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Metal-Free, Green and Efficient Oxidative α Halogenation of Enaminones by Halo acid and DMSO

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Supporting Information

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Material and Methods

General Information

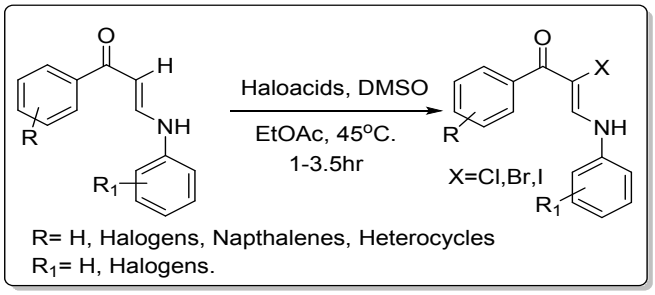
All reactions were carried out in oven-dried glassware, all compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker-400 spectrometers, (^{1}H: 400 MHz, ^{13}C: 100 MHz), and were referenced to the residual peaks of $CDCl_3$ at 7.26 ppm (^{1}H NMR) and $CDCl_3$ at 77.23 ppm (^{13}C NMR). Chemical shifts (δ) are expressed in ppm, and *J* values are given in Hz. Data are reported as follows: Chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, db = doublet broad, m = multiplet), coupling constant (Hz), and integration. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points (m.p.) were determined on digital melting point apparatus and are uncorrected. Mass measurement was performed on Agilent QTOF mass spectrometer with electron spray ionization (ESI) as the ion source. Column chromatography was carried out using commercially available silica gel (230-400 mesh) under pressure.

Materials

Unless otherwise indicated, all reagents were obtained from commercial suppliers used without further purification. PET refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, and all reaction solvents were freshly distilled prior to use.

All the enaminone starting materials were synthesized using the procedure given in literature[1].

General Experimental Procedure for the Preparation of *α*-halogenated enaminone products

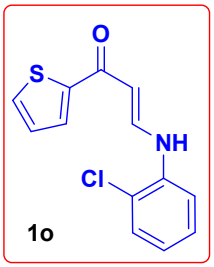


To the solution of enaminone (**1**) (0.45 mmol) in ethyl acetate (2 ml), was added hydrobromic acid (47% aq. HBr, 0.99 mmol) followed by dimethylsulphoxide (0.99 mmol). The reaction mixture was stirred at 45 °C till completion of reaction. The progress of reaction was monitored by TLC. After completion of reaction, evaporated the solvent completely under reduced pressure and the residue was purified by column chromatography to afford pure *α*-halogenated enaminone (**2**).

The above procedure is used for chlorination and iodination reactions using 37% aq. HCl (2.24 mmol) & 57% aq. HI (2.24 mmol) respectively.

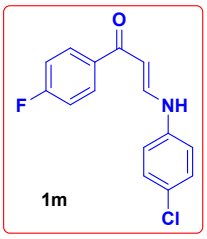
Spectroscopic Data of new enaminone derivatives and α-halogenated enaminones

3-(2-Chlorophenyl)amino-1-(thiophen-2-yl)prop-2-en-1-one (1o):



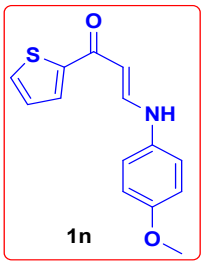
Yellow solid; m.p. 182-184 °C; Rf = (0.7 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.8 (d, *J* = 8.0Hz, 1H, alkene-α-H), 6.77 - 6.83 (m, 1H, ArH), 6.92 - 9.96 (m, 1H, ArH), 6.98 - 7.02 (m, 1H, ArH), 7.03 - 7.09 (m, 1H, ArH), 7.20 - 7.29 (m, 2H, ArH), 7.38 – 7.41 (m, 1H, ArH), 7.48 - 7.51 (m, 1H, ArH), 11.97 (d, *J* = 12.0Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 95.4, 114.0, 122.4, 123.4, 127.7, 127.9, 129.3, 129.9, 131.7, 137.0, 142.4, 145.7, 183.7; MS (ESI): *m/z* calcd for $C_{13}H_{10}ClNOS$ 263.01, found 264.04 [M+H], 266.02 [M+H+2].

3-(4-Chlorophenyl)amino-1-(4-fluorophenyl)prop-2-en-1-one (1m):



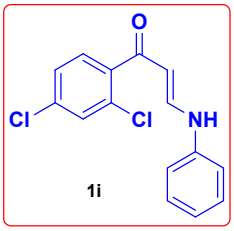
Yellow solid; m.p. 182-184 °C; Rf = (0.8 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.98 (d, *J* = 8.0Hz, 1H, alkene-α-H), 7.0 - 7.05 (m, 2H, ArH), 7.09 - 7.15 (m, 2H, ArH), 7.29 - 7.33 (m, 2H, ArH), 7.40 - 7.47 (m, 1H, ArH), 7.90 - 7.97 (m, 2H, ArH), 12.08 (d, *J* = 12.0Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 93.8, 115.5 (d, *J* = 22Hz), 117.5, 128.8, 129.8, 135.3 (d, *J* = 2.9Hz), 138.8, 144.7, 163.8, 166.3, 189.7; MS (ESI): *m/z* calcd for $C_{15}H_{11}ClFNO$ 275.05, found 276.1 [M+H], 278.1 [M+H+2].

3-(4-Methoxyphenyl)amino-1-(thiophen-2-yl)prop-2-en-1-one (1n):



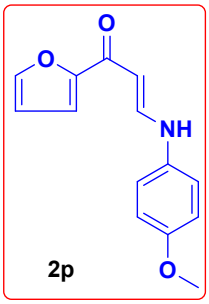
Yellow solid; m.p. 179-181 °C; Rf = (0.8 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.7 (s, 3H, -OMe), 5.75 (d, *J* = 7.6Hz, 1H, alkene-α-H), 6.8 (d, *J* = 7.8Hz, 2H, ArH), 6.94 (d, *J* = 7.8Hz, 2H, ArH), 7.00 - 7.03 (m, 1H, ArH), 7.25 - 7.35 (m, 1H, ArH), 7.43 - 7.45 (m, 1H, ArH), 7.53 - 7.55 (m, 1H, ArH), 11.83 (d, *J* = 12.0Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 55.5, 92.8, 115.0, 117.7, 127.9, 128.6, 131.2, 133.7, 145.4, 146.3, 156.3, 183.3; MS (ESI): *m/z* calcd for $C_{14}H_{13}NO_2S$ 259.06, found 260.09 [M+H].

1-(2,4-Dichlorophenyl)-3-(phenylamino)prop-2-en-1-one (1i):



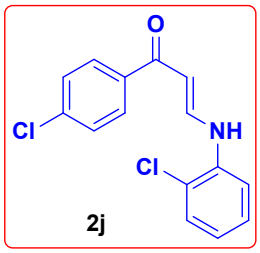
Yellow solid; m.p. 169-171 °C; Rf = (0.8 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.7 (d, *J* = 7.6Hz, 1H, alkene-α-H), 7.09 - 7.14 (m, 1H, ArH), 7.28 – 7.32 (m, 1H, ArH), 7.33 - 7.39 (m, 2H, ArH), 7.43 (d, *J* = 2.0Hz, 1H, ArH), 7.46 - 7.53 (m, 2H, ArH), 11.94 (d, *J* = 12.0Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 97.5, 116.6, 124.2, 127.0, 129.7, 130.1, 130.3, 132.5, 136.0, 138.6, 139.8, 145.3, 190.7; MS (ESI): *m/z* calcd for $C_{15}H_{11}Cl_2NO$ 291.02, found 292.06 [M+H], 293.98 [M+H+2], 295.92 [M+H+4].

1-(Furan-2-yl)-3-(4-methoxyphenylamino)prop-2-en-1-one (1p):



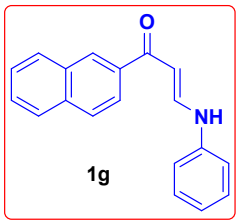
Yellow solid; m.p. 182-184 °C; Rf = (0.8 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 3H, -OMe), 5.77 (d, *J* = 7.6Hz, 1H, alkene-α-H), 6.35 – 6.42 (m, 1H), 6.77 (d, *J* = 9.2Hz, 2H, ArH), 6.92 (d, *J* = 9.2Hz, 2H, ArH), 6.98 (d, *J* = 3.2Hz, 1H, ArH), 7.26 - 7.32 (m, 1H, ArH), 7.42 (d, *J* = 1.2Hz, 1H, ArH), 11.85 (d, *J* = 12.0Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 55.4, 92.5, 111.9, 113.5, 114.8, 117.7, 133.6, 144.7, 145.6, 153.7, 156.2, 179.5; MS (ESI): *m/z* calcd for $C_{14}H_{13}NO_3$ 243.08, found 244.1 [M+H].

1-(4-Chlorophenyl)-3-((2-chlorophenyl)amino)prop-2-en-1-one (1j):



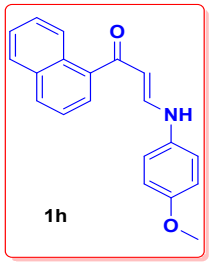
Yellow solid; m.p. 199-201 °C; Rf = (0.7 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.02 (d, *J* = 7.6Hz, 1H, alkene-α-H), 6.72 - 6.78 (m, 1H, ArH), 6.90 - 7.08 (m, 1H, ArH), 7.20 - 7.29 (m, 2H, ArH), 7.41 (d, *J* = 8.2Hz, 2H, ArH), 7.47 - 7.53 (m, 1H, ArH), 7.89 (d, *J* = 8.2Hz, 2H, ArH), 12.39 (d, *J* = 11.6Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 95.0, 115, 117, 119.0, 123.9, 127.6, 127.9, 128.7, 129.4, 130.3, 138.0, 143.5, 189.8; MS (ESI): *m/z* calcd for $C_{15}H_{12}ClNO$ 291.01, found 292.0 [M+H], 294.0 [M+H+2] 296.0 [M+H+4].

1-(Naphthalen-2-yl)-3-(phenylamino)prop-2-en-1-one (1g):



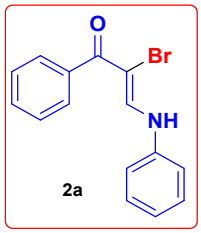
Yellow solid; m.p. 189-191 °C; Rf = (0.8 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (d, *J* = 8.0Hz, 1H, alkene-α-H), 7.07 - 7.17 (m, 3H, ArH), 7.33 - 7.39 (m, 2H, ArH), 7.45 - 7.58 (m, 4H, ArH), 7.71 – 7.74 (m, 1H, ArH), 7.85 - 7.93 (m, 2H, ArH), 8.52 (d, *J* = 8.0Hz, 2H, ArH), 12.14 (d, *J* = 11.6Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 98.3, 116.4, 123.7, 124.7, 125.9, 126.0, 126.8, 128.2, 128.4, 129.7, 130.2, 130.6, 133.8, 138.9, 140.2, 144.6, 195.3; MS (ESI): *m/z* calcd for $C_{19}H_{15}NO$ 273.11, found 274.1 [M+H].

3-(4-Methoxyphenyl)amino)-1-(naphthalen-1-yl)prop-2-en-1-one (1h):



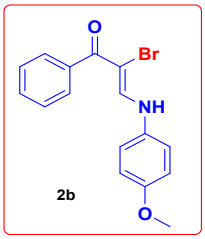
Yellow solid; m.p. 193-195 °C; Rf = 0.8 in 10% (EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3H, -OMe), 5.77 (d, *J* = 7.6Hz, 1H, alkene-α-H), 6.91 (d, *J* = 8.8Hz, 2H, ArH), 7.09 (d, *J* = 8.8Hz, 2H, ArH), 7.40 - 7.58 (m, 4H, ArH), 7.71 (d, *J* = 6.8Hz, 1H, ArH), 7.84 - 7.93 (m, 2H, ArH), 8.52 (d, *J* = 8.4Hz, 1H, ArH), 12.20 (d, *J* = 12.4Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): 55.6, 97.6, 115.1, 118.1, 124.8, 125.8, 126.0, 126.0, 126.7, 128.3, 130.2, 130.4, 133.8, 133.9, 139.2, 145.6, 156.5, 194.9; MS (ESI): *m/z* calcd for $C_{20}H_{17}NO_2$ 303.12, found 304.1 [M+H].

2-Bromo-1-phenyl-3-(phenylamino)prop-2-en-1-one (2a):



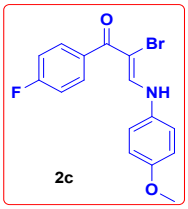
Yellow solid; m.p. 152–154 °C; (200mg, 99%); Rf = (0.35 in 20% EtOAc /PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.9 - 6.92 (m, 2H, ArH), 7.06 - 7.10 (m, 1H, ArH), 7.28 - 7.32 (m, 2H, ArH, -NH), 7.38 – 7.55 (m, 4H, ArH), 7.56 – 7.62 (m, 2H, ArH), 7.87 (d, *J* = 13.60Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.9, 116.6, 118.1, 124.2, 128.5, 129.9, 130.9, 131.1, 132.8, 143.6, 188.3;MS(ESI): *m/z* calcd for $C_{15}H_{12}BrNO$ 301.01; found 302.09 [M+H], 304.01 [M+H+2].

2-Bromo-3-(4-methoxyphenyl)amino-1-phenylprop-2-en-1-one (2b):



Yellow solid; m.p. 178-180 °C; (184mg, 94%); Rf= (0.32 in 20% (EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3H, -OMe), 6.81 (d, *J* = 1.2Hz, 2H), 7.0 - 7.15 (m, 1H), 7.42 - 7.54 (m, 4H), 7.58 - 7.64 (m, 3H, -NH), 7.77 (d, *J* = 13.2Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ =55.9, 102.6, 113.7, 115.04, 116.8, 118.4, 128.5, 130.8, 131.0, 138.8, 143.2, 156.4, 188.2; MS(ESI): *m/z* calcd for $C_{16}H_{14}BrNO_2$ 331.02; found 332.10 [M+H], 334.01 [M+H+2].

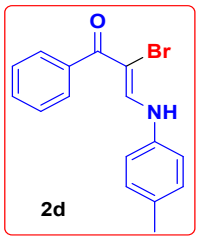
2-Bromo-1-(4-fluorophenyl)-3-((4-methoxyphenyl)amino)prop-2-en-1-one (2c):



Dark brown solid; m.p. 179–181 °C; (183mg, 95%); Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3H, -OMe), 6.83–6.92 (m, 4H, ArH), 7.11-7.22 (m, 3H, ArH + NH), 7.58-7.64 (m, 2H, ArH), 7.74 (d, *J* = 13.6Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 100.6,

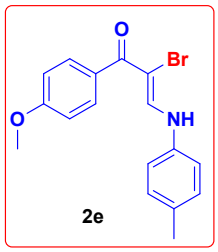
115.2,115.4, 115.6 (d, *J* = 21.0Hz), 115.6 (d, *J* = 21.0Hz), 118.4, 130.7 (d, *J* = 9.0Hz), 130.7 (d, *J* = 9.0Hz), 132.6, 135.1, 144.3, 156.9, 164.2 (d, *J* = 251.0Hz), 186.8; MS(ESI): *m/z* calcd for $C_{16}H_{13}BrFNO_2$ 349.01; found 350.04 [M+H], 352.02 [M+H+2].

2-Bromo-1-phenyl-3-(*p*-tolylamino)prop-2-en-1-one (2d):



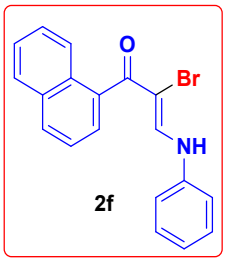
Dark brown solid; m.p. 161–163 °C; (191mg, 96%); Rf = (0.28 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H, -CH_3), 6.81 (d, *J* = 8Hz, 2H, ArH), 7.10 (d, *J* = 8Hz, 2H, ArH), 7.22 (db, *J* = 13.6Hz, 1H, NH), 7.43 – 7.48 (m, 2H, ArH), 7.49 – 7.55 (m, 1H, ArH), 7.57 – 7.63 (m, 2H, ArH), 7.84 (d, *J* = 13.2 Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 101.5, 116.6, 128.4, 128.5, 130.4, 130.8, 134.1, 136.7, 139.0, 143.9, 188.1; MS(ESI): *m/z* calcd for $C_{16}H_{14}BrNO$ 315.02; found 316.04 [M+H], 318.02 [M+H+2].

2-Bromo-1-(4-methoxyphenyl)-3-(p-tolylamino)prop-2-en-1-one(2e):



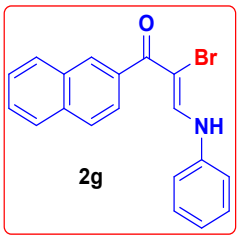
Dark yellow solid; m.p. 159–161 °C; (191mg, 99%); Rf = (0.31 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H, $ArCH_3$), 3.87 (s, 3H, -OMe), 6.83 (d, *J* = 8.4Hz, 2H, ArH), 6.95 (d, *J* = 8.4Hz, 2H, ArH), 6.90 - 7.21 (m, 3H, -NH), 7.60 (d, *J* = 8.8Hz, 2H, ArH), 7.86 (d, *J* = 13.2Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 55.4, 101.4, 116.5, 130.0, 130.8, 131.0, 131.2, 133.8, 136.9, 142.9, 161.9, 187.3; MS(ESI): *m/z* calcd for $C_{17}H_{16}BrNO_2$ 345.03; found 346.05 [M+H], 348.02 [M+H+2].

2-Bromo-1-(naphthalen-1-yl)-3-(phenylamino)prop-2-en-1-one (2f):



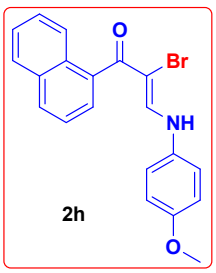
Pale yellow solid; m.p. 175-177 °C; (173mg, 90%); Rf = (0.4 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.72 (d, *J* = 8.0Hz, 2H, ArH), 6.97 (t, *J* = 7.2Hz, 1H, ArH), 7.15 (t, *J* = 8.0Hz,2H, ArH), 7.41 - 7.52 (m, 5H, ArH + NH), 7.71 (d, *J* = 13.6Hz, 1H, C=CH) 7.83-7.98 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 103.2, 116.8, 118.4, 124.5, 125.7, 126.7, 127.2, 128.4, 129.9, 130.3, 130.9, 132.7, 133.8, 136.9, 138.9, 144.4, 188.8; MS(ESI): *m/z* calcd for $C_{19}H_{14}BrNO$ 351.02; found 352.0 [M+H], 354.0 [M+H+2].

2-Bromo-1-(naphthalen-2-yl)-3-(phenylamino)prop-2-en-1-one (2g):



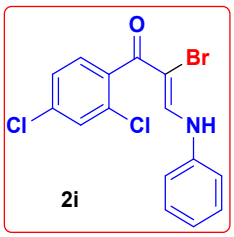
Yellow solid; m.p. 168-170 °C; (181mg, 94%); Rf = (0.35 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.41 (d, *J* = 8.8Hz, 1H, ArH), 7.12 (dd, J_1 = 4.0Hz, J_2 = 8.8Hz, 1H, ArH), 7.45-7.51 (m, 5H, ArH), 7.58 (d, *J* = 2.0Hz, 1H, ArH), 7.63 - 7.67 (m, 1H), 7.73 (d, *J* = 12.8Hz, 1H - NH), 7.84 - 7.97 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 105.8, 113.3, 116.1, 116.2, 124.6, 125.4, 125.8, 126.7, 127.3, 128.4, 130.6, 130.8, 131.8, 133.7, 135.4, 136.0, 136.3, 142.0, 188.7; MS(ESI): *m/z* calcd for $C_{19}H_{14}BrNO$ 351.02; found 352.0 [M+H], 354.0 [M+H+2].

2-Bromo-3-((4-methoxyphenyl)amino)-1-(naphthalen-1-yl)prop-2-en-1-one (2h):



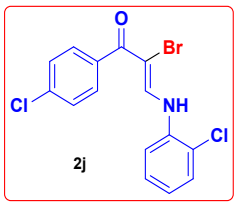
Yellow solid; m.p. 177-179 °C; (171mg, 91%); Rf = (0.32 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70 (s, 3H, -OMe), 6.52 - 6.56 (m, 1H, ArH), 6.64 - 6.68 (m, 1H, ArH), 6.90 (d, *J* = 13.2Hz, 1H,- NH), 6.69 (s, 1H, ArH), 7.05 (d, *J* = 2.8Hz, 1H, ArH), 7.48 - 7.54 (m, 3H, ArH), 7.62 (s, 2H, ArH), 7.87 - 7.89 (m, 1H, ArH), 7.91 - 7.98 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 103.8, 115.1, 118.1, 124.8, 125.4, 125.8, 126.0, 128.3, 130.2, 130.4, 133.8, 133.9, 139.2, 145.6, 156.5, 188.5; MS(ESI): *m/z* calcd for $C_{20}H_{16}BrNO_2$ 381.03; found 382.03 [M+H], 384.02 [M+H+2].

2-Bromo-1-(2,4-dichlorophenyl)-3-(phenylamino)prop-2-en-1-one (2i):



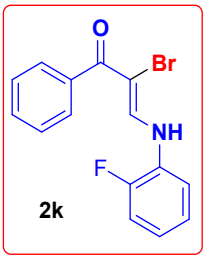
Yellow semi solid; (174mg, 92%); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (d, J = 8.00 Hz, 2H, ArH), 7.13 (t, J = 7.2 Hz, 1H, ArH), 7.25 - 7.38 (m,5H, ArH + NH), 7.48 (d, J = 2 Hz 1H, ArH), 7.63 (d, J = 13.2 Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.9, 117.1, 118.6, 125.1, 127.5, 130.0, 130.3, 133.2, 136.4, 137.2, 139.9, 144.1, 185.0; MS(ESI): *m/z* calcd for $C_{15}H_{10}BrCl_2NO$ 368.93; found 370.05 [M+H], 371.96 [M+H+2], 373.88 [M+H+4], 375.82 [M+H+6].

2-Bromo-1-(4-chlorophenyl)-3-((2-chlorophenyl)amino)prop-2-en-1-one (2j):



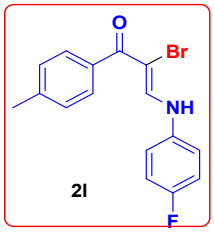
Yellow solid; m.p. 161–163 °C; (185mg 98%); Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.8 (dd, J_1 = 2.0Hz, J = 8.0Hz, 1H, ArH), 6.95 (t, J = 2.0Hz, 1H, ArH), 7.05-7.08 (m, 1H, ArH), 7.22 - 7.24 (m, 1H, ArH), 7.31 (d, J = 12.8 Hz, 1H, -NH), 7.43 – 7.47 (m, 2H, ArH), 7.54 - 7.58 (m, 2H, ArH), 7.79 (d, J = 13.2 Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.5, 114.7, 116.0, 117.0 118.5, 124.5, 129.0, 130.2, 131.2, 136.9, 137.7, 139.6, 142.6, 187.2; MS(ESI): *m/z* calcd for $C_{15}H_{10}BrCl_2NO$ 368.93; found 370.12 [M+H], 372.00 [M+H+2], 373.88 [M+H+4], 375.86 [M+H+6].

2-Bromo-3-((2-fluorophenyl)amino)-1-phenylprop-2-en-1-one (2k):



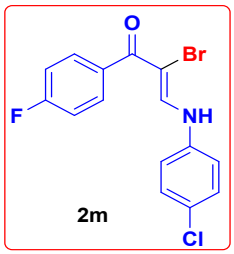
Dark brown solid; m.p. 157–159 °C; (175mg, 97%); Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 (dt, J_1 = 1.6Hz, J_2 = 8.0Hz, 1H, ArH), 6.97 - 7.16 (m, 3H, ArH), 7.35 (d, br, J = 13.2Hz, 1H, -NH), 7.43-7.48 (m, 2H, ArH), 7.49 - 7.55 (m, 1H, ArH), 7.58 - 7.62 (m, 2H, ArH), 7.86 (d, J = 13.2Hz, 1H, C=CH) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 103.3, 116.1, 116.2, 116.4, 124.3 (d, J =7.3 Hz), 124.3 (d, J = 7.3Hz), 125.2 (d, J = 3.7Hz), 125.2 (d, J = 3.7Hz), 128.6 (d, J = 6.7Hz), 128.6 (d, J = 6.7Hz), 131.3, 142.0, 142.7, 151.3 (d, J = 243Hz), 153.7 (d, J = 243Hz), 188.4; MS(ESI): *m/z* calcd for $C_{15}H_{11}BrFNO$ 319.00; found 320.05 [M+H], 322.02 [M+H+2].

2-Bromo-3-((4-fluorophenyl)amino)-1-(p-tolyl)prop-2-en-1-one (2l):



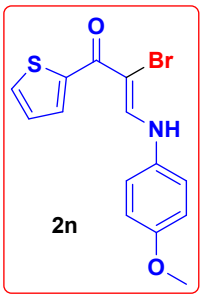
Pale yellow solid; m.p. 173–174 °C; (192mg, 98%); Rf = 0.35 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H, -Me), 6.87 - 6.92 (m, 2H, ArH), 6.99 - 7.06 (m, 2H, ArH), 7.15 (db, J = 13.2Hz, 1H, -NH) 7.24 - 7.28 (m, 2H, ArH) 7.49 - 7.53 (m, 2H, ArH), 7.80 (d, J = 13.2Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.7, 102.1, 116.7 (d, J = 23Hz), 116.9 (d, J = 23Hz), 118.3 (d, J = 8.0Hz), 118.4 (d, J = 8.0Hz), 128.8 (d, J = 44Hz), 129.3 (d, J = 44Hz), 135.8 (d, J = 3Hz), 135.8 (d, J = 3Hz), 136.0, 141.7, 143.7, 158.4 (d, J = 242Hz), 160.8 (d, J = 242Hz), 188.3; MS(ESI): *m/z* calcd for $C_{16}H_{13}BrFNO$ 333.01; found 334.02 [M+H], 336.02 [M+H+2].

2-Bromo-3-((4-chlorophenyl)amino)-1-(4-fluorophenyl)prop-2-en-1-one (2m):



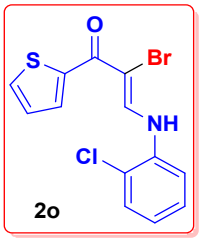
Pale yellow solid; m.p. 168-170 °C; (182mg, 95%); Rf = (0.28 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.87 (d, J = 8.8Hz, 2H, ArH), 7.11 - 7.32 (m, 5H, ArH + NH), 7.60 - 7.66 (m, 2H, ArH), 7.79 (d, J = 12.8Hz 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.0, 115.5 (d, J = 22Hz), 115.7 (d, J = 22Hz), 117.7(d, J = 21Hz), 117.9 (d, J = 21Hz), 129.5(d, J = 54Hz), 130.0 (d, J = 54Hz), 130.8 (d, J = 9Hz), 130.9 (d, J = 9Hz), 134.7,137.7, 142.6, 163.2 (d, J = 251Hz), 165.7 (d, J = 251Hz), 186.9; MS(ESI): *m/z* calcd for $C_{15}H_{10}BrClFNO$ 352.96; found 354.17 [M+H], 356.00 [M+H+2], 357.90 [M+H+4].

2-Bromo-3-(4-methoxyphenyl)amino)-1-(thiophen-2-yl)prop-2-en-1-one (2n):



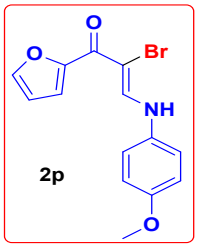
Dark brown semi solid; (185mg, 95%); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H, -OMe), 6.85-6.91 (m, 2H, ArH), 6.95 - 7.01 (m, 2H, ArH), 7.09 - 7.13 (m, 1H, ArH), 7.21 (db, *J* = 13.2Hz, 1H, -NH), 7.56 - 7.62 (m, 2H, ArH), 8.19 (d, *J* = 13.2Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ =55.8, 99.7, 115.3, 118.6, 127.4, 131.3, 131.4, 132.9, 143.1, 149.0, 156.9, 179.1; MS(ESI): *m/z* calcd for $C_{14}H_{12}BrNO_2S$ 336.97; found 338.04 [M+H], 340.02 [M+H+2].

2-Bromo-3-(2-chlorophenyl)amino)-1-(thiophen-2-yl)prop-2-en-1-one (2o):



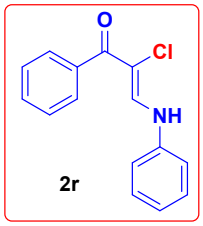
Dark brown semi solid; (93%, 180mg); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.9 - 7.04 (m, 1H, ArH), 7.05 - 7.09 (m, 1H, ArH), 7.13 - 7.17 (m, 1H, ArH), 7.23 - 7.28 (m, 1H, ArH), 7.39 - 7.44 (m, 1H ArH), 7.60 - 7.64 (m, 1H, ArH), 7.66 - 7.70 (m, 1H, ArH), 7.77 (db, *J* = 12.0Hz, 1H, -NH) 8.27 (d, *J* = 13.2Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 102.2, 115.1, 116.2, 127.6, 127.6, 128.4, 130.2, 131.4, 131.8, 132.6, 137.9, 139.2, 180.7; MS(ESI): *m/z* calcd for $C_{13}H_9BrClNOS$ 340.92, found 342.0 [M+H], 344.0 [M+H+2], 345.9[M+H+4].

2-Bromo-1-(furan-2-yl)-3-((4-methoxyphenyl)amino)prop-2-en-1-one (2p):



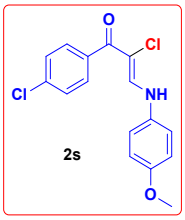
Dark brown solid; m.p. 144–146 °C; (194mg, 98%); Rf = (0.3 in 30% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H, -OMe), 6.53 (dd, J_1 = 2Hz, *J* = 3.6Hz, 1H, ArH), 6.88 - 6.92 (m,2H, ArH) 7.01 - 7.05 (m, 2H, ArH), 7.2 - 7.21 (m, 1H, ArH), 7.30 (d, br, *J* = 13.2Hz 1H, -NH), 7.56 (d, *J* = 0.8Hz, 1H, ArH), 8.65 (d, *J* = 13.6Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 100.1, 112.0, 115.3, 117.4, 118.6, 133.0, 143.4, 144.9, 152.1, 156.9, 173.1; MS(ESI): *m/z* calcd for $C_{14}H_{12}BrNO_3$ 321.00, found 322.08 [M+H], 324.02 [M+H+2].

2-Chloro-1-phenyl-3-(phenylamino)prop-2-en-1-one (2r)[2]:



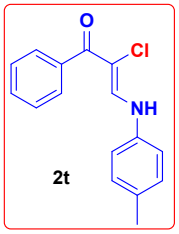
Pale yellow solid; m.p. 162–164 °C; (140mg, 81%); Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.90 - 6.92 (m, 2H, ArH), 7.06 - 7.10 (m, 1H, ArH), 7.28 - 7.32 (m, 2H, ArH, -NH), 7.38 – 7.55 (m, 4H, ArH), 7.56 – 7.62 (m, 2H, ArH), 7.87 (d, *J* = 13.60Hz, 1H, C=CH).

2-Chloro-1-(4-chlorophenyl)-3-((4-methoxyphenyl)amino)prop-2-en-1-one (2s)[2]:



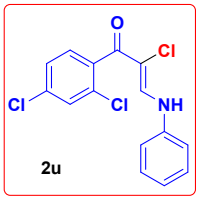
White solid; m.p. 170–172 °C; 129 mg, 77%); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3H, Ar-OCH_3), 6.84 – 6.91 (m, 4H, ArH), 7.19 - 7.34 (m, 4H, ArH + NH), 7.45 (m, 2H, ArH + C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 108.3, 115.1, 118.7, 127.2, 132.2, 136.0, 136.9, 142.8, 157.1, 184.4.

2-Chloro-1-phenyl-3-(p-tolylamino)prop-2-en-1-one(2t)[2]:



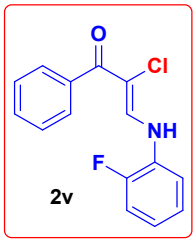
Pale yellow solid; m.p. 160–162 °C; (142mg, 83%); Rf = (0.32 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H, Ar-Me), 6.81 (d, *J* = 8.4Hz, 2H, ArH), 7.09 - 7.17 (m, 3H, ArH + NH), 7.43 - 7.48 (m, 2H, ArH), 7.49 - 7.55 (m, 1H, ArH), 7.59 - 7.63 (m, 2H, ArH), 7.8 (d, *J* = 13.2Hz, 1H, C=CH).

2-Chloro-1-(2,4-dichlorophenyl)-3-(phenylamino) prop-2-en-1-one (2u):



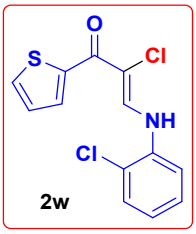
Pale yellow solid; m.p. 145-147 °C; (142mg, 85%); Rf = (0.3 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (d, J = 7.6 Hz, 2H, ArH), 7.09 - 7.15 (m, 1H, ArH), 7.29 - 7.36 (m, 5H, ArH), 7.47 (d, J = 2.0 Hz 1H, ArH), 7.6 (d, J = 13.2 Hz, 1H, -NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.2, 116.8, 124.7, 127.2, 130.0, 130.0, 132.3, 136.2, 136.6, 138.8, 141.8, 144.9, 184.8; MS(ESI): *m/z* calcd for $C_{15}H_{10}Cl_3NO$ 324.98, found 326.17 [M+H], 328.00 [M+H+2], 329.92 [M+H+4], 331.90 [M+H+6].

2-Chloro-3-((2-fluorophenyl)amino)-1-phenylprop-2-en-1-one (2v):



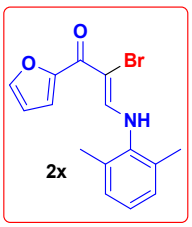
Yellow solid; m.p. 137–139 °C; (137mg,80%); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (dt, J_1 = 1.6 Hz, J_2 =8 Hz, 1H, ArH), 7.08 - 7.19 (m, 3H, ArH), 7.27 (d, J = 11.2Hz, 1H, -NH), 7.44 - 7.48 (m, 2H, ArH), 7.50 - 7.56 (m, 1H, ArH), 7.62 (dd, J_1 = 4.8 Hz, J_2 = 6.8 Hz, 2H,ArH), 7.83 (d, J = 13.2Hz, 1H, C=CH) ;^{13}C NMR (100 MHz, $CDCl_3$): δ =111.0, 115.9, 116.2, 116.4, 124.2 (d, J = 7.0 Hz), 124.2 (d, J = 7.0 Hz), 125.2 (d, J = 4.0Hz), 125.2 (d, J = 4.0 Hz), 128.5 (d, J = 8.0 Hz), 128.5 (d, J = 8.0Hz), 131.3, 138.6, 140.3, 151.3 (d, J = 243.0 Hz), 153.7 (d, J = 243.0 Hz), 188.2; MS(ESI): *m/z* calcd for $C_{15}H_{11}ClFNO$ 275.05, found 276.05 [M+H], 278.02 [M+H+2].

2-Chloro-3-((2-chlorophenyl) amino)-1-(thiophen-2-yl)prop-2-en-1-one (2w):



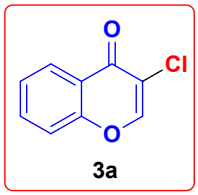
Dark brown semi solid; (134mg, 79%); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 - 7.02 (m, 1H, ArH), 7.07 (d, J = 7.6 Hz, 1H, ArH), 7.11 - 7.15 (m, 1H, ArH), 7.21 - 7.28 (m, 1H, ArH), 7.35 - 7.39 (m, 1H ArH), 7.59 - 7.68 (m, 2H, ArH + NH), 7.77 (dd, J_1 = 0.8 Hz, J_2 = 4 Hz, 1H, ArH), 8.21 (d, J = 13.2 Hz, 1H, C=CH);^{13}C NMR (100 MHz, $CDCl_3$): δ =109.8, 114.9, 123.9, 124.3, 127.6, 128.3, 130.1, 132.2, 132.4, 135.9, 137.4, 142.2, 181.4; MS(ESI): *m/z* calcd for $C_{13}H_9Cl_2NOS$ 296.97, found 298.0 [M+H], 299.9 [M+H+2], 301.9 [M+H+4].

2-Bromo-3-((2,6-dimethylphenyl)amino)-1-(furan-2-yl)prop-2-en-1-one (2x):



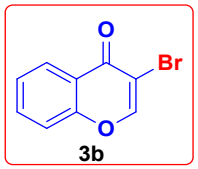
Dark brown semi solid; (149mg ,75%); Rf = (0.3 in 10% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ =2.38 (s, 6H, -Me), 6.51 - 6.53 (m, 1H, ArH), 6.87 (d, J = 13.2 Hz 1H, -NH), 7.11 - 7.20(m, 4H, ArH), 7.50(d, 1H, *J= 0.*8 Hz, ArH), 8.31 (d, J = 13.2 Hz, 1H, C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6, 99.0, 111.9, 120.2, 126.1, 128.9, 129.1, 131.6, 131.8, 138.6, 144.7, 152.5, 180.1; MS(ESI): *m/z* calcd for $C_{13}H_9Cl_2NOS$ 296.97, found 298.02 [M+H], 300.0 [M+H+2].

3-Chloro-4H-chromen-4-one (3a)[3]:



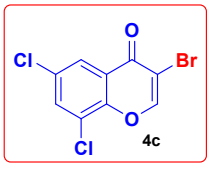
White soilid; m.p. 112-114 °C; Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 - 7.5 (m, 2H, ArH), 7.71 (m, 1H, ArH), 8.15 (s, 1H, C=CH), 8.28 (dd, J_1 = 1.6Hz, J_2 = 1.6Hz, 1H, ArH).

3-Bromo-4H-chromen-4-one (3b)[4]:



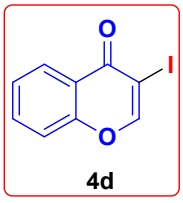
White soilid; m.p. 176-178 °C; Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 - 7.47 (m, 2H, ArH), 7.66 - 7.73 (m, 1H, ArH), 8.21 - 8.26 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.6, 118.1, 123.0, 125.8, 126.3, 134.1, 153.7, 155.9, 172.2

3-Bromo-6,8-dichloro-4H-chromen-4-one (3c)[5]:



White soilid; m.p. 176-178 °C; Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 2.4Hz, 1H, ArH), 8.12 (d, J = 2.4Hz, 1H, ArH), 8.3 (s, 1H, ArH).

3-Iodo-4H-chromen-4-one (3d)[6]:



White solid; m.p. 95-97 °C; Rf = (0.35 in 20% EtOAc/PET); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 - 7.47 (m, 2H, ArH), 7.66 - 7.73 (m, 1H, ArH), 8.21 (dd, J_1 =1.2 Hz, J_2 = 6.8 Hz, 1H, ArH), 8.28 (s, 1H, CH).

Reference and note

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2. H. Xu, P. Zhou, R. Hang, J. Zhou, L. Ling Lu, Y. Shen and F. Chao Yu, *Tetrahedron Letters.*, 2016, **57**, 4965.
3. M. Miliutina, J. Janke, S. Hassan, S. Zaib, J. Iqbal, J. Lecka, J. Sévigny, A. Villinger, A. Friedrich, S. Lochbrunner and P. Langer, *Org. Biomol. Chem.,* 2018, **16**, 717.
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5. S. K. Narwade, S. B. Kale, and B. K. Karale, *Ind. J. Het. Chem.,* 2007, **16**, 275.
6. X. Han, Z. Yue, X. Zhang, Q. He, and C. Yang, *J. Org. Chem.,* 2013, **78** (10), 4850.

GS-TH-O-Cl

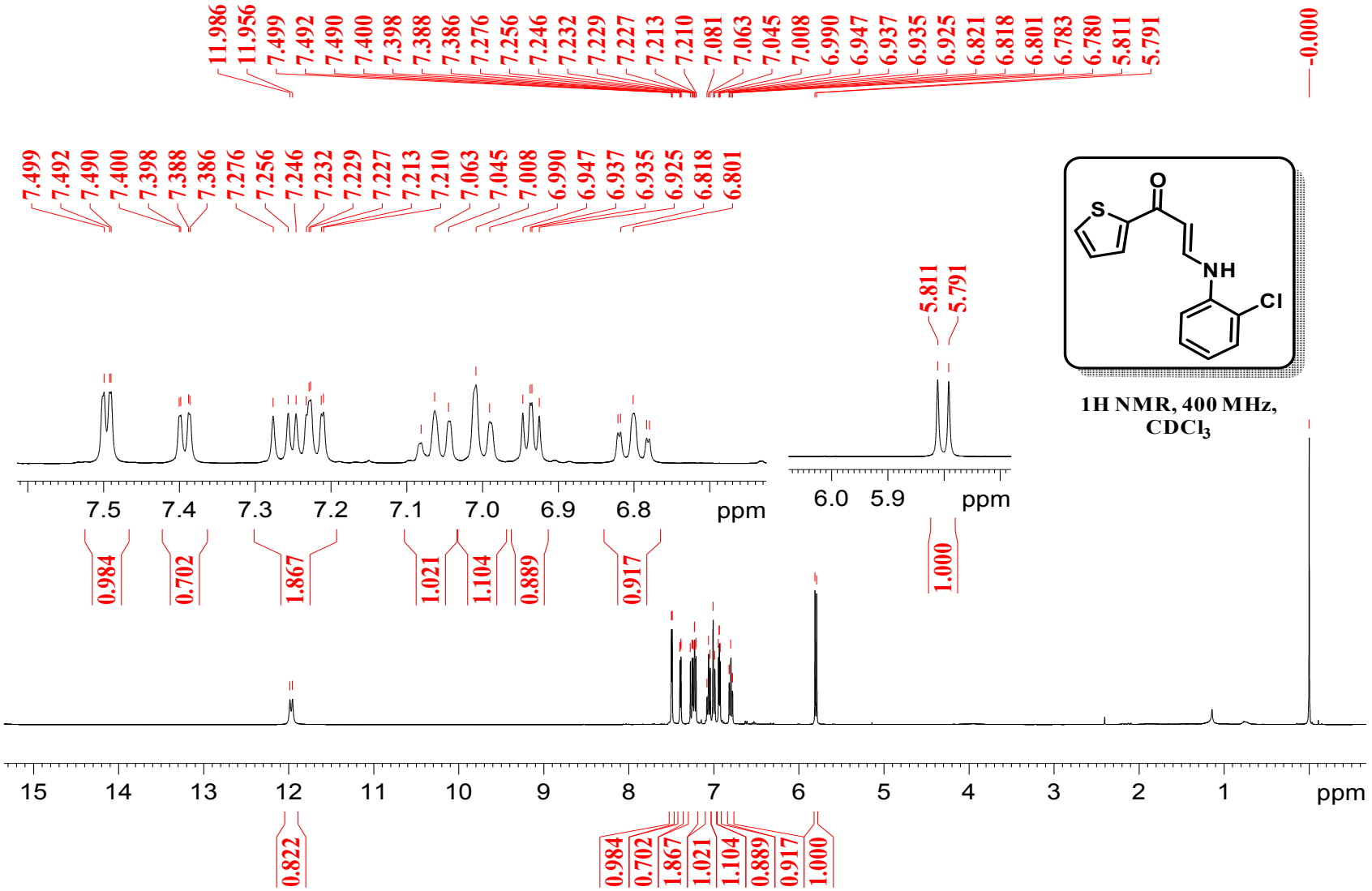


Figure 1: ^{1}H NMR Compound 1o

GS-TH-O-Cl

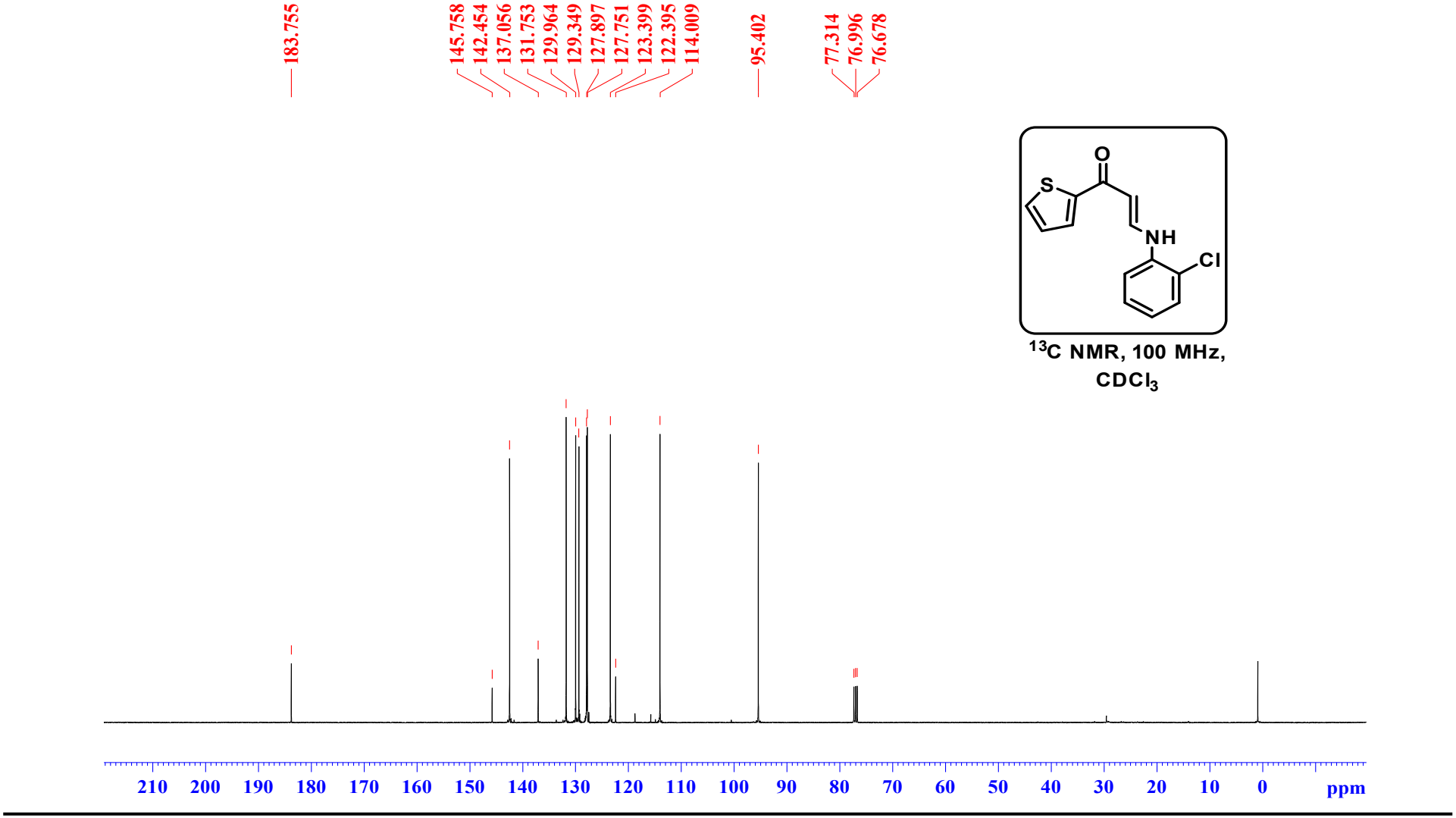

183.755
145.758
142.454
137.056
131.753
129.964
129.349
127.897
127.751
123.399
122.395
114.009
95.402
77.314
76.996
76.678
O
S
NH
Cl
^{13}C NMR, 100 MHz,
$CDCl_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure 2: ^{13}C NMR Compound 1o

GS-F-Cl

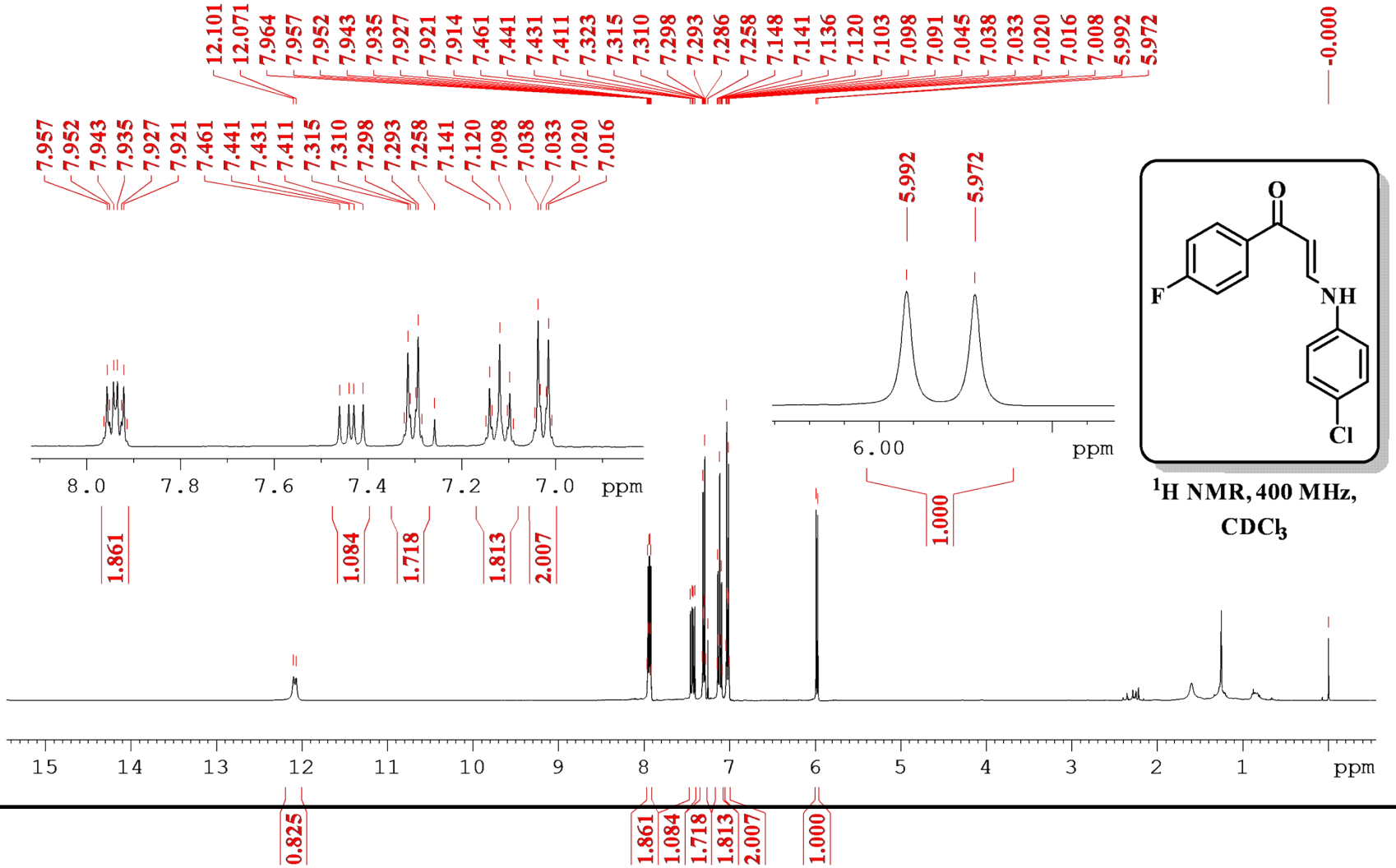


Figure 3: ^{1}H NMR Compound 1m

GS-F-Cl

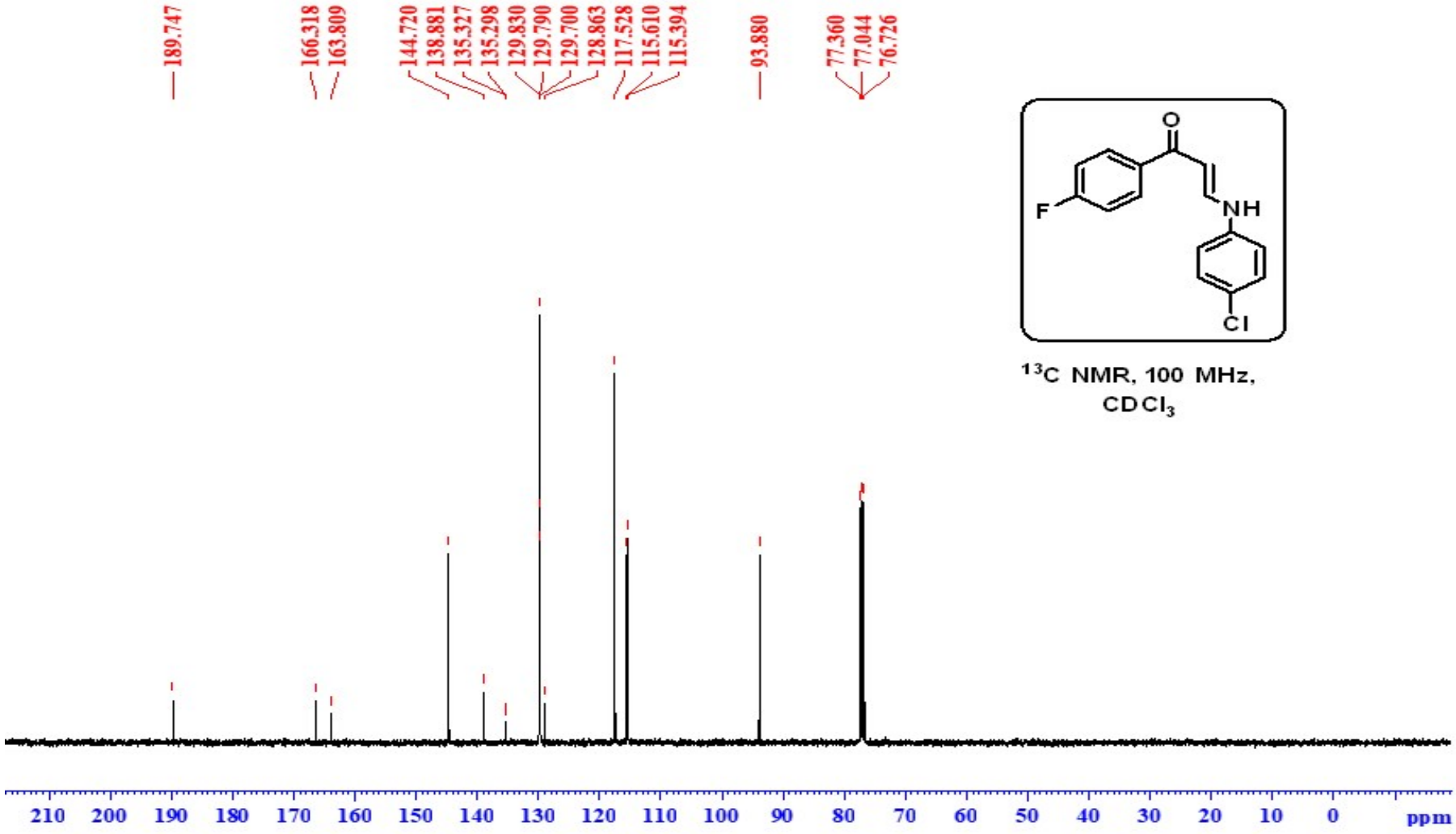

189.747
166.318
163.809
144.720
138.881
135.327
135.298
129.830
129.790
129.700
128.863
117.528
115.610
115.394
93.880
77.360
77.044
76.726
O
F
NH
Cl
^{13}C NMR, 100 MHz,
CDCl$_3$
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure 4: ^{13}C NMR Compound 1m

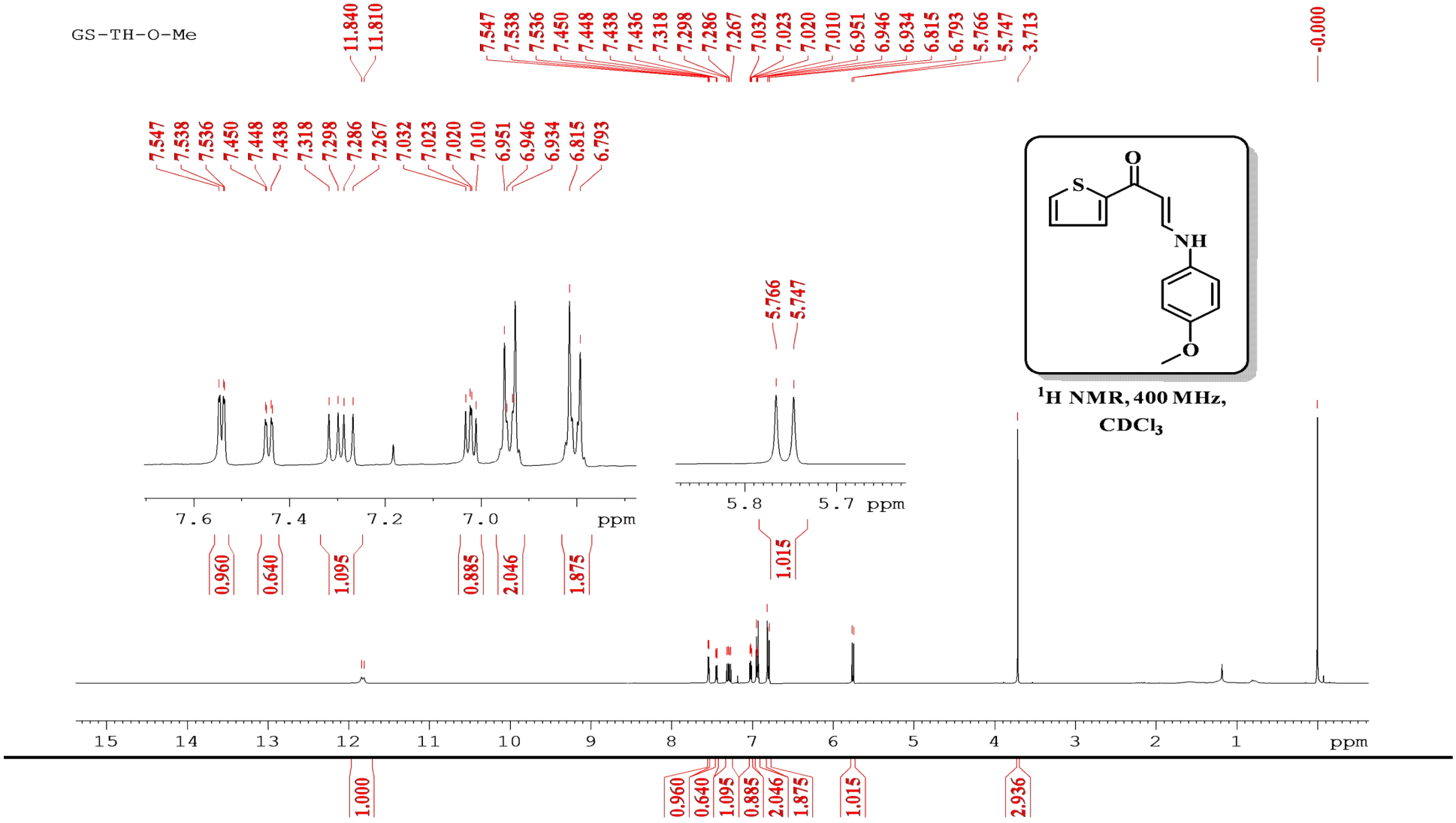


Figure 5: ^{1}H NMR Compound 1n

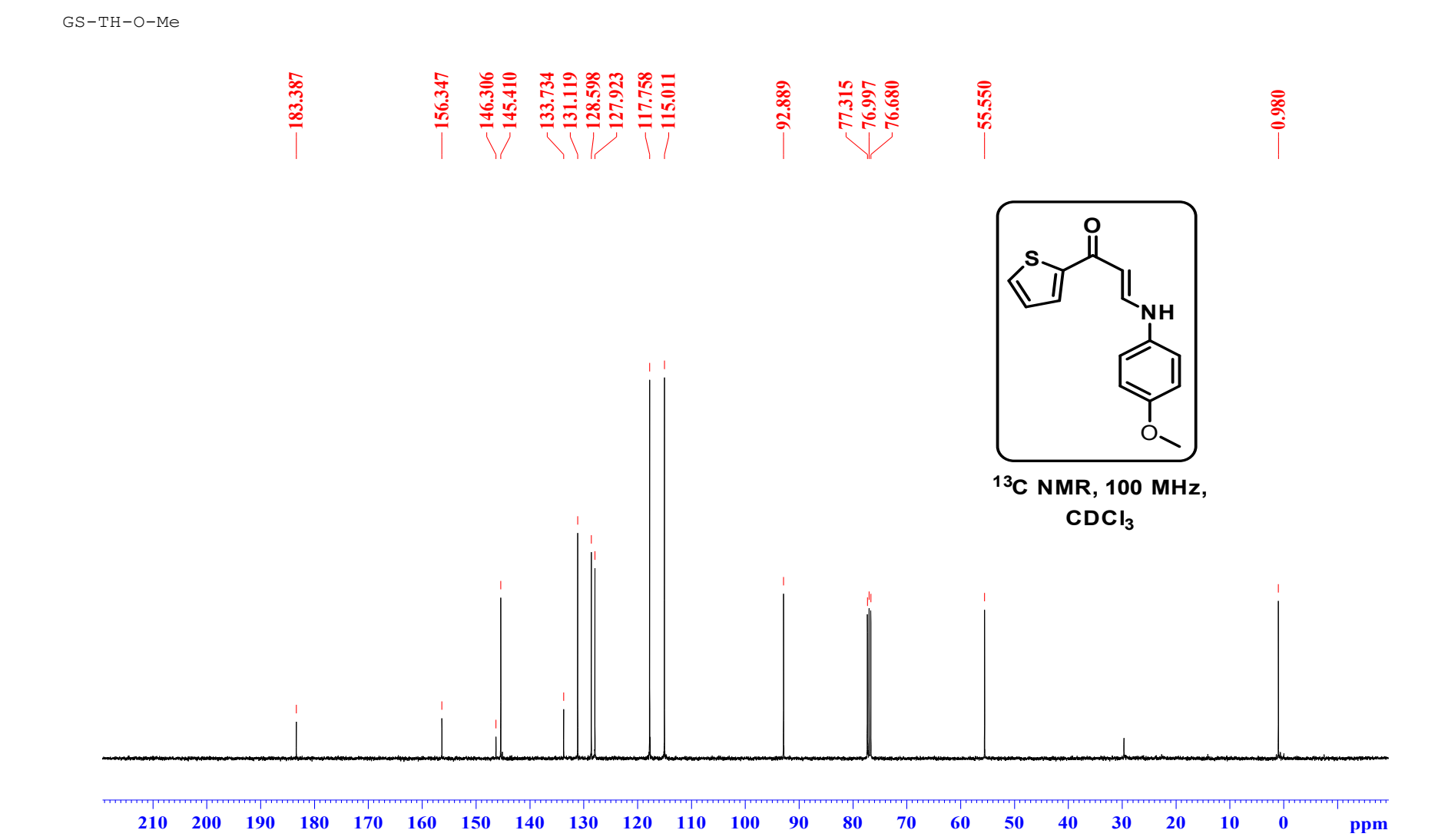


Figure 6: ^{13}C NMR Compound 1n

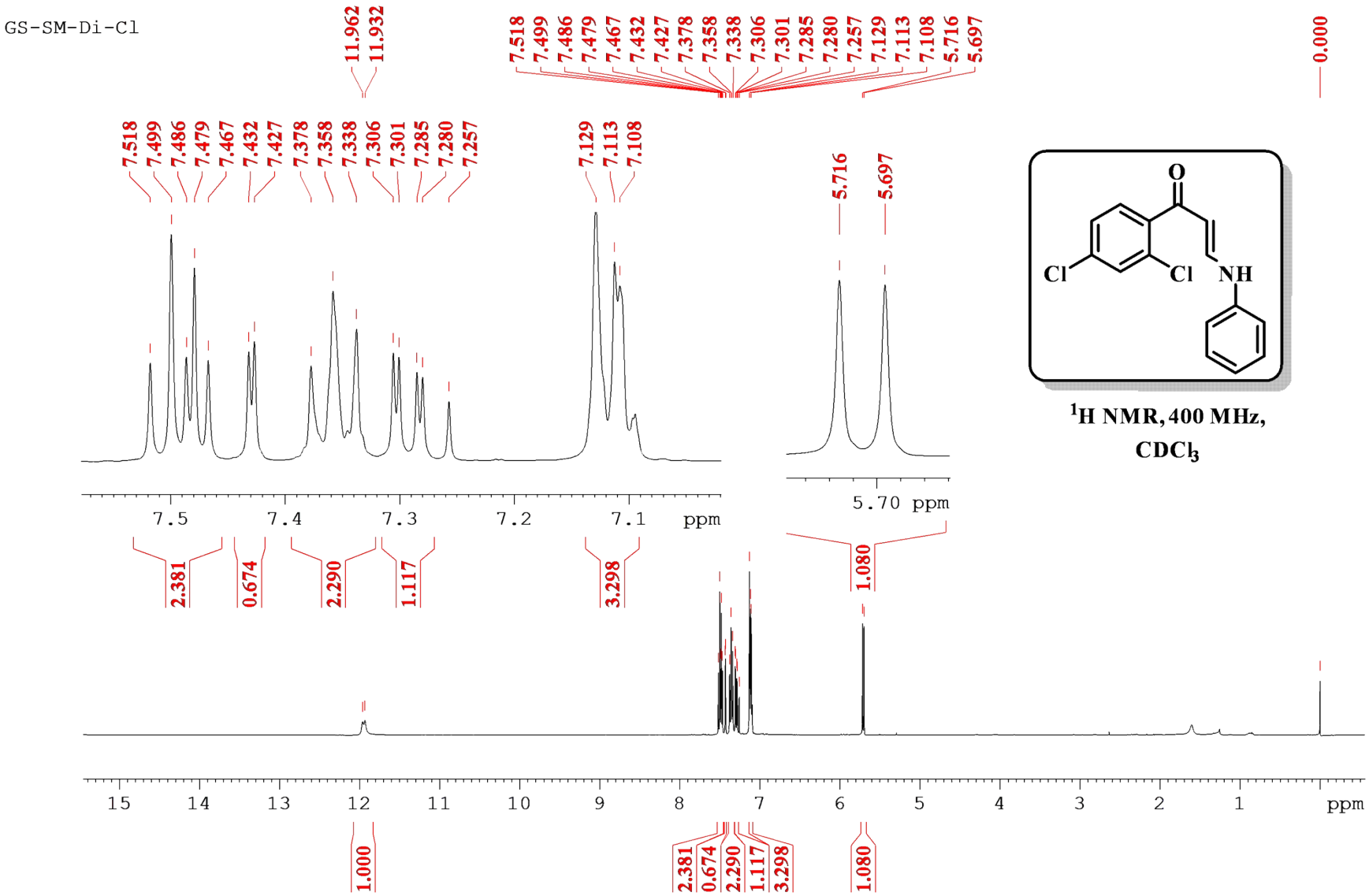


Figure 7: ^{1}H NMR Compound 1i

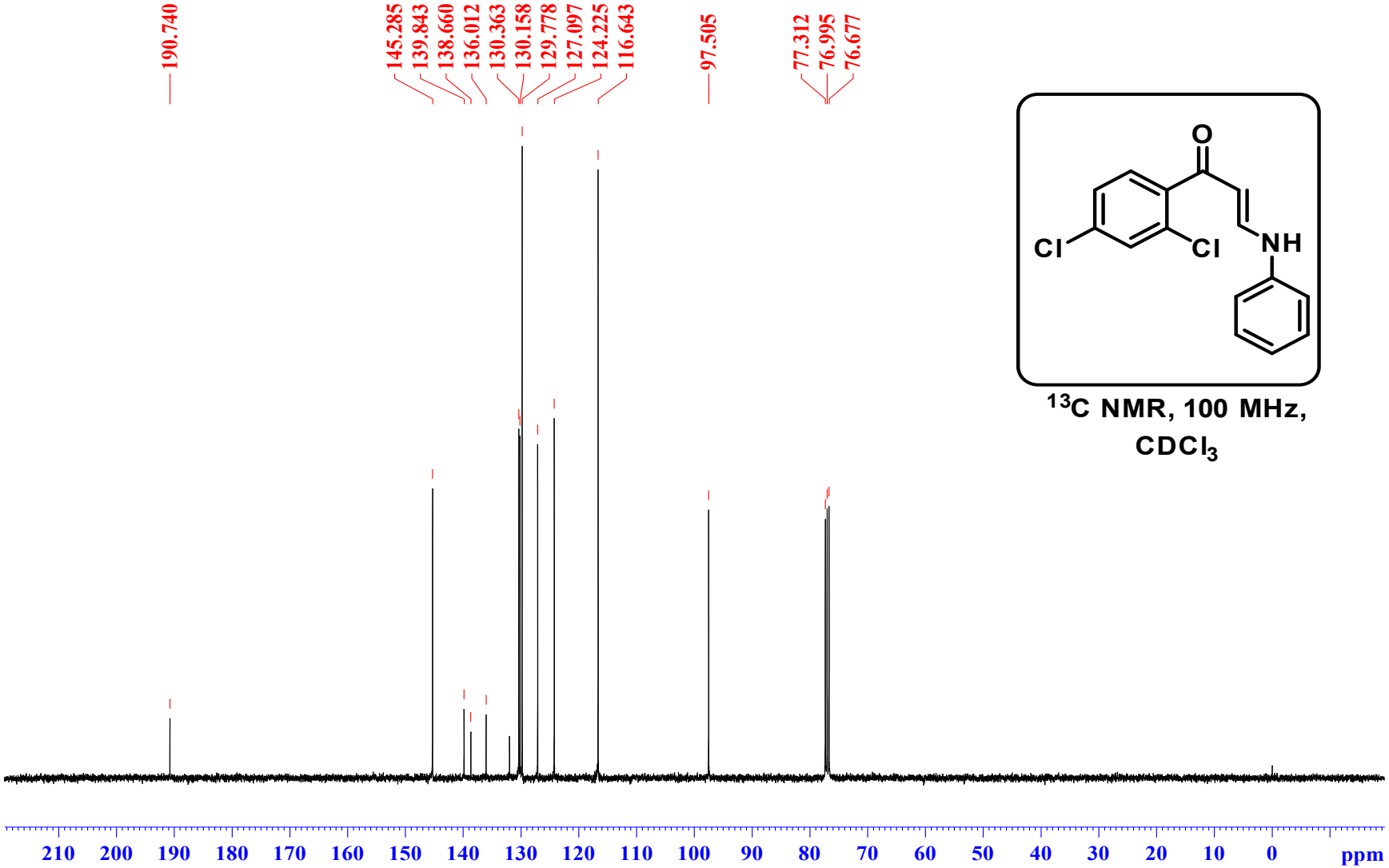


Figure 8: ^{13}C NMR Compound 1i

GS-F-O-Me

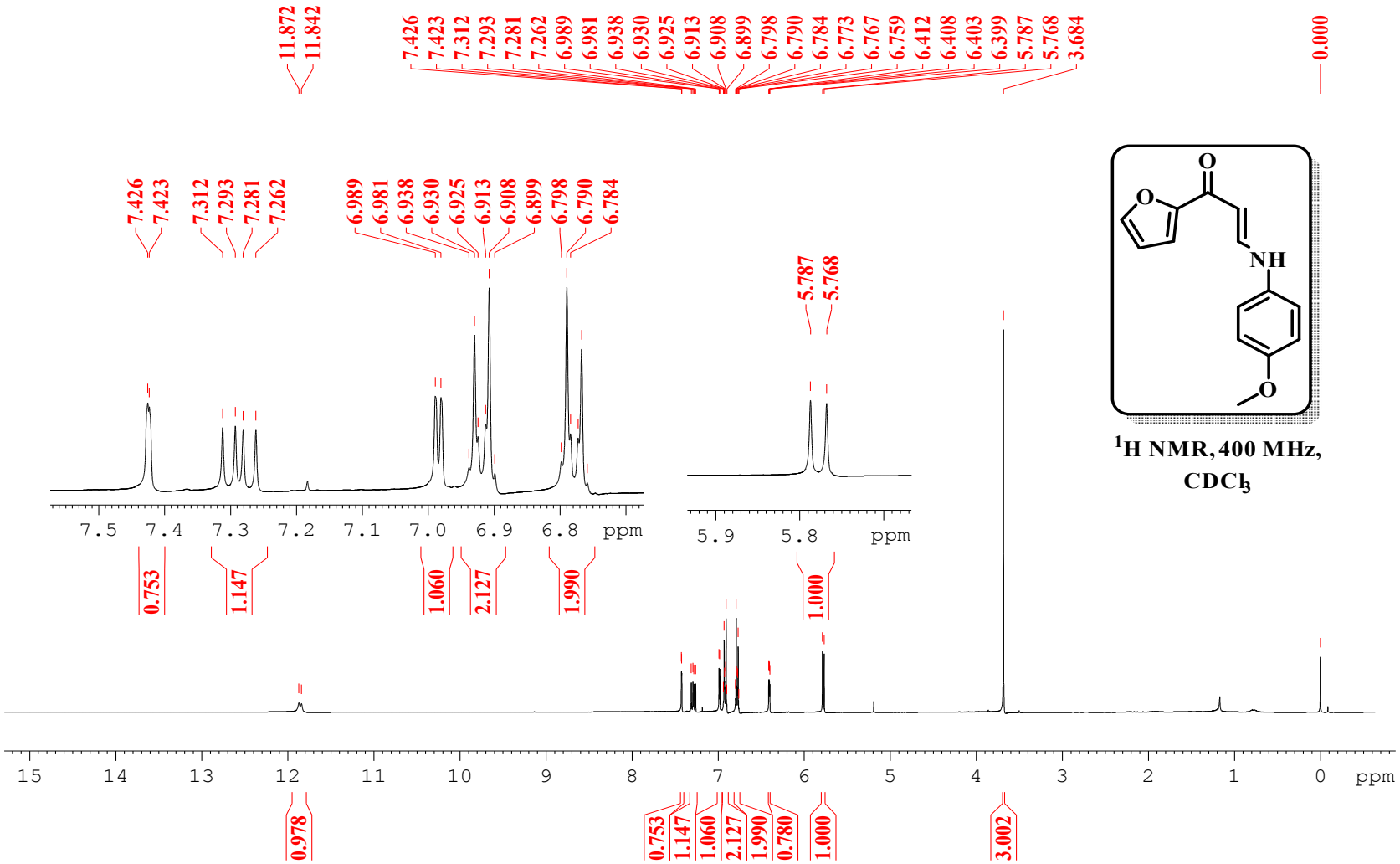


Figure 9: ^{1}H NMR Compound 1p

GS-F-O-Me

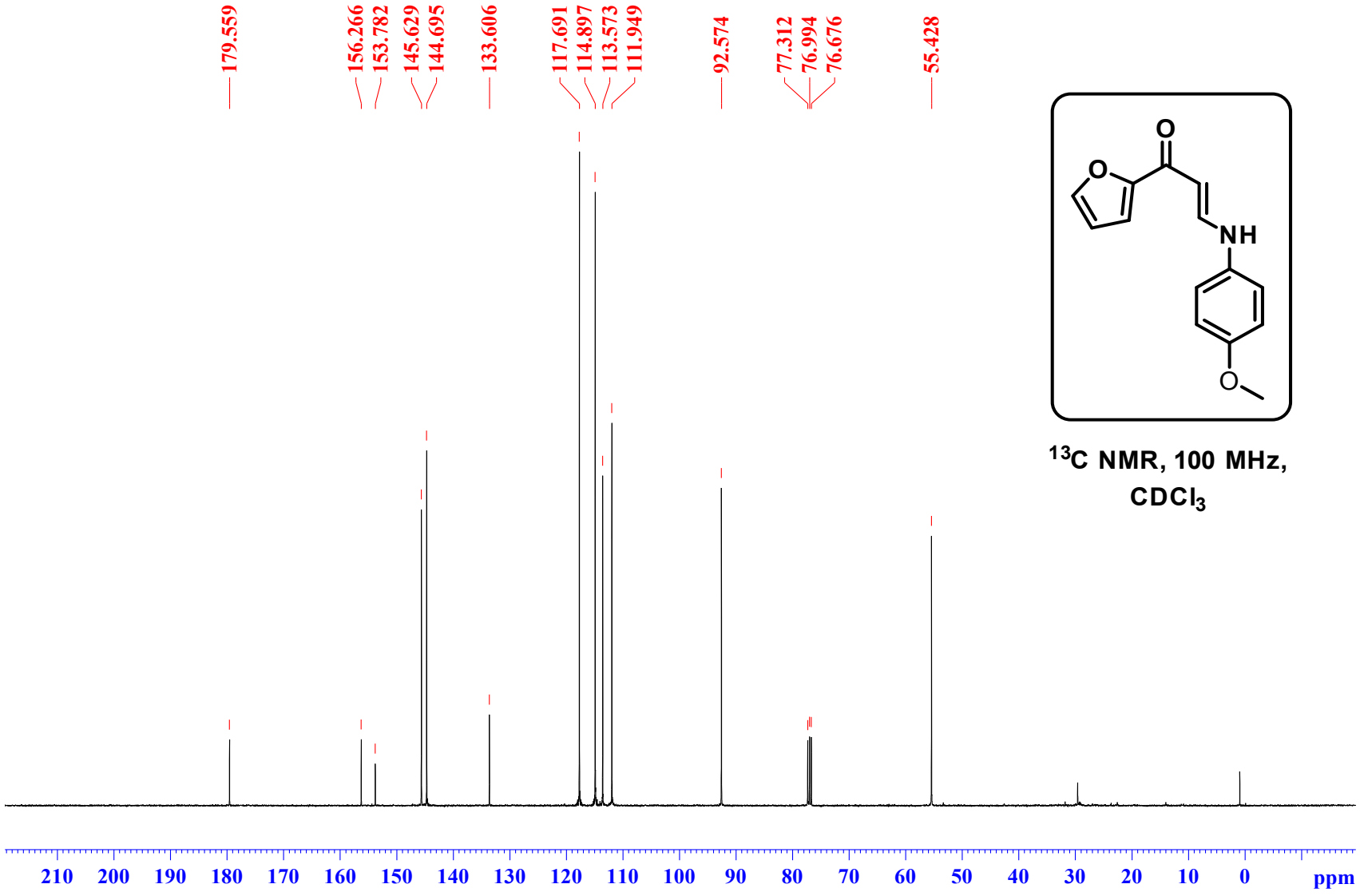


Figure 10: ^{13}C NMR Compound 1p

GS-F-O-Cl

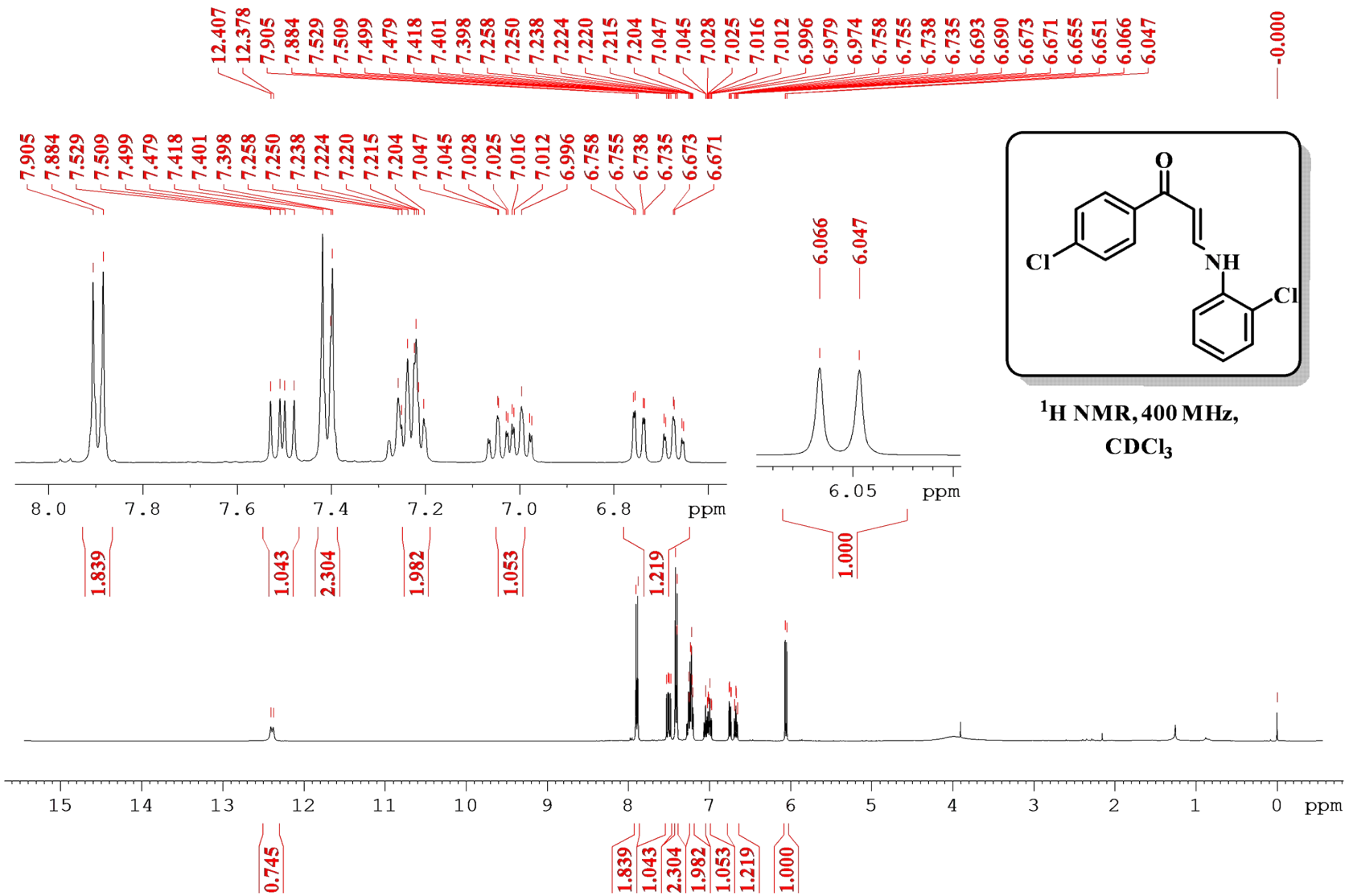


Figure 11: ^{1}H NMR Compound 1j

GS-F-O-Cl

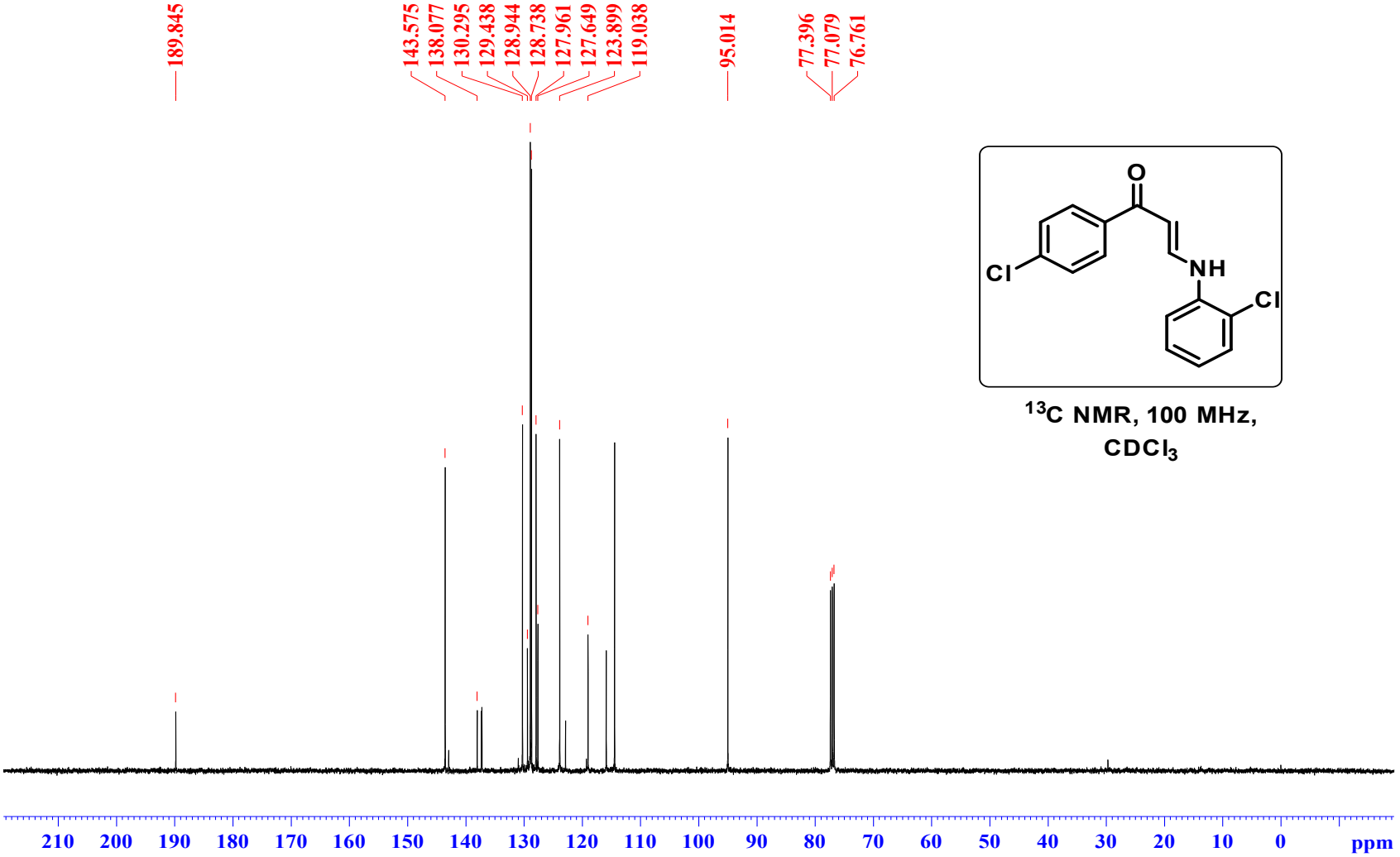


Figure 12: ^{13}C NMR Compound 1j

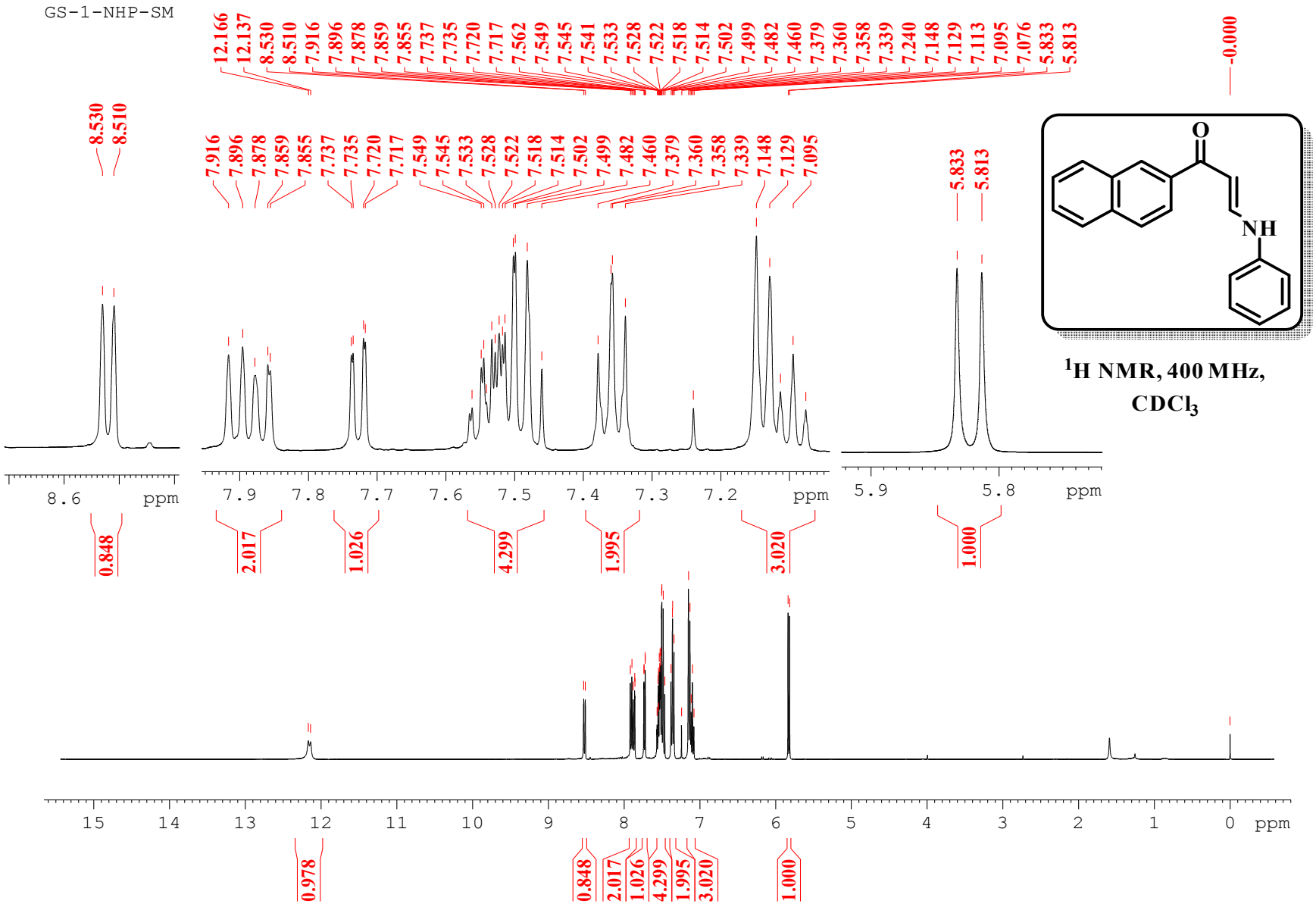


Figure 13: ^{1}H NMR Compound 1g

GS-1-NHP-SM

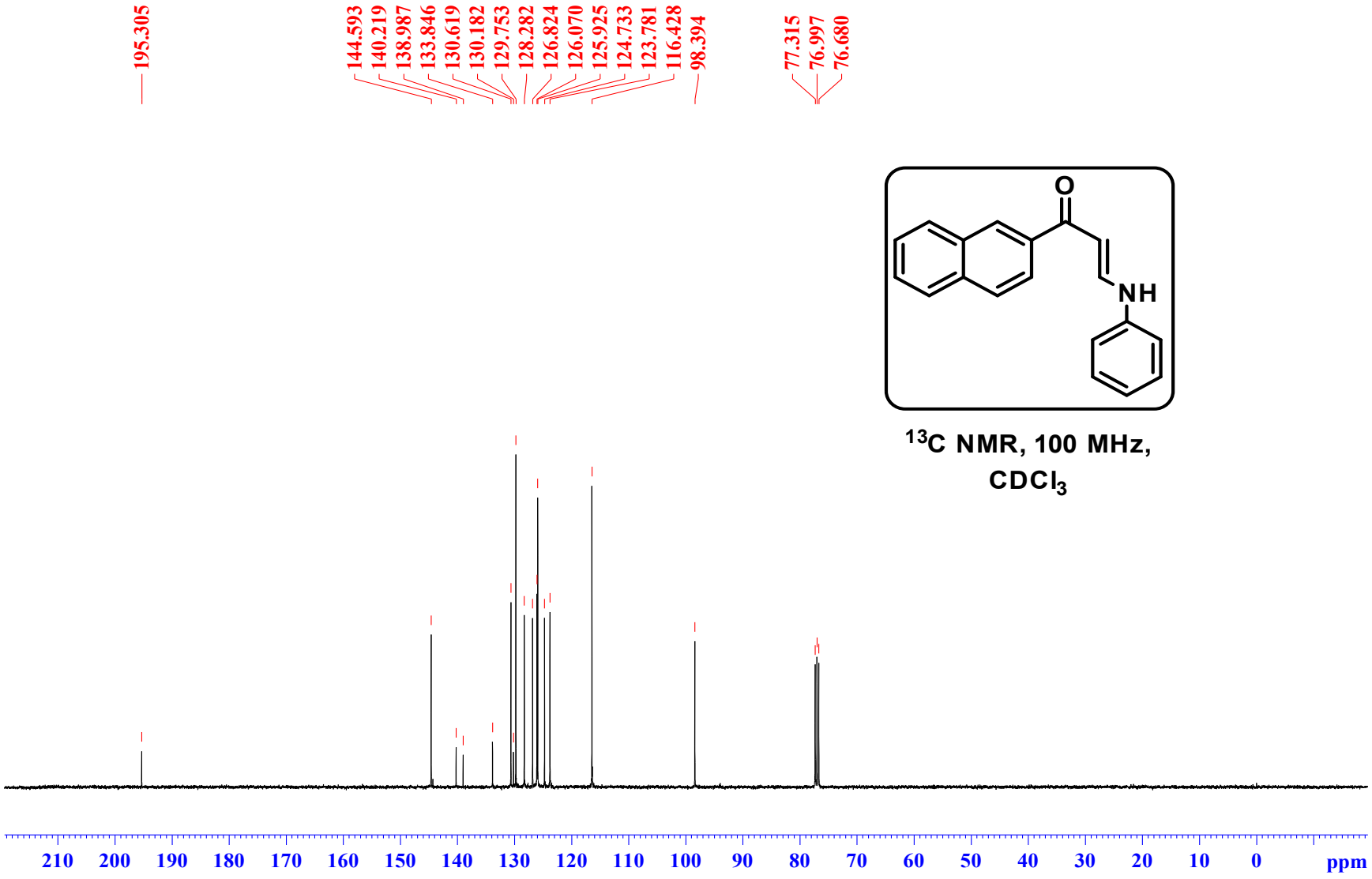


Figure 14: ^{13}C NMR Compound 1g

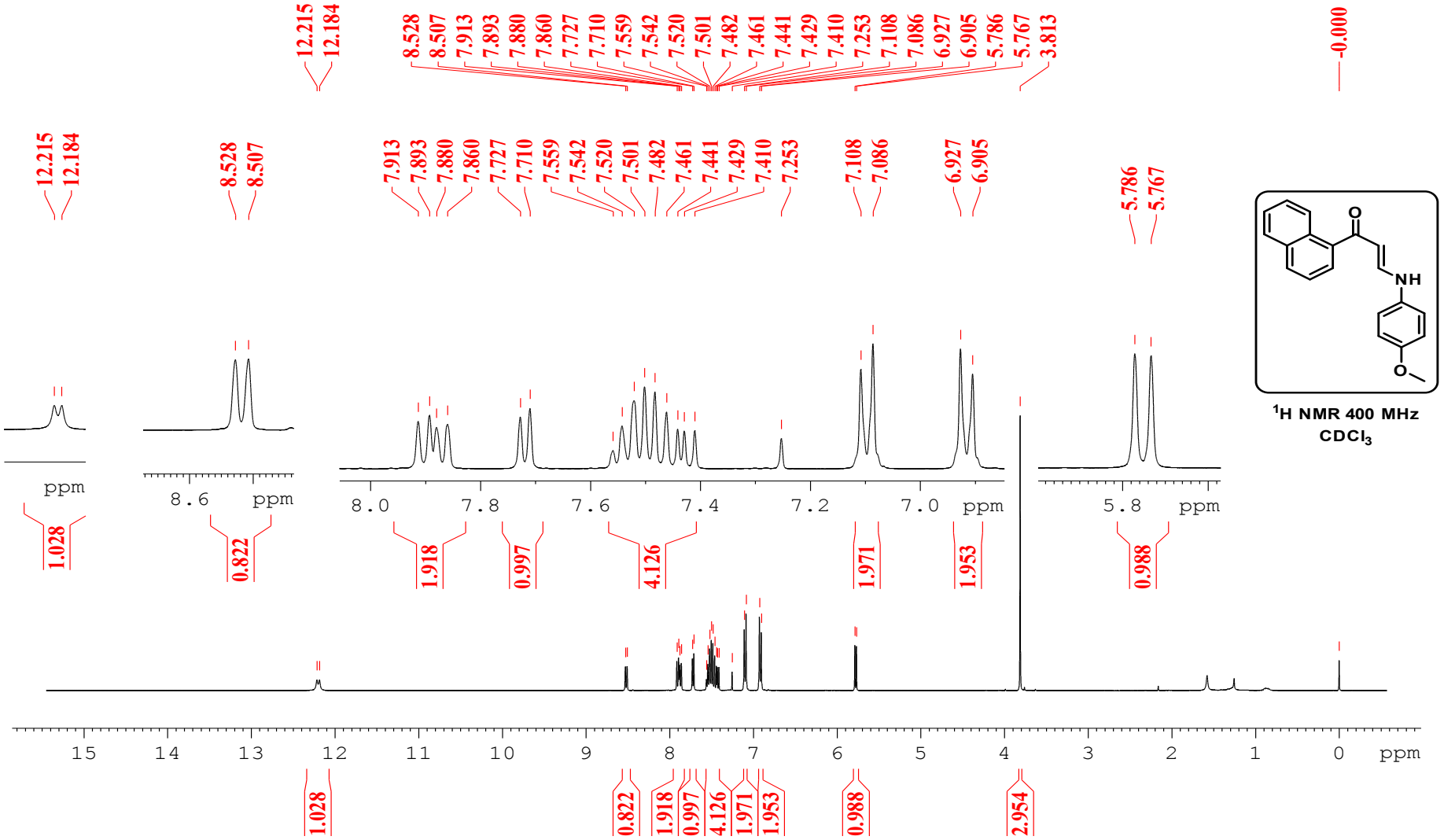


Figure 15: ^{1}H NMR Compound 1h

GS-05-408

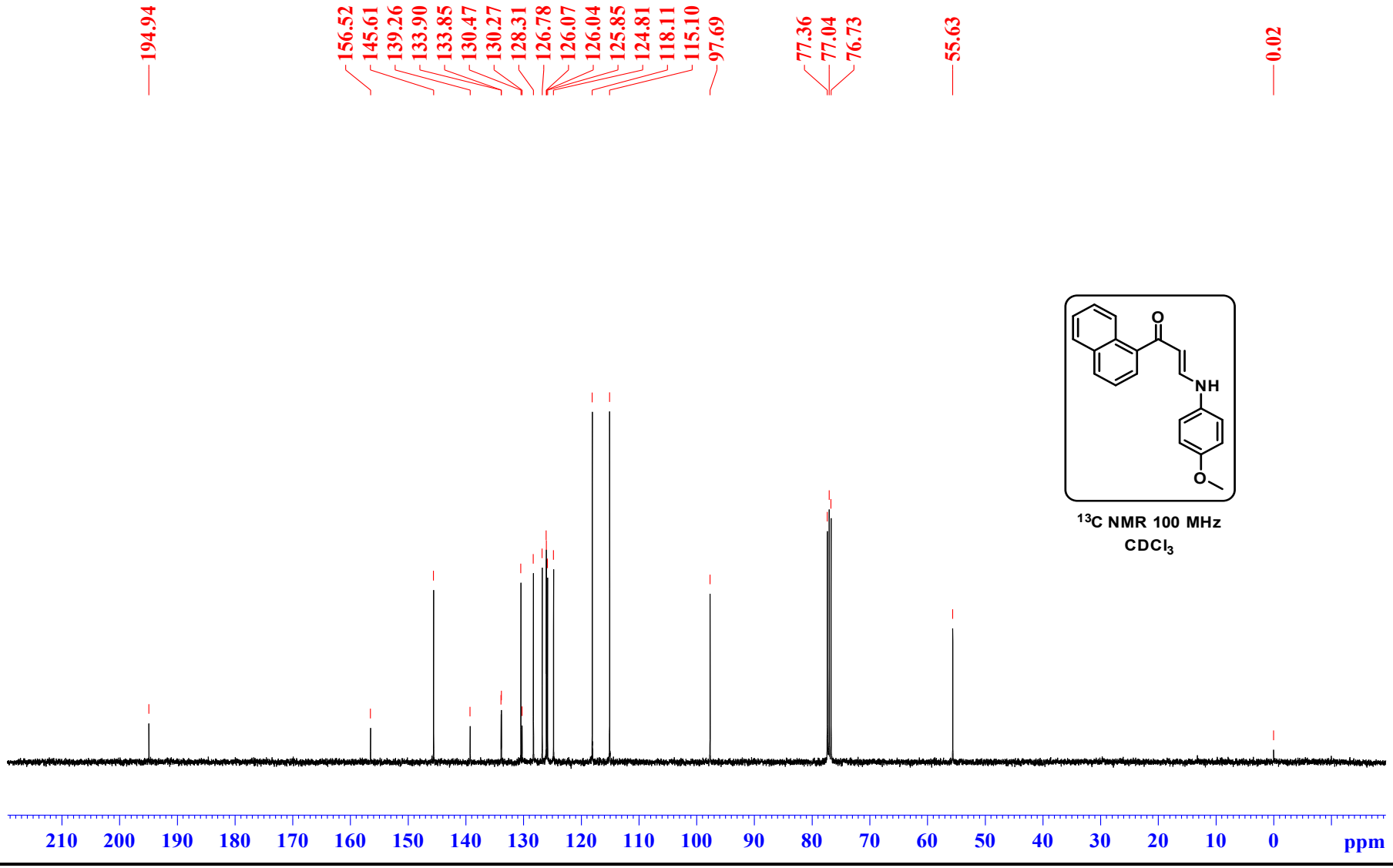

194.94
156.52
145.61
139.26
133.90
133.85
130.47
130.27
128.31
126.78
126.07
126.04
125.85
124.81
118.11
115.10
97.69
77.36
77.04
76.73
55.63
0.02
O
NH
O
13C NMR 100 MHz
CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Figure 16: ^{13}C NMR Compound 1h

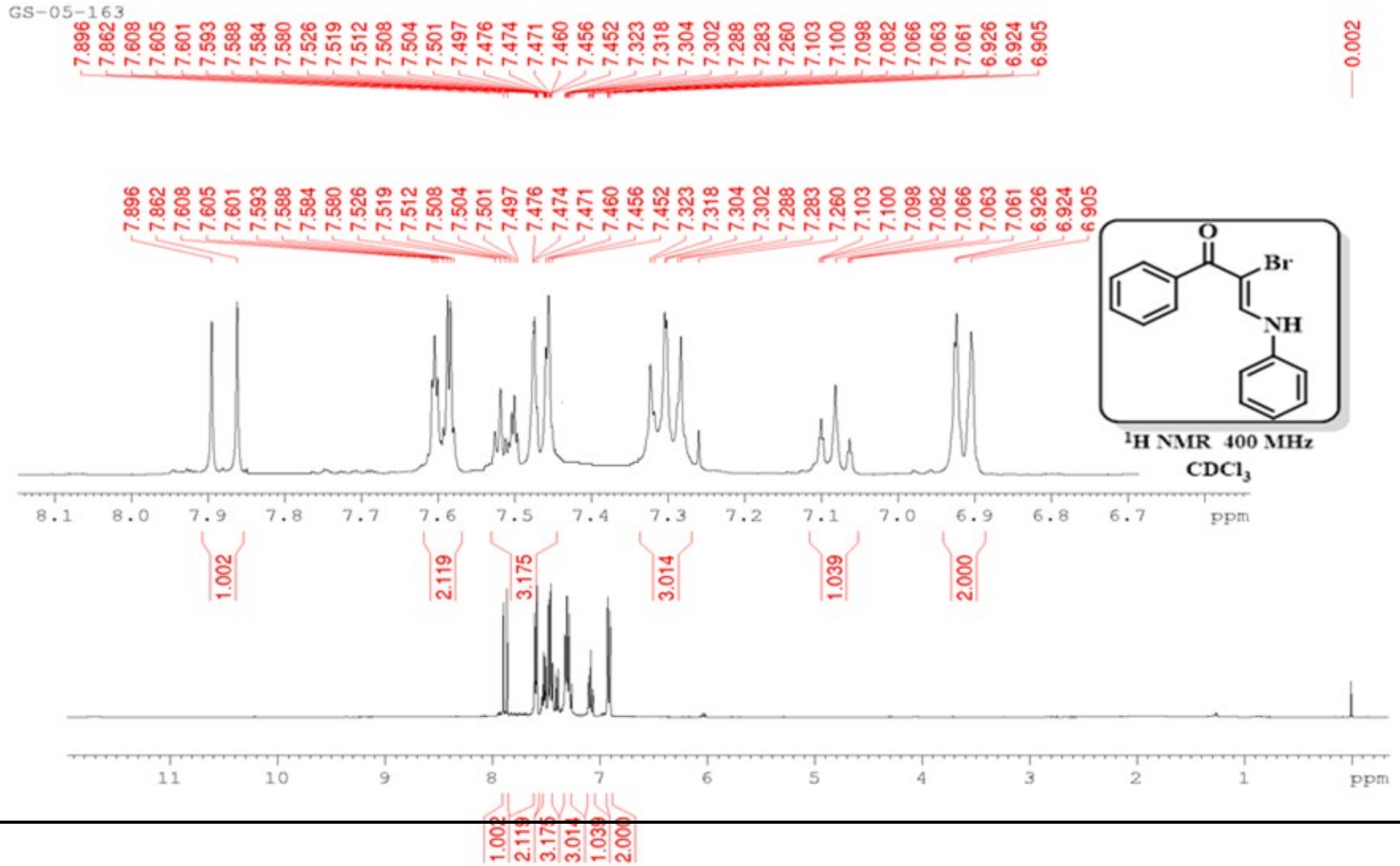


Figure: 17 ^{1}H NMR Compound 2a

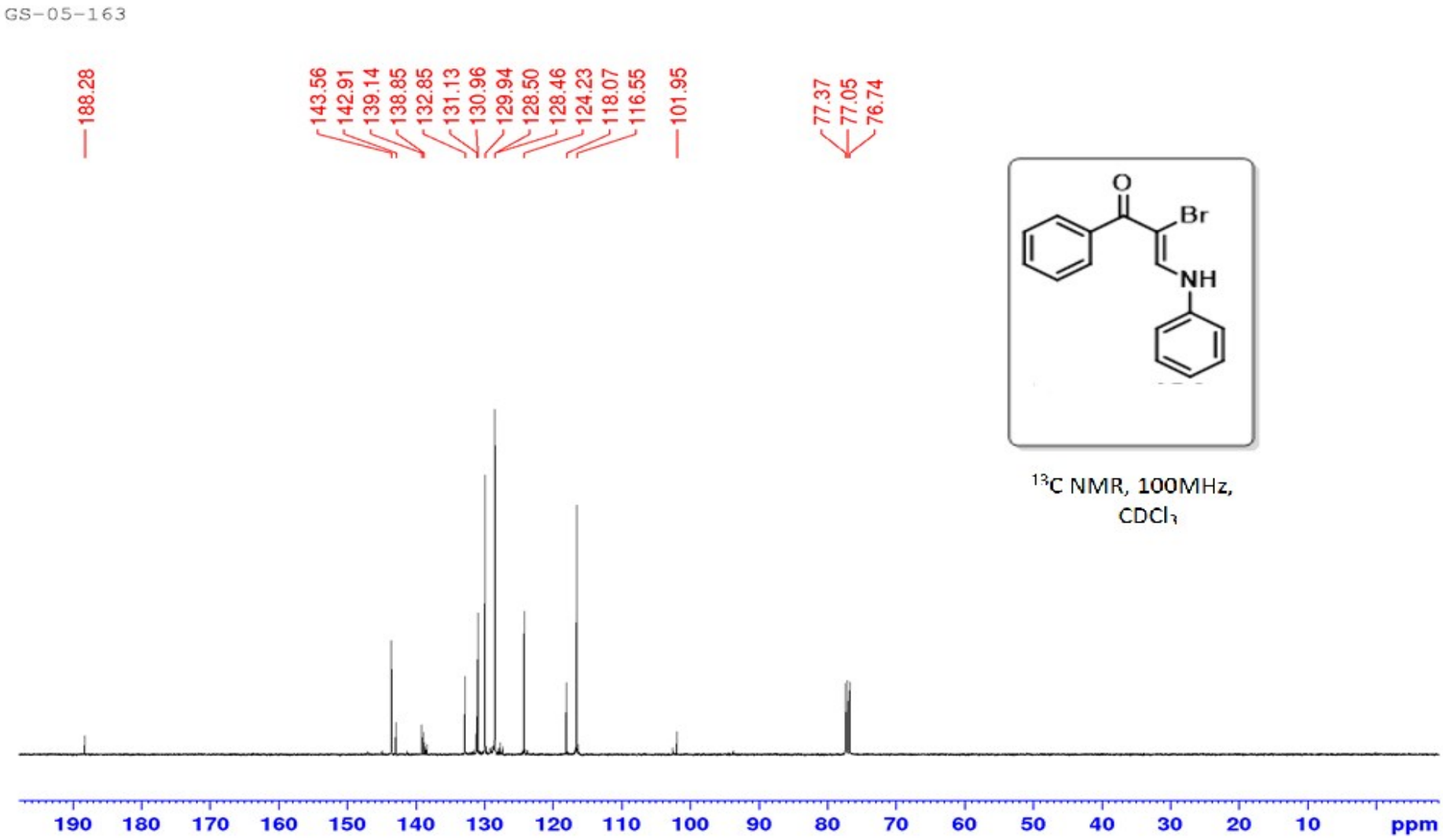


Figure: 18 ^{13}C NMR Compound 2a

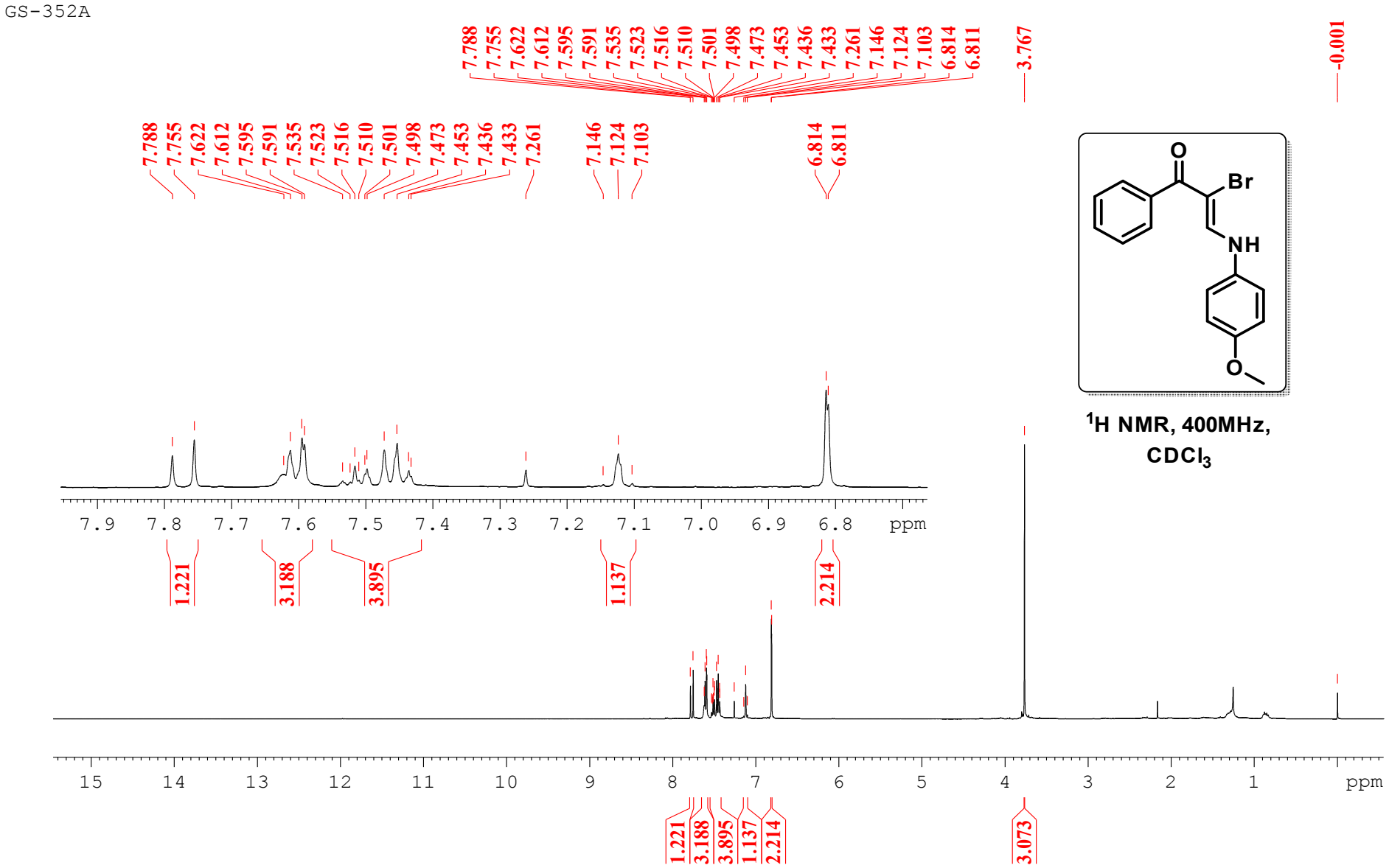


Figure 19: ^{1}H NMR Compound 2b

352A

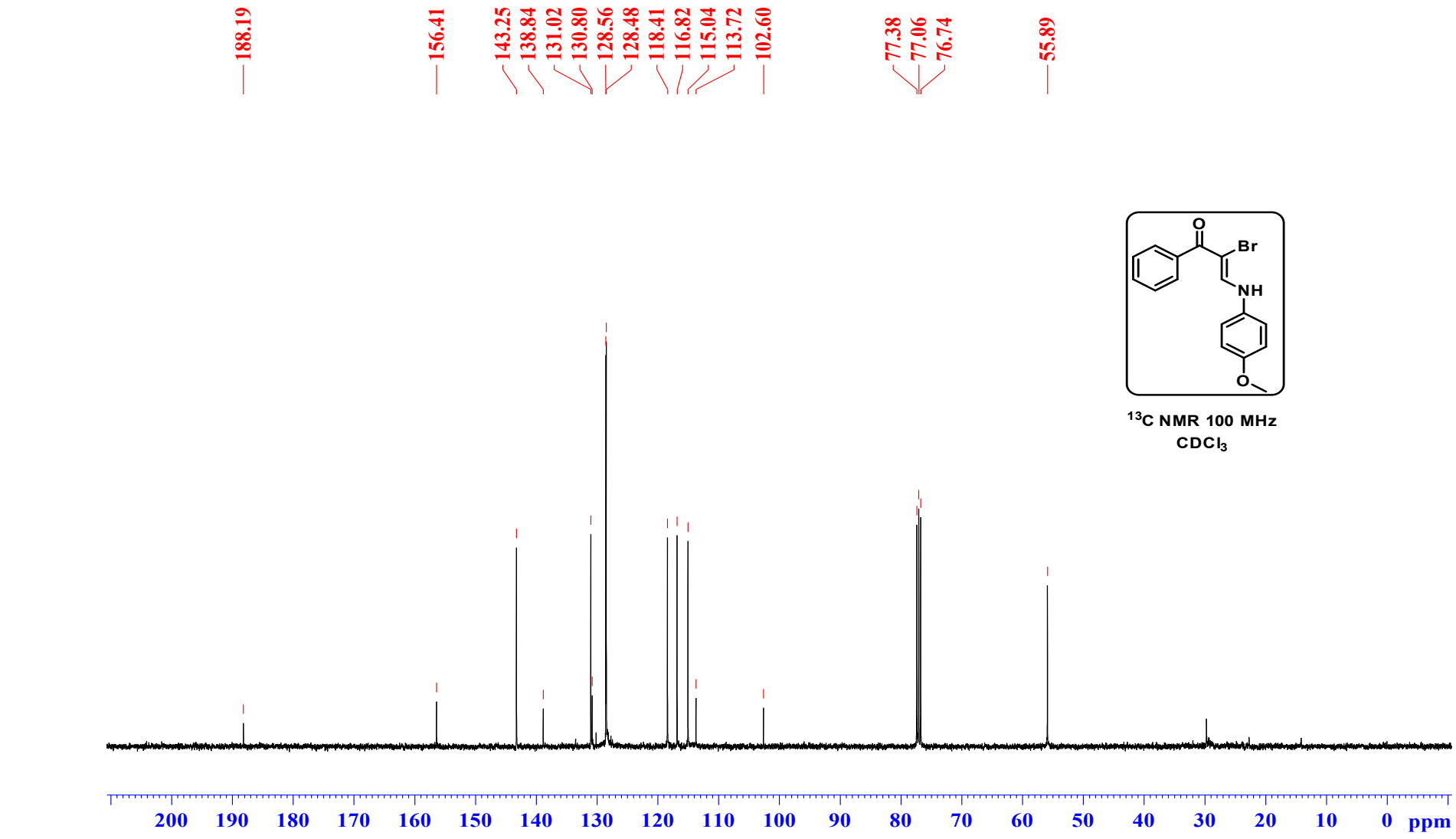


Figure 20: ^{13}C NMR Compound 2b

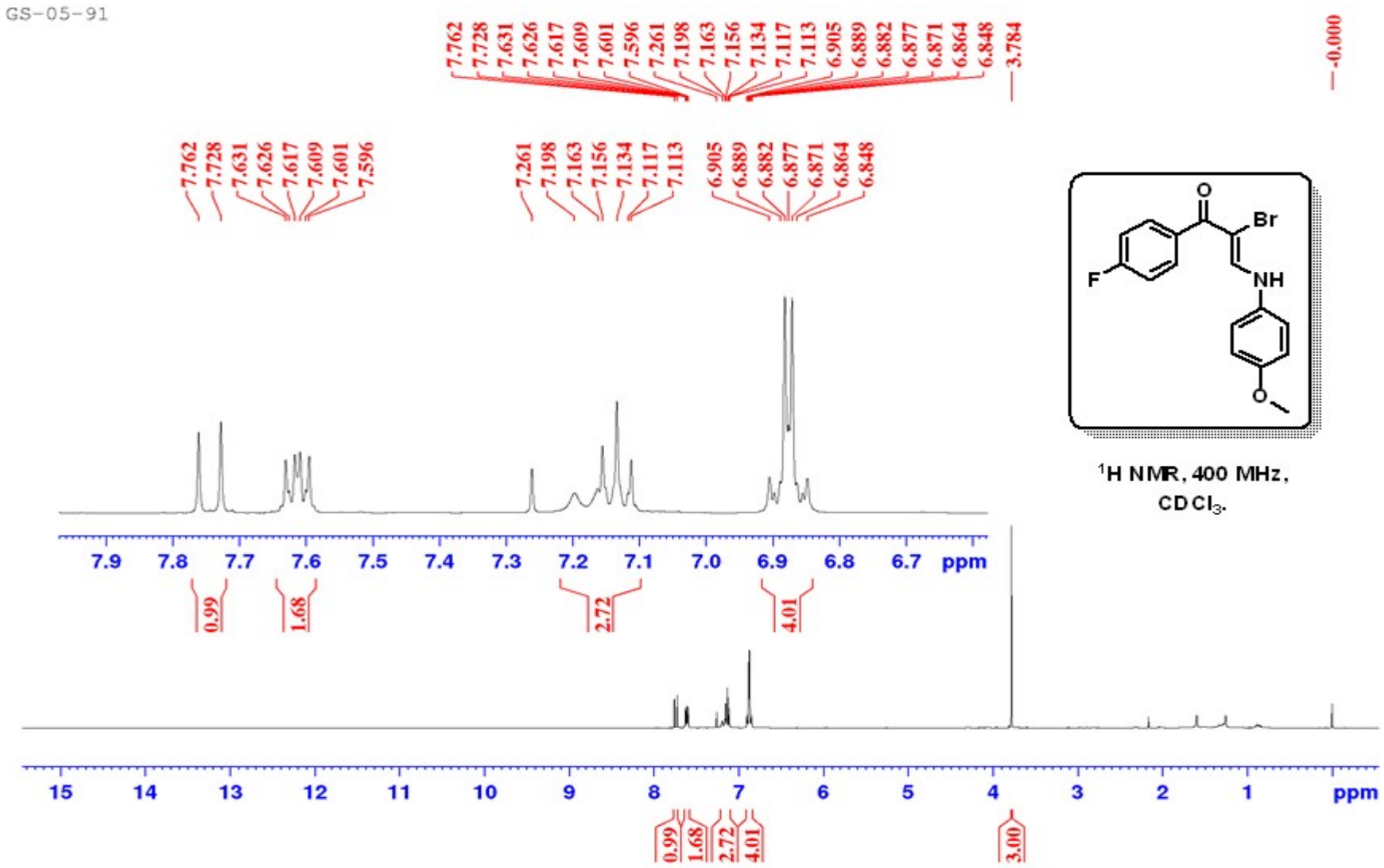
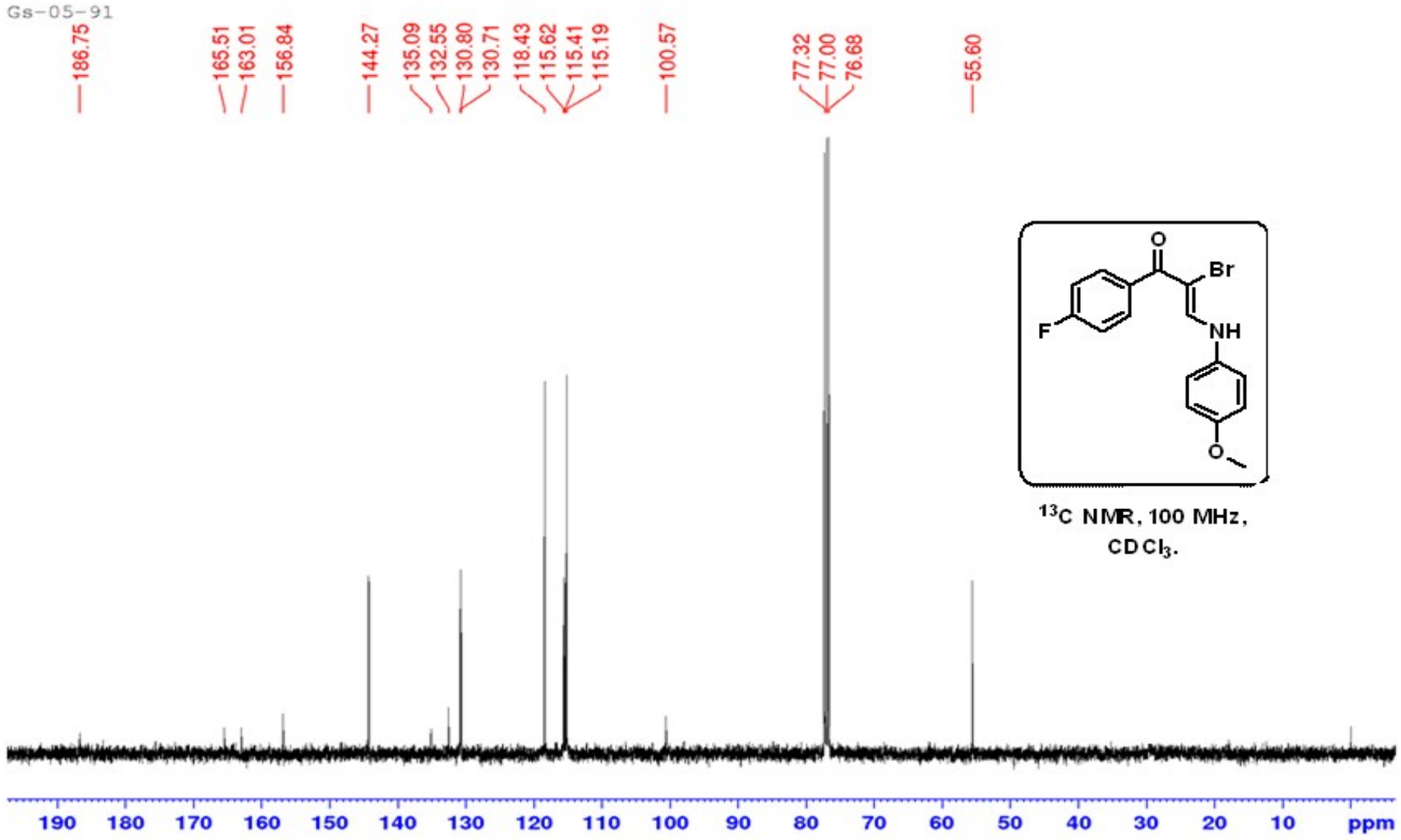


Figure 21: ^{1}H NMR Compound 2c



^{13}C NMR, 100 MHz, $CDCl_3$.

Figure 22: ^{13}C NMR compound 2c

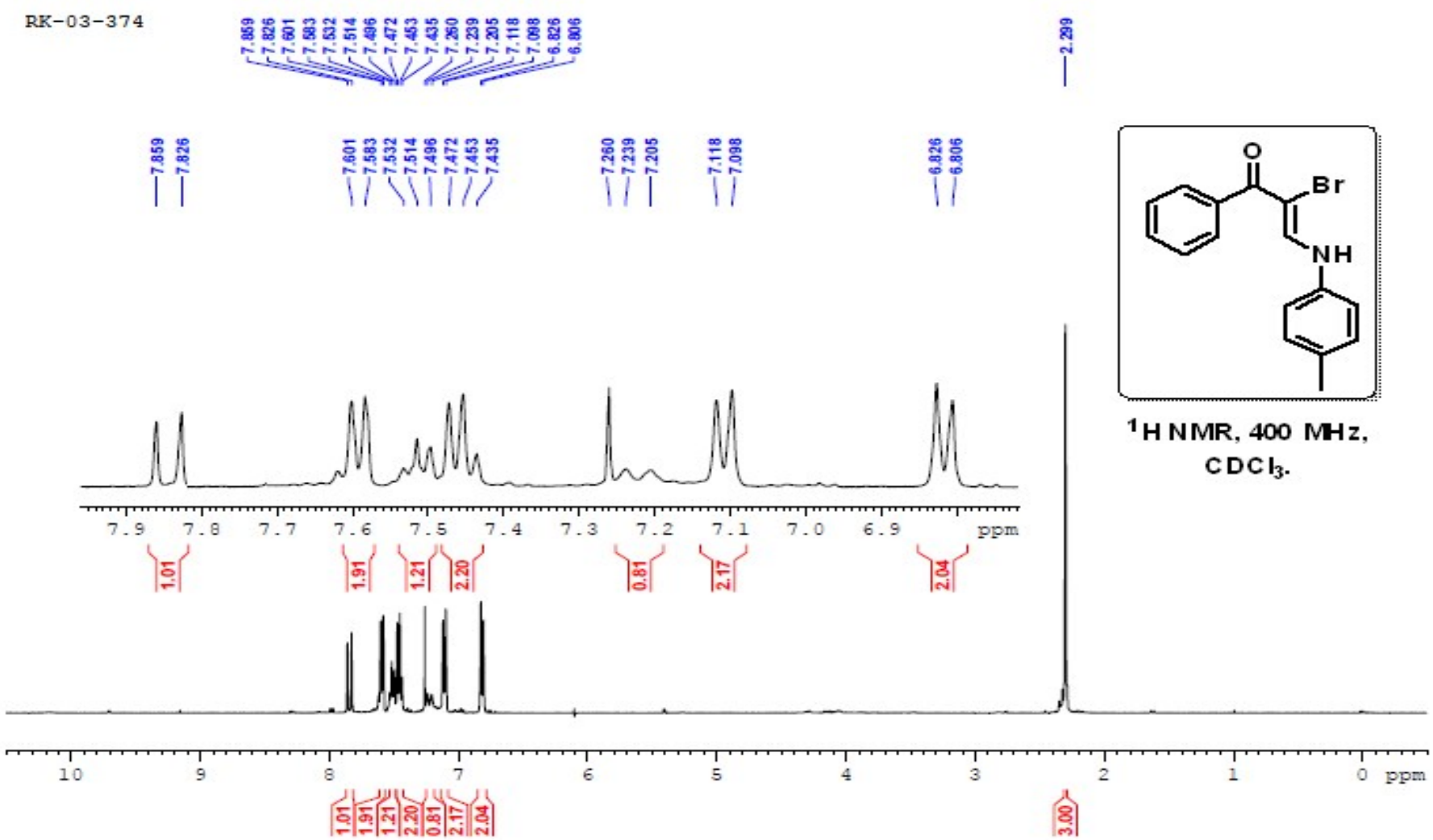


Figure 23 ^{1}H NMR Compound 2d

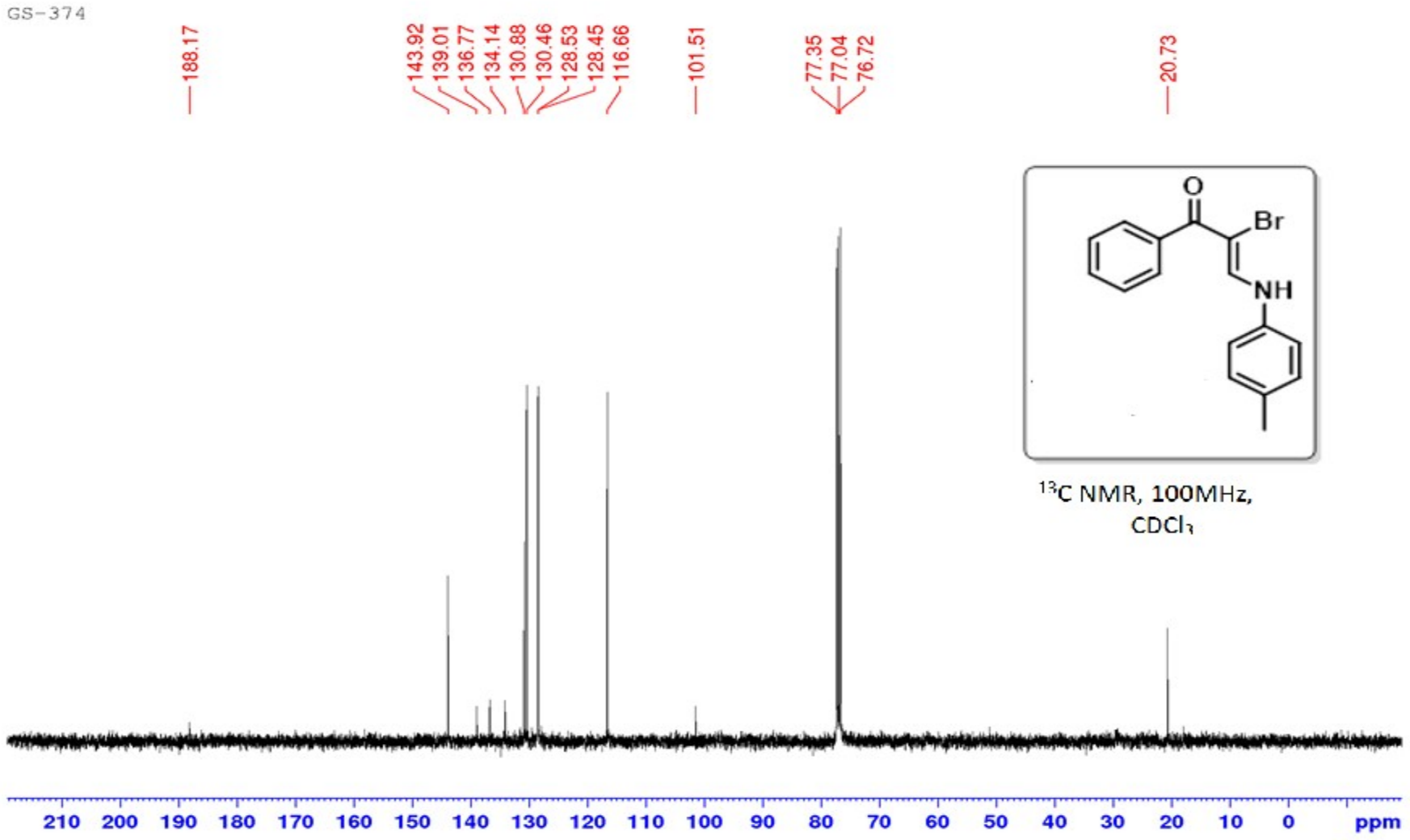


Figure 24: ^{13}C NMR Compound 2d

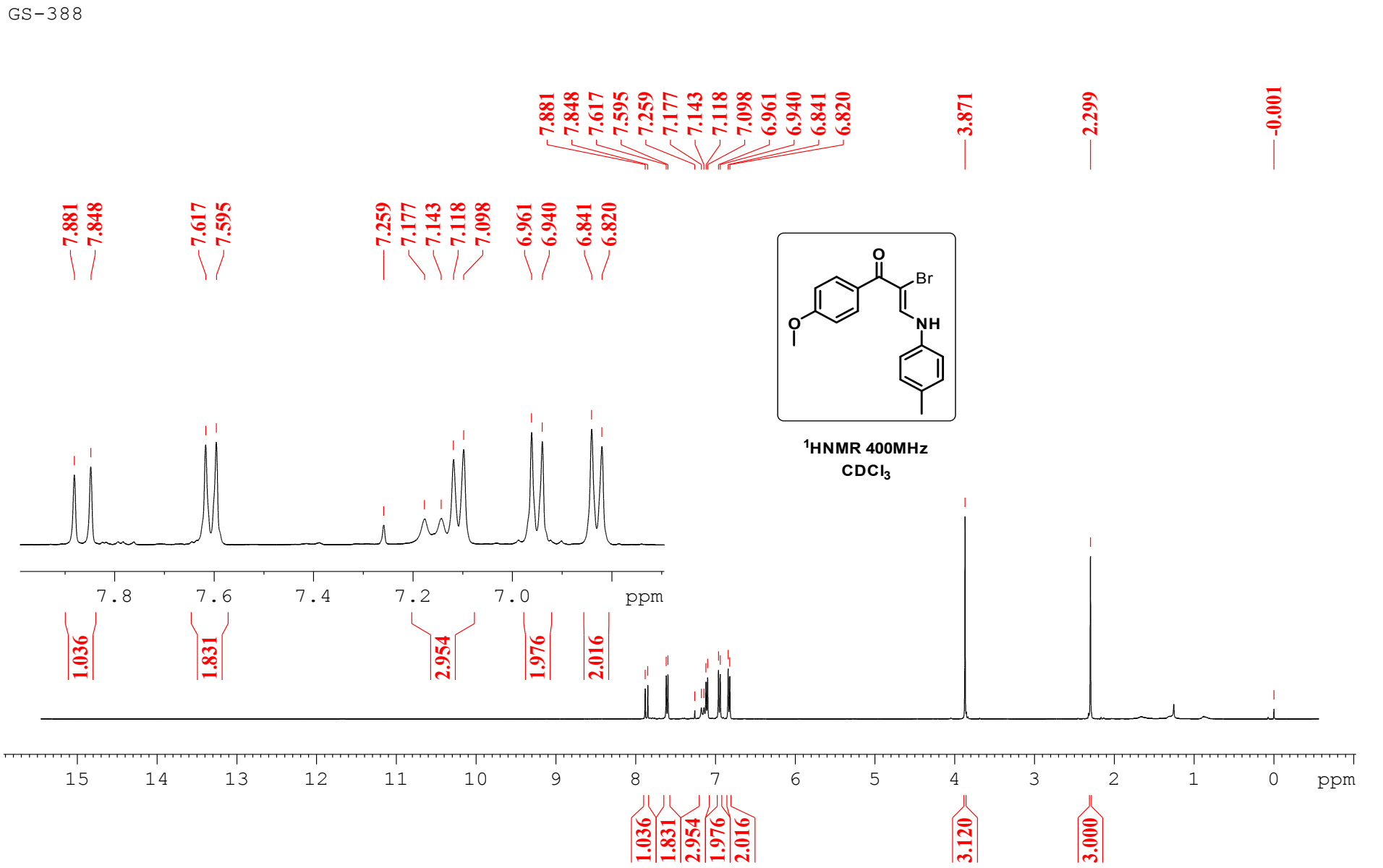


Figure 25: ^{1}H NMR Compound 2e

GS-05-388

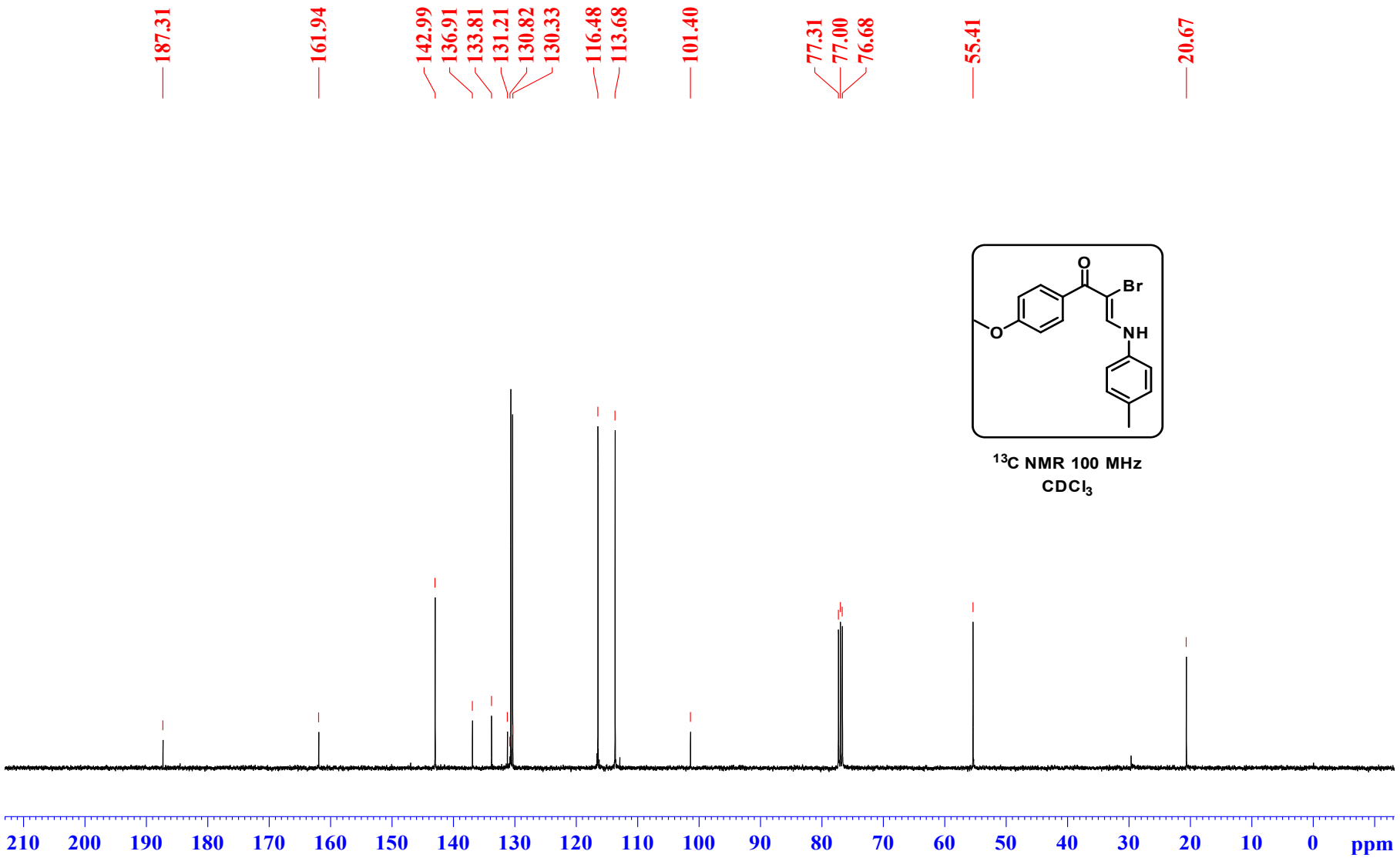


Figure 26: ^{13}C NMR Compound 2e

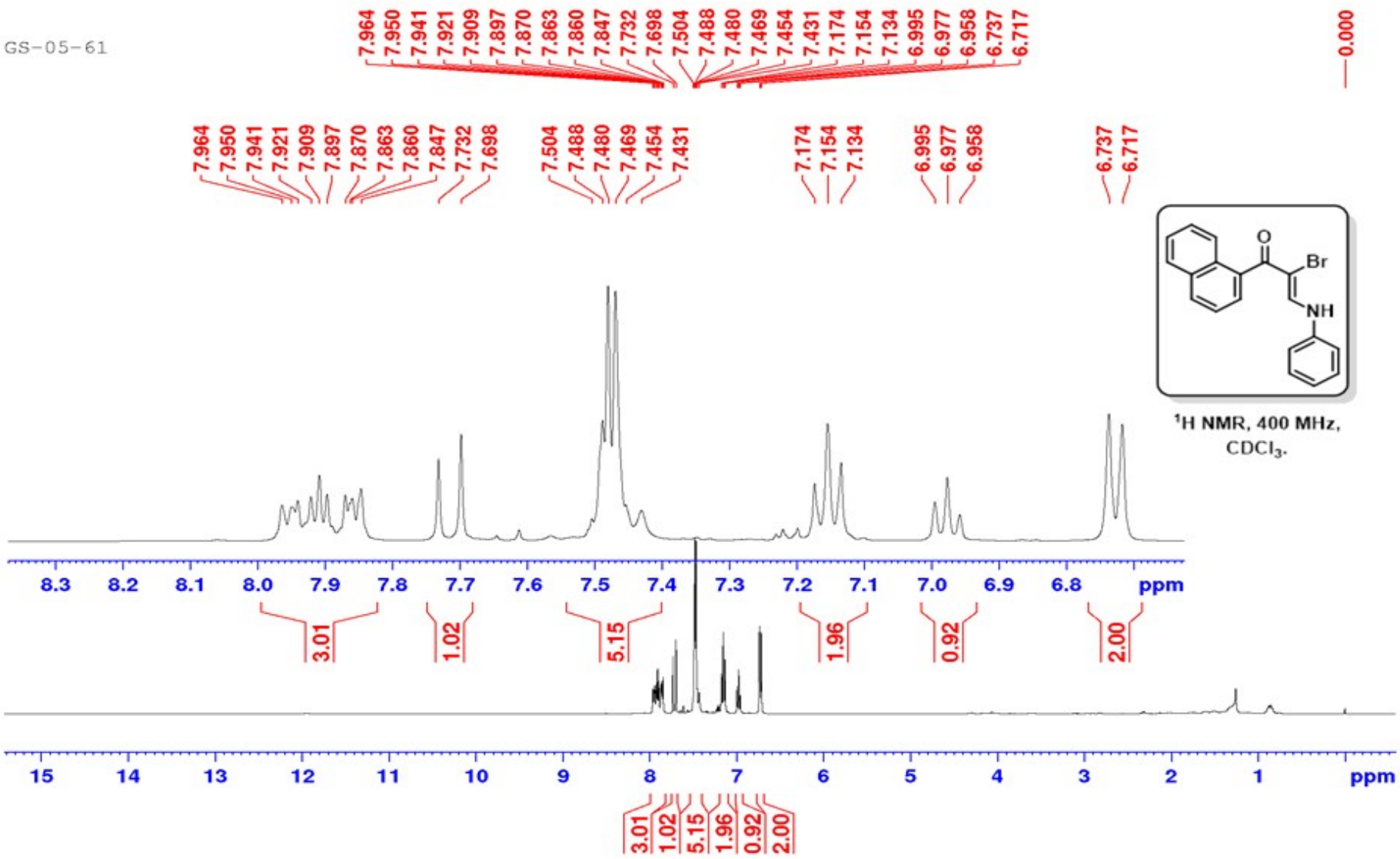
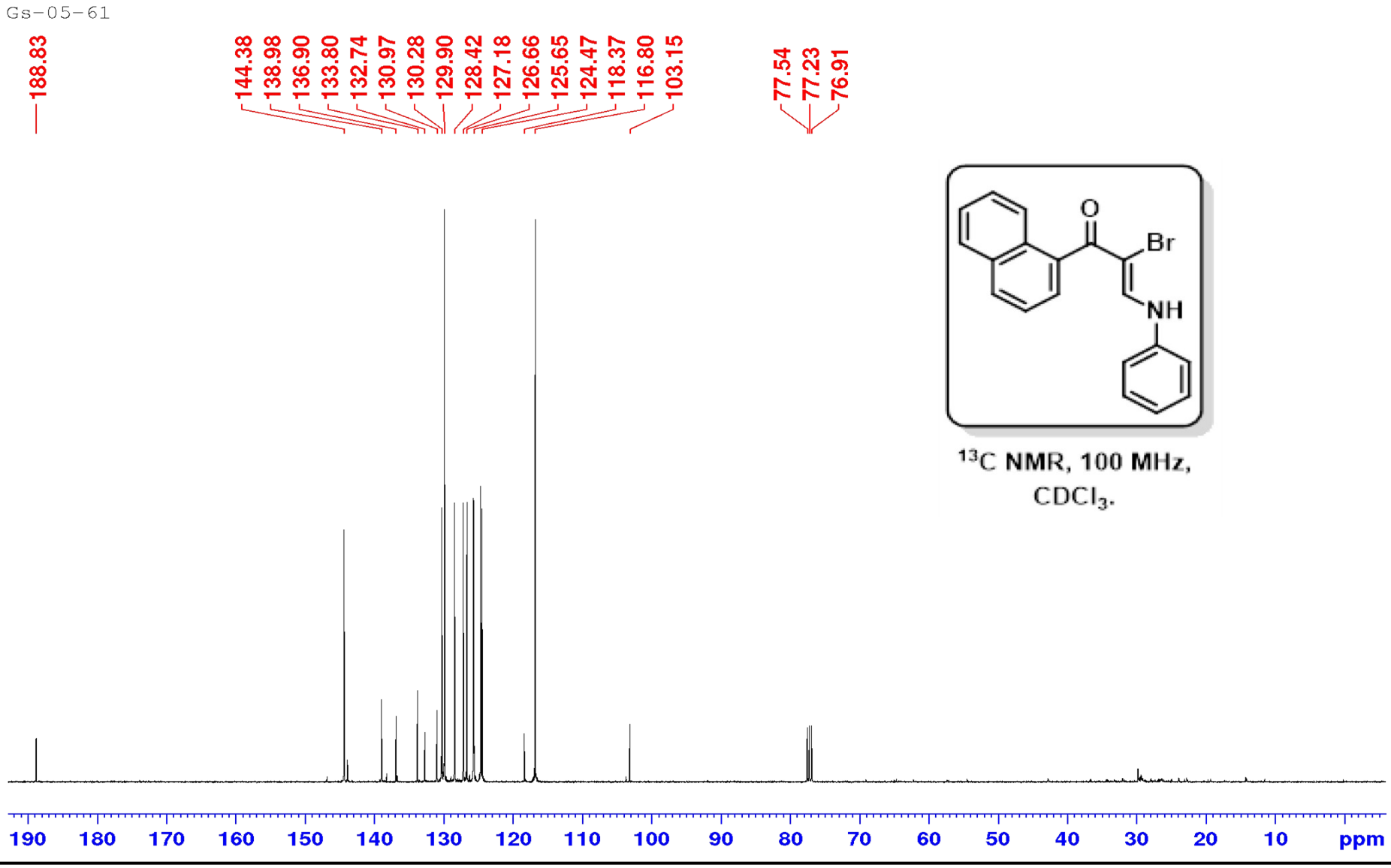


Figure 27: ^{1}H NMR Compound 2f



^{13}C NMR, 100 MHz, $CDCl_3$.

Figure 28: ^{13}C NMR Compound 2f

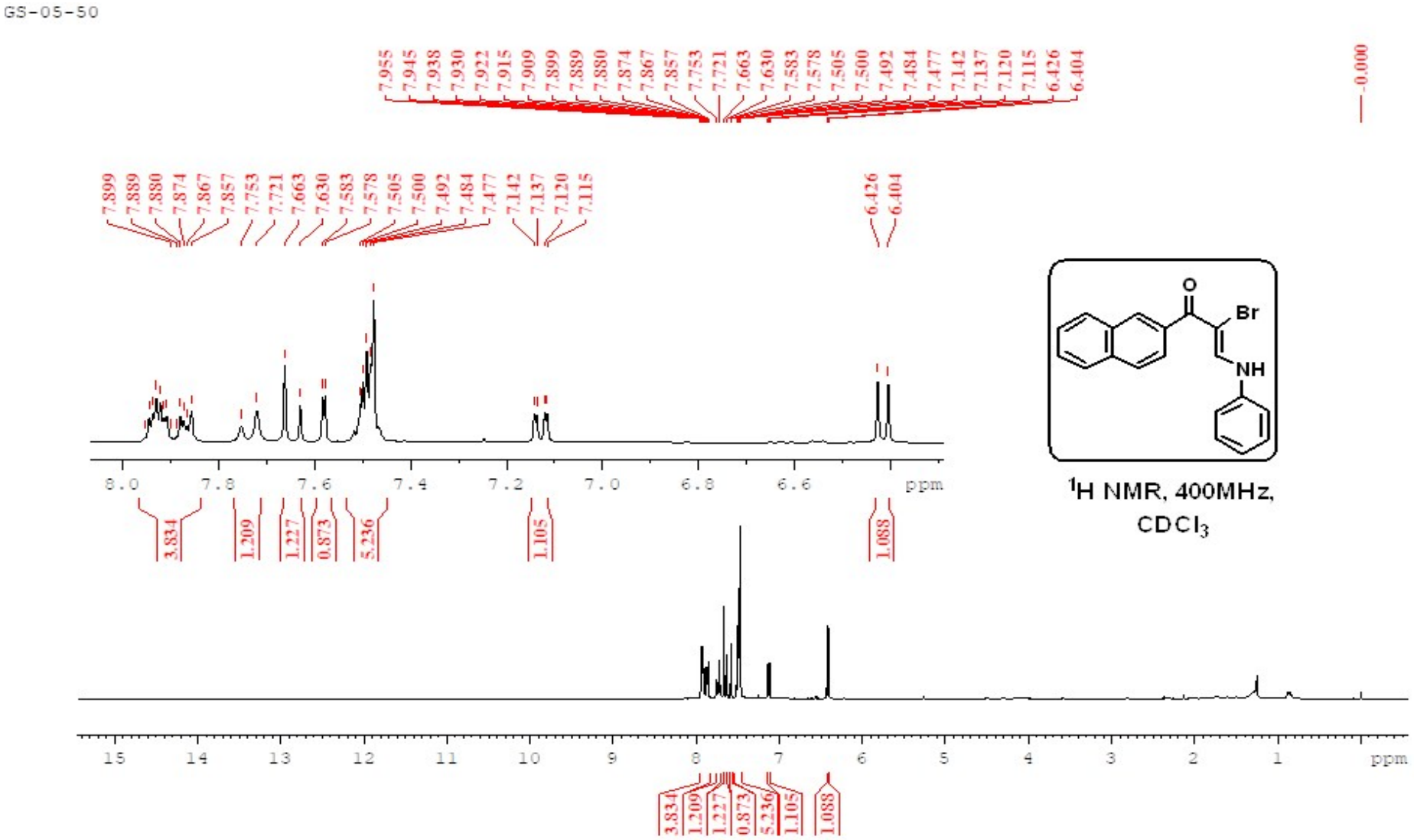


Figure 29: ^{1}H NMR Compound 2g

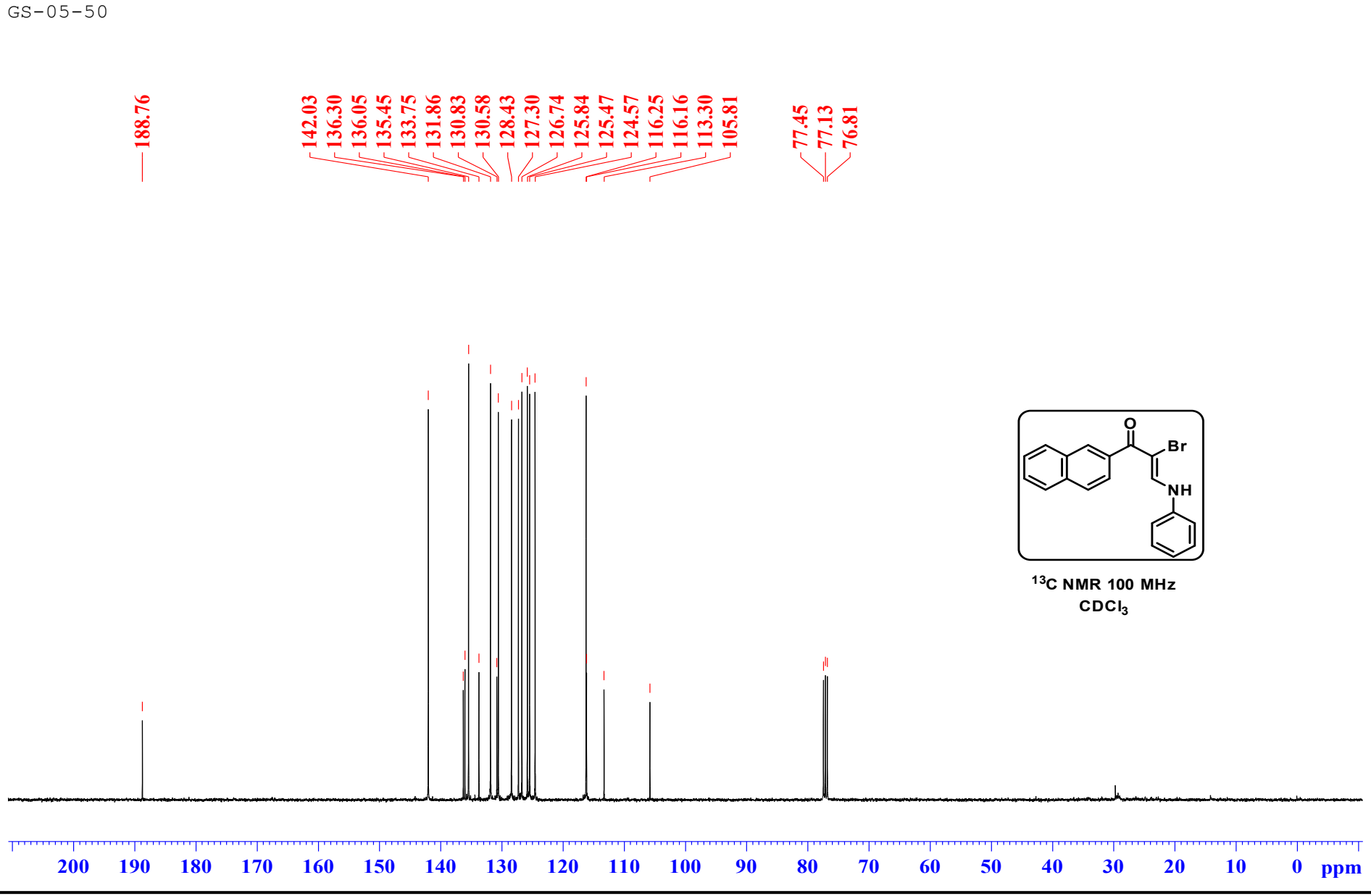


Figure 30: ^{13}C NMR Compound 2g

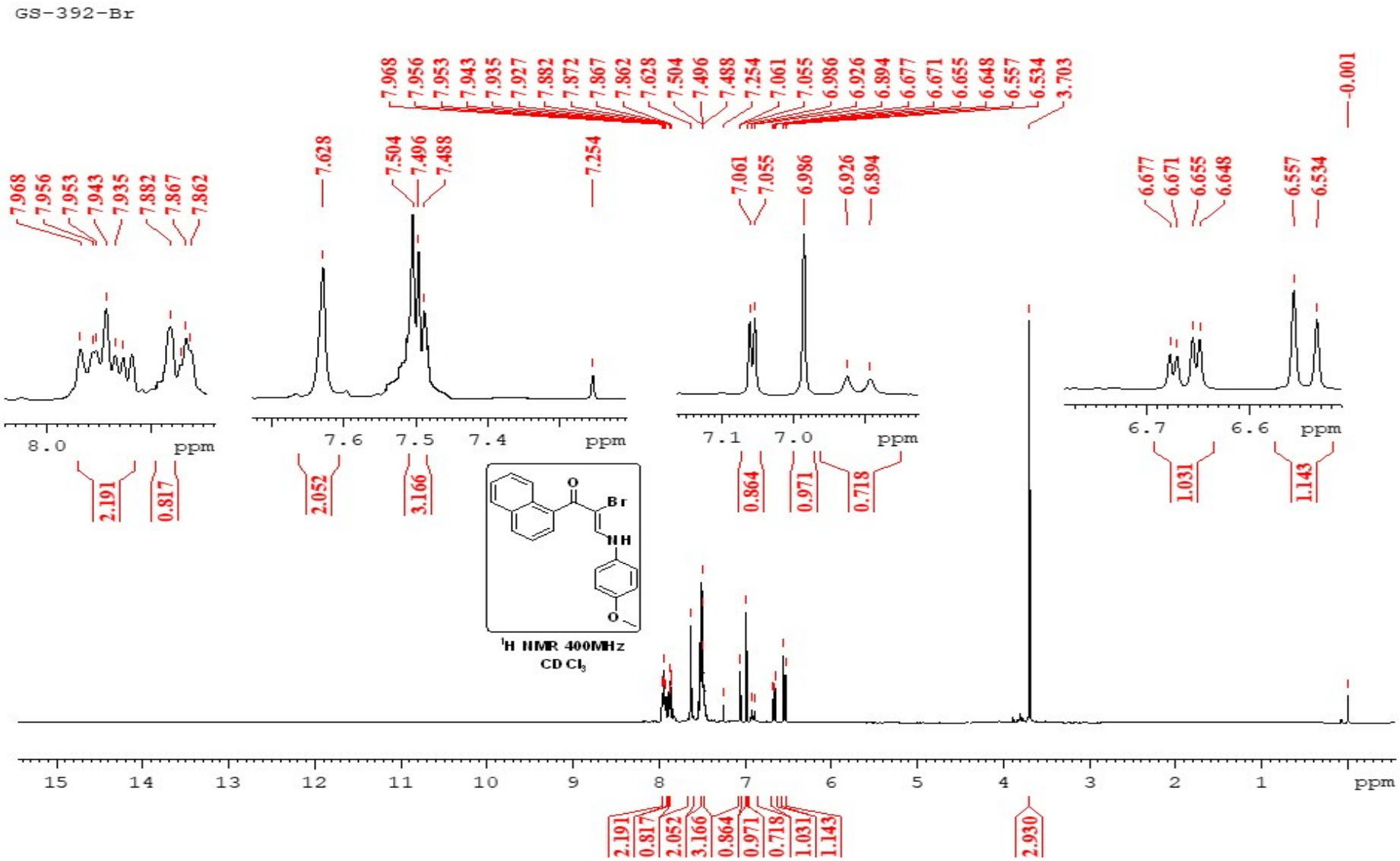


Figure 31: ^{1}H NMR Compound 2h

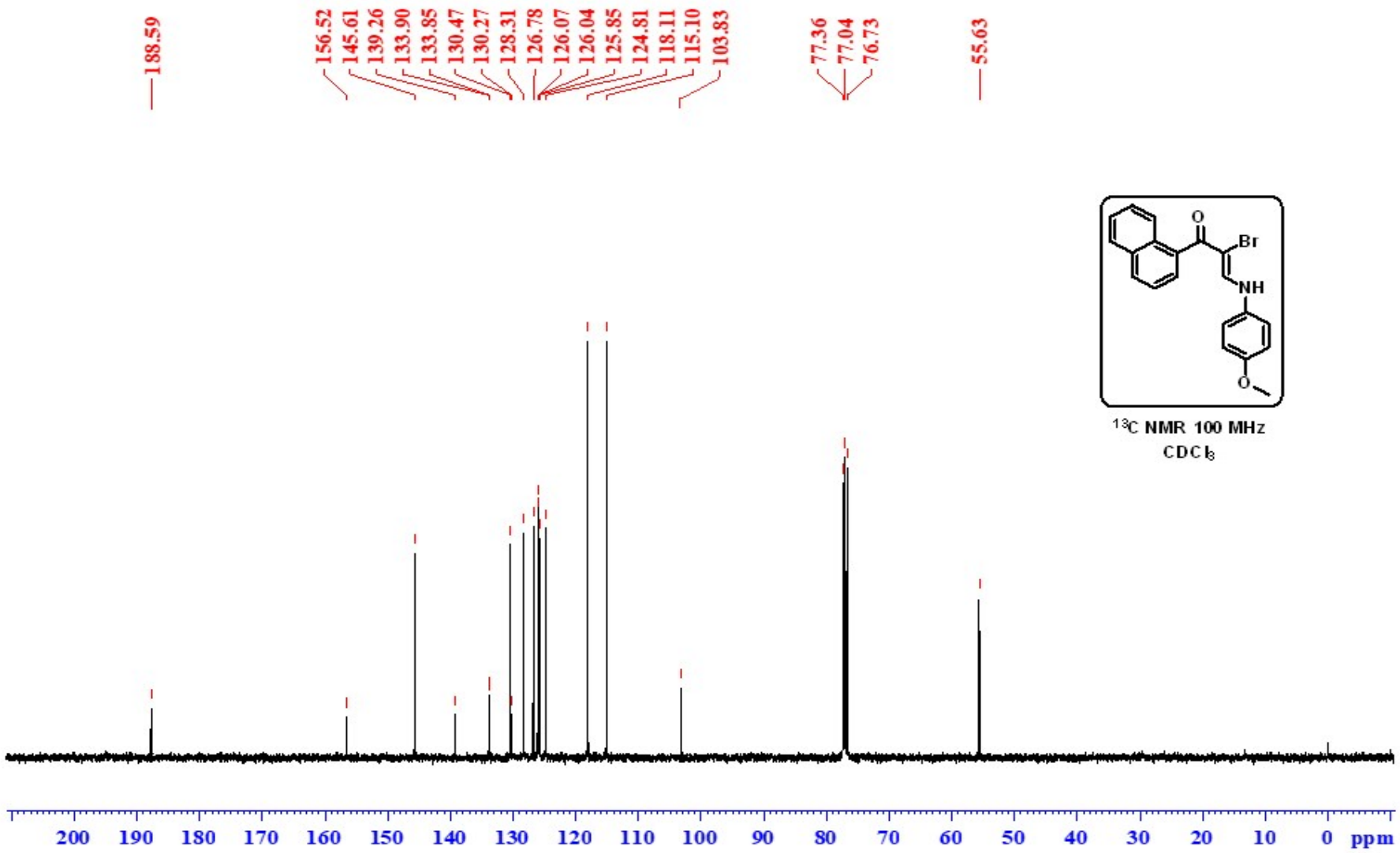


Figure 32: ^{13}C NMR Compound 2h

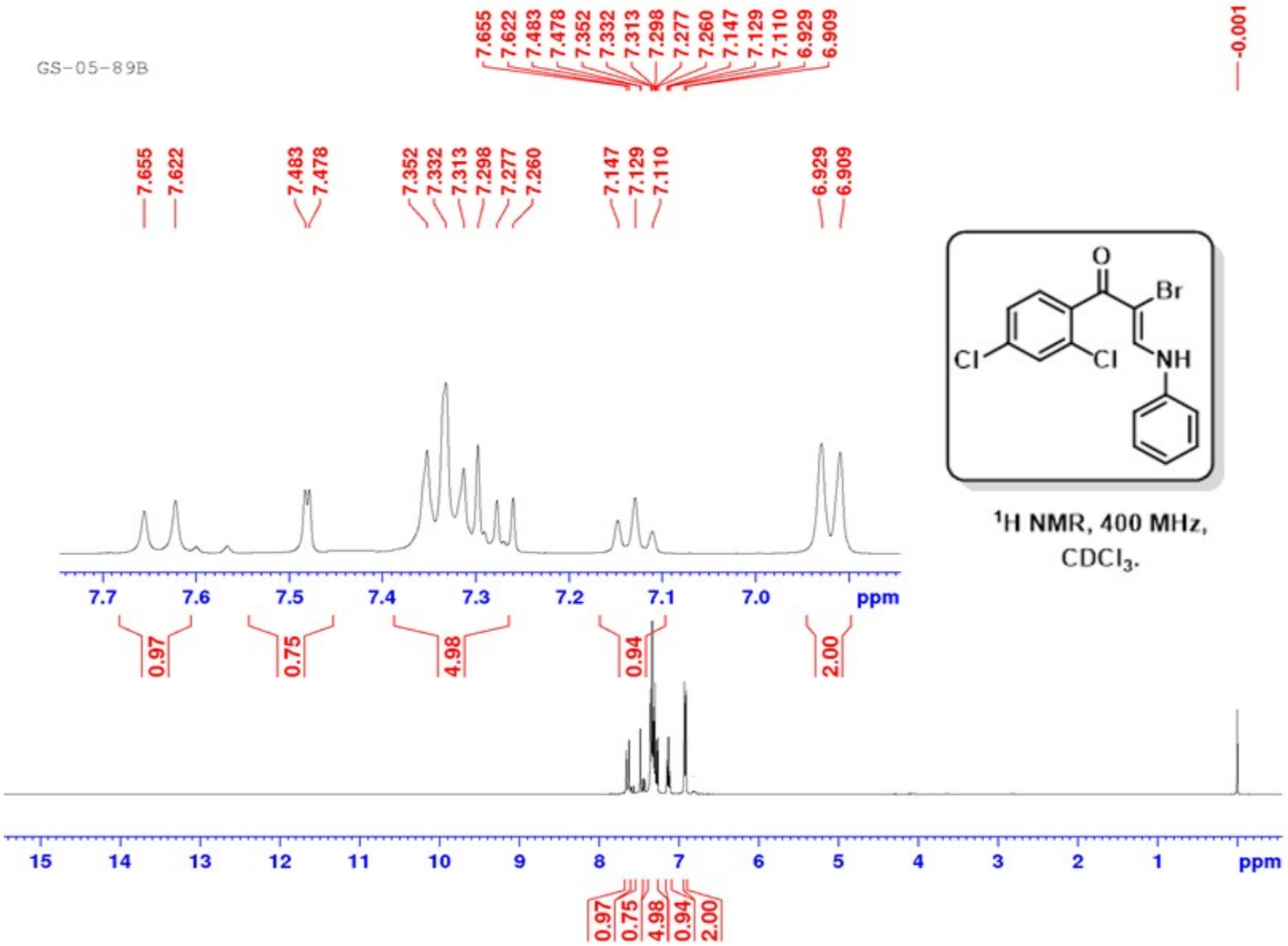


Figure 33: ^{1}H NMR Compound 2i

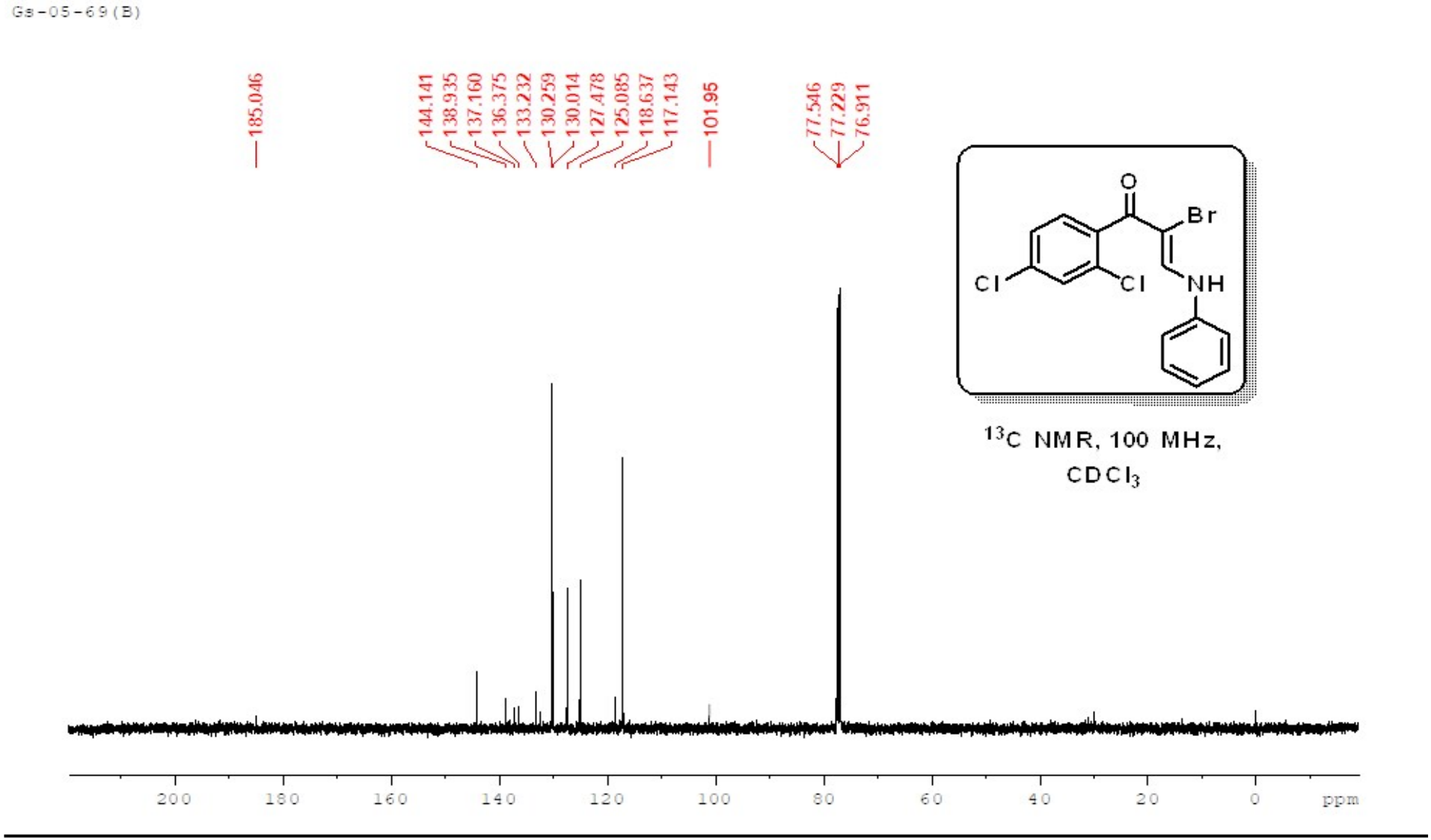


Figure 34: ^{13}C NMR Compound 2i

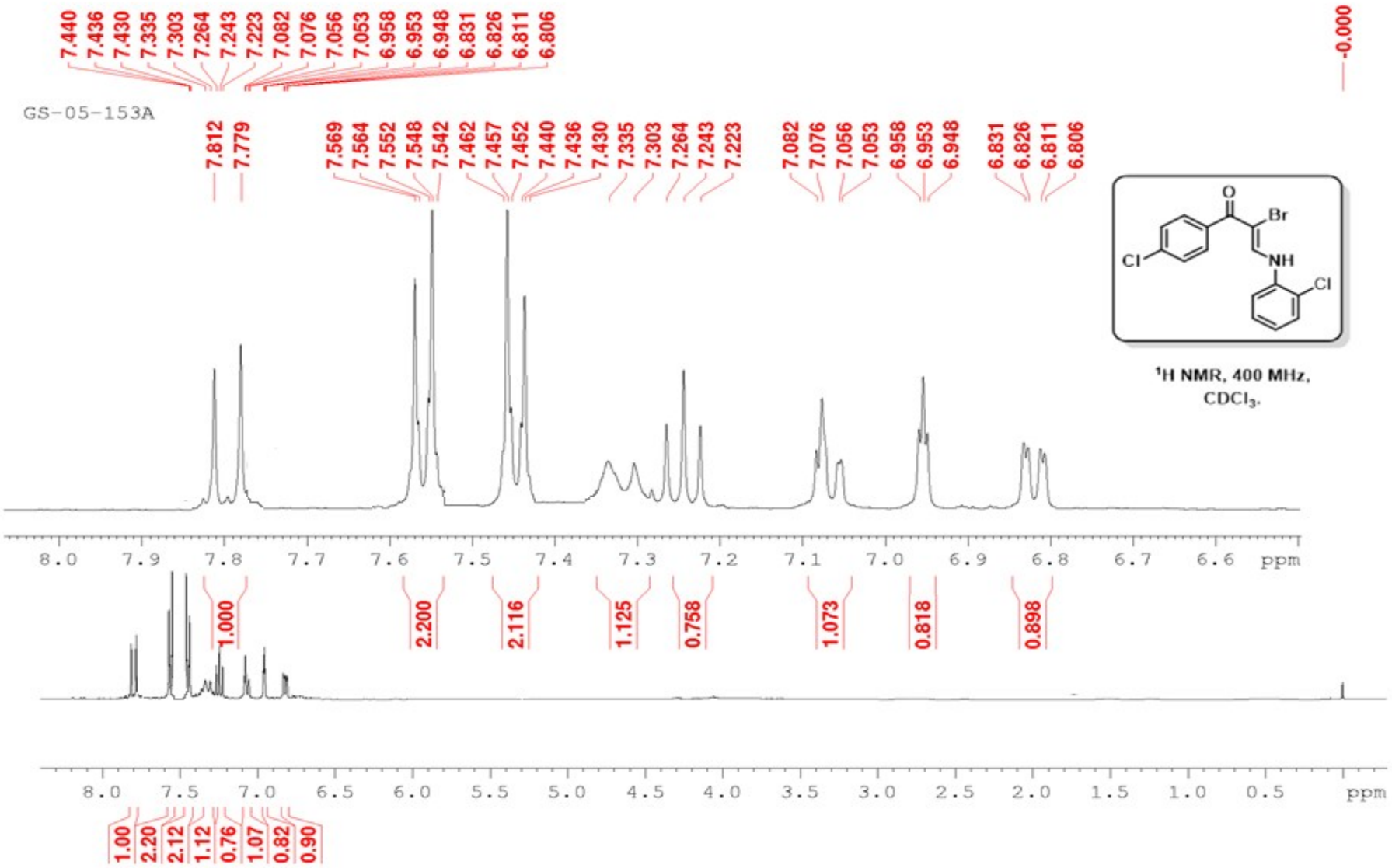
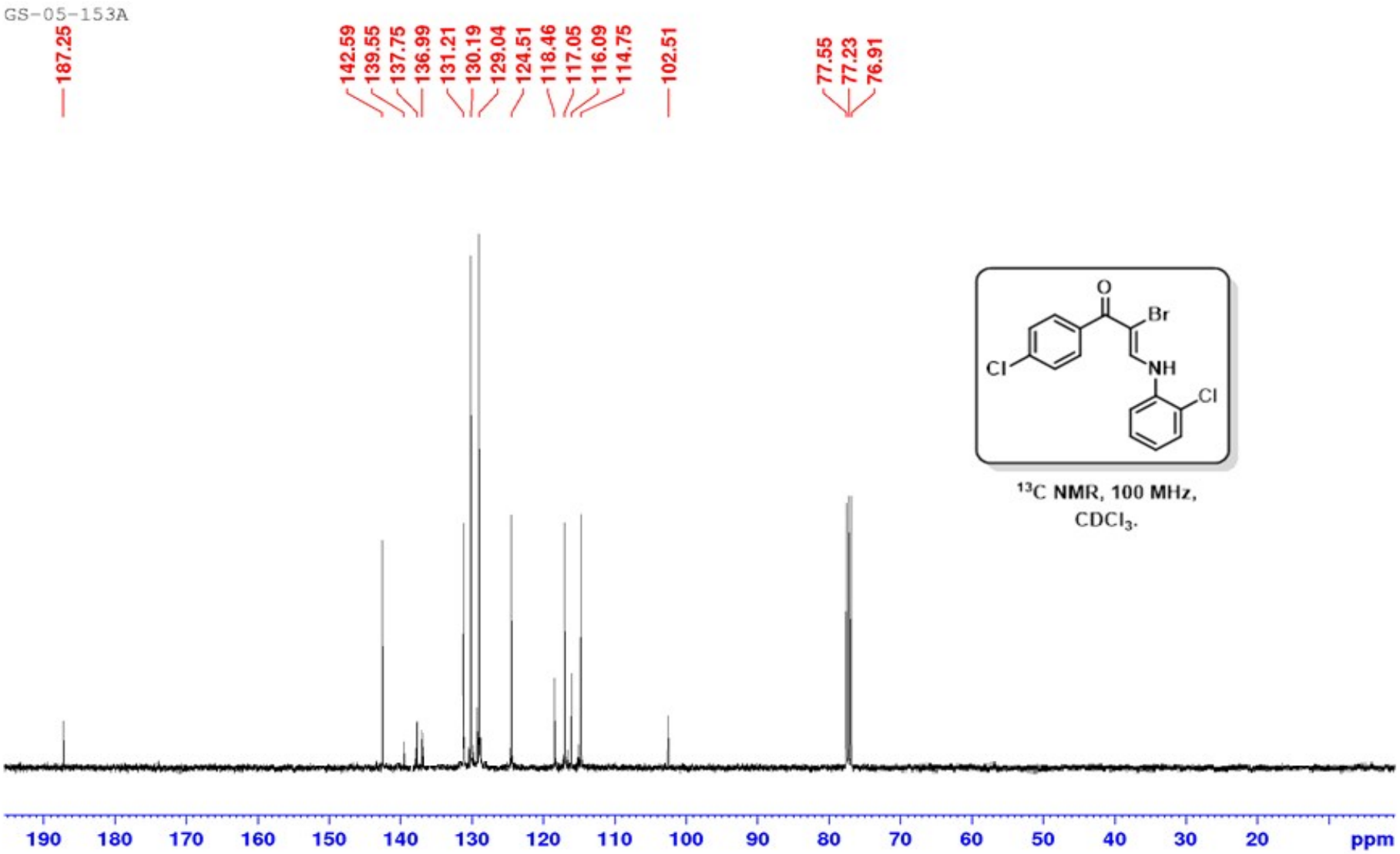


Figure 35: ^{1}H NMR Compound 2j



^{13}C NMR, 100 MHz, $CDCl_3$.

Figure 36: ^{13}C NMR Compound 2j

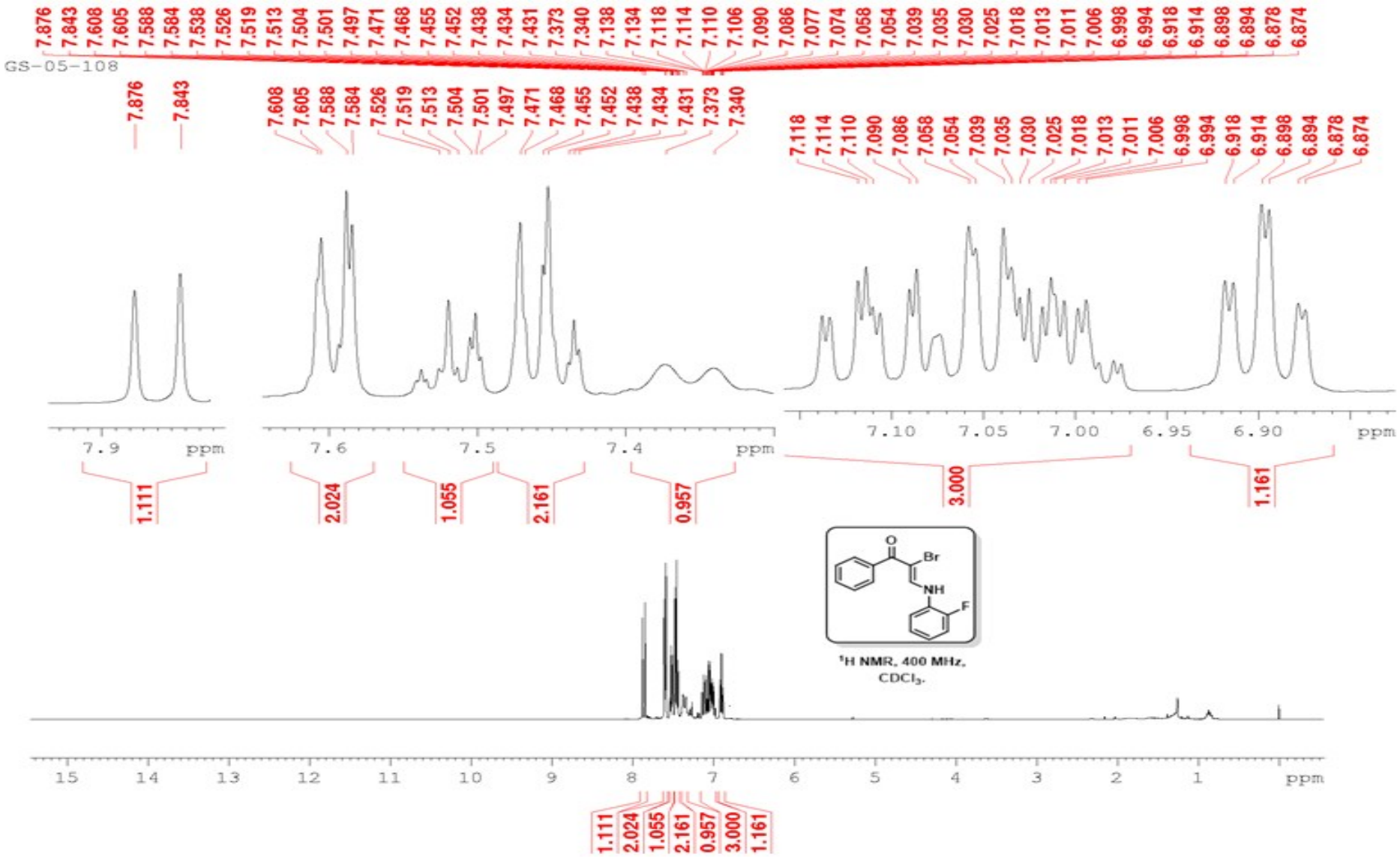
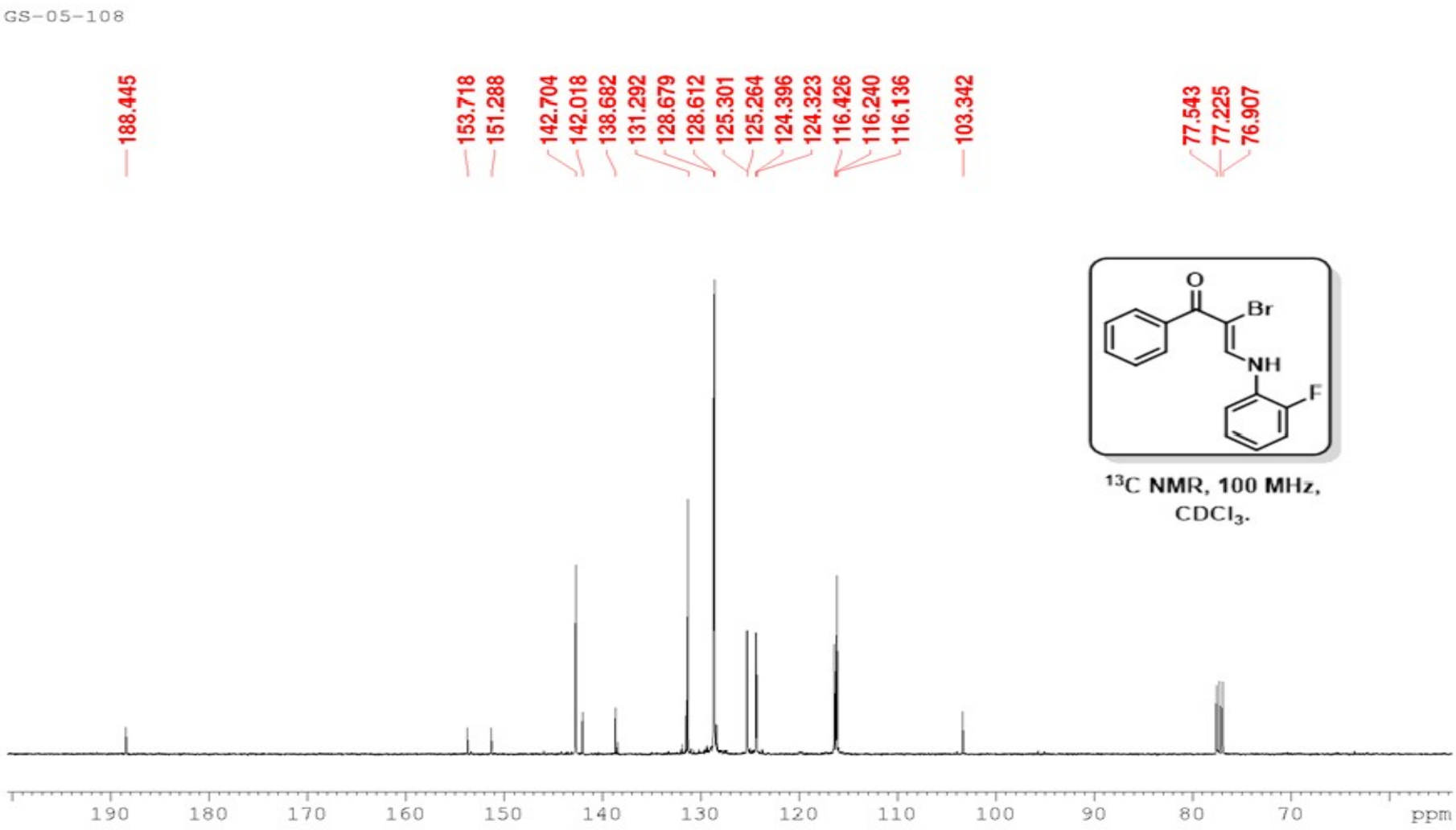


Figure 37: ^{1}H NMR Compound 2k



^{13}C NMR, 100 MHz, $CDCl_3$.

Figure 38: ^{13}C NMR Compound 2k

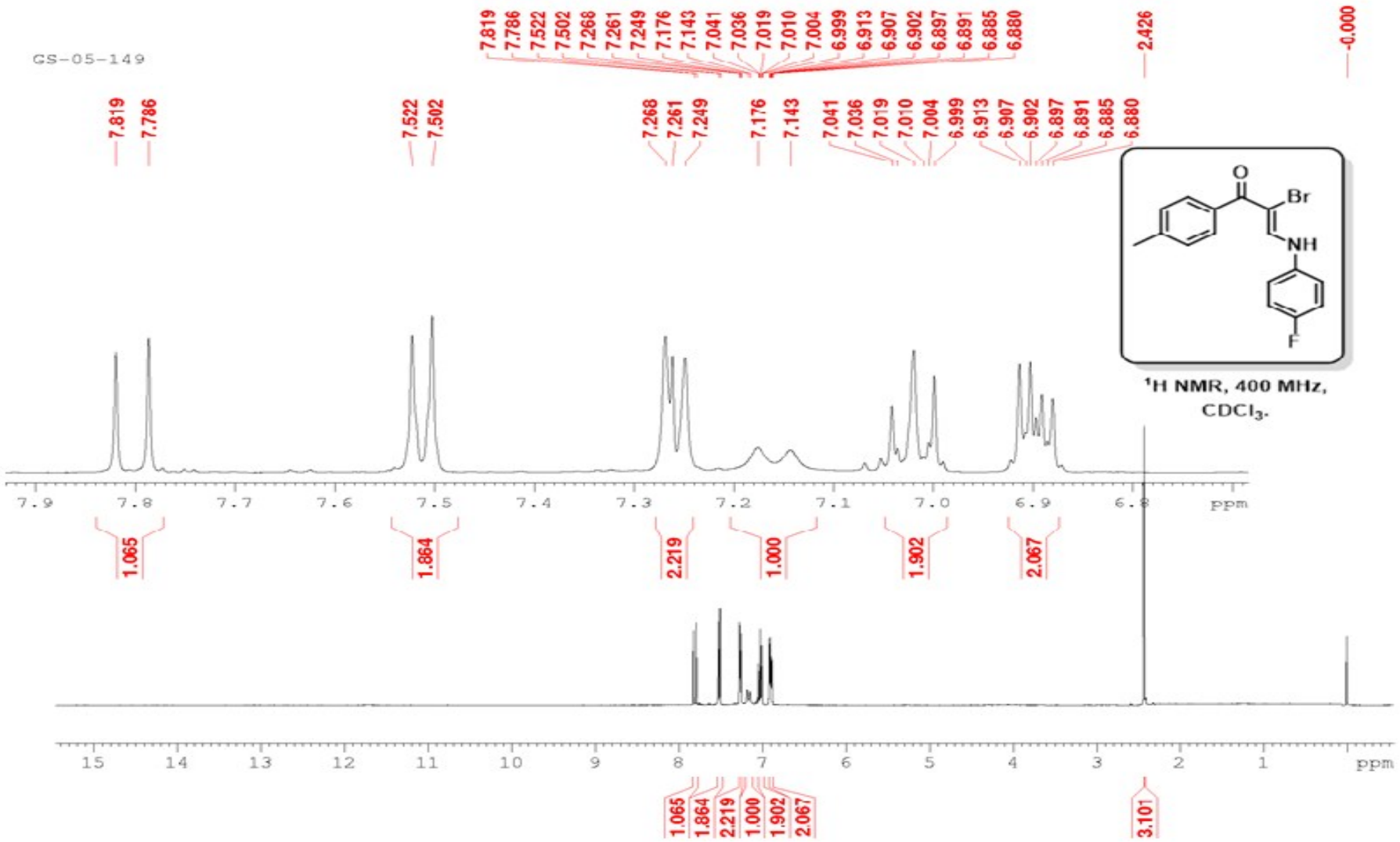


Figure 39: ^{1}H NMR Compound 2l

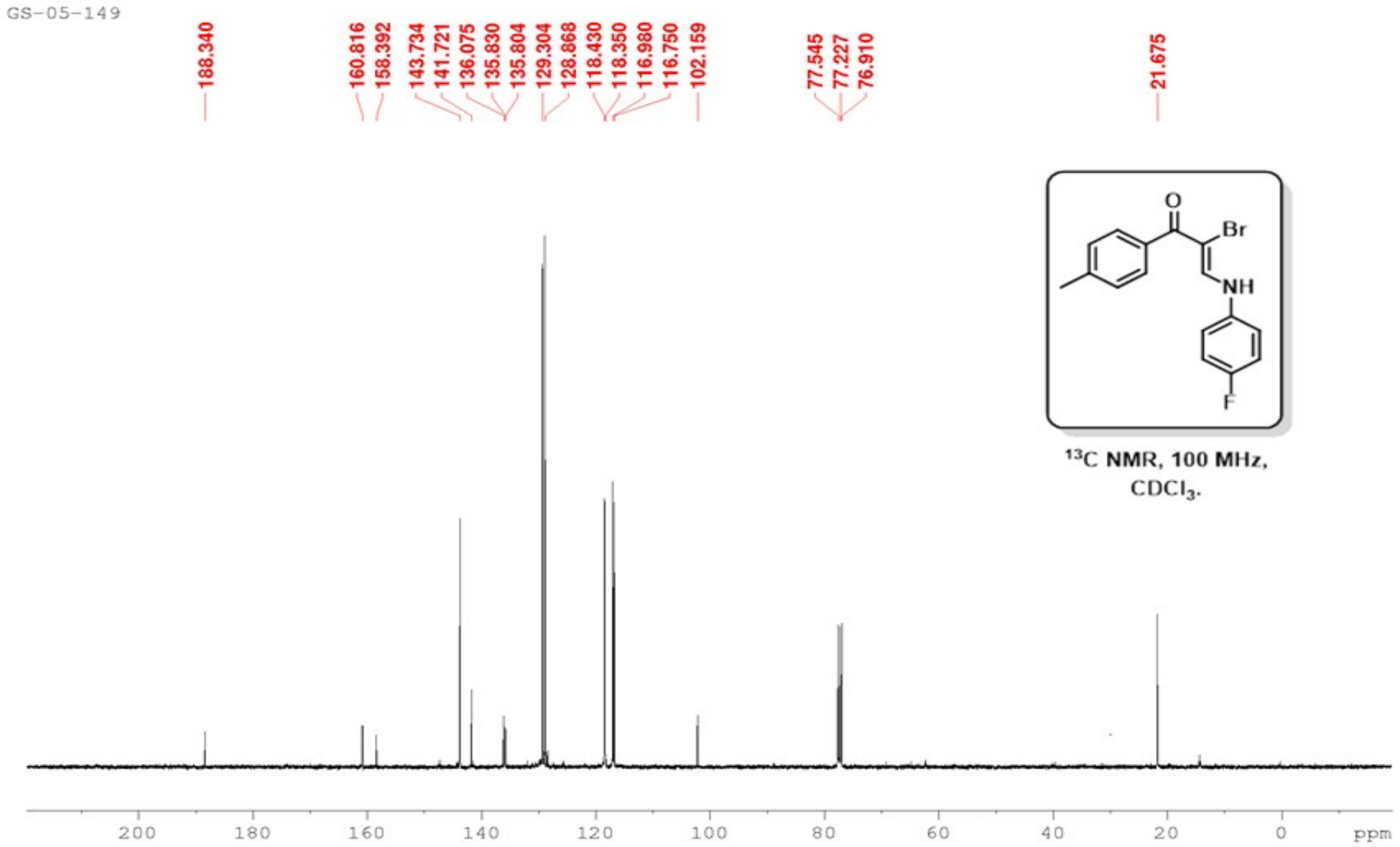


Figure 40: ^{13}C NMR Compound 2l

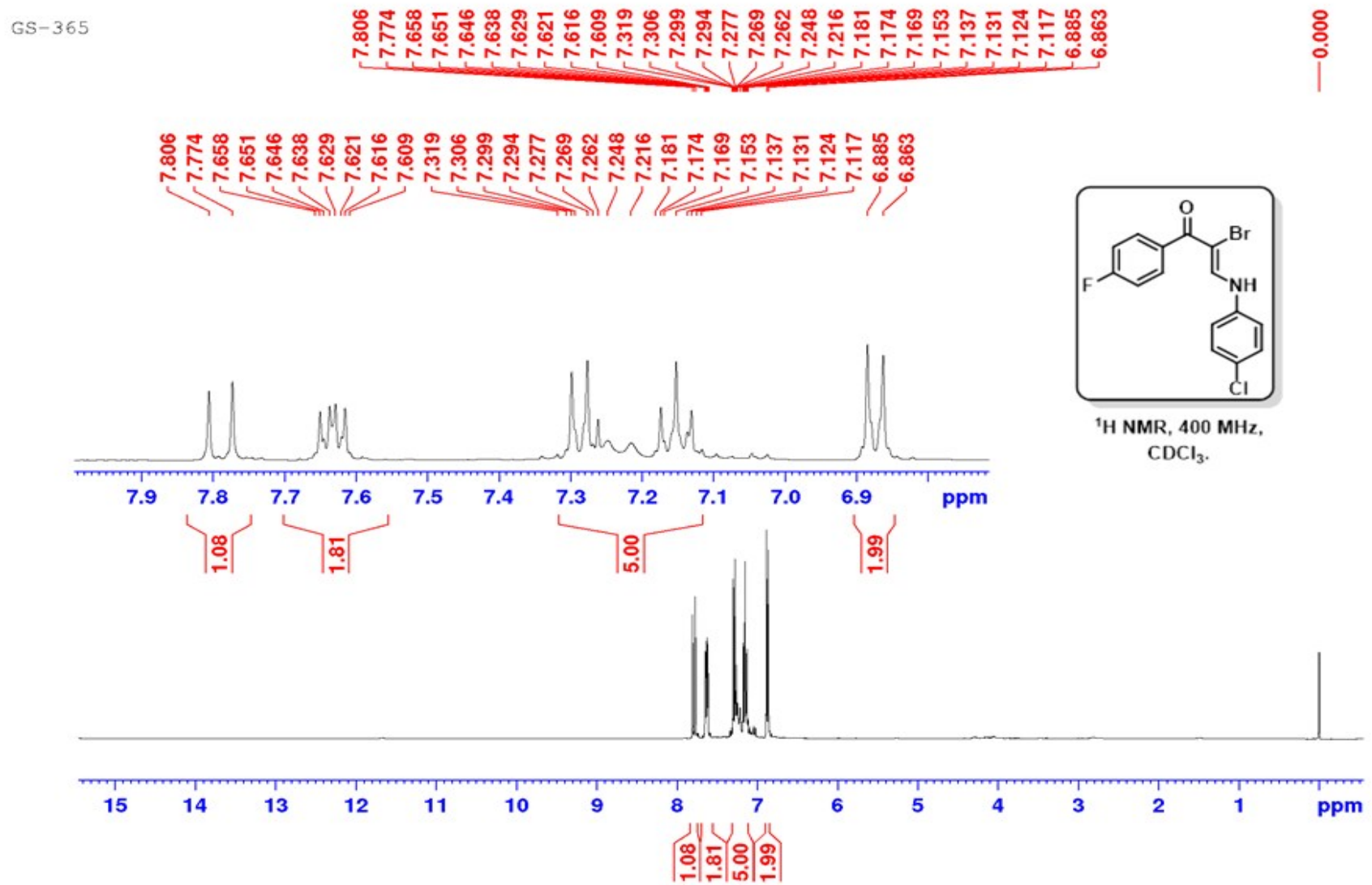


Figure 41: ^{1}H NMR Compound 2m

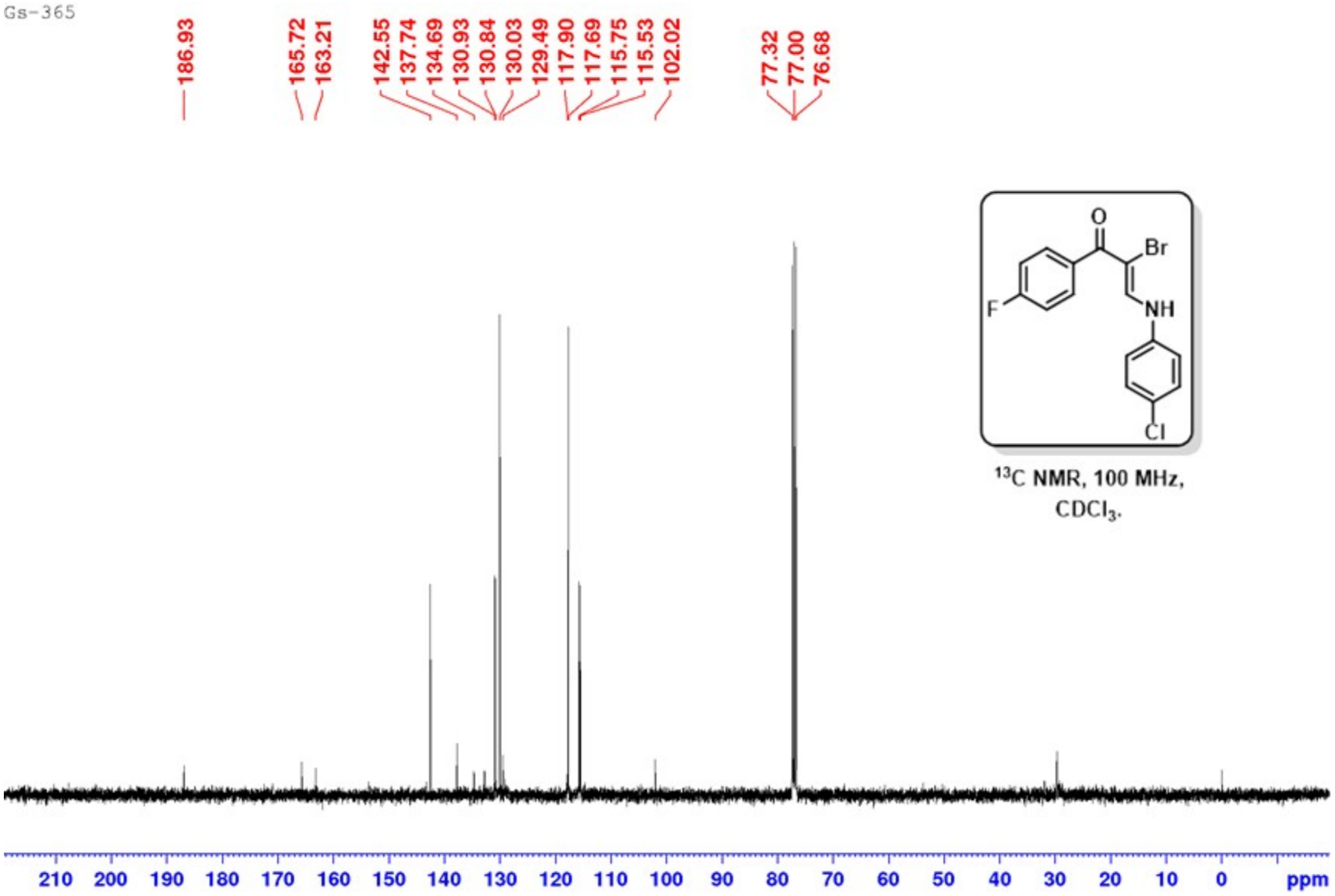


Figure 42: ^{13}C NMR Compound 2m

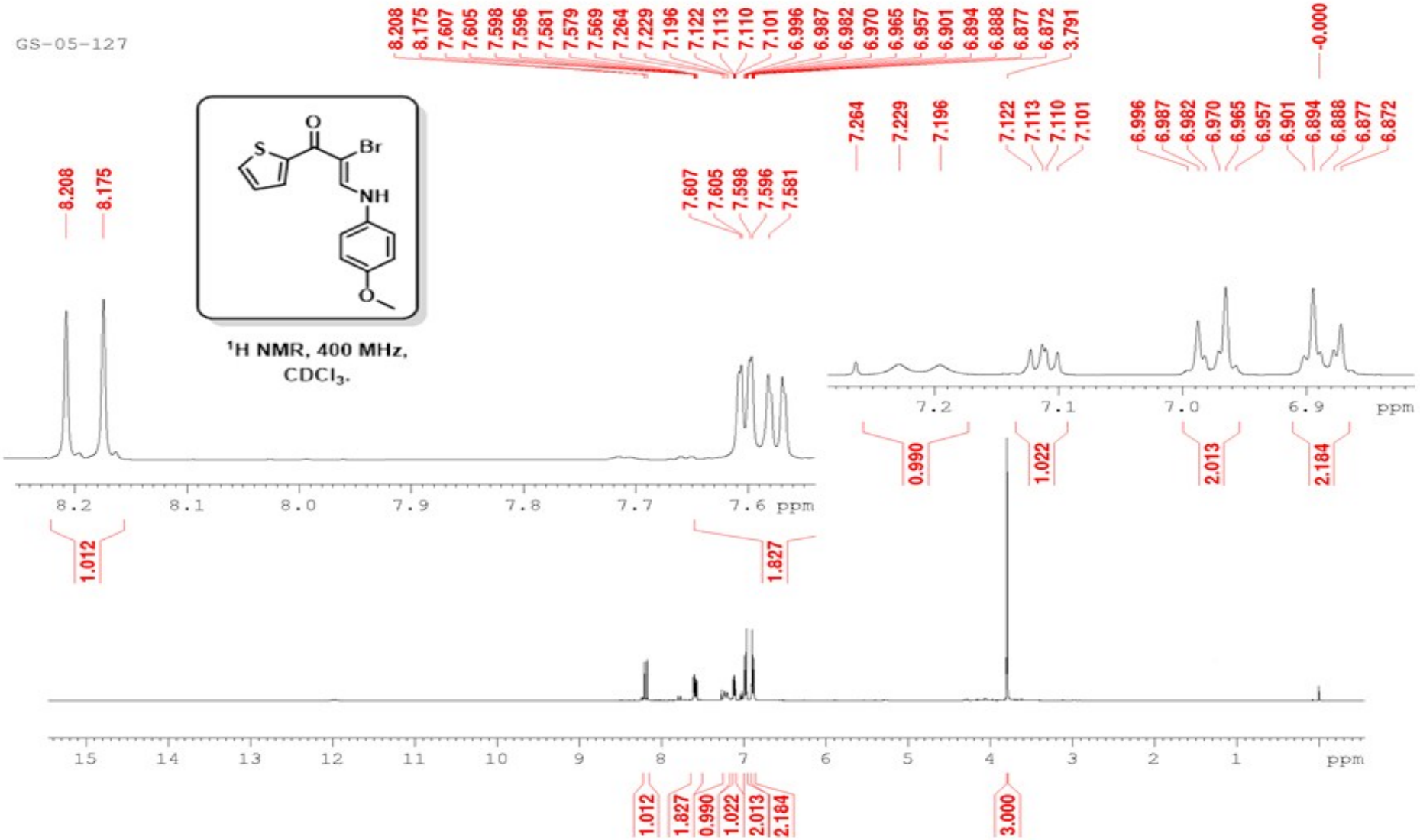


Figure 43: ^{1}H NMR Compound 2n

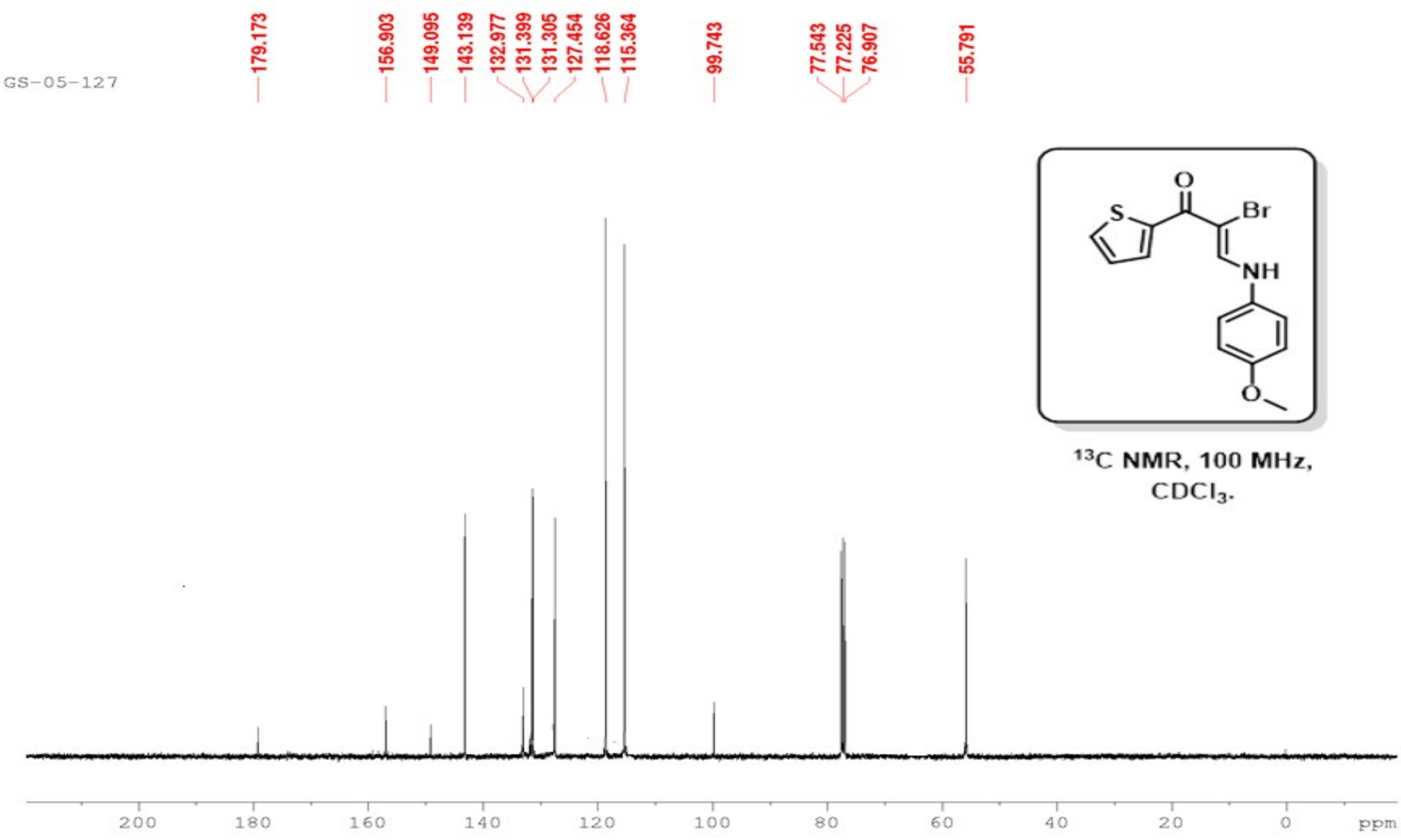


Figure 44: ^{13}C NMR Compound 2n

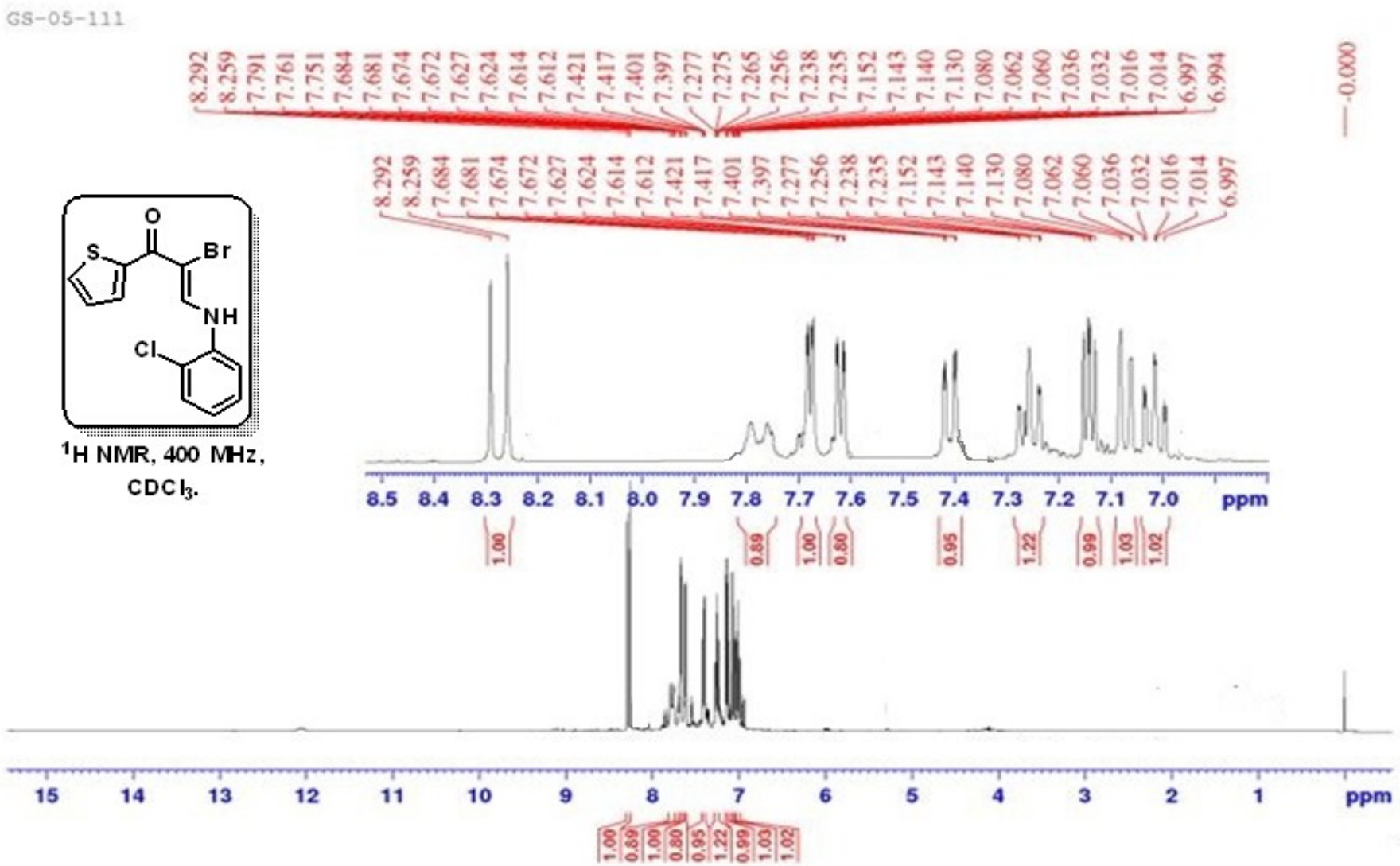


Figure 45 ^{1}H NMR Compound 2o

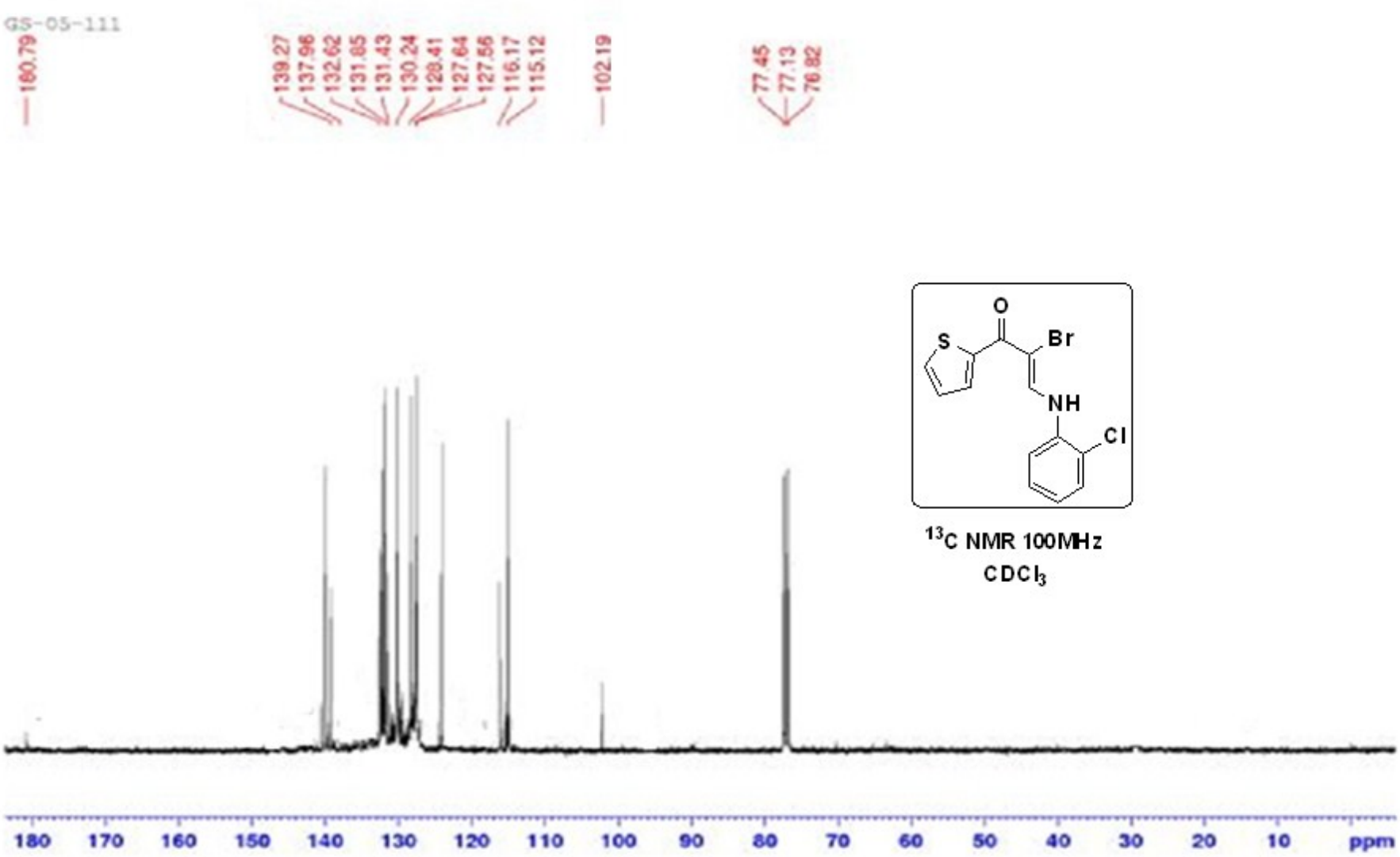


Figure 46: ^{13}C NMR Compound 2o

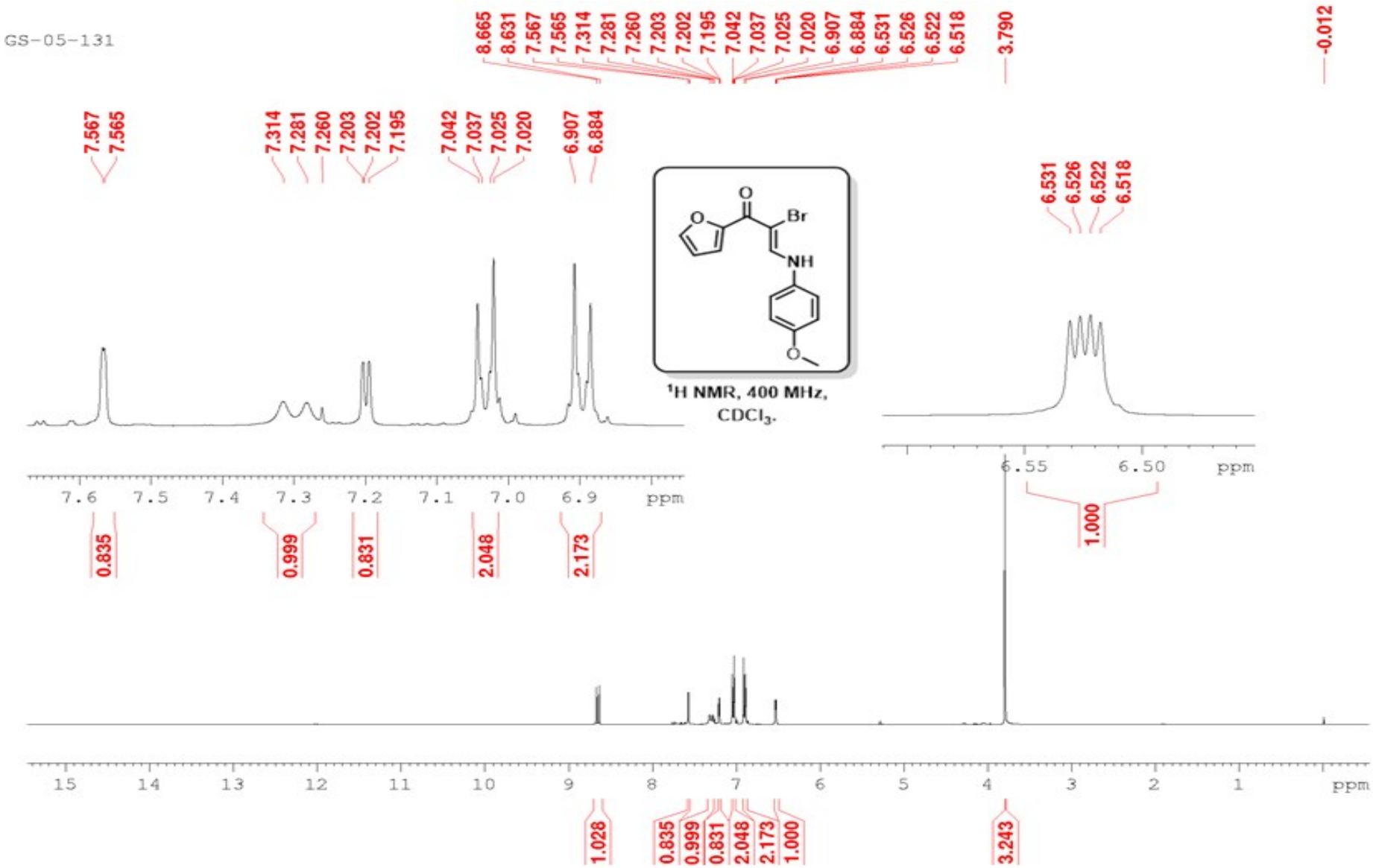


Figure 47: ^{1}H NMR Compound 2p

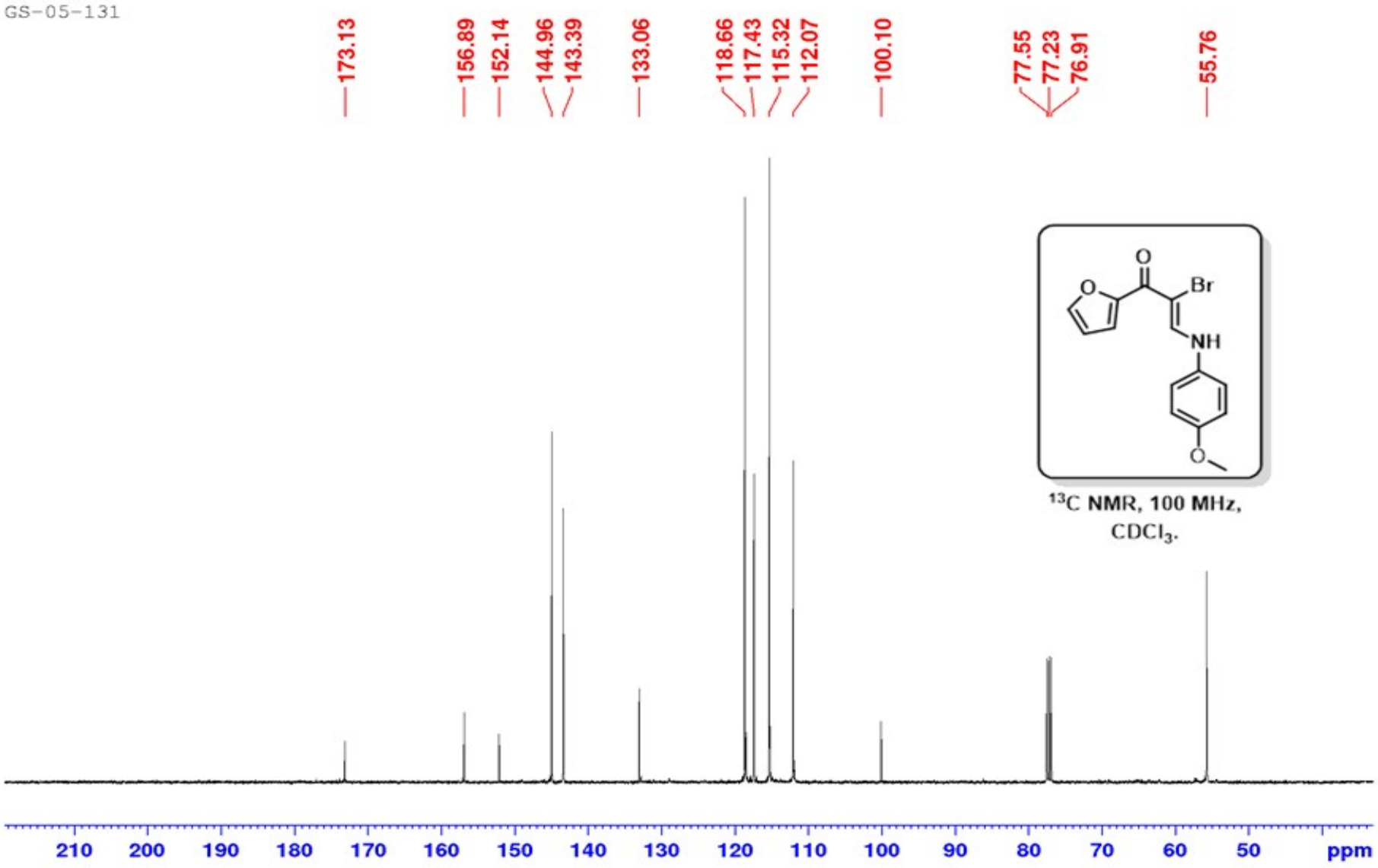


Figure 48: ^{13}C NMR Compound 2p

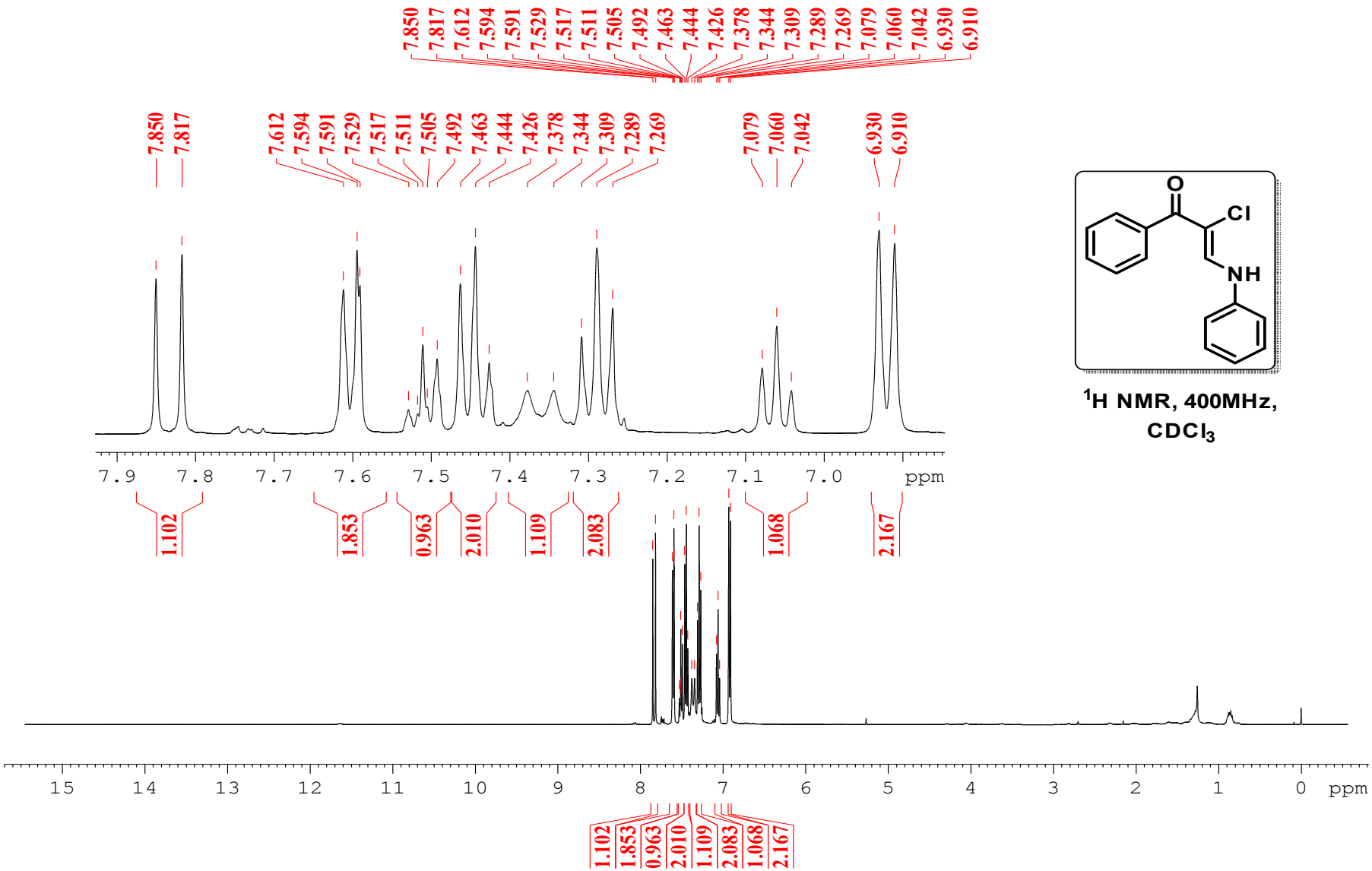


Figure 49: ^{1}H NMR Compound 2r

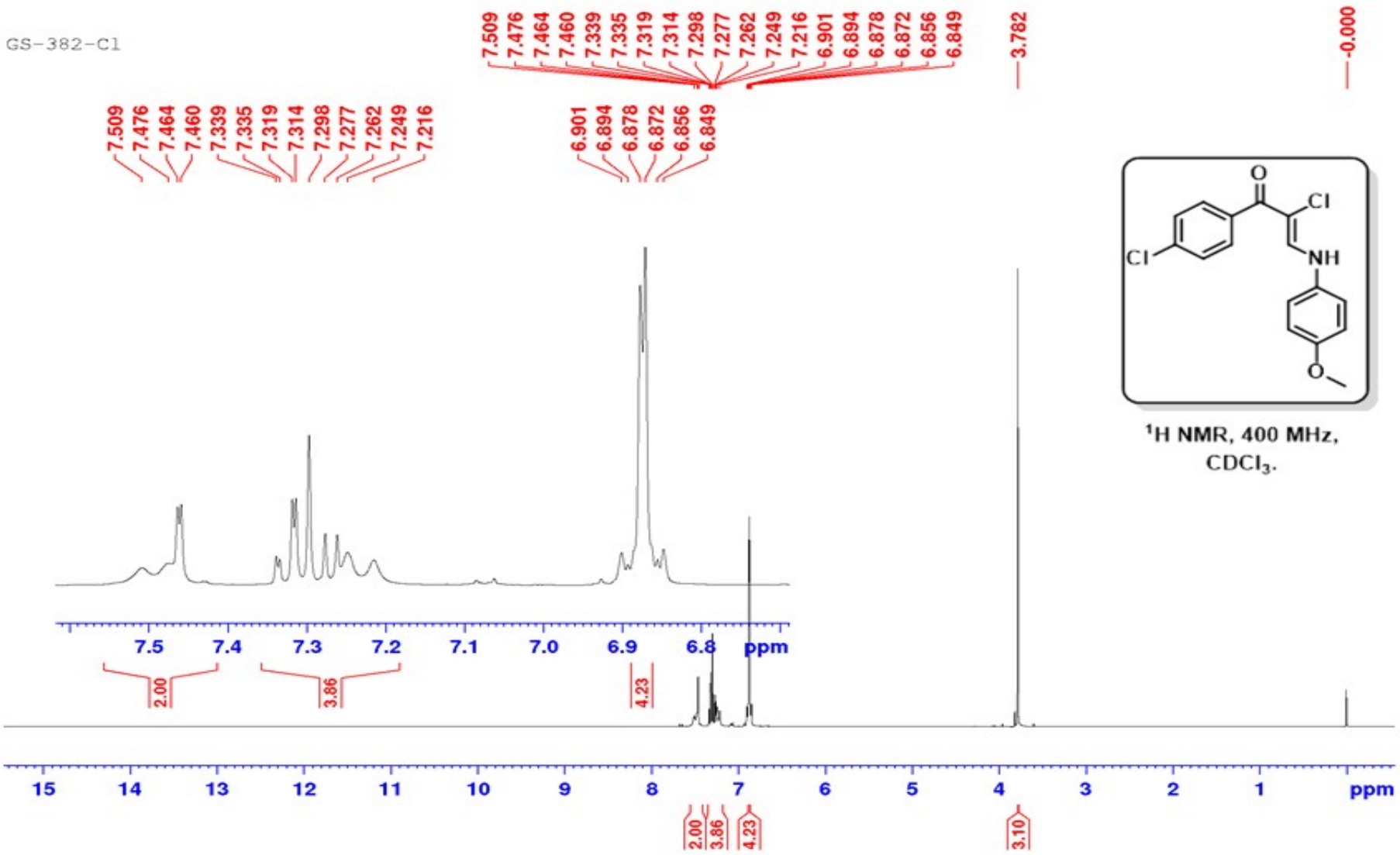


Figure 50: ^{1}H NMR Compound 2s

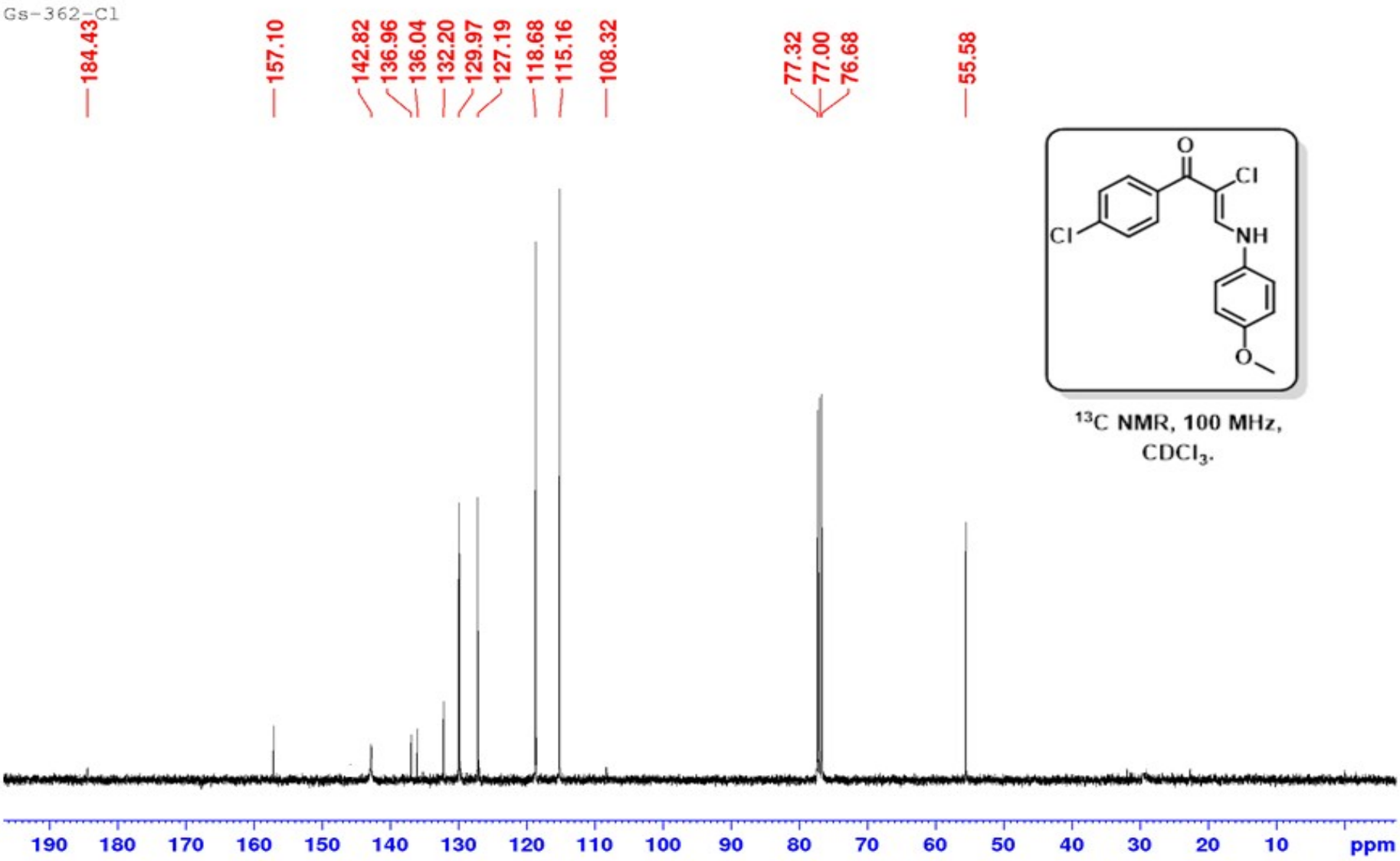


Figure 51: ^{13}C NMR Compound 2s

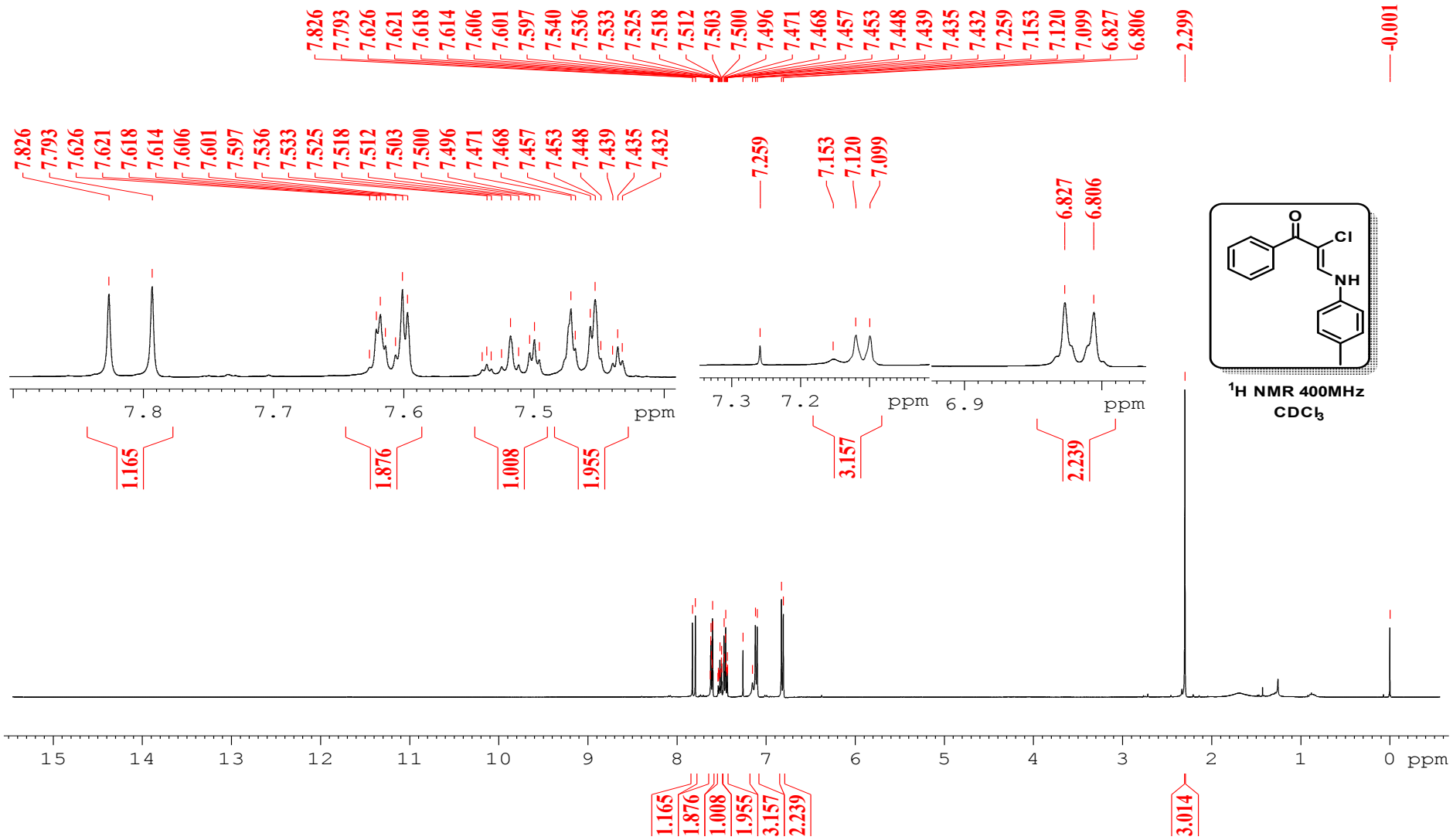


Figure 52: ^{1}H NMR Compound 2t

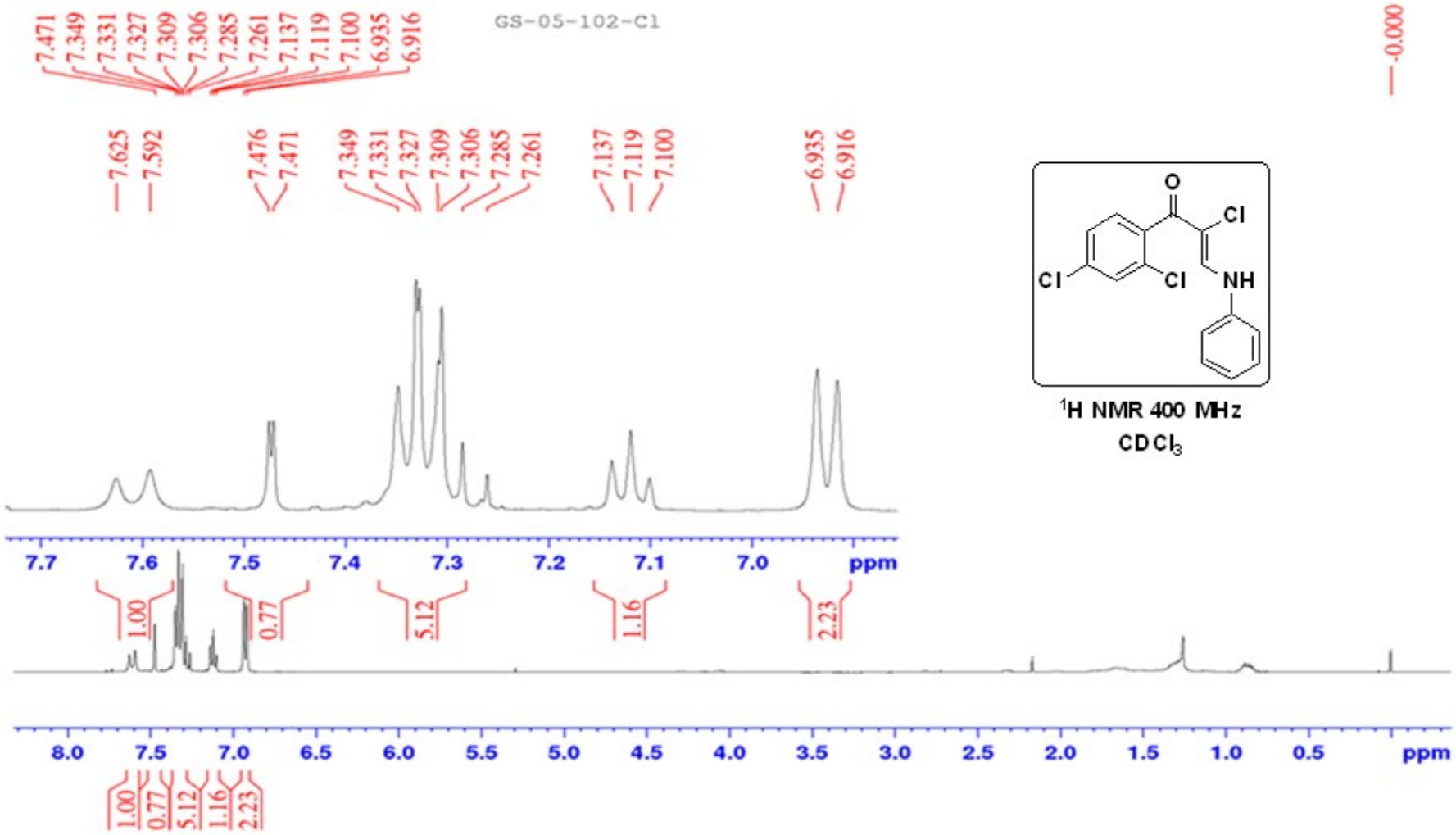


Figure 53: ^{1}H NMR Compound 2u

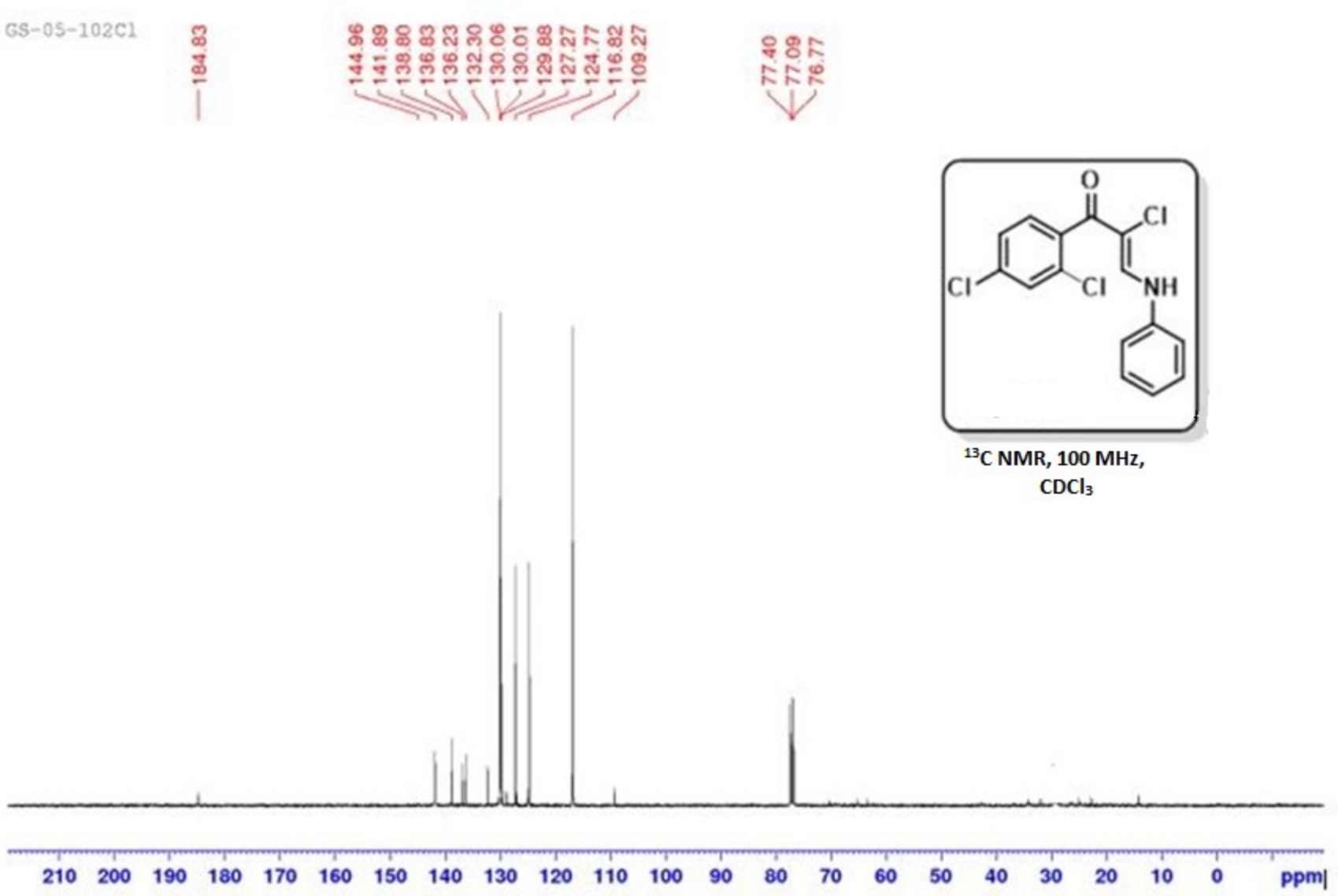


Figure 54: ^{13}C NMR Compound 2u

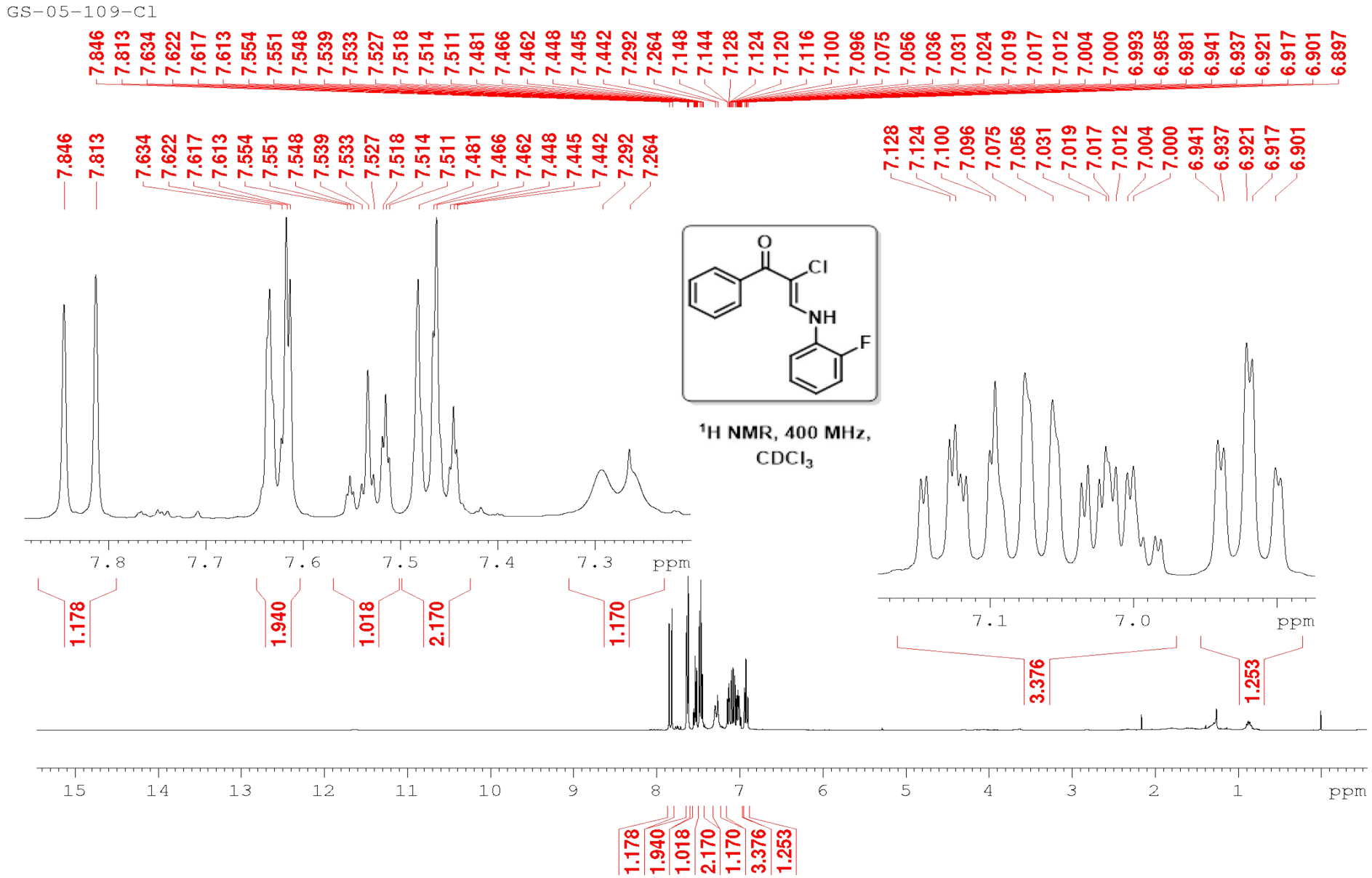


Figure 55: ^{1}H NMR Compound 2v

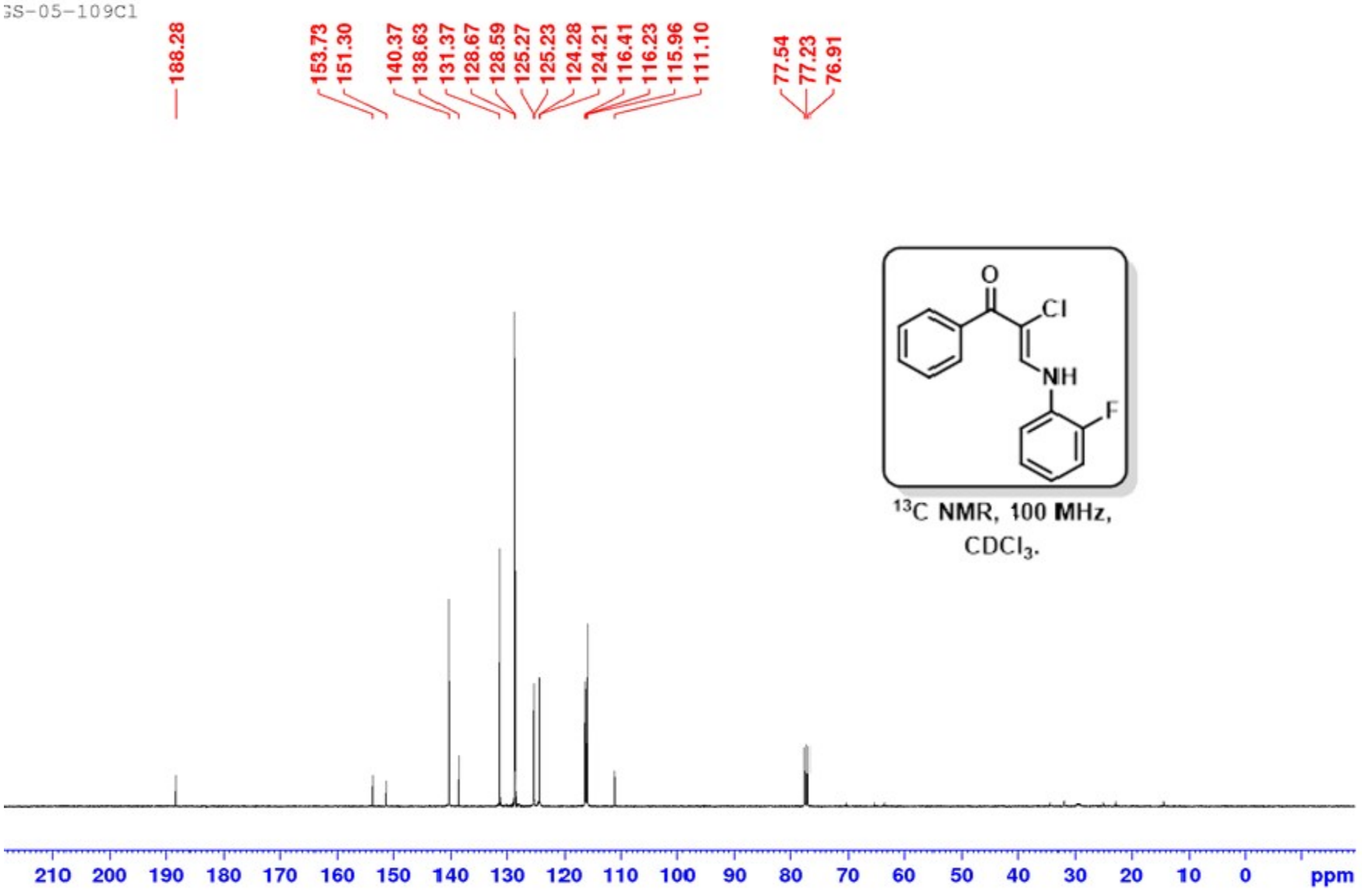


Figure 56: ^{13}C NMR Compound 2v

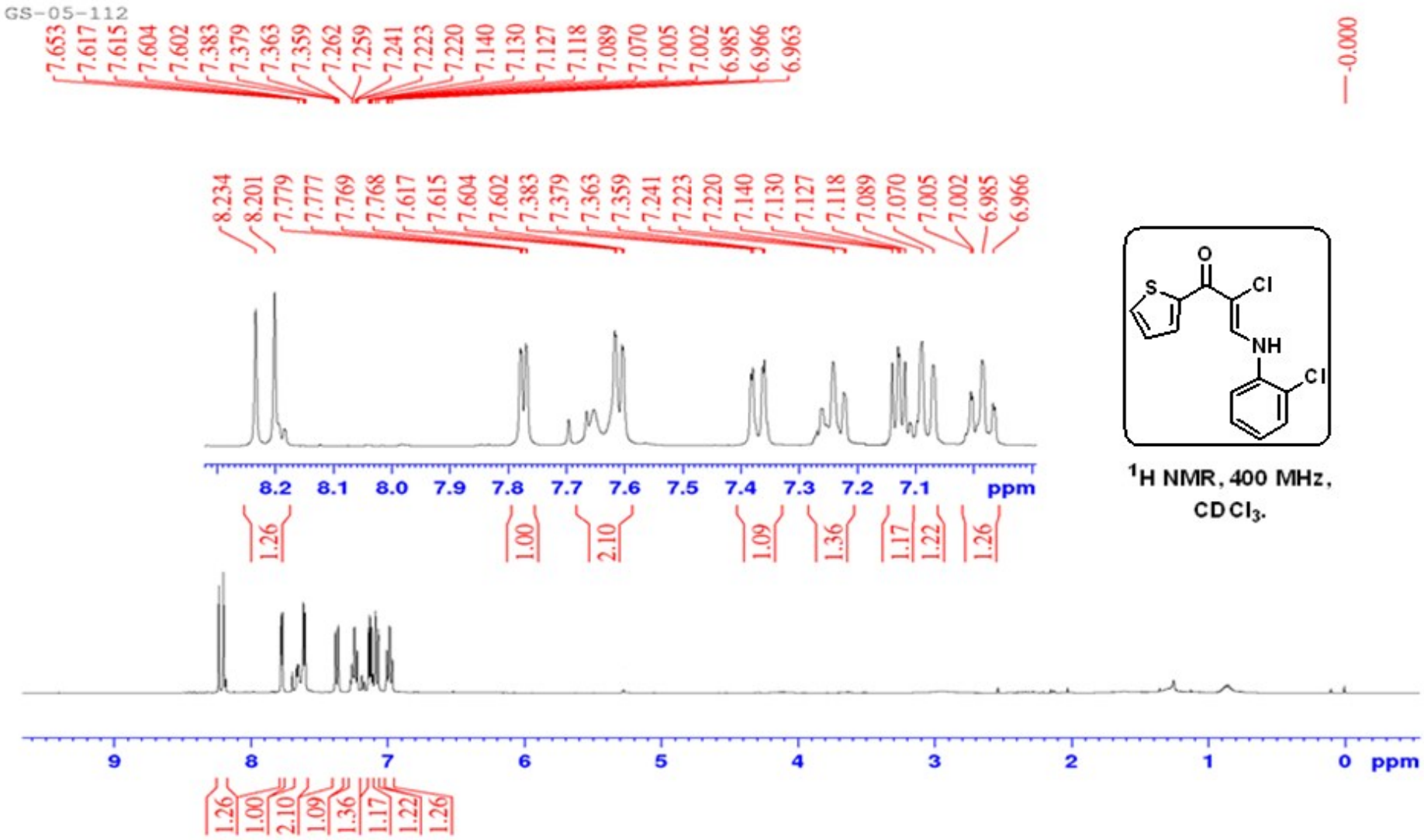


Figure 57: ^{1}H NMR Compound 2w

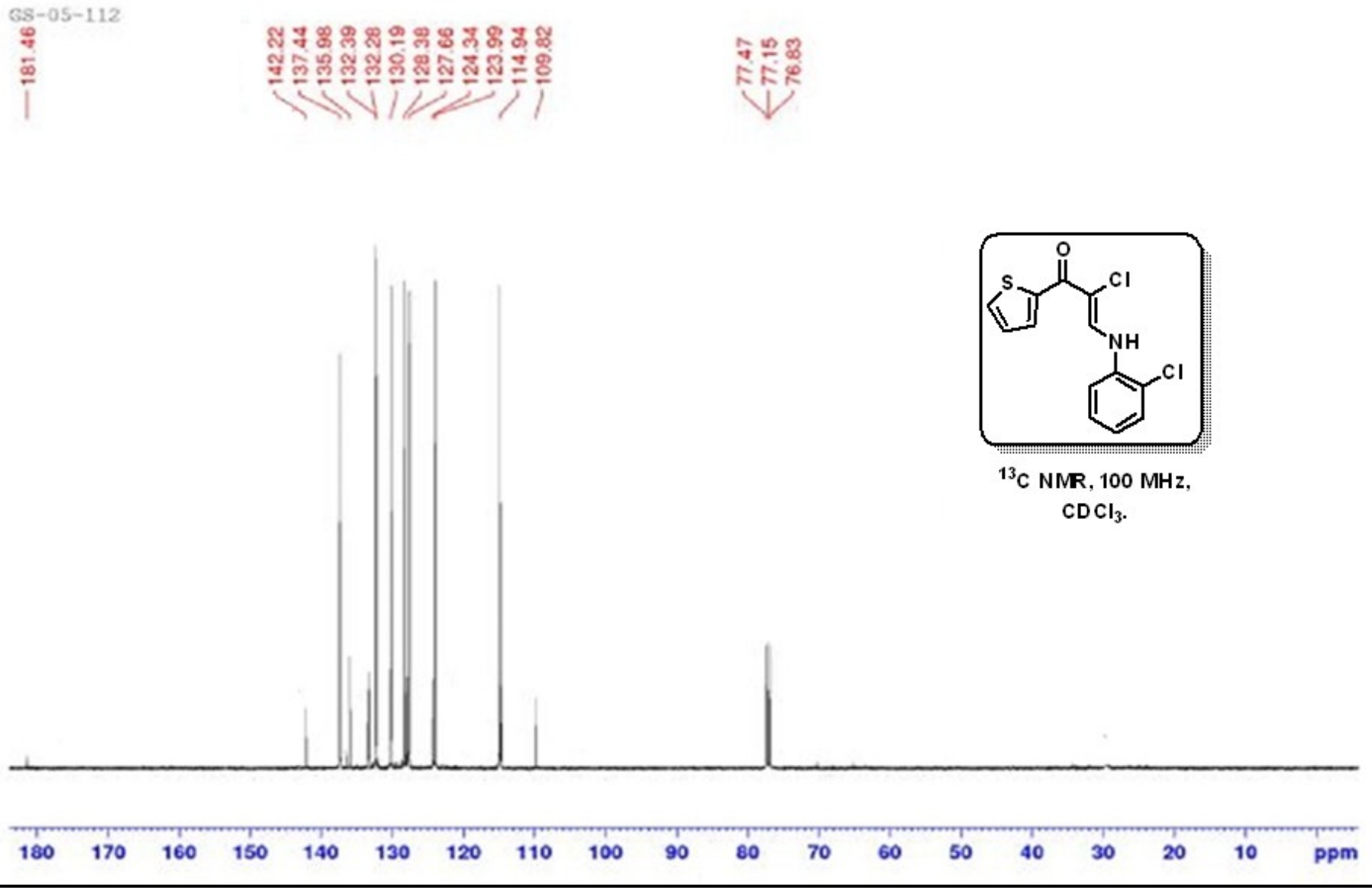


Figure 58: ^{13}C NMR Compound 2w

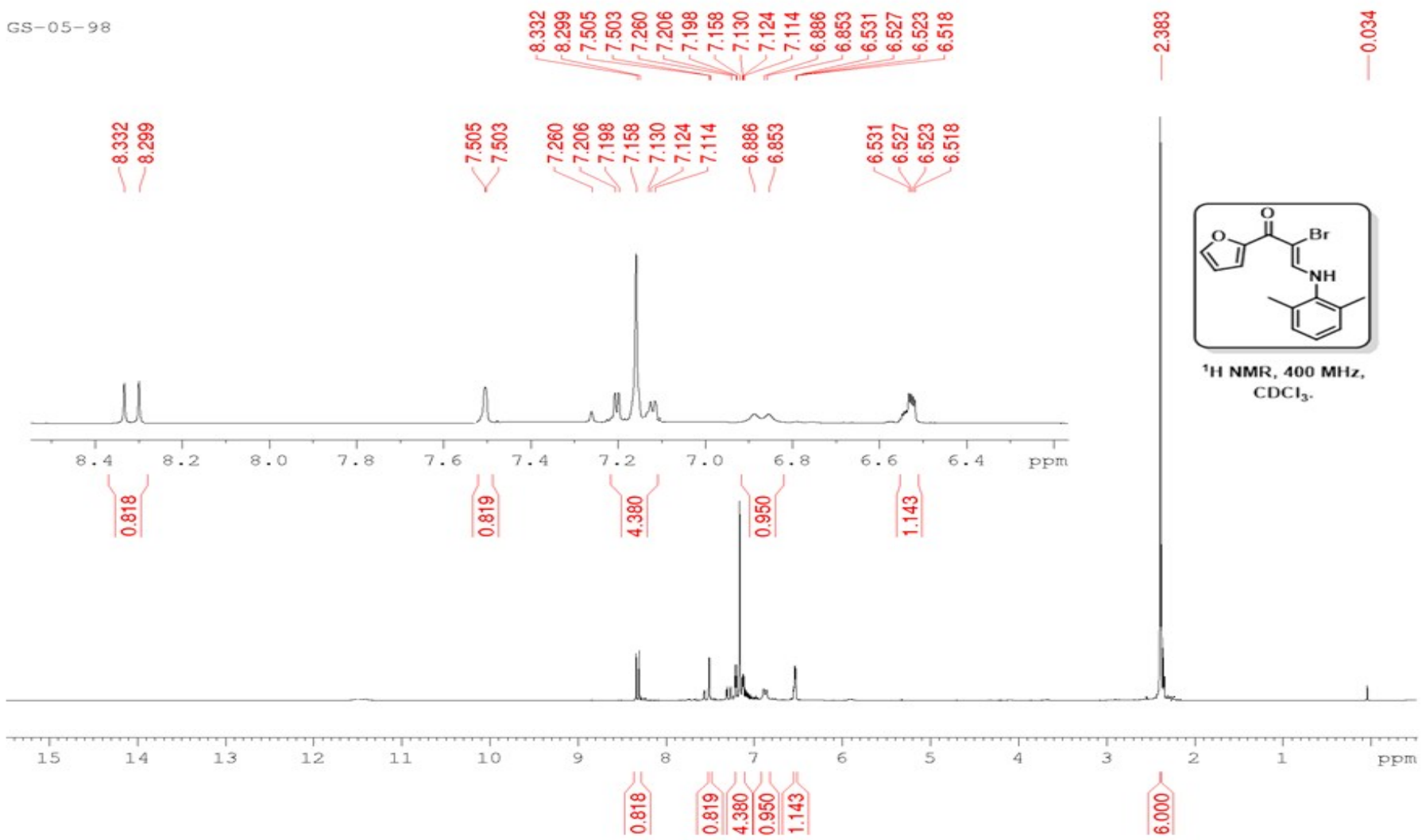


Figure 59: ^{1}H NMR Compound 2x

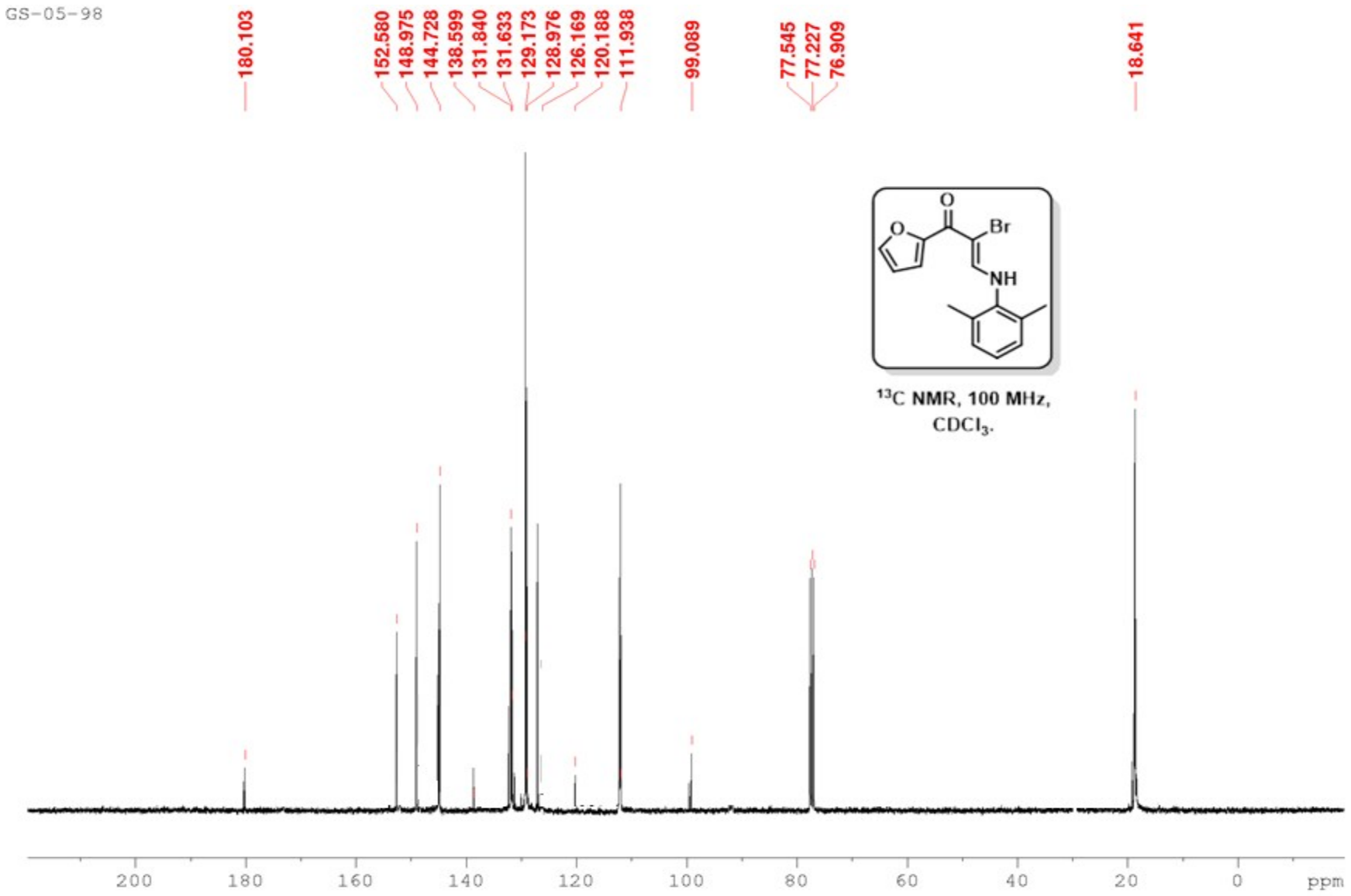


Figure 60: ^{13}C NMR Compound 2x

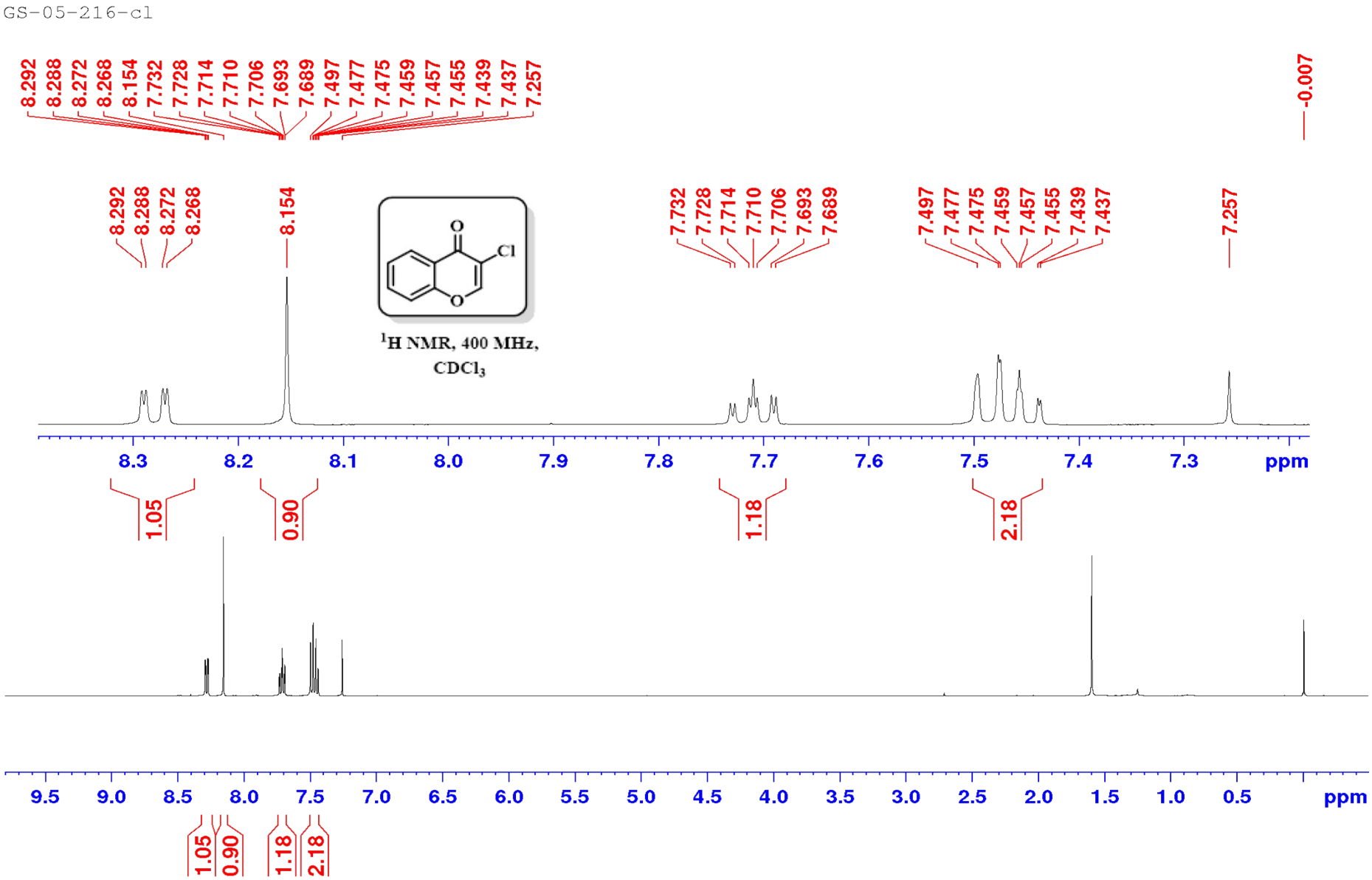


Figure 61: ^{1}H NMR Compound 3a

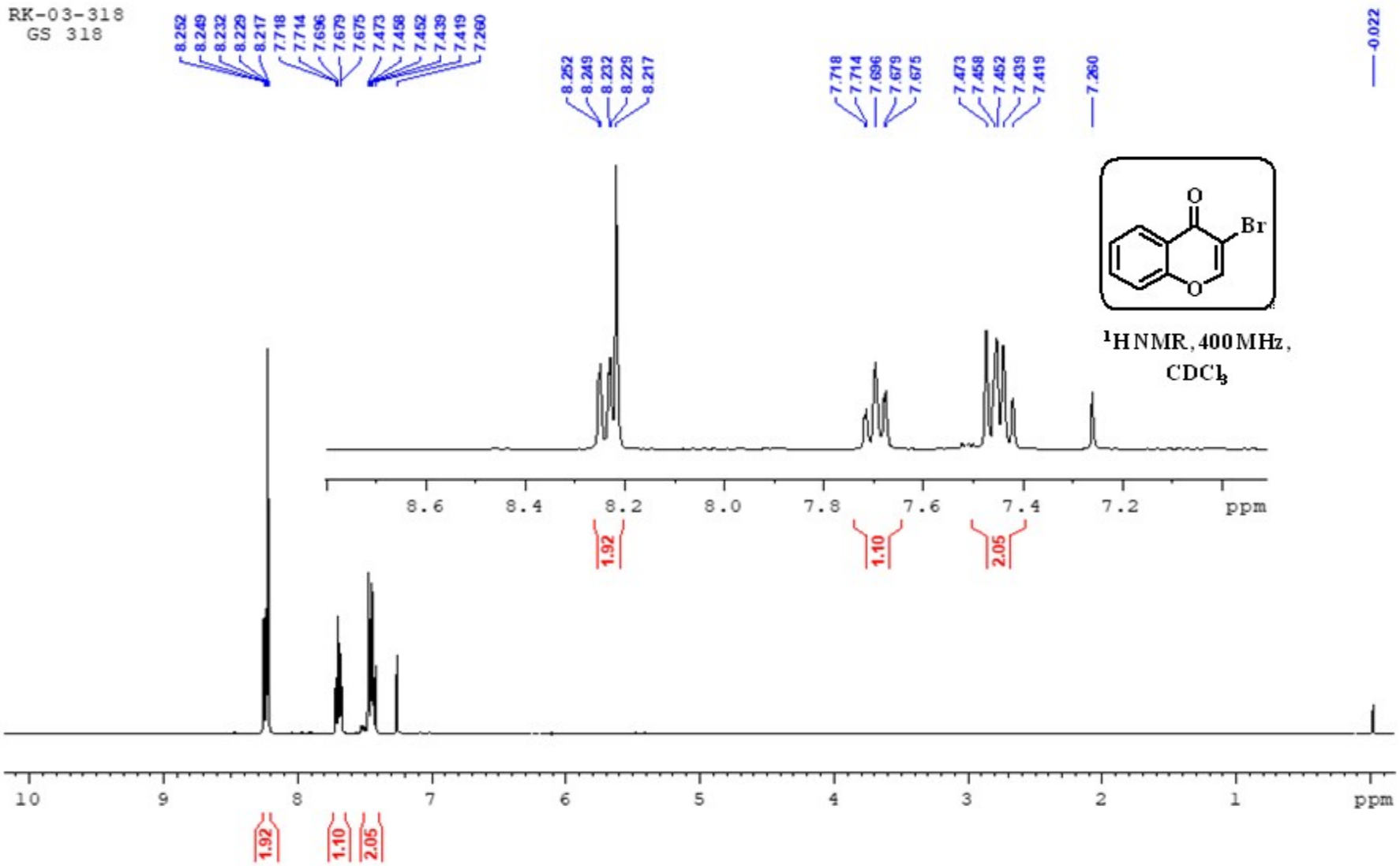


Figure 62: ^{1}H NMR Compound 3b

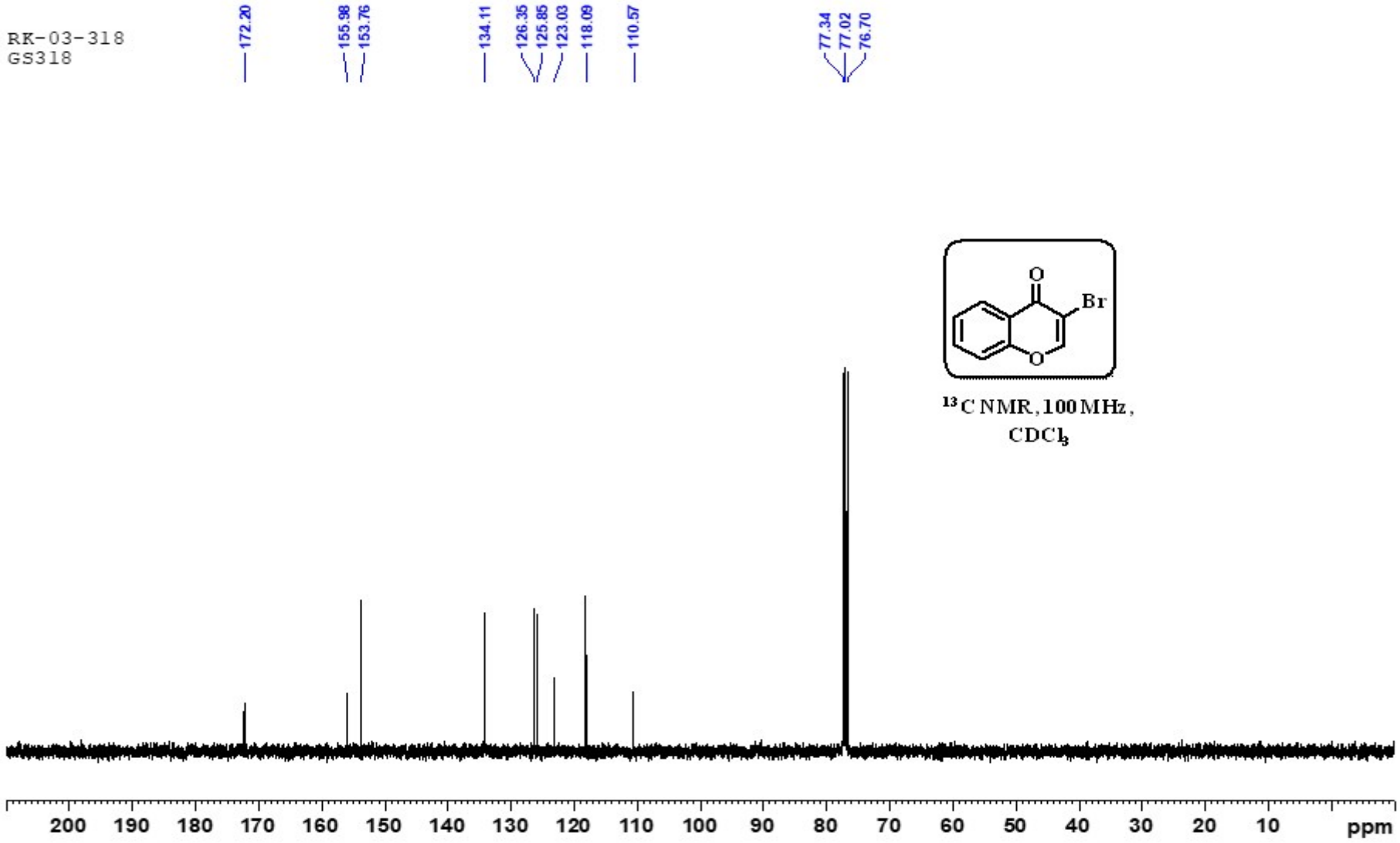


Figure 63: ^{13}C NMR Compound 3b

GS-05-387-Br

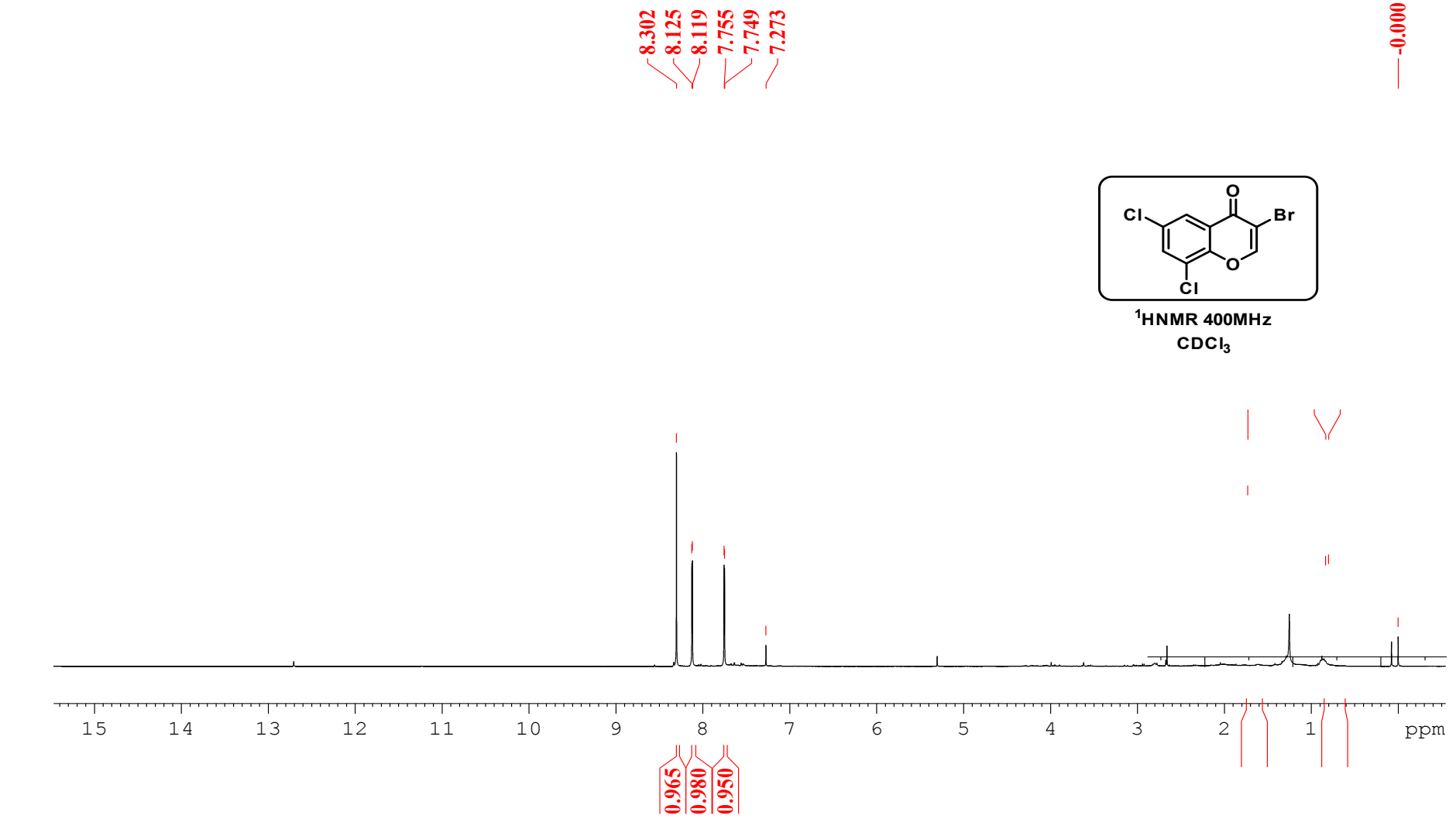

8.302
8.125
8.119
7.755
7.749
7.273
-0.000
Cl
Br
O
O
Cl
1HNMR 400MHz
CDCl3
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.965
0.980
0.950

Figure 64: ^{1}H NMR Compound 3c

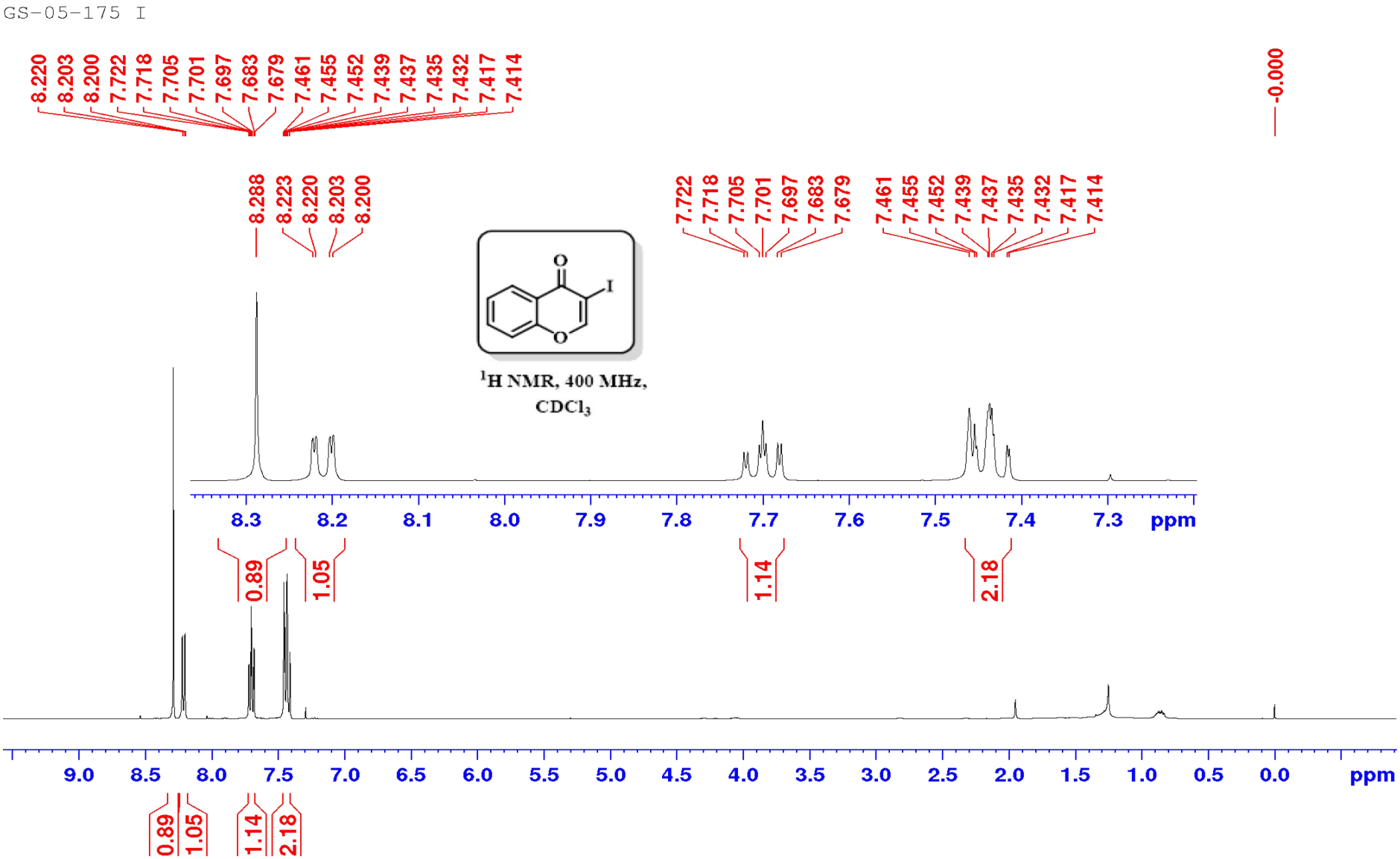


Figure: 65 ^{1}H NMR Compound 3d