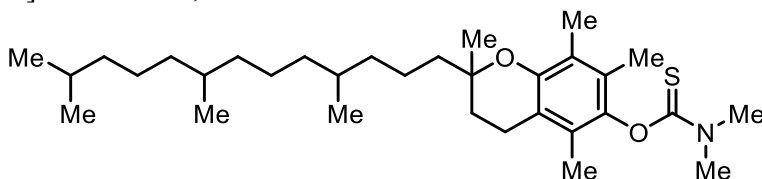
Synthesized by an adapted procedure<sup>9</sup> from O-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) dimethylcarbamothioate (**2w**). To a 20 mL scintillation vial was added 1.0 g of **2w**, 1.0g  $\text{KHF}_2$  (4.0 equiv), 2 mL  $\text{H}_2\text{O}$  and 13 mL MeOH. The vial was equipped with a Teflon coated stir bar, sealed and allowed to stir at r.t. overnight. After, the solution was concentrated and the resulting residue washed with acetone (10 mL x 3). Each wash was collected and filtered through a cotton plug and the combined organics were then concentrated. The solid was then dissolved in 5 mL acetone and then  $\text{Et}_2\text{O}$  was added until further addition yielded no additional precipitate. The white precipitate was collected by vacuum filtration and dried to afford **2s** as a white powder (560 mg, 59%).

$^1\text{H NMR}$  (600 MHz,  $\text{DMSO-d}_6$ ): 7.29 (d,  $J = 8.1$  Hz, 2H), 6.73 (d,  $J = 7.8$  Hz, 2H), 3.34 (s, 3H), 3.28 (s, 3H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  187.1, 151.8, 131.7, 120.2, 42.7, 38.3;  $^{19}\text{F NMR}$  (376 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  -138 **IR** (thin film): 1543, 1501, 1395, 1284, 1211, 1149, 983  $\text{cm}^{-1}$ ; **HRMS** (-ESI):  $m/z$  calculated for  $[\text{M}]^-$ : 248.0528; found: 248.0531



***O*-(2,4,6-trimethylphenyl) dimethylcarbamothioate (2t):** Synthesized by **Method B** from 2,4,6-trimethylphenol in six batches. Each batch was purified by flash chromatography (19:1 hexanes/ethyl acetate) on average giving 4.30 g (86% yield) of a white crystalline solid.

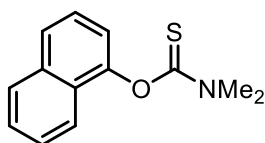
$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.88 (s, 2H), 3.48 (s, 3H), 3.37 (s, 3H), 2.28 (s, 3H), 2.13 (s, 6H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  186.65, 149.0, 135.4, 130.4, 129.3, 43.4, 38.5, 21.0, 16.6; **IR** (thin film): 2924, 2856, 1529, 1482, 1393, 1288, 1196, 1141  $\text{cm}^{-1}$ ; **HRMS (+ESI):**  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 224.1109; found: 224.1102



**(±)-*O*-(2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)**

**dimethylcarbamothioate (2u):** Synthesized by **Method B** from (±)-alpha tocopherol. Purified by flash chromatography (19:1 hexanes/ethyl acetate) giving 4.79 g (94% yield) of a viscous, clear, slightly yellow oil.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.49 (s, 3H), 3.37 (s, 3H), 3.37 (s, 3H), 2.60-2.52 (m, 2H), 2.11 (d, 3H), 2.03 (s, 3H), 1.99 (d, 3H), 1.90-1.68 (m, 2H), 1.65-1.00 (m, 23H), 0.90-0.80 (m, 12H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  187.41, 149.36, 149.28, 143.69, 143.64, 127.40, 125.68, 125.66, 122.91, 122.83, 117.18, 117.11, 74.97, 43.28, 41.39, 41.36, 39.34, 39.06, 38.95, 38.33, 37.53, 37.48, 37.44, 37.42, 37.40, 37.37, 37.35, 37.33, 37.28, 37.27, 37.24, 34.64, 34.51, 32.78, 32.76, 32.75, 32.72, 32.69, 32.66, 32.64, 32.63, 31.58, 31.15, 31.08, 30.66, 30.63, 27.96, 26.89, 25.25, 24.81, 24.80, 24.76, 24.75, 24.44, 24.41, 23.13, 23.10, 22.72, 22.65, 22.62, 21.10, 21.08, 21.06, 20.97, 20.95, 20.69, 20.59, 20.55, 19.75, 19.73, 19.69, 19.68, 19.66, 19.63, 19.61, 19.59, 19.57, 14.13, 13.18, 12.33, 11.91, 11.90. **IR** (thin film): 2924, 2856, 1529, 1482, 1393, 1288, 1196, 1141  $\text{cm}^{-1}$ ; **HRMS (+ESI):**  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 518.4031; found: 518.4016



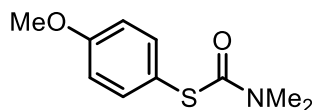
***O*-(1-naphthyl) dimethylcarbamothioate (2v):** Synthesized by **Method A** from 1-Naphthol. Purified by flash chromatography (19:1 hexanes/ethyl acetate) to give 4.10 g (68% yield) of a white crystalline solid.

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.91 – 7.85 (m, 1H), 7.83 – 7.79 (m, 1H), 7.79 – 7.74 (m, 1H), 7.54 – 7.45 (m, 3H), 7.22 (dd,  $J = 7.5, 1.0$  Hz, 1H), 3.53 (s, 3H), 3.51 (s, 3H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.0, 150.0, 134.6, 128.2, 127.5, 126.5, 126.4, 126.2, 125.4, 121.6, 119.6, 43.5, 38.9; **IR** (thin film): 2930, 1598, 1531, 1389, 1286, 1256, 1130, 1013, 799  $\text{cm}^{-1}$ ; **HRMS (+ESI):**  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 232.0796; found: 232.0788

### III. Methods for Cation Radical Accelerated Newman-Kwart Rearrangement and Analytical Data for Rearranged Products

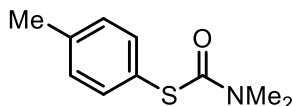
#### Example Method for Cation Radical Accelerate Newman-Kwart Rearrangement

A 2 dram vial equipped with a Teflon coated stir bar was charged with 2.1 mg (0.0047 mmol, 0.01 equiv.) of 2,4,6-tri(p-tolyl)pyrylium tetrafluoroborate and 100 mg (0.47 mmol, 1.0 equiv.) of *O*-(4-methoxyphenyl) dimethylcarbamothioate. The vial was sealed with a Teflon coated septum cap. Next, 1.0 mL of anhydrous acetonitrile (0.5 M with respect to substrate) was added to the vial via syringe. The solution was then sparged with nitrogen gas for 15 minutes (the needle piercings of the septum were covered with a small piece of electrical tape after sparging to minimize solvent loss). The vials were placed on a stir plate and irradiated for 24 hrs. After irradiation, the reaction volume was reduced under vacuum, and the residual solution was loaded onto a silica plug (5 to 7 mL of silica) and eluted with 19:1 (9:1 for more polar products) hexanes/ethyl acetate.



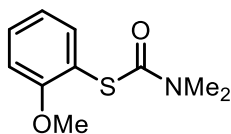
***S*-(4-methoxyphenyl) dimethylcarbamothioate (3a):** Isolated in 95% yield (101 mg), representing an average of two reactions with 106 mg substrate at [0.5 M]. Analytical data were in agreement with previous literature reports.<sup>4</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.39 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.09 (br, 3H), 3.01 (br, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 167.8, 160.6, 137.4, 119.5, 114.7, 55.4, 37.0



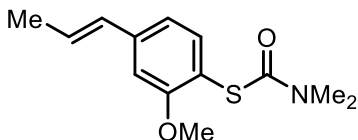
***S*-(4-methylphenyl) dimethylcarbamothioate (3b):** Isolated in 73% yield (73 mg), representing an average of two reactions with 100mg substrate at [0.06 M]. Analytical data were in agreement with previous literature reports.<sup>4</sup>

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.09 (br, 3H), 3.01 (br, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 167.4, 139.5, 135.8, 129.9, 125.2, 37.0, 21.4



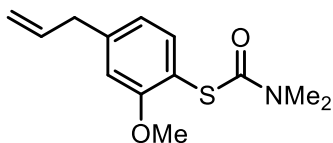
***S*-(2-methoxyphenyl) dimethylcarbamothioate (3d):** Isolated in 79% yield (84 mg), representing an average of two reactions with 106mg substrate at [0.5 M]. Analytical data were in agreement with previous literature reports.<sup>5</sup>

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.46 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.04 – 6.93 (m, 2H), 3.88 (s, 3H), 3.14 (br, 3H), 3.01 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 166.4, 160.2, 138.2, 131.6, 121.1, 116.7, 111.5, 56.2, 37.1, 37.0



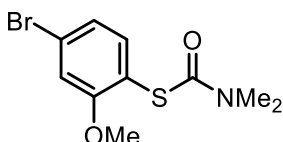
**S-(2-methoxy-4-propenylphenyl) dimethylcarbamothioate (3e)**: Isolated in 99% yield (125 mg), representing an average of two reactions with 126 mg substrate at [0.5 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.36 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 9.4 Hz, 1H), 6.89 (s, 1H), 6.39 (d, *J* = 17.0 Hz, 1H), 6.35 – 6.23 (m, 1H), 3.88 (s, 3H), 3.13 (br, 3H), 3.00 (br, 3H), 1.89 (d, *J* = 8.0 Hz, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 166.6, 160.2, 141.6, 138.2, 130.8, 127.5, 118.8, 114.7, 108.9, 56.1, 37.1, 18.7; **IR** (thin film): 2935, 1667, 1592, 1560, 1463, 1404, 1360, 1289, 1251, 1172, 1096, 1066, 1030 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 252.1058; found: 252.1050



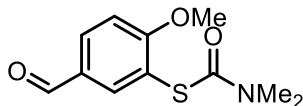
**S-(4-allyl-2-methoxyphenyl) dimethylcarbamothioate (3f)**: Isolated in 97% yield (122 mg), representing an average of two reactions with 126 mg substrate at [0.5 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.36 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 1H), 6.03 – 5.88 (m, 1H), 5.16 – 5.03 (m, 2H), 3.86 (s, 3H), 3.40 (d, *J* = 6.7 Hz, 2H), 3.13 (br, 3H), 3.00 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 166.6, 160.2, 144.2, 138.1, 136.8, 121.4, 116.5, 114.1, 111.9, 56.2, 40.5, 37.0; **IR** (thin film): 2921, 1668, 1595, 1568, 1463, 1405, 1361, 1255, 1169, 1097, 1065, 1032, 909 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 252.1058; found: 252.1050



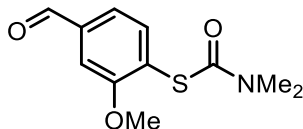
**S-(4-bromo-2-methoxyphenyl) dimethylcarbamothioate (3g)**: Isolated in 96% yield (139 mg), representing an average of two reactions with 145 mg substrate at [0.12 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.31 (d, *J* = 8.1 Hz, 1H), 7.11 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H), 3.86 (s, 3H), 3.12 (br, 3H), 3.00 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 165.7, 160.6, 139.0, 125.3, 124.2, 116.1, 115.2, 56.5, 37.1; **IR** (thin film): 1663, 1576, 1479, 1374, 1254, 1087, 908 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 289.9850; found: 289.9842



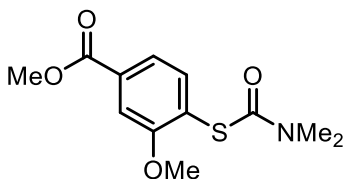
**S-(3-formyl-2-methoxyphenyl) dimethylcarbamothioate (3h)**: Isolated in 89% yield (89 mg), representing an average of two reactions with 100mg substrate at [0.06 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 9.99 (s, 1H) 7.70-7.69 (d, 1H), 7.47-7.46 (d, 1H) 7.45 (s, *J* = 6.6 Hz, *J* = 13.6 Hz, 1H) 3.95 (s, 3H) 3.15 (br, 3H) 3.02 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 190.2, 187.3, 156.9, 143.3, 129.9, 129.9, 125.0, 112.3, 56.4, 43.6, 38.9; **IR** (thin film): 2978.5, 2927.4, 2858.9, 1736.6, 1515.8, 1452.1, 1372.1, 1243.9 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 240.0694; found: 240.0687



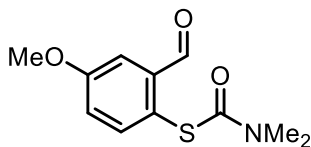
**S-(4-formyl-2-methoxyphenyl) dimethylcarbamothioate (3i)**: Isolated in 95% yield (114 mg), representing an average of two reactions with 120 mg substrate at [0.12 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 9.99 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 9.1 Hz, 1H), 7.45 (s, 1H), 3.95 (s, 3H), 3.15 (br, 3H), 3.02 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 191.80, 191.78, 165.0, 160.3, 138.6, 138.2, 125.1, 123.8, 109.5, 56.5, 37.2, 37.1; **IR** (thin film): 2922, 1693, 1661, 1570, 1484, 1406, 1373, 1290, 1255, 1175, 1096, 1060, 1028, 905 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 240.0694; found: 240.0687



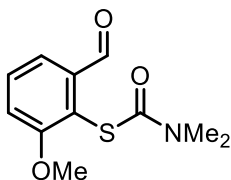
**methyl 4-((dimethylcarbamoyl)thio)-3-methoxybenzoate (3j)**: Isolated in 95% yield (130 mg), representing an average of two reactions with 135 mg substrate at [0.12 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.61 (d, *J* = 1.2 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.14 (br, 3H) 3.01 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 166.7, 165.3, 159.8, 137.7, 132.8, 122.8, 122.0, 112.1, 56.4, 52.5, 37.1; **IR** (thin film): 1720, 1671, 1399, 1290, 1235, 1097 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 270.0800; found: 270.0792



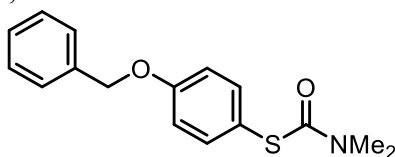
**S-(2-formyl-4-methoxyphenyl) dimethylcarbamothioate (3k)**: Isolated in 56% yield (56 mg), representing an average of two reactions with 100 mg substrate at [0.12 M]. Analytical data were in agreement with previous literature reports.<sup>6</sup>

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 10.33 (s, 1H), 7.54 (d, *J* = 3.0 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.13 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.88 (s, 3H), 3.16 (br, 3H) 3.02 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 191.5, 191.4, 166.0, 161.2, 139.0, 123.5, 121.3, 112.0, 55.8, 37.1



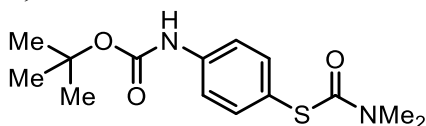
**S-(2-formyl-6-methoxyphenyl) dimethylcarbamothioate (3l):** Isolated in 98% yield (98 mg), representing an average of two reactions with 100 mg substrate at [0.12 M].

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 10.46 (d, *J* = 0.8 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.5, 7.7, 0.8 Hz, 1H), 7.19 (dd, *J* = 8.3, 1.3 Hz, 1H), 3.92 (s, 3H), 3.22 (s, 3H), 3.02 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 191.9, 191.8, 164.9, 160.2, 139.2, 131.2, 120.7, 120.6, 116.3, 56.7, 37.4, 37.3 IR (thin film): 1668, 1574, 1271, 1097 cm<sup>-1</sup>; HRMS (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 240.0694; found: 240.0686



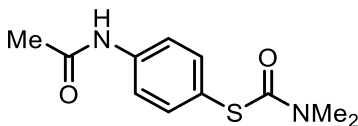
**S-(4-benzyloxyphenyl) dimethylcarbamothioate (3m):** Isolated in 93% yield (134 mg), representing an average of two reactions with 144 mg substrate at [0.12 M].

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.45 – 7.36 (m, 6H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.07 (s, 2H), 3.09 (br, 3H), 3.01 (br, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 167.7, 159.8, 137.4, 136.7, 128.7, 128.2, 127.6, 119.8, 115.6, 70.2, 37.0; IR (thin film): 2924, 1667, 1591, 1572, 1493, 1455, 1403, 1363, 1284, 1242, 1175, 1105, 1089, 1003 cm<sup>-1</sup>; HRMS (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 288.1058; found: 288.1048



**tert-butyl(4-((dimethylcarbamothioyl)thio)phenyl)carbamate (3n):** Isolated in 97% yield (97 mg), representing an average of two reactions with 100mg substrate at [0.12 M] with 5 mol% **1**.

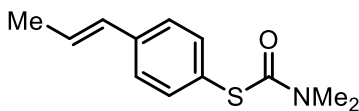
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.38 (s, 4H), 6.58 (s, 1H), 3.05 (d, *J* = 41.8 Hz, 6H), 1.51 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 167.5, 152.5, 139.6, 136.7, 121.9, 118.7, 80.9, 37.0, 28.4; IR (thin film): 2976, 1725, 1650, 1591, 1525, 1399, 1366, 1311, 1235, 1159, 1093 cm<sup>-1</sup>; HRMS (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 297.1273; found: 297.1265



**S-(4-acetamidophenyl) dimethylcarbamothioate (3o):** Isolated in 88% yield (106 mg), representing an average of two reactions with 120 mg substrate at [0.12 M].

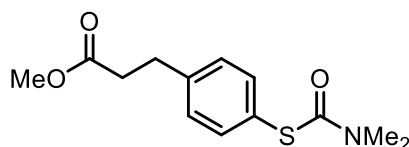
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.87 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.12 (br, 3H), 3.04 (br, 3H), 2.09 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 168.5, 168.1, 168.0, 158.0, 139.5, 136.5, 122.6, 120.3, 120.3, 37.1, 24.6; IR (thin film): 2924, 1644, 1589, 1530,

1399, 1371, 1317, 1248, 1085, 1003  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 239.0854; found: 239.0846



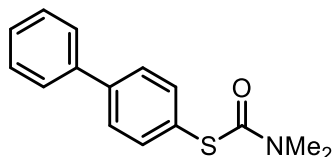
**S-(4-propenylphenyl) dimethylcarbamothioate (3p)**: Isolated in 98% yield (109 mg) as a >19:1 mixture of *E* to *Z* isomers, representing an average of two reactions with 111 mg substrate at [0.12 M].

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J = 8.3$  Hz, 2H), 7.32 (d,  $J = 8.2$  Hz, 2H), 6.39 (d,  $J = 15.8$  Hz, 1H), 6.32 – 6.23 (m, 1H), 3.09 (br, 3H), 3.02 (br, 3H) 1.89 (d,  $J = 6.6$  Hz, 3H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.2, 139.0, 135.9, 130.5, 127.3, 126.6, 37.0, 18.7; **IR** (thin film): 3019, 2934, 1650, 1448, 1402, 1362, 1257, 1088, 961  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 222.0952; found: 222.0945



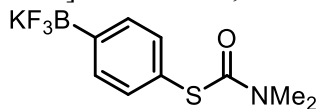
**methyl 3-(4-(dimethylcarbamothioylthio)phenyl)propanoate (3q)**: Isolated in 91% yield (91 mg), representing an average of two reactions with 100 mg substrate at [0.03 M].

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J = 8.1$  Hz, 1H), 7.22 (d,  $J = 8.1$  Hz, 1H), 3.67 (s, 2H), 3.09 (br, 3H), 3.01 (br, 3H), 2.96 (t,  $J = 7.9$  Hz, 1H), 2.66 – 2.60 (m, 1H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.3, 167.2, 141.9, 136.0, 129.1, 126.4, 51.8, 37.0, 35.5, 30.7; **IR** (thin film): 2949, 1737, 1671, 1399, 1290, 1235, 1097  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 268.1007; found: 268.0998



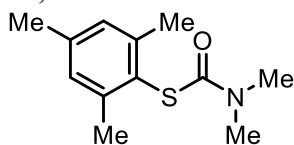
**S-([1,1'-biphenyl]-4-yl) dimethylcarbamothioate (3r)**: Isolated in 96% yield (124 mg), representing an average of two reactions with 129 mg substrate at [0.12 M].

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 – 7.53 (m, 6H), 7.44 (t,  $J = 7.7$  Hz, 2H), 7.36 (t,  $J = 7.4$  Hz, 1H), 3.12 (br, 3H) 3.04 (br, 3H);  **$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.0, 142.2, 140.5, 136.1, 128.9, 127.8, 127.73, 127.3, 123.1, 37.0; **IR** (thin film): 1670, 1478, 1364, 1256, 1040  $\text{cm}^{-1}$ ; **HRMS** (+ESI):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$ : 258.0952; found: 258.0943



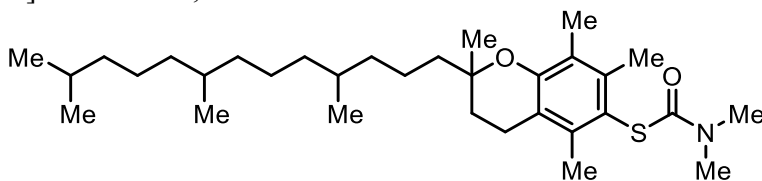
**S-(4-(trifluoro- $\lambda^4$ -boranyl)phenyl) dimethylcarbamothioate, potassium salt (3s)**: Isolated in 80% yield (80 mg), representing an average of two reactions with 100 mg substrate at [0.06 M]. Product was isolated by diluting the reaction mixture with acetone and then precipitating the product by addition of  $\text{Et}_2\text{O}$ .

**<sup>1</sup>H NMR** (600 MHz, DMSO-d<sub>6</sub>): 7.33 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 3.02 (br, 3H), 2.90 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, DMSO-d<sub>6</sub>): δ 166.3, 134.1, 132.3, 124.4, 36.8, 31.1; ; **<sup>19</sup>F NMR** (376 MHz, DMSO-d<sub>6</sub>): δ -139 **IR** (thin film): 1669, 1366, 1202, 1089, 965 cm<sup>-1</sup>; **HRMS** (-ESI): *m/z* calculated for [M]<sup>-</sup>: 248.0528; found: 248.0532



***S*-(2,4,6-trimethylphenyl) dimethylcarbamothioate (3t)**: Isolated in 79% yield (88 mg), representing an average of two reactions with 112 mg substrate at [0.12 M].

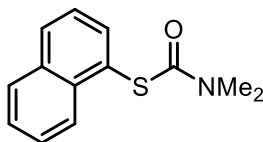
**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 6.96 (s, 2H), 3.16 (br, 3H), 3.08 (br, 3H), 2.37 (s, 6H), 2.27 (s, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 166.4, 143.5, 139.6, 129.2, 124.7, 36.9, 22.0, 21.29; **IR** (thin film): 2921, 1667, 1601, 1458, 1359, 1259, 1096, 1056, 907 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 224.1109; found: 224.1101



**(±)-*S*-(2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)**

**dimethylcarbamothioate (3u)**: Isolated in 99% yield (99 mg), representing an average of two reactions with 100mg substrate at [0.06 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 3.17 (brs, 3H), 3.00 (brs, 3H), 2.62 (t, 2H, *J* = 6 Hz), 2.37 (s, 3H), 2.34 (s, 3H), 2.12 (s, 3H), 1.85-1.70 (m, 2H), 1.62-1.47 (m, 4H), 1.45-1.00 (m, 23H), 0.90-0.80 (m, 12H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 167.51, 153.04, 140.21, 139.51, 123.23, 117.79, 117.64, 75.38, 40.14, 39.35, 37.51, 37.49, 37.44, 37.42, 37.39, 37.37, 37.35, 37.33, 37.26, 37.03, 36.79, 32.78, 32.76, 32.71, 32.68, 31.12, 31.07, 27.97, 24.81, 24.80, 24.45, 24.44, 23.99, 22.73, 22.63, 21.38, 21.05, 21.03, 19.74, 19.68, 19.65, 19.61, 19.58, 18.72, 17.85, 12.59. **IR** (thin film): 2923, 2866, 1669, 1563, 1461, 1359, 1306, 1260, 1157, 1097 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 518.4031; found: 518.4020

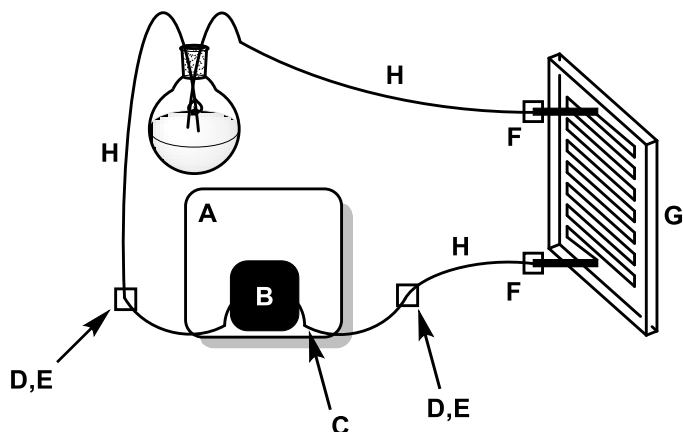


***S*-(1-naphthyl) dimethylcarbamothioate (3v)**: Isolated in 94% yield (109 mg), representing an average of two reactions with 116 mg substrate at [0.5 M].

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.46 (m, 2H), 3.24 (br, 3H), 3.02 (br, 3H); **<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>): δ 166.6, 136.2, 135.3, 134.2, 130.9, 128.6, 127.1, 126.3, 126.2, 125.8, 125.6, 37.1; **IR** (thin film): 1668, 1503, 1360, 1257, 1093, 798 cm<sup>-1</sup>; **HRMS** (+ESI): *m/z* calculated for [M+H]<sup>+</sup>: 232.0796; found: 232.0788

#### IV. Large Scale Flow Synthesis of *S*-(2,4,6-trimethylphenyl)dimethylcarbamothioate (3s)

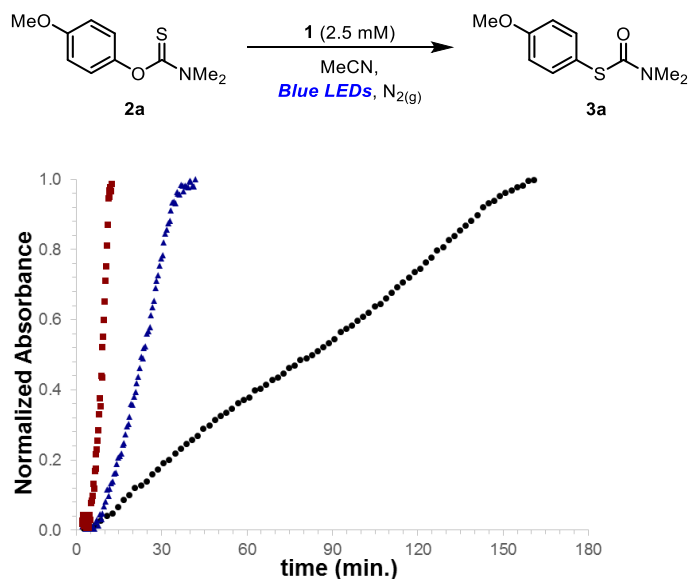
**Figure S1. Diagram of Flow Chemical Apparatus**



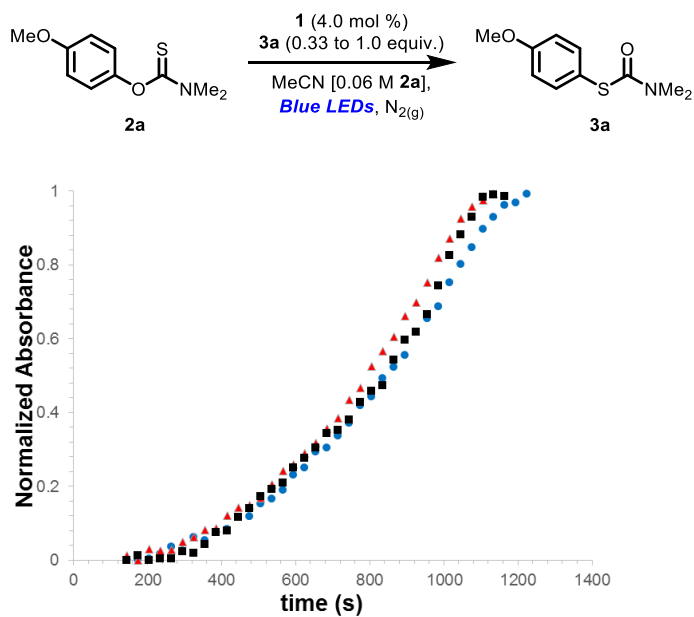
- A.** Masterflex L/S Variable-Speed Drive (Cole-Parmer # EW-07528-30)
- B.** Masterflex L/S Rigid PTFE-Tubing Pump Head (Cole-Parmer # EW-77390-00)
- C.** Masterflex PTFE-tubing 4mm O.D. (Cole-Parmer # EW-77390-50)
- D.** 4MM PTFE Male NPT Compression Adapter (Cole-Parmer # WU-31321-62)
- E.** 1/8" O.D. to 1/8" PTFE Female NPT Compression Adapter (Cole-Parmer # EW-31320-50)
- F.** 1/4-28 flangeless fitting/ferrule for 1/8" O.D. tubing (Sigma-Aldrich SUPELCO # 58686)
- G.** Microreactor (Little Things Factory GmbH # XXL-ST-02)
- H.** PTFE Tubing 1/16" I.D., 1/8" O.D. (Cole-Parmer # WU-06605-27)

A 1 L rbf was charged with 21.5 grams of *O*-(2,4,6-trimethylphenyl)dimethylcarbamothioate (96.4 mmol), followed by 0.38 g of triphenylpyrylium tetrafluoroborate (0.96 mmol, 0.01 equivalents). Next, a teflon coated stir bar was added, followed by 800 mL of acetonitrile. Two 15W PAR38 blue LED floodlamps were positioned on either side of the microreactor (G). The 1 L rbf was clamped in place over a stir plate and moderate stirring was begun. The rbf was fitted with a rubber stopper with two holes drilled through it. Into one hole was placed the PTFE tubing inlet. This tubing was placed several inches below the surface of the solution. Into the second hole was placed the PTFE tubing outlet. This was placed above the surface of the solution to allow visual verification of circulation. The Masterflex L/S Variable-Speed Drive was set to 60 rpm, the occlusion bed of the pump head was adjusted as per the manufacturer's instructions, and the blue LED floodlamps were switched on. The reaction was sampled every 10 to 12 hours and analyzed via  $^1\text{H}$  NMR to determine reaction progress. After 82 hours, all starting material was determined to have been consumed. The solvent was removed under vacuum and the resulting yellow solid was purified via silica gel chromatography (600 mL silica gel, 19:1 to 9:1 to 4:1 petroleum ether/ethyl acetate). After chromatography, 19.7 g (88.2 mmol, 91% yield) of a yellowish white crystalline solid was obtained. The solid was confirmed to be the desired product, *S*-(2,4,6-trimethylphenyl) dimethylcarbamothioate.

## V. Additional Kinetic Data

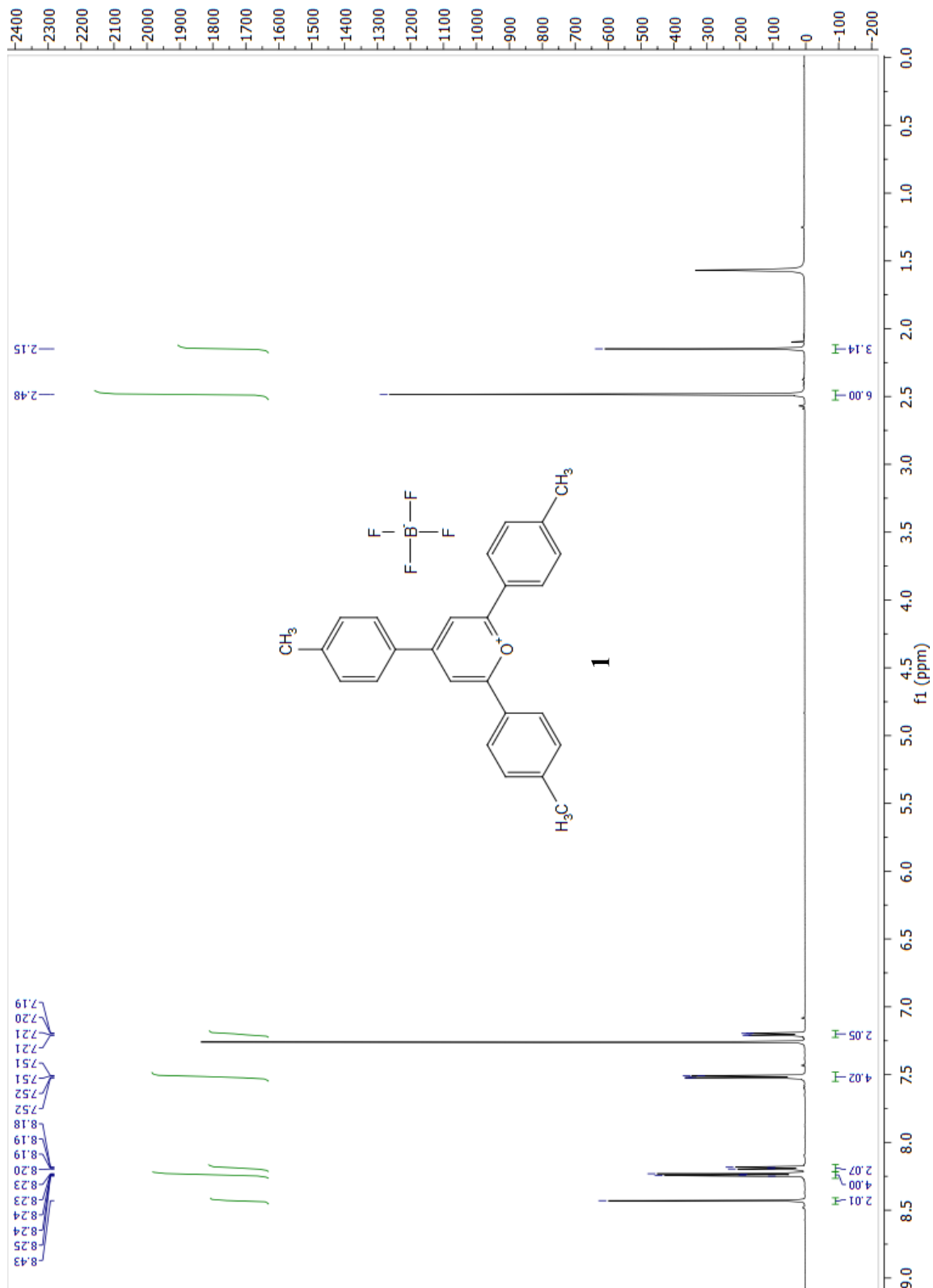


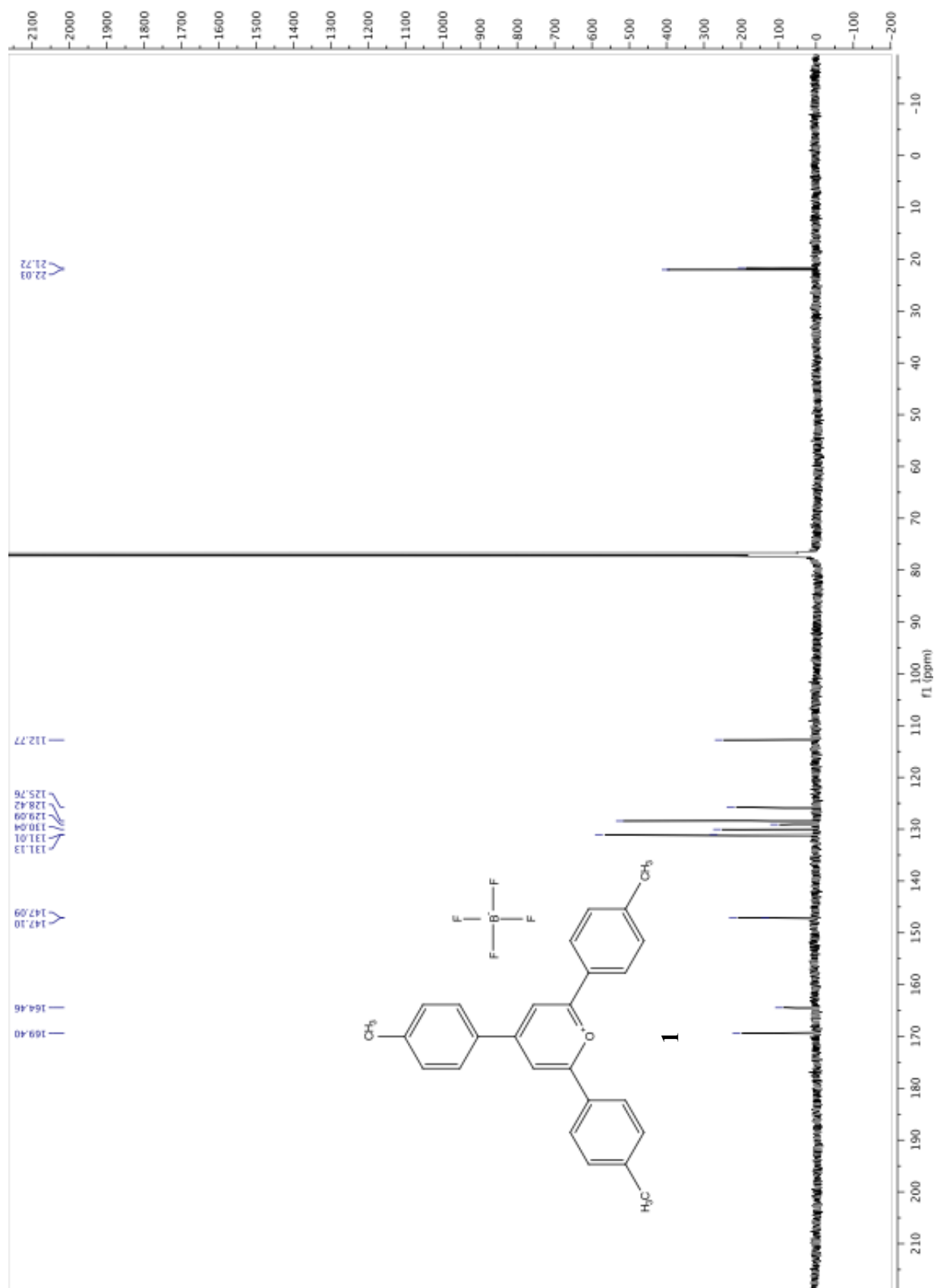
**Figure S1.** Appearance of **3a** monitored by *in situ* IR spectroscopy for the rearrangement of **2a** to **3a**, with blue LED irradiation beginning at two minutes. Conditions: 0.06 M (■), 0.13 M (▲), or 0.25 M (●) starting concentration of **2a**, with [2.5 mM] **1** in 4 mL acetonitrile.

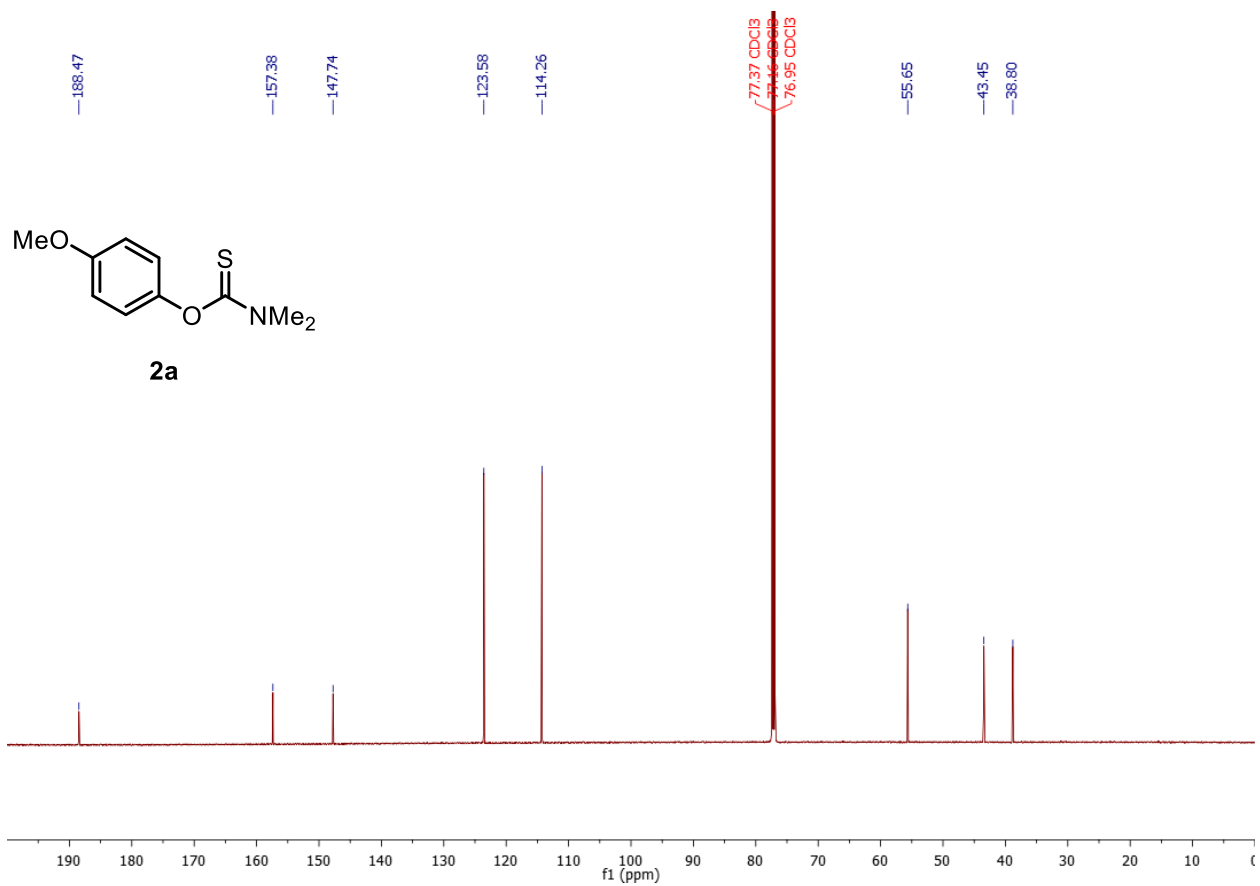
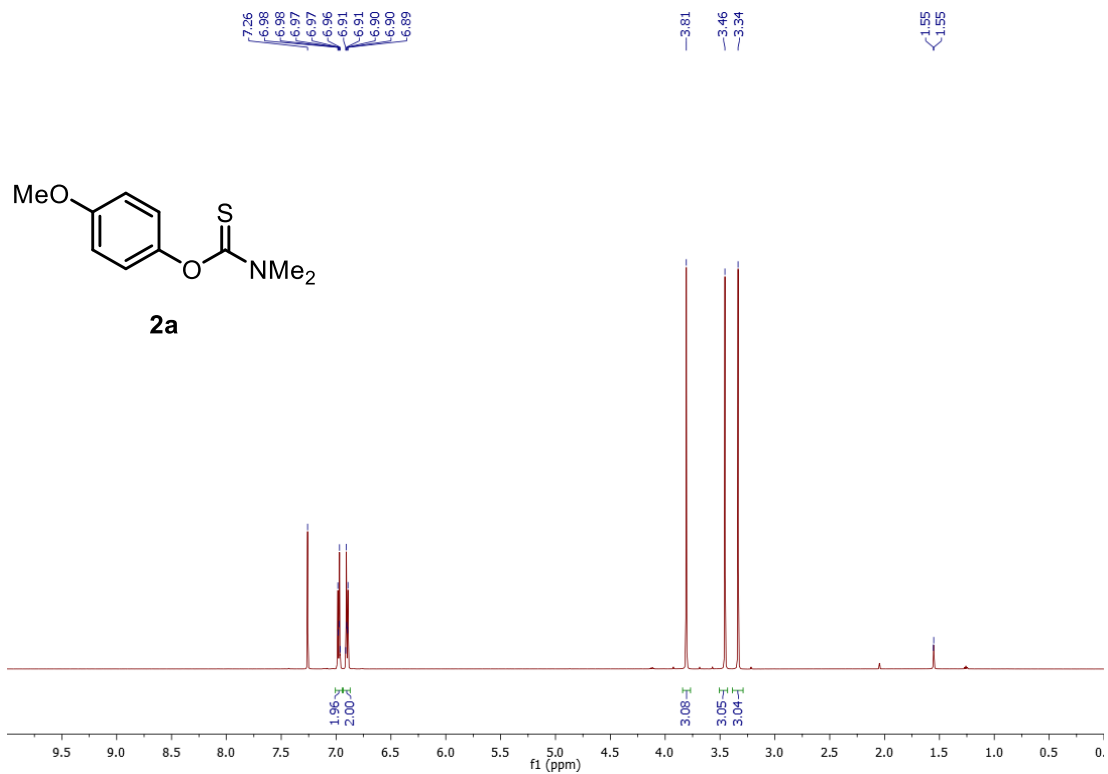


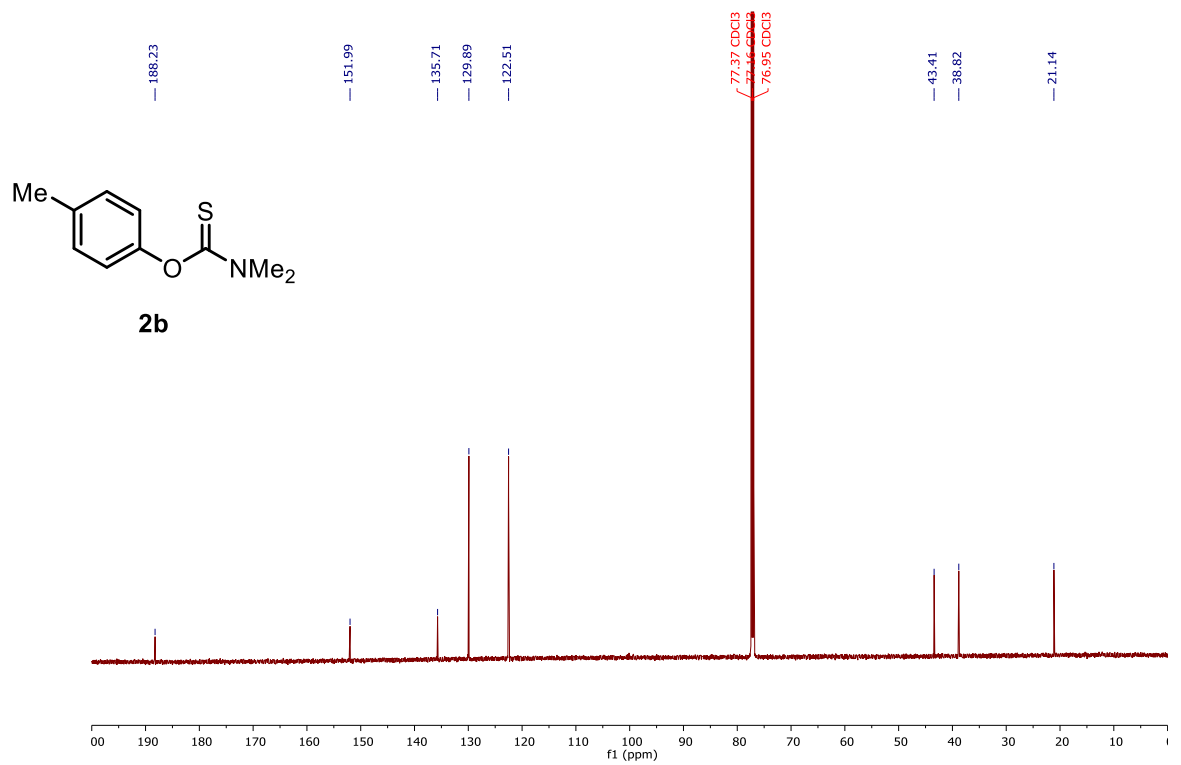
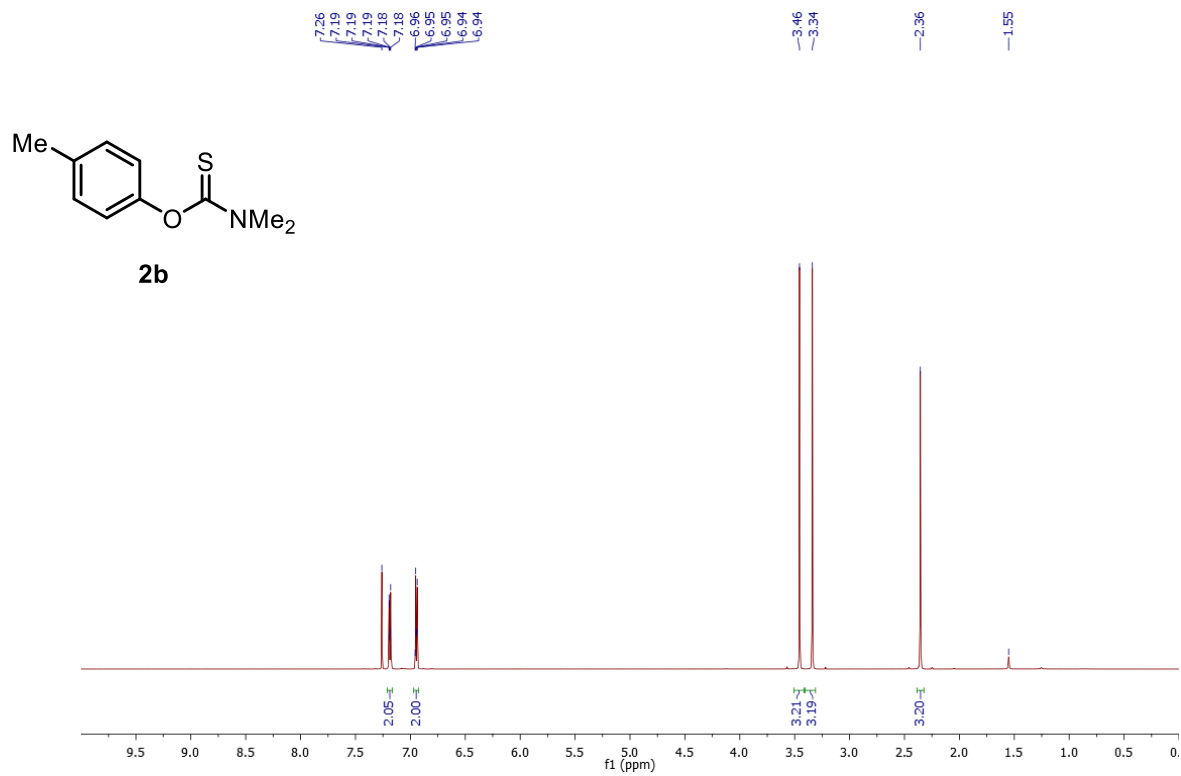
**Figure S2.** Kinetic traces demonstrating lack of product inhibition. Conditions: carried out in a Schlenk tube with 4 mL MeCN, 4.7 mg (0.01 mmol, 4 mol%) **1**, 53 mg (0.25 mmol, 0.06 M) **2a**, and varying amounts of **3a** (0.08 – 0.25 mmol, 0.33 to 1.0 equivalents relative to **2a**) and monitored by *in situ* IR measuring absorbance at 1670 cm<sup>-1</sup>. Irradiation was begun at 120 seconds. 1.0 equivalent of **3a** (■). 0.66 equivalent of **3a** (▲). 0.33 equivalents of **3a** (●).

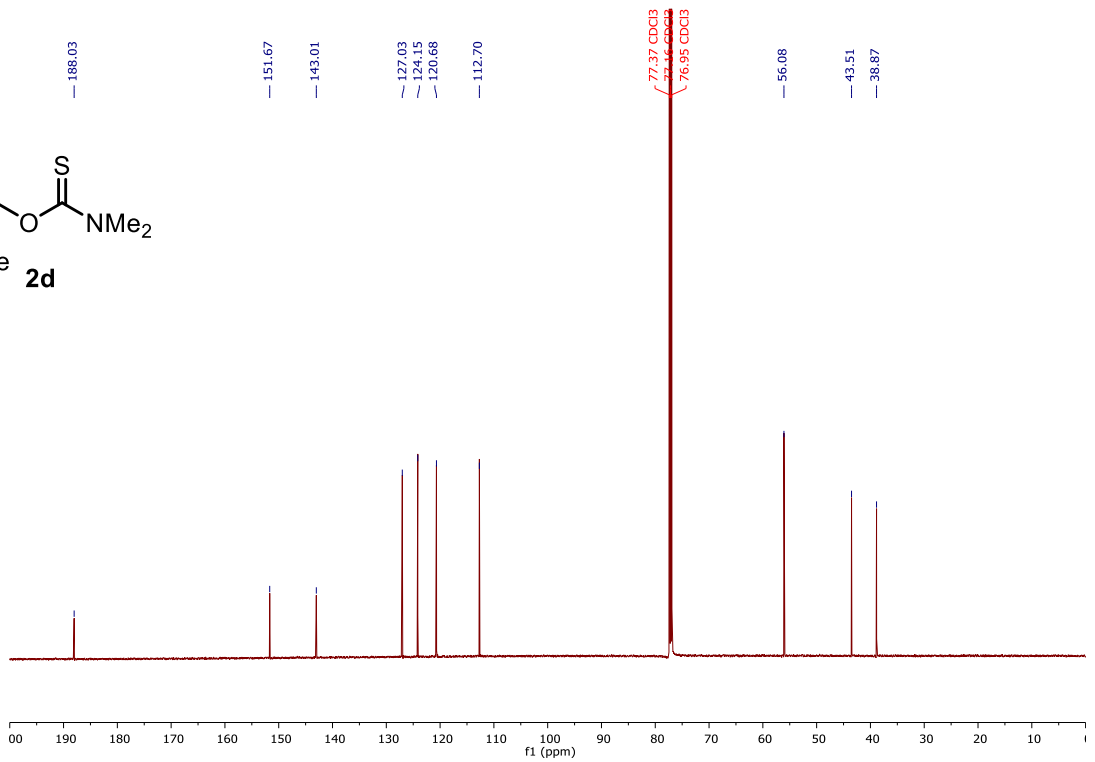
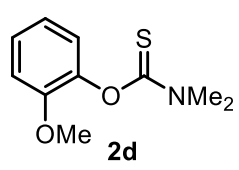
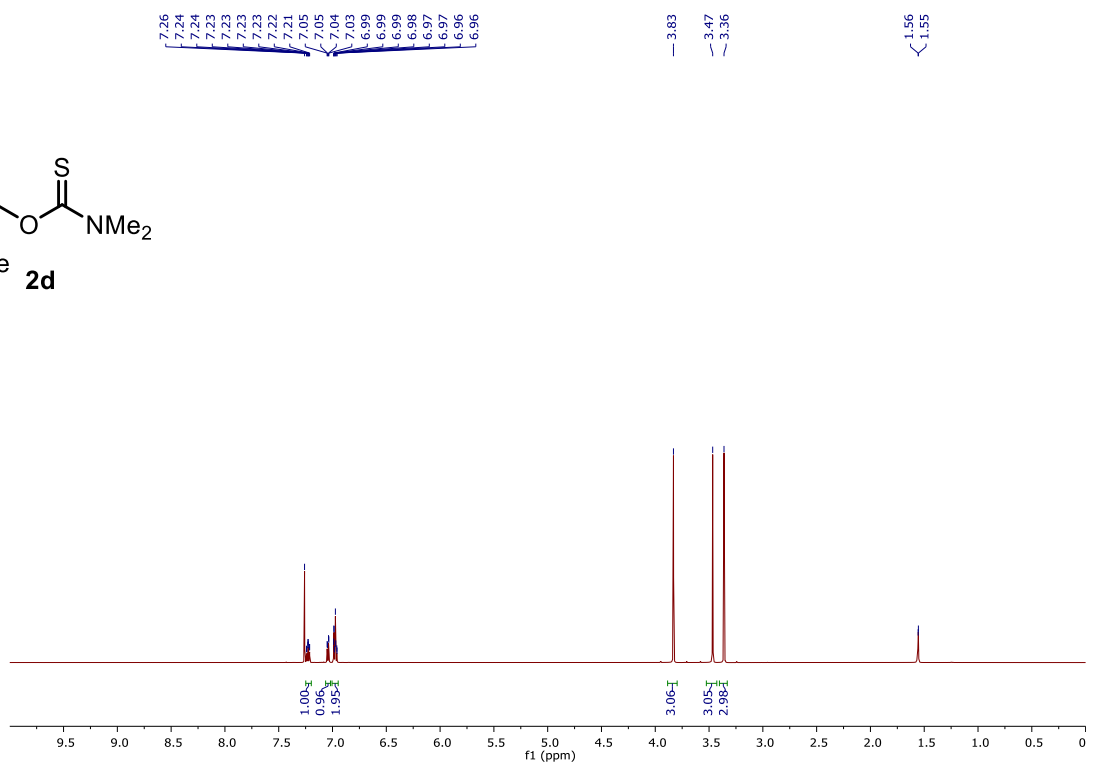
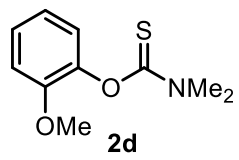
# V. <sup>1</sup>H and <sup>13</sup>C NMR Spectra

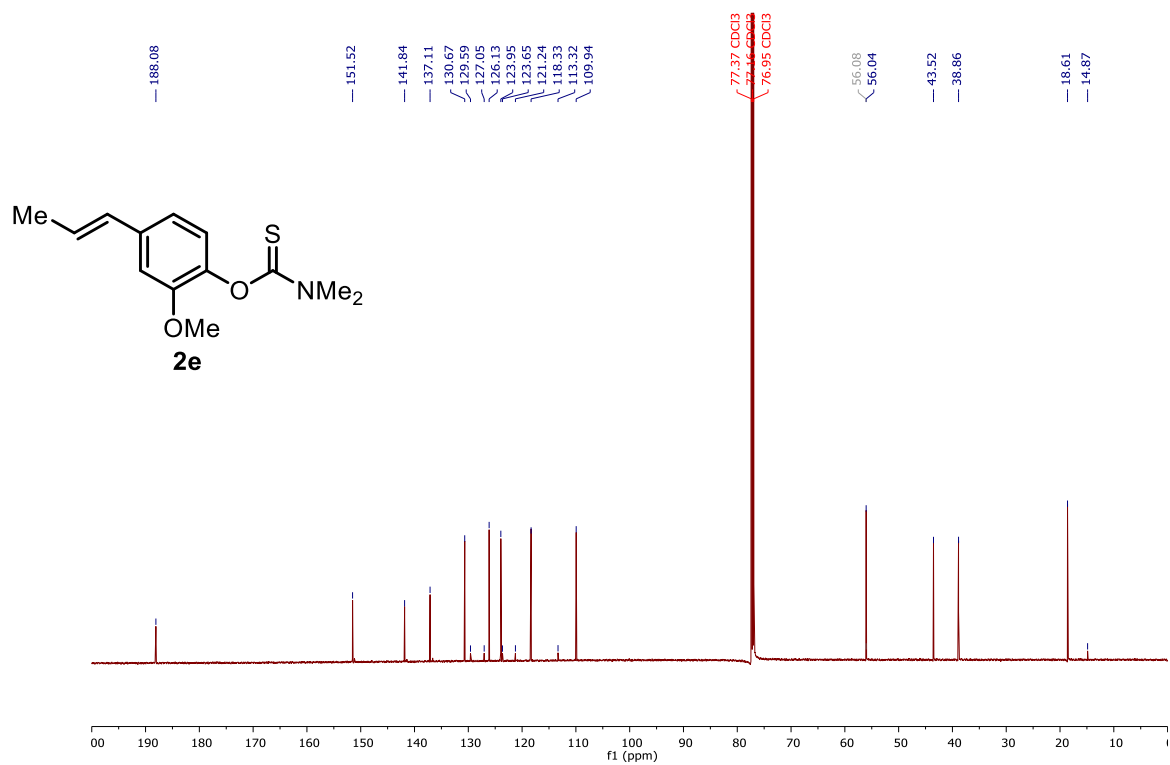
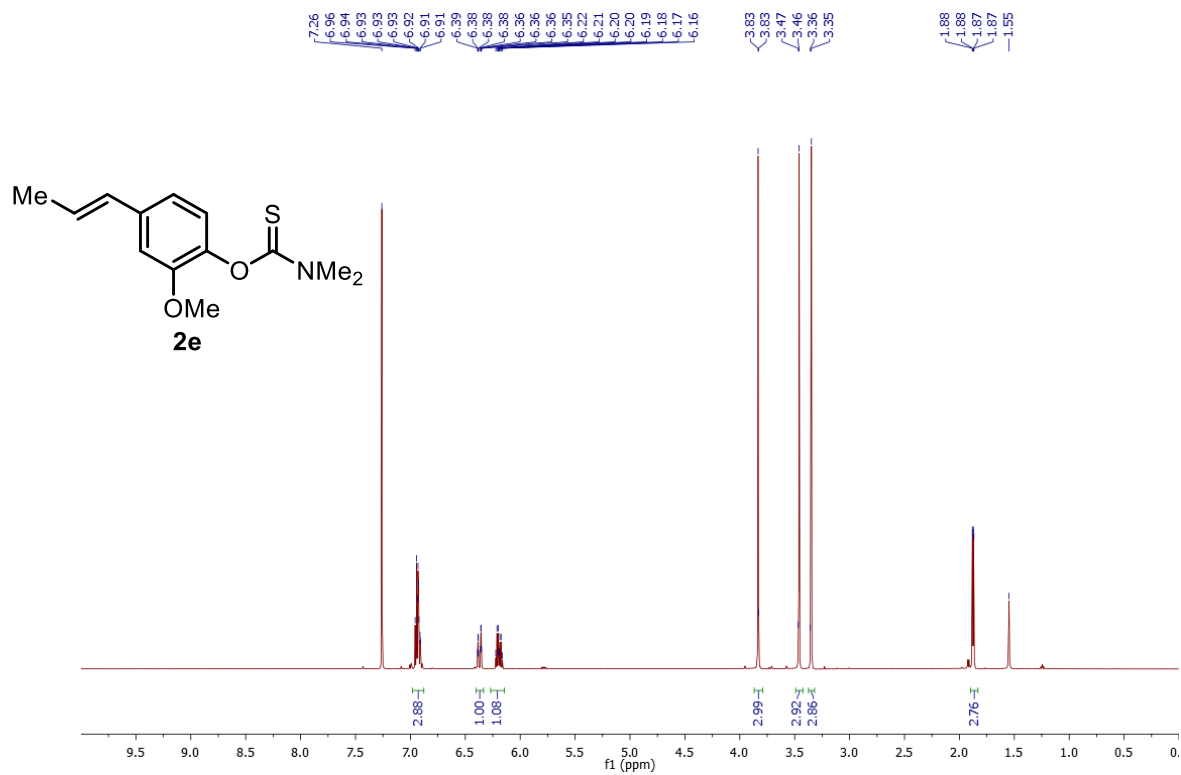


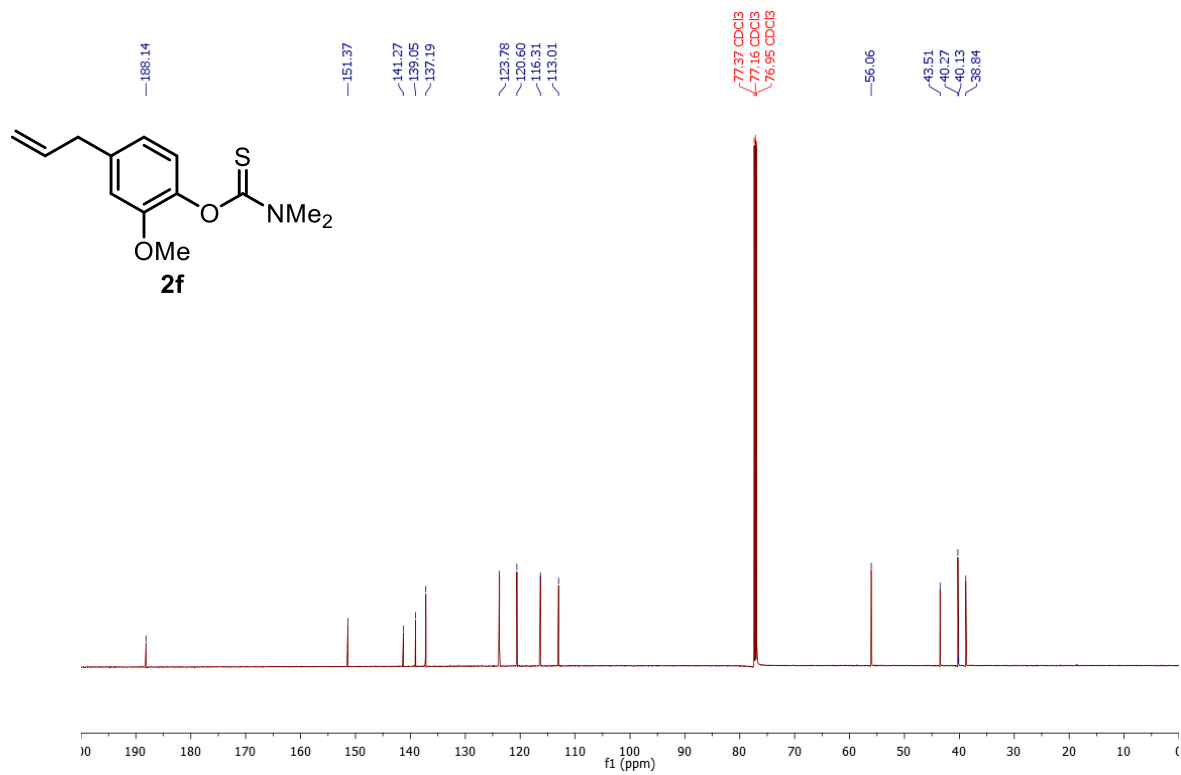
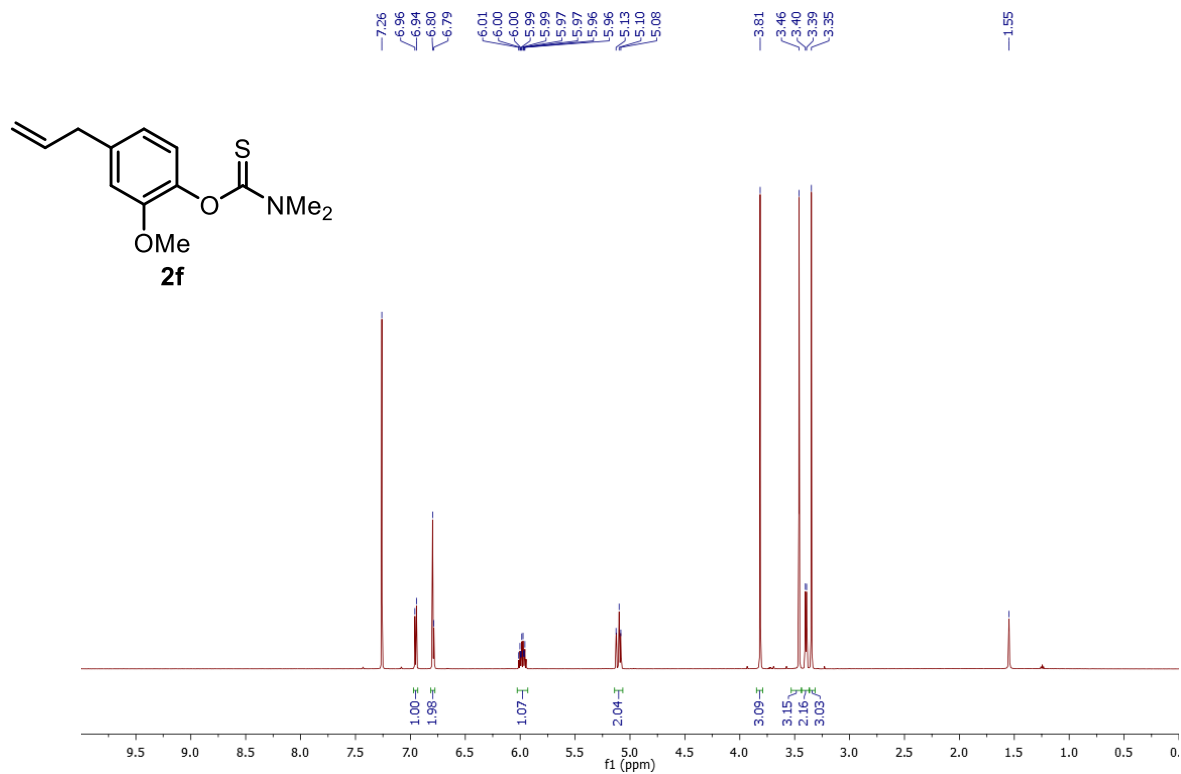


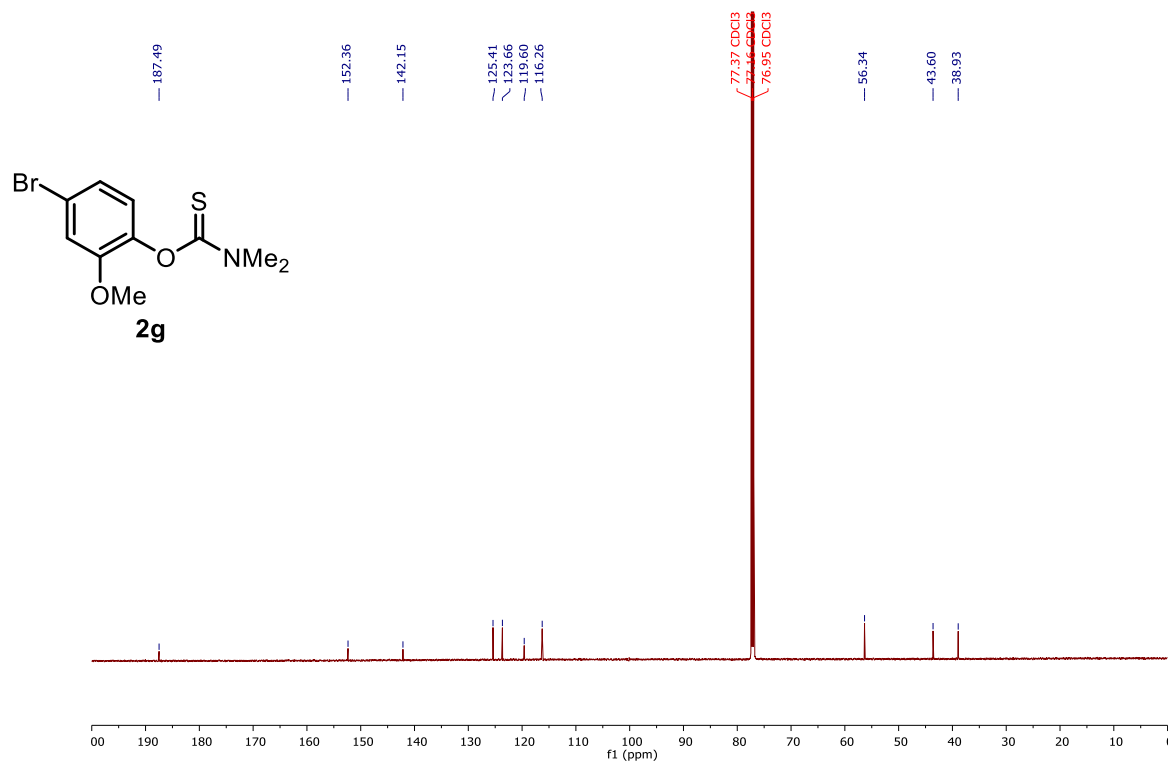
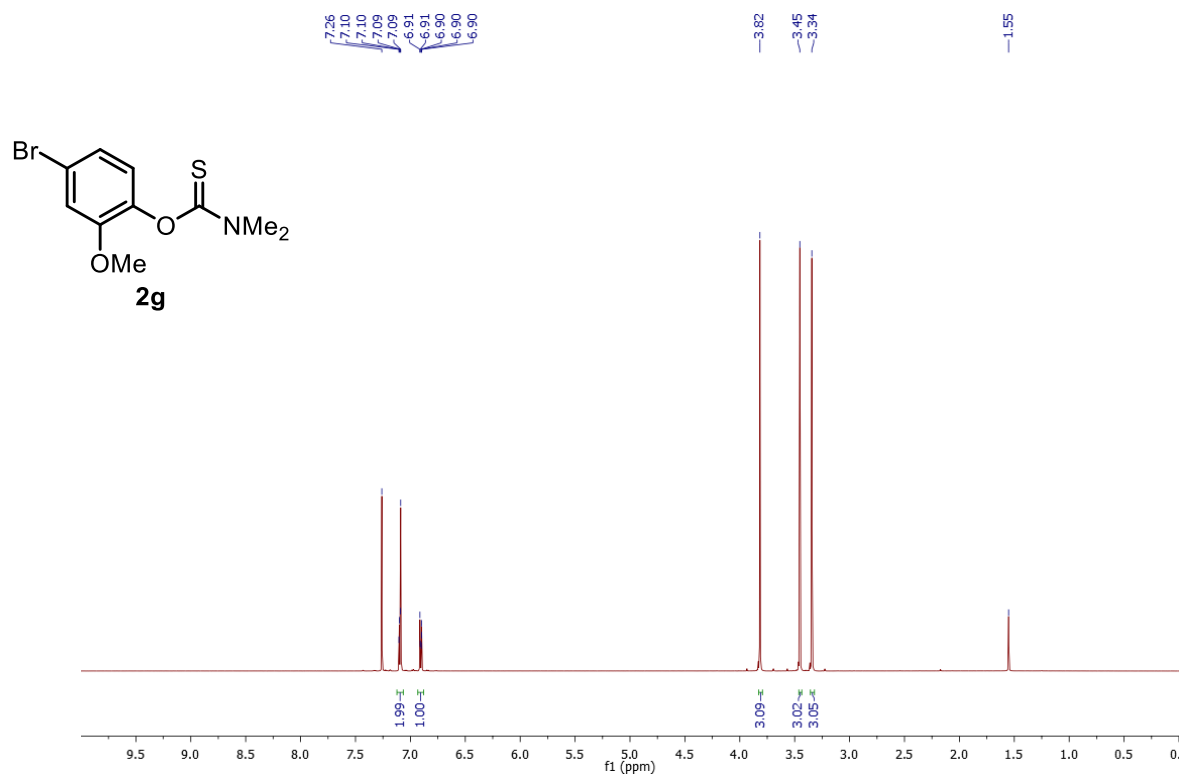


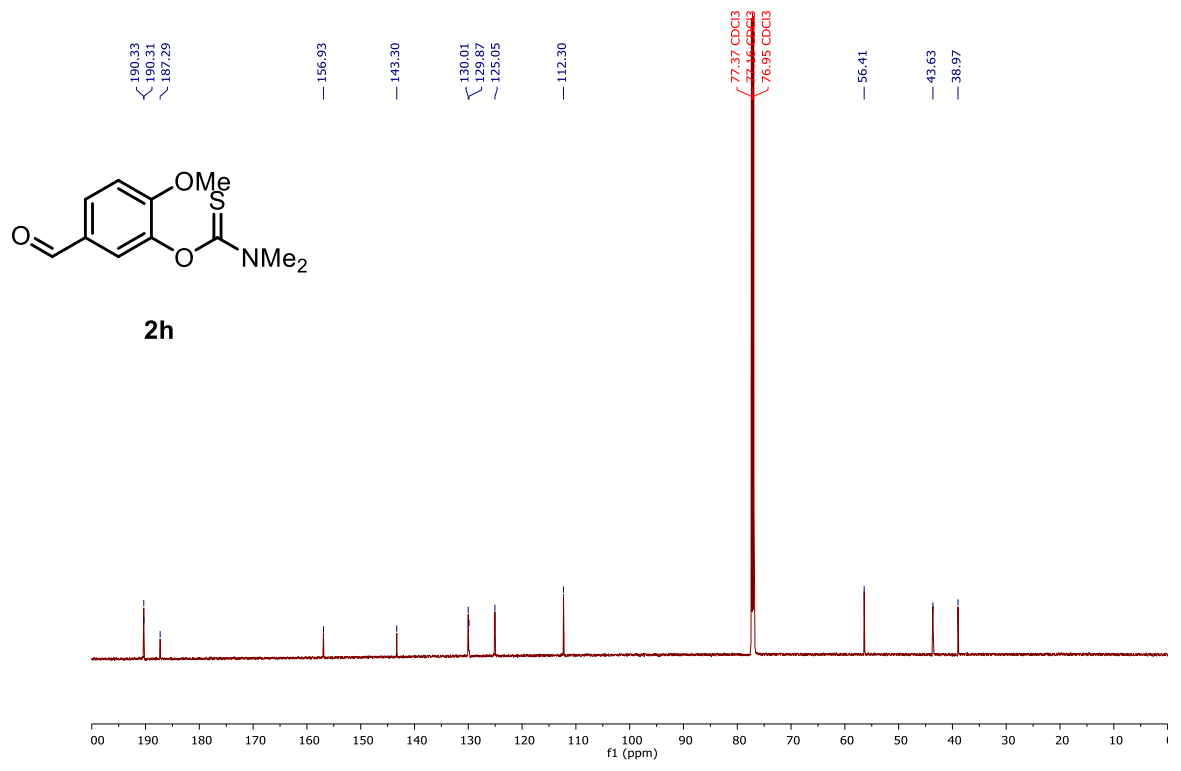
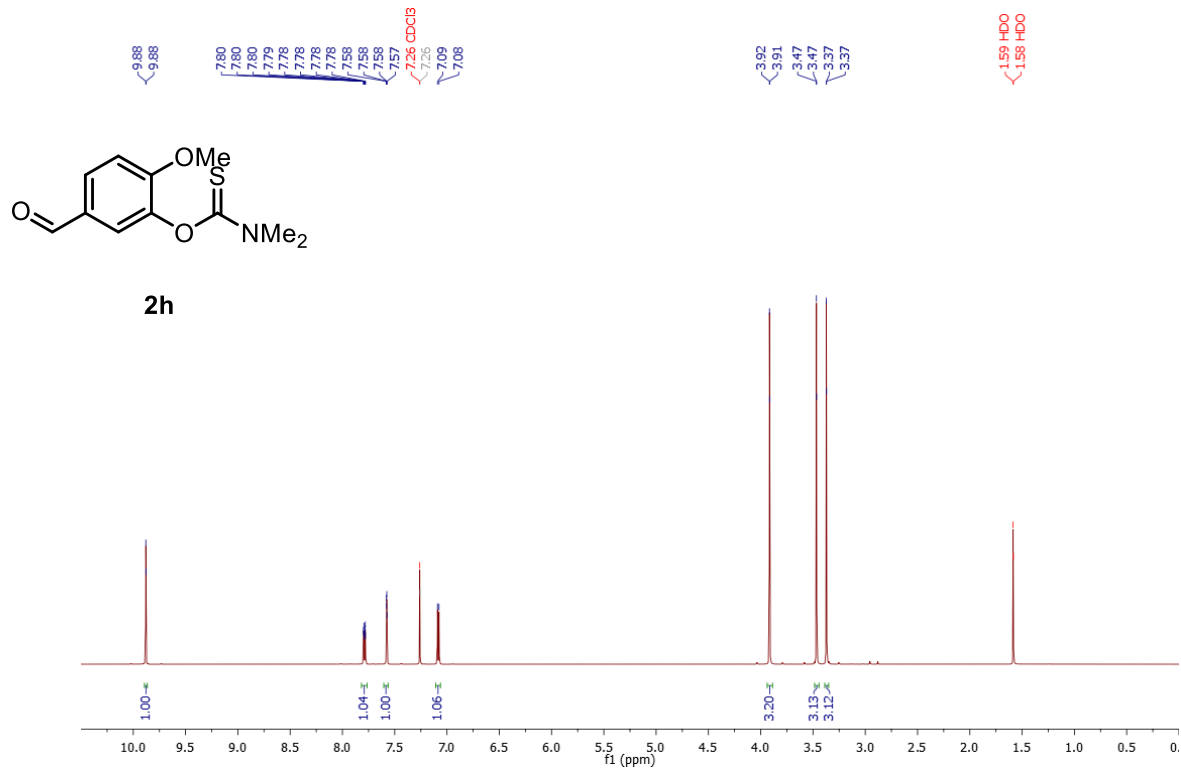


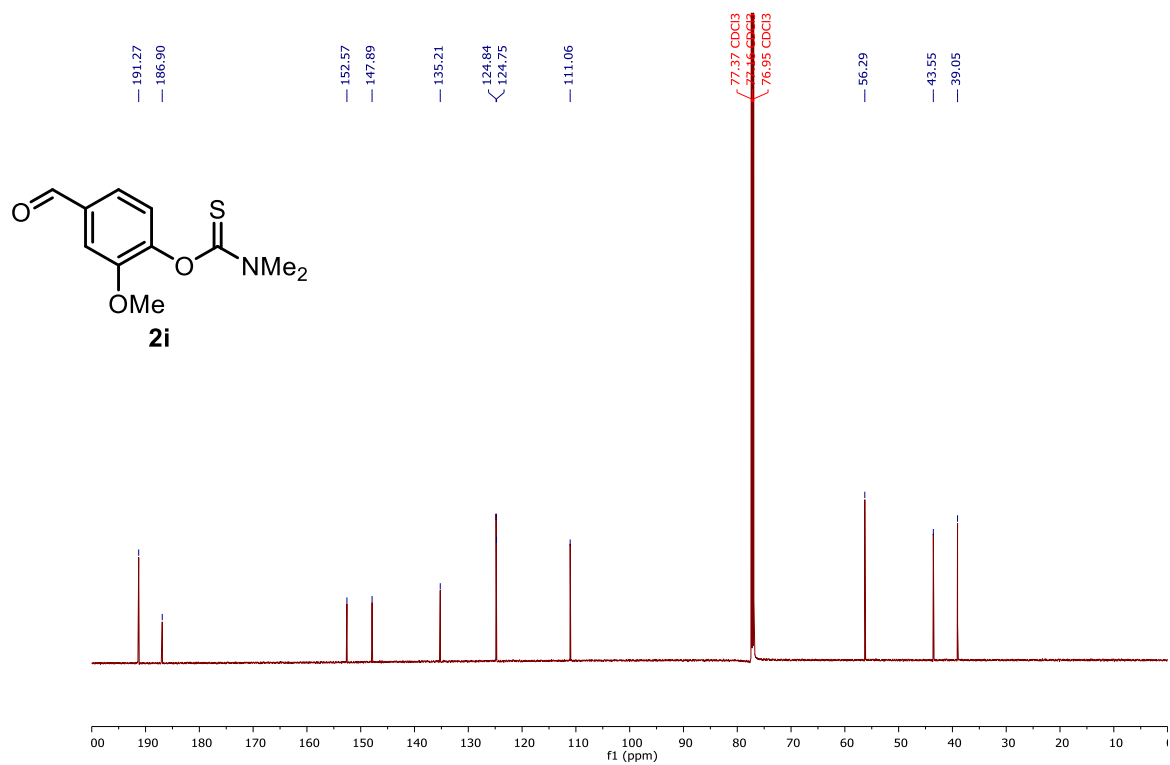
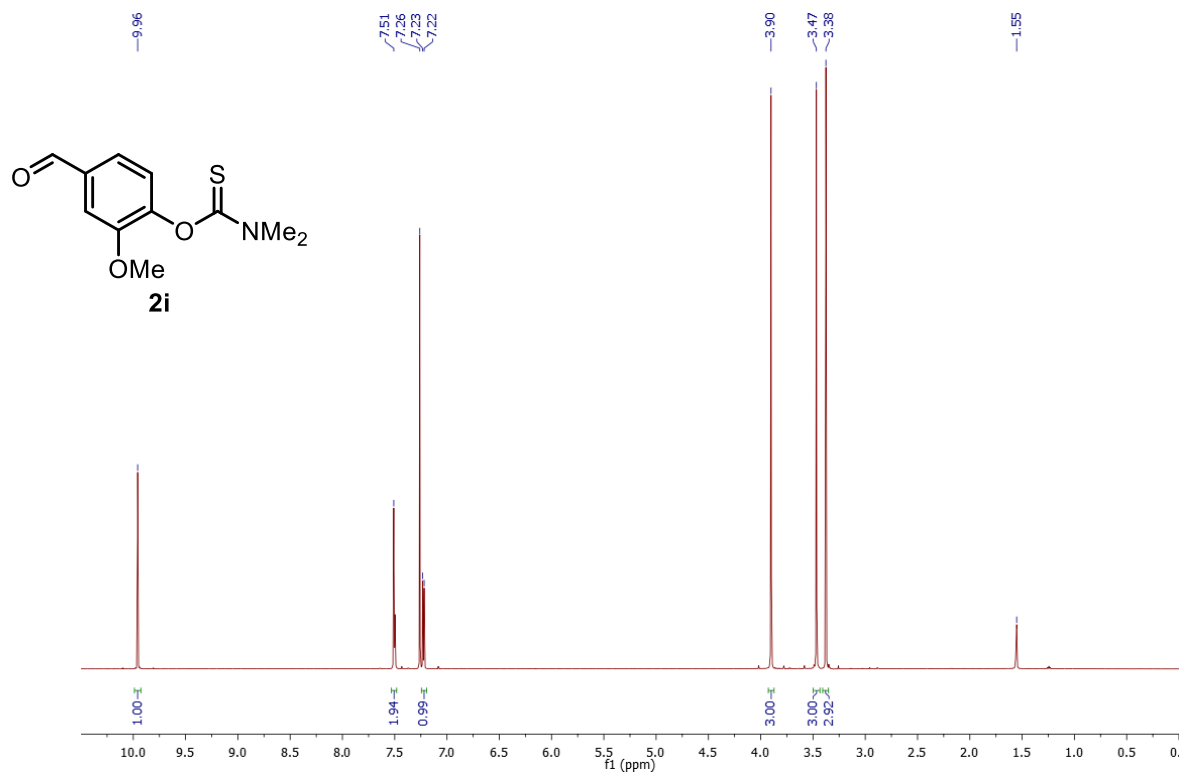


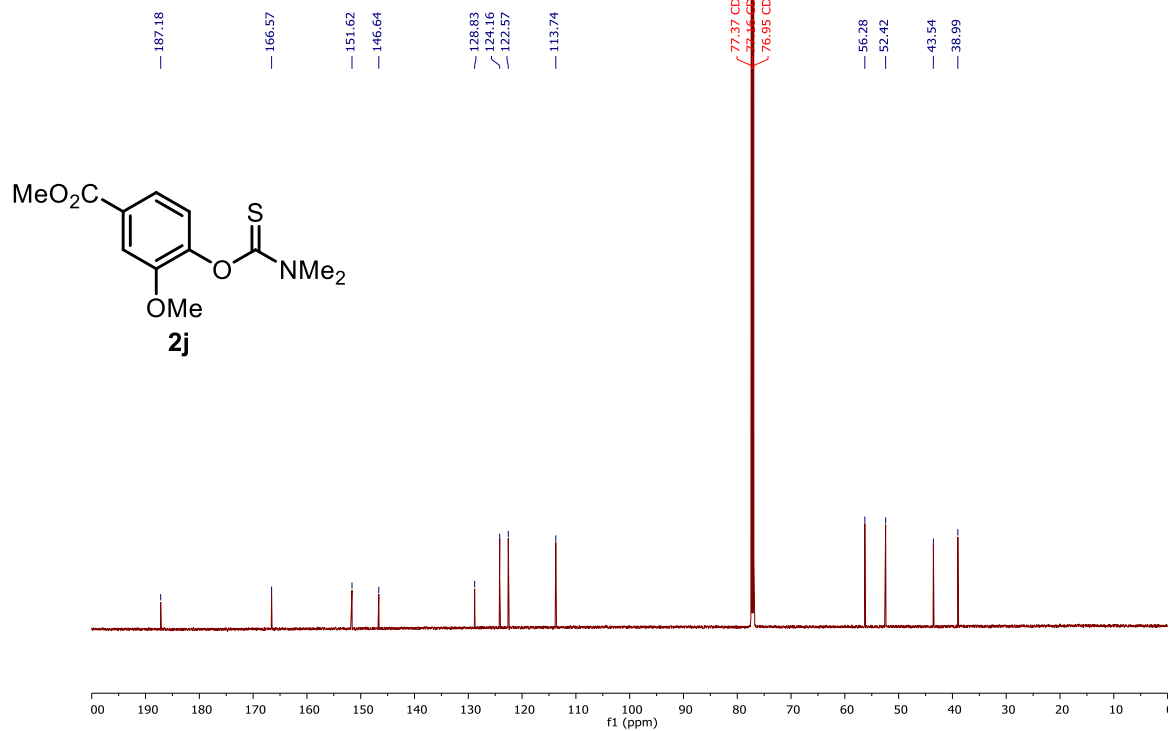
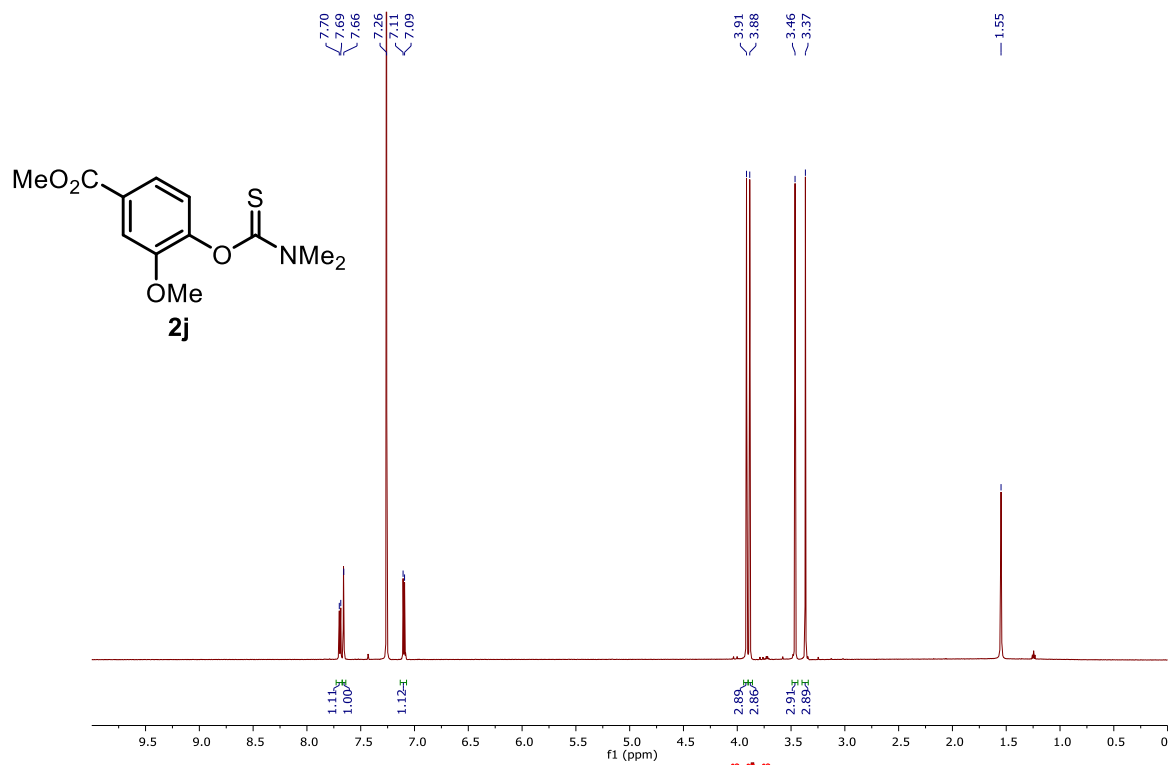


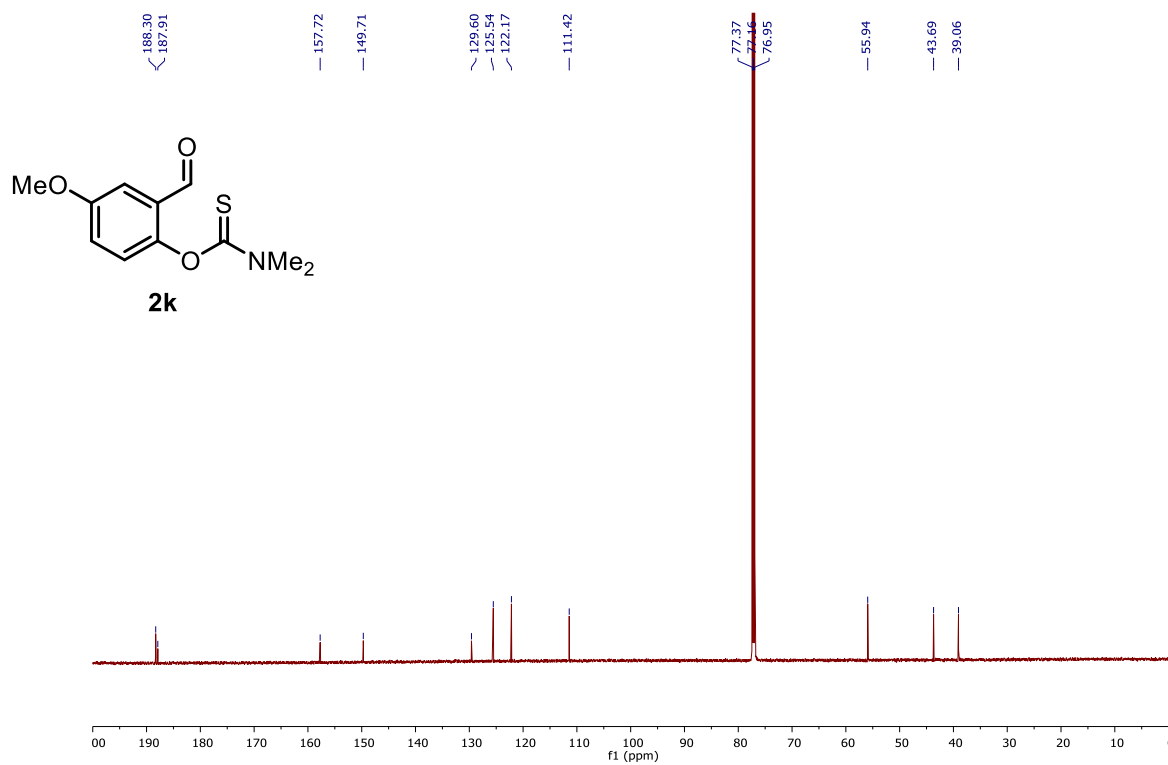
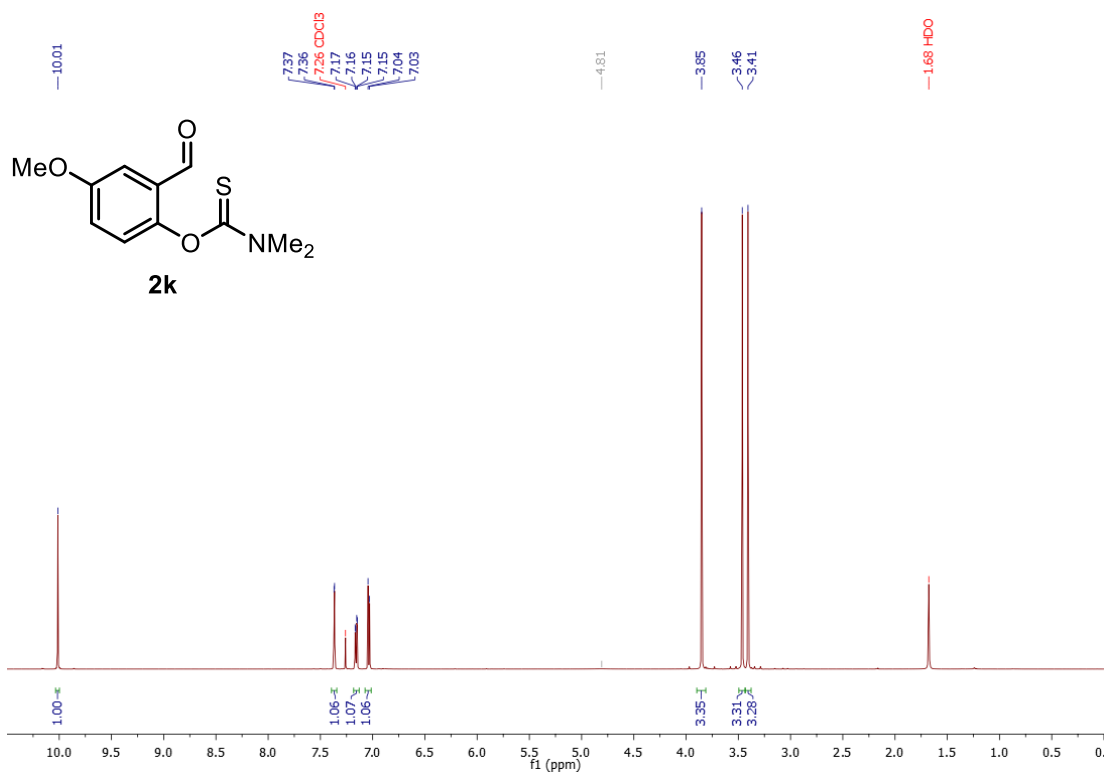


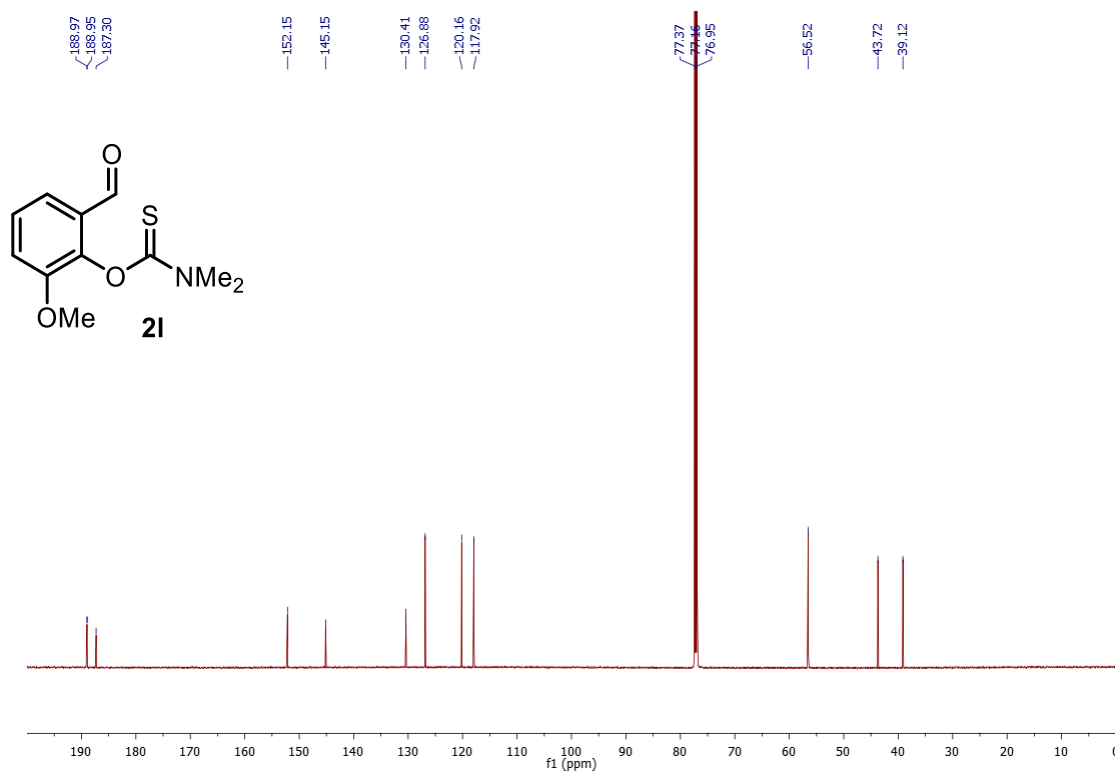
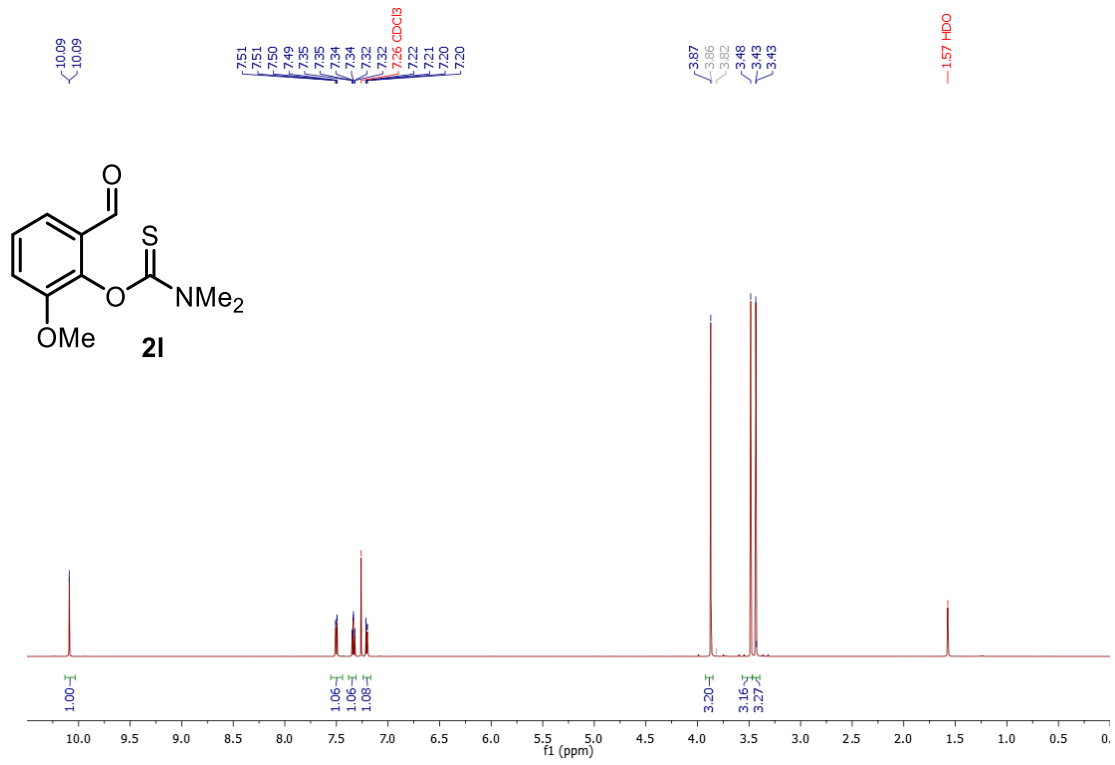


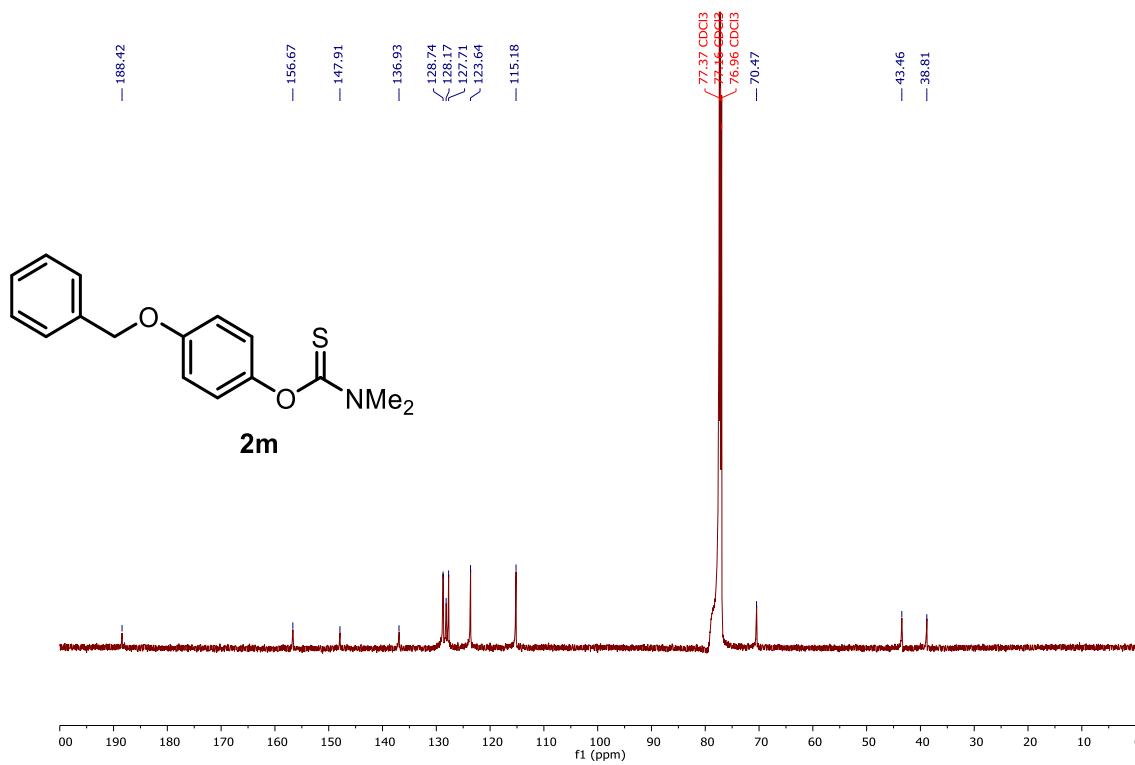
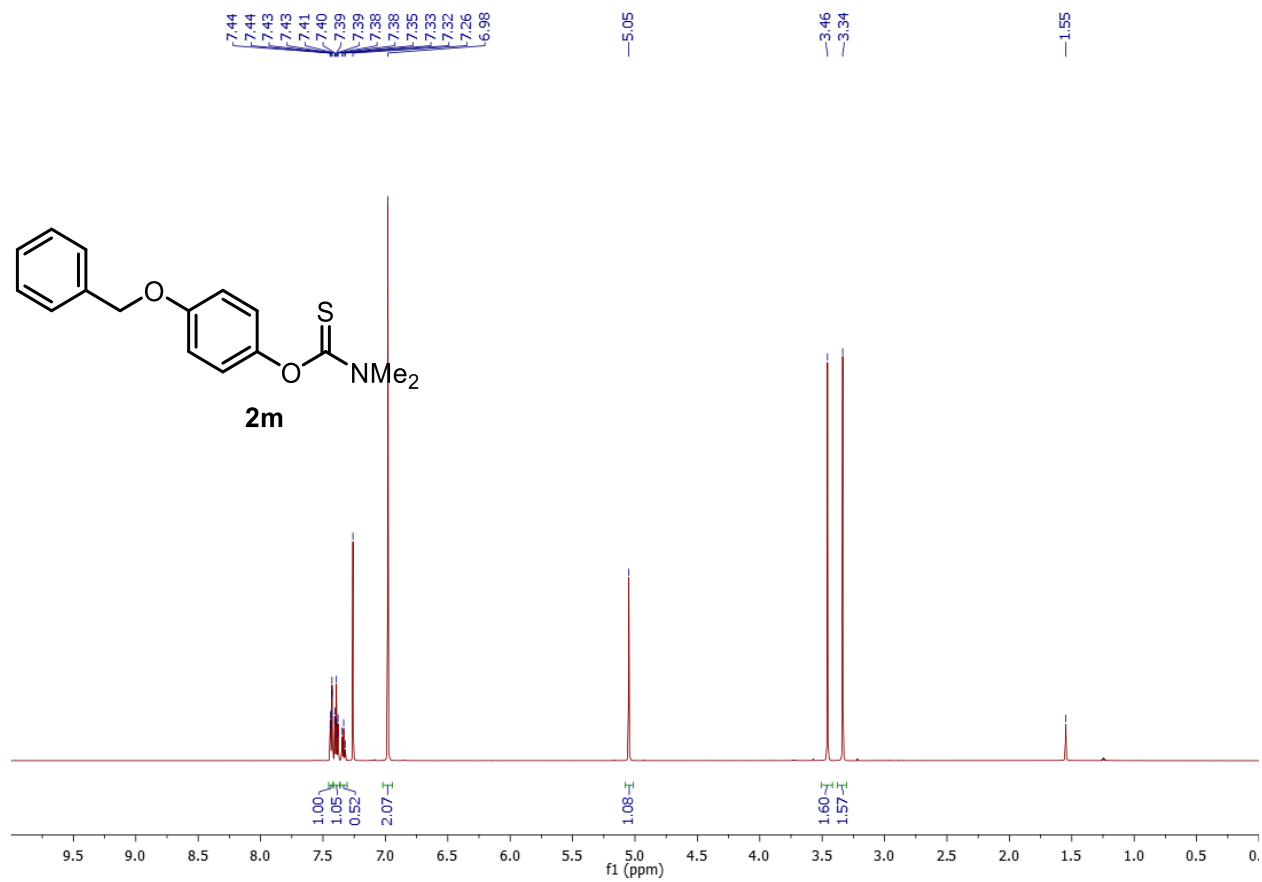


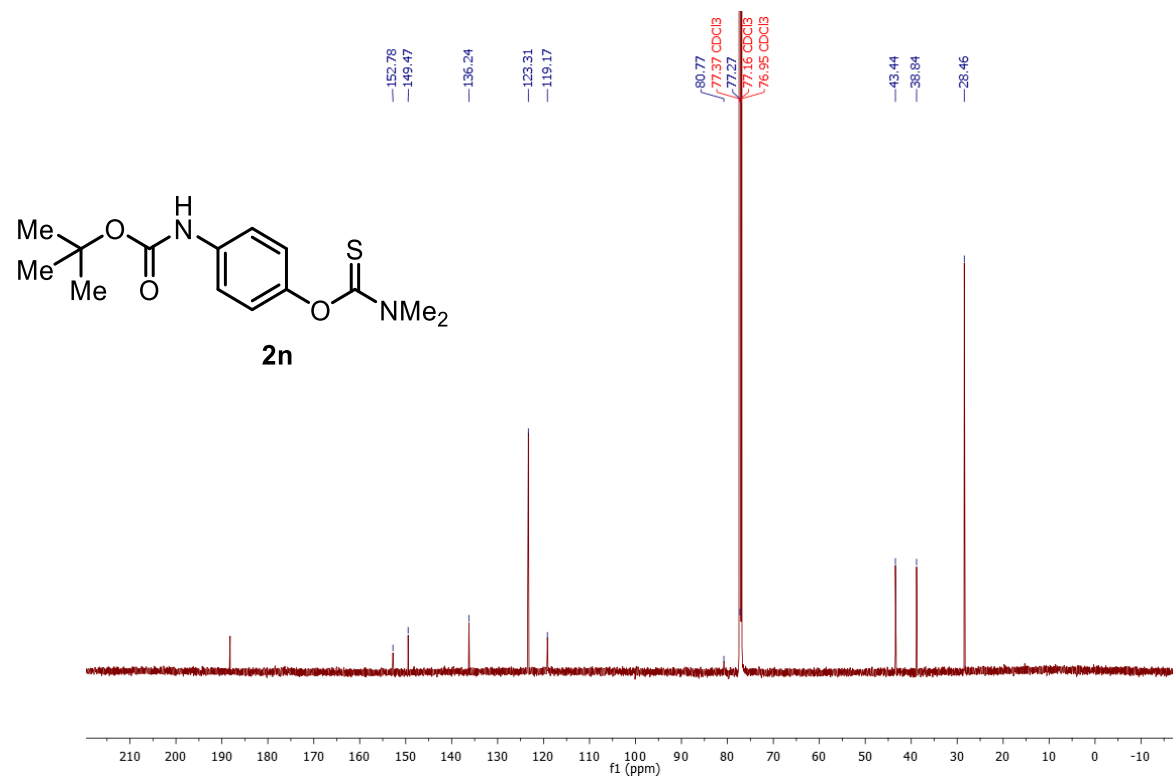
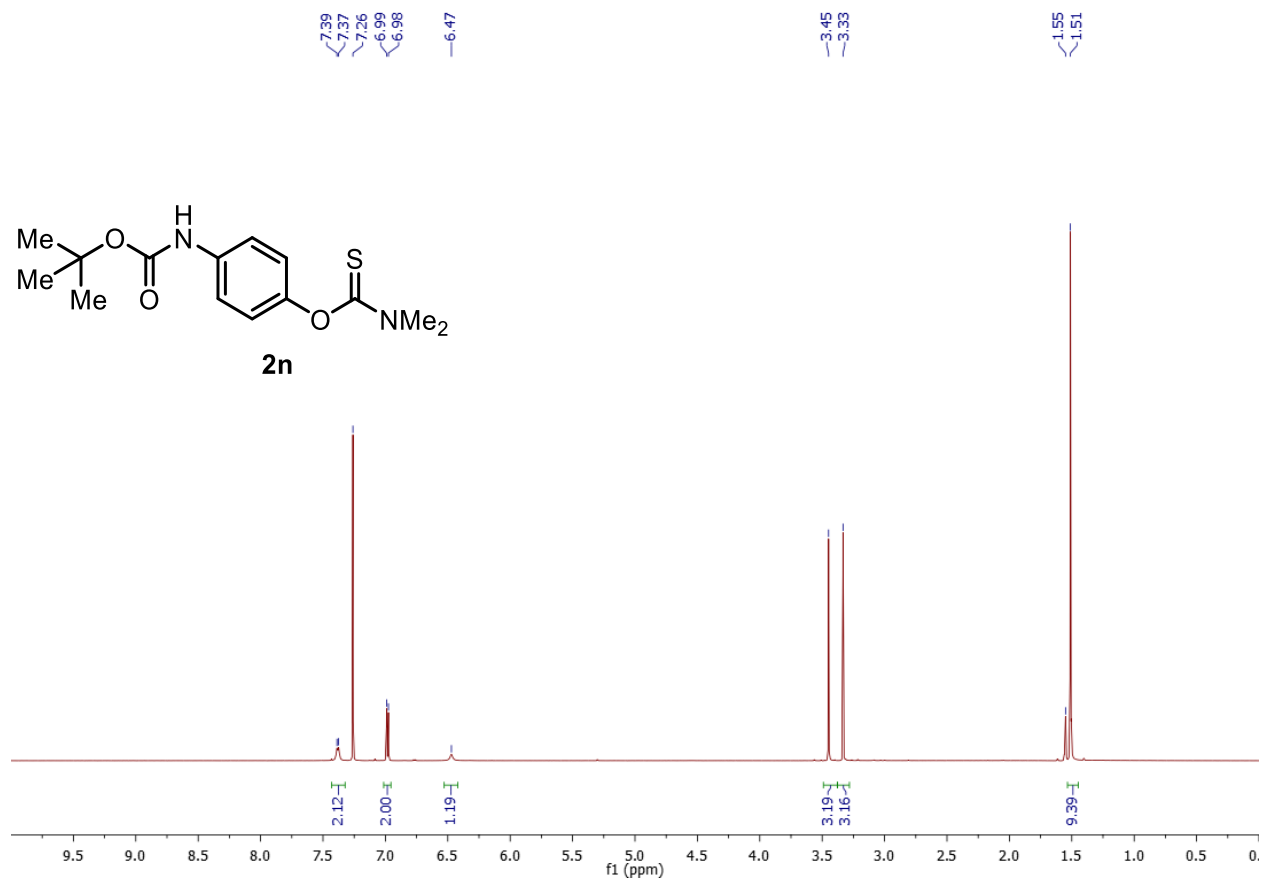


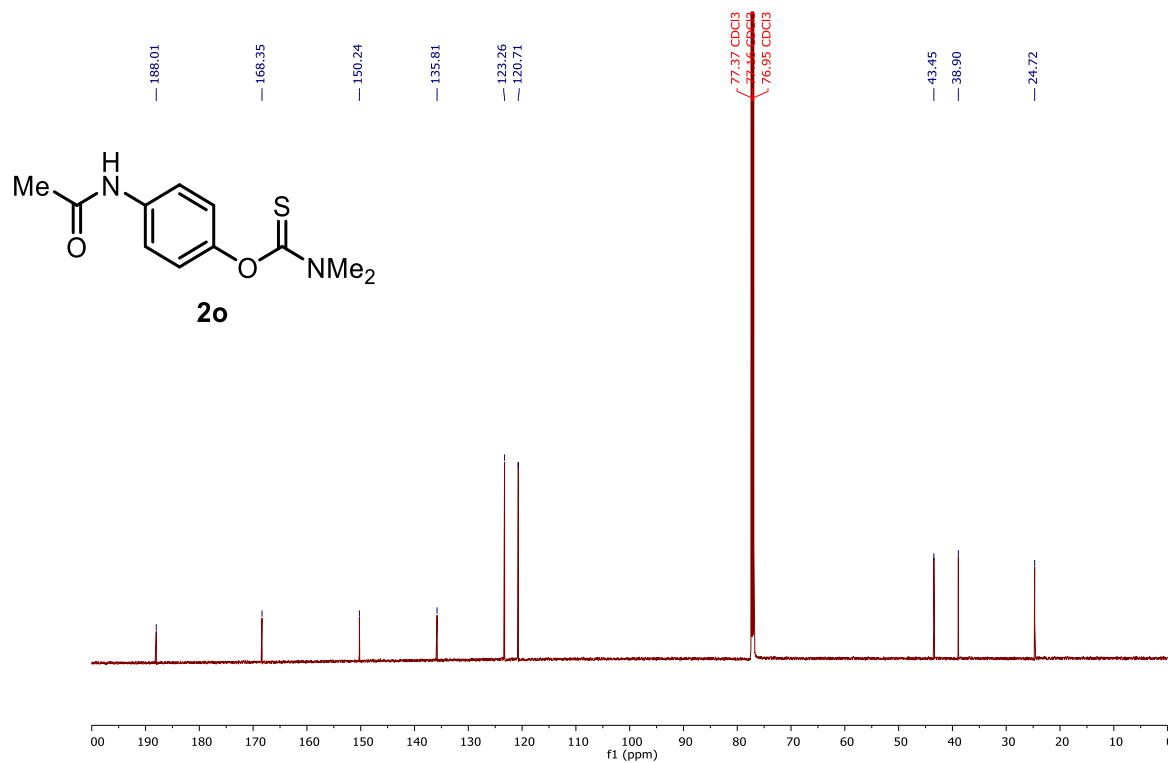
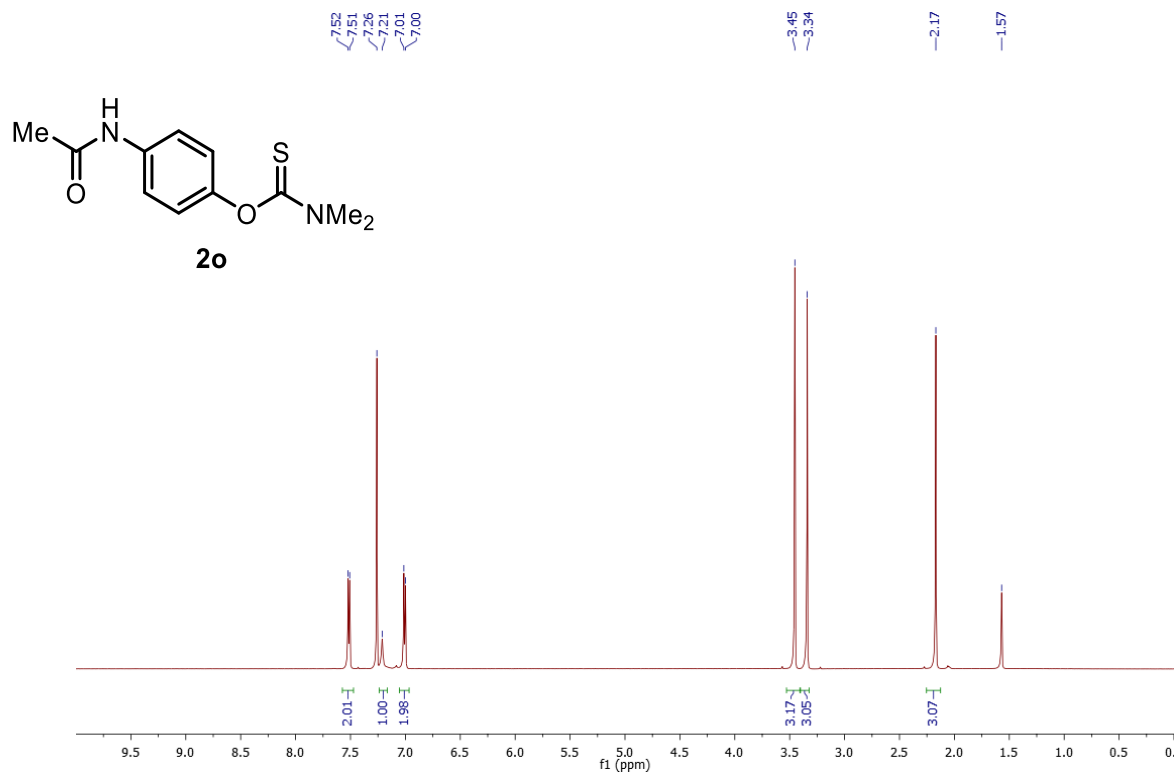


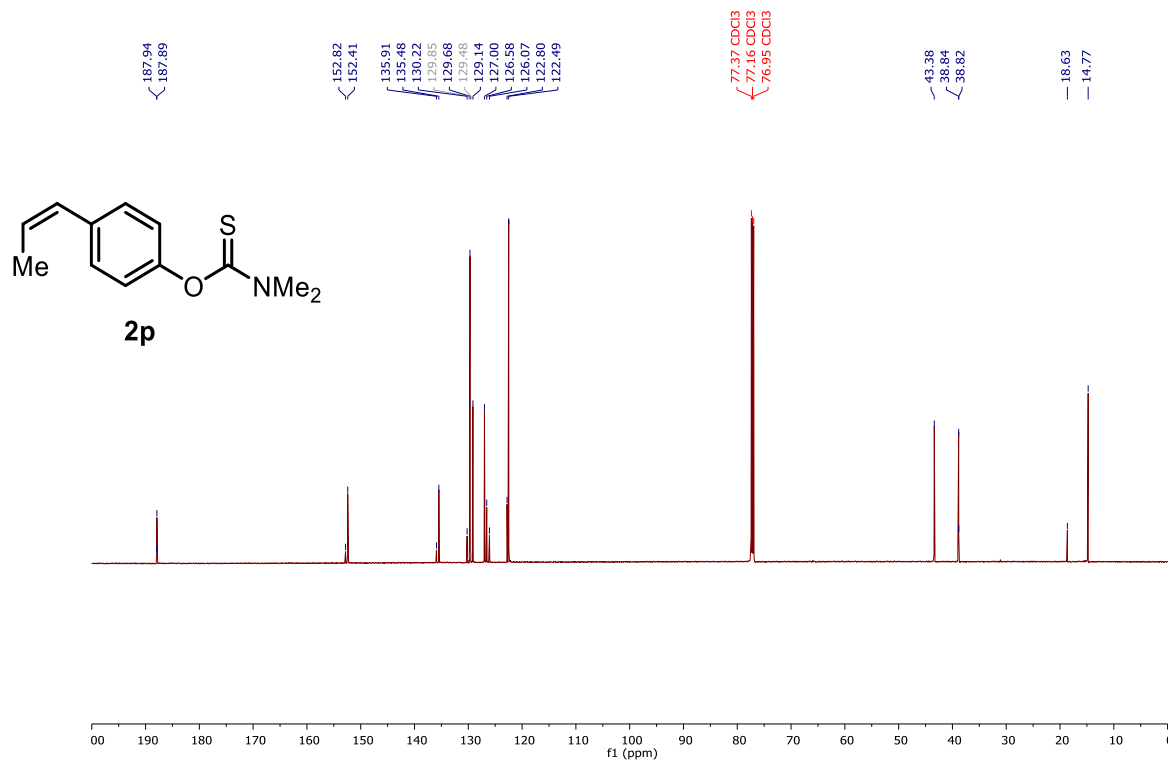
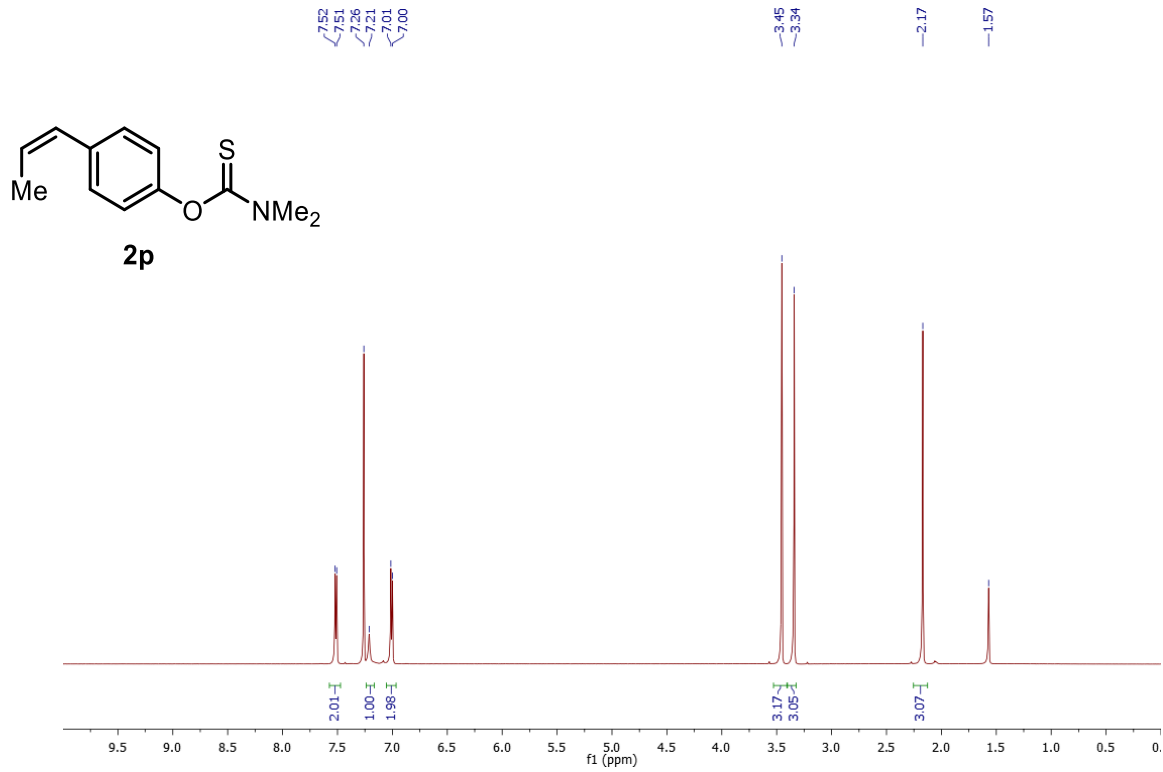


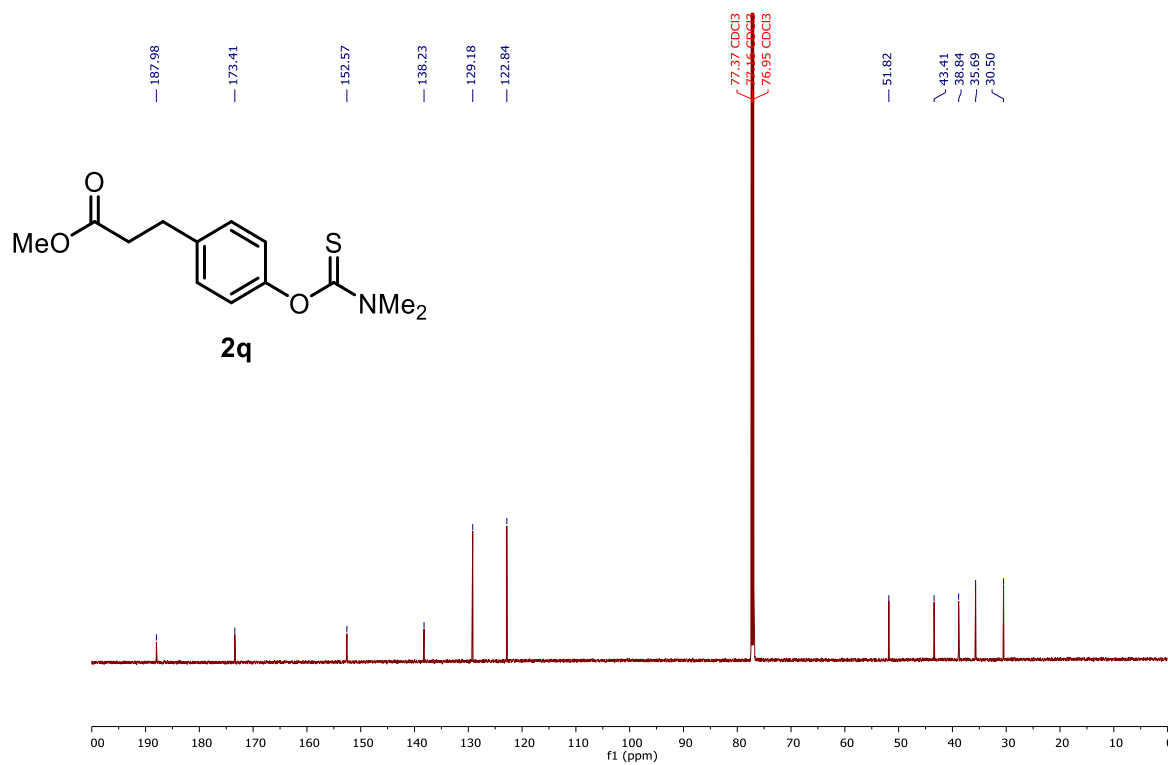
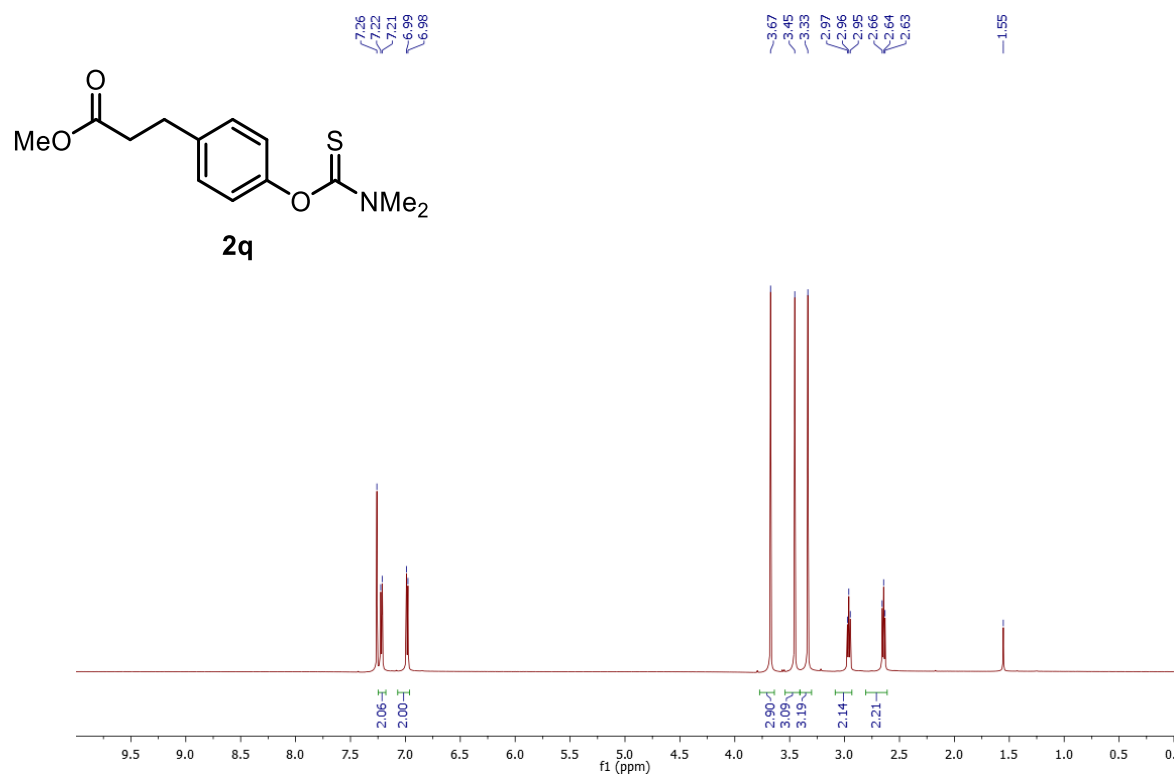


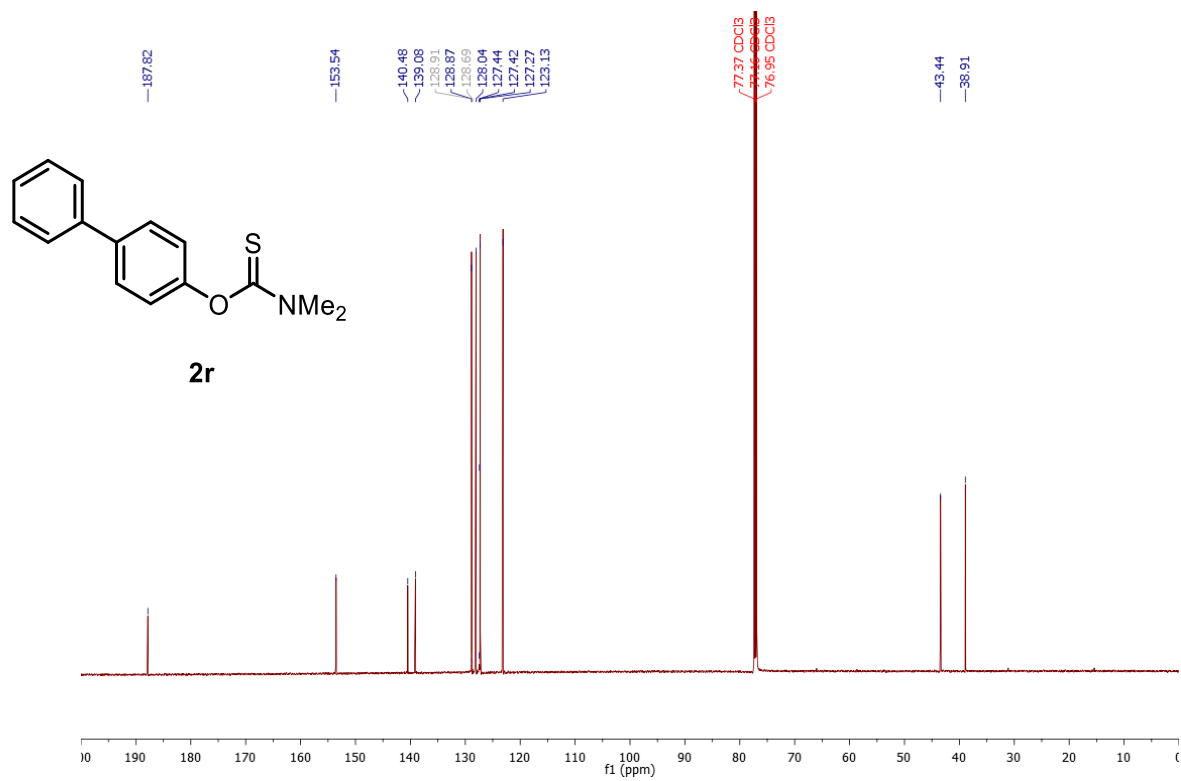
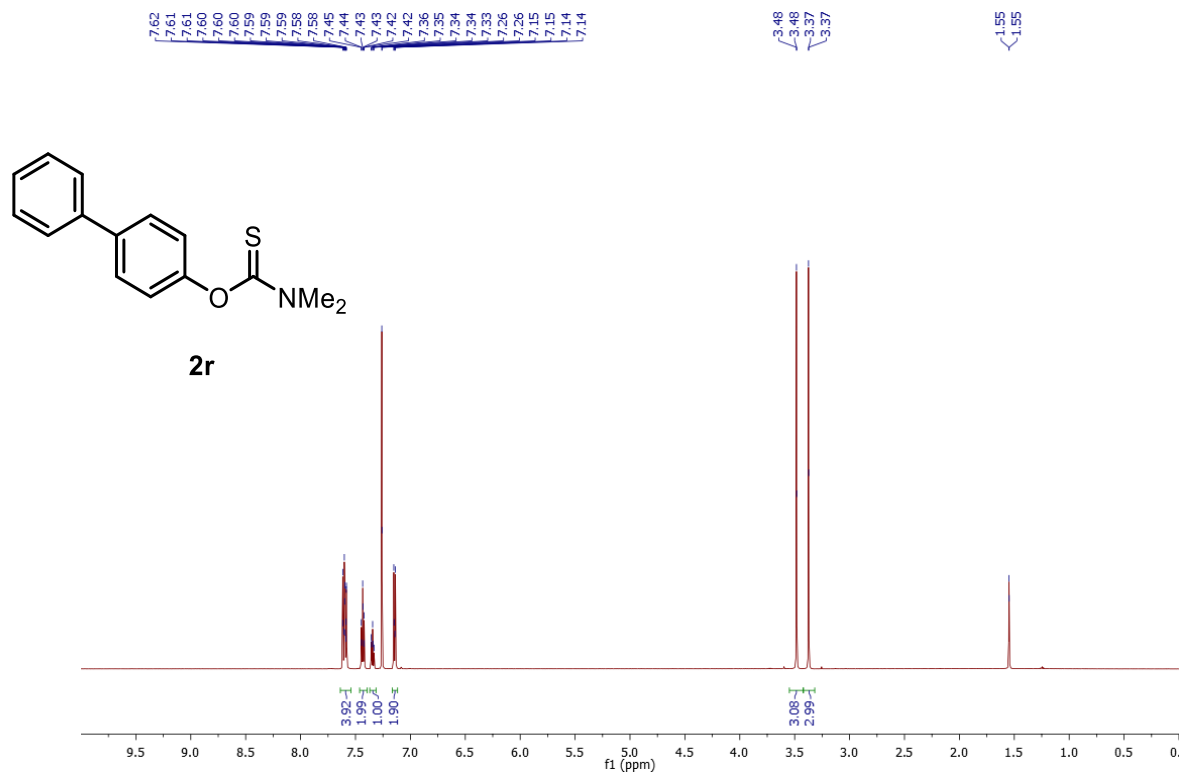


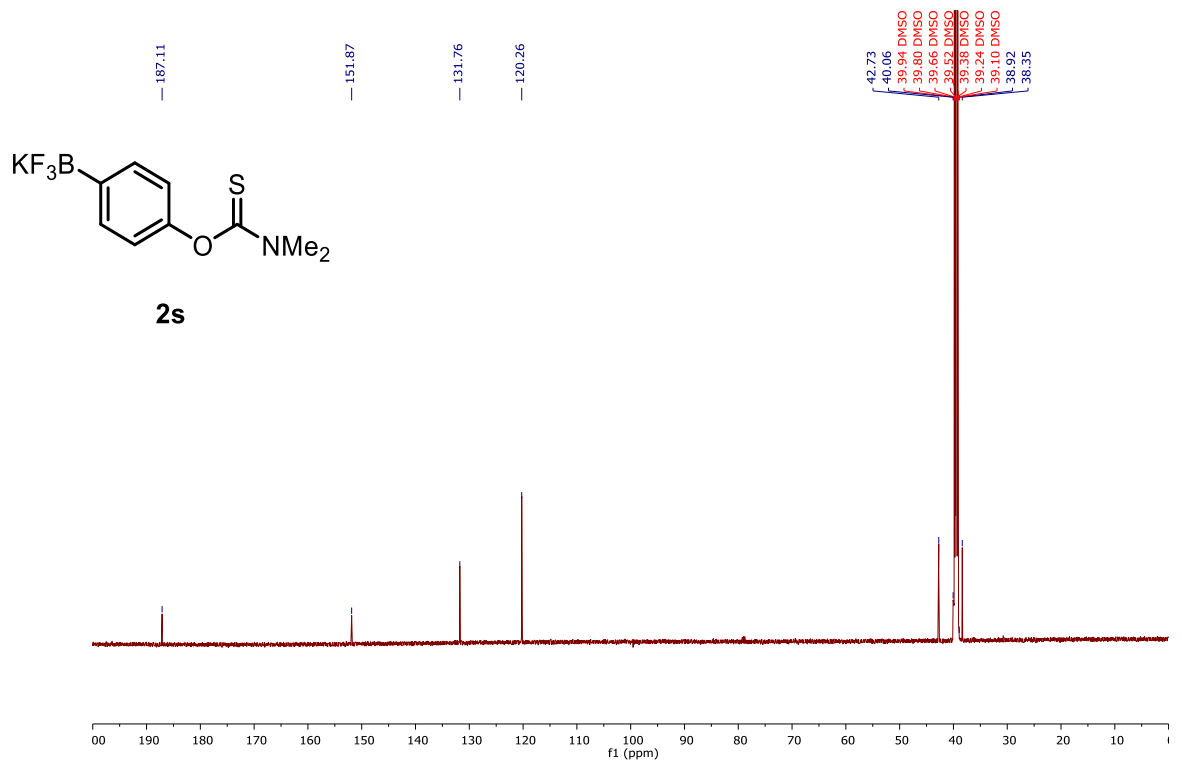
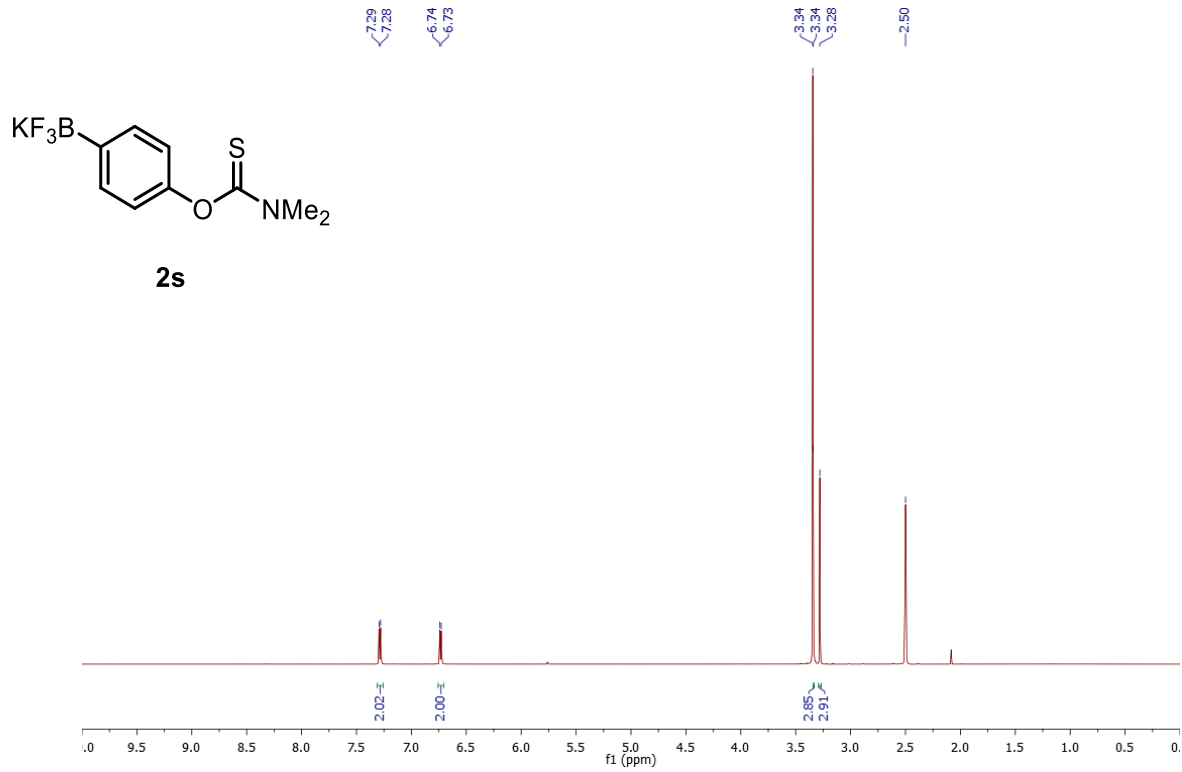


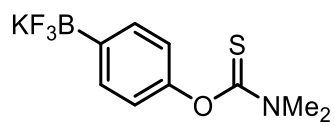




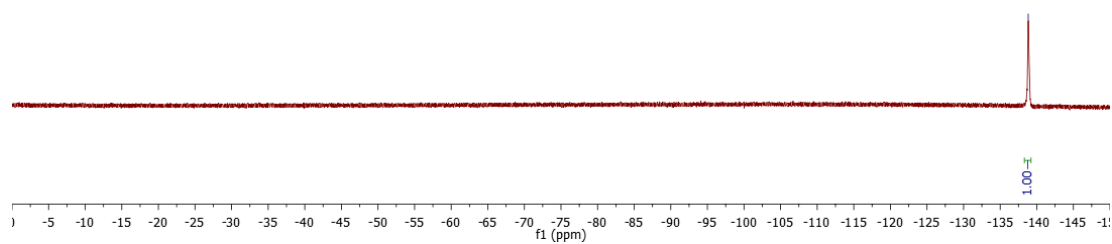


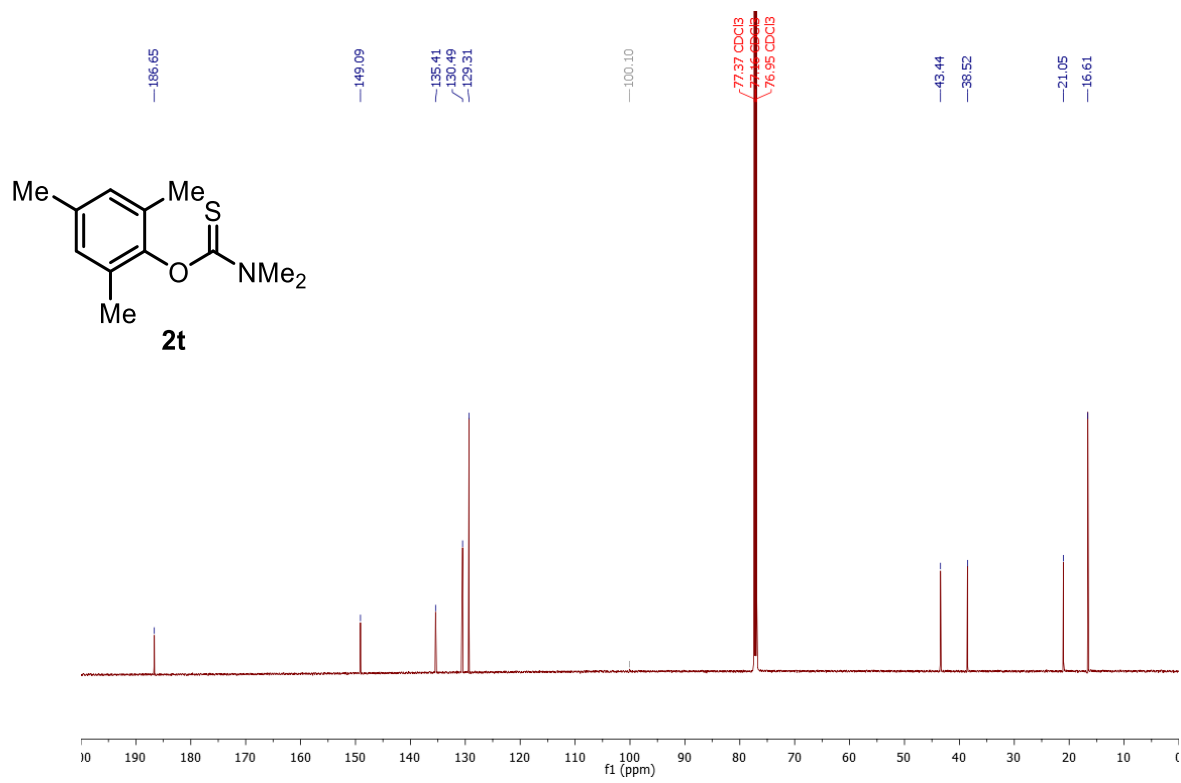
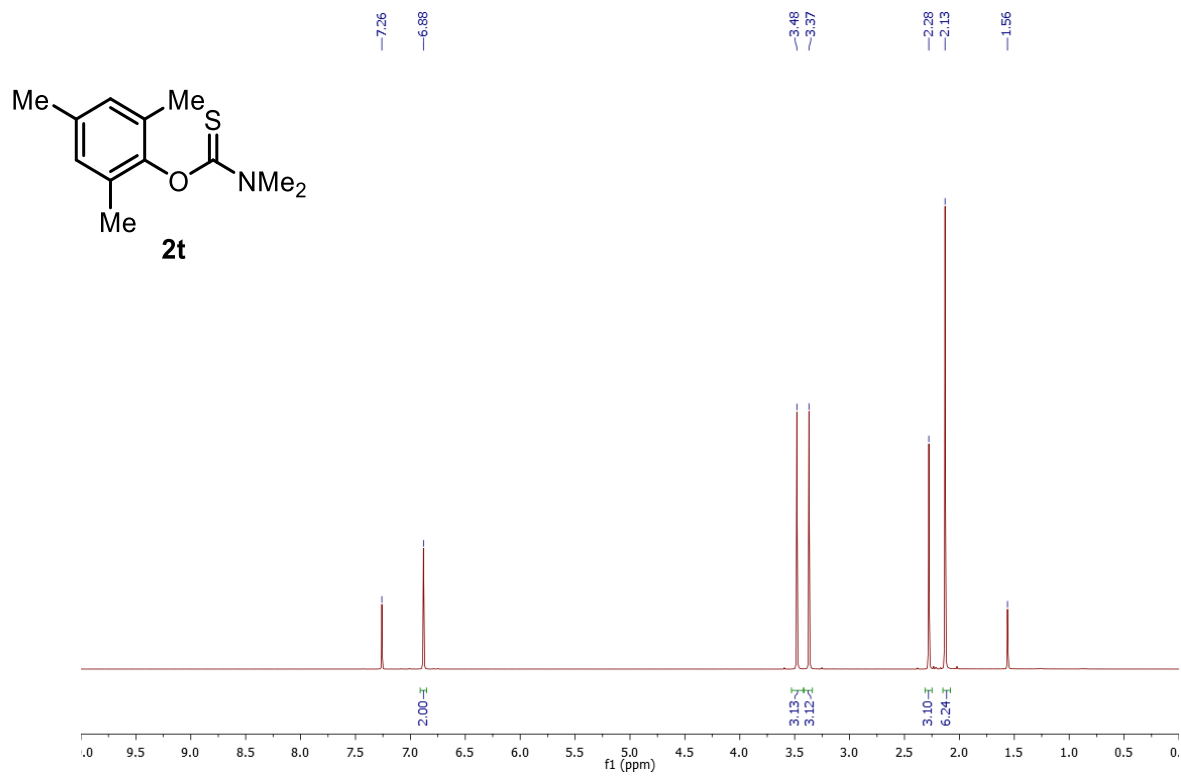




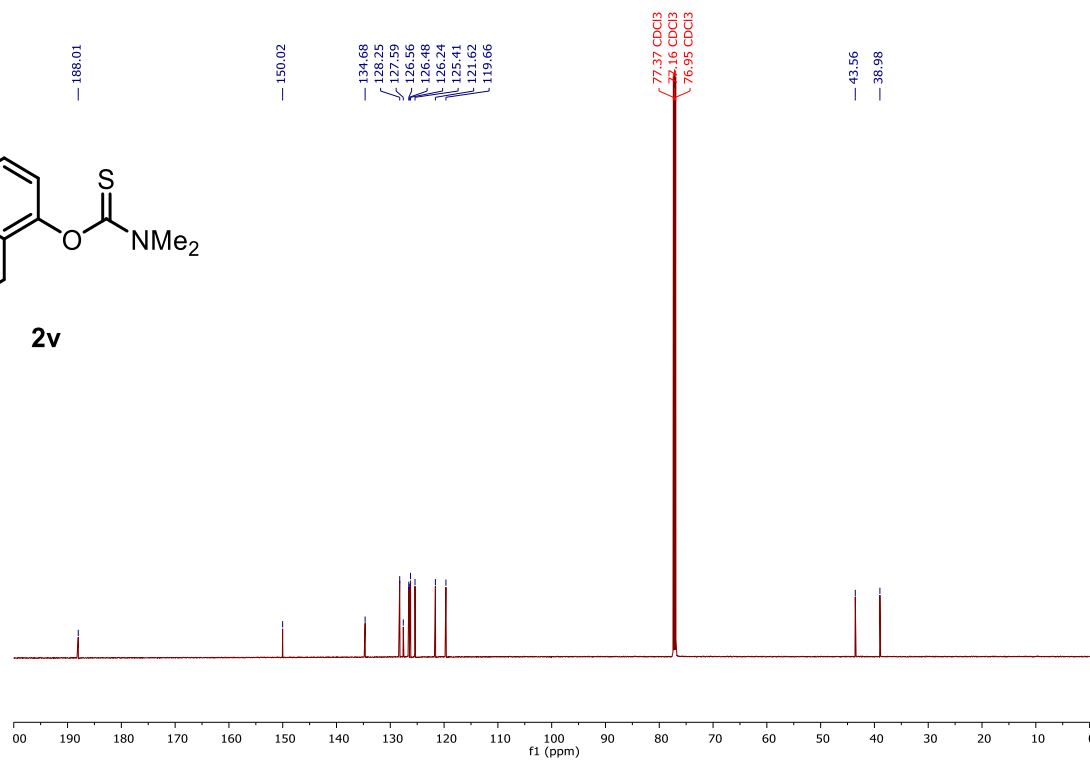
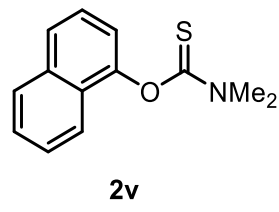
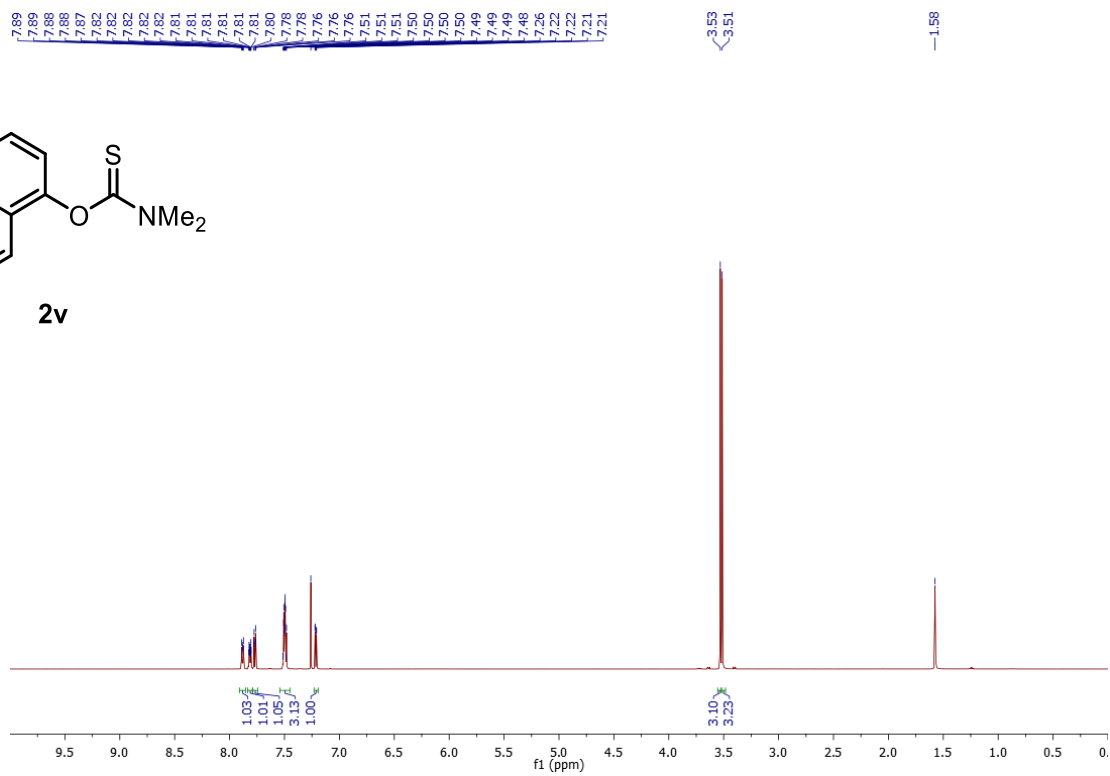
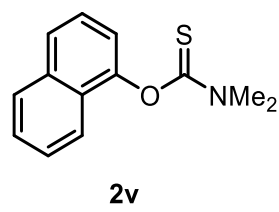


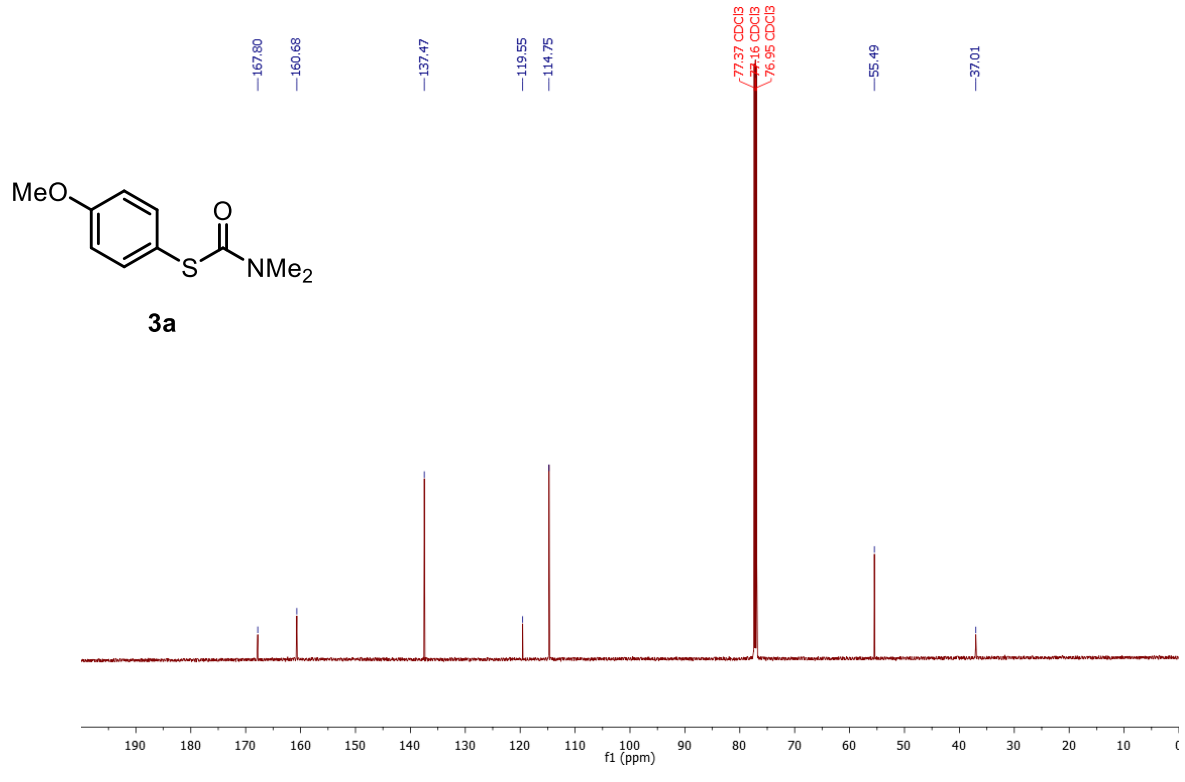
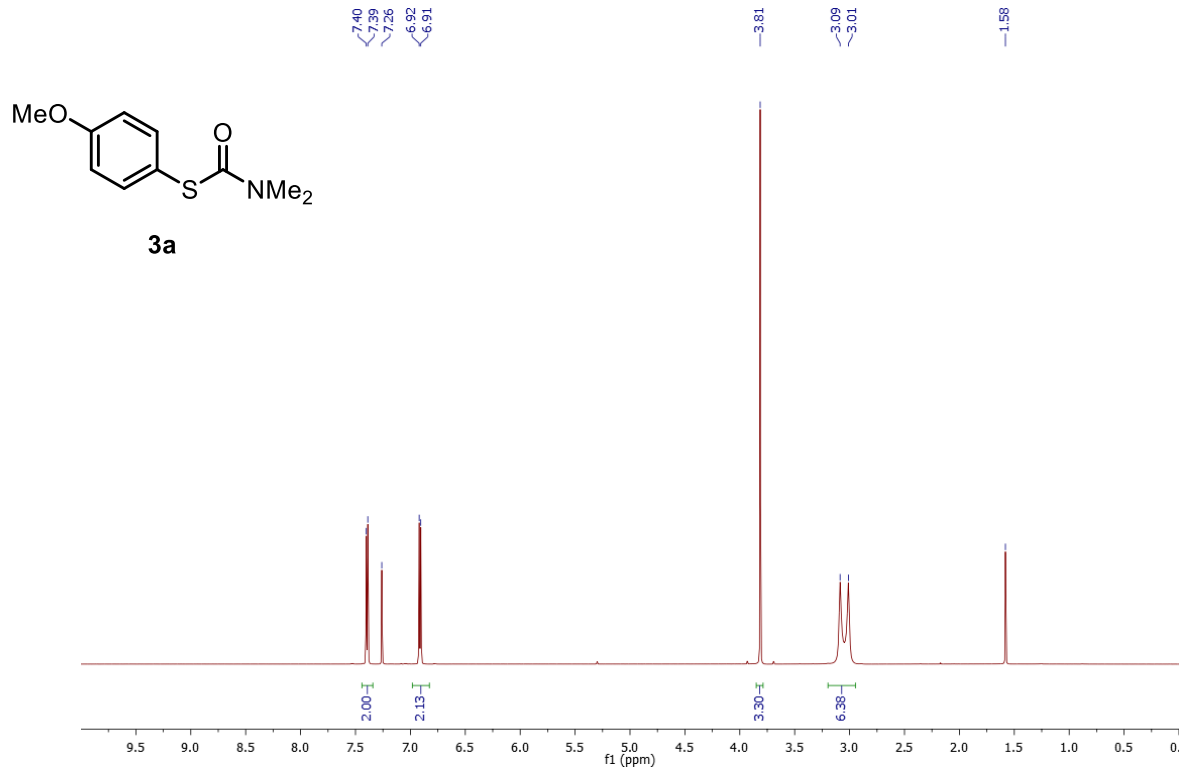
**2s**

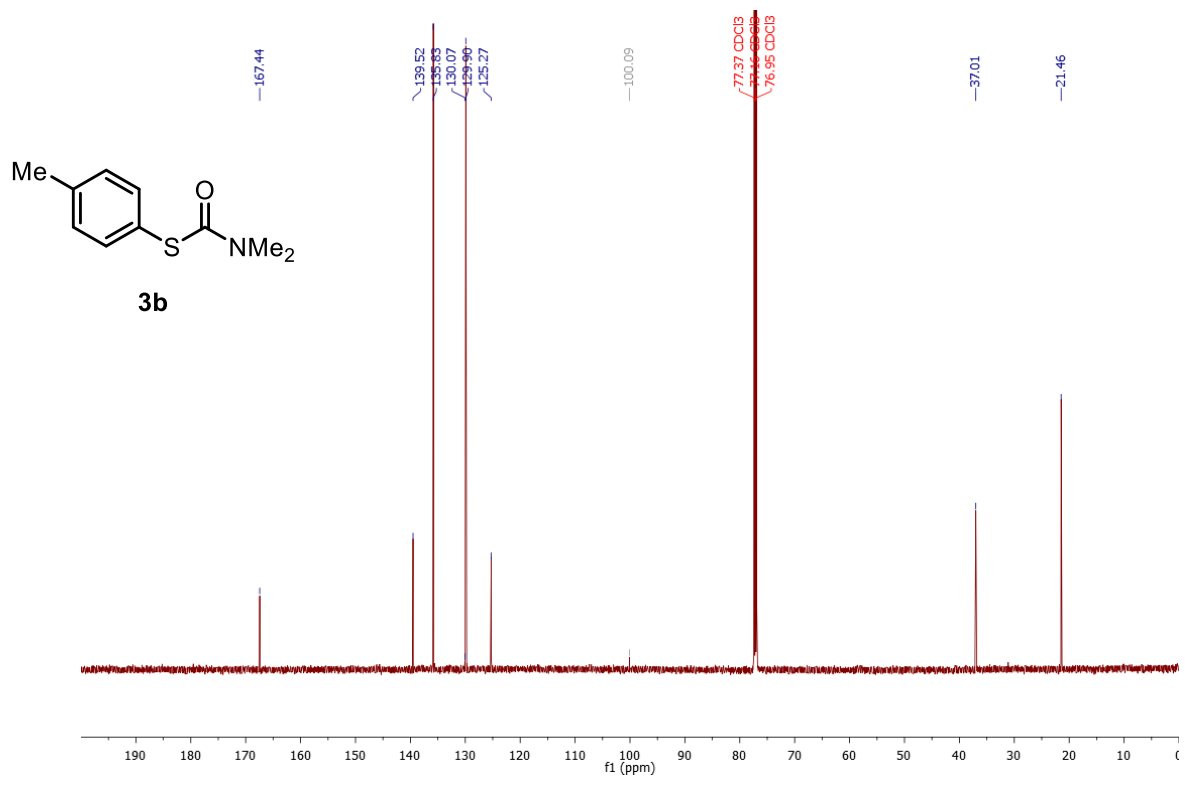
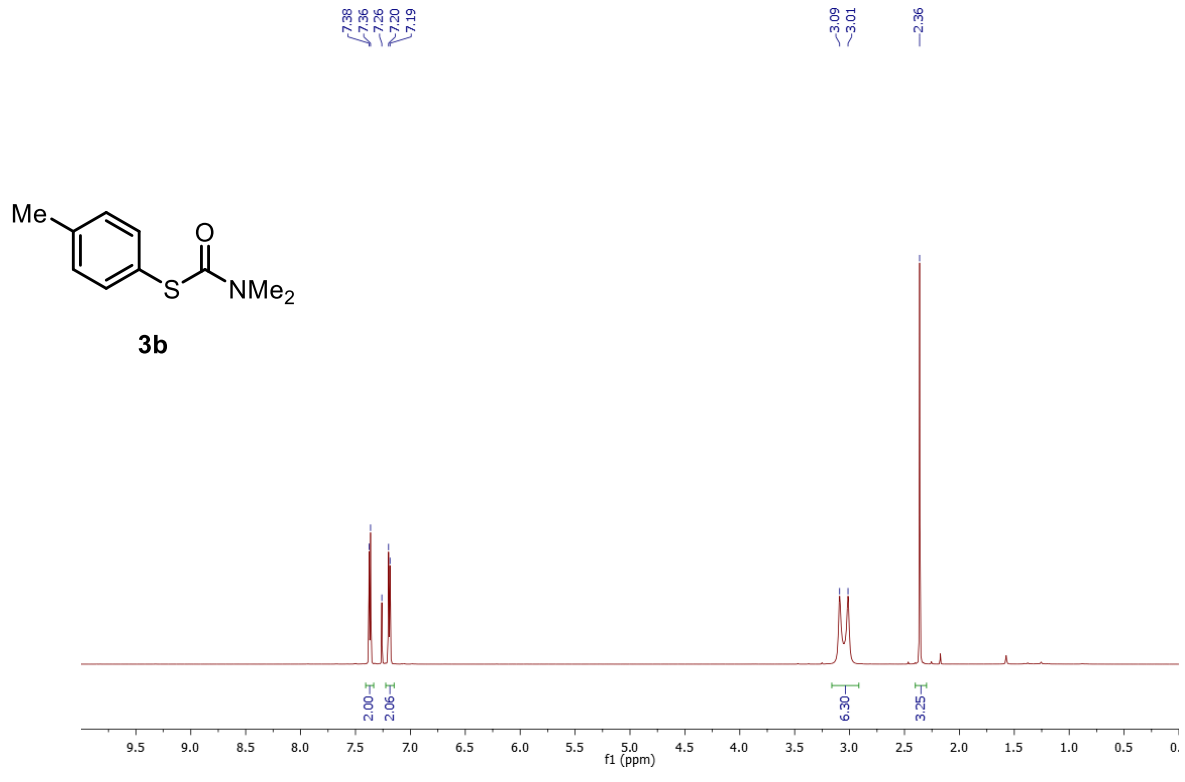


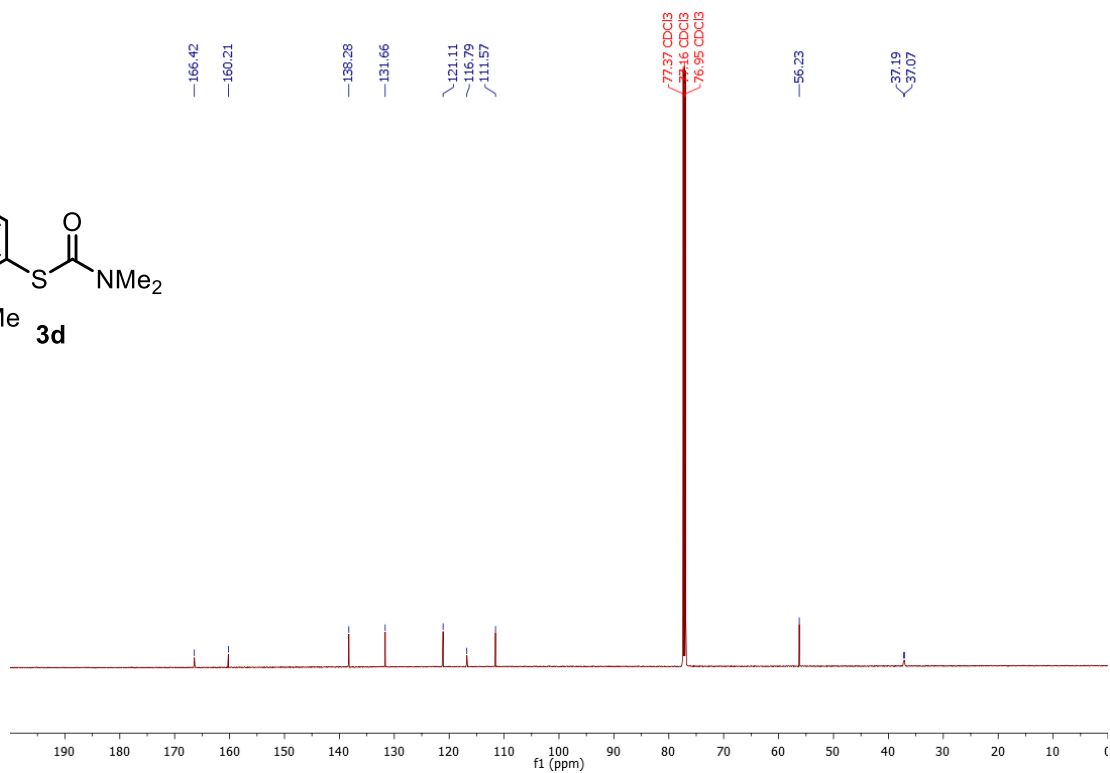
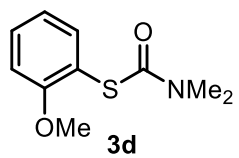
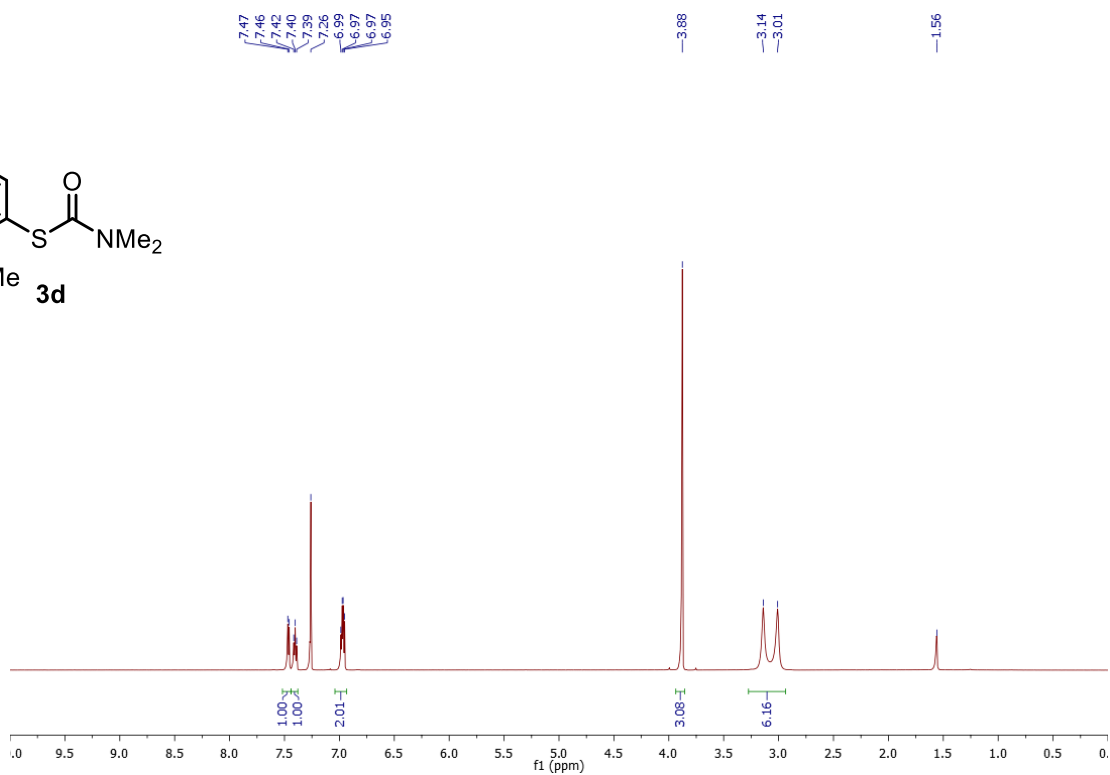
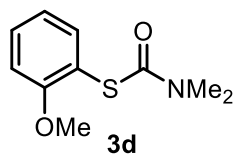


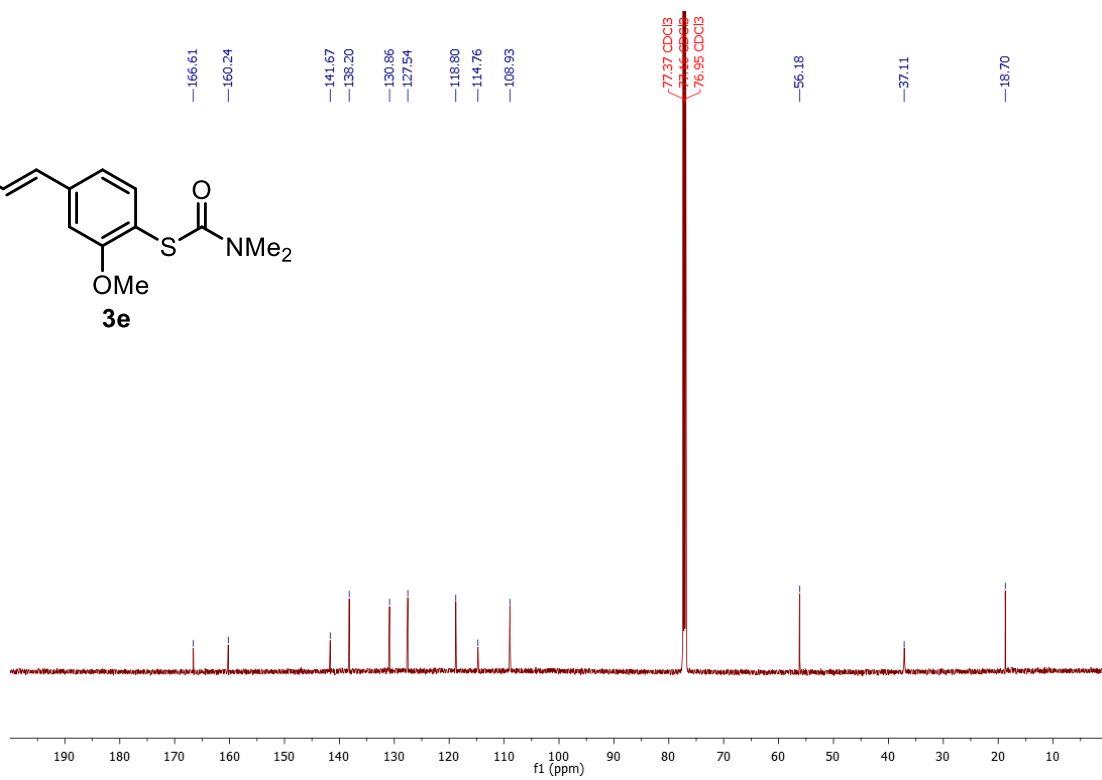
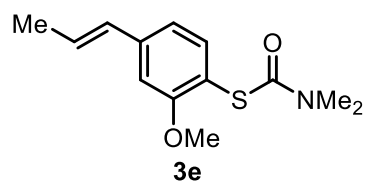
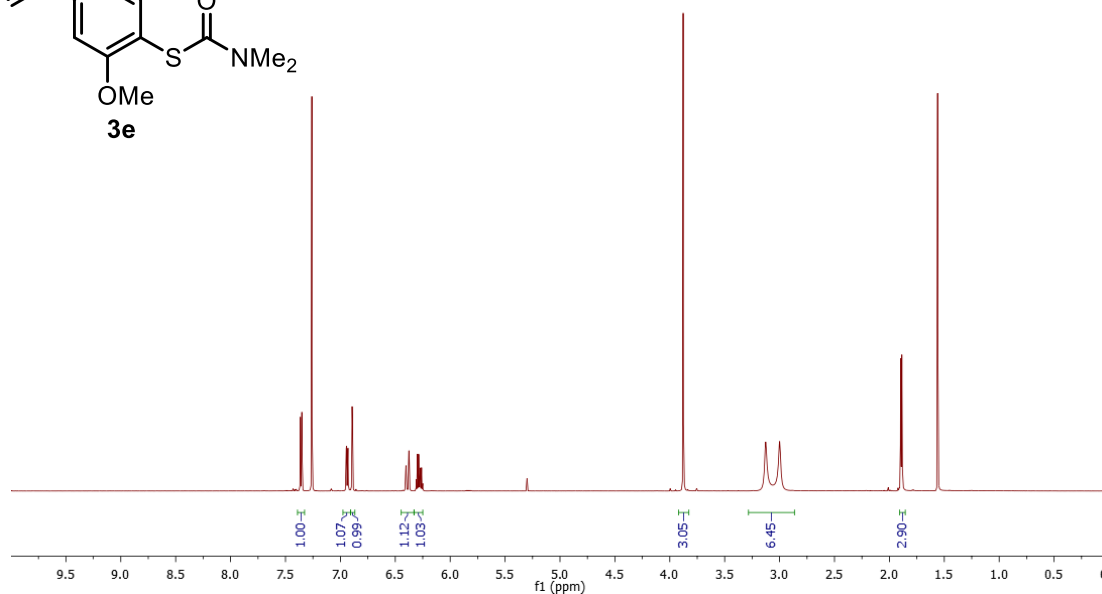
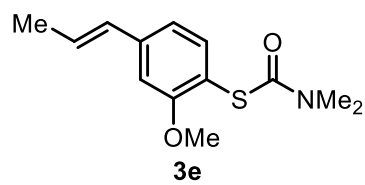


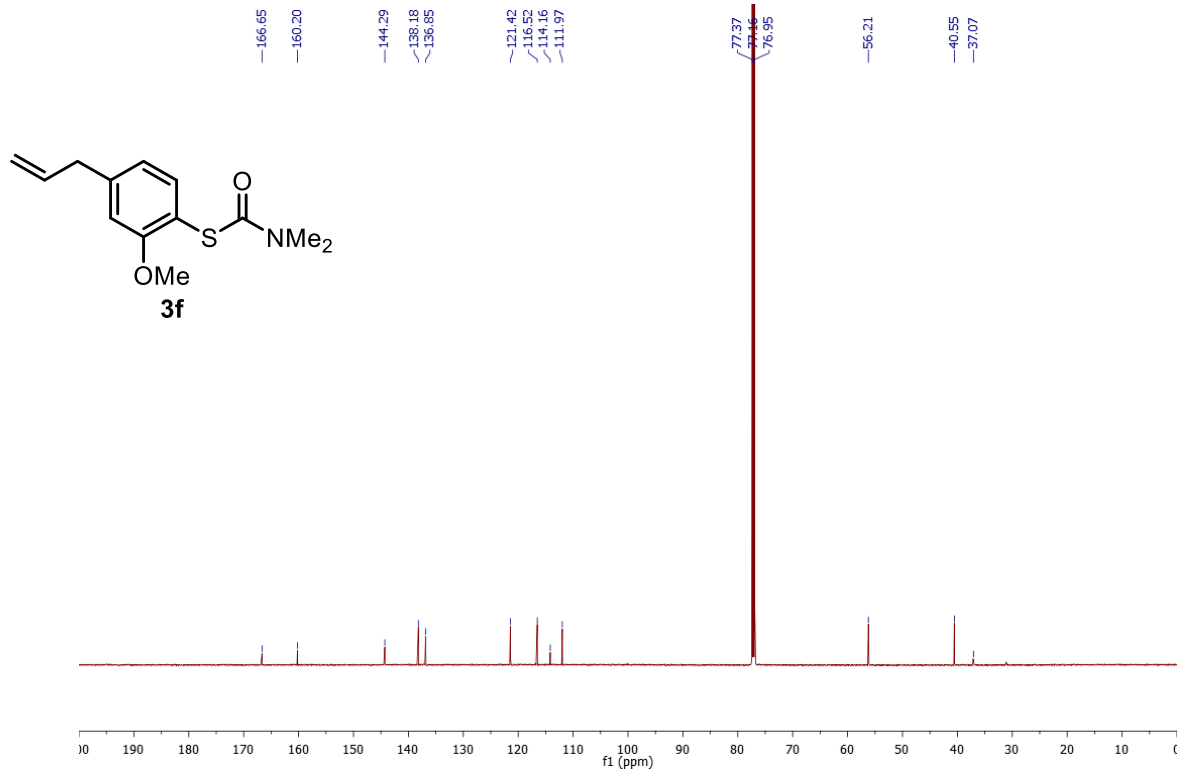
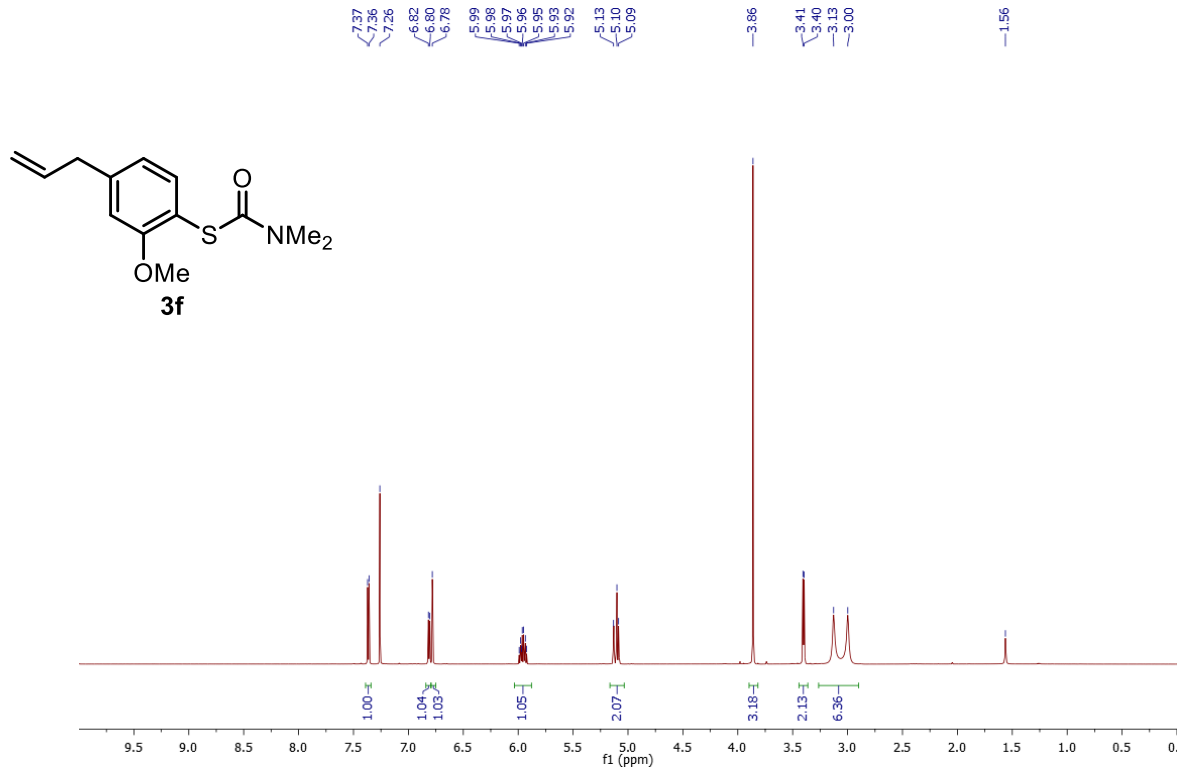


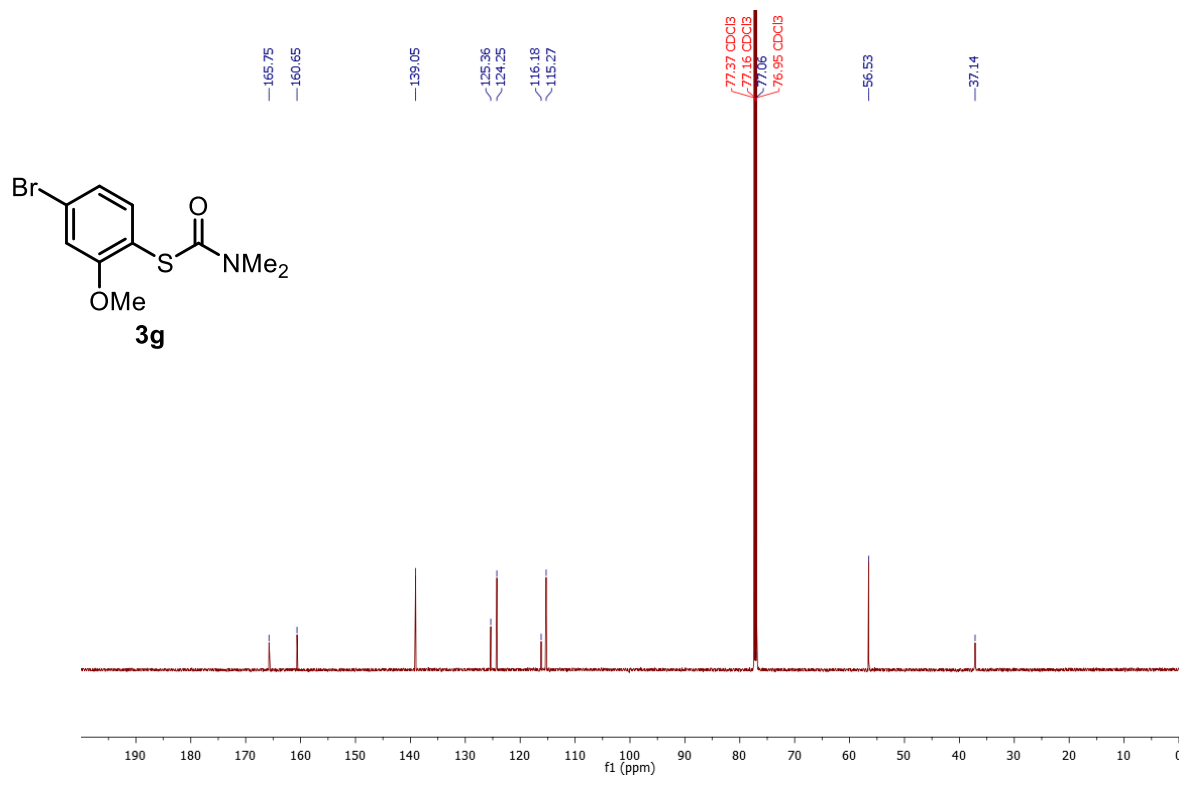
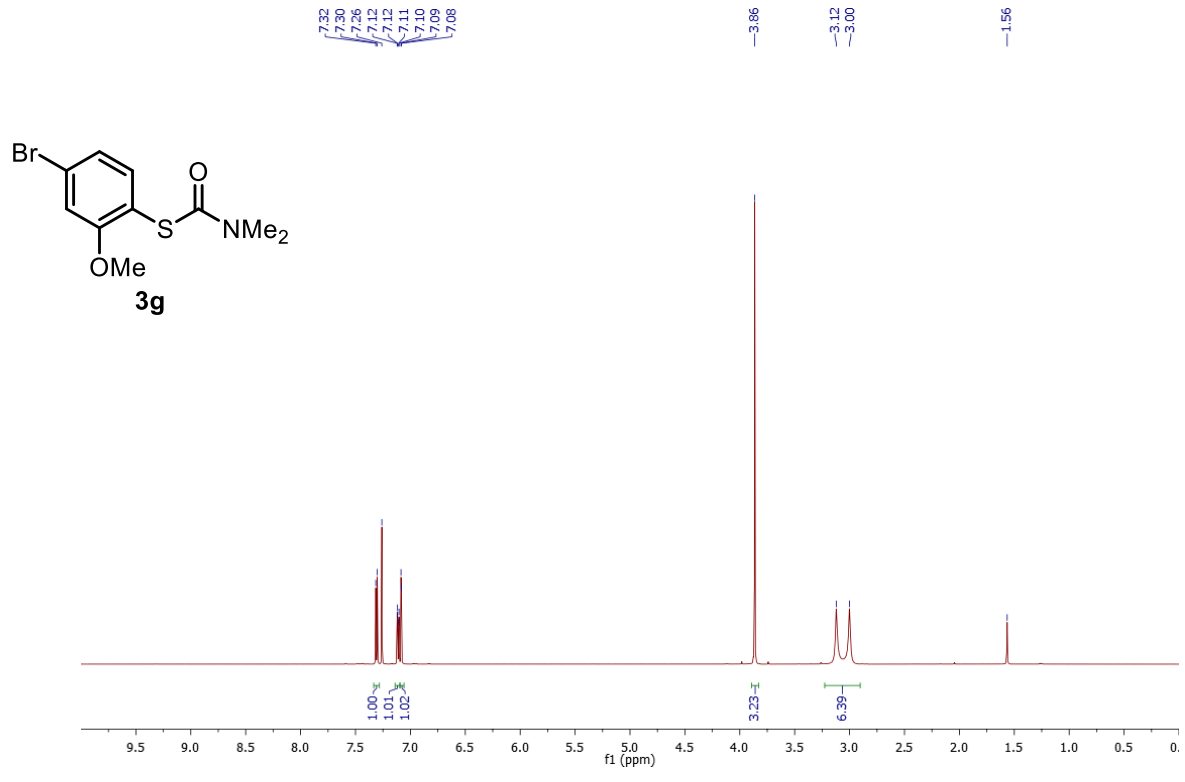


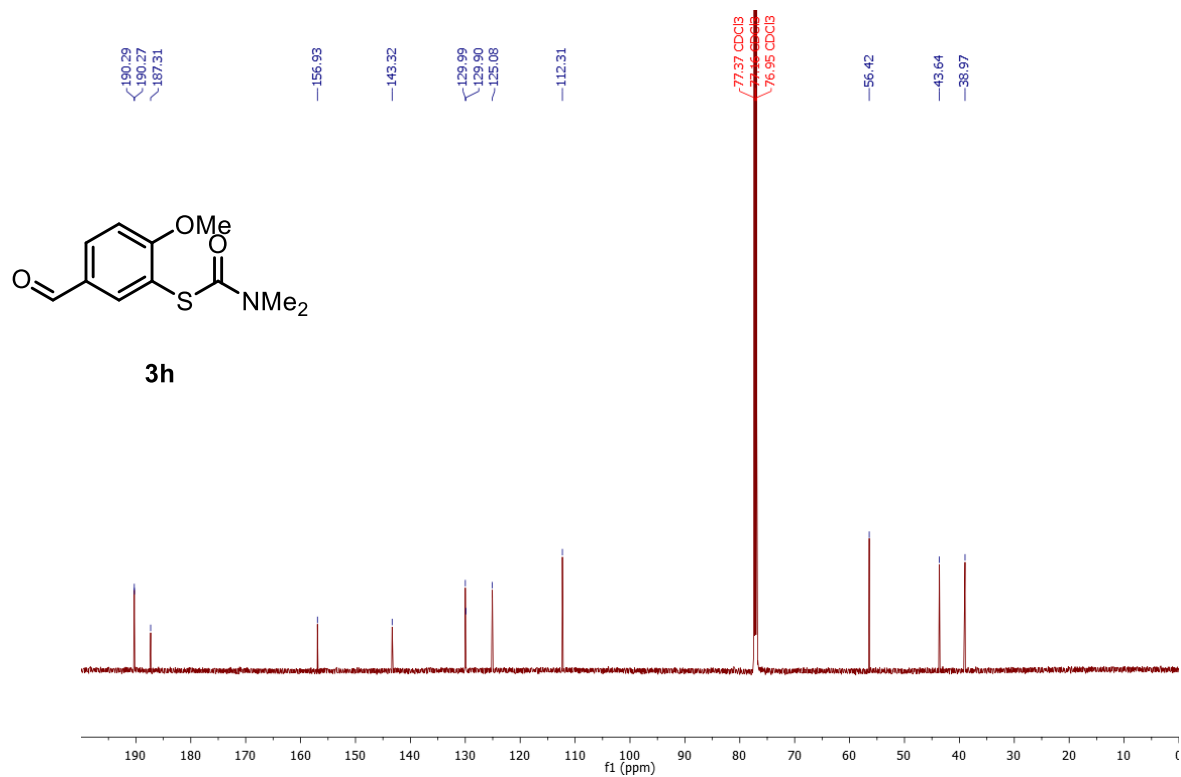
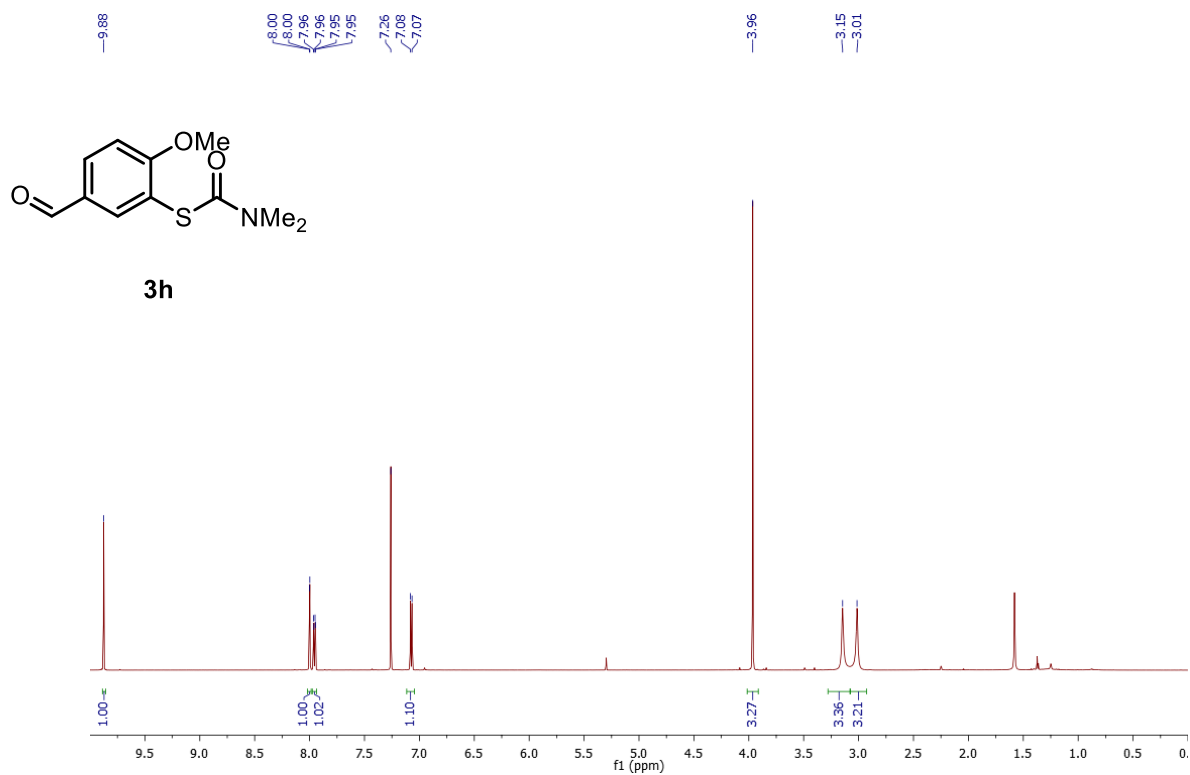


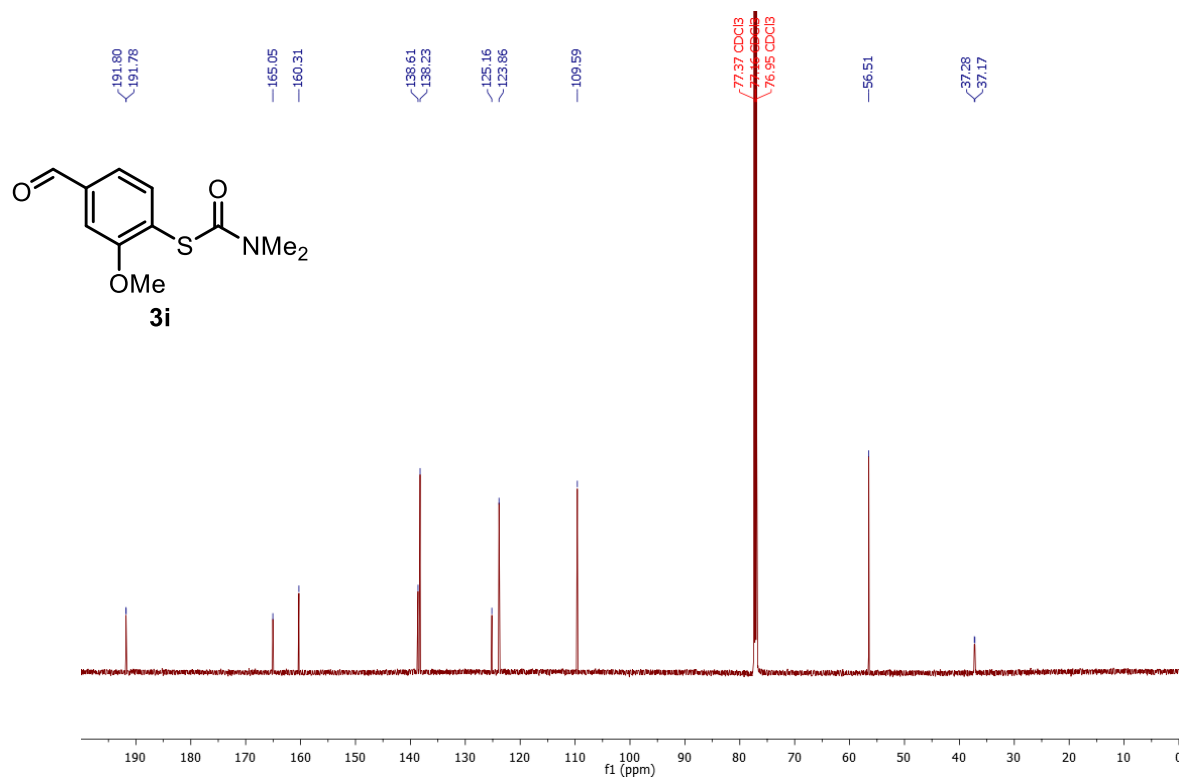
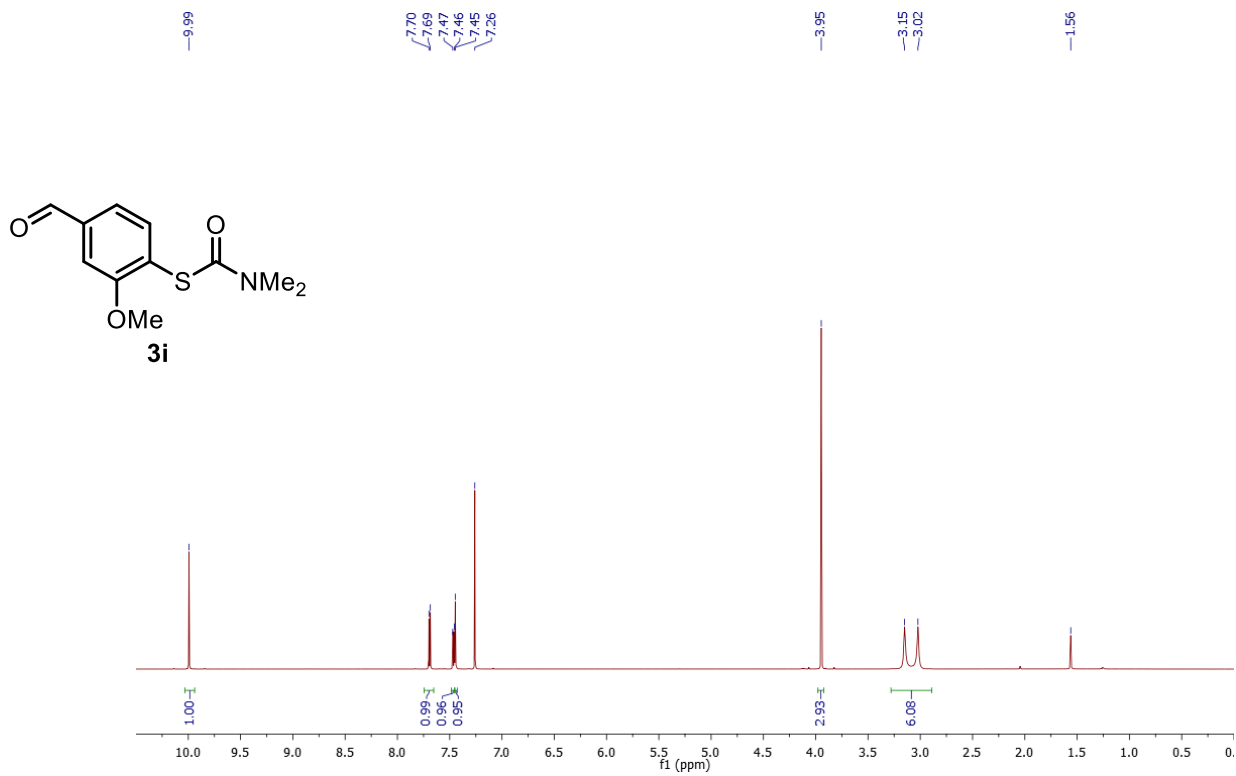


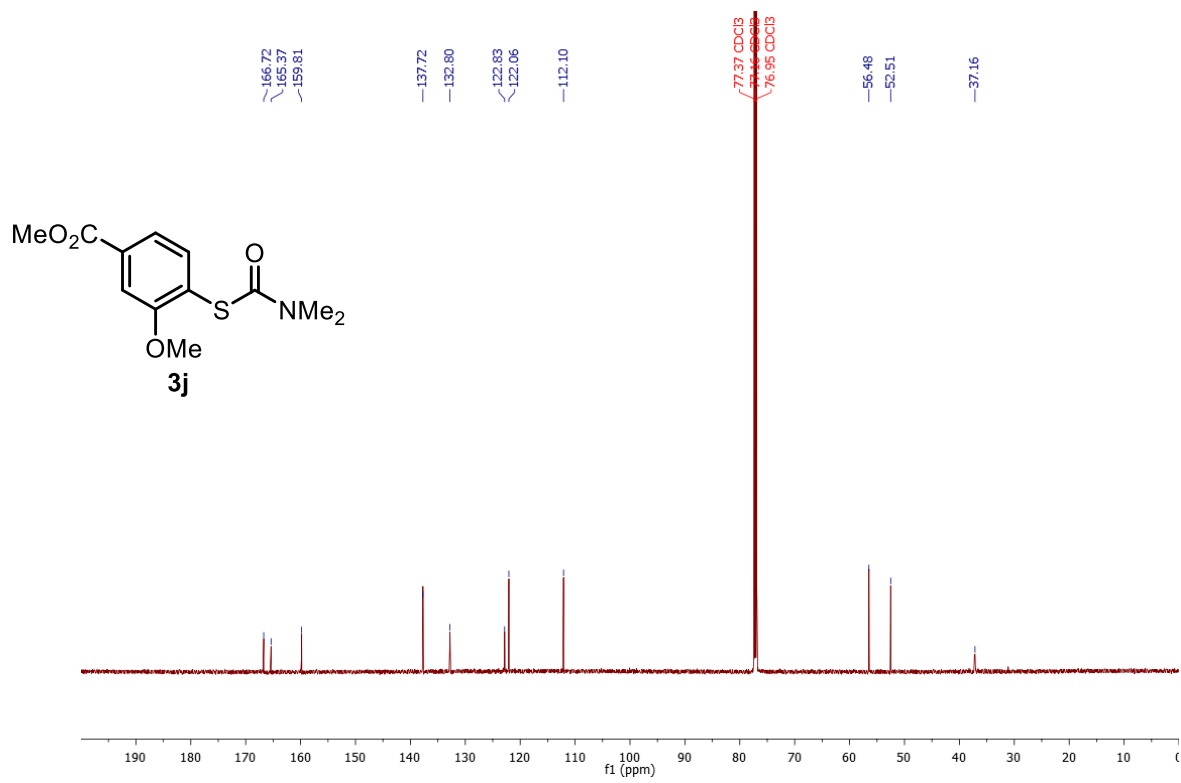
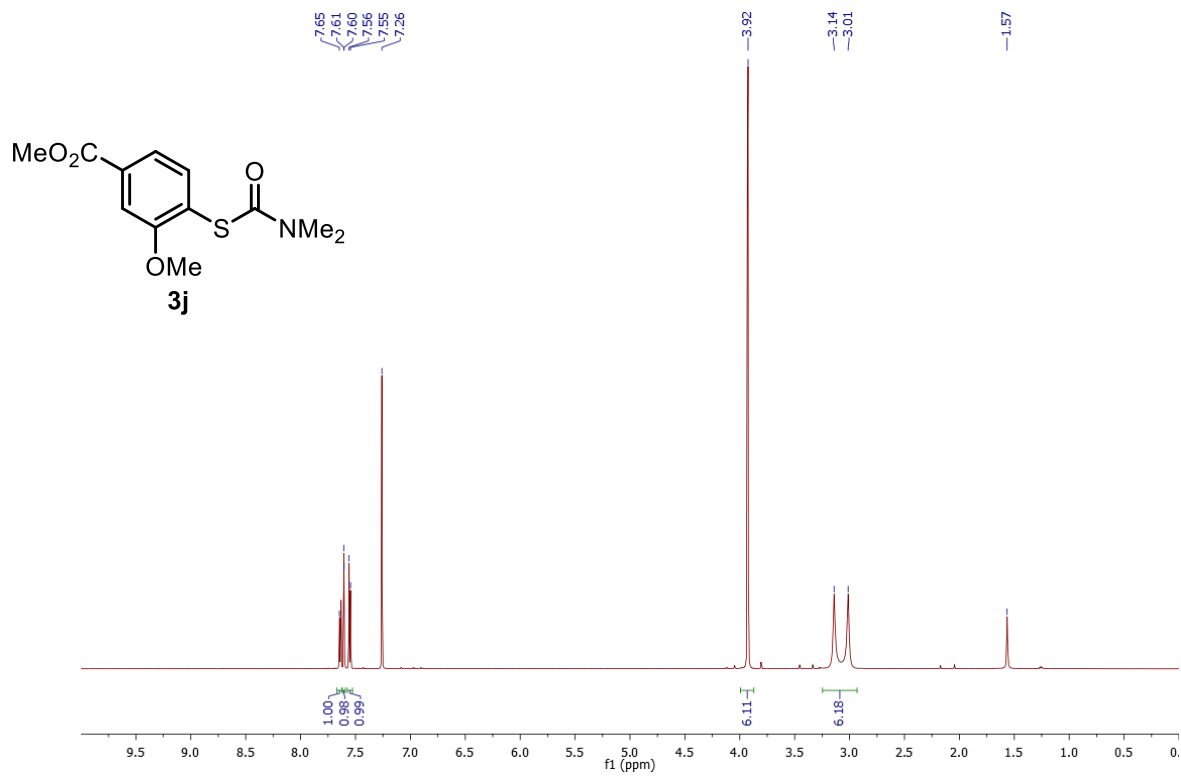


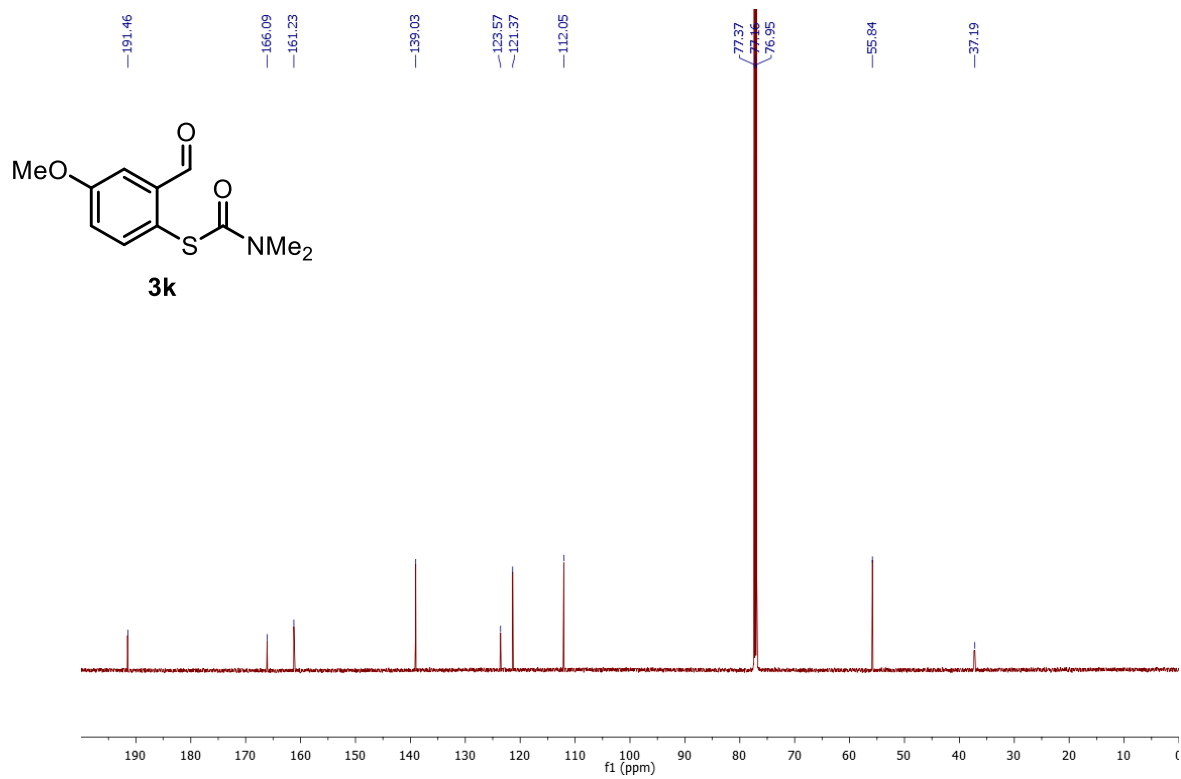
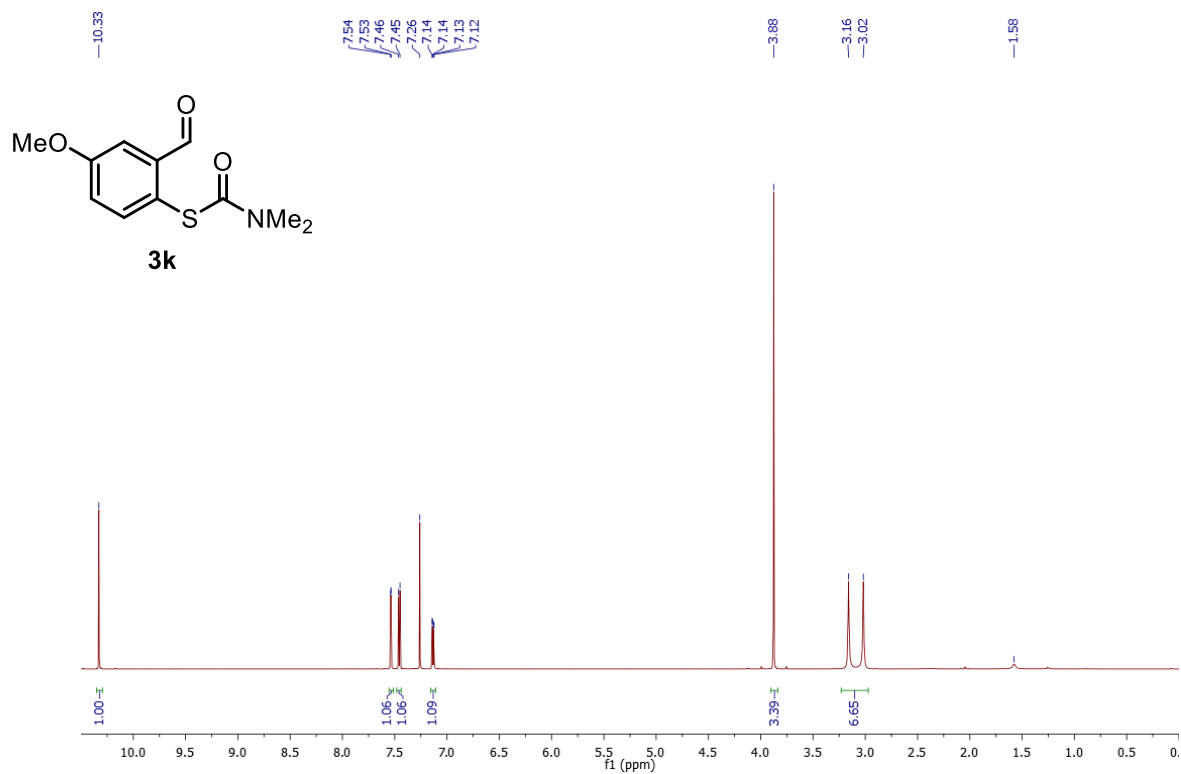


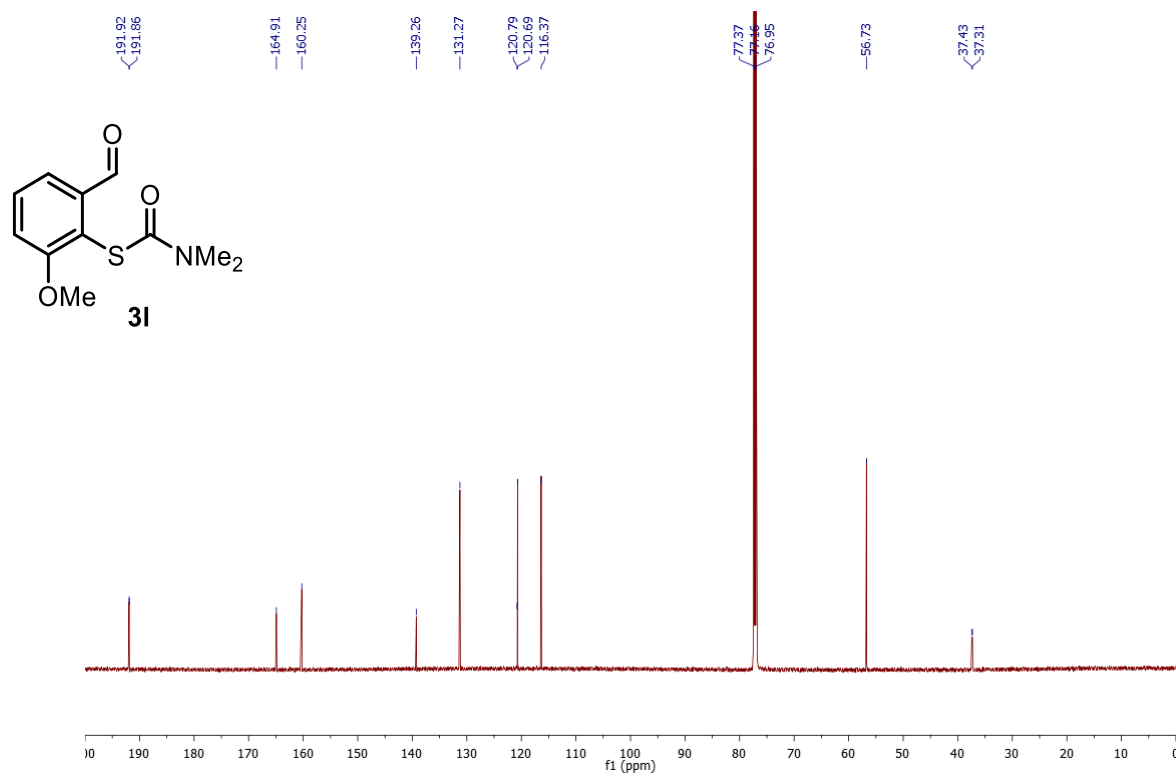
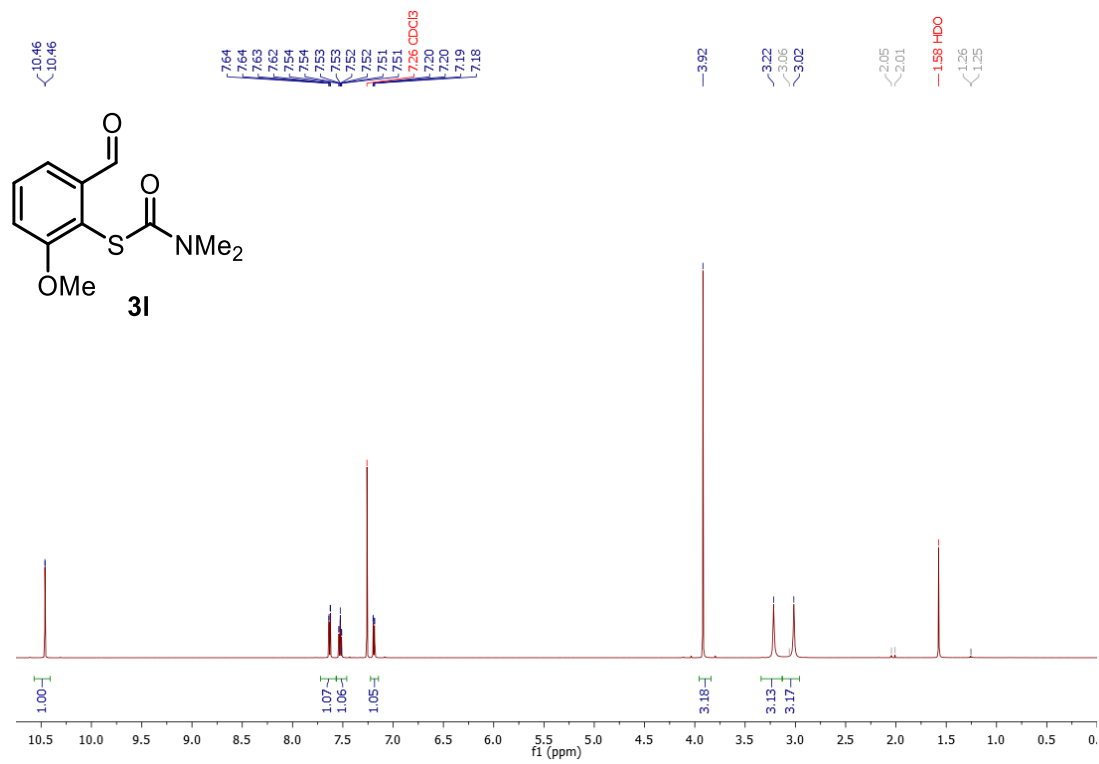


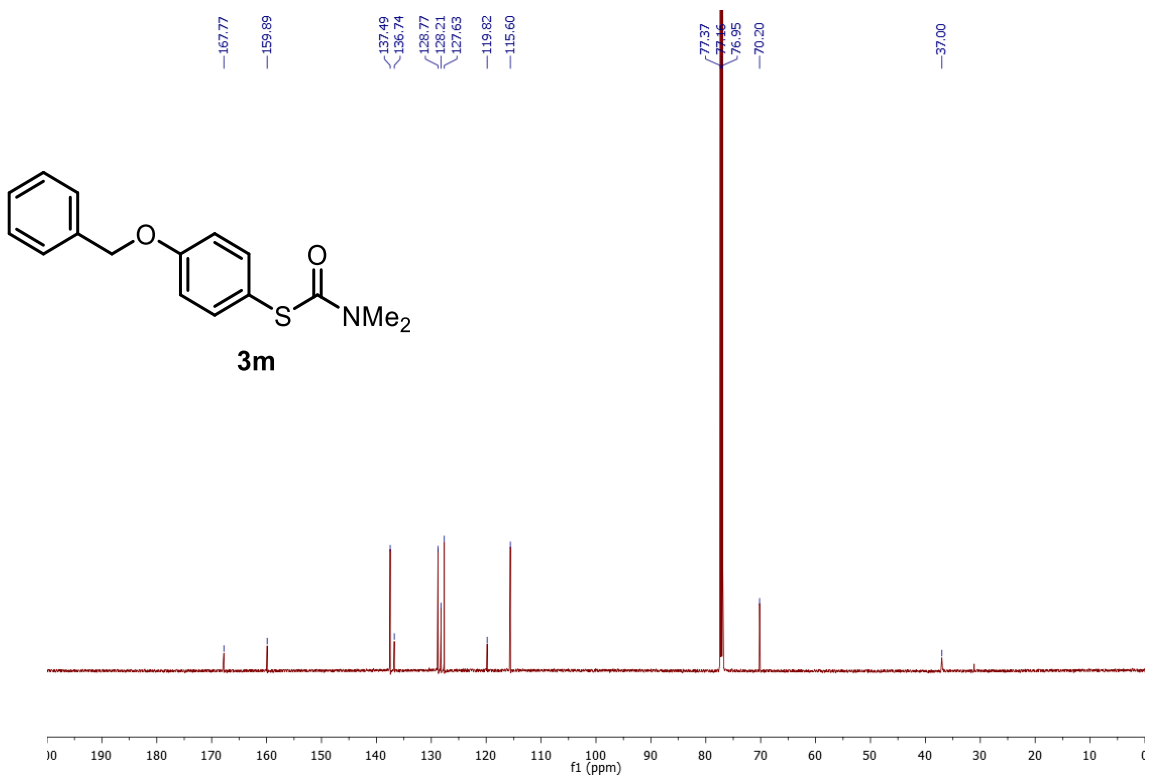
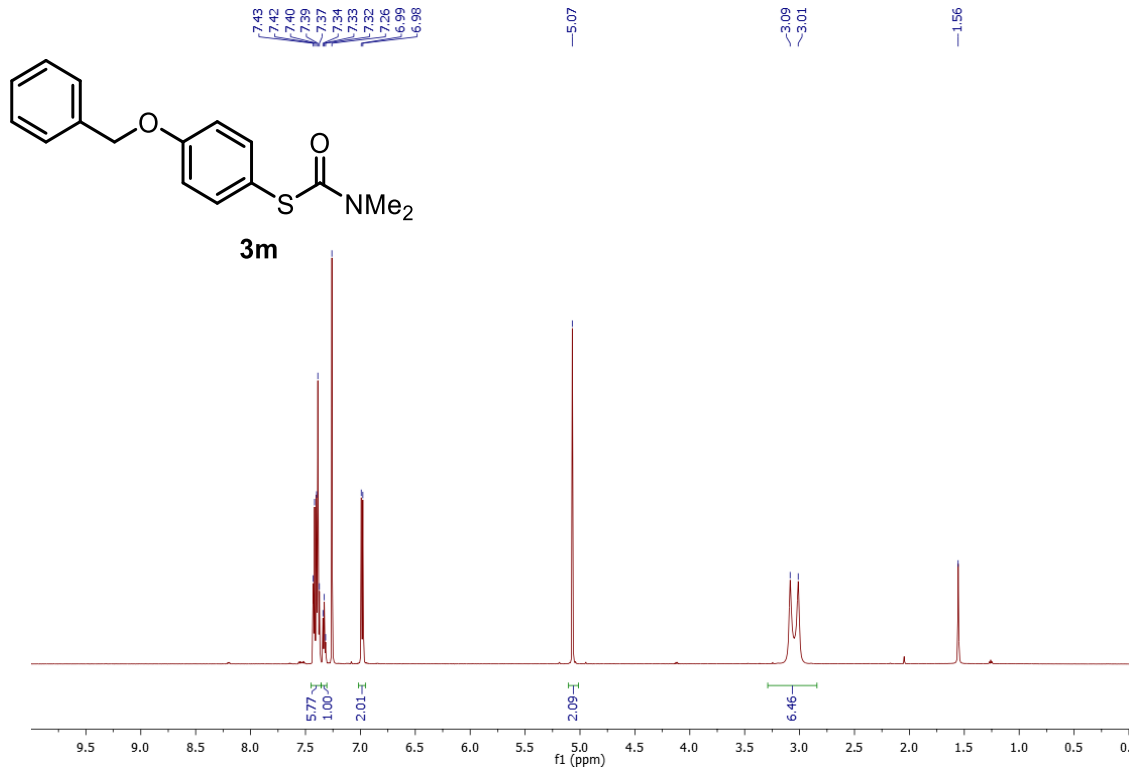


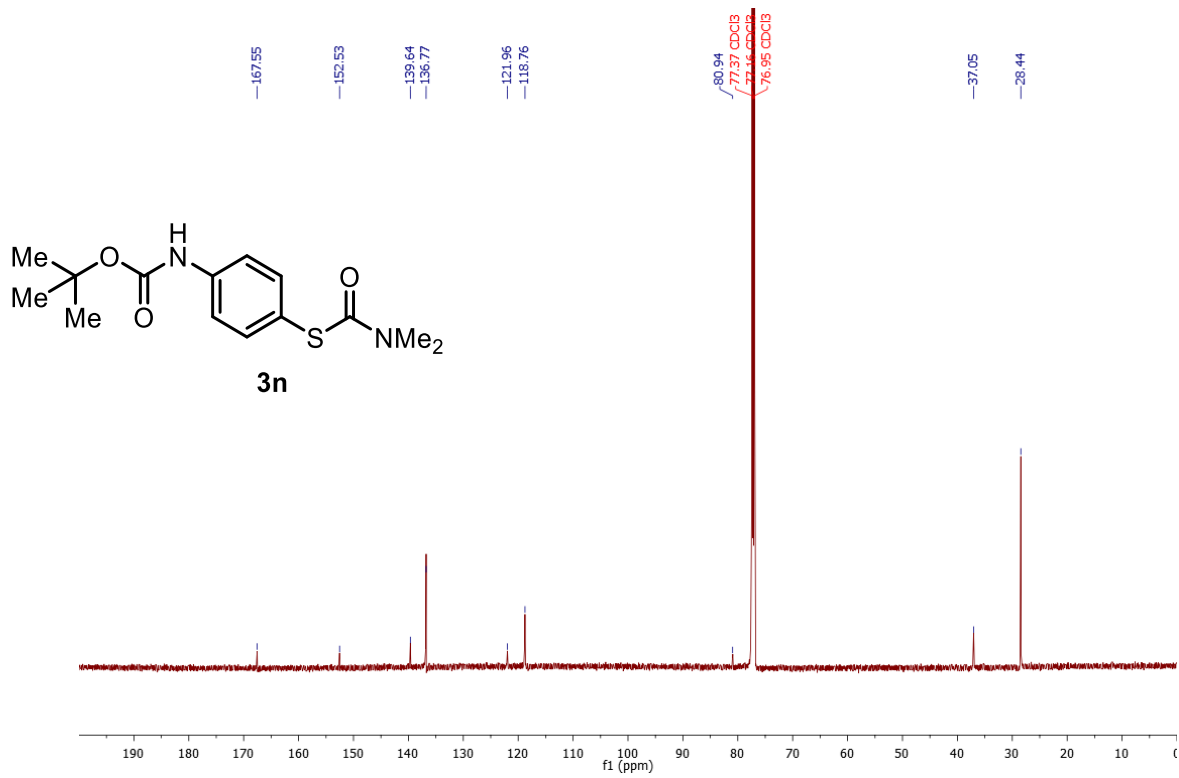
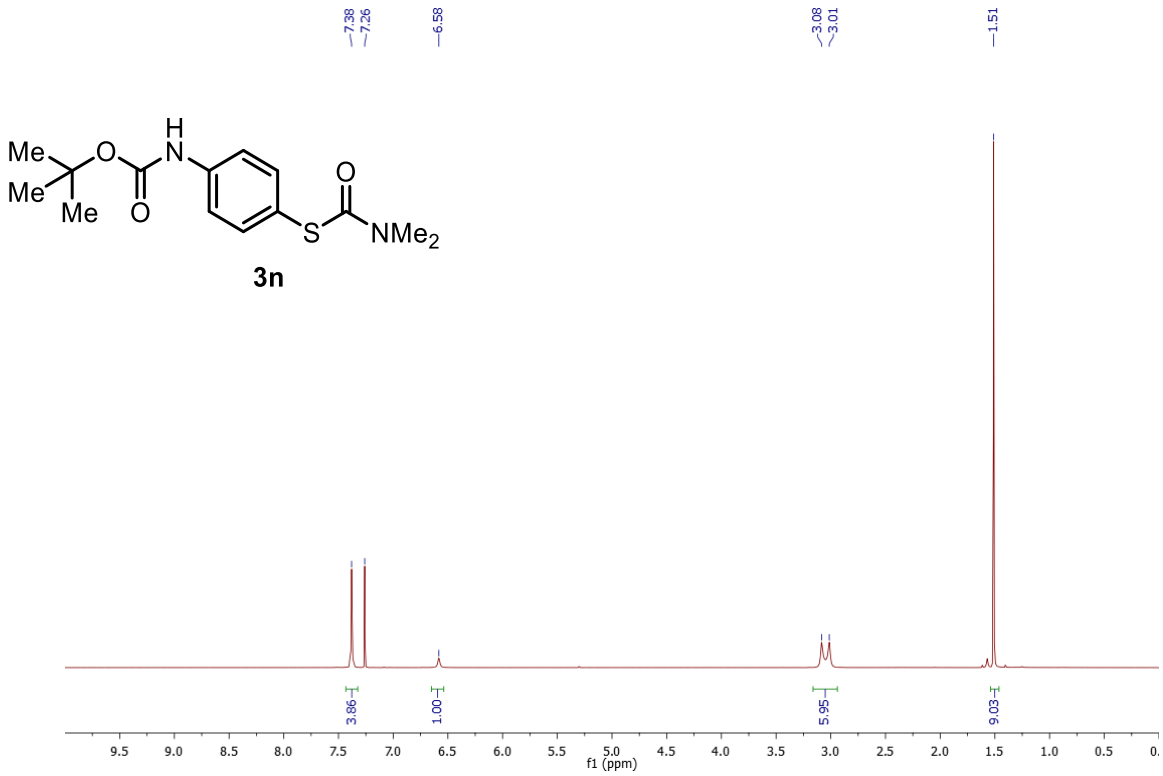


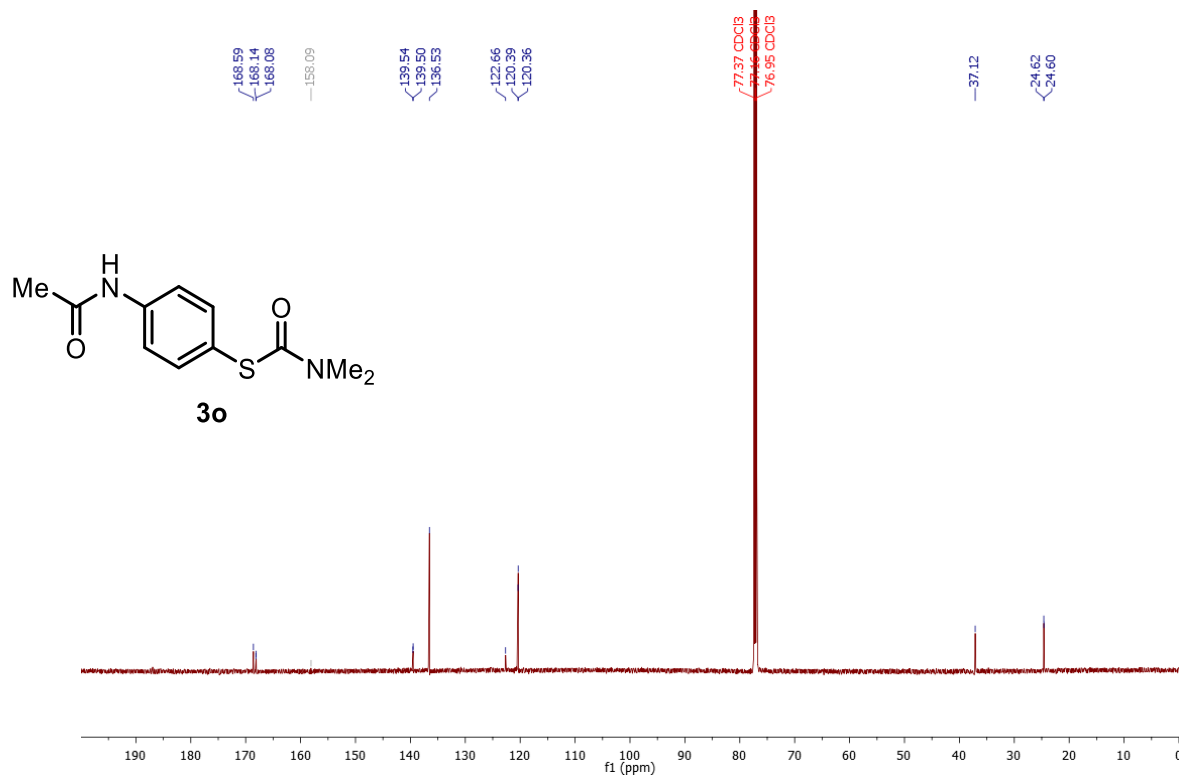
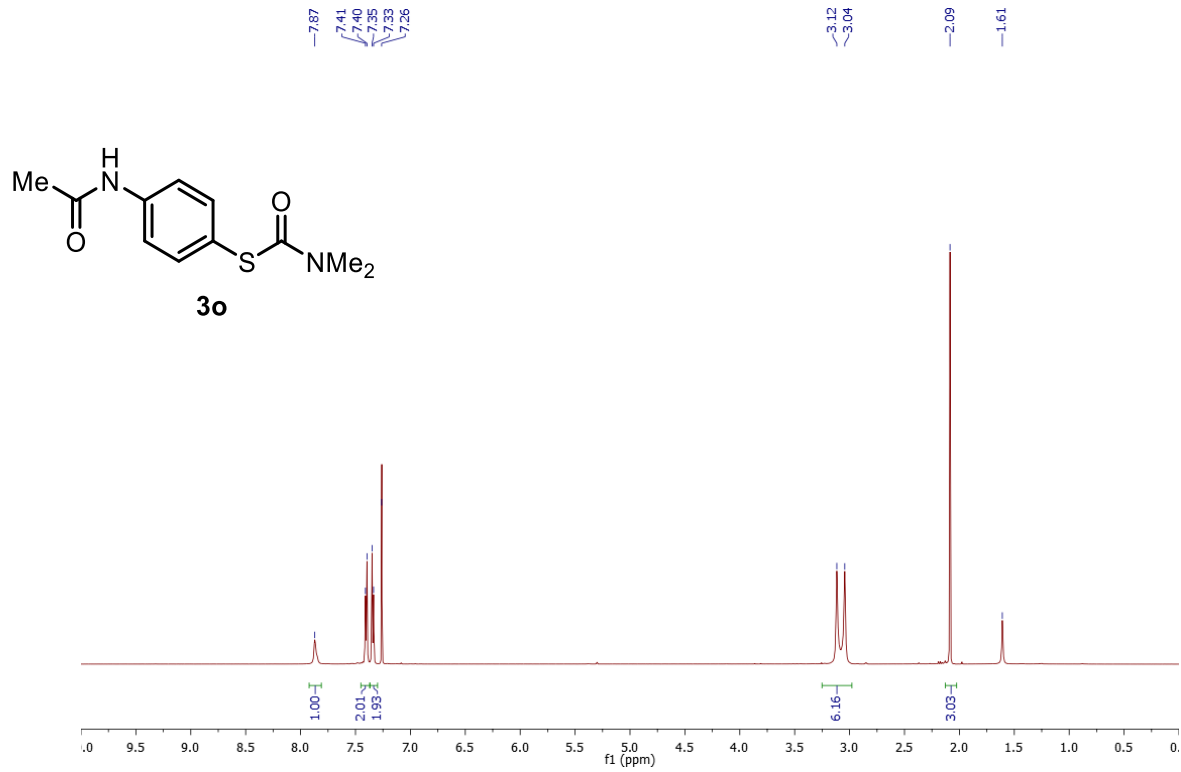


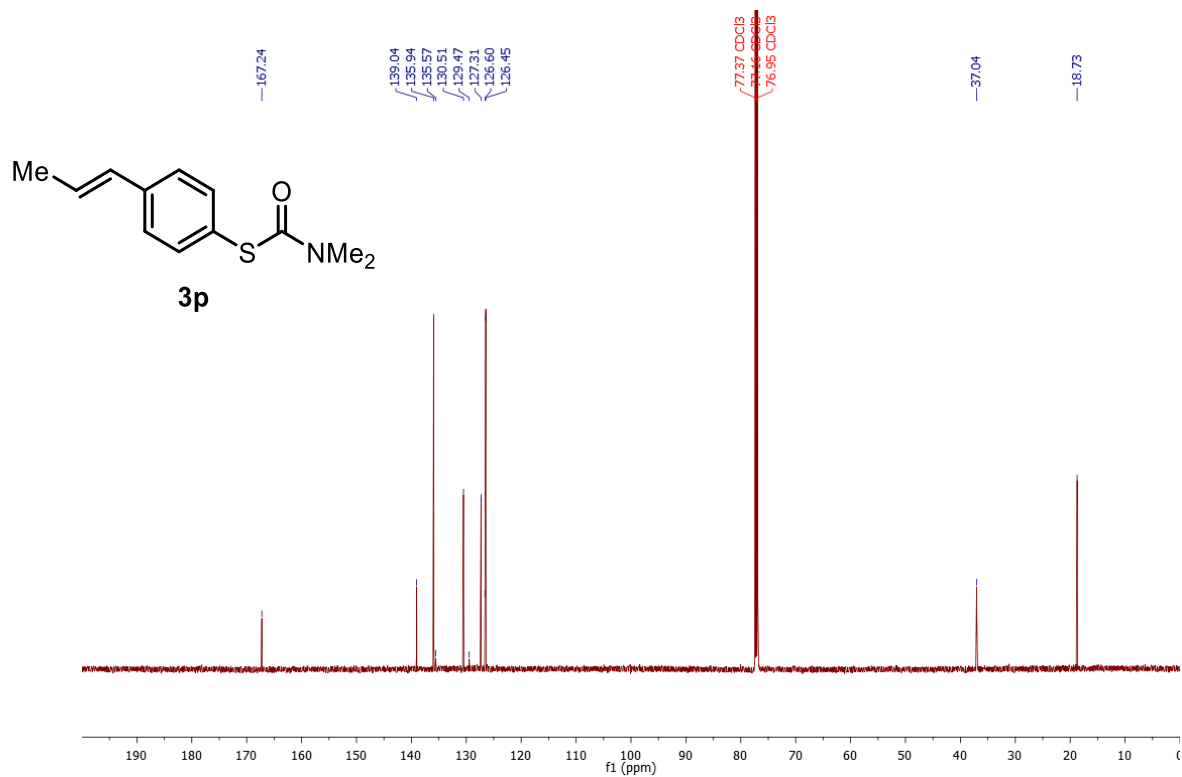
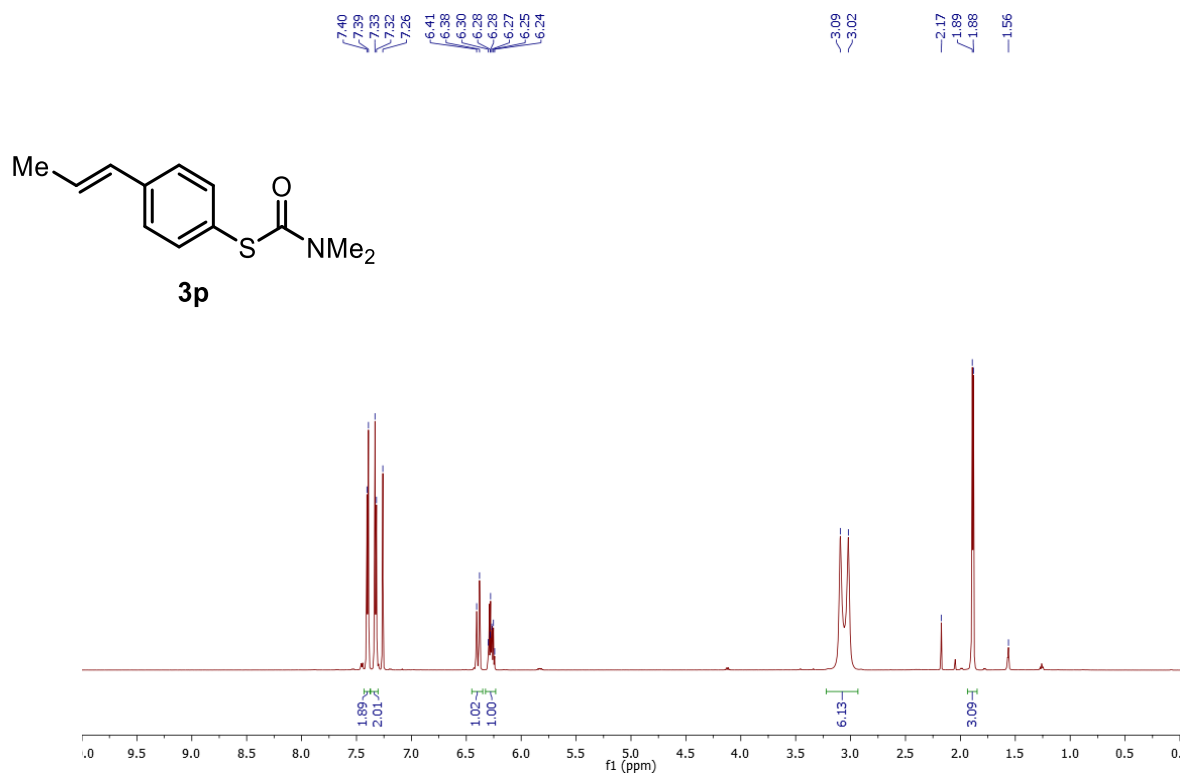


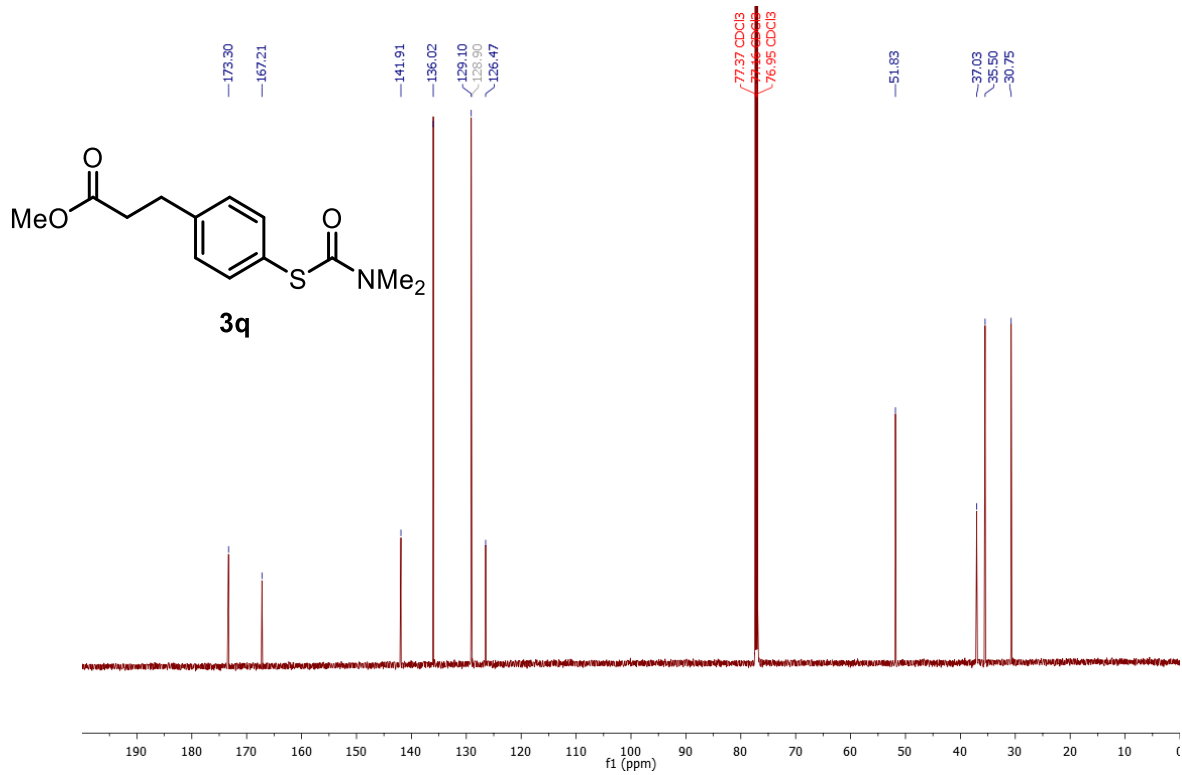
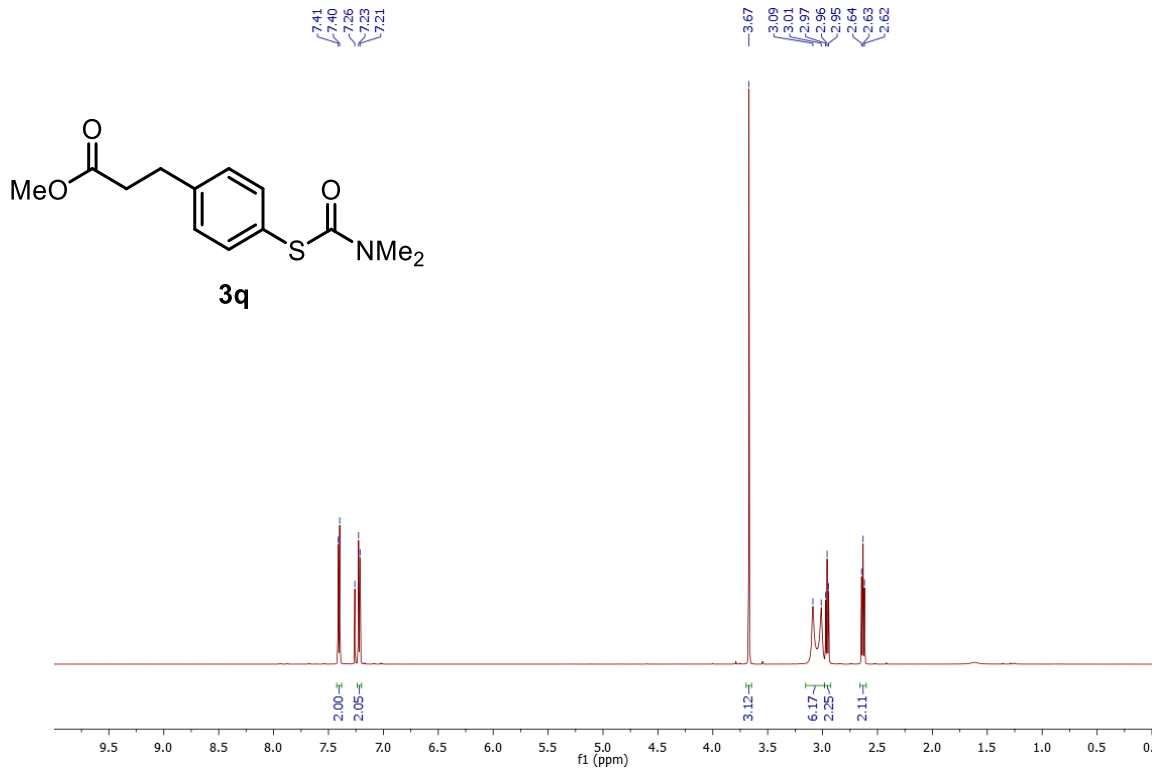


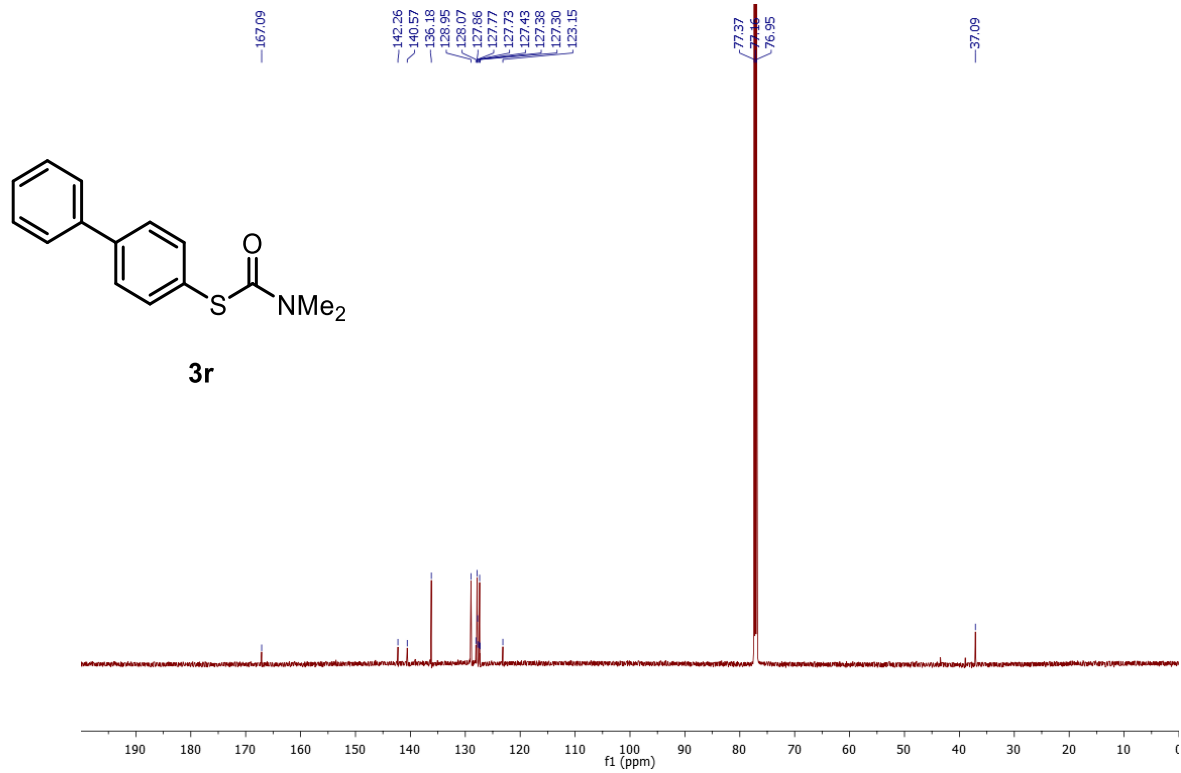
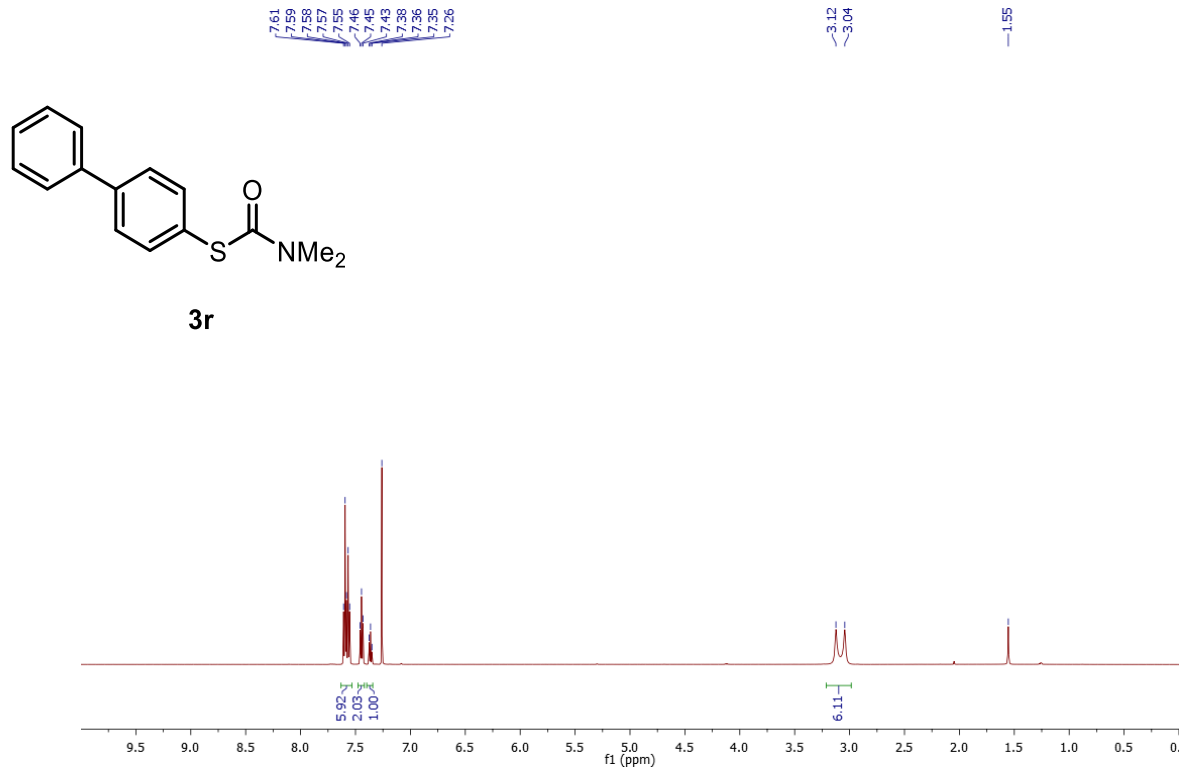


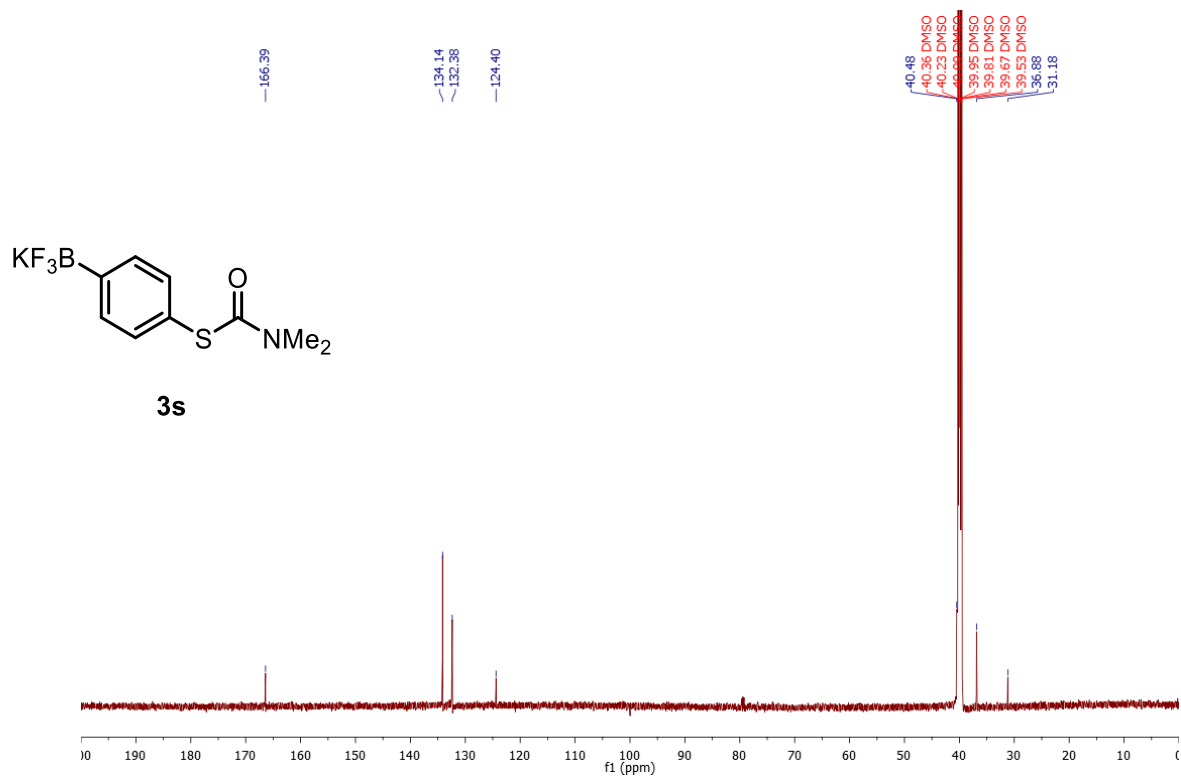
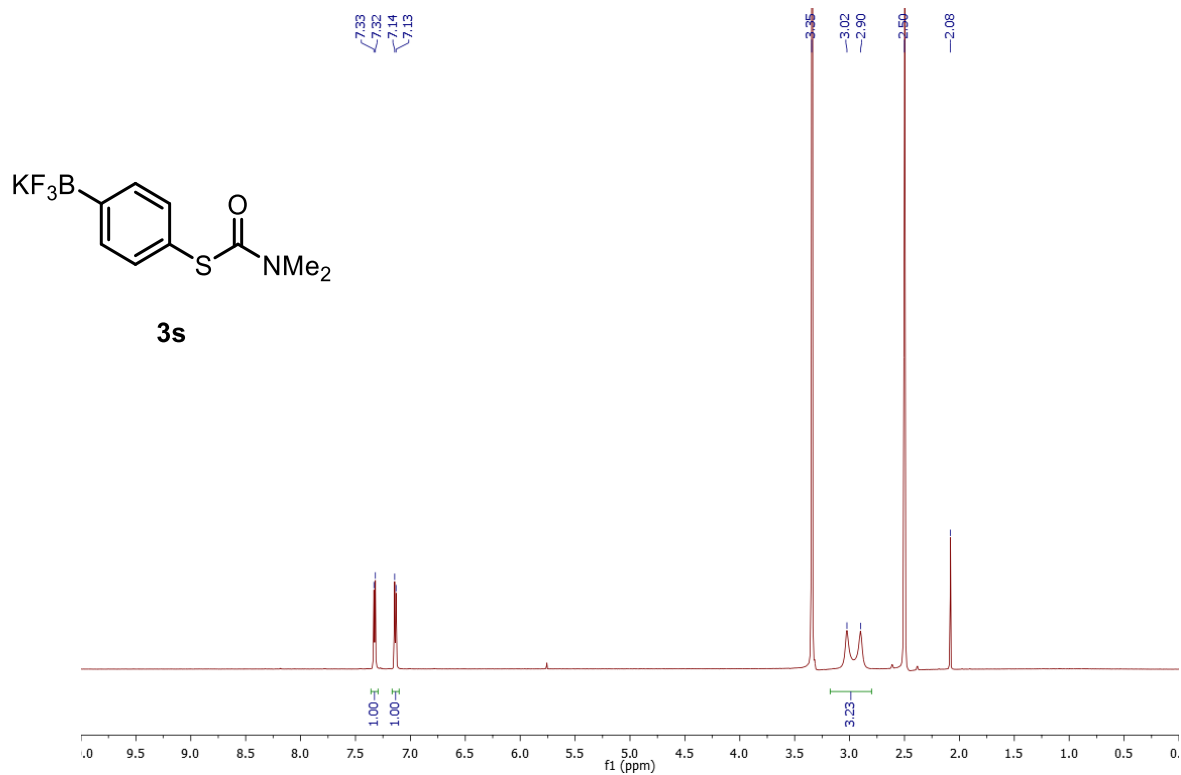


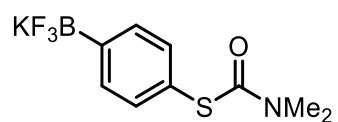




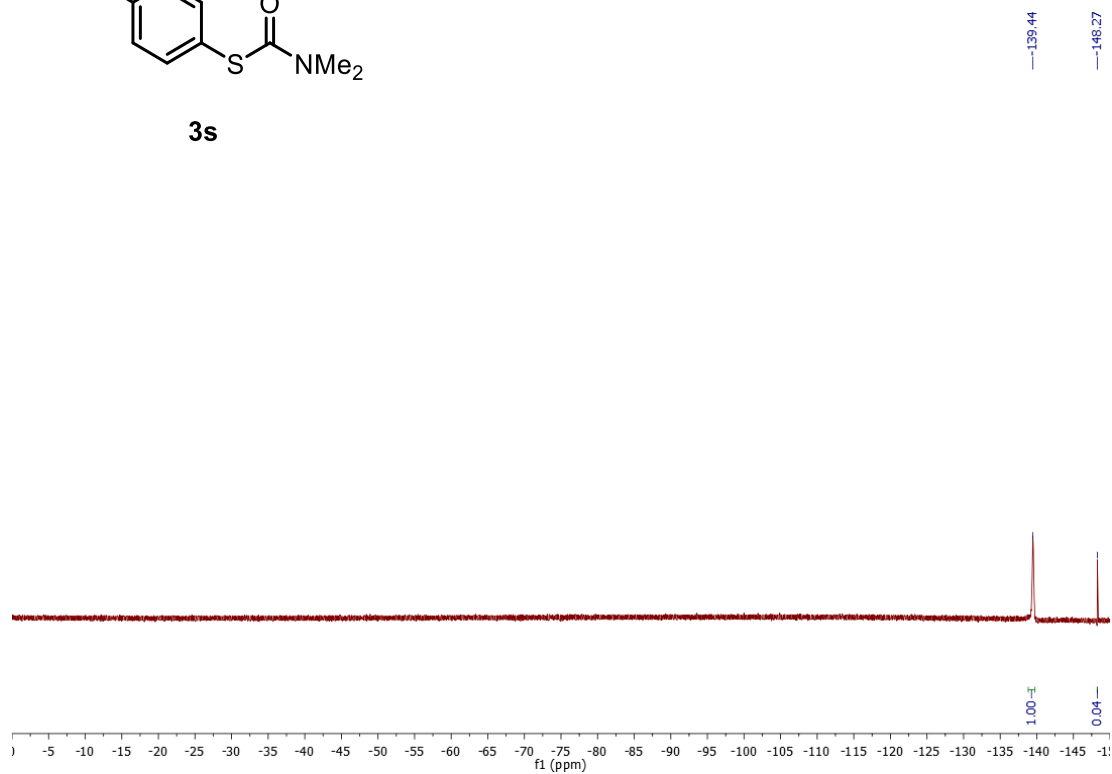


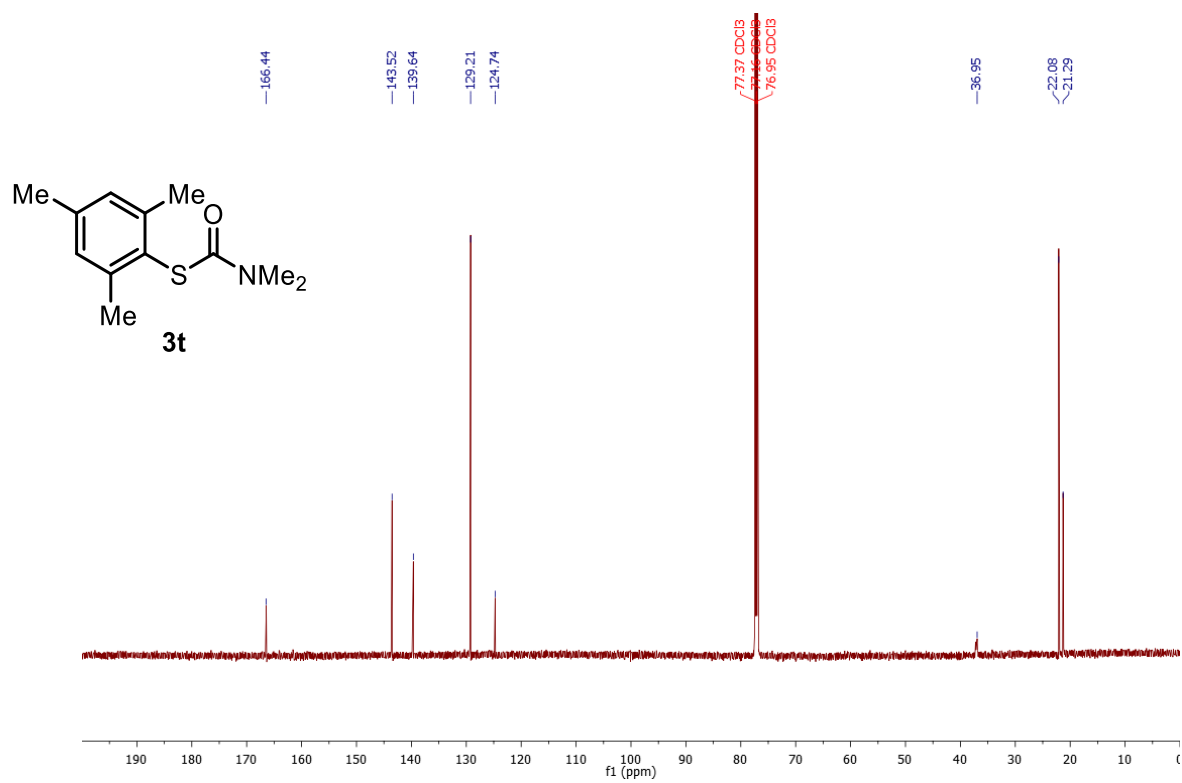
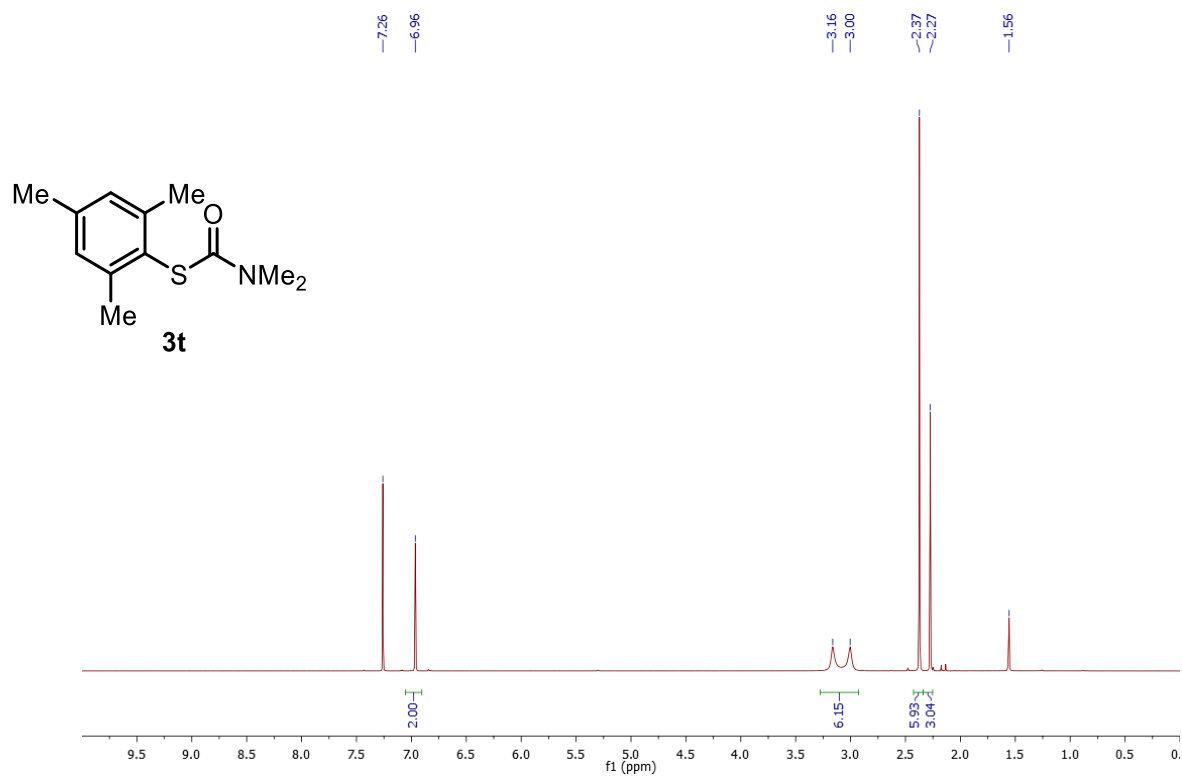


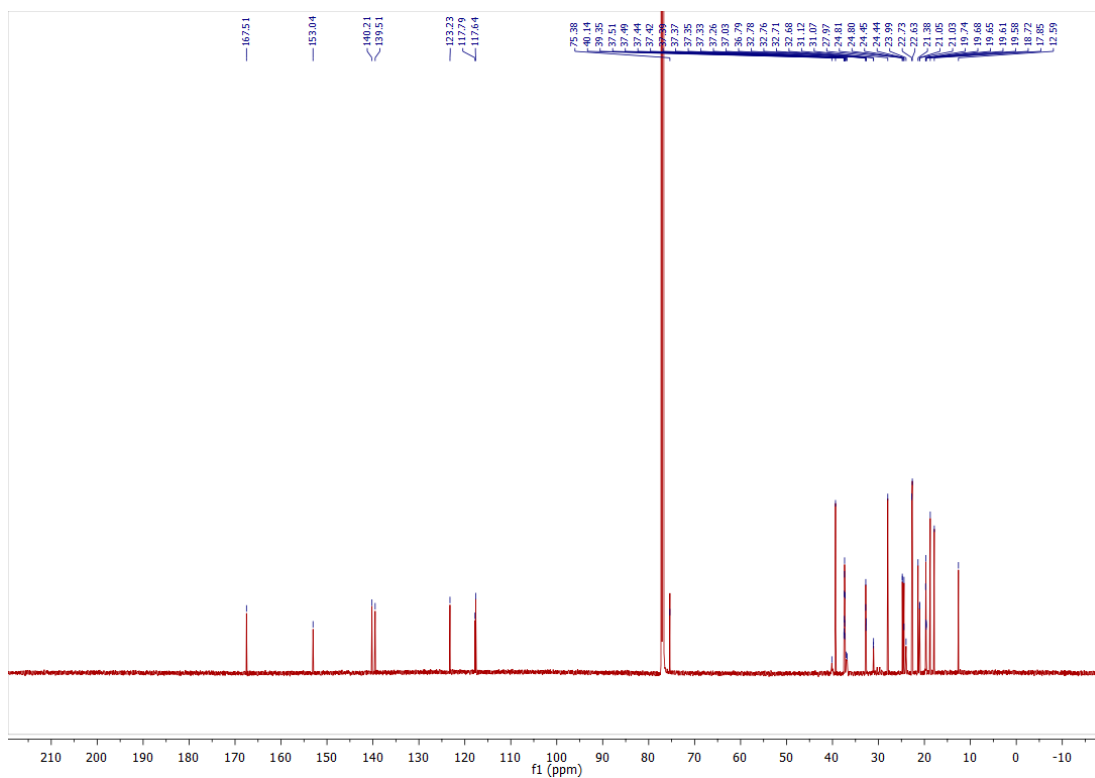
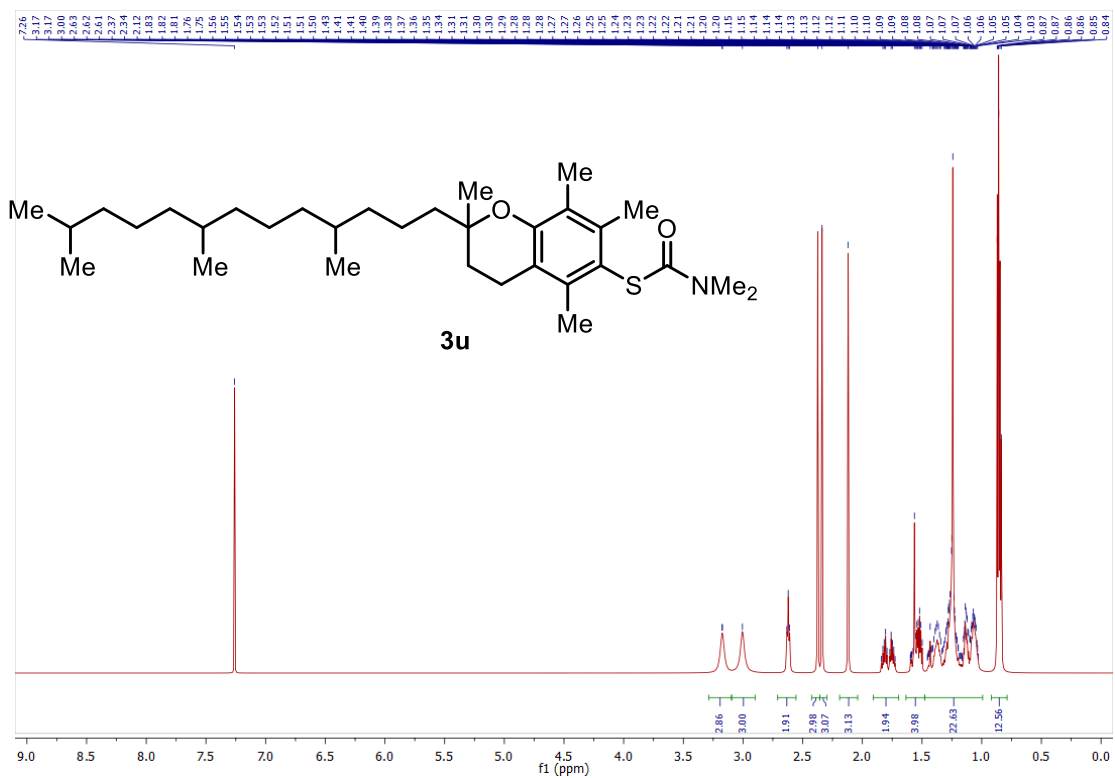


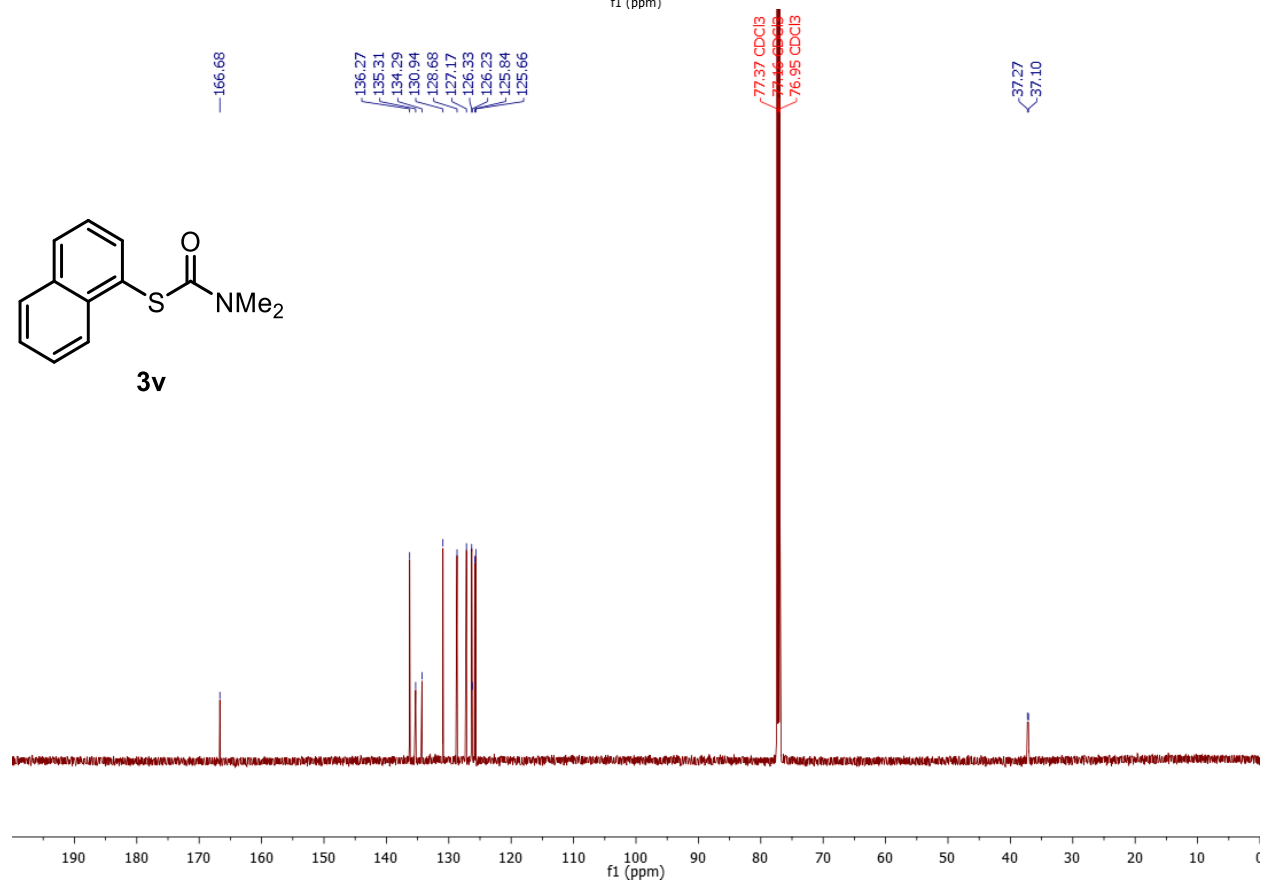
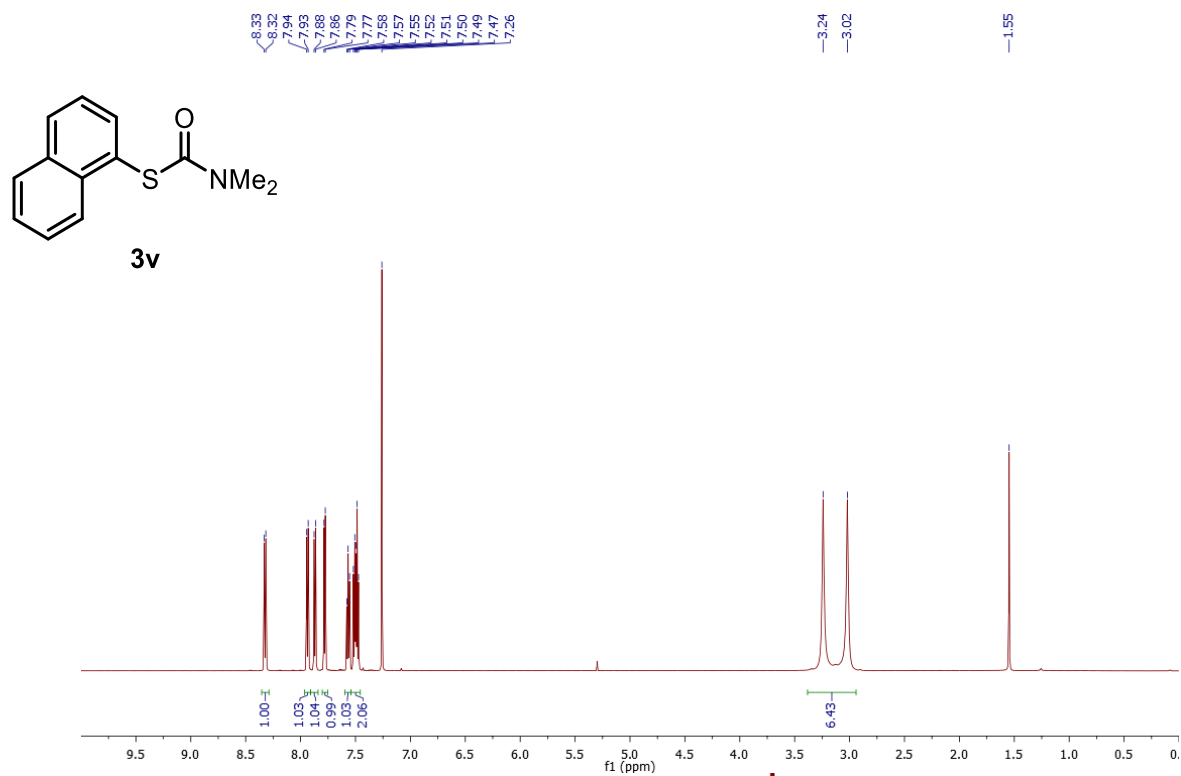


**3s**









## VI. References

- (1) Martiny, M.; Steckhan, E.; Esch, T. *Chem. Ber.* **1993**, *126*, 1671.
- (2) Zhao, Y.; Xie, Y.; Xia, C.; Huang, H. *Adv. Synth. Catal.* **2014**, *356*, 2471.
- (3) Newman, M. S.; Karnes, H. A. *J. Org. Chem.* **1966**, *31*, 3980.
- (4) Harvey, J. N.; Jover, J.; Lloyd-Jones, G. C.; Moseley, J. D.; Murray, P.; Renny, J. S. *Angew. Chem. Int. Ed.* **2009**, *48*, 7612.
- (5) Moseley, J. D.; Sankey, R. F.; Tang, O. N.; Gilday, J. P. *Tetrahedron* **2006**, *62*, 4685.
- (6) Romagnoli, R.; Baraldi, P. G.; Carrion, M. D.; Cruz-Lopez, O.; Tolomeo, M.; Grimaudo, S.; Cristina, A. D.; Pipitone, M. R.; Balzarini, J.; Brancale, A.; Hamel, E. *Bioorg. Med. Chem.* **2010**, *18*, 5114.
- (7) Chen, P.-Y.; Wu, Y.-H.; Hsu, M.-H.; Wang, T.-P.; Wang, E.-C. *Tetrahedron* **2013**, *69*, 653.
- (8) Rauniyar, V.; Hall, D. G. *J. Org. Chem.* **2009**, *74*, 4236.
- (9) Molander, G.A.; Cavalcanti, L. N.; Garcia-Garcia, C. *J. Org. Chem.* **2013**, *78*, 6427