Supporting Information

for

Rh(III)-Catalyzed C−H Activation/Cycloaddition of Benzamides and Methylenecyclopropanes: Divergence in Ring Formation

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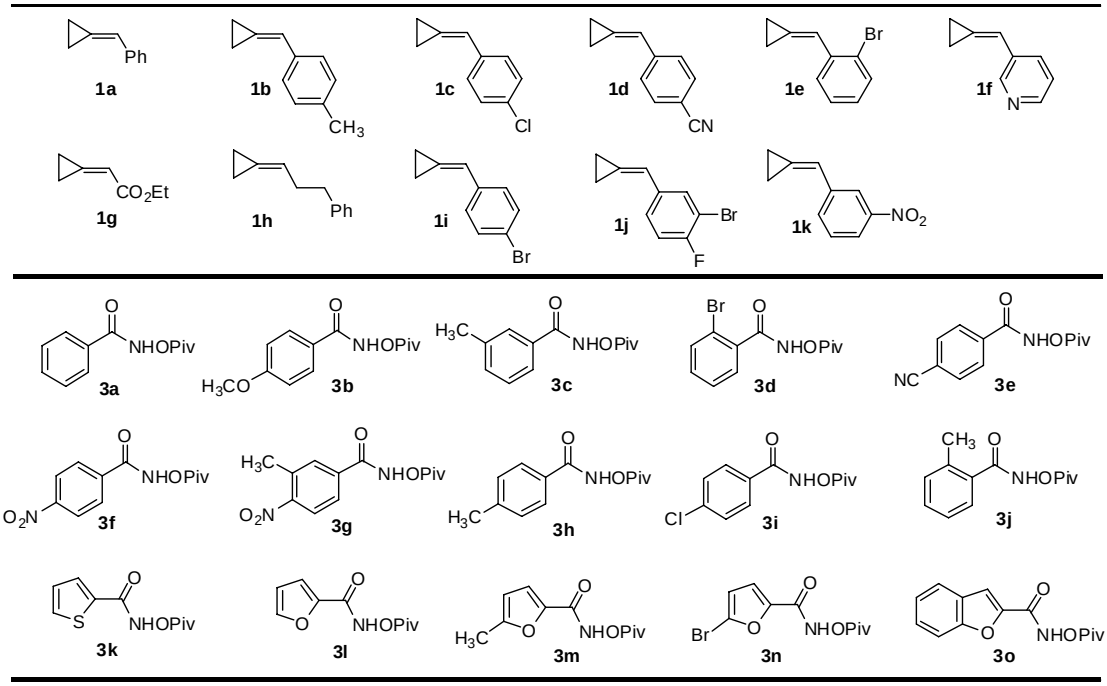
Contents

General Information:

Infrared spectra were obtained on a FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III 500 or BRUKER AVANCE III 400 spectrometer. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were referenced relative to residual solvent signal (^{1}HNMR: δ 7.26 ppm, ^{13}C NMR: δ 77.0 ppm). The following abbreviations are used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). HRMS were performed on Waters GCT Premier Time of Flight Mass Spectrometer (EI) or Agilent Technologies 6224 TOF LC/MS apparatus (ESI). Melting points were measured with micro melting point apparatus.

The methylenecyclopropanes **1**, *N*-methoxybenzamide **2**, and *N*-pivaloyloxybenzamides **3,** were prepared according to the literature. [1], [2] $[Cp^*RhCl_2]_2$, CsOAc, anhydrous MeOH and d_5-benzoic acid were commercial available.

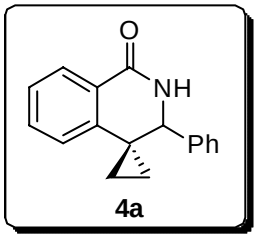


General Procedure:

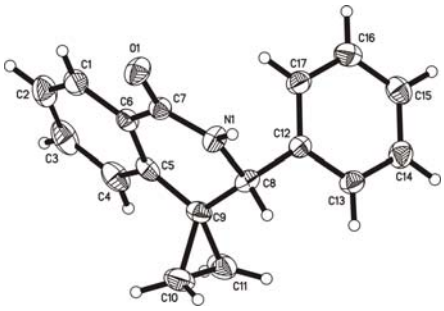
General procedure for synthesis of spiro dihydroisoquinolinones **4**: $[Cp^*RhCl_2]_2$ (2.5 mg, 2 mol%), benzamide (**3a-3j**) (0.2 mmol), CsOAc (38.4 mg, 0.2 mmol) were added to a vial. Methanol (1.0 mL) was added, followed by micro-syringe addition of methylenecyclopropane **1** (0.4 mmol). The micro-syringe was washed with an additional 0.5 mL methanol and added to the reaction solution. The mixture was kept at 30 ^oC under air. After completion (1 h - 2 h), it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:2) as eluent to give the product **4**.

General procedure for synthesis of furan-fused caprolactams **6**: $[Cp^*RhCl_2]_2$ (2.5 mg, 2 mol%), *N*-(pivaloyloxy)furan-2-carboxamide (**3l-3n**) (0.2 mmol), CsOAc (38.4 mg, 0.2 mmol) were added to a vial. Methanol (1.0 mL) was added, followed by micro-syringe addition of methylenecyclopropane **1** (0.4 mmol). The micro-syringe was washed with an additional 0.5 mL methanol and added to the reaction solution. The mixture was kept at 60 ^oC under air. After completion (6 h – 8h), it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:1) as eluent to give the product **6**.

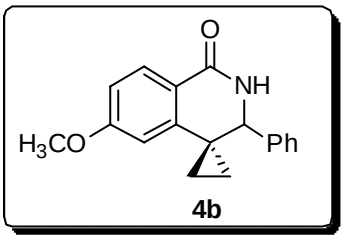
Characterization of Products 4-6:



4a



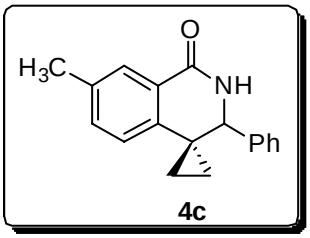
3'-Phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4a). White solid; mp. 172-173 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.14 (dd, J_1 = 1.0 Hz, J_2 = 7.5Hz, 1H), 7.44 (m, 1H), 7.32 (m, 1H), 7.25 (m, 3H), 7.20 (m, 2H), 6.91 (b, 1H), 6.87 (d, J = 7.5 Hz, 1H), 4.37 (d, J = 3.0 Hz, 1H), 1.18 (m, 1H), 1.00 (m, 2H), 0.95 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 141.8, 139.5, 132.9, 129.2, 128.4, 128.1, 128.0, 127.4, 126.3, 121.6, 61.9, 23.3, 16.8, 11.4 ppm; IR (KBr) *v* 3200, 3078, 2910, 1656, 1596, 1467, 1400, 1332, 1272, 1022, 752, 698 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{15}NO$ [M^+] 249.1154; found 249.1150.



4b

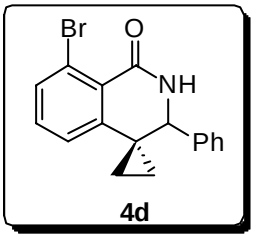
6'-Methoxy-3'-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4b). White solid; mp. 178-180 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.11 (d, J = 8.5 Hz, 1H), 7.26 (m, 3H), 7.22 (m, 2H), 6.83 (dd, J_1 = 2.5 Hz, J_2 = 8.5Hz, 1H), 6.62 (b, 1H), 6.36 (d, J = 2.5 Hz, 1H), 4.33 (d, J = 3.5 Hz, 1H), 3.82 (s, 3H), 1.16 (m, 1H), 1.02 (m, 2H), 0.94 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.0, 163.4, 144.0,

139.7, 130.4, 128.4, 128.0, 127.4, 122.2, 111.0, 107.5, 62.0, 55.3, 23.6, 17.0, 11.5 ppm; IR (KBr) *v* 3179, 2917, 2848, 1663, 1607, 1457, 1407, 1258, 1070, 1026, 826, 708 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{17}NO_2$ [M^+] 279.1259; found 279.1265.



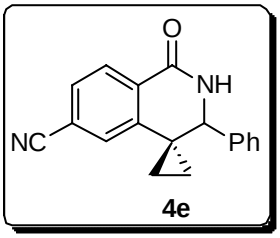
4c

7'-Methyl-3'-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4c). White solid; mp. 206-208 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (s, 1H), 7.27 (m, 4H), 7.20 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.45 (b, 1H), 4.36 (d, *J* = 2.8 Hz, 1H), 2.38 (s, 3H), 1.12 (m, 1H), 0.96 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.3, 139.6, 138.8, 136.0, 133.7, 128.9, 128.5, 128.4, 128.0, 127.4, 121.6, 62.0, 23.1, 20.9, 16.5, 11.2 ppm; IR (KBr) *v* 3191, 3056, 2920, 1655, 1614, 1466, 1431, 1336, 803, 709 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{17}NO$ [M^+] 263.1310; found 263.1307.



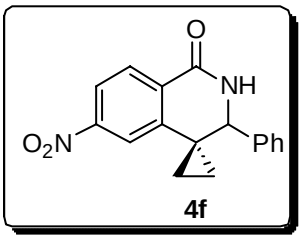
4d

8'-Bromo-3'-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4d). White solid; mp. 201-203 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (dd, J_1 = 0.5 Hz, J_2 = 8.0 Hz, 1H), 7.27 (m, 3H), 7.20 (m, 3H), 6.99 (b, 1H), 6.86 (dd, J_1 = 1.0 Hz, J_2 = 8.0 Hz, 1H), 4.31 (d, *J* = 4.0 Hz, 1H), 1.23 (m, 1H), 1.11 (m, 1H), 1.01 (m, 1H), 0.95 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.0, 144.5, 138.6, 133.7, 132.5, 128.4, 128.3, 128.0, 127.3, 122.8, 121.6, 60.8, 25.2, 15.9, 11.2 ppm; IR (KBr) *v* 3187, 3061, 2924, 1657, 1588, 1550, 1450, 1381, 1287, 960, 772, 721 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}BrNO$ [M^+] 327.0259; found 327.0251.



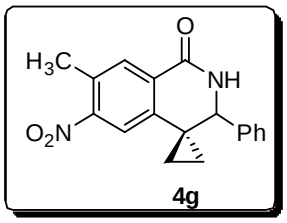
4e

1'-Oxo-3'-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline]-6'-carbonitrile (4e). White solid; mp. 181-183 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.23 (d, J = 10.0 Hz, 1H), 7.60 (dd, J_1 = 1.5 Hz, J_2 = 10.0 Hz, 1H), 7.28 (m, 3H), 7.17 (m, 4H), 4.40 (d, J = 4.0 Hz, 1H), 1.24 (m, 1H), 1.13 (m, 2H), 0.99 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.3, 143.1, 138.6, 132.9, 129.9, 128.8, 128.7, 128.4, 127.2, 125.8, 118.1, 116.2, 61.5, 23.4, 17.5, 11.8 ppm; IR (KBr) v 3227, 3062, 2924, 2221, 1674, 1552, 1453, 1287, 778, 701 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{14}N_2O$ [M^+] 274.1106; found 274.1104.



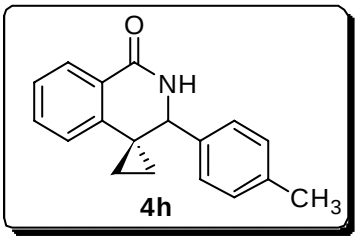
4f

6'-Nitro-3'-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4f). Yellow solid; mp. 155-156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.77 (s, 1H), 7.29 (m, 3H), 7.19 (m, 2H), 6.95 (b, 1H), 4.45 (d, J = 2.4 Hz, 1H), 1.29 (m, 1H), 1.17 (m, 2H), 1.07 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.2, 150.7, 143.9, 138.6, 134.3, 129.6, 128.7, 128.4, 127.2, 121.2, 117.3, 61.6, 23.7, 17.8, 12.0 ppm; IR (KBr) v 3428, 1672, 1617, 1584, 1528, 1341, 1054, 783, 695 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O_3$ [M^+] 294.1004; found 294.1012.



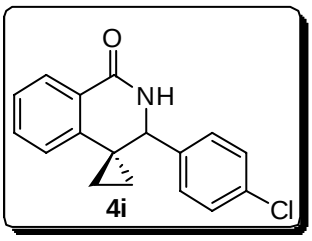
4g

7'-Methyl-6'-nitro-3'-phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4g). Yellow solid; mp. 182-184 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.11 (s, 1H), 7.43 (s, 1H), 7.34 (b, 1H), 7.28 (m, 3H), 7.19 (m, 2H), 4.39 (d, *J* = 3.0 Hz, 1H), 2.60 (s, 3H), 1.28 (m, 1H), 1.14 (m, 2H), 1.00 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.3, 151.7, 141.1, 138.8, 132.8, 132.6, 131.3, 128.7, 128.3, 127.1, 118.4, 61.7, 23.3, 19.8, 17.7, 11.7 ppm; IR (KBr) *v* 3212, 2927, 1665, 1620, 1568, 1516, 1341, 836, 759, 707 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{16}NO_3$ [M^+] 308.1161; found 308.1147.



4h

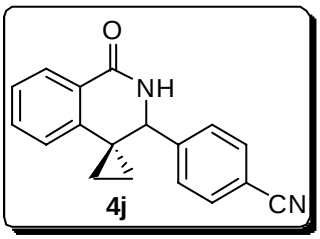
3'-(*p*-Tolyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4h). White solid; mp. 164-165 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.14 (d, *J* = 7.5 Hz, 1H), 7.44 (m, 1H), 7.32 (m, 1H), 7.08 (m, 4H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.69 (b, 1H), 4.38 (s, 1H), 2.29 (s, 3H), 1.10 (m, 1H), 0.98 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 141.9, 137.7, 136.4, 132.8, 129.3, 129.0, 128.0, 127.3, 126.2, 121.5, 61.5, 23.3, 21.0, 16.4, 11.4 ppm; IR (KBr) *v* 3184, 3035, 2911, 1663, 1601, 1571, 1509, 1473, 1406, 1293, 810, 759 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{17}NO$ [M^+] 263.1310; found 263.1302.



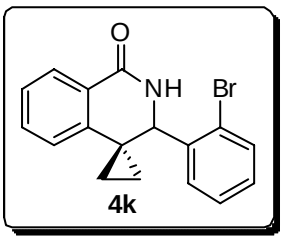
4i

3'-(4-Chlorophenyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4i). White solid; mp. 127-129 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12 (d, *J* = 7.5 Hz, 1H), 7.45 (m, 1H), 7.33 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz,

2H), 7.06 (b, 1H), 6.85 (d, J = 3.0 Hz, 1H), 4.26 (d, J = 2.0 Hz, 1H), 1.28 (m, 1H), 1.06 (m, 1H), 0.98 (m, 1H), 0.93 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.9, 141.4, 138.4, 133.9, 133.0, 129.2, 128.7, 128.6, 128.2, 126.5, 121.6, 61.6, 23.4, 17.6, 11.0 ppm; IR (KBr) v 3203, 3066, 2967, 1660, 1600, 1573, 1468, 1394, 1257, 1090, 799 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}ClNO$ [M^+] 283.0764; found 283.0759.

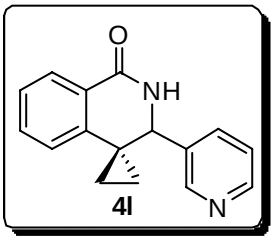


4-(1'-Oxo-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-3'-yl)benzonitrile (4j). Yellow solid; mp. 161-162 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (m, 1H), 7.68 (b, 1H), 7.52 (m, 2H), 7.46 (m, 1H), 7.32 (m, 3H), 6.86 (d, J = 7.5 Hz, 1H), 4.19 (d, J = 3.5 Hz, 1H), 1.47 (m, 1H), 1.19 (m, 1H), 1.02 (m, 1H), 0.94 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 145.7, 140.7, 133.2, 132.2, 129.1, 128.1, 127.9, 126.6, 121.7, 118.4, 111.6, 61.8, 23.1, 19.4, 10.2 ppm; IR (KBr) v 3204, 3071, 2920, 2220, 1659, 1600, 1462, 1392, 1259, 1021, 802, 756 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{14}N_2O$ [M^+] 274.1106; found 274.1104.

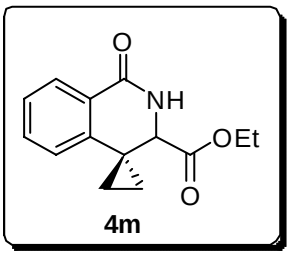


3'-(2-Bromophenyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4k). White solid; mp. 196-197 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 7.50 (m, 2H), 7.34 (m, 1H), 7.23 (m, 1H), 7.11 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.58 (b, 1H), 4.59 (d, J = 4.0 Hz, 1H), 1.45 (m, 1H), 1.23 (m, 1H), 0.98 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.1, 141.9, 139.4, 133.2, 133.1, 129.5, 129.0, 128.9, 128.4, 127.7, 126.4, 124.0, 121.1, 60.7, 21.8, 20.5, 10.9 ppm; IR

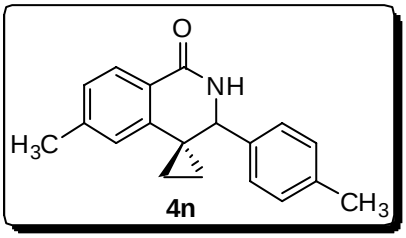
(KBr) *v* 3179, 3037, 2919, 1656, 1600, 1558, 1457, 1410, 1022, 748 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}BrNO$ [M^+] 327.0259; found 327.0254.



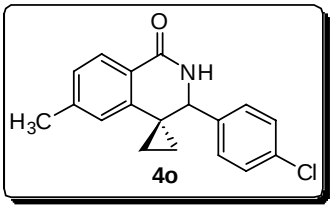
3'-(Pyridin-3-yl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4l). White solid; mp. 175-177 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.47 (m, 2H), 8.11 (d, *J* = 7.5 Hz, 1H), 7.46 (m, 3H), 7.33 (m, 1H), 7.15 (m, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 4.20 (d, *J* = 4.0 Hz, 1H), 1.43 (m, 1H), 1.18 (m, 1H), 1.01 (m, 1H), 0.91 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 149.1, 148.6, 140.8, 134.5, 133.1, 129.1, 128.1, 126.6, 121.7, 60.0, 23.2, 19.2, 10.3 ppm; IR (KBr) *v* 3177, 3032, 2913, 1657, 1600, 1569, 1476, 1408, 1300, 1024, 802, 760, 703 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{14}N_2O$ [M^+] 250.1106; found 250.1103.



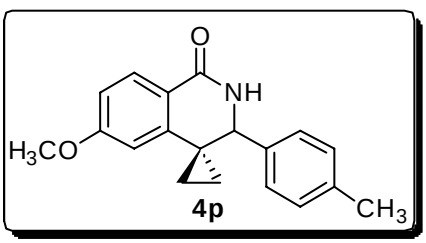
Ethyl 1'-oxo-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline]-3'-carboxylate (4m). White solid; 159-160 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, *J* = 7.6 Hz, 1H), 7.41 (m, 2H), 7.29 (m, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.52 (d, *J* = 4.4 Hz, 1H), 1.58 (m, 1H), 1.34 (m, 1H), 1.23 (m, 1H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.6, 166.4, 140.0, 132.7, 129.0, 128.0, 126.5, 121.1, 61.4, 61.1, 21.2, 20.3, 14.0, 9.5 ppm; IR (KBr) *v* 3192, 3070, 2946, 1728, 1669, 1194, 1024, 765 cm^{-1}; HRMS (ESI) (*m/z*): calcd for $C_{14}H_{15}NO_3$ ([M+H]$^+$), 246.1130; found 246.1138.



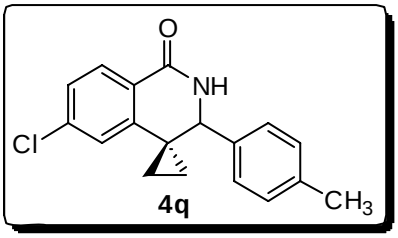
6'-Methyl-3'-(*p*-tolyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4n). White solid; mp. 146-147 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 (d, *J* = 7.5 Hz, 1H), 7.09 (m, 5H), 6.67 (m, 1H), 6.65 (s, 1H), 4.33 (d, *J* = 3.0 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 1.13 (m, 1H), 0.96 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.2, 143.3, 141.7, 137.7, 136.5, 129.1, 128.1, 127.3, 127.1, 126.7, 122.1, 61.7, 23.4, 21.8, 21.0, 16.3, 11.3 ppm; IR (KBr) *v* 3176, 3023, 2920, 1658, 1603, 1560, 1468, 1413, 1284, 819 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO$ [M^+] 277.1467; found 277.1465.



3'-(4-Chlorophenyl)-6'-methyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4o). White solid; mp. 168-170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (m, 3H), 6.64 (s, 1H), 6.59 (b, 1H), 4.22 (d, *J* = 2.0 Hz, 1H), 2.34 (s, 3H), 1.25 (m, 1H), 0.98 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 143.6, 141.1, 138.5, 133.8, 128.60, 128.59, 128.2, 127.3, 126.5, 122.2, 61.6, 23.4, 21.9, 17.8, 10.8 ppm; IR (KBr) *v* 3185, 3060, 2918, 1660, 1611, 1567, 1487, 1394, 1276, 1090, 811 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{16}ClNO$ [M^+] 297.0920; found 297.0913.

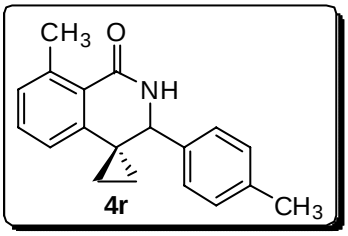


6'-Methoxy-3'-(*p*-tolyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4p). White solid; mp. 177-178 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 8.4 Hz, 1H), 7.08 (m, 4H), 6.81 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 6.56 (m, 1H), 6.34 (d, J = 2.4 Hz, 1H), 4.32 (s, 1H), 3.81 (s, 3H), 2.29 (s, 3H), 1.10 (m, 1H), 0.95 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.0, 163.3, 144.1, 137.7, 136.6, 130.3, 129.0, 127.3, 122.2, 110.9, 107.5, 61.6, 55.2, 23.6, 21.0, 16.6, 11.5 ppm; IR (KBr) v 3179, 2918, 1661, 1602, 1458, 1400, 1324, 1254, 1075, 1029, 803 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO_2$ [M^+] 293.1416; found 293.1411.



4q

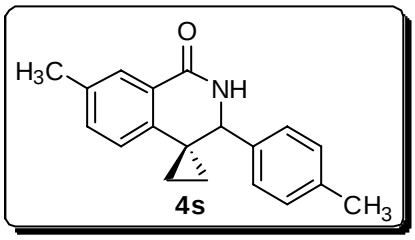
6'-Chloro-3'-(*p*-tolyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4q). White solid; mp. 135-136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.09 (m, 4H), 6.84 (s, 1H), 6.33 (b, 1H), 4.38 (d, J = 2.4 Hz, 1H), 2.31 (s, 3H), 1.04 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.2, 143.9, 139.1, 138.1, 135.9, 129.8, 129.2, 127.7, 127.2, 126.6, 122.1, 61.5, 23.5, 21.0, 16.6, 11.8 ppm; IR (KBr) v 3416, 3187, 2920, 1662, 1590, 1466, 1283, 1094, 840 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}ClNO$ (M^+), 297.0920; found, 297.0922.



4r

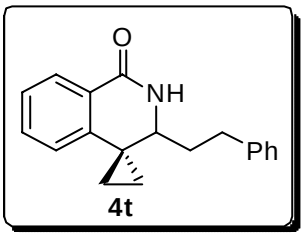
8'-Methyl-3'-(*p*-tolyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4r). White solid; mp. 71-73 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.26 (m, 1H), 7.08 (m, 5H), 6.74 (d, J = 7.5 Hz, 1H), 6.67 (b, 1H), 4.28 (d, J = 3.5 Hz, 1H), 2.74 (s, 3H), 2.29 (s, 3H), 1.11 (m, 1H), 0.99 (m, 1H), 0.92 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125

MHz) δ 166.8, 142.6, 141.1, 137.6, 136.2, 131.6, 130.4, 129.0, 127.8, 127.3, 119.9, 60.9, 24.6, 22.5, 21.0, 15.2, 11.0 ppm; IR (KBr) *v* 3178, 3062, 2916, 1653, 1598, 1506, 1476, 1390, 1275, 1025, 805, 780cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO$ [M^+], 277.1467; found 277.1463.



4s

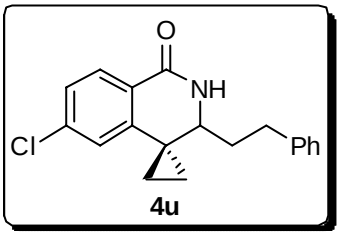
7'-Methyl-3'-(*p*-tolyl)-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4s). White solid; mp. 209-211 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 7.00 (b, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 4.32 (s, 1H), 2.37 (s, 3H), 2.28 (s, 3H), 1.12 (m, 1H), 0.94 (m, 2H), 0.90 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.4, 138.8, 137.6, 136.5, 135.9, 133.5, 129.0, 128.9, 128.4, 127.3, 121.5, 61.6, 23.1, 21.0, 20.9, 16.4, 11.1 ppm; IR (KBr) *v* 3187, 3043, 2911, 1663, 1610, 1571, 1473, 1380, 1282, 1144, 803 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO$ [M^+] 277.1467; found 277.1470.



4t

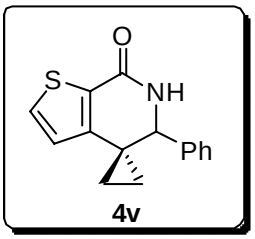
3'-Phenethyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4t). White solid; mp. 91-93 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13 (d, *J* = 7.5 Hz, 1H), 7.81 (m, 1H), 7.45 (m, 1H), 7.32 (m, 1H), 7.26 (m, 2H), 7.17 (m, 3H), 6.88 (d, *J* = 7.5 Hz, 1H), 2.78 (m, 2H), 2.64 (m, 1H), 1.90 (m, 2H), 1.52 (m, 1H), 1.07 (m, 1H), 0.82 (m, 1H), 0.64 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.8, 141.5, 141.2, 132.6, 129.3, 128.4, 128.2, 128.0, 126.1, 125.9, 121.7, 58.5, 36.4, 32.1, 23.2, 20.0, 9.0 ppm; IR (KBr) *v* 3190, 3061, 2921, 1661, 1607, 1563, 1466, 1405, 1307, 1124, 751,

696 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO$ [M^+] 277.1467; found 277.1465.



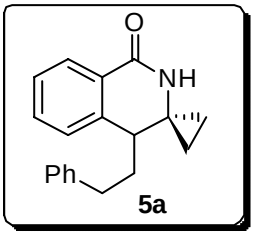
4u

6'-Chloro-3'-phenethyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinolin]-1'-one (4u). White solid; mp. 112-113 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, *J* = 10.5 Hz, 1H), 7.80 (m, 1H), 7.25 (m, 3H), 7.15 (m, 3H), 6.84 (d, *J* = 2.5 Hz, 1H), 2.77 (m, 2H), 2.62 (m, 1H), 1.87 (m, 2H), 1.47 (m, 1H), 1.08 (m, 1H), 0.84 (m, 1H), 0.65 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.0, 143.6, 140.9, 138.8, 129.7, 128.5, 128.2, 127.8, 126.5, 126.0, 122.1, 58.4, 36.4, 32.0, 23.2, 20.2, 9.3 ppm; IR (KBr) *v* 3192, 2924, 2854, 1666, 1596, 1462, 1399, 1130, 837, 747, 696 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{18}ClNO$ [M^+] 311.1077; found 311.1079.



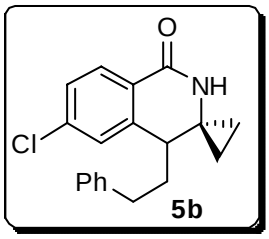
4v

5'-Phenyl-5'*H*-spiro[cyclopropane-1,4'-thieno[2,3-c]pyridin]-7'(6'H)-one (4v). White solid; mp. 201-202 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, *J* = 5.0Hz, 1H), 7.33 (m, 3H), 7.28 (m, 2H), 6.59 (d, *J* = 5.0Hz, 1H), 5.90 (b, 1H), 4.79 (d, *J* = 1.5 Hz, 1H), 1.04 (m, 1H), 0.87 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.2, 150.0, 138.1, 132.2, 130.1, 128.5, 128.4, 127.9, 122.4, 62.7, 22.3, 14.1, 13.3 ppm; IR (KBr) *v* 3187, 3056, 2916, 1655, 1471, 1436, 1402, 1333, 1143, 989, 776, 702 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{13}NOS$ [M^+] 255.0718; found 255.0723.

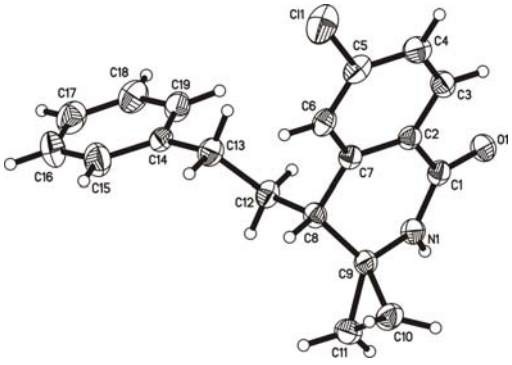


5a

4'-Phenethyl-2',4'-dihydro-1'*H*-spiro[cyclopropane-1,3'-isoquinolin]-1'-one (5a). White solid; mp. 180-182 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12 (dd, J_1 = 1.5 Hz, J_2 = 7.5 Hz, 1H), 7.51 (m, 1H), 7.42 (m, 1H), 7.27 (m, 2H), 7.18 (m, 2H), 7.14 (d, J = 7.0 Hz, 2H), 6.27 (m, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.18(m, 2H), 2.06 (m, 1H), 0.93 (m, 2H), 0.74 (m, 1H), 0.63 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.3, 142.5, 141.6, 132.0, 128.4, 128.2, 128.0, 127.7, 127.2., 125.9, 45.8, 37.9, 35.4, 33.1, 15.0, 10.7 ppm; IR (KBr) *v* 3173, 3059, 2932, 1667, 1594, 1413, 1380, 1079, 794, 744, 697 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO$ [M^+] 277.1467; found 277.1465.

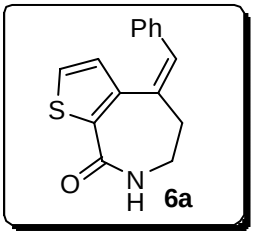


5b

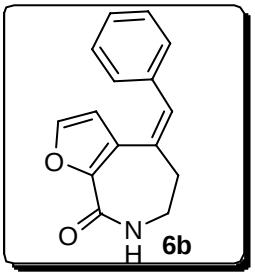


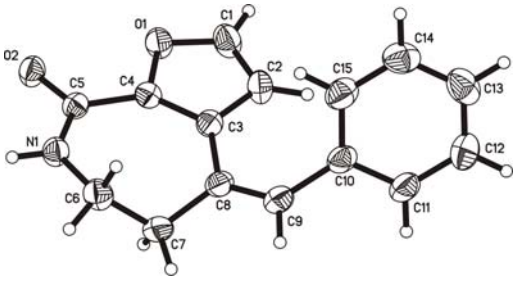
6'-Chloro-4'-phenethyl-2',4'-dihydro-1'*H*-spiro[cyclopropane-1,3'-isoquinolin]-1'-one (5b). White solid; mp. 178-180 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04 (d, J = 10.0 Hz, 1H), 7.37 (dd, J_1 = 2.5 Hz, J_2 = 10.5 Hz, 1H), 7.26 (m, 2H), 7.18 (m, 1H), 7.13 (m, 3H), 6.57 (b, 1H), 2.63 (t, J = 10.5 Hz, 2H), 2.10 (m, 3H), 0.93 (m, 2H), 0.73 (m, 1H), 0.61 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.7, 144.3, 141.2,

138.0, 130.0, 128.5, 128.2, 127.6, 127.5, 126.5, 126.0, 45.6, 37.8, 35.2, 33.1, 14.9, 10.6 ppm; IR (KBr) *v* 3173, 3059, 2932, 1667, 1594, 1413, 1380, 1079, 794, 744, 697 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{18}ClNO$ [M^+] 311.1077; found 311.1079.



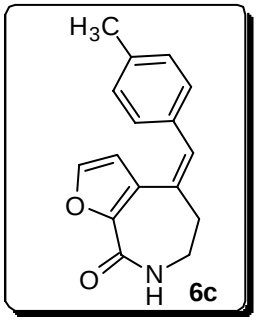
(*Z*)-4-Benzylidene-6,7-dihydro-4*H*-thieno[2,3-c]azepin-8(5*H*)-one (6a). White solid; mp. 183-185 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.20 (m, 4H), 7.06 (d, *J* = 6.5 Hz, 2H), 6.95 (b, 1H), 6.62 (d, *J* = 5.0 Hz, 1H), 6.58 (s, 1H), 3.53 (d, *J* = 5.5 Hz, 2H), 2.95 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.7, 140.9, 136.9, 135.9, 133.5, 130.5, 130.1, 129.1, 129.0, 128.1, 127.2, 42.6, 39.2 ppm; IR (KBr) *v* 3164, 3030, 2926, 1651, 1520, 1473, 1441, 1348, 1166, 957, 765, 714 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{13}NOS$ [M^+] 255.0718; found 255.0723.



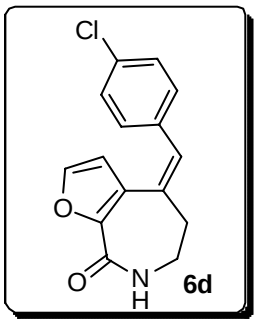


(*Z*)-4-Benzylidene-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6b). Pale yellow solid; mp. 154-156 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (b, 1H), 7.29 (m, 6H), 6.61 (s, 1H), 5.92 (d, *J* = 1.0 Hz, 1H), 3.57 (q, *J* = 4.5 Hz, 2H), 2.84 (t, *J* = 4.5 Hz, 2H)

ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.4, 144.2, 143.7, 137.2, 131.1, 130.3, 129.0, 128.4, 127.6, 127.5, 112.2, 42.2, 38.2 ppm; IR (KBr) *v* 3353, 3183, 2921, 2849, 1662, 1622, 1491, 1412, 1367, 1229, 1029, 763, 704 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{13}NO_2$ [M^+] 239.0946; found 239.0943.

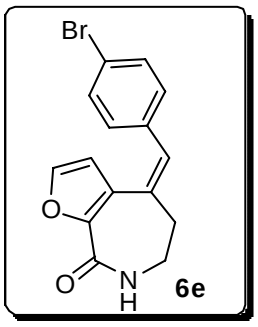


(*Z*)-4-(4-Methylbenzylidene)-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6c). Pale yellow solid; mp. 217-219 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (d, *J* = 1.5 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.94 (b, 1H), 6.57 (s, 1H), 6.01 (d, *J* = 2.0 Hz, 1H), 3.55 (q, *J* = 5.0 Hz, 2H), 2.82 (t, *J* = 4.5 Hz, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.4, 144.1, 143.7, 137.3, 134.2, 131.2, 129.8, 129.1, 128.9, 127.8, 112.2, 42.3, 38.2, 21.2 ppm; IR (KBr) *v* 3193, 3060, 2918, 1653, 1552, 1506, 1495, 1440, 1337, 1265, 1201, 1097, 890, 785 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{15}NO_2$ [M^+] 253.1103; found 253.1105.



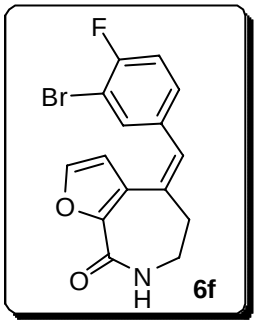
(*Z*)-4-(4-Chlorobenzylidene)-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6d). Pale yellow solid; mp. 221-223 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (b, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.52 (s, 1H), 5.96 (d, *J* = 2.0 Hz, 1H), 3.55 (q, *J* = 4.5 Hz, 2H), 2.82 (t, *J* = 4.5 Hz, 2H) ppm; ^{13}C

NMR ($CDCl_3$, 125 MHz) δ 162.3, 144.4, 143.9, 135.5, 133.3, 131.0, 130.4, 129.6, 128.6, 127.1, 112.0, 42.1, 38.2 ppm; IR (KBr) *v* 3201, 3064, 2923, 1652, 1471, 1201, 1088, 889, 784 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{12}ClNO_2$ [M^+] 273.0557; found 273.0552.



6e

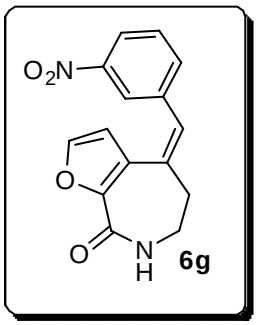
(*Z*)-4-(4-Bromobenzylidene)-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6e). Pale yellow solid; mp. 230-232 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.61 (b, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.49 (s, 1H), 5.97 (d, *J* = 2.0 Hz, 1H), 3.55 (q, *J* = 4.5 Hz, 2H), 2.82 (d, *J* = 4.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.4, 144.4, 143.9, 136.0, 131.6, 131.1, 130.7, 129.6, 127.1, 121.5, 112.0, 42.0, 38.2 ppm; IR (KBr) *v* 3203, 3064, 2923, 1655, 1471, 1200, 1101, 890, 784 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{12}BrNO_2$ [M^+] 317.0051; found 317.0049.



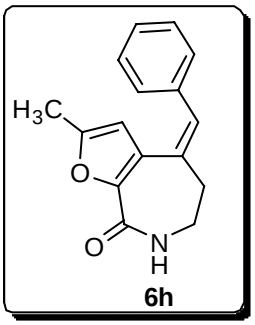
6f

(*Z*)-4-(3-Bromo-4-fluorobenzylidene)-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6f). Pale yellow solid; mp. 193-195 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.08 (b, 1H), 7.44 (dd, J_1 = 2.0 Hz, J_2 = 7.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.14 (m, 1H), 7.06 (m, 1H), 6.45 (S, 1H), 5.95 (d, *J* = 2.0 Hz, 1H), 3.55 (q, *J* = 4.5 Hz, 2H), 2.82 (t, *J* =

4.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.3, 158.3 (d, $J_{C\text{-}F}$ = 247.5 Hz), 144.5, 144.0, 134.6 (d, $J_{C\text{-}F}$ = 3.75 Hz), 133.9, 131.7, 129.7 (d, $J_{C\text{-}F}$ = 6.25 Hz), 128.2, 126.8, 116.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 111.9, 109.0 (d, $J_{C\text{-}F}$ = 21.25 Hz), 42.0, 38.1 ppm; IR (KBr) *v* 3192, 3050, 2928, 1660, 1495, 1478, 1443, 1248, 1206, 882 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{11}BrFNO_2$ [M^+] 334.9957; found 334.9960.

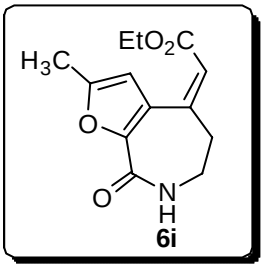


(*Z*)-4-(3-Nitrobenzylidene)-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6g). Dark yellow solid; mp. 207-209 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.13 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (m, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.23 (b, 1H), 6.59 (s, 1H), 5.85 (d, *J* = 2.0 Hz, 1H), 3.58 (q, *J* = 5.0 Hz, 2H), 2.90 (t, *J* = 4.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.9, 148.3, 144.8, 144.3, 138.8, 135.2, 132.9, 129.4, 128.0, 126.3, 123.9, 122.4, 111.6, 42.0, 38.3 ppm; IR (KBr) *v* 3203, 3704, 2924, 1663, 1526, 1348, 1205, 781 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{12}N_2O_4$ [M^+] 284.0797; found 284.0794.



(*Z*)-4-Benzylidene-2-methyl-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6h). Pale yellow solid; mp.163-165 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (m, 5H), 6.92 (b, 1H), 6.55 (s, 1H), 5.58 (d, *J* = 5.0 Hz, 1H), 3.52 (q, *J* = 5.0 Hz, 2H), 2.80 (t, *J* =

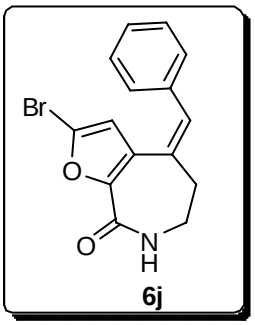
4.5 Hz, 2H), 2.19 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.2, 154.8, 142.4, 137.3, 130.9, 130.6, 129.0, 128.8, 128.3, 127.4, 108.6, 42.3, 38.4, 13.7 ppm; IR (KBr) *v* 3180, 3050, 2923, 1654, 1479, 1438, 1211, 1016, 820 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{15}NO_2$ [M^+] 253.1103; found 253.1102.



6i

(*Z*)-ethyl-(2-methyl-8-oxo-5,6,7,8-tetrahydro-4*H*-furo[2,3-c]azepin-4-ylidene) acetate (6i).

Yellow solid; mp. 172-173 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.16 (b, 1H), 6.33 (s, 1H), 6.13 (s, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.41 (s, 4H), 2.38 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.2, 162.4, 156.2, 147.4, 142.9, 130.0, 116.8, 105.7, 60.2, 39.6, 31.9, 14.2, 13.7 ppm; IR (KBr) *v* 2923, 2853, 1710, 1661, 1464, 1183, 1081, 966 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{13}H_{15}NO_4$ [M^+] 249.1001; found 249.0999.

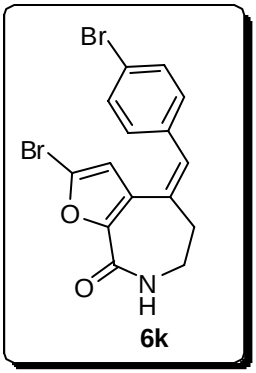


6j

(*Z*)-4-Benzylidene-2-bromo-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6j).

Yellow solid; mp. 219-220 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33 (m, 4H), 7.23 (m, 2H), 6.63 (s, 1H), 5.86 (s, 1H), 3.53 (q, *J* = 4.8 Hz, 2H), 2.82 (t, *J* = 4.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.3, 145.5, 136.6, 132.3, 129.7, 129.4, 128.8, 128.6, 127.9, 126.6, 113.7, 42.0, 38.1 ppm; IR (KBr) *v* 3179, 3054, 2925, 1655, 1493,

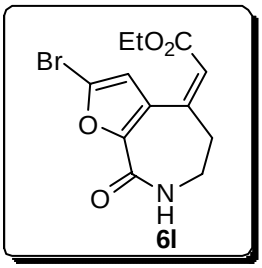
1477, 1187, 932, 705 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{12}BrNO_2$ [M^+] 317.0051; found 317.0049.



6k

(*Z*)-2-bromo-4-(4-bromobenzylidene)-6,7-dihydro-4*H*-furo[2,3-c]azepin-8(5*H*)-one (6k).

Yellow solid; mp. 246-248 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (b, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.52 (s, 1H), 5.92 (s, 1H), 3.53 (q, *J* = 4.4 Hz, 2H), 2.81 (t, *J* = 4.8 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.1, 145.6, 135.4, 131.8, 130.9, 130.6, 130.1, 129.4, 127.0, 122.0, 113.5, 42.0, 38.1 ppm; IR (KBr) *v* 2924, 2853, 1657, 1486, 1185, 1071 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{11}Br_2NO_2$ [M^+] 394.9157; found 394.9161.

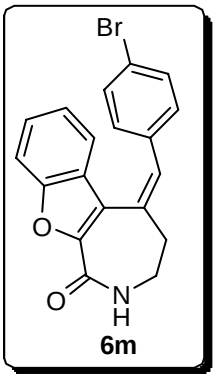


6l

(*Z*)-ethyl 2-(2-bromo-8-oxo-5,6,7,8-tetrahydro-4*H*-furo[2,3-c]azepin-4-ylidene) acetate (6l).

Yellow solid; mp. 125-127 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.88 (b, 1H), 7.01 (s, 1H), 5.86 (s, 1H), 4.20 (q, *J* = 6.8 Hz, 2H), 3.47 (q, *J* = 4.8 Hz, 2H), 2.80 (t, *J* = 4.4 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.4, 161.0,

146.3, 141.1, 127.6, 126.8, 121.0, 114.9, 60.8, 40.7, 38.9, 14.1 ppm; IR (KBr) *v* 2924, 2853, 1718, 1661, 1491, 1182 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{12}BrNO_4$ [M^+] 312.9950; found 312.9952.

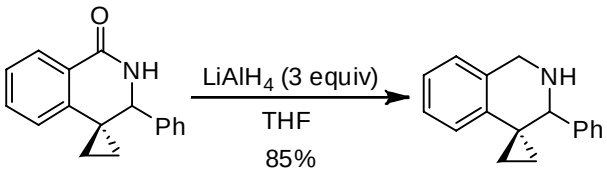


6m

(*Z*)-5-(4-bromobenzylidene)-2,3,4,5-tetrahydro-1*H*-benzofuro[2,3-c]azepin-1-one (6m).

Yellow solid; mp. 237-238 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.30 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 0.8 Hz, 1H), 6.80 (b, 1H), 6.70 (m, 2H), 3.62 (m, 2H), 3.05 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.6, 155.0, 144.9, 135.4, 131.3, 130.6, 130.5, 129.0, 127.1, 124.3, 123.6, 123.4, 123.0, 121.4, 112.3, 42.8, 39.4 ppm; IR (KBr) *v* 2924, 2853, 1655, 1492, 1463, 1186, 1080, 966 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{14}BrNO_2$ [M^+] 367.0208; found 367.0209.

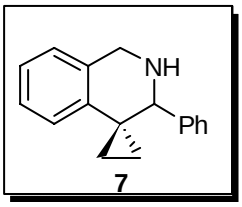
Derivatization of Products to 7 and 8:



4a **7**

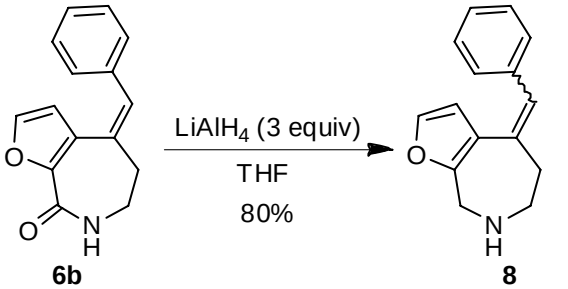
A solution of **4a** (70 mg, 0.28 mmol) in THF (5 mL) protected under Argon was treated with $LiAlH_4$ (32 mg, 0.84 mmol), and the mixture heated at reflux for 8h. Then it was cooled and quenched with water (1.0 mL) (CAUTION), stirred for 10 min at rt and treated with NaOH (0.5 mL of 2 M aqueous solution), stirred for 5 min and

diluted with additional water (5 mL). The solution was extracted with ethyl acetate (10 mL * 2), the combined organic layer were dried (Na_2SO_4), filtered, concentrated under vacuum. The purification was performed by flash column chromatography on basic alumina using ethyl acetate/petroleum ether (v/v, 1:1) as eluent to give the product **7** as pale yellow gel (56 mg, 85%).



7

3'-Phenyl-2',3'-dihydro-1'*H*-spiro[cyclopropane-1,4'-isoquinoline] (7). Pale yellow gel; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.28 (m, 3H), 7.19 (m, 1H), 7.11 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.11 (d, *J* = 16.5 Hz, 1H), 3.97 (d, *J* = 13.5 Hz, 2H), 2.72 (b, 1H), 1.18 (m, 1H), 0.94 (m, 2H), 0.84 (m, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.3, 139.8, 135.5, 128.6, 128.0, 127.2, 126.8, 125.7, 124.8, 121.7, 63.9, 46.4, 21.6, 18.0, 14.2 ppm; IR (KBr) *v* 3393, 3032, 2924, 1613, 1486, 1452, 1372, 1024, 743, 703 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{17}N$ [M^+] 235.1361; found 235.1353.

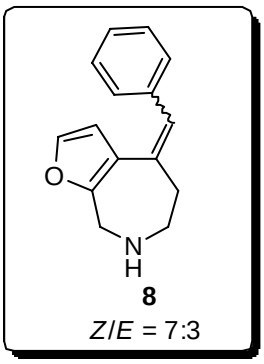


6b **8**

Z/*E* = 7:3

To a solution of $LiAlH_4$ (29 mg, 0.75 mmol) in THF (2 mL) protected under Argon at 0 ^{o}C was added dropwise of THF (2 mL) solution of **4a** (60 mg, 0.25 mmol), the mixture was then heated at reflux for 3h. Then it was cooled and quenched with water (1.0 mL) (CAUTION), stirred for 10 min at rt and treated with NaOH (0.5 mL of 2 M

aqueous solution), stirred for 5 min and diluted with additional water (5 mL). The solution was extracted with ethyl acetate (10 mL * 2), the combined organic layer were dried (Na_2SO_4), filtered, concentrated under vacuum. The purification was performed by flash column chromatography on basic alumina using ethyl acetate/petroleum ether (v/v, 1:1) as eluent to give the inseparable *Z*/*E* mixture **8** as pale yellow gel (45 mg, 80%).



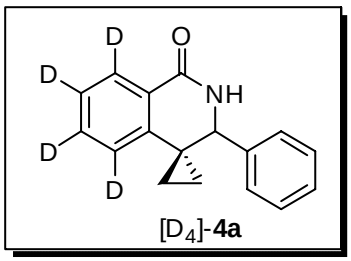
8

Z/*E* = 7:3

4-Benzylidene-5,6,7,8-tetrahydro-4*H*-furo[2,3-c]azepine (8). Pale yellow gel; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (m, 1H), 7.15 (m, 6H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.66 (s, 0.43 H), 6.47 (d, *J* = 2.0 Hz, 0.44H), 6.31 (s, 1H), 5.78 (d, *J* = 2.0 Hz, 1H), 3.96 (s, 0.85H), 3.93 (s, 2H), 3.15 (m, 2H), 3.05 (m, 0.88H), 2.75 (m, 0.91H), 2.54 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.5, 153.7, 140.3, 139.2, 137.7, 137.6, 132.7, 132.4, 129.2, 129.0, 128.2, 127.9, 127.0, 126.6, 126.4, 126.0, 124.2, 120.9, 111.6, 109.7, 50.7, 48.9, 47.1, 46.8, 43.0, 34.5 ppm; IR (KBr) *v* 3321, 3021, 2924, 2853, 1637, 1492, 1445, 1146, 1059, 749, 698 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{15}NO$ [M^+] 225.1154; found 225.1158.

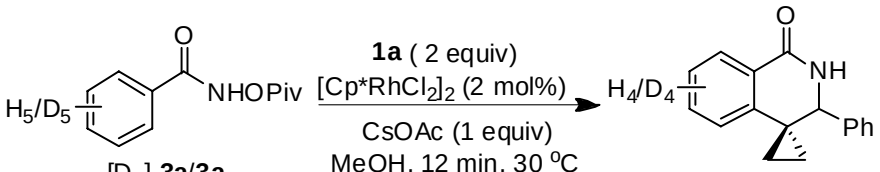
Kinetic Isotope Effect Study:

[D_5]-**3a** was synthesized following literature report,[2] and [D_4]-**4a** was prepared according to general procedure in 75% yield.



[D_4]-**4a**

White solid; mp. 172- 173 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (m, 3H), 7.22 (m, 2H), 6.68 (b, 1H), 4.40 (d, J = 3.0 Hz, 1H), 1.17 (m, 1H), 0.99 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 141.7, 139.4, 132.4, 129.1, 128.5, 128.1, 127.4, 125.8, 121.4, 61.9, 23.3, 16.6, 11.5 ppm; IR (KBr) ν 3214, 3067, 2921, 1656, 1582, 1411, 1320, 1080, 775, 708 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{11}D_4NO$ ([M]$^+$), 253.1405; found, 253.1411.

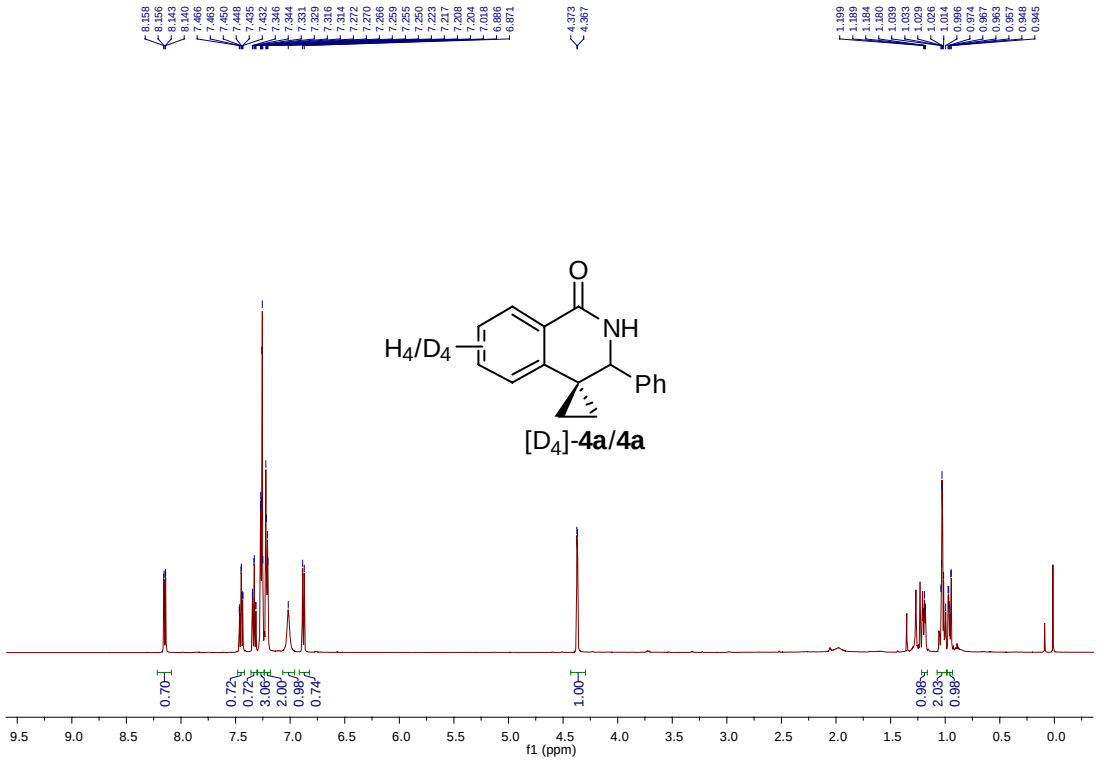


[D_5]-**3a**/**3a**

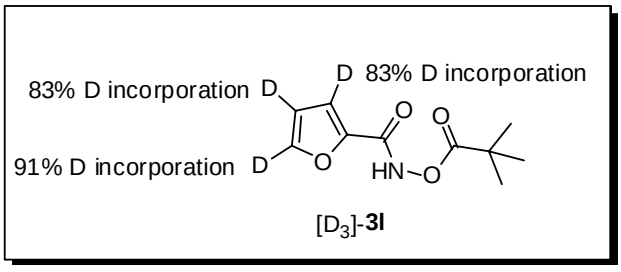
(parallel experiments)

***KIE* = 2.8**

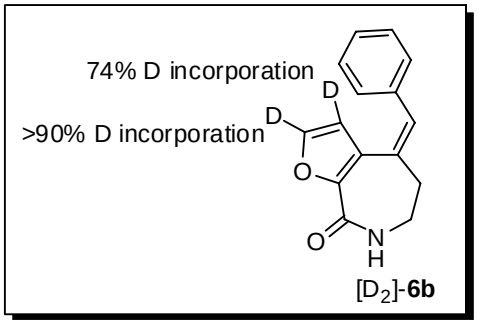
Following general procedure, [Cp*$RhCl_2$]$_2$ (1.2 mg, 2 mol%), benzamide **3a** (22.1 mg, 0.1 mmol), CsOAc (20 mg, 0.1 mmol) were added to a vial. Methanol (0.6 mL) was added, followed by micro-syringe addition of methylenecyclopropane **1a** (26 mg, 0.2 mmol). The micro-syringe was washed with an additional 0.15 mL methanol and added to the reaction solution. In another reaction vial, [D_5]-**3a** (22.6 mg, 0.1 mmol, 1.0 equiv) was used instead of **3a**. The two reactions were allowed to stir at 30 °C for 12 min. Afterwards, the reactions were quenched with water, combined and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4. The product (20 mg, 40% combined yield) was isolated by flash chromatography. The value of K_H/K_D was obtained based on ^{1}HNMR.



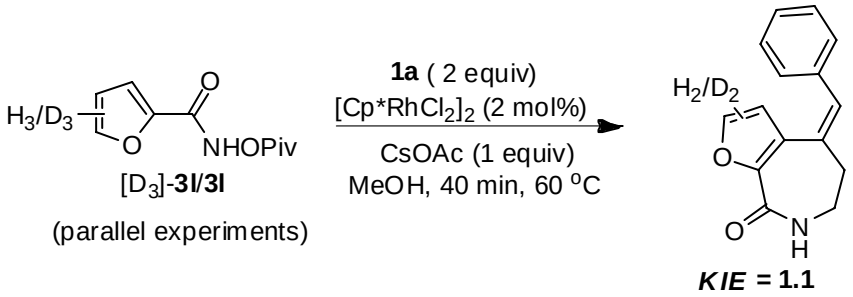
d_3-furan-2-carboxylic acid and [D_3]-**3l** were synthesized following literature report,[3], [2] [D_2]-**6b** was prepared according to general procedure in 64% yield.



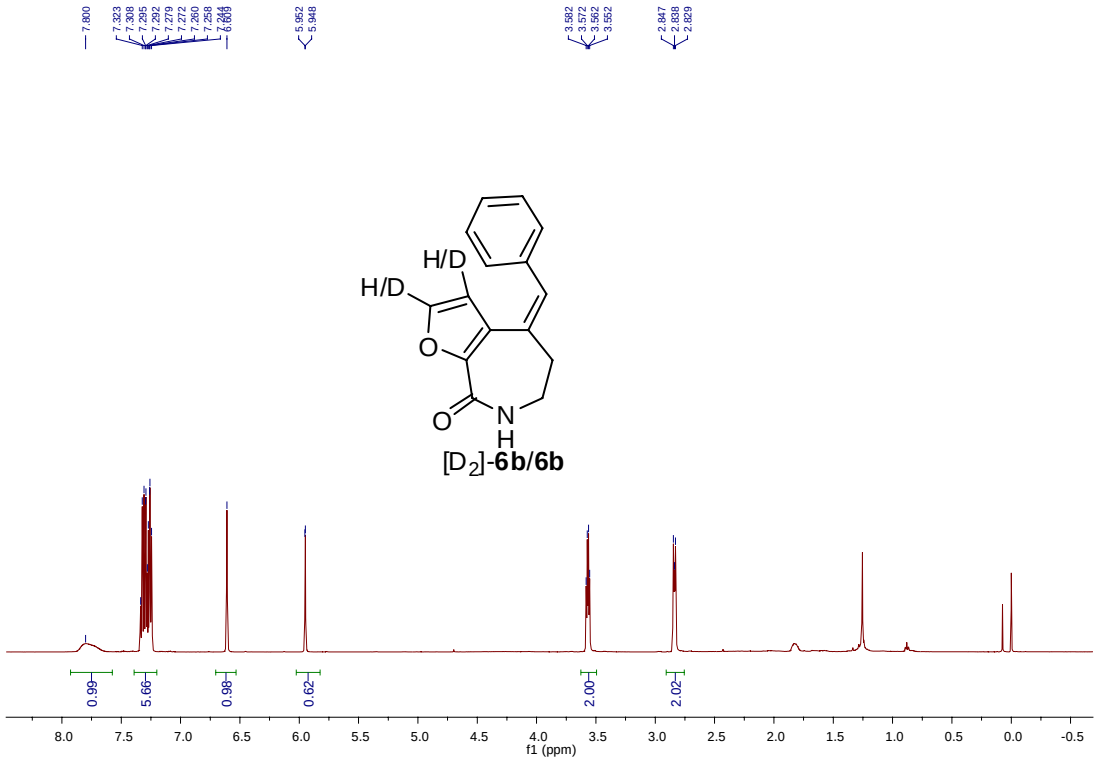
^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.46 (b, 1H), 7.49 (s, 0.09H), 7.23 (m, 0.17H), 6.54 (m, 0.17H), 1.35 (s, 9H) ppm.



^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (m, 3.20 H), 7.25 (m, 1.84H), 6.61 (s, 1H), 5.94 (s, 0.26H), 3.56 (q, J = 6.0 Hz, 2H), 2.84 (t, J = 6.0 Hz, 2H) ppm; ^{13}CNMR ($CDCl_3$, 125 MHz) δ 162.2, 154.8, 142.4, 137.3, 10.9, 130.6, 129.0, 128.8, 128.3, 127.4, 108.6, 42.3, 38.S4 ppm; IR (KBr) v 3204, 3059, 2925, 1683, 1657, 1476, 1438, 1193, 698 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{11}D_2NO_2$ [M^+] 241.1072; found 241.1069.



Following general procedure, $[Cp^*RhCl_2]_2$ (1.2 mg, 2 mol%), amide **3l** (21.1 mg, 0.1 mmol), CsOAc (20 mg, 0.1 mmol) were added to a vial. Methanol (0.6 mL) was added, followed by micro-syringe addition of methylenecyclopropane **1a** (26 mg, 0.2 mmol). The micro-syringe was washed with an additional 0.15 mL methanol and added to the reaction solution. In another reaction vial, [D_3]-**3l** (21.4 mg, 0.1 mmol, 1.0 equiv) was used instead of **3l**. The two reactions were allowed to stir at 60 °C for 40 min. Afterwards, the reactions were quenched with water, combined and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4. The product (20 mg, 42% combined yield) was isolated by flash chromatography. The value of K_H/K_D was obtained based on ^{1}HNMR *considering the deuterium incorporation ratio of starting material* [D_3]-**3l** (83% deuterium incorporation).

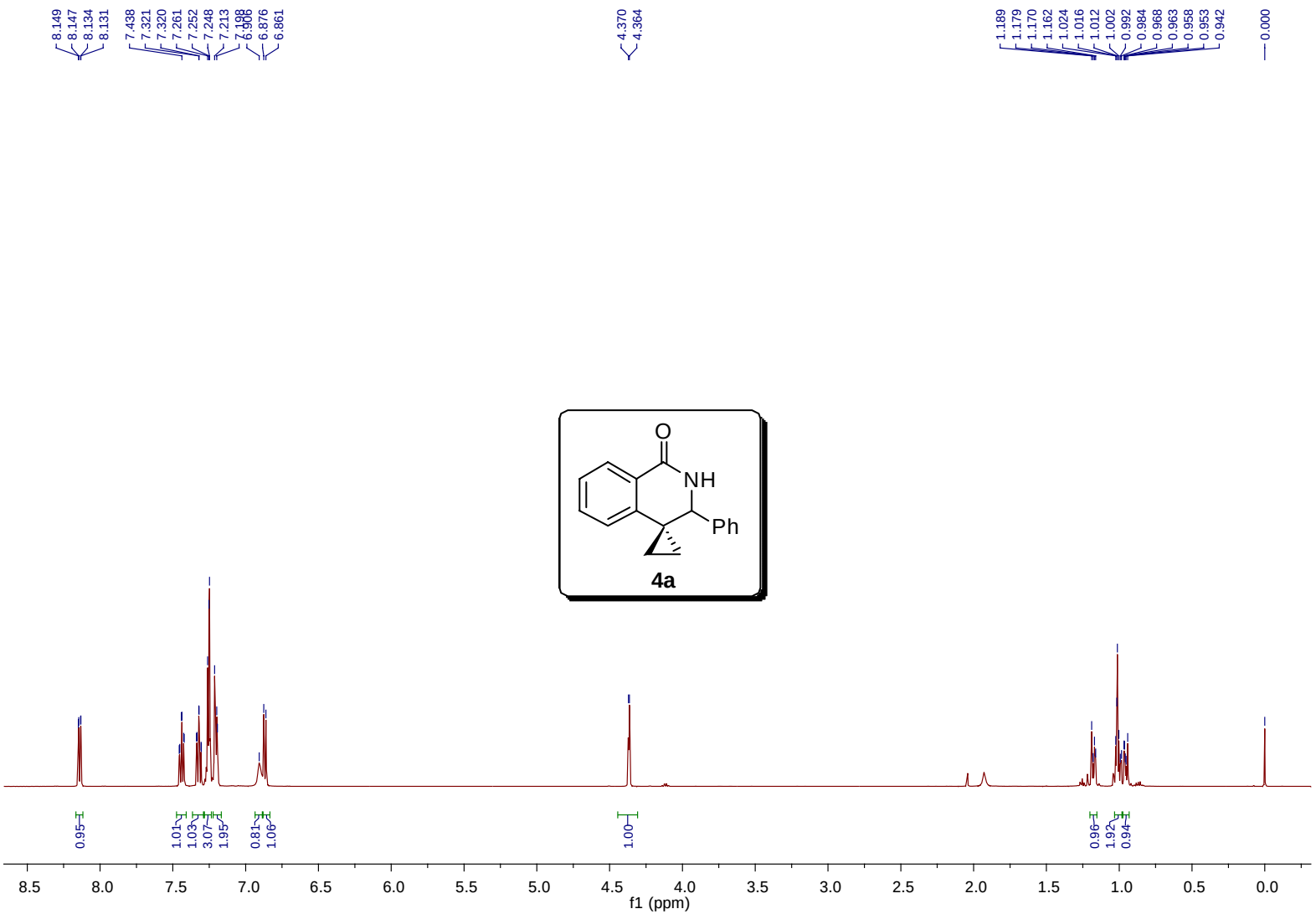


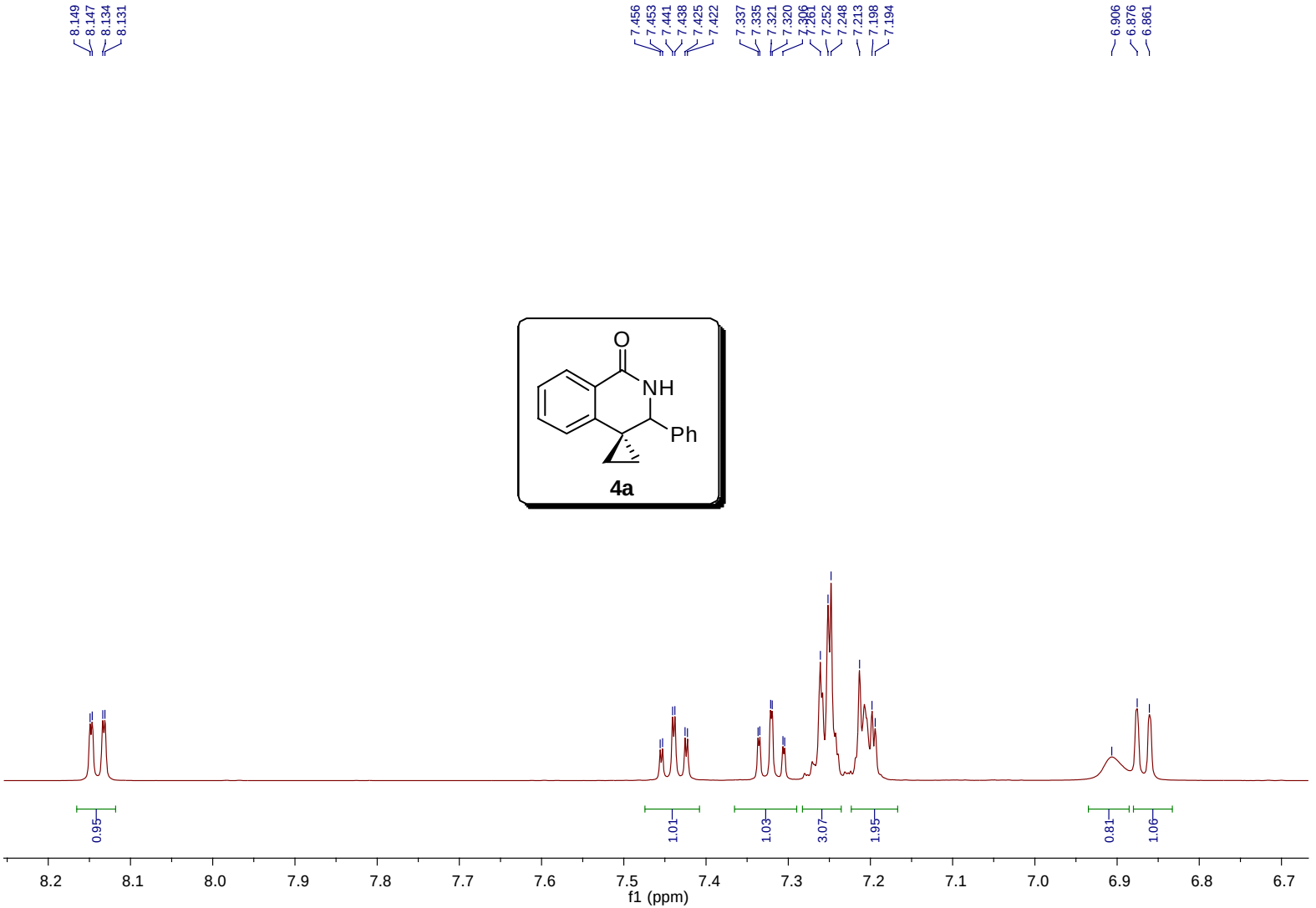
Reference:

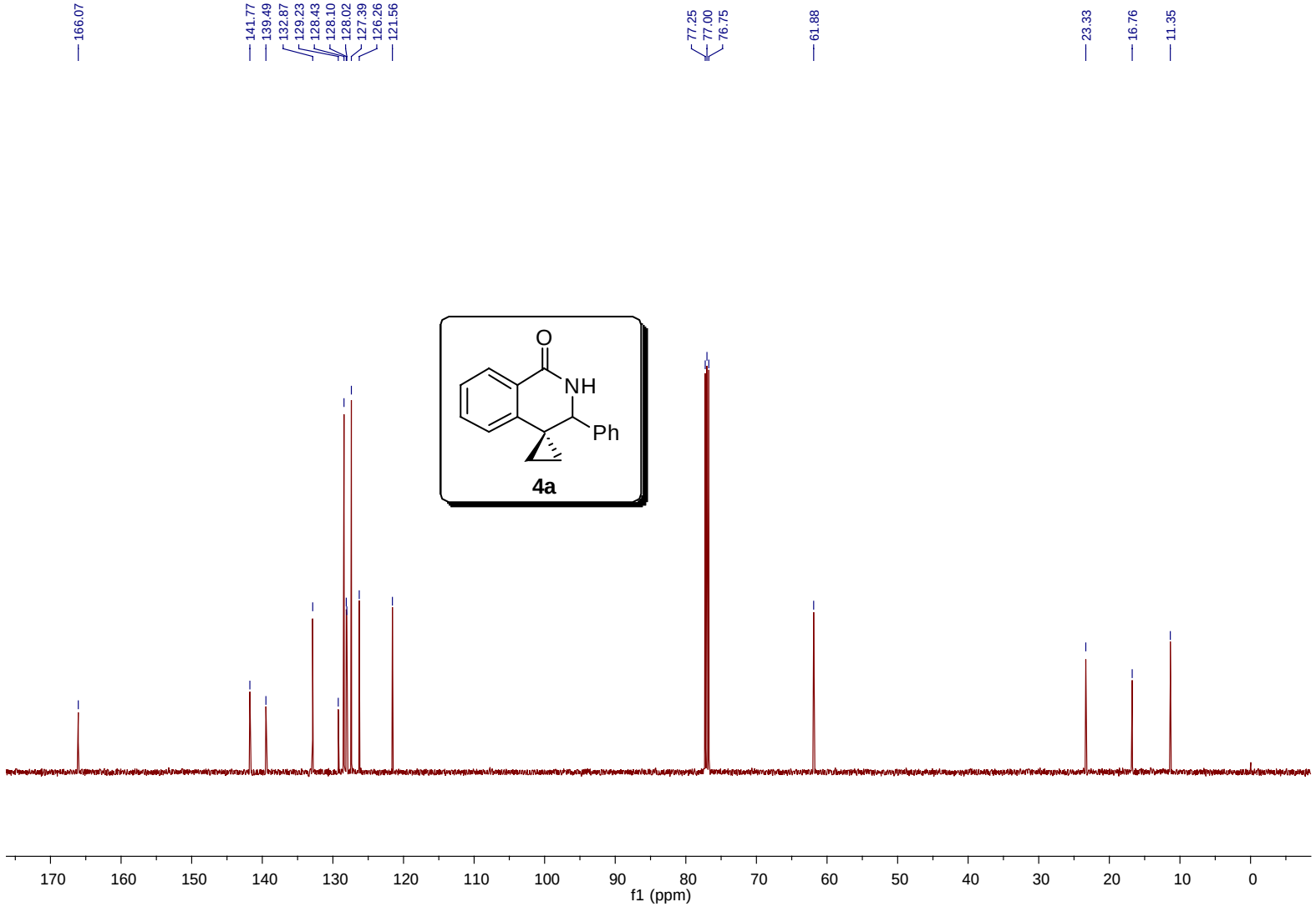
[1] A. Brandi, A. Goti *Chem. Rev*. **1998**, *98*, 589.

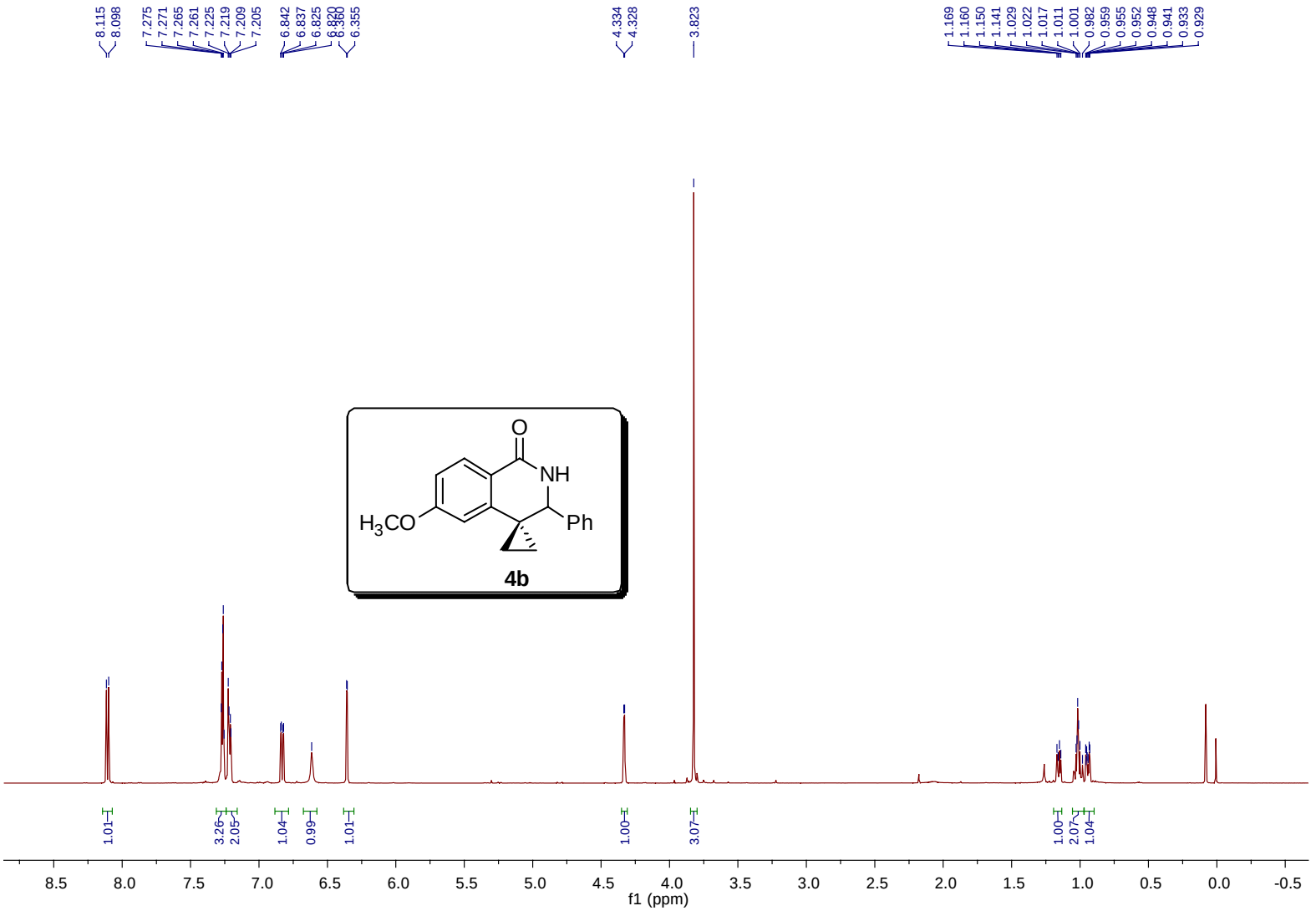
[2] H. Wang, F. Glorius *Angew. Chem., Int. Ed*. **2012**, *51*, 7318-7322.

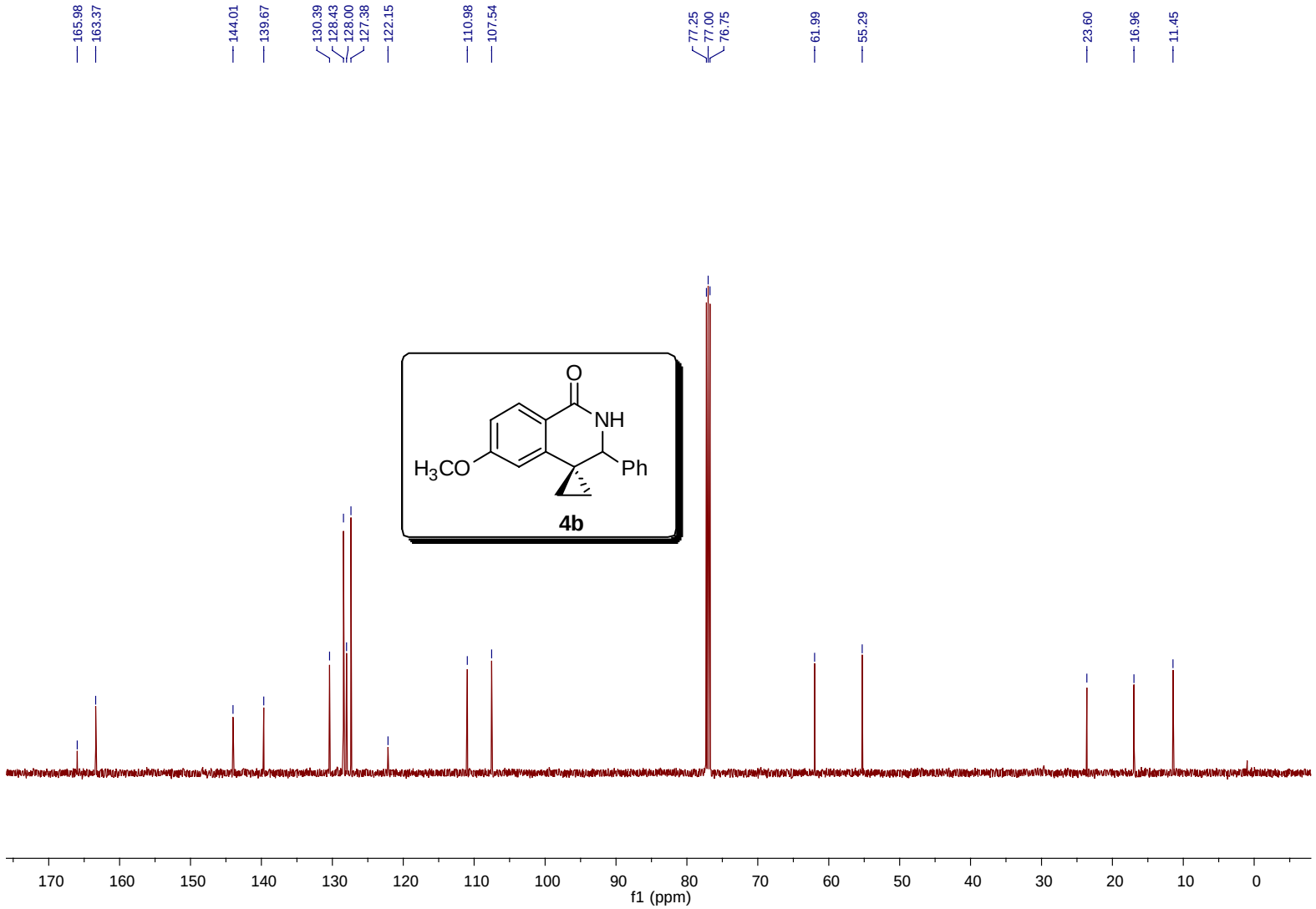
[3] D. J. Chadwick, J. Chambers, G. D. Meakins, R. L. Snowden *J. Chem. Soc*., *Perkin Trans. 1*, **1973**, 201.

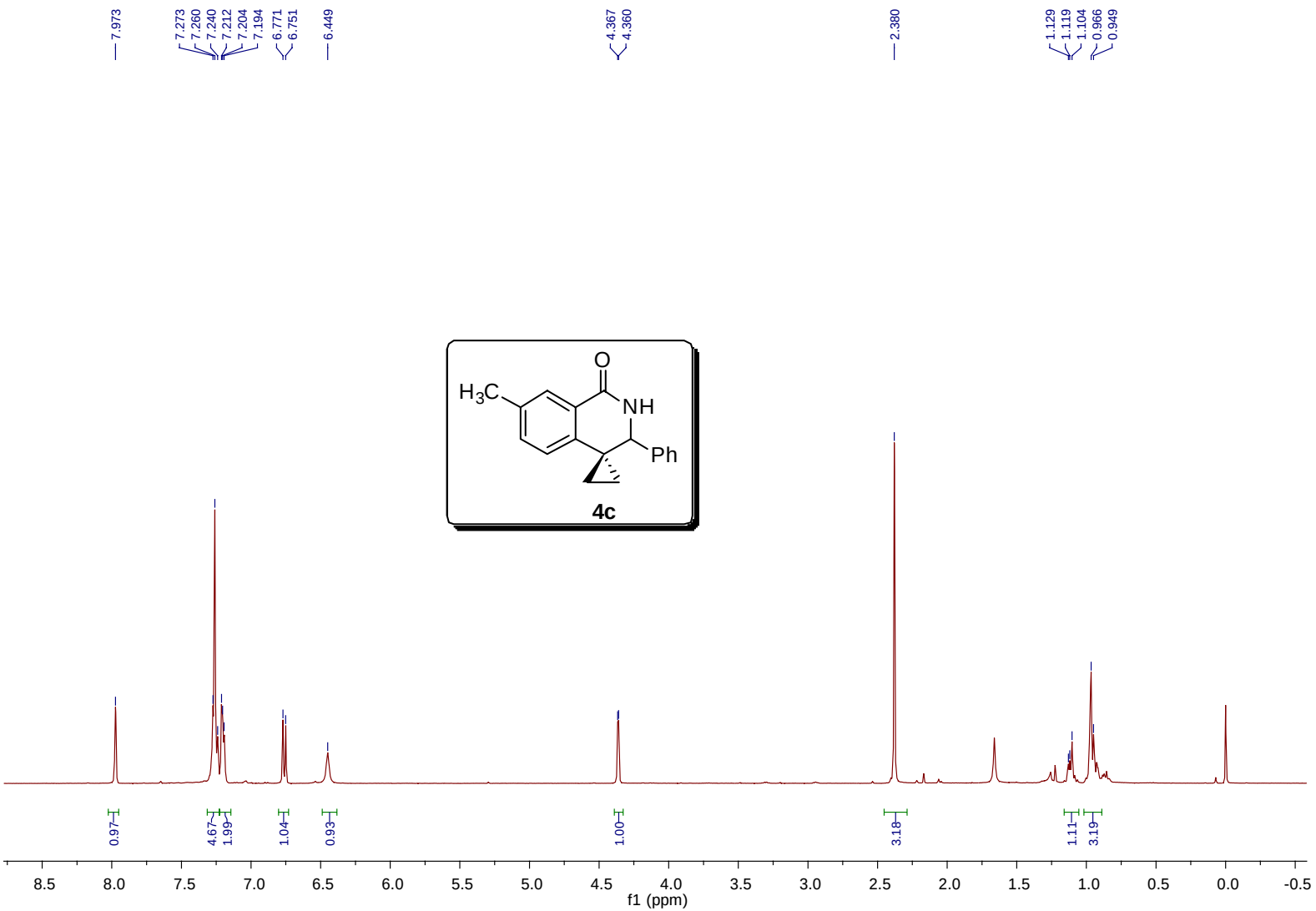


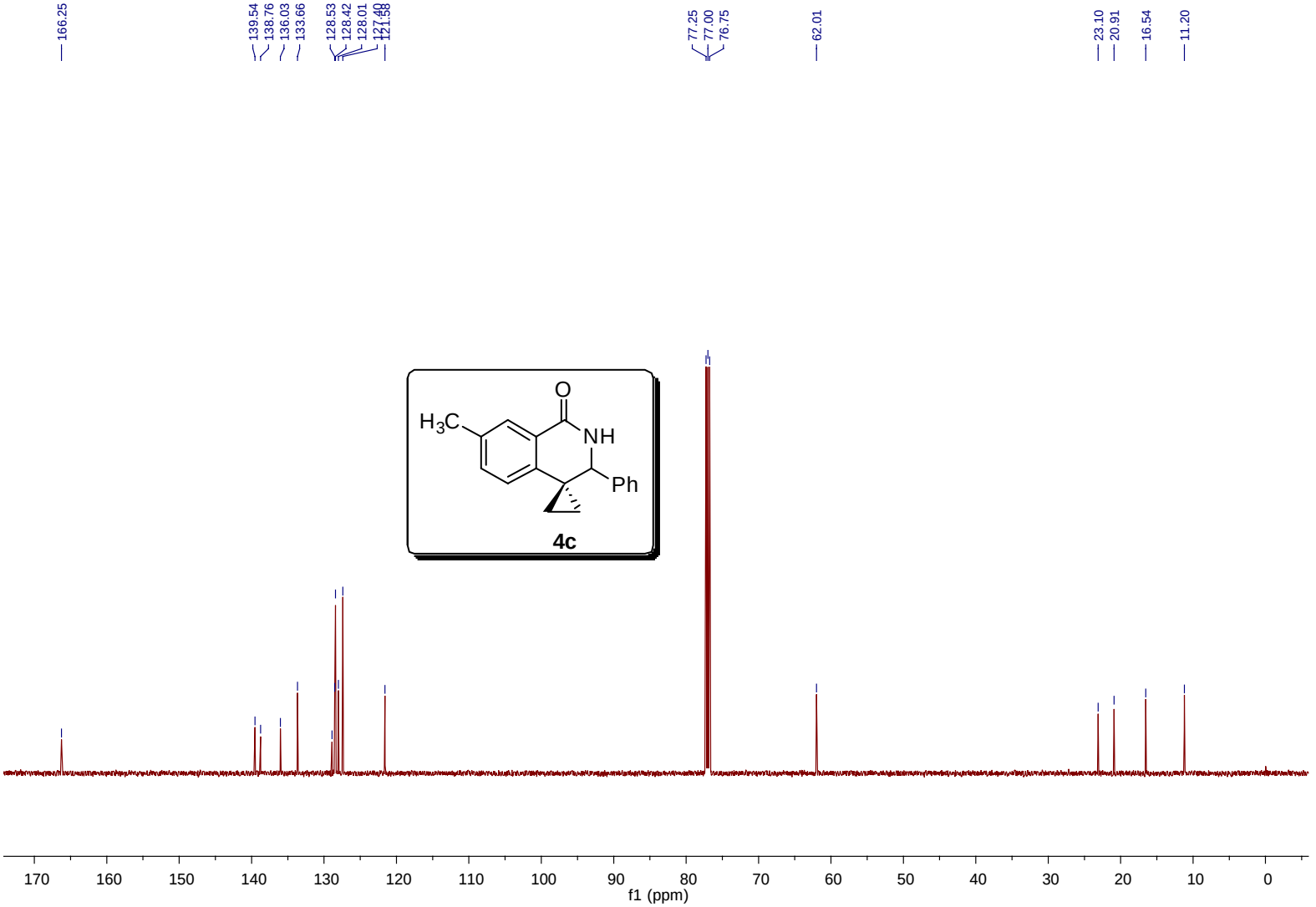


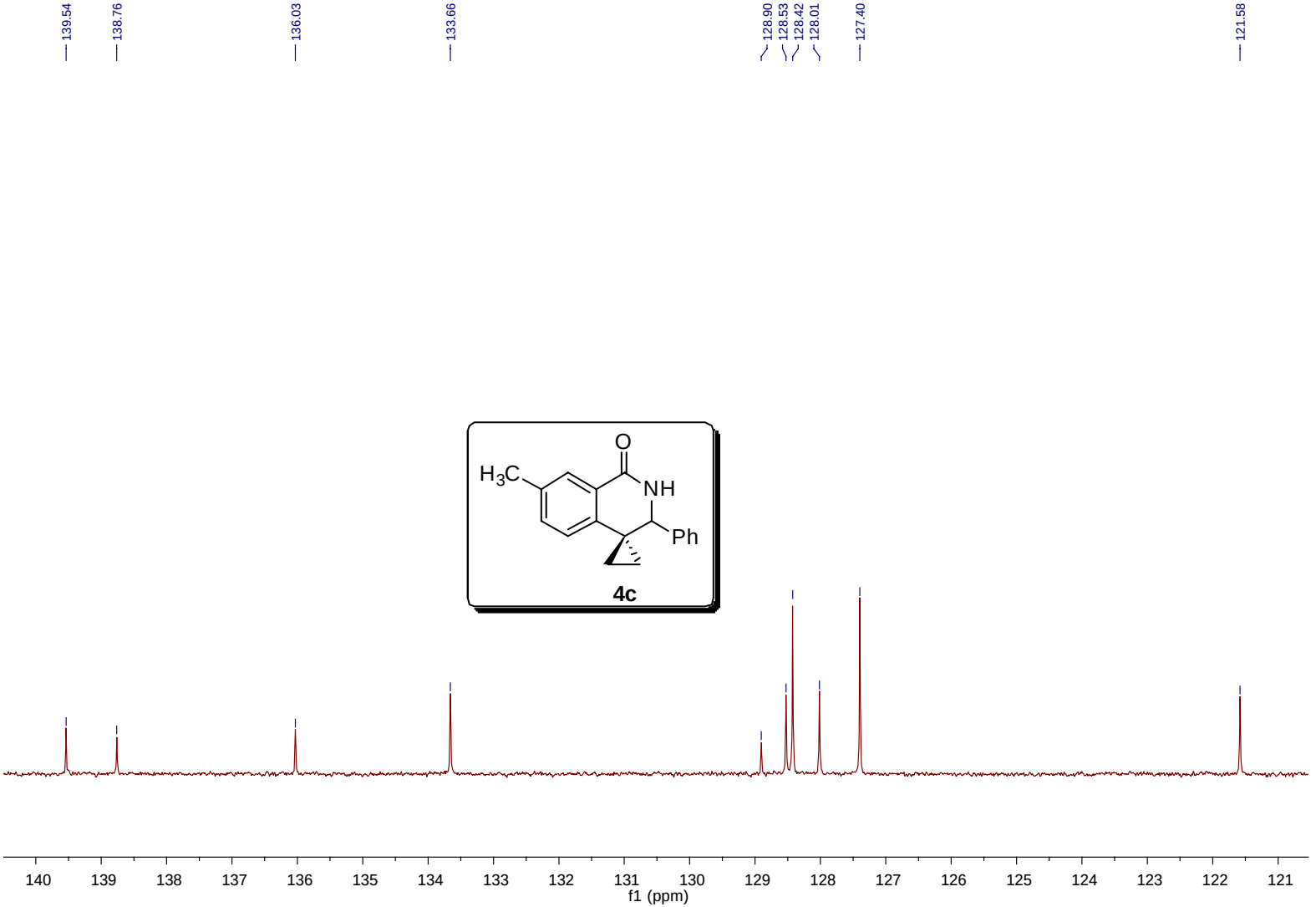


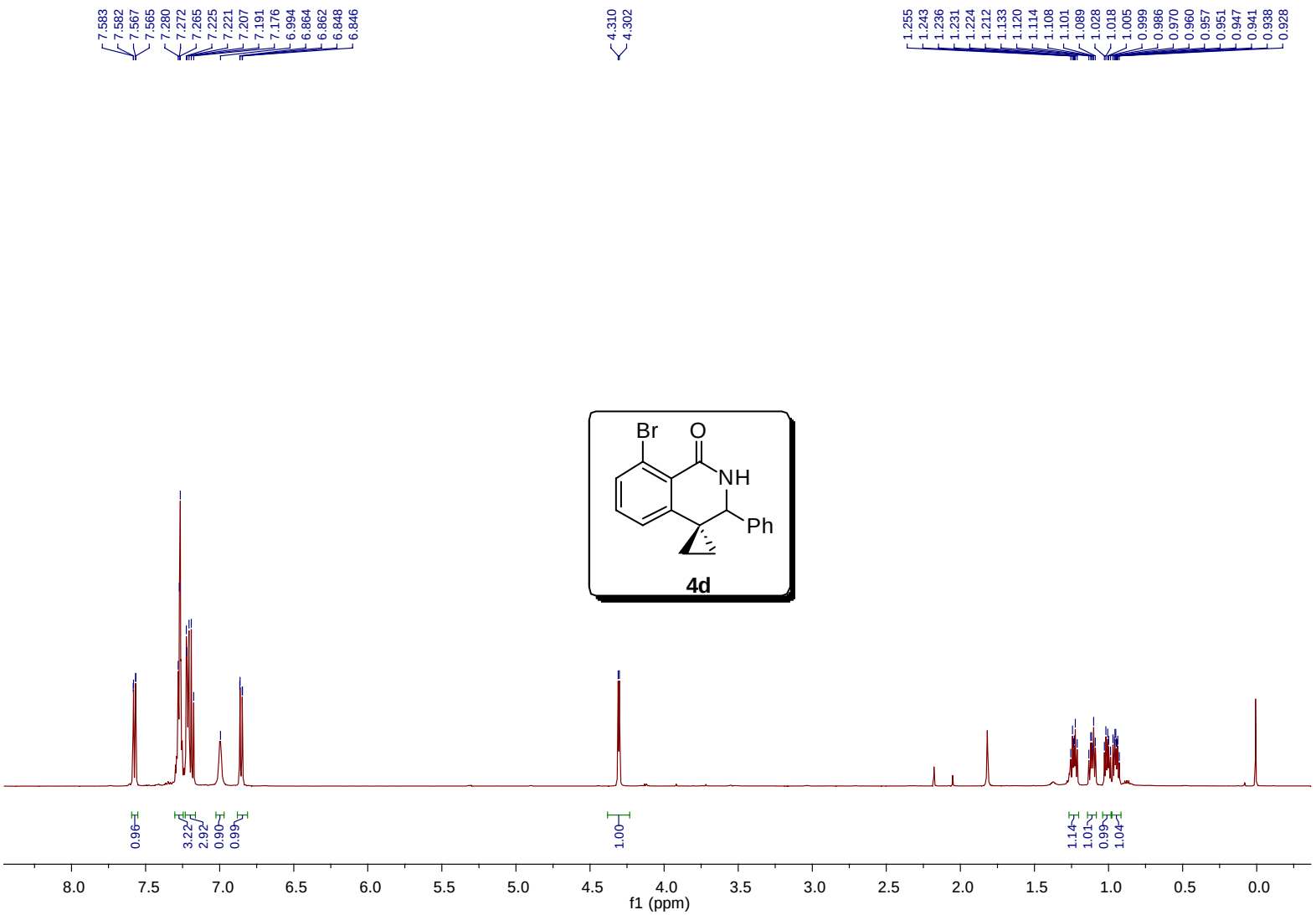


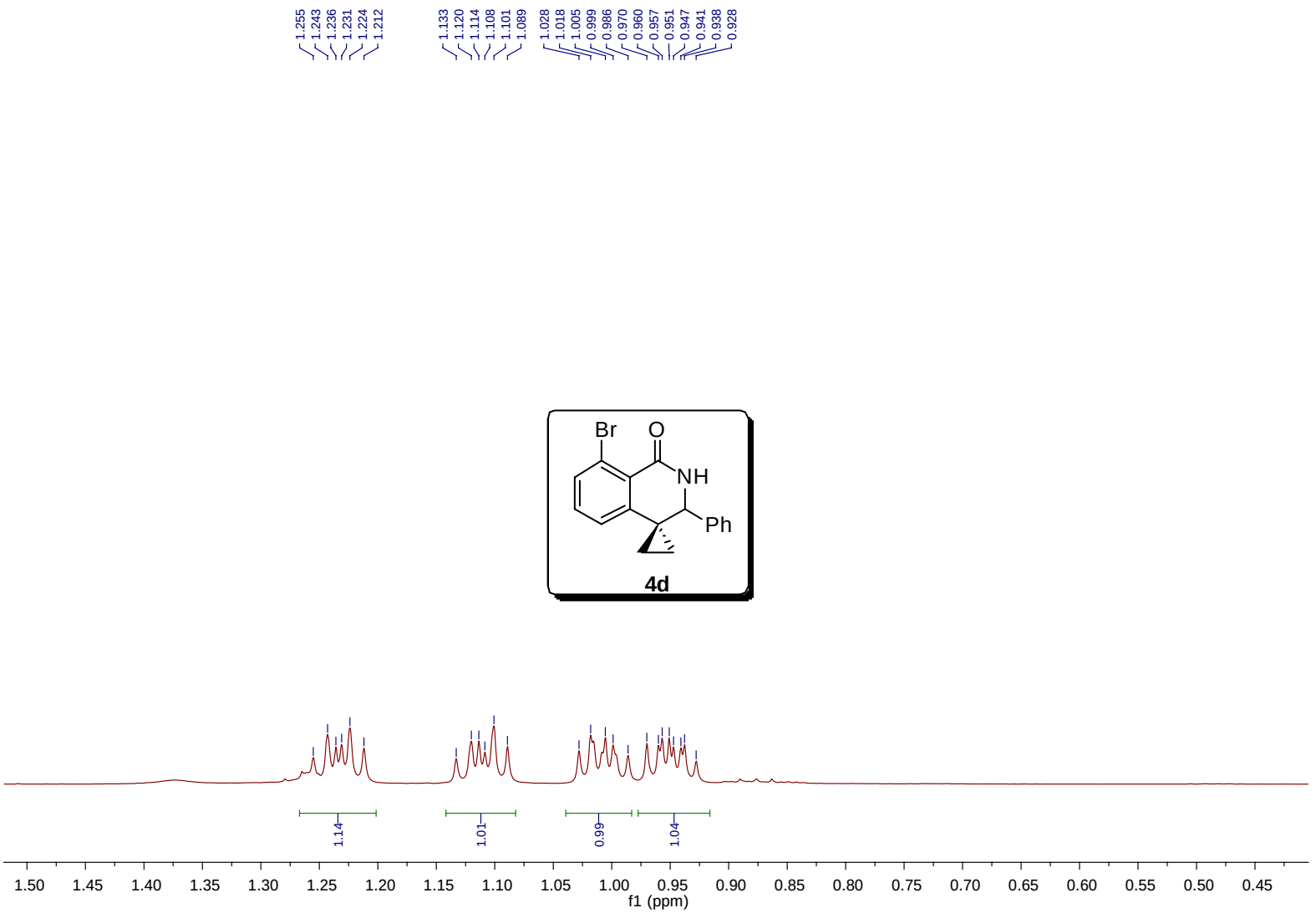


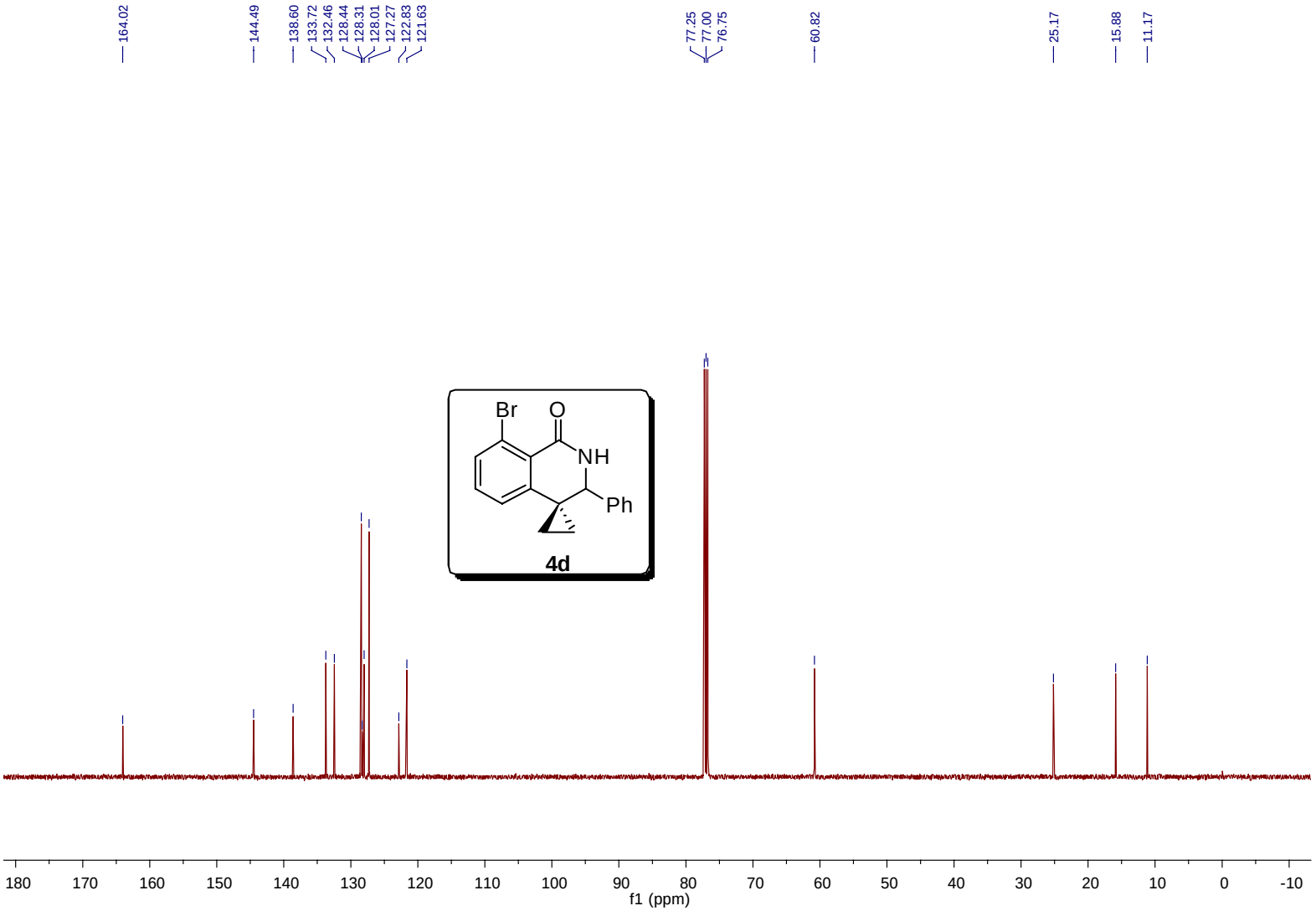


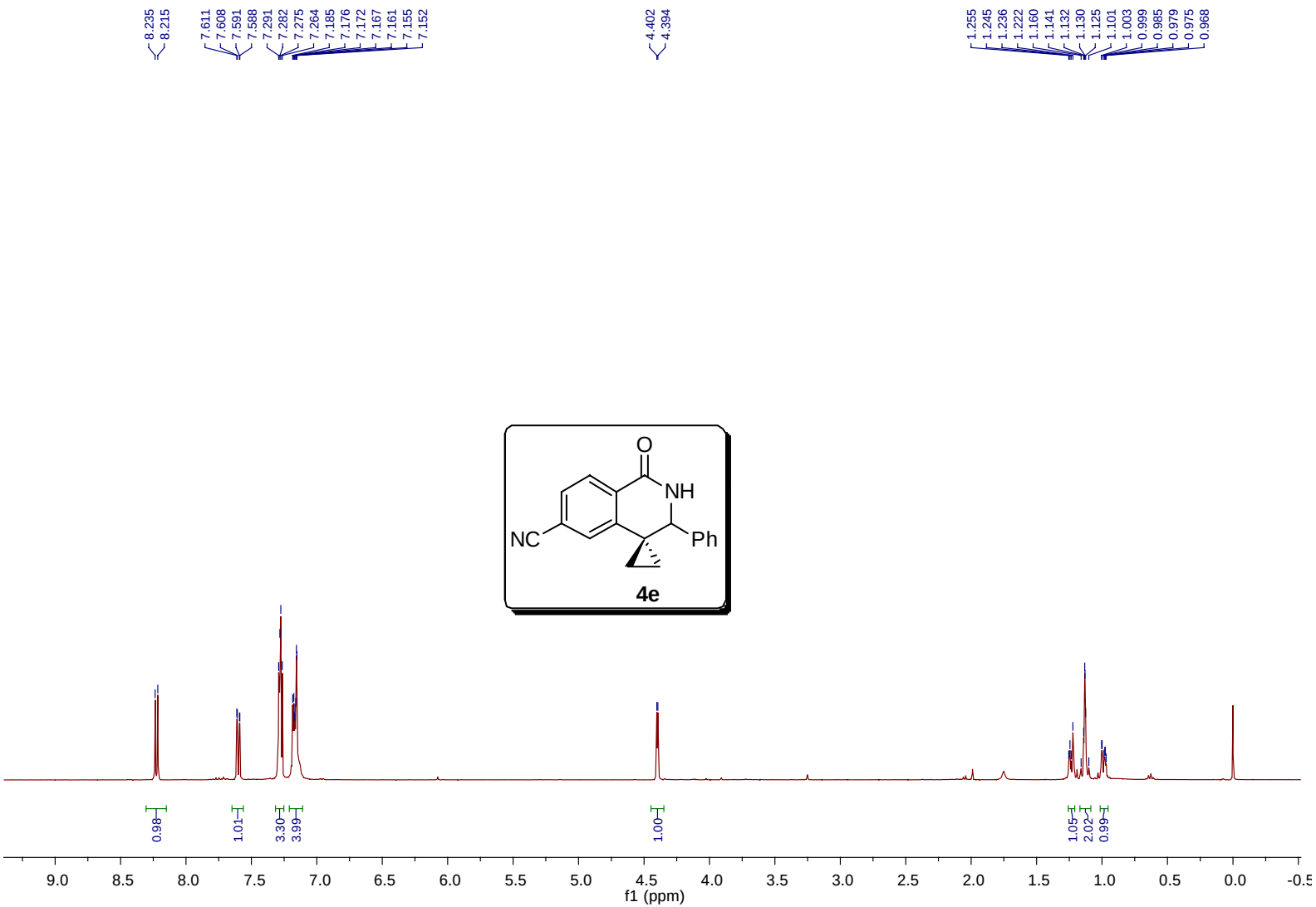


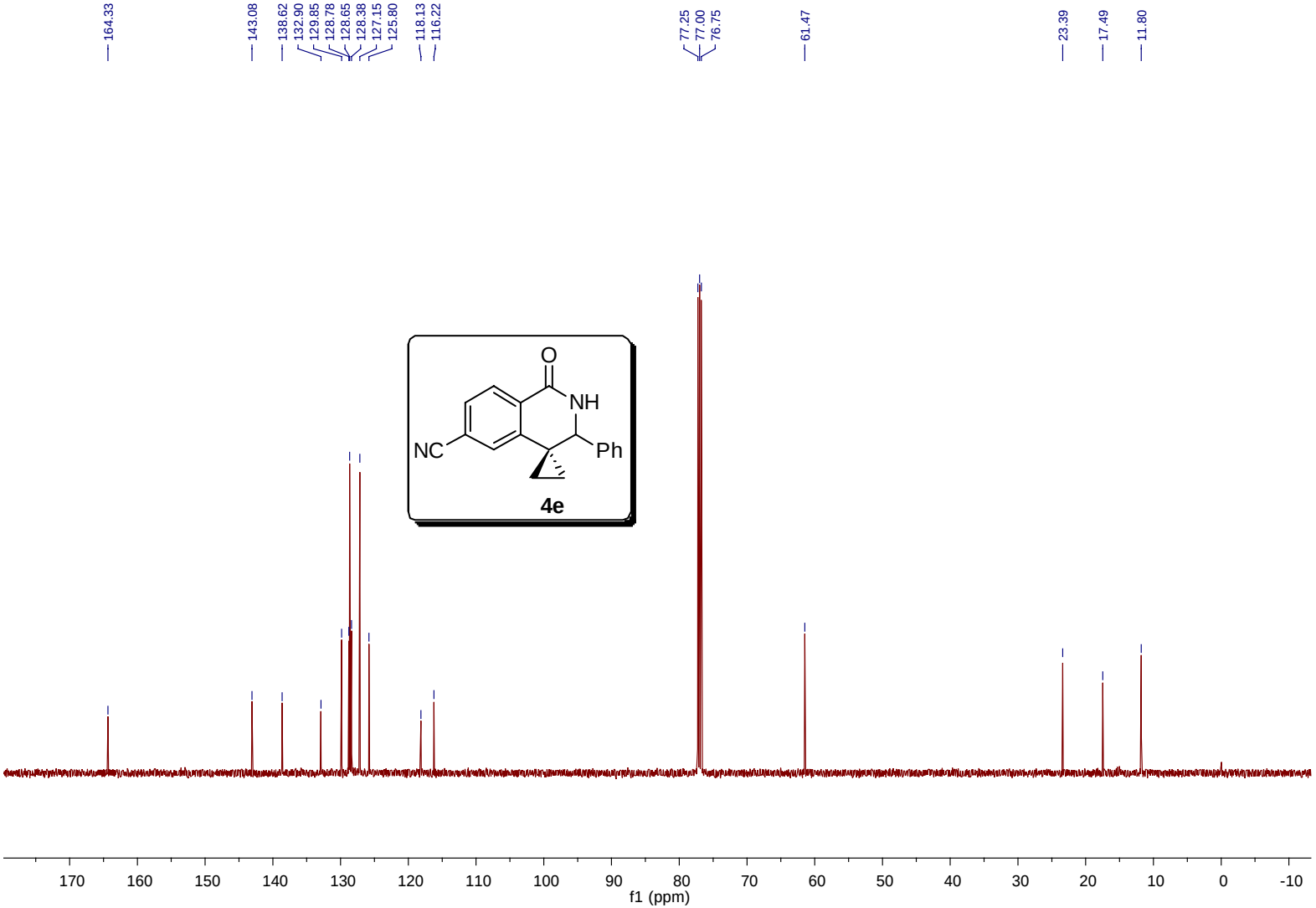


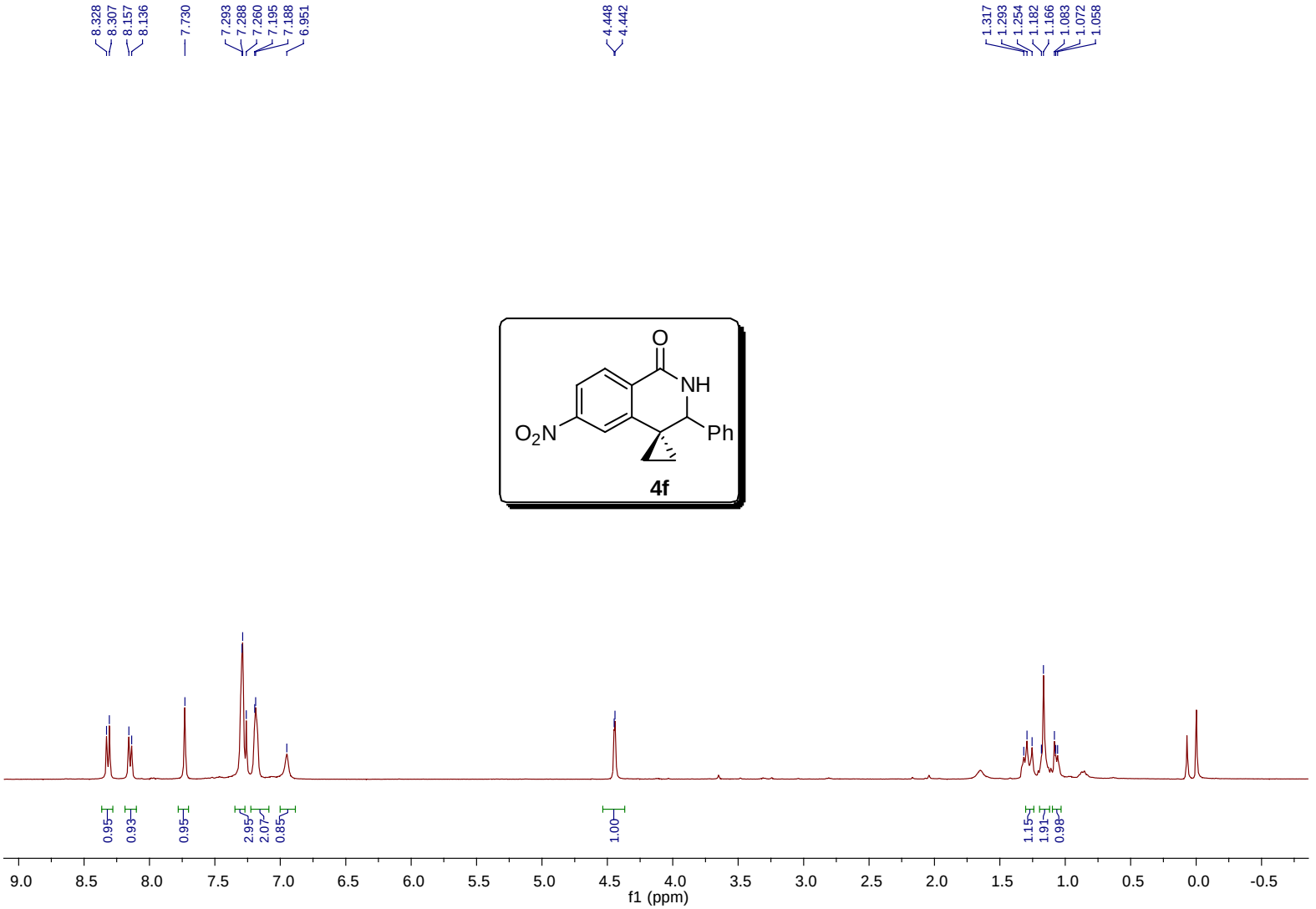


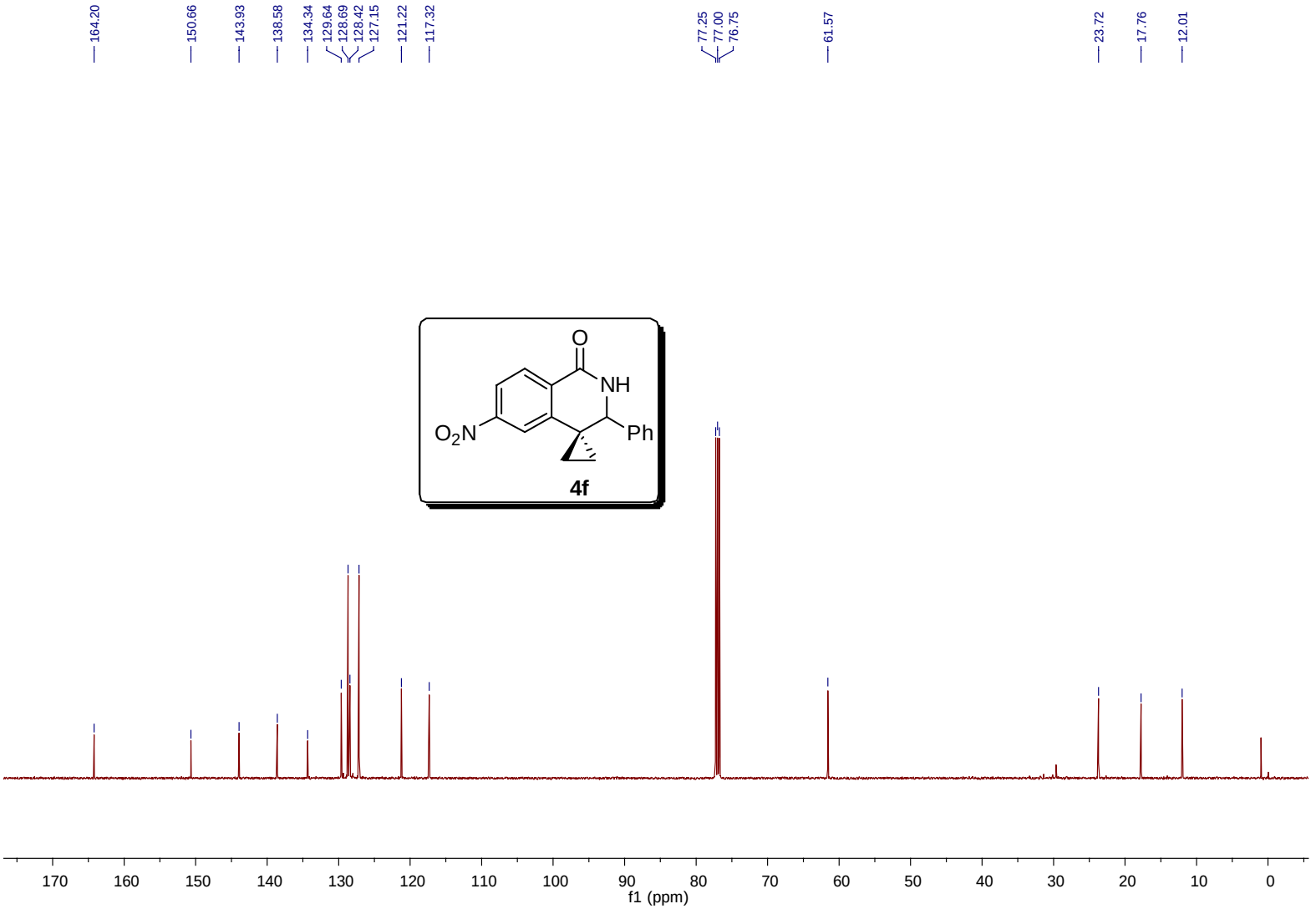


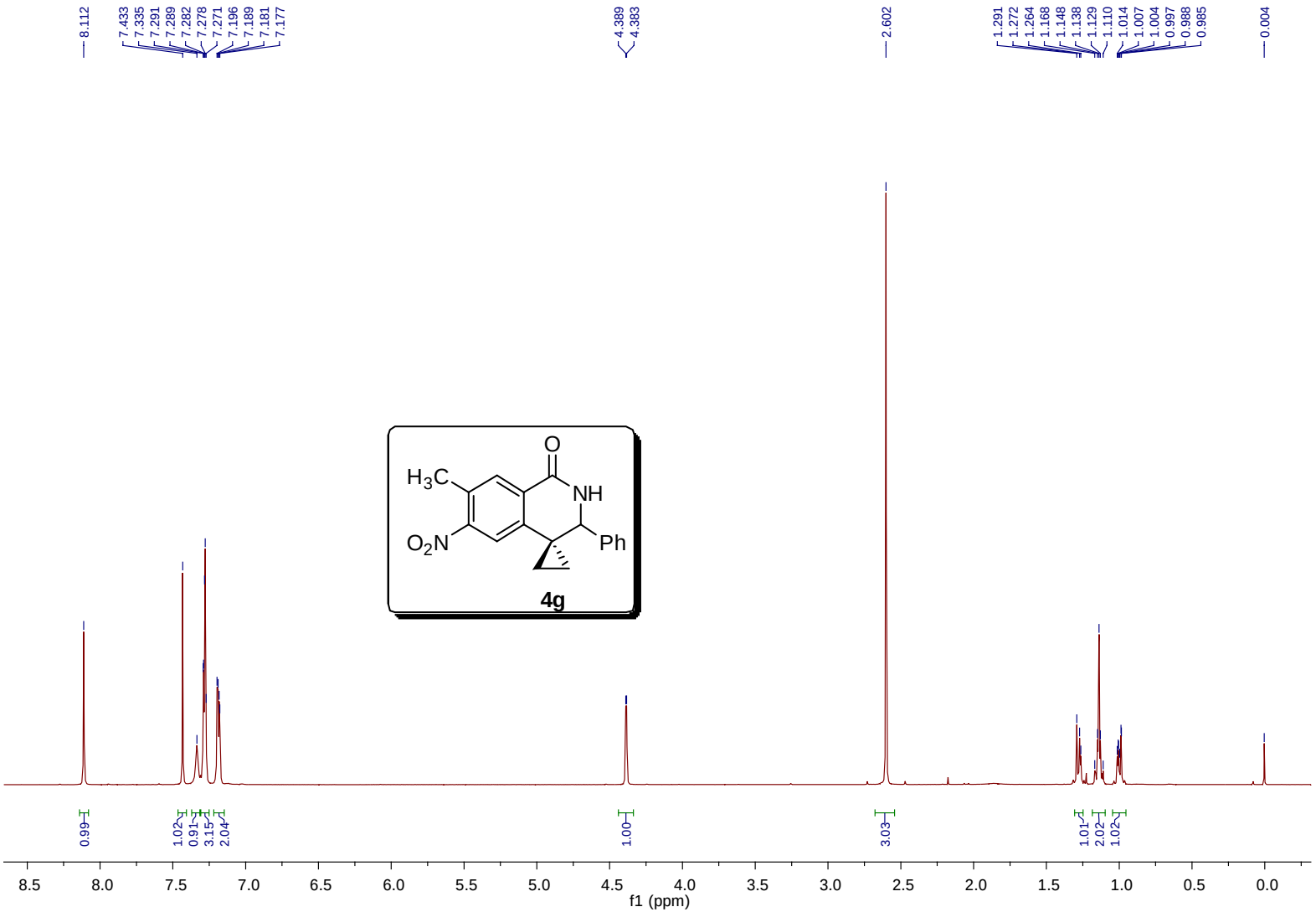


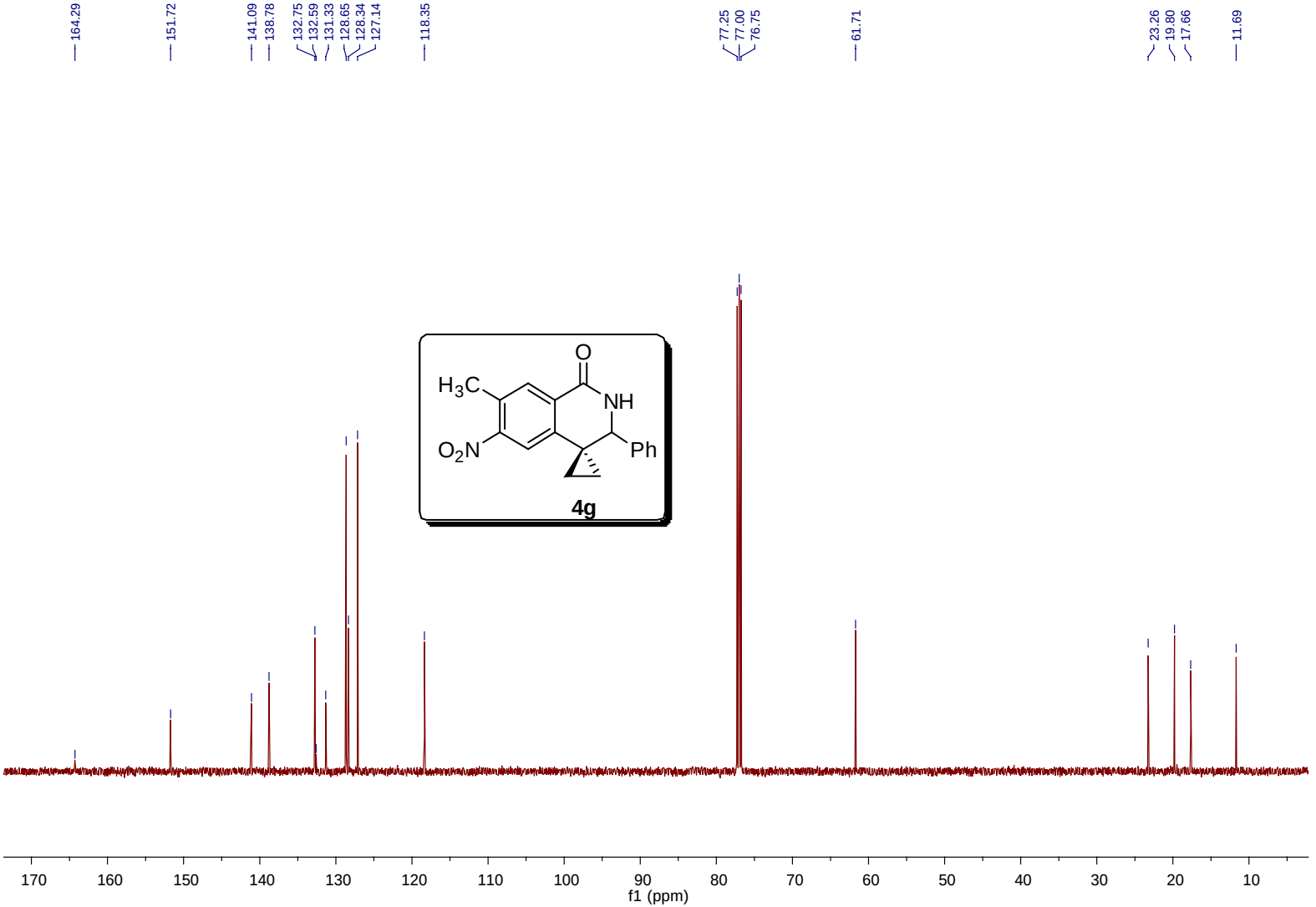


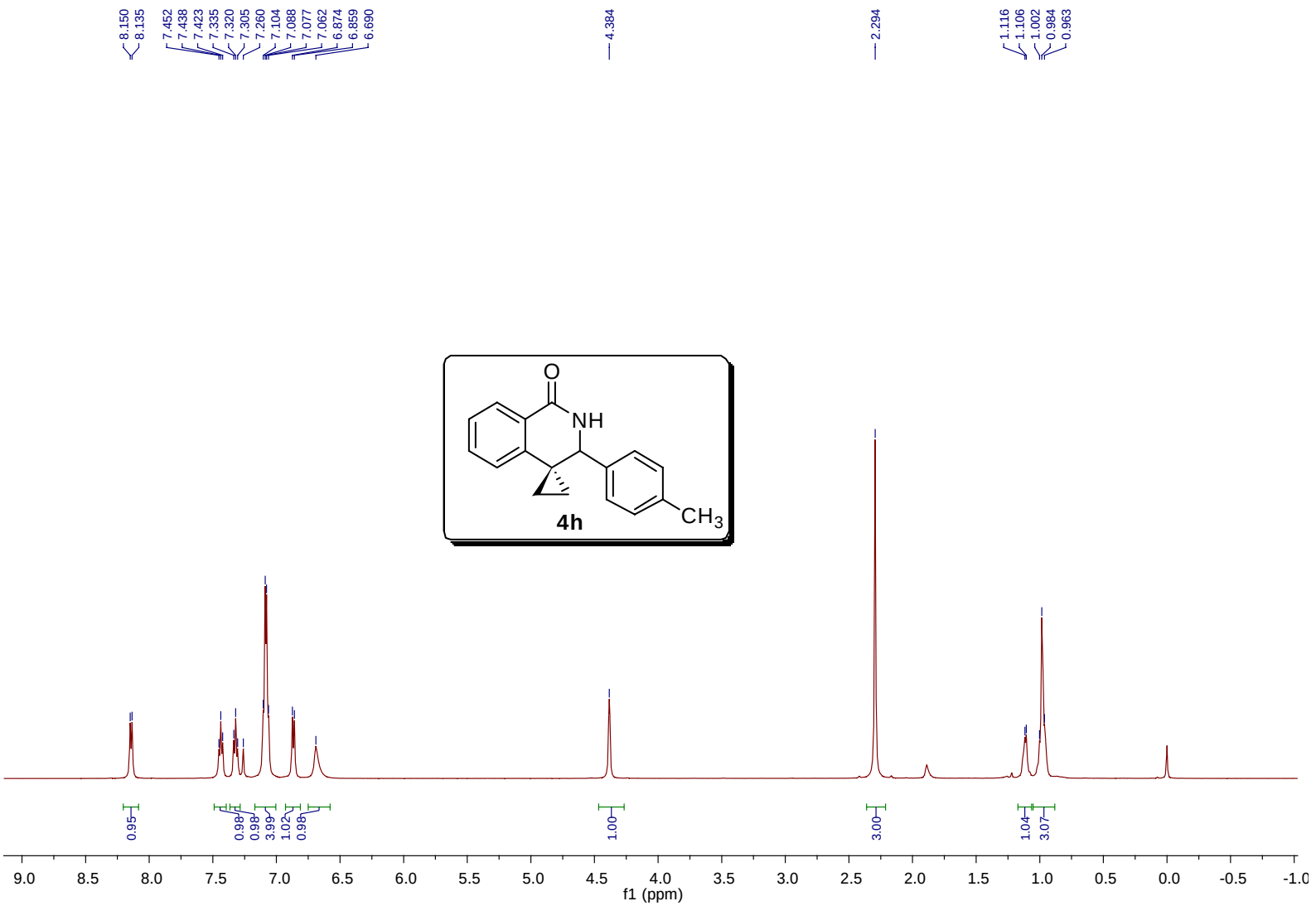


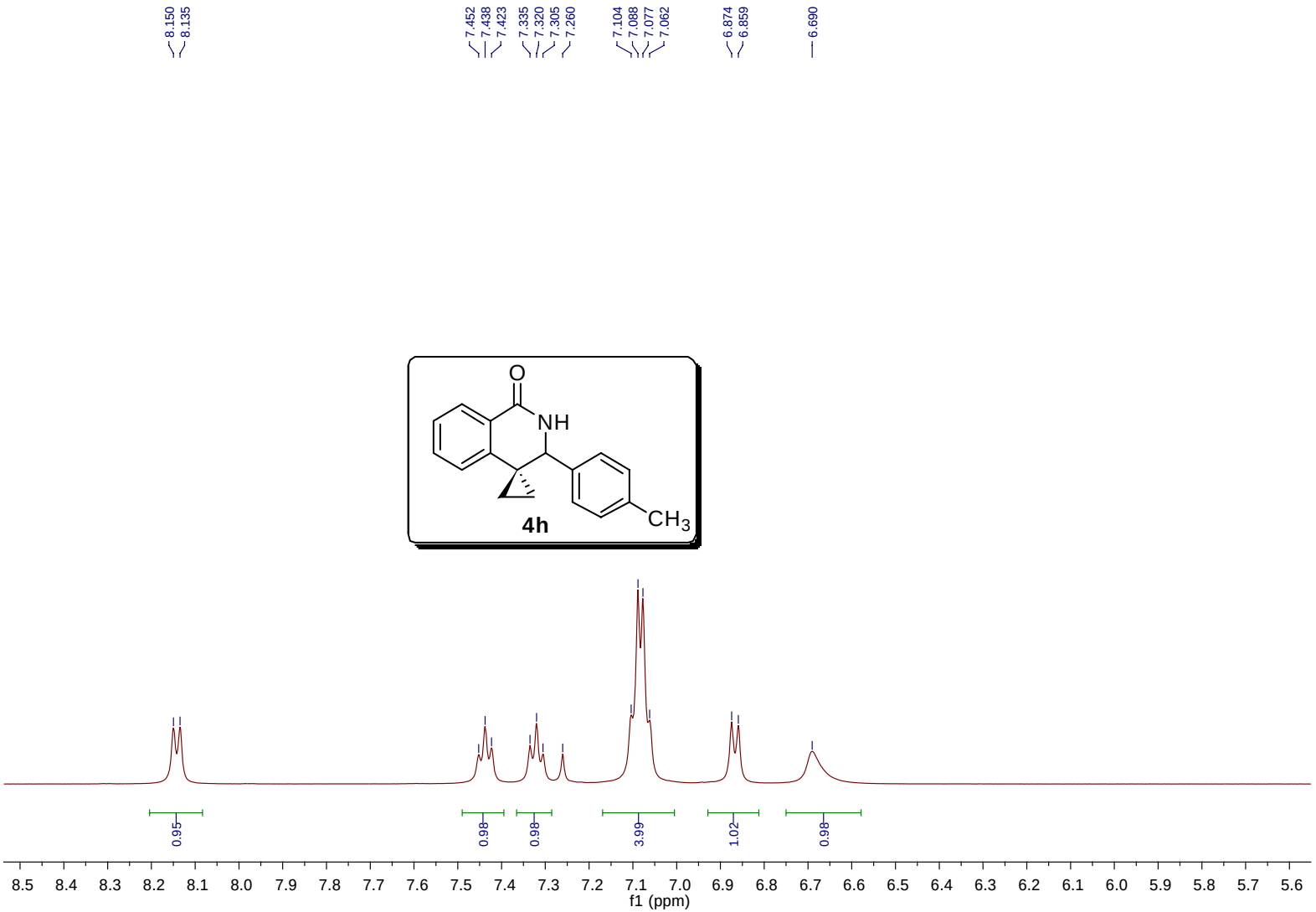


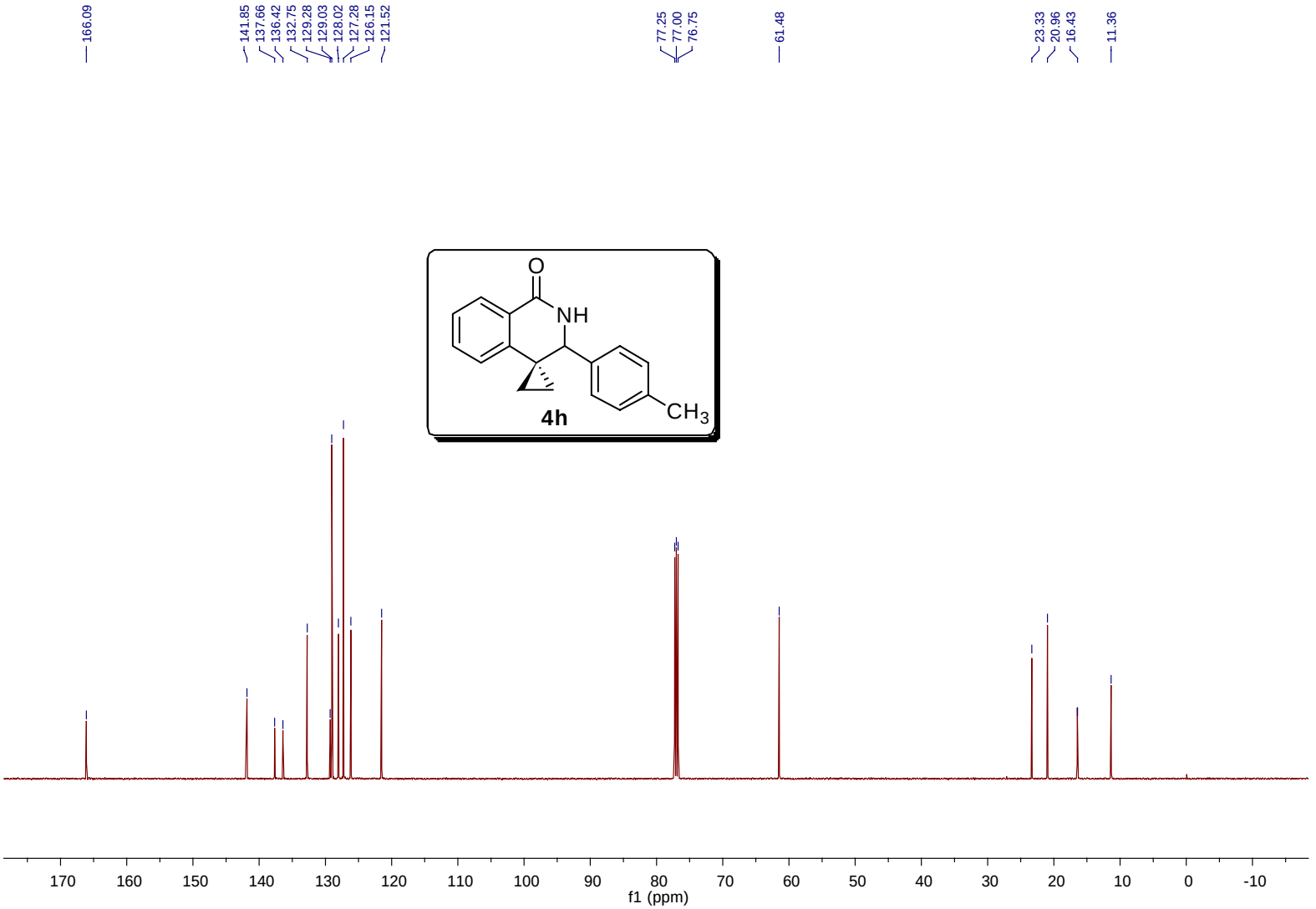


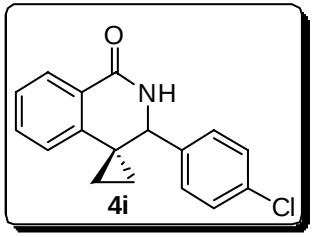


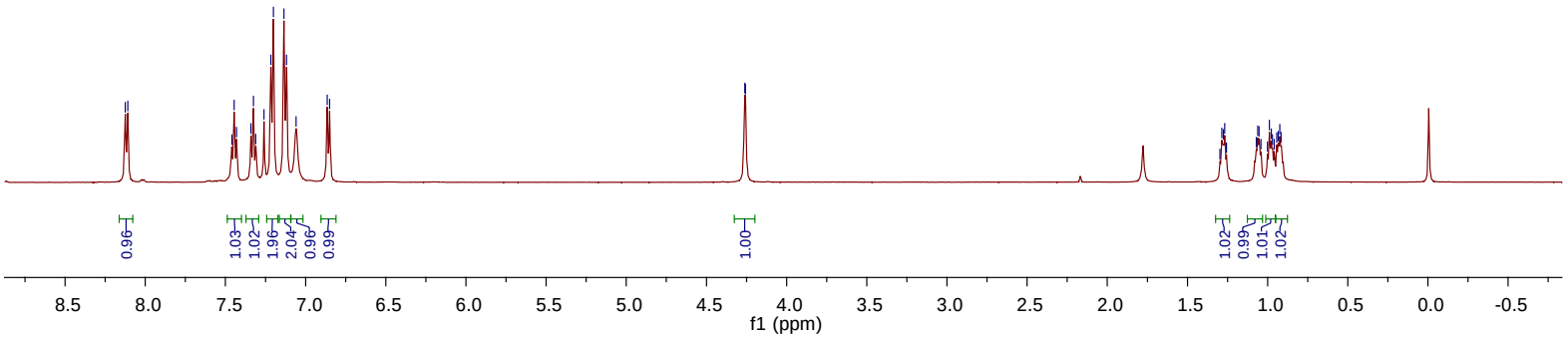


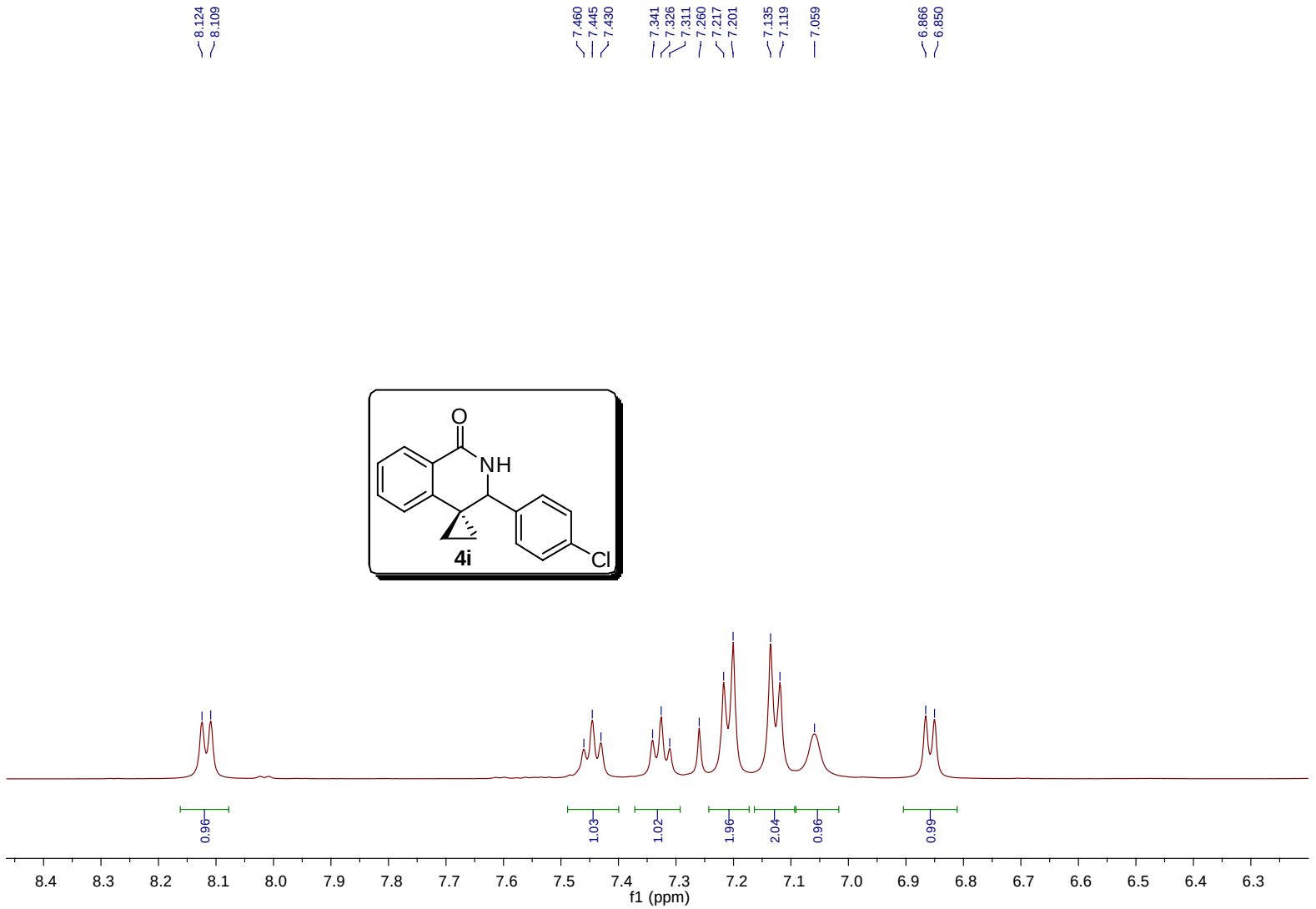








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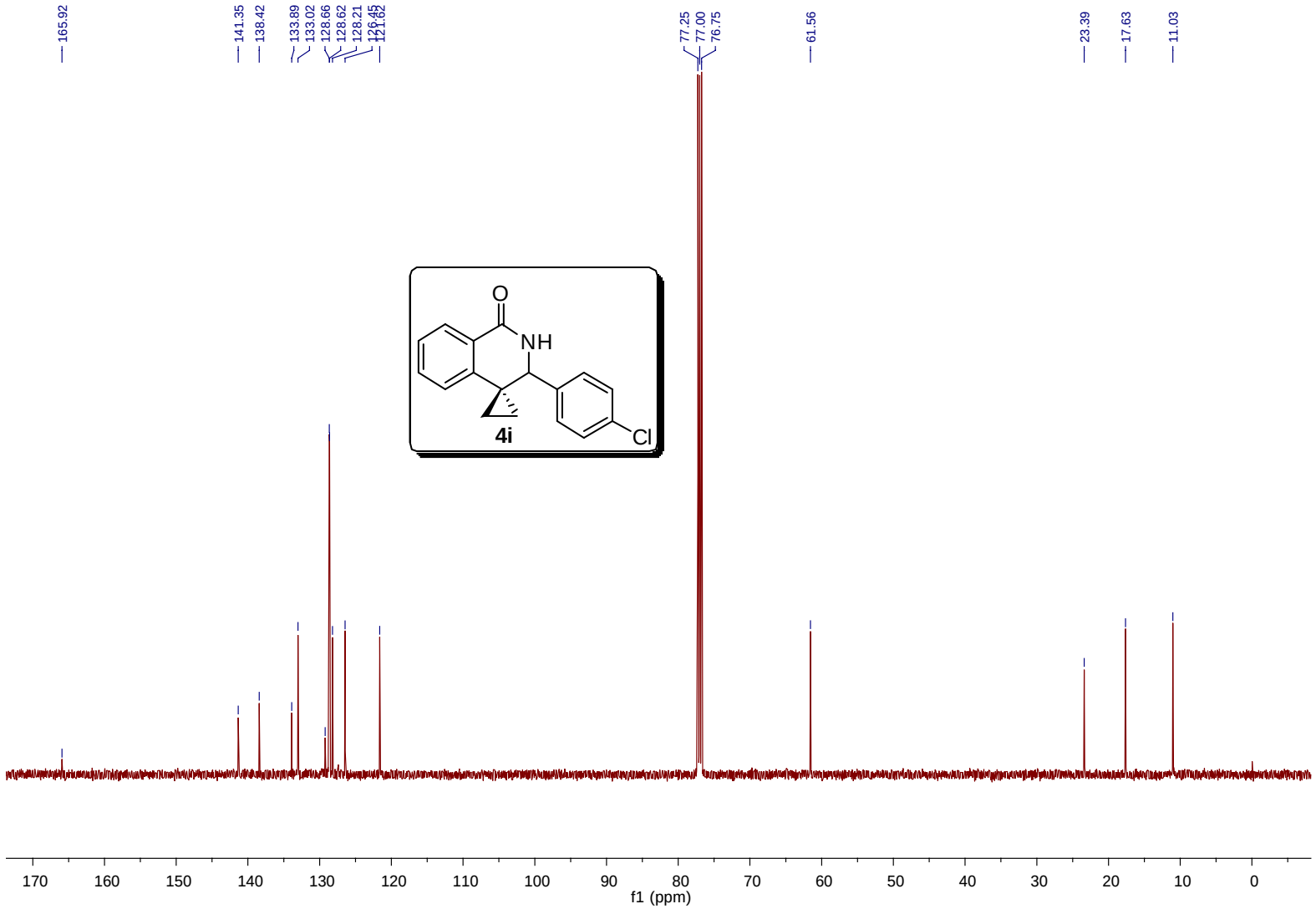

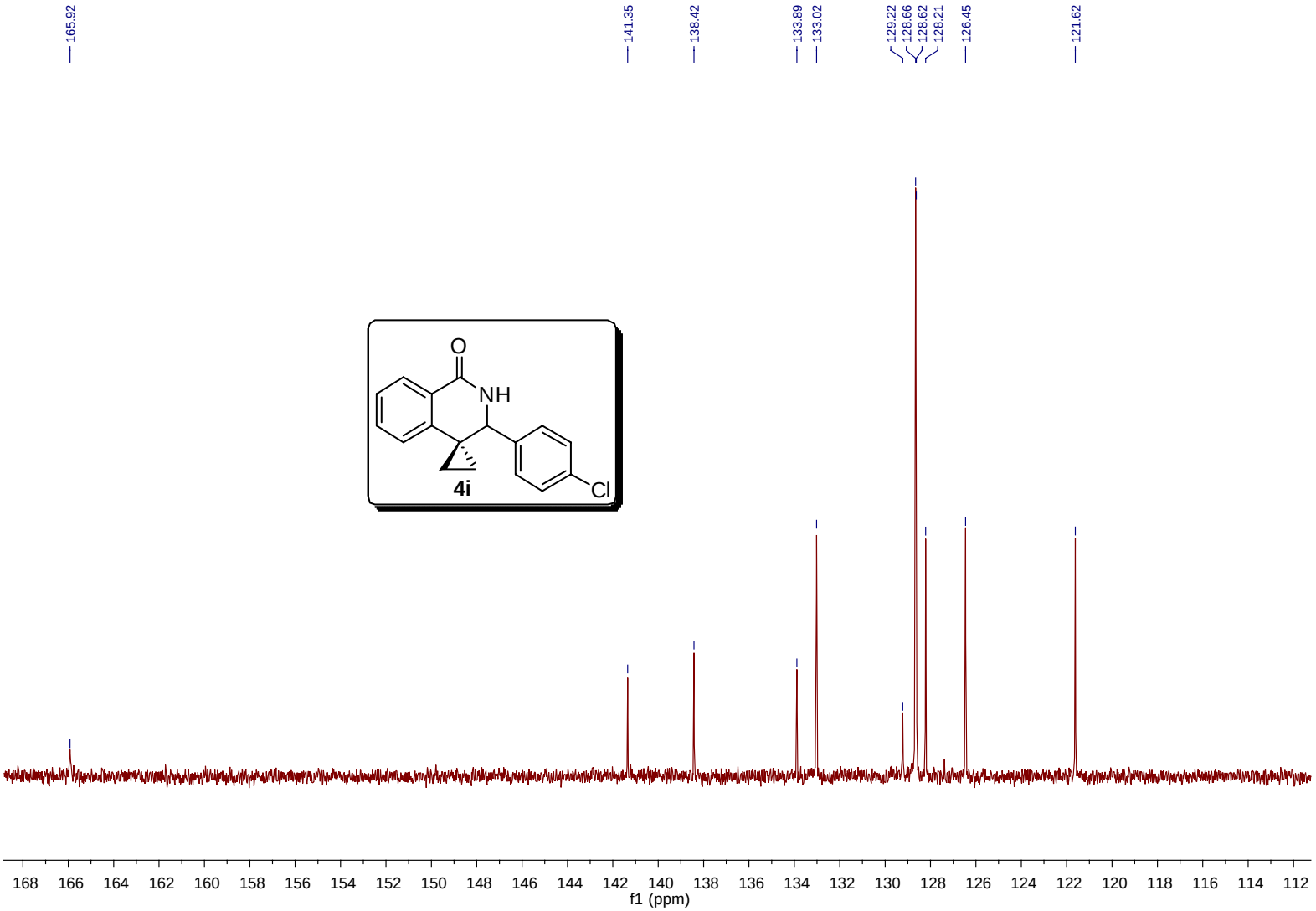

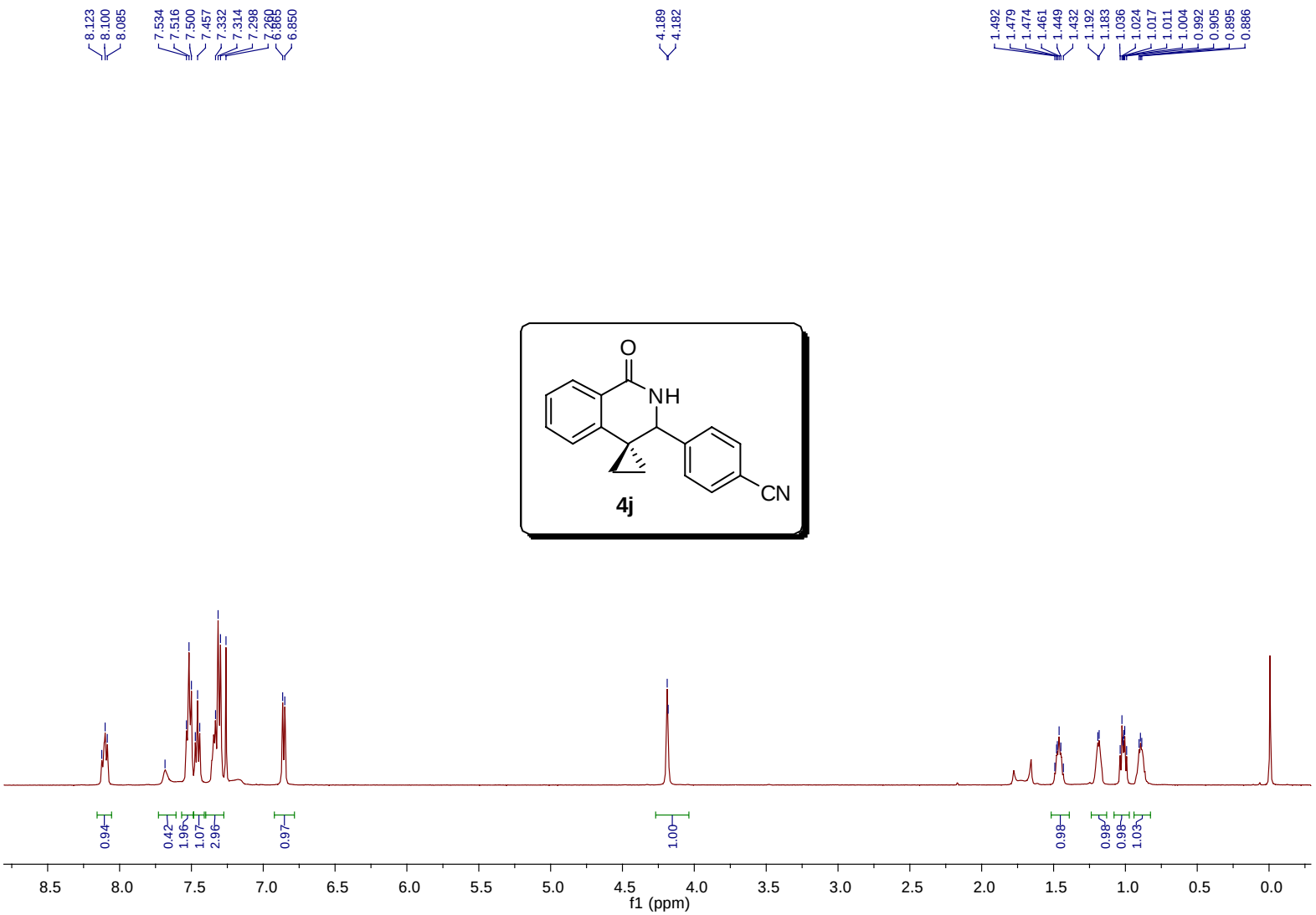

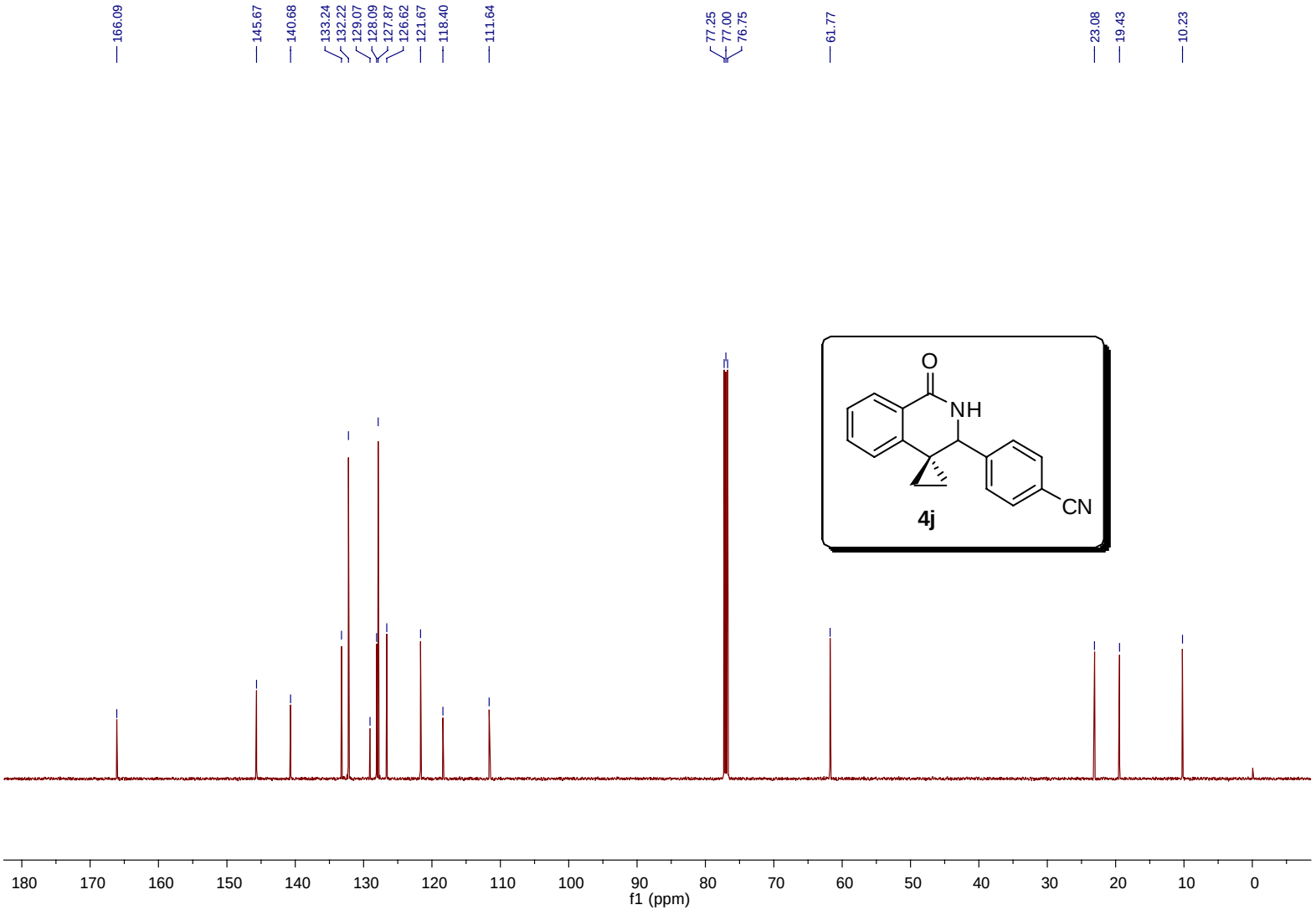

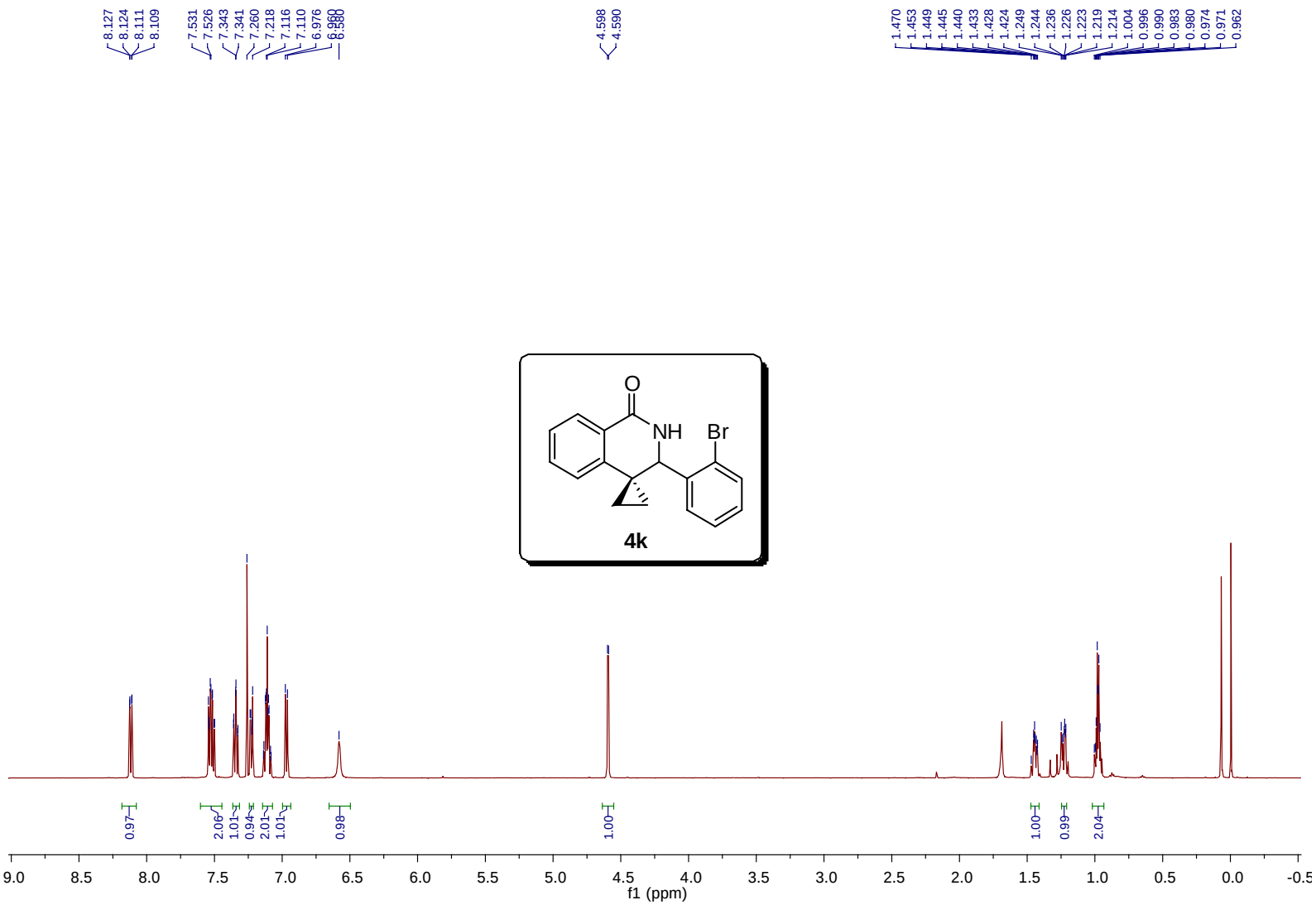

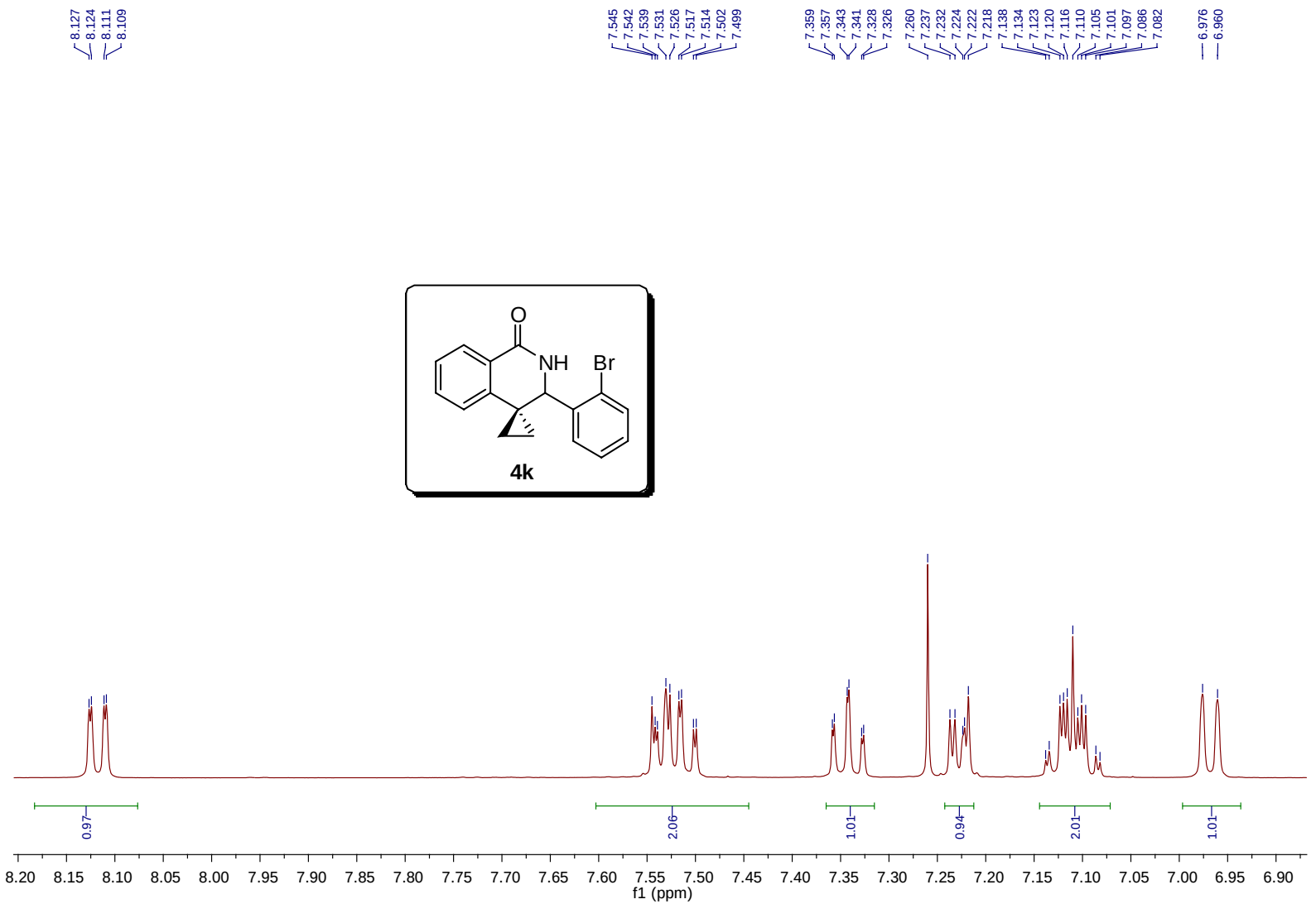

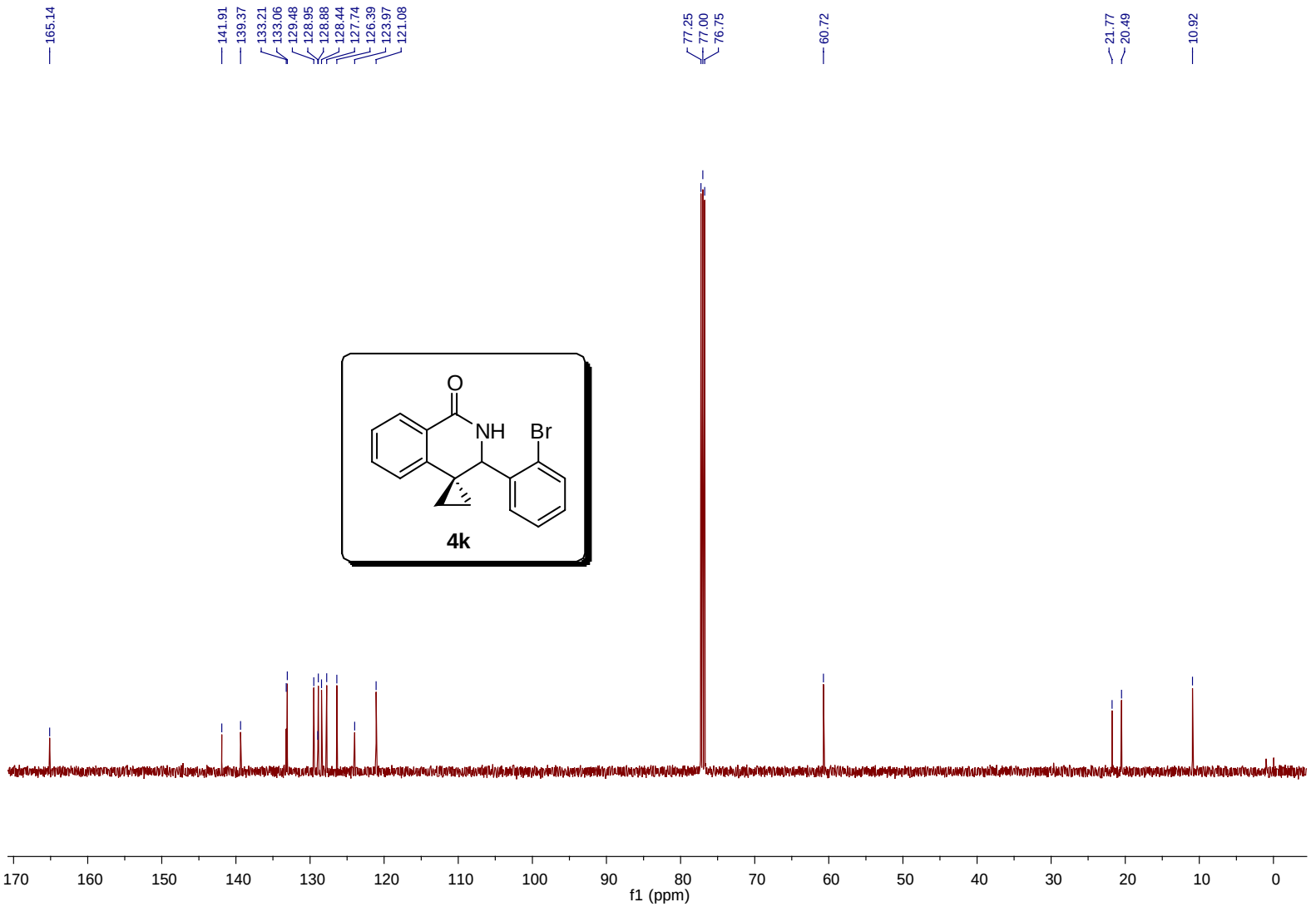

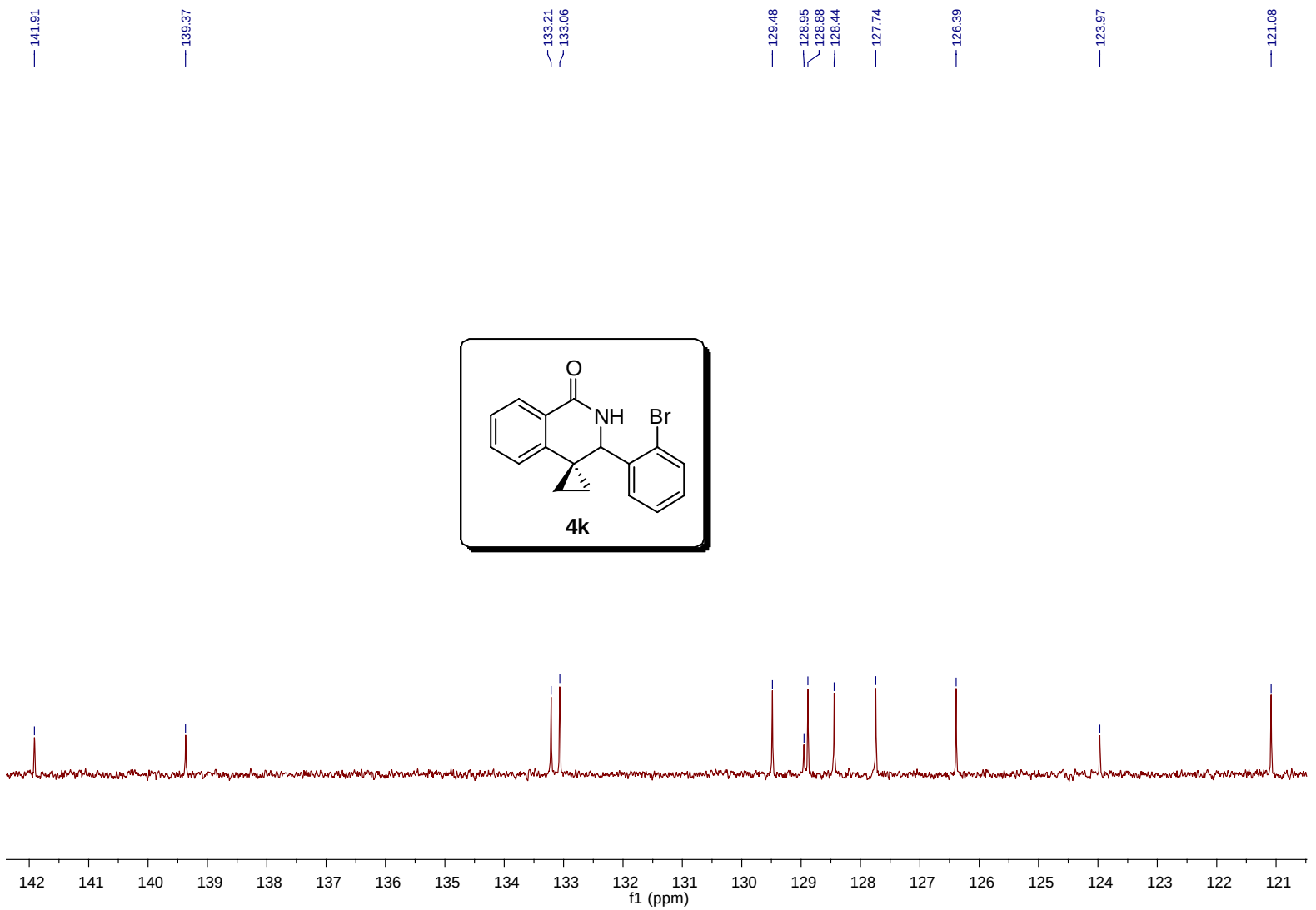

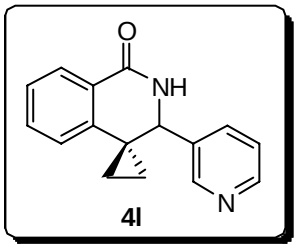

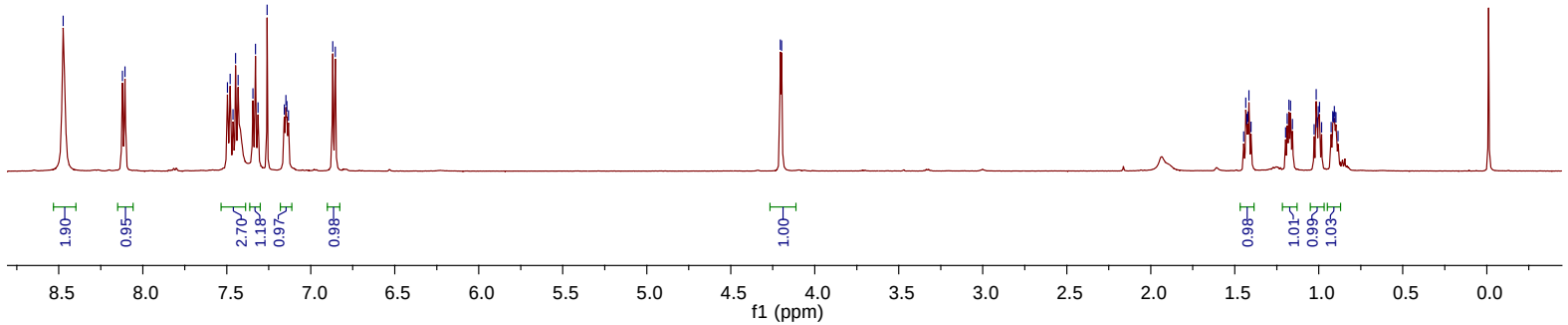

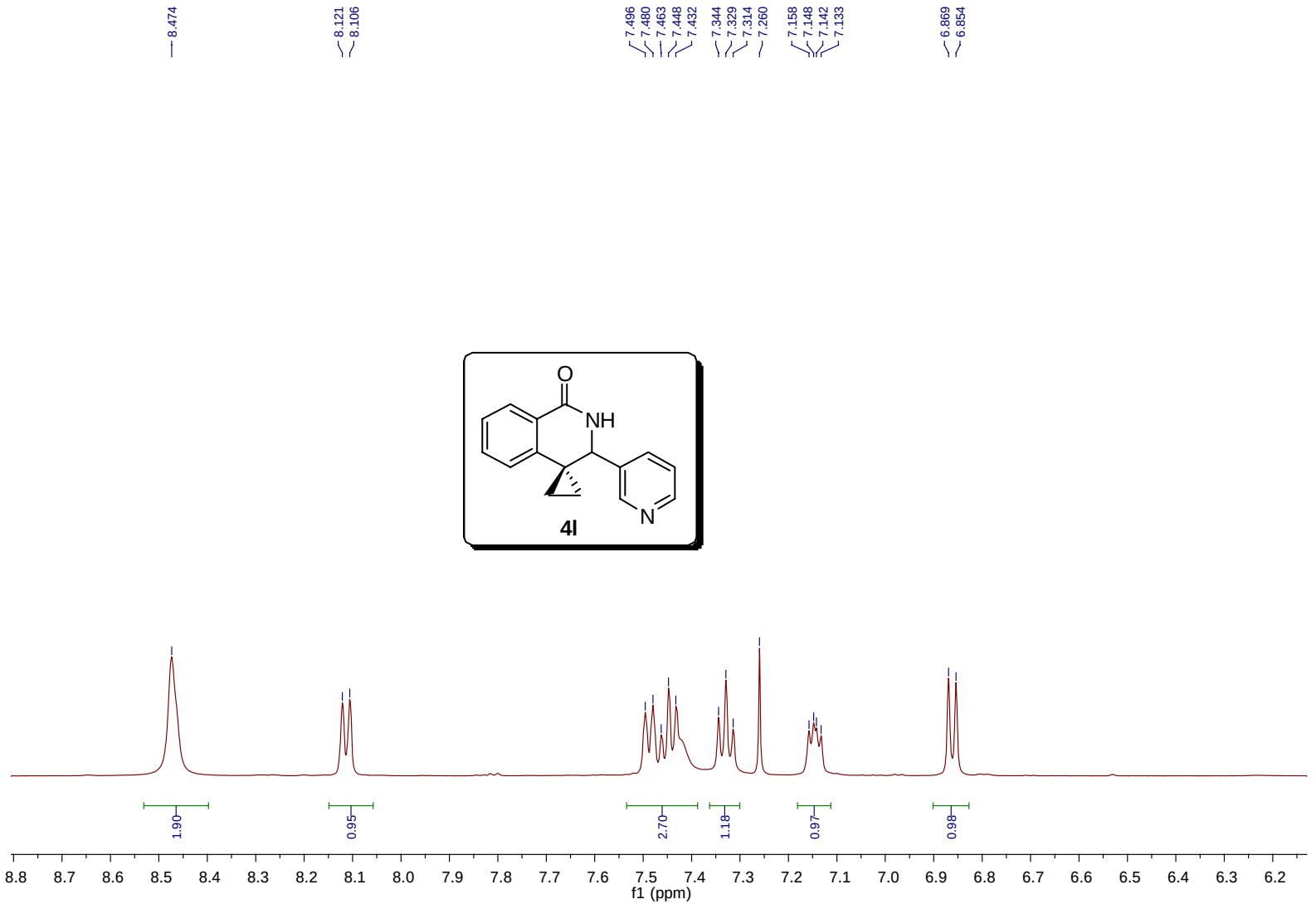

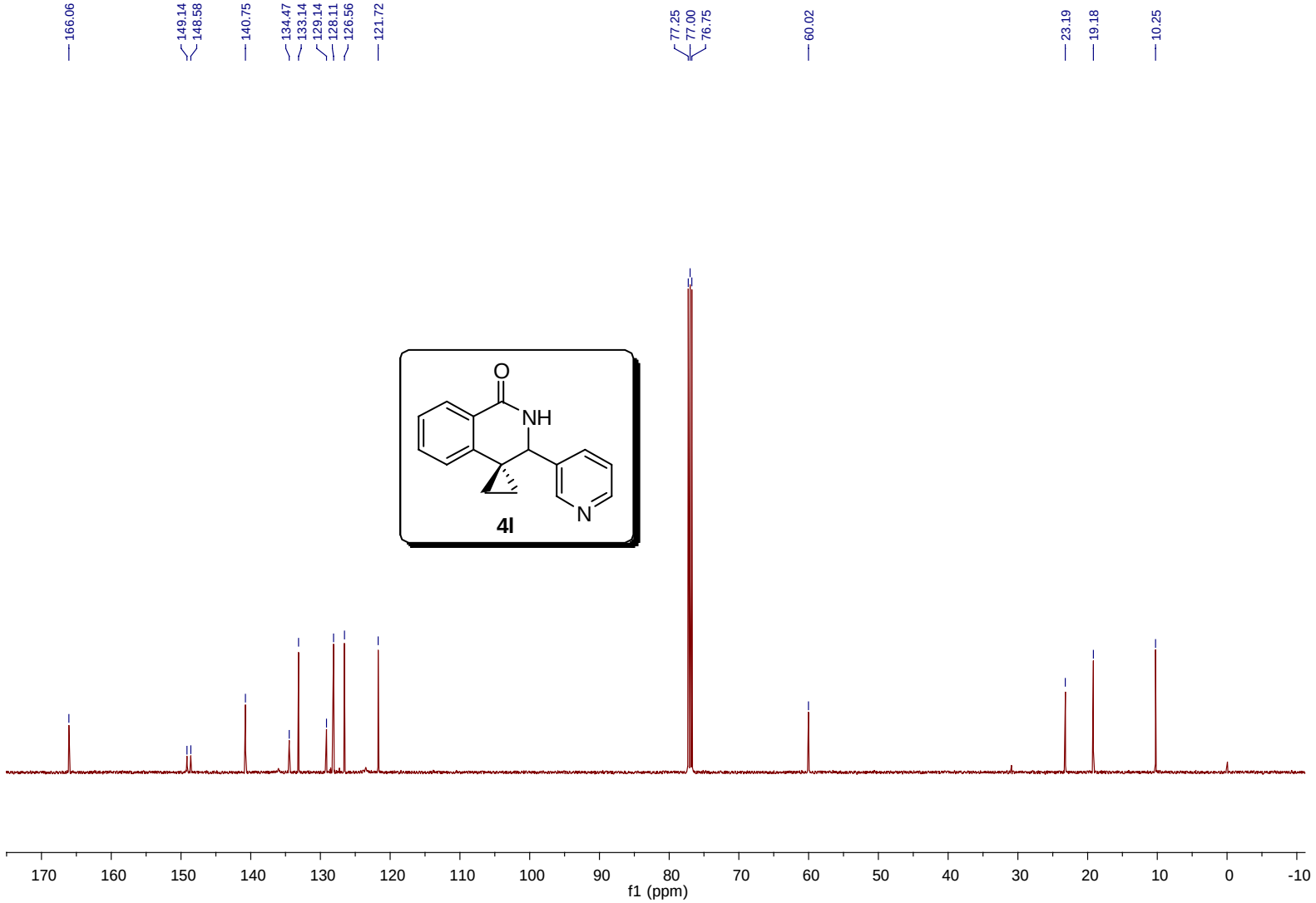

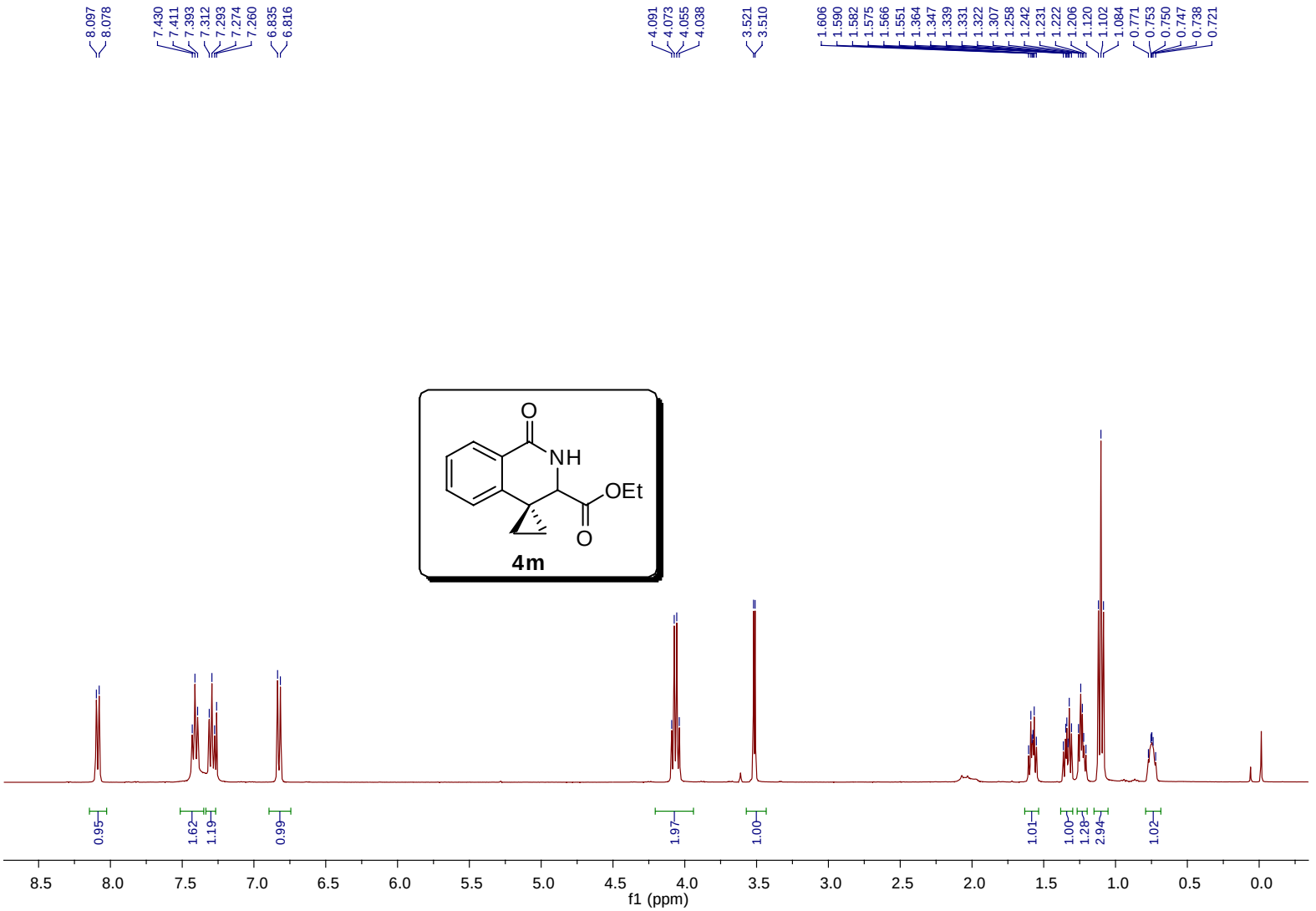

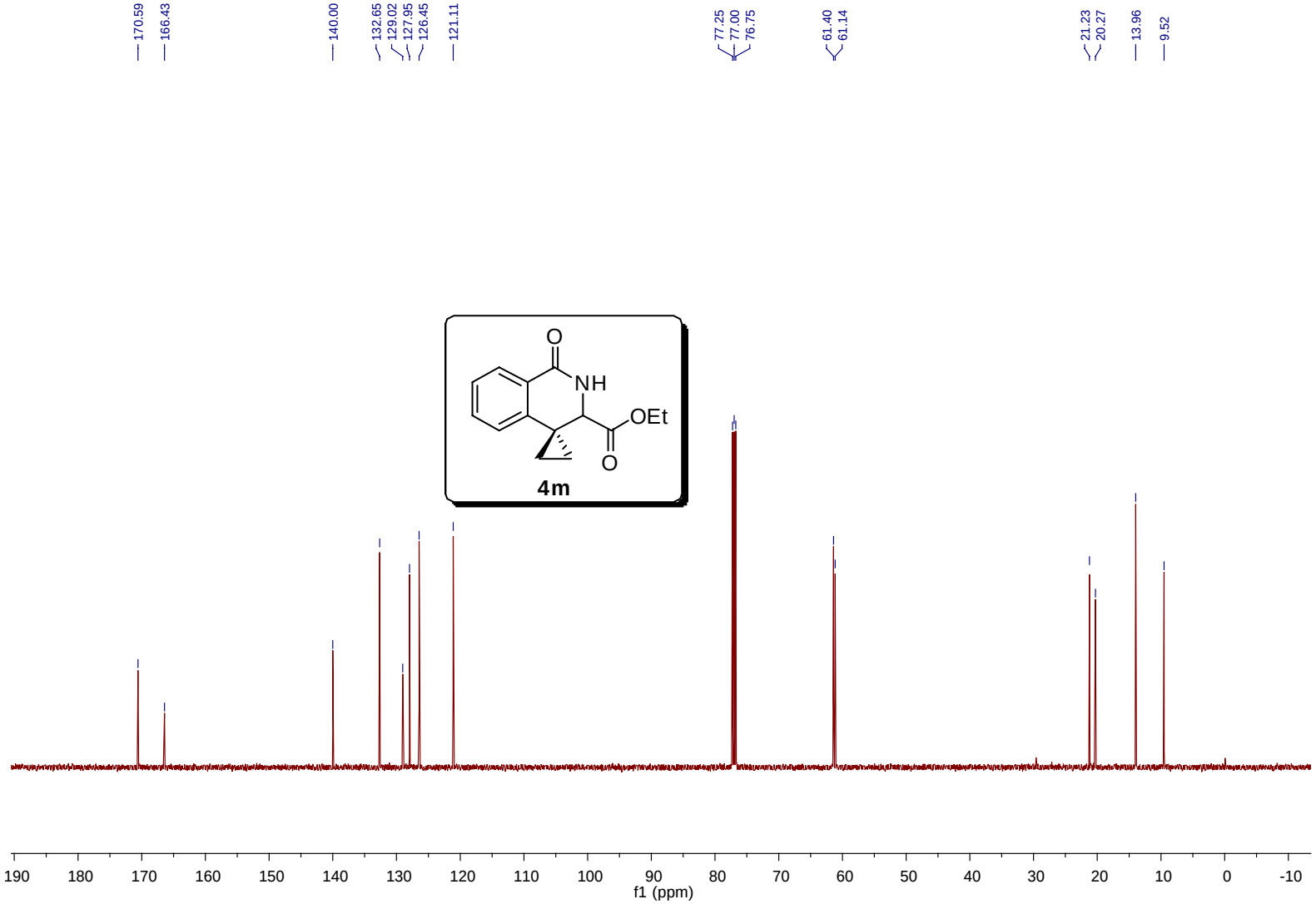

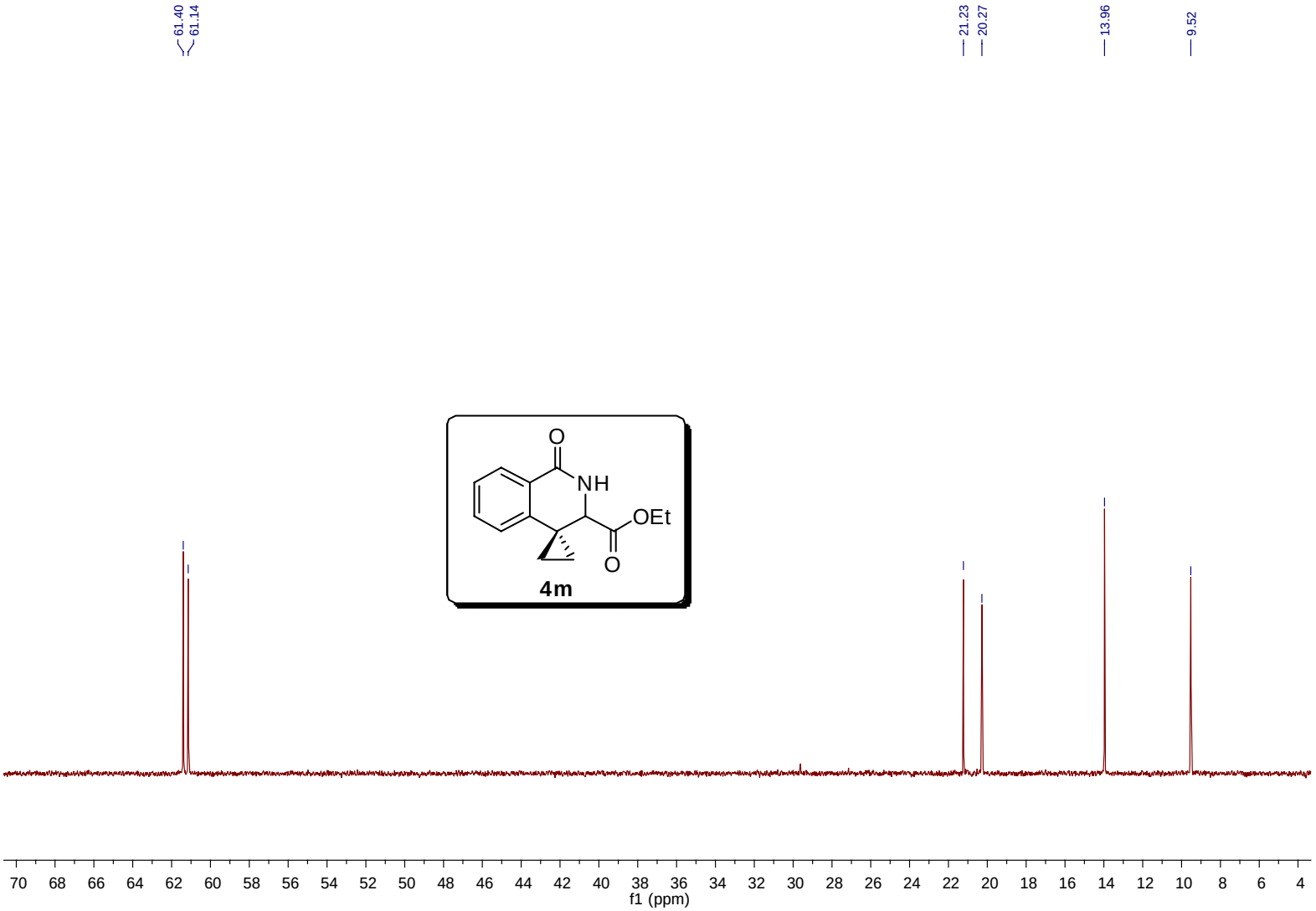

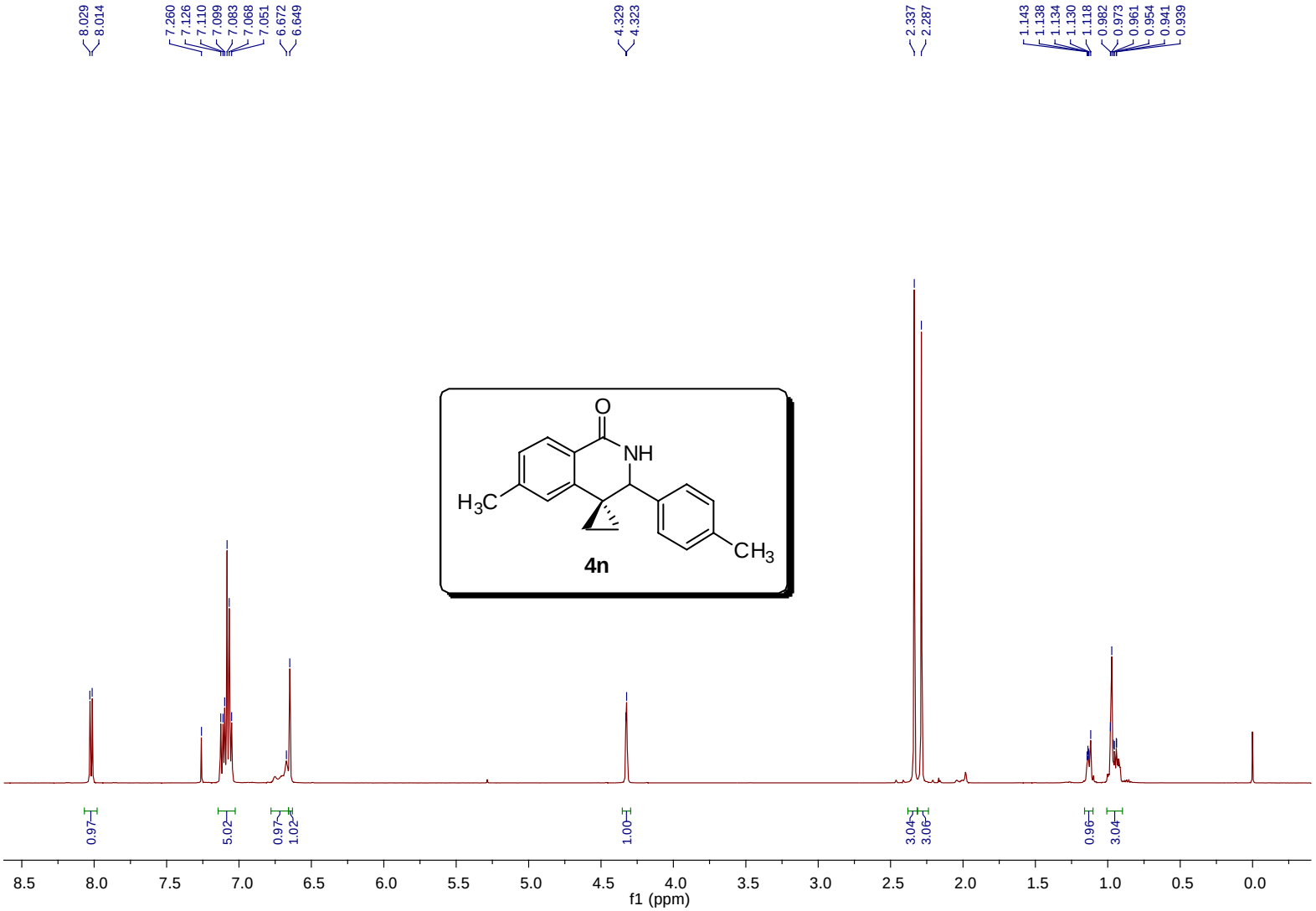

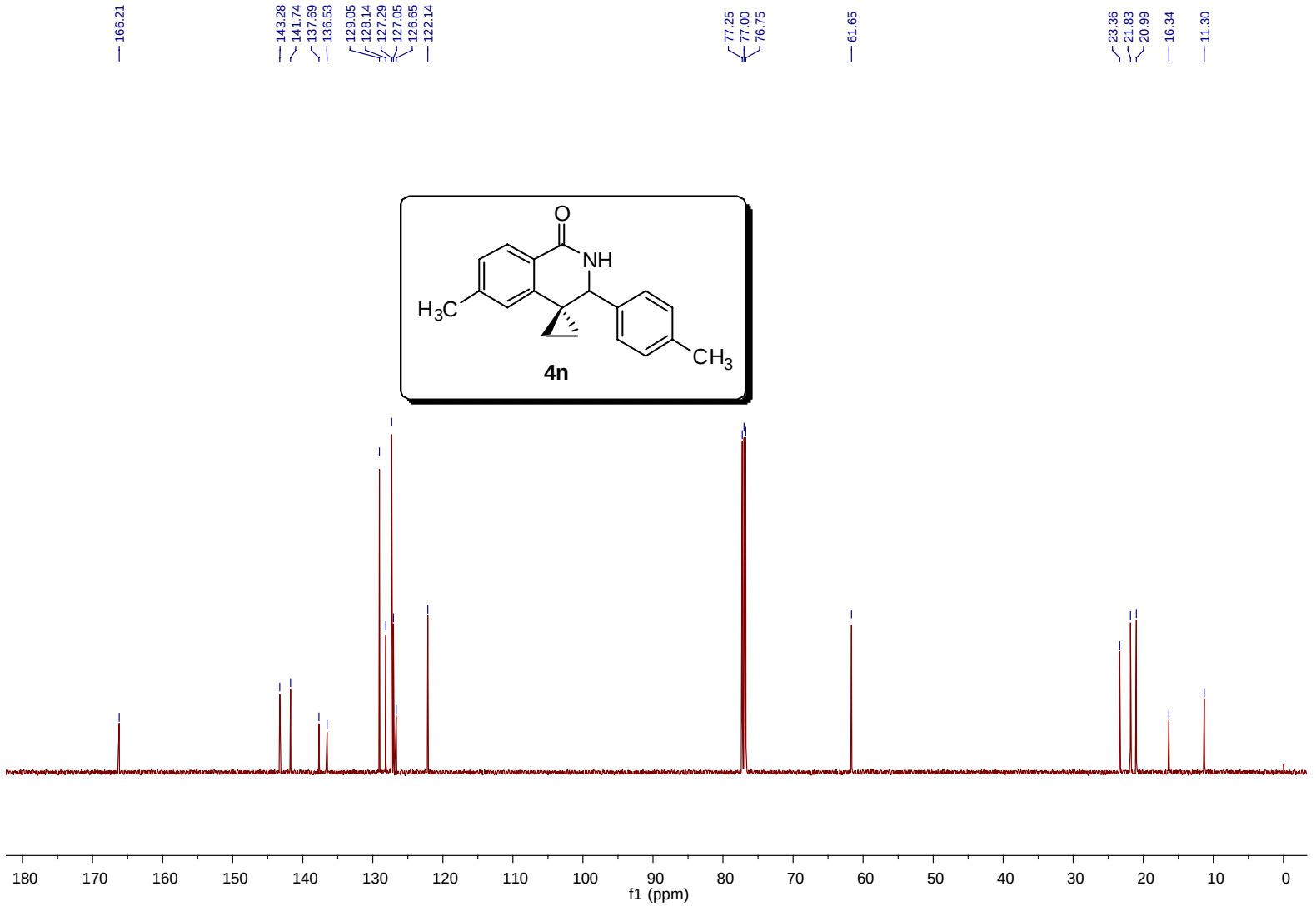

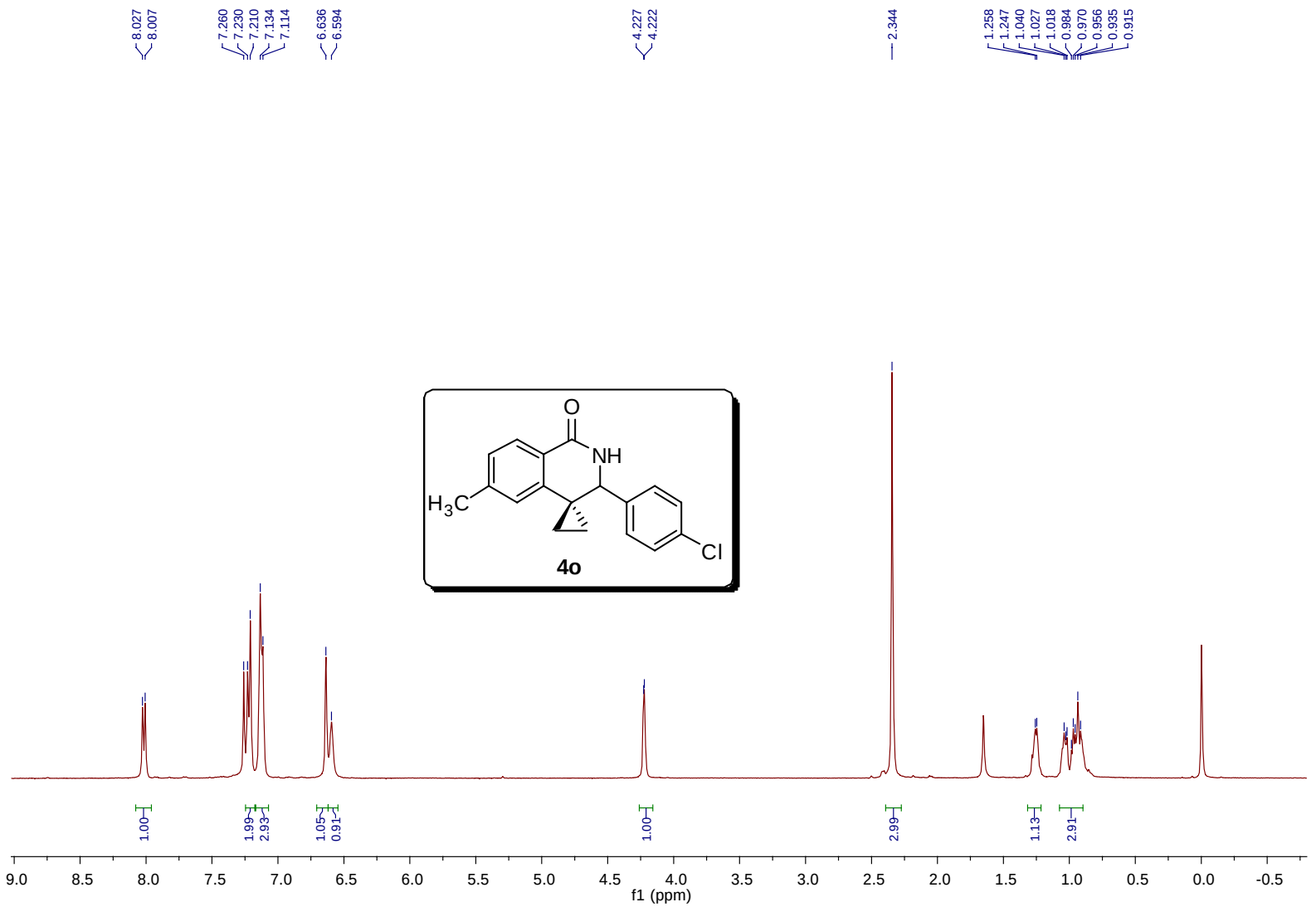

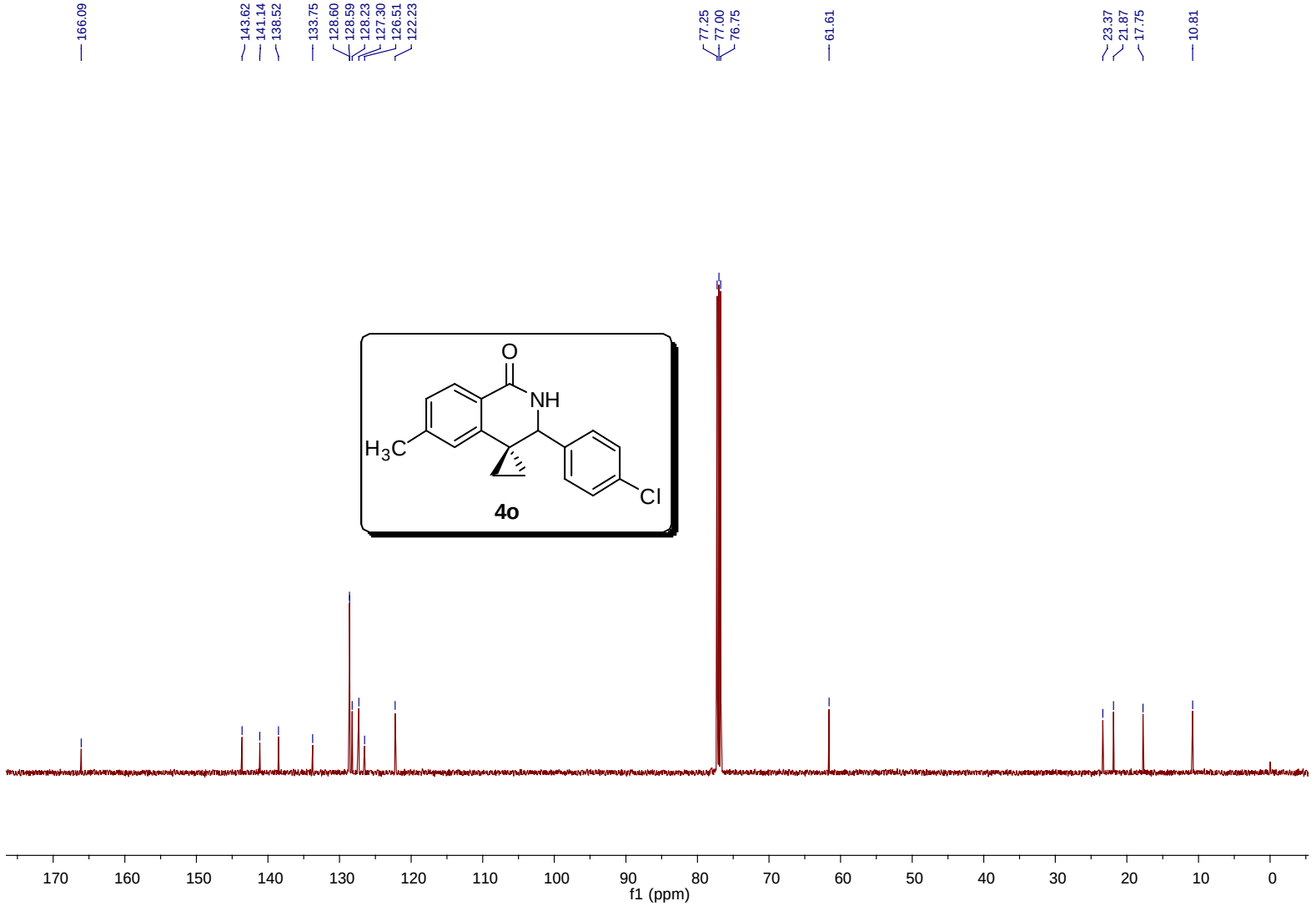

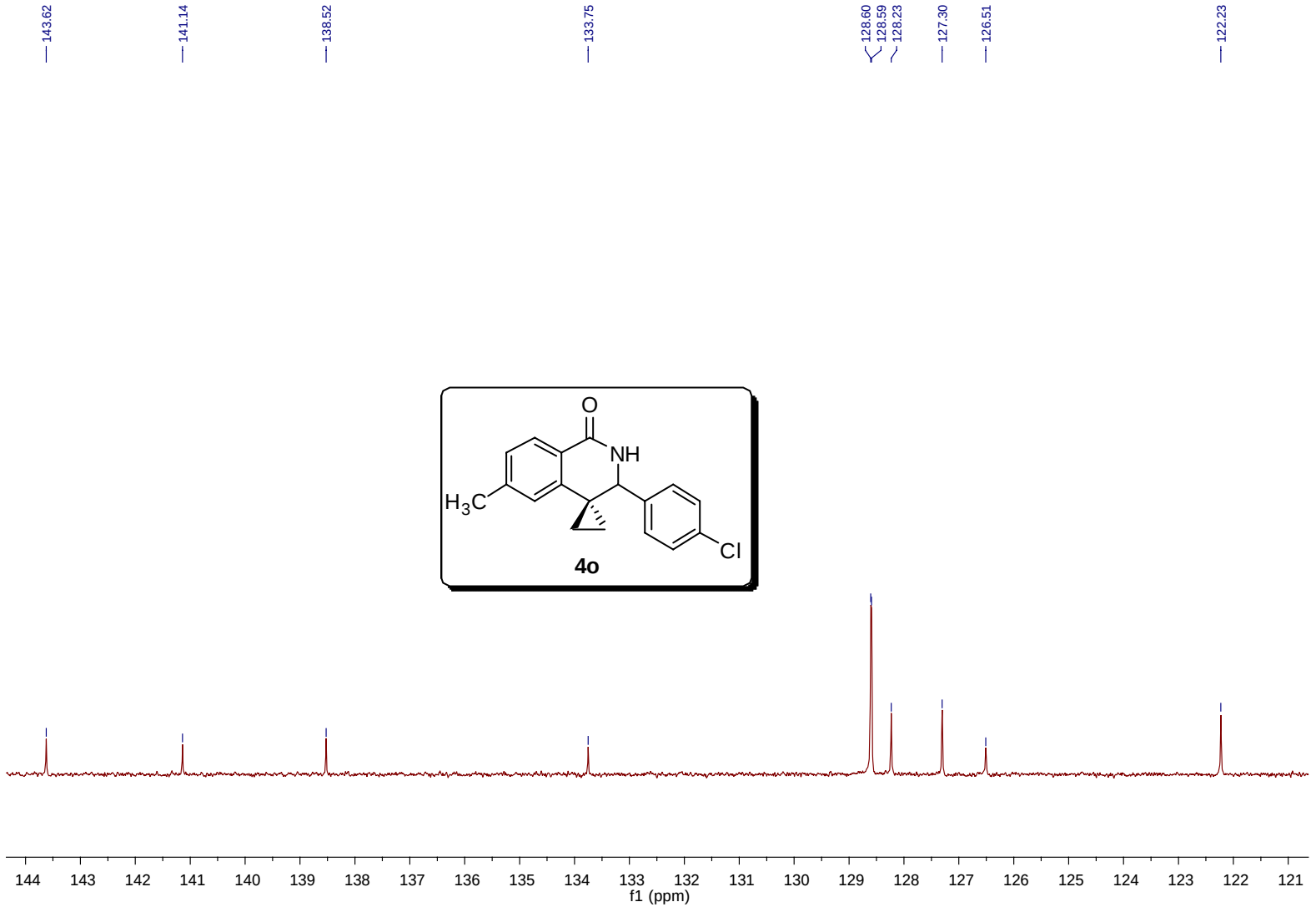

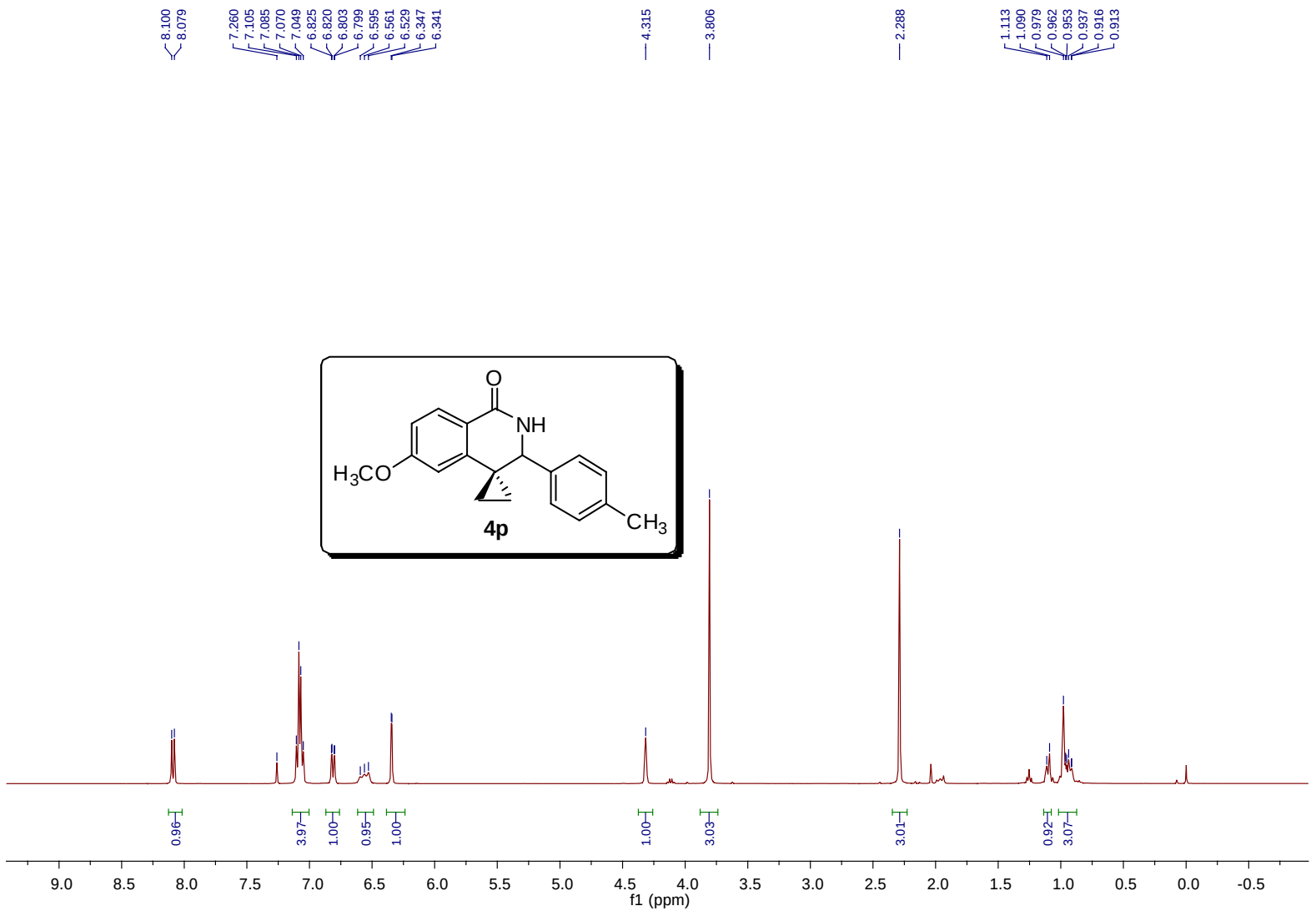

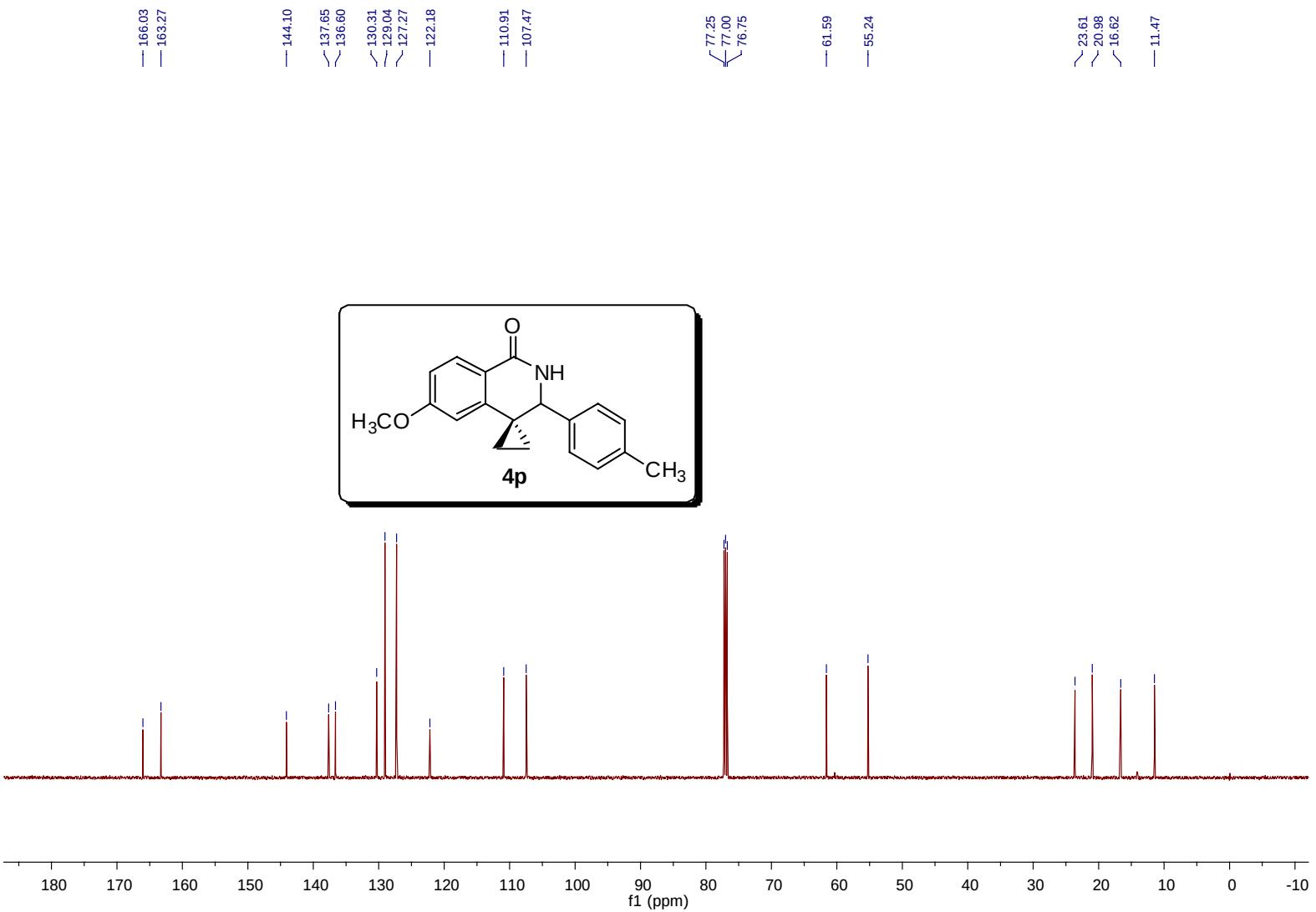

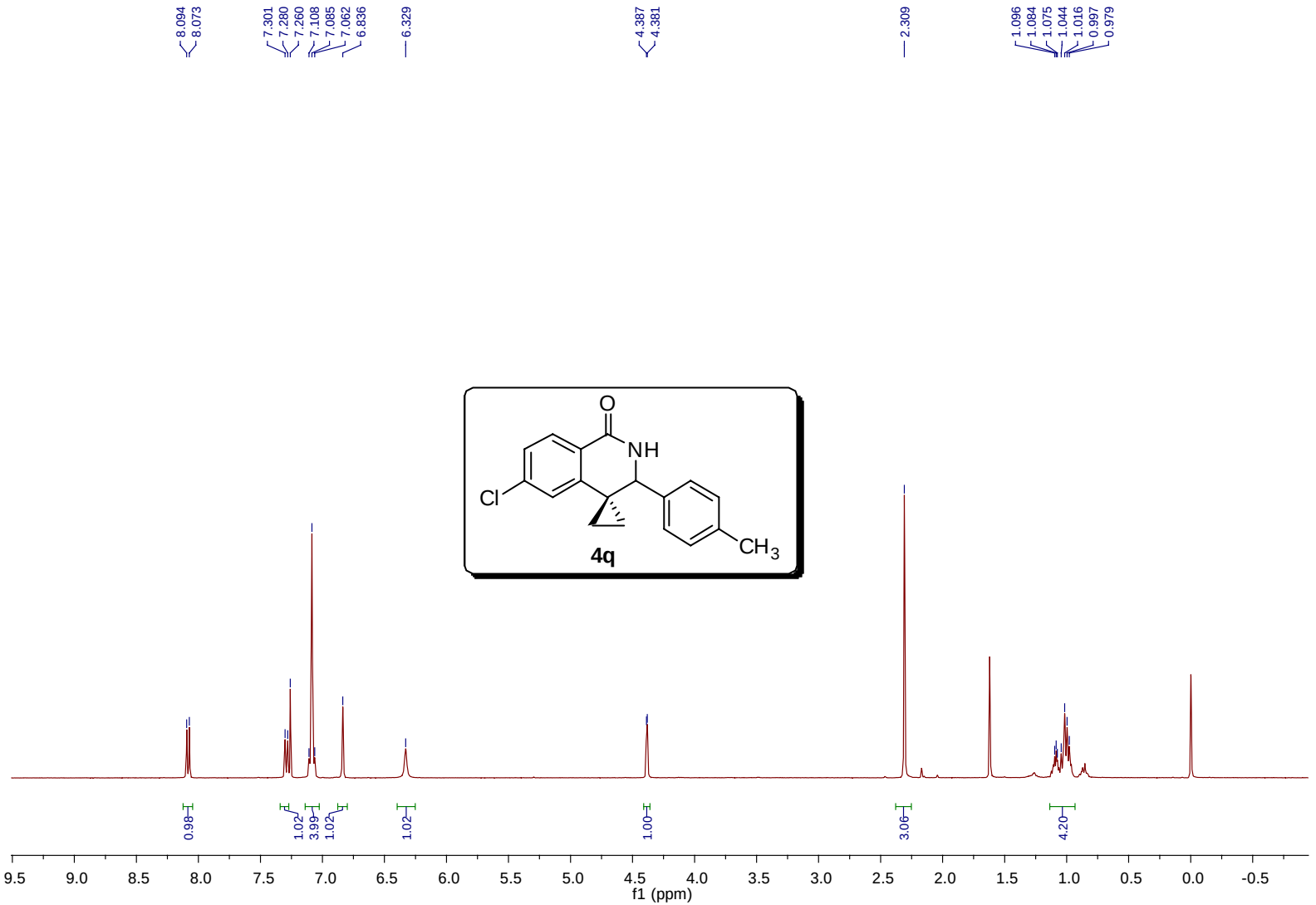

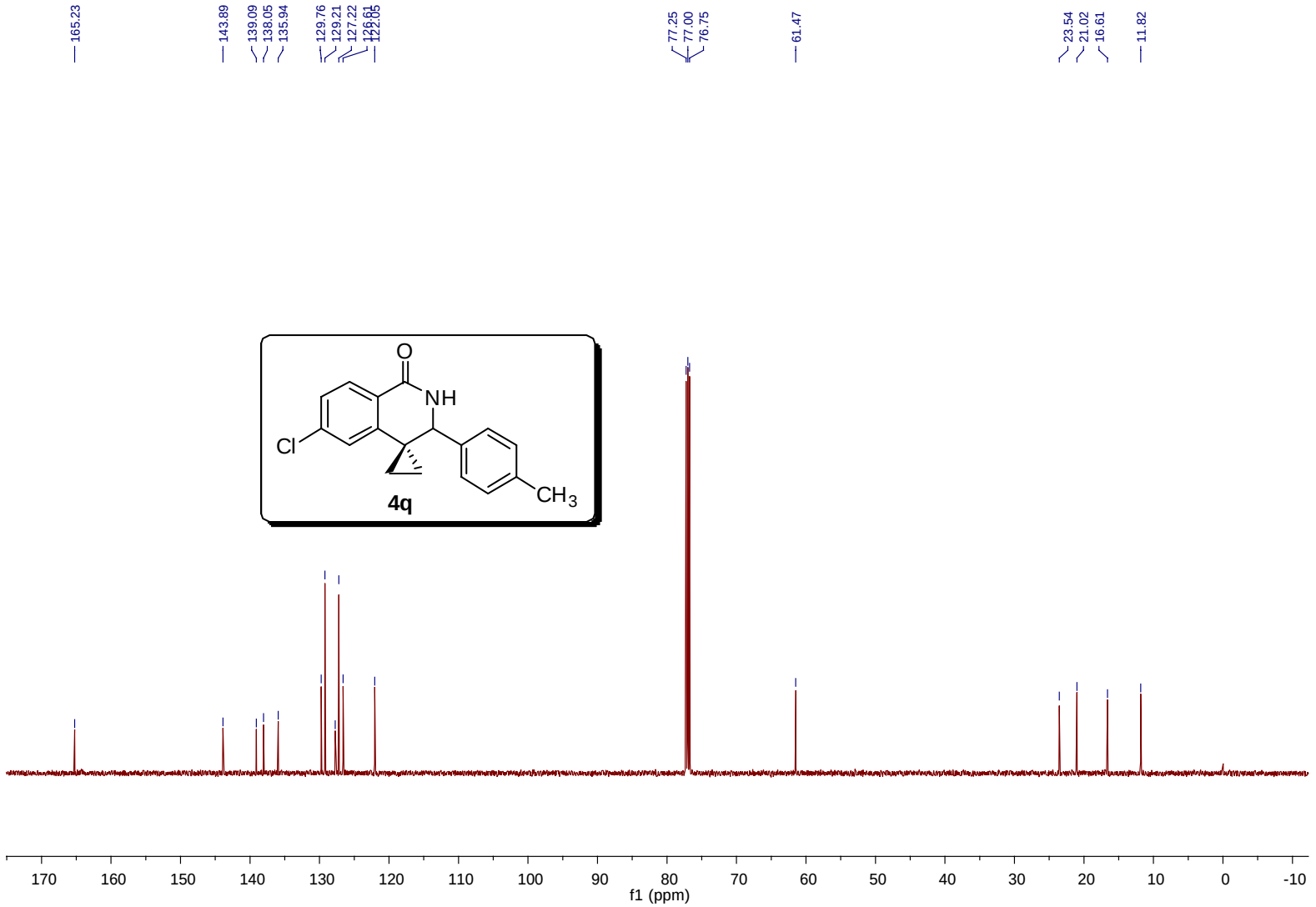

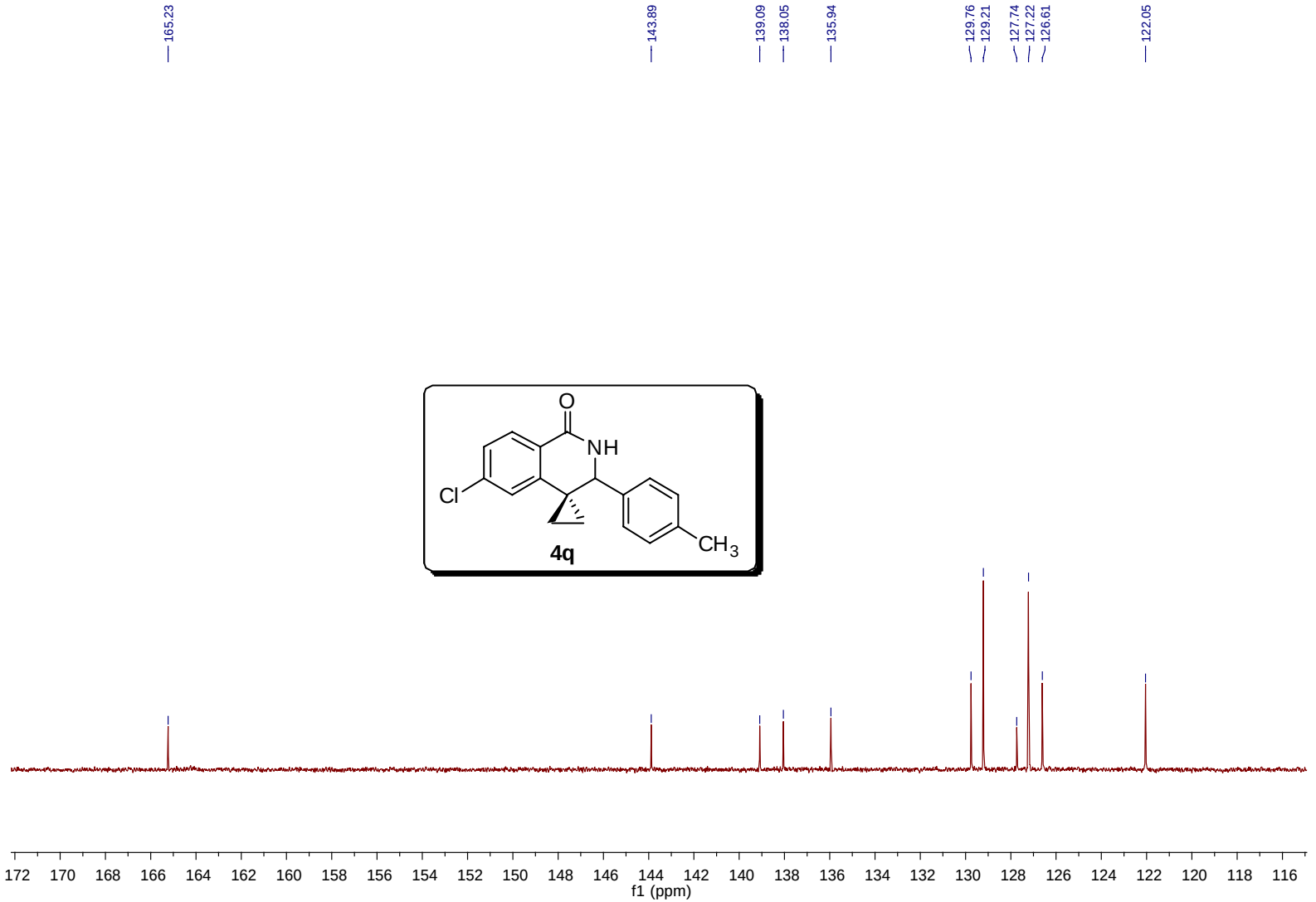

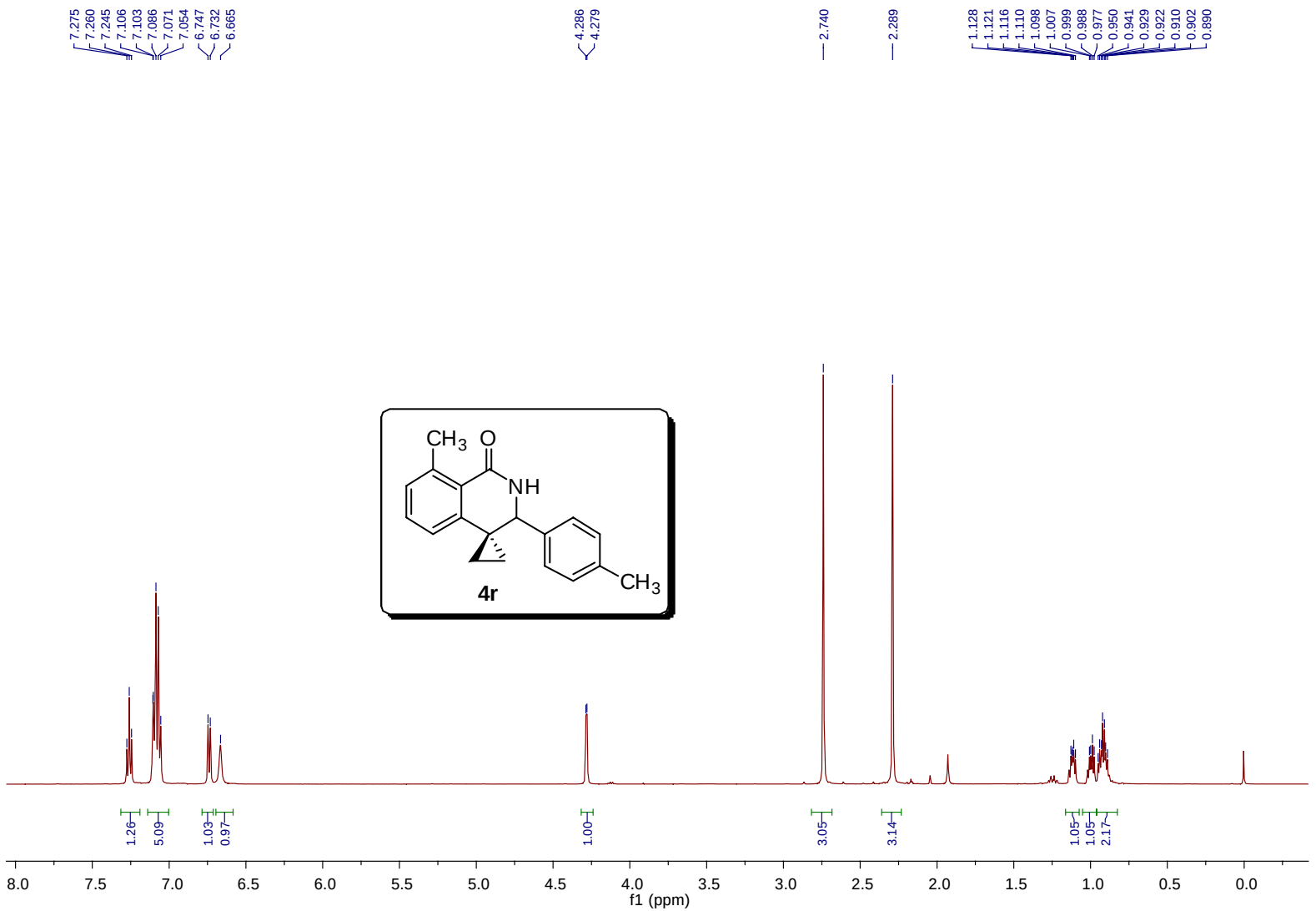

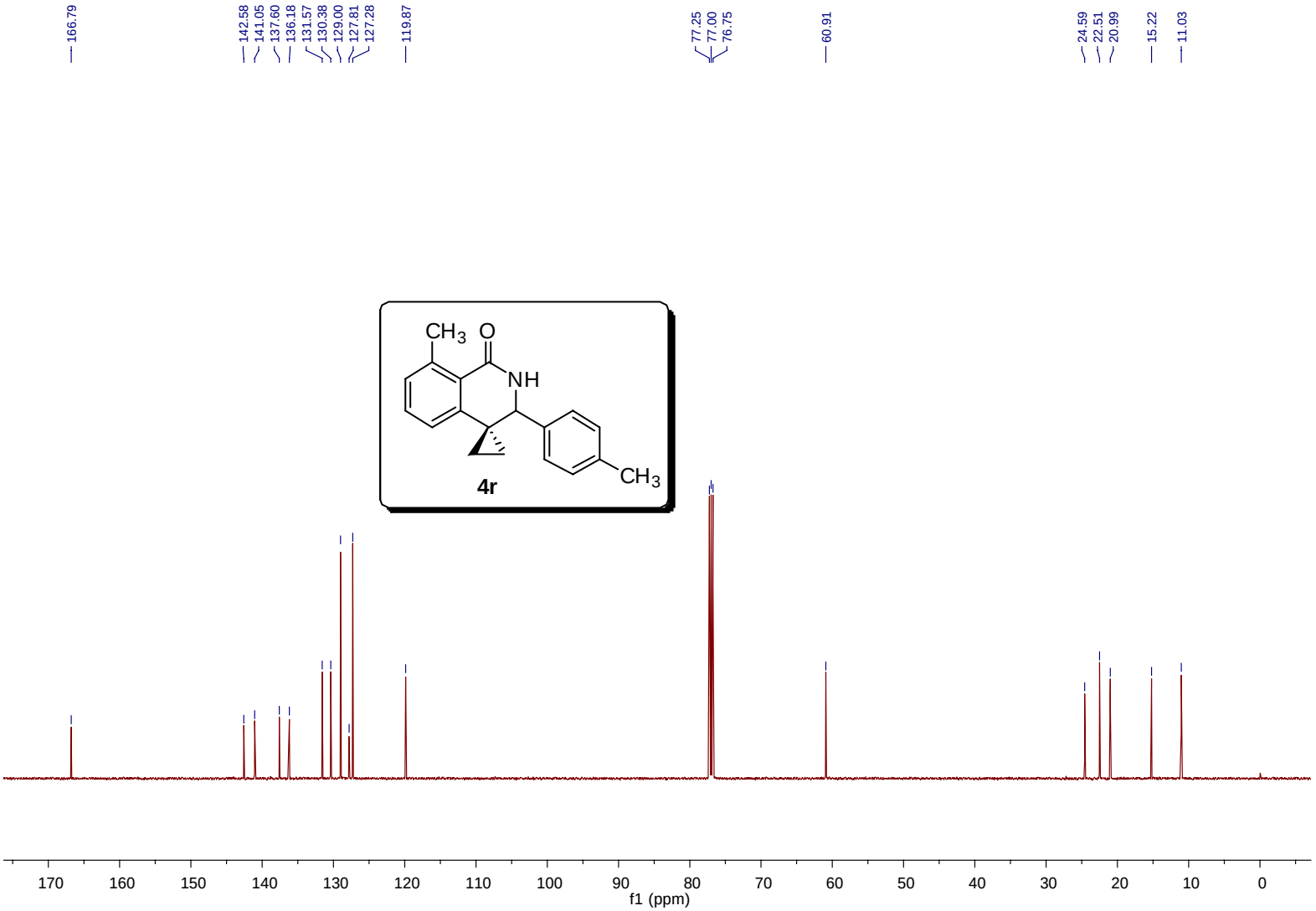

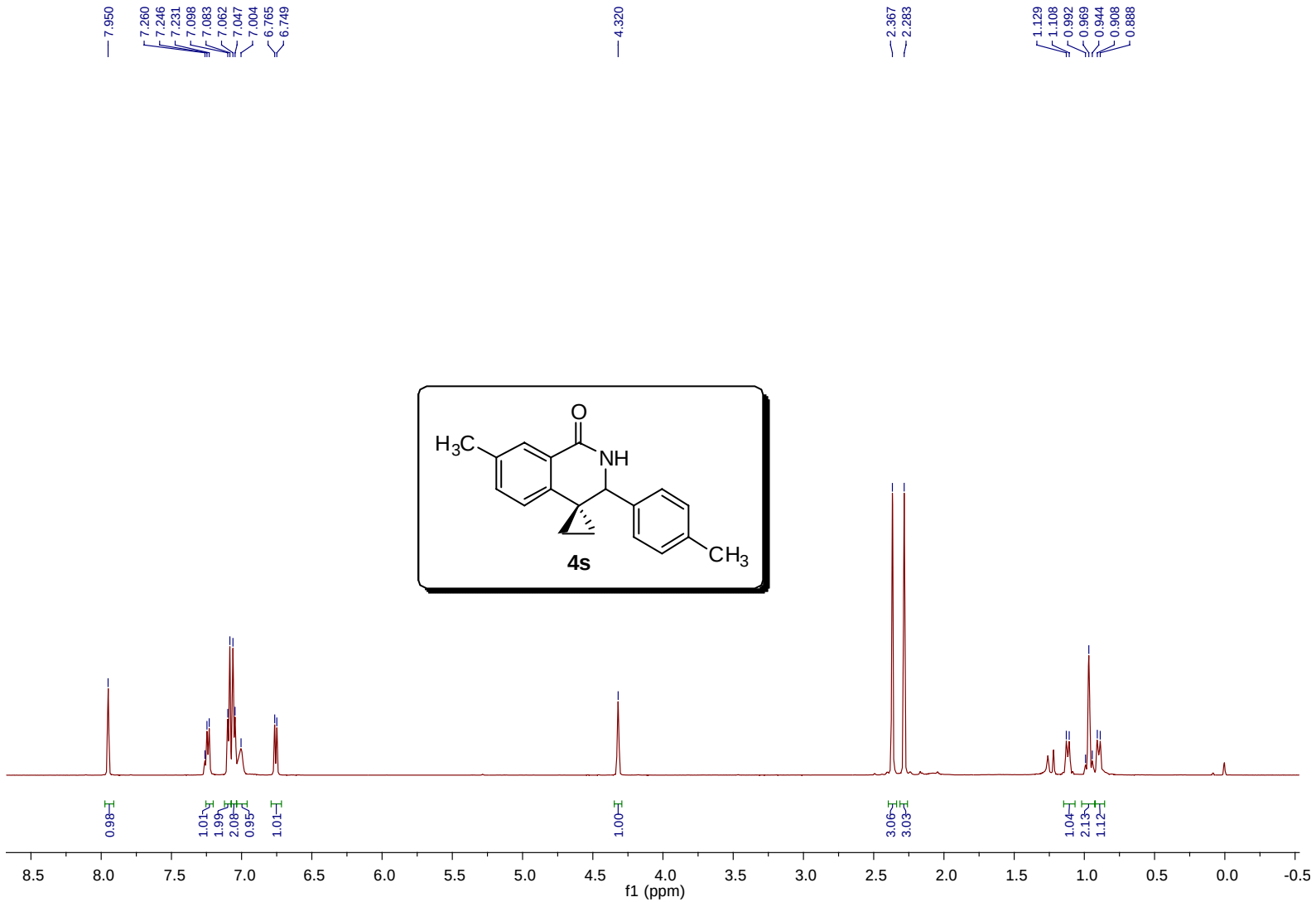

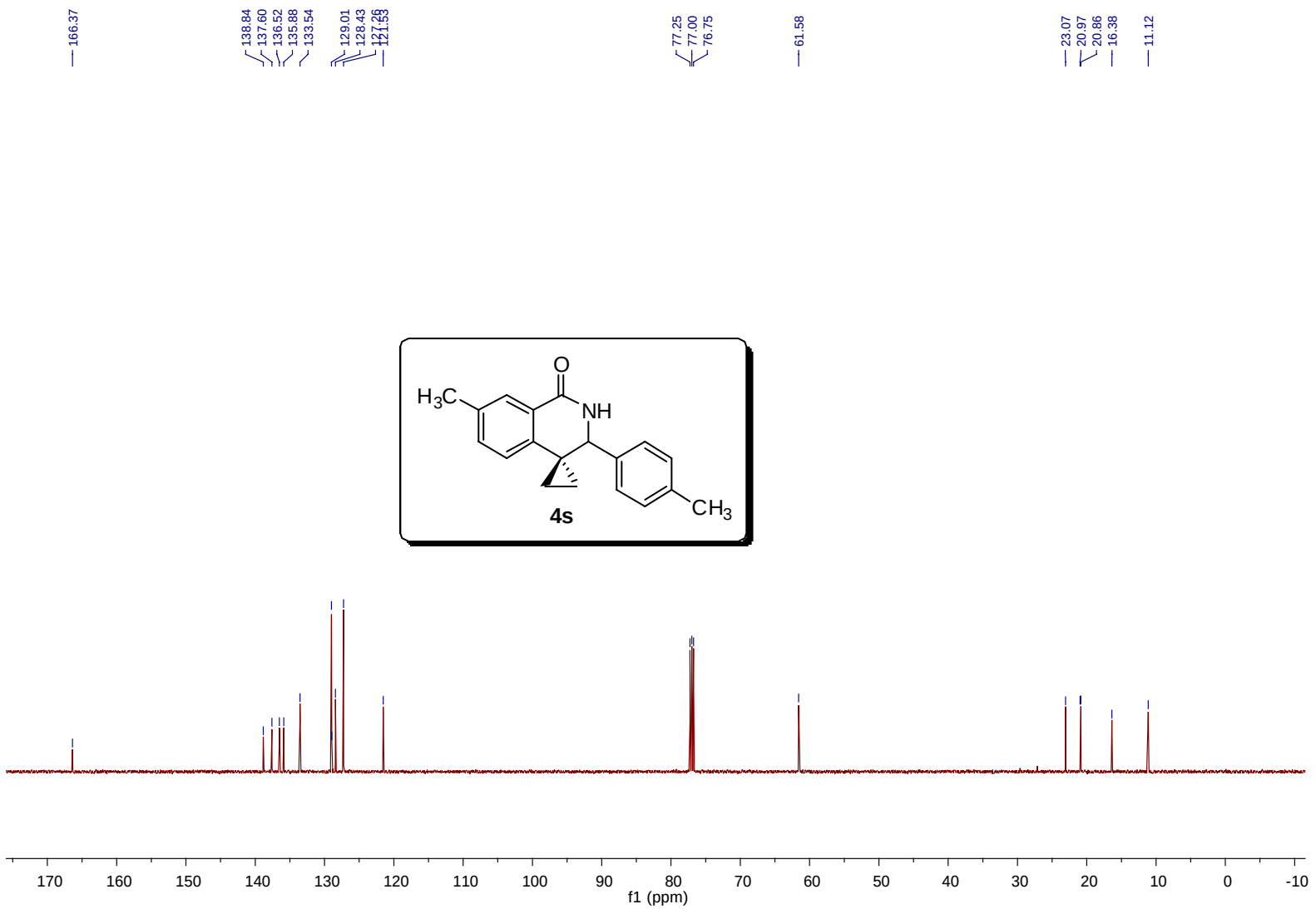

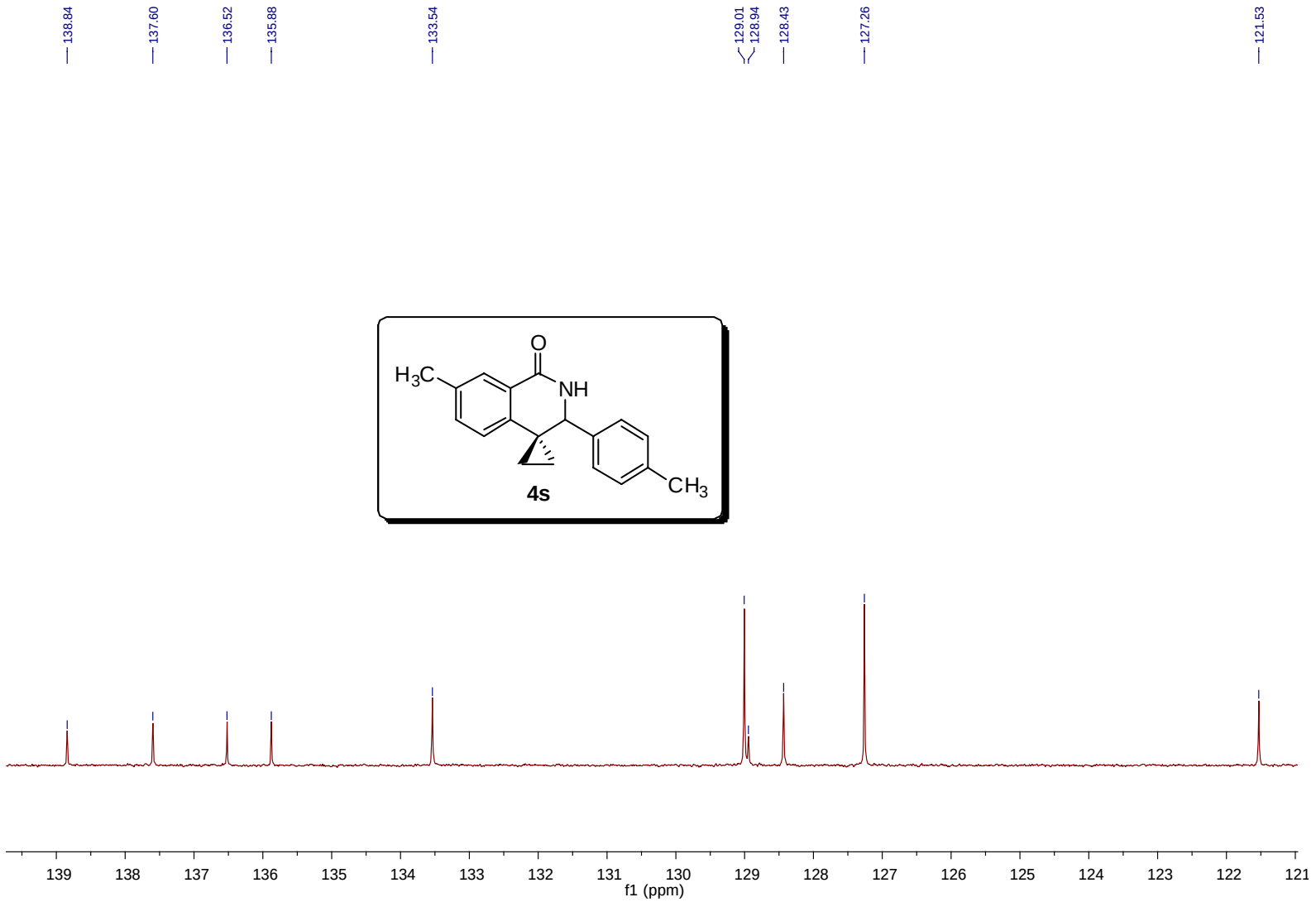

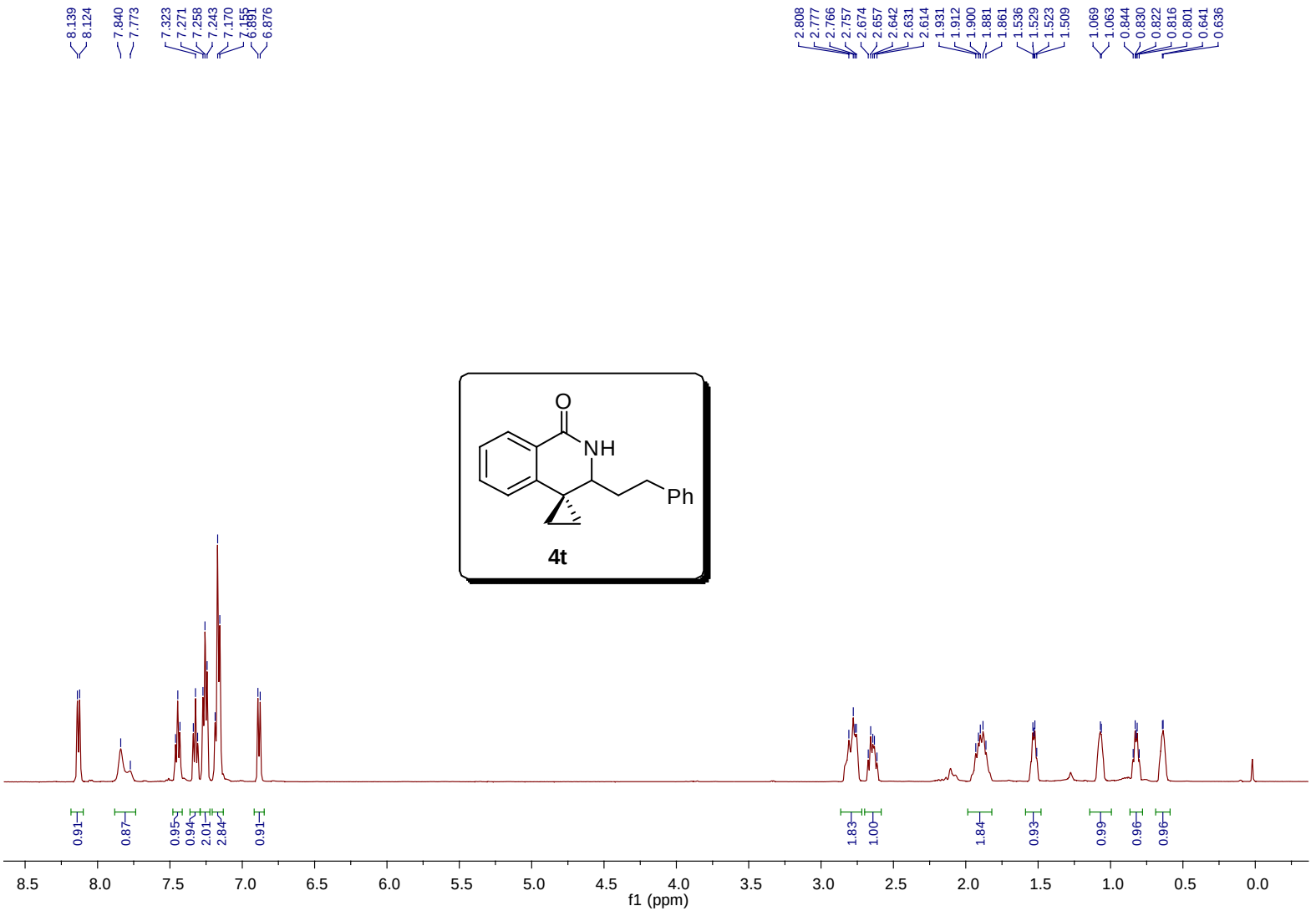

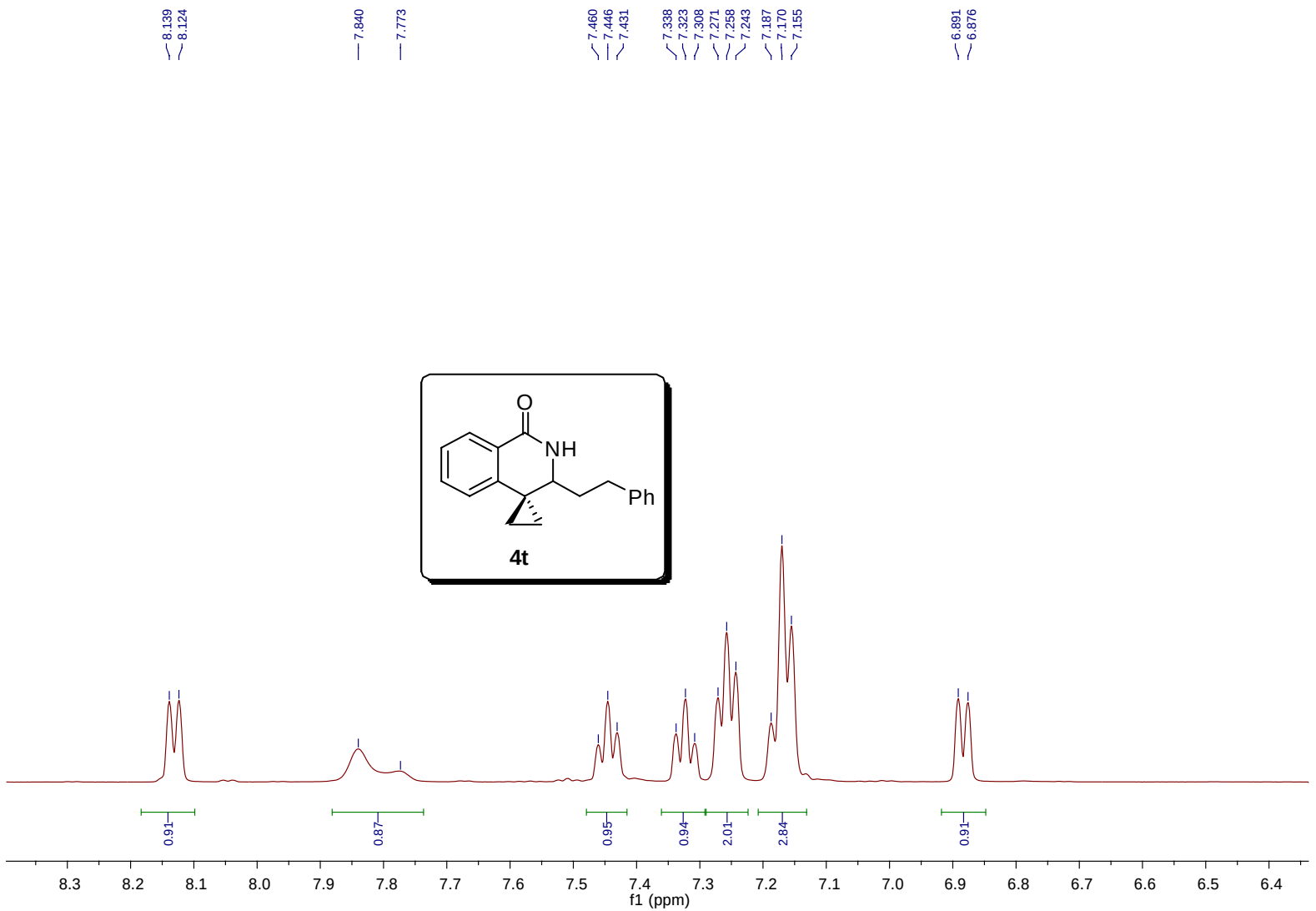

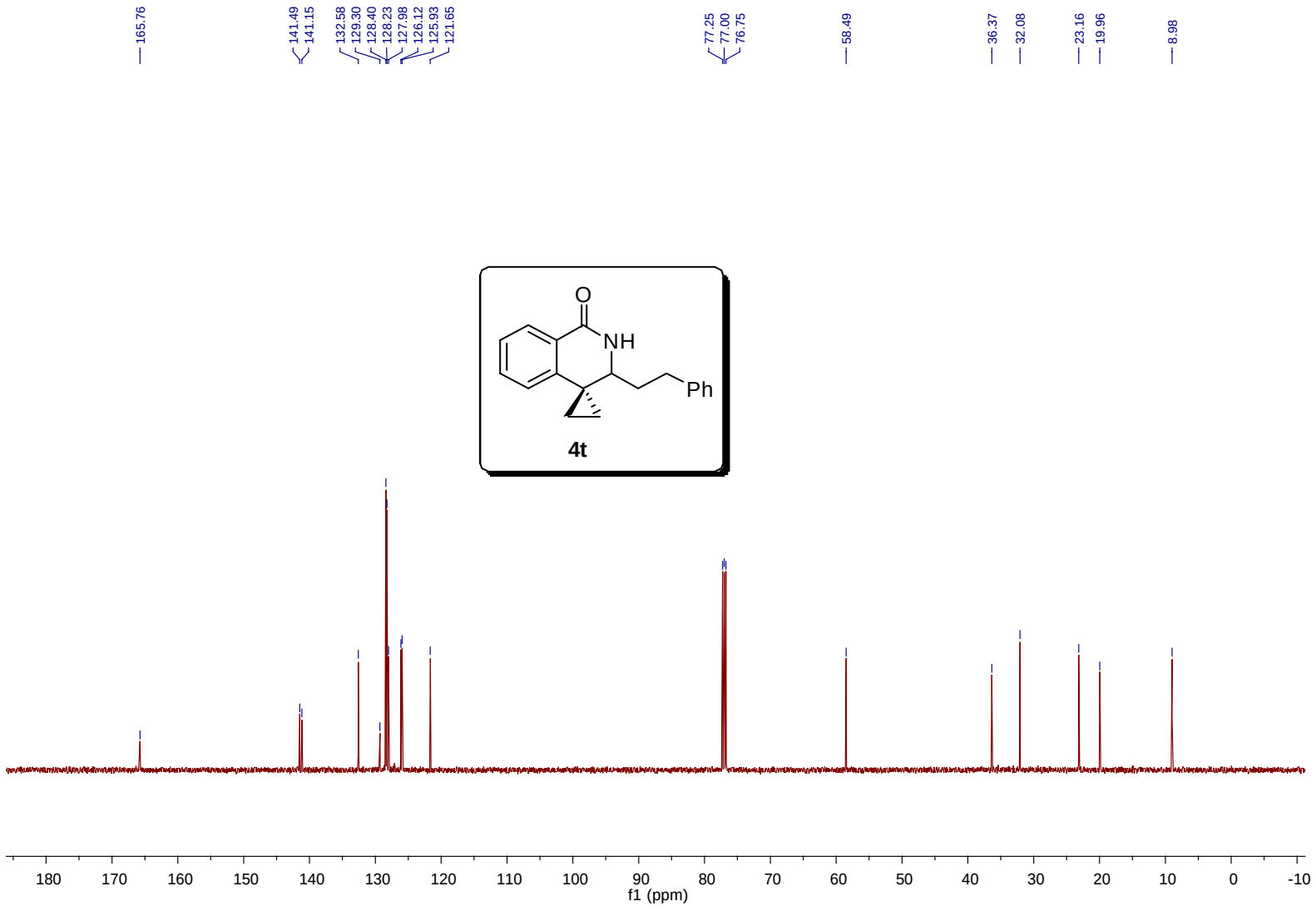

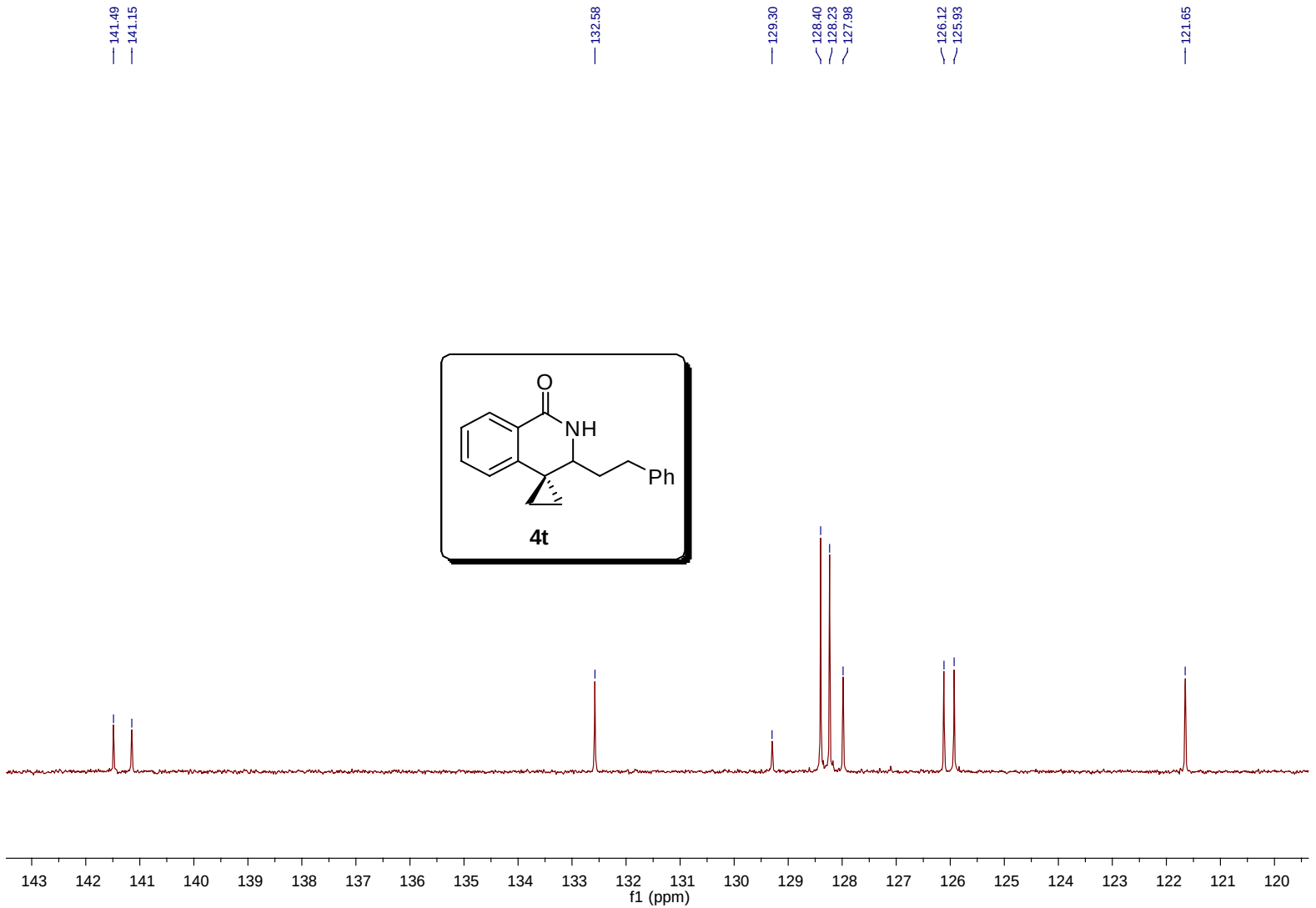

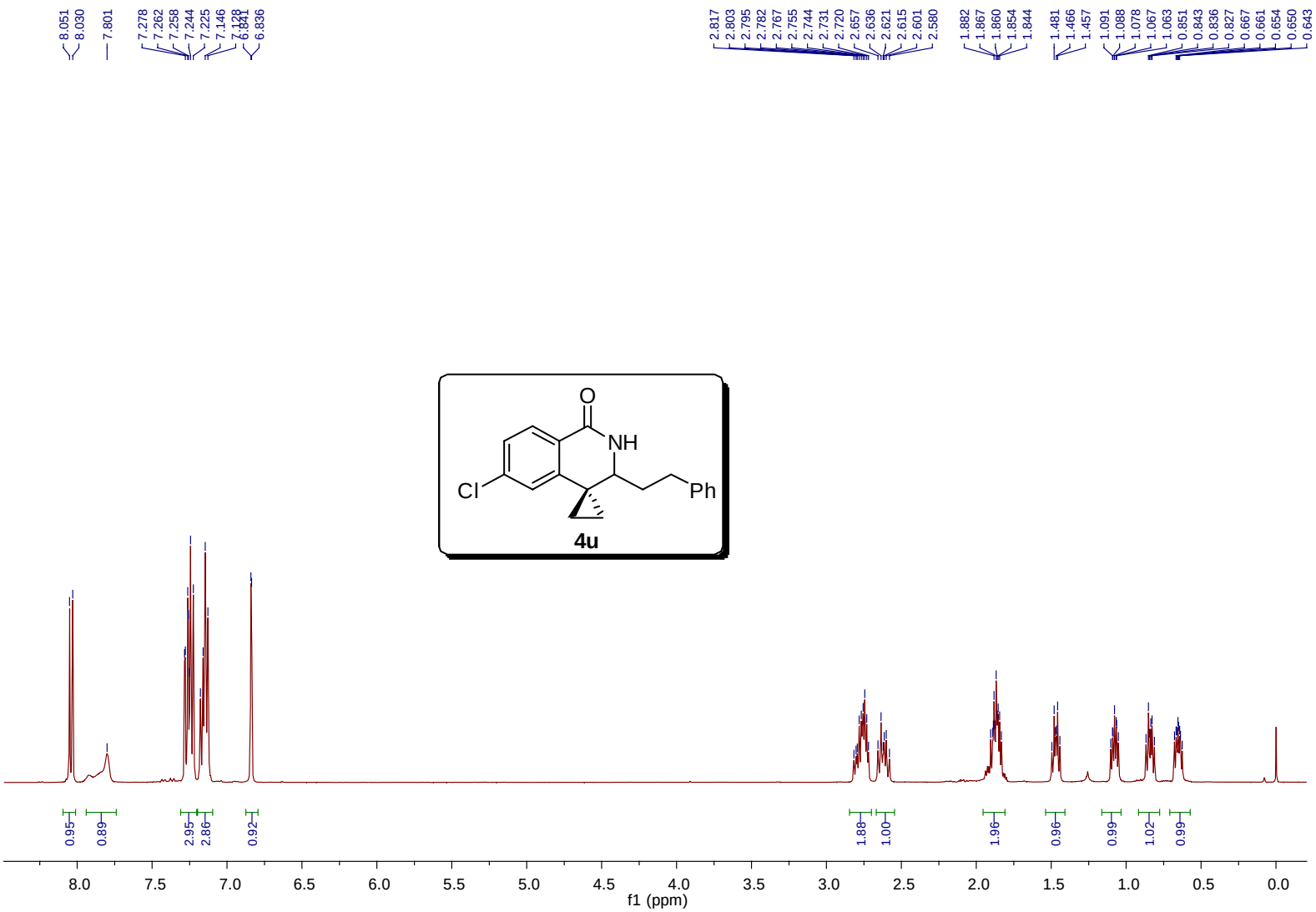

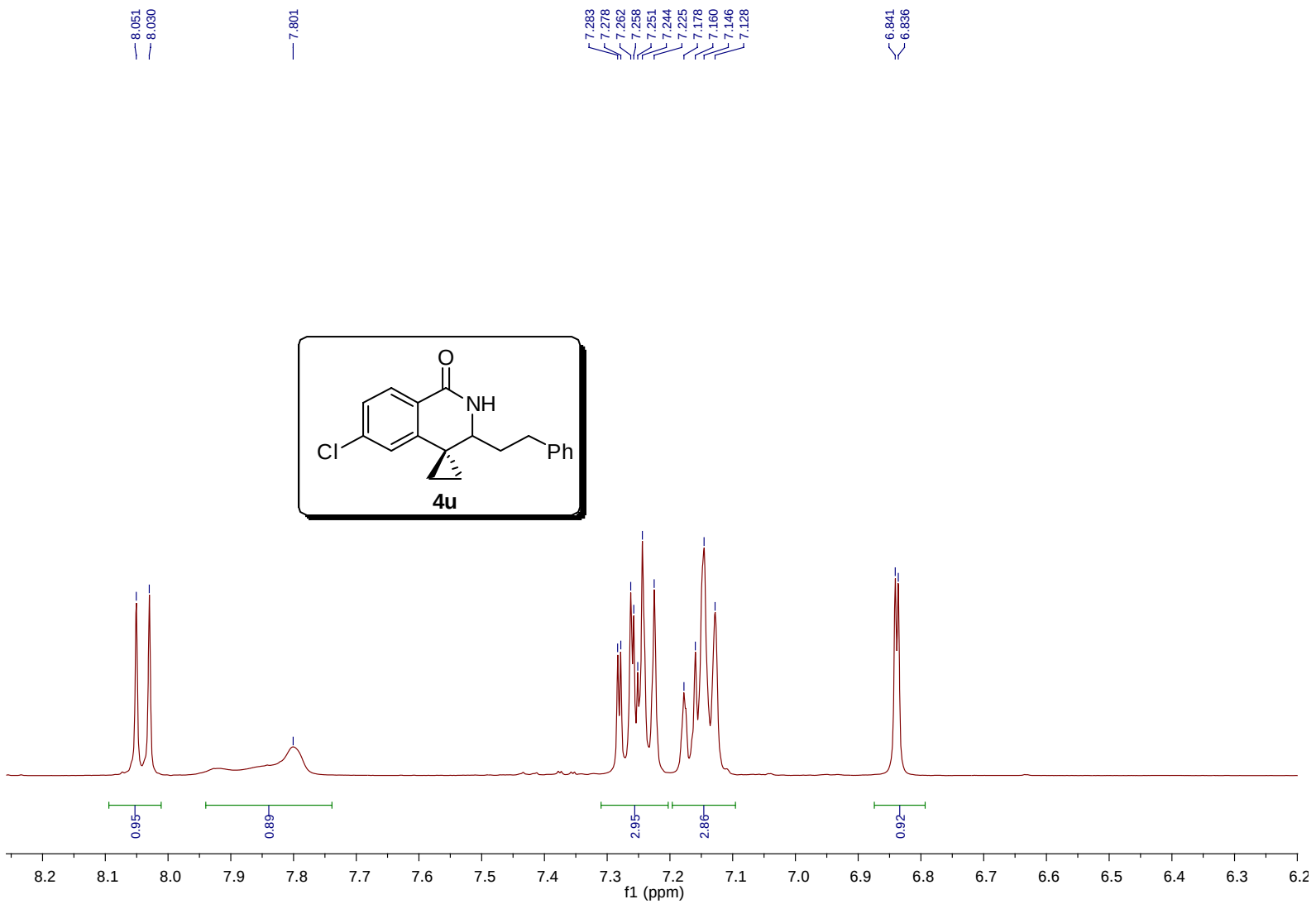

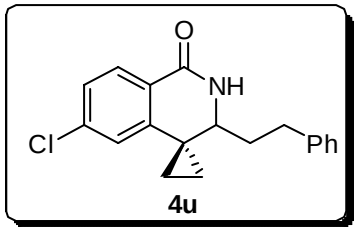

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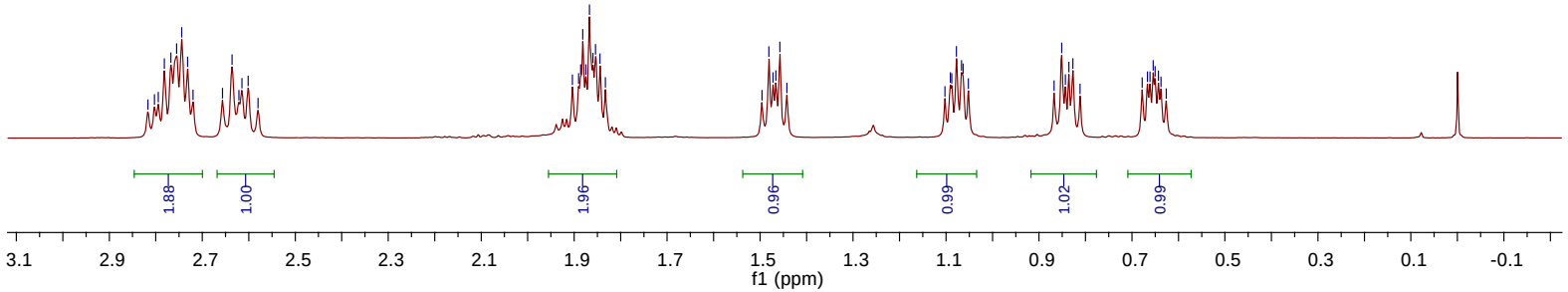

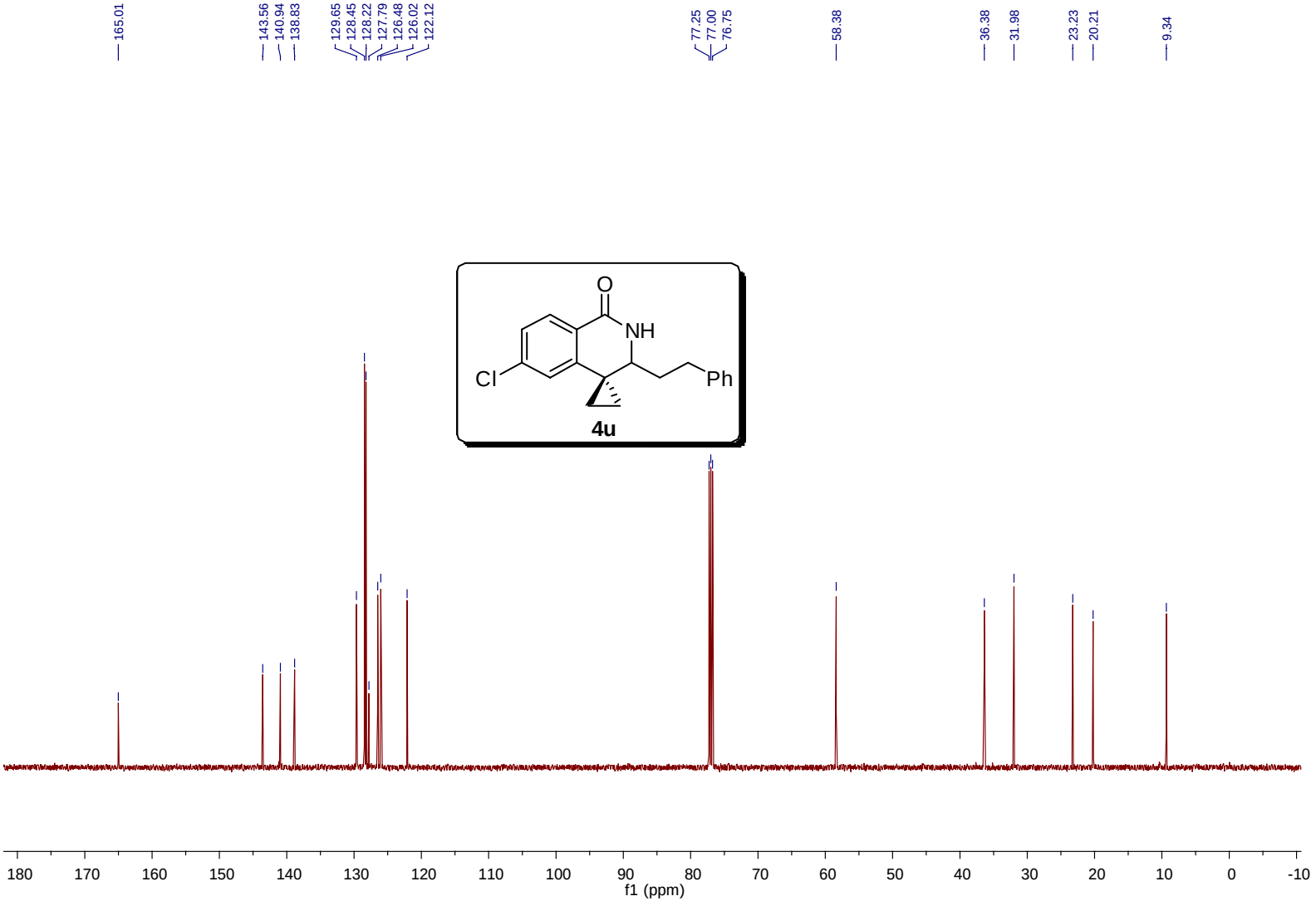

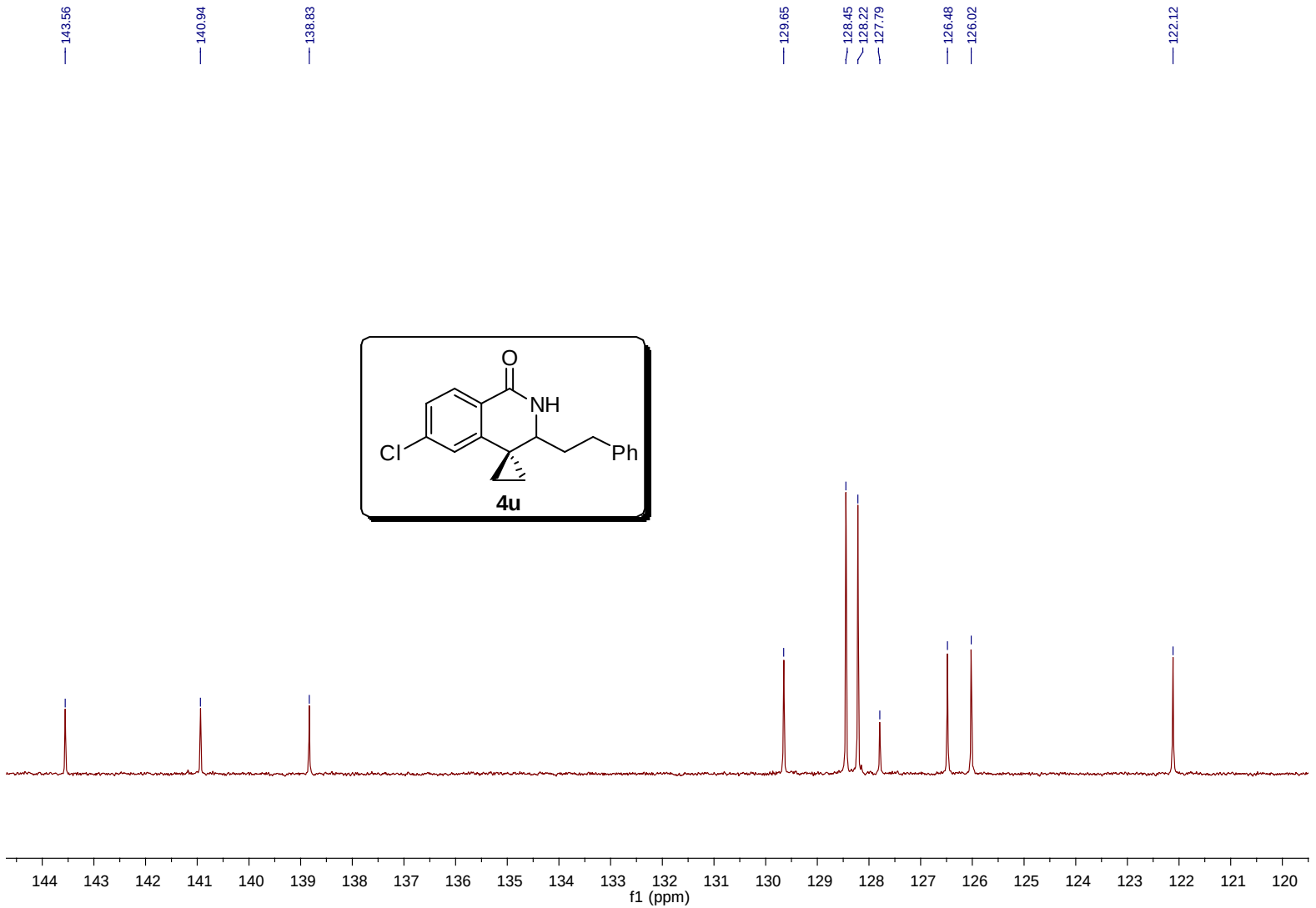

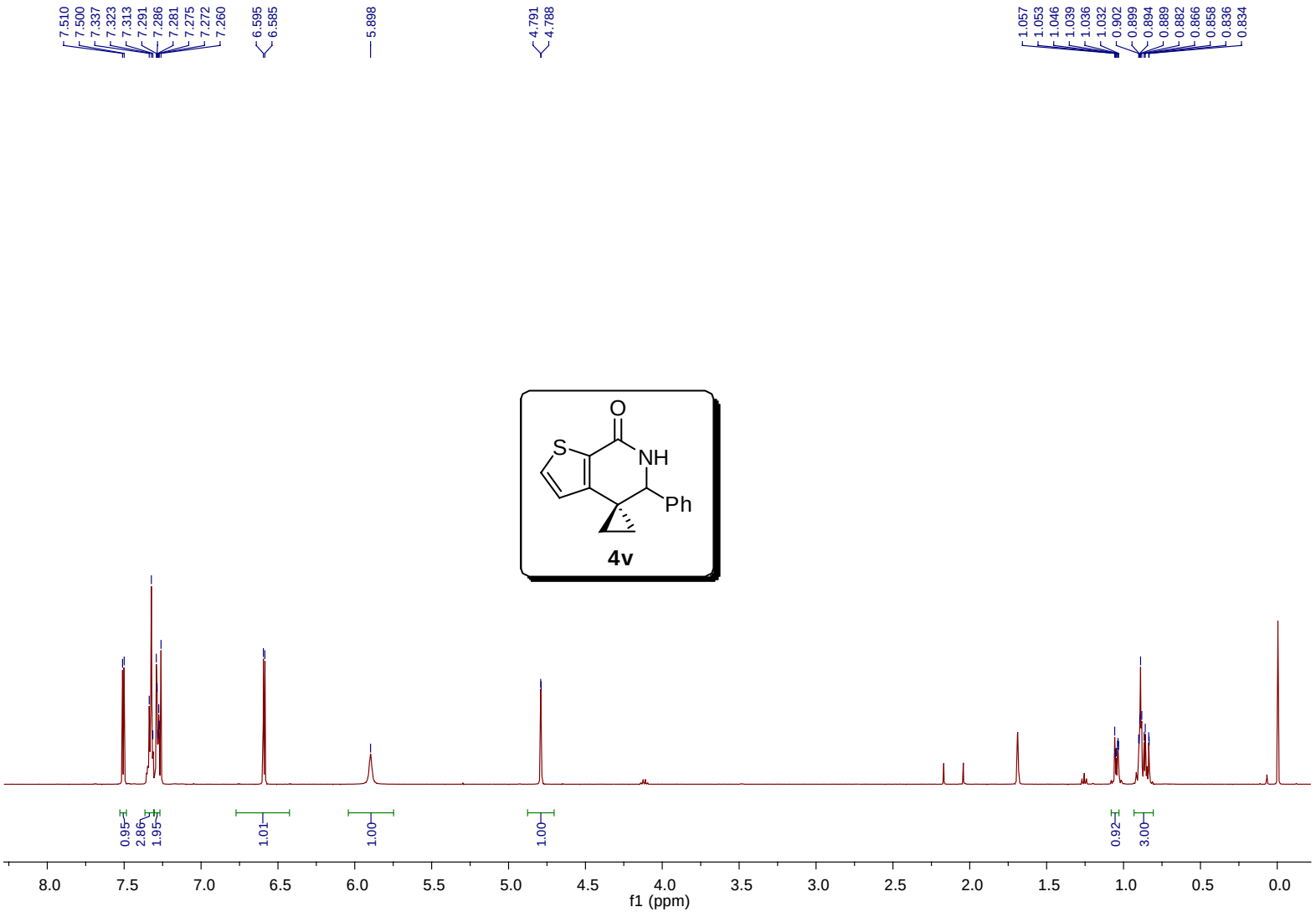

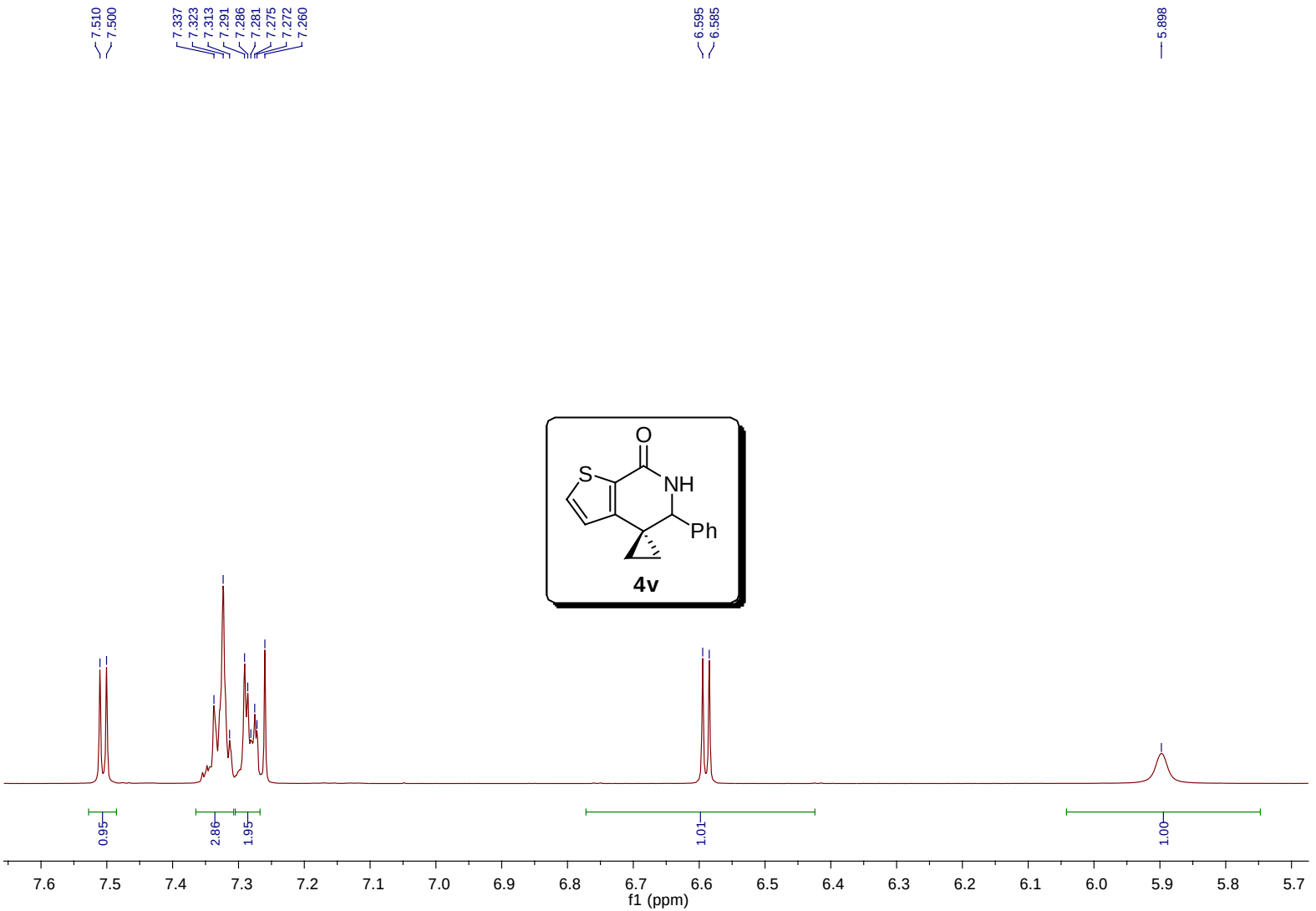

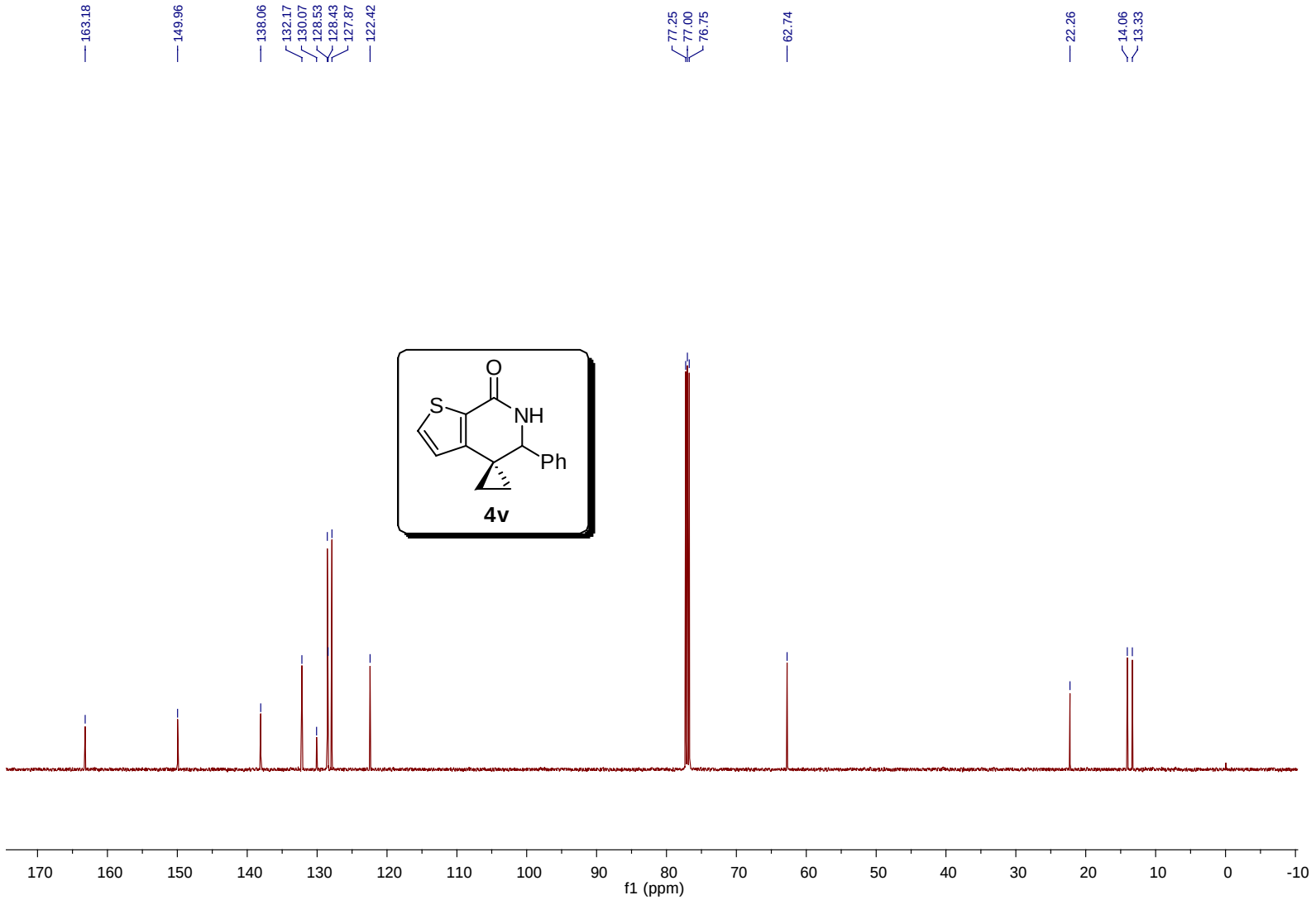

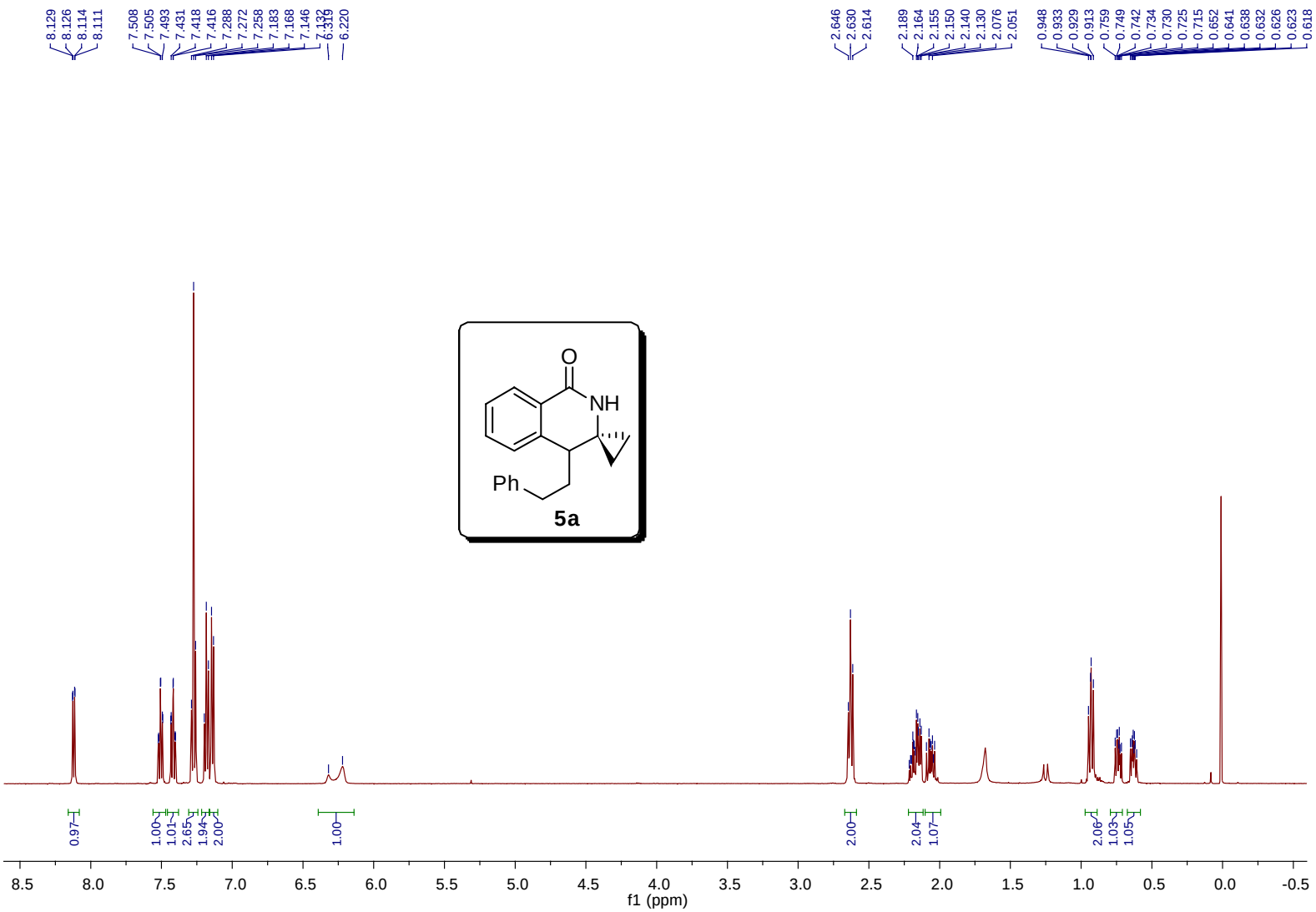

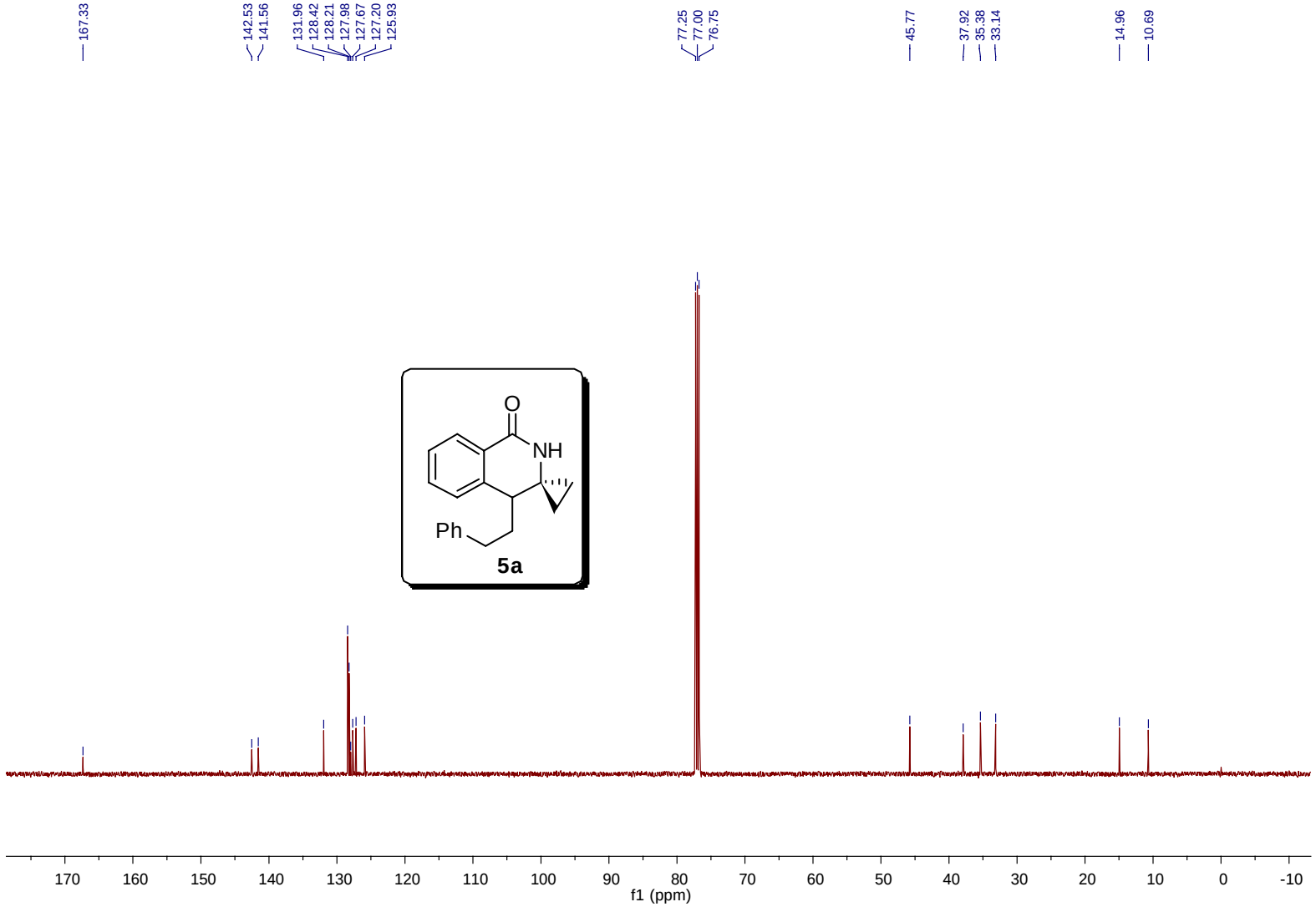

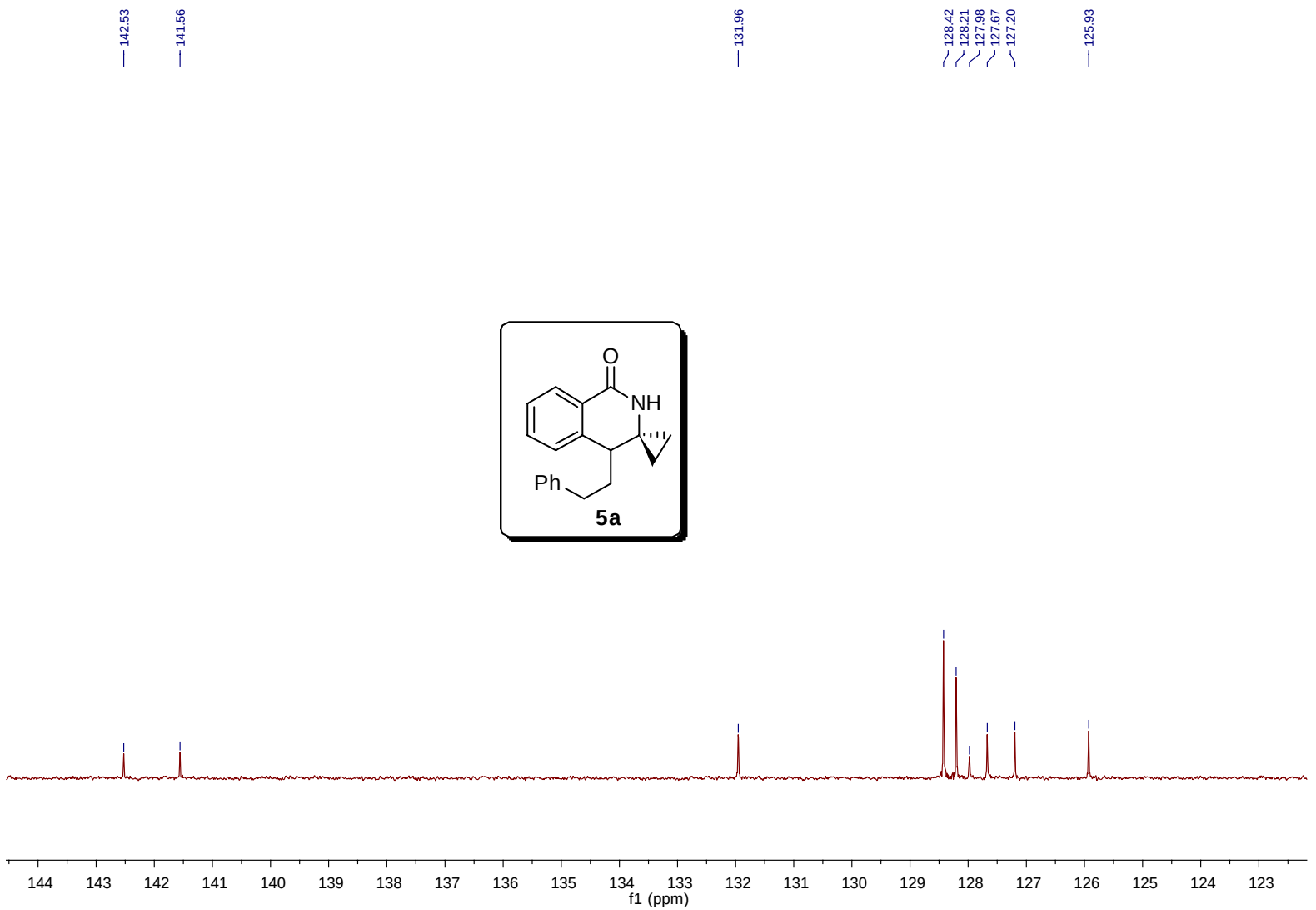

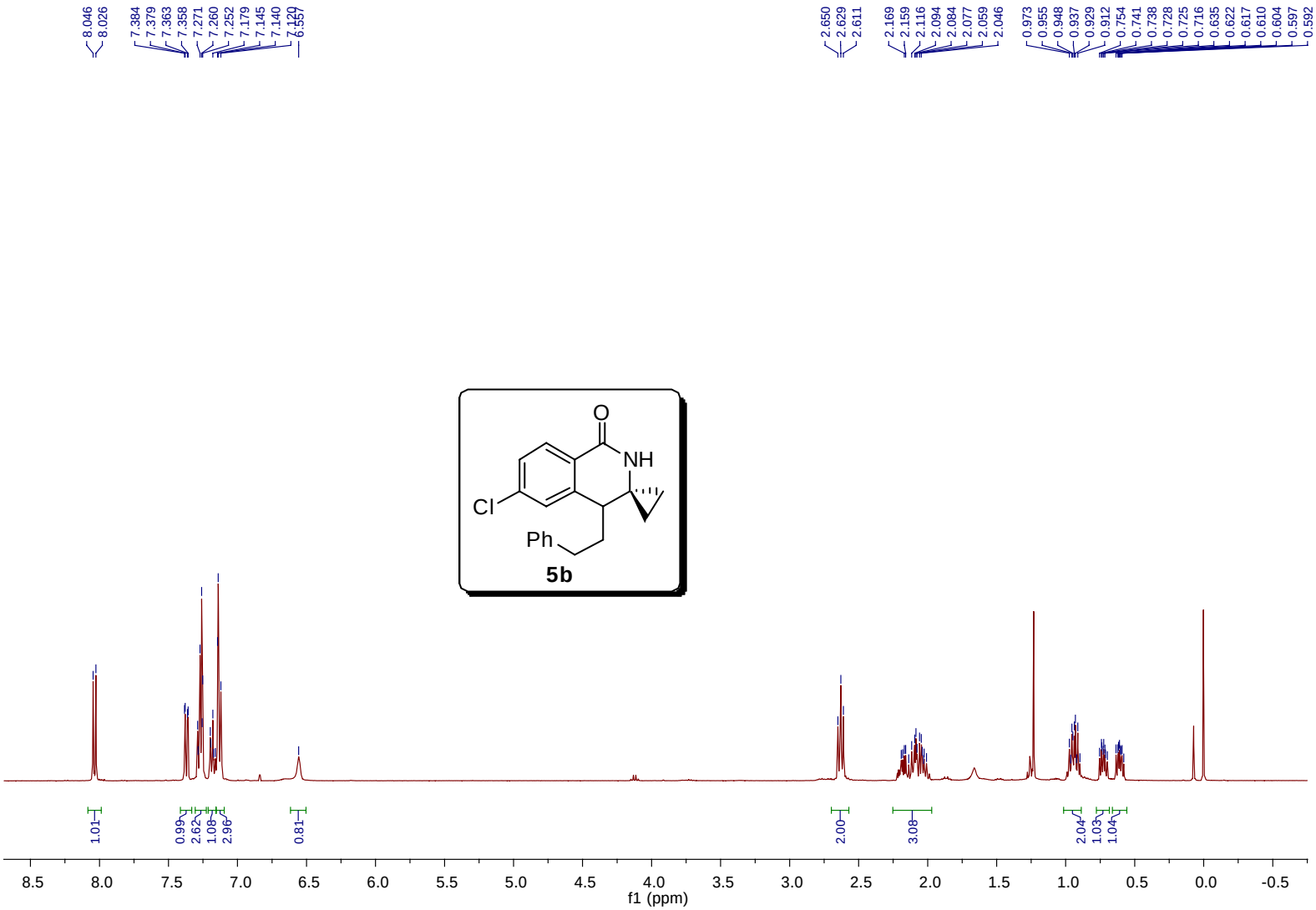

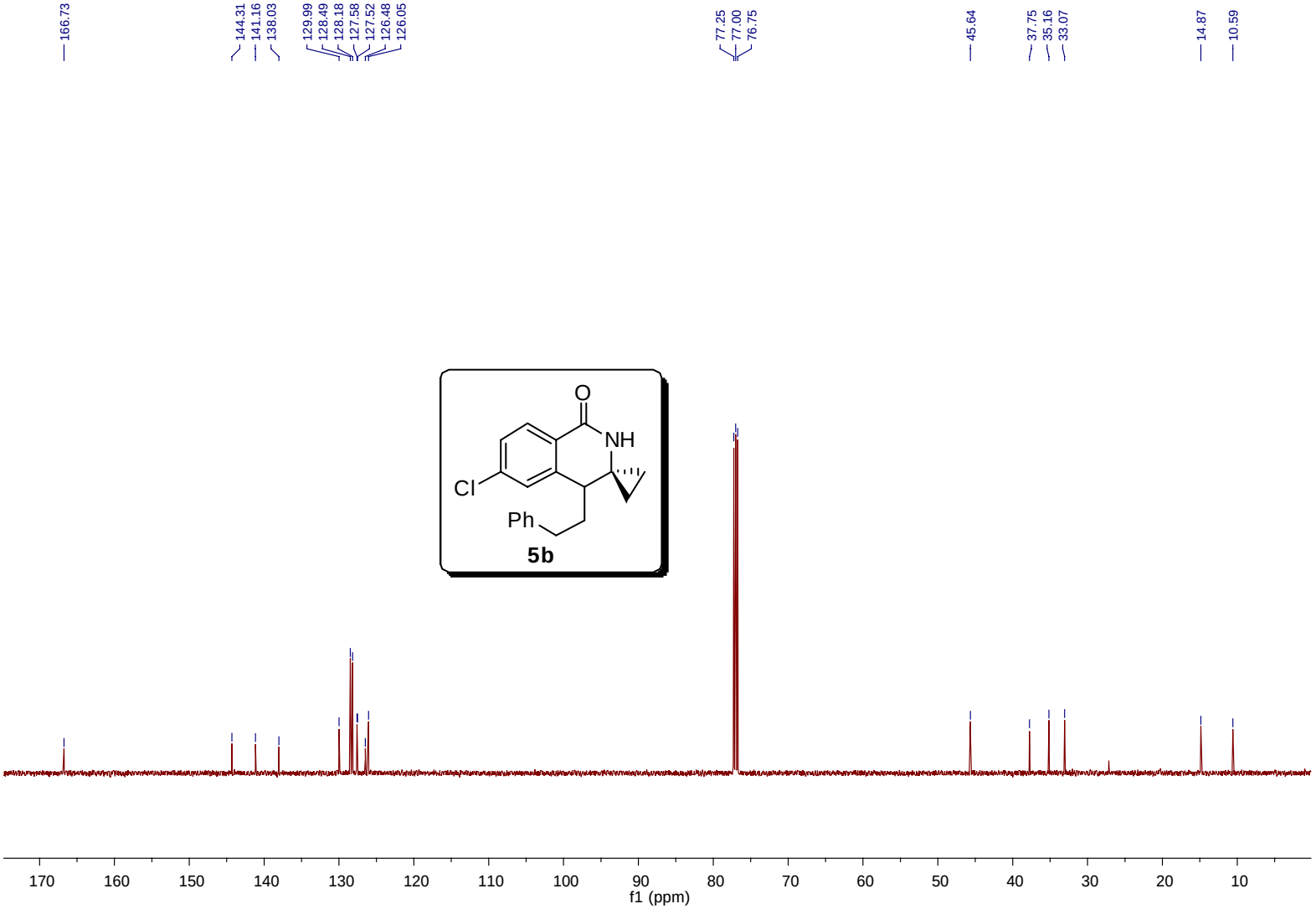

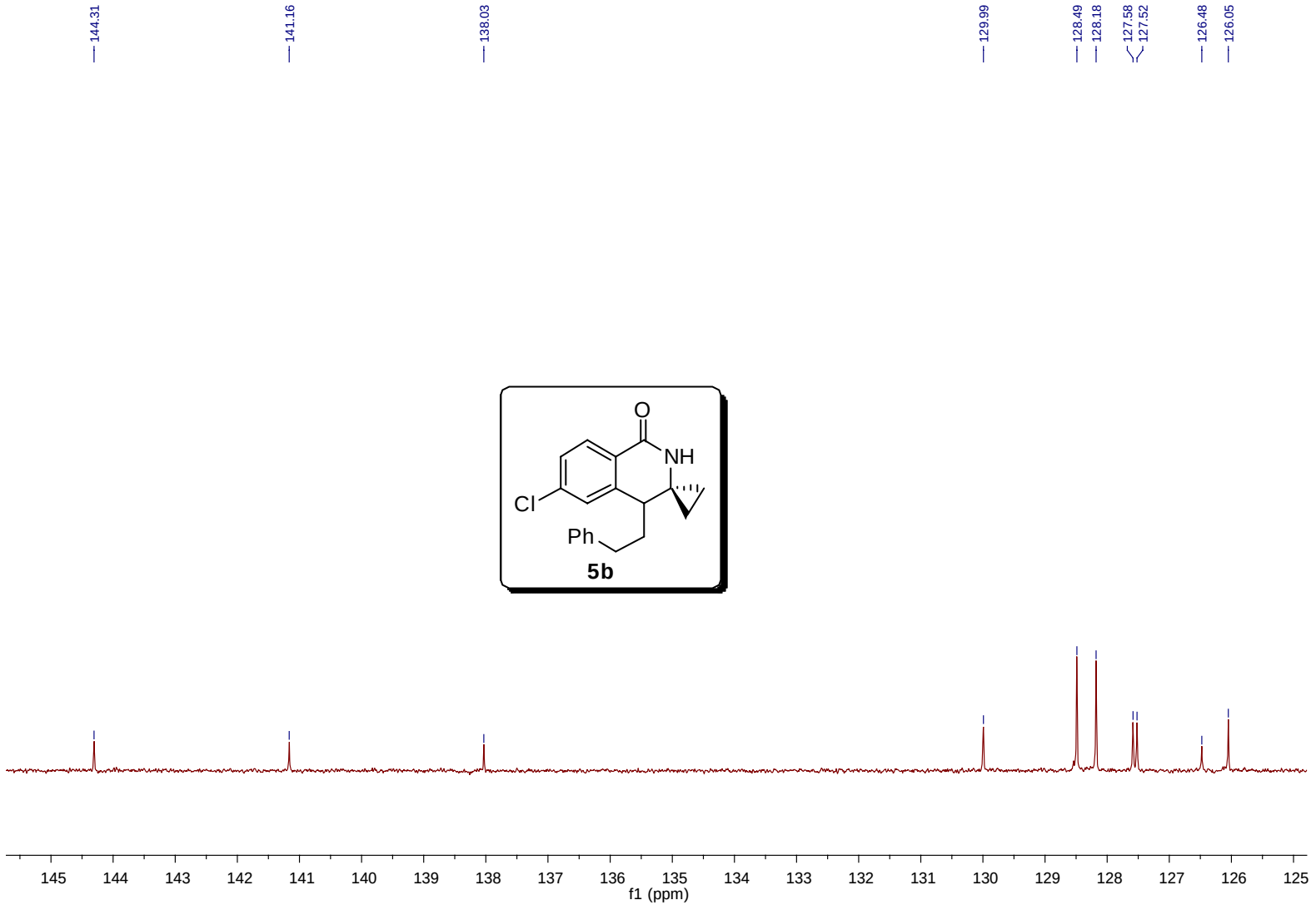

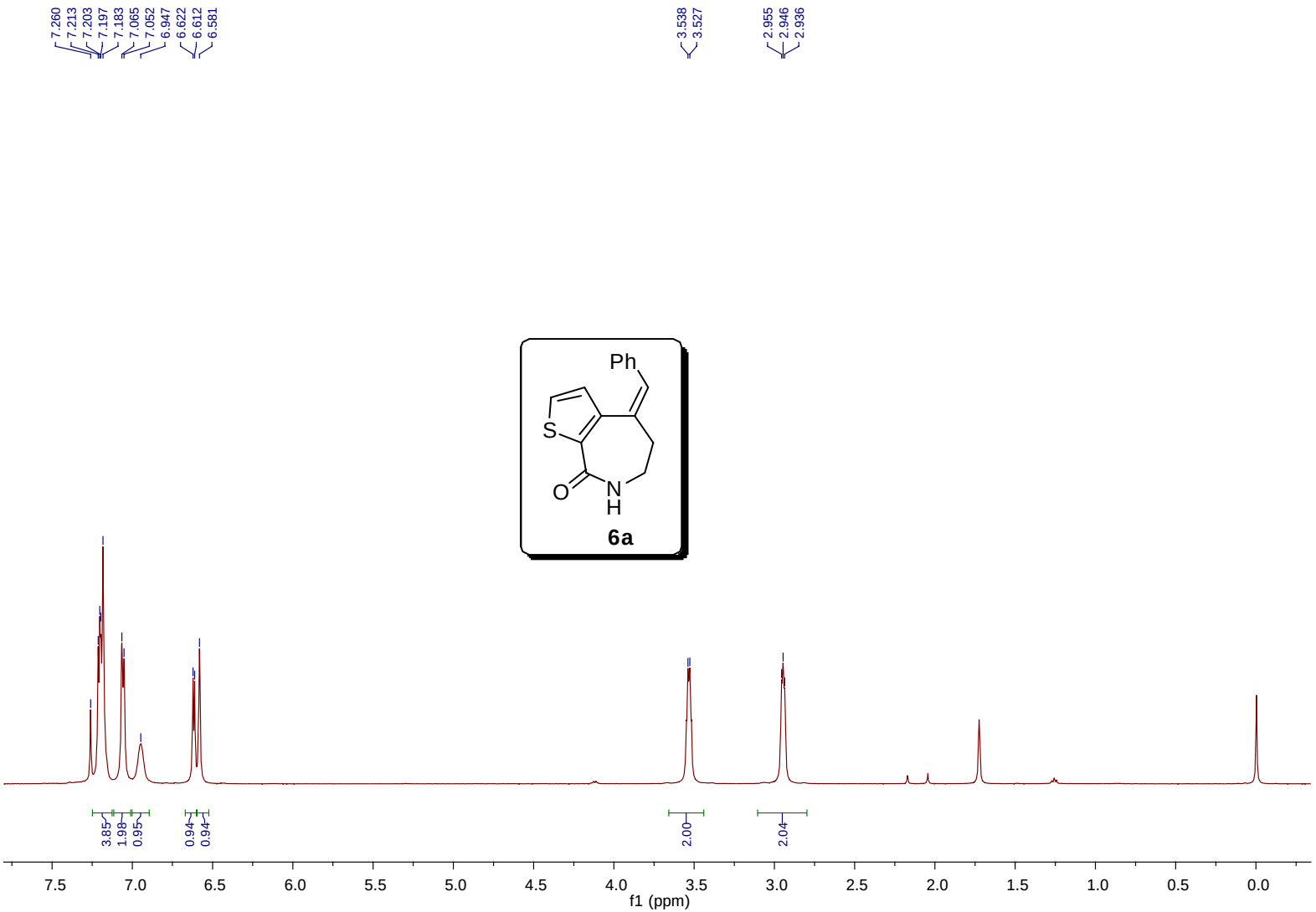

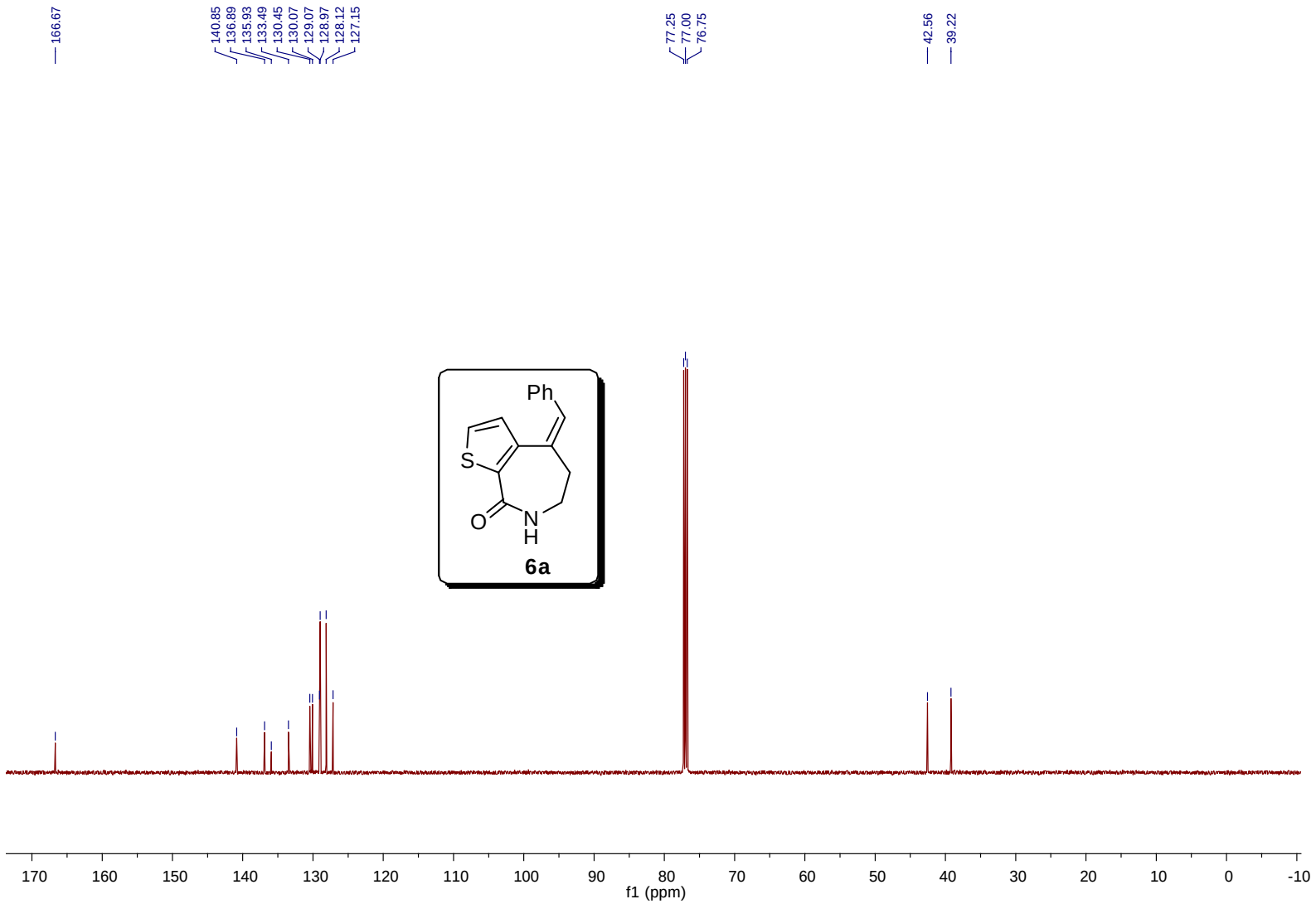

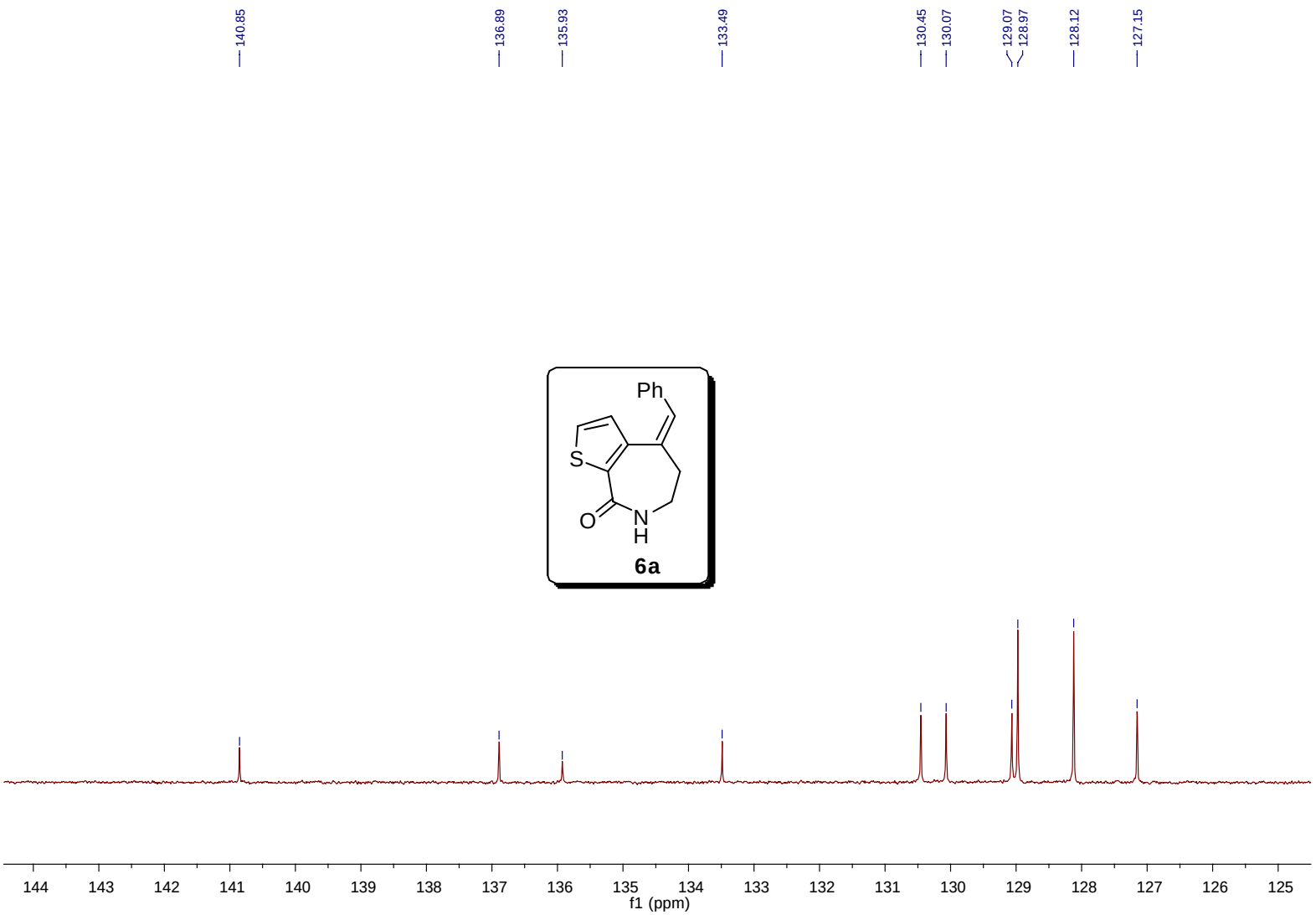

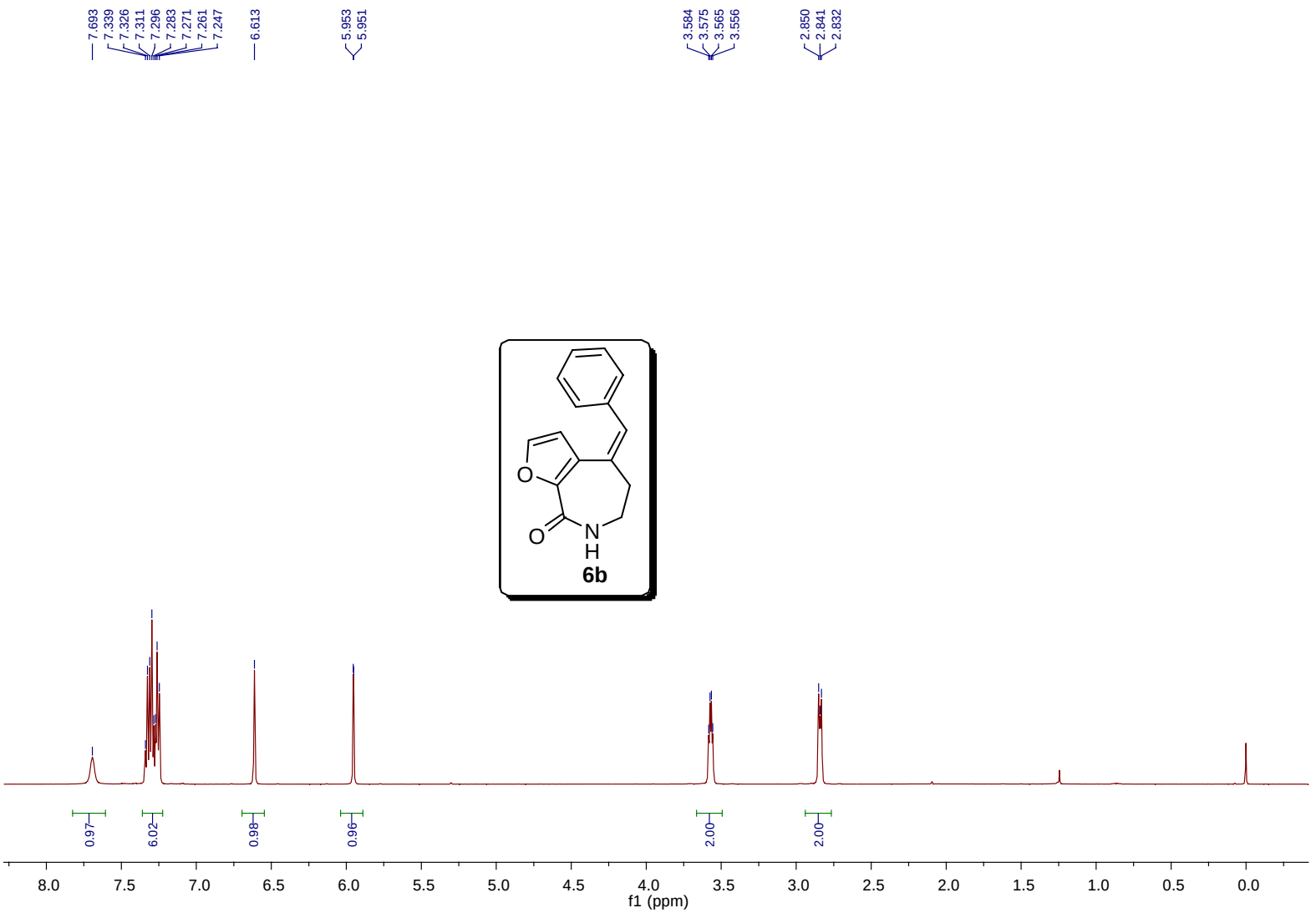

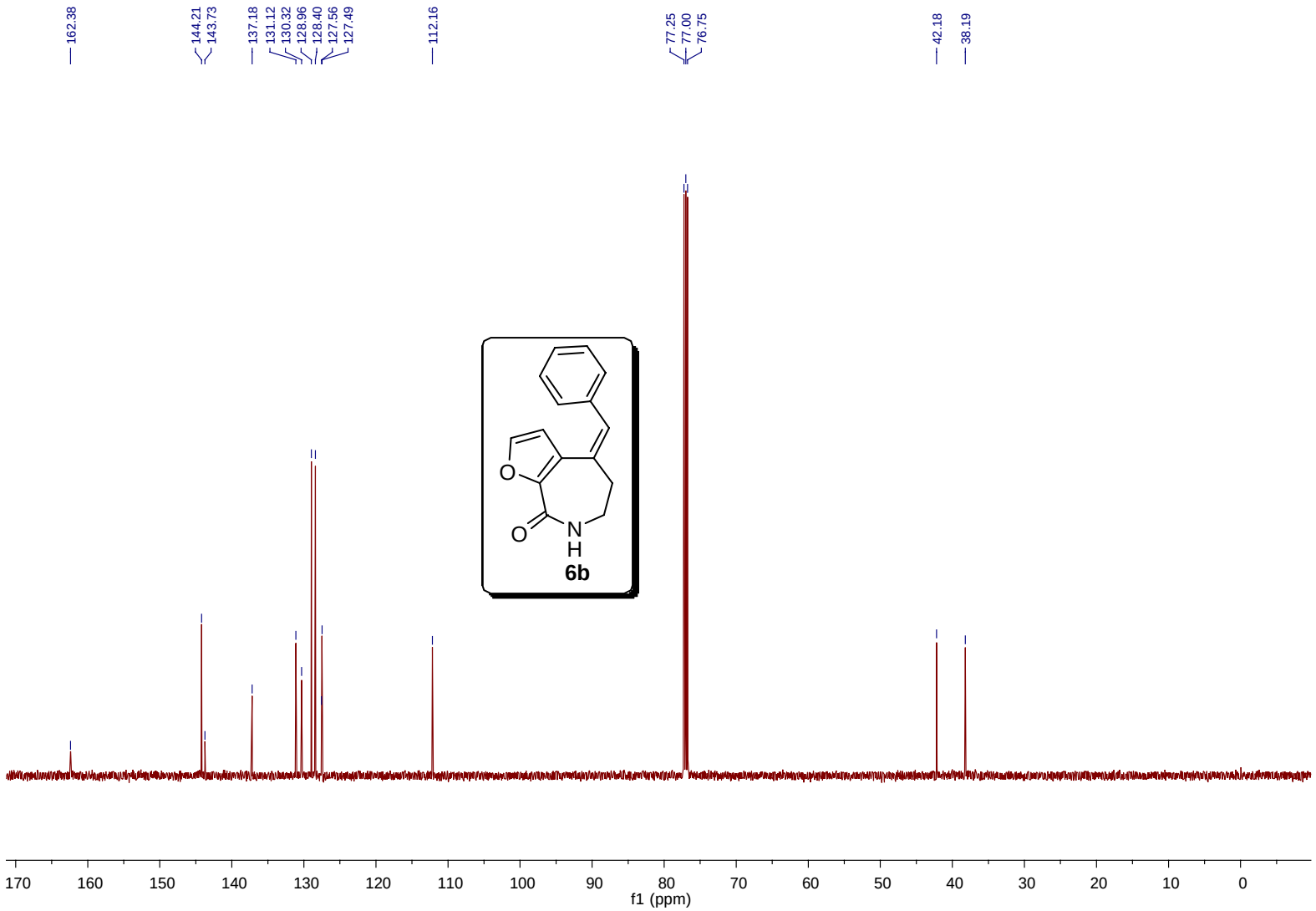

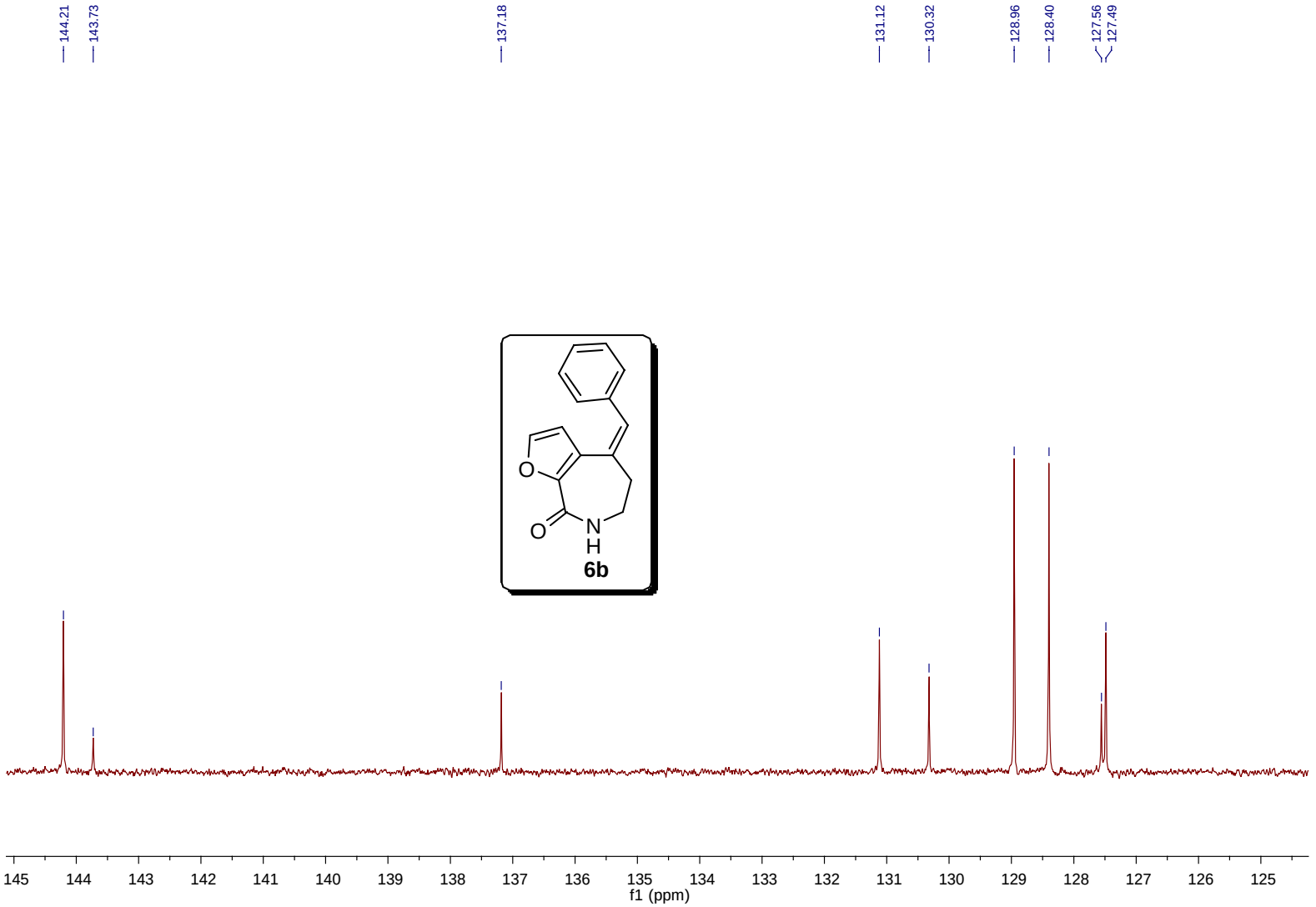

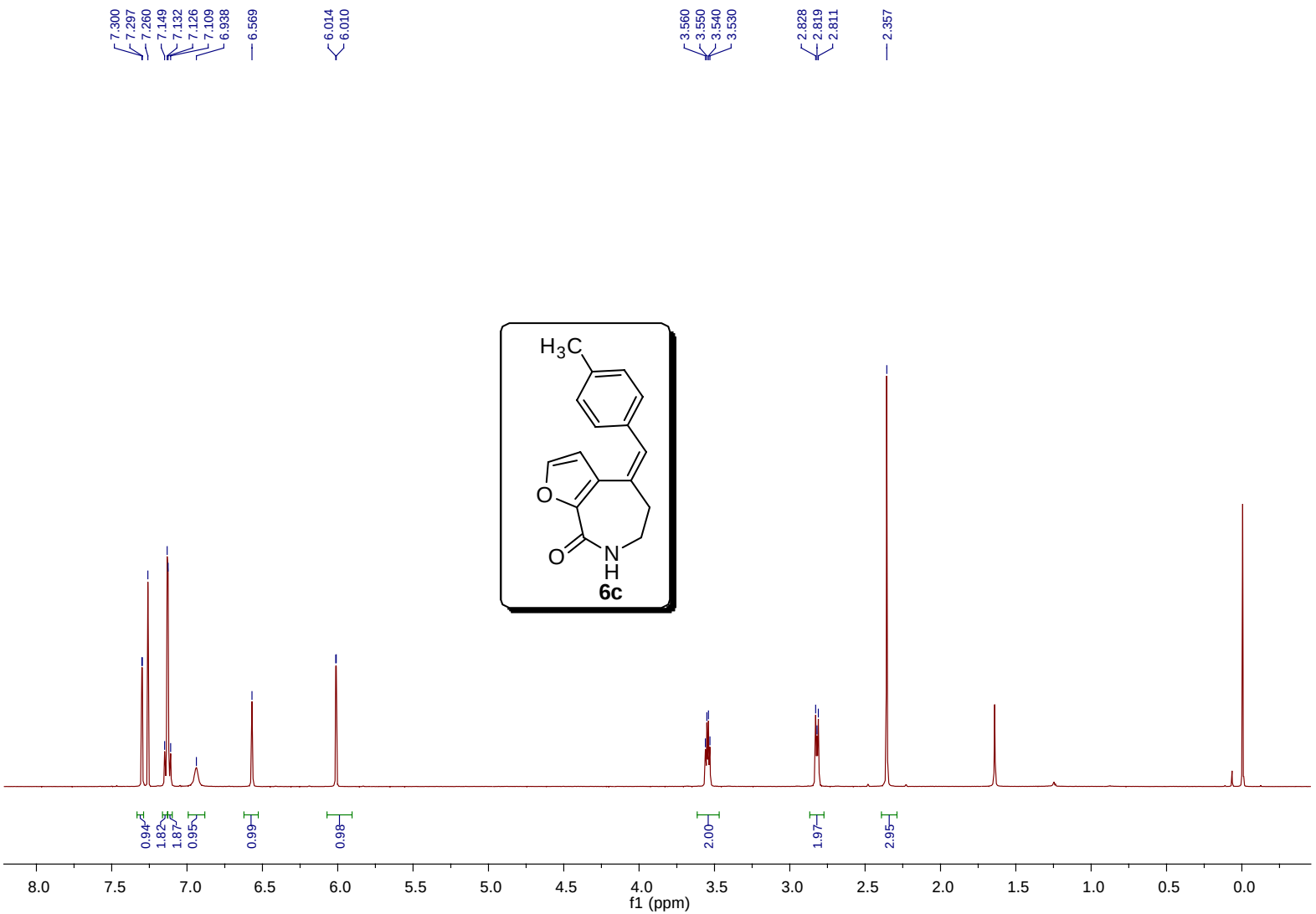

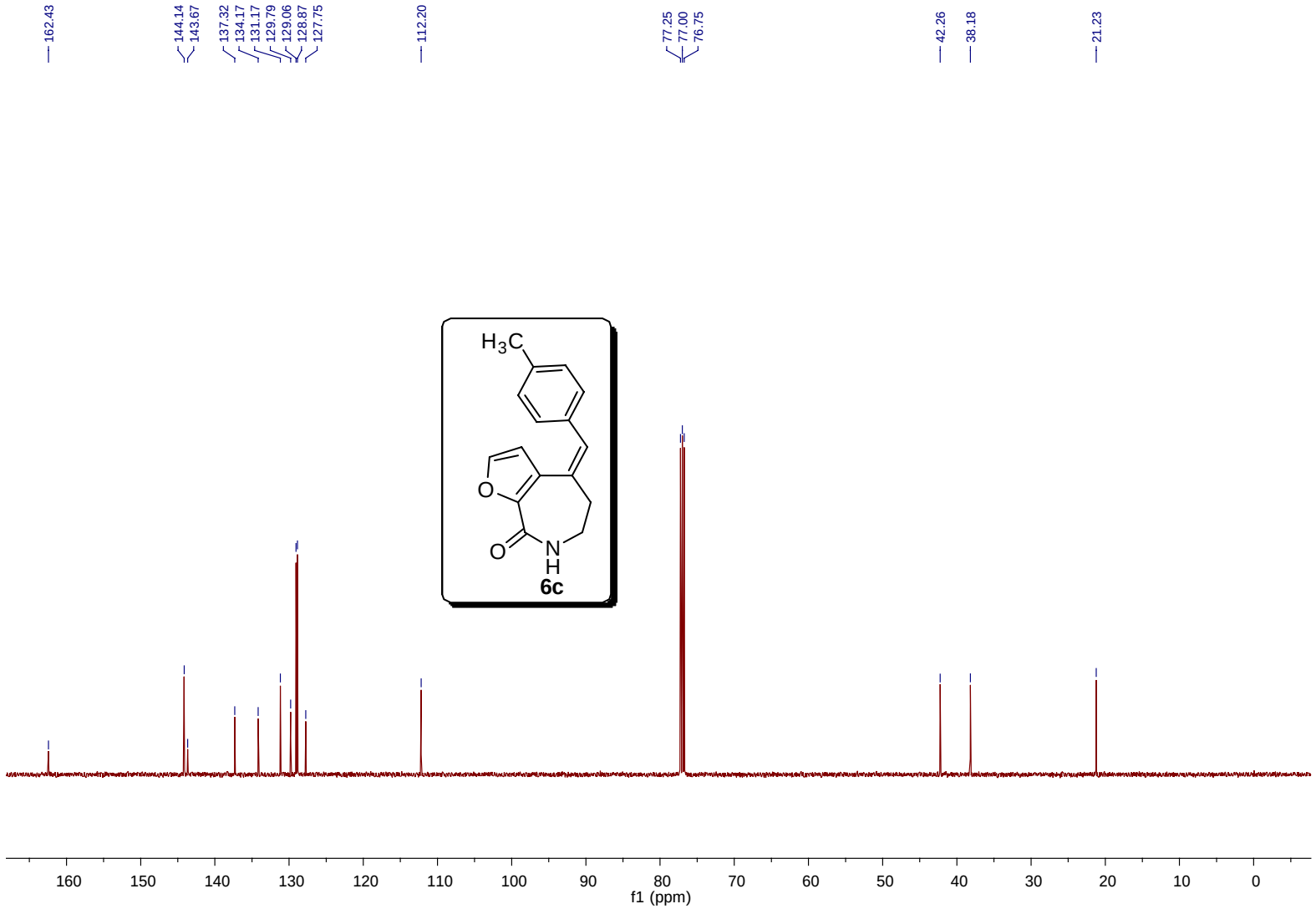

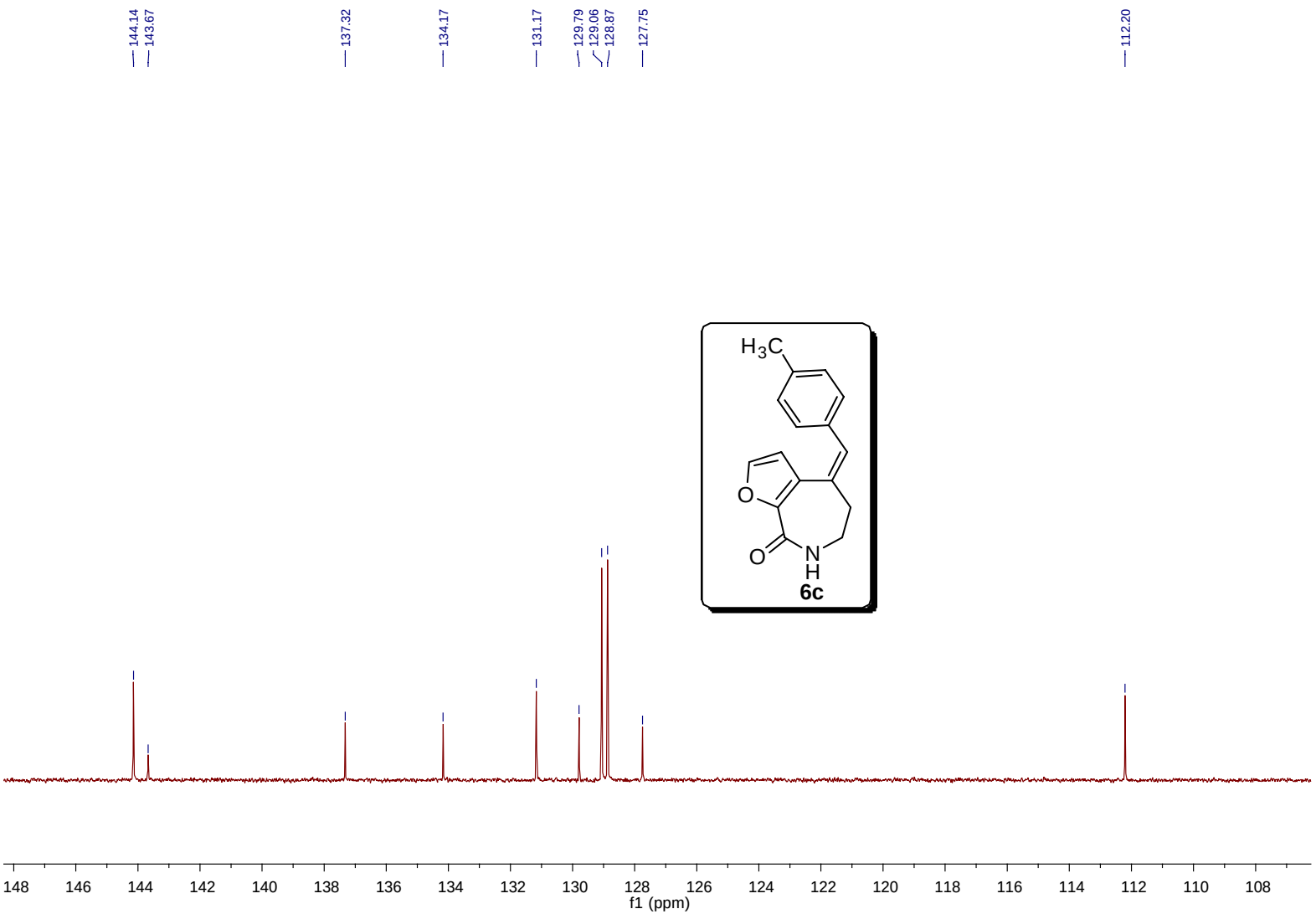

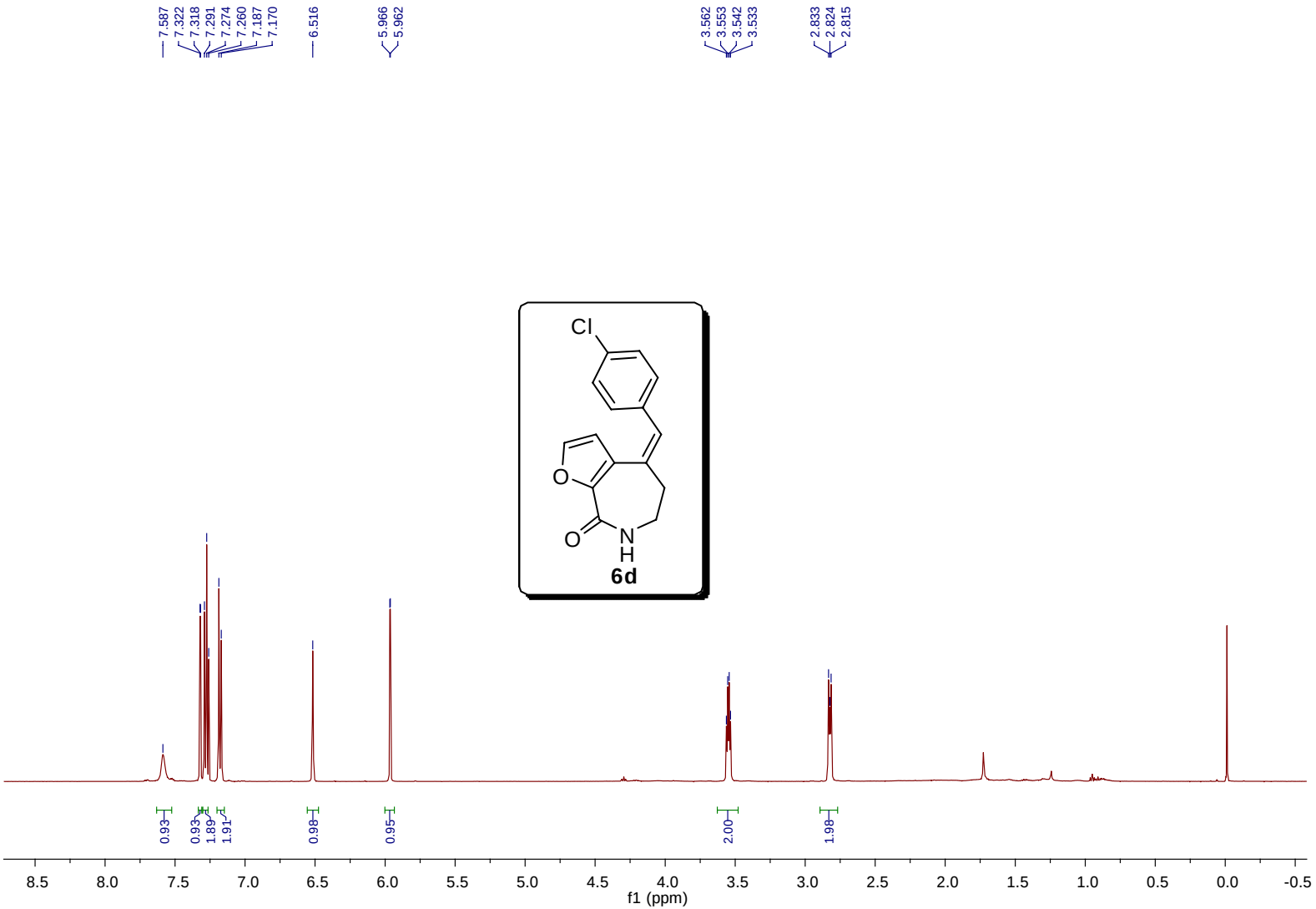

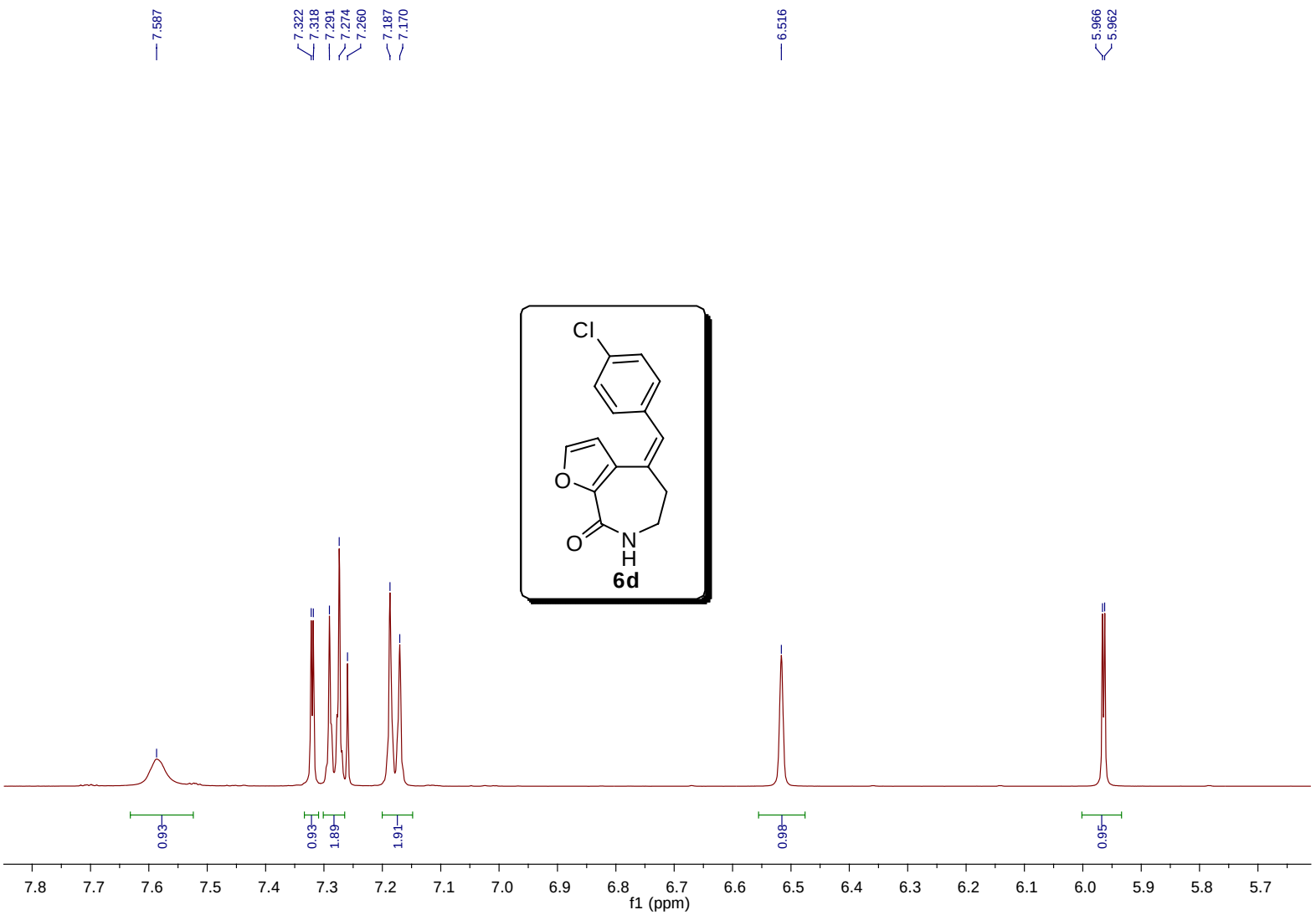

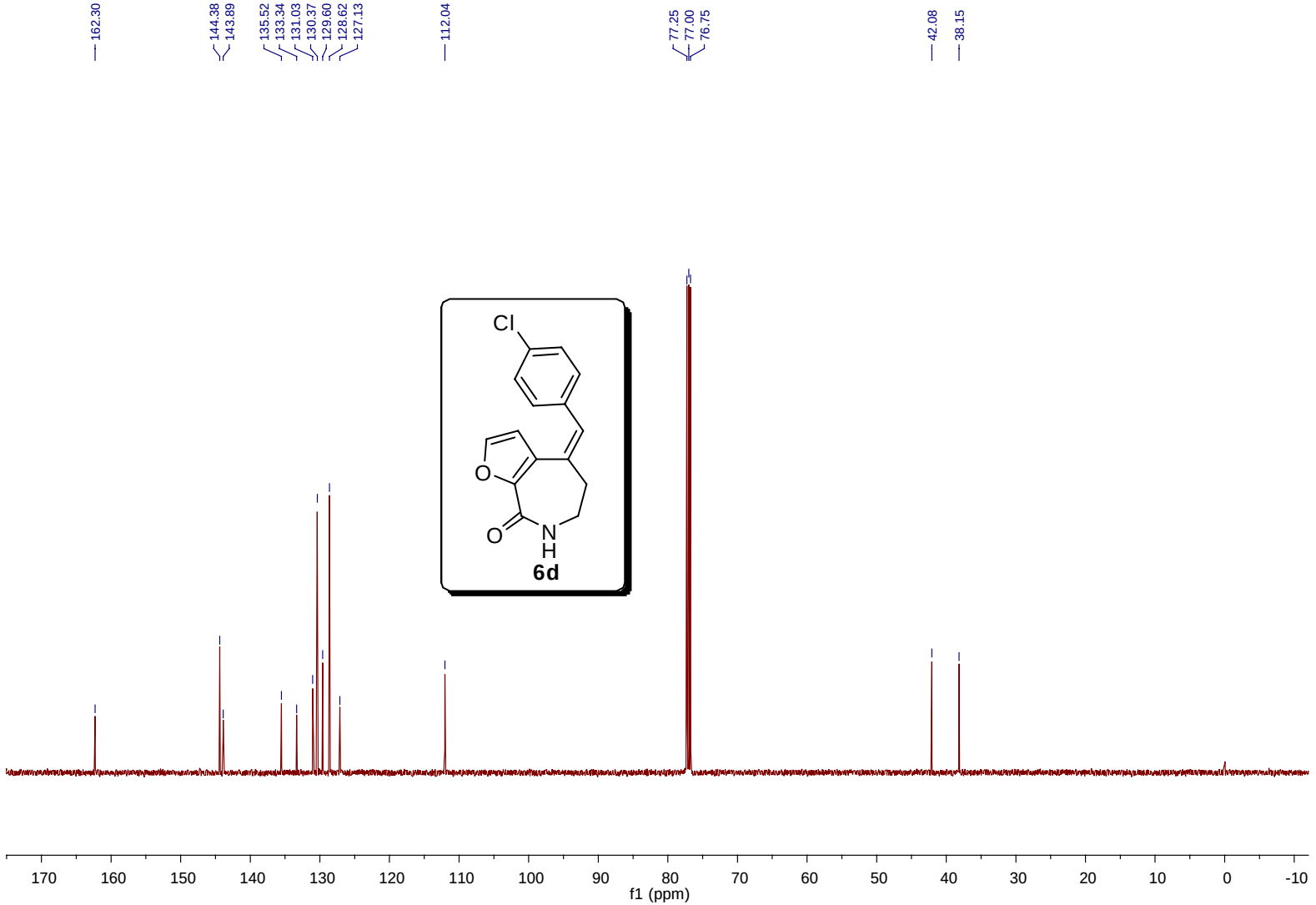

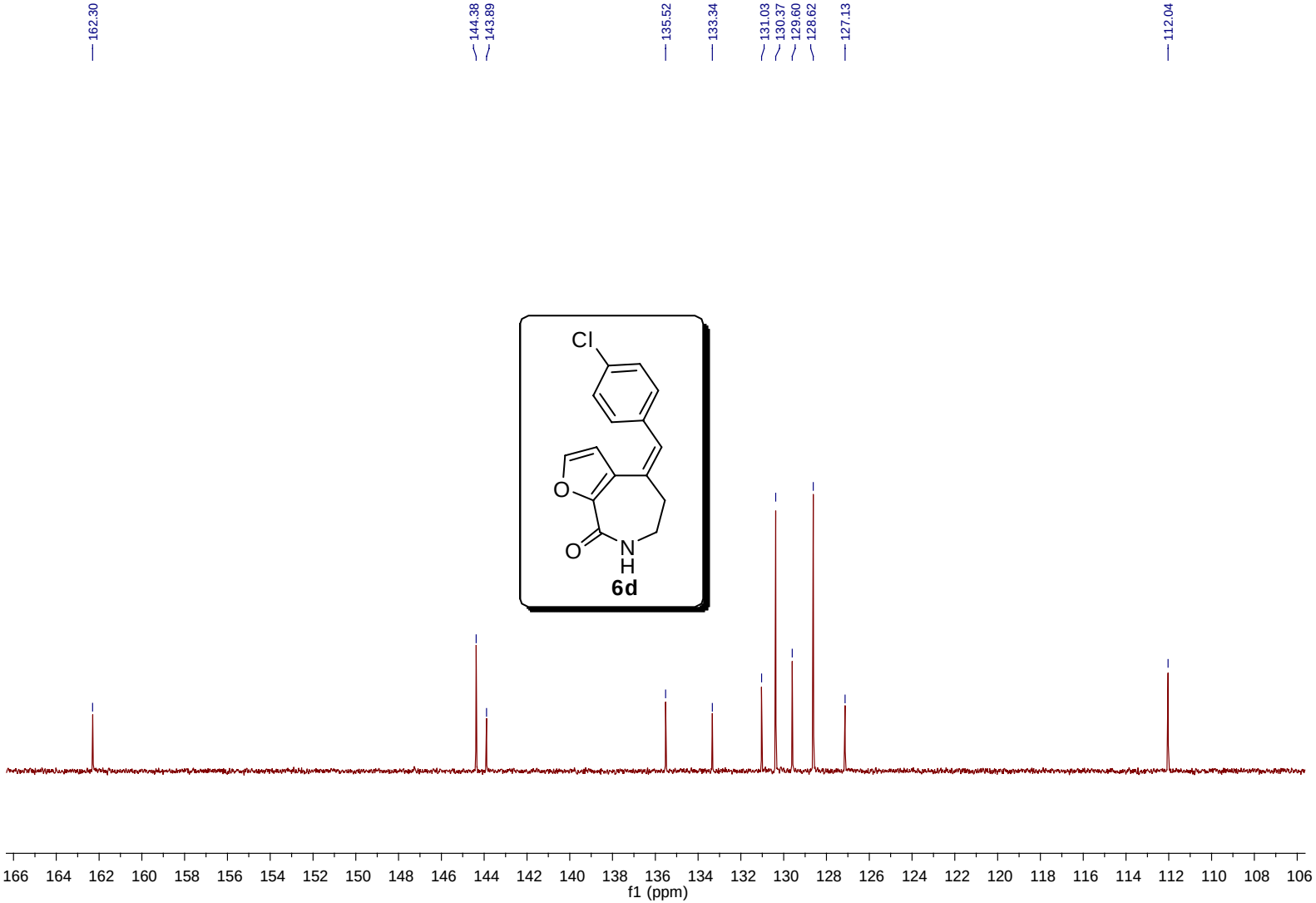

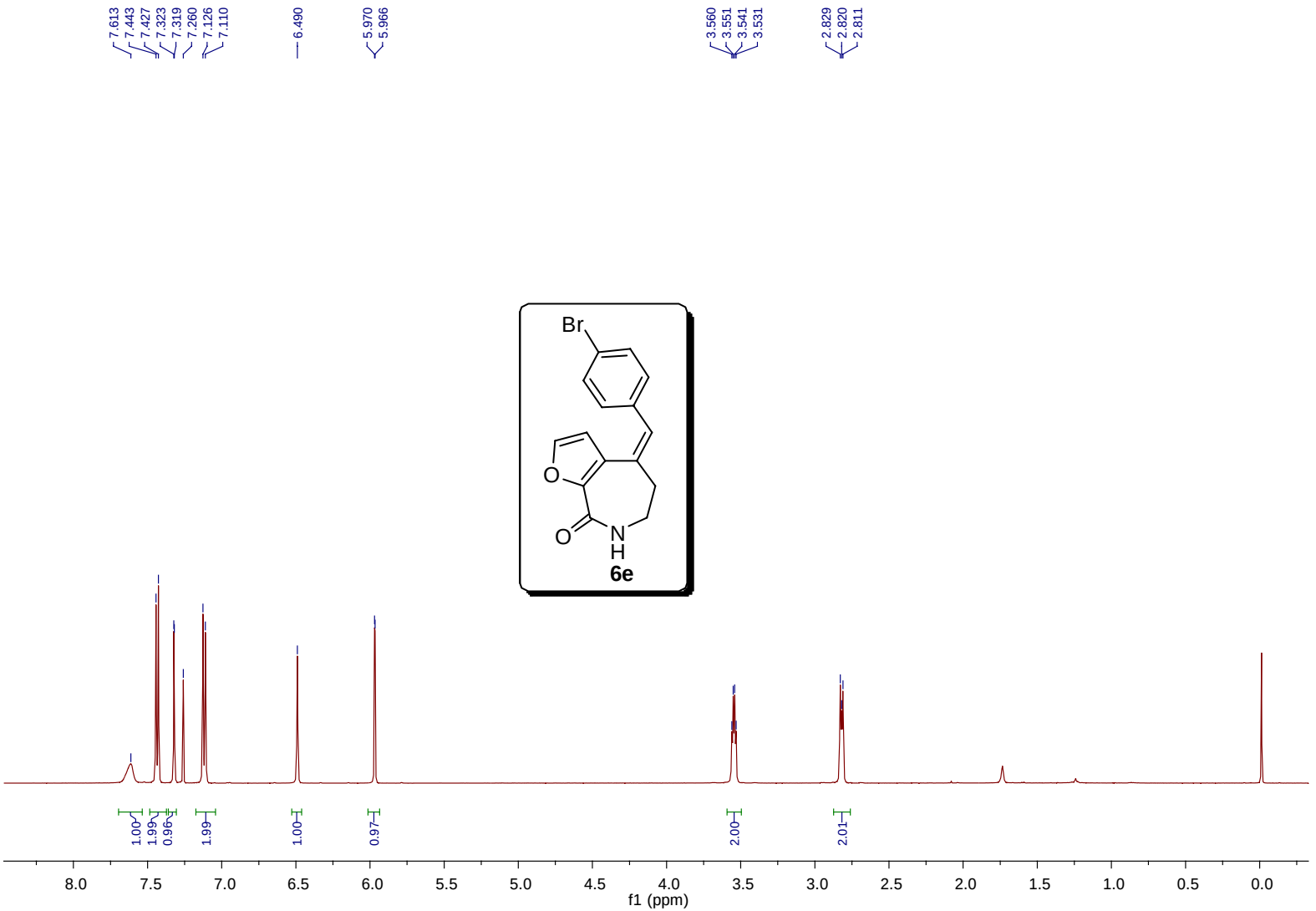

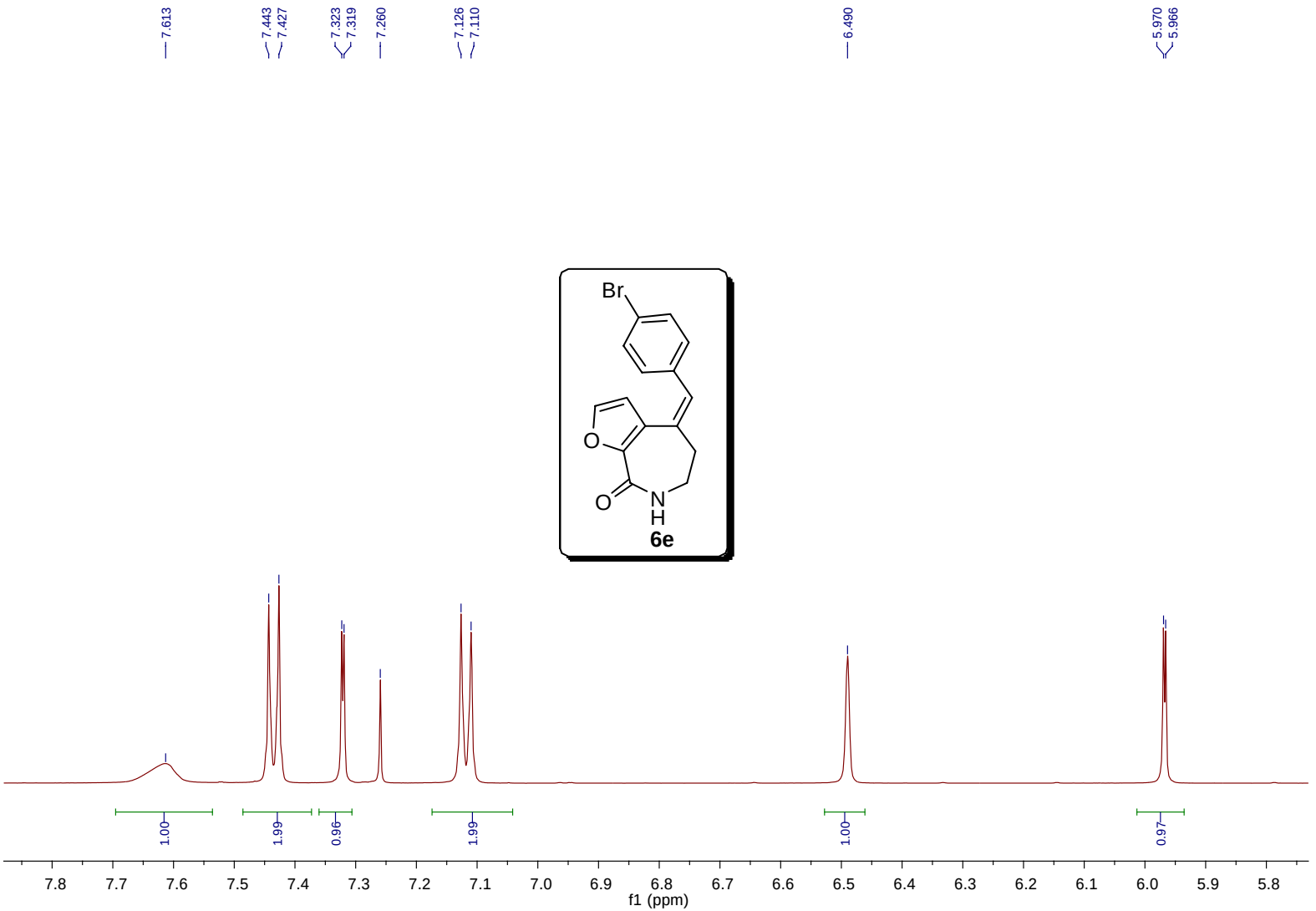

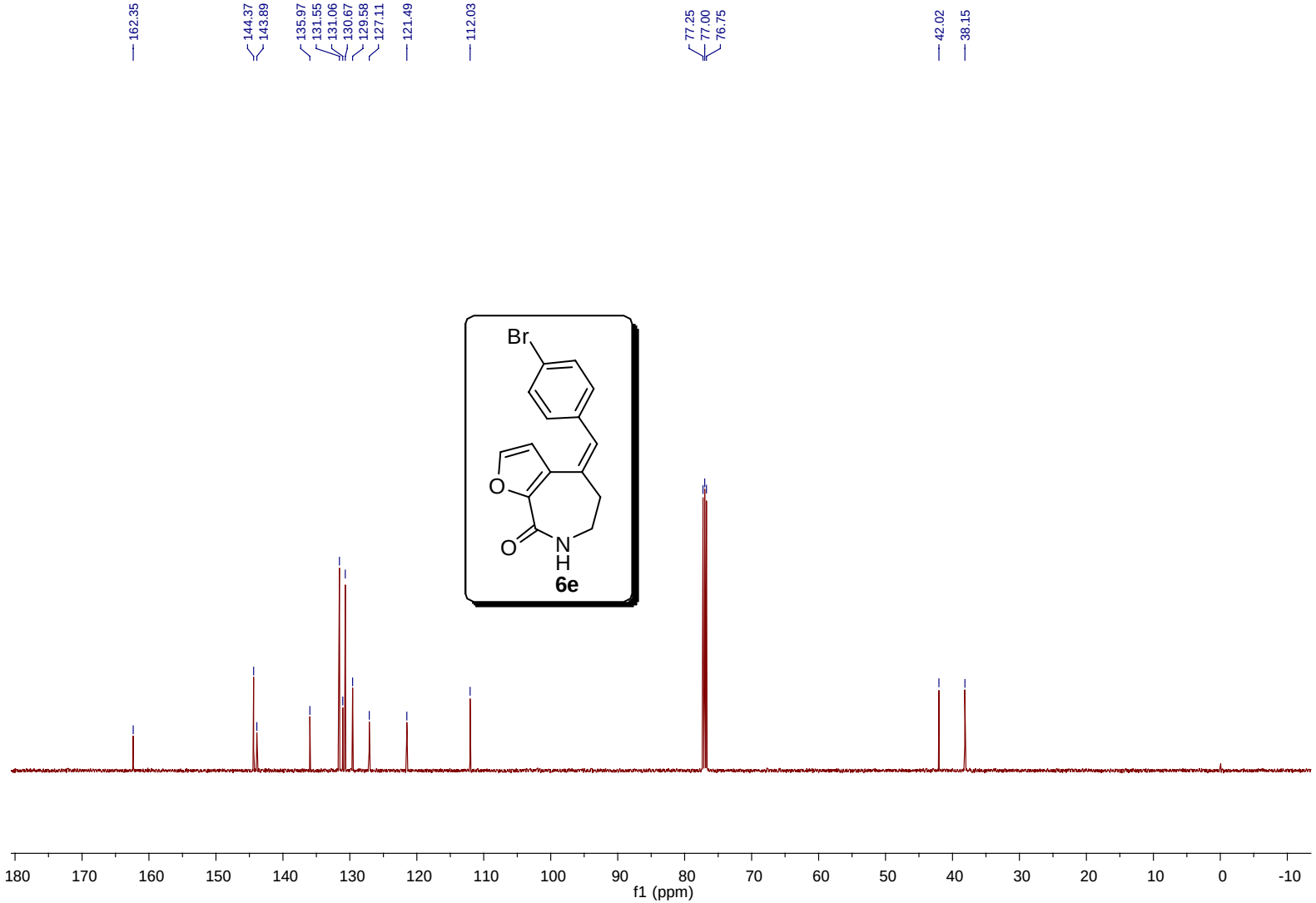

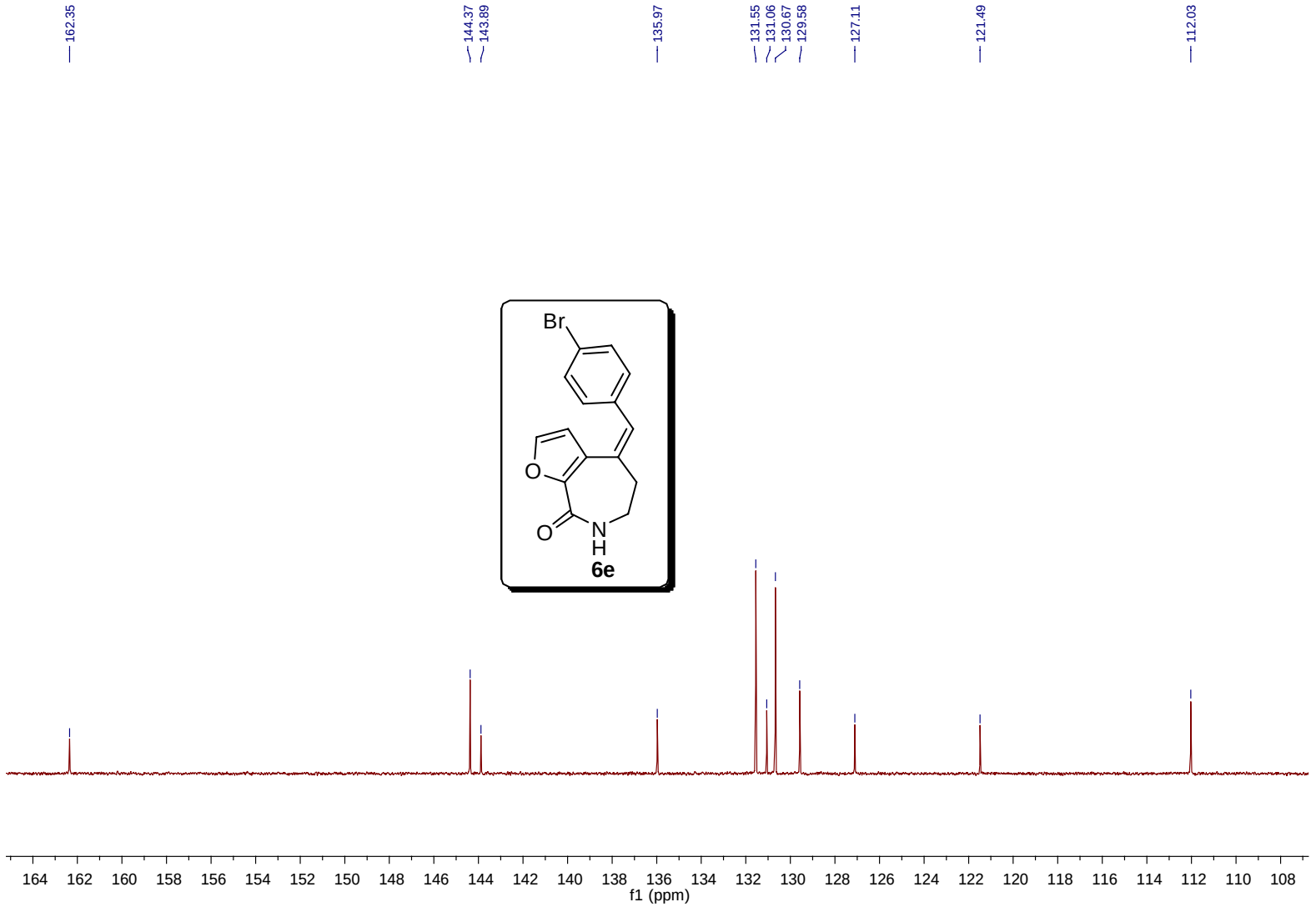

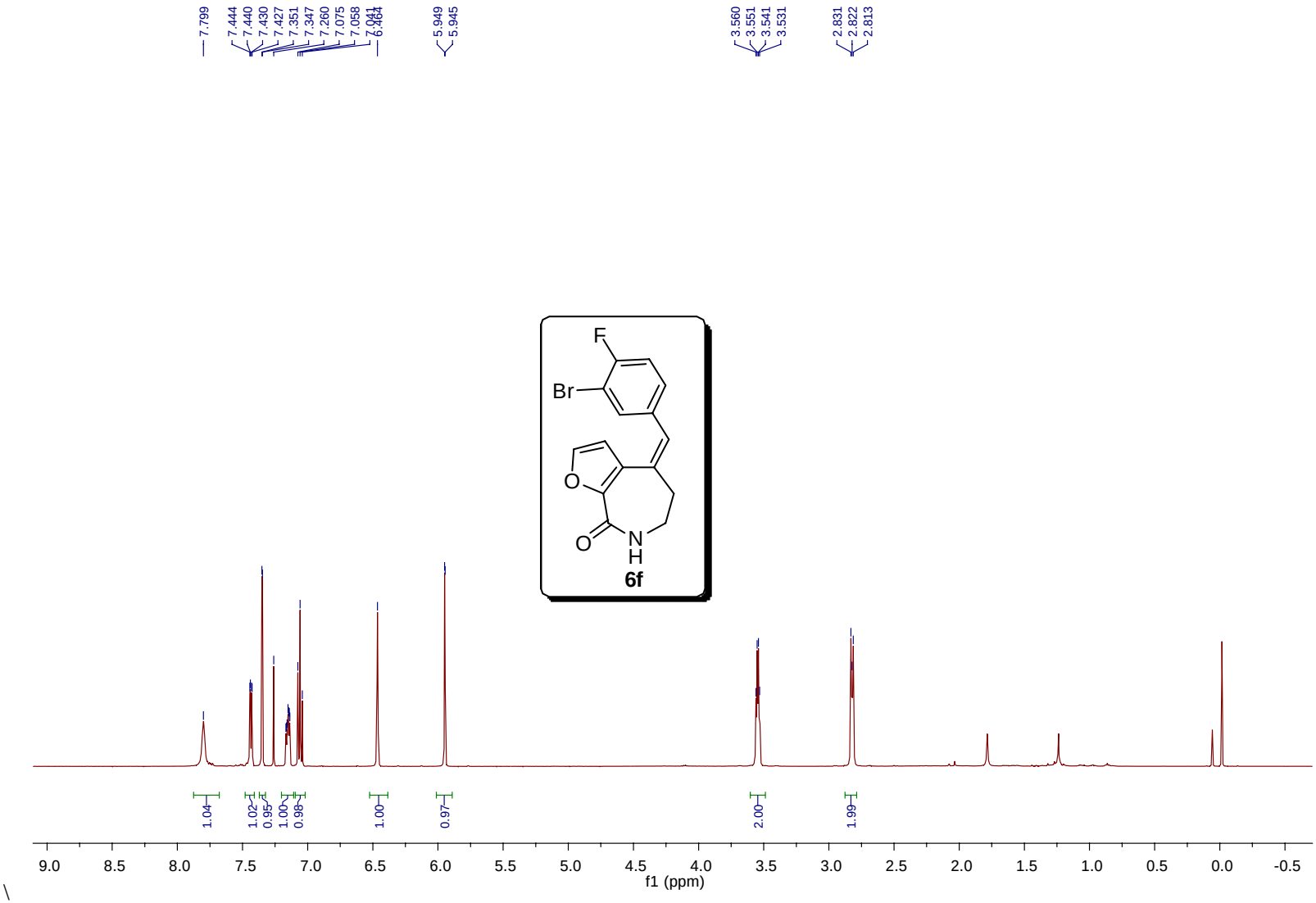

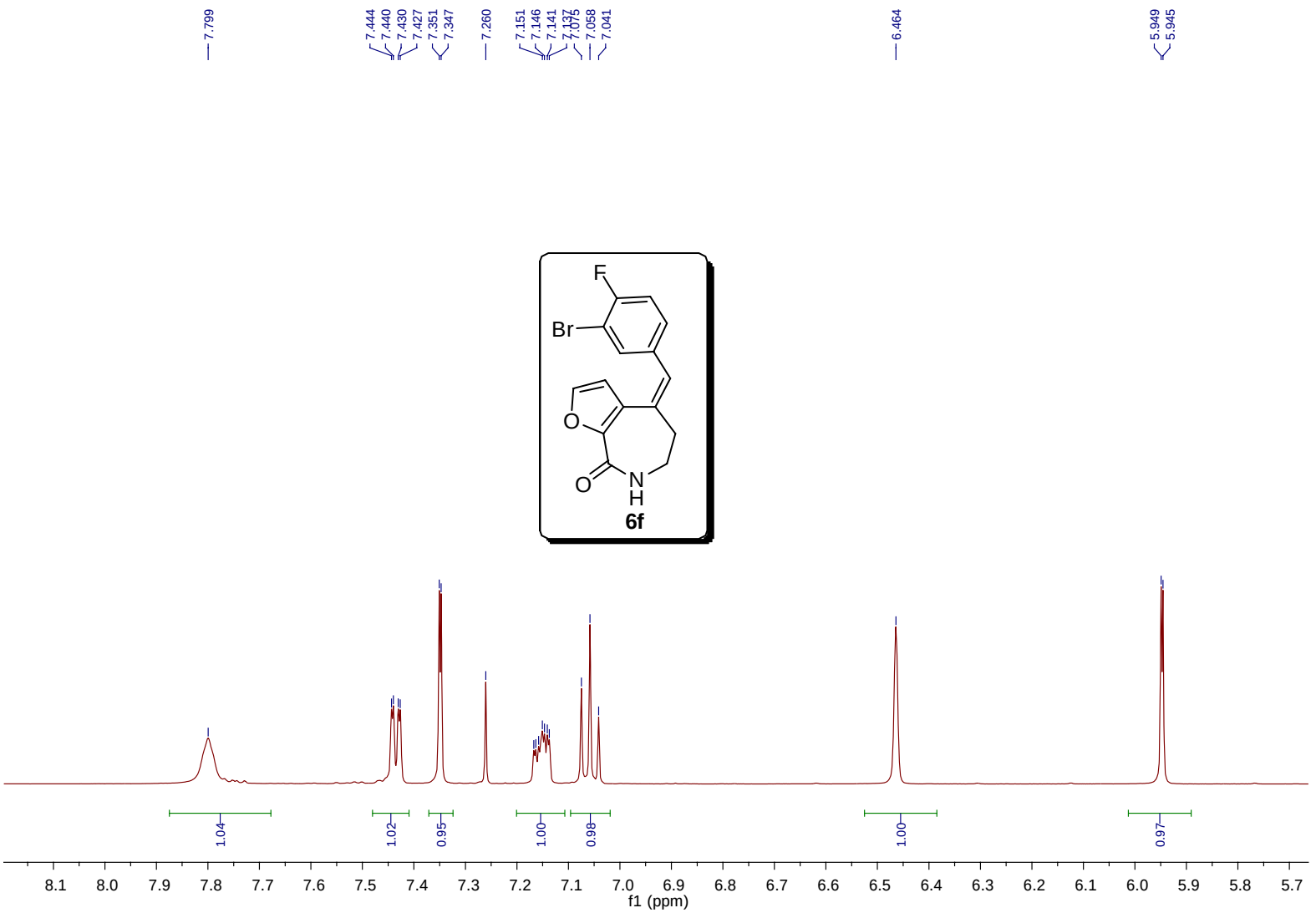

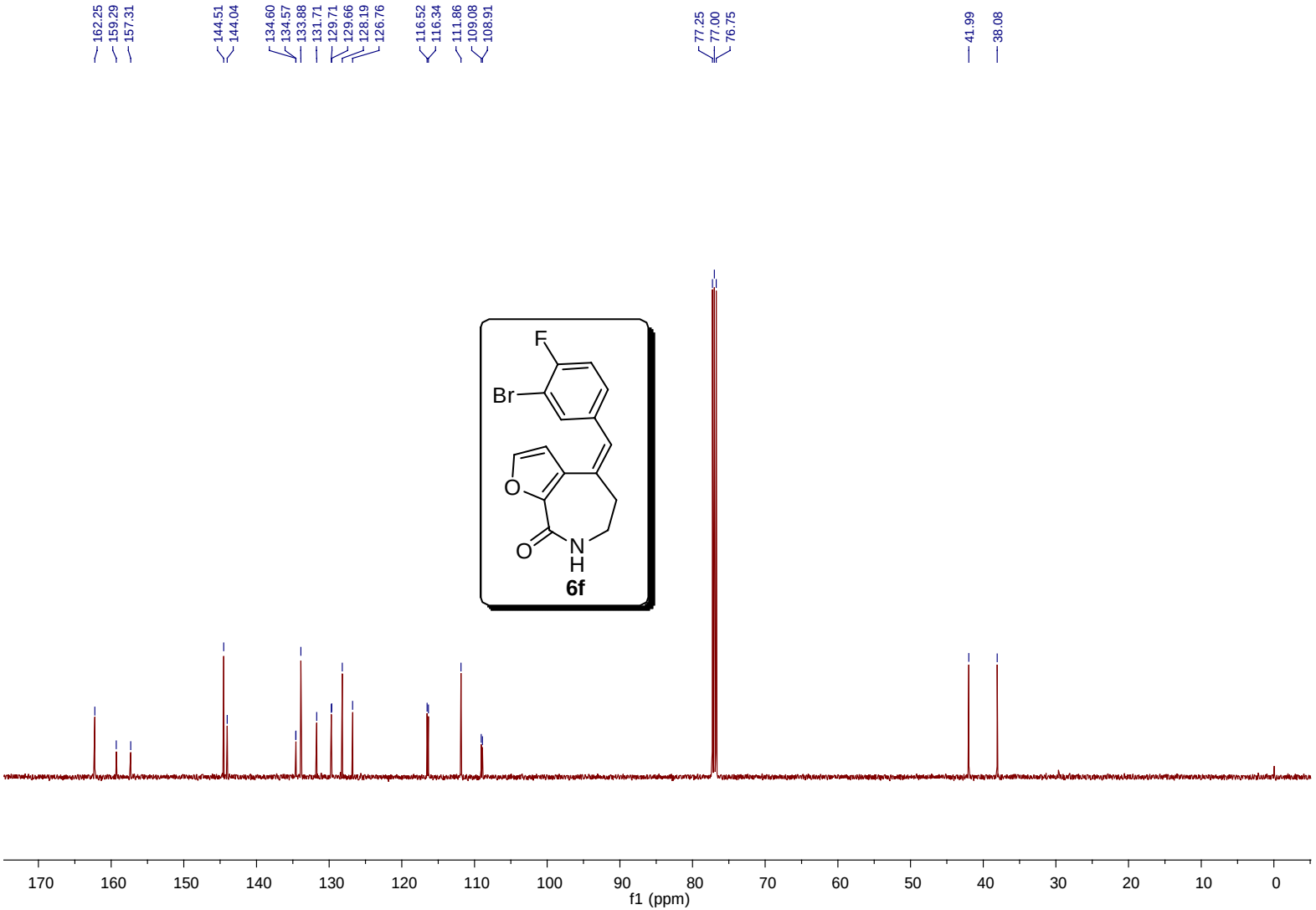

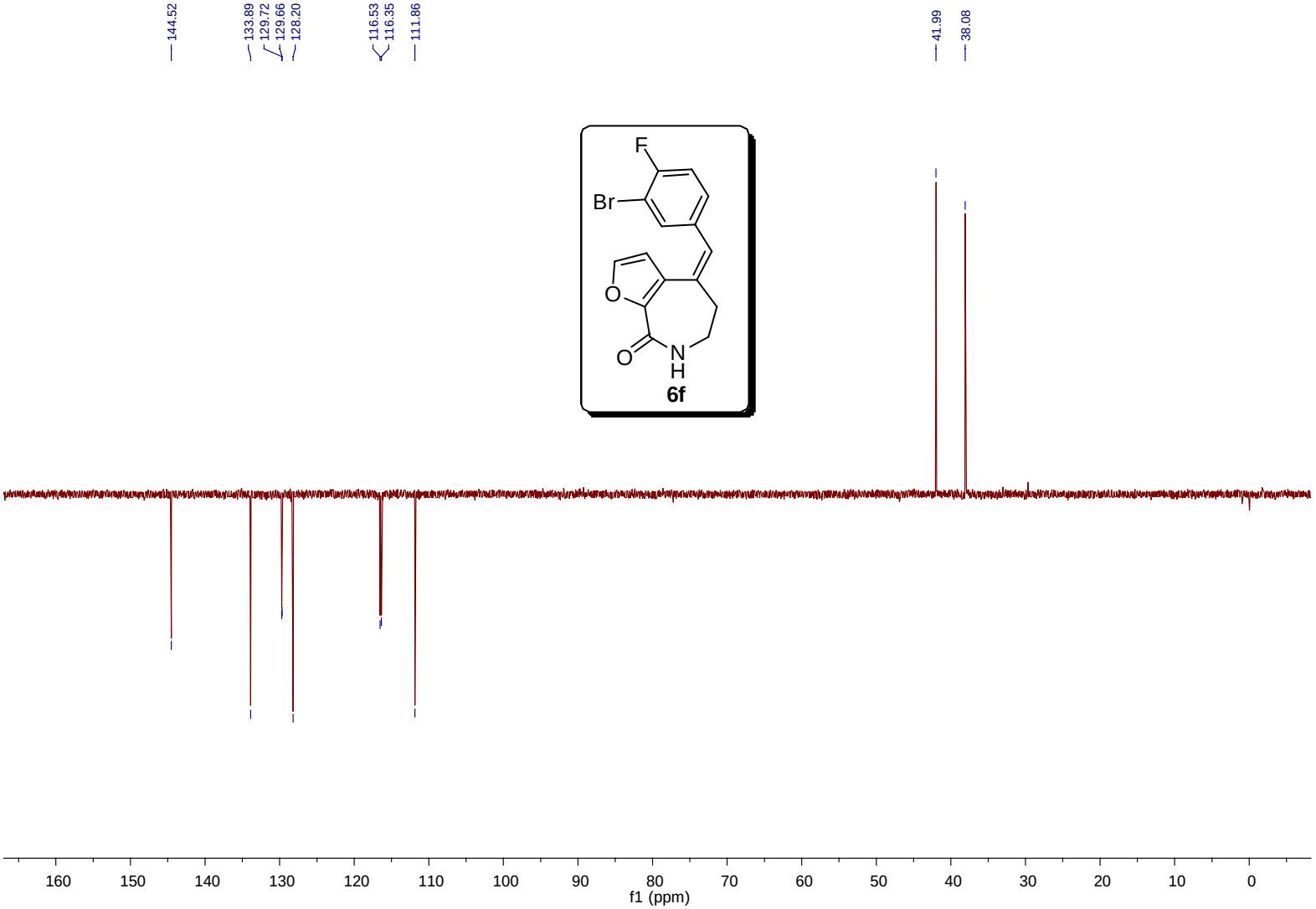

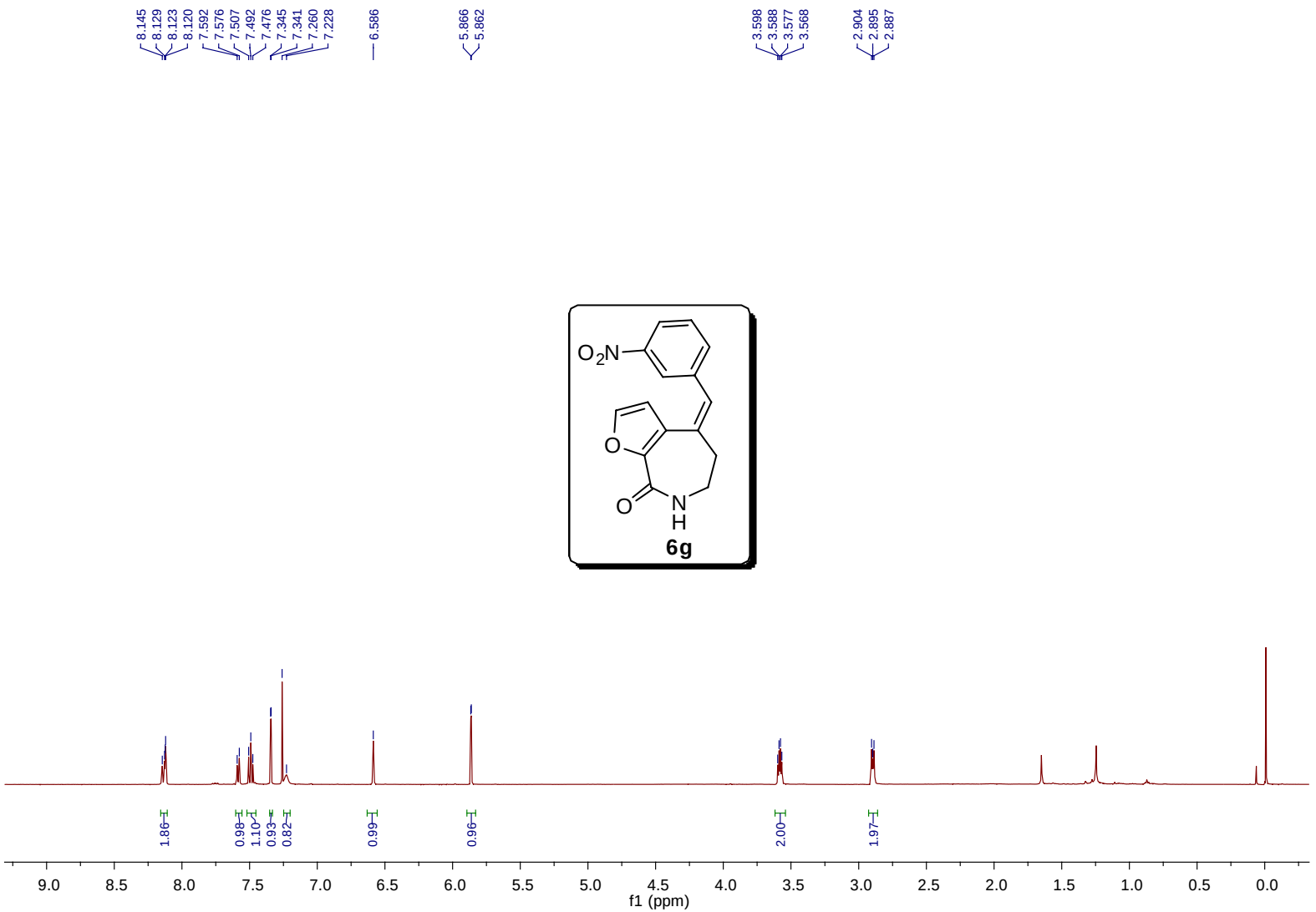

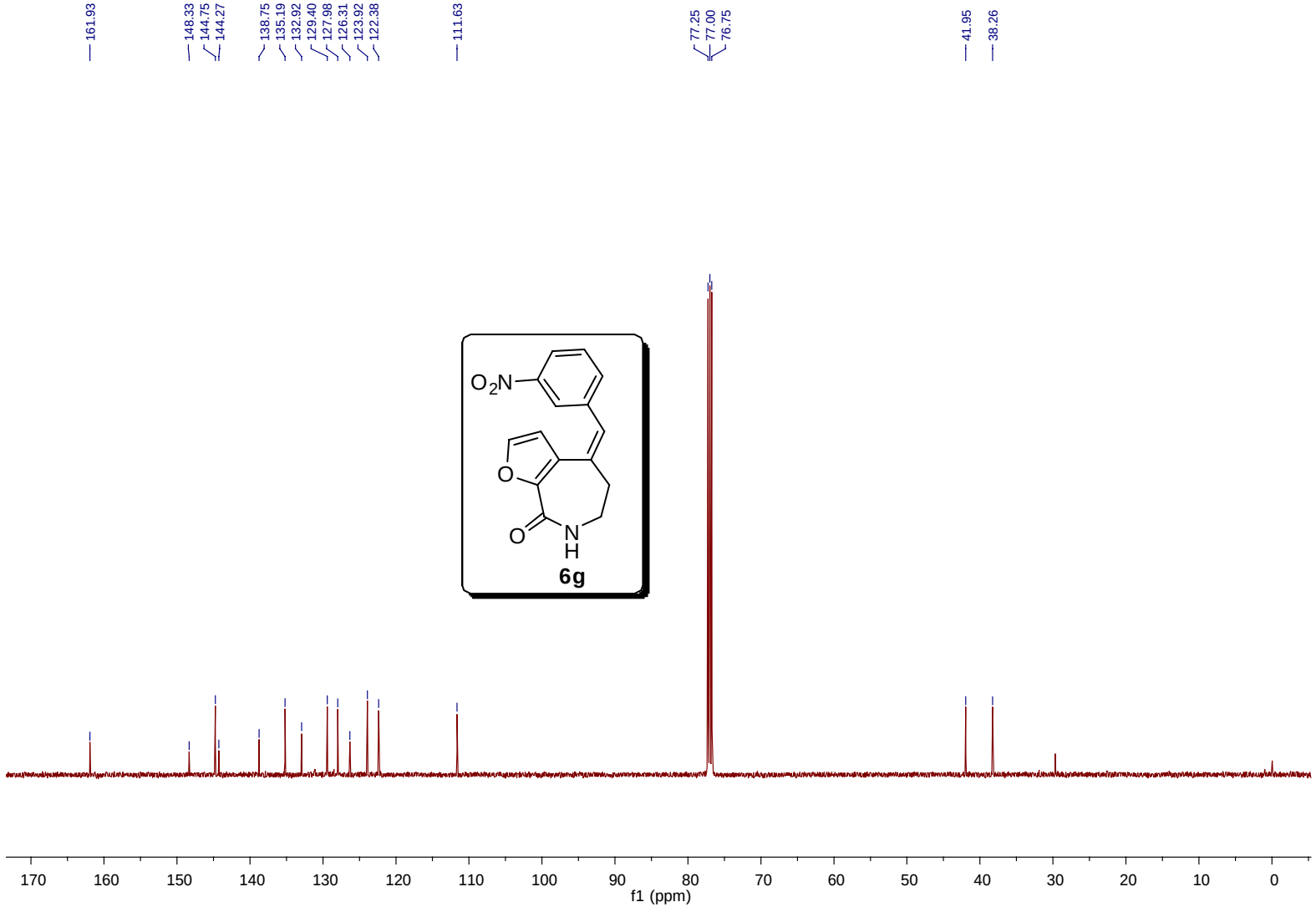

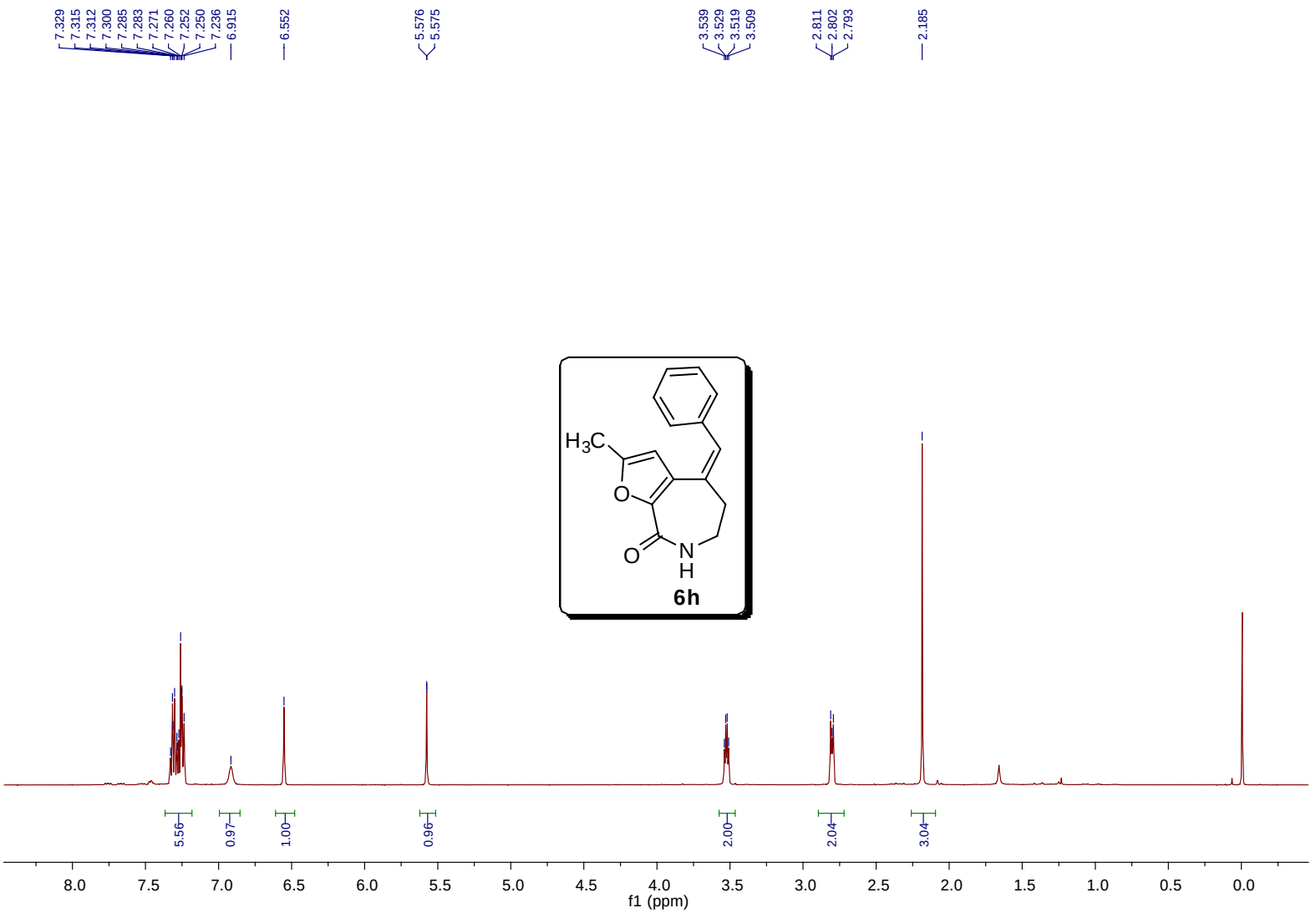

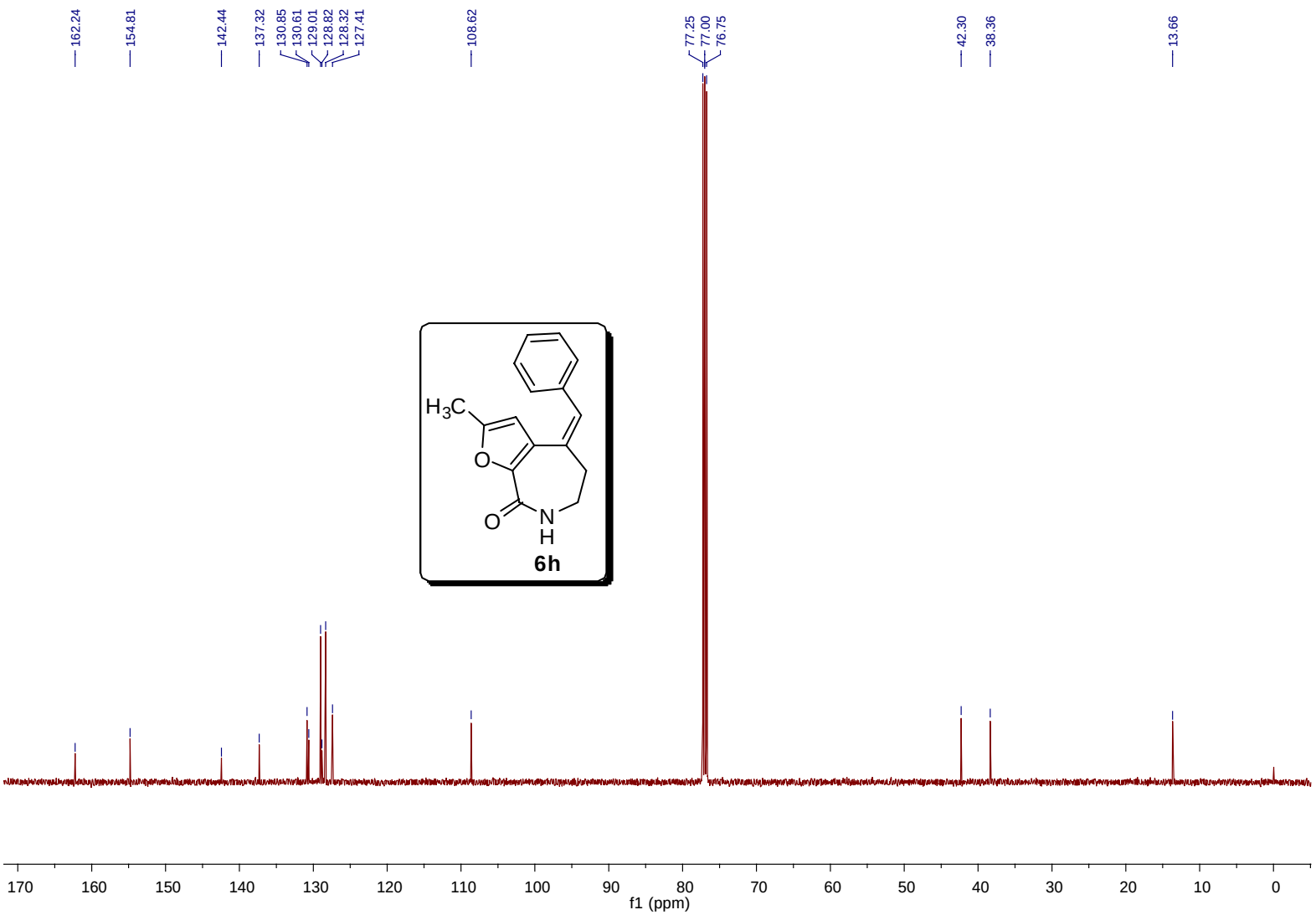

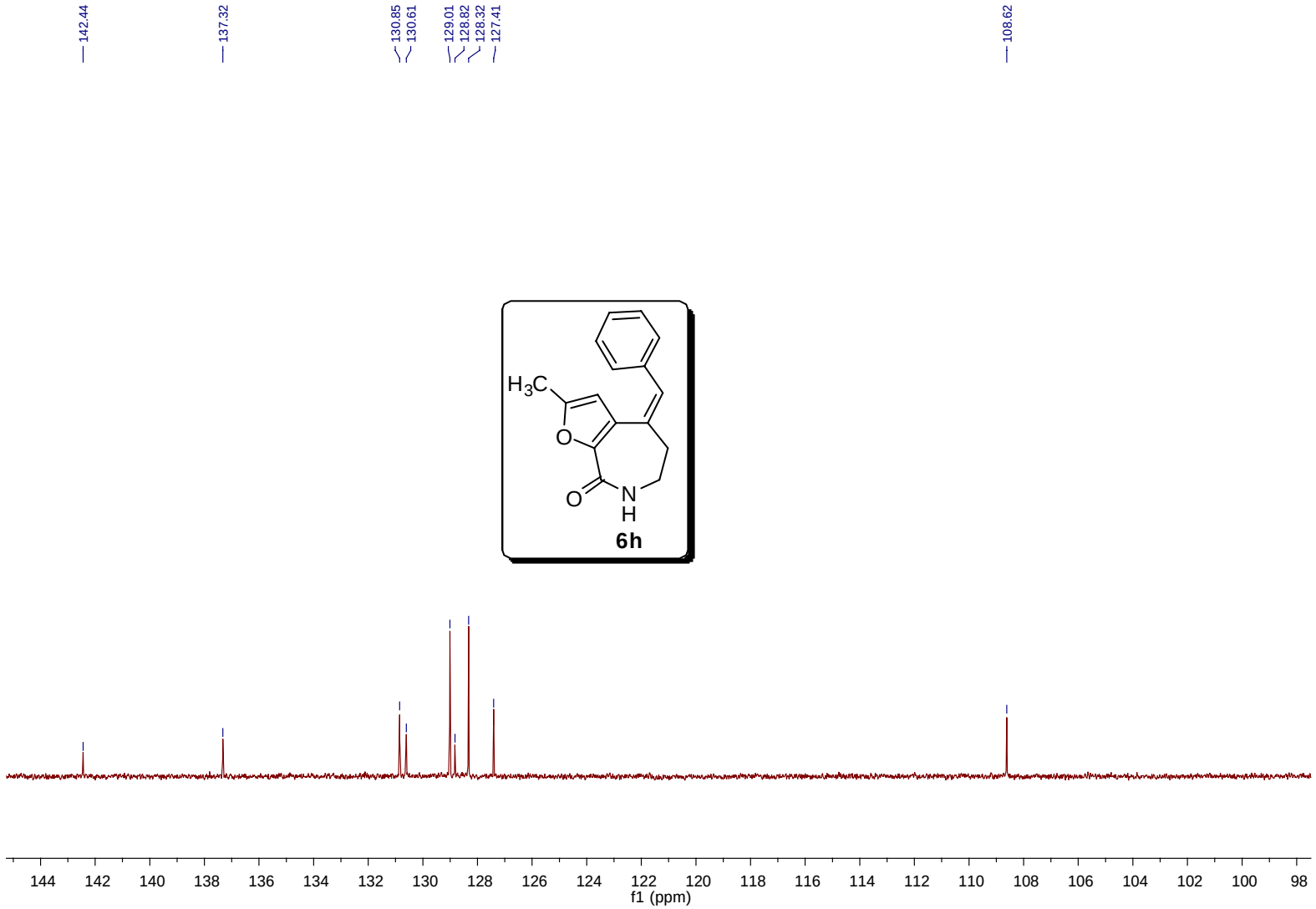

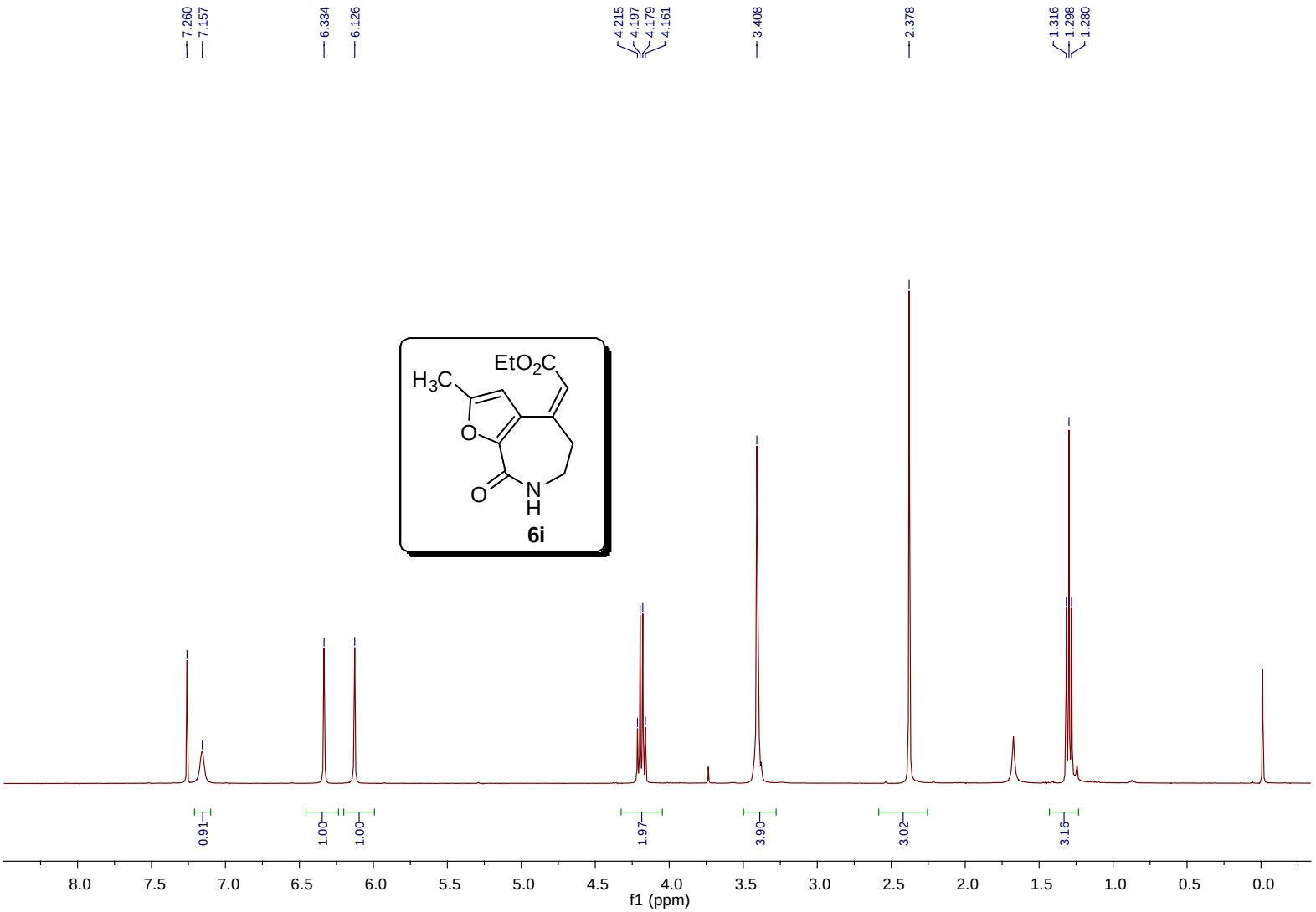

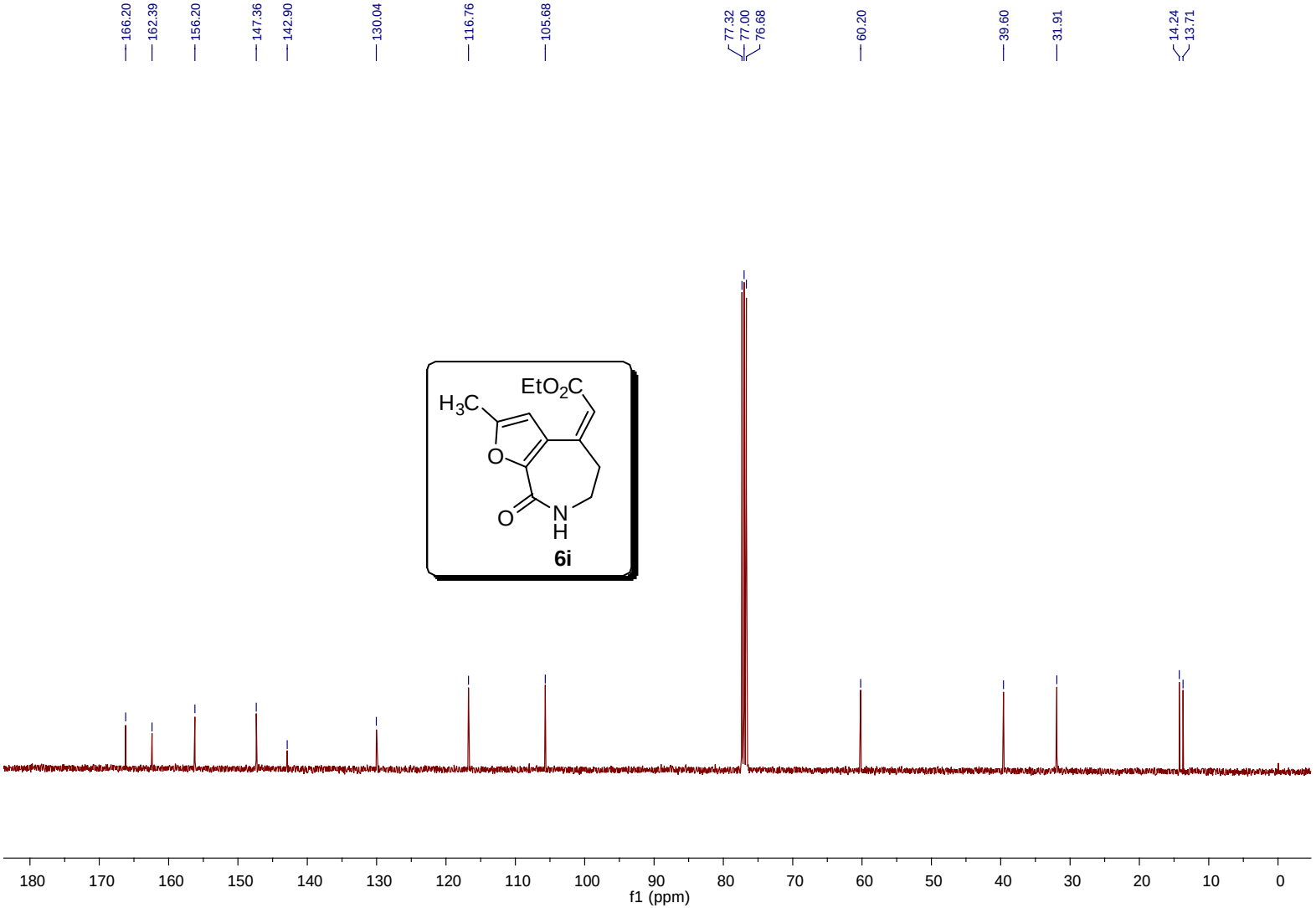

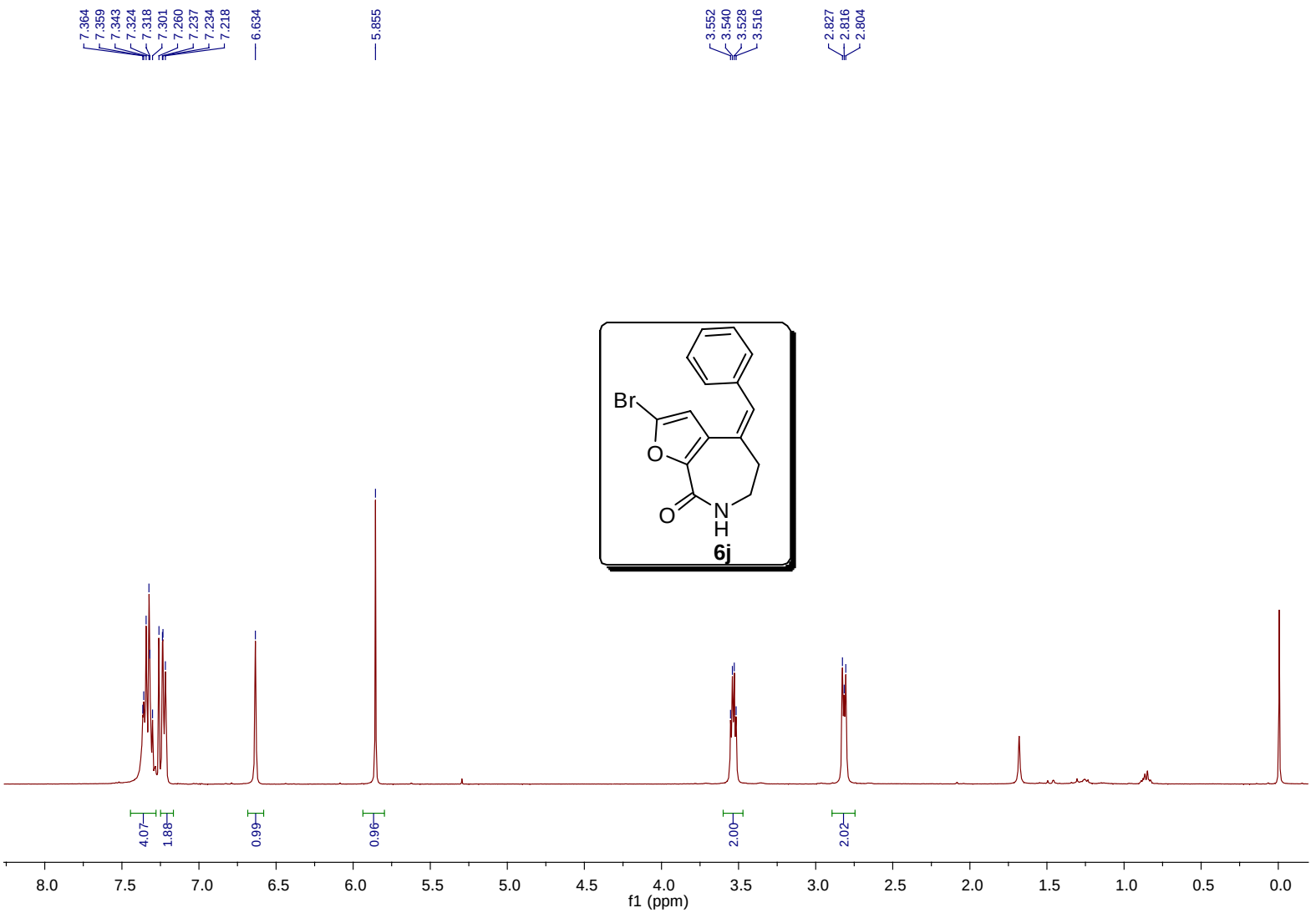

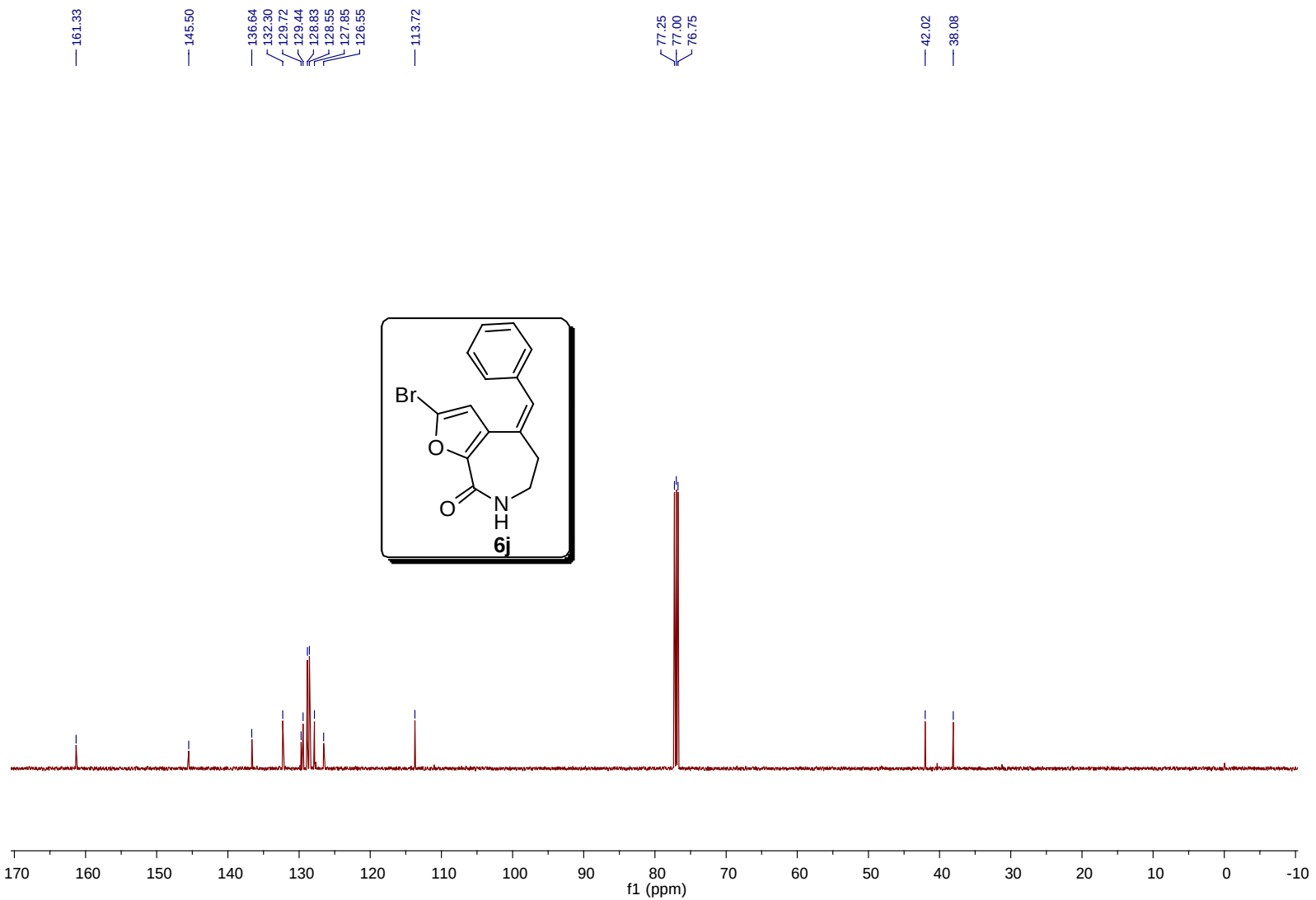

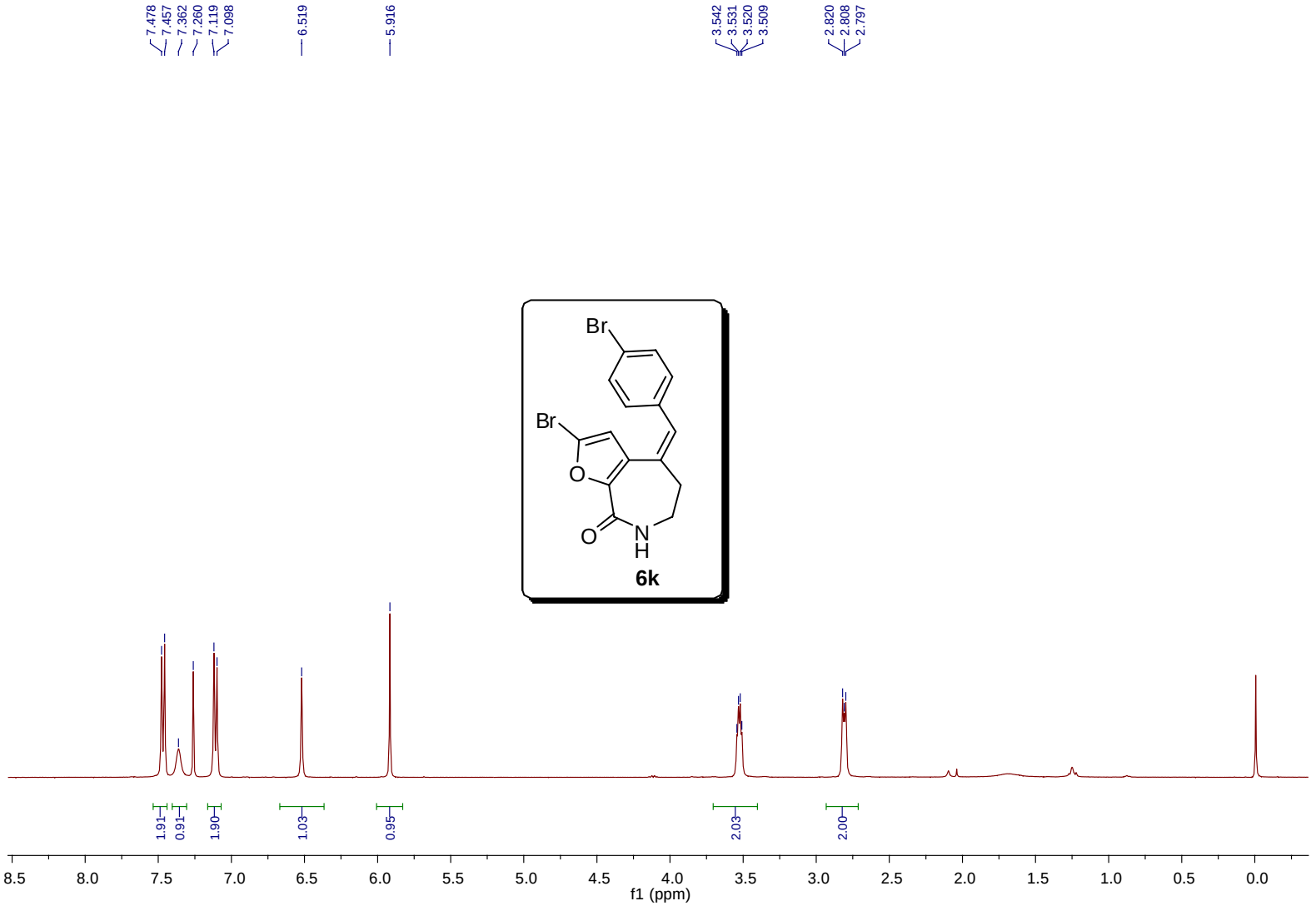

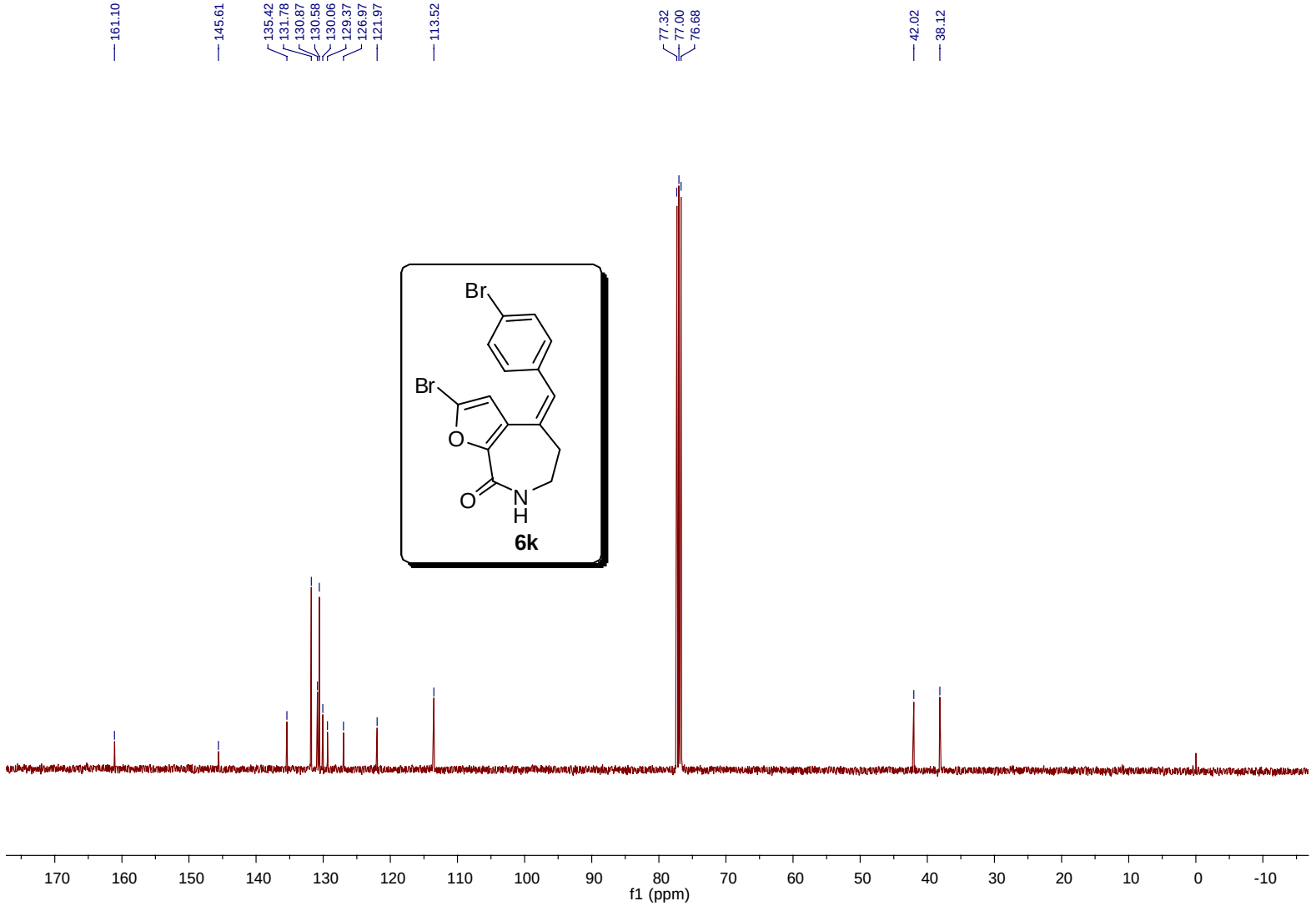

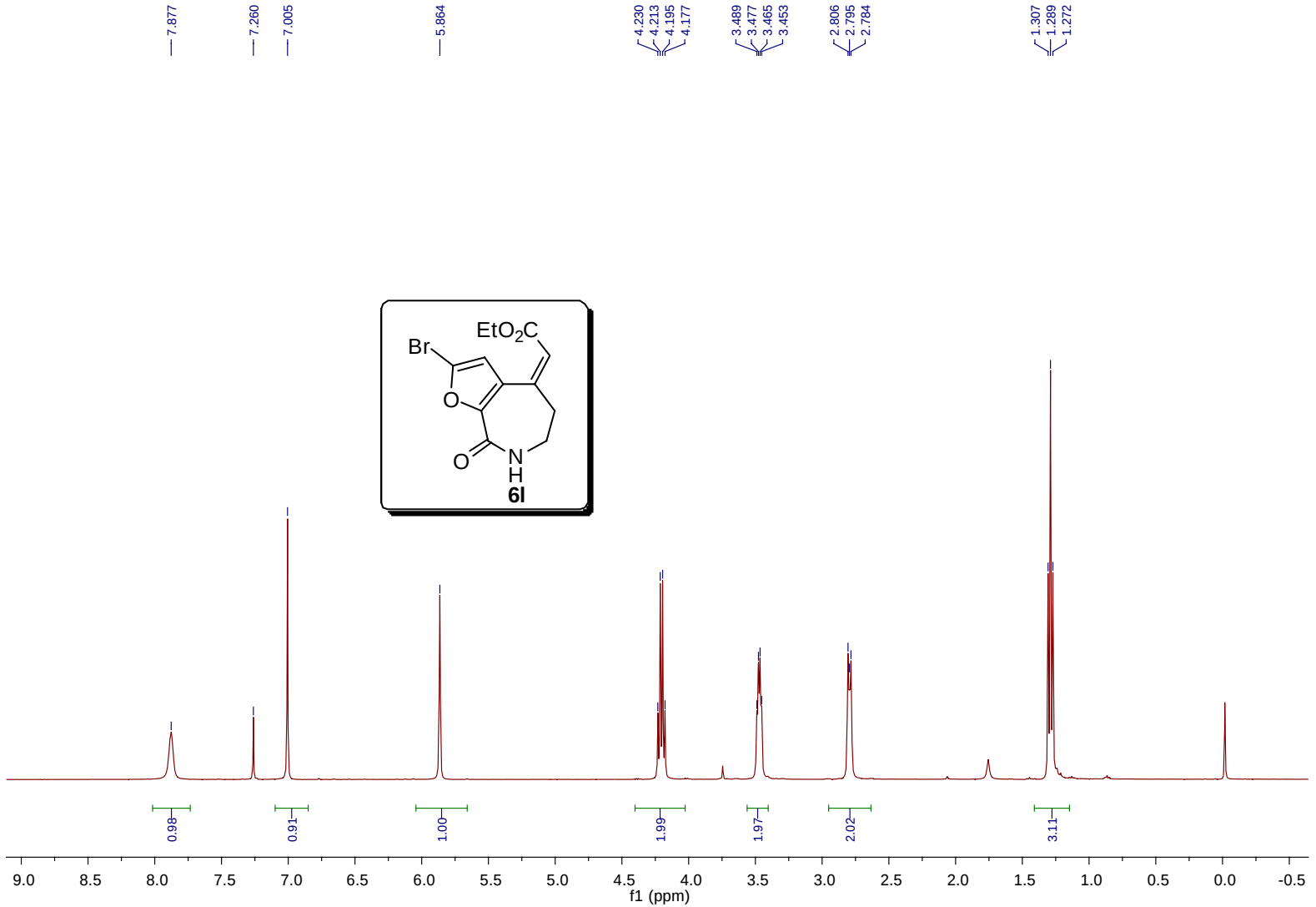

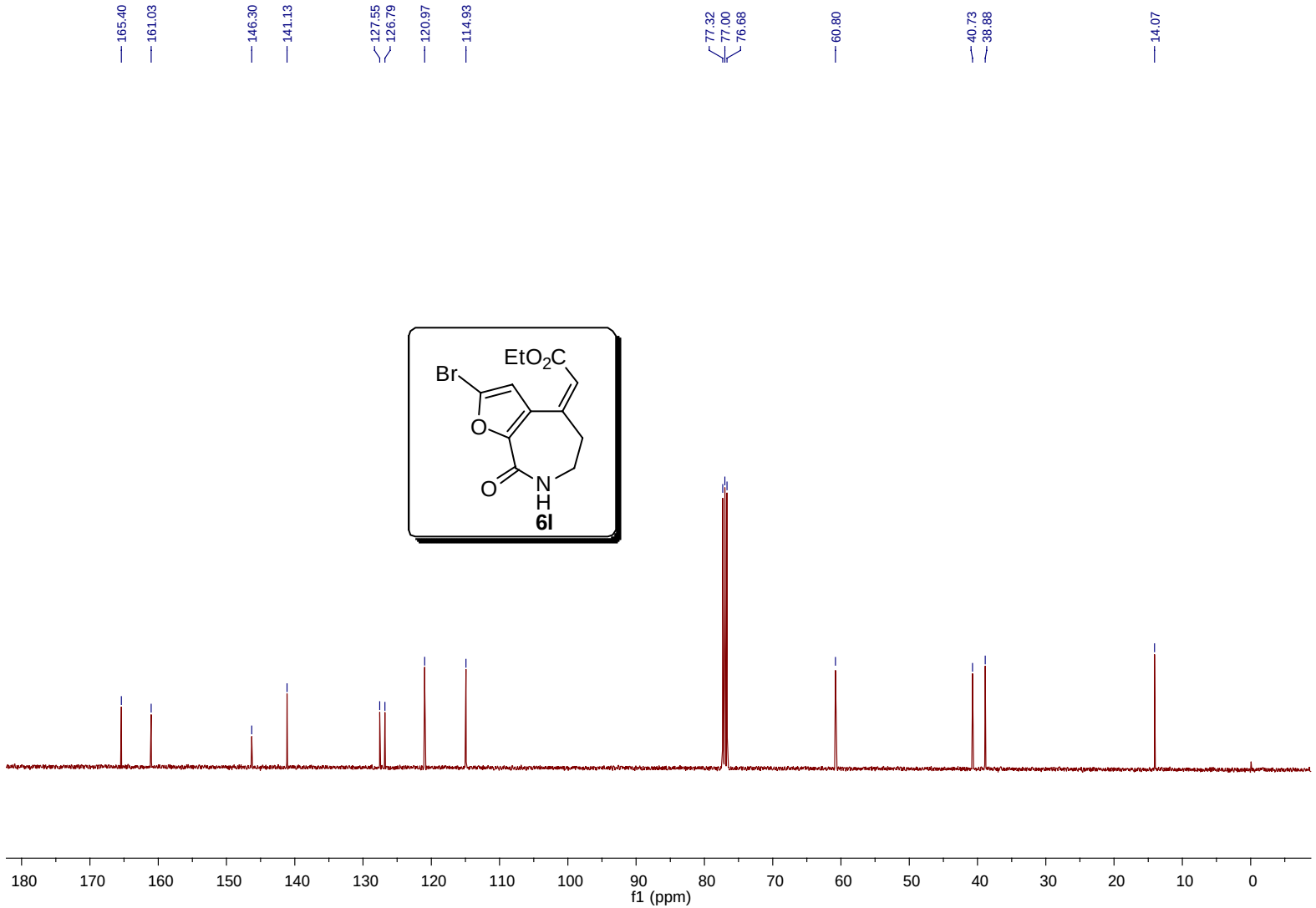

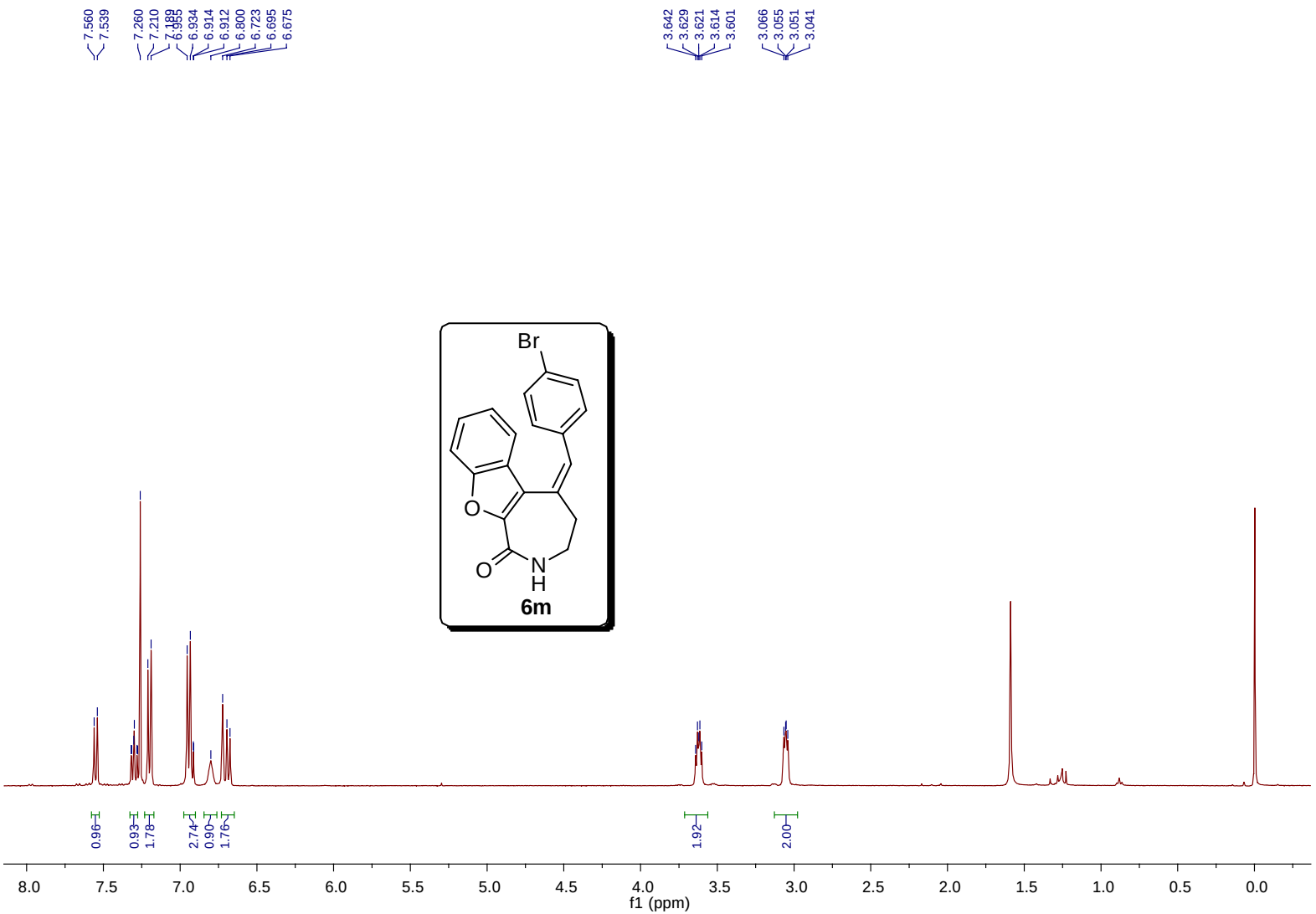

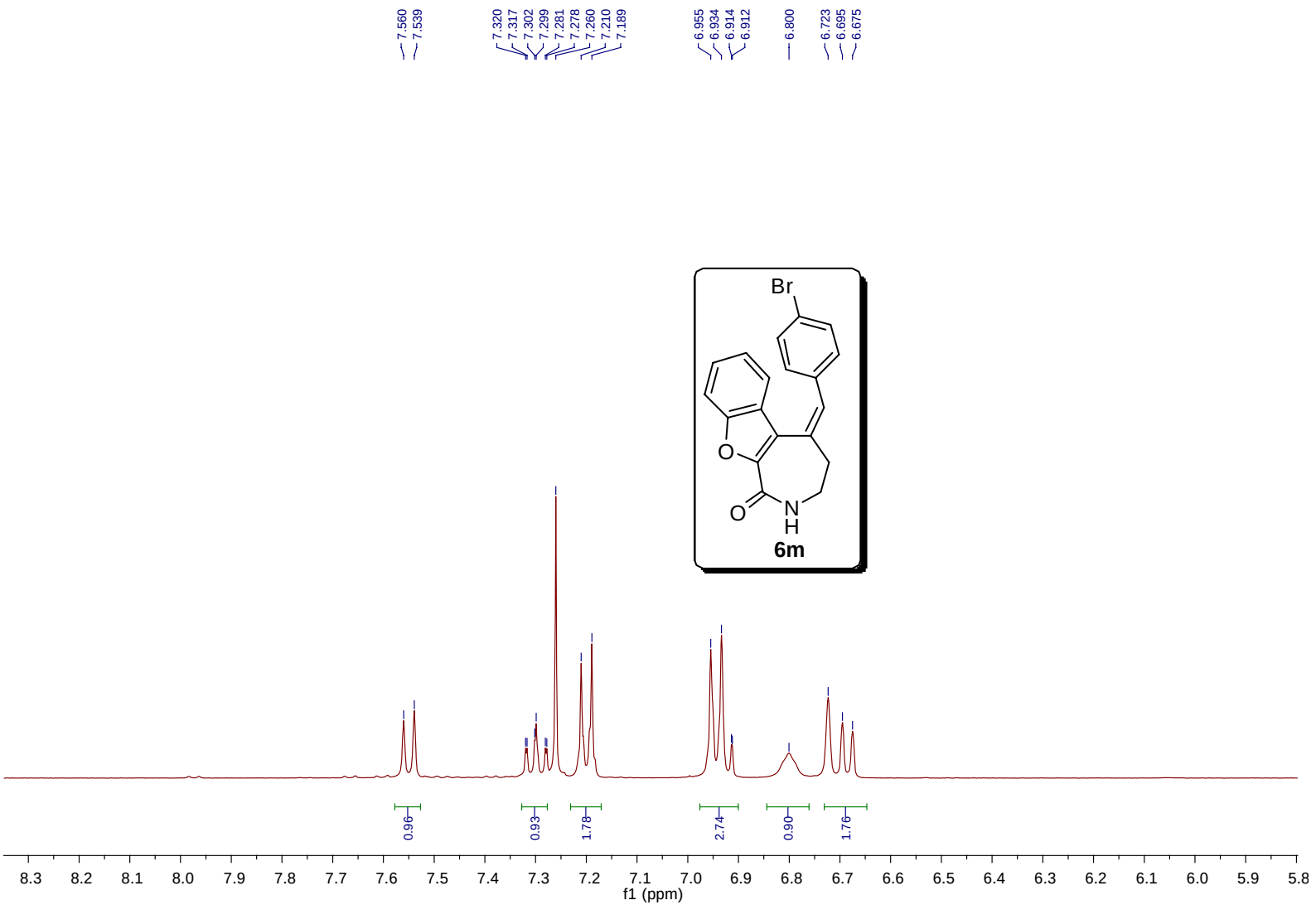

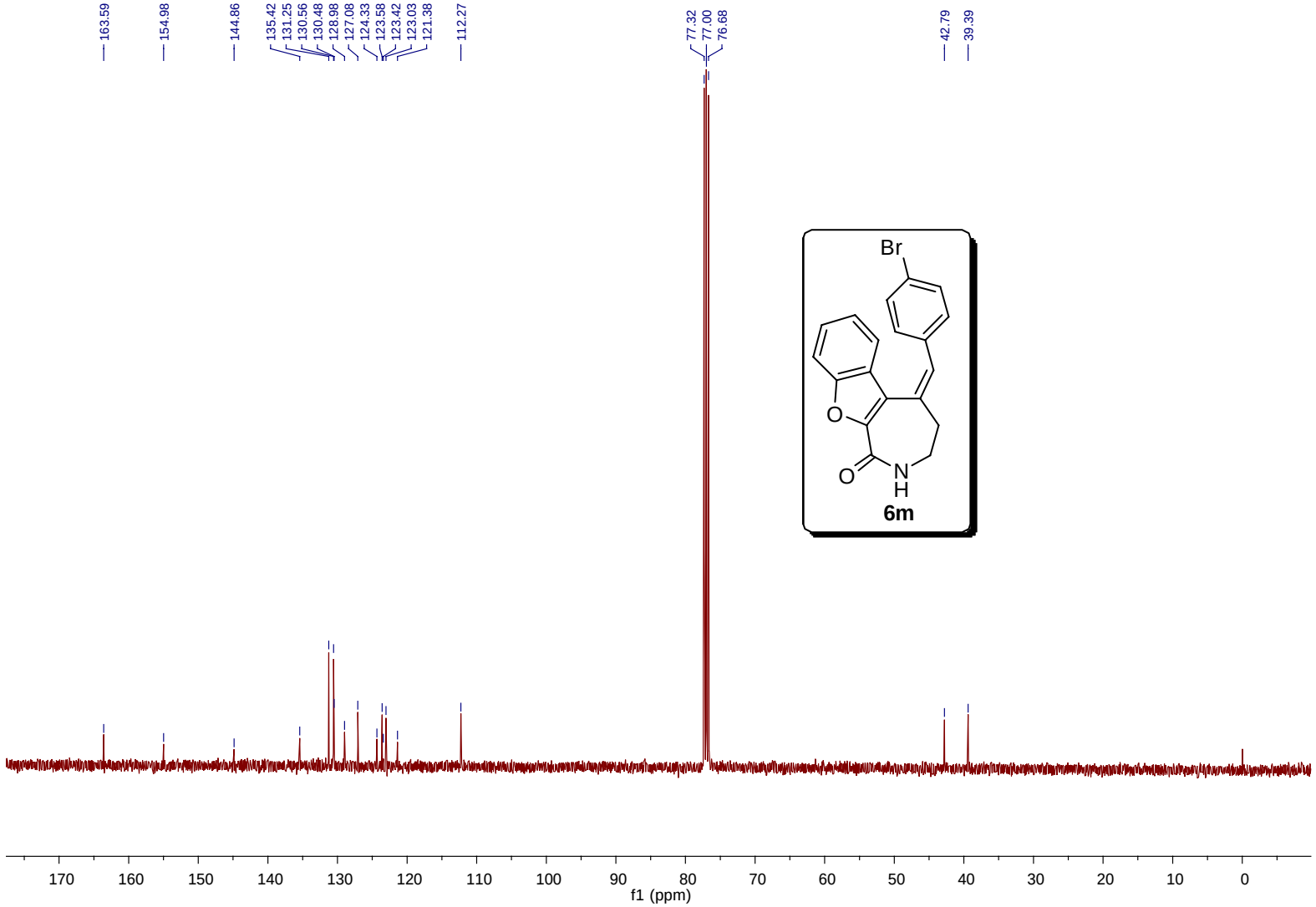

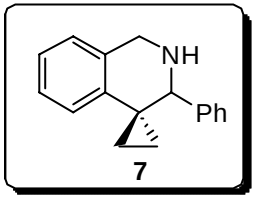

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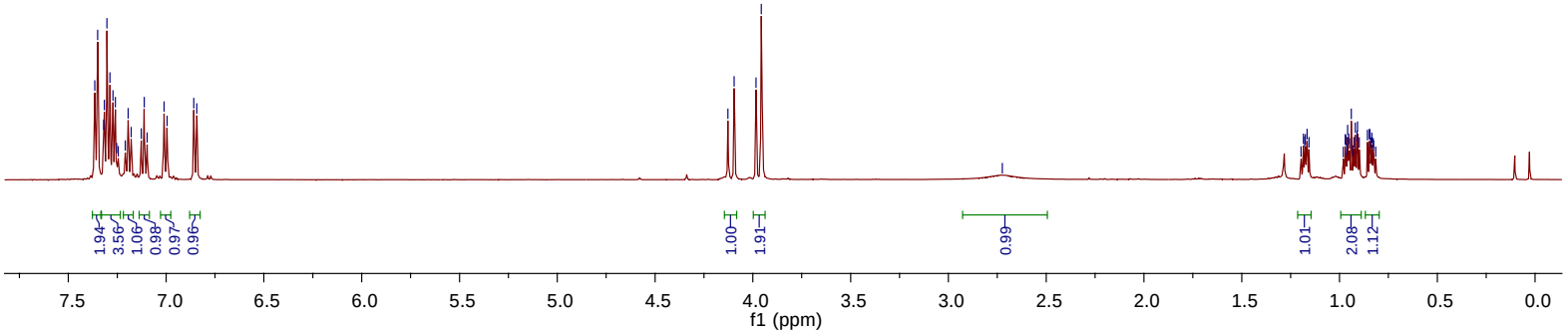
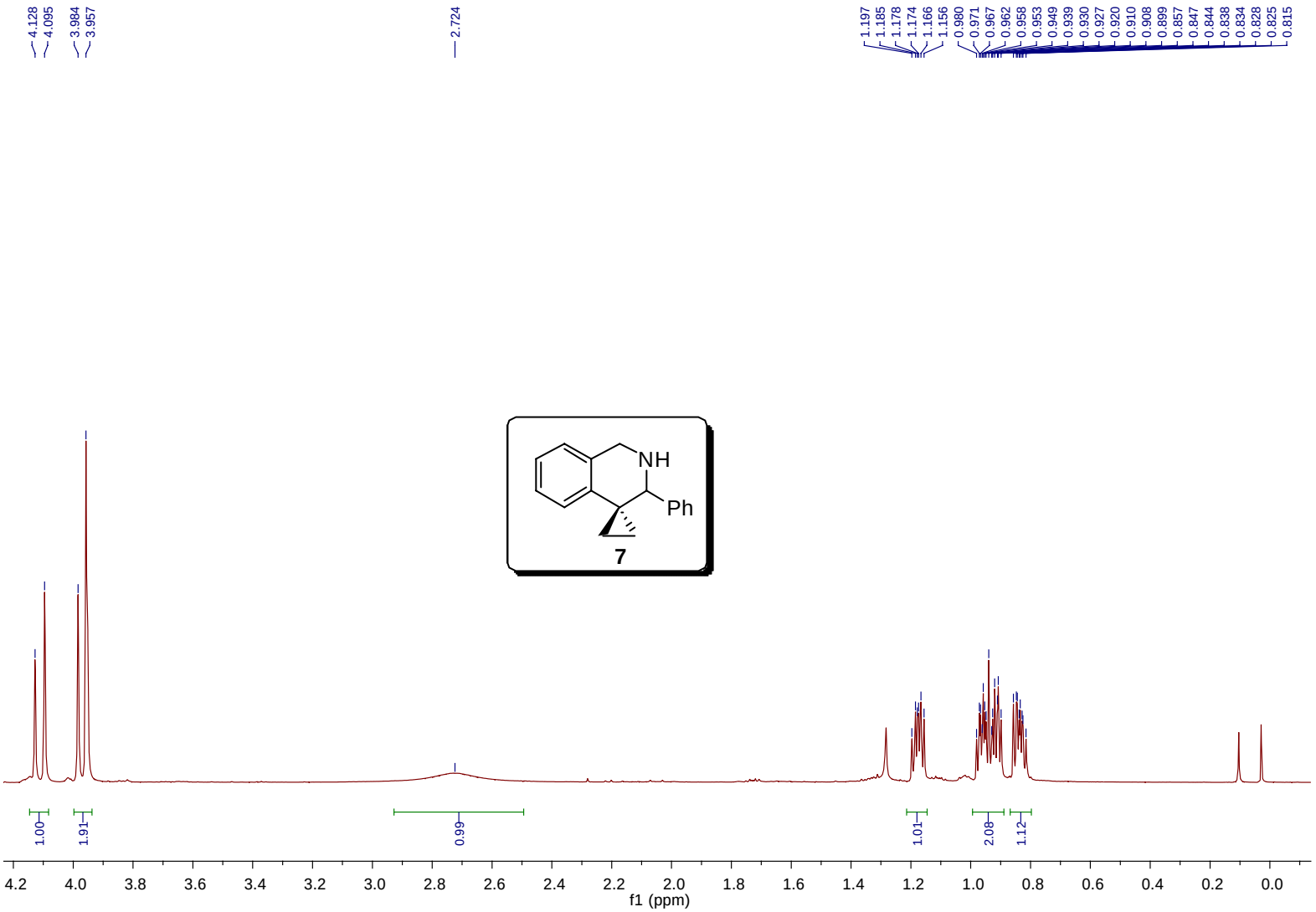
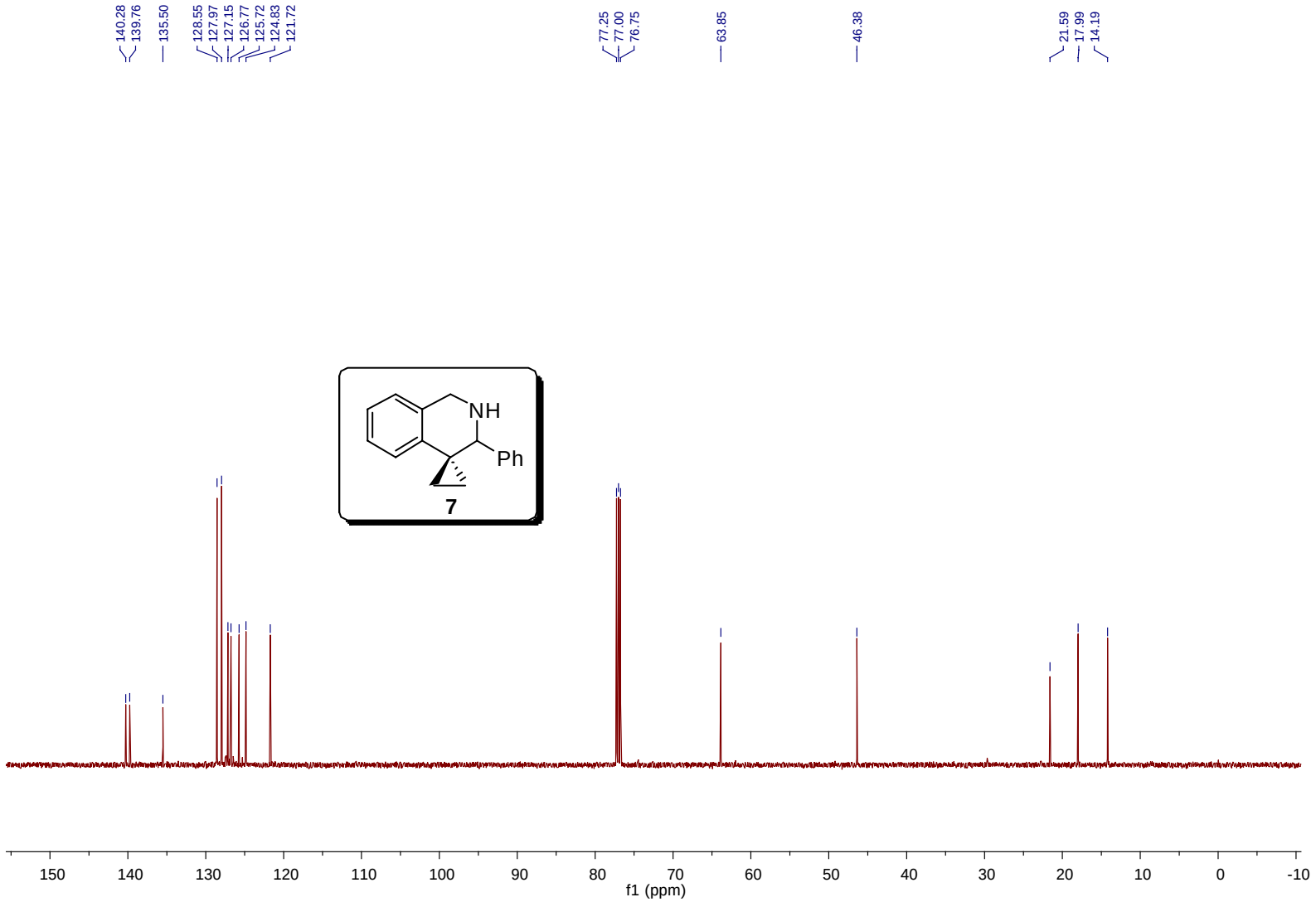
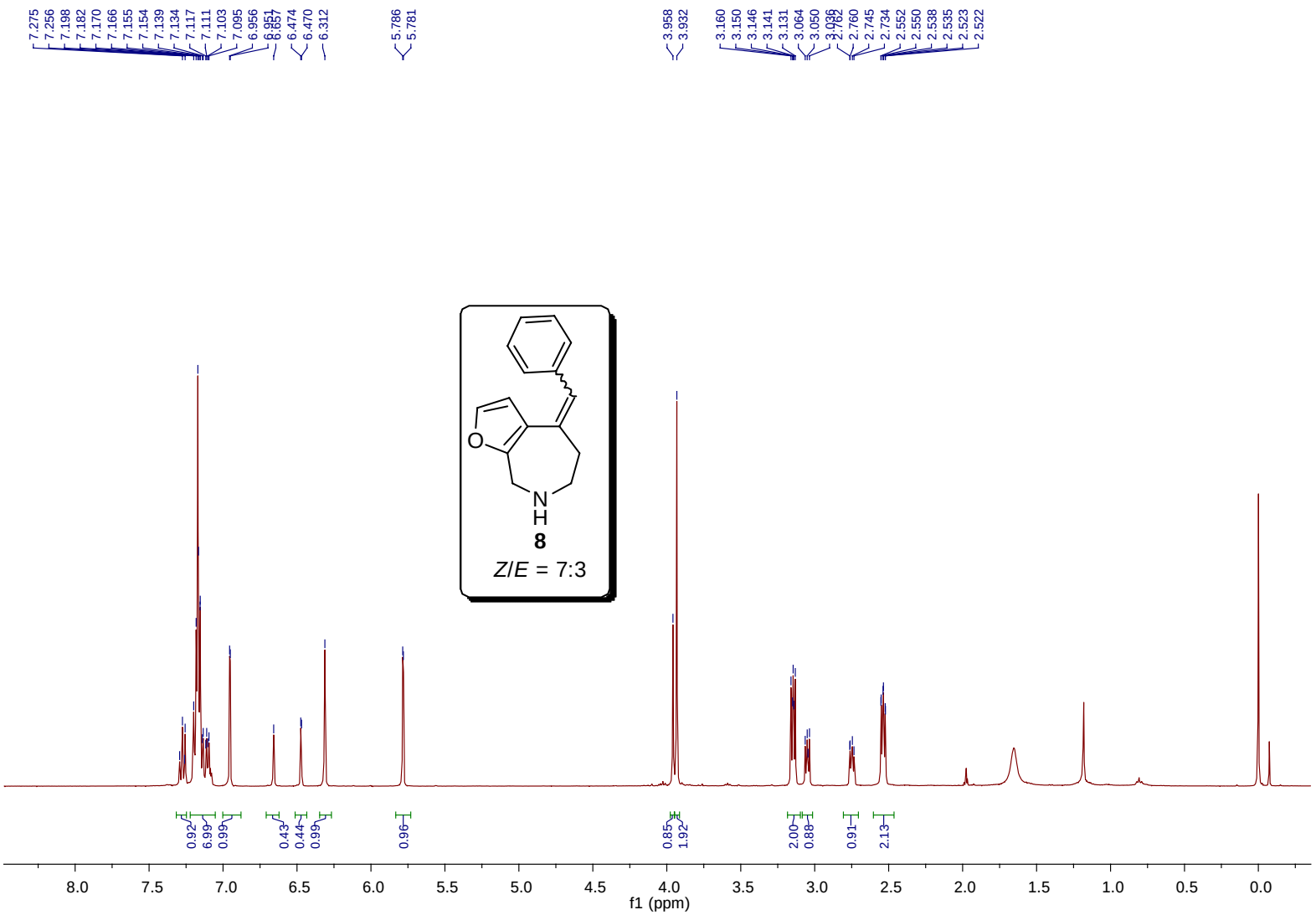
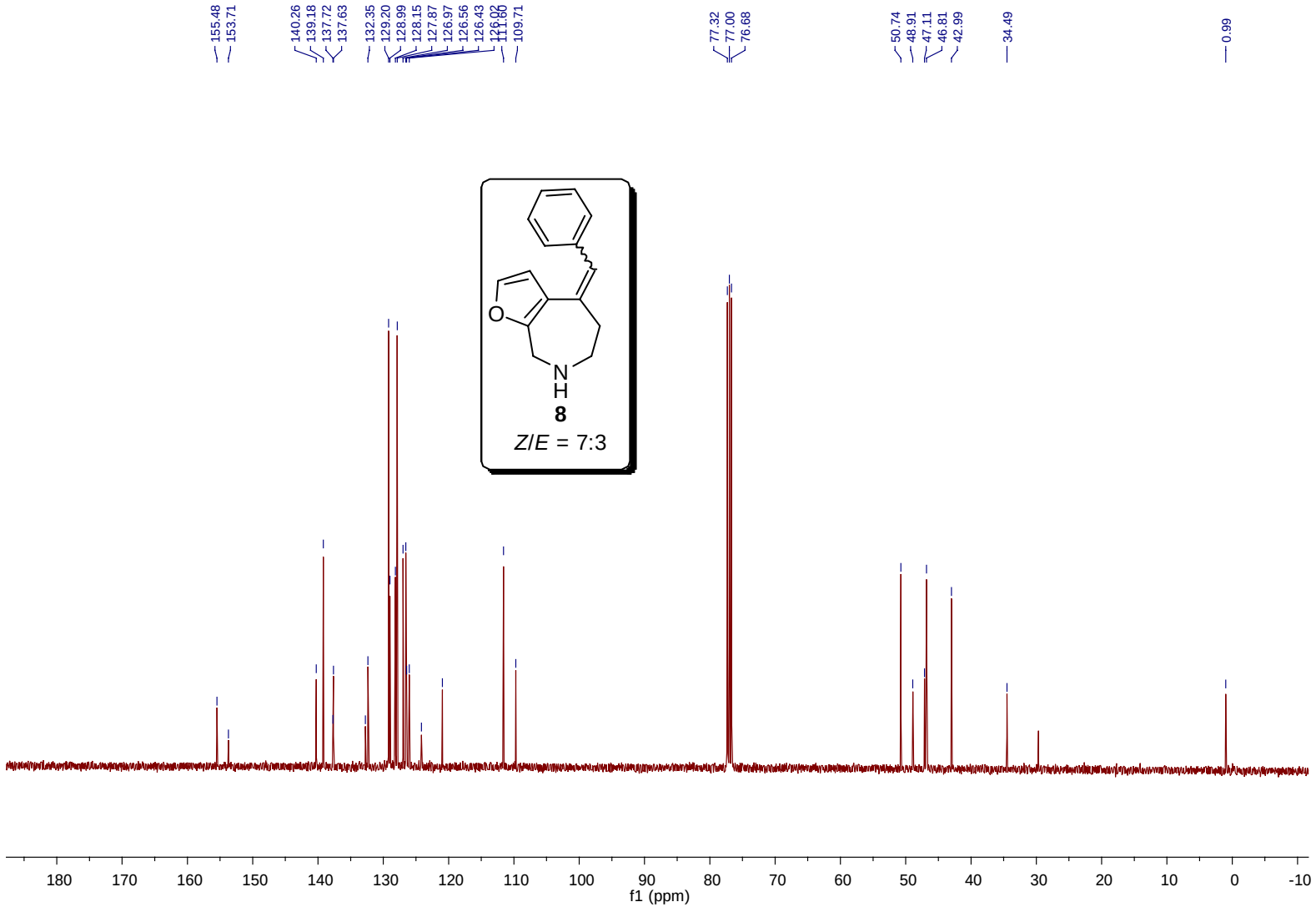
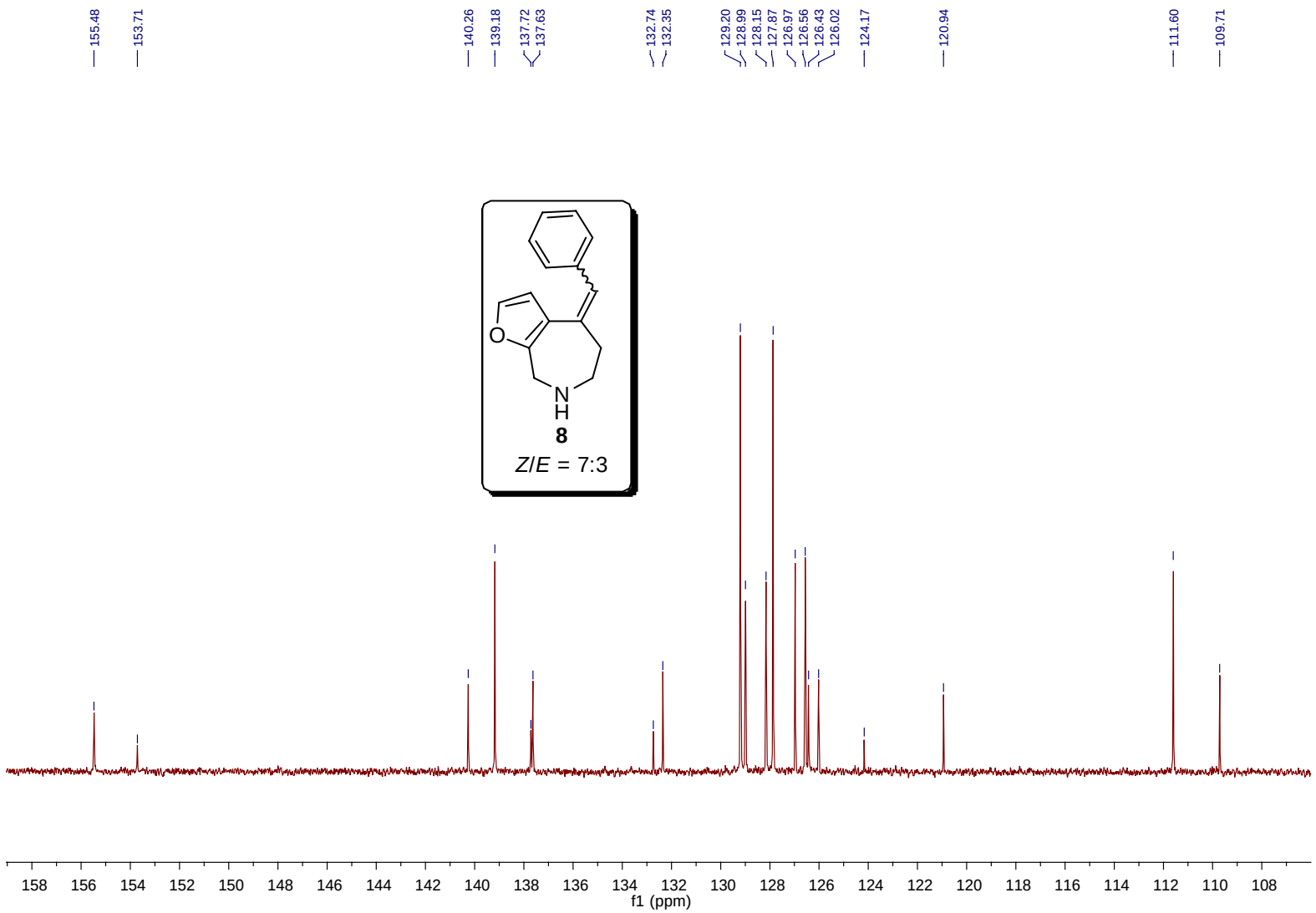


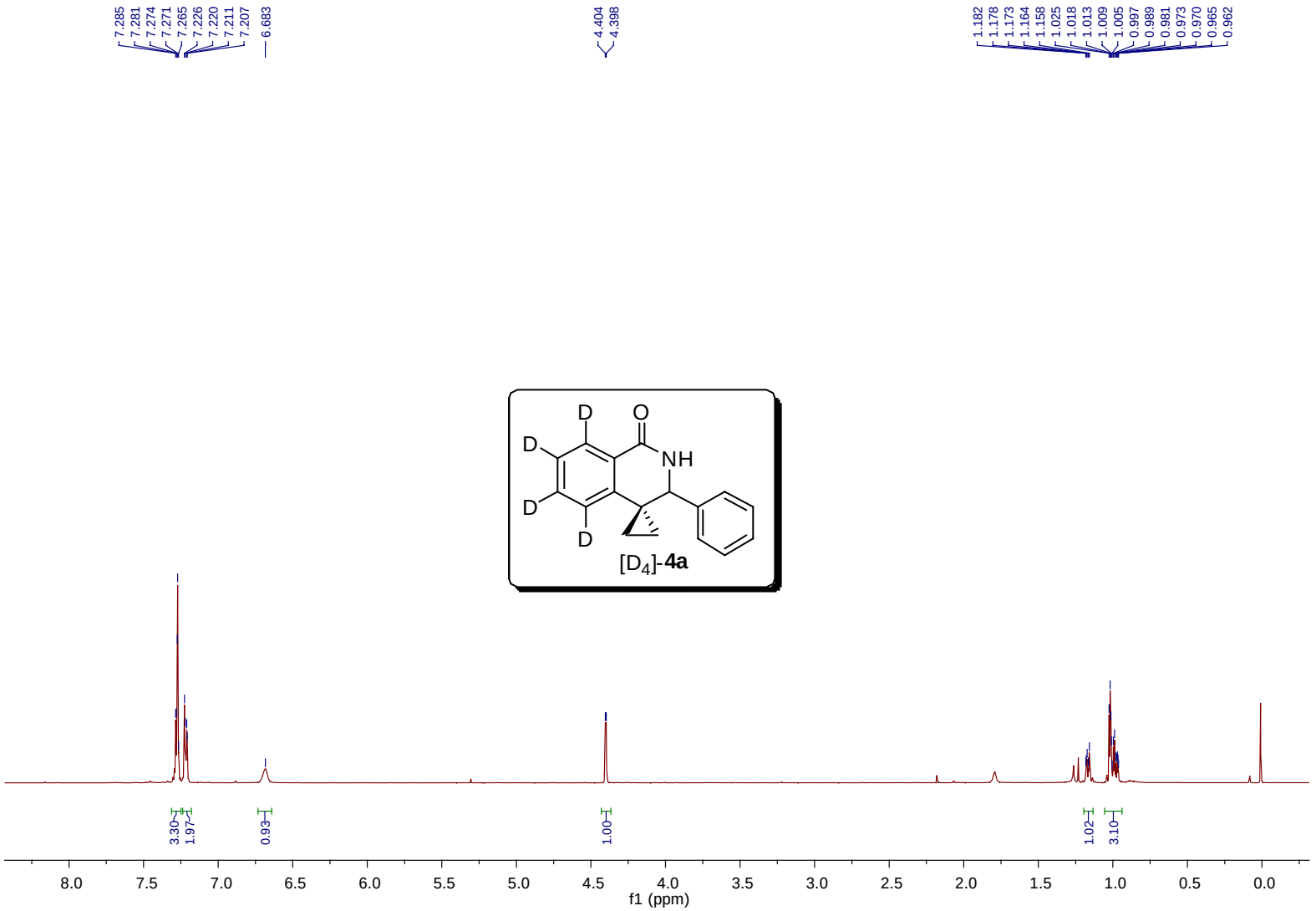


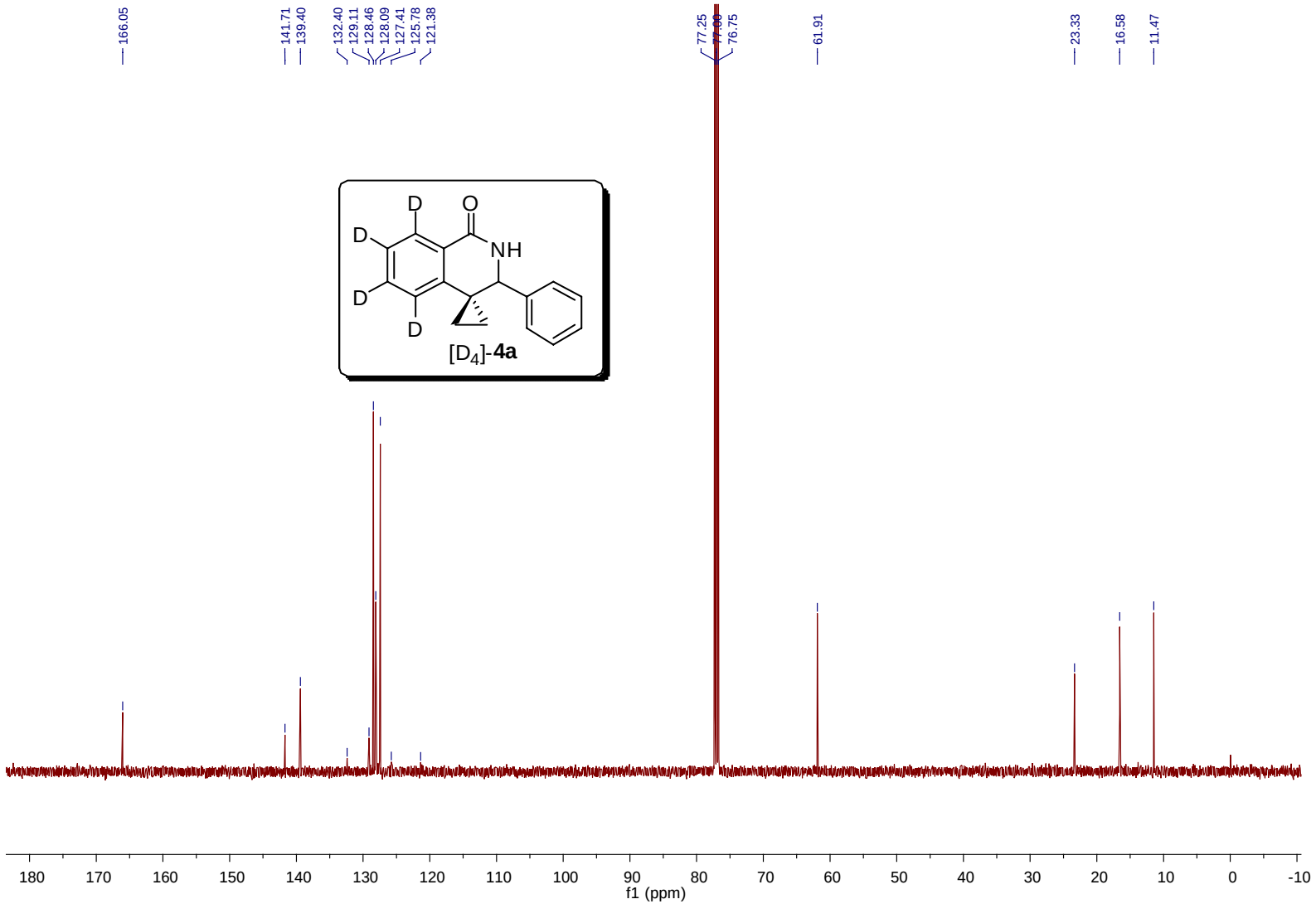


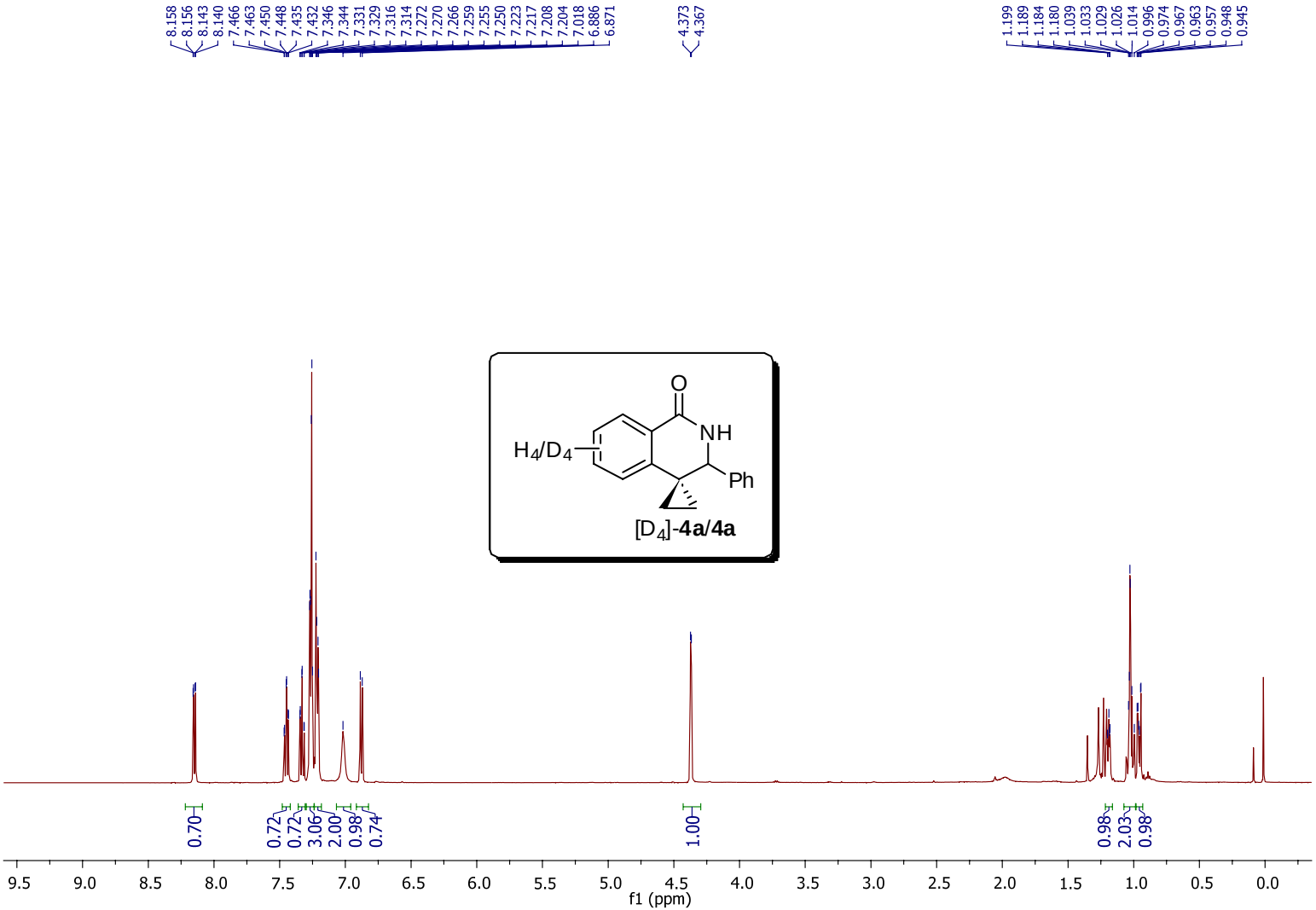


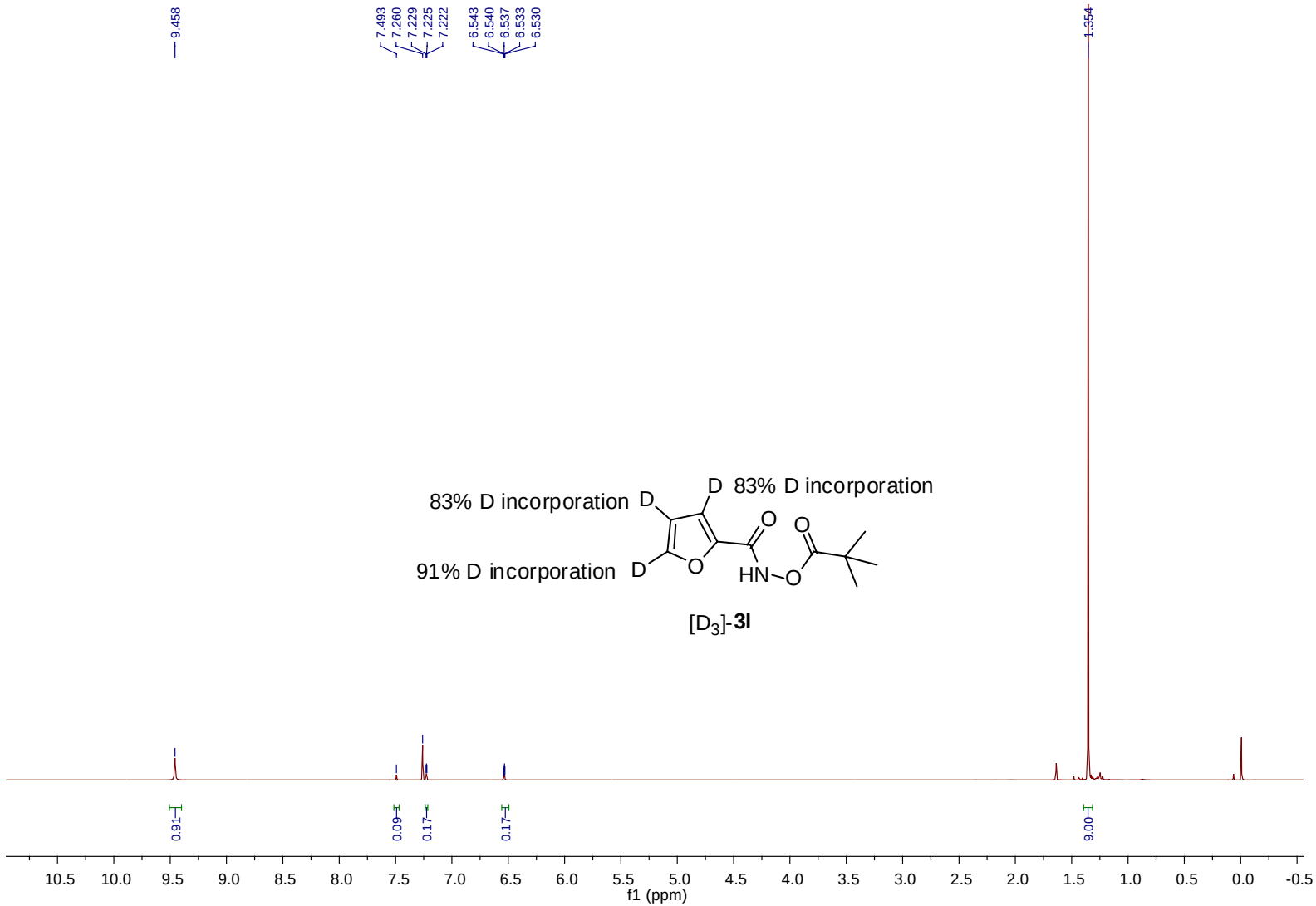




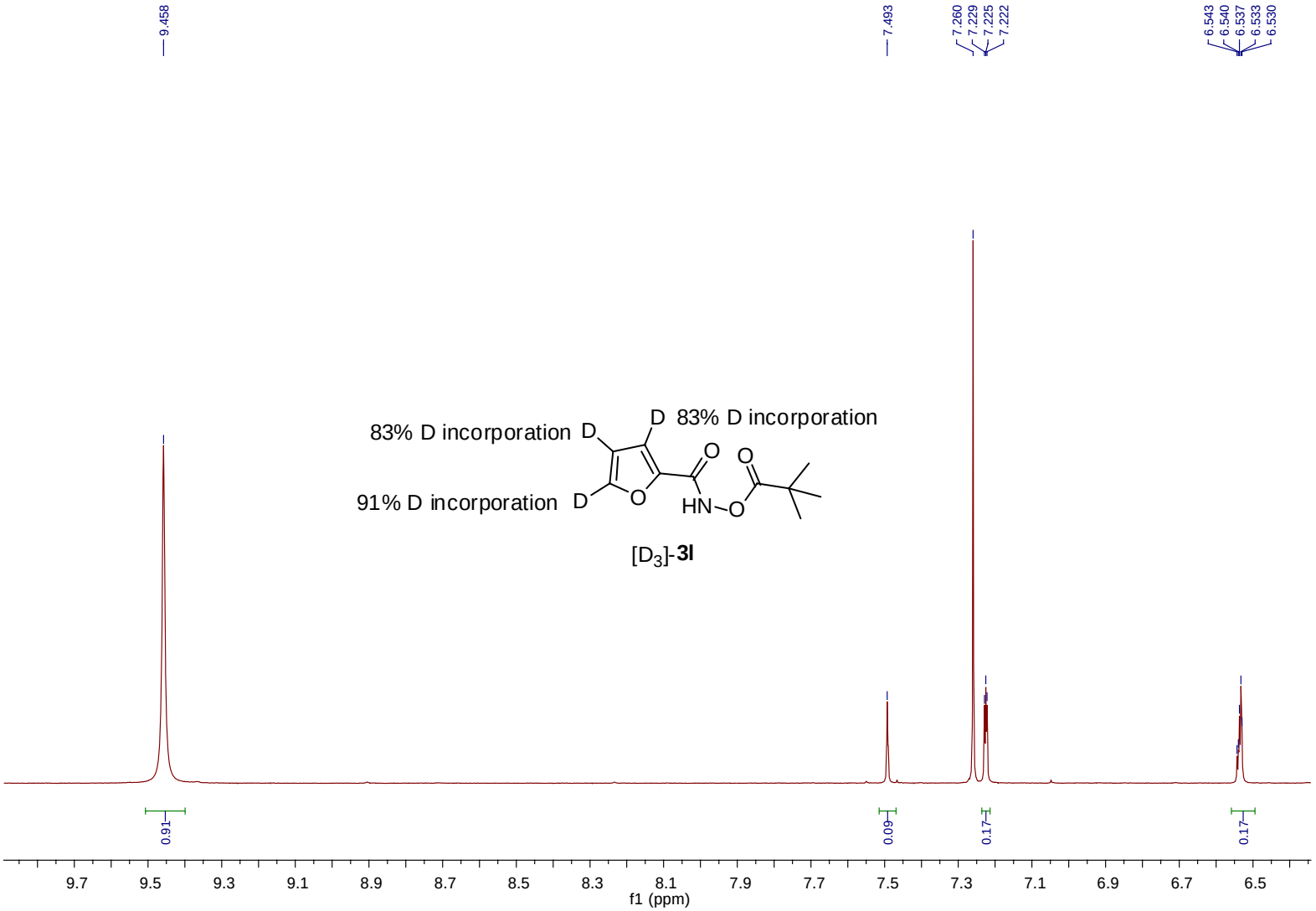








[D_3]-**3l**



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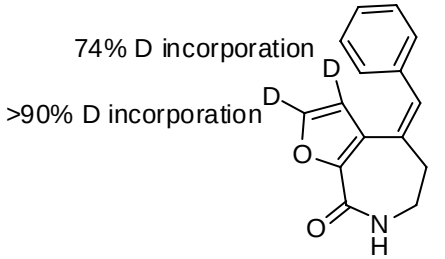

[D_2]-**6b**