Supporting Information

Synthesis of dibenzo cyclohepta[1,2-a]naphthalene derivatives from phenylacetaldehyde and alkynyl benzyl alcohols via sequential electrophilic addition and double Friedel-Crafts reactions

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Table of content

EXPERIMENTAL SECTION

General Information All the reagents were of reagent grade (AR grade) and were used as purchased without further purification. Silica gel (60-120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel GF_{254} (0.25 mm). Melting points were recorded with a Büchi B-540 melting point apparatus. Fourier transform-infra red (FTIR)spectra were recorded on Nicolet Impact-410 instrument either as neat liquid or KBr pellets NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (400 MHz) or ^{13}C (100 MHz). Chemical shifts (δ) are reported in ppm and spin-spin coupling constants (*J*) are given in Hz. HRMS spectra were recorded using Q-TOF premier mass spectrometer. The ratio of enantiomers was determined by HPLC analysis using Chiracel OD columns on Waters 1525 Binary HPLC system. The starting material *ortho*-alkynyl alcohols (**1a, 1b, 1d, 1h, 1i)**,[1] **1j,**[2] **1k**,[3] **1l,**[4] **1m**[5], and **2c**[6] were prepared as per the literature procedure and the spectroscopic data are in good agreement with the literature one.

General Experimental procedure for synthesis of o-alkynyl benzyl alcohols (**1**):

To a stirred solution of substituted 2-iodobenzylalcohol (1.0 mmol, 1.0 equiv.), palladium (II) chloride (2 mol%, 0.02 equiv.), triphenylphosphine (4 mol%, 0.04 equiv.) and copper(I) iodide (8 mol%, 0.08 equiv.) in triethylamine (4 mL) was added 1-ethynyl-benzene derivatives (1.2 mmol, 1.2 equiv.) under nitrogen atmosphere. Then, the reaction was heated at 60 ^oC for 12h. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated NH4Cl solution. The organic layer was extracted with EtOAc (3x20 mL). The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the o-alkynyl benzyl alcohols (1).

Experimental procedure for synthesis of (2-((2-methoxyphenyl)ethynyl)phenyl)methanol (1c):

To a stirred solution of (2-iodophenyl)methanol (234 mg, 1.0 mmol), palladium(II) chloride (3.5 mg, 2 mol%), triphenylphosphine (10.4 mg, 4 mol%) and copper(I) iodide (15 mg, 8 mol%) in triethylamine (4 mL) was added 1-ethynyl-2-methoxybenzene (158 mg, 1.2 mmol) under nitrogen atmosphere. Then, the reaction was heated at 60 ^{o}C for 12h. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated NH_4Cl solution. The organic layer was extracted with EtOAc (3x20 mL). The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the (2-((2-methoxyphenyl)ethynyl)phenyl)methanol (**1c**).

Colorless oil; R_f (hexane/EtOAc 5:1) 0.50; yield 209 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (t, *J* = 7.2 Hz, 1 H), 3.92 (s, 3 H), 4.83 (d, *J* = 7.2 Hz, 2 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.96 (t, *J* = 7.6 Hz, 1 H), 7.25-7.36 (m, 4 H), 7.48 (dd, *J* = 7.6 and 1.6 Hz, 1 H), 7.54 (dd, *J* = 8.0 and 2.4 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 55.9, 64.9, 90.8, 91.9, 110.7, 112.3, 120.9, 122.3, 127.8, 128.3, 128.7, 130.2, 132.0, 132.7, 143.5, 160.2; HRMS (ESI) calcd. for $C_{16}H_{15}O_2$ $(M + H)^+$ 239.1067, found 239.1066.

Methyl 4-((2-(hydroxymethyl)phenyl)ethynyl)benzoate (1e):

Colorless solid; R_f (hexane/EtOAc 5:1) 0.40; mp 108-110 oC; yield 220 mg, 83%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.06 (t, *J* = 5.4 Hz, 1 H), 3.96 (s, 3 H), 4.95 (d, *J* = 6.6 Hz, 2 H), 7.33 (dt, *J* = 7.6 and 1.2 Hz, 1 H), 7.42 (dt, *J* = 7.6 and 1.2 Hz, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.58 (dd, *J* = 7.6 and 1.0 Hz, 1 H), 7.61 (d, *J* = 8.6 Hz, 1 H), 8.06 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$)

δ52.5, 64.1, 89.9, 93.5, 121.0, 127.5, 127.8, 129.5, 129.8, 130.0, 131.7, 132.6, 142.9, 166.7; HRMS (ESI) calcd. for $C_{17}H_{15}O_3$ $(M + H)^+$ 267.1016, found 267.1034.

(2-((3-Methoxyphenyl)ethynyl)phenyl)methanol (1f):

Colorless oil; R_f (hexane/EtOAc 5:1) 0.50; yield 207 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 (s, 1 H), 3.78 (s, 3 H), 4.87 (s, 2 H), 6.88 (dd, *J* = 8.4 and 2.4 Hz, 1 H), 7.03 (s, 1 H), 7.10 (d, *J* = 7.6 Hz, 1 H), 7.20-7.25 (m, 2 H), 7.31 (t, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.50 (d, J = 7.6 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 55.4, 63.8, 86.7, 94.2, 115.2, 116.4, 121.2, 124.0, 124.3, 127.2, 127.5, 128.9, 129.6, 132.2, 142.7, 159.5; HRMS (ESI) calcd. for $C_{16}H_{15}O_2$ $(M + H)^+$ 239.1067, found 239.1067.

(2-(Benzo[*d*][1,3]dioxol-5-ylethynyl)phenyl)methanol (1g):

Colorless oil; R_f (hexane/EtOAc 5:1) 0.60; yield 216 mg, 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (bs, 1 H), 4.87 (s, 2 H), 5.98 (s, 2 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.96 (s, 1 H), 7.05 (dd, *J* = 8.0 and 1.5 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.50 (d, *J* = 7.6 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 64.2, 85.4, 94.4, 101.6, 108.8, 111.7, 116.3, 121.6, 126.5, 127.4, 127.7, 128.7, 132.2, 142.6, 147.8, 148.4; HRMS (ESI) calcd. for $C_{16}H_{13}O_3$ $(M + H)^+$ 253.0859, found 253.0839.

1-(2-(Naphthalen-1-ylethynyl)phenyl)ethanol (1n):

Brown solid; R_f (hexane/EtOAc 4:1) 0.50; mp 105-107 ºC; yield 244 mg, 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (d, *J* = 6.4 Hz, 3 H), 2.19 (bs, 1 H), 5.53-5.59 (m, 1 H), 5.98 (s, 2 H), 7.30 (dt, *J* = 7.6 and 1.5 Hz, 1 H), 7.41 (dt, *J* = 7.6 and 1.5 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.58-7.65 (m, 3 H), 7.76 (d, *J* = 7.6 Hz, 1 H), 7.87 (t, *J* = 7.6 Hz, 2 H), 8.40 (d, *J* = 7.6 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 24.5, 68.9, 92.0, 92.8, 120.8, 121.0, 125.0, 125.5,

126.3, 126.7, 127.2, 127.4, 128.6, 129.2, 129.3, 130.7, 132.7, 133.4, 133.5, 147.8; HRMS (ESI) calcd. for $C_{20}H_{17}O$ $(M + H)^+$ 273.1274, found 273.1284.

Experimental procedure for synthesis of 9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3a):

To a solution of (2-(phenylethynyl)phenyl)methanol (100 mg, 0.5 mmol) and phenylacetaldehyde (66 mg, 0.55 mmol) in toluene was added $BF_3{\cdot}OEt_2$ (0.12 mL, 0.5 mmol) dropwise at 0 ºC under nitrogen atmosphere. The reaction was stirred at 0 ºC for 15 minutes and then brought to room temperature over a period of 15 minutes and then heating at 100 ºC for 1h. After completion of the reaction, the solvent was removed under reduced pressure and diluted with saturated $NaHCO_3$ solution. Then the organic layer was extracted with EtOAc (3x10 mL). The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na_2SO_4 and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel eluted with hexane to give the 9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene.

Colorless solid; R_f (hexane) 0.60; mp 75-77 ºC; yield 102 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (d, J_{ab} = 3.6 Hz, 2 H), 7.33-7.35 (m, 1 H), 7.40-7.43 (m, 4 H), 7.51-7.53 (m, 1 H), 7.61-7.68 (m, 3 H), 7.80-7.82 (m, 1 H), 7.89-7.91 (m, 1 H), 8.05-8.10 (m, 2 H), 8.32 (d, J = 8.0 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 40.7, 125.2, 126.0, 126.3, 126.5, 126.6, 126.7, 127.7, 127.9, 128.0, 128.1, 128.2, 128.3, 129.6, 132.0, 132.7, 133.4, 134.2, 135.8, 136.2, 138.2, 143.6, 144.4; HRMS (ESI) calcd. for $C_{23}H_{17}$ $(M + H)^+$ 293.1325, found 293.1323.

15-Methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3b):

Colorless solid; R_f (hexane) 0.60; mp 74-76 ºC; yield 76 mg, 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3 H), 3.66 (d, J_{ab} = 2.8 Hz, 2 H), 7.20 (t, J = 7.6 Hz, 1 H), 7.24-7.32 (m, 4 H), 7.38 (d, J = 7.6 Hz, 1 H), 7.44-7.50 (m, 2 H), 7.56 (t, J = 8.0 Hz, 1 H), 7.63 (s, 1 H), 7.67-7.70 (m, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.17 (d, J = 8.4 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 20.0, 40.8, 124.4, 125.2, 125.9, 126.0, 126.4, 126.5, 126.6, 127.9, 128.0, 128.4, 128.9, 129.5, 132.2, 132.6, 132.9, 134.0, 134.3, 134.4, 135.8, 138.2, 143.7, 144.3; HRMS (ESI) calcd. for $C_{24}H_{19}$ $(M + H)^+$ 307.1481, found 307.1488.

7-Methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3c):

Colorless solid; R_f (hexane) 0.70; mp 182-184 ºC; yield 92 mg, 60%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.53 (d, J = 5.4 Hz, 3 H), 3.79 (s, 2 H), 7.20 (d, J = 7.2 Hz, 1 H), 7.36-7.39 (m, 1 H), 7.40-7.44 (m, 2 H), 7.45-7.48 (m, 1 H), 7.58-7.67 (m, 3 H), 7.82-7.85 (m, 1 H), 7.91-7.94 (m, 1 H), 8.04-8.08 (m, 2 H), 8.37 (t, J = 7.8 Hz, 1 H); ^{13}CNMR (150 MHz, $CDCl_3$) δ 21.3, 40.7, 125.9, 126.1, 126.2, 126.4, 126.6, 127.3, 127.7, 127.8, 127.9, 128.1, 128.3, 129.6, 131.3, 132.1, 132.6, 133.4, 135.8, 136.1, 137.9, 138.3, 143.7, 144.3; HRMS (ESI) calcd. for $C_{24}H_{22}N$ $(M + NH_4)^+$ 324.1747, found 324.1755.

7,15-Dimethyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3d):

Colorless solid; R_f (hexane) 0.70; mp 87-89 ºC; yield 64 mg, 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3 H), 2.81 (s, 3 H), 3.64 (s, 2 H), 7.03 (d, J = 7.6 Hz, 1 H), 7.21 (s, 1 H), 7.27-7.32 (m, 3 H), 7.38 (d, J = 11.4 Hz, 1 H), 7.47 (t, J = 6.8 Hz, 1 H), 7.56 (t, J = 6.8 Hz, 1 H), 7.63 (s, 1 H), 7.68-7.71 (m, 1 H), 8.08 (d, J = 8.0 Hz, 1 H), 8.20 (d, J = 8.4 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 20.0, 21.4, 40.9, 124.4, 125.8, 125.9, 126.1, 126.5, 126.6, 127.3, 127.9, 128.5, 129.0, 129.6, 131.5, 132.2, 132.6, 132.8, 133.7, 134.4, 135.8, 137.8, 138.4, 143.7, 144.2; HRMS (ESI) calcd. for $C_{25}H_{24}N$ $(M + NH_4)^+$ 338.1903, found 338.1885.

5-Methoxy-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3e):

Colorless solid; R_f (hexane/EtOAc 98:2) 0.50; mp 187-189 °C; yield 77 mg, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 3 H), 3.53-3.63 (m, 2 H), 6.79 (d, *J* = 8.0 Hz, 1 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 7.22-7.32 (m, 4 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.47 (t, *J* = 6.8 Hz, 1 H), 7.70 (t, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.90 (t, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.8, 55.4, 109.1, 119.0, 122.8, 125.6, 125.7, 126.5, 126.7, 127.8, 128.0, 128.2, 128.4, 129.2, 129.3, 131.7, 132.2, 132.6, 136.9, 138.6, 143.8, 146.7, 157.7; HRMS (ESI) calcd. for $C_{24}H_{19}O$ $(M + H)^+$ 323.1430, found 323.1419.

7-Methoxy-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3f):

Colorless solid; R_f (hexane) 0.40; mp 168-170 °C; yield 81 mg, 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73-3.75 (m, 2 H), 3.91 (s, 3 H), 6.87-6.89 (m, 1 H), 7.05 (s, 1 H), 7.37-7.42 (m, 3 H), 7.53-7.61 (m, 3 H), 7.76-7.79 (m, 1 H), 7.85-7.87 (m, 1 H), 7.98-8.02 (m, 2 H), 8.26-8.29 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.0, 55.4, 110.8, 111.8, 125.9, 126.2, 126.5, 126.7, 126.8, 127.5, 127.8, 127.9, 128.1, 128.3, 129.6, 132.1, 133.4, 133.7, 135.6, 136.0, 138.4, 143.3, 145.7, 159.7; HRMS (ESI) calcd. for $C_{24}H_{19}O$ $(M + H)^+$ 323.1430, found 323.1438.

6-Methoxy-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3h):

Colorless solid; R_f (hexane/EtOAc 98:2) 0.50; mp 124-126 °C; yield 77 mg, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (s, 2 H), 3.70 (s, 3 H), 6.85 (dd, *J* = 8.4 and 2.4 Hz, 1 H), 7.08 (d, *J* = 2.0 Hz, 1 H), 7.25-7.29 (m, 4 H), 7.44-7.52 (m, 2 H), 7.65-7.68 (m, 1 H), 7.75 (d, *J* = 8.4 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 8.23 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.8, 55.5, 114.1, 118.0, 126.0, 126.3, 126.4, 126.6, 127.4, 127.6, 128.0, 128.2, 128.3, 129.6, 131.9, 133.4, 135.1, 135.7, 136.3, 137.3, 138.2, 144.0, 157.1; HRMS (ESI) calcd. for $C_{24}H_{19}O$ $(M + H)^+$ 323.1430, found 323.1437.

8-Methoxy-9H-dibenzo[3,4:6,7]cyclohepta[1,2-a]naphthalene (4h):

Colorless solid; R_f (hexane/EtOAc 98:2) 0.55; mp 158-160 ºC; yield 46 mg, 29%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (d, J_{ab} = 12.5 Hz, 1 H), 3.91 (s, 3 H), 4.39 (d, J_{ab} = 12.5 Hz, 1 H), 6.90-6.93 (m, 1 H), 7.14-7.19 (m, 2 H), 7.28-7.34 (m, 2 H), 7.42-7.45 (m, 1 H), 7.47-7.56 (m, 2 H), 7.71-7.73 (m, 1 H), 7.80 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 8.21 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 56.1, 109.7, 125.1, 125.2, 125.9, 126.2, 126.5, 126.8, 127.8, 127.9, 128.0, 128.1, 128.2, 129.4, 132.0, 133.0, 133.3, 135.8, 135.9, 136.3, 138.6, 143.8, 155.5; HRMS (ESI) calcd. for $C_{24}H_{19}O$ $(M + H)^+$ 323.1430, found 323.1428.

7-Methoxy-15-methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3i):

Colorless oil; R_f (hexane/EtOAc 98:2) 0.5; yield 81 mg, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.79 (s, 3 H), 3.60-3.71 (m, 2 H), 3.83 (s, 3 H), 6.77 (dd, *J* = 8.8 and 2.8 Hz, 1 H), 6.93 (d, *J* = 2.8 Hz, 1 H), 7.25-7.32 (m, 3 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.45-7.49 (m, 1 H), 7.53-7.57 (m, 1 H), 7.62 (s, 1 H), 7.67-7.69 (m, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.18 (t, *d* = 8.0 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 19.9, 41.1, 55.5, 110.9, 111.8, 124.4, 125.8, 126.6, 126.7, 127.1, 127.9, 128.4, 128.9, 129.6, 132.3, 132.6, 133.5, 133.9, 134.1, 135.6, 138.4, 143.3, 145.6, 159.5; HRMS (ESI) calcd. for $C_{25}H_{21}O$ $(M + H)^+$ 337.1587, found 337.1606.

5-Methoxy-15-methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3j):

Colorless solid; R_f (hexane/EtOAc 99:1) 0.60; mp 196-198 ºC; yield 50 mg, 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (s, 3 H), 3.55 (s, 3 H), 3.58-3.66 (m, 3 H), 6.82 (d, *J* = 8.2 Hz, 1 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 7.27-7.34 (m, 3 H), 7.45 (t, *J* = 7.6 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.64 (s, 1 H), 7.75 (d, *J* = 7.6 Hz, 2 H), 8.09 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 40.8, 55.4,109.0, 119.0, 123.0, 124.1, 125.3, 125.6, 126.5, 126.7, 127.8, 128.9, 129.0, 129.1, 129.2,

130.9, 131.5, 131.7, 134.1, 136.5, 138.5, 143.8, 146.6, 157.7; HRMS (ESI) calcd. for $C_{25}H_{21}O$ $(M + H)^+$ 337.1587, found 337.1607.

5-Methyl-11*H*-benzo[4',5']naphtho[2'',1'':6',7']cyclohepta[1',2':4,5]benzo[1,2-*d*][1,3]dioxole (3k):

Colorless solid; R_f (hexane, eluted twice) 0.2; mp 102-104 °C; yield 44 mg, 25%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3 H), 3.56 (s, 2 H), 5.87 (d, *J* = 1.2 Hz, 1 H), 6.00 (d, *J* = 1.2 Hz, 1 H), 6.88 (s, 1 H), 6.95 (s, 1 H), 7.29-7.32 (m, 3 H), 7.50 (t, *J* = 6.8 Hz, 1 H), 7.56 (t, *J* = 6.8 Hz, 1 H), 7.62 (s, 1 H), 7.69-7.71 (m, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 8.21 (t, *J* = 8.0 Hz, 1 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 20.0, 40.5, 101.3, 106.9, 112.8, 124.4, 125.9, 126.0, 126.2, 126.7, 127.6, 128.0, 128.3, 128.9, 129.5, 132.2, 132.6, 133.7, 134.1, 135.7, 138.2, 138.3, 143.9, 145.4, 147.6; HRMS (ESI) calcd. for $C_{25}H_{22}NO_2$ $(M + NH_4)^+$ 368.1645, found 368.1657.

16-Methyl-10*H*-benzo[5',6']naphtho[1'',2'':3',4']cyclohepta[1',2':3,4]benzo[1,2-*d*][1,3]dioxole (4k):

Colorless solid; R_f (hexane, eluted twice) 0.3; mp 188-190 °C; yield 26 mg, 15%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (s, 3 H), 3.43 (d, $_{Jab}$ = 12.8 Hz, 1 H), 4.02 (dd, J_{ab} = 12.8 and 1.6 Hz, 1 H), 6.07 (d, *J* = 3.6 Hz, 2H), 6.75 (dd, *J* = 8.0 and 2.8 Hz, 1 H), 7.02 (dd, *J* = 8.0 and 2.0 Hz, 1 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.42 (d, *J* = 6.8 Hz, 1 H), 7.55 (t, *J* = 6.8 Hz, 1 H), 7.61 (t, *J* = 8.0 Hz, 1 H), 7.65 (s, 1 H), 7.74 (d, *J* = 7.2 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H), 8.28 (d, *J* = 8.4 Hz, 1 H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 32.5, 101.3, 105.5, 124.3, 125.9, 126.0, 126.1, 126.2, 126.8, 126.9, 127.8, 128.5, 129.1, 129.3, 129.8, 132.5, 132.7, 133.7, 133.9, 135.7, 139.0, 142.6, 143.9, 146.7; HRMS (ESI) calcd. for $C_{25}H_{22}NO_2$ $(M + NH_4)^+$ 368.1645, found 368.1659.

7-Chloro-15-methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3l):

Colorless solid; R_f (hexane) 0.60; mp 130-132 ºC; yield 24 mg, 15%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, J_{ab} = 2.8 Hz, 2 H), 7.23 (dd, J = 8.4 and 2.0 Hz, 1 H), 7.33-7.37 (m, 3 H), 7.43-7.58 (m, 4 H), 7.70-7.73 (m, 1 H), 7.79 (d, J = 8.4 Hz, 1 H), 7.96-7.99 (m, 2 H), 8.12 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.5, 125.5, 126.2, 126.5, 126.6, 126.7, 127.0, 127.4, 128.1, 128.3, 128.4, 129.7, 131.9, 132.7, 133.4, 133.8, 133.9, 134.6, 136.3, 138.1, 143.0, 145.8; HRMS (ESI) calcd. for $C_{23}H_{19}ClN$ $(M + NH_4)^+$ 344.1201, found 344.1209.

11-Methoxy-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3m):

Colorless gum; R_f (hexane) 0.50; yield 140 mg, 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (d, J_{ab} = 2.8 Hz, 2 H), 3.86 (s, 3 H), 6.87 (dd, J = 8.4 and 2.6 Hz, 1 H), 6.91 (d, J = 2.6 Hz, 1 H), 7.27 (t, J = 8.4 Hz, 1 H), 7.34 (t, J = 7.2 Hz, 1 H), 7.43 (d, J = 7.2 Hz, 1 H), 7.48-7.55 (m, 4 H), 7.63 (d, J = 8.4 Hz, 1 H), 7.77 (d, J = 8.4 Hz, 1 H), 7.94 (d, J = 8.4 Hz, 2 H), 8.16 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.1, 55.6, 112.0, 112.1, 125.3, 125.8, 126.3, 126.7, 127.7, 127.9, 128.1, 128.2, 128.3, 130.7, 131.1, 132.2, 133.2, 134.5, 135.2, 136.0, 144.0, 145.0, 159.7; HRMS (ESI) calcd. for $C_{24}H_{19}O$ $(M + H)^+$ 323.1430, found 323.1432.

11-Methoxy-15-methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3n):

Colorless gum; R_f (hexane) 0.50; yield 130 mg, 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (s, 3 H), 3.63 (d, J_{ab} = 2.8 Hz, 2 H), 3.82 (s, 3 H), 6.83 (dd, J = 8.4 and 2.6 Hz, 1 H), 6.87 (d, J = 2.6 Hz, 1 H), 7.21 (t, J = 8.4 Hz, 1 H), 7.28 (t, J = 7.4 Hz, 1 H), 7.38 (d, J = 7.4 Hz, 1 H), 7.44-7.49 (m, 2 H), 7.54 (t, J = 7.4 Hz, 1 H), 7.60 (s, 1 H), 7.61 (d, J = 8.4 Hz, 1 H), 8.07 (d, J = 8.4 Hz, 2 H), 8.15 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 41.2, 55.5, 111.9, 112.1, 124.3, 125.3, 125.7, 125.9, 126.6, 127.9, 128.3, 128.9, 130.6, 131.1, 132.3, 132.4, 132.9, 133.7, 133.9, 134.7, 135.6, 143.9, 145.0, 159.7; HRMS (ESI) calcd. for $C_{25}H_{21}O$ $(M + H)^+$ 337.1587, found 337.1589.

15-Phenyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3o):

Colorless gum; R_f (hexane) 0.50; yield 74 mg, 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 2 H), 7.25-7.33 (m, 4 H), 7.35-7.38 (m, 2 H), 7.44-7.51 (m, 4 H), 7.54-7.62 (m, 4 H), 7.72-7.74 (m, 1 H), 7.77 (s, 1 H), 8.01-8.04 (m, 1 H), 8.23-8.26 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.9, 125.3, 126.1, 126.2, 126.4, 126.5, 126.7, 127.6, 128.1, 128.2, 128.3, 128.6, 129.2, 129.7, 130.4, 131.7, 132.5, 132.8, 134.3, 135.4, 135.7, 138.1, 140.0, 141.0, 143.8, 144.5; HRMS (ESI) calcd. for $C_{29}H_{21}$ $(M + H)^+$ 369.1638, found 369.1645.

7-Methyl-15-phenyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3p):

Colorless gum; R_f (hexane) 0.50; yield 92 mg, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 3.73 (d, J_{ab} = 6.7 Hz, 2 H), 7.10 (d, J = 8.0 Hz, 1 H), 7.28-7.34 (m, 3 H), 7.36-7.39 (m, 1 H), 7.47-7.51 (m, 4 H), 7.57 (t, J = 7.2 Hz, 2 H), 7.64 (d, J = 7.2 Hz, 2 H), 7.78 (s, 1 H), 8.01-8.04 (m, 1 H), 8.27-8.30 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 40.9, 126.0, 126.1, 126.2, 126.4, 126.6, 126.7, 127.4, 127.6, 128.1, 128.3, 128.6, 129.2, 129.7, 130.4, 131.4, 131.7, 132.6, 132.7, 135.5, 135.6, 138.1, 138.2, 139.8, 141.0, 143.8, 144.3; HRMS (ESI) calcd. for $C_{30}H_{23}$ $(M + H)^+$ 383.1794, found 383.1792.

11*H*-Benzo[5,6]cyclohepta[2,1-*a*:3,4-*a'*]dinaphthalene (3q):

Colorless solid; R_f (hexane) 0.80; mp 190-192 °C; yield 60 mg, 35%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (d, J_{ab} = 13.4 Hz, 1 H), 4.45 (d, J_{ab} = 13.4 Hz, 1 H), 6.90 (d, J = 8.6 Hz, 1 H), 7.08 (dd, J = 7.2 and 1.0 Hz, 1 H), 7.14-7.17 (m, 2 H), 7.22-7.28 (m, 2 H), 7.35-7.47 (m, 4 H), 7.53 (d, J = 8.4 Hz, 1 H), 7.61 (d, J = 7.2 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 7.83 (dd, J = 8.4 and 1.0 Hz, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 7.97 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0, 124.7, 125.7, 125.8, 126.1, 126.6, 127.0, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.1, 128.6, 129.3, 132.9, 133.1, 133.6, 133.7, 134.8, 135.0, 135.4, 136.1, 136.9, 137.3, 138.3, 139.2, 139.5, 140.5, 141.4, 142.1; HRMS (ESI) calcd. for $C_{27}H_{19}$ $(M + H)^+$ 343.1481, found 343.1463.

5-(Naphthalen-1-yl)-11*H*-benzo[*b*]fluorene (4q):

Colorless solid; R_f (hexane) 0.80; mp 90-92 ^oC; yield 76 mg, 45%; ^1H NMR (400 MHz, $CDCl_3$) δ 3.74 (d, J_{ab} = 12.6 Hz, 1 H), 3.79 (d, J_{ab} = 12.6 Hz, 1 H), 7.10-7.12 (m, 1 H), 7.17 (d, *J* = 8.4 Hz, 1 H), 7.22 (dd, *J* = 7.2 and 1.5 Hz, 1 H), 7.25 (d, *J* = 7.2 Hz, 1 H), 7.27-7.30 (m, 1 H), 7.32 (d, *J* = 7.2 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 7.44-7.51 (m, 2 H), 7.56 (d, *J* = 8.4 Hz, 1 H), 7.72 (dd, *J* = 7.2 and 1.5 Hz, 1 H), 7.79-7.88 (m, 3 H), 7.96 (d, *J* = 8.4 Hz, 1 H), 8.00 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.2, 124.8, 125.6, 125.8, 125.9, 126.0, 126.4, 126.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.8, 129.0, 129.1, 130.0, 130.5, 132.4, 132.5, 133.2, 134.0, 137.8, 138.5, 142.8, 144.1; HRMS (ESI) calcd. for $C_{27}H_{19}$ $(M + H)^+$ 343.1481, found 343.1481.

9-Methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (diastereomeric mixture; 3r:4r:: 4:1):

Colorless gum; R_f (hexane) 0.80; yield 60 mg, 40%; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, *J* = 7.2 Hz, 3 H, minor), 1.86 (d, *J* = 7.2 Hz, 3 H, major), 3.79 (q, *J* = 7.2 Hz, 1 H, major), 4.18 (q, *J* = 7.2 Hz, 1 H, minor), 7.22-7.34 (m, 2 H), 7.36-7.44 (m, 3 H), 7.48-7.58 (m, 4 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.82 (d, *J* = 8.4 Hz, 1 H), 7.95-8.00 (m, 2 H), 8.21 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 37.4, 121.6, 121.8, 124.8, 126.0, 126.1, 126.4, 127.8, 127.9, 128.0, 128.1, 128.4, 129.5, 131.7, 131.8, 132.4, 133.4, 134.3, 135.8, 136.2, 138.4, 146.7, 147.5; HRMS (ESI) calcd. for $C_{24}H_{19}$ $(M + H)^+$ 307.1481, found 307.1462.

9-Ethyl-15-methyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (diastereomeric mixture; 3s:4s:: 2:1):

Yellow gum; R_f (hexane) 0.60; yield 162 mg, 85%; ^1H NMR (400 MHz, $CDCl_3$) δ 0.61 (t, *J* = 7.2 Hz, 3 H, minor), 1.01 (t, *J* = 7.2 Hz, 3 H, major), 1.34-1.41 (m, 2 H, minor), 2.36-2.41 (m, 2 H, major), 2.77 (s, 3 H, minor), 2.80 (s, 3 H, major), 3.44 (t, *J* = 8.0 Hz, 1 H, major), 3.81 (t, *J* = 8.0

Hz, 1 H, minor), 7.12-7.37 (m, 11 H), 7.43-7.56 (m, 5 H), 7.60-7.71 (m, 3 H), 8.04-8.15 (m, 2 H), 8.22 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 13.6, 19.9, 20.0, 20.9, 22.6, 45.2, 57.9, 121.9, 122.1, 124.3, 124.4, 124.6, 125.3, 125.8, 125.85, 125.9, 126.0, 126.8, 127.8, 127.85, 127.89, 127.9, 128.4, 128.5, 128.7, 128.8, 128.9, 129.0, 129.6, 130.6, 131.9, 132.3, 132.6, 132.65, 132.7, 133.7, 133.8, 133.9, 134.0, 134.3, 134.5, 134.9, 135.4, 135.8, 137.5, 138.7, 145.7, 146.5, 146.7, 147.2 ; Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.32; H, 6.70.

15-Methyl-9-phenyl-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*a*]naphthalene (3t):

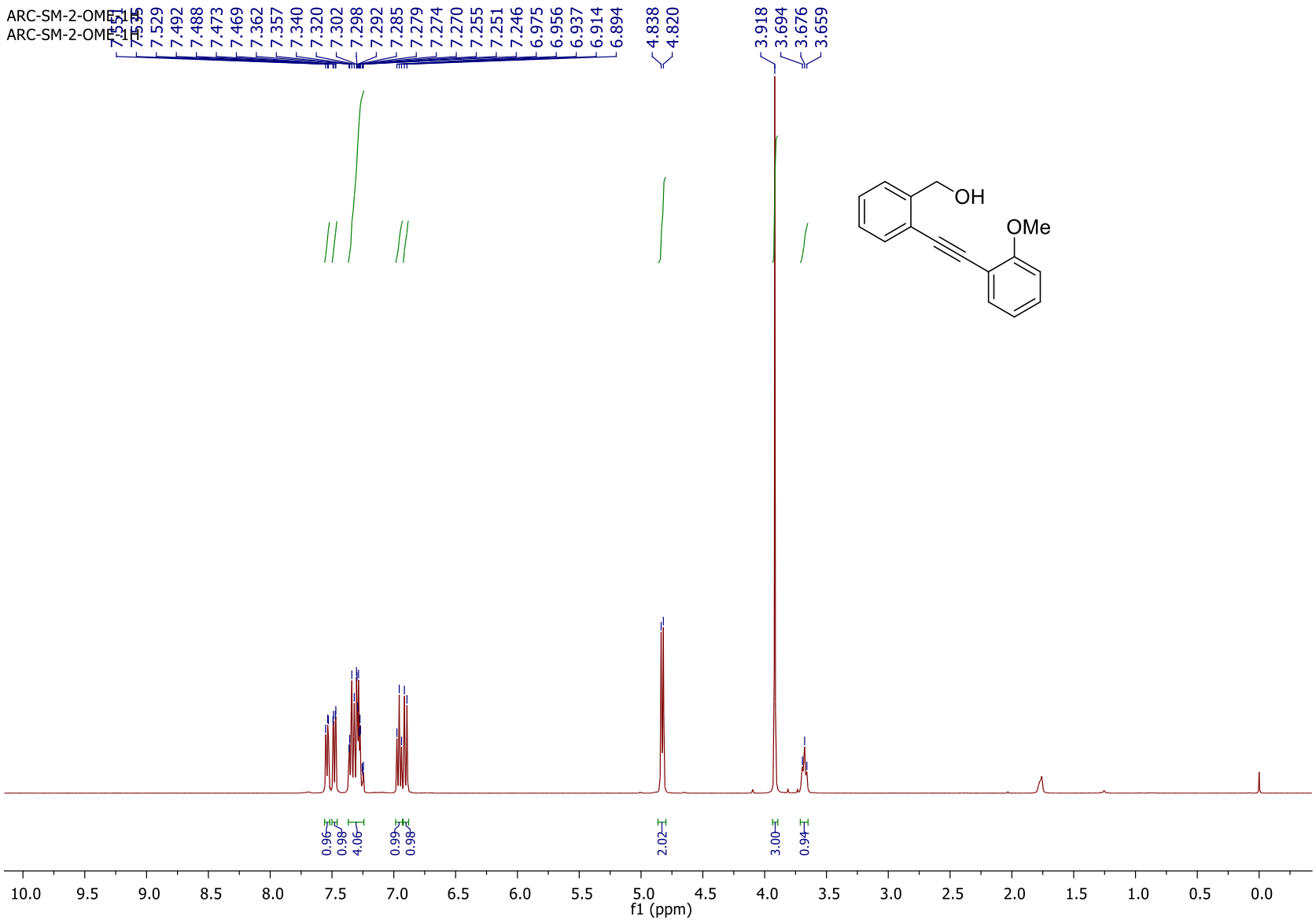
Yellow gum; R_f (hexane) 0.60; yield 118 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3 H), 5.35 (s, 1 H), 6.48 (d, *J* = 7.8 Hz, 1 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 7.15 (d, *J* = 7.4 Hz, 1 H), 7.18(d, *J* = 7.6 Hz, 2 H), 7.21-7.26 (m, 1 H), 7.32 (d, *J* = 7.2 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 7.44-7.51 (m, 2 H), 7.56 (d, *J* = 8.4 Hz, 1 H), 7.27-7.32 (m, 3 H), 7.41-7.47 (m, 2 H), 7.50-7.58 (m, 2 H), 7.62-7.68 (m, 4 H), 8.09 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 54.1, 123.8, 123.9, 125.3, 125.5, 126.7, 127.1, 127.2, 127.7, 128.0, 128.3, 129.0, 129.3, 130.2, 130.6, 130.7, 132.1, 132.6, 133.6, 137.3, 139.5, 140.4, 143.0, 143.2, 149.4; HRMS (ESI) calcd. for $C_{30}H_{23}$ $(M + H)^+$ 383.1794, found 383.1801.

17-Methyl-11*H*-benzo[5,6]cyclohepta[2,1-*a*:3,4-*a'*]dinaphthalene (3u) and 10-Methyl-5-(naphthalen-1-yl)-11*H*-benzo[*b*]fluorine (4u) (3u:4u::2:3):

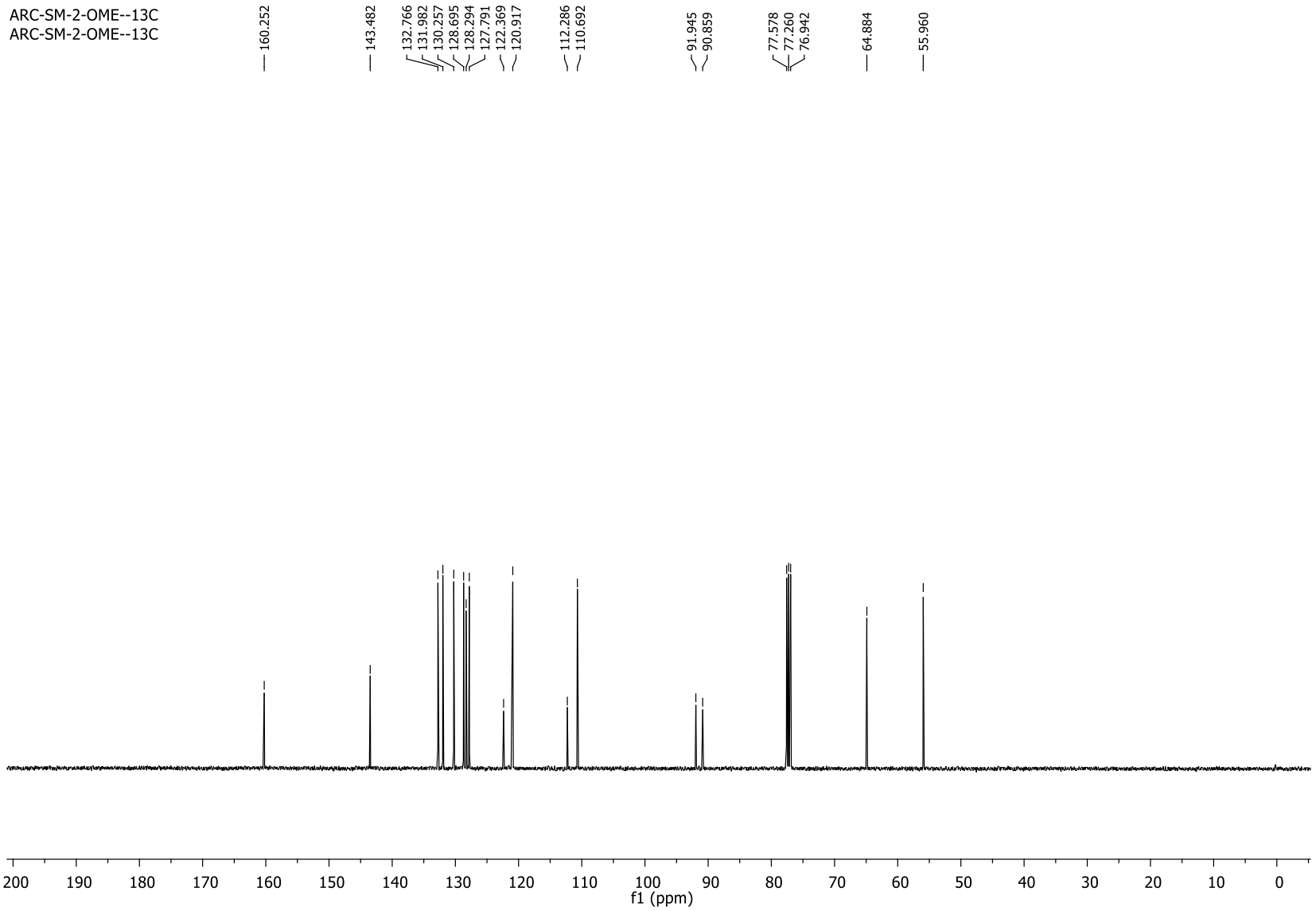
Yellow solid; R_f (hexane) 0.60; mp 180-182-92 ^{o}C; yield 140 mg, 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3 H, **3u**), 2.84 (s, 3 H, **4u**), 3.67 (d, *J* = 13.2 Hz, 1 H, **3u**), 3.71 (d, *J* = 12.6 Hz, 1 H, **4u**), 3.78 (d, *J* = 12.6 Hz, 1 H, **4u**), 4.44 (d, *J* = 13.2 Hz, 1 H, **3u**), 6.90 (d, *J* = 8.6 Hz, 1 H), 7.02-7.12 (m, 3 H), 7.15-7.36 (m, 11 H), 7.38-7.62 (m, 7 H), 7.67-7.72 (m, 3 H), 7.78 (t, *J* = 8.0 Hz, 3 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.0, 37.0, 37.9, 120.4, 121.3, 121.6, 124.0, 124.3, 124.4, 124.7, 125.3, 125.4, 125.5, 125.6, 125.7,

125.74, 125.8, 125.9, 126.2, 126.3, 127.0, 127.2, 127.7, 127.8, 128.0, 128.1, 128.3, 128.4, 128.7, 128.76, 128.8, 129.3, 129.5, 130.3, 131.7, 132.1, 132.3, 132.5, 132.9, 133.1, 133.6, 134.0, 134.2, 134.9, 135.2, 136.1, 136.7, 137.2, 138.7, 141.0, 143.2, 145.1, 145.4, 147.2; HRMS (ESI) calcd. for $C_{28}H_{21}$ $(M + H)^+$ 357.1638, found 357.1636.

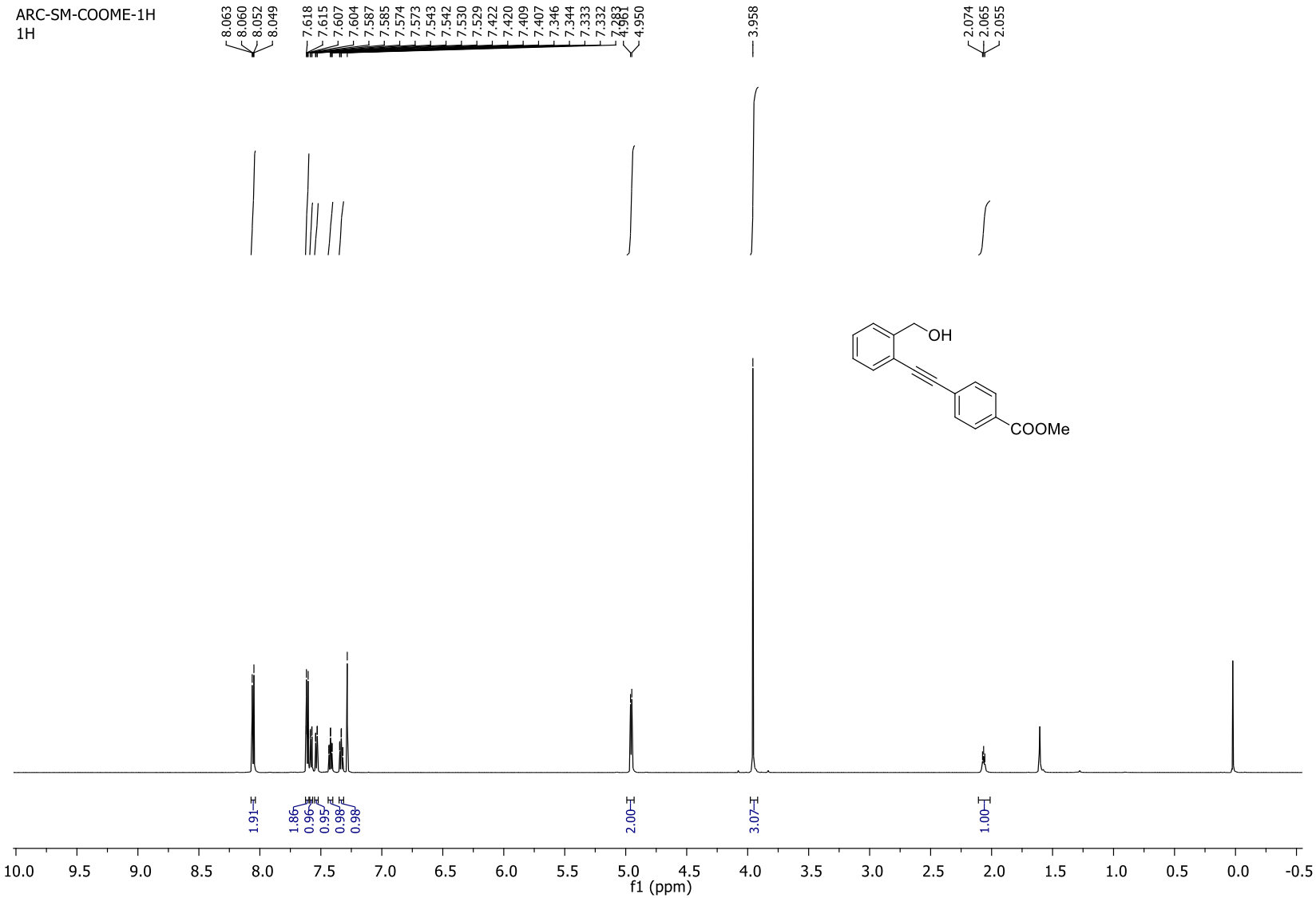
^{1}H Spectrum of **1c**



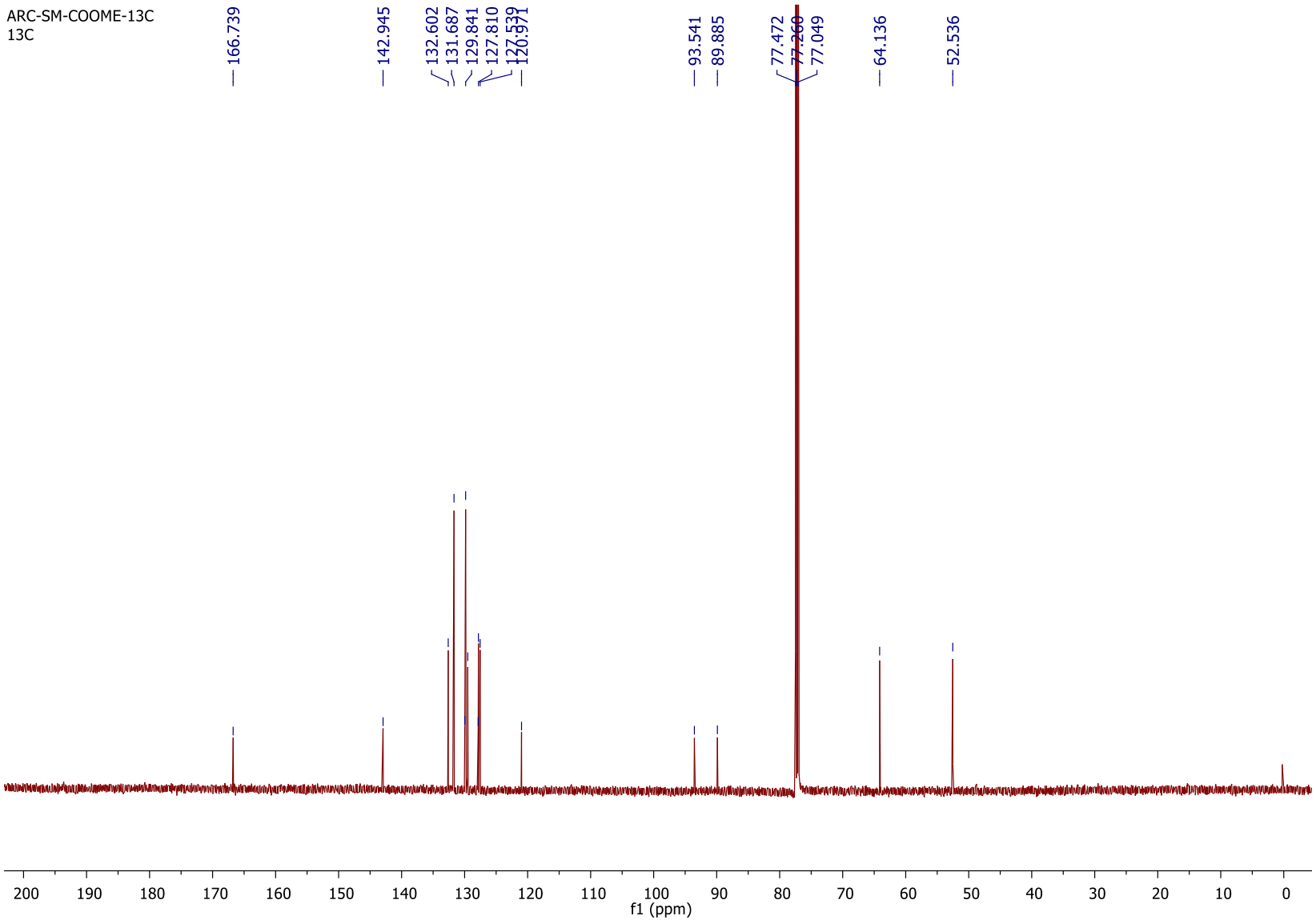
^{13}C Spectrum of **1c**



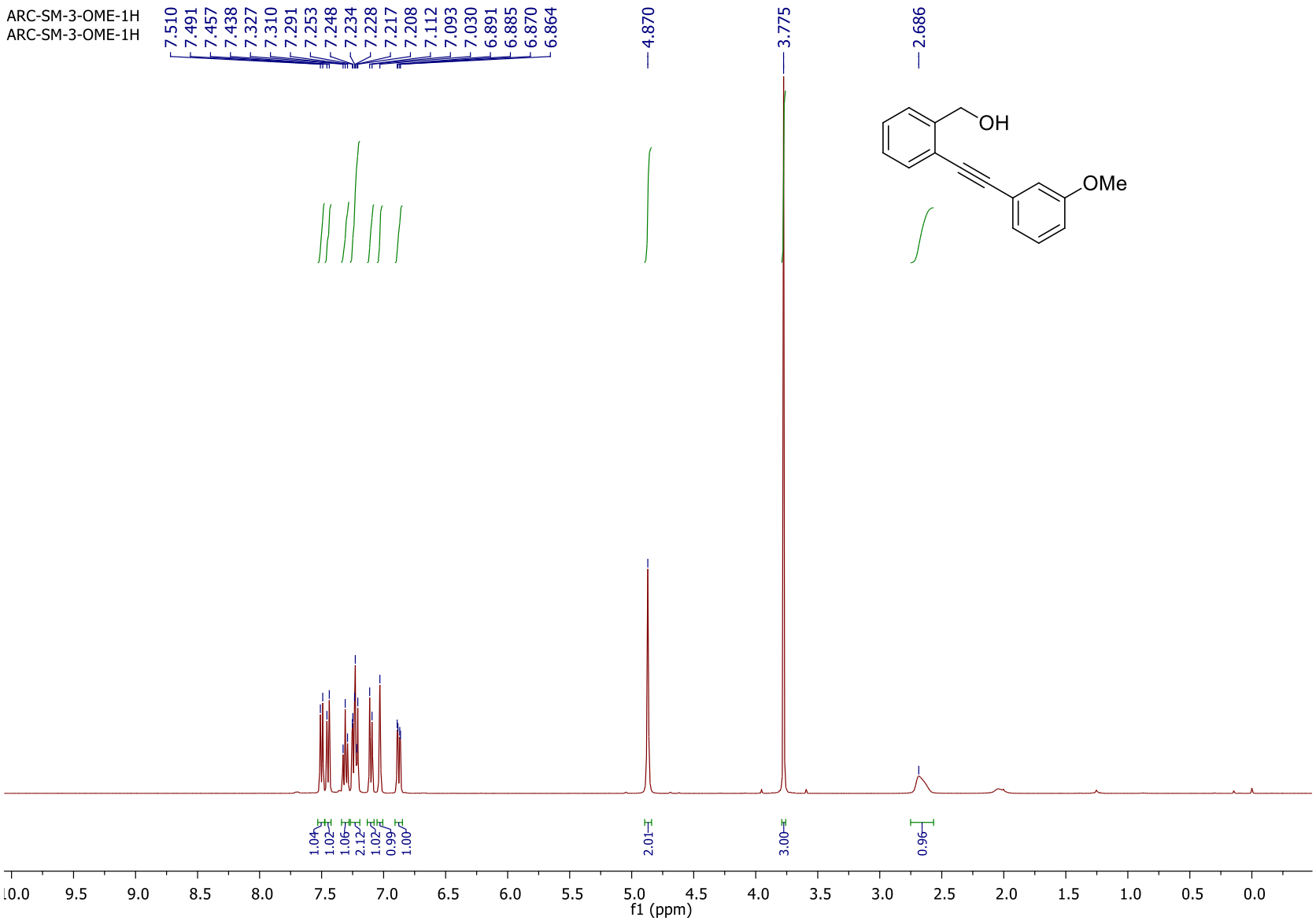
^{1}H Spectrum of **1e**



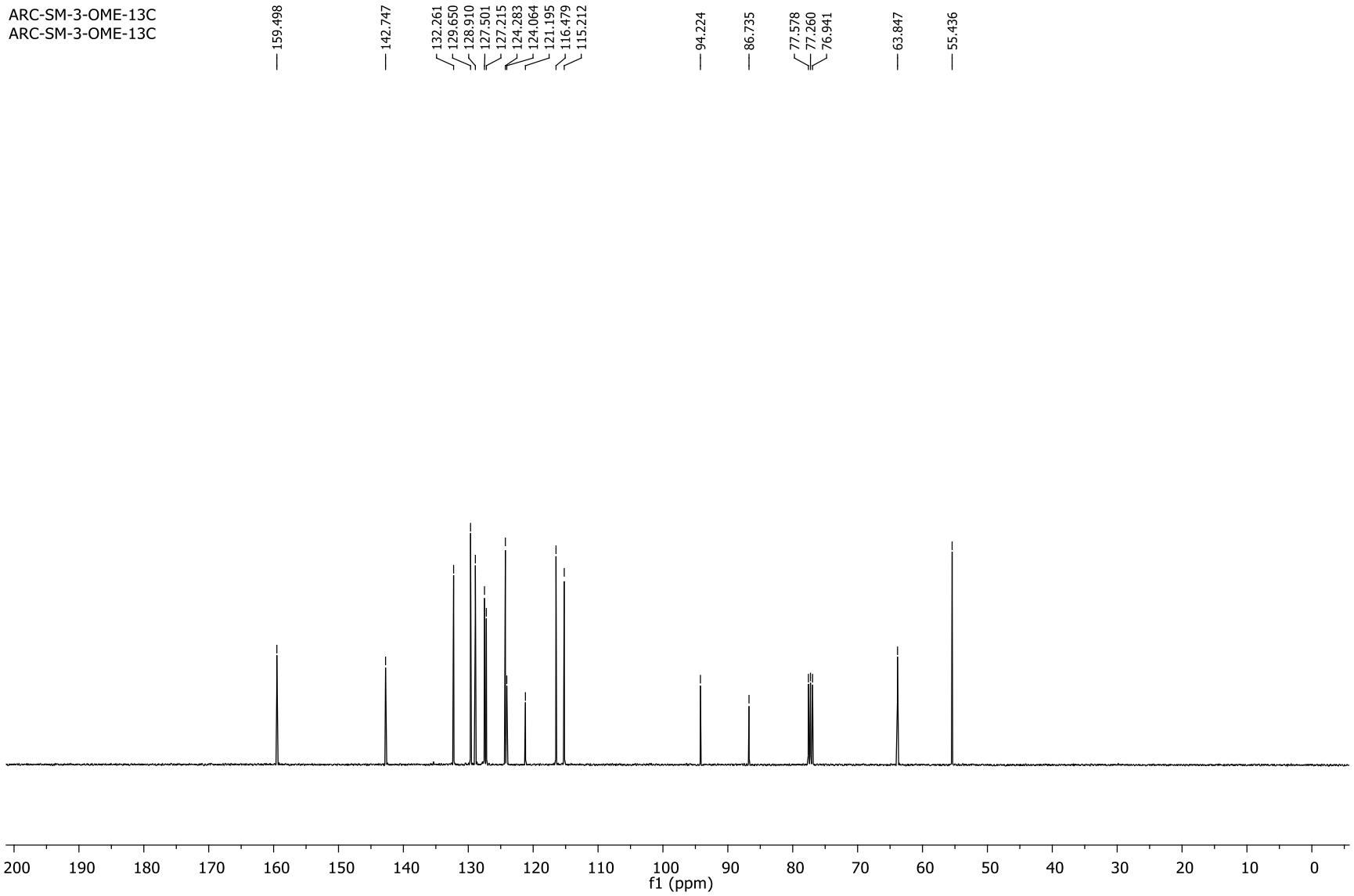
^{13}C Spectrum of **1e**



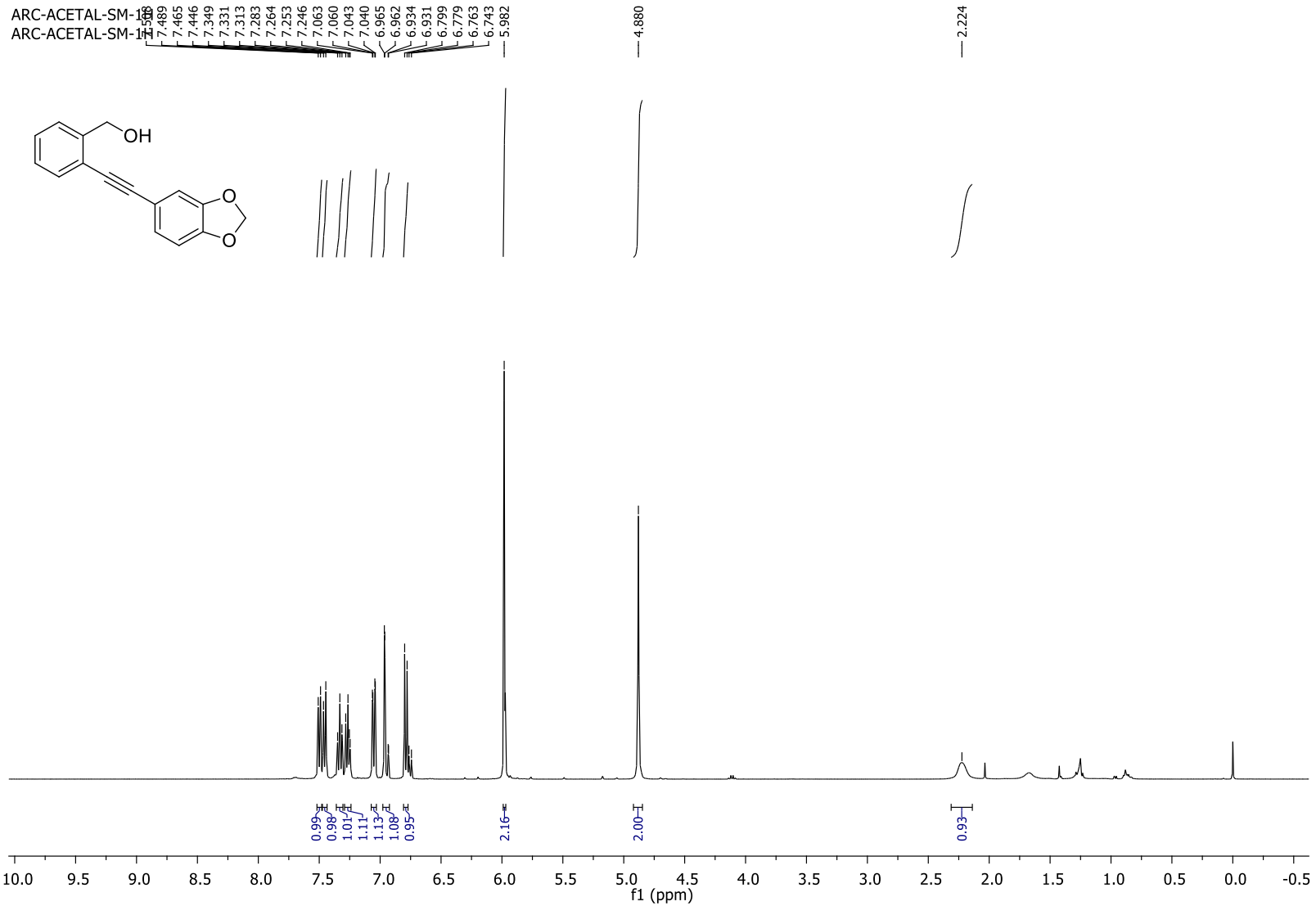
^{1}H Spectrum of **1f**



^{13}C Spectrum of **1f**



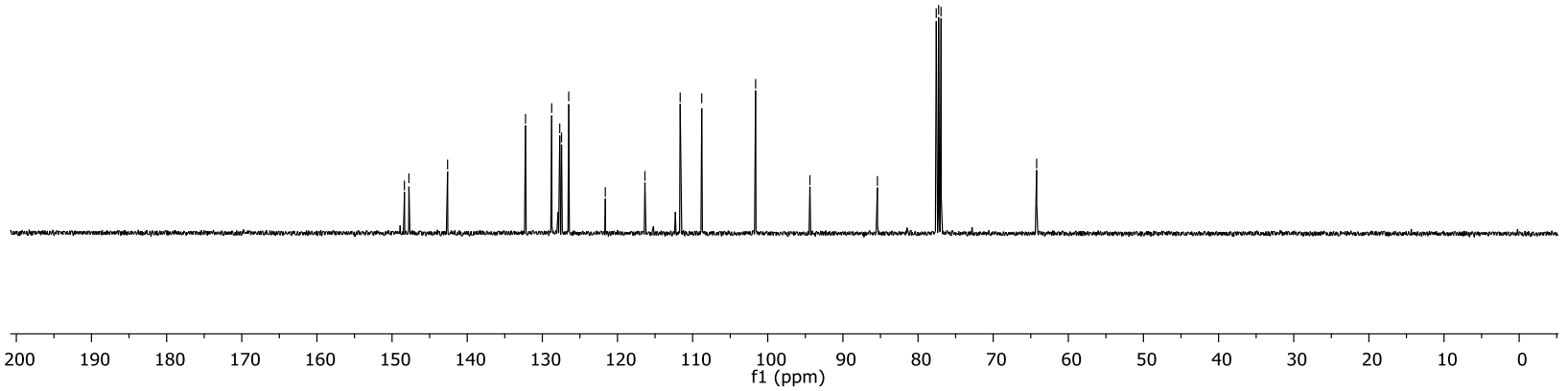
^{1}H Spectrum of **1g**



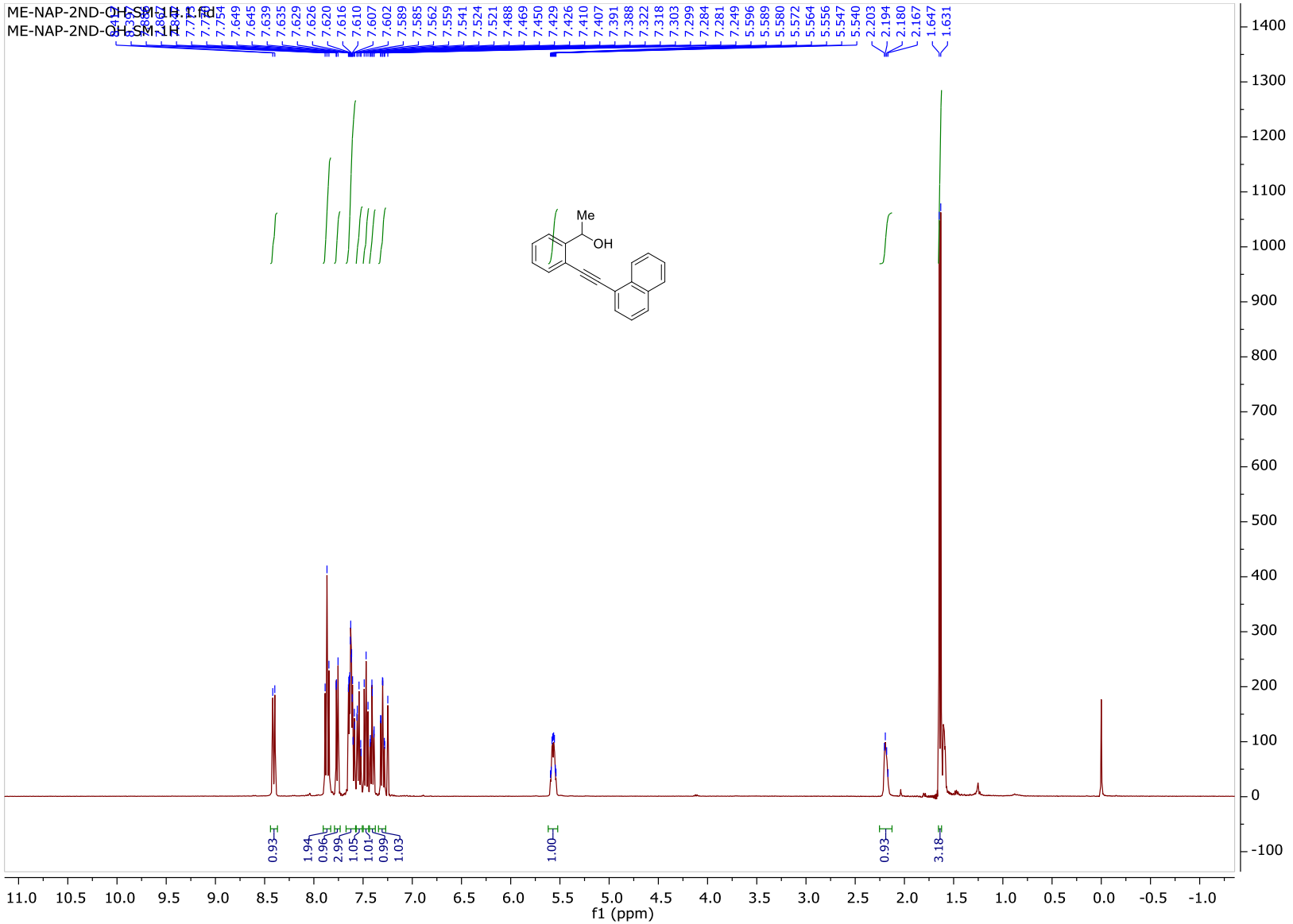
^{13}C Spectrum of **1g**

ARC-ACETAL-SM-13C
ARC-ACETAL-SM-13C

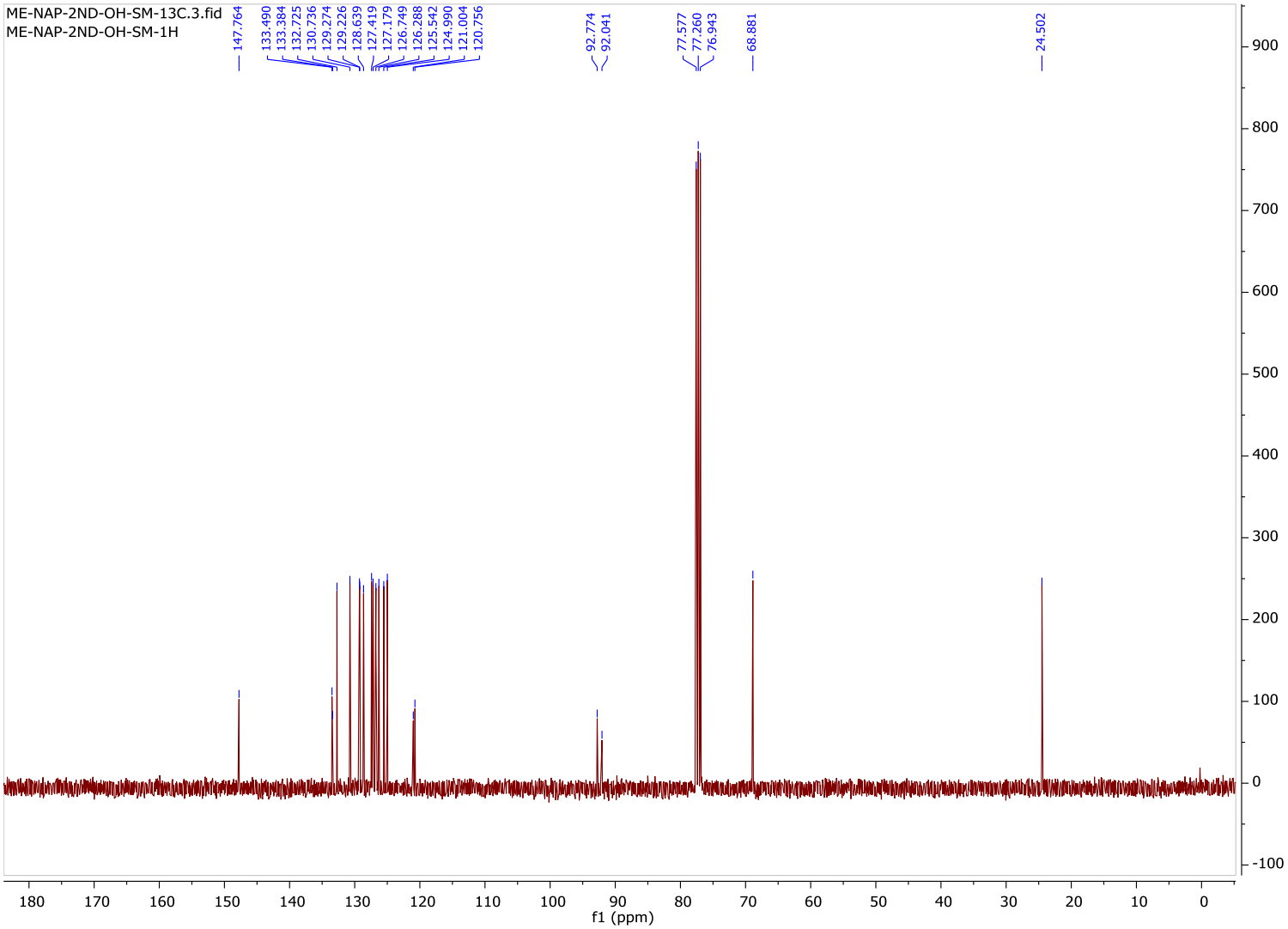
148.362
147.755
142.609
132.240
128.753
127.680
127.443
126.488
121.617
116.346
111.658
108.788
101.620
94.386
85.405
77.578
77.260
76.943
64.219



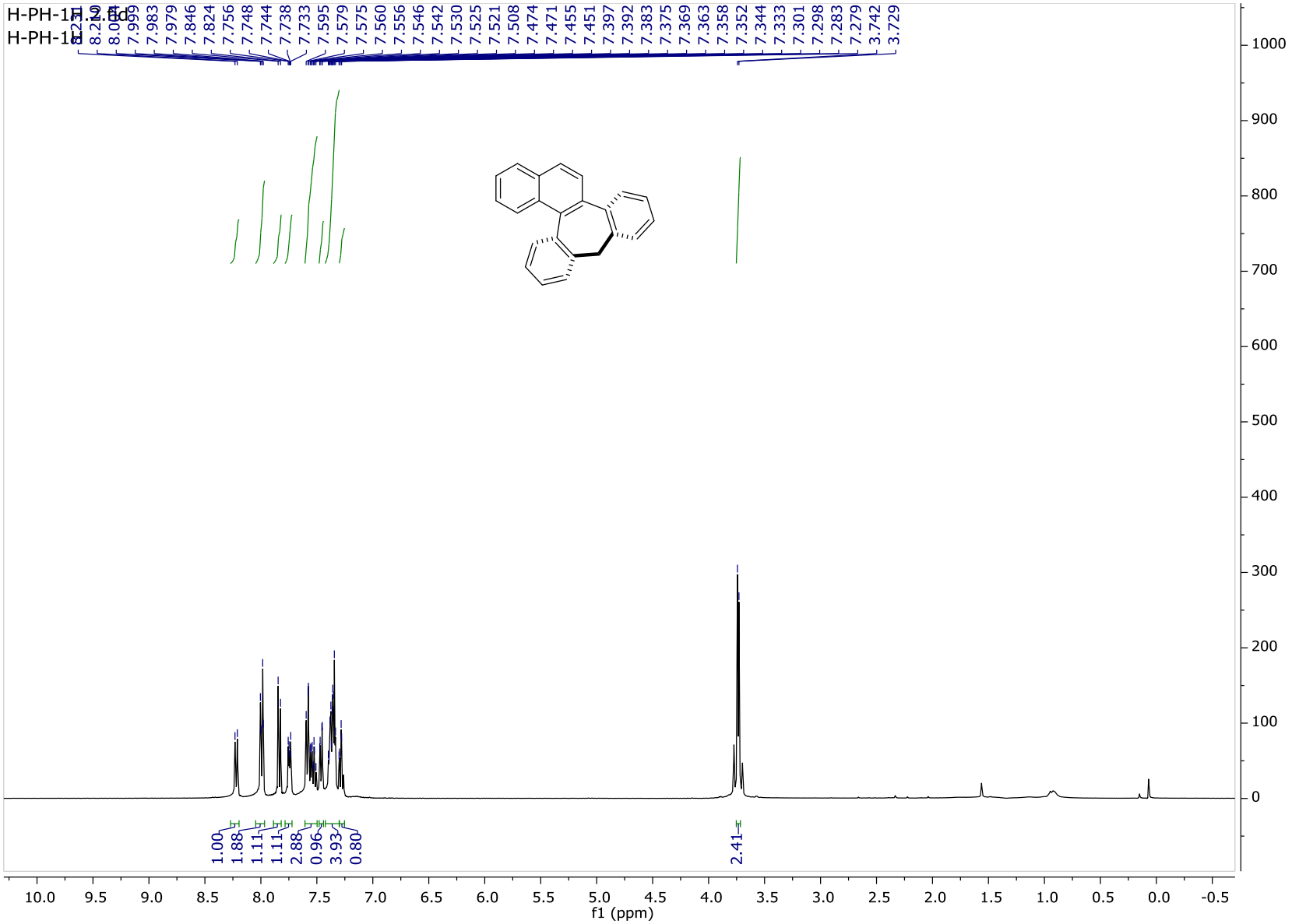
^{1}H Spectrum of **1n**



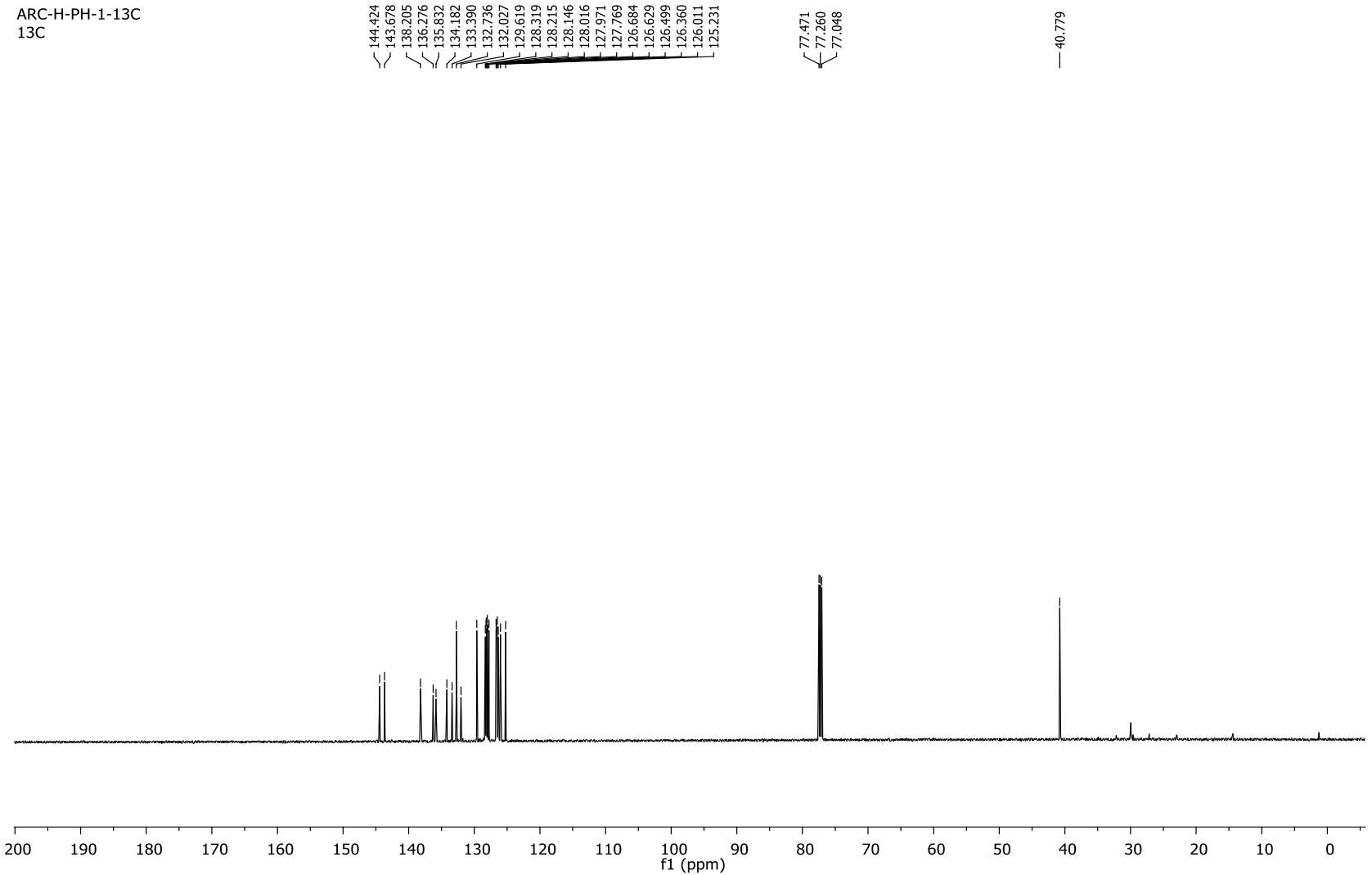
^{13}C Spectrum of **1n**



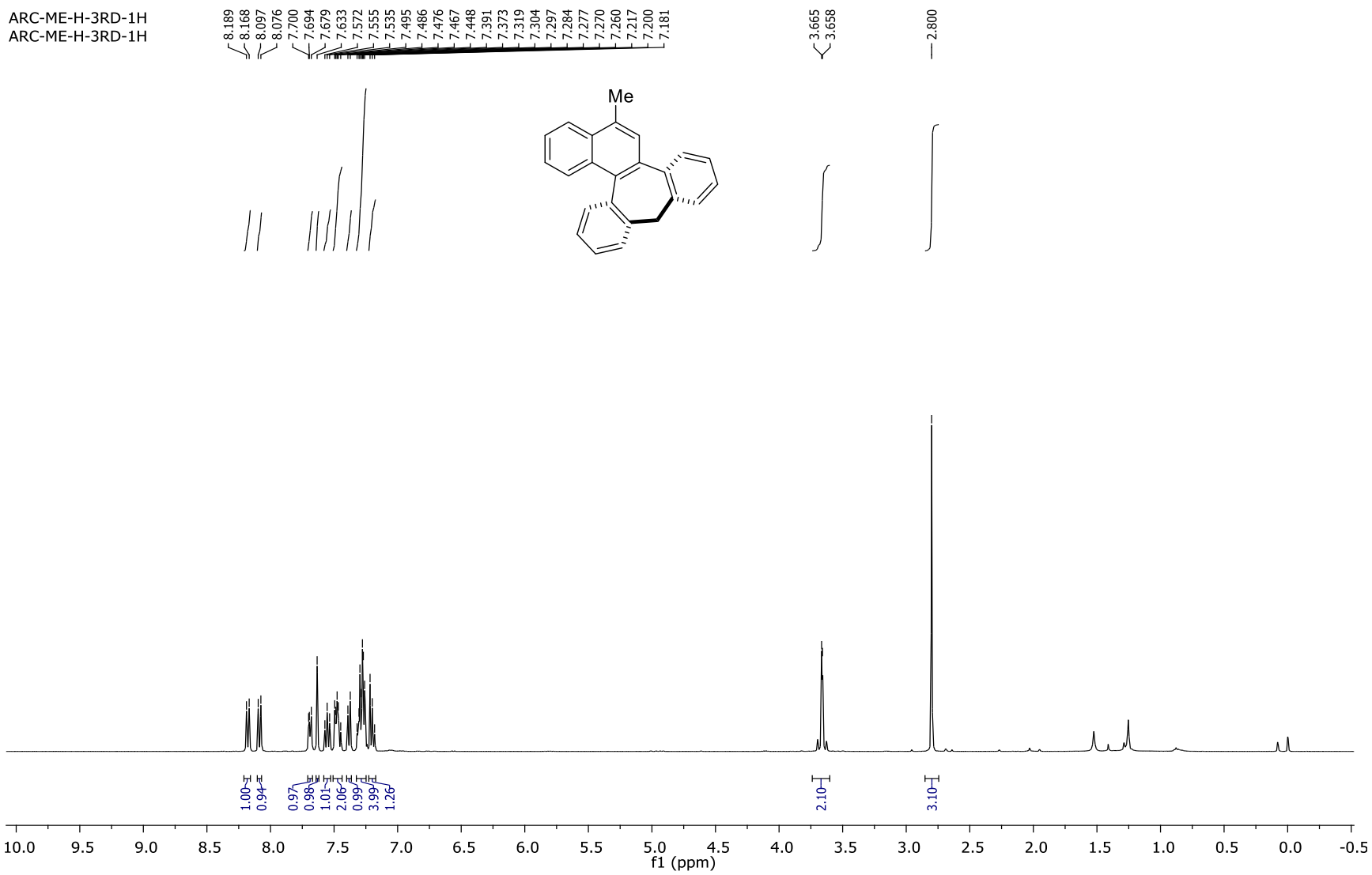
^{1}H Spectrum of **3a**



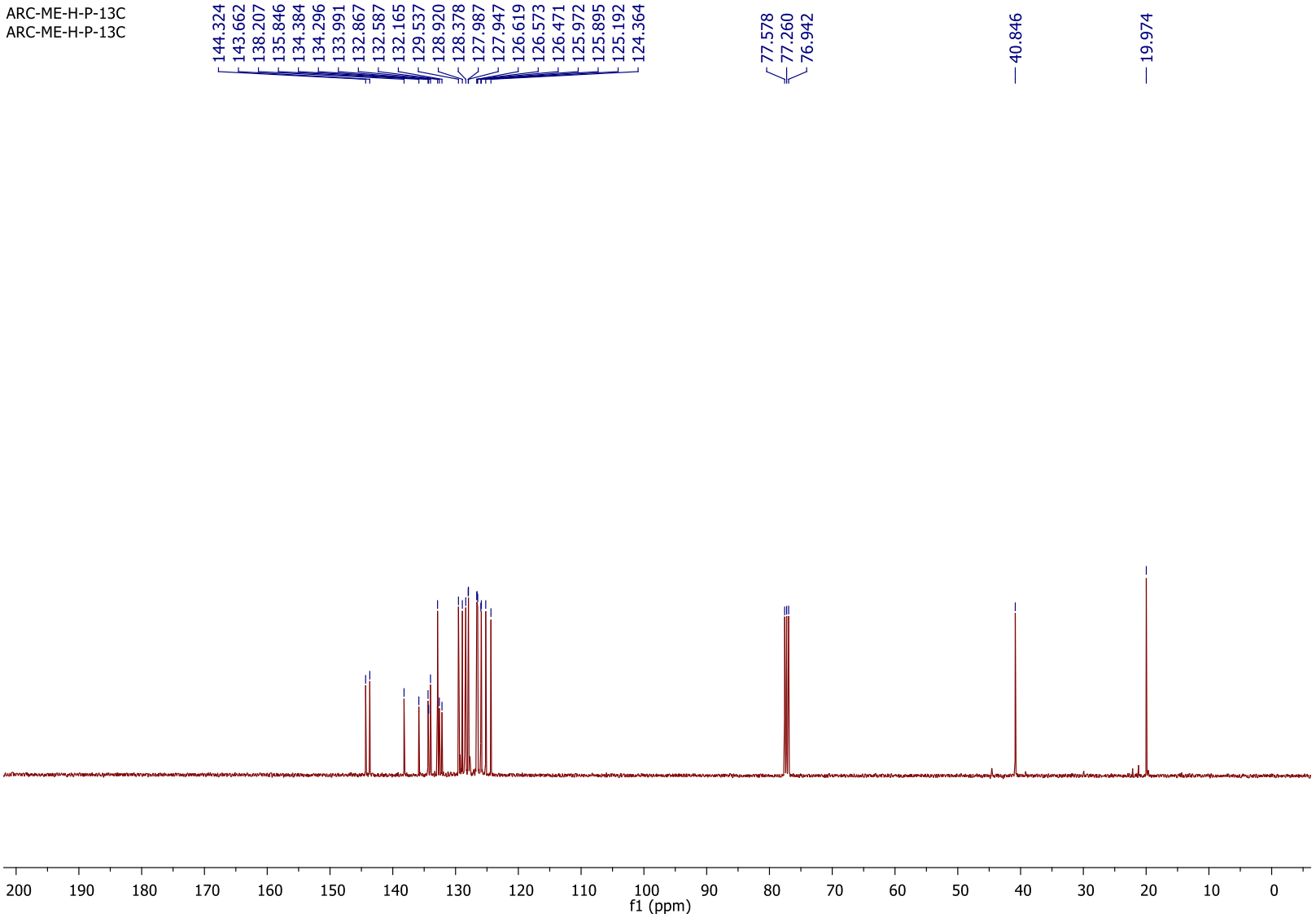
^{13}C Spectrum of **3a**



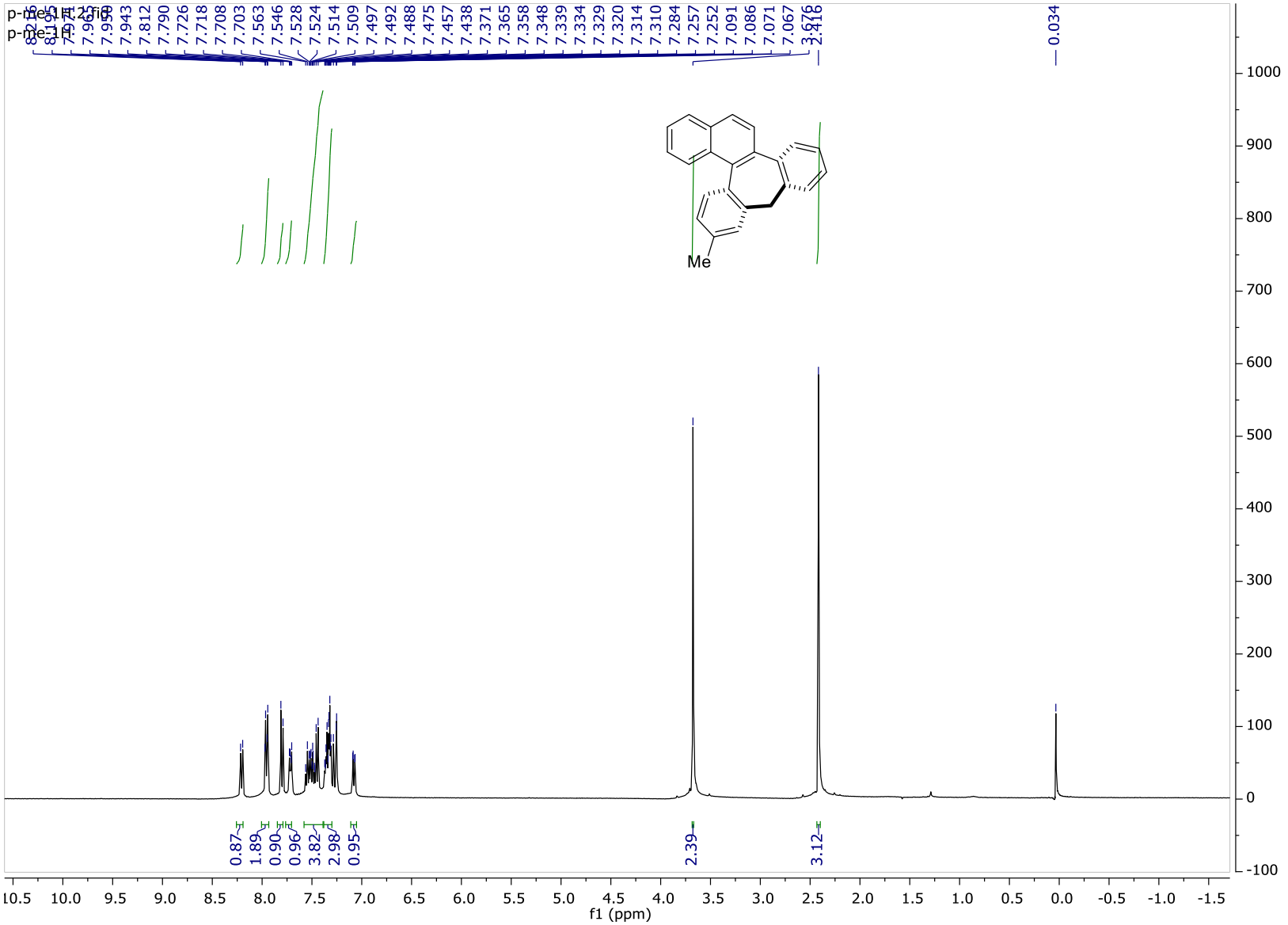
^{1}H Spectrum of **3b**



^{13}C Spectrum of **3b**



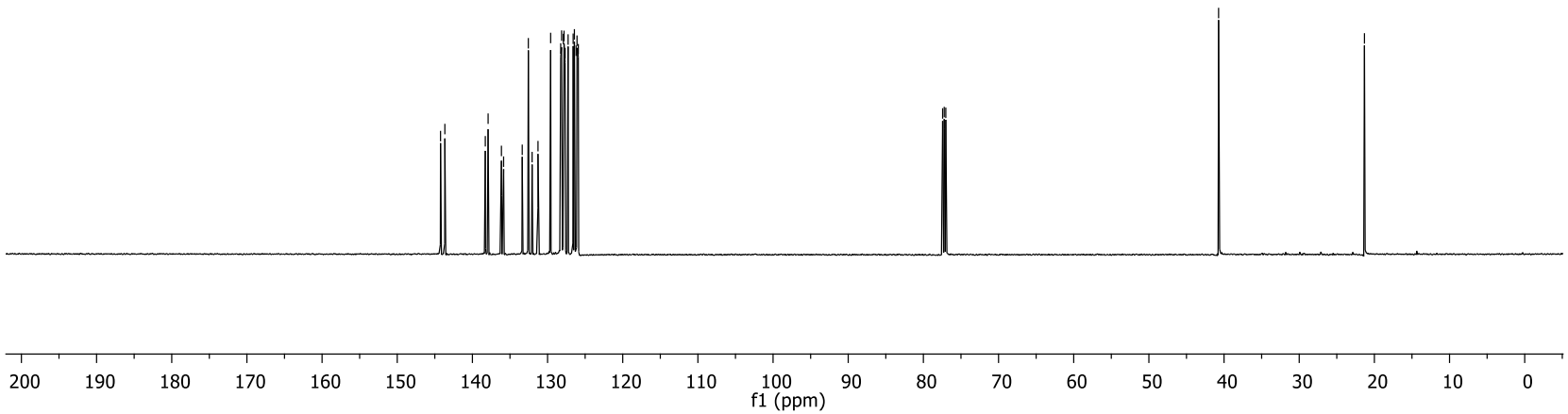
^{1}H Spectrum of **3c**



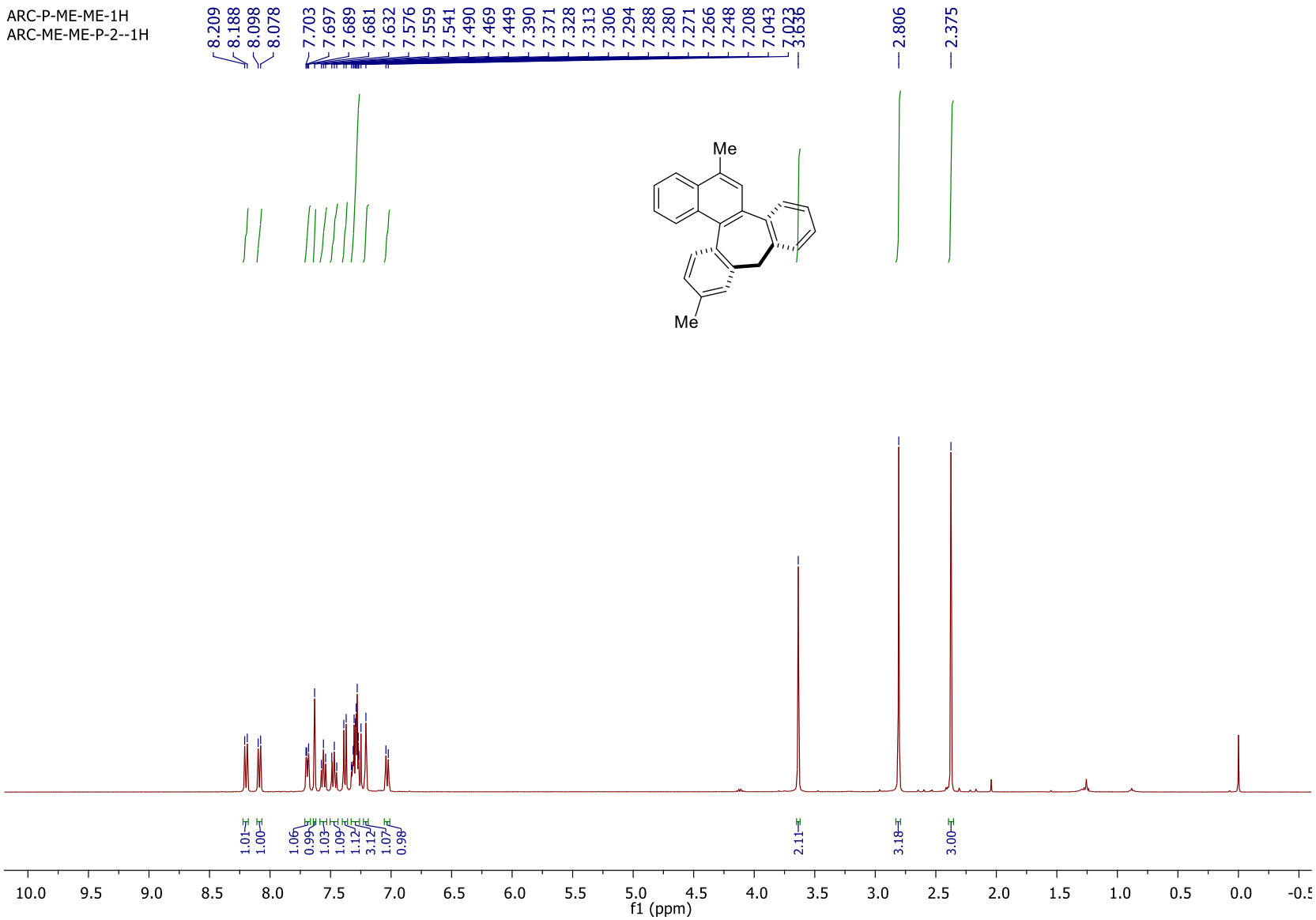
^{13}C Spectrum of **3c**

ARC-P-ME-1-13C
ARC-P-ME-13C

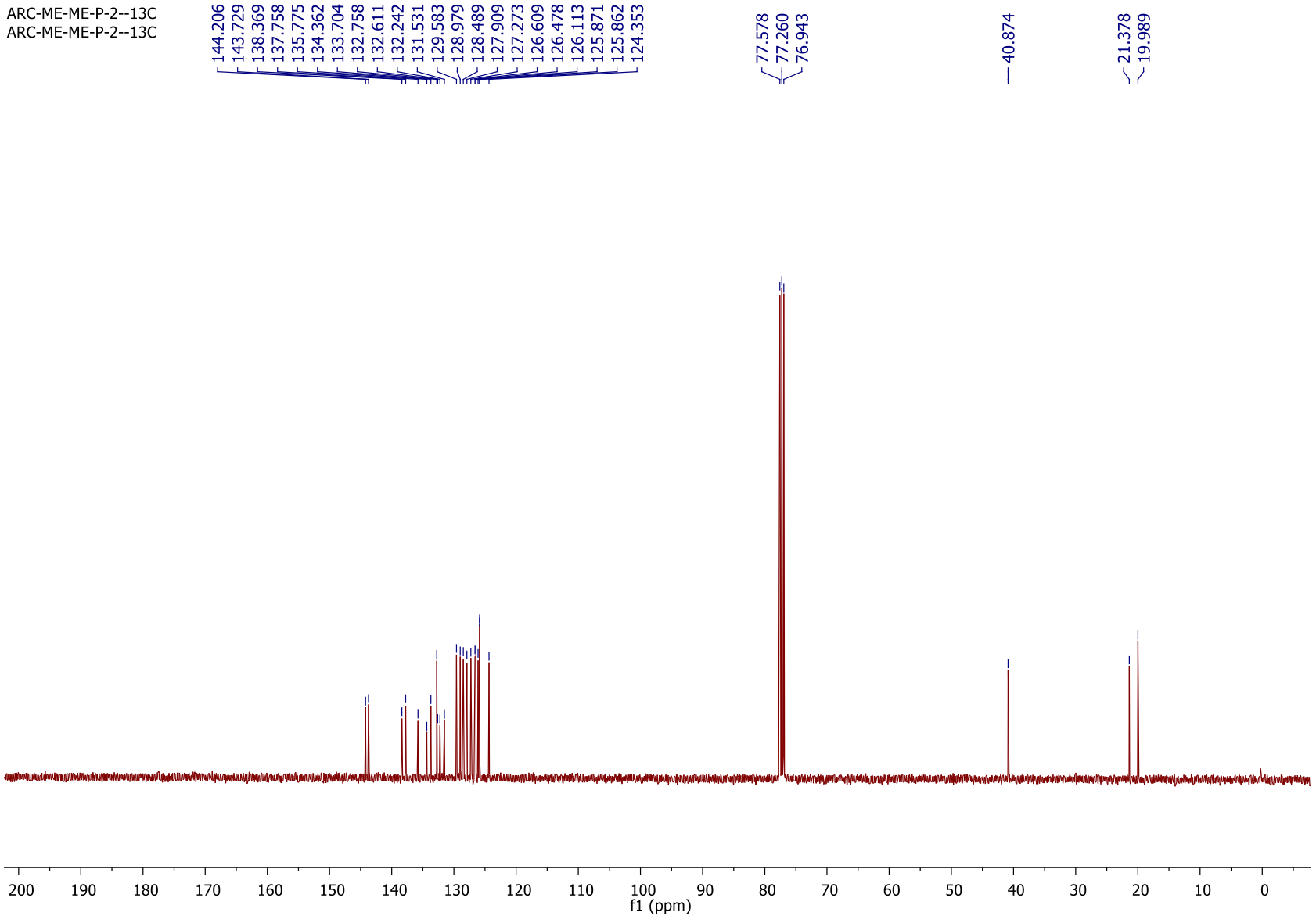
144.238
143.662
138.284
137.911
136.137
135.847
133.370
132.560
132.056
131.274
129.588
128.252
128.130
127.896
127.807
127.661
127.267
126.596
126.431
126.203
126.081
125.907
77.440
77.229
77.017
40.727
21.319



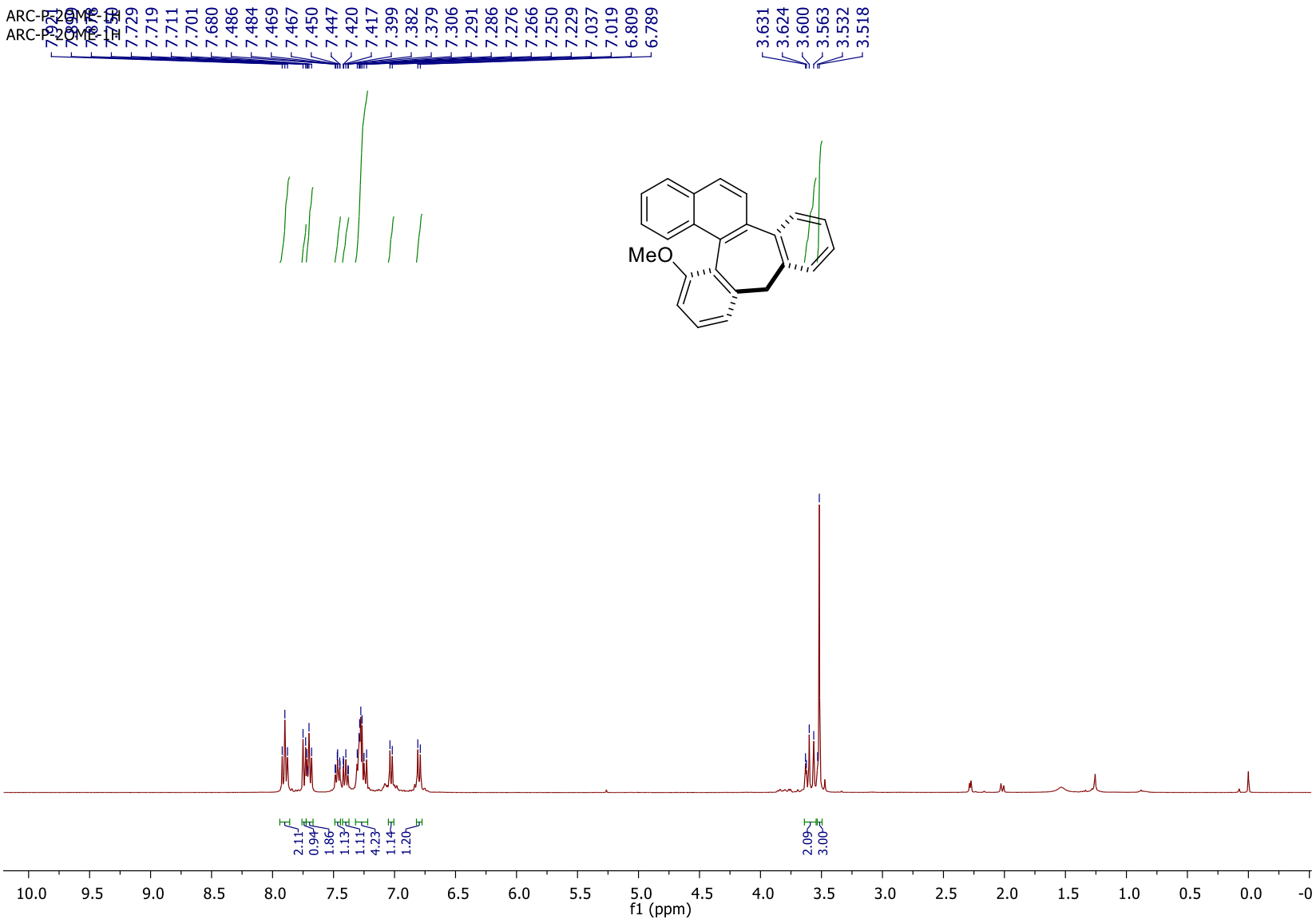
^{1}H Spectrum of **3d**



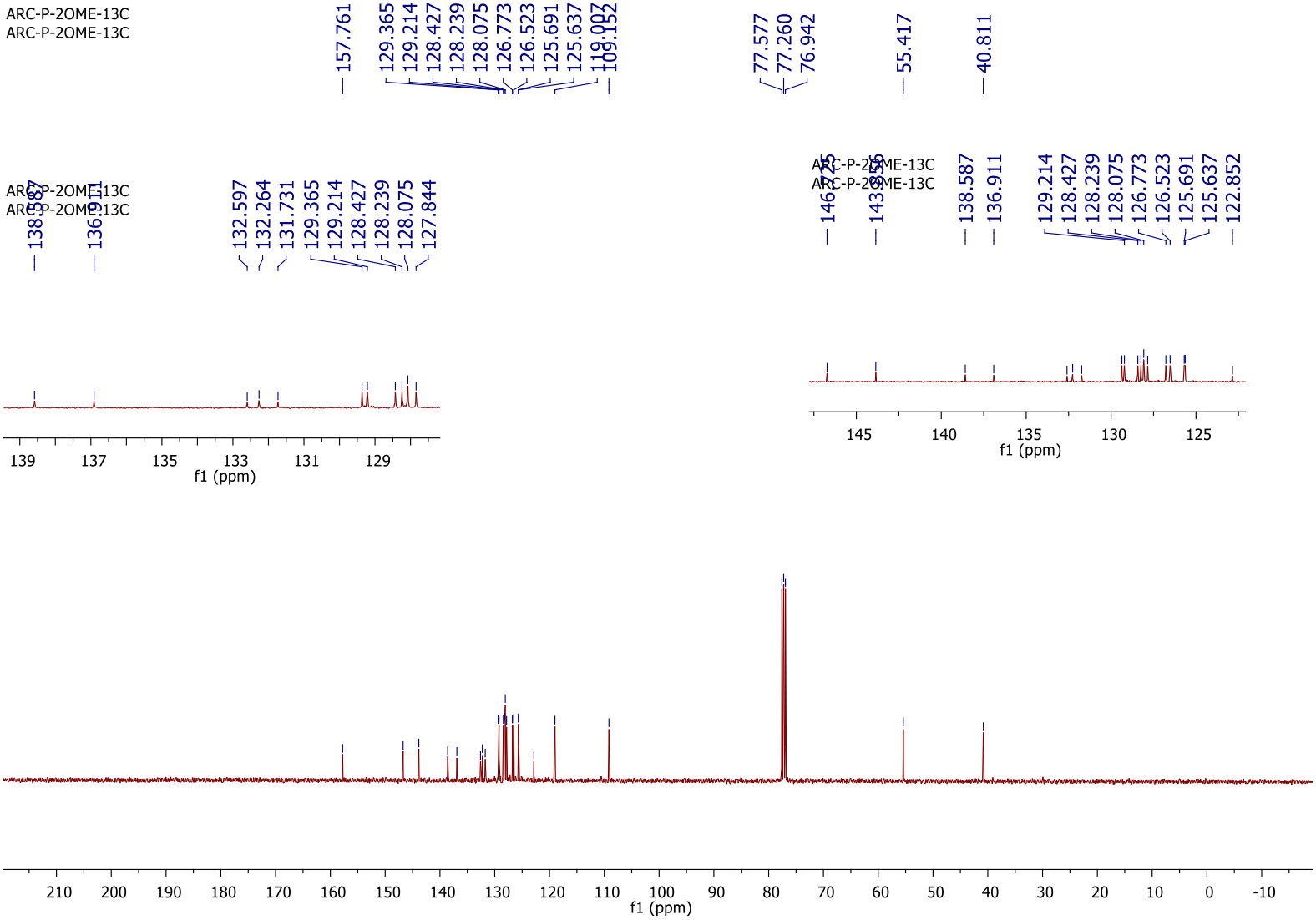
^{13}C Spectrum of **3d**



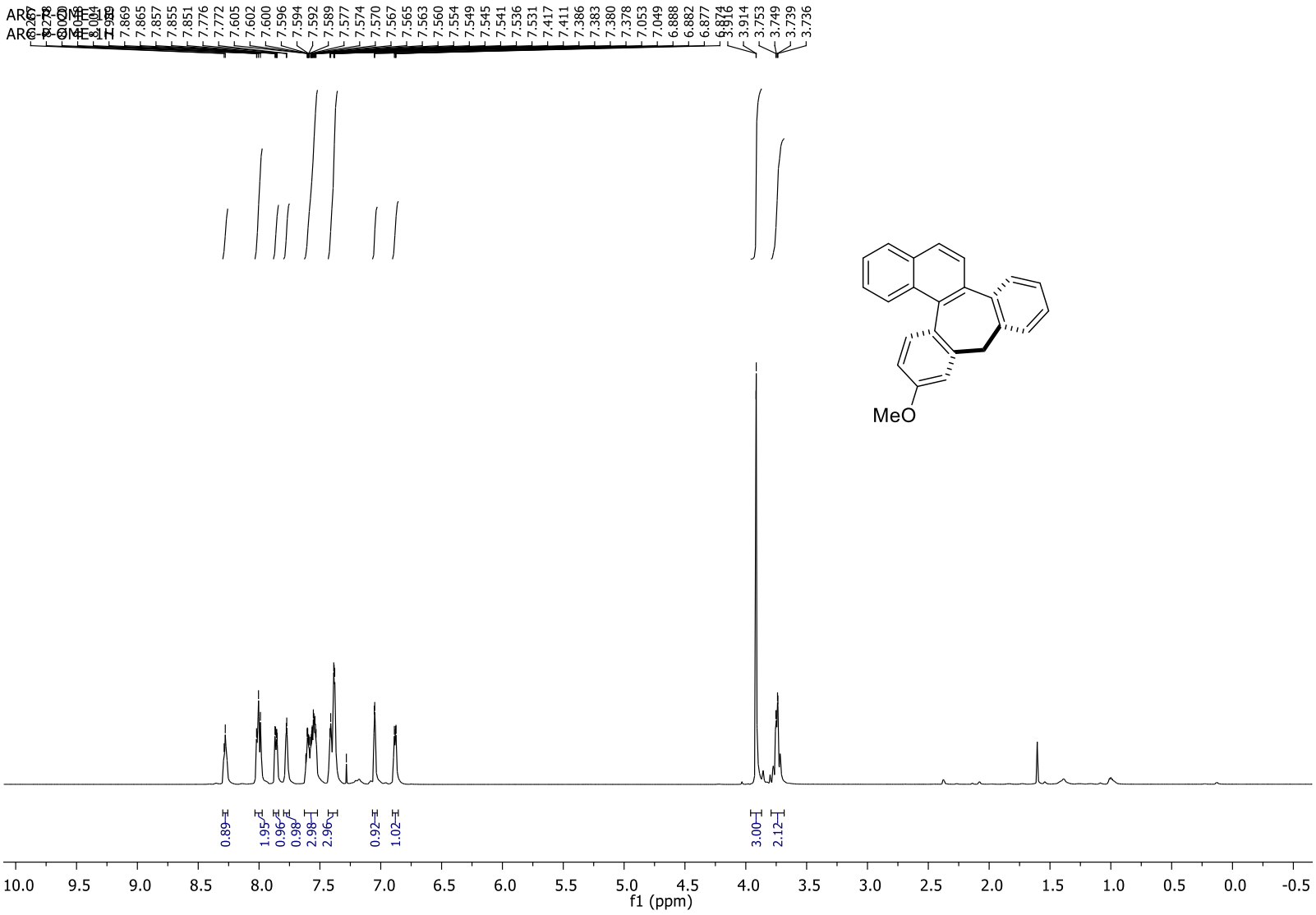
^{1}H Spectrum of **3e**



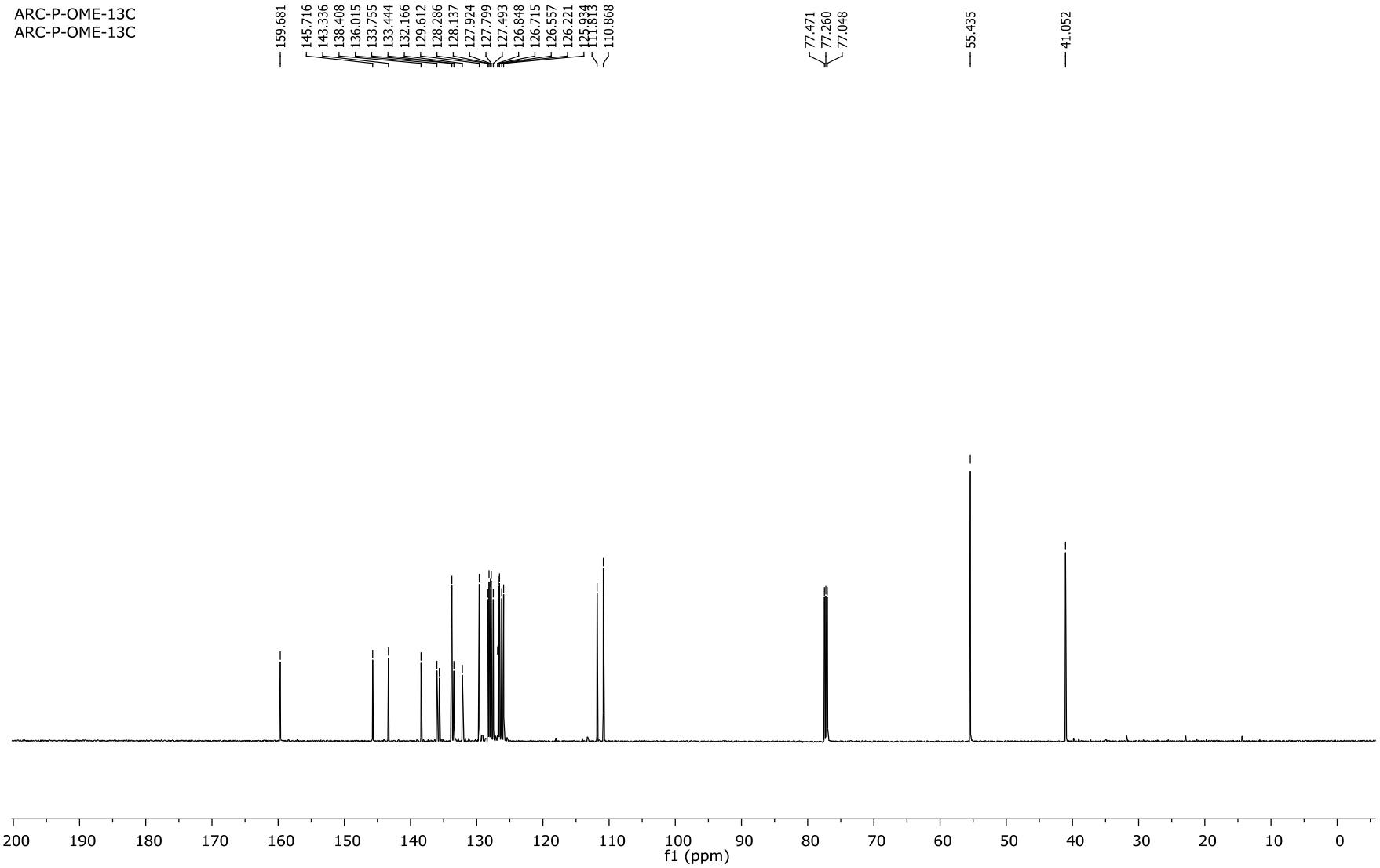
^{13}C Spectrum of **3e**



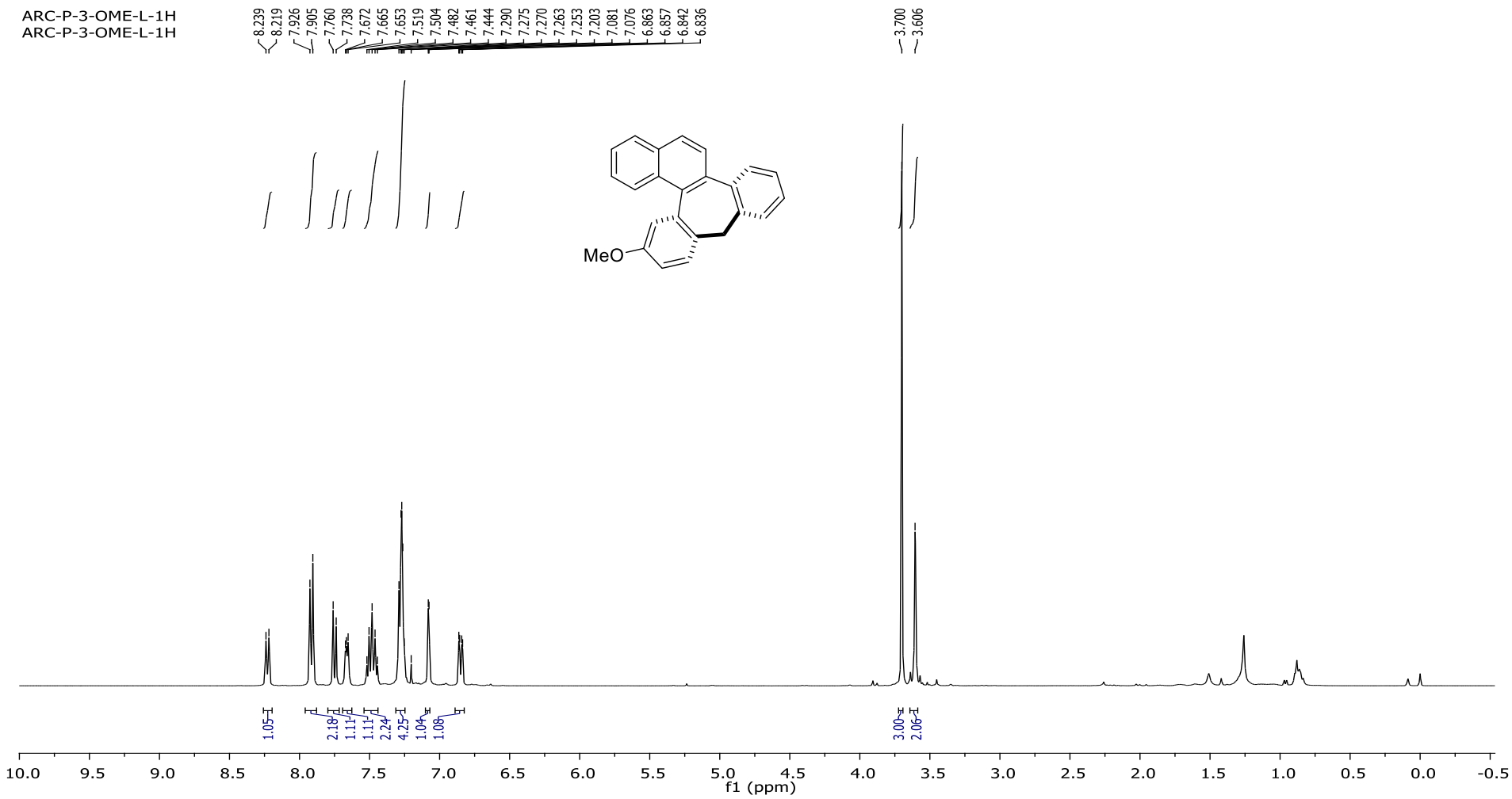
^{1}H Spectrum of **3f**



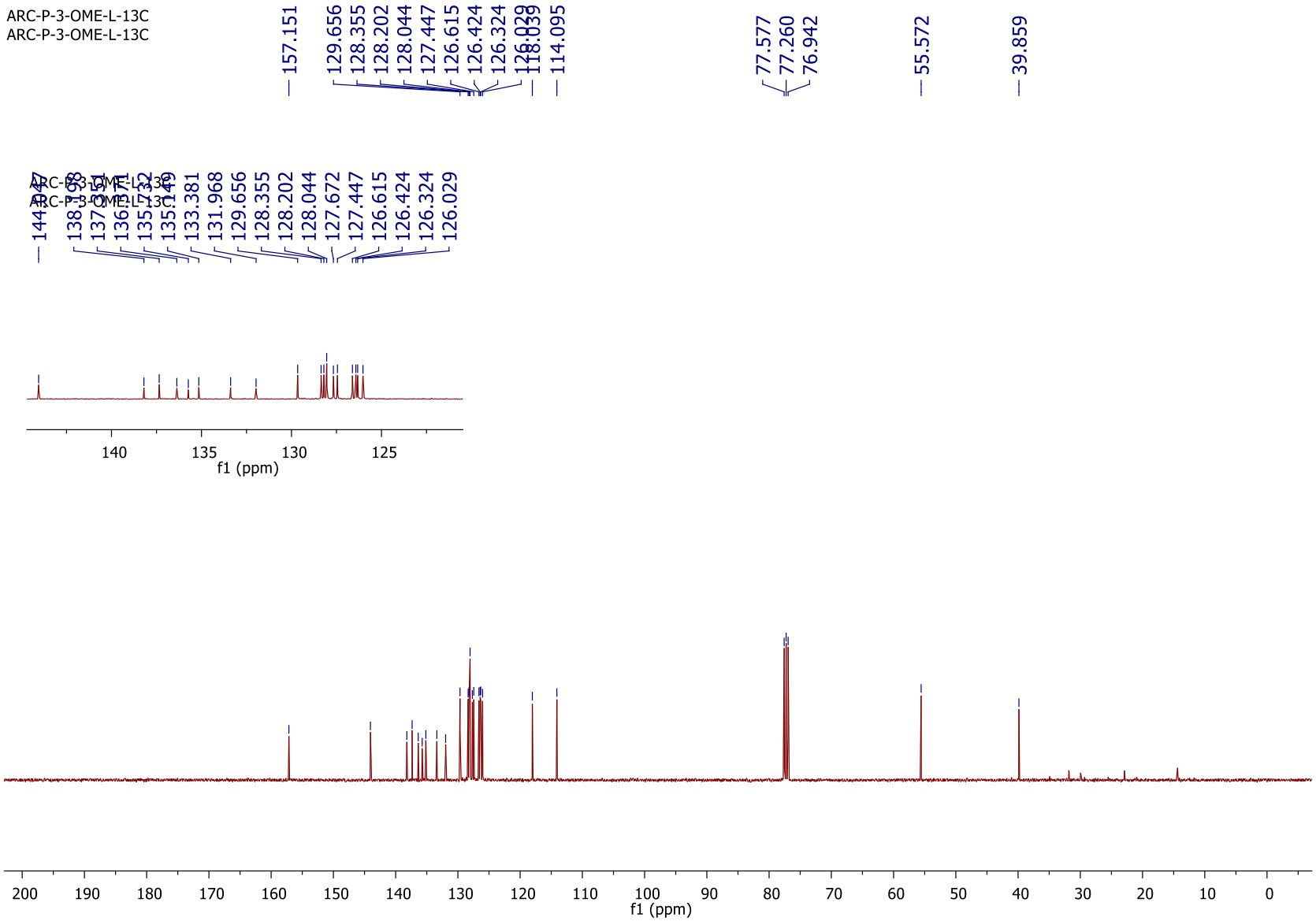
^{13}C Spectrum of **3f**



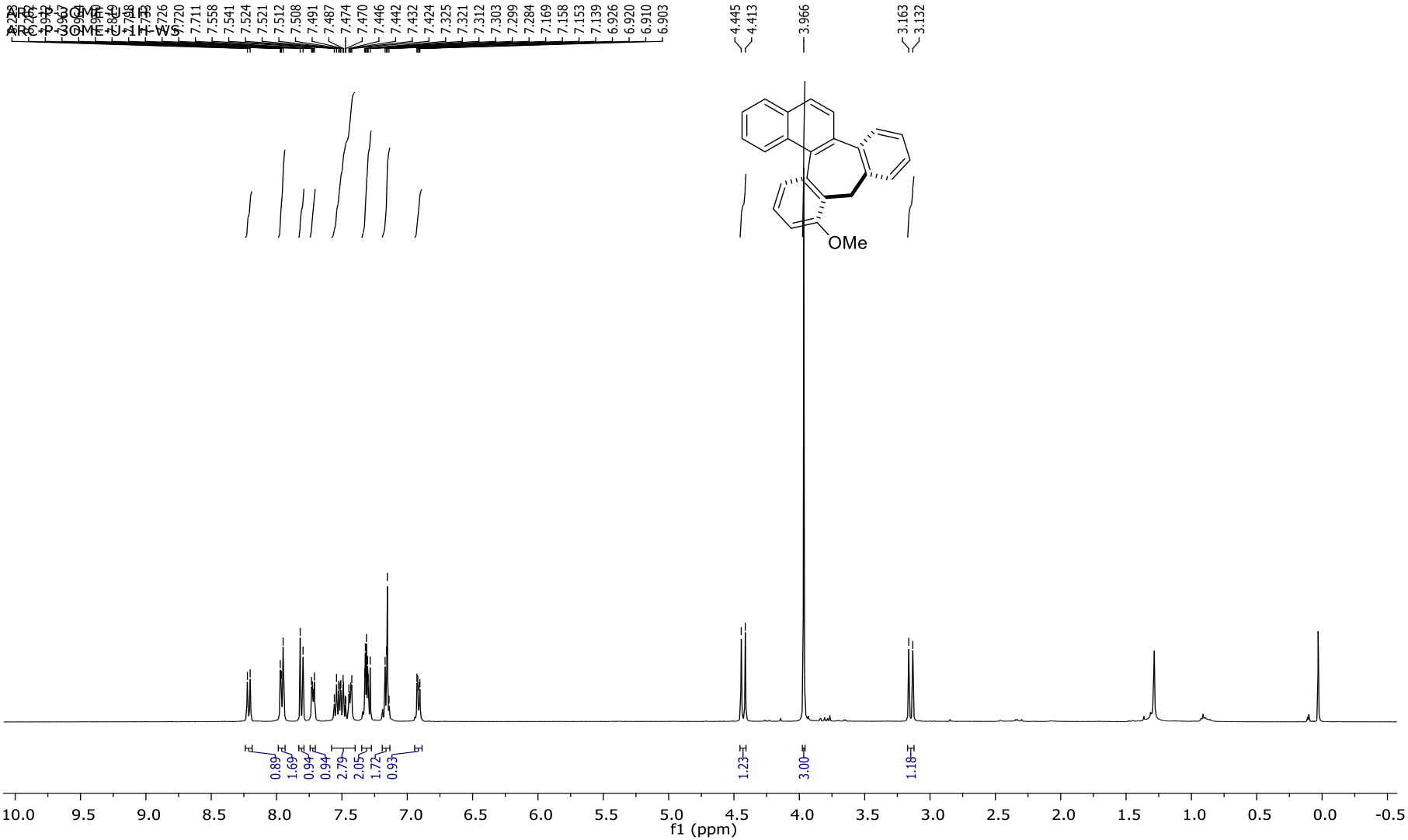
^{1}H Spectrum of **3h**



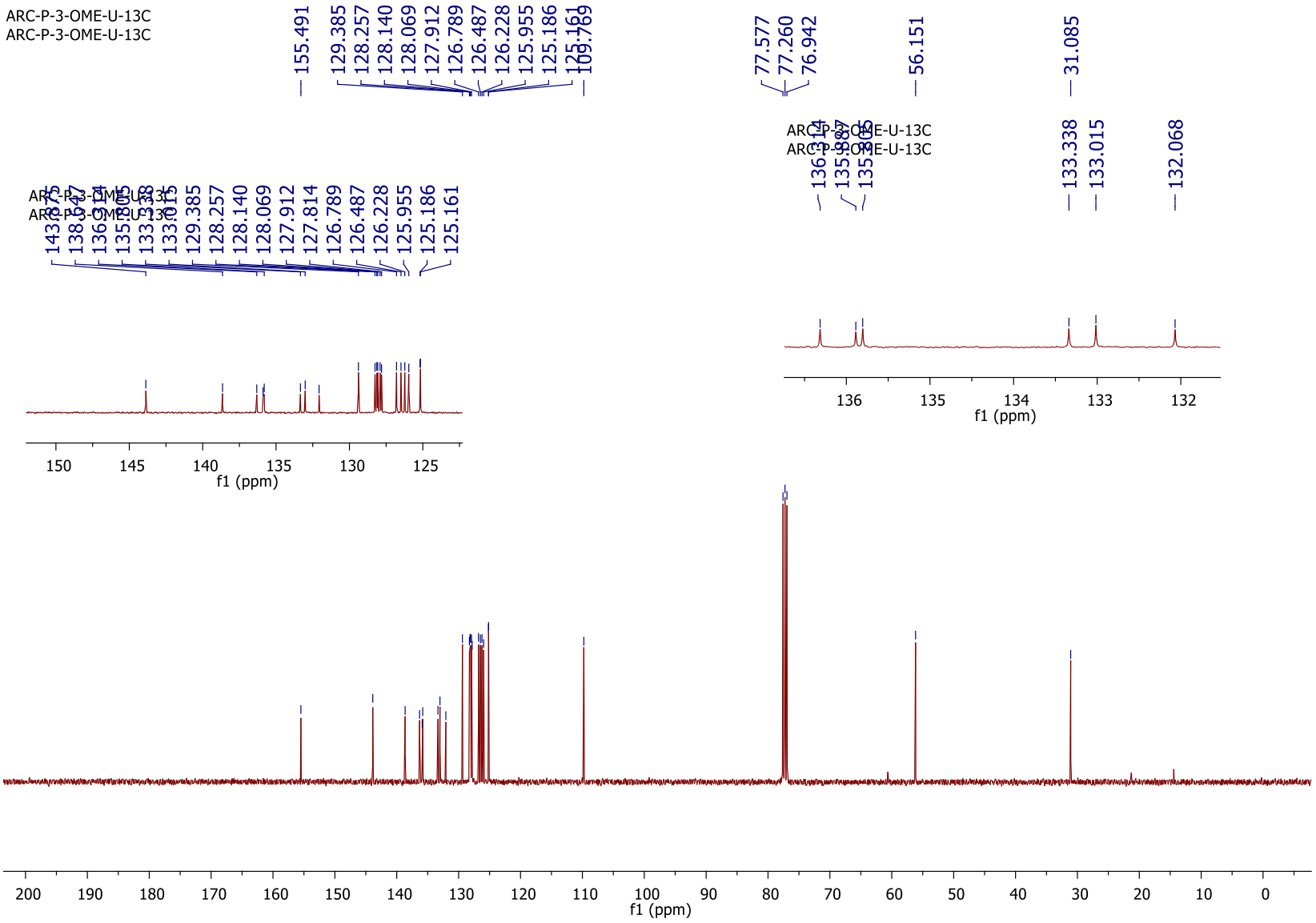
^{13}C Spectrum of **3h**



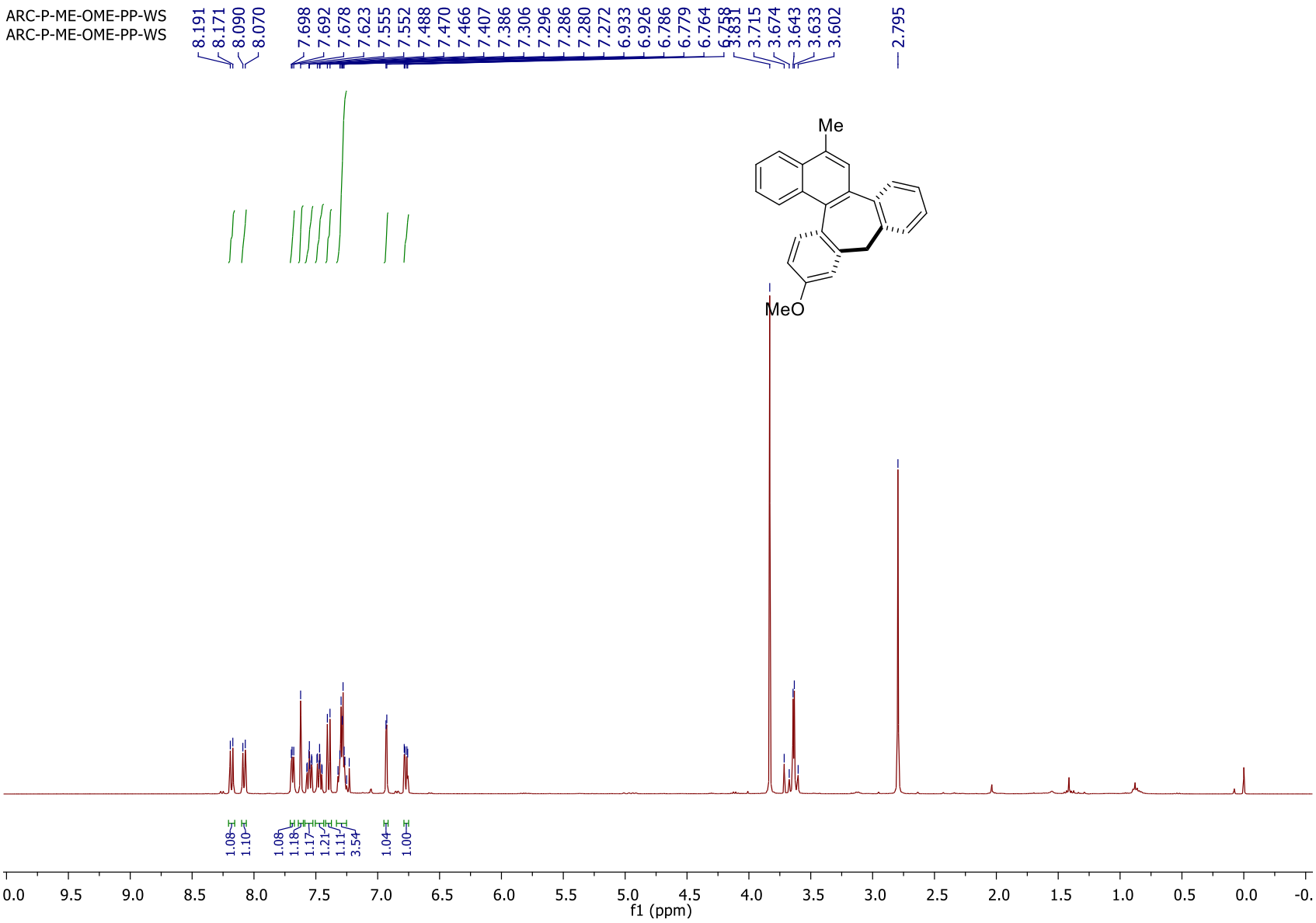
^{1}H Spectrum of **4h**



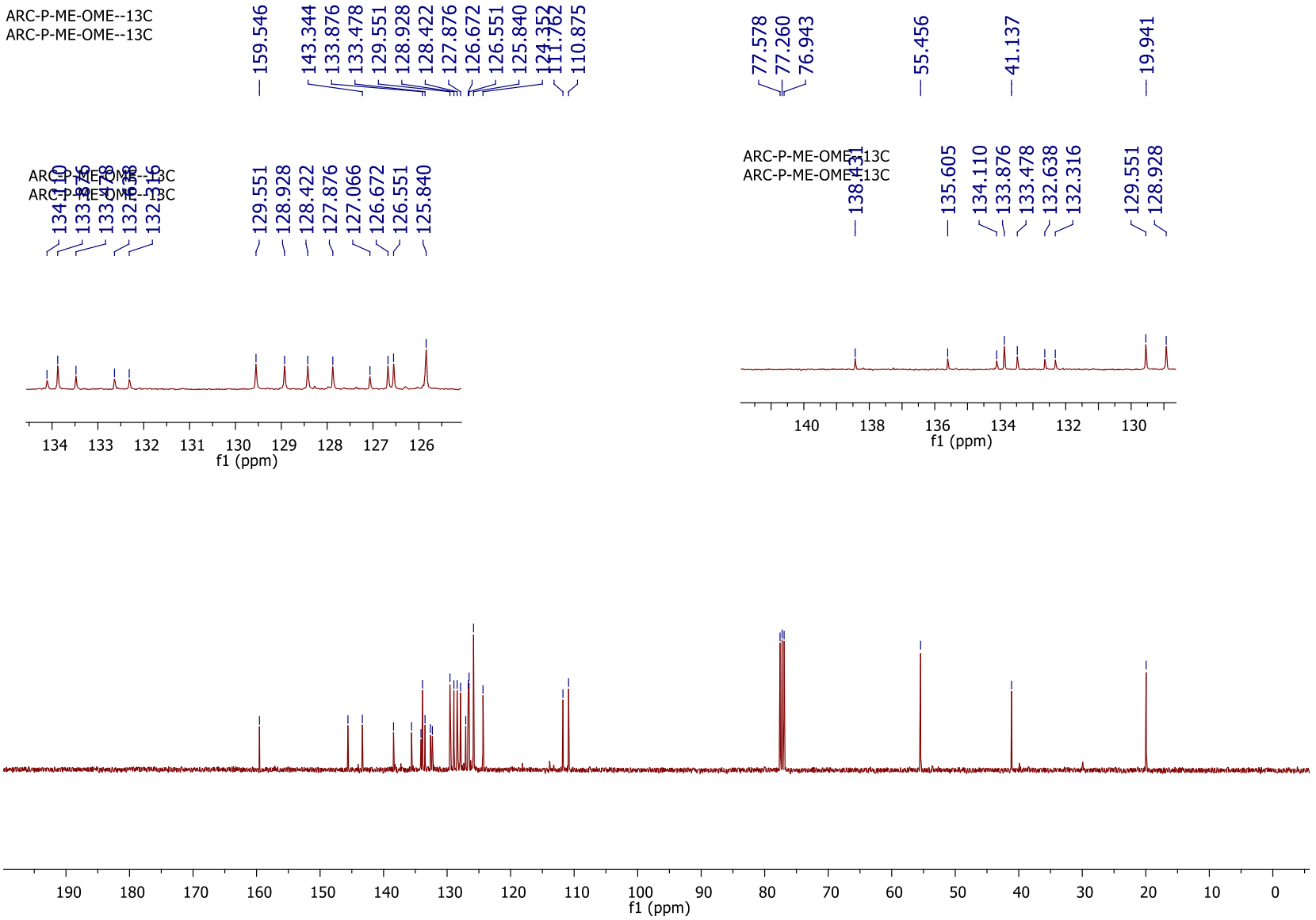
^{13}C Spectrum of **4h**



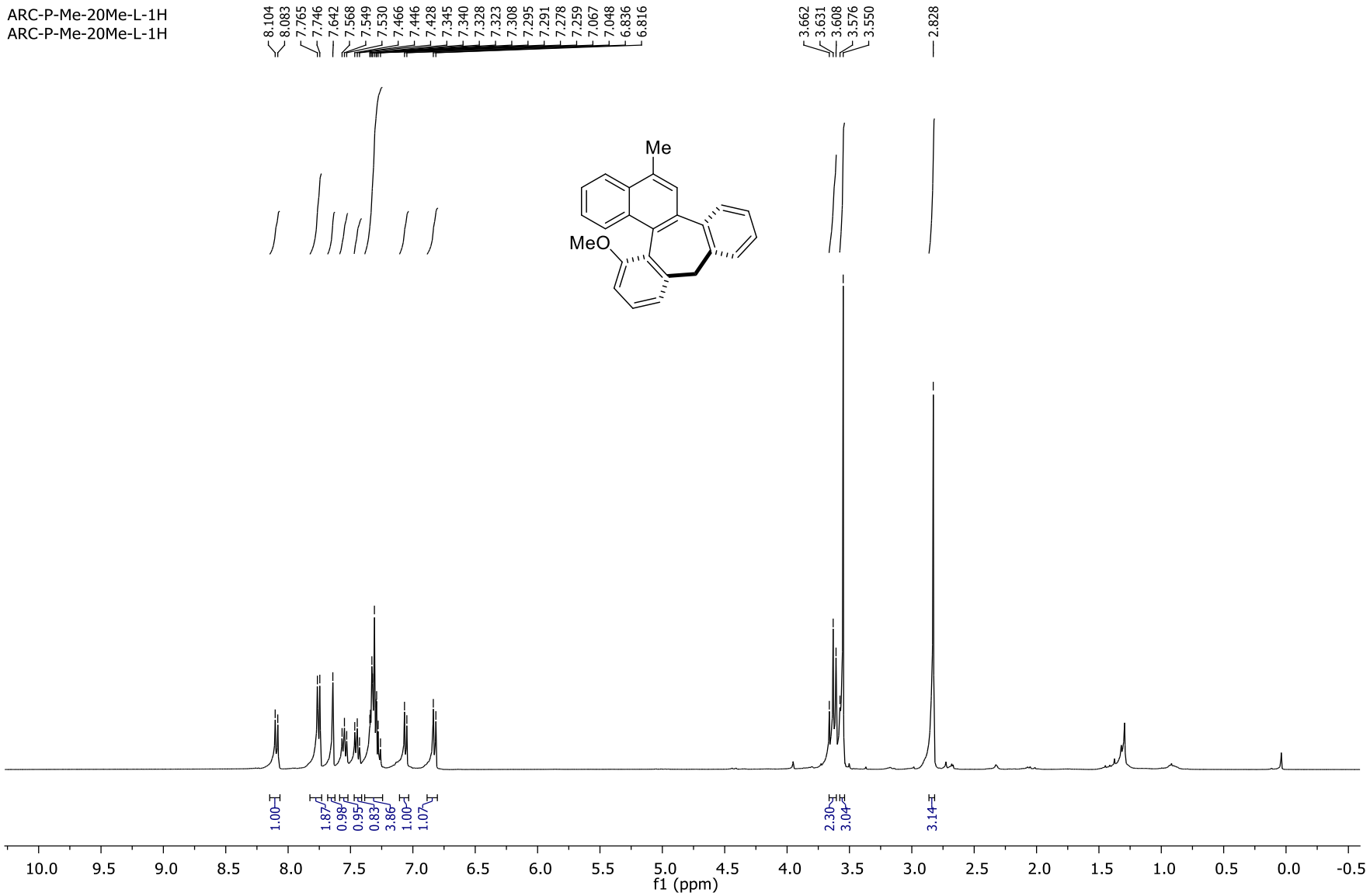
^{1}H Spectrum of **3i**



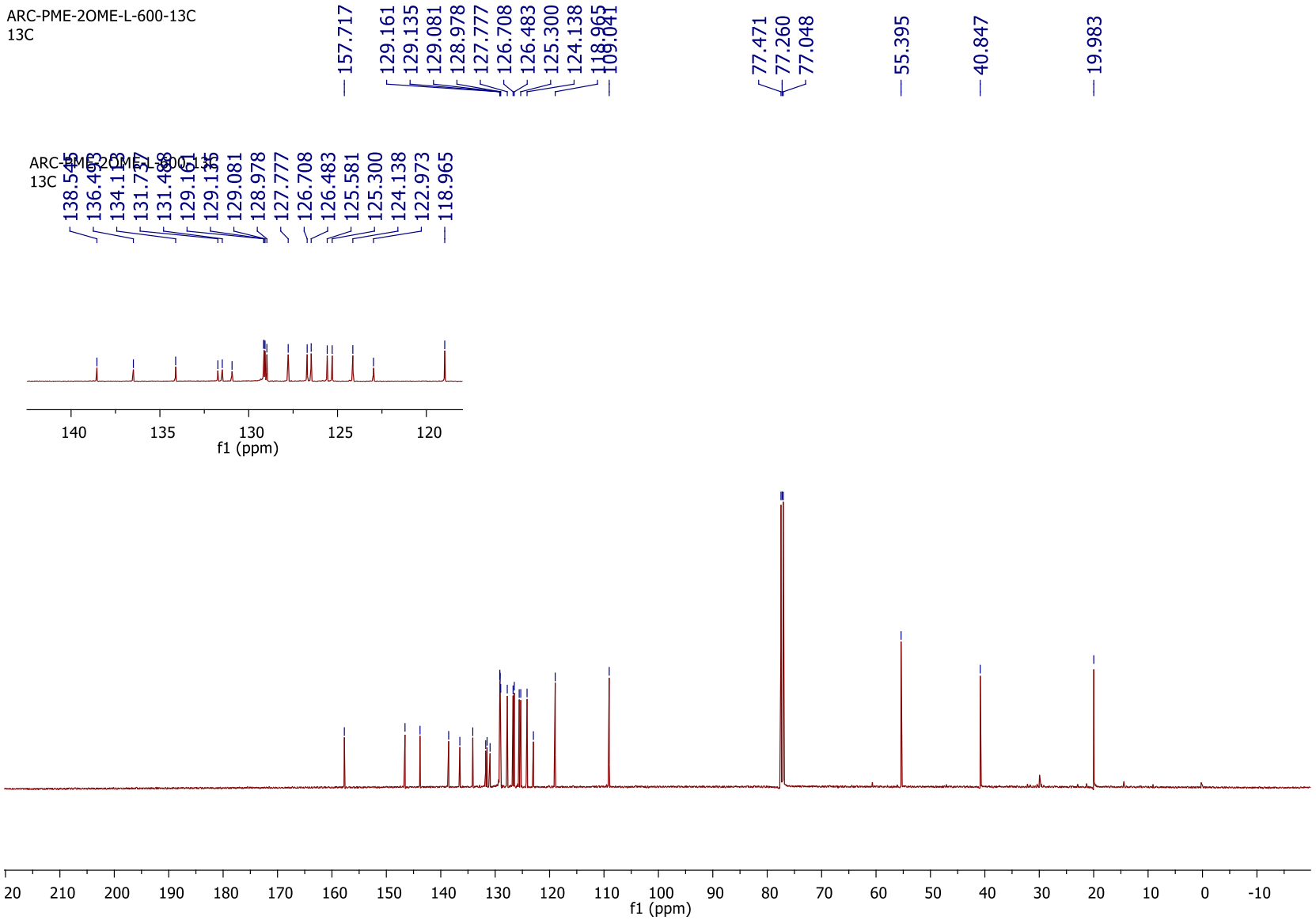
^{13}C Spectrum of **3i**



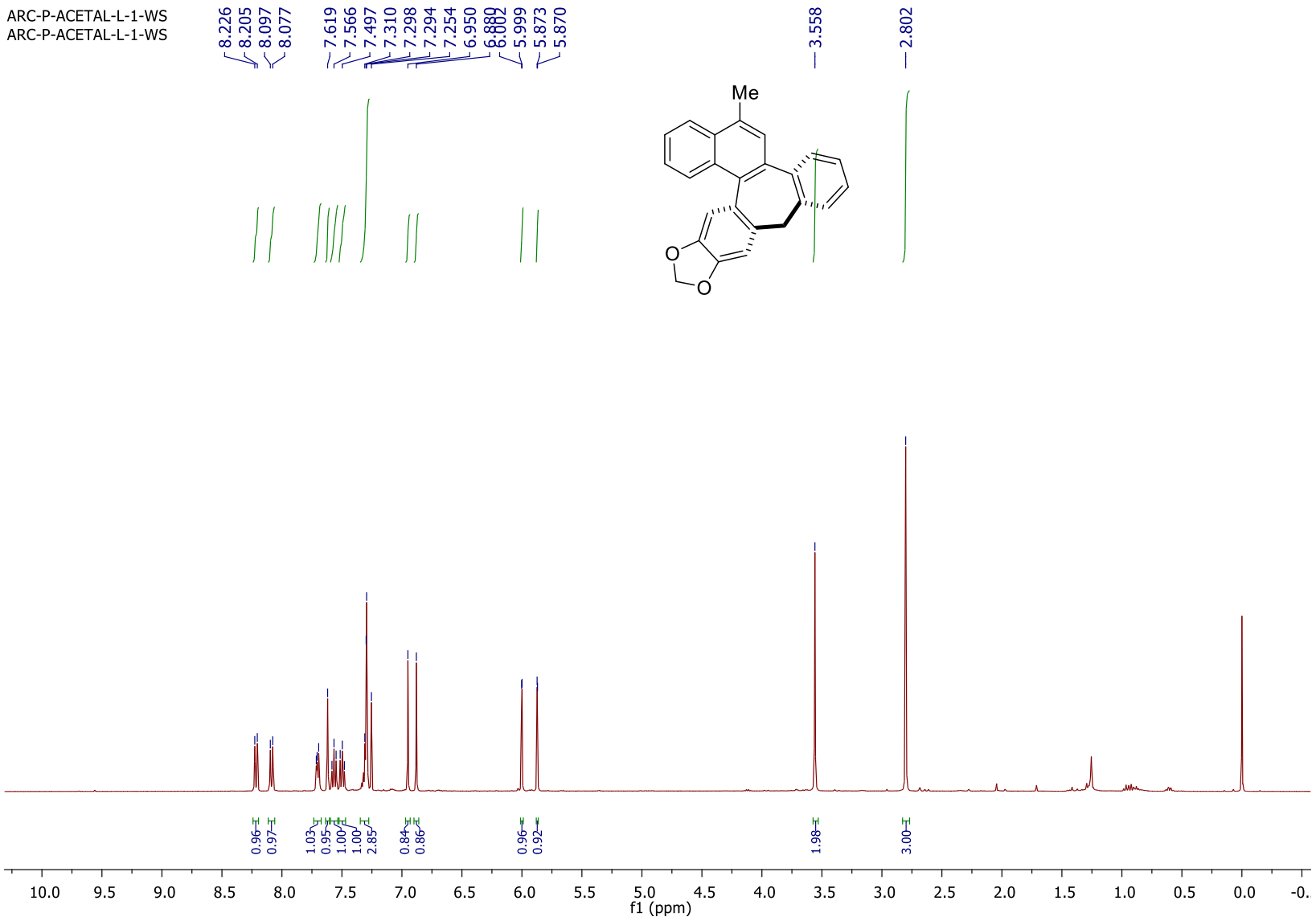
^{1}H Spectrum of **3j**



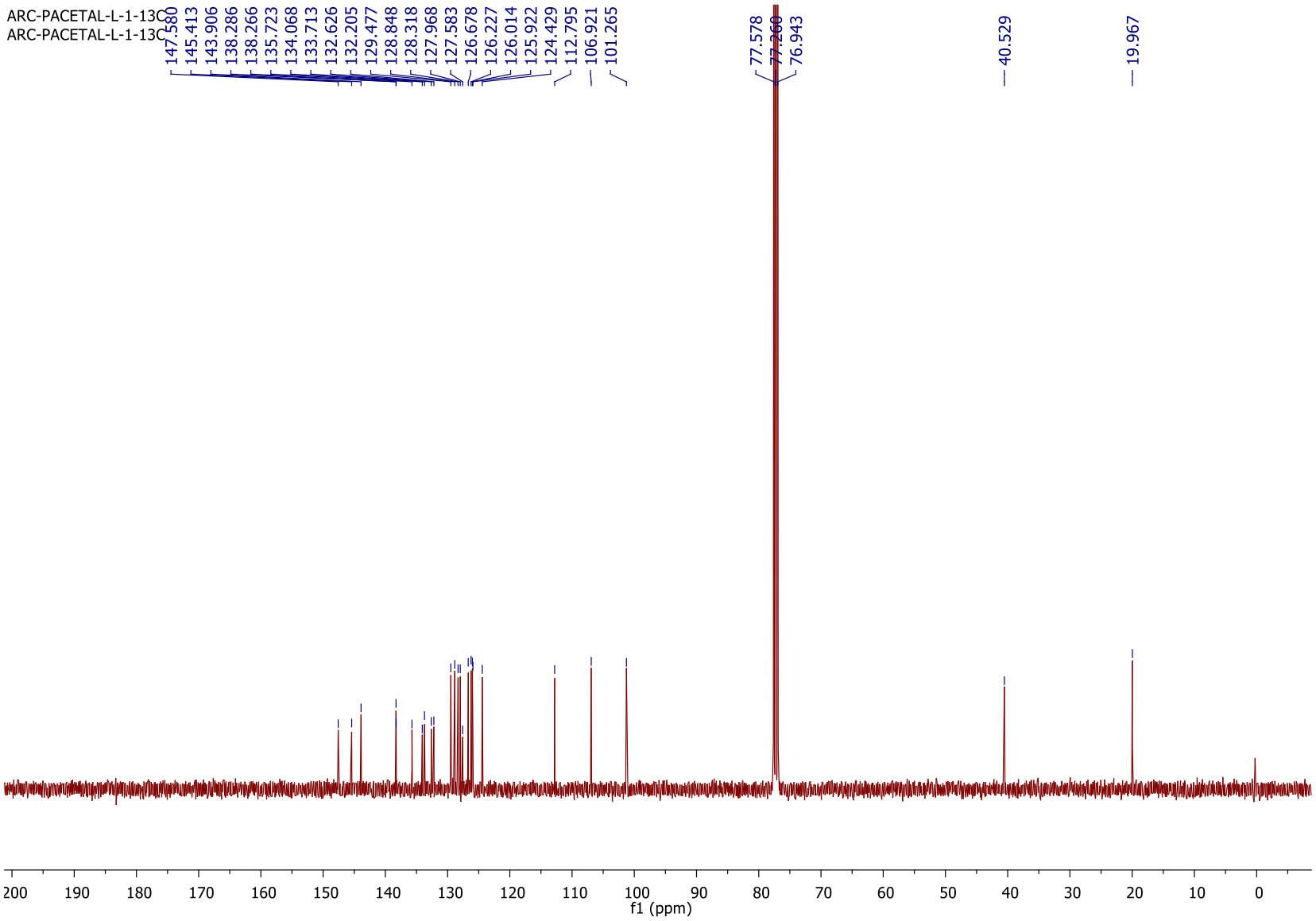
^{13}C Spectrum of **3j**



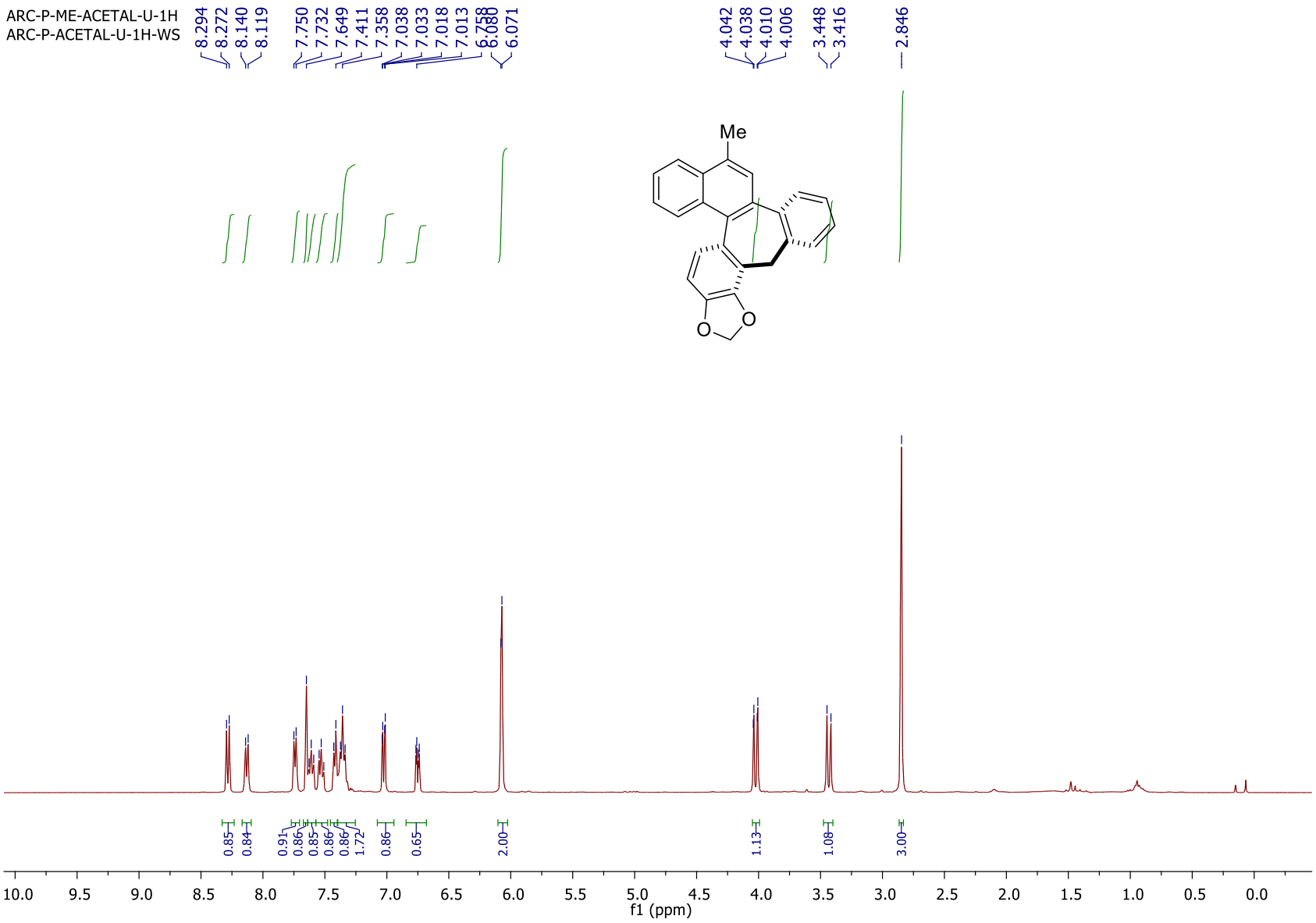
^{1}H Spectrum of **3k**



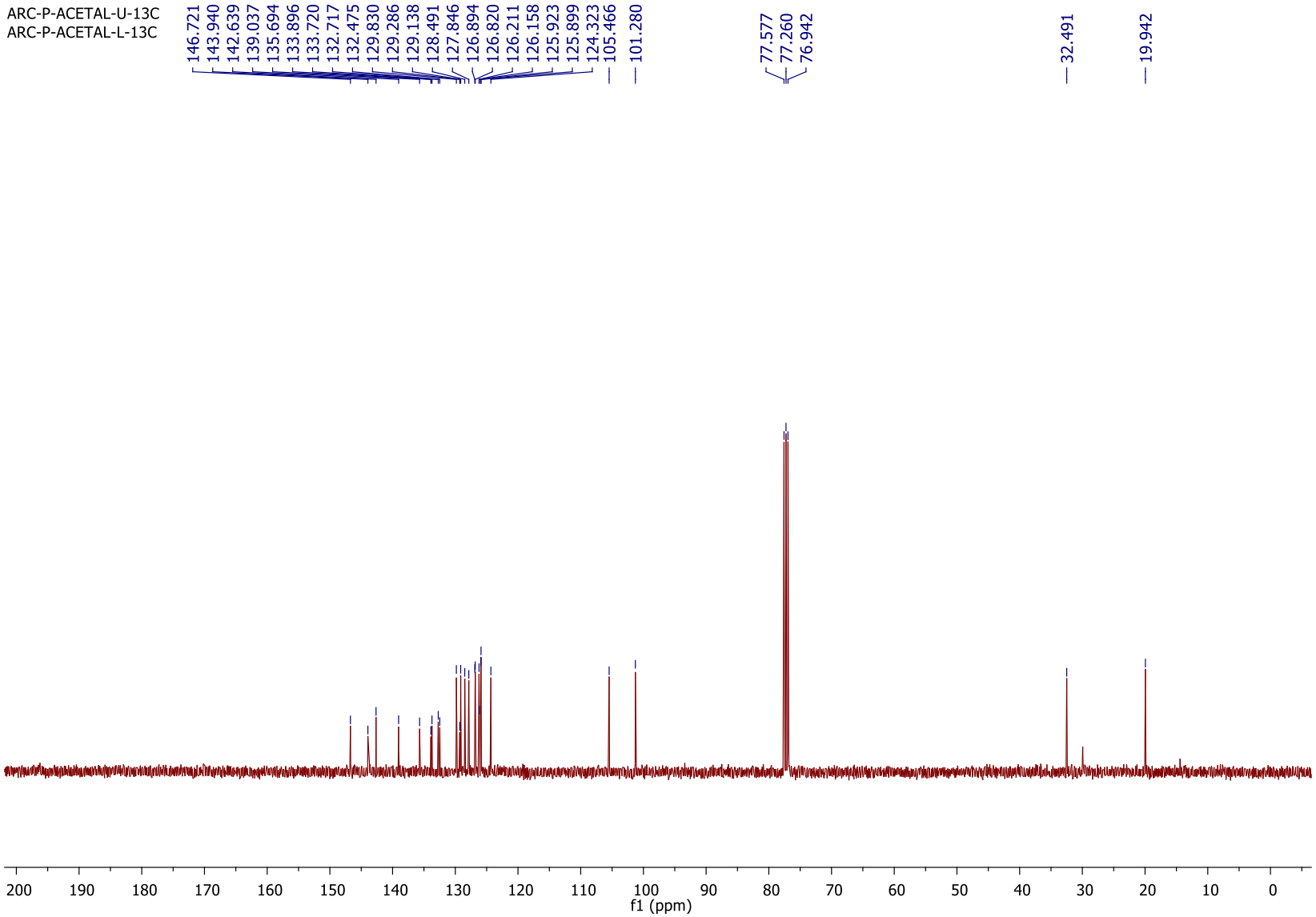
^{13}C Spectrum of **3k**



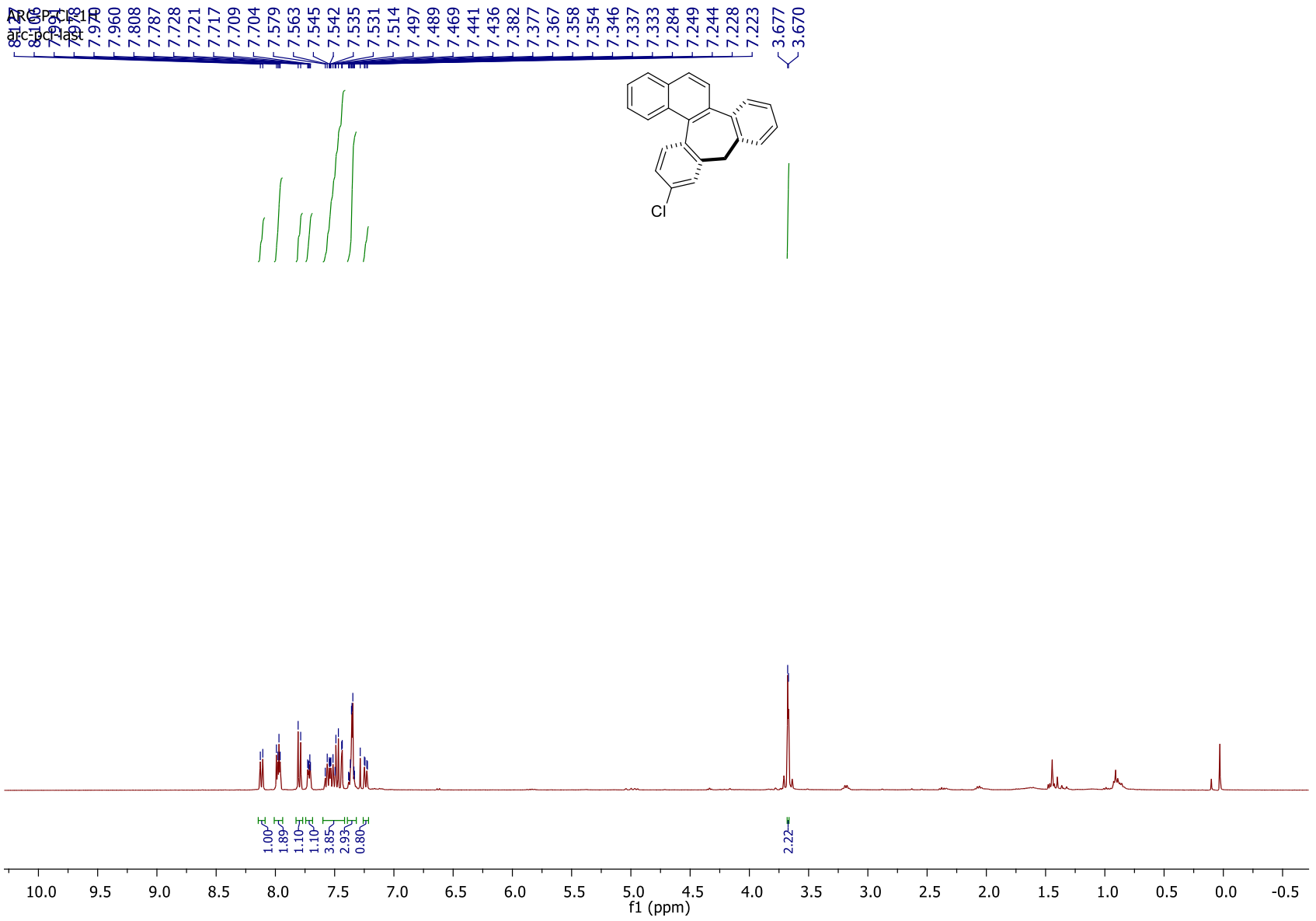
^{1}H Spectrum of **4k**



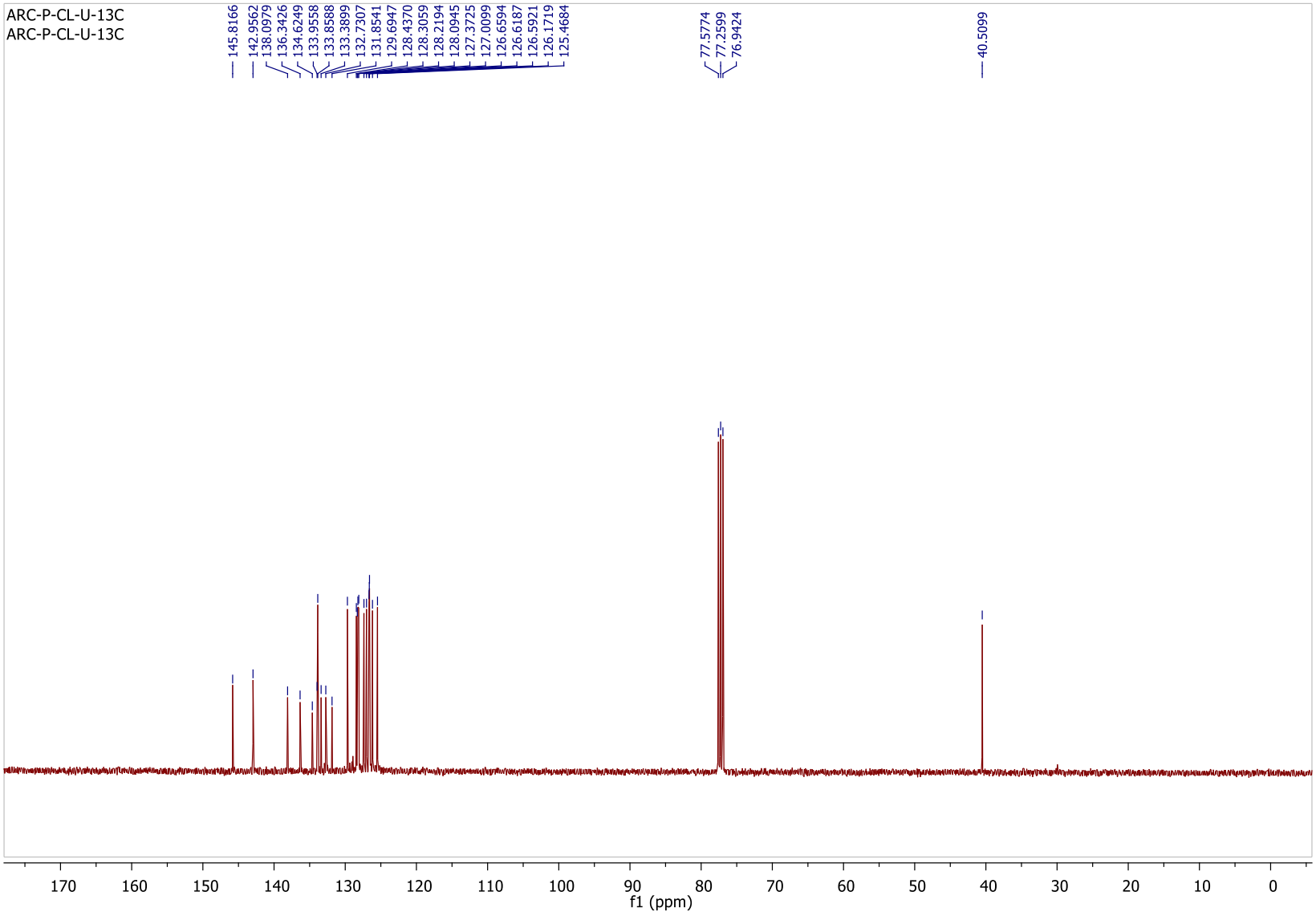
^{13}C Spectrum of **4k**



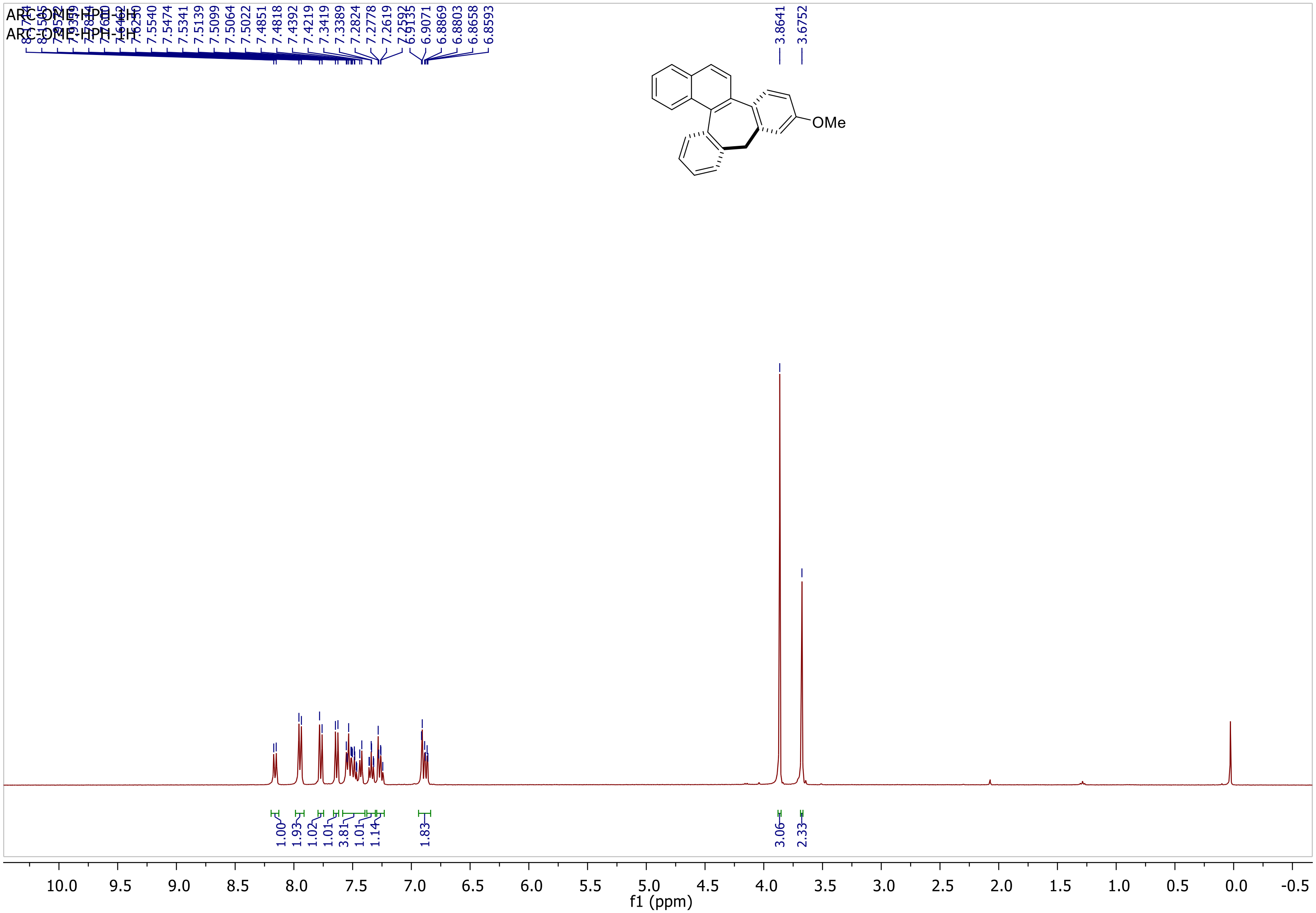
^{1}H Spectrum of **3l**



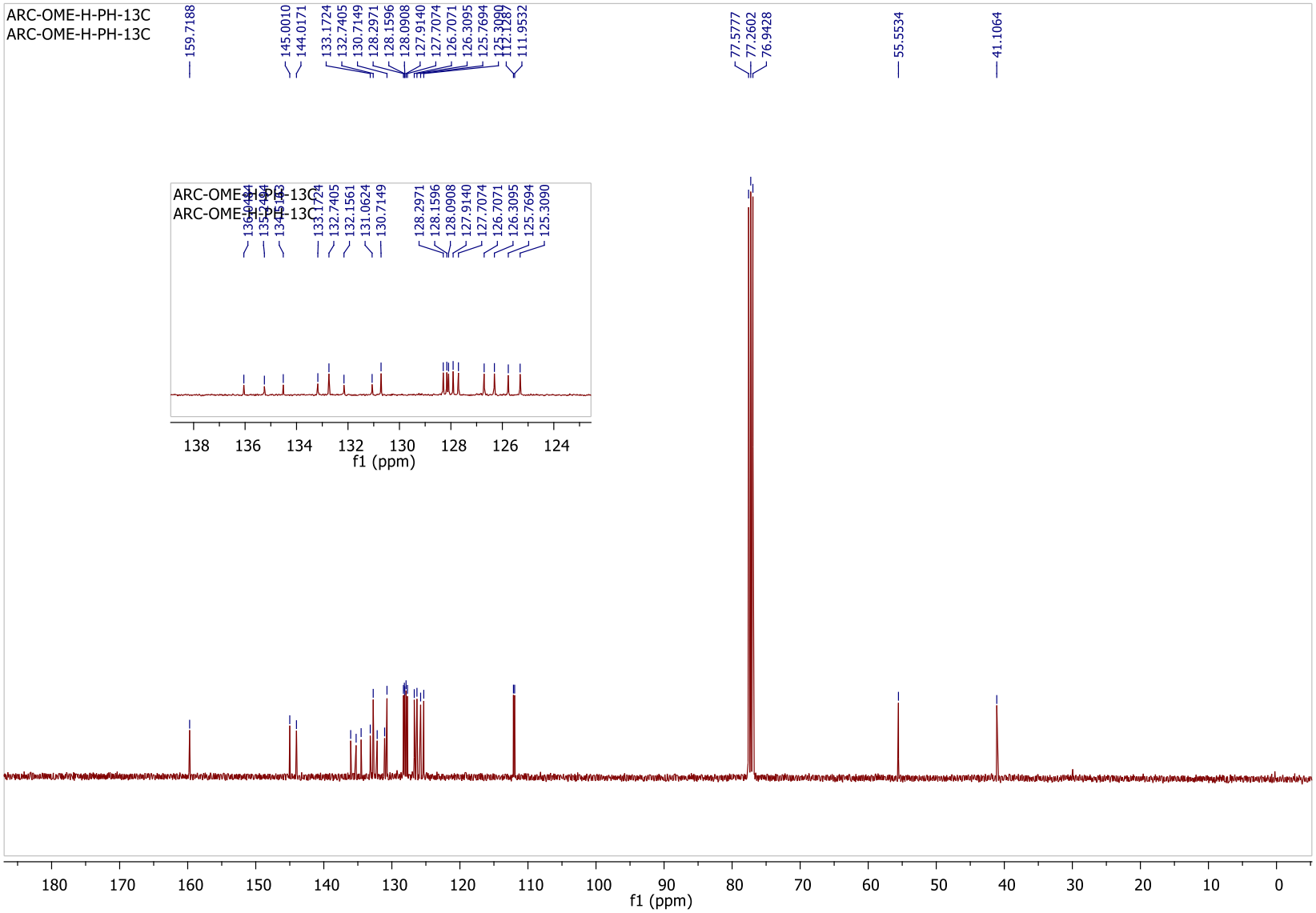
^{13}C Spectrum of **3l**



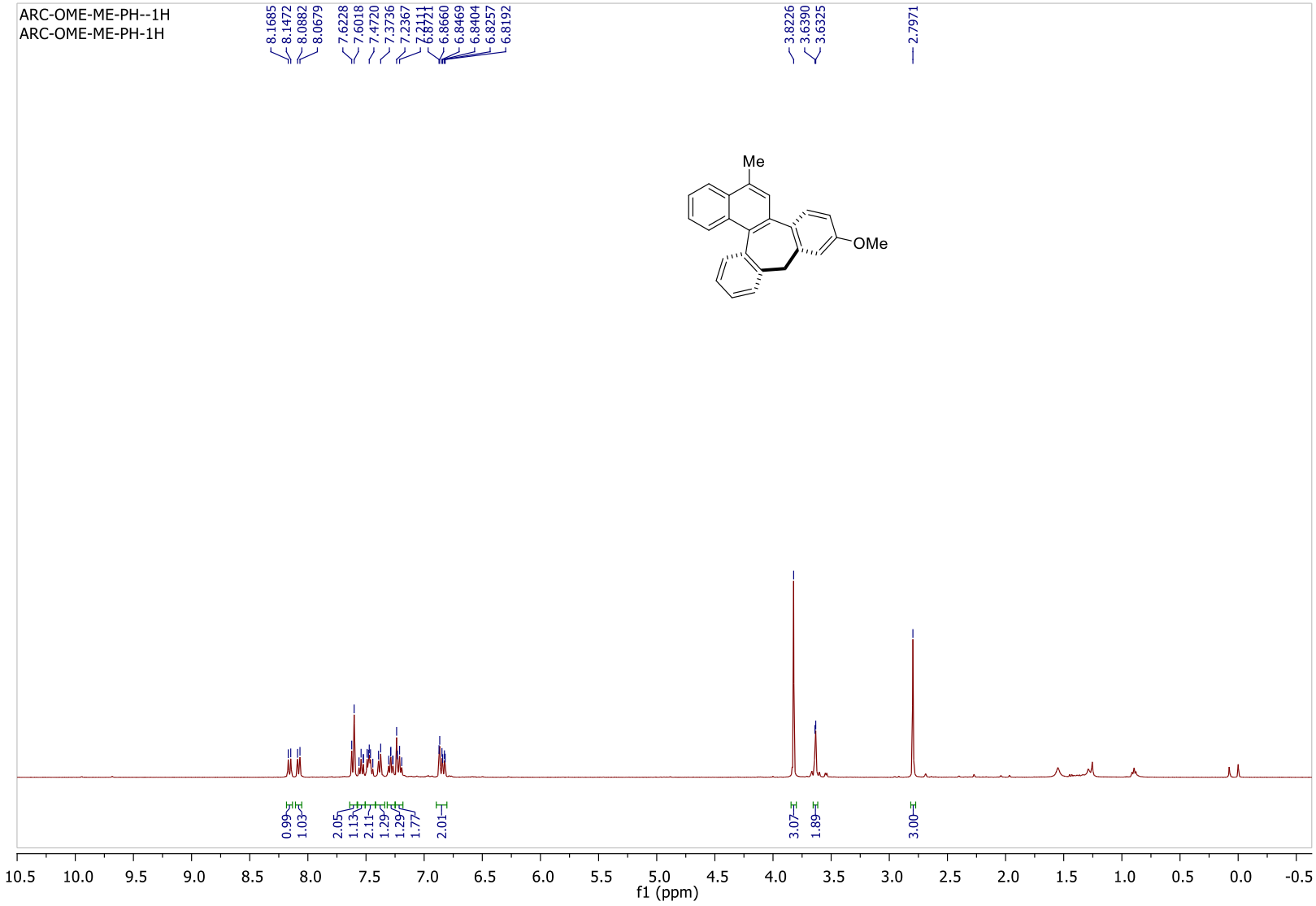
^{1}H Spectrum of **3m**



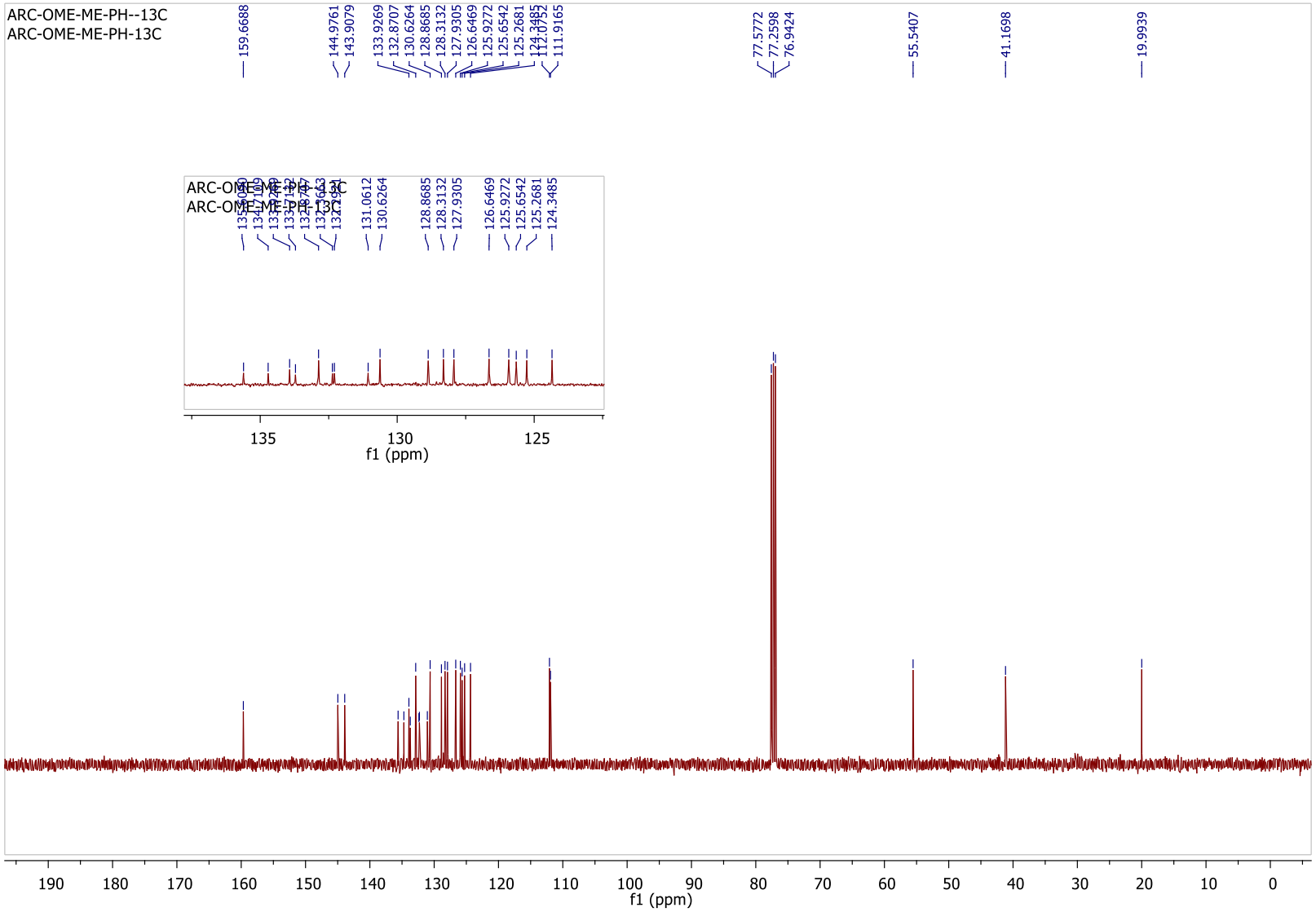
^{13}C Spectrum of **3m**



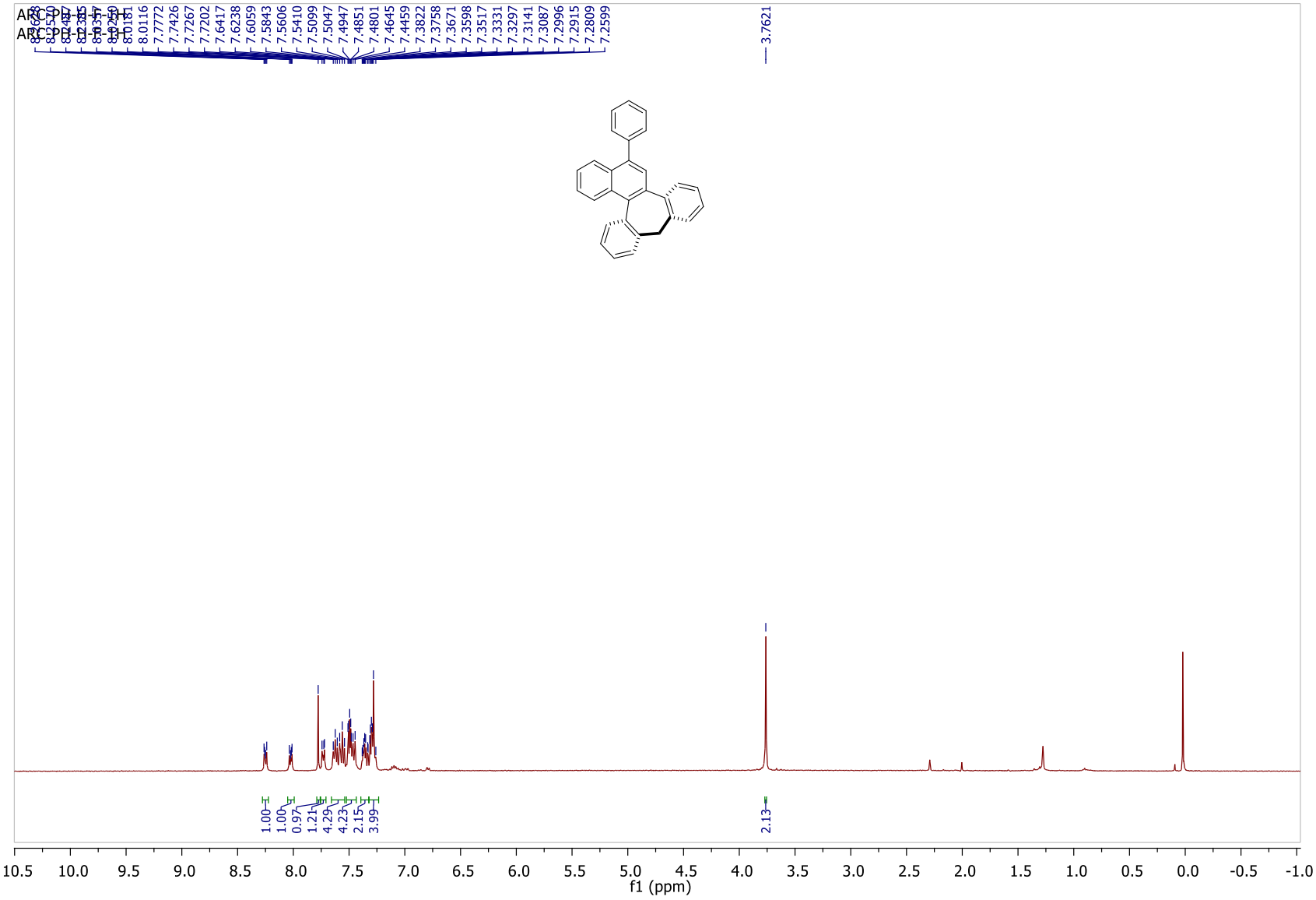
^{1}H Spectrum of **3n**



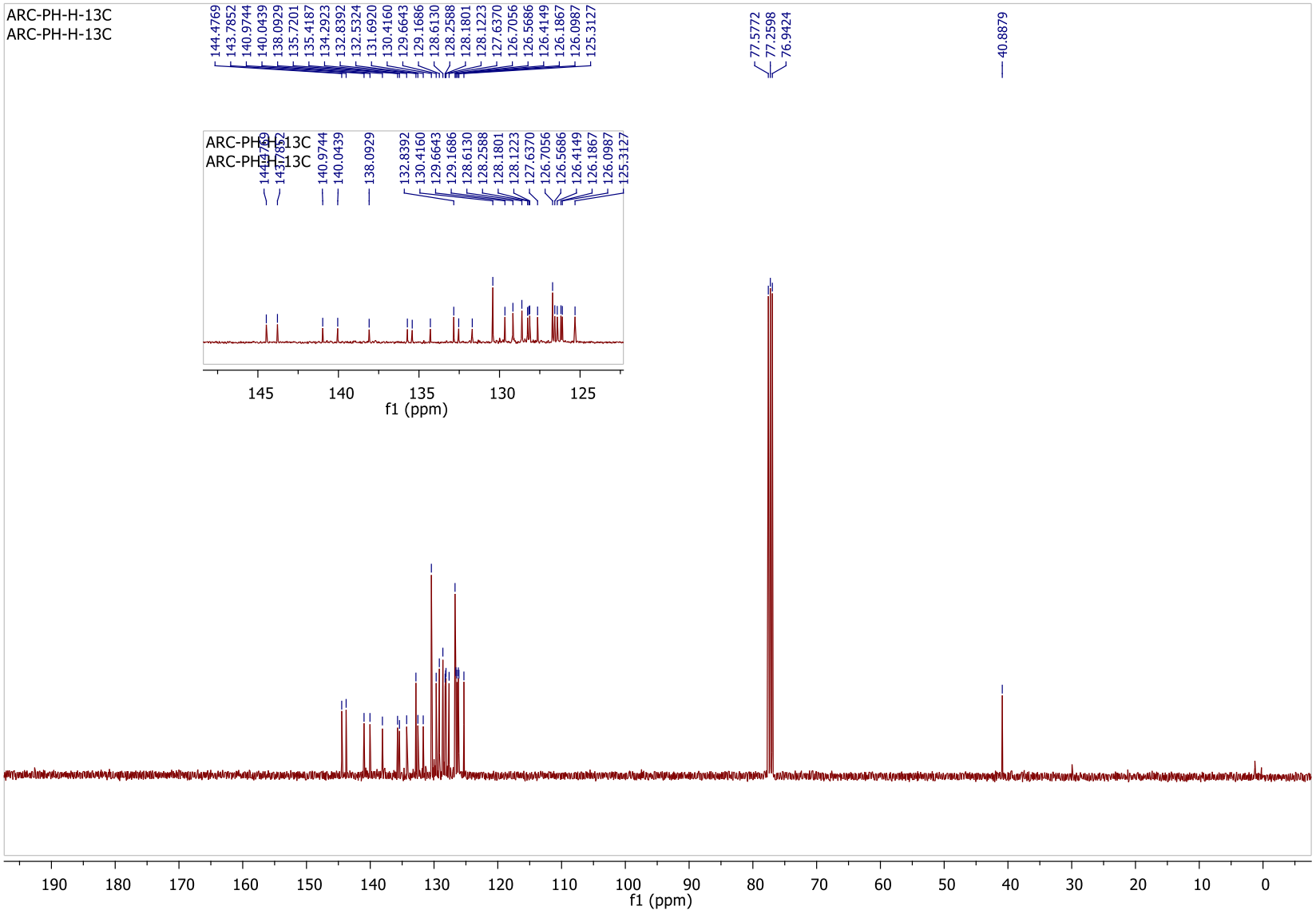
^{13}C Spectrum of **3n**



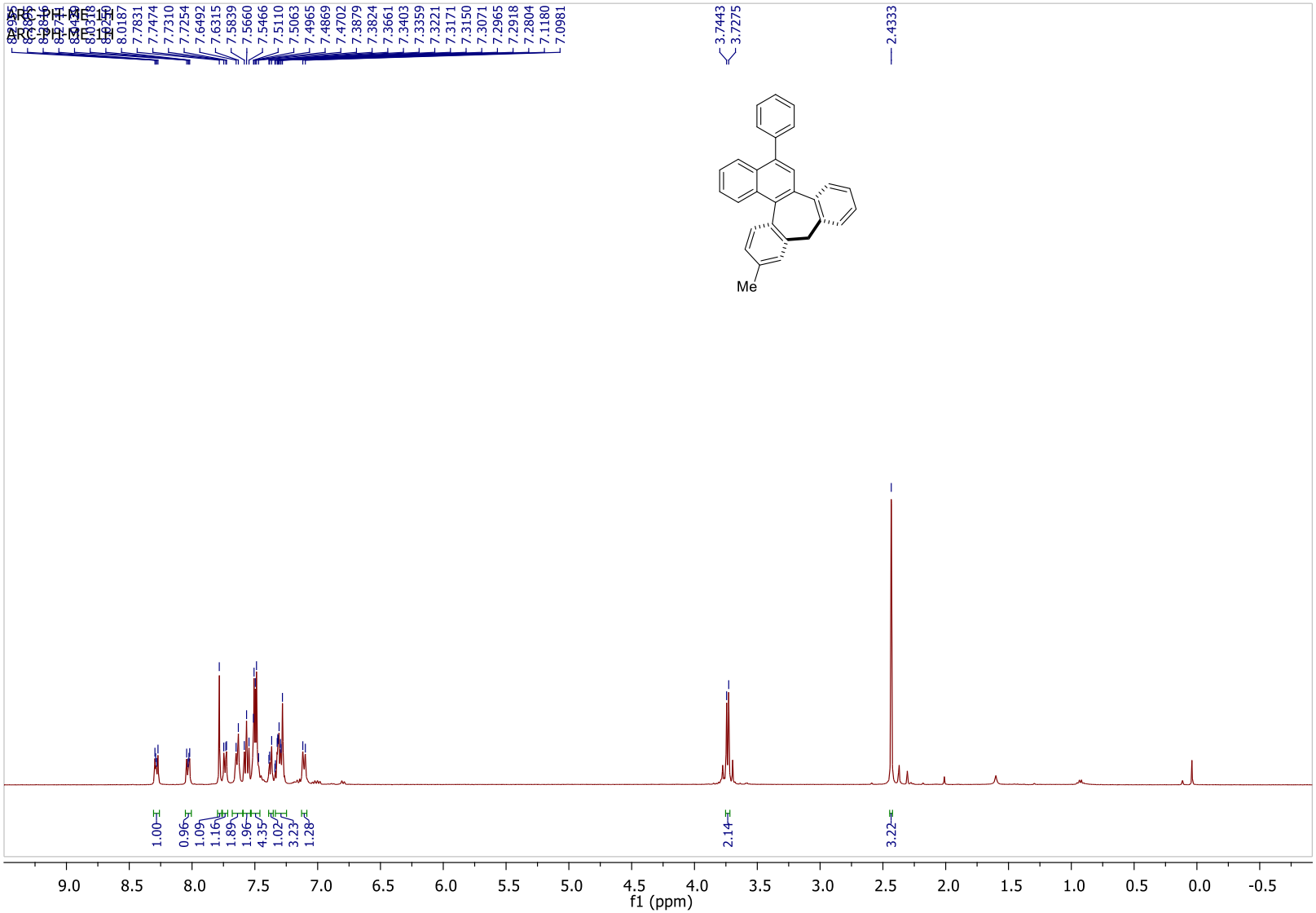
^{1}H Spectrum of **3o**



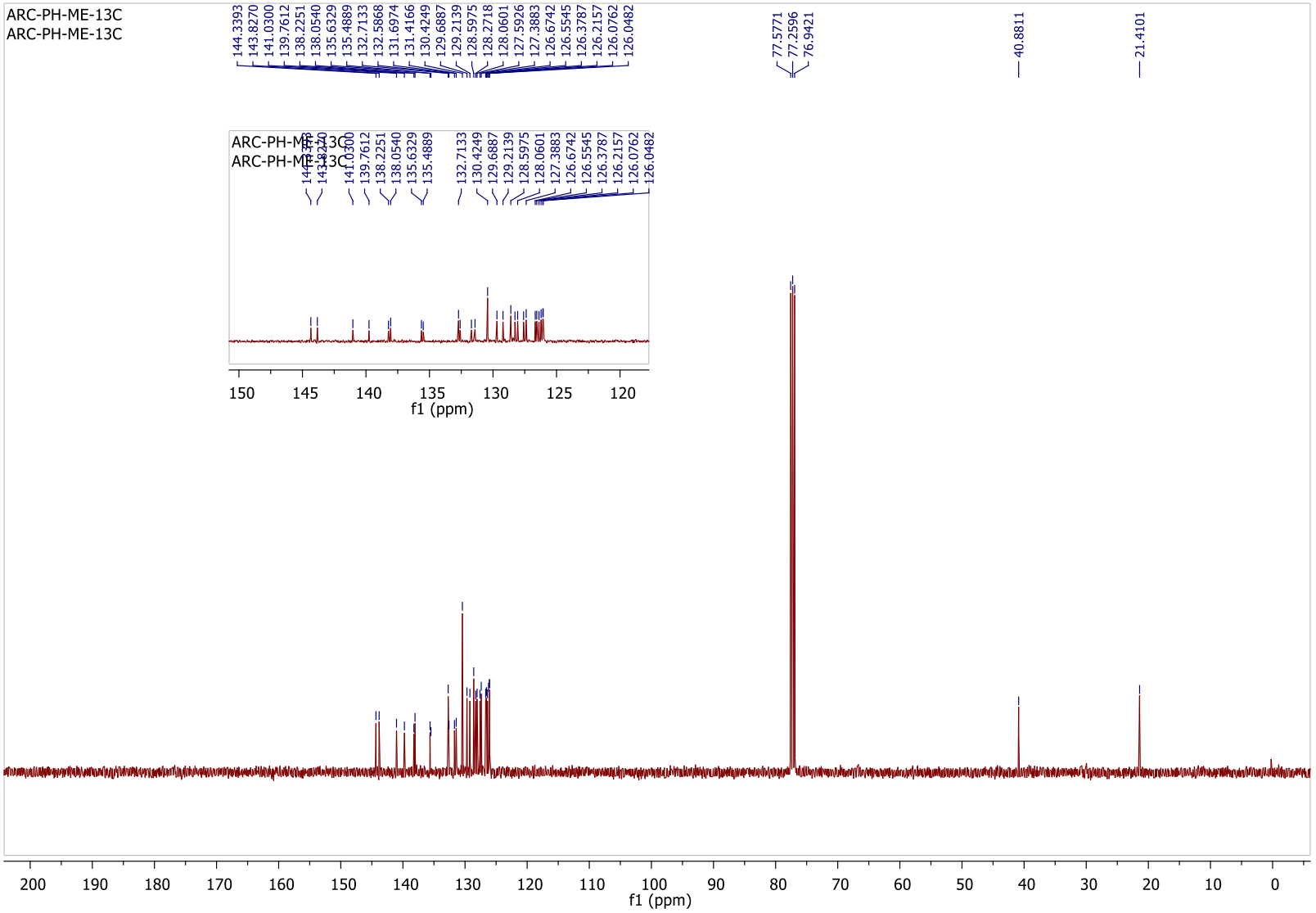
^{13}C Spectrum of **3o**



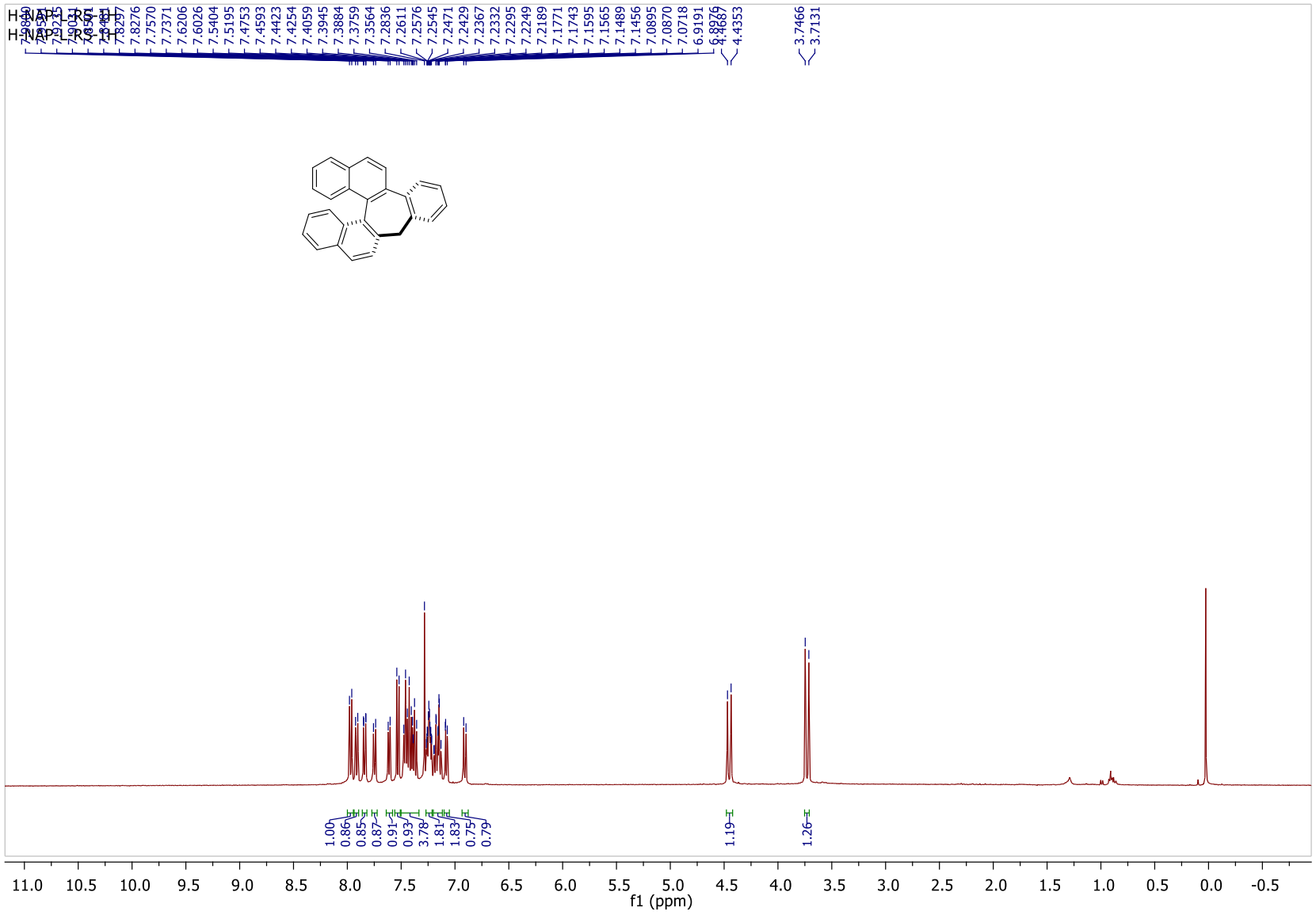
^{1}H Spectrum of **3p**



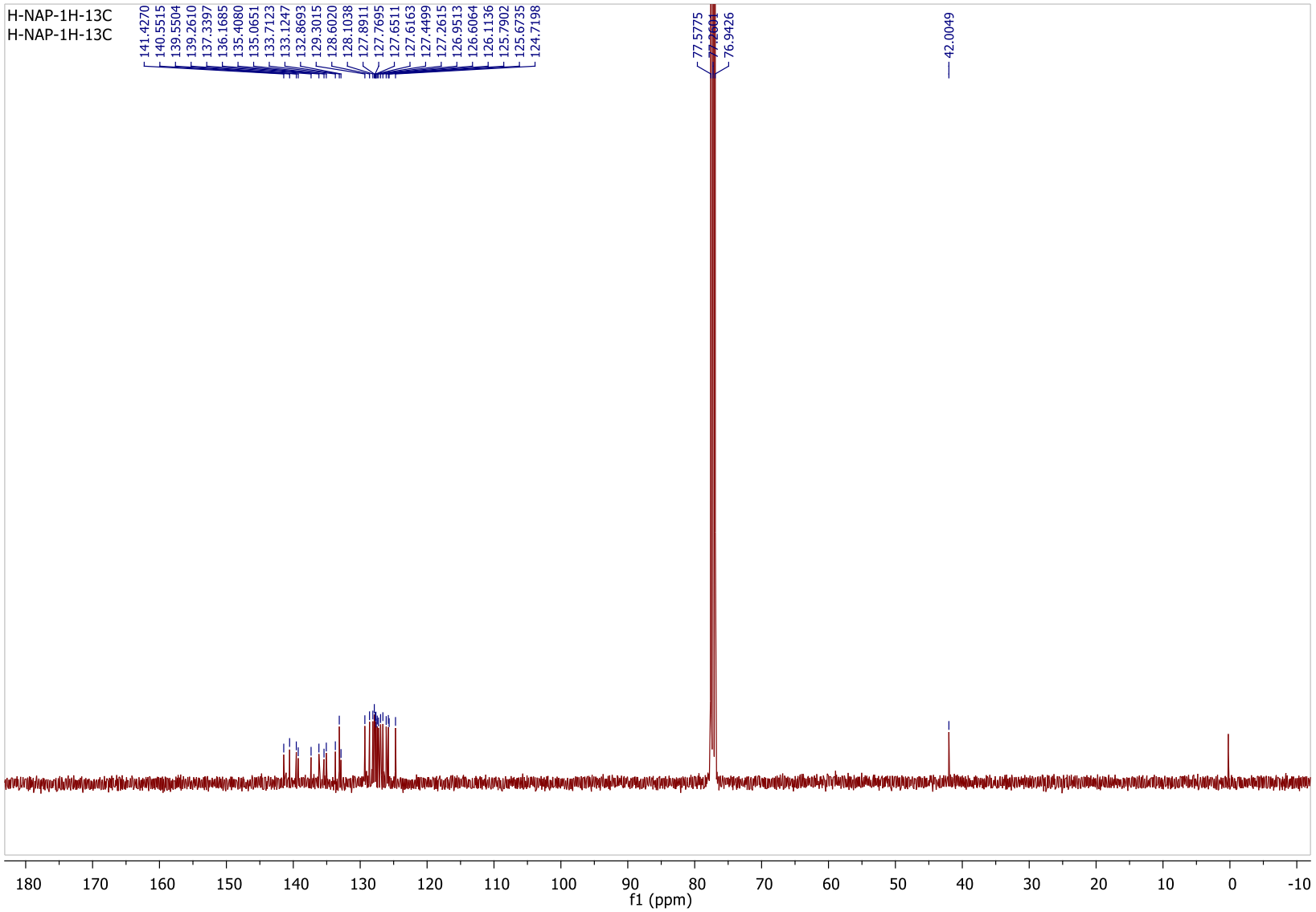
^{13}C Spectrum of **3p**



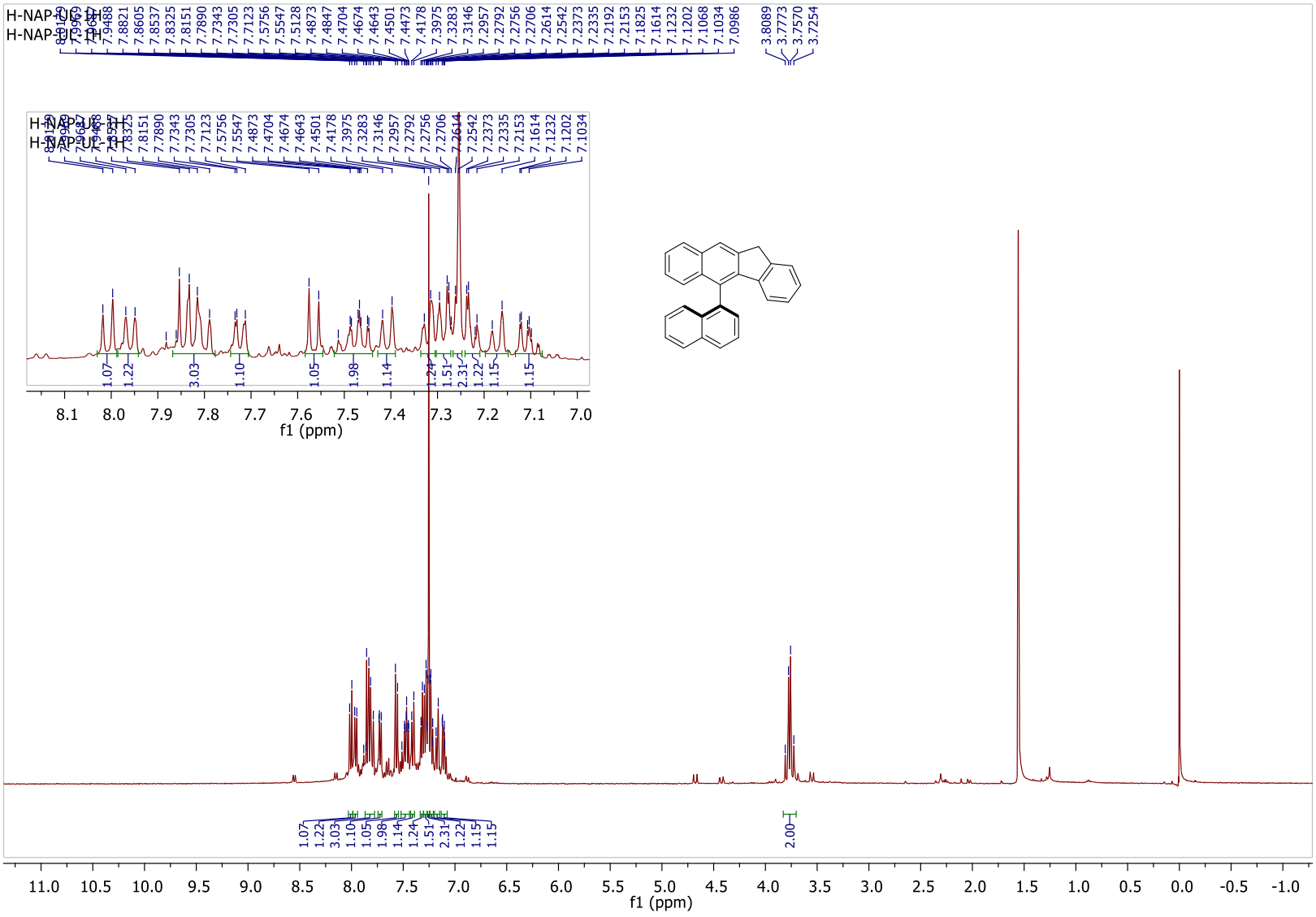
^{1}H Spectrum of **3q**



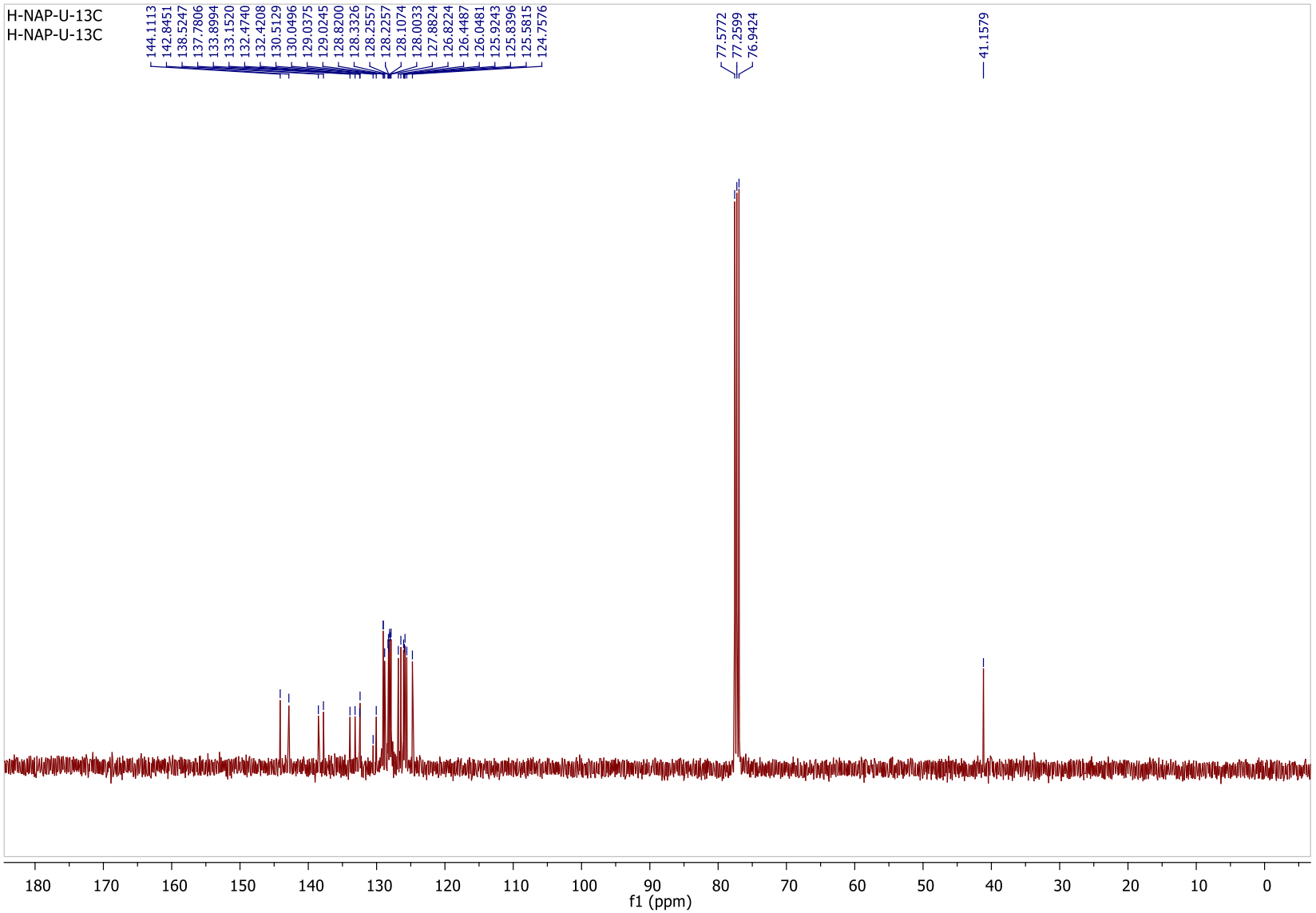
^{13}C Spectrum of **3q**



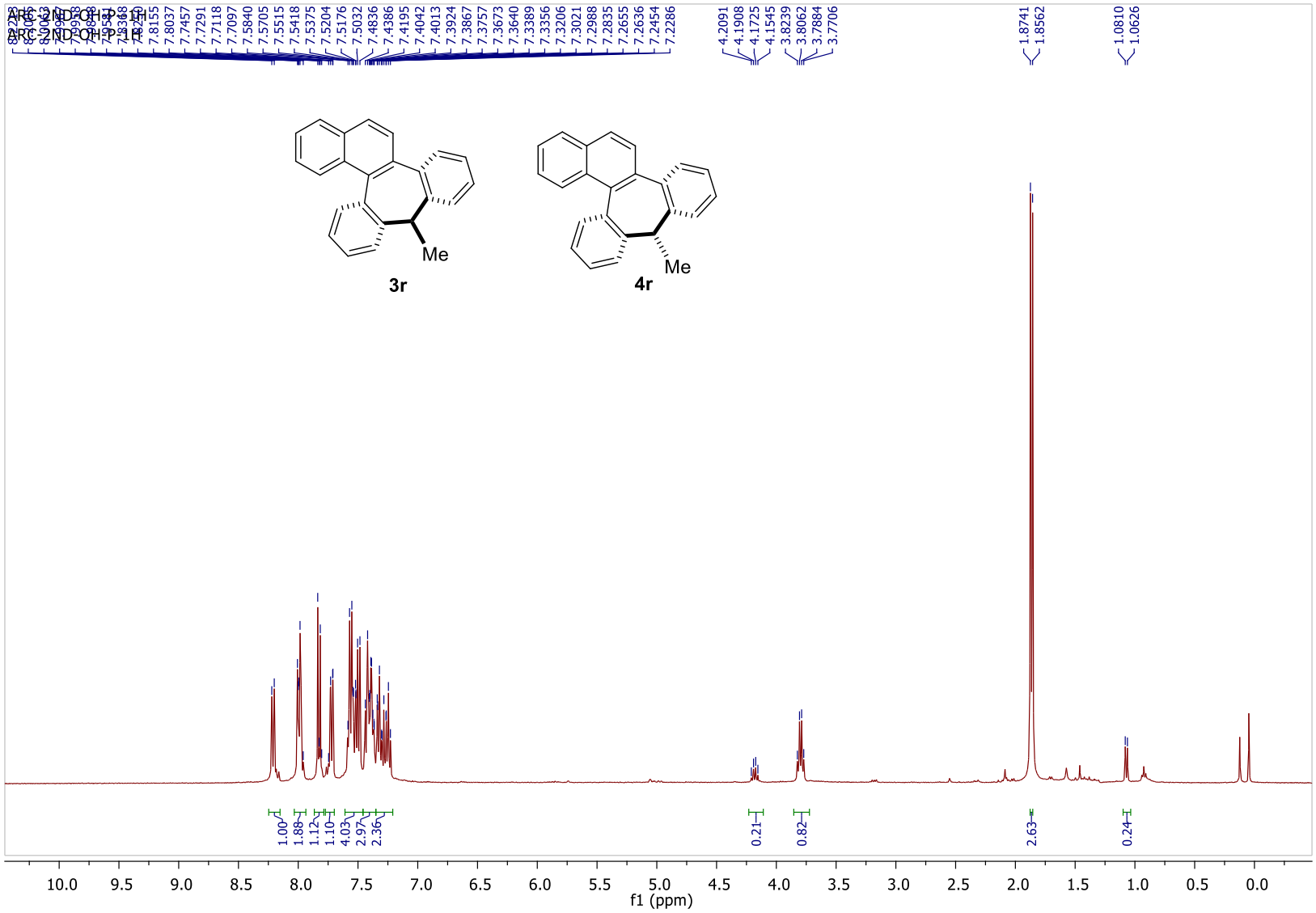
^{1}H Spectrum of **4q**



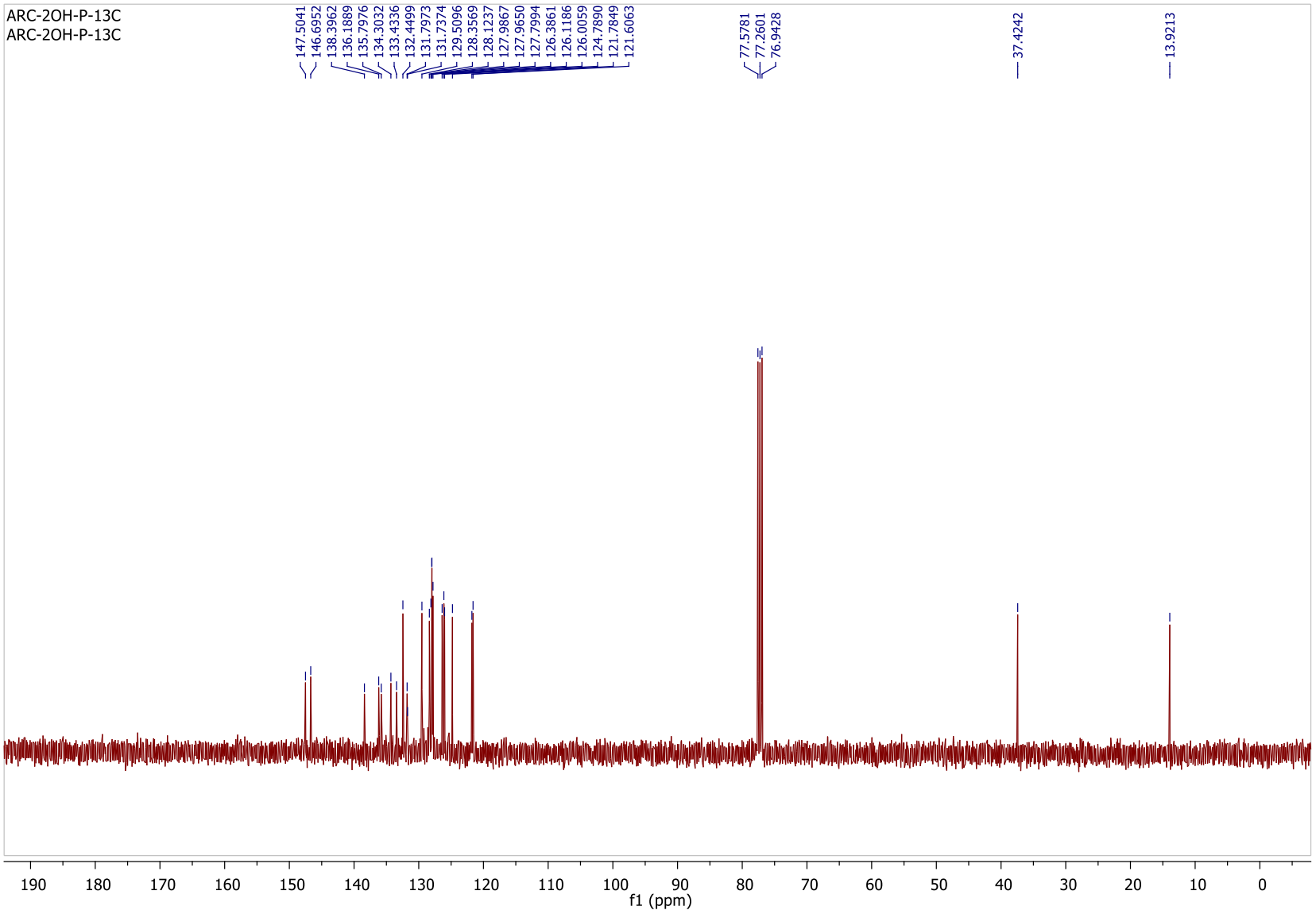
^{13}C Spectrum of **4q**



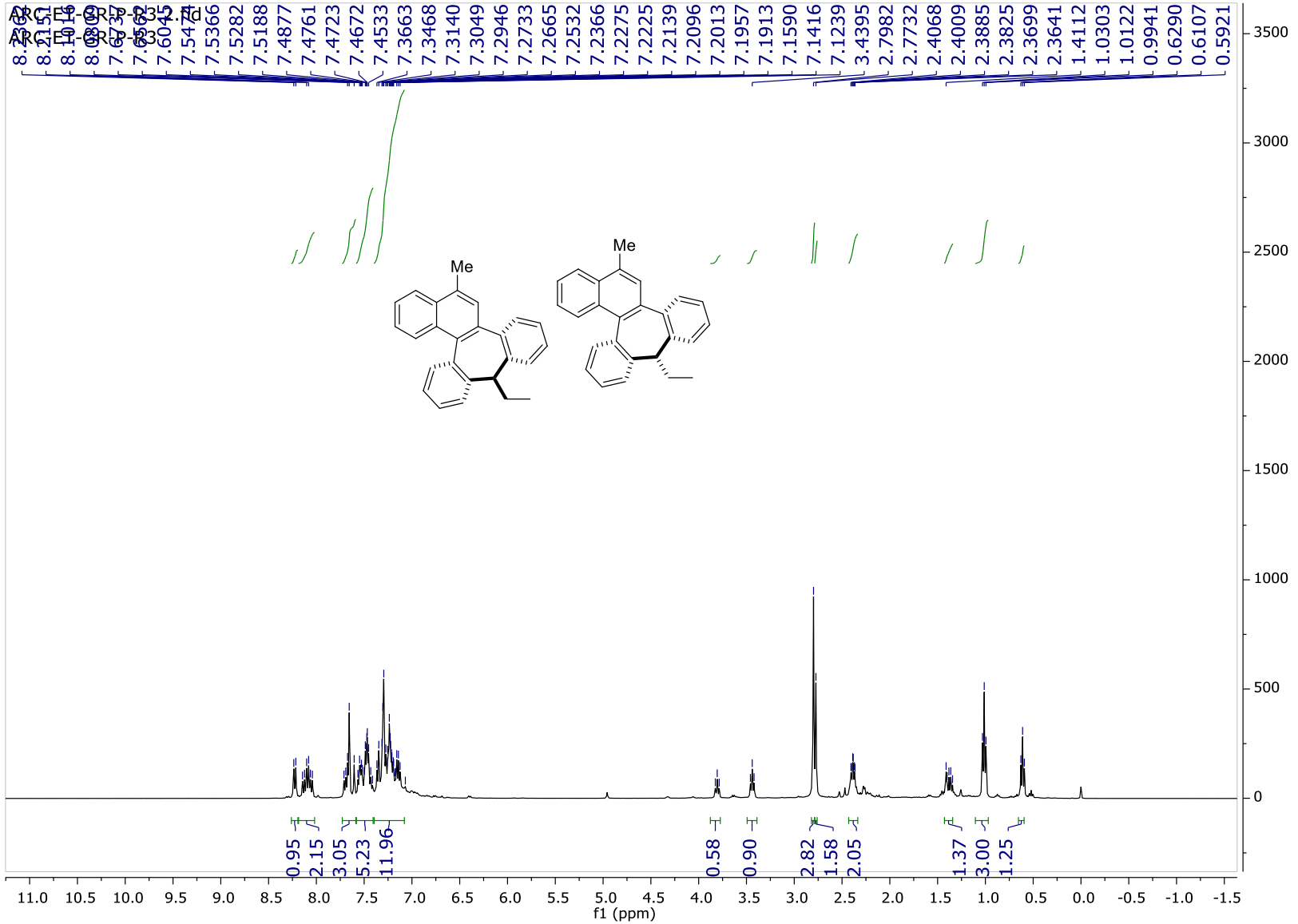
^{1}H Spectrum of **3r** and **4r**



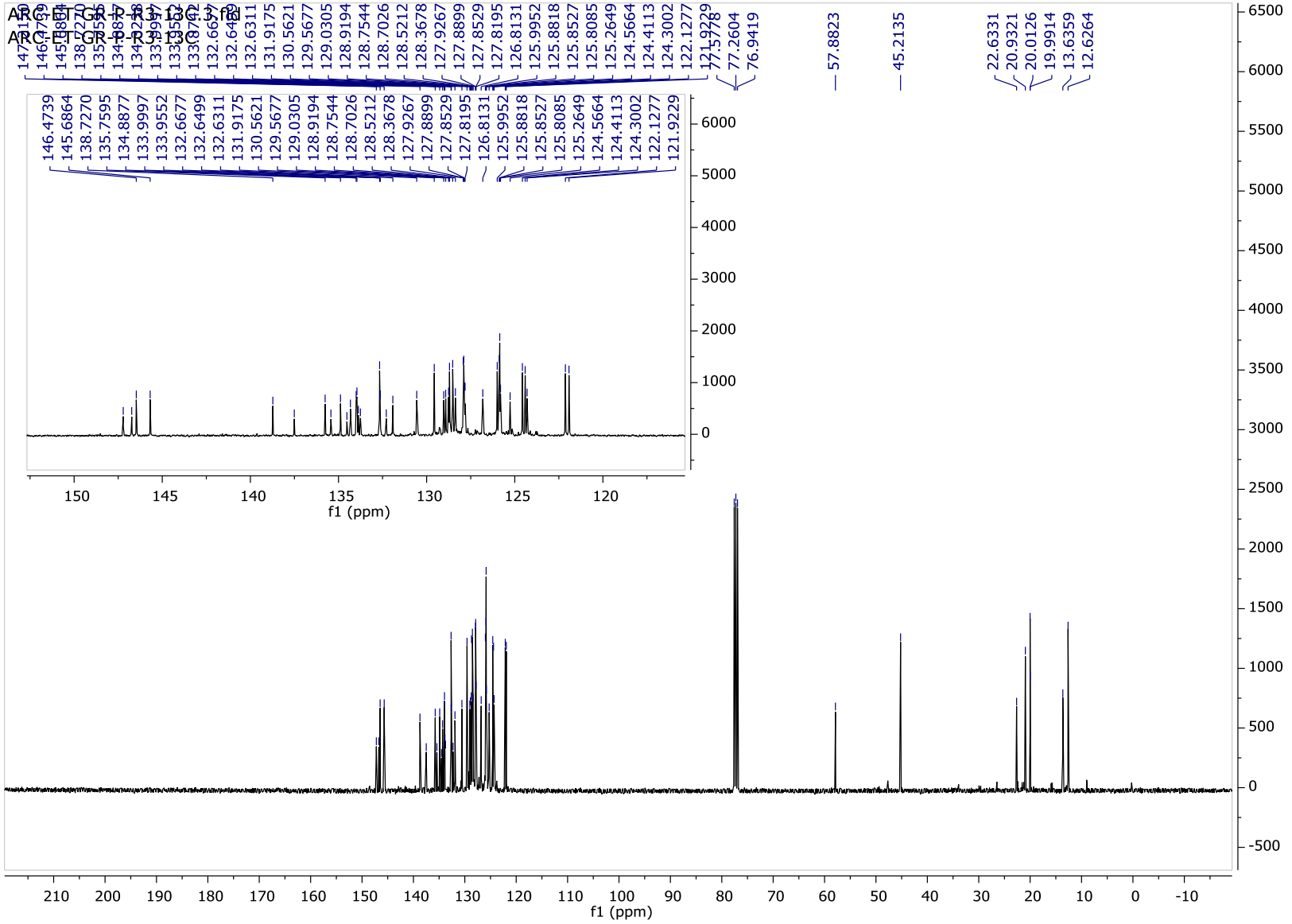
^{13}C Spectrum of **3r** and **4r**



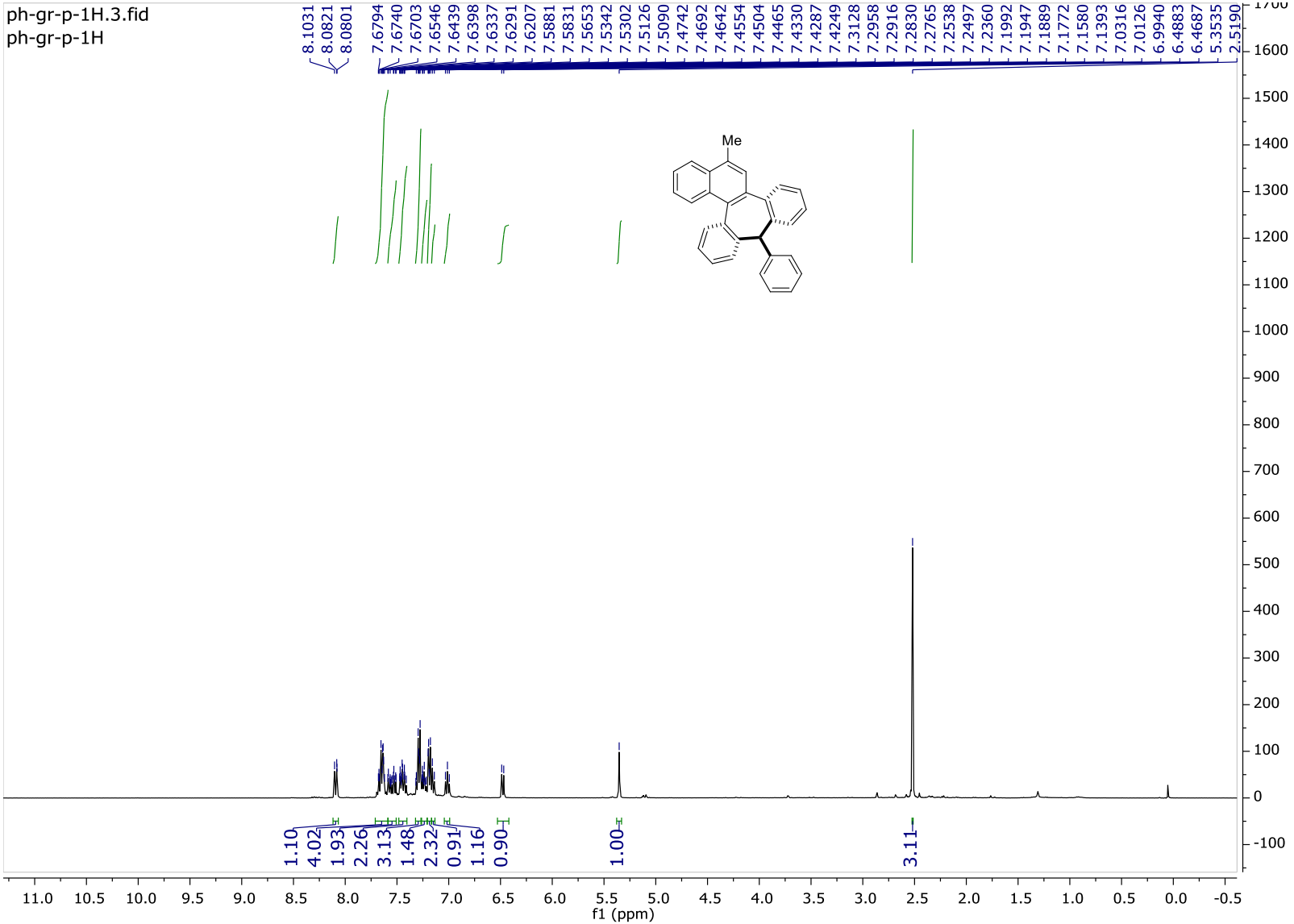
^{1}H Spectrum of **3s** and **4s**



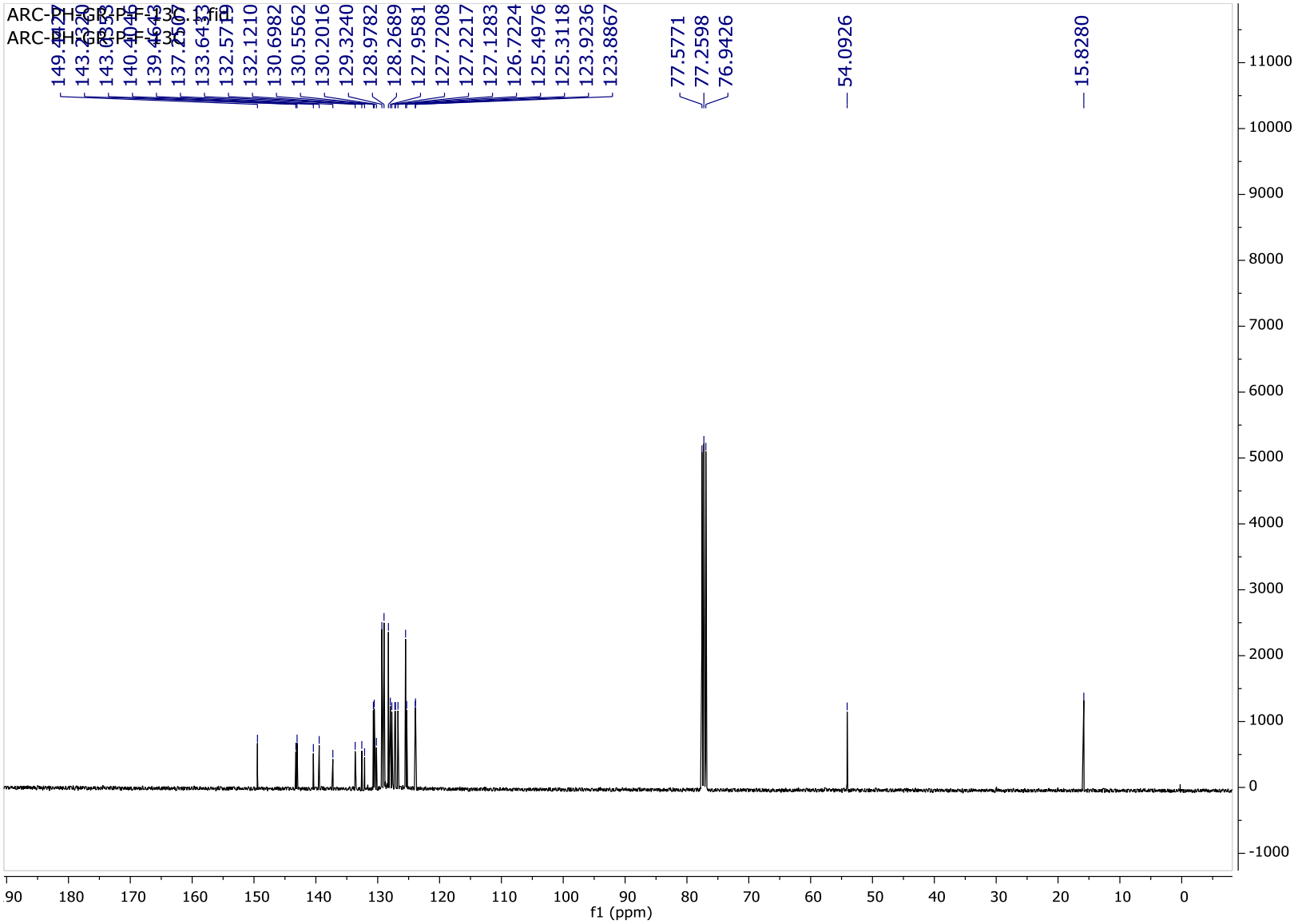
^{13}C Spectrum of **3s** and **4s**



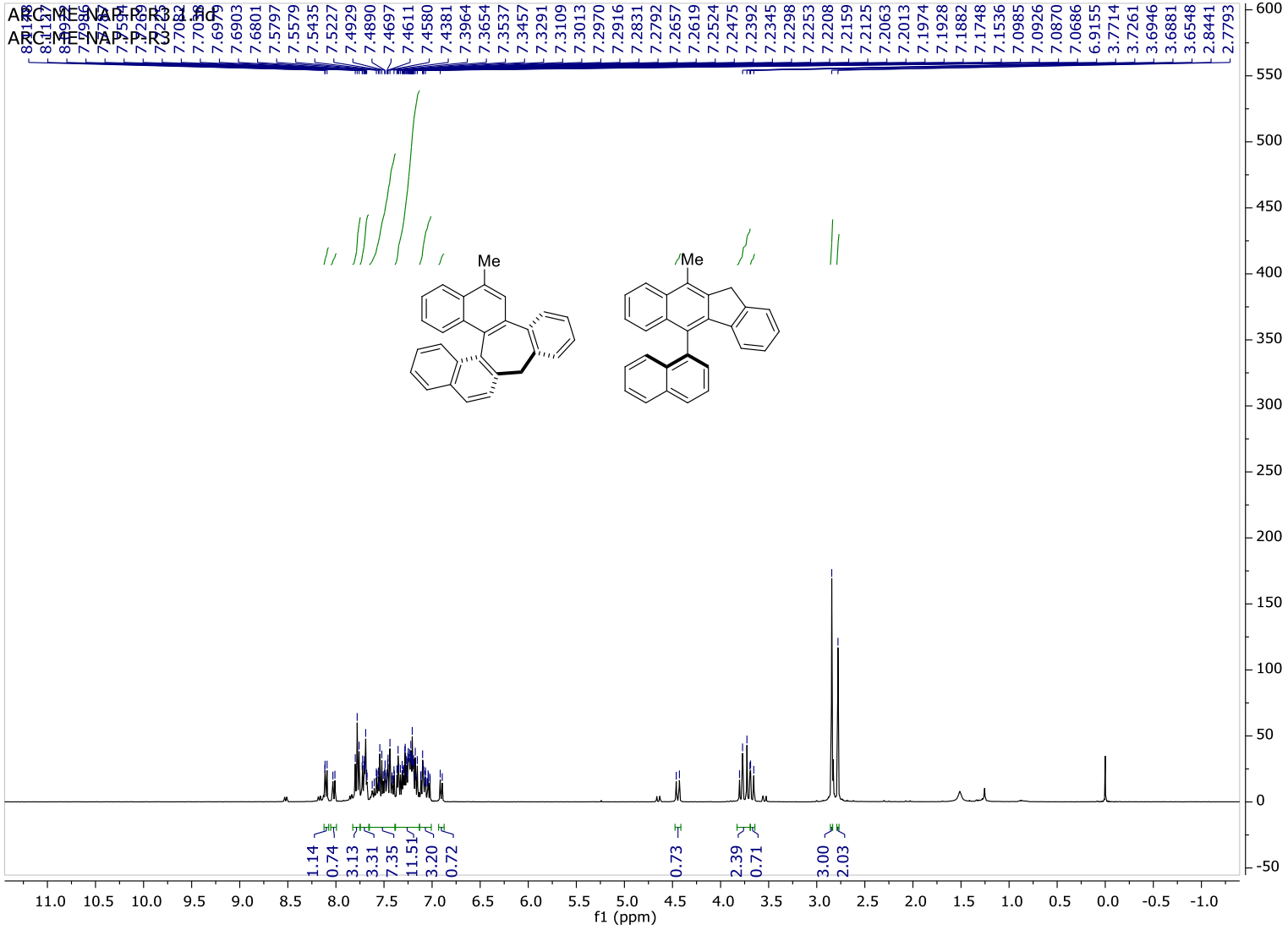
^{1}H Spectrum of **3t**



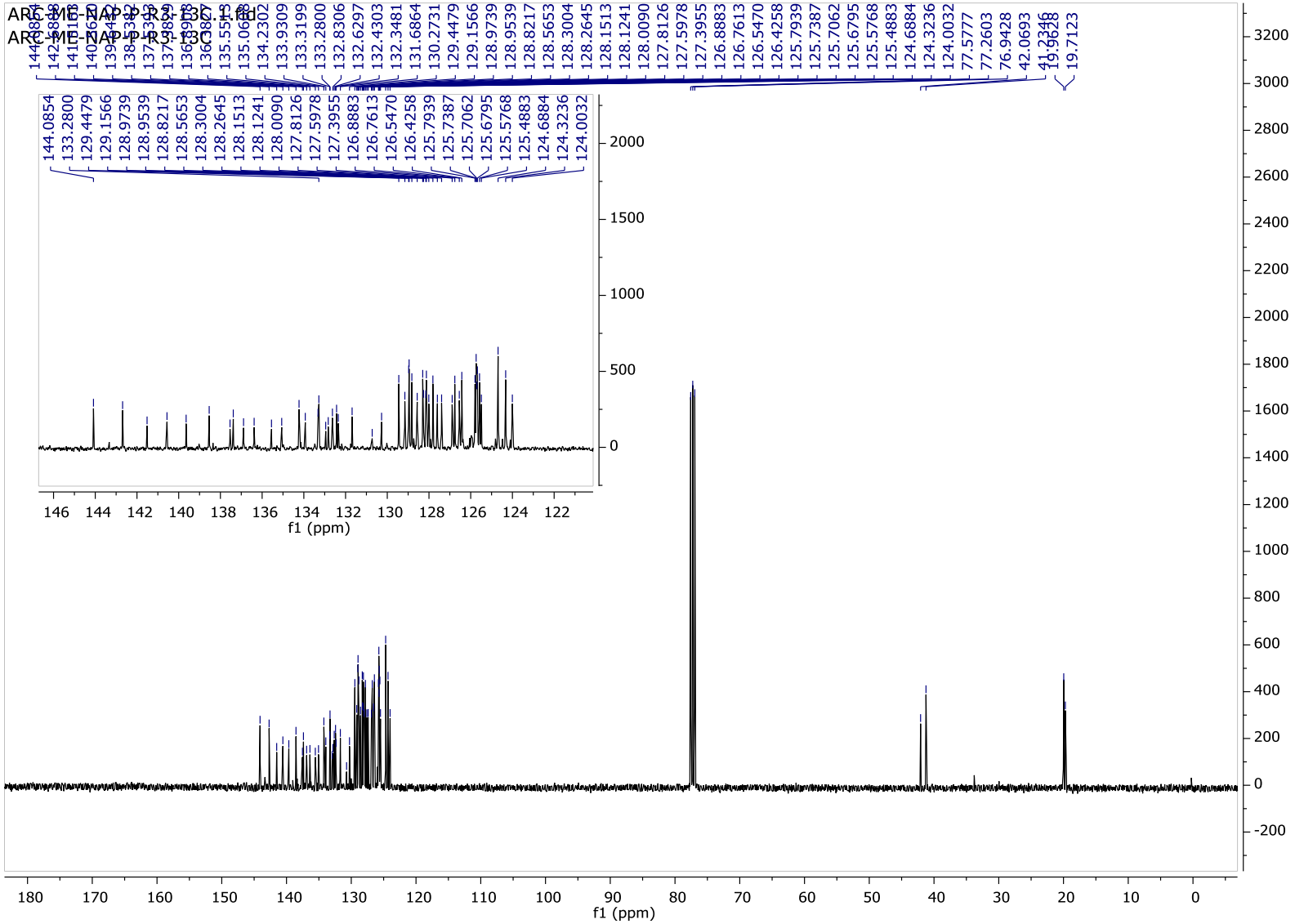
^{13}C Spectrum of **3t**



^{1}H Spectrum of **3u** and **4u**

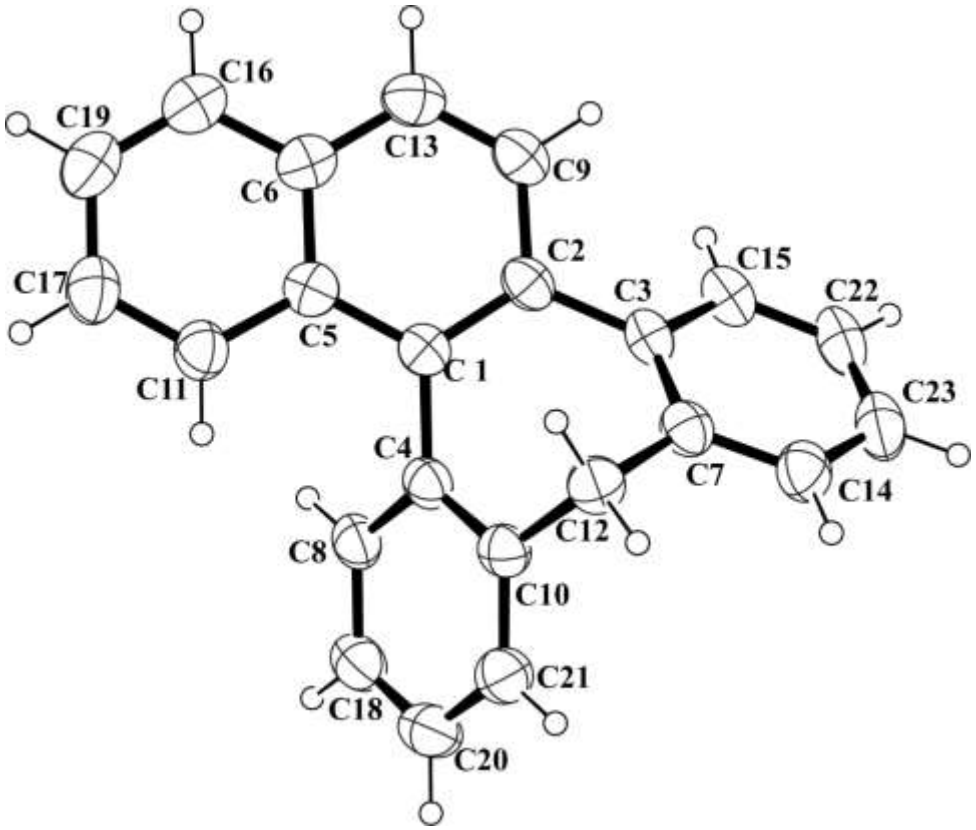


^{13}C Spectrum of **3u** and **4u**



The crystal parameters of compound **3a**

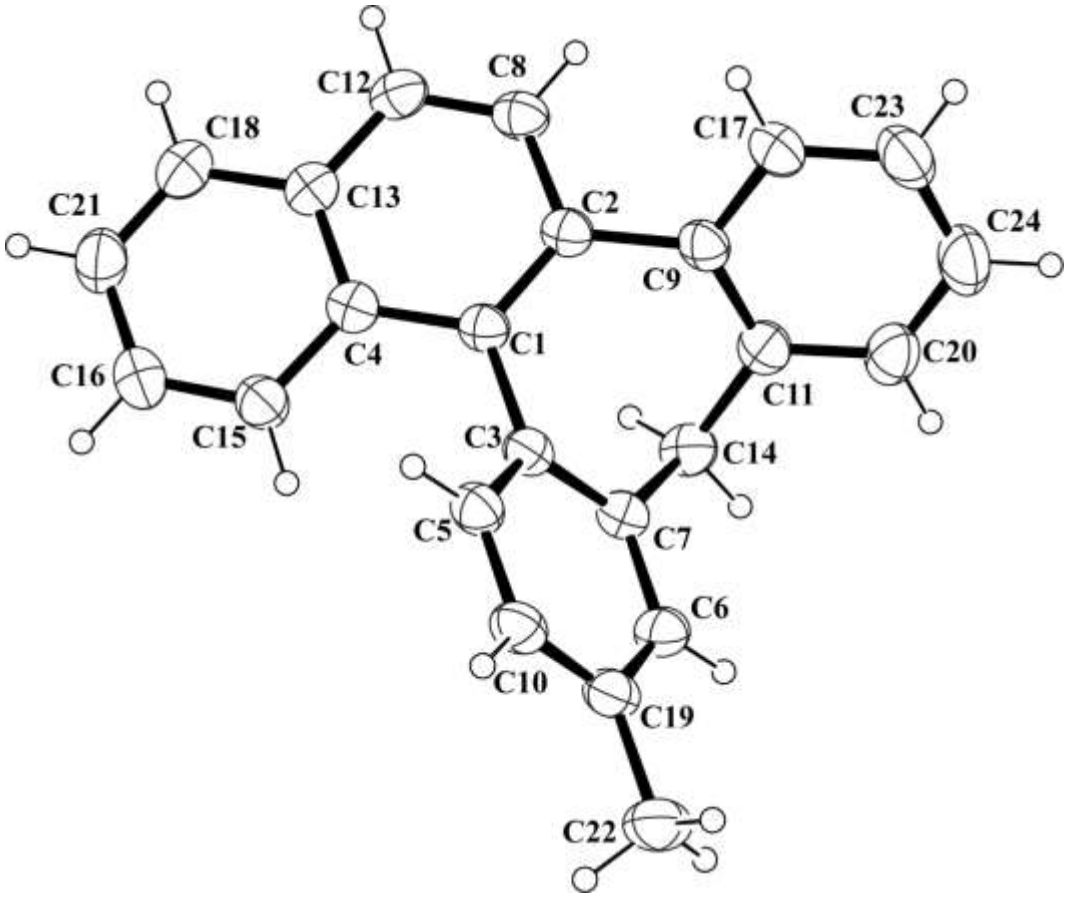
	CCDC 1873106
Formula	$C_{23}H_{16}$
Formula weight	292.36
T/K	293(2)
Crystal system	Triclinic
Space group	P-1
a/Å	8.7105(6)
b/Å	9.7870(7)
c/Å	10.2324(12)
α/°	107.954(7)
β/°	100.920(7)
γ/°	104.829(5)
V/Å^3	767.28(12)
Z	2
Abs. Coeff./mm^{-1}	0.072
Abs. Correction	Multi-Scan
GOF on F^2	1.031
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.0606
	wR2 = 0.1172
R indices [all data]	*R1* = 0.1672
	wR2 = 0.1977



ORTEP diagram of compound **3a**, thermal ellipsoids are drawn on 35% probability level

The crystal parameters of compound **3c**

	CCDC 1873107
Formula	$C_{24}H_{18}$
Formula weight	306.38
T/K	293(2)
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	9.8016(6)
b/Å	12.5556(7)
c/Å	14.0526(8)
α/°	90.00
β/°	108.162(3)
γ/°	90.00
V/Å^3	1643.22(17)
Z	4
Abs. Coeff./mm^{-1}	0.070
Abs. Correction	Multi-Scan
GOF on F^2	1.074
Final *R* indices [$I > 2\sigma(I)$]	*R1* = 0.0517
	wR2 = 0.0715
R indices [all data]	*R1* = 0.1455
	wR2 = 0.1611

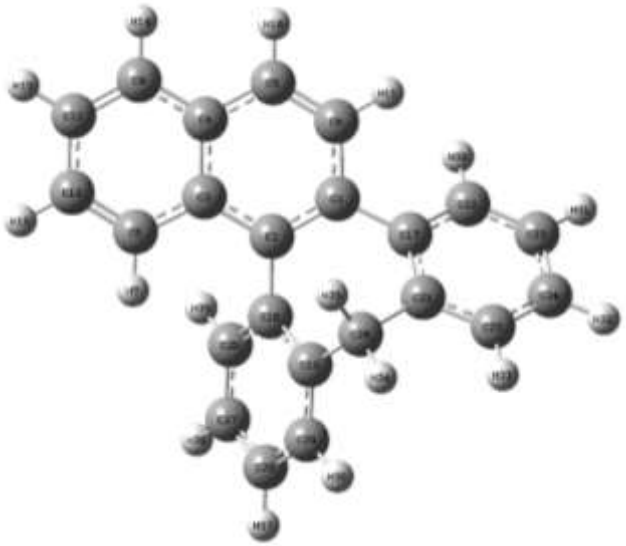


ORTEP diagram of compound **3c**, thermal ellipsoids are drawn on 35% probability level

Table 1: Energy optimized structure of 3a at [DFT-B3LYP/6-311++G(d,p)] level of theory

Compound Name	Method used	Energy (Hartree)
3a	DFT-B3LYP/6-31+G(d,p)	-886.168565
3a	DFT-B3LYP/6-311++G(d,p)	-886.325690

Optimized Structure of compound 3a



Compound 3a [DFT-B3LYP/6-311++G(d,p)]

Table 2: Energy optimized structures of compounds 3q and 4q and their comparison

Compound Name	**Method used**	**Energy (Hartree)**
3q	DFT-B3LYP/6-31+G(d,p)	-1039.815027
4q	DFT-B3LYP/6-31+G(d,p)	-1039.820533
$\Delta E = E_{3q} - E_{4q}$	**DFT-B3LYP/6-31+G(d,p)**	**0.005506 (3.45 kcal/mol)**
3q	DFT-B3LYP/6-311++G(d,p)	-1039.998898
4q	DFT-B3LYP/6-311++G(d,p)	-1040.004372
$\Delta E = E_{3q} - E_{4q}$	**DFT-B3LYP/6-311++G(d,p)**	**0.005474 (3.43 kcal/mol)**

As we can see from Table 1, in DFT-B3LYP/6-31+G(d,p) method, Compound 3q is 0.005506 Hartree (3.45 kcal/mol) higher in energy than that of the Compound 4q. Similarly, in DFT-B3LYP/6-311++G(d,p) method, Compound 3q is 0.005474 Hartree (3.43 kcal/mole) higher in energy than that of the Compound 4q. In other words, Compound 4q is more stable than that of Compound 3q. (1 Hartree = 627.51 kcal/mole)

Optimized Structure of compounds 3q and 4q

Compound 3q [DFT-B3LYP/6-311++G(d,p)]

Compound 4q [DFT-B3LYP/6-311++G(d,p)]

HPLC spectrum of compound **3a**

IIT-Guwahati

Project Name: Demo 20022018

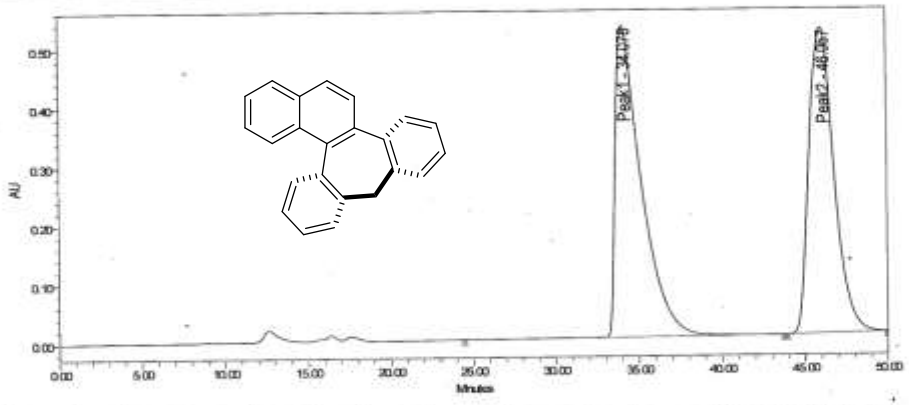
Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	Aro-h-ph	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	11/29/2020 2:39:30 PM IST
Vial:	1	Acq. Method:	Hex_ARC
Injection #:	1	Processed By:	Breeze
Injection Volume:	20.00 ul	Date Processed:	11/29/2020 3:34:13 PM IST
Run Time:	50.00 Minutes	Channel Name:	W489 ChA
Sampling Rate:	1.00 per sec	Channel Desc.:	W489 ChA 254nm
		Sample Set Name:	

Sample Values Used in Calculations: Injection Volume = 20.00 Sample Weight = 1.00000 Dilution = 1.00000



	Peak Name	RT (min)	Peak Type	Area (µV*sec)	%Area	Height (µV)	%Height	Integration Type	Response	Peak Codes	Points Across Peak	Start Time (min)	End Time (min)	Baseline Start (min)
1	Peak1	34.078	Found	5710538[illegible]	51.25	525203	50.48	BB	5.711e+00[illegible]	CBO	119[illegible]	24.467	43.733	24.467
2	Peak2	46.057	Found	5432800[illegible]	48.75	515057	49.52	BB	5.433e+00[illegible]	CBO	364	43.917	49.967	43.917

Report Method: Detailed Individual Report

Page: 1 of 2

Printed: 11/29/202[illegible] 3:34:52 PM Assr/Calculs

HPLC spectrum of compound **3f**

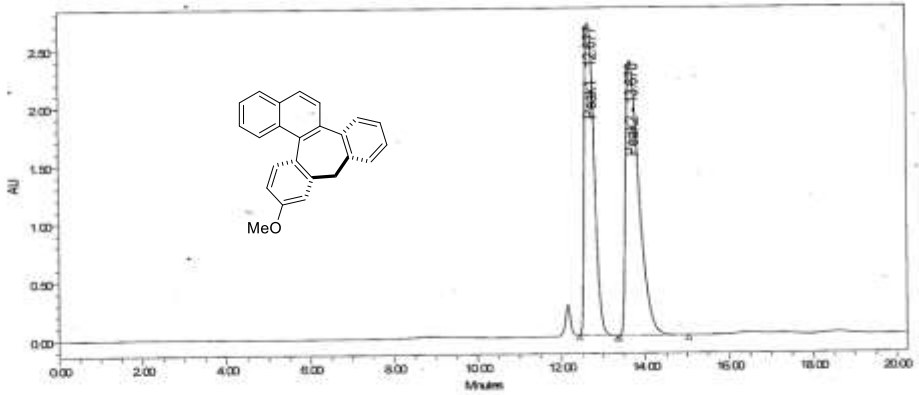
IIT-Guwahati
Project Name: Dame 20032018
Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	Arc-p-OMe	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	11/28/2020 4:54:48 PM IST
Vial:	1	Acq. Method:	Hex_ARC
Injection #:	1	Processed By:	Breeze
Injection Volume:	20.00 ul	Date Processed:	11/28/2020 7:31:43 PM IST
Run Time:	50.00 Minutes	Channel Name:	W2489 Ch1
Sampling Rate:	1.00 per sec	Channel Desc.:	W2489 Ch1 254nm
		Sample Set Name:	

Sample Values Used in Calculations: Injection Volume = 20.00 SampleWeight = 1.00000 Dilution = 1.00000



	Peak Name	RT (min)	Peak Type	Area (µV*sec)	%Area	Height (µV)	%Height	Integration Type	Response	Peak Codes	Points Across Peak	Start Time (min)	End Time (min)
1	Peak1	12.677	Found	4375[illegible]	45.64	2[illegible]	53.12	BB	4.37[illegible]e+007	C20	5[illegible]	12.433	13.35[illegible]
2	Peak2	13.67[illegible]	Found	5211875[illegible]	54.3[illegible]	2[illegible]	46.8[illegible]	BB	5.212e+007	C20	10[illegible]	13.367	15.03[illegible]

Report Method: Detailed Individual Report
Page: 1 of 2

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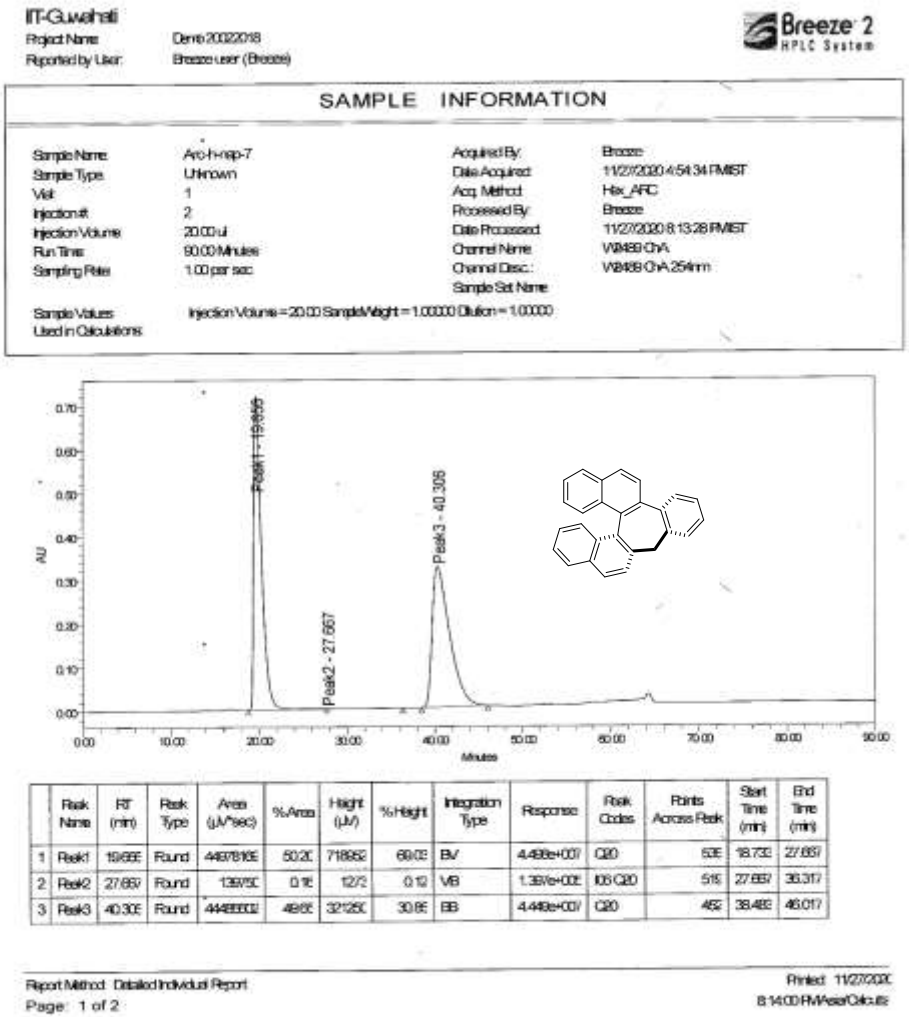
HPLC spectrum of compound **3q**



HPLC spectrum of compound **4q**

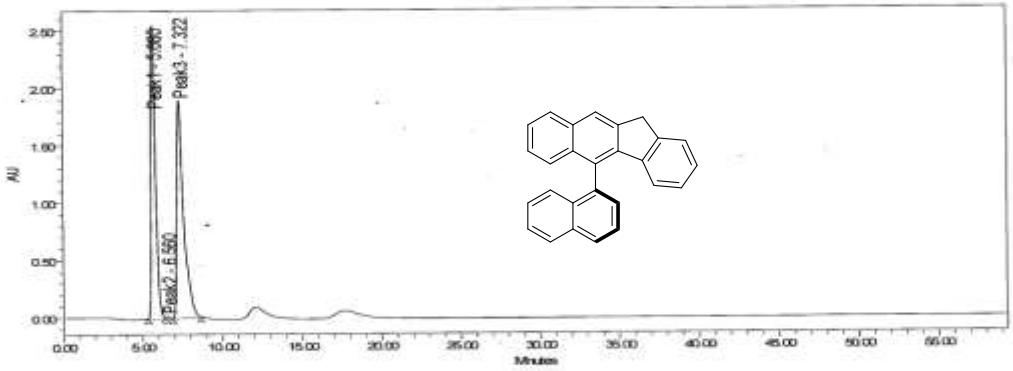
IIT-Guwahati
Project Name: Demo 20122018
Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	Arc-h-nap-6	Acquired By:	Breeze
Sample Type:	Unknown	Date Acquired:	11/27/2020 6:55:09 PM IST
Vial:	1	Acq. Method:	Hex_ARC
Injection #:	3	Processed By:	Breeze
Injection Volume:	20.00 ul	Date Processed:	11/27/2020 8:15:35 PM IST
Run Time:	90.00 Minutes	Channel Name:	W2489 ChA
Sampling Rate:	1.00 per sec	Channel Desc.:	W2489 ChA 254nm
		Sample Set Name:	

Sample Values Used in Calculations: Injection Volume = 20.00 SampleWeight = 1.00000 Dilution = 1.00000



	Peak Name	RT (min)	Peak Type	Area (µV*sec)	%Area	Height (µV)	%Height	Integration Type	Response	Peak Codes	Points Across Peak	Start Time (min)	End Time (min)	Baseline Start (min)
1	Peak1	5.665	Found	4[illegible]346	46.62	258045	57.04	BV	4.986e+007	Q20	62	5.395	6.405	5.395
2	Peak2	6.560	Found	405752	0.38	24235	0.54	VB	4.088e+005	Q20	30	6.405	6.905	5.395
3	Peak3	7.322	Found	5885564	53.00	190110	42.42	BB	5.683e+007	Q20	105	6.905	8.857	6.905

Report Method: Detailed Individual Report
Page: 1 of 2

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