

## Supplementary Information for

### $\alpha$ -Thiocarbonyl Synthesis *via* Fe<sup>II</sup>-Catalyzed Insertion Reaction of $\alpha$ -Diazocarbonyls into S–H Bonds

Hoda Keipour, Angela Jalba, Nour Tanbouza, Virginie Carreras and Thierry Ollevier\*

Département de chimie, Université Laval, 1045 avenue de la Médecine

Québec, QC, G1V 0A6, Canada

#### Table of Contents

General information	S-2
Representative procedure for the S–H insertion into methyl $\alpha$ -( <i>p</i> -methoxyphenyl)- $\alpha$ -diazoacetate	S-2
General procedure for S–H insertion into $\alpha$ -diazoesters	S-3
Characterization of $\alpha$ -thioesters ( <b>2aa–ea</b> )	S-3
Representative procedure for S–H insertion into $\alpha$ -phenyl- $\alpha$ -diazopropan-2-one	S-5
General procedure for S–H insertion of $\alpha$ -diazoketones	S-6
Characterization of $\alpha$ -thioketones ( <b>4a–k</b> )	S-6
Procedure for the reaction of methyl $\alpha$ -phenyl- $\alpha$ -diazoacetate with allyl(phenyl)sulfide	S-9
References	S-10
Copies of <sup>1</sup> H and <sup>13</sup> C NMR spectra	S-11

**General information.** All reactions were performed in flame-dried flasks and tubes under argon atmosphere. Dichloroethane and dichloromethane were distilled from CaH<sub>2</sub>. Fe(OTf)<sub>2</sub> was purchased from Strem (98%). Thin-layer chromatography (TLC) was carried out on 250  $\mu$ m commercial silica gel plates and compounds were visualized using UV absorbance and/or aqueous KMnO<sub>4</sub>. Flash column chromatography was performed on silica gel (230–400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Inova 400 MHz and an Agilent Technologies DD2 500 MHz spectrometer in CDCl<sub>3</sub>. For <sup>1</sup>H NMR (400 MHz), chemical shifts were reported downfield from tetramethylsilane (TMS) used as internal standard ( $\delta$  = 0 ppm) and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (in Hz), and integration. High-resolution mass spectra (HRMS) were recorded on ESI-TOF (time-of-flight) mass spectrometer. IR spectra were recorded on a BOMEM Arid-Zone™ FT-IR spectrometer with a ZnSe ATR accessory and are reported in reciprocal centimeter (cm<sup>-1</sup>). Melting points (mp) are uncorrected and were recorded on a melting point apparatus (MEL-TEMP®).

Caution! Diazo compounds should be handled with caution in a fume hood, as they are presumed to be toxic and potentially explosive. We recommend that their preparation be conducted behind a safety shield, although we have never experienced any explosive incident.

The  $\alpha$ -diazoesters (**1a–e**) and  $\alpha$ -diazoketone **3a** were synthesized according to reported procedures.<sup>1</sup>

### Representative procedure for the S–H insertion into methyl $\alpha$ -(*p*-methoxyphenyl)- $\alpha$ -diazoacetate

In a flame-dried test tube, under argon atmosphere, Fe(OTf)<sub>2</sub> (53 mg, 0.15 mmol, 15 mol%) and 4 Å MS (200 mg) were added and diluted in CH<sub>2</sub>Cl<sub>2</sub> (2.4 mL). Thiophenol (4 mmol) was then introduced dropwise into the mixture. The mixture was heated to 40 °C and the  $\alpha$ -diazoester (1 mmol), diluted in CH<sub>2</sub>Cl<sub>2</sub> (2.4 mL), was added dropwise over 1 h by means of a syringe pump. The mixture was stirred for the specified time and monitored by TLC. Upon completion, the mixture was subsequently filtered through celite and concentrated under reduced pressure (rotary evaporator). The residue was purified by silica gel column chromatography (hexanes/EtOAc, 99:1) to afford methyl  $\alpha$ -(*p*-methoxyphenyl)- $\alpha$ -(phenylthio)acetate (**2ca**) as a colorless oil (213 mg, 0.74 mmol, 74% yield).

### General procedure for S–H insertion into $\alpha$ -diazoesters

In a flame-dried test tube, under argon atmosphere, Fe(OTf)<sub>2</sub> (13.2 mg, 0.0375 mmol, 15 mol%) and 4 Å MS (50 mg) were added and diluted in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL). The thiol (1 mmol) was then introduced dropwise into the mixture. The mixture was heated to 40 °C and the  $\alpha$ -diazoester (0.25 mmol), diluted in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL), was added dropwise over 1 h by means of a syringe pump. The mixture was stirred for the specified time and monitored by TLC. Upon completion, the mixture was subsequently filtered through celite and concentrated under reduced pressure (rotary evaporator). The residue was purified by silica gel column chromatography (hexanes/EtOAc, 99:1) to afford the isolated product.

*Methyl  $\alpha$ -phenyl- $\alpha$ -(phenylthio)acetate (2aa).*<sup>1</sup> The product was obtained as a colorless oil (56 mg, 0.21 mmol, 87% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  7.46–7.43 (m, 2H), 7.39–7.35 (m, 2H),

7.34–7.30 (m, 3H), 7.28–7.26 (m, 3H), 4.92 (s, 1H), 3.68 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  170.9, 135.6, 133.7, 132.6, 129.0, 128.7, 128.5, 128.3, 128.0, 56.3, 52.7 ppm; IR (ZnSe): 2951, 2876, 1717, 1489, 1265, 1145, 1089, 1011, 705  $\text{cm}^{-1}$ .

*Methyl  $\alpha$ -phenyl- $\alpha$ -(*p*-tolylthio)acetate (**2ab**).*<sup>1</sup> The product was obtained as a white solid (64 mg, 0.23 mmol, 94% yield). mp: 60–62 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.4–7.41 (m, 2H), 7.34–7.25 (m, 5H), 7.08 (d,  $J = 8.4$  Hz, 2H), 4.84 (s, 1H), 3.67 (s, 3H), 2.32 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  171.0, 138.4, 135.7, 133.3, 129.9, 129.7, 128.6, 128.5, 128.2, 56.8, 52.7, 21.2 ppm; IR (ZnSe): 2951, 1717, 1433, 1268, 1229, 1006, 811, 762, 695  $\text{cm}^{-1}$ .

*Methyl  $\alpha$ -((*p*-bromophenyl)thio)- $\alpha$ -phenylacetate (**2ac**).*<sup>2</sup> The product was obtained as a white solid (81 mg, 0.24 mmol, 96% yield). mp: 50–54 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.43–7.37 (m, 4H), 7.35–7.30 (m, 3H), 7.23–7.20 (m, 2H), 4.88 (s, 1H), 3.69 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  170.6, 135.2, 134.3, 132.7, 132.1, 128.8, 128.5, 122.5, 56.3, 52.8 ppm; IR (ZnSe): 2945, 1732, 1484, 1428, 1301, 1156, 1092, 1004, 831, 727, 695  $\text{cm}^{-1}$ .

*Methyl  $\alpha$ -((*p*-chlorophenyl)thio)- $\alpha$ -phenylacetate (**2ad**).*<sup>1</sup> The product was obtained as a white solid (64 mg, 0.22 mmol, 88% yield). mp: 58–60 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.4–7.39 (m, 2H), 7.35–7.26 (m, 5H), 7.24–7.22 (m, 2H), 4.86 (s, 1H), 3.69 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  170.6, 135.3, 134.4, 134.3, 131.9, 129.1, 128.7, 128.5, 128.4, 56.4, 52.8 ppm; IR (ZnSe): 2951, 1713, 1495, 1432, 1281, 1235, 1093, 1009, 823  $\text{cm}^{-1}$ .

*Methyl  $\alpha$ -(phenylthio)- $\alpha$ -(*p*-tolyl)acetate (**2ba**).*<sup>1</sup> The product was obtained as white a solid (54 mg, 0.20 mmol, 80% yield). mp: 67–70 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.39–7.32 (m, 4H), 7.28–7.25 (m, 3H), 7.14 (d,  $J = 7.9$  Hz, 2H), 4.89 (s, 1H), 3.67 (s, 3H), 2.33 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100

MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  171.0, 138.2, 133.9, 132.5, 132.4, 129.4, 128.9, 128.3, 127.9, 56.0, 52.7, 21.2 ppm; IR (ZnSe): 3049, 2941, 1740, 1578, 1510, 1434, 1329, 1142, 1078, 792 cm<sup>-1</sup>.

*Methyl  $\alpha$ -(*p*-methoxyphenyl)- $\alpha$ -(phenylthio)acetate (2ca)*.<sup>1</sup> The product was obtained as a white solid (59 mg, 0.20 mmol, 82% yield). mp: 78–80 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  7.39–7.35 (m, 4H), 7.28–7.25 (m, 3H), 6.87–6.83 (m, 2H), 4.88 (s, 1H), 3.80 (s, 3H), 3.67 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  171.1, 159.6, 133.8, 132.6, 129.7, 128.9, 127.9, 127.5, 114.1, 55.6, 55.3, 52.7 ppm; IR (ZnSe): 3002, 2954, 2835, 1718, 1508, 1438, 1252, 1173, 1028, 1003, 830 cm<sup>-1</sup>.

*Methyl  $\alpha$ -(*p*-chlorophenyl)- $\alpha$ -(phenylthio)acetate (2da)*.<sup>1</sup> The product was obtained as a white solid (26 mg, 0.09 mmol, 35% yield). mp: 48–50 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  7.38–7.33 (m, 4H), 7.30–7.25 (m, 5H), 4.86 (s, 1H), 3.68 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  170.5, 134.3, 134.2, 133.1, 133.0, 129.9, 129.0, 128.8, 128.3, 55.7, 52.8 ppm; IR (ZnSe): 3050, 2951, 1716, 1488, 1470, 1293, 1235, 849, 767 cm<sup>-1</sup>.

*Methyl  $\alpha$ -(*p*-bromophenyl)- $\alpha$ -(phenylthio)acetate (2ea)*.<sup>1</sup> The product was obtained as a white solid (53 mg, 0.16 mmol, 63% yield). mp: 48–50 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  7.46–7.43 (m, 2H), 7.36–7.26 (m, 7H), 4.84 (s, 1H), 3.68 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  170.4, 134.8, 133.0, 131.8, 130.2, 129.1, 128.3, 122.4, 55.8, 52.8 ppm; IR (ZnSe): 3051, 2949, 1713, 1483, 1469, 1290, 1231, 838, 767 cm<sup>-1</sup>.

#### Representative procedure for S–H insertion into $\alpha$ -phenyl- $\alpha$ -diazopropan-2-one 3a.

In a flame-dried test tube, Fe(OTf)<sub>2</sub> (35 mg, 0.1 mmol, 10 mol%) and 4 Å molecular sieves (200 mg) were mixed in CH<sub>2</sub>Cl<sub>2</sub> (6 mL). Thiophenol (5 mmol) was introduced into the mixture.  $\alpha$ -Phenyl- $\alpha$ -diazopropan-2-one **3a** (1 mmol) was diluted in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and was added over 1 h using a

syringe pump. The mixture was stirred at 40 °C and monitored by TLC. Upon completion, the mixture was passed through celite and concentrated under vacuum (rotary evaporator). The residue was purified by silica gel flash column chromatography (hexanes/EtOAc, 99:1) to afford the product as a white solid (132 mg, 0.48 mmol, 48% yield).

#### **General procedure for S–H insertion into $\alpha$ -phenyl- $\alpha$ -diazopropan-2-one **3a**.**

In a flame-dried test tube, Fe(OTf)<sub>2</sub> (10 or 20 mol%) and 4 Å molecular sieves (50 mg) were mixed in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL). The thiol (1.25 mmol) was introduced into the mixture.  $\alpha$ -Phenyl- $\alpha$ -diazopropan-2-one **3a** (0.25 mmol) was diluted in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and was added over 1 h using a syringe pump. The mixture was stirred at 40 °C and monitored by TLC. Upon completion, the mixture was passed through celite and concentrated under vacuum (rotary evaporator). The residue was purified by silica gel flash column chromatography (hexanes/EtOAc, 99:1) to afford the product.

*1-(Phenylthio)-1-phenylacetone (4a)*.<sup>3</sup> The product was obtained as a white solid (36 mg, 0.15 mmol, 60% yield). mp: 65–67 °C (lit. 67–68 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  7.35–7.30 (m, 7H), 7.26–7.23 (m, 3H), 4.98 (s, 1H), 2.19 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  203.0, 135.4, 133.6, 132.3, 129.0, 128.9, 128.5, 128.2, 127.7, 64.5, 27.2 ppm; IR (ZnSe): 3045, 2909, 1708, 1478, 1271, 1148, 1024, 687 cm<sup>-1</sup>; HRMS (ESI-TOF): calcd for C<sub>15</sub>H<sub>15</sub>OS<sup>+</sup> [M + H<sup>+</sup>]: 243.0838, found 243.0829.

*1-[(4-Chlorophenyl)thio]-1-phenylacetone (4b)*. The product was obtained as a white solid (48 mg, 0.17 mmol, 70% yield). mp: 27–28 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  7.36–7.27 (m, 5H), 7.25–7.18 (m, 4H), 4.94 (s, 1H), 2.18 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  202.6, 135.2, 134.1,

133.9, 131.9, 129.1, 129.0, 128.5, 128.4, 64.8, 27.4 ppm; IR (ZnSe 3053, 1696, 1475, 1453, 1351, 1092, 852, 738 cm<sup>-1</sup>); HRMS (ESI-TOF): calcd for C<sub>15</sub>H<sub>14</sub>ClOS<sup>+</sup> [M + H<sup>+</sup>]: 277.0448, found 277.0441.

*1-[(4-Bromophenyl)thio]-1-phenylacetone (4c)*. The product was obtained as a white solid (68 mg, 0.21 mmol, 85% yield). mp: 27–28 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 7.38–7.28 (m, 7H), 7.16 (d, *J* = 8.7 Hz, 2H), 4.95 (s, 1H), 2.18 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 202.6, 135.1, 134.0, 132.7, 132.0, 129.0, 128.5, 128.4, 122.1, 64.6, 27.4 ppm; IR (ZnSe): 3398, 2906, 1706, 1486, 1294, 1178, 1069, 773 cm<sup>-1</sup>; HRMS (ESI-TOF): calcd for C<sub>15</sub>H<sub>17</sub>BrNOS<sup>+</sup> [M + NH<sub>4</sub><sup>+</sup>]: 340.0188, found 340.0166.

*1-[(4-Methylphenyl)thio]-1-phenylacetone (4d)*. The product was obtained as a colorless oil (40 mg, 0.16 mmol, 63% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 7.35–7.29 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 4.91 (s, 1H), 2.30 (s, 3H), 2.18 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 203.2, 138.1, 135.5, 132.9, 129.8, 129.8, 128.8, 128.5, 128.2, 64.8, 27.2, 21.1 ppm; IR (ZnSe): 3024, 2916, 1705, 1490, 1246, 1074, 1016, 765 cm<sup>-1</sup>; HRMS (ESI-TOF): calcd for C<sub>16</sub>H<sub>17</sub>OS<sup>+</sup> [M + H<sup>+</sup>]: 257.0995, found 257.0985.

*1-[(2-Methylphenyl)thio]-1-phenylacetone (4e)*. The product was obtained as a colorless oil (27 mg, 0.10 mmol, 42% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 7.36–7.29 (m, 5H), 7.26 (m, 1H), 7.16 (m, 2H), 7.09 (m, 1H), 4.91 (s, 1H), 2.35 (s, 3H), 2.20 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 203.1, 140.0, 135.4, 132.9, 132.4, 130.4, 128.8, 128.4, 128.2, 127.7, 126.5, 63.5, 27.2, 20.6 ppm; IR (ZnSe): 3059, 1708, 1491, 1378, 1202, 1075, 741, 679 cm<sup>-1</sup>; HRMS (ESI-TOF): calcd for C<sub>16</sub>H<sub>17</sub>OS<sup>+</sup> [M + H<sup>+</sup>]: 257.0994, found 257.0983.

*1-[(2-Pyridinyl)thio]-1-phenylacetone (4f)*. The product was obtained as a white solid (23 mg, 0.09 mmol, 38% yield). mp: 62–64 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  8.37 (ddd,  $J = 5.0, 1.9, 1.0$  Hz, 1H), 7.50–7.41 (m, 3H), 7.39–7.30 (m, 3H), 7.18 (dt,  $J = 8.1, 1.0$  Hz, 1H), 6.98 (ddd,  $J = 7.4, 5.0, 1.1$  Hz, 1H), 5.79 (s, 1H), 2.33 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  203.3, 157.5, 149.2, 136.0, 134.2, 129.0, 129.0, 128.4, 121.7, 119.8, 58.5, 28.3 ppm; IR (ZnSe): 3058, 2920, 1712, 1575, 1300, 1147, 745, 700  $\text{cm}^{-1}$ ; HRMS (ESI-TOF): calcd for  $\text{C}_{14}\text{H}_{14}\text{NOS}^+$  [ $\text{M} + \text{H}^+$ ]: 244.0790, found 244.0779.

*1-(Benzylthio)-1-phenylacetone (4g)*. The product was obtained as a white solid (25 mg, 0.1 mmol, 39% yield). mp: 40–41 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.43–7.22 (m, 10H), 4.43 (s, 1H), 3.69 (d,  $J = 13.5$  Hz, 1H), 3.56 (d,  $J = 13.5$  Hz, 1H), 2.09 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  203.2, 137.2, 135.5, 129.0, 128.9, 128.6, 128.5, 128.2, 127.2, 59.7, 35.5, 26.9 ppm; IR (ZnSe): 3025, 2918, 1699, 1487, 1296, 1183, 1027, 692  $\text{cm}^{-1}$ ; HRMS (ESI-TOF): calcd for  $\text{C}_{16}\text{H}_{17}\text{OS}^+$  [ $\text{M} + \text{H}^+$ ]: 257.0994, found 257.0998.

*1-[(4-Chlorobenzyl)thio]-1-phenylacetone (4h)*. The product was obtained as colorless oil (30 mg, 0.10 mmol, 41% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.39–7.26 (m, 7H), 7.20 (d,  $J = 8.3$  Hz, 2H), 4.41 (s, 1H), 3.63 (d,  $J = 13.7$  Hz, 1H), 3.51 (d,  $J = 13.7$  Hz, 1H), 2.09 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  203.1, 135.8, 135.3, 133.0, 130.4, 128.9, 128.6, 128.6, 128.3, 59.7, 34.7, 26.9 ppm; IR (ZnSe): 3027, 2913, 1708, 1488, 1352, 1175, 1029, 770  $\text{cm}^{-1}$ ; HRMS (ESI-TOF): calcd for  $\text{C}_{16}\text{H}_{16}\text{ClOS}^+$  [ $\text{M} + \text{H}^+$ ]: 291.0604, found 291.0593.

*1-[(2-Chlorobenzyl)thio]-1-phenylacetone (4i)*. The product was obtained as colorless oil (43 mg, 0.15 mmol, 59% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.38–7.28 (m, 7H), 7.20 (m, 2H), 4.55 (s, 1H), 3.76 (s, 2H), 2.14 (s, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  203.2, 135.3, 135.0, 134.2, 130.9, 129.8, 128.9, 128.7, 128.5, 128.2, 126.8, 60.2, 33.2, 26.7 ppm; IR (ZnSe): 3055, 1698, 1490, 1351,



1238, 1075, 736, 671  $\text{cm}^{-1}$ ; HRMS (ESI-TOF): calcd for  $\text{C}_{16}\text{H}_{16}\text{ClOS}^+$  [ $\text{M} + \text{H}^+$ ]: 291.0604, found 291.0592.

*1-(Isopropylthio)-1-phenylacetone (4j)*. The product was obtained as colorless oil (23 mg, 0.11 mmol, 44% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.46–7.22 (m, 5H), 4.66 (s, 1H), 2.81 (m, 1H), 2.16 (s, 3H), 1.26 (dd,  $J = 12.3, 6.7$  Hz, 6H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  203.9, 136.1, 128.8, 128.3, 128.0, 59.8, 35.1, 26.3, 23.2 ppm; IR (ZnSe): 2976, 2930, 1667, 1490, 1235, 1109, 925, 557  $\text{cm}^{-1}$ ; HRMS (ESI-TOF): calcd for  $\text{C}_{12}\text{H}_{17}\text{OS}^+$  [ $\text{M} + \text{H}^+$ ]: 209.0994, found 209.0993.

*1-(Butylthio)-1-phenylacetone (4k)*. The product was obtained as colorless oil (17 mg, 0.08 mmol, 31% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  7.47–7.22 (m, 5H), 4.59 (s, 1H), 2.45 (t,  $J = 7.4$  Hz, 2H), 2.17 (s, 3H), 1.64–1.46 (m, 2H), 1.37 (m, 2H), 0.87 (t,  $J = 7.3$  Hz, 3H) ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  203.6, 135.8, 128.8, 128.3, 128.0, 60.6, 31.2, 31.0, 26.4, 21.9, 13.6 ppm; IR (ZnSe): 3055, 2965, 1689, 1481, 1252, 1150, 863, 687  $\text{cm}^{-1}$ ; HRMS (ESI-TOF): calcd for  $\text{C}_{13}\text{H}_{19}\text{OS}^+$  [ $\text{M} + \text{H}^+$ ]: 223.1151, found 223.1149.

#### **Procedure for the reaction of methyl $\alpha$ -phenyl- $\alpha$ -diazoacetate with allyl(phenyl)sulfide**

In a flame-dried test tube, under argon atmosphere,  $\text{Fe}(\text{OTf})_2$  (13.2 mg, 0.0375 mmol, 15 mol%) and 4 Å MS (50 mg) were added and diluted in  $(\text{CH}_2\text{Cl})_2$  (0.5 mL). Allyl(phenyl)sulfide (150 mg, 1 mmol) was then introduced dropwise into the mixture. The mixture was heated to 80 °C and the diazoester (0.5 mmol), diluted in  $(\text{CH}_2\text{Cl})_2$  (0.5 mL), was added dropwise over 1 h by means of a syringe pump. The mixture was stirred for the specified time and monitored by TLC. Upon completion (18 h), the mixture was subsequently filtered through celite and concentrated under

reduced pressure (rotary evaporator). The residue was purified by silica gel column chromatography (hexanes 100 %) to afford the isolated product.

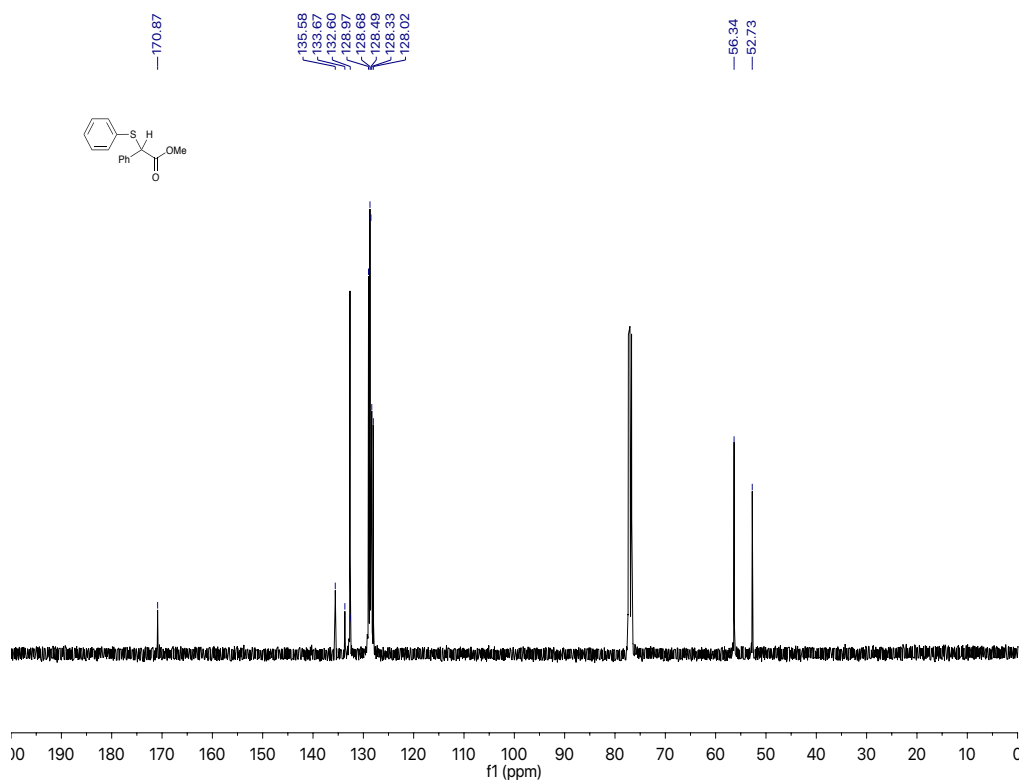
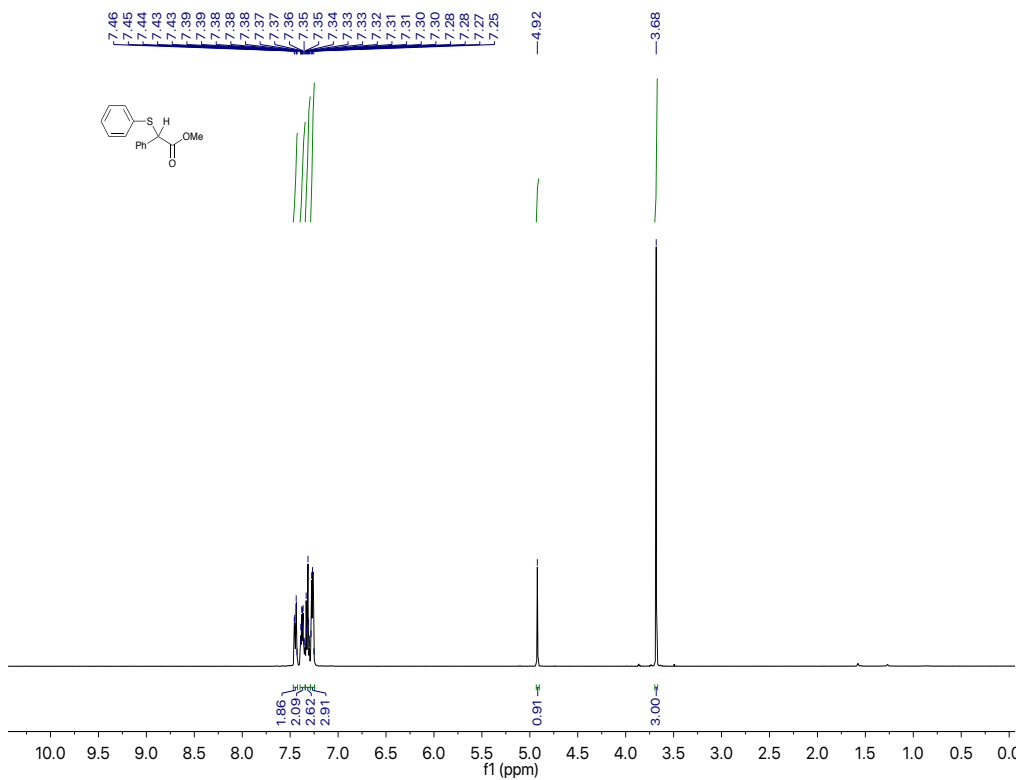
*Methyl 2-phenyl-2-(phenylthio)pent-4-enoate (6a)*.<sup>4</sup> Colorless oil (68 mg, 0.23 mmol, 91% yield); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 7.34-7.26 (m, 6H), 7.22-7.22 (m, 4H), 5.97-5.89 (m, 1H), 5.14-5.07 (m, 2H), 3.71 (s, 3H), 2.94-2.84 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 172.5, 139.9, 137.0, 133.3, 132.8, 130.7, 129.4, 128.6, 128.2, 127.6, 127.5, 118.9, 64.6, 52.8, 40.7. IR (ZnSe): 3059, 2980, 1728, 1439, 1213, 750, 692 cm<sup>-1</sup>.

## References

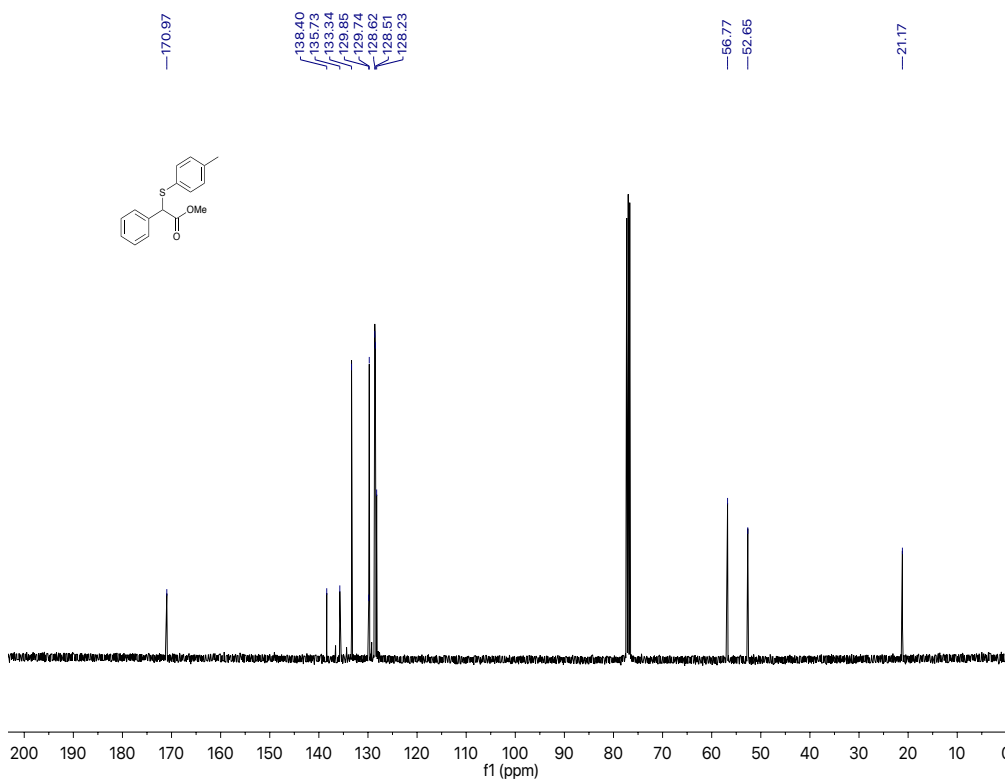
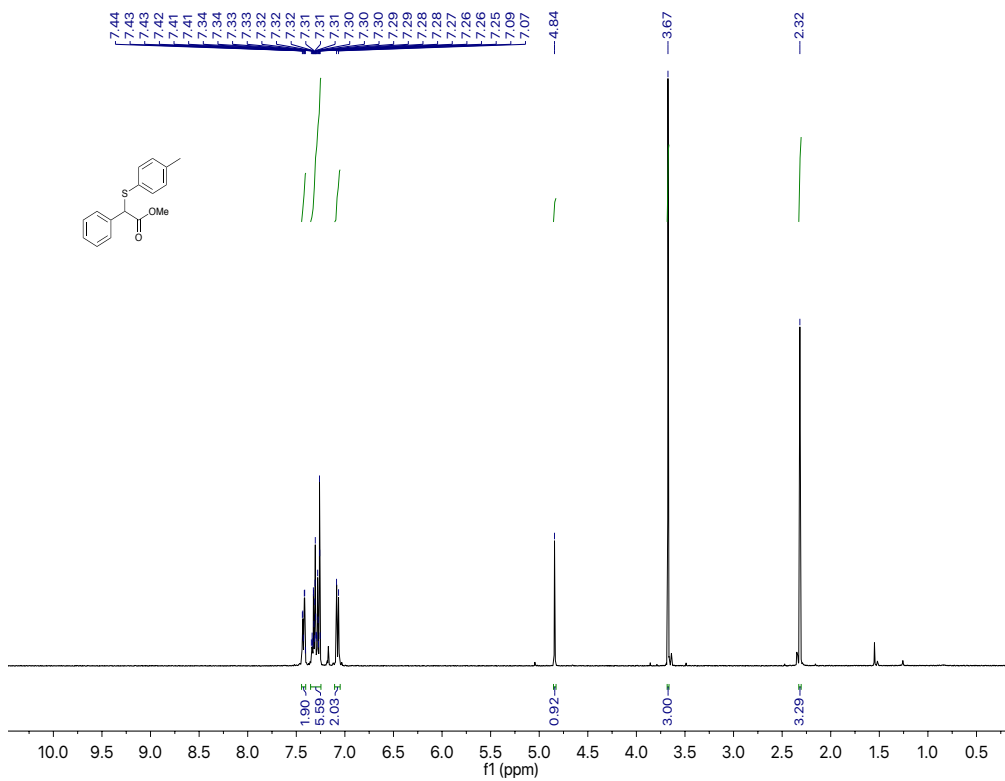
1. H. Keipour, A. Jalba, L. Delage-Laurin and T. Ollevier, *J. Org. Chem.*, 2017, **82**, 3000-3010.
2. Y. Zheng, R. Bian, X. Zhang, R. Yao, L. Qiu, X. Bao and X. Xu, *Eur. J. Org. Chem.*, 2016, **2016**, 3872-3877.
3. A. R. Katritzky, L. Xie, D. Toader and L. Serdyuk, *J. Am. Chem. Soc.*, 1995, **117**, 12015-12016.
4. C.-Y. Zhou, W.-Y. Yu, P. W. H. Chan and C.-M. Che, *J. Org. Chem.*, 2004, **69**, 7072-7082.

# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

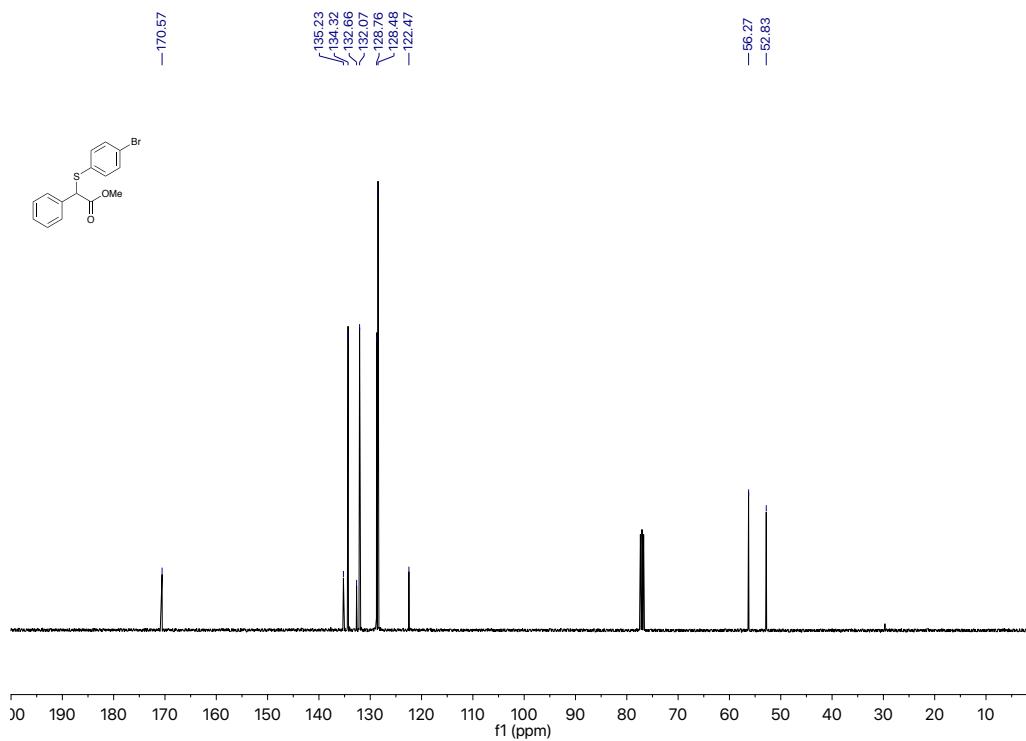
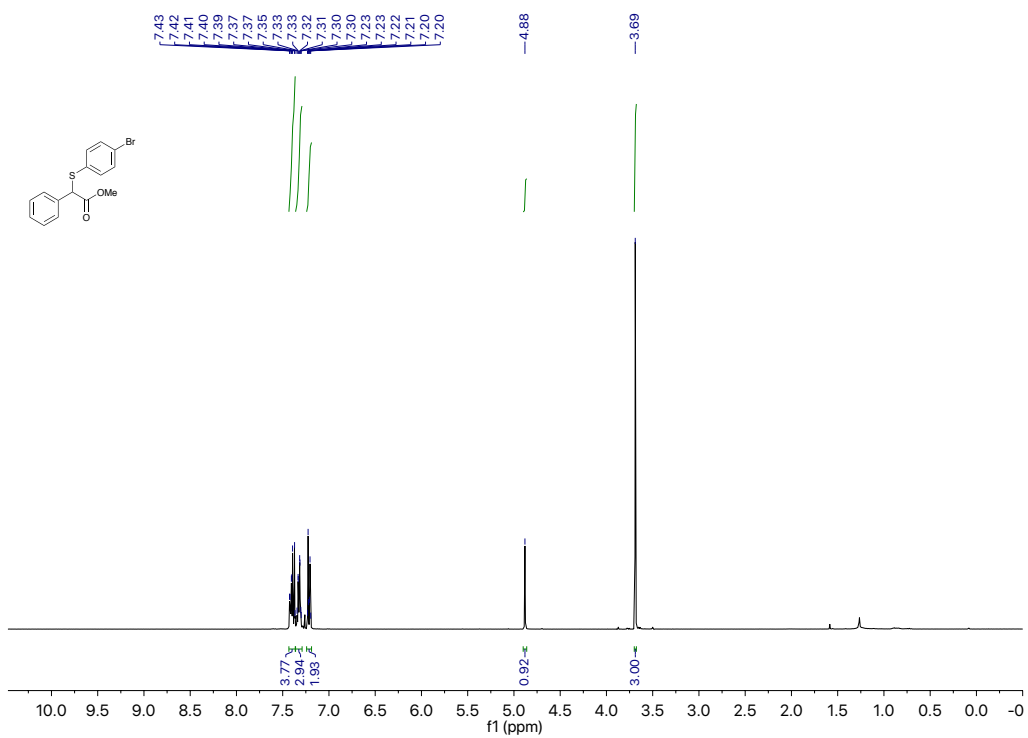
## Methyl $\alpha$ -phenyl- $\alpha$ -(phenylthio)acetate (**2aa**)



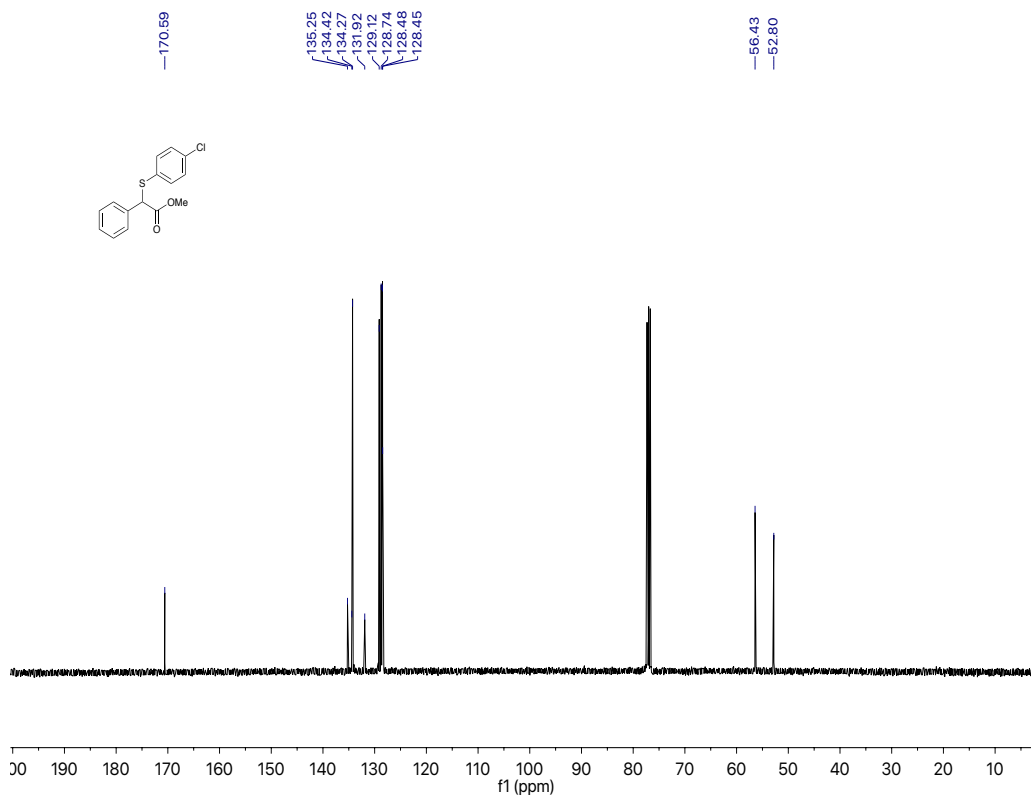
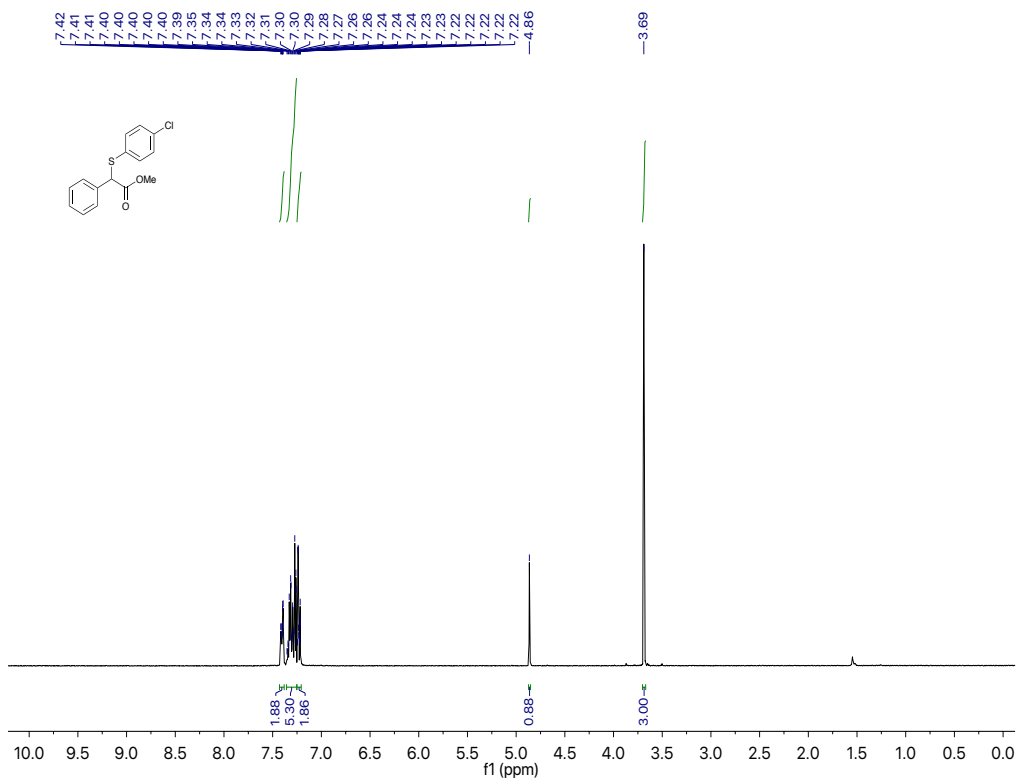
Methyl  $\alpha$ -phenyl- $\alpha$ -(*p*-tolylthio)acetate (**2ab**)



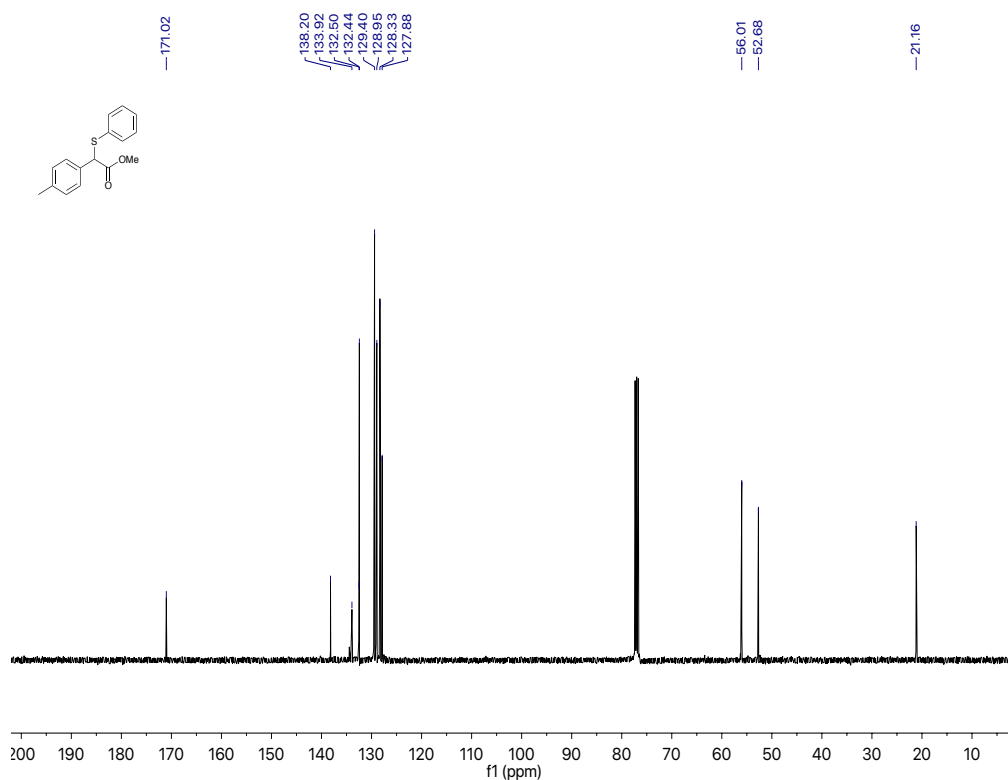
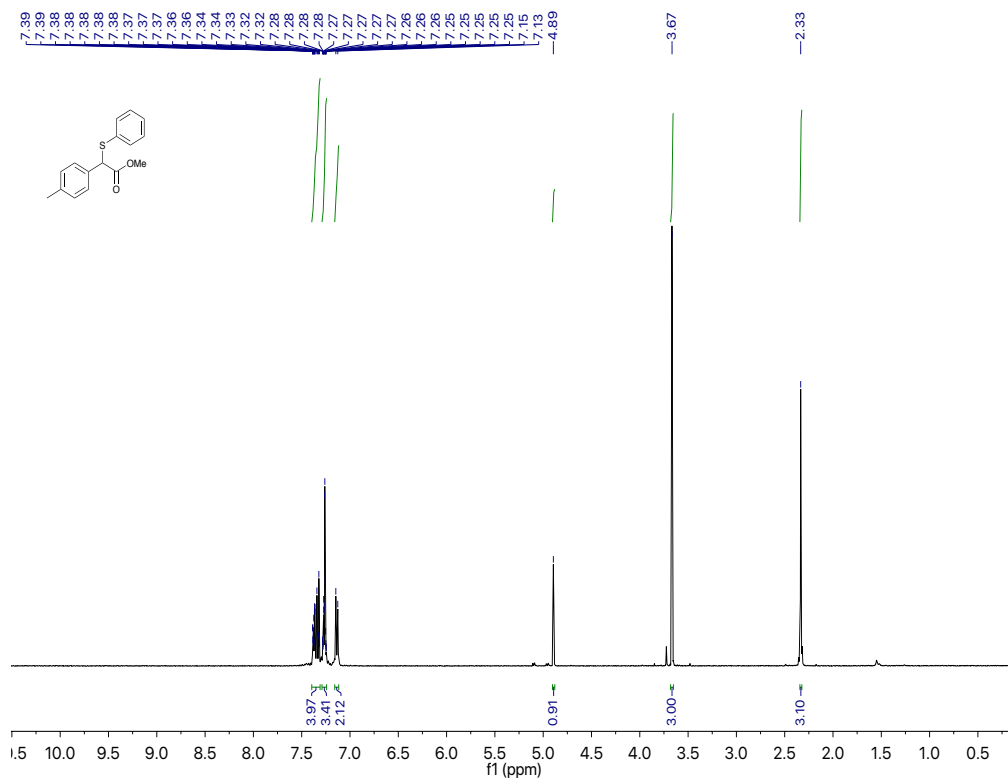
Methyl  $\alpha$ -((*p*-bromophenyl)thio)- $\alpha$ -phenylacetate (**2ac**)



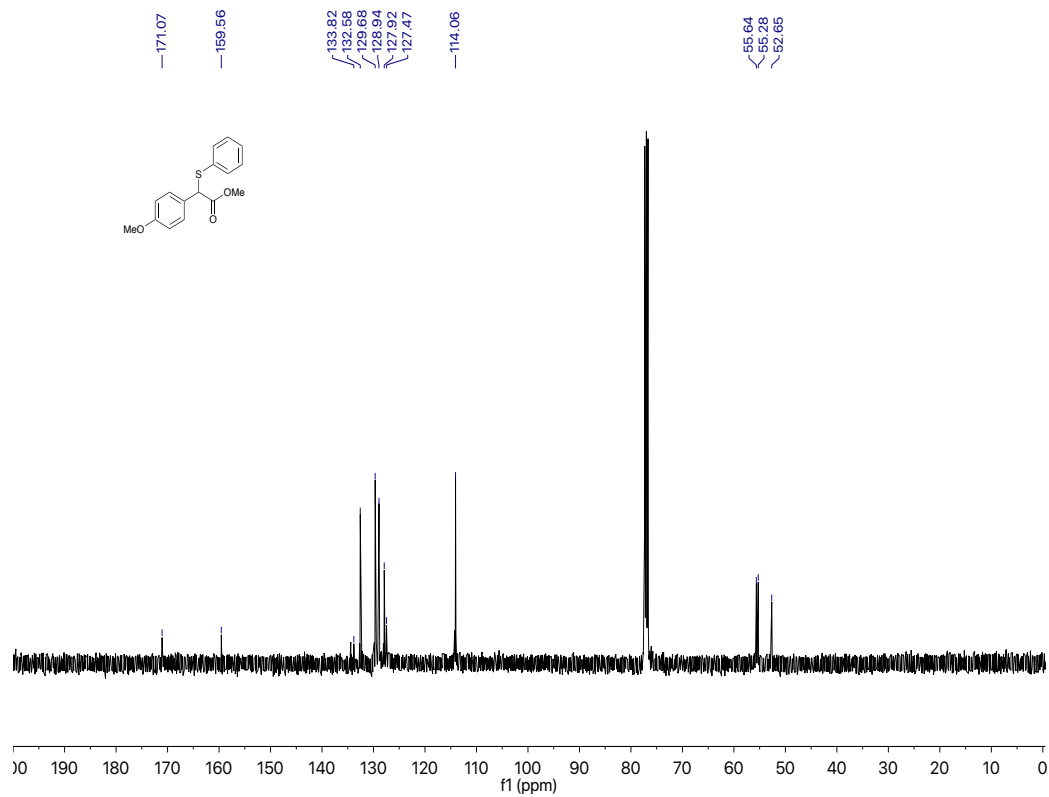
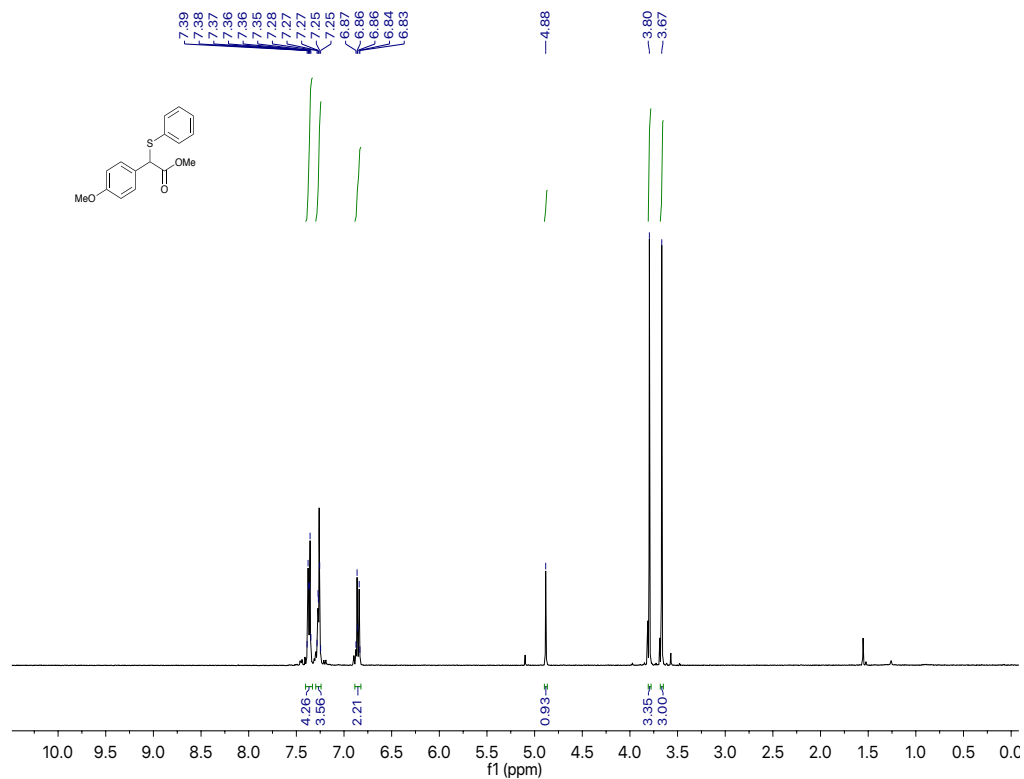
Methyl  $\alpha$ -((*p*-chlorophenyl)thio)- $\alpha$ -phenylacetate (**2ad**)



Methyl  $\alpha$ -(phenylthio)- $\alpha$ -(p-tolyl)acetate (**2ba**)

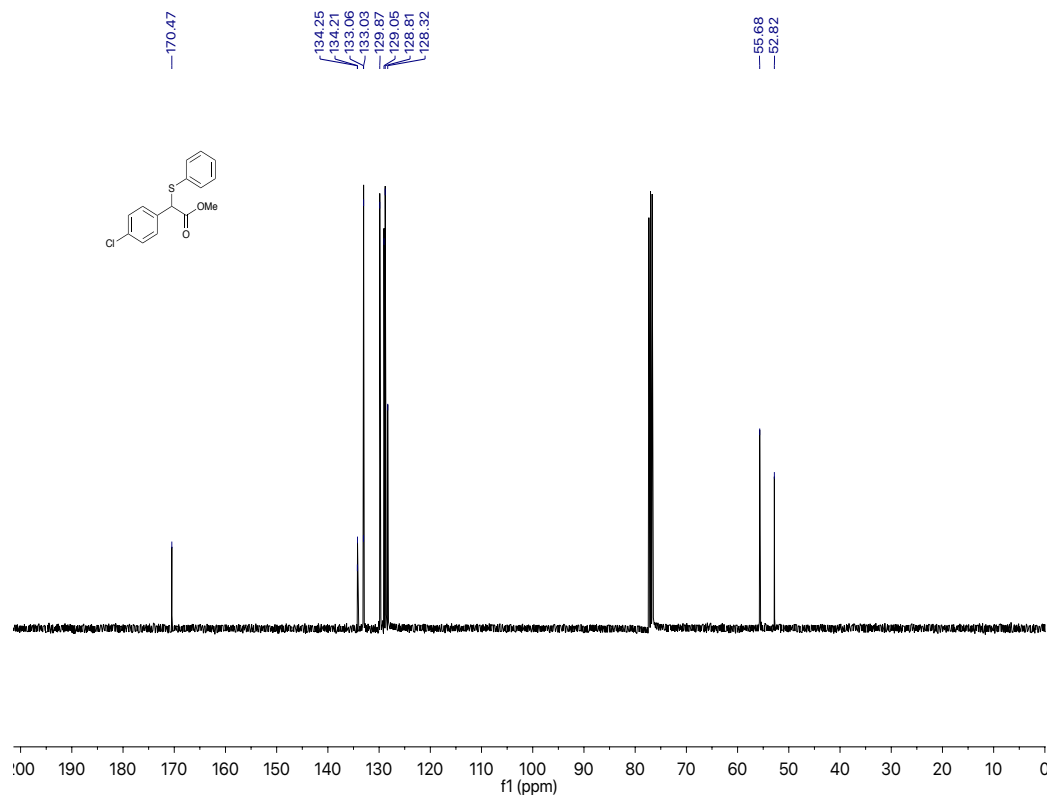
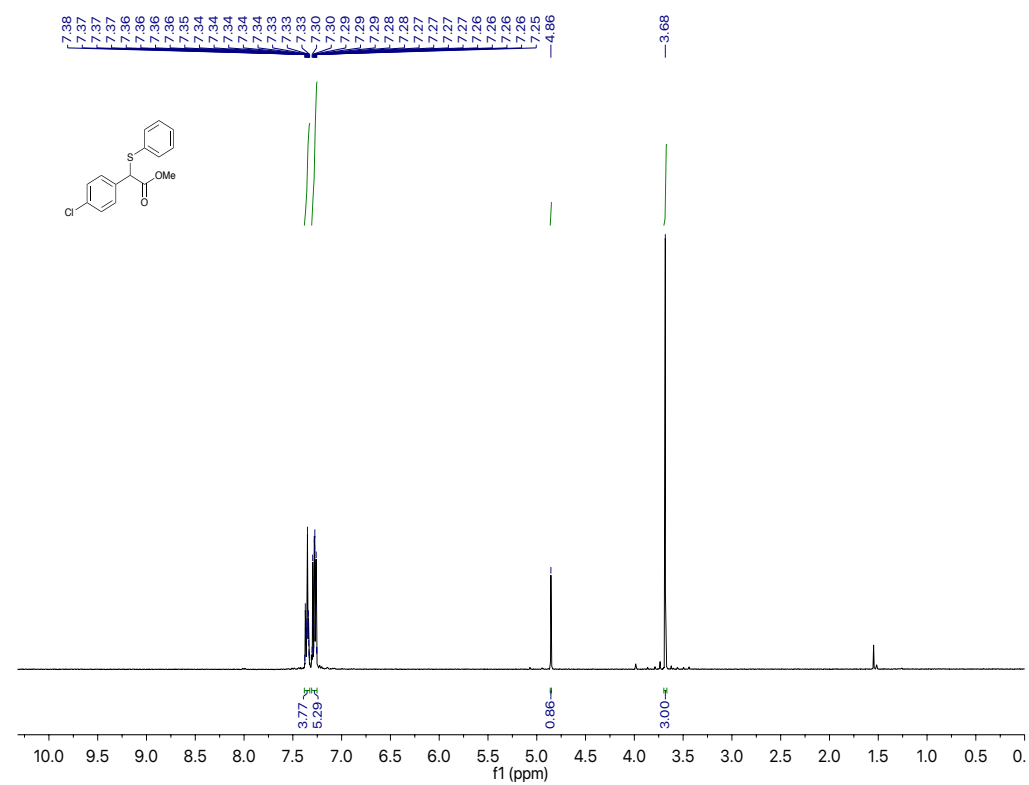


Methyl  $\alpha$ -(*p*-methoxyphenyl)- $\alpha$ -(phenylthio)acetate (**2ca**)

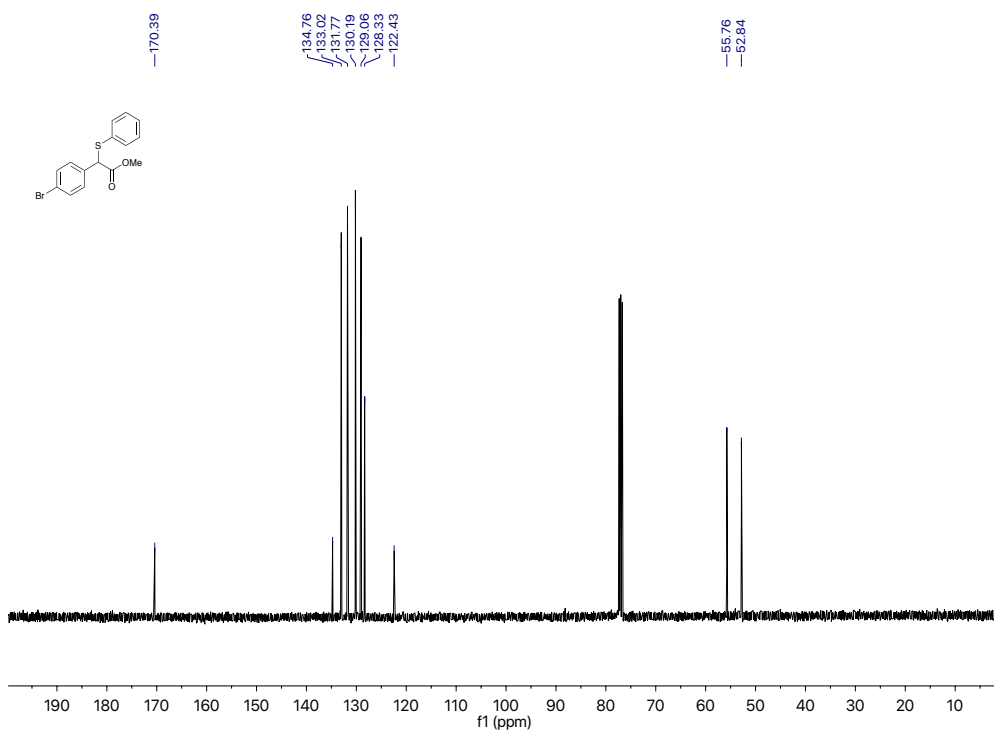
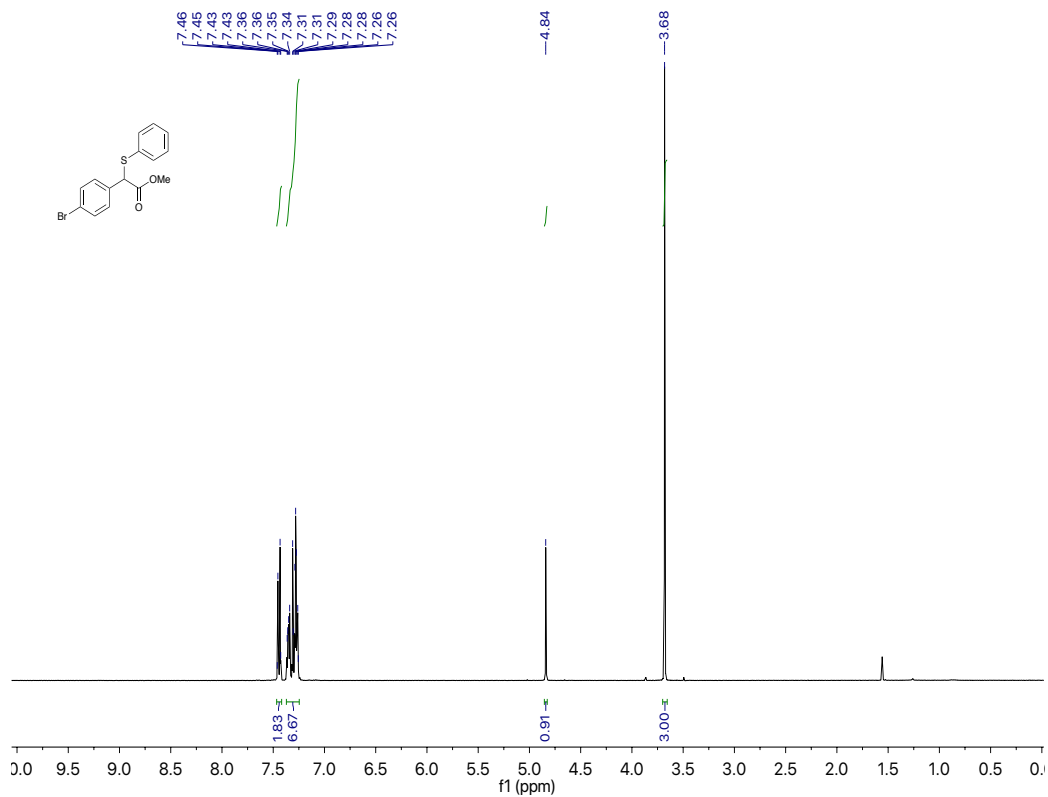




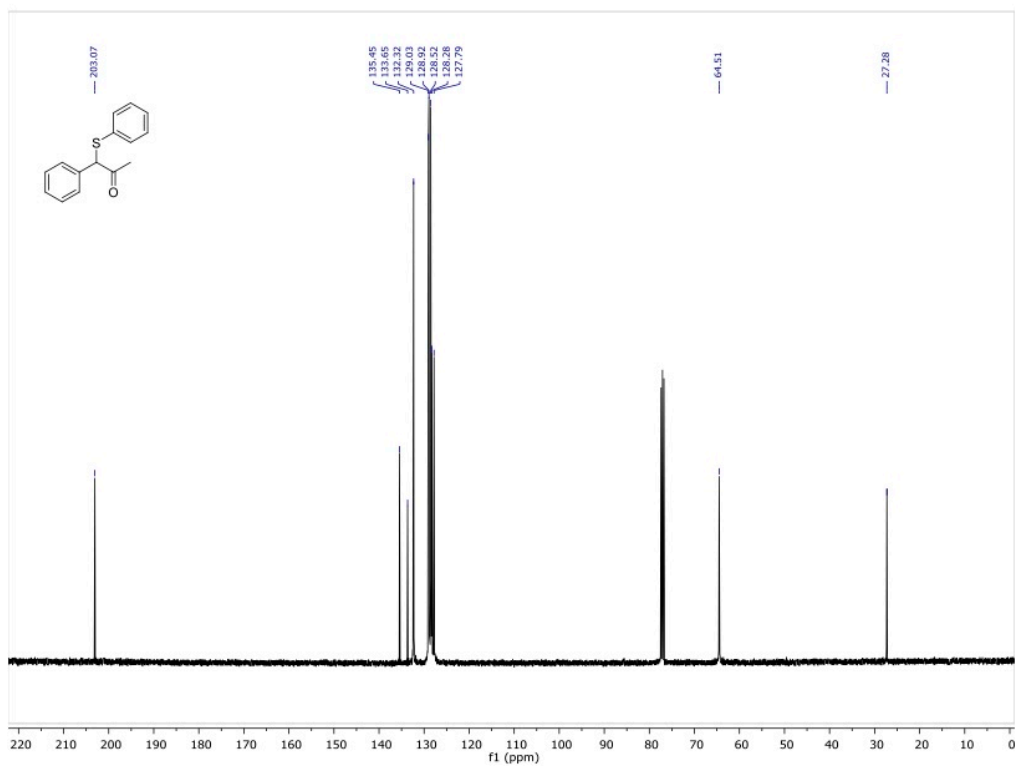
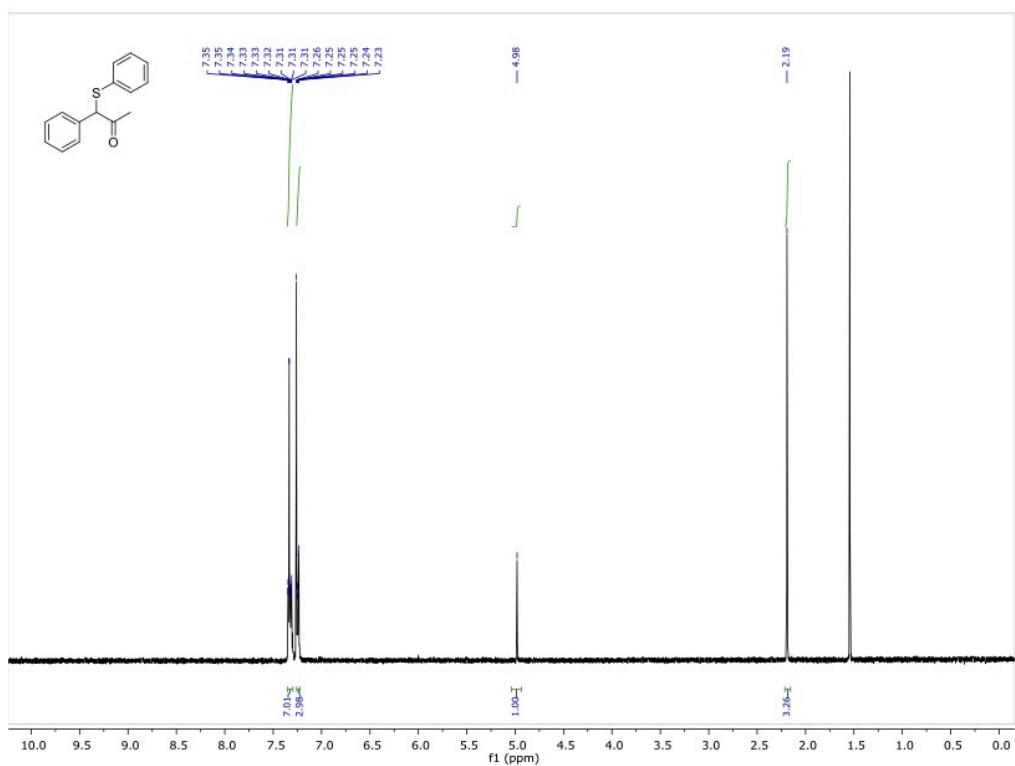
Methyl  $\alpha$ -(*p*-chlorophenyl)- $\alpha$ -(phenylthio)acetate (**2da**)



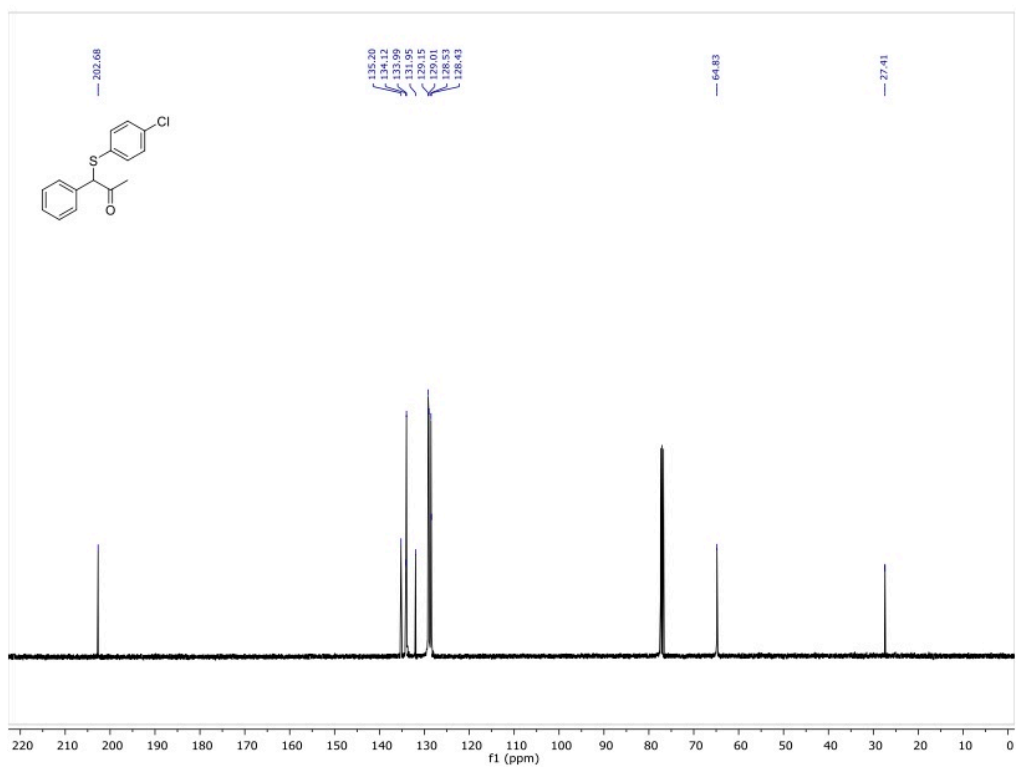
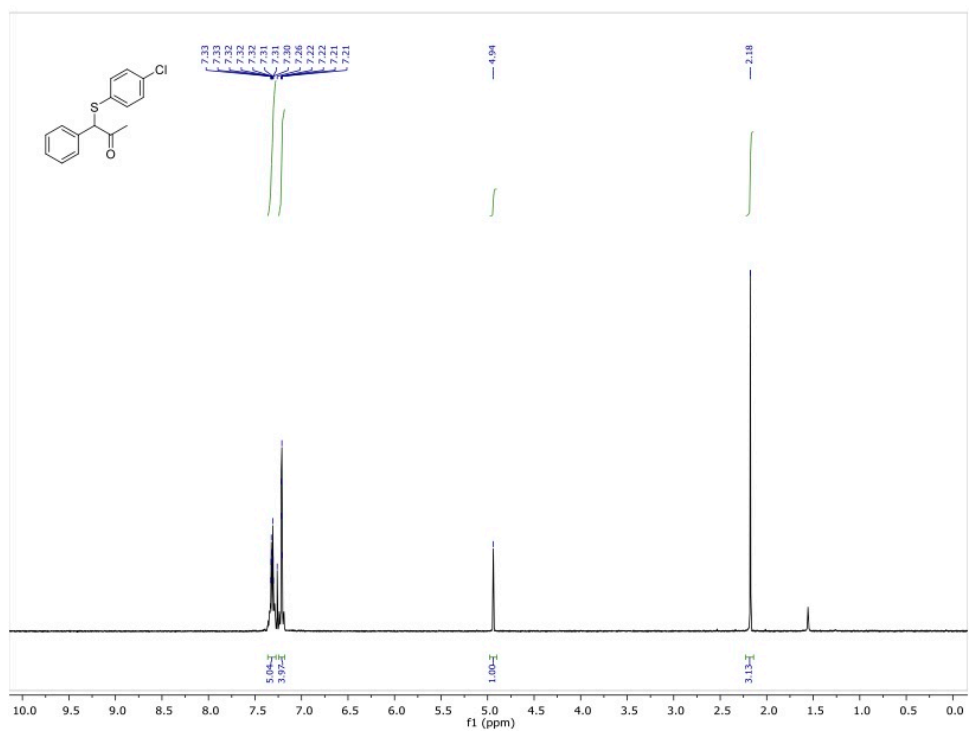
Methyl  $\alpha$ -(*p*-bromophenyl)- $\alpha$ -(phenylthio)acetate (**2ea**)



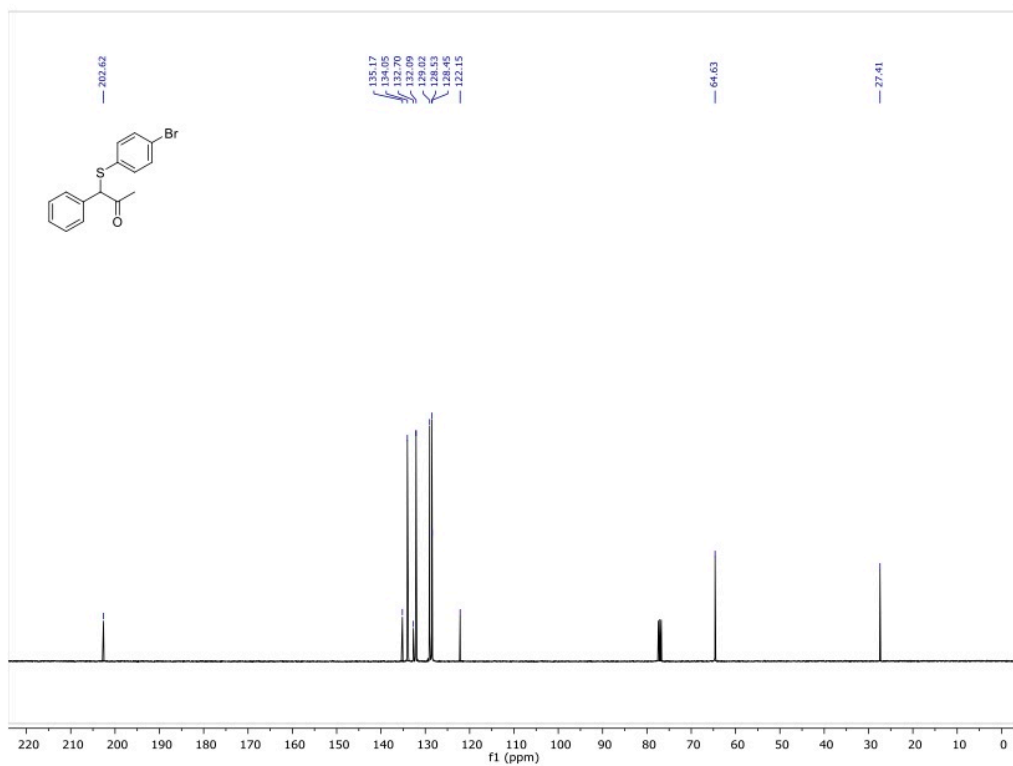
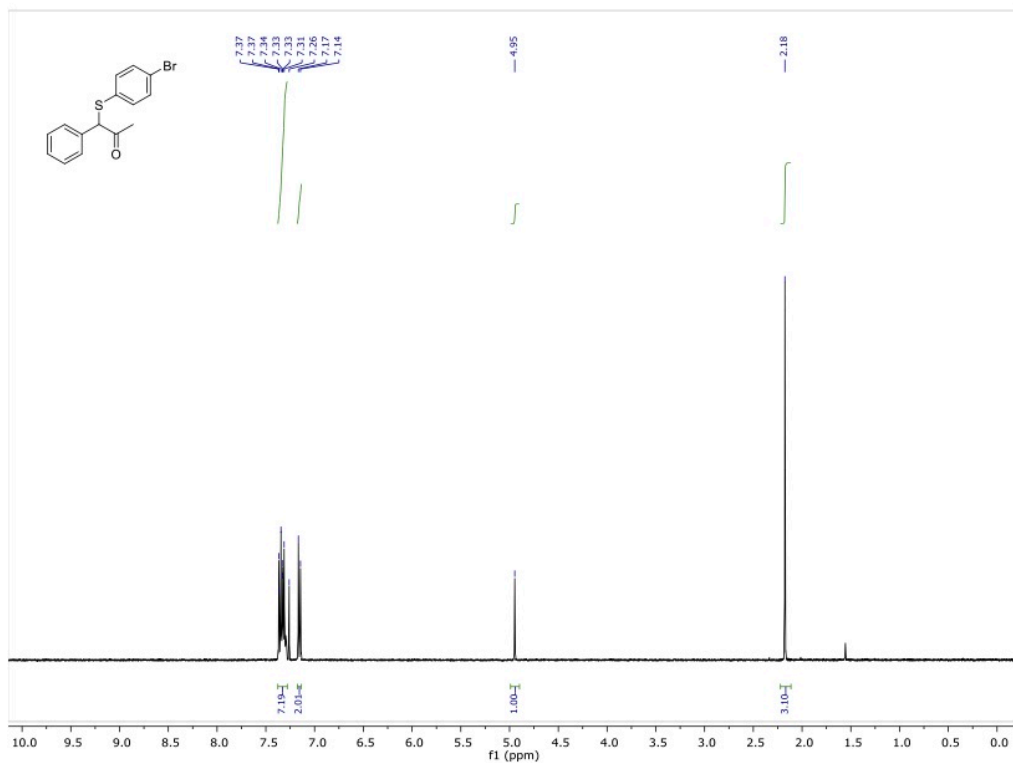
1-(Phenylthio)-1-phenylacetone (**4a**)



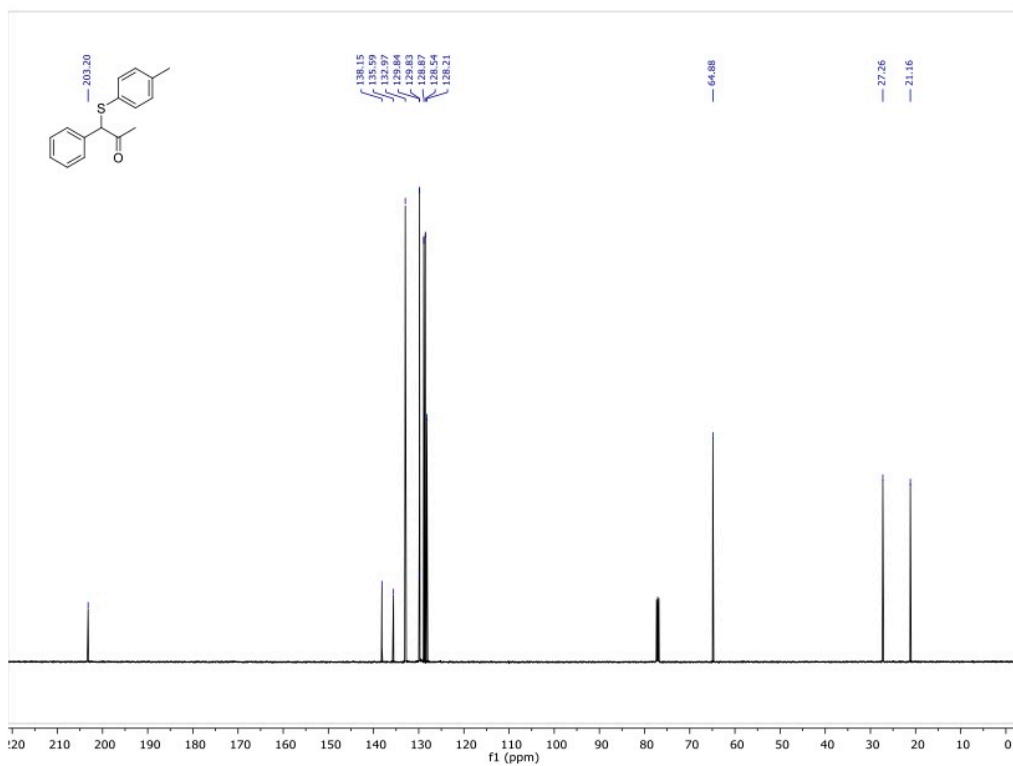
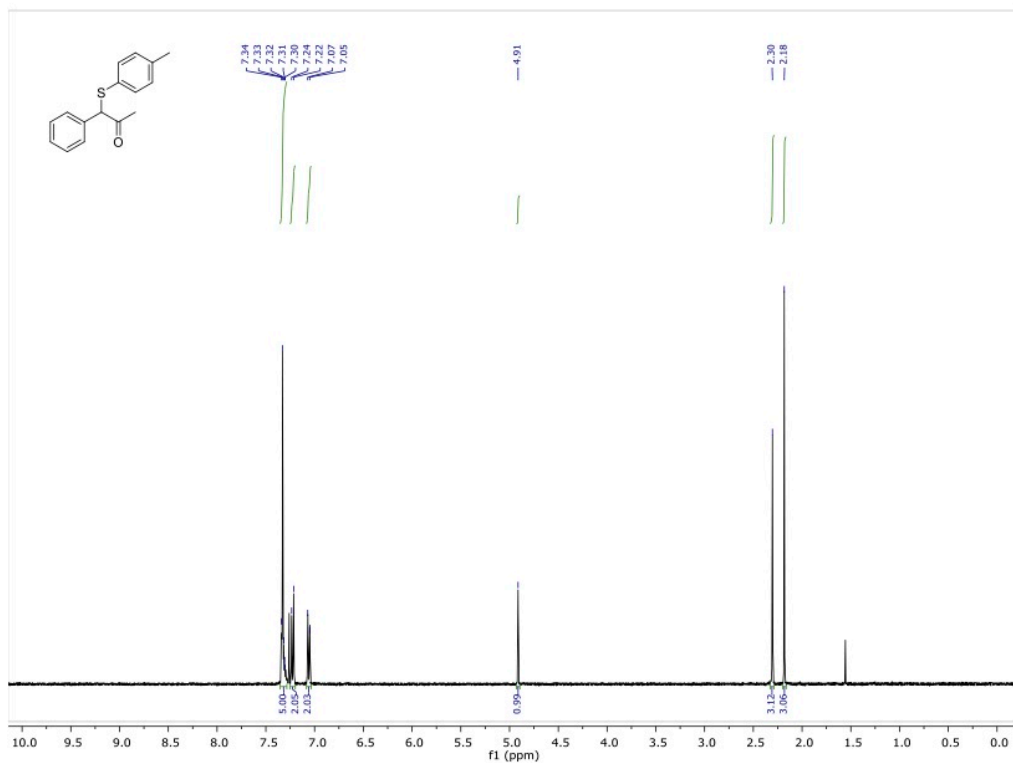
1-[(4-Chlorophenyl)thio]-1-phenylacetone (**4b**)



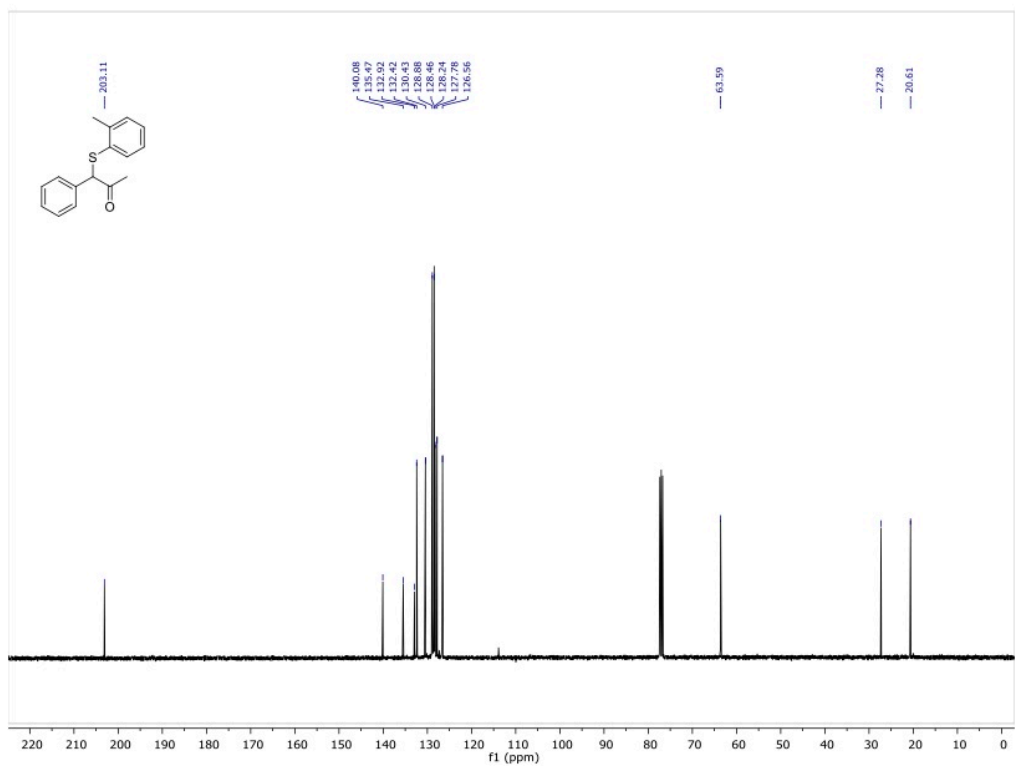
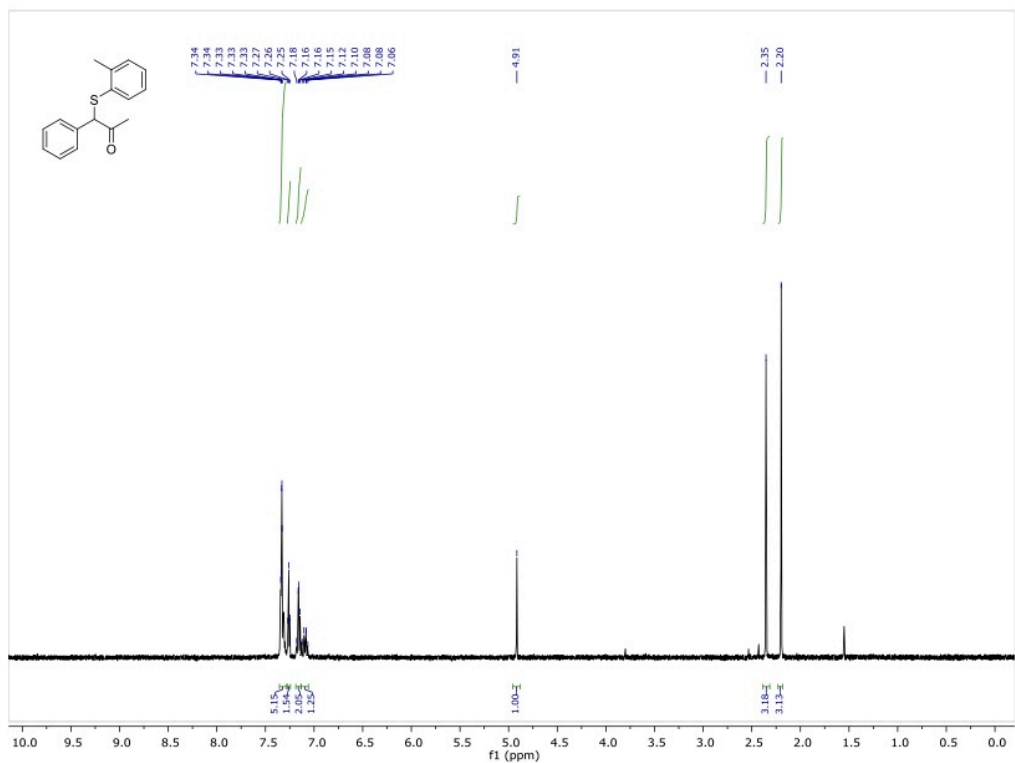
1-[(4-Bromophenyl)thio]-1-phenylacetone (**4c**)



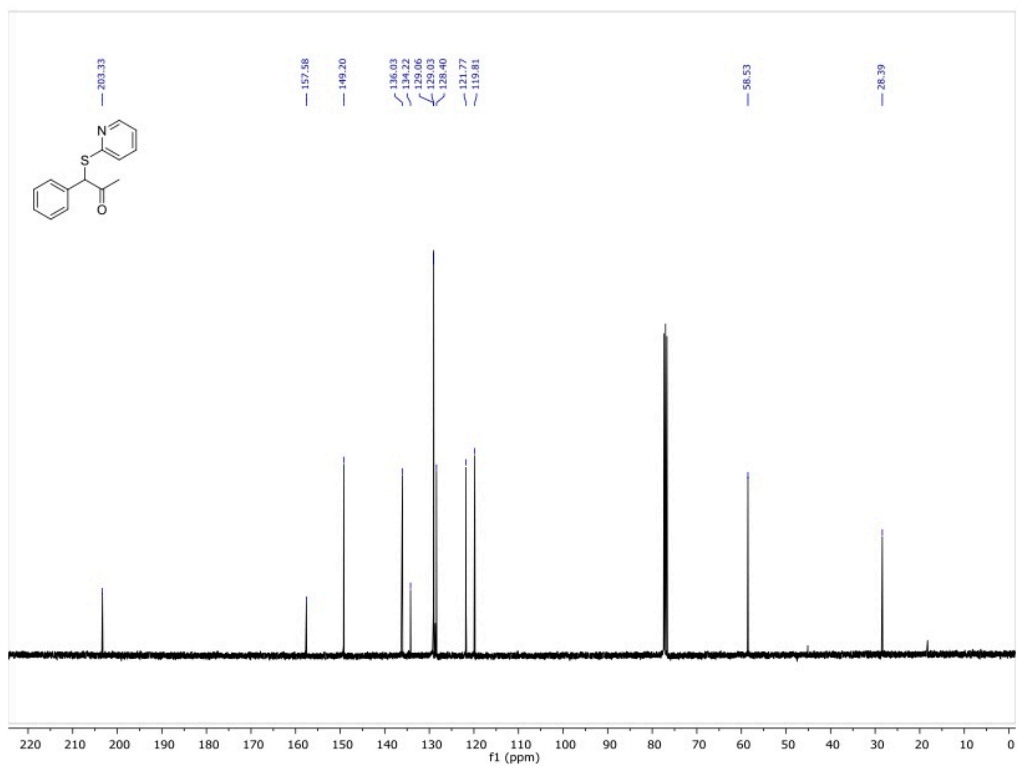
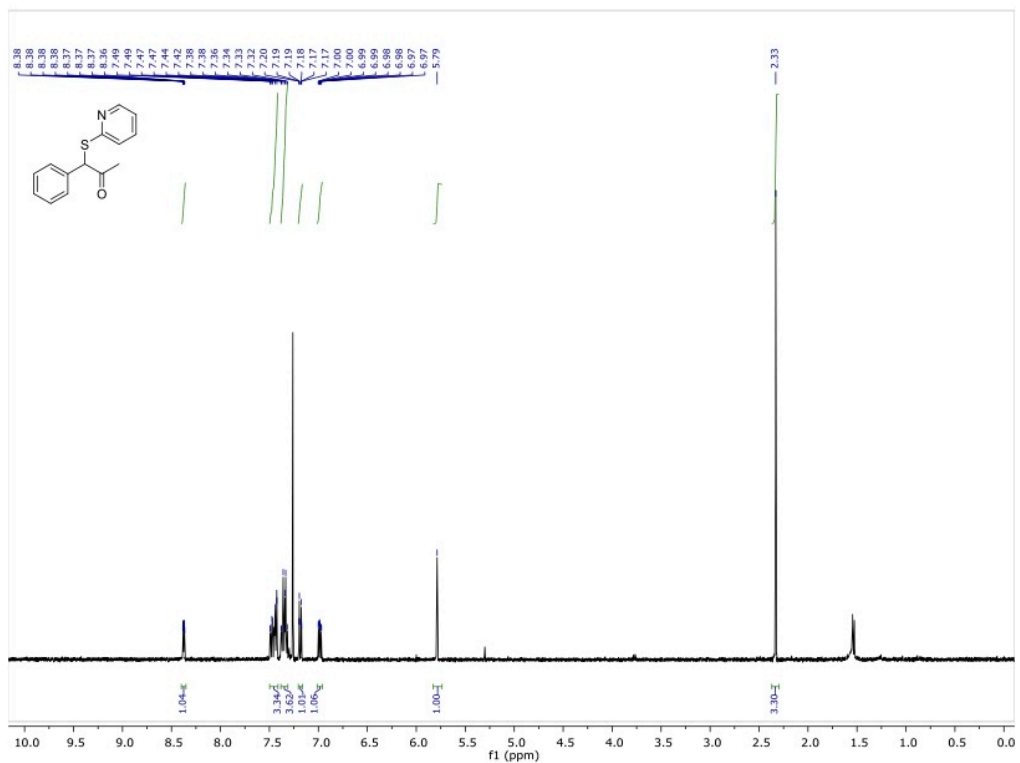
1-[(4-Methylphenyl)thio]-1-phenylacetone (**4d**)



1-[(2-Methylphenyl)thio]-1-phenylacetone (**4e**)

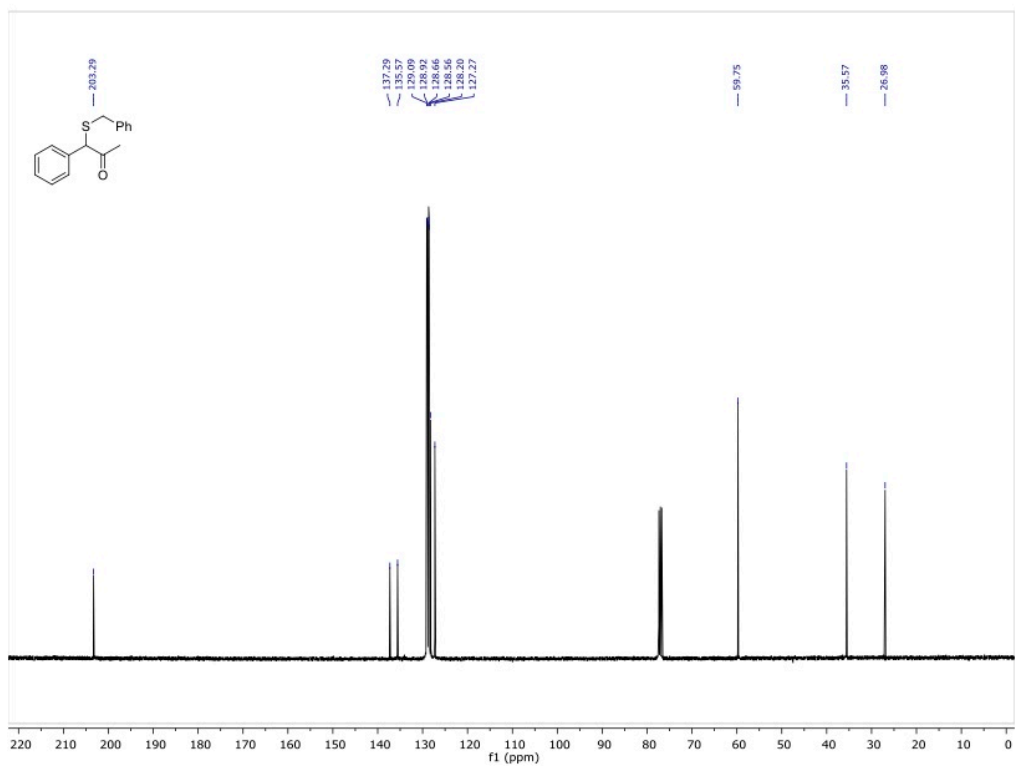
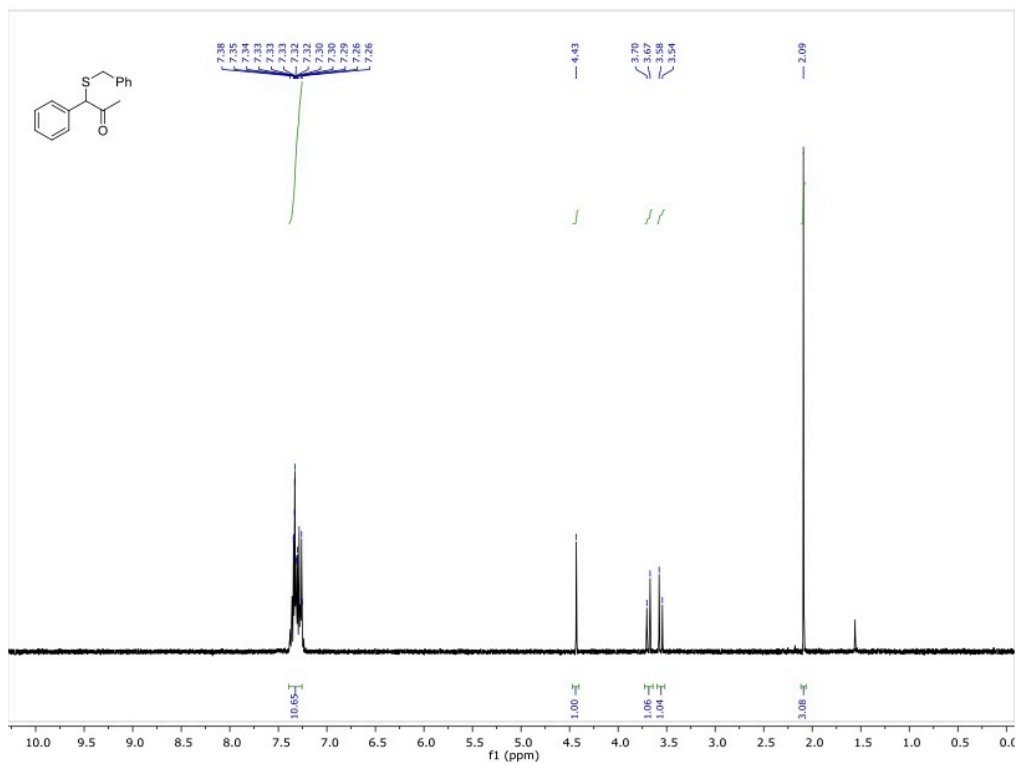


1-[(2-Pyridinyl)thio]-1-phenylacetone (**4f**)

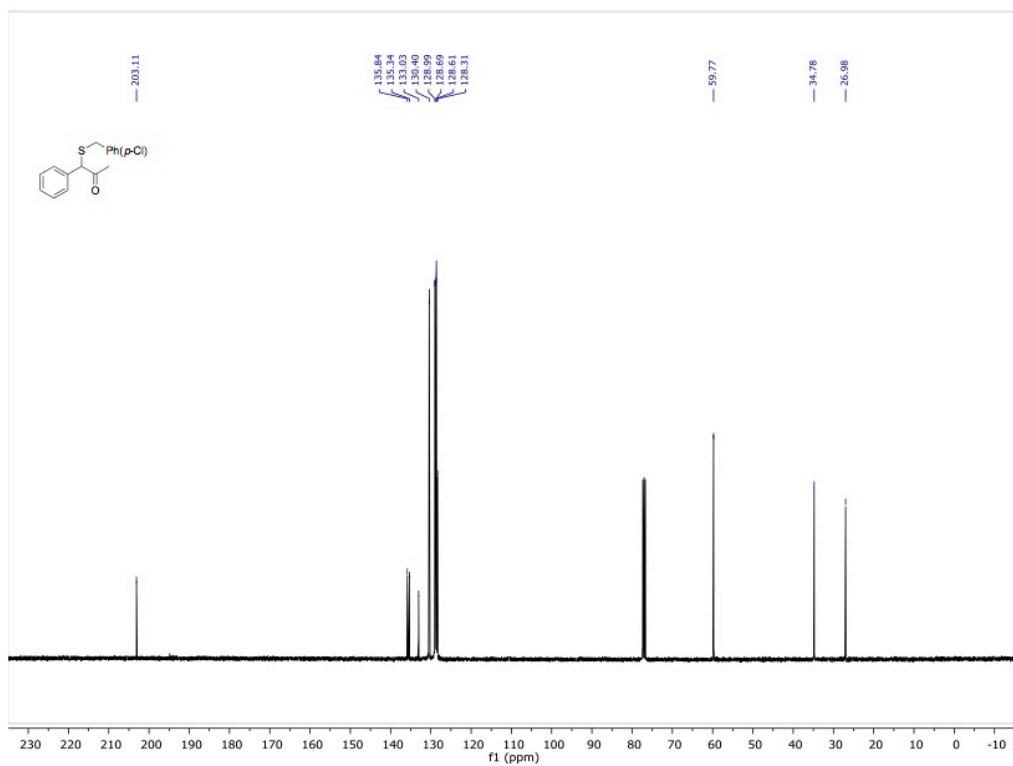
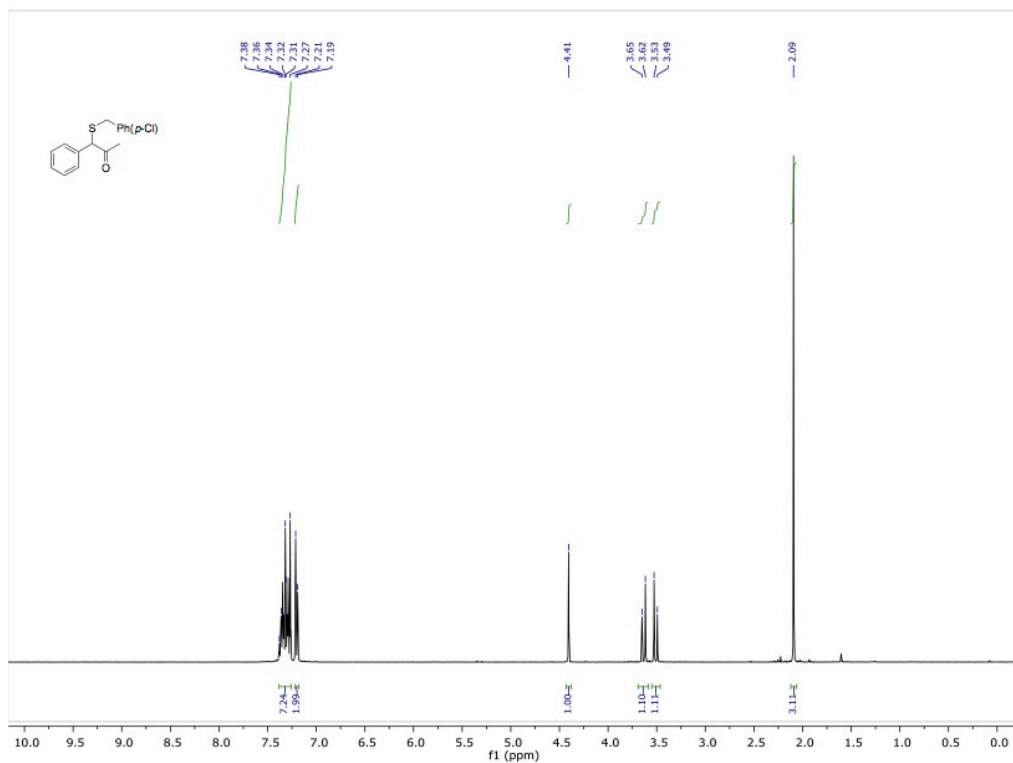




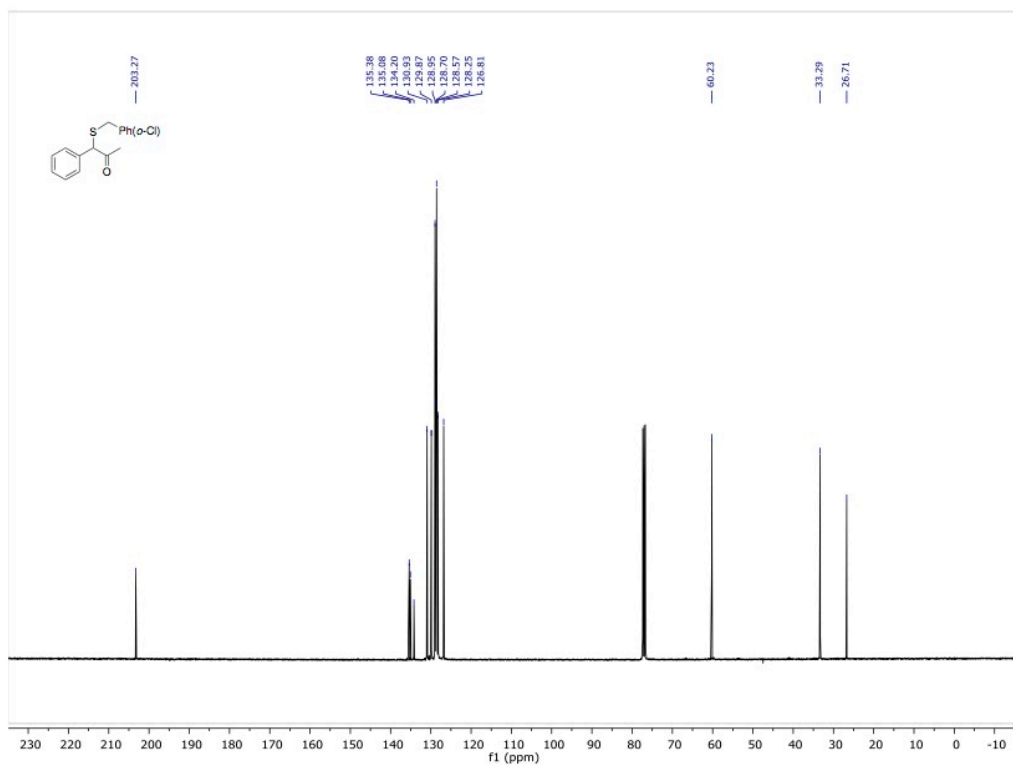
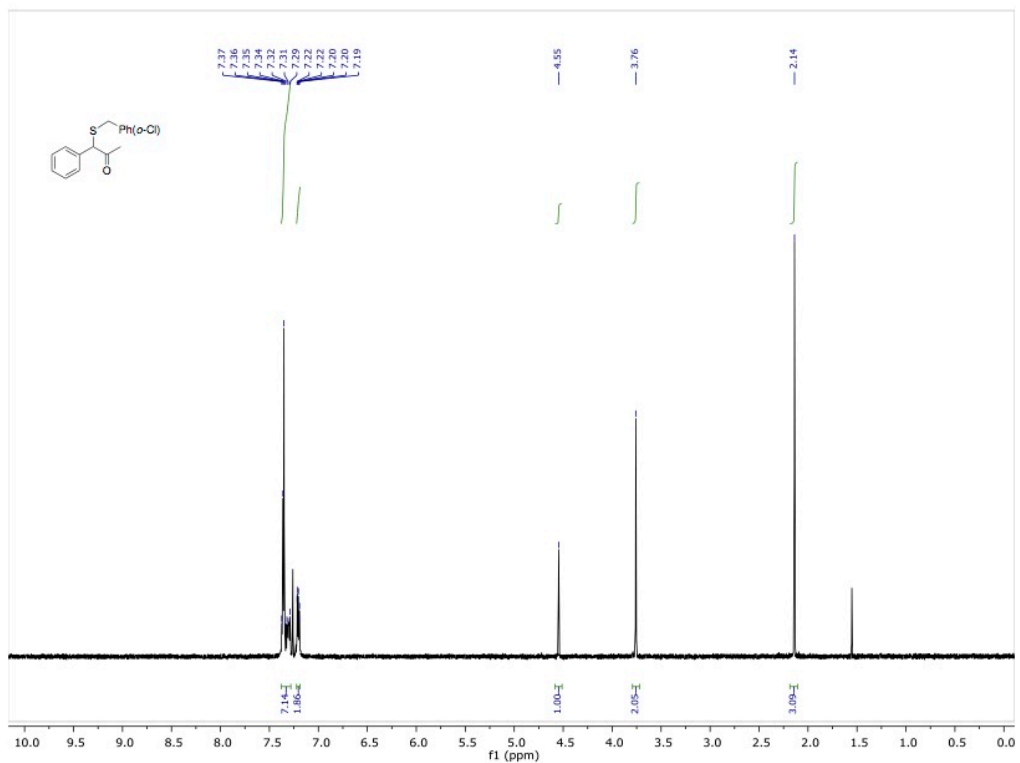
1-(Benzylthio)-1-phenylacetone (**4g**)



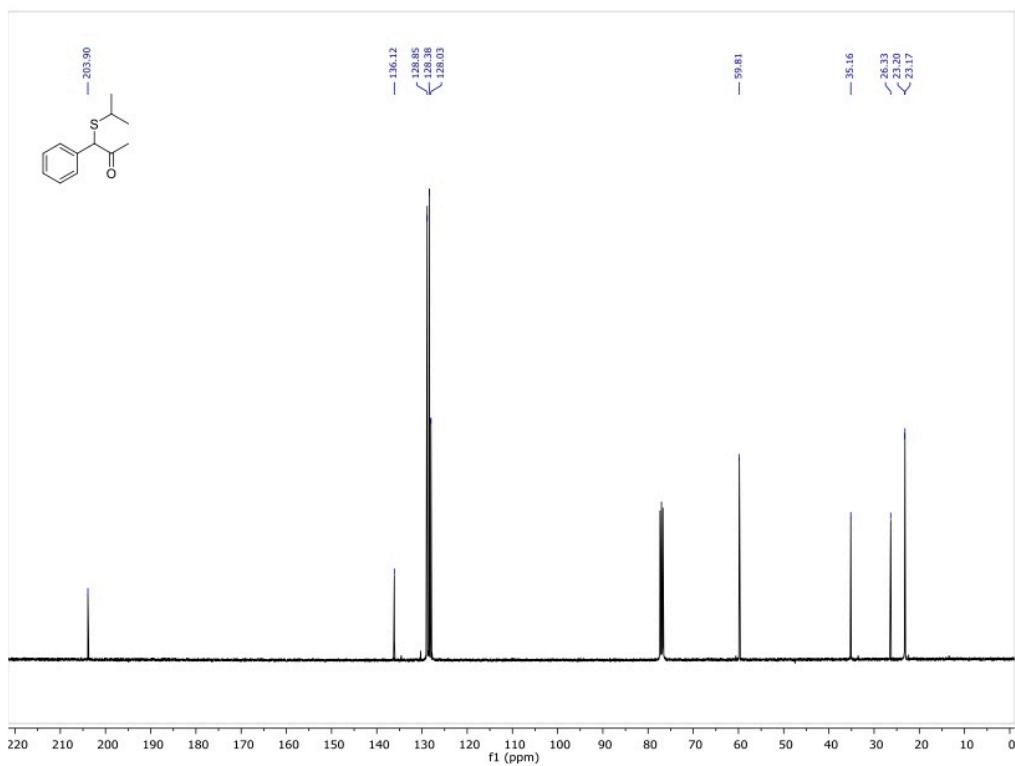
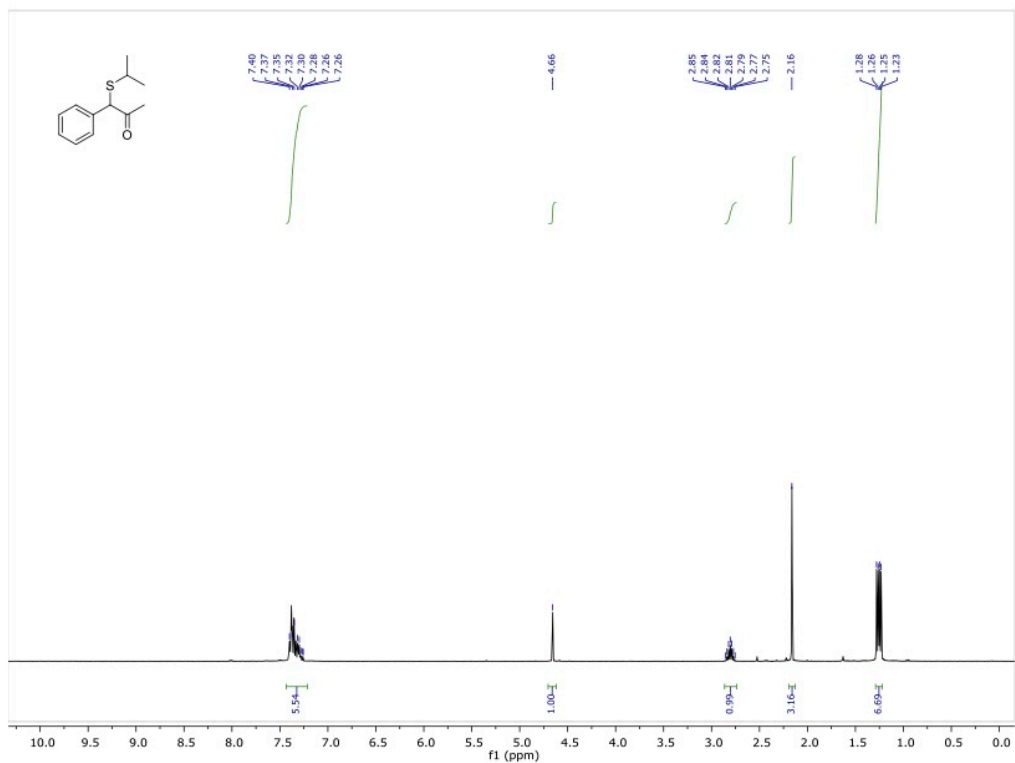
1-[(4-Chlorobenzyl)thio]-1-phenylacetone (**4h**)



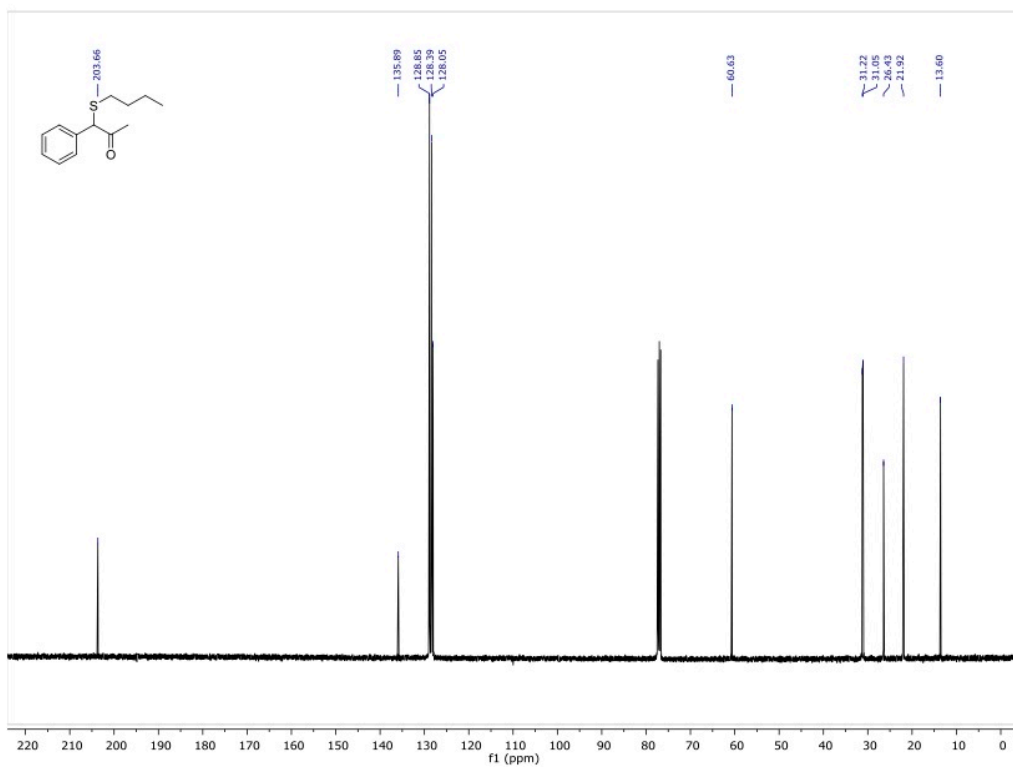
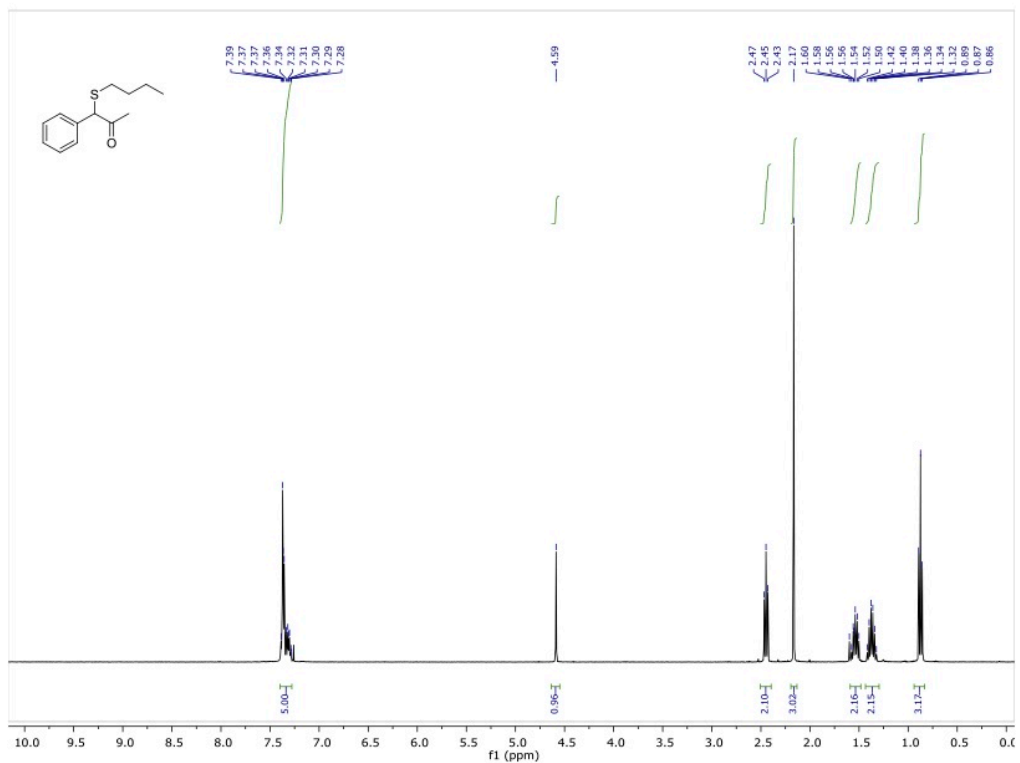
1-[(2-Chlorobenzyl)thio]-1-phenylacetone (**4i**)



1-(Isopropylthio)-1-phenylacetone (**4j**)



1-(Butylthio)-1-phenylacetone (**4k**)



Methyl 2-phenyl-2-(phenylthio)pent-4-enoate (**6a**)

