Supporting Information

for

Rh(III)-Catalyzed C−H Activation/[4+3] Cycloaddition of Benzamides and Vinylcarbenoids: Facile Synthesis of Azepinones

Sunliang Cui,* Yan Zhang, Dahai Wang and Qifan Wu

Institute of Materia Medica and College of Pharmaceutical Sciences,

Zhejiang University, Hangzhou 310058, P.R.China

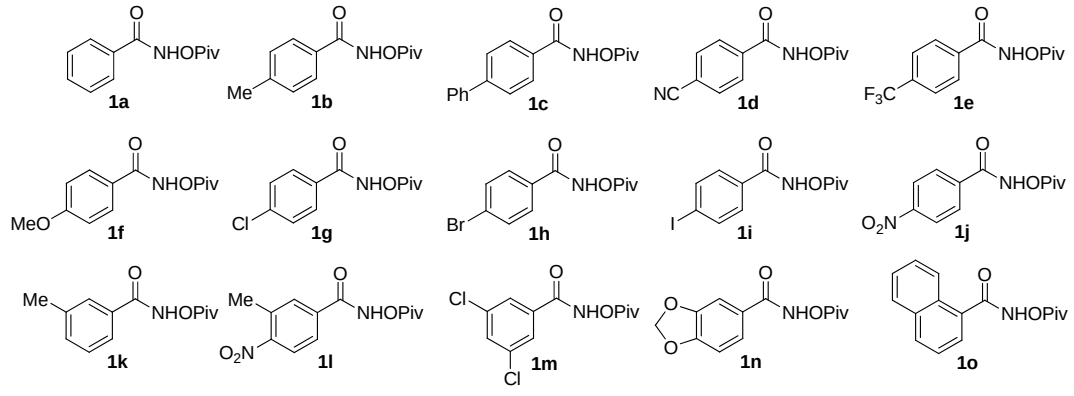
E-mail: slcui@zju.edu.cn

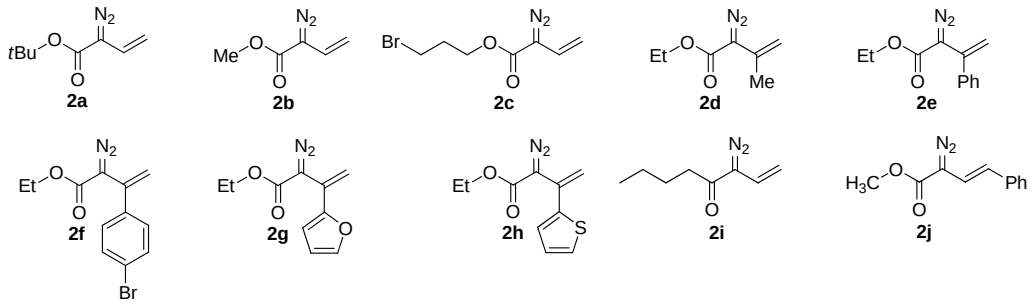
Contents

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}H NMR: 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 *N*-pivaloyloxybenzamides **1,** vinyldiazoacetates and ketone **2**, were prepared according to the literature. [1, 2] $[Cp^*RhCl_2]_2$, CsOAc, anhydrous CH_3CN and d_5-benzoic acid were commercial available.

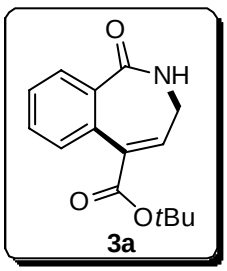




General Procedure:

Typical procedure for synthesis of azepinone: $[Cp^*RhCl_2]_2$ (2.5 mg, 2 mol%), benzamide **1a** (44.2 mg, 0.2 mmol), CsOAc (38.4 mg, 0.2 mmol) were added to a vial. CH_3CN (1.0 mL) was added, followed by micro-syringe addition of *tert*-butyl vinyldiazoacetate **2a** (50.4 mg, 0.3 mmol). The micro-syringe was washed with an additional 0.5 mL CH_3CN and added to the reaction solution. The mixture was kept at room temperature under air. After completion within 6 hours, 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 product **3a** as a white solid (49 mg, 95% yield). White solid; mp. 204-205 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.38 (b, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.50 (m, 2H), 7.45 (m, 1H), 7.28 (m, 1H), 3.51 (t, J = 7.0 Hz, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.7, 165.2, 138.9, 137.6, 134.7, 132.3, 129.8, 129.6, 129.5, 128.3, 81.7, 37.4, 28.0 ppm; IR (KBr) ν 3180, 1703, 1650, 1286, 1177, 1160, 785 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{17}NO_3$ [M^+] 259.1208; found 259.1208.

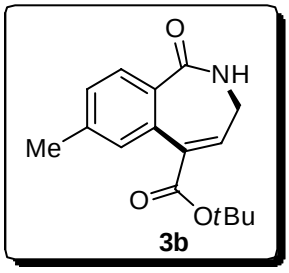
Characterization of Products 3-4:



3a

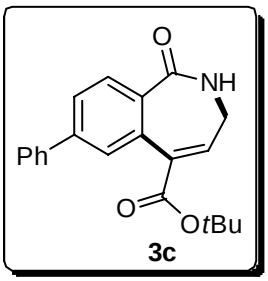
***tert*-Butyl 1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3a).** White solid; mp. 204-205 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.38 (b, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.50 (m, 2H), 7.45 (m, 1H), 7.28 (m, 1H), 3.51 (t, J = 7.0 Hz, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.7, 165.2, 138.9, 137.6, 134.7, 132.3, 129.8, 129.6,

129.5, 128.3, 81.7, 37.4, 28.0 ppm; IR (KBr) *v* 3180, 1703, 1650, 1286, 1177, 1160, 785 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{17}NO_3$ [M^+] 259.1208; found 259.1208.



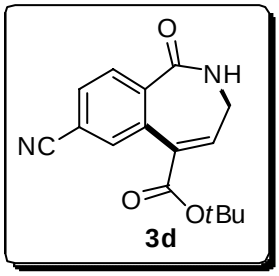
3b

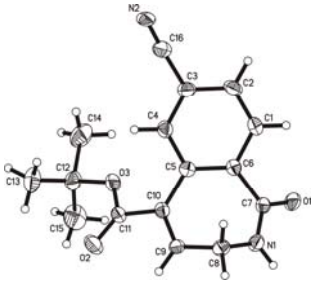
***tert*-Butyl 7-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3b).** Pale yellow solid; mp. 163-165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.33 (b, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.32 (s, 1H), 7.26 (m, 2H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.52 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.3, 140.1, 138.6, 137.6, 132.2, 132.1, 129.9, 129.7, 129.2, 81.6, 37.5, 28.0, 21.4 ppm; IR (KBr) *v* 3176, 3047, 1710, 1652, 1283, 1158 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{19}NO_3$ [M^+] 273.1365; found 273.1358.



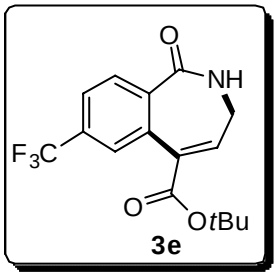
3c

***tert*-Butyl 1-oxo-7-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3c).** White solid; mp. 222-224 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.98 (b, 1H), 7.76 (d, *J* = 1.6 Hz, 1H), 7.68 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.63 (m, 2H), 7.47 (m, 2H), 7.36 (m, 2H), 3.58 (t, *J* = 6.4 Hz, 2H), 1.53 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.5, 165.2, 142.7, 139.9, 139.0, 137.8, 133.4, 132.7, 130.3, 128.9, 128.3, 128.0, 127.2, 127.1, 81.8, 37.6, 28.1 ppm; IR (KBr) *v* 3187, 1702, 1651, 1411, 1280, 1160 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{21}H_{21}NO_3$ [M^+] 335.1521; found 335.1523.

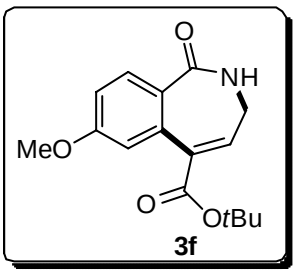




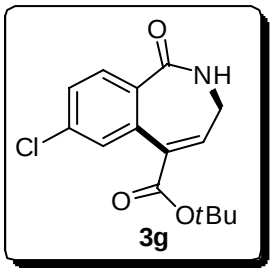
***tert*-Butyl 7-cyano-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3d).** Yellow solid; mp. 204-205 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 1.6 Hz, 1H), 7.71 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.43 (m, 1H), 7.20 (b, 1H), 3.56 (t, J = 7.2 Hz, 2H), 1.54 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 163.9, 140.6, 138.4, 136.2, 133.8, 133.0, 131.2, 130.8, 117.9, 114.0, 82.8, 37.5, 28.0 ppm; IR (KBr) v 2964, 2227, 1703, 1653, 1474, 1288, 1261, 1092, 801 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{16}N_2O_3$ [M^+] 284.1161; found 284.1161.



***tert*-Butyl 1-oxo-7-(trifluoromethyl)-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3e).** White solid; mp. 210-211 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (d, J = 8.0 Hz, 1H), 7.84 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.48 (b, 1H), 7.42 (m, 1H), 3.56 (t, J = 6.4 Hz, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 164.3, 140.4, 137.7, 136.9, 132.9, 131.8 (q, J = 32 Hz), 130.5, 127.0 (q, J = 4 Hz), 124.8 (q, J = 3 Hz), 123.6 (d, J = 272 Hz), 82.5, 37.5, 28.0 ppm; IR (KBr) v 3345, 2960, 1690, 1655, 1316, 1158, 1080 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{16}F_3NO_3$ [M^+] 327.1082; found 327.1092.

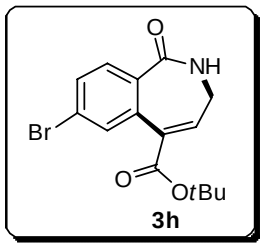


***tert*-Butyl 7-methoxy-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3f).** Pale yellow solid; mp. 192-194 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 (b, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.27 (m, 1H), 7.01 (m, 2H), 3.86 (s, 3H), 3.52 (t, J = 6.4 Hz, 2H), 1.52 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.5, 165.2, 160.4, 138.8, 137.5, 134.0, 131.6, 127.4, 114.6, 114.2, 81.7, 55.3, 37.4, 28.0 ppm; IR (KBr) *v* 3167, 1710, 1649, 1280, 1246, 1170 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{19}NO_4$ [M^+] 289.1314; found 289.1317.



3g

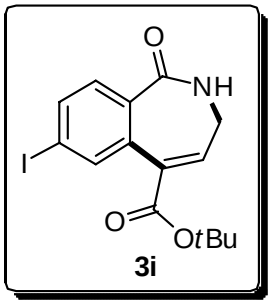
***tert*-Butyl 7-chloro-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3g).** Pale yellow solid; mp. 176-178 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (b, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 2.4 Hz, 1H), 7.42 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.34 (m, 1H), 3.53 (d, J = 7.0 Hz, 2H), 1.52 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 164.5, 139.9, 136.7, 136.2, 133.7, 133.1, 131.2, 129.6, 128.6, 82.2, 37.4, 28.0 ppm; IR (KBr) *v* 3180, 2986, 1705, 1653, 1292, 1165, 846 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{16}ClNO_3$ [M^+] 293.0819; found 293.0808.



3h

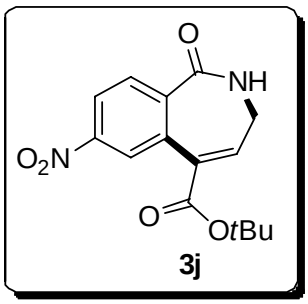
***tert*-Butyl 7-bromo-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3h).** Pale yellow solid; mp. 183-185 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (b, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.58 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 7.35 (m, 1H), 3.54 (t, J = 6.8 Hz, 2H), 1.53 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 164.4, 140.0, 136.6, 133.9, 133.5, 132.6, 131.5, 131.3, 124.6, 82.2, 37.4, 28.0

ppm; IR (KBr) *v* 3183, 2983, 1708, 1654, 1290, 1163 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{16}BrNO_3$ [M^+] 337.0314; found 337.0314.



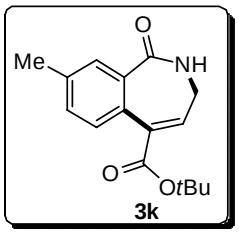
3i

***tert*-Butyl 7-iodo-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3i).** White solid; mp. 202-204 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (m, 2H), 7.79 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.34 (m, 1H), 3.53 (t, J = 6.4 Hz, 2H), 1.53 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.9, 164.4, 140.0, 138.6, 137.3, 136.5, 134.1, 133.8, 131.1, 96.7, 82.2, 37.4, 28.0 ppm; IR (KBr) *v* 3180, 2924, 1699, 1652, 1578, 1280, 1158 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{16}INO_3$ [M^+] 385.0175; found 385.0174.



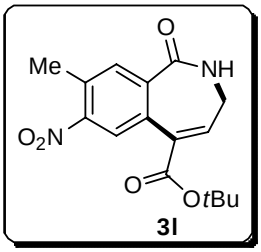
3j

***tert*-Butyl 7-nitro-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3j).** White solid; mp. 202-203 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, J = 2.4 Hz, 1H), 8.26 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.54 (b, 1H), 7.48 (m, 1H), 3.59 (t, J = 6.8 Hz, 2H), 1.54 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 163.8, 148.3, 140.9, 139.8, 136.4, 133.6, 131.4, 125.1, 122.7, 82.9, 37.5, 28.0 ppm; IR (KBr) *v* 3201, 2925, 1710, 1665, 1524, 1346, 1279, 1155 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{16}N_2O_3$ [M^+] 304.1059; found 304.1056.



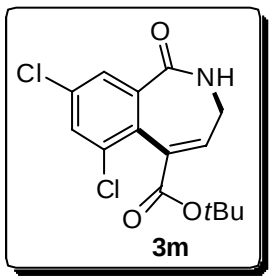
3k

***tert*-Butyl 8-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3k).** Yellow solid; mp. 198-200 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (m, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.31 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.22 (m, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.42 (s, 3H), 1.50 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.4, 165.4, 138.5, 138.0, 137.7, 134.5, 131.0, 130.0, 129.6, 129.5, 81.7, 37.6, 28.0, 21.1 ppm; IR (KBr) v 2964, 2925, 1706, 1649, 1262, 1095, 802 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{19}NO_3$ [M^+] 273.1365; found 273.1366.



3l

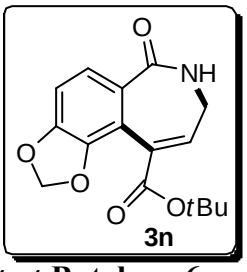
***tert*-Butyl 8-methyl-7-nitro-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3l).** Pale yellow solid; mp. 214-215 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (s, 1H), 7.93 (s, 1H), 7.41 (m, 1H), 7.23 (b, 1H), 3.58 (t, J = 6.4 Hz, 2H), 2.66 (s, 3H), 1.53 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 164.0, 149.6, 140.2, 138.2, 136.3, 134.2, 133.2, 131.2, 126.2, 82.8, 37.5, 28.0, 20.0 ppm; IR (KBr) v 2960, 1710, 1661, 1520, 1342, 1157 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{18}N_2O_5$ [M^+] 318.1216; found 318.1211.



3m

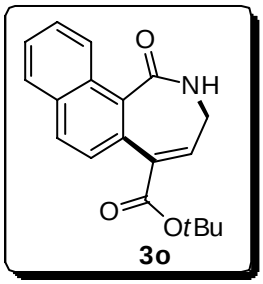
***tert*-Butyl 6,8-dichloro-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (3m).** White solid; mp. 151-153 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, J = 2.0 Hz

, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.32 (b, 1H), 7.27 (m, 1H), 3.55 (m, 2H), 1.47 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 164.2, 139.5, 137.7, 136.9, 135.1, 134.8, 131.8, 130.3, 128.3, 82.3, 37.6, 27.8 ppm; IR (KBr) *v* 3425, 2978, 1719, 1656, 1285, 1159 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{15}Cl_2N_2O_3$ [M^+] 327.0429; found 327.0429.



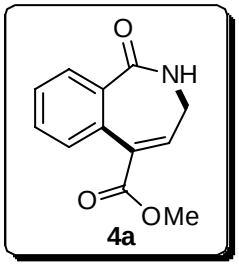
3n

***tert*-Butyl 6-oxo-7,8-dihydro-6*H*-[1,3]dioxolo[4',5':3,4]benzo[1,2-*c*]azepine-10-carboxylate (3n).** White solid; mp. 203-205 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (b, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.17 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 1.47 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 164.7, 149.1, 144.6, 138.9, 134.8, 128.2, 124.9, 115.8, 108.9, 101.6, 81.6, 37.6, 27.9 ppm; IR (KBr) *v* 2975, 2925, 1715, 1654, 1445, 1282, 1251, 1160 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{17}NO_5$ [M^+] 303.1107; found 303.1108.



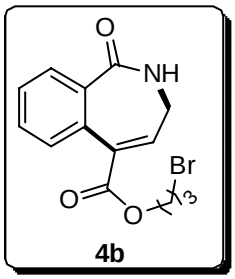
3o

***tert*-Butyl 1-oxo-2,3-dihydro-1*H*-naphtho[1,2-*c*]azepine-5-carboxylate (3o).** Yellow solid; mp. 189-191 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (d, *J* = 8.0 Hz, 1H), 7.88 (m, 2H), 7.57 (m, 3H), 7.42 (m, 1H), 7.34 (b, 1H), 3.54 (m, 2H), 1.53 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 165.1, 140.1, 138.5, 133.1, 131.7, 130.8, 130.6, 129.3, 127.9, 127.3, 127.1, 127.0, 125.8, 82.0, 37.9, 28.1 ppm; IR (KBr) *v* 2974, 2926, 1710, 1654, 1276, 1162, 1086 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{19}NO_3$ [M^+] 309.1365; found 309.1366.



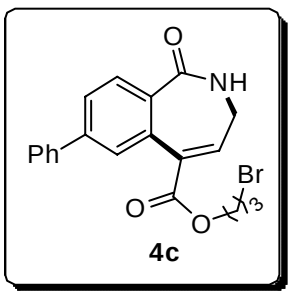
4a

Methyl 1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4a). White solid; mp. 172-174 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (m, 1H), 7.75 (b, 1H), 7.49 (m, 3H), 7.39 (m, 1H), 3.82 (s, 3H), 3.54 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.2, 166.5, 139.9, 136.3, 134.7, 131.8, 130.2, 129.8, 129.4, 128.6, 52.4, 37.5 ppm; IR (KBr) *v* 3186, 3071, 1715, 1659, 1264, 1245, 788 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO_3$ [M^+] 217.0739; found 217.0741.



4b

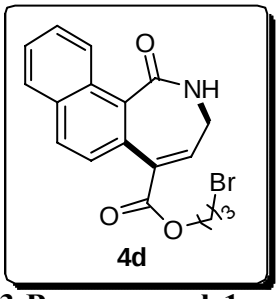
3-Bromopropyl 1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4b). White solid; mp. 95-97 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (b, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.50 (m, 3H), 7.38 (m, 1H), 4.37 (t, *J* = 8.4 Hz, 2H), 3.55 (t, *J* = 6.4 Hz, 2H), 3.43 (t, *J* = 6.4 Hz, 2H), 3.21 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.4, 165.8, 140.2, 136.2, 134.7, 131.7, 130.1, 129.8, 129.3, 128.7, 63.0, 37.5, 31.3, 29.3 ppm; IR (KBr) *v* 3177, 1716, 1649, 1241, 783 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{14}H_{14}BrNO_3$ [M^+] 323.0157; found 323.0150.



4c

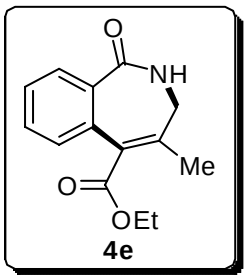
3-Bromopropyl 1-oxo-7-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate

(4c). White solid; mp. 173-174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.80 (b, 1H), 7.73 (m, 2H), 7.63 (m, 2H), 7.43 (m, 4H), 4.40 (t, *J* = 6.0 Hz, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 3.22 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.2, 165.8, 143.0, 140.3, 139.6, 136.2, 133.4, 132.1, 130.5, 128.9, 128.1, 128.0, 127.3, 63.1, 37.6, 31.5, 29.3 ppm; IR (KBr) *v* 2962, 1717, 1648, 1418, 1263, 1094, 1025 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{20}H_{18}BrNO_3$ [M^+] 399.0470; found 399.0464.



4d

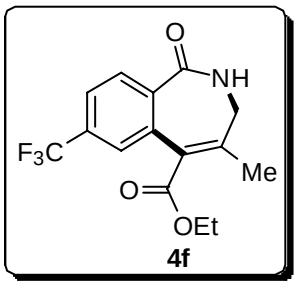
3-Bromopropyl 1-oxo-2,3-dihydro-1*H*-naphtho[1,2-*c*]azepine-5-carboxylate (4d). Yellow solid; mp. 68-70 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.50 (d, *J* = 8.0 Hz, 1H), 7.89 (m, 3H), 7.59 (m, 2H), 7.51 (m, 2H), 4.40 (m, 2H), 3.63 (m, 1H), 3.47 (m, 3H), 2.22 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 165.8, 141.7, 136.6, 133.1, 131.8, 130.5, 130.1, 129.5, 128.0, 127.5, 127.11, 127.08, 125.5, 63.0, 37.8, 31.3, 29.4 ppm; IR (KBr) *v* 2963, 1718, 1652, 1262, 1237, 1088 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{16}BrNO_3$ [M^+] 373.0314; found 373.0318.



4e

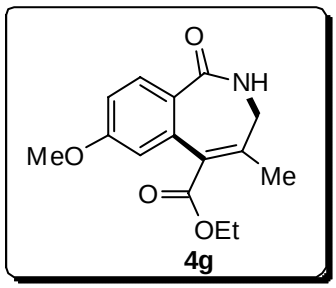
Ethyl 4-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4e). White solid; mp. 159-161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (m, 2H), 7.44 (m, 2H), 7.28 (m, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.49 (d, *J* = 6.0 Hz, 2H), 2.21 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 168.2, 144.7, 134.0, 133.8, 132.0, 130.4, 129.9, 127.9, 127.7, 61.1, 44.8, 21.1, 14.1 ppm; IR (KBr)

v 3177, 1713, 1655, 1475, 1097, 817 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{14}H_{15}NO_3$ [M^+] 245.1052; found 245.1049.



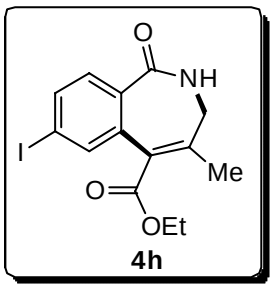
4f

Ethyl 4-methyl-1-oxo-7-(trifluoromethyl)-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4f). White solid; mp. 126-128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (b, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 (b, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.50 (d, *J* = 6.0 Hz, 2H), 2.27 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 167.2, 147.7, 136.8, 134.8, 132.2 (q, *J* = 32 Hz), 130.8, 130.6, 125.2 (q, *J* = 4 Hz), 124.4 (q, *J* = 4 Hz), 123.4 (d, *J* = 271 Hz), 61.4, 45.1, 21.3, 14.0 ppm; IR (KBr) *v* 3335, 1725, 1625, 1334, 1304, 1220, 1131, 1083 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{14}F_3NO_3$ [M^+] 313.0926; found 313.0930.



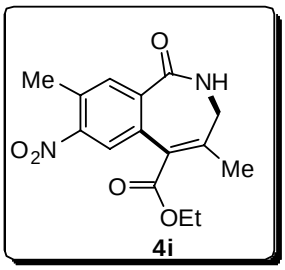
4g

Ethyl 7-methoxy-4-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4g). White solid; mp. 129-131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.64 (b, 1H), 6.95 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 3.48 (d, *J* = 6.4 Hz, 2H), 2.17 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.8, 168.2, 160.9, 144.1, 135.7, 132.04, 131.98, 126.5, 114.2, 112.2, 61.1, 55.4, 44.8, 21.1, 14.1 ppm; IR (KBr) *v* 3171, 2919, 1726, 1650, 1296, 1229 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{17}NO_4$ [M^+] 275.1158; found 275.1153.



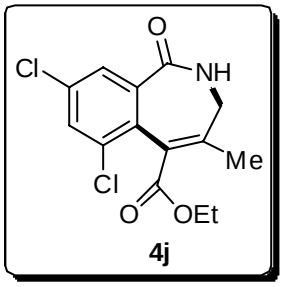
4h

Ethyl 7-iodo-4-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4h). White solid; mp. 178-180 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (b, 1H), 7.73 (dd, J_1 = 8.0 Hz, J_2= 1.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 4.27 (q, J = 7.2 Hz, 2H), 3.46 (d, J = 6.4 Hz, 2H), 2.20 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 167.5, 146.5, 136.9, 136.8, 135.6, 133.2, 131.3, 130.6, 97.2, 61.3, 44.8, 21.2, 14.1 ppm; IR (KBr) *v* 3283, 1717, 1620, 1222, 1045 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{14}H_{14}INO_3$ [M^+] 371.0018; found 371.0020.



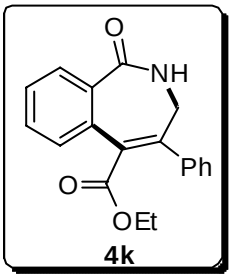
4i

Ethyl 4,8-dimethyl-7-nitro-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4i). Pale yellow solid; mp. 192-194 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 1H), 7.93 (s, 1H), 7.77 (b, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.52 (d, J = 6.4 Hz, 2H), 2.64 (s, 3H), 2.28 (s, 3H), 1.29 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 166.9, 149.8, 147.7, 137.3, 134.4, 133.1, 132.8, 130.3, 124.5, 61.6, 45.2, 21.4, 19.9, 14.1 ppm; IR (KBr) *v* 2925, 1724, 1667, 1519, 1343, 1215, 1066 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{16}N_2O_3$ [M^+] 304.1059; found 304.1059.



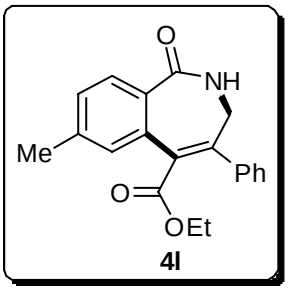
4j

Ethyl 6,8-dichloro-4-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4j). Pale yellow solid; mp. 198-200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (b, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 4.15 (m, 2H), 3.57 (m, 1H), 3.37 (m, 1H), 2.37 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 165.9, 151.8, 137.3, 134.8, 134.4, 132.4, 131.6, 127.9, 127.8, 61.2, 46.1, 20.5, 13.8 ppm; IR (KBr) *v* 3334, 1725, 1623, 1228, 1092, 812 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{14}H_{13}Cl_2NO_3$ [M^+] 313.0272; found 313.0276.



4k

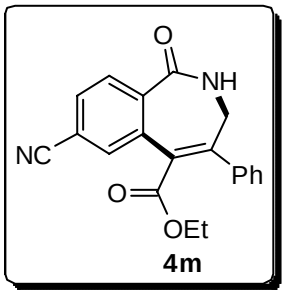
Ethyl 1-oxo-4-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4k). White solid; mp. 205-207 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.64 (b, 1H), 7.49 (m, 3H), 7.35 (m, 5H), 4.02 (q, *J* = 6.8 Hz, 2H), 3.87 (d, *J* = 6.4 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 168.5, 144.8, 139.4, 134.0, 133.9, 133.5, 130.8, 130.4, 128.6, 128.5, 128.4, 127.7, 127.3, 61.2, 45.0, 13.6 ppm; IR (KBr) *v* 2924, 1717, 1651, 1461, 1260, 1025 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{17}NO_3$ [M^+] 307.1208; found 307.1211.



4l

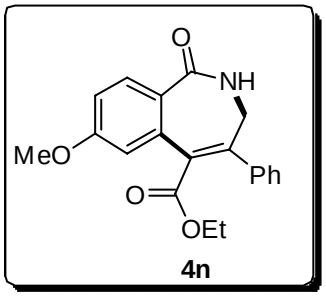
Ethyl 7-methyl-1-oxo-4-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4l). White solid; mp. 200-202 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.33 (m, 8H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.85 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 0.94 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 168.6, 144.4, 141.2, 139.5, 134.0, 133.4, 131.3, 130.5, 129.6, 129.5, 128.3, 128.0, 127.3, 61.2, 45.0,

21.5, 13.6 ppm; IR (KBr) *v* 3177, 2924, 1719, 1659, 1227, 1084, 1022 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{20}H_{19}NO_3$ [M^+] 321.1365; found 321.1367.



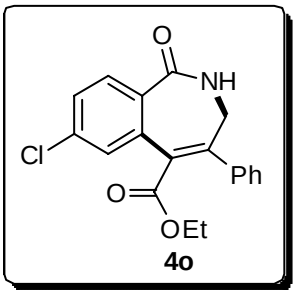
4m

Ethyl 7-cyano-1-oxo-4-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4m). White solid; mp. 188-190 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 9.4 Hz, 1H), 7.90 (d, *J* = 1.6 Hz, 1H), 7.79 (b, 1H), 7.71 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.40 (m, 3H), 7.33 (m, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.88 (d, *J* = 6.4 Hz, 2H), 0.92 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.9, 167.6, 147.4, 138.9, 137.6, 134.4, 131.8, 131.32, 131.25, 128.9, 128.7, 127.2, 117.7, 114.8, 61.7, 44.9, 13.5 ppm; IR (KBr) *v* 3315, 2958, 2925, 2230, 1716, 1661, 1623, 1461, 1264, 1088, 1029 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{20}H_{16}N_2O_3$ [M^+] 332.1161; found 332.1161.



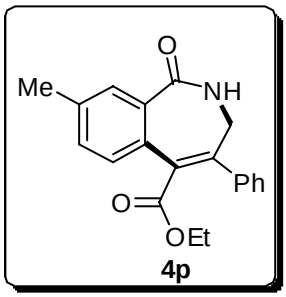
4n

Ethyl 7-methoxy-1-oxo-4-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4n). White solid; mp. 181-183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.38 (m, 6H), 7.01 (m, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.86 (m, 5H), 0.95 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.4, 168.4, 161.1, 144.7, 139.4, 135.1, 133.7, 132.5, 128.5, 128.4, 127.3, 126.7, 114.8, 112.3, 61.2, 55.4, 45.0, 13.6 ppm; IR (KBr) *v* 3173, 1720, 1656, 1604, 1294, 1239, 1041, 771 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{20}H_{19}NO_4$ [M^+] 337.1314; found 337.1310.



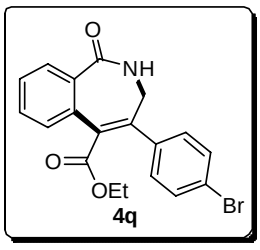
4o

Ethyl 7-chloro-1-oxo-4-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4o). Pale red solid; mp. 168-170 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.59 (b, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.43 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.35 (m, 5H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.86 (d, *J* = 6.4 Hz, 2H), 0.94 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 167.9, 146.1, 139.1, 137.1, 135.0, 132.7, 132.4, 132.0, 128.8, 128.6, 127.6, 1273, 61.5, 44.9, 13.5 ppm; IR (KBr) *v* 3178, 3062, 1722, 1662, 1588, 1452, 1201, 1024 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{16}ClNO_3$ [M^+] 341.0819; found 341.0820.



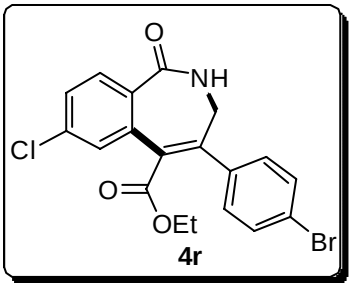
4p

Ethyl 8-methyl-1-oxo-4-phenyl-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4p). Pale yellow solid; mp. 177-179 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (s, 1H), 7.34 (m, 7H), 7.11 (b, 1H), 4.02 (q, *J* = 6.8 Hz, 2H), 3.86 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.4, 168.6, 143.8, 139.5, 138.9, 134.0, 133.7, 131.8, 130.8, 128.6, 128.3, 127.8, 127.3, 61.2, 45.0, 21.2, 13.6 ppm; IR (KBr) *v* 2958, 2924, 1717, 1664, 1088, 1035 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{20}H_{19}NO_3$ [M^+] 321.1365; found 321.1361.



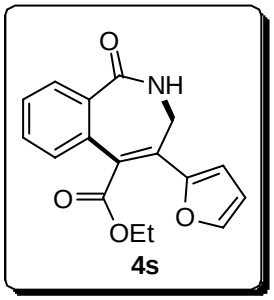
4q

Ethyl 4-(4-bromophenyl)-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4q). White solid; mp. 177-179 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (dd, J_1= 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.49 (m, 5H), 7.32 (b, 1H), 7.22 (d, J = 8.4 Hz, 2H), 4.05 (q, J = 7.2 Hz, 2H), 4.83 (d, J = 6.4 Hz, 2H), 1.01 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 168.1, 143.4, 138.2, 134.5, 133.9, 133.2, 131.8, 131.0, 130.5, 129.0, 128.9, 127.7, 122.7, 61.5, 44.8, 13.7 ppm; IR (KBr) *v* 2930, 1721, 1657, 1462, 1261, 1205, 800 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{16}BrNO_3$ [M^+] 385.0314; found 385.0318.



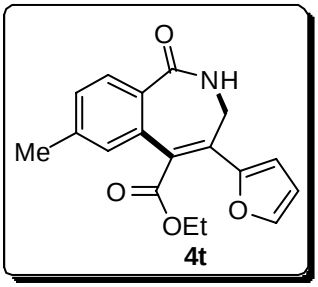
4r

Ethyl 4-(4-bromophenyl)-7-chloro-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4r). White solid; mp. 228-230 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.4 Hz, 1H), 7.52 (m, 3H), 7.45 (dd, J_1= 8.4 Hz, J_2= 1.6 Hz, 1H), 7.42 (b, 1H), 7.20 (d, J = 8.4 Hz, 2H), 4.06 (q, J = 7.2 Hz, 2H), 3.83 (d, J = 6.4 Hz, 2H), 1.01 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 167.6, 144.7, 137.9, 137.3, 134.7, 133.3, 132.3, 132.1, 131.9, 129.1, 128.9, 127.7, 122.9, 61.7, 44.8, 13.6 ppm; IR (KBr) *v* 2960, 2925, 1720, 1656, 1461, 1261, 1082, 1024 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{15}BrClNO_3$ [M^+] 418.9924; found 418.9917.



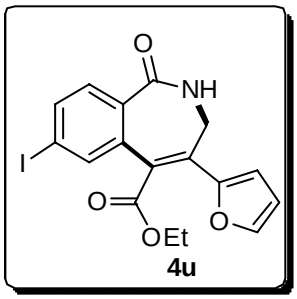
4s

Ethyl 4-(furan-2-yl)-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4s). Red solid; mp. 78-80 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, *J* = 7.2 Hz, 1H), 7.78 (b, 1H), 7.47 (m, 4H), 6.65 (d, *J* = 3.2 Hz, 1H), 6.46 (m, 1H), 4.32 (q, *J* = 6.8 Hz, 2H), 3.87 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 168.7, 150.2, 144.0, 133.8, 133.3, 131.0, 130.7, 129.9, 129.7, 128.6, 127.1, 112.0, 111.4, 61.7, 40.8, 14.0 ppm; IR (KBr) *v* 1722, 1655, 1259, 1234, 1203, 1025 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{15}NO_4$ [M^+] 297.1001; found 297.1002.



4t

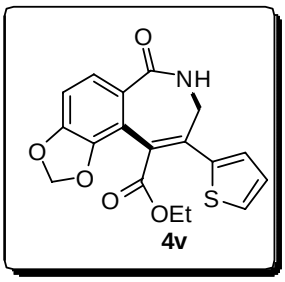
Ethyl 4-(furan-2-yl)-7-methyl-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4t). Red solid; mp. 83-85 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.67 (b, 1H), 7.45 (d, *J* = 1.2 Hz, 1H), 7.27 (m, 2H), 6.63 (d, *J* = 3.6 Hz, 1H), 6.45 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.86 (m, 2H), 2.39 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 168.8, 150.3, 143.9, 141.4, 133.2, 131.1, 130.8, 129.8, 129.63, 129.56, 127.4, 112.0, 111.3, 61.6, 40.9, 21.5, 14.0 ppm; IR (KBr) *v* 3396, 1721, 1654, 1235, 1026 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{17}NO_4$ [M^+] 311.1158; found 311.1153.



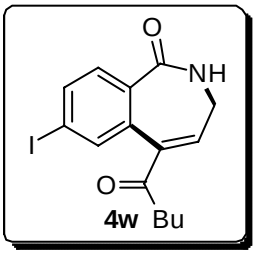
4u

Ethyl 4-(furan-2-yl)-7-iodo-1-oxo-2,3-dihydro-1*H*-benzo[*c*]azepine-5-carboxylate (4u). Red solid; mp. 88-90 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, *J* = 1.6 Hz, 1H), 7.78 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.63 (b, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 6.66 (d, *J* = 3.2 Hz, 1H), 6.48 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H),

3.87 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 168.2, 149.9, 144.3, 137.6, 135.9, 134.9, 133.1, 132.1, 130.9, 128.2, 112.2, 112.0, 98.0, 61.9, 40.8, 14.0 ppm; IR (KBr) ν 3404, 1721, 1655, 1578, 1251, 1022, 742 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}INO_4$ [M^+] 422.9968; found 422.9966.

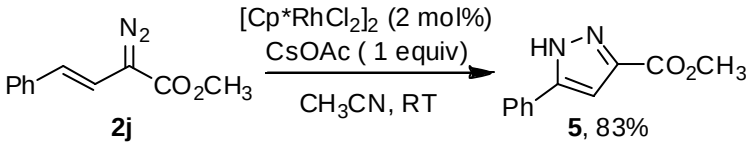


Ethyl 6-oxo-9-(thiophen-2-yl)-7,8-dihydro-6*H*-[1,3]dioxolo[4',5':3,4]benzo[1,2-*c*] azepine-10-carboxylate (4v). White solid; mp. 220-222 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (d, J = 8.4 Hz, 1H), 7.41 (dd, J_1 = 4.2 Hz, J_2 = 1.2 Hz, 1H), 7.15 (m, 1H), 7.04 (m, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.81 (b, 1H), 6.04 (s, 2H), 4.14 (q, J = 6.8 Hz, 2H), 3.95 (m, 2H), 1.12 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.4, 167.3, 149.3, 145.0, 139.9, 138.8, 128.5, 128.2, 127.8, 127.6, 127.4, 125.7, 116.9, 109.1, 102.0, 61.4, 46.7, 13.7 ppm; IR (KBr) ν 2923, 1720, 1652, 1442, 1247, 1035 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{15}NO_5S$ [M^+] 357.0671; found 357.0668.



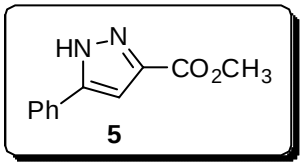
7-Iodo-5-pentanoyl-2,3-dihydro-1*H*-benzo[*c*]azepin-1-one (4w). White solid; mp. 167-169 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (dd, J_1= 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.68 (m, 2H), 7.26 (b, 1H), 7.13 (m, 1H), 3.57 (t, J = 6.8 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H), 1.63 (m, 2H), 1.36 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.7, 170.3, 143.7, 138.1, 137.8, 134.1, 133.5, 131.5, 97.1, 39.4, 37.6, 26.4, 22.3, 13.9 ppm; IR (KBr) ν 2956, 2926, 1654, 1578, 1147, 1079 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{16}INO_2$ [M^+] 369.0226; found 369.0222.

Synthesis of Pyrazole 5:



2j

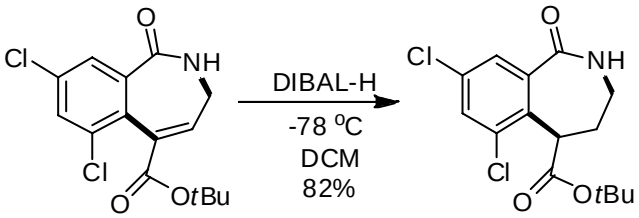
When styryldiazoacetate **2j** was subject to the standard reaction condition, pyrazole **5** was obtained exclusively in 83% yield.



5

methyl 5-phenyl-1H-pyrazole-3-carboxylate (5). Yellow solid; mp. 183-185 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 12.0 (b, 1H), 7.73 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.0 Hz, 2H), 7.35 (t, J = 7.0 Hz, 1H), 7.08 (s, 1H), 3.87 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.1, 149.4, 130.6, 128.9, 128.4, 125.7, 105.6, 52.2 ppm; HRMS (ESI) (*m/z*): calcd for $C_{11}H_{10}N_2O_2$ $[M+H]^+$ 203.0821; found 203.0813.

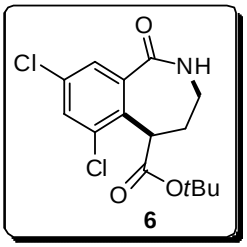
Derivation of Product 3m to 6 and 7:



3m **6**

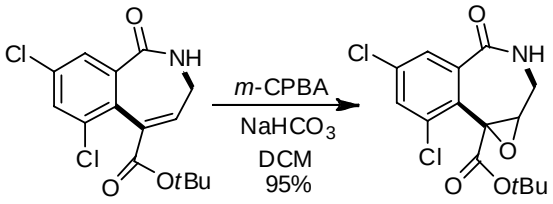
Azepinone **3m** (0.12 mmol, 40 mg) was added to Schlenk tube, vacuumed and refilled with argon for three times. Anhydrous DCM (2 mL) was added and the solution was stirred for 10 mins at RT. Then the reaction solution was cooled -78 ^{o}C, and DIBAL-H (0.24 mL, 1.5 M in toluene) was added. The reaction solution was stirred for 20 mins and poured into aqueous solution of Rochelle's salt (2 mL). The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic

layer was washed with brine, dried over $MgSO_4$. The solvent was removed by rotary evaporation. The residue was subject to flash chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:2) as eluent to give product **6** (33 mg, 82%) as a white solid.



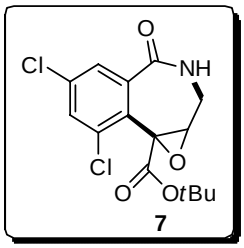
6

***tert*-Butyl 6,8-dichloro-1-oxo-2,3,4,5-tetrahydro-1*H*-benzo[*c*]azepine-5-carboxylate (6).** White solid; mp. 150-151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 2.0 Hz, 1H), 7.54 (d, J = 2.4 Hz, 1H), 6.54 (b, 1H), 4.52 (d, J = 7.6 Hz, 1H), 3.24 (m, 1H), 2.97 (m, 2H), 1.97 (m, 1H), 1.33 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.0, 170.4, 138.0, 134.6, 133.9, 132.5, 131.4, 128.2, 82.4, 43.8, 38.9, 31.8, 27.9 ppm; IR (KBr) ν 2925, 1730, 1672, 1251, 1153 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{17}Cl_2NO_3$ [M^+] 329.0585; found 329.0577.



3m **7**

Azepinone **3m** (0.2 mmol, 65.6 mg) was added to flask, DCM (10 mL) was added and the solution was stirred for 5 min, aqueous $NaHCO_3$ solution (0.5 M, 10 mL) was added afterward. *m*-CPBA (69 mg, 0.4 mmol) was added to the biphasic solution and the solution was kept at RT for 24 h. Then the mixture was poured into separatory funnel, the organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with $NaHCO_3$ solution, brine, dried over $MgSO_4$. The solvent was removed by rotary evaporation. The residue was subject to flash chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:1) as eluent to give product **7** (65 mg, 95%) as white solid.

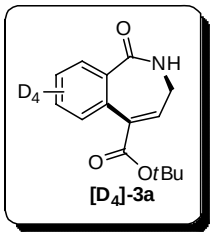


7

***tert*-Butyl 6,8-dichloro-4-oxo-2,3,4,8b-tetrahydro-1a*H*-benzo[*c*]oxireno[2,3-*e*] azepine-8b-carboxylate (7).** White solid; mp. 69-71 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.47 (b, 1H), 3.94 (m, 1H), 3.83 (m, 1H), 2.91 (m, 1H), 1.38 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.0, 166.2, 137.6, 136.3, 135.5, 132.1, 128.9, 128.7, 83.9, 61.4, 57.6, 43.4, 27.6 ppm; IR (KBr) *v* 2980, 1735, 1666, 1370, 1163 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{15}Cl_2NO_4$ [M^+] 343.0378; found 343.0379.

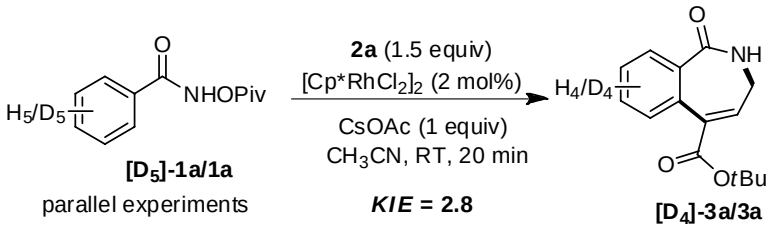
Kinetic Isotope Effect Study

[D_4]-**3a** was prepared according to general procedure in 70% yield.

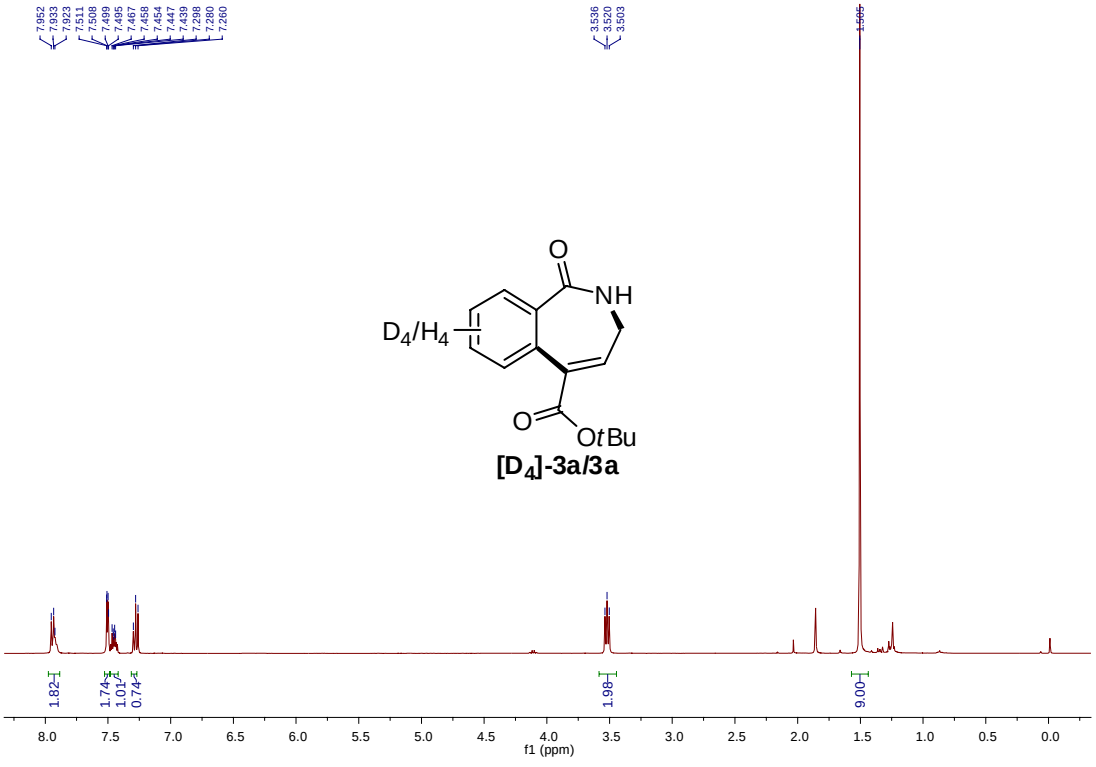


[D_4]-3a

White solid; mp. 203-205 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (m, 1H), 6.96 (b, 1H), 3.53 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 171.1, 165.2, 138.4, 138.1, 134.5, 132.1, 81.9, 37.6, 28.0 ppm; IR (KBr) *v* 2924, 2853, 1713, 1656, 1461, 1274, 1148 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{13}D_4NO_3$ [M^+] 263.1460; found 263.1460.



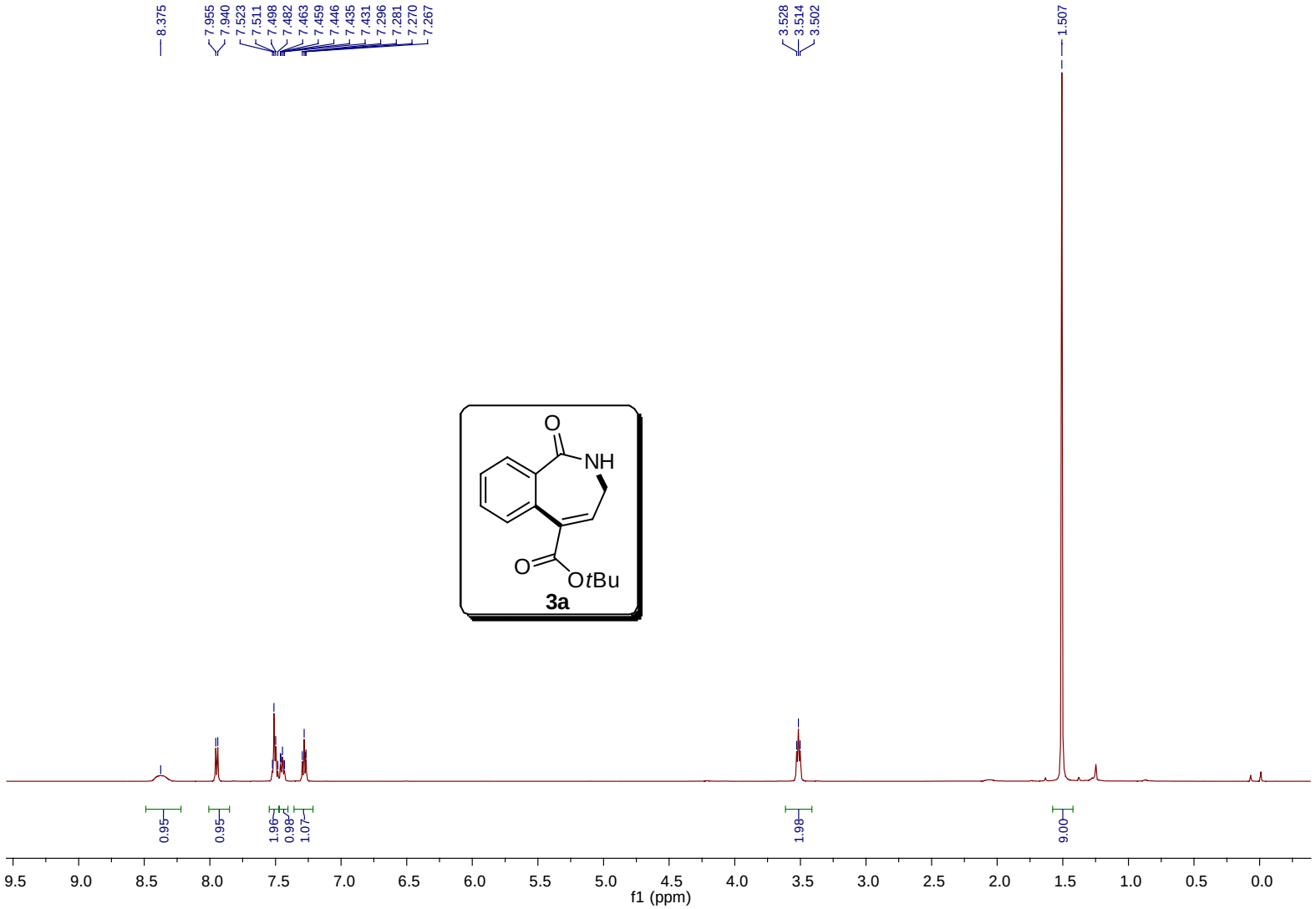
Following general procedure, $[Cp^*RhCl_2]_2$ (0.6 mg, 2 mol%), benzamide **1a** (22.1 mg, 0.1 mmol), CsOAc (20 mg, 0.1 mmol) were added to a vial. CH_3CN (0.6 mL) was added, followed by micro-syringe addition of vinyldiazoacetate **2a** (25.2 mg, 0.15 mmol). The micro-syringe was washed with an additional 0.15 mL CH_3CN and added to the reaction solution. In another reaction vial, $[D_5]$-**1a** (22.6 mg, 0.1 mmol, 1.0 equiv) was used instead of **1a**. The two reactions were allowed to stir at RT for 20 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 (15.6 mg, 30% combined yield) was isolated by flash chromatography. The value of K_H/K_D was obtained based on ^{1}HNMR.

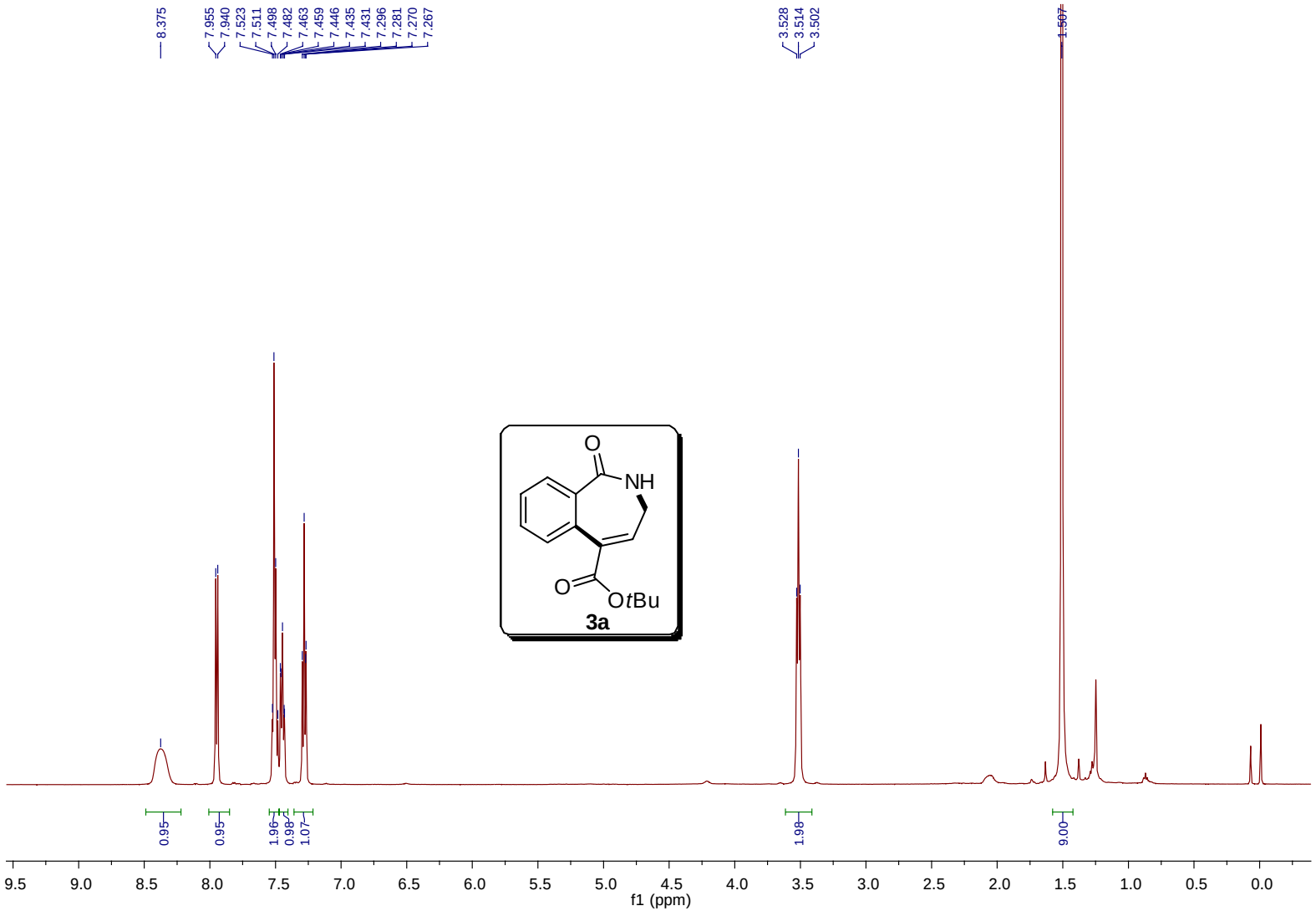


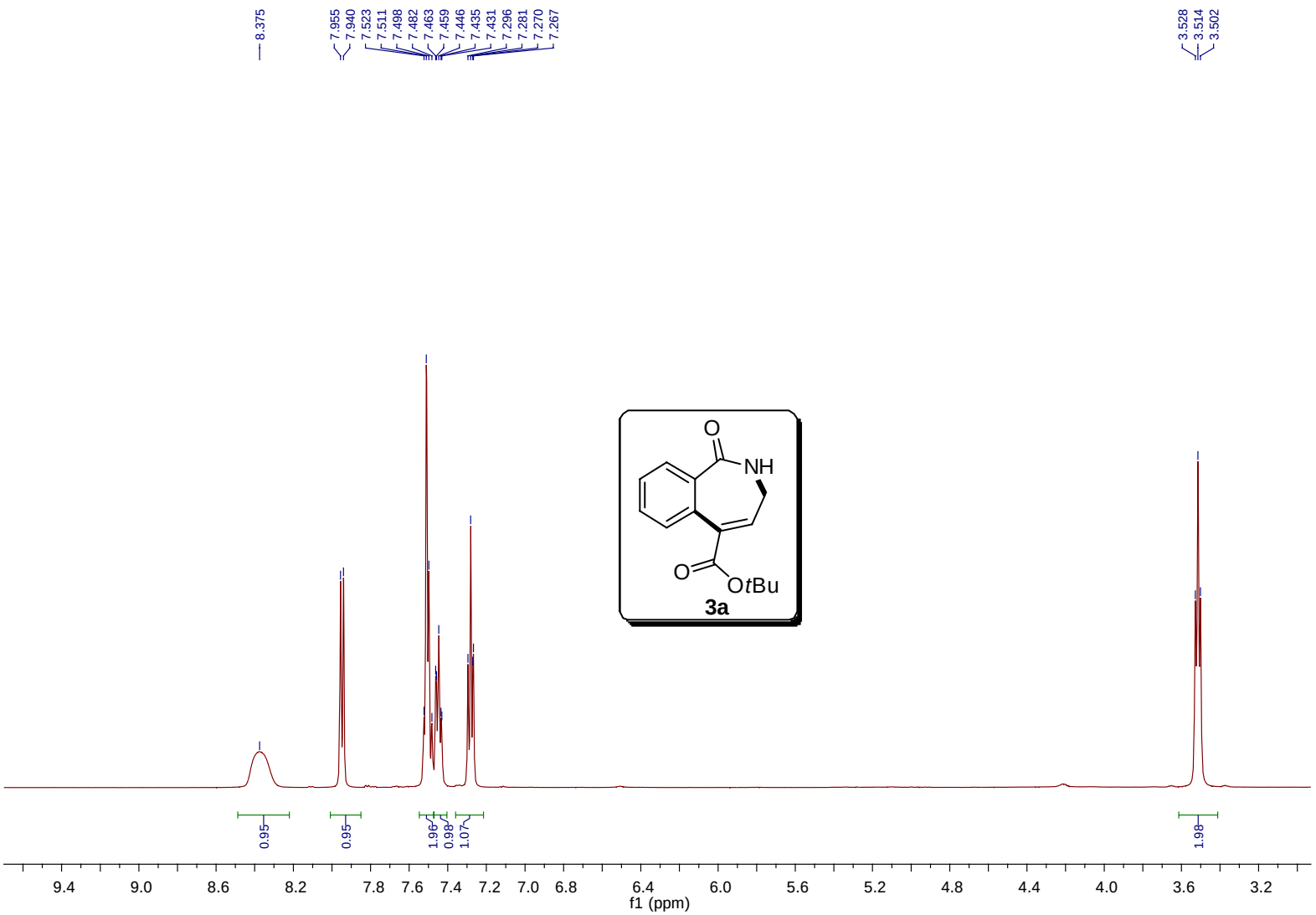
Reference:

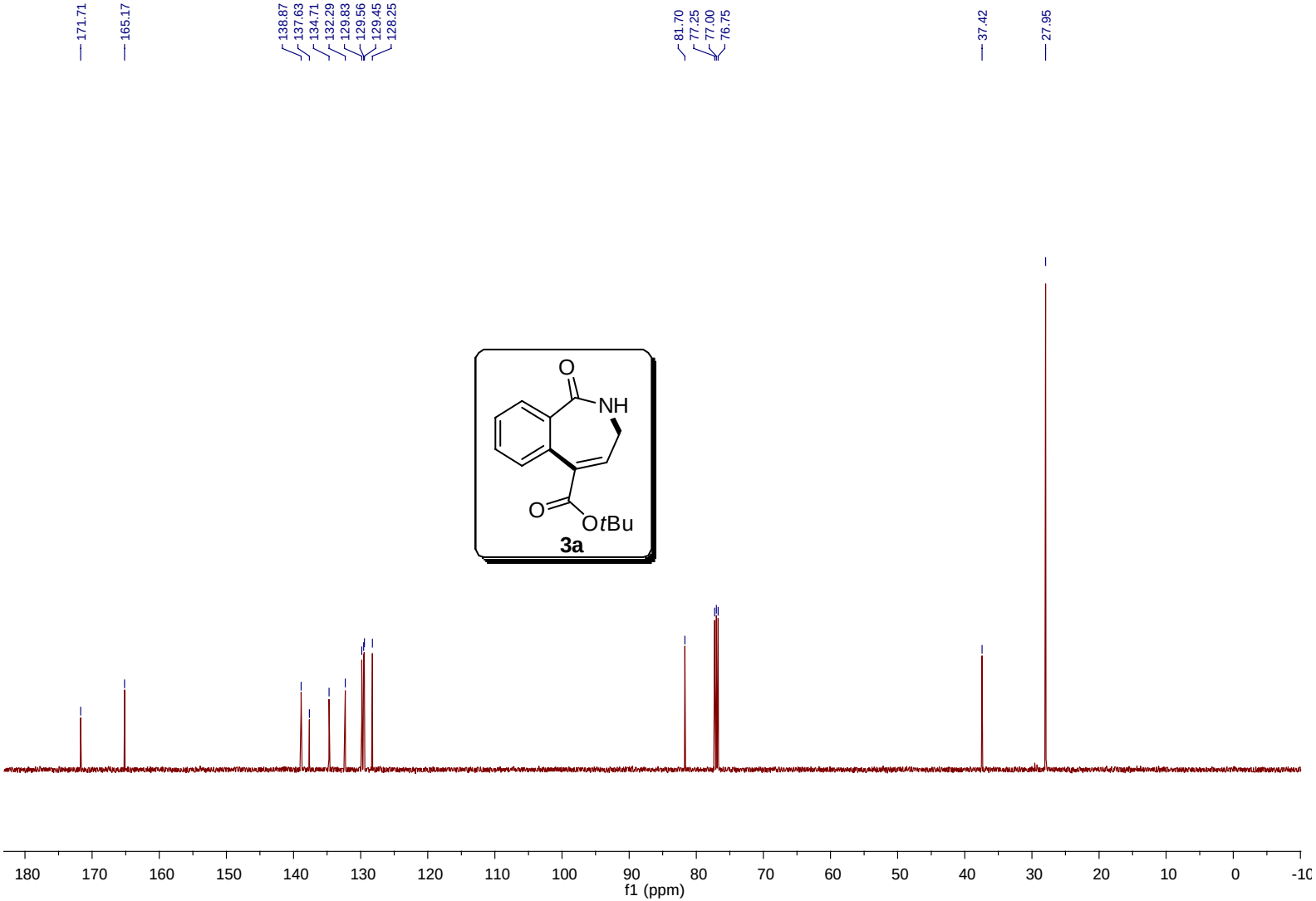
1 H. Wang, F. Glorius, *Angew. Chem., Int. Ed*., 2012, **51**, 7318-7322.

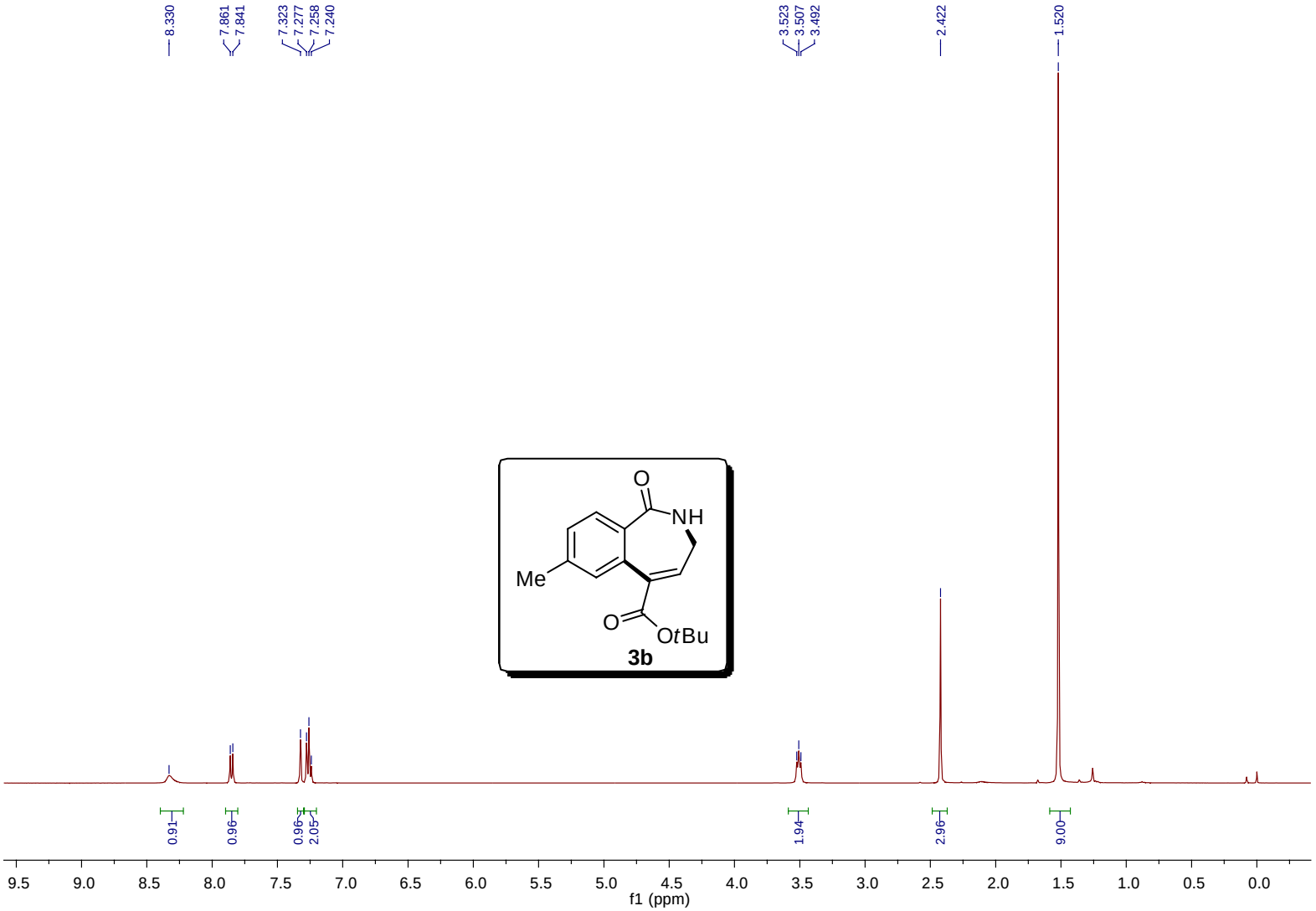
2 (a) H. M. L. Davies, B. Hu, E. Saikali, P. R. Bruzinski, *J. Org. Chem*., 1994, **59**, 4535-4541; (b) V. V. Pagar, A. M. Jdhav, R.-S. Liu, *J. Am. Chem. Soc*., 2011, **133**, 20728-20731.

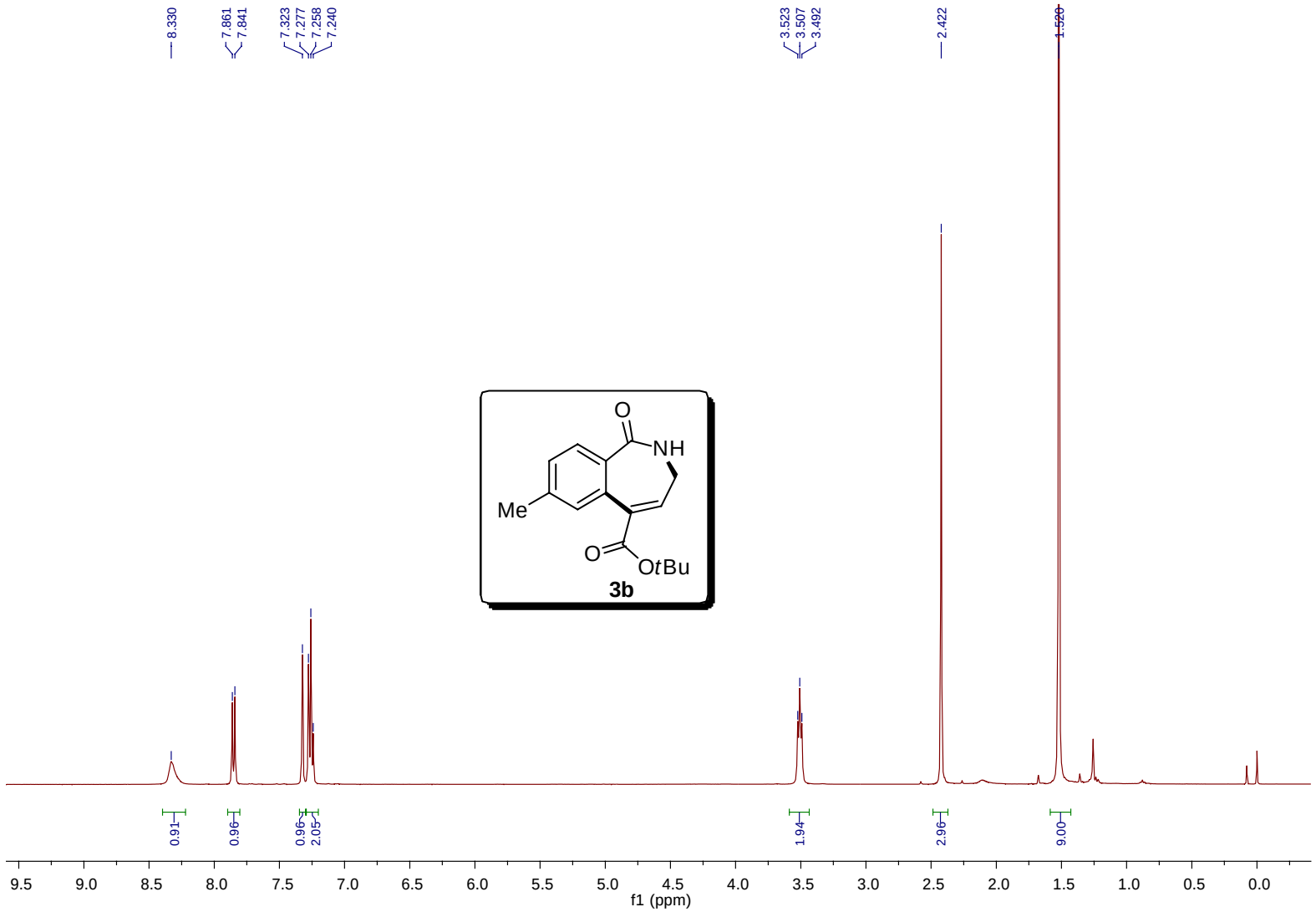


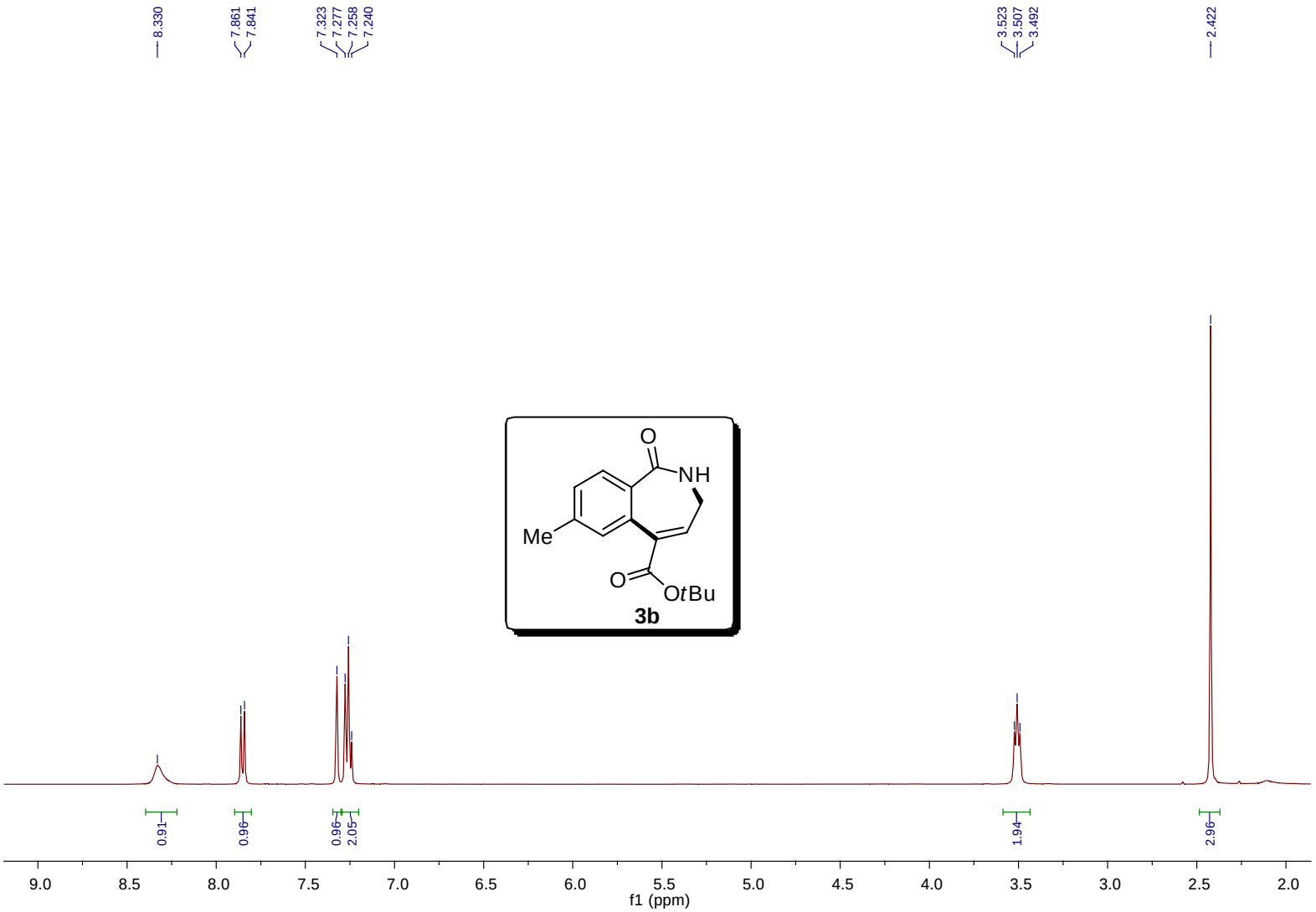


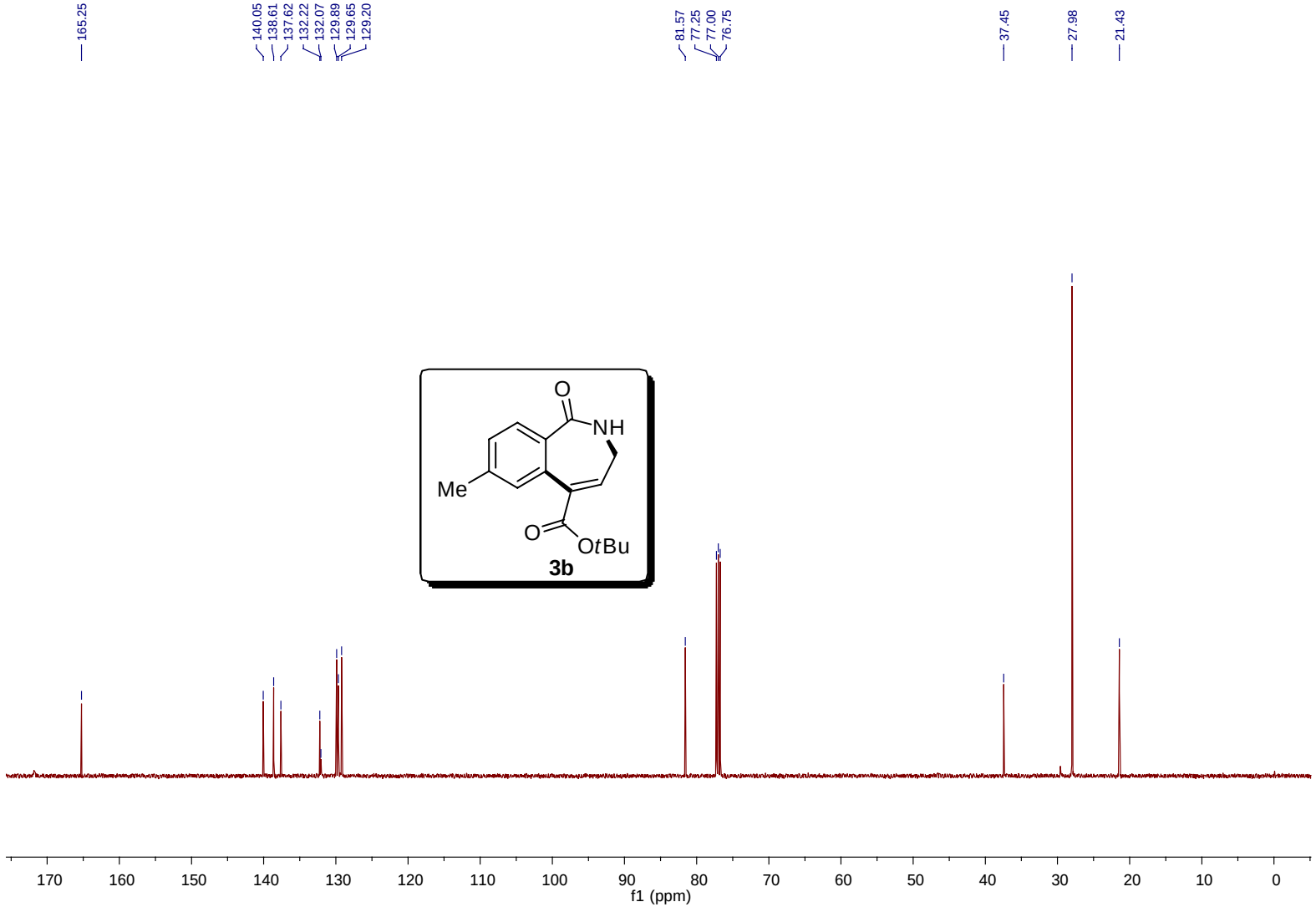


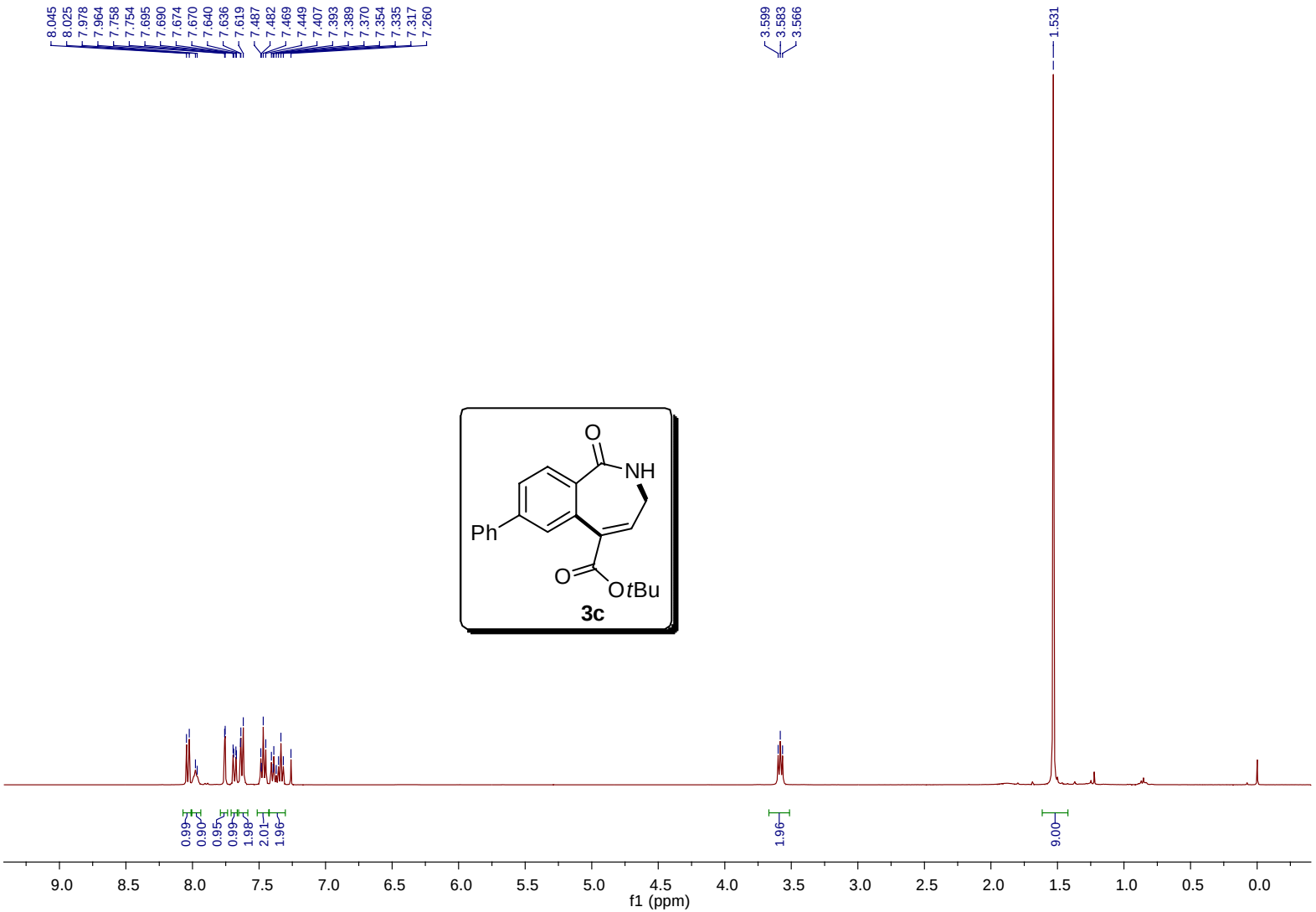


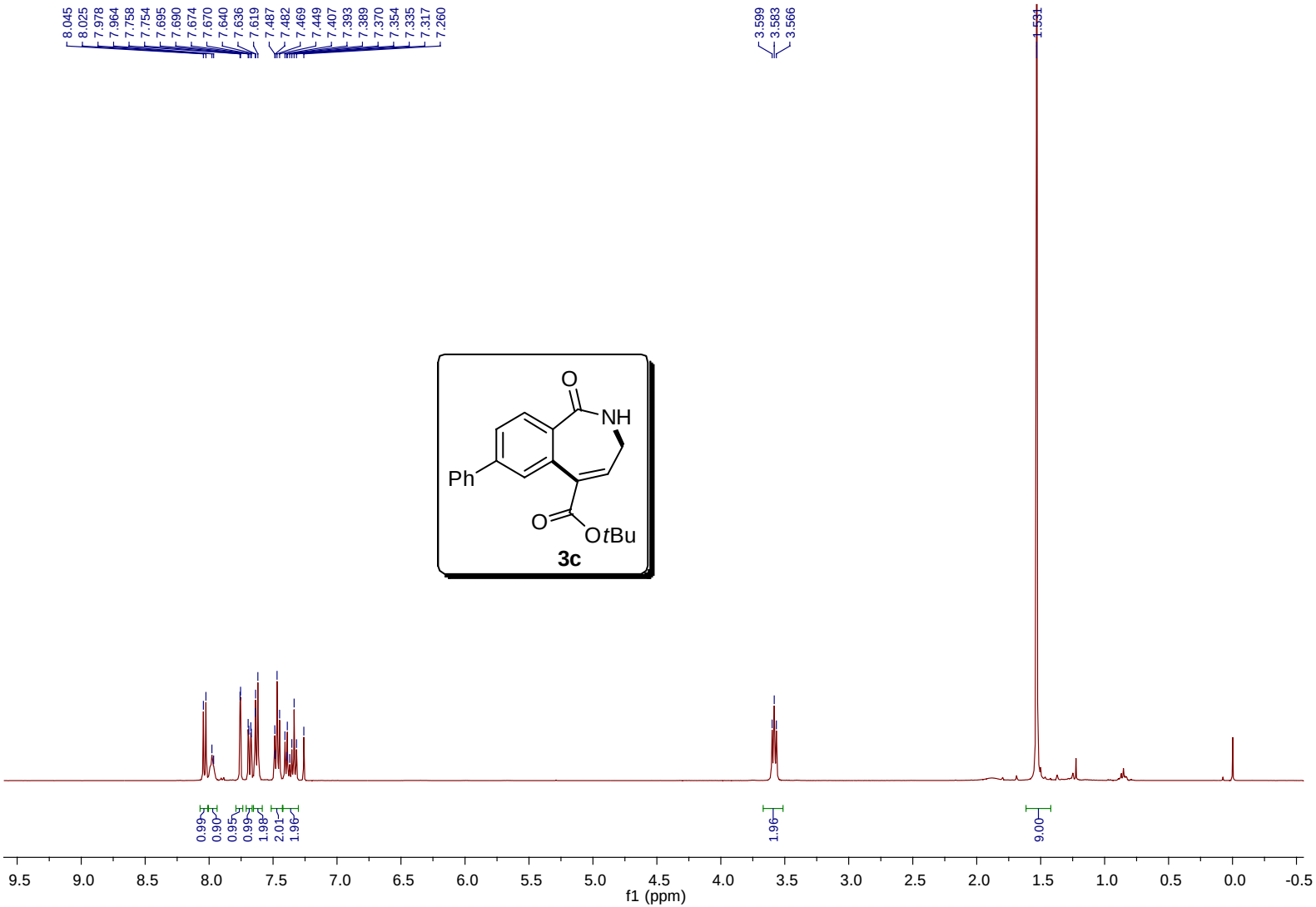


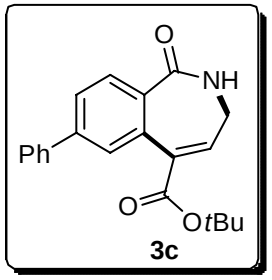




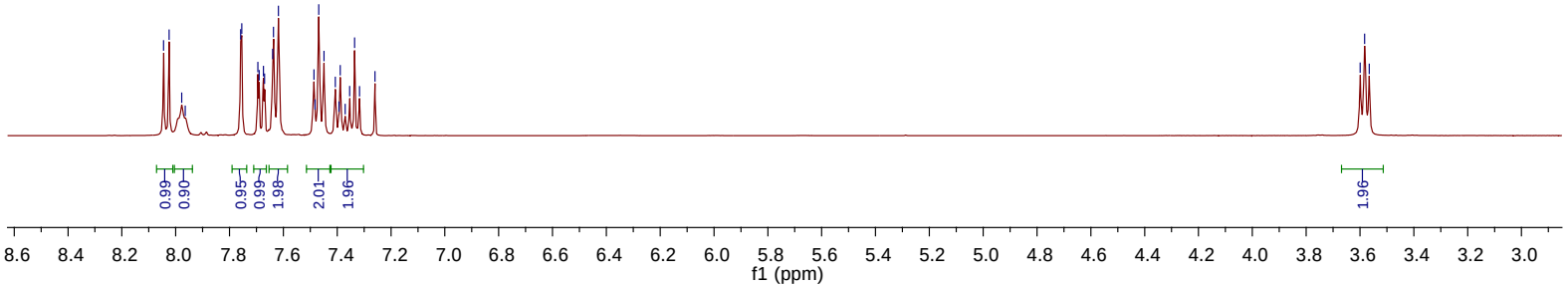


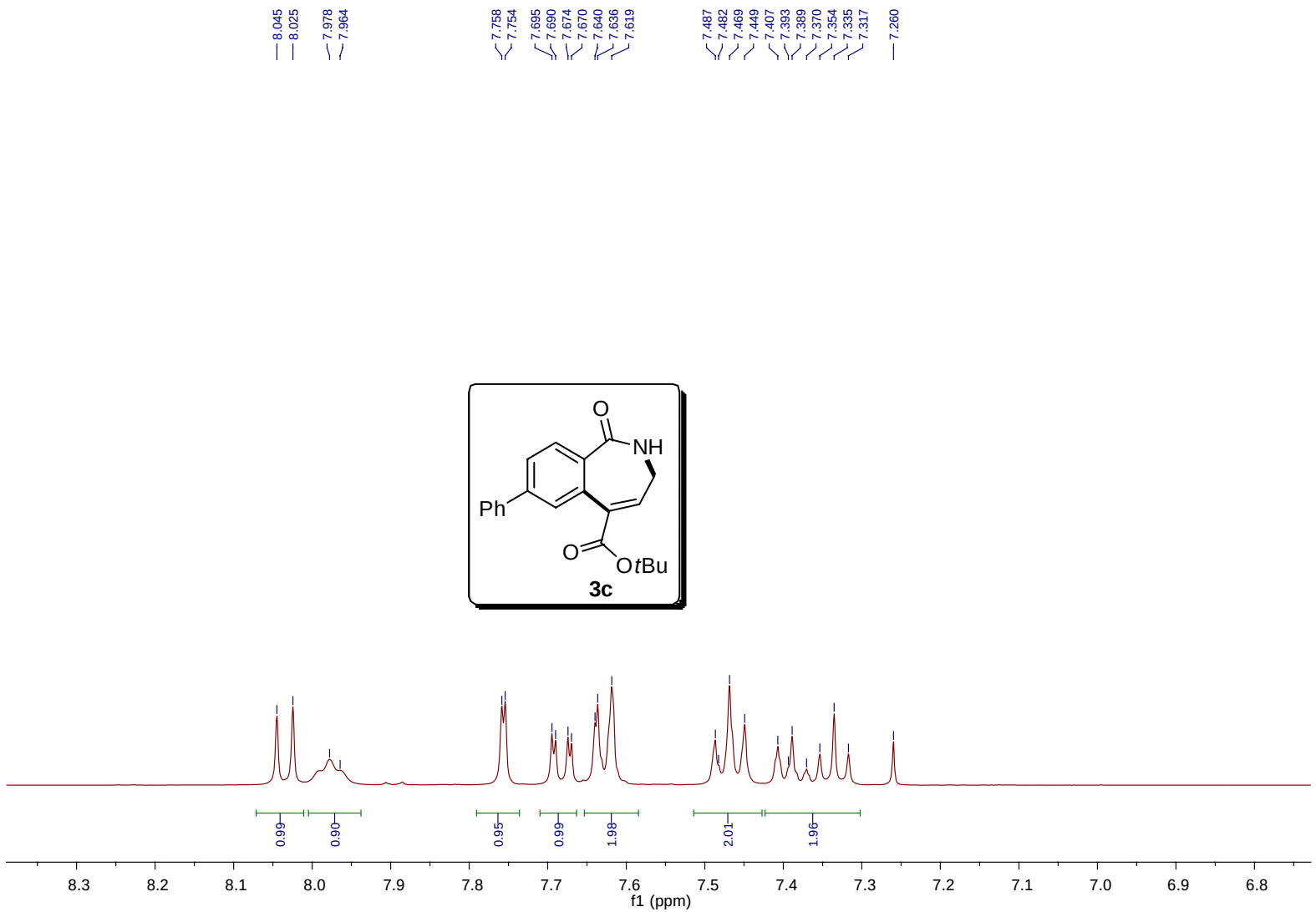


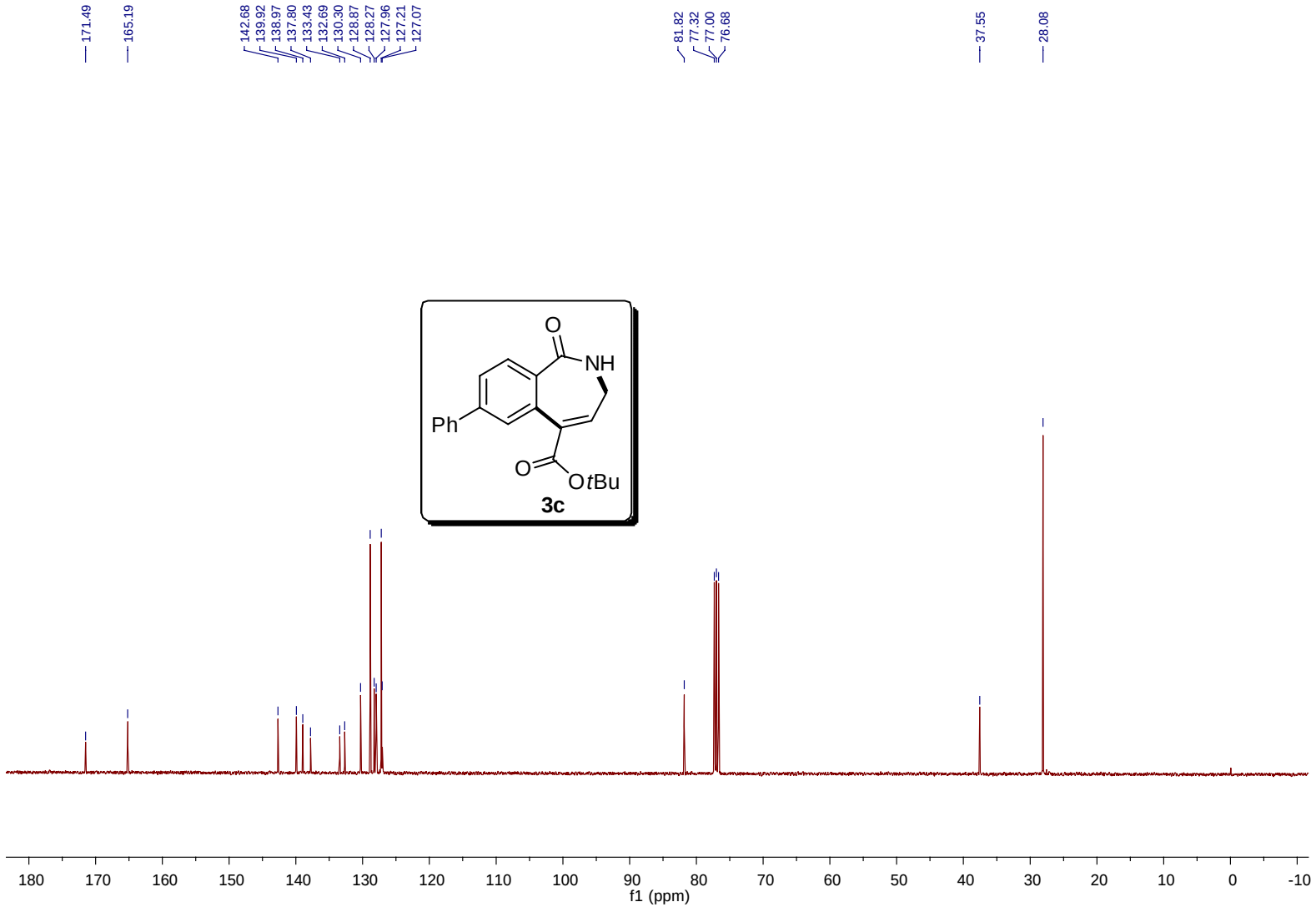


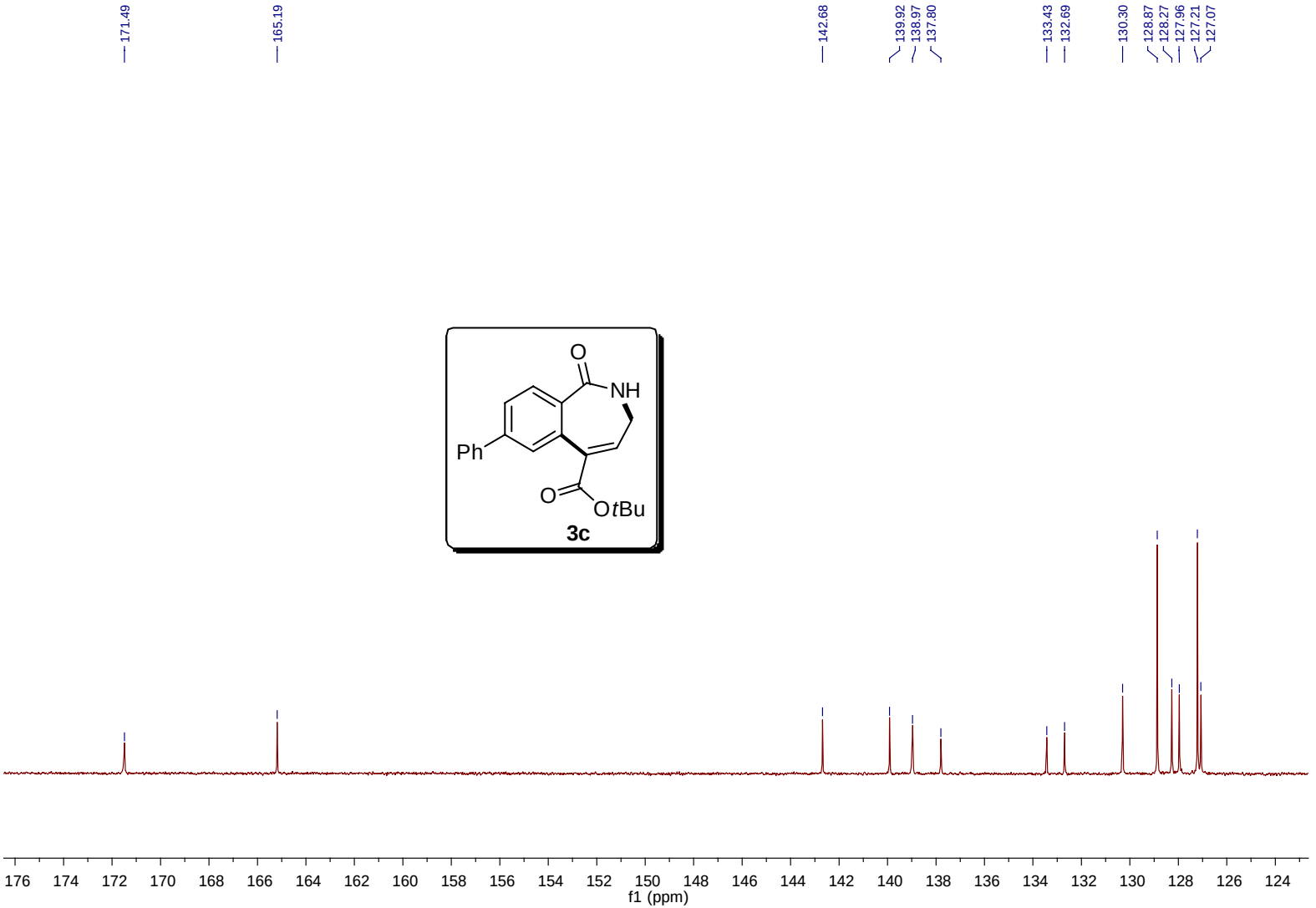


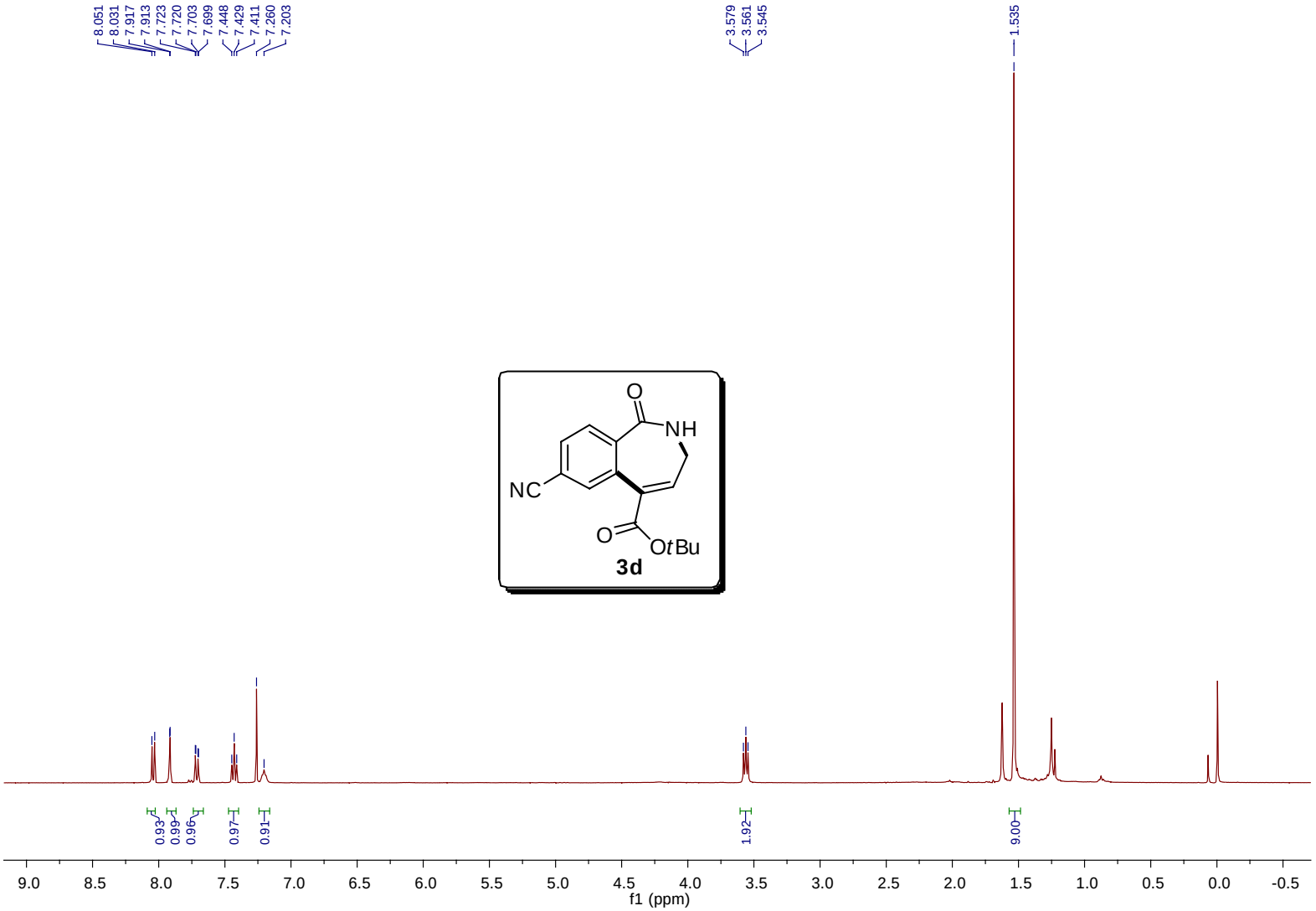
3c

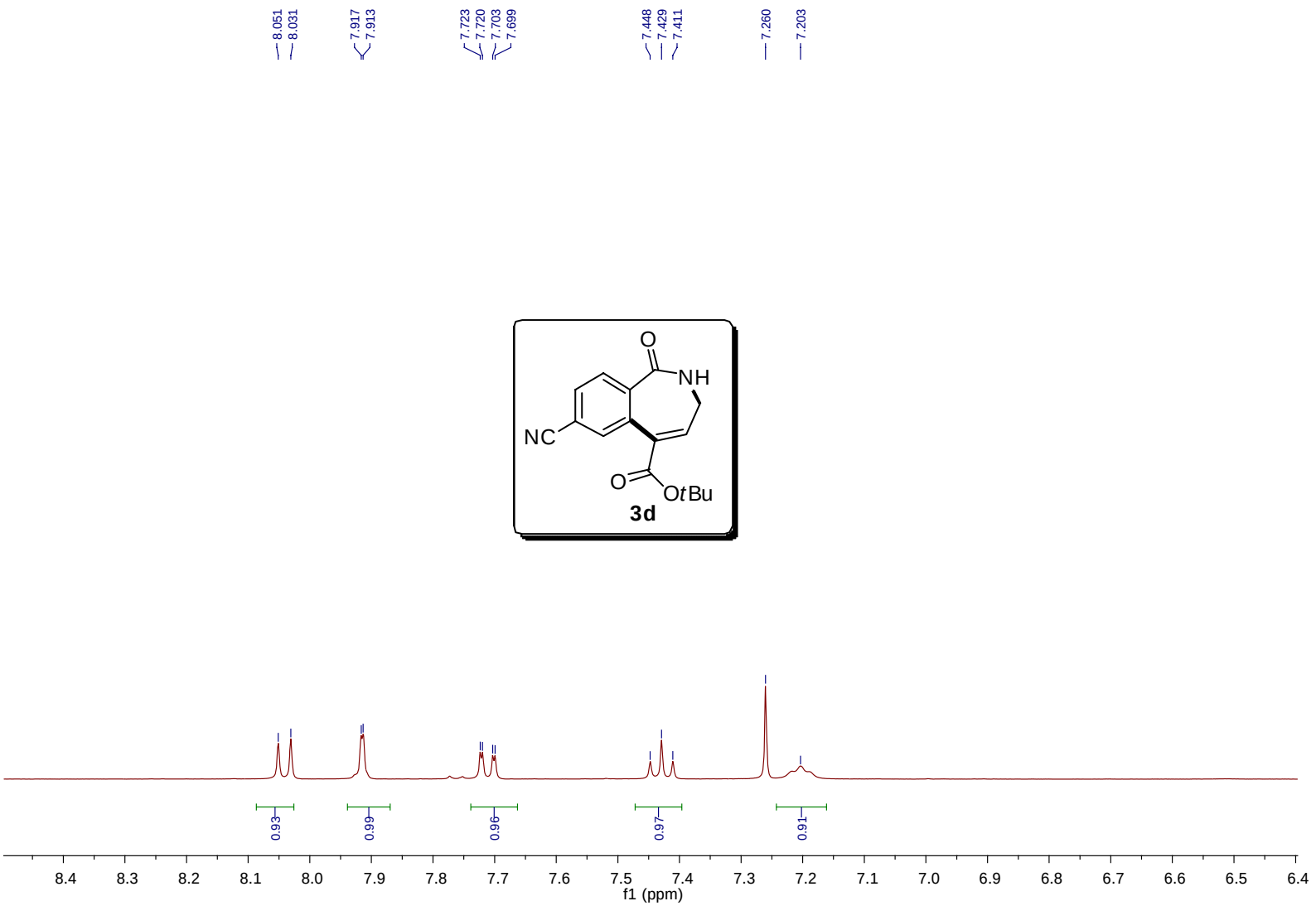


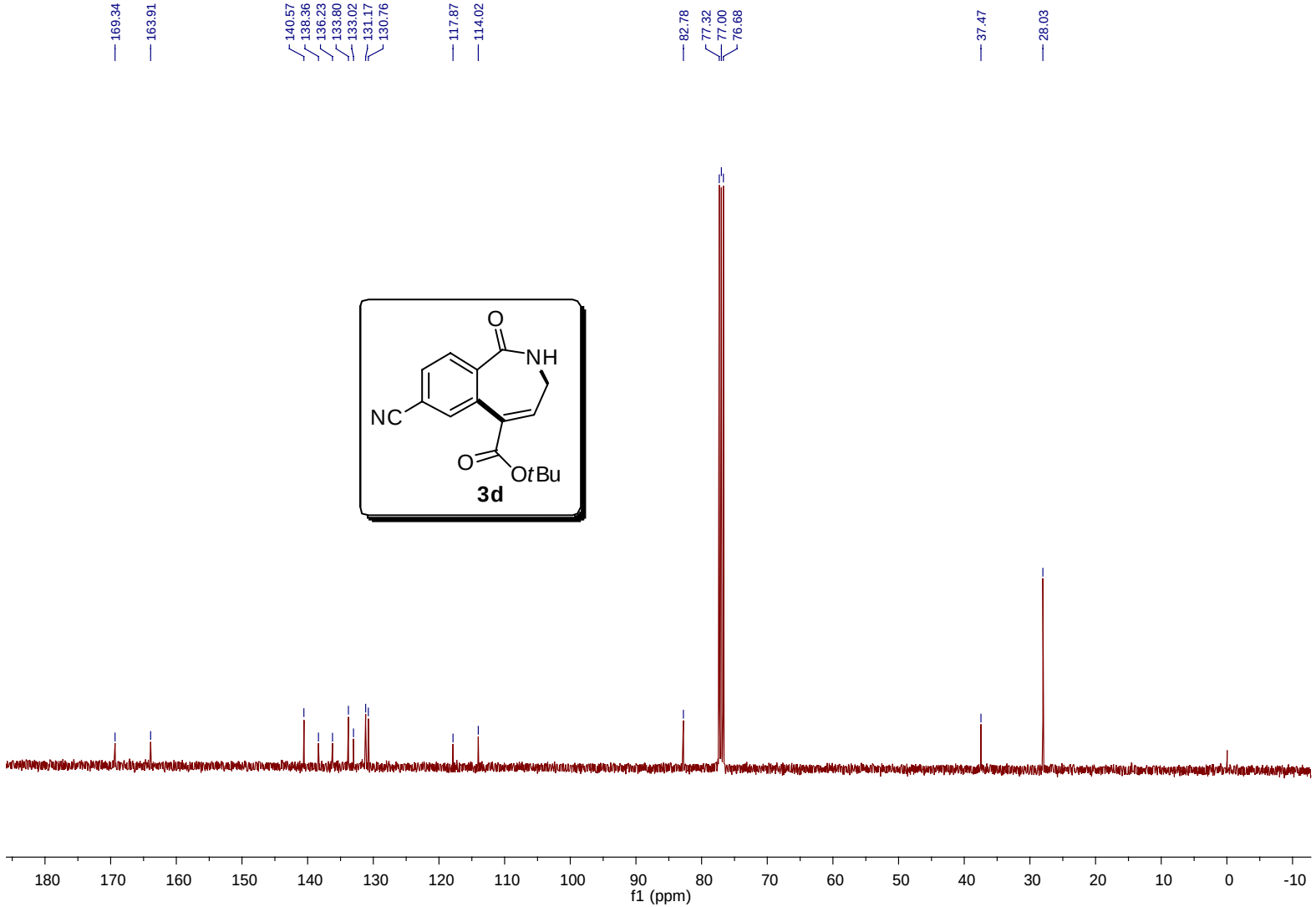


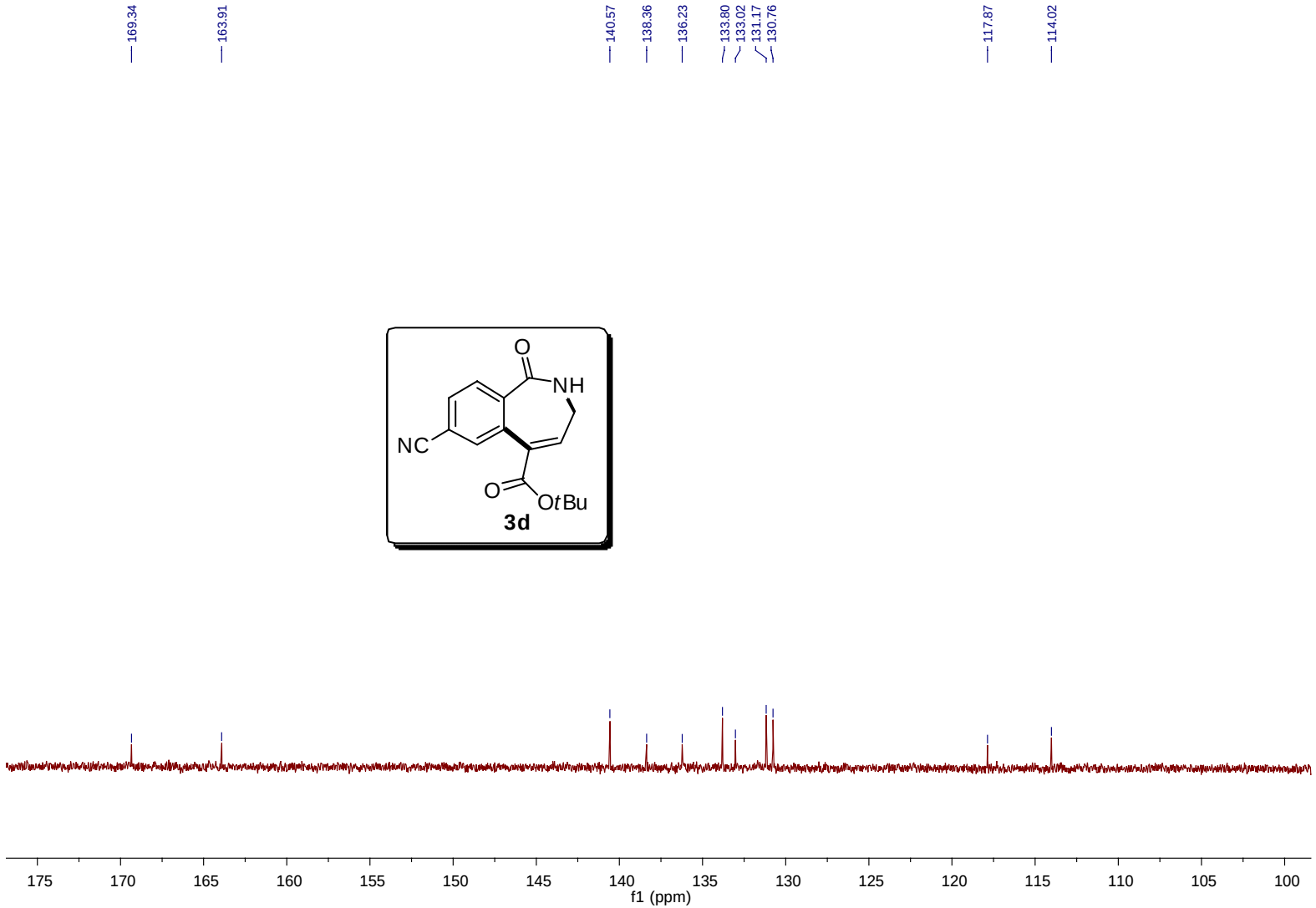


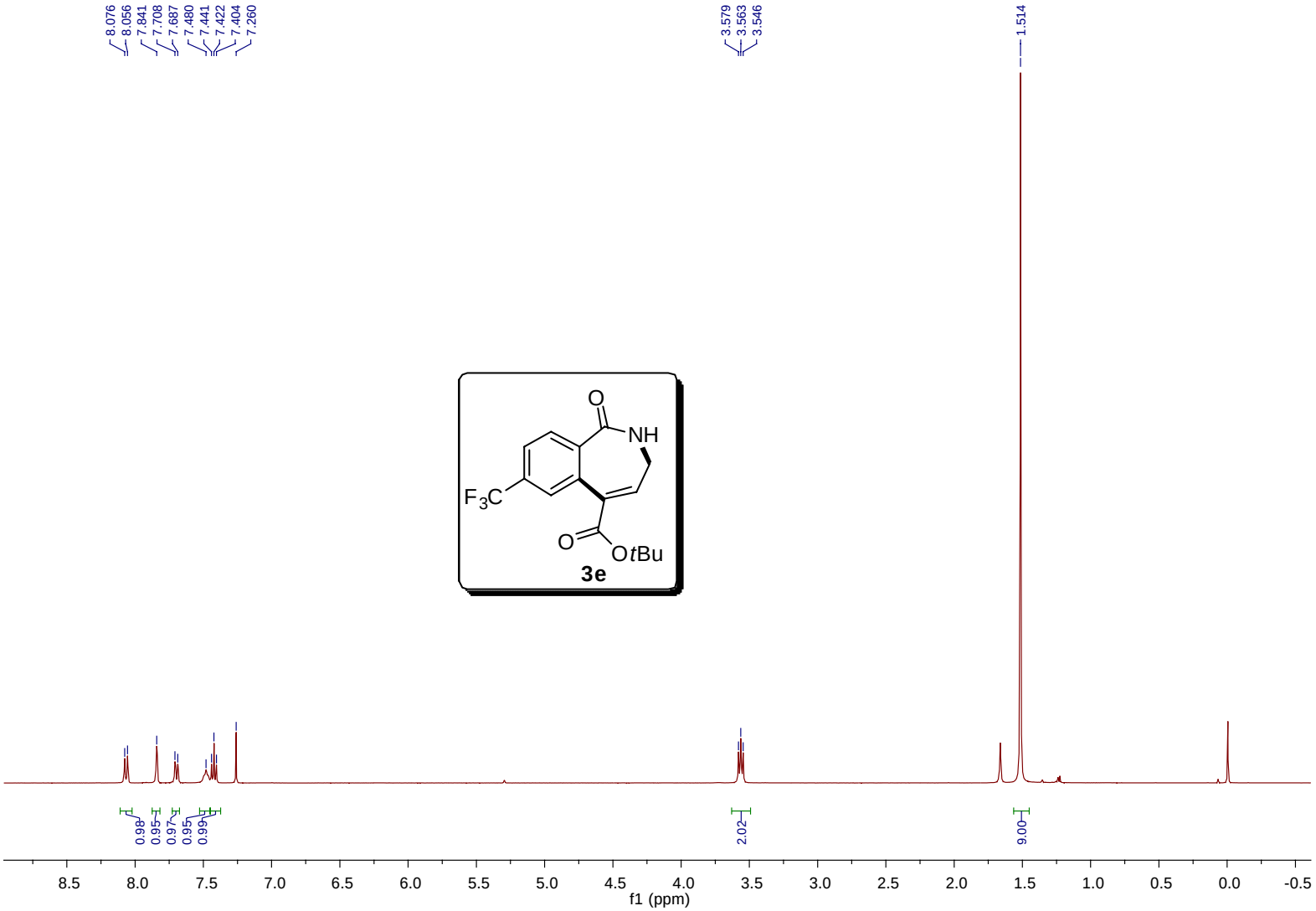


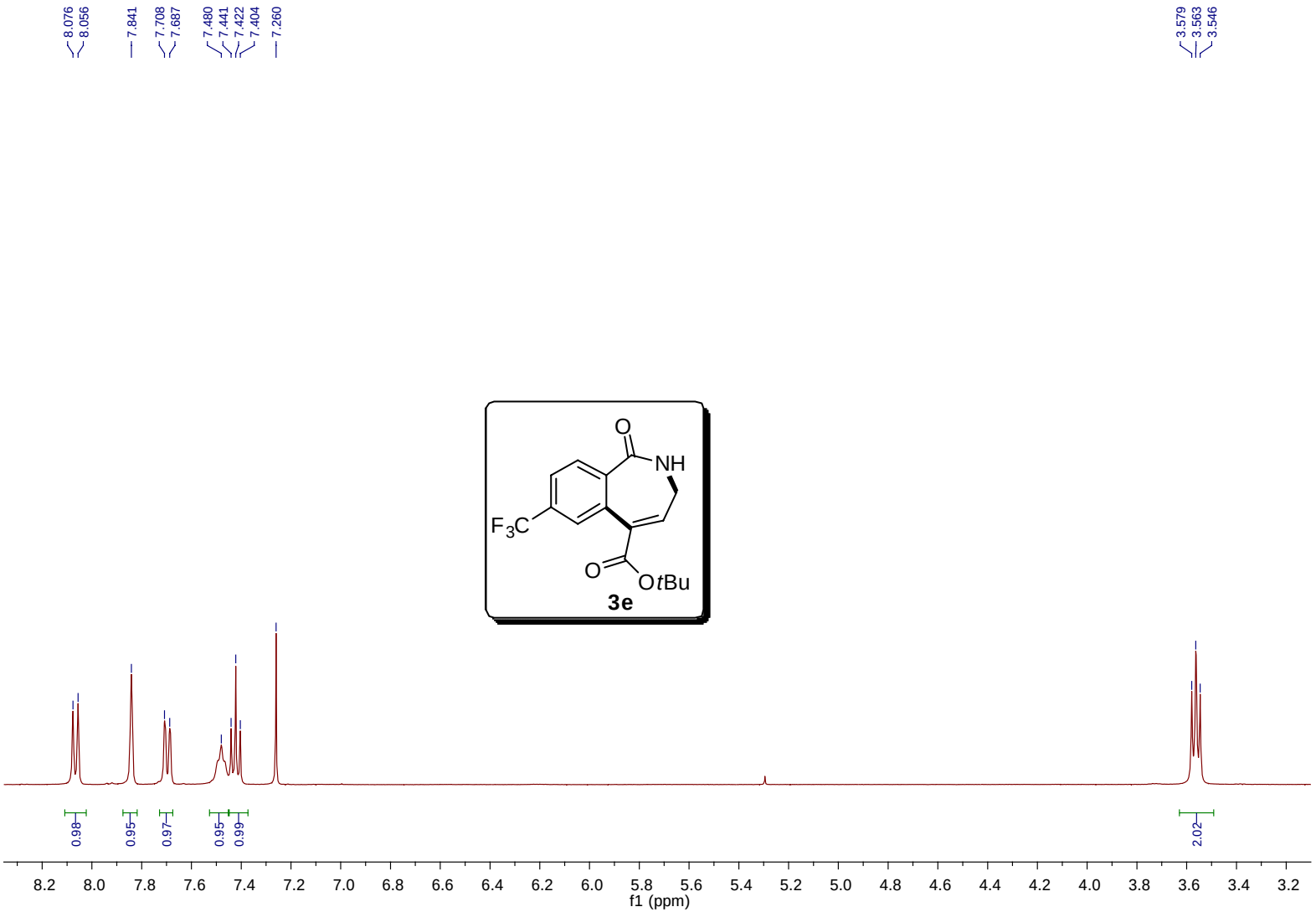


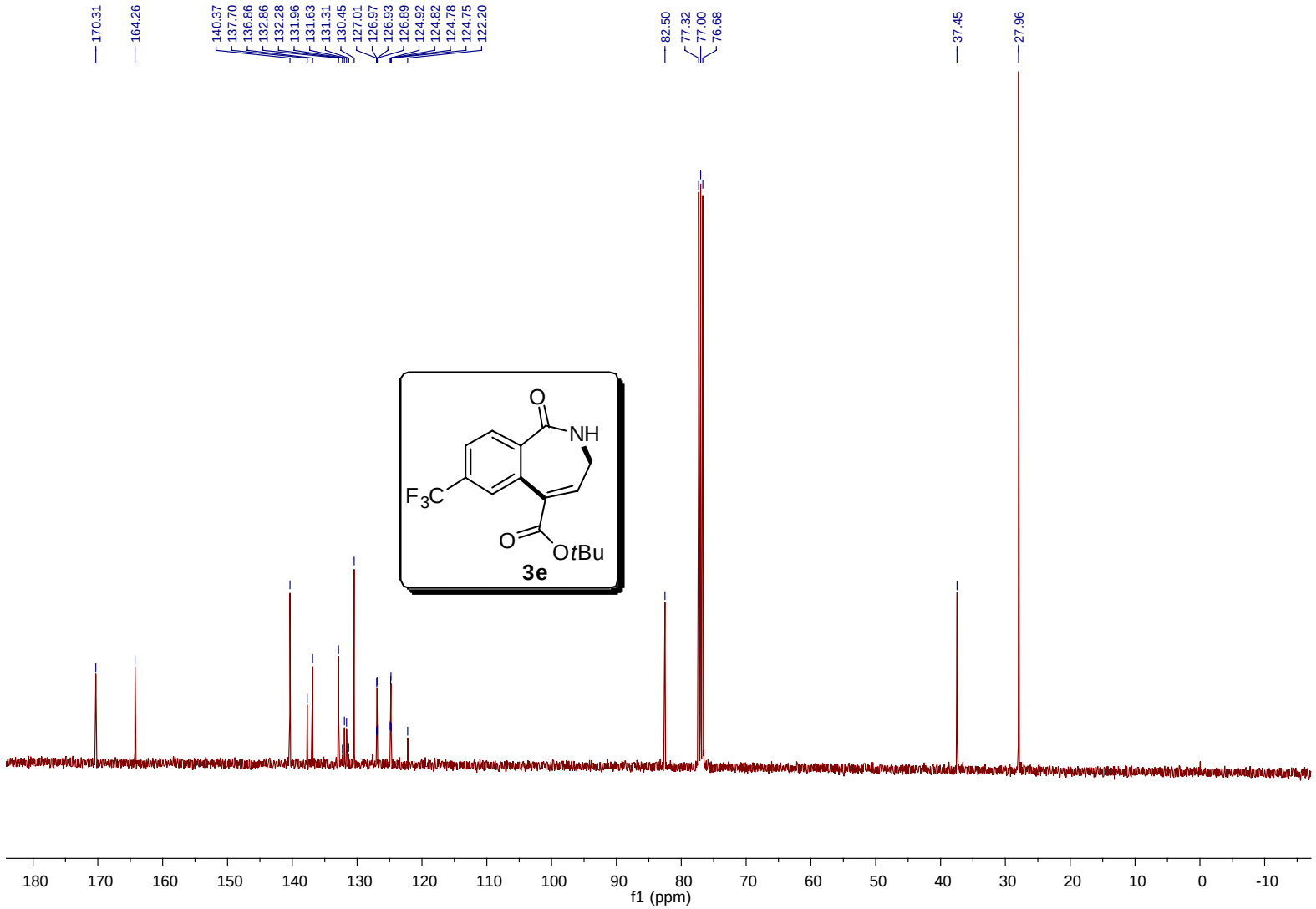


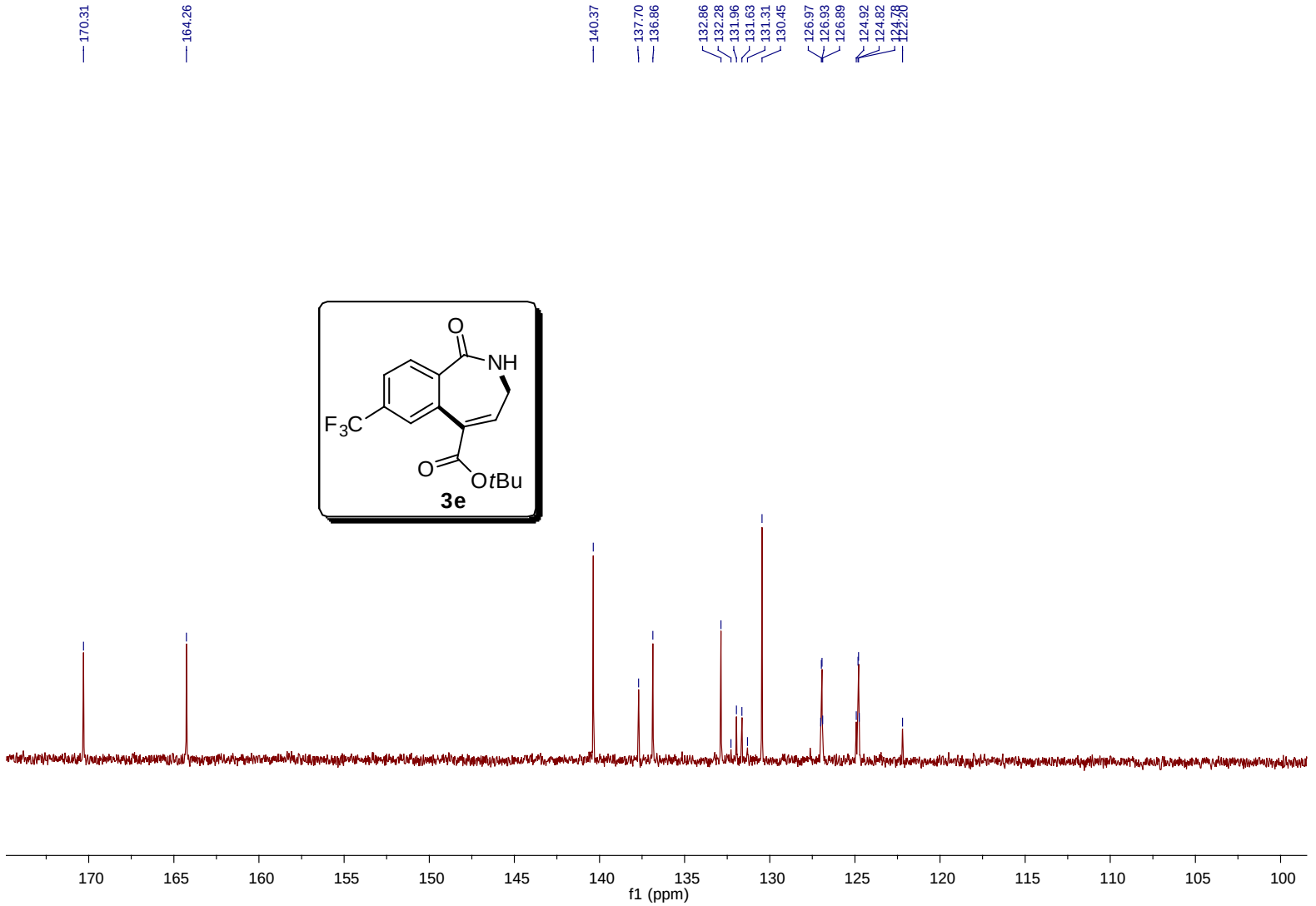


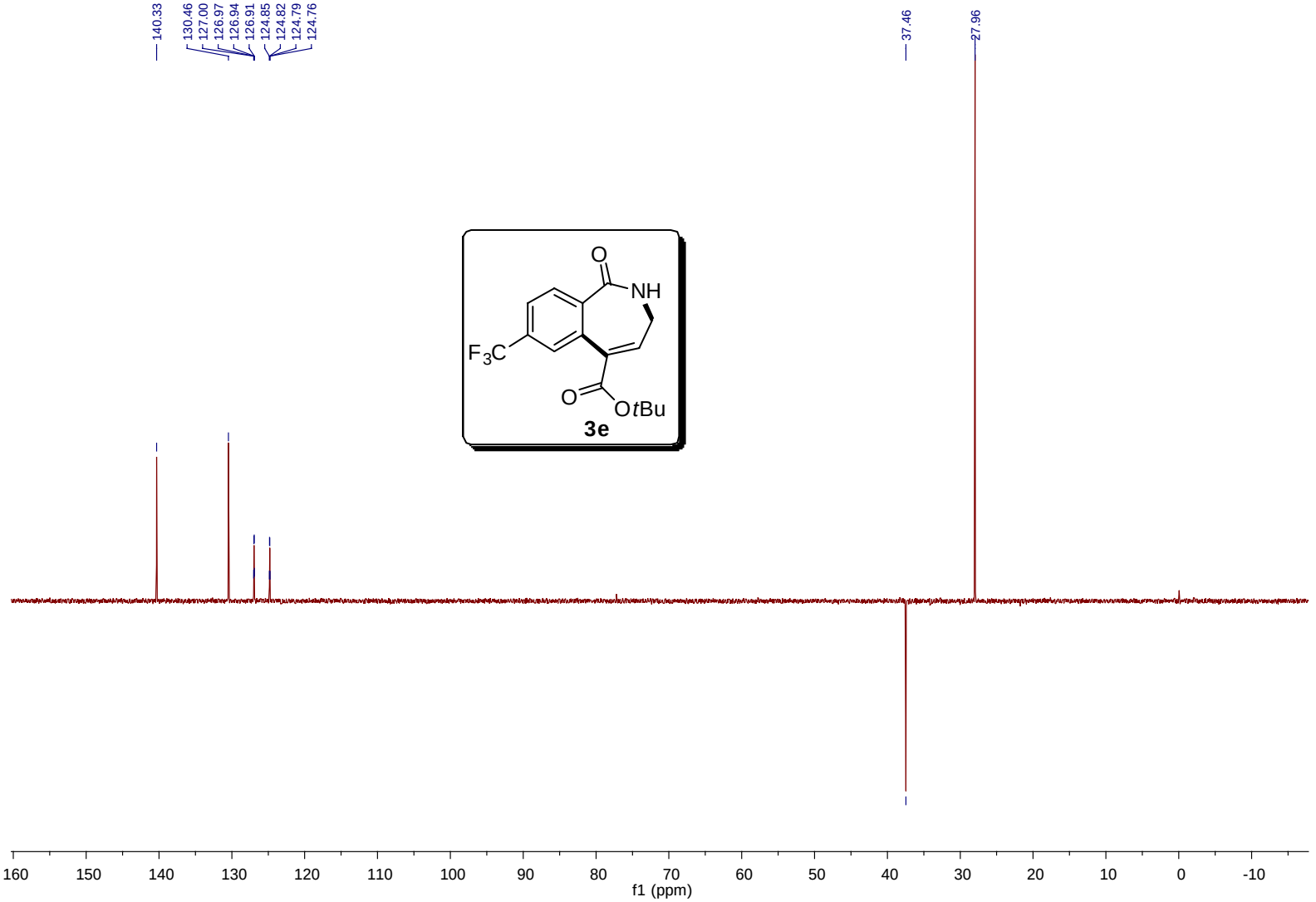


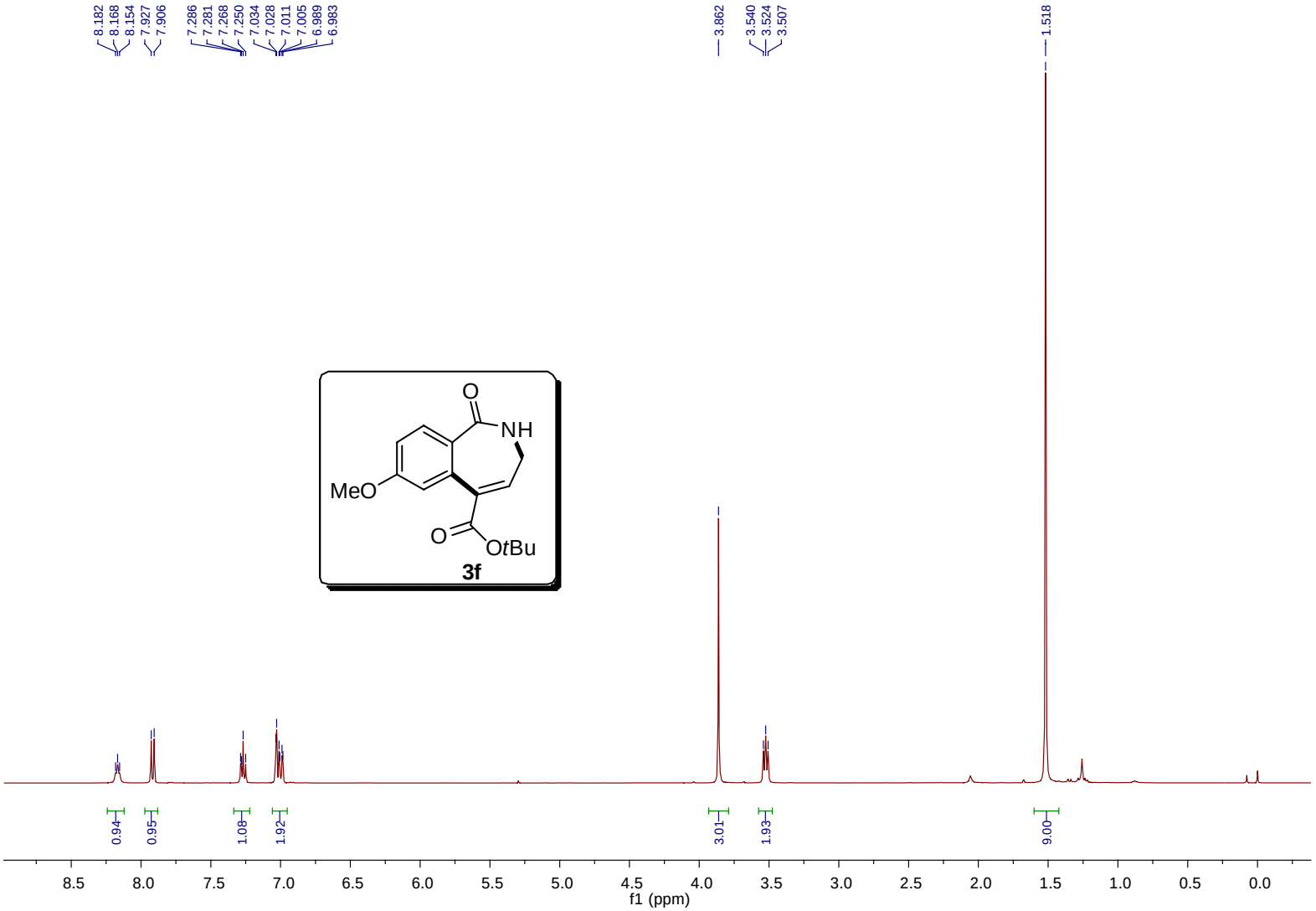


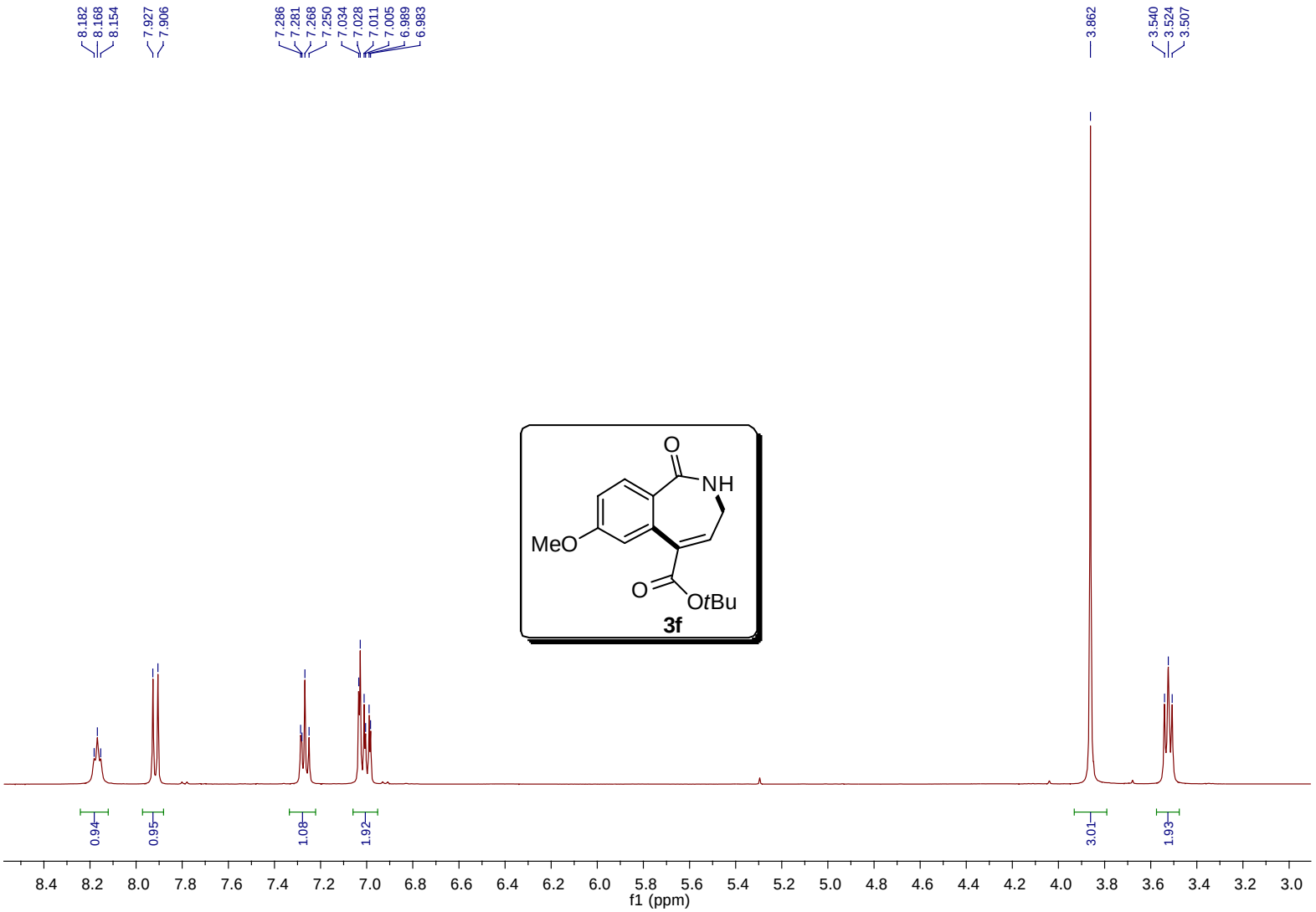


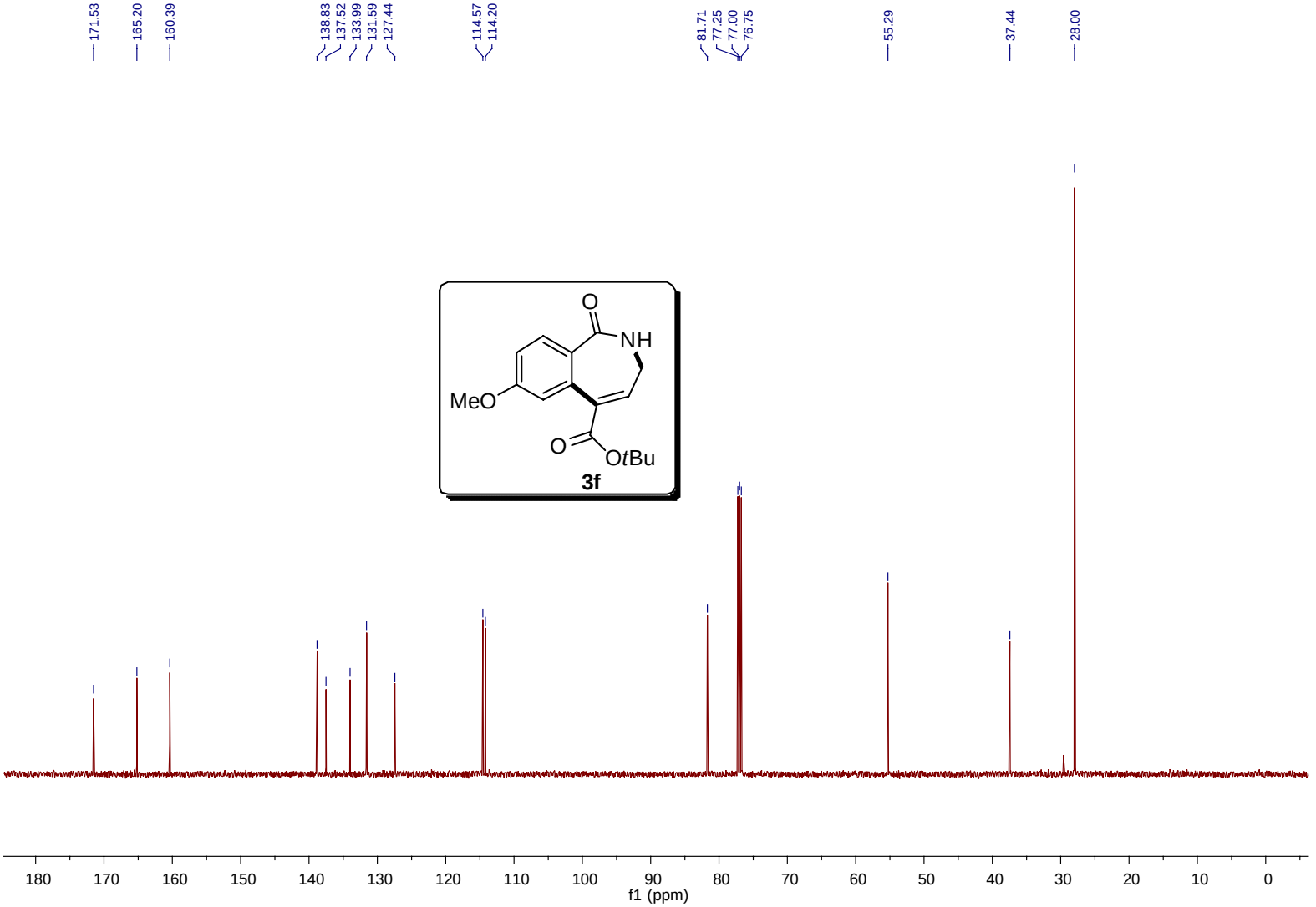


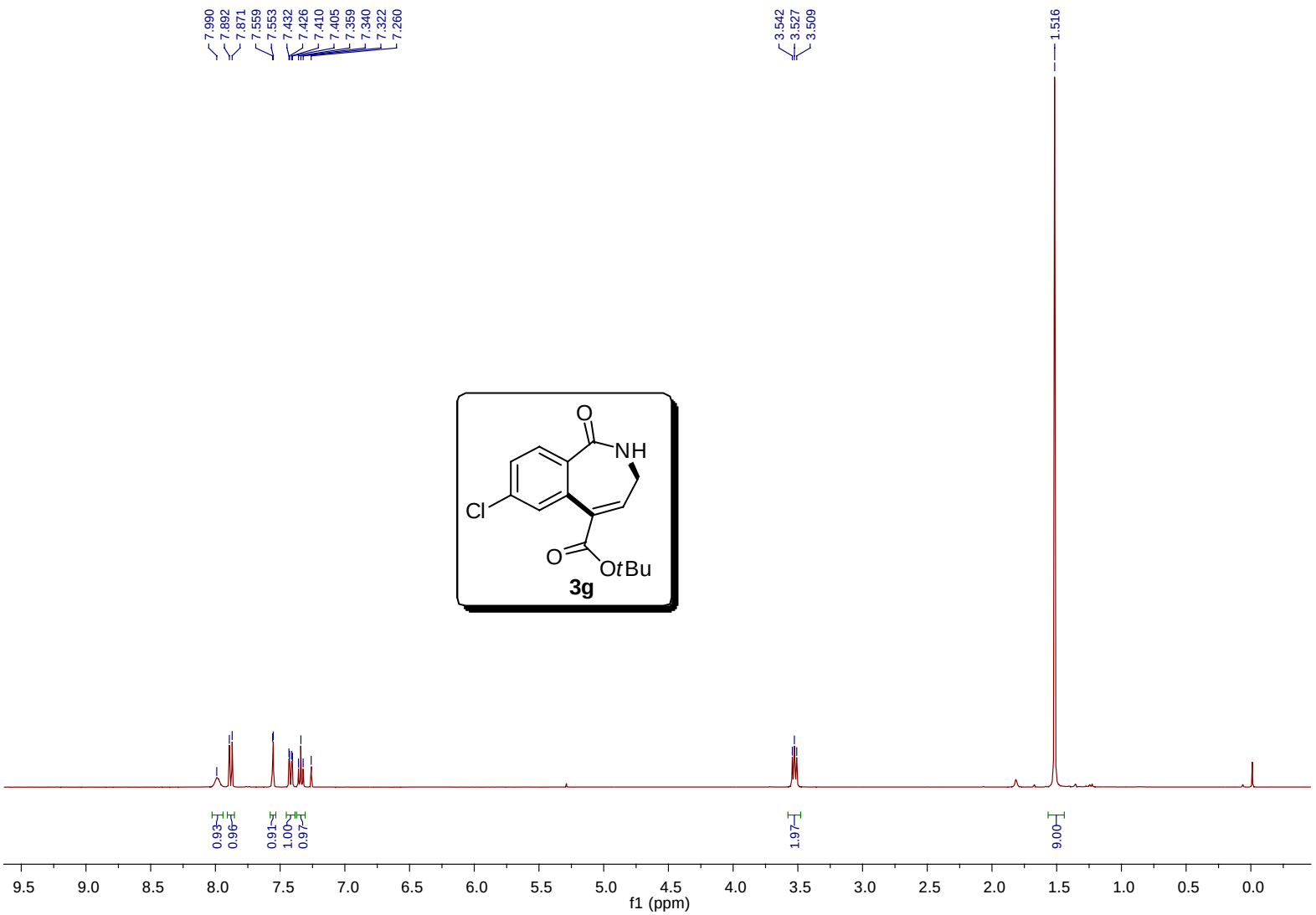


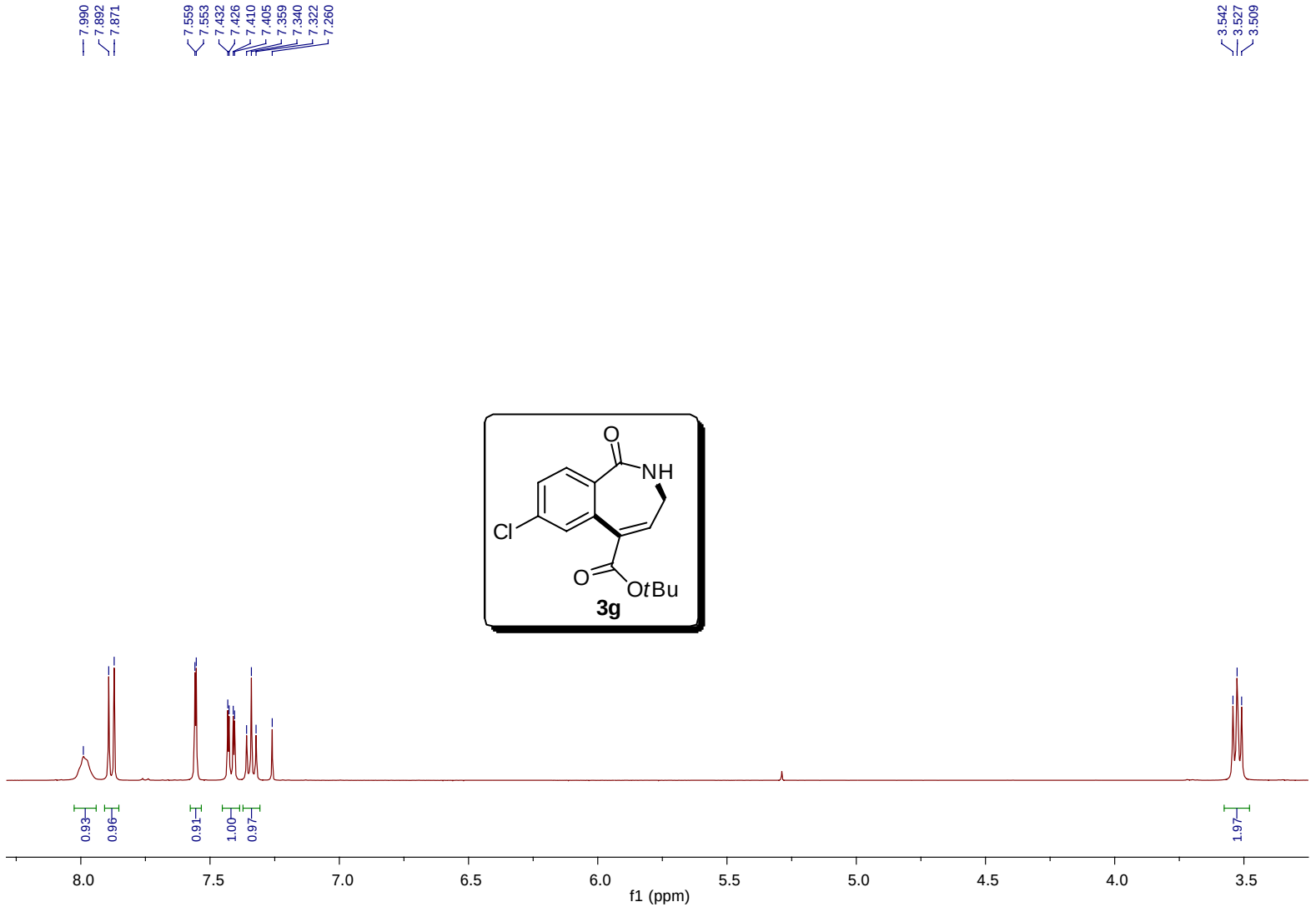


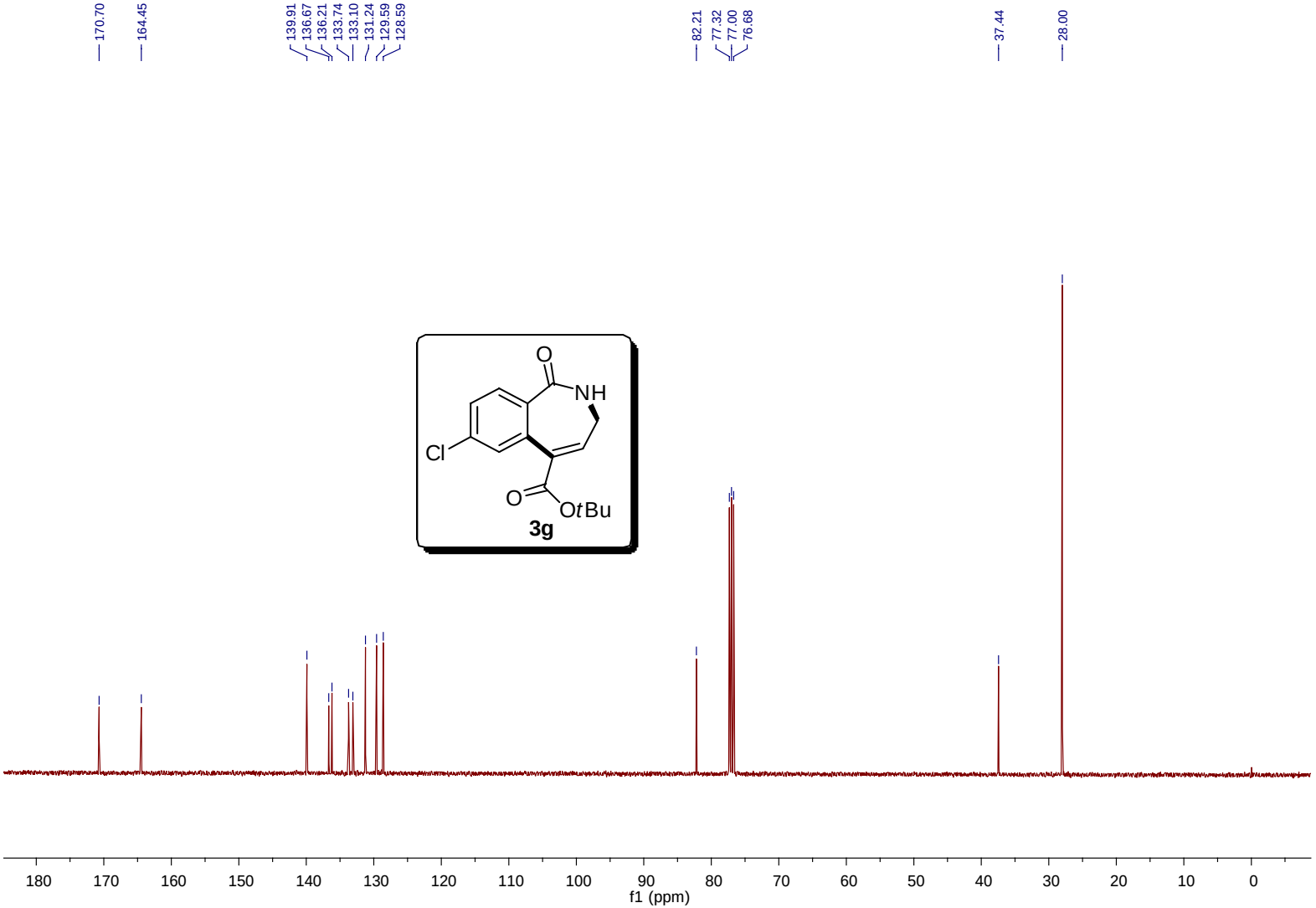


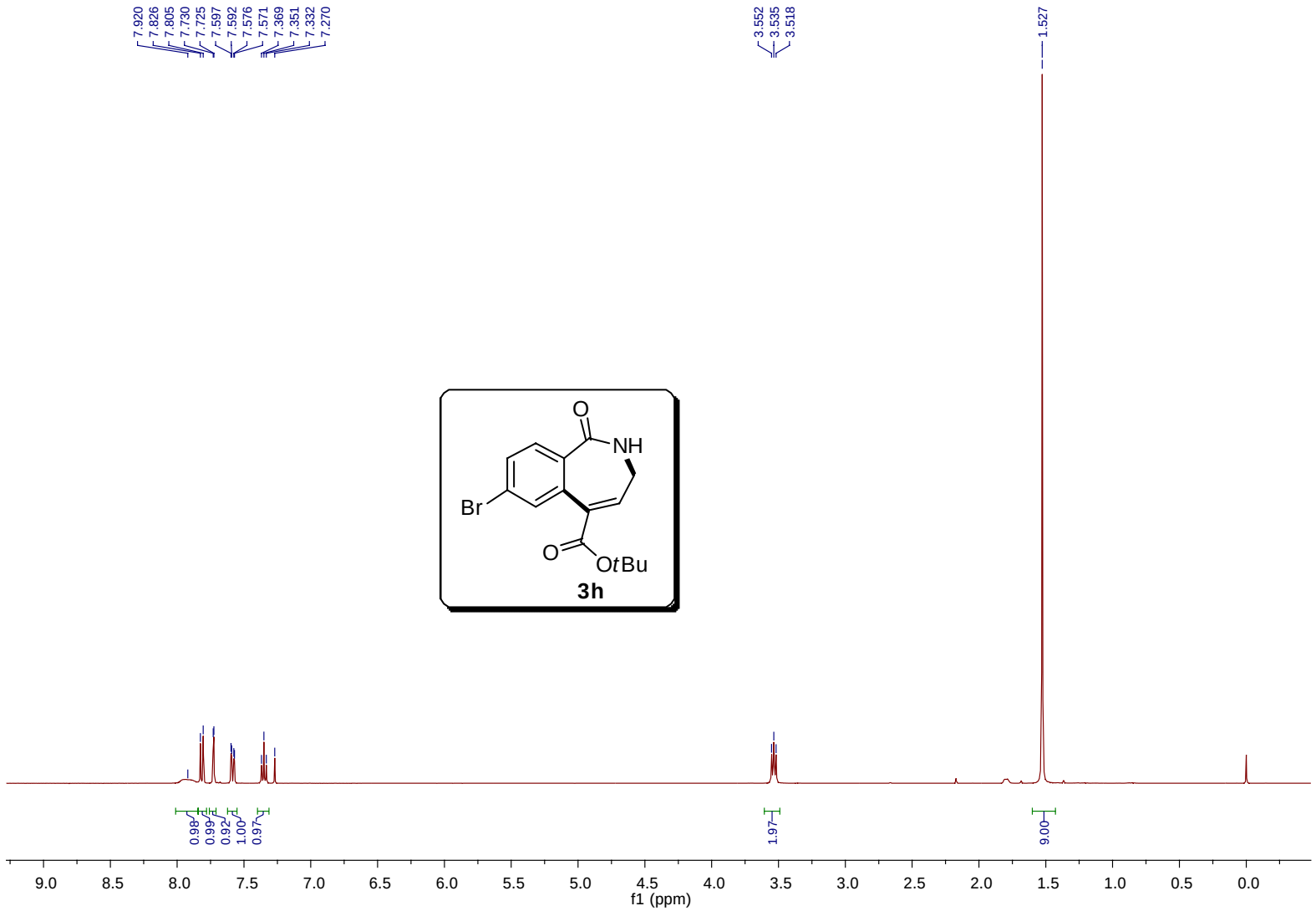


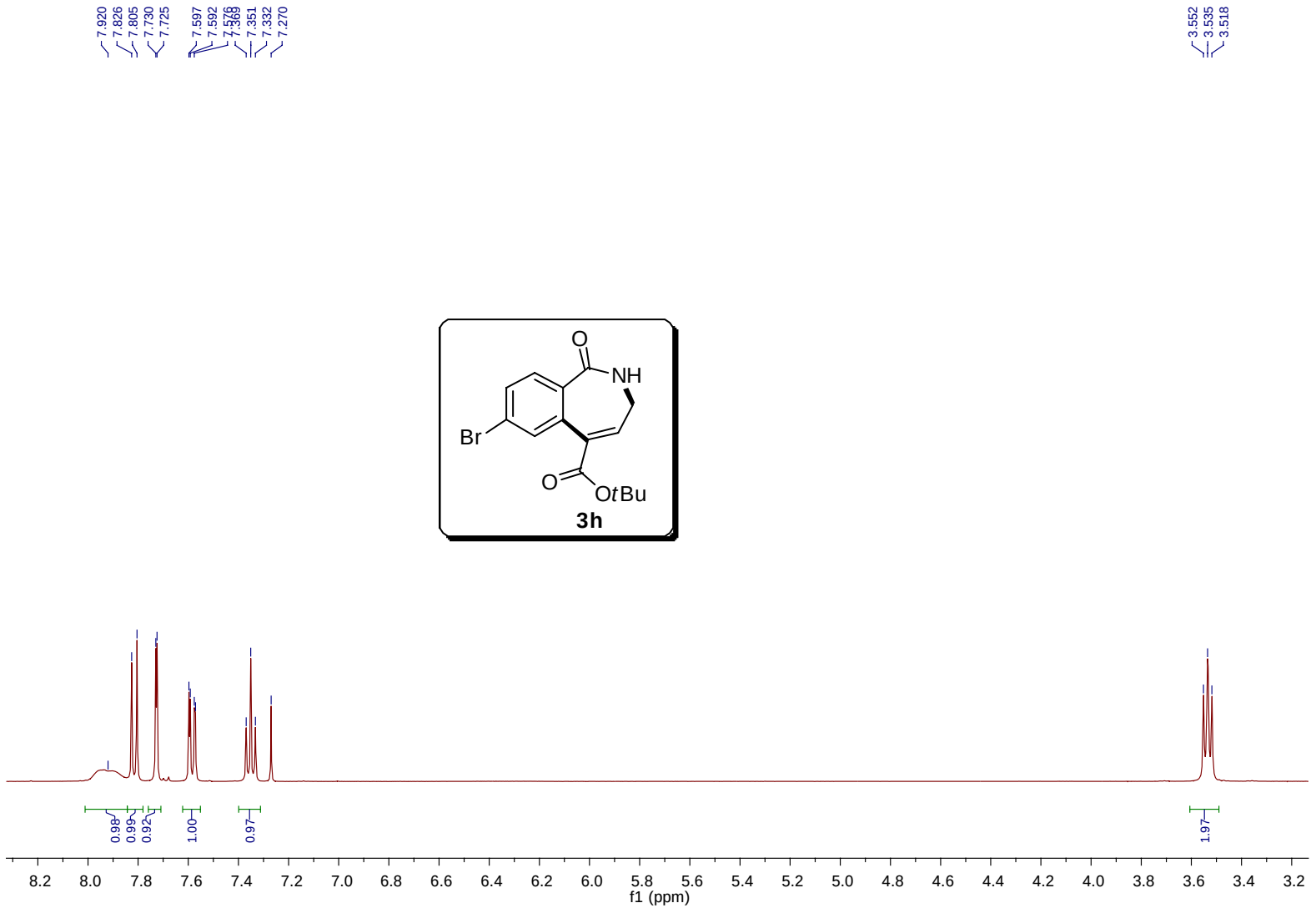


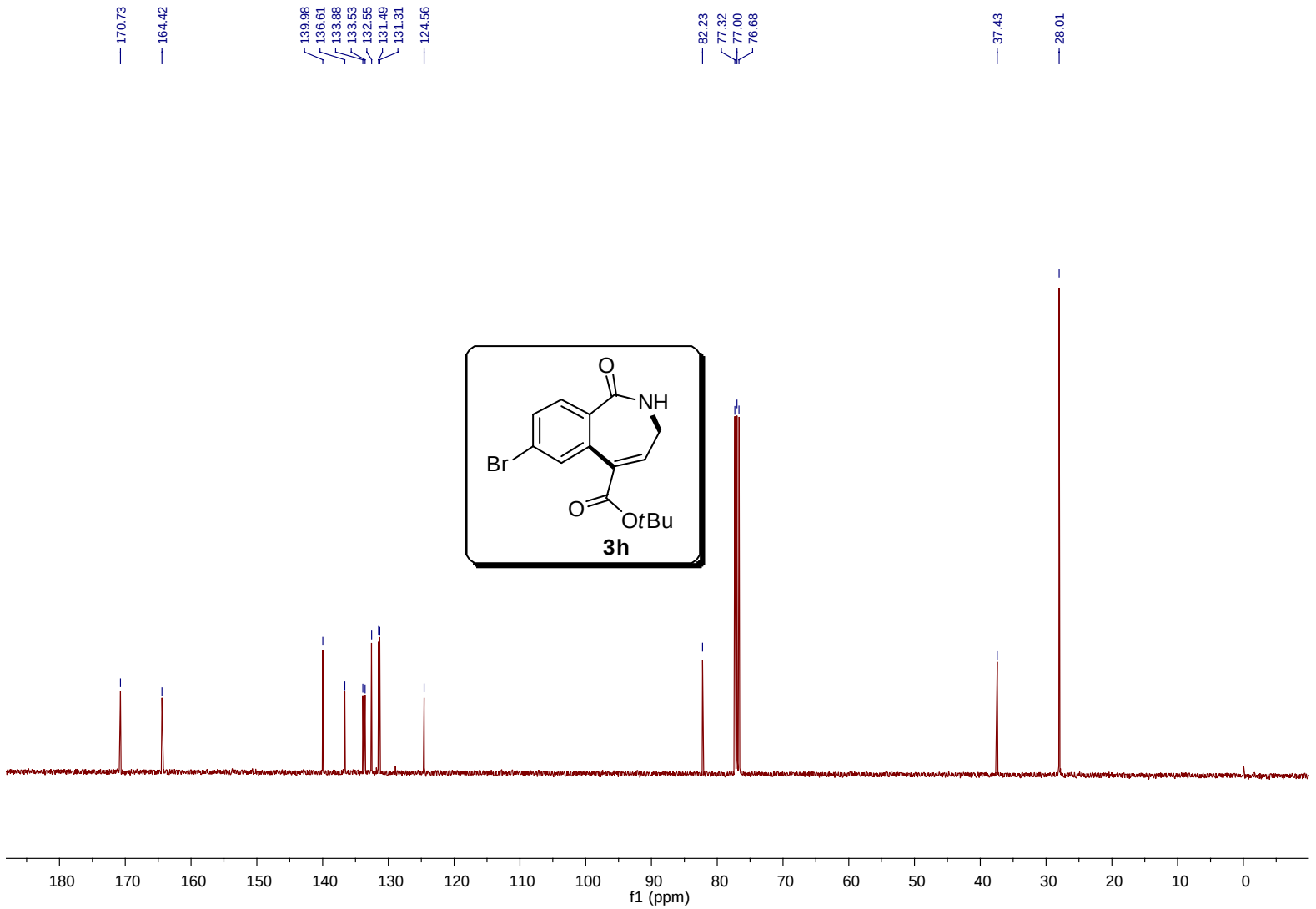


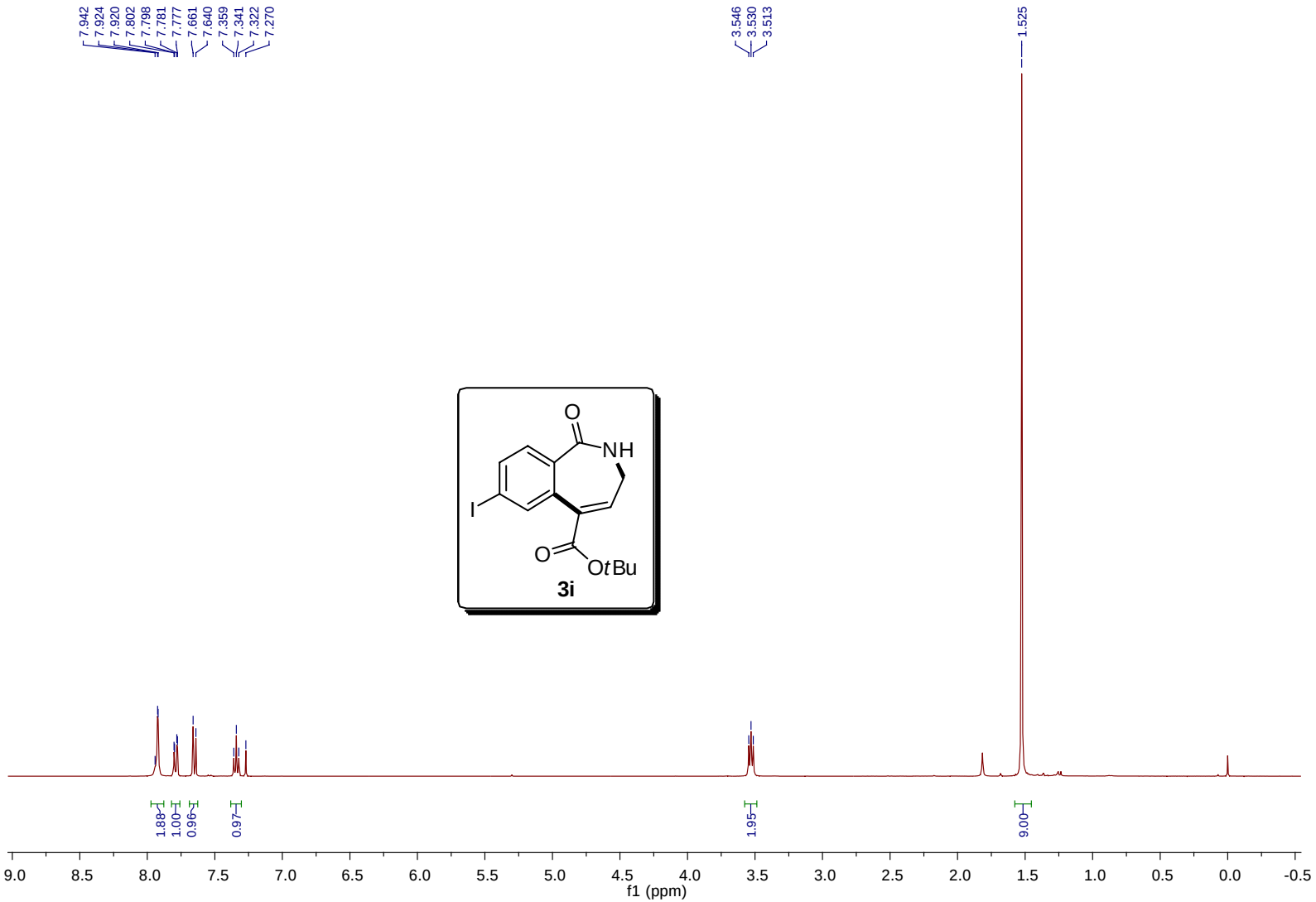


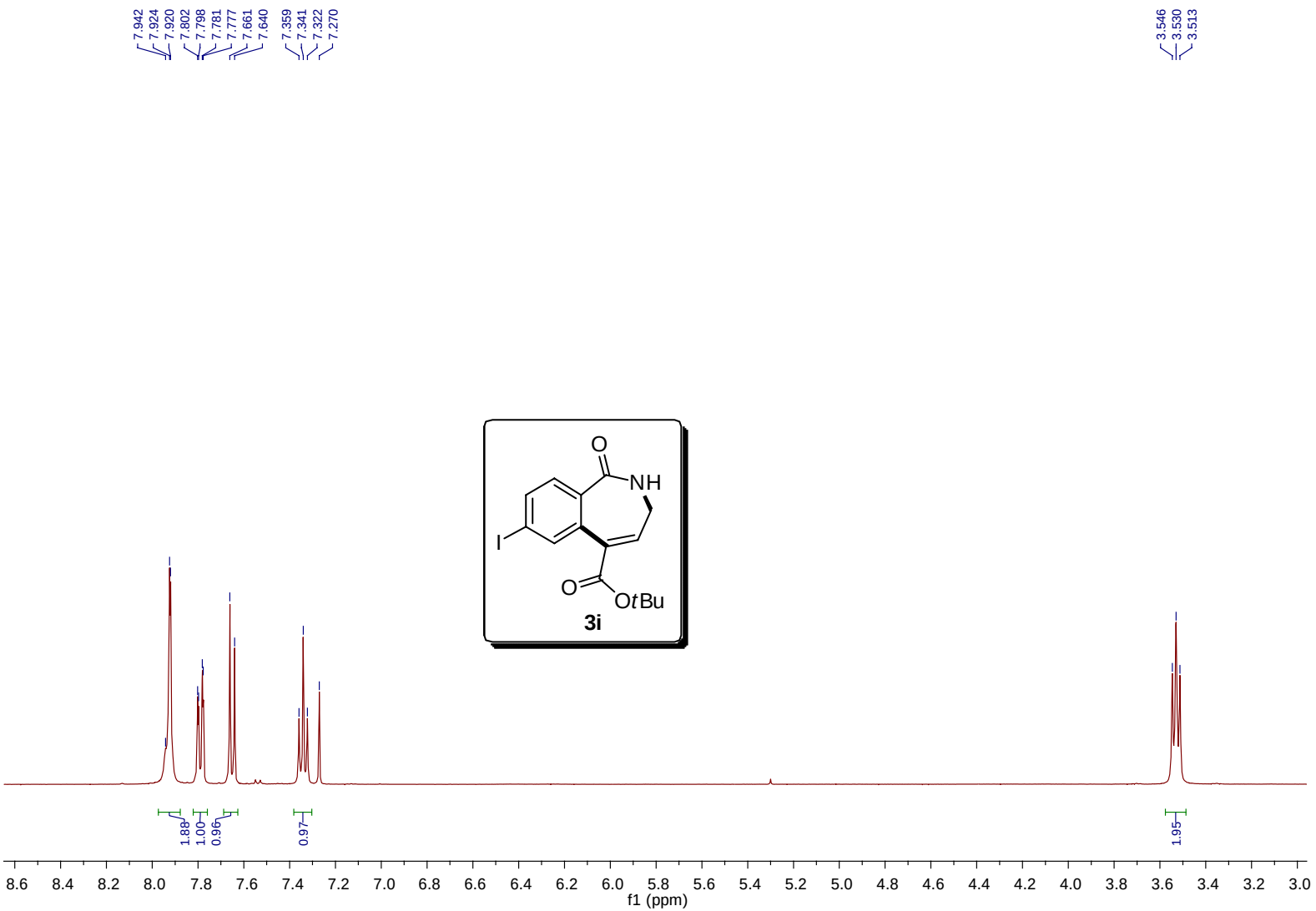


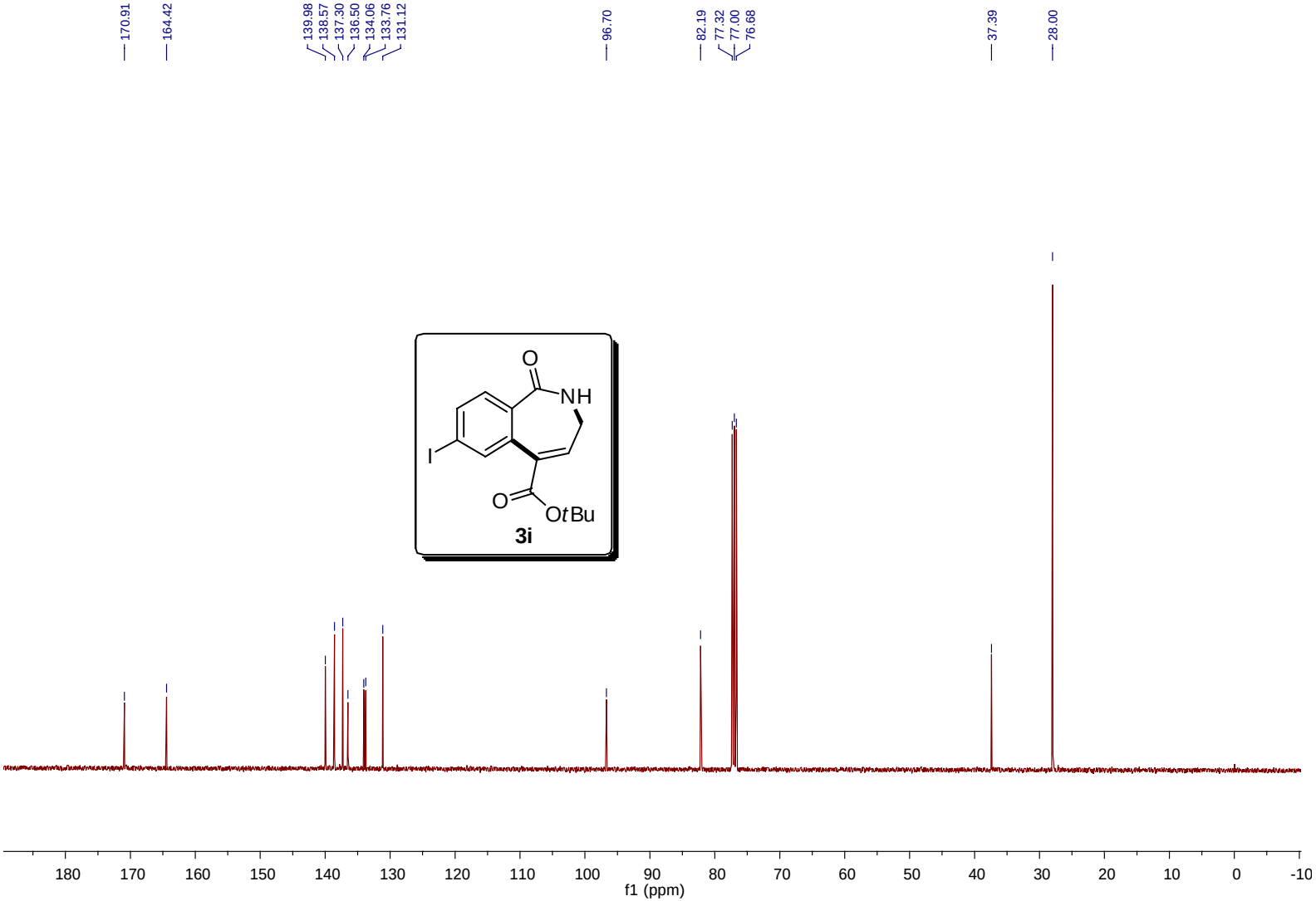


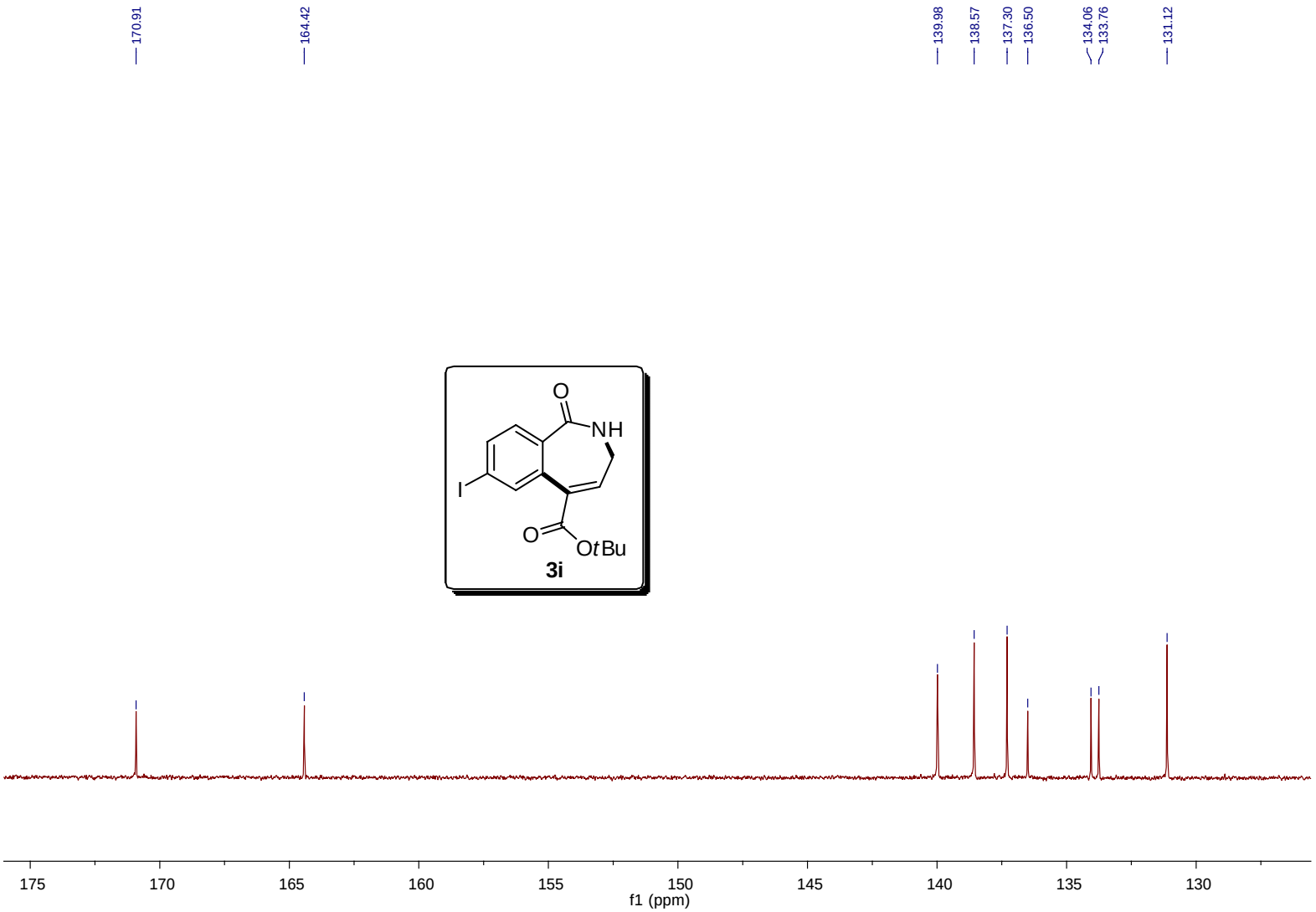


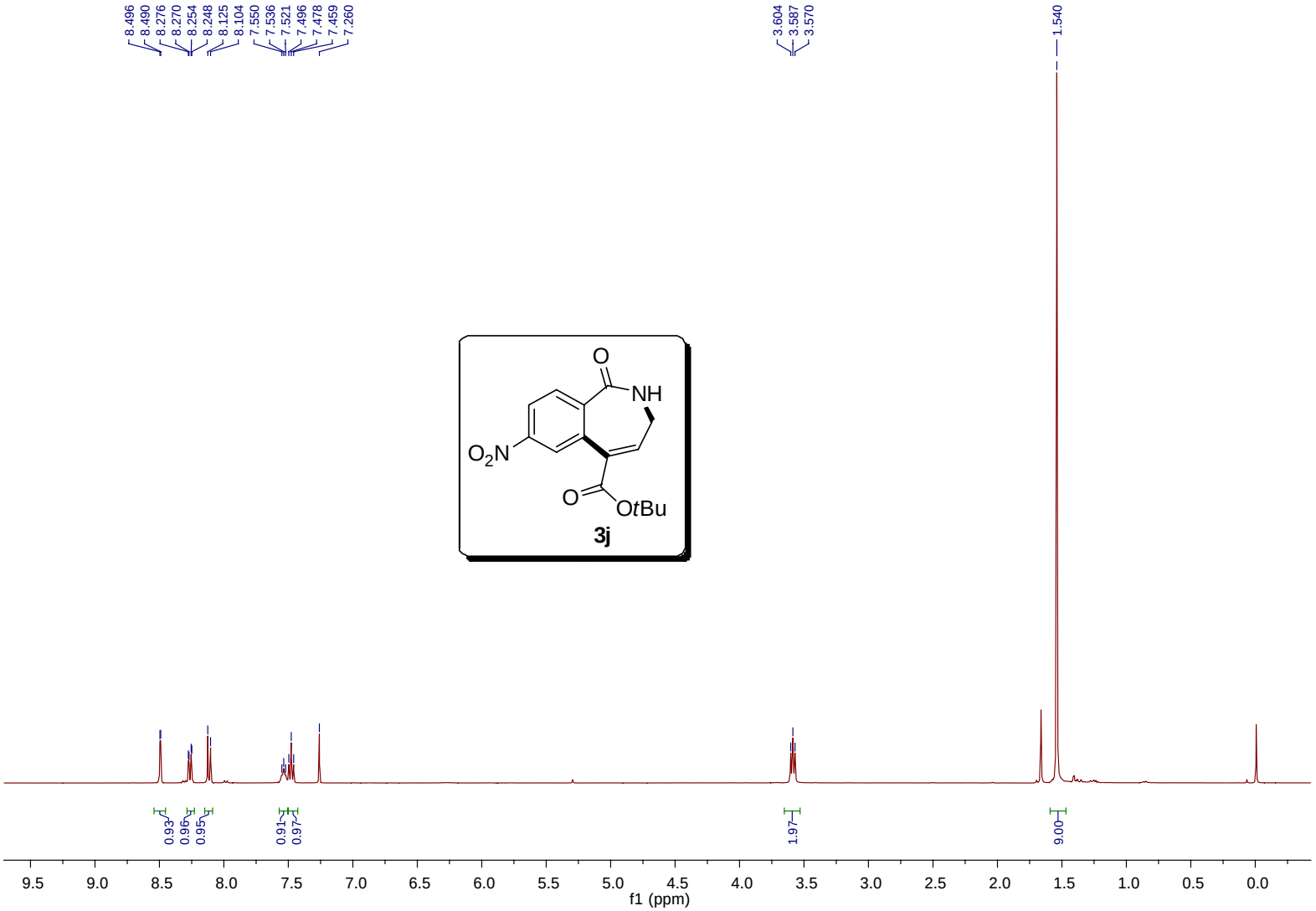


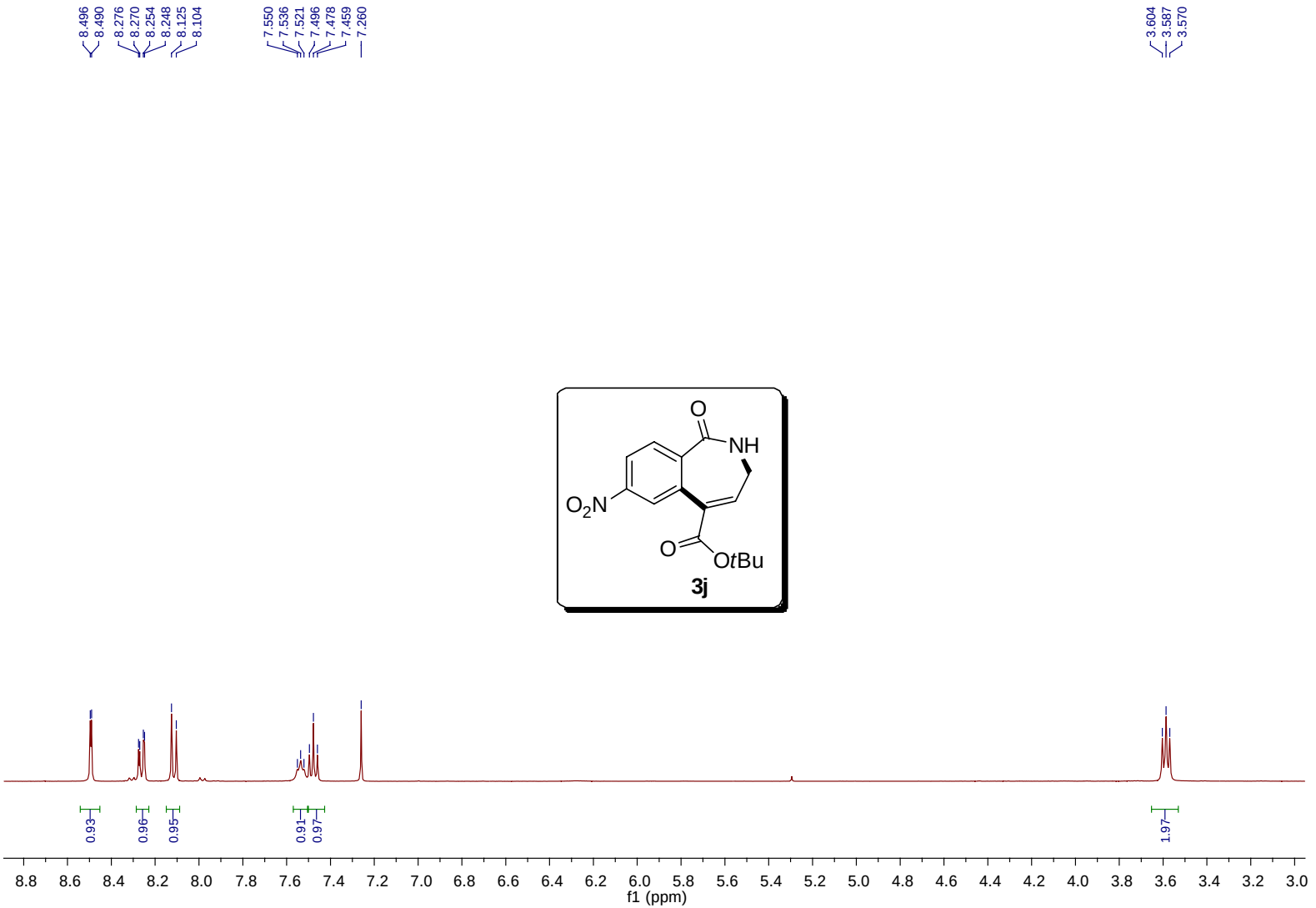


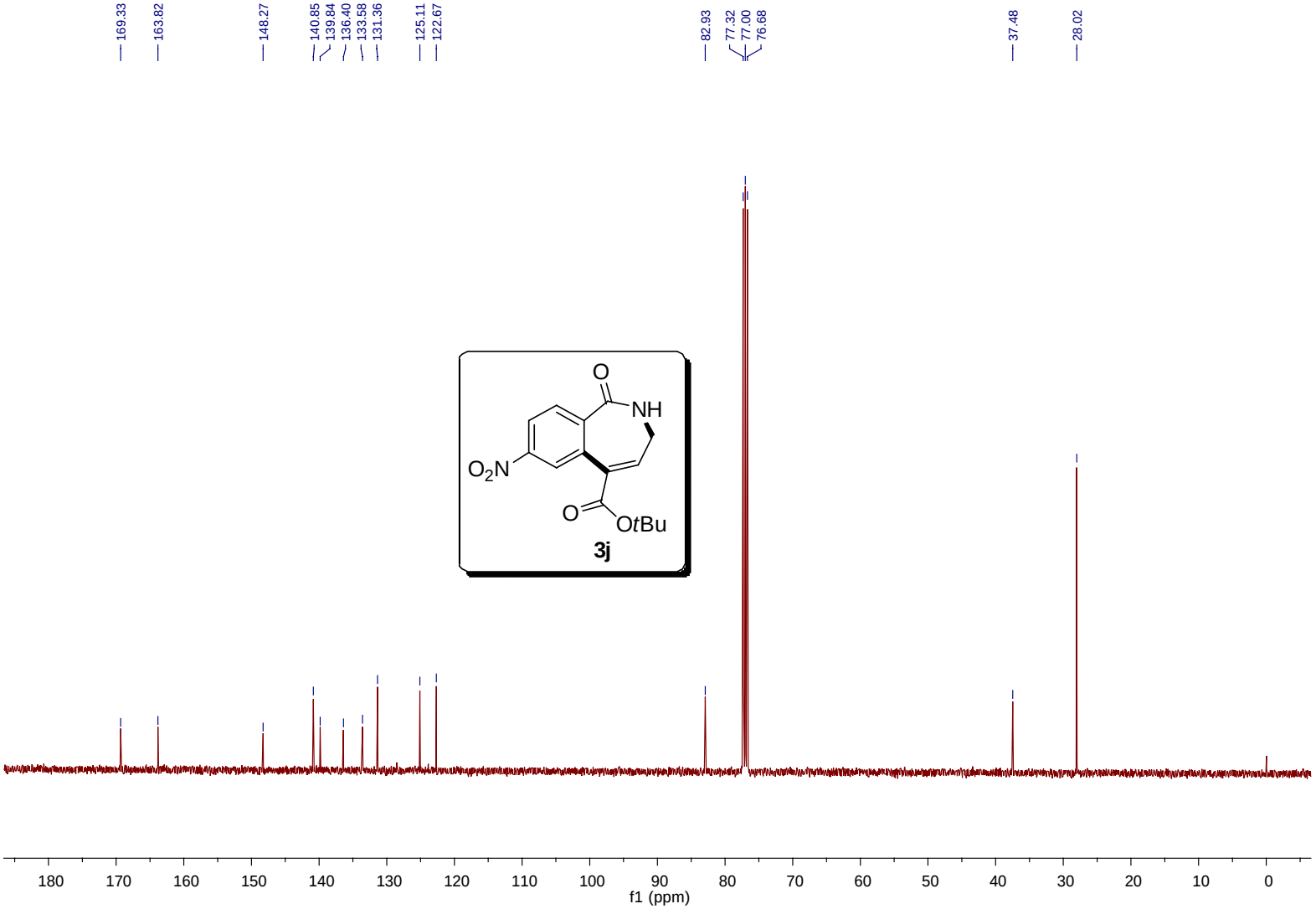


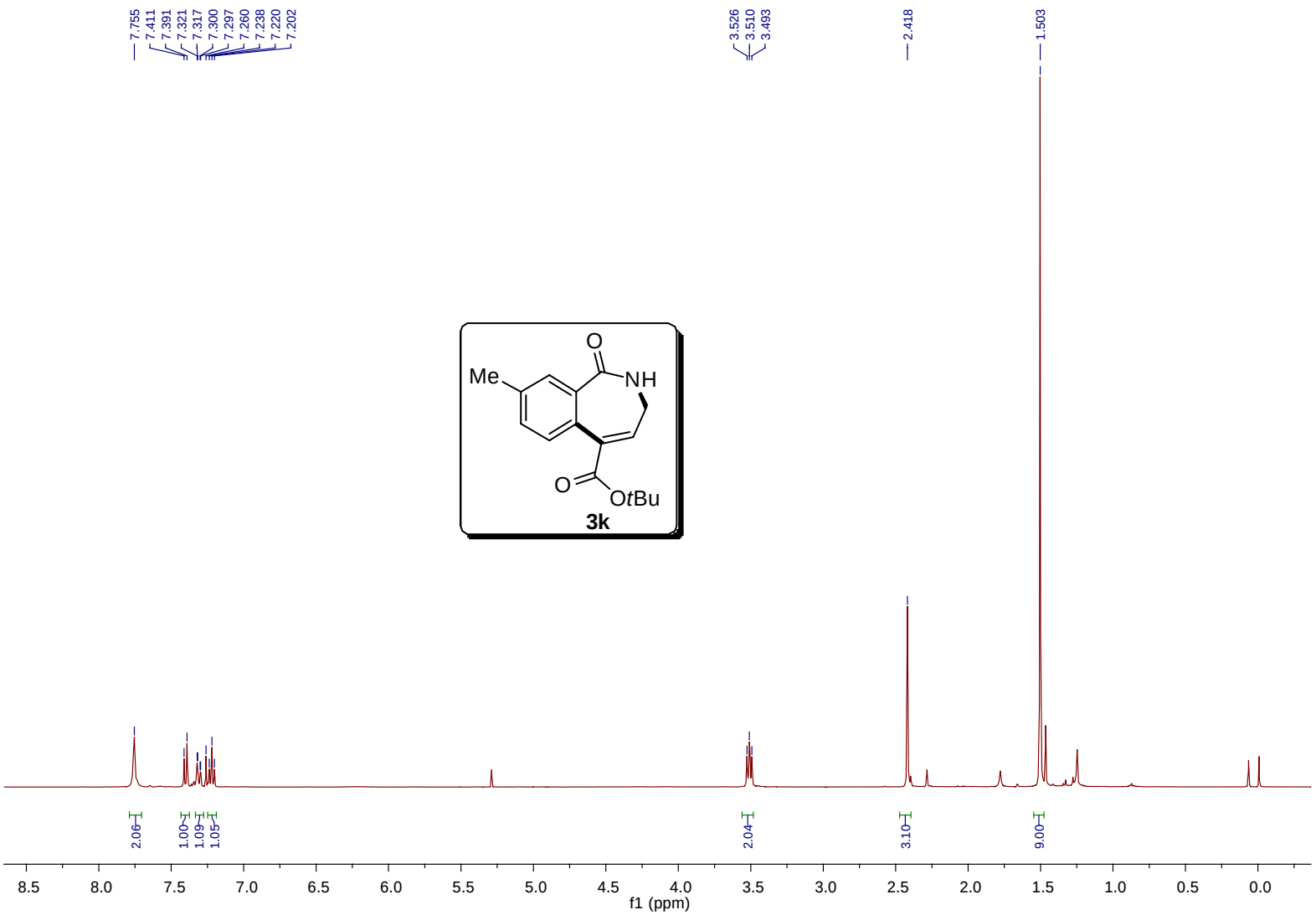


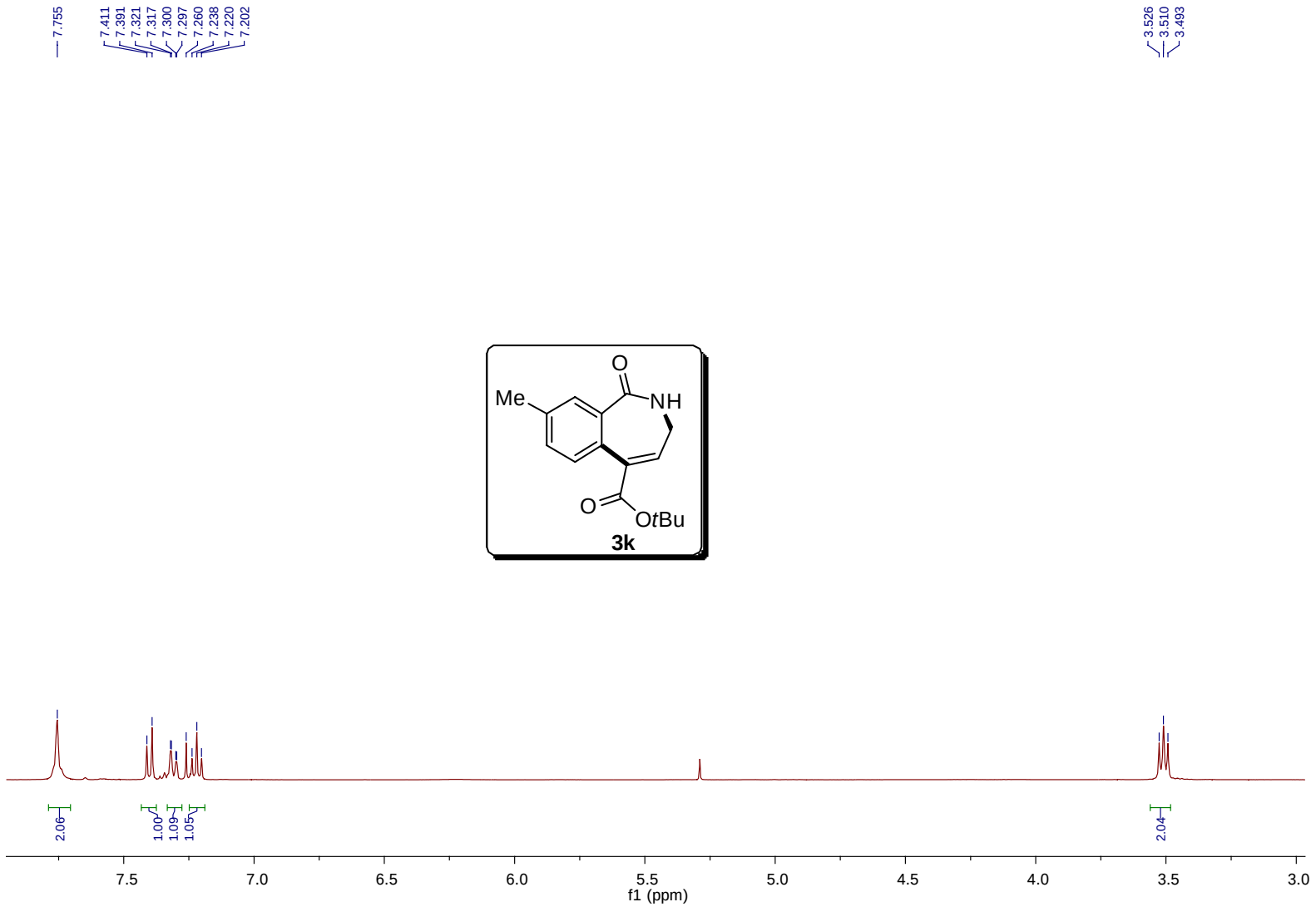


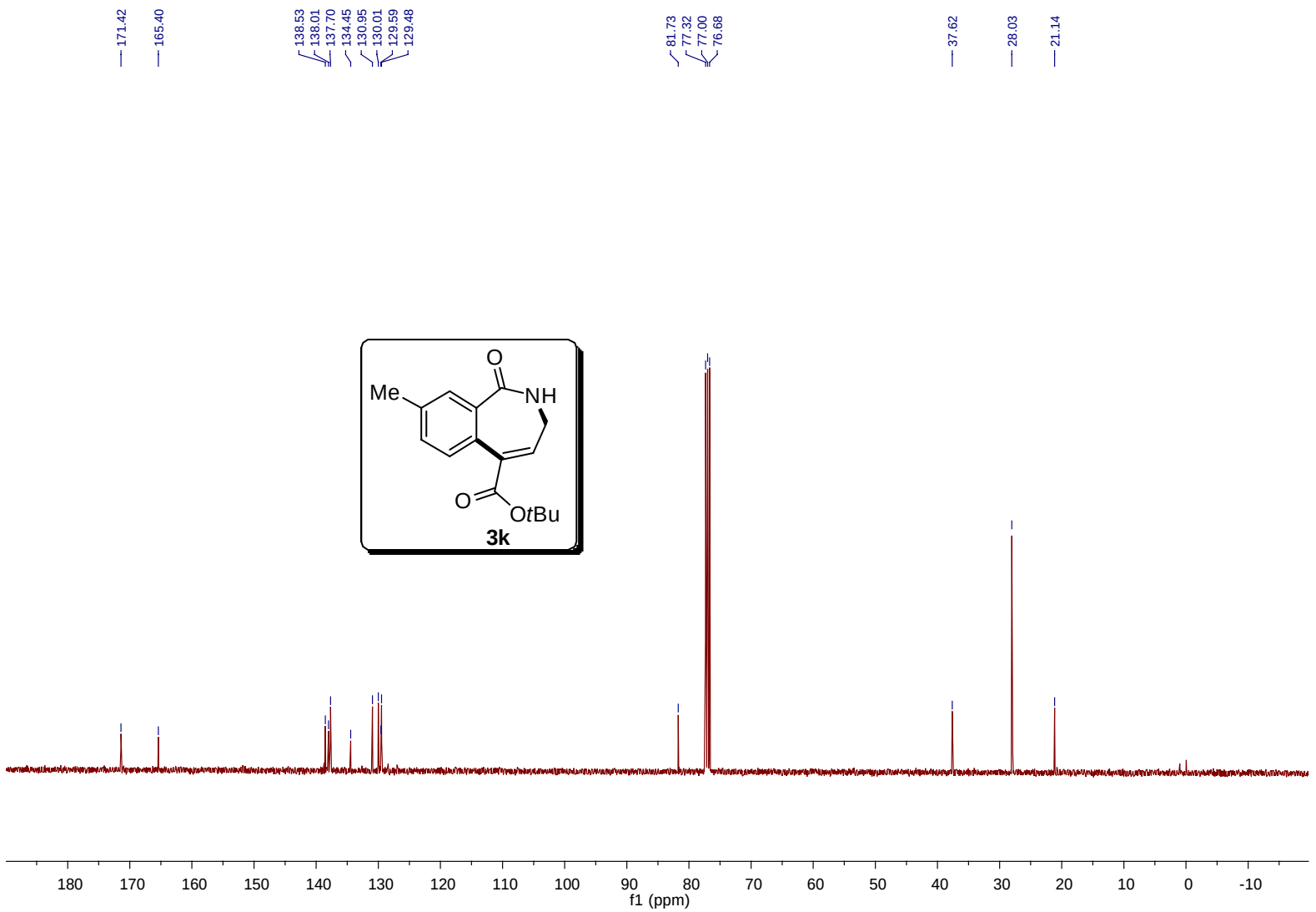


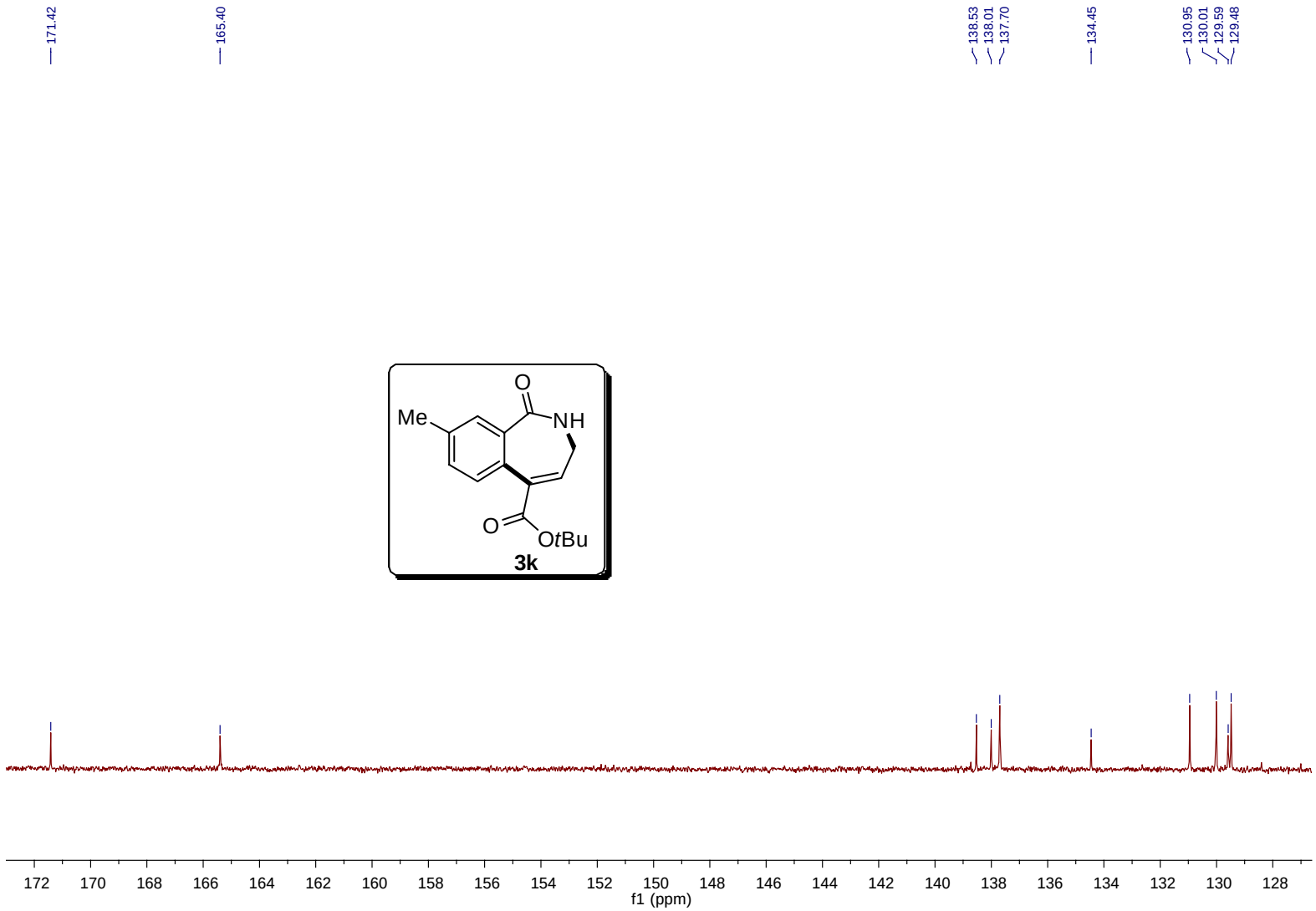


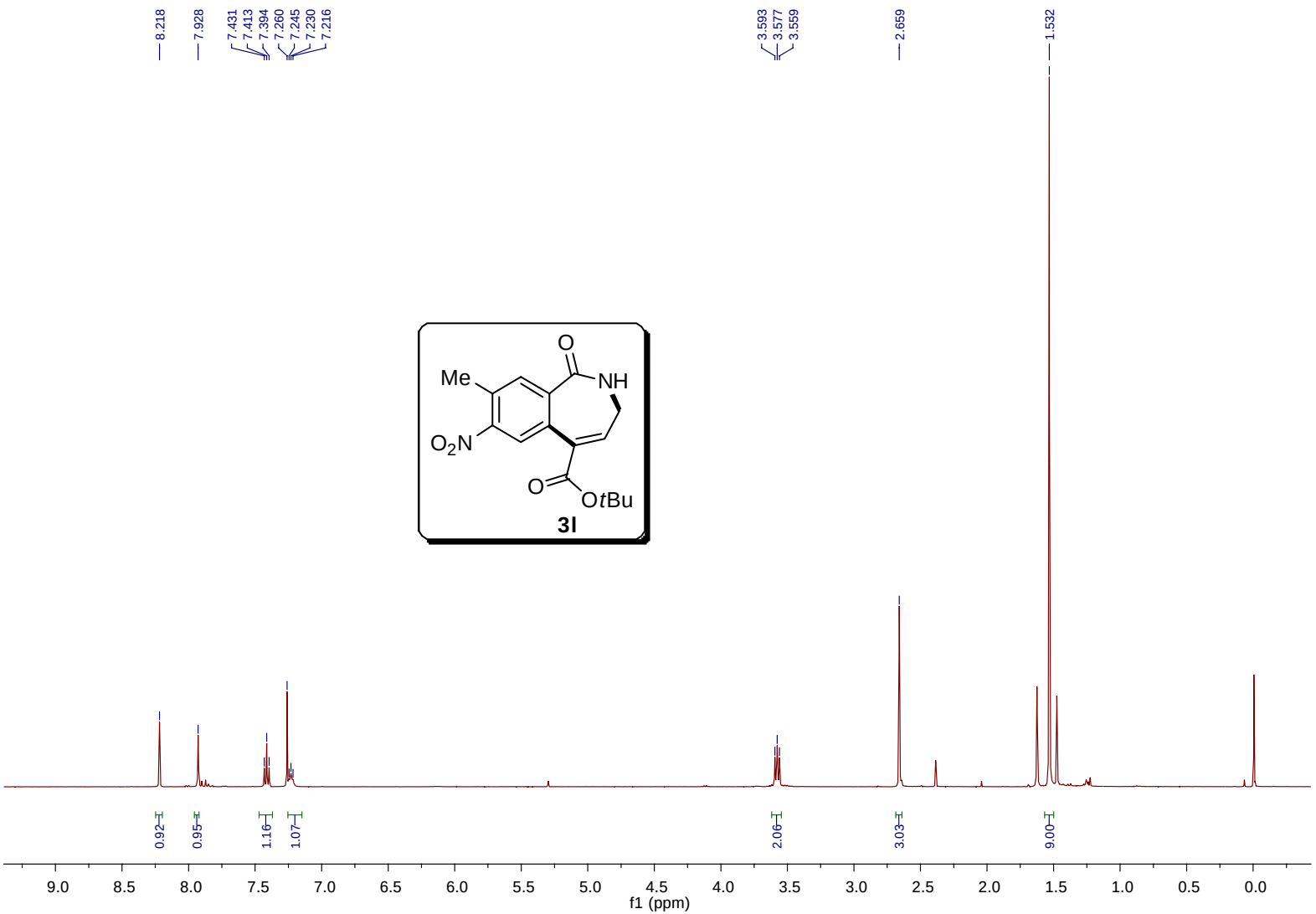


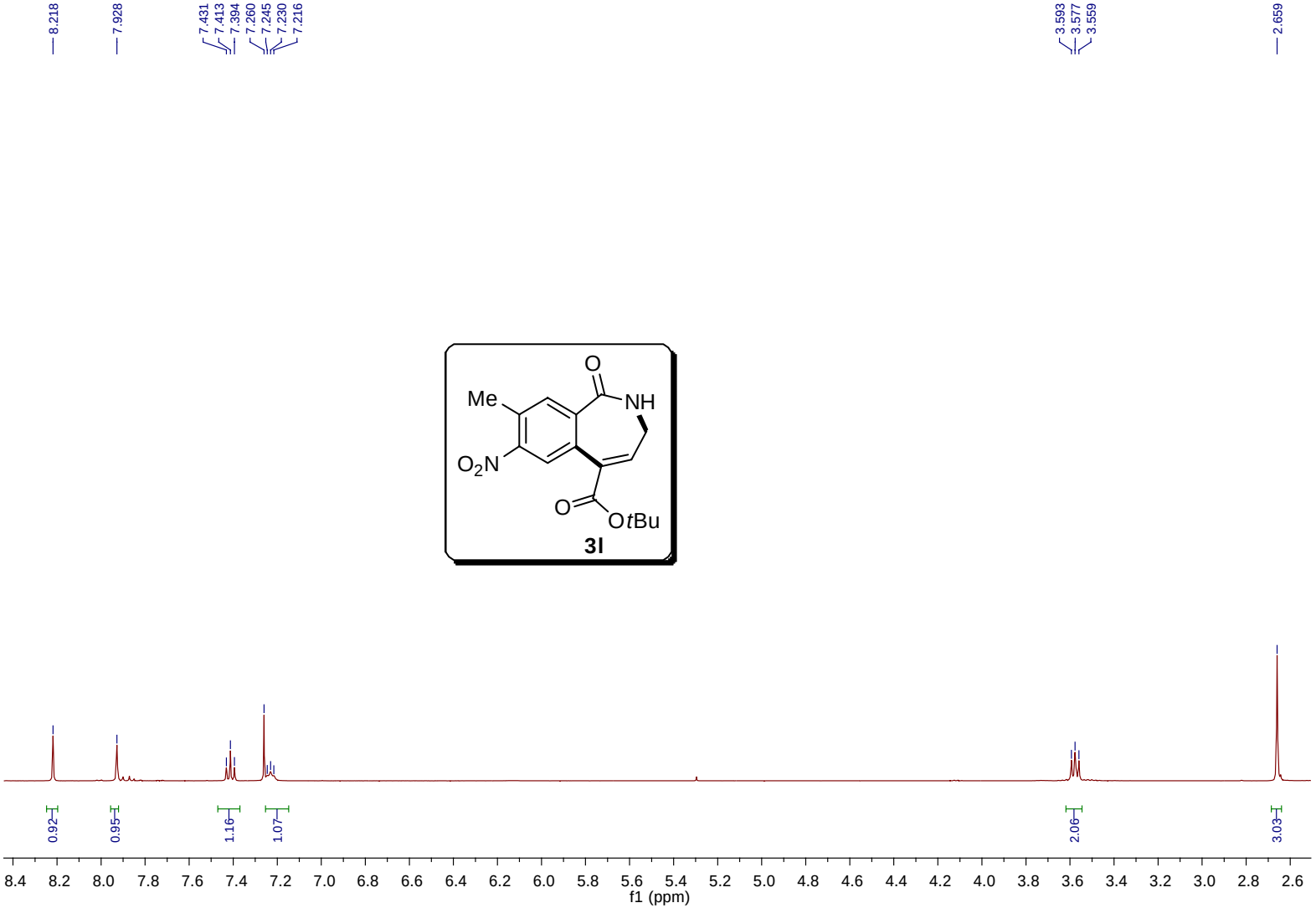


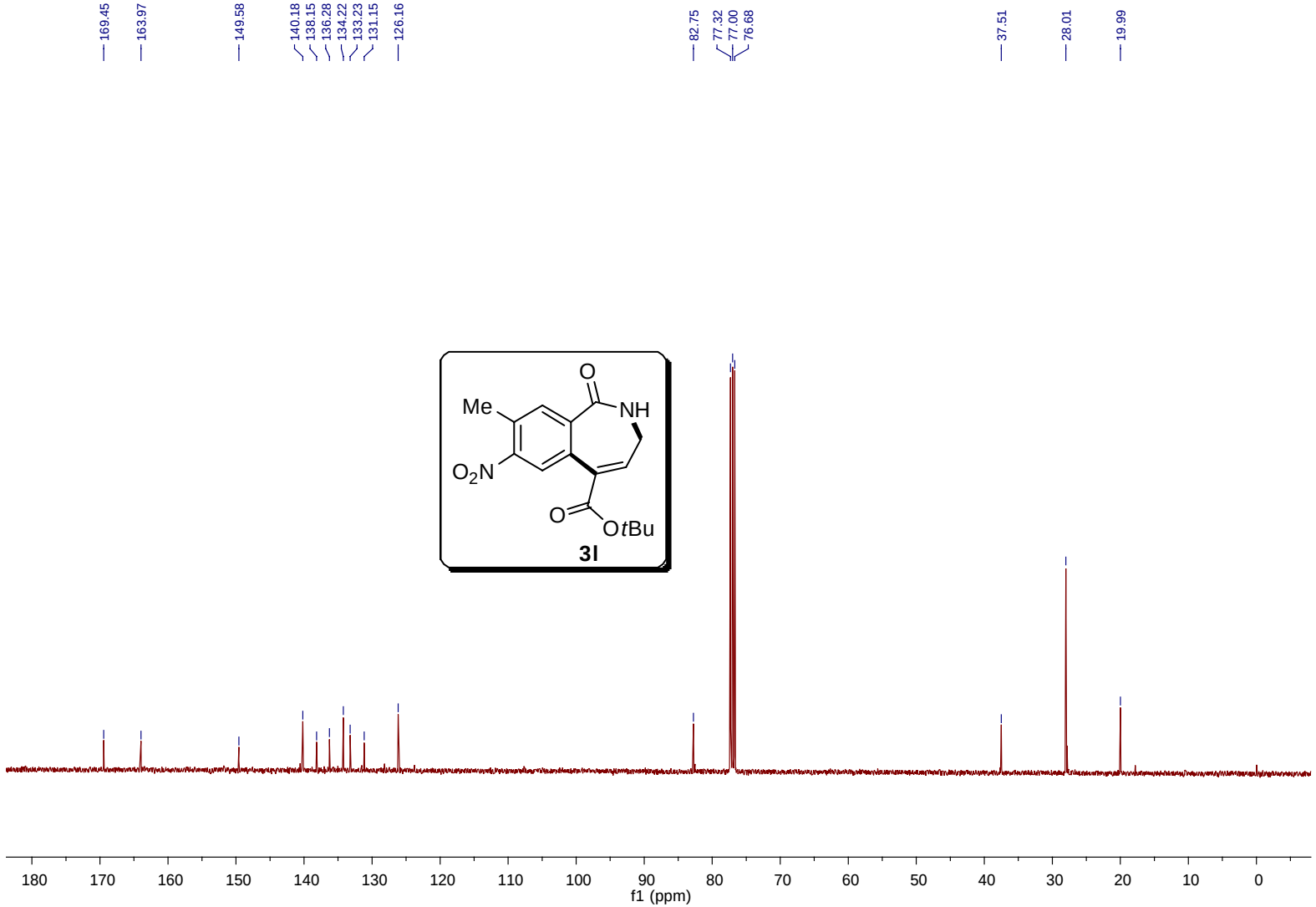


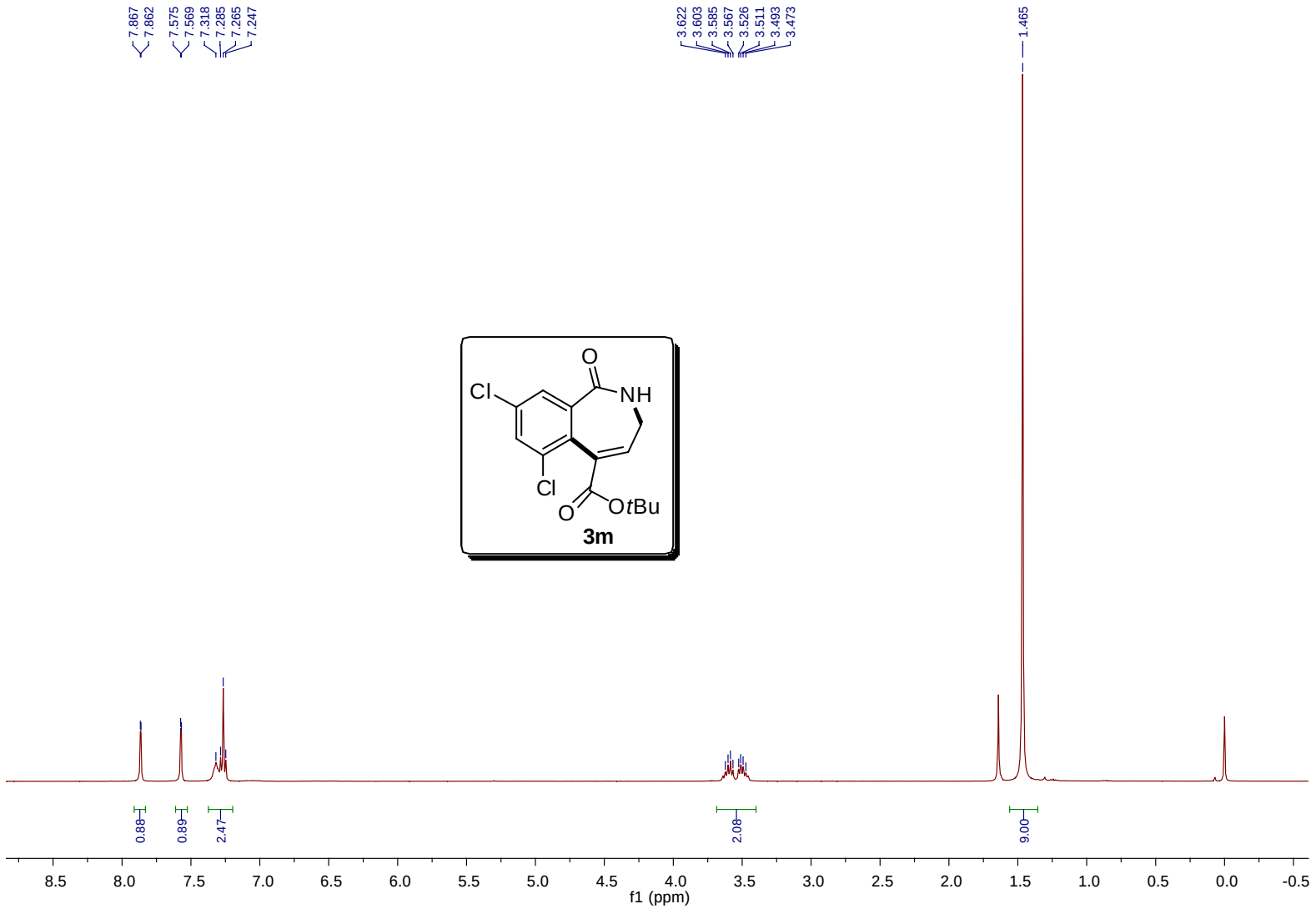


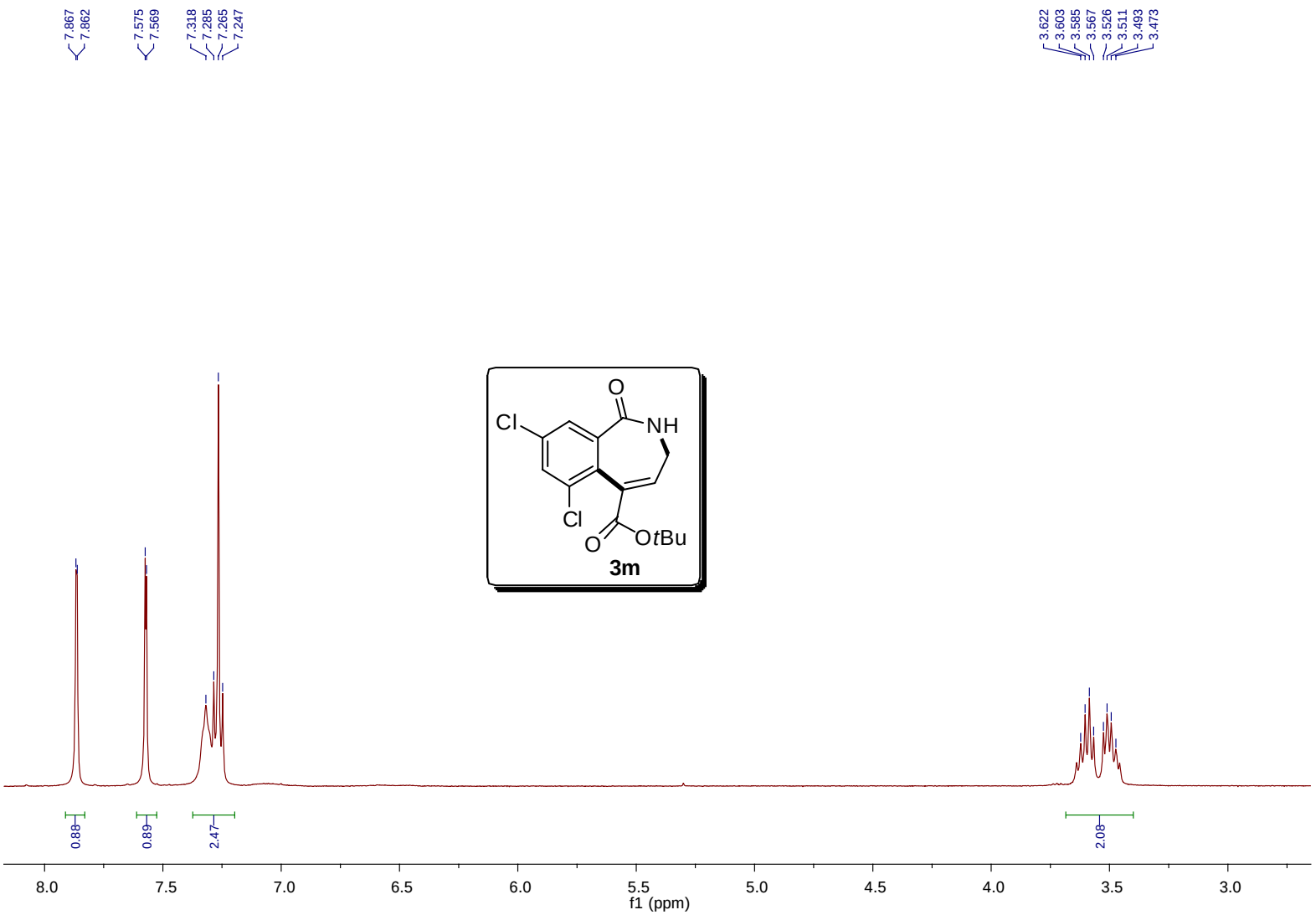


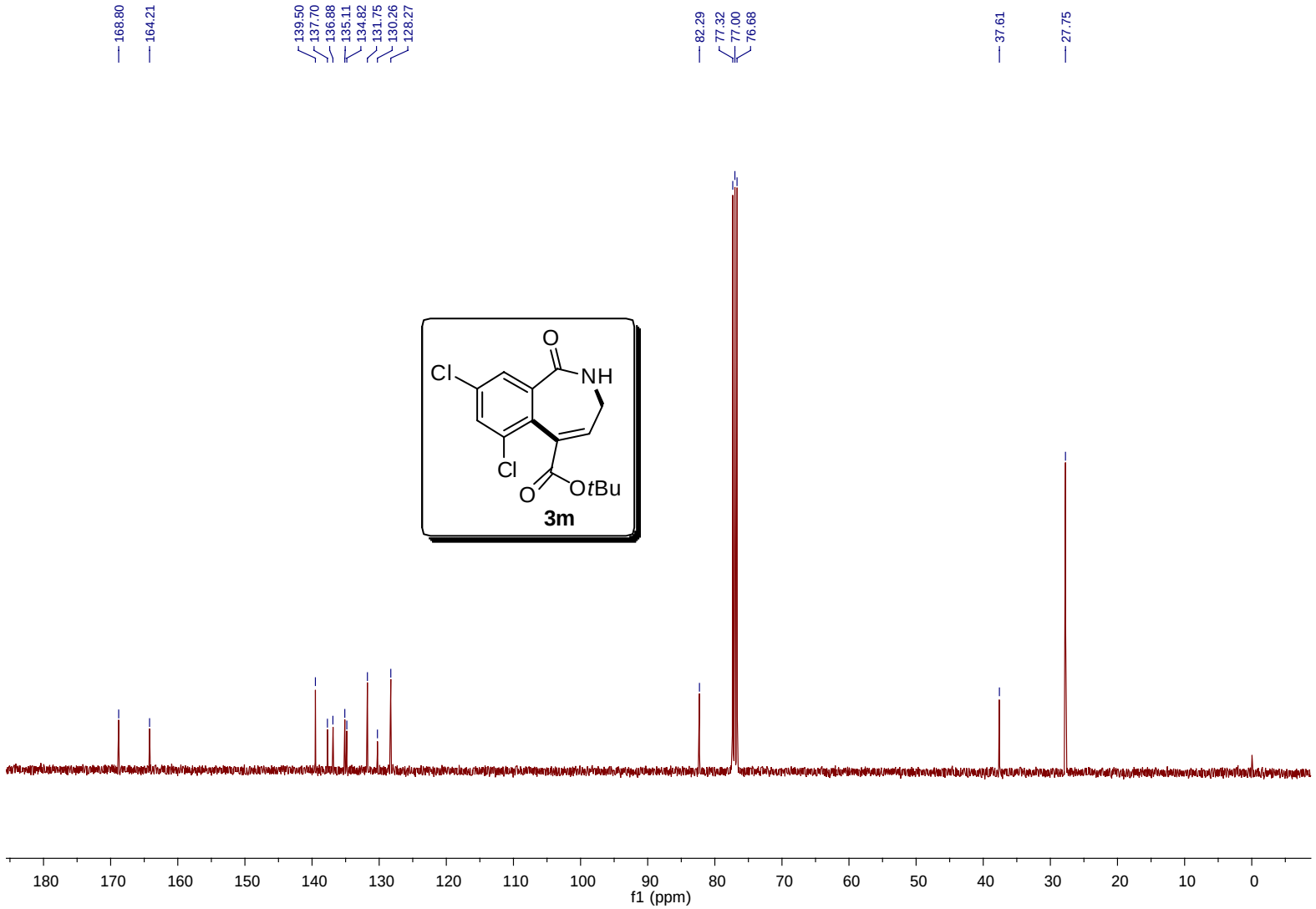


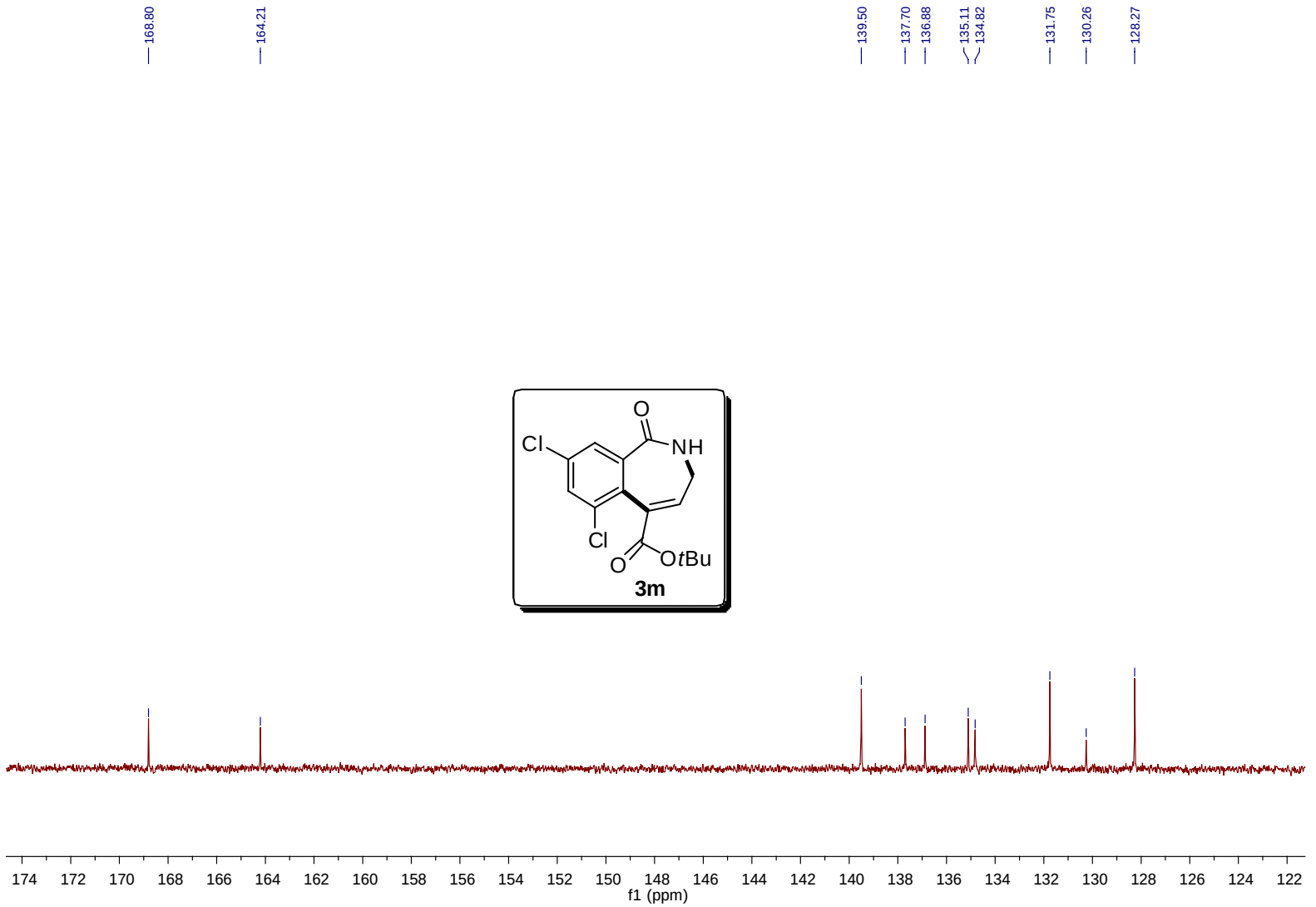


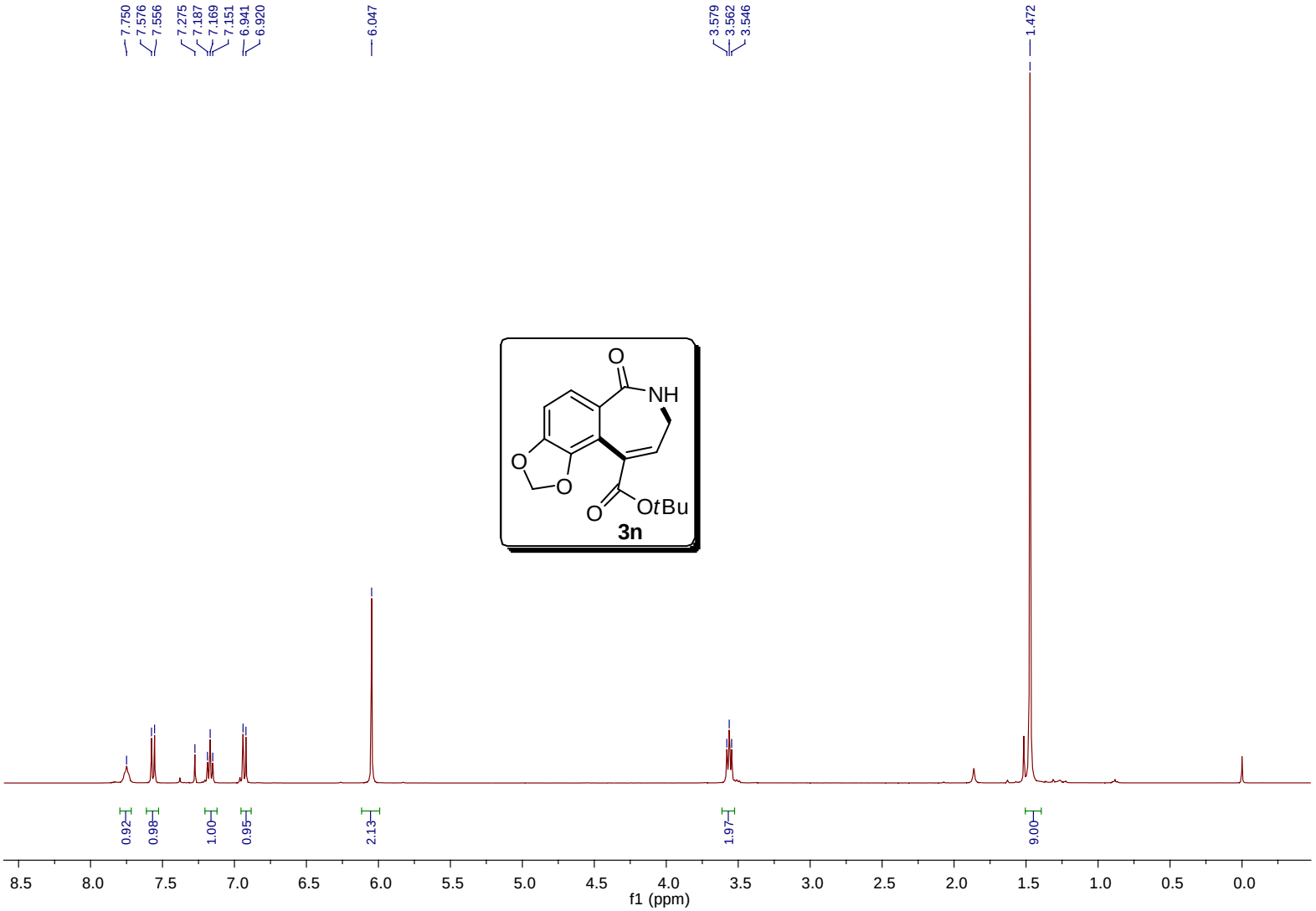


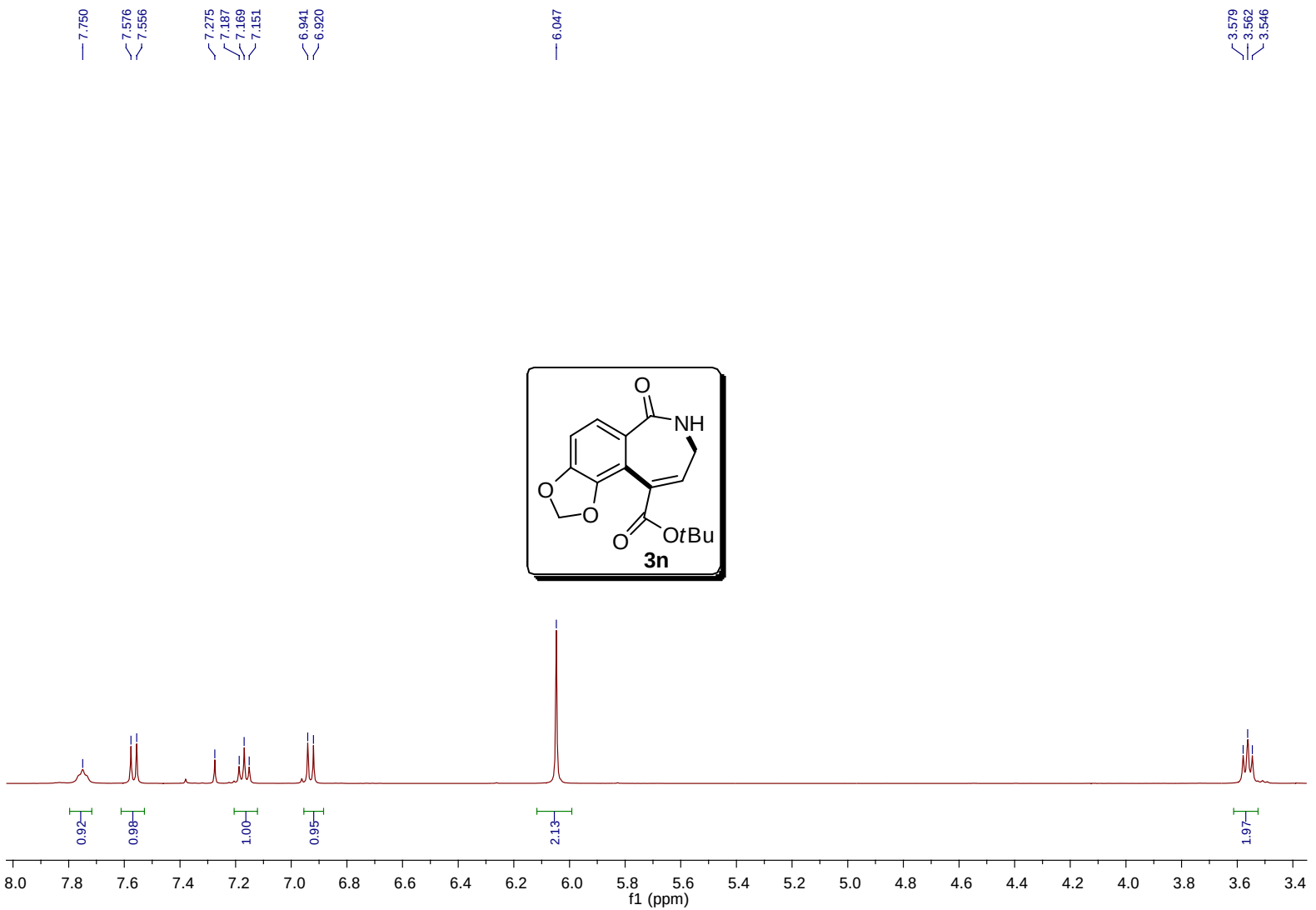


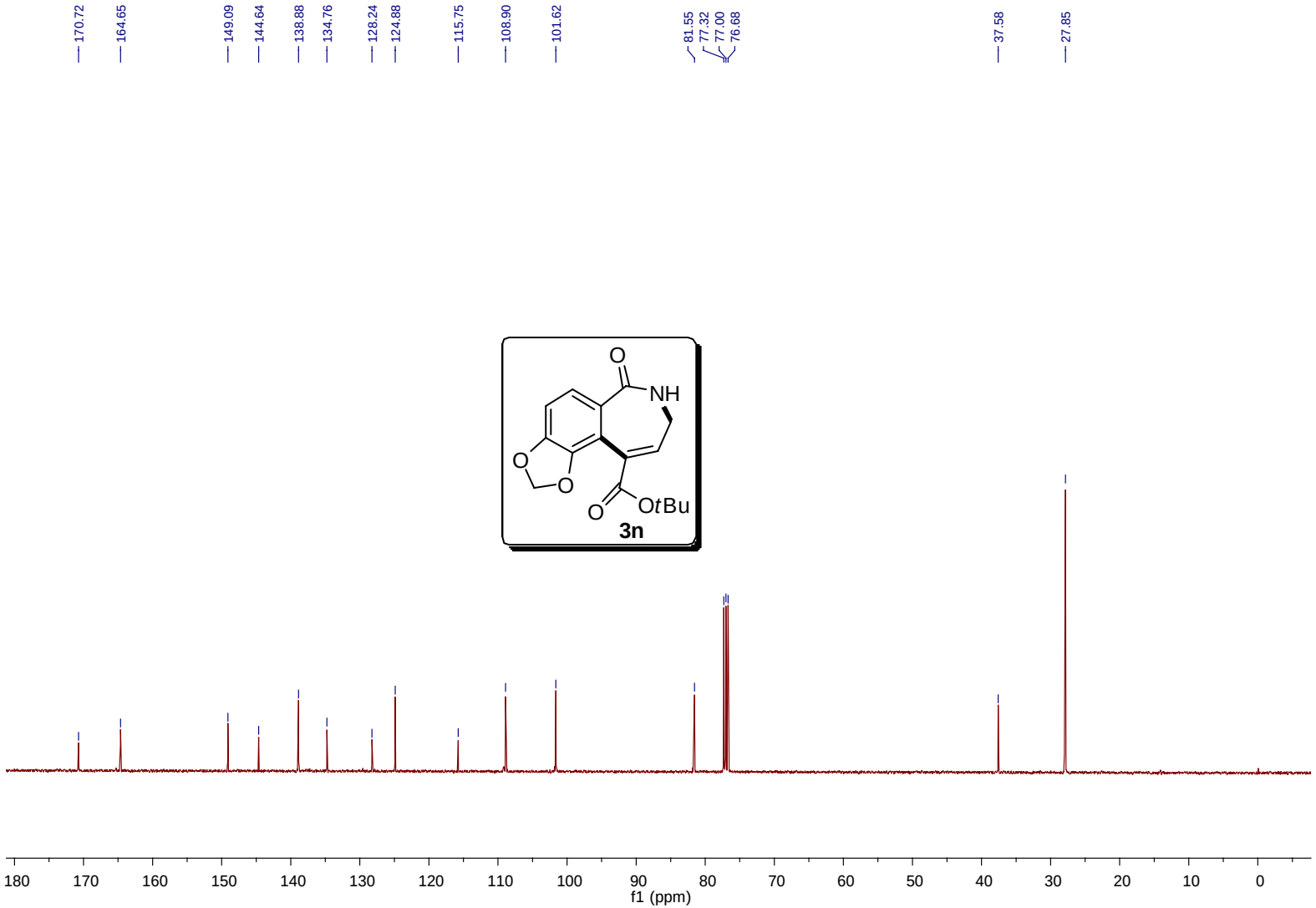


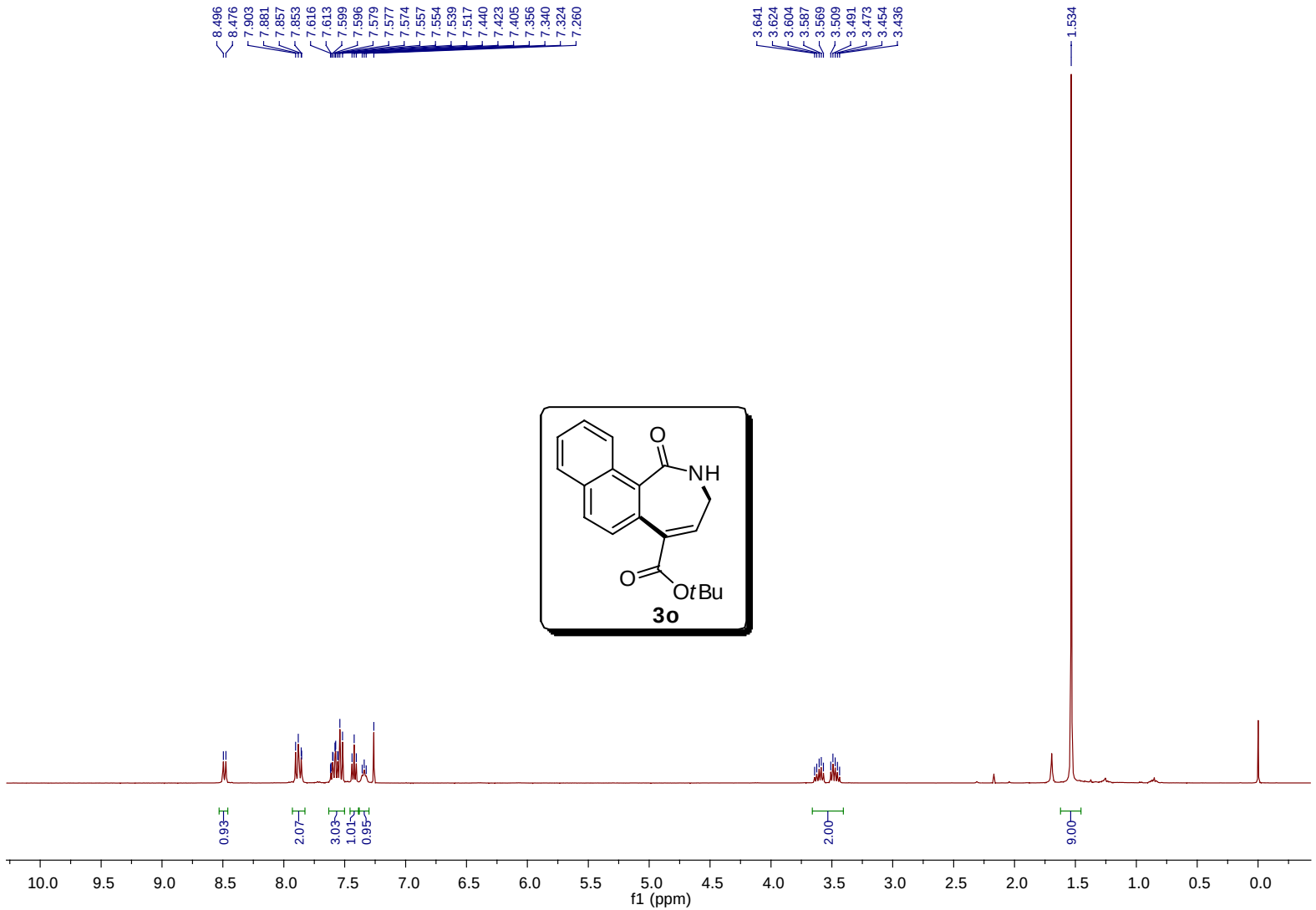


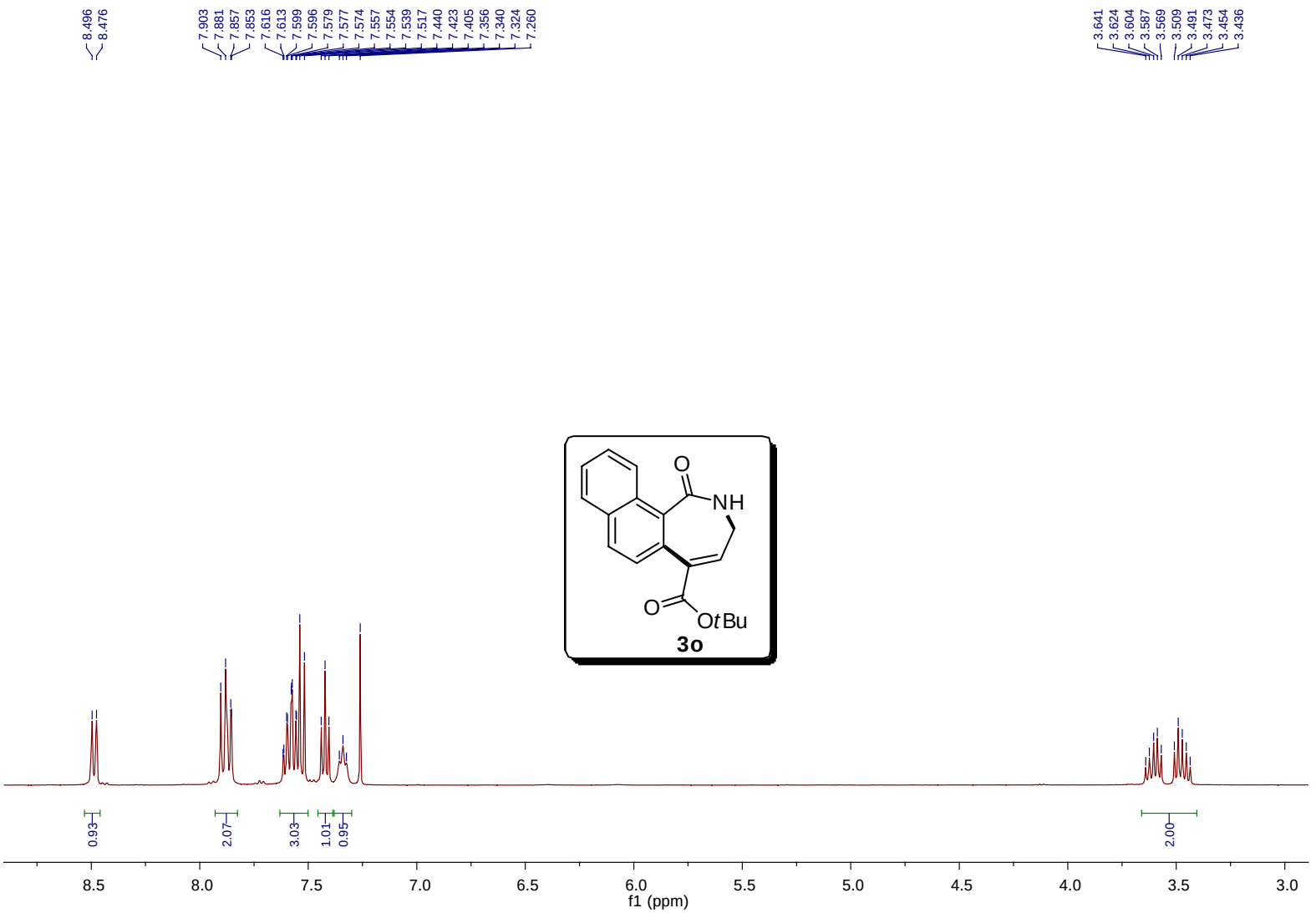


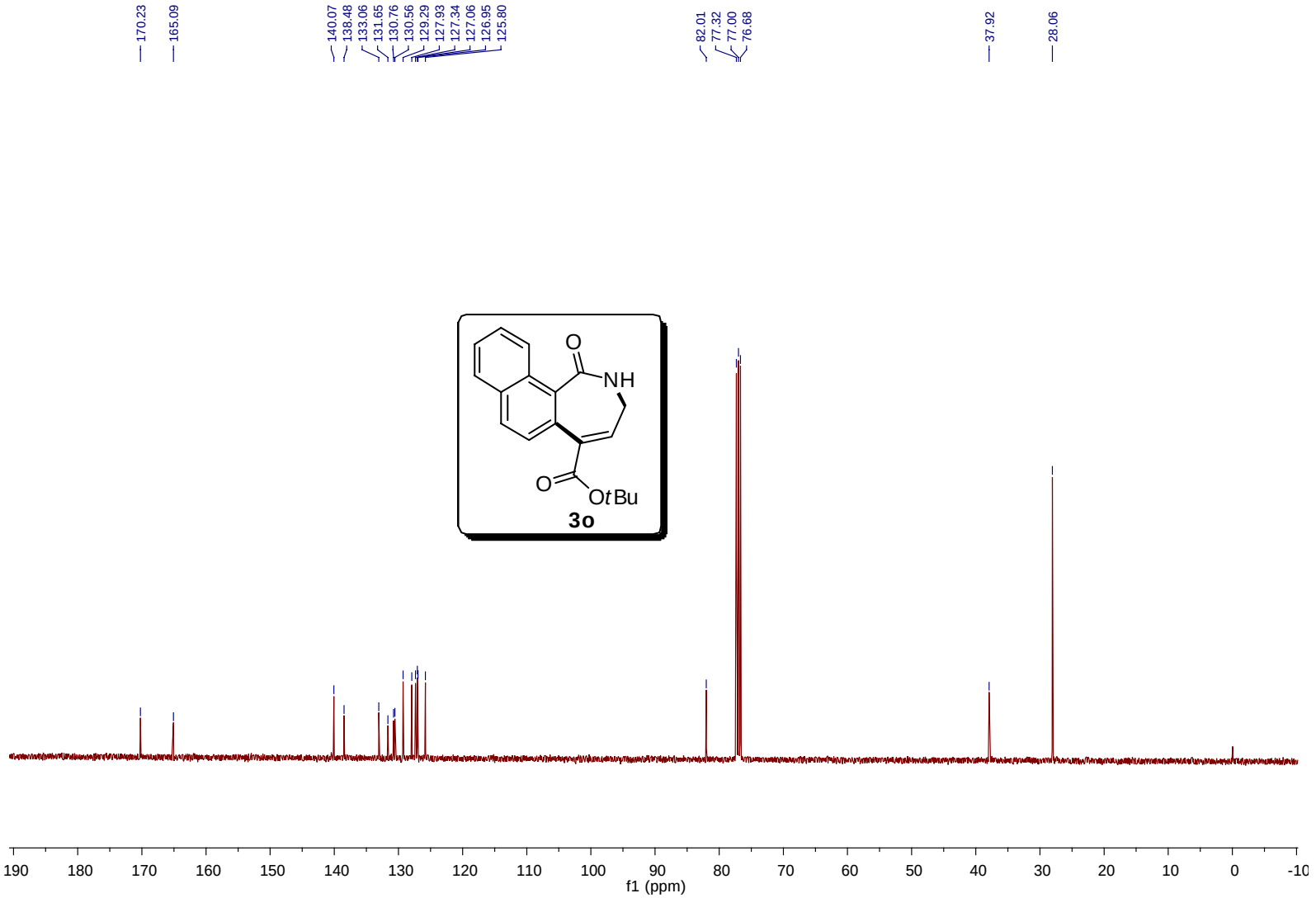


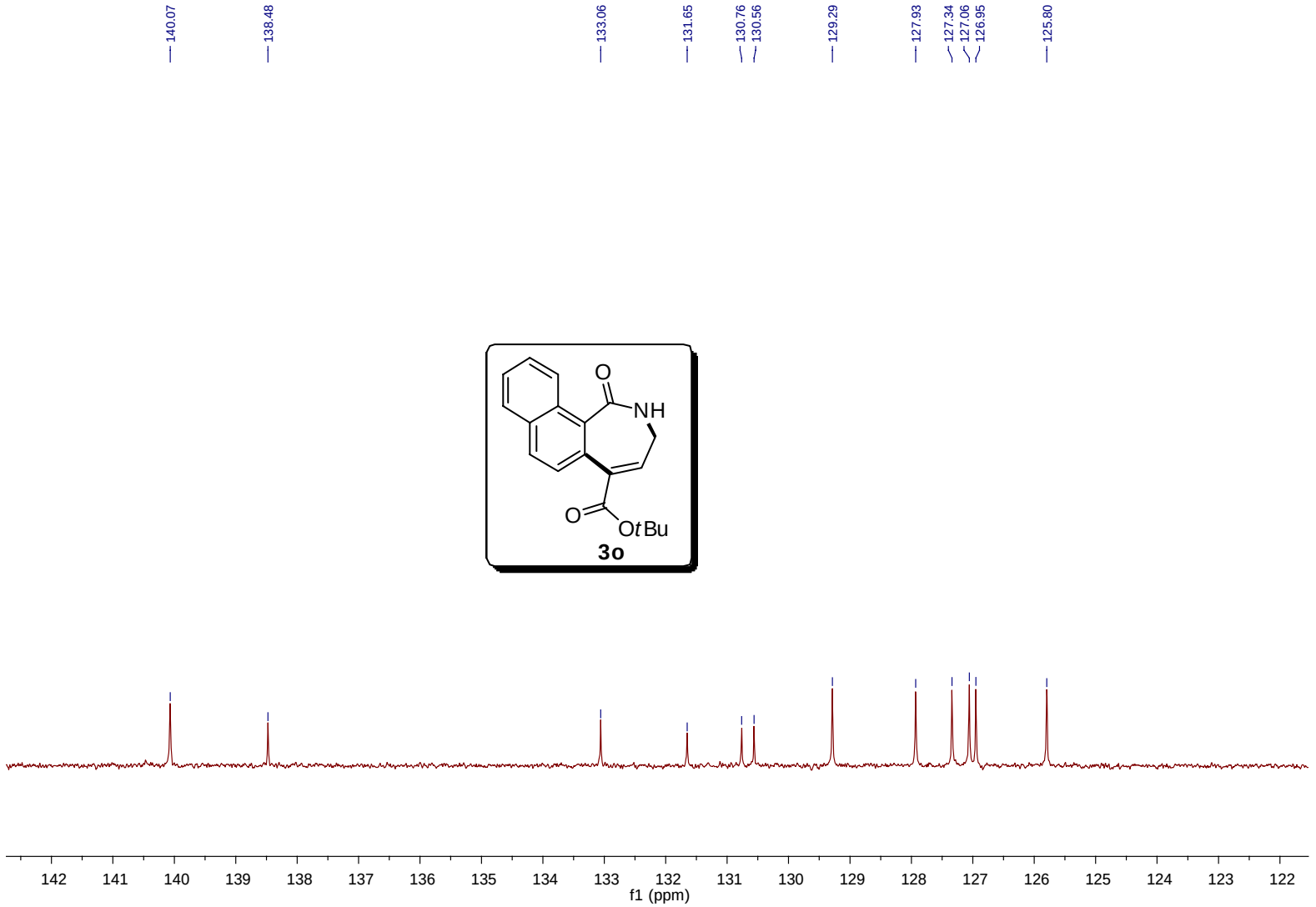


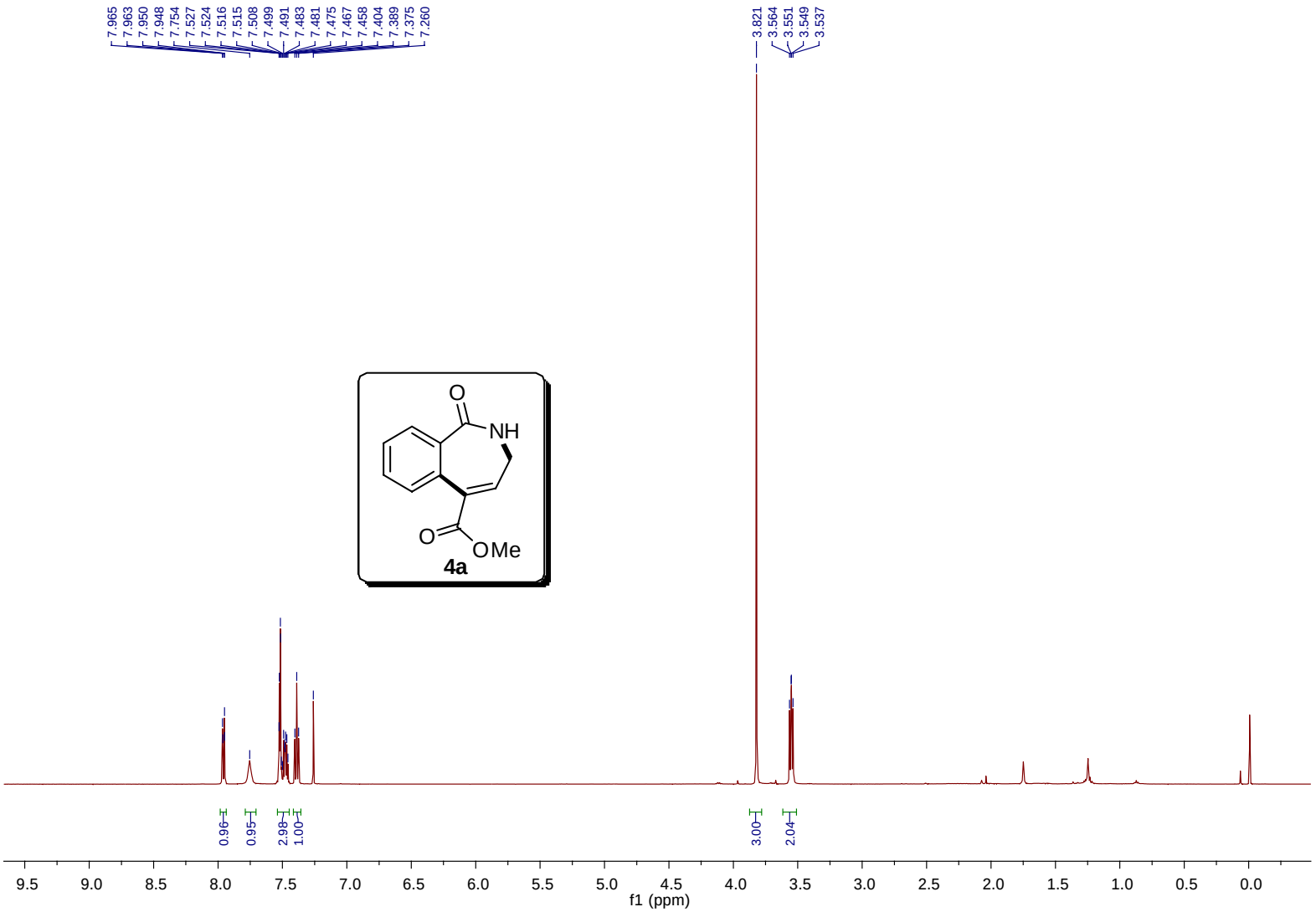


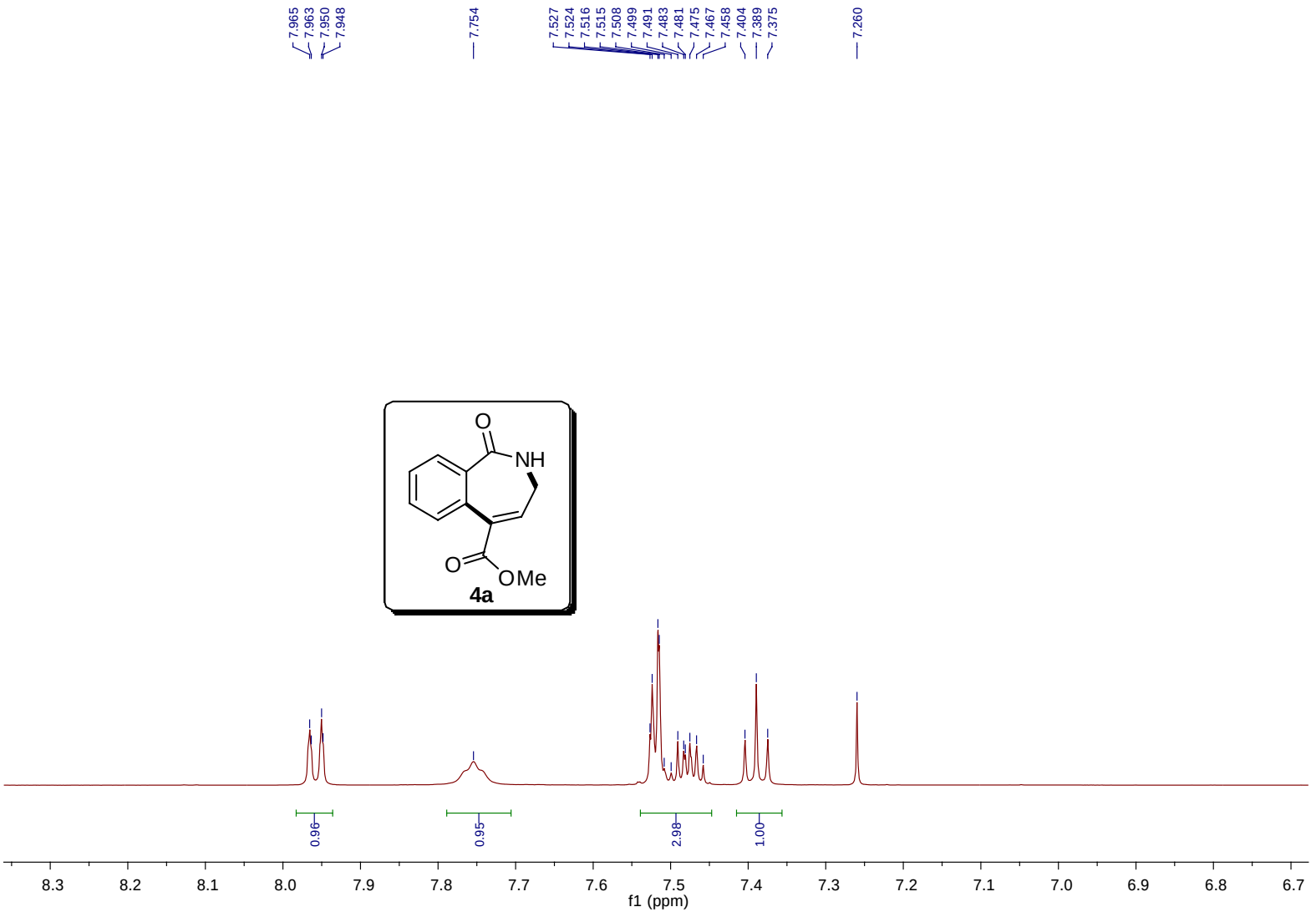


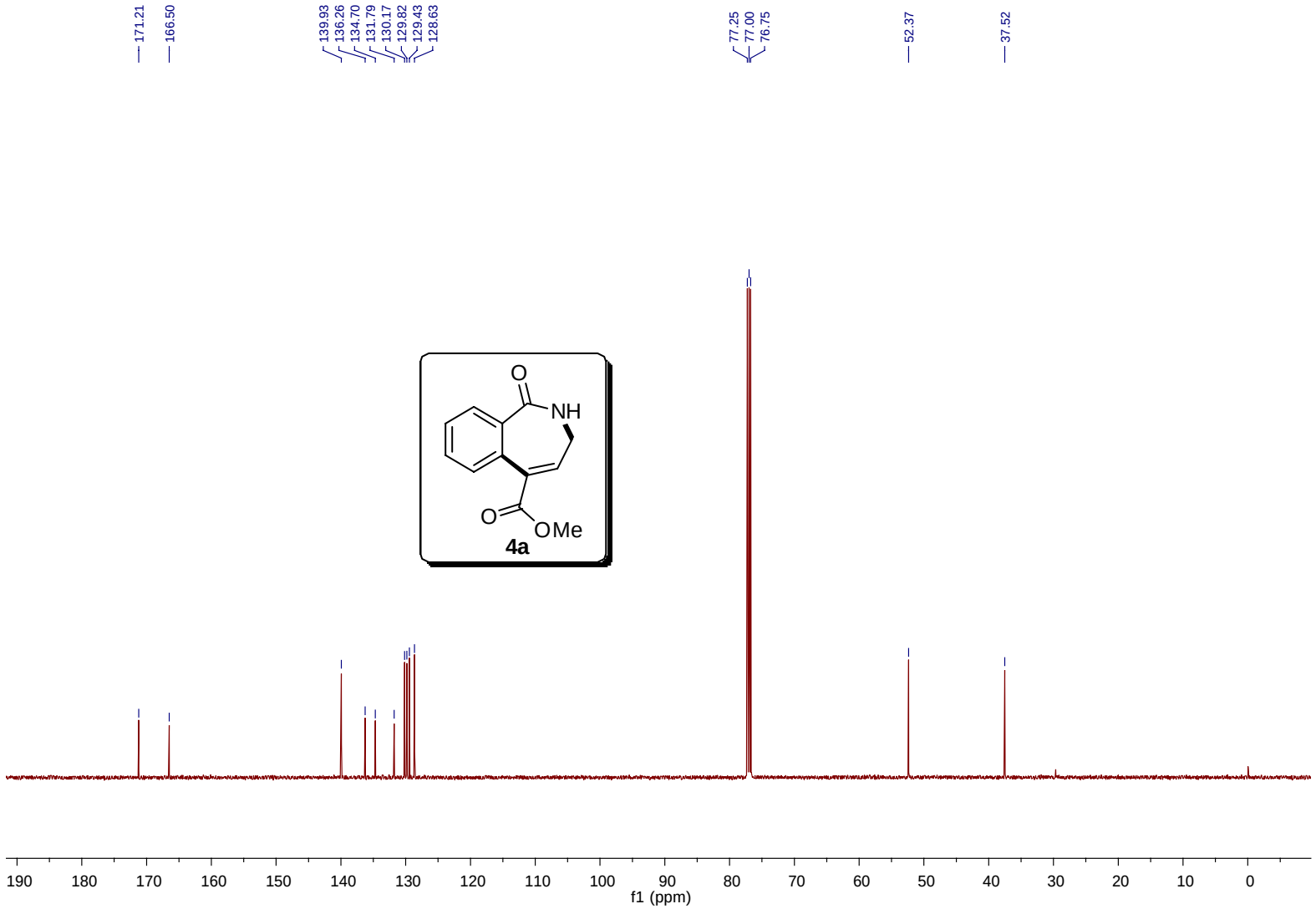


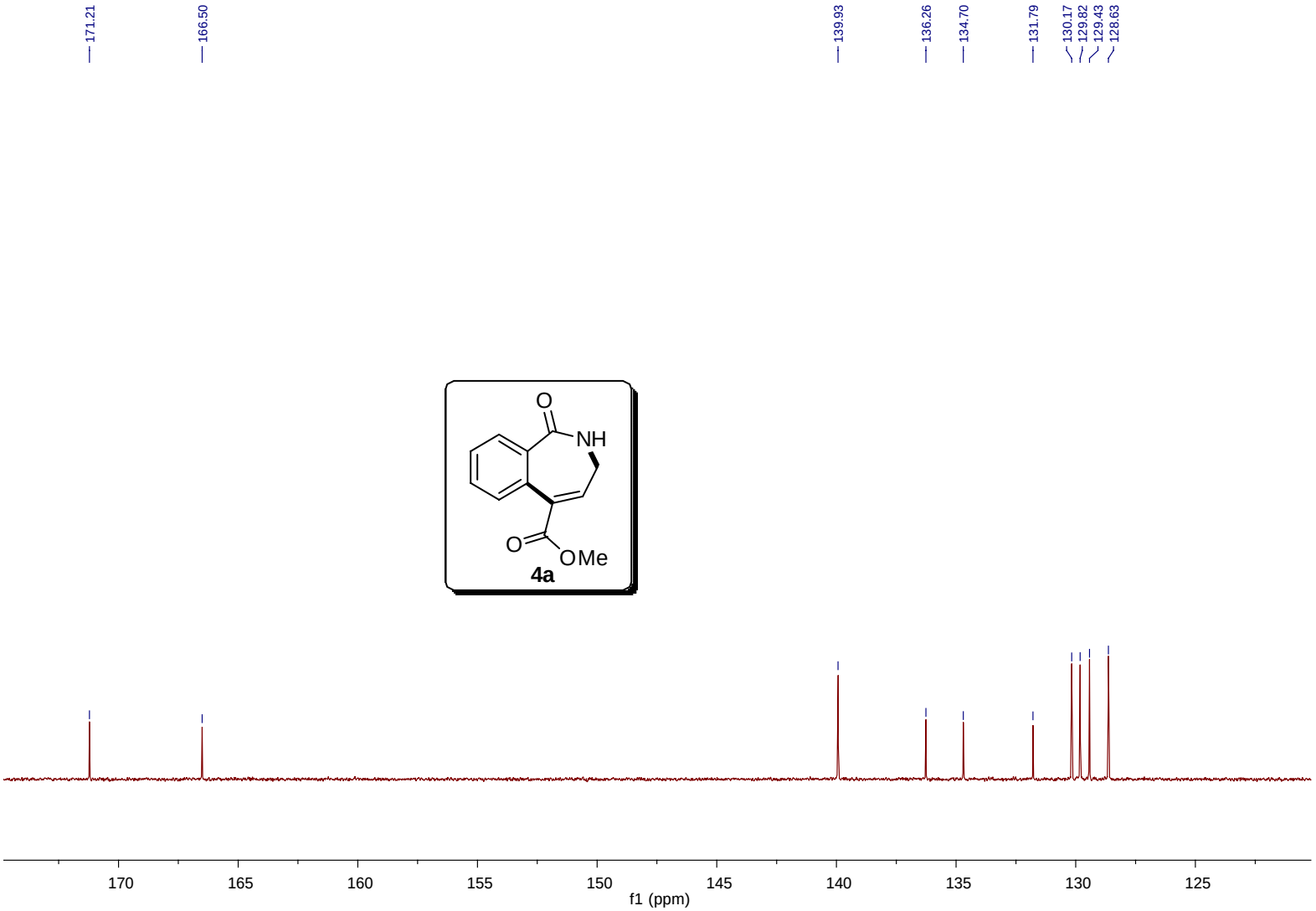


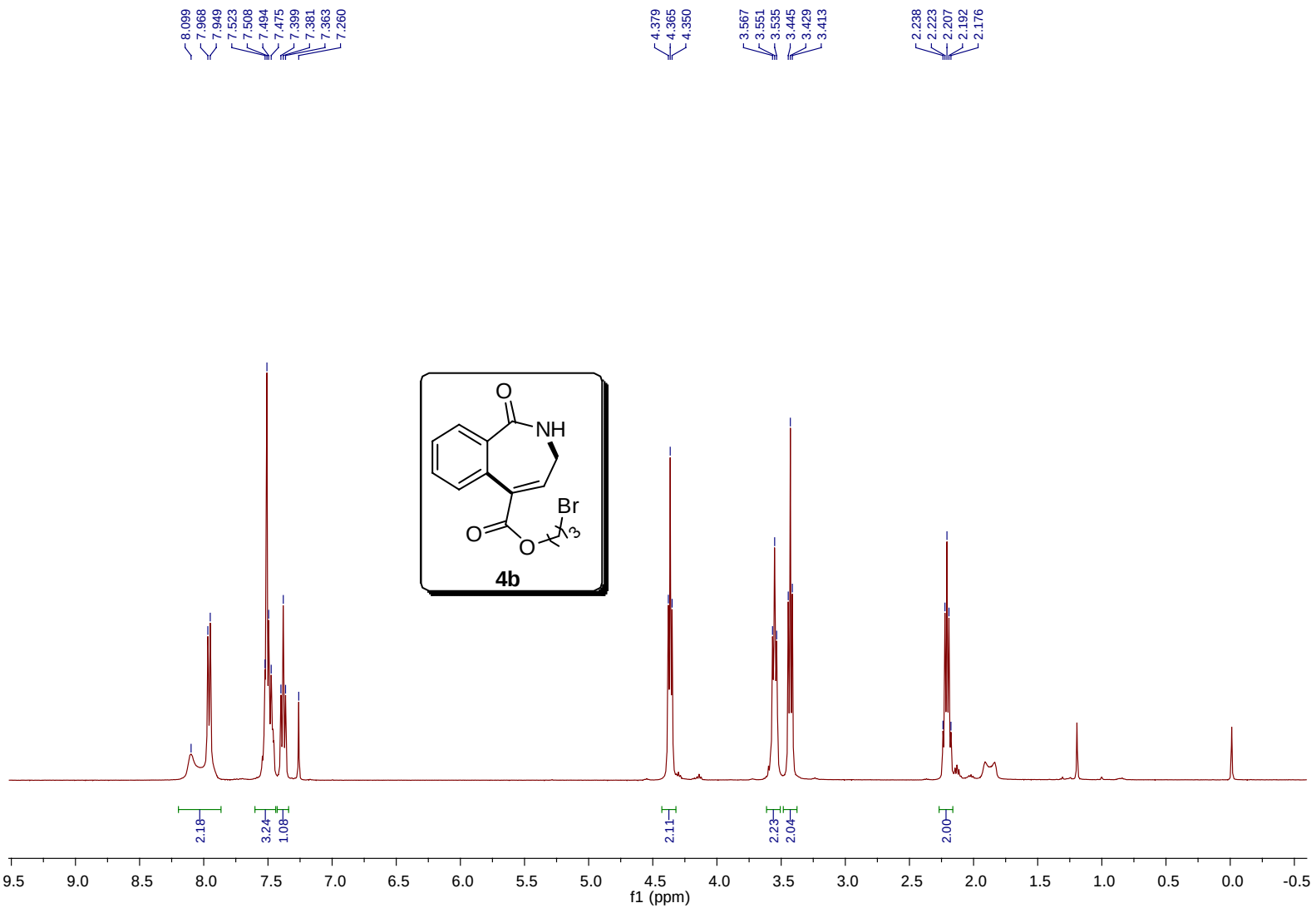


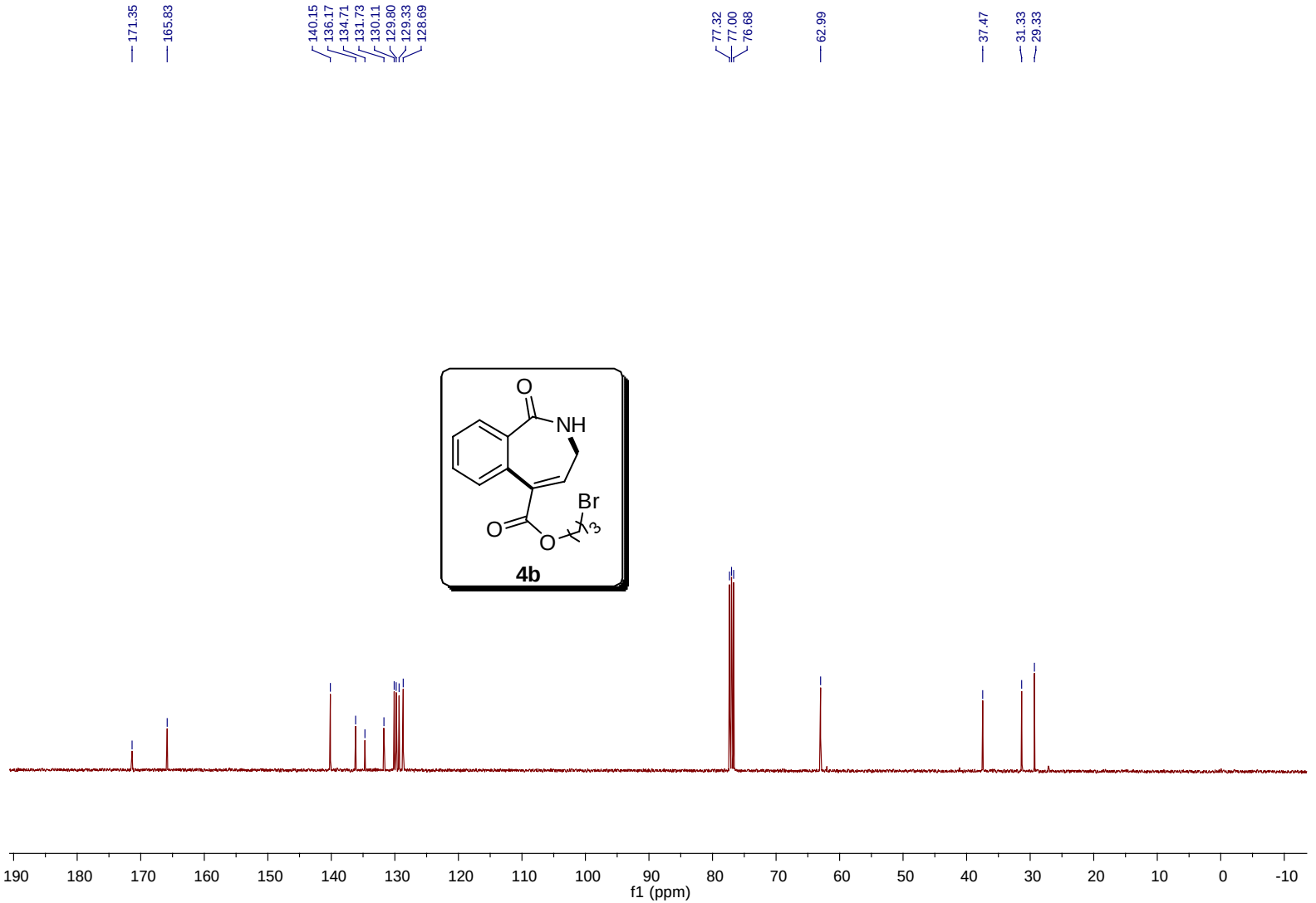


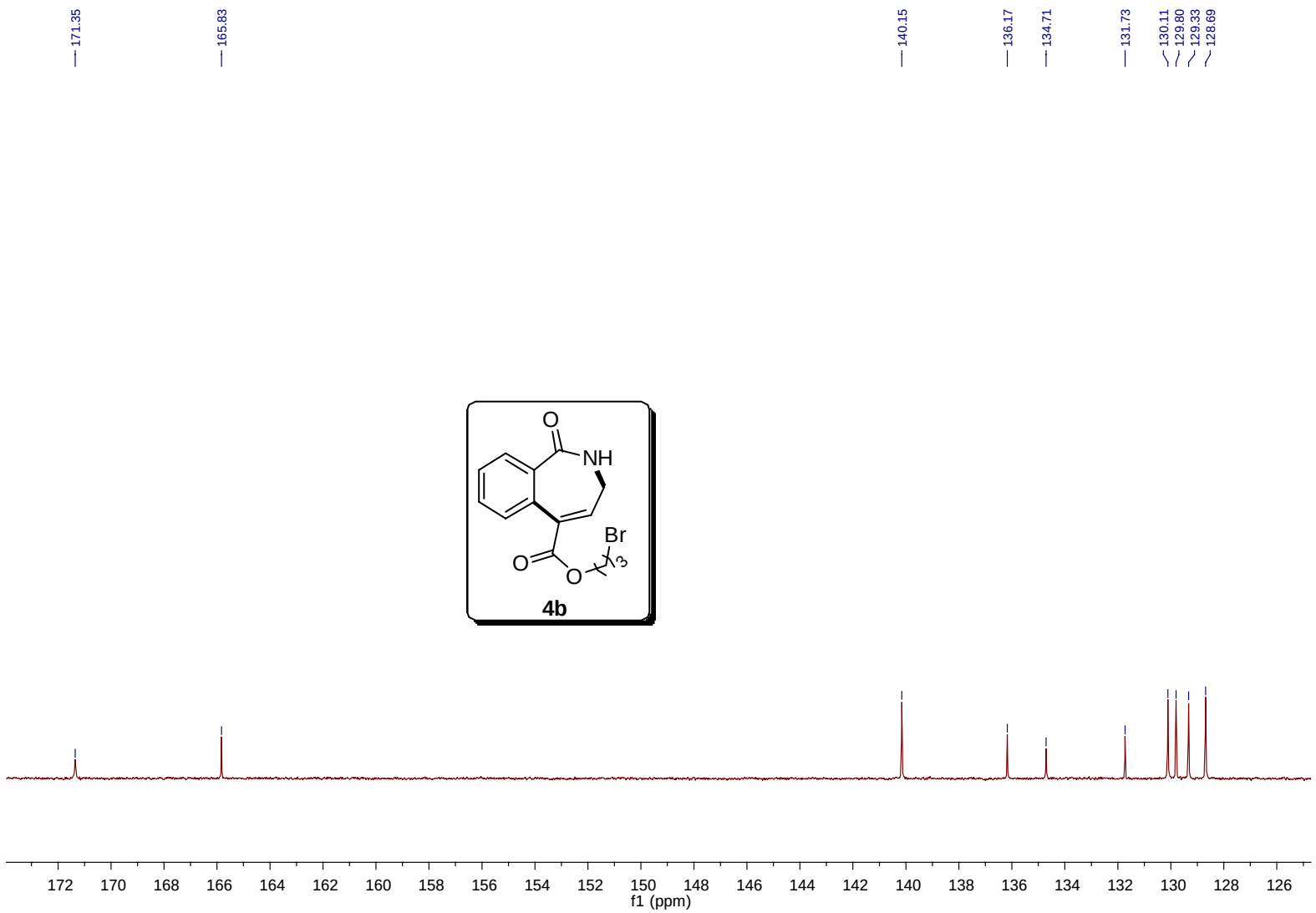


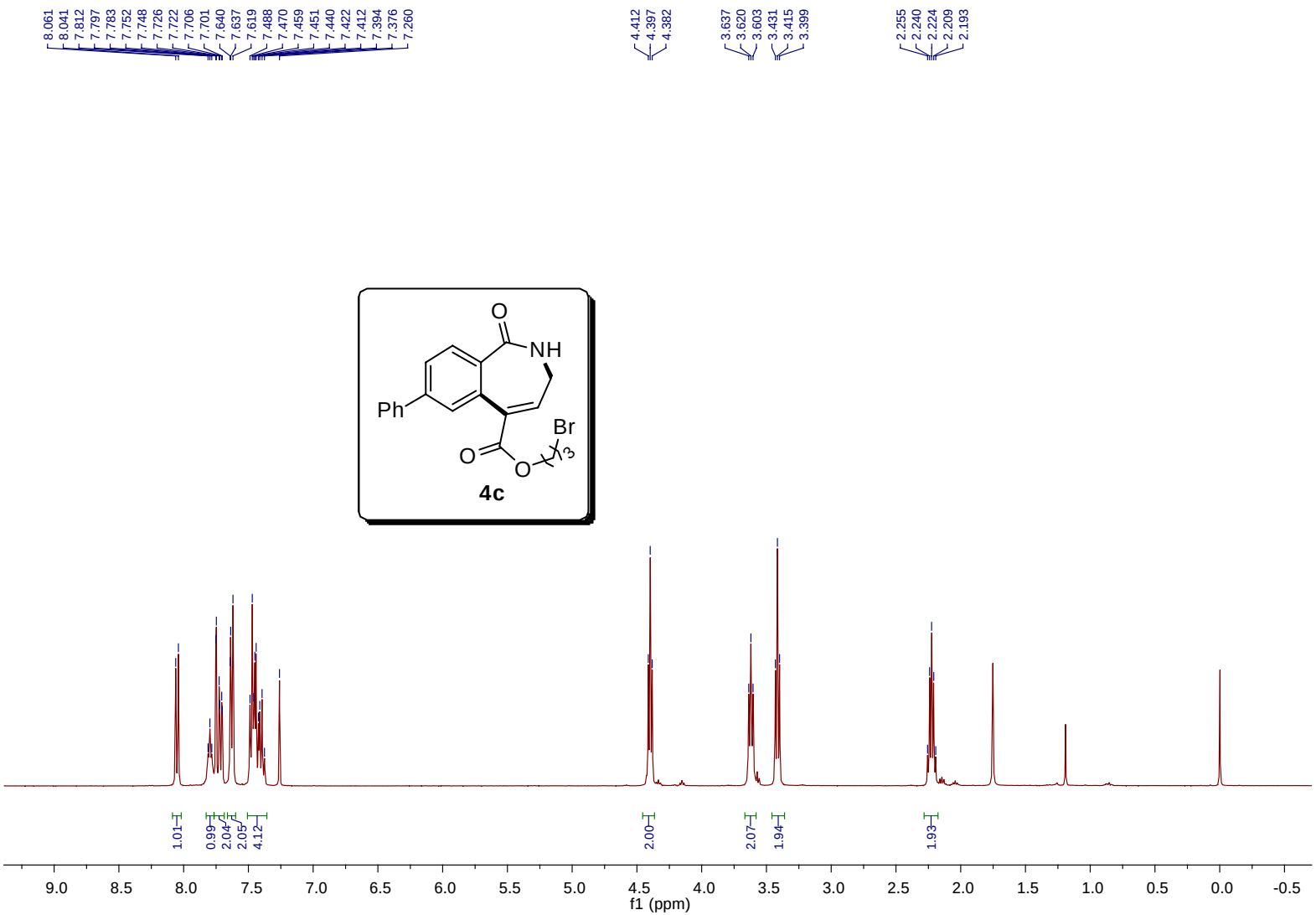


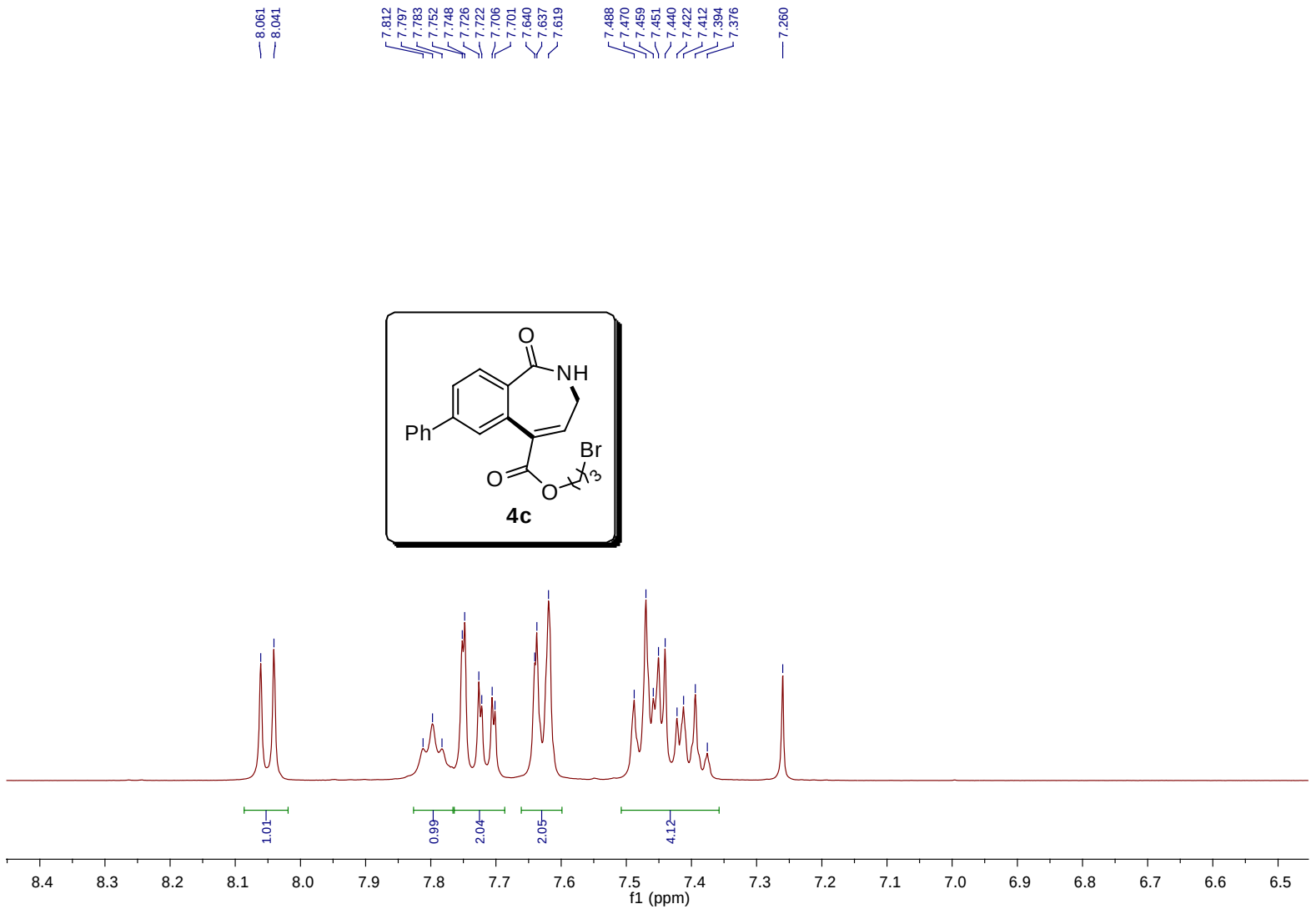


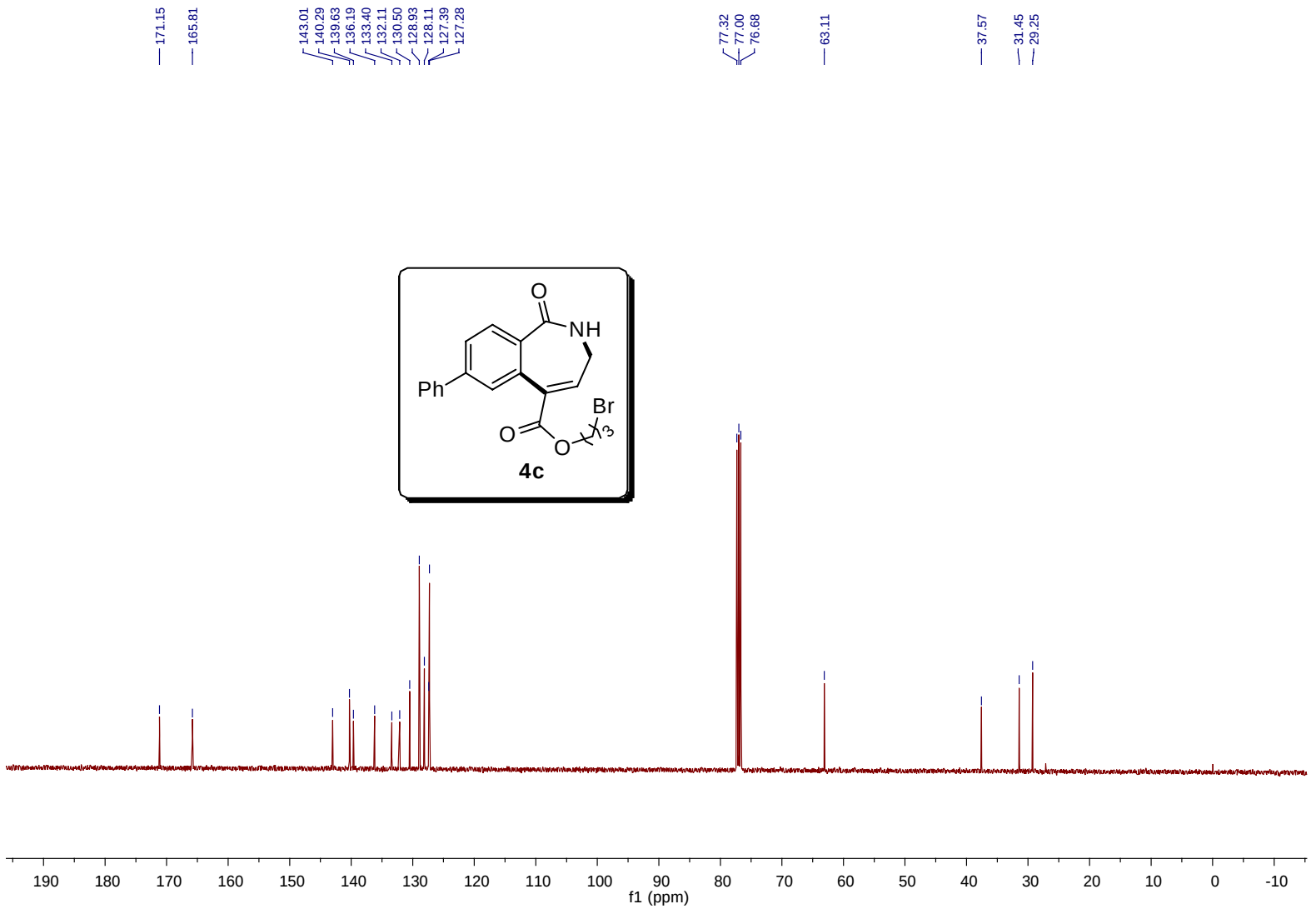


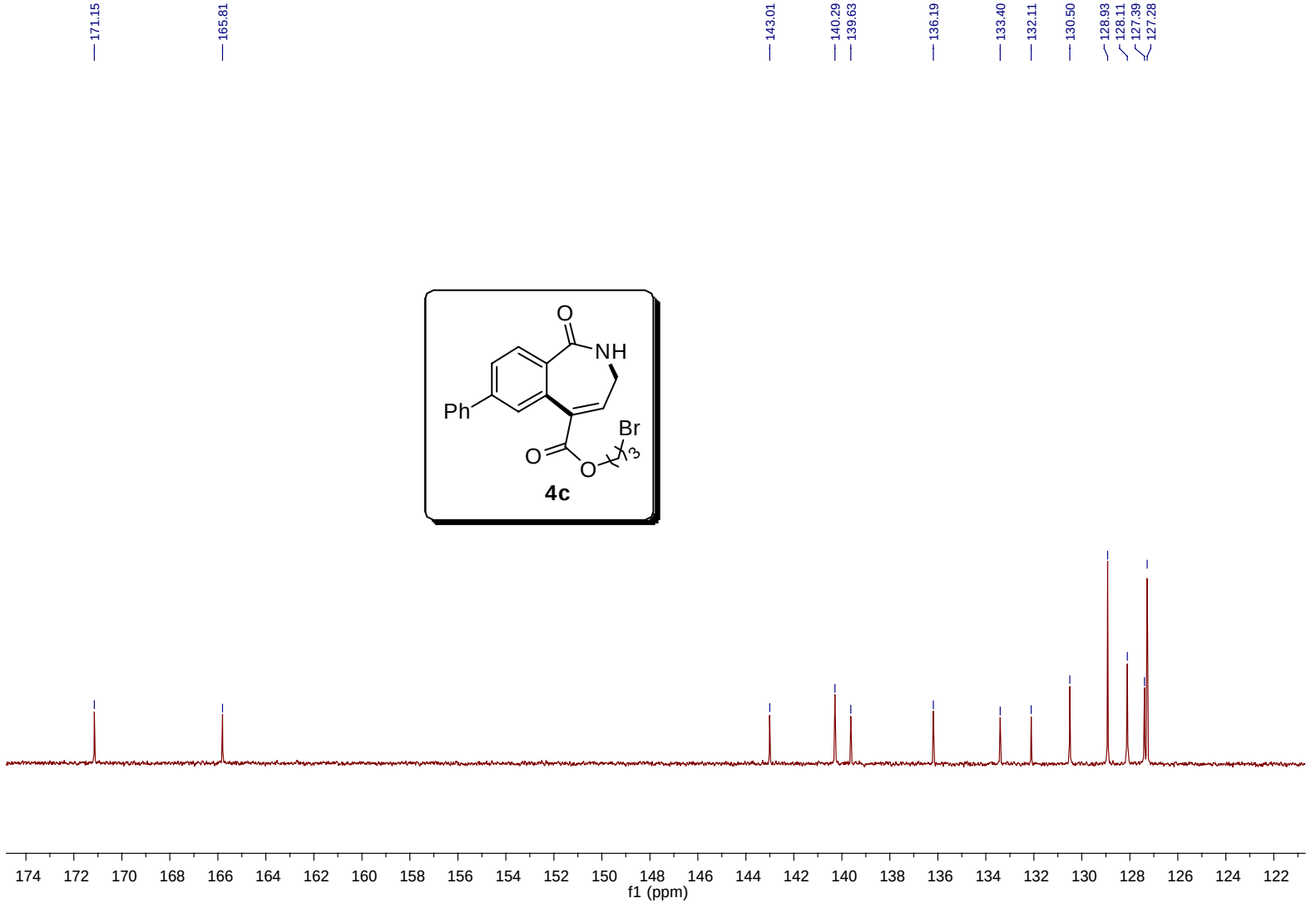


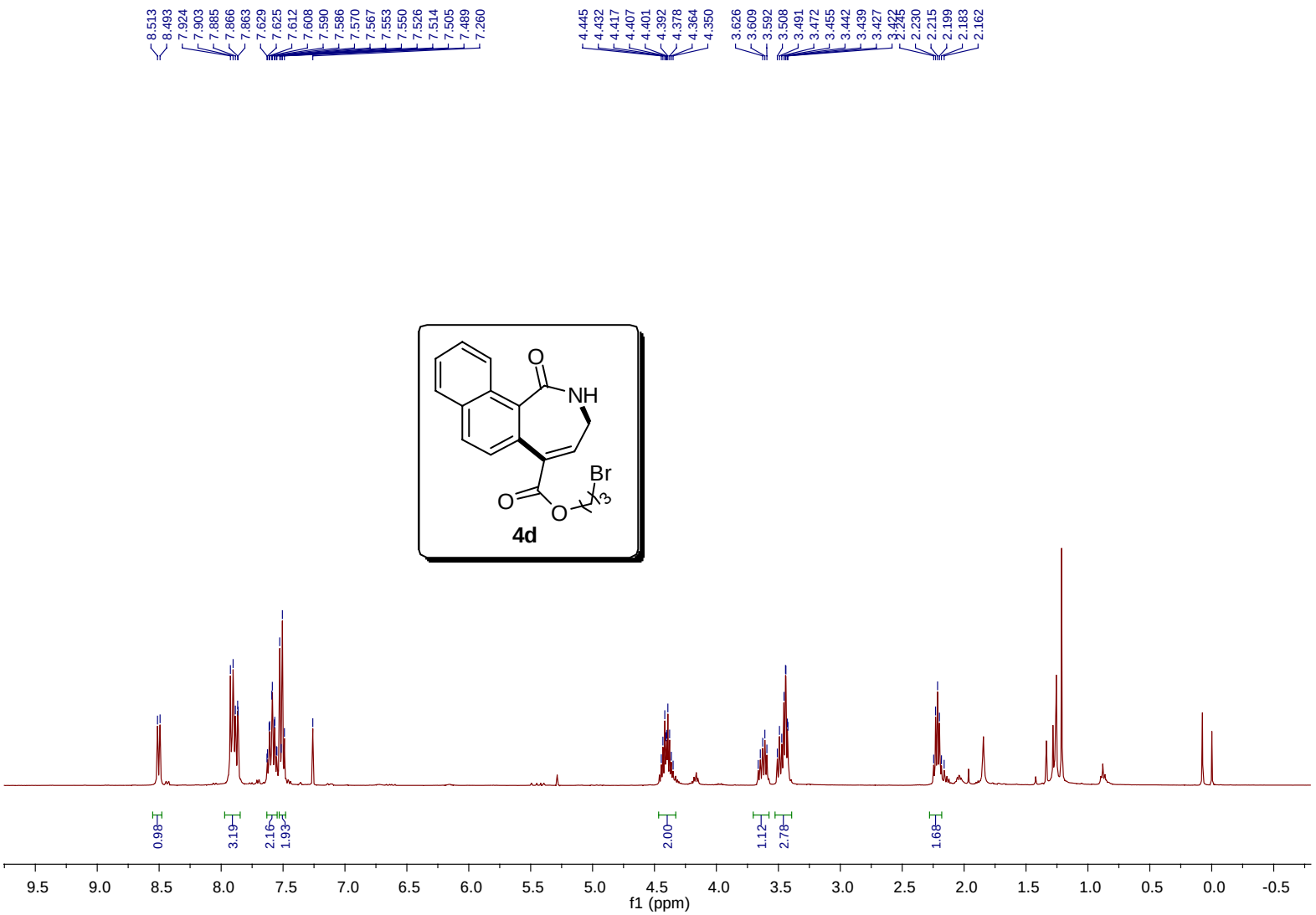


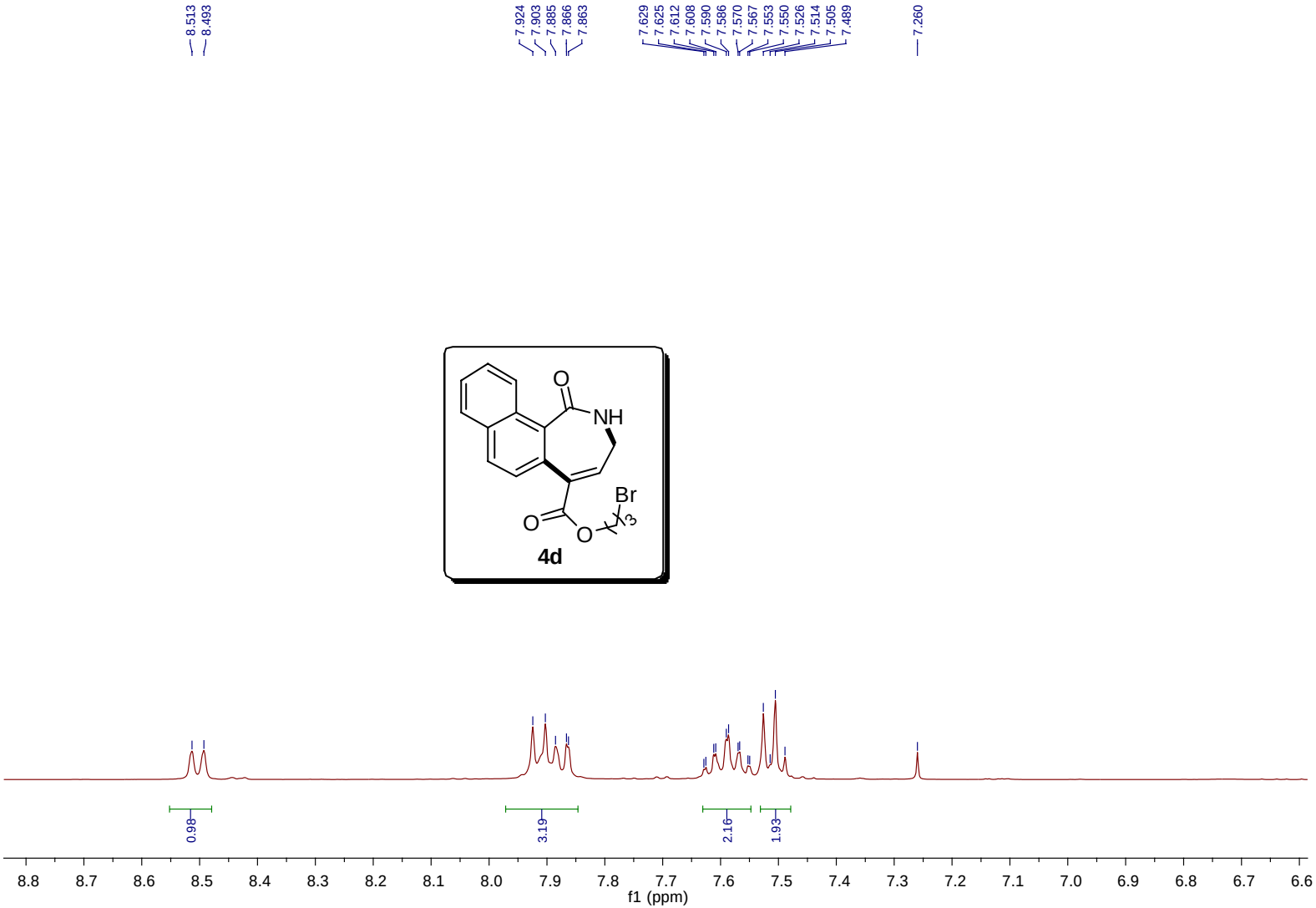


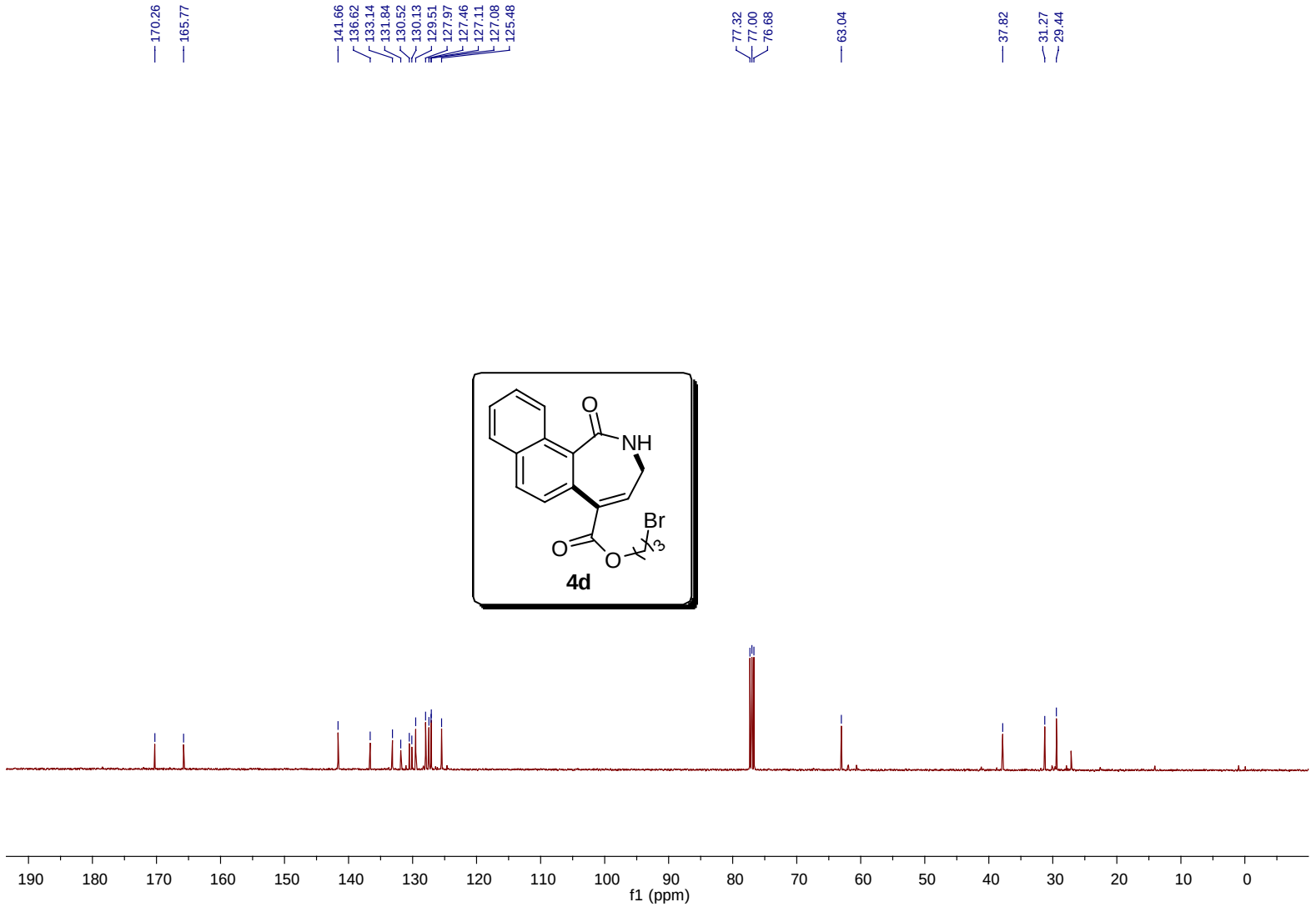


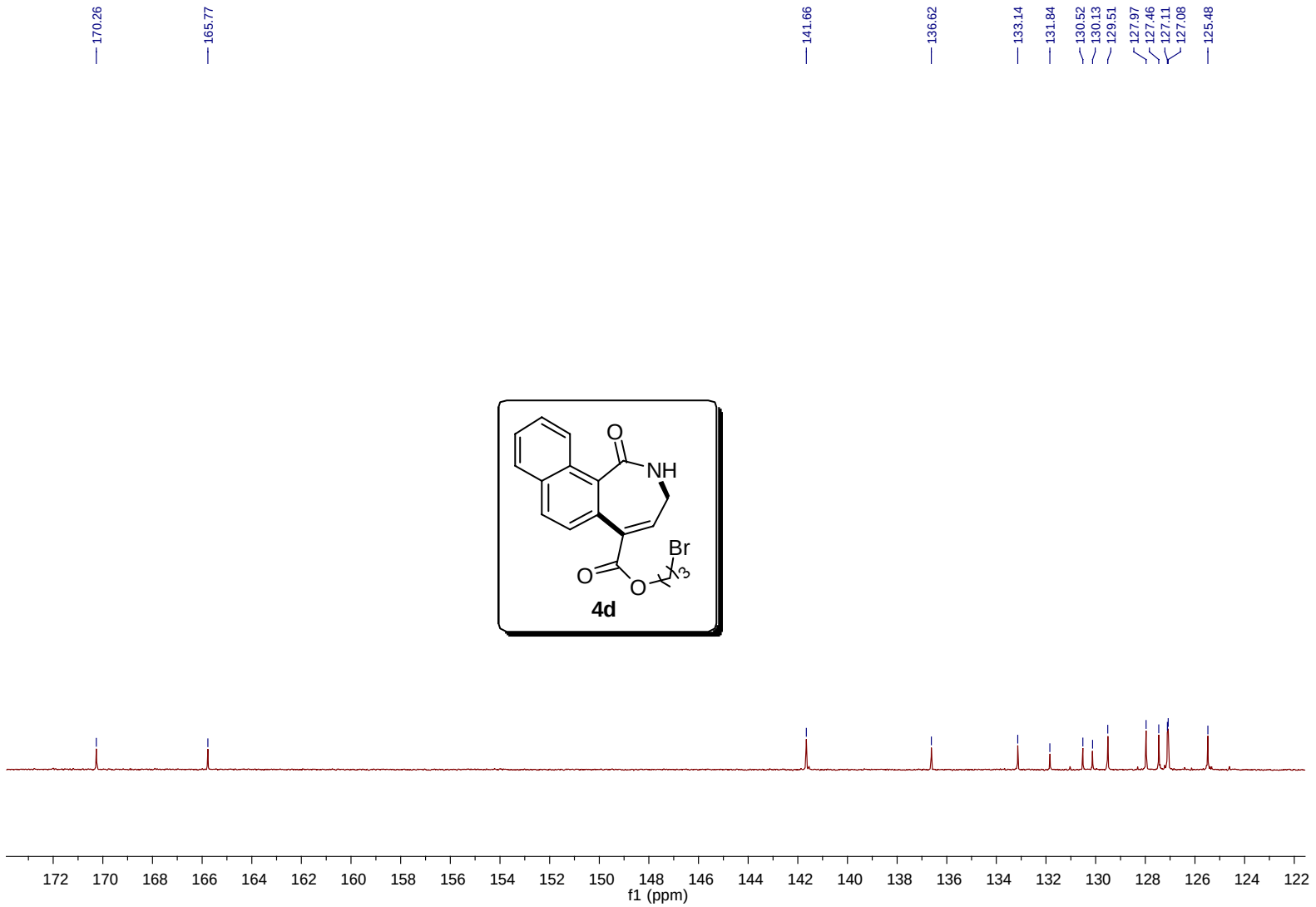


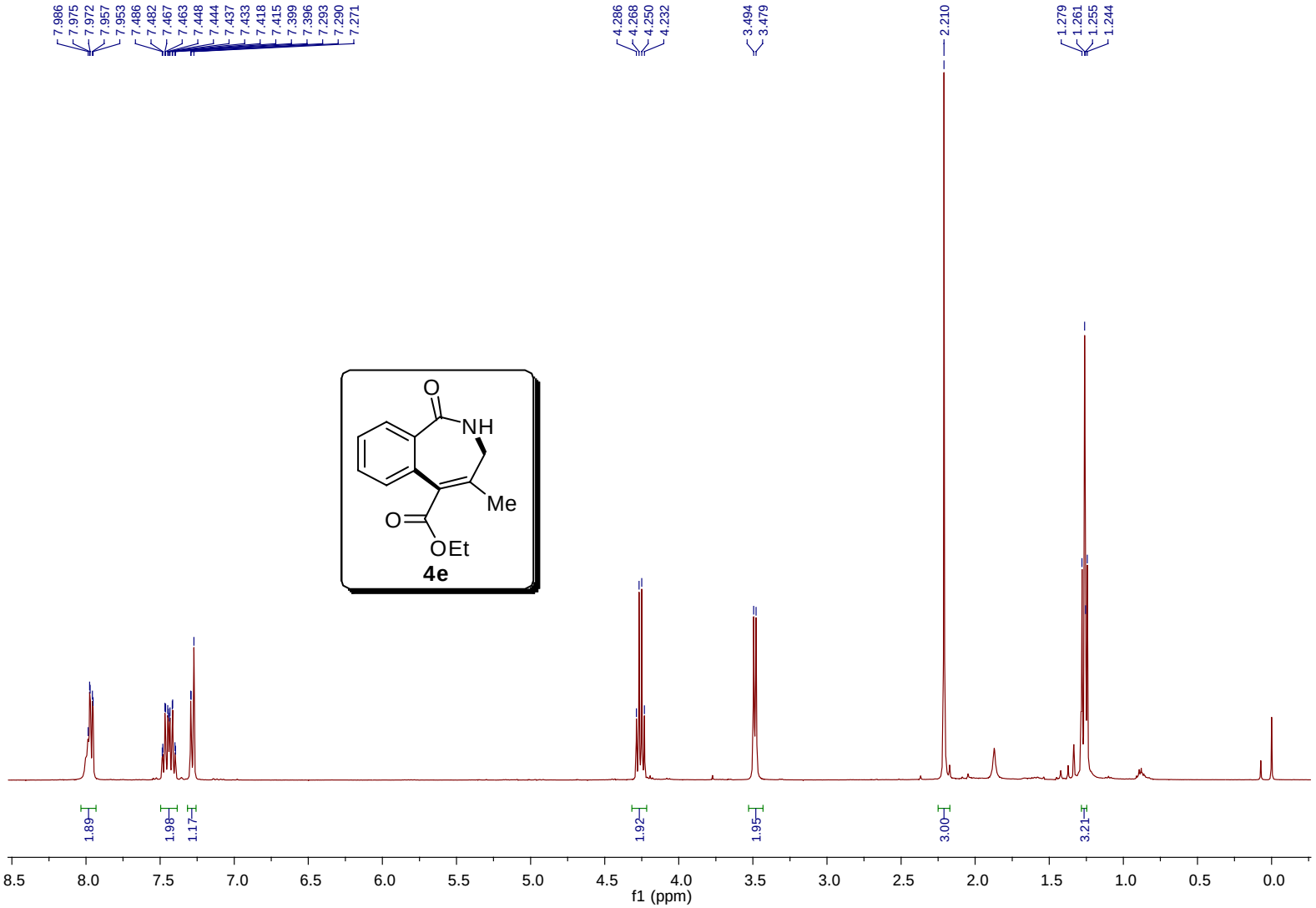


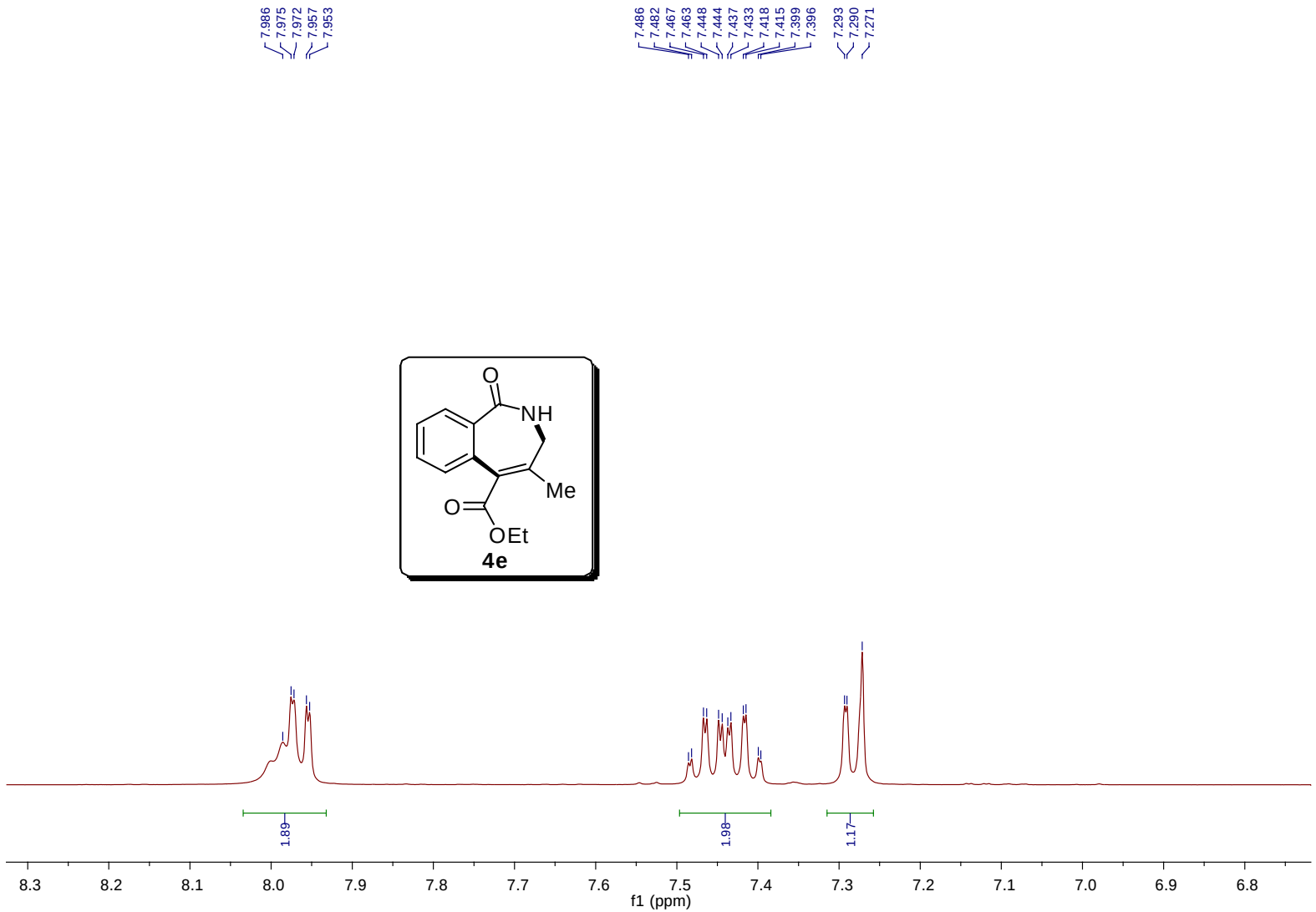


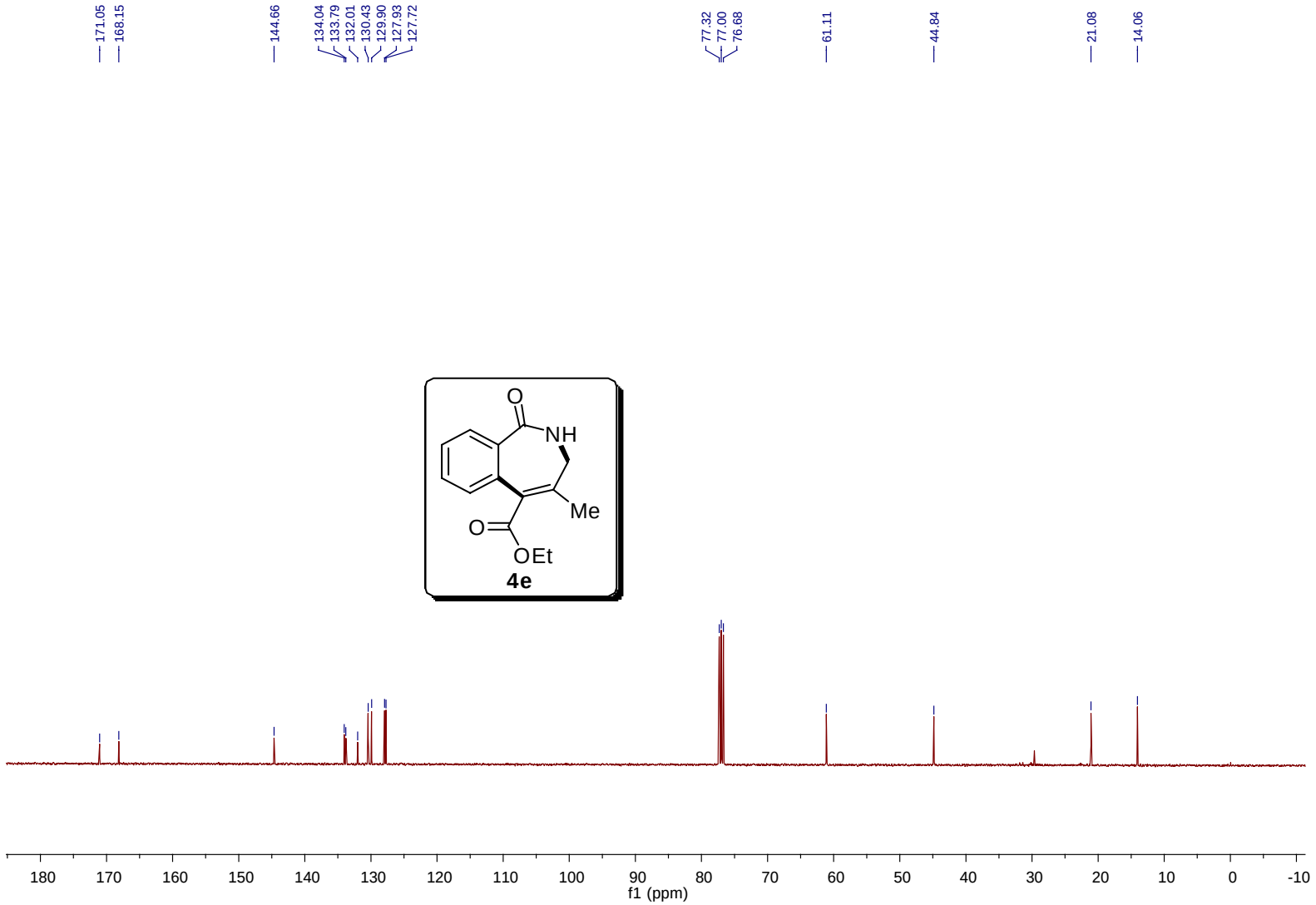

8.513
8.493
7.924
7.903
7.885
7.866
7.863
7.629
7.625
7.612
7.608
7.590
7.586
7.570
7.567
7.553
7.550
7.526
7.514
7.505
7.489
7.260
O
NH
Br
O
O
4d
0.98
3.19
2.16
1.93
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)

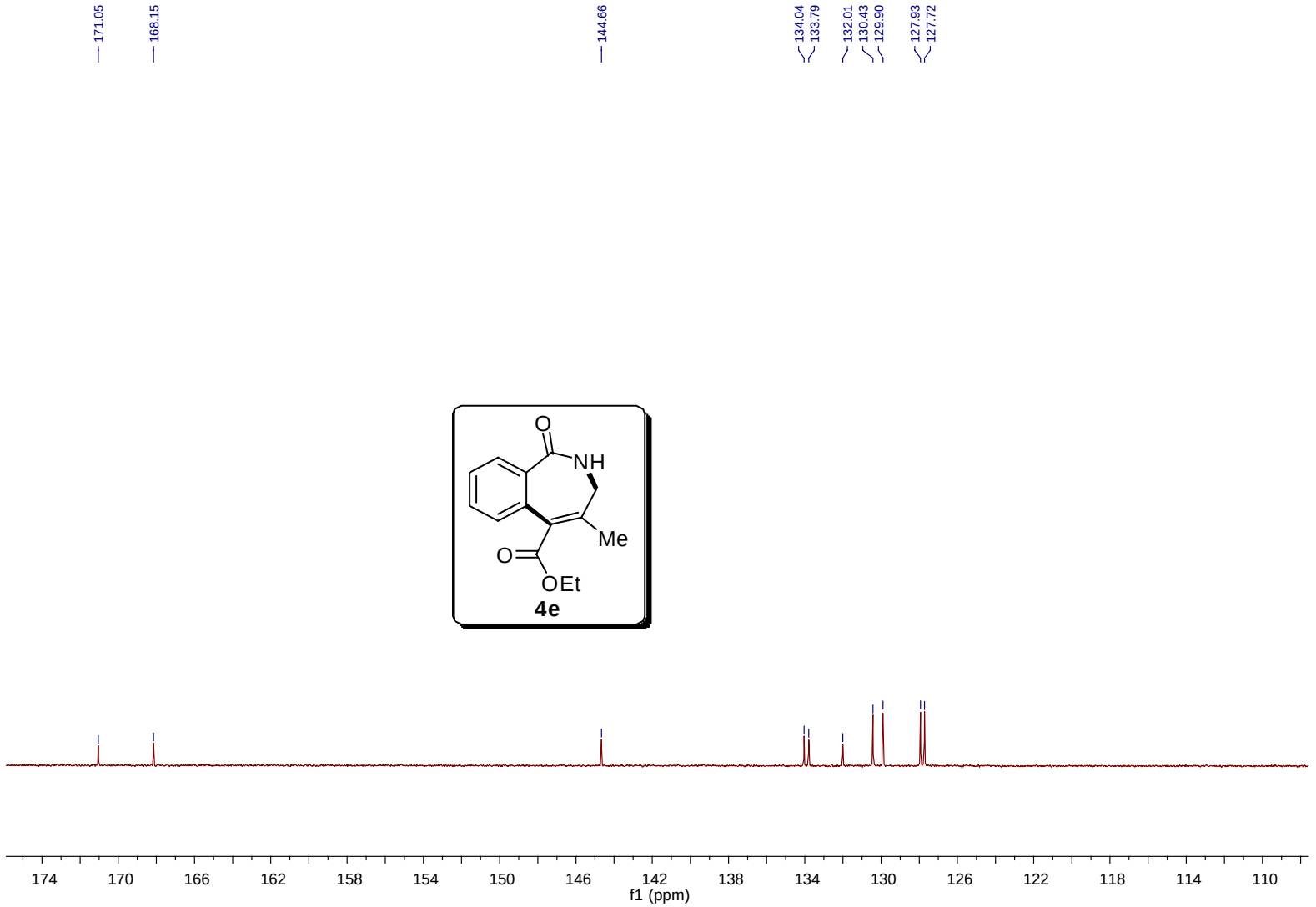


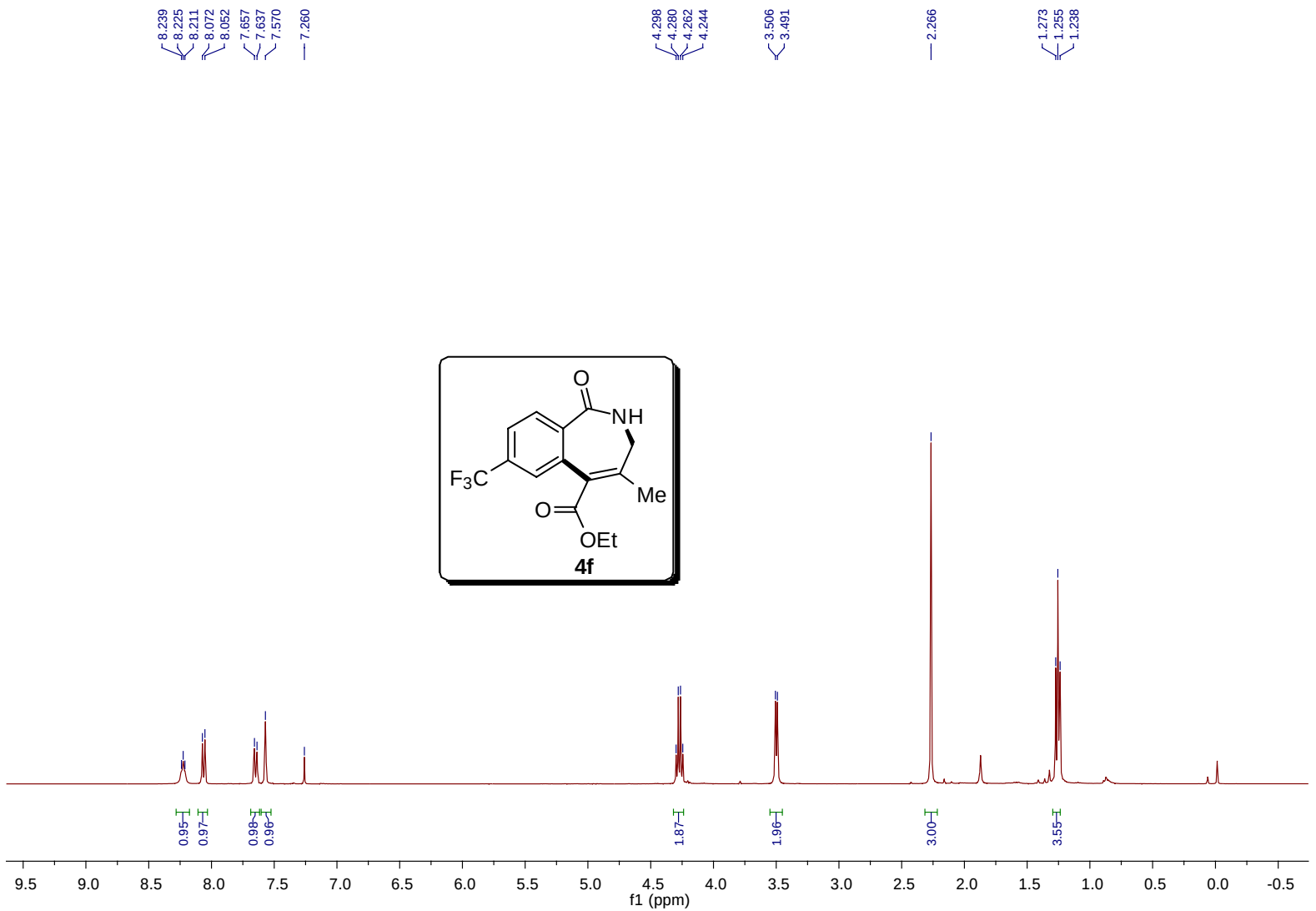


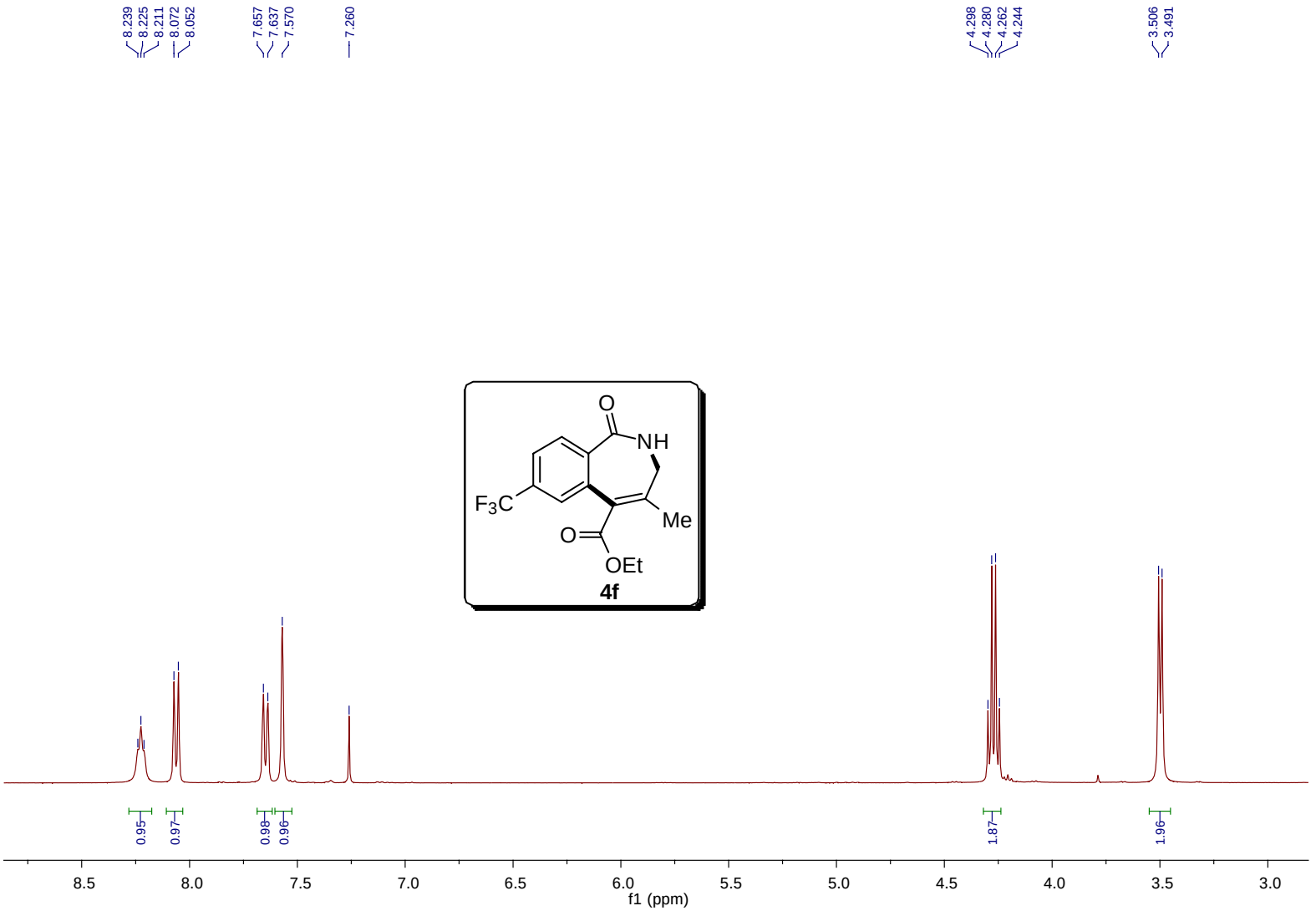


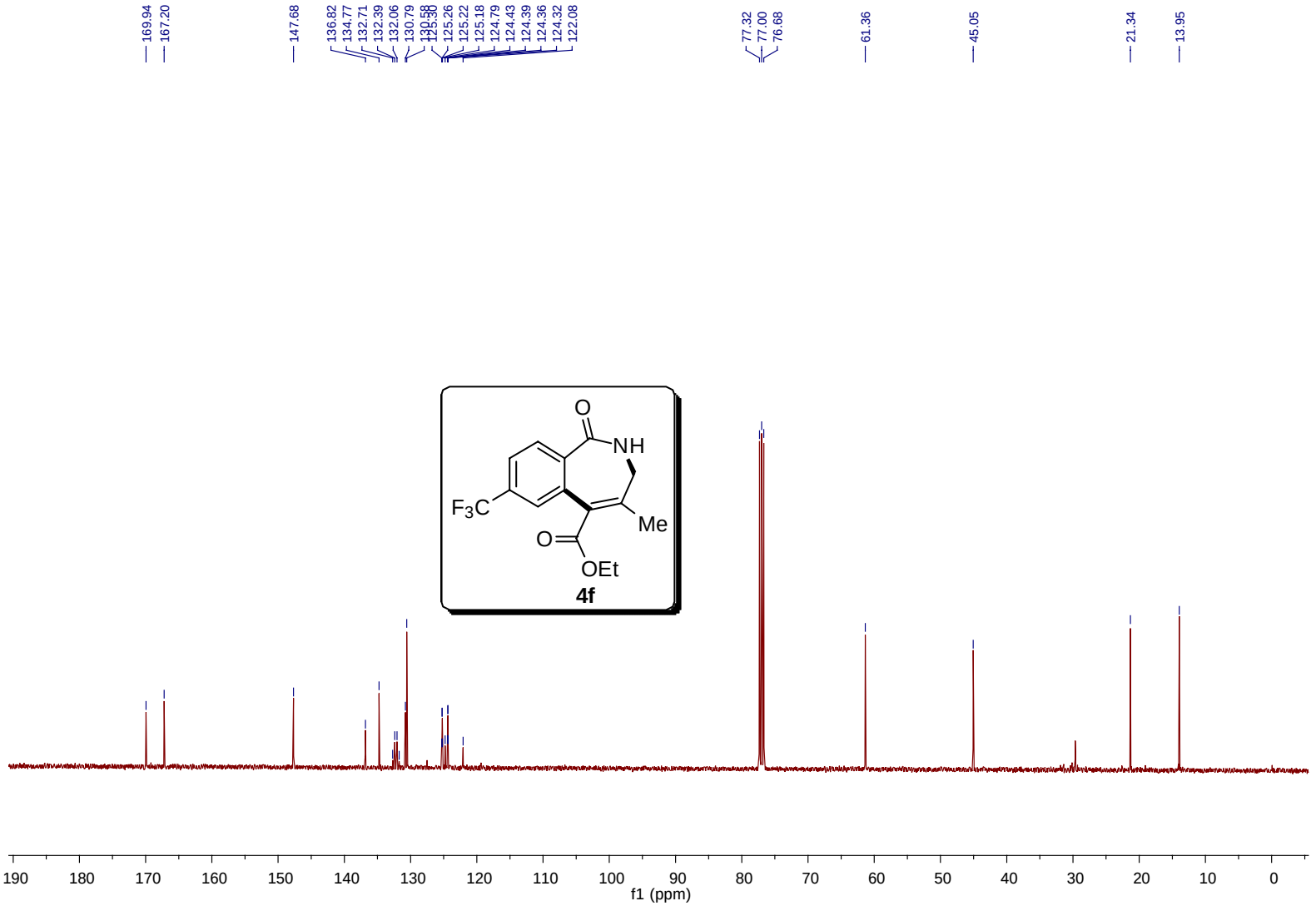


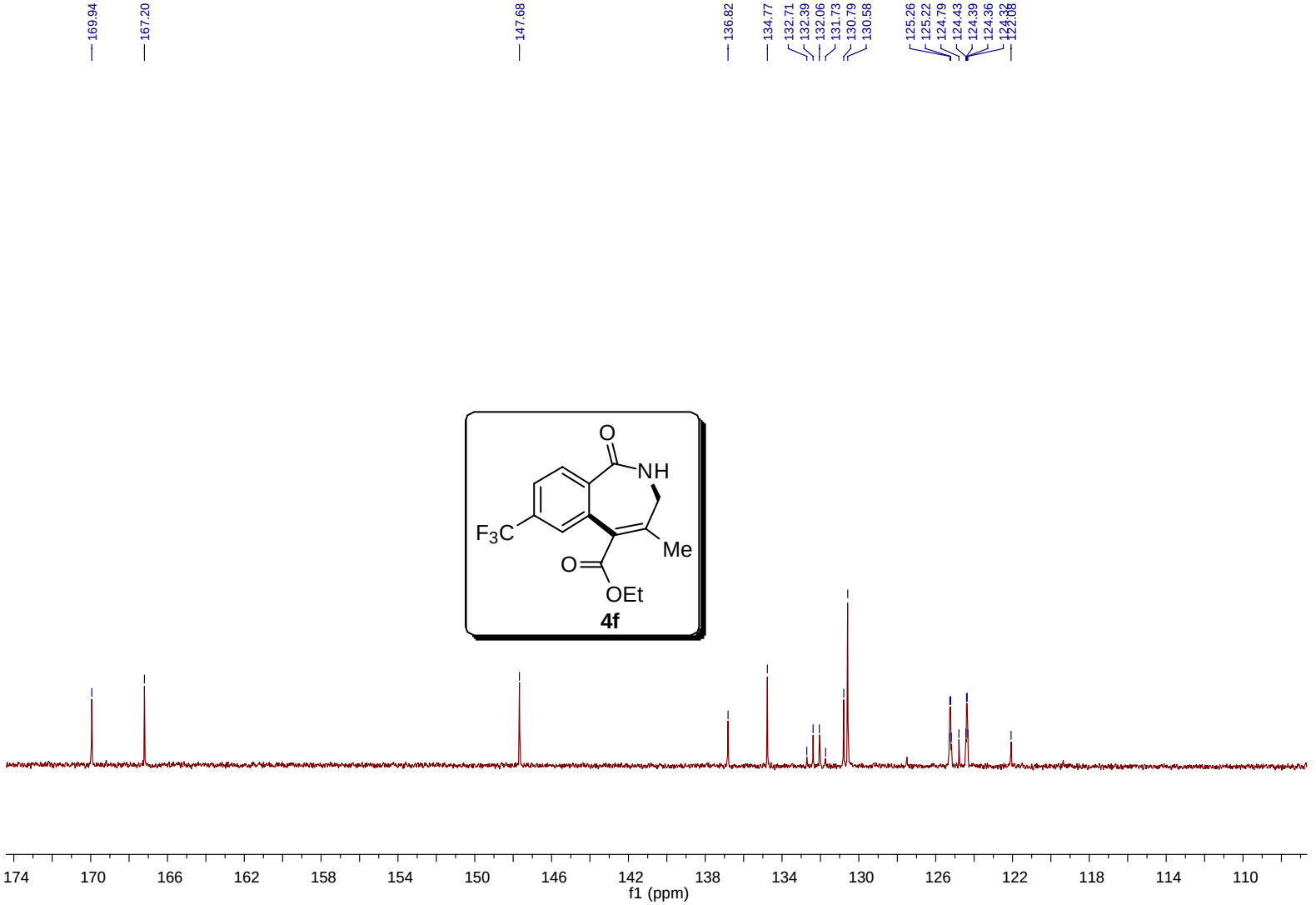


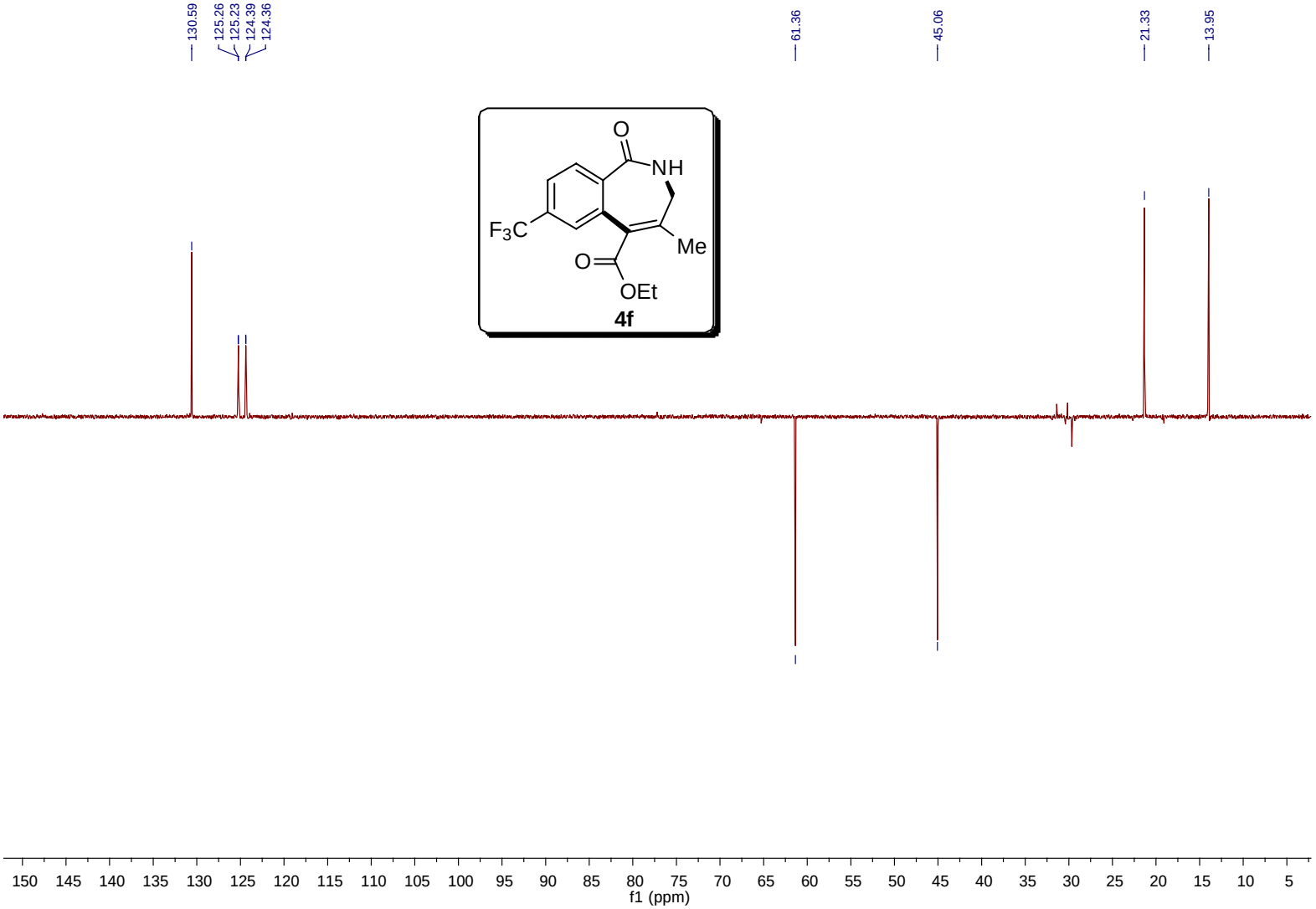


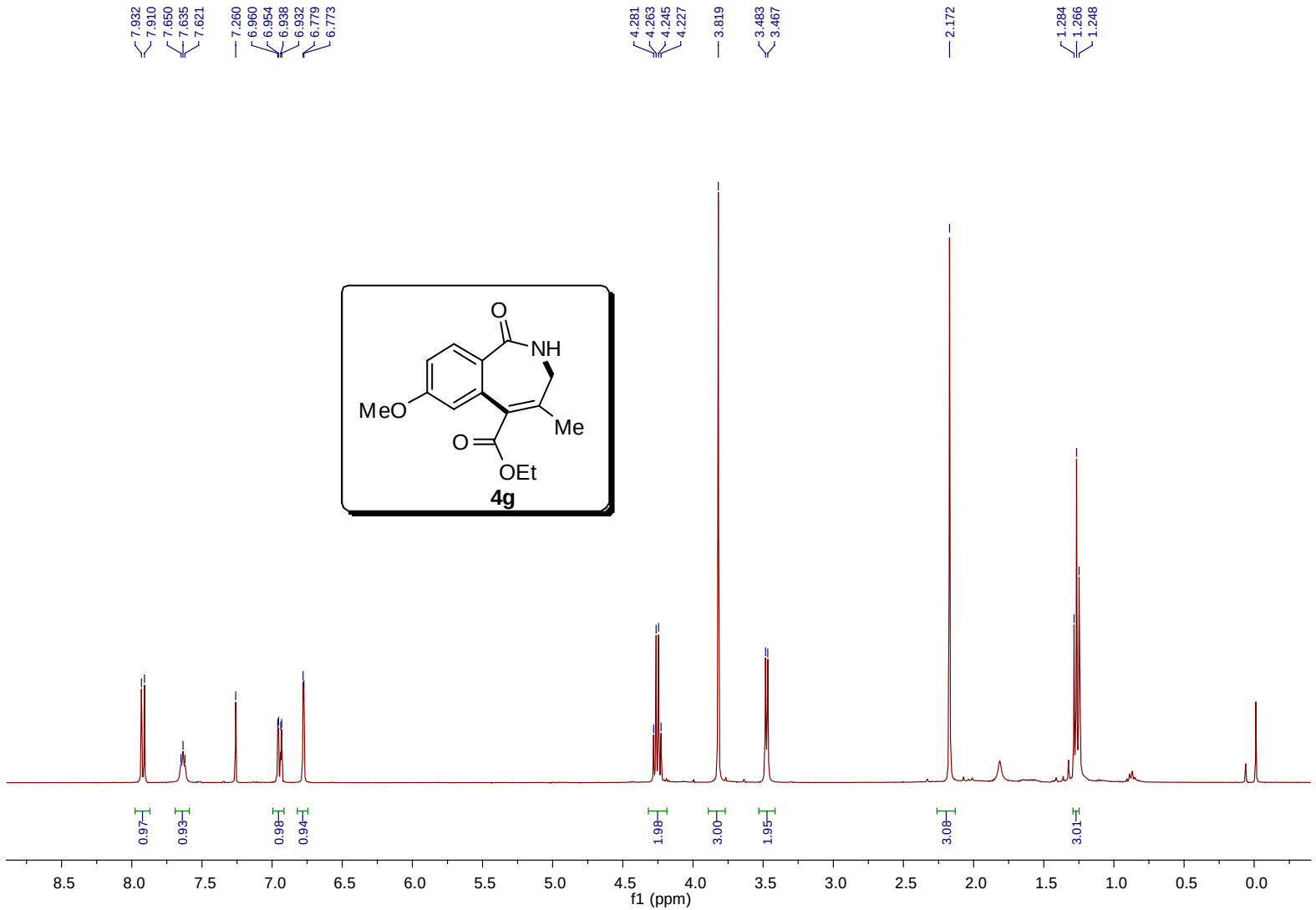


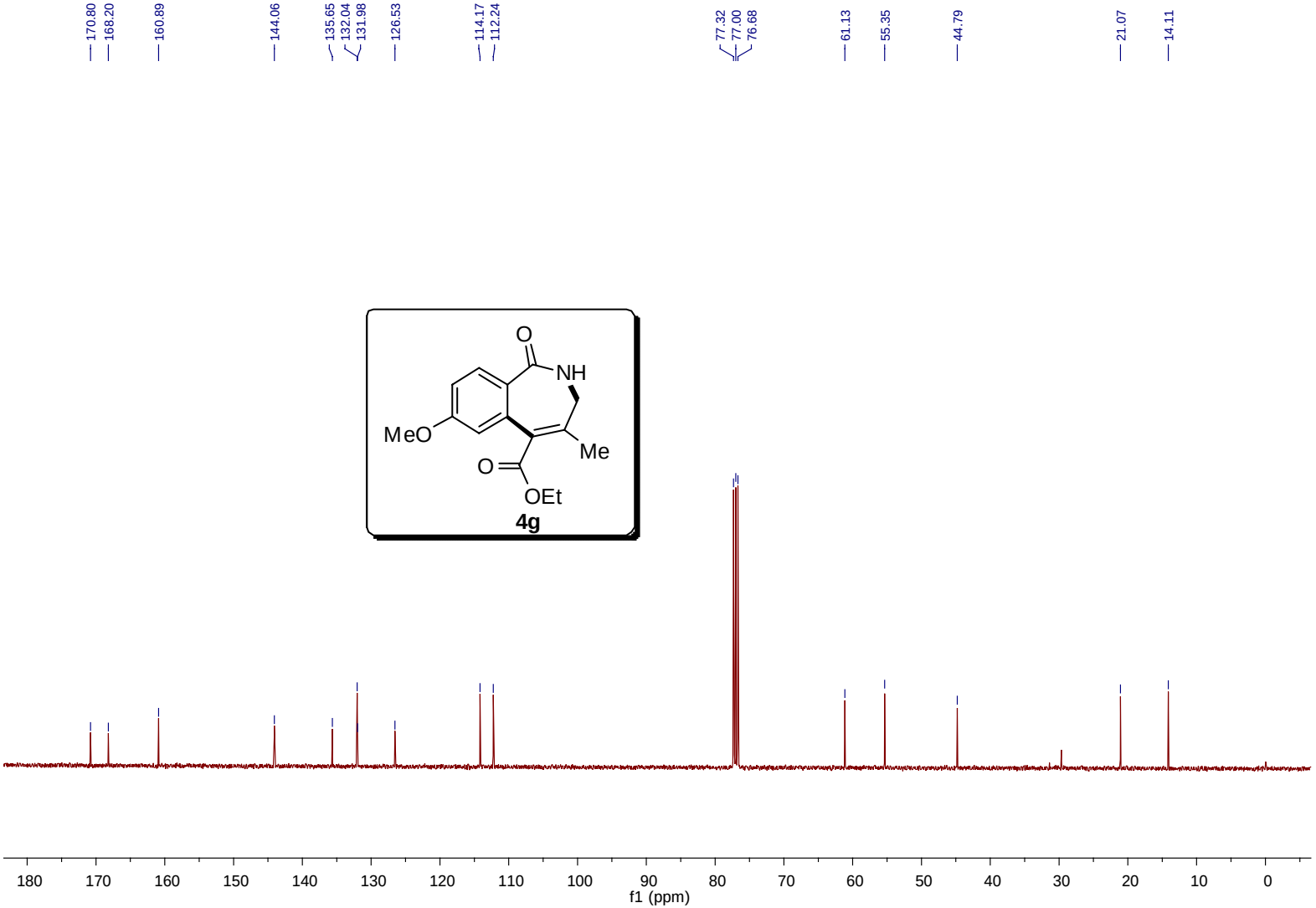


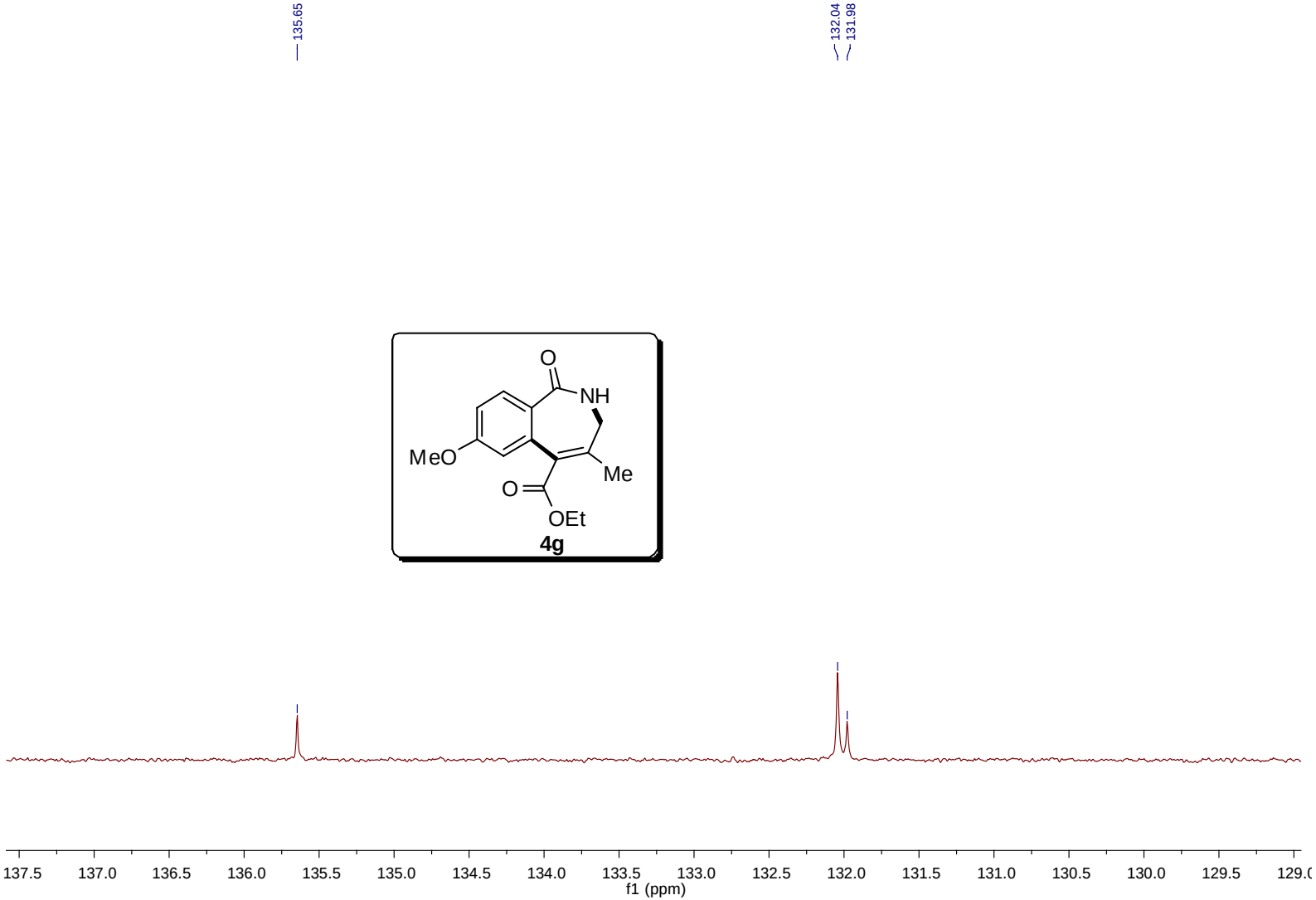


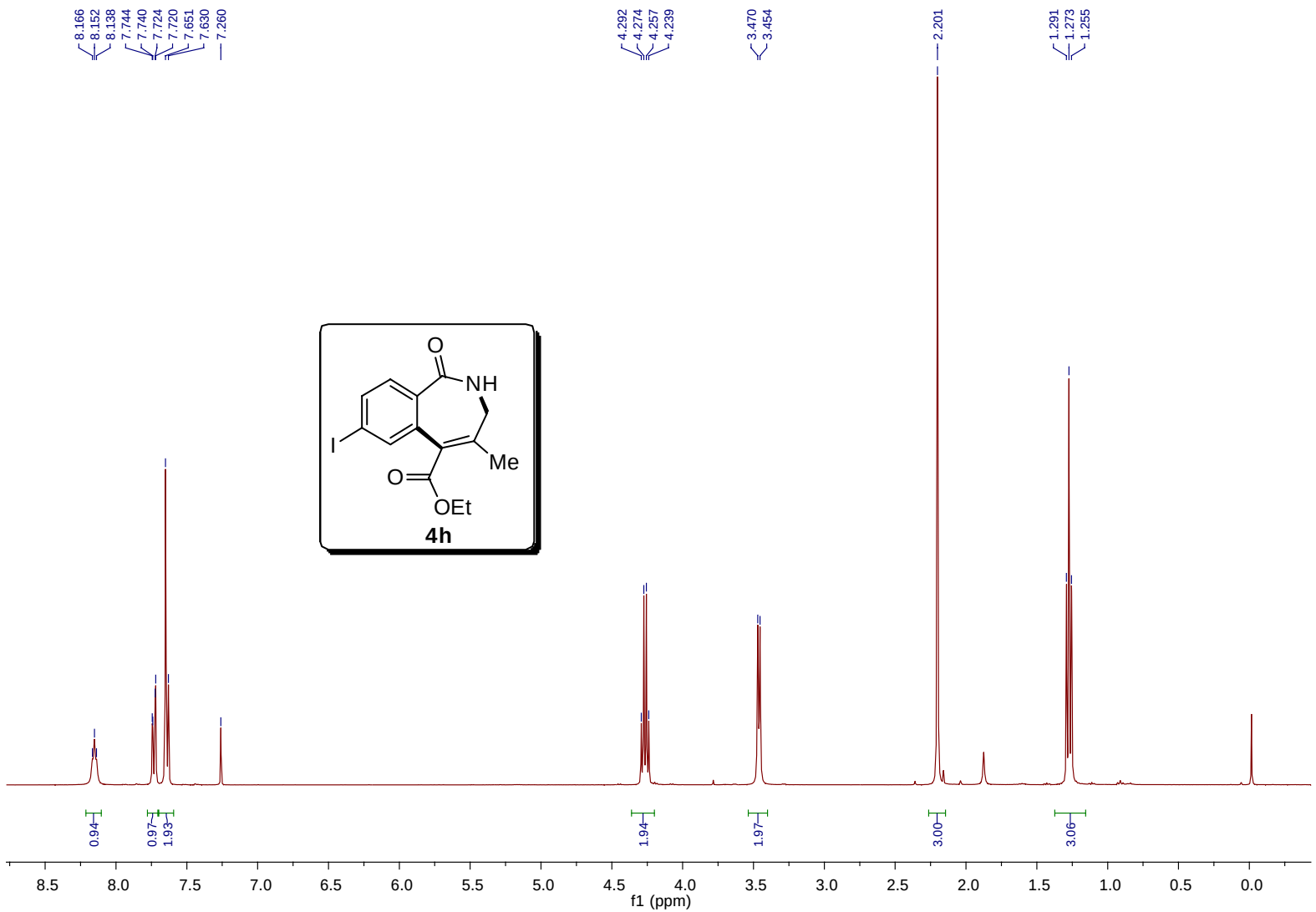


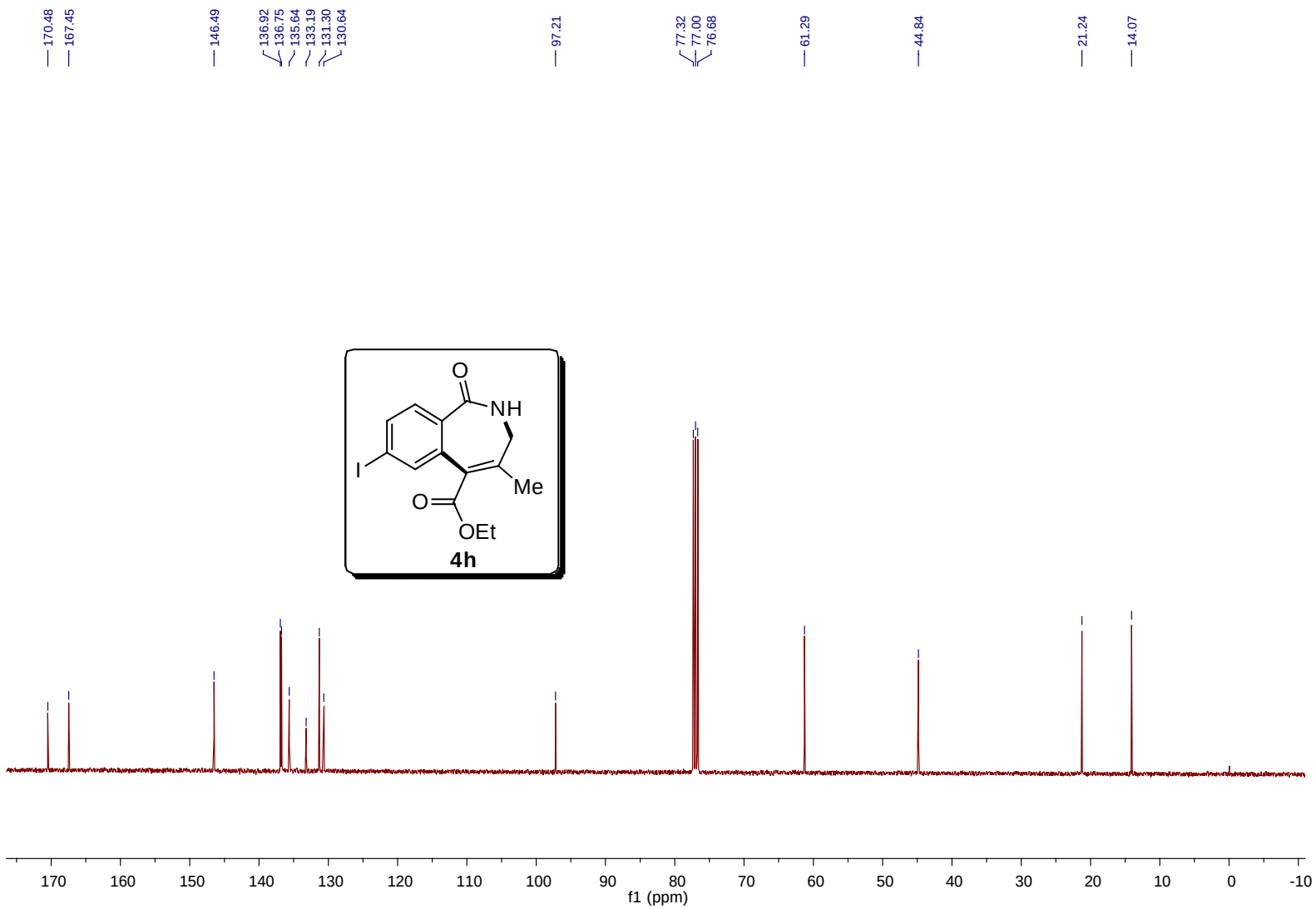


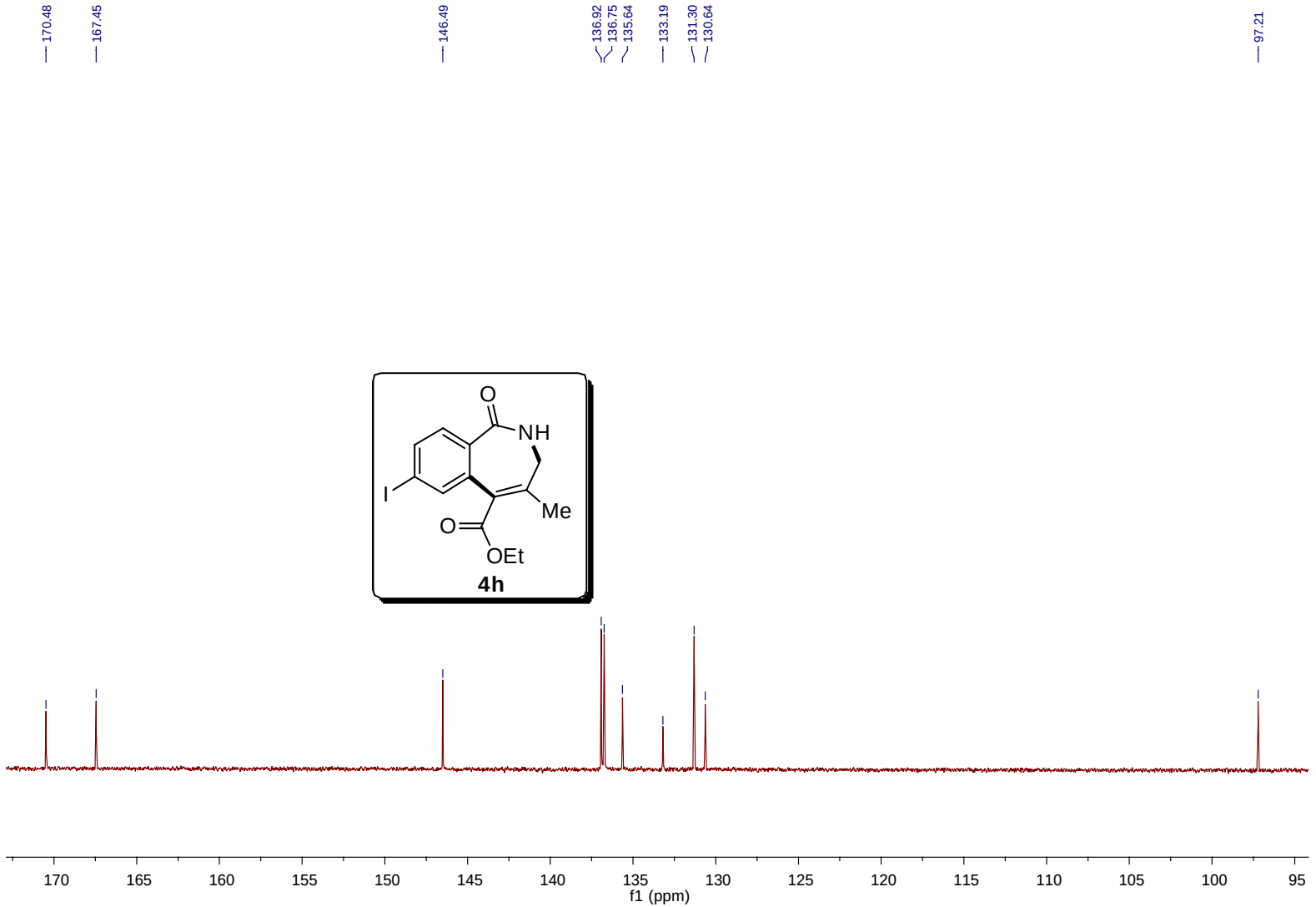


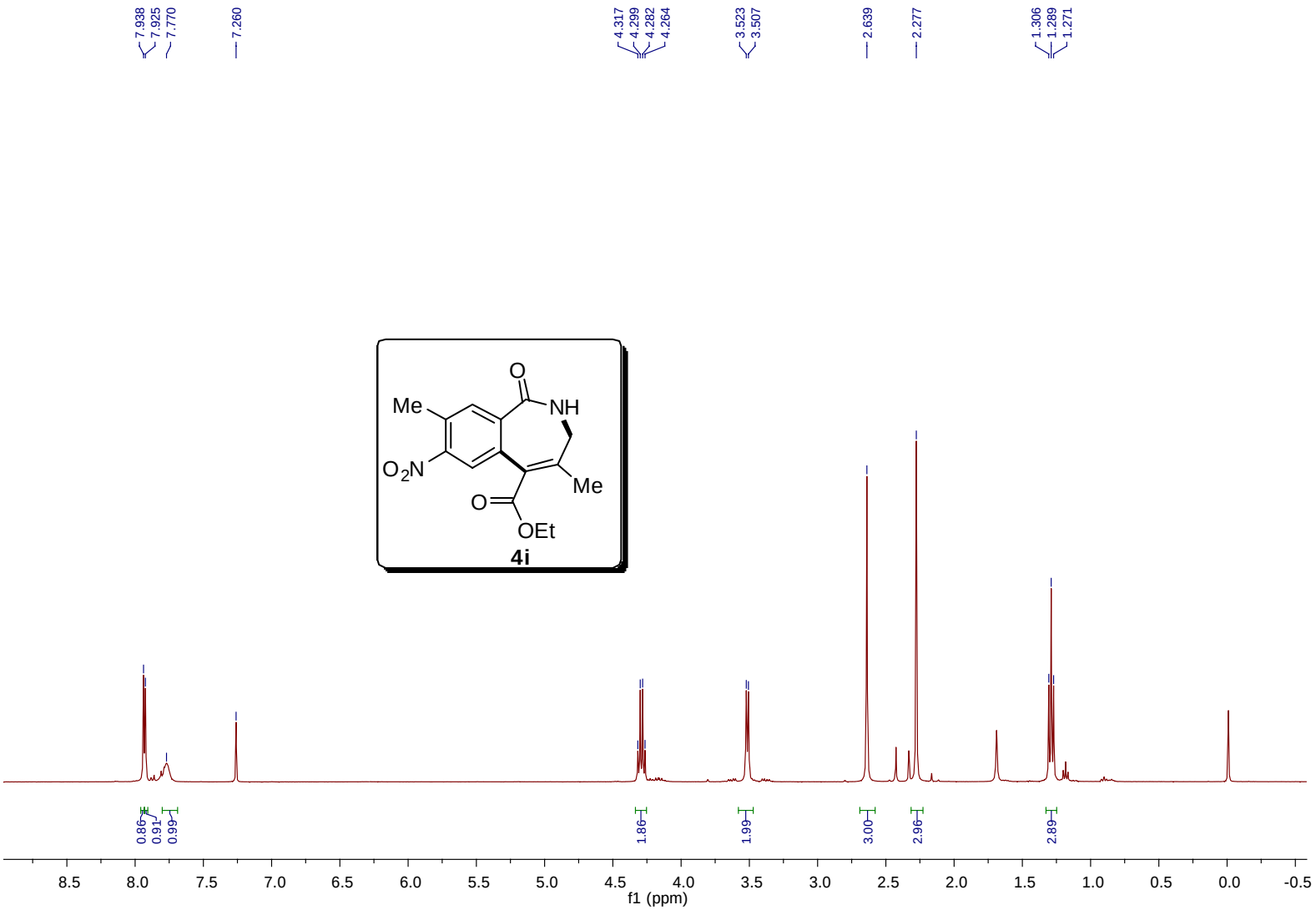


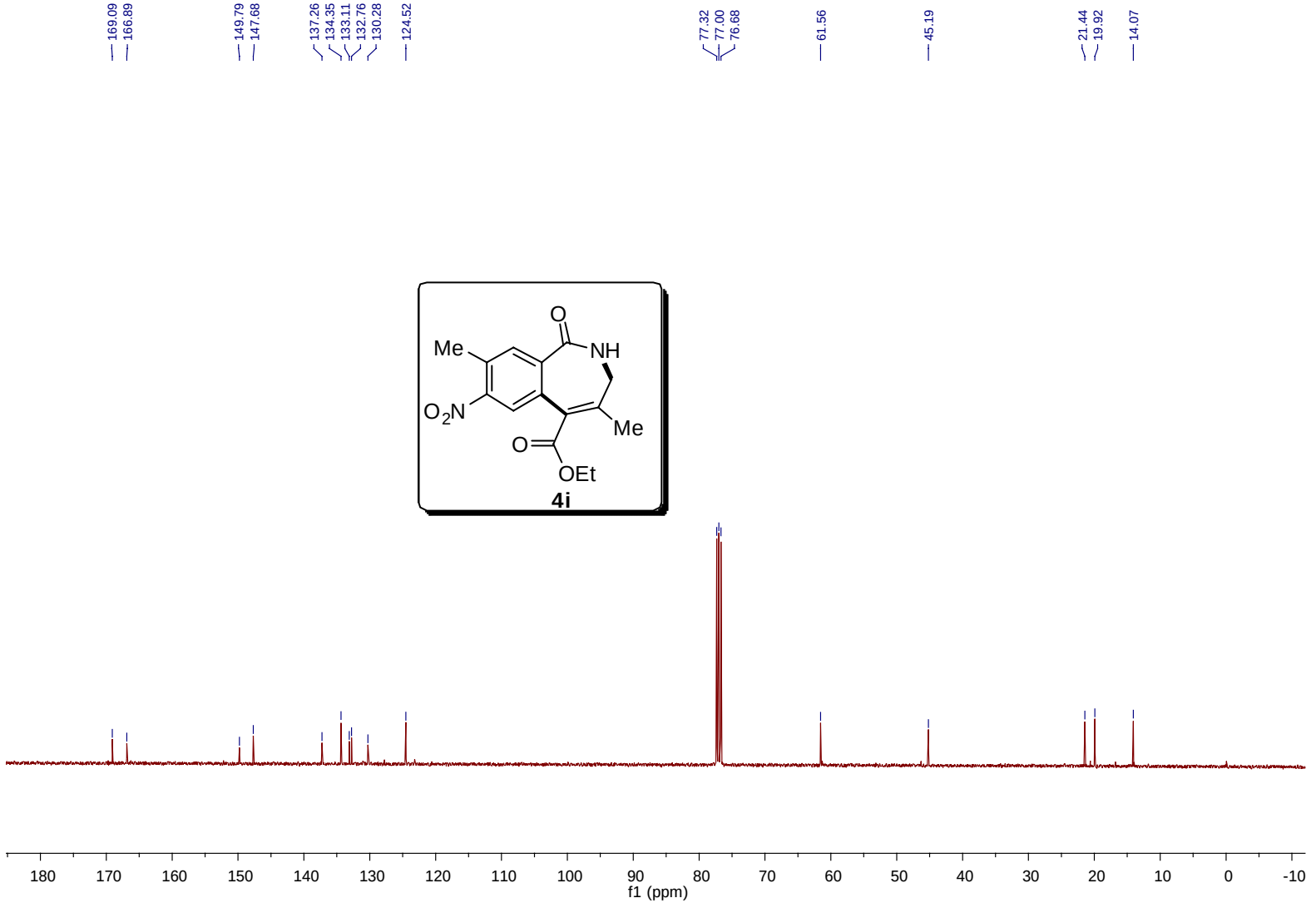


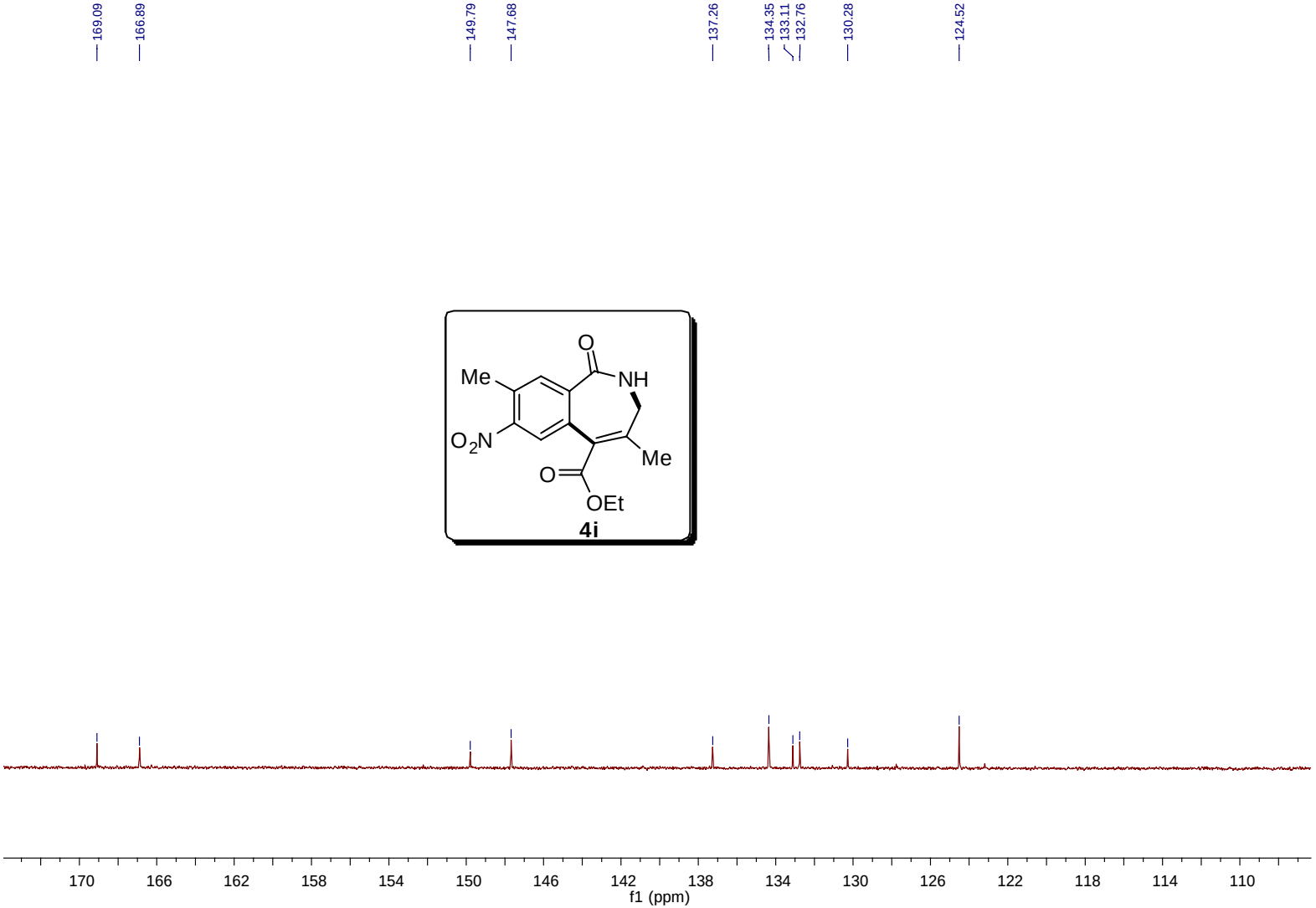


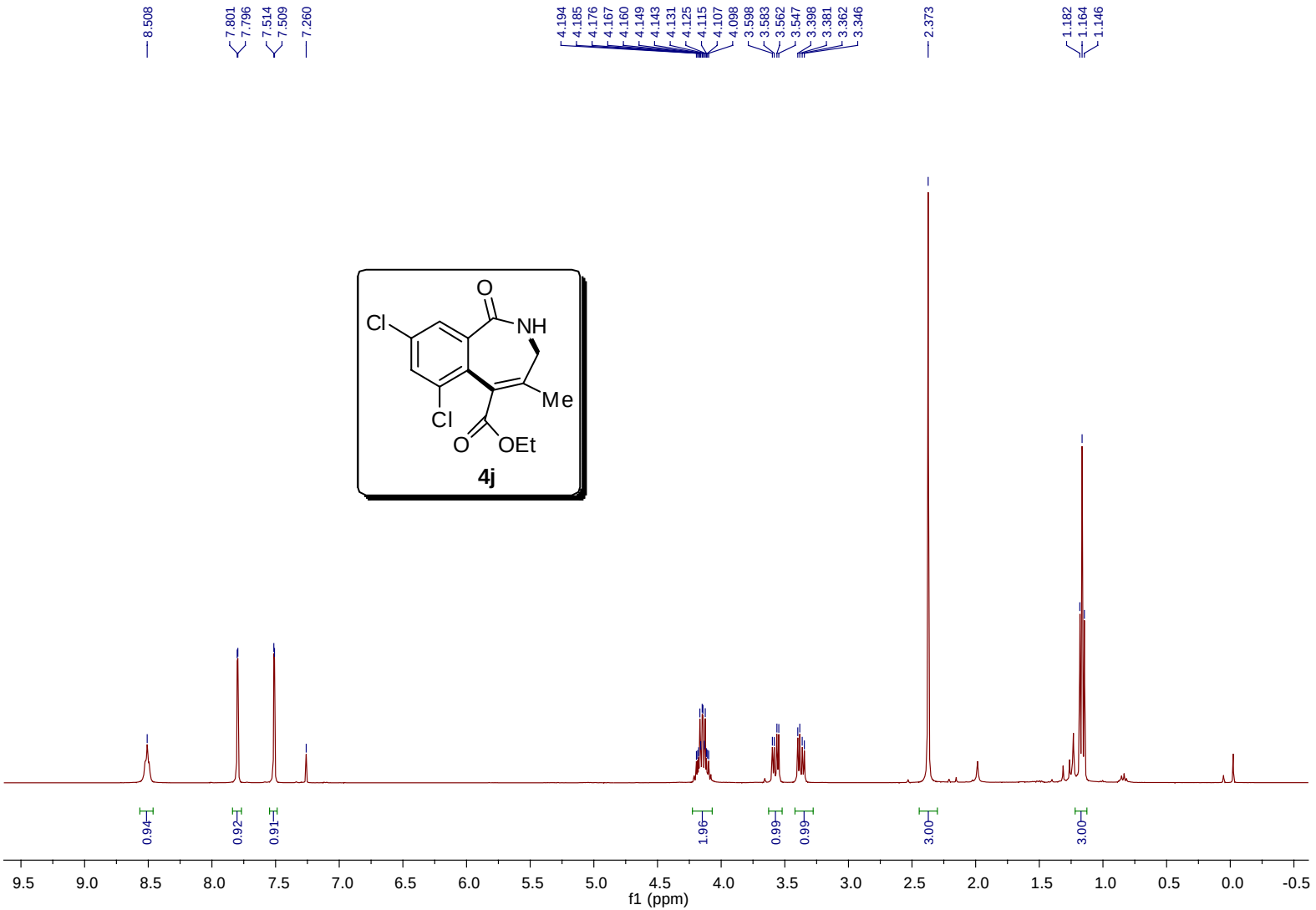


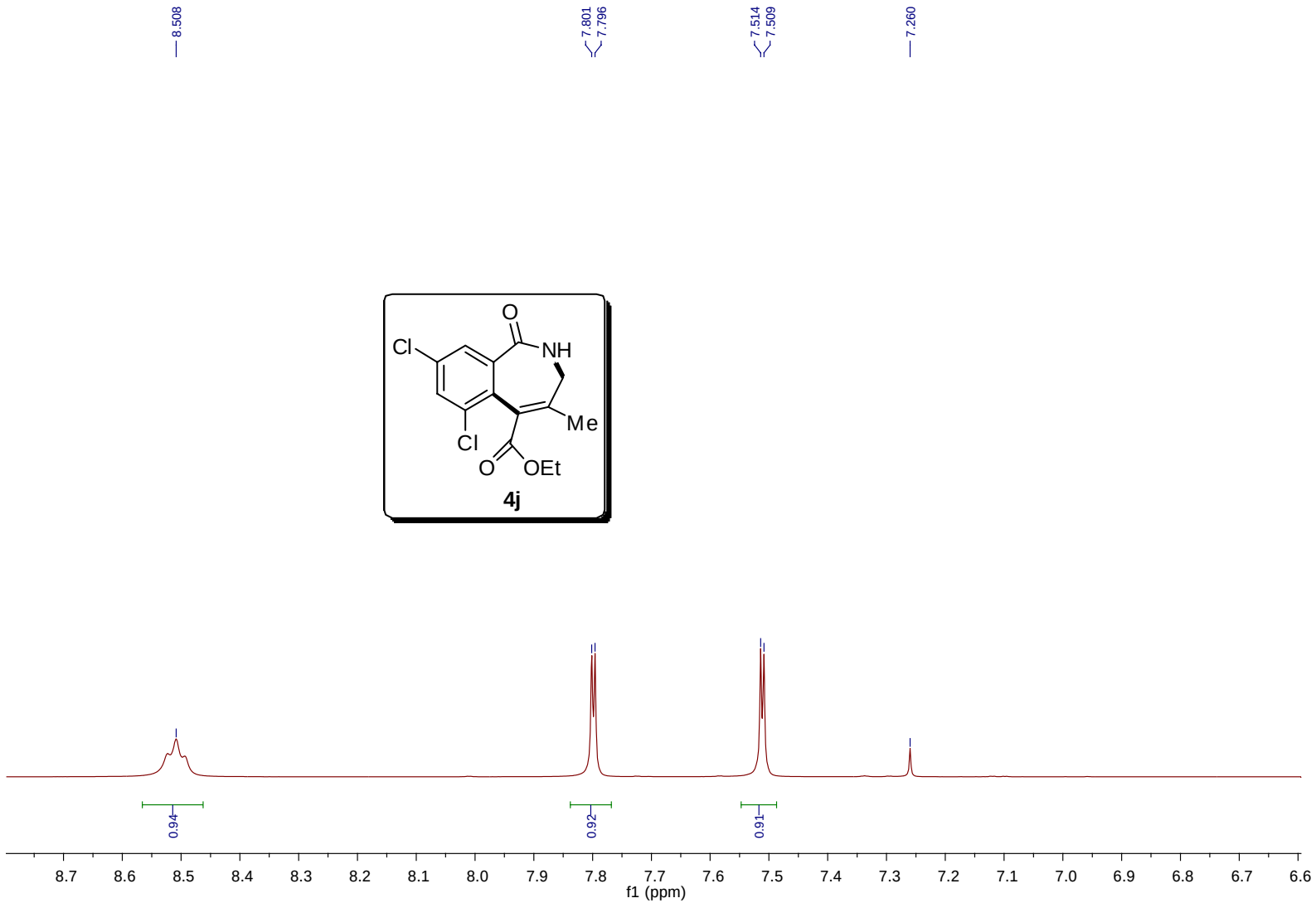


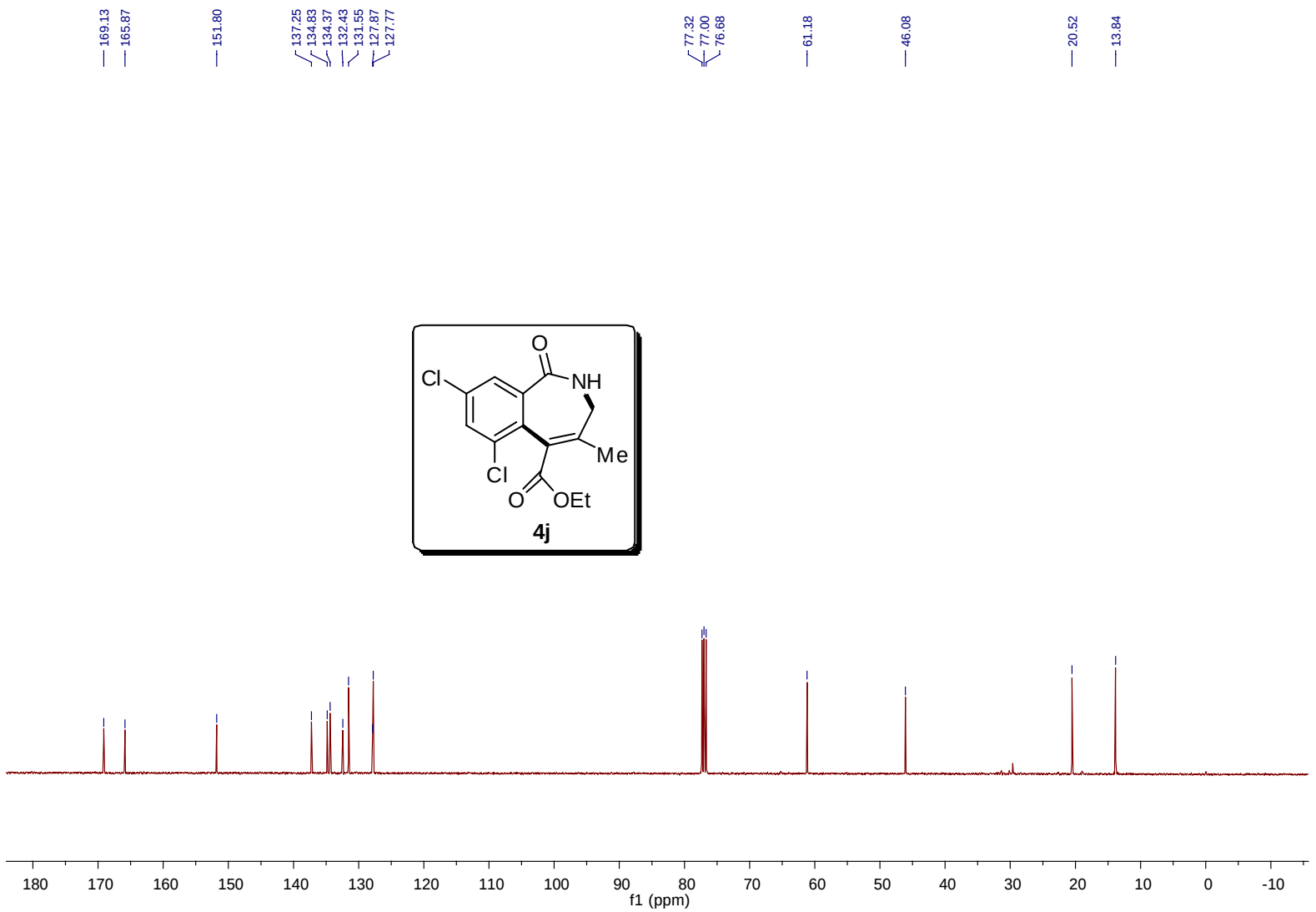


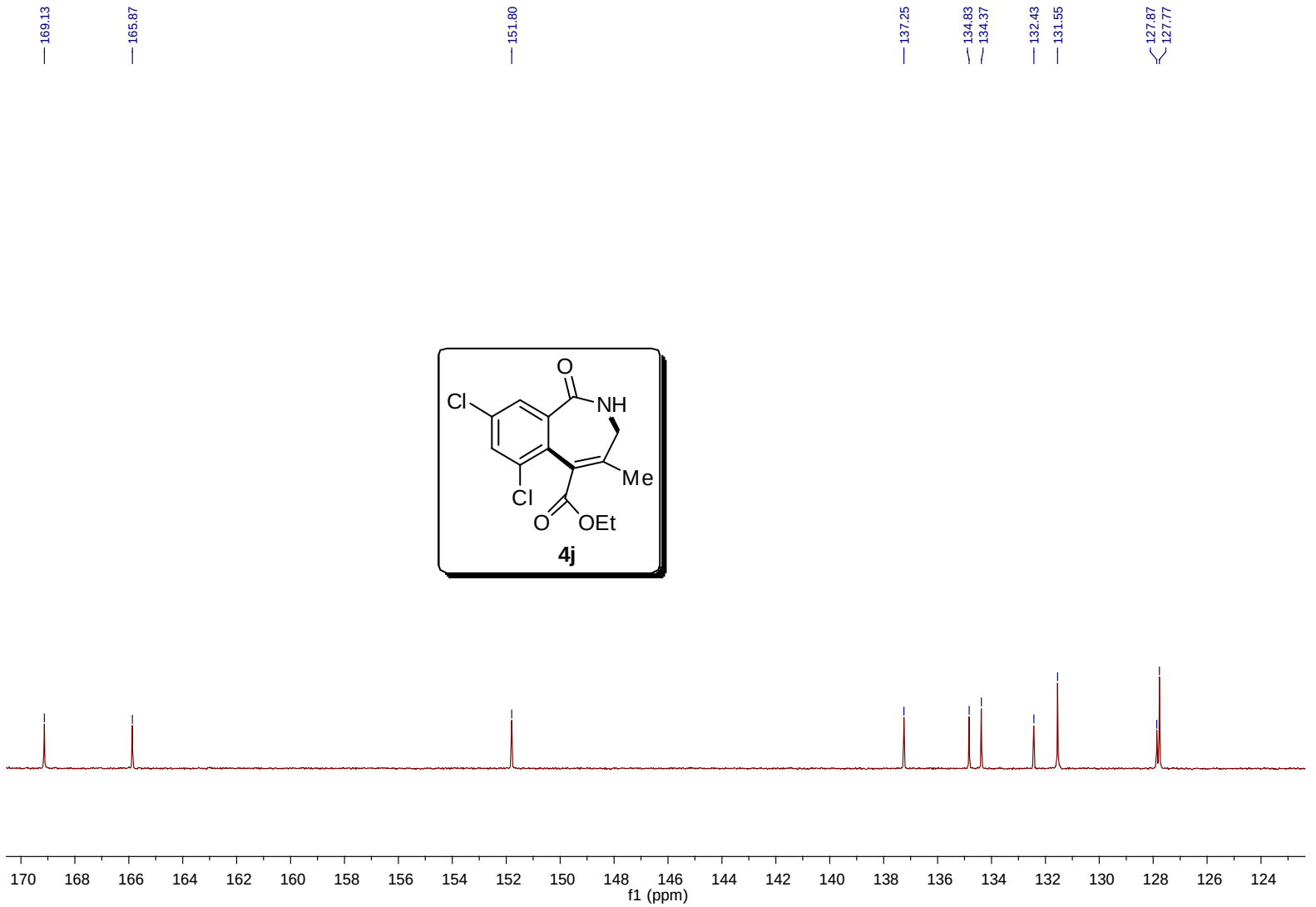


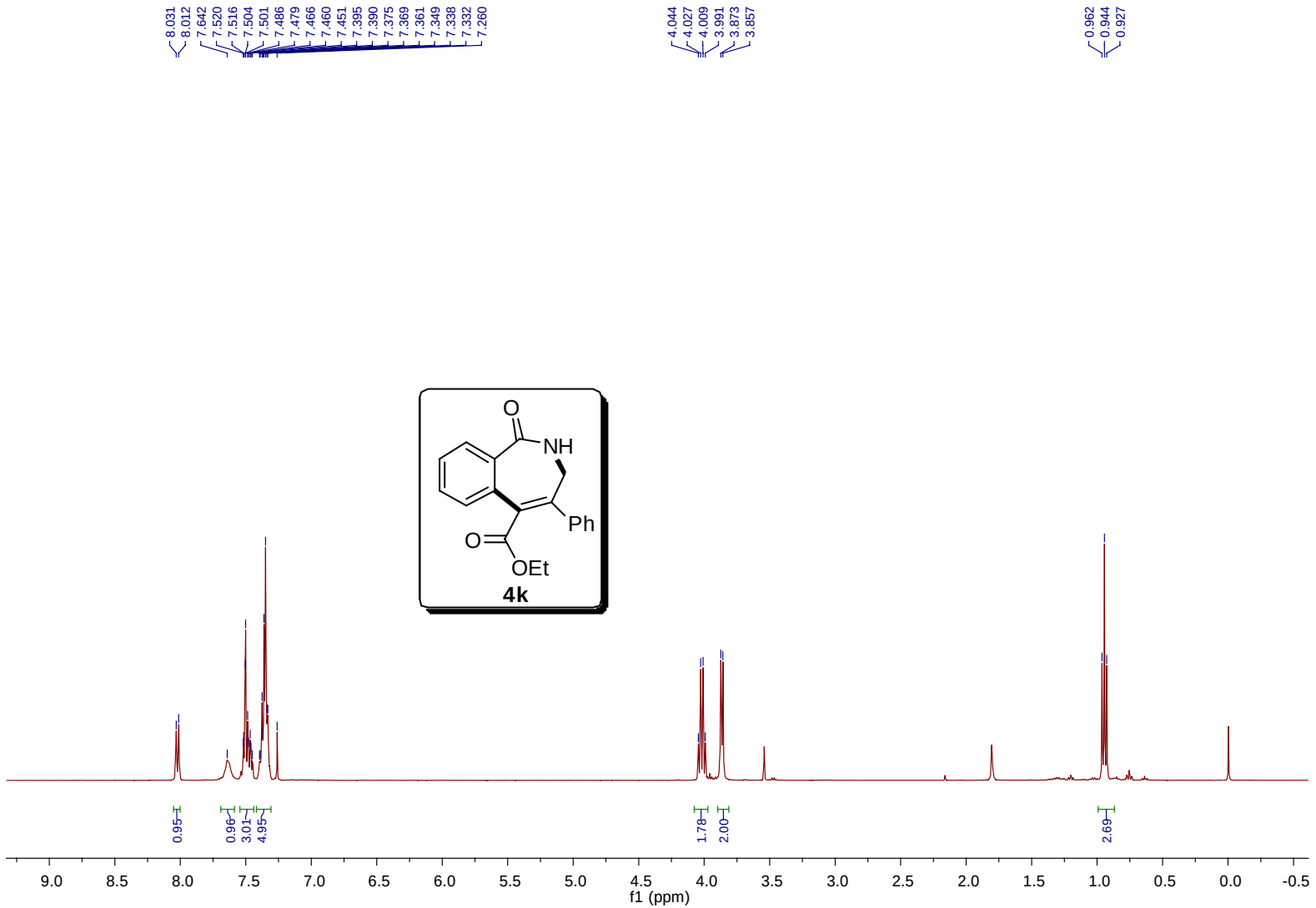


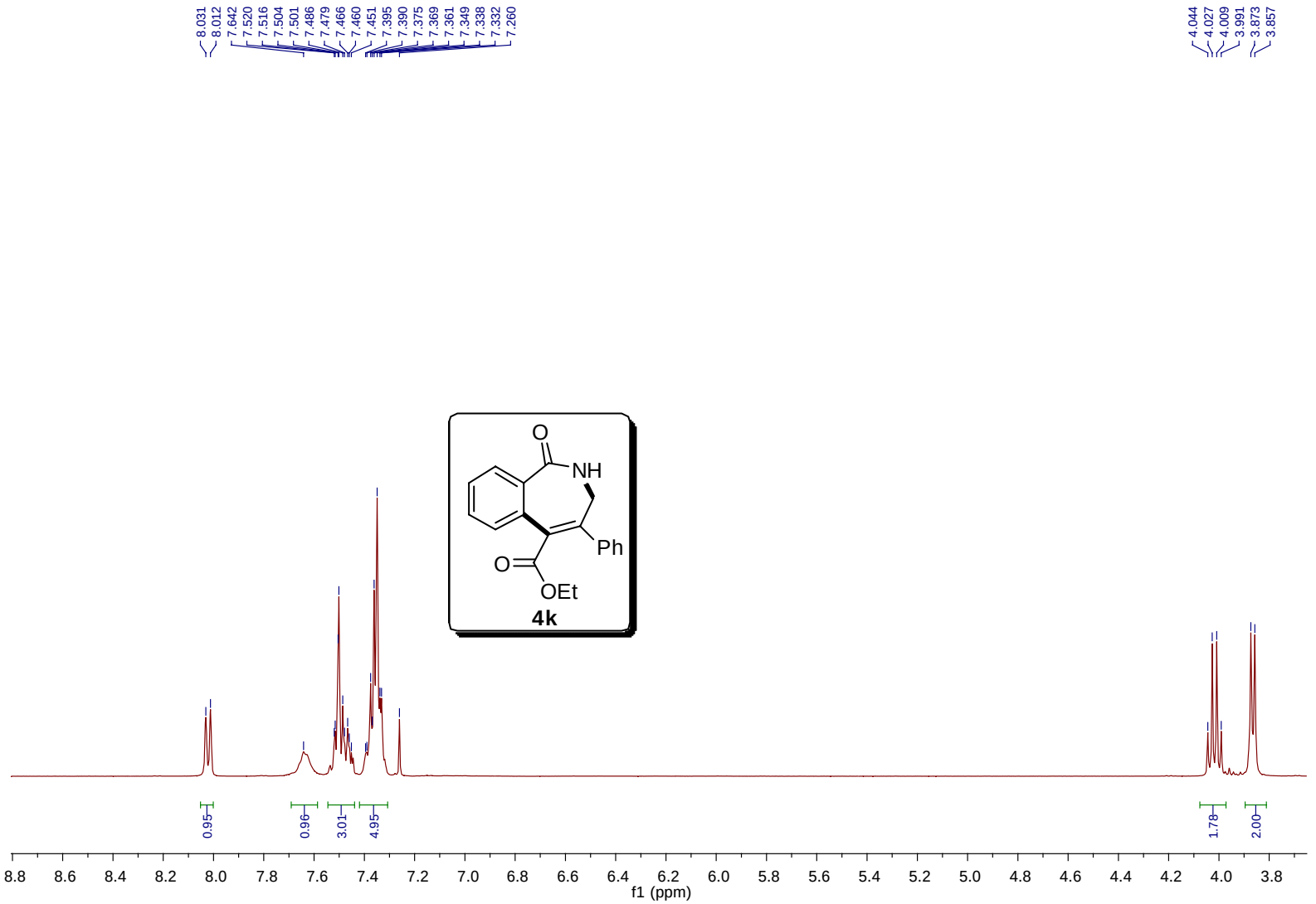


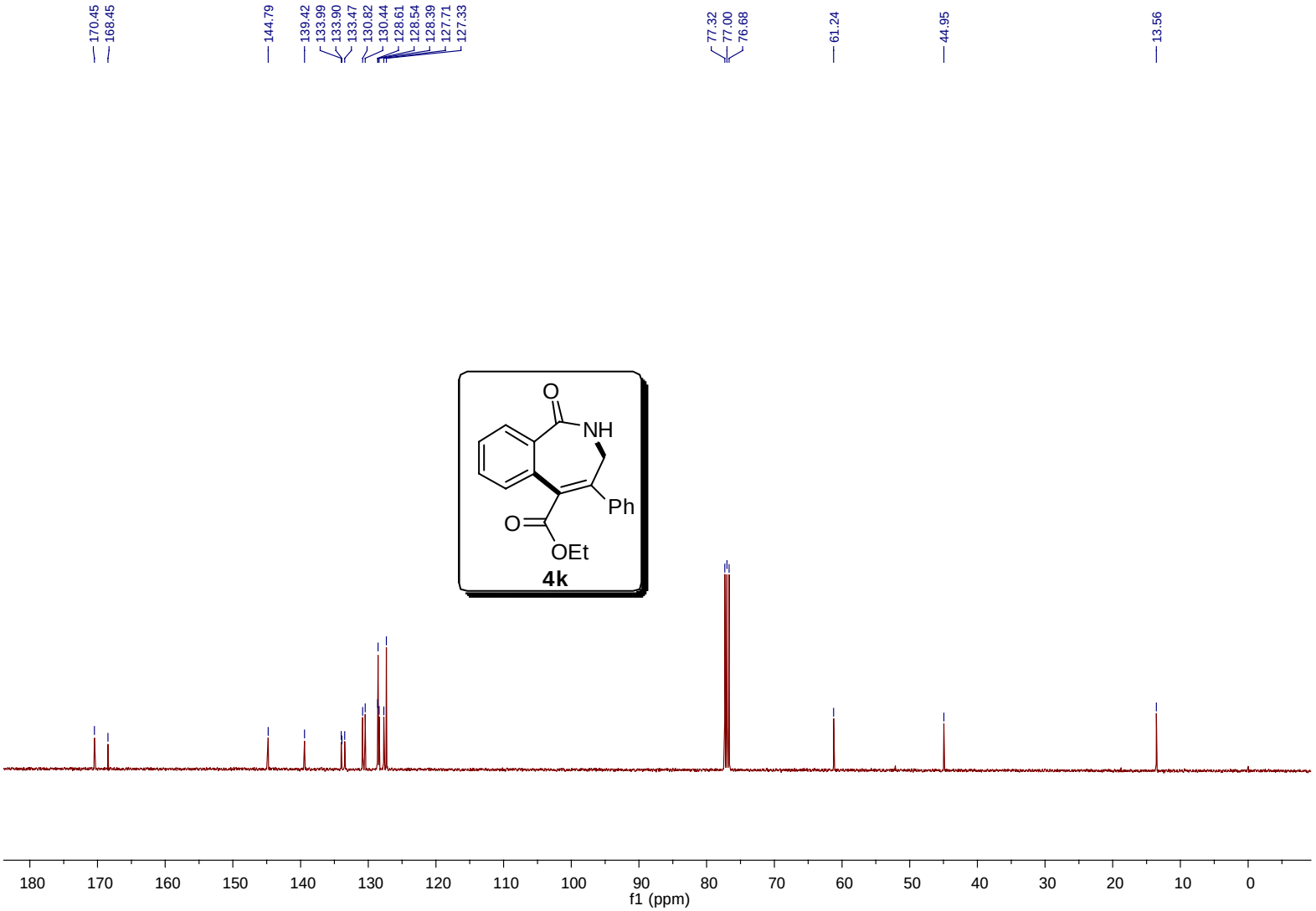


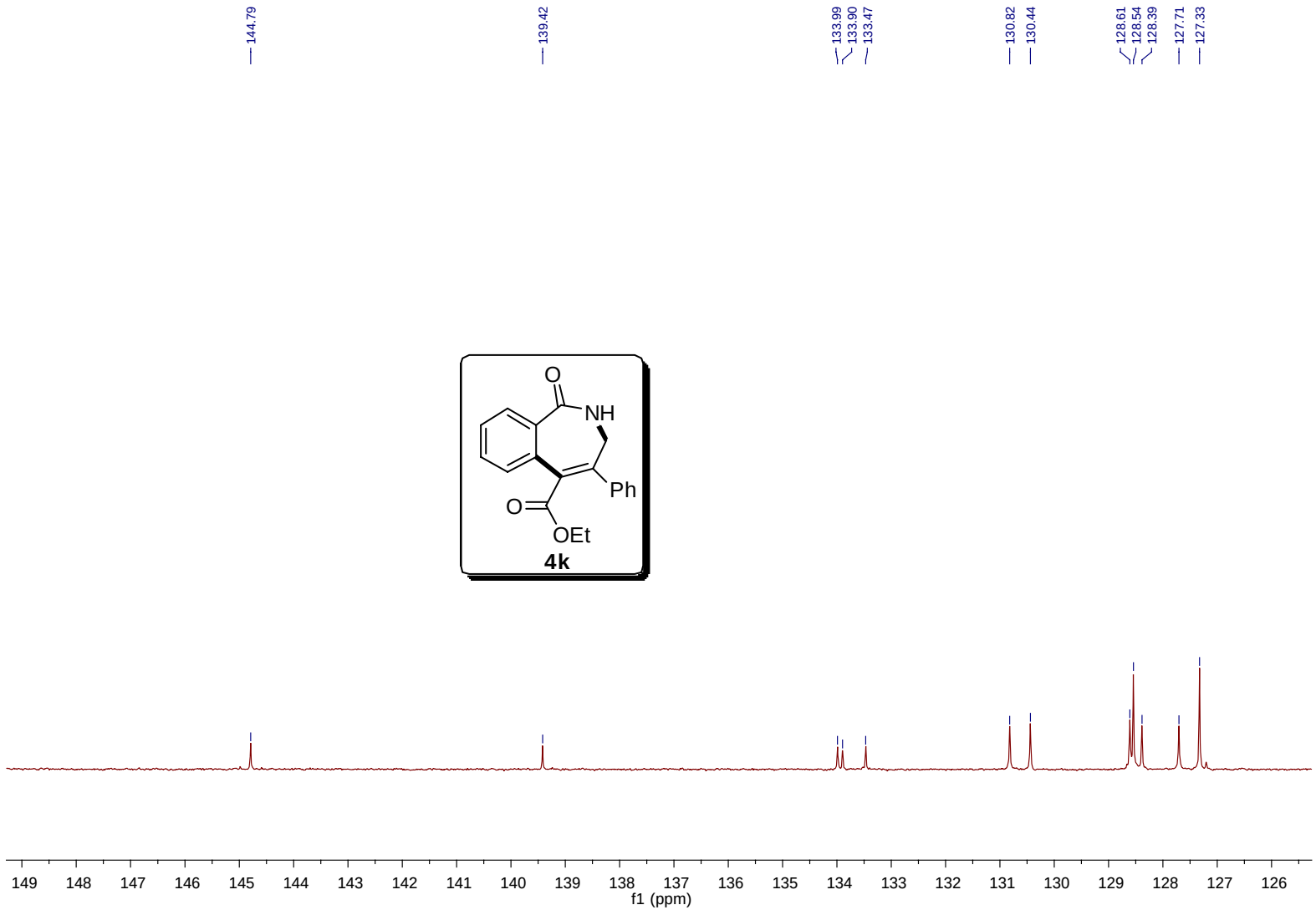


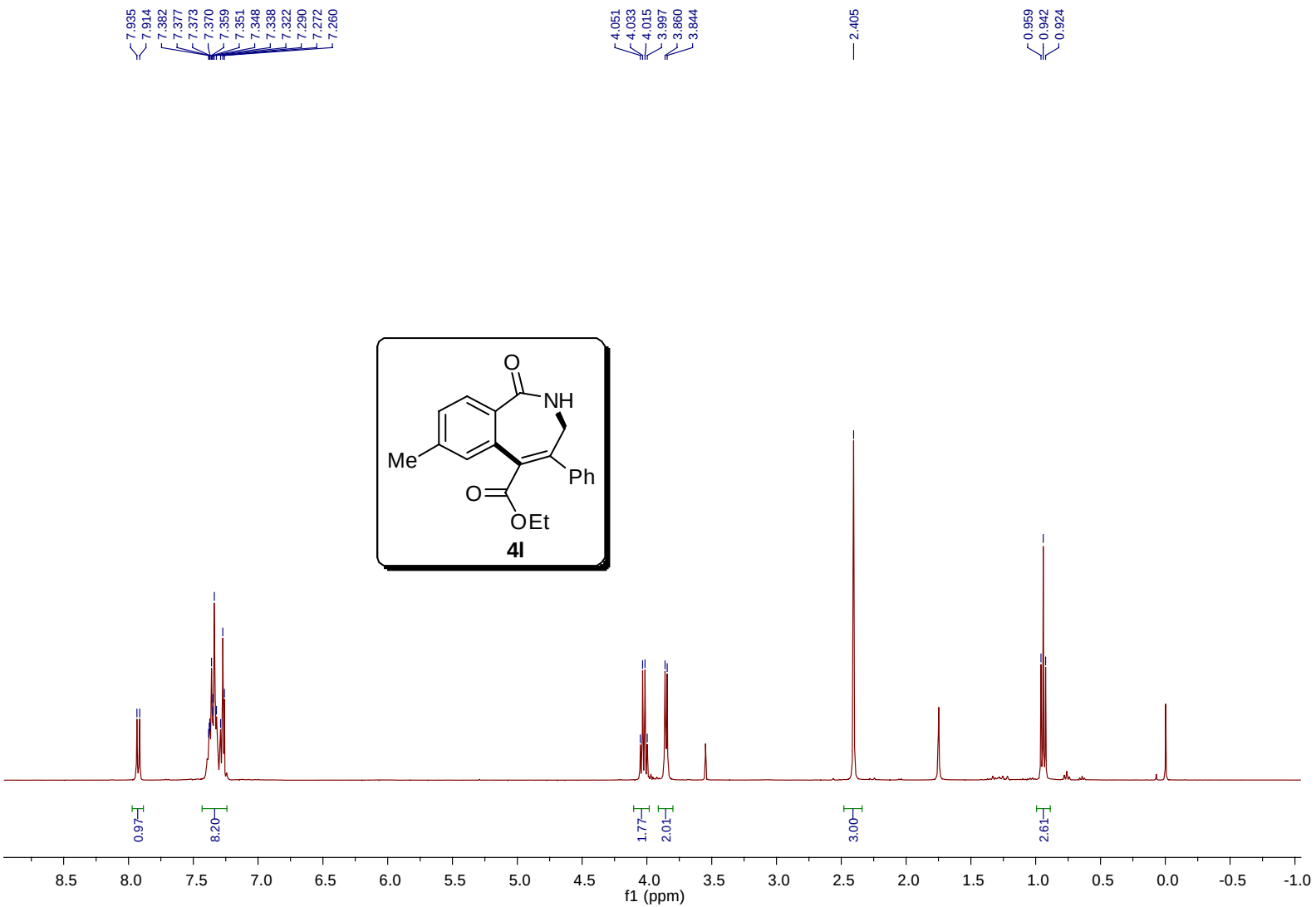


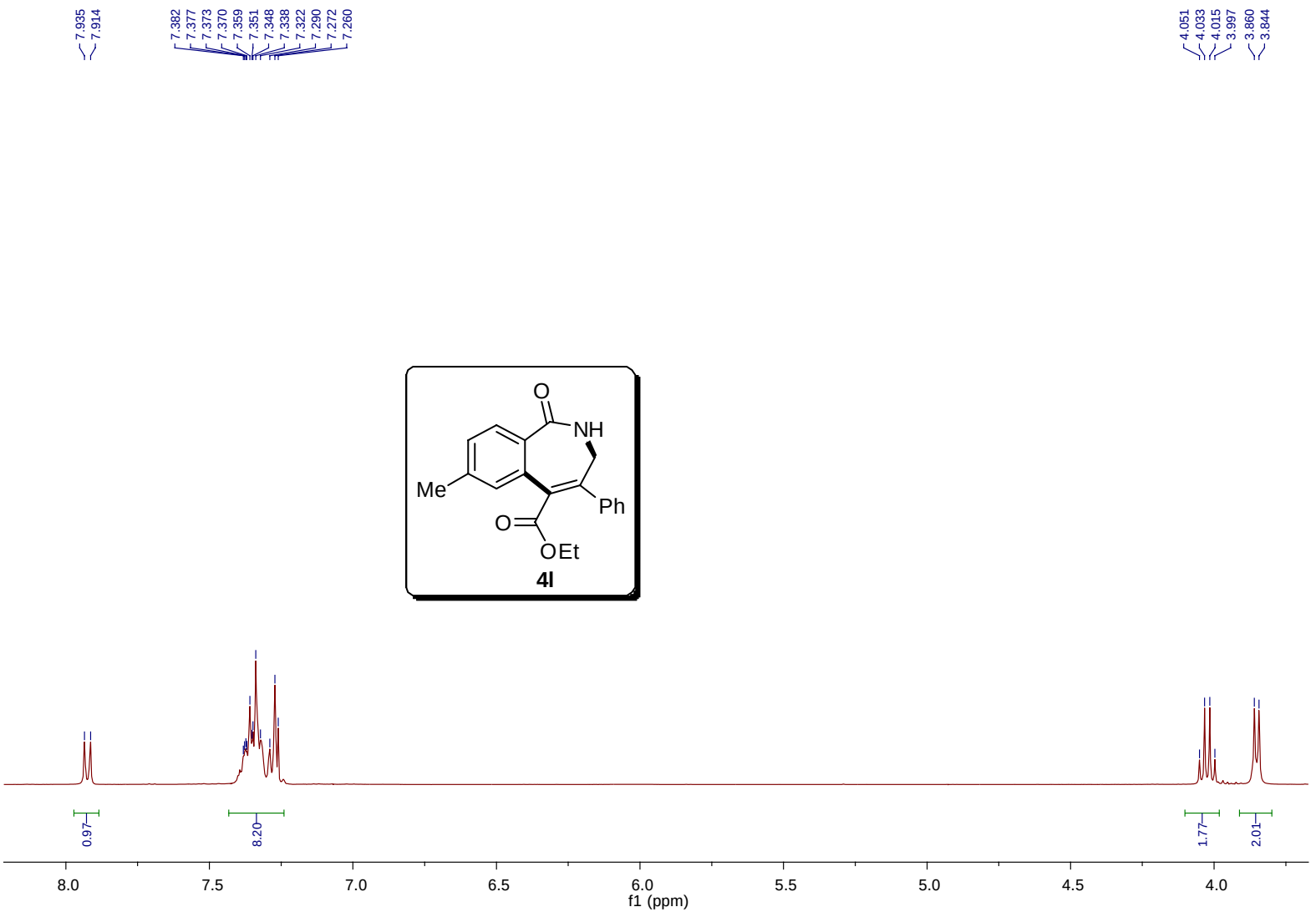


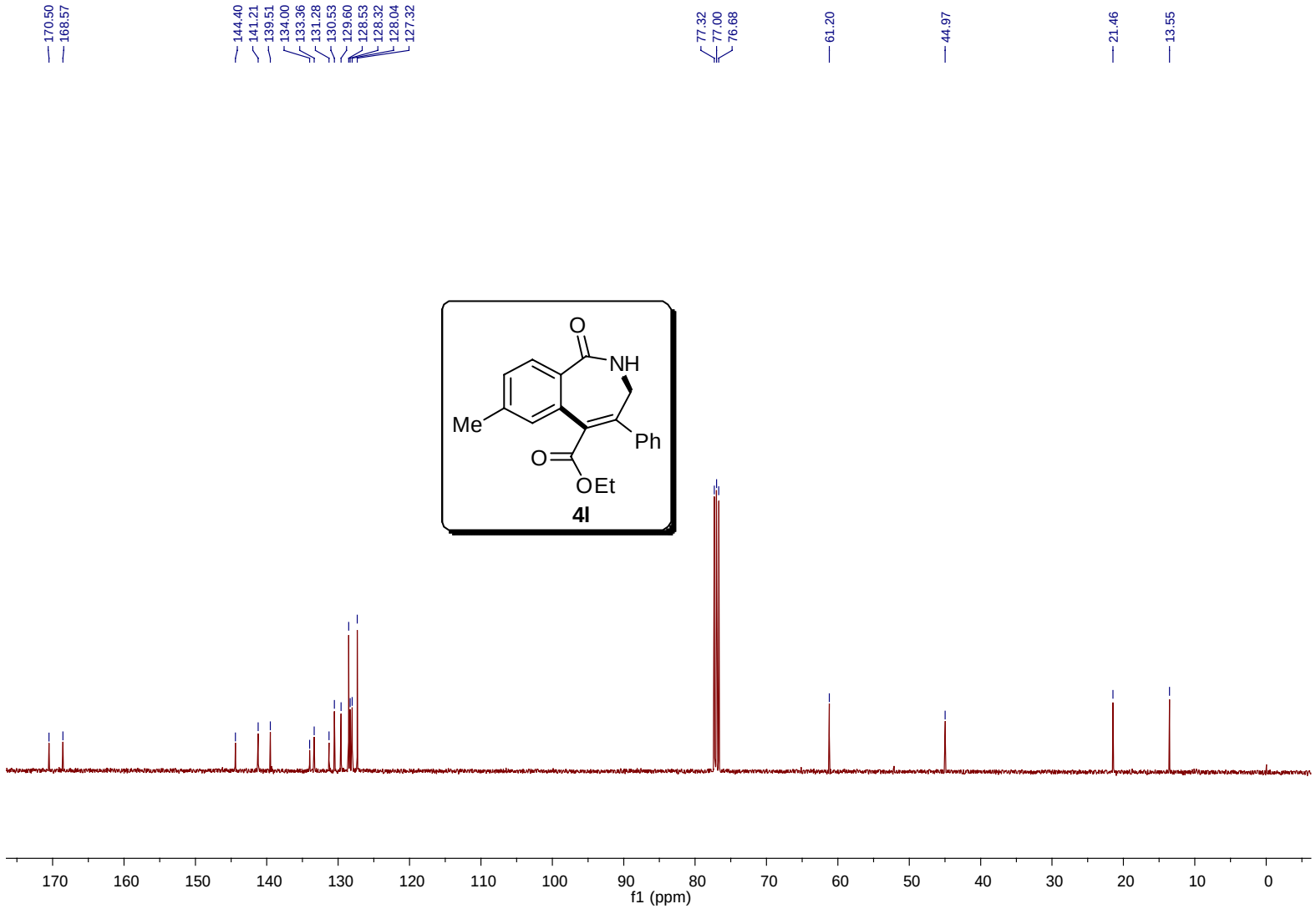


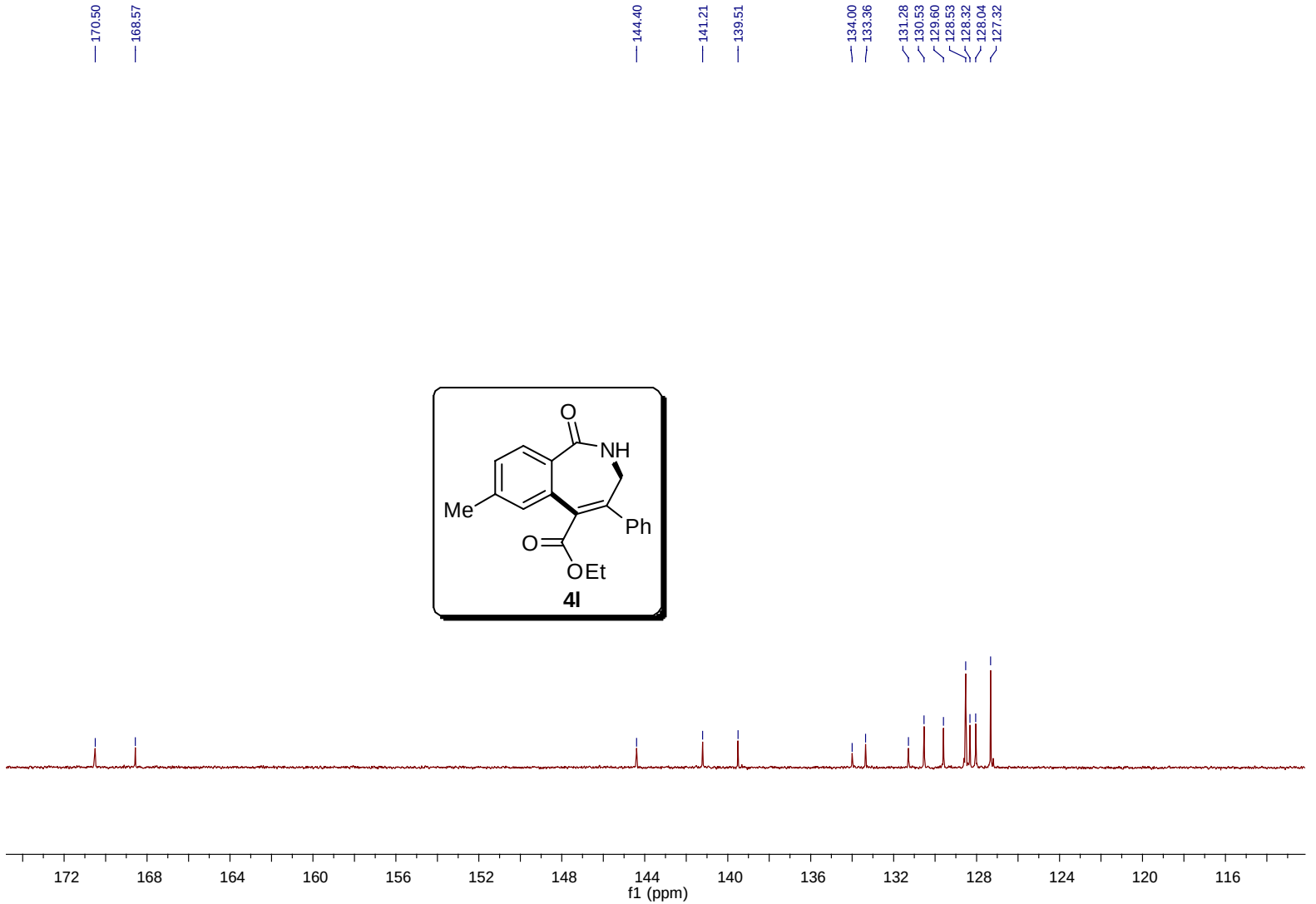


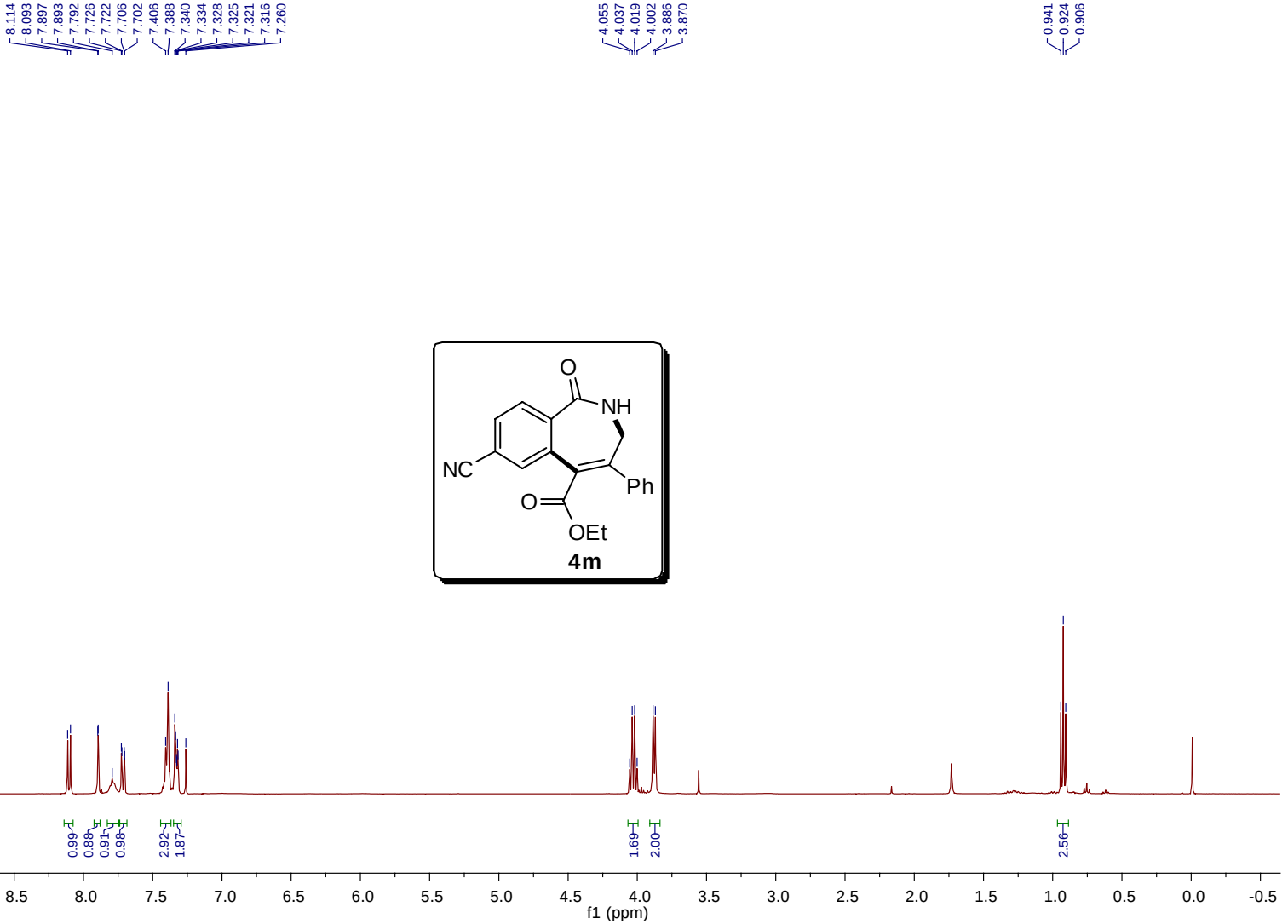


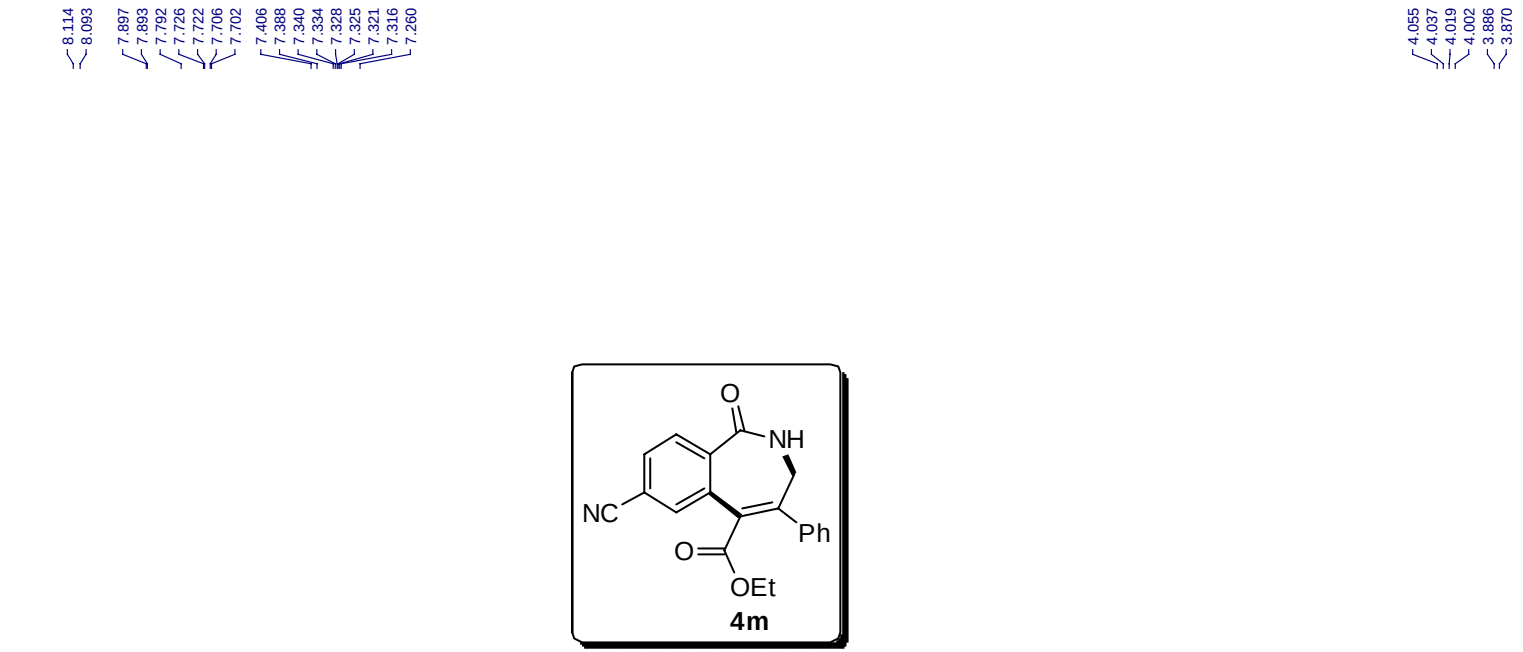


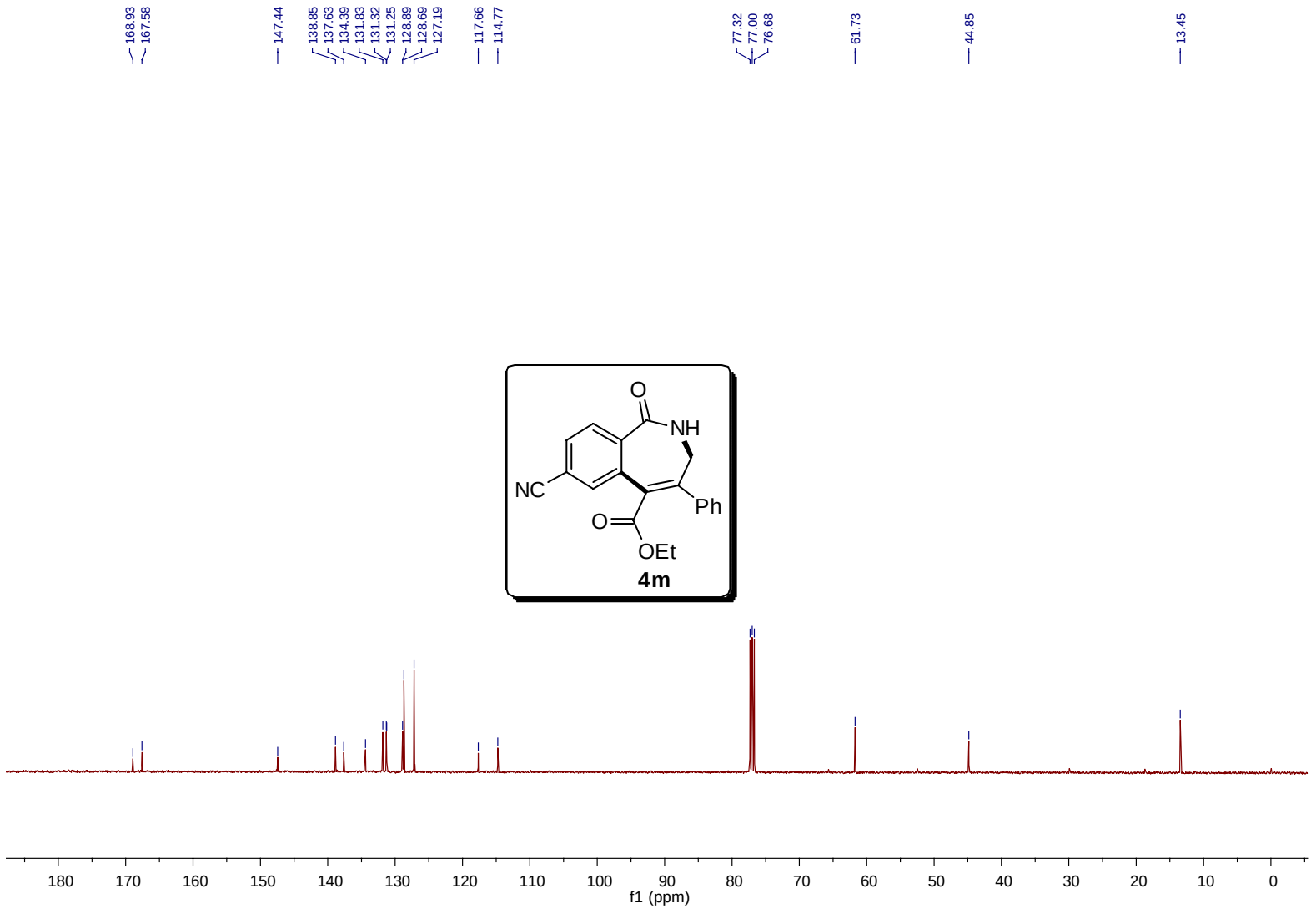


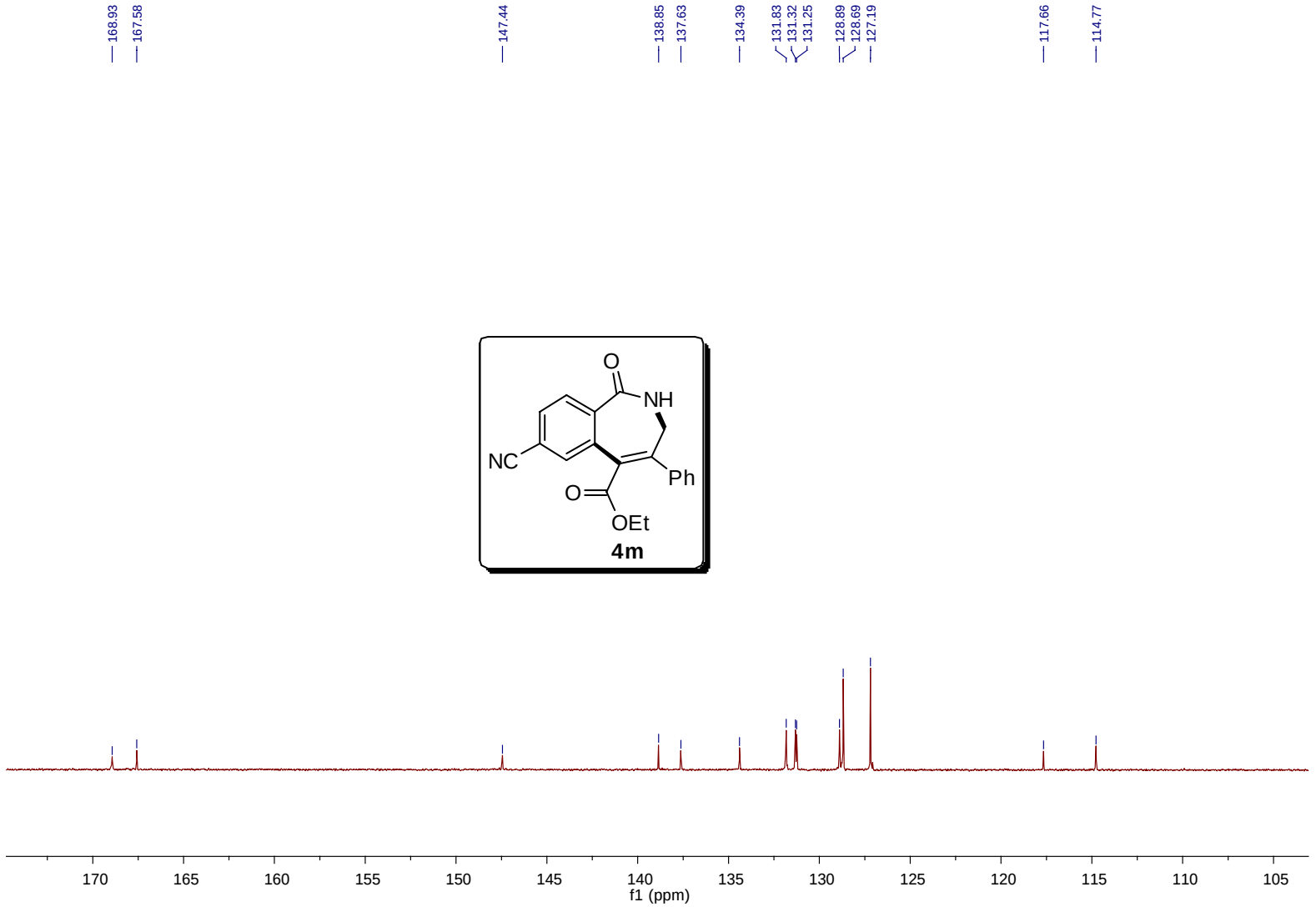


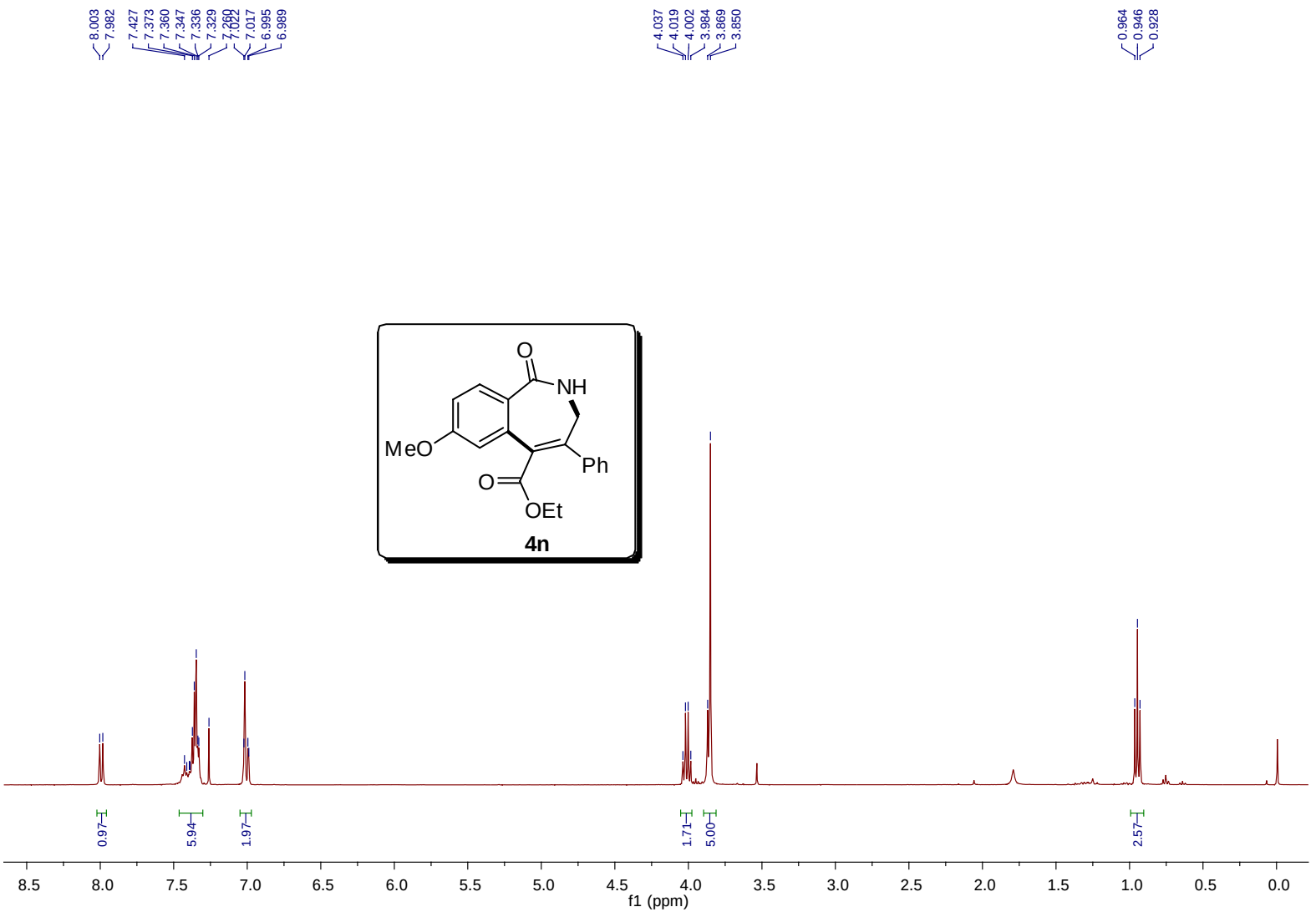


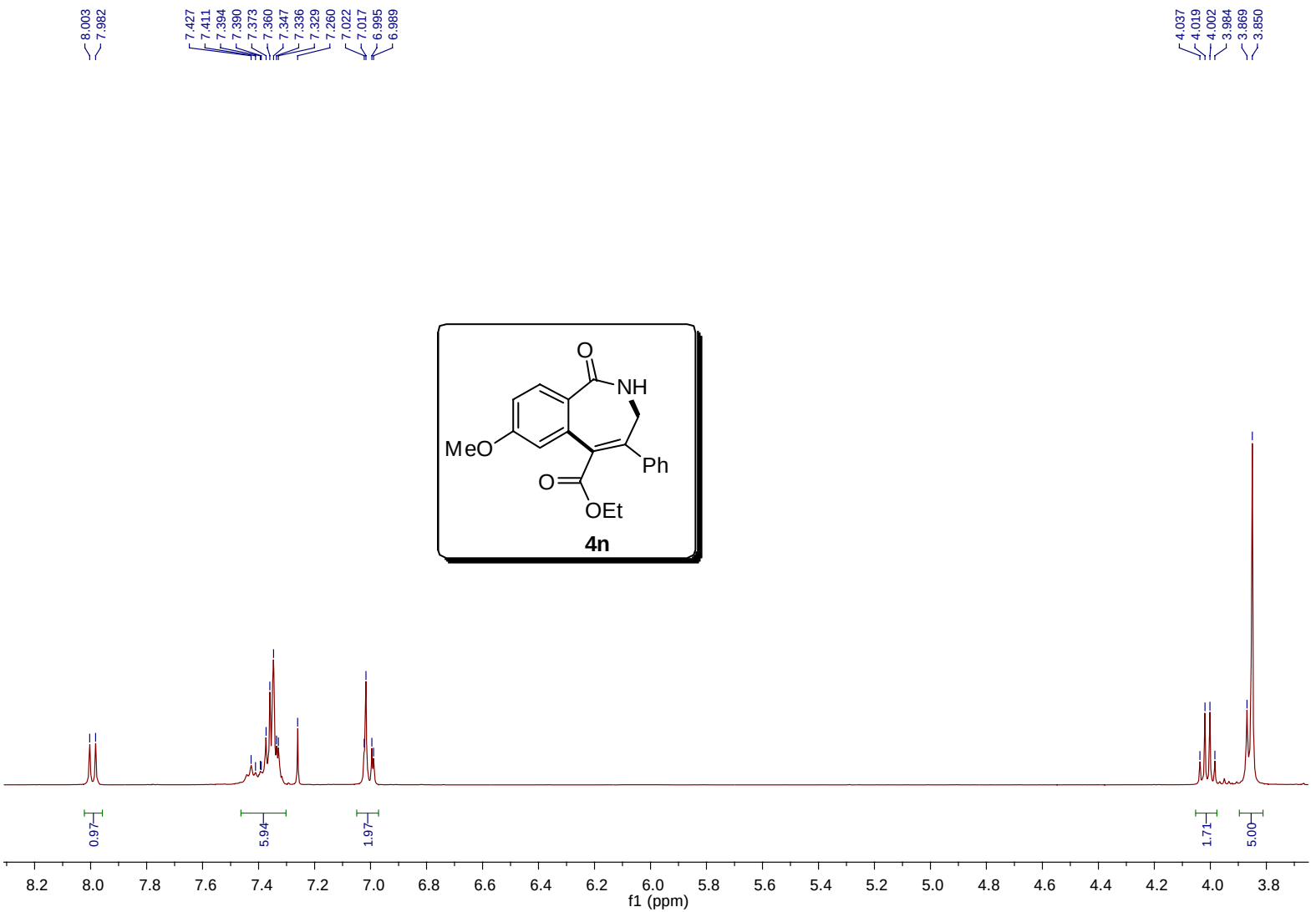


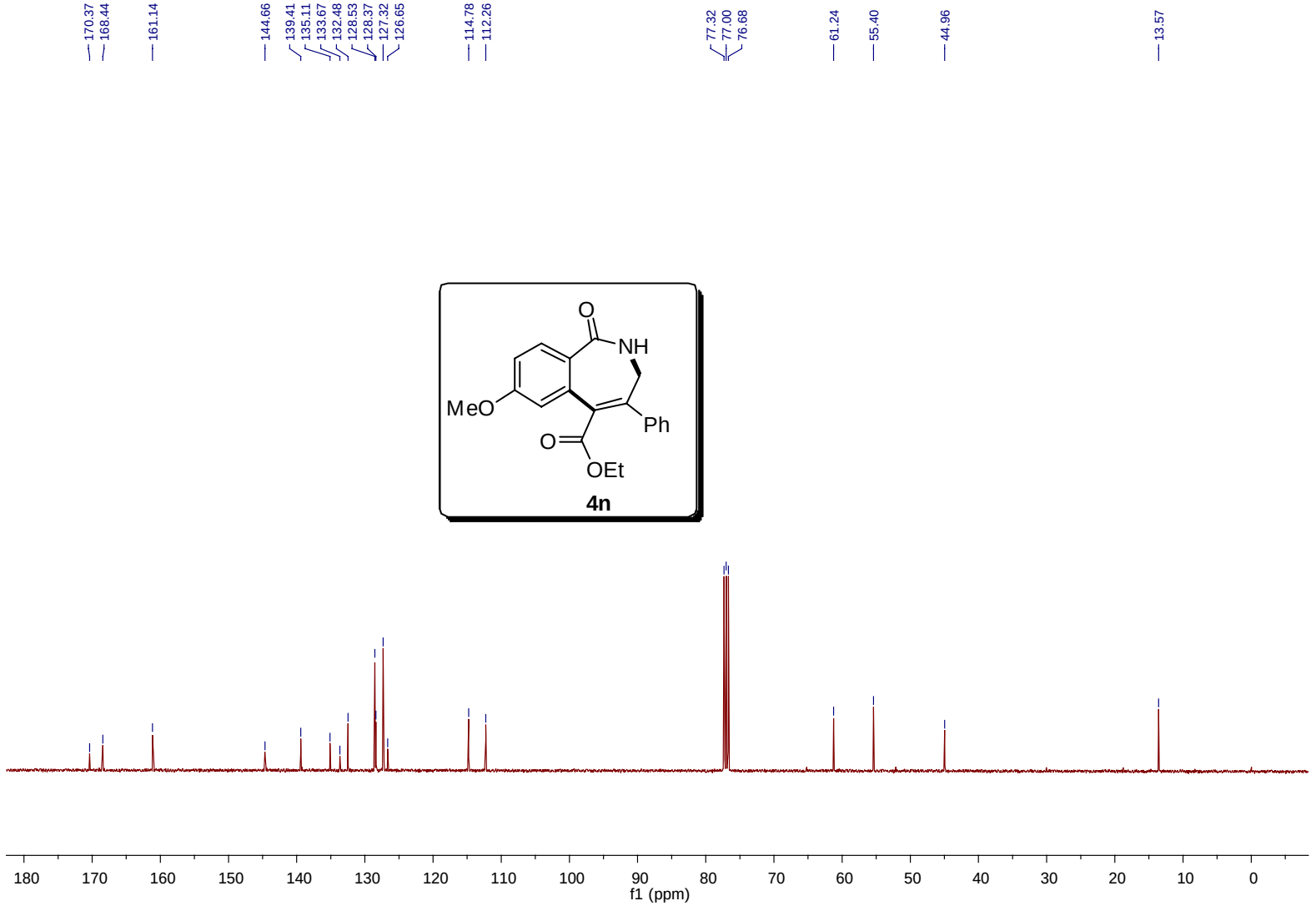


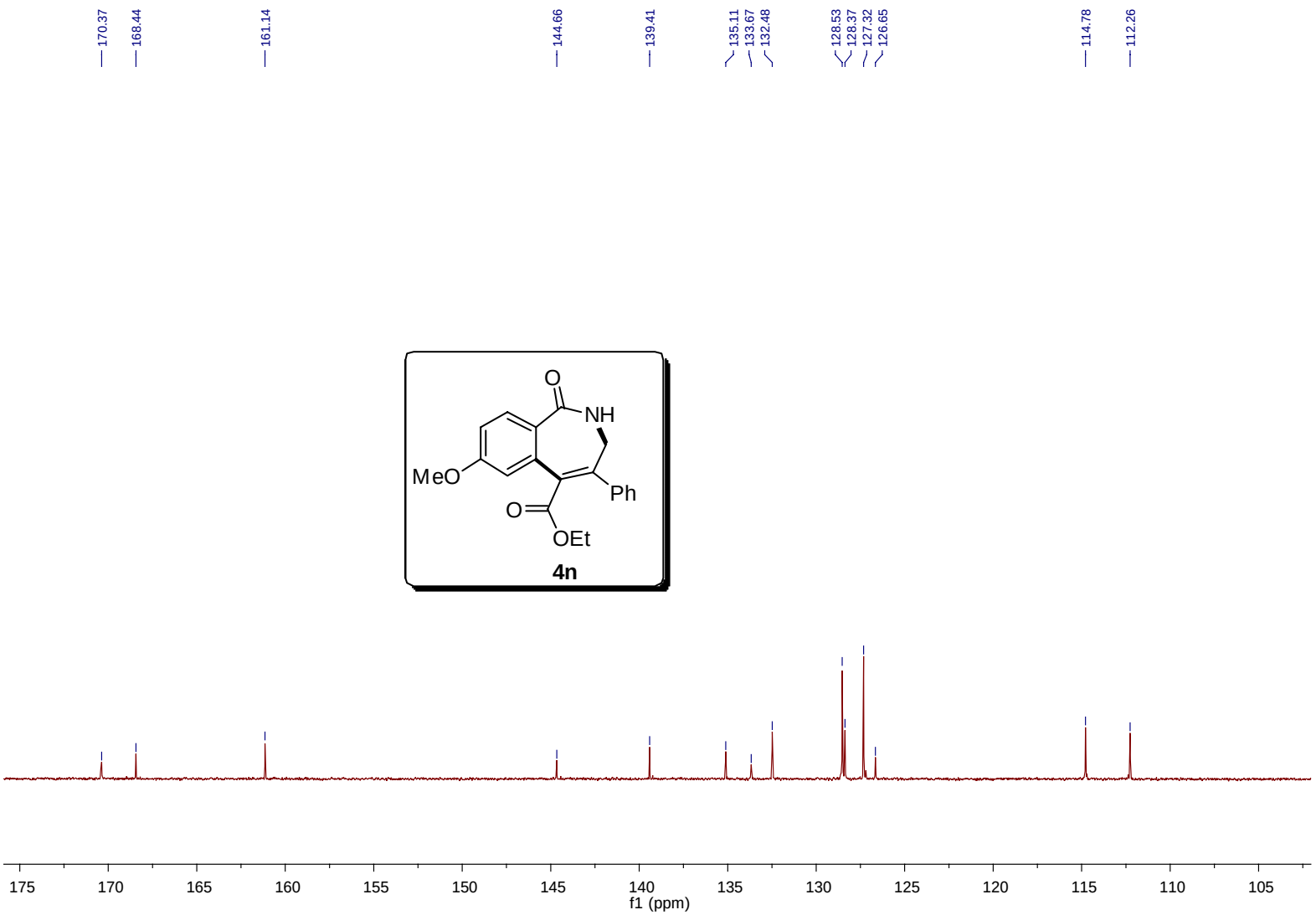


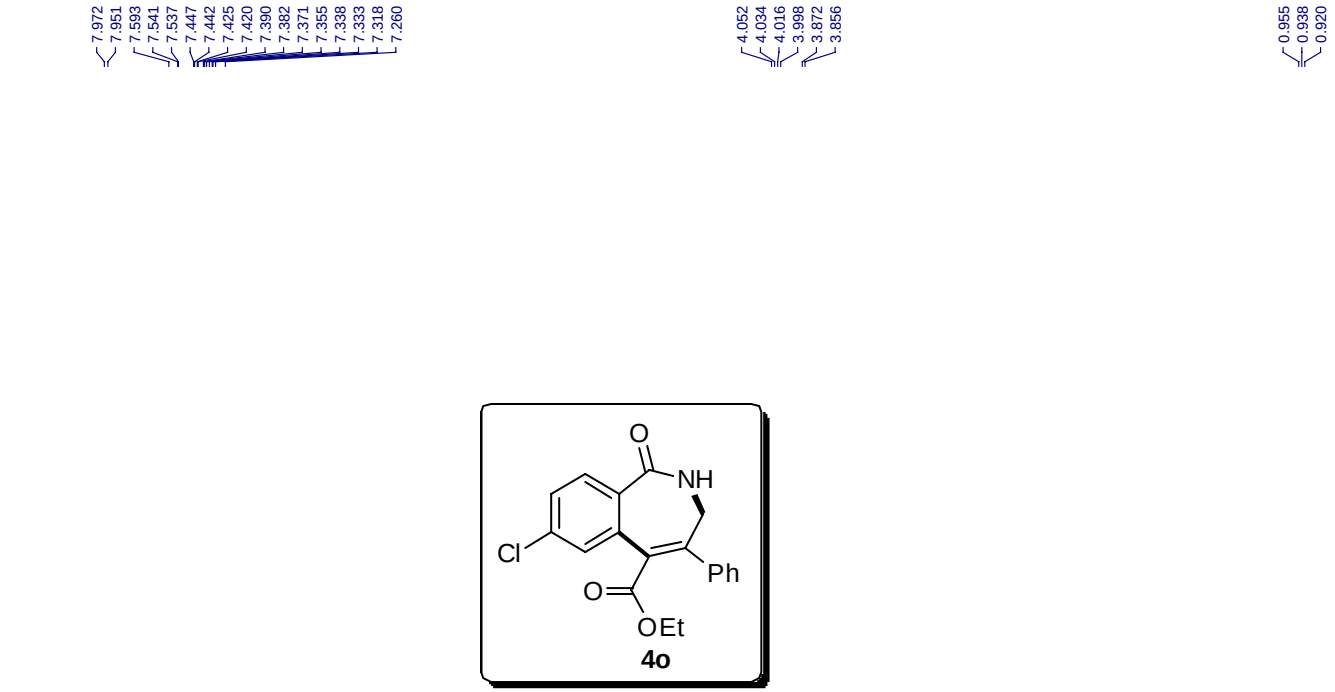


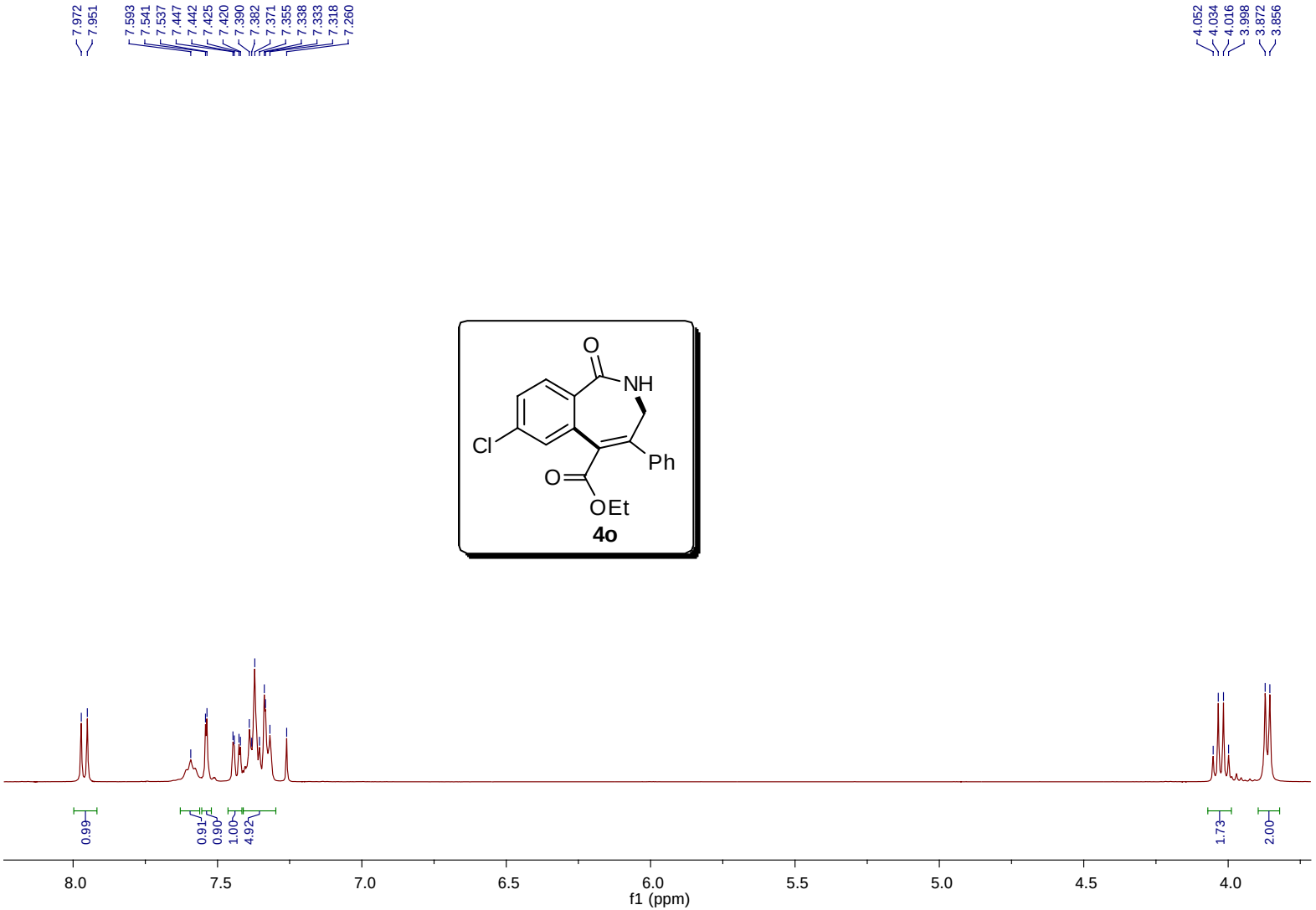


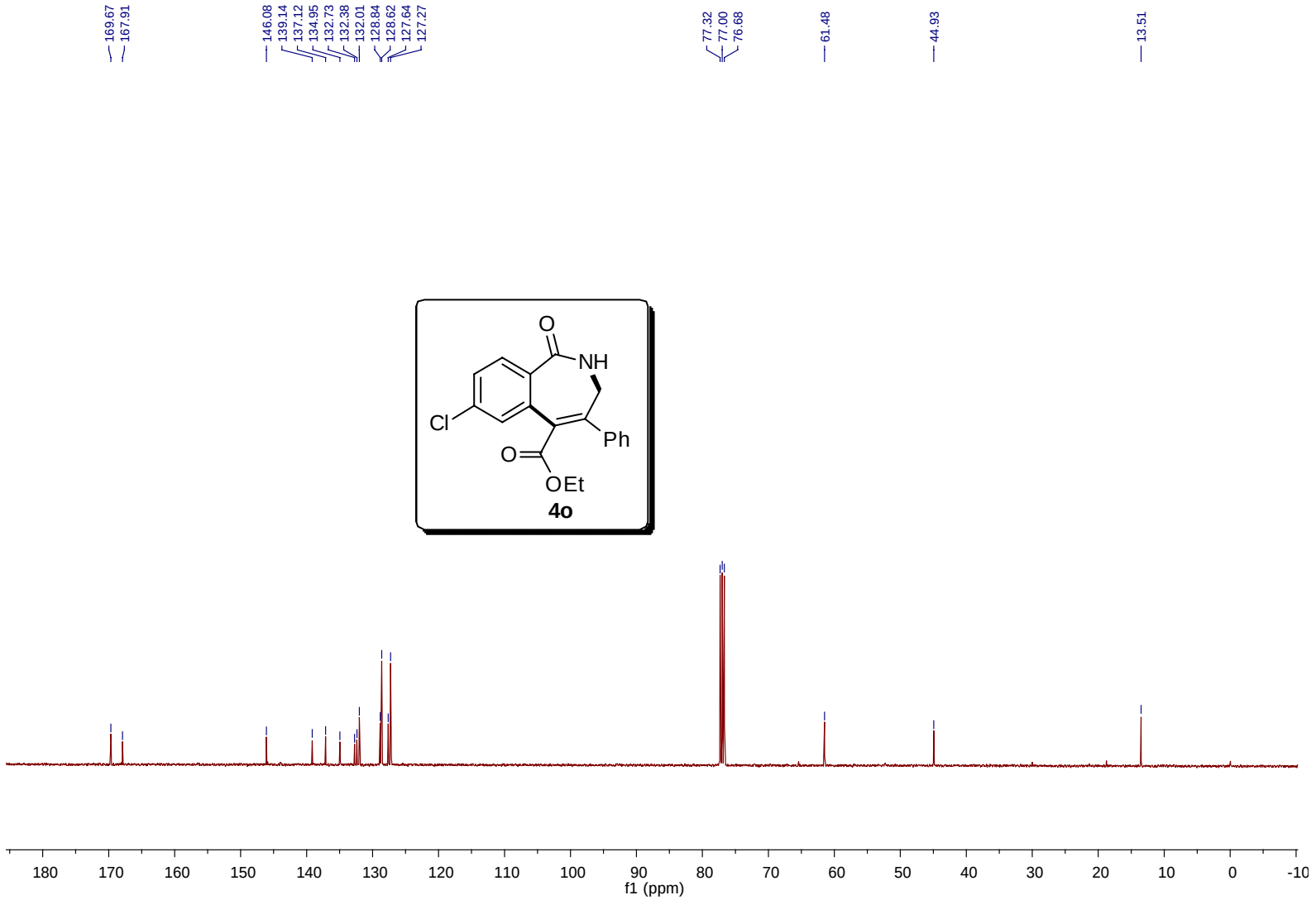


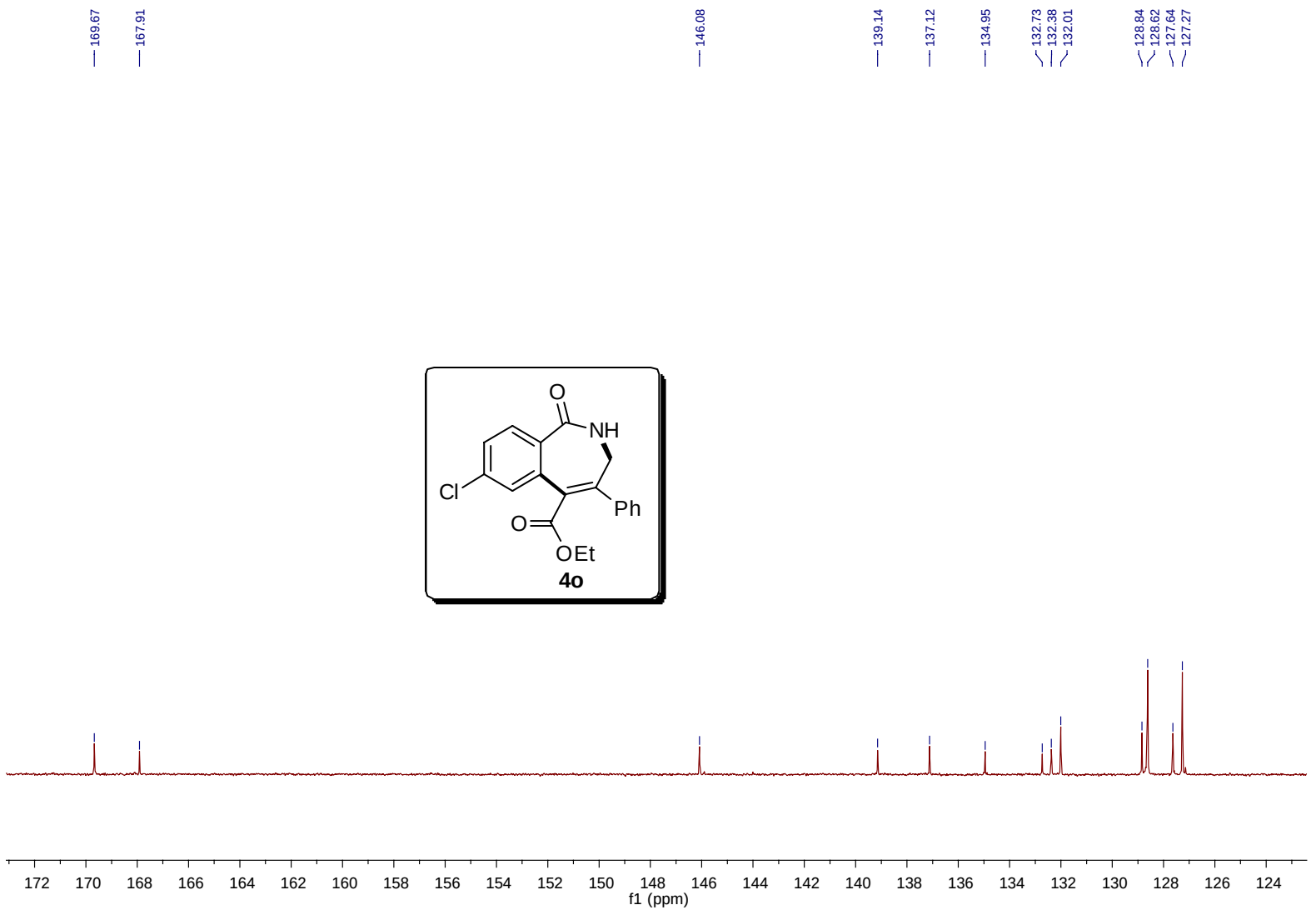


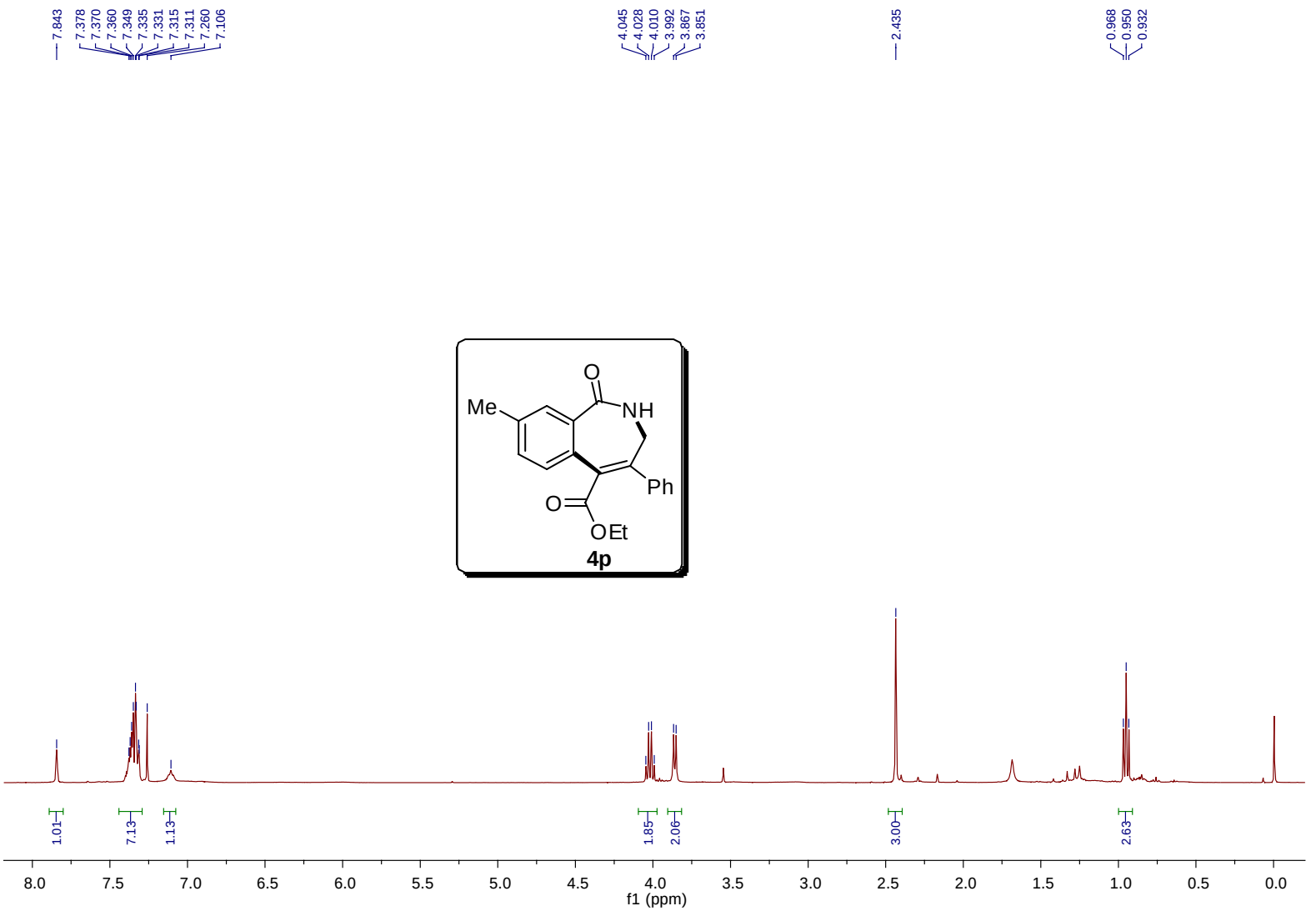


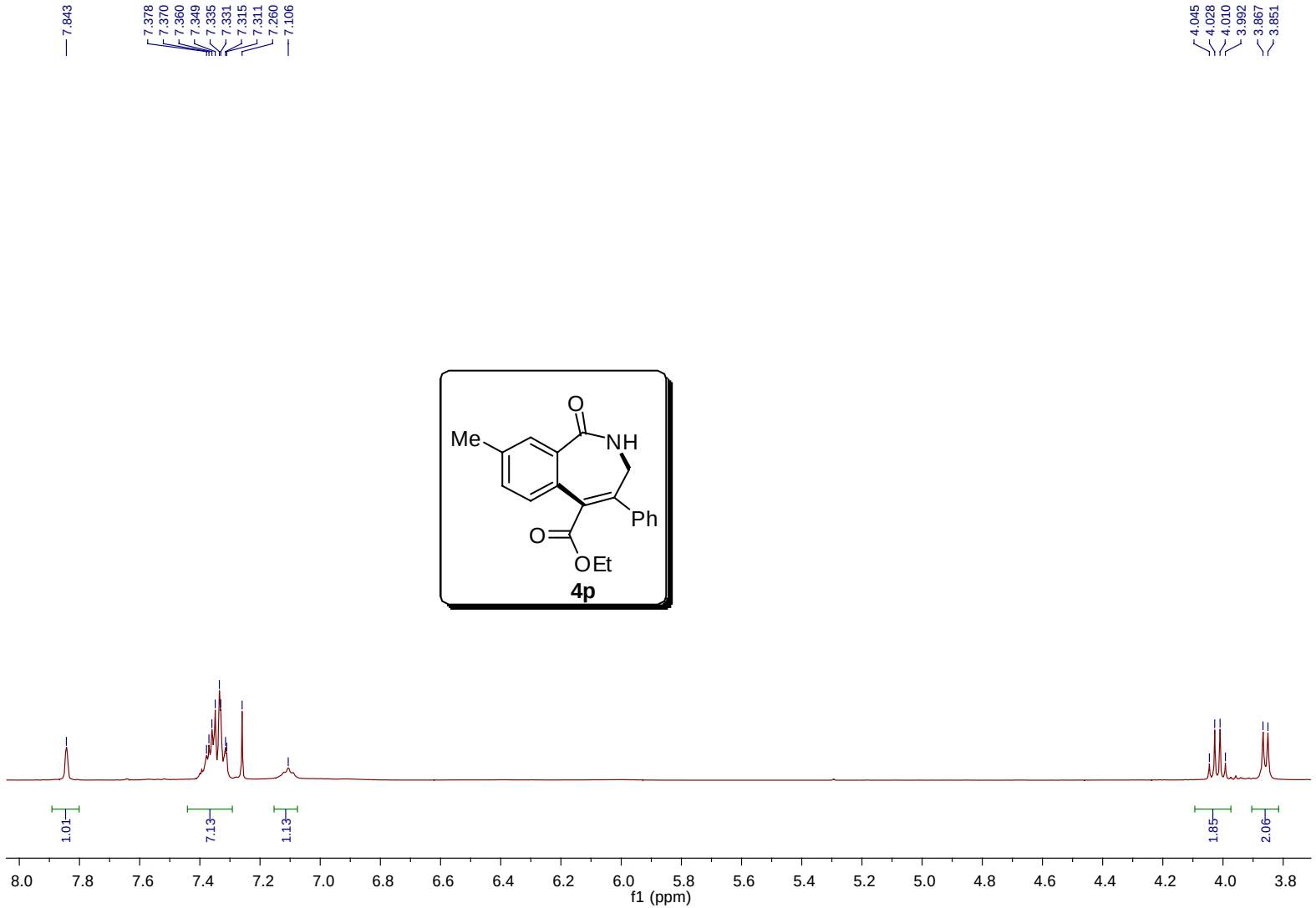


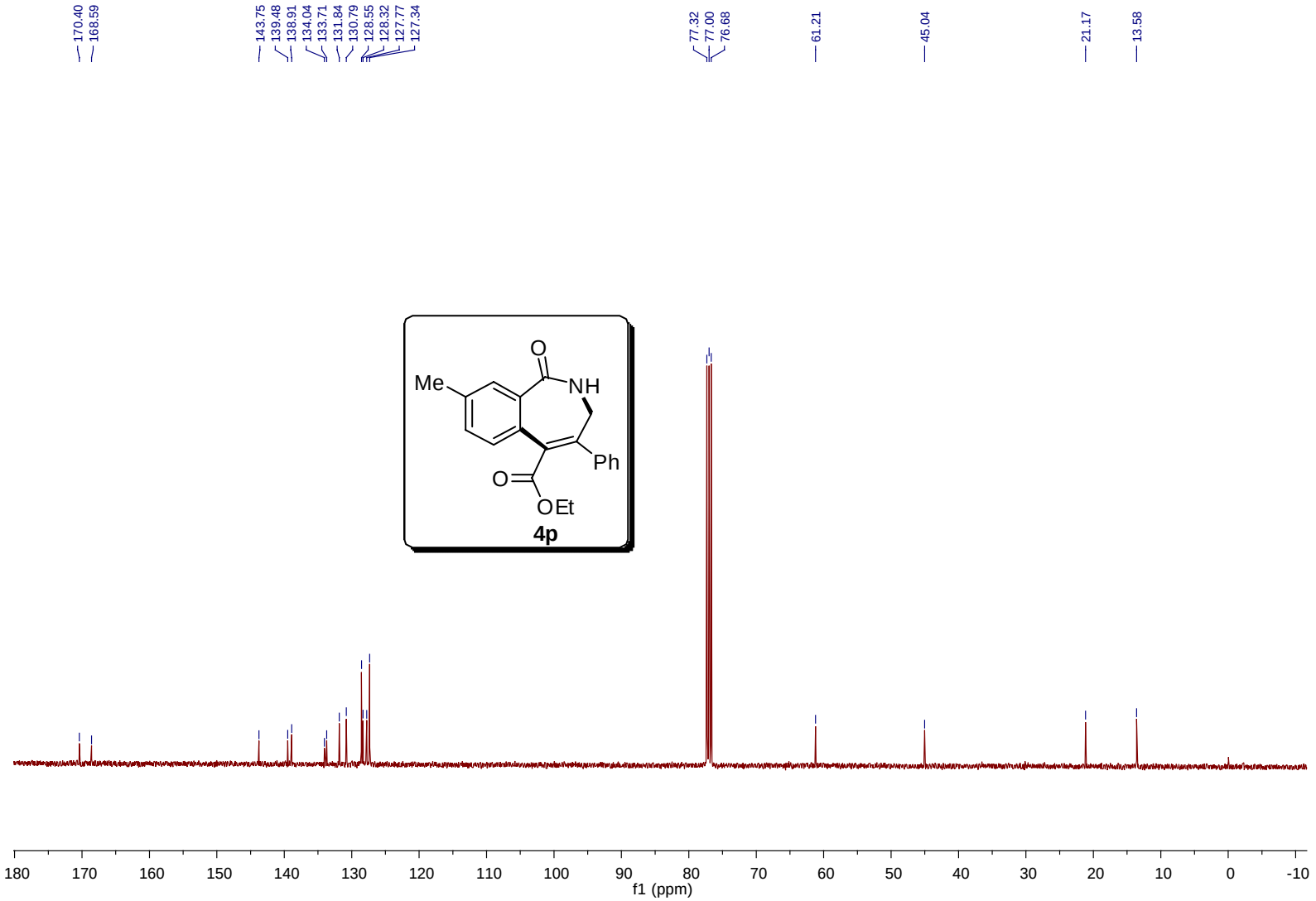


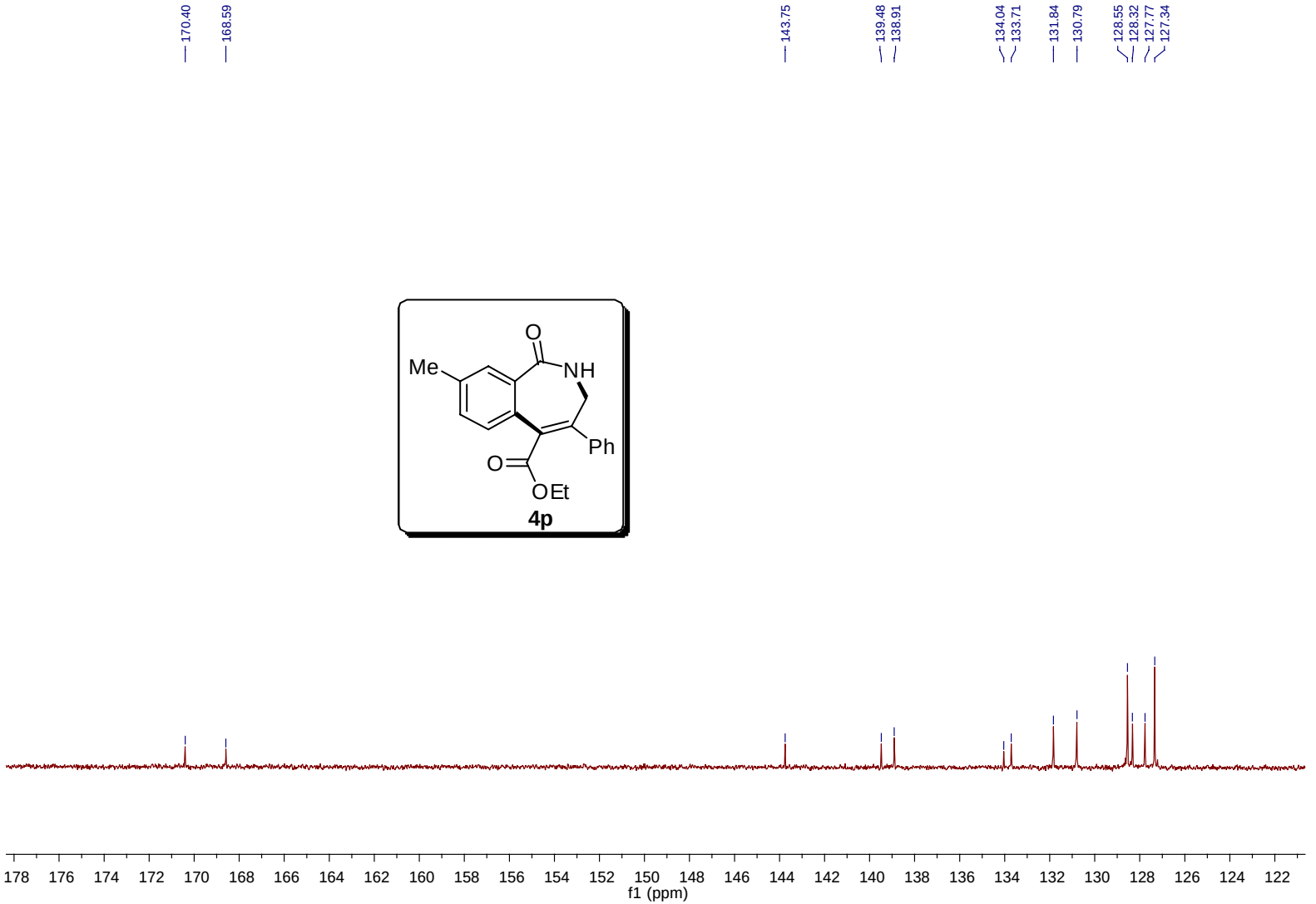


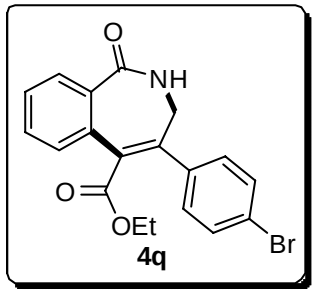




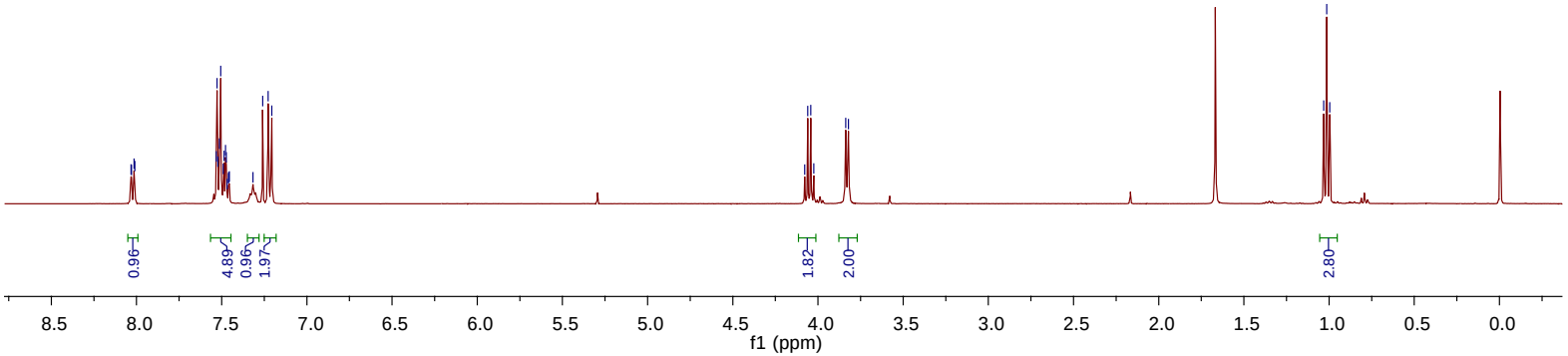


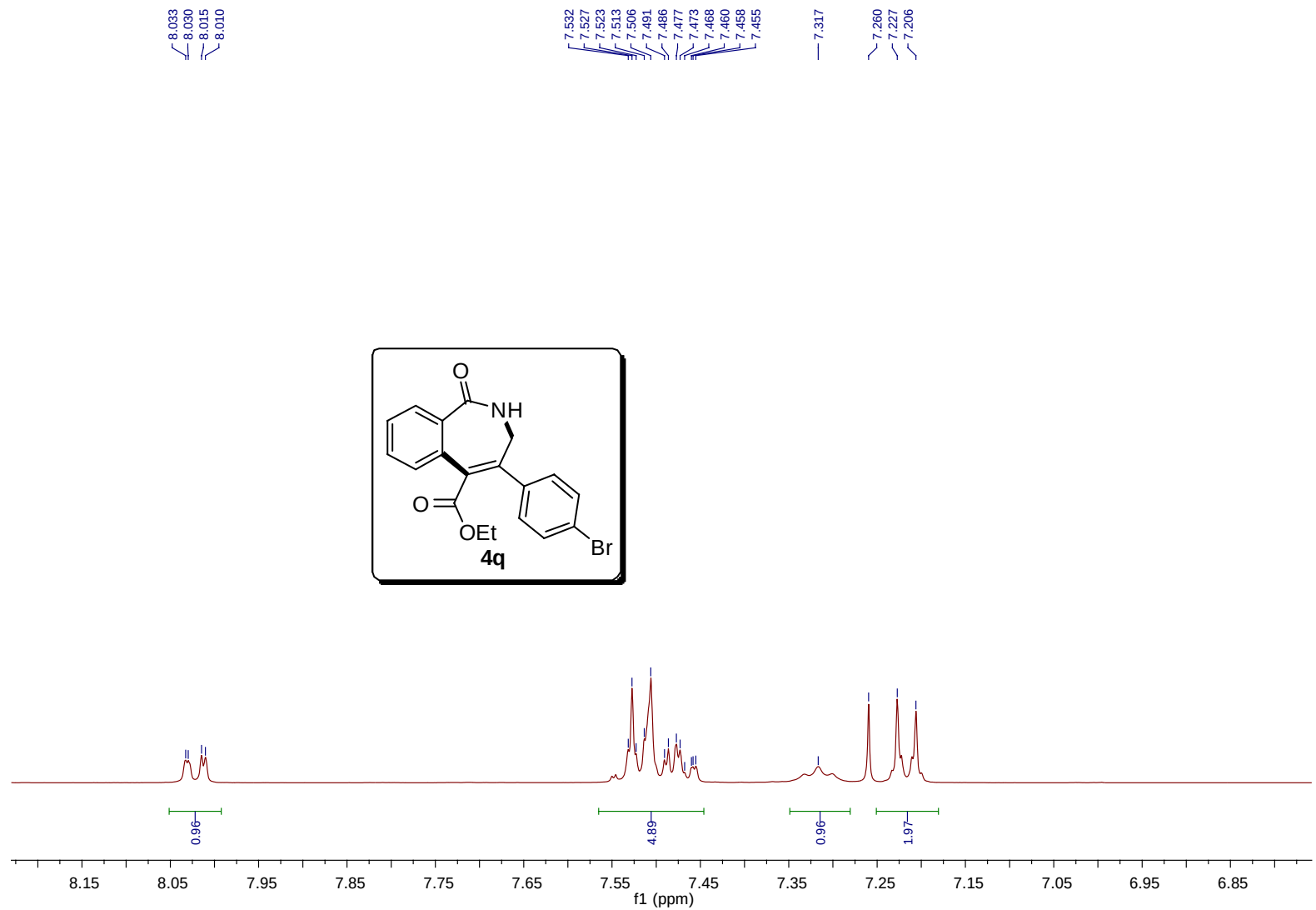


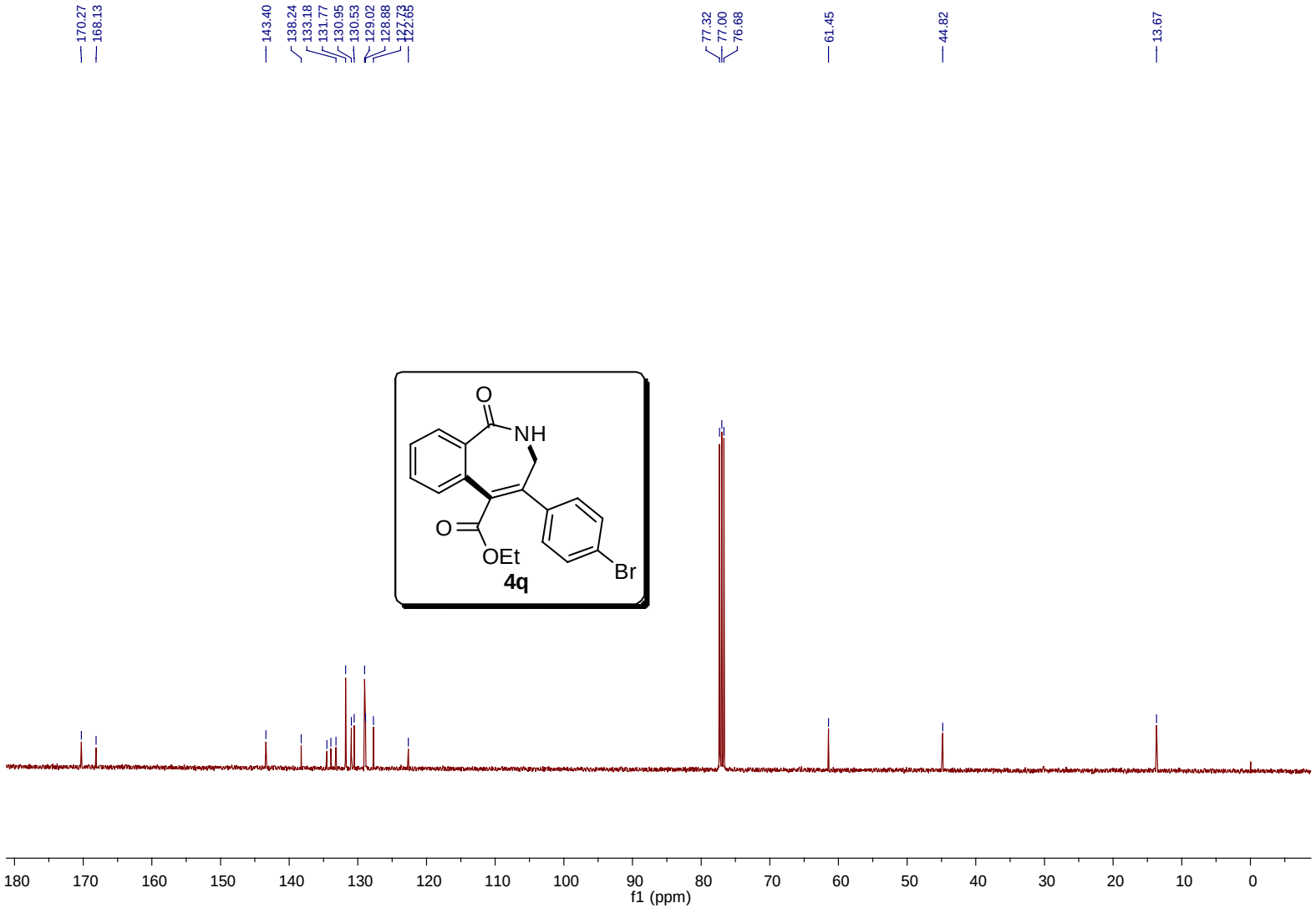


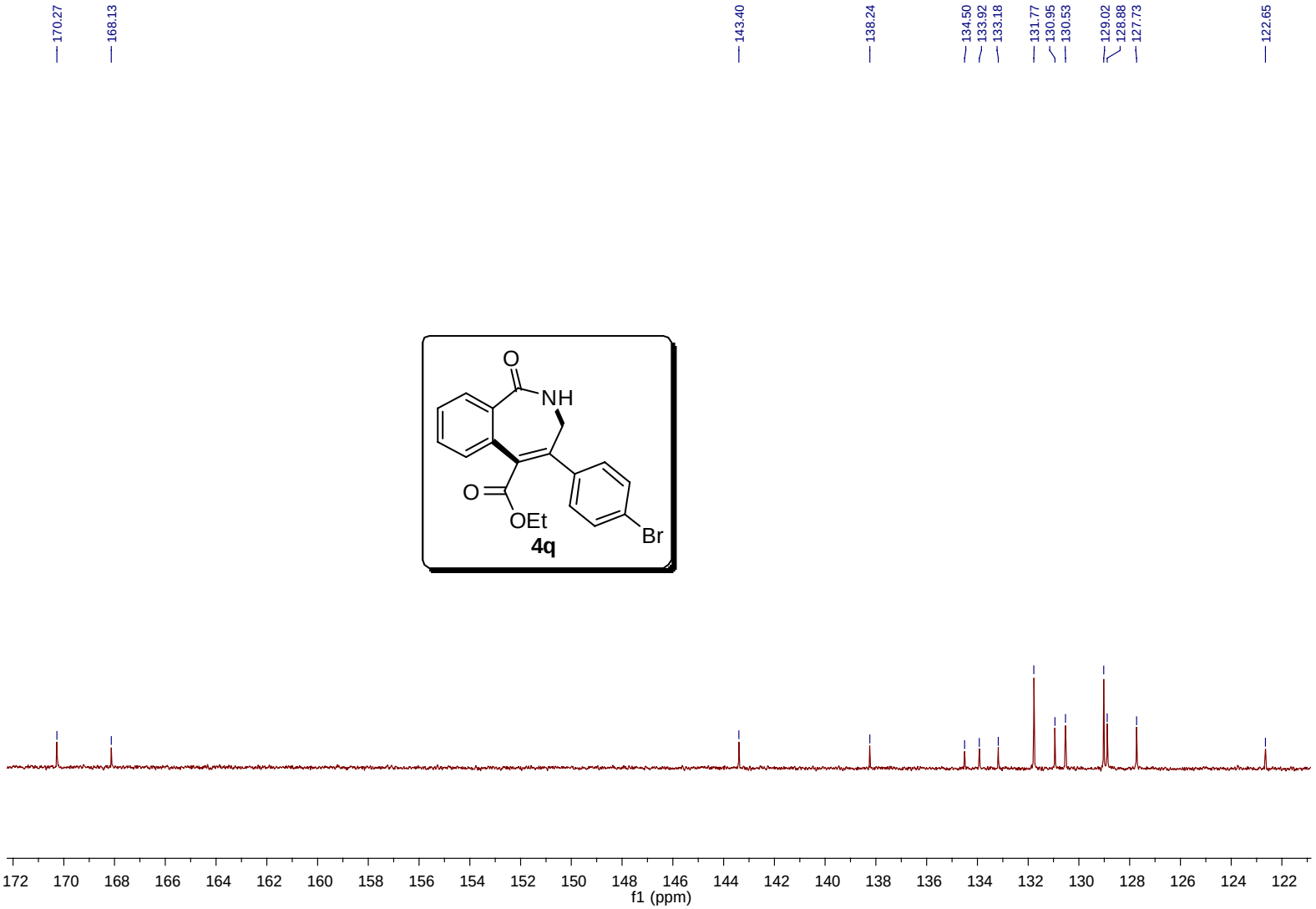


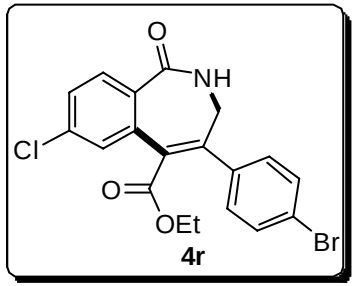
4q

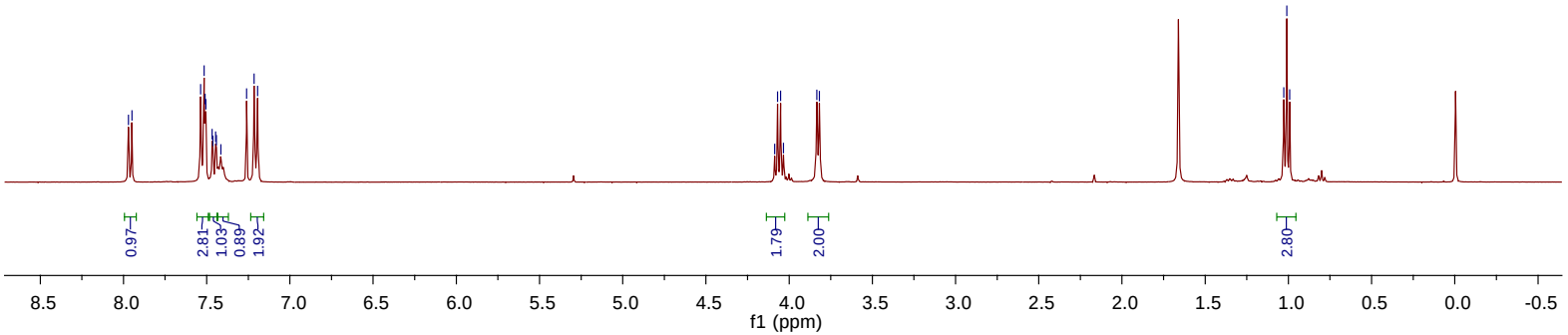


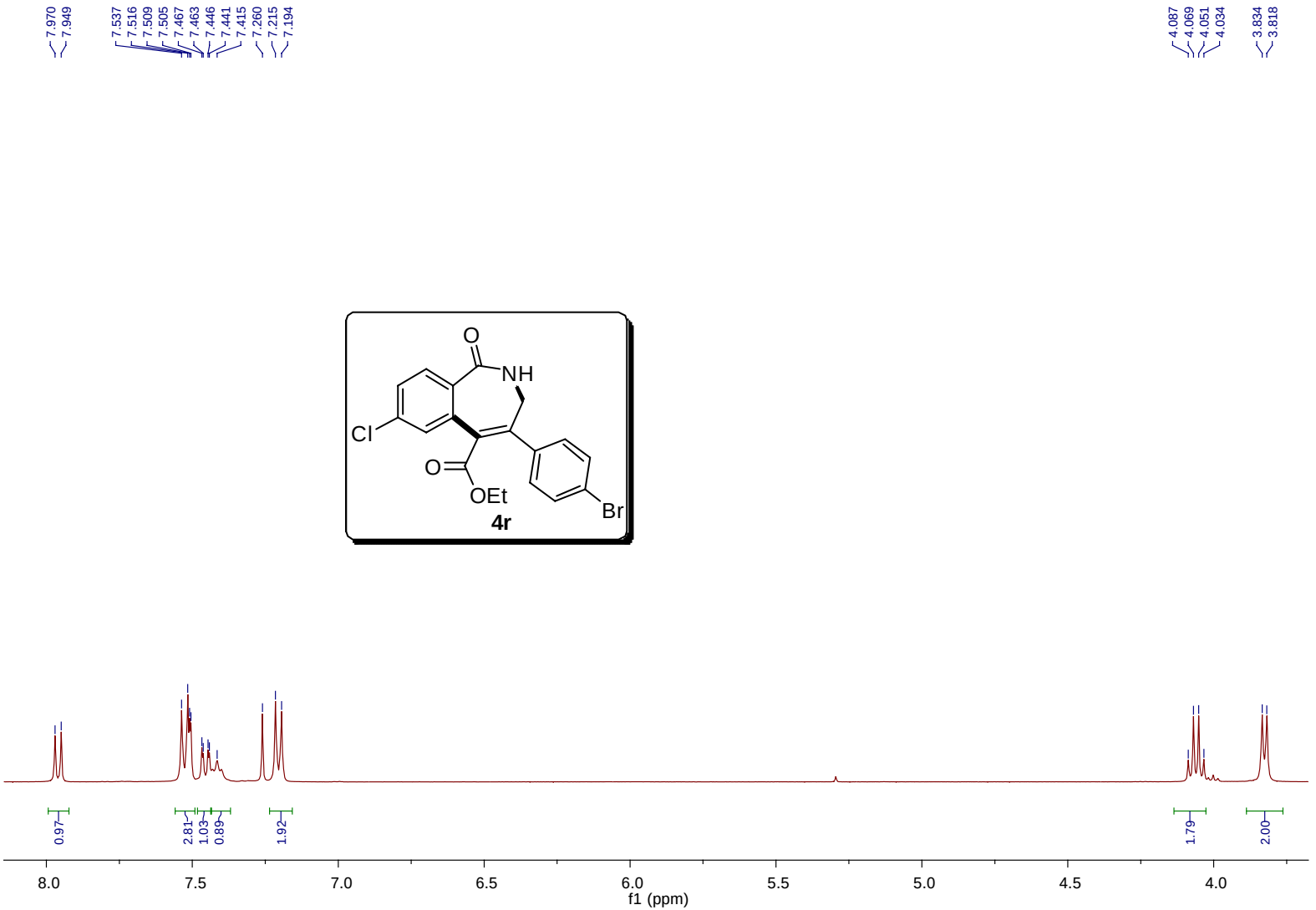


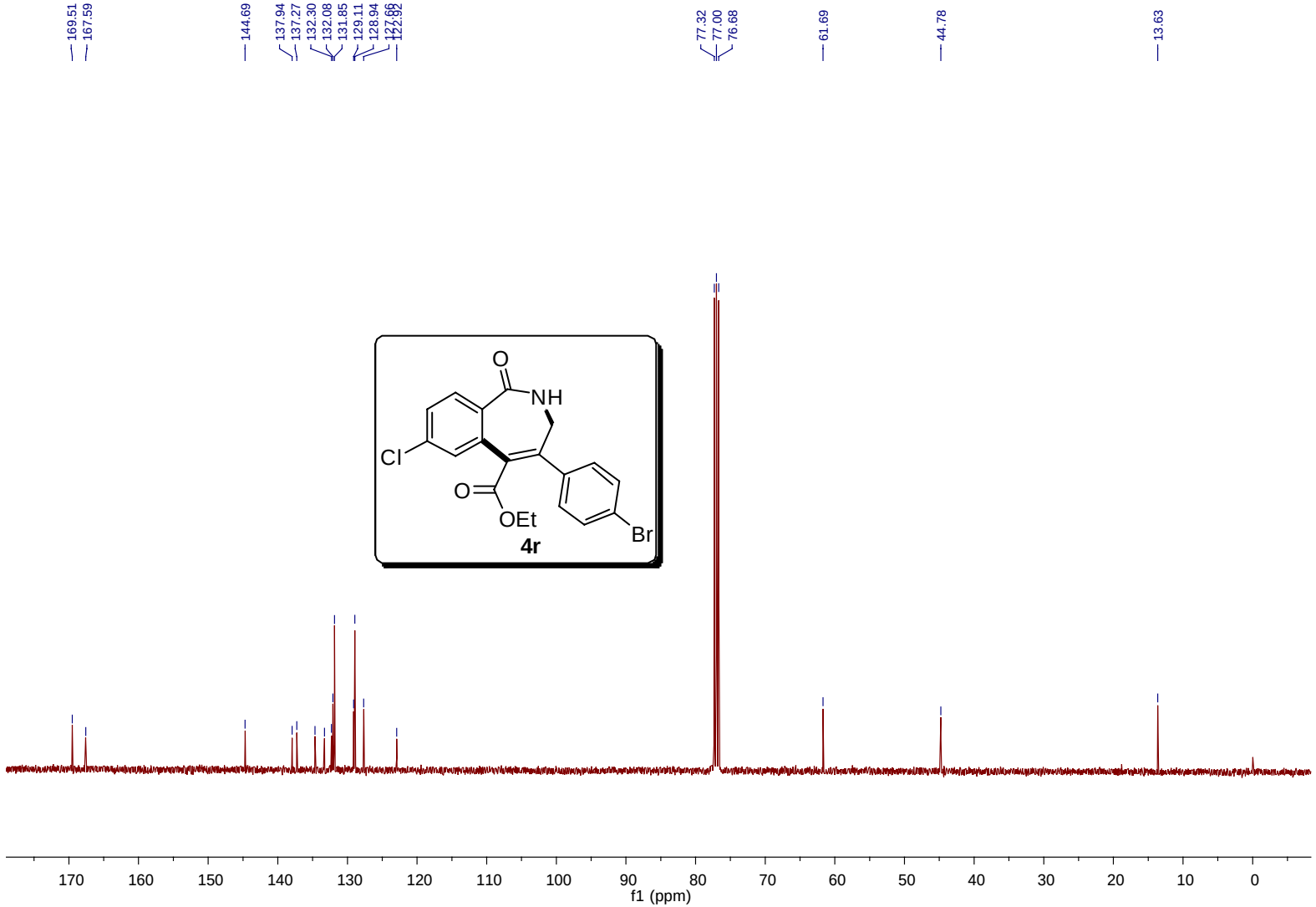


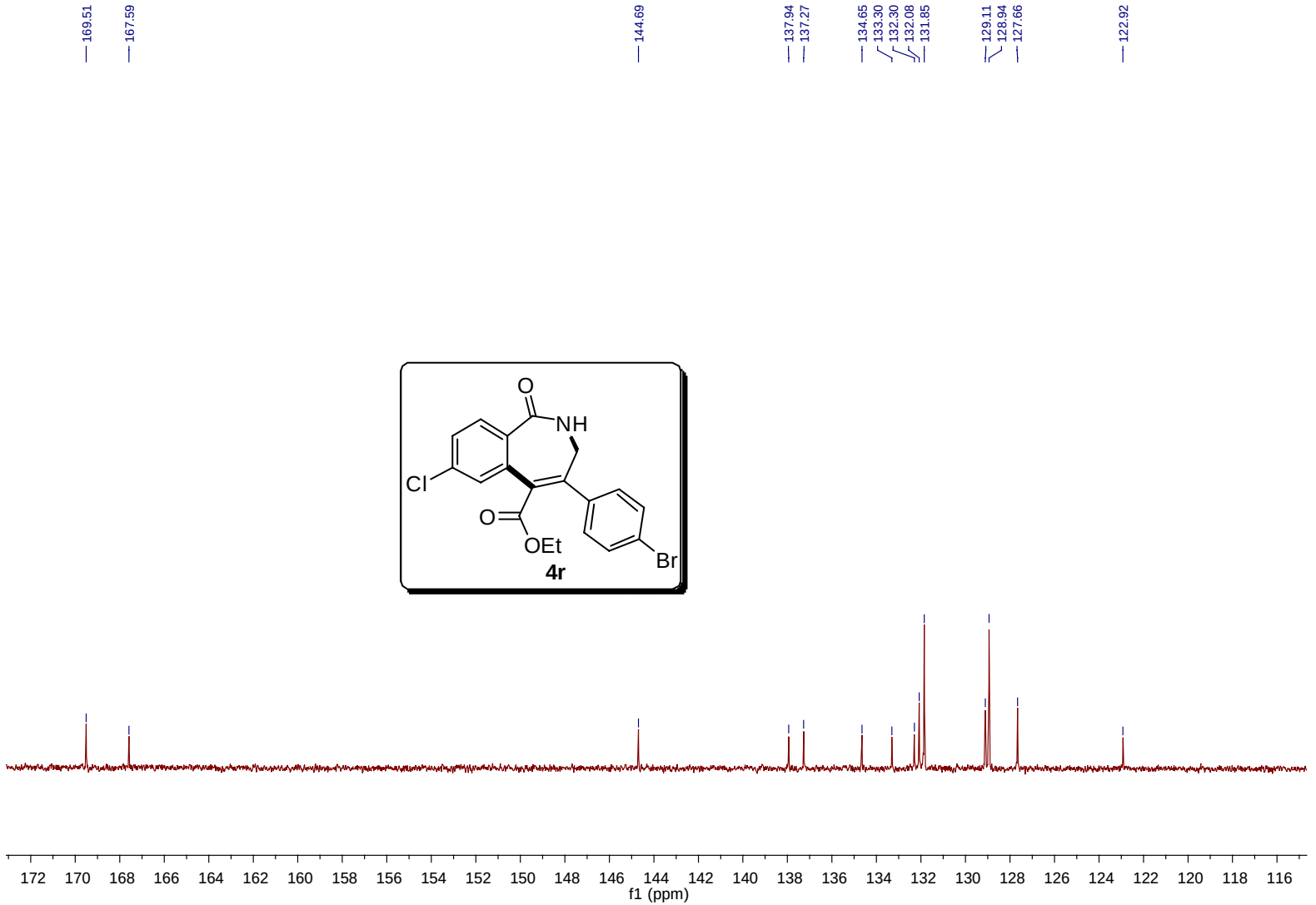


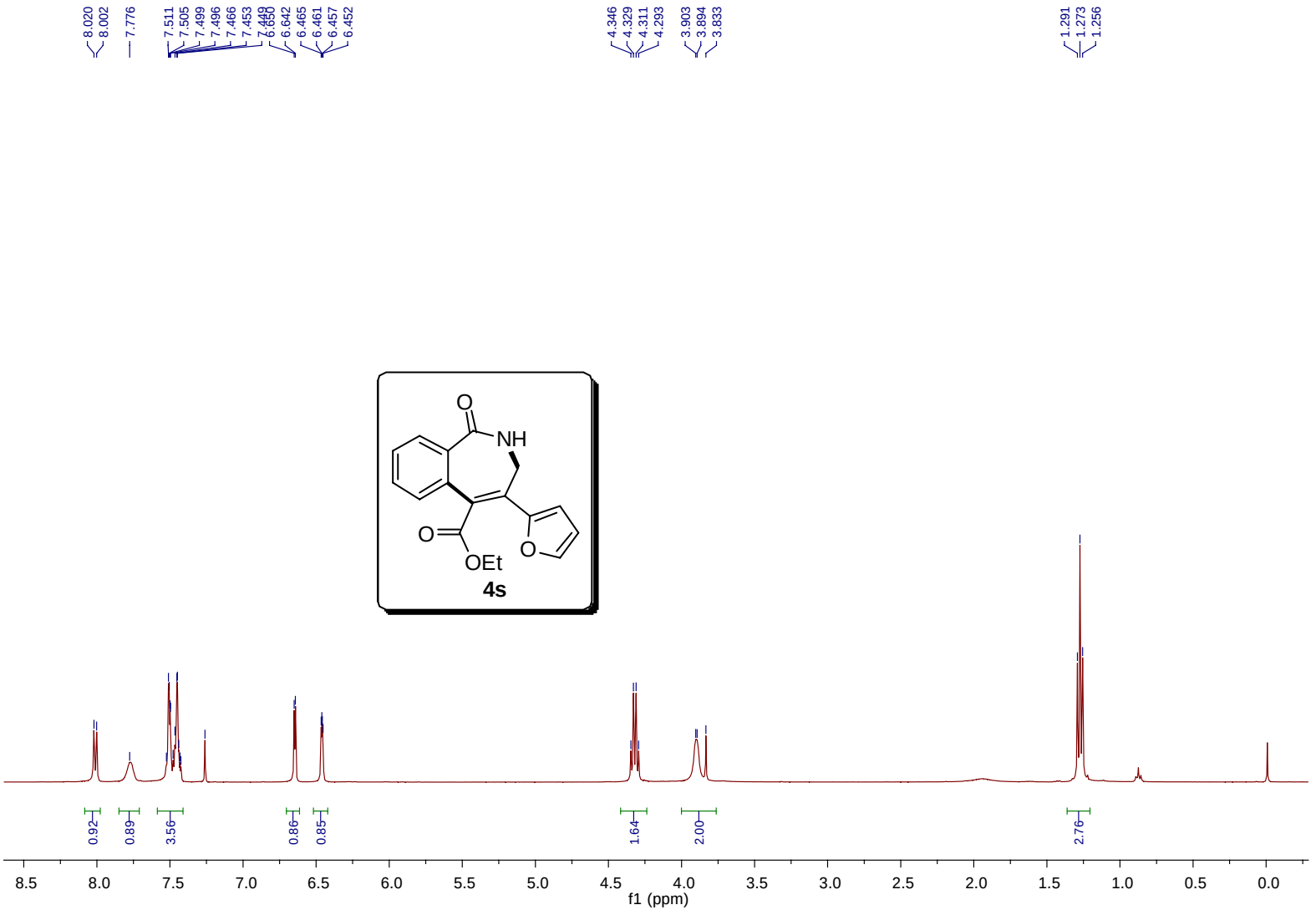


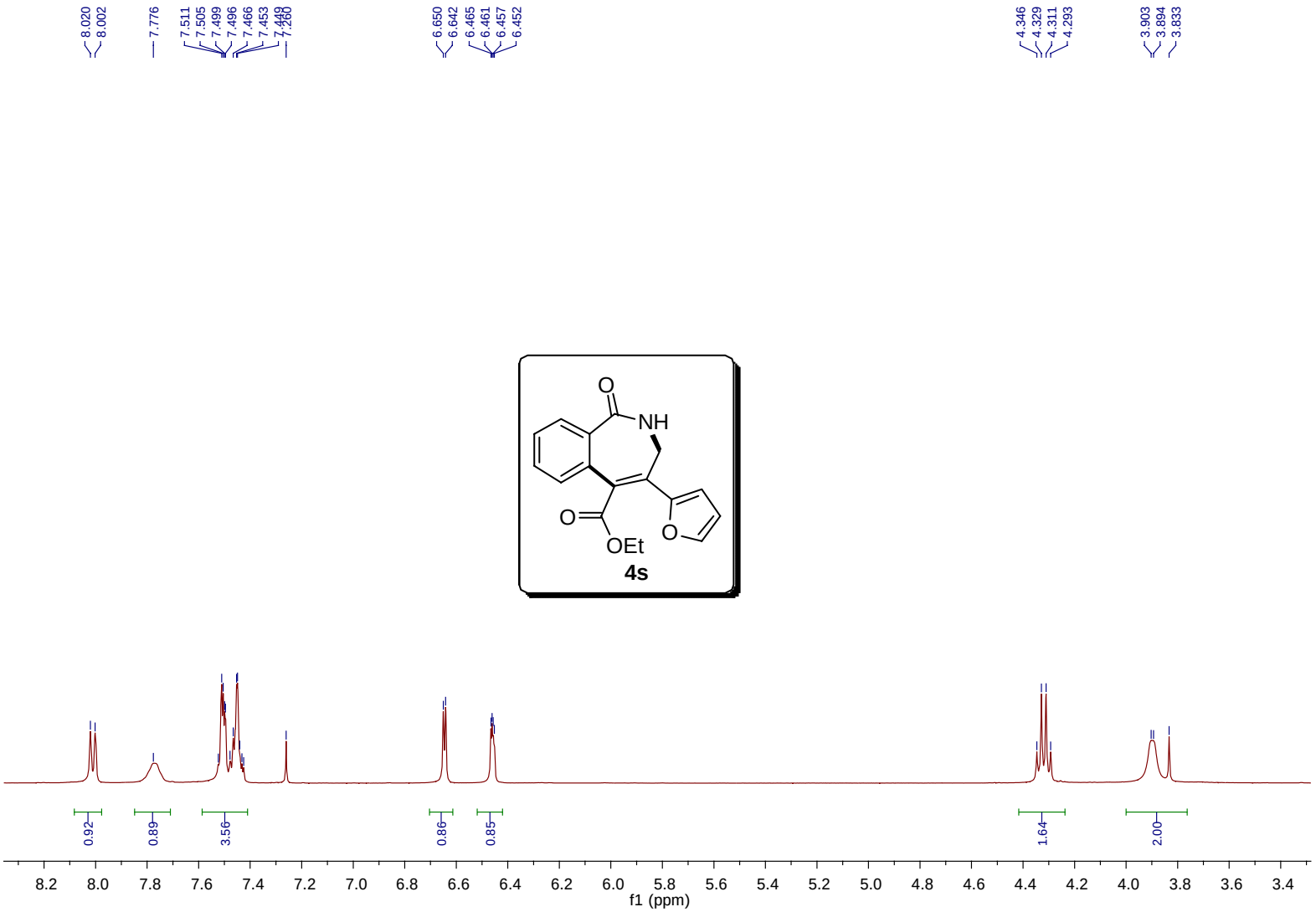


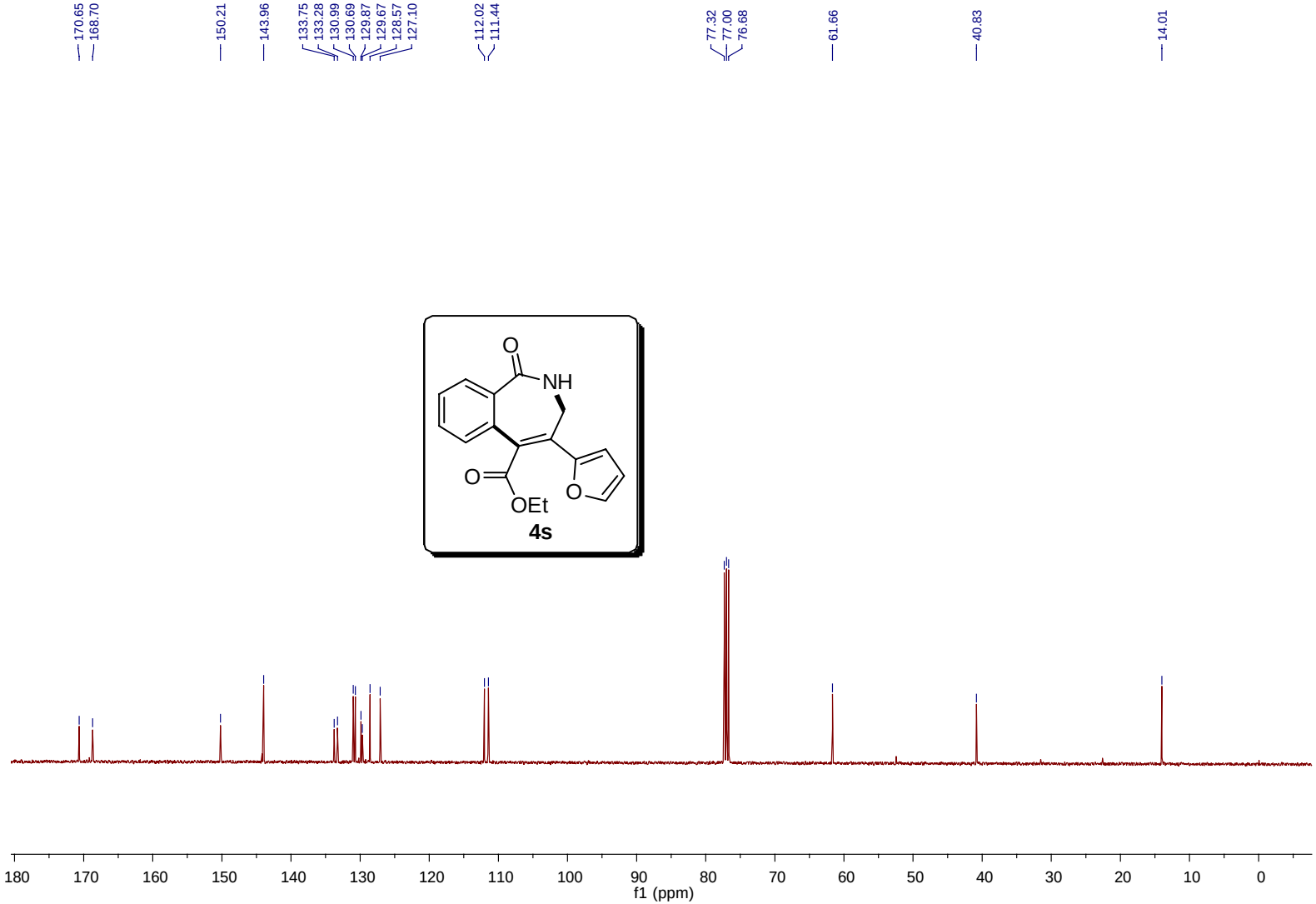


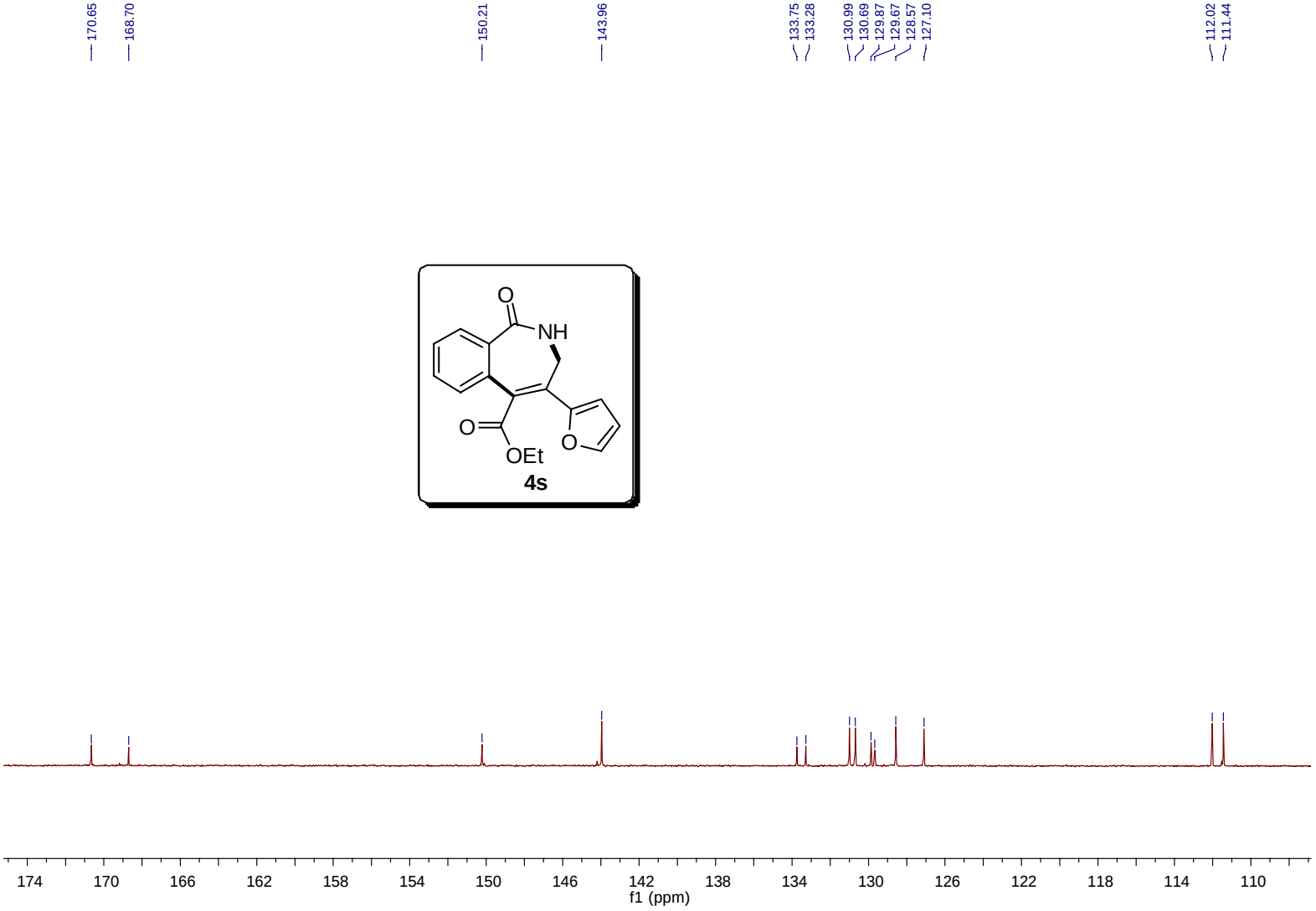


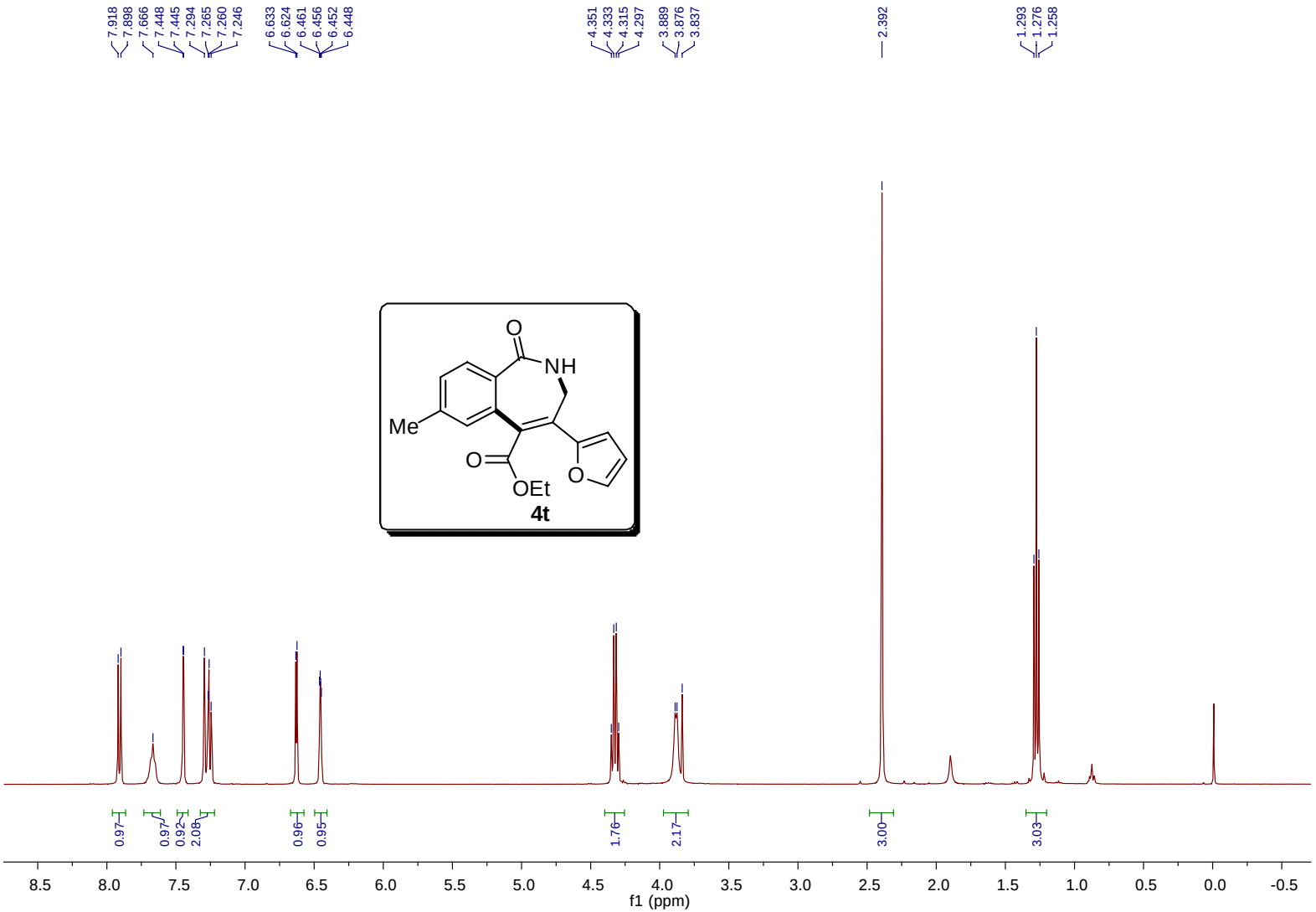


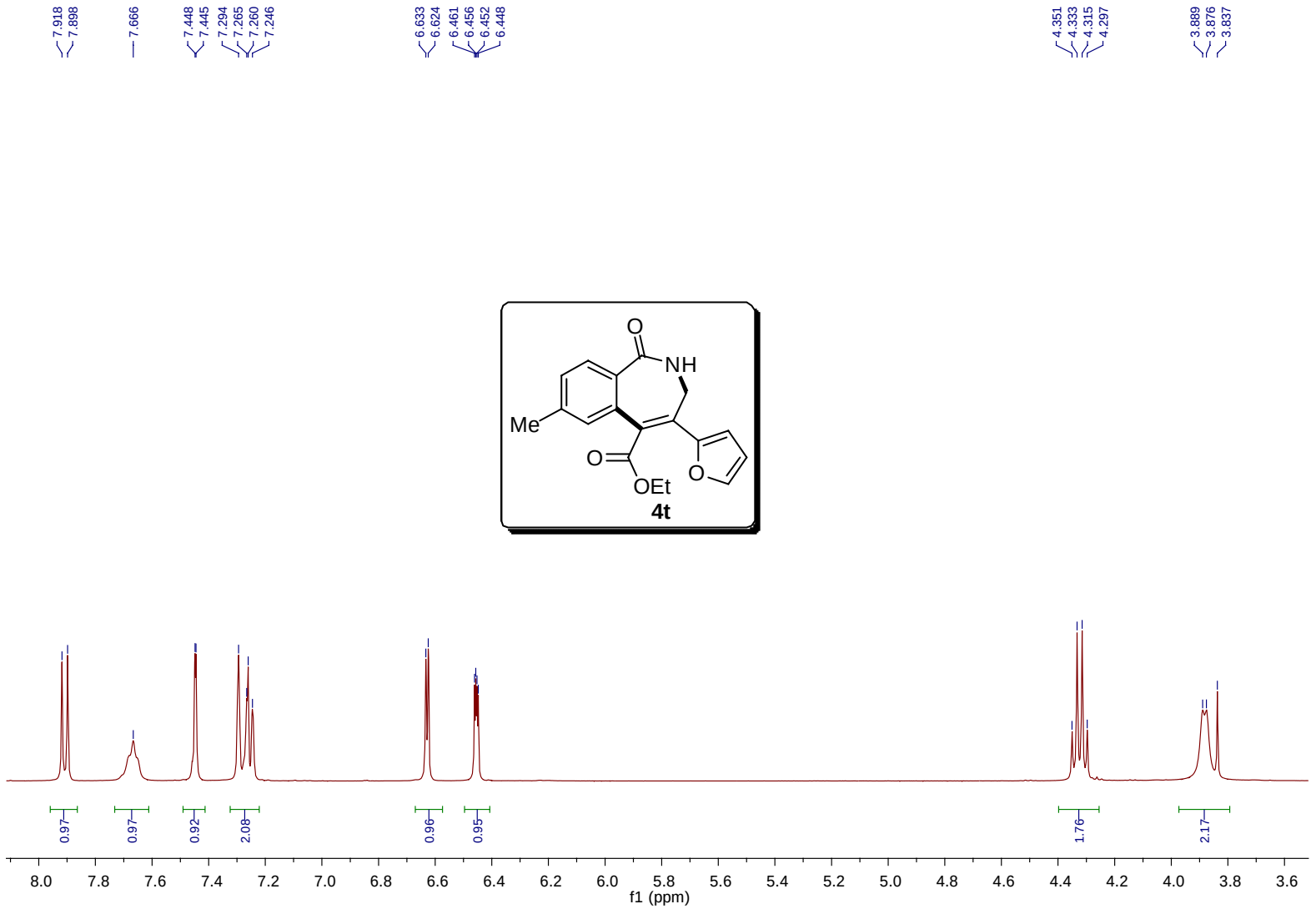


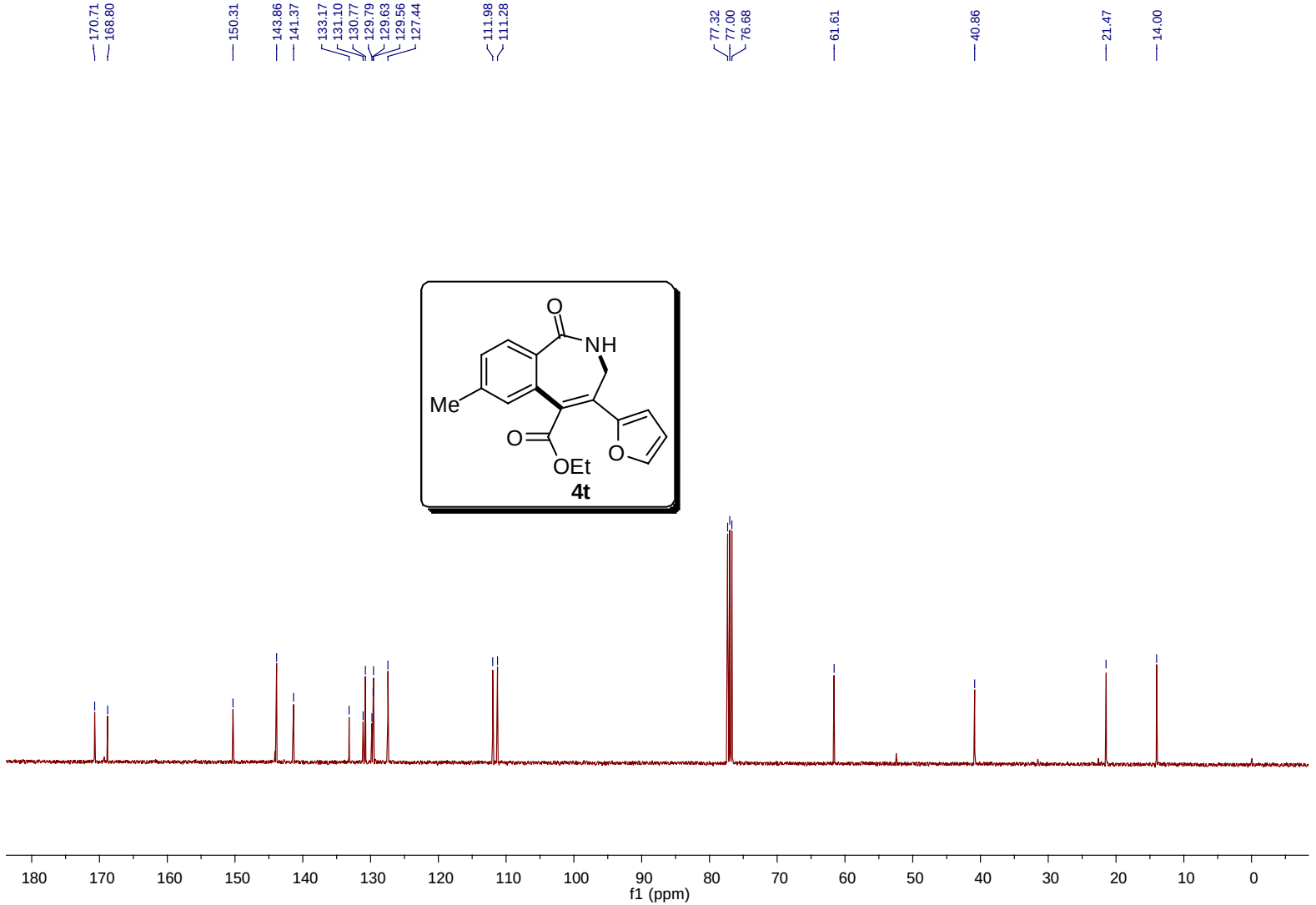


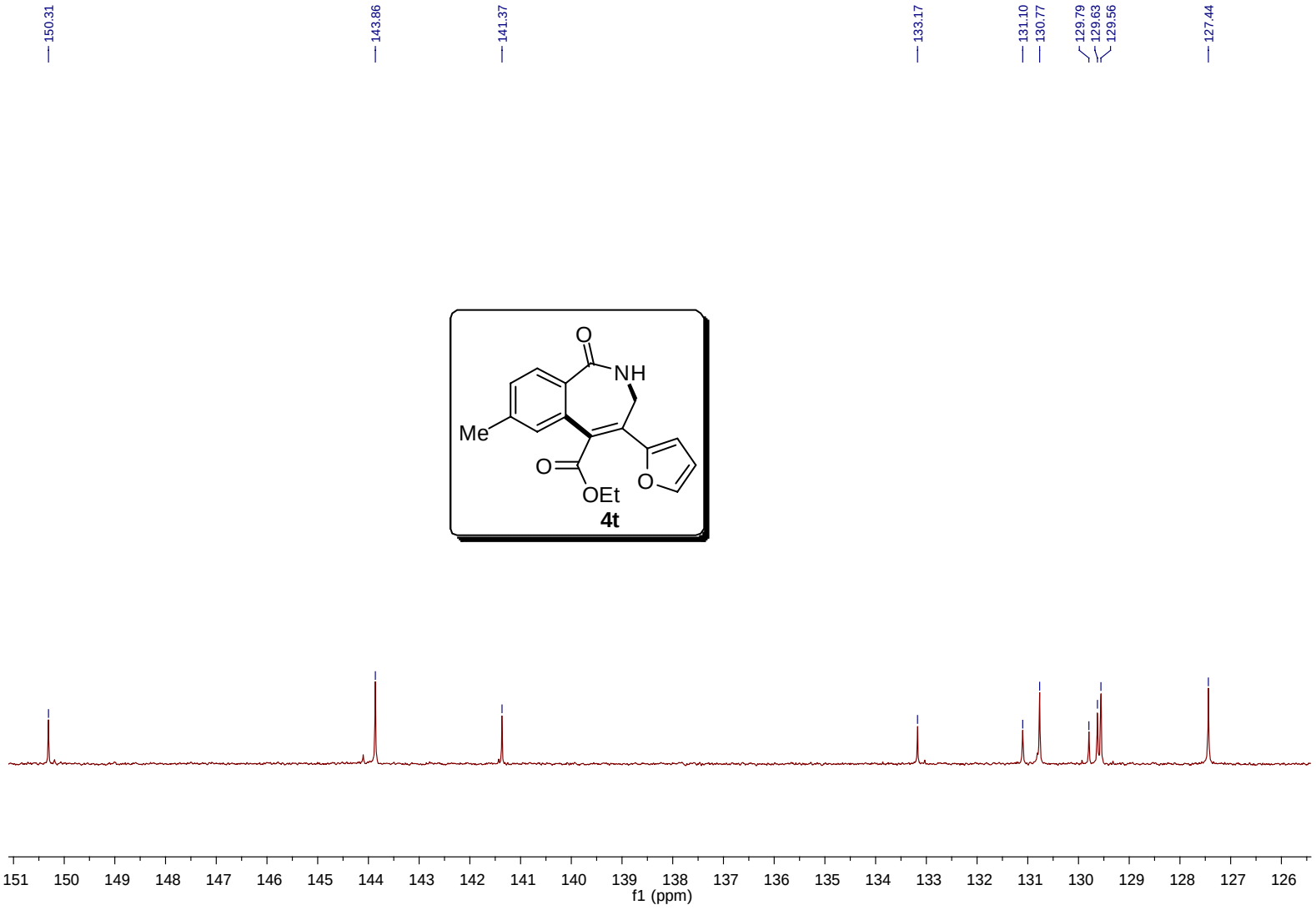


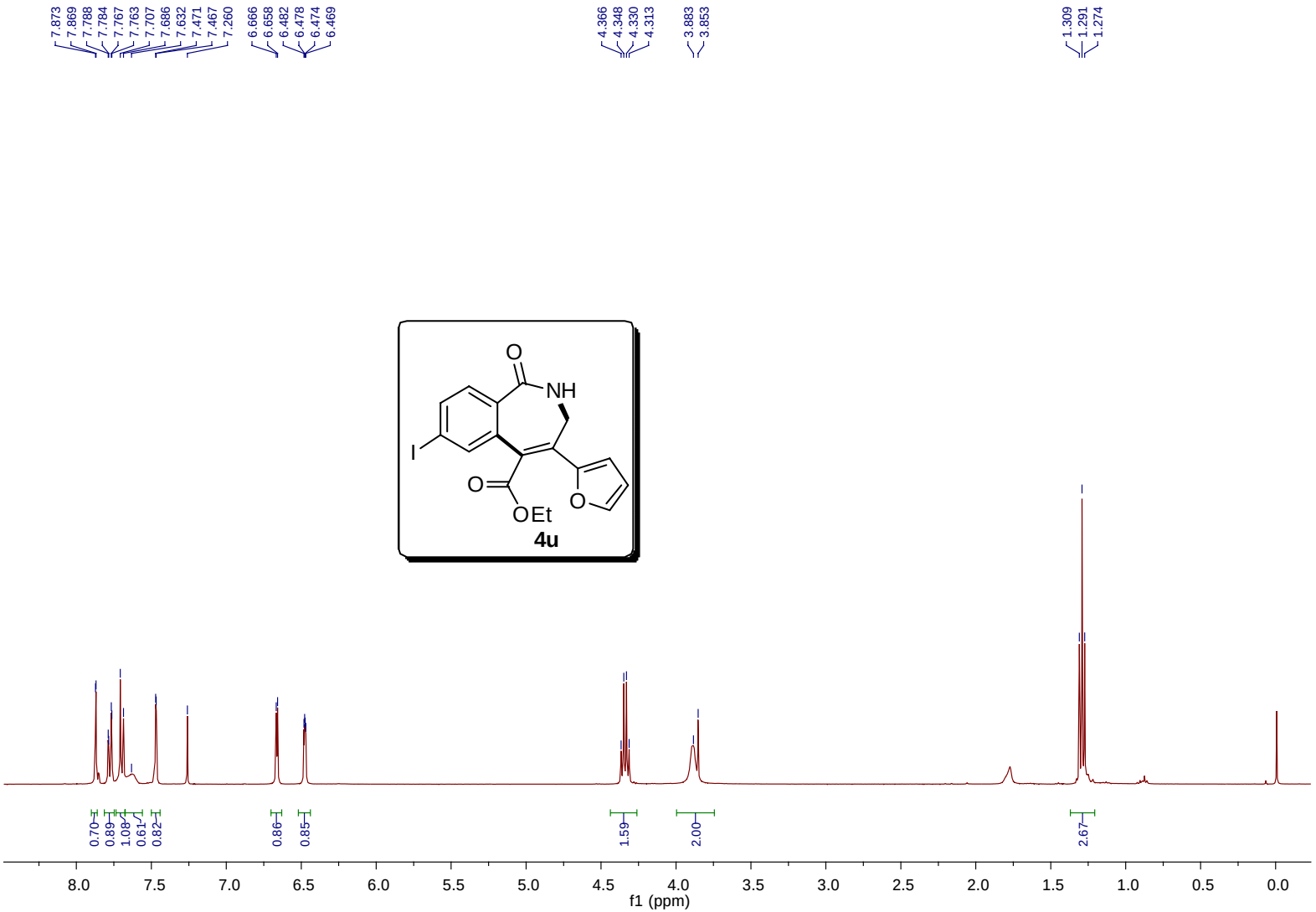


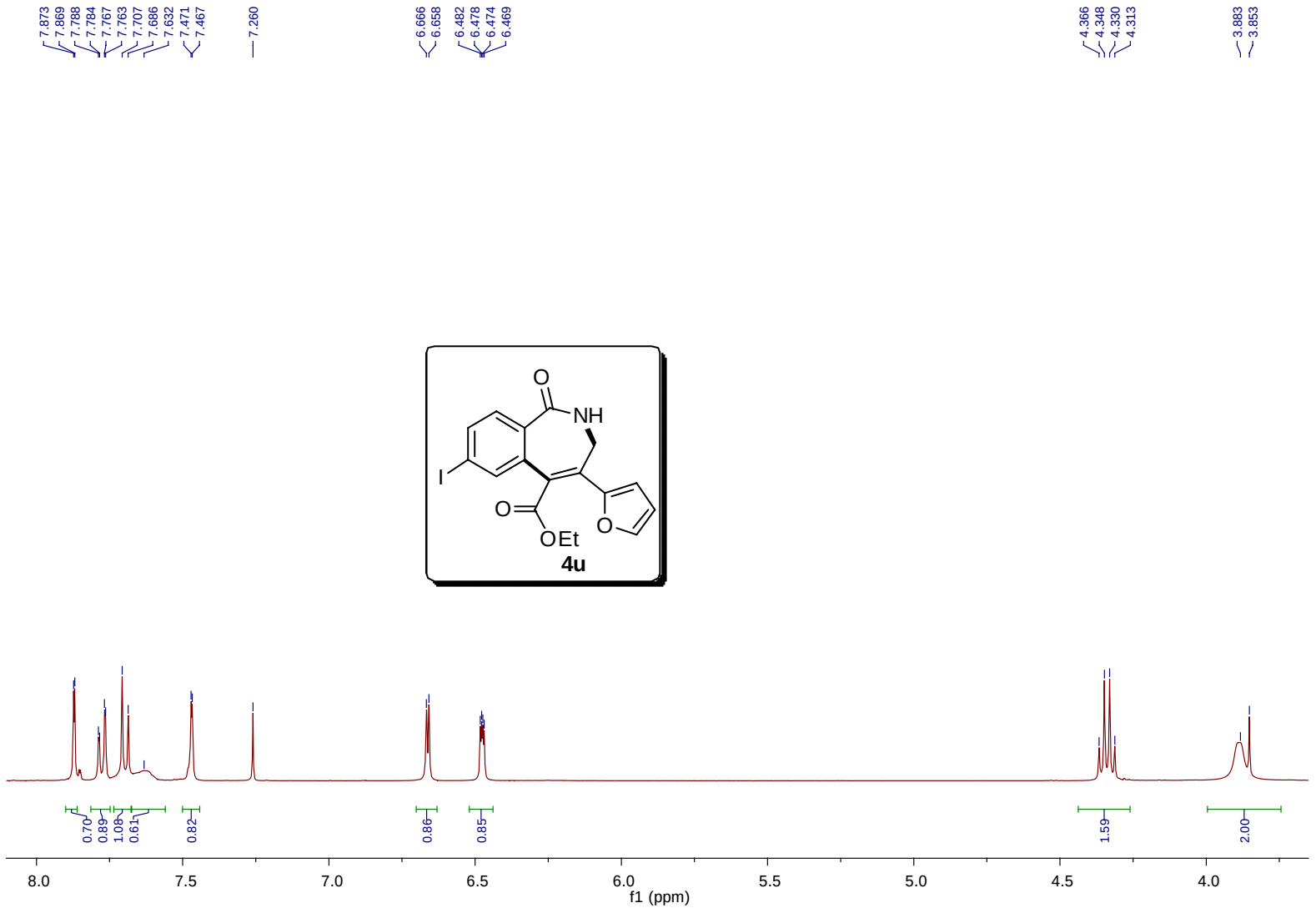


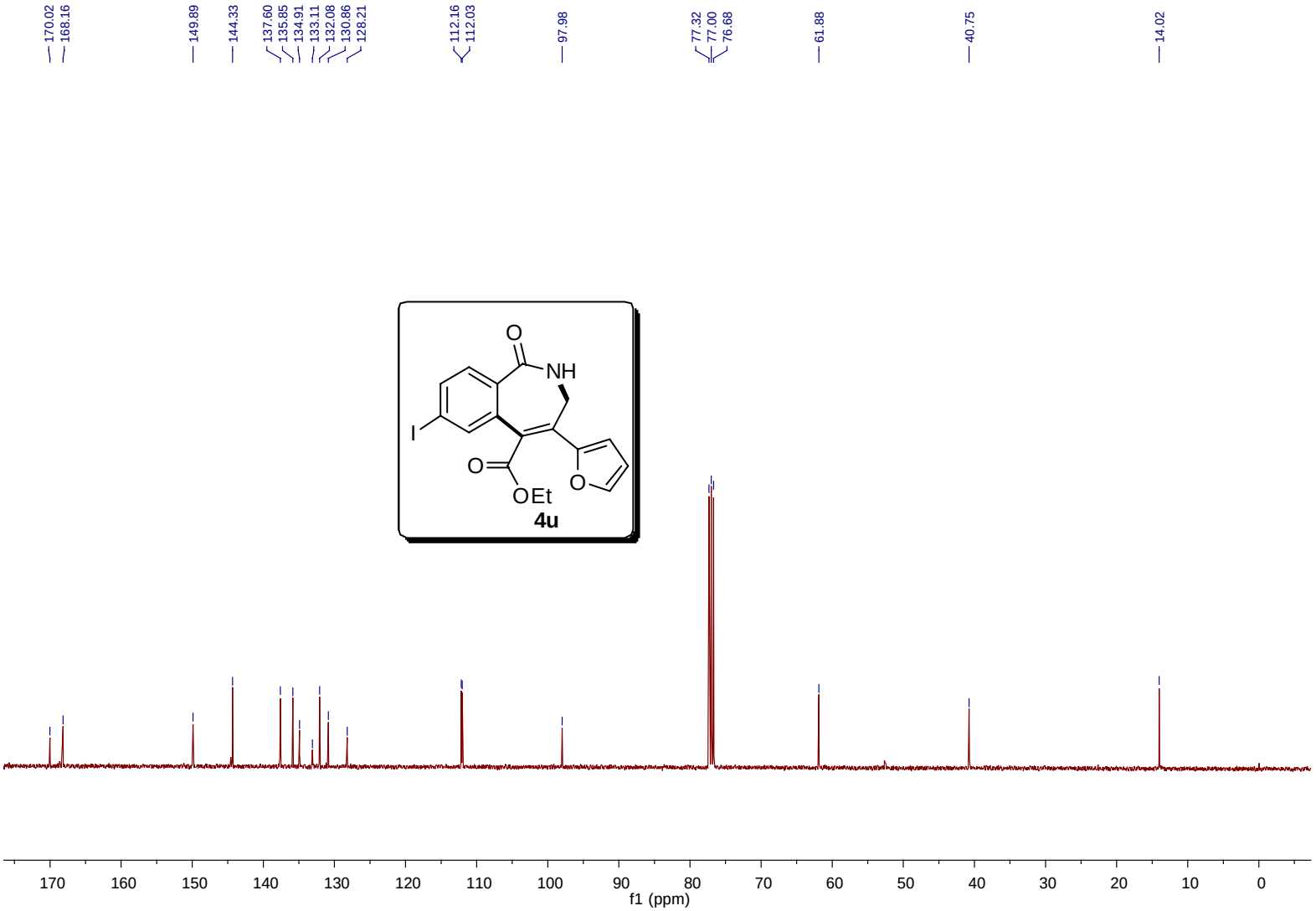


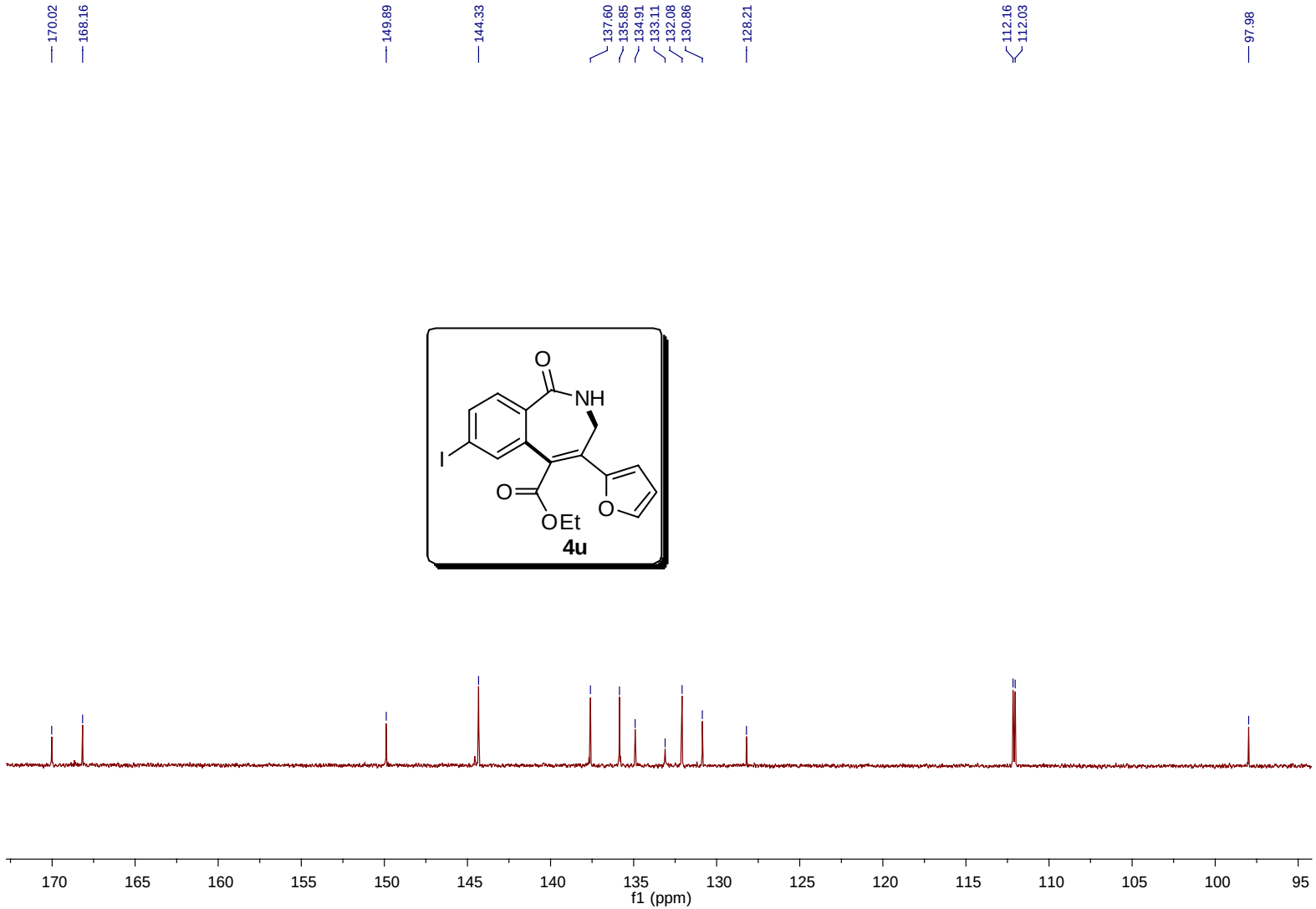


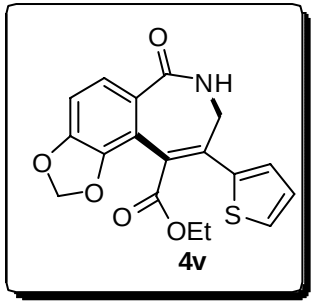


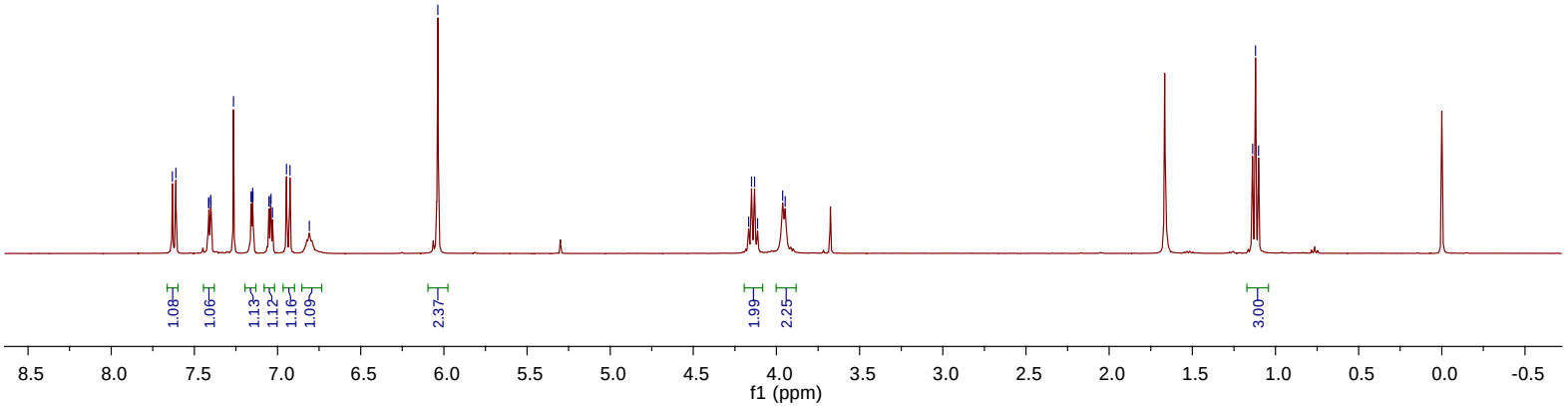


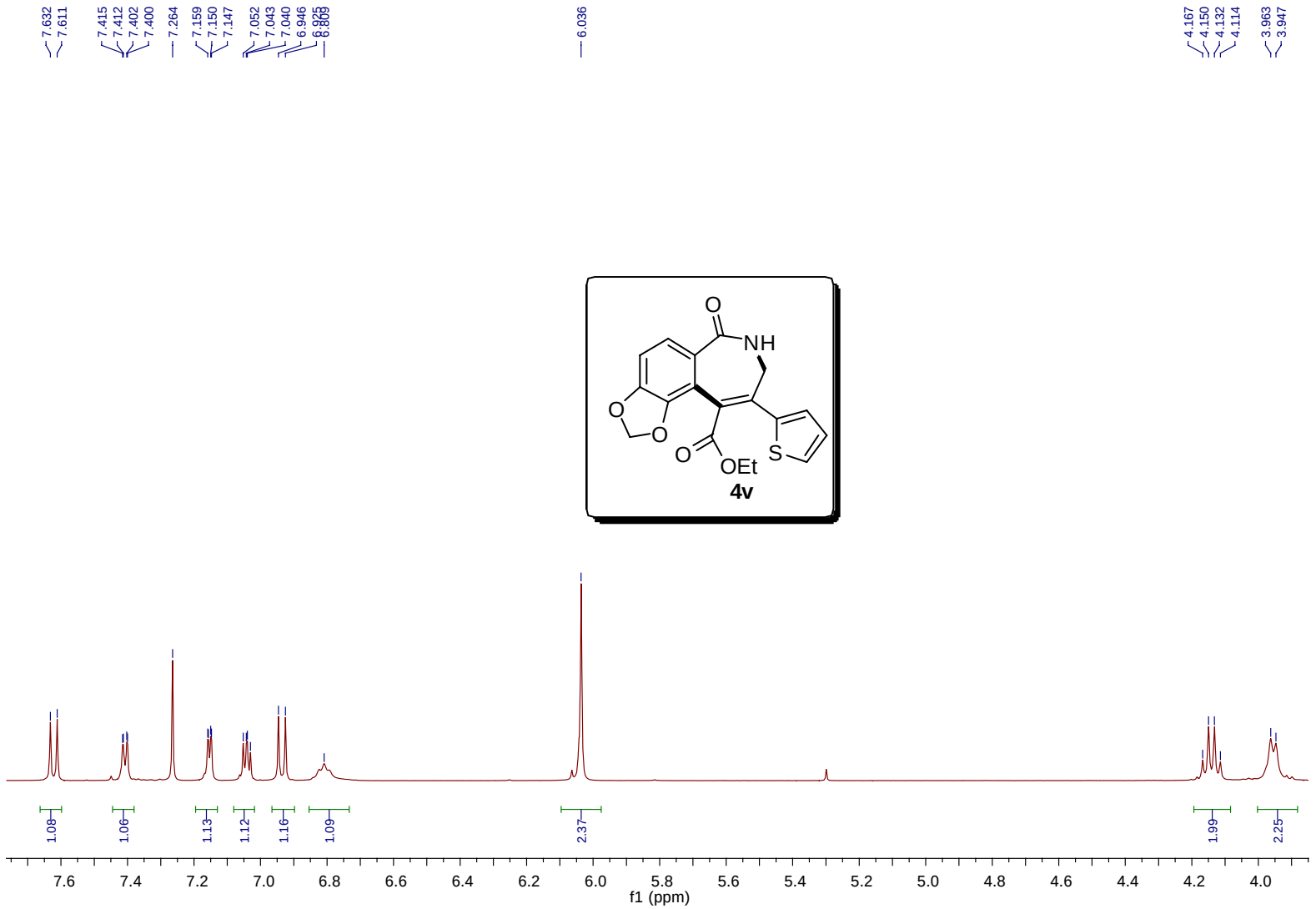


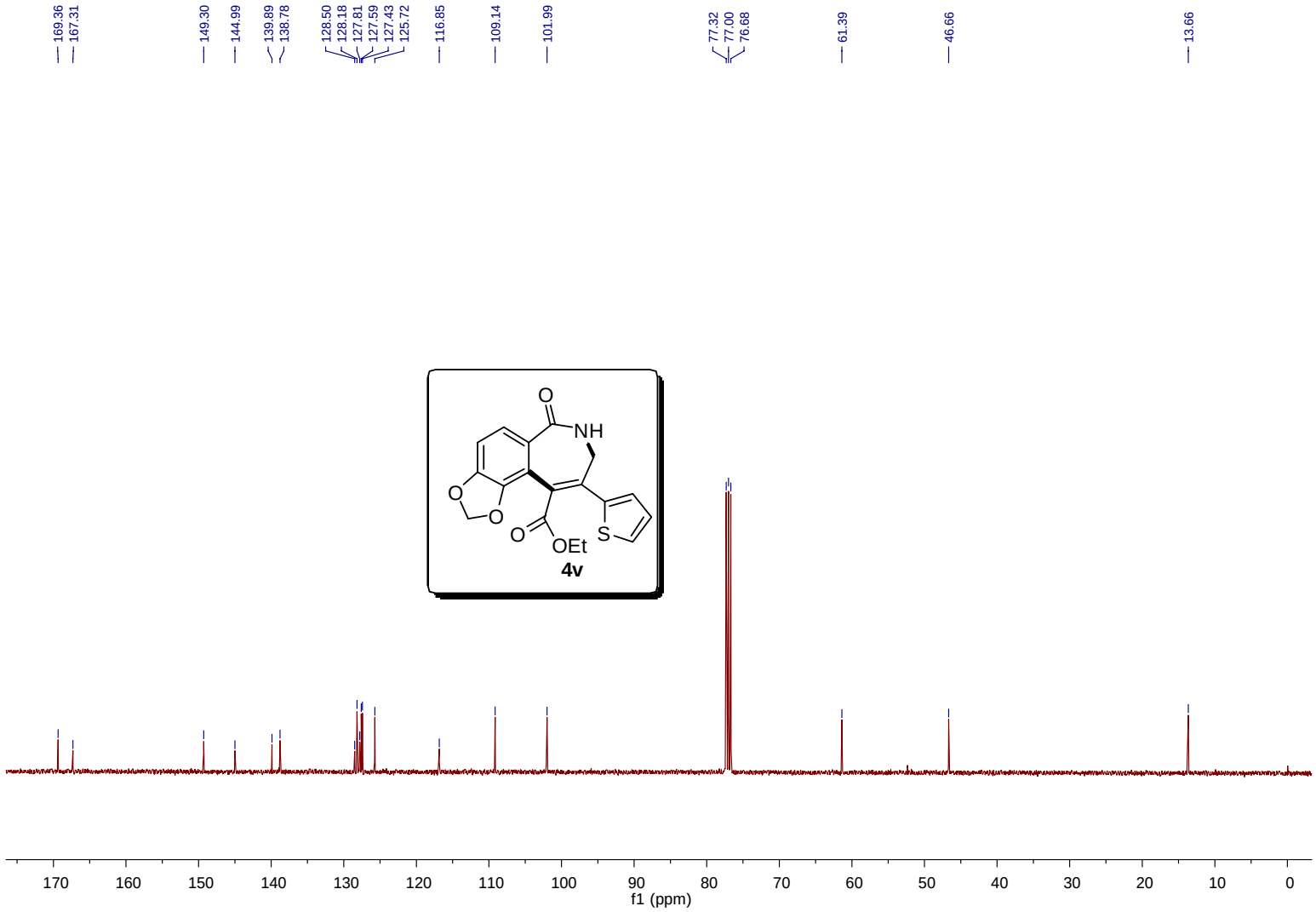


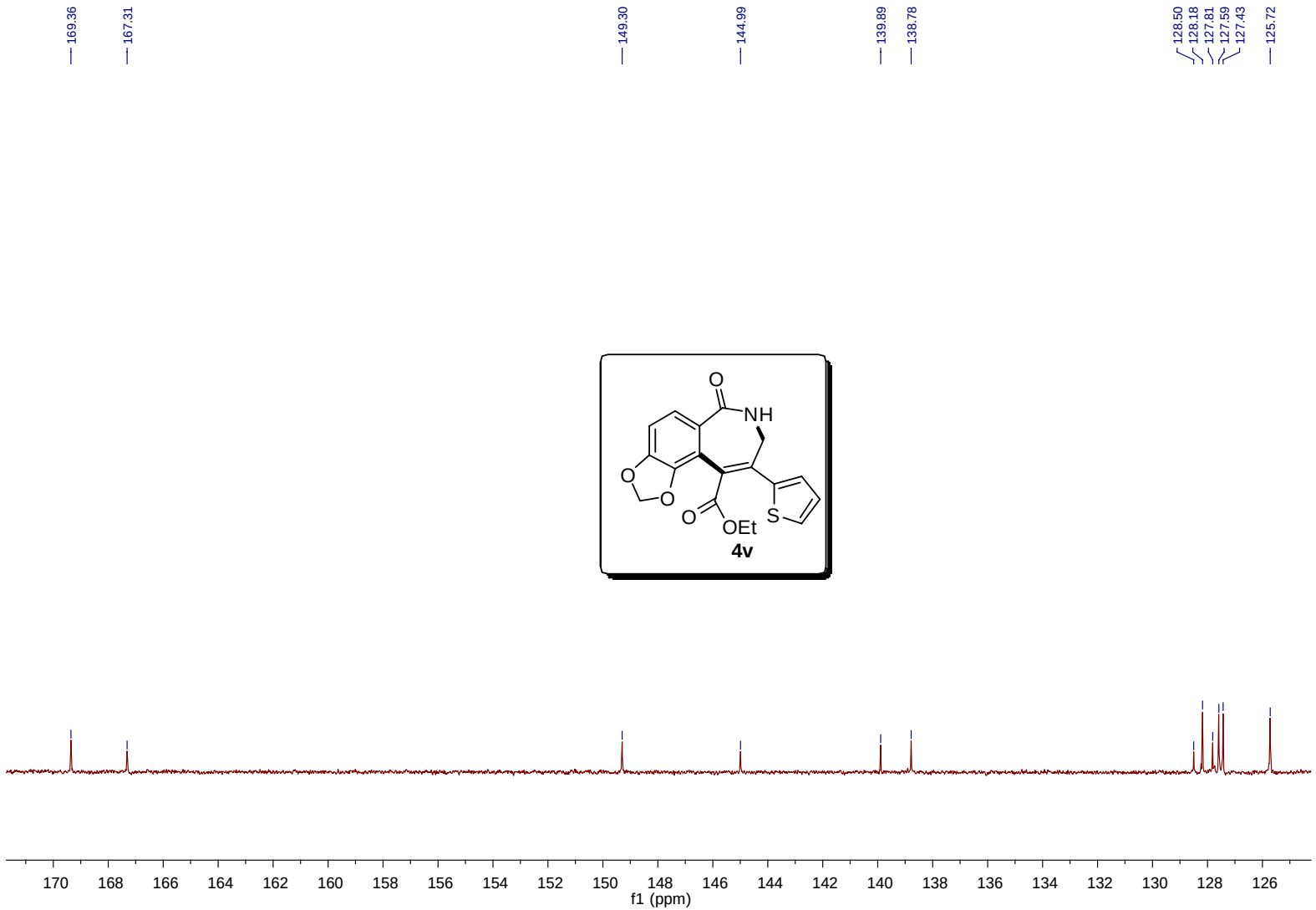


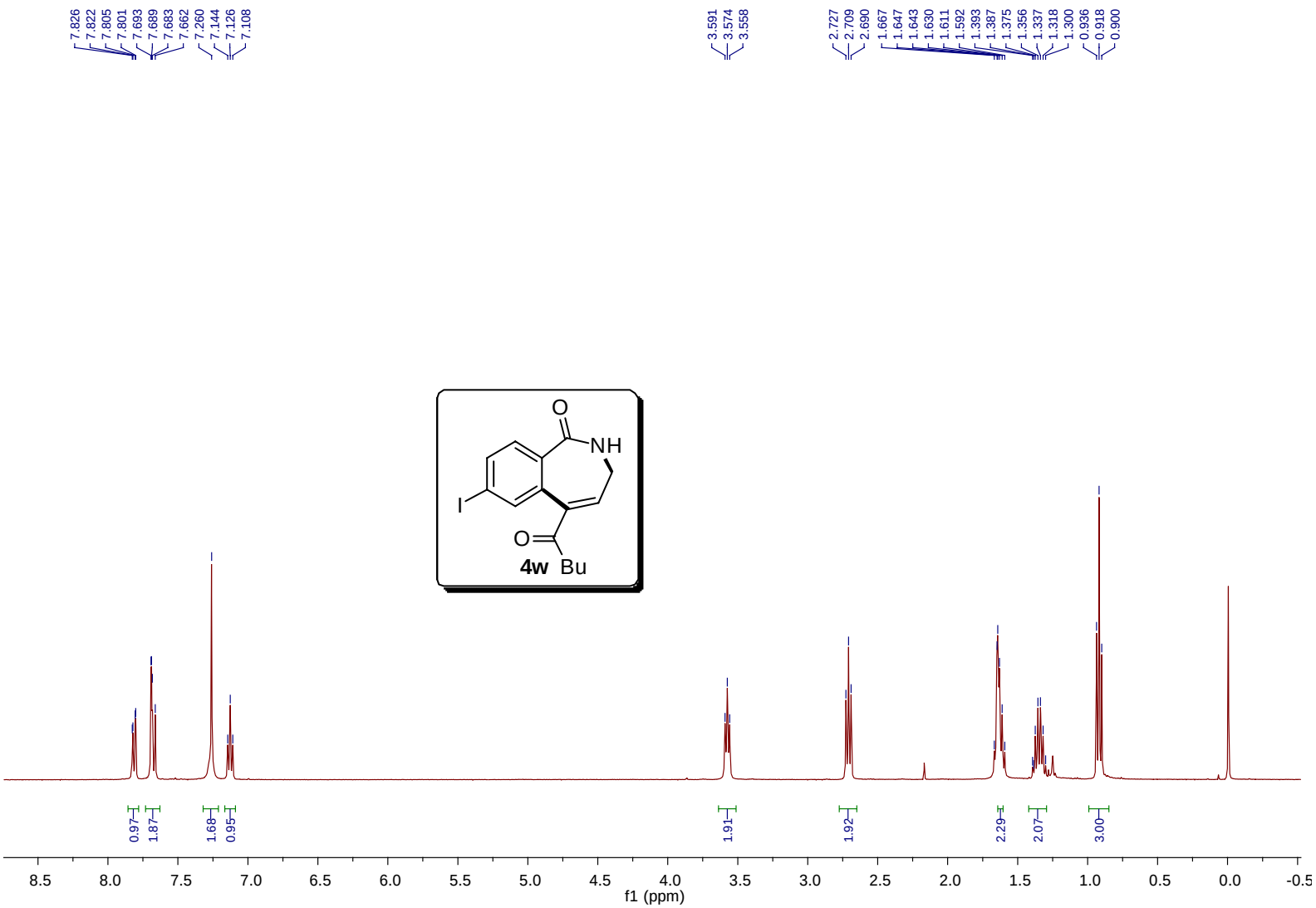


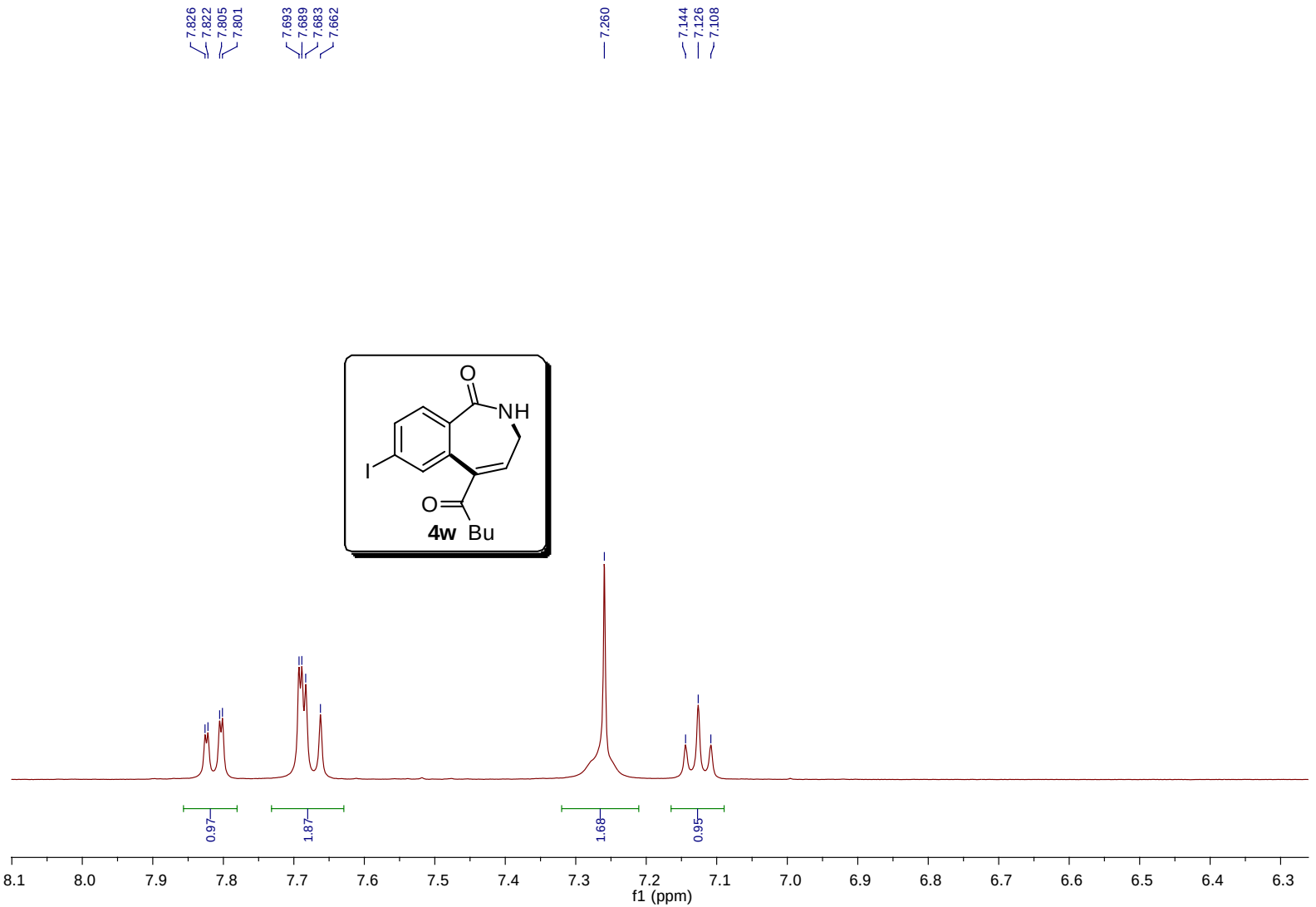


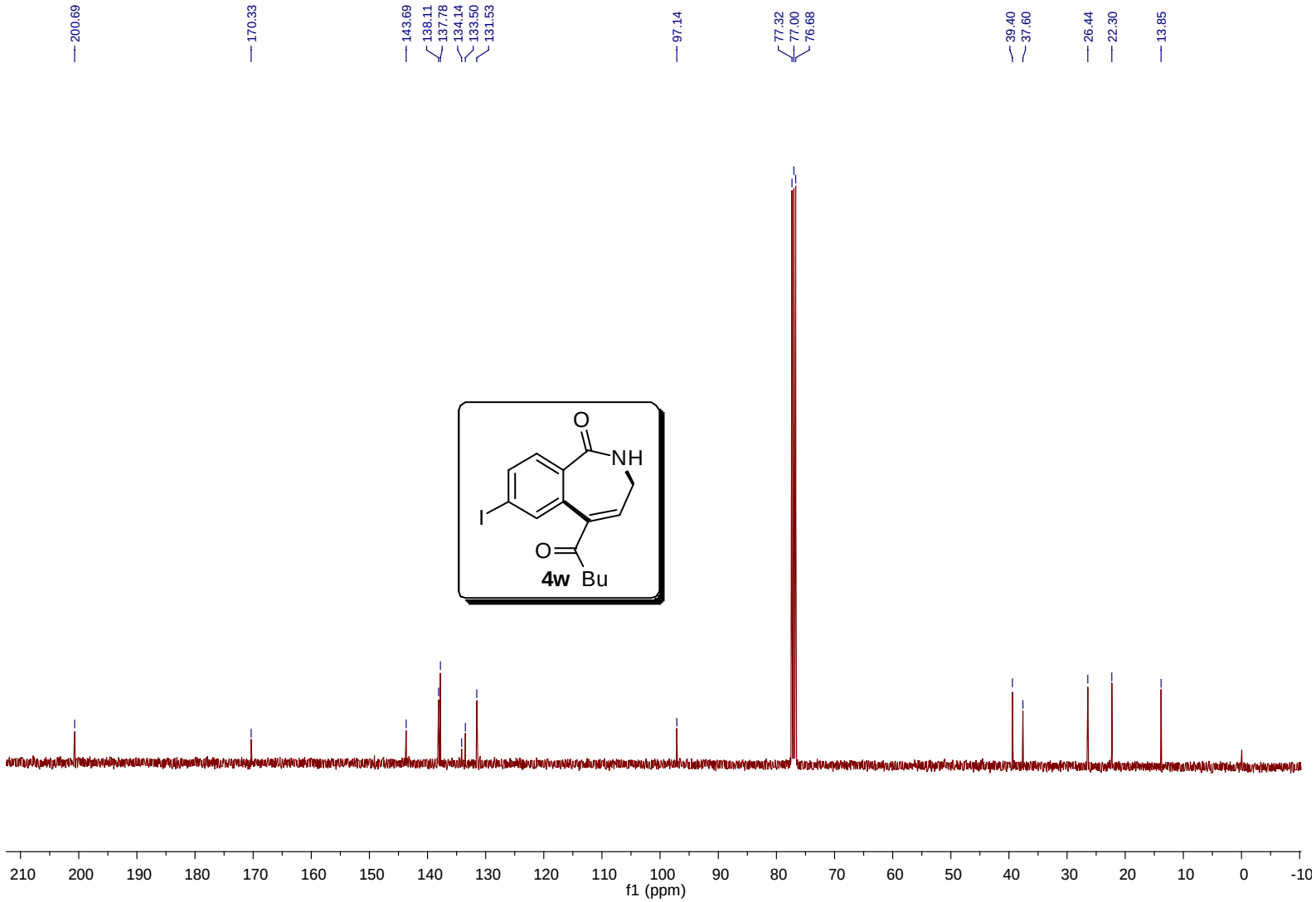


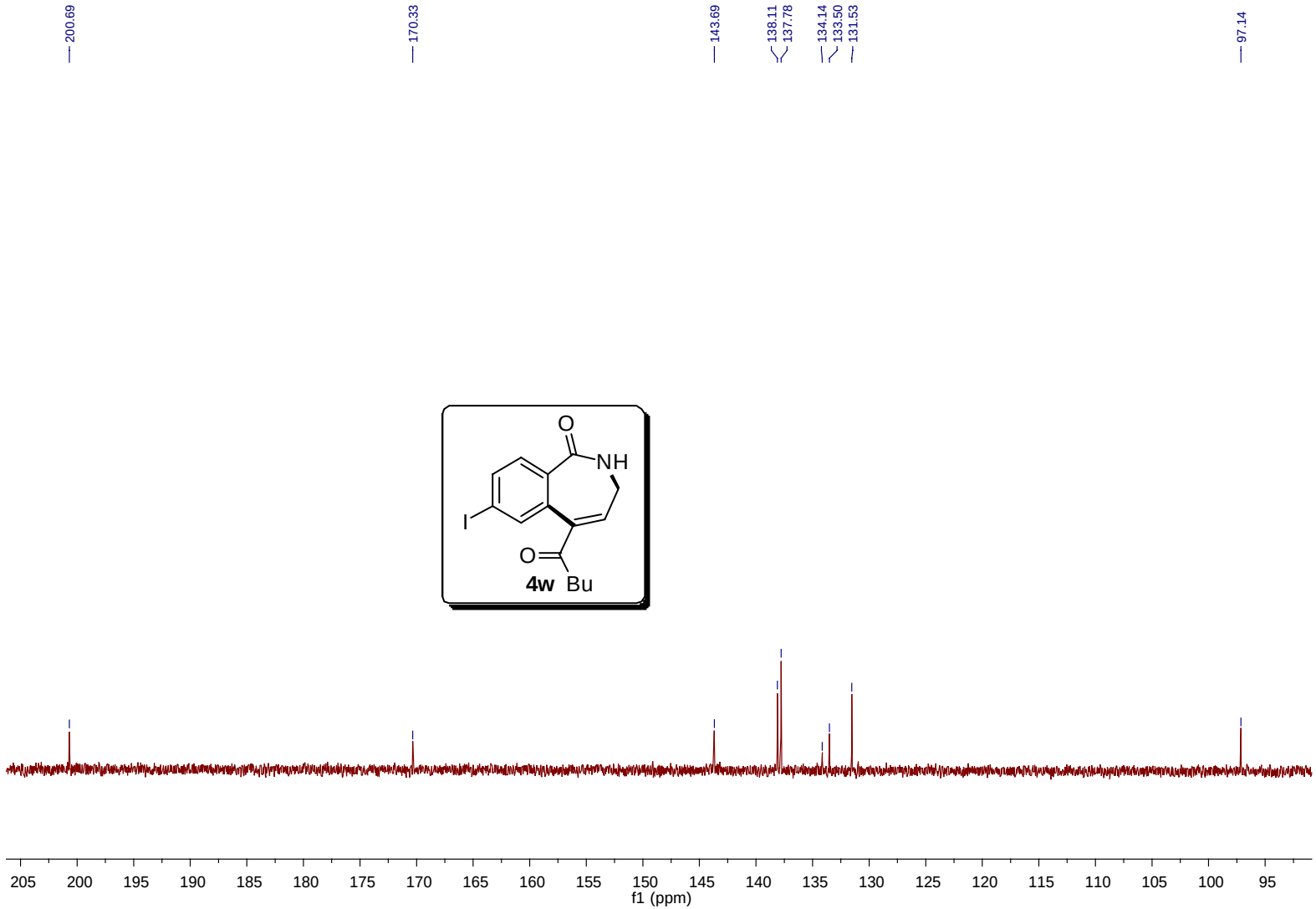


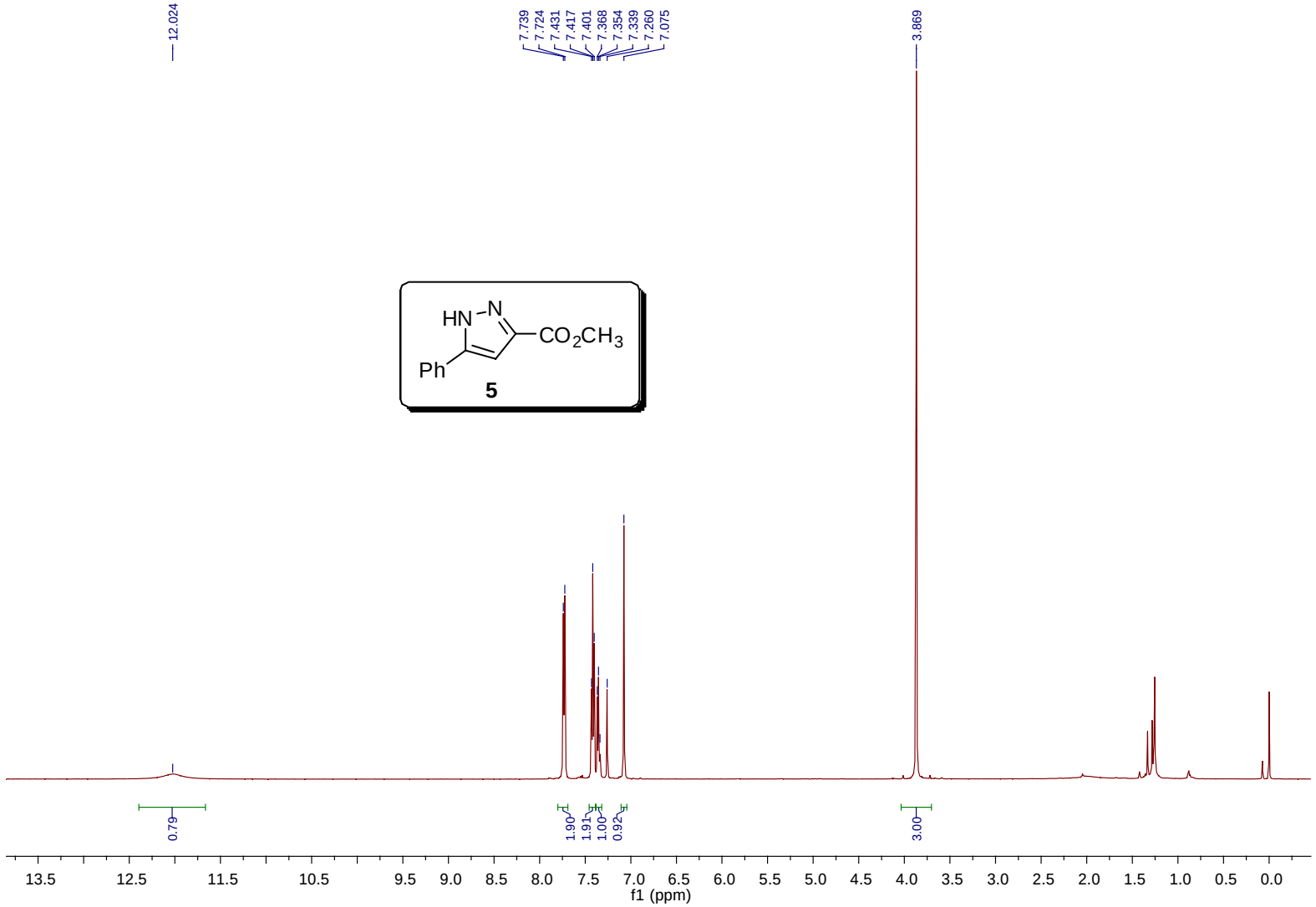


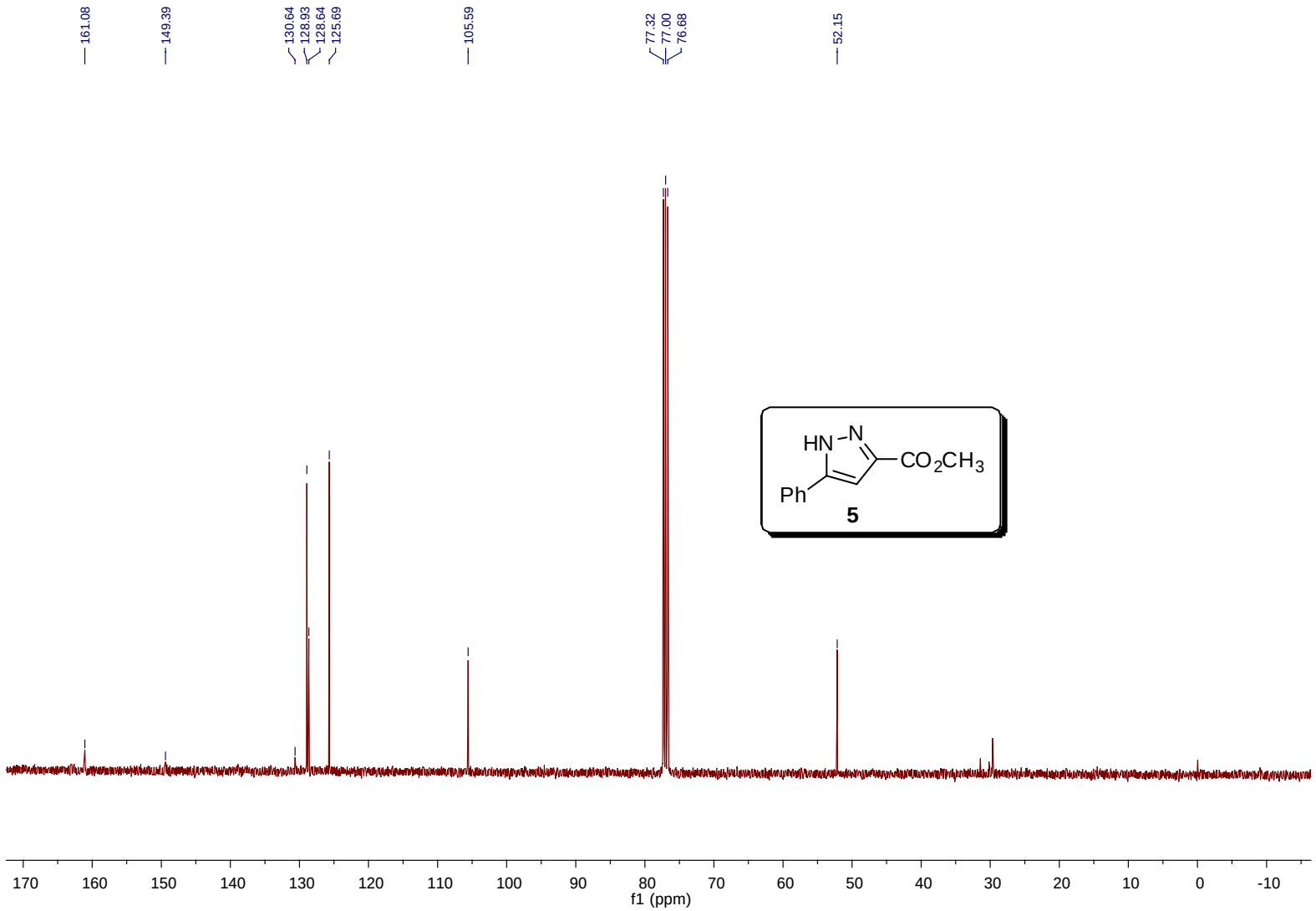


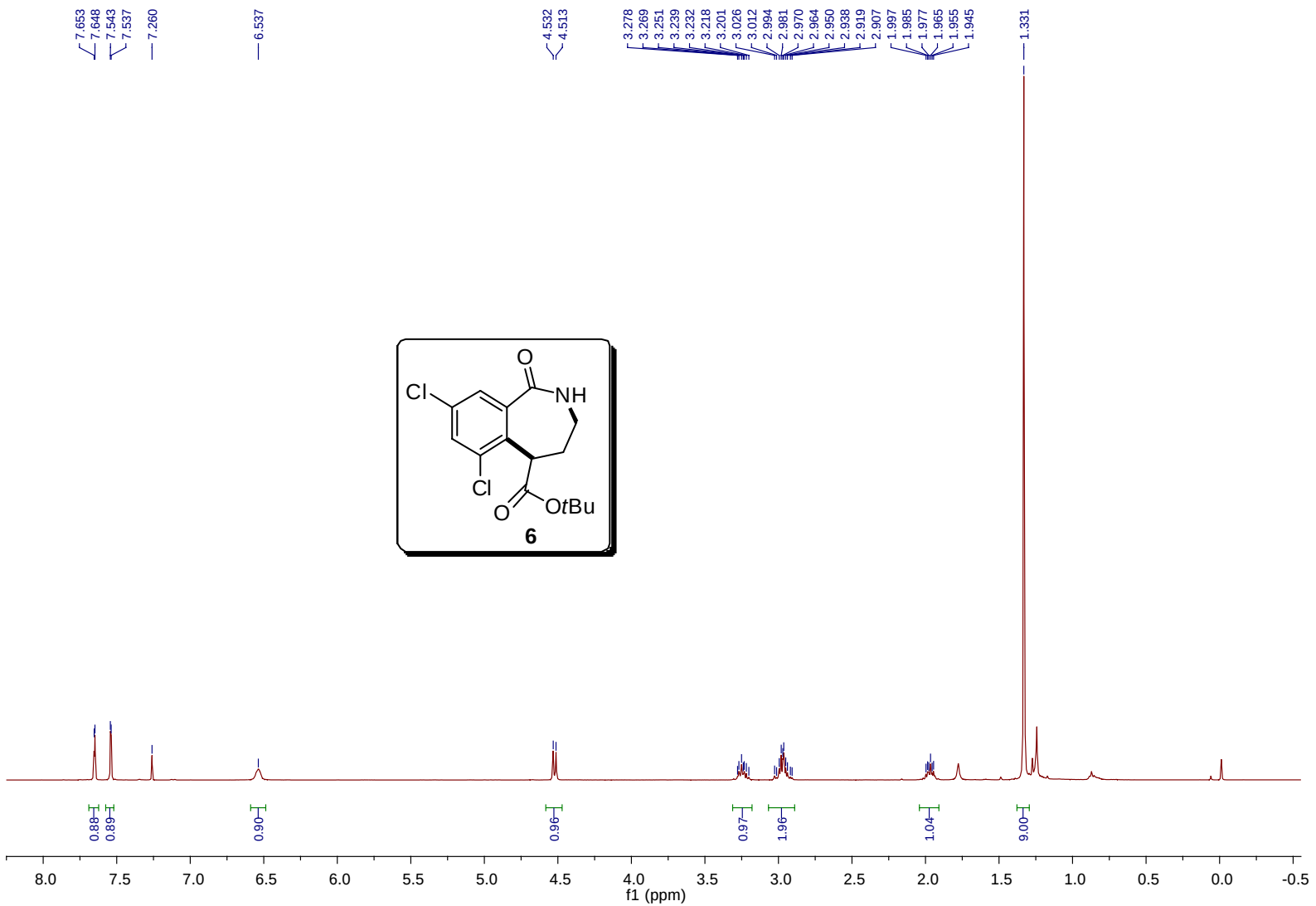


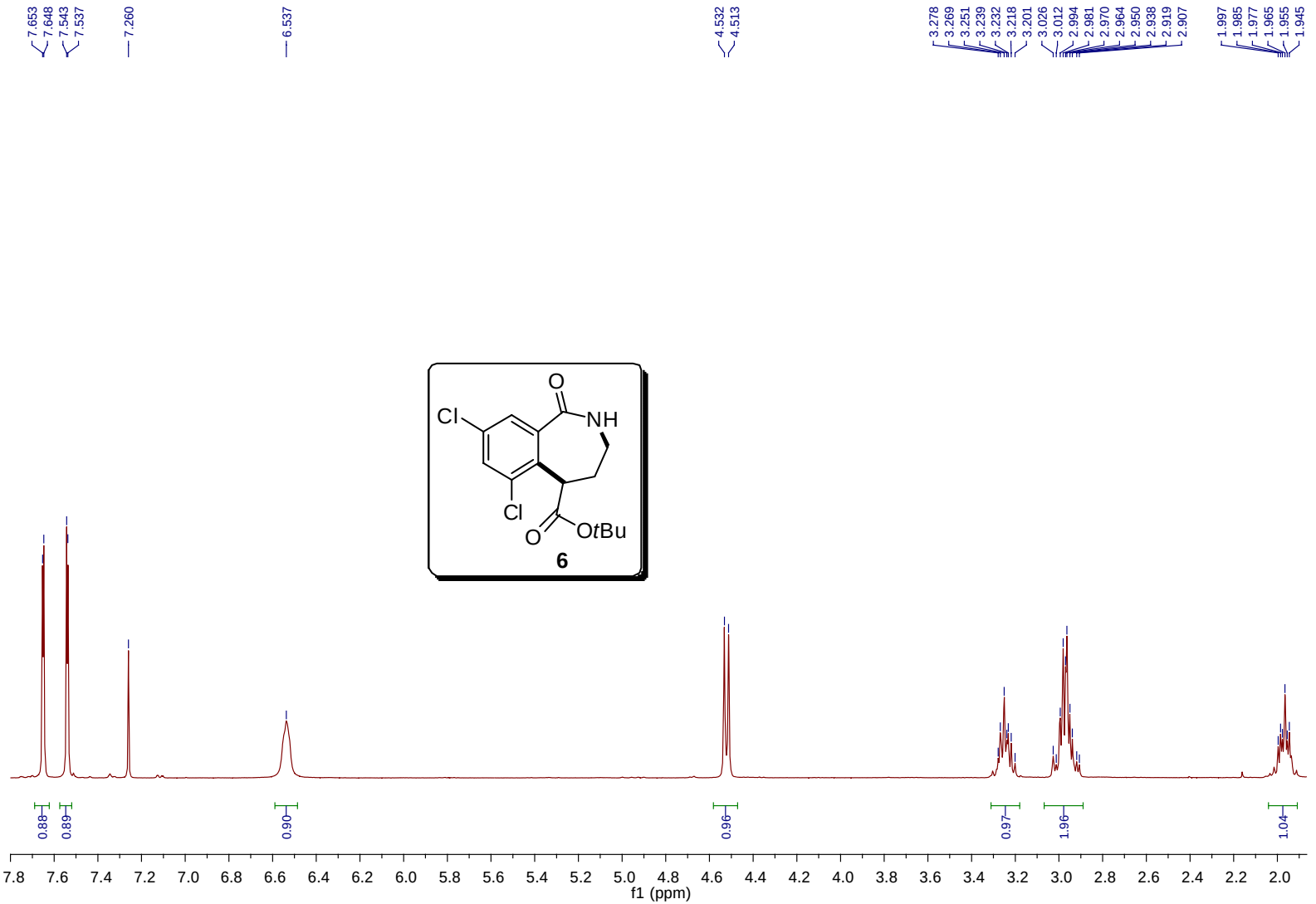


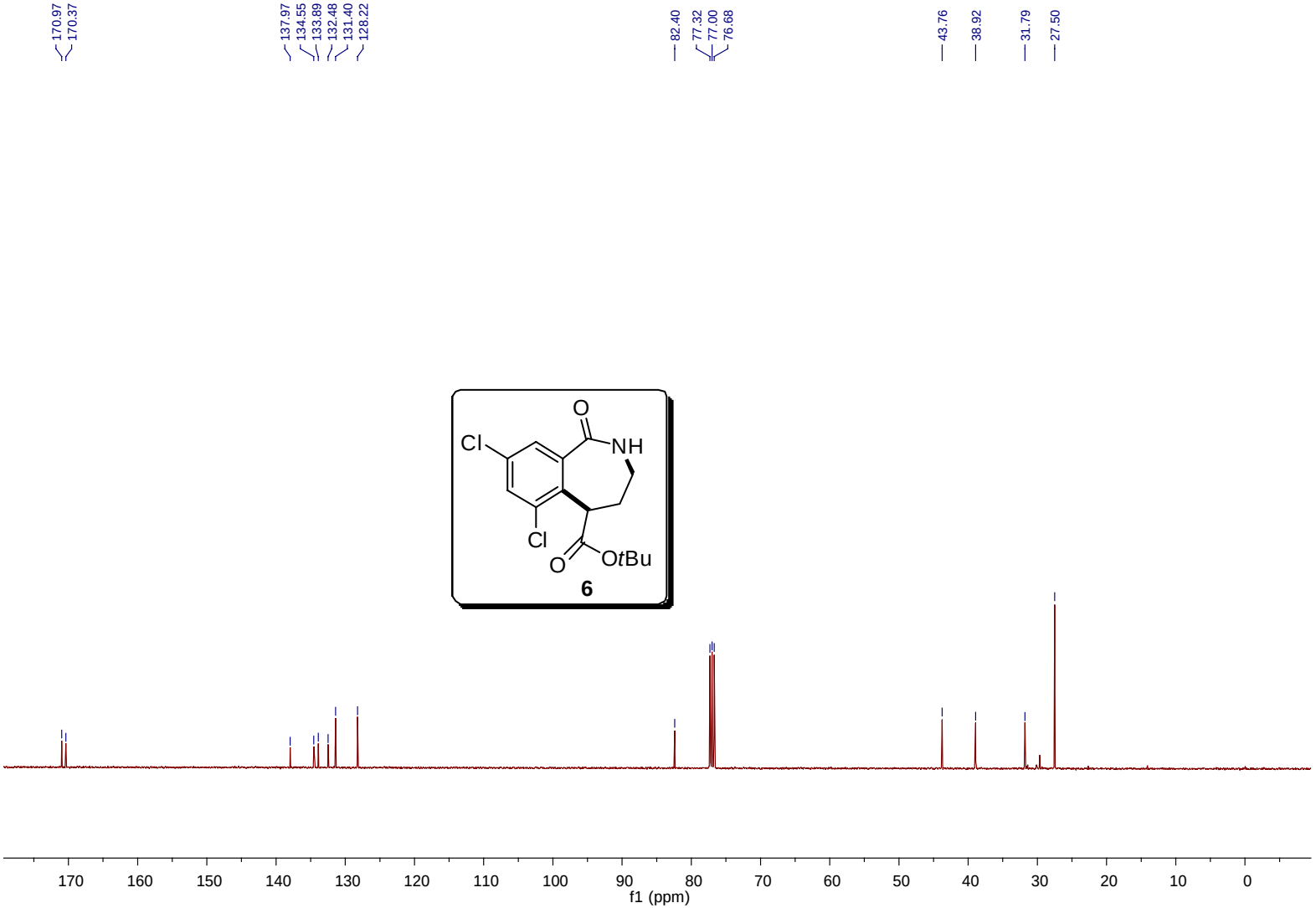


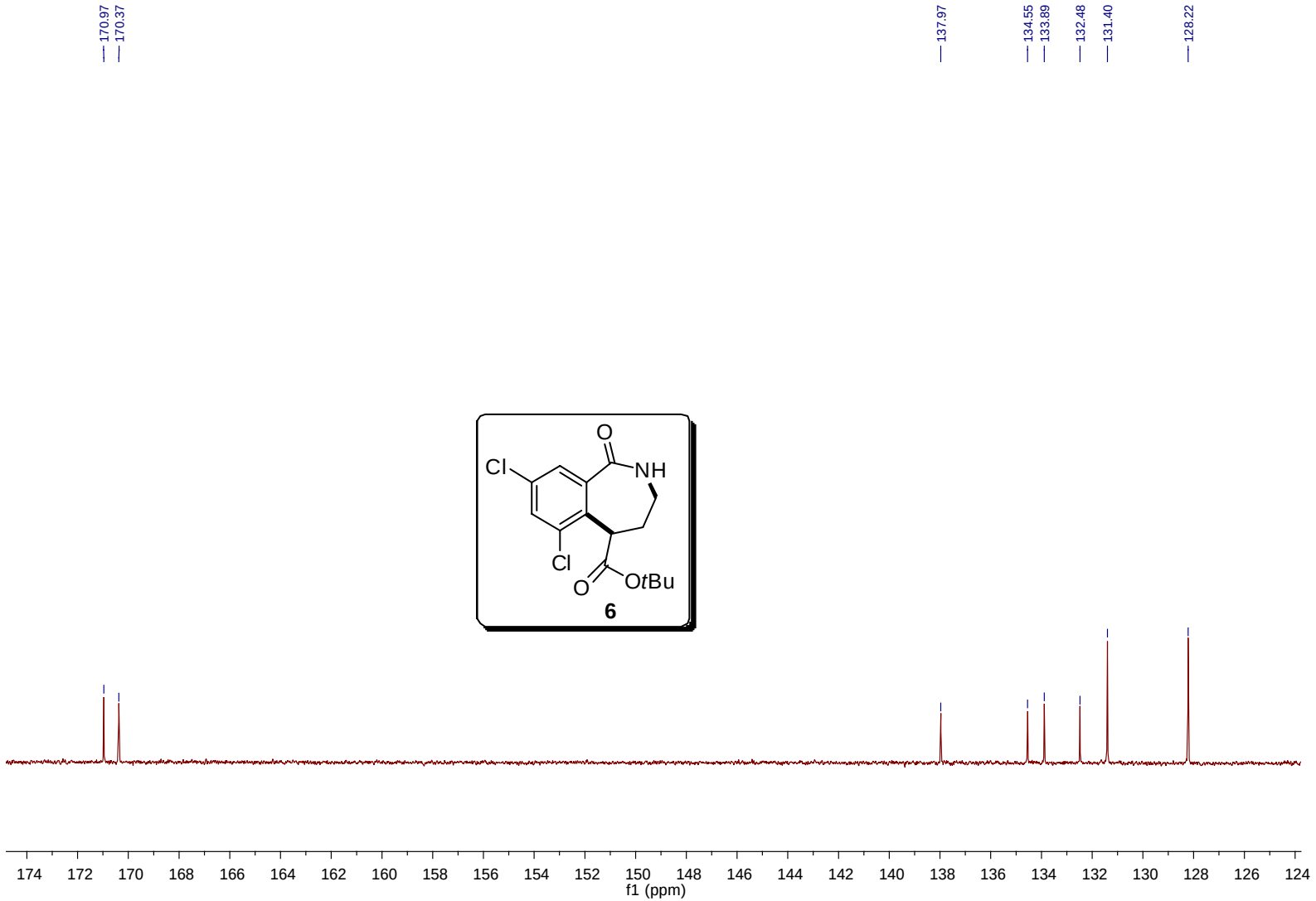


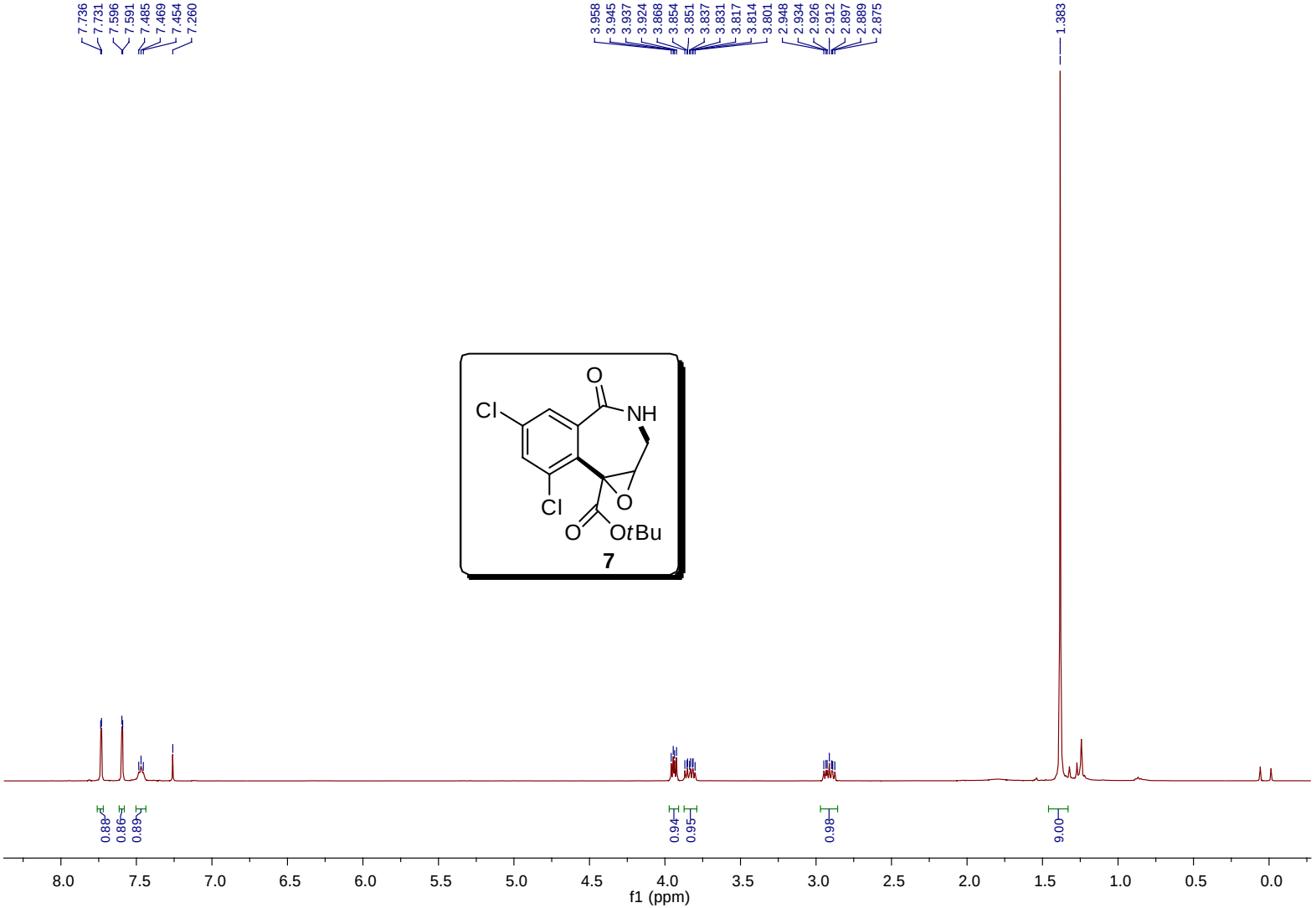


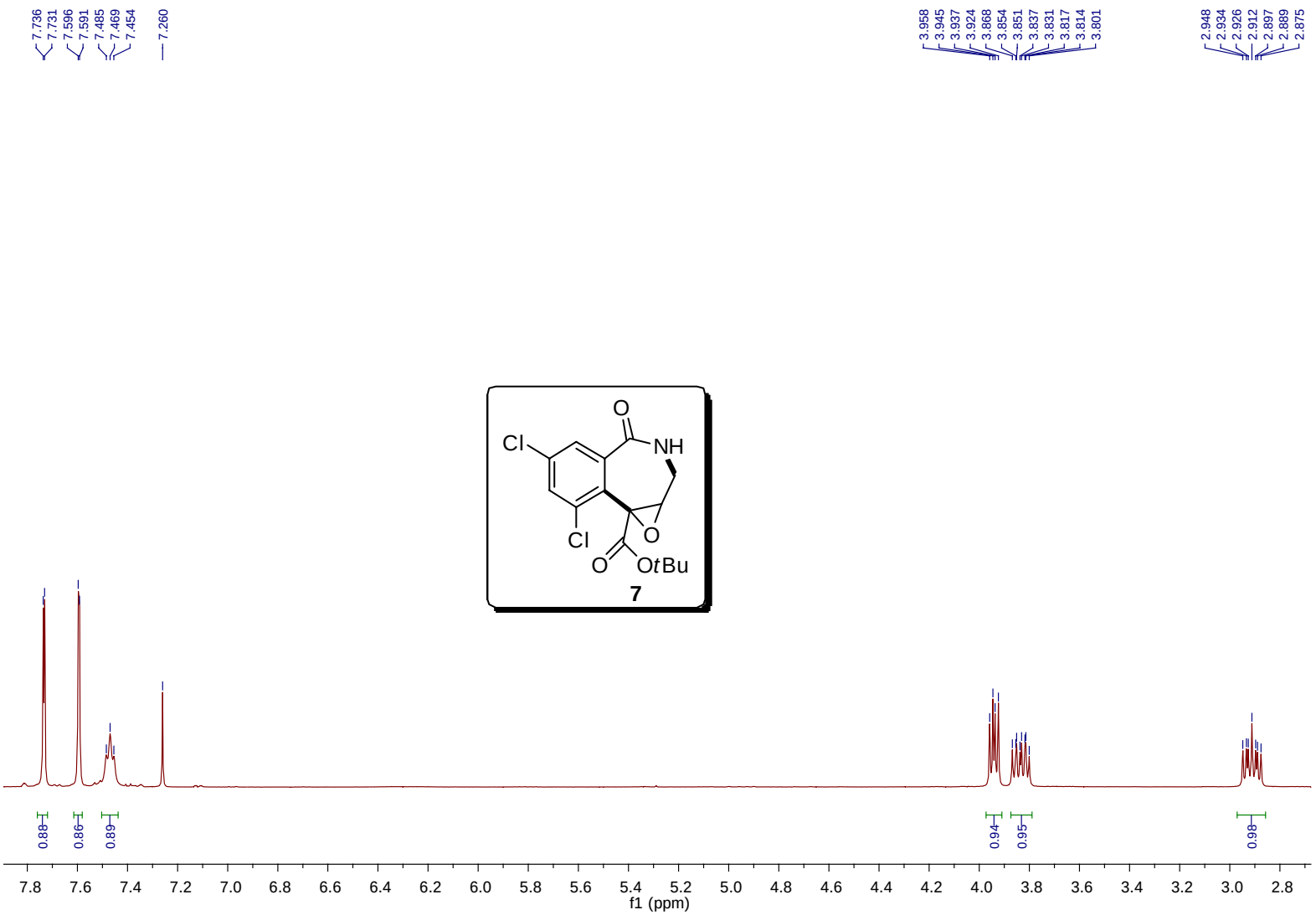


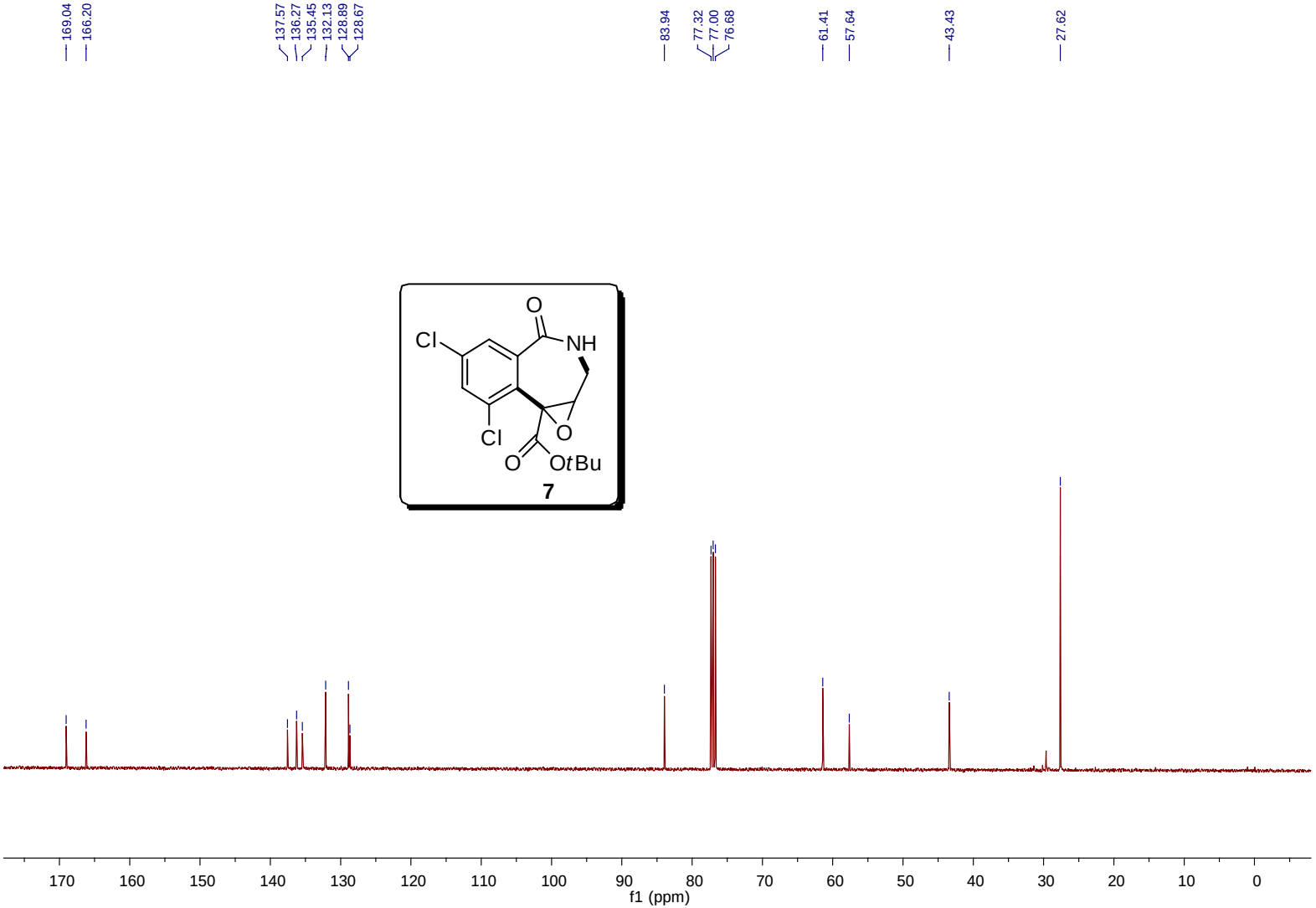


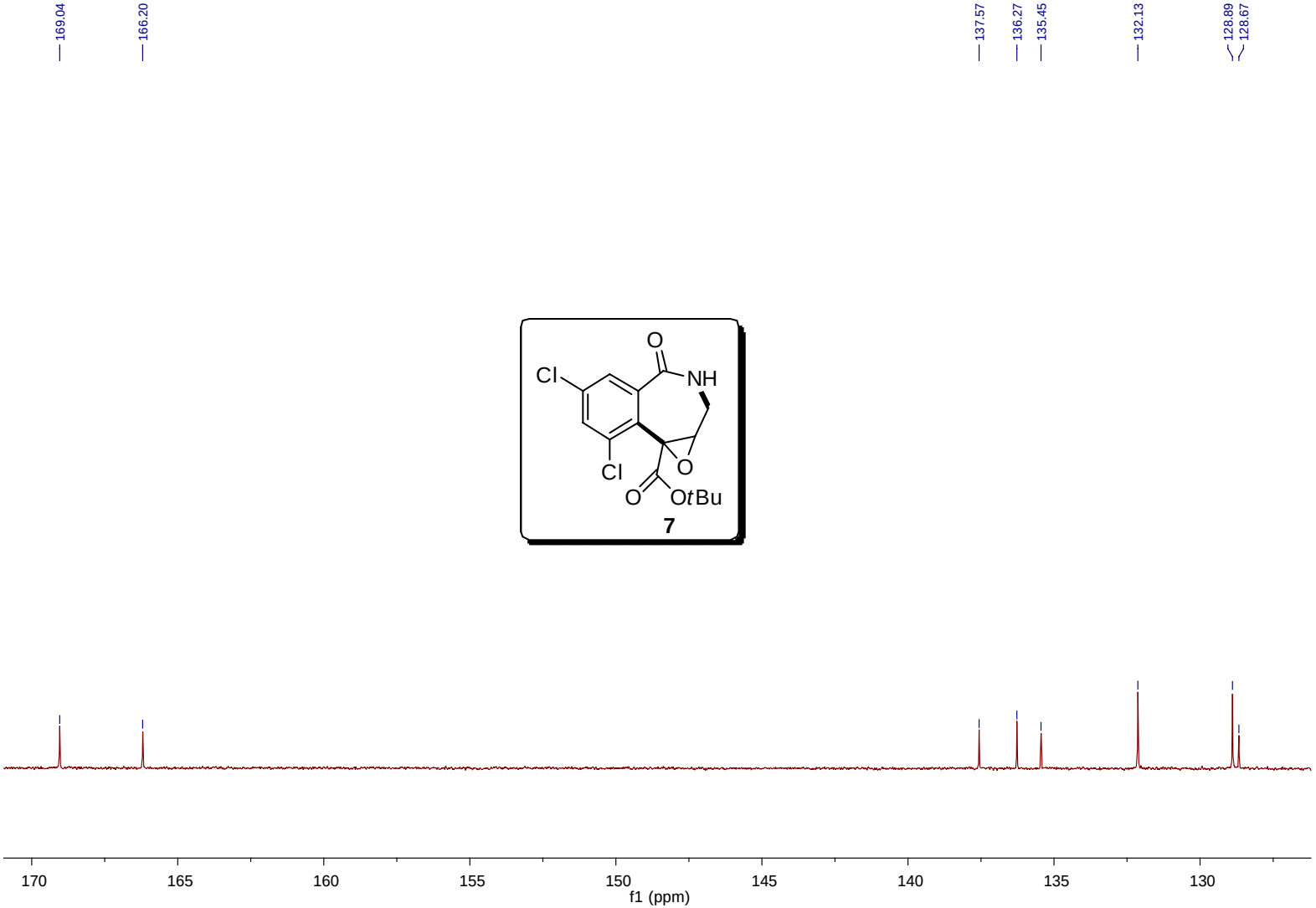


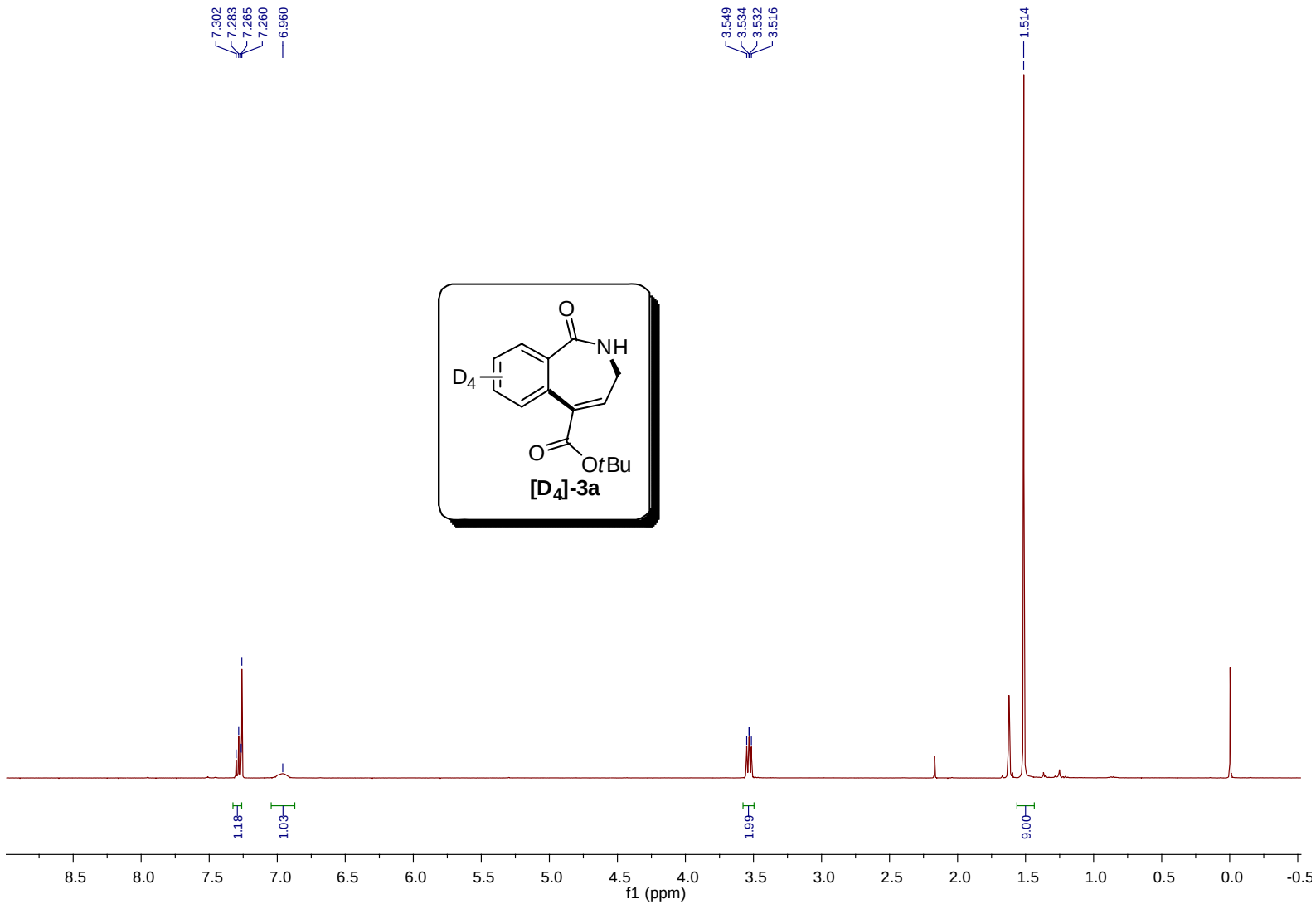


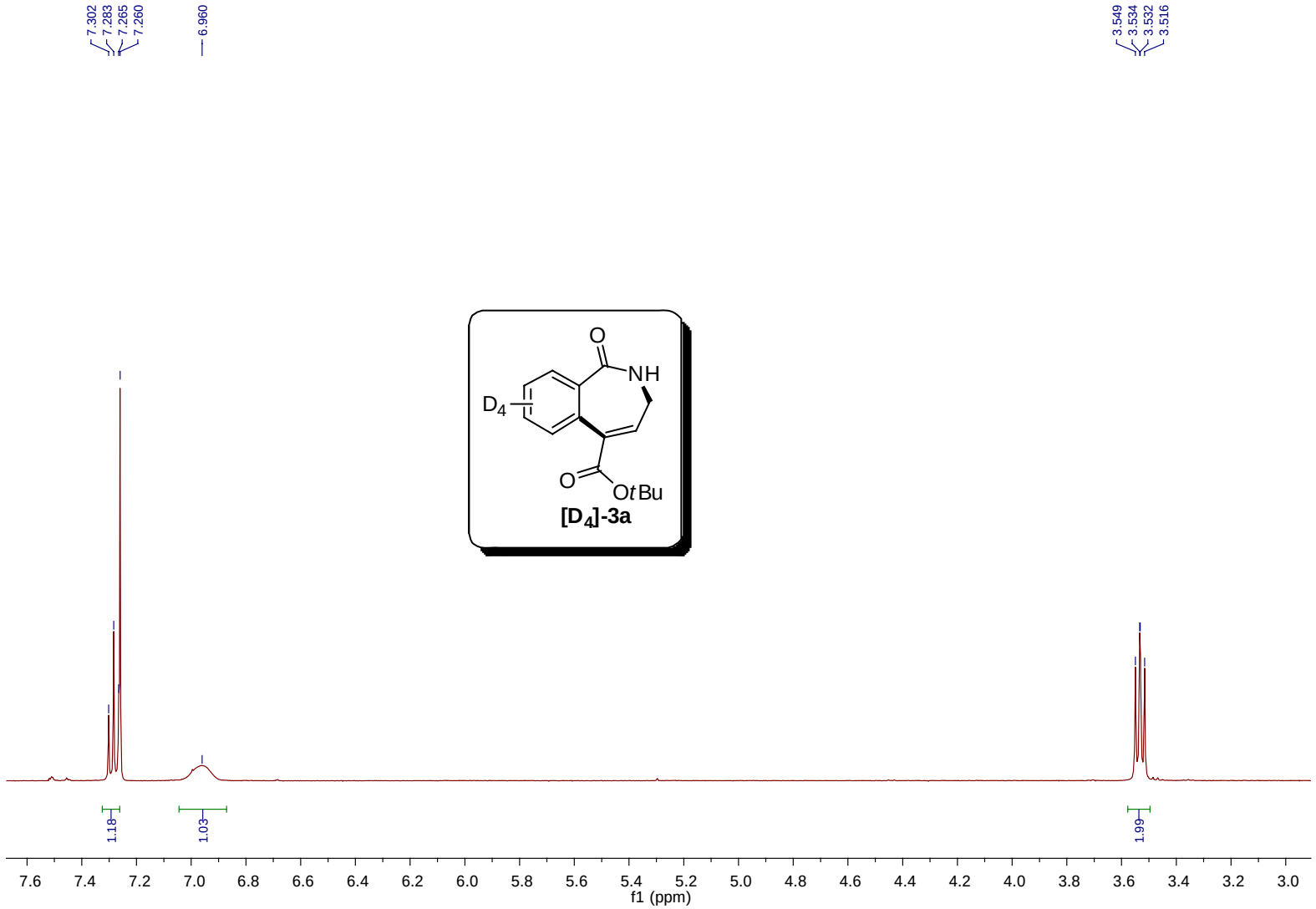


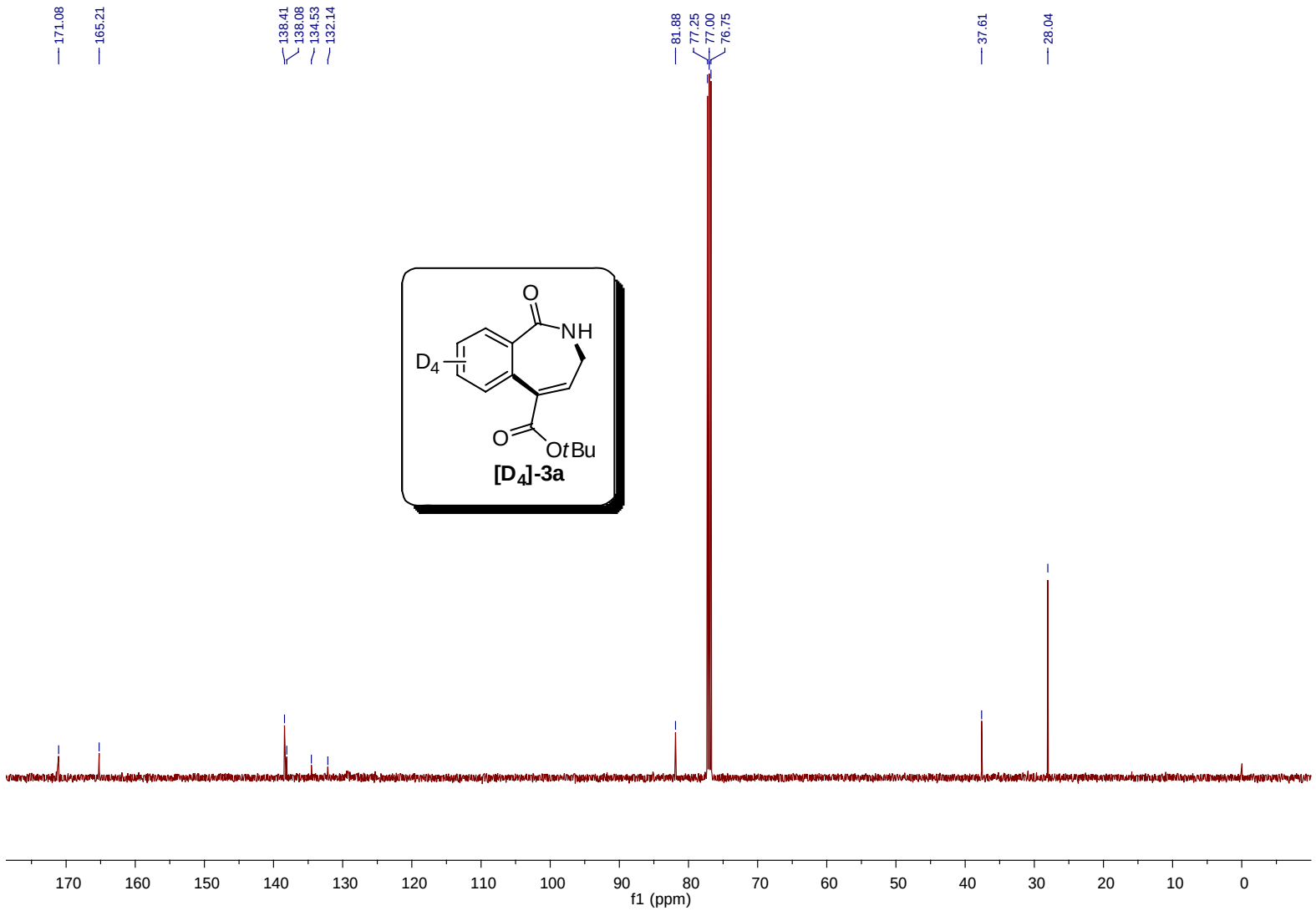


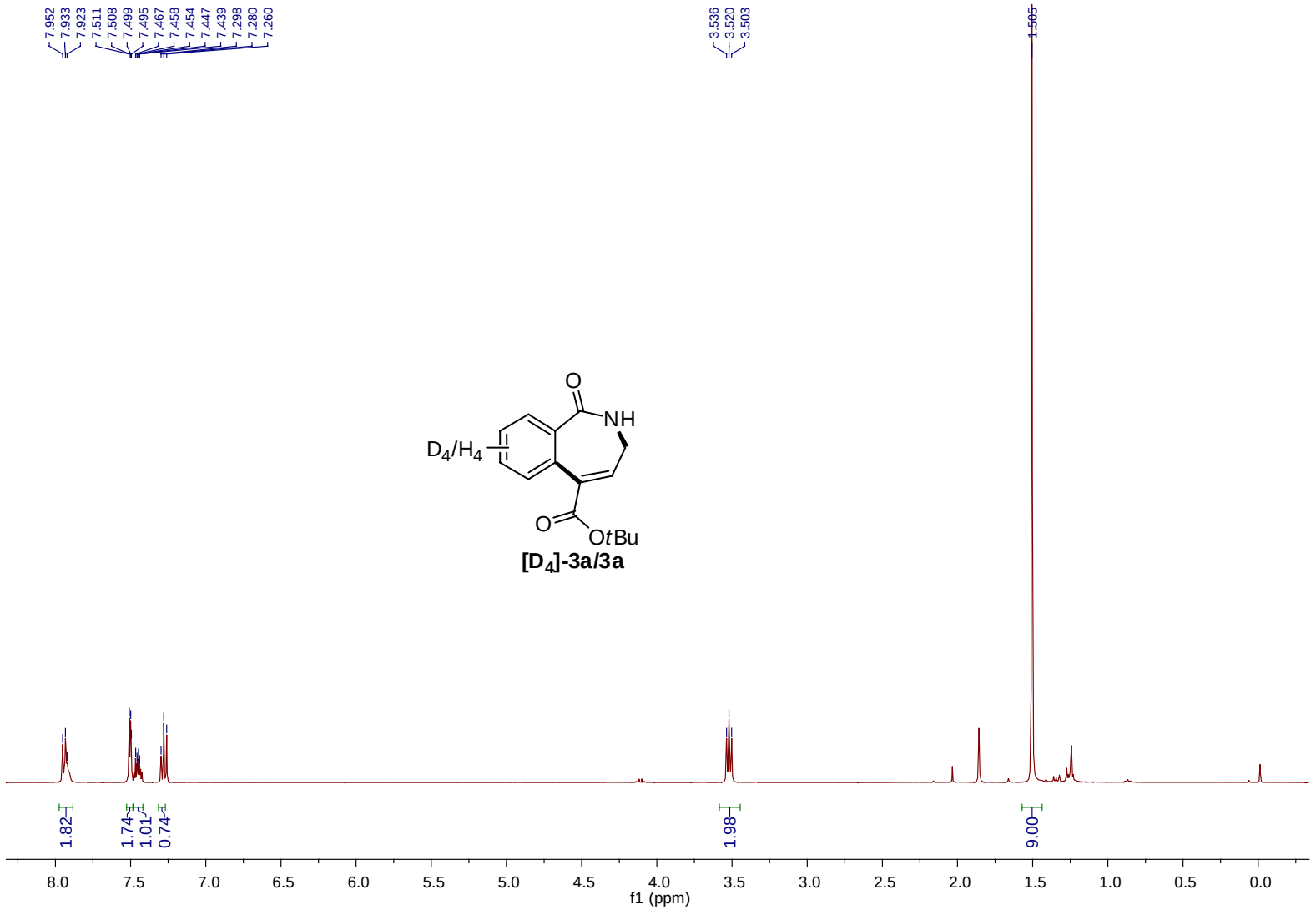




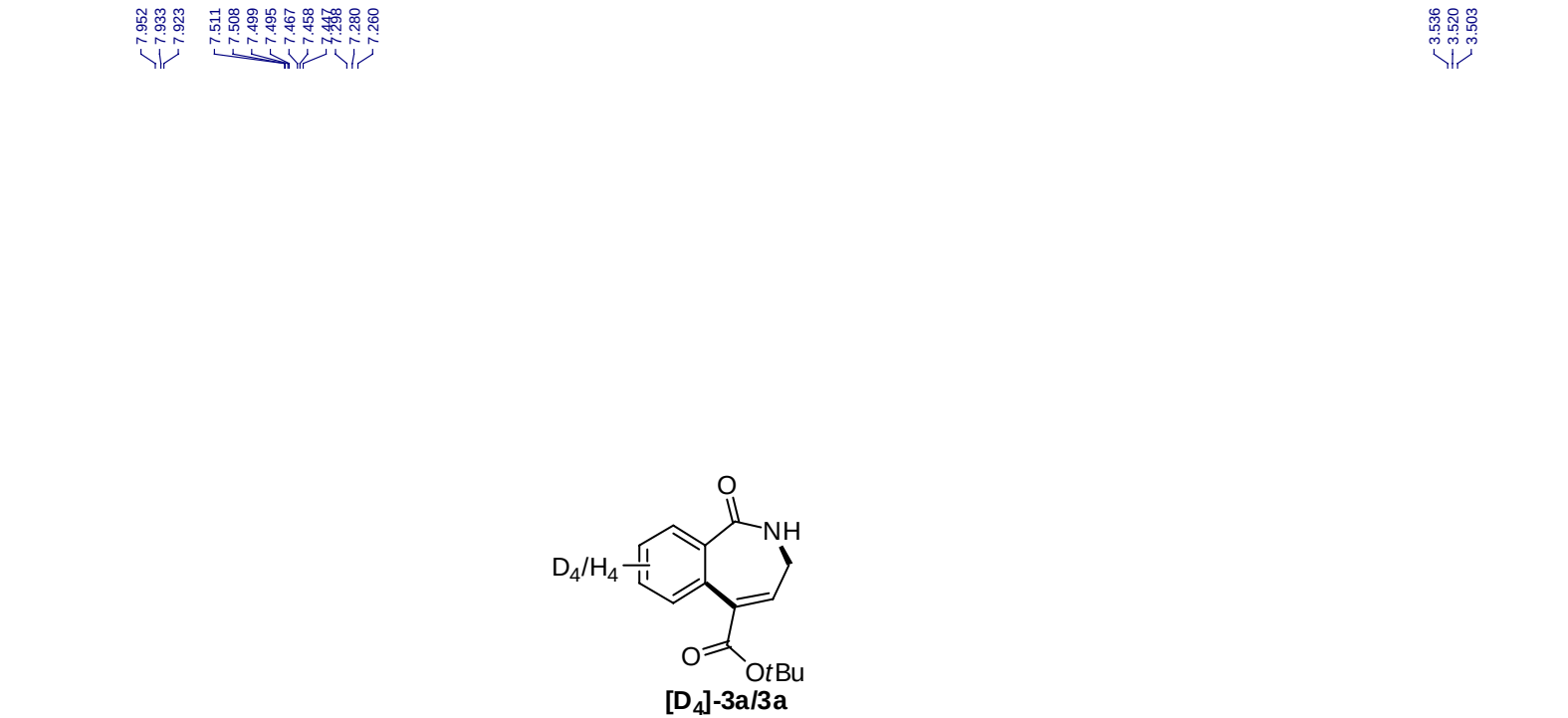








[D$_4$]-3a/3a



[D$_4$]-3a/3a