

# **Samarium Diiodide-Mediated Radical Thioetherification of Alkyl Bromides with Thiols by Ruthenium Catalysis**

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### **List of Known Compounds/General Methods**

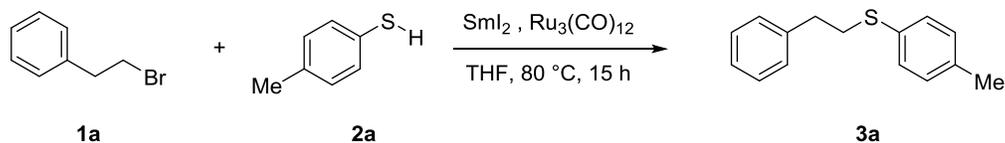
Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving SmI<sub>2</sub> were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using <sup>1</sup>H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by <sup>1</sup>H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker spectrometers at 500 (<sup>1</sup>H NMR) and 125 MHz (<sup>13</sup>C NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl<sub>3</sub> peak (7.27 and 77.2 ppm, <sup>1</sup>H NMR and <sup>13</sup>C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP6890 GC System and Agilent 5977C inert XL EI/CI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 45 °C. The injector temperature was 280 °C. The detector temperature was 280 °C. For runs with the initial oven temperature of 45 °C, temperature was increased with a 20 °C/min ramp after 45 °C hold for 2.5 min to a final temperature of 280 °C, then hold at 280 °C for 2 min (splitless mode of injection, total run time of 16.25 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. <sup>1</sup>H NMR and <sup>13</sup>C NMR data are given for all compounds in the Supporting Information. <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS data are reported for all new compounds.

## Experimental Procedures

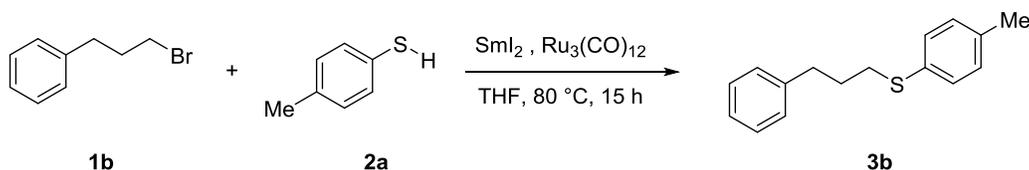
**General Procedure for SmI<sub>2</sub>-Mediated Radical Thioetherification of Alkyl Bromides.** An oven-dried Schlenk tube equipped with a stir bar was charged with alkyl bromides (1.0 equiv), 4-methylbenzenethiol (3.0 equiv), Ru<sub>3</sub>(CO)<sub>12</sub> (5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The Schlenk tube was then transferred to the glovebox, samarium diiodide (typically, 2.0 equiv, 0.1 M in THF) were added with vigorous stirring at room temperature. The Schlenk tube was then transferred out of the glovebox and placed in a preheated oil bath at 80 °C, which was stirred for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature. The reaction mixture was added saturated NaHCO<sub>3</sub> solution (10 mL) and washed with ethyl acetate (3×10 mL). The obtained solution was dried with anhydrous sodium sulfate, filtrated, concentrated to get crude product. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/ethyl acetate) afforded the title product.

**Representative Procedure for SmI<sub>2</sub>-Mediated Radical Thioetherification of Alkyl Bromides.** An oven-dried Schlenk tube equipped with a stir bar was charged with (3-bromopropyl)benzene (39.8 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenethiol (74.5 mg, 0.6 mmol, 3.0 equiv), Ru<sub>3</sub>(CO)<sub>12</sub> (6.4 mg, 0.01 mmol, 5 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. The Schlenk tube was then transferred to the glovebox, samarium diiodide (4.0 mL, 0.1 M in THF, 0.40 mmol, 2.0 equiv) were added with vigorous stirring at room temperature. The Schlenk tube was then transferred out of the glovebox and placed in a preheated oil bath at 80 °C, which was stirred for 15 h. After the indicated time, the reaction mixture was cooled down to room temperature. The reaction mixture was added saturated NaHCO<sub>3</sub> solution (10 mL) and washed with ethyl acetate (3×10 mL). The obtained solution was dried with anhydrous sodium sulfate, filtrated, concentrated to get crude product. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexane/ethyl acetate) afforded the title product. Yield 90% (43.6 mg, 0.090 mmol). Characterization data are included in the section below.

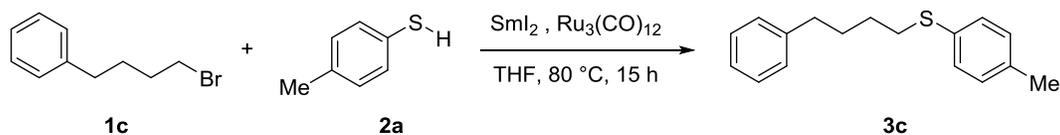
## Characterization Data

1-Methyl-4-[(2-phenylethyl)thio]benzene (Scheme 1, 3a)<sup>1</sup>

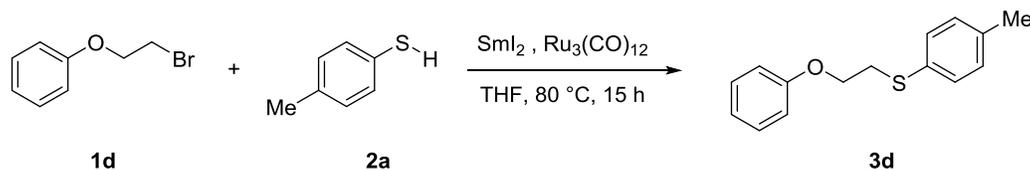
According to the general procedure, the reaction of (2-bromoethyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 92% yield (42.0 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.23-7.20 (m, 4H), 7.15-7.10 (m, 3H), 7.04 (d, *J* = 4.0 Hz, 2H), 3.05 (t, *J* = 4.0 Hz, 2H), 2.82 (t, *J* = 4.0 Hz, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.44, 136.32, 132.55, 130.21, 129.84, 128.62, 128.59, 126.50, 35.92, 35.85, 21.13.

1-Methyl-4-[(3-phenylpropyl)thio]benzene (Scheme 1, 3b)<sup>1</sup>

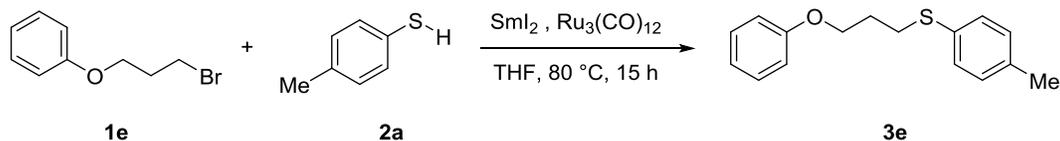
According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 90% yield (43.6 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22-7.18 (m, 2H), 7.17-7.14 (m, 2H), 7.13-7.08 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.90-1.82 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.49, 136.15, 132.72, 130.12, 129.75, 128.61, 128.48, 126.04, 34.74, 33.75, 30.79, 21.10.

**1-Methyl-4-[(4-phenylbutyl)thio]benzene (Scheme 1, 3c)<sup>2</sup>**

According to the general procedure, the reaction of (4-bromobutyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 97% yield (49.7 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.19 (t, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 4.0 Hz, 2H), 7.11-7.07 (m, 3H), 7.01 (d, *J* = 4.0 Hz, 2H), 2.82 (t, *J* = 4.0 Hz, 2H), 2.54 (t, *J* = 4.0 Hz, 2H), 2.24 (s, 3H), 1.70-1.65 (m, 2H), 1.61-1.56 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.14, 134.94, 131.86, 128.94, 128.61, 127.36, 127.28, 124.73, 34.36, 33.24, 29.41, 27.73, 19.98.

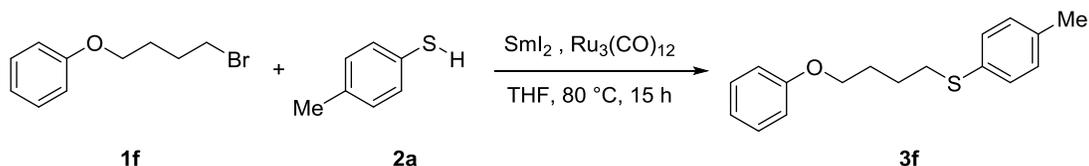
**1-Methyl-4-[(2-phenoxyethyl)thio]benzene (Scheme 1, 3d)<sup>2</sup>**

According to the general procedure, the reaction of (2-bromoethoxy)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 80% yield (39.1 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.26 (d, *J* = 4.0 Hz, 2H), 7.20-7.17 (m, 2H), 7.04 (d, *J* = 4.0 Hz, 2H), 6.87 (t, *J* = 4.0 Hz, 2H), 6.78 (d, *J* = 4.0 Hz, 2H), 4.04 (t, *J* = 4.0 Hz, 2H), 3.17 (t, *J* = 4.0 Hz, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 128.49, 136.94, 131.62, 130.85, 129.94, 129.58, 121.09, 114.68, 66.66, 33.57, 21.14.

**(3-Phenoxypropyl)(*p*-tolyl)sulfane (Scheme 1, 3e)**

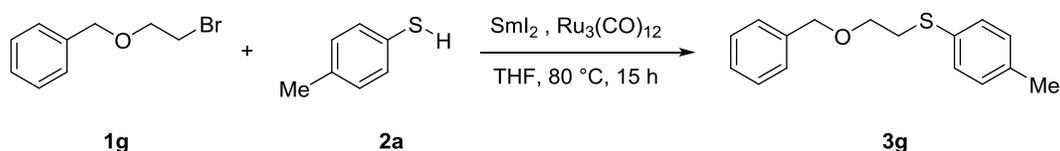
According to the general procedure, the reaction of (3-bromopropoxy)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 82% yield (42.4 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22-7.18 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 12.0 Hz, 2H), 3.98 (t, *J* = 8.0 Hz, 2H), 3.00 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 2.03-1.97 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.91, 136.33, 132.39, 130.22, 129.82, 129.54, 120.81, 114.58, 66.00, 31.02, 29.06, 21.11. **HRMS (ESI-TOF) m/z** calcd for C<sub>16</sub>H<sub>19</sub>OS (M<sup>+</sup>+H) 259.1151, found 259.1159.

#### (4-Phenoxybutyl)(*p*-tolyl)sulfane (Scheme 1, 3f)



According to the general procedure, the reaction of (4-bromobutoxy)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (53.4 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (t, *J* = 8.0 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 3.88 (t, *J* = 8.0 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.87-1.81 (m, 2H), 1.77-1.70 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 159.01, 136.21, 132.70, 130.21, 129.78, 129.53, 120.71, 114.56, 67.23, 34.24, 28.37, 25.94, 21.12. **HRMS (ESI-TOF) m/z** calcd for C<sub>17</sub>H<sub>20</sub>OS (M<sup>+</sup>) 272.1235, found 272.1231.

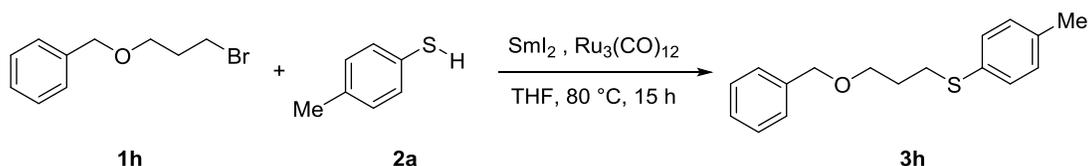
#### (2-(Benzyloxy)ethyl)(*p*-tolyl)sulfane (Scheme 1, 3g)



According to the general procedure, the reaction of ((2-bromoethoxy)methyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv)

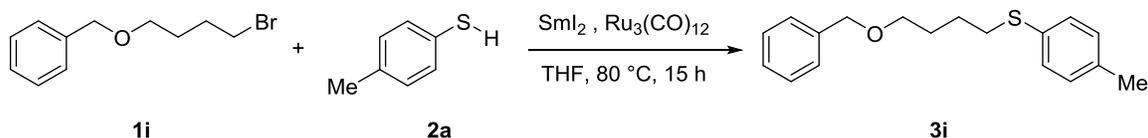
and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 71% yield (36.7 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.29-7.18 (m, 7H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.45 (s, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 138.14, 136.49, 132.20, 130.38, 129.82, 128.51, 127.82, 127.79, 73.14, 68.95, 34.07, 21.11. **HRMS (ESI-TOF) m/z** calcd for C<sub>16</sub>H<sub>19</sub>OS (M<sup>+</sup>+H) 259.1151, found 259.1160.

### 1-Methyl-4-[[3-(phenylmethoxy)propyl]thio]benzene (Scheme 1, 3h)<sup>3</sup>



According to the general procedure, the reaction of ((3-bromopropoxy)methyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 90% yield (49.0 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.29-7.17 (m, 7H), 7.01 (d, *J* = 4.0 Hz, 2H), 4.41 (s, 2H), 3.50 (t, *J* = 8.0 Hz, 2H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.87-1.81 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 138.50, 136.14, 132.72, 130.09, 129.76, 128.49, 127.73, 127.69, 73.06, 68.66, 31.21, 29.57, 21.10.

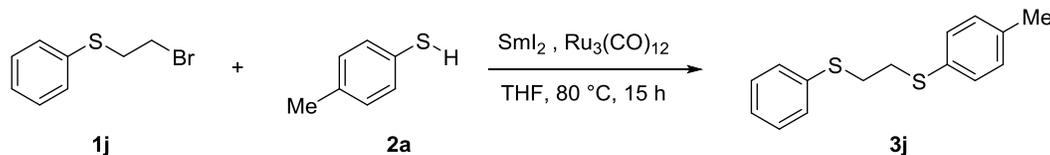
### (4-(Benzyloxy)butyl)(*p*-tolyl)sulfane (Scheme 1, 3i)



According to the general procedure, the reaction of ((4-bromobutoxy)methyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 87% yield (49.8 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.28-7.16 (m, 7H), 7.01 (d, *J* = 4.0 Hz, 2H), 4.41 (s, 2H), 3.40 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.66-1.63 (m, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 138.61, 136.06, 132.91, 130.06, 129.74, 128.47, 127.73, 127.64, 72.98, 69.84, 34.27,

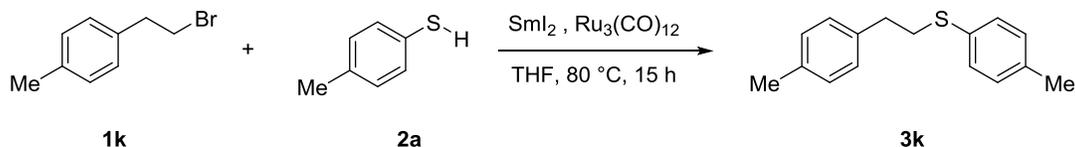
28.87, 26.11, 21.11. **HRMS (ESI-TOF) m/z** calcd for C<sub>18</sub>H<sub>22</sub>OS (M<sup>+</sup>) 286.1391, found 286.1388.

#### 1-Methyl-4-[[2-(phenylthio)ethyl]thio]benzene (Scheme 1, 3j)<sup>4</sup>

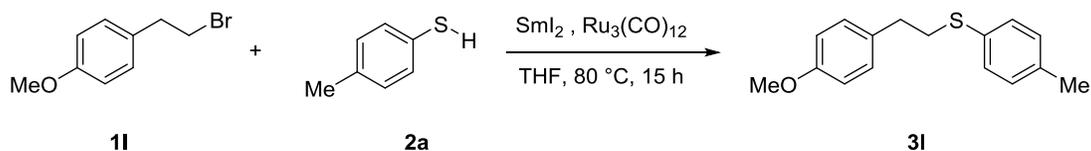


According to the general procedure, the reaction of (2-bromoethyl)(phenyl)sulfane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 48% yield (25.0 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.25-7.17 (m, 7H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.00-2.95 (m, 4H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.99, 135.22, 131.22, 131.03, 130.13, 129.93, 129.12, 126.56, 34.11, 33.36, 21.15.

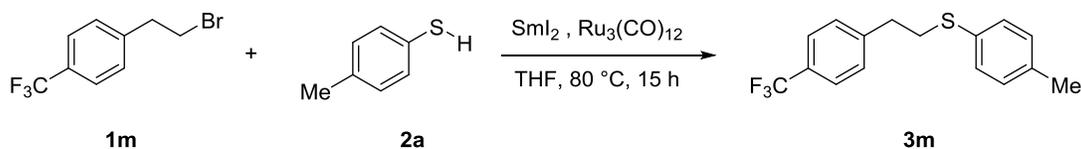
#### 1-Methyl-4-[[2-(4-methylphenyl)ethyl]thio]benzene (Scheme 1, 3k)<sup>5</sup>



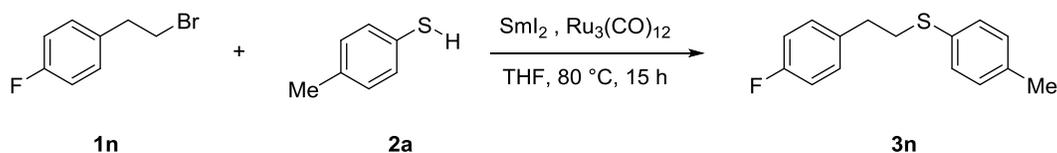
According to the general procedure, the reaction of 1-(2-bromoethyl)-4-methylbenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 85% yield (41.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.05-6.99 (m, 6H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.25 (d, *J* = 3.0 Hz, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 137.36, 136.23, 136.02, 132.62, 130.12, 129.81, 129.27, 128.49, 35.99, 35.37, 21.15, 21.12.

**1-Methoxy-4-[2-[(4-methylphenyl)thio]ethyl]benzene (Scheme 1, 3l)<sup>2</sup>**

According to the general procedure, the reaction of 1-(2-bromoethyl)-4-methoxybenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 96% yield (49.6 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.19 (t, *J* = 8.0 Hz, 2H), 7.05-7.02 (m, 4H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.33, 136.30, 132.70, 132.59, 130.20, 129.88, 129.64, 114.04, 55.42, 36.22, 34.98, 21.18.

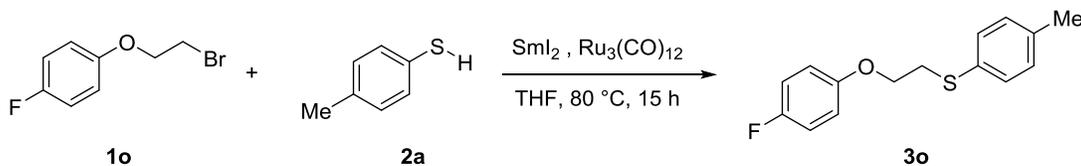
**(4-(Benzyloxy)butyl)(*p*-tolyl)sulfane (Scheme 1, 3m)<sup>6</sup>**

According to the general procedure, the reaction of 1-(2-bromoethyl)-4-(trifluoromethyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 88% yield (52.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 143.24, 135.57, 130.89, 129.45, 128.78, 127.89, 124.44 (q, *J*<sup>F</sup> = 4.0 Hz), 123.23 (q, *J*<sup>F</sup> = 299.0 Hz), 34.57, 34.47, 20.00. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -62.22.

**1-Methoxy-4-[2-[(4-methylphenyl)thio]ethyl]benzene (Scheme 1, 3n)<sup>6</sup>**

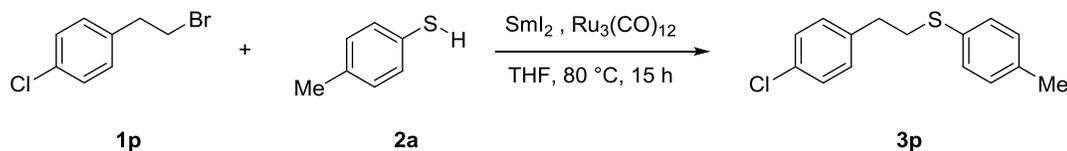
According to the general procedure, the reaction of 1-(2-bromoethyl)-4-fluorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 63% yield (31.0 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (d, *J* = 4 Hz, 2H), 7.08-7.03 (m, 4H), 6.90 (t, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 161.73 (d, *J*<sup>F</sup> = 245.4 Hz), 136.53, 136.10 (d, *J*<sup>F</sup> = 3.0 Hz), 132.40, 130.12 (d, *J*<sup>F</sup> = 8.1 Hz), 129.93, 115.40 (d, *J*<sup>F</sup> = 22.2 Hz), 36.16, 35.03, 21.19. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -116.61.

### (2-(4-Fluorophenoxy)ethyl)(*p*-tolyl)sulfane (Scheme 1, 3o)



According to the general procedure, the reaction of 1-(2-bromoethoxy)-4-fluorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 85% yield (44.6 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 8.0 Hz, 2H), 6.72-6.69 (m, 2H), 3.99 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 157.48 (d, *J*<sup>F</sup> = 239.4 Hz), 154.62 (d, *J*<sup>F</sup> = 2.0 Hz), 137.02, 131.54, 130.91, 129.95, 115.87 (d, *J*<sup>F</sup> = 32.3 Hz), 115.80 (d, *J*<sup>F</sup> = 1.0 Hz), 67.44, 33.62, 21.13. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -123.89. **HRMS (ESI-TOF) m/z** calcd for C<sub>15</sub>H<sub>15</sub>FOS (M<sup>+</sup>) 262.0828, found 262.0824.

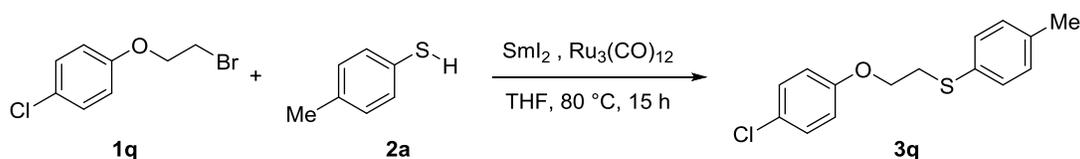
### 1-Chloro-4-[2-[(4-methylphenyl)thio]ethyl]benzene (Scheme 1, 3p)<sup>1</sup>



According to the general procedure, the reaction of 1-(2-bromoethyl)-4-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv)

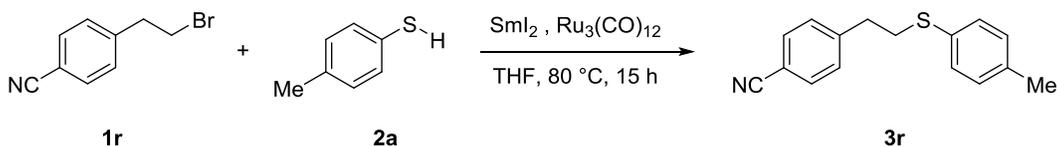
and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 95% yield (49.9 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.19 (t, *J* = 8.0 Hz, 4H), 7.05-7.02 (m, 4H), 3.02 (d, *J* = 8.0 Hz, 2H), 2.78 (d, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 137.66, 135.42, 131.14, 131.09, 129.30, 128.89, 128.75, 127.55, 34.76, 33.99, 20.01.

#### (2-(4-Chlorophenoxy)ethyl)(*p*-tolyl)sulfane (Scheme 1, 3q)



According to the general procedure, the reaction of 1-(2-bromoethoxy)-4-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 84% yield (46.7 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 12 Hz, 2H), 4.00 (t, *J* = 8.0 Hz, 2H), 3.15 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 156.00, 135.98, 130.31, 129.88, 128.85, 128.32, 124.84, 114.85, 65.95, 32.45, 20.02. **HRMS (ESI-TOF) m/z** calcd for C<sub>15</sub>H<sub>15</sub>ClOS (M<sup>+</sup>) 278.0532, found 278.0532.

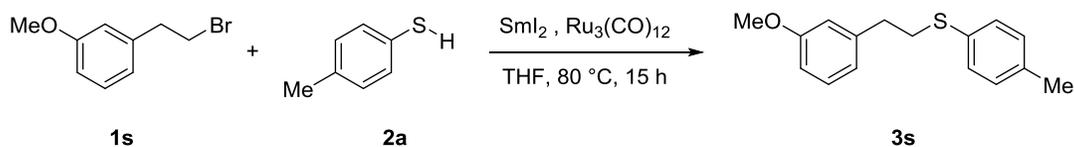
#### 4-(2-(*p*-Tolylthio)ethyl)benzonitrile (Scheme 1, 3r)



According to the general procedure, the reaction of 4-(2-bromoethyl)benzonitrile (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 80% yield (40.5 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz,**

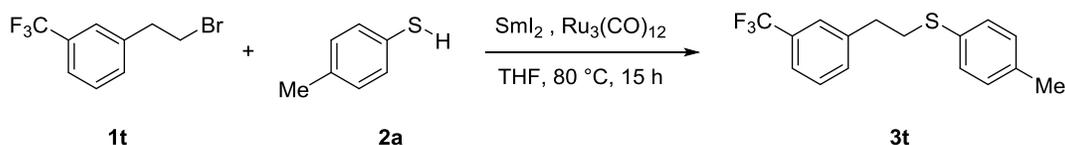
**CDCl<sub>3</sub>**)  $\delta$  145.89, 136.94, 132.43, 131.81, 130.77, 130.01, 129.59, 119.11, 110.46, 35.84, 35.56, 21.20. **HRMS (ESI-TOF) m/z** calcd for C<sub>16</sub>H<sub>15</sub>NS (M<sup>+</sup>) 253.0925, found 253.0923.

**(3-Methoxyphenethyl)(p-tolyl)sulfane (Scheme 1, 3s)**<sup>6</sup>

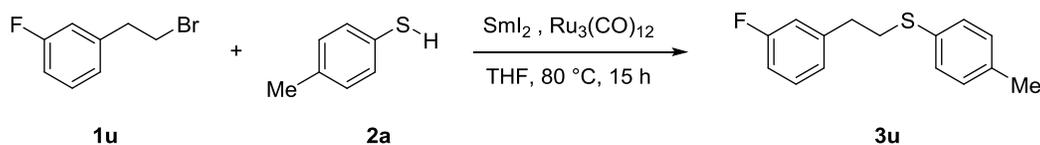


According to the general procedure, the reaction of 1-(2-bromoethyl)-3-methoxybenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 84% yield (43.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.71-6.65 (m, 3H), 3.72 (s, 3H), 3.05 (t, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  164.38, 156.17, 141.63, 132.58, 129.06, 128.38, 127.88, 127.31, 124.42, 113.38, 82.63, 66.87, 38.52, 33.43, 30.87, 28.55, 28.40, 28.31, 25.05, 23.57, 21.66, 13.11.

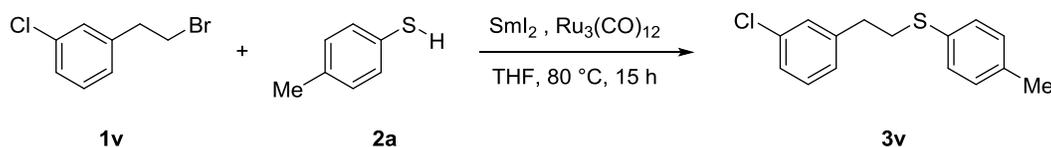
**p-Tolyl(3-(trifluoromethyl)phenethyl)sulfane (Scheme 1, 3t)**



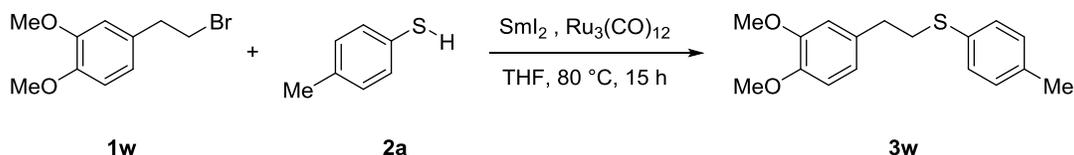
According to the general procedure, the reaction of 1-(2-bromoethyl)-3-(trifluoromethyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 83% yield (49.2 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.41-7.28 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  141.26, 136.78, 132.17, 132.04, 131.06, 130.72, 129.98, 129.04, 125.47 (q, *J*<sup>F</sup> = 3.0 Hz), 123.45 (d, *J*<sup>F</sup> = 4.0 Hz), 122.96, 35.87, 35.64, 21.20. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -62.90. **HRMS (ESI-TOF) m/z** calcd for C<sub>16</sub>H<sub>15</sub>F<sub>3</sub>S (M<sup>+</sup>) 296.0847, found 296.0845.

**1-Fluoro-3-[2-[(4-methylphenyl)thio]ethyl]benzene (Scheme 1, 3u)<sup>1</sup>**

According to the general procedure, the reaction of 1-(2-bromoethyl)-3-fluorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 83% yield (40.9 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22-7.14 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.89-6.79 (m, 3H), 3.03 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 143.05 (d, *J*<sup>F</sup> = 246.4 Hz), 142.95 (d, *J*<sup>F</sup> = 7.1 Hz), 136.64, 132.25, 130.53, 130.06 (d, *J*<sup>F</sup> = 8.1 Hz), 129.96, 124.37 (d, *J*<sup>F</sup> = 3.0 Hz), 115.59 (d, *J*<sup>F</sup> = 21.2 Hz), 113.36 (d, *J*<sup>F</sup> = 21.2 Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -113.30.

**1-Chloro-3-[2-[(4-methylphenyl)thio]ethyl]benzene (Scheme 1, 3v)<sup>1</sup>**

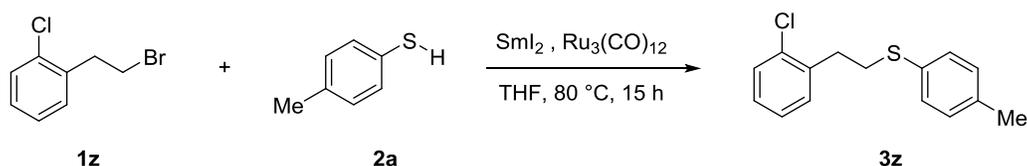
According to the general procedure, the reaction of 1-(2-bromoethyl)-3-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 99% yield (52.0 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (d, *J* = 8.0 Hz, 2H), 7.16-7.03 (m, 5H), 2.68 (s, 2H), 6.99-6.96 (m, 1H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 142.41, 136.65, 134.36, 132.19, 130.57, 129.95, 129.87, 128.84, 126.92, 126.74, 35.79, 35.54, 21.19.

**Benzene, 1,2-dimethoxy-4-[2-[(4-methylphenyl)thio]ethyl]- (Scheme 1, 3w)<sup>7</sup>**



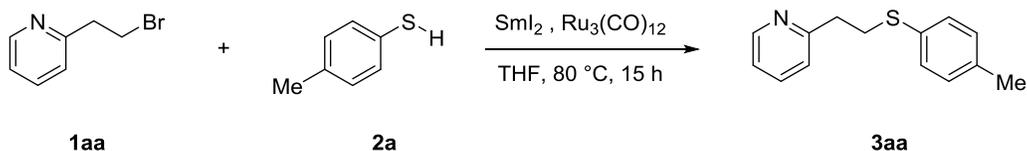
**NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.21 (t,  $J = 8.0$  Hz, 2H), 7.15-7.08 (m, 2H), 7.04 (d,  $J = 8.0$  Hz, 2H), 7.00-6.91 (m, 2H), 3.05 (t,  $J = 6.0$  Hz, 2H), 2.86 (t,  $J = 6.0$  Hz, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  142.10 (d,  $J^F = 10.1$  Hz), 137.80, 135.14, 130.57 (d,  $J^F = 7.1$  Hz), 129.14 (d,  $J^F = 15.2$  Hz), 128.53 (d,  $J^F = 9.1$  Hz), 125.76 (d,  $J^F = 13.1$  Hz), 115.21 (d,  $J^F = 21.2$  Hz), 83.91, 24.67. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -118.32. **HRMS (ESI-TOF) m/z** calcd for C<sub>15</sub>H<sub>15</sub>FS (M<sup>+</sup>) 246.0878, found 246.0875.

**(2-Chlorophenethyl)(*p*-tolyl)sulfane (Scheme 1, 3z)<sup>6</sup>**

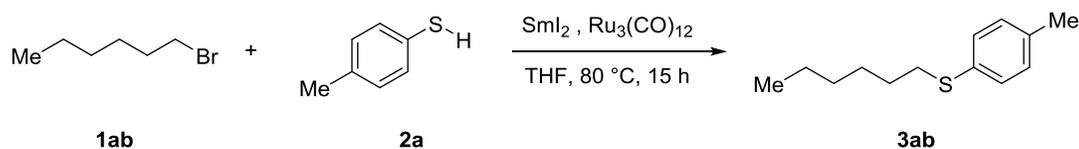


According to the general procedure, the reaction of 1-(2-bromoethyl)-2-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 61% yield (32.1 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.27-7.22 (m, 1=3H), 7.14-7.08 (m, 3H), 7.05 (d,  $J = 8.0$  Hz, 2H), 3.08-3.04 (m, 2H), 2.96-2.92 (m, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  137.91, 136.35, 134.02, 132.28, 130.94, 130.20, 129.82, 129.67, 128.05, 126.94, 33.95, 33.85, 21.12..

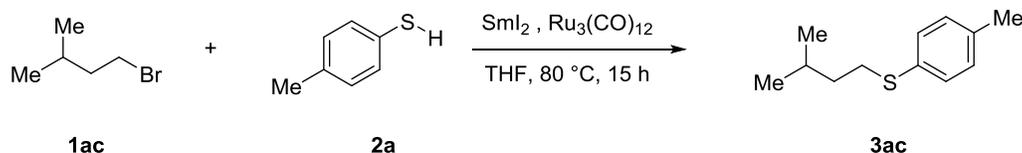
**2-[2-[(4-Methylphenyl)thio]ethyl]pyridine (Scheme 1, 3aa)<sup>8</sup>**



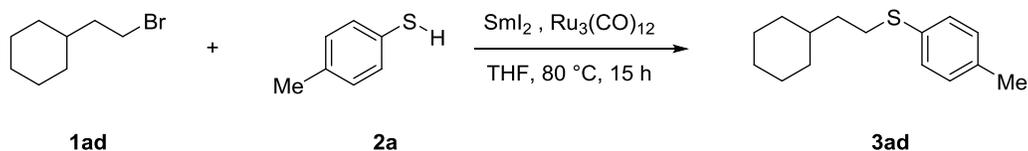
According to the general procedure, the reaction of 2-(2-bromoethyl)pyridine (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 61% yield (28.0 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.47 (s, 1H), 7.53 (t,  $J = 8.0$  Hz, 1H), 7.21 (t,  $J = 8.0$  Hz, 2H), 7.08-7.02 (m, 4H), 3.23 (t,  $J = 8.0$  Hz, 2H), 3.01 (t,  $J = 8.0$  Hz, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  159.85, 149.39, 136.59, 136.36, 132.33, 130.37, 129.82, 123.48, 121.64, 37.90, 34.00, 21.11.

**1-(Hexylthio)-4-methylbenzene (Scheme 1, 3ab)<sup>9</sup>**

According to the general procedure, the reaction of 1-bromohexane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 80% yield (3.3 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.58-1.52 (m, 2H), 1.37-1.31 (m, 2H), 1.23-1.20 (m, 4H), 0.81 (d, *J* = 8.0 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 135.90, 133.22, 129.82, 129.69, 34.43, 31.48, 29.30, 28.59, 22.64, 21.08, 14.11.

**1-Methyl-4-[(3-methylbutyl)thio]benzene (Scheme 1, 3ac)<sup>10</sup>**

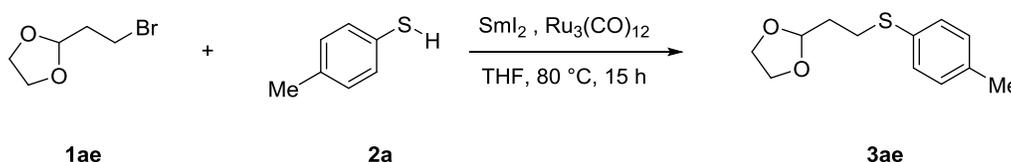
According to the general procedure, the reaction of 1-bromo-3-methylbutane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 87% yield (33.8 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.69-1.59 (m, 1H), 1.47-1.41 (m, 2H), 0.83 (d, *J* = 8.0 Hz, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 135.90, 133.20, 129.75, 129.70, 38.26, 32.41, 27.51, 22.36, 21.08.

**(2-Cyclohexylethyl)(*p*-tolyl)sulfane (Scheme 1, 3ad)**

According to the general procedure, the reaction of (2-bromoethyl)cyclohexane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and

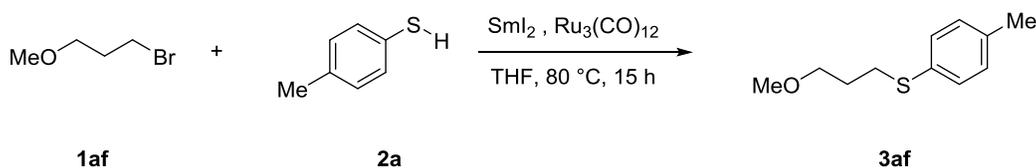
Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 85% yield (39.8 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.66-1.63 (m, 2H), 1.56-1.26 (m, 6H), 1.17-1.07 (m, 3H), 0.86-0.78 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 135.82, 133.28, 129.69, 129.63, 37.03, 36.83, 33.09, 31.95, 26.64, 26.31, 21.08. **HRMS (ESI-TOF) m/z** calcd for C<sub>15</sub>H<sub>23</sub>S (M<sup>+</sup>+H) 235.1515, found 235.1523.

### 2-[2-[(4-Methylphenyl)thio]ethyl]-1,3-dioxolane (Scheme 1, 3ae)<sup>11</sup>



According to the general procedure, the reaction of 2-(2-bromoethyl)-1,3-dioxolane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 74% yield (33.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (s, 1H), 7.18 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.90 (t, *J* = 8.0 Hz, 1H), 3.91-3.85 (m, 2H), 3.83-3.77 (m, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.93-1.88 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.30, 132.35, 130.17, 129.80, 103.20, 65.07, 33.68, 28.68, 21.09.

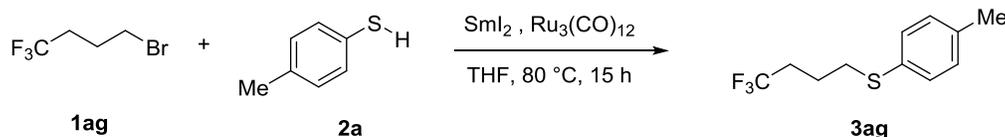
### 1-[(3-Methoxypropyl)thio]-4-methylbenzene (Scheme 1, 3af)<sup>2</sup>



According to the general procedure, the reaction of 1-bromo-3-methoxypropane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 82% yield (32.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (s, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.39 (t, *J* = 8.0 Hz, 2H), 3.24 (s,

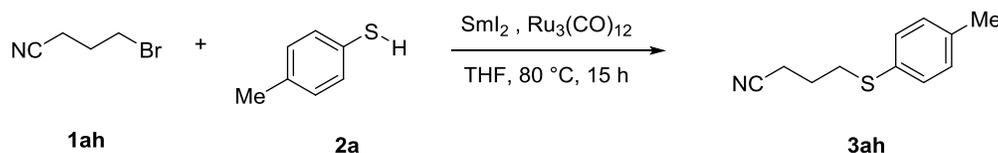
3H), 2.89 (t,  $J = 8.0$  Hz, 2H), 2.24 (s, 3H), 1.83-1.76 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  136.13, 132.70, 130.05, 129.75, 71.04, 58.72, 31.09, 29.40, 21.08.

### 1-Methyl-4-[(4,4,4-trifluorobutyl)thio]benzene (Scheme 1, 3ag)<sup>12</sup>

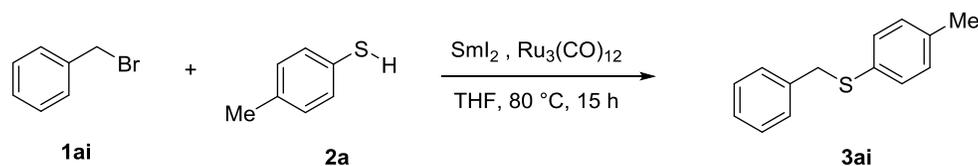


According to the general procedure, the reaction of 4-bromo-1,1,1-trifluorobutane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 76% yield (35.6 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.20 (d,  $J = 8.0$  Hz, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 2.85 (t,  $J = 8.0$  Hz, 2H), 2.26 (s, 3H), 2.20-2.13 (m, 2H), 1.81-1.76 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  135.85, 130.36, 129.87, 128.83, 125.97 (d,  $J^F = 277.8$  Hz), 32.63, 31.42 (q,  $J^F = 28.3$  Hz), 20.60 (d,  $J^F = 3.0$  Hz), 20.01. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -65.59.

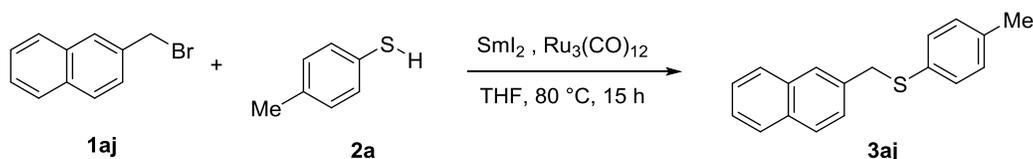
### 4-[(4-Methylphenyl)thio]butanenitrile (Scheme 1, 3ah)<sup>2</sup>



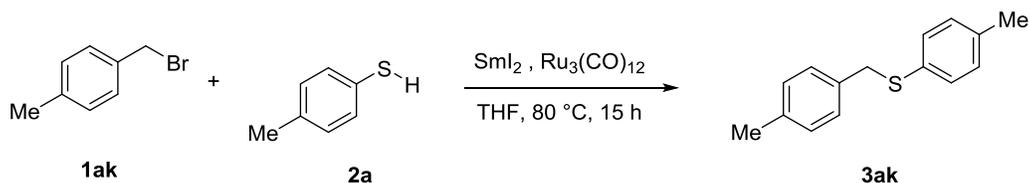
According to the general procedure, the reaction of 4-bromobutanenitrile (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 79% yield (30.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.21 (d,  $J = 8.0$  Hz, 2H), 7.05 (d,  $J = 8.0$  Hz, 2H), 2.91 (t,  $J = 8.0$  Hz, 2H), 2.44 (t,  $J = 8.0$  Hz, 2H), 2.26 (s, 3H), 1.89-1.82 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  137.24, 131.13, 130.91, 130.04, 119.21, 33.39, 24.91, 21.14, 15.94.

**1-Methyl-4-[(phenylmethyl)thio]benzene (Scheme 1, 3ai)<sup>5</sup>**

According to the general procedure, the reaction of (bromomethyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 43% yield (18.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.29-7.24 (m, 5H), 7.20 (d, *J* = 12.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.06 (s, 2H), 2.30 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 137.88, 136.67, 132.55, 130.80, 129.71, 128.93, 128.53, 127.17, 39.87, 21.15.

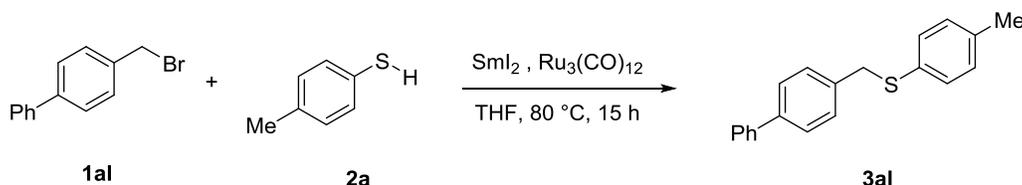
**2-[[4-Methylphenyl]thio]methyl]naphthalene (Scheme 1, 3aj)<sup>13</sup>**

According to the general procedure, the reaction of 2-(bromomethyl)naphthalene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 48% yield (25.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.74-7.66 (m, 3H), 7.57 (s, 1H), 7.39-7.36 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 4.0 Hz, 2H), 4.15 (s, 2H), 2.22 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 135.66, 134.21, 132.26, 131.52, 131.29, 129.84, 128.61, 127.21, 126.68, 126.62, 126.35, 126.03, 125.05, 124.73, 39.12, 20.02.

**1-Methyl-4-[[4-methylphenyl]methyl]thio]benzene (Scheme 1, 3ak)<sup>5</sup>**

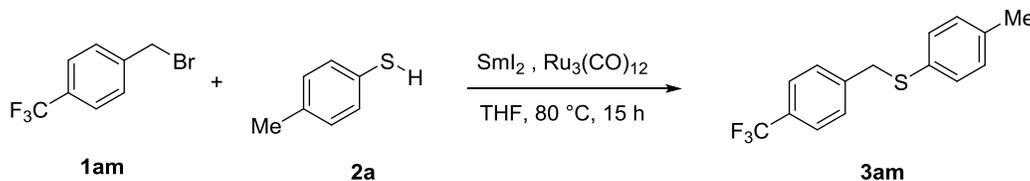
According to the general procedure, the reaction of 1-(bromomethyl)-4-methylbenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 54% yield (24.7 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 4H), 3.97 (s, 2H), 2.24 (d, *J* = 4.0 Hz, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.82, 136.50, 134.72, 132.82, 130.56, 129.68, 129.23, 128.80, 39.49, 21.20, 21.14.

#### 4-[[4-Methylphenylthio]methyl]-1,1'-biphenyl (Scheme 1, 3al)<sup>14</sup>



According to the general procedure, the reaction of 4-(bromomethyl)-1,1'-biphenyl (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 40% yield (23.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.04 (s, 2H), 2.24 (d, *J* = 4.0 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.86, 140.05, 136.97, 136.74, 132.50, 130.85, 129.75, 129.34, 128.85, 127.34, 127.26, 127.11, 39.60, 21.15.

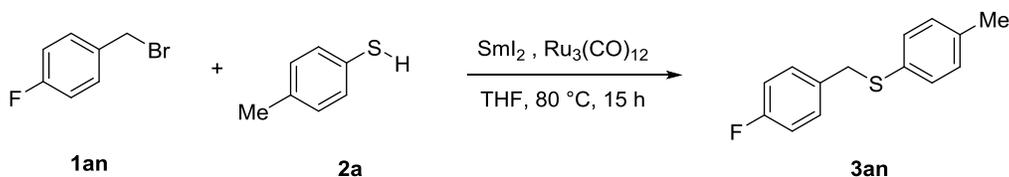
#### 1-[[4-Methylphenylthio]methyl]-4-(trifluoromethyl)benzene (Scheme 1, 3am)<sup>14</sup>



According to the general procedure, the reaction of 1-(bromomethyl)-4-(trifluoromethyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 53% yield (29.9 mg). Yellow oil. **<sup>1</sup>H NMR**

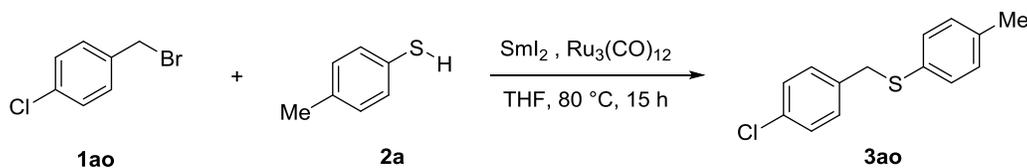
**(400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.44 (d,  $J$  = 8.0 Hz, 2H), 7.26 (d,  $J$  = 8.0 Hz, 2H), 7.12 (d,  $J$  = 8.0 Hz, 2H), 7.00 (d,  $J$  = 8.0 Hz, 2H), 4.00 (s, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  148.17, 142.39, 137.29, 131.49, 131.37, 129.85, 129.17, 125.44 (d,  $J^F$  = 4.0 Hz), 113.96, 39.62, 21.15. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -62.11.

### 1-Fluoro-4-[[4-(4-methylphenyl)thio]methyl]benzene (Scheme 1, 3an)<sup>5</sup>

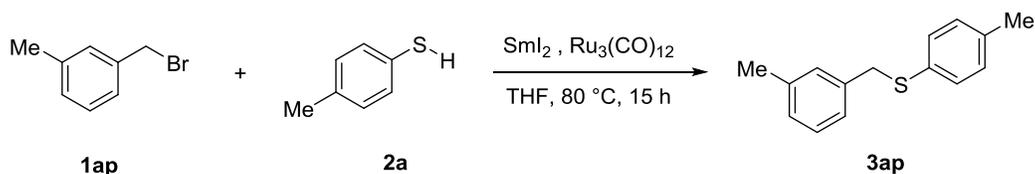


According to the general procedure, the reaction of 1-(bromomethyl)-4-fluorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 83% yield (38.6 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.14-7.11 (m, 4H), 6.99 (d,  $J$  = 8.0 Hz, 2H), 6.88 (t,  $J$  = 8.0 Hz, 2H), 3.95 (s, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  137.22 (d,  $J^F$  = 52.5 Hz), 134.49, 133.69 (d,  $J^F$  = 7.1 Hz), 132.01, 131.16, 130.44 (d,  $J^F$  = 8.1 Hz), 129.75, 115.34 (d,  $J^F$  = 22.2 Hz), 39.23, 21.1567. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -115.43.

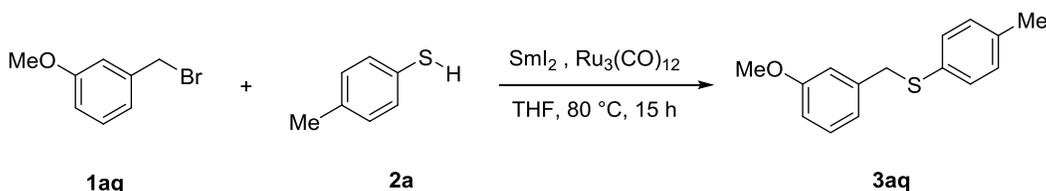
### 1-Chloro-4-[[4-(4-methylphenyl)thio]methyl]benzene (Scheme 1, 3ao)<sup>13</sup>



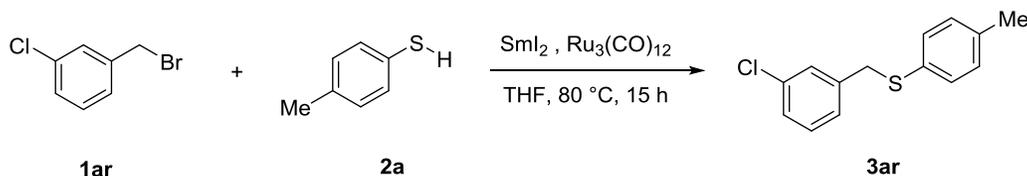
According to the general procedure, the reaction of 1-(bromomethyl)-4-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 58% yield (28.9 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.16 (d,  $J$  = 8.0 Hz, 2H), 7.12-7.08 (m, 4H), 6.99 (d,  $J$  = 8.0 Hz, 2H), 3.93 (s, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  137.06, 136.56, 132.90, 131.81, 131.24, 130.22, 129.78, 128.63, 39.34, 21.16.

**1-Methyl-3-[[4-methylphenyl]thio]methyl]benzene (Scheme 1, 3ap)<sup>5</sup>**

According to the general procedure, the reaction of 1-(bromomethyl)-3-methylbenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 60% yield (27.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.14 (d, *J* = 4.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.02-6.96 (m, 5H), 3.97 (s, 2H), 2.24 (s, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 138.19, 137.65, 136.56, 132.80, 130.61, 129.68, 129.28, 128.41, 127.96, 125.96, 39.81, 21.44, 21.13.

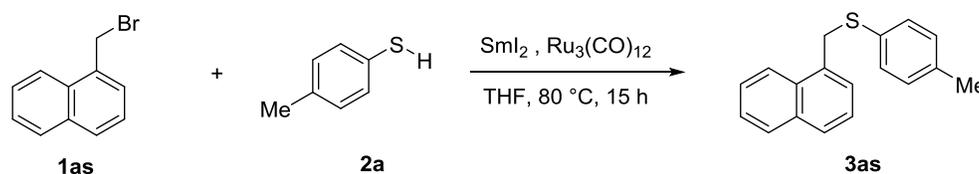
**1-Methoxy-3-[[4-methylphenyl]thio]methyl]benzene (Scheme 1, 3aq)<sup>5</sup>**

According to the general procedure, the reaction of 1-(bromomethyl)-3-methoxybenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 50% yield (24.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.15 (d, *J* = 4.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 2H), 3.69 (s, 3H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 159.69, 139.43, 136.69, 132.55, 130.81, 129.71, 129.50, 121.27, 114.21, 112.96, 55.25, 39.90, 21.13.

**1-Chloro-3-[[4-methylphenyl]thio]methyl]benzene (Scheme 1, 3ar)<sup>5</sup>**

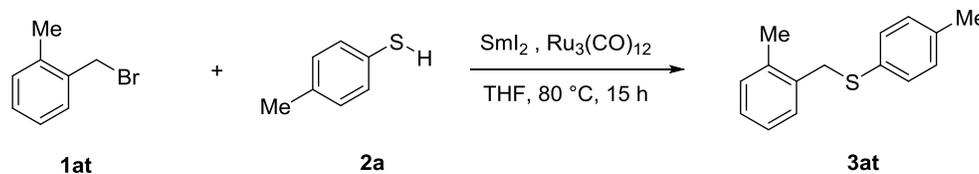
According to the general procedure, the reaction of 1-(bromomethyl)-3-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 44% yield (21.9 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17 (s, 1H), 7.13-7.11 (m, 4H), 7.05-7.03 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.06, 137.13, 134.24, 131.78, 131.24, 129.80, 129.71, 129.01, 127.34, 127.05, 39.54, 21.15.

### 1-[[4-Methylphenyl]thio]methyl]naphthalene (Scheme 1, 3as)<sup>15</sup>



According to the general procedure, the reaction of 1-(bromomethyl)naphthalene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 56% yield (29.6 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 4.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.50-7.41 (m, 2H), 7.28-7.23 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.44 (s, 2H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 135.76, 132.92, 132.05, 131.75, 130.42, 130.07, 128.61, 127.75, 127.14, 126.27, 125.15, 124.77, 124.21, 123.93, 36.92, 20.05.

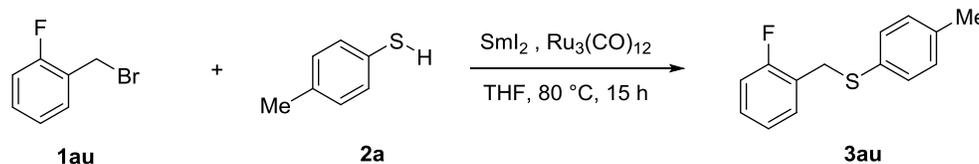
### 1-Methyl-2-[[4-methylphenyl]thio]methyl]benzene (Scheme 1, 3at)<sup>16</sup>



According to the general procedure, the reaction of 1-(bromomethyl)-2-methylbenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 40% yield (18.3 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.09-7.08 (m, 2H), 7.03-7.00 (m, 4H), 3.99 (s, 2H),

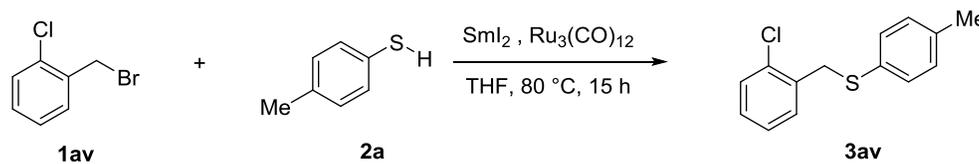
2.31 (s, 3H), 2.25 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.80, 135.47, 132.78, 131.18, 130.52, 129.87, 129.70, 127.50, 126.03, 38.21, 21.16, 19.28.

### 1-Fluoro-2-[[4-methylphenyl]thio]methyl]benzene (Scheme 1, 3au)<sup>5</sup>

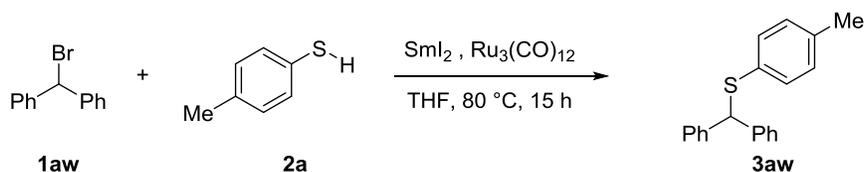


According to the general procedure, the reaction of 1-(bromomethyl)-2-fluorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 74% yield (34.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17-7.11 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.97-6.92 (m, 2H), 4.01 (s, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.88 (d, *J*<sup>F</sup> = 39.4 Hz), 131.46, 130.95 (d, *J*<sup>F</sup> = 4.0 Hz), 129.73, 128.91 (d, *J*<sup>F</sup> = 8.1 Hz), 124.06 (d, *J*<sup>F</sup> = 3.0 Hz), 123.29 (d, *J*<sup>F</sup> = 3.0 Hz), 115.43 (d, *J*<sup>F</sup> = 25.3 Hz), 33.00, 21.17. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -117.81.

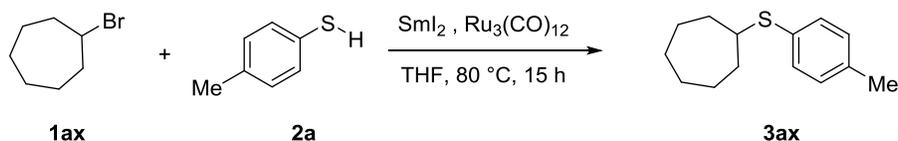
### 1-Chloro-2-[[4-methylphenyl]thio]methyl]benzene (Scheme 1, 3av)<sup>16</sup>



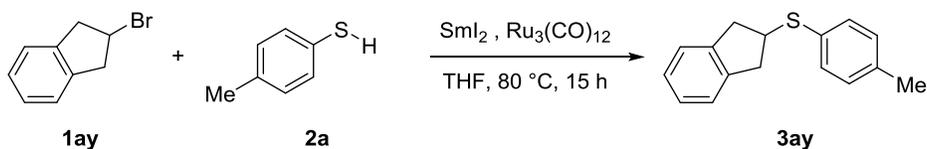
According to the general procedure, the reaction of 1-(bromomethyl)-2-chlorobenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 58% yield (28.9 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.29 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12-7.03 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.09 (s, 2H), 2.24 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 137.12, 135.61, 134.12, 131.93, 131.63, 130.82, 129.75, 128.57, 126.77, 37.79, 21.18.

**1-[(Diphenylmethyl)thio]-4-methylbenzene (Scheme 1, 3aw)<sup>17</sup>**

According to the general procedure, the reaction of (bromomethylene)dibenzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 80% yield (46.5 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.33 (d, *J* = 8.0 Hz, 4H), 7.21 (t, *J* = 8.0 Hz, 4H), 7.15-7.11 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.39 (s, 1H), 2.18 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 137.12, 135.61, 134.12, 131.63, 130.82, 129.75, 128.57, 126.77, 37.79, 21.18.

**[(4-Methylphenyl)thio]cycloheptane (Scheme 1, 3ax)<sup>12</sup>**

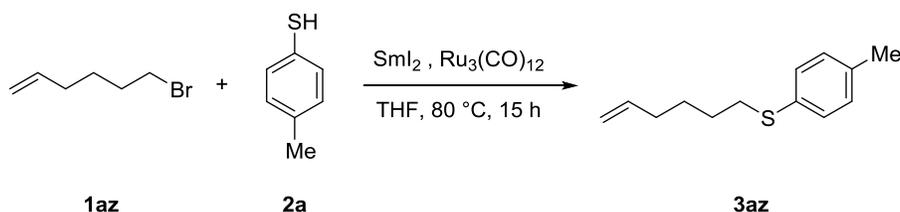
According to the general procedure, the reaction of bromocycloheptane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 64% yield (28.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.22-3.15 (m, 1H), 2.25 (s, 3H), 1.96-1.89 (m, 2H), 1.68-1.61 (m, 2H), 1.52-1.46 (m, 8H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 157.70, 136.67, 132.17, 129.66, 48.65, 34.73, 28.31, 26.01, 21.16.

**2,3-Dihydro-2-[(4-methylphenyl)thio]-1H-indene (Scheme 1, 3ay)<sup>18</sup>**

According to the general procedure, the reaction of 2-bromo-2,3-dihydro-1H-indene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and

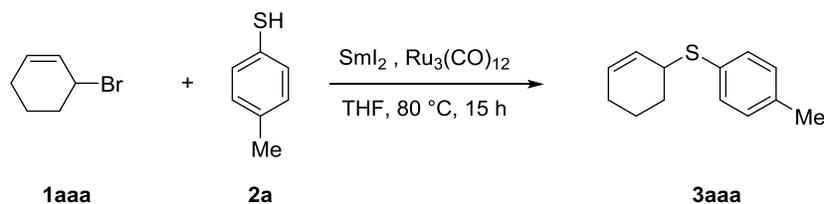
Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 41% yield (19.7 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.13-7.05 (m, 6H), 4.01-3.94 (m, 1H), 3.29-3.23 (m, 2H), 2.94-2.88 (m, 2H), 2.27 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.64, 135.78, 131.05, 130.57, 128.70, 125.60, 123.48, 44.92, 39.08, 20.06.

### 1-(5-Hexen-1-ylthio)-4-methylbenzene (Scheme 2, 3az)<sup>11</sup>



According to the general procedure, the reaction of 6-bromohex-1-ene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 62% yield (25.6 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.82-5.72 (m, 1H), 5.01-4.91 (m, 2H), 2.87 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.07-2.01 (m, 2H), 1.66-1.59 (m, 2H), 1.54-1.46 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 138.57, 136.00, 133.06, 129.90, 129.71, 114.77, 34.27, 33.34, 28.70, 28.06, 21.08.

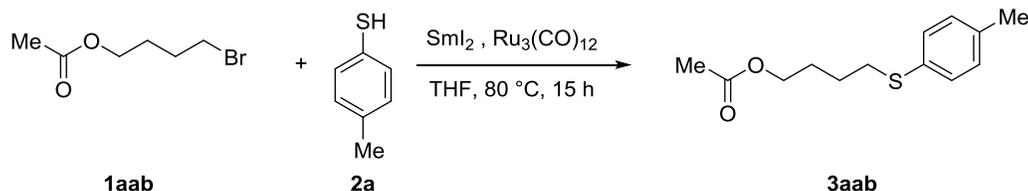
### 1-(2-Cyclohexen-1-ylthio)-4-methylbenzene (Scheme 2, 3aaa)<sup>19</sup>



According to the general procedure, the reaction of 3-bromocyclohex-1-ene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 72% yield (29.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.77-5.73 (m, 1H), 5.71-5.68 (m, 1H), 3.70 (s, 1H), 2.26 (s, 3H), 1.96-1.95 (m, 2H), 1.85-1.79 (m, 2H), 1.71-1.67 (m, 1H), 1.58-

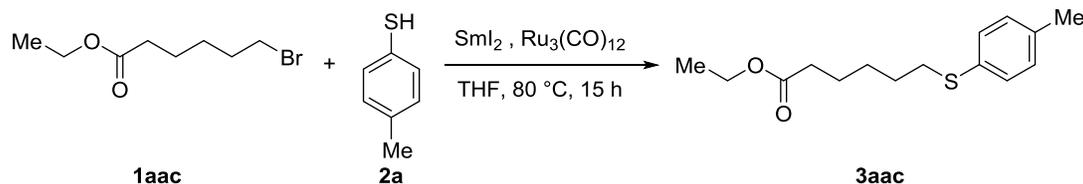
1.54 (m, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 137.26, 132.32, 130.35, 129.71, 128.39, 127.20, 44.60, 28.84, 25.05, 21.24, 19.52.

#### 4-(*p*-Tolylthio)butyl acetate (Scheme 2, 3aab)

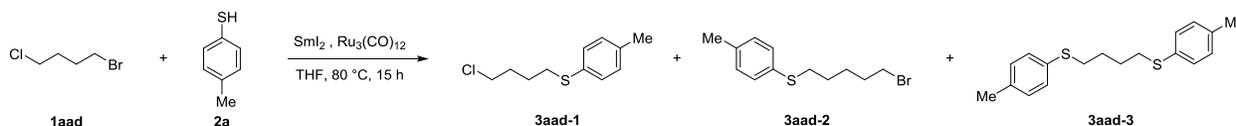


According to the general procedure, the reaction of 4-bromobutyl acetate (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 70% yield (33.4 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.99 (t, *J* = 8.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H), 1.96 (s, 3H), 1.72-1.66 (m, 2H), 1.64-1.57 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.25, 136.33, 132.51, 130.31, 129.78, 64.00, 34.14, 27.68, 25.73, 21.10, 21.06. **HRMS (ESI-TOF) m/z** calcd for C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>S (M<sup>+</sup>) 238.1026, found 238.1024.

#### Ethyl 6-[(4-methylphenyl)thio]hexanoate (Scheme 2, 3aac)<sup>11</sup>



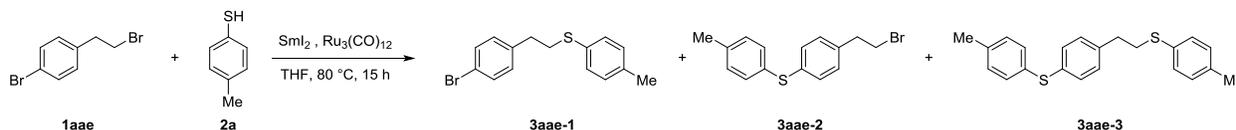
According to the general procedure, the reaction of ethyl 6-bromohexanoate (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 59% yield (31.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.07-4.02 (m, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 2.21 (t, *J* = 8.0 Hz, 2H), 1.59-1.52 (m, 4H), 1.41-1.35 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 173.74, 136.09, 132.88, 130.04, 129.13, 60.34, 34.26, 28.96, 28.30, 24.59, 22.17, 21.09, 14.34.

**(4-Chlorobutyl)(*p*-tolyl)sulfane (Scheme 2, 3aad-1)**<sup>20</sup>

According to the general procedure, the reaction of 1-bromo-4-chlorobutane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 44% yield (18.8 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.20 (s, 1H), 7.18 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.47 (t, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H), 1.88-1.81 (m, 2H), 1.73-1.66 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.39, 132.42, 130.32, 129.81, 44.56, 33.83, 31.45, 26.47, 21.11.

**1,4-Bis(*p*-tolylthio)butane (Scheme 2, 3aad-3)**<sup>21</sup>

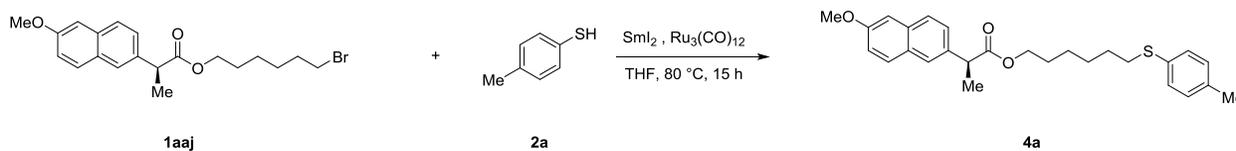
According to the general procedure, the reaction of 1-bromo-4-chlorobutane (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 52% yield (31.5 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.16 (d, *J* = 8.0 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 4H), 2.81-2.77 (m, 4H), 2.25 (s, 6H), 1.68-1.64 (m, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 136.22, 132.66, 130.21, 129.75, 34.05, 28.27, 21.10.

**(4-Bromophenethyl)(*p*-tolyl)sulfane (Scheme 2, 3aae-1)**<sup>1</sup>

According to the general procedure, the reaction of 1-bromo-4-(2-bromoethyl)benzene (0.20 mmol, 1.0 equiv), 4-methylbenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 88% yield (54.1 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.01 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 3H). **<sup>13</sup>C NMR**

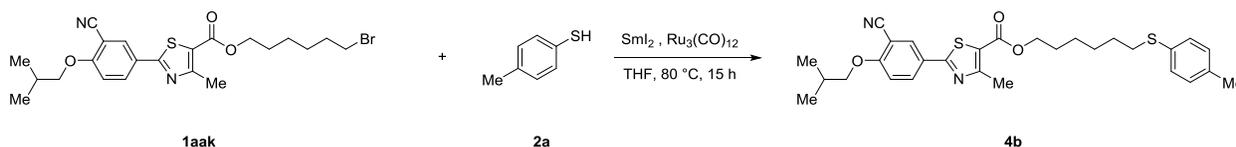
**(101 MHz, CDCl<sub>3</sub>)**  $\delta$  139.30, 136.55, 132.19, 131.62, 130.44, 130.41, 129.88, 120.31, 35.80, 35.17, 21.14.

### 6-(*p*-Tolylthio)hexyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (Scheme 2, 4a)



According to the general procedure, the reaction of 6-bromohexyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 84% yield (36.7 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.61 (t, *J* = 8.0 Hz, 3H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 2H), 7.07-6.99 (m, 4H), 4.01-3.96 (m, 2H), 3.84 (s, 3H), 3.79-3.72 (m, 1H), 2.74-2.67 (m, 2H), 2.24 (s, 3H), 1.66-1.54 (m, 2H), 1.49-1.45 (m, 5H), 1.43-1.10 (m, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  174.78, 157.70, 135.77, 133.75, 130.21, 129.86, 129.75, 129.71, 129.37, 129.00, 127.22, 126.31, 126.00, 119.06, 105.66, 64.33, 55.40, 45.57, 34.03, 29.10, 28.48, 27.64, 25.65, 21.09, 18.54. **HRMS (ESI-TOF) m/z** calcd for C<sub>27</sub>H<sub>33</sub>O<sub>3</sub>S (M<sup>+</sup>+H) 437.2145, found 437.2178.

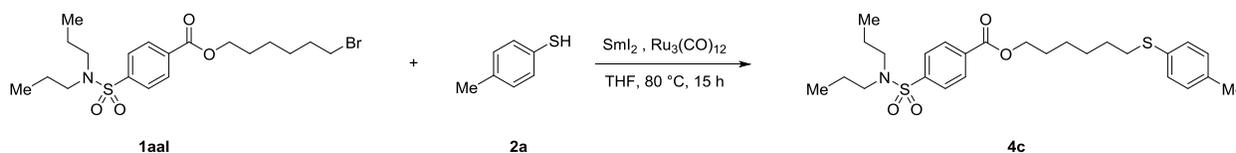
### 6-(*p*-Tolylthio)hexyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (Scheme 2, 4b)



According to the general procedure, the reaction of 6-bromohexyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 71% yield (37.1 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.11 (d, *J* = 4.0 Hz, 1H), 8.03-8.00 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.21 (t, *J* = 8.0 Hz, 2H), 3.83 (d, *J* = 4.0 Hz, 2H), 2.82 (t, *J* = 8.0 Hz, 2H), 2.69 (s,

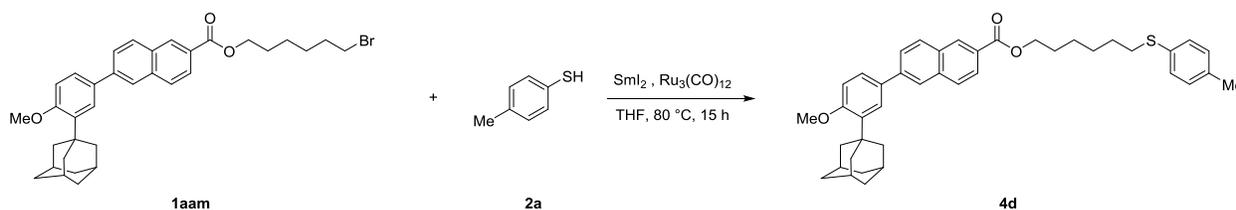
3H), 2.24 (s, 3H), 2.15-2.12 (m, 1H), 1.71-1.65 (m, 2H), 1.63-1.57 (m, 2H), 1.45-1.34 (m, 4H), 1.02 (d,  $J = 4.0$  Hz, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  167.29, 162.58, 162.20, 161.21, 136.06, 132.97, 132.66, 132.19, 129.93, 129.73, 126.09, 121.96, 115.50, 112.69, 103.06, 65.39, 34.32, 29.13, 28.60, 28.40, 28.24, 25.68, 21.08, 19.15, 17.57. **HRMS (ESI-TOF)  $m/z$**  calcd for C<sub>29</sub>H<sub>35</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub> (M<sup>+</sup>+H) 523.2084, found 523.2083.

### 6-(*p*-Tolylthio)hexyl 4-(*N,N*-dipropylsulfamoyl)benzoate (Scheme 2, 4c)



According to the general procedure, the reaction of 6-bromohexyl 4-(*N,N*-dipropylsulfamoyl)benzoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 77% yield (37.9 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.1 (d,  $J = 8.0$  Hz, 2H), 7.85 (d,  $J = 8.0$  Hz, 2H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.08 (d,  $J = 8.0$  Hz, 2H), 4.32 (t,  $J = 8.0$  Hz, 2H), 3.08 (d,  $J = 8.0$  Hz, 4H), 2.87 (t,  $J = 8.0$  Hz, 2H), 2.30 (s, 3H), 1.79-1.73 (m, 2H), 1.68-1.47 (m, 10H), 0.85 (t,  $J = 4.0$  Hz, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  165.41, 144.24, 136.11, 133.80, 132.92, 130.27, 129.96, 129.74, 127.08, 65.69, 50.02, 34.33, 29.15, 28.61, 28.43, 25.69, 22.02, 21.09, 11.25. **HRMS (ESI-TOF)  $m/z$**  calcd for C<sub>26</sub>H<sub>38</sub>NO<sub>4</sub>S<sub>2</sub> (M<sup>+</sup>+H) 492.2237, found 492.2244.

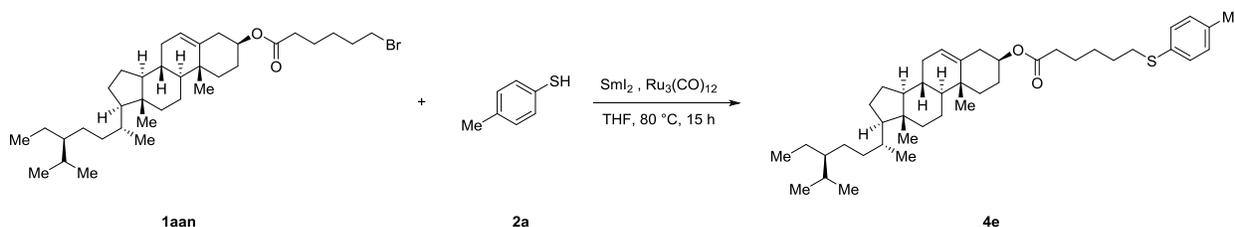
### 6-(*p*-Tolylthio)hexyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (Scheme 2, 4d)



According to the general procedure, the reaction of 6-bromohexyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 49% yield

(30.3 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.52 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 4.30 (t, *J* = 8.0 Hz, 2H), 3.84 (s, 3H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 2.11 (s, 6H), 2.03 (s, 3H), 1.73 (s, 6H), 1.63-1.67 (m, 2H), 1.50 (s, 2H), 1.45-1.43 (m, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 166.99, 159.01, 141.42, 139.09, 136.42, 136.03, 132.99, 131.34, 130.82, 129.97, 129.80, 129.73, 128.29, 127.29, 126.54, 126.07, 125.82, 125.68, 124.82, 112.19, 36.14, 55.26, 40.69, 37.29, 37.21, 34.37, 29.19, 28.77, 28.52, 28.00, 25.79, 21.09. **HRMS (ESI-TOF) m/z** calcd for C<sub>41</sub>H<sub>47</sub>O<sub>3</sub>S (M<sup>+</sup>+H) 619.3240, found 619.3242.

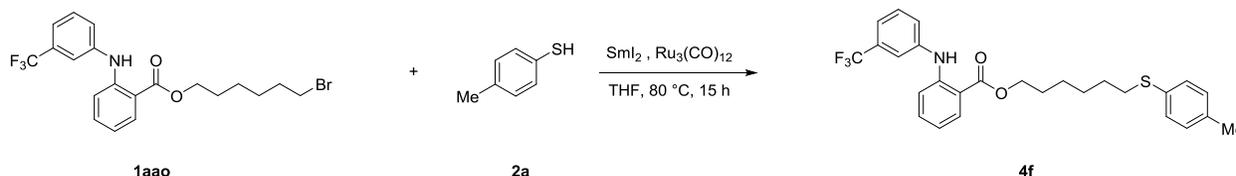
**(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*)-5-Ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 6-(*p*-tolylthio)hexanoate (Scheme 2, 4e)**



According to the general procedure, the reaction of (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*)-5-ethyl-6-methylheptan-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 6-bromohexanoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 54% yield (34.3 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.31 (s, 1H), 4.58-4.50 (m, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 2H), 2.19 (t, *J* = 8.0 Hz, 2H), 1.95-1.89 (m, 2H), 1.80-1.73 (m, 3H), 1.64-1.57 (m, 2H), 1.55-1.51 (m, 1H), 1.43-1.33 (m, 6H), 1.22-1.05 (m, 10H), 0.99 (t, *J* = 8.0 Hz, 1H), 0.95 (s, 3H), 0.92-0.89 (m, 1H), 0.86-0.83 (m, 3H), 0.79-0.77 (m, 3H), 0.76-0.69 (m, 6H), 0.62 (d, *J* = 8.0 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 173.37, 139.83, 136.08, 132.84, 130.02, 129.73, 122.73, 73.90, 56.77, 16.09, 51.37, 50.10, 45.90, 42.39, 41.97, 40.60, 39.80, 38.23, 37.07, 36.68, 36.24, 34.60, 34.25, 33.79, 31.94, 29.76, 28.95, 28.27, 27.88, 26.12, 24.67, 23.10, 21.09,

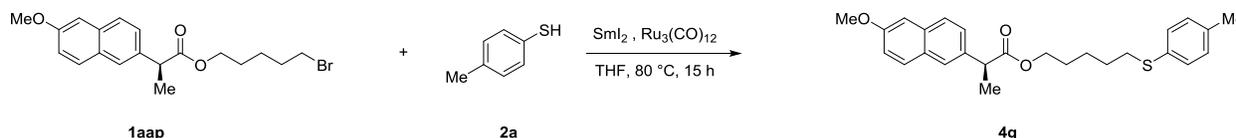
19.91, 19.41, 19.11, 12.32, 11.94. **HRMS (ESI-TOF) m/z** calcd for C<sub>42</sub>H<sub>67</sub>O<sub>2</sub>S (M<sup>+</sup>+H) 635.4856, found 635.4861.

### 6-(*p*-Tolylthio)hexyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (Scheme 2, 4f)



According to the general procedure, the reaction of 6-bromohexyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 91% yield (44.4 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.32-7.25 (m, 1H), 7.16 (t, *J* = 8.0 Hz, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 3.84 (t, *J* = 6.6 Hz, 2H), 3.72 (s, 1H), 1.71-1.64 (m, 2H), 1.36 (t, *J* = 8.0 Hz, 2H), 1.21-1.18 (m, 12H), 1.15 (s, 12H), 0.81 (t, *J* = 6.6 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 168.55, 146.77, 141.76, 136.07, 134.27, 132.97, 131.90 (q, *J<sup>F</sup>* = 96.8.0 Hz), 131.82, 130.38, 129.98, 129.74, 124.54, 124.06 (q, *J<sup>F</sup>* = 821.1 Hz), 119.57 (d, *J<sup>F</sup>* = 5.1 Hz), 118.38, 118.02 (q, *J<sup>F</sup>* = 12.1 Hz), 114.38, 113.28, 64.91, 34.35, 29.18, 28.65, 28.47, 25.77, 21.08. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -62.43. **HRMS (ESI-TOF) m/z** calcd for C<sub>27</sub>H<sub>29</sub>F<sub>3</sub>NO<sub>2</sub>S (M<sup>+</sup>+H) 488.1866, found 488.1871.

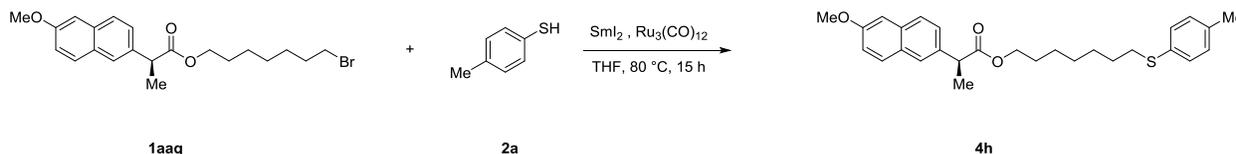
### 5-(*p*-Tolylthio)pentyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (Scheme 2, 4g)



According to the general procedure, the reaction of 5-bromopentyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 54% yield (22.8 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.61 (t, *J* = 8.0 Hz, 3H), 7.34-7.31 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.07-7.04 (m, 1H), 7.01 (t, 3H), 4.00-3.96 (m, 2H), 3.83 (s, 3H), 3.79-3.73 (m, 1H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 1.52-1.43 (m, 9H). **<sup>13</sup>C NMR (101**

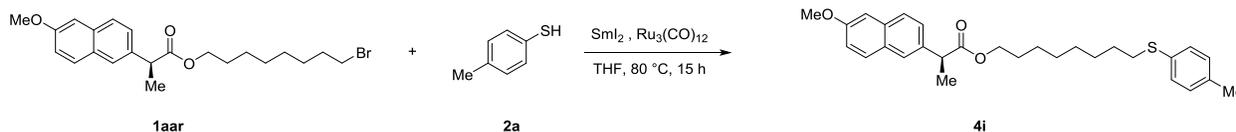
**MHz, CDCl<sub>3</sub>)**  $\delta$  174.81, 157.71, 136.05, 135.87, 133.76, 132.88, 129.95, 129.72, 129.36, 129.00, 127.20, 126.34, 126.03, 119.07, 105.66, 64.64, 55.39, 45.59, 34.15, 28.80, 28.19, 25.07, 21.09, 18.50. **HRMS (ESI-TOF) m/z** calcd for C<sub>26</sub>H<sub>31</sub>O<sub>3</sub>S (M<sup>+</sup>+H) 423.1988, found 423.2000.

### 7-(*p*-Tolylthio)heptyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (Scheme 2, 4h)



According to the general procedure, the reaction of 7-bromoheptyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 65% yield (29.3 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.61 (t, *J* = 8.0 Hz, 3H), 7.34-7.31 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07-7.04 (m, 1H), 7.03-7.00 (m, 3H), 3.99-3.95 (m, 2H), 3.83 (s, 3H), 3.79-3.73 (m, 1H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.53-1.44 (m, 7H), 1.23-1.12 (m, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  174.86, 157.69, 135.95, 135.93, 133.76, 133.14, 129.84, 129.71, 129.36, 129.01, 127.18, 126.36, 126.01, 119.04, 105.66, 64.86, 55.39, 45.61, 34.32, 29.11, 28.74, 28.64, 28.52, 25.73, 21.08, 18.54. **HRMS (ESI-TOF) m/z** calcd for C<sub>28</sub>H<sub>35</sub>O<sub>3</sub>S (M<sup>+</sup>+H) 451.2301, found 451.2319.

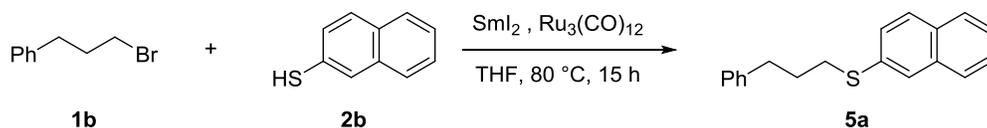
### 8-(*p*-Tolylthio)octyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (Scheme 2, 4i)



According to the general procedure, the reaction of 8-bromooctyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv), SmI<sub>2</sub> (0.20 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.005 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 67% yield (31.1 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.61 (t, *J* = 8.0 Hz, 3H), 7.34-7.32 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07-7.01 (m, 4H), 3.98 (t, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.79-3.74 (m, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.52-1.44 (m, 7H), 1.27-1.13 (m, 4H), 1.12-1.09

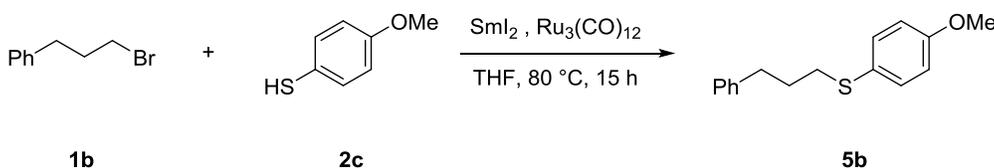
(m, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.86, 157.69, 135.93, 133.75, 133.18, 129.83, 129.71, 129.36, 129.01, 127.17, 126.79, 126.37, 126.01, 119.03, 105.65, 64.92, 55.40, 45.62, 34.34, 29.25, 29.08, 29.05, 28.69, 28.58, 25.79, 21.08, 18.57. **HRMS (ESI-TOF) m/z** calcd for C<sub>29</sub>H<sub>37</sub>O<sub>3</sub>S (M<sup>+</sup>+H) 465.2458, found 465.2457.

### 2-[(3-Phenylpropyl)thio]naphthalene (Scheme 3, 5a)<sup>22</sup>

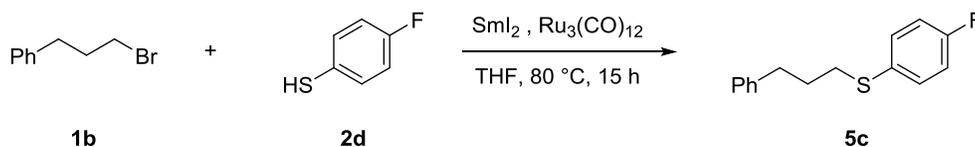


According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), naphthalene-2-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 83% yield (46.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.72-7.60 (m, 4H), 7.41-7.31 (m, 3H), 7.23-7.15 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.98-1.91 (m, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.23, 133.04, 132.75, 130.63, 127.52, 127.42, 127.31, 126.67, 126.28, 125.97, 125.48, 124.99, 124.51, 33.68, 31.60, 29.55.

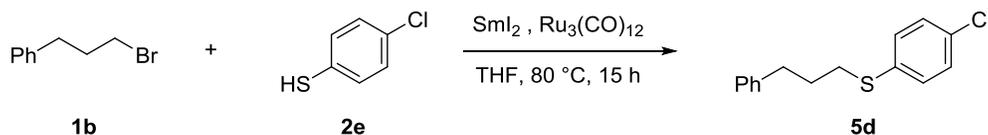
### 1-Methoxy-4-[(3-phenylpropyl)thio]benzene (Scheme 3, 5b)<sup>2</sup>



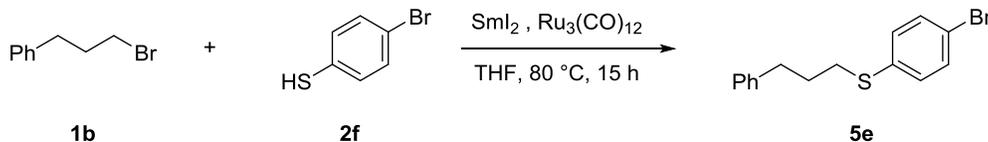
According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 90% yield (46.5 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.28-7.24 (m, 2H), 7.21 (t, *J* = 4.0 Hz, 2H), 7.13-7.07 (m, 3H), 6.77-6.74 (m, 2H), 3.72 (s, 3H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.86-1.79 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 158.94, 141.56, 133.29, 132.52, 128.59, 128.47, 126.00, 114.63, 55.43, 35.22, 34.66, 30.88.

**1-Fluoro-4-[(3-phenylpropyl)thio]benzene (Scheme 3, 5c)<sup>22</sup>**

According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 4-fluorobenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 82% yield (40.4 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.25-7.18 (m, 4H), 7.14-7.07 (m, 3H), 6.93-6.87 (m, 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.88-1.81 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 161.81 (d, *J<sup>F</sup>* = 247.5 Hz), 141.32, 132.31 (d, *J<sup>F</sup>* = 8.1 Hz), 131.31 (d, *J<sup>F</sup>* = 4.0 Hz), 128.58, 128.52, 126.11, 116.07 (d, *J<sup>F</sup>* = 22.2 Hz), 34.65, 34.33, 30.72. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -115.70.

**1-Chloro-4-[(3-phenylpropyl)thio]benzene (Scheme 3, 5d)<sup>2</sup>**

According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 4-chlorobenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 88% yield (46.3 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.23-7.15 (m, 6H), 7.10 (t, *J* = 8.0 Hz, 3H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 1.91-1.83 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.20, 135.16, 131.88, 130.51, 129.08, 128.59, 128.55, 126.16, 34.69, 33.15, 30.58.

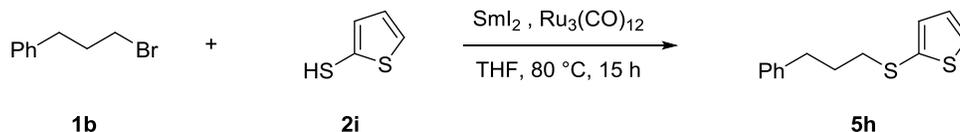
**1-Bromo-4-[(3-phenylpropyl)thio]benzene (Scheme 3, 5e)<sup>23</sup>**

According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 4-bromobenzenethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and



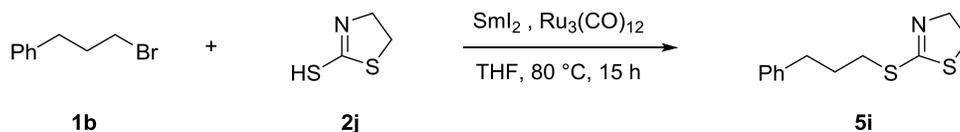
4.0 Hz), 122.13 (d,  $J^F = 18.2$  Hz), 114.61 (d,  $J^F = 22.2$  Hz), 83.91, 24.67. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -109.87.

### 2-[(3-Phenylpropyl)thio]thiophene (Scheme 3, 5h)<sup>25</sup>

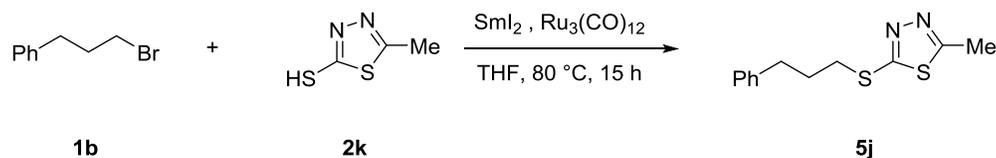


According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), thiophene-2-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 39% yield (18.3 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.43 (d,  $J = 8.0$  Hz, 1H), 7.23 (t,  $J = 8.0$  Hz, 2H), 7.14 (t,  $J = 8.0$  Hz, 3H), 7.09 (d,  $J = 4.0$  Hz, 1H), 6.94 (d,  $J = 8.0$  Hz, 1H), 3.33 (t,  $J = 8.0$  Hz, 2H), 2.71 (t,  $J = 8.0$  Hz, 2H), 2.14-2.07 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  135.76, 132.39, 128.66, 128.60, 127.86, 126.29, 34.25, 34.05, 33.22.

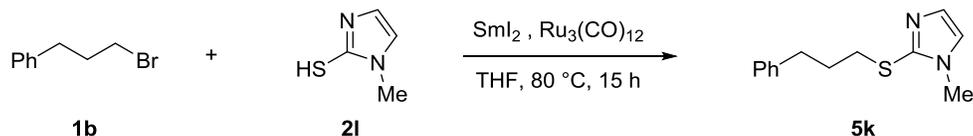
### 2-((3-Phenylpropyl)thio)-4,5-dihydrothiazole (Scheme 3, 5i)<sup>26</sup>



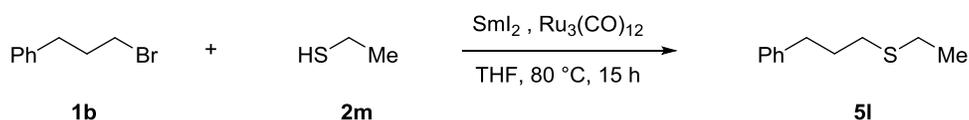
According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 4,5-dihydrothiazole-2-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 57% yield (27.1 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.22 (t,  $J = 8.0$  Hz, 2H), 7.13 (d,  $J = 8.0$  Hz, 3H), 4.19 (t,  $J = 8.0$  Hz, 2H), 3.37 (t,  $J = 8.0$  Hz, 2H), 3.14 (t,  $J = 8.0$  Hz, 2H), 2.68 (t,  $J = 8.0$  Hz, 2H), 2.02-1.95 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  150.29, 140.92, 128.59, 128.57, 126.21, 62.70, 34.95, 34.65, 32.91, 30.82.

**2-Methyl-5-[(3-phenylpropyl)thio]-1,3,4-thiadiazole (Scheme 3, 5j)**

According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 5-methyl-1,3,4-thiadiazole-2-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 51% yield (25.5 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 3H), 3.23 (t, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 2.09-2.02 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 165.70, 165.07, 140.89, 128.59, 126.22, 34.66, 33.49, 30.74, 15.72. **HRMS (ESI-TOF) *m/z*** calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>S<sub>2</sub> (M<sup>+</sup>) 250.0598, found 250.0597.

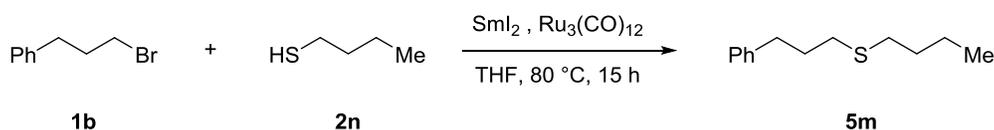
**1-Methyl-2-[(3-phenylpropyl)thio]-1H-imidazole (Scheme 3, 5k)**

According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 1-methyl-1H-imidazole-2-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 87% yield (40.4 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22-7.20 (m, 1H), 7.18 (s, 1H), 7.11 (t, *J* = 8.0 Hz, 3H), 7.01 (s, 1H), 6.86 (s, 1H), 3.55 (s, 3H), 3.02 (t, *J* = 8.0 Hz, 2H), 2.68 (t, 2H), 1.95-1.88 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.87, 141.26, 128.85, 128.58, 128.51, 126.09, 122.22, 34.62, 33.78, 33.45, 31.35. **HRMS (ESI-TOF) *m/z*** calcd for C<sub>13</sub>H<sub>17</sub>N<sub>2</sub>S (M<sup>+</sup>+H) 233.1107, found 233.1113.

**[3-(Ethylthio)propyl]benzene (Scheme 3, 5l)<sup>27</sup>**

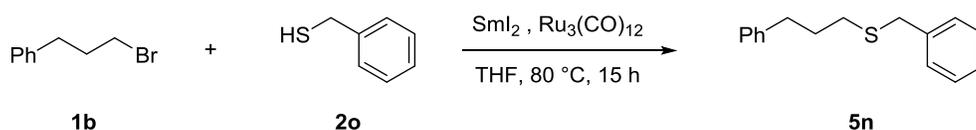
According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), ethanethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 56% yield (20.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.24-7.20 (m, 2H), 7.13-7.11 (m, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.50-2.44 (m, 4H), 1.88-1.81 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 140.62, 127.46, 127.35, 124.87, 33.85, 30.11, 29.97, 24.83, 13.78.

### [3-(Butylthio)propyl]benzene (Scheme 3, 5m)<sup>28</sup>

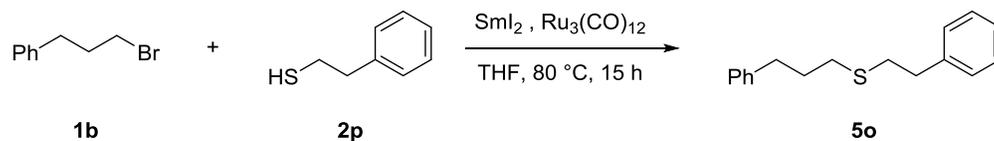


According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), butane-1-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 39% yield (16.3 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.22 (t, *J* = 8.0 Hz, 2H), 7.14-7.10 (m, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.47-2.42 (m, 4H), 1.88-1.80 (m, 2H), 1.46 (t, *J* = 8.0 Hz, 2H), 1.36-1.30 (m, 2H), 0.84 (t, *J* = 8.0 Hz, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.75, 128.57, 128.46, 125.97, 34.95, 31.86, 31.56, 31.30, 22.12, 13.80, 1.03.

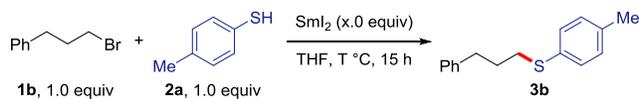
### [3-[(Phenylmethyl)thio]propyl]benzene (Scheme 3, 5n)<sup>28</sup>



According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), phenylmethanethiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 19% yield (9.2 mg). Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.25-7.20 (m, 5H), 7.18-7.06 (m, 5H), 3.63 (s, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.36 (t, *J* = 8.0 Hz, 2H), 1.84-1.77 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.65, 138.63, 128.92, 128.57, 128.46, 126.99, 125.97, 36.26, 34.88, 30.90, 30.72.

**Phenethyl(3-phenylpropyl)sulfane (Scheme 3, 5o)**

According to the general procedure, the reaction of (3-bromopropyl)benzene (0.20 mmol, 1.0 equiv), 2-phenylethane-1-thiol (0.60 mmol, 3.0 equiv), SmI<sub>2</sub> (0.40 mmol, 2.0 equiv) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.01 mmol, 5 mol%) in THF (0.1 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 84% yield (43.1 mg). *New Compound*. Yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.24-7.19 (m, 4H), 7.16-7.10 (m, 6H), 2.81-2.77 (m, 2H), 2.71-2.67 (m, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.47 (t, *J* = 8.0 Hz, 2H), 1.88-1.80 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.64, 140.73, 128.73, 128.58, 128.50, 126.53, 126.44, 126.03, 36.45, 34.92, 33.68, 31.67, 31.24. **HRMS (ESI-TOF) m/z** calcd for C<sub>17</sub>H<sub>20</sub>SNa (M<sup>+</sup>+Na) 279.1178, found 279.1179.

**Table S1.** Summary of optimizations.<sup>a</sup>

entry	catalyst	temp (°C)	yield (%)
1		80 °C	16
2	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> (5 mol%)	80 °C	16
3	Ni(dppp)Cl <sub>2</sub> (5 mol%)	80 °C	39
4	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl (2 mol%)	80 °C	32
5	CuI (5 mol%)	80 °C	21
6	AgBF <sub>4</sub> (5 mol%)	80 °C	<2
7	NaBF <sub>4</sub> (5 mol%)	80 °C	<2
8	FeCl <sub>3</sub> (5 mol%)	80 °C	22
9	CoI <sub>2</sub> (5 mol%)	80 °C	33
10	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	65
11	Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub> (5 mol%)	80 °C	17
12	Ru(PPh <sub>3</sub> ) <sub>3</sub> (CO)HCl (5 mol%)	80 °C	25
13	Ru(PPh <sub>3</sub> ) <sub>2</sub> (Cp)Cl (5 mol%)	80 °C	16
14	Ru(PPh <sub>3</sub> ) <sub>2</sub> (indenyl)Cl (5 mol%)	80 °C	22
15	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub> (5 mol%)	80 °C	<2
16	RuCl <sub>3</sub> (5 mol%)	80 °C	<2
17	Ru(acac) <sub>3</sub> (5 mol%)	80 °C	37
18 <sup>b</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	77
19 <sup>c</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	80
20 <sup>d</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	85
21 <sup>e</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	90
22 <sup>b</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	60 °C	55
23 <sup>b</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	100 °C	79
24 <sup>b</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	120 °C	72
25 <sup>e,f</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	0
26 <sup>g</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	69
27 <sup>e,h</sup>	Ru <sub>3</sub> (CO) <sub>12</sub> (5 mol%)	80 °C	78

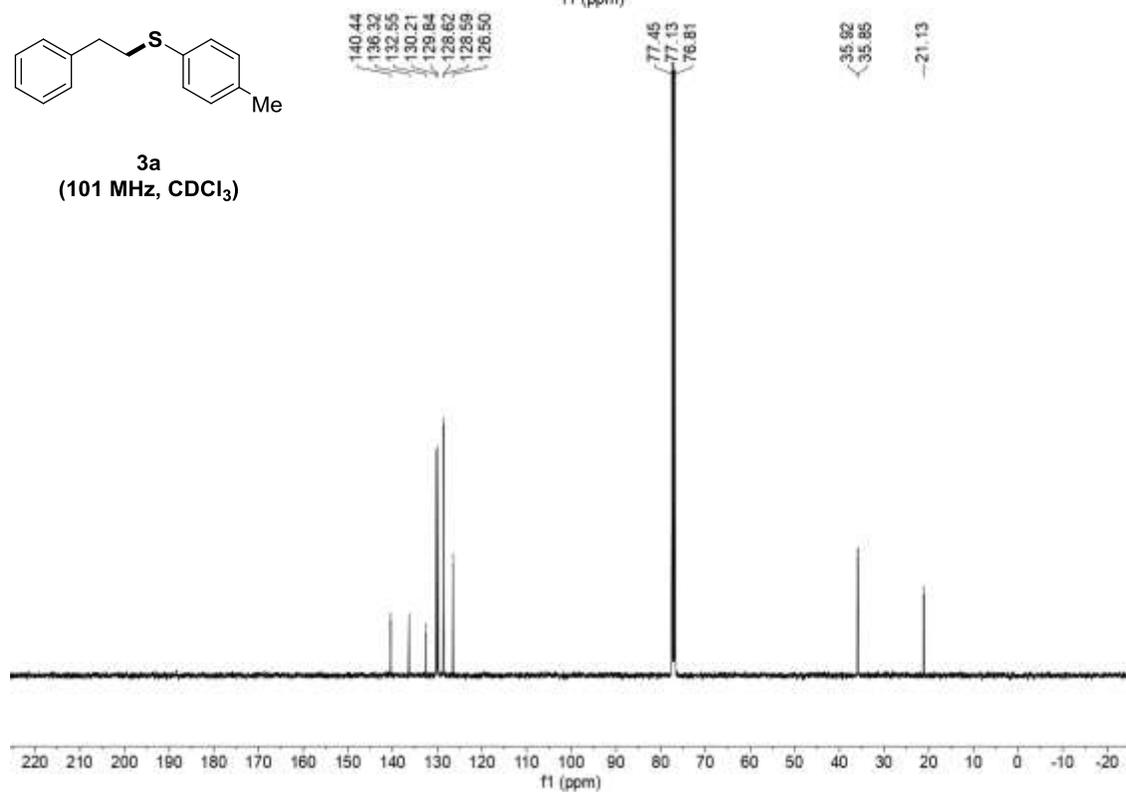
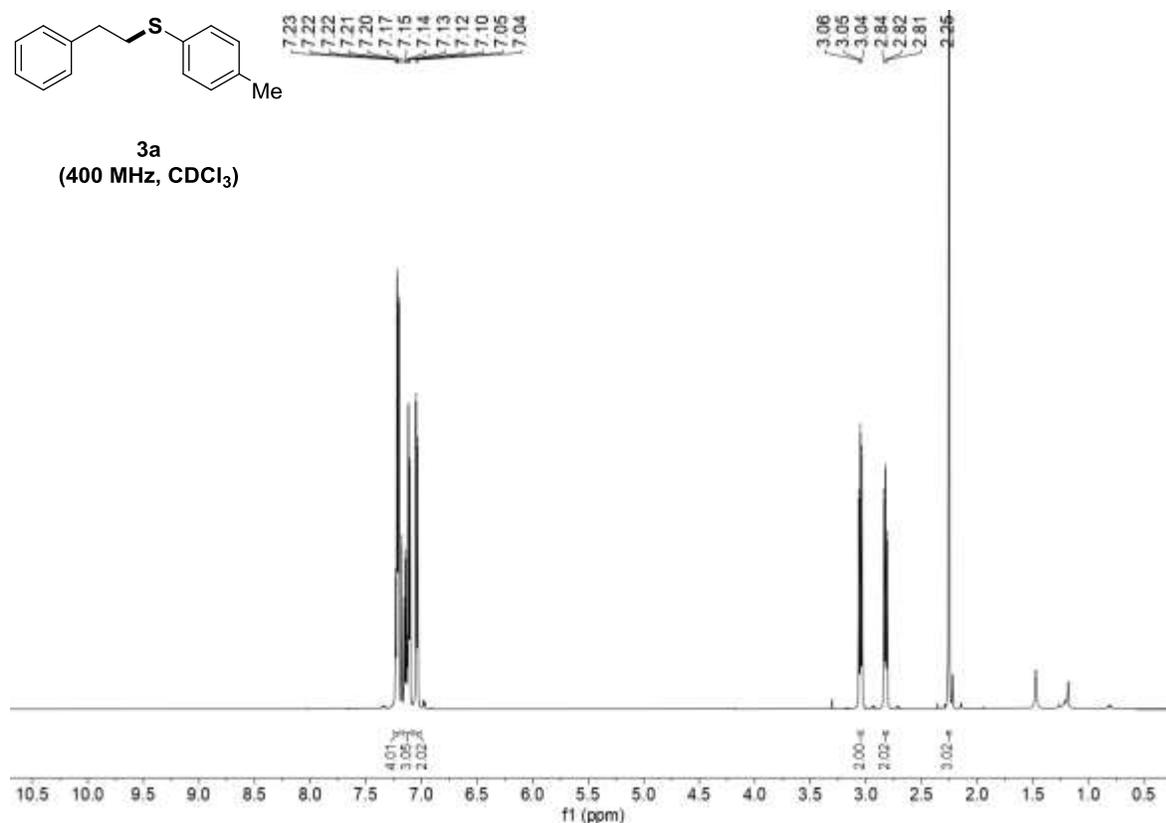
<sup>a</sup>Conditions: **1b** (0.1 mmol, 1.0 equiv), **2a** (1.0 equiv), SmI<sub>2</sub> (2.0 equiv), catalyst (x mol%), THF, 15 h; <sup>b</sup>**2a** (1.5 equiv); <sup>c</sup>**2a** (2.0 equiv); <sup>d</sup>**2a** (2.5 equiv); <sup>e</sup>**2a** (3.0 equiv); <sup>f</sup>without SmI<sub>2</sub>; <sup>g</sup>SmI<sub>2</sub> (1.0 equiv); <sup>h</sup>SmI<sub>2</sub> (1.5 equiv).

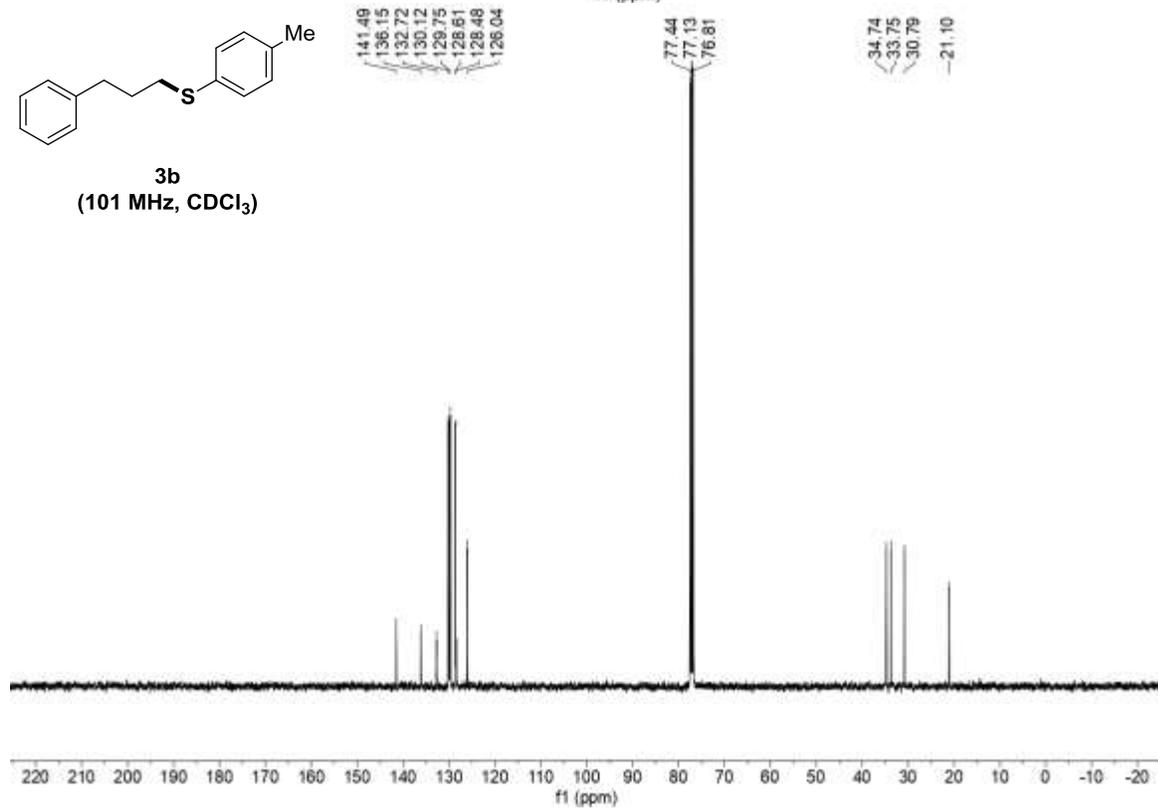
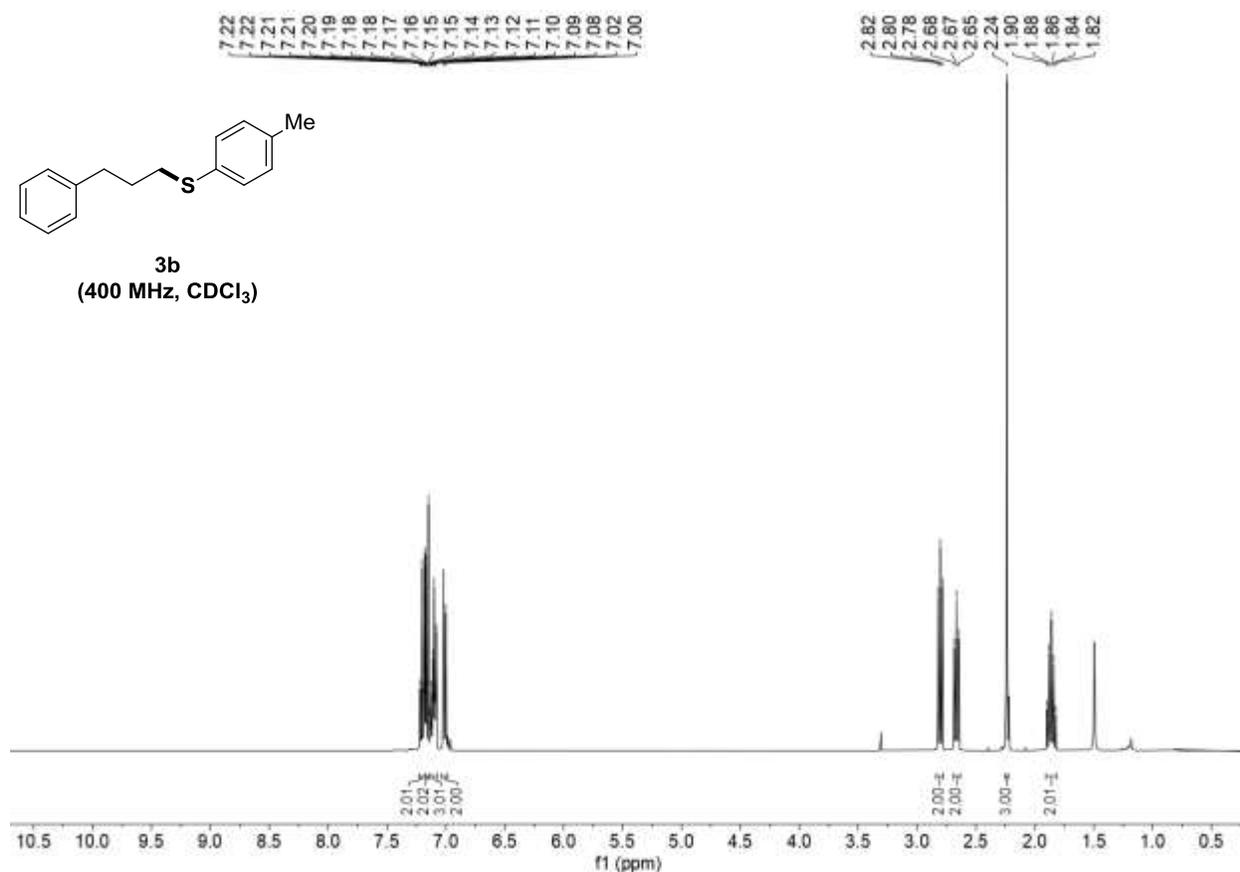
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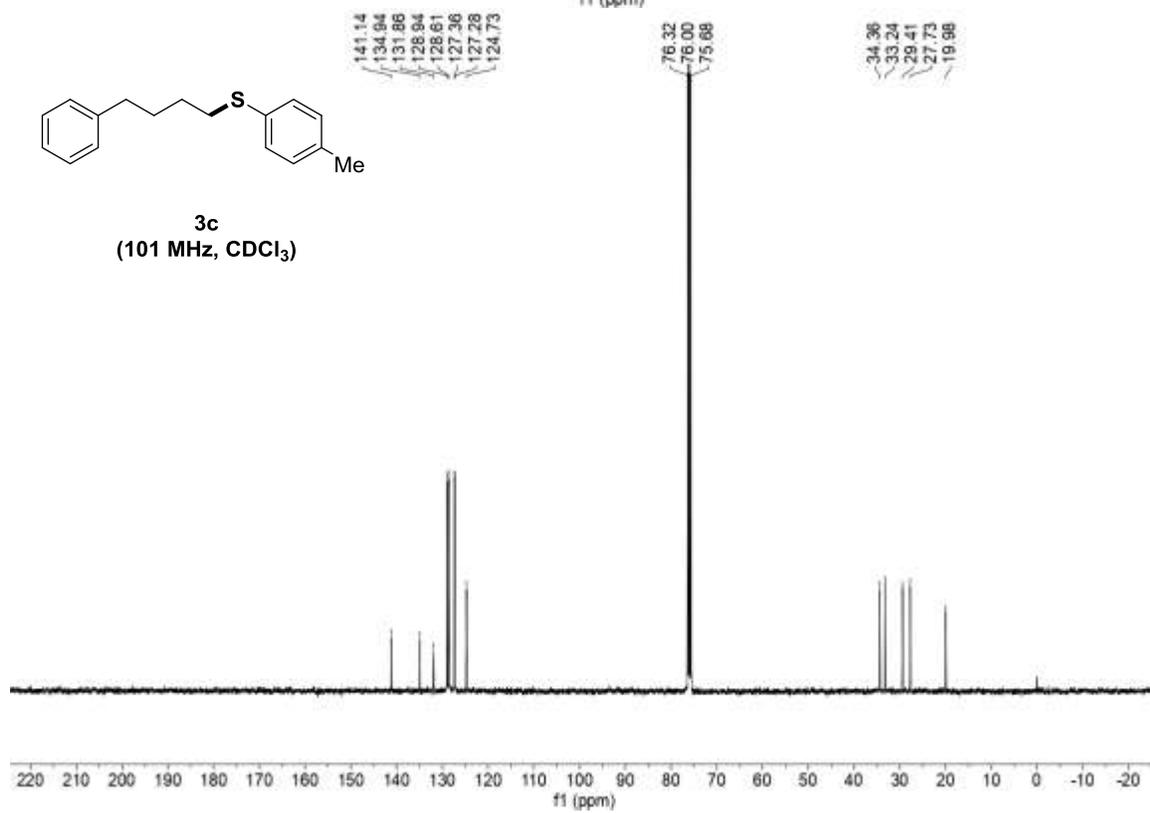
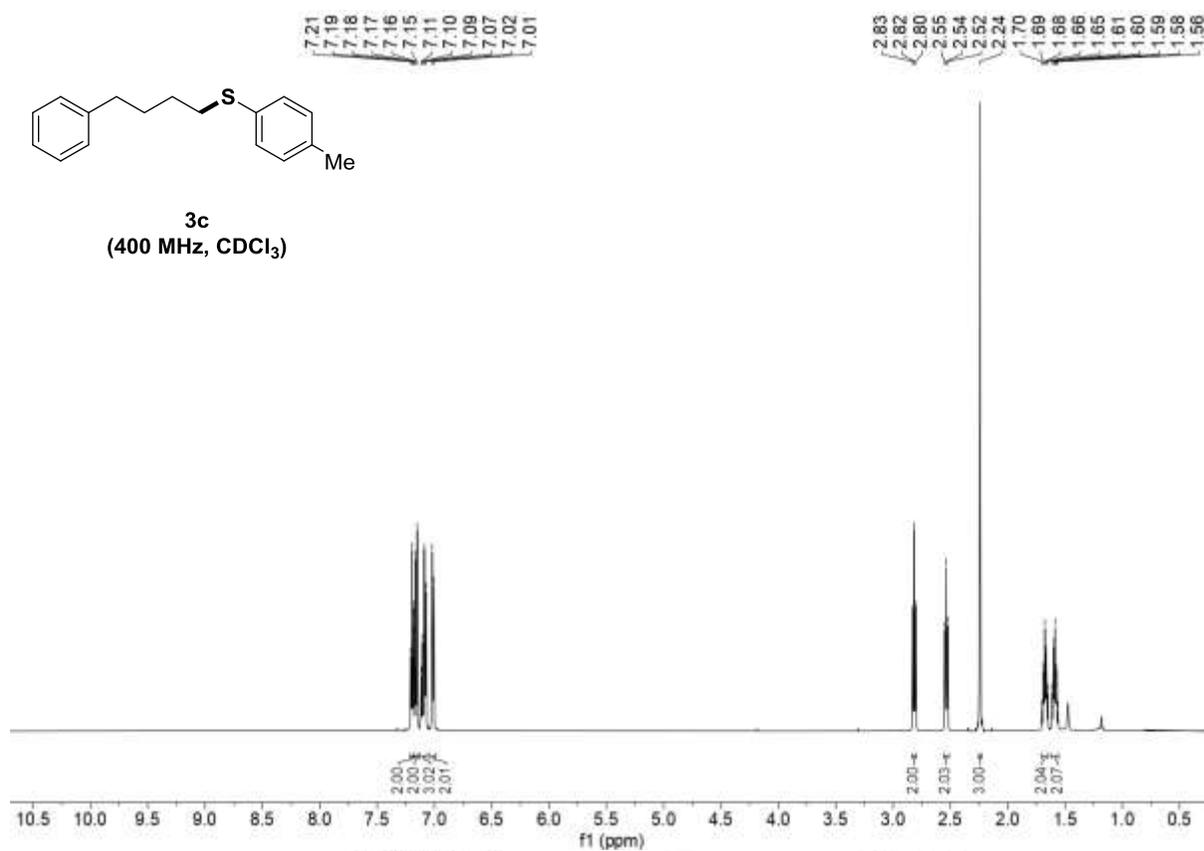
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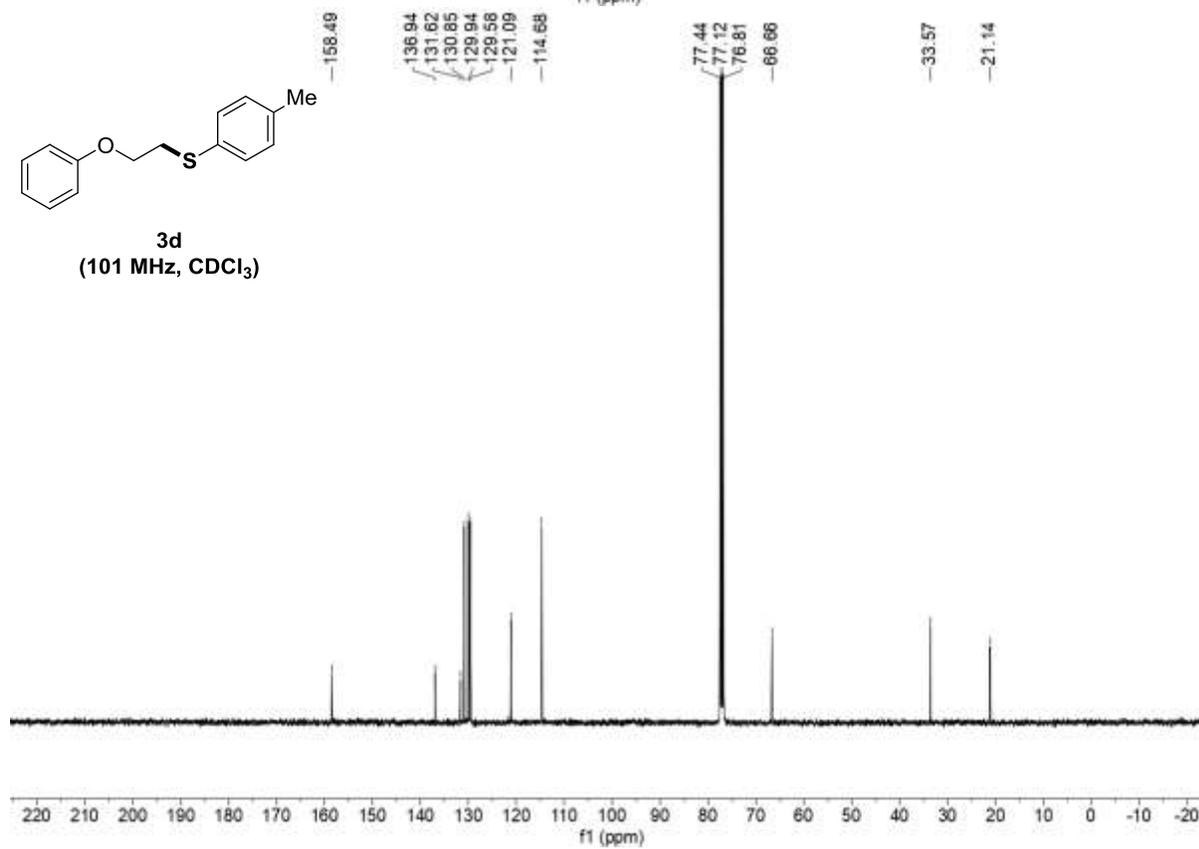
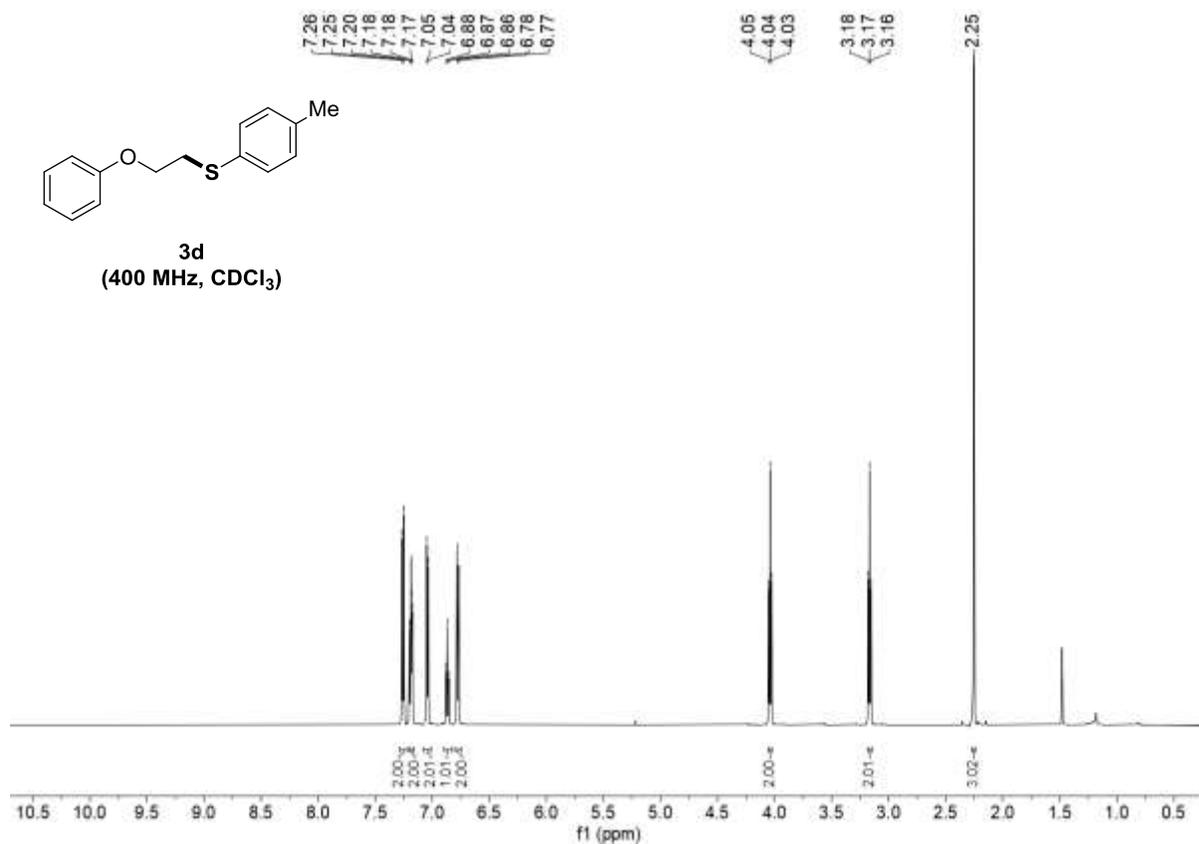
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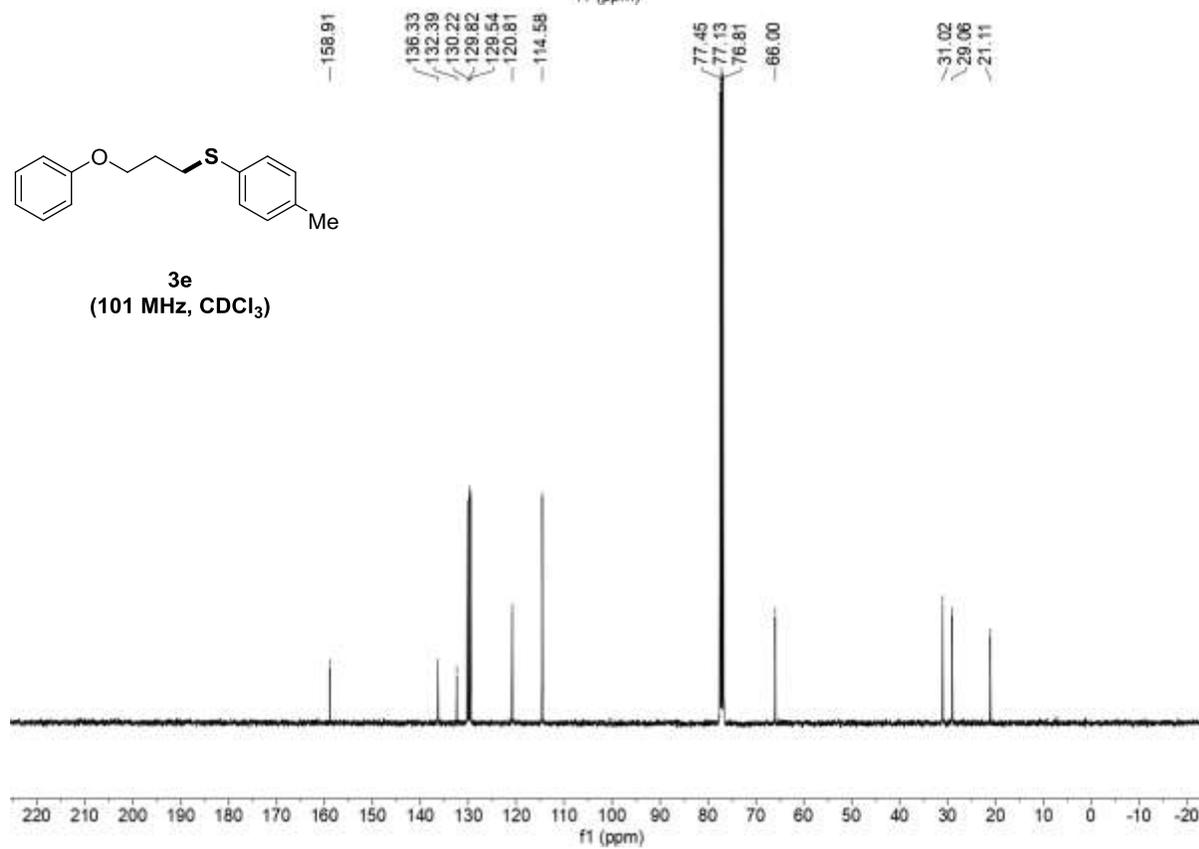
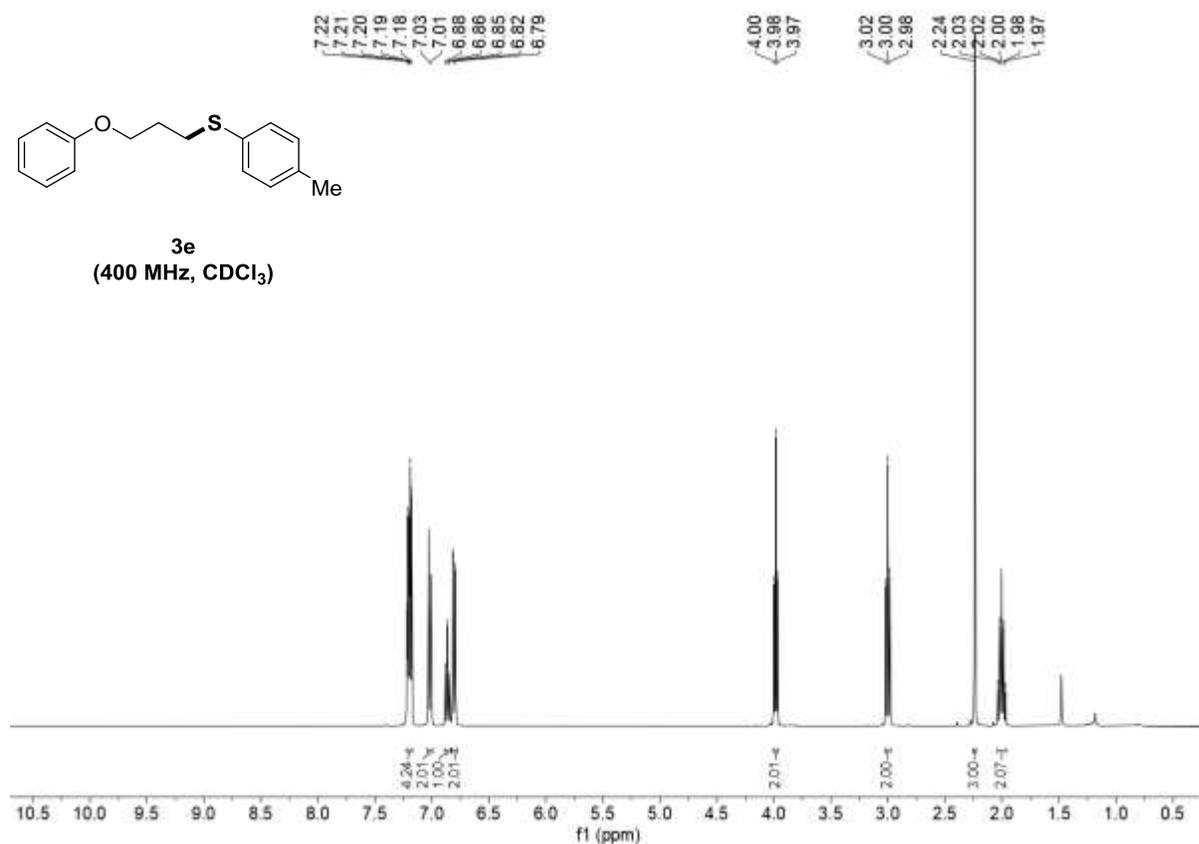
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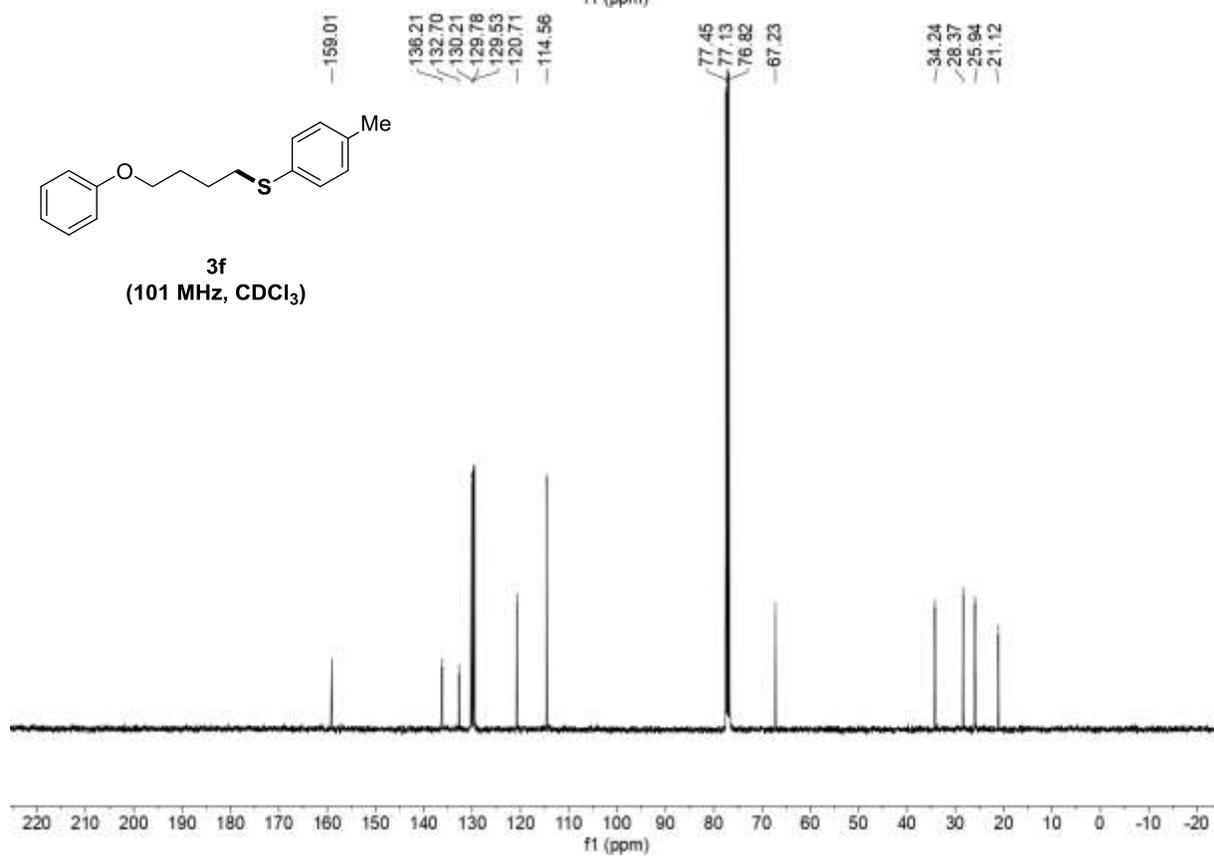
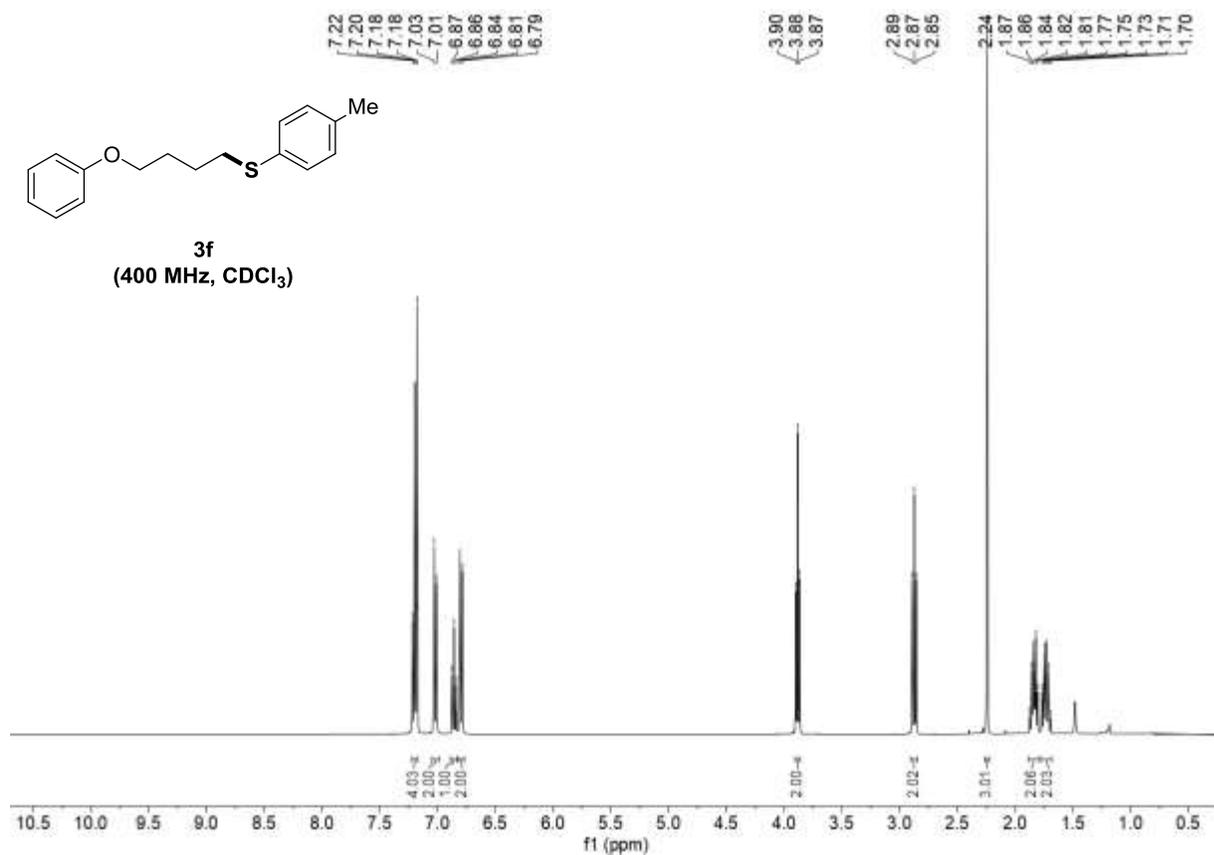


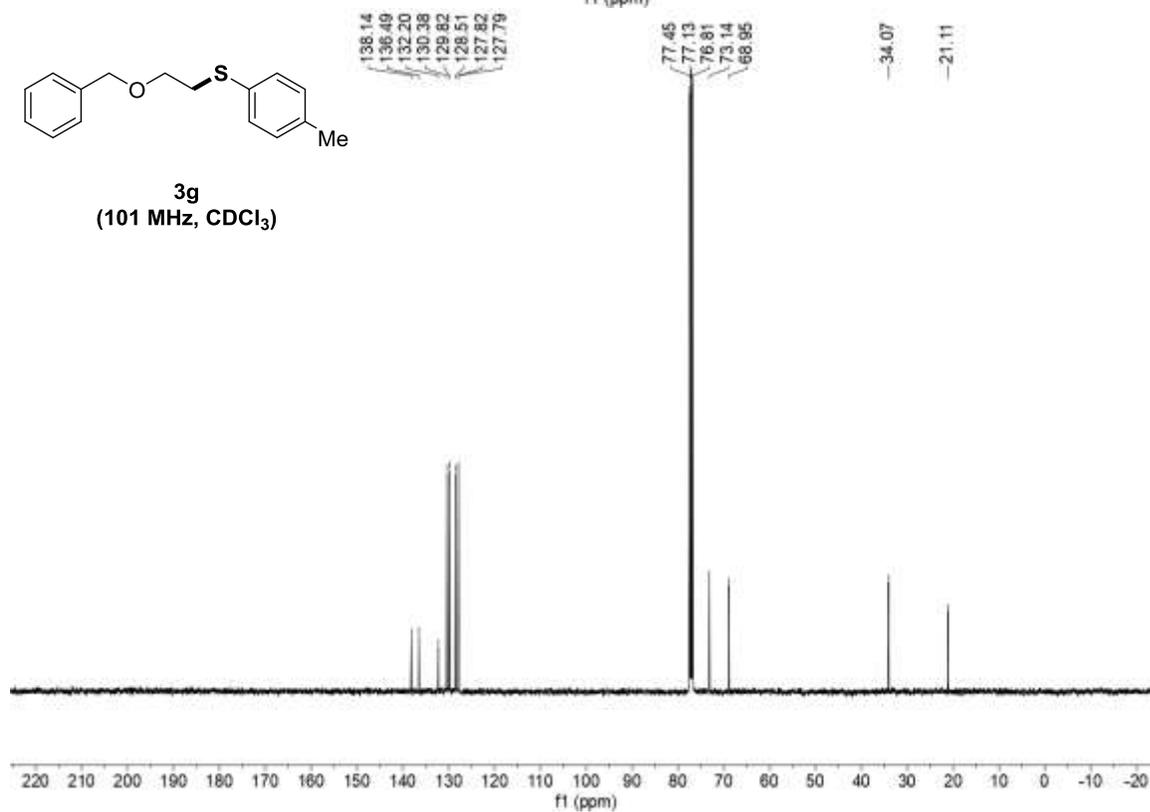
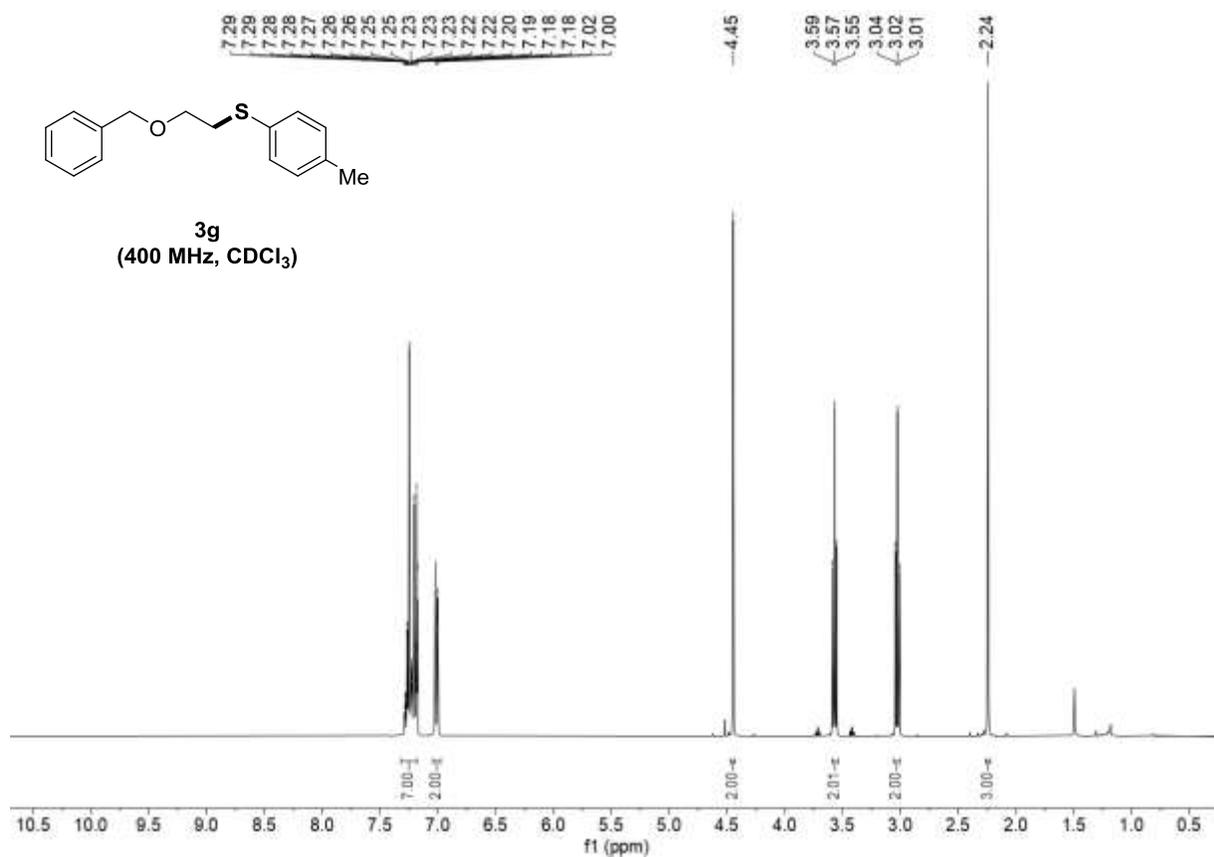


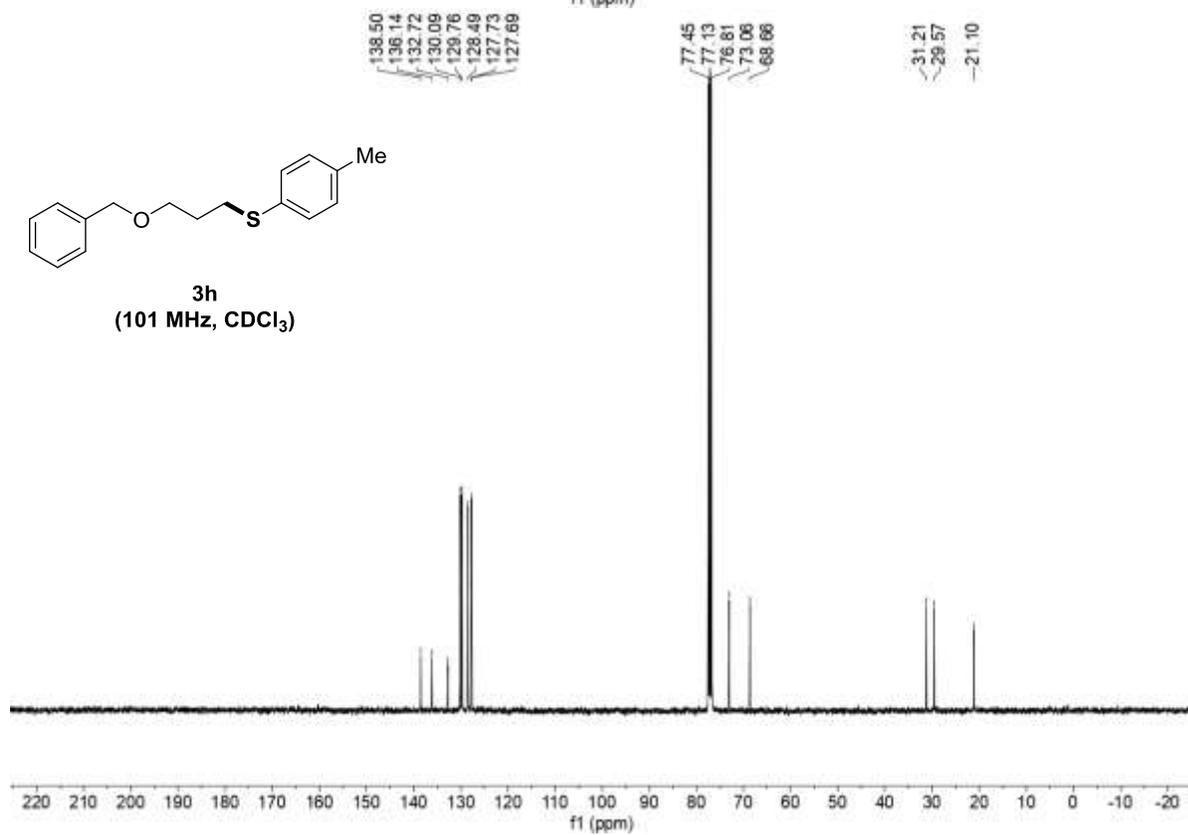
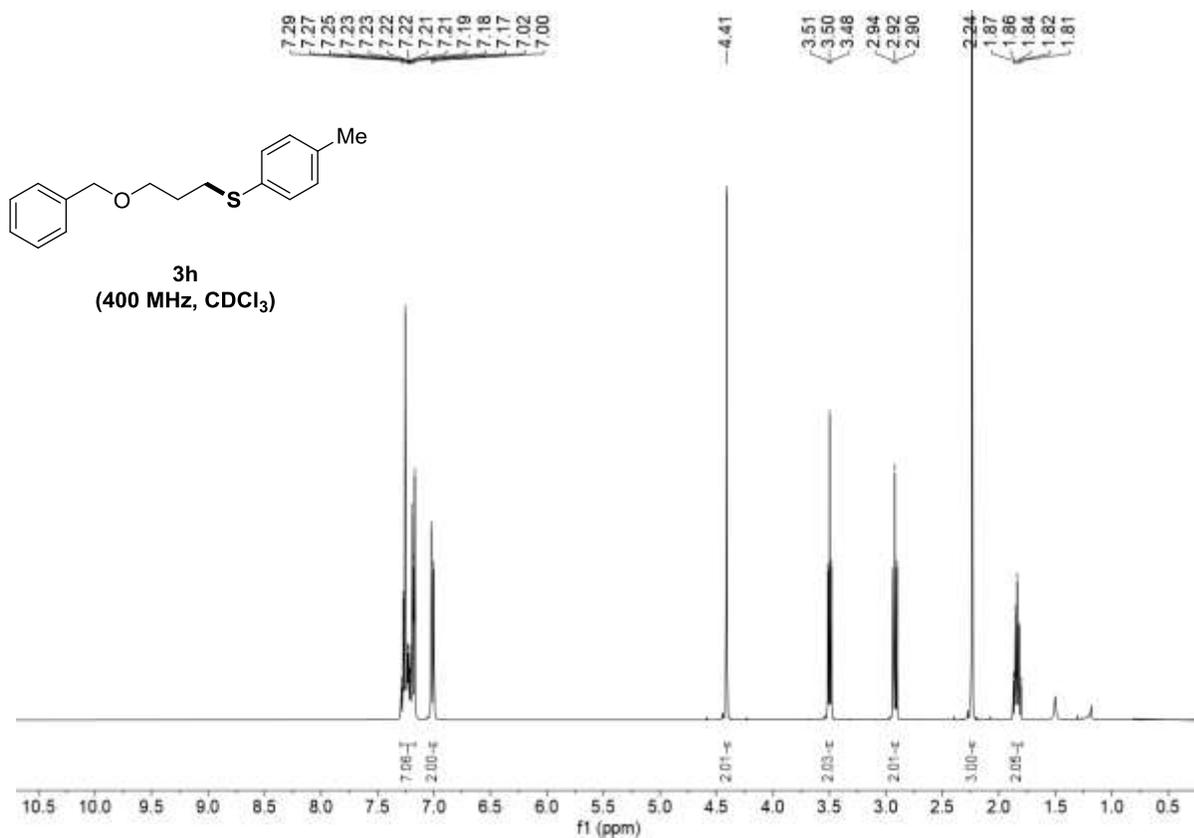


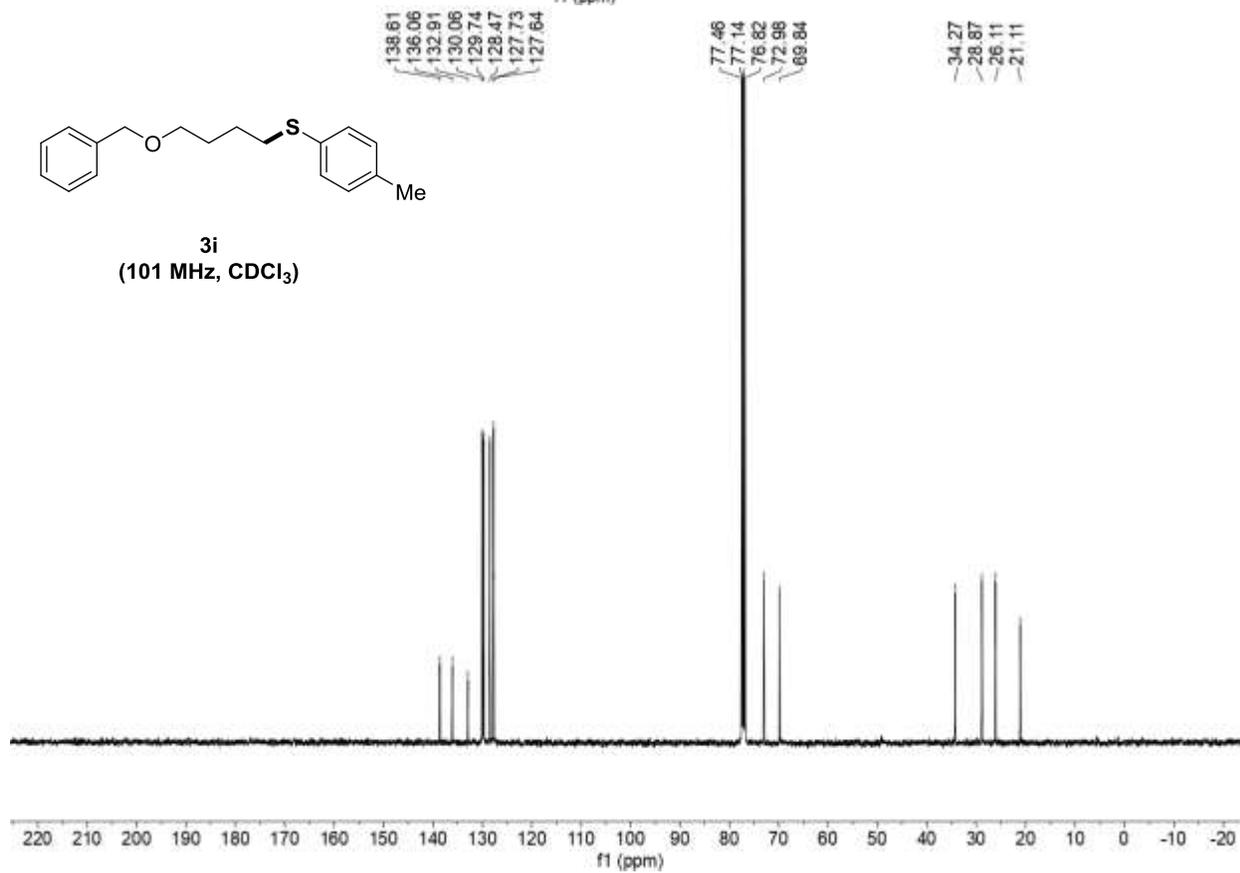
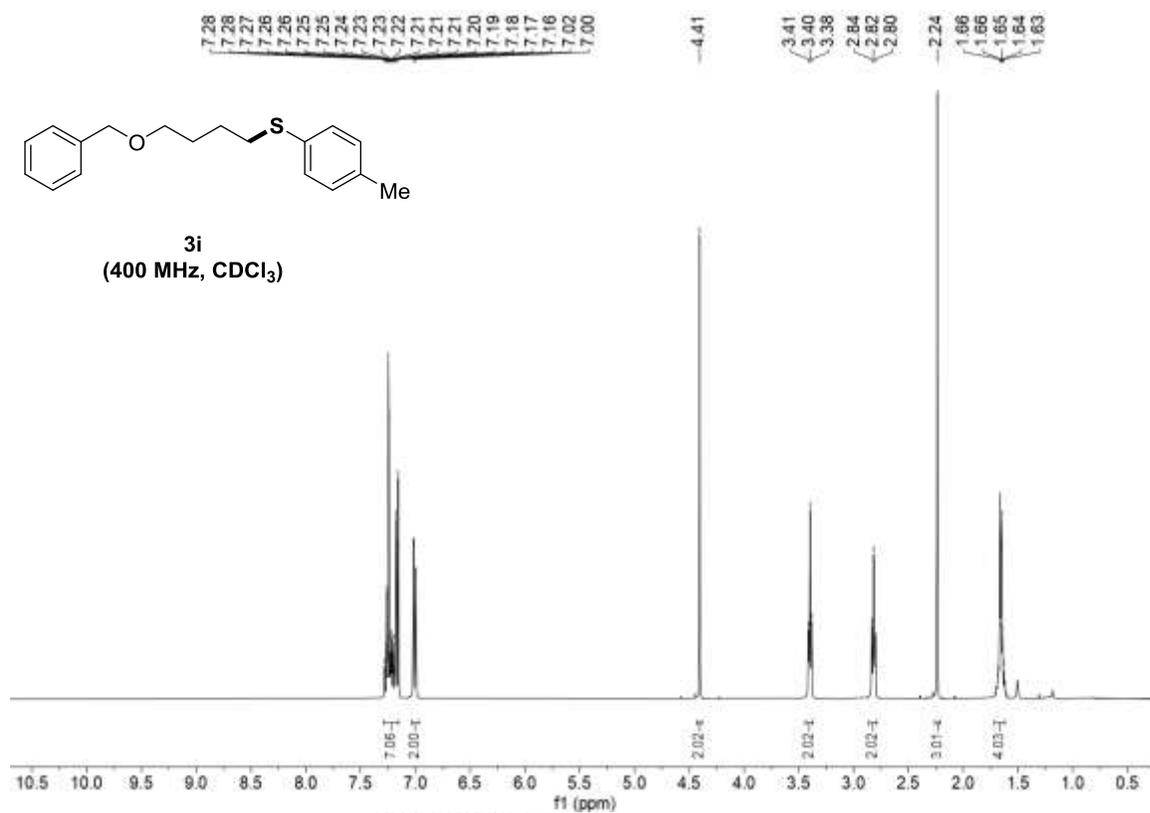


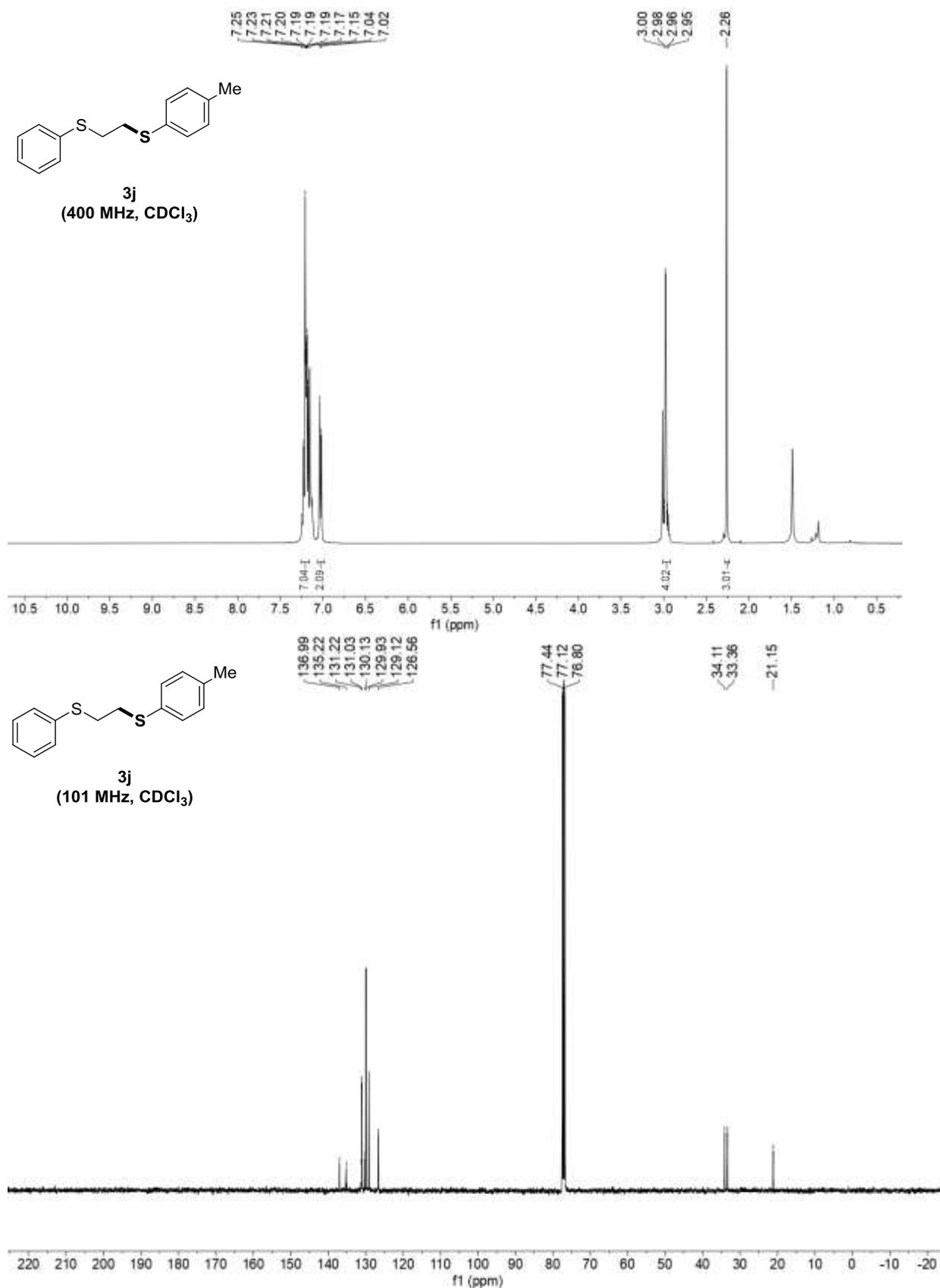


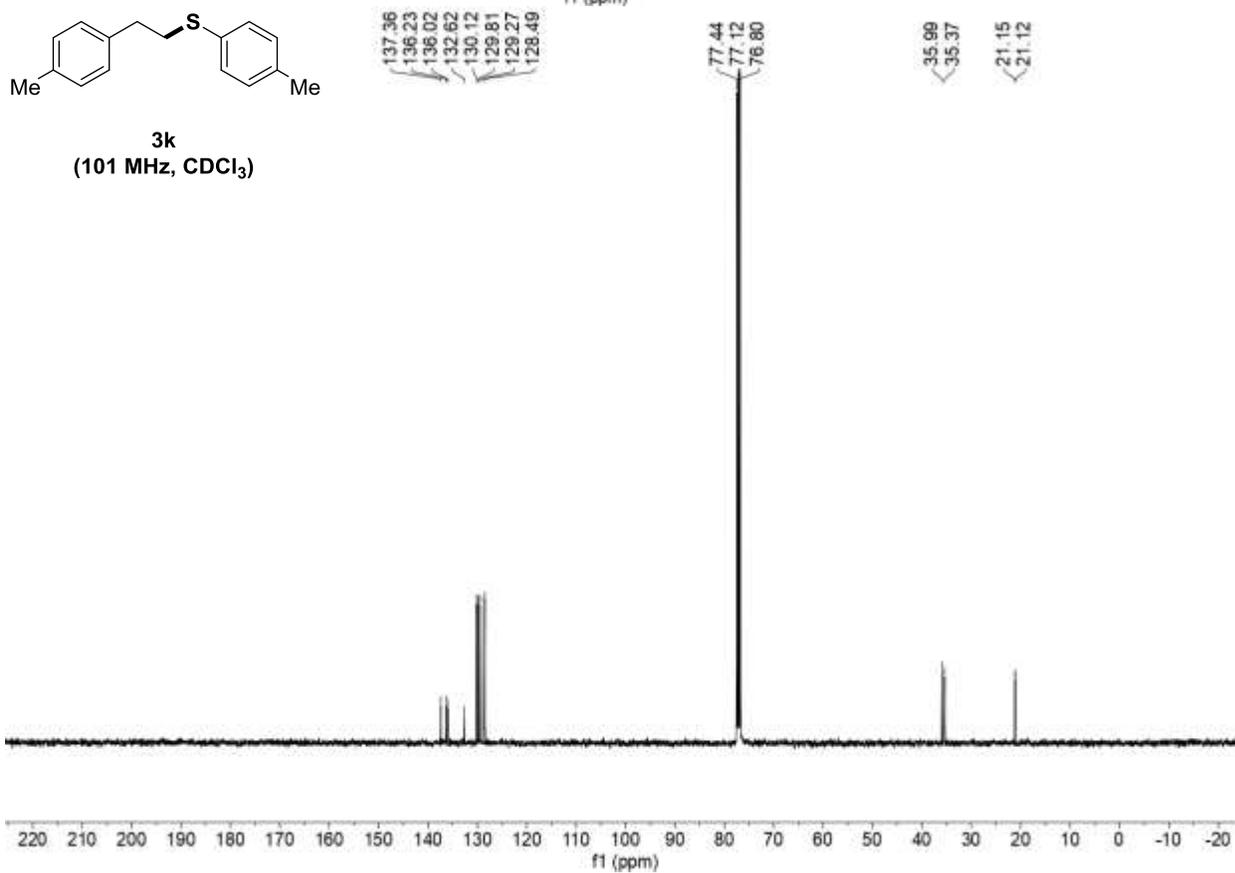
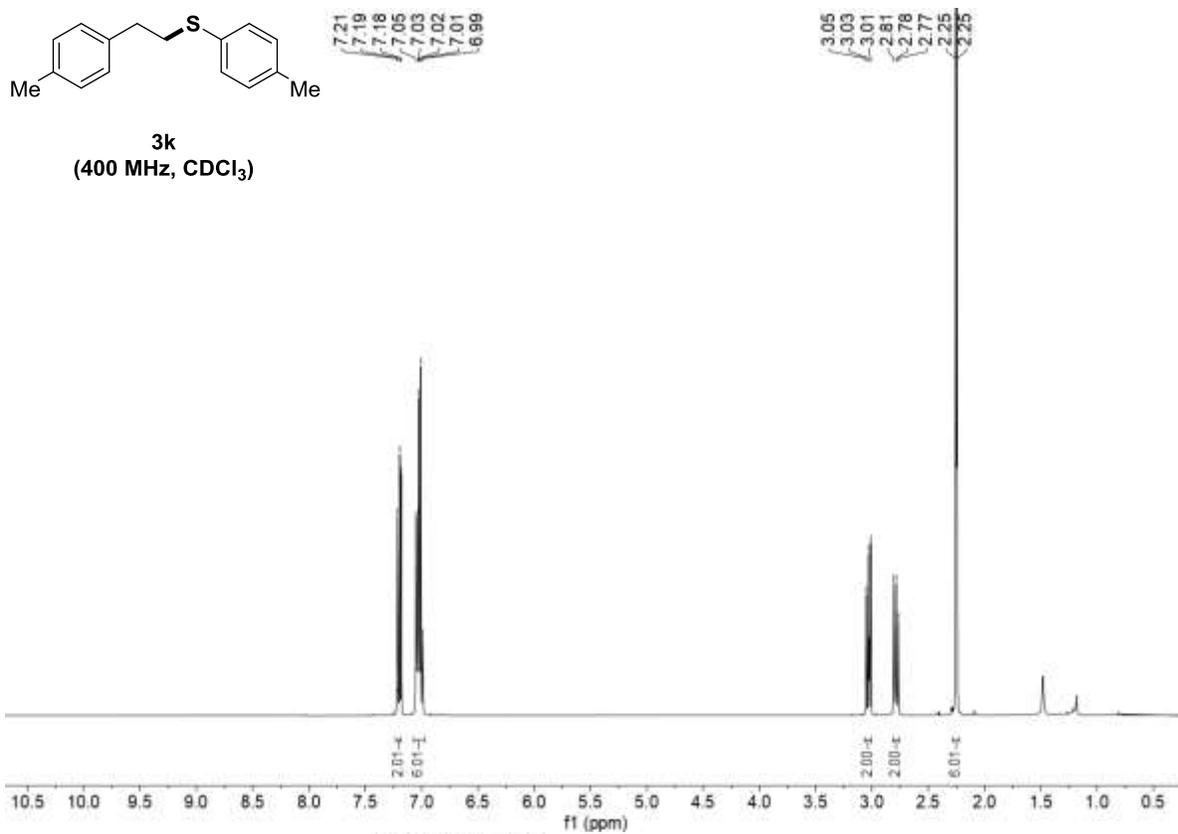


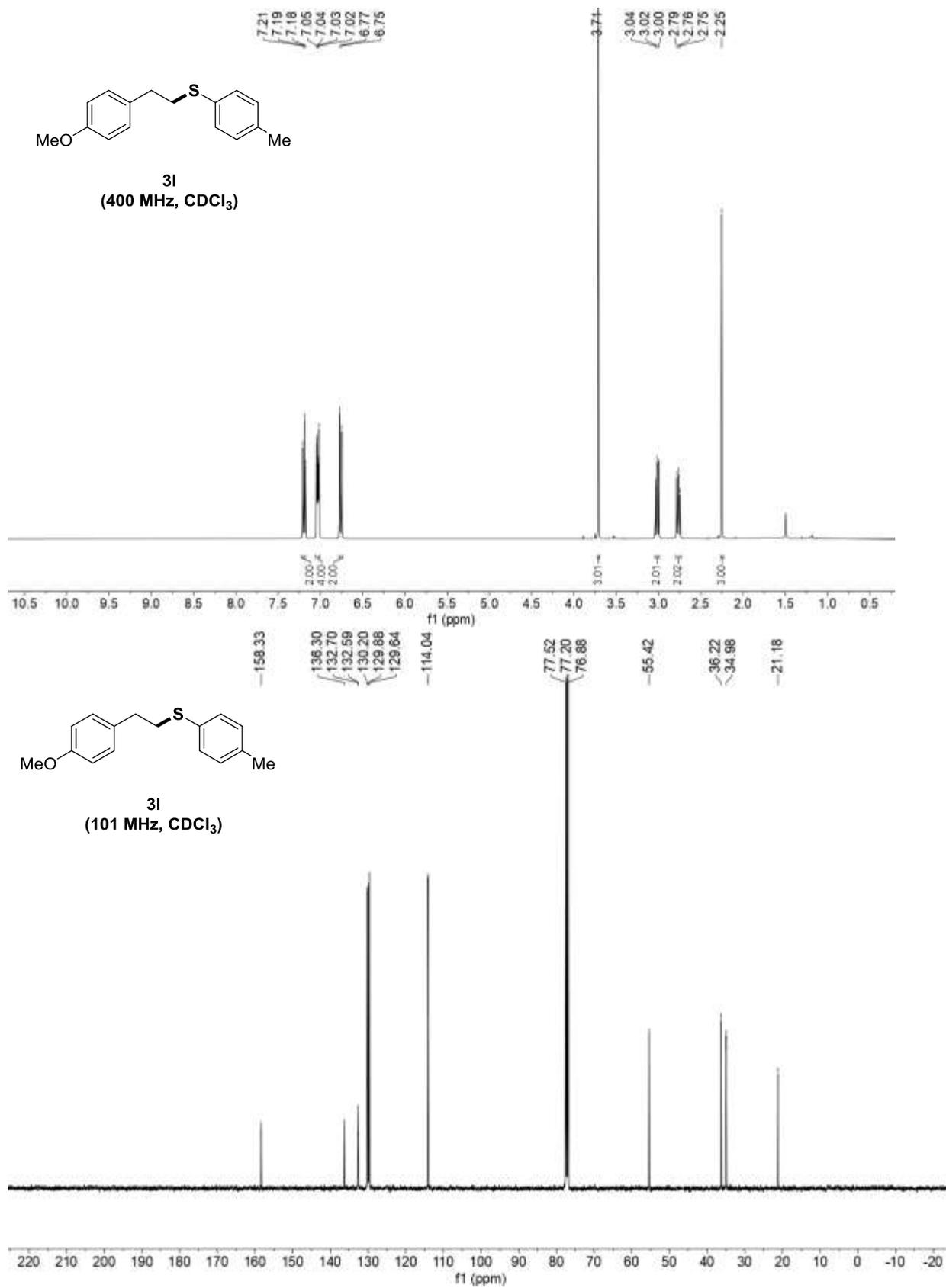


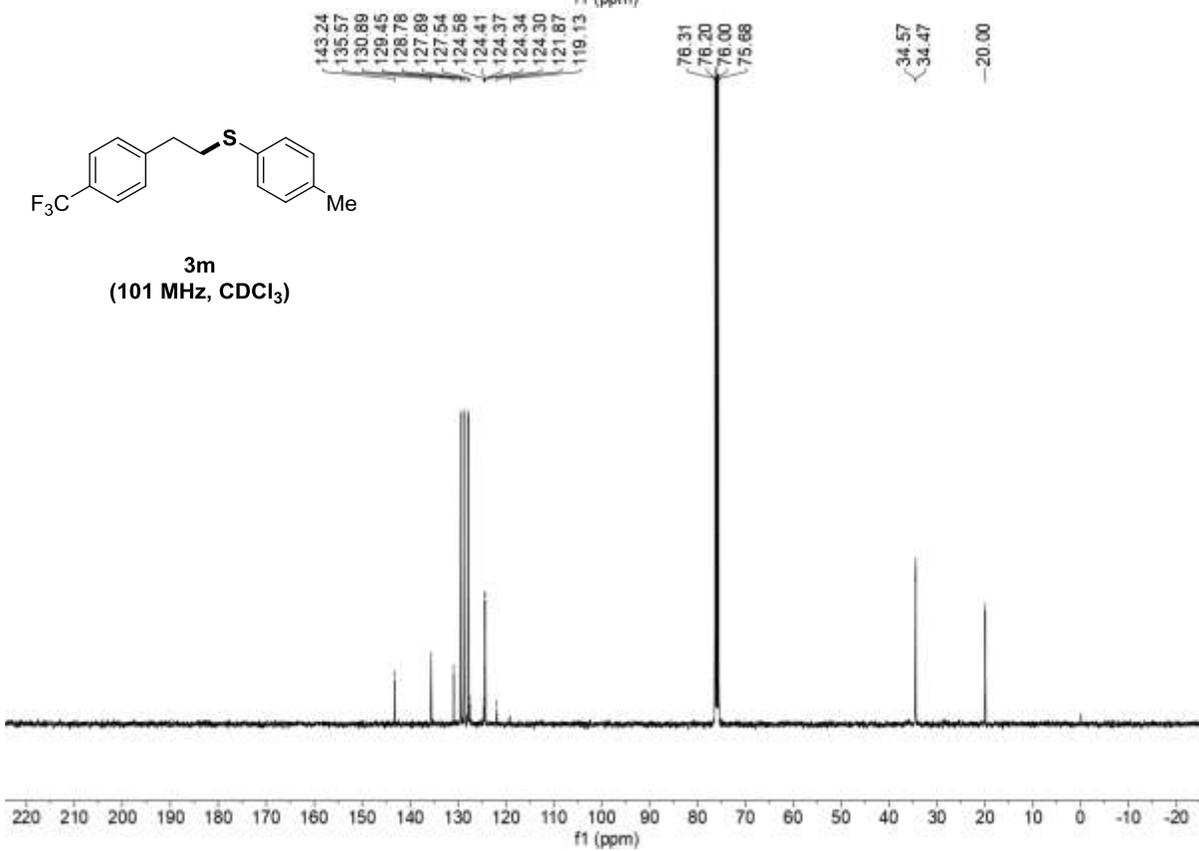
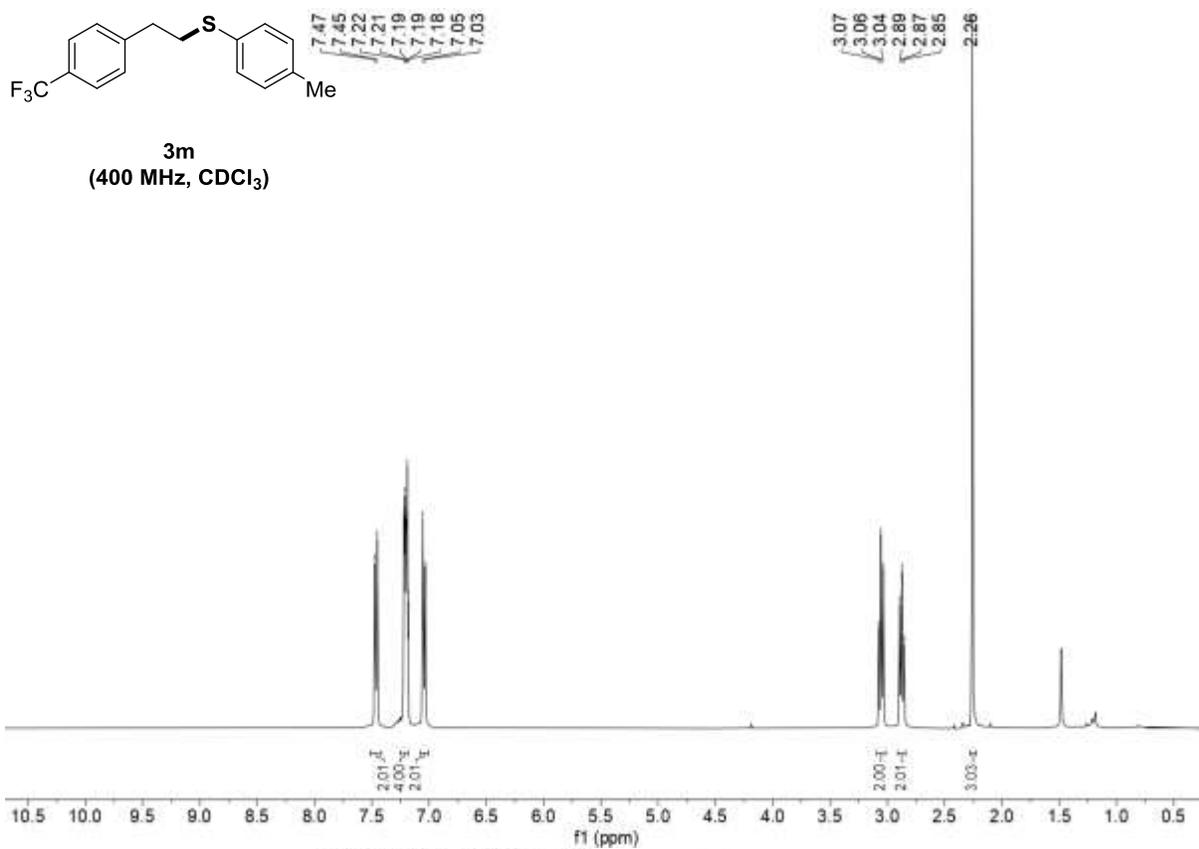


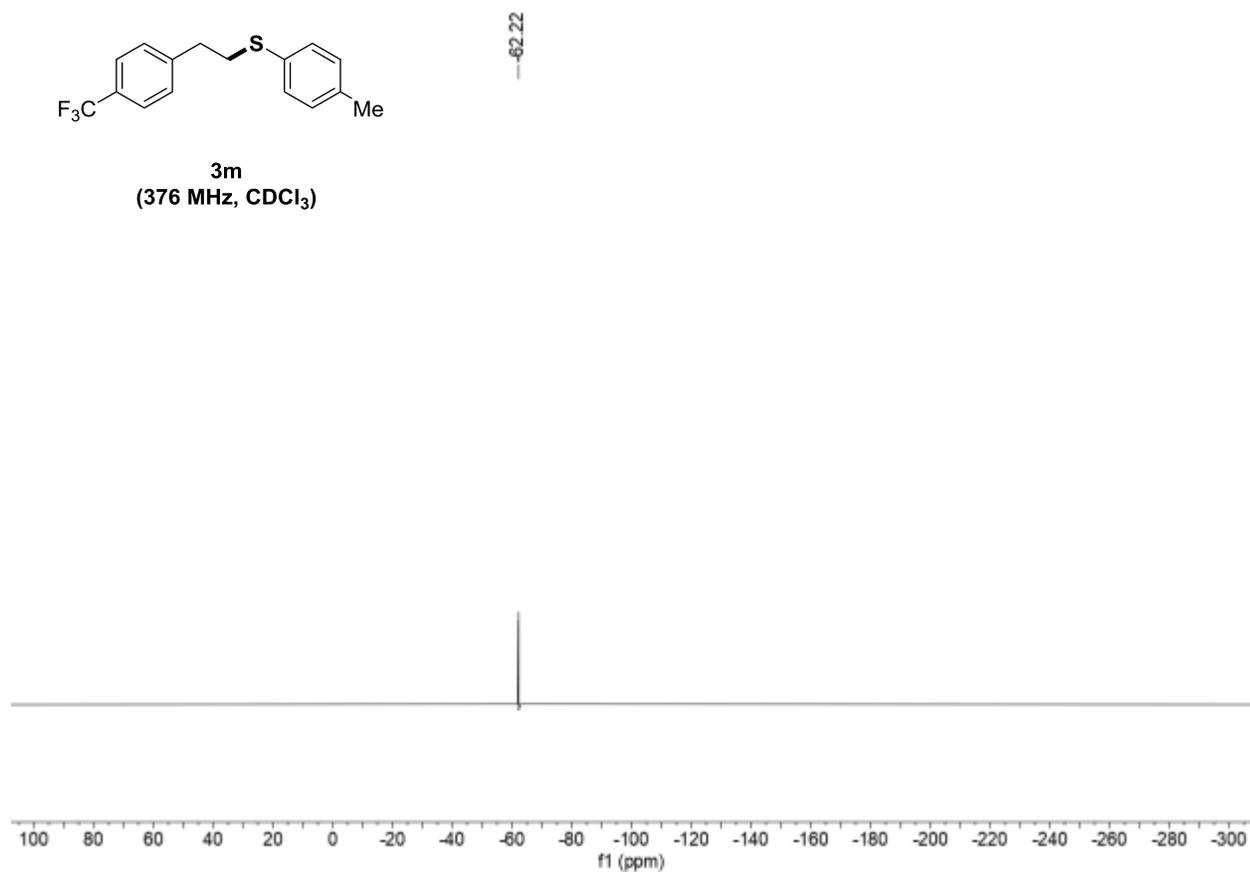


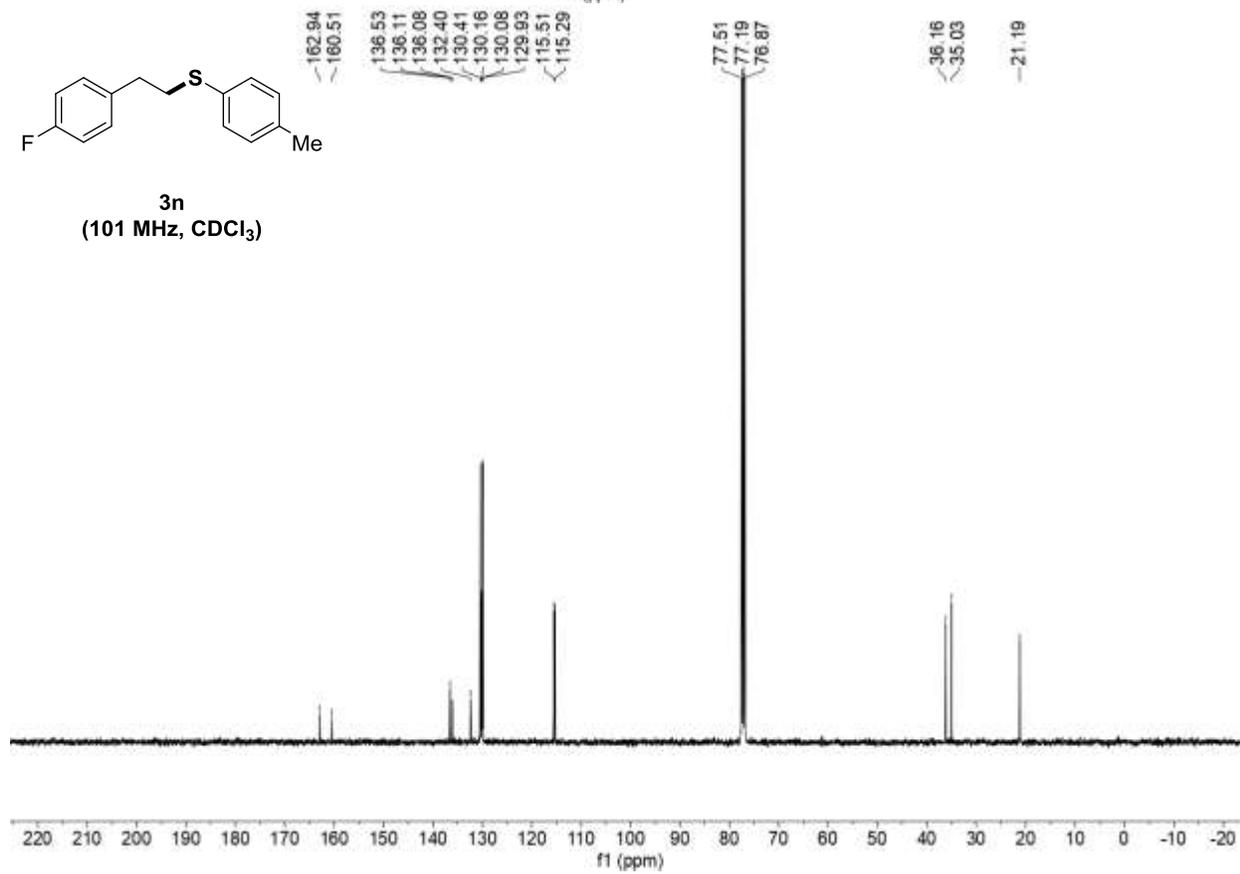
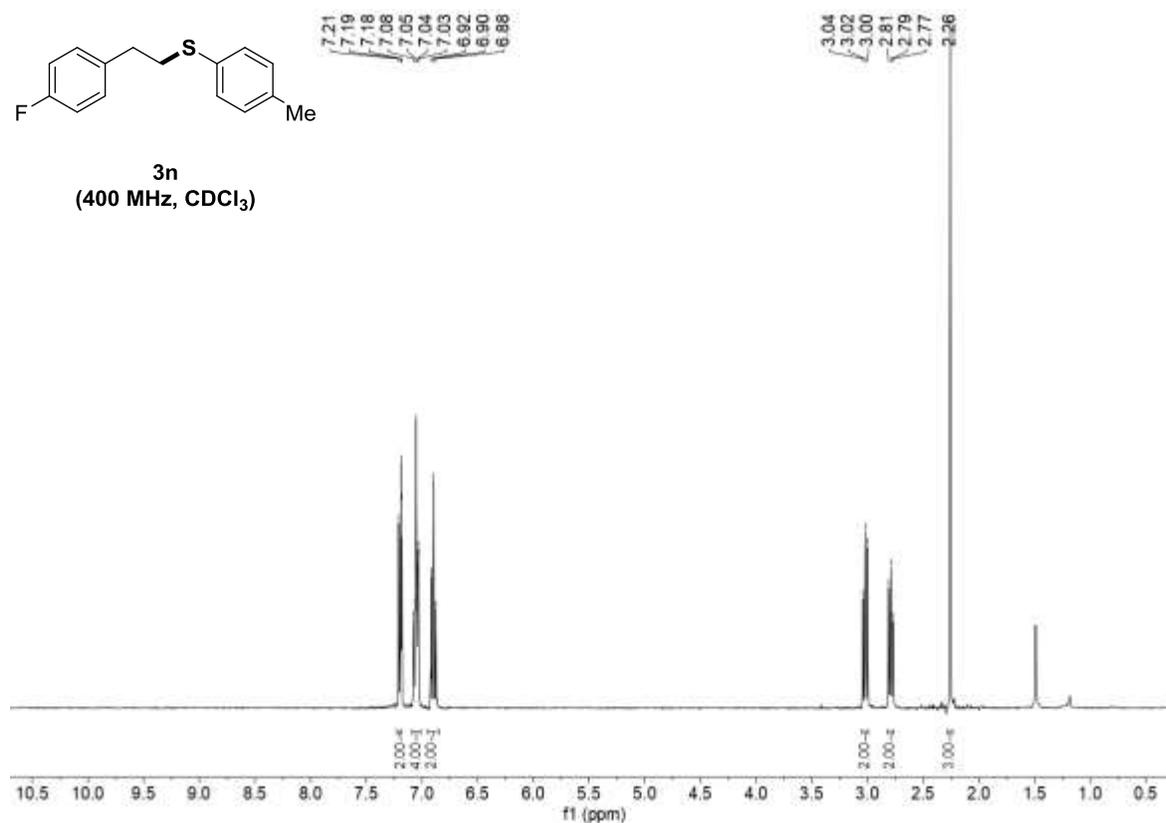


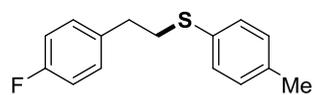




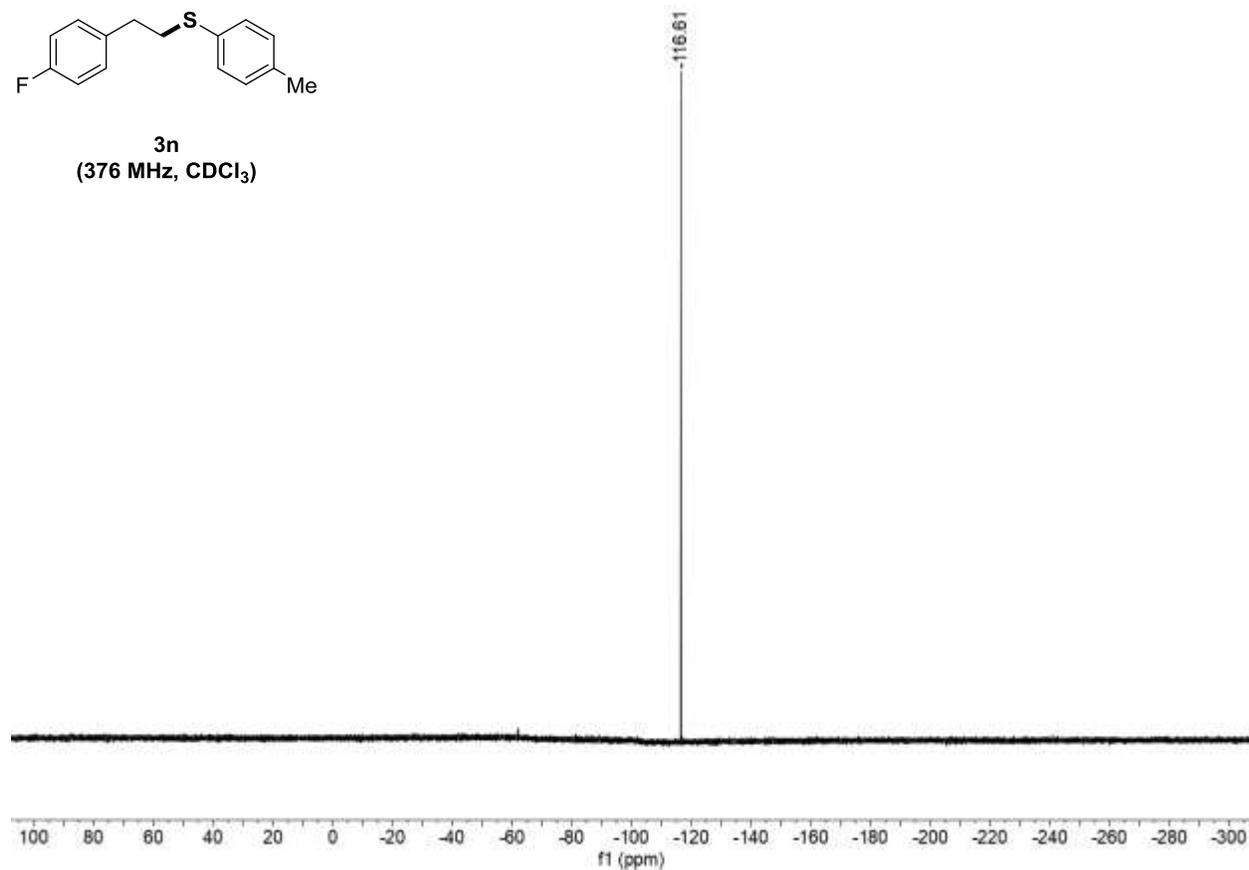


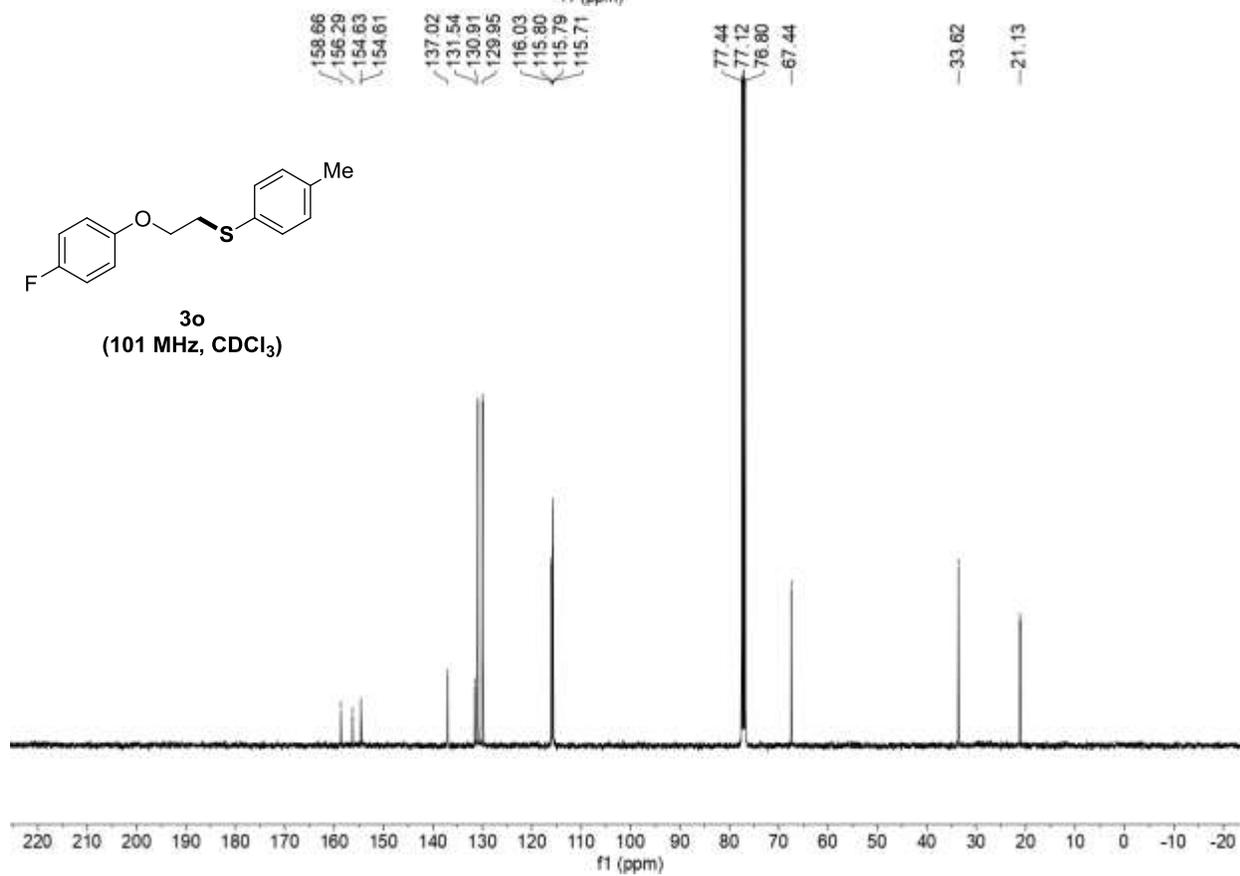
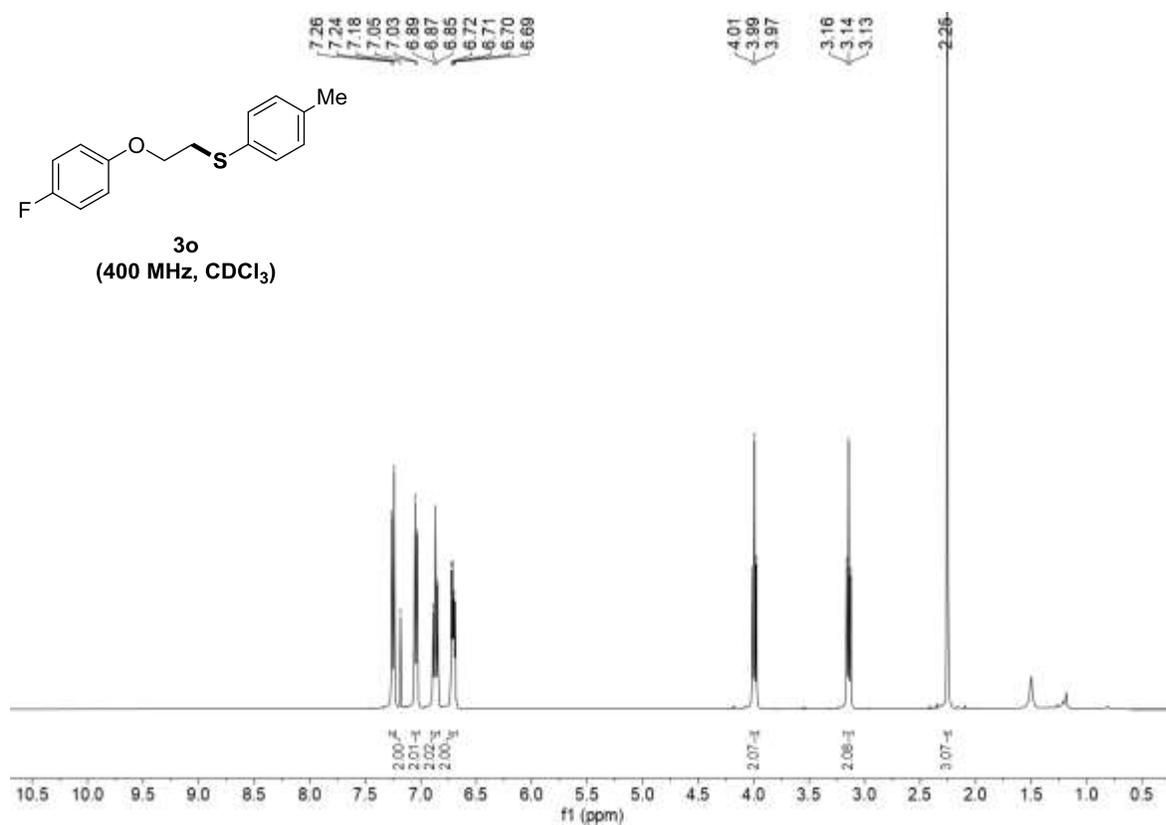


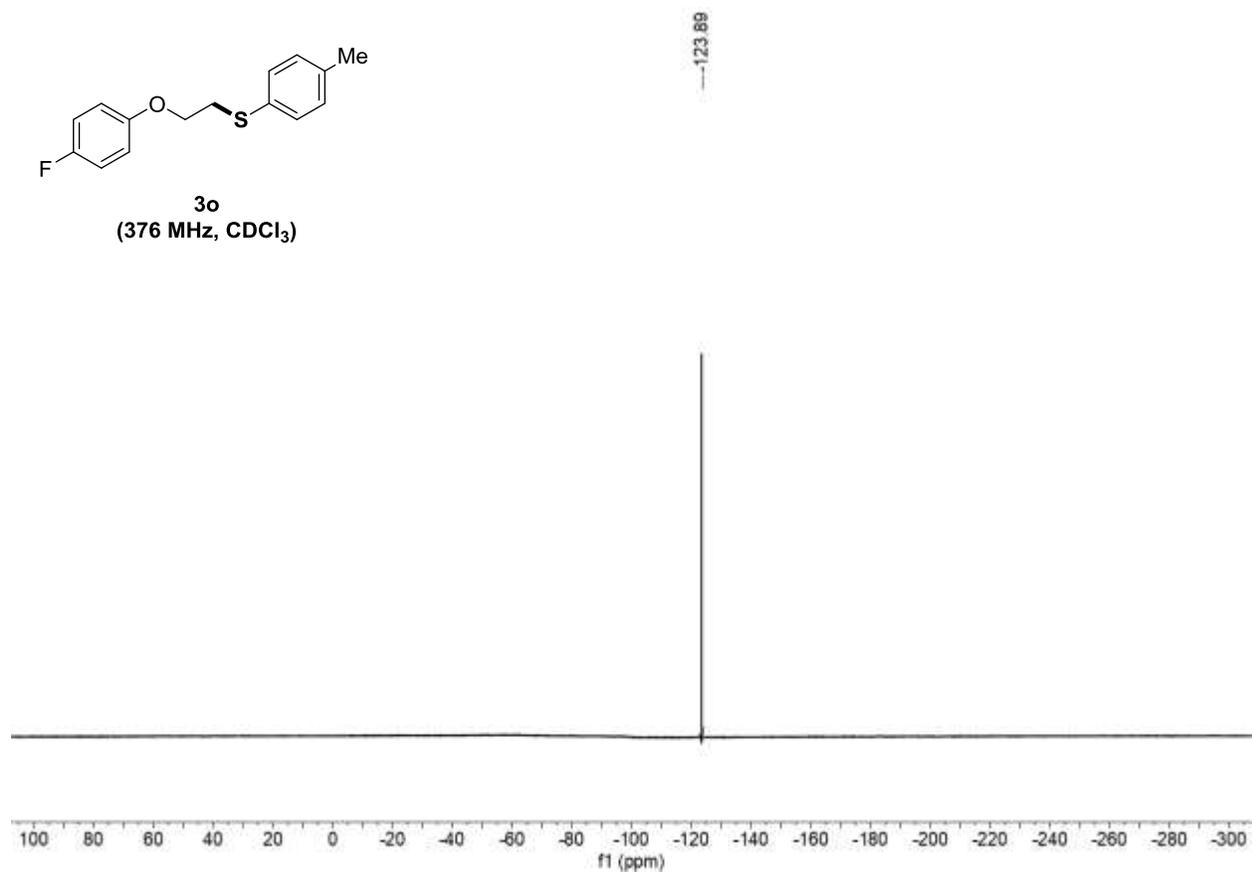


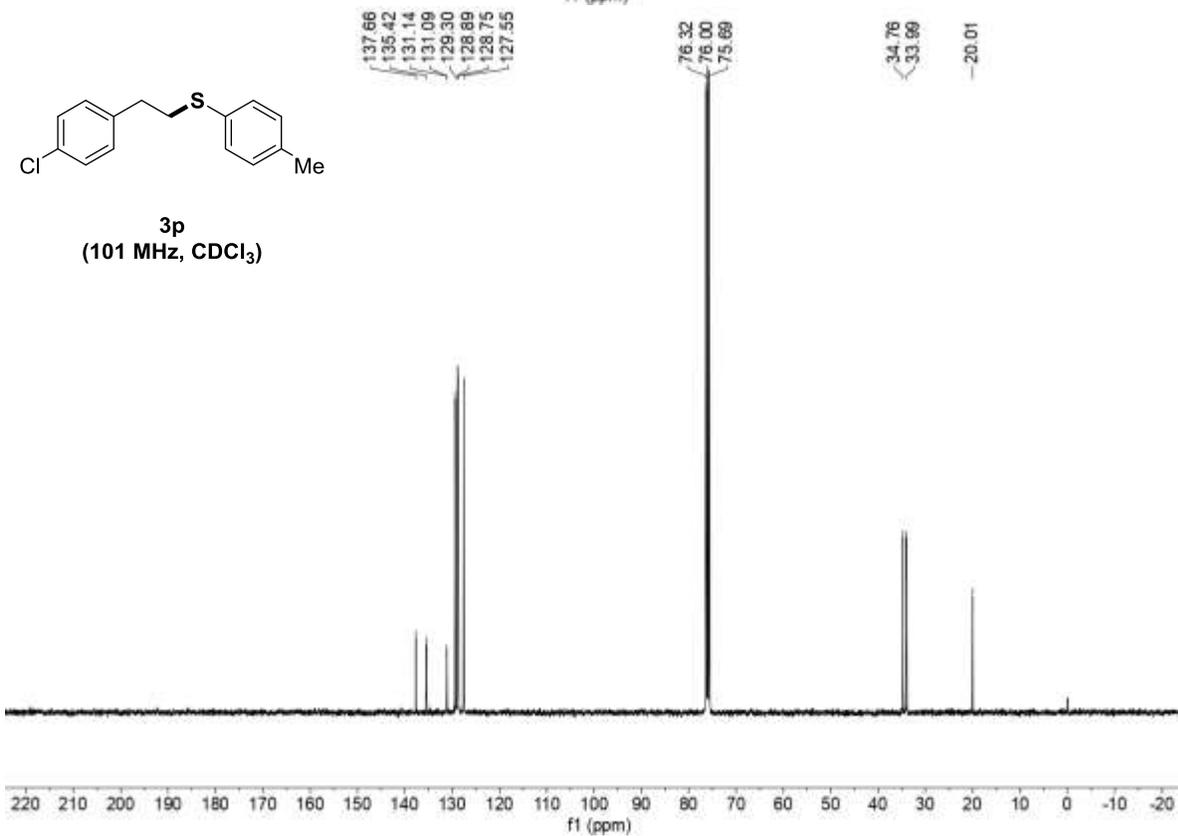
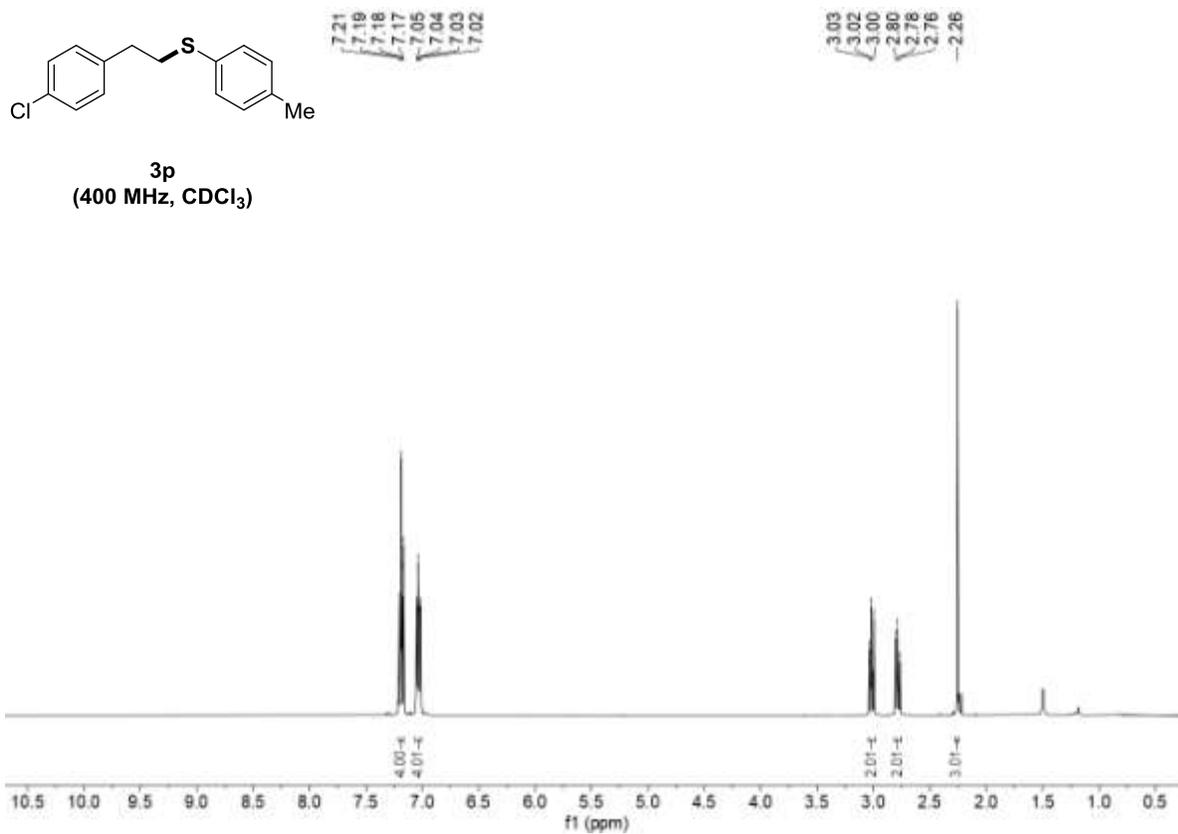


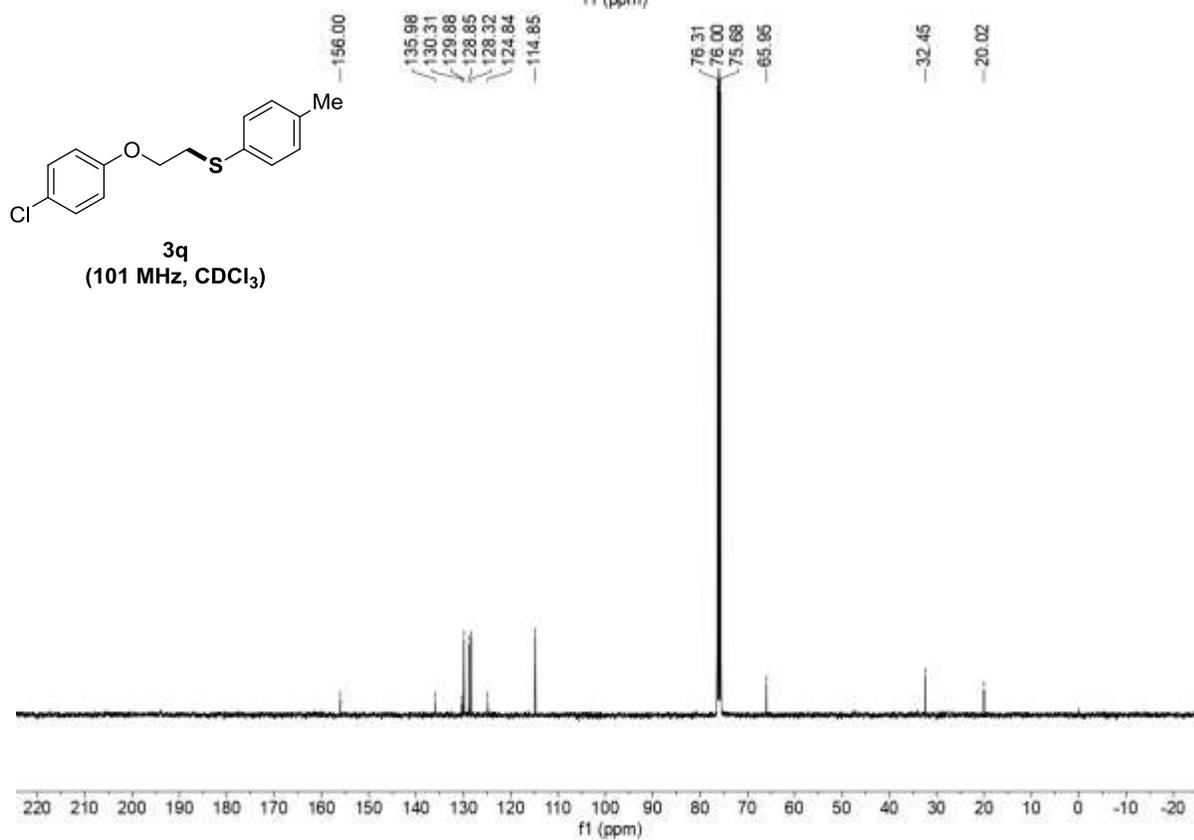
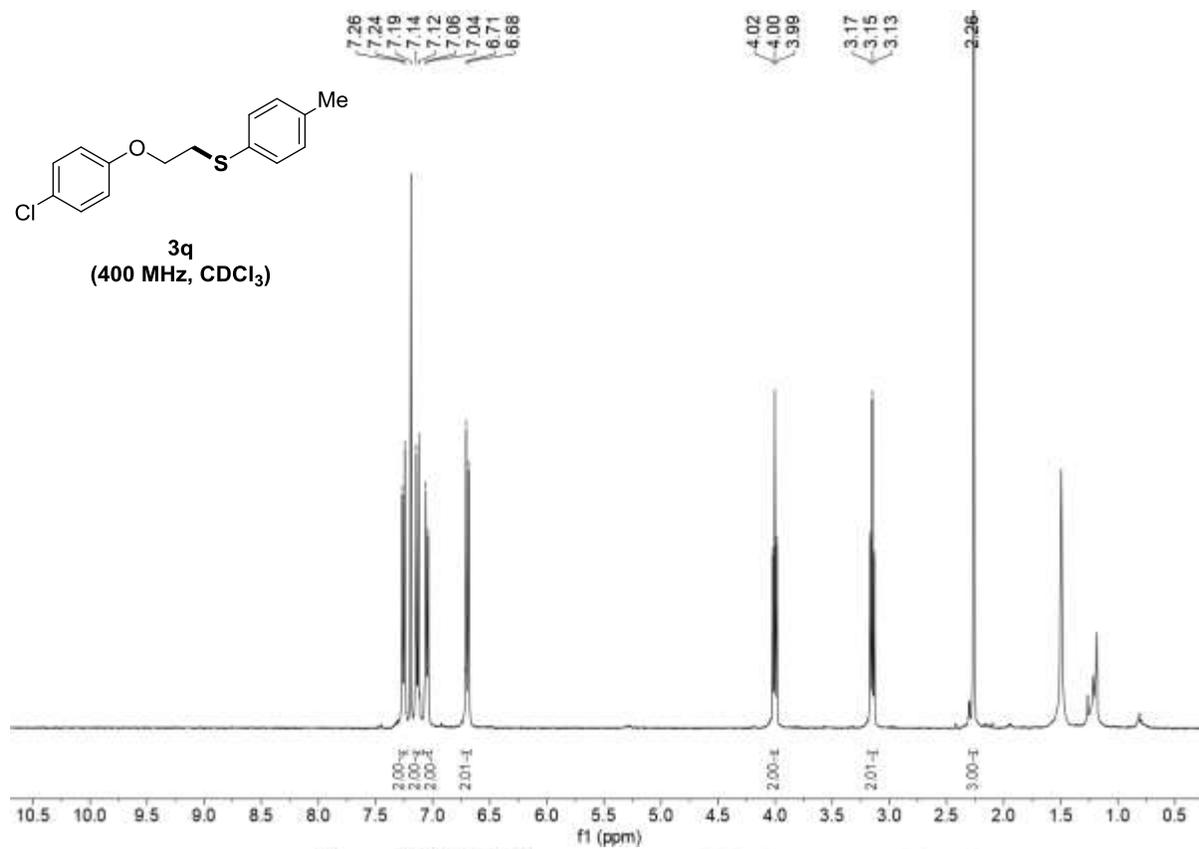
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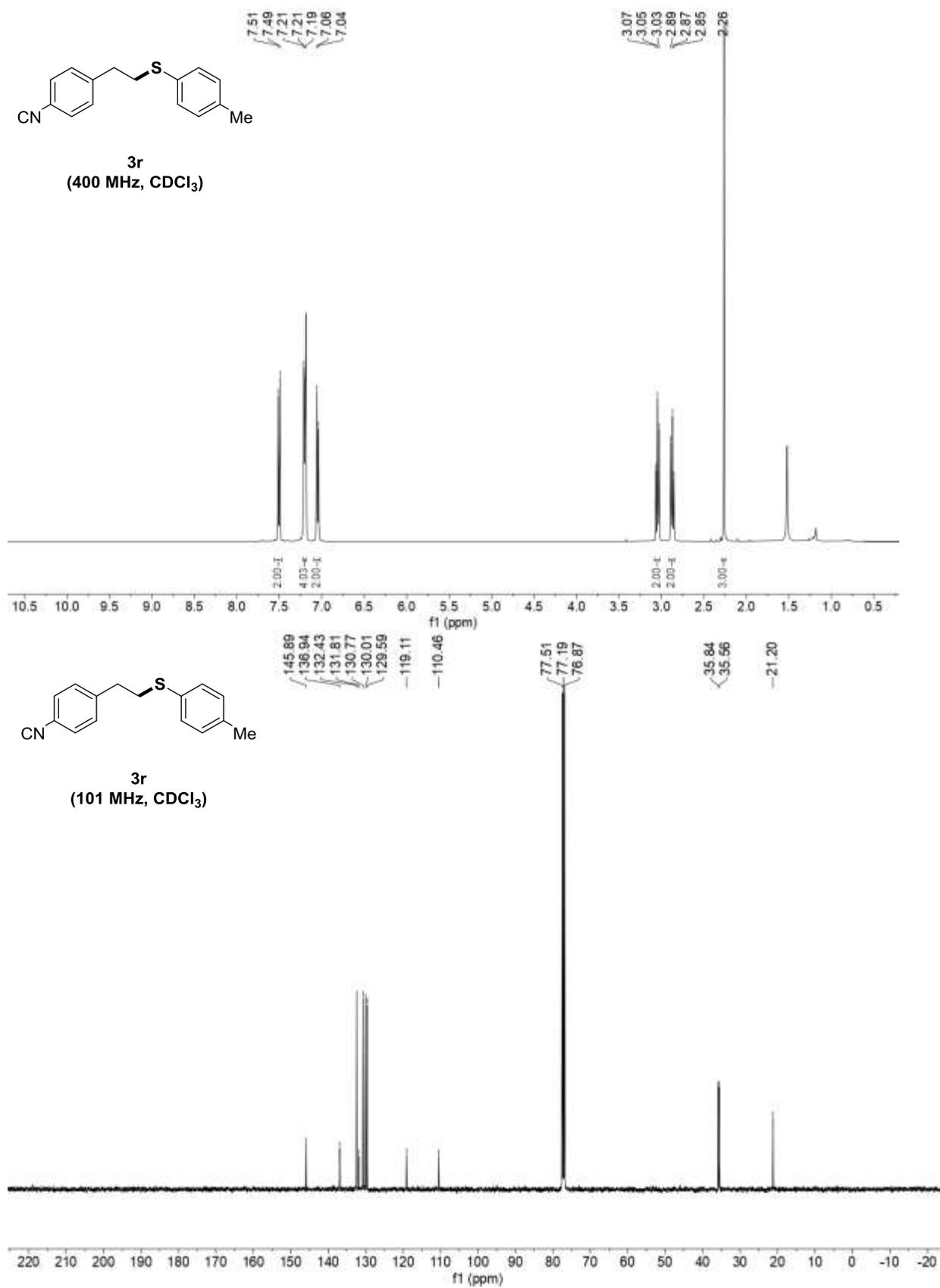


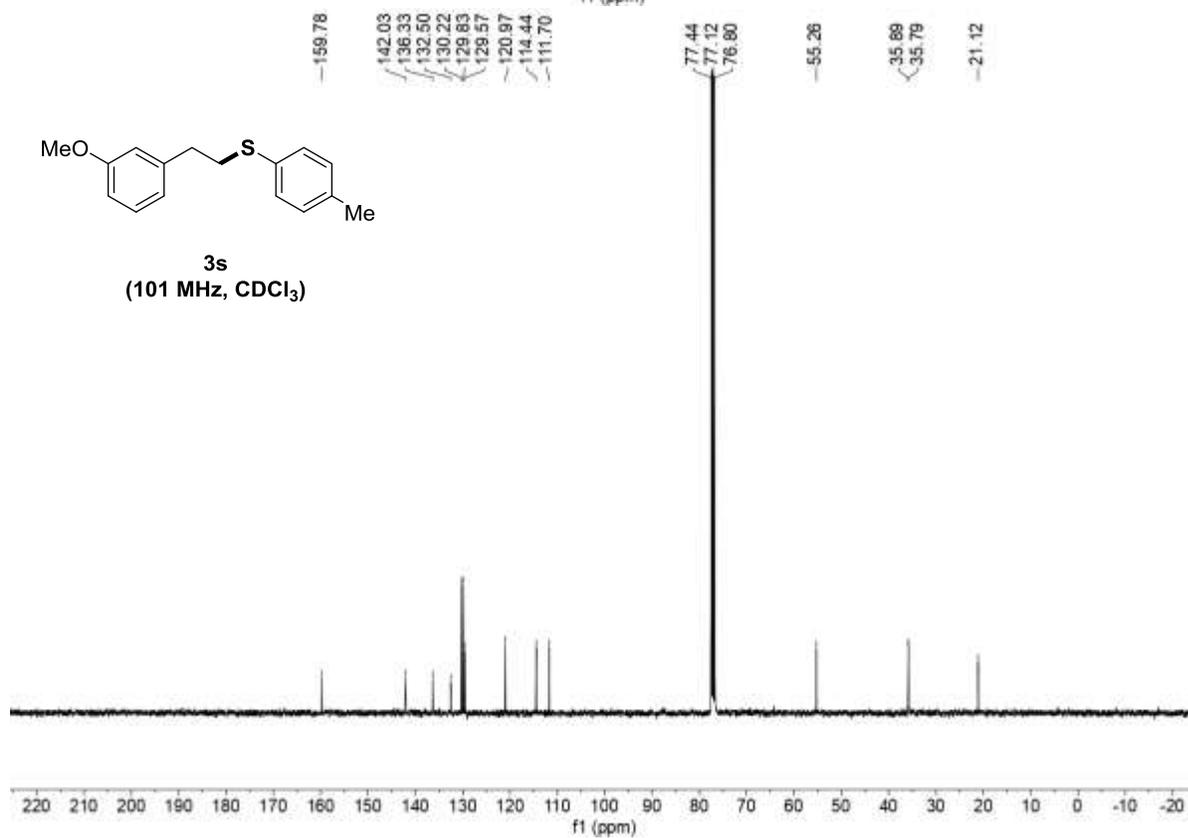
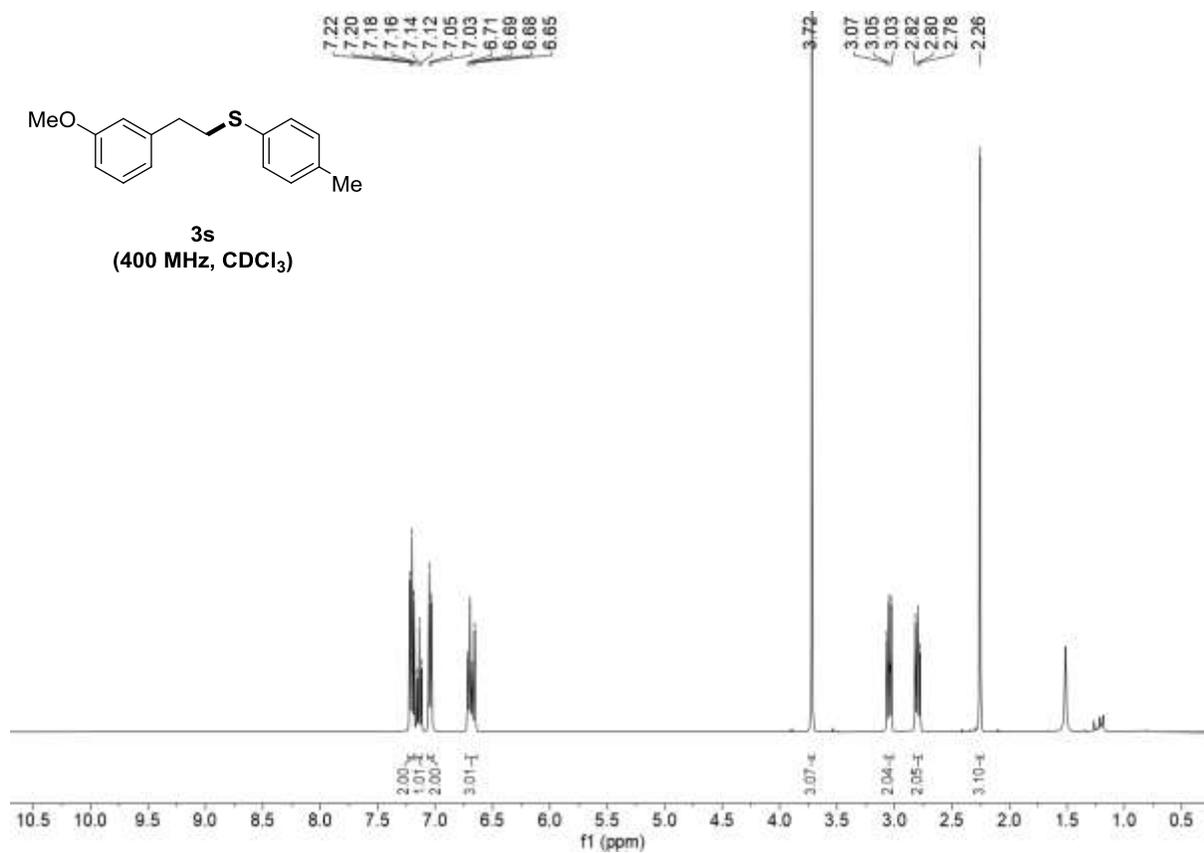


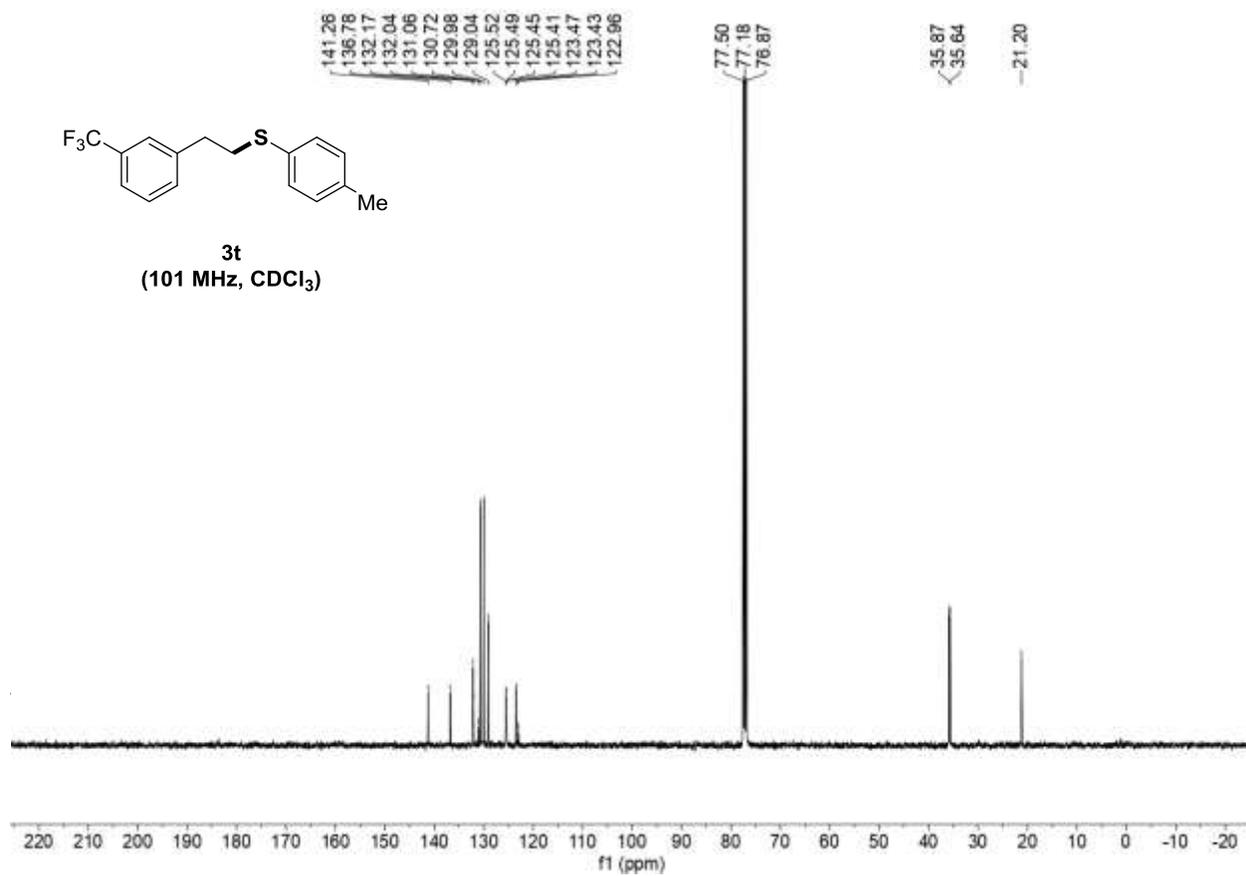
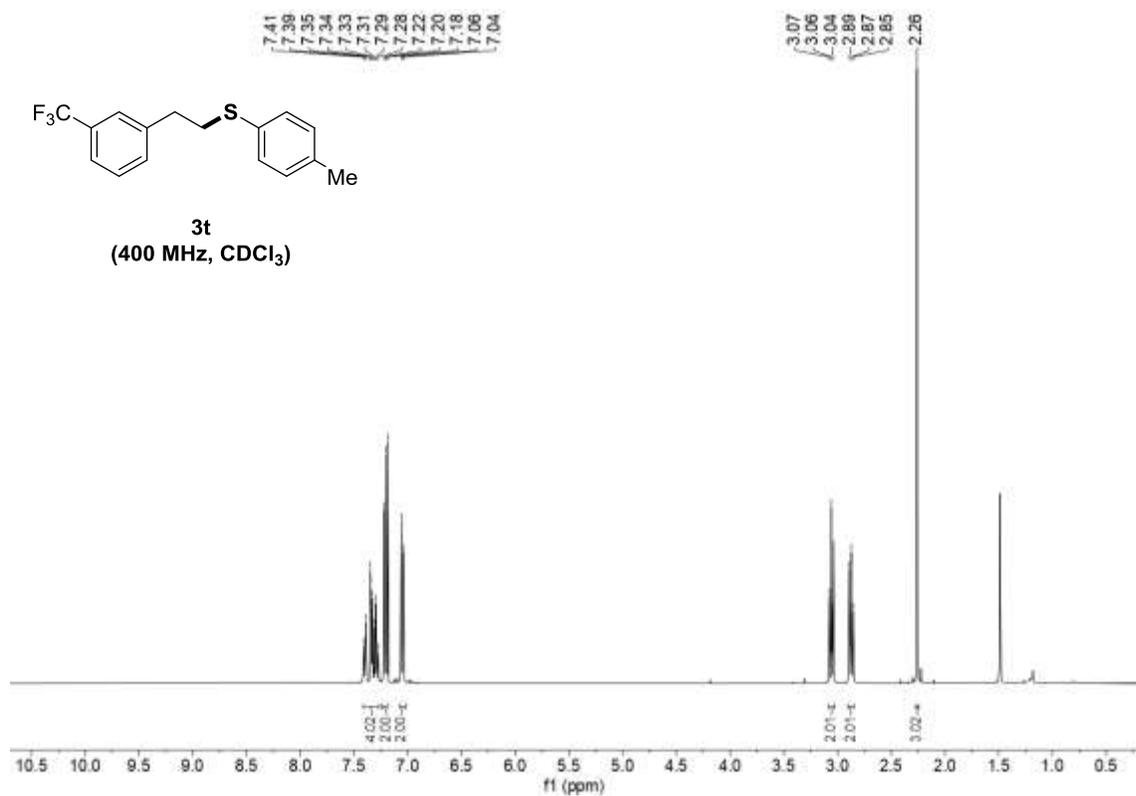


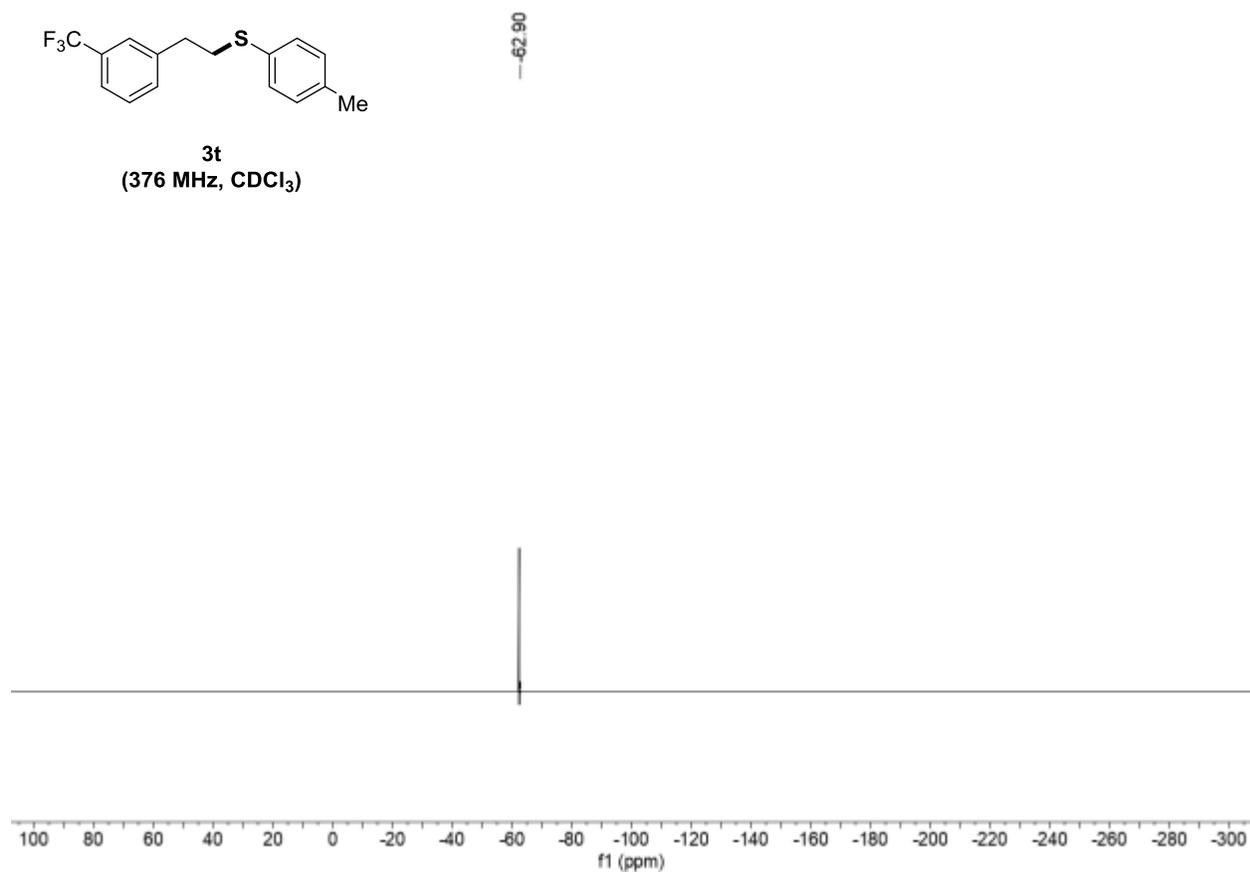


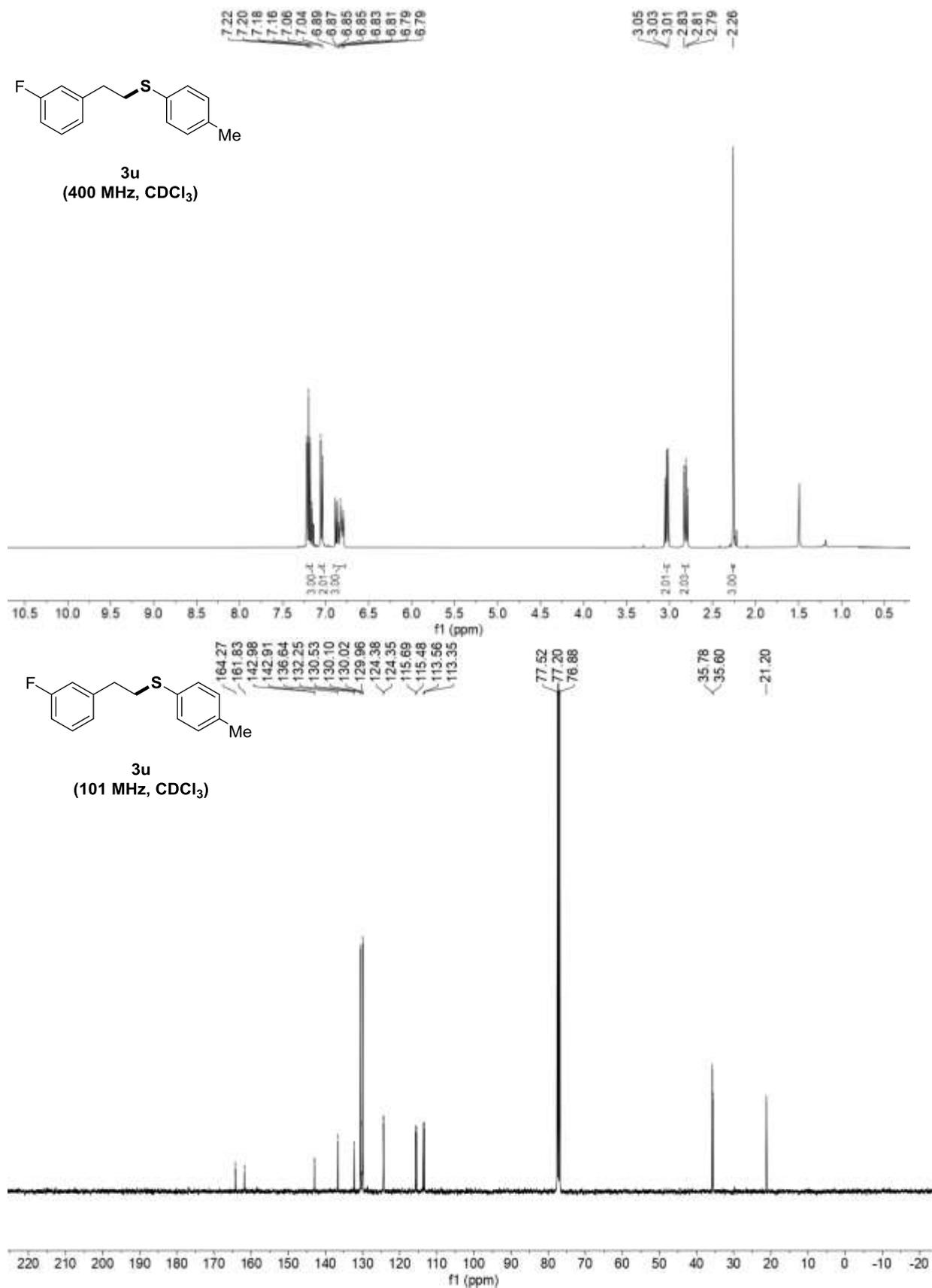


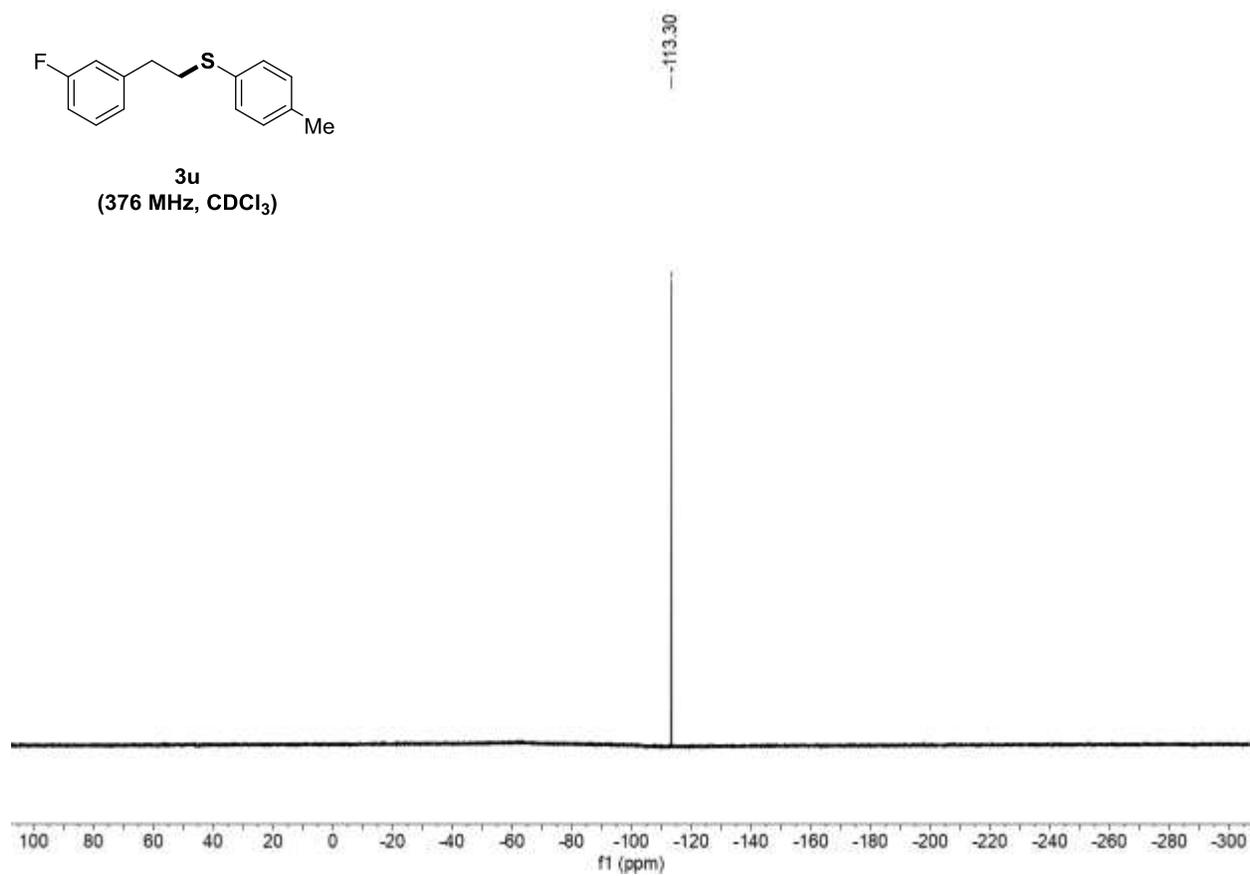


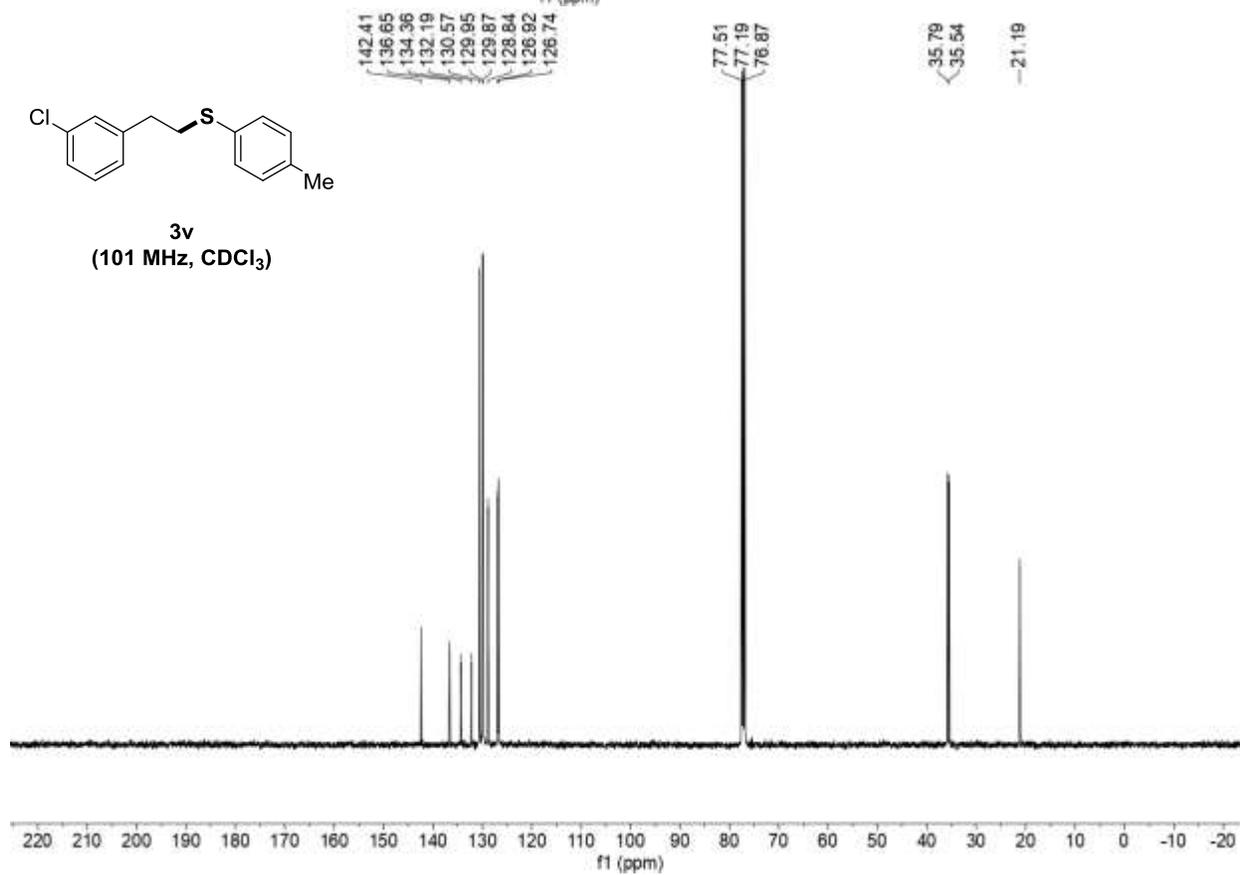
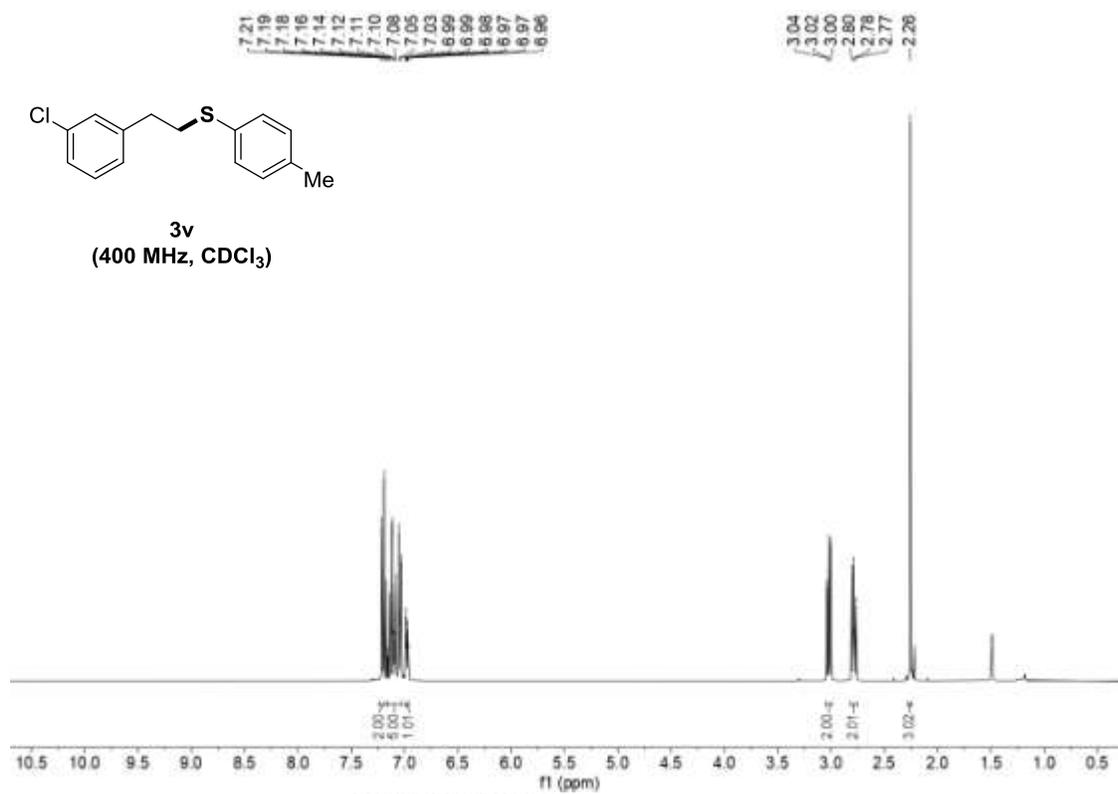


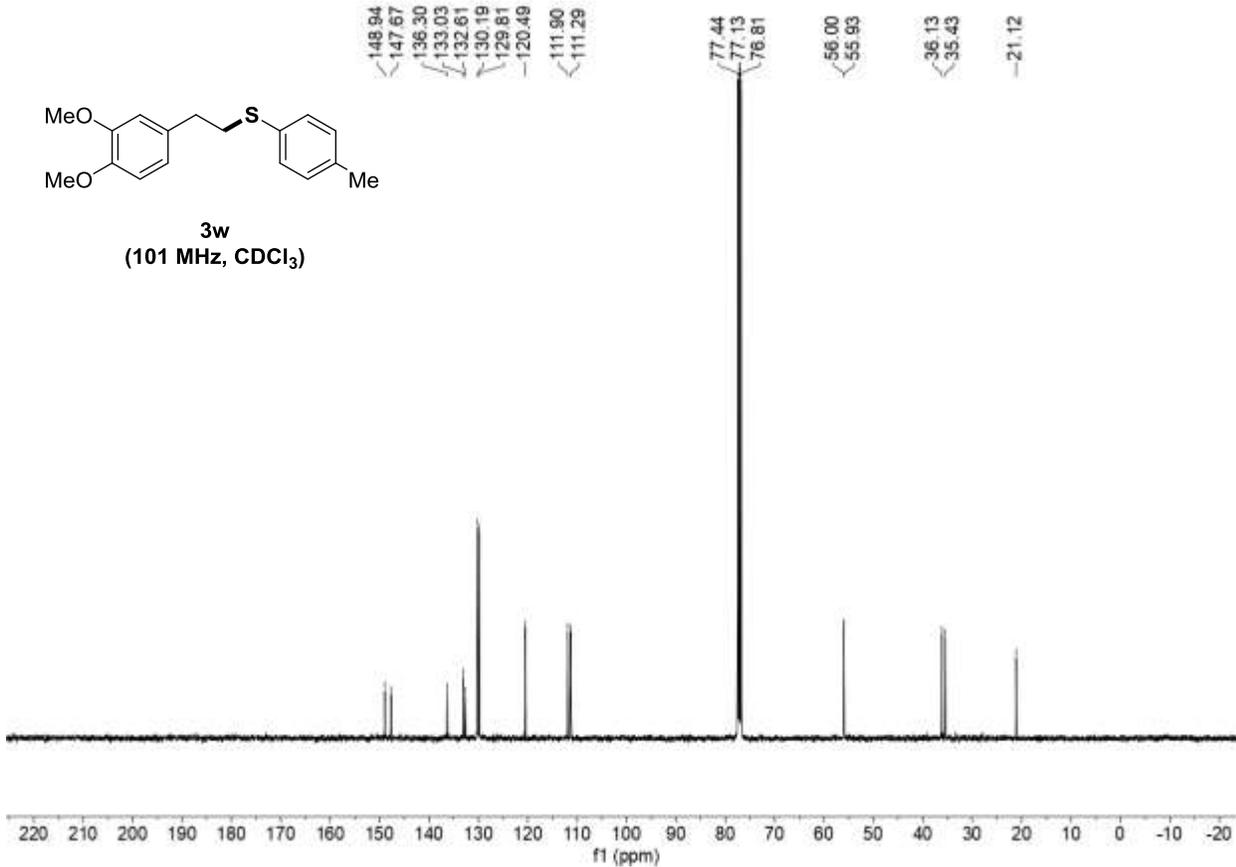
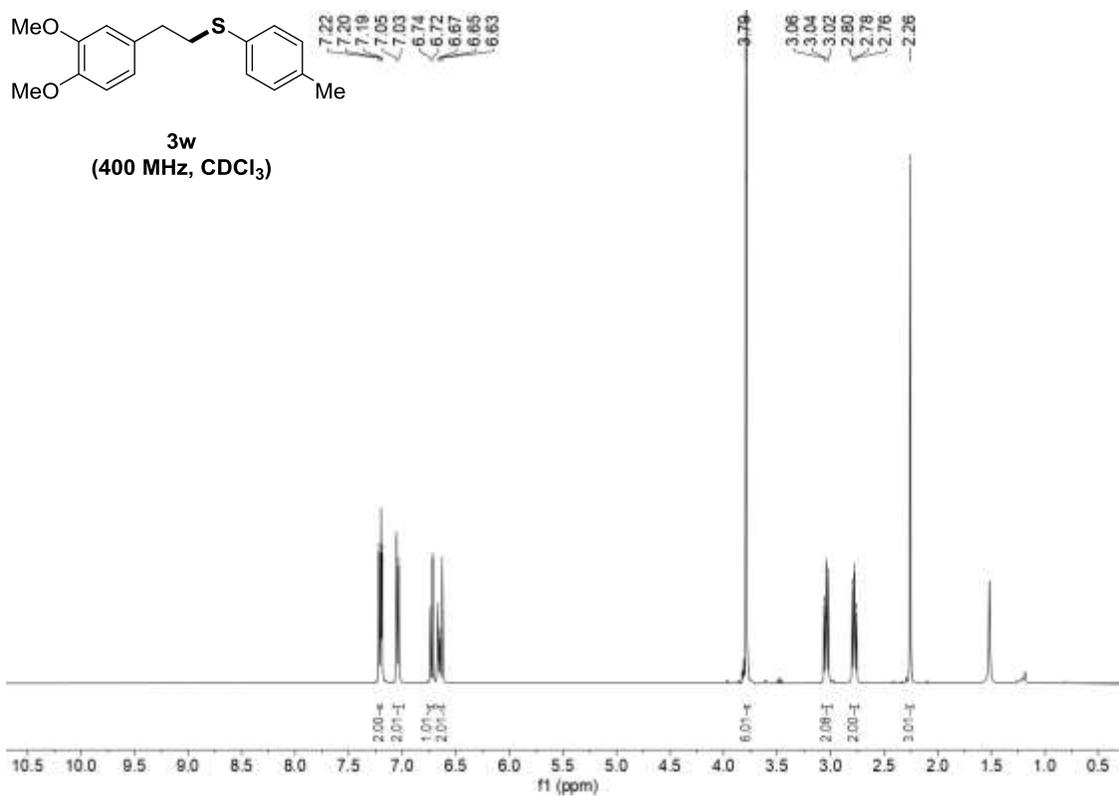


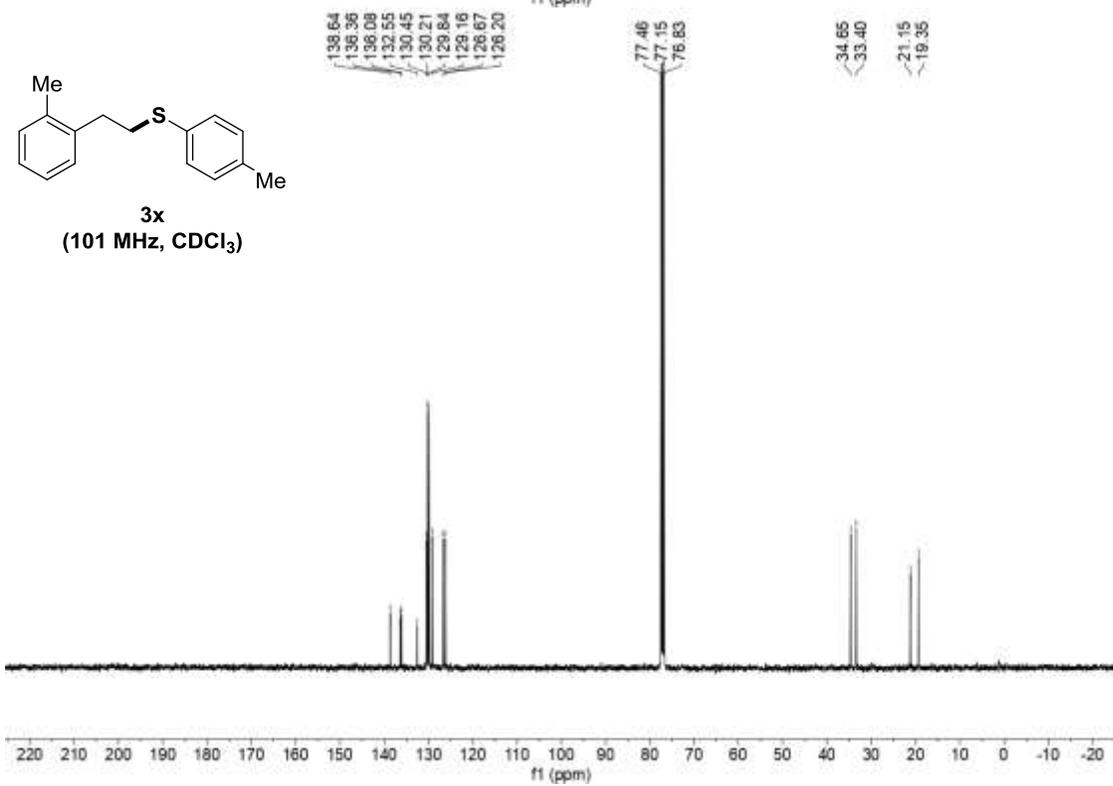
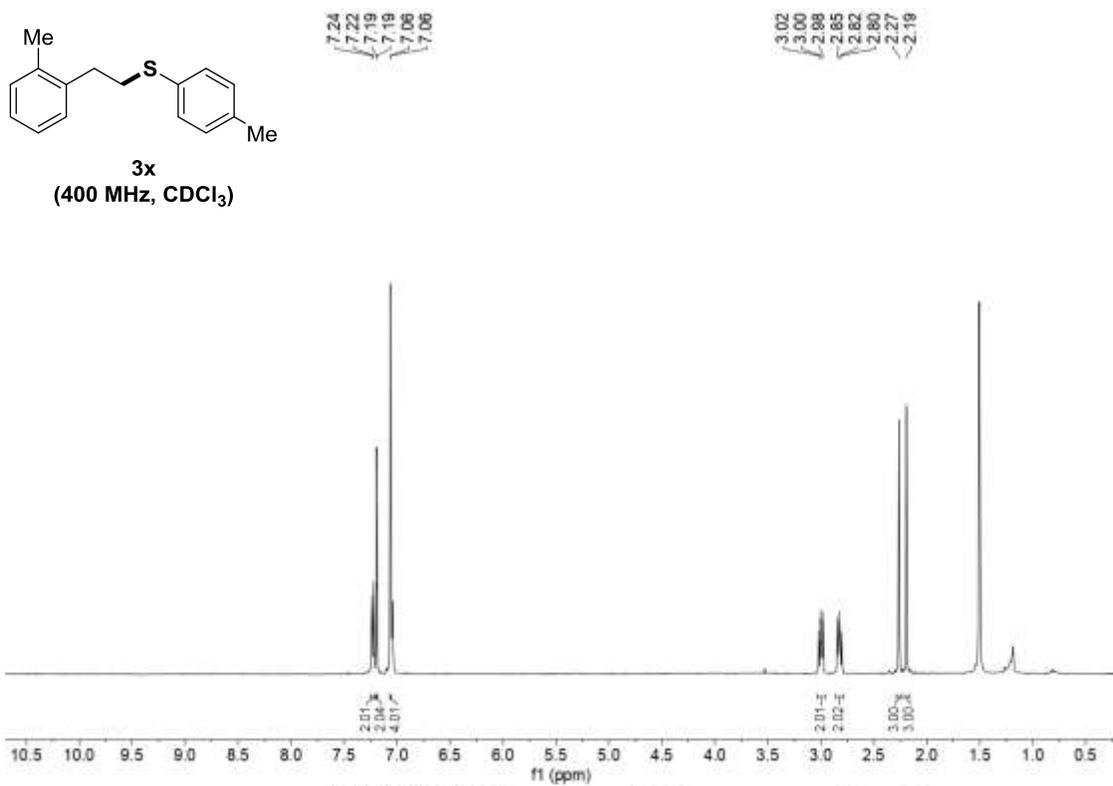


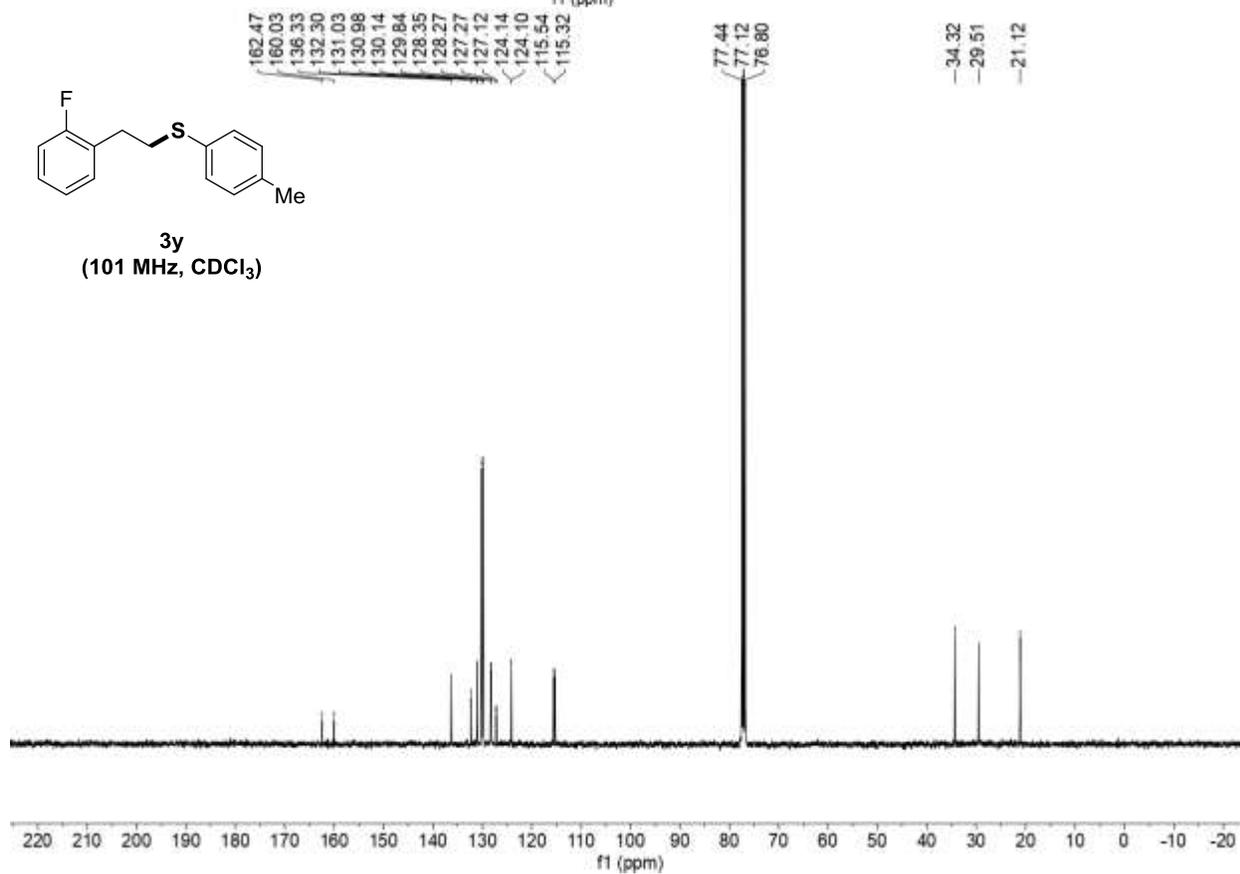
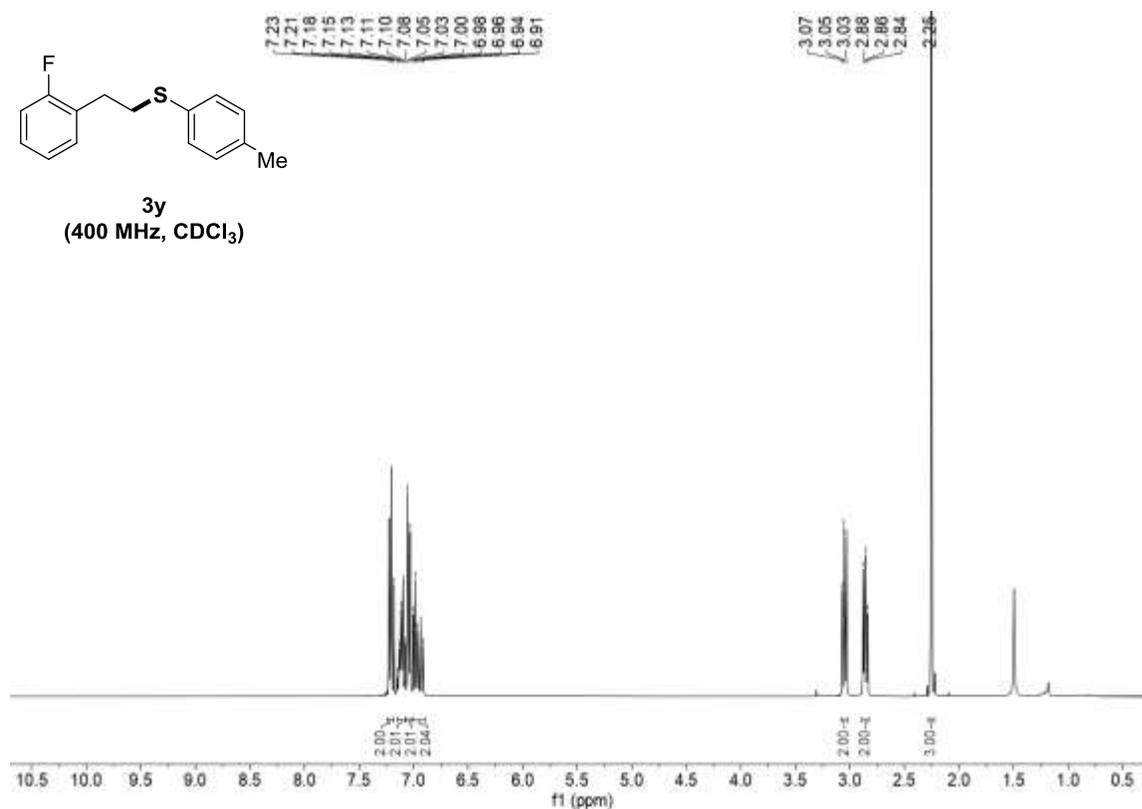


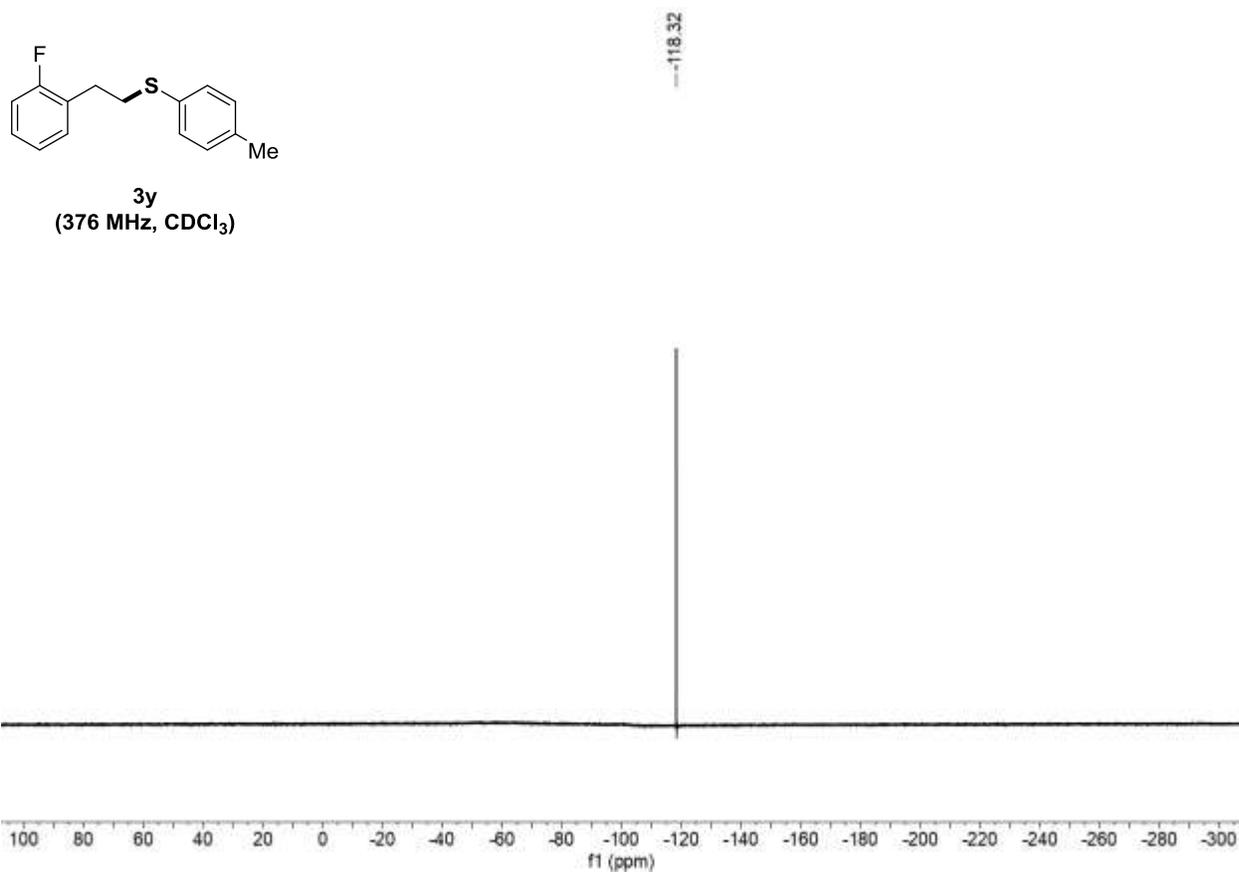


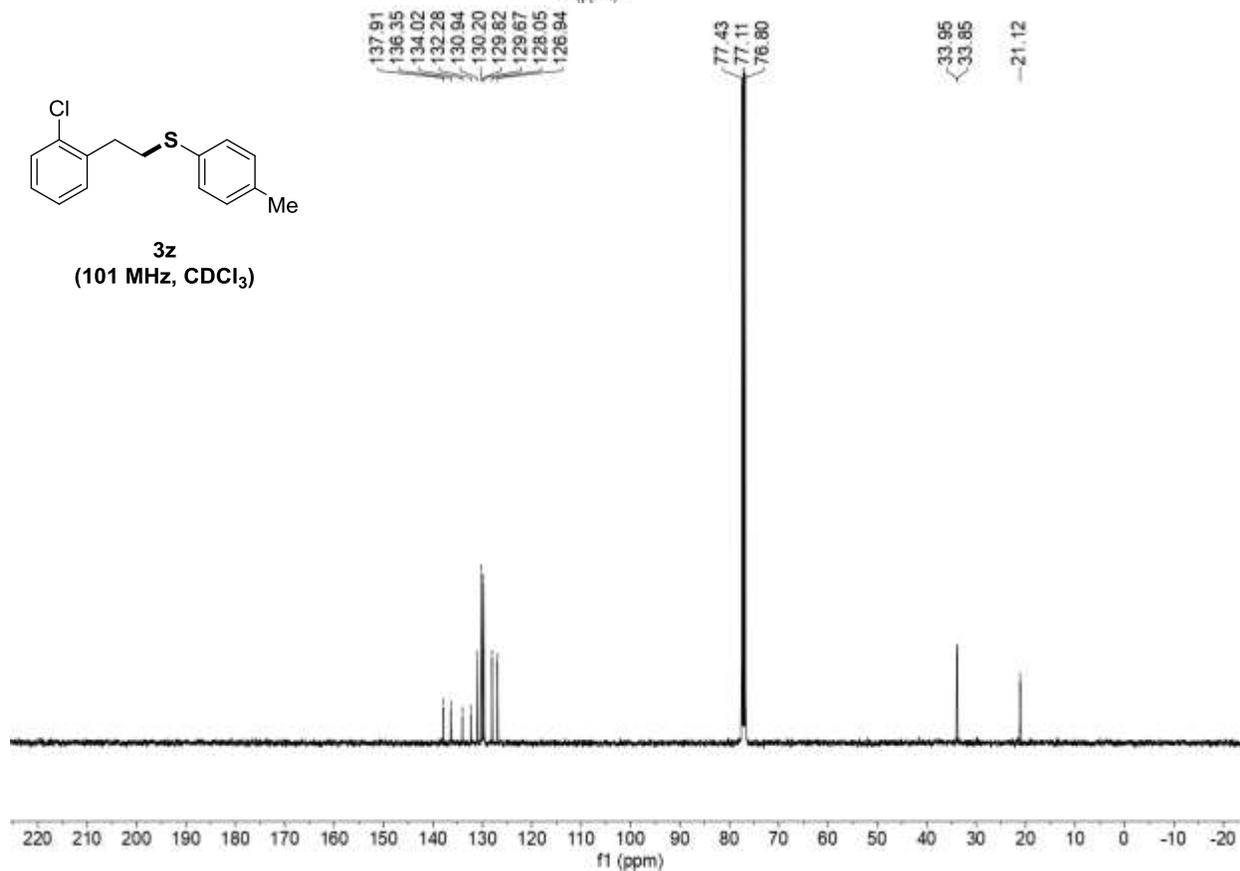
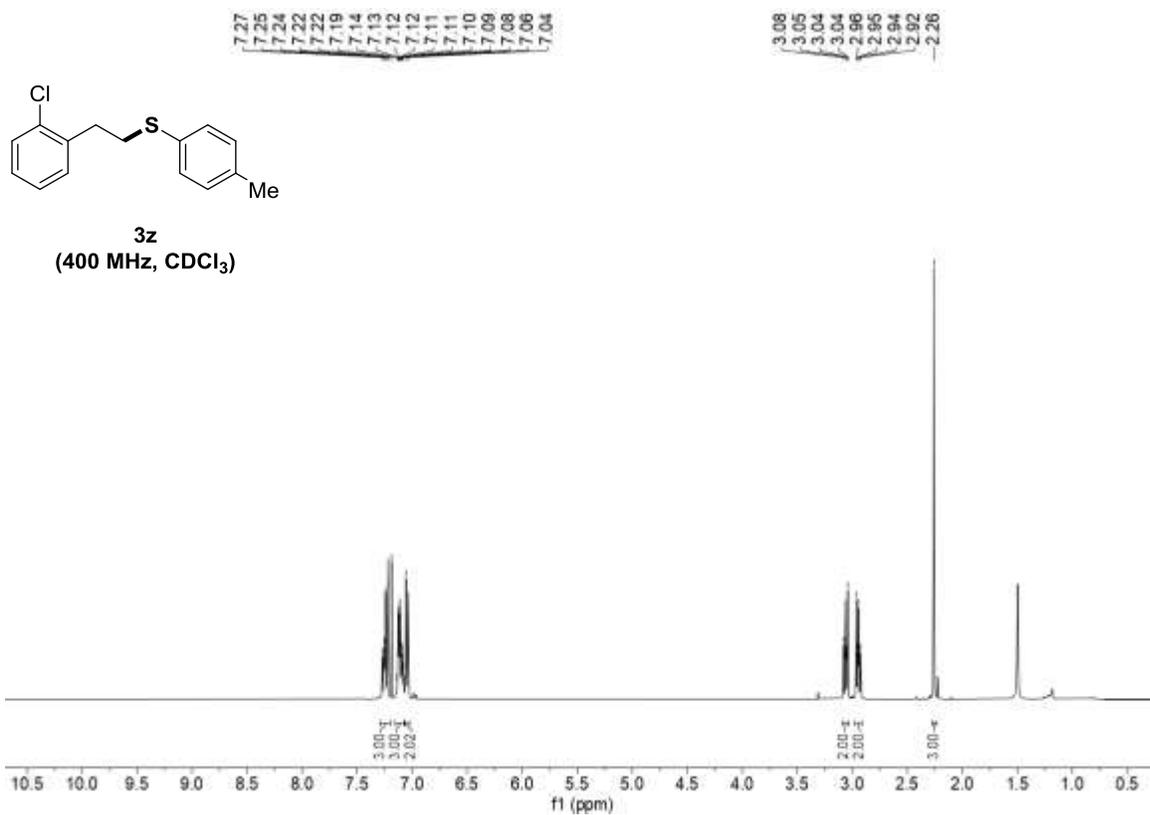


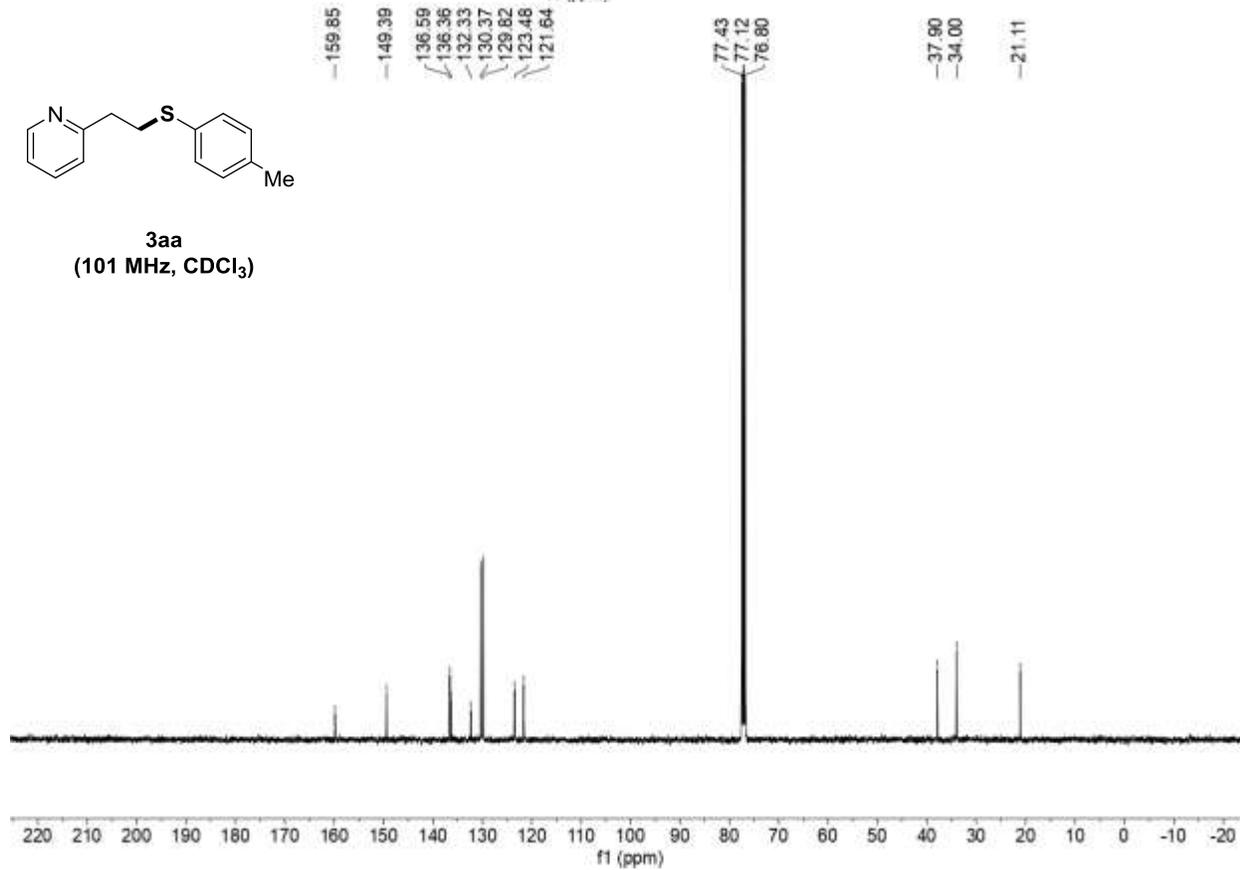
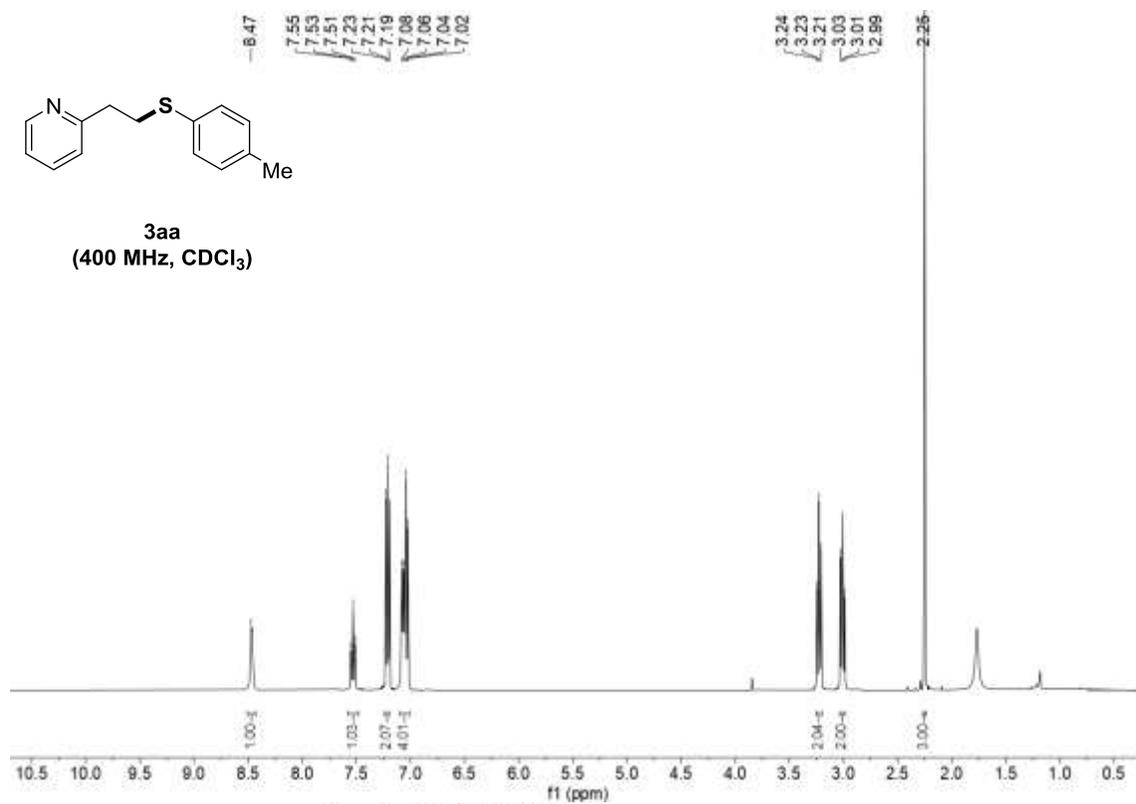


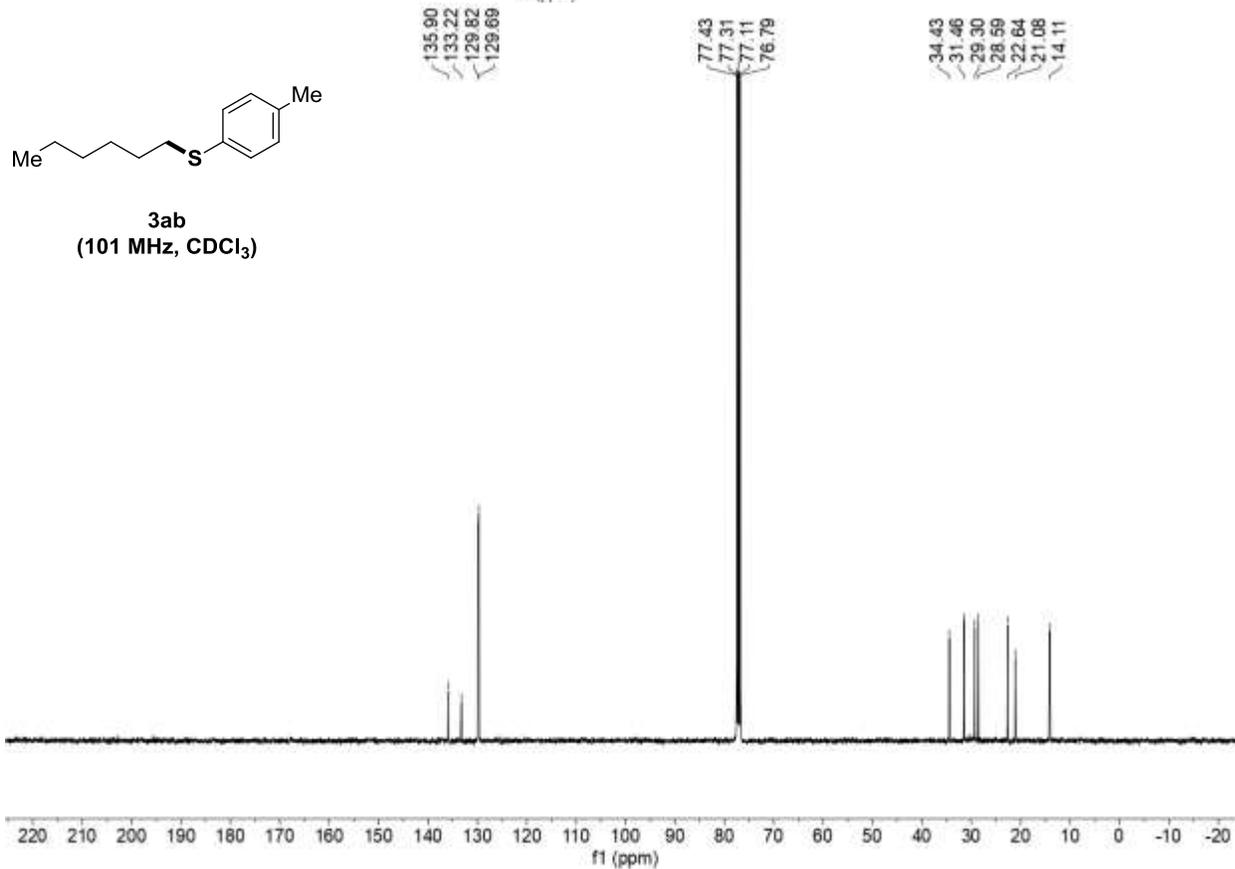
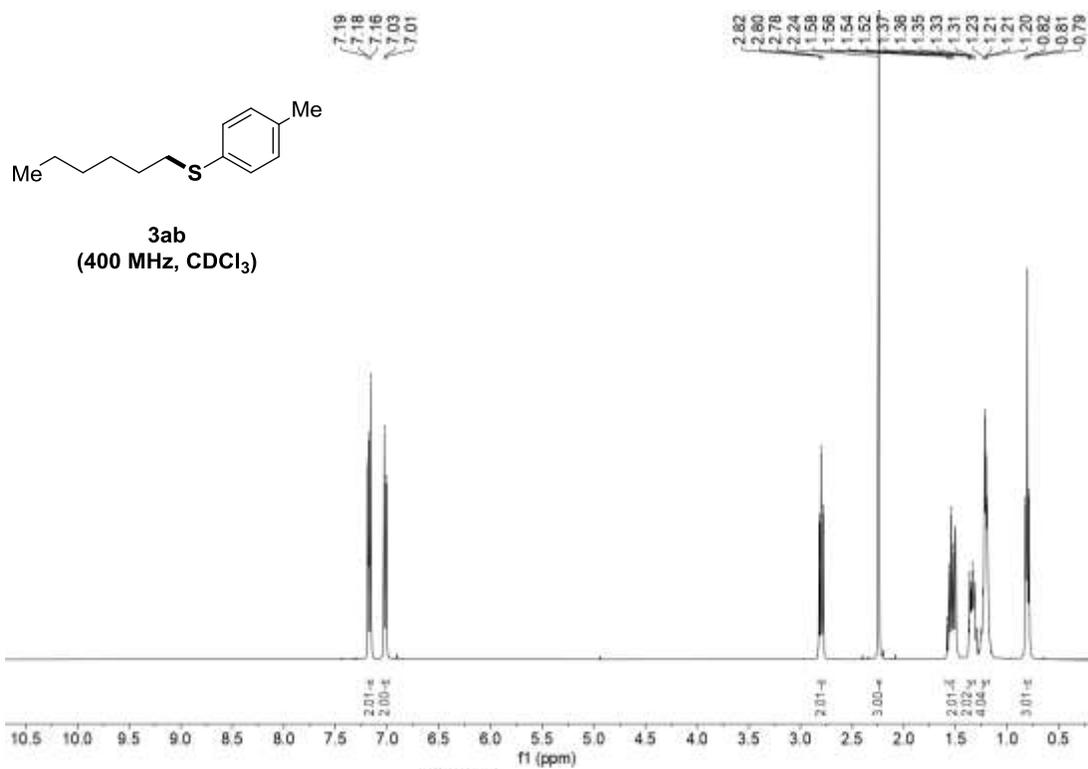


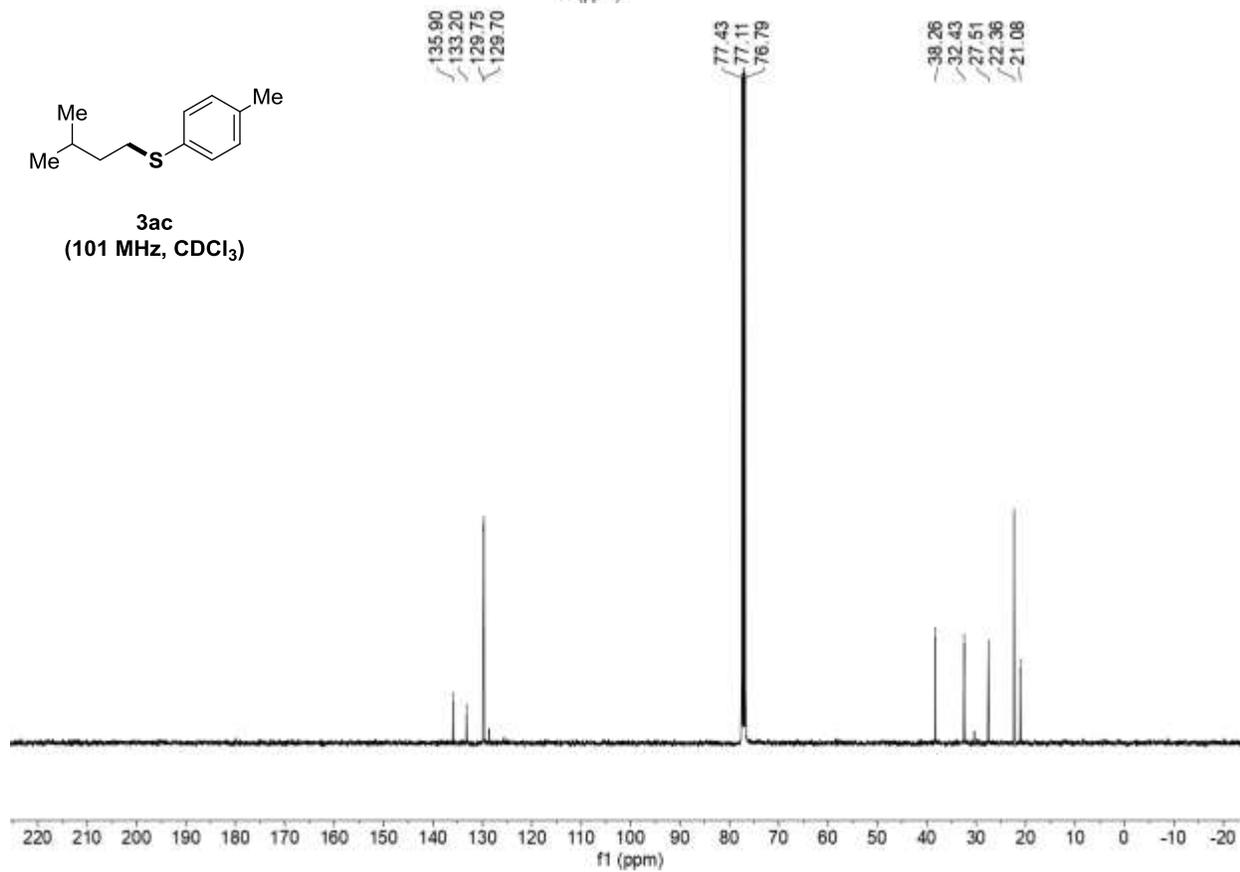
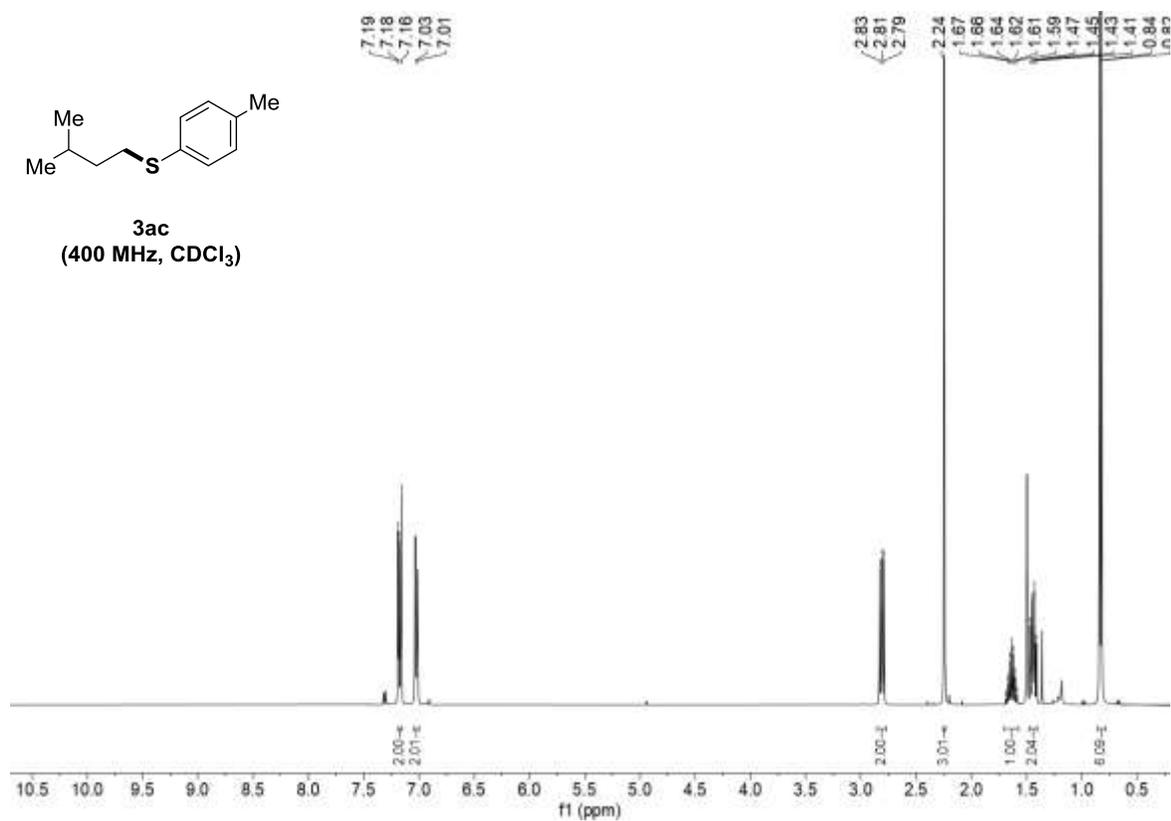


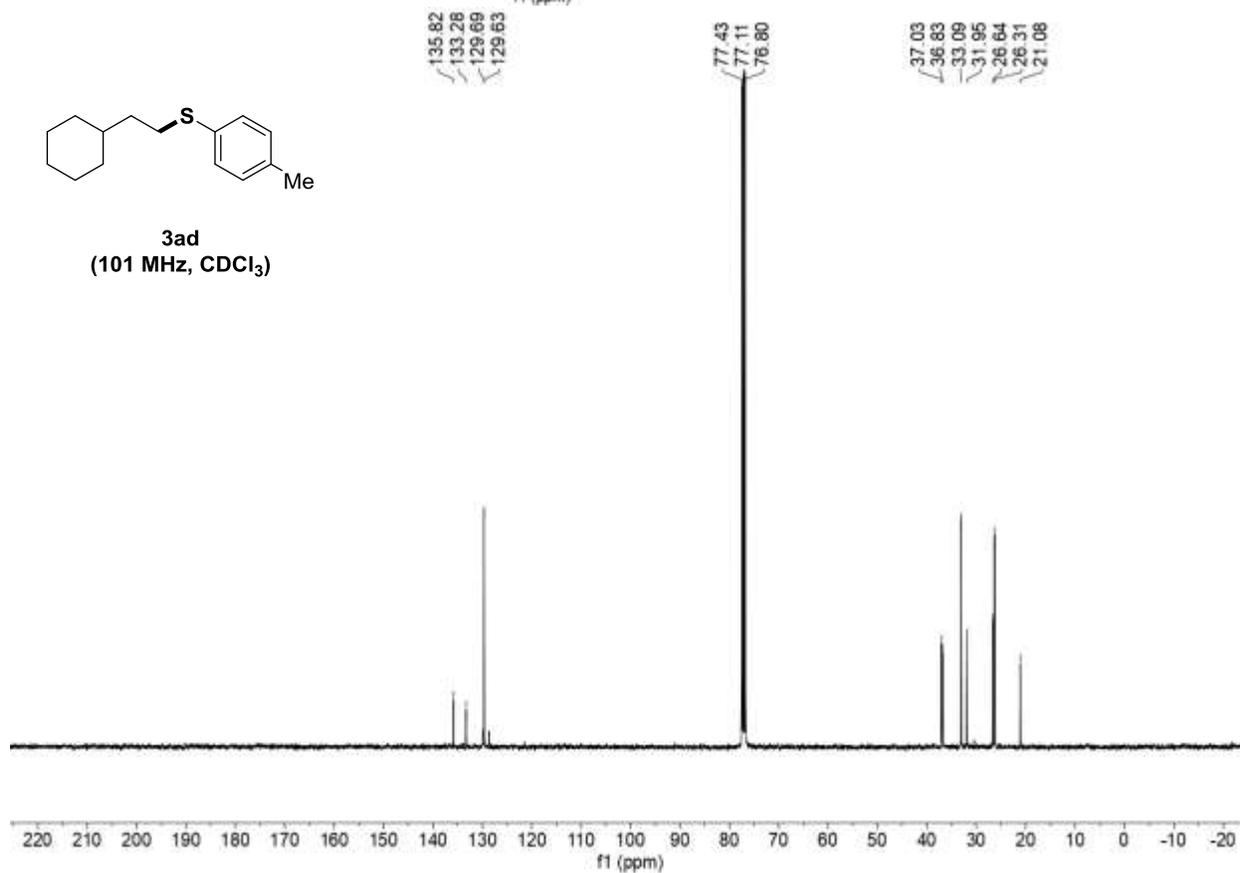
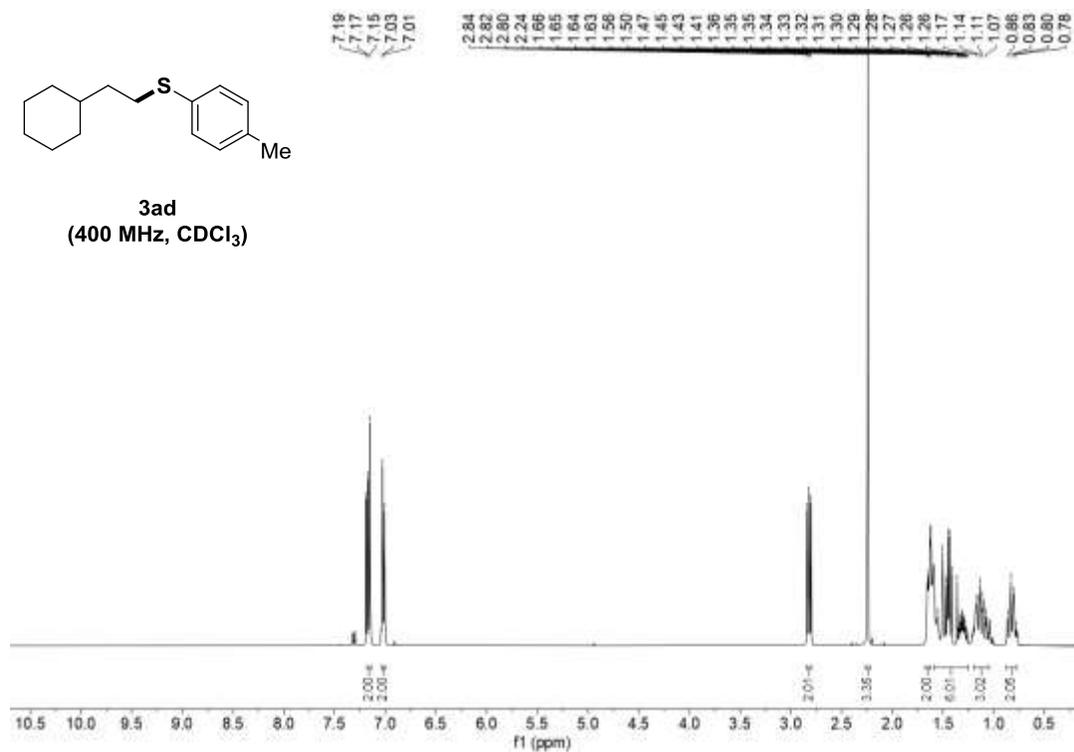


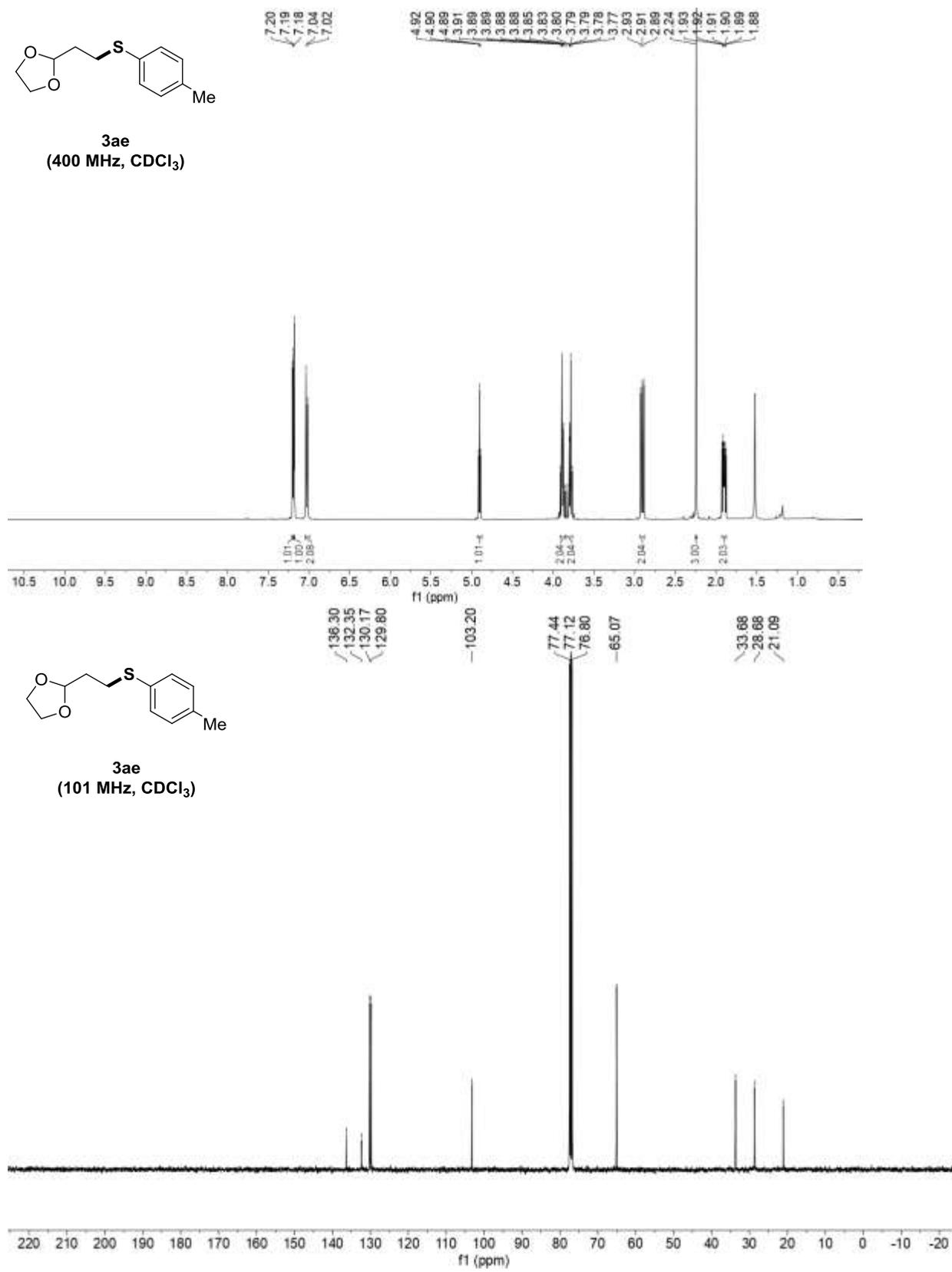


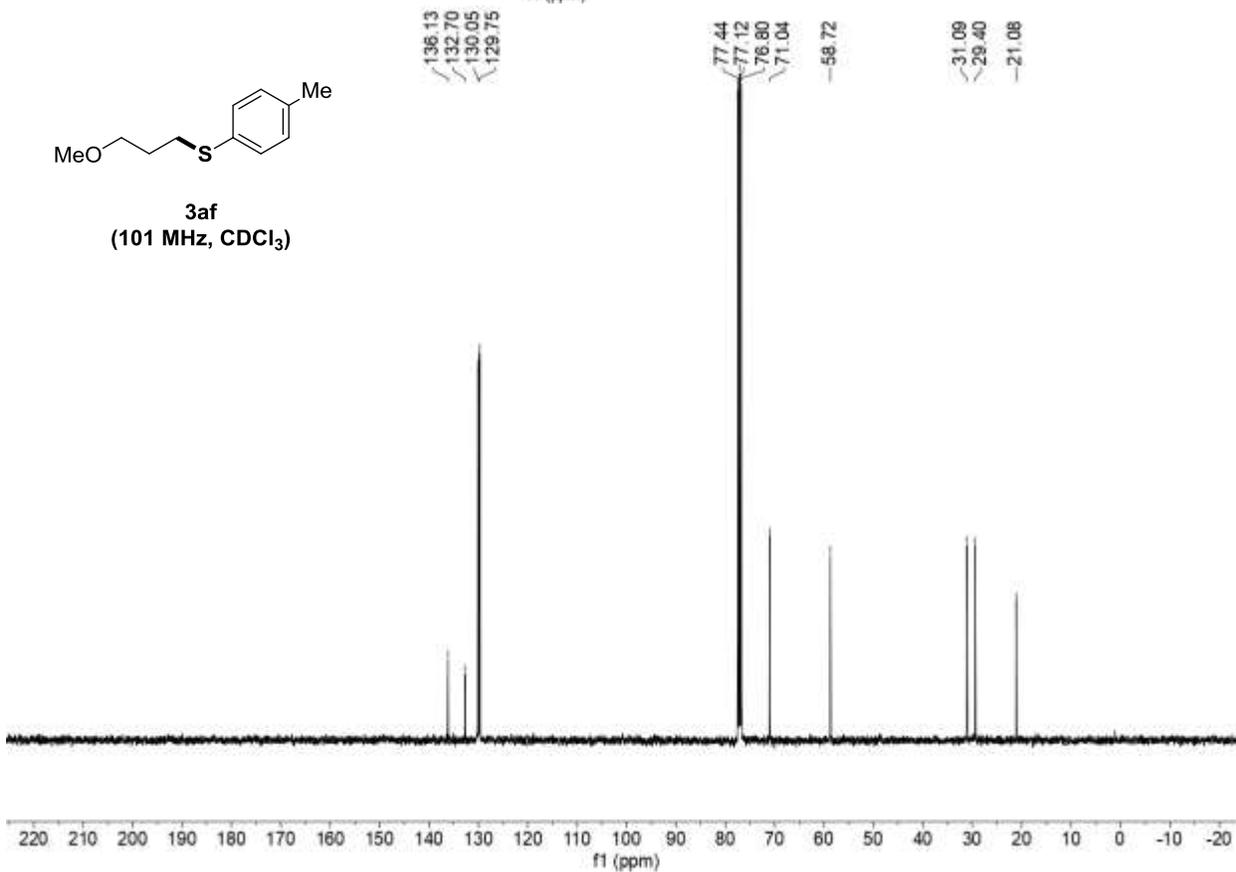
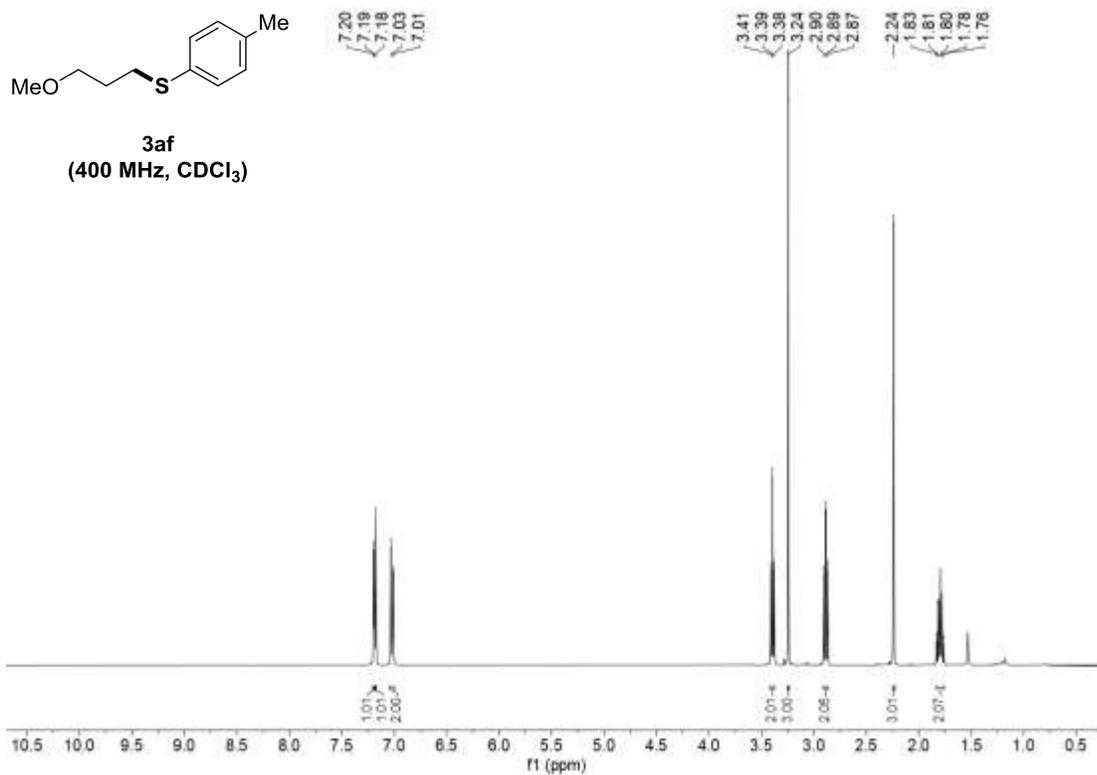


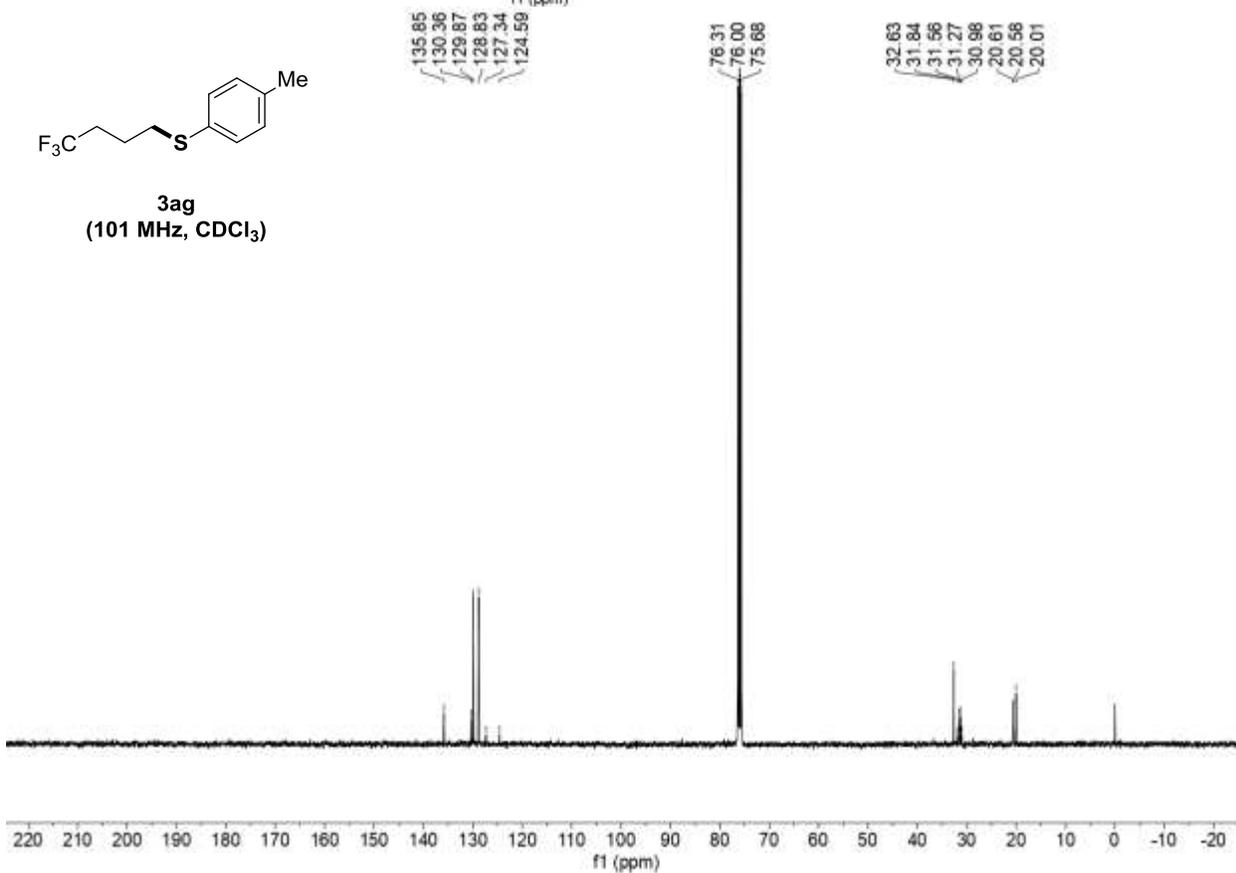
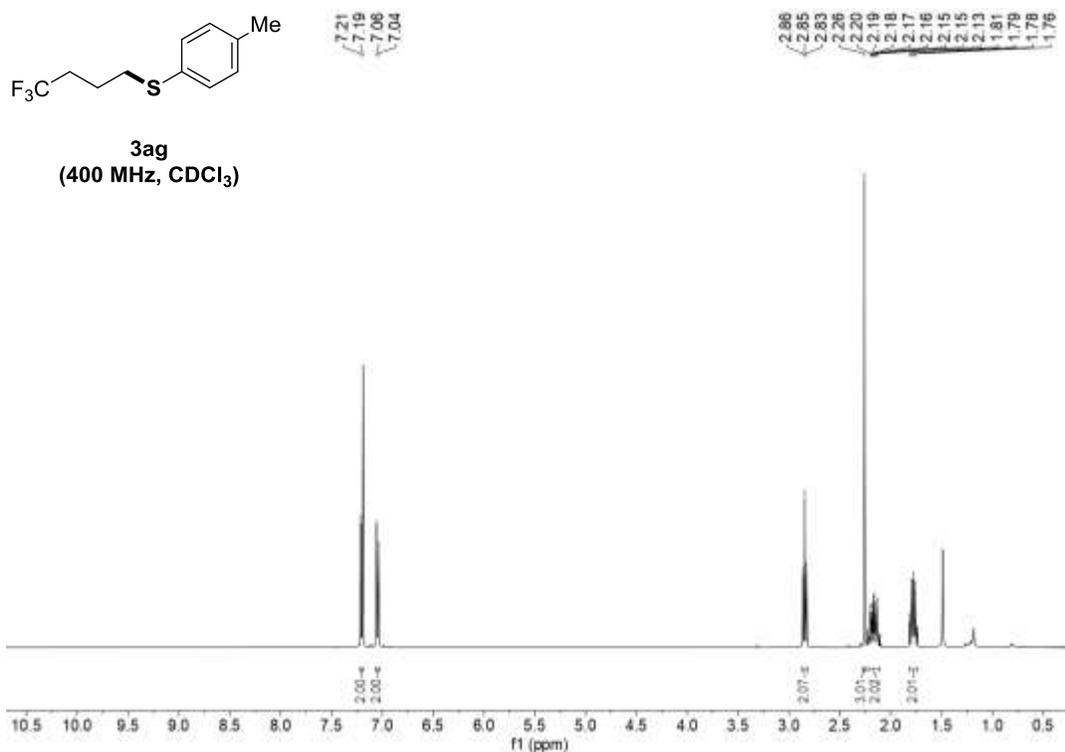


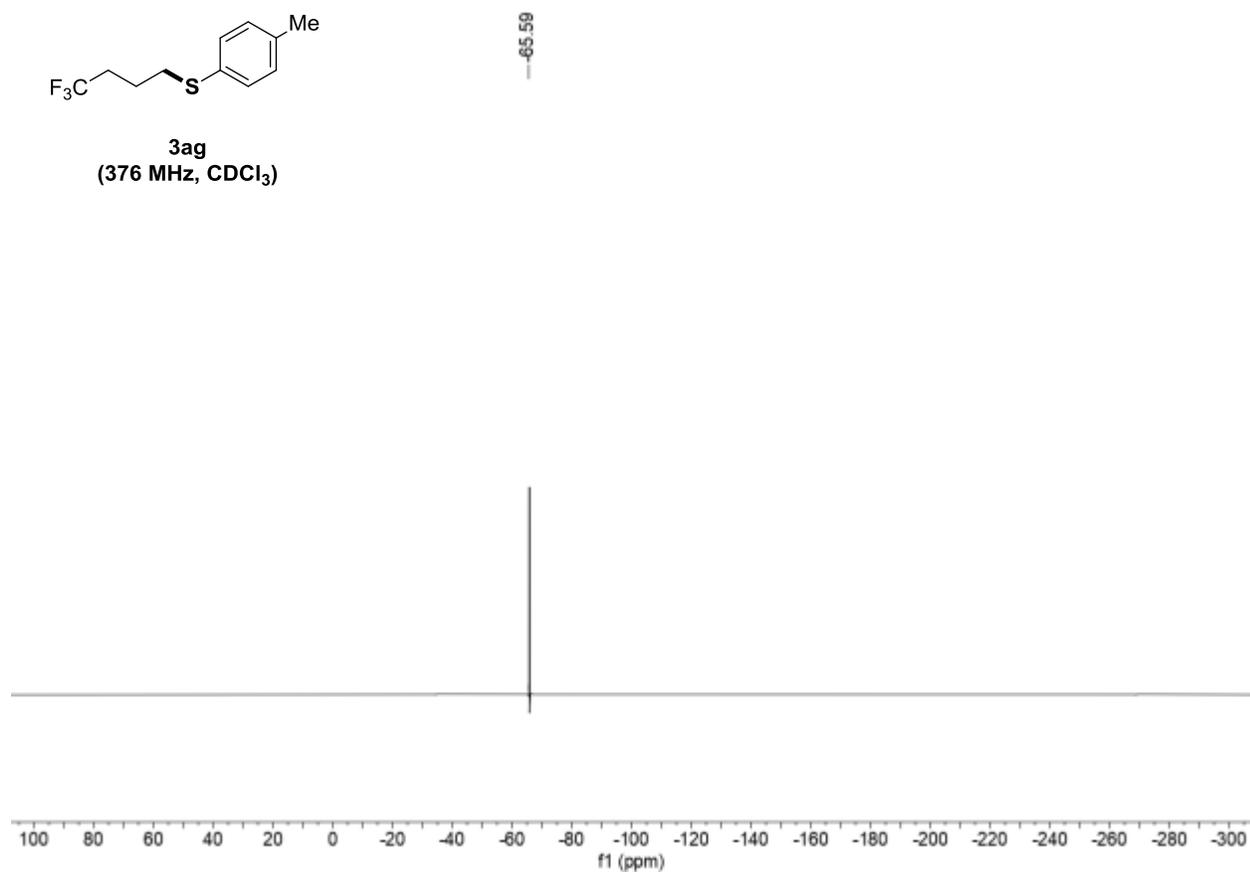


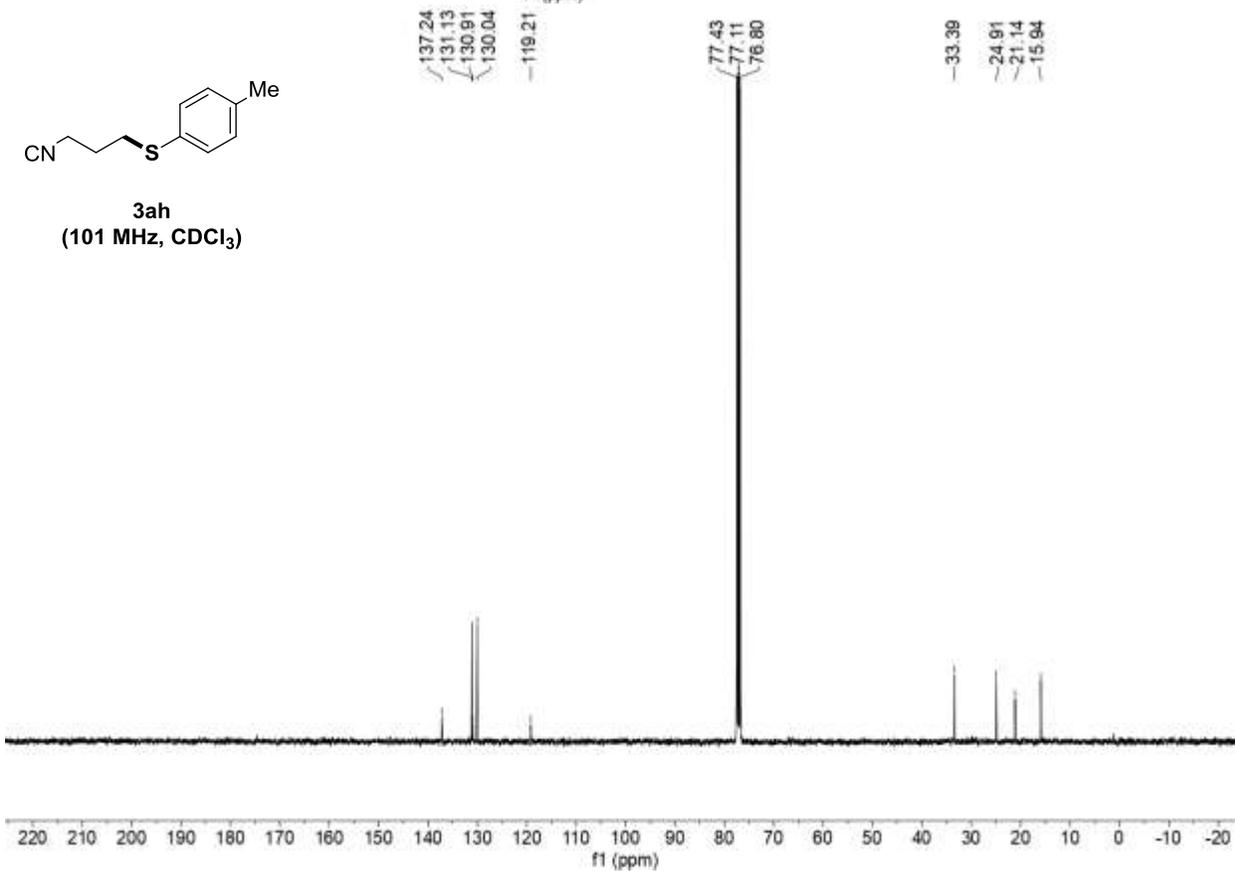
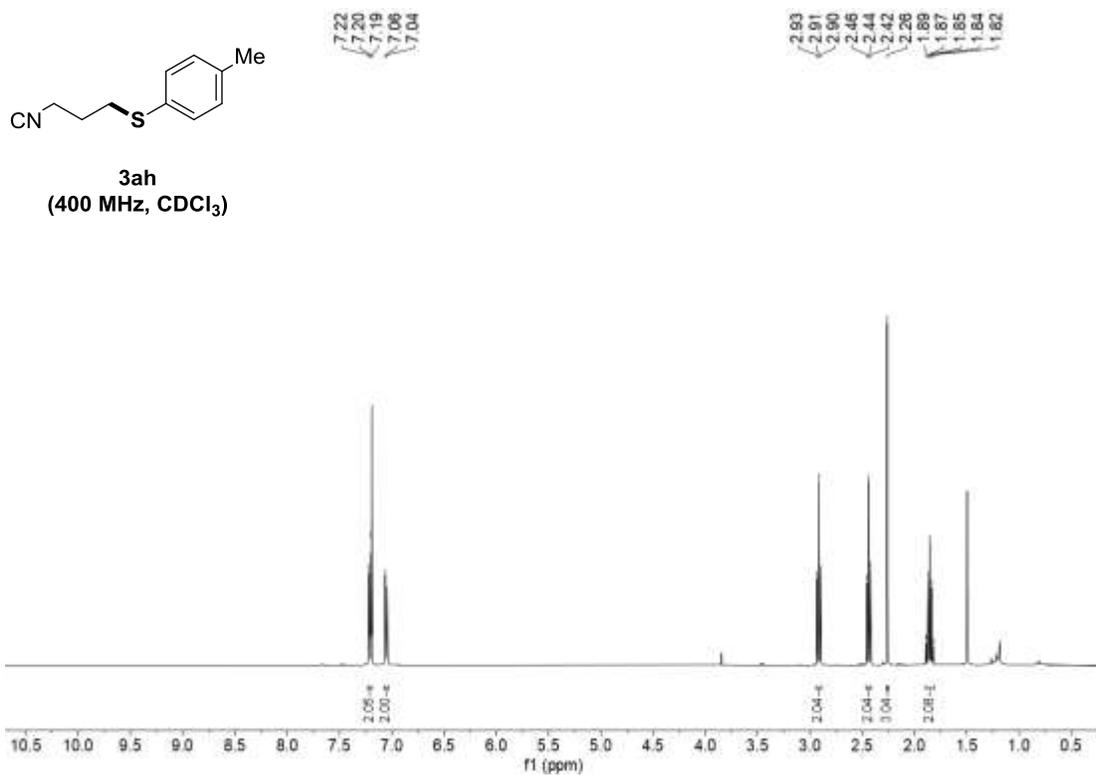


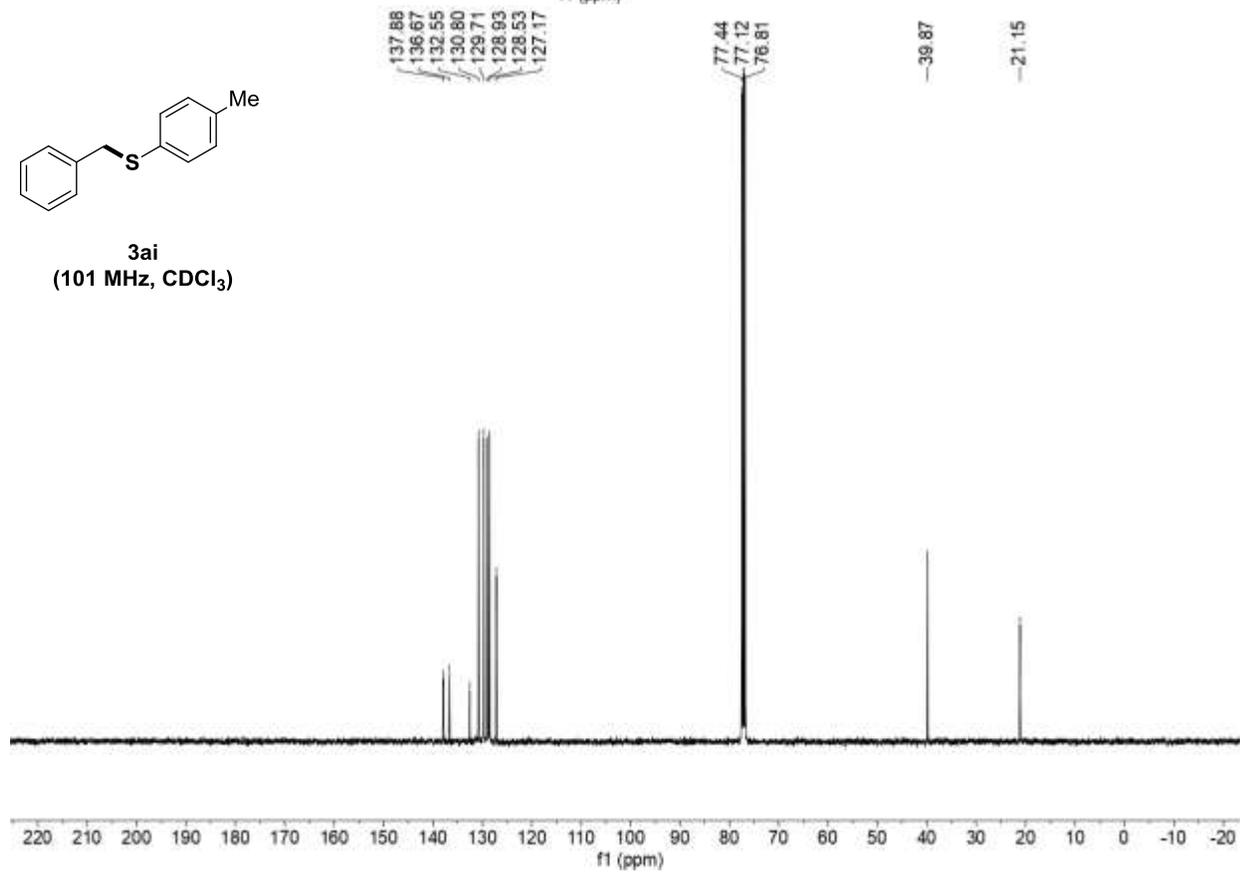
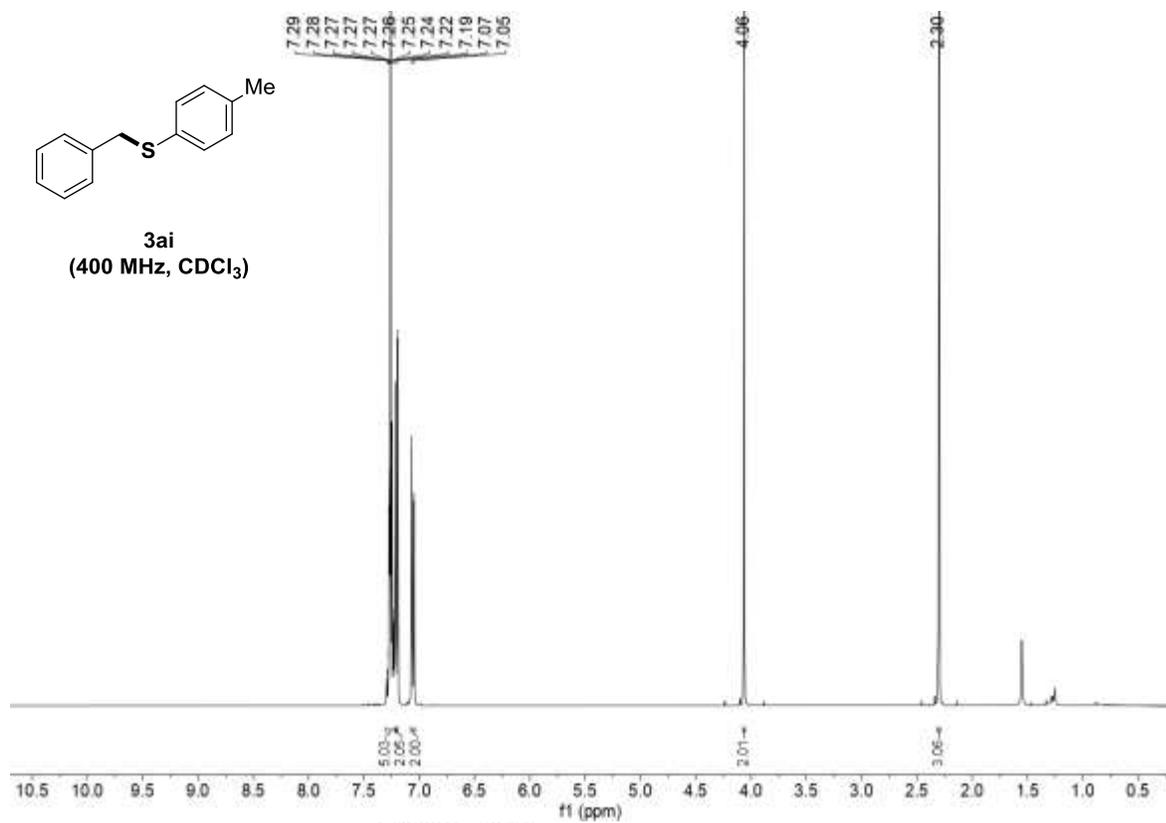




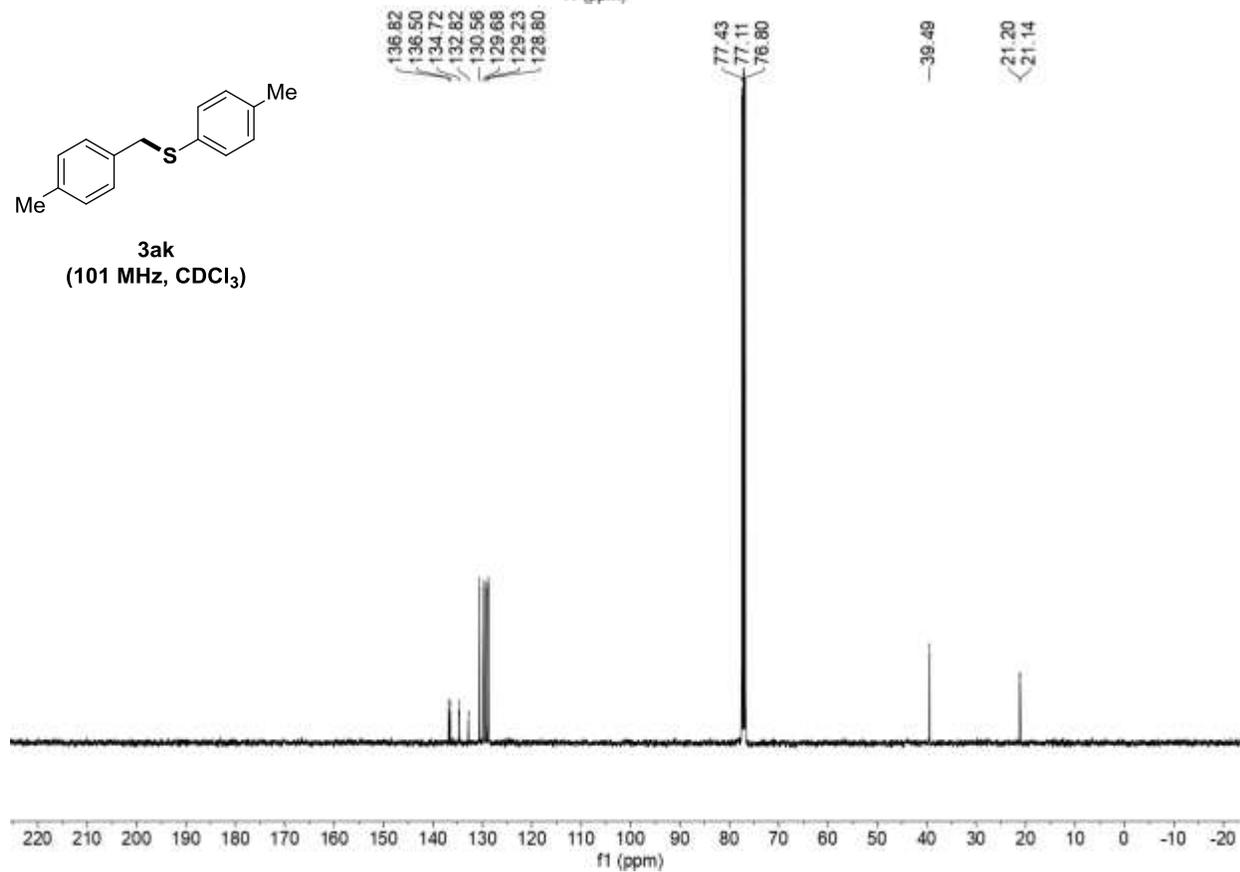
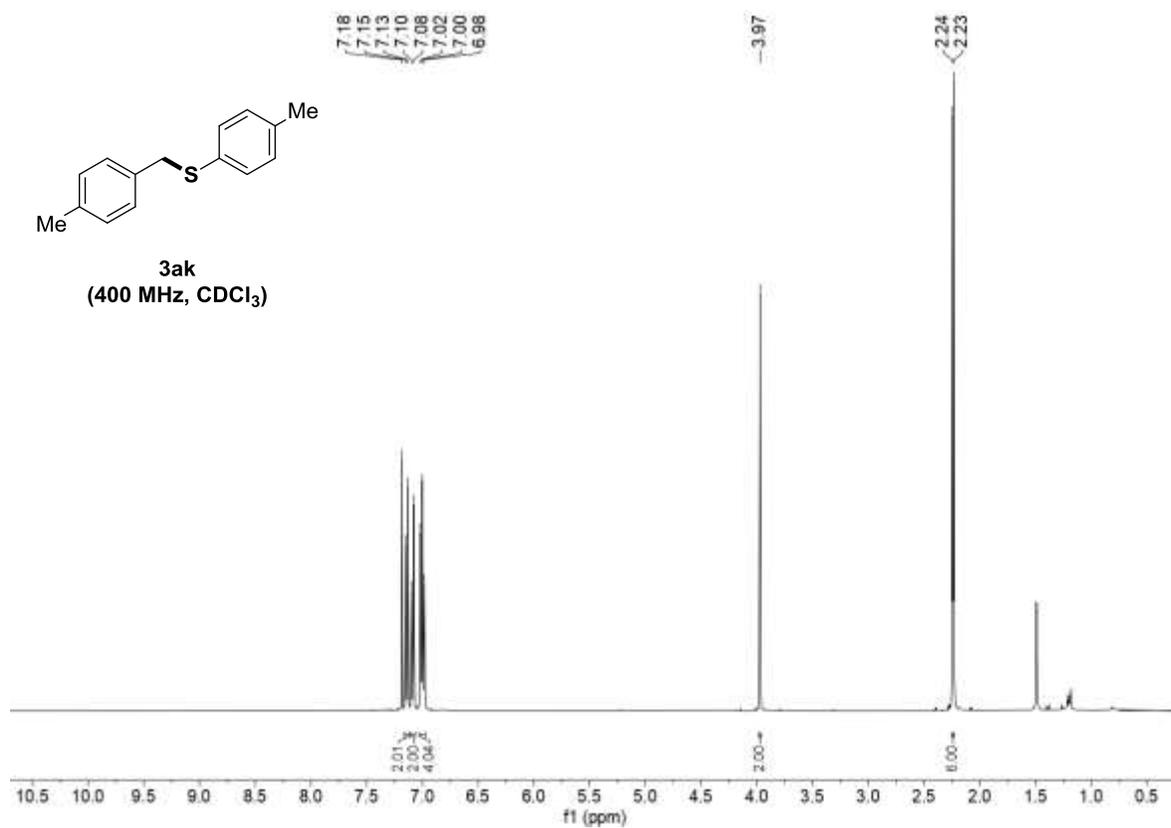


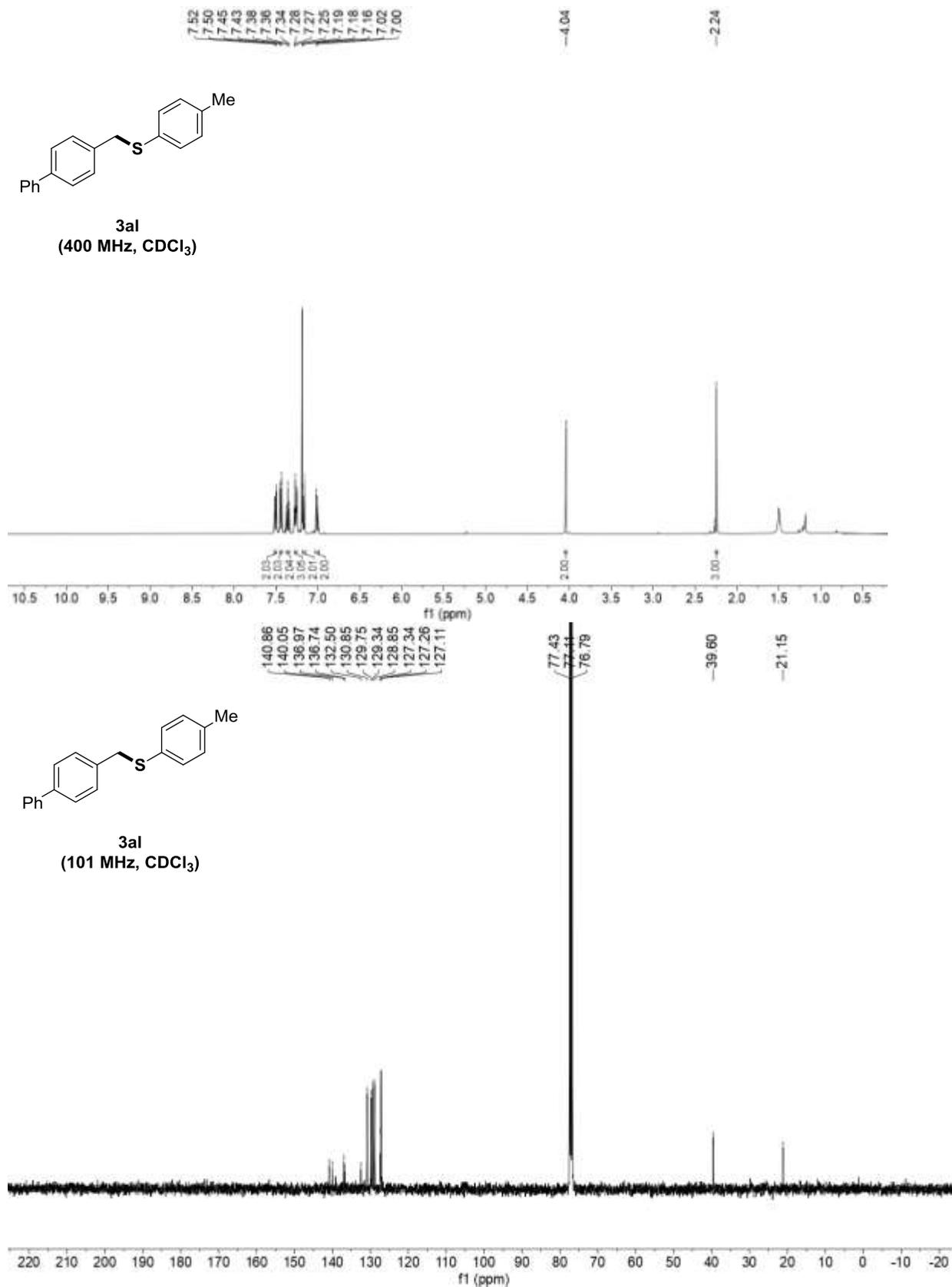




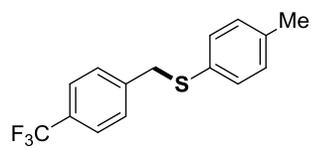










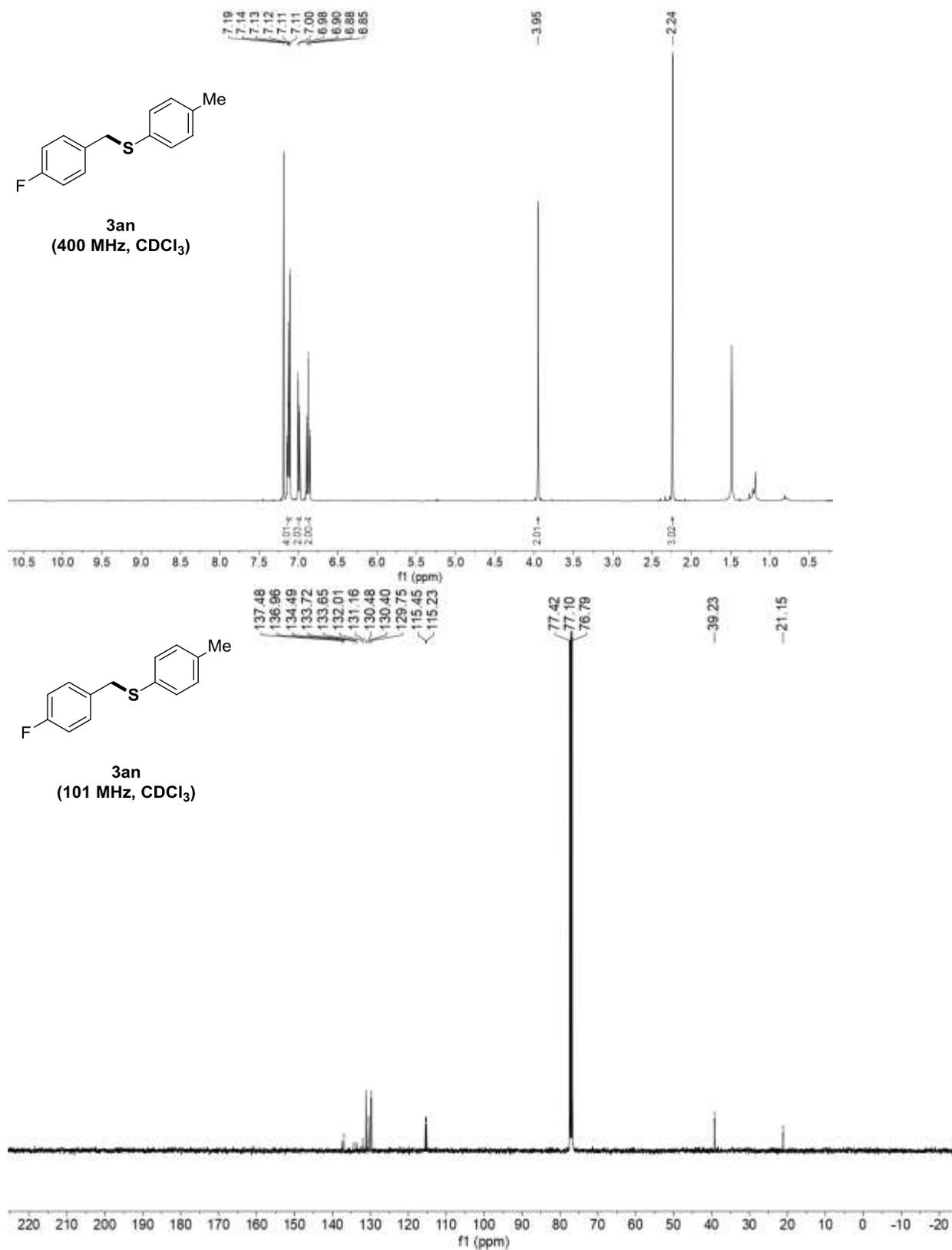


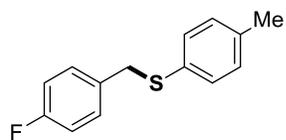
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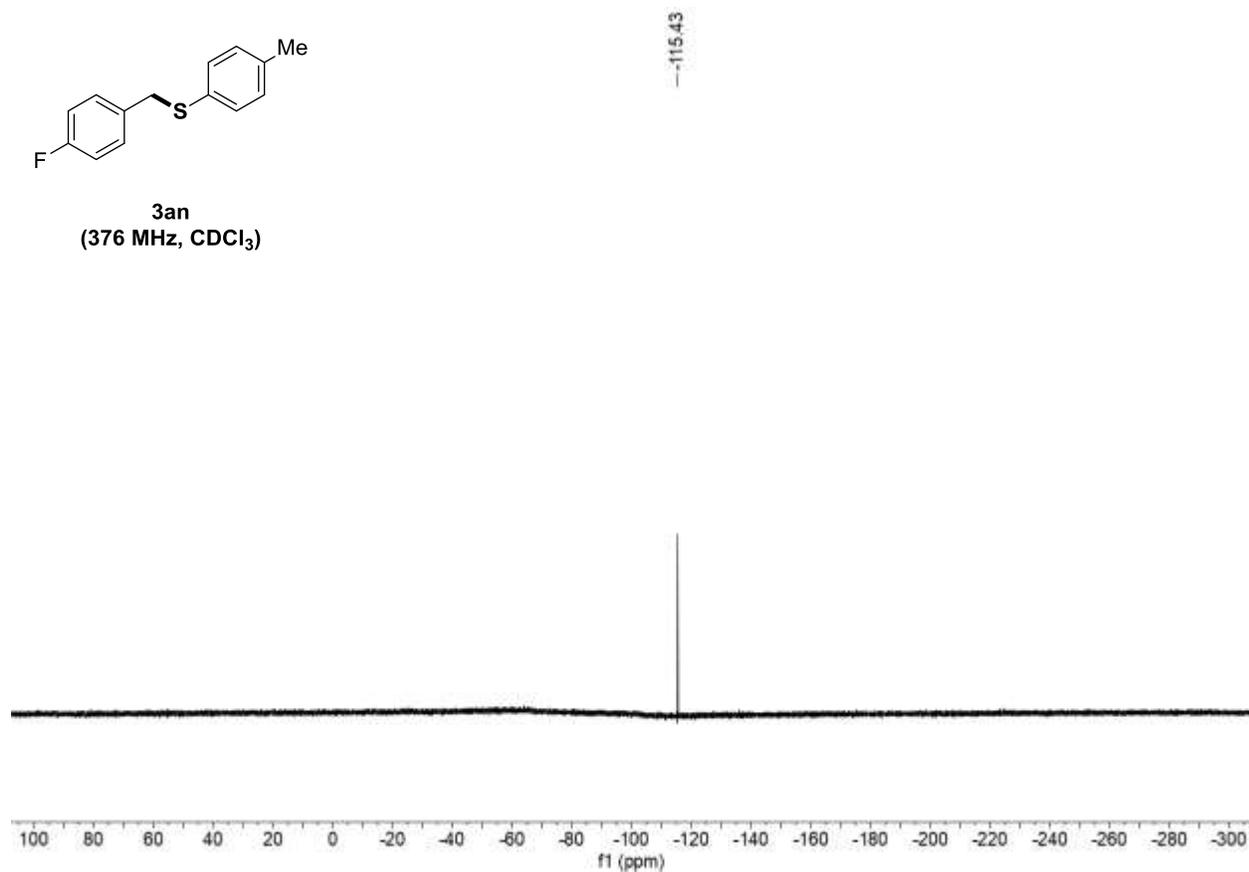


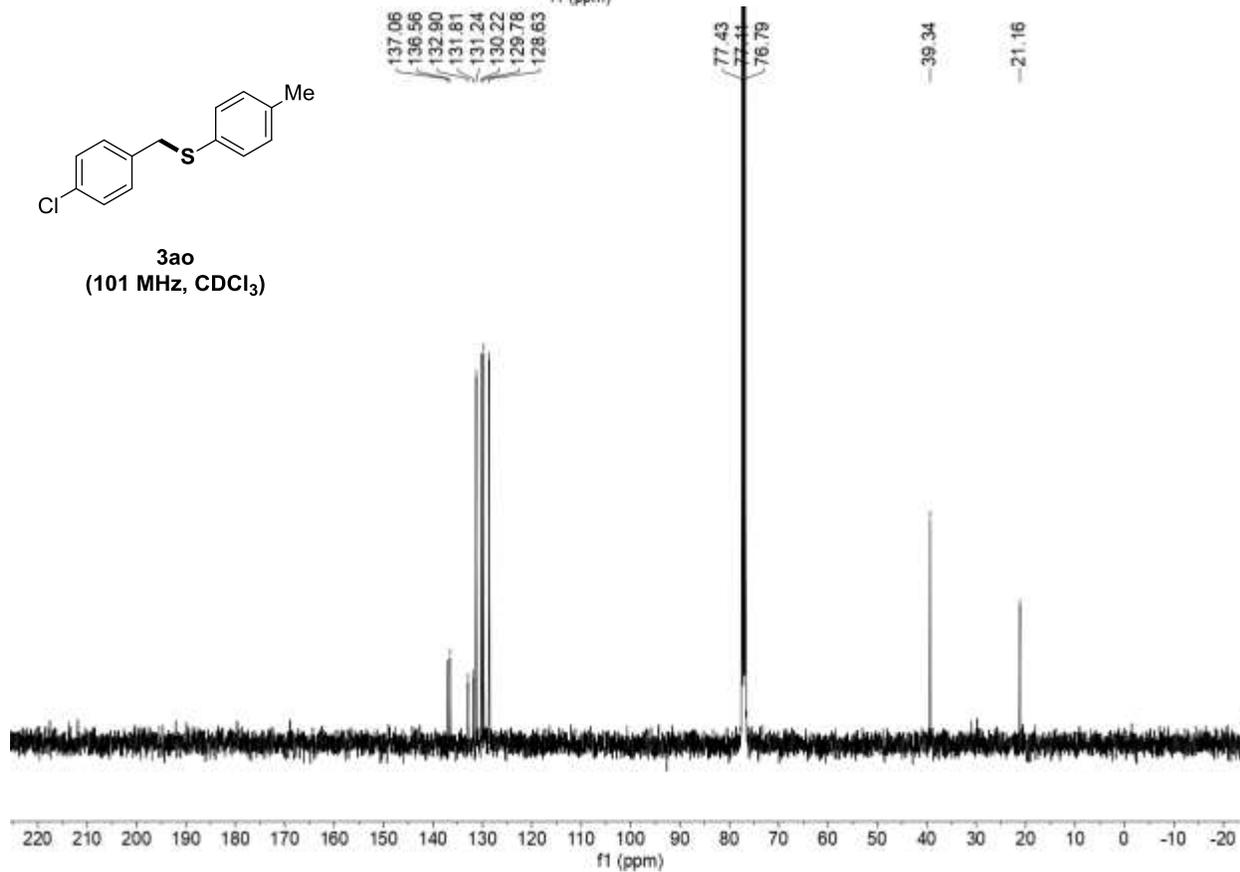
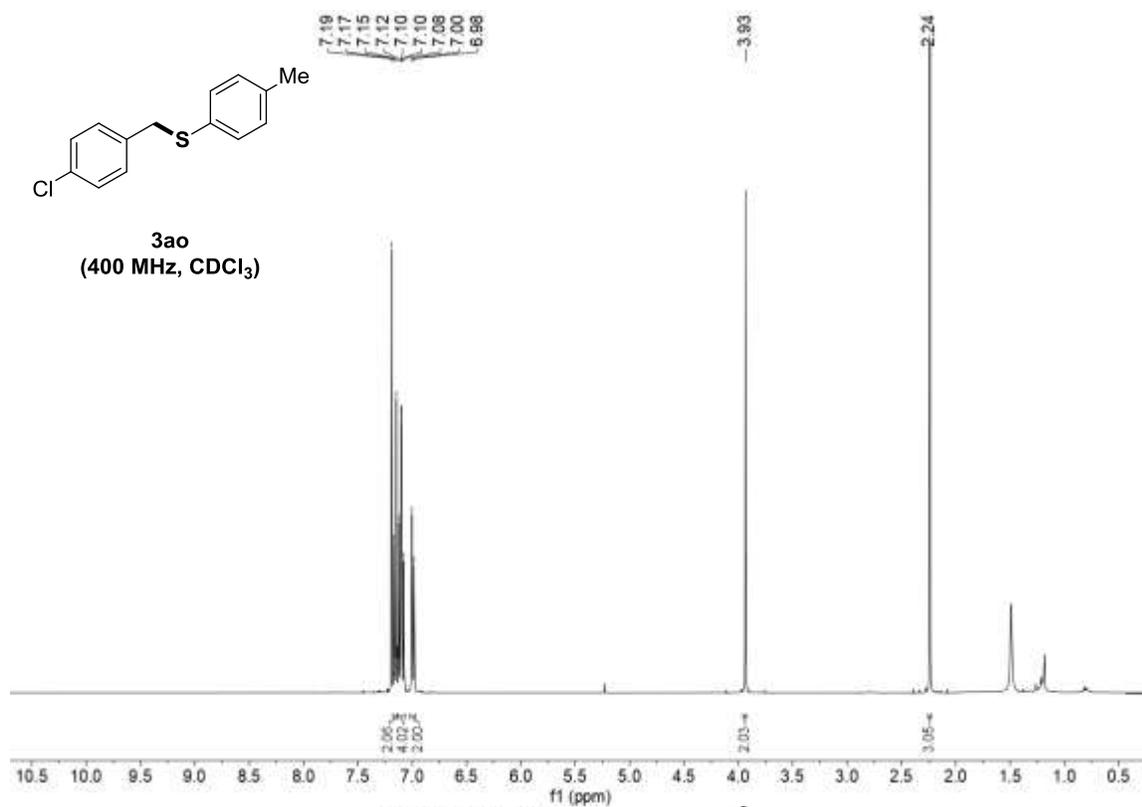
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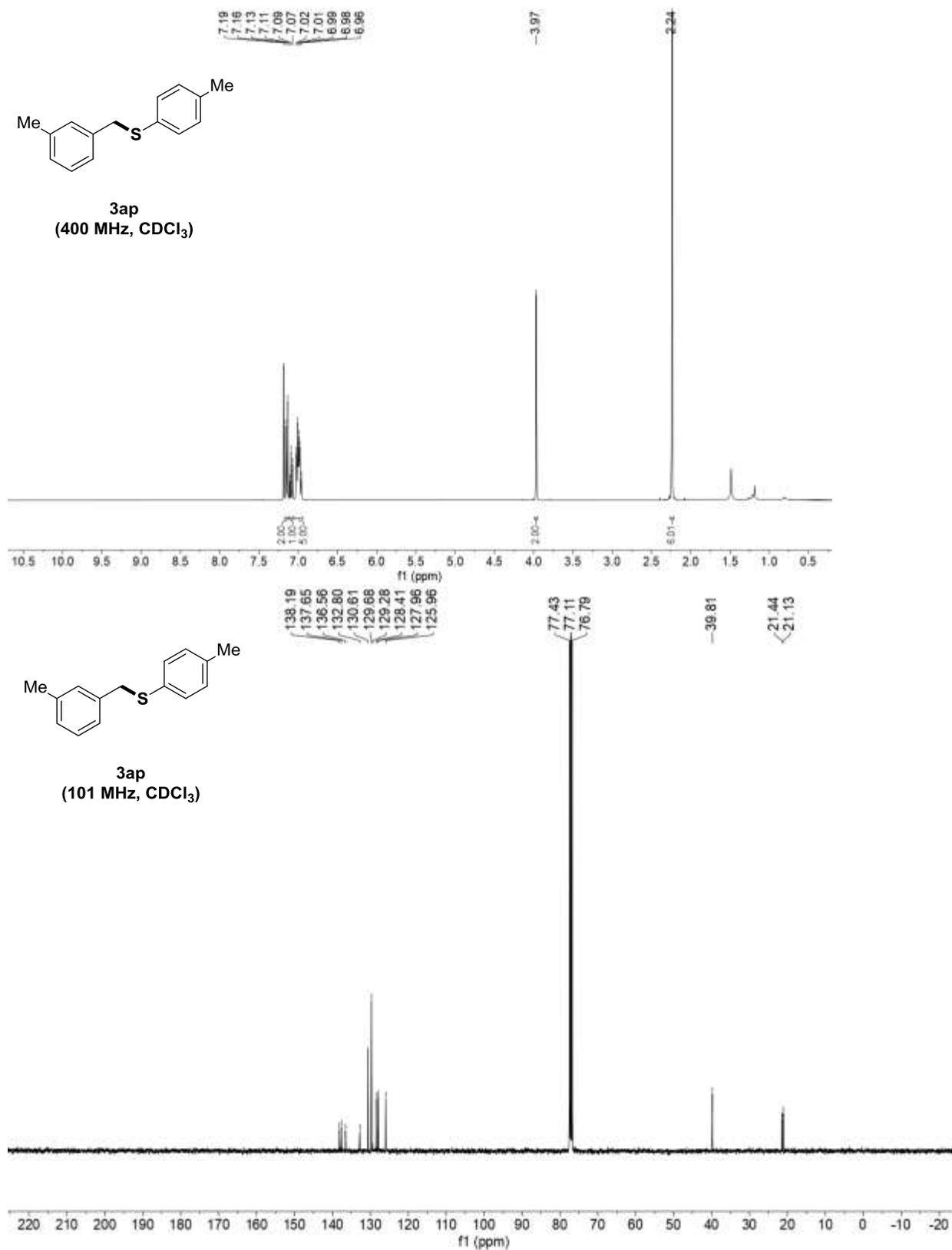


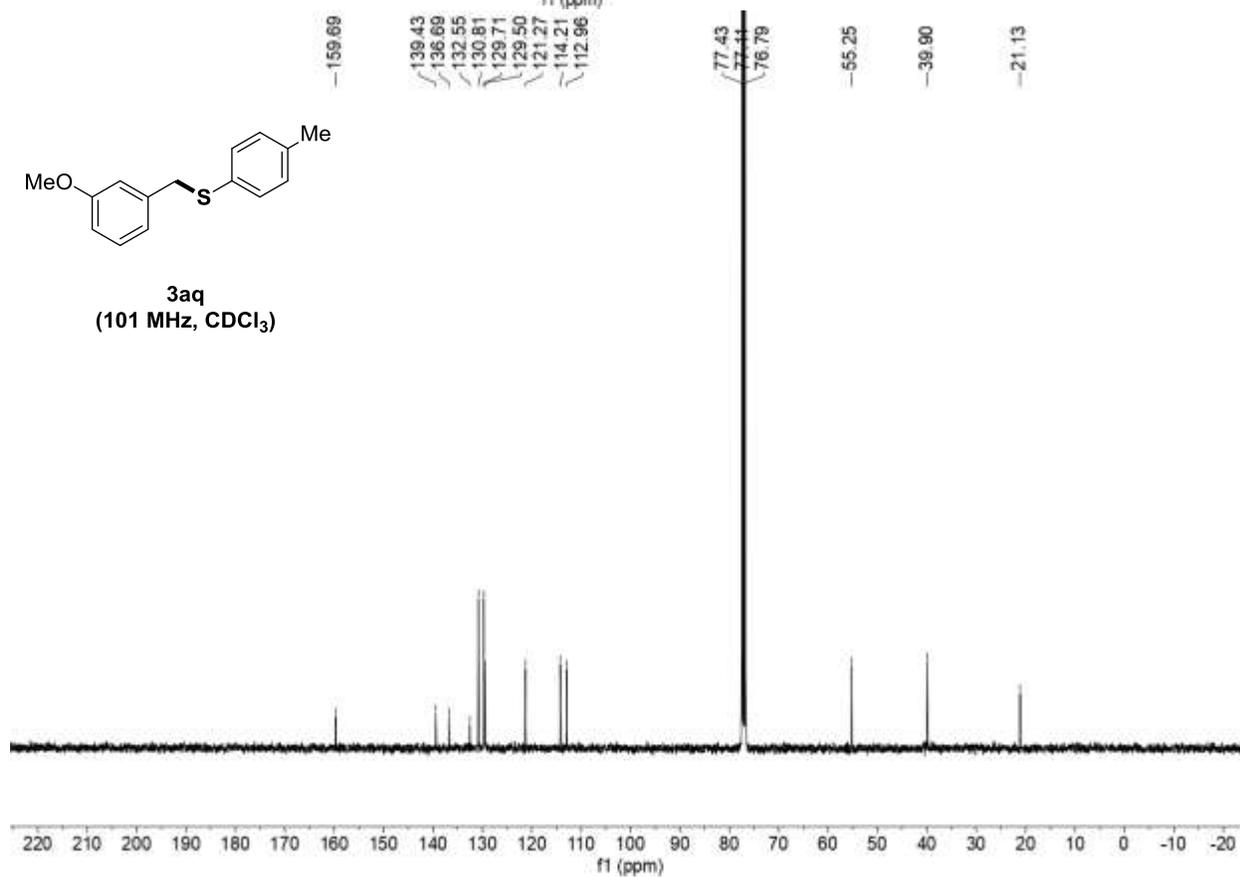
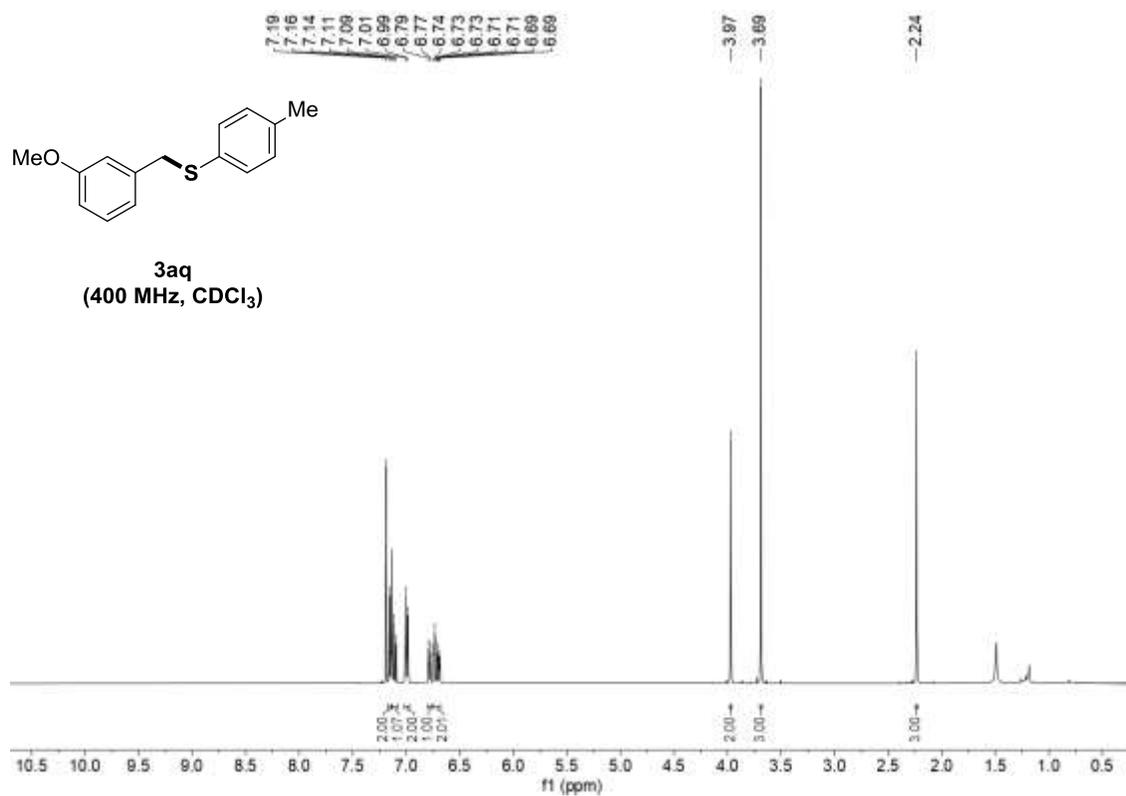


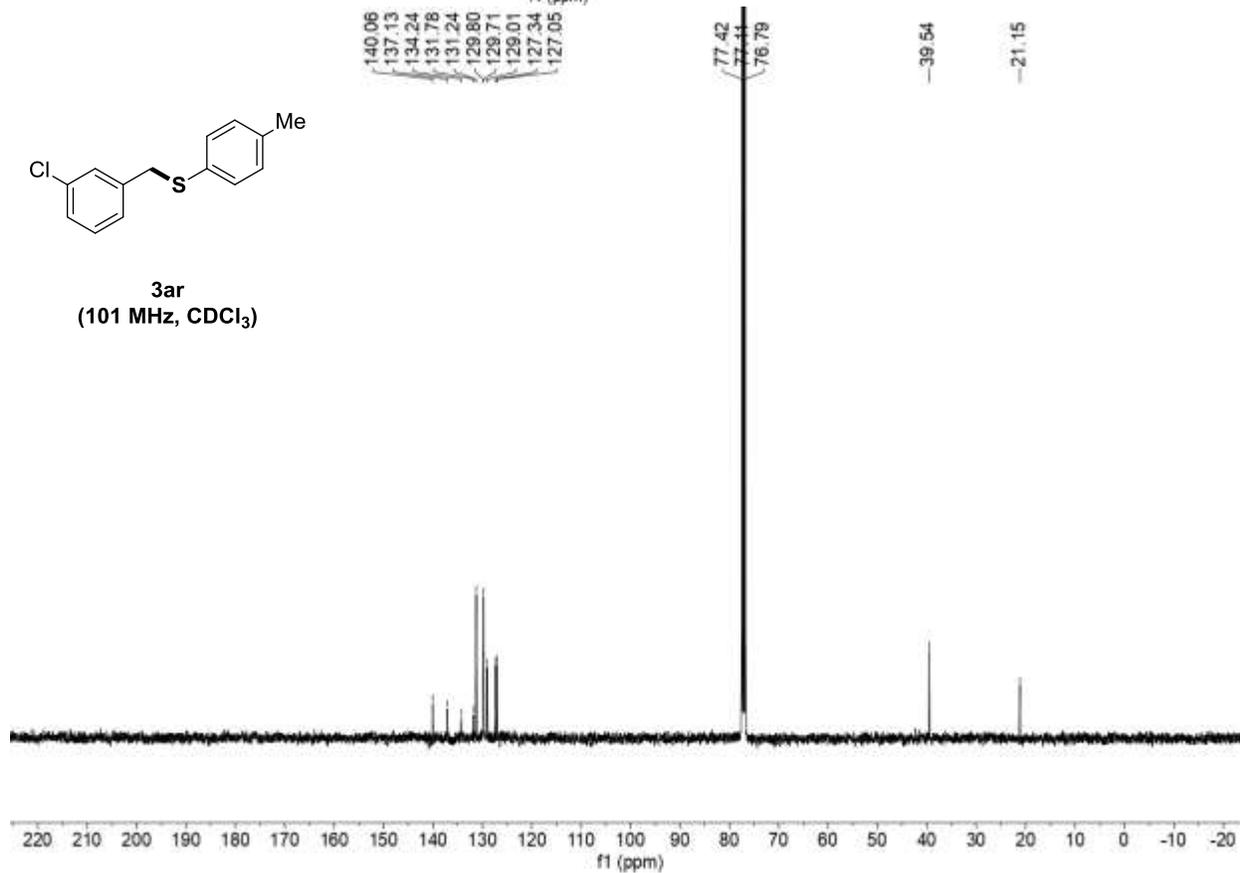
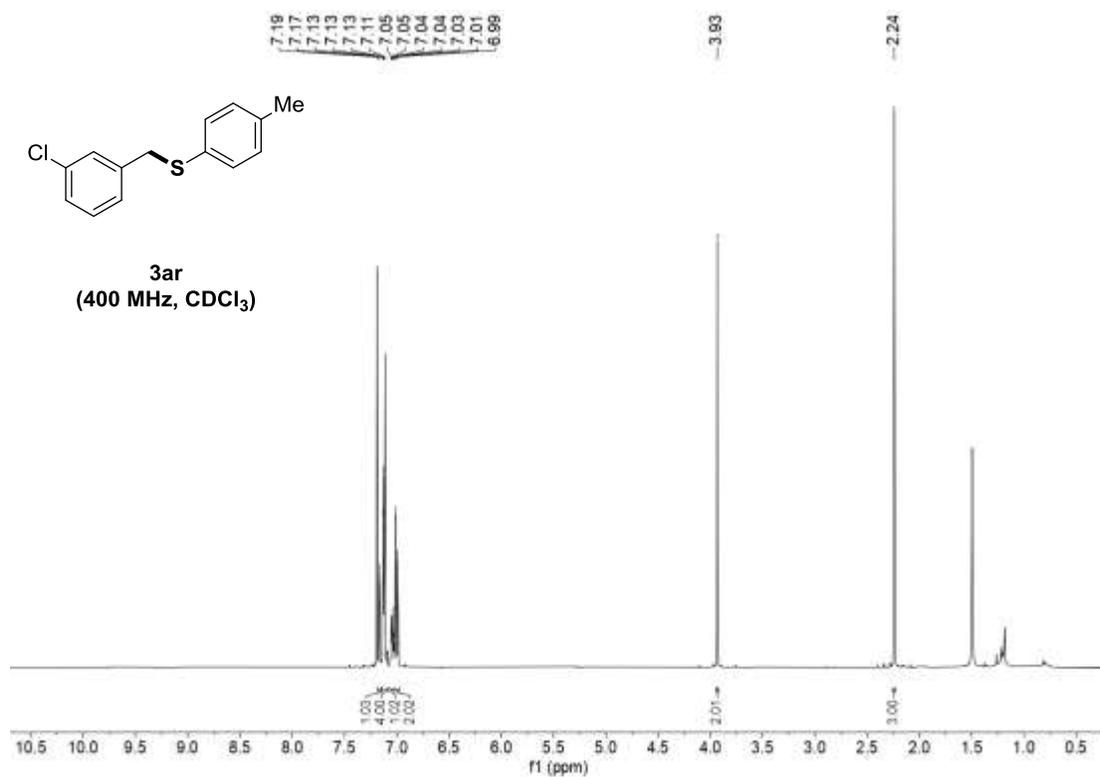
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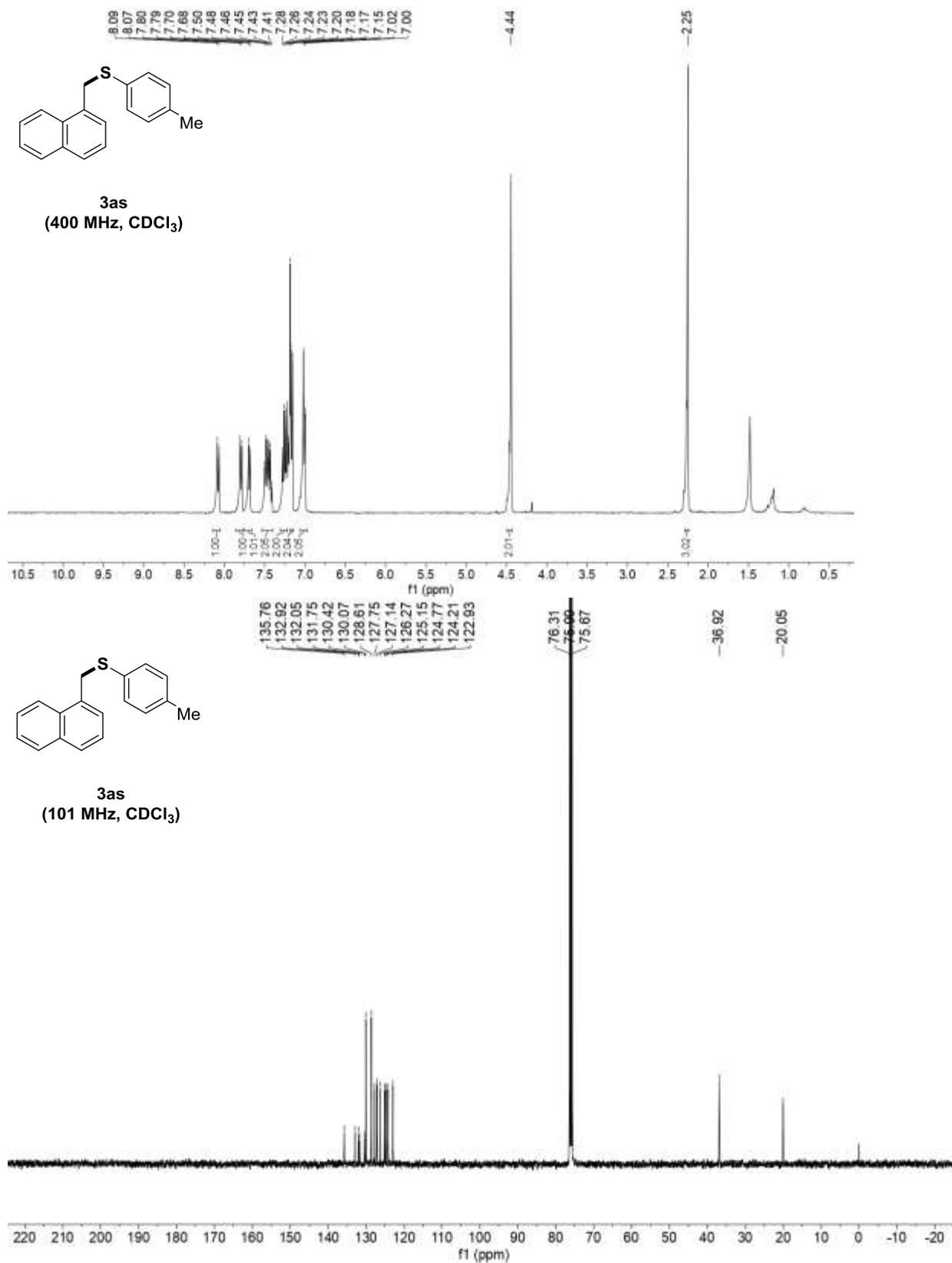


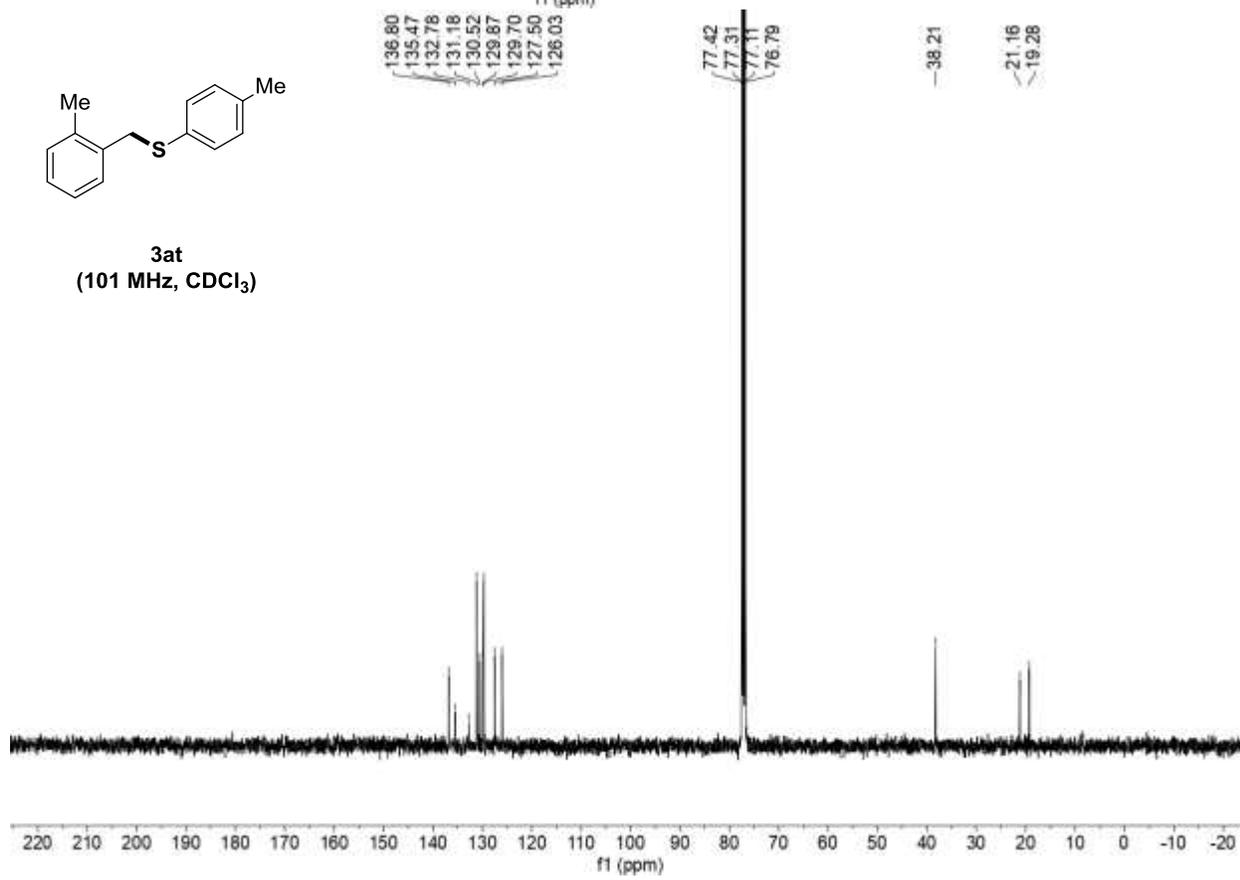
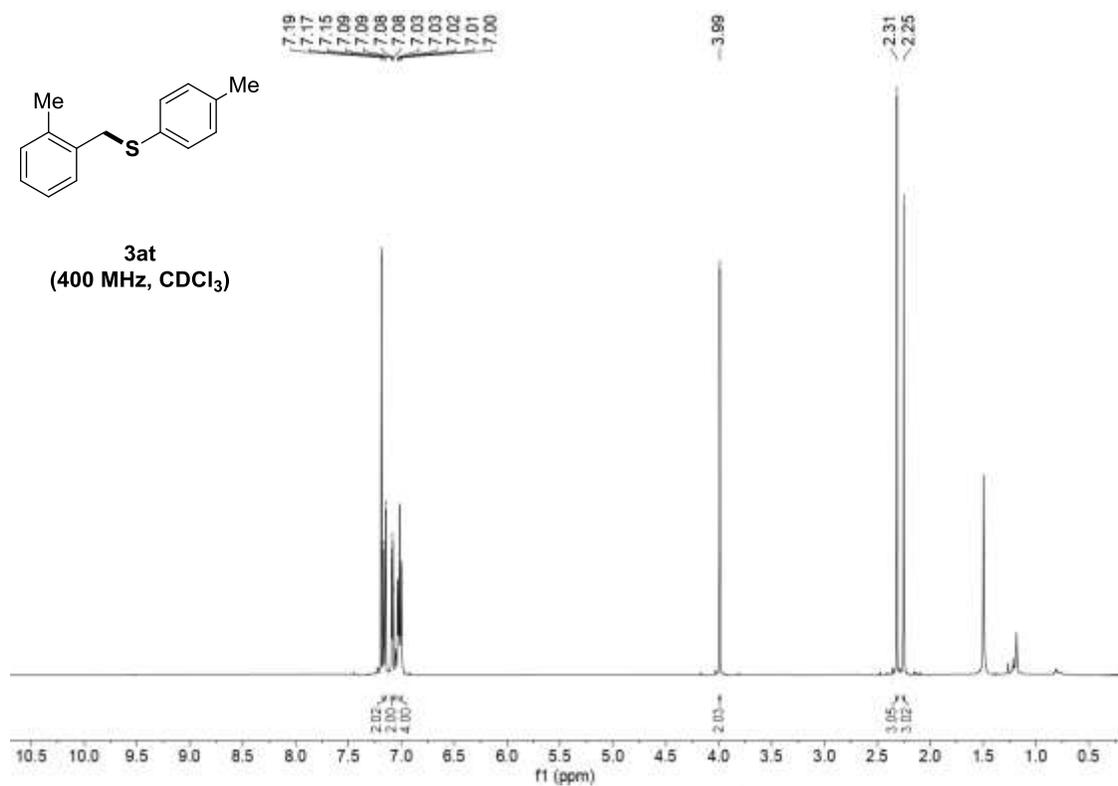


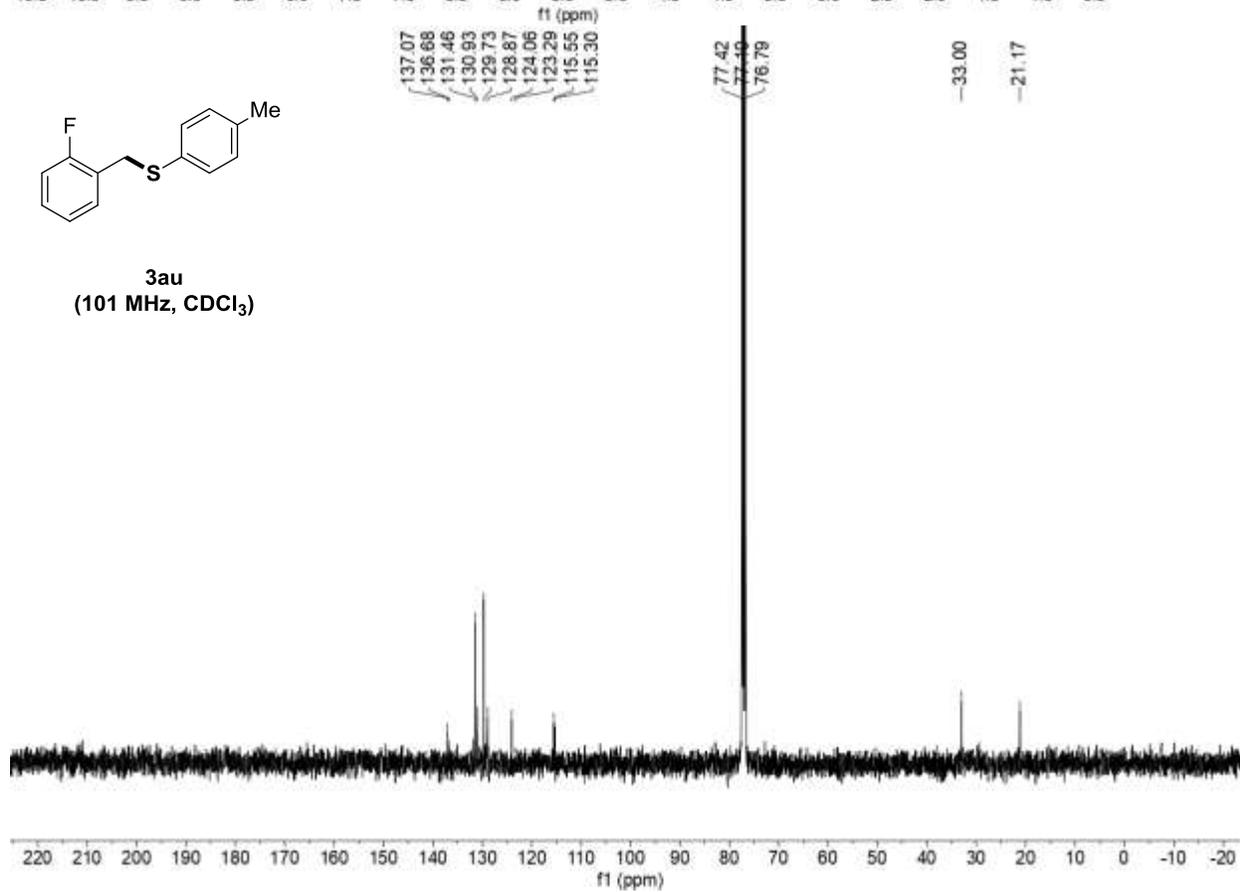
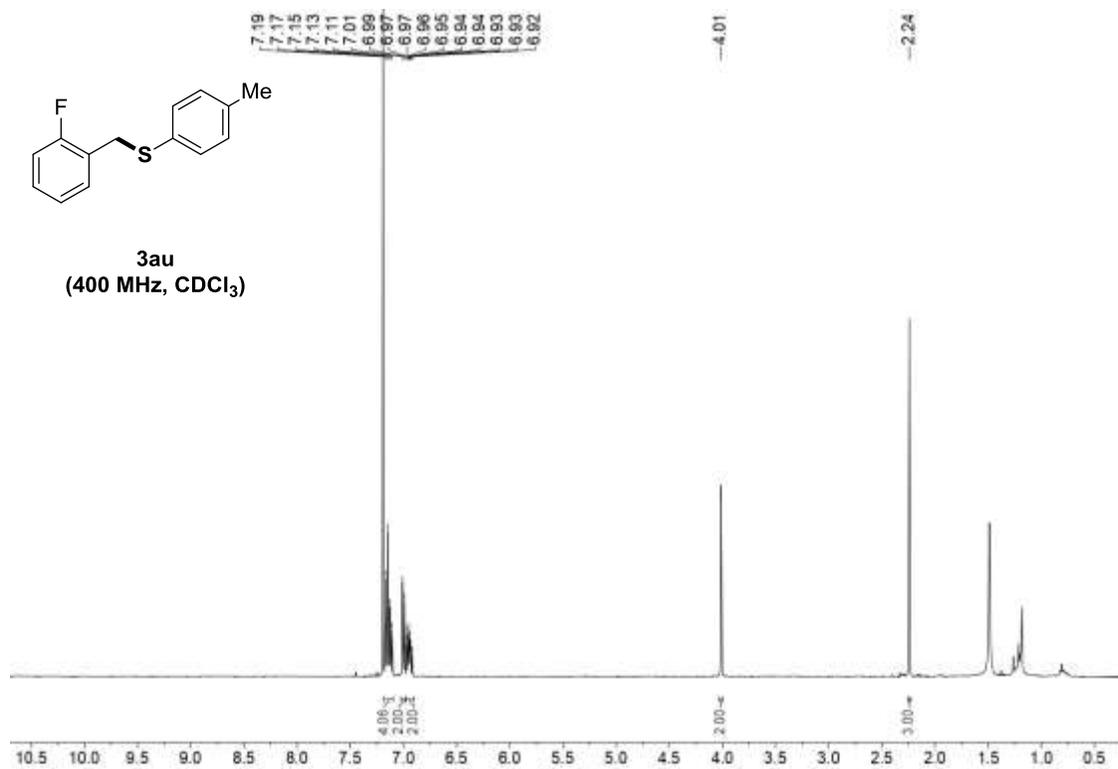


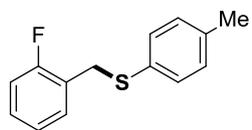




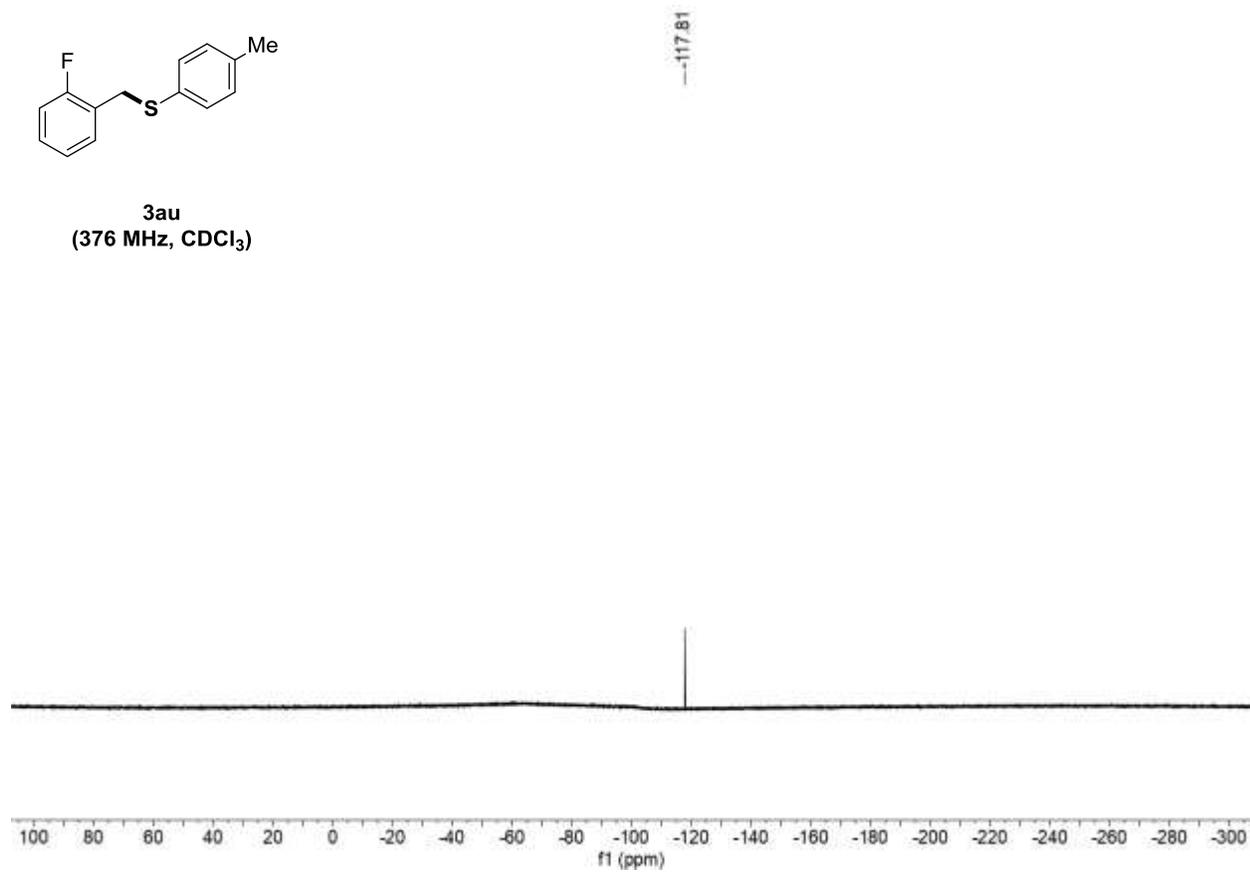


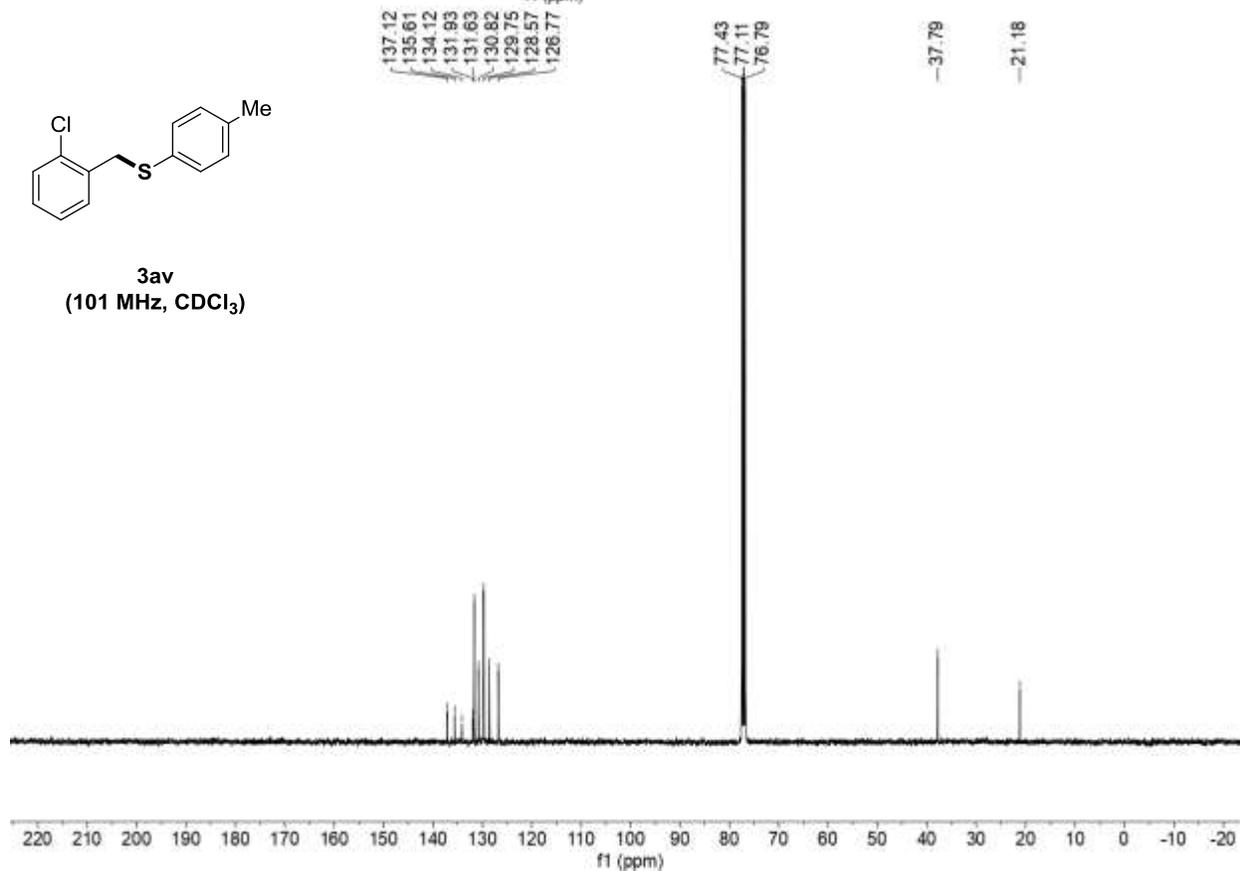
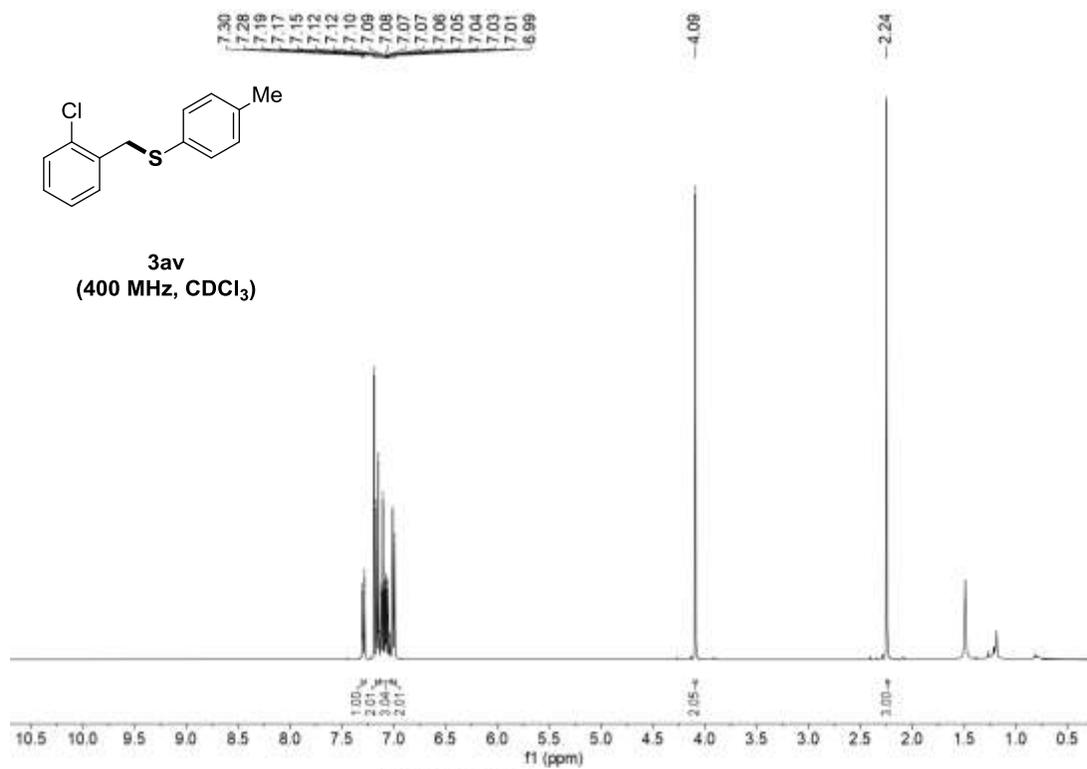


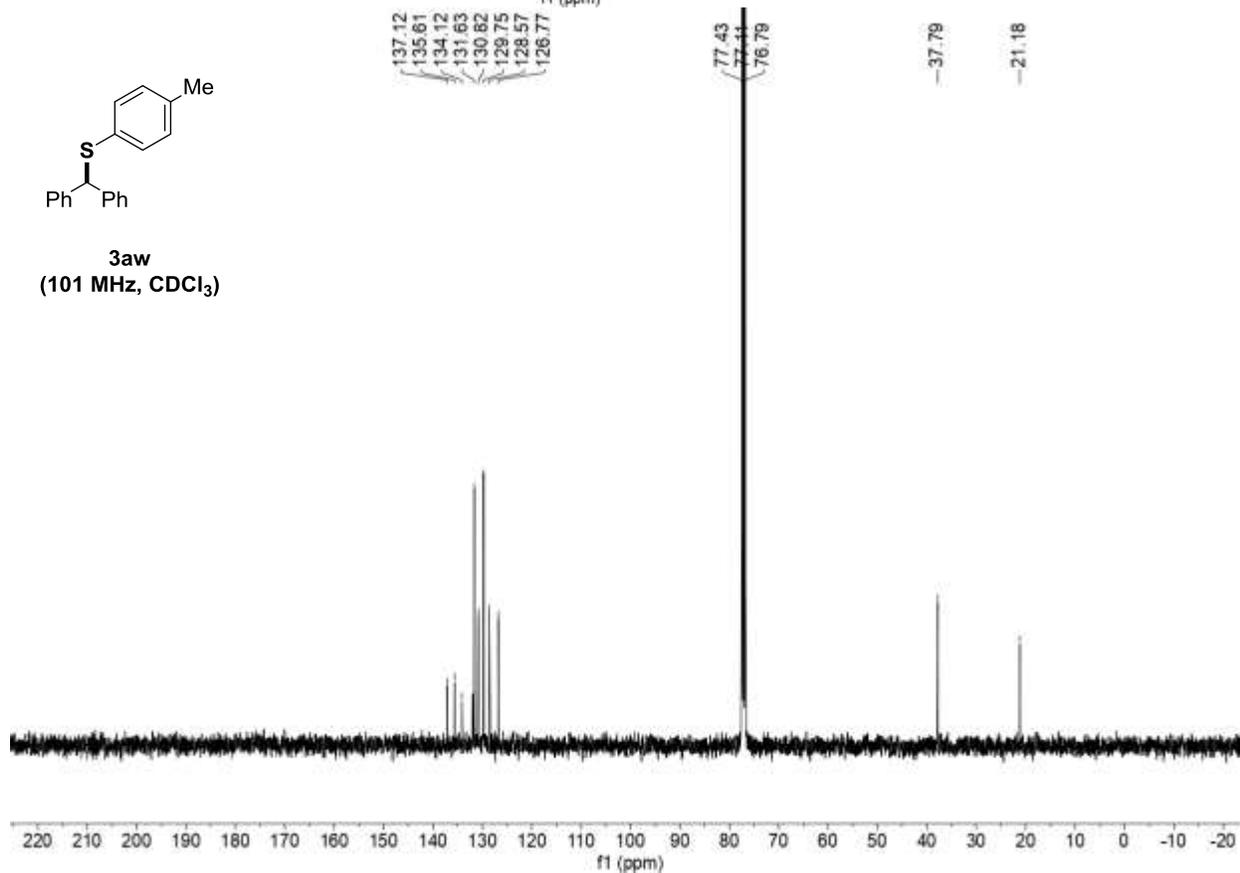
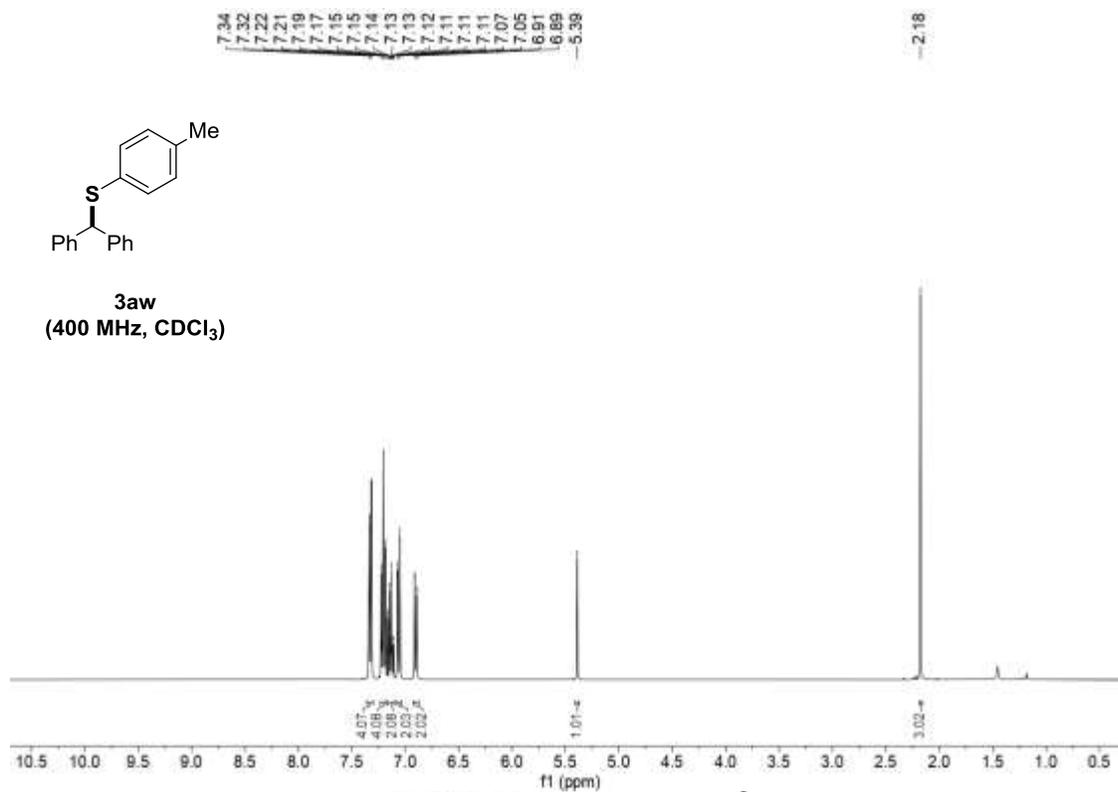


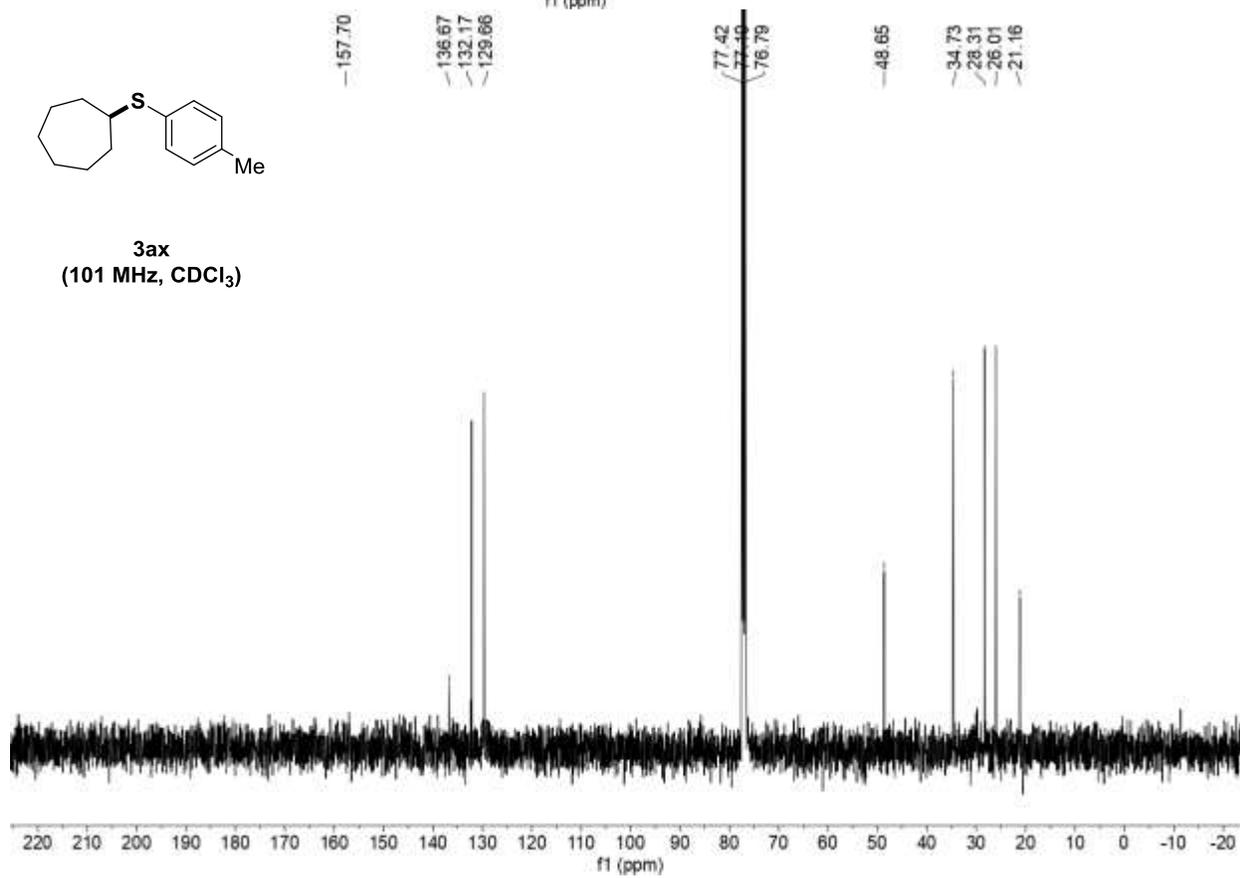
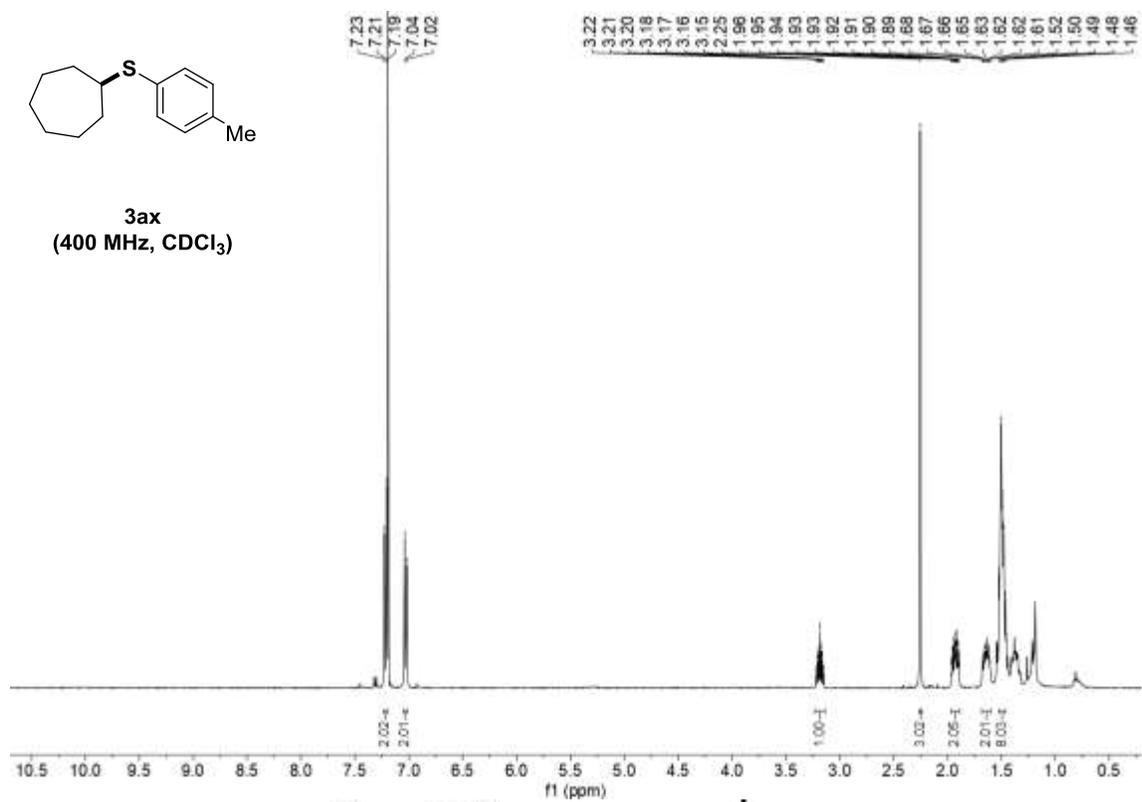


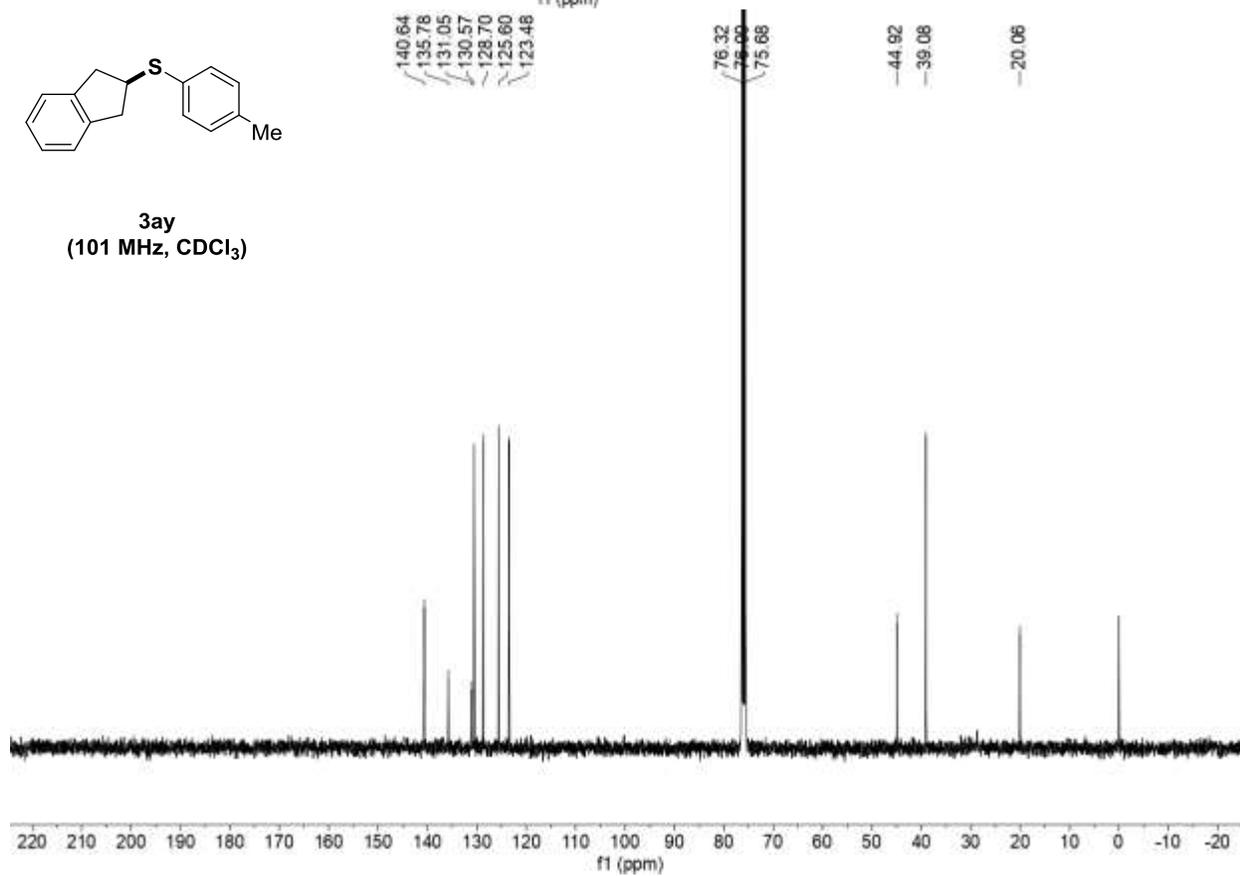
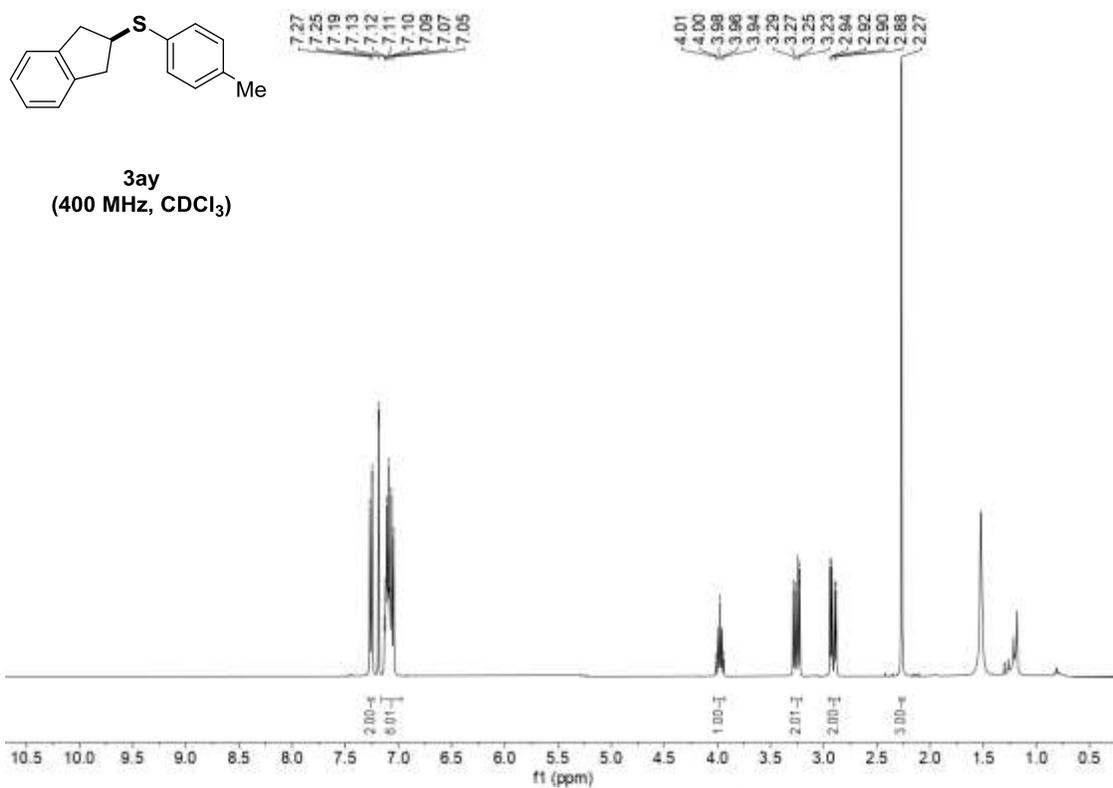
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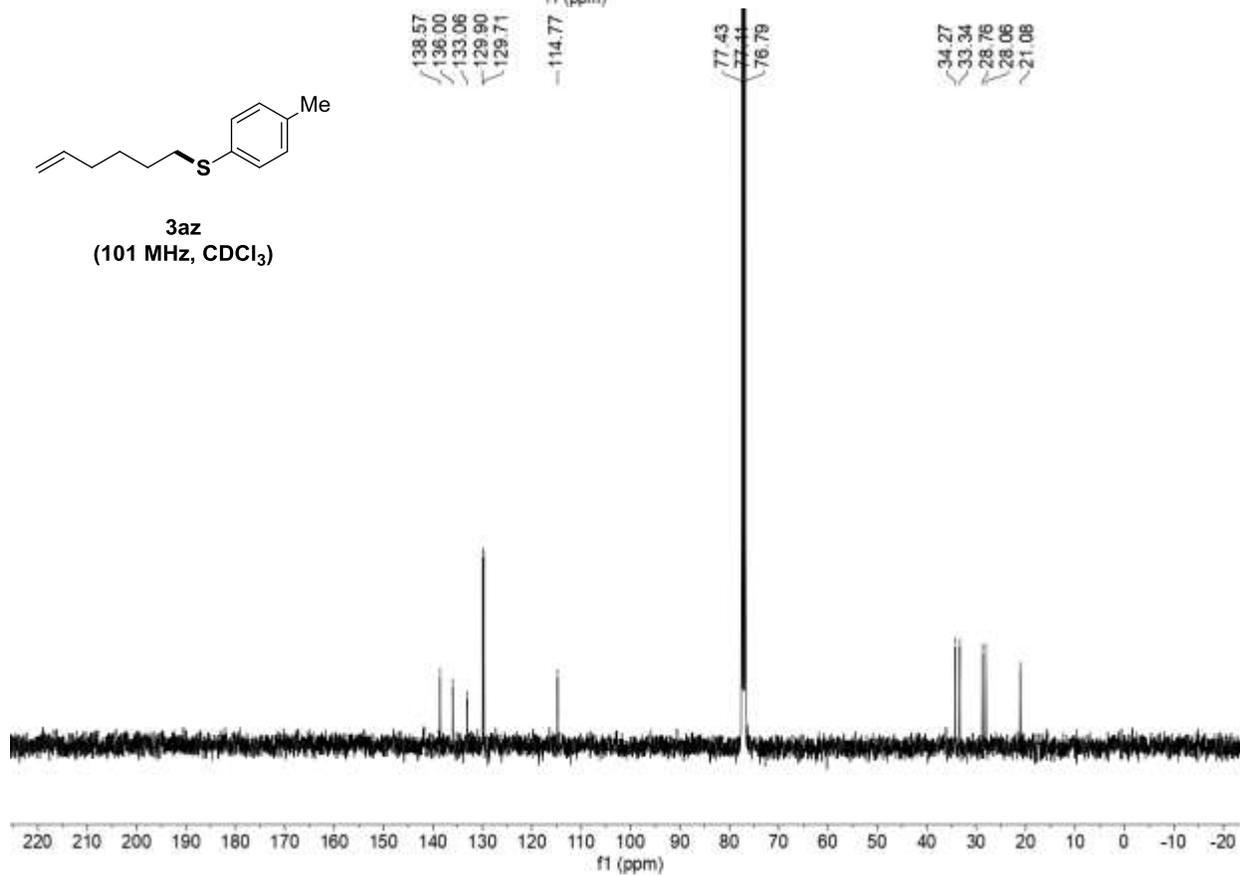
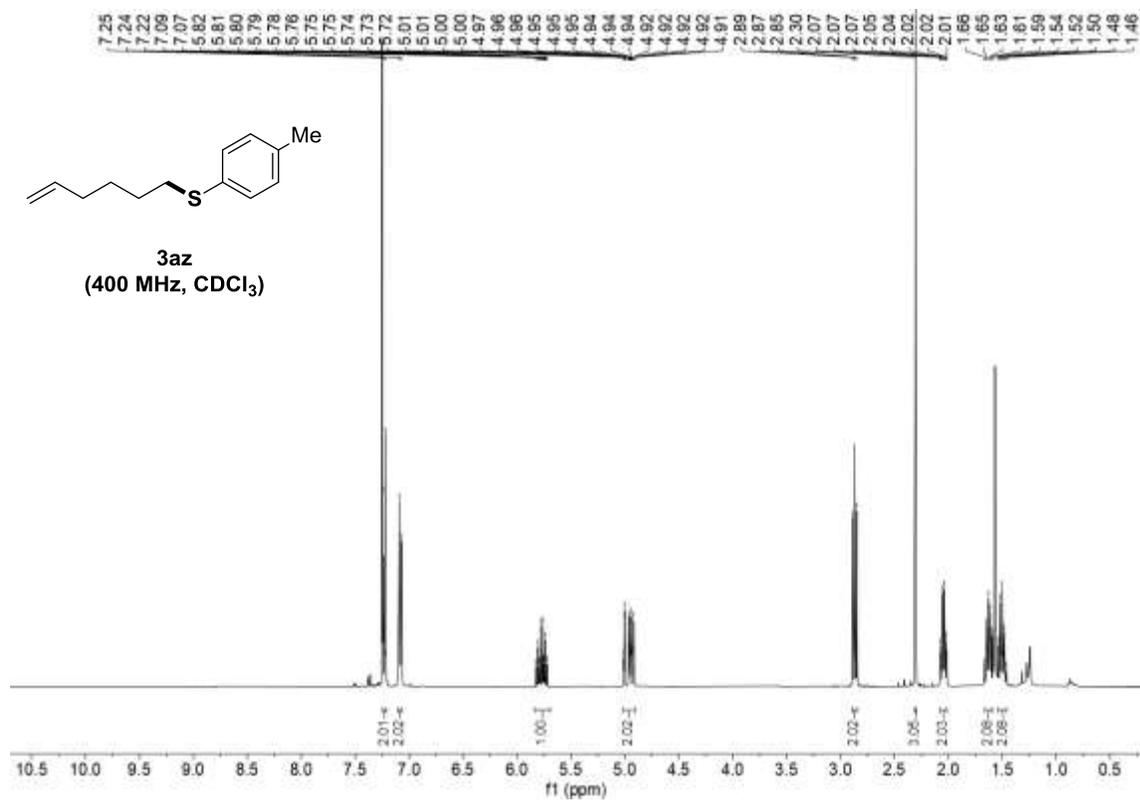


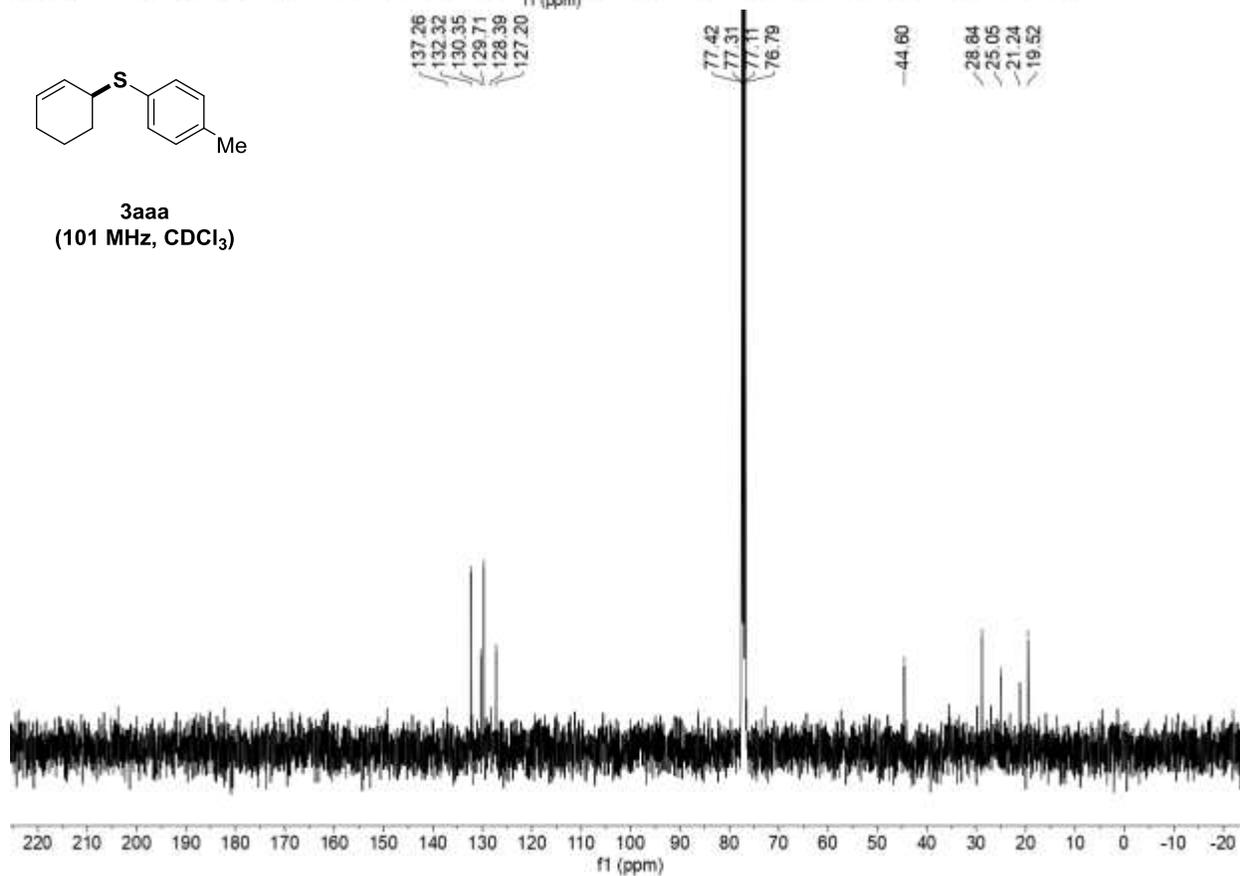
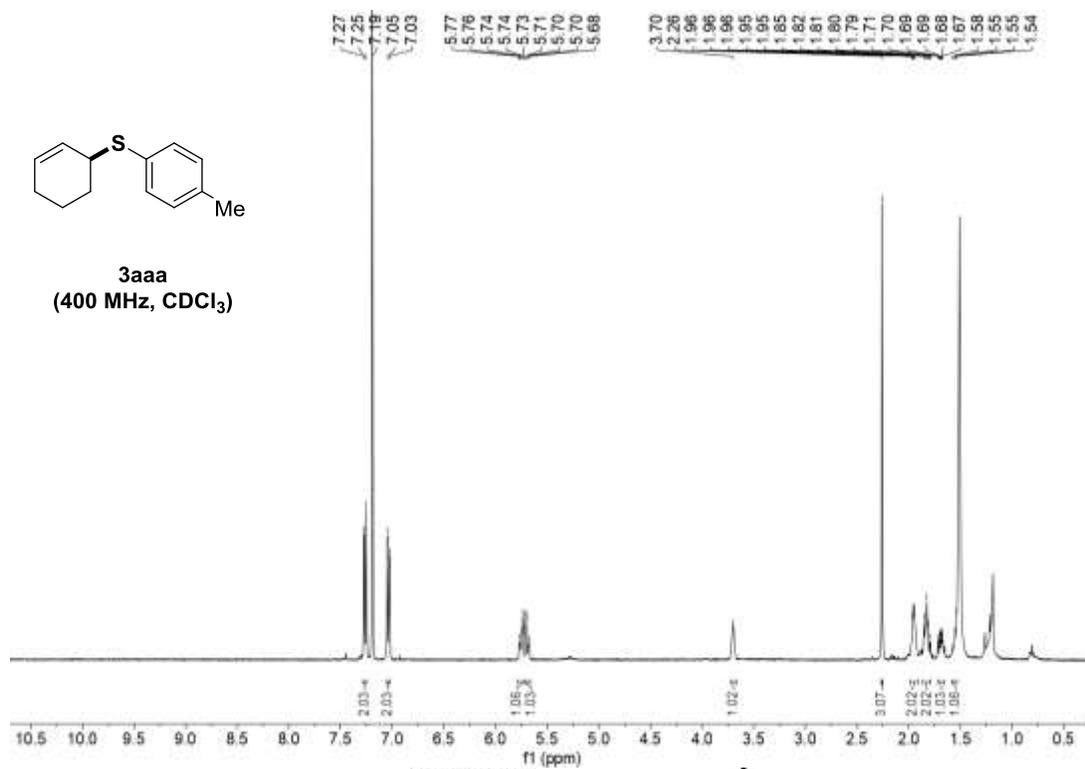


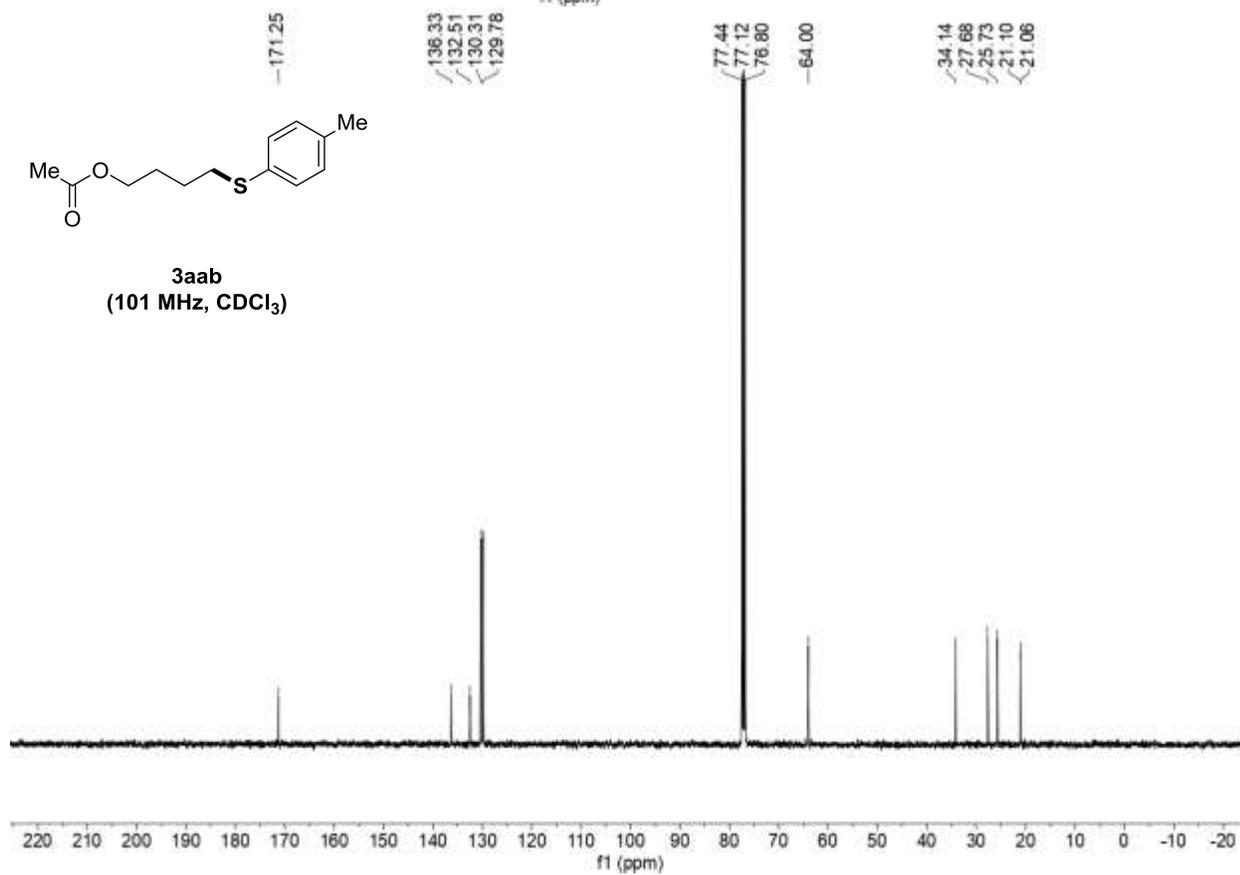
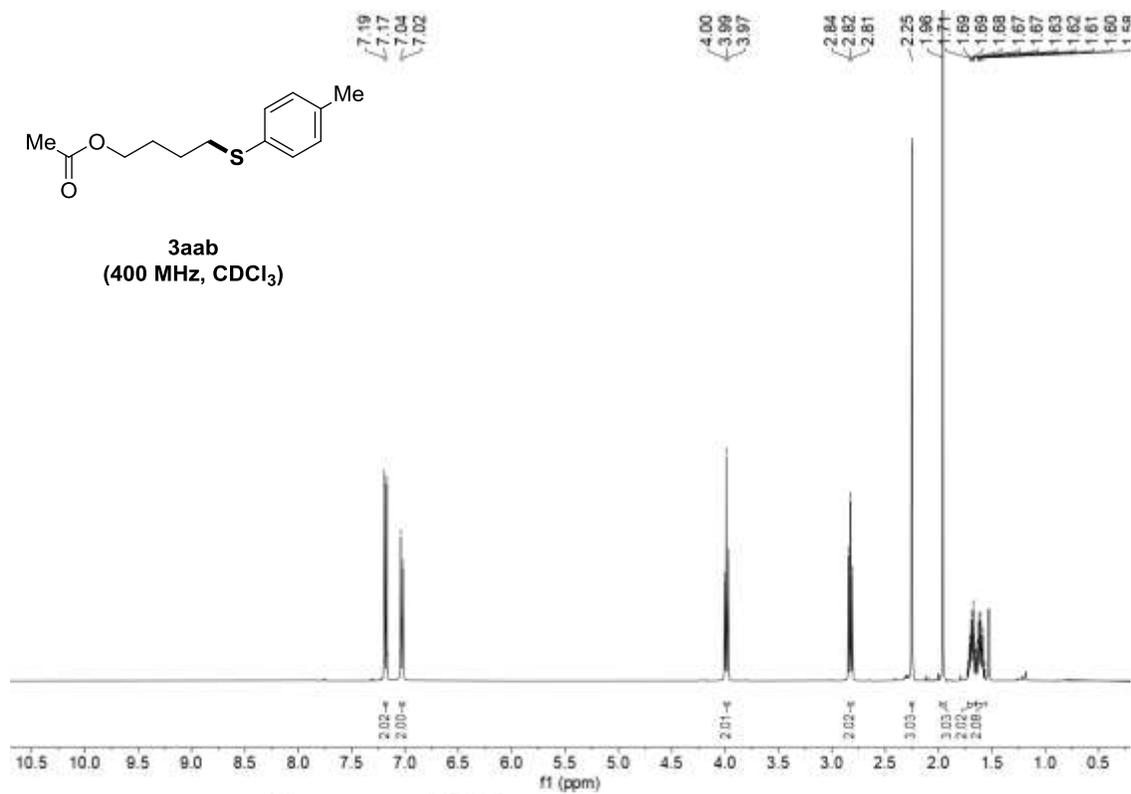


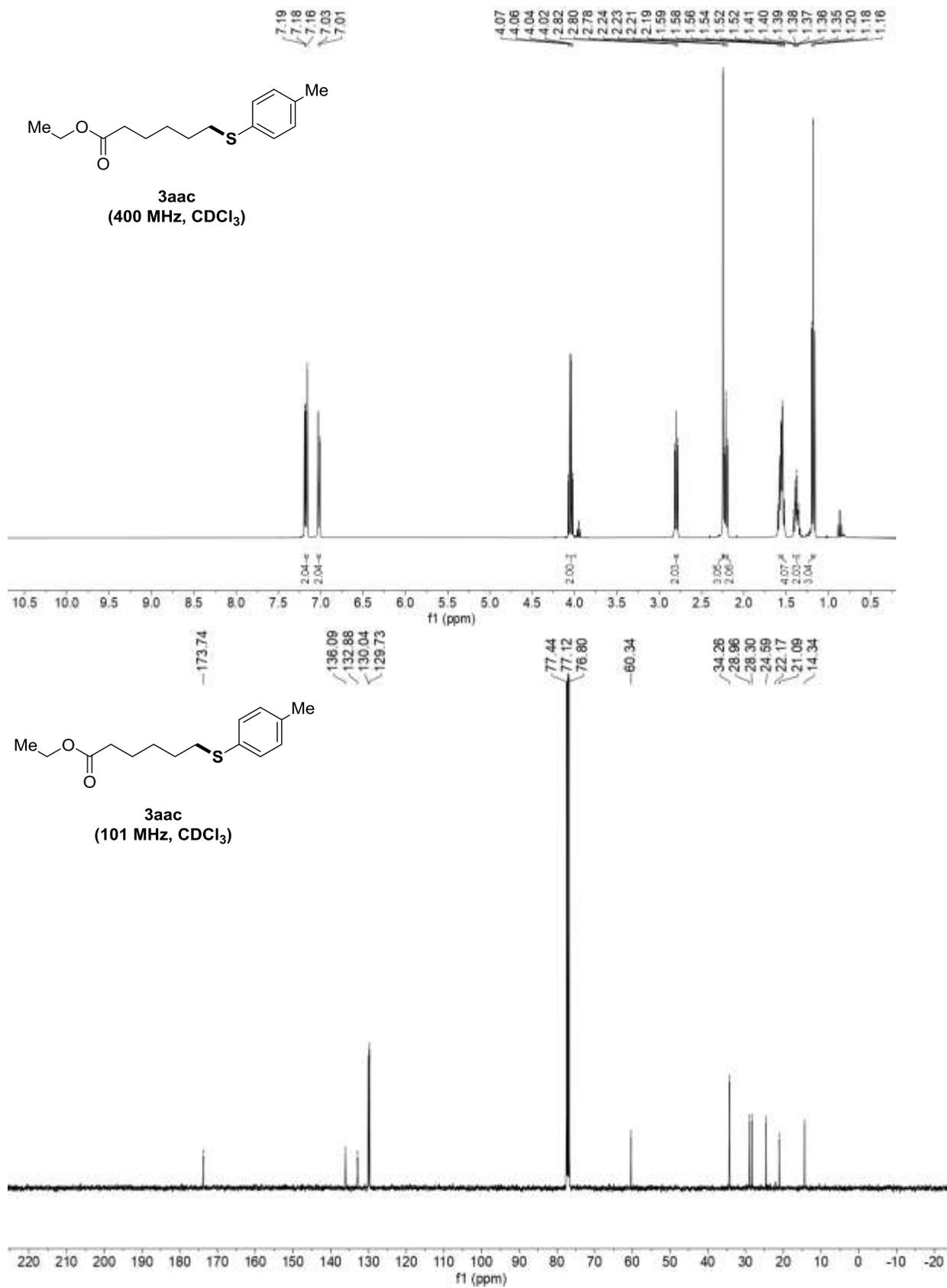


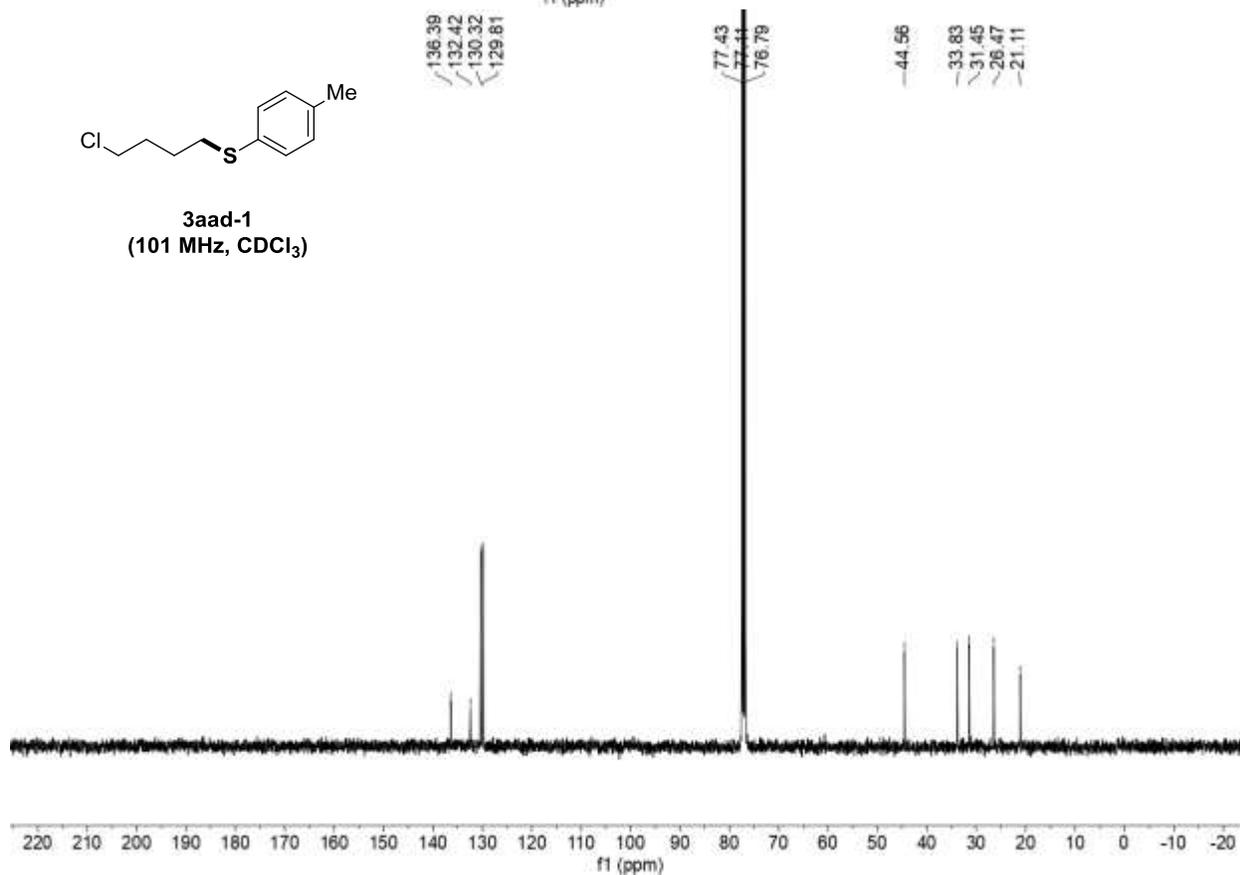
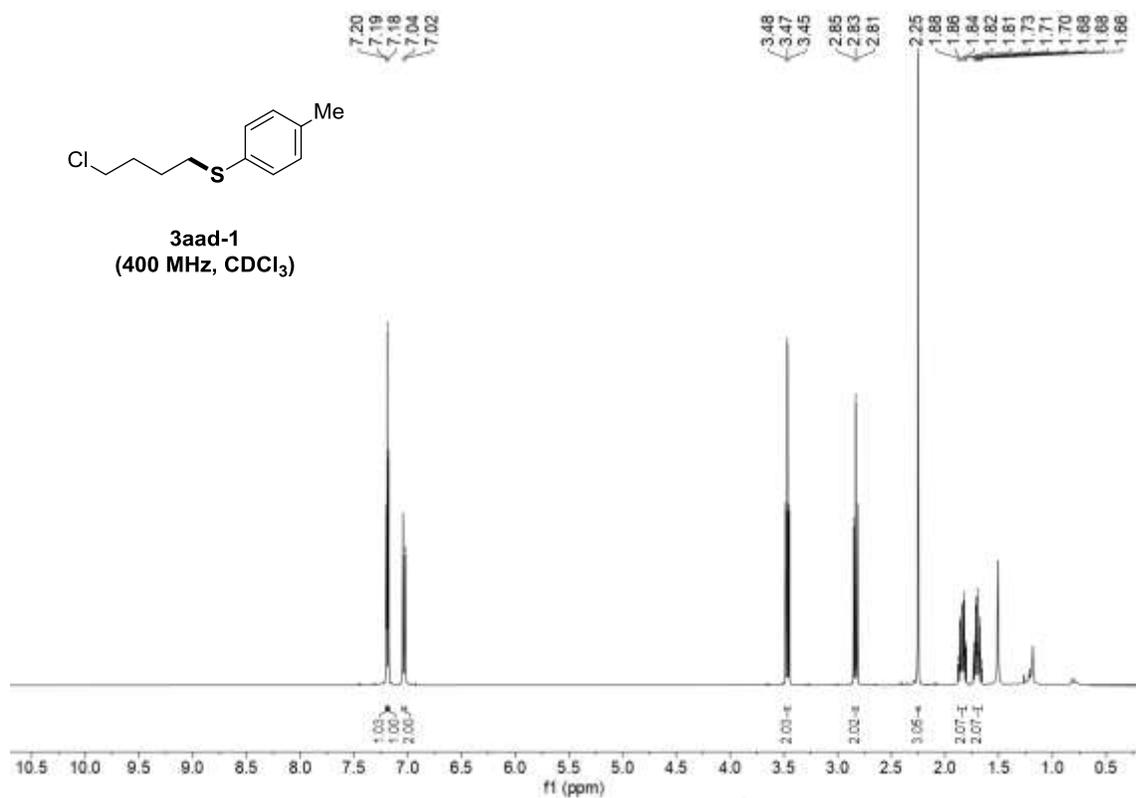


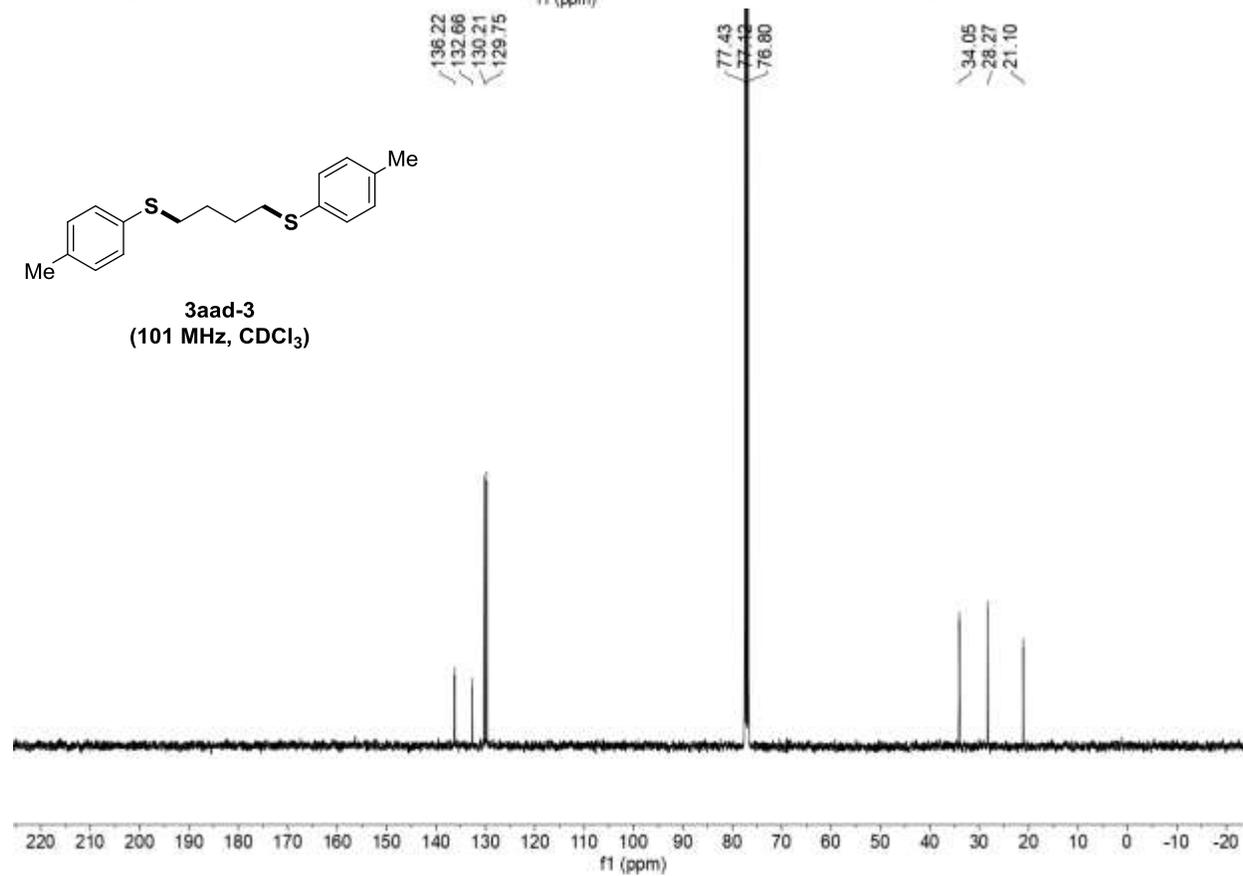
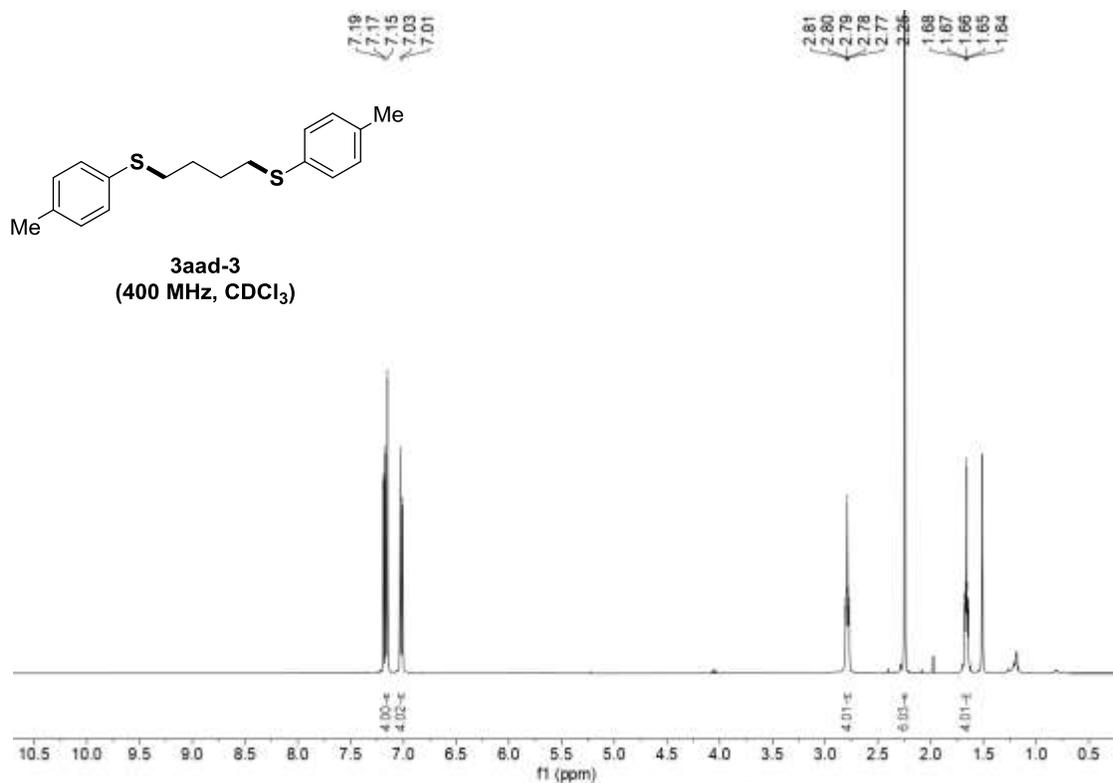


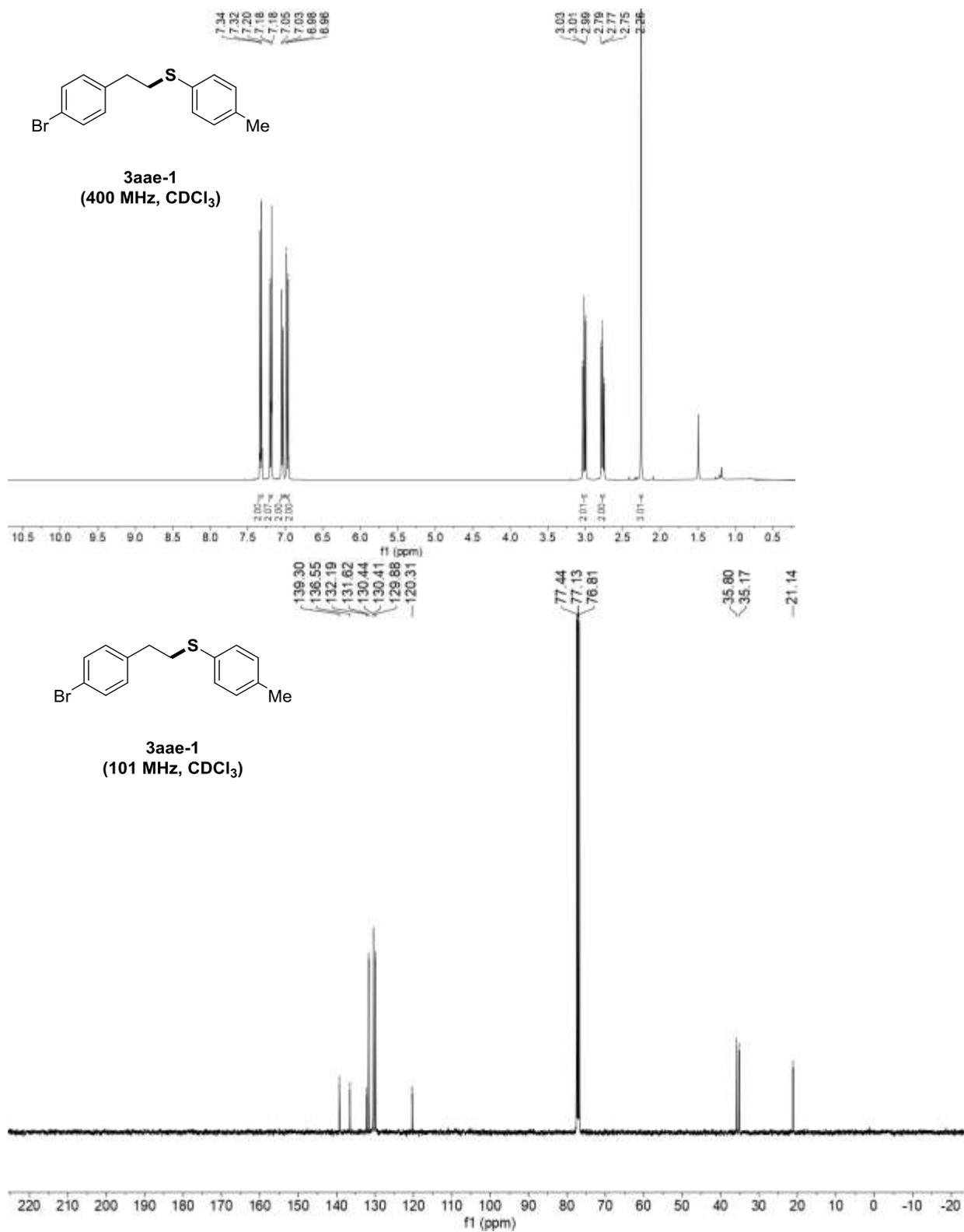


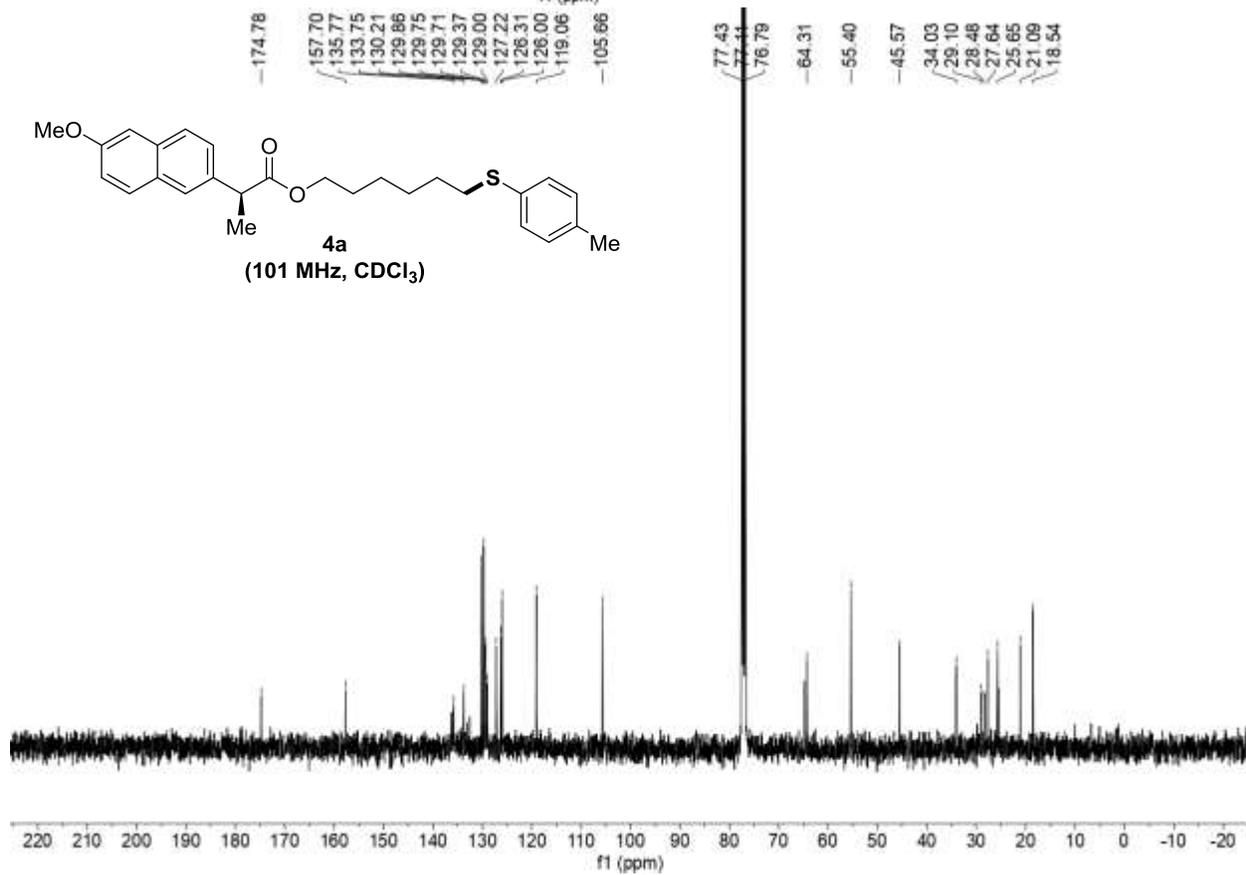
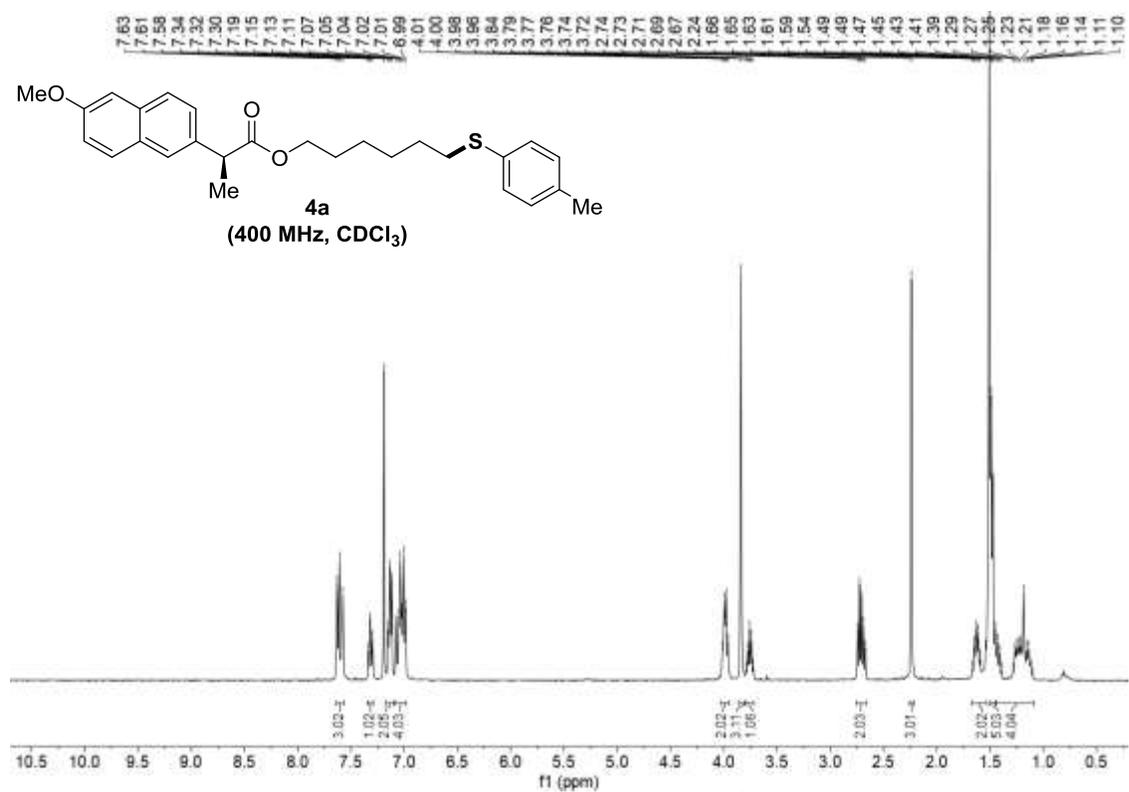


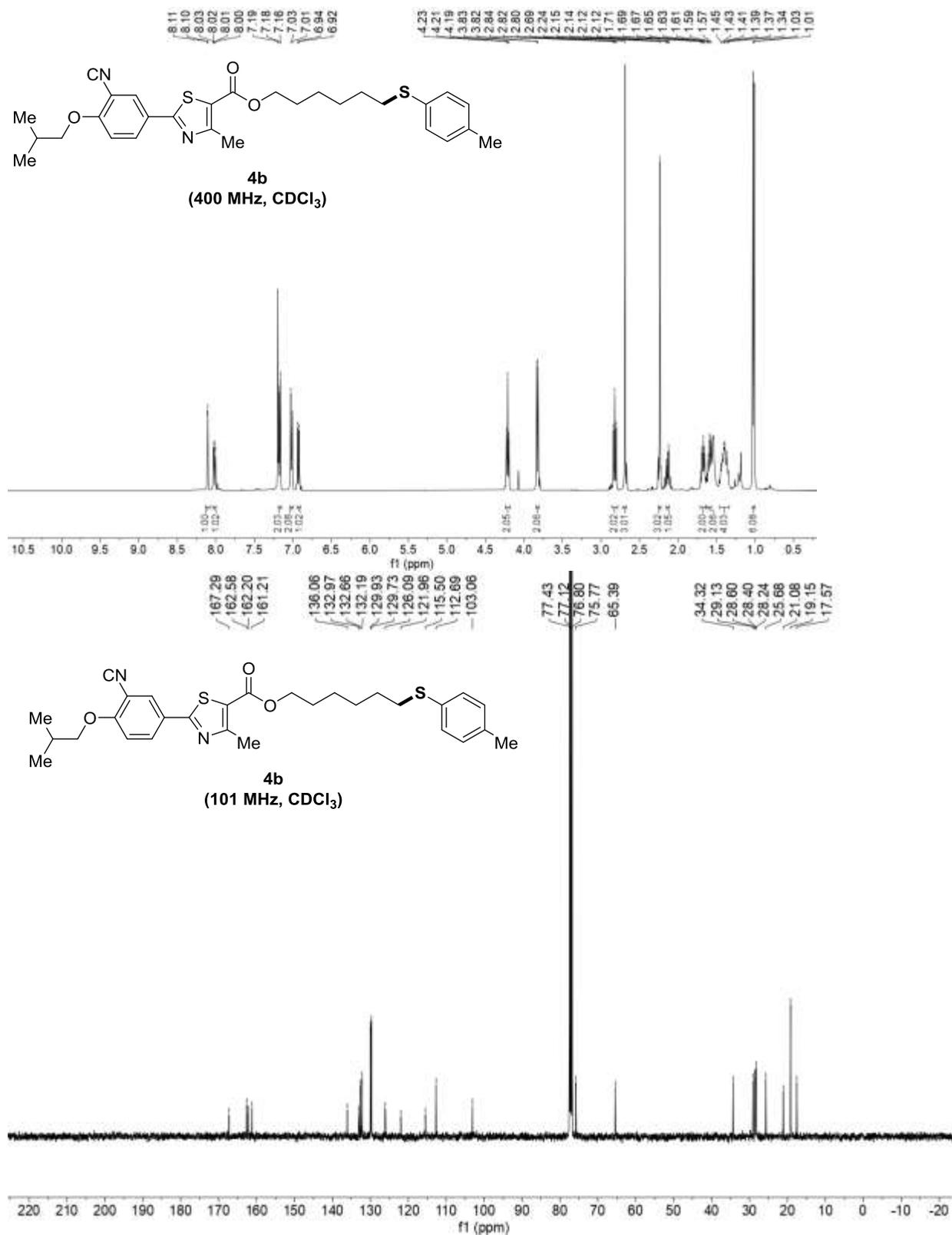


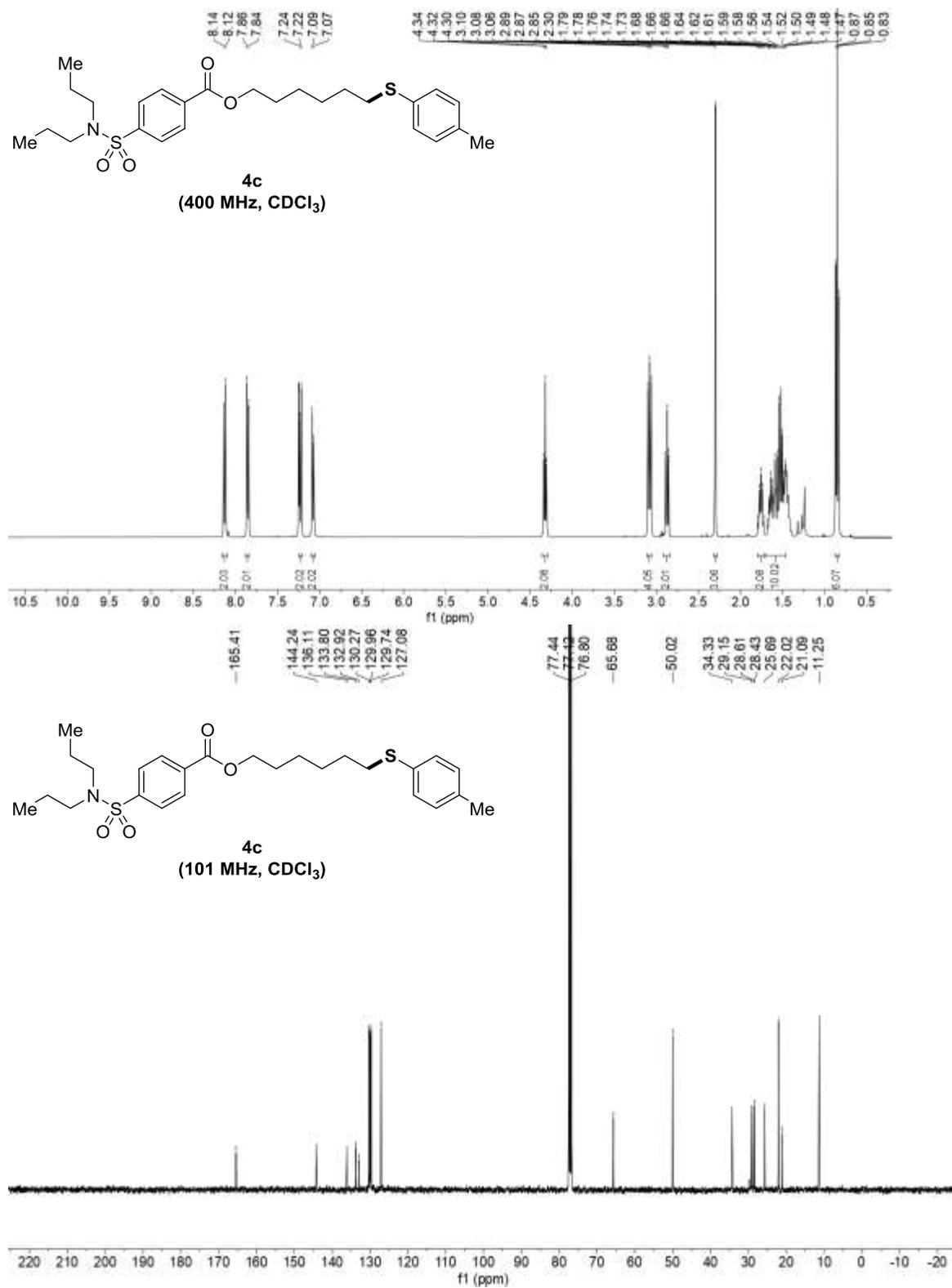


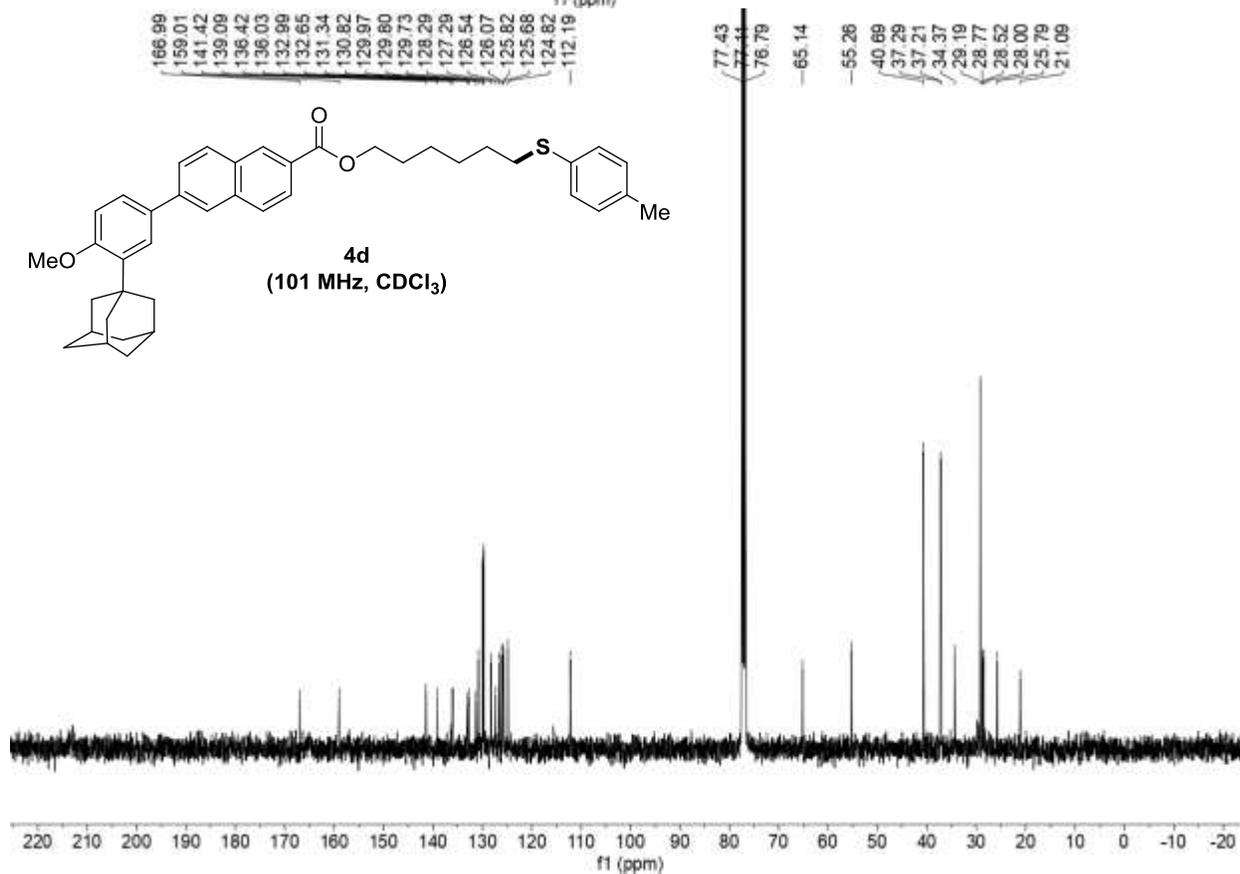
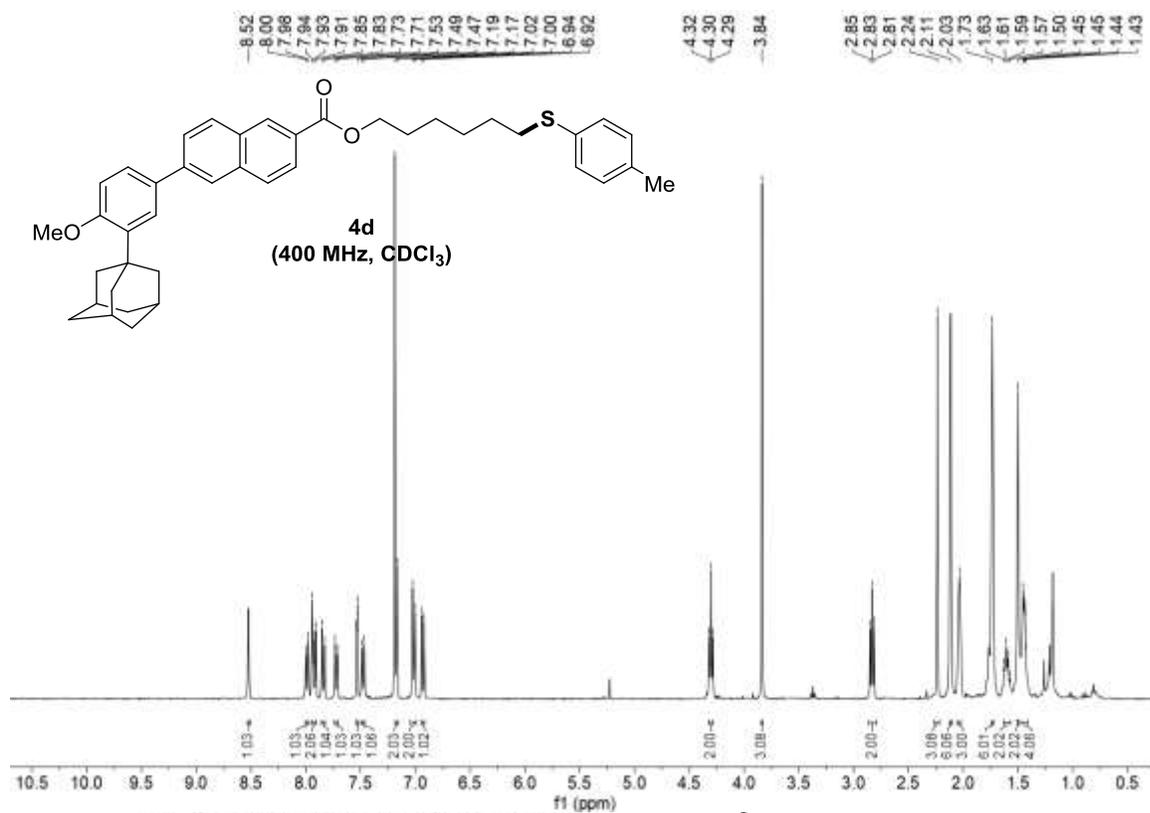


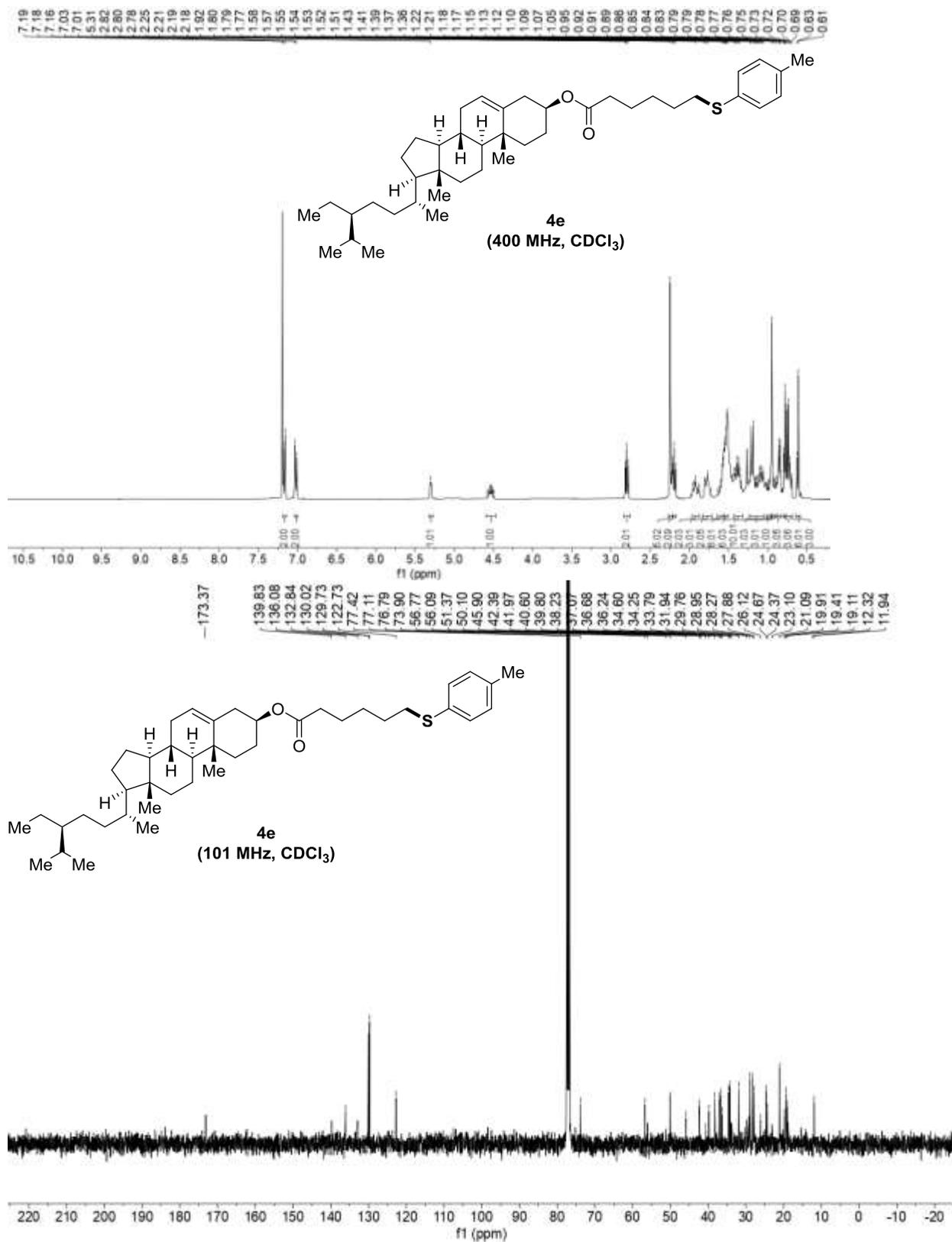


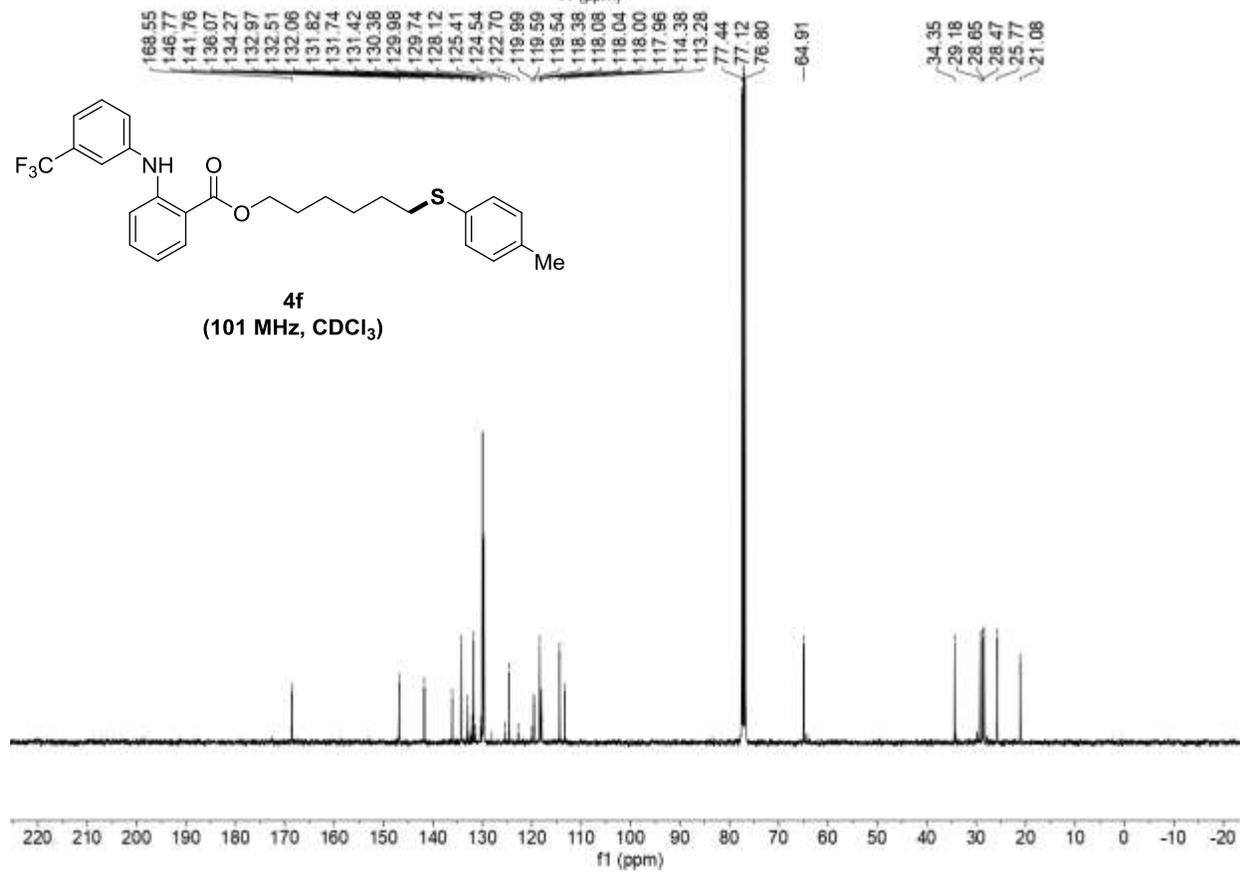
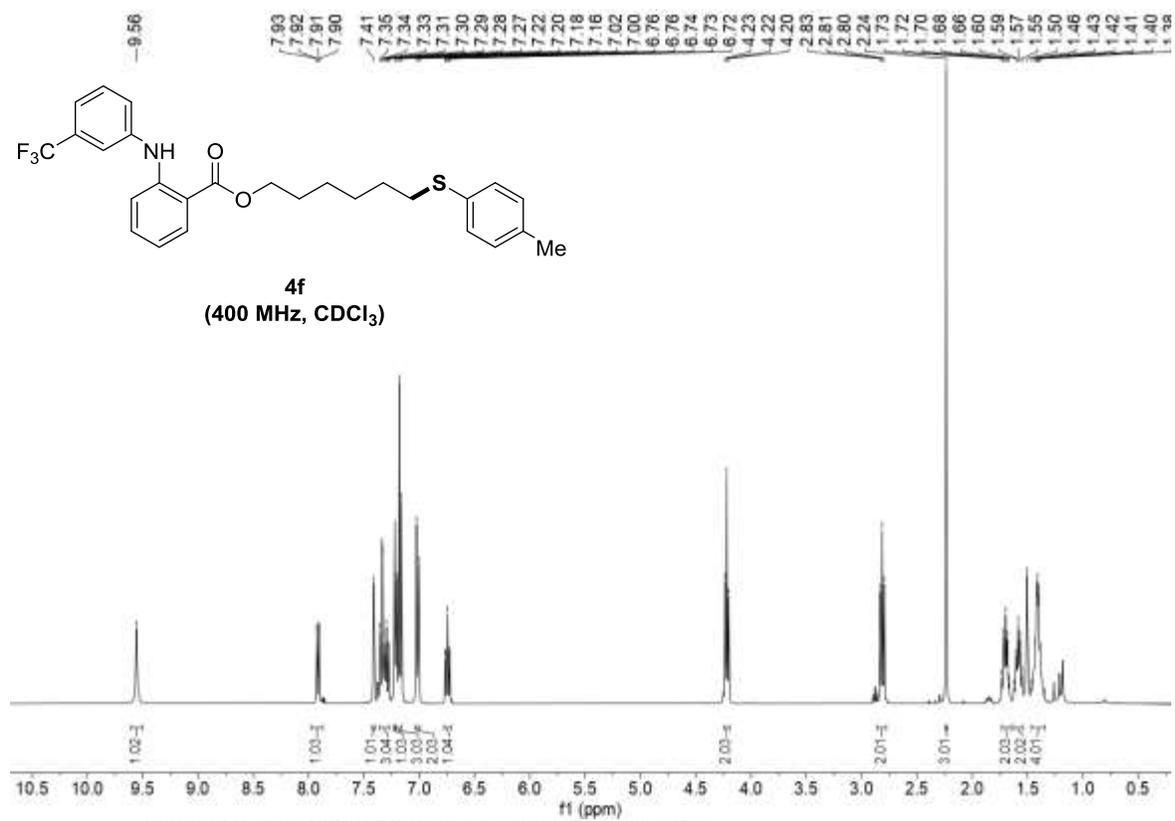


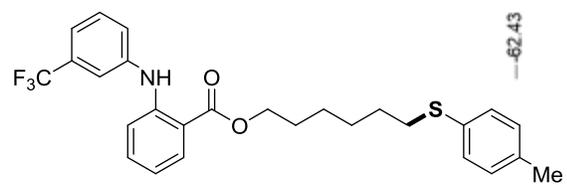




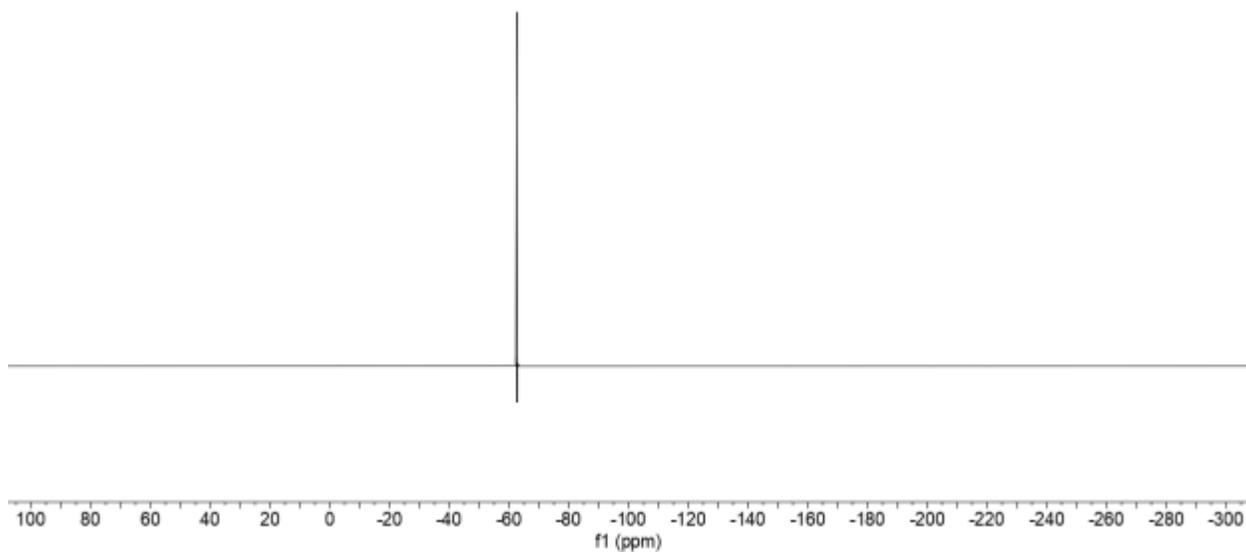


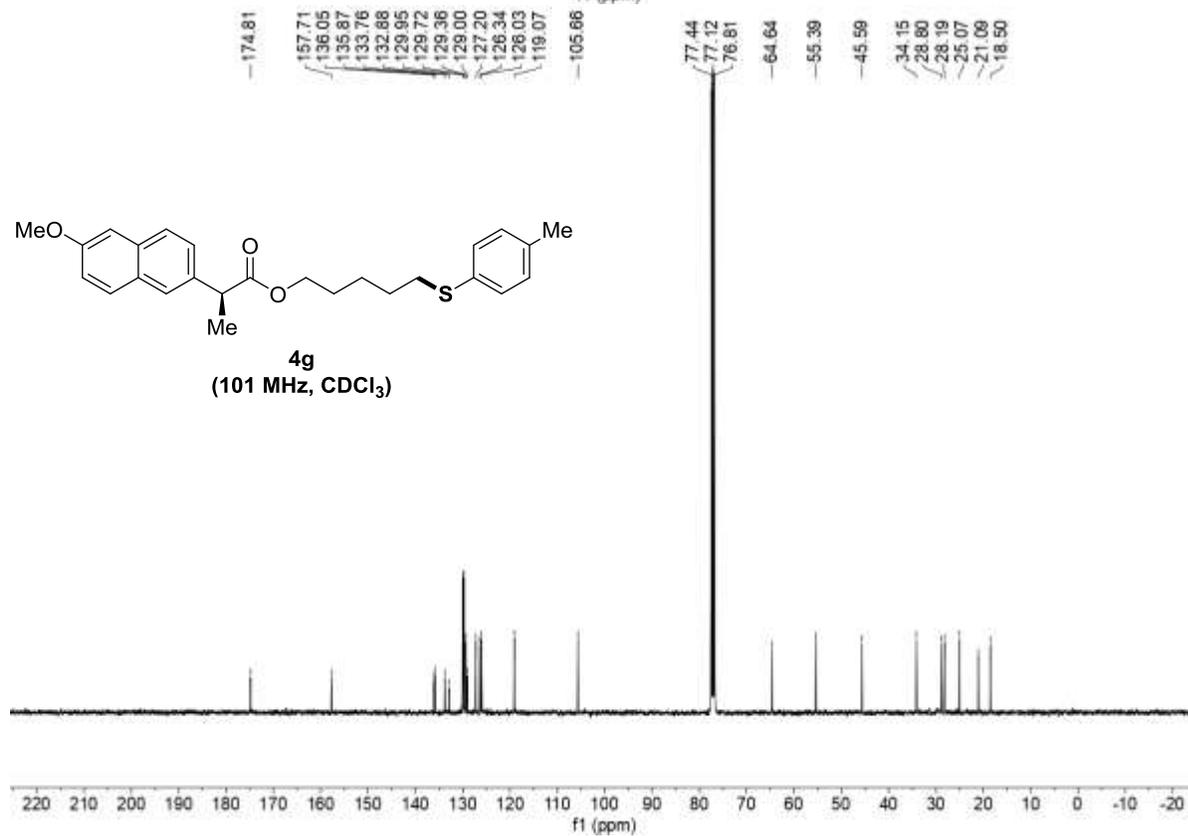
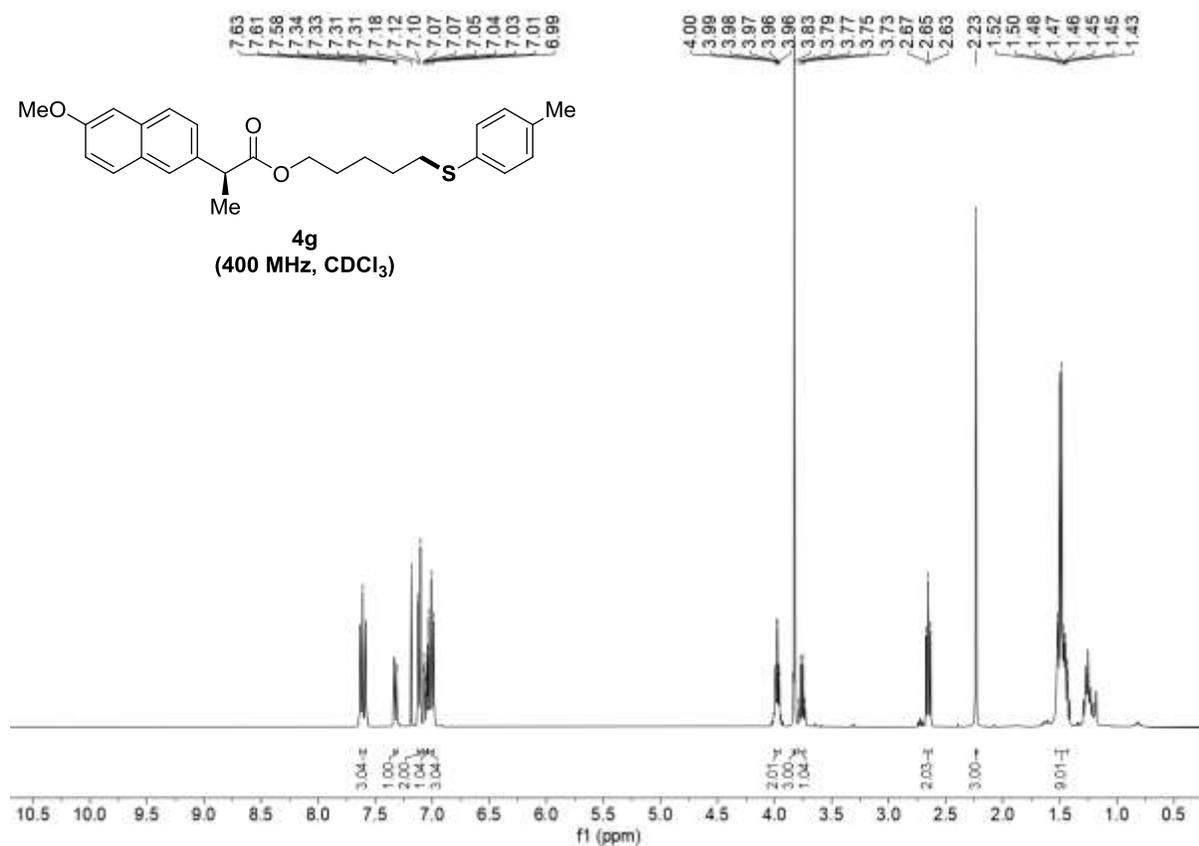


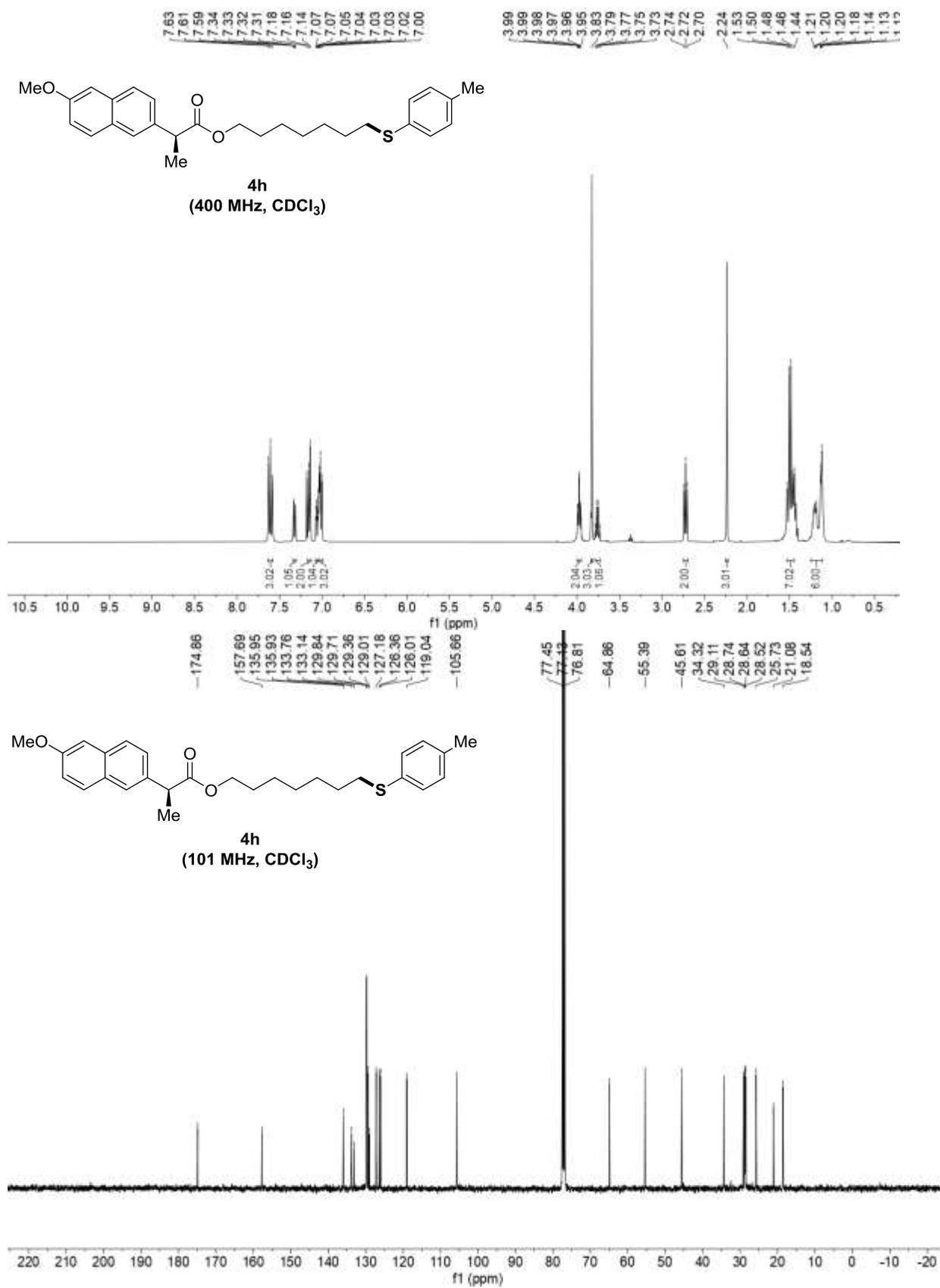


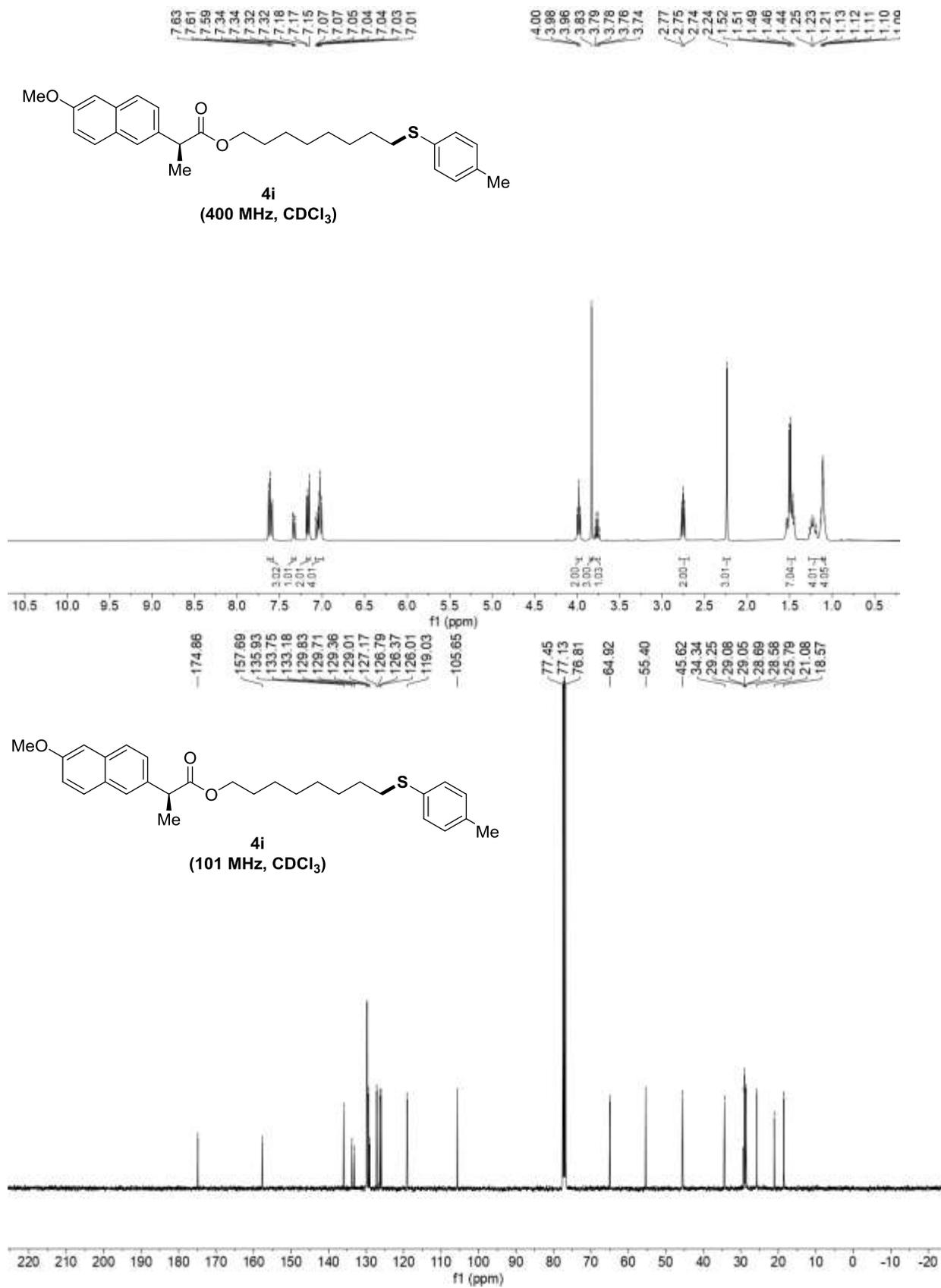


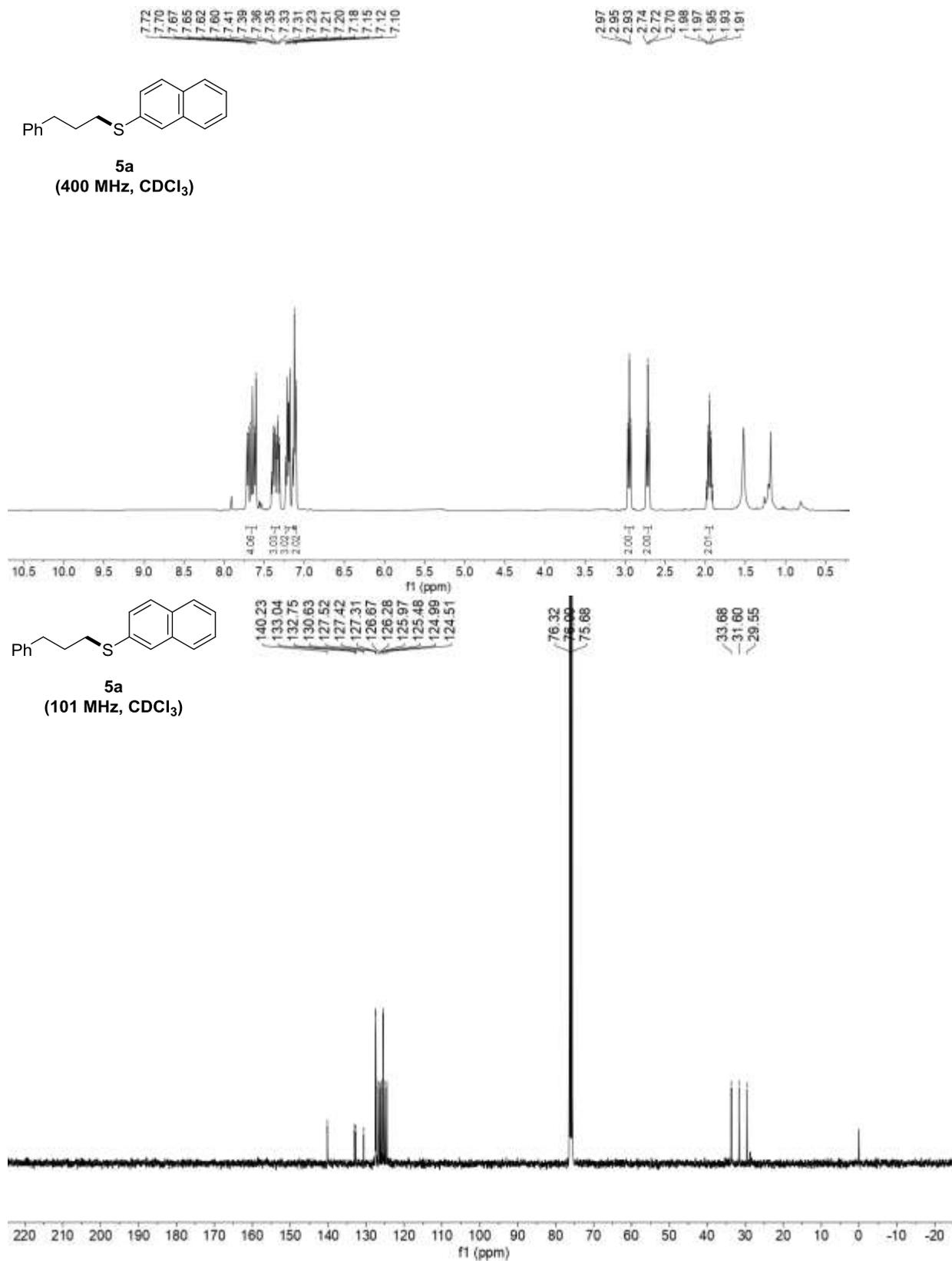
**4f**  
(376 MHz, CDCl<sub>3</sub>)

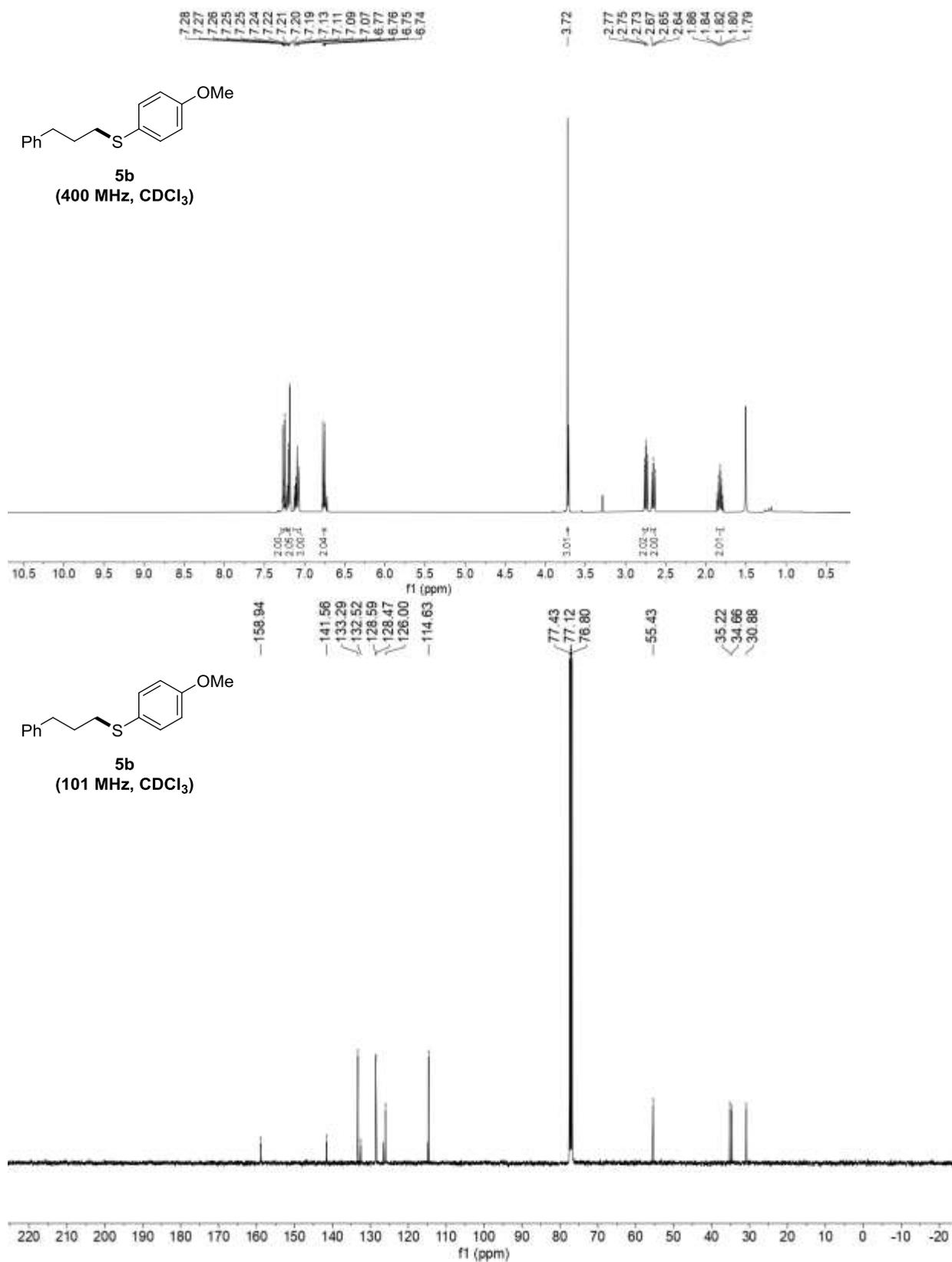


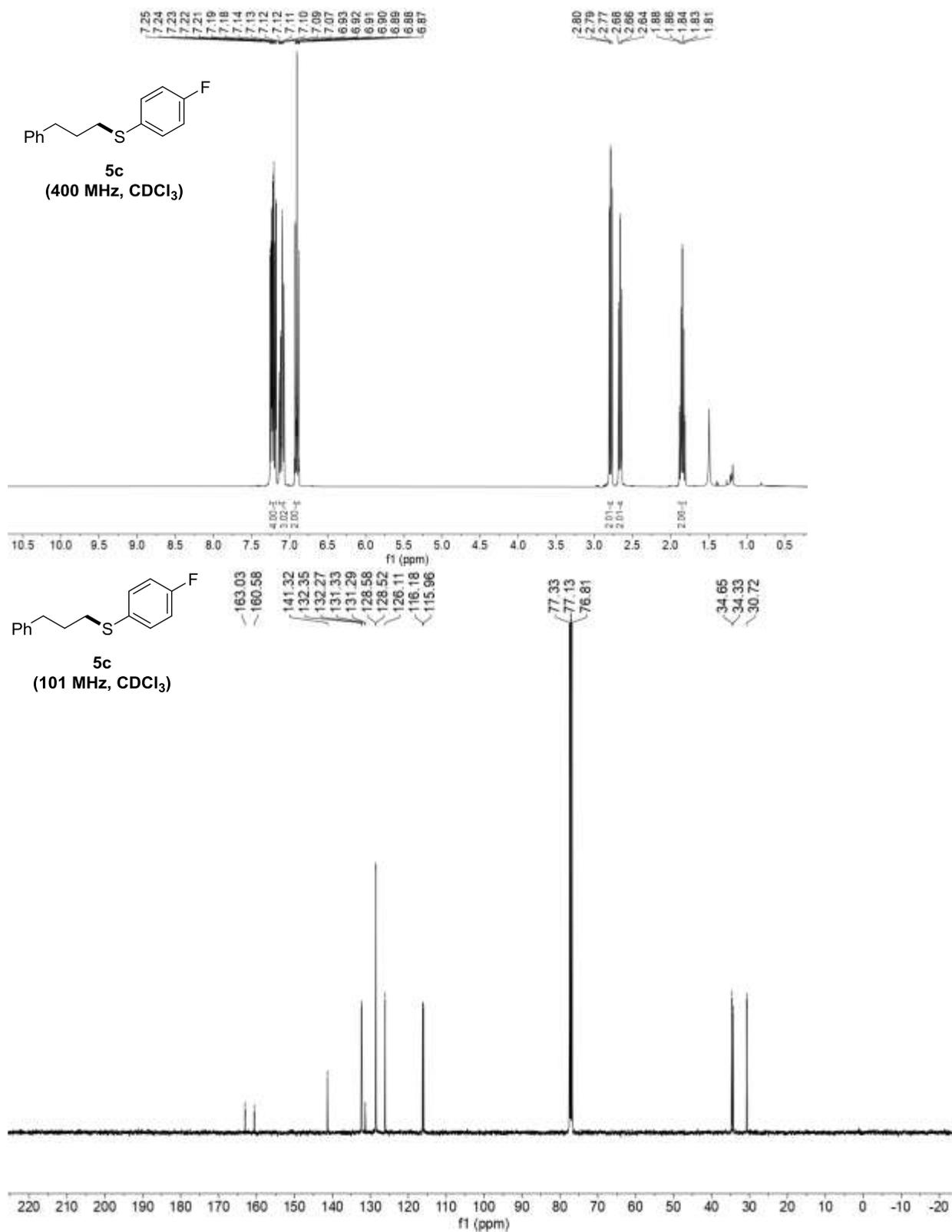


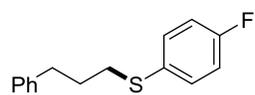




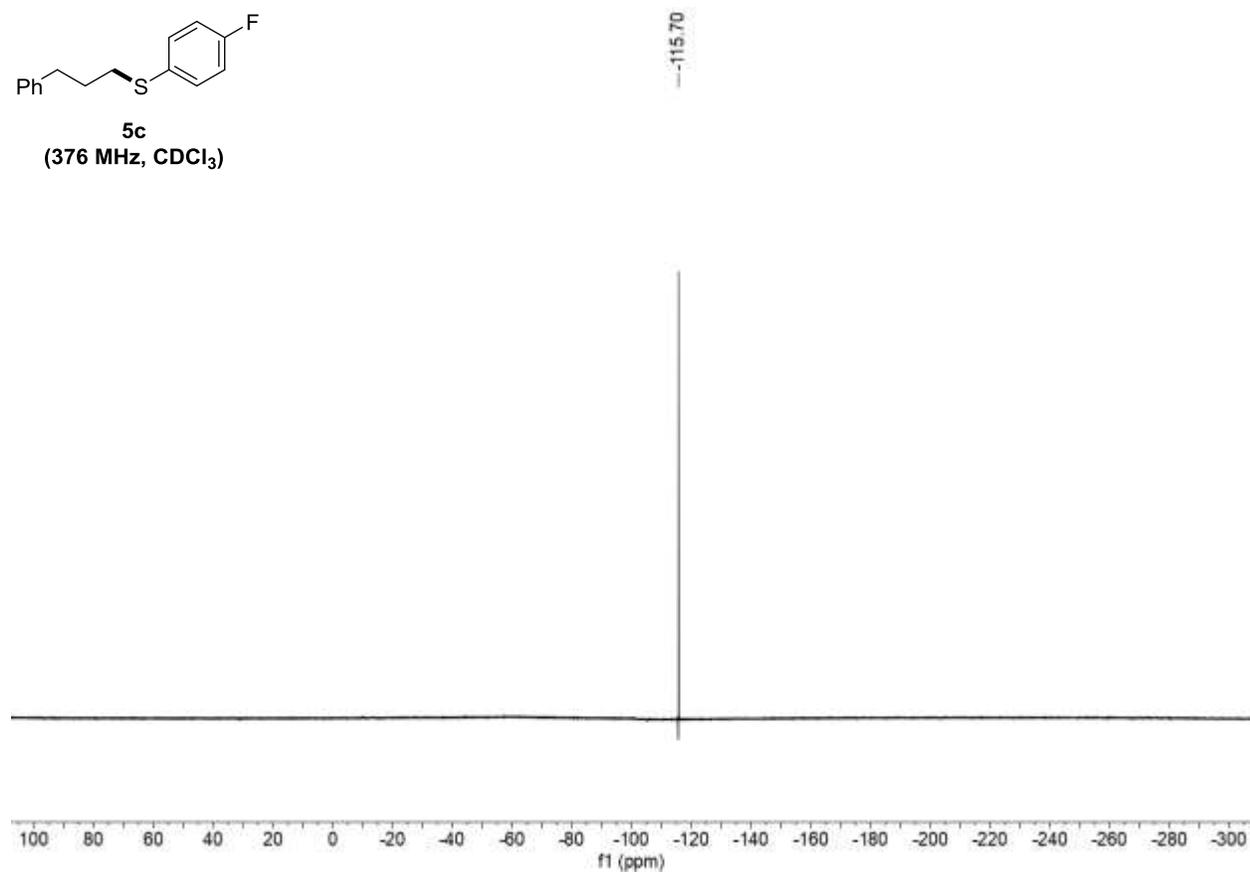


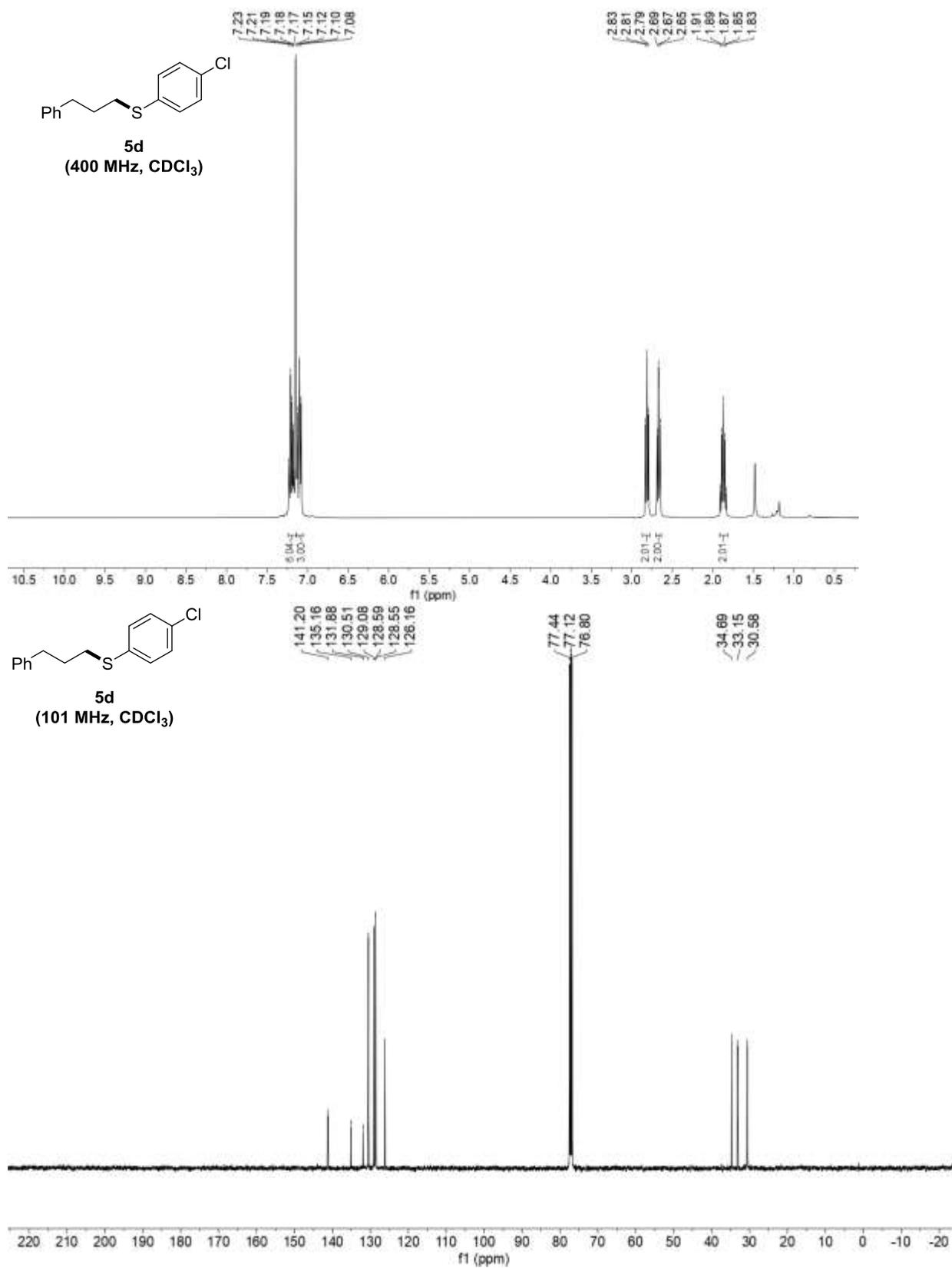


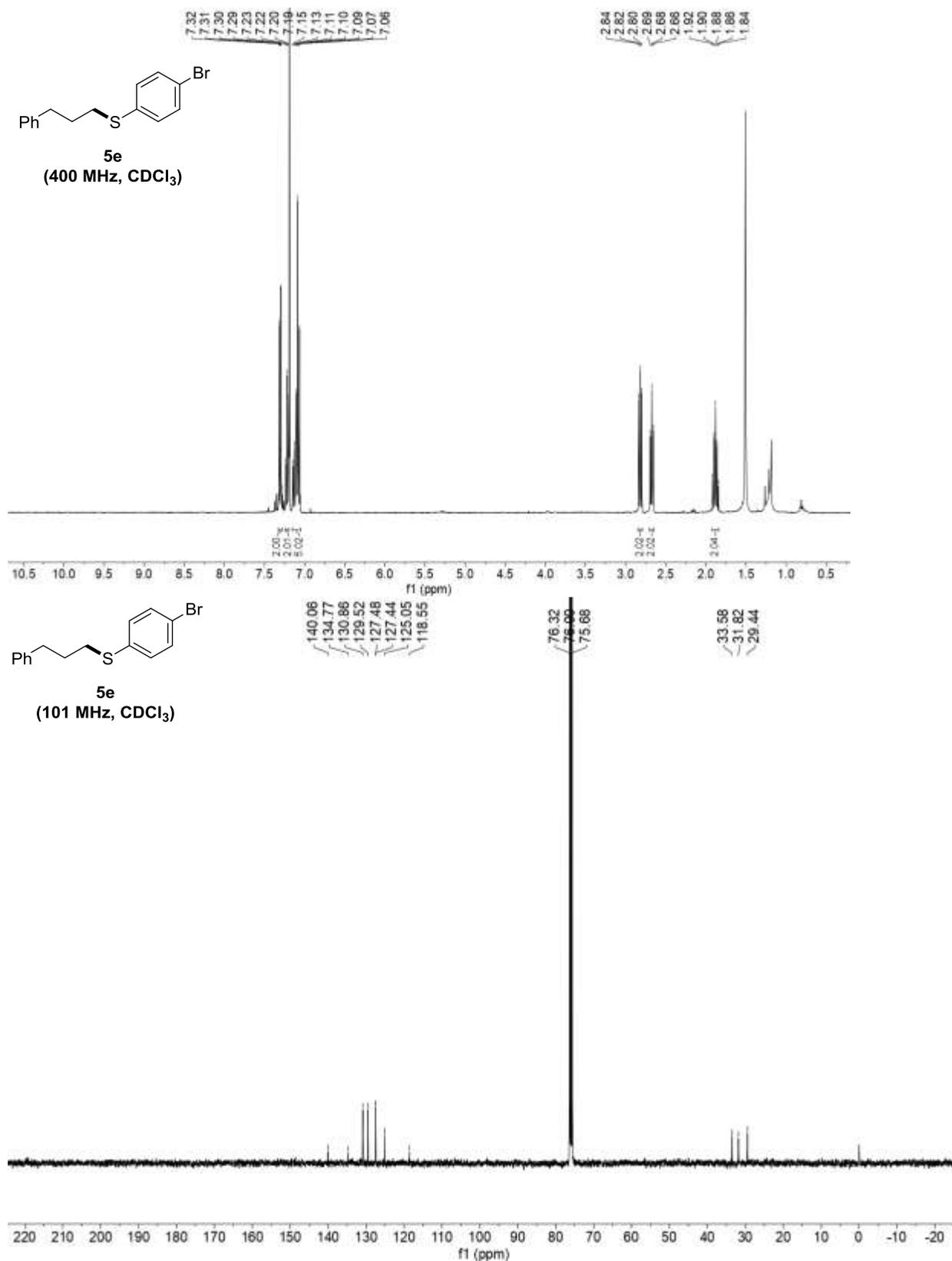


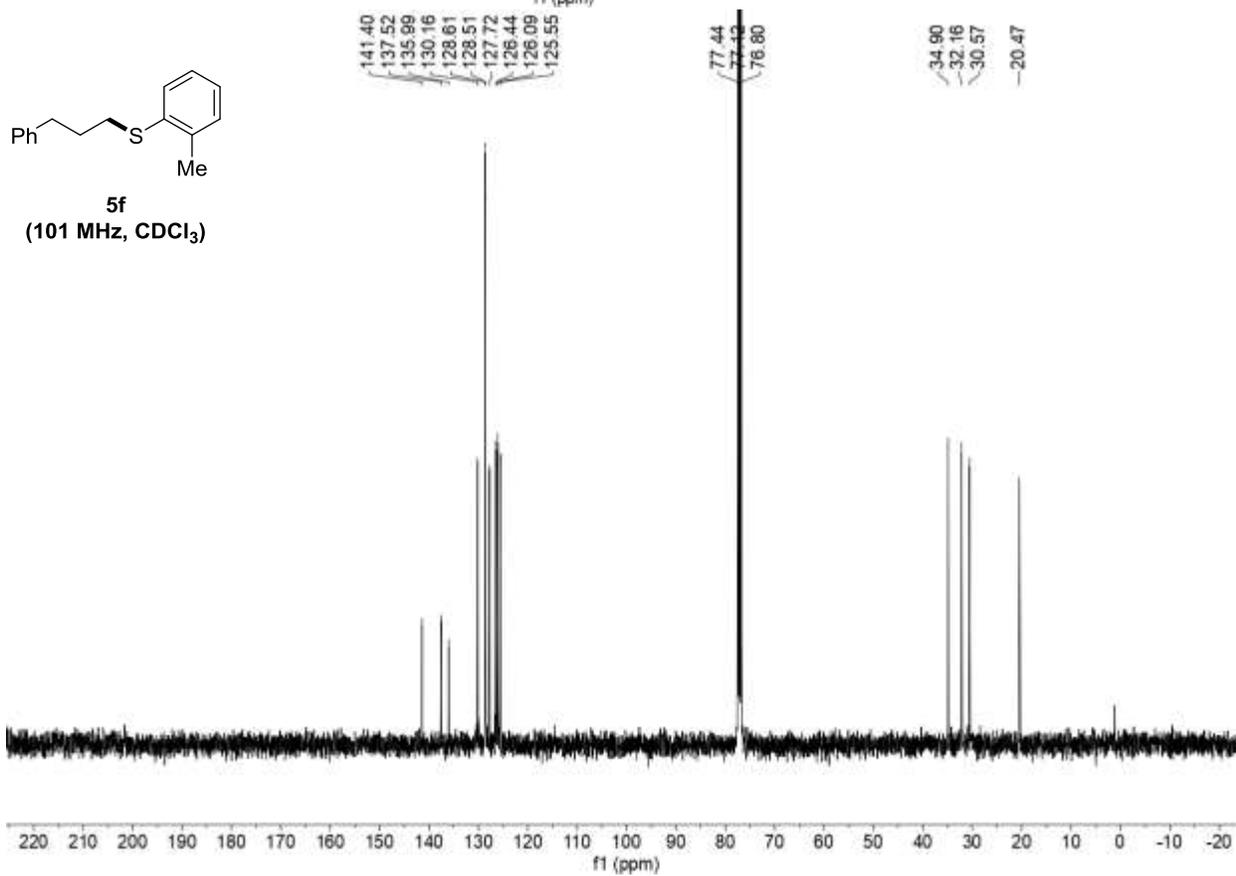
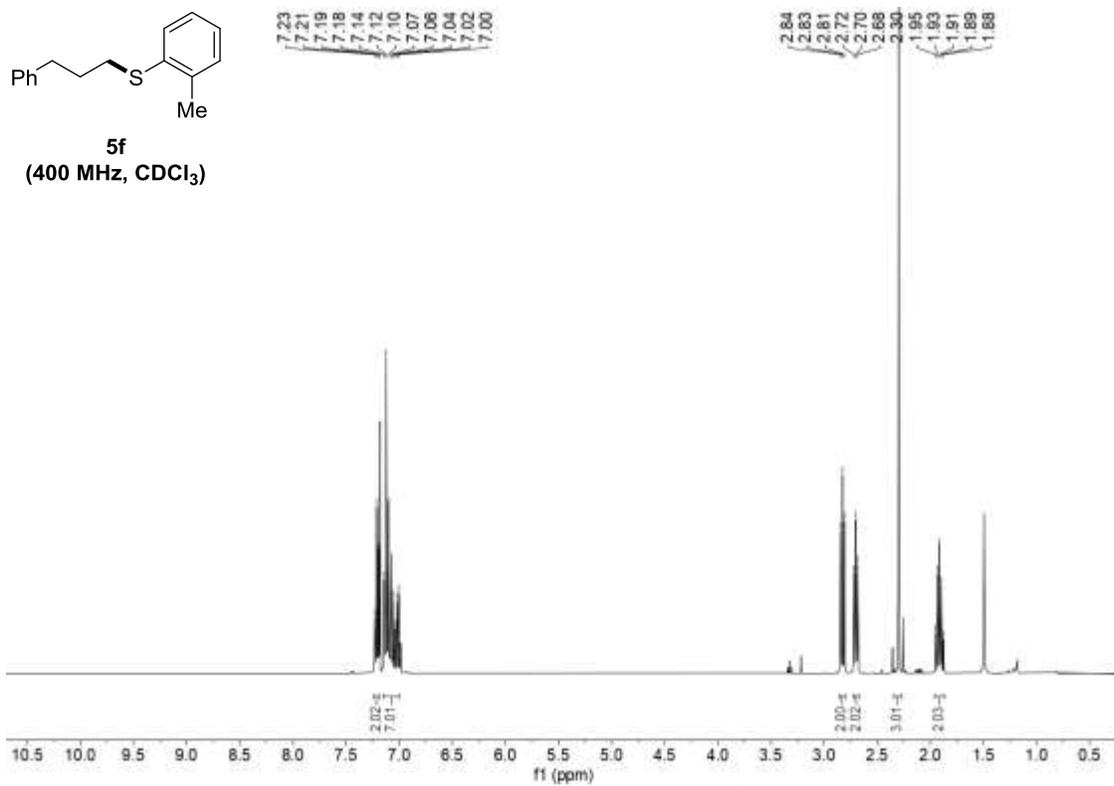


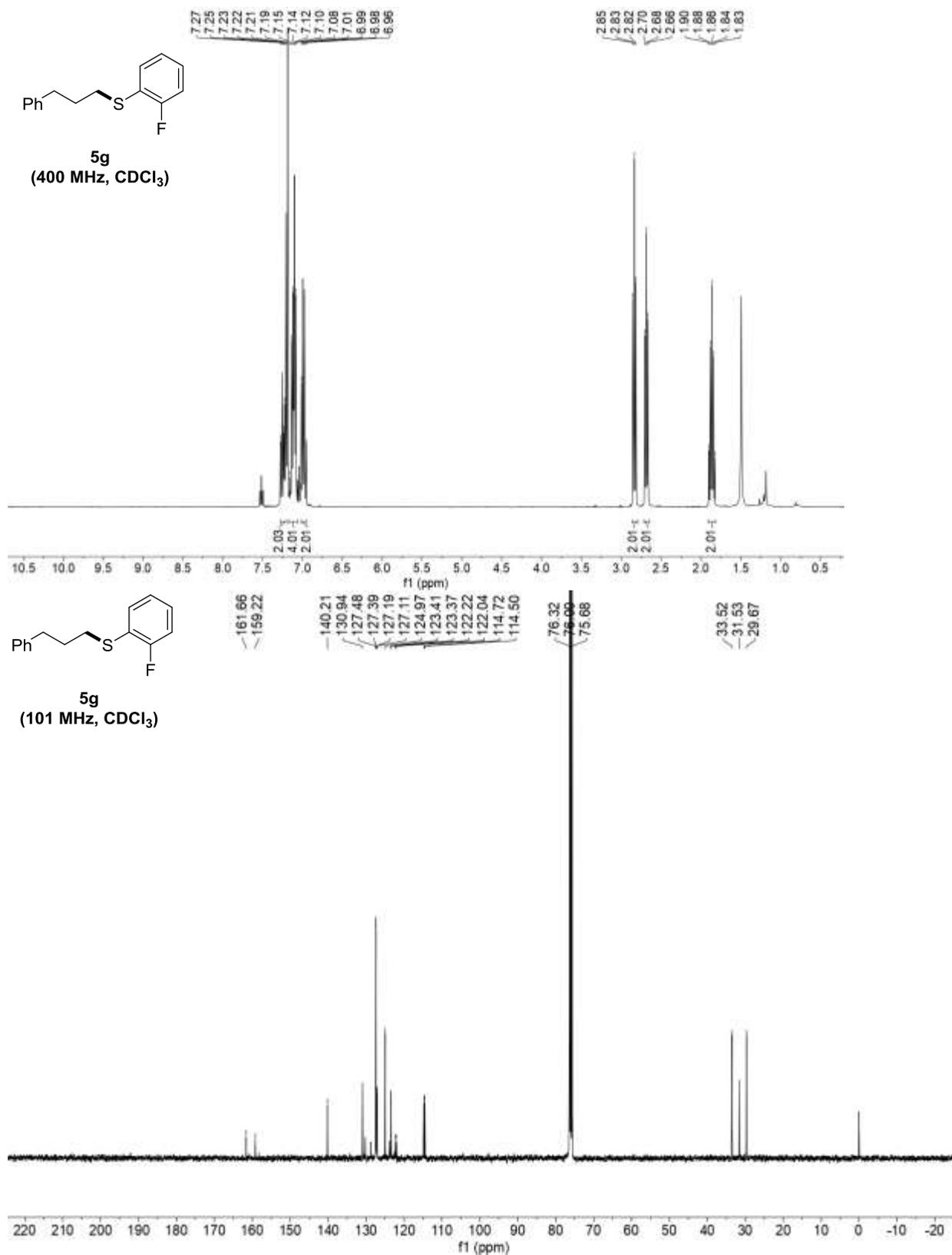
**5c**  
(376 MHz, CDCl<sub>3</sub>)

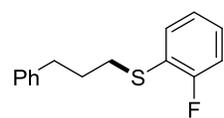




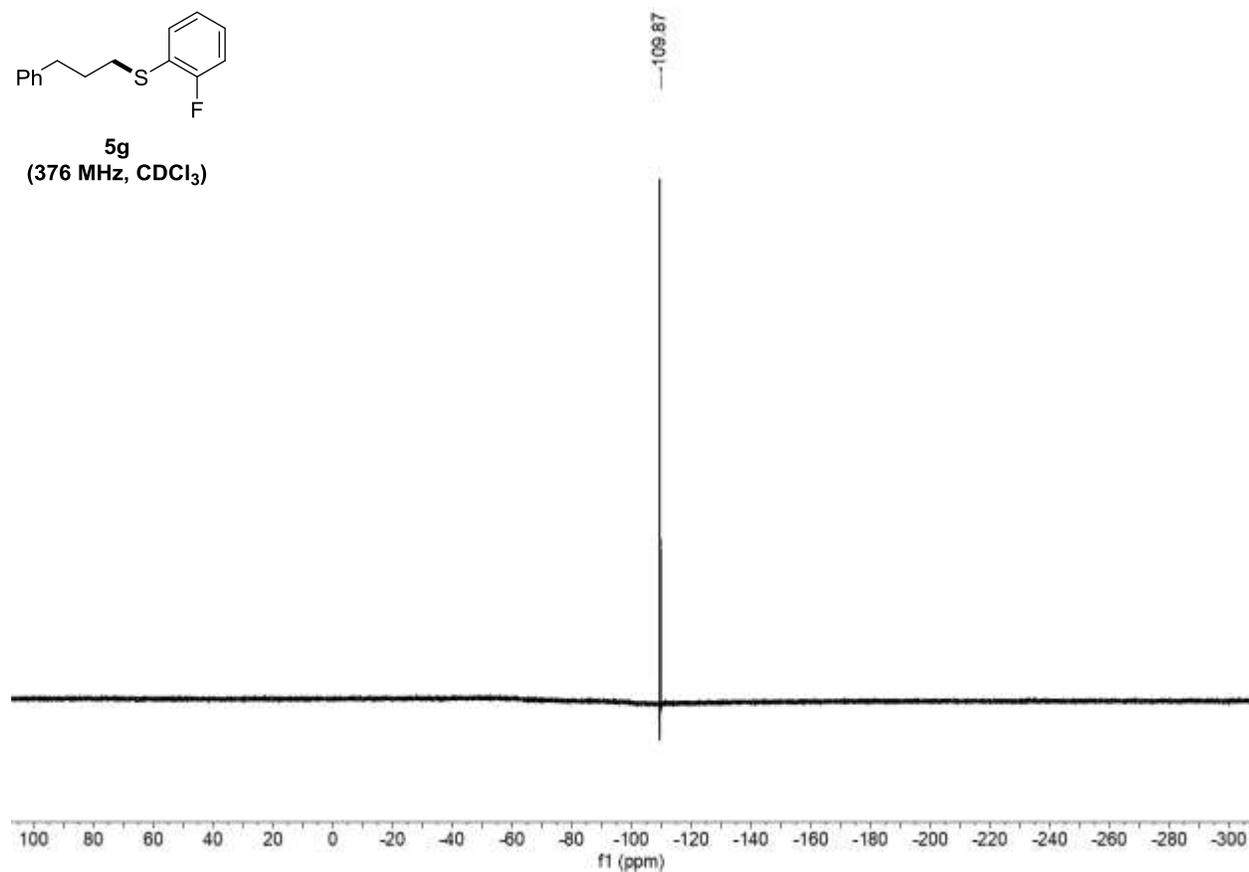


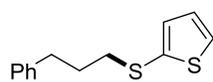




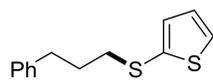
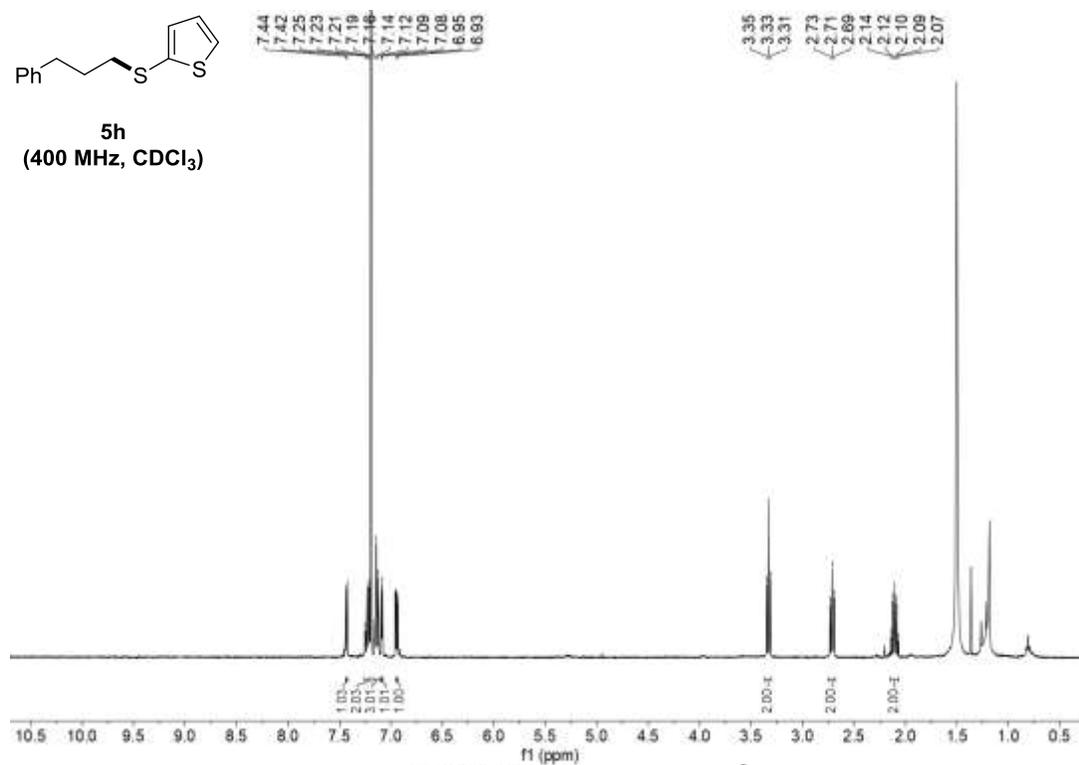


**5g**  
(376 MHz, CDCl<sub>3</sub>)

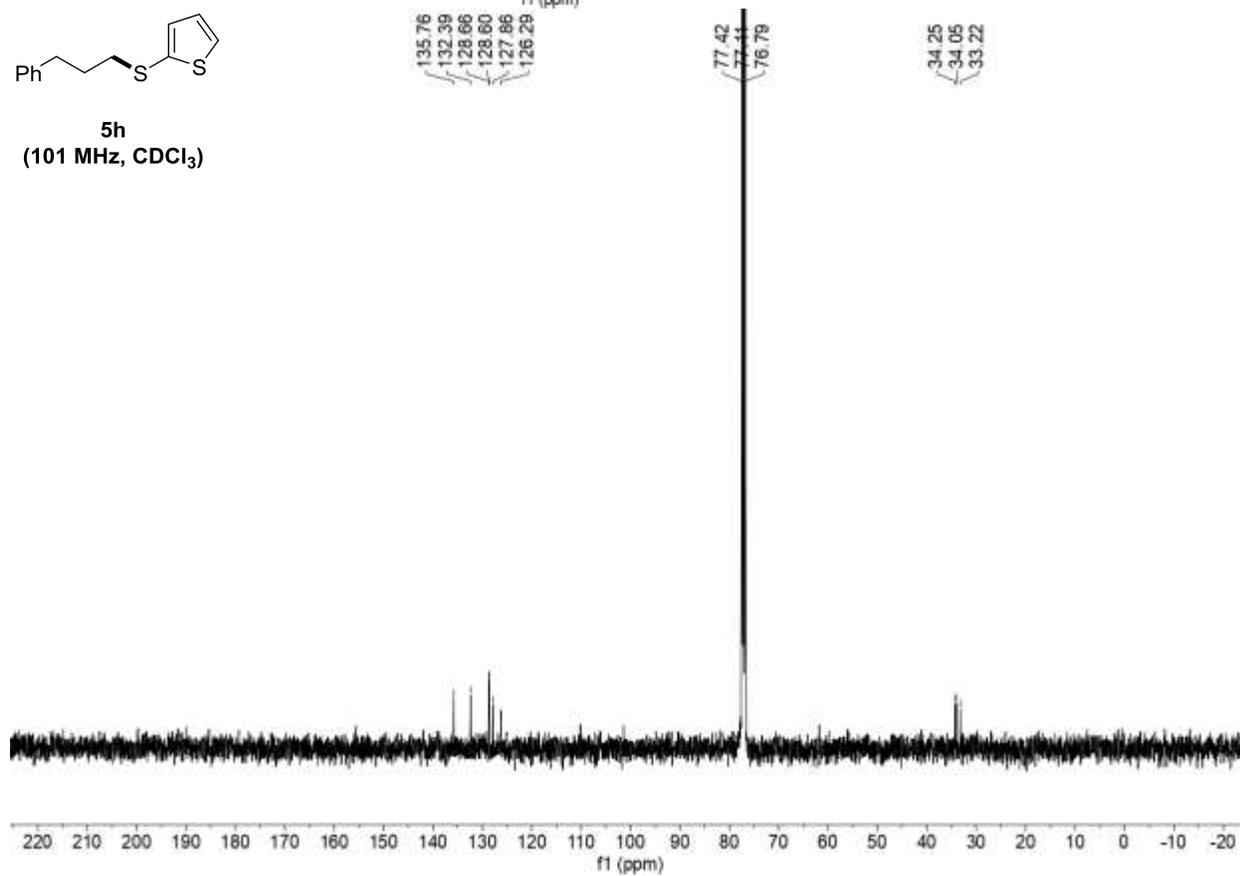


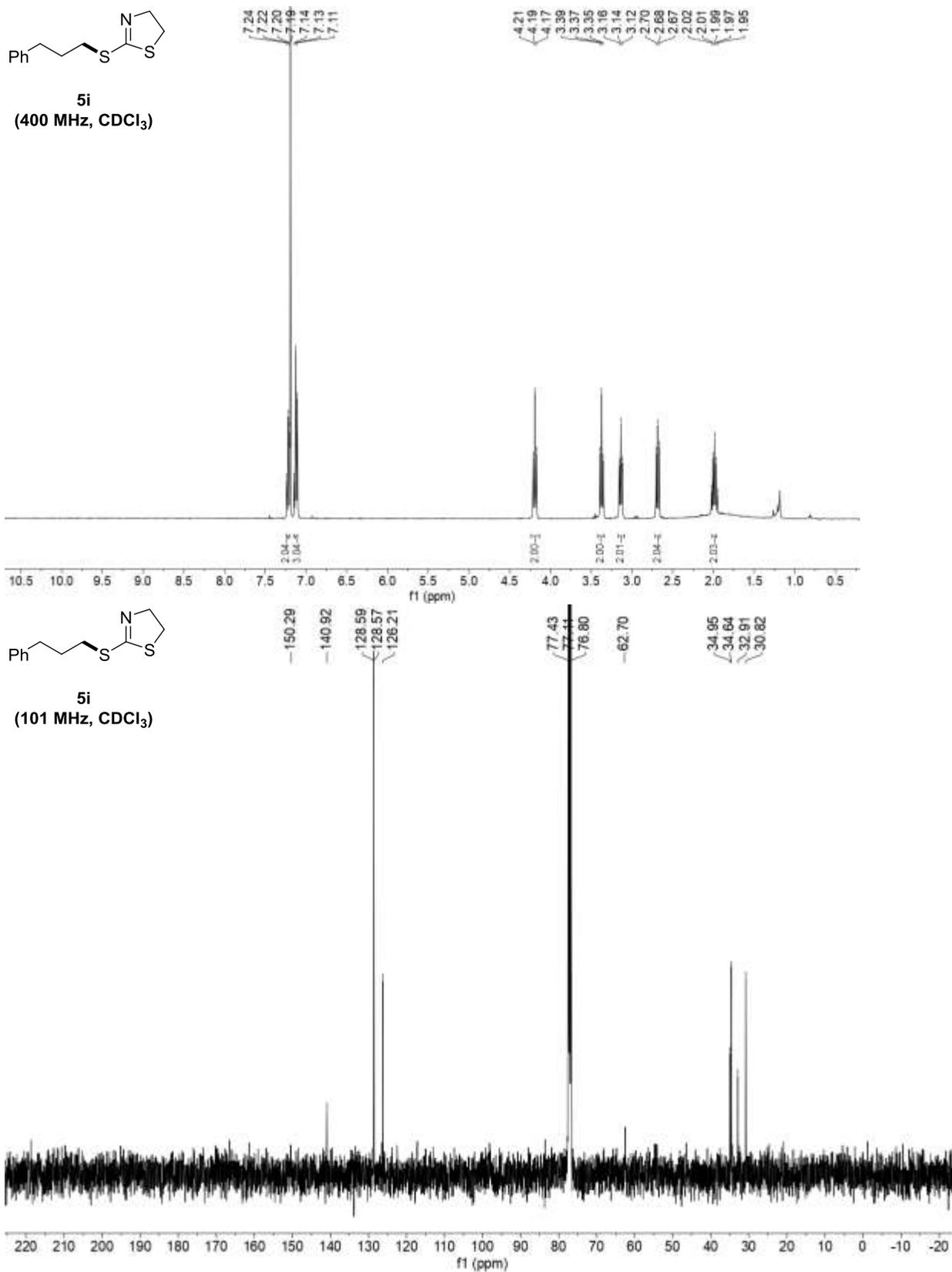


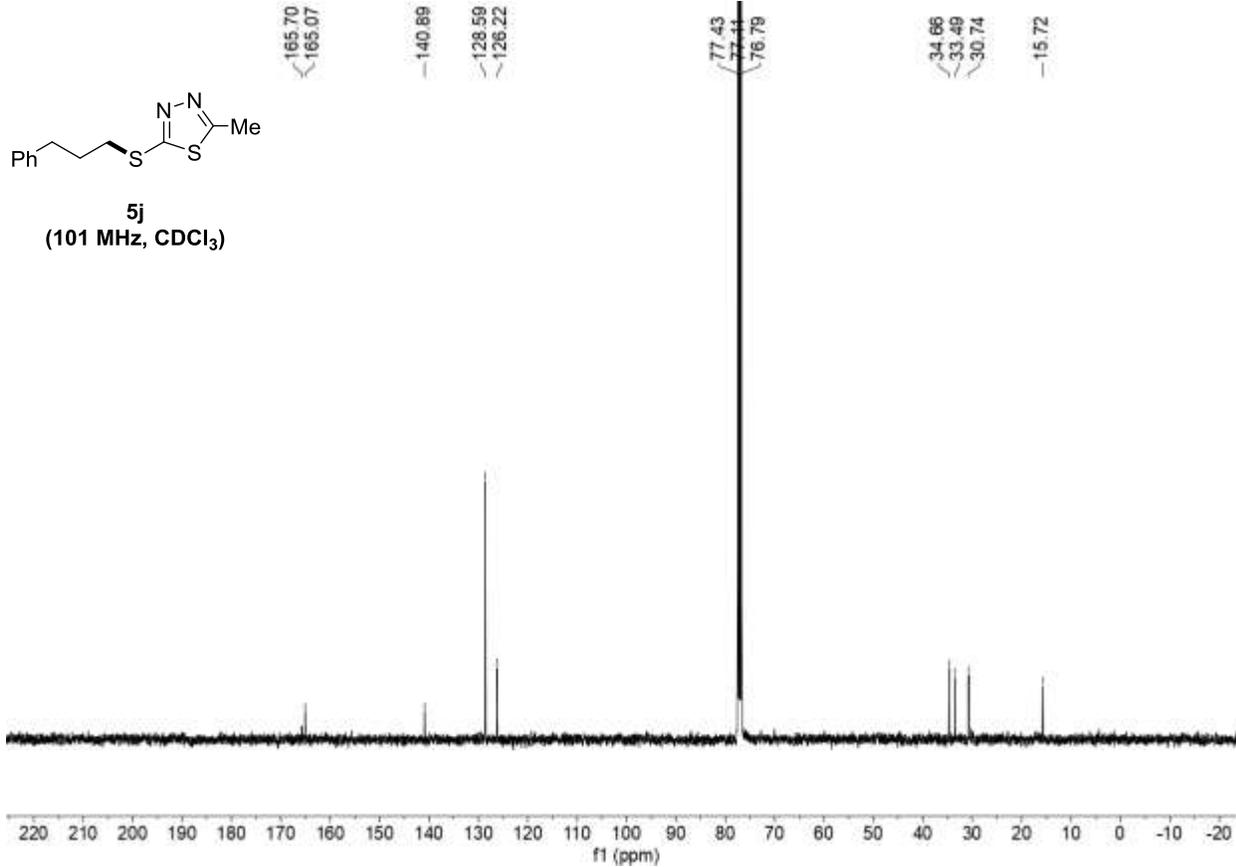
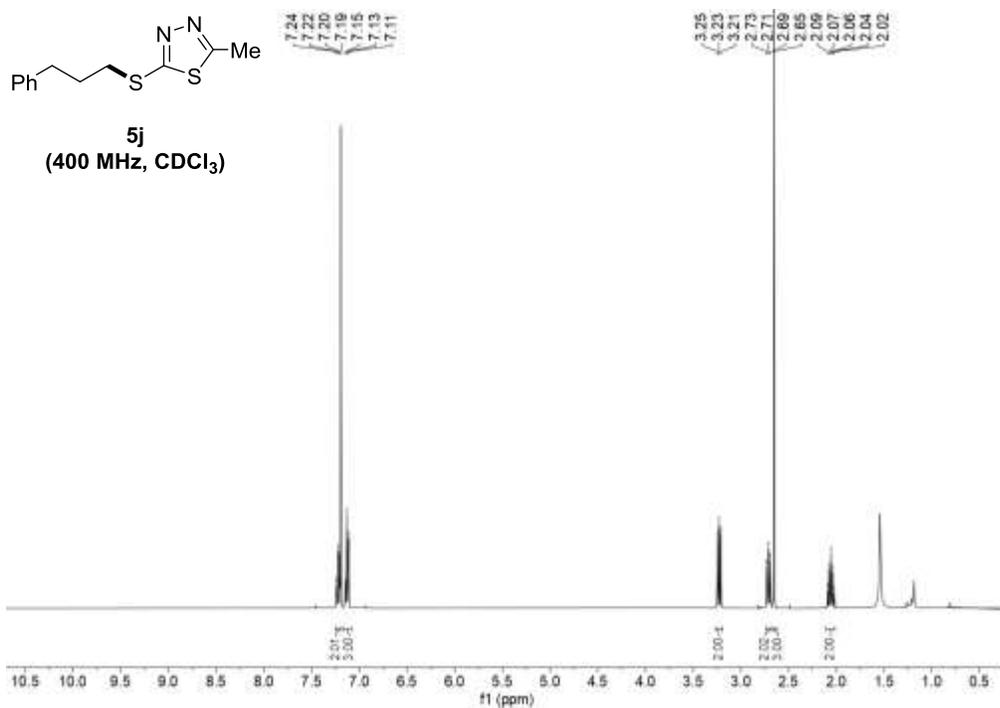
**5h**  
(400 MHz, CDCl<sub>3</sub>)

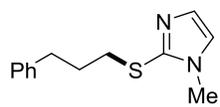


**5h**  
(101 MHz, CDCl<sub>3</sub>)

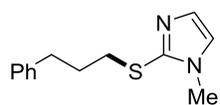
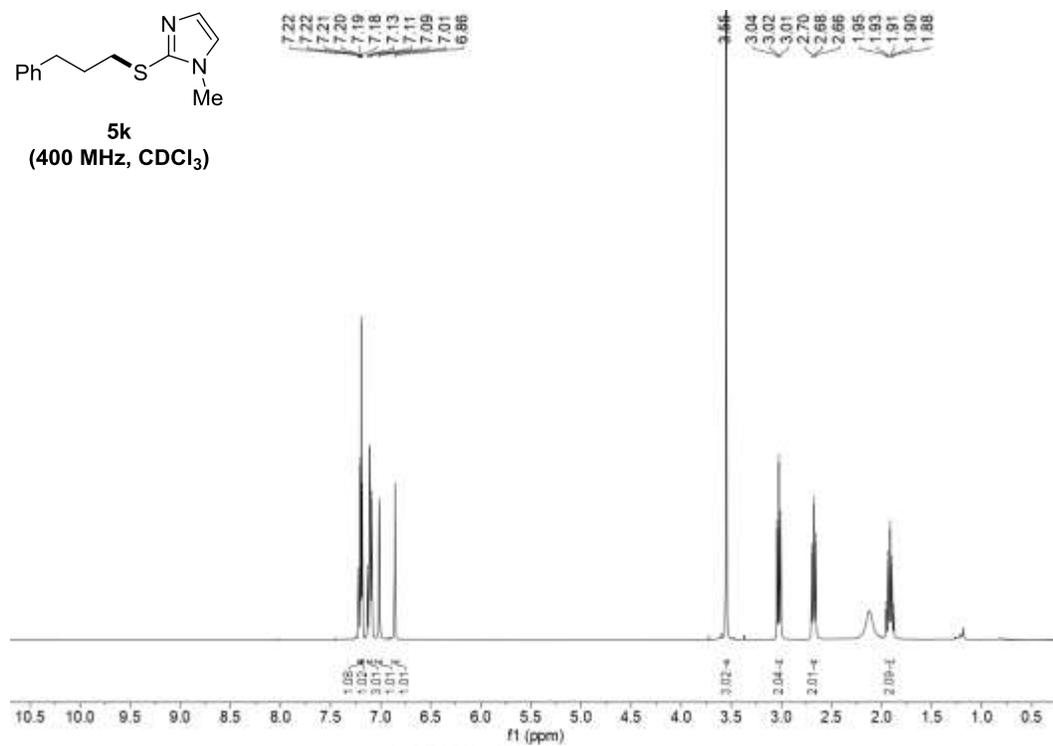




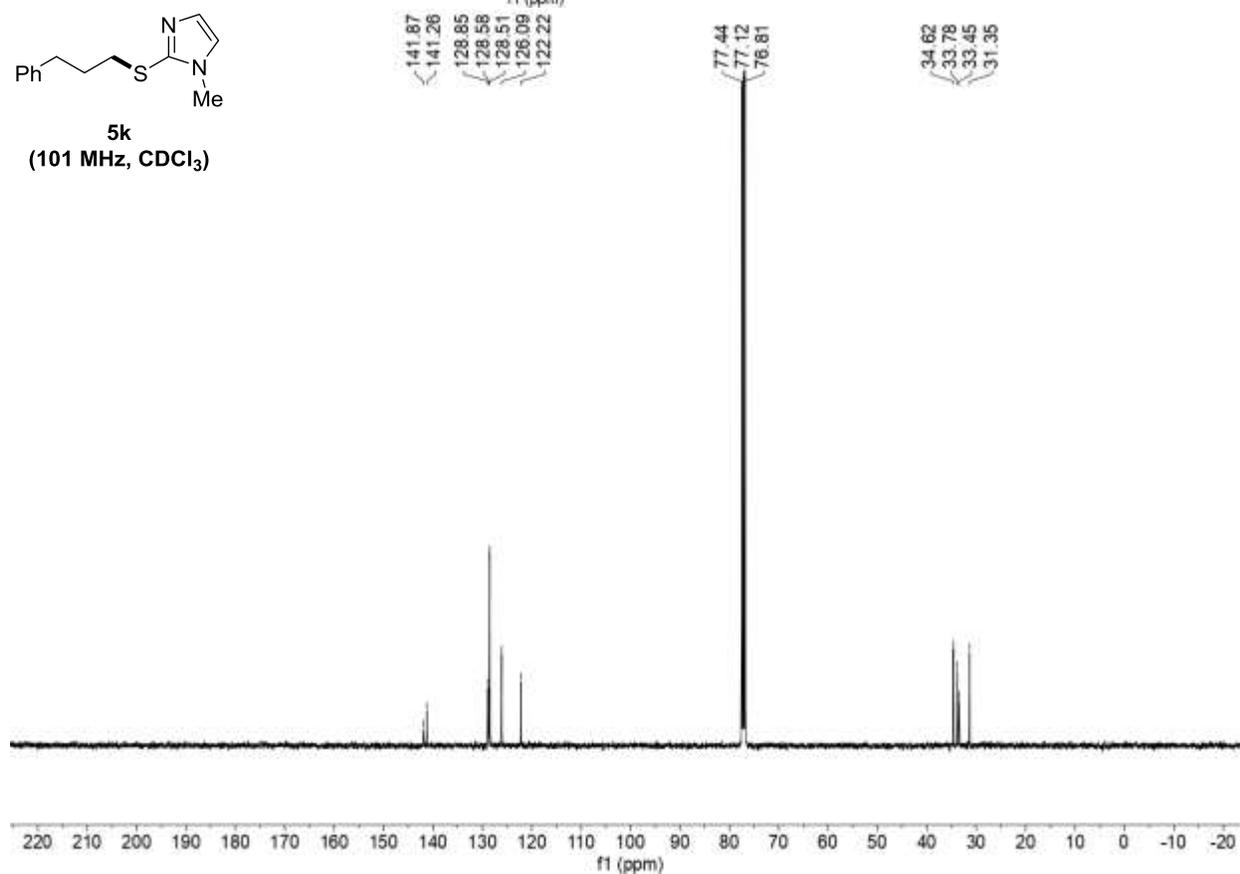


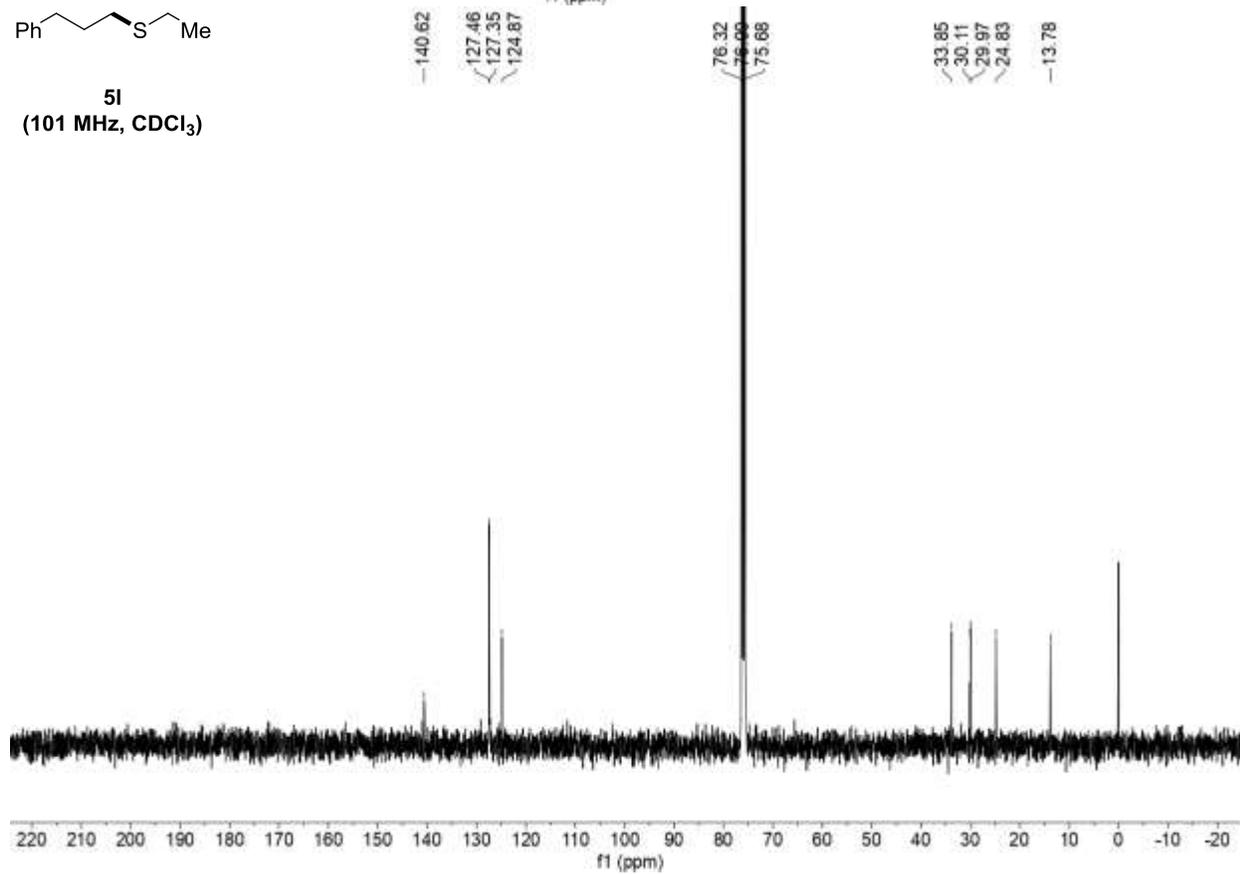
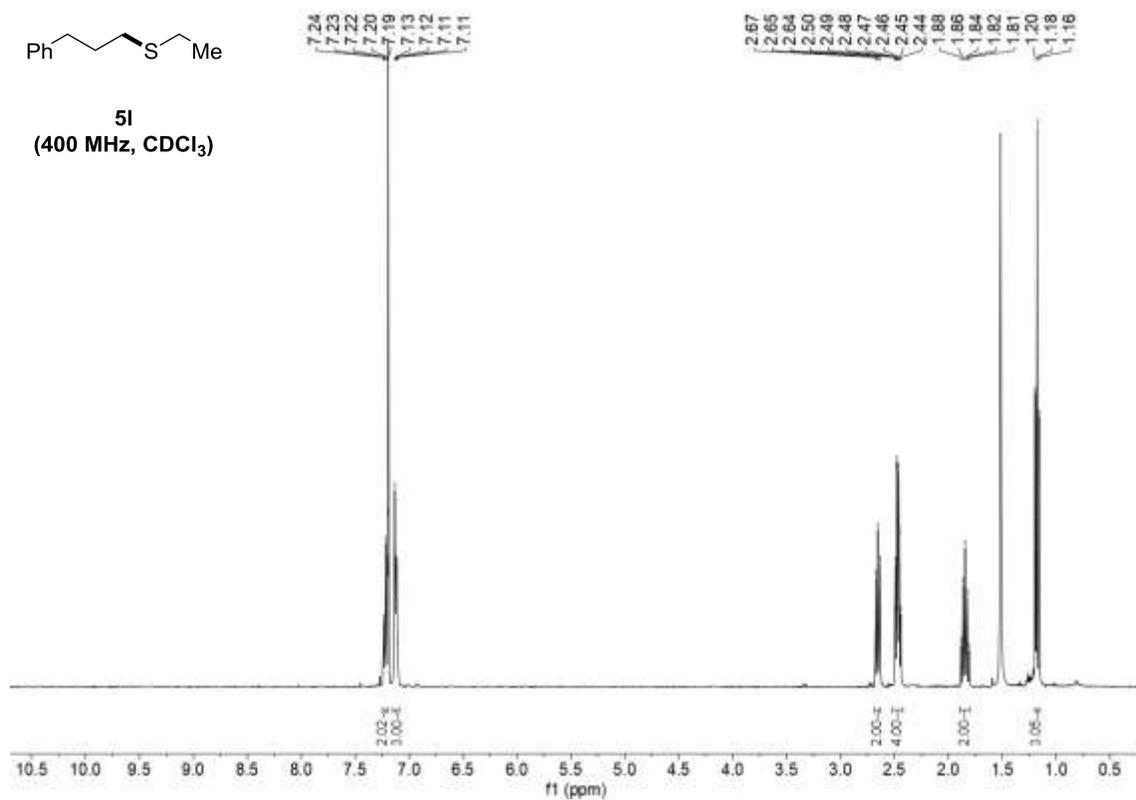


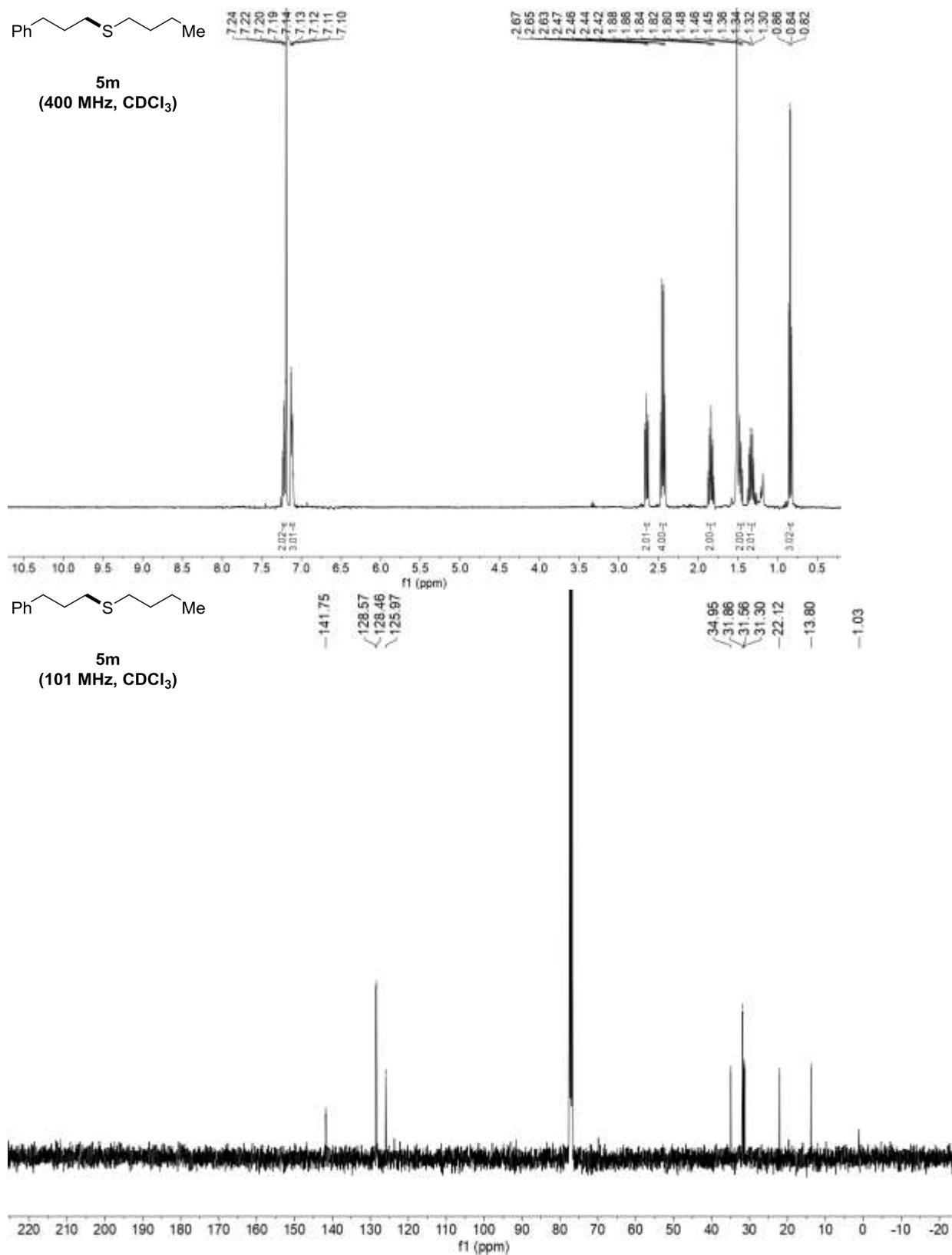
**5k**  
(400 MHz, CDCl<sub>3</sub>)

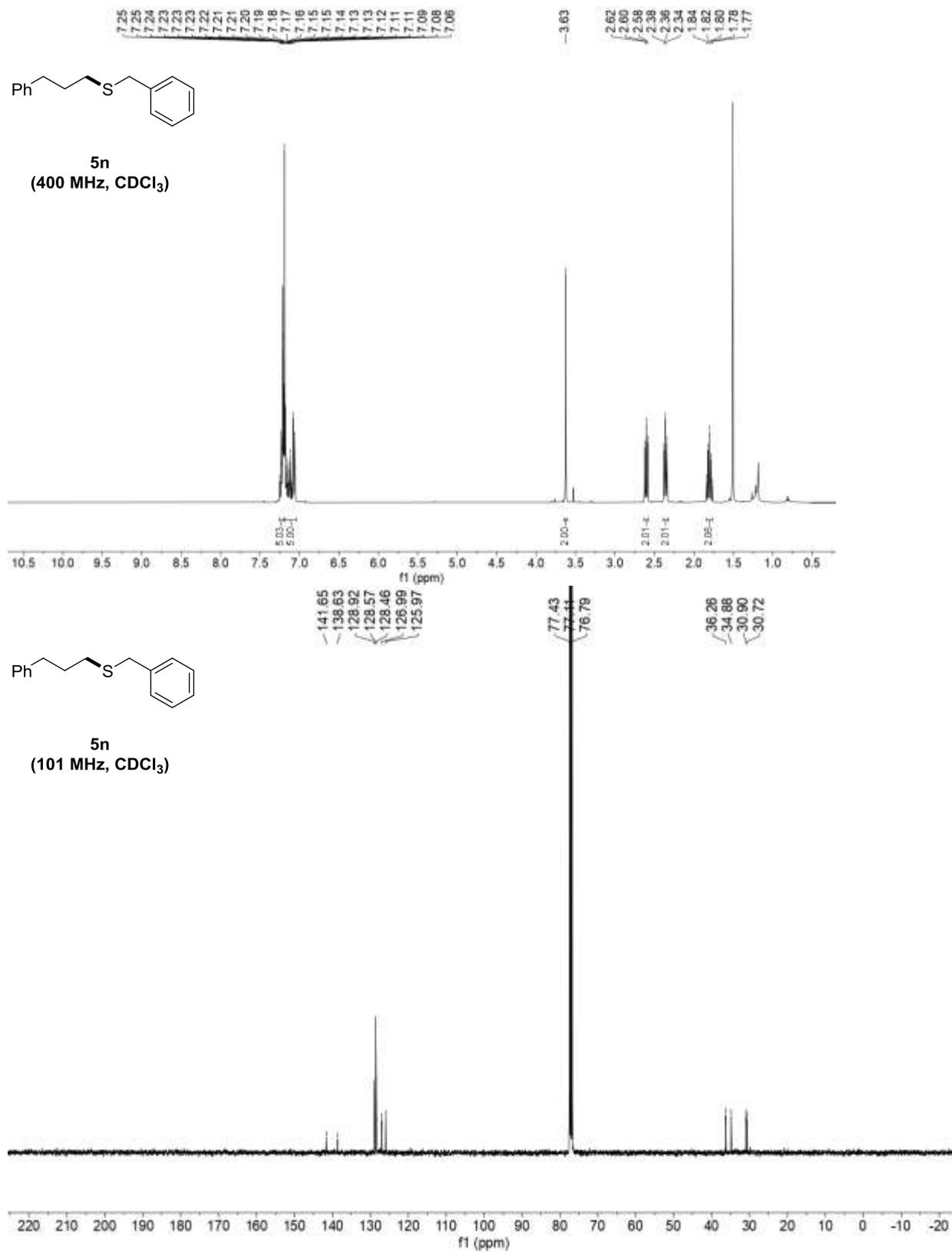


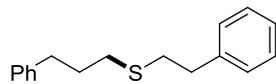
**5k**  
(101 MHz, CDCl<sub>3</sub>)



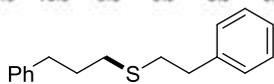
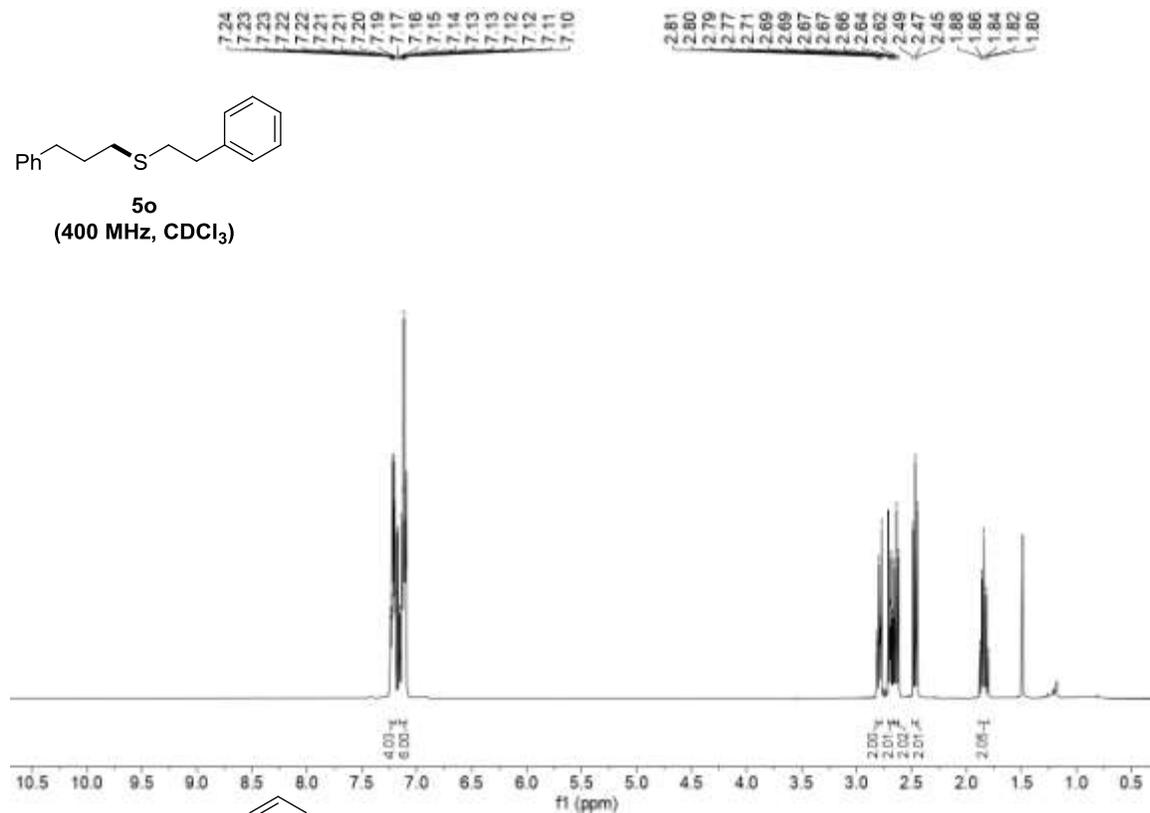








**5o**  
(400 MHz, CDCl<sub>3</sub>)



**5o**  
(101 MHz, CDCl<sub>3</sub>)

