

Supporting Information

Metal-free oxidative coupling of aryl acetylene with elemental sulphur and amines: A facile access to α -ketothioamides

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Table of contents

1 Experimental Section

1.1 General information.....S2

1.2 Synthesis of α -ketothioamidesS2

2 ¹H and ¹³C data of the compoundsS2

3 References.....S6

4 Copies of ¹H and ¹³C NMR Spectra.....S8

1. Experimental Section

1.1. General Information

All starting materials and commercial reagent were purchased from Alfa Aesar, Sigma Aldrich, Avra, Spectrochem, TCI. Thin Layer Chromatography plates were visualized by exposure to ultraviolet light (UV) with 254 nm of wavelength and then further analyzed by using iodine chamber. Thin-layer chromatography was performed using pre-coated plates. Column chromatography was performed in 120 to 200 mesh size silica gel. The reactions were carried out in round bottom flask and sealed tube. and all NMR spectra were recorded by Bruker Avance 400 spectrometer (^1H at 400 MHz and ^{13}C at 100 MHz). Chemical shifts for ^1H NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 ; δ 7.26 ppm). Similarly, ^{13}C NMR spectra have been reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl_3 ; δ 77.0 ppm). The ^1H NMR and ^{13}C NMR of the known products were compared with literature reports.

1.2 Synthesis of 2-morpholino-1-phenyl-2-thioxoethan-1-one (4a):

Phenylacetylene (**1**, 1 mmol, 102 mg), morpholine (**2**, 2 mmol, 174 mg), elemental sulphur (**3**, 2 mmol) was mixed in a sealed tube. Then the mixture was stirred after the addition of the iodine (253 mg, 1 equiv.) and DMSO solvent (2 mL) at 80 °C for 12 h under open atmosphere. After completion, monitoring by TLC, the mixture was cooled to room temperature and 20 mL of cold water was added to the mixture. then extracted with EtOAc three times (3×20 mL). The extract was washed with 10% Na_2SO_3 solution (w/w), dried over anhydrous Na_2SO_4 and evaporation. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **4a**.

2-morpholino-1-phenyl-2-thioxoethan-1-one (4a):¹ Yield: 80%, 188 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.62 (dt, $J = 8.7, 1.2$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 4.40 – 4.25 (m, 2H), 3.97 – 3.84 (m, 2H), 3.75 – 3.66 (m, 2H), 3.63 – 3.56 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.71, 187.91, 134.47, 133.27, 129.85, 128.98, 66.44 (d, $J = 12.0$ Hz), 51.94, 47.13.

2-morpholino-2-thioxo-1-(p-tolyl)ethan-1-one (4b):¹ Yield: 74%, 184 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.2$ Hz, 2H), 7.29 (d,

$J = 8.0$ Hz, 2H), 4.35 – 4.28 (m, 2H), 3.92 – 3.87 (m, 2H), 3.71 – 3.64 (m, 2H), 3.61 – 3.56 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.00, 187.91, 145.75, 130.74, 129.99, 129.71, 66.45 (d, $J = 12.4$ Hz), 51.91, 47.10, 21.90.

1-(4-fluorophenyl)-2-morpholino-2-thioxoethan-1-one (4c):² Yield: 77%, 194 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dd, $J = 8.9, 5.3$ Hz, 2H), 7.17 (t, $J = 8.6$ Hz, 2H), 4.35 – 4.30 (m, 2H), 3.94 – 3.86 (m, 2H), 3.74 – 3.66 (m, 2H), 3.63 – 3.56 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.18, 186.38, 167.73, 165.17, 132.67 (d, $J = 9.7$ Hz), 129.74 (d, $J = 2.9$ Hz), 116.40, 116.18, 66.45 (d, $J = 14.9$ Hz), 51.96, 47.18.

1-(4-chlorophenyl)-2-morpholino-2-thioxoethan-1-one (4d):¹ Yield: 75%, 201 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.5$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 4.35 – 4.29 (m, 2H), 3.93 – 3.87 (m, 2H), 3.73 – 3.66 (m, 2H), 3.63 – 3.56 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.94, 186.44, 141.04, 131.75, 131.21, 129.35, 66.45 (d, $J = 14.8$ Hz), 51.96, 47.18.

1-(3-bromophenyl)-2-morpholino-2-thioxoethan-1-one (4e):³ Yield: 70%, 218 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (t, $J = 1.8$ Hz, 1H), 7.90 (d, $J = 10.3$ Hz, 1H), 7.73 (d, $J = 7.0$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 4.36 – 4.29 (m, 2H), 3.93 – 3.87 (m, 2H), 3.74 – 3.67 (m, 2H), 3.63 – 3.57 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.51, 185.95, 137.23, 135.24, 132.36, 130.50, 128.44, 123.21, 66.45 (d, $J = 13.9$ Hz), 52.00, 47.22.

1-(4-bromophenyl)-2-morpholino-2-thioxoethan-1-one (4f):² Yield: 72%, 224 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 8.6$ Hz, 1H), 7.68 – 7.59 (m, 1H), 4.36 – 4.23 (m, 1H), 3.96 – 3.82 (m, 1H), 3.74 – 3.65 (m, 1H), 3.65 – 3.51 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.85, 186.58, 132.25 (d, $J = 15.9$ Hz), 131.24, 129.87, 66.44 (d, $J = 15.1$ Hz), 51.96, 47.18.

1-(2-methoxyphenyl)-2-morpholino-2-thioxoethan-1-one (4g):⁴ Yield: 66%, 174 mg, purified by petroleum ether/EtOAc = 5:1; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.55 (ddd, $J = 8.5, 7.4, 1.8$ Hz, 1H), 7.16 – 7.05 (m, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 4.32 – 4.19 (m, 2H), 3.91 – 3.88 (m, 2H), 3.87 (s, 3H), 3.79 – 3.74 (m, 2H), 3.71 – 3.65 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.33, 186.62, 159.15, 135.54, 131.82, 121.53, 112.56, 66.24, 66.00, 56.14, 51.71, 46.95.

2-morpholino-1-(thiophen-2-yl)-2-thioxoethan-1-one (4h):⁴ Yield: 69%, 166 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (ddd, *J* = 6.0, 4.4, 1.1 Hz, 2H), 7.16 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.34 – 4.25 (m, 2H), 3.93 – 3.85 (m, 2H), 3.76 – 3.61 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 194.34, 181.03, 140.34, 136.17, 135.60, 128.64, 66.56, 66.33, 52.02, 47.32.

1-phenyl-2-(piperidin-1-yl)-2-thioxoethan-1-one (4i):¹ Yield: 72%, 187 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.95 (m, 2H), 7.65 – 7.56 (m, 1H), 7.48 (dd, *J* = 10.6, 4.7 Hz, 2H), 4.32 – 4.16 (m, 2H), 3.61 – 3.46 (m, 2H), 1.88 – 1.72 (m, 4H), 1.67 – 1.59 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.46, 188.00, 134.16, 133.47, 129.81, 128.84, 53.01, 48.13, 26.44, 25.36, 24.09.

1-(4-fluorophenyl)-2-(piperidin-1-yl)-2-thioxoethan-1-one (4j):¹ Yield: 67%, 168 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 4.27 – 4.22 (m, 2H), 3.56 – 3.51 (m, 2H), 1.85 – 1.75 (m, 4H), 1.63 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.96, 186.49, 167.57, 165.02, 132.58 (d, *J* = 9.6 Hz), 129.92 (d, *J* = 2.9 Hz), 116.24, 116.02, 53.03, 48.17, 26.50, 25.35, 24.06.

1-(4-chlorophenyl)-2-(piperidin-1-yl)-2-thioxoethan-1-one (4k):¹ Yield: 64%, 170 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.90 (m, 2H), 7.48 – 7.42 (m, 2H), 4.27 – 4.21 (m, 2H), 3.56 – 3.48 (m, 2H), 1.87 – 1.73 (m, 5H), 1.63 (s, 2H), 1.34 – 1.17 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 193.66, 186.57, 140.66, 131.94, 131.16, 129.22, 53.04, 48.18, 29.71, 26.51, 25.37, 24.05.

1-(3-bromophenyl)-2-(piperidin-1-yl)-2-thioxoethan-1-one (4l): Yield: 62%, 192 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (t, *J* = 1.7 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.71 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 4.27 – 4.20 (m, 2H), 3.56 – 3.49 (m, 2H), 1.86 – 1.75 (m, 4H), 1.64 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.29, 186.02, 136.93, 135.44, 132.45, 130.39, 128.41, 123.10, 53.10, 48.21, 29.71, 26.50, 25.37, 24.07. HRMS (ESI) calcd for C₁₃H₁₅BrNOS [M+H]⁺ 312.0052; found 312.0058.

1-(4-bromophenyl)-2-(piperidin-1-yl)-2-thioxoethan-1-one (4m):⁵ Yield: 68%, 210 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 4.35 – 4.17 (m, 1H), 3.64 – 3.43 (m, 1H), 1.90 – 1.69 (m, 2H), 1.63 (d, *J* = 4.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 193.59, 186.67, 132.28 (d, *J* = 15.4 Hz), 131.21, 129.50, 53.05, 48.19, 26.51, 25.37, 24.05.

1-(2-methoxyphenyl)-2-(piperidin-1-yl)-2-thioxoethan-1-one (4n): Yield: 59%, 155 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.96 (m, 1H), 7.56 – 7.49 (m, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.18 (t, *J* = 5.3 Hz, 2H), 3.85 (s, 3H), 3.63 – 3.59 (m, 2H), 1.74 (dd, *J* = 36.3, 5.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 196.79, 186.46, 159.25, 135.29, 131.86, 124.38, 121.33, 112.52, 56.03, 52.81, 47.96, 25.61, 25.23, 24.15. HRMS (ESI) calcd for C₁₄H₁₈NO₂S [M+H]⁺ 264.1053; found 264.1060.

2-(piperidin-1-yl)-1-(thiophen-2-yl)-2-thioxoethan-1-one (4o):⁵ Yield: 65%, 155 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (ddd, *J* = 6.0, 4.4, 1.1 Hz, 2H), 7.15 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.33 – 4.04 (m, 2H), 3.67 – 3.38 (m, 2H), 1.89 – 1.71 (m, 4H), 1.69 – 1.58 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 193.04, 181.31, 140.49, 135.73, 135.29, 128.54, 53.10, 48.32, 26.50, 25.33, 24.05.

2-(4-(2-methoxyphenyl)piperazin-1-yl)-1-phenyl-2-thioxoethan-1-one (4p): Gummy mass, Yield: 71%, 241 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 7.89 (m, 2H), 7.69 – 7.56 (m, 1H), 7.49 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.06 (ddd, *J* = 8.0, 7.1, 2.1 Hz, 1H), 6.99 – 6.80 (m, 3H), 4.62 – 4.42 (m, 2H), 3.87 (s, 3H), 3.82 – 3.68 (m, 2H), 3.36 – 3.22 (m, 2H), 3.09 (dd, *J* = 5.9, 4.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.44, 188.02, 152.24, 139.72, 134.33, 133.42, 129.90, 128.93, 124.10, 121.14, 118.70, 111.46, 55.48, 51.92, 50.70, 50.05, 47.13. HRMS (ESI) calcd for C₁₉H₂₁N₂O₂S [M+H]⁺ 341.1318; found 341.1323.

1-(3-methoxyphenyl)-2-(4-(2-methoxyphenyl)piperazin-1-yl)-2-thioxoethan-1-one (4q): Gummy mass, Yield: 63%, 233 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.49 – 7.38 (m, 1H), 6.98 (ddd, *J* = 6.5, 6.0, 3.1 Hz, 2H), 6.90 – 6.80 (m, 4H), 4.40 – 4.25 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.74 (d, *J* = 4.9 Hz, 2H), 3.20 – 3.13 (m, 2H), 3.10 – 3.03 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 196.90, 185.58, 158.14, 151.19, 138.93, 134.45, 130.72, 123.30, 122.94, 120.33, 120.09, 117.49, 111.47, 110.39, 55.04, 54.44, 50.59, 48.90 (d, *J* = 9.0 Hz), 45.91. HRMS (ESI) calcd for C₂₀H₂₃N₂O₃S [M+H]⁺ 371.1424; found 371.1430.

1-(4-chlorophenyl)-2-(4-(2-methoxyphenyl)piperazin-1-yl)-2-thioxoethan-1-one (4r): Gummy mass, Yield: 70%, 261 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.12 – 6.99 (m, 1H), 6.99 – 6.83 (m, 3H), 4.55 – 4.41 (m, 2H), 3.87 (s, 3H), 3.80 – 3.65 (m, 2H), 3.33 – 3.16 (m, 2H), 3.16 – 2.98 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.68, 186.55, 152.24, 140.89, 139.64, 131.92,

131.24, 129.30, 124.16, 121.15, 118.71, 111.47, 55.49, 51.95, 50.74, 50.06, 47.19. HRMS (ESI) calcd for C₁₉H₂₀ClN₂O₂S [M+H]⁺ 375.0929; found 375.0933.

1-(3-bromophenyl)-2-(4-(2-methoxyphenyl)piperazin-1-yl)-2-thioxoethan-1-one (4s):

Gummy mass, Yield: 66%, 275 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (t, *J* = 1.7 Hz, 1H), 7.99 – 7.82 (m, 1H), 7.73 (ddd, *J* = 8.0, 1.8, 0.9 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.15 – 7.03 (m, 1H), 6.98 – 6.76 (m, 3H), 4.56 – 4.39 (m, 2H), 3.87 (s, 3H), 3.81 – 3.62 (m, 2H), 3.30 (dd, *J* = 17.5, 12.4 Hz, 2H), 3.09 (dd, *J* = 16.0, 11.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.28, 186.05, 152.27, 139.65, 137.09, 135.42, 132.52, 130.47, 128.49, 124.17, 123.19, 121.16, 118.77, 111.50, 55.51, 52.00, 50.72, 50.04, 47.22. HRMS (ESI) calcd for C₁₉H₂₀BrN₂O₂S [M+H]⁺ 419.0423; found 419.0429.

1-(4-bromophenyl)-2-(4-(2-methoxyphenyl)piperazin-1-yl)-2-thioxoethan-1-one (4t):

Gummy mass, Yield: 69%, 288 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 – 6.81 (m, 3H), 4.53 – 4.41 (m, 2H), 3.94 – 3.81 (m, 3H), 3.82 – 3.65 (m, 2H), 3.35 – 3.16 (m, 2H), 3.16 – 2.99 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.60, 186.69, 152.22, 139.62, 132.31 (d, *J* = 3.3 Hz), 131.28, 129.73, 124.16, 121.14, 118.70, 111.45, 55.48, 51.94, 50.73, 50.05, 47.18. HRMS (ESI) calcd for C₁₉H₂₀BrN₂O₂S [M+H]⁺ 419.0423; found 419.0430.

1-phenyl-2-thiomorpholino-2-thioxoethan-1-one (4u):⁶ Yield: 75%, 188 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.08 – 7.89 (m, 9H), 7.62 (ddd, *J* = 8.7, 2.5, 1.3 Hz, 5H), 7.50 (t, *J* = 7.7 Hz, 10H), 4.59 (s, 10H), 3.88 – 3.81 (m, 11H), 2.90 (t, *J* = 5.1 Hz, 10H), 2.71 (d, *J* = 2.6 Hz, 11H). ¹³C NMR (101 MHz, CDCl₃) δ 196.11, 187.74, 134.43, 133.23, 129.91, 128.93, 54.64, 49.70, 28.24, 27.30.

1-(4-bromophenyl)-2-thiomorpholino-2-thioxoethan-1-one (4v): Gummy mass, Yield: 67%, 219 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.6 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 4.57 (s, 1H), 3.92 – 3.71 (m, 1H), 2.89 (t, *J* = 5.1 Hz, 1H), 2.70 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 195.22, 186.42, 132.21 (d, *J* = 20.0 Hz), 131.29, 129.85, 54.69, 49.78, 28.31, 27.31. HRMS (ESI) calcd for C₁₂H₁₃BrNOS₂ [M+H]⁺ 329.9616; found 329.9622.

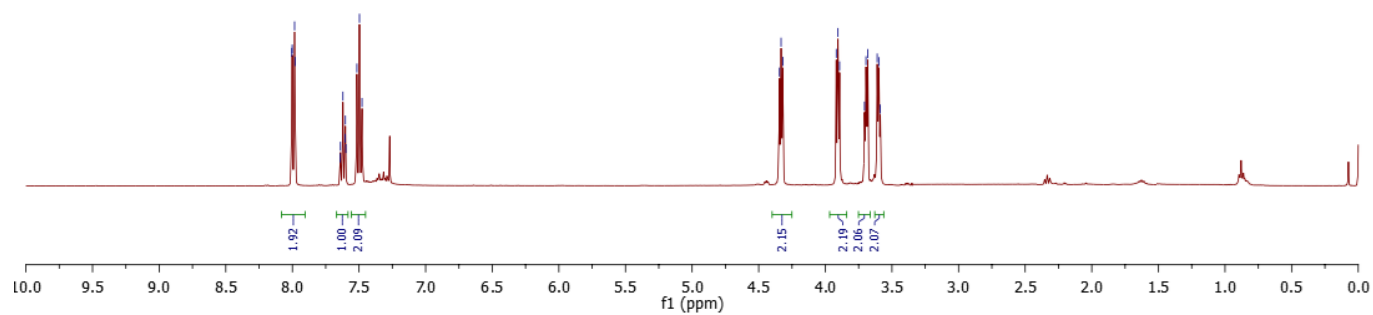
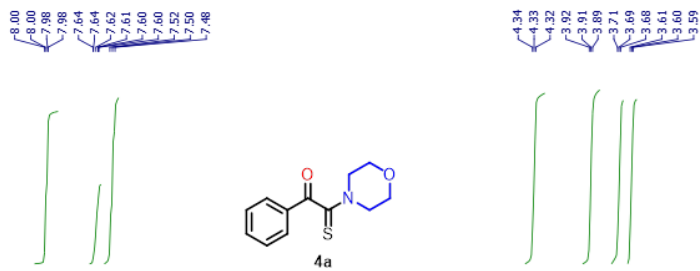
2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-phenyl-2-thioxoethan-1-one (4w):⁷ Yield: 54%, 151 mg, purified by petroleum ether/EtOAc = 5:1; ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.75 (m, 2H), 7.62 – 7.47 (m, 1H), 7.41 (dd, *J* = 15.6, 8.1 Hz, 2H), 7.25 – 7.06 (m, 4H), 5.26 (s, 1H), 4.63 (s, 1H), 4.35 (t, *J* = 6.3 Hz, 1H), 3.86 – 3.69 (m, 1H), 2.95 (dt, *J* = 91.5, 6.0 Hz, 2H). ¹³C

NMR (101 MHz, CDCl₃) δ 195.75, 188.03, 134.31 (d, $J = 6.8$ Hz), 133.41, 133.07, 131.09 (d, $J = 16.3$ Hz), 129.94 (d, $J = 4.3$ Hz), 128.91 (d, $J = 3.5$ Hz), 128.47, 127.26 (d, $J = 3.8$ Hz), 126.92 (d, $J = 13.2$ Hz), 125.96, 52.58, 49.36 (d, $J = 12.2$ Hz), 45.87, 29.28, 27.95.

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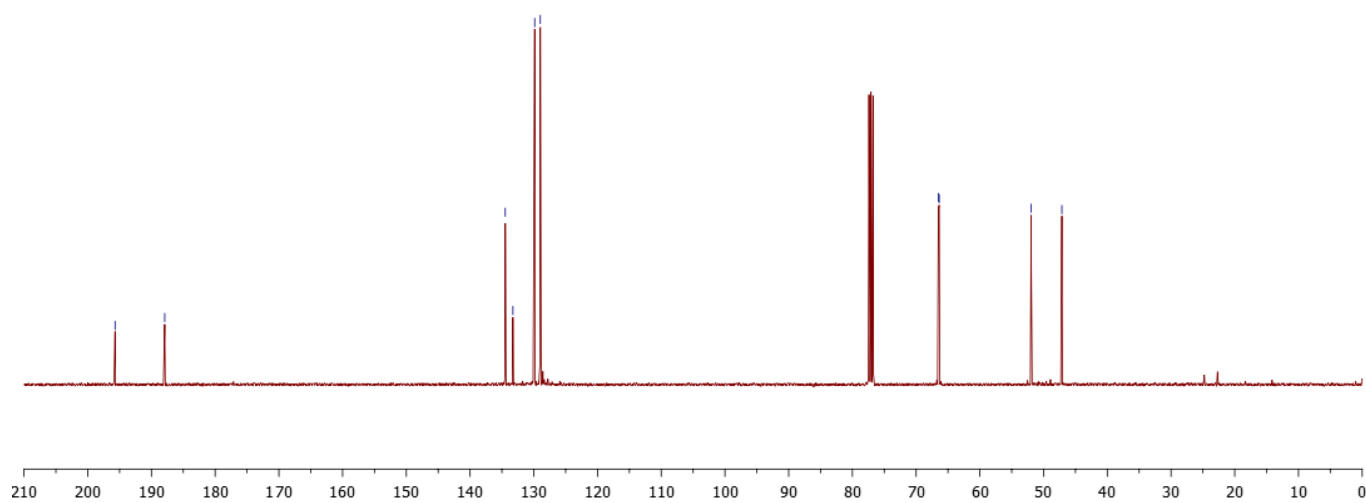
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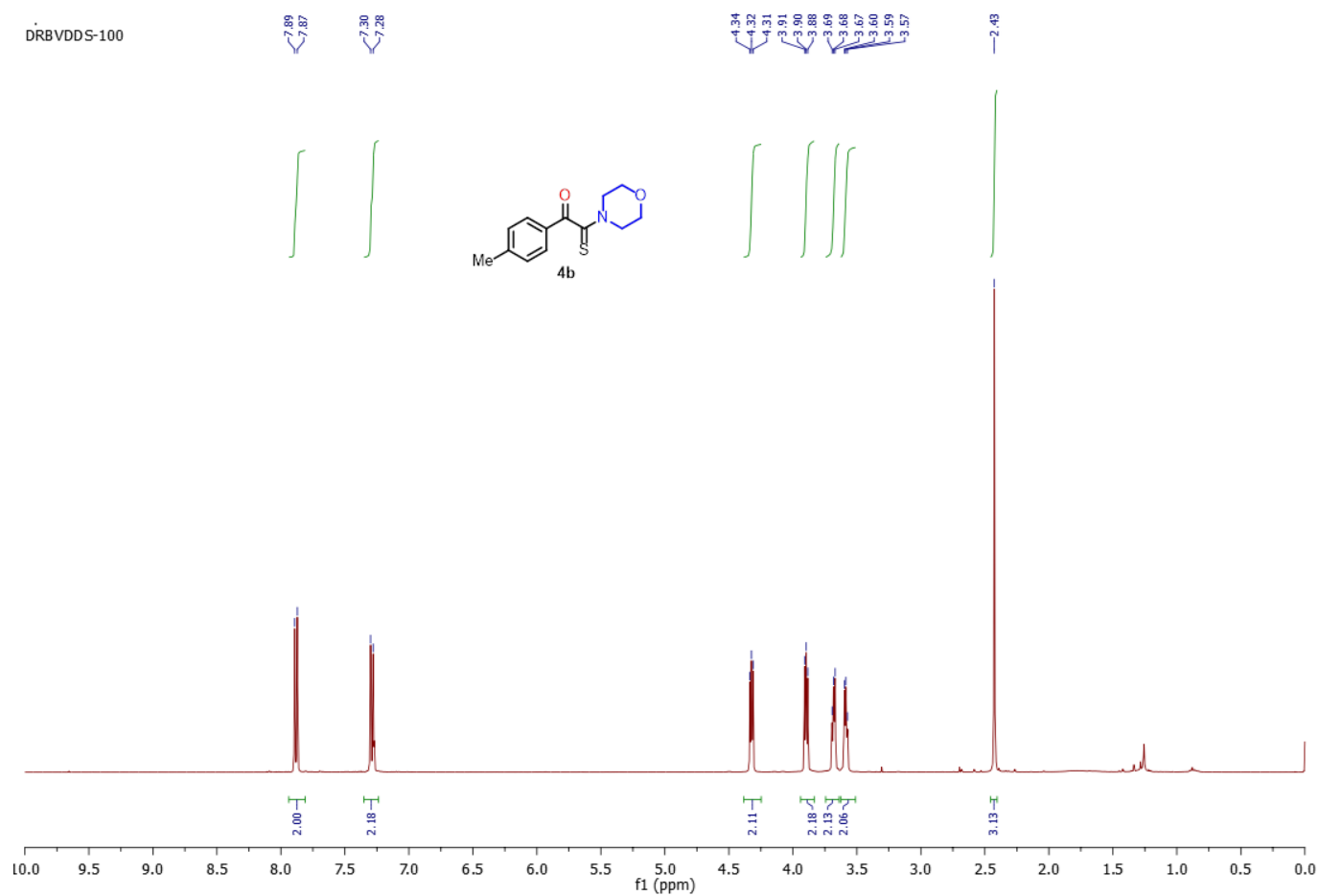
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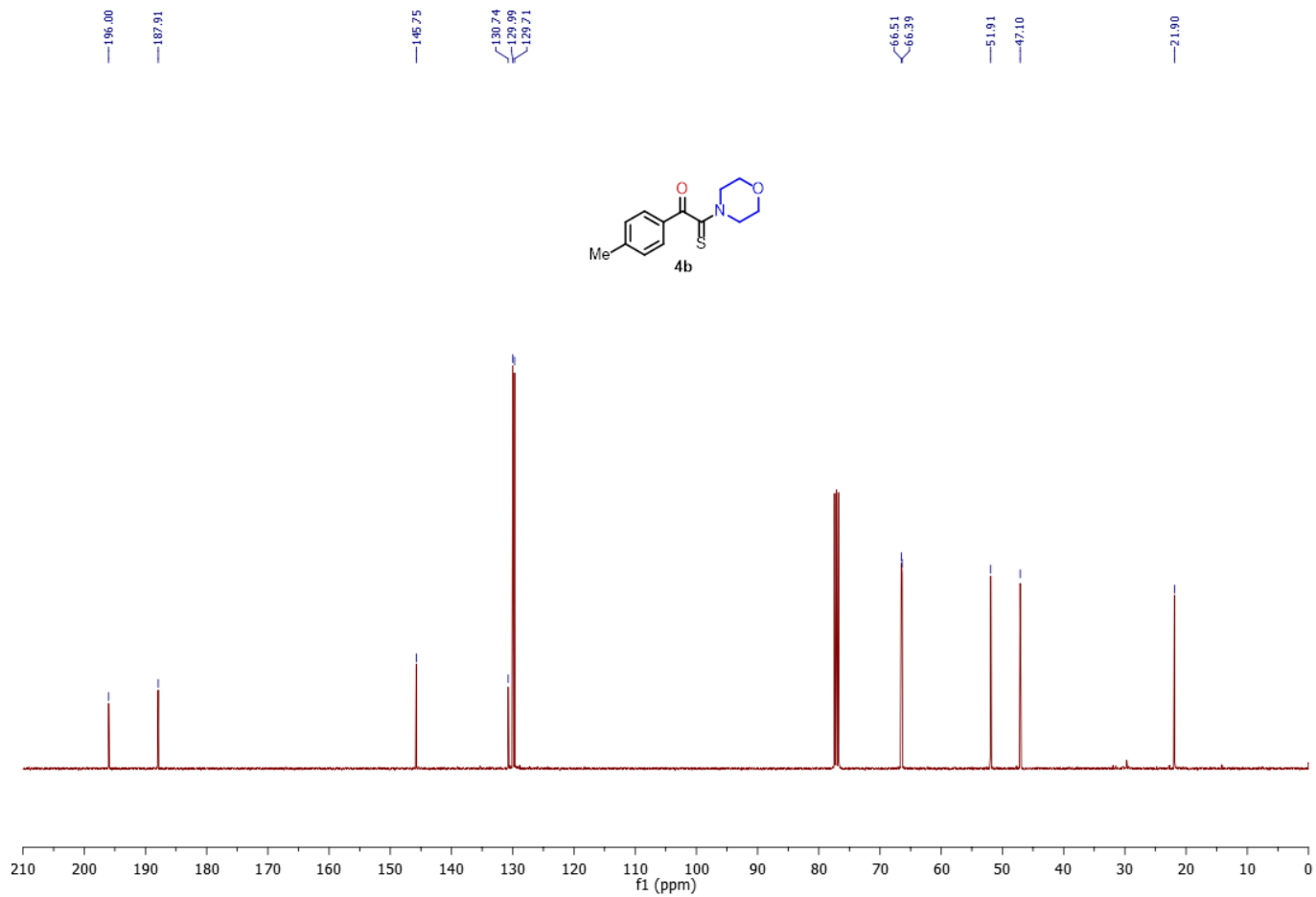
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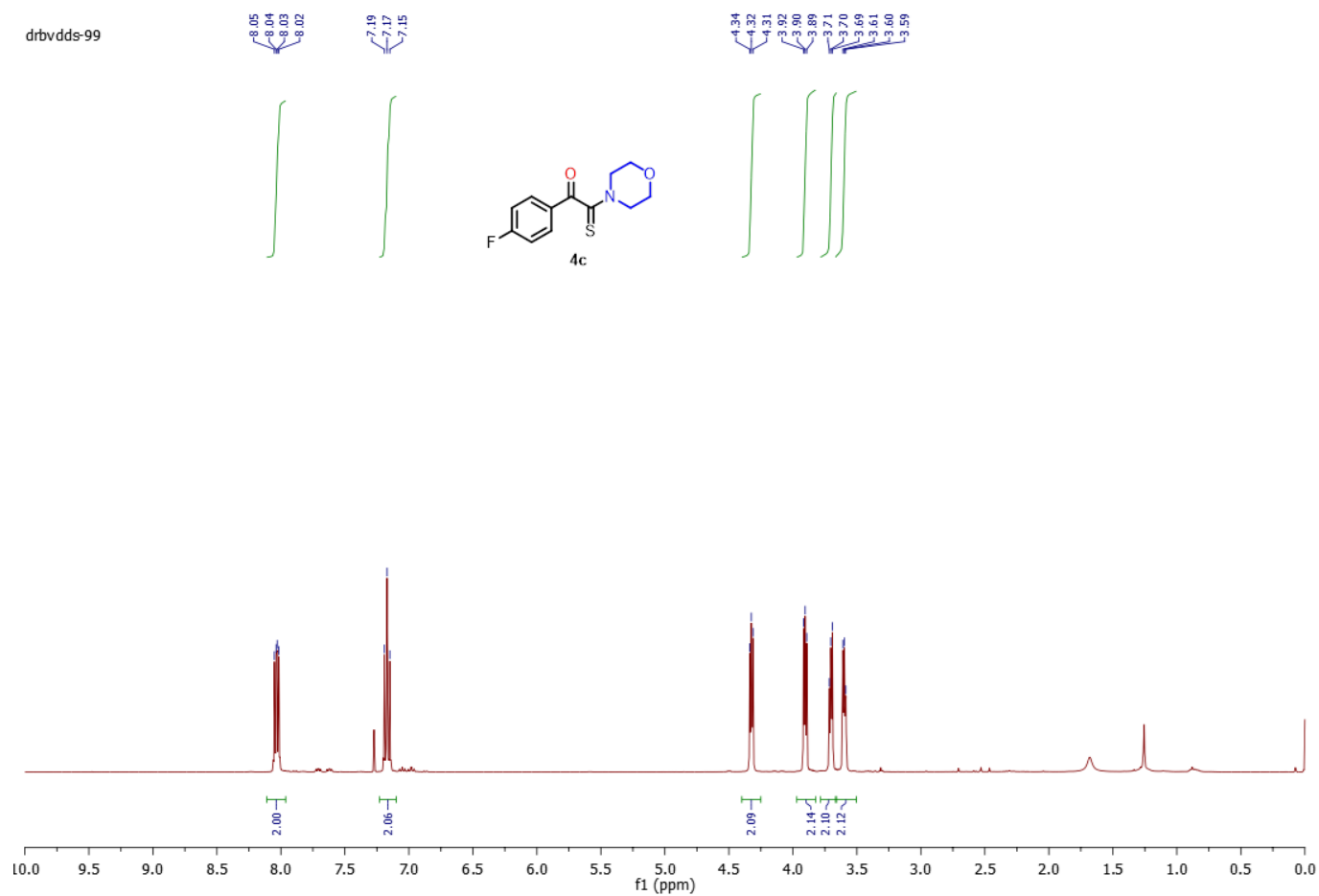


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116.40

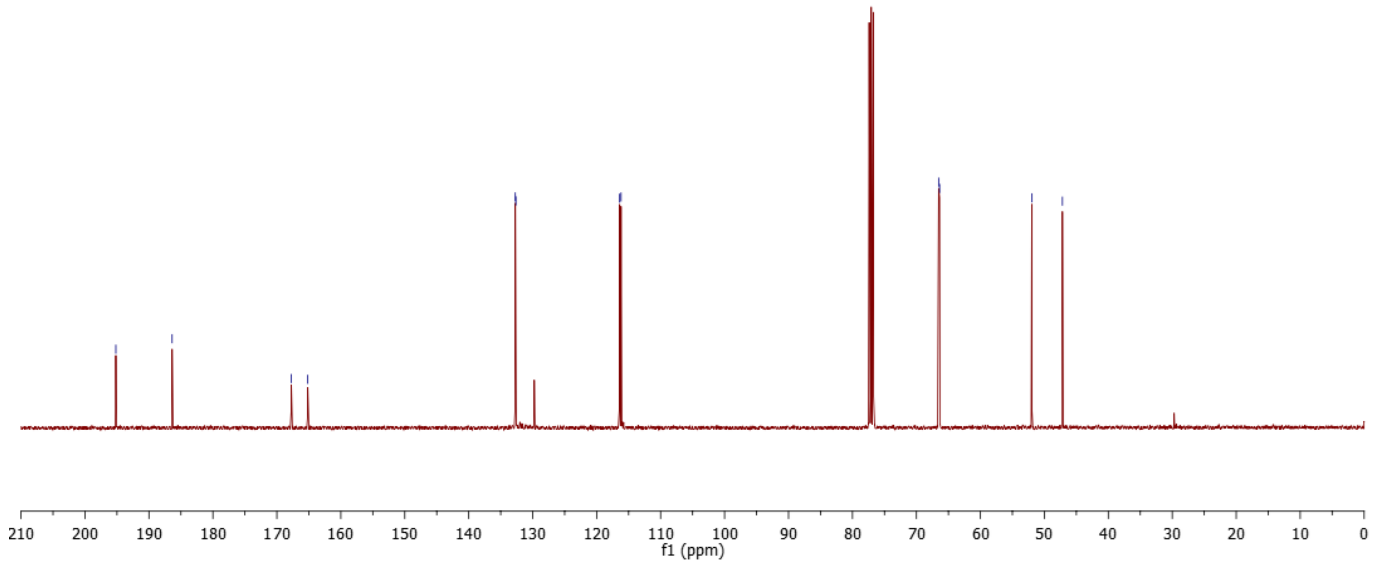
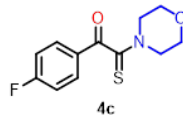
116.18

66.53

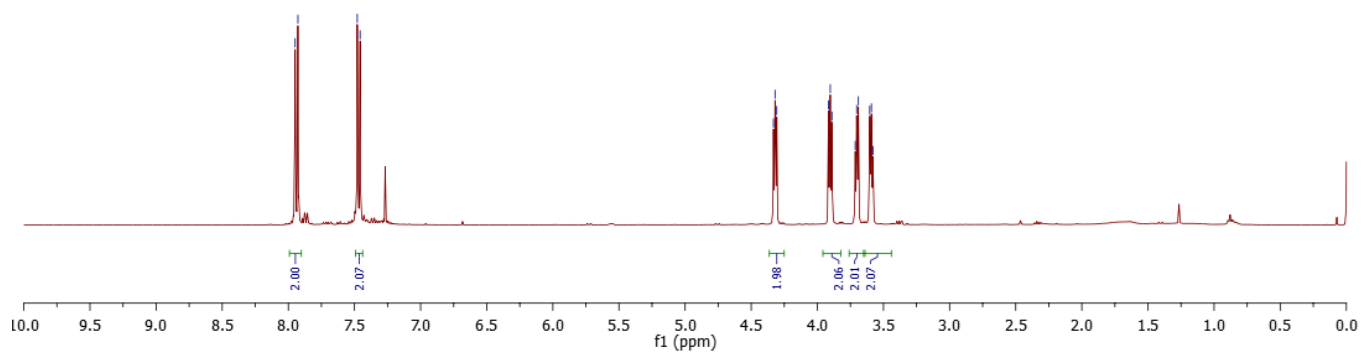
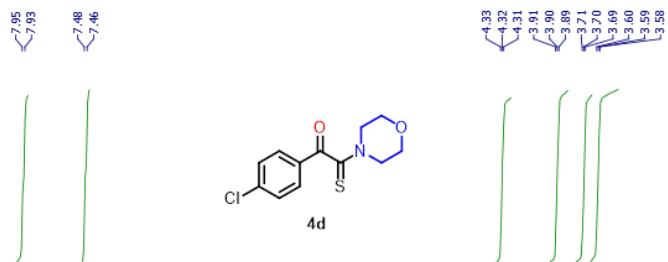
66.38

51.96

47.18



DRBVDDS-98



194.94

186.44

141.04

131.75

131.21

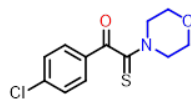
129.35

66.53

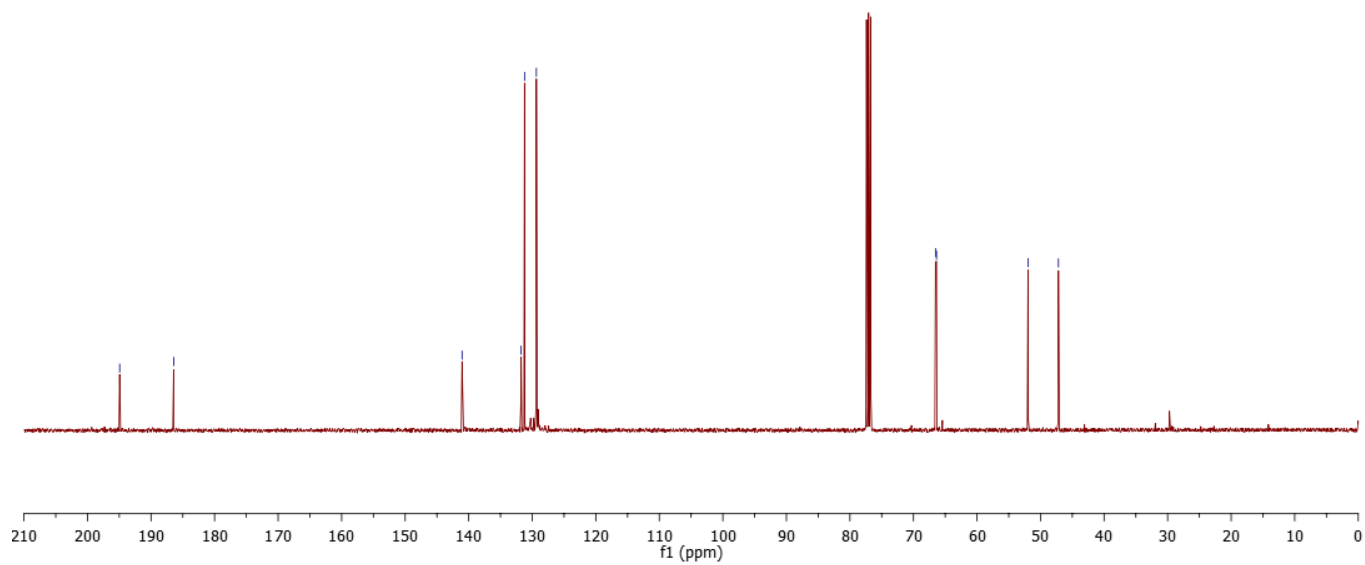
66.38

51.96

47.18



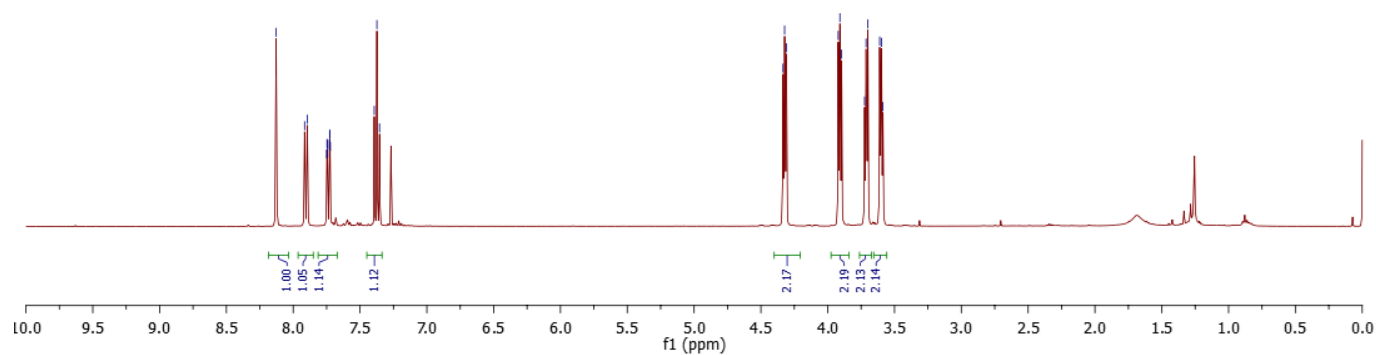
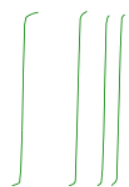
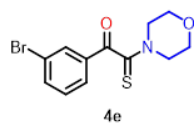
4d



DRBVDDS-101

7.813
7.791
7.789
7.755
7.754
7.774
7.774
7.753
7.753
7.722
7.739
7.737
7.735

4.333
4.327
4.311
3.927
3.911
3.900
3.721
3.721
3.700
3.664
3.600
3.589



—194.51

—185.95

—137.23

—135.24

—132.51

—130.50

—128.44

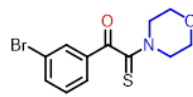
—123.21

—66.52

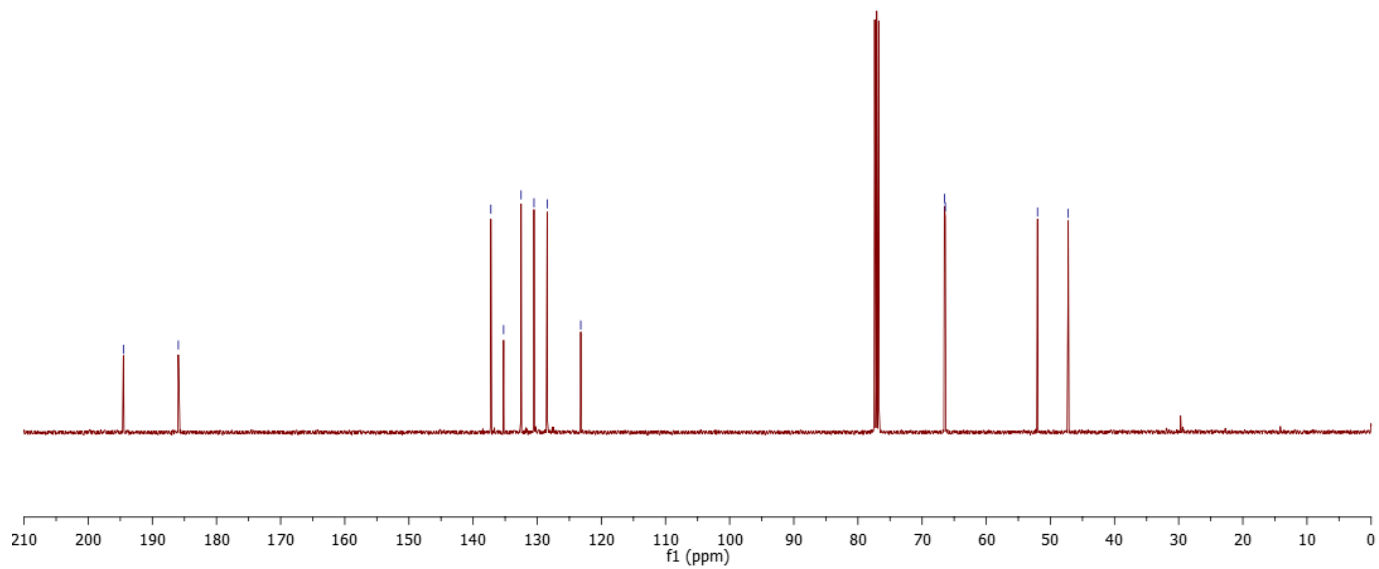
—66.38

—52.00

—47.22



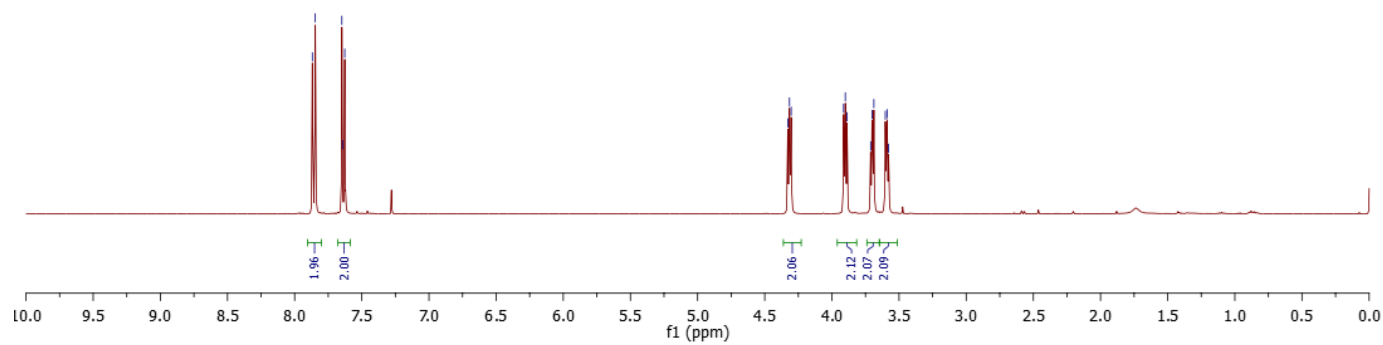
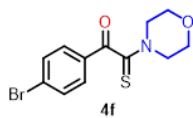
4e



DRBVDDS-140

7.87
7.85
7.85
7.84
7.83

4.33
4.32
4.30
3.91
3.90
3.89
3.71
3.69
3.60
3.59
3.58



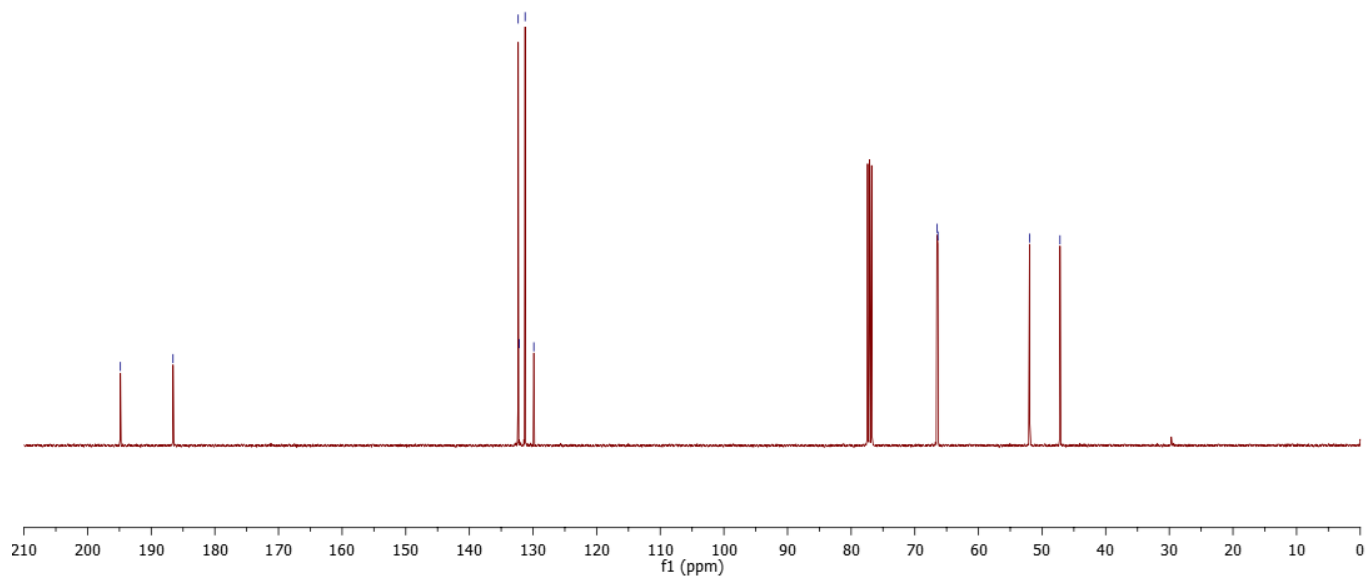
194.85

186.58

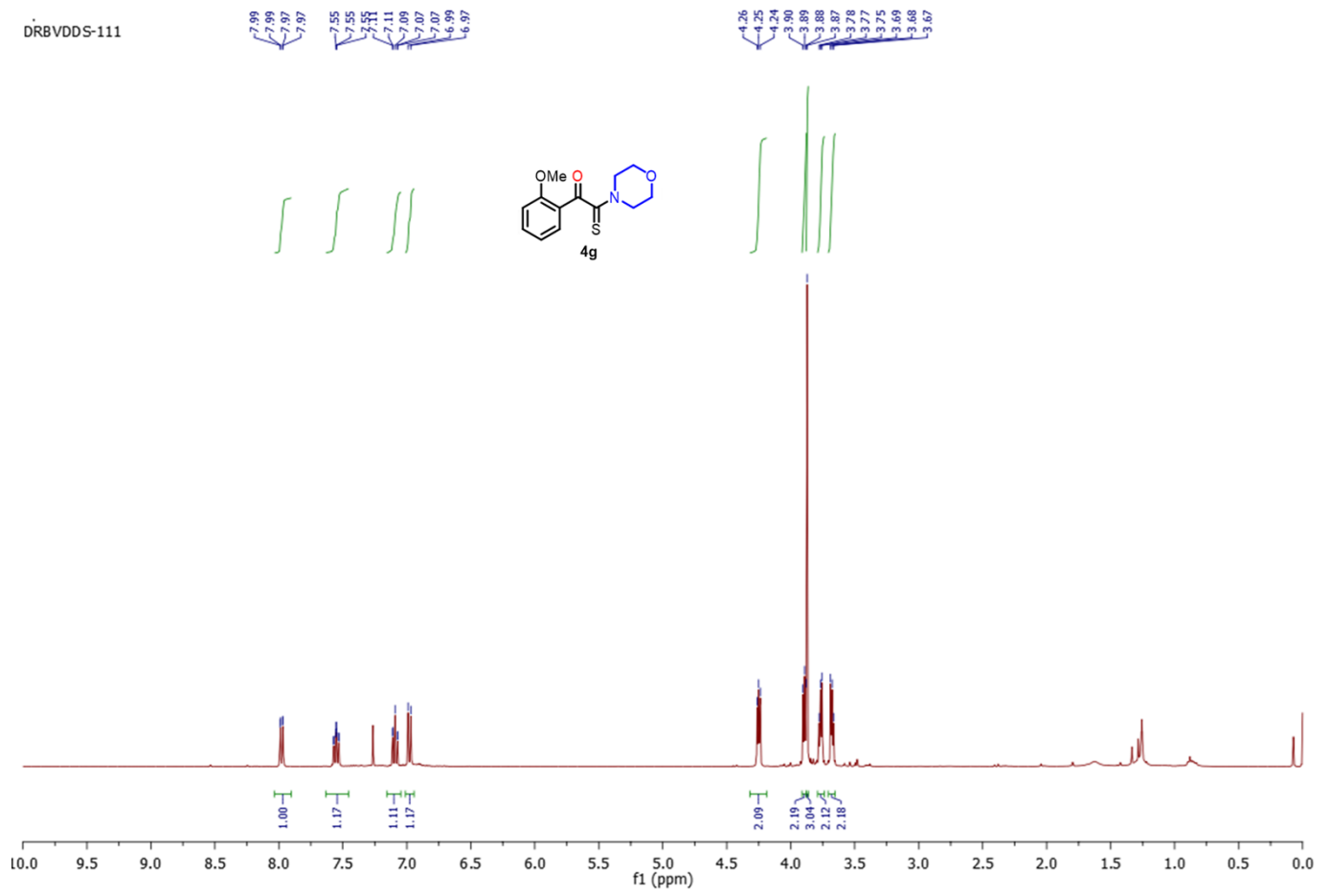
132.33
132.17
131.24
129.87

66.51
66.36

51.96
47.18



DRBVDDS-111



DS111

198.33

186.62

159.15

135.54

131.82

121.53

112.56

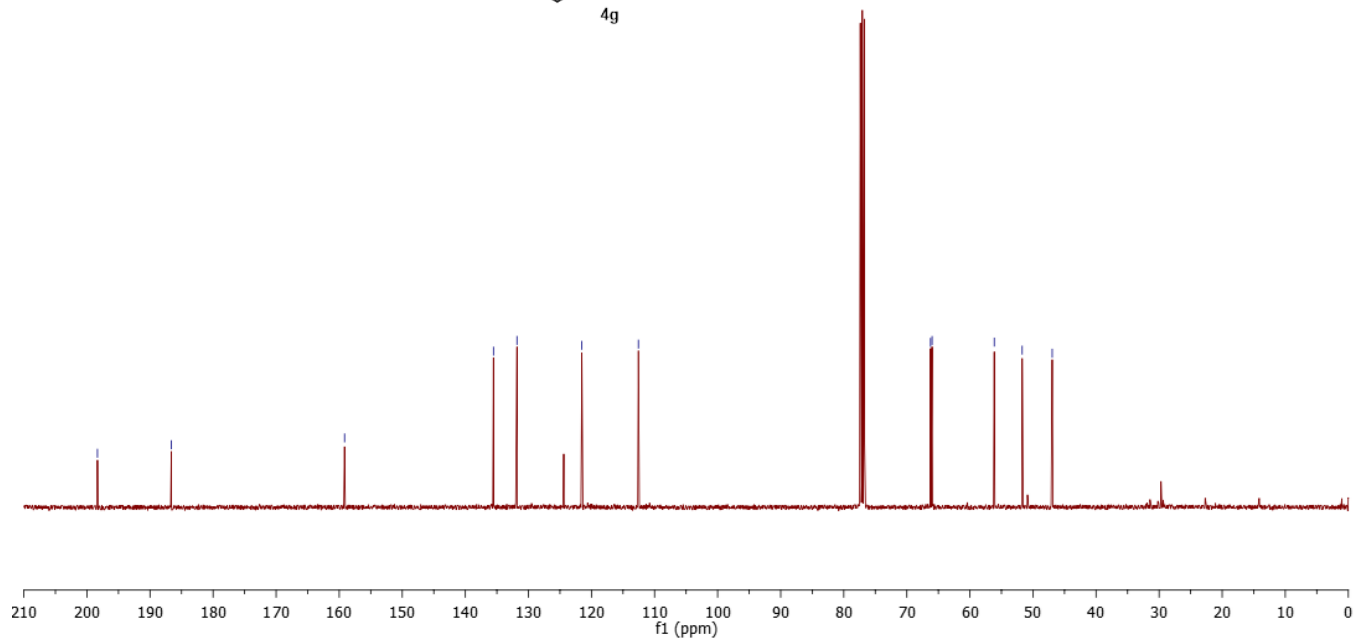
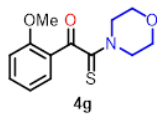
66.24

66.00

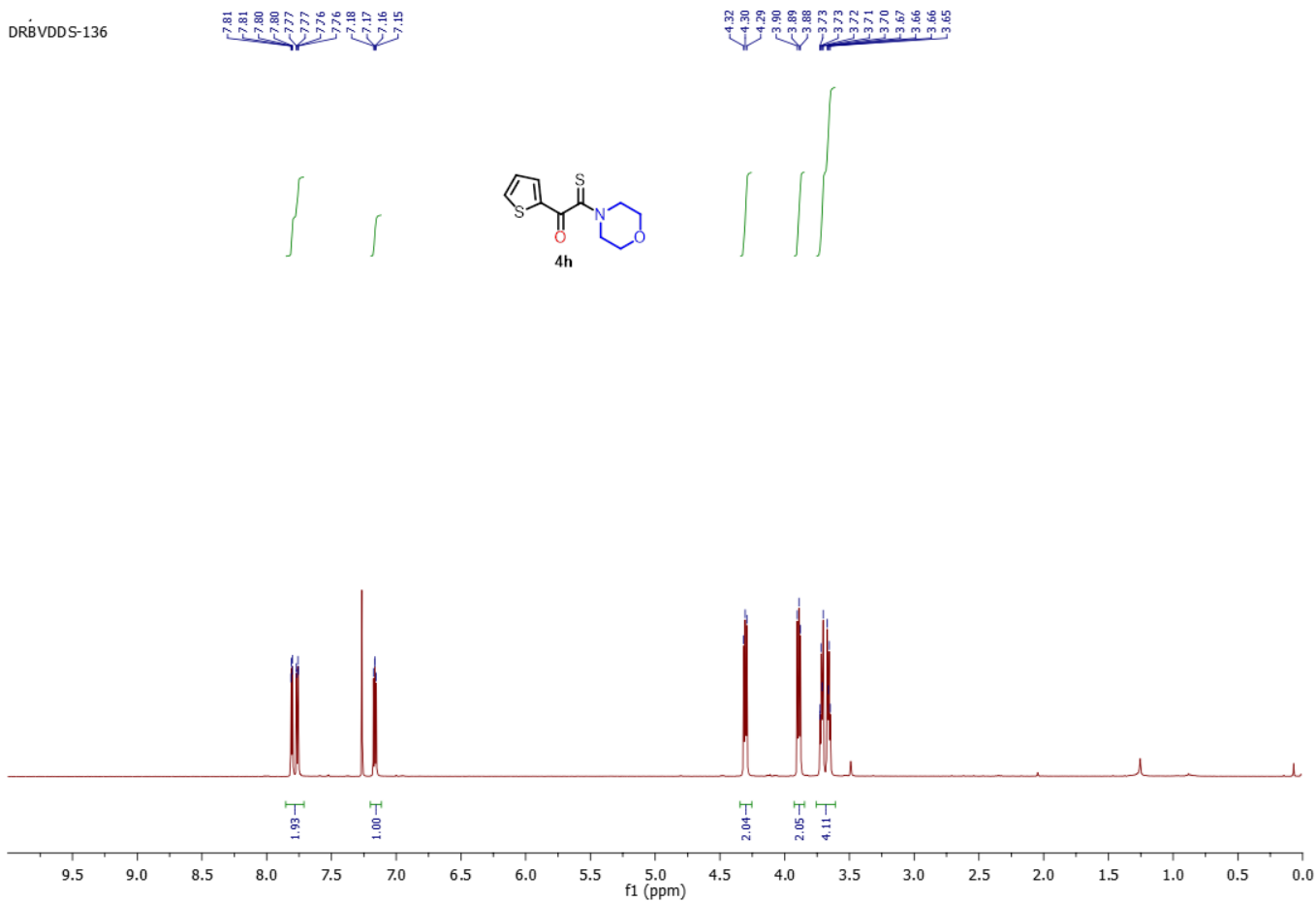
56.14

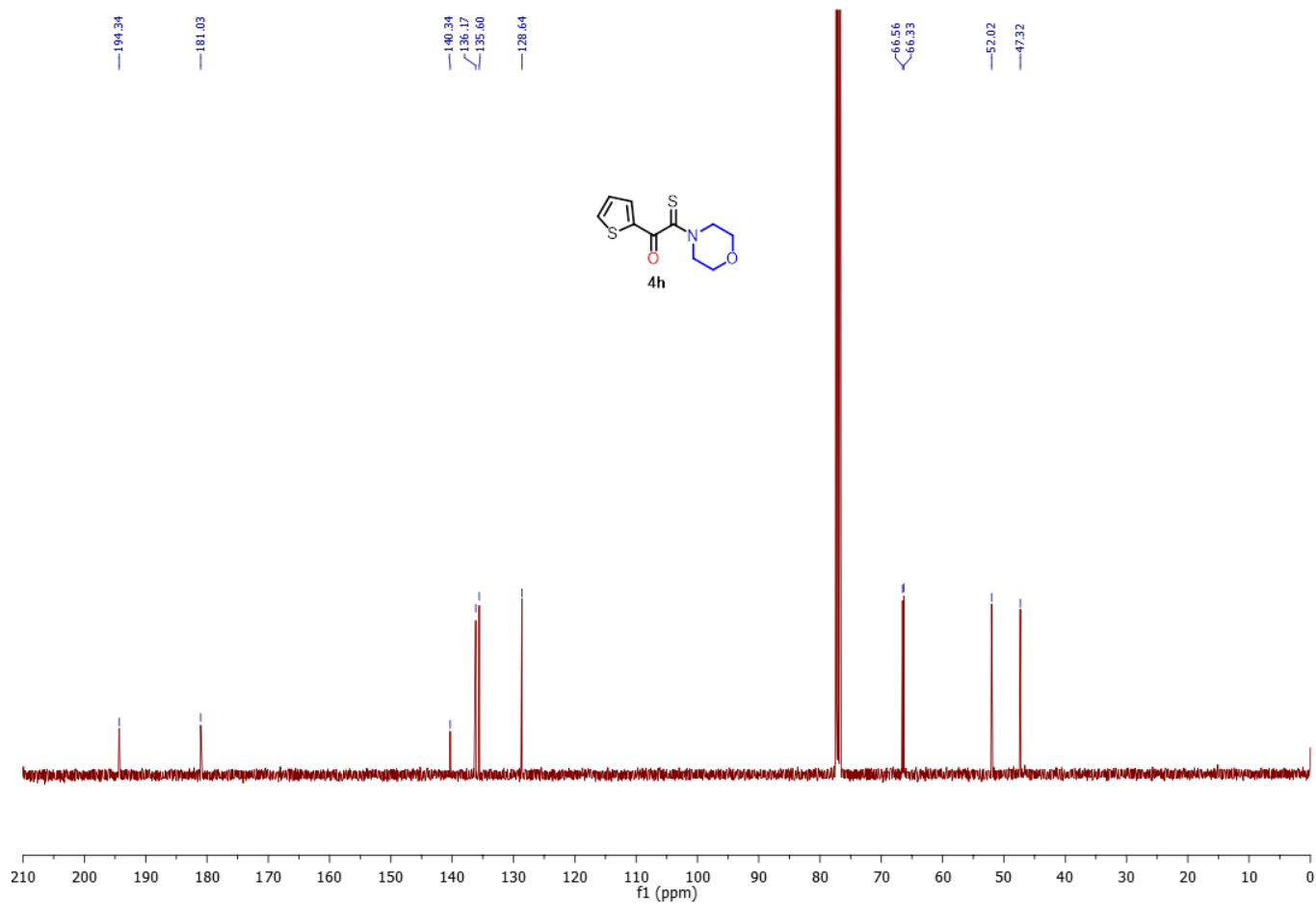
51.71

46.95

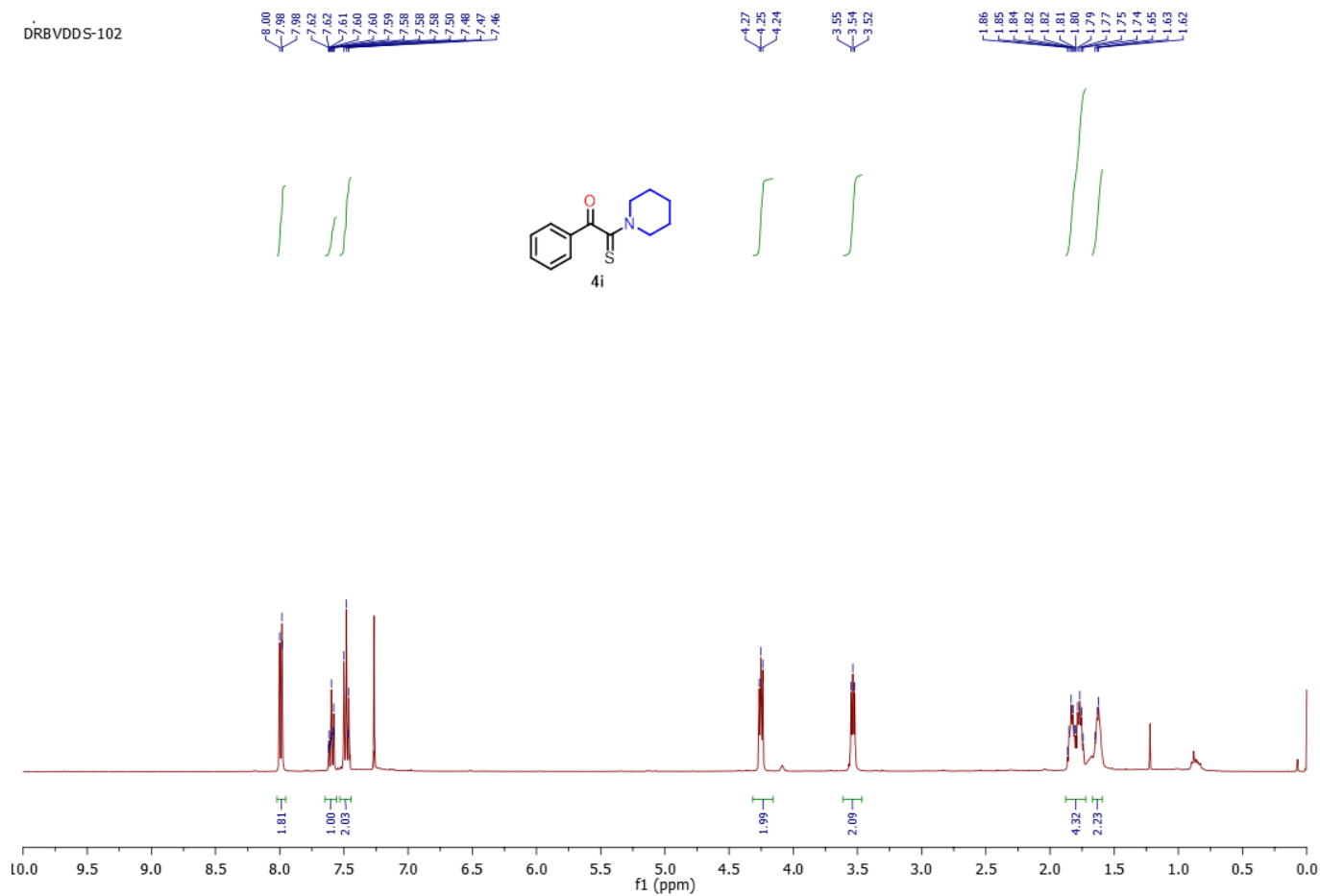


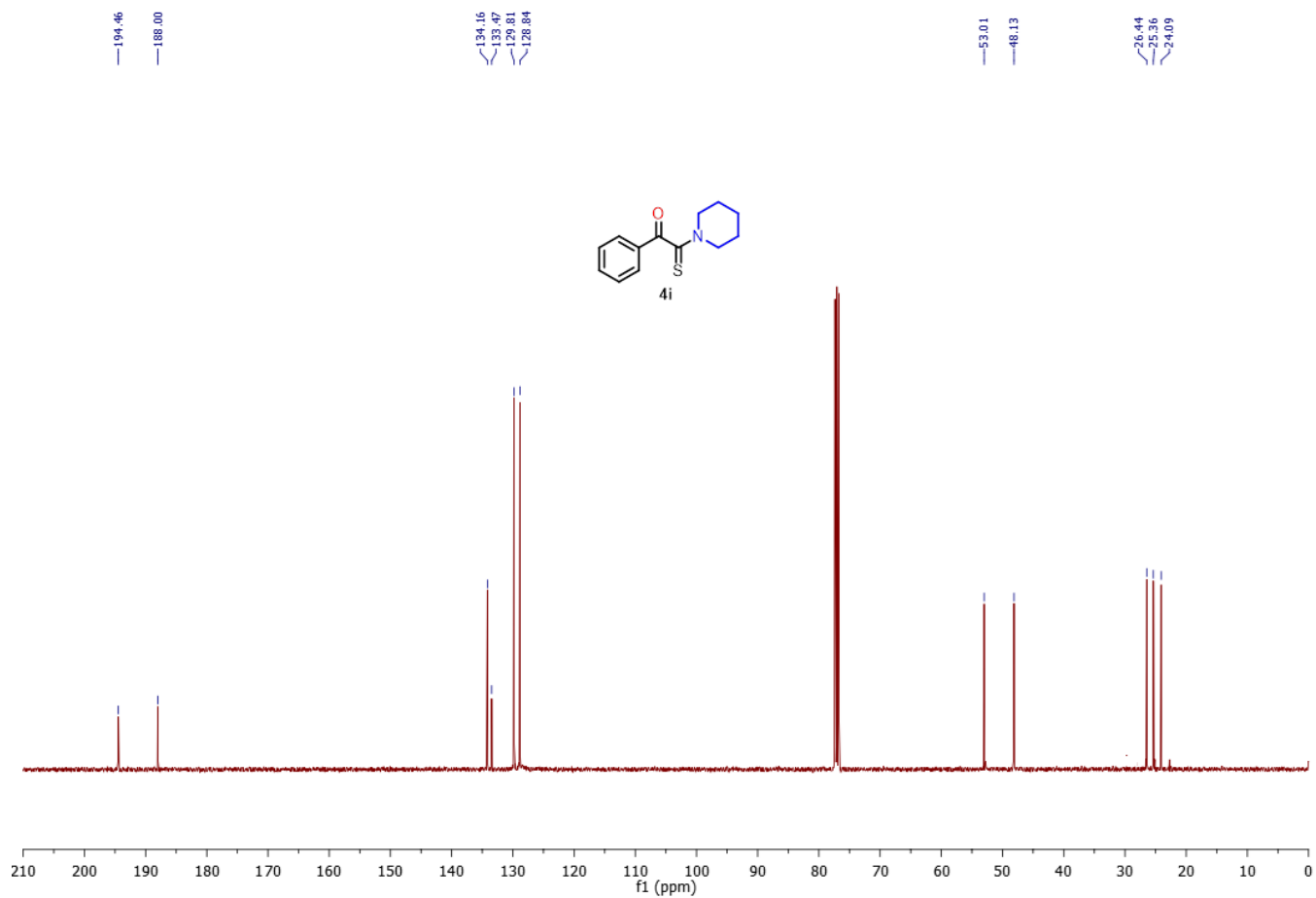
DRBVDDS-136



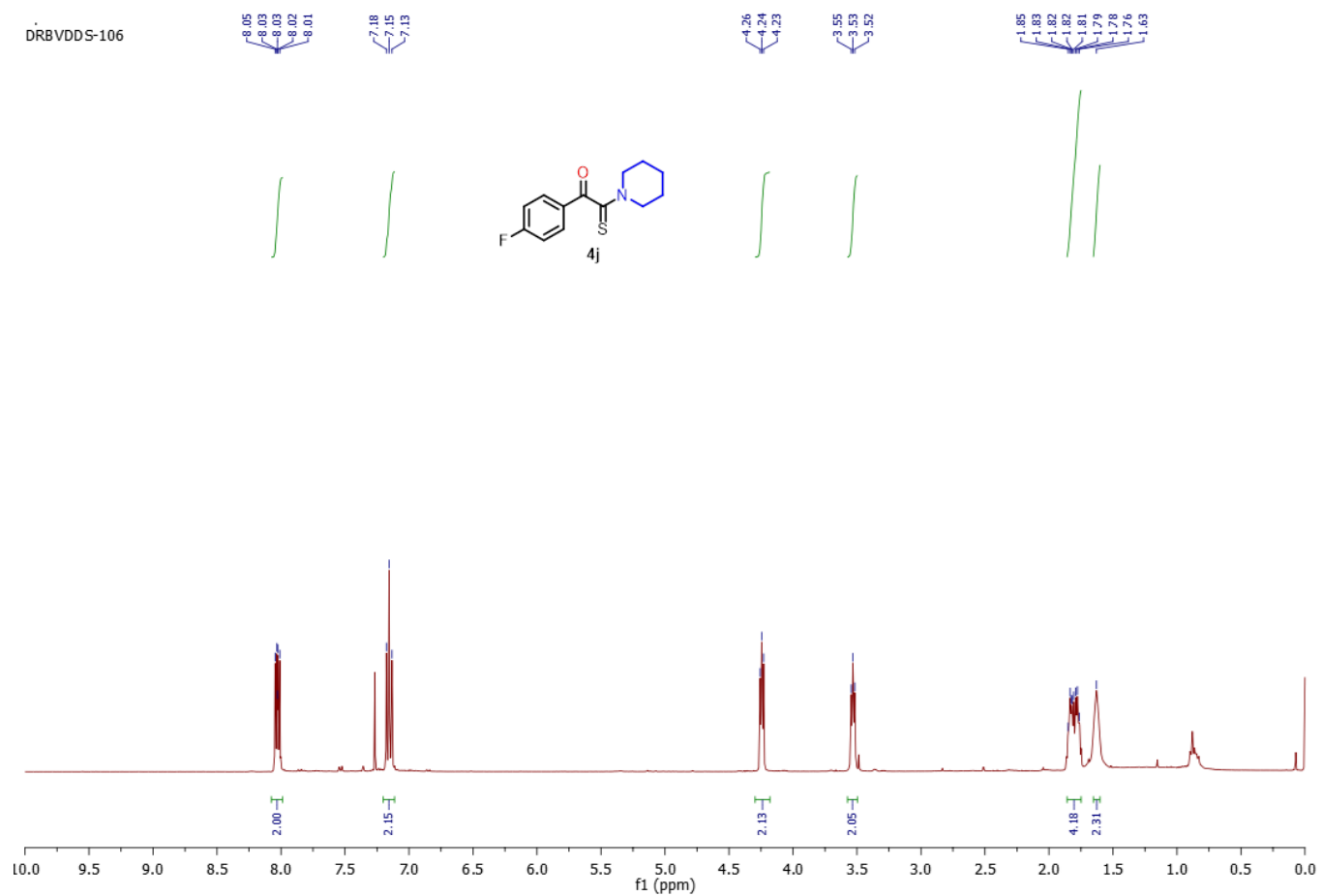


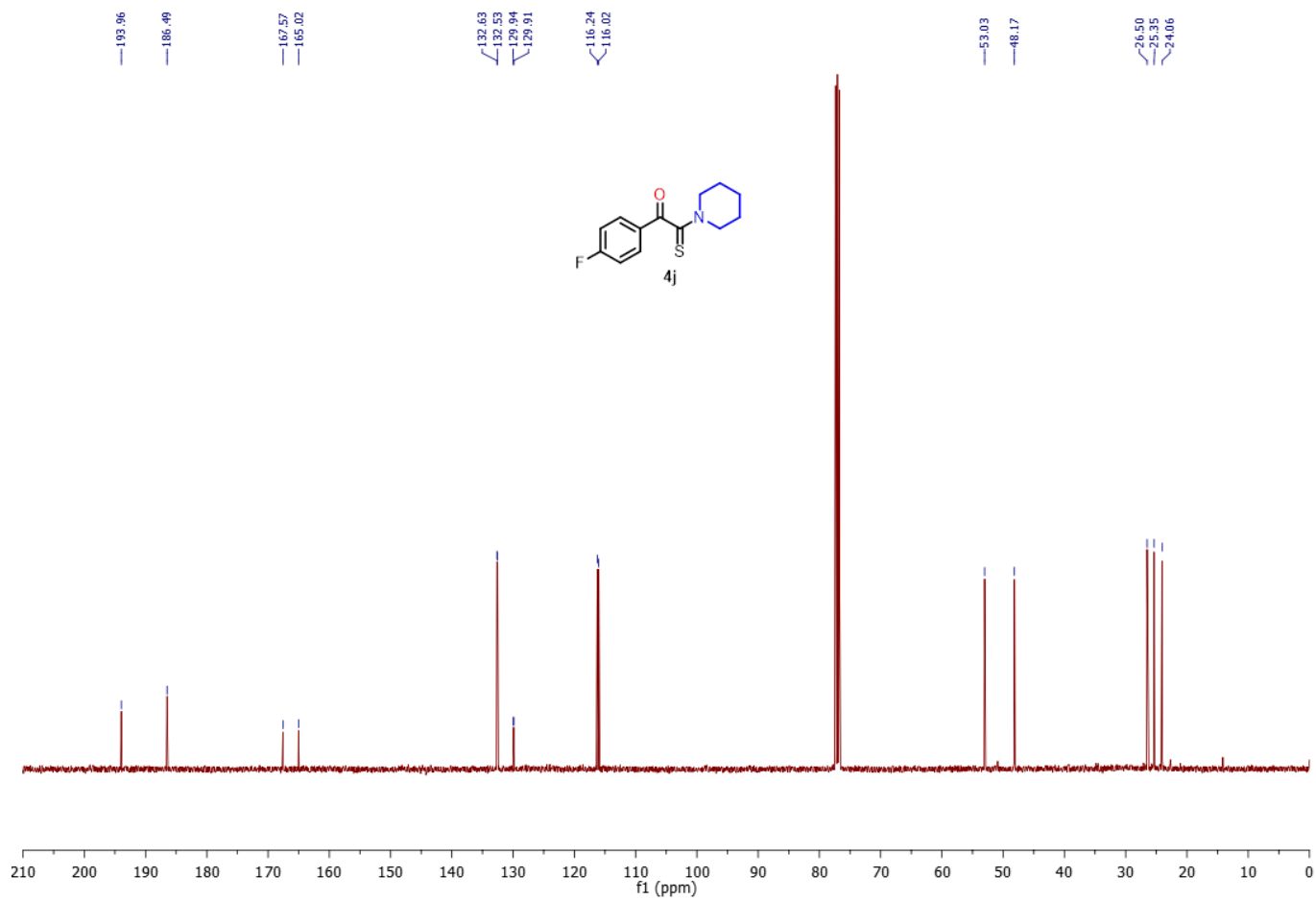
DRBVDDS-102



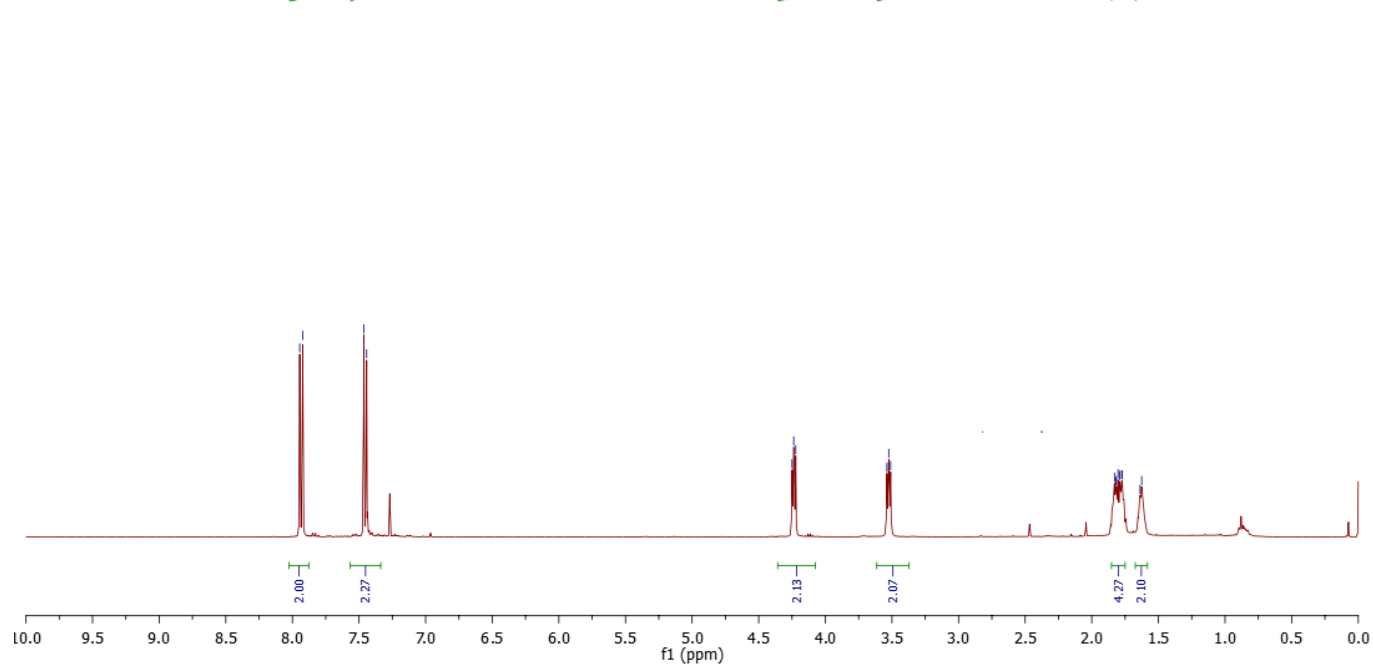
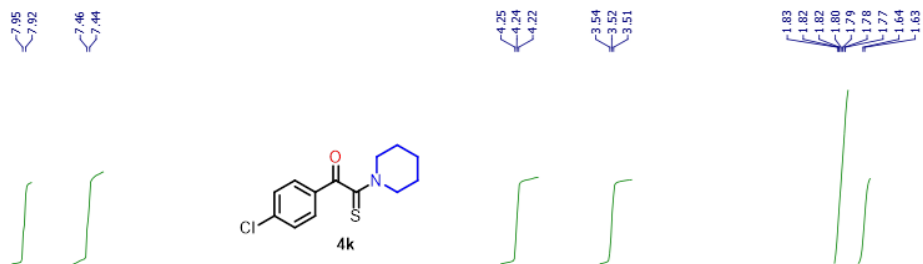


DRBVDDS-106





DRBVDDS-104



193.66

186.53

140.66

131.94

131.16

129.22

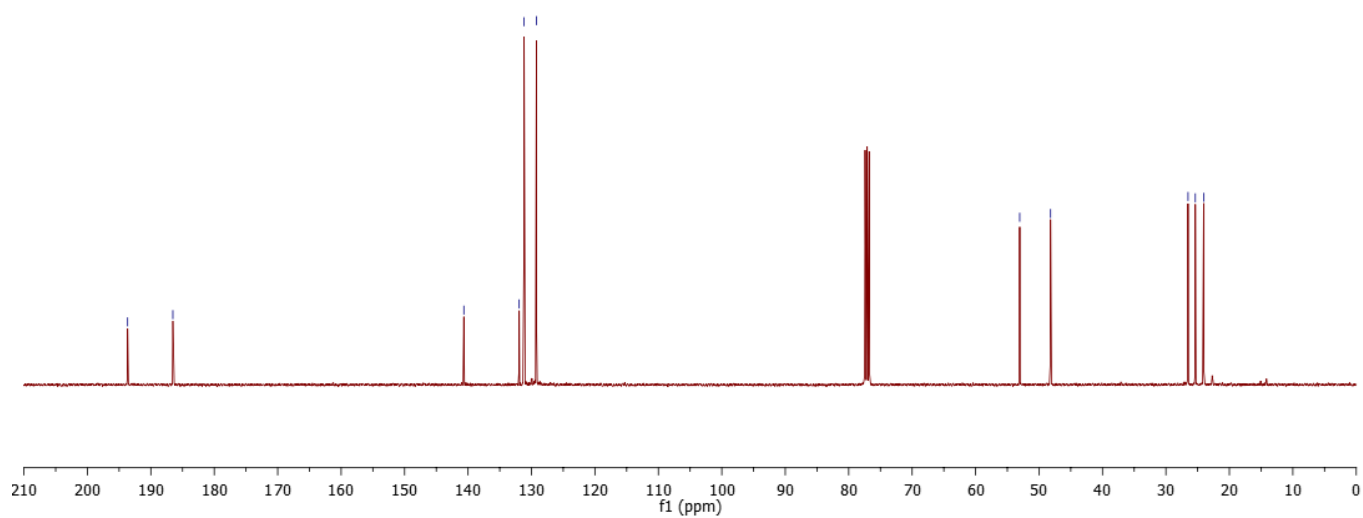
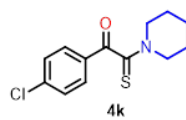
53.04

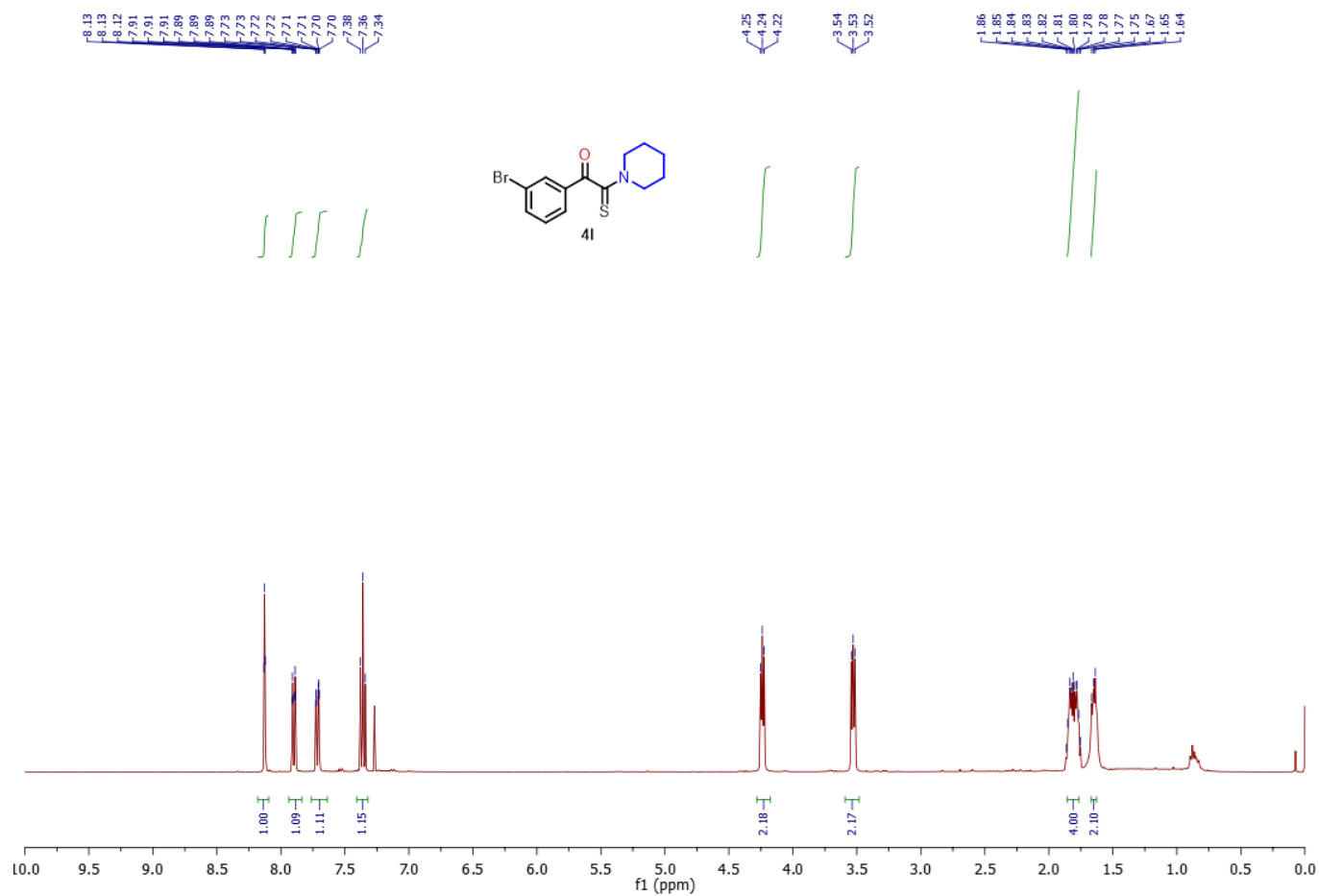
48.18

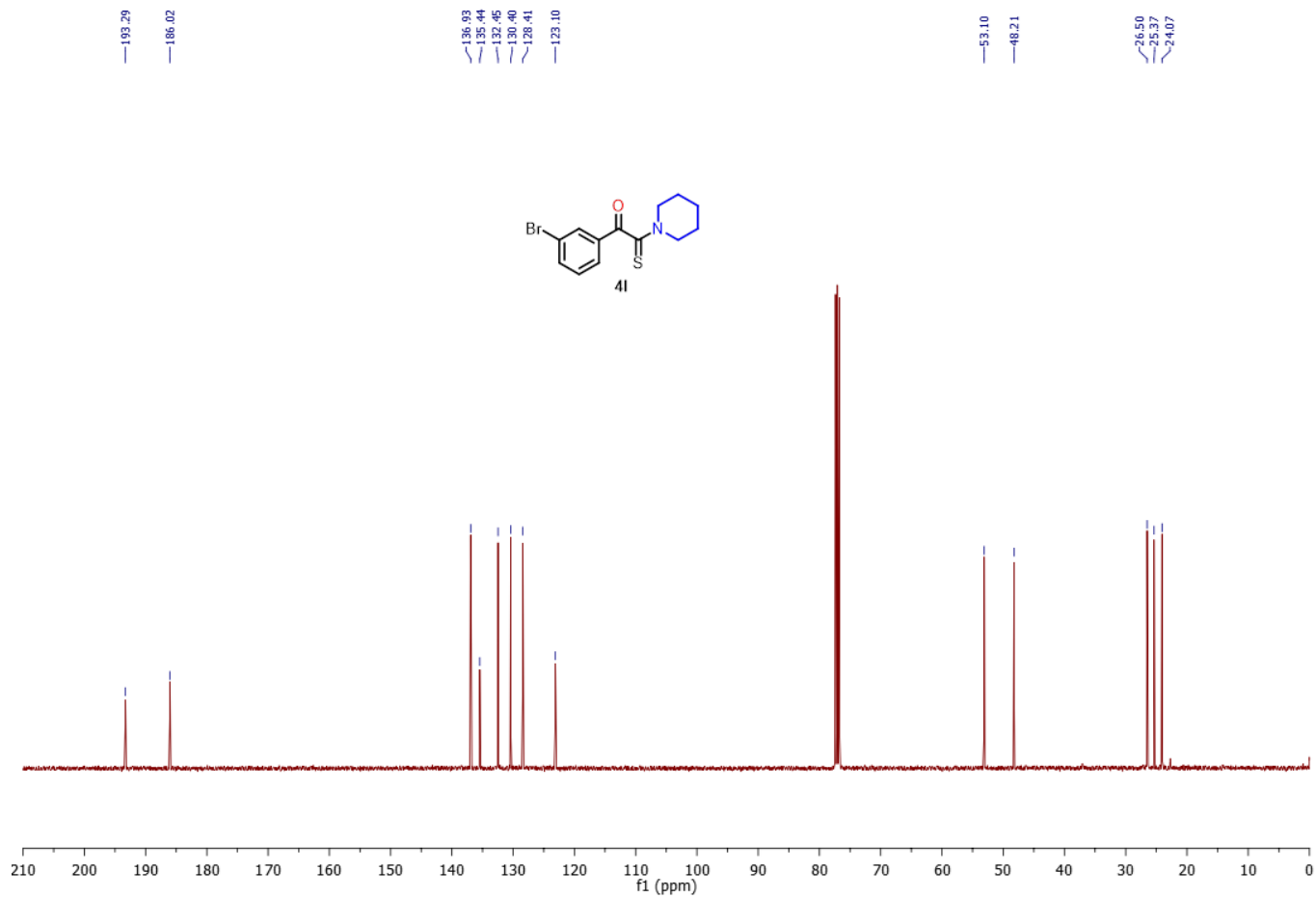
26.51

25.37

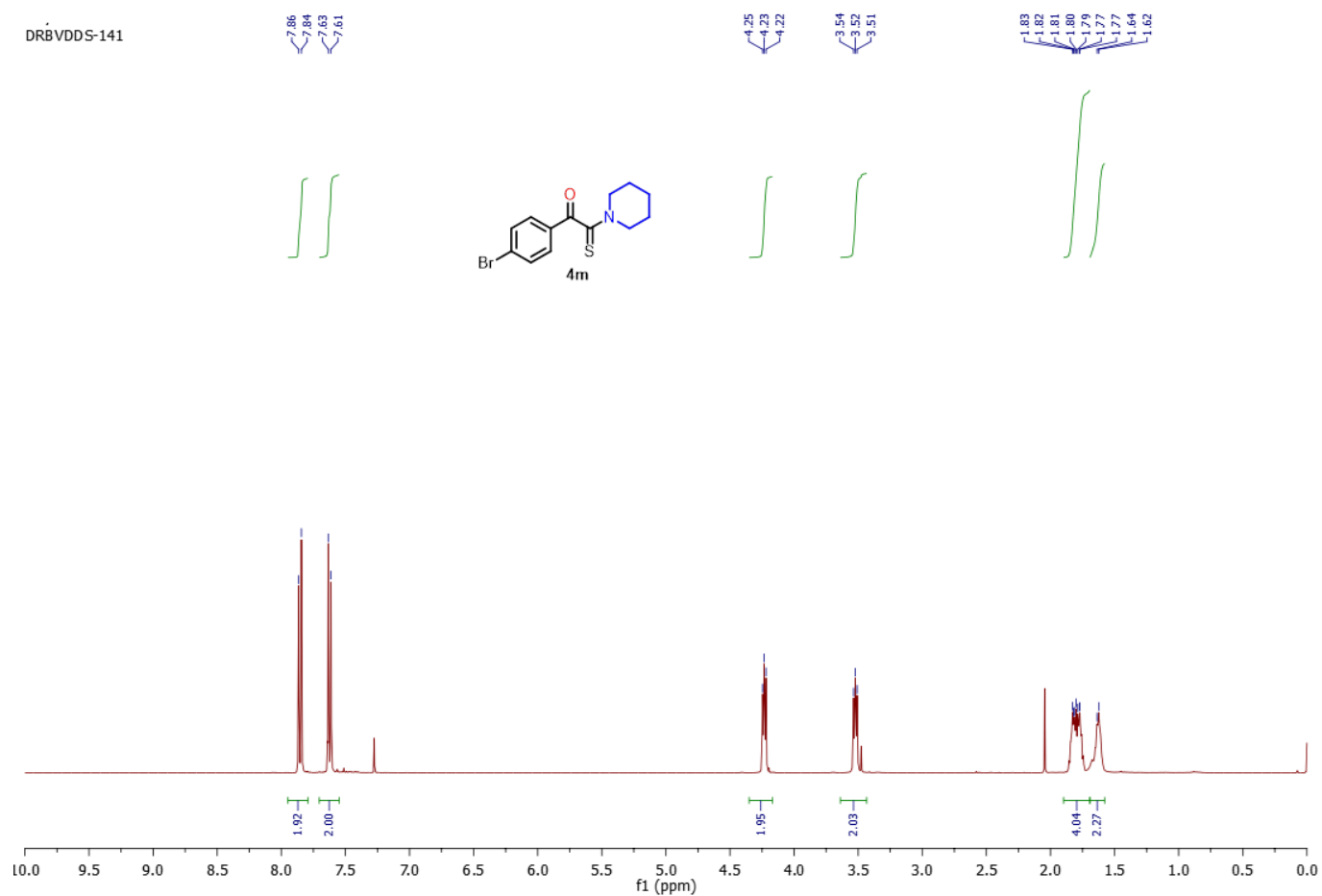
24.05







DRBVDDS-141



DS141

193.59

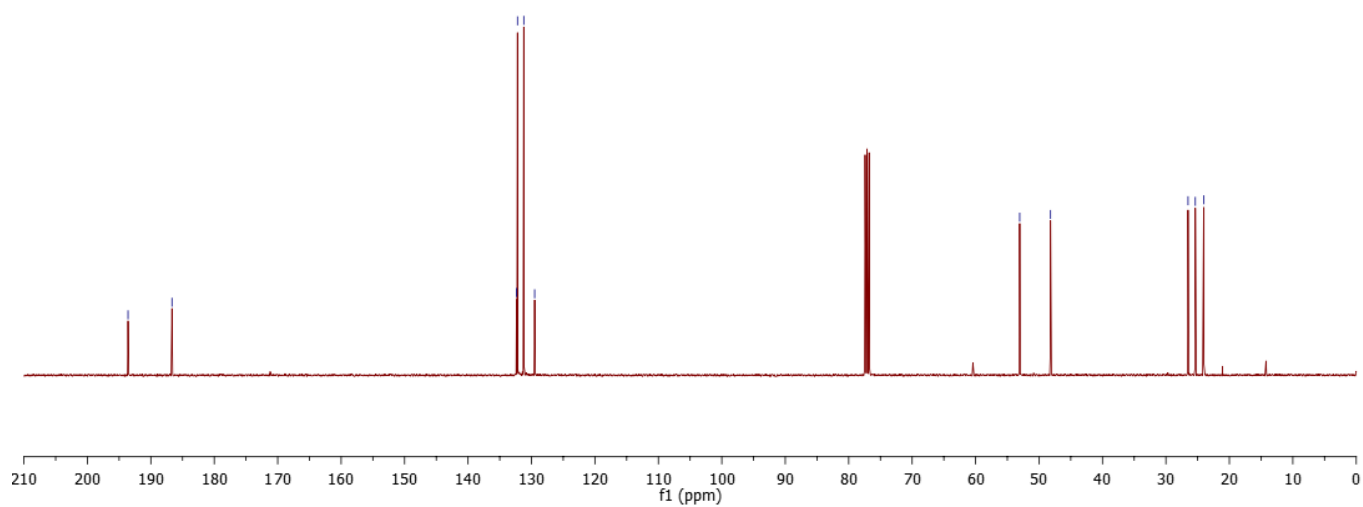
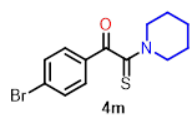
186.67

132.36
132.21
31.21
29.50

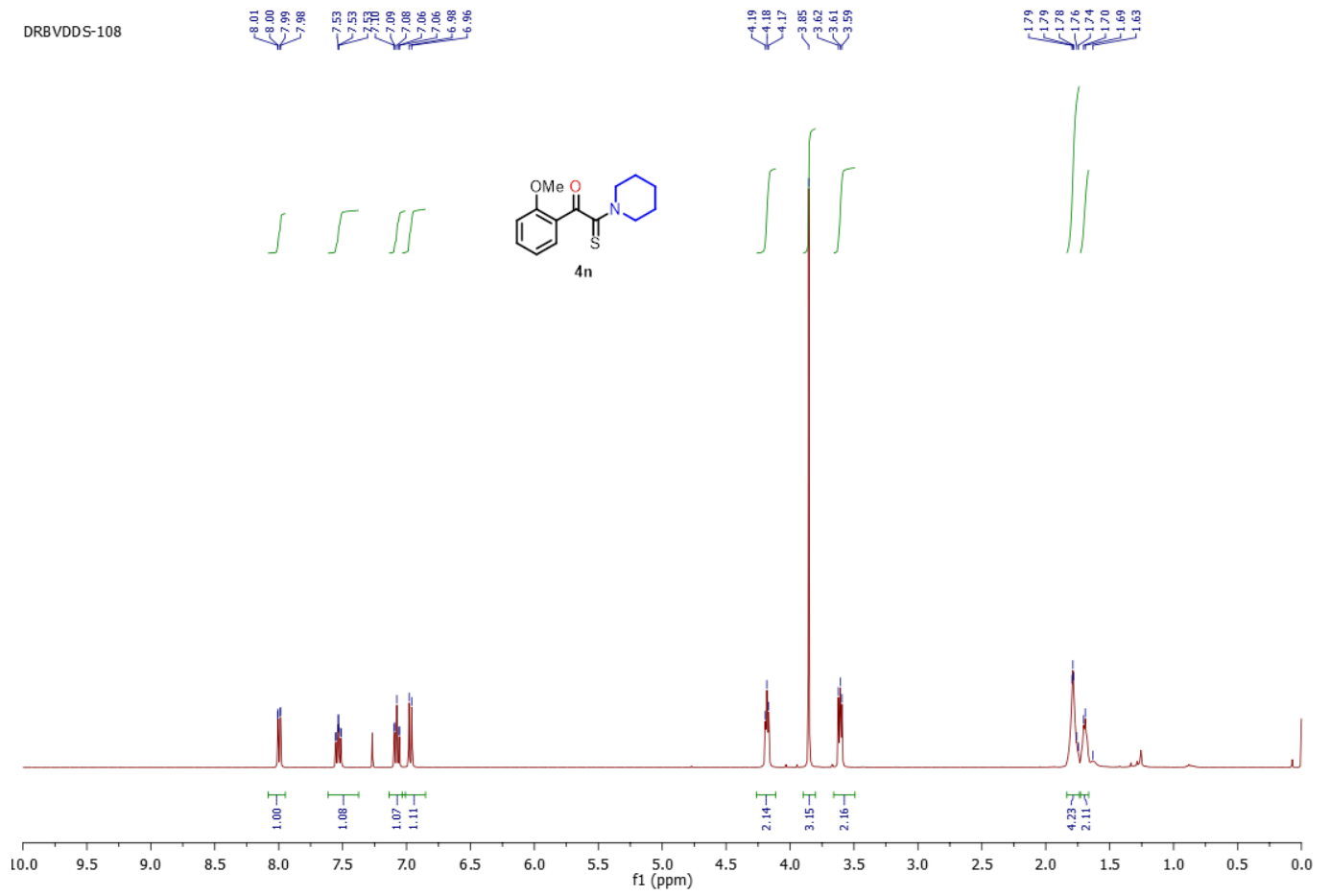
53.05

48.19

26.51
26.37
24.05



DRBVDDS-108



196.79

186.46

159.25

135.29

131.86

124.38

121.33

112.52

56.03

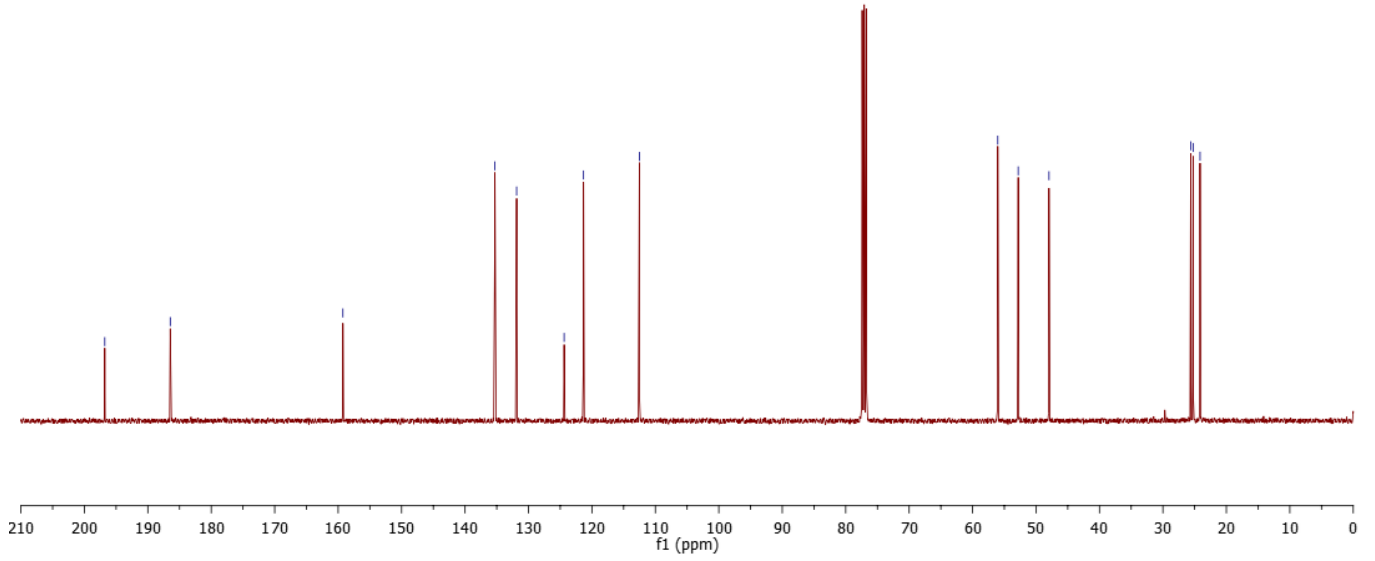
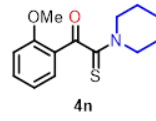
52.81

47.96

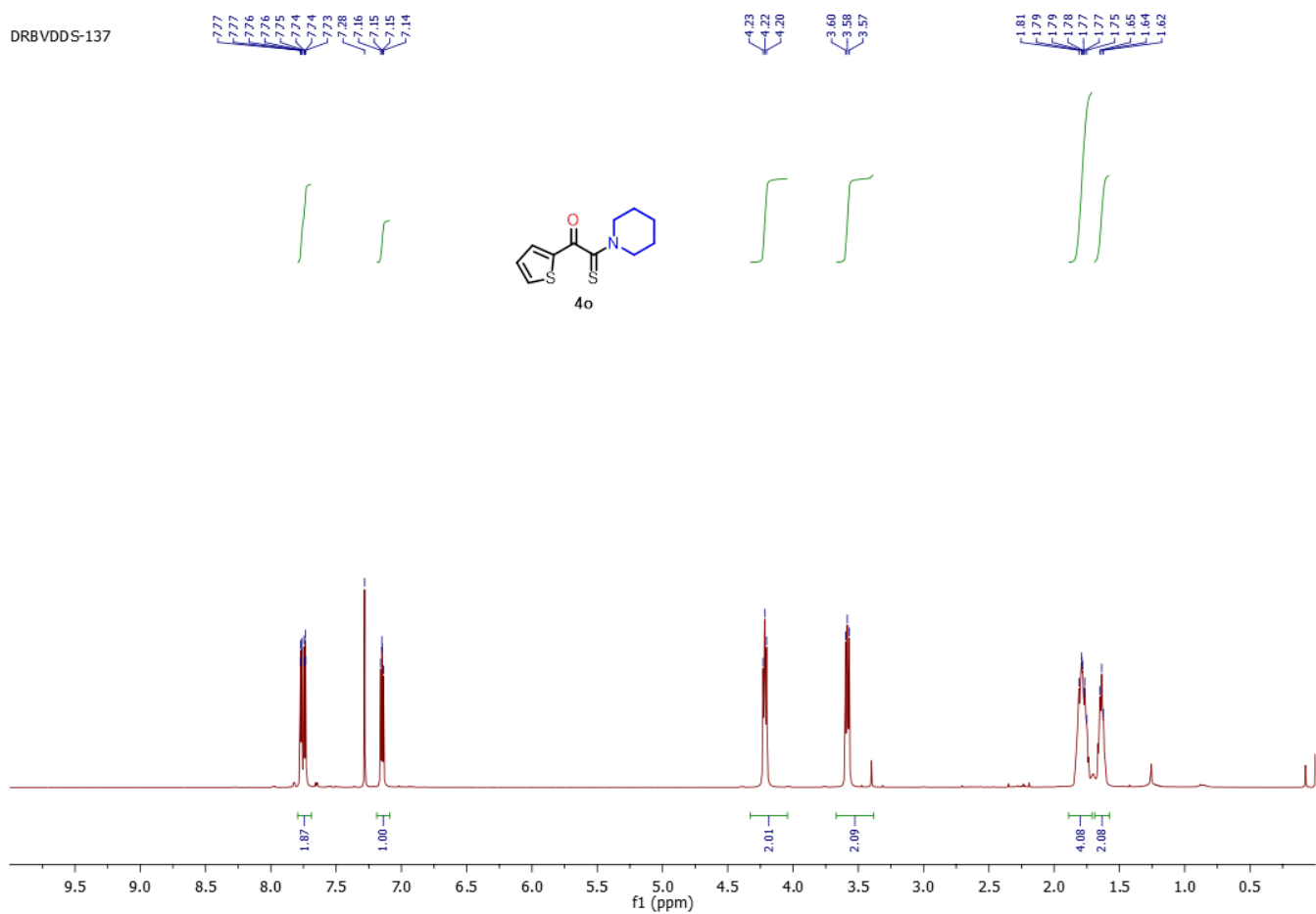
25.61

23.73

21.15



DRBVDDS-137



DS137

—193.04

—181.31

—140.49

—135.73

—135.29

—128.54

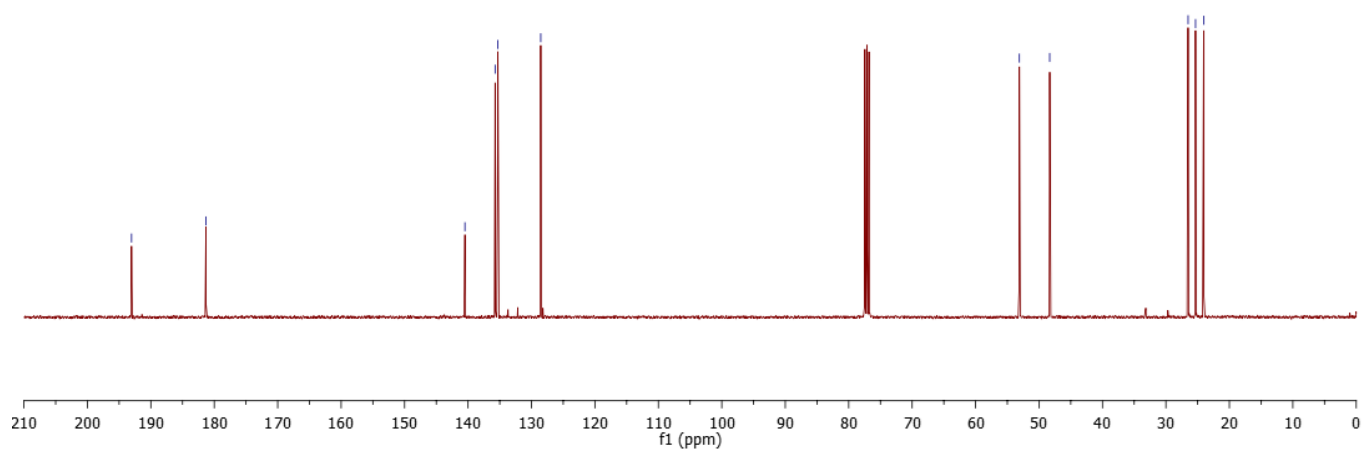
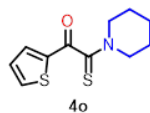
—53.10

—48.32

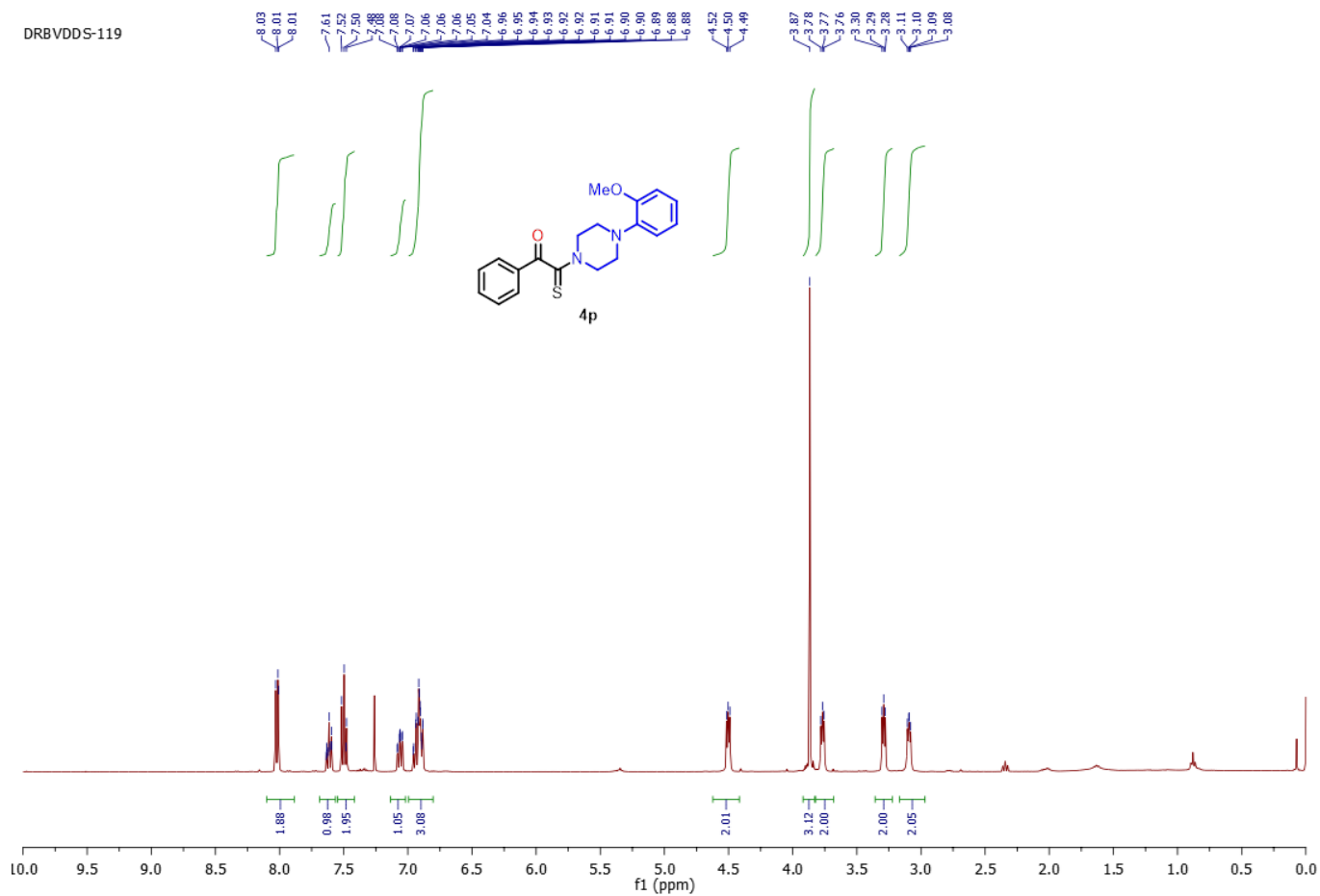
—26.50

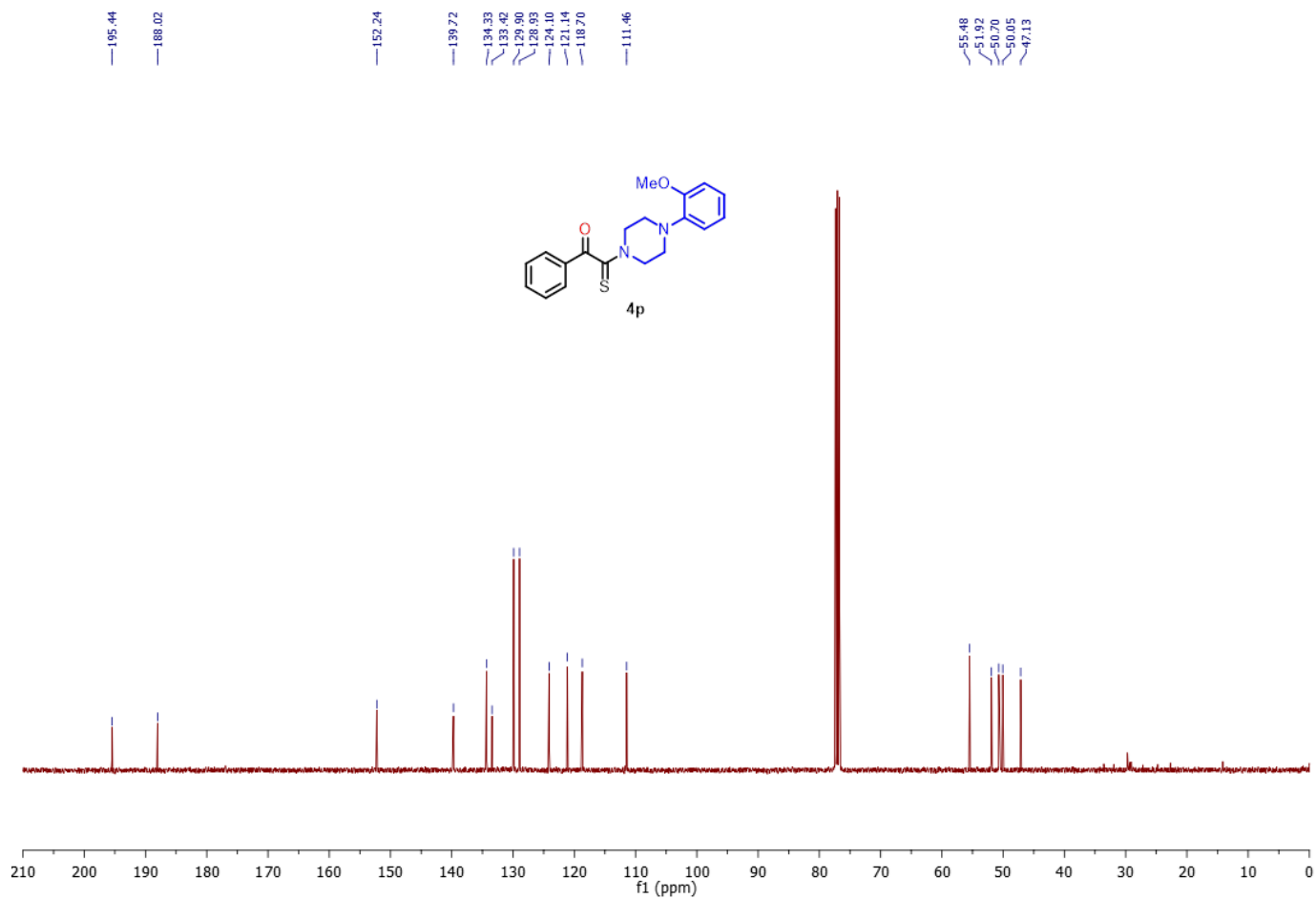
—26.33

—24.05

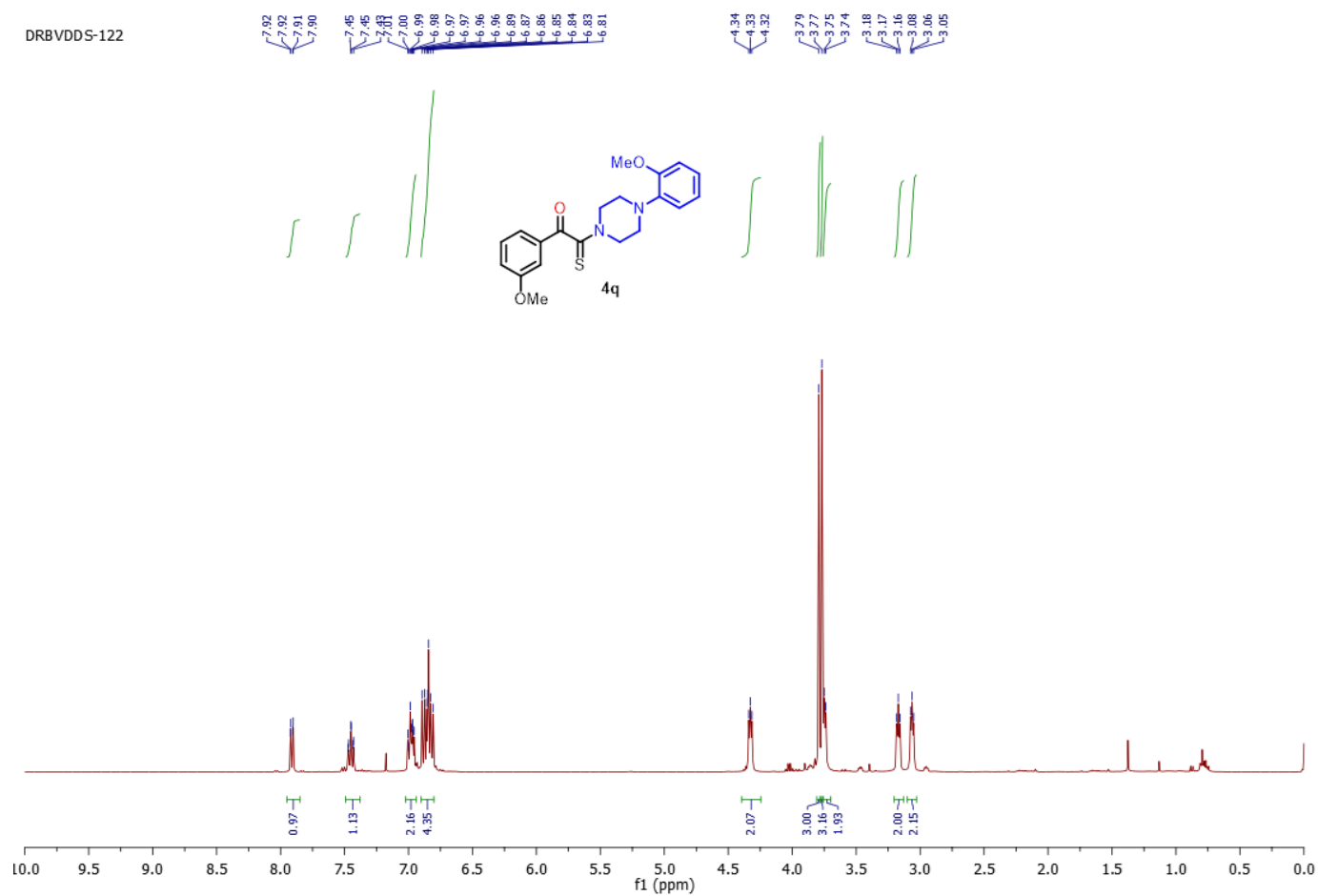


DRBVDDS-119





DRBVDDS-122



DS122

196.90

185.58

158.14

151.19

138.03

134.45

130.72

123.30

122.94

120.33

120.09

117.49

111.47

110.39

55.04

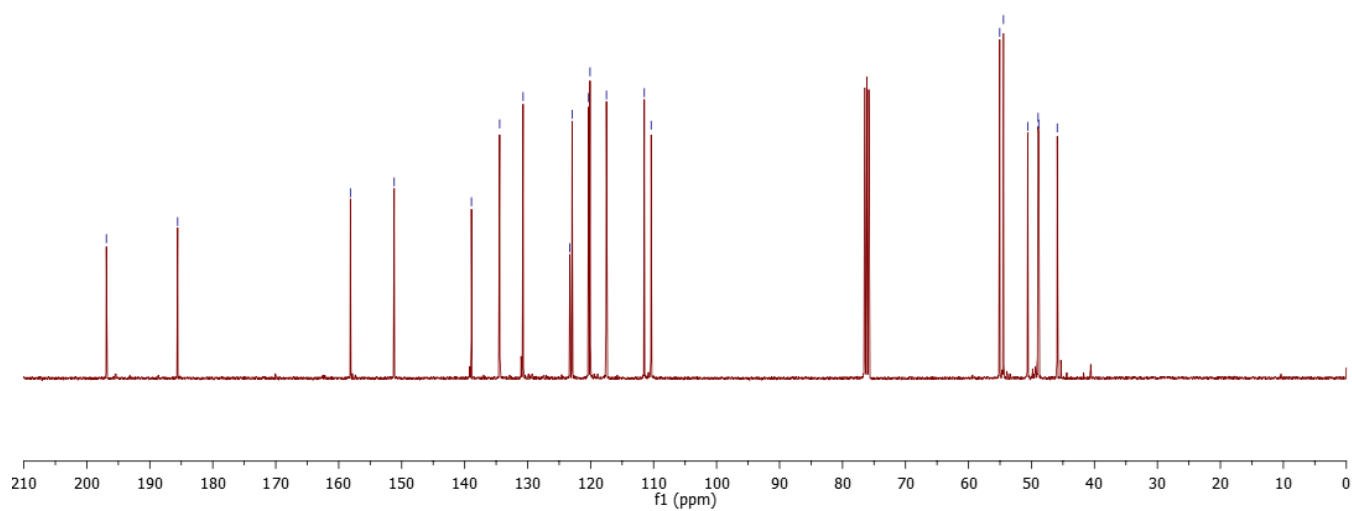
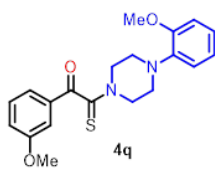
54.44

50.59

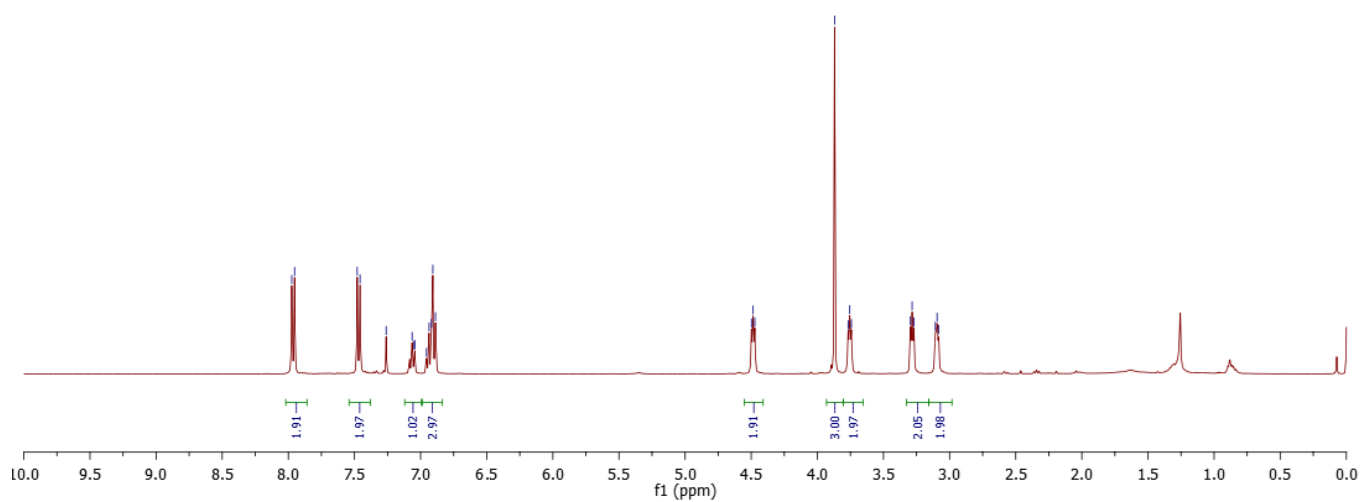
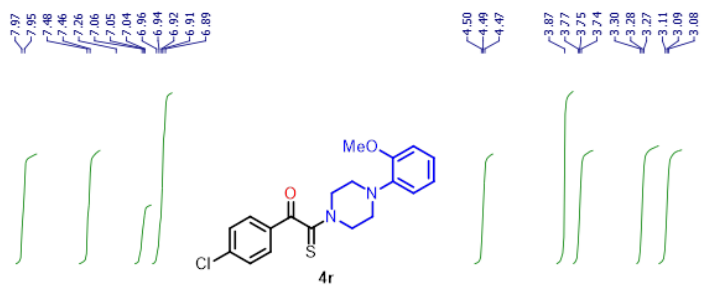
48.94

48.85

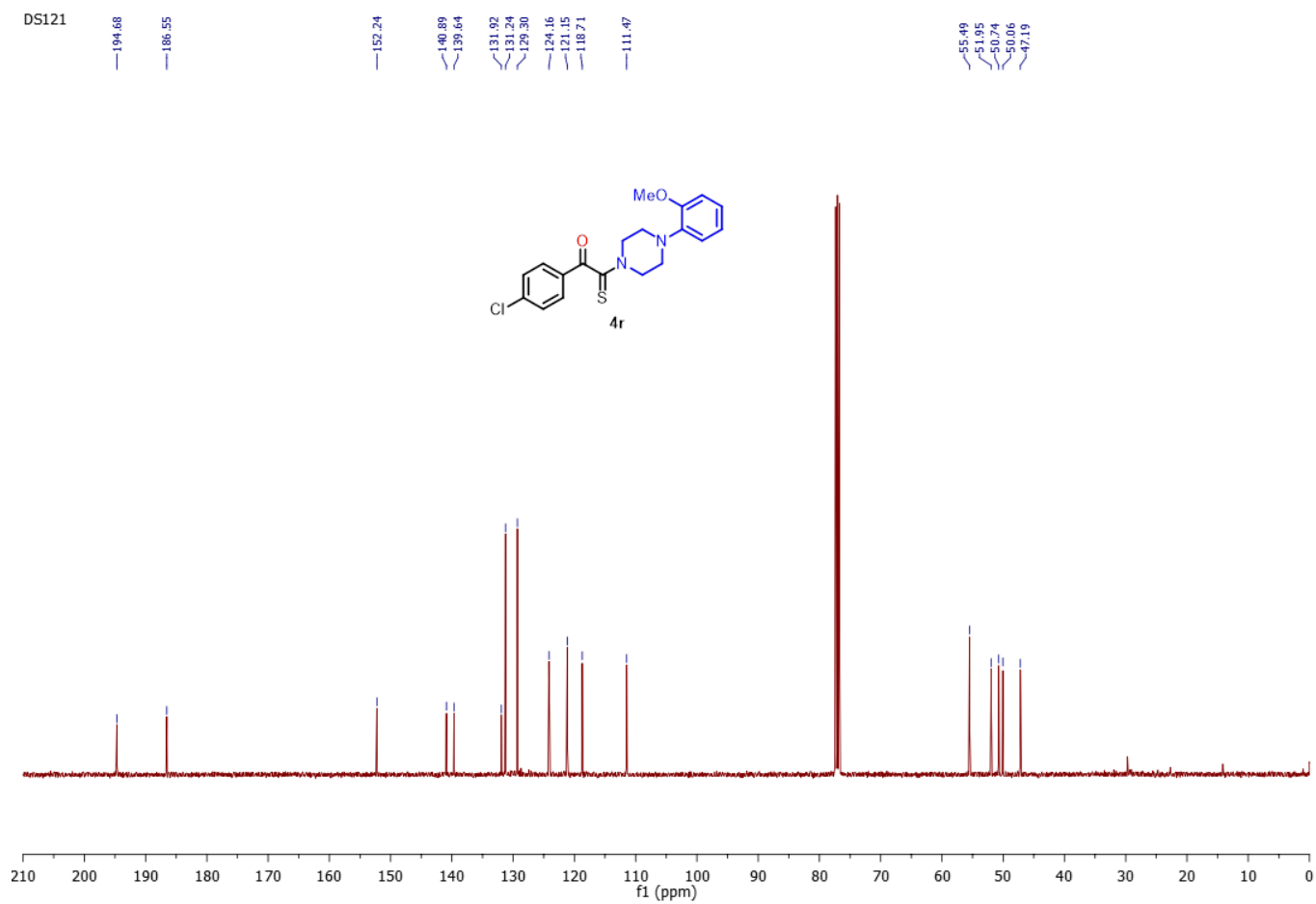
45.91



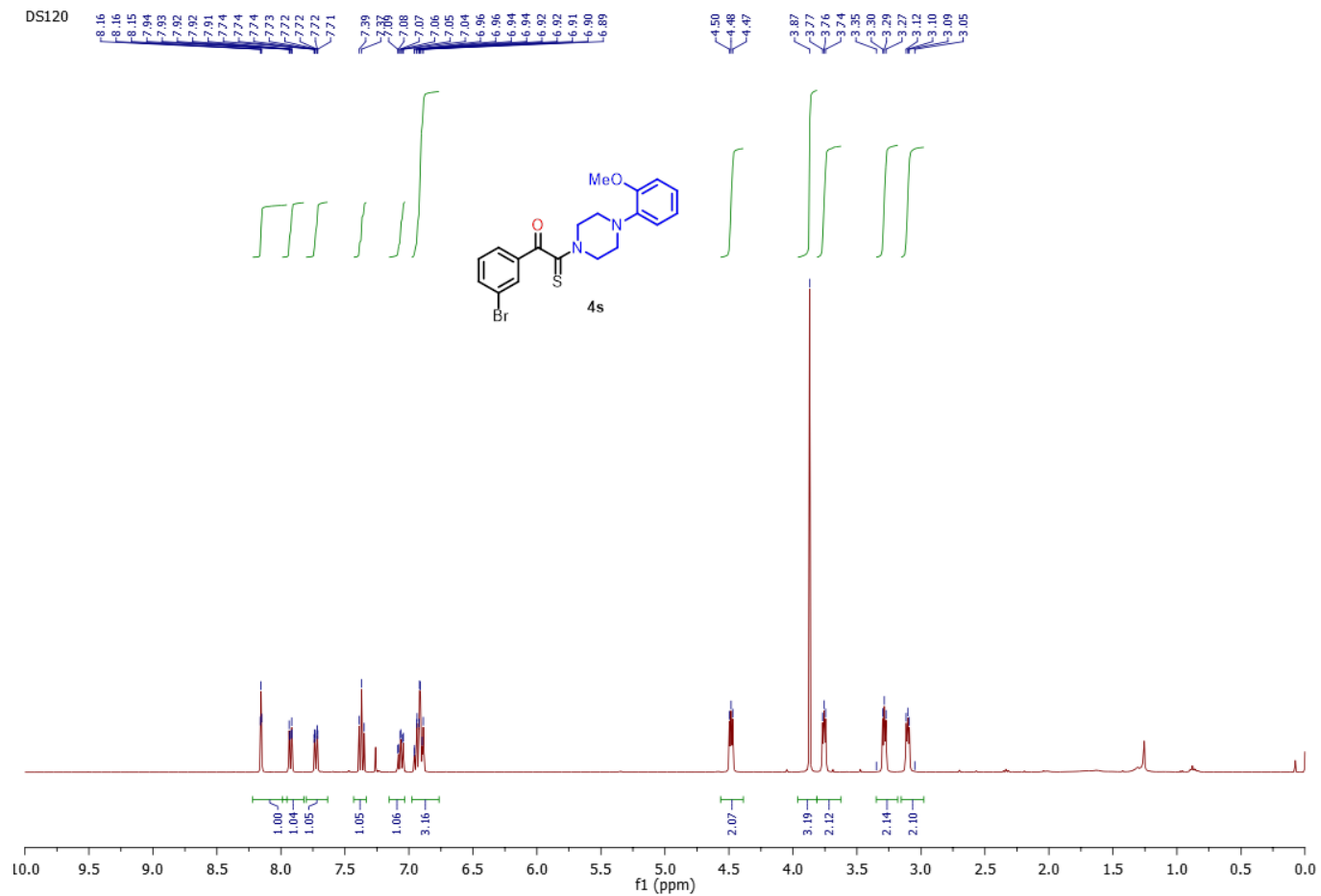
DRBVDDS-121



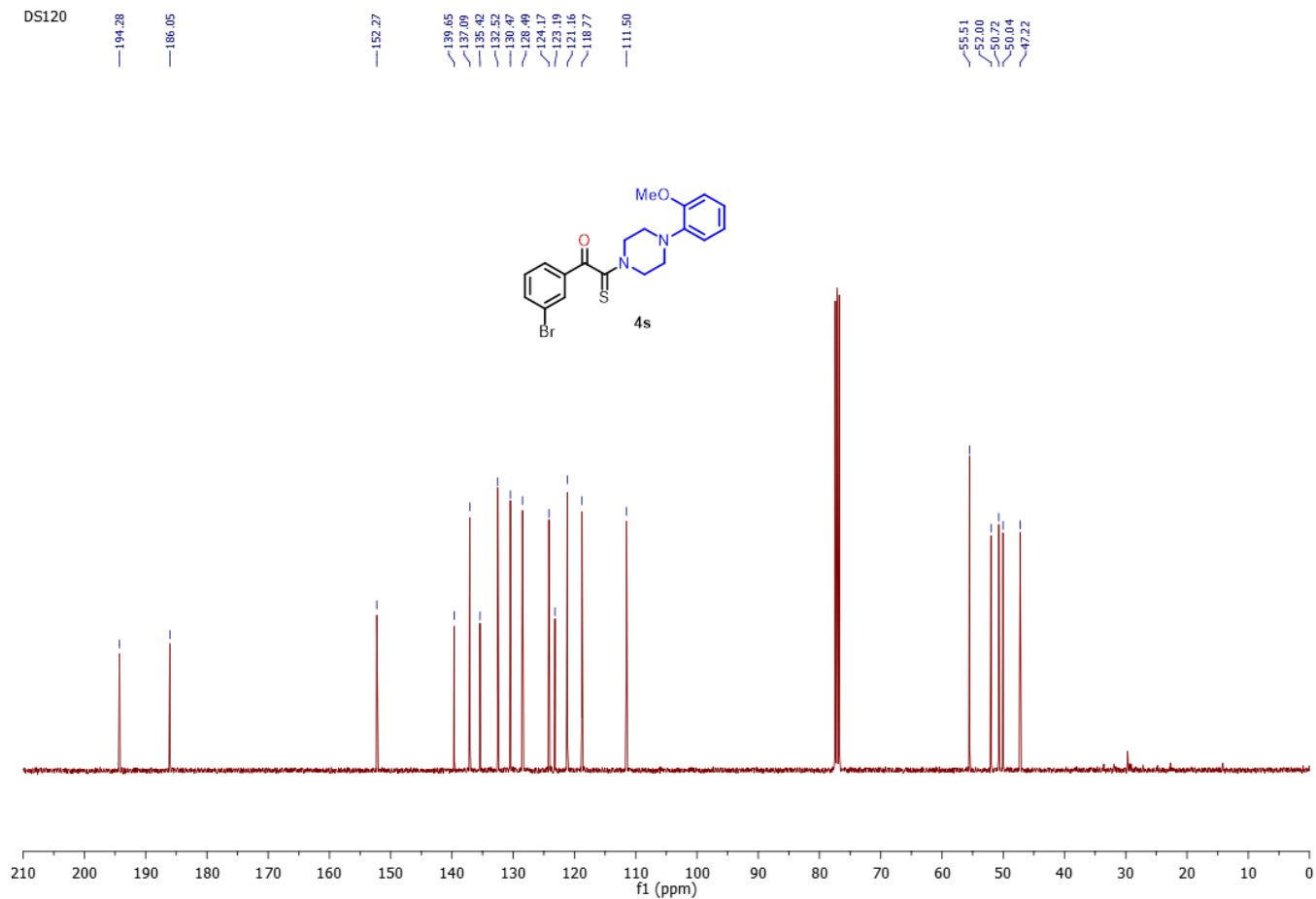
DS121



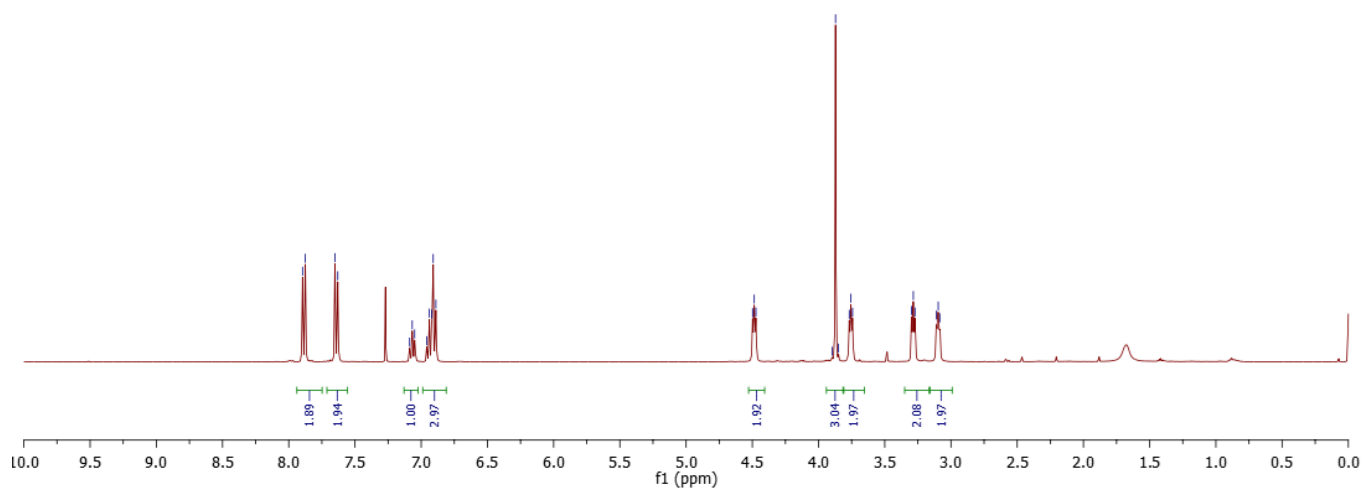
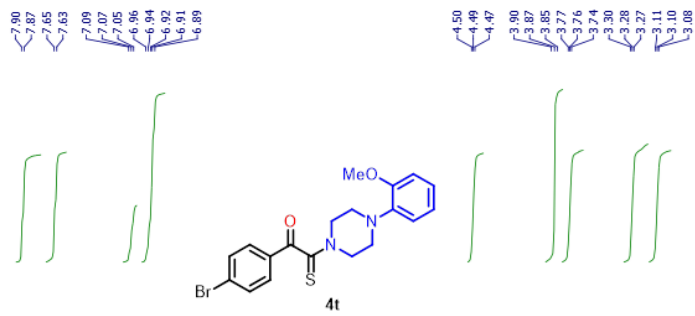
DS120



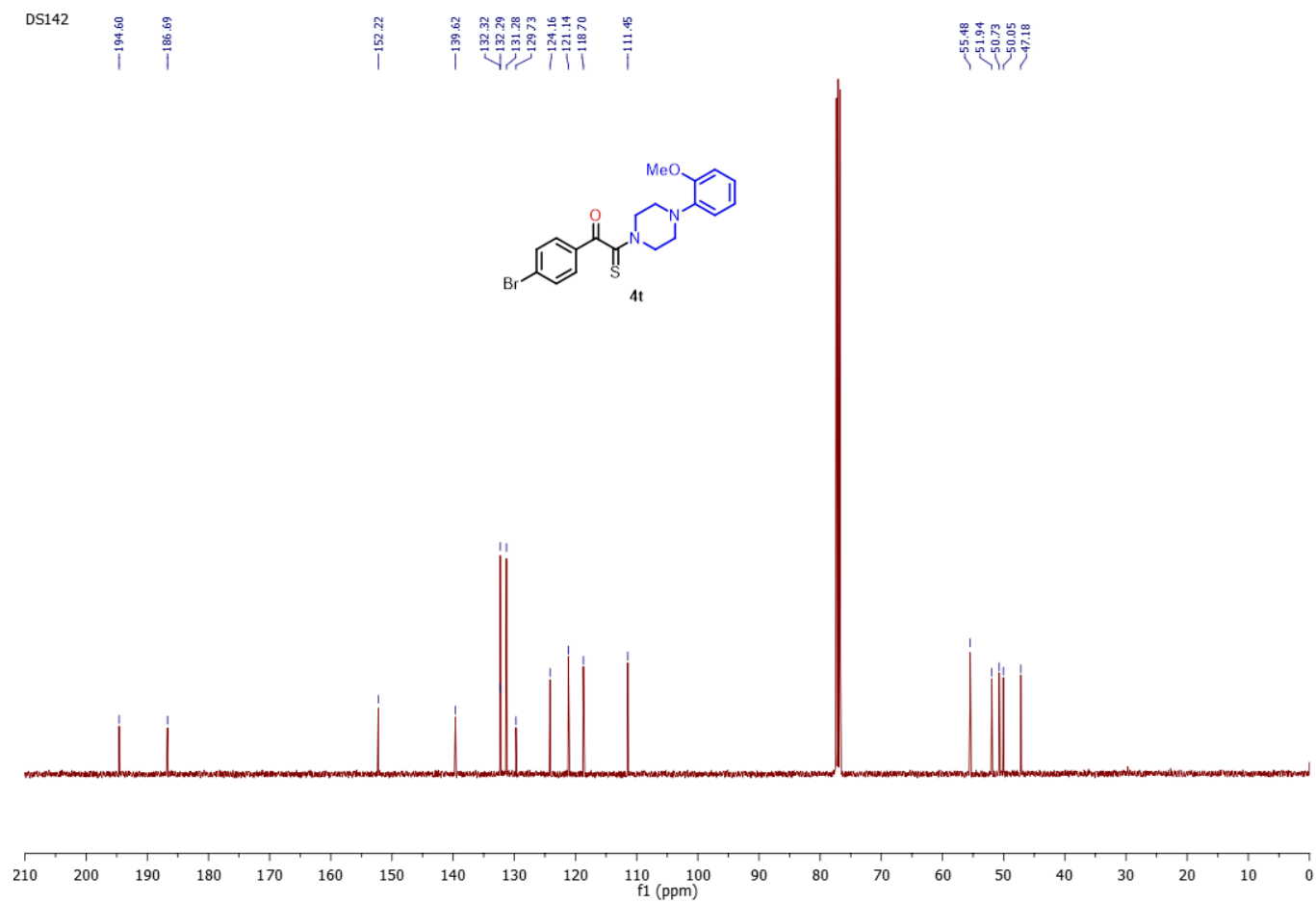
DS120



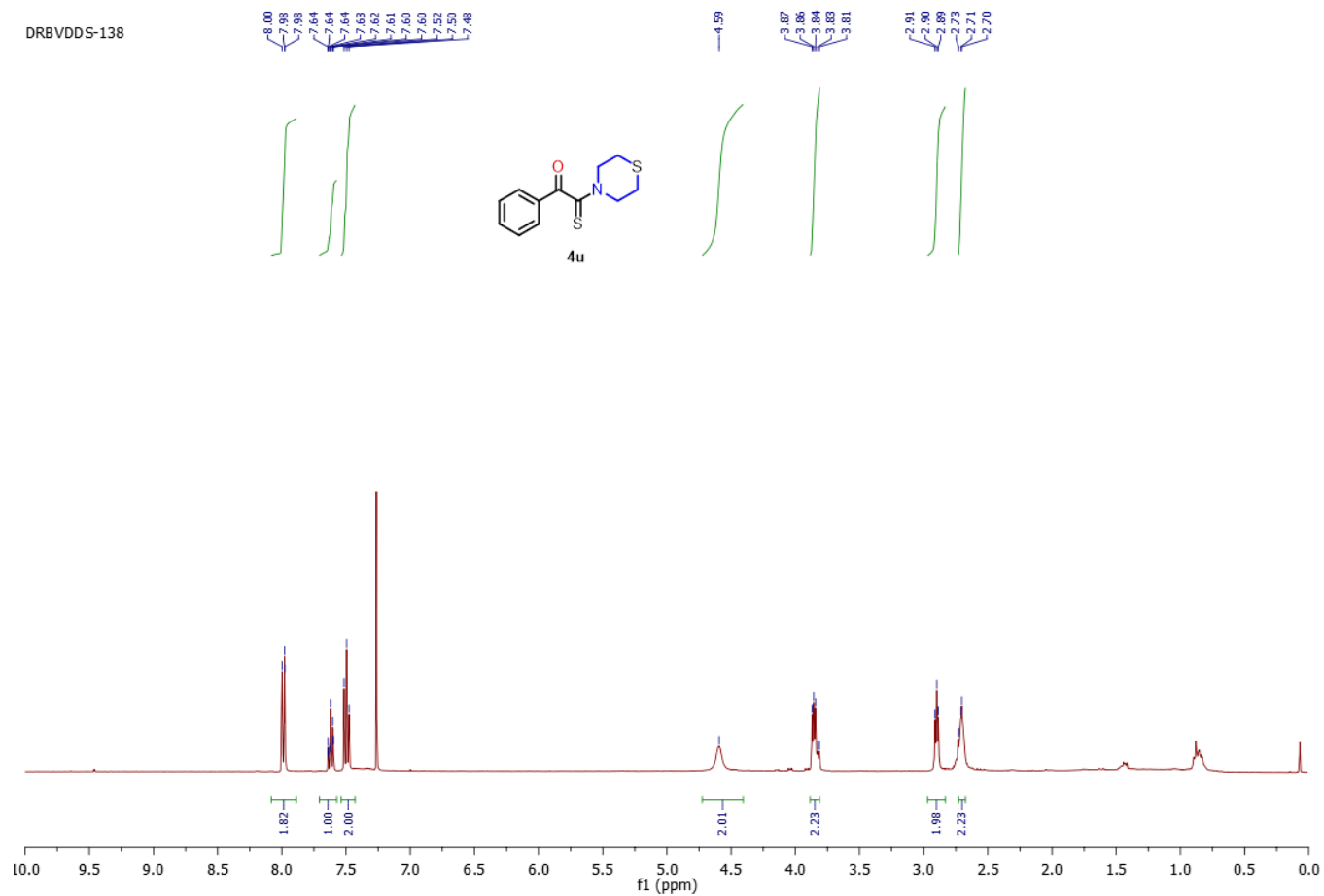
DRBVDDS-142



DS142



DRBVDD5-138



DS138

196.11

187.4

134.43

133.23

129.91

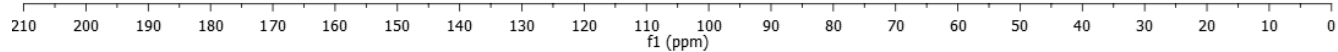
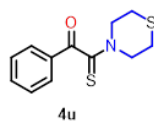
128.93

54.64

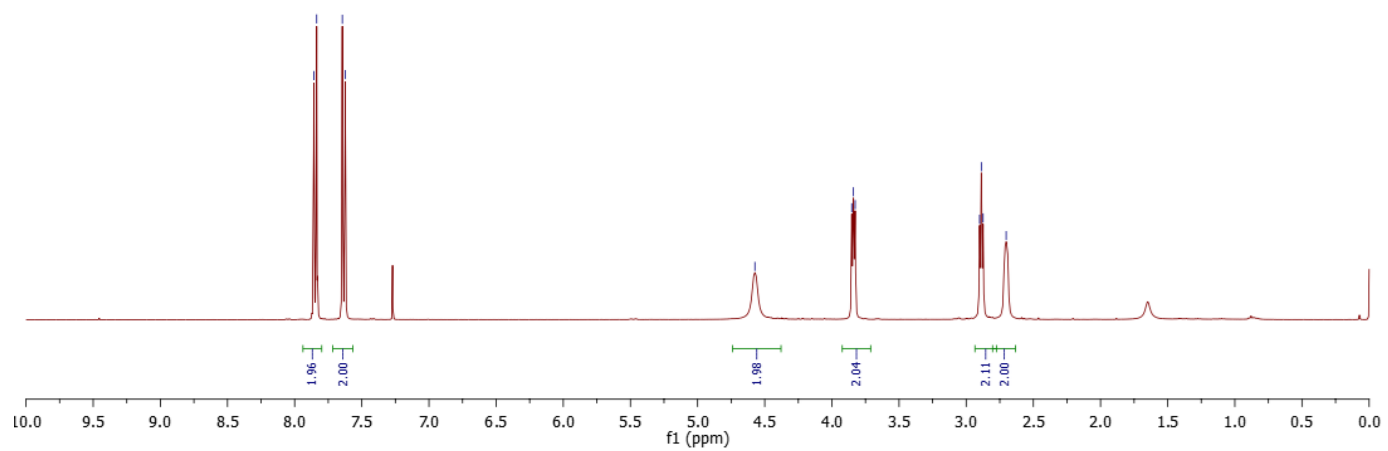
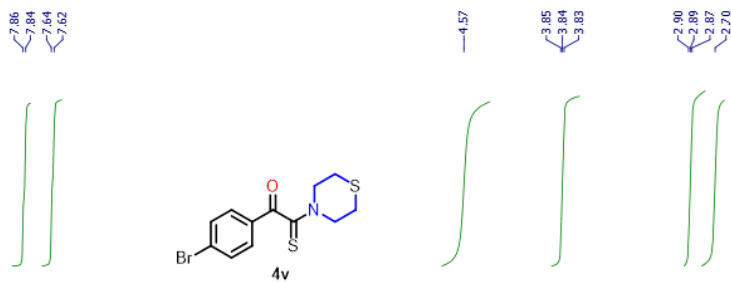
49.70

28.24

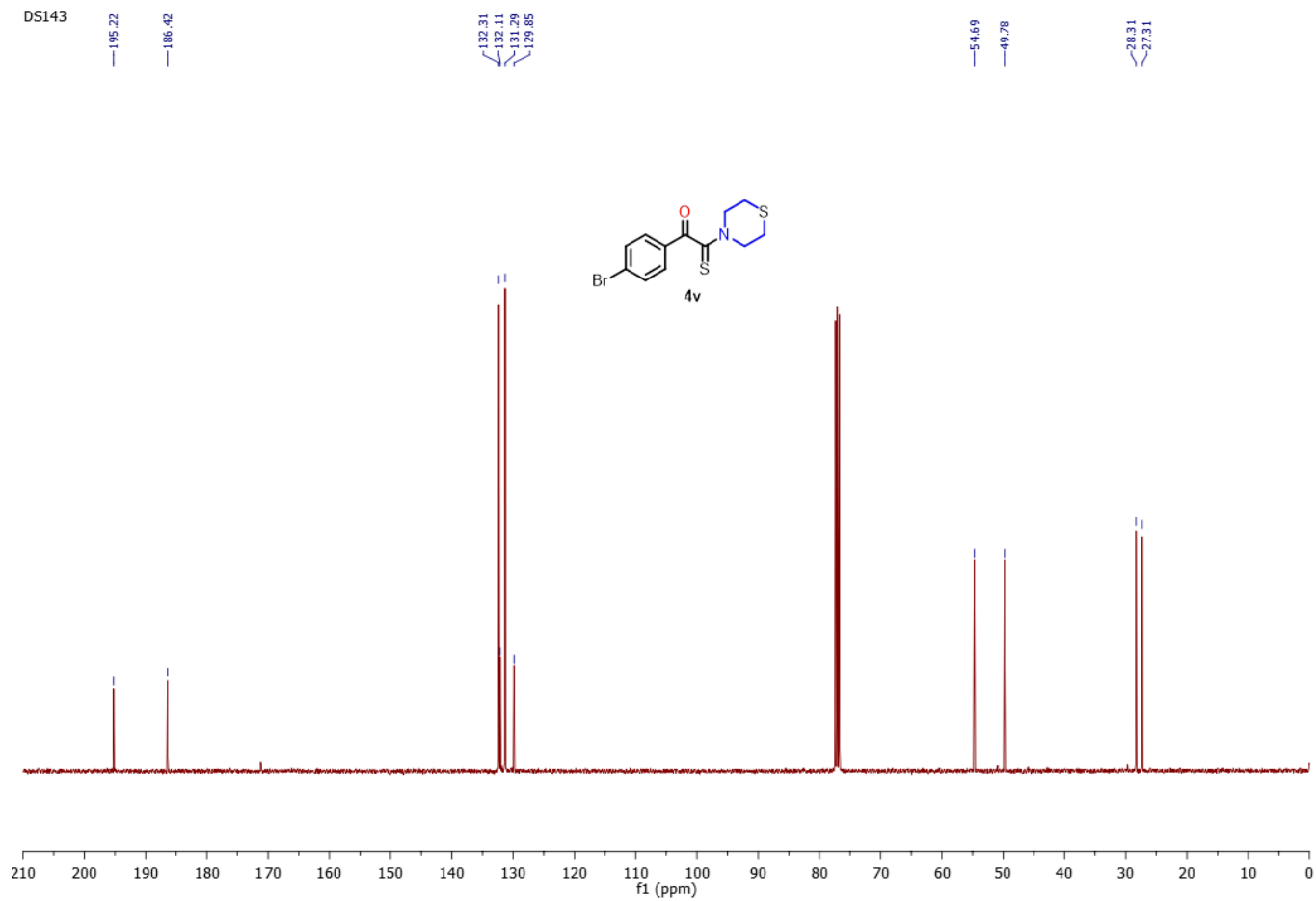
27.30



DRBVDDS-143



DS143



DRB VDDS 146 US

