Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Cooperativity within the catalyst: alkoxyamide as a catalyst for bromocyclization and bromination of (hetero)aromatics

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Experimental Section:

General: All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen atmosphere. Heptane was used as received from the commercial source. All other solvents were obtained from Merck India and were dried according to the standard literature procedure. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm); and visualized under UV light or dipping into $KMnO_4$ solution. Silica gel (particle size 100-200 mesh) and neutral alumina were purchased from SRL India for performing column chromatography. The ^1H NMR spectroscopic data were recorded with a Bruker 400, 500 or 600 MHz instruments. Proton-decoupled ^{13}C NMR spectra ($^{13}C\{^1H\}$) were similarly recorded with a 101, 126 or 151 MHz instruments by using a broad-band decoupled mode. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton or carbon signals in $CDCl_3$ (δ = 7.26, 77.16). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. For the description of ^{13}C NMR spectra, for two symmetrical carbons '2C' and for four symmetrical carbons '4C' are denoted in the parenthesis next to the respective chemical shift values. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublets dt: doublet of triplets, td: triplet of doublets, ddd: doublet of doublet of doublets, m: multiplet, br: broad. Infrared (IR) spectra were recorded by Perkin Elmer FTIR spectrometer, and reported in terms of wave number (cm^{-1}). High-resolution mass spectra were recorded with the ESI (+ve) method using a time-of-flight (TOF) mass analyzer. Other chemicals were obtained from commercial sources and used without further purification. Starting materials [**2a–2d**][1], **2e**[2], **2f**[1], **2g**[3], **2h**[4], [**2i–2j**][1], **2k**[3], **2l**[1], **2m**[3], **2n**[5], **2o**[3], **2p**[6] and **2q**[7] were synthesized according to the standard literature procedure. Compounds [**4a** and **4b**][8], [**4c** and **4d**][9], **4e**[10], **4f**[11], [**6a-6f**][12] and **8r**[13] were synthesized according to literature reported methods. Starting materials [**8a-8q**] and [**8s-8t**] are commercially available.

Synthesis of Alkoxyamide Catalyst (1c): 1-Butanesulfonyl chloride (1.0 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (5.0 mL) and *N*-methoxyamine hydrochloride (1.0 equiv.) was added. Then pyridine (2.0 equiv.) was added and the mixture was stirred at room temperature for 4 h. The mixture was quenched with water, extracted with CH_2Cl_2 (10 mL x 3), dried over anhydrous Na_2SO_4 and solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography and the corresponding alkoxyamide catalyst **1c** (151 mg, 90%) was isolated as a light orange oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.02 (s, 1H), 3.82 (s, 3H), 3.20 (dd, *J* = 8.8, 7.2 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.52 – 1.48 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 65.3, 48.7, 25.0, 21.7, 13.6. **DEPT 135** (126 MHz, $CDCl_3$): δ (ppm) 65.3 (CH_3), 48.7 (CH_2), 25.0 (CH_2), 21.7 (CH_2), 13.6 (CH_3). **FTIR:** ν_{max} (neat)/ cm^{-1} = 3320, 2963, 2877, 1466, 1397, 1328, 1150, 1048. **HRMS (ESI) m/z:** $[M + NH_4]^+$ calcd for $C_5H_{17}N_2O_3S$, 185.0954; found 185.0953. Compounds **1a**[14], **1b**[15] and **1d**[16] were characterized according to the literature procedure.

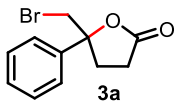
General Procedure for the Alkoxyamide-Catalyzed Bromolactonization (GP I): To a mixture of alkenoic acid **2** (0.5 mmol, 1.0 equiv) and catalyst **1c** (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added *N*-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na_2SO_3 solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by flash silica-gel column chromatography to yield the corresponding cyclized products **3**.

General Procedure for Bromo Cycloetherification and Bromo Cycloamination (GP II): To a mixture of alkenoic acid **4** (0.5 mmol, 1.0 equiv) and catalyst **1c** (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added *N*-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na_2SO_3 solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude residue was purified by flash silica-gel column chromatography to yield the corresponding cyclized products **5**.

General Procedure for the Bromocyclization of Tryptophans, Tryptamines and Tryptophols (GP III): To a solution of tryptophan or tryptamine or tryptophol derivative **6** (0.5 mmol, 1.0 equiv) and catalyst **1c** (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added *N*-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na_2SO_3 solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash silica-gel column chromatography to yield the corresponding products **7**.

General Procedure for the Bromination of Aromatic and Heteroaromatic Compounds (GP IV): To a mixture of aromatic/ heteroaromatic compound **8** (0.5 mmol, 1.0 equiv) and catalyst **1c** (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added *N*-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na_2SO_3 solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash silica-gel column chromatography to yield the corresponding brominated products **9**.

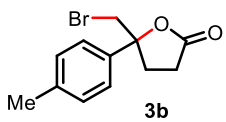
5-(Bromomethyl)-5-phenyldihydrofuran-2(3*H*)-one (3a):[3]



3a

The titled compound **3a** was synthesized according to the **GP I** and the product was isolated as colourless oil (119.9 mg, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.41 – 7.32 (m, 5H), 3.74 (d, *J* = 11.6 Hz, 1H), 3.69 (d, *J* = 11.6 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.60 – 2.48 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 175.6, 140.8, 129.0 (2C), 128.8, 125.0 (2C), 86.5, 41.1, 32.5, 29.2.

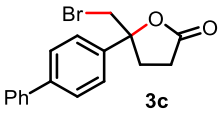
5-(Bromomethyl)-5-(p-tolyl)dihydrofuran-2(3*H*)-one (3b):[3]



3b

The titled compound **3b** was synthesized according to the **GP I** and the product was isolated as colourless oil (124 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 3.73 (d, *J* = 11.4 Hz, 1H), 3.67 (d, *J* = 11.4 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.57 – 2.49 (m, 2H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 175.7, 138.8, 137.9, 129.6 (2C), 125.0 (2C), 86.6, 41.2, 32.5, 29.2, 21.2.

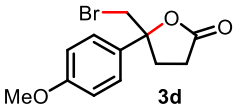
5-([1,1'-Biphenyl]-4-yl)-5-(bromomethyl)dihydrofuran-2(3*H*)-one (3c):[1]



3c

The titled compound **3c** was synthesized according to the **GP I** and the product was isolated as white solid (107.6 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.64 – 7.57 (m, 4H), 7.50 – 7.44 (m, 4H), 7.39 – 7.36 (m, 1H), 3.79 (d, *J* = 11.3 Hz, 1H), 3.73 (d, *J* = 11.3 Hz, 1H), 2.90 – 2.79 (m, 2H), 2.65 – 2.53 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 175.6, 141.8, 140.2, 139.7, 129.0 (2C), 127.9, 127.7 (2C), 127.3 (2C), 125.6 (2C), 86.5, 41.1, 32.5, 29.2.

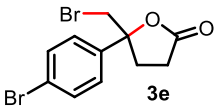
5-(Bromomethyl)-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one (3d):[3]



3d

The titled compound **3d** was synthesized according to the **GP I** and the product was isolated as colourless oil (118.3 mg, 83%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.33 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H) 3.71 (d, *J* = 11.3 Hz, 1H), 3.65 (d, *J* = 11.3 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.57 – 2.50 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 175.7, 159.9, 132.7, 126.4 (2C), 114.3 (2C), 86.5, 55.5, 41.3, 32.3, 29.3.

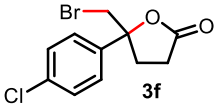
5-(Bromomethyl)-5-(4-bromophenyl)dihydrofuran-2(3*H*)-one (3e):[2]



3e

The titled compound **3e** was synthesized according to the **GP I** and the product was isolated as colourless oil (153.6 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.54 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.70 (d, *J* = 11.4 Hz, 1H), 3.65 (d, *J* = 11.4 Hz, 1H), 2.85 – 2.75 (m, 2H), 2.57 – 2.48 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 175.2, 140.0, 132.2 (2C), 126.9 (2C), 123.0, 86.1, 40.6, 32.5, 29.1.

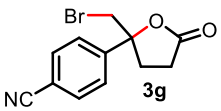
5-(Bromomethyl)-5-(4-chlorophenyl)dihydrofuran-2(3*H*)-one (3f):[3]



3f

The titled compound **3f** was synthesized according to the **GP I** and the product was isolated as colourless oil (127.4 mg, 88%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.38 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 3.70 (d, *J* = 11.4 Hz, 1H), 3.65 (d, *J* = 11.4 Hz, 1H), 2.85 – 2.76 (m, 2H), 2.57 – 2.49 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 175.2, 139.4, 134.9, 129.2 (2C), 126.6 (2C), 86.1, 40.7, 32.5, 29.1.

4-(2-(Bromomethyl)-5-oxotetrahydrofuran-2-yl)benzonitrile (3g):[3]

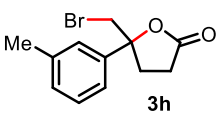


3g

The titled compound **3g** was synthesized according to the **GP I** and the product was isolated as white solid (116 mg, 83%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 3.71 (d, *J* = 11.4 Hz, 1H), 3.67 (d, *J* = 11.4 Hz, 1H), 2.89 – 2.79 (m, 2H), 2.60 – 2.52 (m, 2H). **^{13}C NMR**

(151 MHz, $CDCl_3$): δ (ppm) 174.8, 146.0, 132.8 (2C), 126.1 (2C), 118.2, 113.0, 85.9, 40.1, 32.6, 28.9.

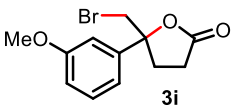
5-(Bromomethyl)-5-(m-tolyl)dihydrofuran-2(3*H*)-one (3h):



3h

The titled compound **3h** was synthesized according to the **GP I** and the product was isolated as yellow oil (118.4 mg, 88%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.29 (t, *J* = 7.8 Hz, 1H), 7.23 (s, 1H), 7.17 (dd, *J* = 12.9, 7.8 Hz, 2H), 3.73 (d, *J* = 11.4 Hz, 1H), 3.69 (d, *J* = 11.4 Hz, 1H), 2.84 – 2.76 (m, 2H), 2.58 – 2.50 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 175.8, 140.8, 138.8, 129.5, 128.9, 125.7, 122.1, 86.6, 41.2, 32.5, 29.2, 21.7. **FTIR:** ν_{max} (neat)/ cm^{-1} = 3028, 2924, 1608, 1417, 1242, 1158, 1035. **HRMS (ESI) m/z:** $[M + H]^+$ calcd for $C_{12}H_{14}BrO_2$, 269.0712; found 269.0710.

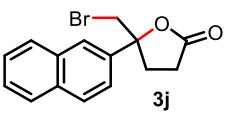
5-(Bromomethyl)-5-(3-methoxyphenyl)dihydrofuran-2(3*H*)-one (3i):[3]



3i

The titled compound **3i** was synthesized according to the **GP I** and the product was isolated as yellow oil (141 mg, 99%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.32 (t, *J* = 7.8 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.88 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.82 (s, 3H), 3.74 (d, *J* = 11.4 Hz, 1H), 3.69 (d, *J* = 11.4 Hz, 1H), 2.83 – 2.77 (m, 2H), 2.58 – 2.51 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 175.7, 160.1, 142.5, 130.1, 117.2, 114.1, 111.1, 86.5, 55.5, 41.1, 32.6, 29.2.

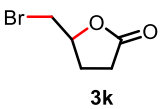
5-(Bromomethyl)-5-(naphthalen-2-yl)dihydrofuran-2(3*H*)-one (3j):[3]



3j

The titled compound **3j** was synthesized according to the **GP I** and the product was isolated as colourless oil (137.3 mg, 90%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.94 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.55 – 7.50 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 1H), 3.81 (dd, *J* = 13.8, 11.4 Hz, 2H), 2.93 – 2.81 (m, 2H), 2.70 – 2.65 (m, 1H), 2.60 – 2.54 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 138.0, 133.2, 133.1, 129.1, 128.5, 127.8, 127.0, 124.4, 122.5, 86.7, 40.9, 32.6, 29.2.

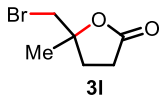
5-(Bromomethyl)dihydrofuran-2(3*H*)-one (3k):[3]



3k

The titled compound **3k** was synthesized according to the **GP I** and the product was isolated as colourless oil (61 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 4.76 – 4.70 (m, 1H), 3.57 – 3.50 (m, 2H), 2.68 – 2.50 (m, 2H), 2.47 – 2.38 (m, 1H), 2.15 – 2.06 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 176.2, 78.0, 34.2, 28.4, 26.3.

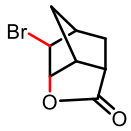
5-(Bromomethyl)-5-methyldihydrofuran-2(3*H*)-one (3l):[3]



3l

The titled compound **3l** was synthesized according to the **GP I** and the product was isolated as colourless oil (86 mg, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 3.53 (d, *J* = 10.8 Hz, 1H), 3.47 (d, *J* = 10.8 Hz, 1H), 2.76 – 2.59 (m, 2H), 2.42 – 2.35 (m, 1H), 2.12 – 2.04 (m, 1H), 1.57 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): 175.8, 84.2, 39.5, 31.7, 29.3, 25.6.

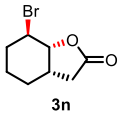
(±)-6-Bromohexahydro-2*H*-3,5-methanocyclopenta[*b*]furan-2-one (3m):[3]



3m

The titled compound **3m** was synthesized according to the **GP I** and the product was isolated as colourless oil (88 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 4.93 (d, *J* = 5.0 Hz, 1H), 3.85 (d, *J* = 2.2 Hz, 1H), 3.24 (td, *J* = 4.9, 1.1 Hz, 1H), 2.68 (d, *J* = 2.9 Hz, 1H), 2.57 (dd, *J* = 11.2, 4.6 Hz, 1H), 2.34 (dd, *J* = 11.5, 1.4 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.81 – 1.74 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 179.4, 87.8, 53.6, 46.0, 45.7, 37.7, 35.9, 34.1.

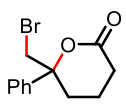
(±)-7-Bromohexahydrobenzofuran-2(3*H*)-one (3n):[5]



3n

The titled compound **3n** was synthesized according to the **GP I** and the product was isolated as colourless oil (101.8 mg, 93%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 4.59 (t, *J* = 4.4 Hz, 1H), 4.45 (dd, *J* = 8.4, 4.1 Hz, 1H), 2.79 – 2.73 (m, 1H), 2.60 (dd, *J* = 16.9, 6.9 Hz, 1H), 2.28 (dd, *J* = 16.9, 3.5 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.96 – 1.92 (m, 1H), 1.80 – 1.75 (m, 2H), 1.56 – 1.51 (m, 1H), 1.34 – 1.28 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 176.1, 81.6, 48.5, 36.8, 32.7, 29.5, 26.4, 18.8.

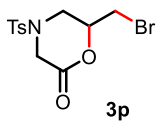
6-(Bromomethyl)-6-phenyltetrahydro-2*H*-pyran-2-one (3o):[3]



3o

The titled compound **3o** was synthesized according to the **GP I** and the product was isolated as colourless oil (105 mg, 78%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.42 – 7.34 (m, 5H), 3.68 (d, *J* = 11.4 Hz, 1H), 3.64 (d, *J* = 11.4 Hz, 1H), 2.53 – 2.35 (m, 4H), 1.87 – 1.81 (m, 1H), 1.63 – 1.59 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 170.6, 140.5, 129.2 (2C), 128.7, 125.6 (2C), 85.3, 41.7, 30.2, 29.2, 16.4.

6-(Bromomethyl)-4-tosylmorpholin-2-one (3p):

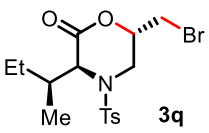


3p

The titled compound **3p** was synthesized according to the **GP I** and the product was isolated as gummy liquid (137.5 mg, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.75 – 4.69 (m, 1H), 4.04 (d, *J* = 17.6 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.56 – 3.48 (m, 2H), 3.12 (dd, *J* = 12.9, 7.8 Hz,

1H), 2.47 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 163.5, 145.3, 131.7, 130.5 (2C), 128.0 (2C), 77.1, 47.1, 45.3, 29.5, 21.8. **FTIR:** ν_{max} (neat)/ cm^{-1} = 2924, 2854, 1752, 1354, 1255, 1166, 1090, 975. **HRMS (ESI) m/z:** $[M + K]^+$ calcd for $C_{12}H_{14}BrKNO_4S$, 385.9458; found 385.9464.

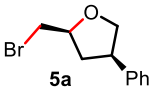
(3*S*,6*S*)-6-(Bromomethyl)-3-((*S*)-sec-butyl)-4-tosylmorpholin-2-one (3q):



3q

The titled compound **3q** was synthesized according to the **GP I** and the product was isolated as gummy liquid (155.6 mg, 77%) with 2:1 diastereomeric ratio. The reported signals are for the major diastereomer and the integration of the total diastereomers are shown because of the overlap of protons of two diastereomers. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 4.34 – 4.33 (m, 1 H), 4.19 – 4.12 (m, 1H), 4.10 – 4.02 (m, 1H), 3.39 – 3.34 (m, 3H), 2.44 (s, 3H), 2.07 – 2.01 (m, 1H), 1.67 – 1.59 (m, 2H), 1.04 (d, *J* = 6.7 Hz, 2H), 1.01 – 0.99 (m, 1H), 0.95 – 0.87 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 166.1, 145.0, 136.3, 130.5 (2C), 127.4 (2C), 75.2, 60.2, 42.9, 38.7, 30.8, 26.3, 21.7, 15.9, 11.5. **FTIR:** ν_{max} (neat)/ cm^{-1} = 2967, 1746, 1598, 1455, 1349, 1213, 1089, 965. **HRMS (ESI) m/z:** $[M + K]^+$ calcd for $C_{16}H_{22}BrKNO_4S$, 442.0084; found 442.0088.

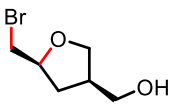
(±)-2-(Bromomethyl)-4-phenyltetrahydrofuran (5a):[17]



5a

The titled compound **5a** was synthesized according to the **GP II** and the product was isolated as colourless oil (89.2 mg, 74%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 3H), 4.37 – 4.32 (m, 1H), 4.24 (t, *J* = 8.1 Hz, 1H), 3.88 (t, *J* = 8.8 Hz, 1H), 3.57 – 3.51 (m, 3H), 2.58 – 2.53 (m, 1H), 1.95 – 1.90 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 140.9, 128.8 (2C), 127.4 (2C), 127.0, 79.1, 75.0, 45.8, 39.6, 36.0.

(±)-(5-(Bromomethyl)tetrahydrofuran-3-yl)methanol (5b):

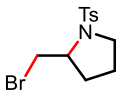


5b

The titled compound **5b** was synthesized according to the **GP II** and the product was isolated as colourless oil (93 mg, 95%) with 2:1 diastereomeric ratio. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 4.23 (quint, *J* = 6.4 Hz, 1H), 4.13 (q, *J* = 6.8 Hz, 2H), 4.05 (t, *J* = 7.8 Hz, 1H), 3.92 (t, *J* = 8.0 Hz, 2H), 3.78 (t, *J* = 7.4 Hz, 2H), 3.68 – 3.56 (m, 8H), 3.45 (d, *J* = 5.4 Hz, 4H), 3.43 – 3.36 (m, 2H), 2.58 – 2.52 (m, 7.1 Hz, 3H), 2.25 – 2.20 (m, 2H), 1.91 (t, *J* = 6.8 Hz, 2H), 1.81 (s, 4H), 1.47 – 1.41 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 78.7, 78.0, 71.3, 64.7, 64.4, 42.2, 41.8, 35.8, 35.5, 33.8, 33.3.

FTIR: ν_{max} (neat)/ cm^{-1} = 3392, 2935, 2870, 1643, 1421, 1361, 1222. **HRMS (ESI) m/z:** $[M + H]^+$ calcd for $C_6H_{12}BrO_2$, 195.0015; found 195.0016.

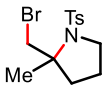
2-(Bromomethyl)-1-tosylpyrrolidine (5c):[9]



5c

The titled compound **5c** was synthesized according to the **GP II** and the product was isolated as white foam (133.6 mg, 84%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.85 – 3.81 (m, 1H), 3.77 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.49 – 3.45 (m, 1H), 3.35 (t, *J* = 9.7 Hz, 1H), 3.17 – 3.13 (m, 1H), 2.44 (s, 3H), 1.97 – 1.92 (m, 1H), 1.88 – 1.81 (m, 1H), 1.77 – 1.70 (m, 1H), 1.58 – 1.53 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 143.9, 134.2, 130.0 (2C), 127.7 (2C), 60.5, 49.9, 36.2, 30.4, 23.9, 21.7.

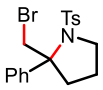
2-(Bromomethyl)-2-methyl-1-tosylpyrrolidine (5d):[9]



5d

The titled compound **5d** was synthesized according to the **GP II** and the product was isolated as white foam (134.5 mg, 81%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.75 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.84 (d, *J* = 10.1 Hz, 1H), 3.75 (d, *J* = 10.1 Hz, 1H), 3.43 – 3.39 (m, 1H), 3.35 – 3.31 (m, 1H), 2.41 (s, 3H), 2.30 – 2.26 (m, 1H), 1.89 – 1.82 (m, 1H), 1.80 – 1.75 (m, 1H), 1.73 – 1.67 (m, 2H), 1.56 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 143.3, 137.9, 129.6 (2C), 127.4 (2C), 67.4, 50.0, 41.1, 39.4, 24.2, 22.6, 21.6.

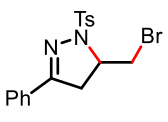
2-(Bromomethyl)-2-phenyl-1-tosylpyrrolidine (5e):[10]



5e

The titled compound **5e** was synthesized according to the **GP II** and the product was isolated as white solid (118.3 mg, 60%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.33 – 7.32 (m, 2H), 7.26 – 7.24 (m, 5H), 7.09 – 7.07 (m, 2H), 4.47 (d, *J* = 10.7 Hz, 1H), 4.28 (d, *J* = 10.7 Hz, 1H), 3.69 (q, *J* = 7.4 Hz, 1H), 3.61 (q, *J* = 7.3 Hz, 1H), 2.68 (dt, *J* = 14.4, 7.6 Hz, 1H), 2.36 (s, 3H), 2.24 (dt, *J* = 13.3, 6.8 Hz, 1H), 2.06 – 1.91 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 142.7, 141.2, 137.2, 129.0 (2C), 128.1 (2C), 127.4, 127.18 (2C), 127.15 (2C), 71.7, 50.4, 41.9, 39.4, 22.9, 21.4.

5-(Bromomethyl)-3-phenyl-1-tosyl-4,5-dihydro-1*H*-pyrazole (5f):[11]



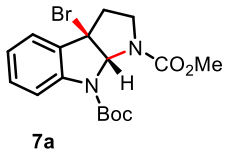
5f

The titled compound **5f** was synthesized according to the **GP II** and the product was isolated as white solid (133.7 mg, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.20 – 4.12 (m, 1H), 4.00 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.61 (t, *J* = 9.7 Hz, 1H), 3.28 (dd, *J* = 17.5, 10.9 Hz, 1H), 3.12 (dd, *J* = 17.5, 8.8 Hz, 1H), 2.39 (s, 3H). **^{13}C**

NMR (126 MHz, $CDCl_3$): δ (ppm) 157.4, 144.8, 132.0, 131.0, 130.5, 129.8 (2C), 128.82 (2C), 128.76 (2C), 127.1 (2C), 62.0, 40.0, 35.3, 21.8.

Bromocyclization of Tryptophans, Tryptamines and Tryptophols:

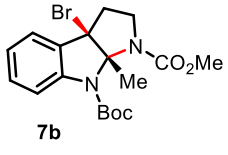
(±)-8-(*tert*-Butyl) 1-methyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,8-dicarboxylate (7a):[12]



7a

The titled compound **7a** was synthesized according to the **GP III** and the product was isolated as light yellow oil (82.4 mg, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.64 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.38 (s, 1H), 3.81 – 3.77 (m, 1H), 3.74 (s, 3H), 2.90 – 2.82 (m, 2H), 2.78 – 2.71 (m, 1H), 1.59 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 154.9, 152.3, 142.1, 132.5, 130.6, 124.3, 123.8, 117.5, 84.2, 82.3, 62.2, 52.9, 46.4, 41.2, 28.4.

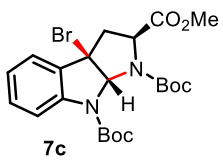
(±)-8-(*tert*-Butyl) 1-methyl-3a-bromo-8a-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (7b):[12]



7b

The titled compound **7b** was synthesized according to the **GP III** and the product was isolated as light yellow oil (85.3 mg, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.72 (s, 1H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.1 Hz, 1H), 3.64 (s, 3H), 3.49 – 3.43 (m, 1H), 2.95 – 2.84 (m, 2H), 2.69 – 2.61 (m, 1H), 2.11 (s, 3H), 1.59 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.1, 142.2, 131.7, 130.4, 123.8, 123.2, 118.3, 88.4, 82.0, 70.4, 52.4, 45.9, 36.1, 28.5, 24.6.

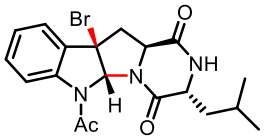
1,8-di-*tert*-Butyl 2-methyl (2*S*,3a*R*,8a*R*)-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-*b*]indole-1,2,8-tricarboxylate (7c):[12]



7c

The titled compound **7c** was synthesized according to the **GP III** and the product was isolated as white foam (96.7 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.56 (s, 1H), 7.37 – 7.30 (m, 2H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.39 (s, 1H), 3.89 (dd, *J* = 10.3, 6.3 Hz, 1H), 3.74 (s, 3H), 3.21 (dd, *J* = 12.6, 6.3 Hz, 1H), 2.82 (dd, *J* = 12.6, 10.3 Hz, 1H), 1.59 (s, 9H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 171.5, 152.2, 141.6, 132.9, 130.6, 124.4, 123.2, 118.8, 83.8, 82.3, 81.5, 59.7, 59.5, 52.4, 42.0, 28.3, 28.2.

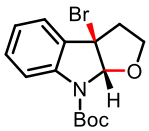
(3*R*,5a*R*,10b*R*,11a*S*)-6-Acetyl-10*b*-bromo-3-isobutyl-2,3,6,10b,11,11a-hexahydro-4*H*-pyrazino[1',2':1,5]pyrrolo[2,3-*b*]indole-1,4(5a*H*)-dione (7d):[12]



7d

The titled compound **7d** was synthesized according to the **GP III** followed by treatment with TFA in dichloromethane and the product was isolated after two steps as white solid (37.8 mg, 36%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.27 (s, 1H), 6.15 (s, 1H), 3.96 – 3.89 (m, 2H), 3.37 (dd, *J* = 12.9, 5.7 Hz, 1H), 2.96 (dd, *J* = 12.8, 11.5 Hz, 1H), 2.70 (s, 3H), 2.04 – 1.97 (m, 1H), 1.76 – 1.69 (m, 1H), 1.57 – 1.50 (m, 1H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 170.7, 167.6, 166.3, 142.1, 131.7, 131.3, 125.8, 123.5, 119.7, 85.2, 59.2, 58.8, 53.3, 43.6, 38.8, 24.6, 23.7, 23.4, 21.2.

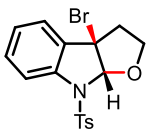
(±)-*tert*-Butyl-3a-bromo-2,3,3a,8a-tetrahydro-8*H*-furo[2,3-*b*]indole-8-carboxylate (7e):[12]



7e

The titled compound **7e** was synthesized according to the **GP III** and the product was isolated as gummy liquid (84.2 mg, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.77 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.16 (s, 1H), 3.96 (t, *J* = 8.1 Hz, 1H), 3.49 – 3.41 (m, 1H), 2.90 – 2.82 (m, 1H), 2.75 (dd, *J* = 11.7, 4.1 Hz, 1H), 1.56 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.0, 141.8, 131.9, 130.6, 125.0, 123.8, 115.1, 100.9, 82.4, 67.9, 61.8, 45.2, 28.5.

(±)-3a-Bromo-8-tosyl-3,3a,8,8a-tetrahydro-2*H*-furo[2,3-*b*]indole (7f):[12]

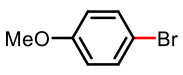


7f

The titled compound **7f** was synthesized according to the **GP III** and the product was isolated as light yellow foam (77 mg, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.24 (s, 1H), 4.03 – 3.98 (m, 1H), 3.43 (ddd, *J* = 11.1, 9.2, 4.8 Hz, 1H), 2.88 – 2.80 (m, 1H), 2.74 – 2.70 (m, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.6, 140.7, 135.8, 132.6, 130.8, 129.9 (2C), 127.6 (2C), 125.4, 125.0, 114.4, 103.4, 68.1, 61.5, 44.8, 21.7.

(*Hetero*)-Aromatic Bromination:

1-Bromo-4-methoxybenzene (9a):[18]

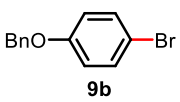


9a

The titled compound **9a** was synthesized according to the **GP IV** and the product was isolated as clear liquid (82.2 mg, 88%). **^{1}H NMR** (400 MHz,

$CDCl_3$): δ (ppm) 7.38 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 158.9, 132.4 (2C), 115.9 (2C), 113.0, 55.6.

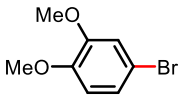
1-(Benzyloxy)-4-bromobenzene (9b):[18]



9b

The titled compound **9b** was synthesized according to the **GP IV** and the product was isolated as white solid (114.4 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.43 – 7.32 (m, 7H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.04 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 158.0, 136.7, 132.4 (2C), 128.8 (2C), 128.3, 127.6 (2C), 116.8 (2C), 113.3, 70.4.

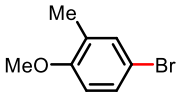
4-Bromo-1,2-dimethoxybenzene (9c):[18]



9c

The titled compound **9c** was synthesized according to the **GP IV** and the product was isolated as colourless oil (95.5 mg, 88%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.02 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 149.8, 148.4, 123.5, 114.9, 112.8, 112.6, 56.2, 56.1.

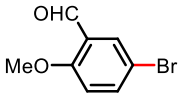
4-Bromo-1-methoxy-2-methylbenzene (9d):[18]



9d

The titled compound **9d** was synthesized according to the **GP IV** and the product was isolated as colourless oil (75.4 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.25 (d, *J* = 7.2 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 2.19 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 157.0, 133.3, 129.5, 129.1, 112.5, 111.6, 55.6, 16.2.

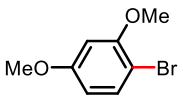
5-Bromo-2-methoxybenzaldehyde (9e):[19]



9e

The titled compound **9e** was synthesized according to the **GP IV** and the product was isolated as light yellowish solid (80.6 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 10.37 (s, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 188.5, 160.9, 138.4, 131.1, 126.2, 113.8, 113.6, 56.1.

1-Bromo-2,4-dimethoxybenzene (9f):[20]

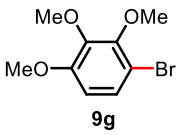


9f

The titled compound **9f** was synthesized according to the **GP IV** and the product was isolated as colourless oil (98.8 mg, 91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.40 (d, *J* = 8.6 Hz, 1H), 6.49 (s, 1H), 6.40 (d, *J* = 8.7 Hz,

1H), 3.87 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 160.5, 156.8, 133.3, 106.3, 102.8, 100.3, 56.4, 55.8.

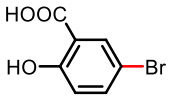
1-Bromo-2,3,4-trimethoxybenzene (9g):[21]



9g

The titled compound **9g** was synthesized according to the **GP IV** and the product was isolated as light yellow oil (122.3 mg, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.20 (d, *J* = 8.9 Hz, 1H), 6.58 (d, *J* = 9.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 153.6, 151.3, 143.9, 126.9, 109.0, 108.7, 61.3, 61.2, 56.4.

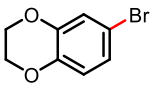
5-Bromo-2-hydroxybenzoic acid (9h):[22]



9h

The titled compound **9h** was synthesized according to the **GP IV** and the product was isolated as white solid (89.6 mg, 85%). The isolated product **9h** contained 6% of **8h**. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 10.32 (s, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.60 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 173.6, 161.3, 139.9, 133.2, 120.0, 112.9, 111.4.

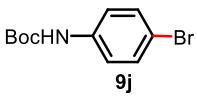
6-Bromo-2,3-dihydrobenzo[*b*][1,4]dioxine (9i):[23]



9i

The titled compound **9i** was synthesized according to the **GP IV** and the product was isolated as colourless oil (100 mg, 93%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.01 (d, *J* = 2.3 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 4.24 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 144.5, 143.0, 124.4, 120.4, 118.7, 112.9, 64.4, 64.3.

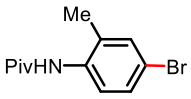
***tert*-Butyl (4-bromophenyl)carbamate (9j):**[18]



9j

The titled compound **9j** was synthesized according to the **GP IV** and the product was isolated as white solid (117 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 2H), 6.48 (bs, 1H), 1.51 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.6, 137.6, 132.0 (2C), 120.2 (2C), 28.4.

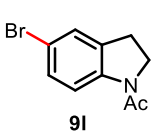
***N*-(4-Bromo-2-methylphenyl)pivalamide (9k):**[24]



9k

The titled compound **9k** was synthesized according to the **GP IV** and the product was isolated as white solid (124 mg, 92%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.76 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.31 (s, 2H), 7.18 (s, 1H), 2.22 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 176.6, 135.1, 133.1, 130.9, 129.9, 124.4, 117.7, 39.9, 27.8, 17.6.

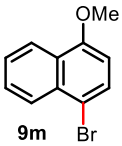
1-(5-Bromoindolin-1-yl)ethan-1-one (9l):[24]



9l

The titled compound **9l** was synthesized according to the **GP IV** and the product was isolated as white solid (102 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.06 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 4.04 (t, *J* = 8.5 Hz, 2H), 3.16 (t, *J* = 8.5 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 168.9, 142.2, 133.5, 130.5, 127.7, 118.4, 116.0, 49.0, 27.8, 24.2.

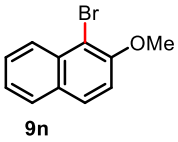
1-Bromo-4-methoxynaphthalene (9m):[18]



9m

The titled compound **9m** was synthesized according to the **GP IV** and the product was isolated as white solid (117 mg, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.28 (d, *J* = 8.3 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 3.99 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 155.4, 132.6, 129.6, 127.9, 127.0, 126.95, 126.1, 122.6, 113.4, 104.7, 55.8.

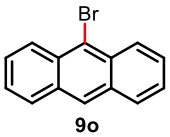
1-Bromo-2-methoxynaphthalene (9n):[18]



9n

The titled compound **9n** was synthesized according to the **GP IV** and the product was isolated as white solid (109 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.23 (d, *J* = 8.6 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 9.3 Hz, 1H), 4.03 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 153.9, 133.3, 130.0, 129.1, 128.2, 127.9, 126.3, 124.4, 113.8, 108.8, 57.2.

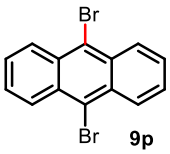
9-Bromoanthracene (9o):[20]



9o

The titled compound **9o** was synthesized according to the **GP IV** and the product was isolated as yellow solid (104 mg, 81%). In a second fraction, dibrominated product **9p** was also isolated (10.5 mg, 8% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 8.9 Hz, 2H), 8.45 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.62 – 7.59 (m, 2H), 7.53 – 7.49 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 132.3, 130.7, 128.8 (2C), 127.8 (2C), 127.4 (2C), 127.3, 125.8 (2C), 122.5.

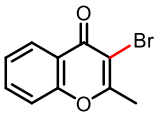
9,10-Dibromoanthracene (9p):[20]



9p

The titled compound **9p** was synthesized according to the **GP IV** and the product was isolated as yellow solid (143 mg, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.61 – 8.57 (m, 4H), 7.65 – 7.61 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 131.2 (4C), 128.4 (4C), 127.6 (4C), 123.7 (2C).

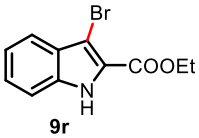
3-Bromo-2-methyl-4*H*-chromen-4-one (9q):[25]



9q

The titled compound **9q** was synthesized according to the **GP IV** and the product was isolated as white solid (59.7 mg, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.23 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 (ddd, *J* = 8.5, 7.4, 1.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 172.4, 164.1, 155.5, 134.0, 126.6, 125.7, 122.0, 117.7, 109.9, 21.8.

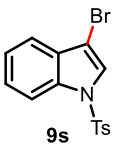
Ethyl 3-Bromo-1*H*-indole-2-carboxylate (9r):[26]



9r

The titled compound **9r** was synthesized according to the **GP IV** and the product was isolated as white solid (110 mg, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.07 (bs, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.23 – 7.21 (m, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 161.1, 135.4, 128.2, 126.7, 124.3, 121.6, 121.5, 112.1, 98.5, 61.6, 14.5.

3-Bromo-1-tosyl-1*H*-indole (9s):[27]

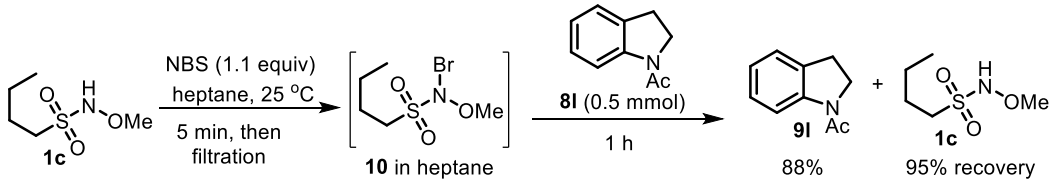


9s

The titled compound **9s** was synthesized according to the **GP IV** and the product was isolated as white solid (89 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 145.5, 134.9, 134.4, 130.2 (2C), 129.9, 127.0 (2C), 125.9, 124.9, 124.0, 120.2, 113.7, 99.7, 21.7.

Control Experiments:

Bromocyclization Using Stoichiometric Amount of 10:



In a reaction tube, 1.1 equiv. of NBS was added to a solution of **1c** (83.6 mg, 0.5 mmol) in heptane. The reaction tube was covered with aluminium foil and the reaction was stirred for 5 min at room temperature. After completion, the insoluble succinimide was filtered and the filtrate was collected. Then 0.5 mmol of the alkenoic acid **8l** was added to the solution and the mixture was stirred for 15 minutes at room temperature. The reaction was quenched with saturated solution of $Na_2S_2O_3$. The reaction mixture was concentrated and purified by column chromatography to isolate 88% of **9l** and catalyst **1c** was recovered (79.4 mg, 95%) almost in quantitative yield.

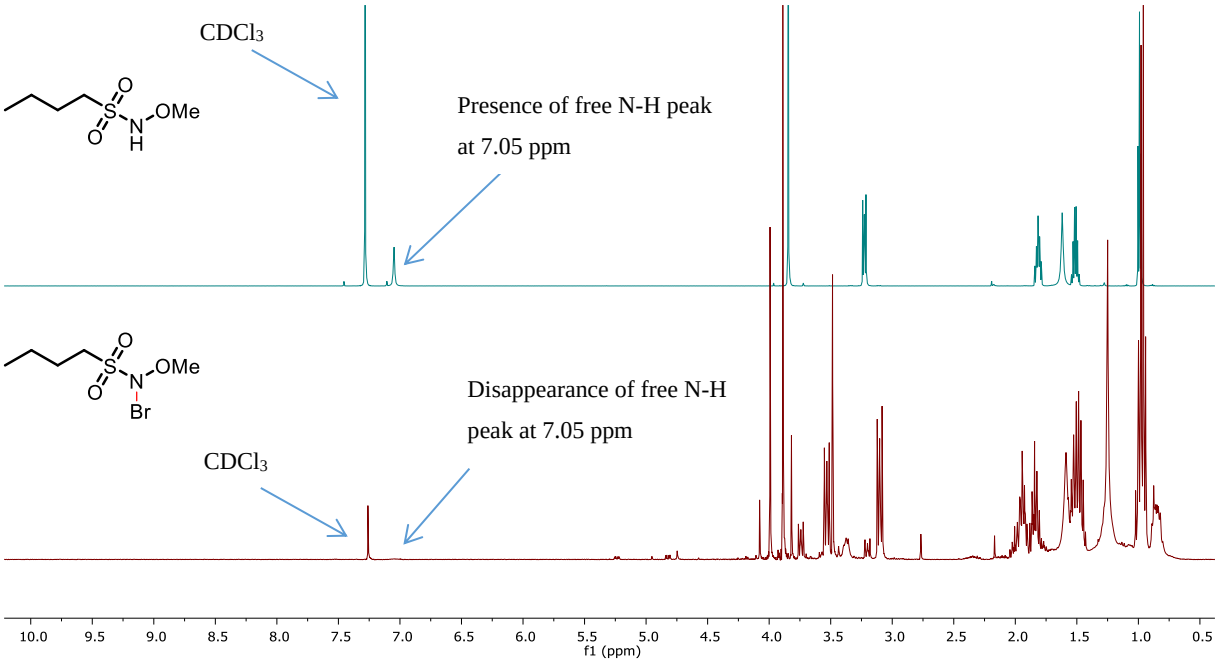
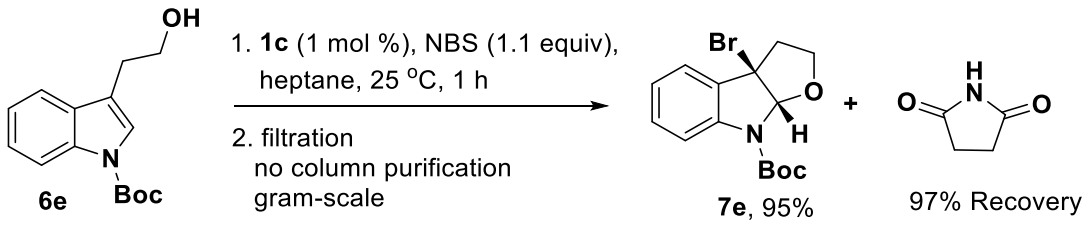


Figure S1. ^{1}H NMR study of crude **10**.

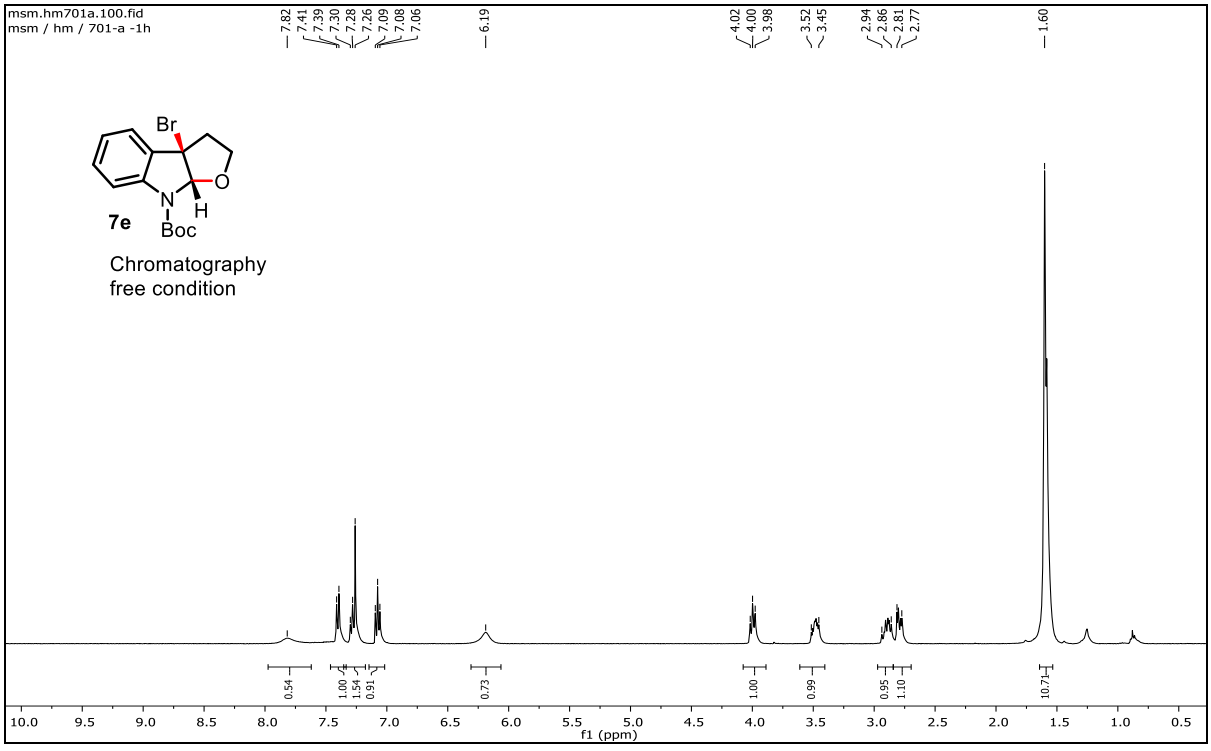
Alternatively, we also attempted to isolate the intermediate **10** by following the same procedure as discussed above to obtain **10** as a solution in heptane. The solvent was then evaporated and the crude residue containing **10** was quickly re-dissolved in $CDCl_3$ and NMR was recorded immediately. The ^{1}H NMR analysis of crude **10** revealed that N-H peak of **1c** at 7.05 ppm disappeared (Figure S1). It was found that although the intermediate **10** is stable in heptane

solution for some time, it undergoes rapid decomposition in the absence of any solvent. The stability of **10** also varies from solvent to solvent.

Chromatography-Free Gram-Scale Synthesis:



To a solution of *N*-Boc tryptophol **6e (**1.3 g, 5 mmol) in 25 mL hexane, 1 mol % of **1c** (8.4 mg) and NBS (1.1 equiv., 0.98 g) were added. After stirring the resulting mixture at room temperature for 1 h, the insoluble succinimide was separated by filtration. The filtrate was then concentrated to obtain tetrahydrofuroindoline **7e** (1.6 g, 95%) in analytically pure form as indicated by ^{1}H NMR analysis (Figure S2). Pure succinimide (confirmed by ^{1}H NMR analysis) was recovered in 97% yield. No column chromatography was performed in this entire isolation process.



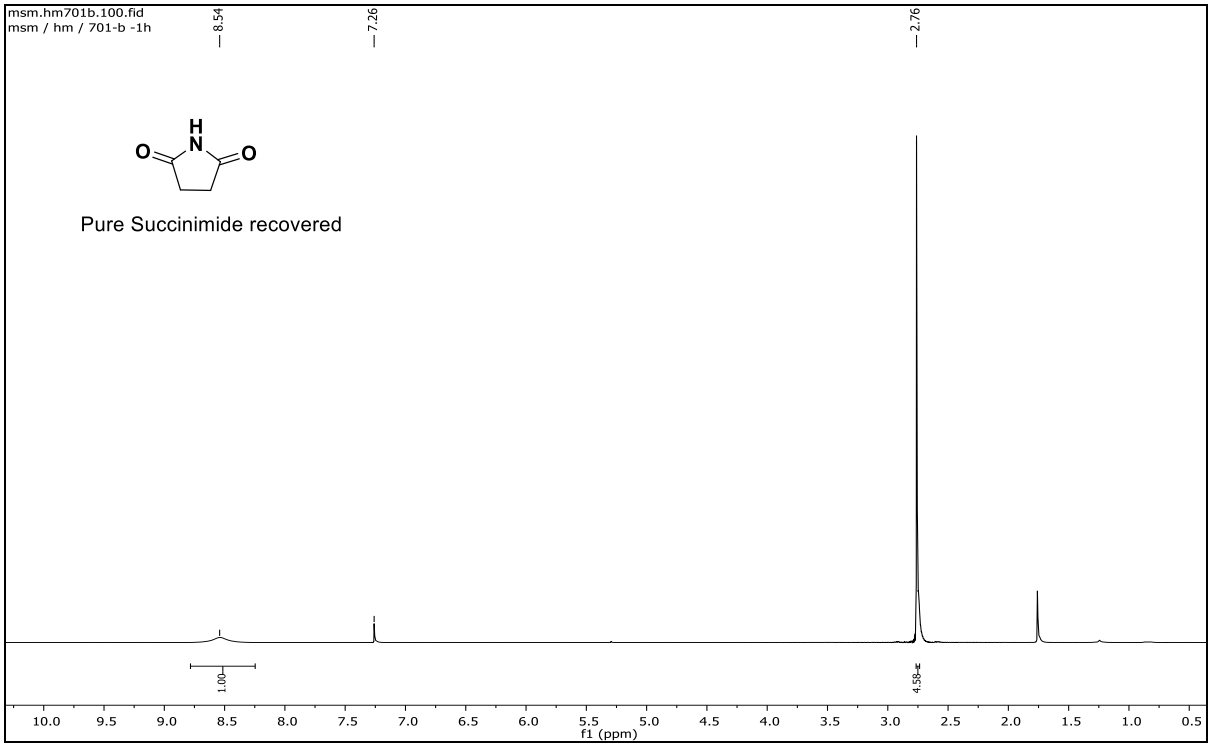
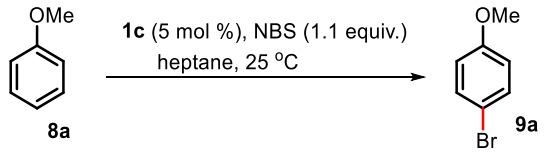


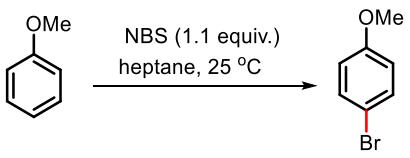
Figure S2: Chromatography-free gram-scale synthesis.

Kinetic Studies:

Effect of Catalyst on the Reaction Profile: Catalyzed vs Uncatalyzed Reaction of Anisole Bromination:



Anisole Bromination in the Presence of Catalyst: Anisole (1 mmol) was dissolved in 10 ml of heptane and 5 mol % of **1c** and 1.05 mmol of NBS were added successively. The reaction mixture was stirred in the absence of light. Periodically, aliquots of the reaction mixture were taken and quenched with $Na_2S_2O_3$ solution. The conversion from **8a** to **9a** was followed up by ^1H NMR analysis of aliquots. Product conversion was plotted as a function of time.



Anisole Bromination in the Absence of Catalyst: Anisole (1 mmol) was dissolved in 10 ml of heptane and 1.05 mmol of NBS was added. The reaction mixture was stirred in the absence of light. Periodically, aliquots of the reaction mixture were taken and quenched with $Na_2S_2O_3$ solution. The conversion from **8a** to **9a** was followed up by NMR analysis of aliquots.

With Catalyst

Time (h)	Conversion to 9a (%) (with catalyst)
0	0
2	0
4	0
5	0
6	0
7	0
8	9.1
8.5	16.7
9.5	23.1
10.5	28.6
11.5	37.5
12	44.4
12.5	51.2
13.5	63.6
14.25	72.9
14.5	76.1
14.75	78.0
15	80.3
15.5	84.8
16	88.1
16.5	92.2

Without Catalyst

Time (h)	Conversion to 9a (%) (without catalyst)
0	0
3	0
5	0
7	0
8	0
9	0
10	0
11	0
12.25	0
13.5	0
14.25	0
15	0
16	0
24	0

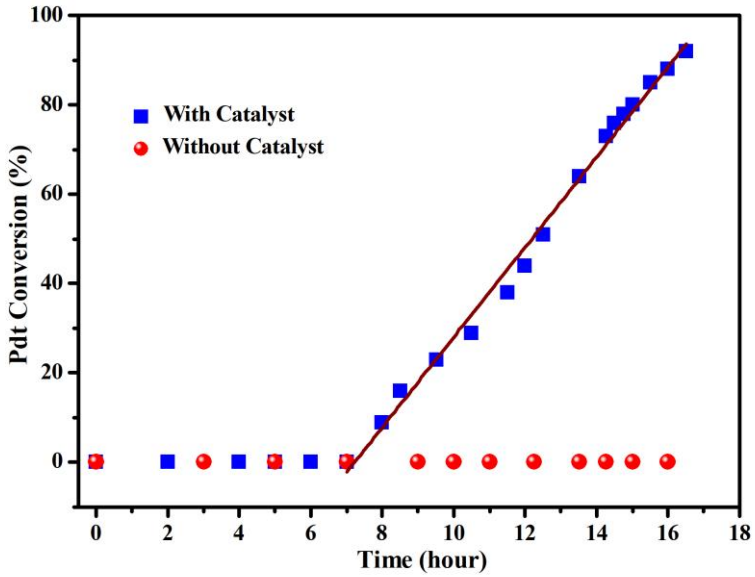
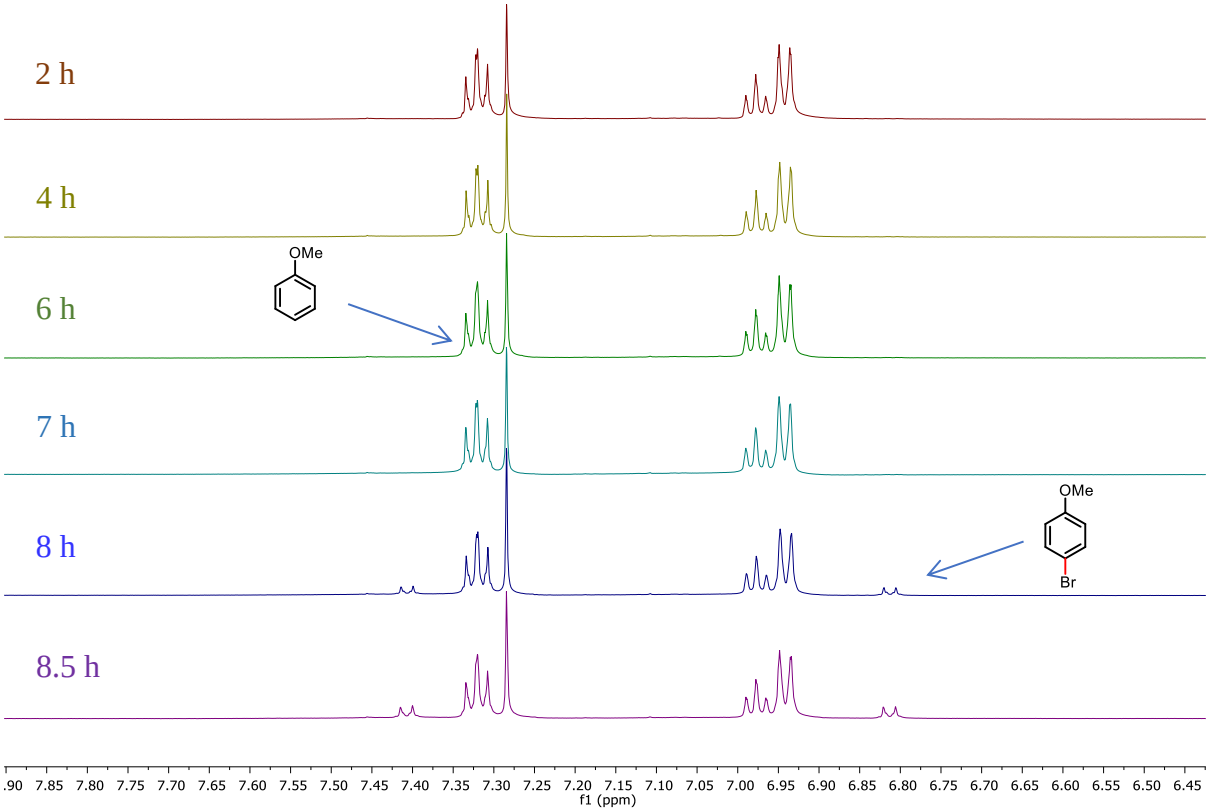
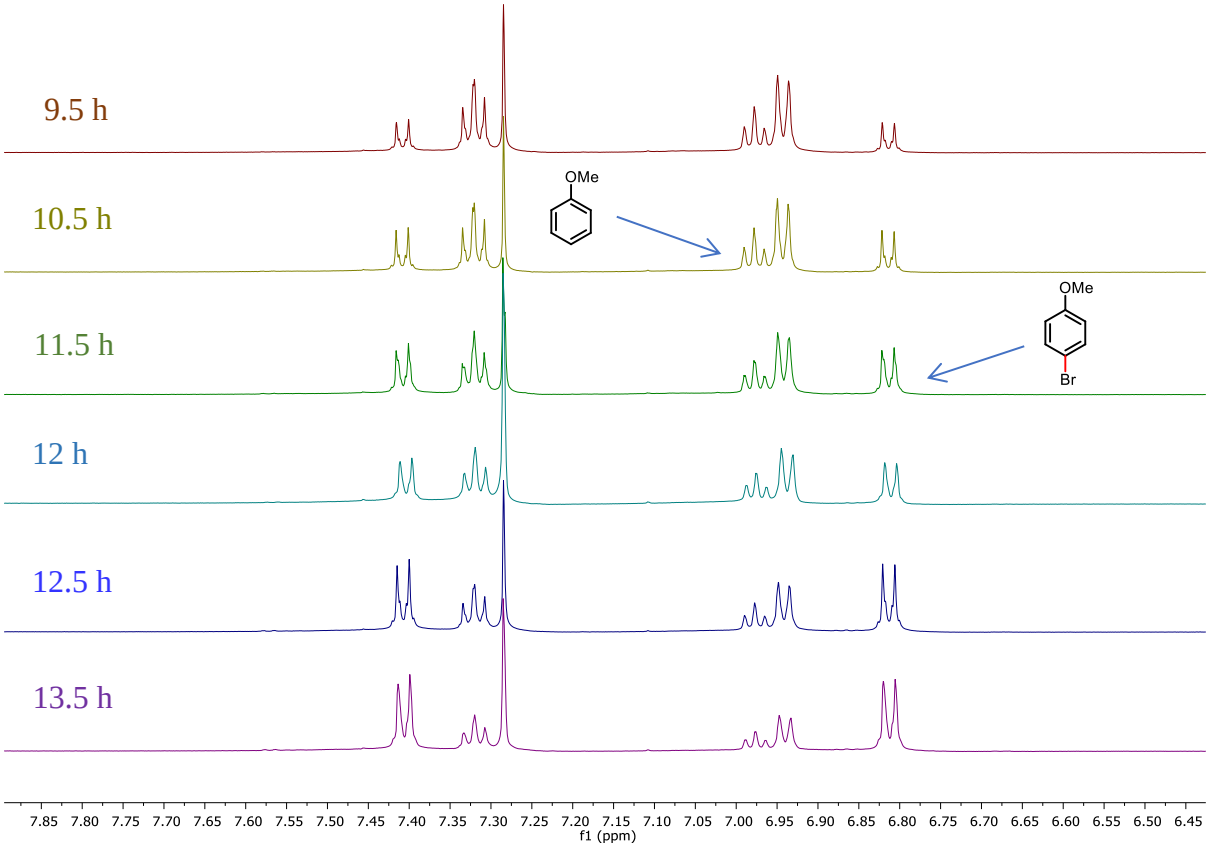
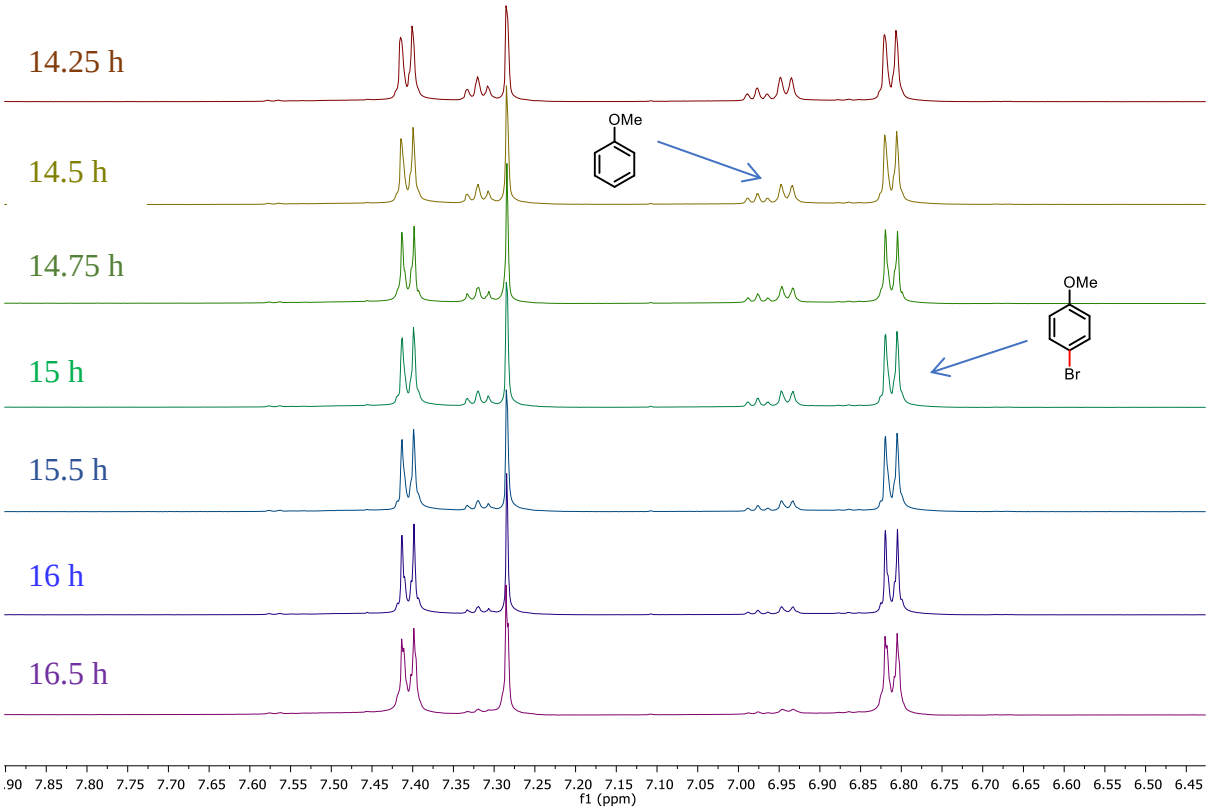


Figure S3. Effect of catalyst on the reaction profile: catalyzed vs uncatalyzed reaction of anisole bromination.

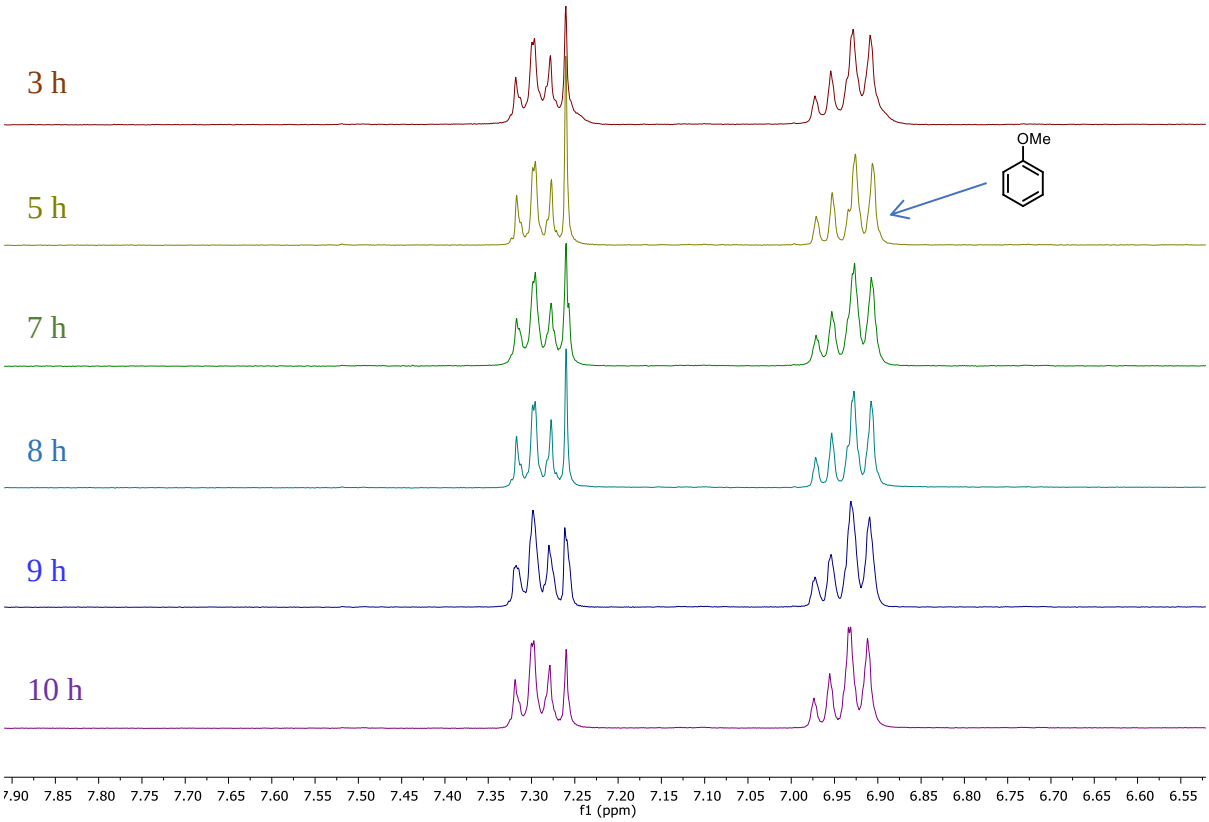
Stacked NMR spectra of anisole bromination in presence of catalyst

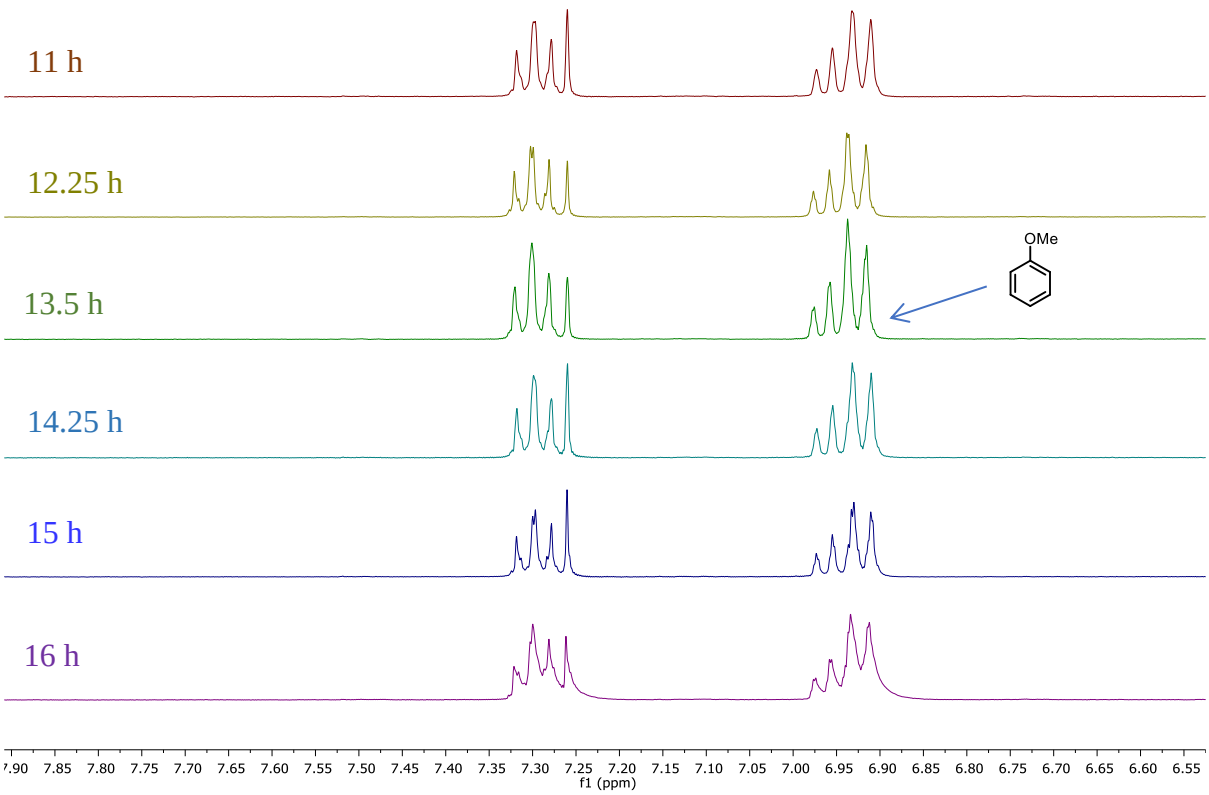






Stacked NMR spectra of anisole bromination without catalyst





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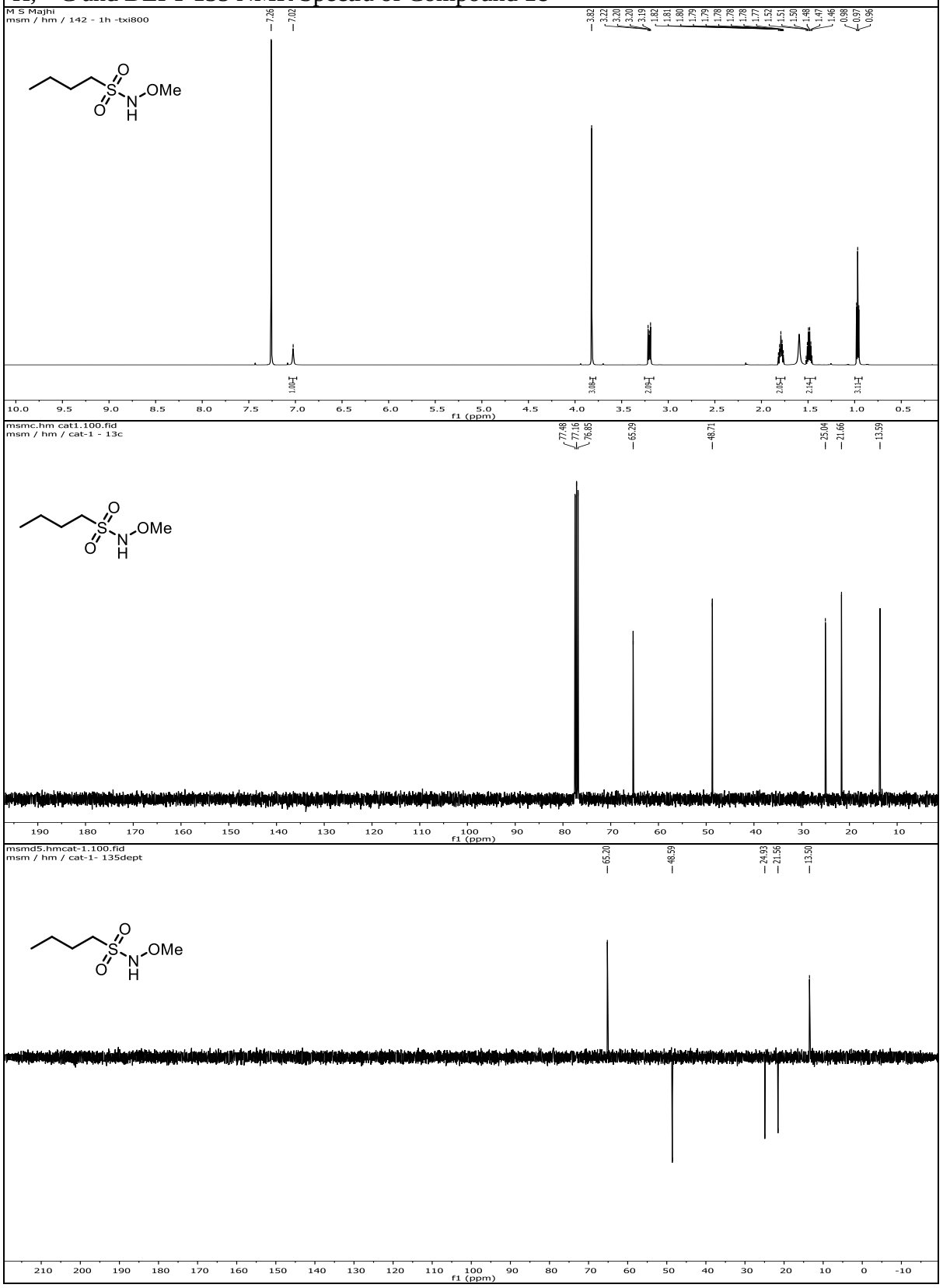
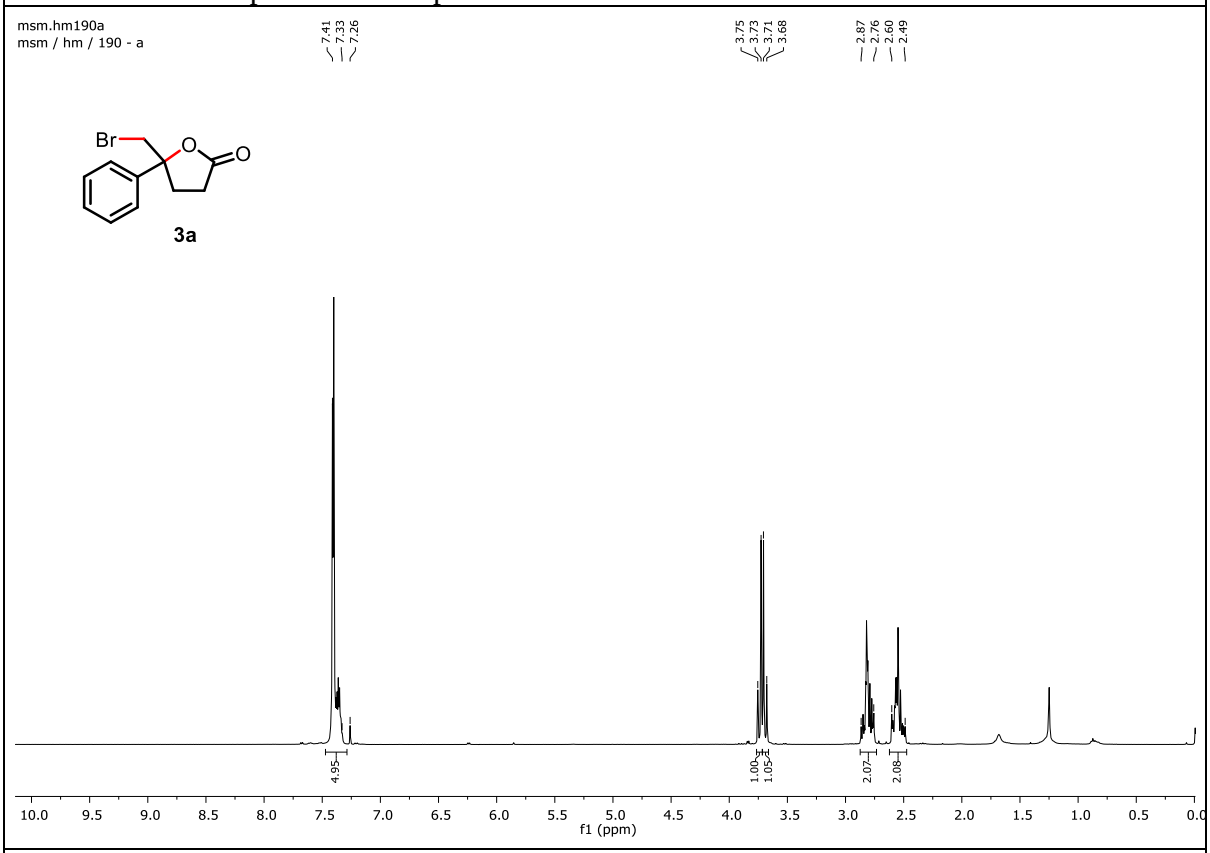
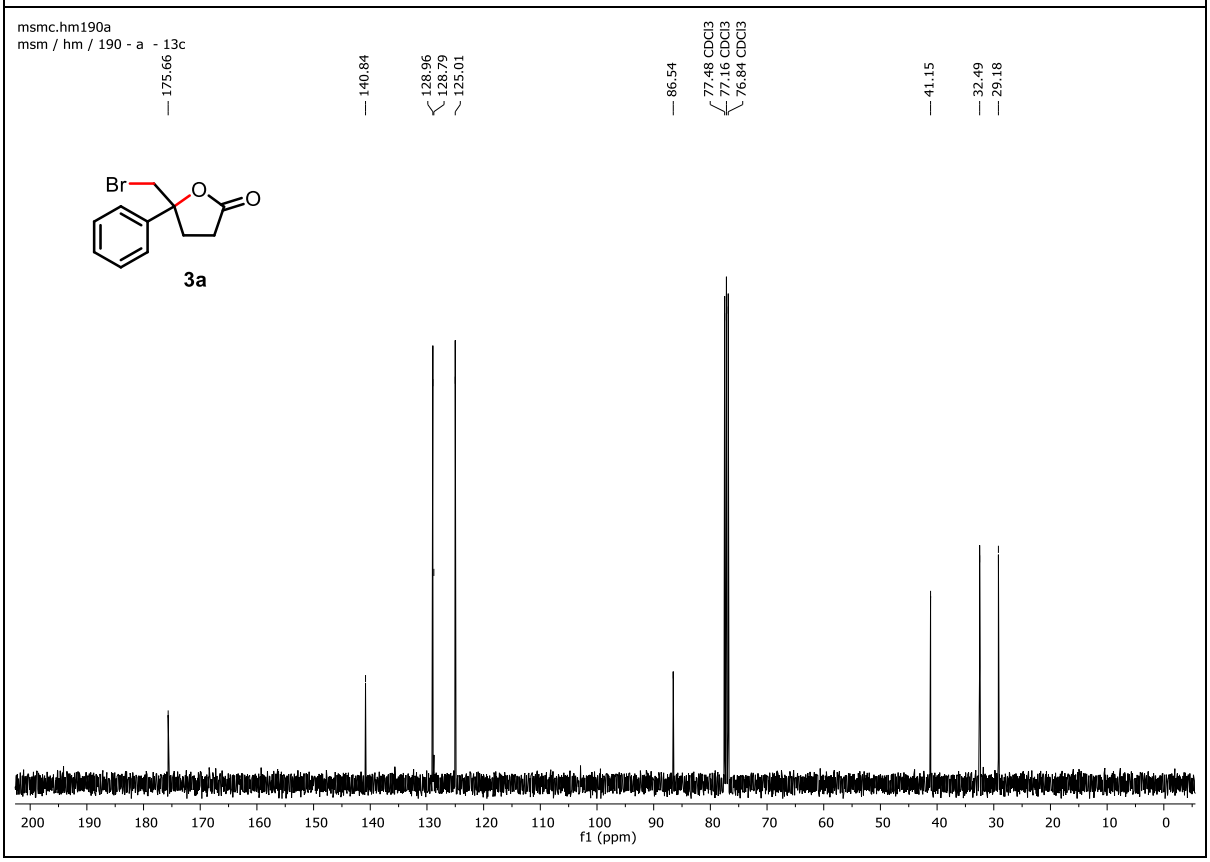
^{1}H, ^{13}C and DEPT 135 NMR Spectra of Compound **1c**



^{1}H and ^{13}C NMR Spectra of Compound **3a**





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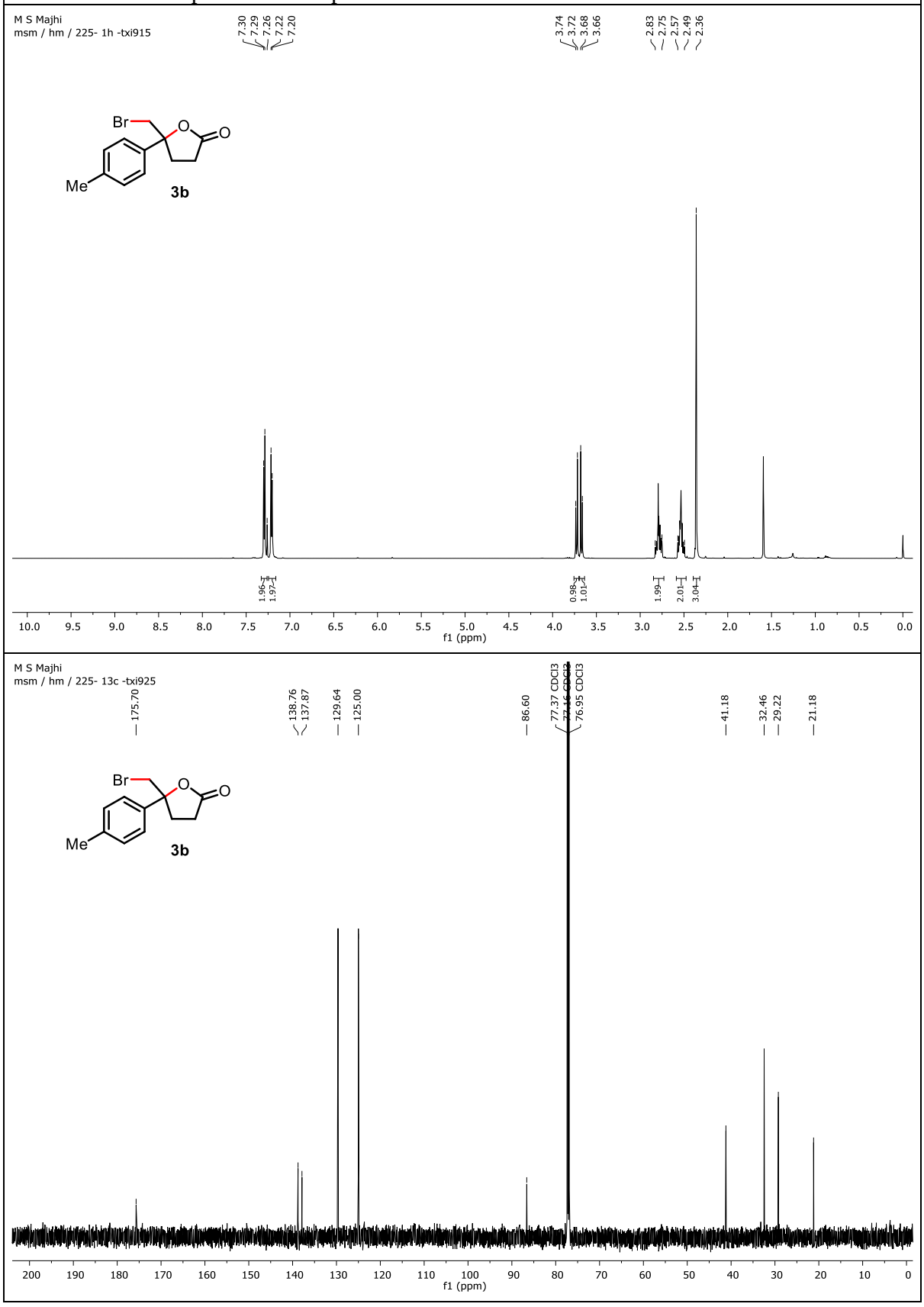

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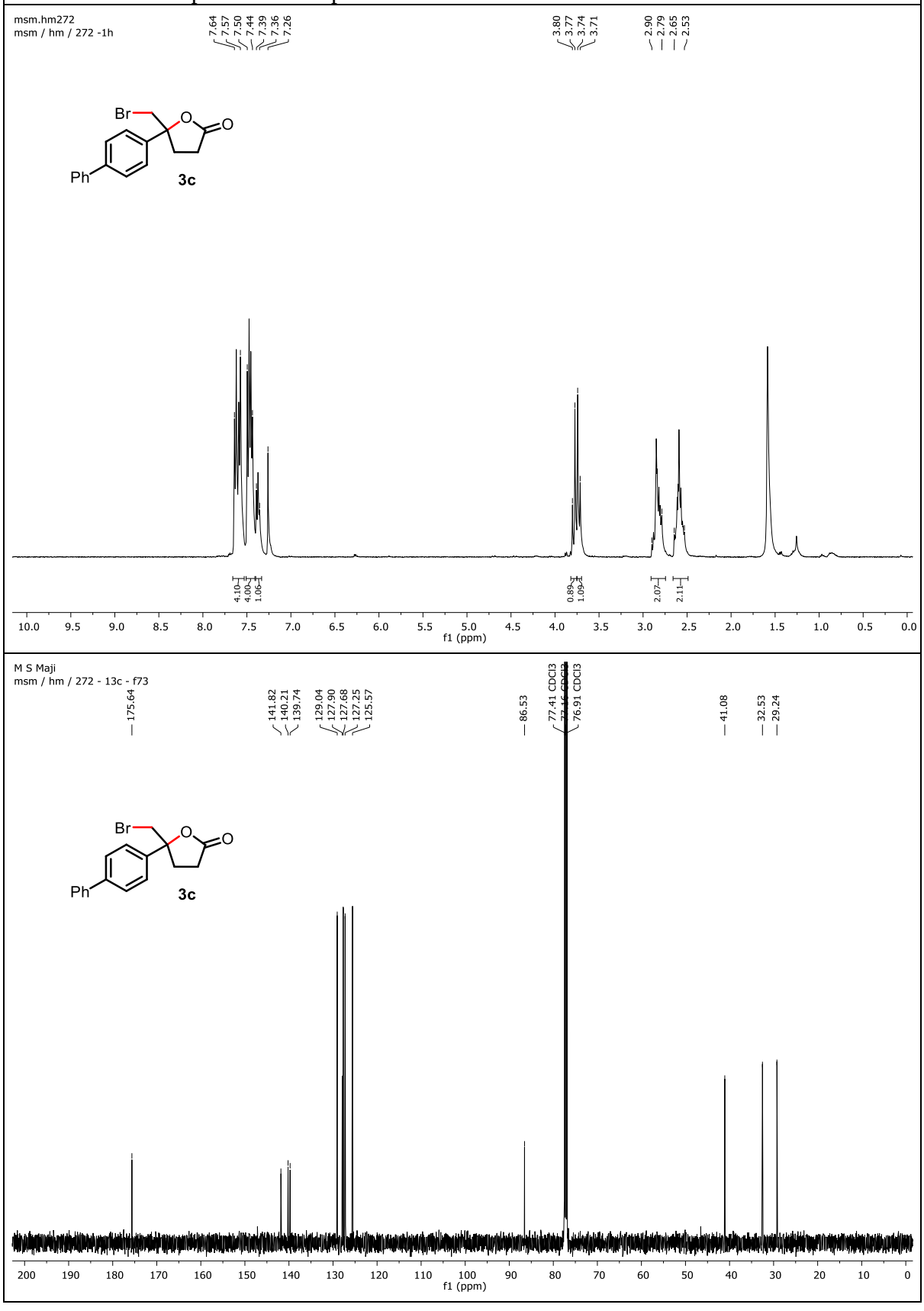
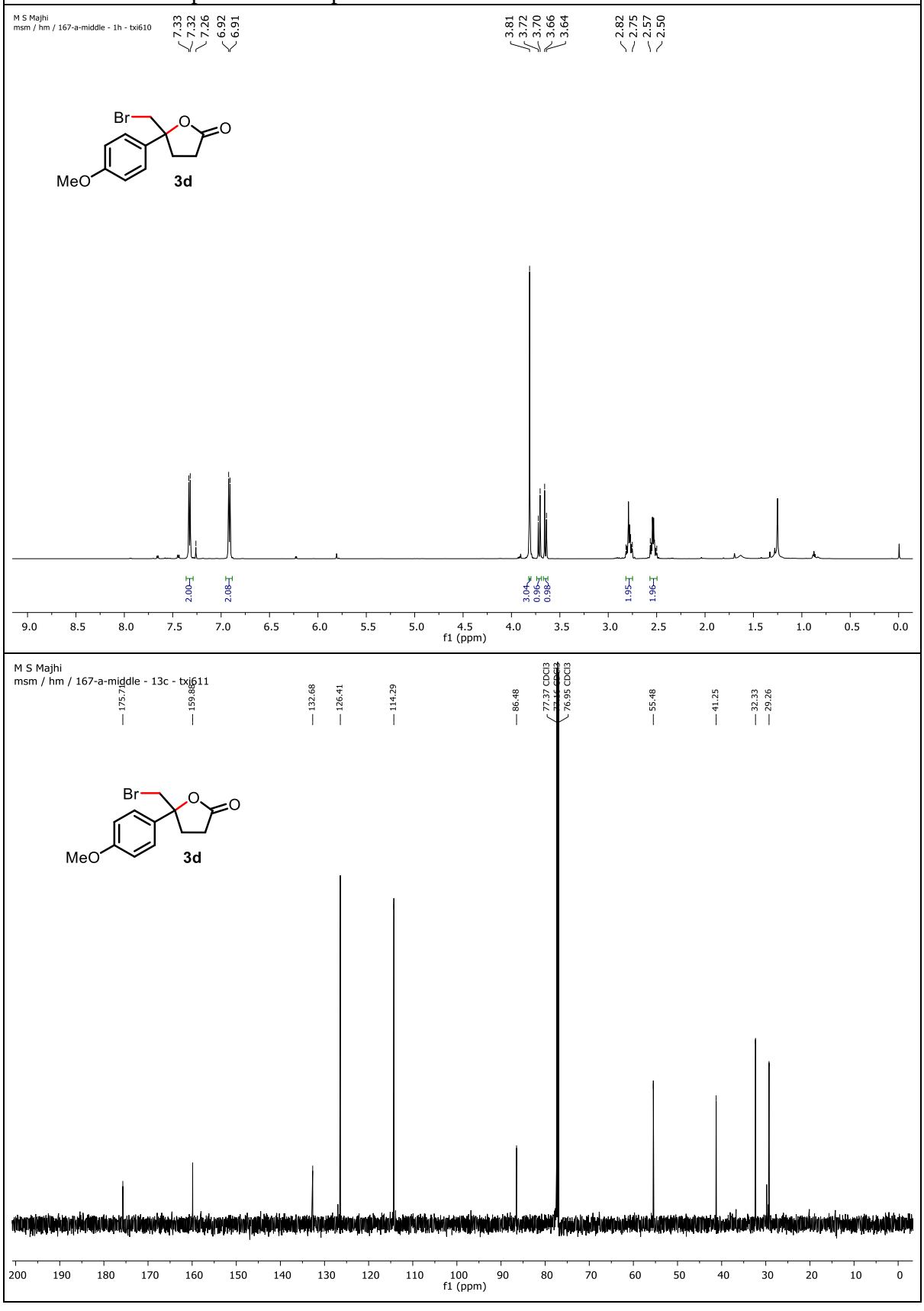
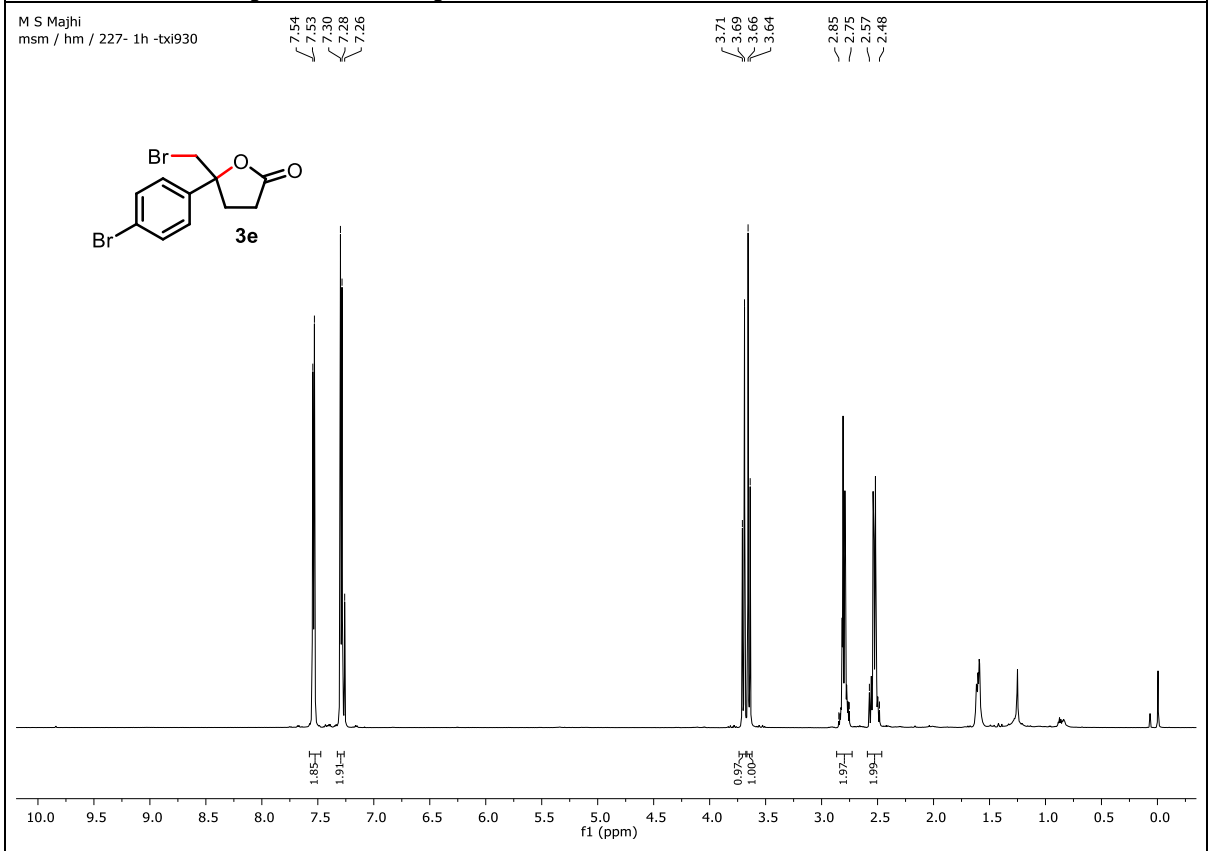
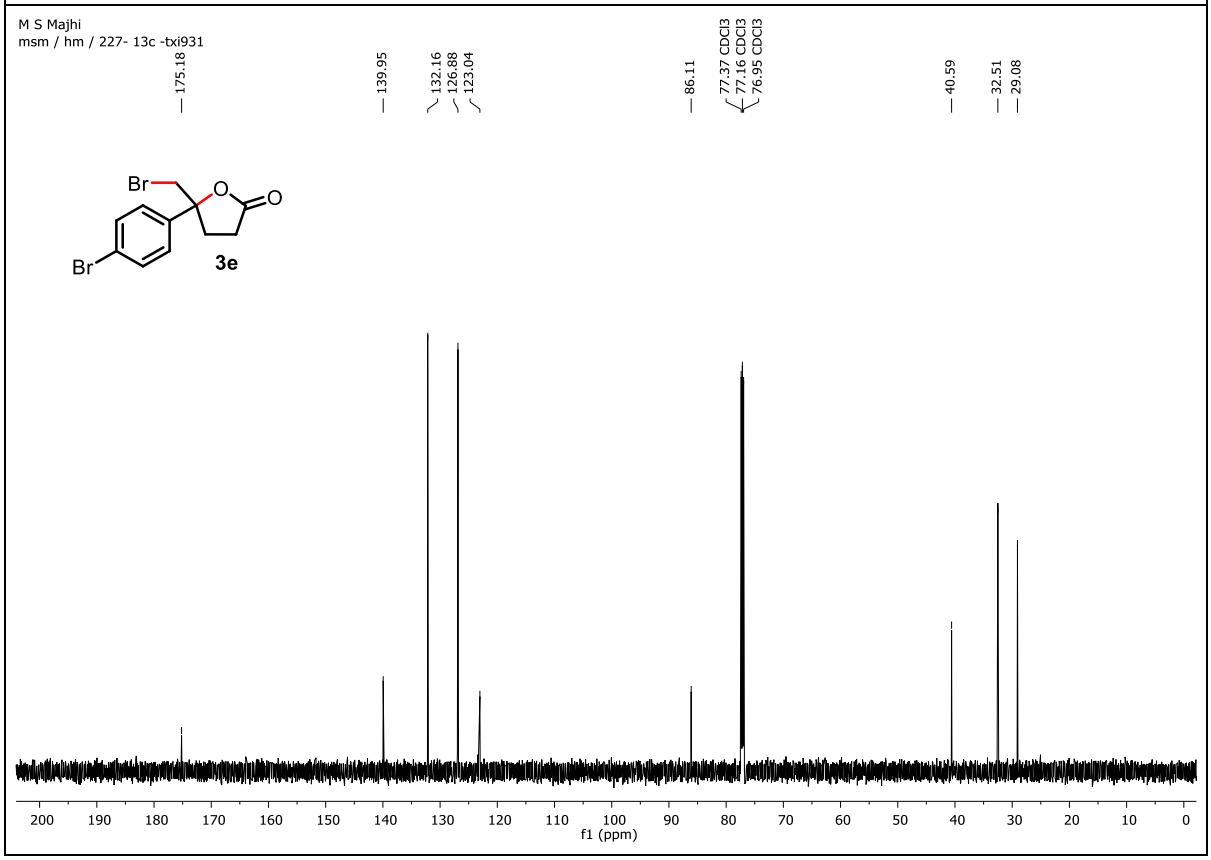


^{1}H and ^{13}C NMR Spectra of Compound **3d**



^{1}H and ^{13}C NMR Spectra of Compound **3e**





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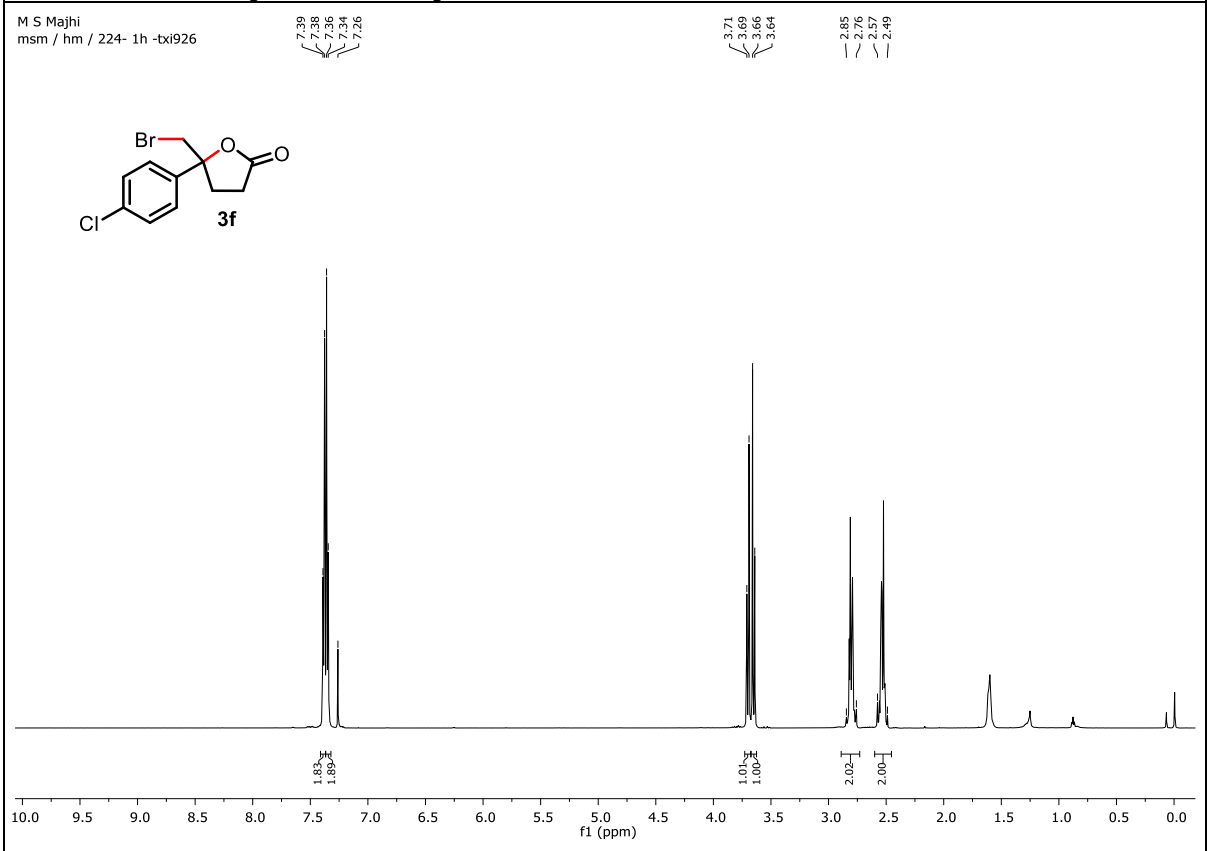

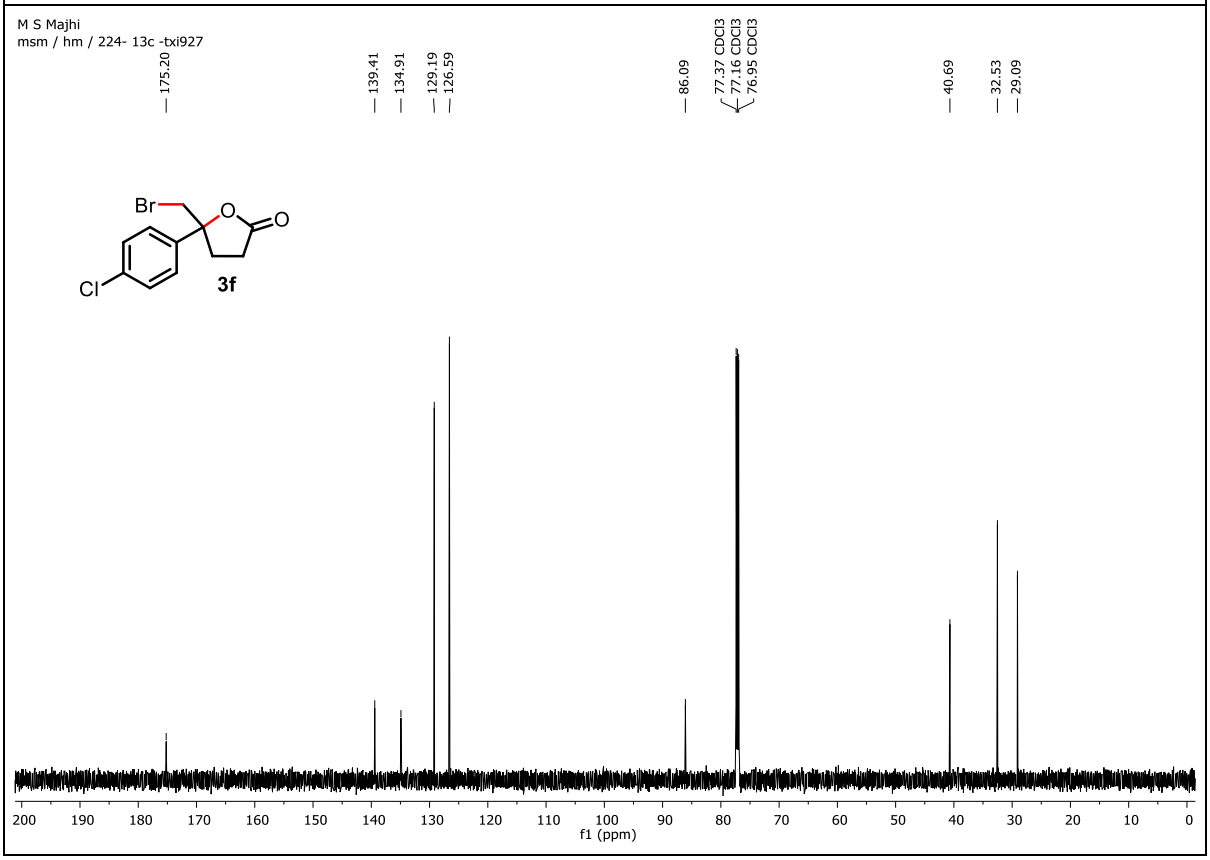

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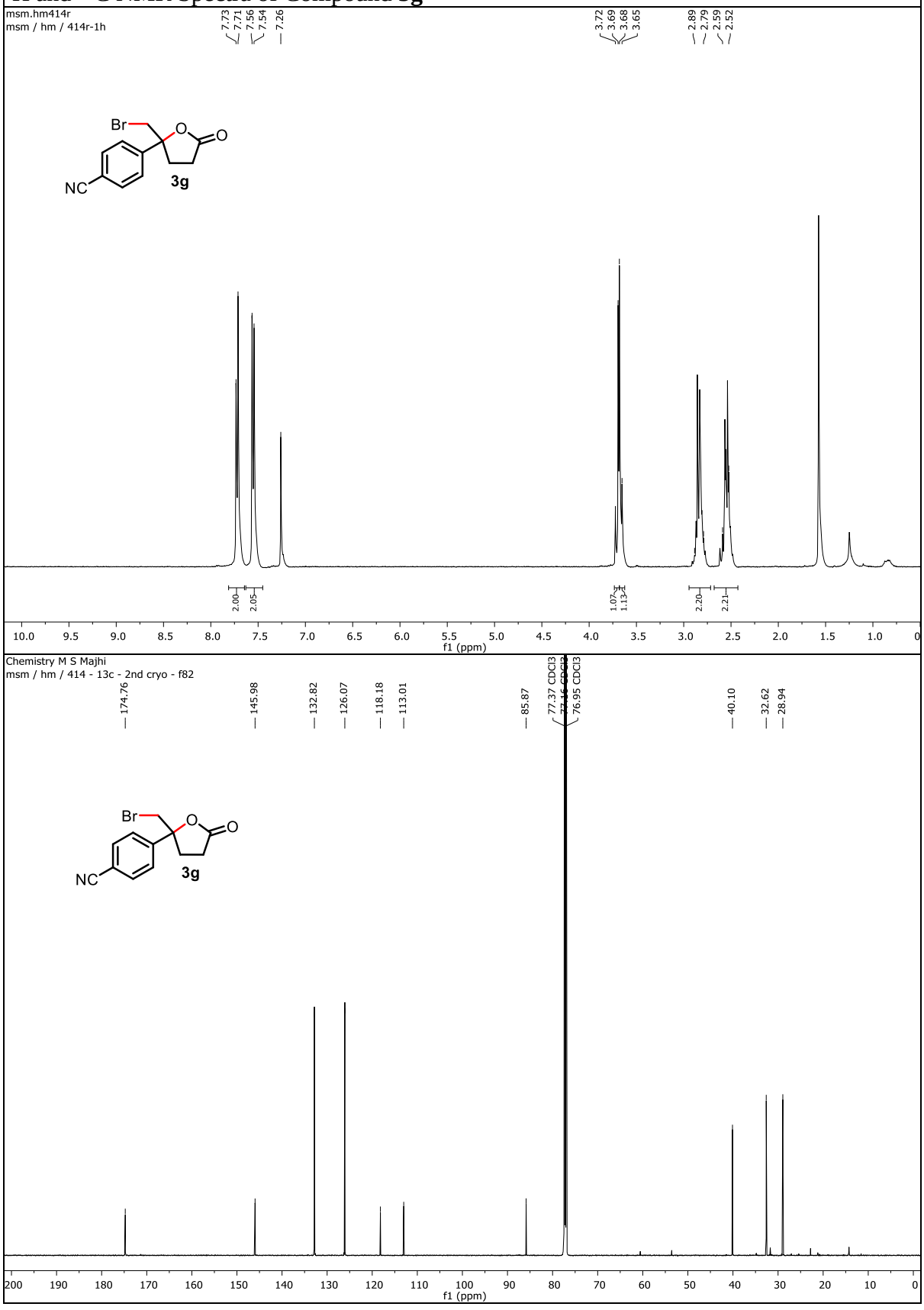

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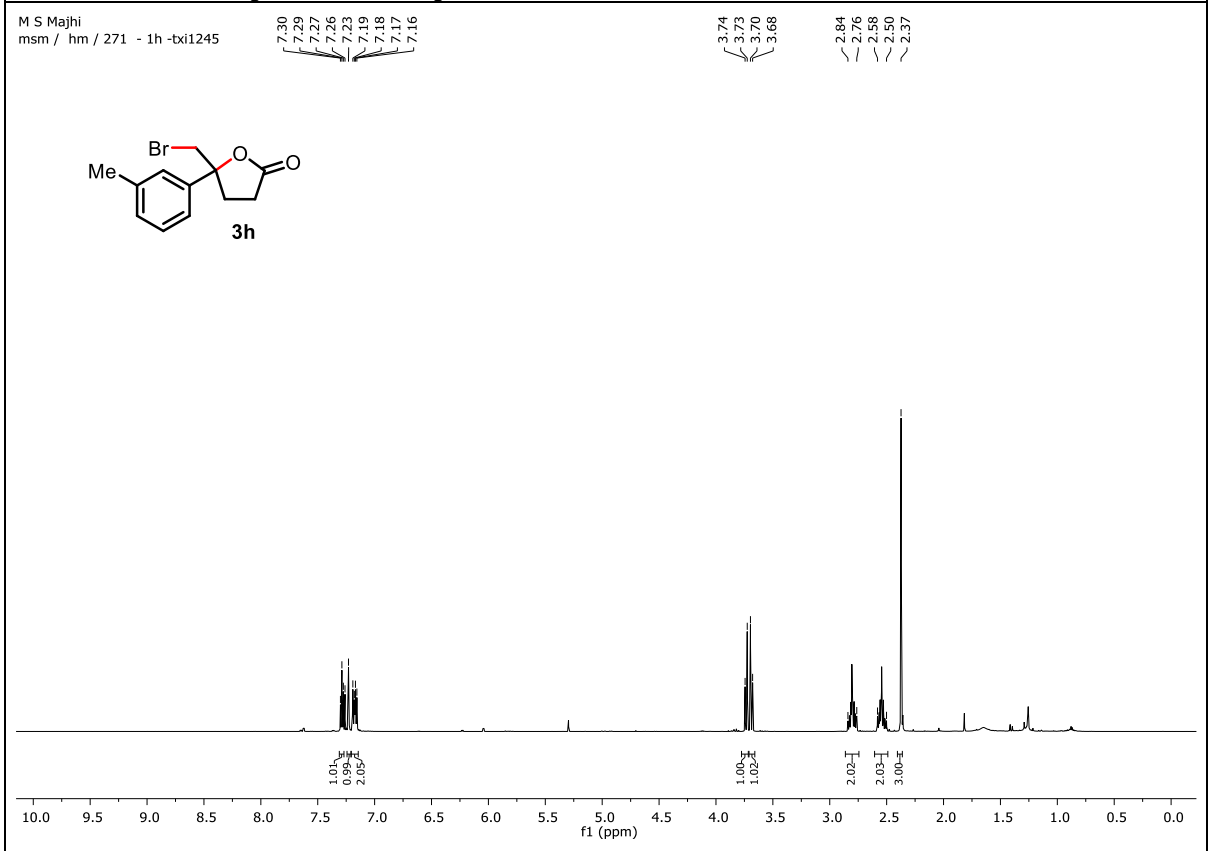

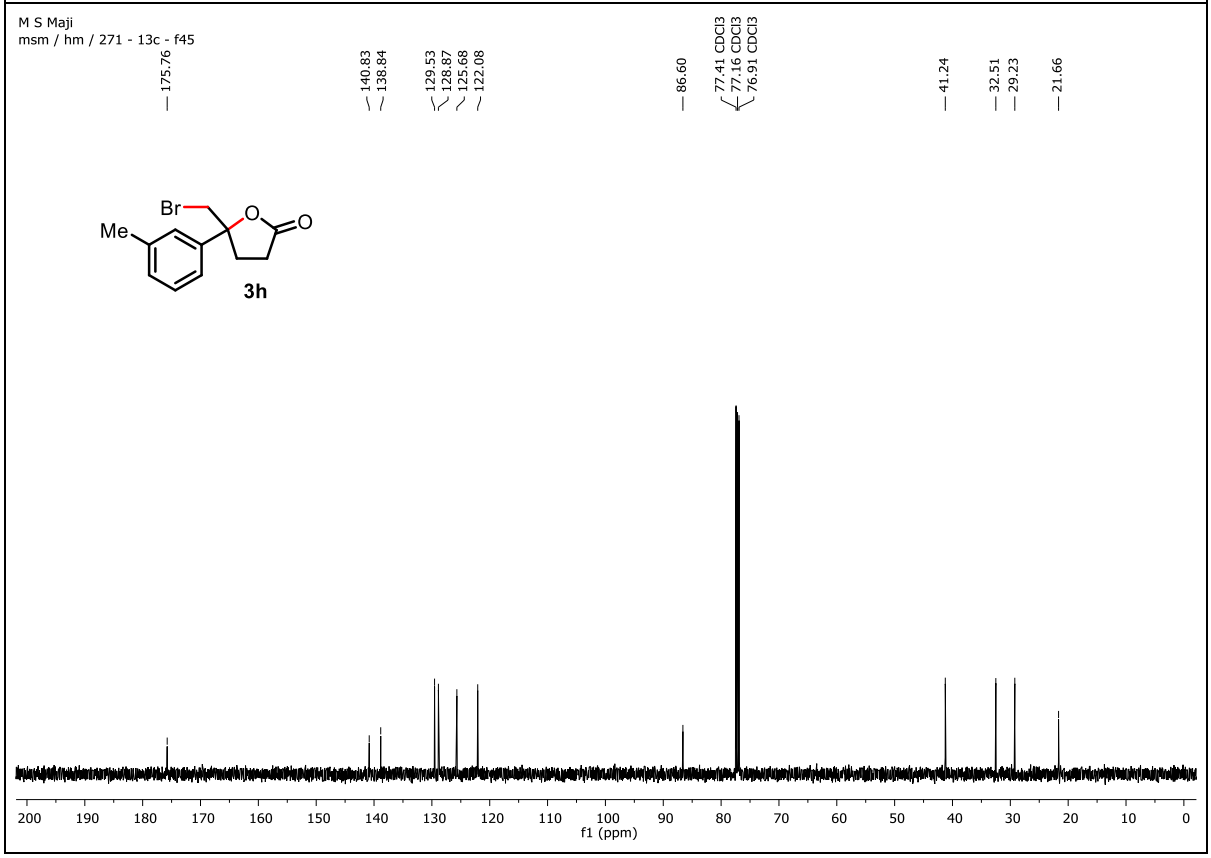

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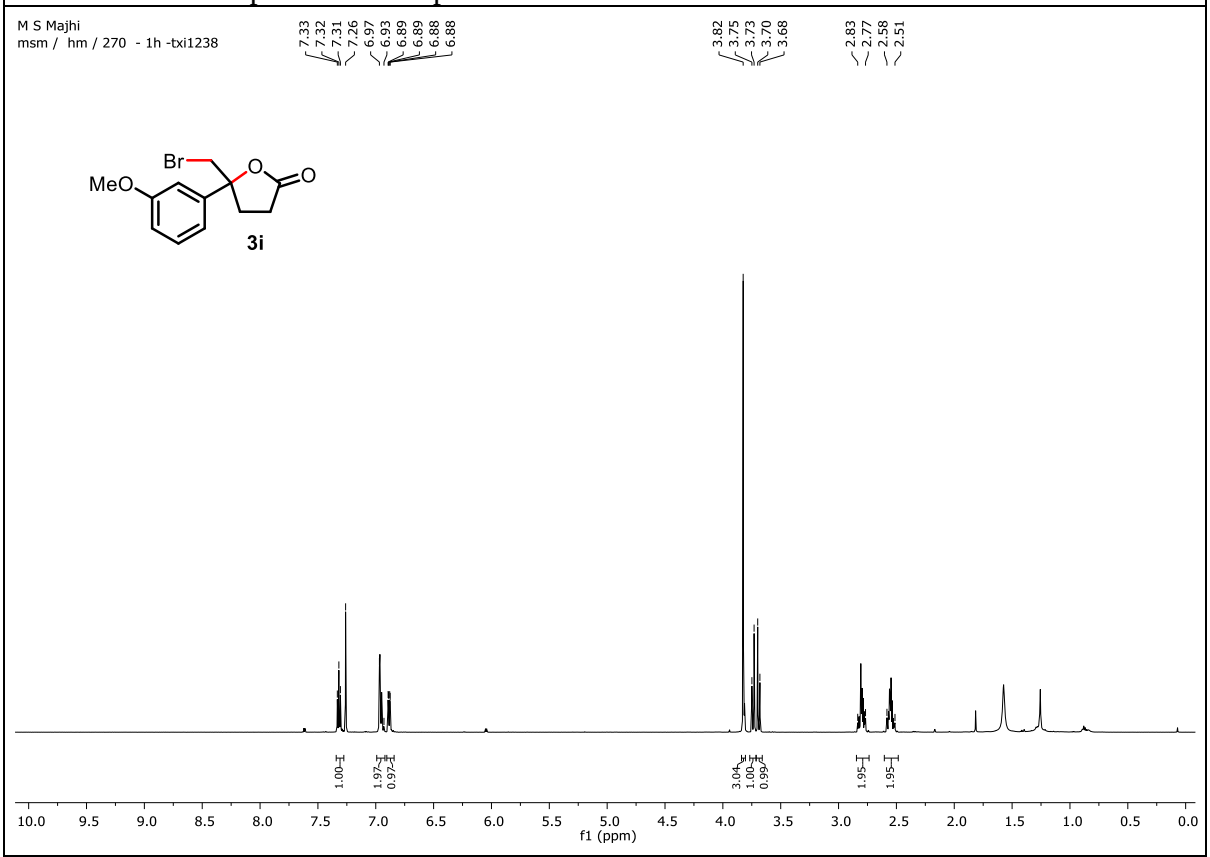

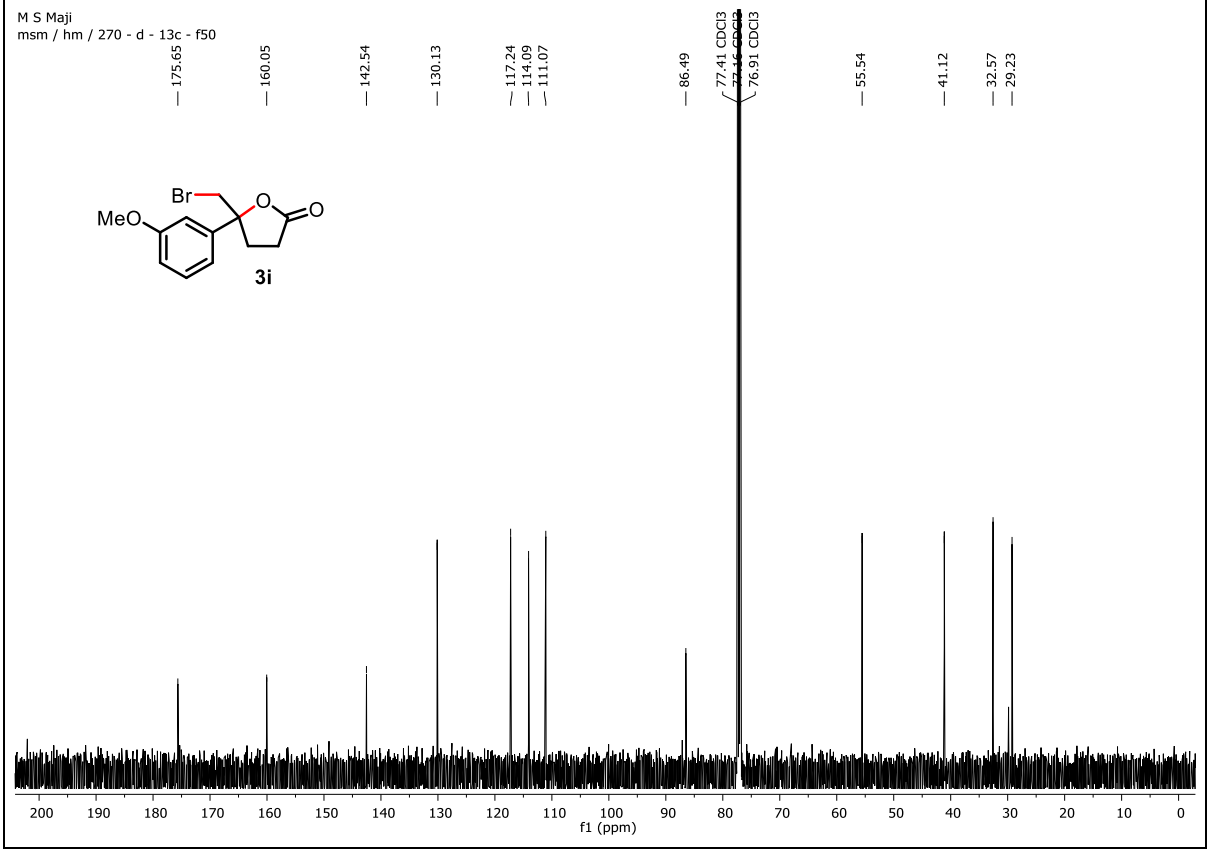

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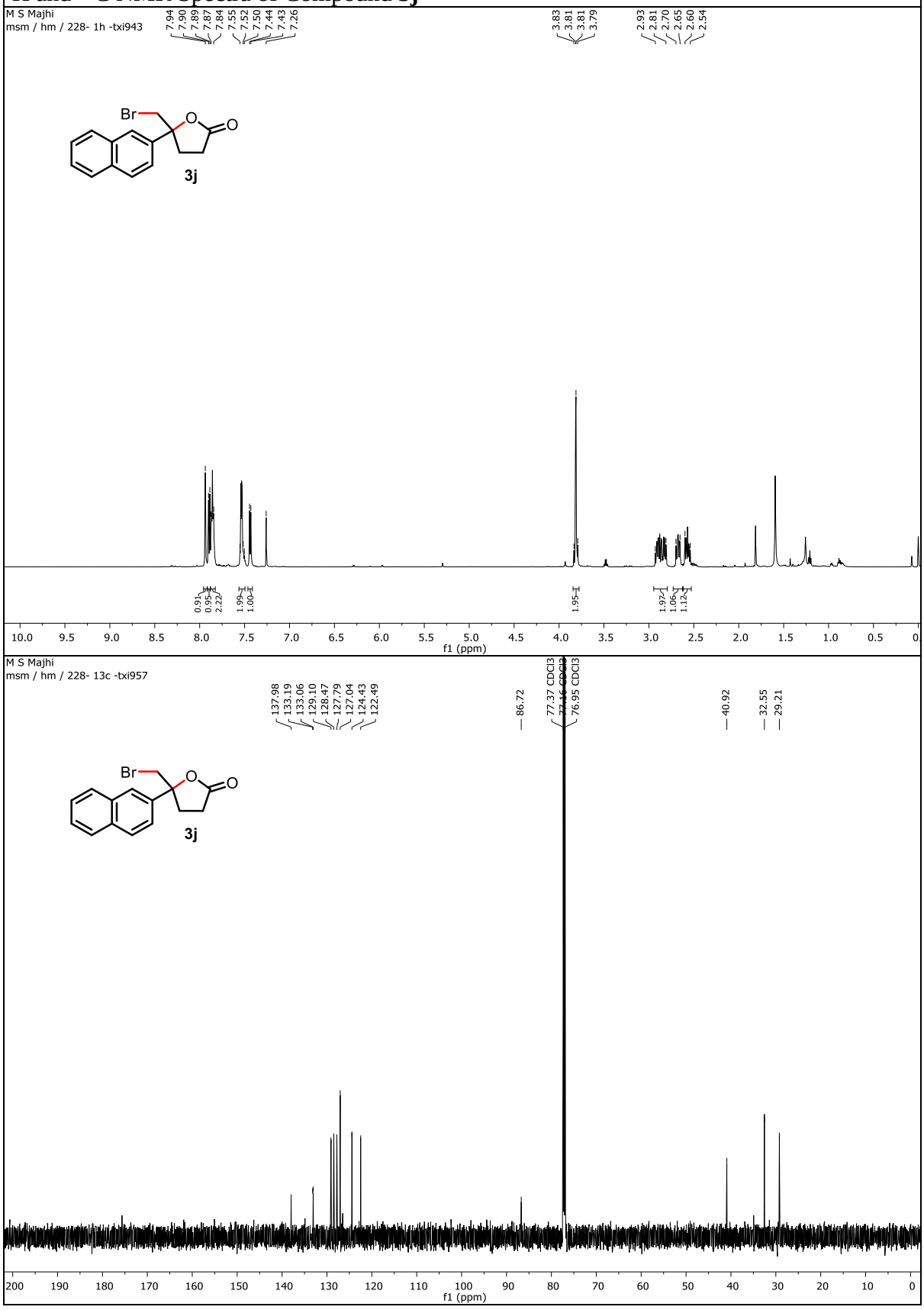

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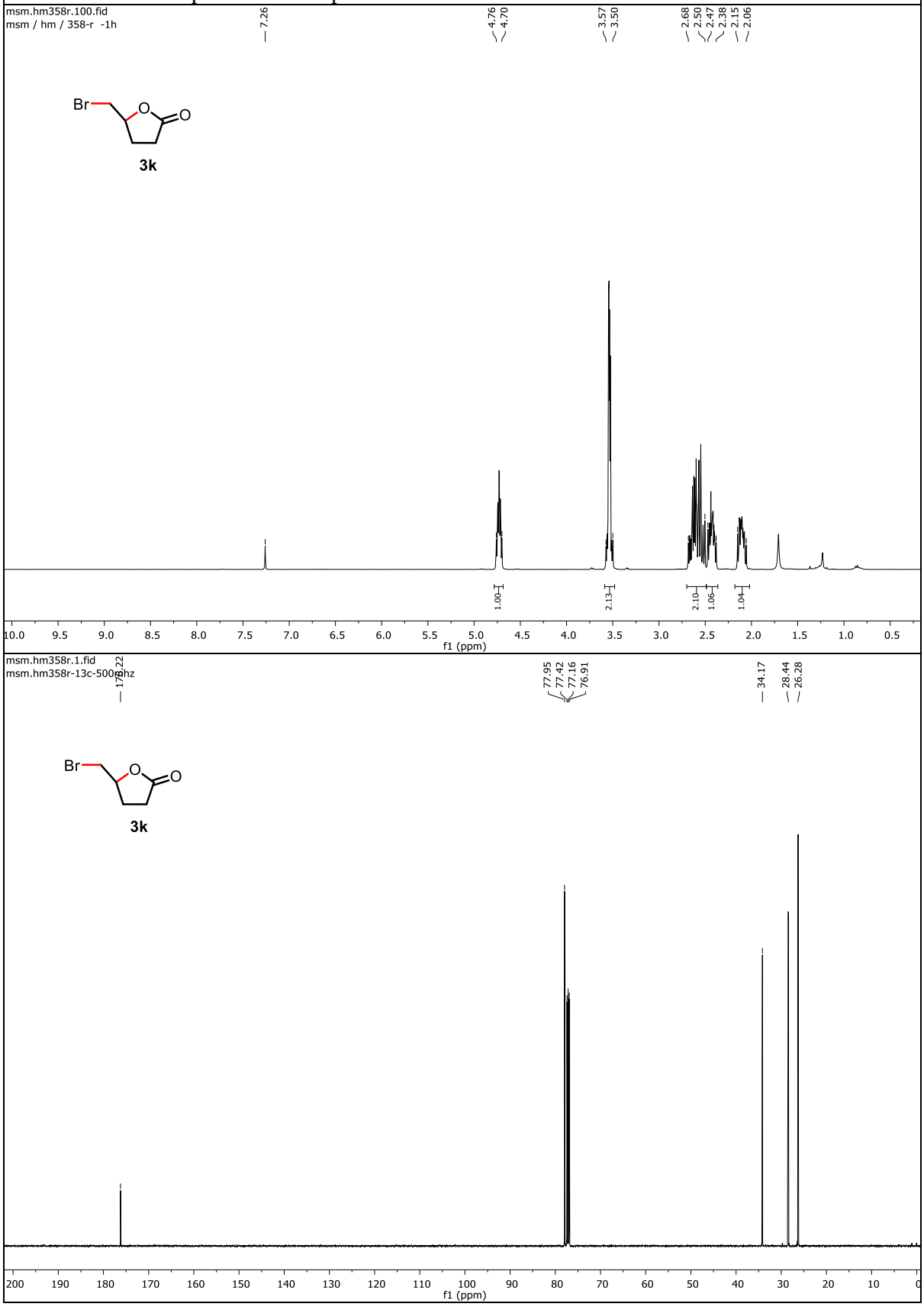

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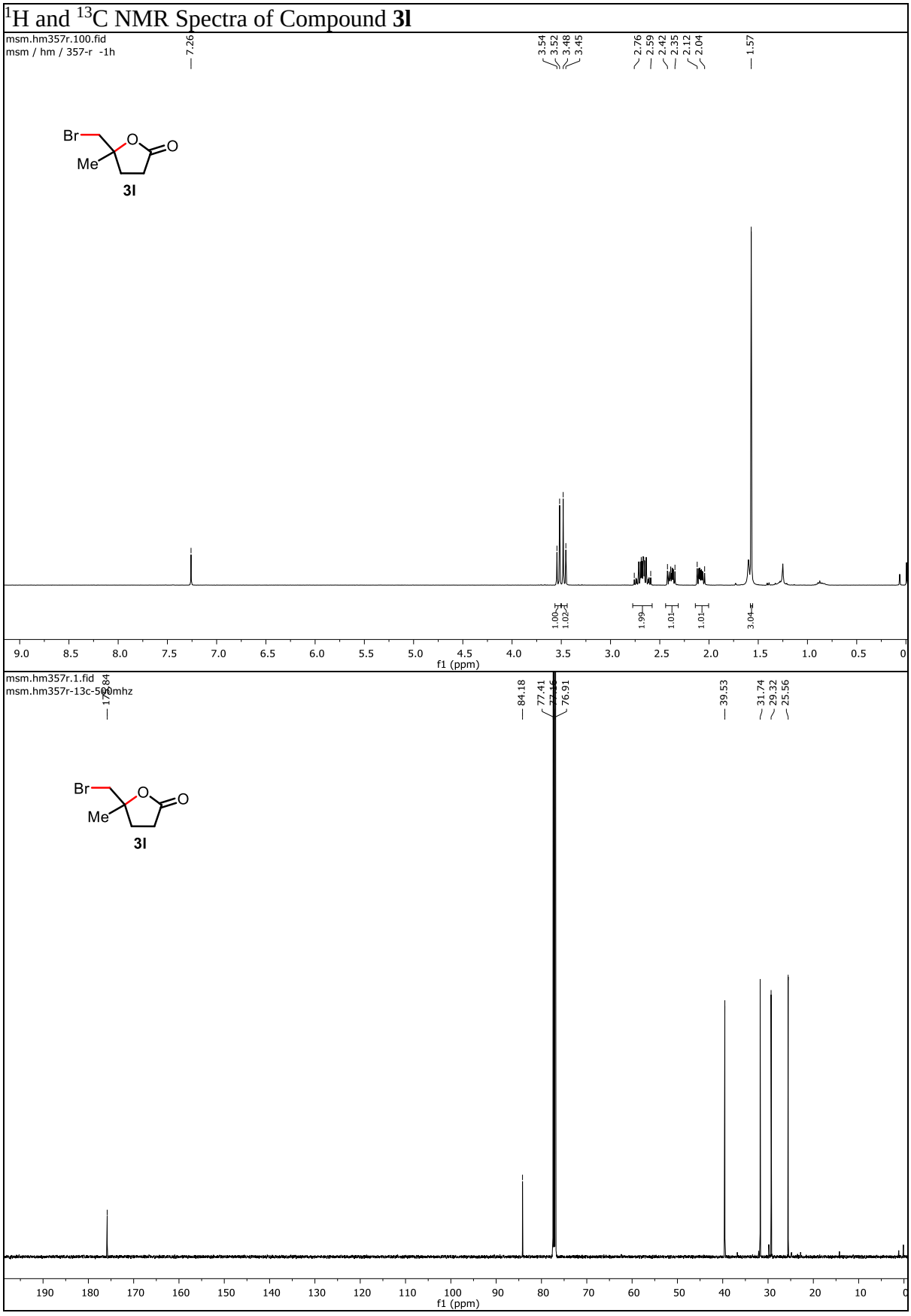

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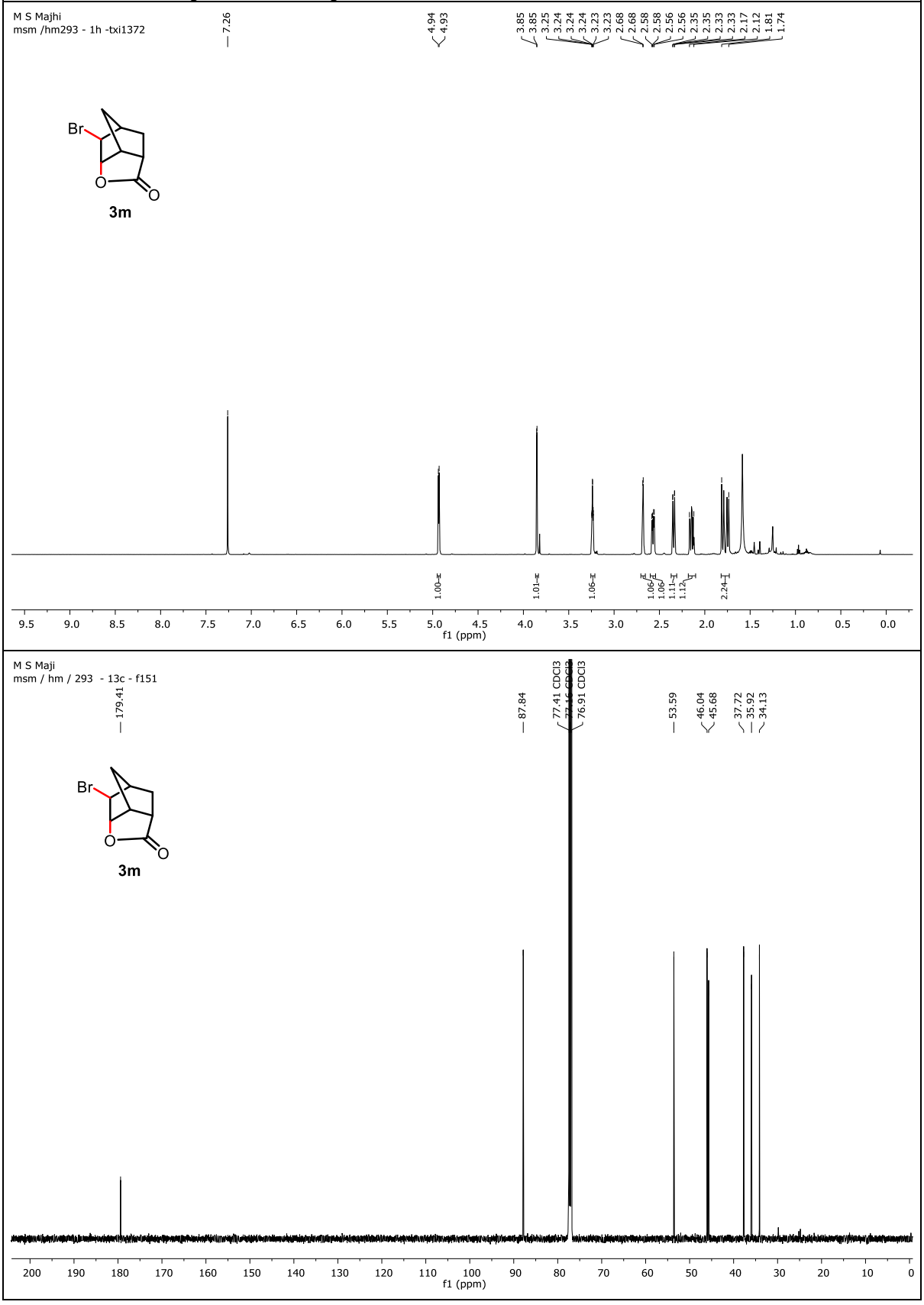

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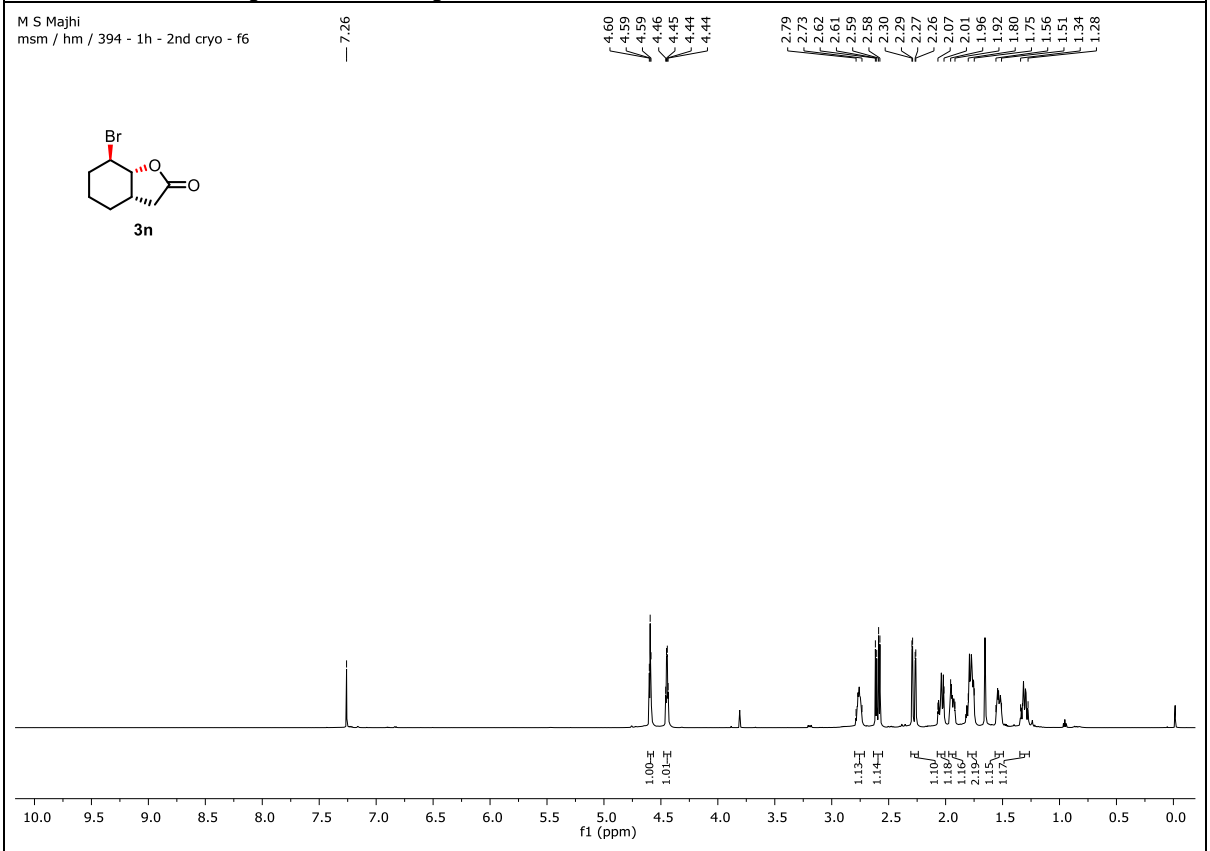
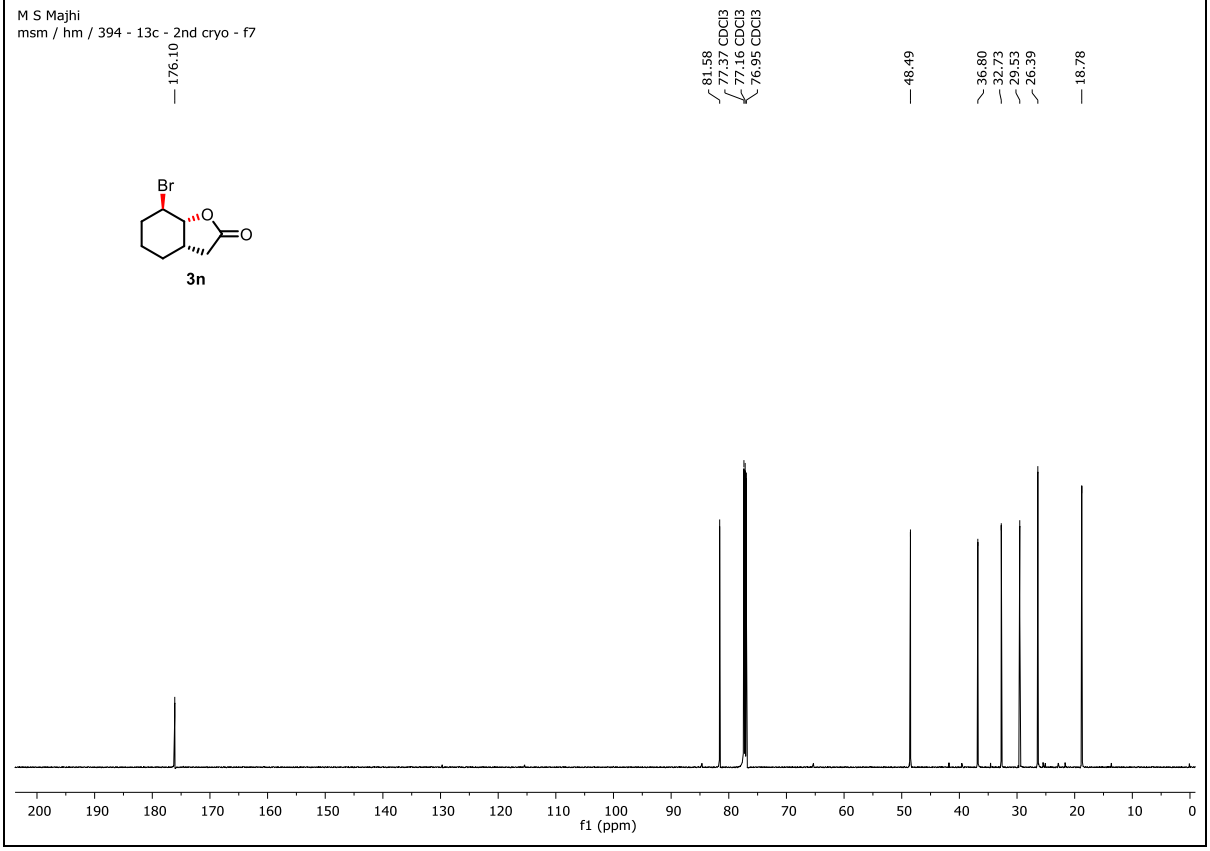
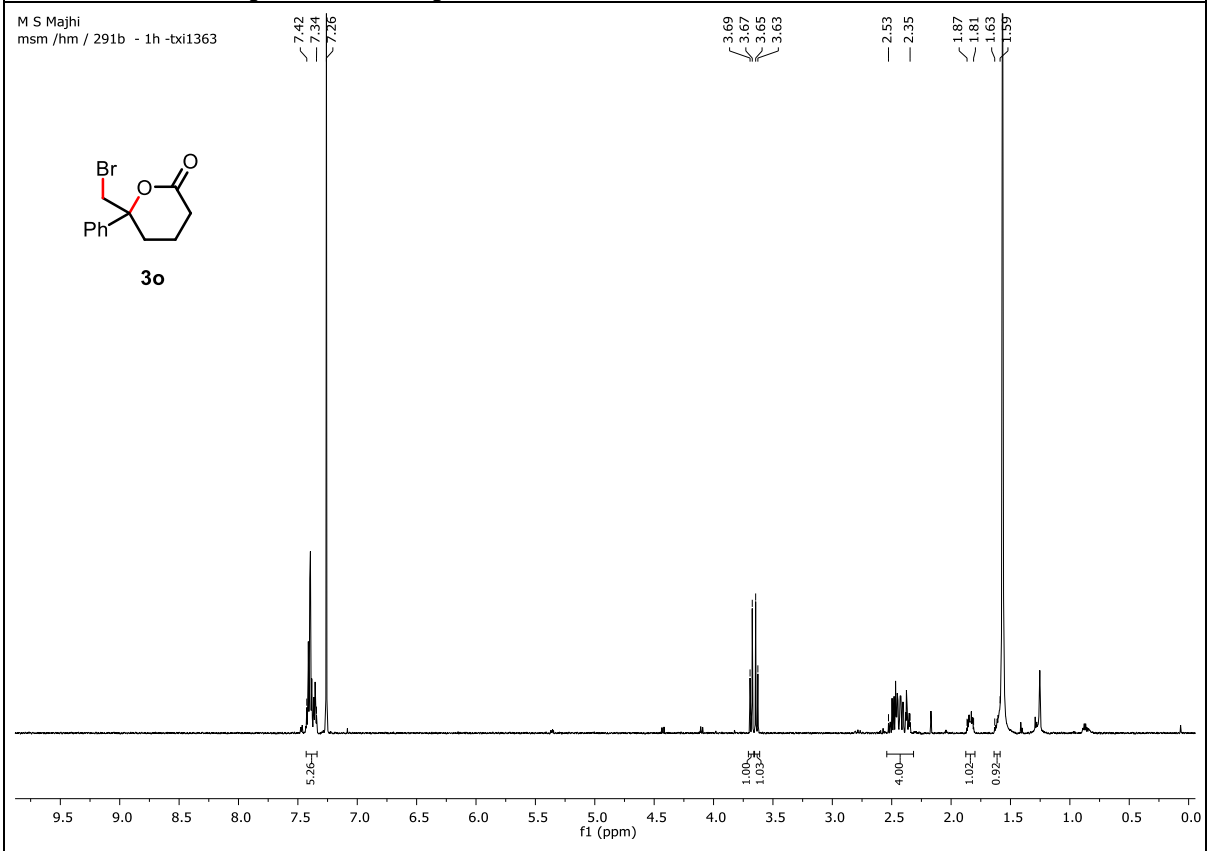
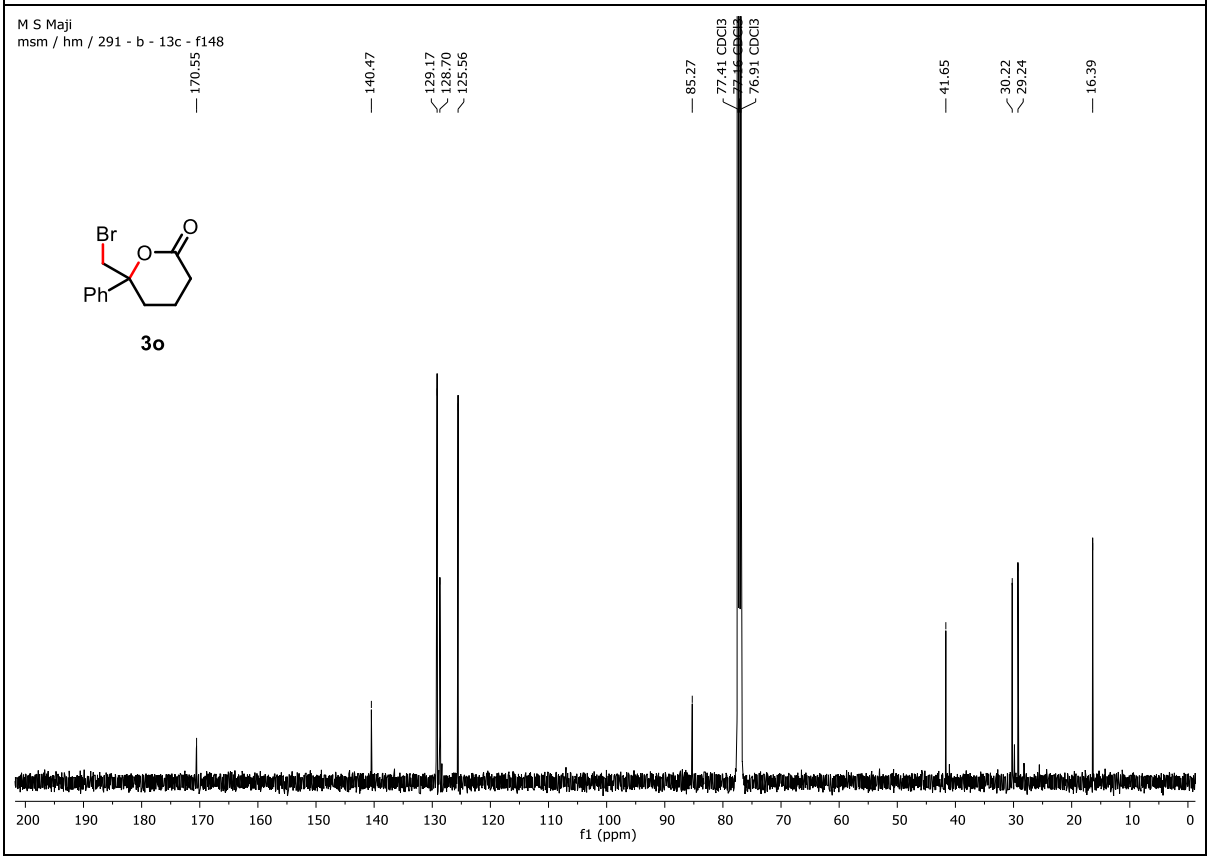


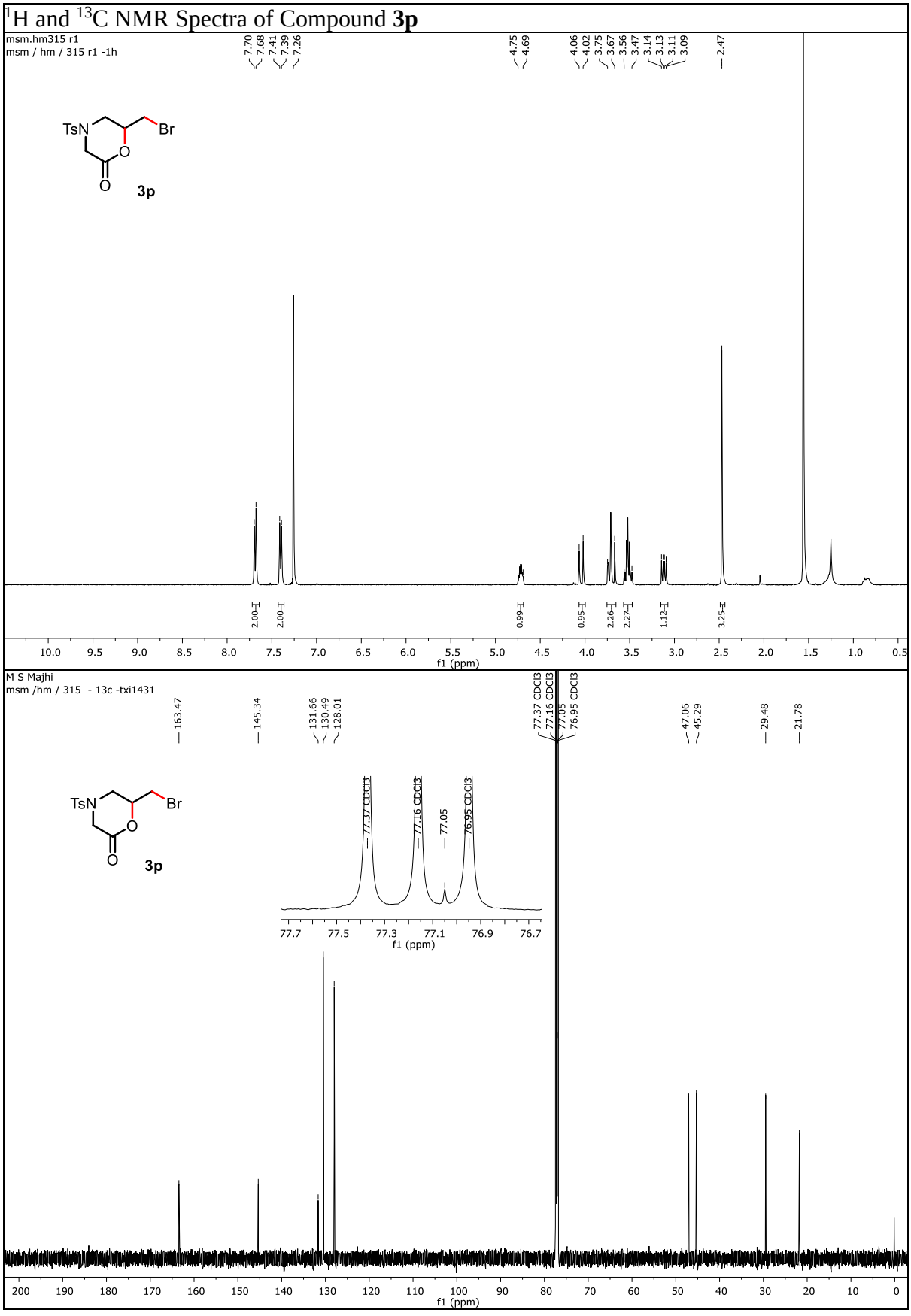


^{1}H and ^{13}C NMR Spectra of Compound **3o**

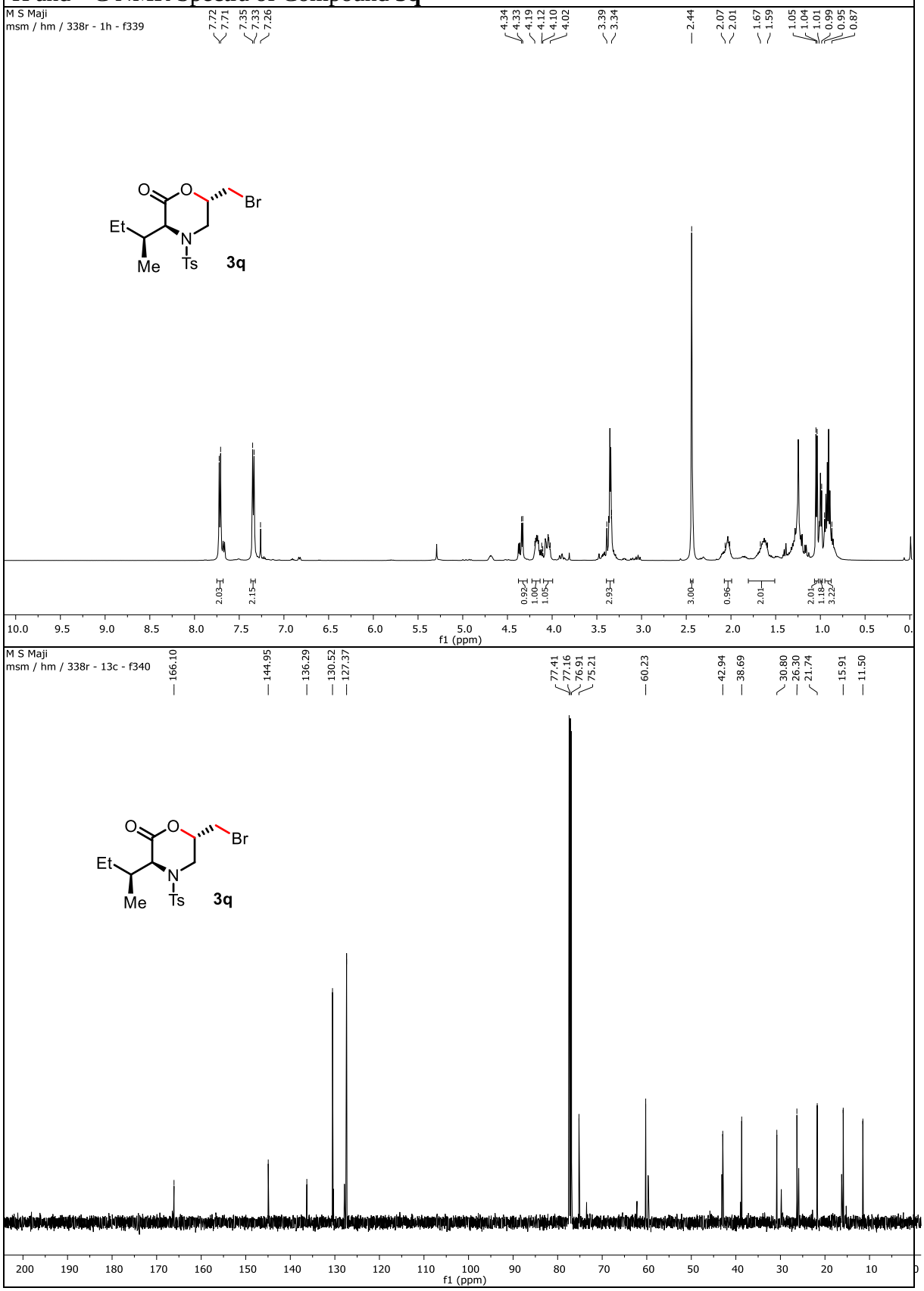




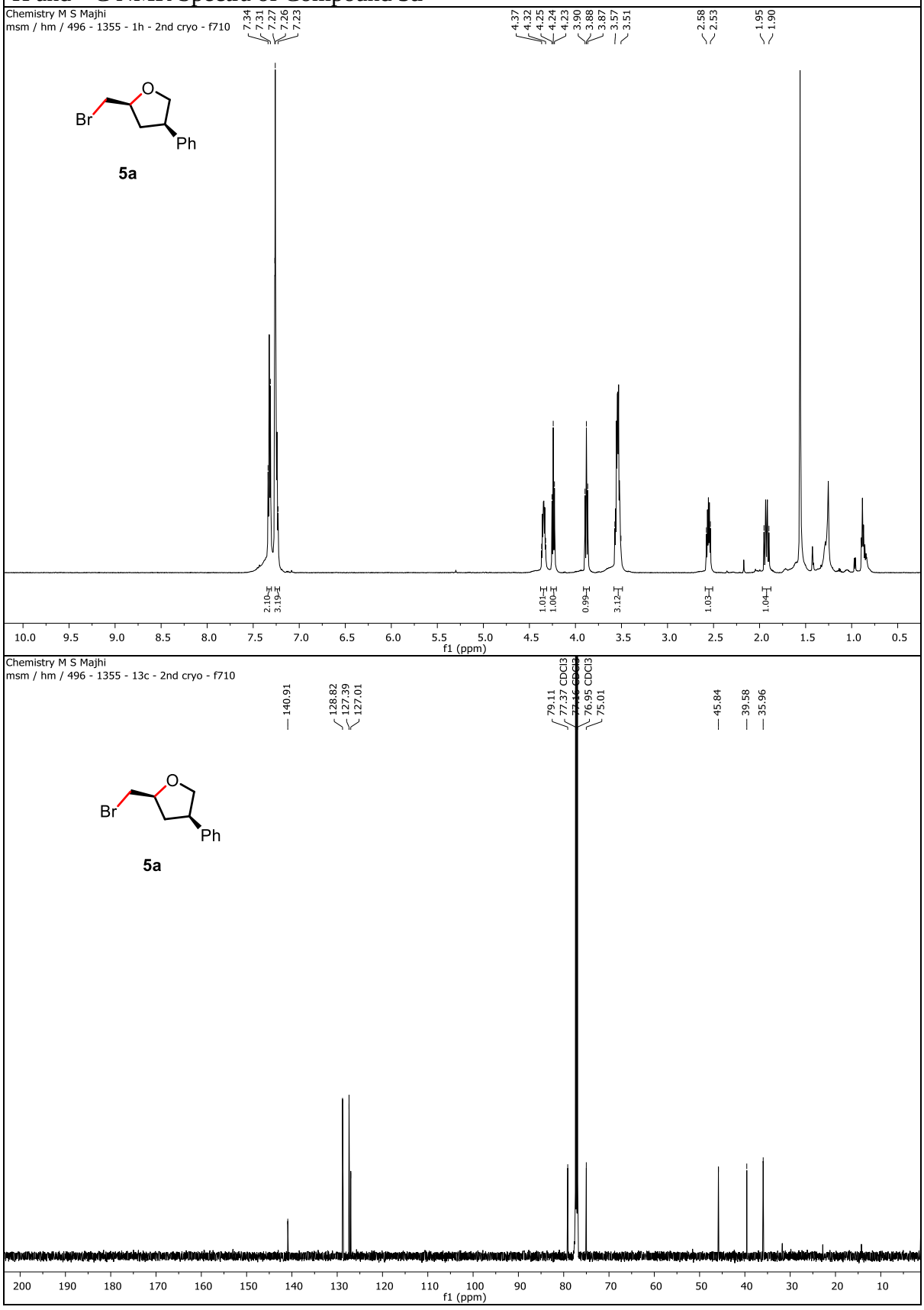
^{1}H and ^{13}C NMR Spectra of Compound **3p**



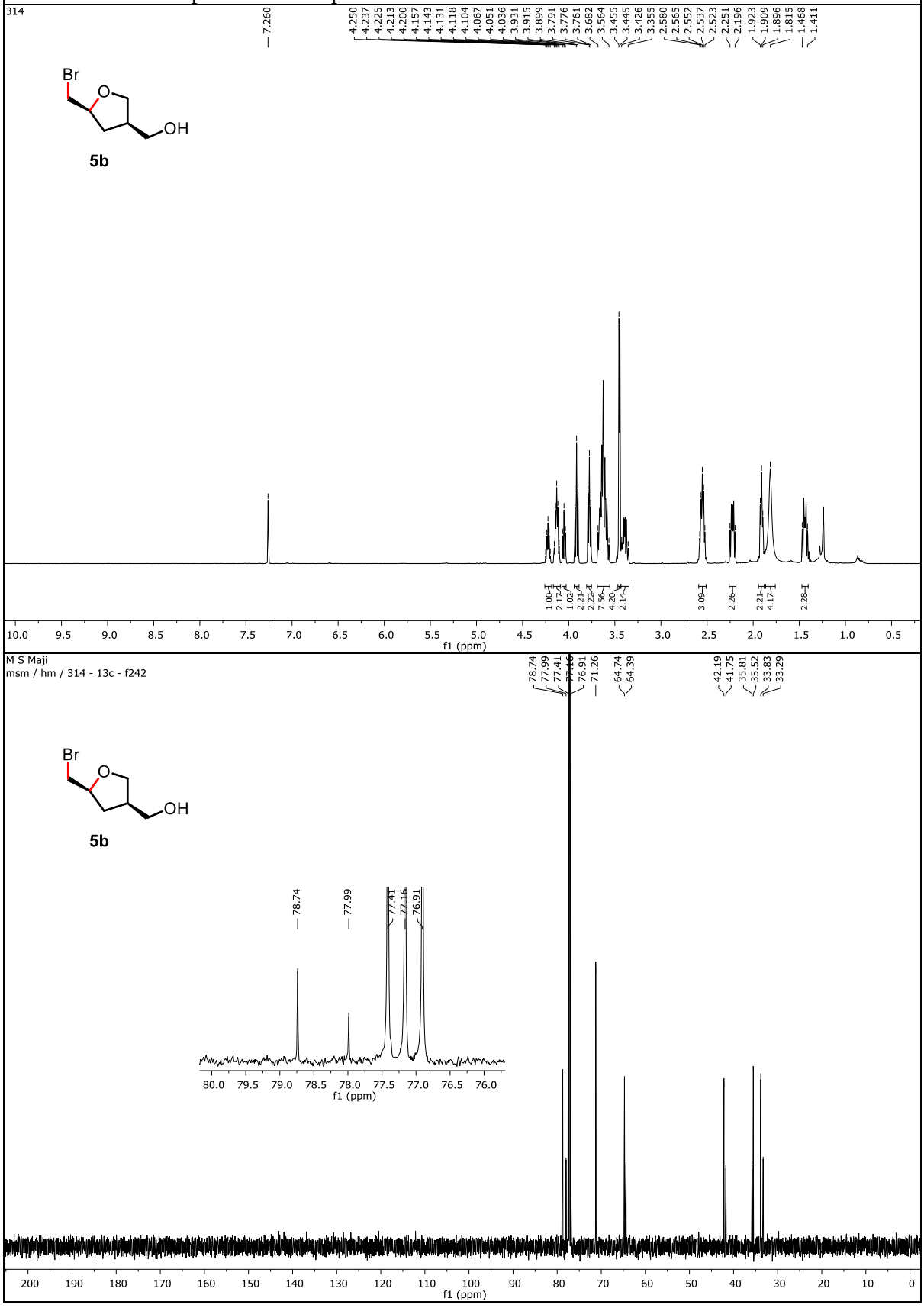
^{1}H and ^{13}C NMR Spectra of Compound **3q**



^{1}H and ^{13}C NMR Spectra of Compound **5a**



^{1}H and ^{13}C NMR Spectra of Compound **5b**



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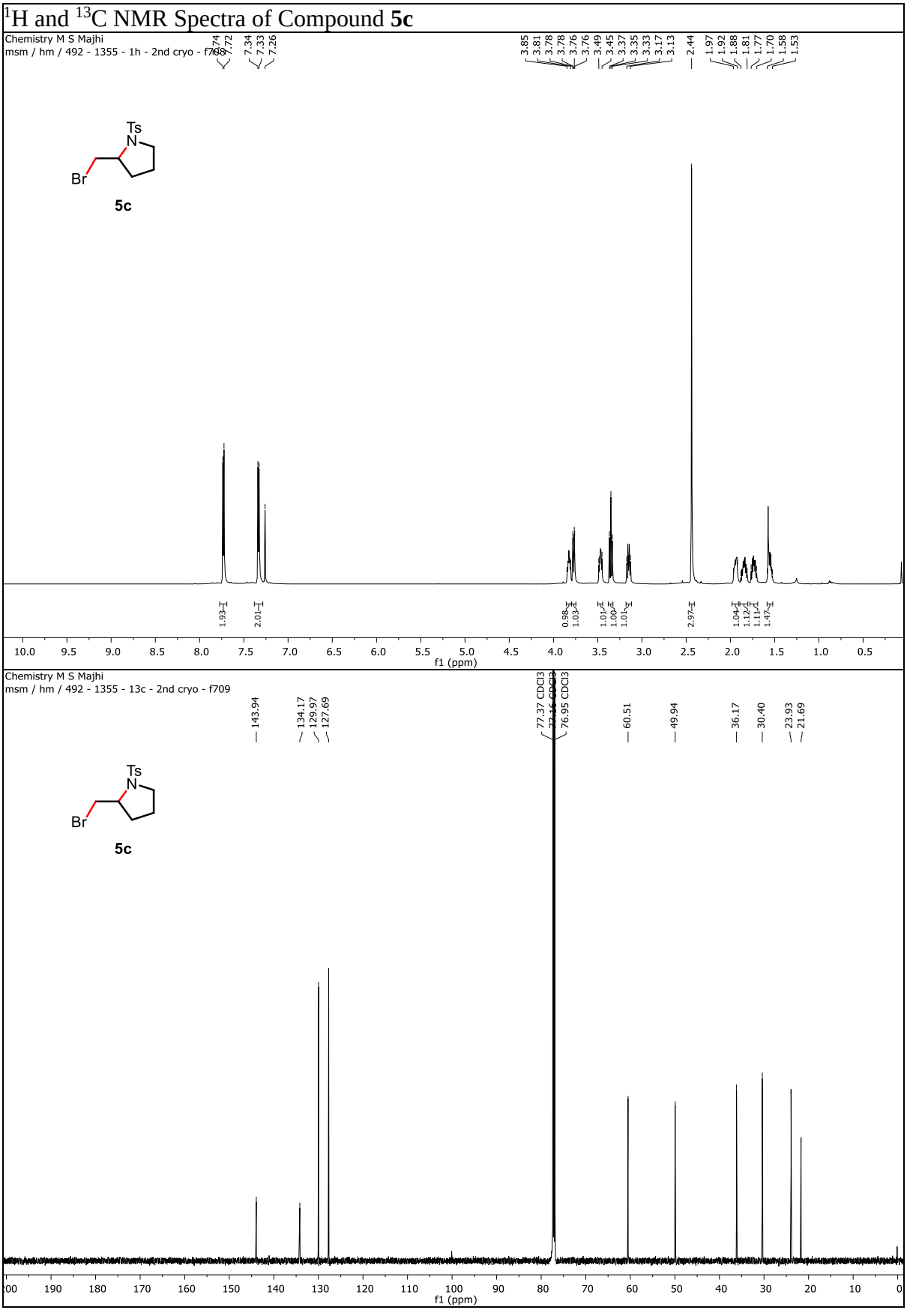
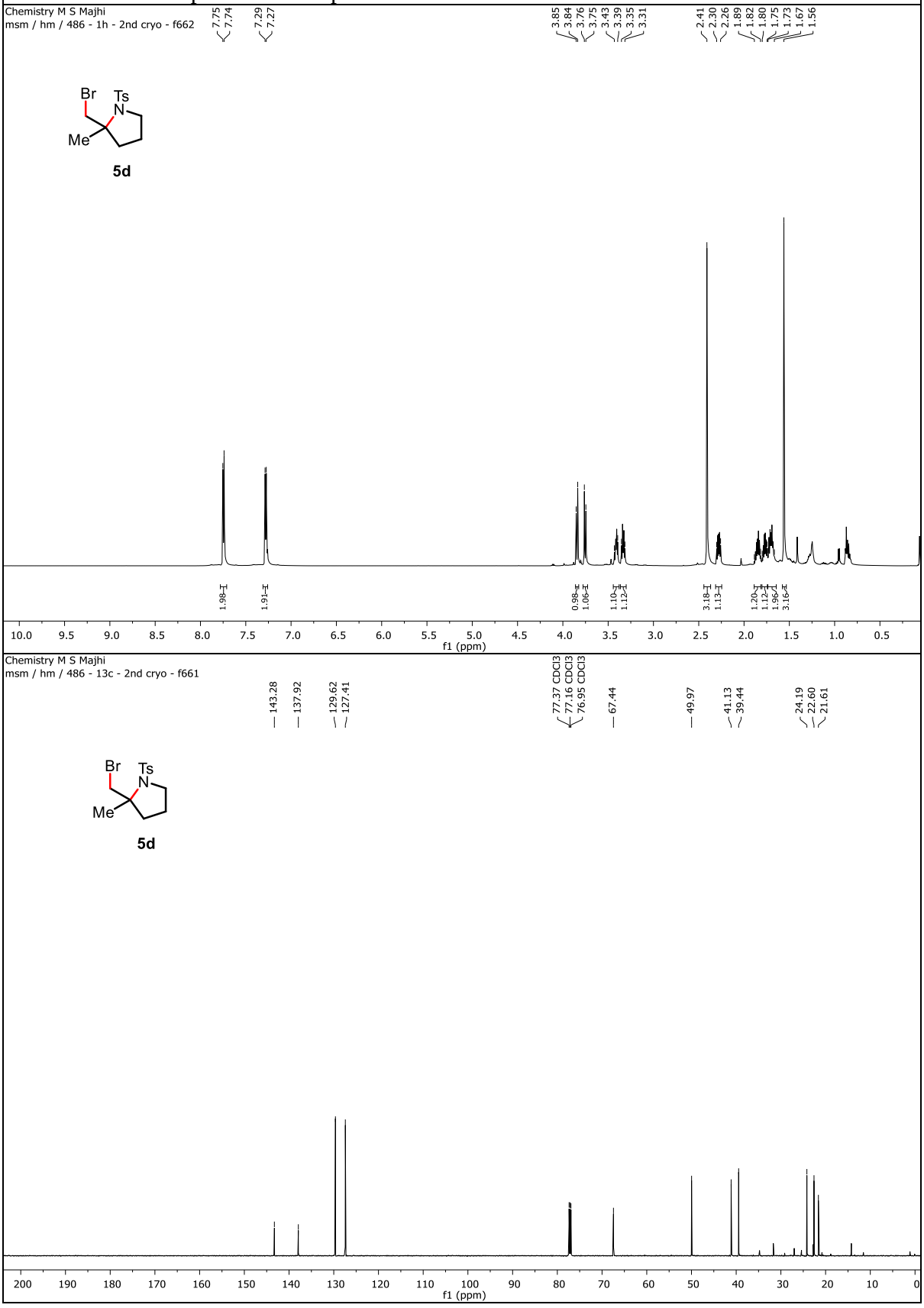


^{1}H and ^{13}C NMR Spectra of Compound **5d**



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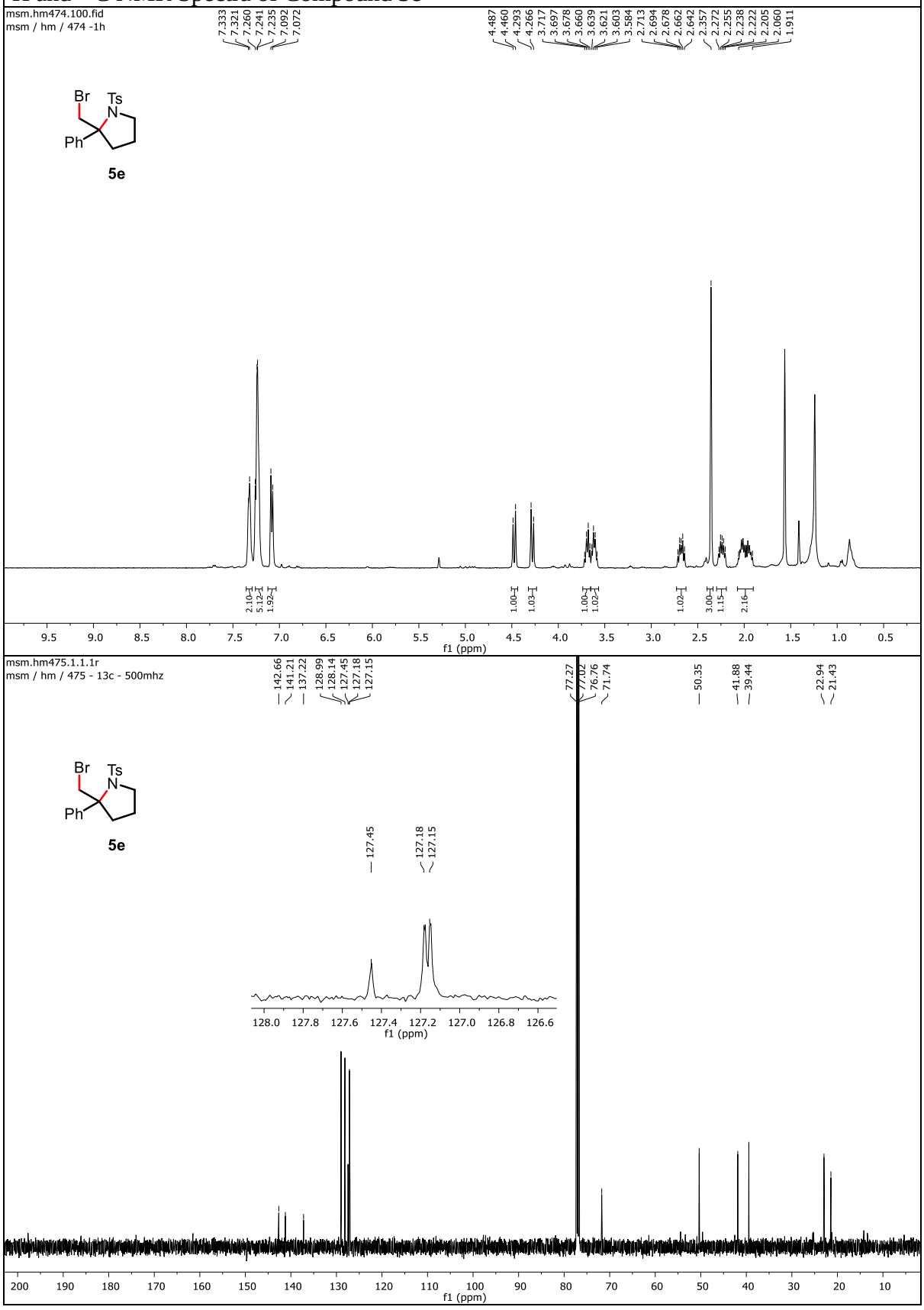
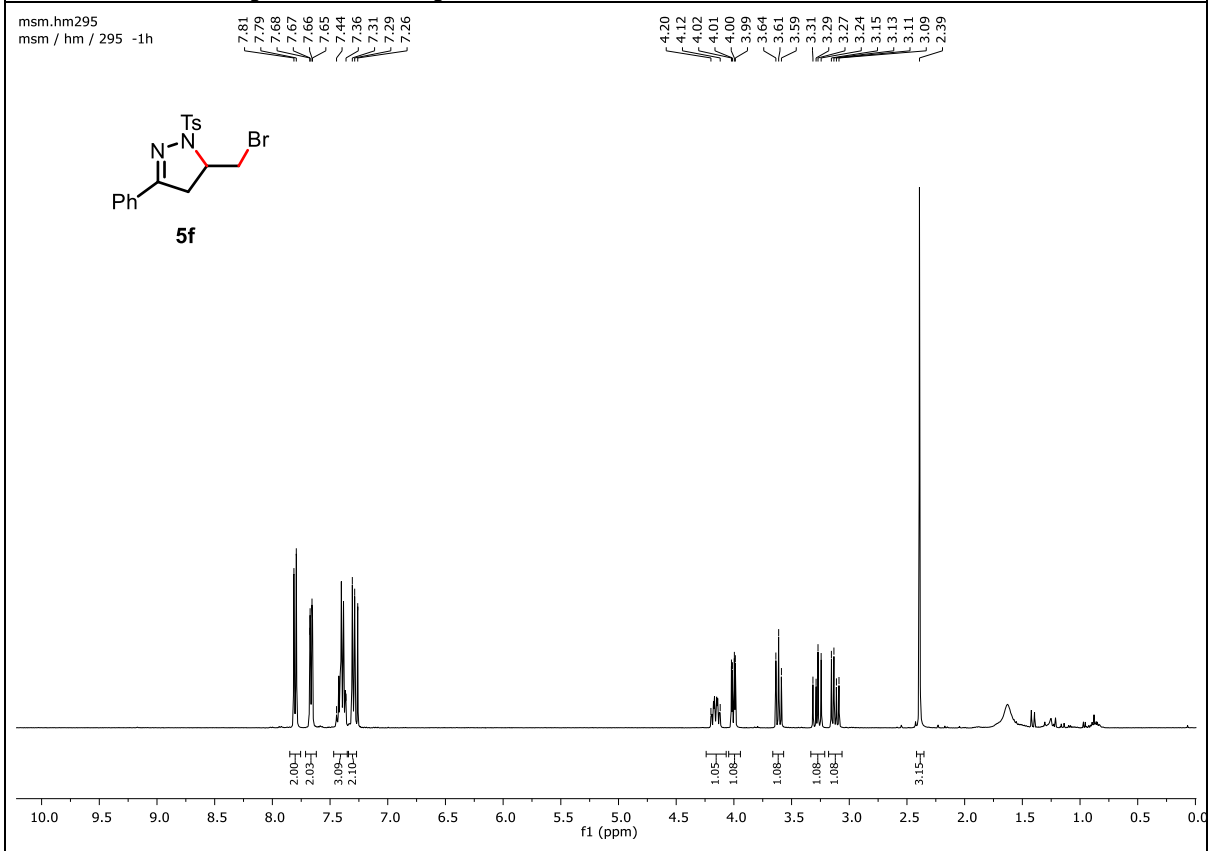
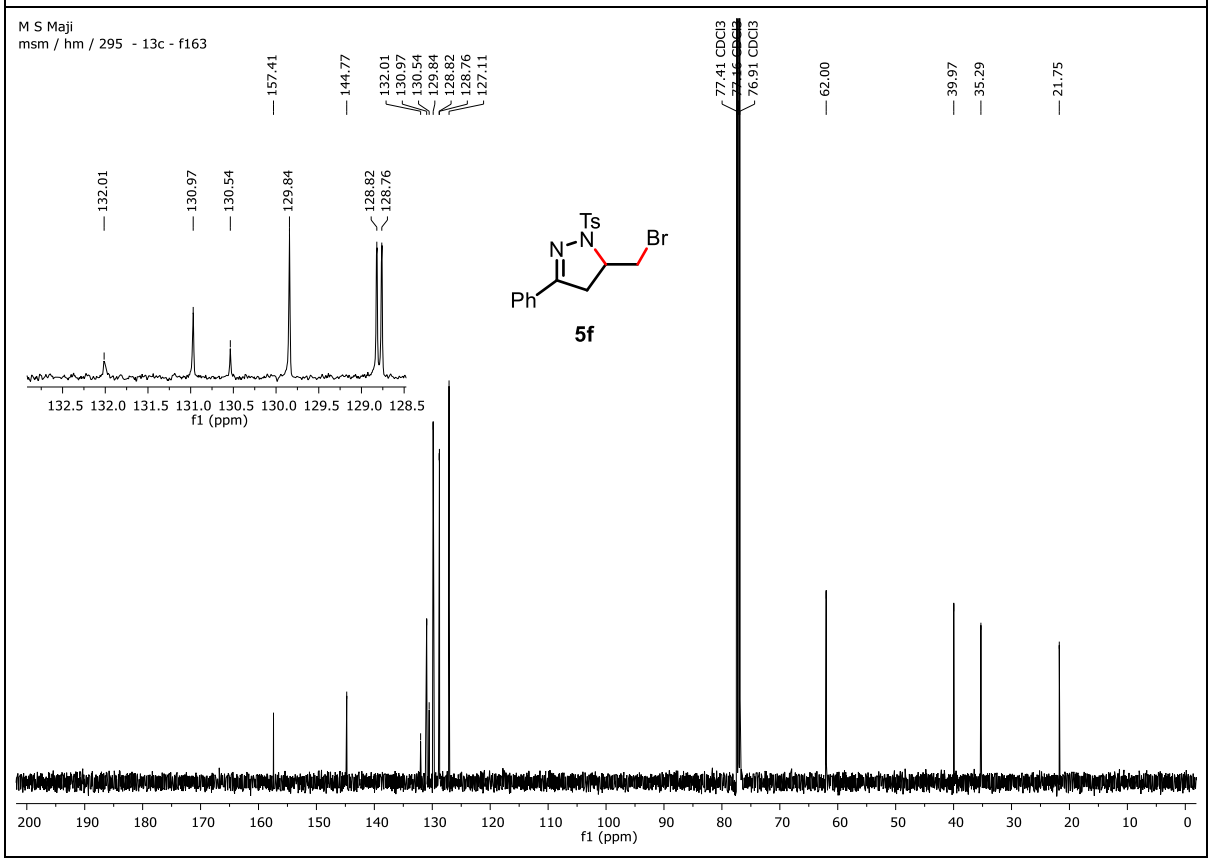
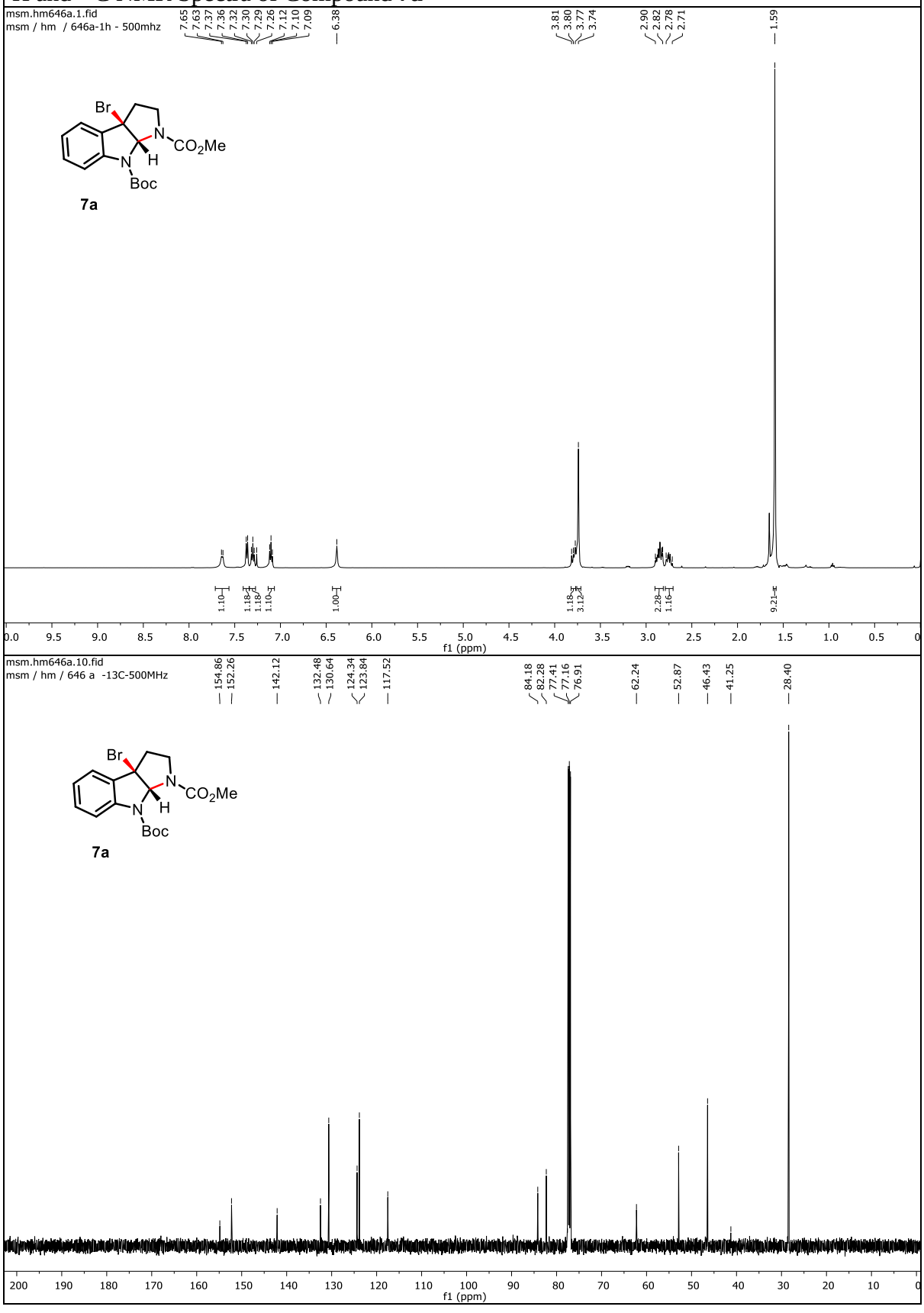


^{1}H and ^{13}C NMR Spectra of Compound **5f**

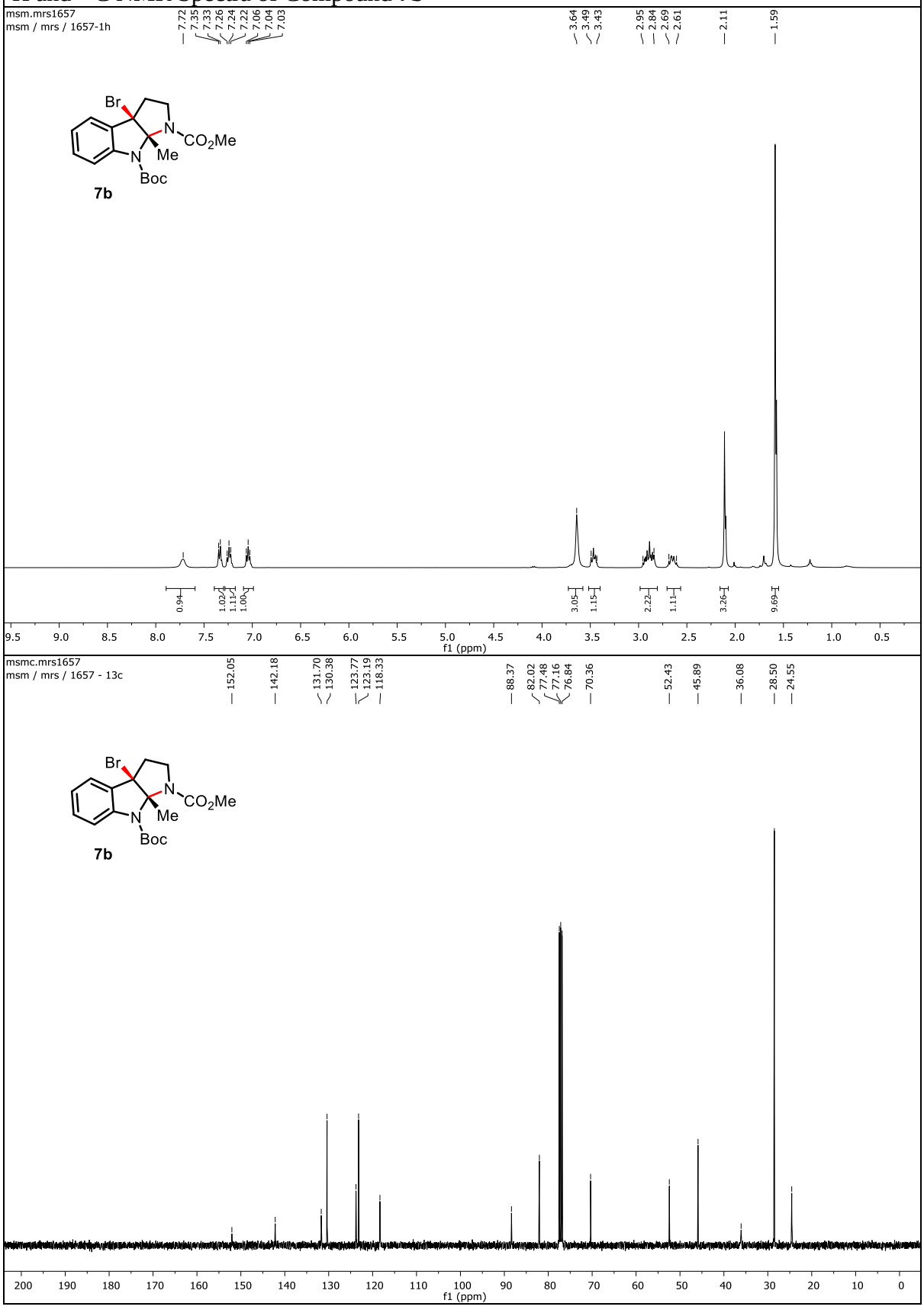




^{1}H and ^{13}C NMR Spectra of Compound **7a**



^{1}H and ^{13}C NMR Spectra of Compound **7b**



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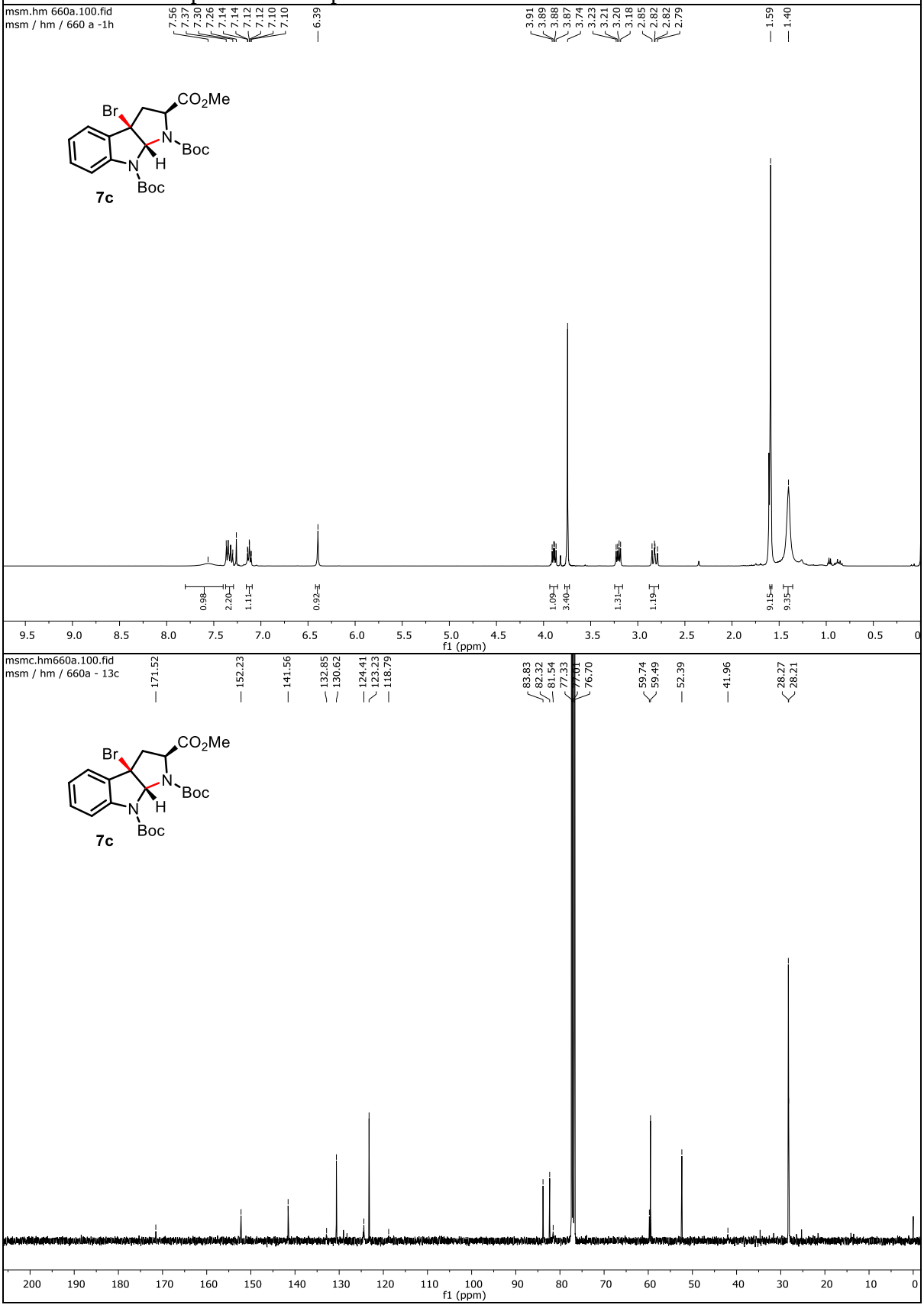
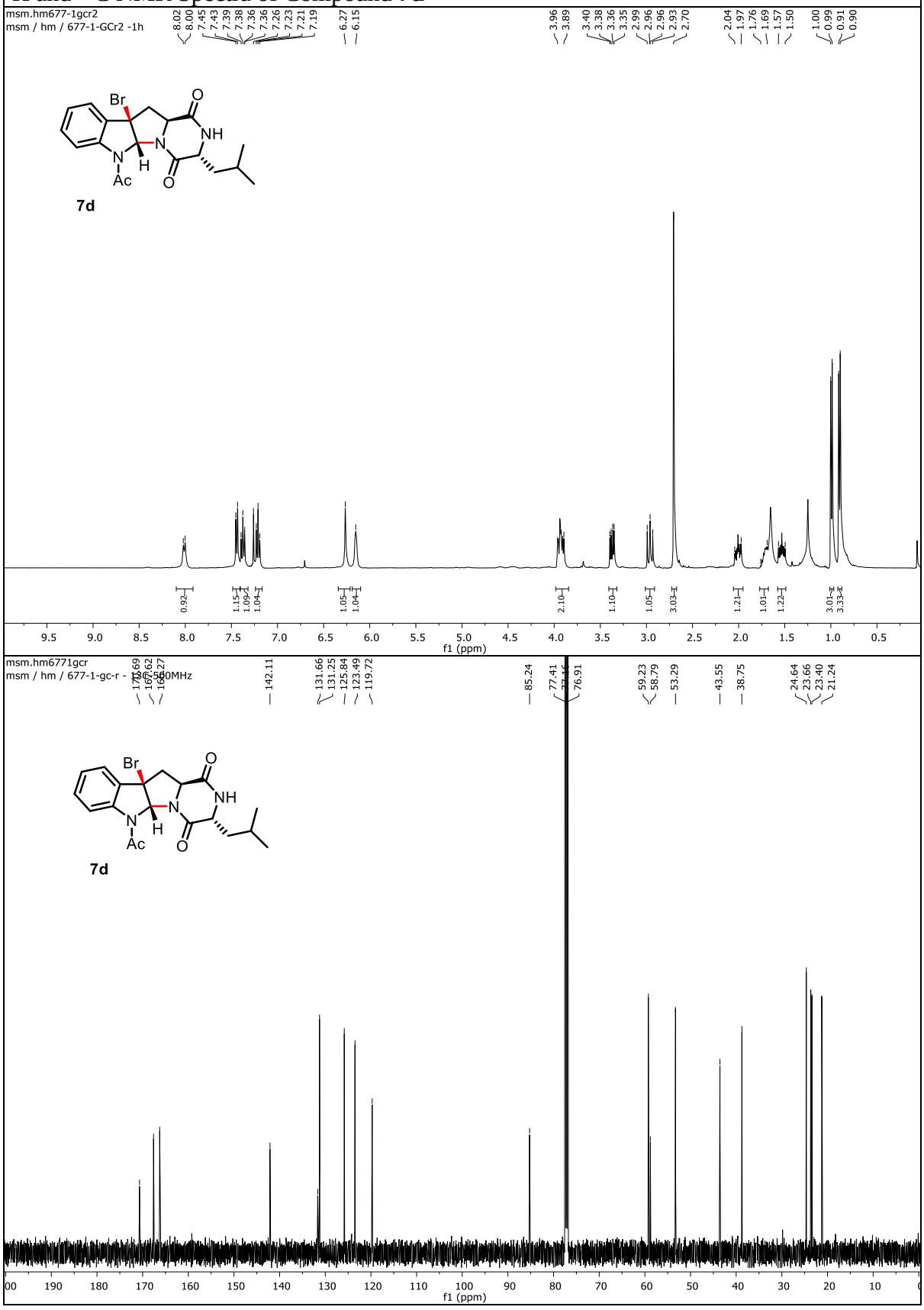


^{1}H and ^{13}C NMR Spectra of Compound **7d**



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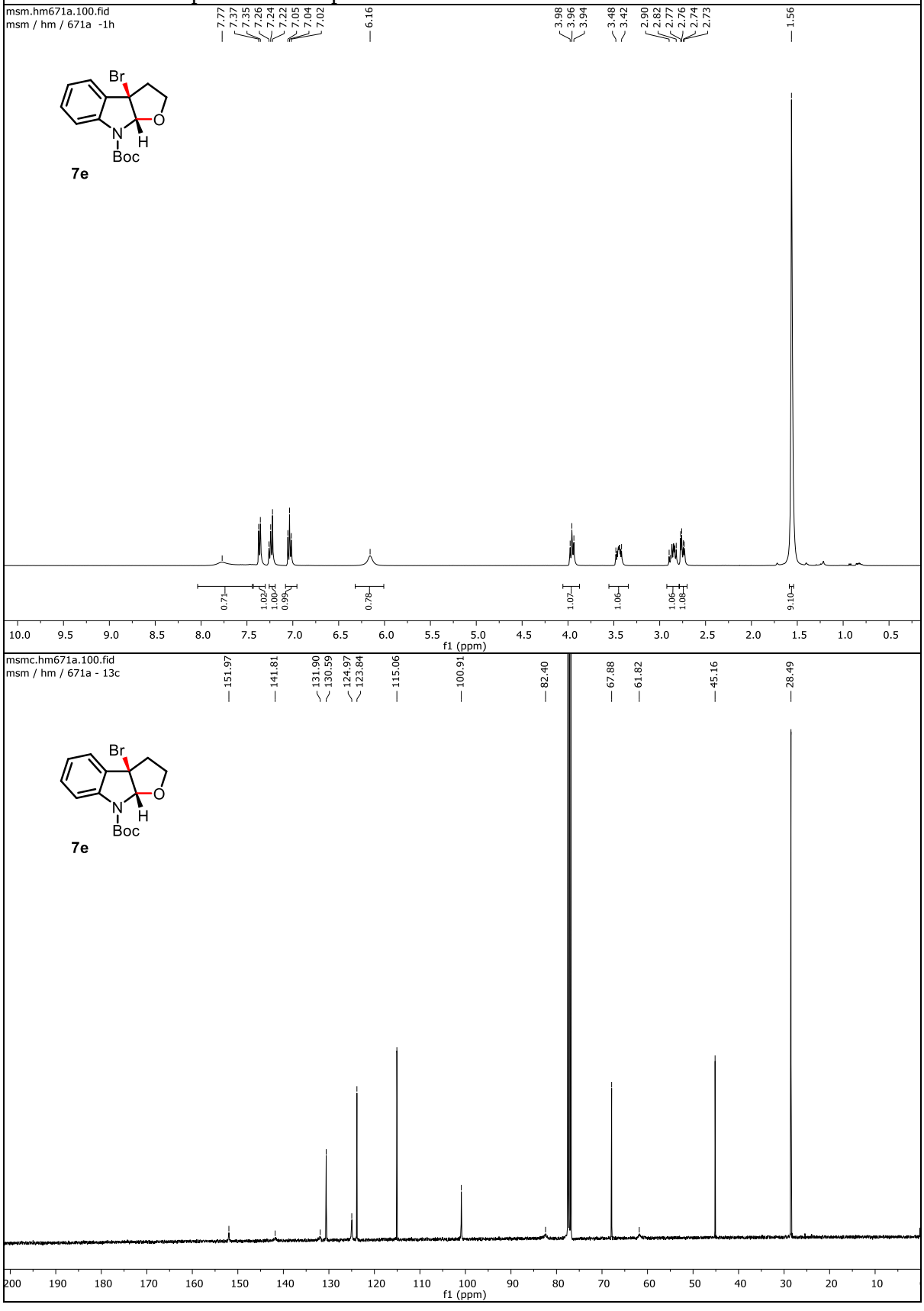
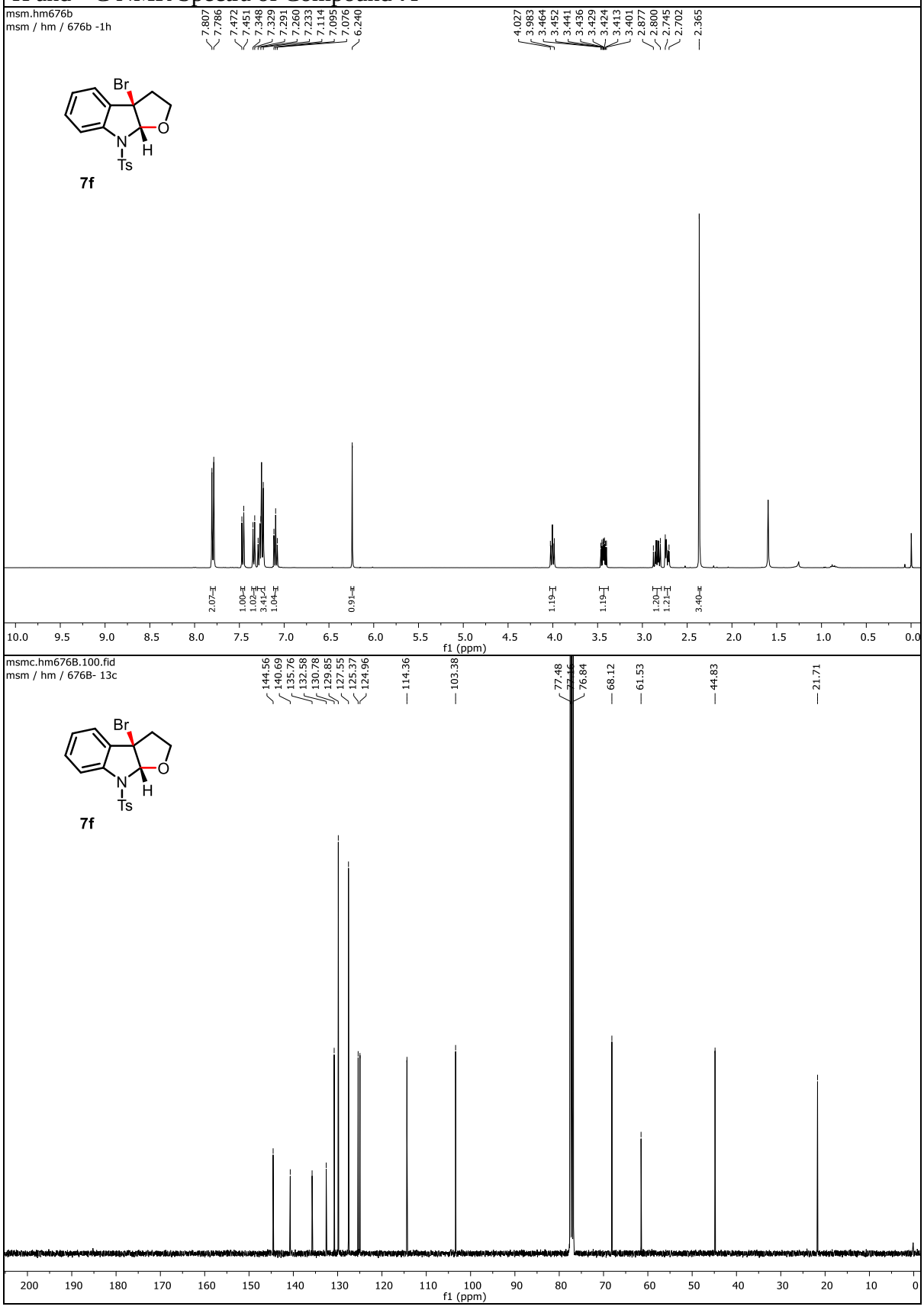
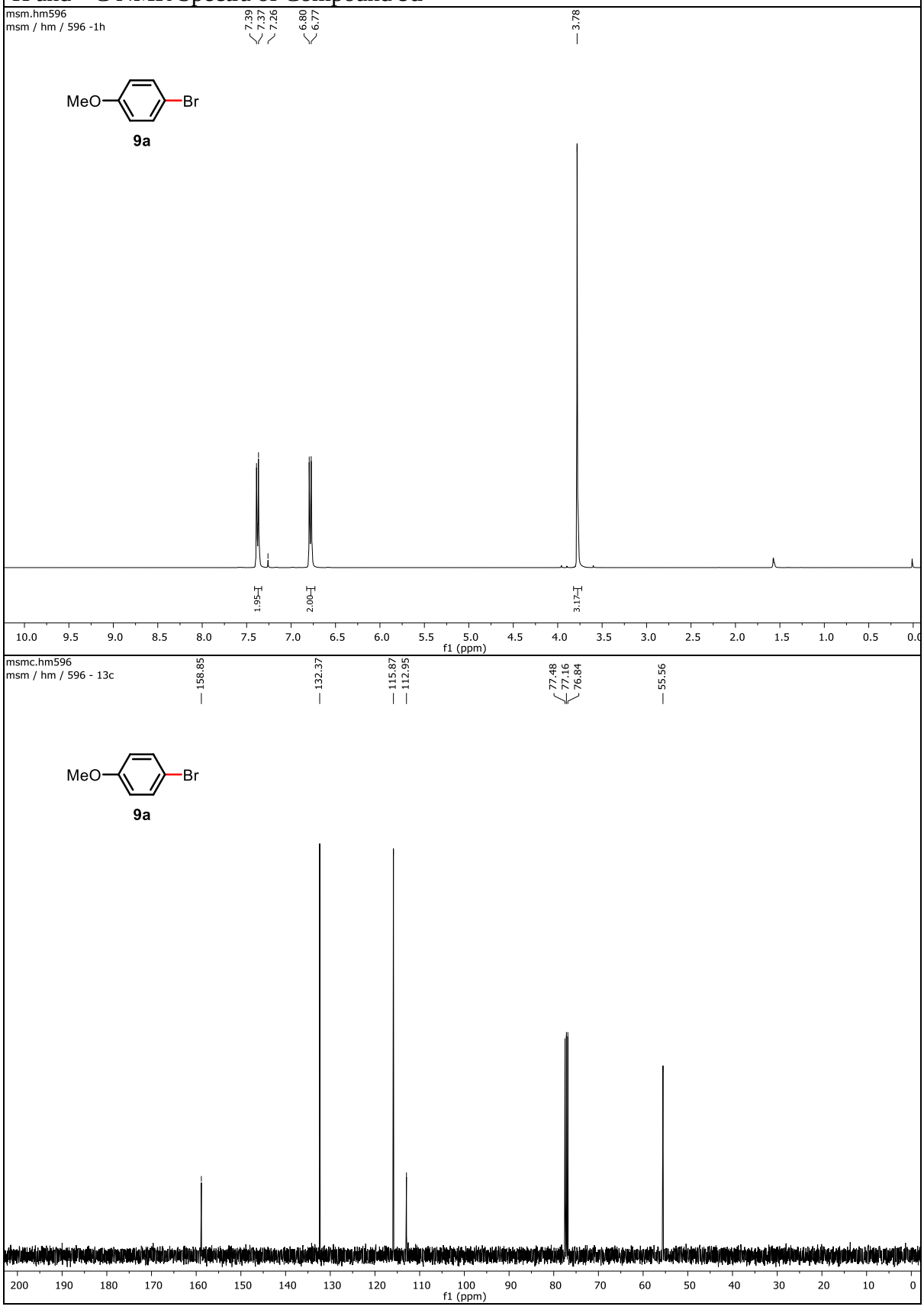


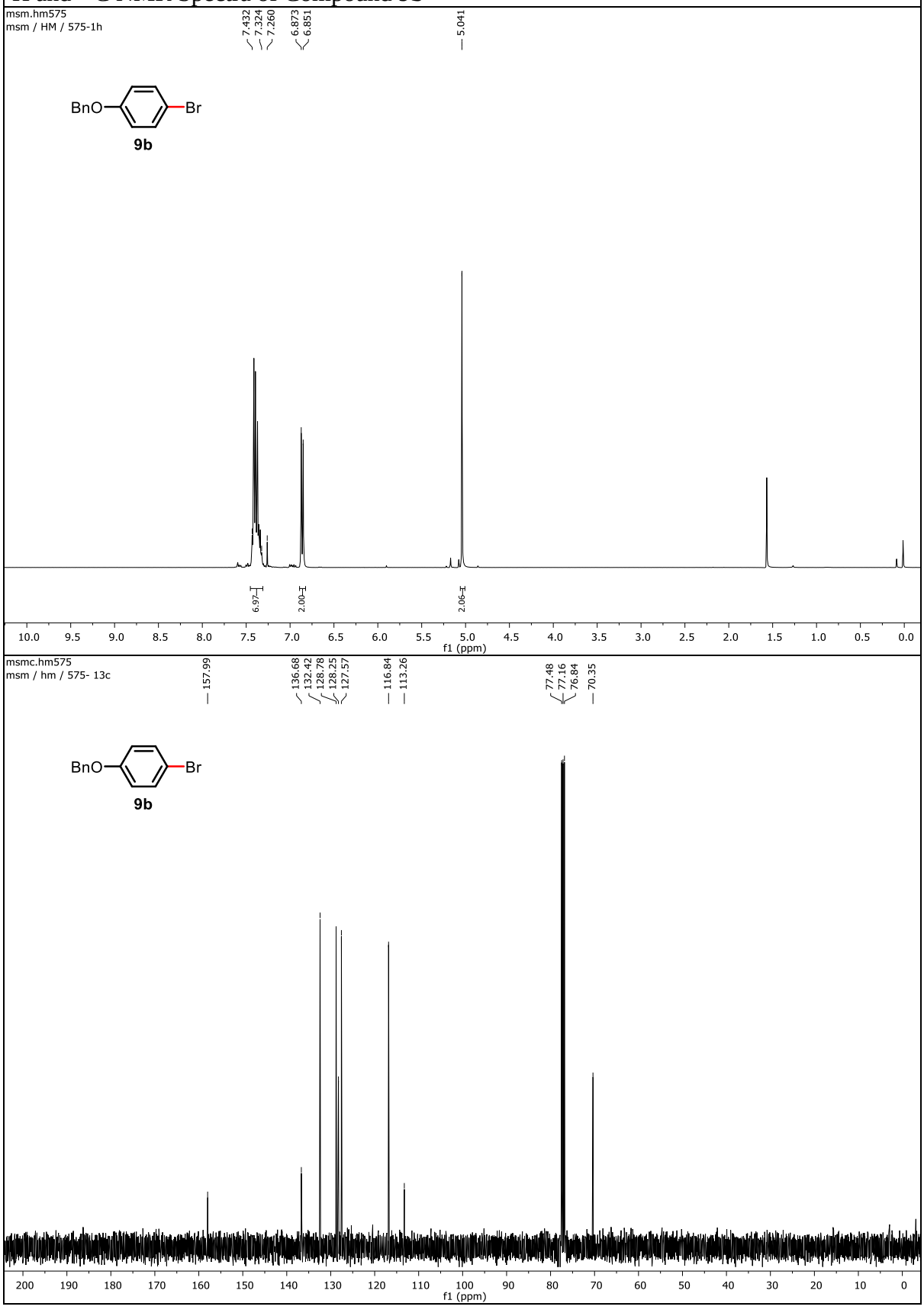
^{1}H and ^{13}C NMR Spectra of Compound **7f**



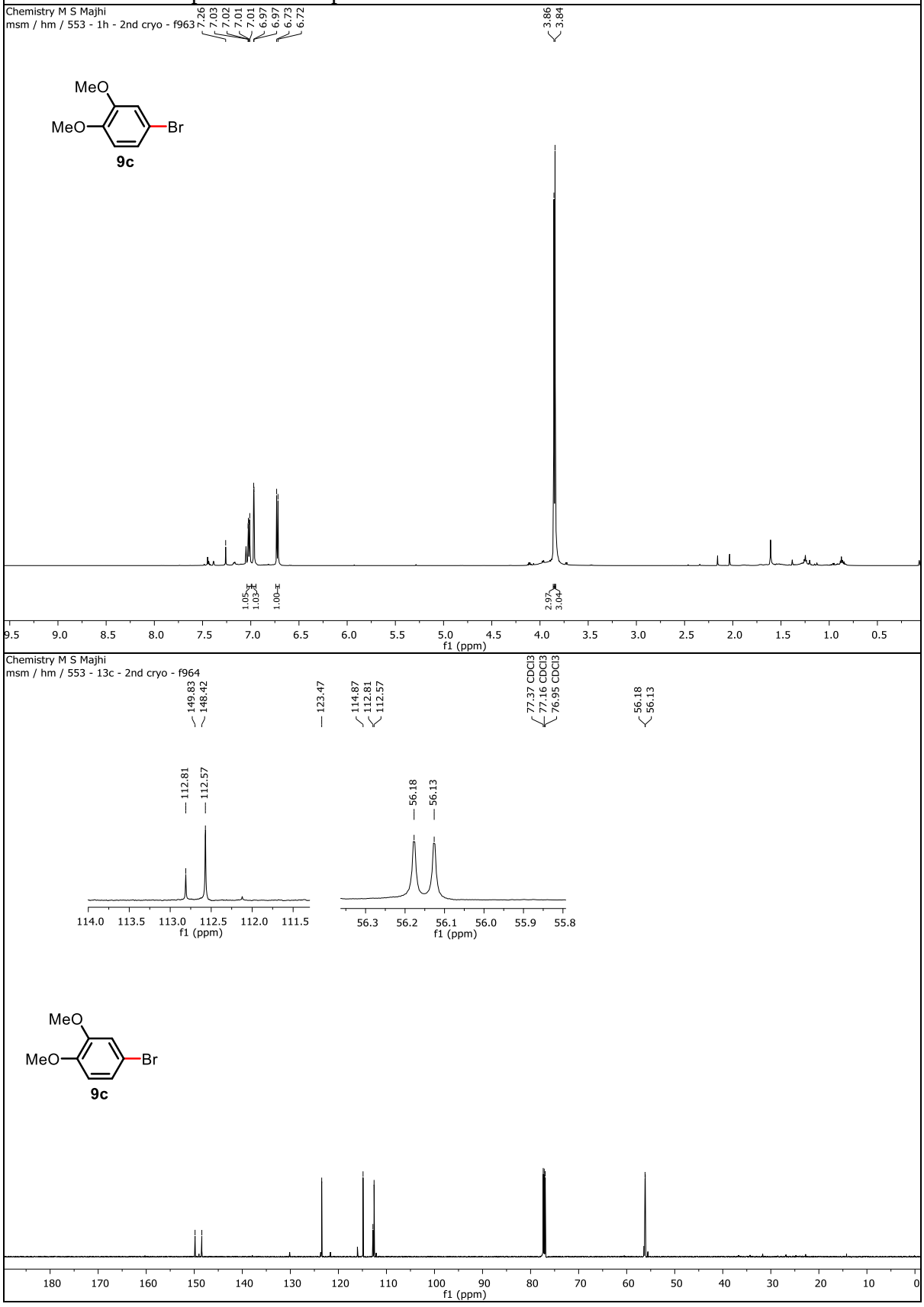
^{1}H and ^{13}C NMR Spectra of Compound **9a**



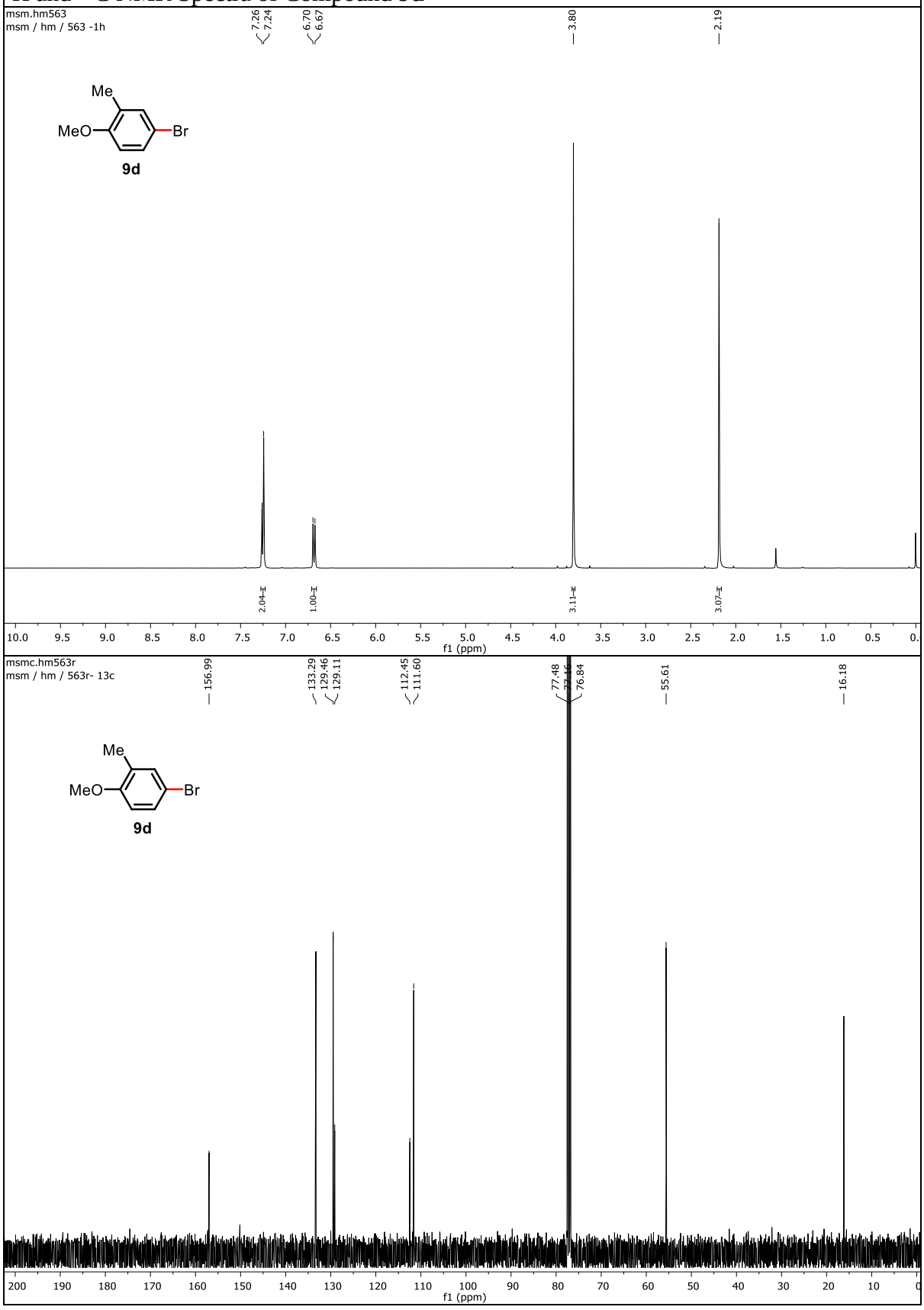
^{1}H and ^{13}C NMR Spectra of Compound **9b**



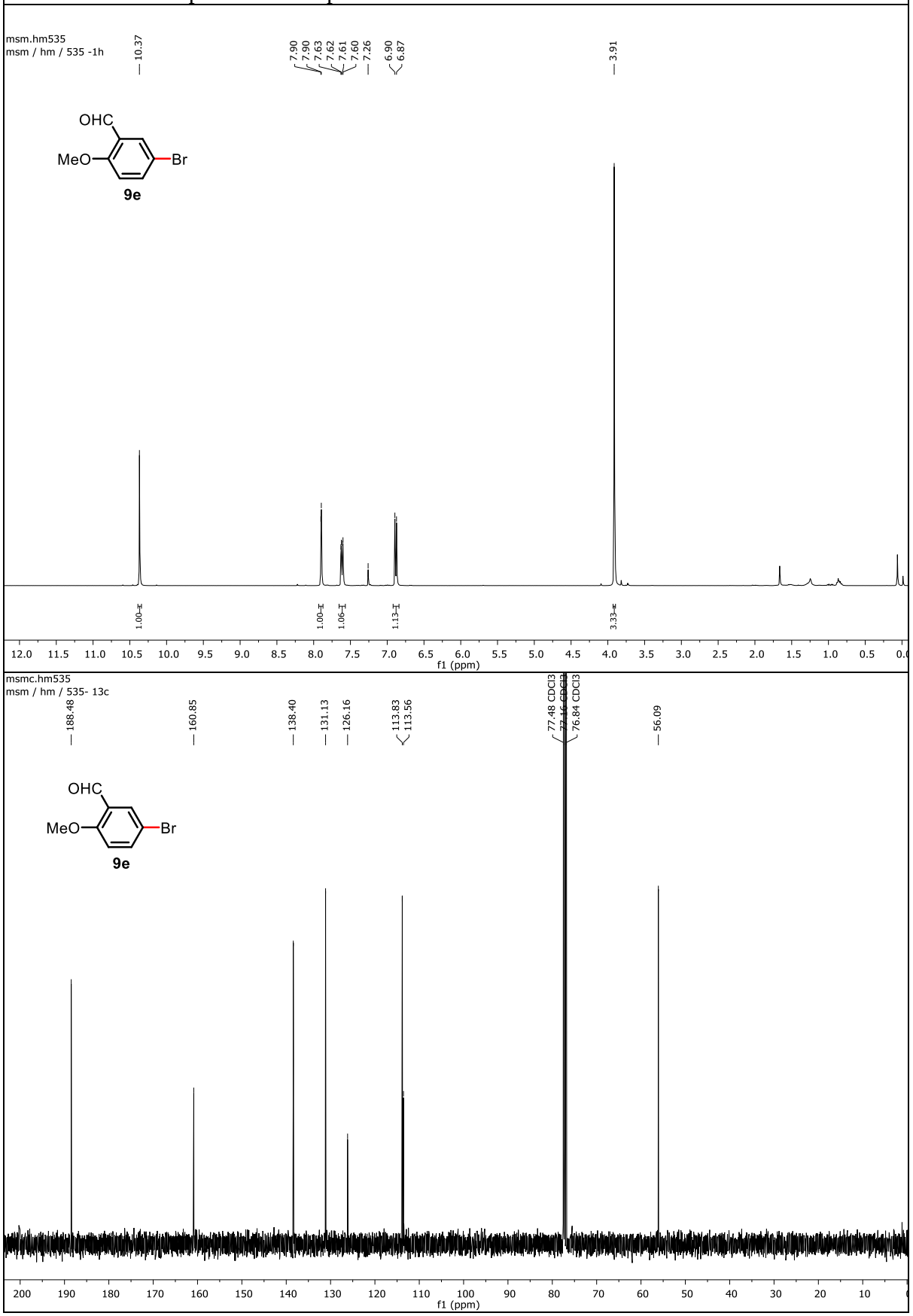
^{1}H and ^{13}C NMR Spectra of Compound **9c**



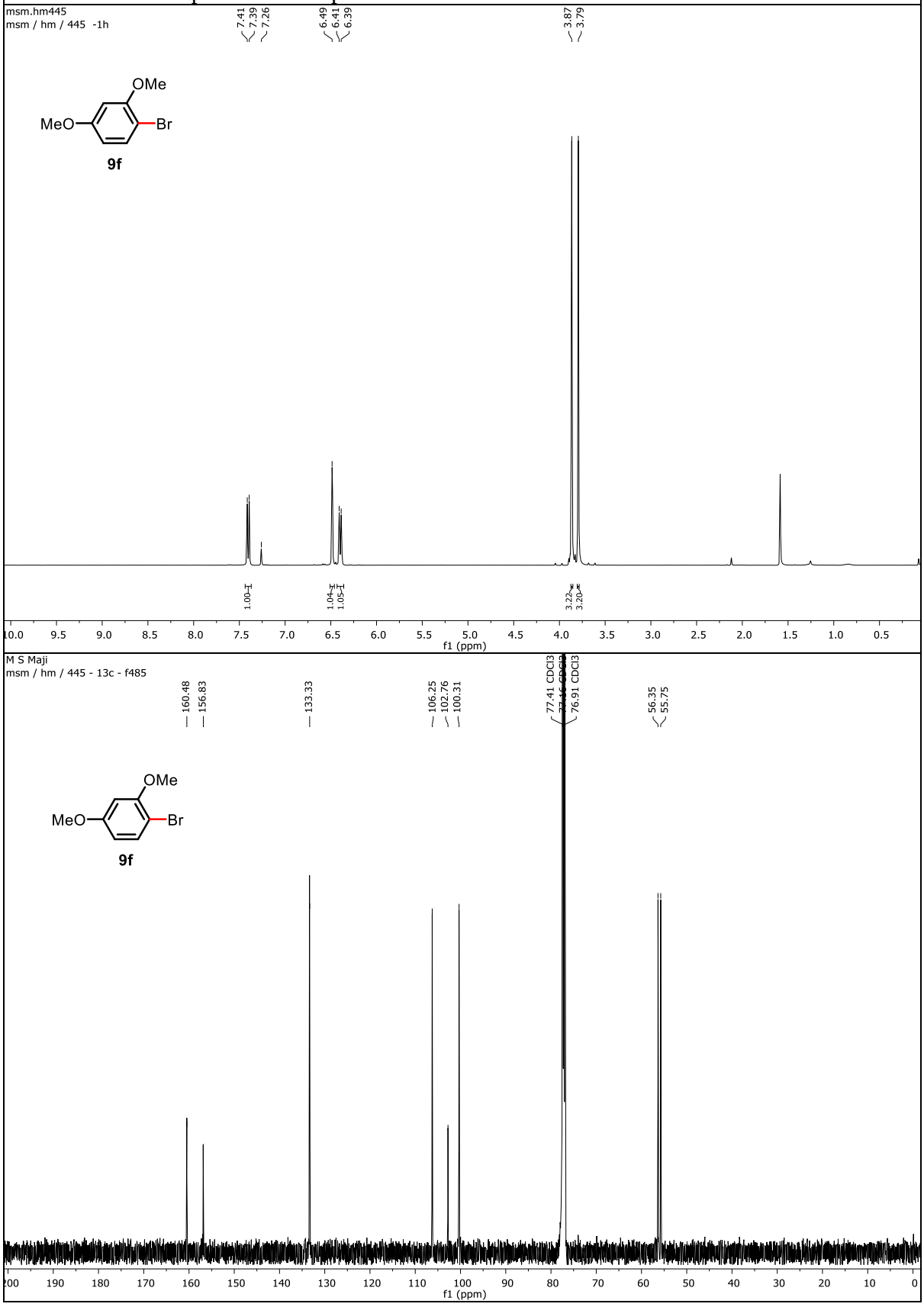
^{1}H and ^{13}C NMR Spectra of Compound **9d**



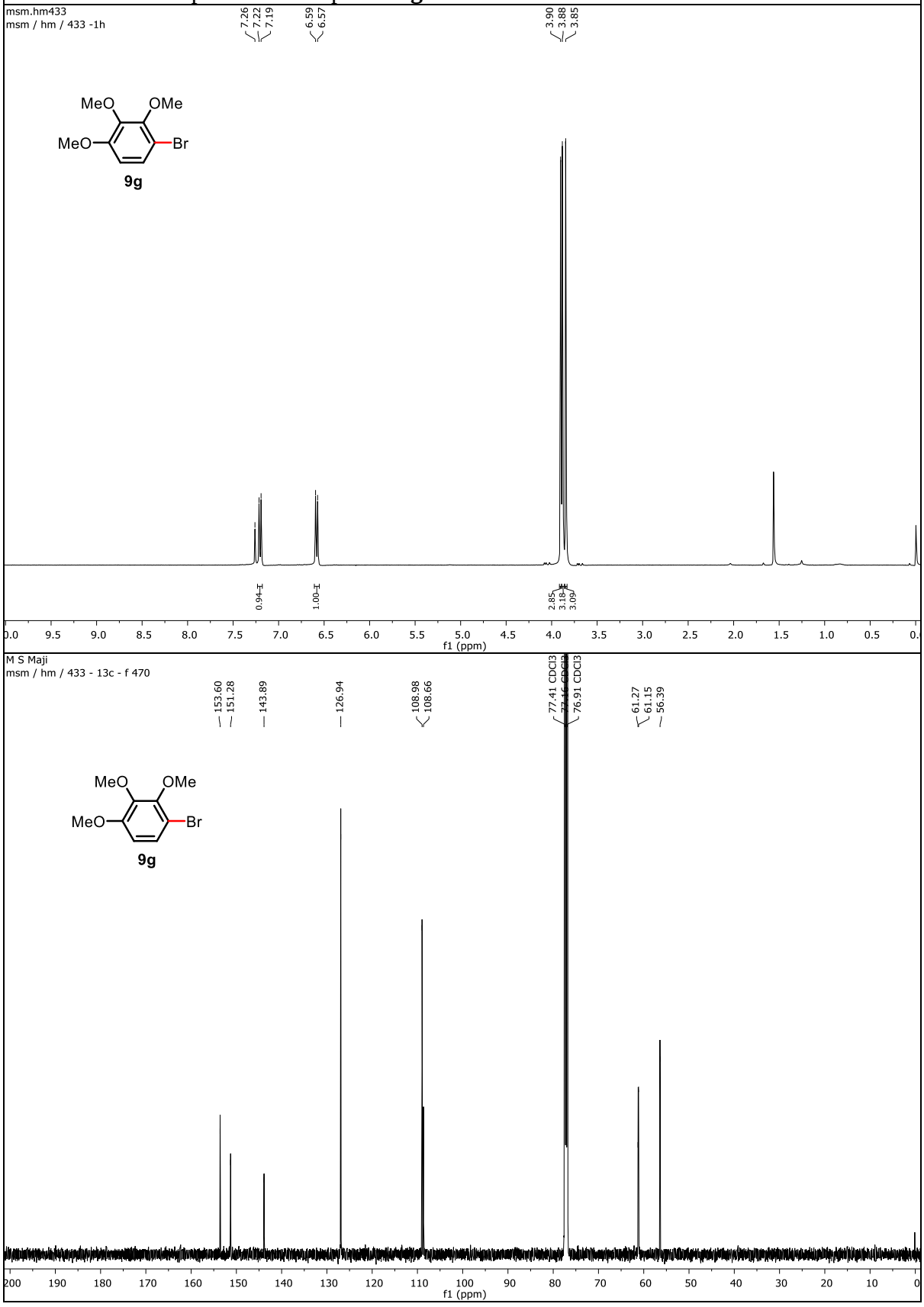
^{1}H and ^{13}C NMR Spectra of Compound **9e**



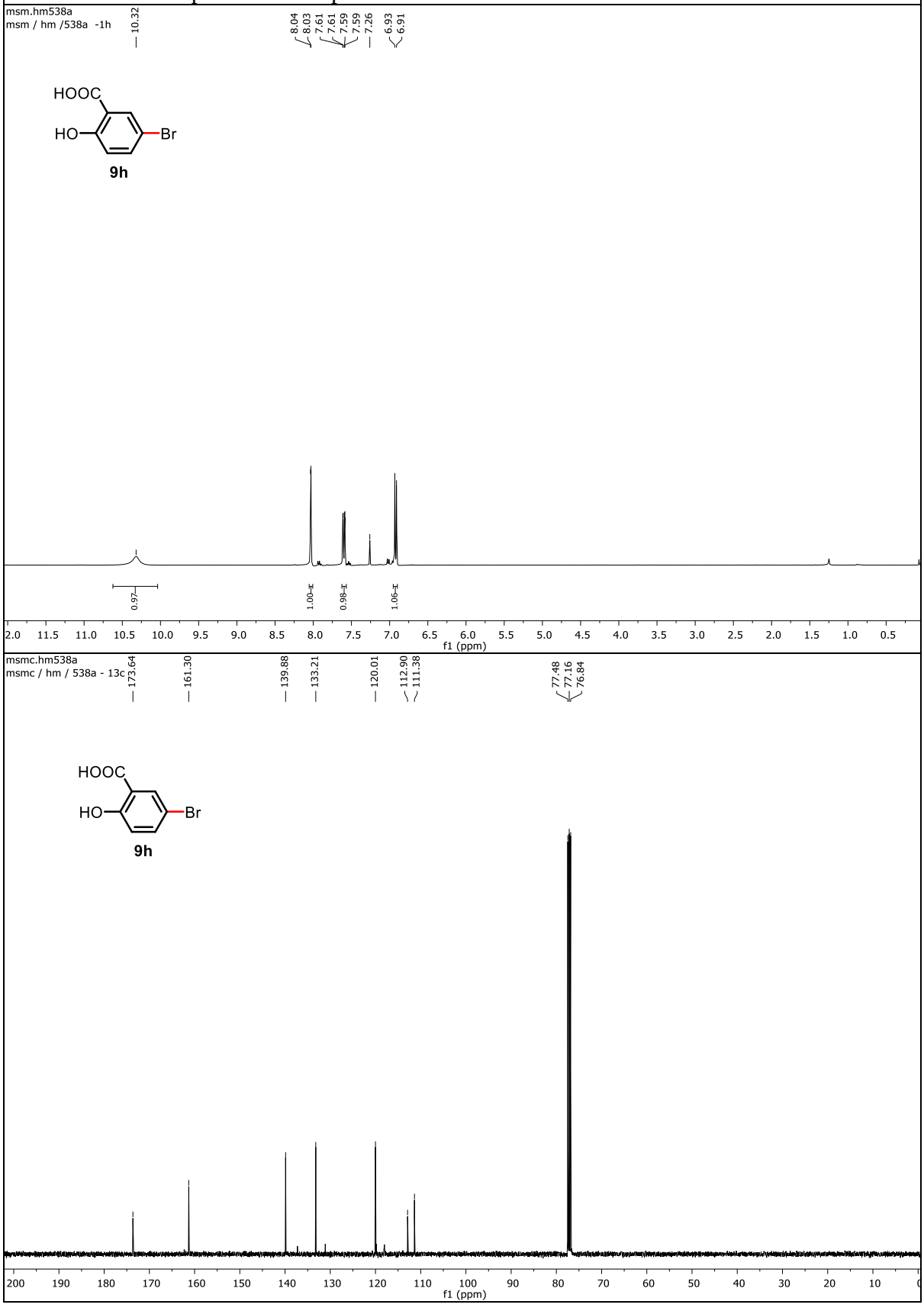
^{1}H and ^{13}C NMR Spectra of Compound **9f**



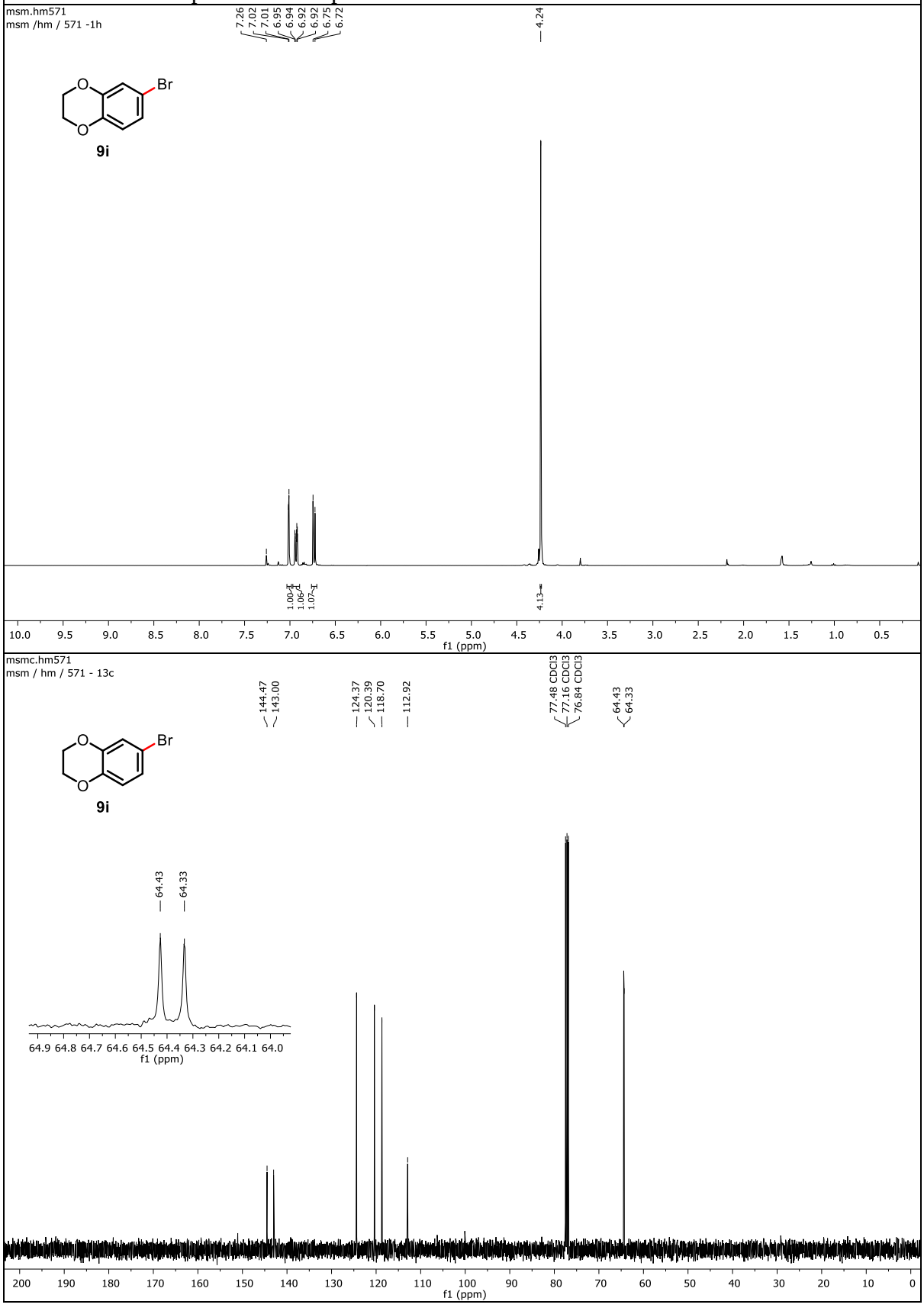
^{1}H and ^{13}C NMR Spectra of Compound **9g**



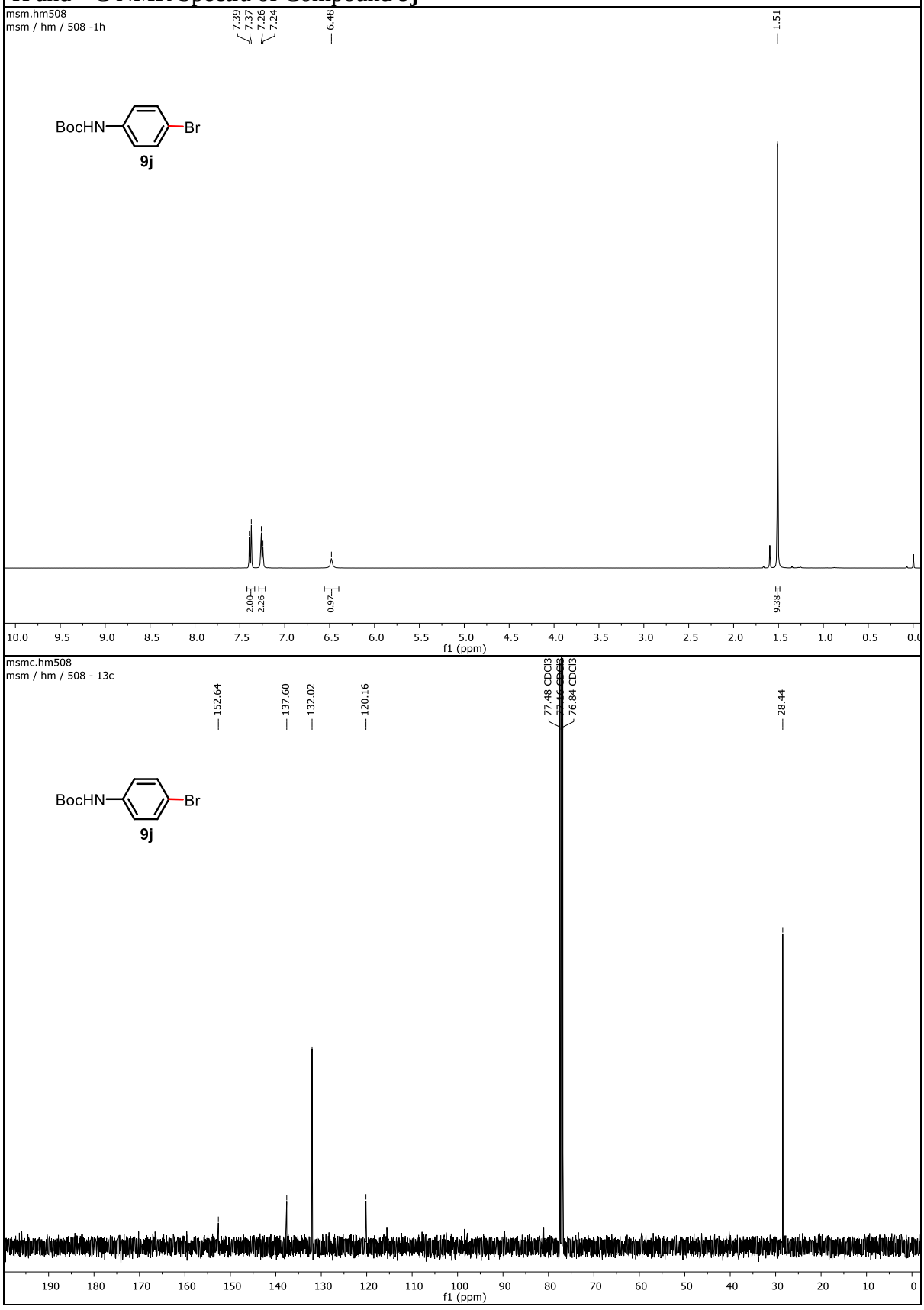
^{1}H and ^{13}C NMR Spectra of Compound **9h**



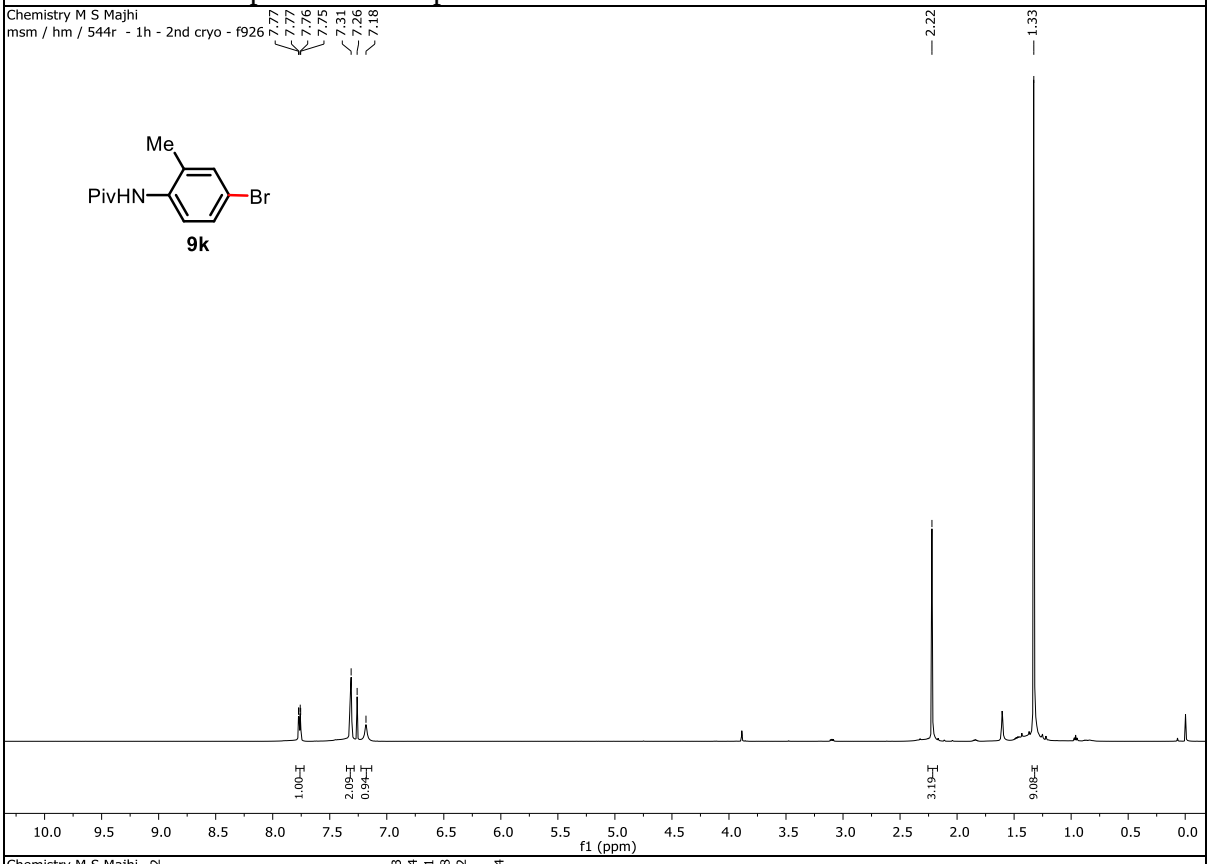
^{1}H and ^{13}C NMR Spectra of Compound **9i**

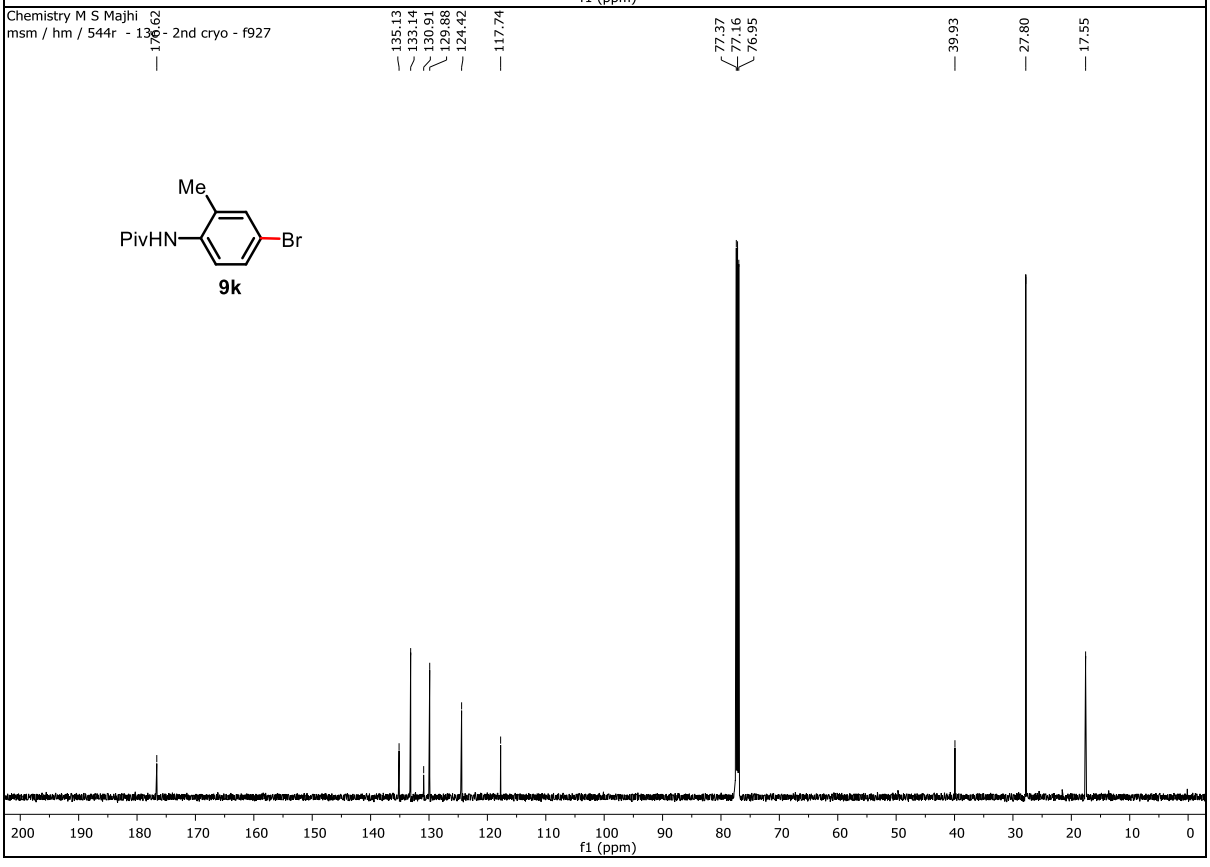


^{1}H and ^{13}C NMR Spectra of Compound **9j**

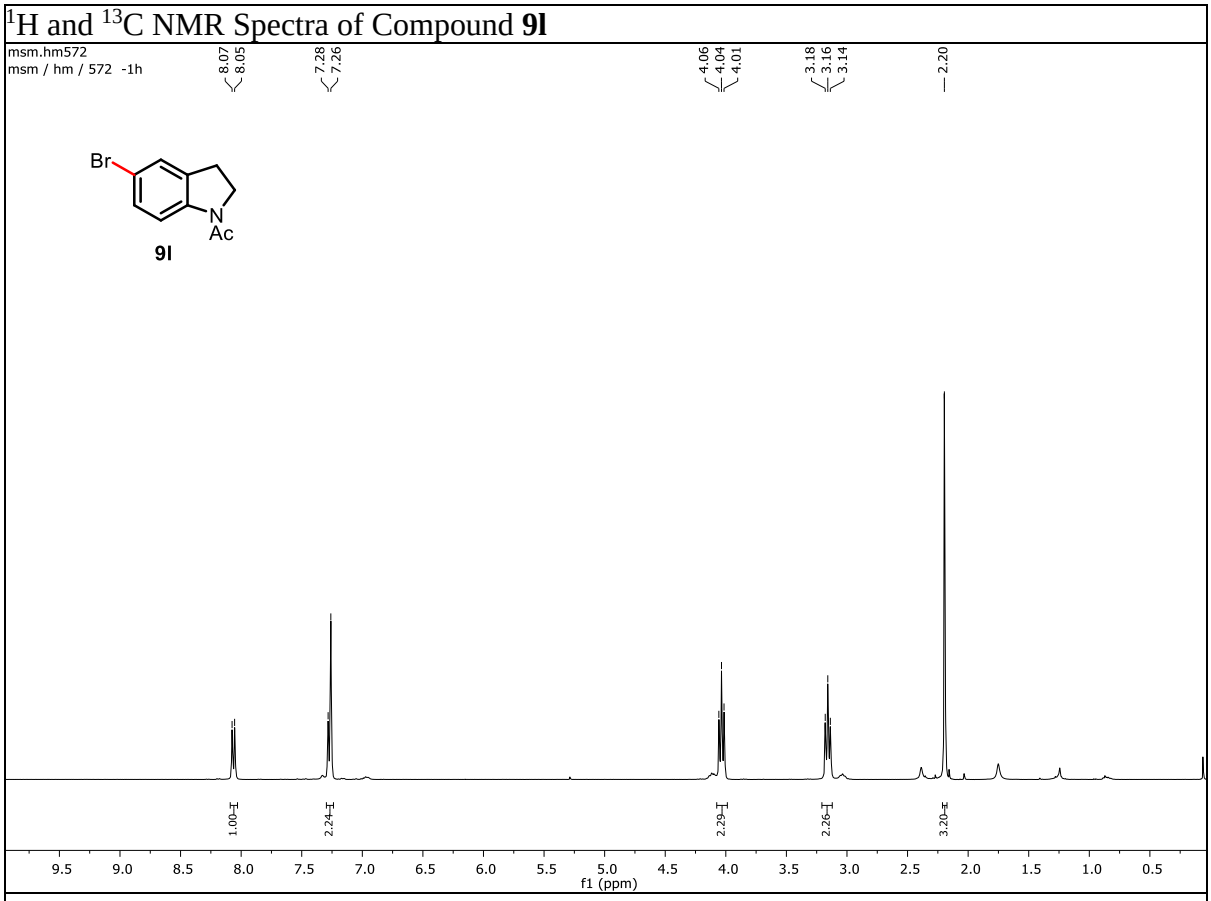


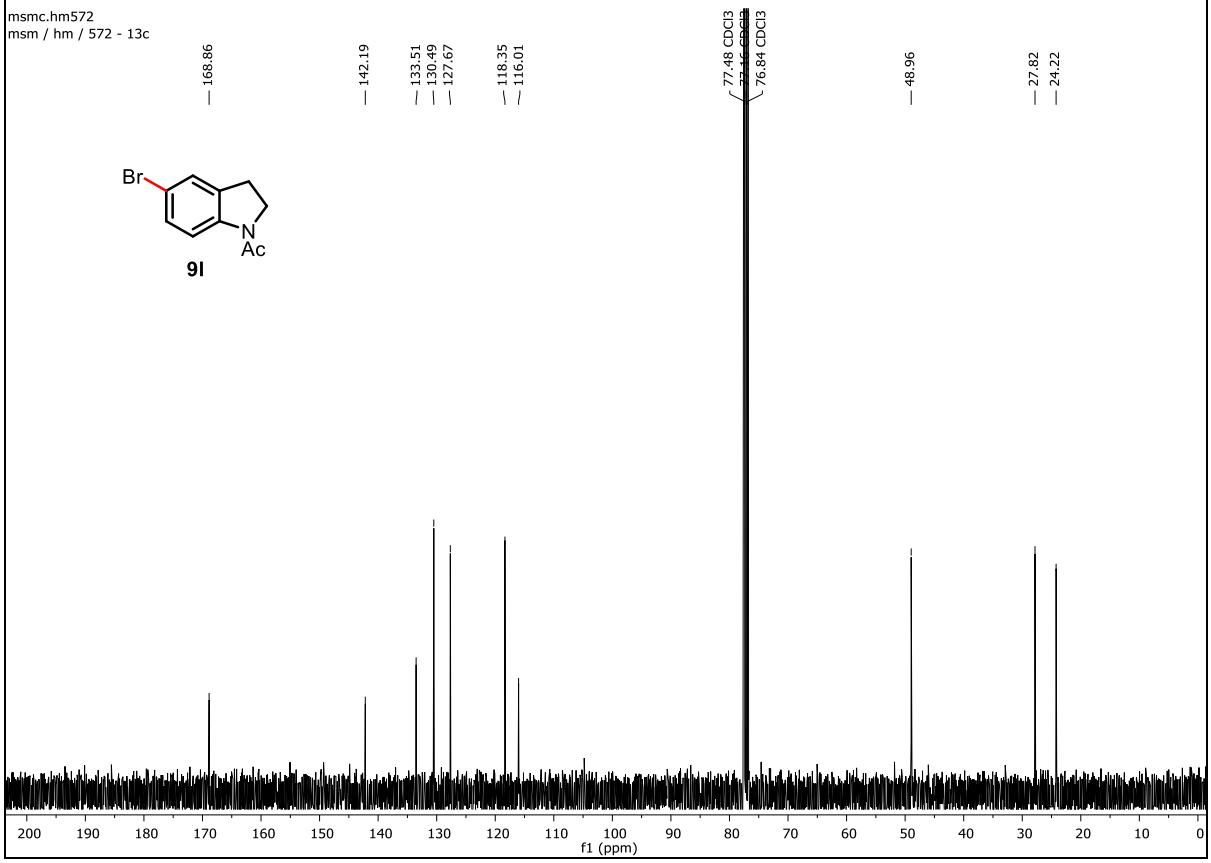
^{1}H and ^{13}C NMR Spectra of Compound **9k**



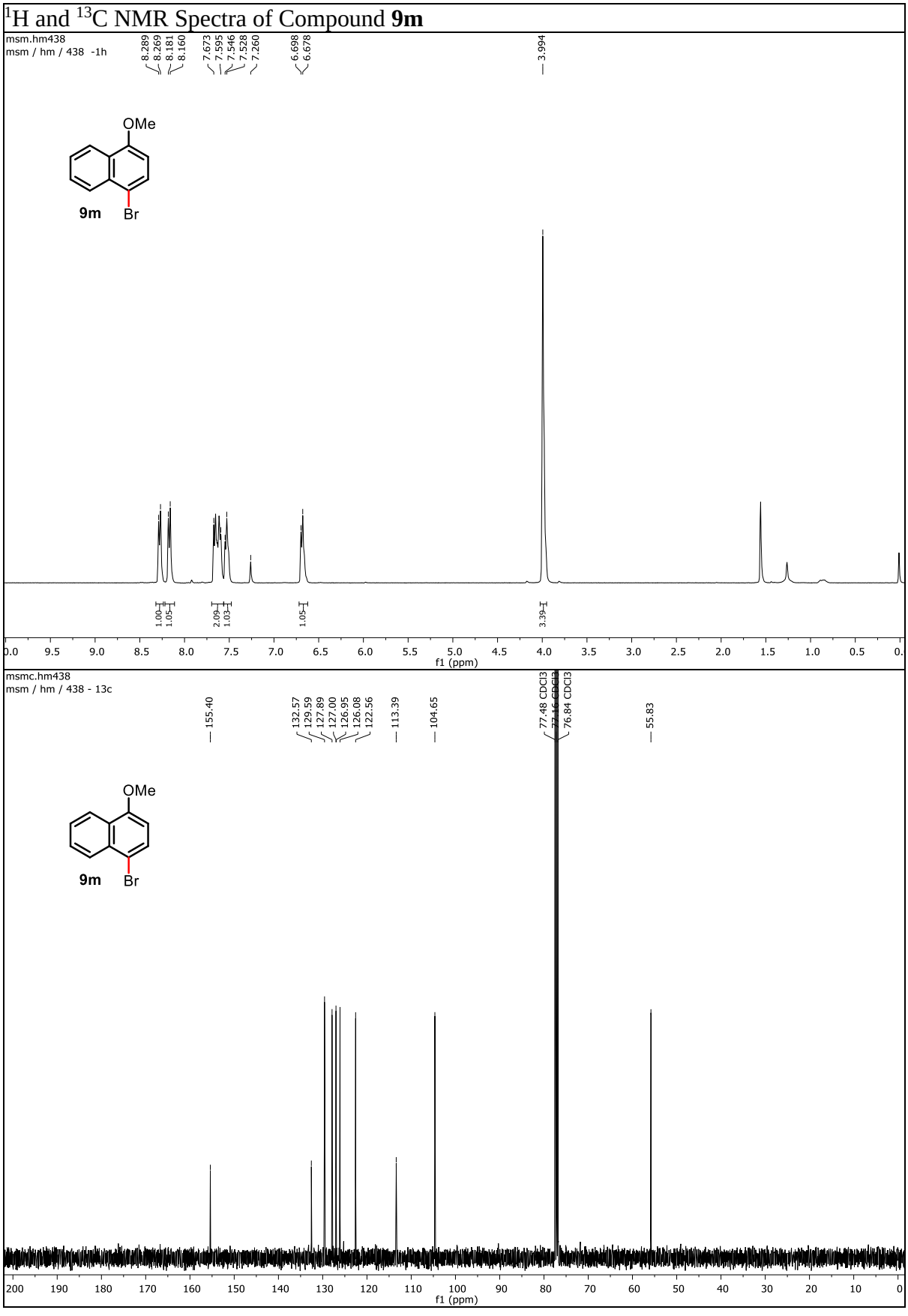


^{1}H and ^{13}C NMR Spectra of Compound **9l**

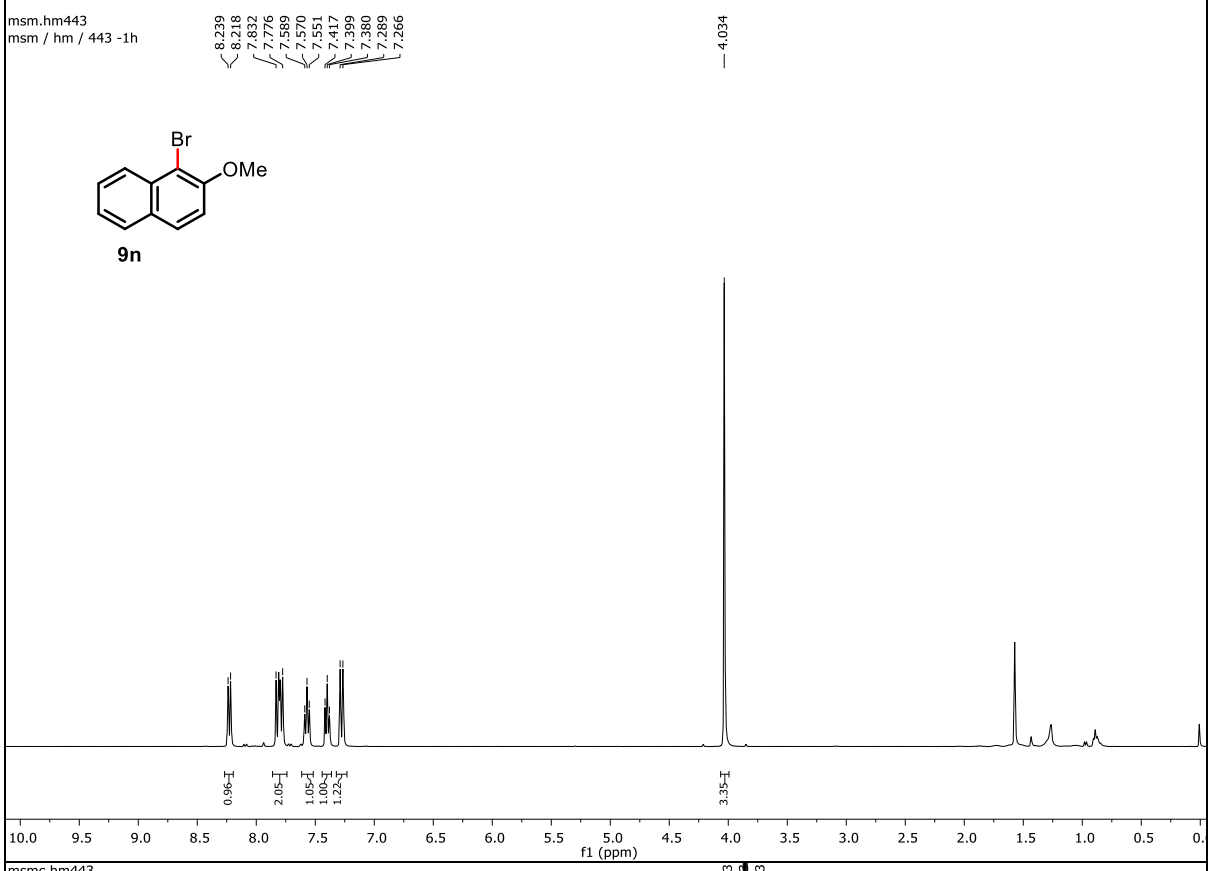


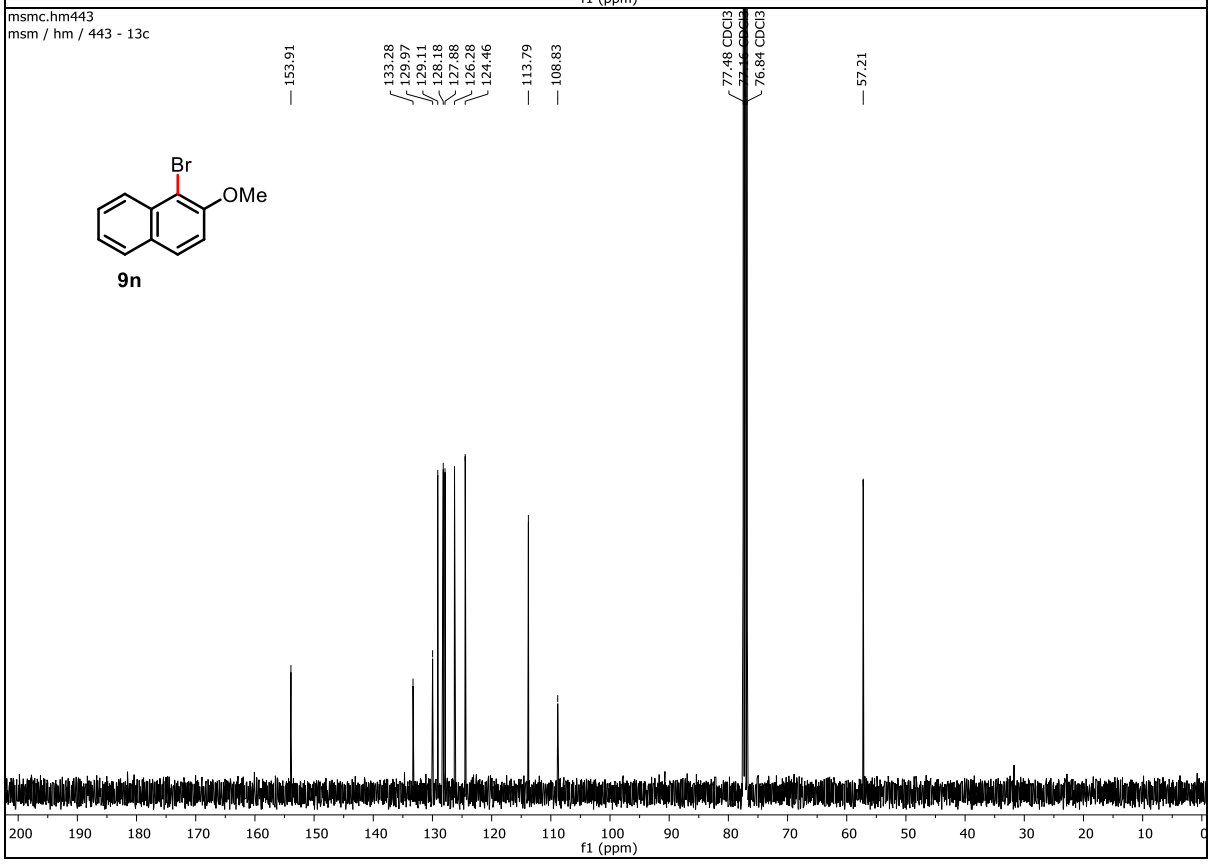


^{1}H and ^{13}C NMR Spectra of Compound **9m**

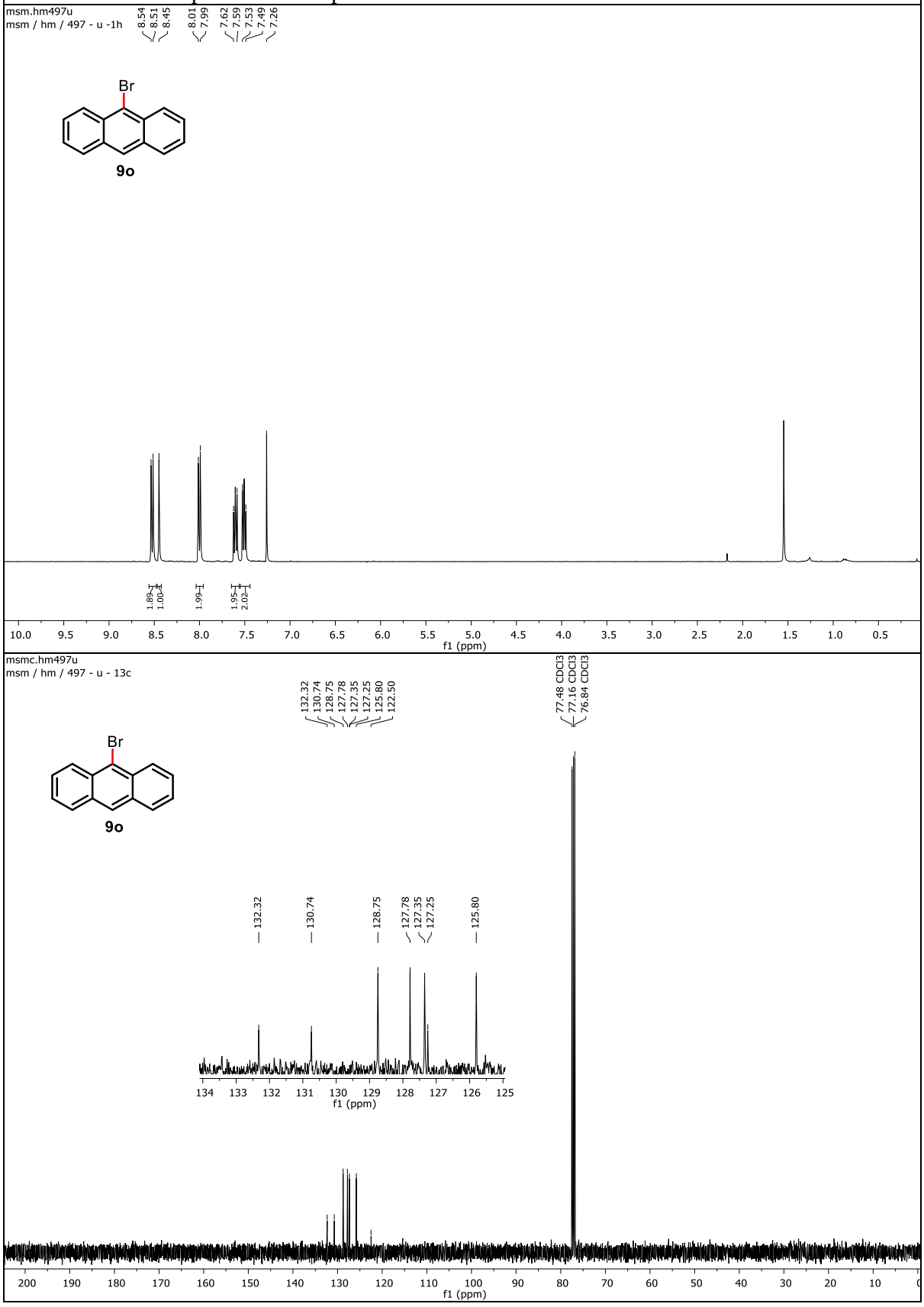


^{1}H and ^{13}C NMR Spectra of Compound **9n**

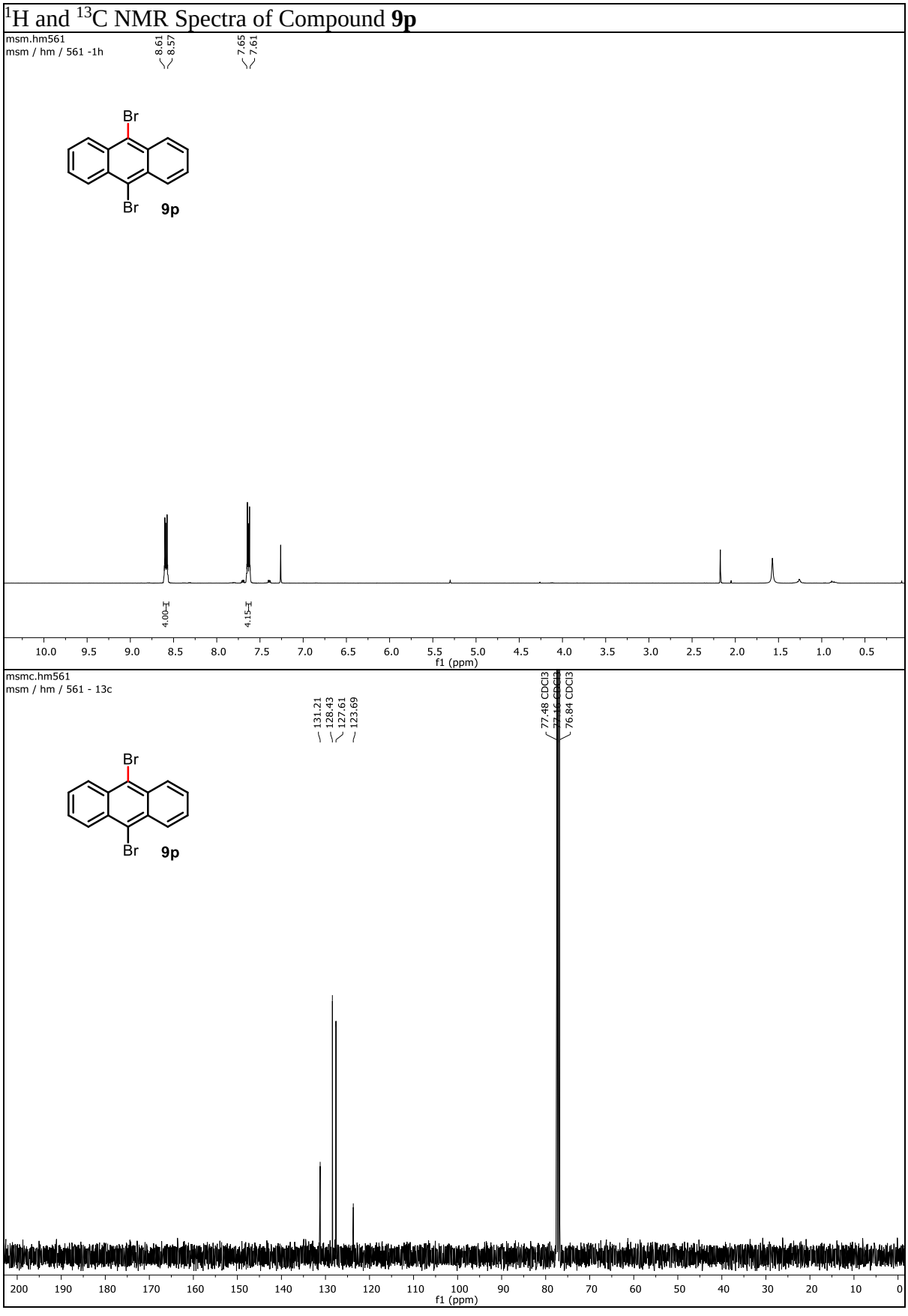




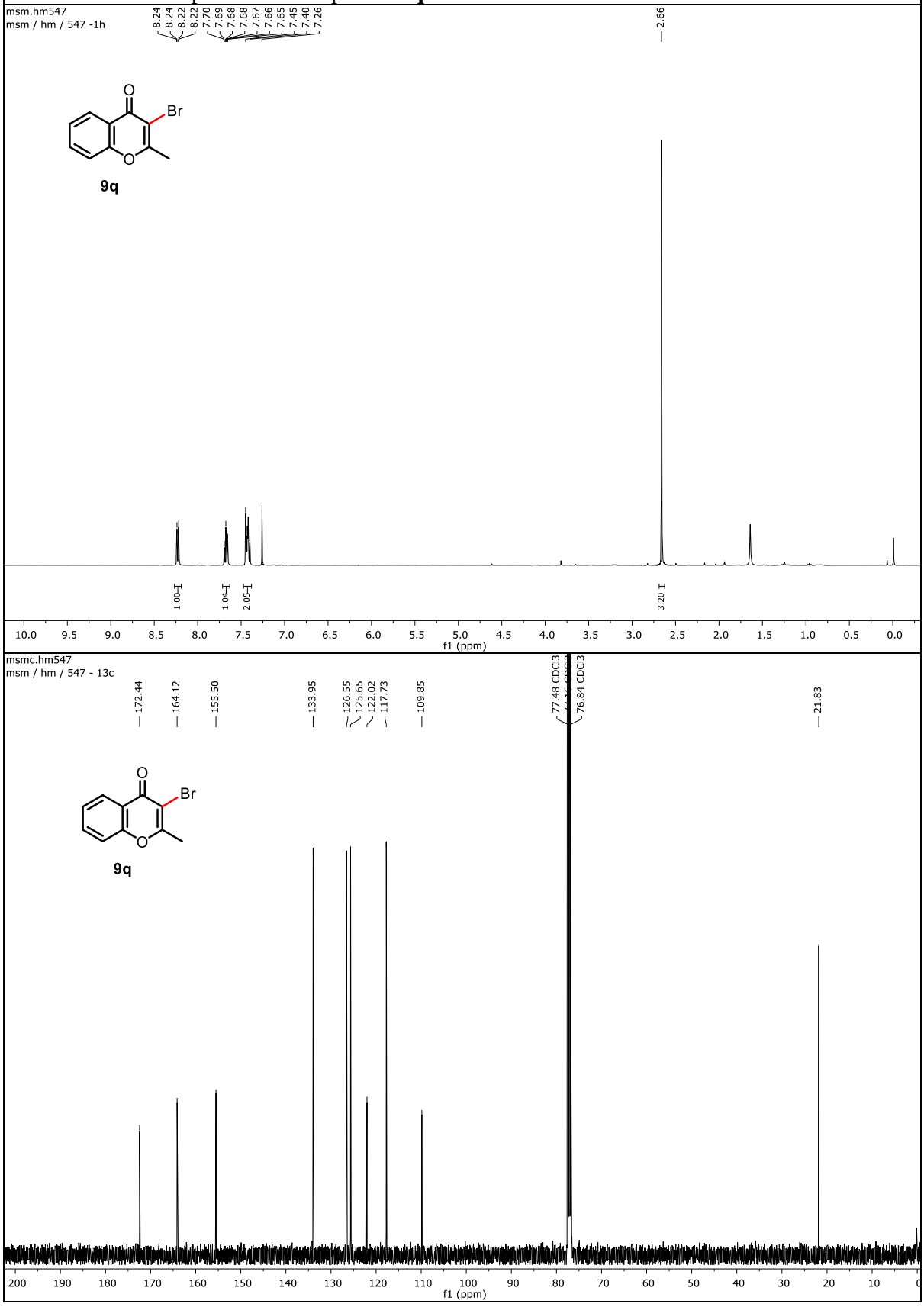
^{1}H and ^{13}C NMR Spectra of Compound **9o**



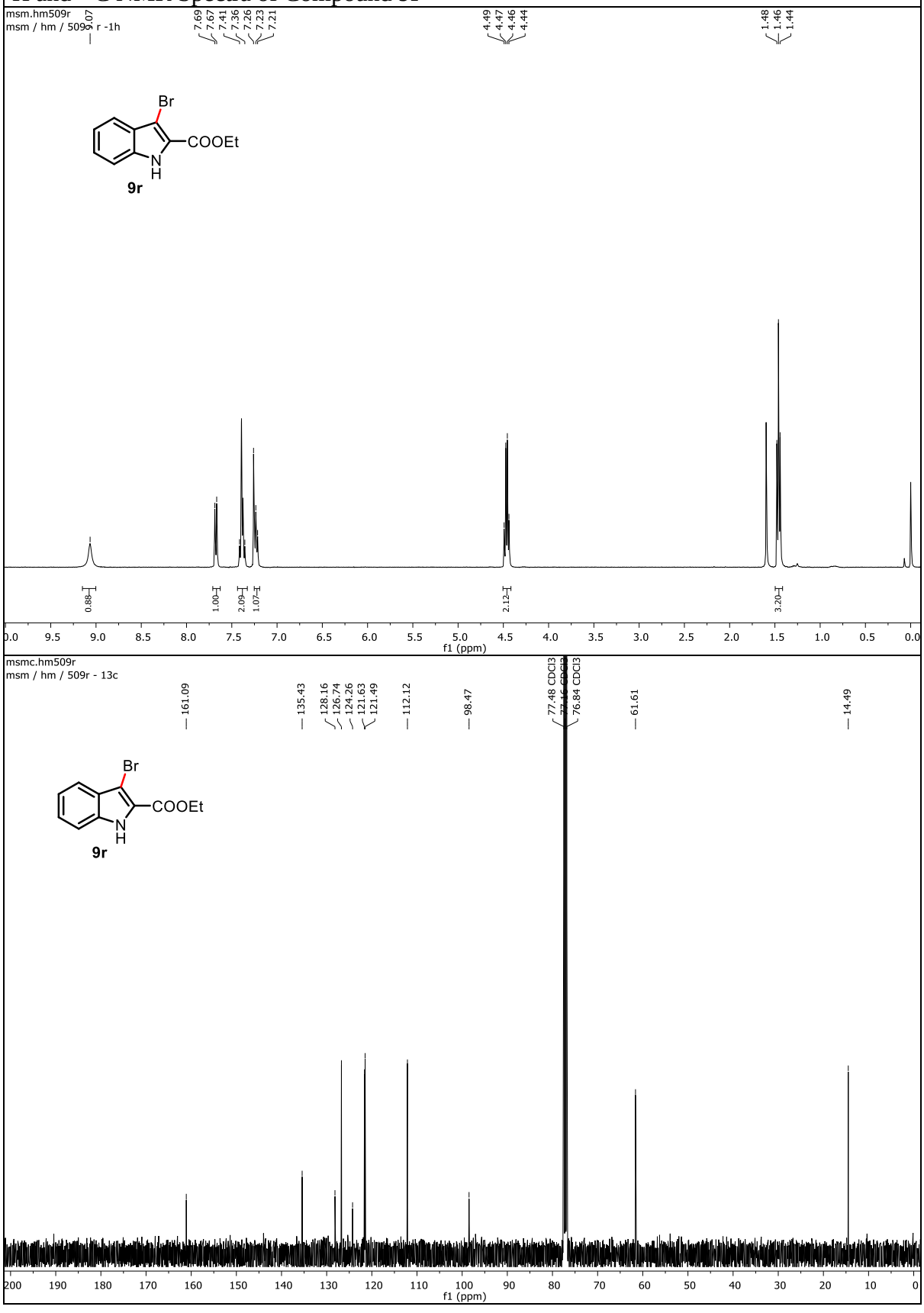
^{1}H and ^{13}C NMR Spectra of Compound **9p**



^{1}H and ^{13}C NMR Spectra of Compound **9q**



^{1}H and ^{13}C NMR Spectra of Compound **9r**



^{1}H and ^{13}C NMR Spectra of Compound **9s**