Electronic Supplementary Information for

TfOH-catalysed domino-double annulation of arenes with propargylic alcohols: A unified approach to indene polycyclic systems

Beeraiah Baire* and Bhavna Yadav

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036

Tamil Nadu, INDIA.

Email: beeru@iitm.ac.in

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1. General Information:

General Methods: All the solvents were distilled prior to use. Dry solvents were prepared according to the standard procedures. All other reagents were used as received from either Aldrich or Lancaster chemical companies. Reactions requiring inert atmosphere were carried out under nitrogen atmosphere. Infrared (IR) spectra were recorded on a JASCO 4100 FT-IR spectrometer. ^{1}H NMR spectra were measured on Bruker AVANCE 400 MHz and 500 MHz spectrometers in $CDCl_3$ solution. Chemical shifts were reported in ppm relative to solvent signals. ^{13}C NMR spectra were recorded on Bruker 100 MHz and 125 MHz spectrometers with complete proton decoupling in $CDCl_3$ solution. Chemical shifts were reported in ppm from the residual solvent as an internal standard.

The high-resolution mass spectra (HRMS) were performed on Micromass QTOF micro mass spectrometer equipped with a Harvard apparatus syringe pump. X-ray crystallographic data were recorded using Bruker-AXS Kappa CCD-Diffractometer with graphite monochromator MoKα radiation (λ=0.7107 A). For thin layer chromatography (TLC) analysis throughout this work, E-merck precoated TLC plates (silica gel 60 F254 grade, 0.25 mm) were used. Acme (India) silica gel (60-120 mesh) was used for column chromatography.

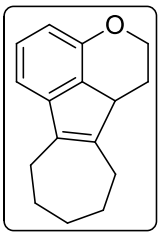
Characterization data for all new compounds is given below and soft copy of each ^{1}H, ^{13}C NMR spectra for all new compounds were given in this supporting information file.

2. Experimental procedures for all new compounds:

2A. General procedure for the synthesis ofcyclopenta[*de*]chromene frameworks (4a-4l).

Propargylic alcohol **1** (1 equiv.) was dissolved in 1,2-dichloroethane (3.5 mL - 7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, trifluoromethanesulfonic acid (TfOH) (0.2 equiv.; µl Hamilton syringe) was added and reaction mixture was stirred at 50 ºC (or room temperature) for 2-4 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane delivered the corresponding cyclopenta[*de*]chromene **4**.

1,2,7,8,9,10,11,11*b*-Octahydroazuleno[1,2,3-*de*]chromene(4a)



Propargylic alcohol **1a** (30 mg, 0.122 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.024 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 20 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane delivered the corresponding cyclopenta[*de*]chromene **4a** (26 mg, 0.114 mmol, 94%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.02 (1H, t, *J* = 7.5 Hz), 6.93 (1H, d, *J*= 7.2Hz), 6.73 (1H, d, *J* = 7.3Hz), 4.33-4.18 (2H, m), 3.47 (1H, d, *J* = 9.8Hz), 2.74-2.32 (4H, m), 1.84-1.83 (1H, m), 1.82-1.63 (4H, m) and 1.41-1.28 (3H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 150.4, 147.4, 143.6, 131.5, 125.7, 125.2, 115.6, 112.2, 67.3, 54.6, 32.1, 31.2, 30.4, 28.4, 27.5and 24.5 ppm.

IR (neat): 3055, 2986, 2926, 2855, 2306, 1597, 1475, 1425, 1265, 1039, 896, 746 and 708 cm^{-1}.

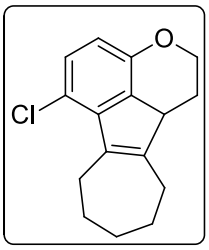
HR ESI-MS:$[C_{16}H_{19}O]^+$= $[M+H]^+$requires 227.1430; found 227.1432.

TLC: R_f= 0.4 (Hexane).

6-Chloro-1,2,7,8,9,10,11,11*b*-octahydroazuleno[1,2,3-*de*]chromene (4b)

Propargylic alcohol **1b** (31 mg, 0.111 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.022 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 2.5 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined

organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane delivered the corresponding cyclopenta[*de*]chromene **4b** (25 mg, 0.096 mmol, 87%) as a pale-yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.89 (1H, d, *J* = 8.4Hz), 6.66 (1H, d, *J* = 8.4Hz),4.26-4.19 (2H, m), 3.60 (1H, d, *J* = 9.9Hz), 2.78-2.52 (5H, m), 1.97-1.59 (5H, m), 1.44-1.17 (1H, m) and 1.23-1.17 (1H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 149.1, 144.8, 142.8, 133.1, 125.5, 125.5, 121.6, 114.5, 67.4, 55.0, 30.9, 29.9, 28.8, 28.3, 27.1and 24.2 ppm.

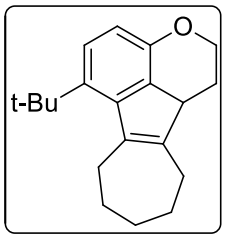
IR (neat): 3051, 2932, 2929, 2360, 2340, 1723, 1585, 1472, 1255, 896 and 807 cm^{-1}.

HR ESI-MS:$[C_{16}H_{18}ClO]^+$= $[M+H]^+$requires 261.1041; found 261.1188.

TLC: R_f= 0.4 (Hexane).

6-(*Tert*-butyl)-1,2,7,8,9,10,11,11*b*-octahydroazuleno[1,2,3-*de]*chromene (4c)

Propargylic alcohol **1c** (30 mg, 0.099 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.019 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 1.5 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane delivered the corresponding cyclopenta[*de*]chromene **4c** (26 mg, 0.092 mmol, 93%) as a pale-yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.09 (1H, d, *J* = 8.5Hz), 6.71 (1H, d, *J* = 8.4Hz), 4.24-4.19 (2H, m), 3.77 (1H, d, *J* = 9.5 Hz), 2.73-2.54 (5H, m), 2.06-1.59 (6H, m), 1.44 (9H, s) and 1.19-1.13 (1H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 148.5, 144.2, 143.7, 139.3, 131.5, 124.8, 124.7, 113.1, 66.8, 55.3, 35.9, 34.4, 32.4, 30.5, 29.8, 28.2, 26.5 and 24.2 ppm.

IR (neat): 3042, 2928, 2361, 2336, 2252, 1646, 1562, 1550, 1538, 1515, 1041, 887 and 743 cm^{-1}.

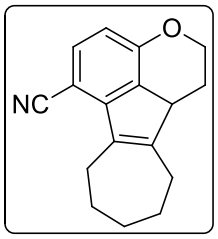
HR ESI-MS:$[C_{20}H_{27}O]^+$= $[M+H]^+$requires 283.2056; found 283.2048.

TLC: R_f= 0.4 (Hexane).

1,2,7,8,9,10,11,11*b*-Octahydoazuleno[1,2,3-*de*]chromene-6-carbonitrile (4d)

Propargylic alcohol **1d** (30 mg, 0.111 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.022 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 4.5 h (the reaction was monitored by TLC analysis). The reaction was quenched

with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding chromene derivative **4d** (22 mg, 0.087 mmol, 79%) as a pale yellow semi-solid.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.26 (1H, d, *J* = 8.3Hz), 6.75 (1H, d, *J* = 8.2Hz), 4.34-4.23 (2H, m), 3.68 (1H, d, *J* = 9.6Hz), 2.74-2.54 (5H, m), 2.04-1.92 (2H, m), 1.87-1.80 (3H, m) and 1.74-1.65 (2H, m)ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 153.6, 150.3, 145.6, 132.4, 129.8, 124.7, 118.5, 113.7, 99.4, 67.6, 55.0, 30.8, 30.0, 28.2, 27.1 and 23.9 ppm.

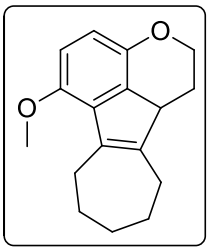
IR (neat): 3429, 2929, 2856, 2371, 2224, 1604, 1489, 1261, 1118, 1035, 825 and 736cm^{-1}.

HR ESI-MS: $[C_{17}H_{21}N_2O]^+$= $[M+ NH_4]^+$ requires 269.1648; found 269.1634.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

6-Methoxy-1, 2, 7, 8, 9, 10, 11, 11*b*-octahydroazuleno [1,2,3-*de*]chromene (4e)

Propargylic alcohol **1e** (30 mg, 0.109 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.021 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4e** (24 mg, 0.093 mmol, 85%) as a pale yellow semi-solid.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.68 (1H, d, *J* = 8.5Hz), 6.52 (1H, d, *J* = 8.5Hz),4.26-4.12 (2H, m), 3.82 (3H, s), 3.60 (1H, d, *J* = 9.3Hz), 2.73-2.46 (5H, m), 1.95-1.90 (1H, m), 1.85-1.77(2H, m), 1.73-1.59 (2H, m) and 1.43-1.15 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 150.3, 144.9, 144.5, 132.9, 132.4, 125.9, 112.9, 108.1, 67.4, 55.8, 53.8, 31.1, 30.2, 29.5, 28.3, 27.3and 24.4 ppm.

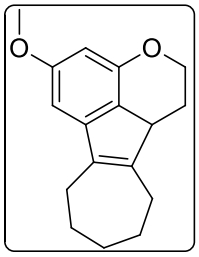
IR (neat): 3055, 2987, 2926, 2853, 1599, 1492, 1428, 1320, 1265, 1037, 896 and 741 cm^{-1}.

HR ESI-MS: $[C_{17}H_{21}O_2]^+$= $[M+H]^+$requires 257.1536; found 257.1544.

TLC: R_f= 0.4 (Hexane).

5-Methoxy-1,2,7,8,9,10,11,11*b*-octahydroazuleno[1,2,3-*de*]chromene (4f)

Propargylic alcohol **1f** (30 mg, 0.109 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen



atmosphere. Then, TfOH (0.021 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane delivered the corresponding cyclopenta[*de*]chromene **4f** (24 mg, 0.093 mmol, 86%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.56 (1H, s), 6.34 (1H, s), 4.32-4.13 (2H, m), 3.78 (3H, s), 3.43 (1H, d), 2.70-2.21 (4H, m),2.39-2.19(6H, m)and1.91-1.57 (2H, m) ppm.

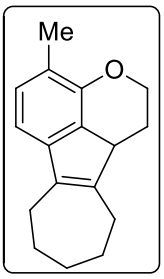
^{13}C NMR (100 MHz, $CDCl_3$):δ = 159.2, 150.4, 148.0, 140.8, 125.1, 124.9, 103.1, 98.6,67.6, 55.9, 54.6, 32.4, 31.1, 30.2, 28.2,27.6 and 24.4 ppm.

IR (neat): 3053, 2922, 2845, 2359, 1607, 1541, 1491, 1440, 1274, 1198, 1147, 1107, 1037, 836 and 736 cm^{-1}.

HR ESI-MS: $[C_{17}H_{21}O_2]^+ = [M+H]^+$ requires 257.1536; found 257.1544.

TLC: R_f= 0.4(Hexane).

4-Methyl-1,2,7,8,9,10,11,11*b*-octahydroazuleno[1,2,3-*de*]chromene (4g)



Propargylic alcohol **1g** (30 mg, 0.116 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.023 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 25 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4g** (23 mg, 0.095 mmol, 82%) as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.77 (1H, d, *J* = 8.0Hz), 4.23 (1H, d, *J* = 8.0Hz), 4.24-4.21 (2H, m), 3.51 (1H, d, *J* = 9.6Hz), 2.75-2.43 (5H, m), 2.34 (3H, s) and 1.97-1.59 (7H, m) ppm.

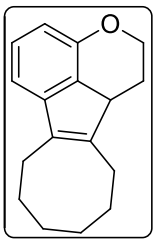
^{13}C NMR (100 MHz, $CDCl_3$):δ = 147.7, 143.8, 142.4, 130.2, 125.8, 124.9, 124.7, 111.6, 66.2, 53.3, 29.0, 28.9, 28.8, 27.2, 26.2, 23.5 and 17.0ppm.

IR (neat): 3033, 2915, 2360, 1634, 1579, 1490, 1452, 1101, 1043, 757and 673 cm^{-1}.

HR ESI-MS: $[C_{17}H_{21}O]^+ = [M+H]^+$ requires 241.1587; found 241.1592.

TLC: R_f= 0.4 (Hexane).

2,7,8,9,10,11,12,12*b*-Octahydro-1*H*-cycloocta[4,5]cyclopenta[1,2,3-*de*]chromene (4h)



Propargylic alcohol **1h** (30 mg, 0.116 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.023 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 50 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4h** (23 mg, 0.095 mmol, 82%) as pale-yellow oil.

^{1}H NMR (400 MHz,$CDCl_3$):δ = 7.02 (1H, t, *J* = 7.5Hz), 6.93 (1H, d), 6.73 (1H, d, *J* = 7.9Hz), 4.37-4.14 (2H, m), 3.48 (1H, s), 2.76-2.69(3H, m), 2.42-2.33 (2H, m), 2.05-2.02 (1H, m), 1.84-1.81 (1H, m), 1.64-1.48 (4H, m) and 1.29-1.16 (3H, m) ppm.

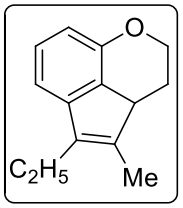
^{13}C NMR (100 MHz, $CDCl_3$):δ = 150.6, 146.3, 142.7, 132.0, 126.6, 125.1, 115.6, 112.2, 67.3, 53.6, 29.7, 26.9, 26.5, 26.0, 25.5, 24.7 and 24.6 ppm.

IR (neat): 3049, 2913, 2360, 2340, 1710, 1598, 1551, 1477, 1256, 1101and 750 cm^{-1}.

HR ESI-MS: $[C_{17}H_{21}O]^+$= $[M+H]^+$ requires 241.1587; found 241.1594.

TLC: R_f= 0.4 (Hexane).

4-Ethyl-5-methyl-3,3*a*-dihydro-2*H*-cyclopenta[*de*]chromene (4i)



Propargylic alcohol **1i** (45 mg, 0.206 mmol) was dissolved in 1,2-dichloroethane (5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.041 mmol, 4 µL) was added and reaction mixture was stirred at 50 ºC for 1 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4i** (37 mg, 0.184 mmol, 90%) as a pale-yellow oil.

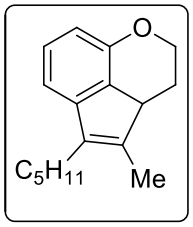
^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.01-6.95 (2H, m), 6.72 (1H, d, *J* = 7.5Hz), 4.29-4.20 (2H, m), 3.30 (1H, s), 2.77-2.74 (2H, m), 2.09-1.99 (1H, m), 1.91 (3H, s), 1.75-1.64 (1H, m) and 0.71 (3H, t, *J* = 7.3Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ =150.5, 146.4, 136.1, 132.2, 126.9, 125.1, 116.2, 112.3, 67.4, 54.8, 24.5, 22.7, 12.0 and 9.6ppm.

IR (neat): 3055, 2983, 2929, 2306, 1596, 1474, 1423, 1264, 1036, 896 and 743 cm^{-1}.

TLC: R_f= 0.4 (Hexane).

5-Methyl-4-pentyl-3,3*a*-dehydro-2*H*-cyclopenta[*de*]chromene (4j)



Propargylic alcohol **1j** (60 mg, 0.230 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.046 mmol, 4 µL) was added and reaction mixture was stirred at 50 ºC for 1 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4j** (48 mg, 0.198 mmol, 86%) as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.01-6.95 (2H, m), 6.70 (1H, d, *J* = 7.2 Hz), 4.28-4.20 (2H, m), 3.33 (1H, s), 2.76-2.74 (2H, m), 2.03-1.88 (4H, m), 1.66-1.56 (3H, m), 1.29-1.10 (3H, m) and 0.91-0.84 (4H, m)ppm.

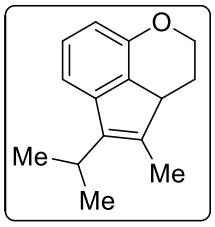
^{13}C NMR (100 MHz, $CDCl_3$):δ = 150.5, 146.8, 136.7, 132.1, 126.6, 125.1, 116.2, 112.3, 67.4, 53.9 32.3, 30.0, 25.3, 24.5, 22.6, 14.2 and 12.1 ppm.

IR (neat): 3054, 2986, 2960, 2933, 2360, 1617, 1600, 1475, 1265, 739 and 705 cm^{-1}.

HR ESI-MS: $[C_{17}H_{26}NO]^+$= $[M+NH_4]^+$requires 260.2009; found 260.2026.

TLC: R_f = 0.4 (Hexane).

5-Isopropyl-4-methyl-3-3*a*-dihydro-2*H*-cyclopenta[*de*]chromene (4k)



Propargylic alcohol **1k** (30 mg, 0.129 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.025 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 1 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4k** (26 mg, 0.121 mmol, 94%) as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.04-6.95 (2H, m), 6.72 (1H, d, *J* = 7.3Hz), 4.24-4.21 (2H, t, *J* = 5.6Hz), 3.28 (1H, s), 2.76-2.74(2H, m), 2.40-2.31 (1H, m), 1.93 (3H, s), 1.30-1.22 (3H, m)and0.52 (3H, d, *J* = 6.8Hz) ppm.

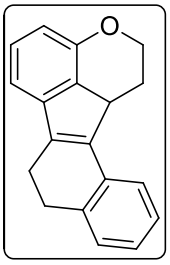
^{13}C NMR (100 MHz, $CDCl_3$):δ = 150.4, 144.7, 135.9, 132.7, 127.2, 124.9, 117.3, 112.4, 67.4, 60.2,28.7, 24.4, 21.6, 16.3 and 12.5 ppm.

IR (neat): 2959, 2873, 1702, 1590, 1475, 1366, 1255, 1228, 1056, 994 and 759 cm^{-1}.

HR ESI-MS: $[C_{15}H_{19}O]^+$= $[M+H]^+$ requires 215.1430; found 215.1433.

TLC: R_f =0.4 (Hexane).

2, 7, 8, 12*c*-Tetrahydro-1*H*-benzo[6,7]indeno[1,2,3-*de*]chromene (4l)



Propargylic alcohol **1l** (30 mg, 0.107 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.021 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 14 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding chromene derivative **4l** (21 mg, 0.080 mmol, 75%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.56 (1H, d, *J* = 7.4Hz), 7.24-7.23 (2H, m), 7.18-7.16 (1H, m), 7.10-7.08 (2H, m), 6.80-6.79 (1H, d, *J* = 6.9Hz), 4.47-4.16 (2H, m), 3.60 (1H, d, *J* = 13.7Hz),3.26-3.09 (3H, m), 2.64-2.61 (1H, m)and 1.57-1.45 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 151.9, 146.0, 137.0, 136.6, 133.3, 132.6, 129.3, 126.7, 126.3, 126.2, 126.0, 125.9, 115.9, 113.0, 67.1, 50.6, 30.9, 28.4 and 26.6ppm.

IR (neat): 3566, 3055, 2986, 2360, 2306, 1620, 1541, 1485, 1453, 1421, 1265, 1077, 1055, 1036, 1019, 896, 742 and 706 cm^{-1}.

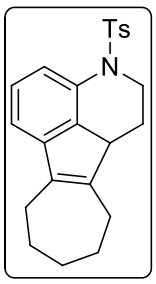
HR ESI-MS: $[C_{19}H_{17}O]^+$= $[M+H]^+$requires 261.1274; found 261.1311.

TLC: R_f=0.4(Hexane).

2B. Synthesis ofcyclopenta[*de*]quimoline frameworks (9a-9i)

Following **the Experimental procedure 2A**, a class of cyclopenta[*de*]quinolineframeworks were synthesised.

3-Tosyl-2,3,7,8,9,10,11,11*b*-0ctahydro-1*H*-azuleno[1,2,3-*de*]quinoline (9a)



Propargylic alcohol **8a** (30 mg, 0.075 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.015 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 1 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9a** (25 mg, 0.065 mmol, 89%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.57-7.52 (3H, m), 7.15 (2H, d, *J* = 8.0Hz), 7.09-7.07 (2H, m), 3.99-3.81 (2H, m), 3.36 (1H, d, *J* = 8.9Hz), 2.51-2.40 (2H, m), 2.34 (3H, s), 2.29-2.25 (3H, m), 1.87-180(1H, m), 1.70-1.52(3H, m) and 1.36-1.19 (3H, m) ppm.

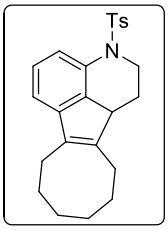
^{13}C NMR (100 MHz, $CDCl_3$):δ = 146.7, 146.2, 143.5, 137.3, 135.9, 130.8, 129.6, 127.3, 127.1, 124.7, 120.0, 119.0, 53.9, 46.8, 31.8, 31.1, 29.8, 28.3, 27.5, 22.1 and 21.6 ppm.

IR (neat): 2926, 2853, 1653, 1597, 1457, 1263, 1216, 1164, 1123, 1093, 1035, 1012, 815, 770 and 751 cm^{-1}

HR ESI-MS: $[C_{23}H_{25}KNO_2S]^+$= $[M+K]^+$requires 418.1238; found 418.1255.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

3-Tosyl-2,3,7,8,9,10,11,11*b*-octahydro-1*H*-azuleno[1,2,3-*de*]quinoline (9b)



Propargylic alcohol **8b** (30 mg, 0.072 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.014 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 1 h 10 min. (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9b** (22 mg, 0.055 mmol, 78%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.63-7.58 (1H, m), 7.46-7.43 (2H, m), 7.17-7.08 (4H, m), 4.26-4.17(1H, m), 3.62-3.55 (1H, m), 3.35 (1H, s), 2.53-2.22 (7H, m), 2.08-1.84 (3H, m), 1.74-1.52 (3H, m), 1.41-1.29 (2H, m) and 0.89-0.79 (2H, m) ppm.

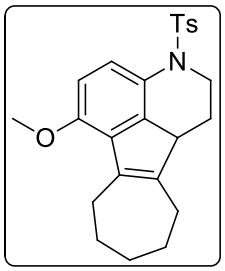
^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.5, 145.4, 143.5, 137.2, 136.9, 129.8, 129.7, 127.1, 126.5, 124.8, 121.0, 119.5, 53.1, 46.9, 29.9, 29.5, 27.2, 26.5, 26.0, 25.3, 24.1 and 21.9 ppm.

IR (neat): 3443, 2929, 2854, 1645, 1467, 1367, 1242, 1123, 1087, 1053, 889 and 737 cm^{-1}.

HR ESI-MS: $[C_{24}H_{28}NO_2S]^+$= $[M+H]^+$requires 394.1835; found 394.1829.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

6-Methoxy-3-tosyl-2,3,7,8,9,10,11,11*b*-octahydro-1*H*-azuleno[1,2,3-*de*]quinoline (9c)



Propargylic alcohol **8c** (29 mg, 0.0654 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.013 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 10 min. (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9c** (22 mg, 0.0537 mmol, 82%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.52 (1H, d, *J* = 8.7Hz), 7.46 (2H, d, *J* = 8.1Hz), 7.13 (2H, d, *J* = 8.7Hz), 6.63 (1H, d, *J* = 8.7Hz), 3.94-3.74 (2H, m), 3.85 (3H, s), 3.47 (1H, d, *J* = 8.2Hz), 2.54-2.36 (2H, m), 2.23 (3H, s), 2.17-2.02 (2H, m), 1.82-1.79 (1H, m) and 1.59 (7H, m) ppm.

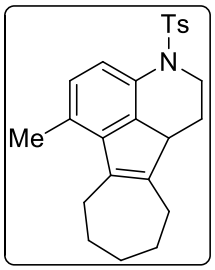
^{13}C NMR (100 MHz, $CDCl_3$):δ=152.9, 147.0, 143.4, 137.9, 137.2, 131.5, 129.6, 127.1, 127.1, 124.5, 122.6, 107.7, 55.5, 52.9, 46.8, 31.1, 29.6, 28.2, 27.3, 21.6 and 21.5 ppm.

IR (neat): 2926, 2852, 2364, 2338, 1598, 1492, 1445, 1350, 1259, 1163, 1087, 1045, 809 and 738 cm^{-1}.

HR ESI-MS: $[C_{24}H_{28}NO_3S]^+$= $[M+H]^+$ requires 410.1784; found 410.1772**.**

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

6-Methyl-3-tosyl-2,3,7,8,9,10,11,11b-octahydro-1H-azuleno[1,2,3-de]quinoline (9d)



Propargylic alcohol **8d** (60 mg, 0.145 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.029 mmol, 3 µL) was added and reaction mixture was stirred at 50 ºC for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9d** (40 mg, 0.101 mmol, 70%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.51 (2H, d, *J* = 8.4Hz), 7.46 (1H, d, *J* = 7.6Hz), 7.14 (2H, d, *J* = 7.6Hz), 6.86 (1H, d, *J* = 8.0Hz), 3.93-3.80 (2H, m), 3.41 (1H, d,*J* = 8.4Hz), 2.50-2.38 (2H, m), 2.34 (7H, s), 2.10 (2H, s), 1.90-1.76 (1H, m), 1.82-1.51 (4H, m) and 1.33-1.10 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.8, 144.1, 143.3, 137.2, 135.7, 129.5, 129.3, 128.7, 127.2, 127.0, 126.5, 120.6, 53.3, 46.6, 30.7, 29.5, 29.3, 28.0, 27.0, 21.7, 21.4 and 18.2 ppm.

IR (neat): 2946, 2855, 2834, 1712, 1450, 1353, 1222, 1092, 977, 813, 783 and 711 cm^{-1}.

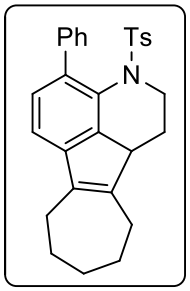
HR ESI-MS: $[C_{24}H_{28}NO_2S]^+$ = $[M+H]^+$requires 394.1835; found 394.1818.

TLC: R_f= 0.4 (9:1, Hex/EtOAc).

4-Phenyl-3-tosyl-2,3,7,8,9,10,11,11*b*-octahydro-1*H*-azuleno[1,2,3-*de*]quinoline (9e)

Propargylic alcohol **8e** (30 mg, 0.063 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.012 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 10 min. (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent

was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9e** (23 mg, 0.060 mmol, 84%) as a pale-yellow gummy liquid.



^{1}H NMR (400 MHz,$CDCl_3$):δ = 7.48 (2H, d, *J*= 6.8Hz), 7.37-7.27 (3H, m), 7.23 (1H, d, *J* = 7.8Hz)), 7.13(3H, d, *J* = 7.8Hz), 7.02 (2H, d, *J* = 7.8Hz), 4.16 (1H, bs), 3.41 (2H, s), 2.56-2.38 (4H, m), 2.32 (3H, s), 1.89-1.60 (6H, m) and 1.40-1.29 (2H, m) ppm.

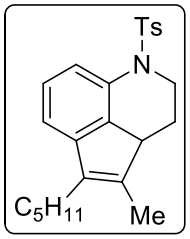
^{13}C NMR (100 MHz, $CDCl_3$*)*:δ =148.0, 145.7, 143.2, 141.1, 139.7, 136.8, 136.8, 129.2, 129.1, 128.2, 127.8, 127.7, 127.6,127.2, 126.5, 120.8, 53.4, 47.1, 31.8, 31.1, 29.8, 28.6, 27.3, 22.0 and 21.5 ppm.

IR (neat): 3356, 2946, 2834, 1656, 1454, 1222, 1146, 1027, 968, 815 and 768 cm^{-1}.

HR ESI-MS: $[C_{29}H_{30}NO_2S]^+$= $[M+H]^+$ requires 456.1992; found 456.1995.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

5-Methyl-4-pentyl-1-tosyl-1,2,3,3*a*-tetrahydrocyclopenta[*de*]quinoline (9f)



Propargylic alcohol **8f** (60 mg, 0.145 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.029 mmol, 3 µL) was added and reaction mixture was stirred at 50 ºC for 1 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9f** (49 mg, 0.123 mmol, 85%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.59-7.57 (1H, m), 7.50 (2H, d, *J*= 8.3Hz), 7.13-7.07 (4H, m), 4.05-3.99 (1H, m), 3.80-3.73 (1H, m), 3.26 (1H, s), 2.33 (3H, s), 2.28-2.15 (2H, m), 2.04-1.83 (2H, m), 1.79 (3H, s), 1.65-1.56 (2H, m) and 0.96-0.81 (7H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.9, 143.4, 139.1, 137.3, 136.6, 130.9, 129.6, 128.1, 127.0, 124.6, 120.4, 119.5, 53.1, 46.8, 32.2, 29.8, 24.3, 22.6, 22.0, 21.6, 14.2 and 12.1 ppm.

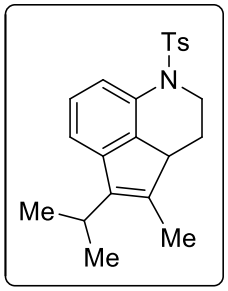
IR (neat): 3056, 2929, 2857, 1597, 1470, 1352, 1266, 1165, 1092, 1041, 897, 809, 740 and 668 cm^{-1}.

HR ESI-MS: $[C_{24}H_{29}NNaO_2S]^+$= $[M+Na]^+$requires 418.1811; found 418.1822.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

4-Isopropyl-5-methyl-1-tosyl-1,2,3,3*a*-tetrahydrocyclopenta[*de*]quinoline (9g)

Propargylic alcohol **8g** (30 mg, 0.077 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen



atmosphere. Then, TfOH (0.015 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 2 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9g** (25 mg, 0.068 mmol, 88%) as pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.58 (1H, d, *J* = 8.7Hz), 7.45 (2H, d, *J* = 8.0Hz), 7.18 (1H, d, *J* = 7.0Hz), 7.10-7.05 (3H, m), 4.12-4.06 (1H, m), 3.71-3.64 (1H, m), 3.18 (1H, s), 2.34-2.23 (5H, m), 2.16-2.161 (1H, m), 1.78 (3H, s), 1.15 (3H, d, *J* = 6.9Hz) and 0.33 (3H, d, *J* = 6.9Hz) ppm.

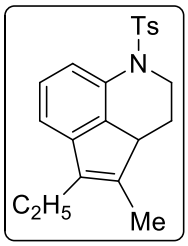
^{13}C NMR (100 MHz, $CDCl_3$):δ = 144.0, 143.3, 138.9, 137.3, 137.2, 130.8, 129.5, 128.6, 127.0, 124.4, 121.0, 120.8, 59.4, 46.8, 28.9, 21.7, 21.5, 21.3, 16.1 and 12.6 ppm.

IR (neat): 3056, 2963, 2856, 2364, 1594, 1463, 1351, 1268, 1164, 1053, 820, 742 and 660 cm^{-1}.

HR ESI-MS: $[C_{22}H_{25}NO_2S]^+$= $[M+H]^+$requires 368.1679; found 368.1680.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

4-Ethyl-5-methyl-1-tosyl-1,2,3,3*a*-tetrahydrocyclopenta[*de*]quinoline (9h)



Propargylic alcohol **8h** (60 mg, 0.161 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.032 mmol, 3 µL) was added and reaction mixture was stirred at 50 ºC for 3 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9h** (47 mg, 0.133 mmol, 83%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.59-7.57 (1H, m), 7.49 (2H, d, *J* = 8.2Hz), 7.12-7.08 (4H, m), 4.05-3.99 (1H, m), 3.80-3.73 (1H, m), 3.26 (1H, s), 2.32 (3H, s), 2.27-2.16 (2H, m), 2.05-1.92 (1H, m),1.78 (3H,m), 1.75-1.65 (1H, m) and 0.44 (3H, t, *J* = 7.3Hz) ppm.

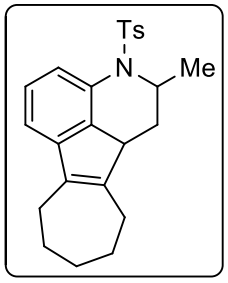
^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.5, 143.4, 138.7, 137.2, 136.8, 130.9, 129.6, 128.4, 127.0, 124.7, 120.5, 119.5, 53.9, 49.9, 22.4, 21.9, 21.6, 12.0 and 8.5 ppm.

IR (neat): 2961, 2929, 2855, 2360, 2340, 1712, 1598, 1552, 1527, 1470, 1353, 1223, 1164, 1092, 1041, 977, 816, 783 and 711 cm^{-1}.

HR ESI-MS: $[C_{21}H_{24}NO_2S]^+$= $[M+H]^+$requires 354.1522; found 354.1514.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

2-Methyl-3-tosyl-2,3,7,8,9,10,11,11*b*-octahydro-1*H*-azuleno[1,2,3-*de*]quinoline (9i)



Propargylic alcohol **8i** (30 mg, 0.073 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.014 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 5 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with ethyl acetate/n-hexane (10: 90 v/v) gave the corresponding quinoline derivative **9i** (20 mg, 0.032 mmol, 83%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.60-7.58 (1H, m), 7.52 (2H, d, *J*= 8.2Hz), 7.16-7.07 (4H, m), 4.76-4.69 (1H, m), 3.40-3.38 (1H, m), 2.53-2.36 (2H, m), 2.34 (3H, s), 2.31-2.17 (3H, m), 2.08-1.95 (2H, m), 1.86-1.74 (2H,m),1.67-1.60 (3H, m) and 1.07 (3H, d, *J* = 6.7Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ =148.0, 146.4, 143.4, 137.3, 129.7, 128.1, 127.1, 127.1, 125.8, 125.0, 121.6, 118.9, 54.0, 51.6, 32.1, 31.0, 29.7, 28.1, 27.9, 27.3, 21.6 and 20.1 ppm.

IR (neat): 3443, 2929, 2854, 1645, 1467, 1367, 1242, 1123, 1087, 1053, 889 and 737 cm^{-1}.

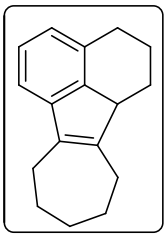
HR ESI-MS: $[C_{24}H_{28}NO_2S]^+$= $[M+H]^+$ requires 394.1835; found 394.1829.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

2C.Synthesis ofacenaphthylene frameworks (11a-11g)

Following **the Experimental procedure 2A**, a class of acenaphthylene frameworks were synthesised.

2, 3, 7, 8, 9, 10, 11,11*b*-Octahydro-1*H*-cyclohepta[*a*]acenaphthylene (11a)



Propargylic alcohol **10a** (60 mg, 0.247 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.049 mmol, 4 µL) was added and reaction mixture was stirred at rt for 20 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11a** (54 mg, 0.24 mmol, 97%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.18 (1H, d, *J* = 7.0Hz), 7.08-7.00 (2H, m), 3.41 (1H, d, *J* = 10.2Hz), 2.79 (2H, t, *J* = 5.8Hz), 2.69-2.34 (5H, m), 1.97-1.83 (5H, m), 1.70-1.61 (2H, m), 1.45-1.36(1H, m) and 1.34-1.24 (1H, m) ppm.

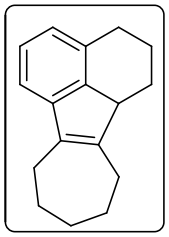
^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.9, 144.4, 142.9, 132.0, 131.0, 124.7, 123.7, 119.9, 53.6, 32.4, 31.3, 30.6, 28.6, 27.6, 27.4, 23.6 and 23.2 ppm.

IR (neat): 3047, 2925, 2852, 1703, 1600, 1451, 1266, 1093, 1047 and 766 cm^{-1}.

HR ESI-MS: $[C_{17}H_{21}]^+$= $[M+H]^+$ requires 225.1638; found 225.1625.

TLC: R_f= 0.4 (Hexane).

1,2,3,7,8,9,10,10*b*-Octahydrofluoranthene (11b)



Propargylic alcohol **10b** (30 mg, 0.131 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.025 mmol, 2 µL) was added and reaction mixture was stirred at rt for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11b** (27 mg, 0.123 mmol, 94%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.21 (1H, d, *J* = 6.5Hz), 7.07-7.02 (2H, m), 3.10-3.07 (1H, m), 2.81-2.77 (2H, m), 2.59 (2H, s), 2.51 (1H, d, *J* = 12Hz), 2.23 (1H, t, *J* = 12.1Hz), 2.00-1.95 (3H, m), 1.90-1.87 (1H, m), 1.58-1.50 (2H, m), 1.26-1.18(1H, m) and 1.00-0.92 (1H, m)ppm.

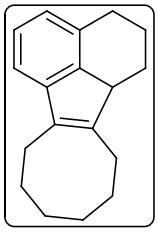
^{13}C NMR (100 MHz, $CDCl_3$):δ =145.6, 143.5, 141.5, 131.6, 128.8, 124.8, 123.7, 119.9, 50.5, 32.3, 27.7, 27.6, 26.4, 25.9, 23.7and 22.9 ppm.

IR (neat):2928, 2852, 2361, 2336, 1692, 1646, 1562, 1550, 1538, 1514, 1451, 1265, 1056, 760 and 740 cm^{-1}.

HR ESI-MS: $[C_{16}H_{19}]^+$= $[M+H]^+$ requires 211.1481; found 211.1477.

TLC: R_f= 0.4 (Hexane).

1,2,3,6*b*,7,8,9,10,11,12,12*a*,12*b*-Odecahydrocycloocta[*a*]acenaphthylene (11c)



Propargylic alcohol **10c** (49 mg, 0.183 mmol) was dissolved in 1,2-dichloroethane (6 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.035 mmol, 3 µL) was added and reaction mixture was stirred at rt for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11c** (42 mg, 0.176 mmol, 97%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.15 (1H, d, *J* = 6.8Hz), 7.06-6.99 (2H, m), 3.37 (1H, s), 2.78-2.73 (3H, m), 2.62-2.47 (2H, m), 2.38-2.36 (2H, m), 2.01-1.97 (2H, m), 1.89-1.80(2H,m), 1.69-1.58 (1H, m), 1.53-1.42 (4H, m) and 1.27-1.20 (2H, m) ppm.

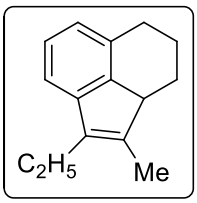
^{13}C NMR (100 MHz, $CDCl_3$):δ =144.9, 143.5, 133.0, 131.3, 124.8, 123.8, 120.0, 52.8, 29.6, 27.6, 27.1, 26.7, 26.2, 25.5, 24.7, 23.7and 23.6 ppm.

IR (neat): 2930, 2854, 2374, 1682, 1602, 1518, 1404, 1201, 1135, 1044, 845, 802 and 723 cm^{-1}.

HR ESI-MS: $[C_{18}H_{23}]^+$= $[M+H]^+$ requires 239.1794; found 239.1789.

TLC: R_f= 0.4 (Hexane).

2-Ethyl-1-methyl2*a*,3,4,5-tetrahydroacenaphthylene (11d)



Propargylic alcohol **10d** (30 mg, 0.130 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.026 mmol, 2 µL) was added and reaction mixture was stirred at rt for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11d** (24 mg, 0.121 mmol, 93%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$)*:*δ = 7.26-7.21 (1H, d,*J* = 6.9Hz), 7.03-6.96 (2H, m), 3.24 (1H, s), 2.76-2.74 (2H, m), 2.54-2.51 (2H, m), 1.92-1.88 (1H, m), 1.71-1.69 (3H, m), 0.91-0.87 (1H, m), 0.86-0.87(2H, m) and 0.69 (3H, t, *J* = 8.0Hz) ppm.

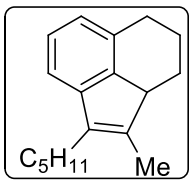
^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.5, 143.6, 137.6, 132.9, 131.3, 124.8, 123.7, 120.6, 53.8, 29.8, 27.6, 23.7, 23.3, 22.8, 12.1 and 9.6 ppm.

IR (neat): 3418, 2928, 2856, 1712, 1681, 1595, 1461, 1373, 1266, 768 cm^{-1}.

HR ESI-MS: $[C_{15}H_{19}]^+$= $[M+H]^+$requires 199.1481; found 199.1478.

TLC: R_f= 0.4 (Hexane).

2-Methyl-2-pentyl-2*a*,3,4,5-tetrahydroaceaphthylene (11e)



Propargylic alcohol **10e** (30 mg, 0.116 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.022 mmol, 2 µL) was added and reaction mixture was stirred at rt for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11e** (27 mg, 0.112 mmol, 97%) as a pale-yellow gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.18(1H, d, *J*= 6.9Hz), 7.03-6.97 (2H, m), 3.26 (1H, s), 2.81-2.72 (2H, m), 2.55-2.53 (2H, m), 2.01-1.86 (7H, m), 1.63-1.55 (2H, m), 1.41-1.32 (2H, m) and 0.94-0.84 (5H, m) ppm.

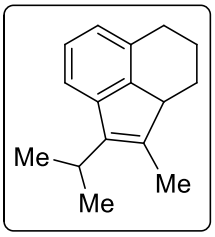
^{13}C NMR (100 MHz,$CDCl_3$):δ=145.5, 143.6, 137.6, 132.9, 131.3, 124.8, 123.7, 120.6, 53.0, 32.5, 30.2, 27.7, 25.4, 23.8, 22.7, 14.3 and 12.2 ppm.

IR (neat): 2928, 2853, 1682, 1601, 1519, 1467, 1403, 1201, 1135, 1045 and 465 cm^{-1}.

HR ESI-MS: $[C_{18}H_{25}]^+$= $[M+H]^+$ requires 241.1951; found, 241.1942.

TLC: R_f= 0.4 (Hexane).

2-Isopropyl-1-methyl-2*a*,3,4,5-tetrahydroacenaphthylene (11f)



Propargylic alcohol **10f** (70 mg, 0.323 mmol) was dissolved in 1,2-dichloroethane (8 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.064 mmol, 5 µL) was added and reaction mixture was stirred at rt for 10 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11f** (63 mg, 0.296 mmol, 92%) as a pale-yellow oil.

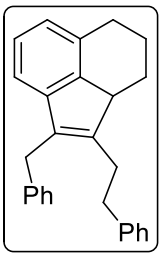
^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.23-7.20(1H, m), 7.01-6.95 (2H, m), 3.20 (1H, s), 2.81-2.69 (2H, m), 2.54-2.51 (2H, m), 2.38-2.29 (1H, m), 1.97-1.81 (5H, m), 1.21 (3H, d, *J* = 7.0Hz) and 0.50 (3H, d, *J* = 6.8Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 144.2, 143.4, 136.8, 133.7, 131.1, 124.9, 123.5, 121.6, 59.3, 28.9, 27.8, 23.8, 23.4, 21.7, 16.6 and 12.7 ppm.

IR (neat):3055, 2962, 2932, 2857, 2366, 1713, 1595, 1459, 1266, 1041, 898 and 740 cm^{-1}.

TLC: R_f= 0.4 (Hexane).

1-Benzyl-2-phenethyl-2a,3,4,5-tetrahydroacenaphthylene (11g)



Propargylic alcohol **10g** (60 mg, 0.160 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.031 mmol, 3 µL) was added and reaction mixture was stirred at rt for 20 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding acenaphthylene derivative **11g** (52 mg, 0.148 mmol, 93%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31-7.12 (10H, m), 6.96-6.94 (1H, d, *J* = 7.2Hz), 6.865 (1H, t, *J* = 7.2Hz), 6.52 (1H, d, *J* = 7.2Hz), 3.63 (1H, s), 3.28-3.23 (1H, q), 2.87-2.71 (4H, m), 2.64-2.27 (5H, m) and 1.84-1.79 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 144.8, 142.7, 142.1, 140.8, 140.6, 134.2, 131.7, 129.4, 128.5, 128.4, 128.3, 126.2, 126.0, 125.0, 123.8, 121.3, 51.9, 37.2, 36.3, 29.0, 27.5, 23.6 and 23.3 ppm.

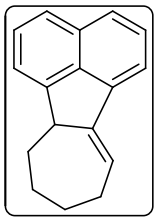
IR (neat): 2952, 2857, 2765, 2366, 1613, 1595, 1439, 1375, 1301, 1266, 1041, 956, 856, and 710 cm^{-1}.

HR ESI-MS: $[C_{27}H_{26}K]^+$= $[M+K]^+$ requires 389.1666; found 389.1968.

TLC: R_f= 0.4 (Hexane).

2D. Procedure for the aromatization of acenaphthylene framework 11a to

7, 8, 9, 10, Tetrahydro-6*bH*-cyclohepta[*a*]acenaphthylene (12a).



The compound **11a** (60 mg, 0.245 mmol) and DDQ (168 mg, 0.737 mmol) in 1,2- dichloroethane (7 mL) were stirred for 2 h at 55 ºC. The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with n-hexane delivered the oxidized product **12a** (47 mg, 0.213 mmol, 87%) as a white-solid.

^{1}H NMR (400 MHz, $CDCl_3$*):*δ = 7.59 (2H, d, *J* = 7.8Hz), 7.48-7.43 (3H, m), 7.24-7.22 ((1H, d, *J* = 7.4Hz), 6.74-6.70 (1H, m), 4.11 (1H, d, *J* = 11.7Hz), 2.52-2.45 (1H, m), 2.39-2.21 (3H, m), 1.96-1.80 (2H, m) and 1.50-1.37 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 147.8, 146.7, 141.4, 138.7, 131.5, 128.2, 128.0, 124.0, 123.3, 122.6, 117.9, 114.5 49.7, 34.2, 32.4, 29.4 and 28.5 ppm.

IR (neat): 2924, 2850, 2360, 2335, 1587, 1463, 1267, 1180, 1125, 1031, 756, 680 and 680 cm^{-1}.

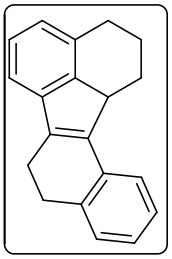
HR ESI-MS: $[C_{17}H_{16}]^+ = [M+H]^+$ requires 221.1325; found 221.0960.

TLC: R_f= 0.4 (Hexane).

M.P.: 70-75 °C

2E.Synthesis for pentacyclic frameworks: daldinone A andhypoxylonol A (13 & 14).

4 5,6,6a,11,12-Hexahydrobenzo[*f*]fluoranthene (13)



Propargylic alcohol **15** (60 mg, 0.217 mmol) was dissolved in 1,2-dichloroethane (7 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.043 mmol, 4 µL) was added and reaction mixture was stirred at 50 ºC for 1 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding pentacyclic acenaphthylene derivative **13** (35 mg, 0.135 mmol, 63%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.63 (1H, d, *J* = 7.7Hz), 7.30 (1H, d, *J* = 7.2Hz), 7.25-7.22 (2H, m), 7.17-7.10 (2H, m), 7.06 (1H, d, *J* = 7.4Hz), 3.52 (1H, d, *J* = 13.5Hz), 3.19-3.02 (3H, m), 2.93-2.77 (3H, m), 2.64-2.59 (1H, m), 2.17-2.11 (1H, m) 1.89-1.80 (1H, m) and 1.49-1.40 (1H, m) ppm.

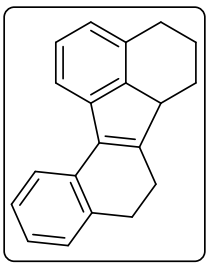
^{13}C NMR (100 MHz,$CDCl_3$):δ = 145.0, 143.8, 137.7, 137.1, 133.8, 133.1, 132.8, 129.3, 126.6, 126.5, 126.1, 125.3, 124.9, 120.4, 49.7, 31.0, 28.7, 27.5, 25.7and 23.9 ppm.

IR (neat):3342, 2926, 2851, 1592, 1455, 1120, 1035, 911, 745, 698, 533 and 490 cm^{-1}.

HR ESI-MS: $[C_{20}H_{19}]^+ = [M+H]^+$ requires 259.1481; found; 259.1489.

TLC: R_f= 0.4 (Hexane).

1,2,3,11,12,12b-Hexahydrobenzo[j]fluoranthene (14)



Propargylic alcohol **16** (30 mg, 0.108 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.021 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 0.5 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding pentacyclic acenaphthylene derivative **14** (24 mg, 0.092 mmol, 83%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.52 (1H, d, *J* = 7.2Hz), 7.47 (1H, d, *J* = 6.0Hz), 7.16-7.04 (4H, m), 6.98 (1H, d, *J* = 7.2Hz), 4.35 (1H, s), 3.00-2.87 (2H, m), 2.80-2.64 (3H, m), 2.59-2.38 (3H, m) and1.94-1.72 (2H, m)ppm.

^{13}C NMR (100 MHz,$CDCl_3$):δ = 144.4, 141.4, 138.7, 138.6, 136.6, 132.0, 130.5, 127.8, 126.2, 126.2, 125.4, 125.0, 123.7, 122.7, 52.6, 30.8, 27.5, 23.4, 23.4and 23.2 ppm.

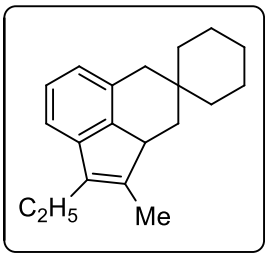
IR (neat): 3346, 2923, 2840, 1560, 1450, 1100, 1030, 907, 740, 698, 560 and 499 cm^{-1}.

HR ESI-MS: $[C_{20}H_{19}]^+ = [M+H]^+$ requires 259.1481; found. 259.1489.

TLC: R_f= 0.4 (Hexane).

2F. Synthesis for the spiro-pentacyclic core of Incarviatone A (17a-17c).

5'-Ethyl-4'-methyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[*de*]chromene] (17a)



Propargylic alcohol **18a** (35 mg, 0.123 mmol) was dissolved in 1,2-dichloroethane (3.5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.021 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 0.5 h (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding spirocyclic acenaphthylene derivative **17a** (27 mg, 0.101 mmol, 81%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.17 (1H, d, *J* = 7.2Hz), 7.06-6.97 (2H, m), 3.32 (1H, s), 2.72-2.66 (2H, m), 2.40-2.39 (2H, s), 2.07-1.98 (1H, m), 1.95 (3H, s), 1.77-1.72 (1H, m), 1.35-1.33 (5H, m), 1.31-1.29 (5H, m) and 0.63 (3H, t, *J* = 7.2Hz) ppm.

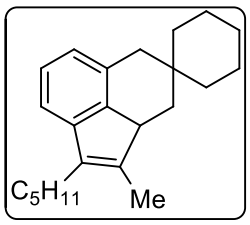
^{13}C NMR (100 MHz, $CDCl_3$):δ = 144.3, 143.7, 138.2, 132.6, 128.2, 125.3, 123.8, 120.2, 54.1, 37.0, 36.3, 34.8, 29.8, 26.7, 22.7, 22.0, 12.0 and 9.2 ppm.

IR (neat): 3029**,** 2927, 2851, 2345, 1496, 1450, 1288, 1245, 1133, 933, 780 and 738 cm^{-1}.

HR ESI-MS: $[C_{20}H_{27}]^+ = [M+H]^+$ requires 267.2107; found. 267.2108.

TLC: R_f = 0.2 (Hexane).

2-Methyl-1-pentyl-3,5-dihydro-2*a*H-spiro[acenaphthylene-4,1'-cyclohexane] (17b)



Propargylic alcohol **18b** (20 mg, 0.0613 mmol) was dissolved in 1,2-dichloroethane (2 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.01 mmol, 1 µL) was added and reaction mixture was stirred at 50 ºC for 25 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding spirocyclic acenaphthylene derivative **17b** (18 mg, 0.0510 mmol, 94%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.19 (1H, d, *J* = 7.2Hz), 7.05-6.97 (2H, m), 3.32 (1H, s), 2.71-2.62 (2H, m), 2.43-2.351 (2H, m), 1.95 (3H, s), 1.70-1.57 (2H, m), 1.53-1.40 (5H, m), 1.33-1.17 (11H, m) and 0.93-0.84 (4H, m) ppm.

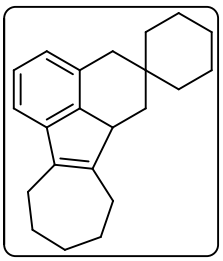
^{13}C NMR (100 MHz, $CDCl_3$):δ = 146.1, 144.9, 143.5, 138.9, 138.7, 132.3, 129.2, 125.3, 123.8, 120.3, 53.3, 39.1, 36.9, 36.5, 34.7, 32.3, 30.0, 26.7, 25.0, 22.6, 22.0, 14.1 and 12.1 ppm.

IR (neat): 2957, 2925, 2853, 2361, 1731, 1465, 1290, 1243, 780, 759 and 734 cm^{-1}.

HR ESI-MS: $[C_{23}H_{36}N]^+ = [M+NH_4]^+$ requires 326.2842; found. 326.2834.

TLC: R_f = 0.2 (Hexane).

1,3,7,8,9,10,11,11b-Octahydrospiro[cyclohepta[a]acenaphthylene-2,1'-cyclohexane] (17c)



Propargylic alcohol **18c** (45 mg, 0.145 mmol) was dissolved in 1,2-dichloroethane (5 mL), and the resulting solution was stirred at room temperature under a positive nitrogen atmosphere. Then, TfOH (0.029 mmol, 2 µL) was added and reaction mixture was stirred at 50 ºC for 20 min (the reaction was monitored by TLC analysis). The reaction was quenched with saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried ($MgSO_4$) and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash column chromatography. Elution with n-hexane gave the corresponding spirocyclic acenaphthylene derivative **17c** (38 mg, 0.310 mmol, 89%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.13 (1H, d, *J* = 6.8Hz), 7.05-7.01 (1H, t, *J* = 7.2Hz), 6.96 (1H, d, *J* = 7.2Hz), 3.42 (1H, s), 2.73-2.53 (4H, m), 2.37-2.29 (3H, m), 1.89-1.64 (4H, m), 1.64-1.56 (1H, m), 1.4-1.35 (6H, m) and 1.36-1.28 (6H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 145.8, 145.4, 142.9, 131.5, 129.1, 125.3, 123.9, 119.8, 53.9, 39.2, 36.9, 36.7, 34.9, 32.2, 31.4, 30.0, 28.4, 28.0, 26.8 and 22.0 ppm.

IR (neat): 3028, 2927, 2853, 2324, 2145, 1496, 1448, 1085, 1023, 911, 770, 755 and 715 cm^{-1}.

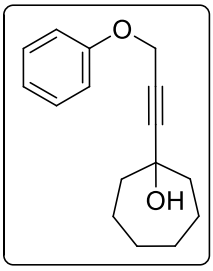
HR ESI-MS: $[C_{22}H_{29}]^+ = [M+H]^+$ requires 293.2264; found. 293.2283.

TLC: R_f = 0.2 (Hexane).

3. Experimental procedures for all starting materials:

3A. Synthesis of O-linked propargylic alcohols (1a-1l)

1-(3-Phenoxyprop-1-yn-1-yl)cycloheptanol(1a)



To a stirred and 0 ºC cooled solution of the ether derivative (200 mg, 1.514 mmol) in anhydrous THF (5 mL) was added n- BuLi (1.2 mL, 1.968 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (220 mg, 1.968 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1a** (250 mg, 1.023 mmol, 68%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31-7.27 (2H, m), 6.99-6.96 (3H,m), 4.73 (2H, s), 2.01-1.95 (3H, m), 1.83-1.77 (2H, m) and 1.67-1.49 (7H, m) ppm.

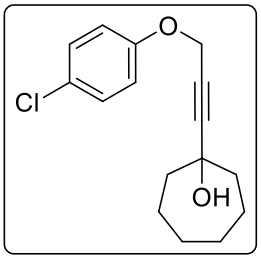
^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.5, 129.2, 121.2, 114.9, 91.9, 78.1, 71.6, 56.0, 42.7, 27.8 and 21.9 ppm.

IR (neat): 3442, 2931, 2760, 2356, 2306, 1634, 1429, 1266, 1023, 897 and 742 cm^{-1}.

HR ESI-MS: $[C_{16}H_{24}NO_2]^+ = [M+NH_4]^+$ requires 262.1802; found 262.1799.

TLC:R_f = 0.4 (9:1, Hexane/EtOAc).

1-(3-(4-Chlorophenoxy)prop-1-yn-1-yl)cycloheptanol(1b)



To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.602 mmol) in anhydrous THF (5 mL) was added n- BuLi (0.5 mL, 0.783 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (87 mg, 0.783 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1b** (113 mg, 0.406 mmol, 67%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.25-7.22 (2H, m), 6.92-6.88 (2H, m), 4.71 (2H, s), 1.99-1.94 (2H, m), 1.83-1.77 (2H, m) and 1.65-1.45 (8H, m) ppm.

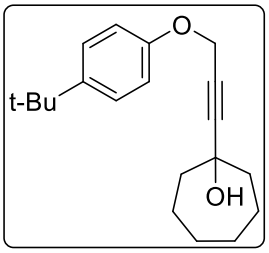
^{13}C NMR (100 MHz, $CDCl_3$):δ = 156.4, 129.4, 126.5, 116.6, 92.7, 78.0, 72.0, 56.7, 43.0, 28.1 and 22.2 ppm.

IR (neat): 3400, 2928, 2856, 2367, 1589, 1491, 1372, 1285, 1222, 1096, 1022, 824 and 745 cm^{-1}.

HR ESI-MS: $[C_{16}H_{19}ClNaO_2]^+ = [M+Na]^+$ requires 301.0966; found 301.0945.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(3-(4-(*tert*-Butyl)phenoxy)prop-1-yn-1-yl)cycloheptanol (1c)



To a stirred and 0 ºC cooled solution of the ether derivative (150 mg, 0.797 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.7 mL, 1.036 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (116 mg, 1.036 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^v/_v$) delivered the corresponding propargylic alcohol **1c** (180 mg, 0.599 mmol, 75%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (2H, d, *J* = 8.6Hz), 6.90 (2H, d *J* = 8.6Hz), 4.70 (2H, s), 2.01-1.95 (3H, m), 1.83-1.77 (2H, m), 1.63-1.48 (7H, m) and 1.29 (9H, s) ppm.

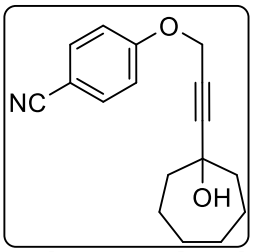
^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 144.3, 126.3, 114.8, 92.1, 78.8, 72.0, 56.6, 43.1, 34.3, 31.7, 28.1 and 22.3 ppm.

IR (neat): 3110, 2993, 2914, 1709, 1623, 1582, 1486, 1375, 1308, 1278, 1227, 1167, 1068, 1044, 959, 905, 832, 788, 707 and 619 cm^{-1}.

HR ESI-MS: $[C_{20}H_{32}O_2]^+ = [M+NH_4]^+$ require 318.2428; found 318.2436.

TLC: R_f= 0.4 (9:1, Hex/EtOAc).

4-(3-(1-Hydroxycycloheptyl)prop-2-yn-1-yl)oxy)benzonitrile (1d)



To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.636 mmol) in anhydrous THF (5 mL) was added n- BuLi (0.5 mL, 0.827 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (93 mg, 0.827 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^v/_v$) delivered the corresponding propargylic alcohol **1d** (120 mg, 0.445 mmol, 71%) as a pale-yellow oil.

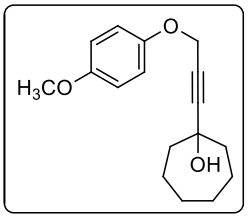
^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.59 (2H, d, *J* = 8.4Hz), 7.043 (2H, d, *J* = 8.7Hz), 4.79 (2H, s), 2.36 (1H, bs), 2.04-1.09 (2H, m), 1.83-1.77 (2H, m) and 1.60-1.42 (8H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 160.9, 134.0, 119.1, 115.8, 104.6, 93.4, 76.9, 71.8, 56.5, 42.8, 28.0 and 22.1 ppm.

IR (neat): 3442, 2935, 1602, 1511, 1459, 1349, 1290, 1247, 1162, 1035, 777 and 593 cm^{-1}.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(3-(4-Methoxyphenoxy)prop-1yn-1-yl)cycloheptanol (1e)



To a stirred and 0 ºC cooled solution of the ether derivative (200 mg, 1.234 mmol) in anhydrous THF (5 mL), was added n-BuLi (1 mL, 1.604 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (180 mg, 1.604 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1e** (210 mg, 0.765 mmol, 62%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 6.94-6.89 (2H, m), 6.85-6.81 (2H, m), 4.67 (2H, s), 3.77 (3H, s), 2.00-1.95 (3H, m), 1.83-1.77 (2H, m), 1.64-1.58 (2H, m), 1.56-1.53 (4H, m) and 1.49-1.44(2H, m) ppm.

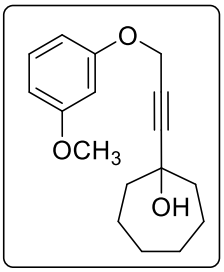
^{13}C NMR (100 MHz, $CDCl_3$):δ = 154.5, 152.0, 116.5, 114.7, 92.2, 78.7, 71.9, 57.3, 55.9, 43.0, 28.1 and 22.2 ppm.

IR (neat): 3110, 2993, 2914, 1709, 1623, 1582, 1486, 1375, 1308, 1278, 1227, 1167, 1068, 1044, 959, 905, 832, 788 and 619 cm^{-1}.

HR ESI-MS: $[C_{17}H_{26}O_3N]^+ = [M+NH_4]^+$ require 292.1913; found 292.1916.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(3-(4-Methoxyphenoxy)prop-1-yl)cycloheptanol (1f)



To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.617 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.5 mL, 0.802 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (90 mg, 0.802 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl

acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1f** (80 mg, 0.291 mmol, 47%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.20-7.16 (1H, m), 6.58-6.53 (3H, m), 4.70 (2H, s), 3.78 (3H, s), 2.01-1.96 (2H, m), 1.84-1.75 (2H, m), 1.65-1.56 (4H, m) and 1.54-1.45(4H, m) ppm.

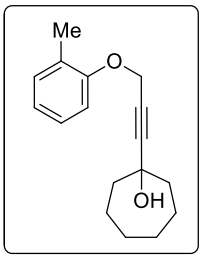
^{13}C NMR (100 MHz, $CDCl_3$):δ = 160.9, 159.1, 130.0, 107.2, 107.2, 101.7, 92.3, 78.4, 71.9, 56.4, 55.4, 43.0, 28.1 and 22.2 ppm.

IR (neat): 3133, 2929, 2914, 1708, 1620, 1580, 1485, 1380, 1338, 1268, 1220, 1170, 1060, 1044, 959, 905, 780 and 619 cm^{-1}.

HR ESI-MS: $[C_{17}H_{26}O_3N]^+ = [M+NH_4]^+$ require 292.1907; found 292.1915.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(3-(*o*-(Tolyloxy)prop-yn-1-yl)cycloheptanol (1g)



To a stirred and 0 ºC cooled solution of the ether derivative (150 mg, 1.027 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.8 mL, 1.335 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cycloheptanone (149 mg, 1.335 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1g** (160 mg, 0.619 mmol, 61%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.09-7.07 (2H, d, *J* = 8.3Hz), 6.88-6.85 (2H, m), 4.69 (2H, s), 2.28 (3H, s), 2.01-1.95 (3H m), 1.85-1.77 (3H, m) and 1.65-1.45(6H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 155.8, 130.9, 130.0, 115.2, 92.2, 78.7, 72.0, 56.6, 43.1, 28.1, 22.3 and 20.7ppm.

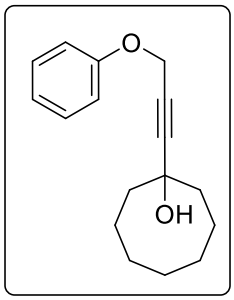
IR (neat): 3140, 2990, 2929, 1709, 1620, 1562, 1466, 1355, 1368, 1270, 1220, 1170, 1068, 960, 830, 780, 775 and 619 cm^{-1}.

HR ESI-MS: $[C_{17}H_{23}O_2]^+ = [M+H]^+$ require 259.1693; found 259.1699.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

1-(3-phenoxyprop-1-yn-1-yl)cyclooctanol(1h)

To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.757 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.984 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the cyclooctanone (124 mg, 0.984 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1h** (115 mg, 0.445 mmol, 59%) as a pale-yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31-7.26 (2H, m), 7.00-6.96 (3H, m), 4.72 (2H, s), 1.97-1.83 (5H, m) and 1.73-1.59 (9H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.8, 129.6, 121.6, 115.2, 92.2, 77.5, 71.6, 56.4, 38.1, 28.0, 24.6 and 22.1 ppm.

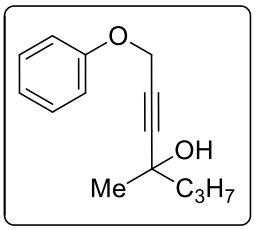
IR (neat):3118, 2901, 2373, 1590, 1499, 1458, 1418, 1268, 1217, 1121, 1034, 926, 755 and 692 cm^{-1}.

HR ESI-MS: $[C_{17}H_{26}NO_2]^+ = [M+NH_4]^+$ requires 276.1958; found 276.1916.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

4-Methyl-1-phenoxyhept-2-yn-ol (1i)

To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.757 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.984 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the pentan-2-one (84 mg, 0.984 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was eaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^{v}/_{v}$) delivered the corresponding propargylic alcohol **1i** (137 mg, 0.628 mmol, 82%) as a pale-yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.27 (2H, m), 6.96-6.95 (3H, m), 4.70 (2H, s), 2.12(1H, *b*s), 1.671-1.55 (2H m), 1.45 (5H, s) and 0.92-0.89 (3H, m)ppm.

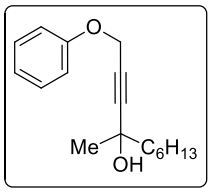
^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.8, 129.6, 121.6, 115.2, 91.4, 78.3, 68.4, 56.3, 45.9, 29.7, 18.1 and 14.3 ppm.

IR (neat): 3134, 2990, 2929, 1790, 1620, 1580, 1480, 1317, 1318, 1278, 1160, 1044, 959, 780 and 699 cm^{-1}.

HR ESI-MS: $[C_{14}H_{22}NO_2]^+ = [M+NH_4]^+$ require 236.1651; found 236.1655.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

(4-Methyl-1-phenoxydec-2-yn-ol (1j)



To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.757 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.984 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the octan-2-one (97 mg, 0.984 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^v/_v$) delivered the corresponding propargylic alcohol **1j** (140 mg, 0.538 mmol, 71%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.26 (2H, m), 6.99-6.95 (3H, m), 4.70 (2H, s), 2.09 (1H, bs), 1.67-1.56 (2H m), 1.41 (1H, s), 1.41-1.37 (2H, m), 1.30-1.25 (6 H, m) and 0.89-0.86 (3H, m) ppm.

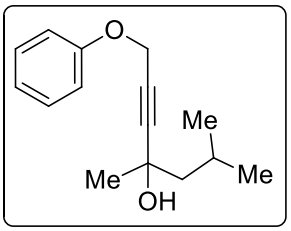
^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.8, 129.6, 121.6, 115.2, 91.4, 78.3, 68.4, 56.3, 43.7, 31.9, 29.7, 29.5, 24.7, 22.7 and 14.3 ppm.

IR (neat): 3110, 2914, 1709, 1623, 1582, 1486, 1375, 1308, 1278, 1227, 1167, 1068, 1044, 959, 905, 832, 788 and 717cm^{-1}.

HR ESI-MS: $[C_{17}H_{25}O_2]^+ = [M+H]^+$require 261.1849; found 261.1822.

TLC:R_f = 0.4 (9:1, Hexane/EtOAc).

4,6-Dimethyl-1-phenoxyhept-2-yn-ol (1k)



To a stirred and 0 ºC cooled solution of the ether derivative (70 mg, 0.530 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.4 mL, 0.689 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the 2-methyl pentan-2-one (68 mg, 0.689 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^v/_v$) delivered the corresponding propargylic alcohol **1k** (90 mg, 0.387 mmol, 73%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.27 (2H, m), 6.96-6.95 (3H, m), 4.70 (2H, s), 2.12 (1H, bs), 1.671-1.55 (2H m), 1.45 (3H, s) and 0.92-0.89 (6H, m) ppm.

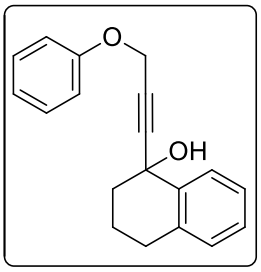
^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.8, 129.6, 121.6, 115.2, 91.4, 78.3, 68.4, 56.3, 45.9, 29.7, 18.1 and 14.3 ppm.

IR (neat): 3412, 2955, 2928, 2869, 1598, 1495, 1371, 1263, 1216, 1173, 1155, 1035, 990, 923, 770 and 691 cm^{-1}.

HR ESI-MS:$[C_{15}H_{21}O_2]^+ = [M+H]^+$ require 233.1536; found 233.1544.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(3-Phenoxyprop-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (1l)



To a stirred and 0 ºC cooled solution of the ether derivative (100 mg, 0.757 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.984 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, the 1-tetralone (143 mg, 0.984 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 $^v/_v$) delivered the corresponding propargylic alcohol **1l** (130 mg, 0.467 mmol, 61%) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.64-7.62 (1H, m), 7.28-7.24(2H, m), 7.22-7.17 (2H, m), 7.07-7.05 (1H, m), 6.98-6.86 (3H, m), 4.70 (2H, s), 2.82-2.69 (2H, m), 2.53(1H, *b*s), 2.16-2.13 (2H, m) and 1.99-1.80 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.8, 138.7, 136.1, 129.6, 129.2, 128.3, 128.0, 126.7, 121.6, 115.3, 91.6, 79.4, 67.9, 56.4, 38.8, 29.2 and 19.1 ppm.

IR (neat): 3436, 2927, 2854, 2356, 1580, 1480, 1266, 1096, 1020, 896, 766, 750 and 700 cm^{-1}.

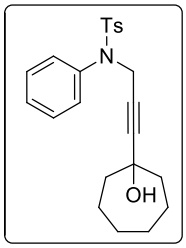
HR ESI-MS: $[C_{19}H_{18}NaO_2]^+ = [M+NH_4]^+$ require 301.1199; found 301.1189.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

3B. Synthesis of N-linkedpropargylic alcohols (8a-8i)

Following **the Experimental procedure 3A**, the precursor alcohols were prepared.

***N*-(3-(1-Hydroxycycloheptyl)prop-2-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (8a)**



To a stirred and -78 ºC cooled solution of 4-methyl-*N*-phenyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (170 mg, 0.596 mmol) in anhydrous THF (5 mL) was added n- BuLi (0.5 mL, 0.775 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, cycloheptanone (87 mg, 0.775 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8a** (150 mg, 0.377 mmol, 63%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.54 (1H, d, *J* = 8.2Hz), 7.34-7.29 (3H, m), 7.24 (2H, d), 7.21-7.19 (2H, m), 4.44 (2H, s), 2.41 (3H, s), 1.98-1.57 (10H, m) and 1.41-1.15 (4H, m)ppm.

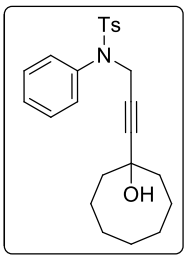
^{13}C NMR (100 MHz, $CDCl_3$):δ = 160.8, 159.0, 130.0, 107.2, 101.7, 92.3, 78.4, 71.9, 56.4, 55.4, 53.6, 43.0, 28.1 and 22.2 ppm.

IR (neat): 3066, 2993, 2914, 1709, 1623, 1582, 1486, 1375, 1308, 1278, 1227, 1068, 1044, 959, 788 and 755cm^{-1}.

HR ESI-MS: $[C_{23}H_{31}N_2O_3S]^+ = [M+NH_4]^+$ require 415.2050; found 415.2057.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

***N*-(3-(1-hydroxycyclooctyl)prop-2-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide(8b)**



To a stirred and -78 ºC cooled solution of propargyl amine derivative (150 mg, 0.526 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.4 mL, 0.684 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, cyclooctanone (86 mg, 0.684 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8b** (120 mg, 0.291 mmol, 55%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.56 (2H, d, *J* = 8.0Hz), 7.32-7.29 (3H, m), 7.28-7.20 (4H, m), 4.46 (2H, s), 2.41 (3H, s), 1.80-1.73 (2H, m), 1.83-1.50 (7H, m) and 1.47-1.33 (5H, m) ppm.

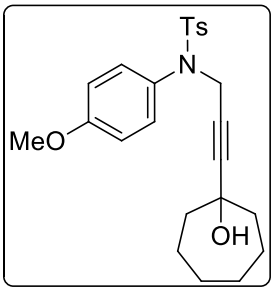
^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.7, 139.4, 135.8, 129.4, 129.0, 128.7, 128.2, 128.1, 90.3, 71.2, 41.3, 37.8, 27.9, 24.3, 21.9 and 21.8 ppm.

IR (neat): 3143, 2926, 2374, 1592, 1500, 1351, 1164, 1092, 859, 811, 758, 696 and 662 cm^{-1}.

HR ESI-MS: $[C_{24}H_{33}N_2O_3S]^+ = [M+NH_4]^+$ requires 429.2206; found 429.2223.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

N-(3-(1-Hydroxycycloheptyl)prop-2-yn-1-yl)-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (8c)



To a stirred and -78 ºC cooled solution of propargyl amine derivative (100 mg, 0.317 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.3 mL, 0.412 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, cyclo-heptanone (46 mg, 0.412 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8c** (80 mg, 0.187 mmol, 59%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.56 (2H, d, *J* = 8.2Hz), 7.25 (2H, d, *J* = 9.1Hz), 7.12-7.08 (2H, m), 6.83-7.6.78 (3H, m), 4.42 (2H, s), 3.79 (3H, s),2.42 (3H, s), 2.09-1.87 (6H, m)and 1.80-1.62 (6H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 159.5, 143.7, 136.0, 131.9, 130.4, 129.5, 128.2, 114.2, 90.5, 77.8, 71.7, 55.6, 42.8, 28.1, 22.0 and 21.7 ppm.

IR (neat): 3442, 2935, 2340, 1602, 1560, 1500, 1459, 1349, 1290, 1247, 1162, 1035, 777 and 593 cm^{-1}.

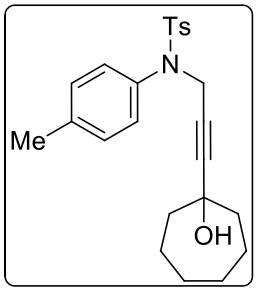
HR ESI-MS: $[C_{24}H_{33}N_2O_4S]^+ = [M+NH_4]^+$ require 445.2156; found 445.2142.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

N-(3-(1-Hydroxycycloheptyl)prop-2-yn-1-yl)-4-methyl-N-(p-tolyl)benzenesulfonamide (8d)

To a stirred and -78 ºC cooled solution of propargyl amine derivative (100 mg, 0.334 mmol) in anhydrous THF (5 mL) was added n-BuLi (0.3 mL, 0.434 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, cycloheptanone (49 mg, 0.434 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred

at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:90 v/v) delivered the alcohol **8d** (120 mg, 0.291 mmol, 87%) as a pale-yellow colored oil.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.57 (2H, d, *J* = 8.0Hz), 7.25 (2H, d, *J* = 8.0Hz), 7.16-7.05 (4H, m), 4.43 (2H, s), 2.41 (3H, s), 2.33 (3H, s), 1.77-1.62 (5H, m), 1.58-1.42 (4H, m) and 1.35-1.19 (3H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.6, 138.3, 136.8, 136.2, 129.7, 129.4, 128.7, 128.2, 90.4, 77.8, 42.8, 41.5, 28.0, 22.0, 21.6 and 21.2 ppm.

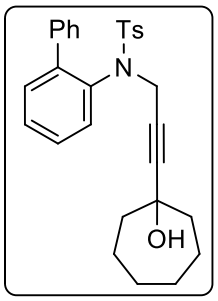
IR (neat): 3448, 2909, 2342, 1665, 1561, 1466, 1290, 1280, 1163, 1040, 786 and 699 cm^{-1}.

HR ESI-MS: $[C_{24}H_{33}N_2O_3S]^+ = [M+NH_4]^+$ requires 429.2206; found 429.2194.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

N-(1-1'-Biphenyl]-2-yl)-*N*-(3-(1-hydroxycycloheptyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (8e)

To a stirred and -78 ºC cooled solution of propargyl amine derivative (200 mg, 0.553 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.5 mL, 0.719 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, cycloheptanone (80 mg, 0.719 mmol)in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8e** (193 mg, 0.468 mmol, 85%) as a pale-yellow colored oil.



^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.64 (2H, d, *J* = 7.6Hz), 7.54 (2H, d, *J* = 6.9Hz), 7.42-7.38 (5H, m), 7.28-7.26 (3H, m), 7.08(1H, d, *J* = 7.8Hz), 4.43 (1H, bs), 3.75 (1H, bs), 2.43 (3H, s),1.78-1.57 (6H, m) and 1.3-1.21 (6H, m) ppm.

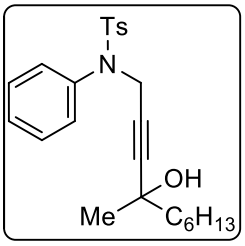
^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.8, 142.7, 139.0, 137.4, 136.7, 131.7, 129.6, 129.4, 129.2, 128.9, 128.4, 128.3, 127.8, 90.9, 71.6, 42.8, 41.2, 29.8, 28.2, 21.9 and 21.7 ppm.

IR (neat): 3621, 2924, 2850, 2374, 1690, 1647, 1584, 1467, 1413, 1266, 1120, 1034, 756 and 542 cm^{-1}.

HR ESI-MS: $[C_{29}H_{35}N_2O_3S]^+ = [M+NH_4]^+$ require 491.2363; found 491.2367.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

***N*-(4-Hydroxy-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (8f)**



To a stirred and -78 ºC cooled solution of propargyl amine derivative (150 mg, 0.526 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.5 mL, 0.684 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, octan-2-one (87 mg, 0.684 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8f** (130 mg, 0.314 mmol, 60%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.55 (2H, d, *J* = 8.1Hz), 7.34-7.29 (3H, m), 7.23 (4H, d), 4.44 (2 H, s), 2.41 (3H, s), 1.41-1.2 (11H, m) and 0.90-0.87 (5H, m) ppm.

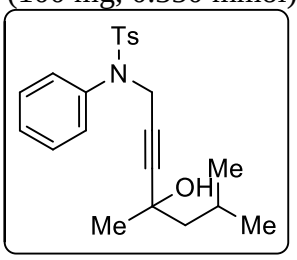
^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.8, 139.5, 136.0, 129.5, 129.1, 128.7, 118.9, 113.8, 89.7, 77.6, 68.1, 53.9, 43.5, 41.4, 31.9, 29.5, 29.5, 24.6, 22.8, 21.7 and 14.3 ppm.

IR (neat): 3435, 2929, 2856, 1598, 1493, 1455, 1353, 1308, 1219, 1164, 1094, 1031, 859, 770 and 726 cm^{-1}.

HR ESI-MS: $[C_{24}H_{35}N_2O_3S]^+ = [M+NH_4]^+$ require 431.2363; found 431.2370.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

***N*-(4-Hydroxy-4,6-dimethylhept-2-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (8g)**



To a stirred and -78 ºC cooled solution of propargyl amine derivative (100 mg, 0.350 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.5 mL, 0.456 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, methyl-isobutyl ketone (46 mg, 0.456 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8g** (90 mg, 0.535 mmol, 67%) as a pale-yellow colored oil.

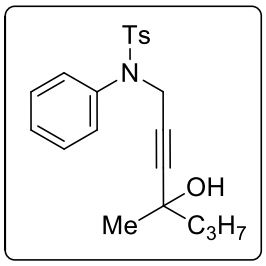
^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.55 (2H, d, *J* = 8.0Hz), 7.31-7.30 (3H, m), 7.25-7.21 (4H, m),4.45 (2H, s), 2.41 (3H, s),1.76 (1H, *b*s), 1.70-1.60 (1H, m), 1.40-1.39 (2H, m), 1.28 (3H, s)and 0.86 (6H, t, *J* = 7.0Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.8, 139.5, 135.9, 129.5, 129.1, 128.7, 128.3, 128.2, 89.9, 77.8, 68.1, 51.4, 41.4, 30.7, 25.1, 24.3, 24.1 and 21.7 ppm.

IR (neat): 3587, 3304, 3055, 2873, 2306, 1454, 1422, 1093, 1052, 1027, 946, 897, 824, 656 and 543cm^{-1}.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

***N*-(4-Hydroxy-4-methylhept-2-yn-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (8h)**



To a stirred and -78 ºC cooled solution of propargyl amine derivative (200 mg, 0.701 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.912 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, 2-pentanone (78 mg, 0.912 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8h** (150 mg, 0.404 mmol, 58%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.54 (2H, d, *J* = 8.2Hz), 7.34-7.29 (3H, m), 7.24 (2H, d), 7.21-7.19 (2H, m), 4.44 (2 H, s), 2.41 (3H, s),1.49-1.36 (2H, m), 1.26 (3H s), 1.23-1.16(2H, m)and 0.84 (3H, m) ppm.

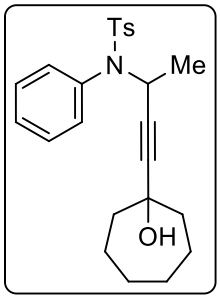
^{13}C NMR (100 MHz, $CDCl_3$):δ = 160.8, 159.0, 130.0, 107.2, 101.7, 92.3, 78.4, 71.9, 56.4, 55.4, 53.6, 43.0, 28.1 and 22.2 ppm.

IR (neat): 3110, 2993, 2914, 1709, 1623, 1582, 1486, 1375, 1308, 1278, 1227, 1167, 1068, 1044, 959, 905, 832, 788, 707 and 619 cm^{-1}.

HR ESI-MS: $[C_{21}H_{26}NO_3S]^+$ = $[M+H]^+$require 372.1628; found 372.1635.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

***N*-(4-(1-Hydroxycycloheptyl)but-3-yn-2-yl)-4-methyl-*N*-phenylbenzenesulfonamide (8i)**



To a stirred and -78 ºC cooled solution of propargyl amine derivative (200 mg, 0.668 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.869 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at -78 ºC for 30 min, cycloheptanone (97 mg, 0.869 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (20:80 v/v) delivered the alcohol **8i** (170 mg, 0.413 mmol, 62%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (2H, d, *J* = 7.8Hz), 7.36-7.29 (3H, m), 7.26-7.22(4H, m), 5.35-5.29 (1H, m,),2.43(3H, s), 1.78-1.64 (7H, m) and 1.28-1.23 (8H, m) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 137.3, 136.0, 131.8, 129.4, 129.0, 128.9, 128.4, 90.0, 82.4, 71.6, 46.9, 42.9, 28.2, 22.2, 22.1, 21.7, 21.2 and 14.4 ppm.

IR (neat): 3621, 2924, 2850, 2374, 1690, 1647, 1584, 1467, 1413, 1266, 1120, 1034 and 756 cm^{-1}.

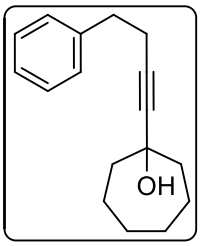
HR ESI-MS: $[C_{24}H_{29}NNaO_3S]^+$ = $[M+Na]^+$ require 434.1760; found 434.1751.

TLC: R_f = 0.4 (8:2, Hexane/EtOAc).

3C. Synthesis for the C-linked propargylic alcohols (10a-10g)

Following **the Experimental procedure 3A**, the carban linkedpropargylic alcohols was prepared.

1-(4-Phenylbut-1-yn-1-yl)cycloheptanol (10a)



To an ice-cold solution of but-3-yn-1-ylbenzene (200 mg, 1.538 mmol) in anhydrous THF (5 mL), was added n-BuLi (1.3 mL, 1.999 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, cycloheptanone (224 mg, 1.999 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10a** (290 mg, 1.196 mmol, 79%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.26 (2H, m), 7.21-7.19 (3H, m), 2.80 (2H, t, *J* = 7.3 Hz), 2.50 (2H, t, *J* = 7.3Hz), 2.02 (1H, bs), 1.97-1.90 (2H, m), 1.79-1.73 (2H, m) and 1.65-1.47 (8H, m) ppm.

^{13}C NMR (100 MHz, CDCl3): δ = 141.1, 128.9, 128.7, 126.7, 86.4, 83.4, 72.3, 43.7, 35.6, 28.4, 22.6 and 21.3 ppm.

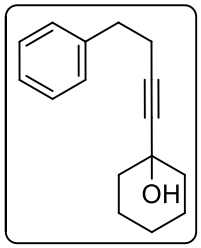
IR (neat): 3432, 2930, 2855, 1695, 1599, 1453, 1338, 1200, 1024, 911, 746 and 699 cm^{-1}.

HR ESI-MS: $[C_{17}H_{26}NO]^+$ = $[M+NH_4]^+$ requires 260.2009; found 260.2039.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(4-Phenylbut-1-yn-1-yl)cyclohexanol (10b)

To an ice-cold solution of but-3-yn-1-ylbenzene (100 mg, 0.769 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.7 mL, 1 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, cyclohexanone (98 mg, 1 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2



h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10b** (140 mg, 0.613 mmol, 79%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.25 (2H, m), 7.22-7.18(3H, m), 2.83-2.79 (2H, t, *J* = 7.4Hz), 2.51-2.48 (2H, t, *J* = 7.4Hz), 1.93-1.78 (5H, m), 1.46-1.41 (4H, m) and 0.93-0.83 (1H, m) ppm.

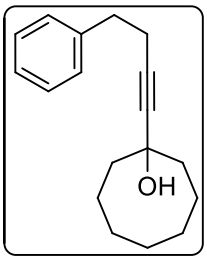
^{13}C NMR (125 MHz, $CDCl_3$):δ = 140.9, 128.7, 128.5, 126.4, 86.0, 83.0, 71.7, 38.7, 35.4, 28.1, 24.7, 22.3 and 21.0 ppm.

IR (neat): 3436, 2993, 2855, 1646, 1451, 1264, 1061, 959, 754, 698and 437 cm^{-1}.

HR ESI-MS: $[C_{16}H_{24}NO]^+ = [M+NH_4]^+$ requires 246.1852; found 246.1853.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(4-Phenylbut-1-yn-1-yl)cyclooctanol (10c)



To an ice-cold solution of but-3-yn-1-ylbenzene (100 mg, 0.769 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.7 mL, 1 mmol, 1.6 *M* in THF)dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, cyclooctanone (126 mg, 1 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10c** (130 mg, 0.507 mmol, 66%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.26 (2H, m), 7.22-7.21 (3H, m), 2.82 (2H, t, *J* = 6.9Hz), 2.51 (2H, t, *J* = 6.3Hz), 1.86-1.80 (3H, m), 1.64-1.58 (3H, m), 1.54-1.43 (8H, m) and 1.25-1.19 (1H, m) ppm.

^{13}C NMR (125 MHz, $CDCl_3$):δ = 140.9, 128.7, 128.5, 126.4, 85.0, 84.1, 69.0, 40.4, 35.4, 25.4, 23.5 and 21.0 ppm.

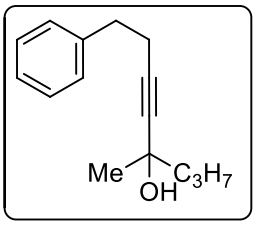
IR (neat): 3431, 2927, 2853, 2340, 2140, 1692, 1456, 1266, 1052, 984, 896 and 742 cm^{-1}.

HR ESI-MS: $[C_{18}H_{28}NO]^+ = [M+NH_4]^+$ requires 274.2165; found 274.2145.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

(S)-4-Methyl-8-phenyloct-5-yn-4-ol (10d)

To an ice-cold solution of but-3-yn-1-ylbenzene (150 mg, 1.153 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.9 mL, 1.498 mmol, 1.6 *M* in THF) dropwise under a positive



N_2 atmosphere. After stirring at 0 ºC for 30 min, 2-pentanone (129 mg, 1.498 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10d** (180 mg, 0.832 mmol, 72%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.25 (2H, m), 7.22-7.18(3H, m), 2.85 (2H, t, *J* = 7.4Hz), 2.49 (2H, t, *J* = 7.4Hz), 1.93-1.78 (5H, m), 1.46-1.41 (4H, m) and 0.931-0.835 (1H, m)ppm.

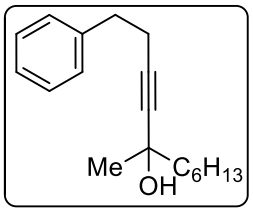
^{13}C NMR (100 MHz, $CDCl_3$):δ = 140.9, 128.7, 128.5, 126.4, 86.0, 83.0, 71.7, 38.7, 35.4, 28.1, 24.7, 22.3 and 21.0 ppm.

IR (neat): 3441, 2954, 2355, 1707, 1658, 1588, 1572, 1056, 1026, 754 and 695 cm^{-1}.

HR ESI-MS: $[C_{15}H_{21}O]^+$= $[M+H]^+$ requires 217.1587; found 217.1589.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

(S)-4-Methyl-8-phenyloct-5-yn-4-ol (10e)



To an ice-cold solution of but-3-yn-1-ylbenzene (150 mg, 1.153 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.9 mL, 1.498 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, 2-octanone (192 mg, 1.498 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10e** (220 mg, 0.851 mmol, 74%) as a pale-yellow colored oil.

^{1}H NMR (500 MHz, $CDCl_3$):δ = 7.33-7.27 (2H, m), 7.22-7.19(3H, m), 2.80 (2H, t, *J* = 7.52Hz), 2.48(2H, t, *J* = 7.51Hz), 1.90 (1H, *b*s), 1.64-1.93 (2H, m), 1.42 (3H, s), 1.33-1.26 (8H, m) and 0.91-0.88 (3H, m)ppm.

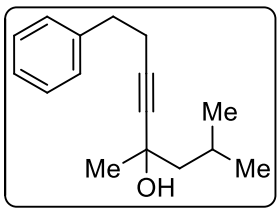
^{13}C NMR (100 MHz, $CDCl_3$):δ = 140.8, 128.7, 128.5, 126.4, 85.1, 83.0, 68.5, 44.1, 35.3, 32.0, 30.2, 29.6, 24.9, 22.8, 21.0 and 14.3 ppm.

IR (neat): 3441, 2928, 2856, 1668, 1589, 1460, 1267, 1121, 1030 and 751 cm^{-1}.

HR ESI-MS: $[C_{18}H_{30}NO]^+$= $[M+NH_4]^+$requires 276.2322; found 276.2328.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

(S)-2,4-Dimethyl-8-phenyloct-5-yn-4-ol (10f)



To an ice-cold solution of but-3-yn-1-ylbenzene (150 mg, 1.153 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.9 mL, 1.498 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, 4-methylpentan-2-one (150 mg, 1.498 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10f** (180 mg, 0.782 mmol, 68%) as a pale-yellow colored oil

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30-7.25 (2H, m), 7.22-7.18(3H, m), 2.81 (2H, t, *J* = 7.4Hz), 2.49 (2H, t, *J* = 7.4Hz), 1.93-1.78 (5H, m), 1.46-1.41 (4H, m) and 0.931-0.835 (1H, m) ppm.

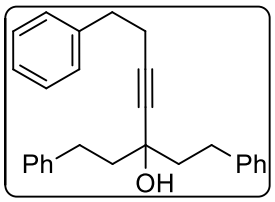
^{13}C NMR (100 MHz, $CDCl_3$):δ = 140.9, 128.7, 128.5, 126.4, 86.0, 83.0, 71.7, 38.7, 35.4, 28.1, 24.7, 22.3 and 21.0 ppm.

IR (neat): 3441, 2954, 2345, 2178, 1707, 1540, 1461, 1374, 1150, 1056, 923 and 702 cm^{-1}.

HR ESI-MS: $[C_{16}H_{23}O]^+ = [M+H]^+$ requires 231.1743; found 231.1759.

TLC: R_f= 0.4 (9:1, Hexane/EtOAc).

3-Phenethyl-1,7-diphenylhept-4-yn-3-ol (10g)



To an ice-cold solution of but-3-yn-1-ylbenzene (150 mg, 1.153 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.9 mL, 1.498 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, 1,5-diphenylpentan-3-one (357 mg, 1.498 mmol) in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **10 g** (210 mg, 0.570 mmol, 50%) as a pale-yellow colored oil

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.48-6.88 (15H, m), 2.90-2.46 (5H, m), 1.83-1.74 (2H, m), 1.68-1.54 (2H, m), 1.33-1.21 (2H, m) and 0.97-0.84 (1H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.6, 142.1, 128.6, 128.5, 128.4, 128.1, 126.7, 125.9, 123.8, 121.4, 119.4, 70.9, 68.3, 39.3, 38.1, 34.9, 34.6, 33.1, 32.1 and 29.8 ppm.

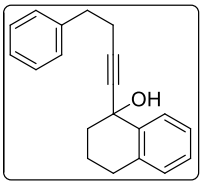
IR (neat): 3412, 2929, 2870, 2340, 1860, 1707, 1461, 1373, 1140, 1122, 1050, 923 and 702 cm^{-1}.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

3D. Synthesis of daldinone A and hypoxylonol A precursor.

Following **the Experimental procedure 3A**, precursor propargylic alcohols were prepared.

1-(4-Phenylbut-1-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (15)



To an ice-cold solution of but-3-yn-1-ylbenzene (100 mg, 0.768 mmol) in anhydrous THF (5 mL), was added n-BuLi (0.6 mL, 0.999 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, 1-tetralone (146 mg, 0.999 mmol)in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **15** (130 mg, 0.470 mmol, 61%) as a pale-yellow colored oil

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.67-7.64 (1H, m), 7.29-7.25 (2H, m), 7.22-7.18 (5H, m), 7.08-7.05(1H, m), 2.83-2.72 (4H, m), 2.51 (2H, t, *J* = 7.4Hz), 2.20 (1H, *br*s), 2.17-2.09 (2H,m), 2.01-1.93 (1H, m) and 1.89-1.82 (1H, m) ppm.

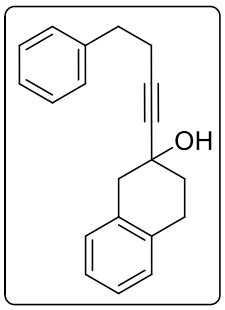
^{13}C NMR (100 MHz, $CDCl_3$):δ = 157.5, 129.2, 121.2, 114.9, 91.9, 78.1, 71.6, 56.0, 42.7, 27.8 and 21.9 ppm.

IR (neat): 3110, 3066, 2993, 2914, 1709, 1623, 1582, 1486, 1375, 1308, 1278, 1227, 1167, 1068, 1044, 959, 905, 832, 788, 707 and 619 cm^{-1}.

HR ESI-MS: $[C_{20}H_{20}ONa]^+ = [M+Na]^+$ requires 299.1406; found 299.1391.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-(4-Phenylbut-1-yn-1-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (16)



To an ice-cold solution of but-3-yn-1-ylbenzeneylbenzene (200 mg, 1.537 mmol) in anhydrous THF (5 mL), was added n-BuLi (1.2 mL, 1.998 mmol, 1.6 *M* in THF) dropwise under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, 2-tetralone (291 mg, 1.998 mmol)in anhydrous THF (5 mL) was added and the reaction mixture was stirred at room and temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered the alcohol **16** (244 mg, 0.883 mmol, 56 %) as a pale-yellow colored oil

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.75-7.57 (9H, m), 3.69-3.45 (4H m), 3.26-2.96 (4H, m) and 2.70-2.46 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 159.5, 137.4, 134.2, 131.9, 130.0, 129.6, 129.0, 128.8, 128.7, 128.4, 88.1, 86.5, 71.6, 69.9, 69.9 and 55.4 ppm.

IR (neat): 3110, 2990, 2929, 1729, 1620, 1480, 1278, 1160, 1168, 955, 836, 788 and 755 cm^{-1}.

HR ESI-MS: $[C_{20}H_{20}ONa]^+$ = $[M+Na]^+$ requires 299.1406; found 299.1391.

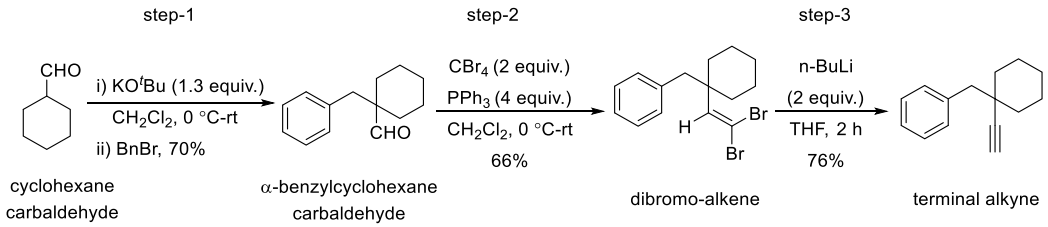
TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

3E. Synthesis of spiro-alkyne

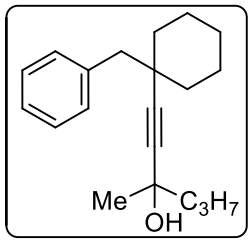
Step-1: To a solution of cyclohexanecarbaldehyde (200 mg, 1.783 mmol, 1.0 equiv.) in CH_2Cl_2 (6 mL) was added *t*-BuOK (260 mg, 2.317 mmol, 1.3 equiv.) and BnBr (915 mg, 5.349, 3.0 equiv.). The reaction mixture was stirred at room temperature for 12 h, and then it was diluted with water (10 mL) and extracted with EtOAc (2 x 15 mL). The organic layers were washed with water (5 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude residue was purified by flash chromatography. Elution with n-hexane delivered the corresponding α-benzylated aldehyde (260 mg, 1.286 mmol, 72%) as a colorless oil.

Step-2: To a solution of Ph_3P (1349mg, 5.145 mmol, 4.0 equiv.) in CH_2Cl_2 (3 mL) was added CBr_4 (852 mg, 2.572 mmol, 2.0 equiv.) at 0 ºC. After stirring for 1 h at 0 ºC, a solution of α–benzyl-cyclohexane carbaldehyde (260 mg, 1.286 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL) was added and the reaction mixture was further stirred at room temperature for 3 h. Dilution with cold n-hexane (20 mL), filtration through a plug of Celite (n-hexane, 20 mL) and concentration under reduced pressure gave a crude residue which was purified by flash chromatography. Elution with ethyl acetate/hexane (1: 99 v/v) delivered the corresponding dibromoalkene (304 mg, 0.853 mmol, 66%) as a white solid.

Step-3: To an ice-cold solution of the dibromoalkene (300 mg, 0.842 mmol, 1.0 equiv.) in THF (7 mL) was added n-BuLi (0.7 mL, 1.09 mmol, 1.6 *M* solution in THF) dropwise and under a positive N2 atmosphere. The solution was stirred at room temperature for 2 h and quenched with water (10 mL). The mixture was then extracted with EtOAc (2 x 15 mL) and the organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude residue which was purified by flash chromatography. Elution with ethyl acetate/hexane (1:99 v/v) delivered the corresponding terminal alkyne (125 mg, 0.630 mmol, 74%) as a colorless oil.[1]



(S)-1-(1-Benzylcyclohexyl)-3-methylhex-1-yn-3-ol (18a)



To an ice-cold solution of (1-ethynylcyclohexyl)methyl)benzene (60 mg, 0.302 mmol) in anhydrous THF (5 mL) was added n-BuLi (0.3 mL, 0.393 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, pentan-2-one (34 mg, 0.393 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered alcohol **18a** (40 mg, 0.140 mmol, 47%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.28-7.26 (5H, m), 2.59 (2H, s), 1.94 (1H, *b*s), 1.63-1.45 (8H, m), 1.40-1.36 (5H, m), 1.22-1.10 (4H, m) and 0.87-0.83 (5H, m) ppm.

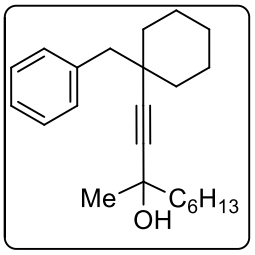
^{13}C NMR (100 MHz, $CDCl_3$):δ = 137.9, 130.8, 127.5, 126.2, 88.2, 88.0, 68.3, 49.1, 46.2, 37.8, 37.6, 30.2, 26.1, 23.1, 18.2 and 14.3 ppm.

IR (neat): 3433, 2925, 2854, 1710, 1592, 1454, 1377, 1275, 1025, 912, 850 and 769 cm^{-1}.

HR ESI-MS: $[C_{20}H_{28}NaO]^+ = [M+Na]^+$ requires 307.2032; found 307.2061.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc)

1-((1-Benzylcyclohexyl)ethynyl)cycloheptanol (18b)



To an ice-cold solution of (1-ethynylcyclohexyl)methyl)benzene (60 mg, 0.302 mmol) in anhydrous THF (5 mL) was added n-BuLi (0.3 mL, 0.393 mmol, 1.6 *M* in THF) dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, octan-2-one (50 mg, 0.393 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered alcohol **18b** (52 mg, 0.159 mmol, 53%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.26-7.20 (5H, m), 2.67 (2H, s), 1.67-1.57 (10H, m), 1.28-1.10 (12H, m) and 0.90-0.87 (4H, m) ppm.

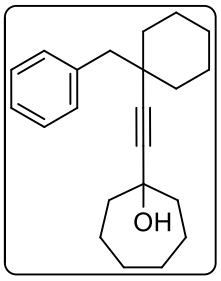
^{13}C NMR (100 M, $CDCl_3$):δ = 137.8, 130.8, 127.9, 123.3, 86.2, 86.1, 66.5, 49.2, 44.0, 37.8, 37.8, 37.7, 31.9, 30.2, 29.5, 26.1, 24.9, 23.1, 22.6 and 14.2 ppm.

IR (neat): 3440, 2958, 2924, 2960, 2853, 1712, 1592, 1452, 1378, 1263, 757 and 737 cm^{-1}.

HR ESI-MS: $[C_{23}H_{35}O]^+ = [M+H]^+$ requires 327.2682; found 327.2087.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

1-((1-Benzylcyclohexyl)ethynyl)cycloheptanol (18c)



To an ice-cold solution of (1-ethynylcyclohexyl)methyl)benzene (122 mg, 0.615 mmol) in anhydrous THF (5 mL) was added n-BuLi (0.5 mL, 0.800 mmol, 1.6 *M* in THF)dropwise and under a positive N_2 atmosphere. After stirring at 0 ºC for 30 min, cycloheptanone (89 mg, 0.800 mmol) in anhydrous THF (5 mL) was added and the solution was stirred at room temperature for 2 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (15 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and filtered. The solvent was evaporated off under reduced pressure and the crude residue was purified by flash chromatography. Elution with ethyl acetate/n-hexane (10:90 v/v) delivered alcohol **18c** (150 mg, 0.483 mmol, 79%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.26-7.19 (5H, m), 2.68 (1H, s), 2.50-2.47 (2H, m), 1.98-1.93 (2H, m), 1.81-1.75 (2H, m), 1.68-1.62 (9H, m), 1.58-1.47 (6H, m) and 1.25-1.18 (2H, m) ppm.

^{13}C NMR (100 MHz, $CDCl_3$):δ = 137.8, 130.8, 127.9, 126.3, 89.0, 88.5, 72.1, 49.3, 43.5, 37.8, 37.7, 27.9, 26.1, 23.2 and 22.4 ppm.

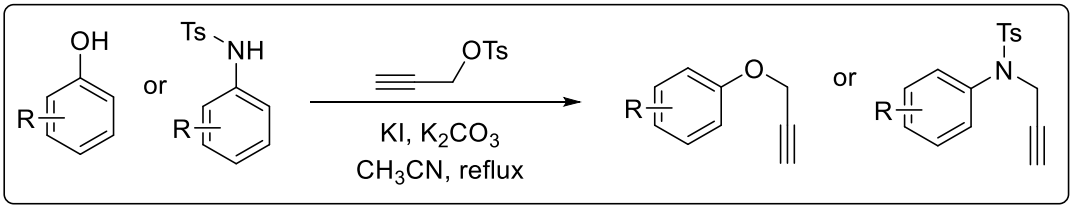
IR (neat): 3309, 2952, 2923, 2852, 1704, 1491, 1453, 918, 909, 849, 791, 758, 748 and 699 cm^{-1}.

HR ESI-MS: $[C_{22}H_{31}O]^+ = [M+H]^+$ requires 311.2369; found 311.1993.

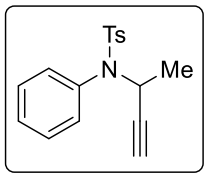
TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

A General procedure for the synthesis of propargyl ether/amines with terminal alkynes:

A solution of the substituted phenol or aniline derivative (1 equiv.), propargyl tosylate (1.3 equiv.), a catalytic amount of KI (0.2 equiv.) and K_2CO_3 (2 equiv.) in dry acetonitrile was refluxed for 12-15 h. The solvent was evaporated off under reduced pressure and the crude residue was directly purified by flash chromatography. Elution with acetate/hexane (10:90 v/v) delivered the corresponding propargyl ether/amine as a pale-yellow colored oil (80-85%). [2-6]



Procedure for the preparation of *N*-(but-3-yn-2-yl)-4-methyl-*N*-phenylbenzenesulfonamide (S_1)



4-Methyl-*N*-phenylbenzenesulfonamide (200 mg, 0.809 mmol) and but-3-yn-2-ol (74 mg, 1.05 mmol) were dissolved in anhydrous THF (41 mL) at 0 °C and under a nitrogen atmosphere. Then, Ph_3P (276 g, 1.05 mmol) was added portion wise, the reaction mixture was stirred for 10 min, and then DEAD (216 mg, 1.07 mmol) was slowly added. The resulting solution was heated at 70 °C for 20 h. The reaction mixture was allowed to cool to room temperature, diluted with cold n-hexane (20 ml) and filtered through a plug of Celite (n-hexane, 20 ml).The filtrate was concentrated, and the crude residue was purified by flash chromatography. Elution with ethyl acetate/hexane (10:90 v/v) delivered the product **S1** (60 mg, 0.267 mmol, 33%) as a pale-yellow colored oil.

^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.60 (2H, d, *J* = 8.0Hz), 7.37-7.28 (3H, m), 7.23-7.21 (4H, m), 5.37-5.29 (1H, m), 2.41 (3H, s) and 1.29 (1H, d, *J* = 7.2Hz) ppm.

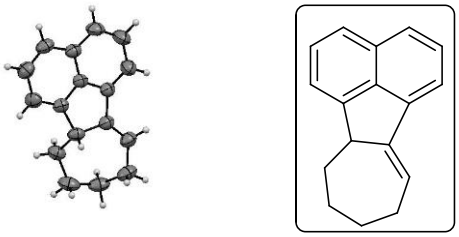
^{13}C NMR (100 MHz, $CDCl_3$):δ = 143.5, 136.7, 135.7, 131.7, 129.2, 128.9, 128.8, 128.2 82.9, 73.5, 46.5, 21.8 and 21.7 ppm.

IR (neat): 3261, 2923, 1598, 1494, 1343, 1159, 1091, 921, 813, 754, 662 and 559 cm^{-1}.

HR ESI-MS:$[C_{17}H_{21}N_2O_2S]^+ = [M+NH_4]^+$ requires 317.1318: found 317.1404.

TLC: R_f = 0.4 (9:1, Hexane/EtOAc).

4. Single crystal X-ray diffraction analysis of 7, 8, 9, 10-tetrahydro-6*bH*-cyclohepta[*a*]acenaphthylene12a

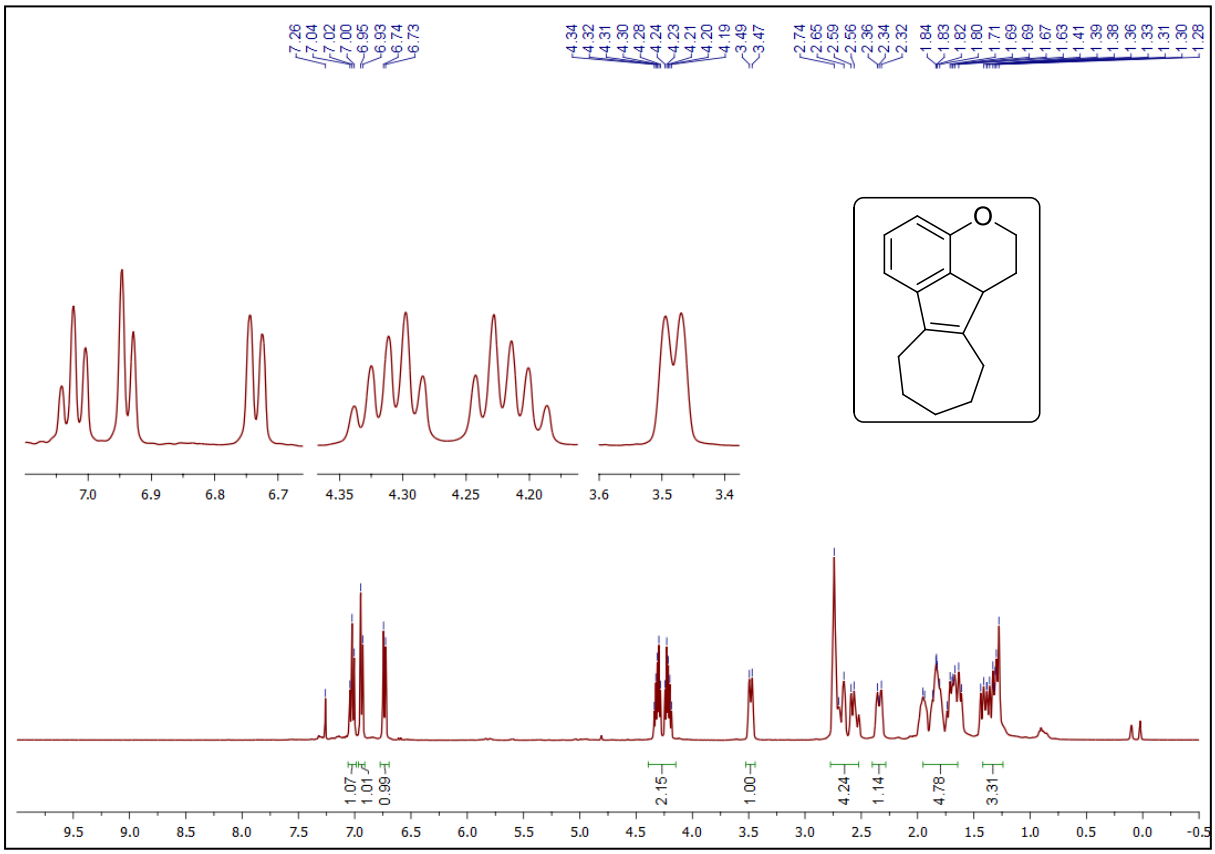
Crystallographic Data and Structure Refinements Summary of Compound 12a	
Molecular Structure (ORTEP Diagram) For compound **12a**	
CCDC number	CCDC2079834
Formula	$C_{17}H_{16}$
Formula weight	220.30
Color of the crystal	White
Temperature (K)	296(2)
Wave length (Å)	0.71073 Å
Crystal system	Triclinic
Space group	P -1
a (Å)	7.5288(3)
b (Å)	b = 8.6068(3)
c (Å)	c = 10.6262(4)
α (°)	9081.5606(18)
β (°)	72.1189(19)
γ (°)	67.1244(18)
Volume ($Å^3$)	603.47(4)
Z	2
Calculated density (Mg/m^3)	1.212

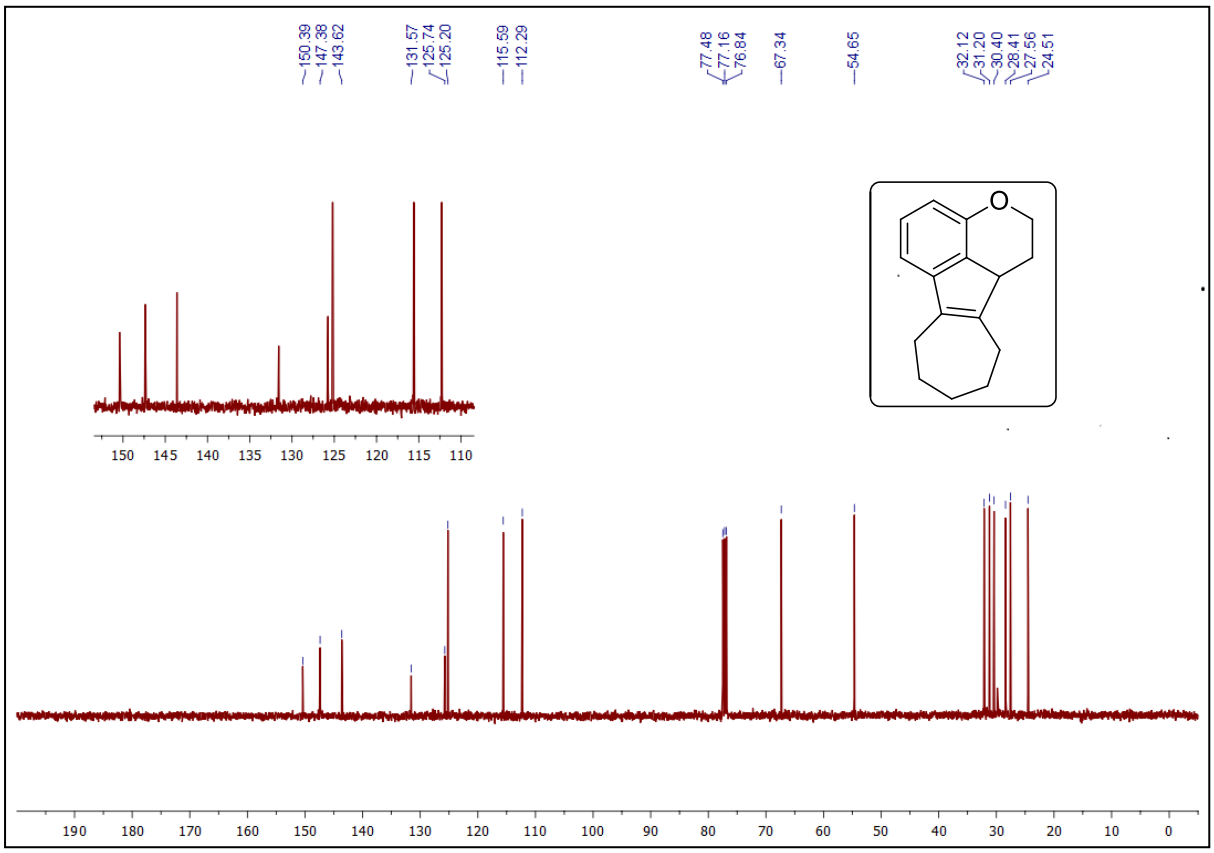
Absorption coefficient, μ (mm^{-1})	0.068
F (000)	236
Crystal size	0.250 x 0.220 x 0.100 mm^3
θ range for data collection (°)	2.015 to 24.987
Number of unique reflections	9624
Number of parameters	155
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.1029
R indices (all data)	R1 = 0.0646, wR2 = 0.1173
Largest diff. peak and hole ($e.Å^{-3}$)	0.161 and -0.113
Goodness-of-fit on F^2	1.038

5.References:

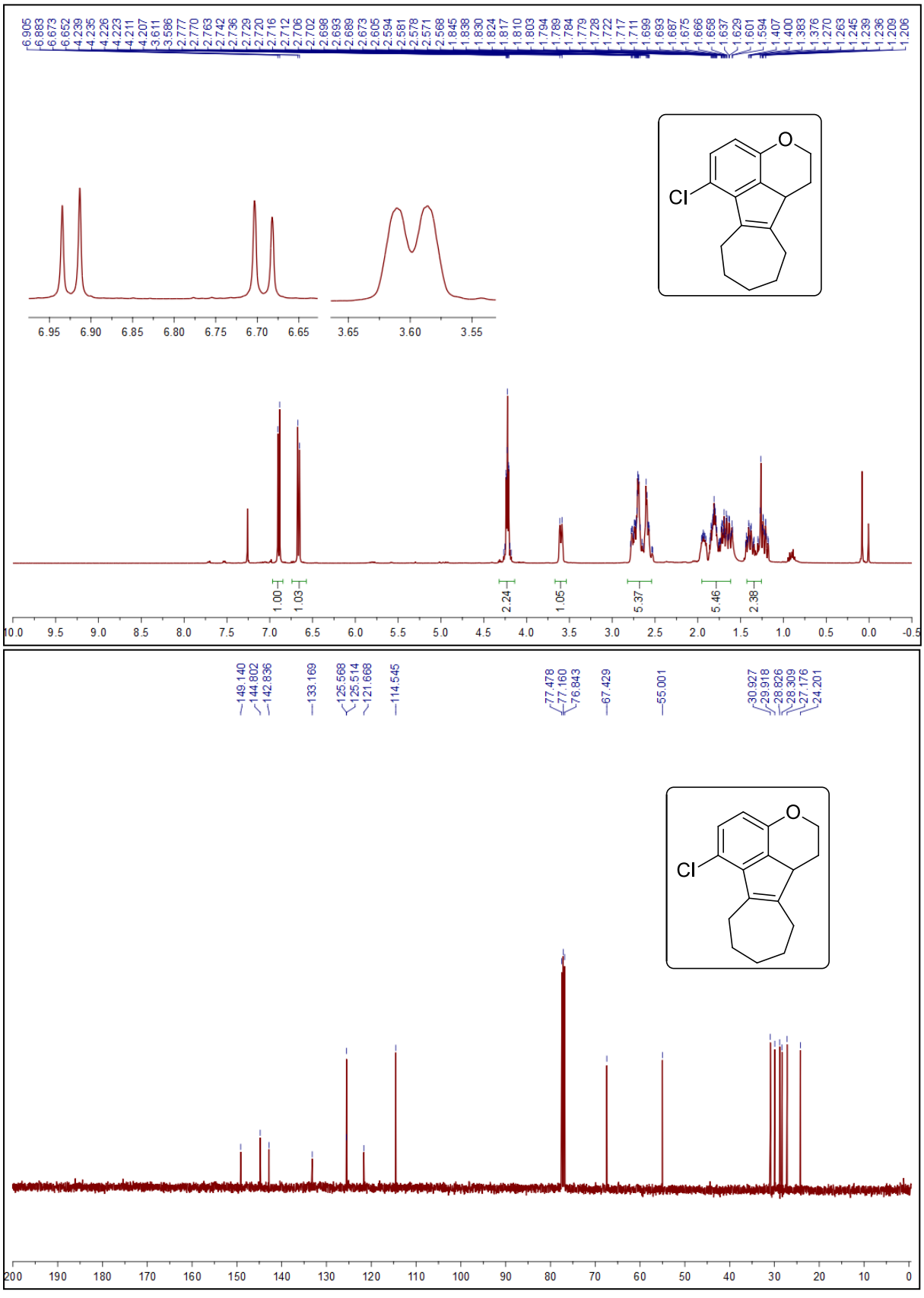
1. H. Wu, R. Andres, Q. Wang, J. Zhu, *Angew. Chem., Int. Ed.* 2019, **58**, 499– 503.
2. Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem., Int. Ed*. 2012, **51**, 1915-1918
3. L. Alonso-Marañón, M. M. Martínez, L. A. Sarandeses, J. P. Sestelo, *Org. Biomol.Chem*.2015, **13**, 379-387.
4. V. S. P. R. Lingam, R. Vinodkumar, K. Mukkanti, A. Thomas, B. Goalie. *Tetrahedron Lett*.,2008, **49**, 4260–4264.
5. B. Roy, I. Ansary, S. Samanta, K. C. Majumdar, *Tetrahedron Lett*., 2012, **53**, 5119-5122
6. M. Ito, A. Takaki, M. Okamura, K. S. Kanyiva, T. Shibata, *Eur. J. Org. Chem*. 2021, **2021**, 1688-1692.

^{1}H and ^{13}C NMR Spectra of Compound **4a**. (Solvent $CDCl_3$, 400 MHz)

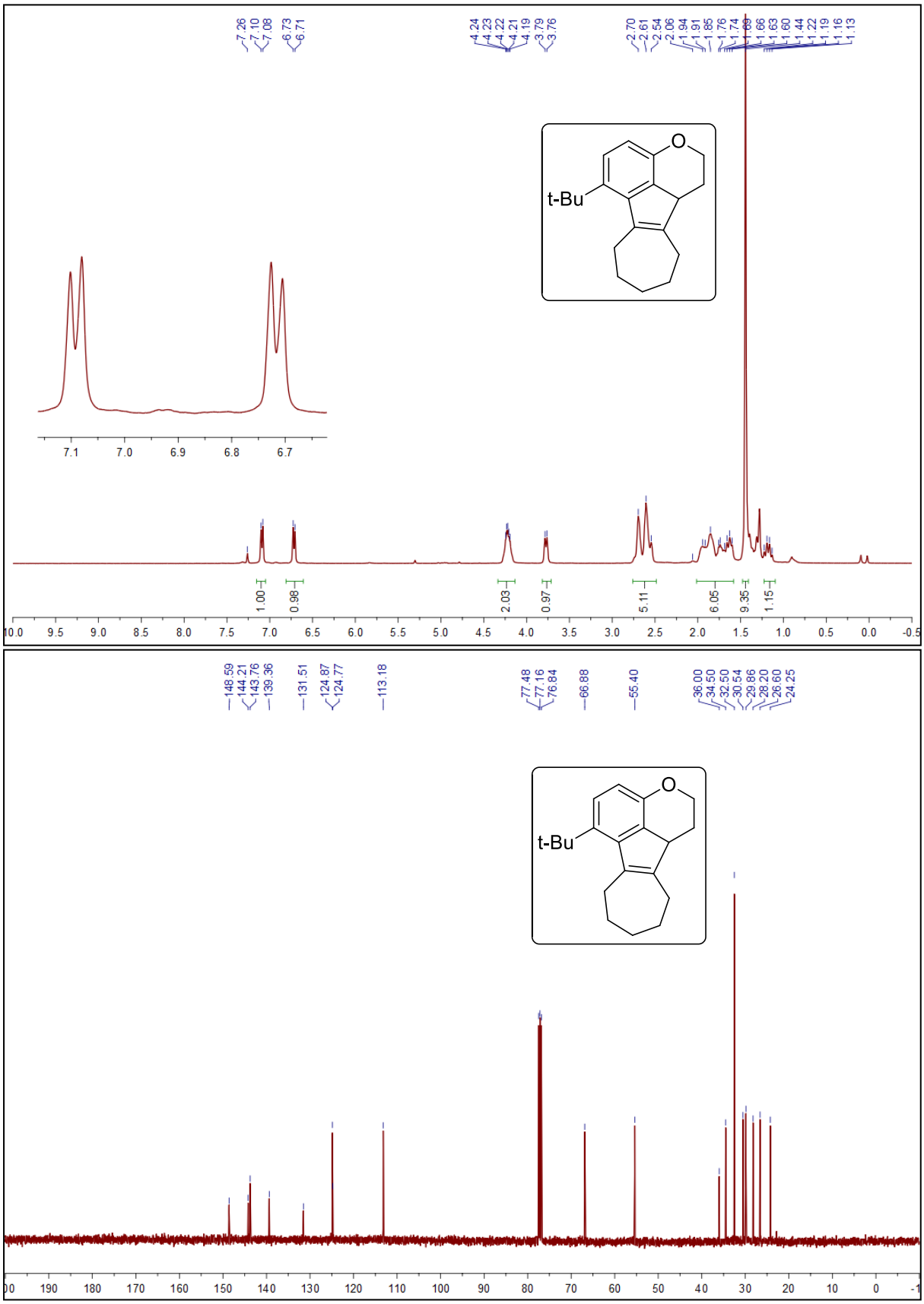




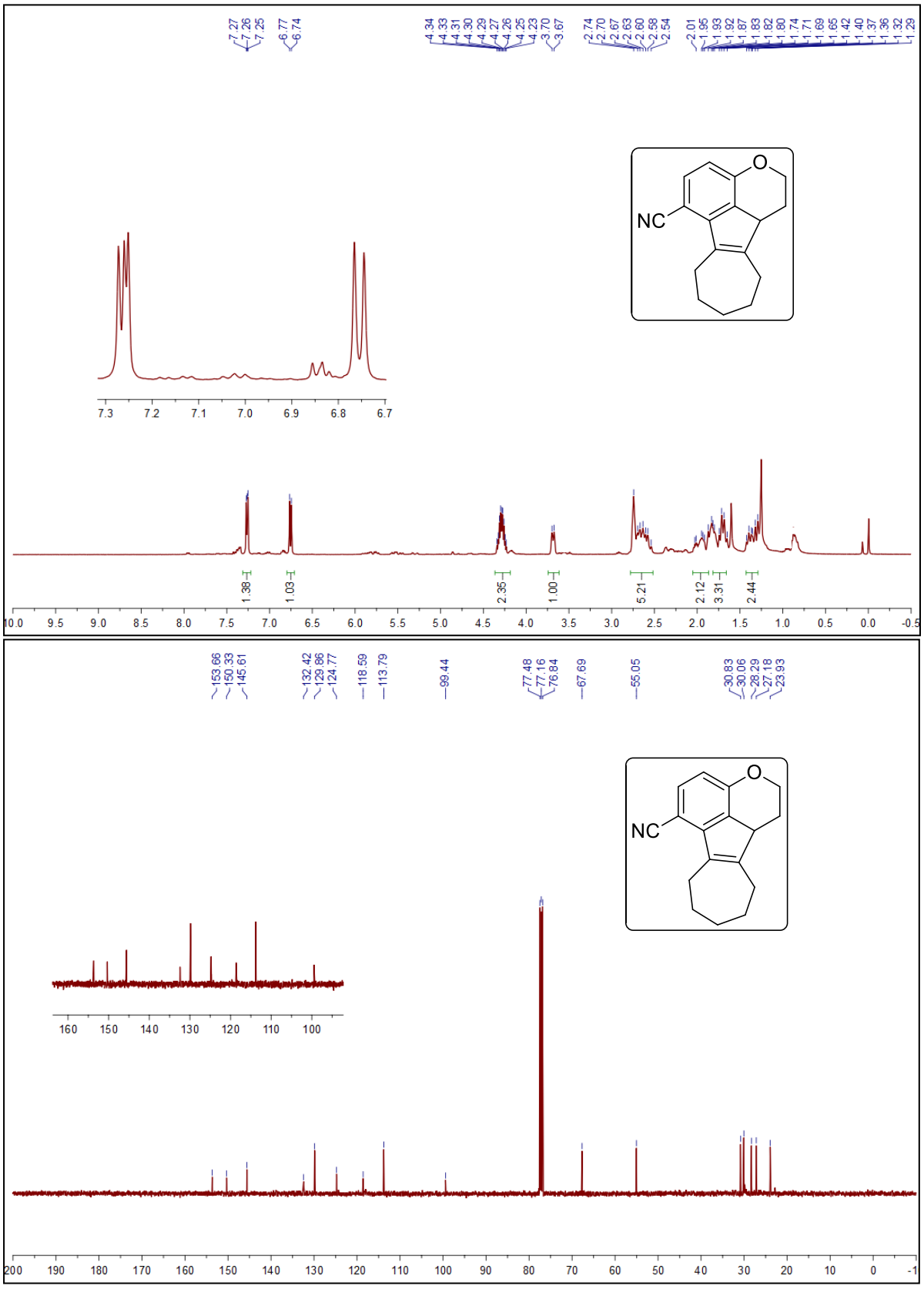
^{1}H and ^{13}C NMR Spectra of Compound **4b**. (Solvent $CDCl_3$, 400 MHz)



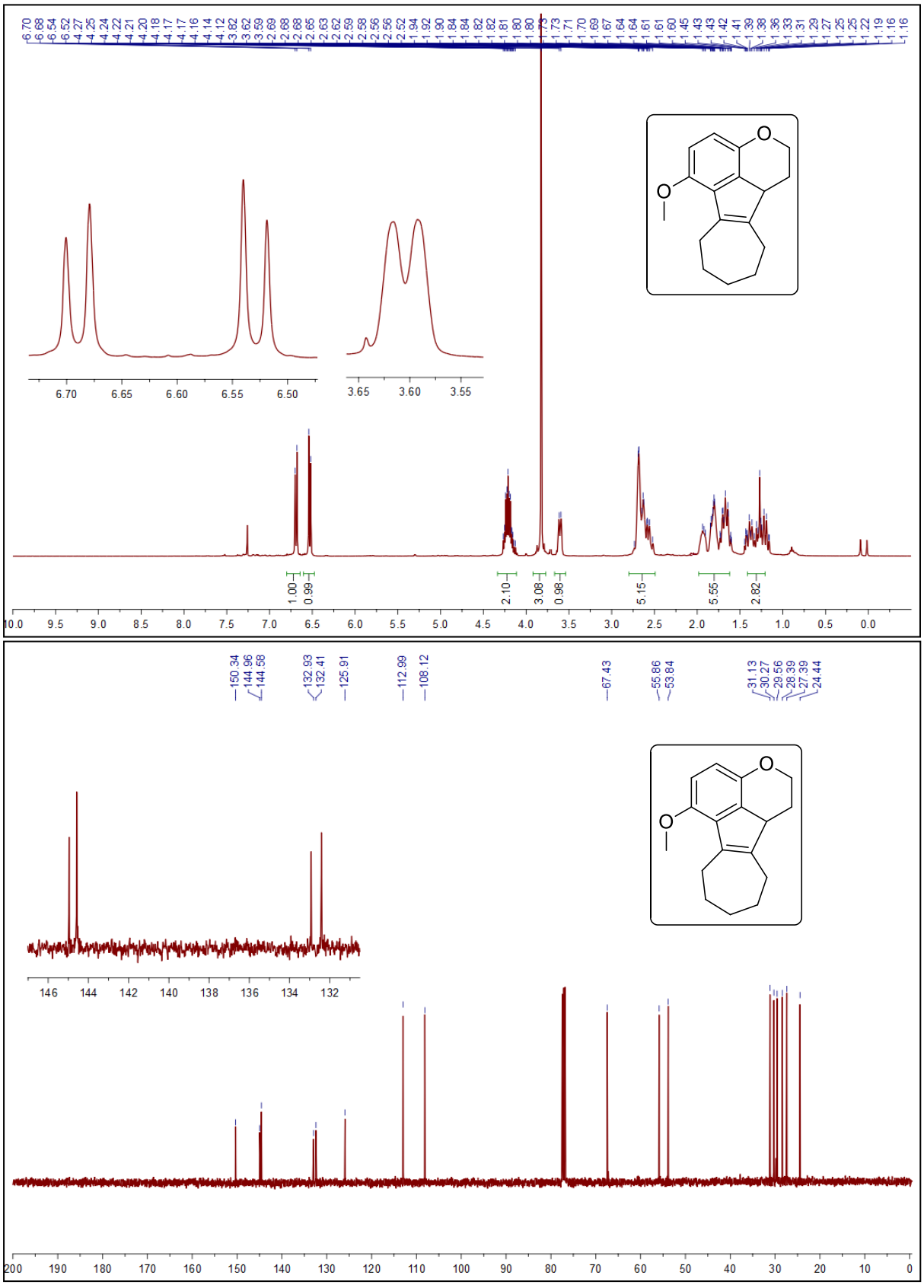
^{1}H and ^{13}C NMR Spectra of Compound **4c**. (Solvent $CDCl_3$, 400 MHz)



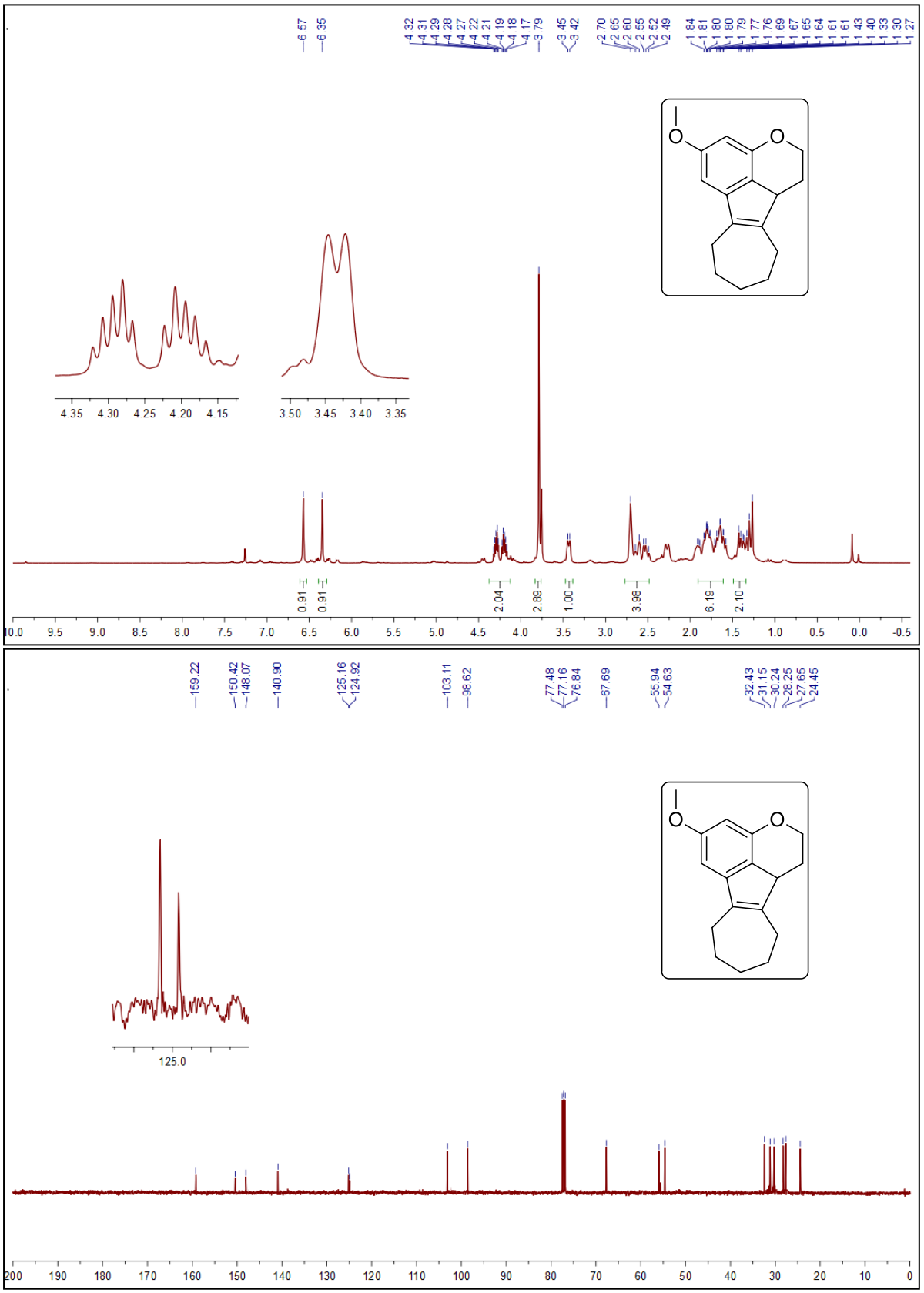
^{1}H and ^{13}C NMR Spectra of Compound **4d**. (Solvent $CDCl_3$, 400 MHz)



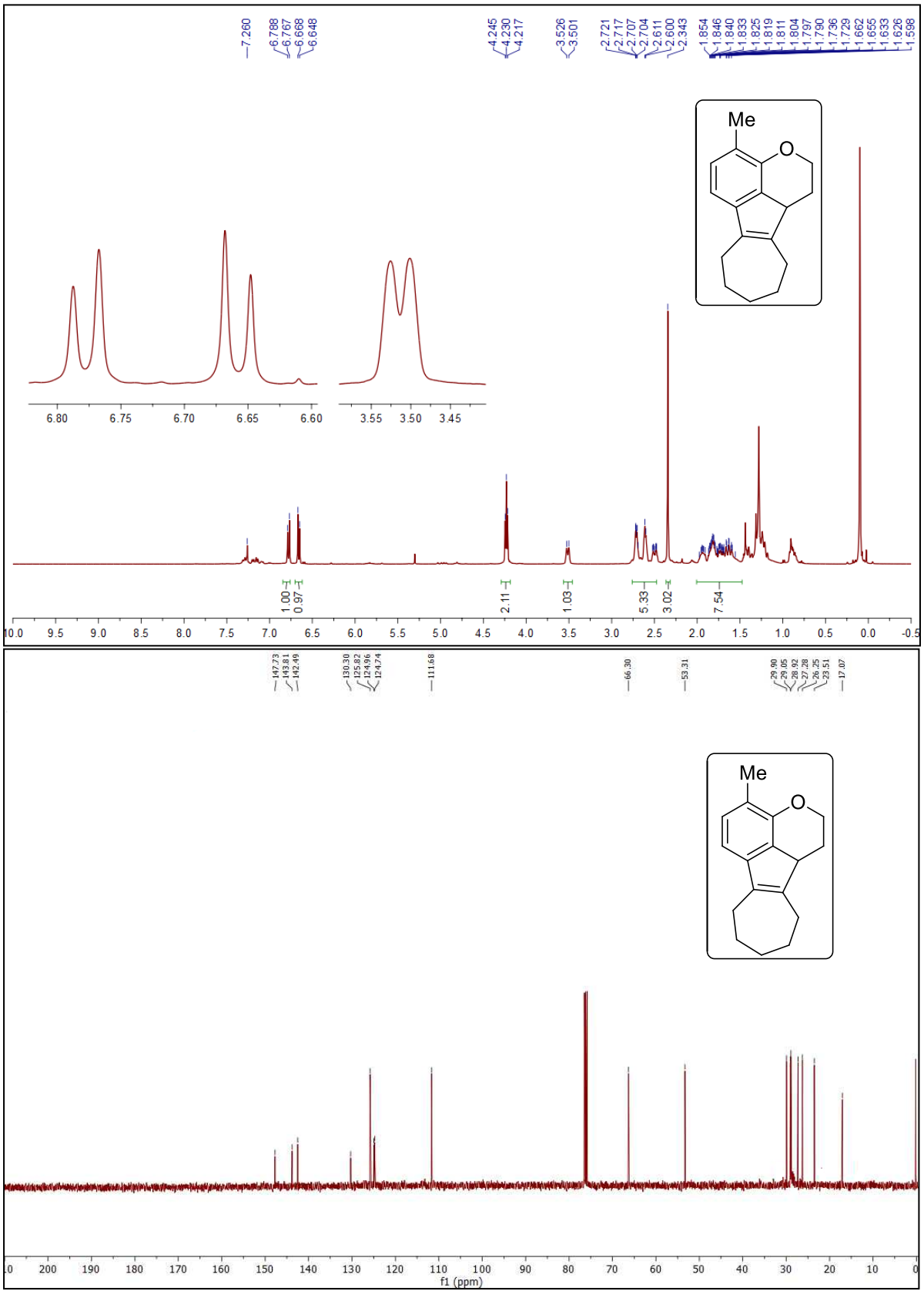
^{1}H and ^{13}C NMR Spectra of Compound **4e**. (Solvent $CDCl_3$, 400 MHz)



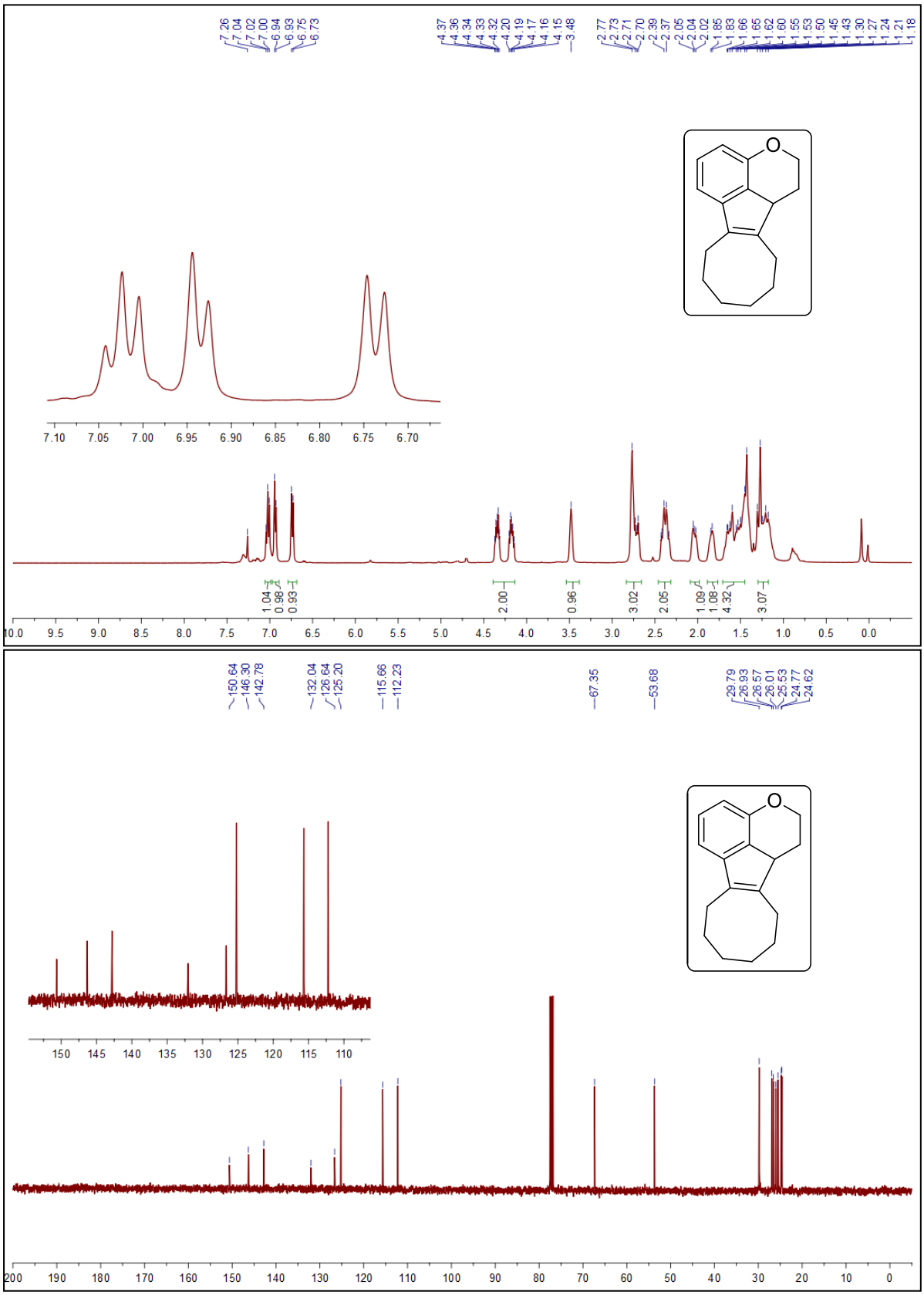
^{1}H and ^{13}C NMR Spectra of Compound **4f**. (Solvent $CDCl_3$, 400 MHz)



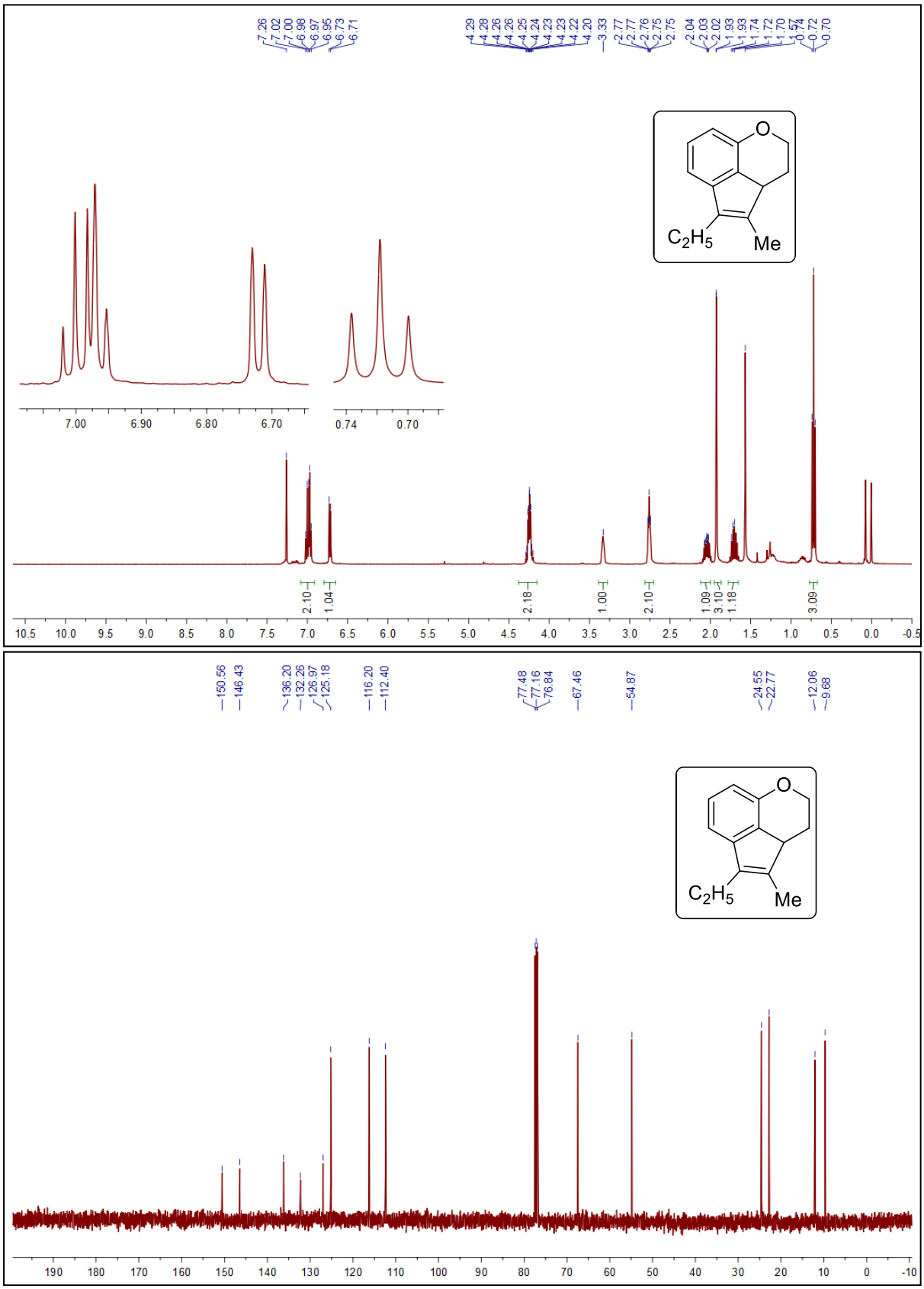
^{1}H and ^{13}C NMR Spectra of Compound **4g**. (Solvent $CDCl_3$, 400 MHz)



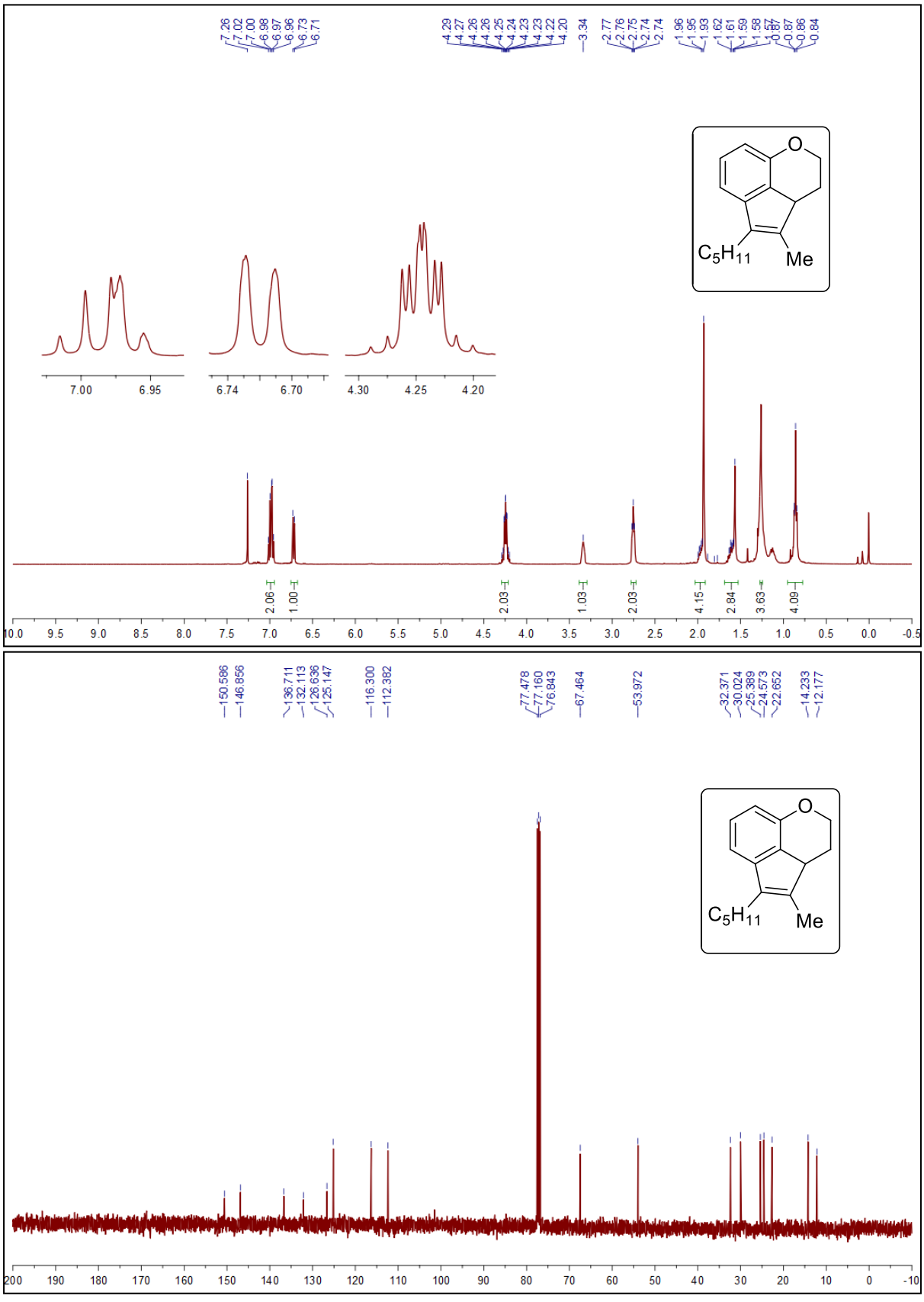
^{1}H and ^{13}C NMR Spectra of Compound **4h**. (Solvent $CDCl_3$, 400 MHz)



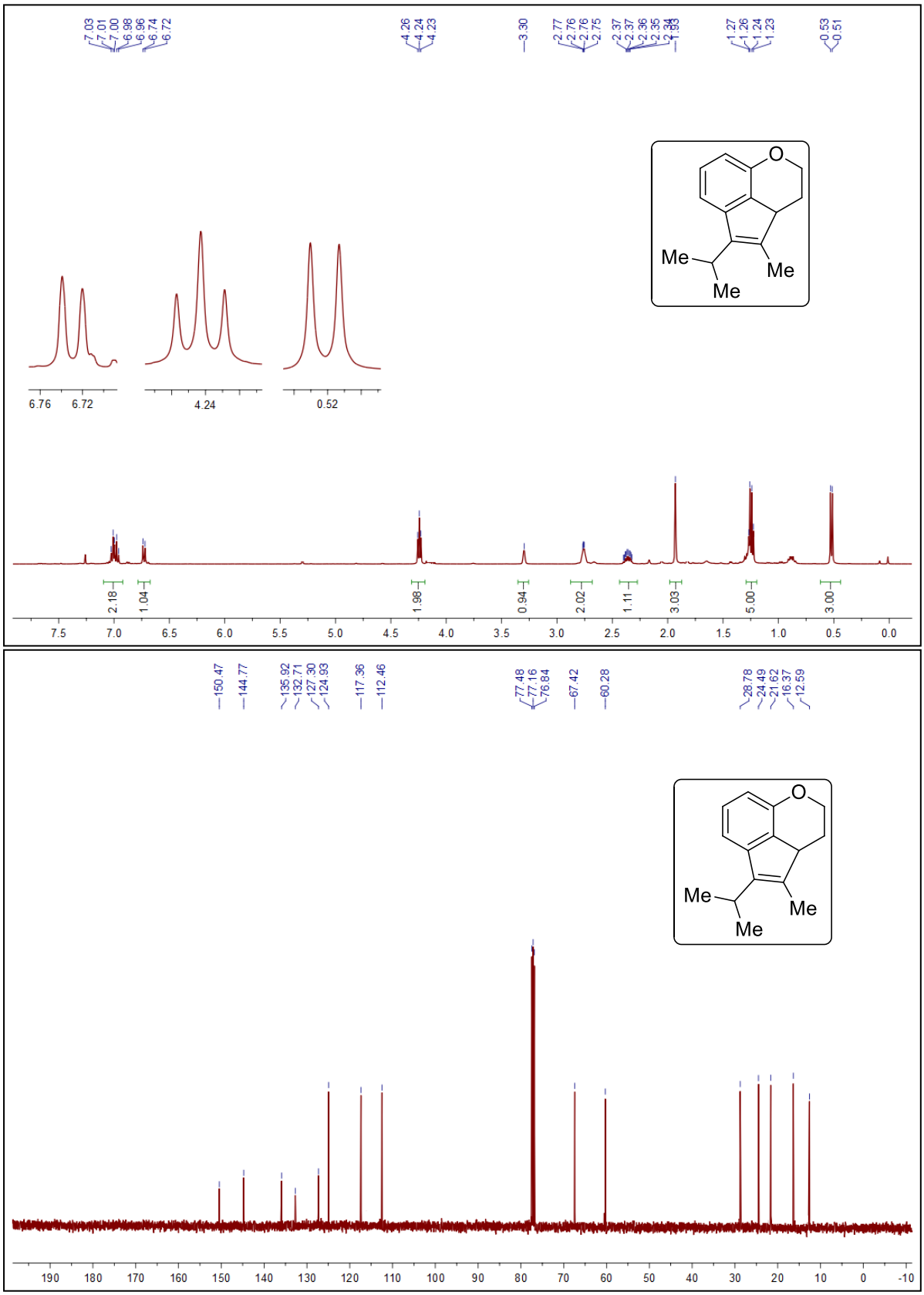
^{1}H and ^{13}C NMR Spectra of Compound **4i**. (Solvent $CDCl_3$, 400 MHz)



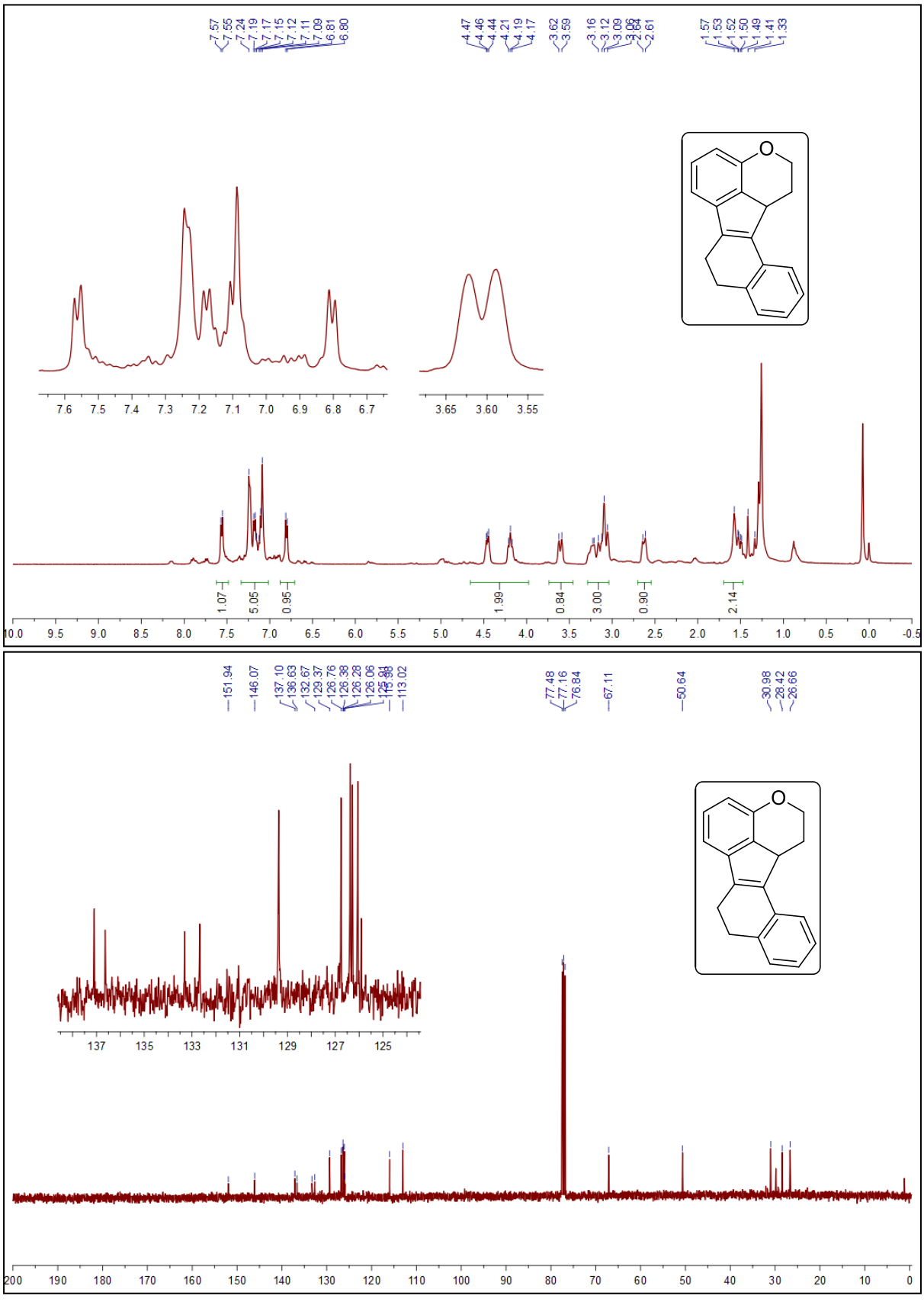
^{1}H and ^{13}C NMR Spectra of Compound **4j**. (Solvent $CDCl_3$, 400 MHz)



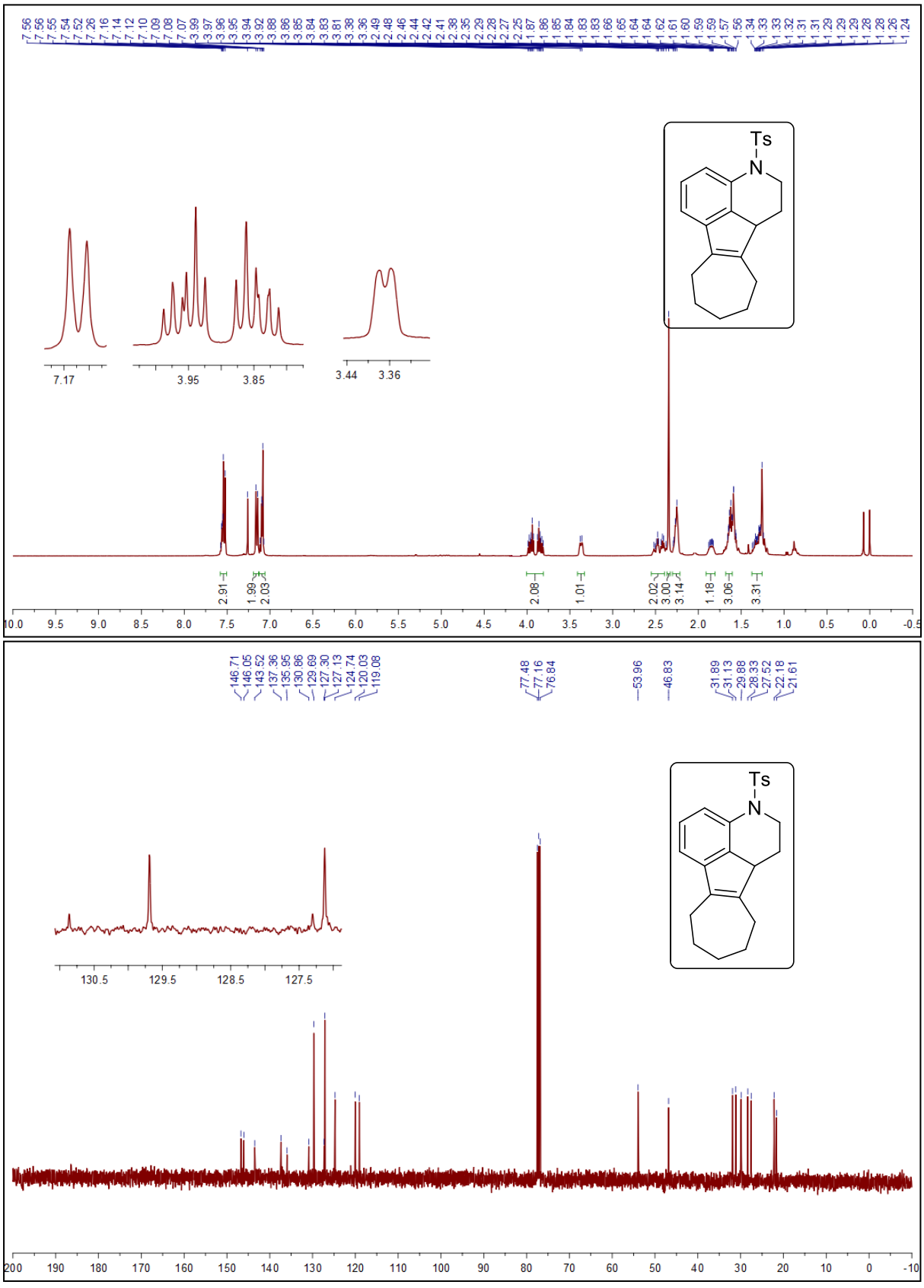
^{1}H and ^{13}C NMR Spectra of Compound **4k**. (Solvent $CDCl_3$, 400 MHz)



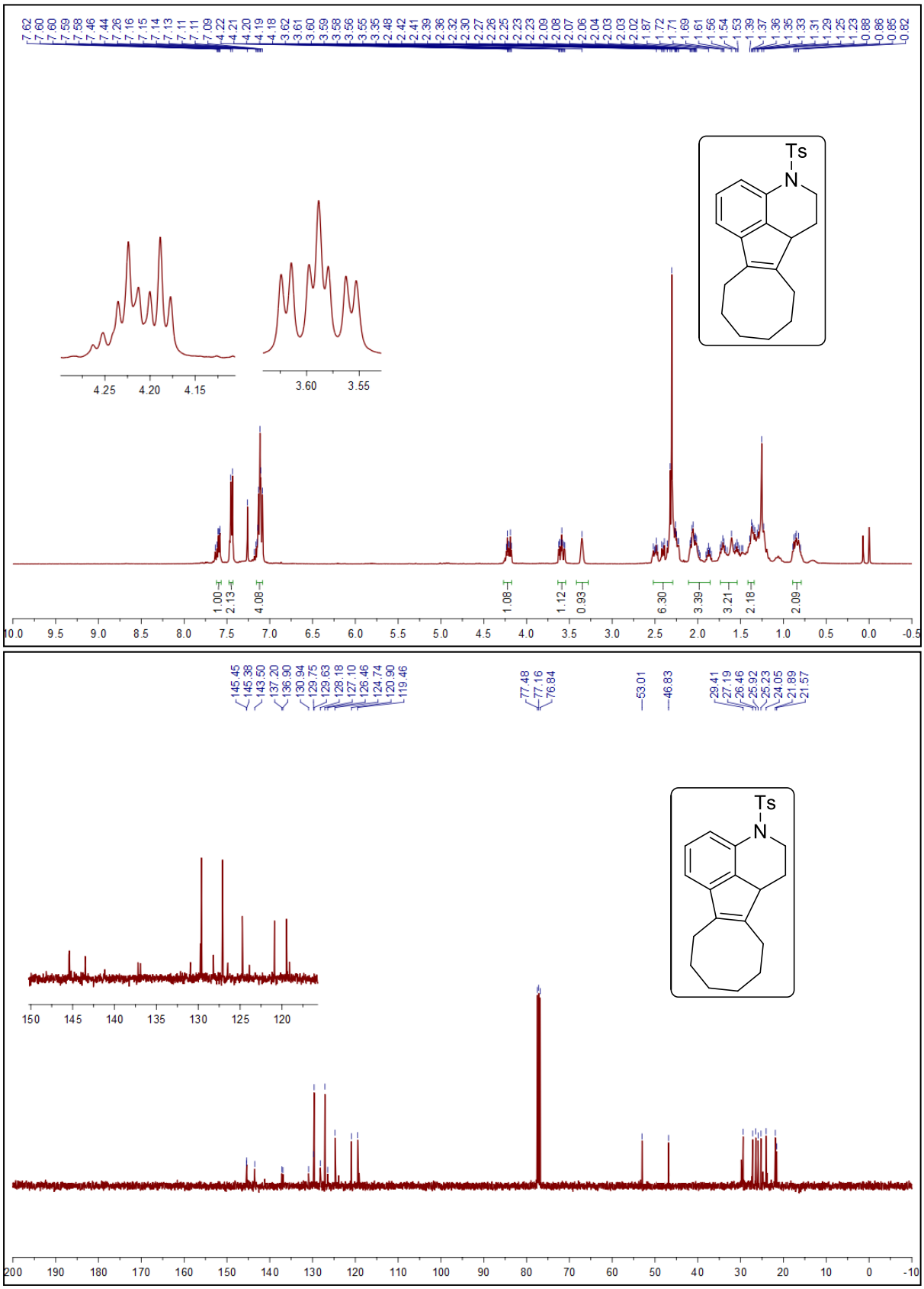
^{1}H and ^{13}C NMR Spectra of Compound **4l**. (Solvent $CDCl_3$, 400 MHz)



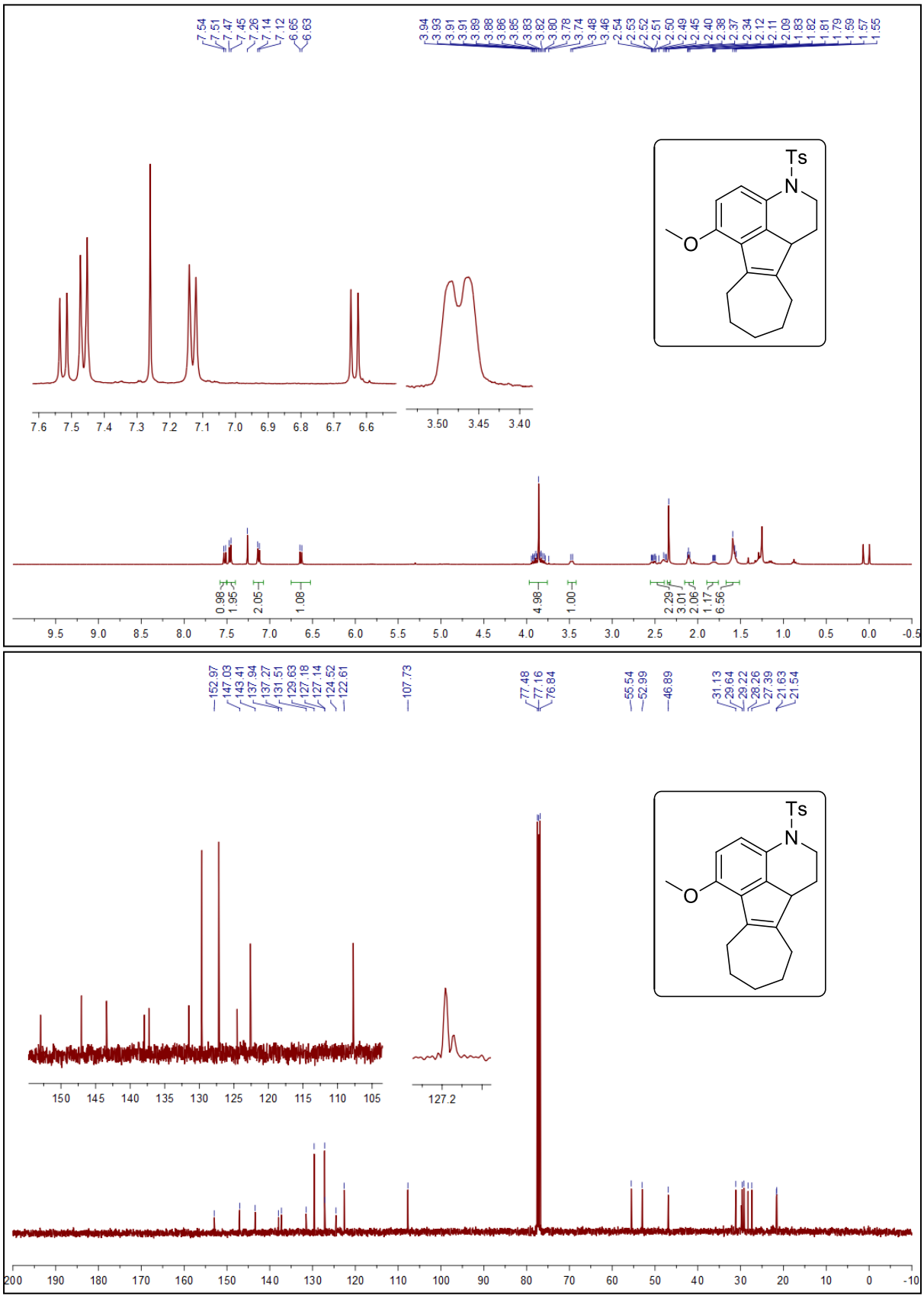
^{1}H and ^{13}C NMR Spectra of Compound **9a**. (Solvent $CDCl_3$, 400 MHz)



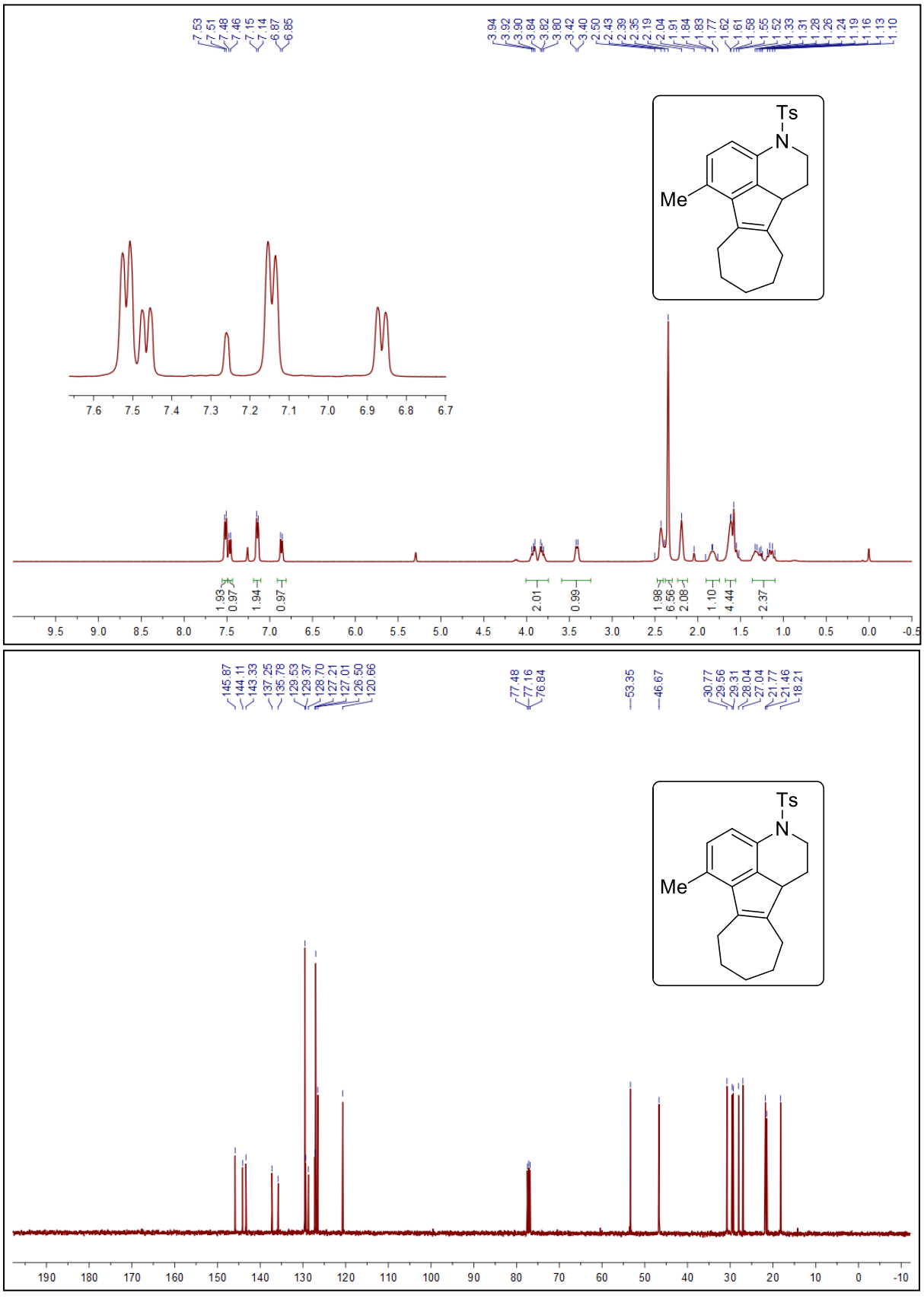
^{1}H and ^{13}C NMR Spectra of Compound **9b**. (Solvent $CDCl_3$, 400 MHz)



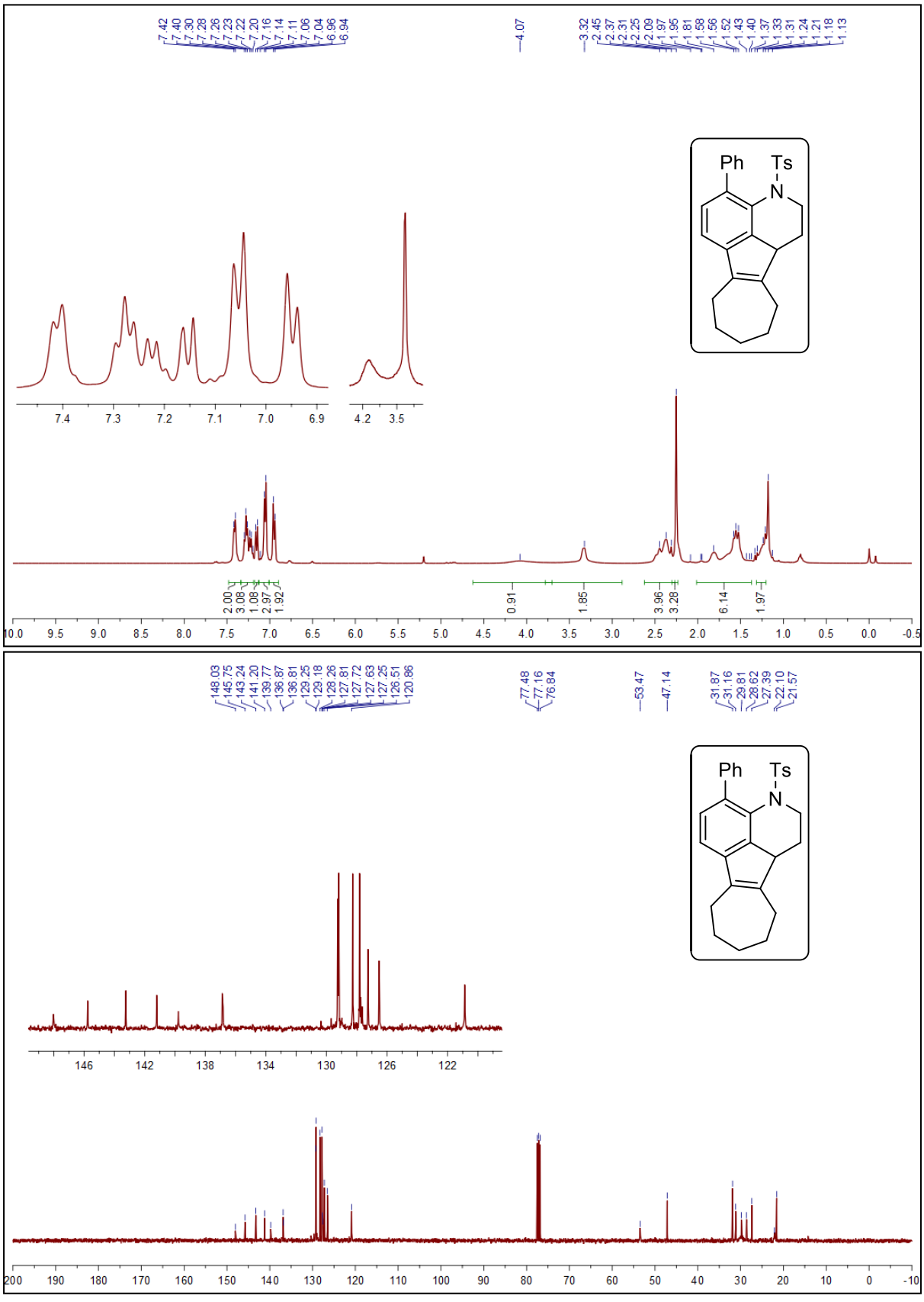
^{1}H and ^{13}C NMR Spectra of Compound **9c**. (Solvent $CDCl_3$, 400 MHz)



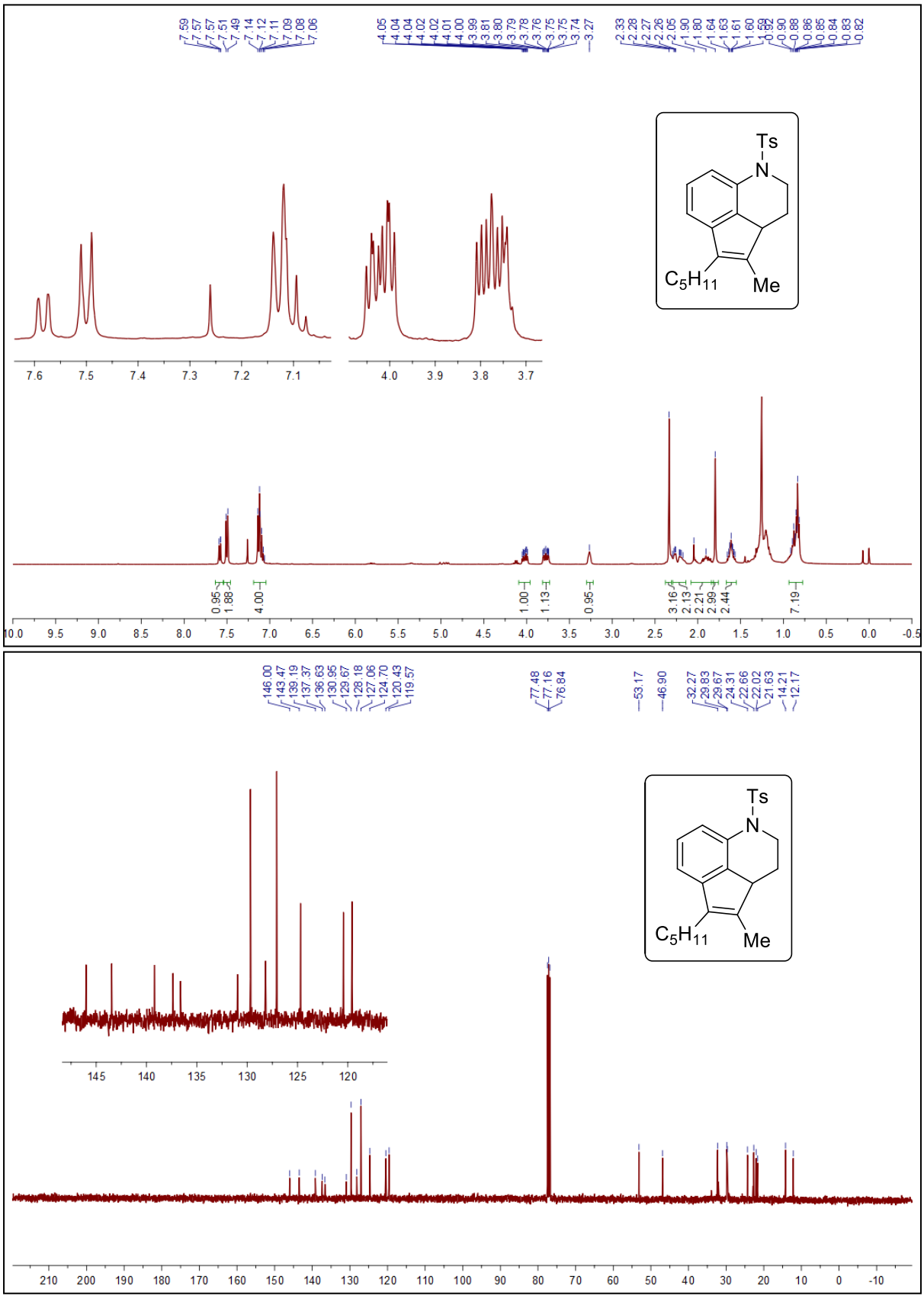
^{1}H and ^{13}C NMR Spectra of Compound **9d**. (Solvent $CDCl_3$, 400 MHz)



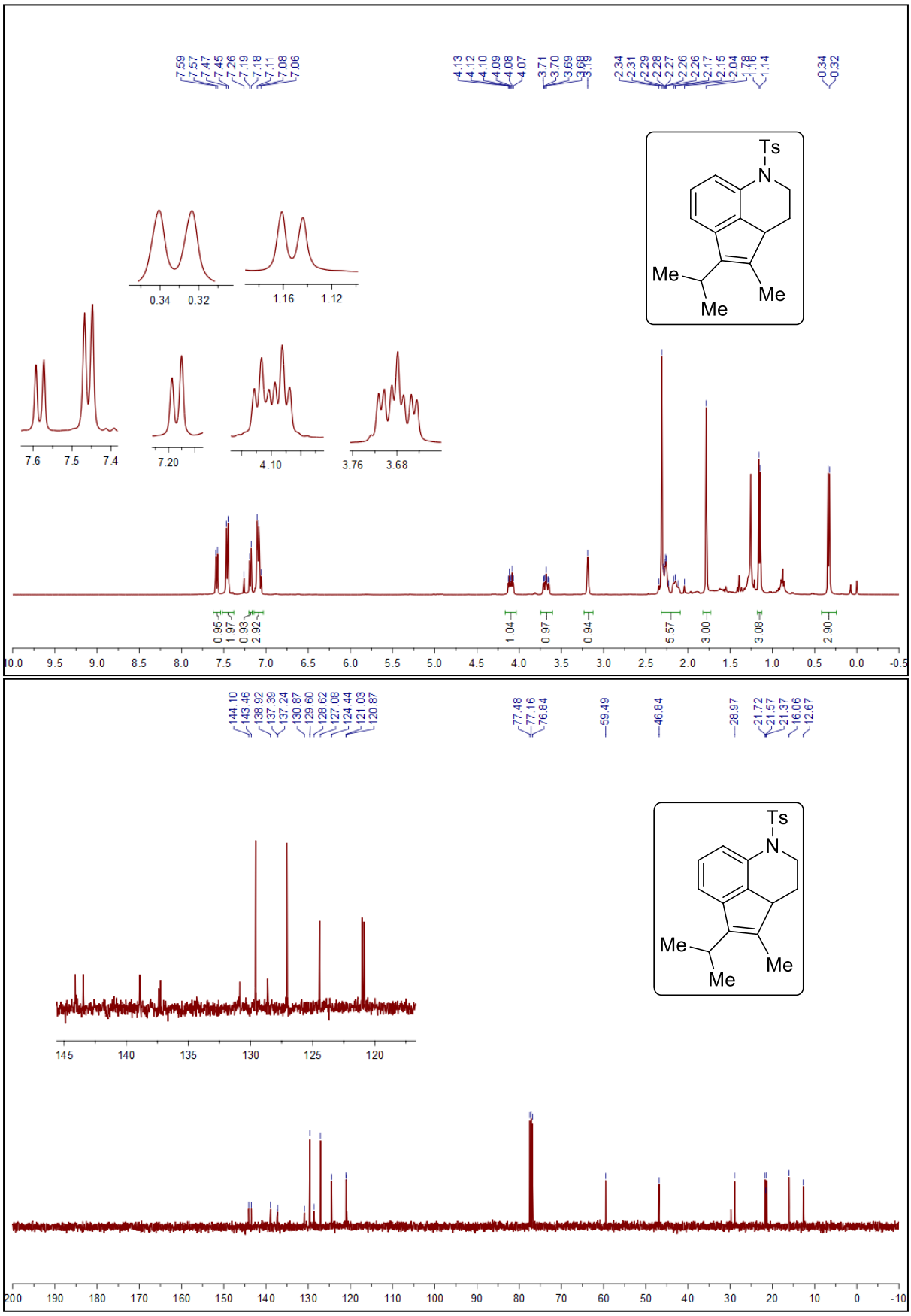
^{1}H and ^{13}C NMR Spectra of Compound **9e**. (Solvent $CDCl_3$, 400 MHz)



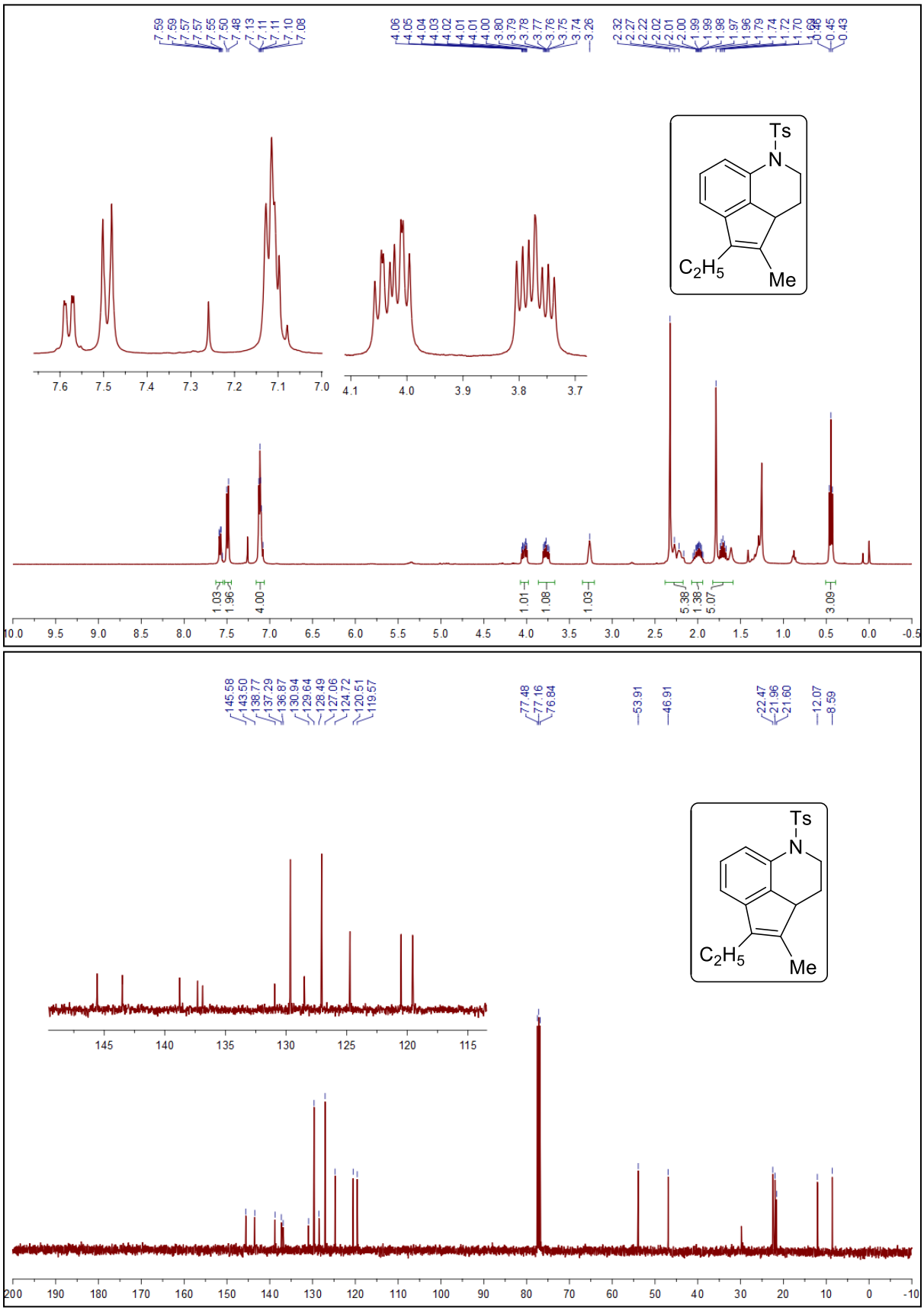
^{1}H and ^{13}C NMR Spectra of Compound **9f**. (Solvent $CDCl_3$, 400 MHz)



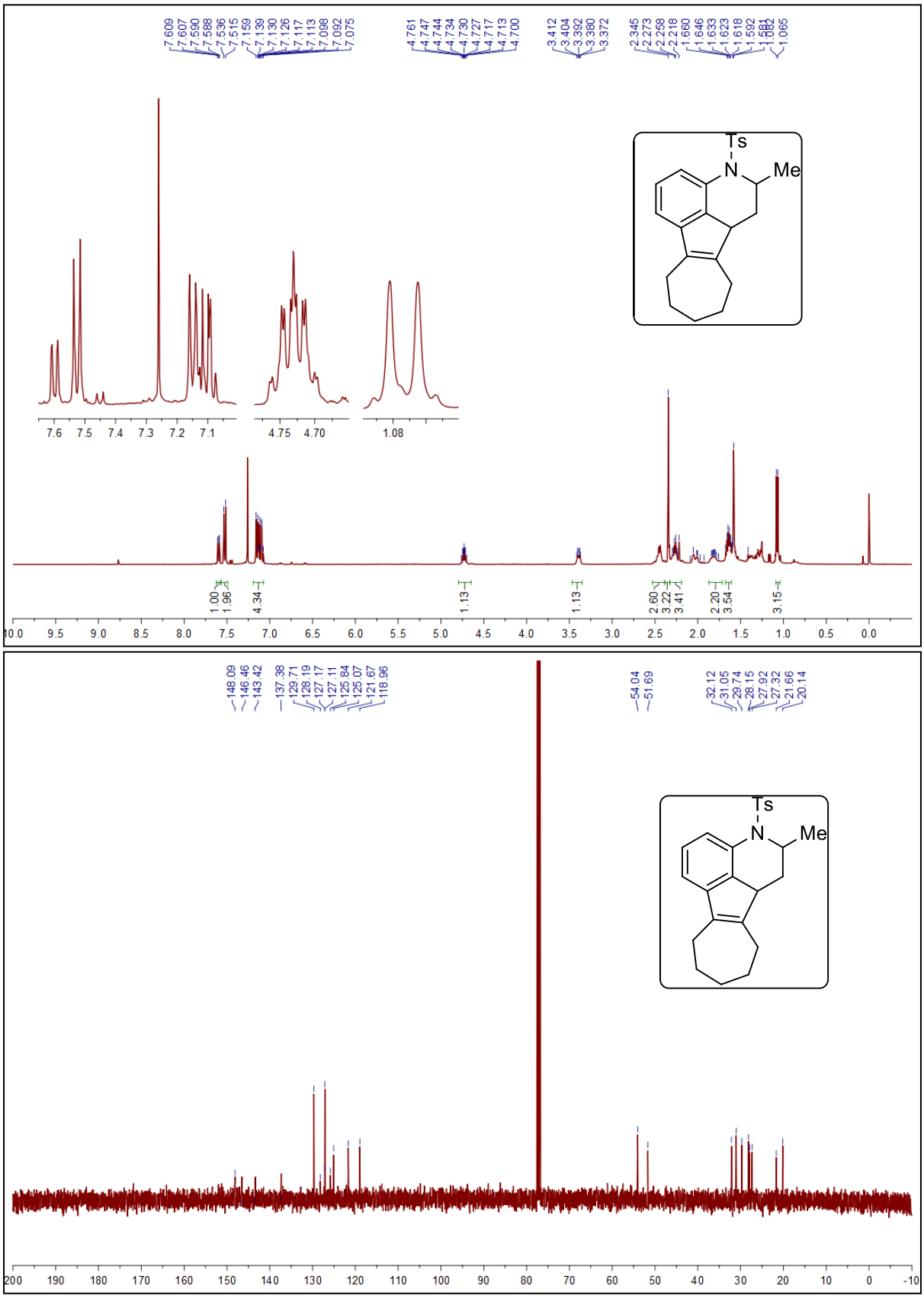
^{1}H and ^{13}C NMR Spectra of Compound **9g**. (Solvent $CDCl_3$, 400 MHz)



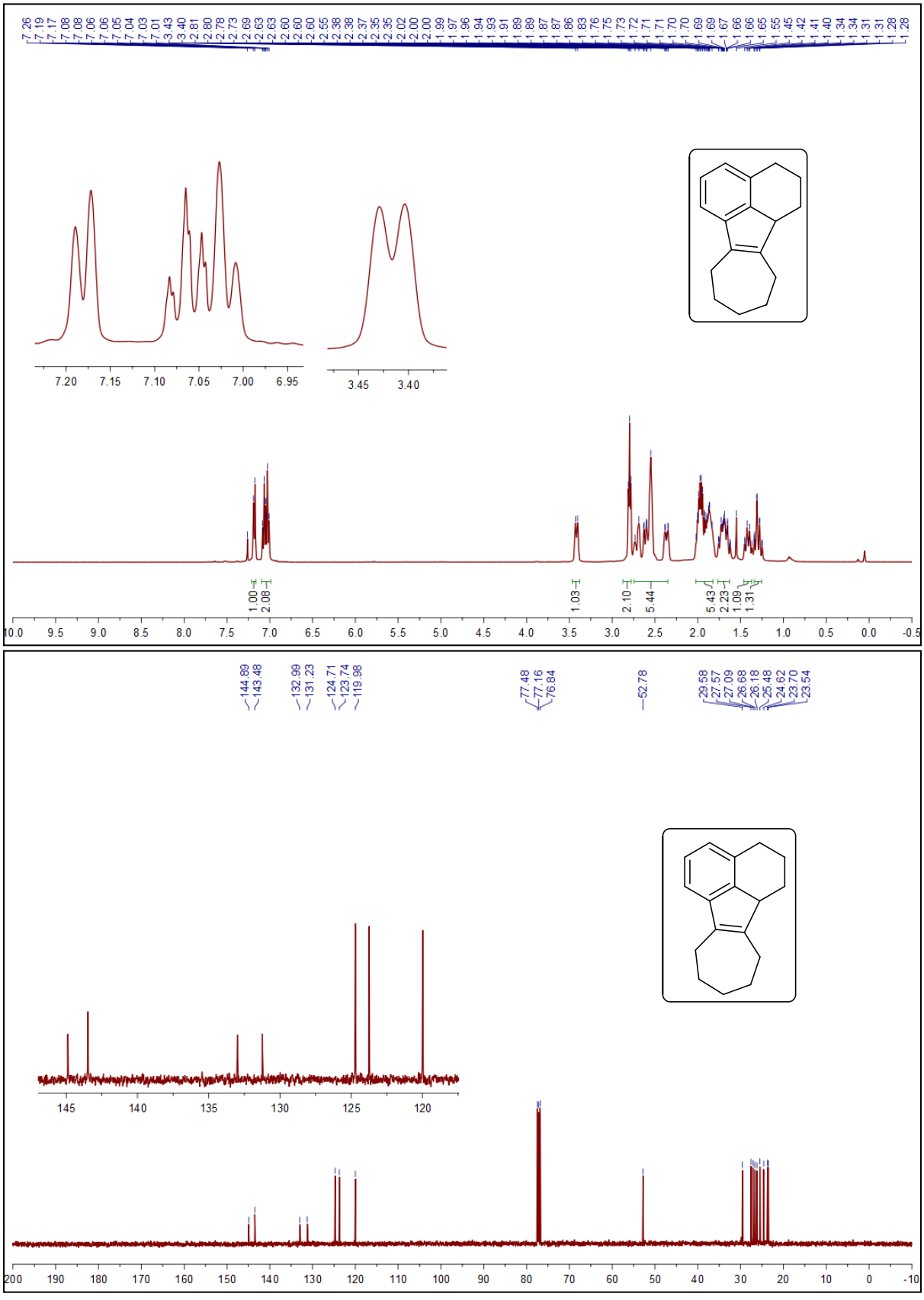
^{1}H and ^{13}C NMR Spectra of Compound **9h**. (Solvent $CDCl_3$, 400 MHz)



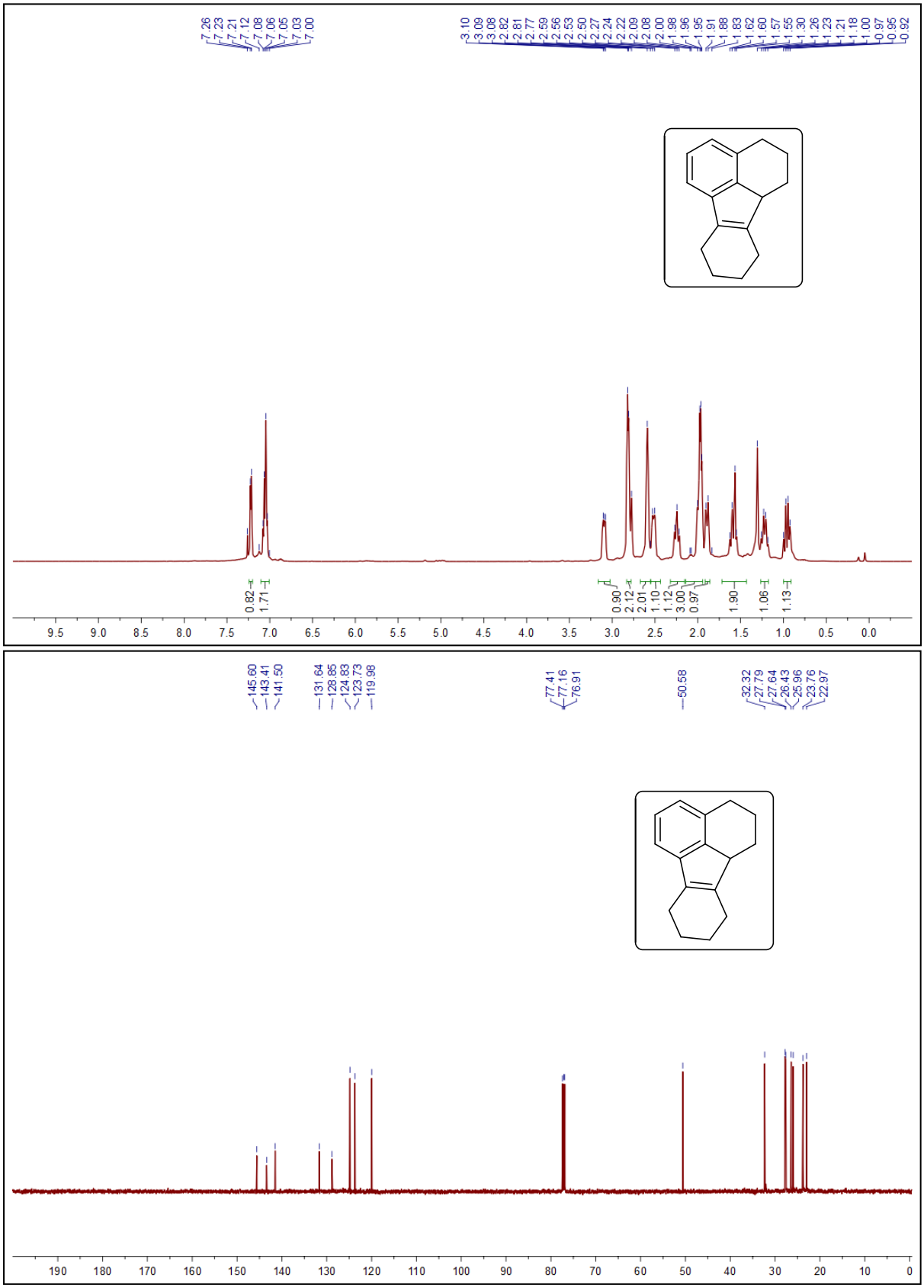
^{1}H and ^{13}C NMR Spectra of Compound **9i**. (Solvent $CDCl_3$, 400 MHz)



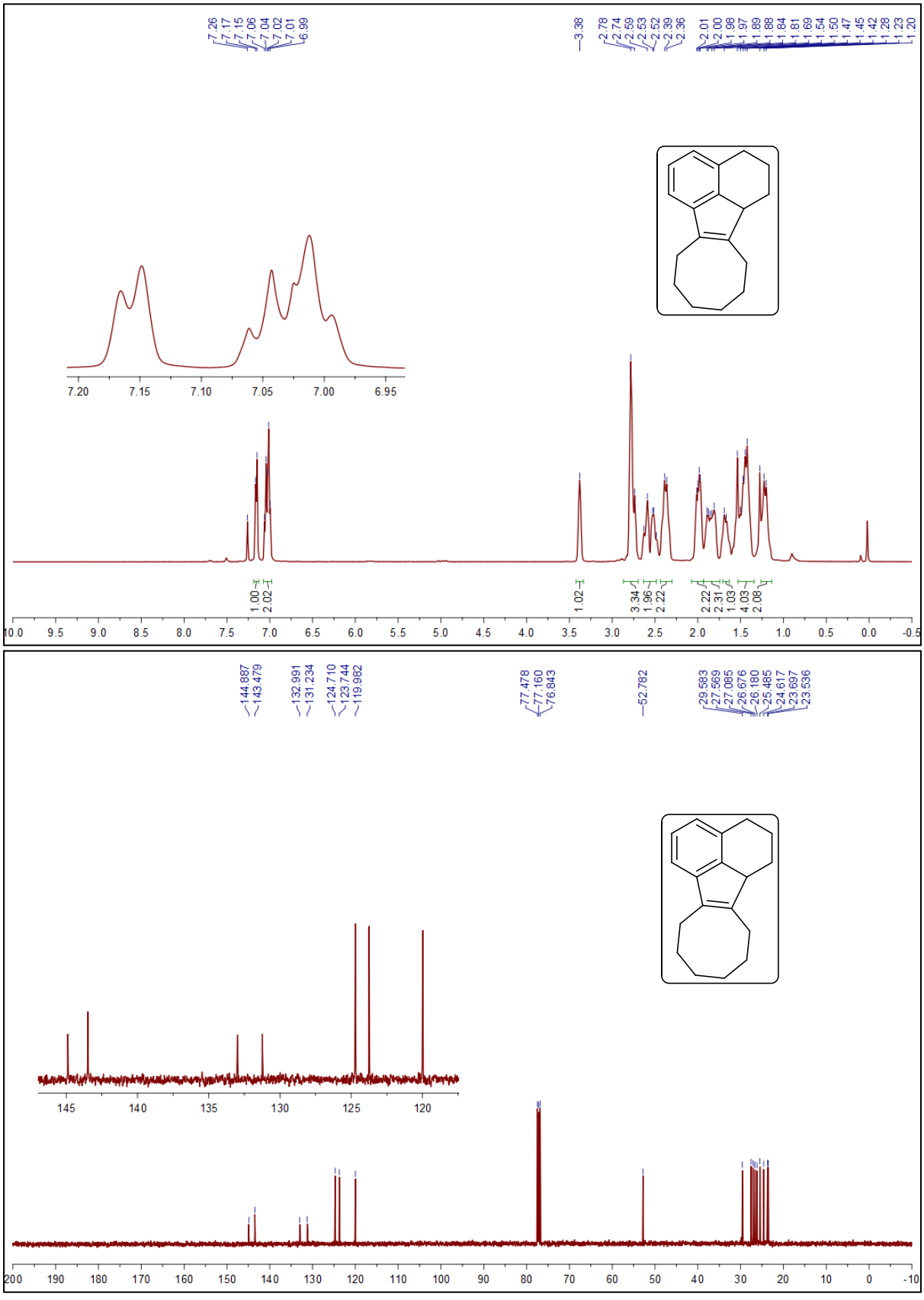
^{1}H and ^{13}C NMR Spectra of Compound **11a**. (Solvent $CDCl_3$, 400 MHz)



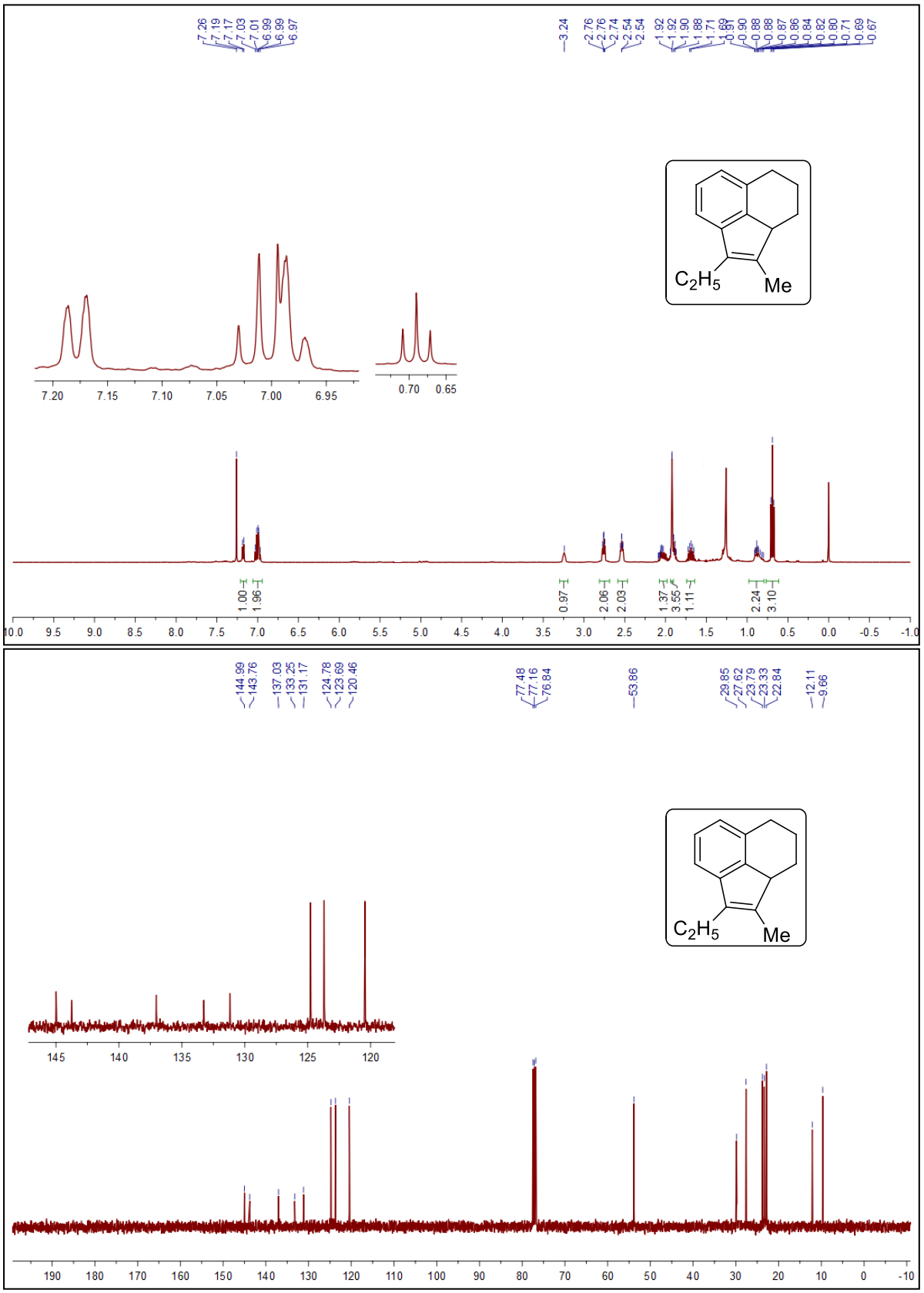
^{1}H and ^{13}C NMR Spectra of Compound **11b**. (Solvent $CDCl_3$, 400 MHz)



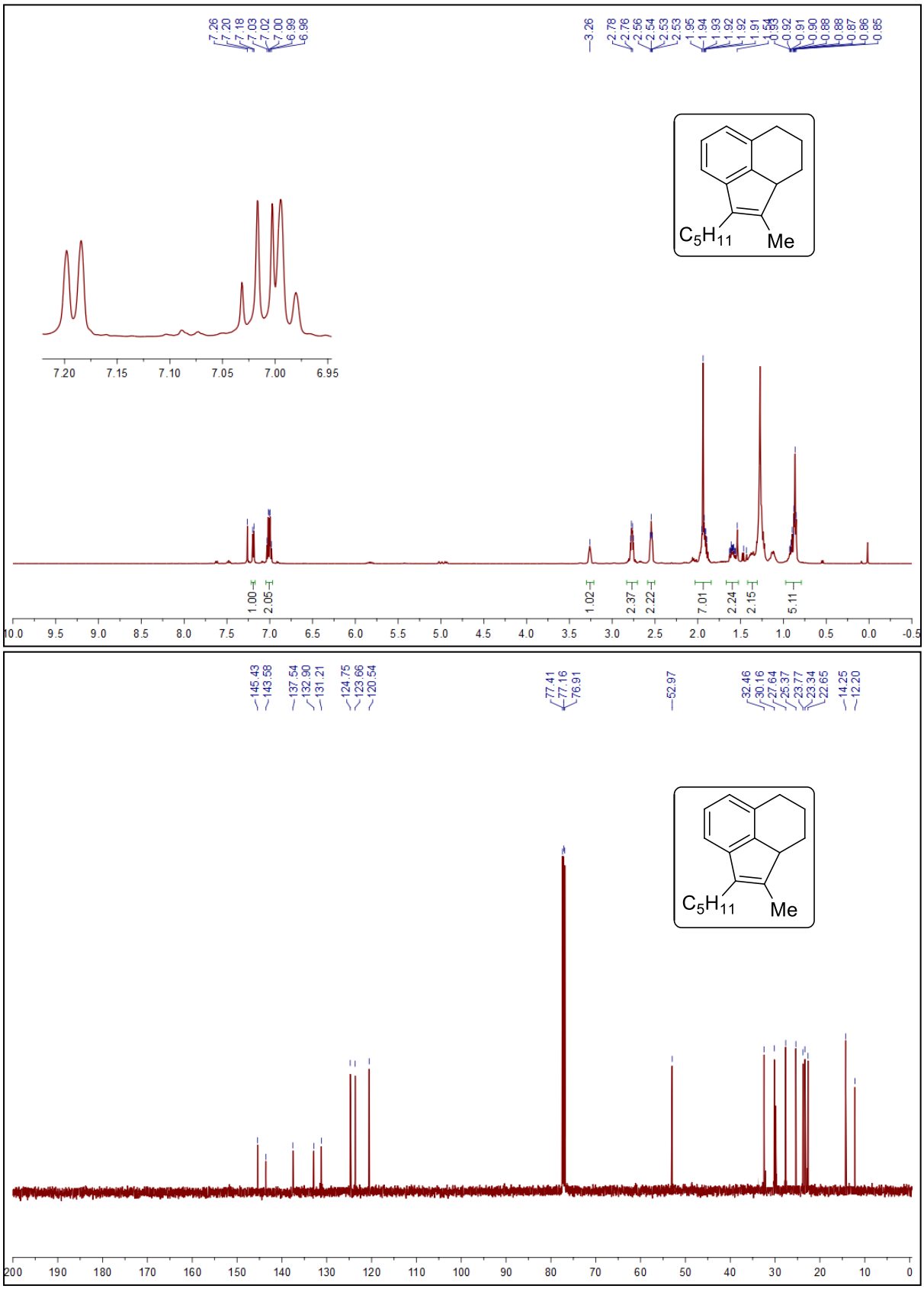
^{1}H and ^{13}C NMR Spectra of Compound **11c**. (Solvent $CDCl_3$, 400 MHz)



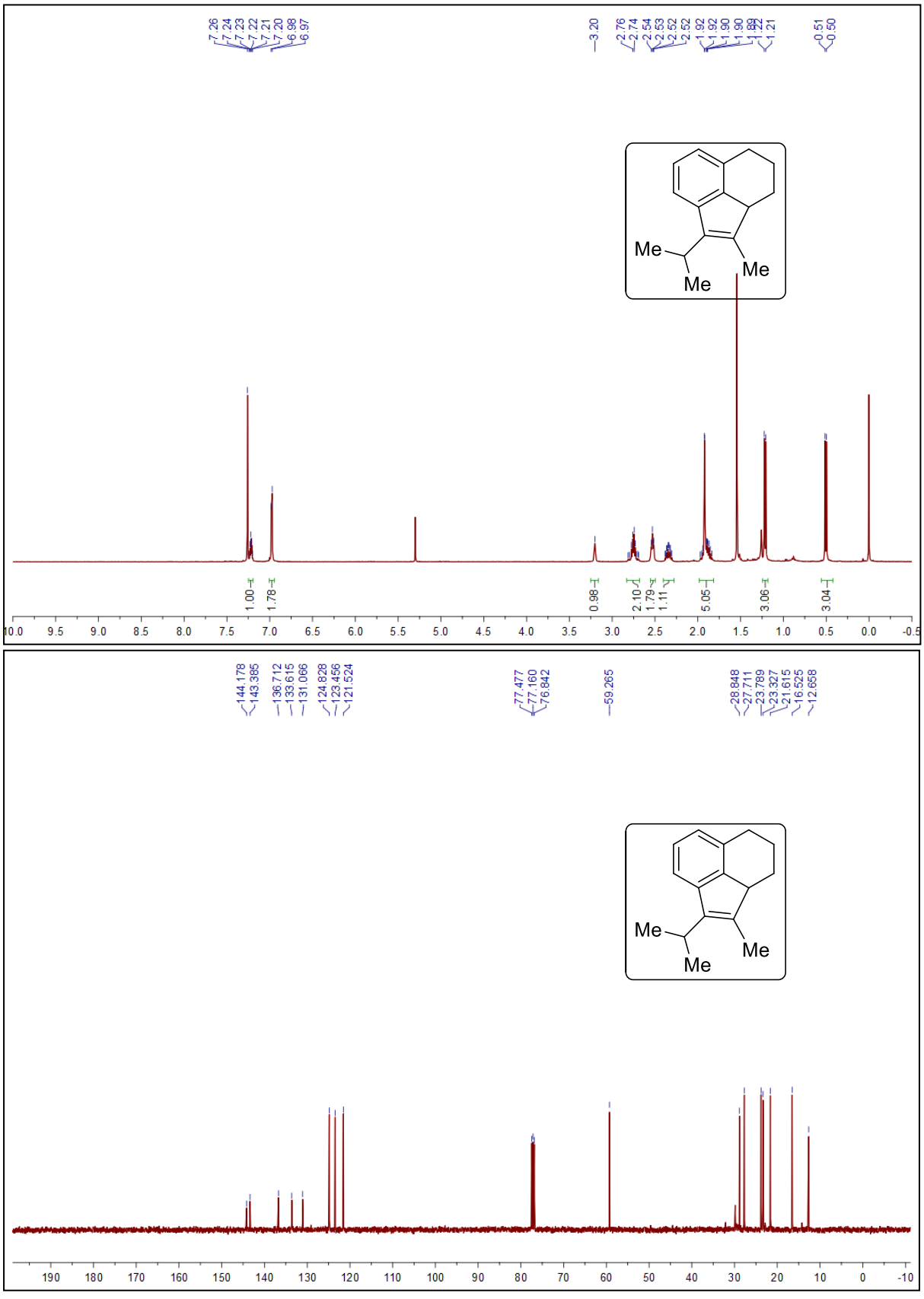
^{1}H and ^{13}C NMR Spectra of Compound **11d**. (Solvent $CDCl_3$, 400 MHz)



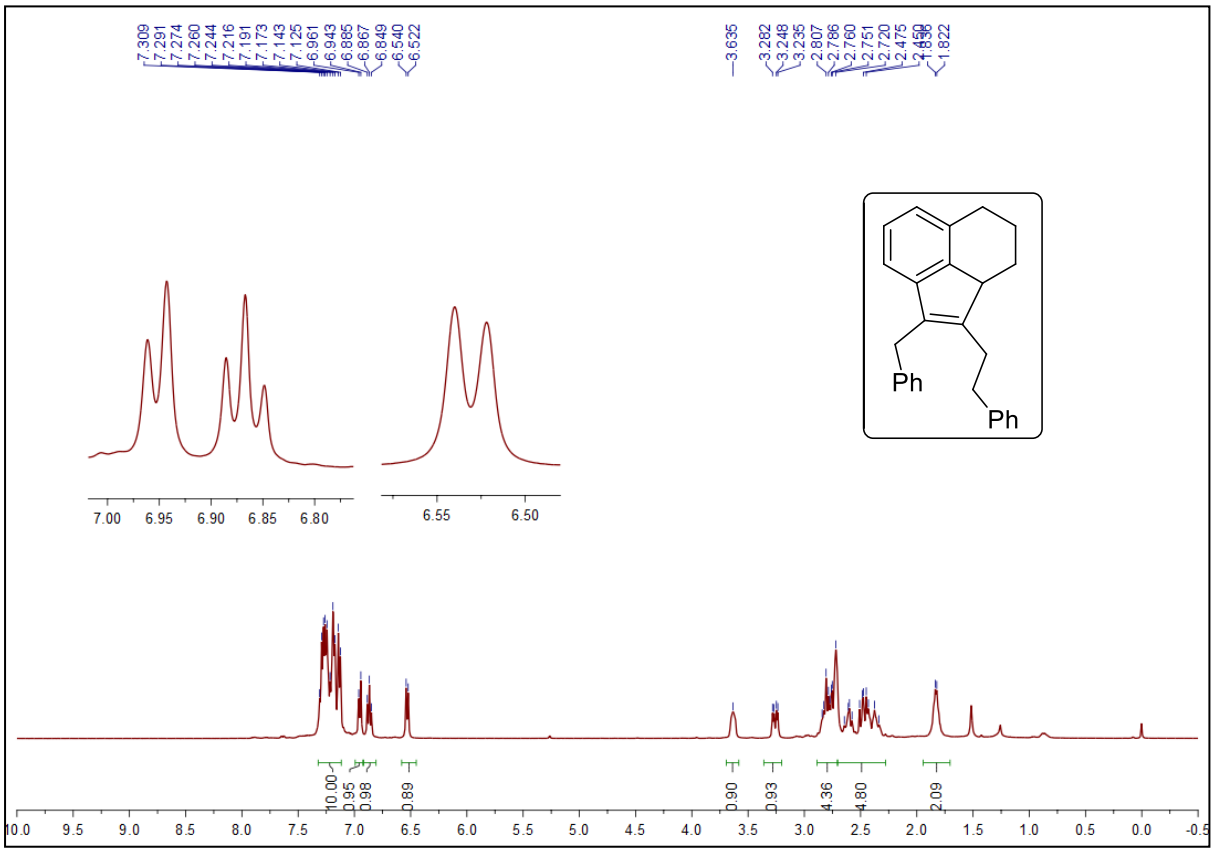
^{1}H and ^{13}C NMR Spectra of Compound **11e**. (Solvent $CDCl_3$, 400 MHz)

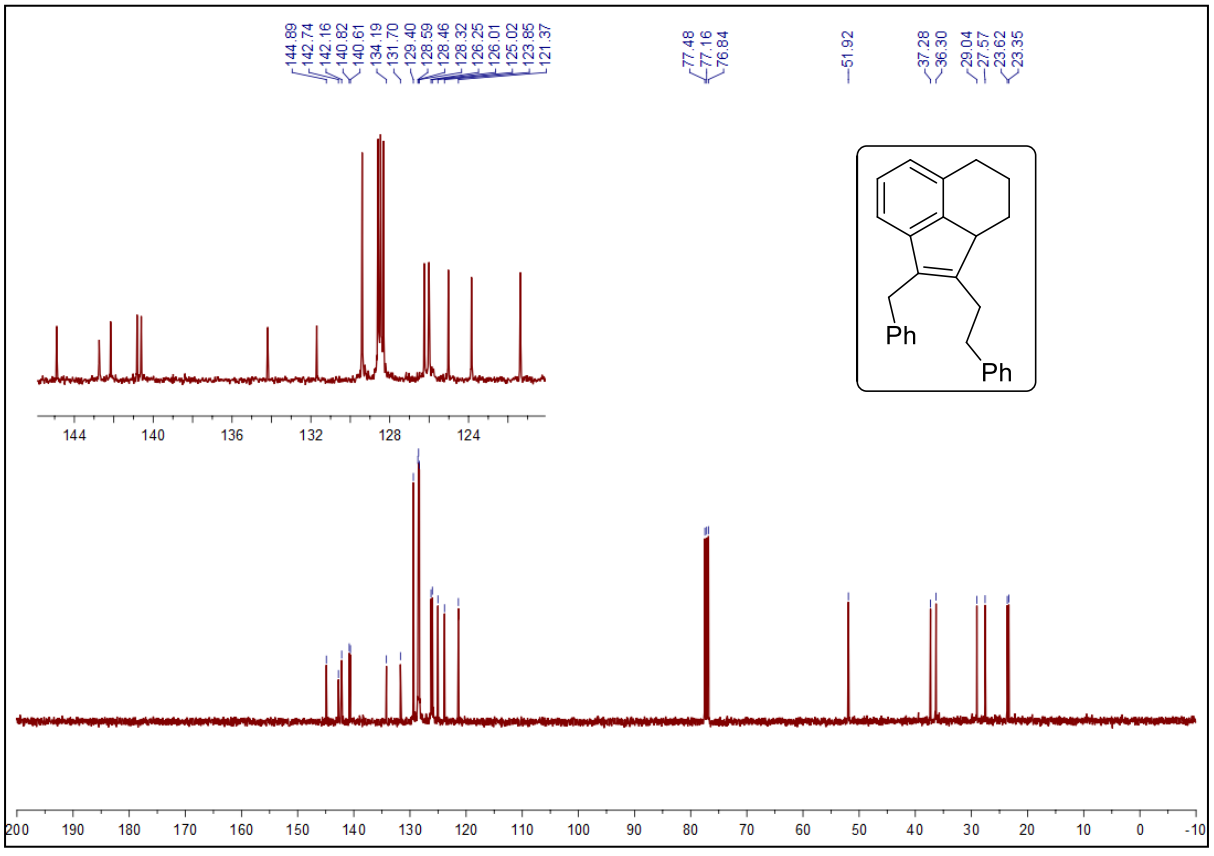


^{1}H and ^{13}C NMR Spectra of Compound **11f**. (Solvent $CDCl_3$, 400 MHz)

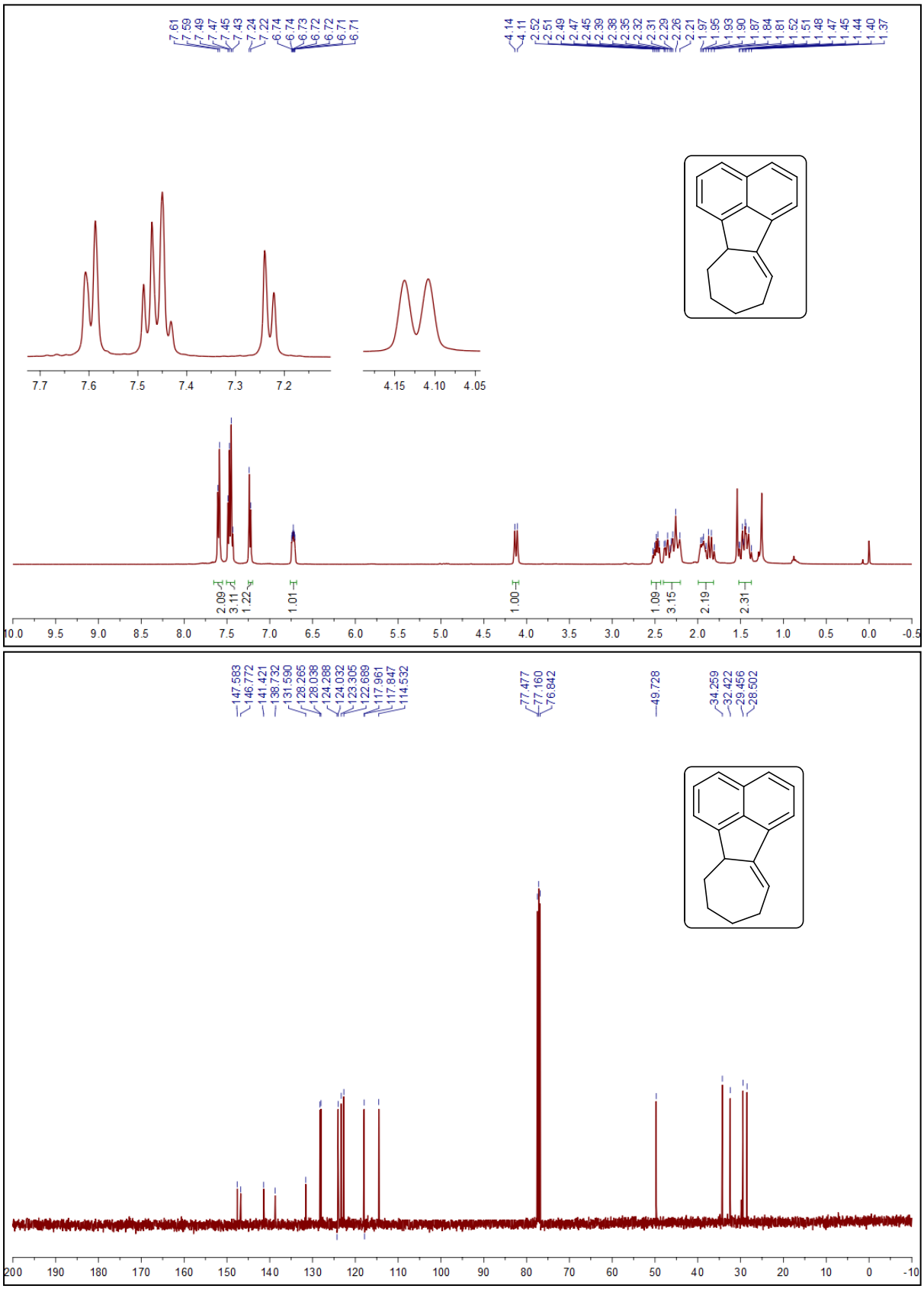


^{1}H and ^{13}C NMR Spectra of Compound **11g**. (Solvent $CDCl_3$, 400 MHz)

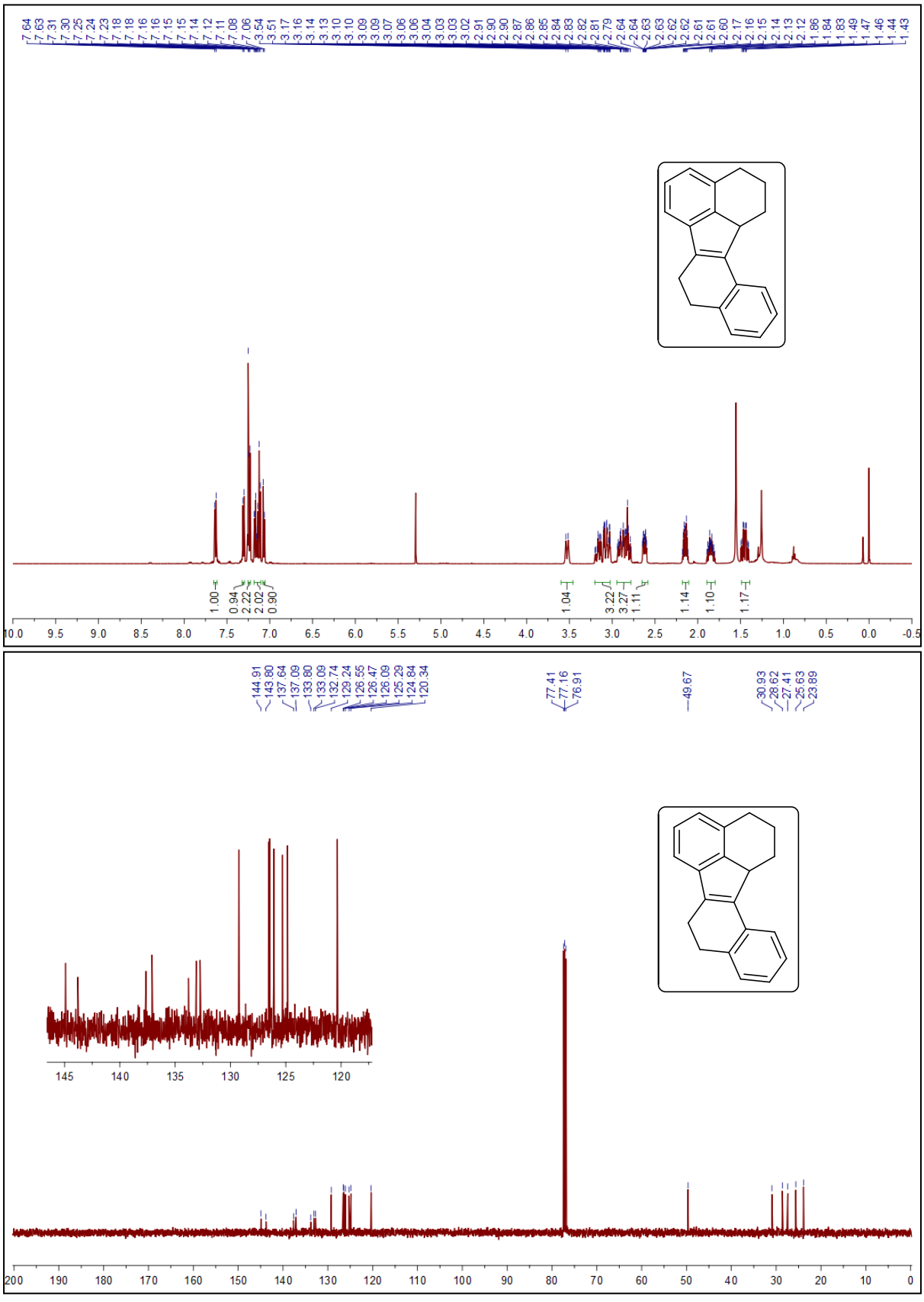




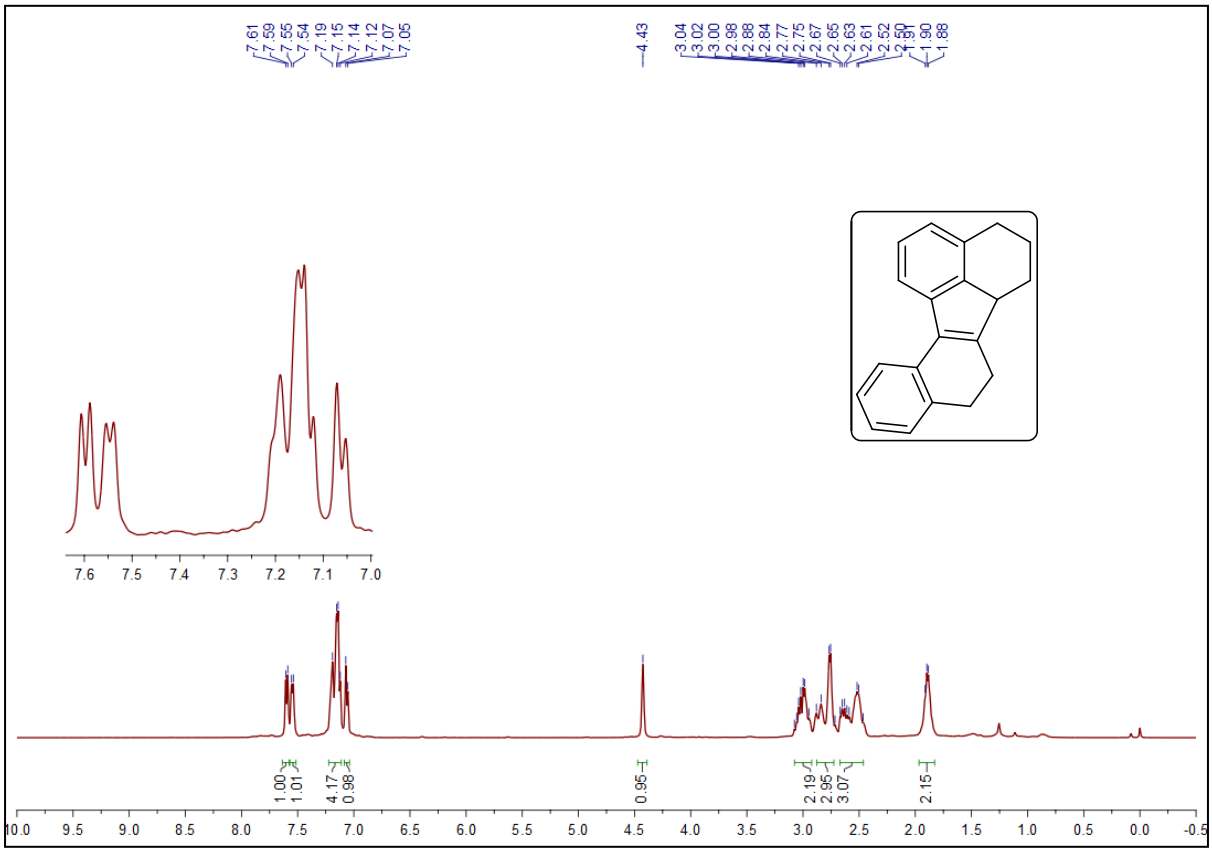
^{1}H and ^{13}C NMR Spectra of Compound **12a**. (Solvent $CDCl_3$, 400 MHz)

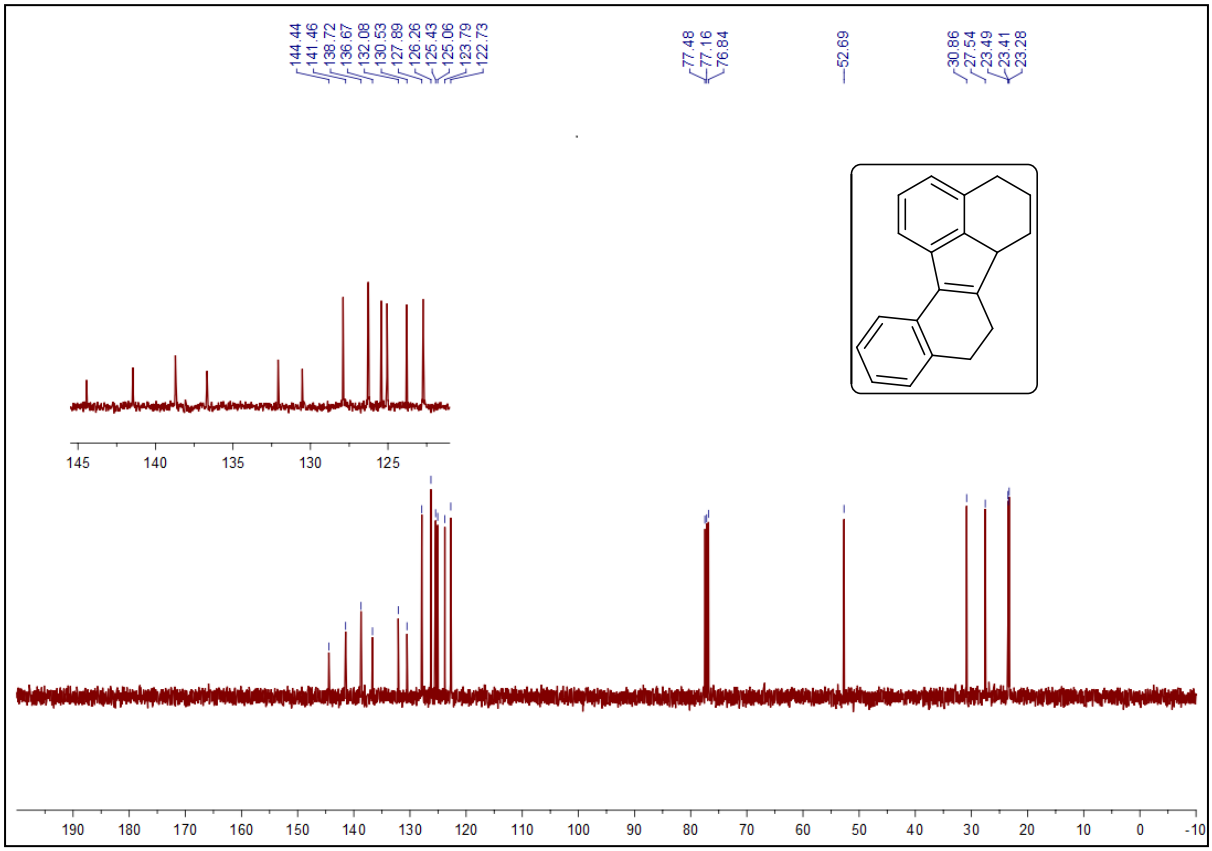


^{1}H and ^{13}C NMR Spectra of Compound **13**. (Solvent $CDCl_3$, 400 MHz)

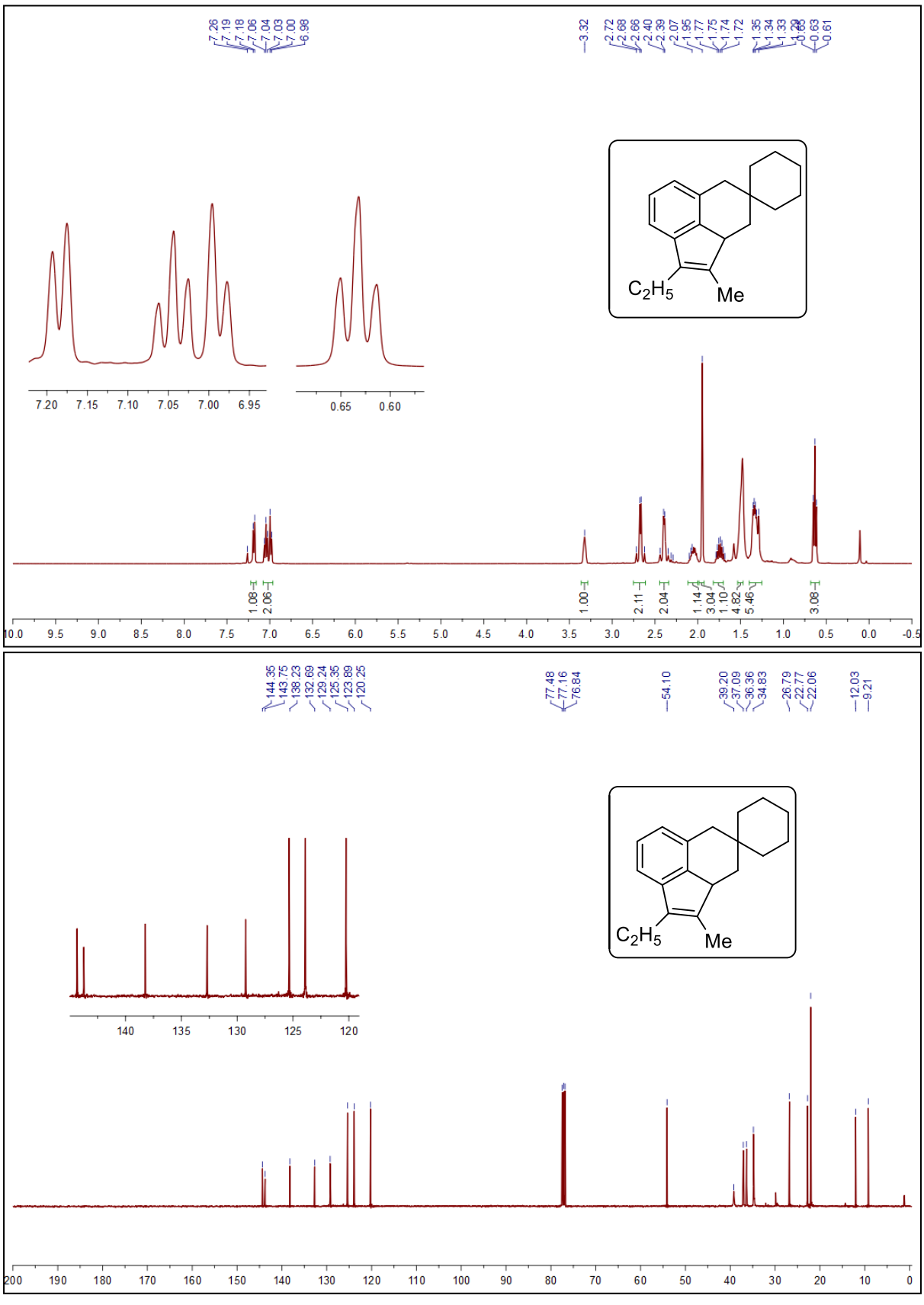


^{1}H and ^{13}C NMR Spectra of Compound **14**. (Solvent $CDCl_3$, 400 MHz)

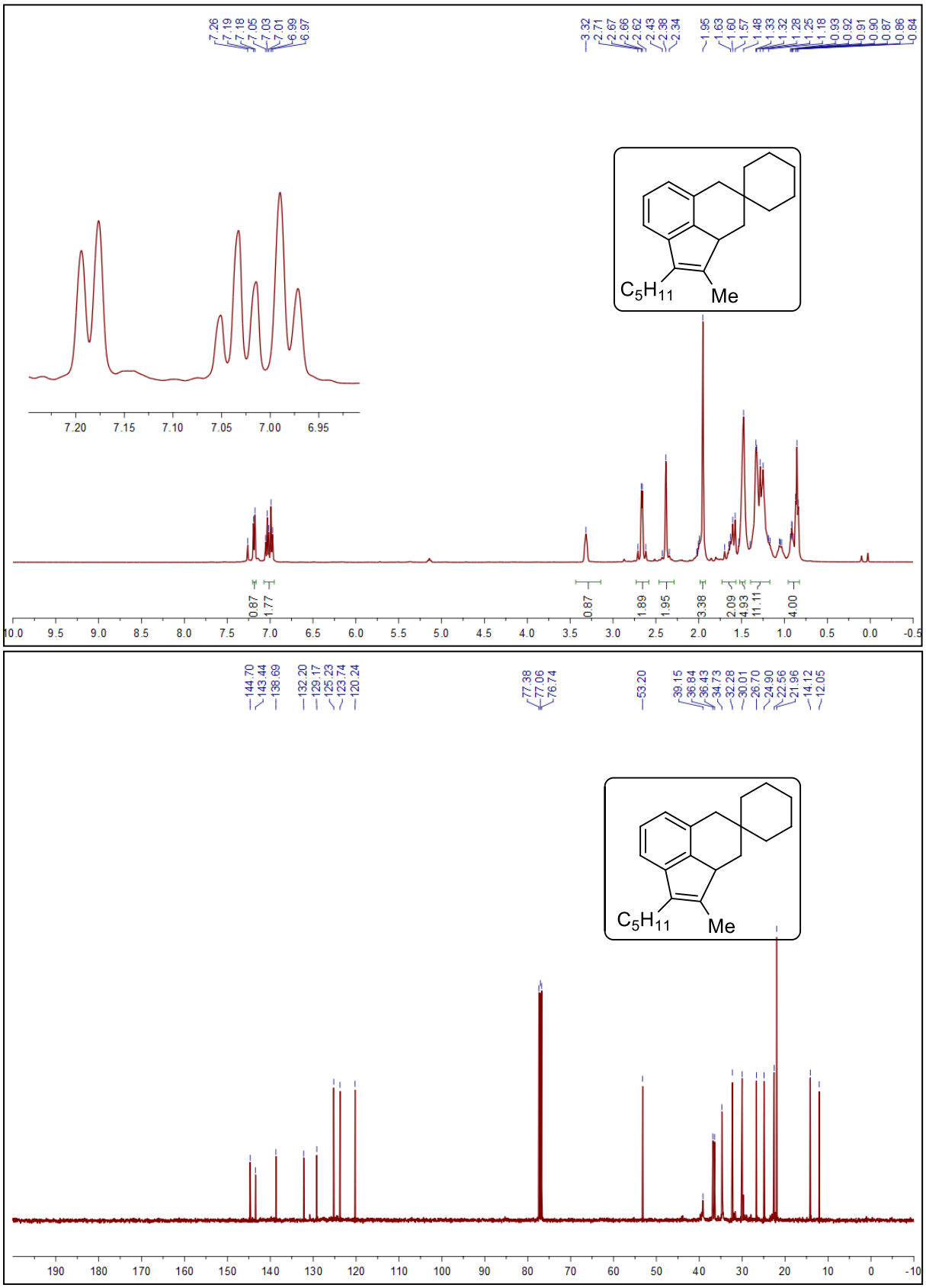




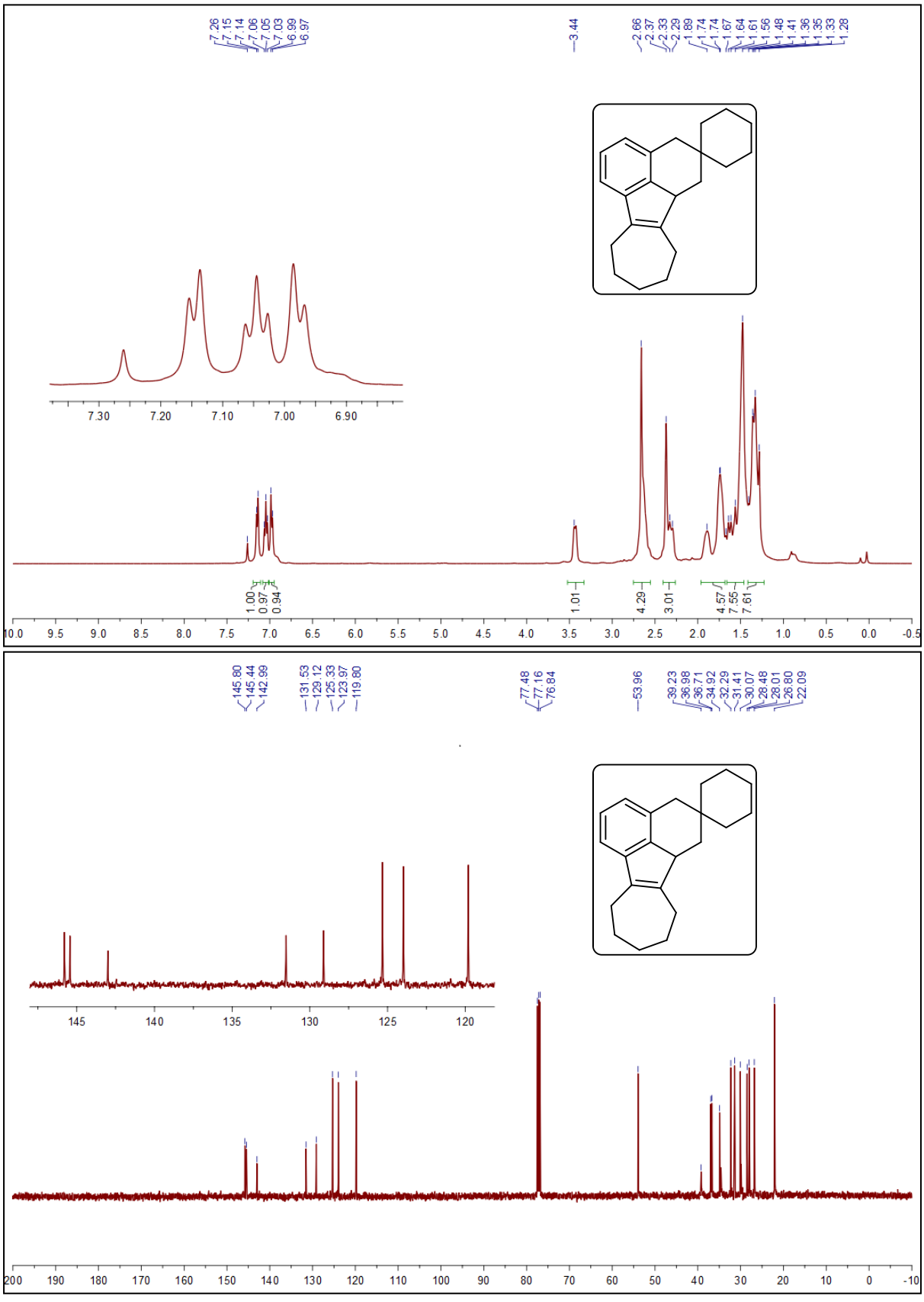
^{1}H and ^{13}C NMR Spectra of Compound **17a**. (Solvent $CDCl_3$, 400 MHz)



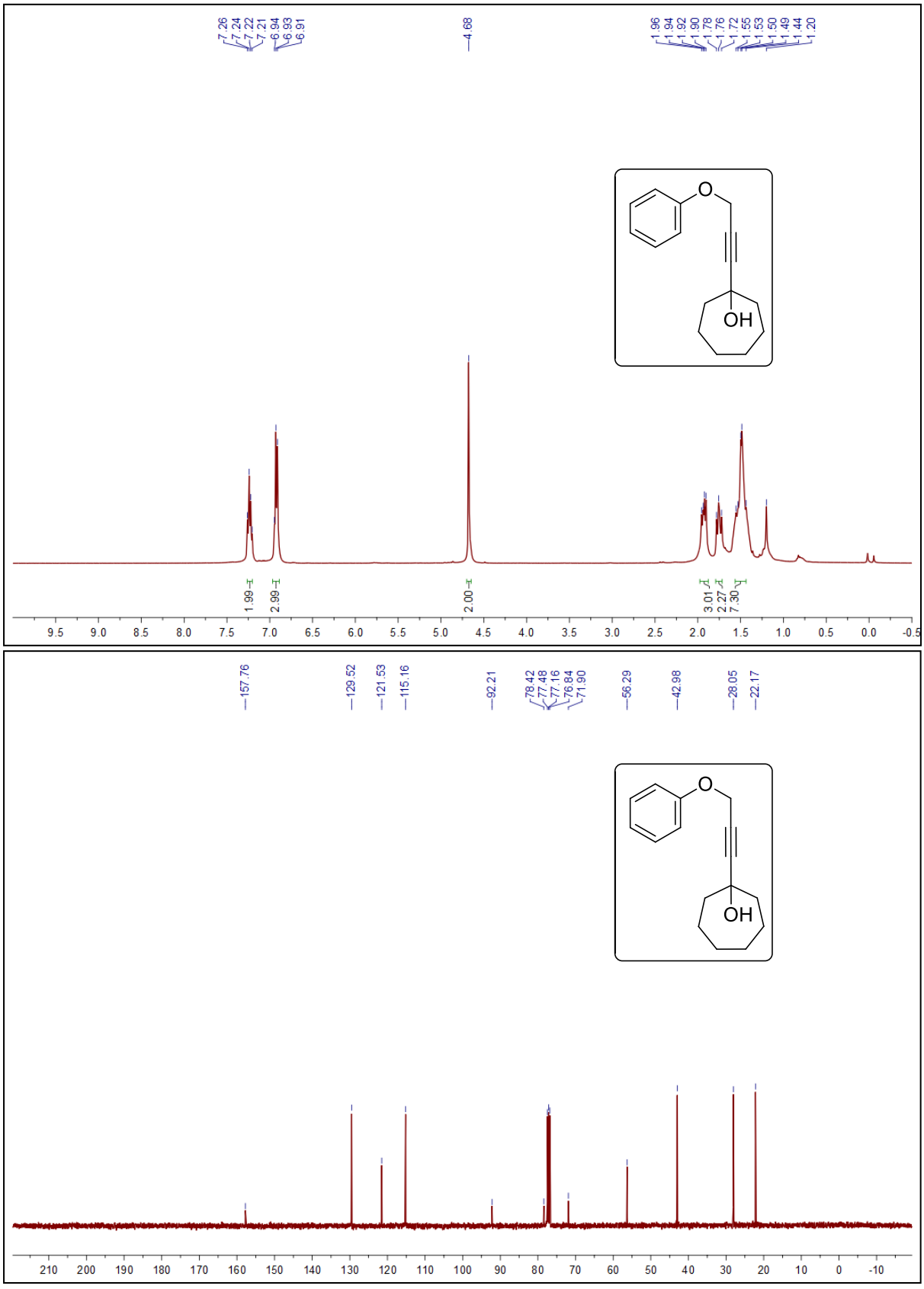
^{1}H and ^{13}C NMR Spectra of Compound **17b**. (Solvent $CDCl_3$, 400 MHz)



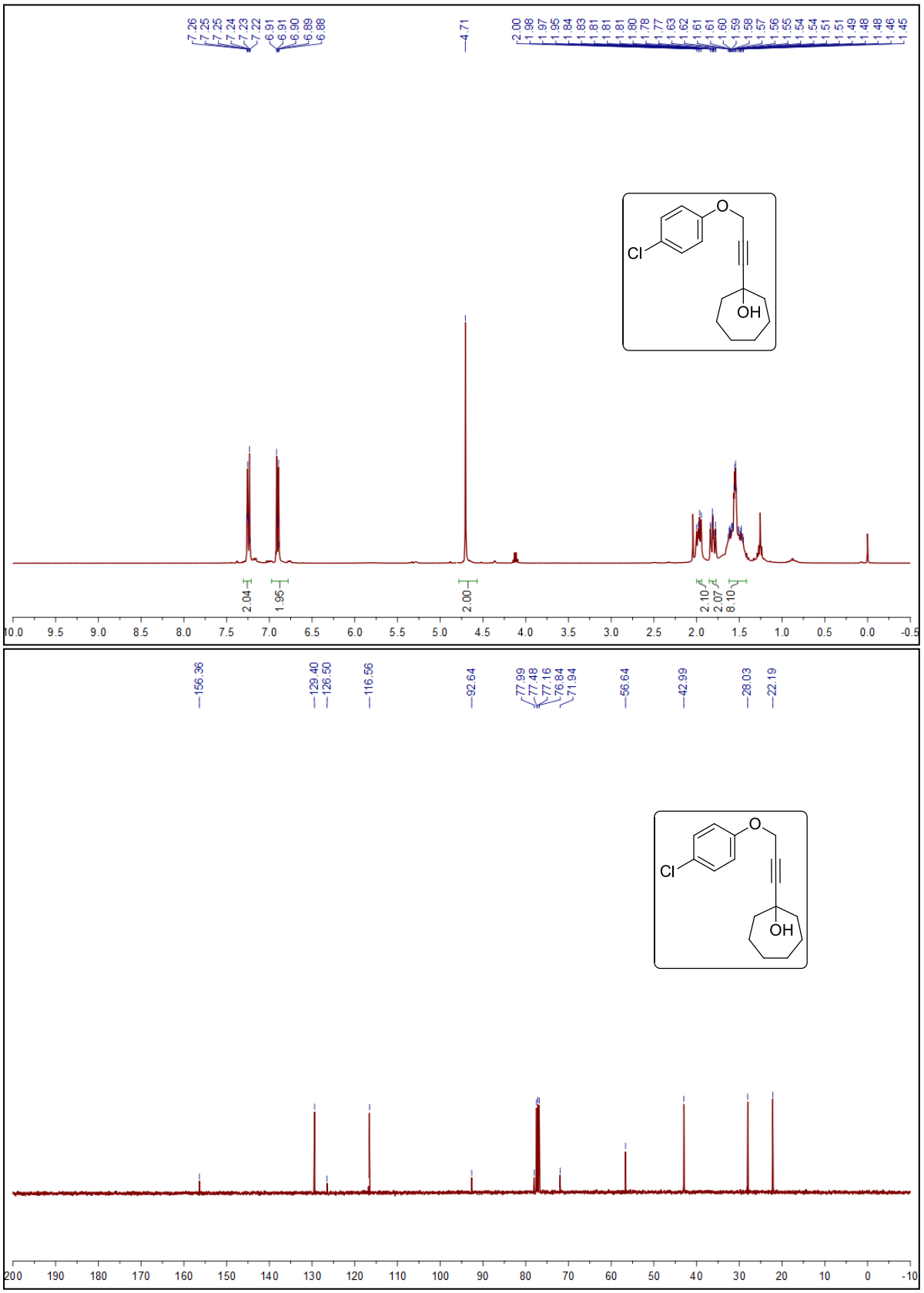
^{1}H and ^{13}C NMR Spectra of Compound **17c**. (Solvent $CDCl_3$, 400 MHz)



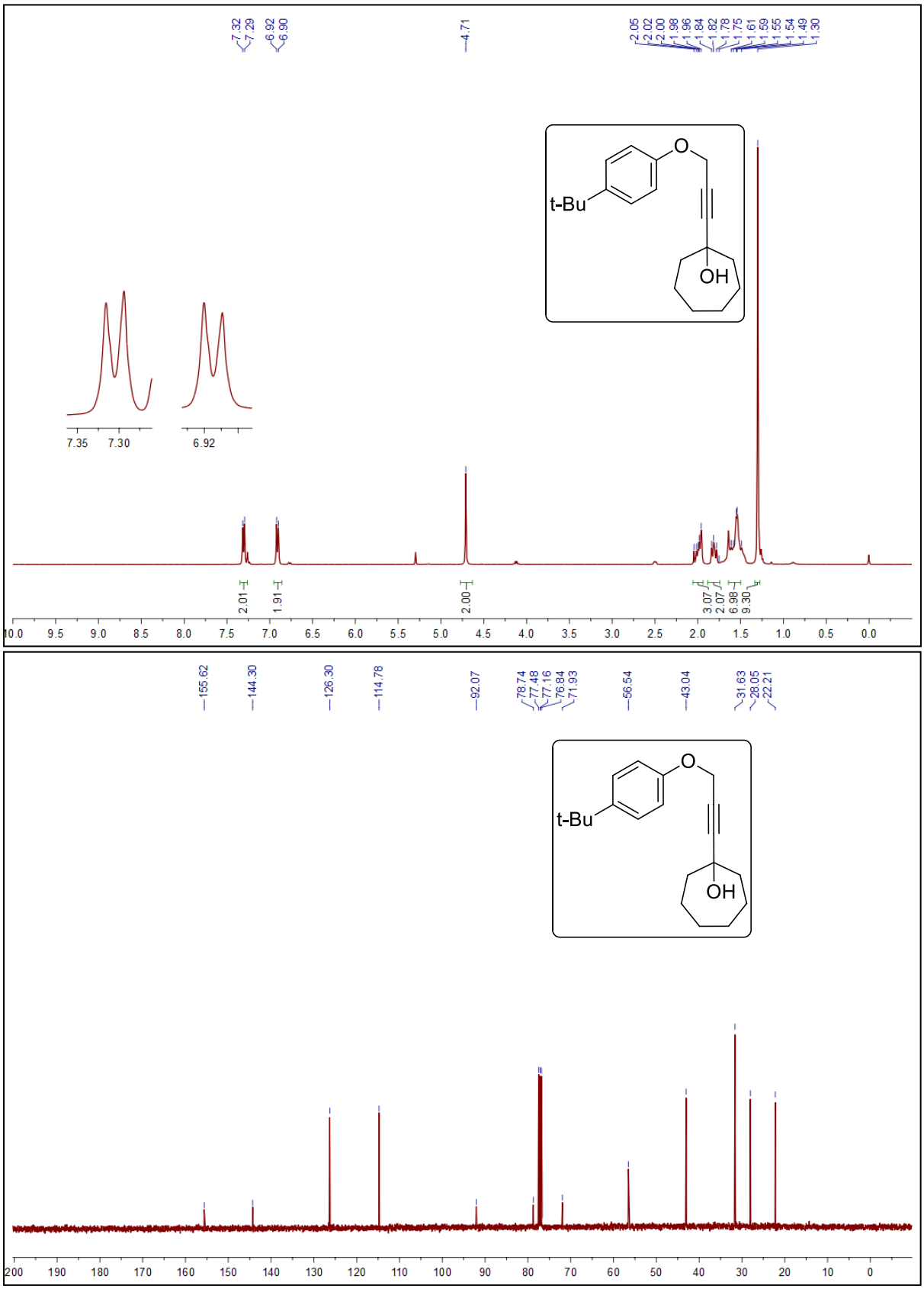
^{1}H and ^{13}C NMR Spectra of Compound **1a**. (Solvent $CDCl_3$, 400 MHz)



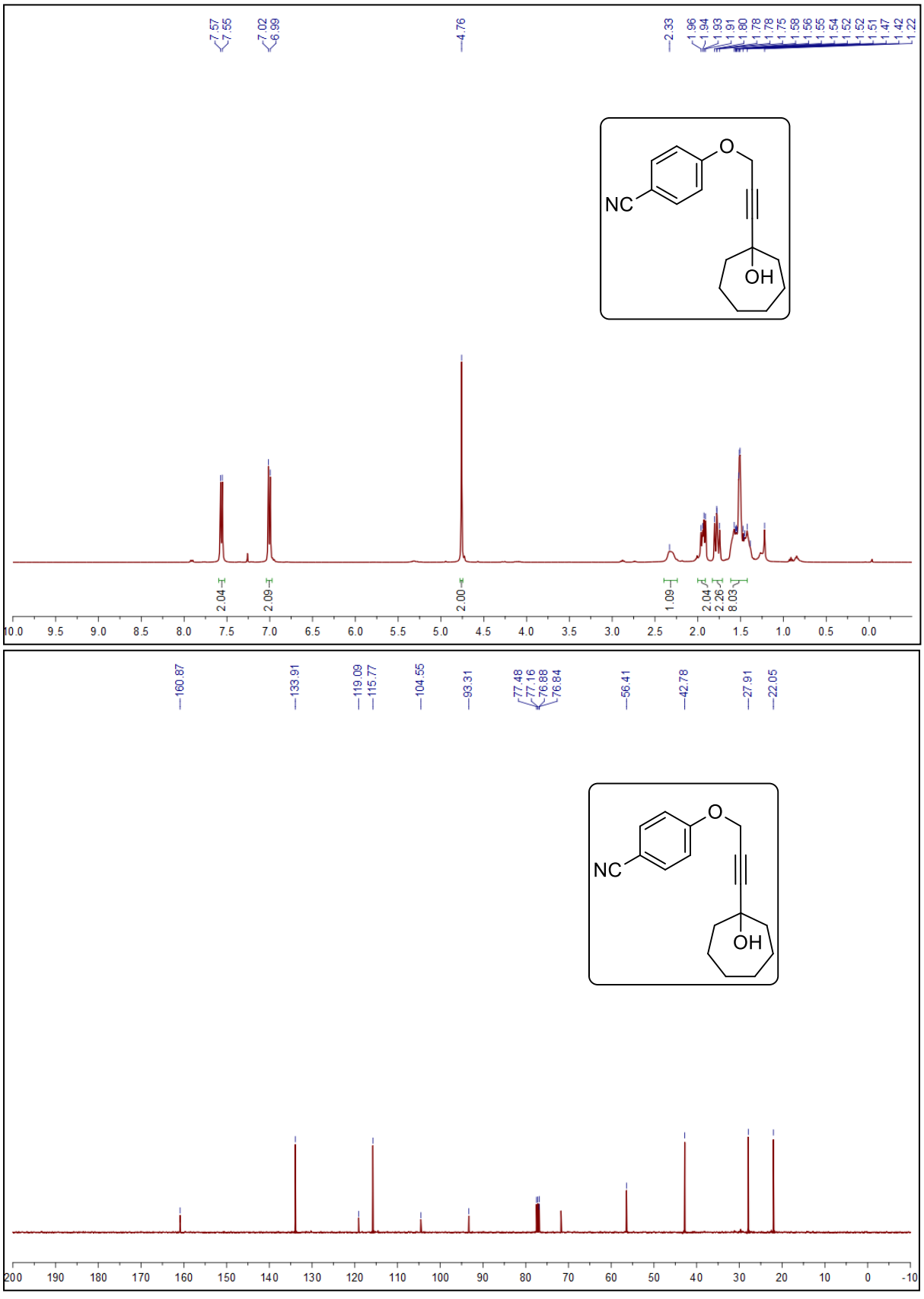
^{1}H and ^{13}C NMR Spectra of Compound **1b**. (Solvent $CDCl_3$, 400 MHz)



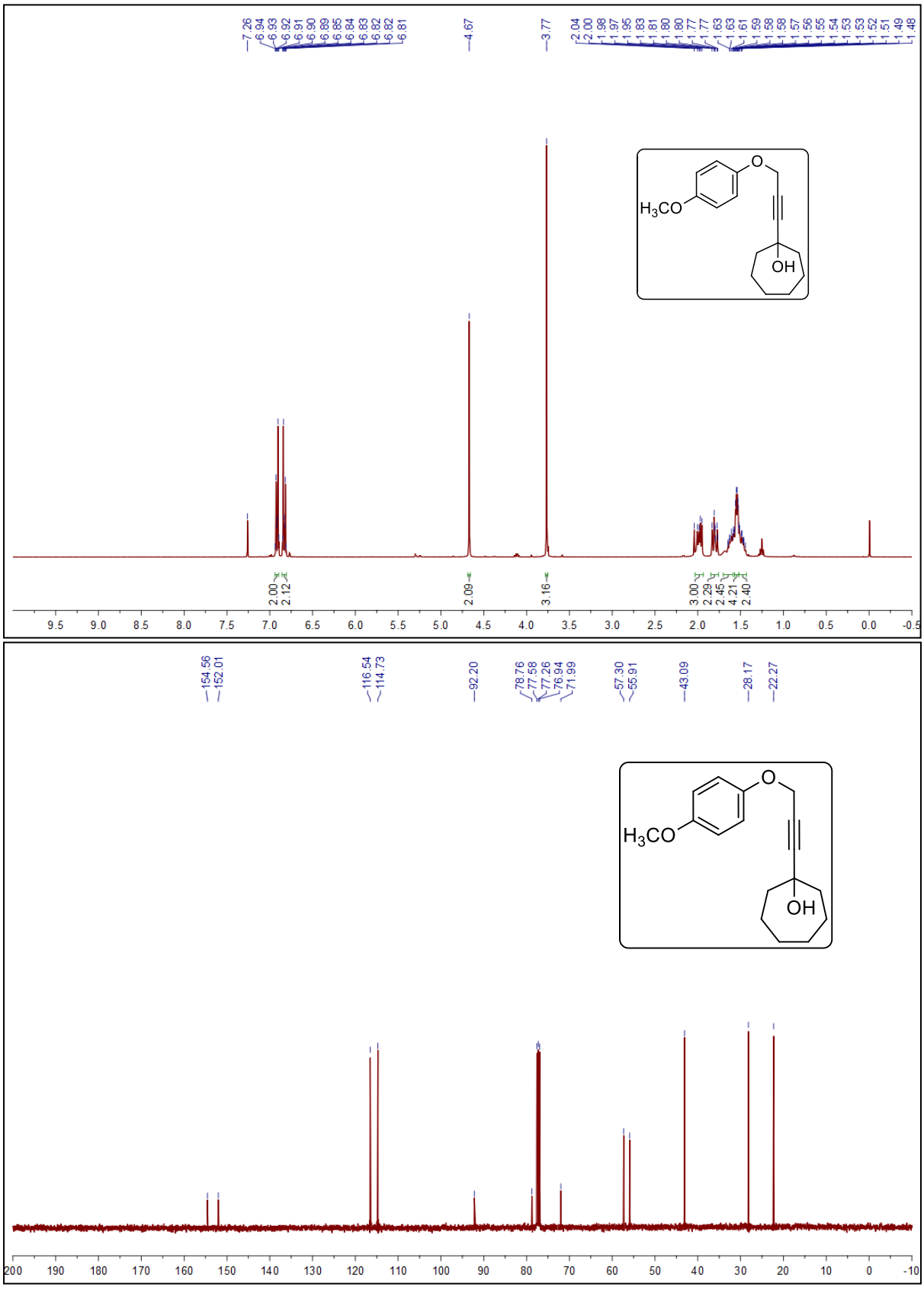
^{1}H and ^{13}C NMR Spectra of Compound **1c**. (Solvent $CDCl_3$, 400 MHz)



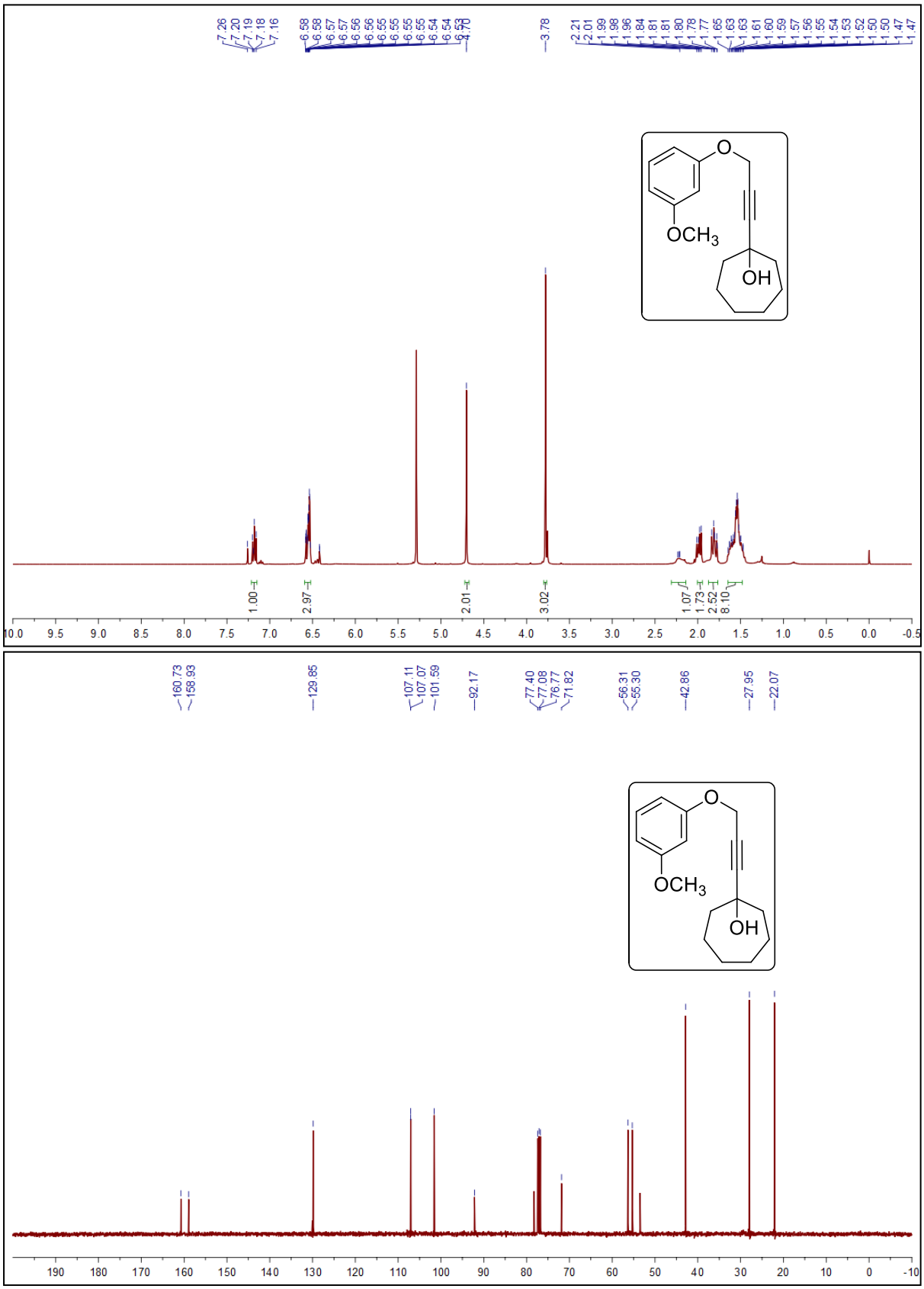
^{1}H and ^{13}C NMR Spectra of Compound **1d**. (Solvent $CDCl_3$, 400 MHz)



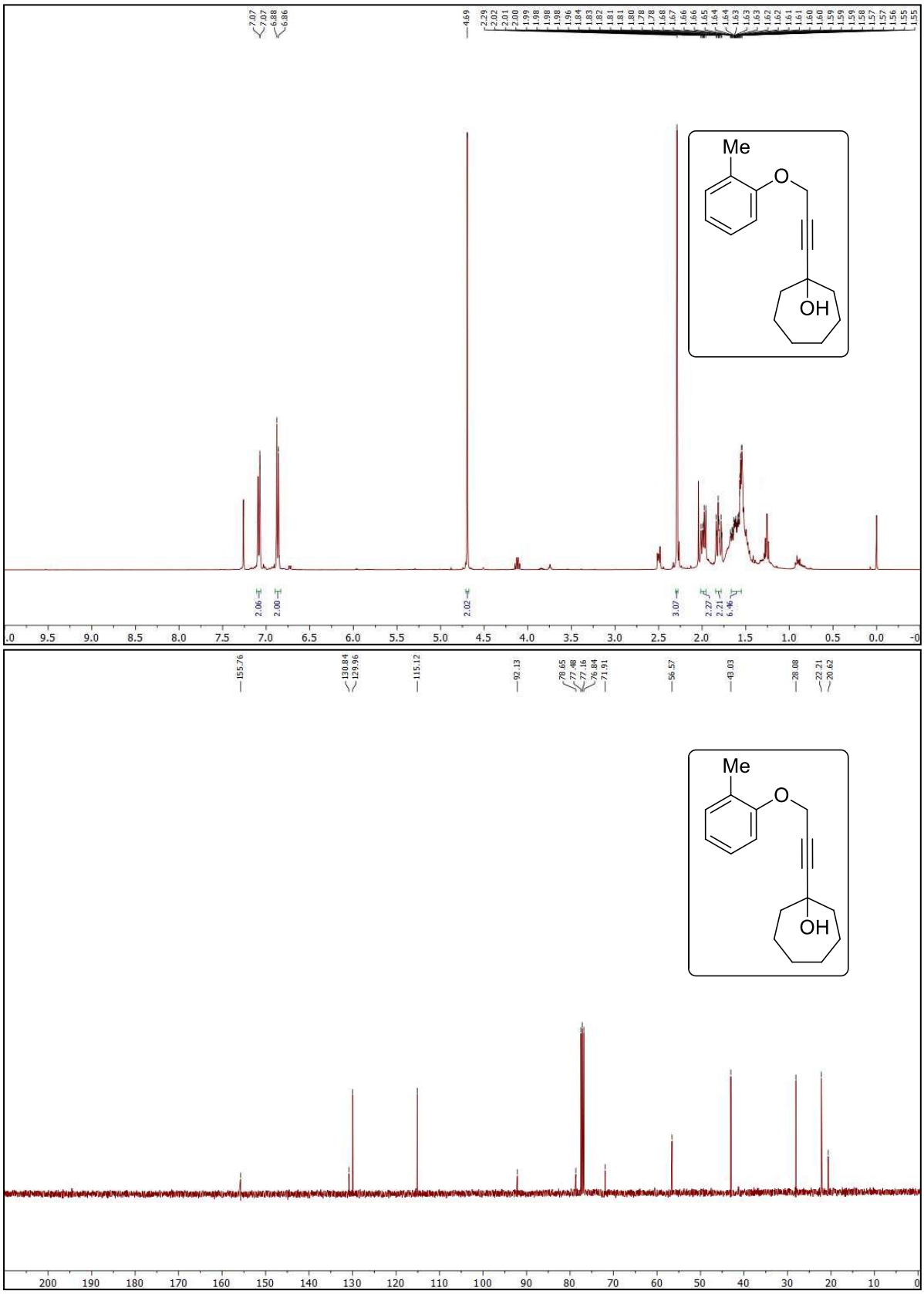
^{1}H and ^{13}C NMR Spectra of Compound **1e**. (Solvent $CDCl_3$, 400 MHz)



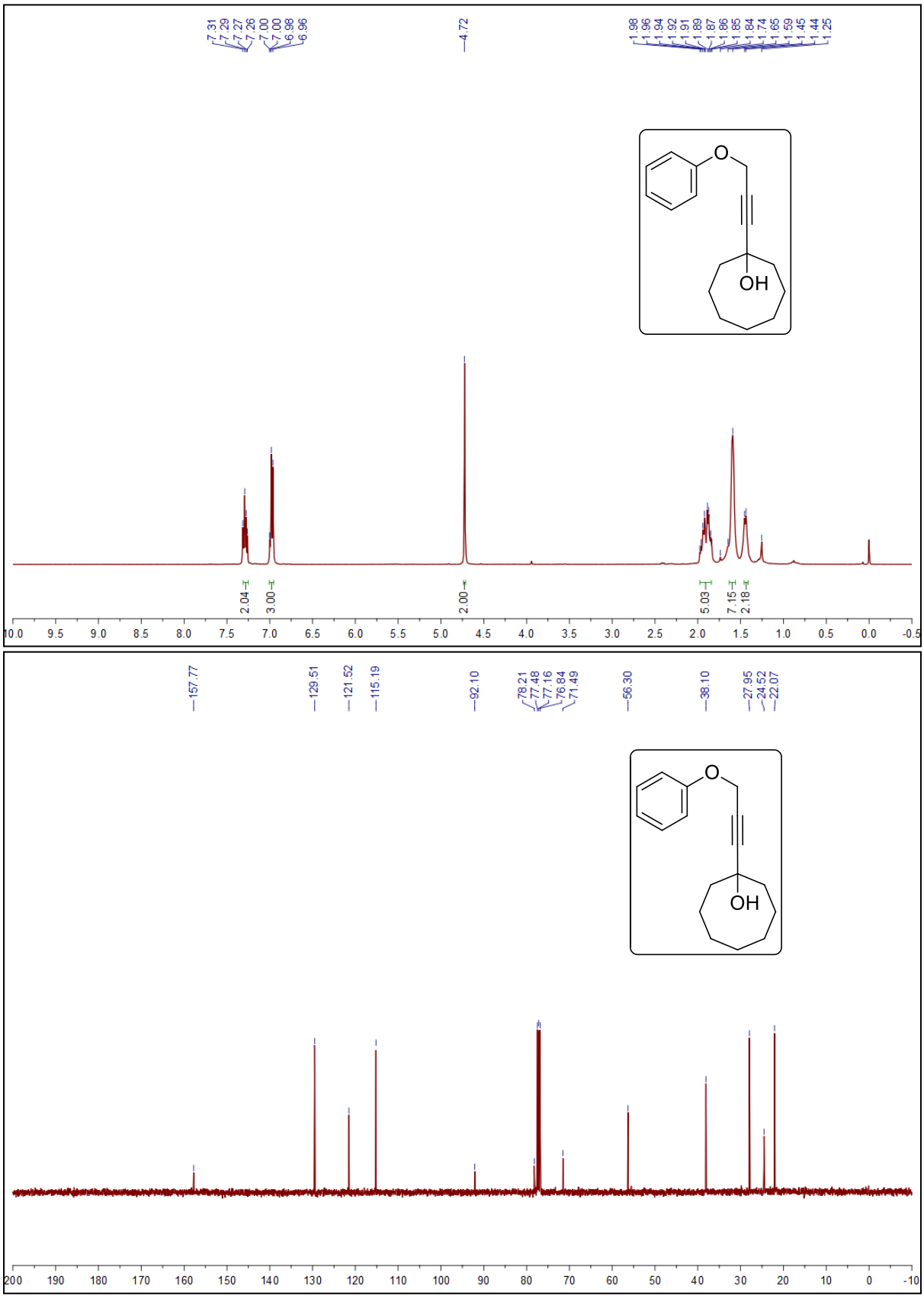
^{1}H and ^{13}C NMR Spectra of Compound **1f**. (Solvent $CDCl_3$, 400 MHz)



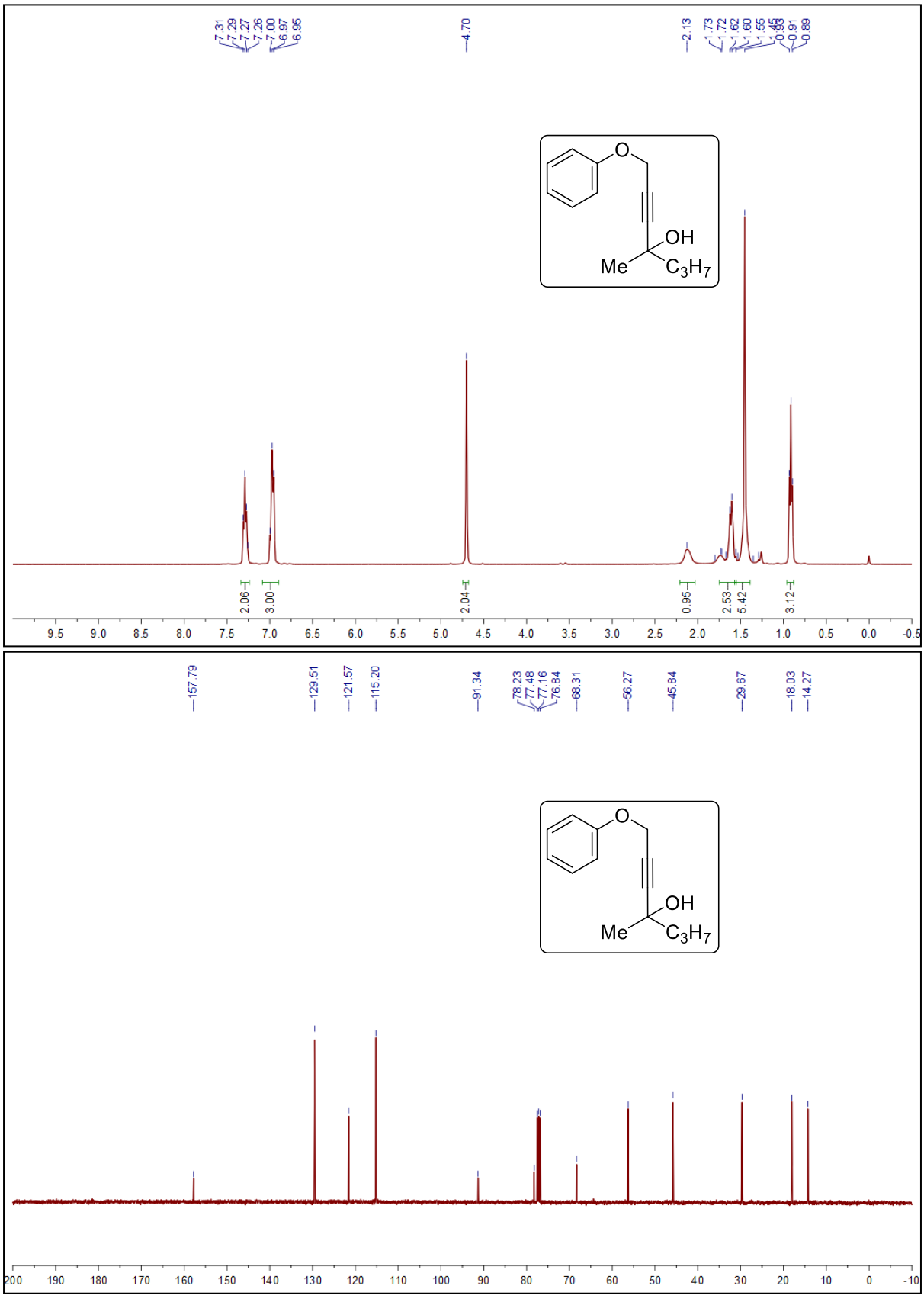
^{1}H and ^{13}C NMR Spectra of Compound **1g**. (Solvent $CDCl_3$, 400 MHz)



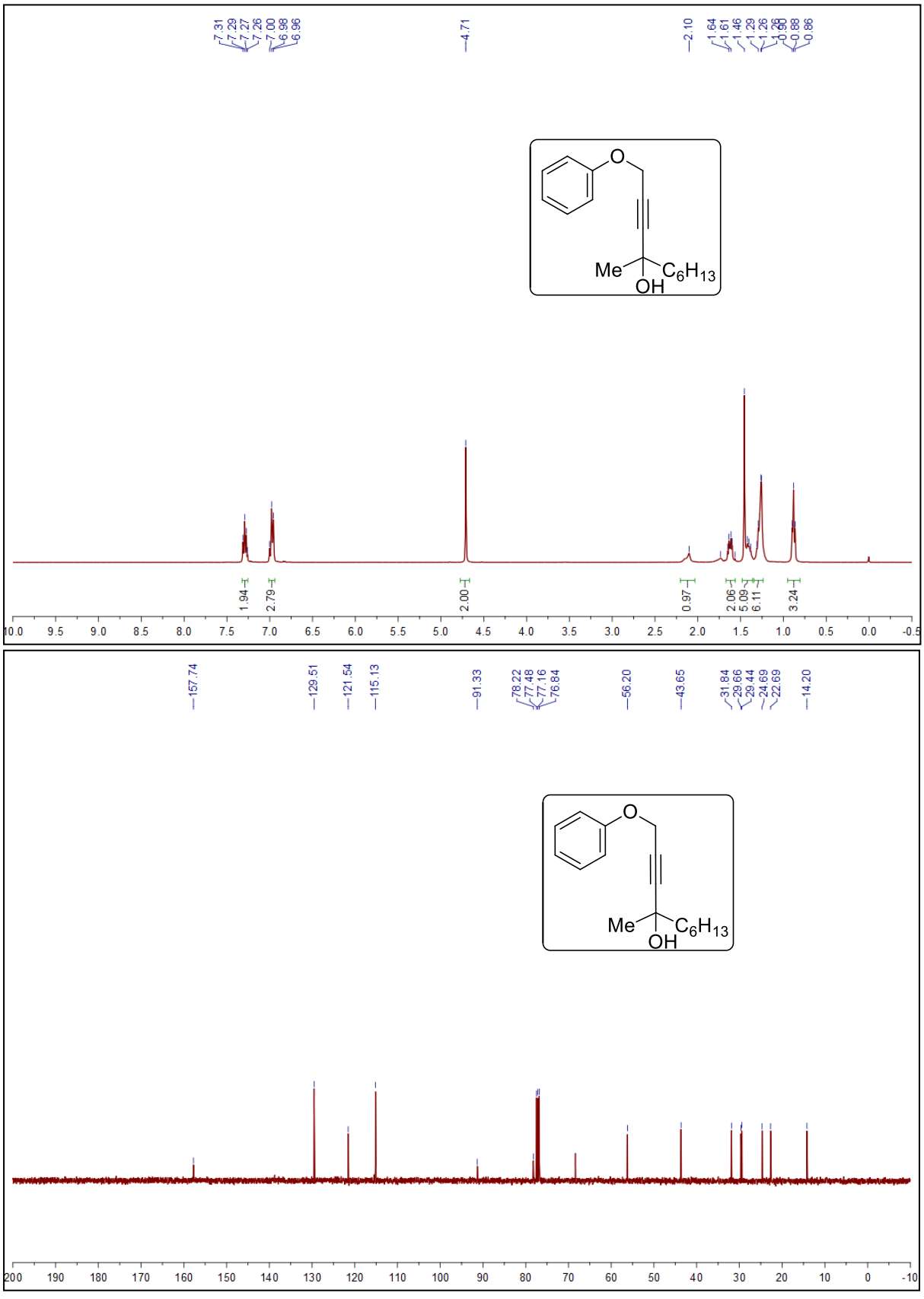
^{1}H and ^{13}C NMR Spectra of Compound **1h**. (Solvent $CDCl_3$, 400 MHz)



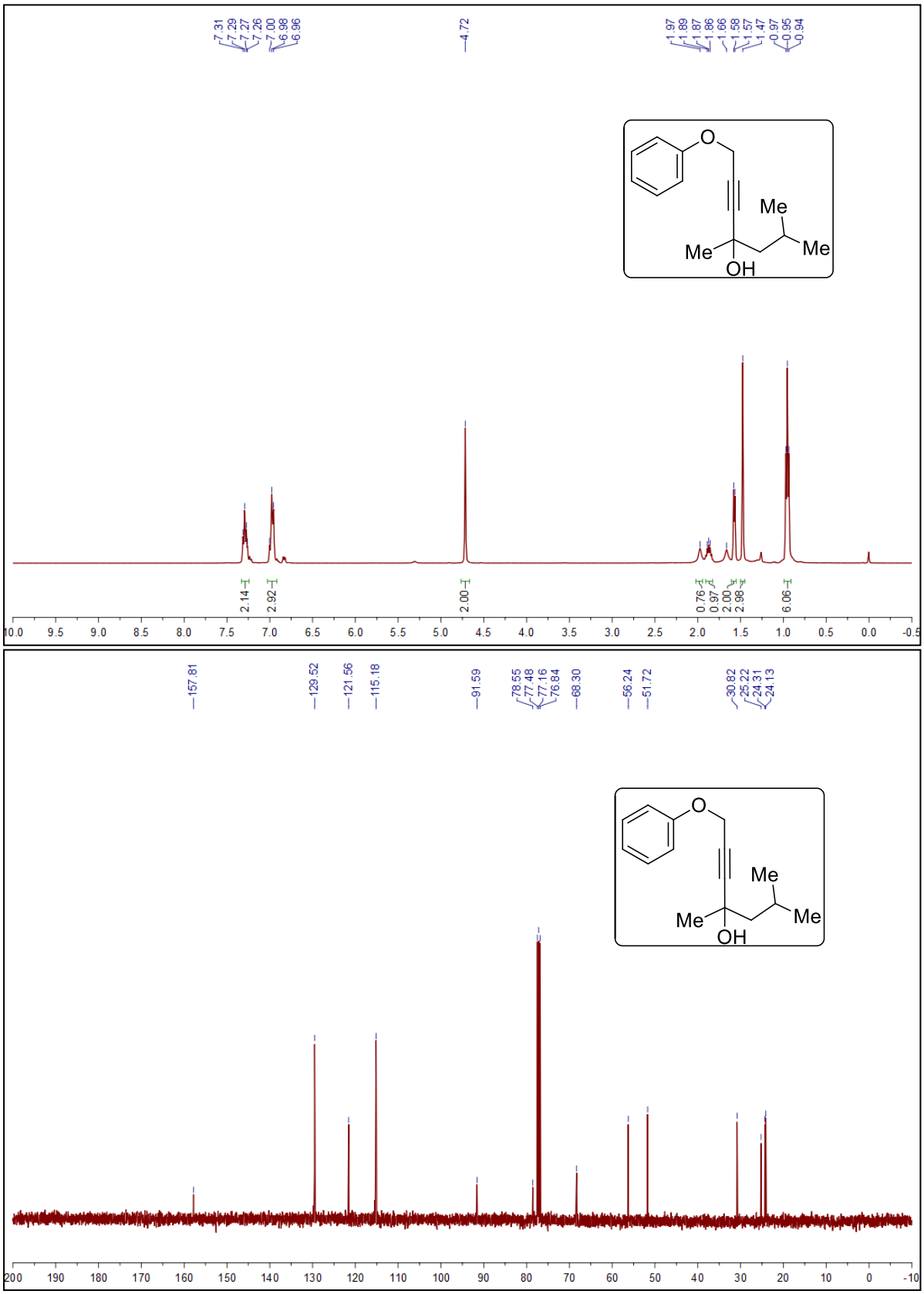
^{1}H and ^{13}C NMR Spectra of Compound **1i**. (Solvent $CDCl_3$, 400 MHz)



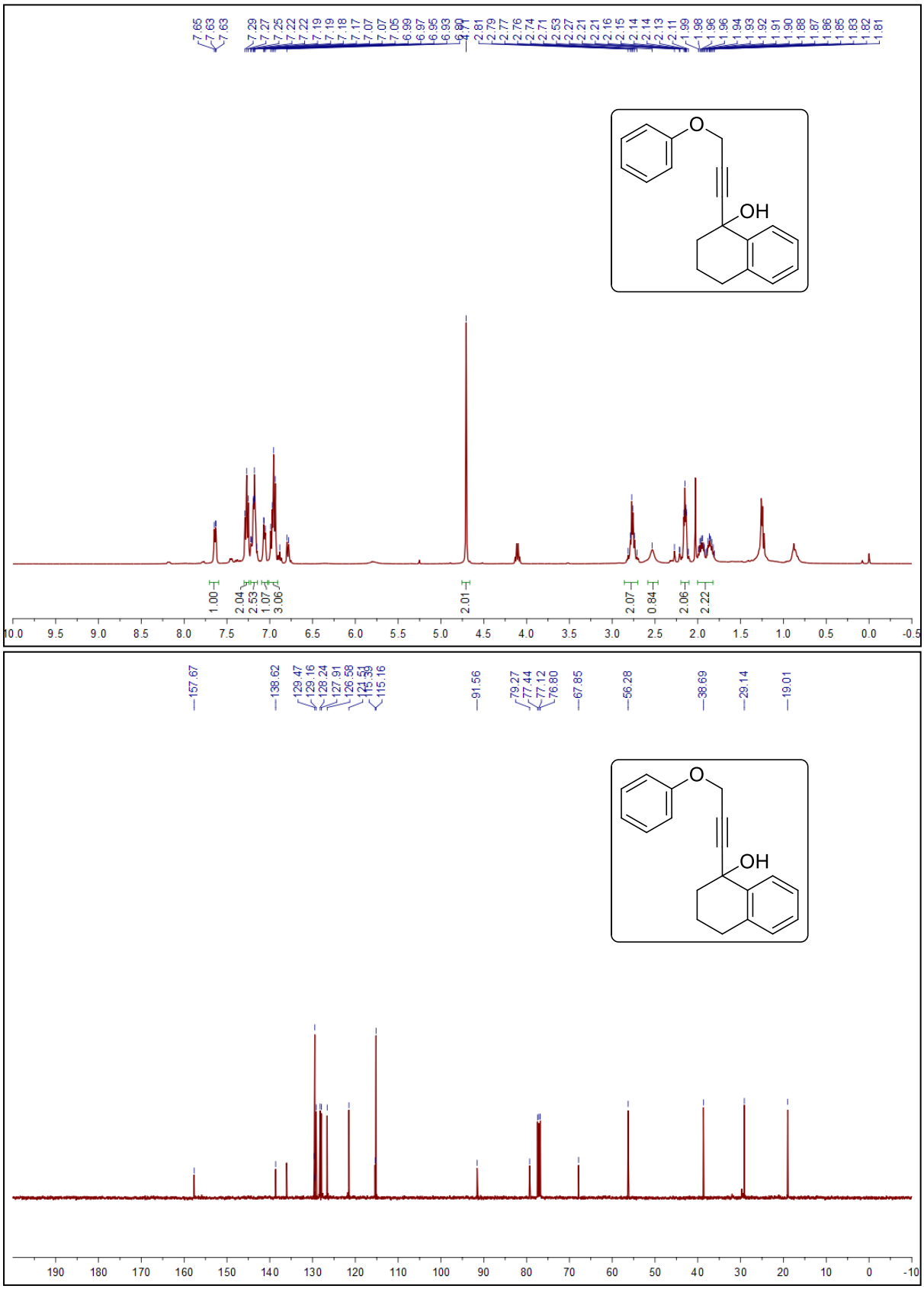
^{1}H and ^{13}C NMR Spectra of Compound **1j**. (Solvent $CDCl_3$, 400 MHz)



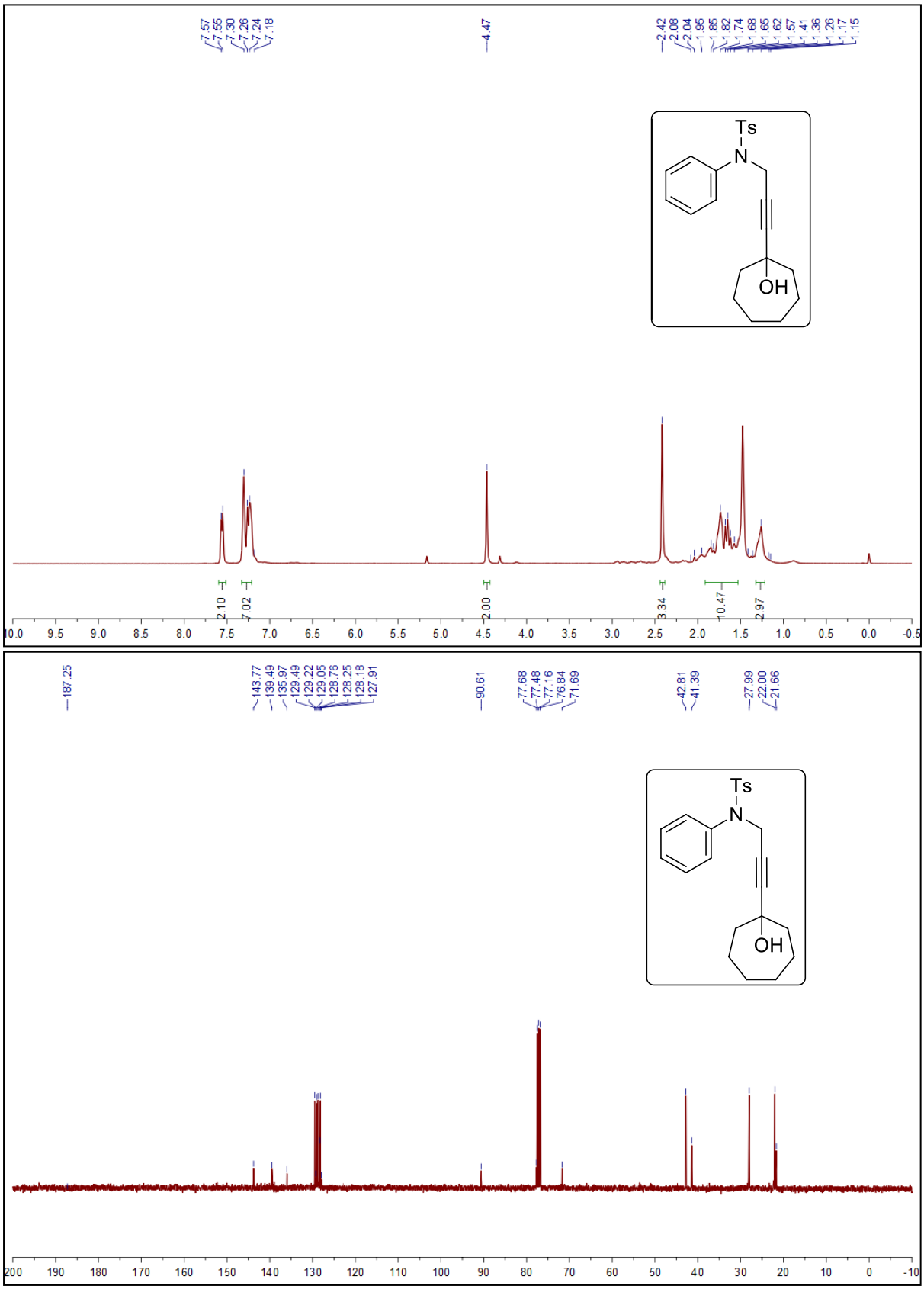
^{1}H and ^{13}C NMR Spectra of Compound **1k**. (Solvent $CDCl_3$, 400 MHz)



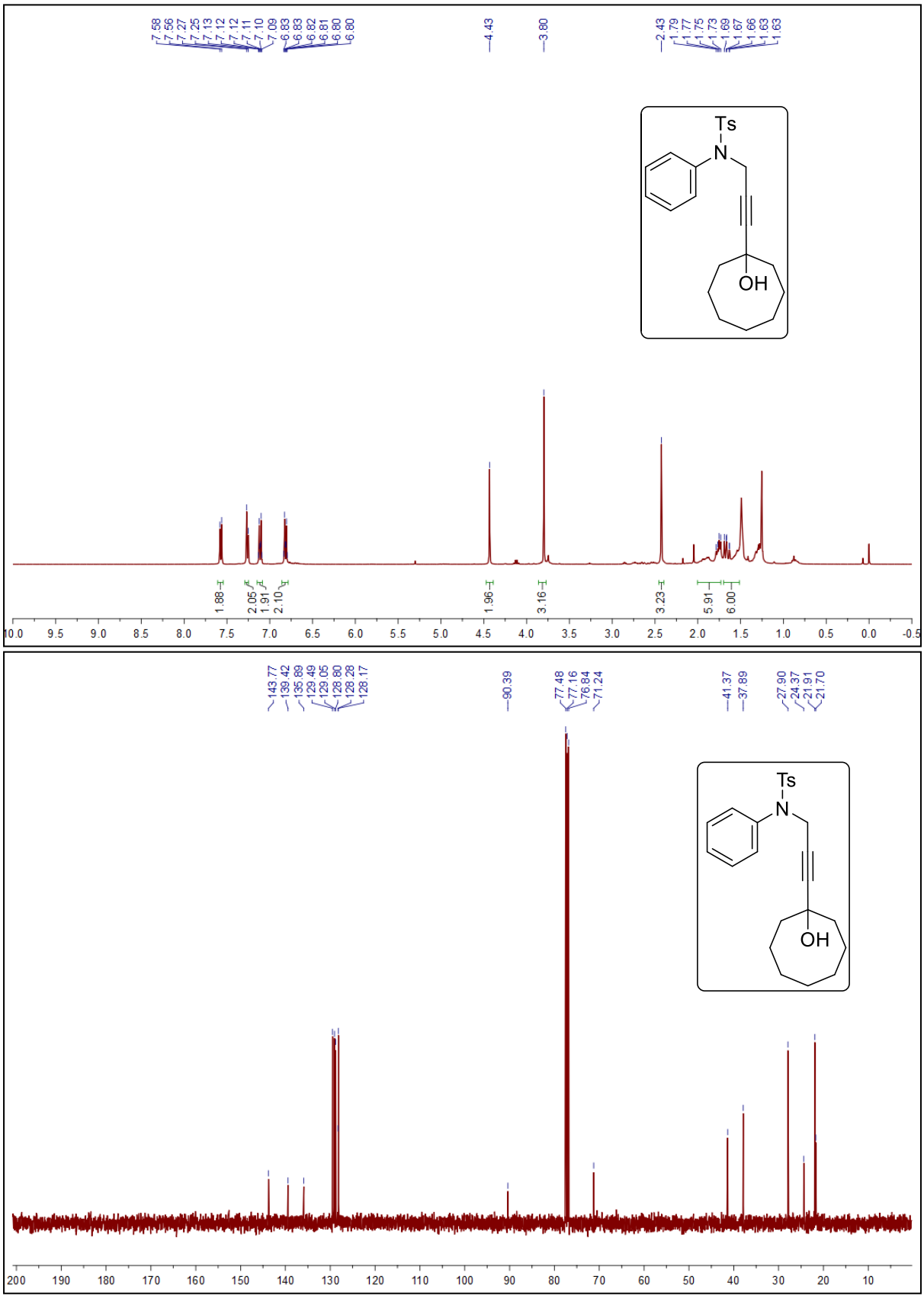
^{1}H and ^{13}C NMR Spectra of Compound **1l**. (Solvent $CDCl_3$, 400 MHz)



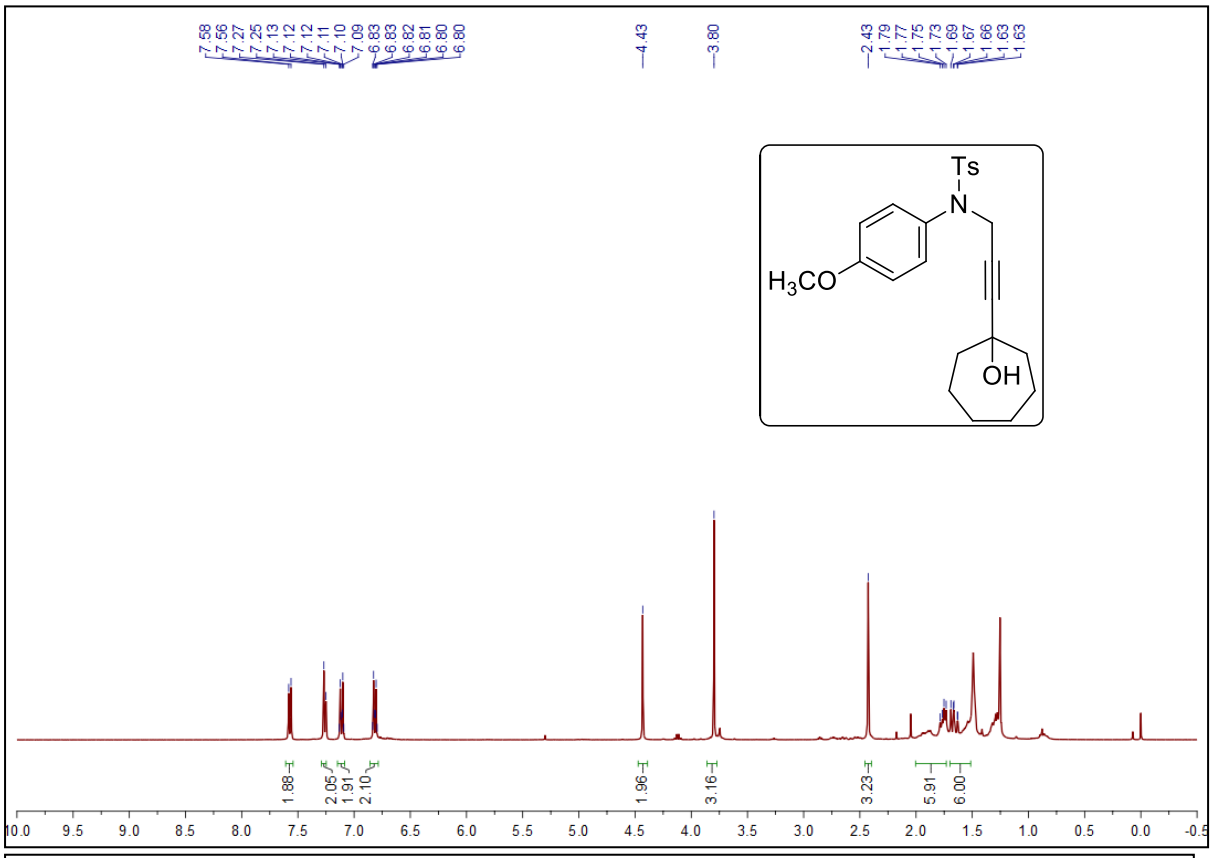
^{1}H and ^{13}C NMR Spectra of Compound **8a**. (Solvent $CDCl_3$, 400 MHz)

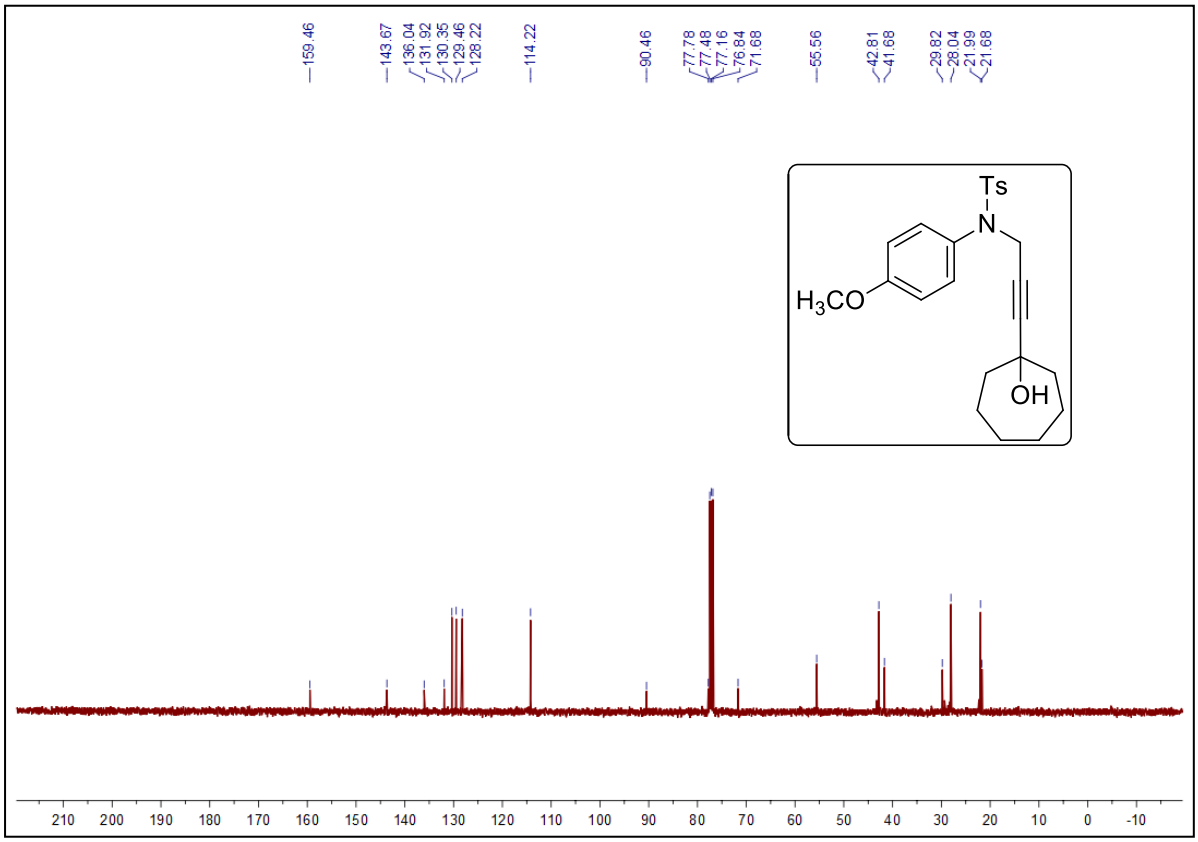


^{1}H and ^{13}C NMR Spectra of Compound **8b**. (Solvent $CDCl_3$, 400 MHz)

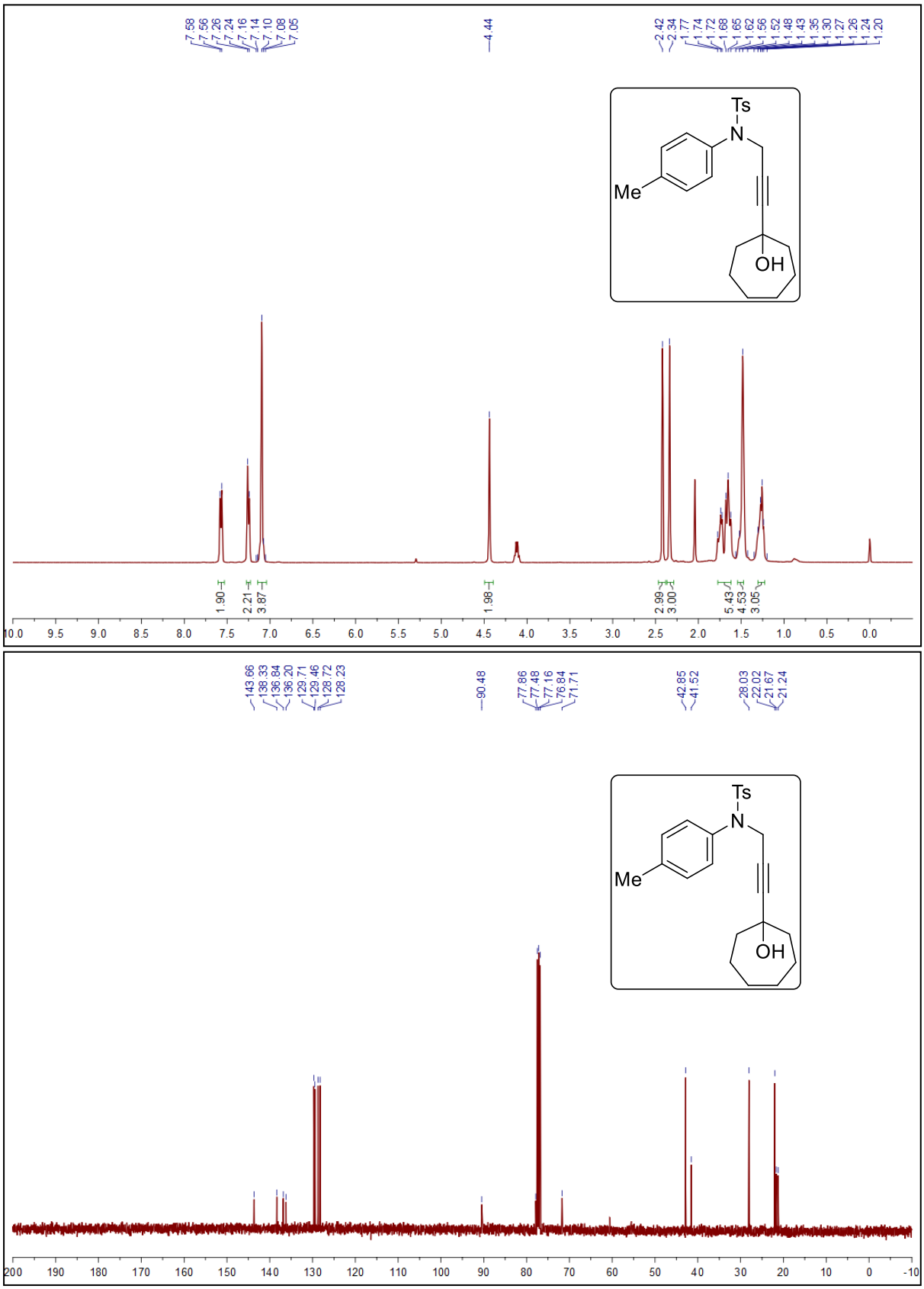


^{1}H and ^{13}C NMR Spectra of Compound **8c**. (Solvent $CDCl_3$, 400 MHz)

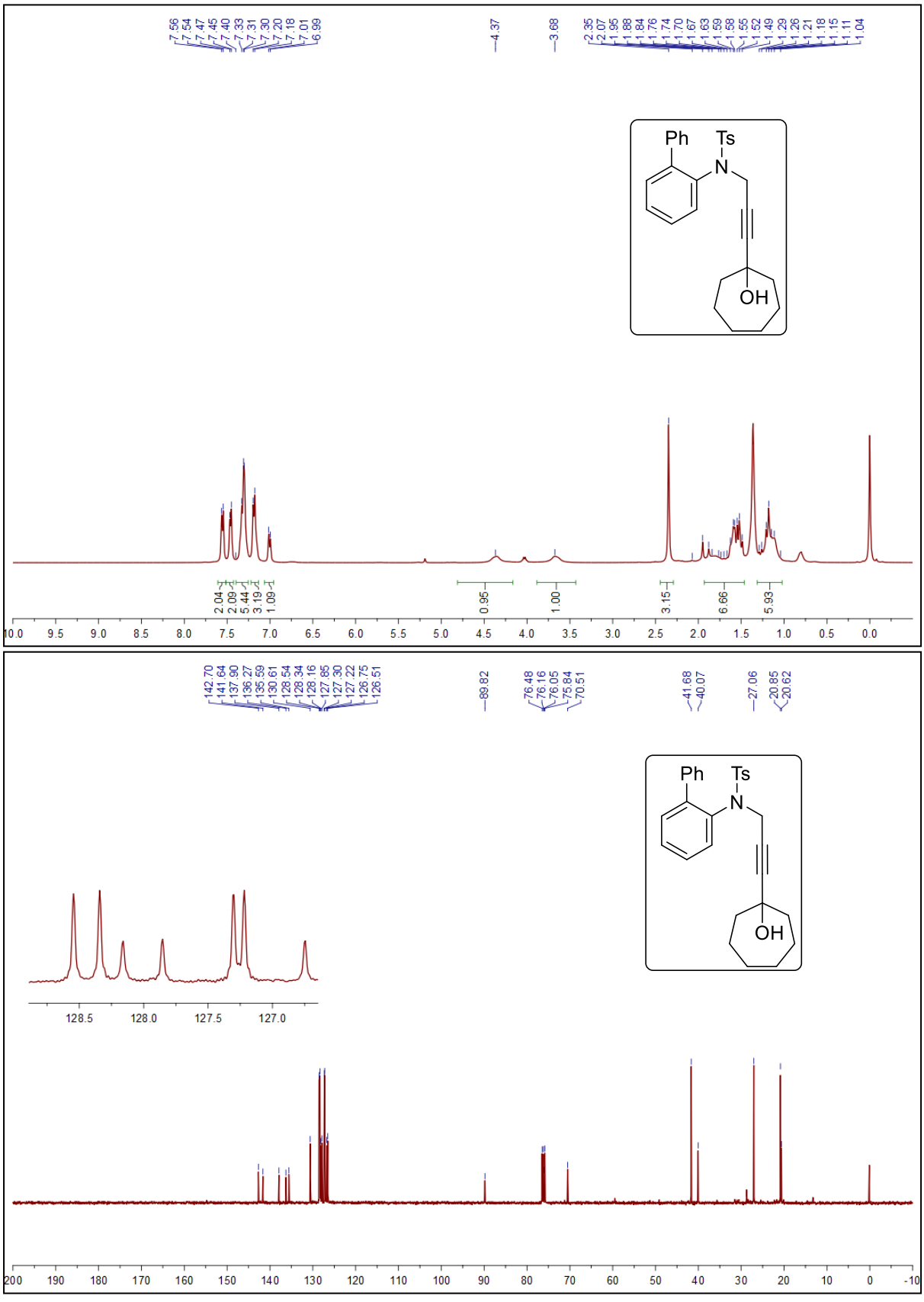




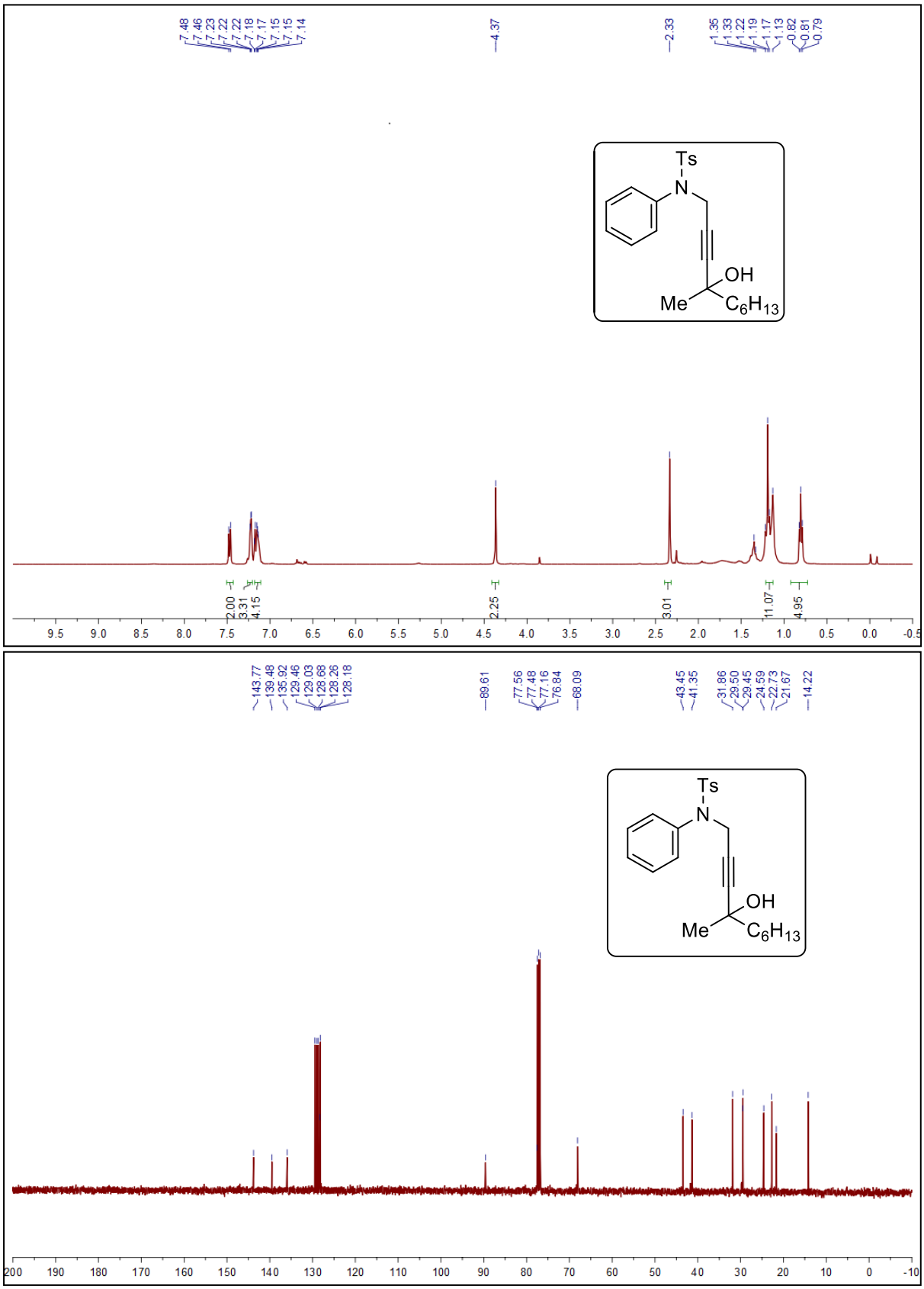
^{1}H and ^{13}C NMR Spectra of Compound **8d**. (Solvent $CDCl_3$, 400 MHz)



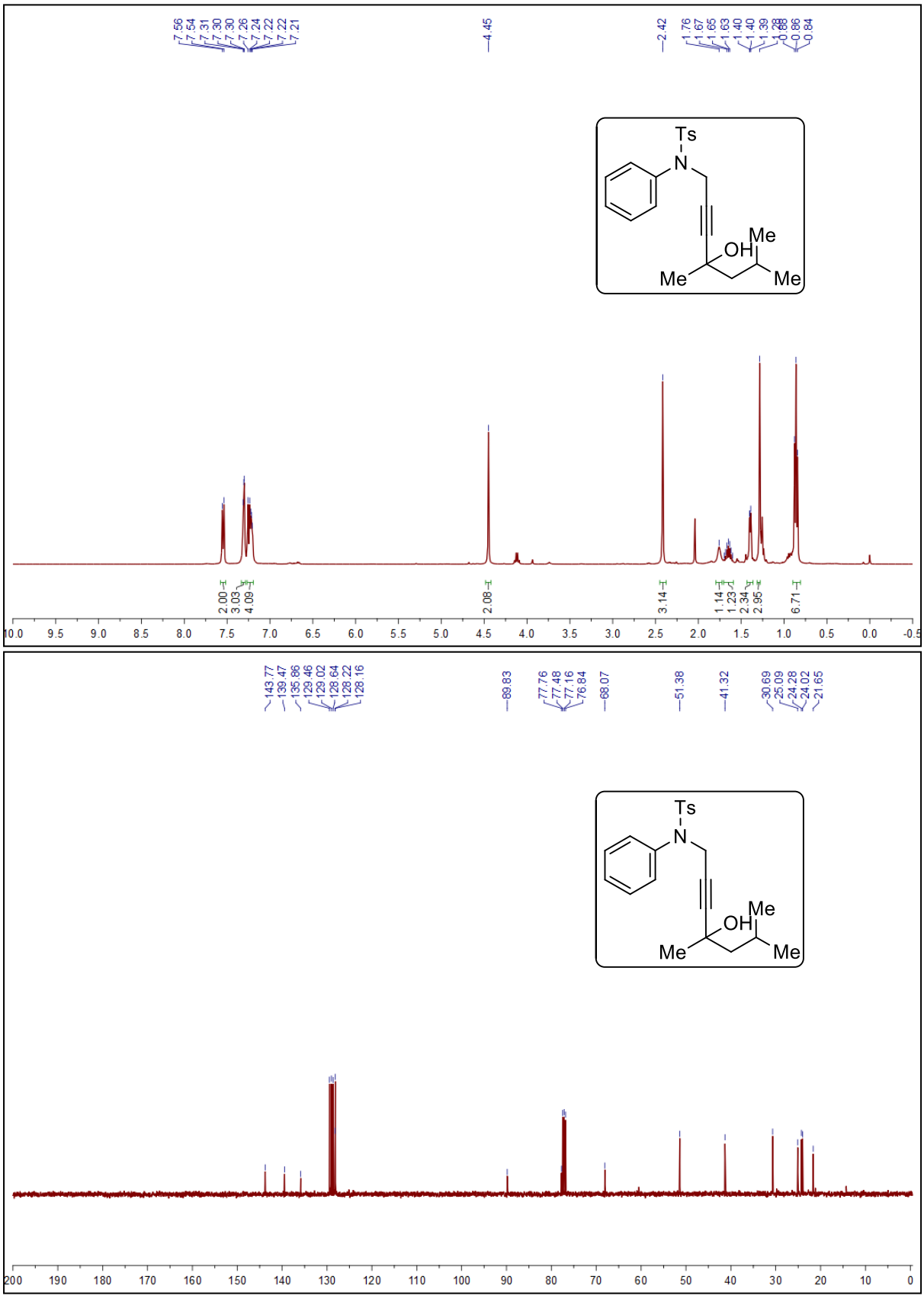
^{1}H and ^{13}C NMR Spectra of Compound **8e**. (Solvent $CDCl_3$, 400 MHz)



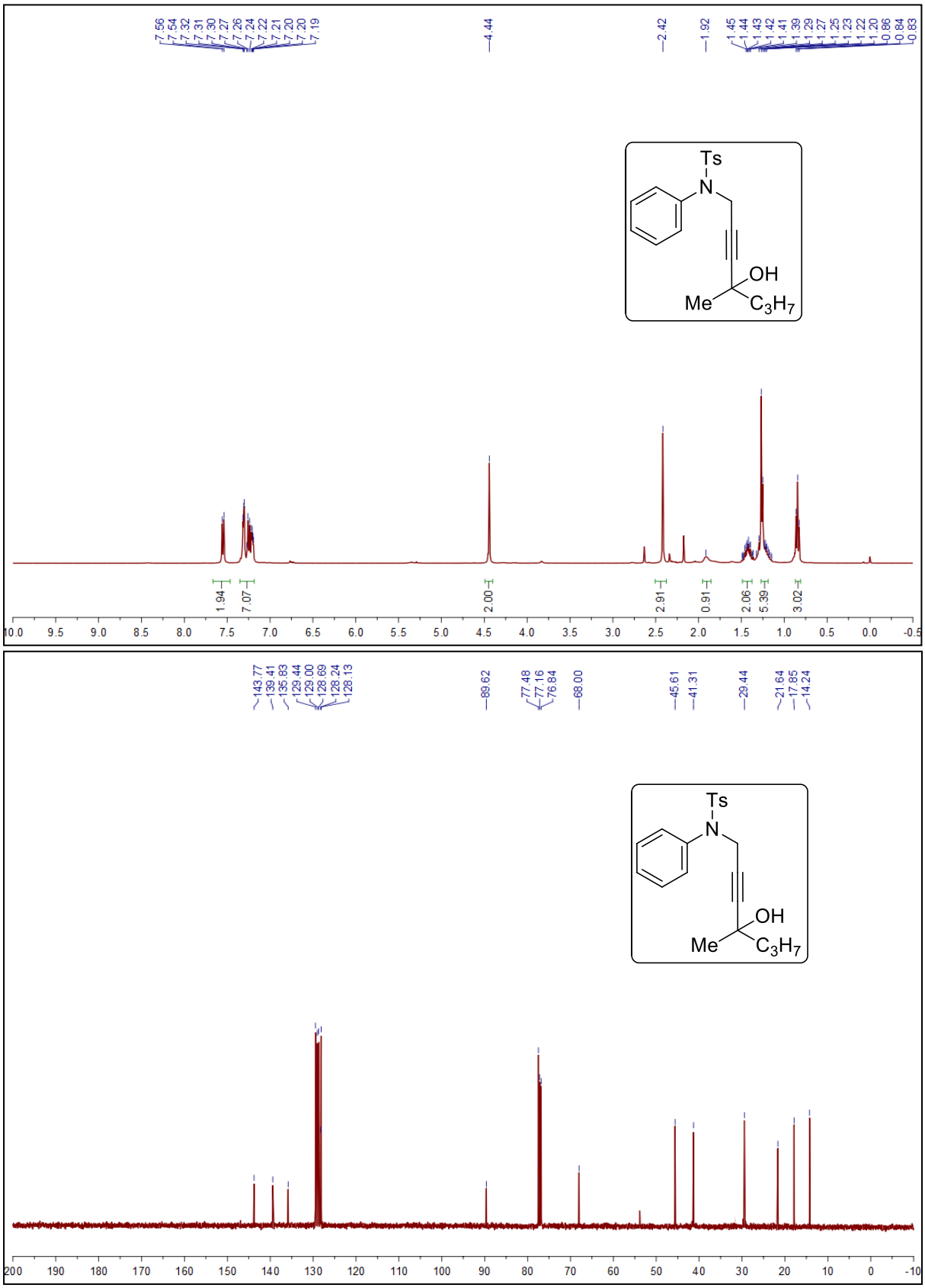
^{1}H and ^{13}C NMR Spectra of Compound **8f**. (Solvent $CDCl_3$, 400 MHz)



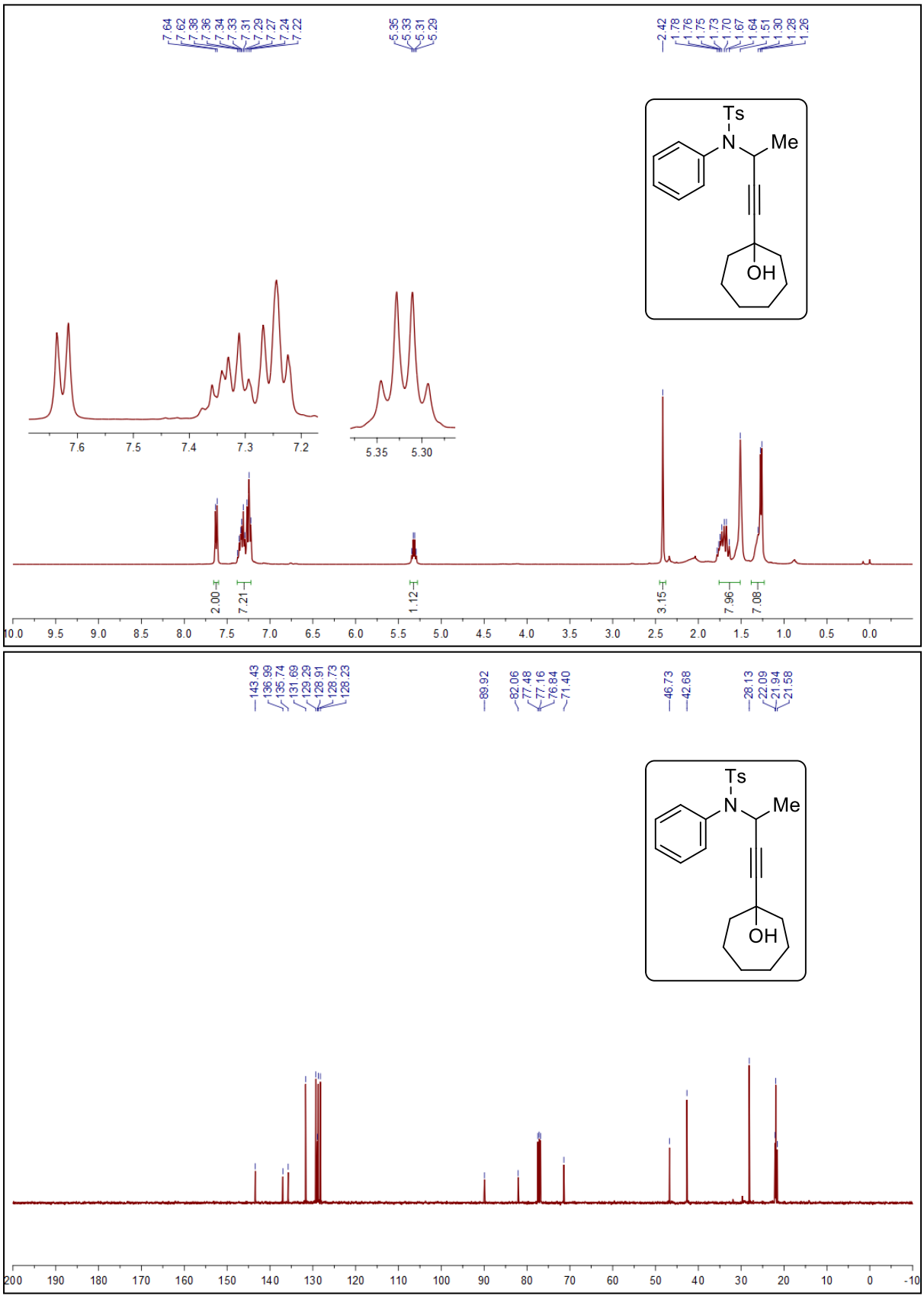
^{1}H and ^{13}C NMR Spectra of Compound **8g**. (Solvent $CDCl_3$, 400 MHz)



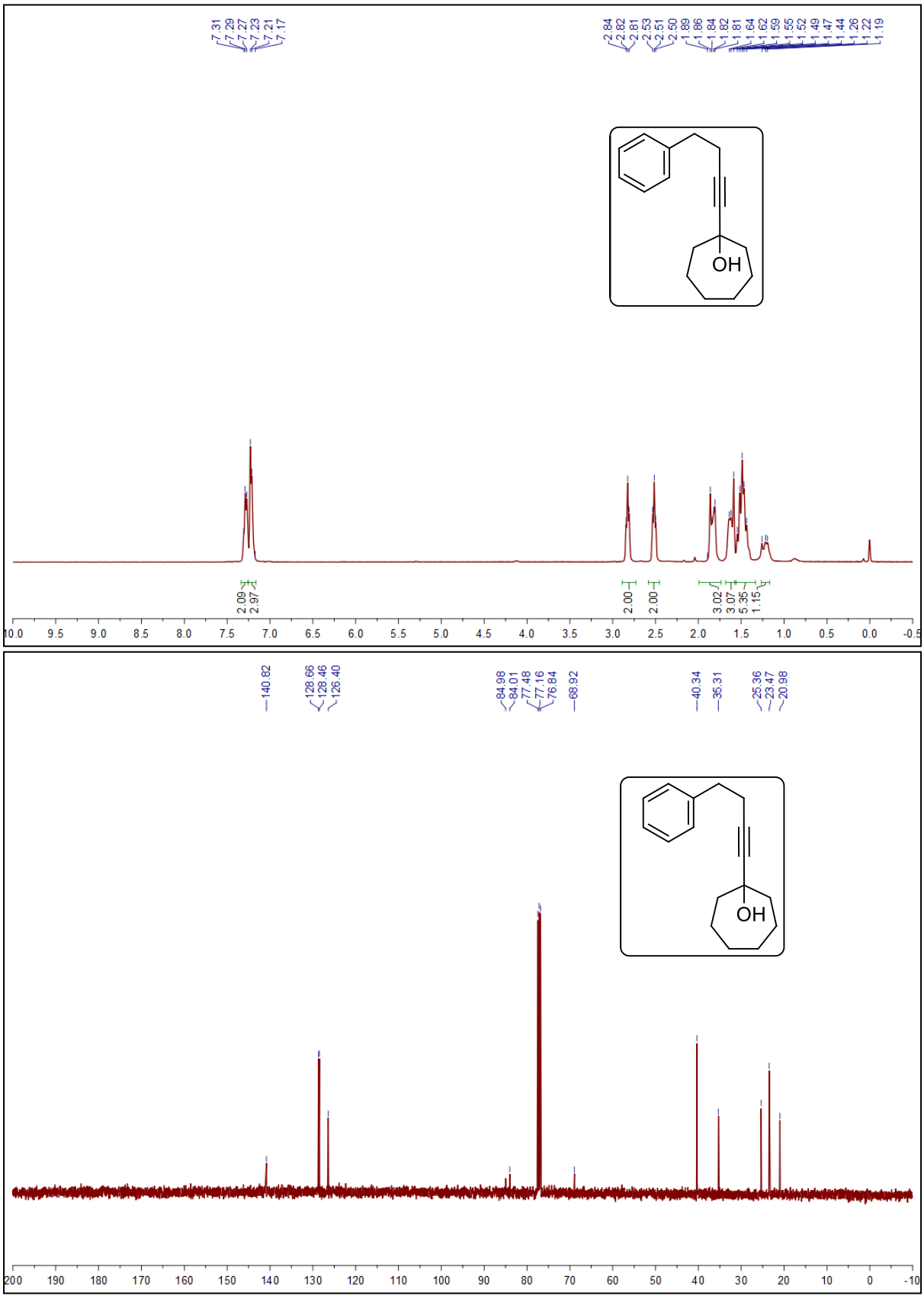
^{1}H and ^{13}C NMR Spectra of Compound **8h**. (Solvent $CDCl_3$, 400 MHz)



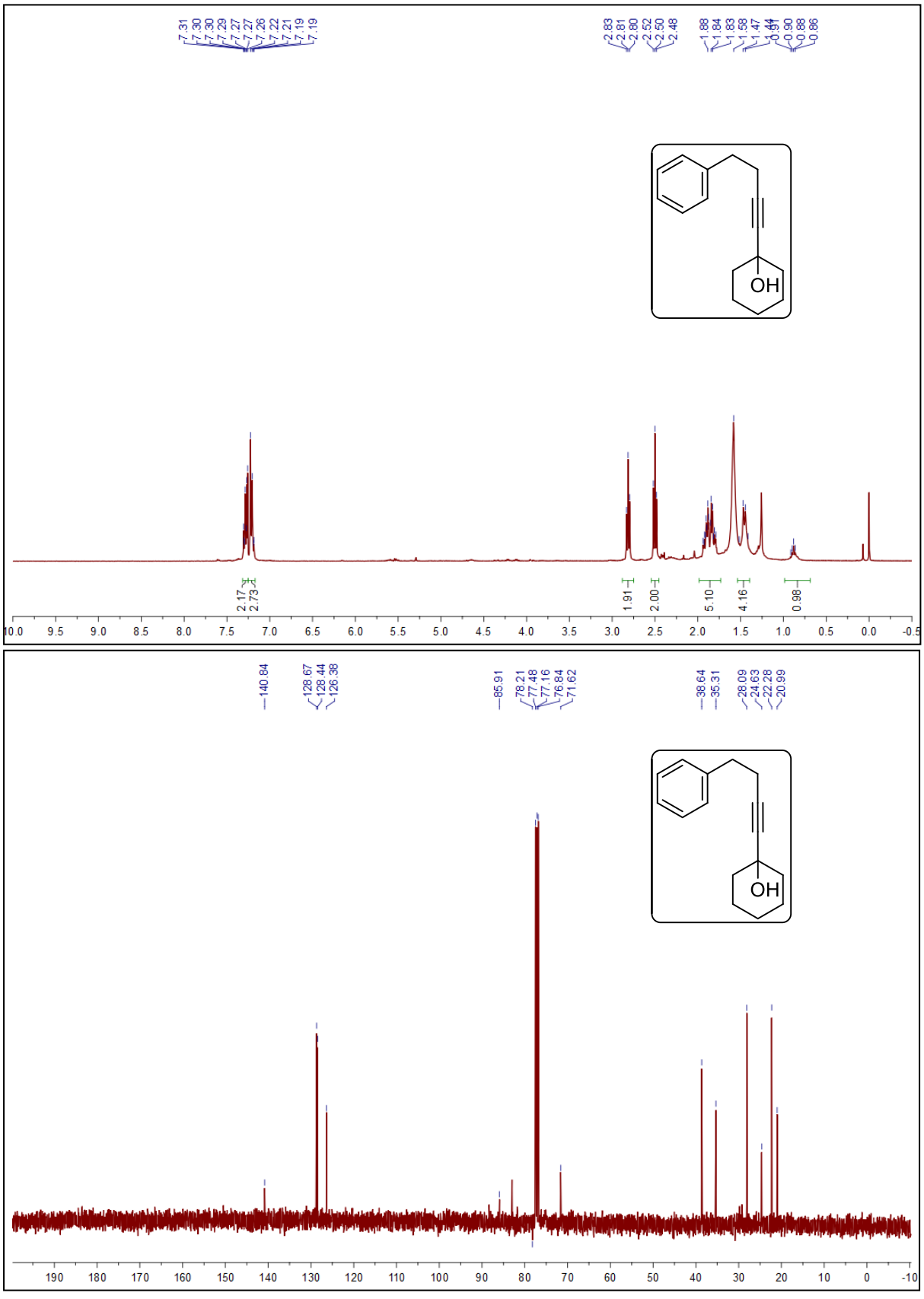
^{1}H and ^{13}C NMR Spectra of Compound **8i**. (Solvent $CDCl_3$, 400 MHz)



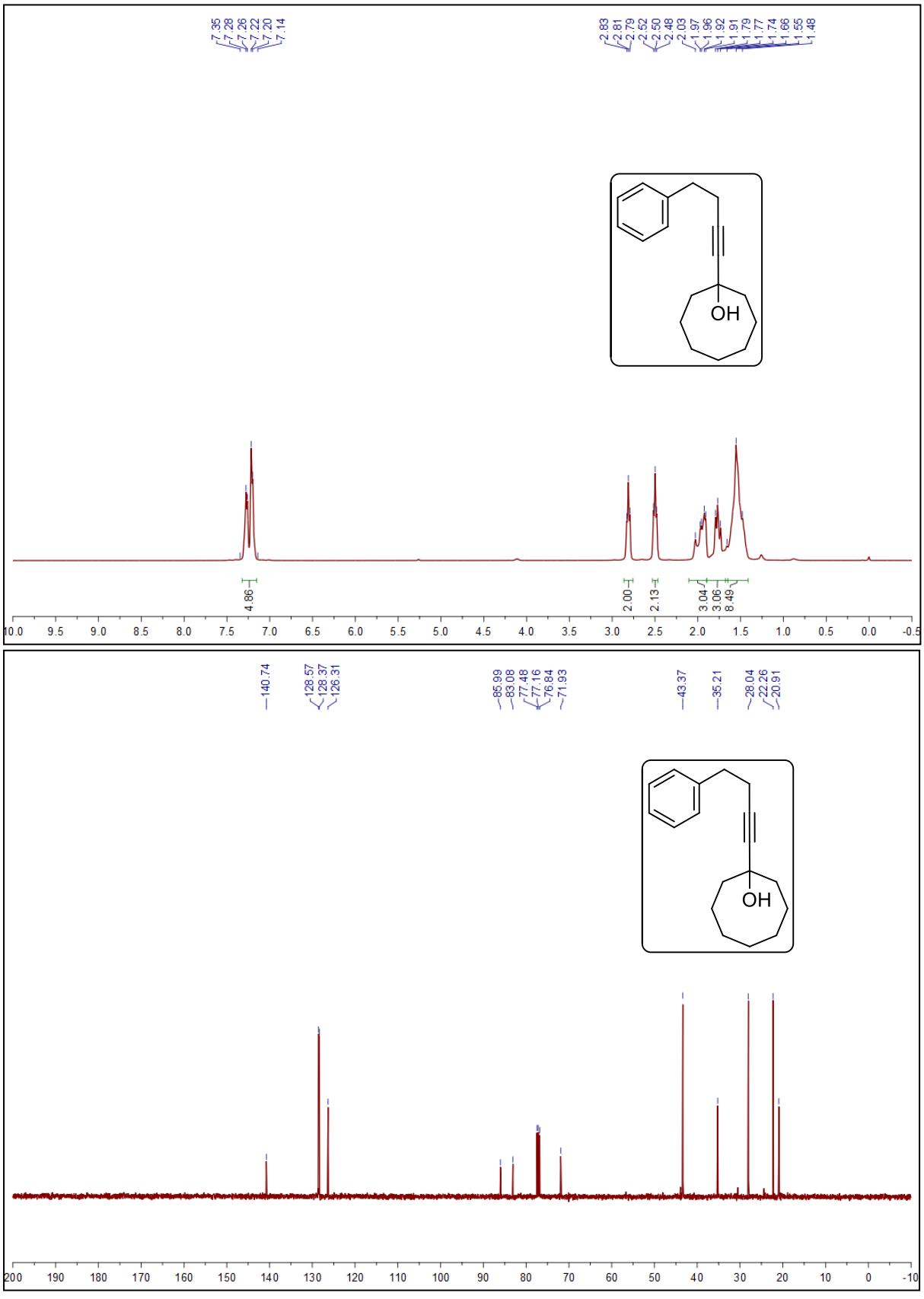
^{1}H and ^{13}C NMR Spectra of Compound **10a**. (Solvent CDCl3, 400 MHz)



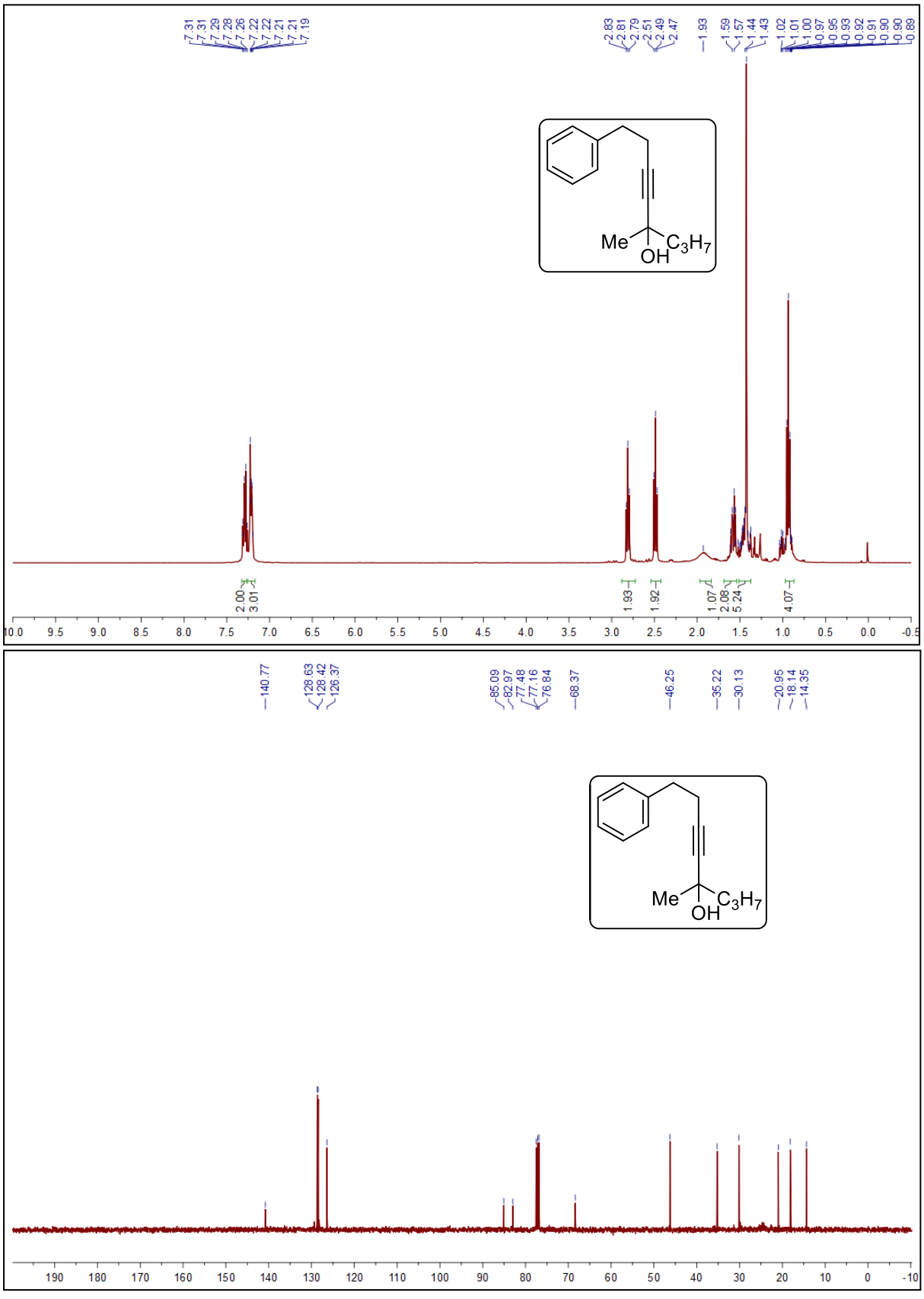
^{1}H and ^{13}C NMR Spectra of Compound **10b**. (Solvent $CDCl_3$, 400 MHz)



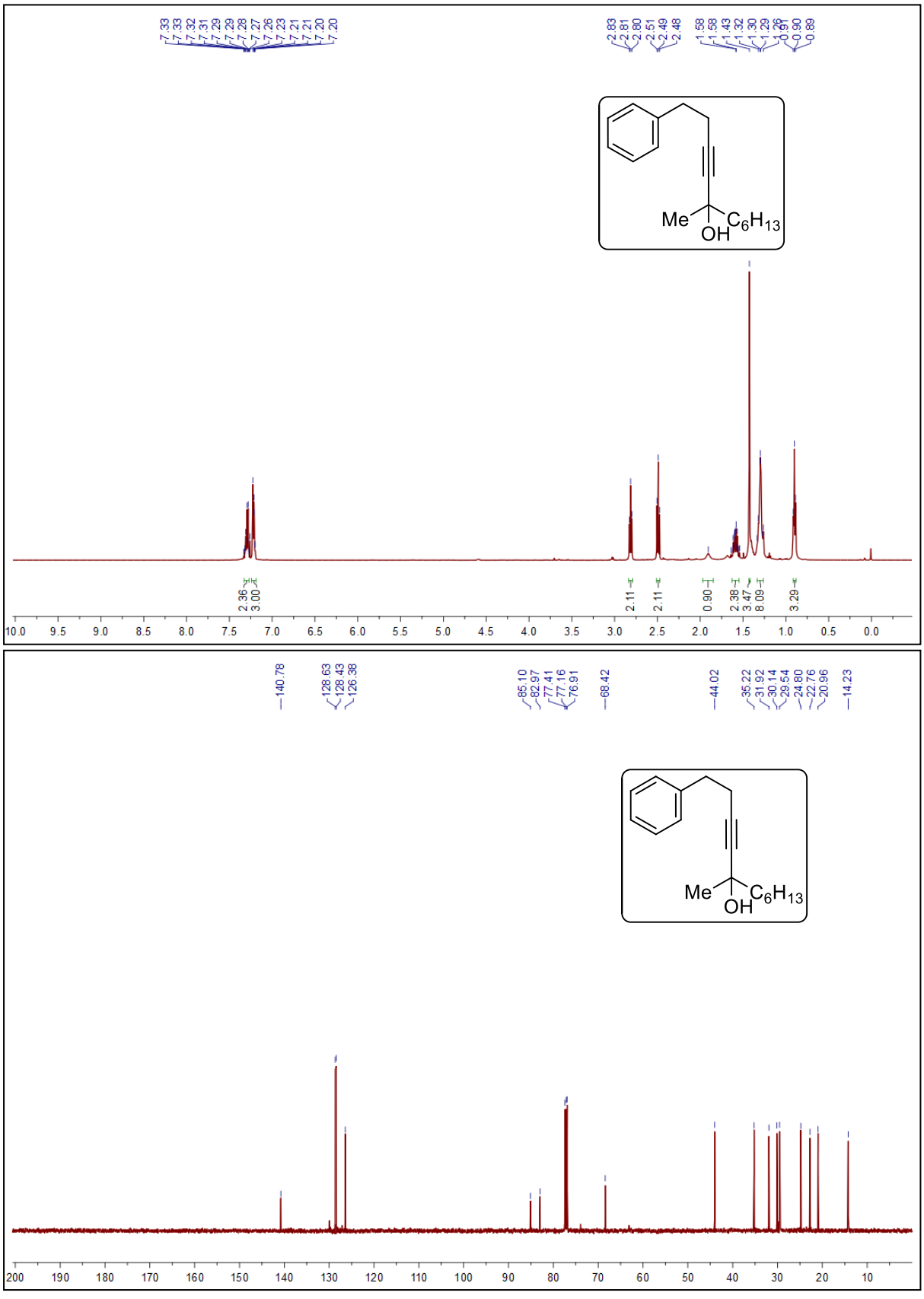
^{1}H and ^{13}C NMR Spectra of Compound **10c**. (Solvent $CDCl_3$, 400 MHz)



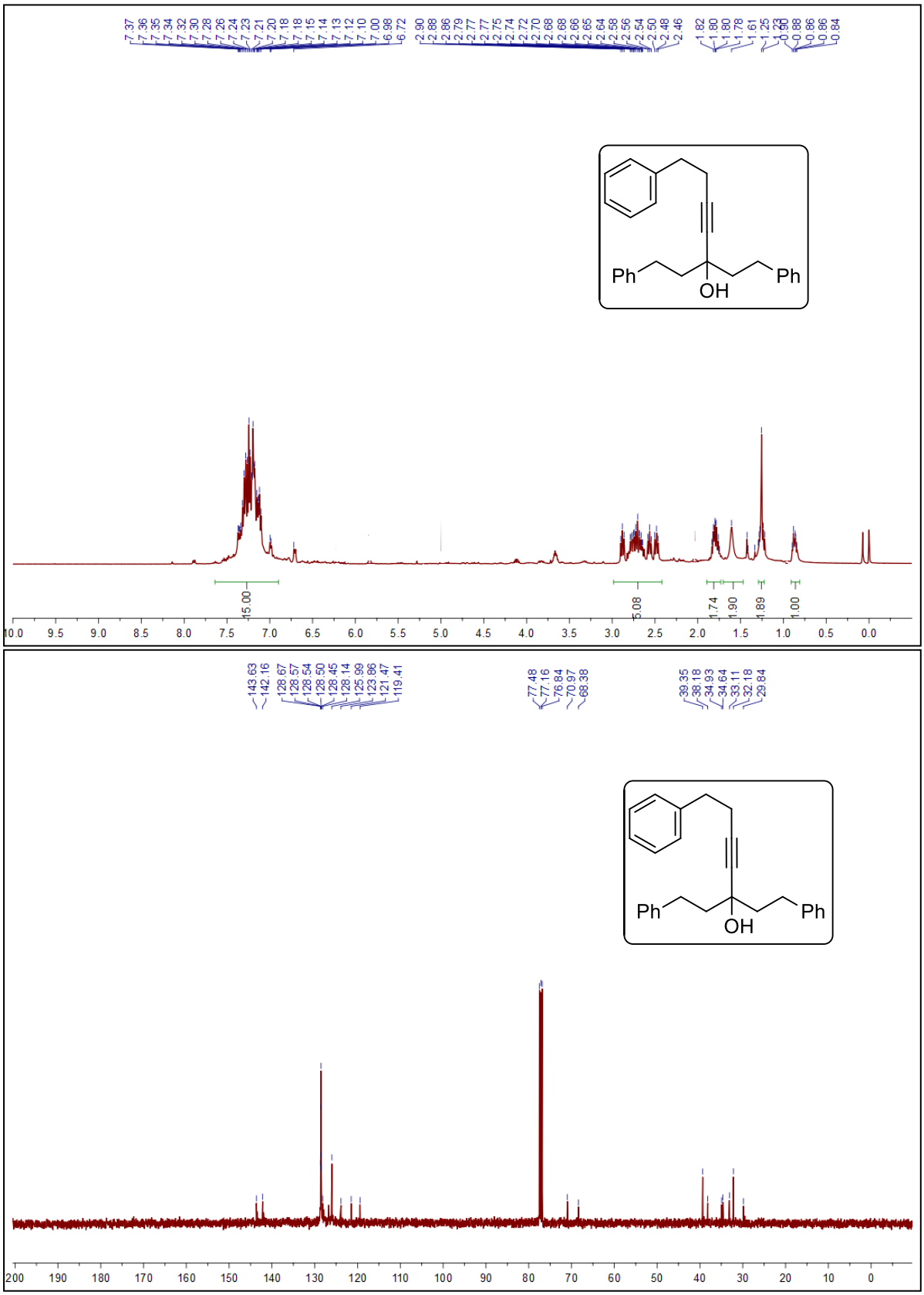
^{1}H and ^{13}C NMR Spectra of Compound **10d**. (Solvent $CDCl_3$, 400 MHz)



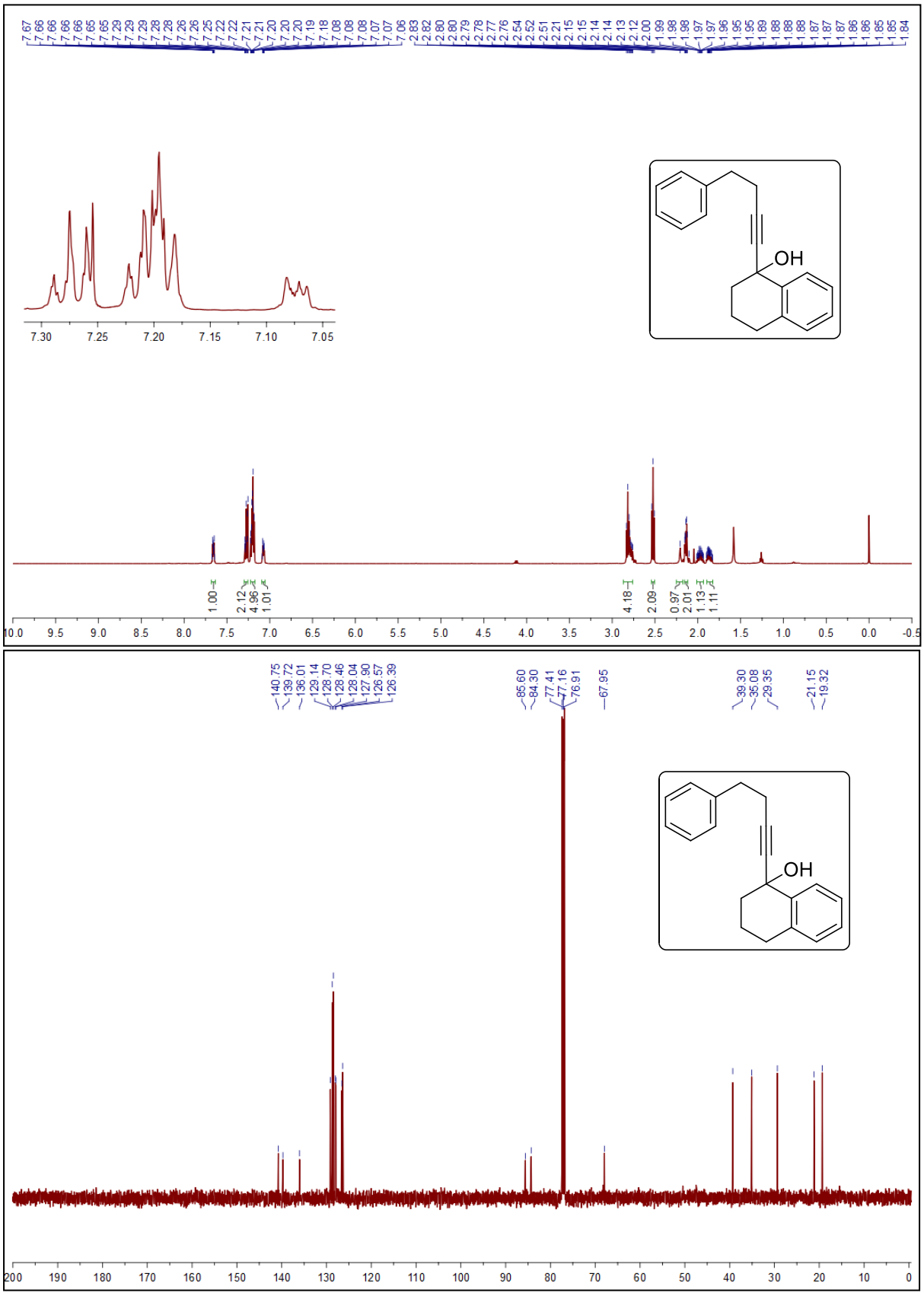
^{1}H and ^{13}C NMR Spectra of Compound **10e**. (Solvent $CDCl_3$, 400 MHz)



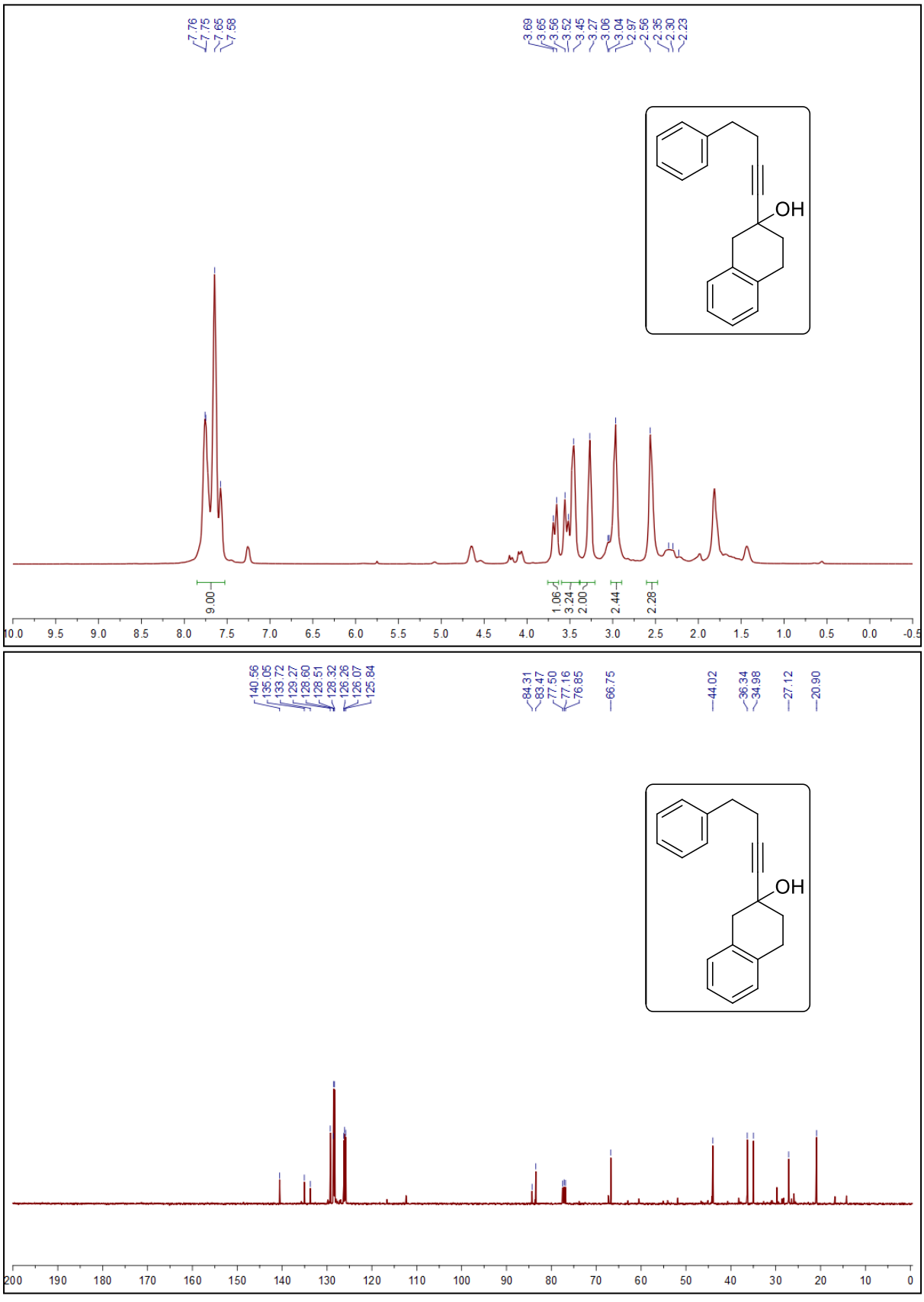
^{1}H and ^{13}C NMR Spectra of Compound **10g**. (Solvent $CDCl_3$, 400 MHz)



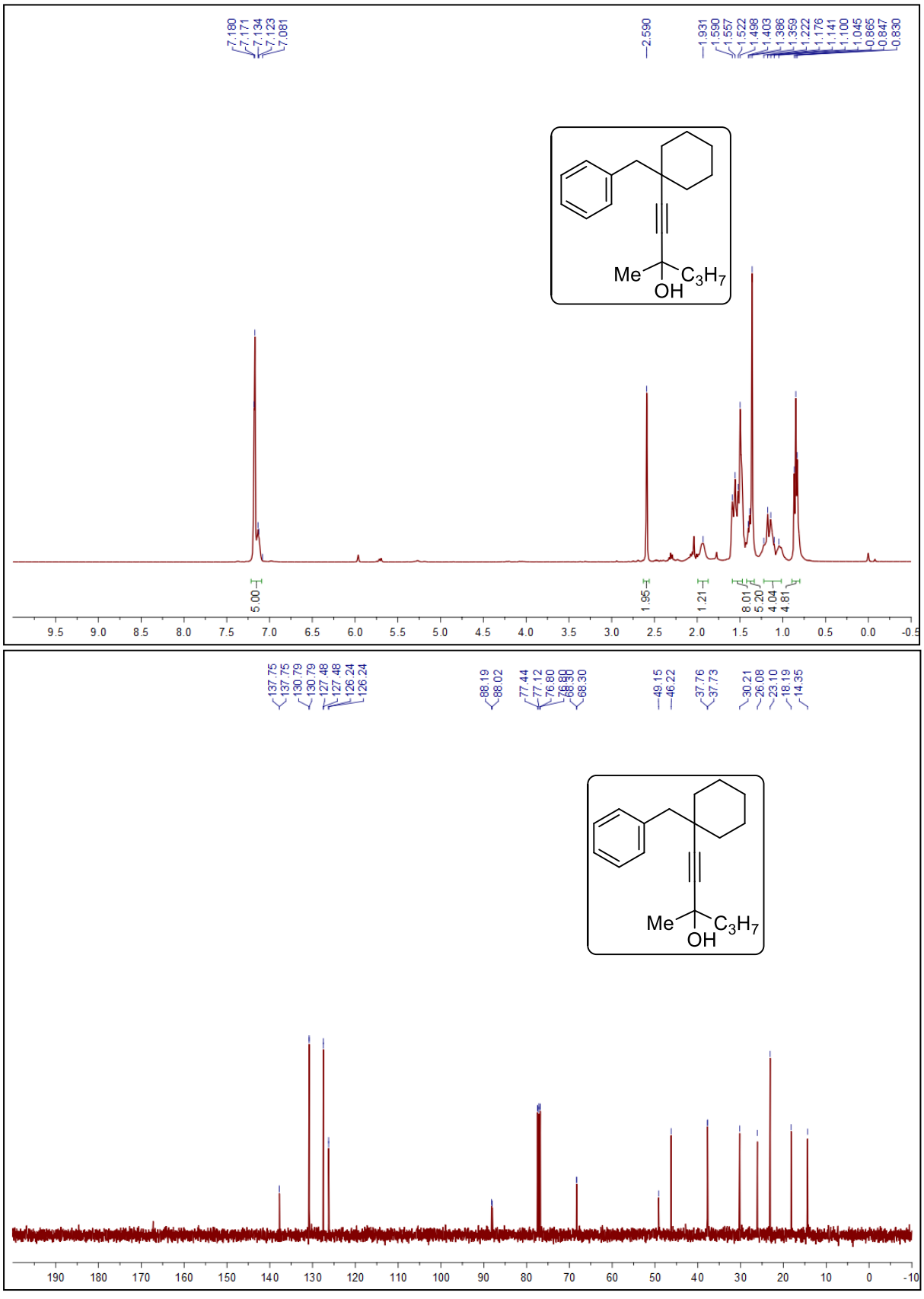
^{1}H and ^{13}C NMR Spectra of Compound **15**. (Solvent $CDCl_3$, 400 MHz)



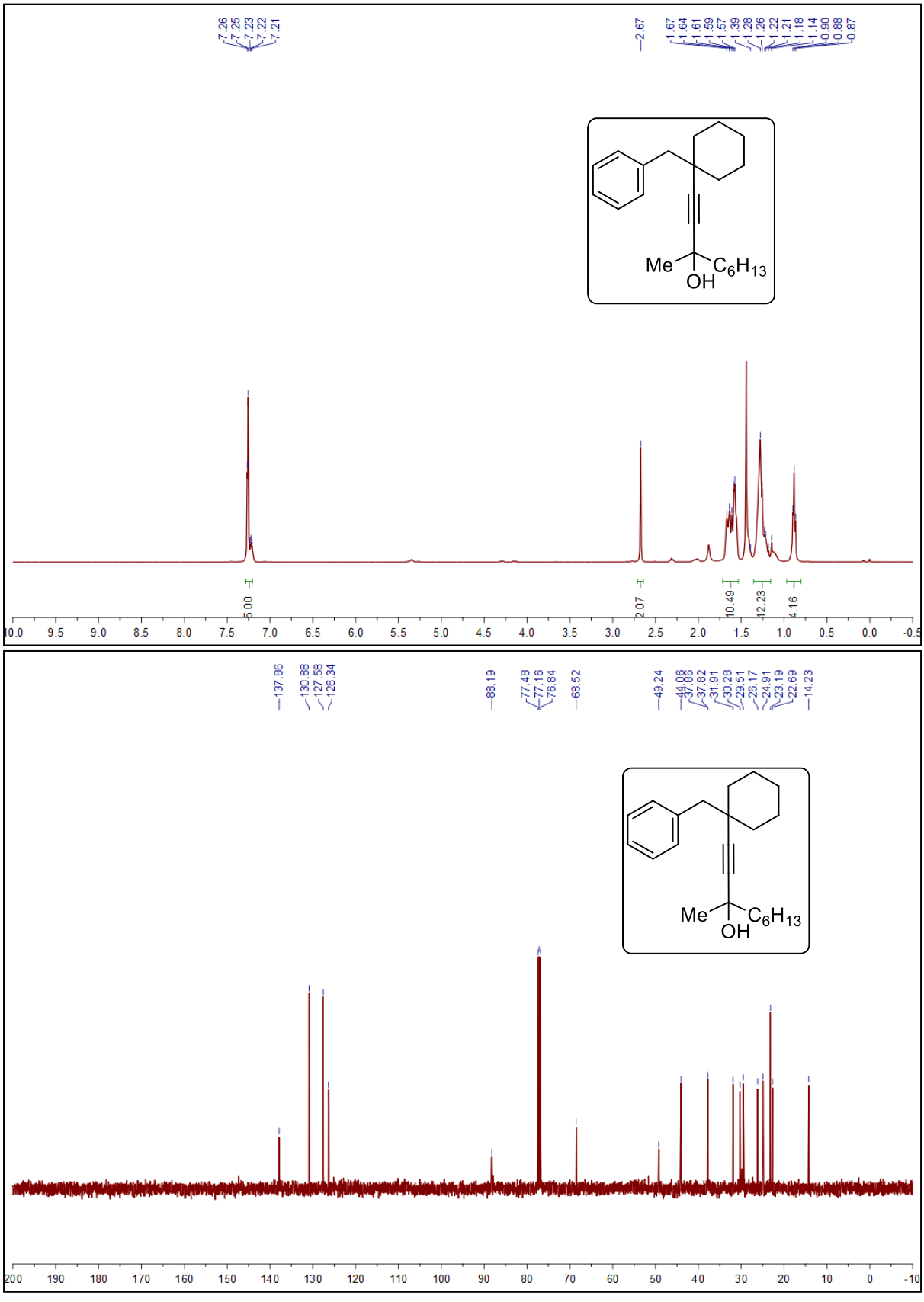
^{1}H and ^{13}C NMR Spectra of Compound **16**. (Solvent $CDCl_3$, 400 MHz)



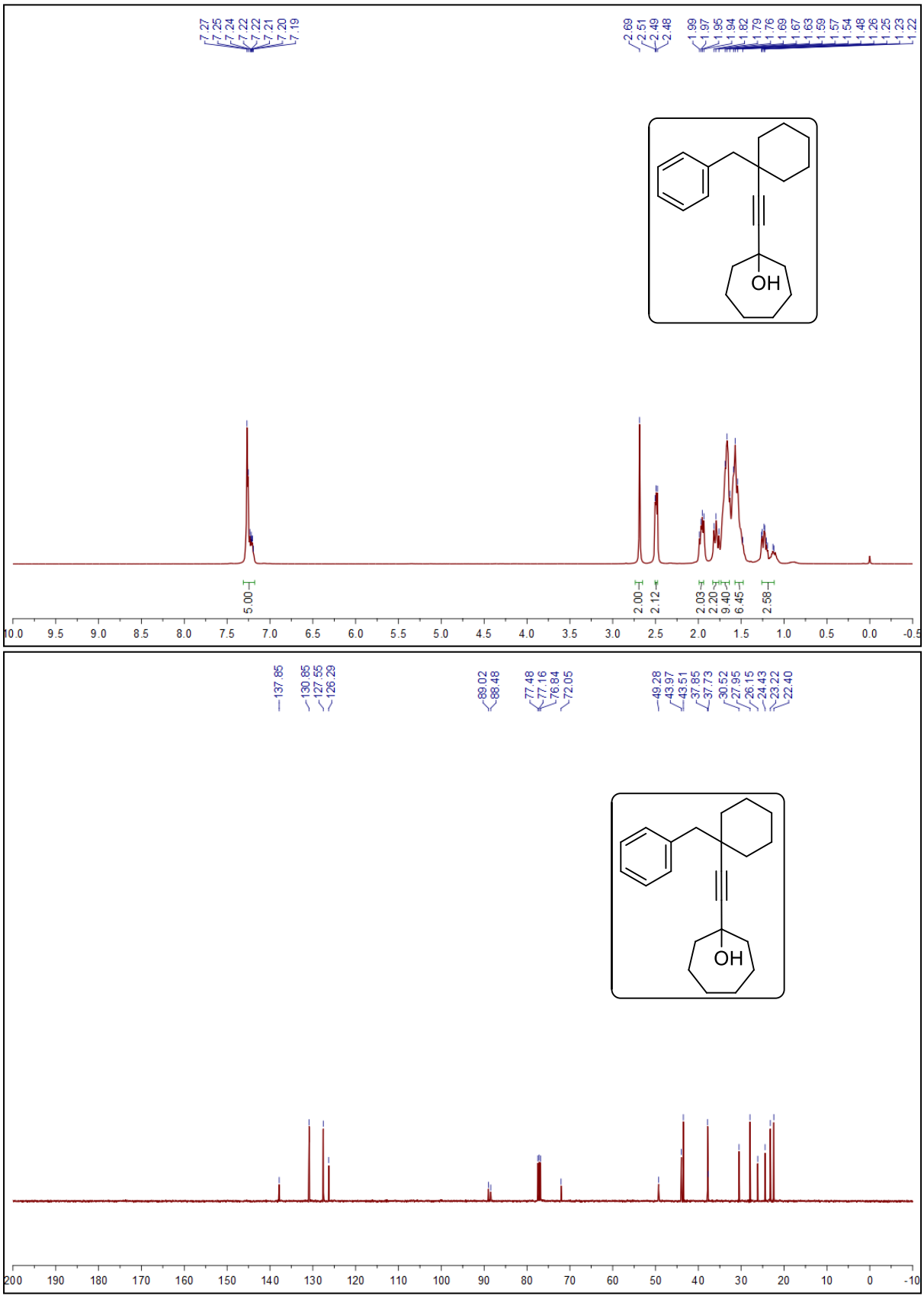
^{1}H and ^{13}C NMR Spectra of Compound **18a**. (Solvent $CDCl_3$, 400 MHz)



^{1}H and ^{13}C NMR Spectra of Compound **18b**. (Solvent $CDCl_3$, 400 MHz)



^{1}H and ^{13}C NMR Spectra of Compound **18c**. (Solvent $CDCl_3$, 400 MHz)



^{1}H and ^{13}C NMR Spectra of Compound **S_1.** (Solvent $CDCl_3$, 400 MHz)

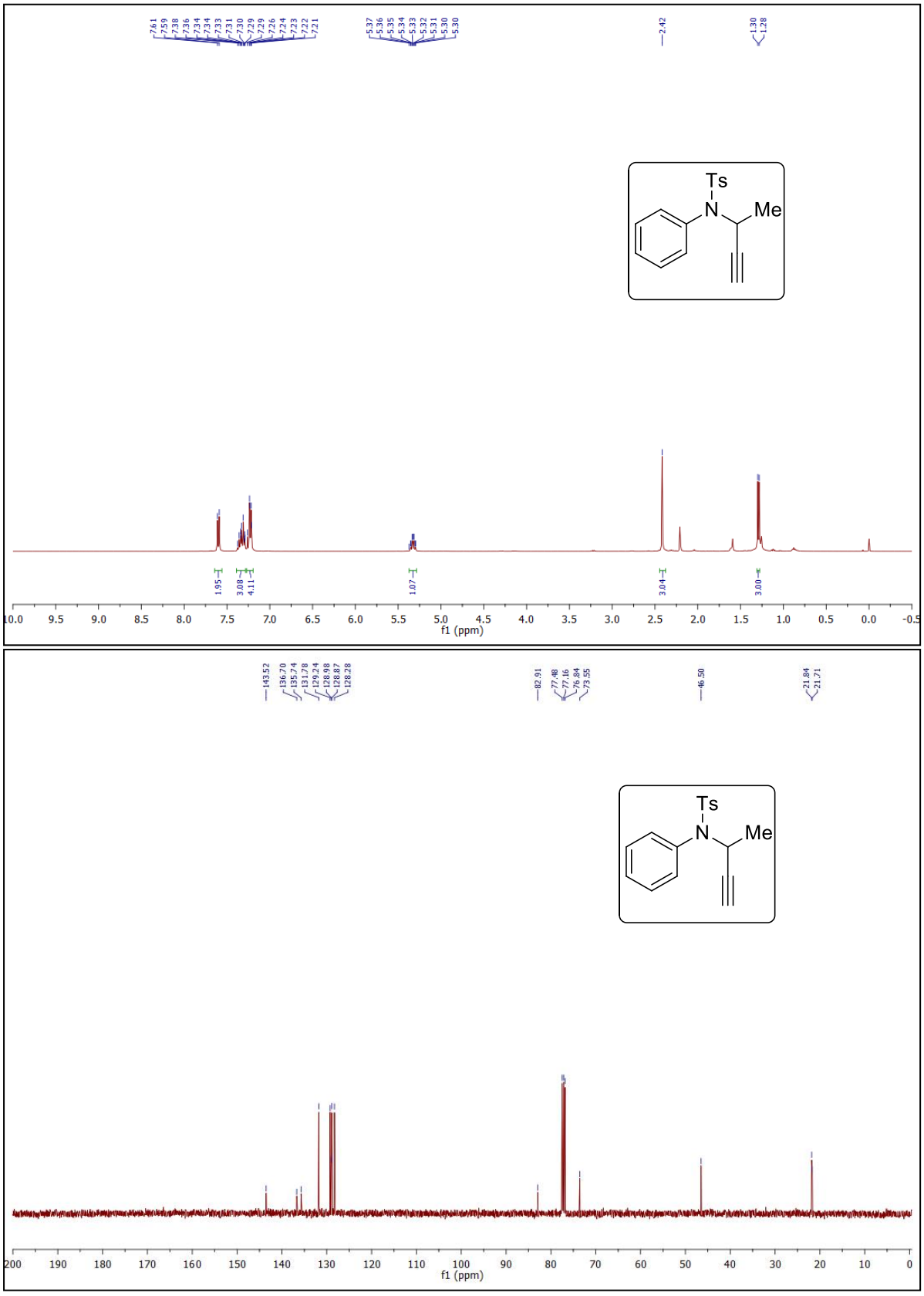
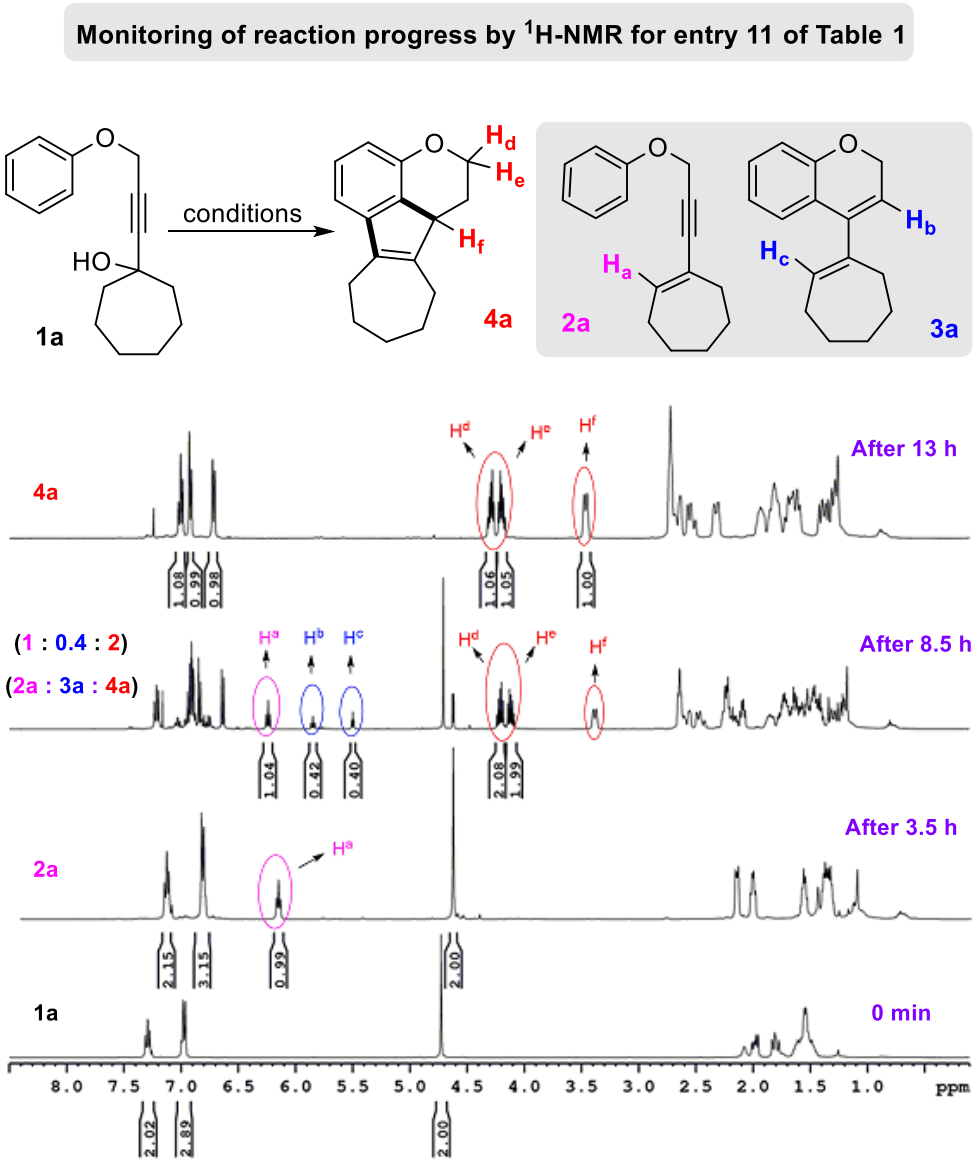


Figure 1: ^{1}H-NMR analysis of reaction progress (entry 11, Table 1 of MS)

Figure 1:


Monitoring of reaction progress by ^{1}H-NMR for entry 11 of Table 1
conditions
HO
1a
4a
2a
3a
H_a
H_b
H_c
H_d
H_e
H_f
After 13 h
After 8.5 h
After 3.5 h
0 min
(1 : 0.4 : 2)
(2a : 3a : 4a)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm