This journal is © The Royal Society of Chemistry 2009

Supporting Information

Iterative Synthesis of Acenes via Homo-elongation

Chih-Hsiu Lin*; Ke-Han.Lin; Bikash Pal; Li-Der Tsou

Institute of Chemistry, Academia Sinica,

128 Academia Road, Nankang, Taipei, Taiwan

chl@chem.sinica.edu.tw

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

This journal is © The Royal Society of Chemistry 2009

Table of Contents

General experimental procedures……3-6

Spectral characterization for diesters 1-14, diols 1a-13a, dialdehydes 1b-13b…....6-19

Spectral characterization for dinitriles 15-27…….....19-24

Spectral characterization for compounds 28-35……..……24-31

^{1}H, ^{13}C NMR spectra of diesters 1-14, diols 1a-13a, dialdehydes 1b-13b……32-111

^{1}H, ^{13}C NMR spectra of 15-27……...……112-142

^{1}H, ^{13}C NMR spectra of 28-35….....143-161

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

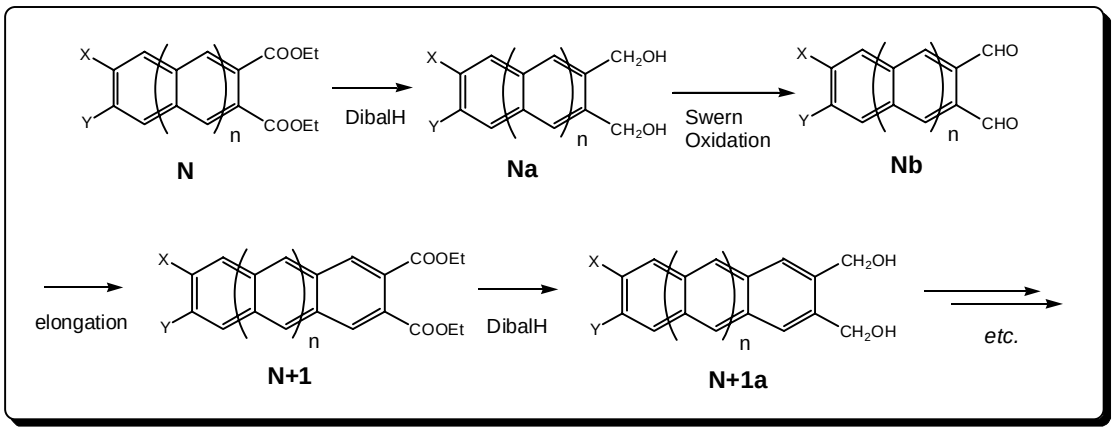
Instruments and General Experimental Set-ups:

Nuclear magnetic resonance spectra were taken on Brucker AMX-400 (400 MHz), Brucker AV-400 (400 MHz), or Brucker AV-500 (500 MHz) spectrometer. Infrared spectrum data were measured on a Thermo Nicolet Avatar 360 E.S.P. FT-IR spectrometer. Samples were pressed into KBr tablet or deposited on NaCl pellet from CH_2Cl_2 solution. High resolution mass spectra were taken on JEOL JMS-700 10kV.

All reactions were performed under 1 atmosphere of inert gas (dried nitrogen) and mixed well with magnetic stirring devices. Reagent grade chemicals and solvents were used in all reactions. Reaction vessels were oven dried before use. Tetrahydrofuran was distilled over metallic sodium with benzophenone radical anion as the indicator. Dichloromethane was distilled from CaH_2. Flash column chromatography was performed with Merck silica gel 60 (1.11567.9025, 0.040-0.063 according to their order mm) as the stationary phase. All ratios of reported mixed eluents are based on volume.

General procedures for iterative elongation reactions:

The numbering of the acene diester compounds, diol and dialdehyde synthetic intermediates appear in the main text and supporting material is defined in the following scheme. All other compounds (including the acene dinitrile products) are numbered based on the order of their appearance in the text.



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

This journal is © The Royal Society of Chemistry 2009

Optimized general procedure for the elongation of [N]acene dialdehydes to [N+1] acene diesters: The triethylphosphine (1.3-1.4 equivalents) was added dropwise via syringe to a stirred CH_2Cl_2 solution of diethyl maleate (1.2-1.3 equivalents, 2 mmol/mL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 30 min. The Wittig reagent thus generated was added dropwise via syringe to a stirred CH_2Cl_2 solution of dialdehyde (1 equivalent, 5 mmol/mL) at 0 °C. After the completion of the addition, a CH_2Cl_2 solution of DBU (0.1 equivalent, 5 mmol/mL) was added dropwise via syringe to the reaction mixture. The reaction mixture was stirred at room temperature for another 3 hr. Water was added to quench the reaction and the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over anhydrous $MgSO_4$ and the volatiles were removed under reduced pressure. The resulting slurry was purified by column chromatography on silica gel (hexane-CH_2Cl_2, 1:1 and 1:3 to pure CH_2Cl_2).

The reaction was also carried out by adding the phosphine to a CH_2Cl_2 (minimum amount to dissolve the reactants) mixed solution of diethyl maleate and dialdehyde at -78 °C. DBU (CH_2Cl_2 solution) was then added before the reaction was warmed back to room temperature. The reaction was monitored by TLC (3-20 hr, solvent system CH_2Cl_2) and worked up as described upon the completion of the elongation. Tributyl or trioctyl phosphine can also be used in place of triethyl phosphine. Neither of these variations have much bearing on the final yields of naphthalene and anthracene products. Yet, for the bidirectional elongation reaction, the optimized procedure is necessary to ensure good yields.

General procedure for reduction of [N]acene diesters to bis(hydroxymethyl) [N]acene: A diisobutylaluminium hydride solution in toluene (1.0 M) was added dropwise via syringe to a stirred solution of ester in toluene (4-5 equivalents of reductant per ester group) at -50 °C under nitrogen atmosphere and stirring was

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

continued at -50 °C for 12 hr. The reaction mixture was quenched by the dropwise addition of methanol via syringe. A saturated solution of sodium potassium tartarate was added and the reaction mixture was extracted with ethyl acetate three times and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the desired product was obtained as a white solid. Not all of these diol products have complete characterizations (^{1}H NMR, ^{13}C NMR, IR, HR Mass) due to solubility problems. However, we are confident with their structural assignment since the products from subsequent transformations are all well characterized. LAH can also be used for the reduction of naphthalene diesters. In some cases, THF was added during the extraction process to solublize the diol products.

General procedure for oxidation of bis(methanol)-[N]acene to [N]acene dialdehydes: A solution of DMSO and CH_2Cl_2 (volume ratio = 1:2, 10-15 ml per mmol of starting diol) was added dropwise via syringe to a stirred solution of oxalyl chloride (3 equivalents per alcohol) in CH_2Cl_2 (10 ml) at -80 °C under nitrogen atmosphere and stirring was continued for 30 min. After that, a solution of diol in DMSO and CH_2Cl_2 (volume ratio = 1:2, 10-15 ml per mmol of starting diol) was added dropwise via syringe at the same temperature and the reaction mixture was further stirred for 12 hr at -80 °C. The reaction mixture was quenched by the dropwise addition of triethylamine (distilled, 5 ml per mmol of starting diol) via syringe and the reaction was stirred at room temperature for another 30 min. Water was added and the reaction mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with water three times and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure and the desired aldehydes thus obtained are often used in the next elongation step without further purification.

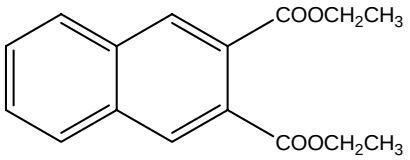
General procedure for the elongation of [N]acene dialdehydes to [N+1]acene dinitriles: A solution of triethylphosphine (1.0 M in THF, 1.2 equivalents) was

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

diluted with CH_2Cl_2 (equal volume to THF solution). This phosphine solution was added dropwise via syringe to a stirred CH_2Cl_2 solution of fumaronitrile (1.5 mL/ mmol, 1.1 equivalents) at 0 °C under nitrogen atmosphere. Then the reaction mixture was stirred at the same temperature for 30 min. The Wittig reagent was then added dropwise via syringe to a stirred CH_2Cl_2 solution of dialdehyde (1 mmol per 5 ml) at 0 °C. The reaction mixture was warmed back to room temperature and stirred for an additional 3 hr. Water was added and the reaction mixture was extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The resulting slurry was purified by flash chromatography on silica gel (hexane-dichloromethane to pure dichloromethane). The desired product was obtained as tan yellow solid.

An alternative procedure is to add the phosphine solution to a mixed solution of fumaronitrile and the dialdehyde at -78 °C. A CH_2Cl_2 solution of DBU (0.1 equivalent) was then added before the reaction mixture was warmed back to room temperature. The progress of the reaction was monitored with TLC chromatography. After the completion of the elongation reaction (3-10 hr), the product was purified as described above. As in the reaction to produce diesters, tributyl or trioctyl phosphine can also be used in place of triethyl phosphine. As before, neither of these variations have much bearings on the final yields of naphthalene and anthracene products. Yet, the optimized procedure is necessary to ensure good yields in bidirectional elongation reaction.

1: Naphthalene-2,3-dicarboxylic acid diethyl ester

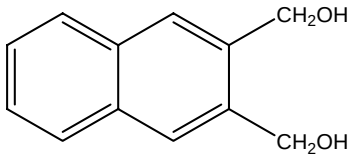


Yield: 86 %; IR (KBr, ν) 2983, 1724, 1631, 1467, 1369, 1285, 1199, 1046 cm^{-1};

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

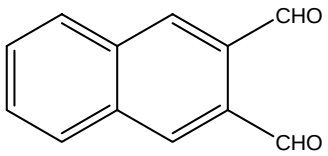
^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.37 (t, *J* = 7.2 Hz, 6H), 4.40 (q, *J* = 7.2 Hz, 4H), 7.59-7.62 (m, 2H), 7.88-7.92 (m, 2H), 8.23 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.15, 61.62, 128.42, 128.59, 128.82, 129.98, 133.33, 167.72; MS (FAB): HRMS. ($M+H^+$), $C_{16}H_{17}O_4$, Calc: 273.1127; Found: 273.1131.

1a: (3-Hydroxymethyl-naphthalen-2-yl)-methanol



Yield: 86 %; IR (KBr, ν) 3207, 2932, 2874, 1600, 1445, 1091, 1006, 989, 886, 744 cm^{-1}; ^{1}H NMR (Acetone-d_6, 400 MHz, ppm): δ 4.46 (t, *J* = 5.4 Hz, 2H), 4.87 (d, *J* = 5.4 Hz, 4H), 7.46-7.48 (m, 2H), 7.85-7.88 (m, 2H), 7.9 (s, 2H); ^{13}C NMR (Acetone-d_6, 100 MHz, ppm): δ 63.32, 126.68, 127.34, 128.42, 133.88, 139.23; MS (FAB): HRMS. (M^+) $C_{12}H_{12}O_2$, Calc: 188.0837; Found: 188.0841.

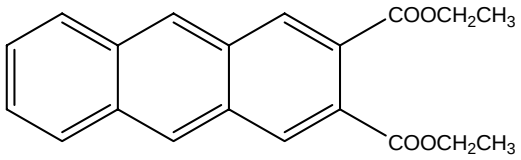
1b: Naphthalene-2,3-dicarbaldehyde



Yield: 83 %; IR (KBr, ν) 3102, 3078, 3034, 2230, 1621, 1465, 1362, 1276, 914, 909, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.72-7.74 (m, 2H), 8.03-8.05 (m, 2H), 8.44 (s, 2H), 10.62 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 129.63, 129.99, 132.84, 134.41, 192.45; MS (FAB): HRMS. ($M+H^+$), $C_{12}H_9O_2$, Calc: 185.0603; Found: 185.06.

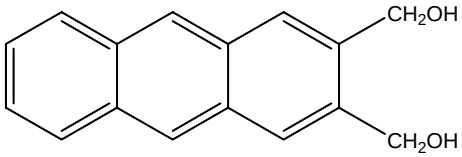
2: Anthracene-2,3-dicarboxylic acid diethyl ester

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



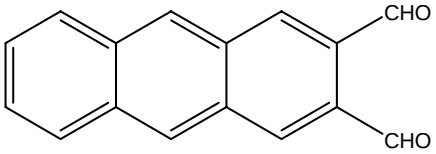
Yield: 86 %; IR (KBr, ν) 2980, 2941, 2905, 1720, 1368, 1299, 1231, 1056, 926, 874, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.41 (t, *J* = 7.2 Hz, 6H), 4.42 (q, *J* = 7.2 Hz, 4H), 7.53-7.55 (m, 2H), 8.02-8.04 (m, 2H), 8.42 (s, 2H), 8.50 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.17, 61.58, 126.70, 127.84, 127.92, 128.32, 130.38, 131.05, 132.96, 167.71; MS (FAB): HRMS. (M^+), $C_{20}H_{18}O_4$, Calc: 322.1205; Found: 322.1199.

2a: (3-Hydroxymethyl-anthracen-2-yl)-methanol



Yield: 77 %; IR (KBr, ν) 3211, 2925, 2855, 1684, 1438, 1344, 1117, 1037, 1012, 903, 737 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 4.74 (d, *J* = 3.6 Hz, 4H), 5.28 (t, *J* = 4.0 Hz, 2H), 7.47-7.49 (m, 2H), 8.03 (s, 2H), 8.05-8.07 (m, 2H), 8.51 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 60.76, 124.65, 125.21, 125.37, 127.98, 130.56, 131.16, 138.24; MS (EI): HRMS. (M^+), $C_{16}H_{14}O_2$, Calc: 238.0994; Found: 238.0998.

2b: Anthracene-2,3-dicarbaldehyde

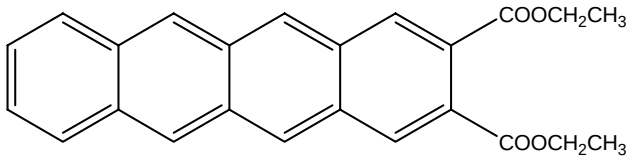


Yield: 81 %; IR (KBr, ν) 1941, 1757, 1712, 1473, 916, 909 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.62-7.64 (m, 2H), 8.08-8.11 (m, *2*H), 8.62 (s, 2H), 8.64 (s, 2H), 10.65 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 127.75, 128.63, 129.51, 130.89,

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

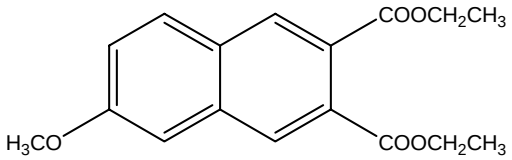
132.02, 133.78, 136.38, 192.39; MS (FAB): HRMS. ($M+H^+$), $C_{16}H_{11}O_2$, Calc: 235.0759; Found: 235.0758.

3: Naphthacene-2,3-dicarboxylic acid diethyl ester



Yield: 55 %; IR (KBr, ν) 2981, 2934, 2905, 1719, 1674, 1368, 1263, 1054, 927, 874, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.42 (t, *J* = 7.1 Hz, 6H), 4.42 (q, *J* = 7.0 Hz, 4H), 7.43-7.46 (m, 2H), 8.00-8.03 (m, 2H), 8.41 (s, 2H), 8.69 (s, 2H), 8.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.23, 61.57, 125.98, 126.92, 127.65, 128.30, 128.49, 129.81, 130.96, 131.62, 132.24, 167.69; MS (FAB): HRMS. (M^+), $C_{24}H_{20}O_4$, Calc: 372.1362; Found: 372.1362.

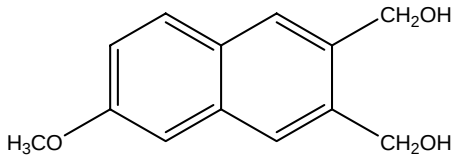
4: 6-Methoxy-naphthalene-2,3-dicarboxylic acid diethyl ester



Yield: 86 %; IR (Neat, ν) 2982, 1722, 1631, 1473, 1283, 1205, 1125, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.34-1.40 (m, 6H), 3.90 (s, 3H), 4.33-4.42 (m, 4H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.22 (dd, *J* = 2.5 Hz, 2.4 Hz, 1H), 7.78 (d, *J* = 8.9 Hz, 1H), 8.03 (s, 1H), 8.19 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.13, 14.16, 55.41, 61.43, 61.56, 106.32, 121.21, 126.02, 128.25, 128.57, 129.95, 130.10, 130.16, 135.12, 159.65, 167.47, 168.22; MS (FAB): HRMS. (M^+), $C_{17}H_{18}O_5$, Calc: 302.1154; Found: 302.1152.

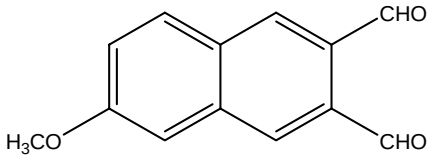
4a: (3-Hydroxymethyl-6-methoxy-naphthalen-2-yl)-methanol

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



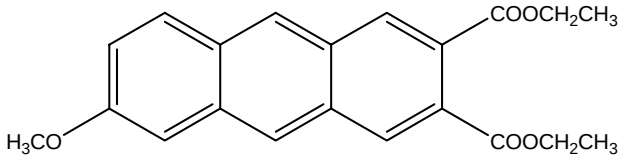
Yield: 80 %; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.90 (s, 3H), 4.86 (d, *J* = 4.0 Hz, 4H), 7.11 (d, *J* = 5.8 Hz, 2H), 7.69 (s, 1H), 7.71 (s, 1H), 7.72(s, 1H).

4b: 6-Methoxy-naphthalene-2,3-dicarbaldehyde



Yield: 91 %; IR (Neat, ν) 1762, 1684, 1618, 1471, 1390, 1208, 1181, 1142, 1024, 884 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.97 (s, 3H), 7.30 (br, 1H), 7.38 (dd, *J* = 6.4 Hz, 2.4 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 8.30 (s, 1H), 8.36 (s, 1H), 10.53 (s, 1H), 10.66 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 55.88, 107.74, 122.95, 129.93, 131.14, 131.37, 132.63, 133.65, 134.87, 136.61, 161.12, 192.49, 192.93; MS (FAB): HRMS. ($M+H^+$), $C_{13}H_{11}O_3$, Calc: 215.0708; Found: 215.0704.

5: 6-Methoxy-anthracene-2,3-dicarboxylic acid diethyl ester

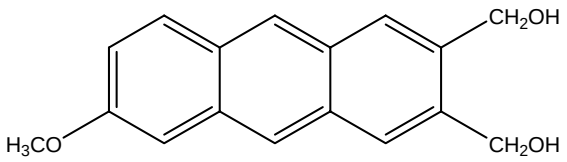


Yield: 60 %; IR (Neat, ν) 2361, 1630, 1478, 1418, 1297, 1272, 1255, 1216, 1116, 1060, 1022 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.39-1.42 (m, 6H), 3.97 (s, 3H), 4.39-4.44 (m, 4H), 7.21(s, 1H), 7.23 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 8.31 (d, *J* = 2.6 Hz, 2H), 8.31 (d, *J* = 3.0 Hz, 2H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.23 (2XC), 55.40, 61.54, 61.61, 103.84, 121.97, 125.63, 126.83, 127.89, 128.43, 129.12, 129.63, 130.05, 130.29, 131.15, 131.43, 134.46, 158.27, 167.70, 168.08; MS (FAB): HRMS.

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

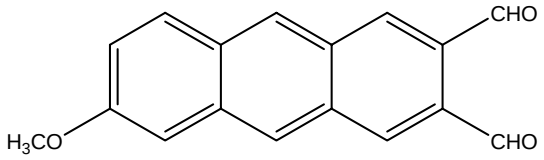
(M^+), $C_{21}H_{20}O_5$, Calc: 352.1311; Found: 352.1321.

5a: (3-Hydroxymethyl-6-methoxy-anthracen-2-yl)-methanol



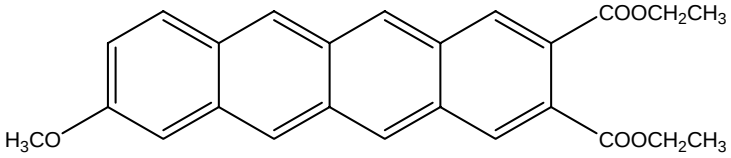
Yield: 89 %; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.91 (s, 3H), 4.71 (d, *J* = 7.2 Hz, 4H), 7.14 (dd, *J* = 7.1 Hz, 2.0 Hz, 1H), 7.37 (s, 1H), 7.96 (s, 3H), 8.34 (s, 1H), 8.43 (s, 1H).

5b: 6-Methoxy-anthracene-2,3-dicarbaldehyde



Yield: 90 %; IR (KBr, ν) 2361, 1693, 1628, 1481, 1425, 1285, 1227, 1178, 914 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.99 (s, 3H), 7.27 (s, 1H), 7.29 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 8.46 (s, 1H), 8.55 (s, 2H), 8.58 (s, 1H), 10.60 (s, 1H), 10.67 (s, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 55.46, 104.09, 122.84, 127.16, 129.33, 129.50, 130.23, 130.27, 131.18, 131.50, 132.18, 135.35, 136.80, 158.98, 192.33, 192.56; MS (FAB): HRMS. ($M+H^+$), $C_{17}H_{13}O_3$, Calc: 265.0865; Found: 265.0866.

6: 8-Methoxy-naphthacene-2,3-dicarboxylic acid diethyl ester

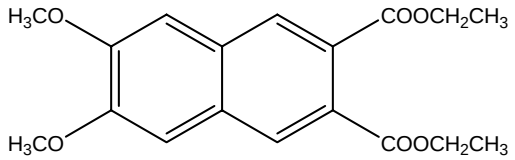


Yield: 43 %; IR (KBr, ν) 1722, 1631, 1470, 1303, 1266, 1116, 1023, 923 cm^{-1}; ^{1}H

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

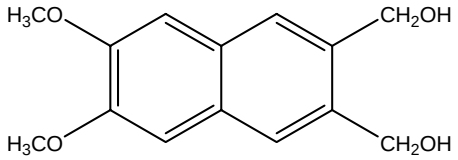
NMR ($CDCl_3$, 400 MHz, ppm): δ 1.33 (t, *J* = 7.0 Hz, 6H), 3.96 (s, 3H), 4.32 (q, *J* = 7.0 Hz, 4H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 8.51 (s, 1H), 8.53 (s, 1H), 8.70 (s, 1H), 8.83 (s, 1H) , 8.95 (s, 1H), 9.00 (s, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.33, 14.43, 55.74, 61.63 (2XC), 103.49, 127.06, 127.50, 127.68, 128.08, 128.99, 129.37, 129.66, 129.87, 130.23, 130.53, 131.45, 131.49, 131.83, 131.99, 133.55, 136.08, 157.62, 167.33, 167.41; MS (FAB): HRMS. (M^+), $C_{25}H_{22}O_5$, Calc: 402.1467; Found: 402.1466.

7: 6,7-Dimethoxy-naphthalene-2,3-dicarboxylic acid diethyl ester



Yield: 80 %; IR (KBr, ν) 2981, 2937, 1720, 1625, 1511, 1482, 1292, 1246, 1154, 1053, 864 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.36 (t, *J* = 7.5 Hz, 6H), 3.96 (s, 6H), 4.36 (q, *J* = 7.2 Hz, 4H), 7.12 (s, 2H), 8.04 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.12, 55.94, 61.38, 106.65, 127.22, 128.14, 129.46, 151.31, 167.92; MS (FAB): HRMS. ($M+H^+$), $C_{18}H_{21}O_6$, Calc: 333.1338; Found: 333.1345.

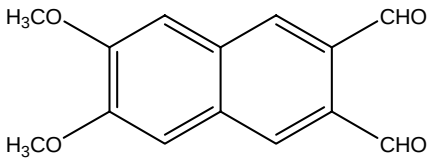
7a: (3-Hydroxymethyl-6,7-dimethoxy-naphthalen-2-yl)-methanol



Yield: 89 %; IR (KBr, ν) 3210, 2925, 2856, 1613, 1513, 1463, 1442, 1412, 1263, 1217, 1152, 1010, 902, 755 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz, ppm): δ 3.01 (s, 6H), 3.80 (d, *J* = 5.5 Hz, 4H), 4.27 (t, *J* = 5.3 Hz, 2H), 6.41 (s, 2H), 6.86 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 55.37, 60.86, 106.33, 124.11, 127.69, 135.93, 149.03; MS (FAB): HRMS. (M^+), $C_{14}H_{16}O_4$, Calc: 248.1049; Found: 248.1046.

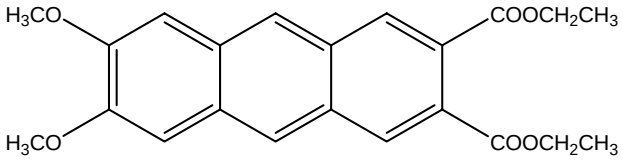
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

7b: 6,7-Dimethoxy-naphthalene-2,3-dicarbaldehyde



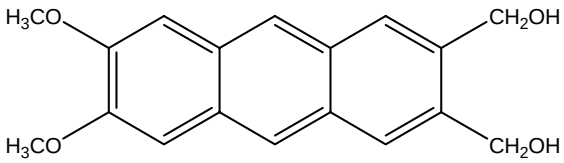
Yield: 92 %; IR (KBr, ν) 2921, 2834, 1687, 1612, 1513, 1481, 1435, 1249, 1160,1006, 900 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 4.04 (s, 6H), 7.28 (s, *2*H), 8.28 (s, 2H), 10.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 56.16, 107.54, 130.79, 131.49, 132.25, 152.49, 192.38; MS (FAB): HRMS. ($M+H^+$), $C_{14}H_{13}O_4$, Calc: 245.0814; Found: 245.0810.

8: 6,7-Dimethoxy-anthracene-2,3-dicarboxylic acid diethyl ester



Yield: 71 %; IR (KBr, ν) 2979, 2933, 1719, 1635, 1493, 1428, 1305, 1219, 1157, 1117, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.39 (t, *J* = 7.0 Hz, 6H), 4.02 (s, 6H), 4.40 (q, *J* = 7.0 Hz, 4H), 7.17 (s, 2H), 8.23 (s, 2H), 8.30 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.19, 55.94, 61.49, 104.95, 125.31, 127.15, 129.66, 130.18, 130.48, 151.03, 167.97; MS (FAB): HRMS. (M^+), $C_{22}H_{22}O_6$, Calc: 382.1416; Found: 382.1407.

8a: (3-Hydroxymethyl-6,7-dimethoxy-anthracen-2-yl)-methanol

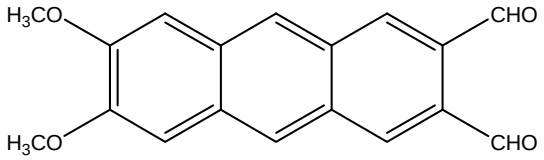


Yield: 68 %; IR (KBr, ν) 3249, 2925, 2854, 1685, 1654, 1635, 1493, 1292, 1226, 1154,

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

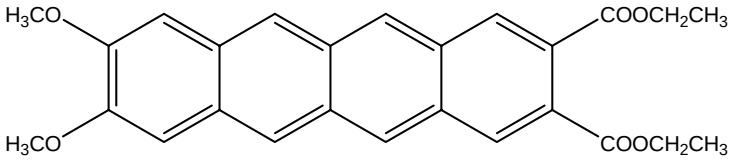
1007, 909 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 3.93 (s, 6H), 4.72 (d, *J* = 5.6 Hz, 4H), 5.22 (t, *J* = 5.6 Hz, 2H), 7.36 (s, 2H), 7.91 (s, 2H), 8.27 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 55.40, 60.92, 104.96, 123.13, 124.49, 128.14, 129.51, 137.04, 149.72; MS (FAB): HRMS. (M^+), $C_{18}H_{18}O_4$, Calc: 298.1205; Found: 298.1197.

8b: 6,7-Dimethoxy-anthracene-2,3-dicarbaldehyde



Yield: 89 %; IR (KBr, ν) 2928, 2859, 1681, 1572, 1493, 1429, 1307, 1229, 1190,1157, 913 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 4.07 (s, 6H), 7.26 (s, 2H), 8.40 (s, 2H), 8.53 (s, 2H) 10.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 56.14, 105.27, 126.90, 130.21, 131.20, 131.43, 135.79, 151.84, 192.59; MS (FAB): HRMS. ($M+H^+$), $C_{18}H_{15}O_4$, Calc: 295.0970; Found: 295.0970.

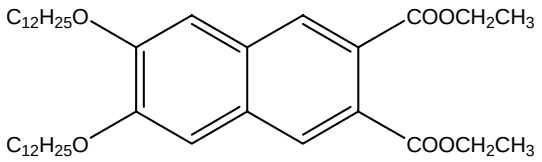
9: 8,9-Dimethoxy-naphthacene-2,3-dicarboxylic acid diethyl ester



Yield: 52 %; IR (KBr, ν) 2925, 2855, 1764, 1725, 1705, 1623, 1493, 1428, 1221, 1156 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.41 (t, *J* = 7.0 Hz, 6H), 4.04 (s, 6H), 4.42 (q, *J* = 7.0 Hz, 4H), 7.15 (s, 2H), 8.37 (s, 2H), 8.41 (s, 2H), 8.58 (s, 2H) ; ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.22, 55.94, 61.50, 104.28, 124.08, 127.19, 127.56, 129.40, 129.83, 130.50, 131.53, 159.89, 167.83; MS (FAB): HRMS. (M^+), $C_{26}H_{24}O_6$, Calc: 432.1573; Found: 432.1569.

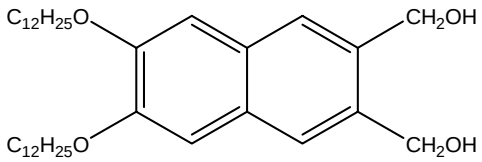
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

10: 6,7-Bis-dodecyloxy-naphthalene-2,3-dicarboxylic acid diethyl ester



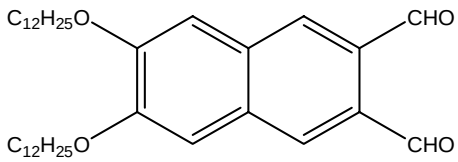
Yield: 71 %; IR (KBr, ν) 2954, 2920, 2850, 1724, 1716, 1623, 1511, 1472, 1302, 1253, 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.86 (t, *J* = 6.5 Hz, 6H), 1.25-1.28 (m, 32H), 1.37 (t, *J* = 7.0 Hz, 6H), 1.46-1.52 (m, 4H), 1.86-1.91 (m, 4H), 4.09 (t, *J*=6.5 Hz, 4H), 4.37 (q, *J* = 7.0 Hz, 4H), 7.13 (s, 2H), 8.02 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.09, 14.19, 22.67, 26.03, 28.94, 29.35, 29.39, 29.61, 29.65, 29.68, 31.91, 61.38, 68.91, 107.80, 126.96, 128.15, 129.51, 151.36, 168.10; MS (FAB): HRMS. (M^+), $C_{40}H_{64}O_6$, Calc: 640.4703; Found: 640.4688.

10a: (6,7-Bis-dodecyloxy-3-hydroxymethyl-naphthalen-2-yl)-methanol



Yield: 89 %; IR (KBr, ν) 3296, 2919, 2849, 1611, 1505, 1465, 1414, 1260, 1214, 1173, 999 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.86 (t, *J* = 6.8 Hz, 6H), 1.24-1.29 (m, 32H), 1.47-1.53 (m, 4H), 1.83-1.90 (m, 4H), 4.07 (t, *J*=6.8 Hz, 4H), 4.80 (s, 4H), 7.06 (s, 2H), 7.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.09, 22.67, 26.07, 29.09, 29.35, 29.44, 29.63, 29.65, 29.69, 31.91, 64.68, 68.89, 107.68, 127.41, 128.91, 135.04, 149.95; MS (FAB): HRMS. (M^+), $C_{36}H_{60}O_4$, Calc: 556.4492; Found: 556.4490.

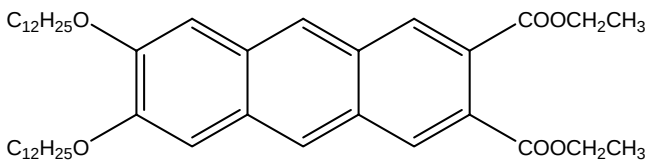
10b: 6,7-Bis-dodecyloxy-naphthalene-2,3-dicarbaldehyde



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

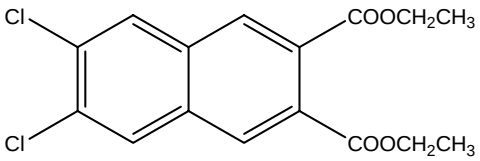
Yield: 95 %; IR (KBr, ν) 2921, 2851, 1759, 1682, 1509, 1486, 1466, 1389, 1274, 1215,1120 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.86 (t, *J* = 6.4 Hz, 6H), 1.25-1.28 (m, 32H), 1.50-1.52 (m, 4H), 1.88-1.93 (m, 4H), 4.14 (t, *J* = 6.4 Hz, 4H), 7.25 (s, 2H), 8.24 (s, 2H), 10.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.06, 22.64, 25.97, 28.84, 29.32, 29.57, 29.61, 29.65, 31.88, 69.07, 108.46, 130.77, 131.29, 132.29, 152.51, 192.51; MS (FAB): HRMS. ($M+H^+$), $C_{36}H_{57}O_4$, Calc: 553.4257; Found: 553.4243.

11: 6,7-Bis-dodecyloxy-anthracene-2,3-dicarboxylic acid diethyl ester



Yield: 45 %: IR (KBr, ν) 2958, 2923, 2852, 1724, 1713, 1492, 1467, 1310, 1224, 1162 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.86 (t, *J* = 6.4 Hz, 6H), 1.25-1.28 (m, 32H), 1.38 (t, *J*=7.0 Hz, 6H), 1.48-1.54 (m, 4H), 1.90-1.94 (m, 4H), 4.14 (t, *J* = 6.4 Hz, 4H), 4.40 (q, *J*=7.0 Hz, 4H), 7.17 (s, 2H), 8.23 (s, 2H) , 8.31 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.11, 14.22, 22.68, 26.06, 28.91, 29.34, 29.37, 29.60, 29.63, 29.67, 31.91, 61.48, 68.80, 105.80, 125.14, 126.93, 129.55, 130.34, 130.55, 151.02, 168.08; MS (FAB): HRMS. (M^+) $C_{44}H_{66}O_6$, Calc: 690.4859; Found: 690.4857.

12: 6,7-Dichloro-naphthalene-2,3-dicarboxylic acid diethyl ester

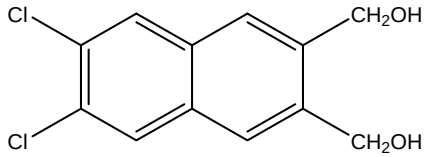


Yield: 55 %; IR (KBr, ν) 3068, 2980, 2903, 1720, 1625, 1473, 1445, 1290, 1268, 1132, 1058, 933 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.38 (t, *J* = 7.1 Hz, 6H), 4.40 (q,

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

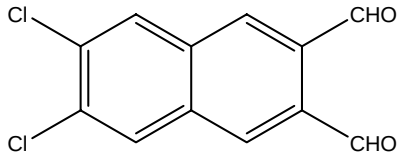
J = 7.1 Hz, 4H), 8.01 (s, 2H), 8.12 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.13, 61.92, 128.82, 129.44, 130.17, 132.15, 133.20, 167.05; MS (FAB): HRMS. ($M+H^+$), $C_{16}H_{15}Cl_2O_4$, Calc: 341.0347; Found: 341.0349.

12a: (6,7-Dichloro-3-hydroxymethyl-naphthalen-2-yl)-methanol



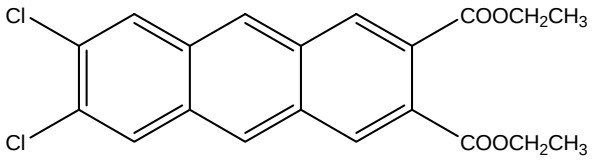
Yield: 88 %; IR (KBr, ν) 3280, 3195, 2905, 2856, 1484, 1444, 1383, 1275, 1214, 1048, 981 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 4.67 (d, *J* = 5.3 Hz, 4H), 5.33 (t, *J* = 5.3 Hz, 2H), 7.92 (s, 2H), 8.25 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 60.17, 123.65, 127.91, 128.58, 131.16, 139.94; MS (EI): HRMS. (M^+), $C_{12}H_{10}Cl_2O_2$, Calc: 256.0058; Found: 256.0056.

12b: 6,7-Dichloro-naphthalene-2,3-dicarbaldehyde



Yield: 94 %; IR (KBr, ν) 3082, 2928, 2872, 1691, 1615, 1439, 1270, 1168, 1124, 920, 871 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.16 (s, 2H), 8.34 (s, 2H), 10.59 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 130.35, 132.98, 133.17, 133.77, 134.95, 191.75; MS (FAB): HRMS. ($M+H^+$) $C_{12}H_7Cl_2O_2$, Calc: 252.9823; Found: 252.9819.

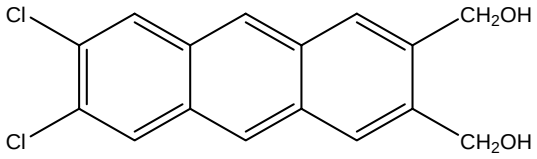
13: 6,7-Dichloro-anthracene-2,3-dicarboxylic acid diethyl ester



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

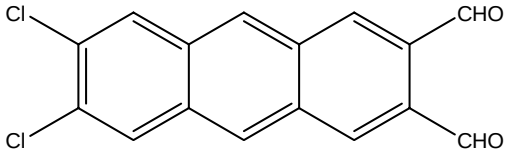
Yield: 60 %; IR (KBr, ν) 2983, 2903, 1716, 1460, 1416, 1367, 1298, 1245, 1129, 1116, 933 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.41 (t, *J* = 7.1 Hz, 6H), 4.42 (q, *J* = 7.1 Hz, 4H), 8.13 (s, 2H), 8.36 (s, 2H), 8.37 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.19, 61.79, 127.04, 128.87, 128.92, 130.68, 130.88, 131.03, 131.38, 167.05; MS (FAB): HRMS. (M^+), $C_{20}H_{16}Cl_2O_4$, Calc: 390.0426; Found: 390.0426.

13a: (6,7-Dichloro-3-hydroxymethyl-anthracen-2-yl)-methanol



Yield: 90 %; IR (KBr, ν) 3220, 2925, 2856, 1766, 1430, 1287, 1113, 1041, 1006, 971, 911 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 4.73 (d, *J* = 5.3 Hz, 4H), 5.33 (t, *J* = 5.3 Hz, 2H), 8.03 (s, 2H), 8.43 (s, 2H), 8.56 (s, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 60.49, 124.39, 125.05, 127.63, 129.00, 129.61, 131.16, 139.35; MS (EI): HRMS. (M^+) $C_{16}H_{12}Cl_2O_2$, Calc: 306.0214; Found: 306.0210.

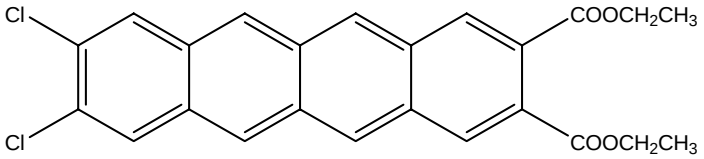
13b: 6,7-Dichloro-anthracene-2,3-dicarbaldehyde



Yield: 93 %; IR (KBr, ν) 2925, 2854, 1685, 1613, 1463, 1424, 1329, 1287, 1188, 1113, 971, 803; cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 8.62 (s, 2H), 8.78 (s, 2H), 8.95 (s, 2H) 10.54 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 129.50, 130.08, 130.83, 131.65, 132.11, 133.20, 135.68, 193.41; MS (EI): HRMS. (M^+), $C_{16}H_8Cl_2O_2$, Calc: 301.9901; Found: 301.9900.

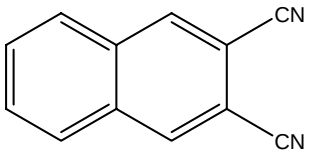
14: 8,9-Dichloro-naphthacene-2,3-dicarboxylic acid diethyl ester

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



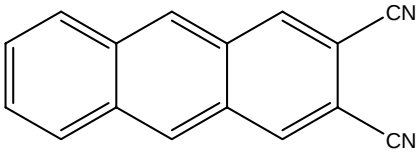
Yield: 46 %; IR (KBr, ν) 2988, 2935, 1736, 1720, 1472, 1421, 1368, 1303, 1263, 1237, 1108, 1056, 926 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.42 (t, *J* = 7.2 Hz, 6H), 4.30 (q, *J* = 7.2 Hz, 4H), 8.14 (s, 2H), 8.41 (s, 2H), 8.60 (s, 2H), 8.72 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.22, 61.71, 126.37, 128.26, 128.66, 128.78, 130.40, 130.45, 130.55, 131.17, 131.49, 167.51; MS (EI): HRMS. (M^+) $C_{24}H_{18}Cl_2O_4$, Calc: 440.0582; Found: 440.0583.

15: Naphthalene-2,3-dicarbonitrile



Yield: 72 %; IR (KBr, ν) 3078, 3034, 2230, 1622, 1465, 1387, 1362, 1276, 1185, 909, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.78-7.80 (m, 2H), 7.96-7.98 (m, 2H), 8.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 110.11, 115.86, 128.71, 130.85, 133.18, 135.95; MS (FAB): HRMS. ($M+H^+$), $C_{12}H_7N_2$, Calc: 179.0609; Found: 179.0606.

16: Anthracene-2,3-dicarbonitrile

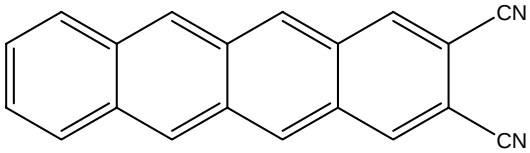


Yield: 62 %; IR (KBr, ν) 3089, 3054, 3019, 2230, 1630, 1531, 1411, 1344, 1180, 925, 747 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 7.75-7.77 (m, 2H), 8.26-8.29 (m, 2H), 8.82 (s, 2H), 9.06 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 106.82,

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

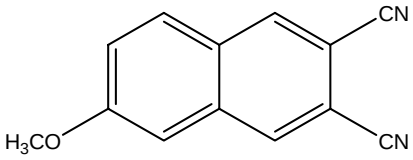
116.66, 128.37, 128.68, 128.90, 129.01, 133.32, 138.29; MS (FAB): HRMS. (M^+) $C_{16}H_8N_2$, Calc: 228.0687; Found: 228.0688.

17: Naphthacene-2,3-dicarbonitrile



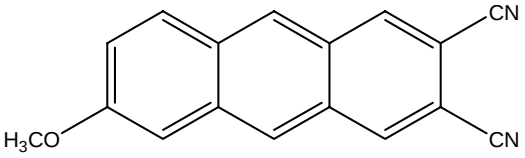
Yield: 63 %; IR (KBr, ν) 3032, 2944, 2232, 1760, 1690, 1646, 1451, 1296, 1182, 927, 754 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz, ppm): δ 7.60-7.63 (m, 2H), 8.21-8.23 (m, 2H), 9.05 (s, 2H), 9.07 (s, 2H), 9.13 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 106.08, 114.53, 116.80, 126.97, 127.80, 128.12, 128.39, 130.08, 130.74, 139.19; MS (EI): HRMS. (M^+): $C_{20}H_{10}N_2$, Calc: 278.0844; Found: 278.0848.

18: 6-Methoxy-naphthalene-2,3-dicarbonitrile



Yield: 40 %; IR (KBr, ν) 2363, 2231, 1795, 1621, 1500, 1394, 1209, 1139, 1012, 904, 827 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.97 (s, 3H), 7.19 (d, J = 2.0 Hz, 1H), 7.38 (dd, J = 6.7 Hz, 2.3 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 8.19 (s, 1H), 8.23 (s, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 55.77, 106.39, 107.42, 110.69, 116.01, 116.15, 123.72, 128.63, 130.18, 134.18, 135.14, 135.33, 161.26; MS (FAB): HRMS. ($M+H^+$), $C_{13}H_9N_2O$, Calc: 209.0715; Found: 209.0714.

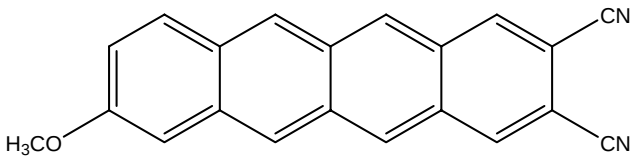
19: 6-Methoxy-anthracene-2,3-dicarbonitrile



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

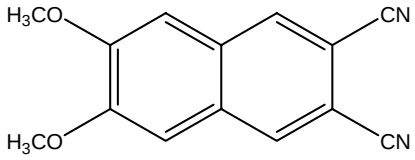
Yield: 60 %; IR (KBr, ν) 2361, 2229, 1632, 1475, 1418, 1225, 1177, 918, 460 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.99 (s, 3H), 7.25 (d, *J* = 2.2 Hz, 1H), 7.32 (d, *J* = 9.2 Hz, 1H), 7.97(d, *J* = 9.2 Hz, 1H), 8.37 (s, 1H), 8.44 (s, 1H), 8.46 (d, *J* = 2.7 Hz, 2H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 56.04, 104.97, 106.01, 107.41, 117.15, 117.24, 123.57, 126.82, 128.07, 129.20, 130.02, 130.32, 130.92, 135.60, 138.00, 138.66, 159.29; MS (FAB): HRMS. (M^+), $C_{17}H_{10}N_2O$, Calc: 258.0793; Found: 258.0789.

20: 8-Methoxy-naphthacene-2,3-dicarbonitrile



Yield: 57 %; IR (KBr, ν) 3028, 2271, 2363, 2226, 1773, 1633, 1415, 1299, 1177, 921 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.98 (s, 3H), 7.28 (dd, *J* = 7.1 Hz, 2.3 Hz, 1H), 7.49 (s, 1H), 8.14 (d, *J* = 9.3 Hz, 1H), 8.81 (s, 1H), 8.93 (s, 1H), 9.01 (s, 1H), 9.02 (s, 1H) , 9.04 (s, 1H), 9.06 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 55.46, 103.19, 105.43, 106.02, 116.84, 118.67, 122.67, 124.82, 127.45, 127.83, 128.29, 128.83, 129.61, 129.69, 130.15, 130.25, 131.26, 133.95, 138.88, 139.11, 157.74; MS (EI) m/z (rel intensity): 554 ($[M+H]^+$, 100), 552 (35), 383 (11), 215 (16), 188 (15); HRMS. (M^+), $C_{21}H_{12}O_1N_2$, Calc: 308.0950; Found: 308.0956.

21: 6,7-Dimethoxy-naphthalene-2,3-dicarbonitrile

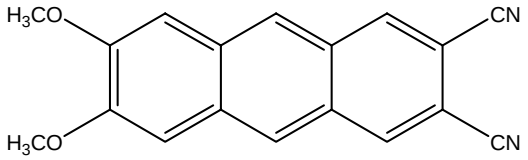


Yield: 80 %; IR (KBr, ν) 2987, 2951, 2231, 1614, 1513, 1475, 1416, 1273, 1185, 1159, 1005, 910, 909 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 4.04 (s, 6H), 7.17 (s, 2H),

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

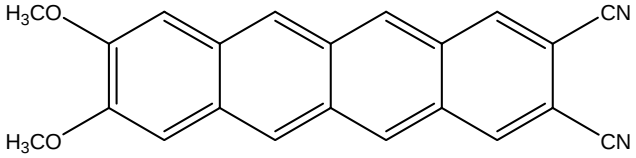
8.11 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 56.37, 106.56, 108.34, 116.36, 129.91, 133.42, 153.10; MS (FAB): HRMS. ($M+H^+$), $C_{14}H_{11}N_2O_2$, Calc: 239.0821; Found: 239.0819.

22: 6,7-Dimethoxy-anthracene-2,3-dicarbonitrile



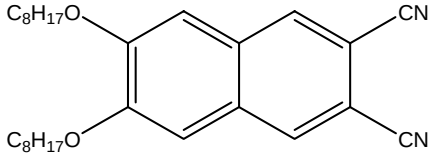
Yield: 49 %; IR (KBr, ν) 3017, 2832, 2229, 1631, 1568, 1492, 1429, 1303, 1236, 1158, 1008, 924 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.99 (s, 6H), 7.58 (s, 2H), 8.60 (s, 2H), 8.94 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 56.29, 105.88, 106.08, 117.34, 126.39, 128.62, 137.90, 152.36; MS (FAB): HRMS. ($M+H^+$), $C_{18}H_{13}N_2O_2$, Calc: 289.0977; Found: 289.0980.

23: 8,9-Dimethoxy-naphthacene-2,3-dicarbonitrile



Yield: 40 %; IR (KBr, ν) 2942, 2830, 2225, 1684, 1631, 1560, 1488, 1432, 1248, 1206, 1157, 922 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 3.98 (s, 6H), 7.46 (s, 2H), 8.68 (s, 2H), 8.90 (s, 2H), 8.94 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz, ppm): δ 56.12, 104.84, 105.72, 117.33, 124.89, 127.91, 129.22, 130.54, 130.92, 139.21, 151.70; MS (EI): HRMS. (M^+), $C_{22}H_{14}N_2O_2$, Calc: 338.1055; Found: 338.1055.

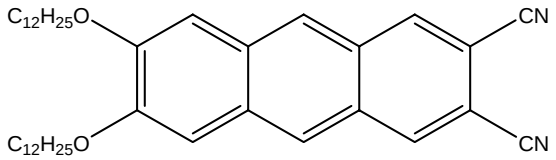
24: 6,7-Bis-octyloxy-naphthalene-2,3-dicarbonitrile



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

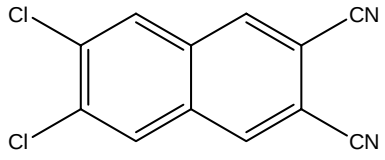
Yield: 41 %; IR (KBr, ν) 2950, 2918, 2855, 2232, 1613, 1504, 1470, 1423, 1271, 1218, 1175, 996 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.87 (t, *J* = 6.4 Hz, 6H), 1.28-1.35 (m, 16H), 1.47-1.52 (m, 4H), 1.88-1.92 (m, 4H), 4.12 (t, *J* = 6.4 Hz, 4H), 7.12 (s, 2H), 8.07 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.09, 22.64, 25.95, 28.78, 29.22, 29.27, 31.77, 62.23, 107.20, 107.83, 116.54, 129.80, 133.29, 152.98; MS (EI): HRMS. (M^+), $C_{28}H_{38}N_2O_2$, Calc: 434.2933; Found: 434.2941.

25: 6,7-Bis-dodecyloxy-anthracene-2,3-dicarbonitrile



Yield: 61 %; IR (KBr, ν) 2955, 2922, 2850, 2230, 1629, 1497, 1465, 1433, 1308, 1240, 1162, 920, 894 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.86 (t, *J* = 6.5 Hz, 6H), 1.24-1.28 (m, 32H), 1.35-1.39 (m, 4H), 1.91-1.94 (m, 4H), 4.16 (t, *J* = 6.5 Hz, 4H), 7.21 (s, 2H), 8.27 (s, 2H), 8.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.10, 22.68, 26.05, 28.88, 29.37, 29.62, 29.66, 29.70, 30.91, 31.92, 60.04, 105.72, 107.01, 116.60, 125.45, 128.52, 131.60, 136.72, 152.31; MS (FAB): HRMS. ($M+H^+$), $C_{40}H_{57}N_2O_2$, Calc: 597.4420; Found: 597.4417.

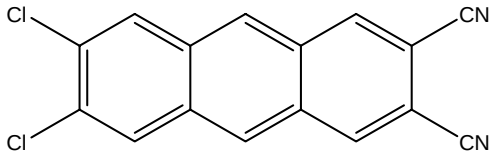
26: 6,7-Dichloro-naphthalene-2,3-dicarbonitrile



Yield: 77 %; IR (KBr, ν) 3063, 2928, 2858, 2236, 1617, 1576, 1439, 1355, 1174, 1123, 981; cm^{-1}; ^{1}H NMR (Acetone-d_6, 500 MHz, ppm): δ 8.50 (s, 2H), 8.74 (s, 2H); ^{13}C NMR (Acetone-d_6, 125 MHz, ppm): δ 112.13, 116.57, 131.08, 133.36, 135.65, 135.40; MS (EI): HRMS. (M^+), $C_{12}H_4Cl_2N_2$, Calc: 245.9752; Found: 245.9749.

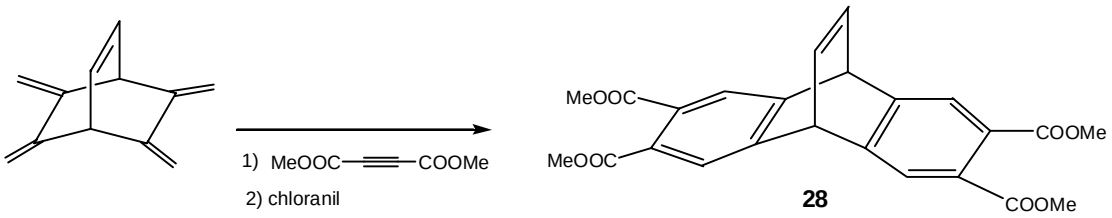
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

27: 6,7-Dichloro-anthracene-2,3-dicarbonitrile



Yield**:** 51 %; IR (KBr, ν) 3038, 2929, 2230, 1689, 1648, 1430, 1410, 1327, 1114, 974, 928 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.69 (s, 2H), 8.87 (s, 2H), 9.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 108.34, 116.89, 128.98, 130.21, 131.56, 132.34, 138.76; MS (EI): HRMS. (M^+), $C_{16}H_6Cl_2N_2$, Calc: 295.9908; Found: 295.9912.

28: 9,10-Dihydro-9,10-ethenoanthracene-2,3,6,7-tetracarboxylic acid tetramethyl ester



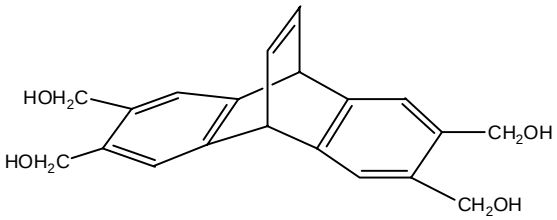
Freshly distilled dimethylacetylenedicarboxylate (12 ml, 76.8 mmol) was added dropwise via syringe to a stirred solution of 2,3,5,6-tetrakis(methylene)-bicyclo[2.2.2]oct-7-ene (7.0 g, 10.9 mmol) in toluene (50 ml) at room temperature under nitrogen atmosphere and stirring was continued at room temperature for 12 hr. The solvent was evaporated under reduced pressure to give the intermediate (colorless oil, 97%) which was used without any further purification for the next step. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.14 (s, 8H), 3.73 (s, 12H), 4.10 (t, J = 2.8 Hz, 2H), 6.72 (t, J = 2.8 Hz, 2H).

Chloranil (15.0 g, 61 mmol) was added all at once to a stirred solution of the Diels-Alder adduct from last step (4.76 g, 10.8 mmol) in toluene (50 ml) at room temperature and the reaction mixture was refluxed at 130 °C for 7 hr under nitrogen

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

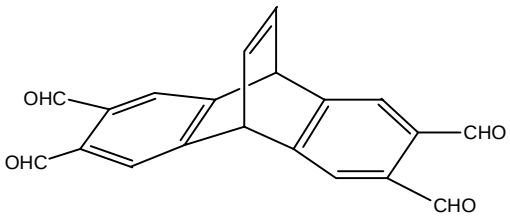
atmosphere. After cooling to room temperature, the solid was filtered off and washed with ether. The filtrate was concentrated under reduced pressure. The resulting slurry was purified by column chromatography on silica gel (passed hexane-dichloromethane = 1:1 and then dichloromethane to remove all chloranil and impurity) using ether as eluent. The desired product was obtained as a white solid (4.38 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 3.84 (s, 12H), 5.27 (t, *J* = 3.6 Hz, 2H), 6.97 (t, *J* = 3.6 Hz, 2H), 7.60 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.54, 52.55, 123.61, 129.07, 138.36, 148.05, 167.80.

28a: : 9,10-Dihydro-2,3,6,7-tetrakis(hydroxymethyl)-9,10-ethenoanthracene



Yield 92%, ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 4.41 (d, *J* = 5.4 Hz, 8H), 4.90 (t, *J* = 5.4 Hz, 4H)), 5.20 (t, *J* = 3.6 Hz, 2H), 6.98 (t, *J* = 3.6 Hz, 2H), 7.29 (s, 4H).

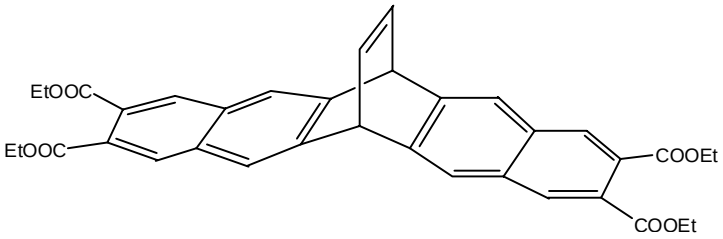
28b: 9,10-Dihydro-2,3,6,7-tetrakis(carbaldehyde)-9,10-ethenoanthracene



Yield: 76%, ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.54 (brt, 2H), 7.07 (t, *J* = 3.6 Hz, 2H), 7.90 (s, 4H), 10.46 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.95, 125.27, 134.36, 138.06, 150.17, 191.44.

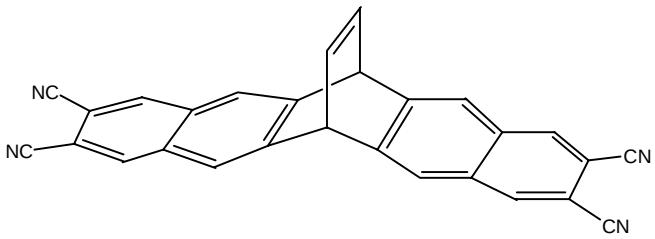
29: 6,13-Dihydro-6,13-etheno-2,3,9,10-tetracarboxylic acid tetraethyl ester pentacene

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



Yield 72%, IR (KBr, ν) 2981, 2355, 1722, 1445, 1371, 1277, 1207, 1125, 1049 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.35 (t, *J* = 7.1 Hz, 12H), 4.36 (q, *J* = 7.1 Hz, 8H), 5.37 (d, *J* = 3.8 Hz, 2H), 7.04 (t, *J* = 3.7 Hz, 2H), 7.76 (s, 4H), 8.09 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.12, 50.06, 61.54, 122.07, 128.74, 129.42, 131.87, 137.93, 144.24, 167.77; MS (EI, m/e, relative intensity %) 592 (M^+, 100), 547 (12), 519 (45), 491 (10), 445 (22); HRMS Calcd for C_{36} $H_{32}O_8$: 592.2097, Found: 592.2106.

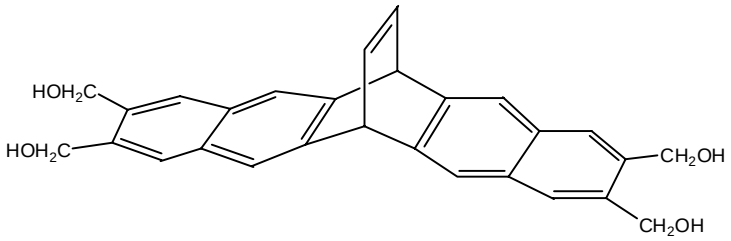
30. 6,13-Dihydro-6,13-etheno-2,3,9,10-tetracyano pentacene



Yield 65%, IR (KBr, ν) 2912, 2850, 2360, 2334, 2222, 1593, 1399, 1258, 1087, 1017, 910, 797 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 5.80 (t, *J* = 3.6 Hz, 2H), 7.16 (t, *J* = 3.6 Hz, 2H), 8.12 (s, 4H), 8.71 (s, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 48.95, 108.56, 116.49, 122.51, 131.63, 135.81, 138.01, 146.38; MS (EI, m/e, relative intensity %) 404 (M^+, 100), 378 (18), 302 (5), 202 (8); HRMS Calcd for C_{28} $H_{12}N_4$: 404.1062, Found: 404.1058.

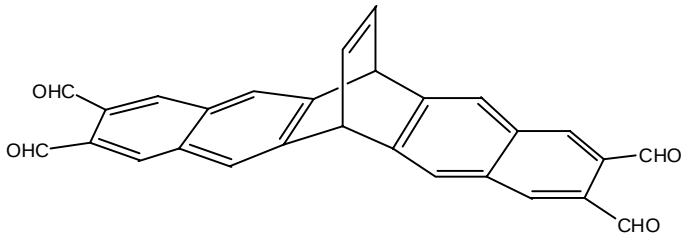
29a: 6,13-Dihydro-6,13-etheno-2,3,9,10-tetrakis(hydroxymethyl) pentacene

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



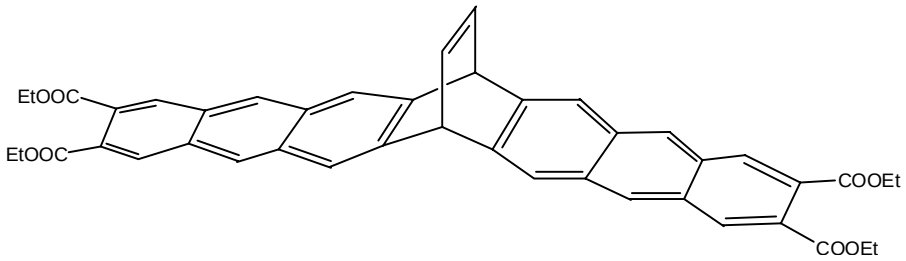
(Impure), ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 4.63 (d, *J* = 4.8 Hz, 8H), 5.17 (brt, 4H)), 5.42 (brt, 2H), 7.08 (brt, 2H), 7.73 (s, 4H), 7.76 (s, 4H).

29b: 6,13-Dihydro-6,13-etheno-2,3,9,10-tetrakis(carbaldehyde) pentacene



(Impure), ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.49 (brt, 2H), 7.07 (t, *J* = 3.6 Hz, 2H), 7.91 (s, 4H), 8.29 (s, 4H), 10.54 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 50.14, 123.21, 132.84, 133.13, 133.59, 137.80, 145.57, 192.34.

31: 7,16-Dihydro-7,16-etheno-2,3,11,12-tetracarboxylic acid tetraethyl ester heptacene

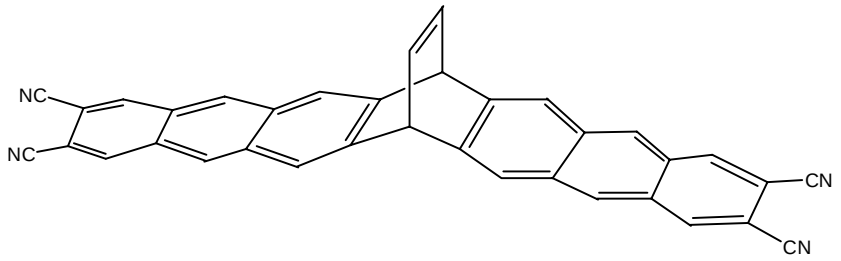


Yield 70 %, IR (KBr, ν) 2980, 2361, 1721, 1591, 1430, 1364, 1293, 1242, 1119, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.38 (t, *J* = 7.1 Hz, 12H), 4.40 (q, *J* = 7.1 Hz, 8H), 5.37 (t, *J* = 3.6 Hz, 2H), 7.04 (t, *J* = 3.6 Hz, 2H), 7.90 (s, 4H), 8.3507 (s, 4H), 8.3578 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.20, 49.78, 61.58, 121.41, 127.26, 127.73, 130.62, 130.89, 132.08, 137.35, 141.98, 167.79; MS (EI, m/e,

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

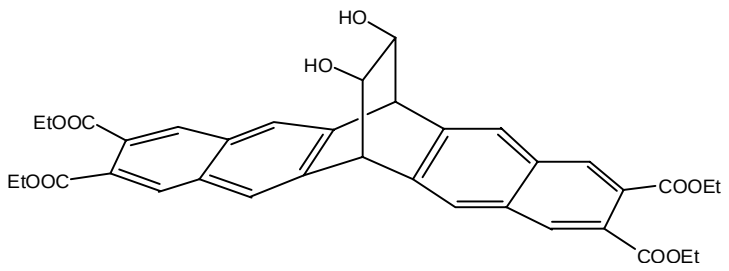
relative intensity %) 692 (M^+, 100), 642 (80), 592 (18), 490 (65), 460 (16); HRMS Calcd for $C_{44}H_{36}O_8$: 692.2410, Found: 692.2407.

32: 7,16-Dihydro-7,16-etheno-2,3,11,12-tetracyano heptacene



Yield 62%, IR (KBr, ν) 2919, 2361, 2341, 2229, 1590, 1409, 1257, 1019, 799, 670 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz, ppm): δ 5.67 (brt, 2H), 7.15 (brt, 2H), 8.17 (s, 4H), 8.71 (s, 4H), 8.95 (s, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 48.60, 106.57, 116.70, 121.67, 128.14, 129.18, 132.39, 137.54, 137.92, 143.40; MS (EI, m/e, relative intensity %) 504 (M^+, 35), 454 (42), 453 (36),183 (18), 167 (20), 149 (42), 104 (100); HRMS Calcd for $C_{36}H_{16}N_4$: 504.1375, Found: 504.1362.

33: 6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic acid tetraethyl ester-*cis*-23,24-diol:

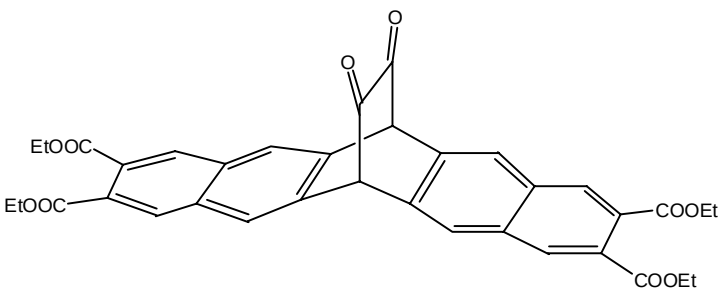


To a stirred acetone solution of 4-methylmorpholine-N-oxide (110 mg, 0.94 mmol / 20 ml), a 2.5 % (w) solution of osmium tetroxide in *t*-butanol (0.16 ml, diluted with 2 ml acetone) was slowly added under a nitrogen atmosphere at 0 °C. The mixture

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

was stirred for 20 min at 0 °C. An acetone solution of **32** (150 mg, 0.25 mmol / 20 ml) was then added slowly. The mixture was stirred at room temperature for an additional 5 hr. Sodium dithionite (150 mg) was added to the reaction mixture and the slurry was stirred for another 20 min to yield a heterogeneous solution. The solvent was removed under reduced pressure at 40 °C and the residue was purified by column chromatography on silica gel (passed dichloromethane to remove impurity) using ethyl acetate as eluent. The desired product was obtained as a brownish solid (140 mg, yield 89%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.40-1.20 (m, 12H), 4.23 (brs, 2H), 4.37 (q, J = 7.1 Hz, 8H), 4.70 (brs, 2H), 7.86 (s, 2H), 7.91 (s, 2H), 8.16 (s, 2H), 8.19 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.13, 51.35, 61.66, 61.71, 67.87, 124.20, 125.93, 128.83, 128.99, 129.63, 132.75, 138.52, 139.68, 167.68; MS (FAB, m/e, relative intensity %) 627 ($[M+H]^+$, 67.9); HRMS Calcd for $C_{36}H_{35}O_{10}$: 627.2230, Found: 627.2246.

34: 6,13-Dihydro-6,13-ethenopentacene-2,3,9,10-tetracarboxylic acid tetraethyl ester-23,24-dione

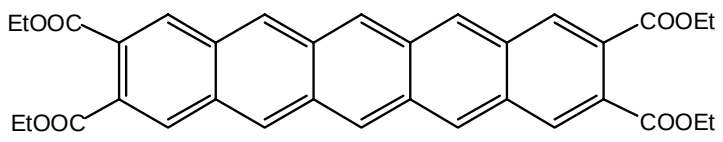


A solution of DMSO and CH_2Cl_2 (1:2, 6 ml) was added dropwise via syringe to a stirred solution of oxalyl chloride (0.2 ml, 2.4 mmol) in CH_2Cl_2 (4 ml) at -80 °C under nitrogen atmosphere. The mixture was stirred for 30 min. A solution of **33** (140 mg, 0.22 mmol) in DMSO and CH_2Cl_2 (1:2, 9 ml) was added slowly via syringe at the same temperature and the reaction mixture was further stirred for 3 hr before

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

triethylamine (0.75 ml, distilled) was slowly added. The reaction mixture was stirred at the low temperature for another 1 hr before warming it back to room temperature. Water (50 ml) was added at this point and the reaction mixture was extracted three times with CH_2Cl_2. The combined organic layer was washed with water three times and dried over anhydrous $MgSO_4$. The solution was concentrated in vacuo and the remaining solid was purified by column chromatography on silica gel (passed hexane: dichloromethane =1:1 and then dichloromethane to remove impurity) using a mixture of dichloromethane and ethylacetate (7:1) as eluent. The desired product was obtained as a brownish-yellow solid (84 mg, yield 61%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.38 (t, J = 7.1 Hz, 12H), 4.39 (q, J = 7.1 Hz, 8H), 5.36 (s, 2H), 8.00 (s, 4H), 8.21 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.13, 60.69, 61.92, 126.22, 129.78, 130.24, 133.59, 134.11, 167.18, 183.76; MS (FAB, m/e, relative intensity %) 623 ($[M+H]^+$, 29.4); HRMS Calcd for $C_{36}H_{31}O_{10}$: 623.1917, Found: 623.1904.

35: Pentacene-2,3,9,10-tetracarboxylic acid tetraethyl ester:

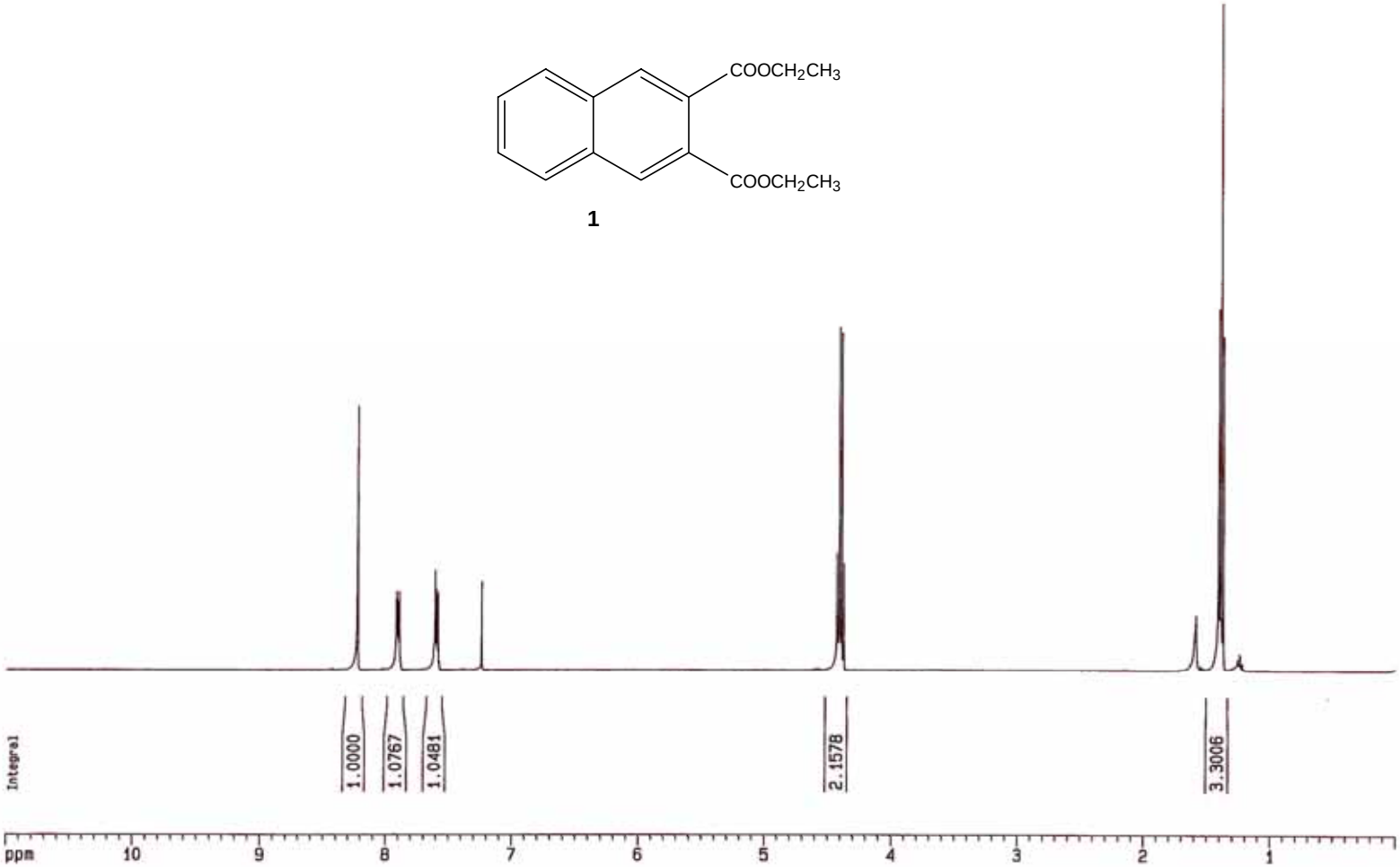


A $CDCl_3$ solution of **34** (20 mg, 0.032 mmol in 2 ml) was taken in NMR tube under nitrogen atmosphere. The NMR tube was sealed by septum with parafilm. While the solution was irradiated under a 365nm UVlamp, the photochemical conversion was monitored by NMR spectrum until completion (8 hr). Flash chromatography (under nitrogen atmosphere, dichloromethane: ethyl acetate = 20:1) provided pure sample of **35** (70-80 %). IR (Neat, ν) 2981, 2929, 1721, 1454, 1369, 1275, 1218, 1122, 1048,

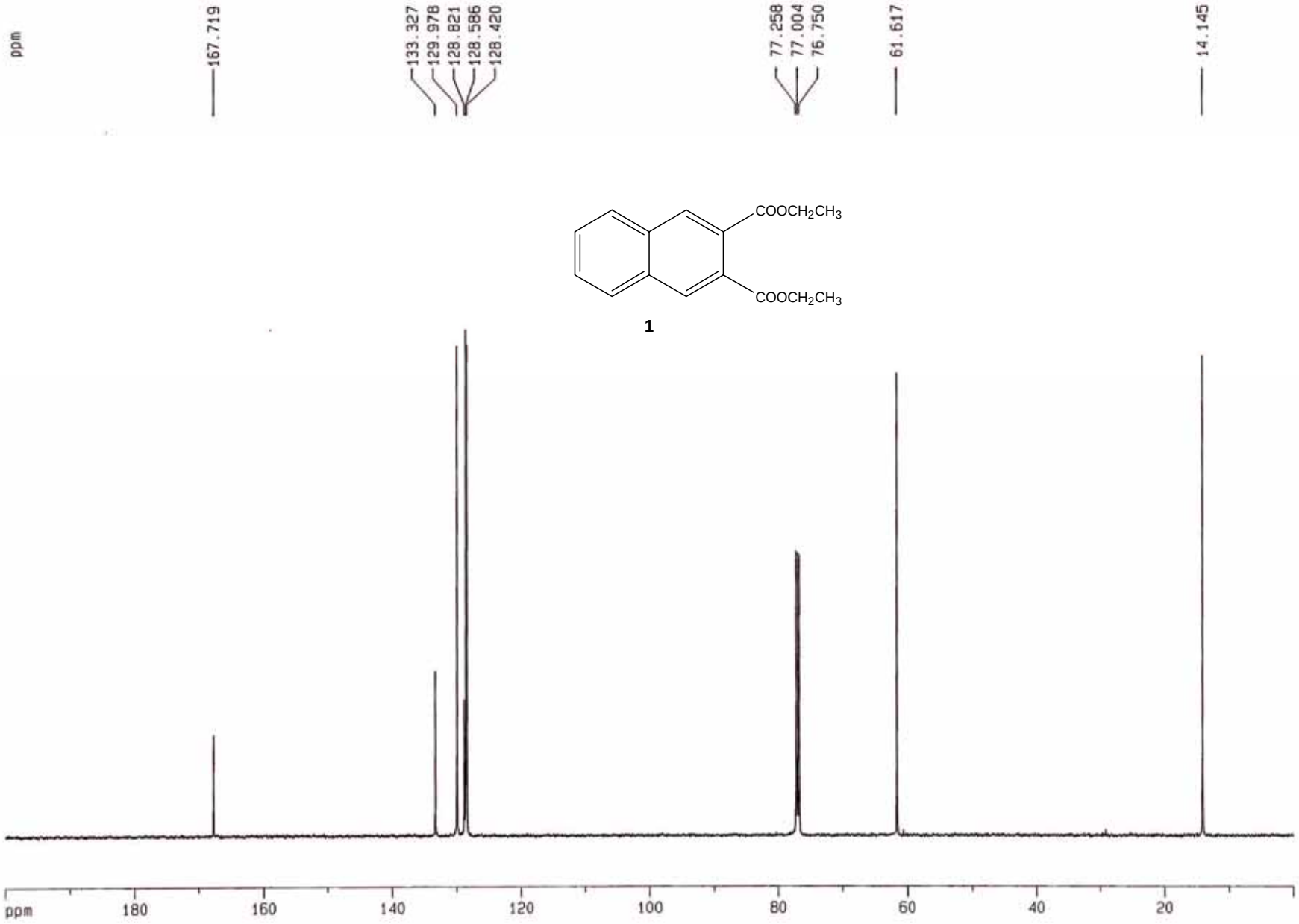
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

1019, 927, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.41 (t, *J* = 7.1 Hz, 12H), 4.41 (q, *J* = 7.1 Hz, 8H), 8.37 (s, 4H), 8.77 (s, 4H), 9.03 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 14.14, 61.68, 128.14, 128.18, 128.98, 130.26, 131.09, 131.81, 167.51; MS (FAB, m/e, relative intensity %) 566 (M^+, 100); HRMS Calcd for $C_{34}H_{30}O_8$: 566.1941, Found: 566.1938.

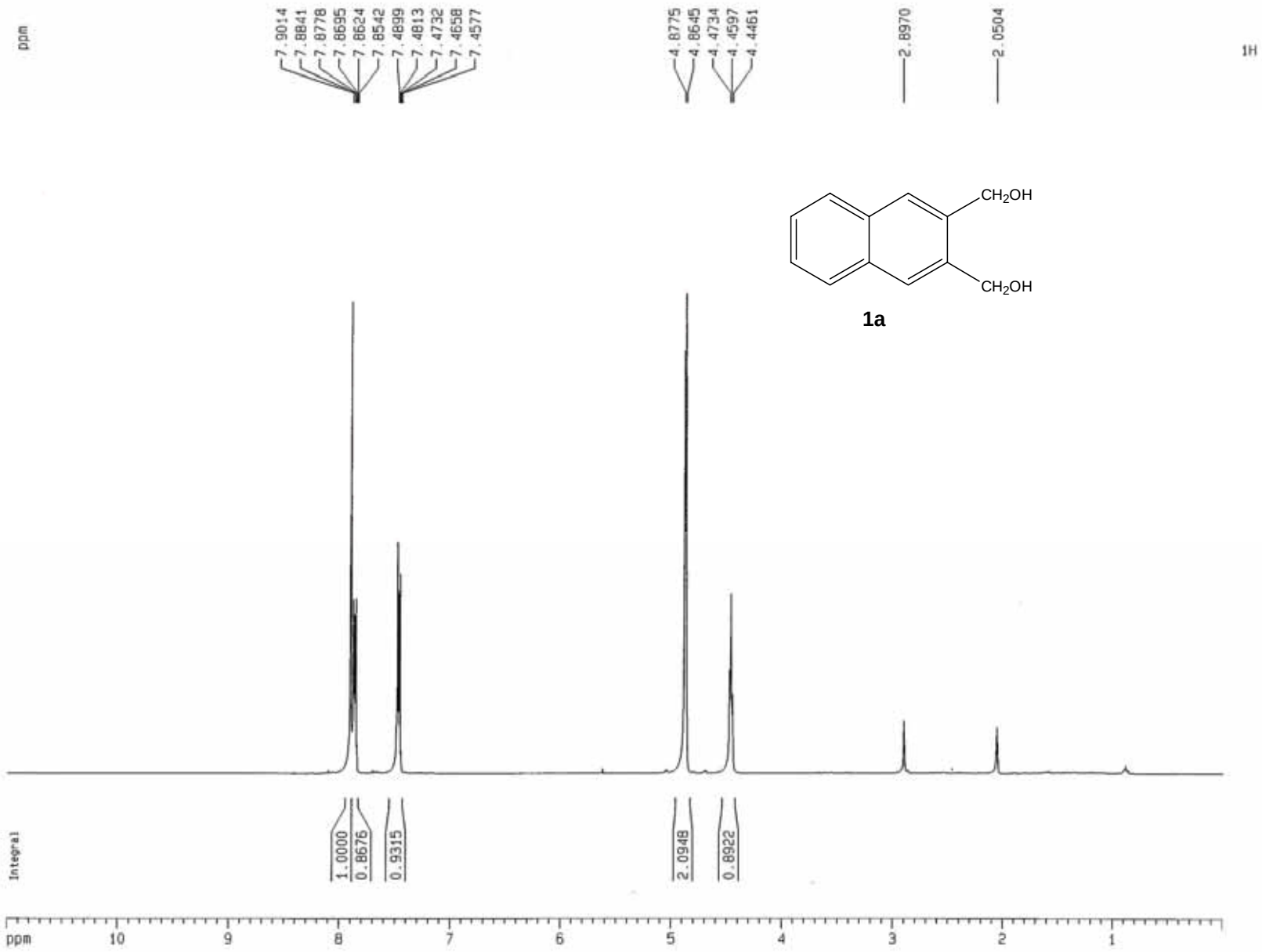
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



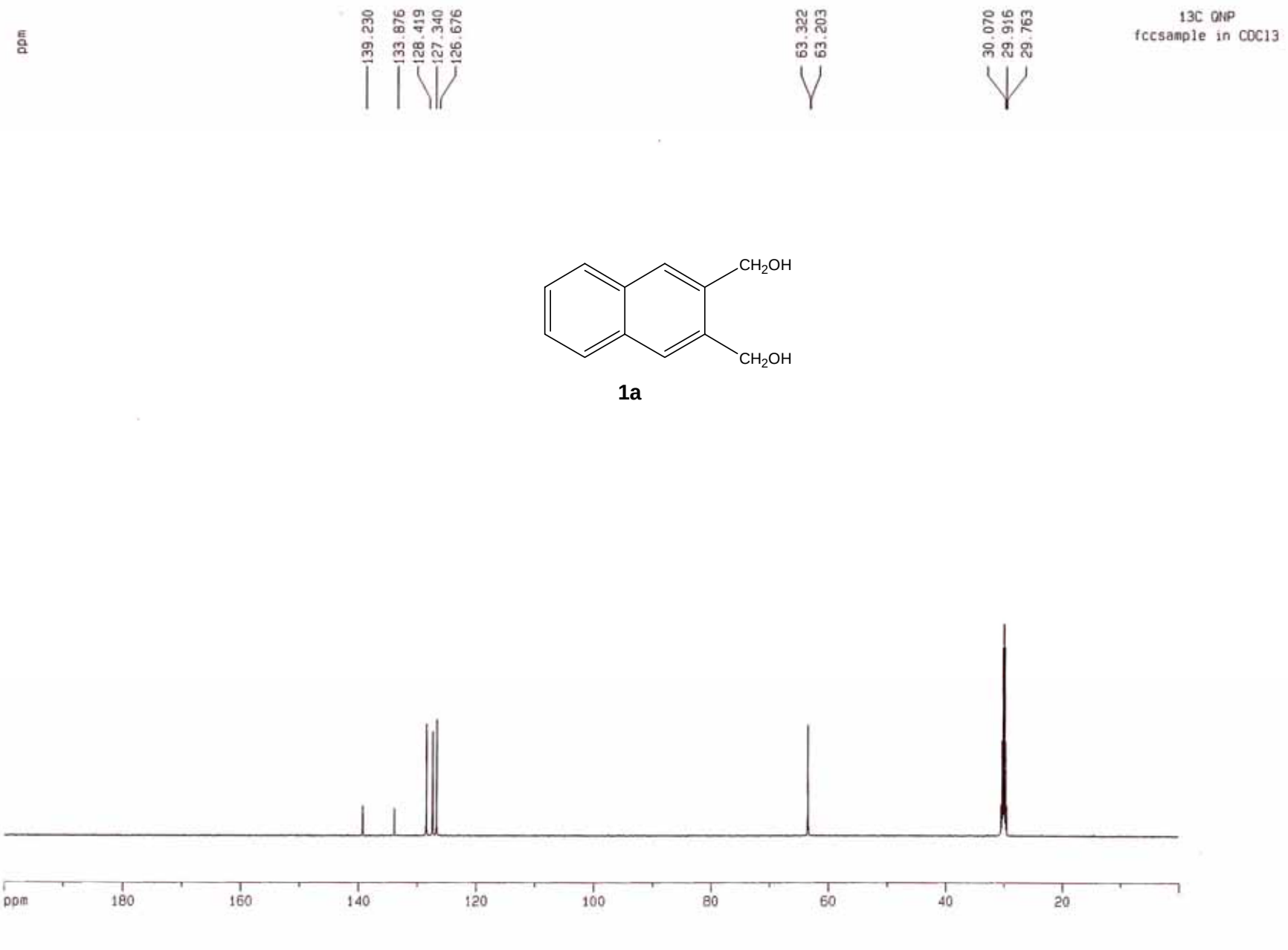
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

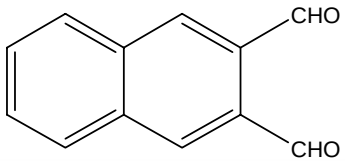


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

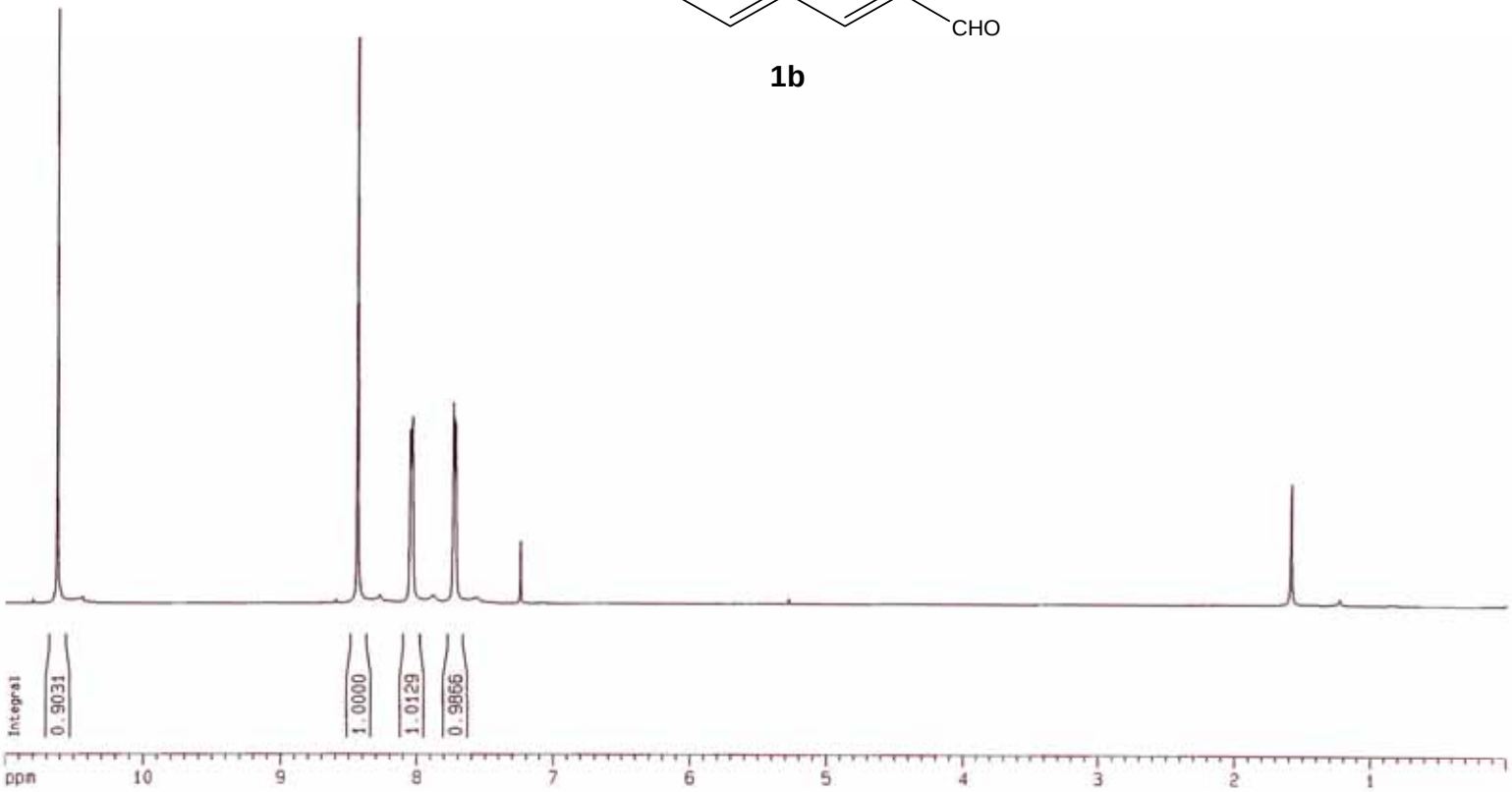


1a

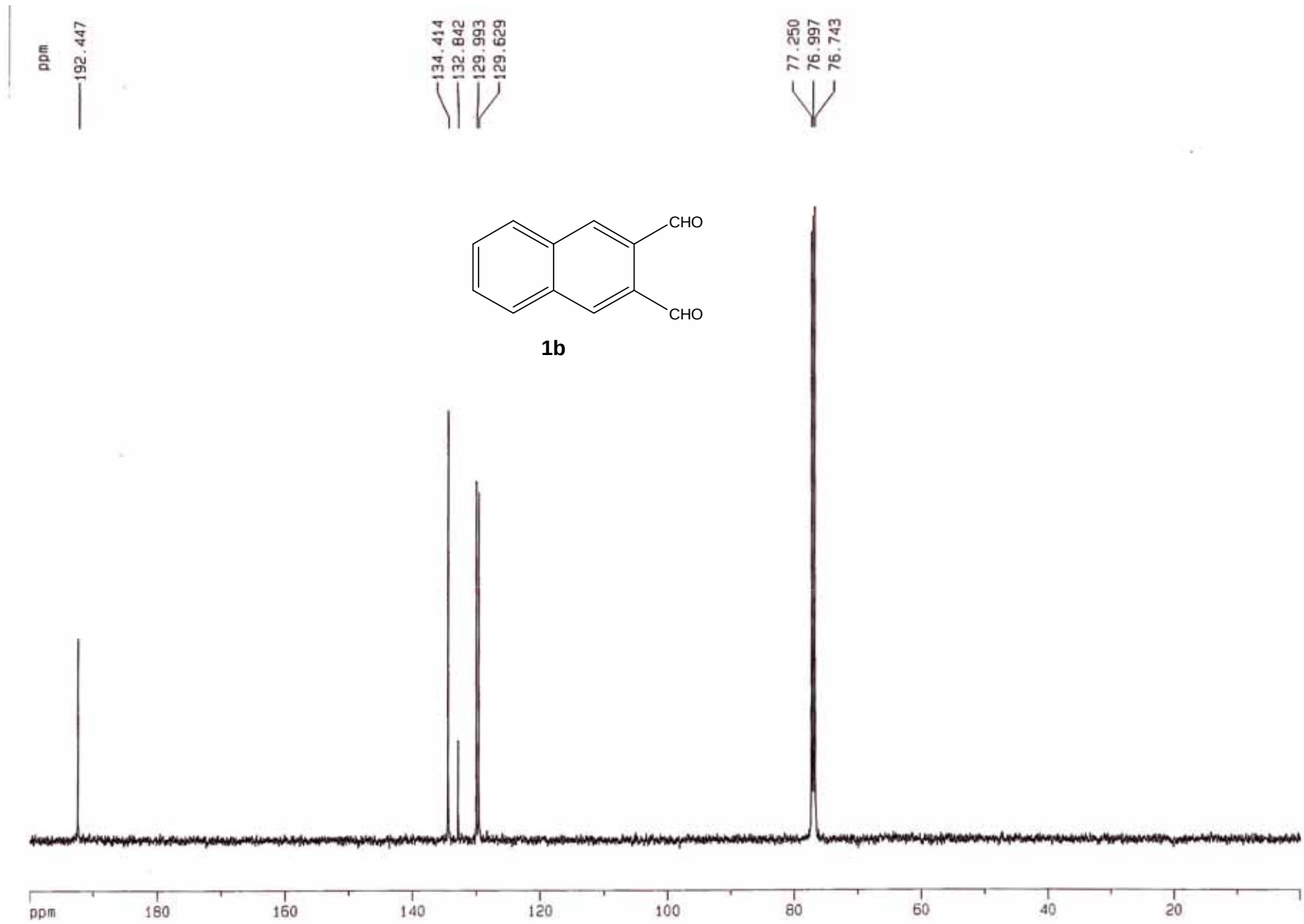
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



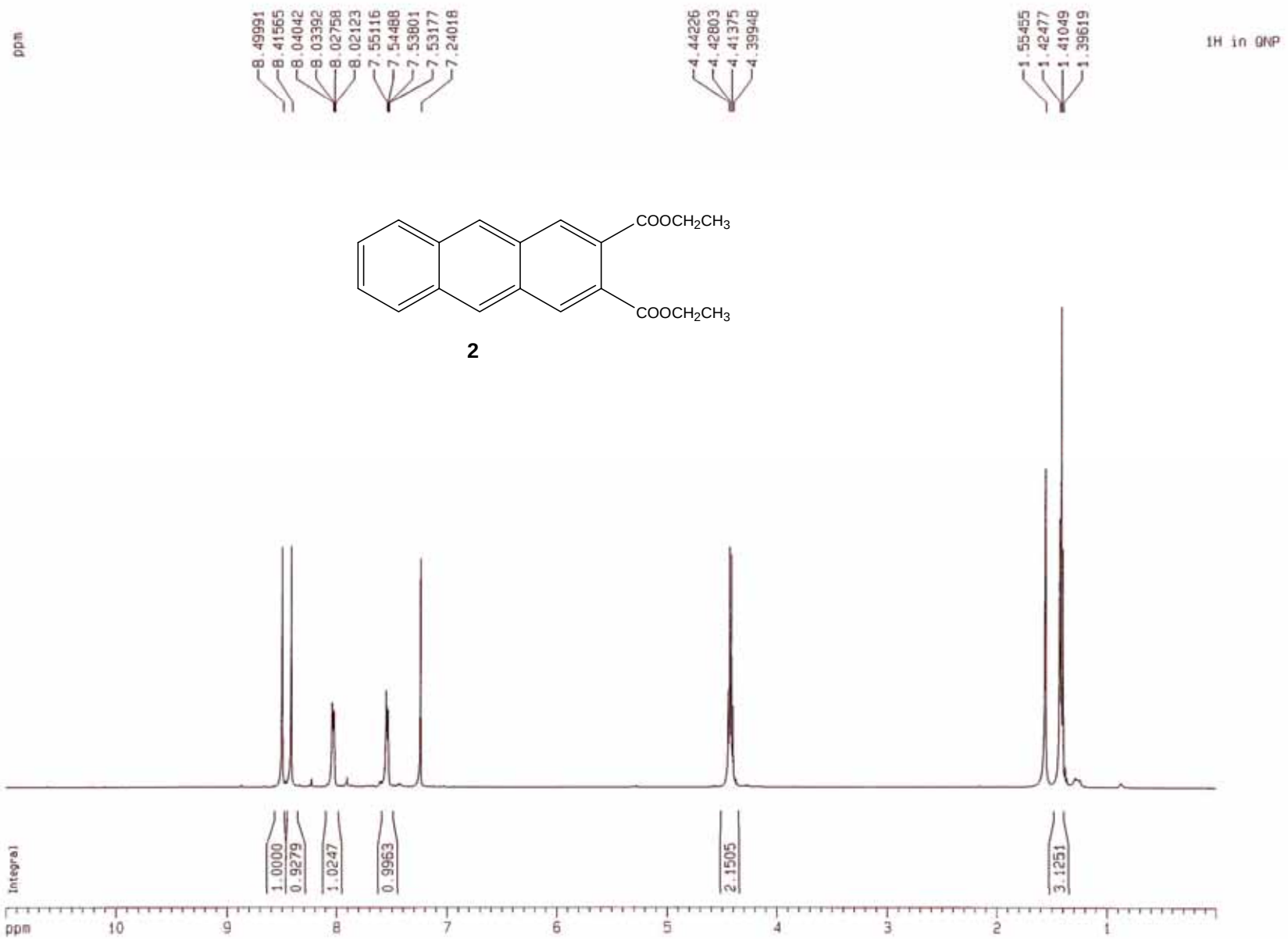
1b



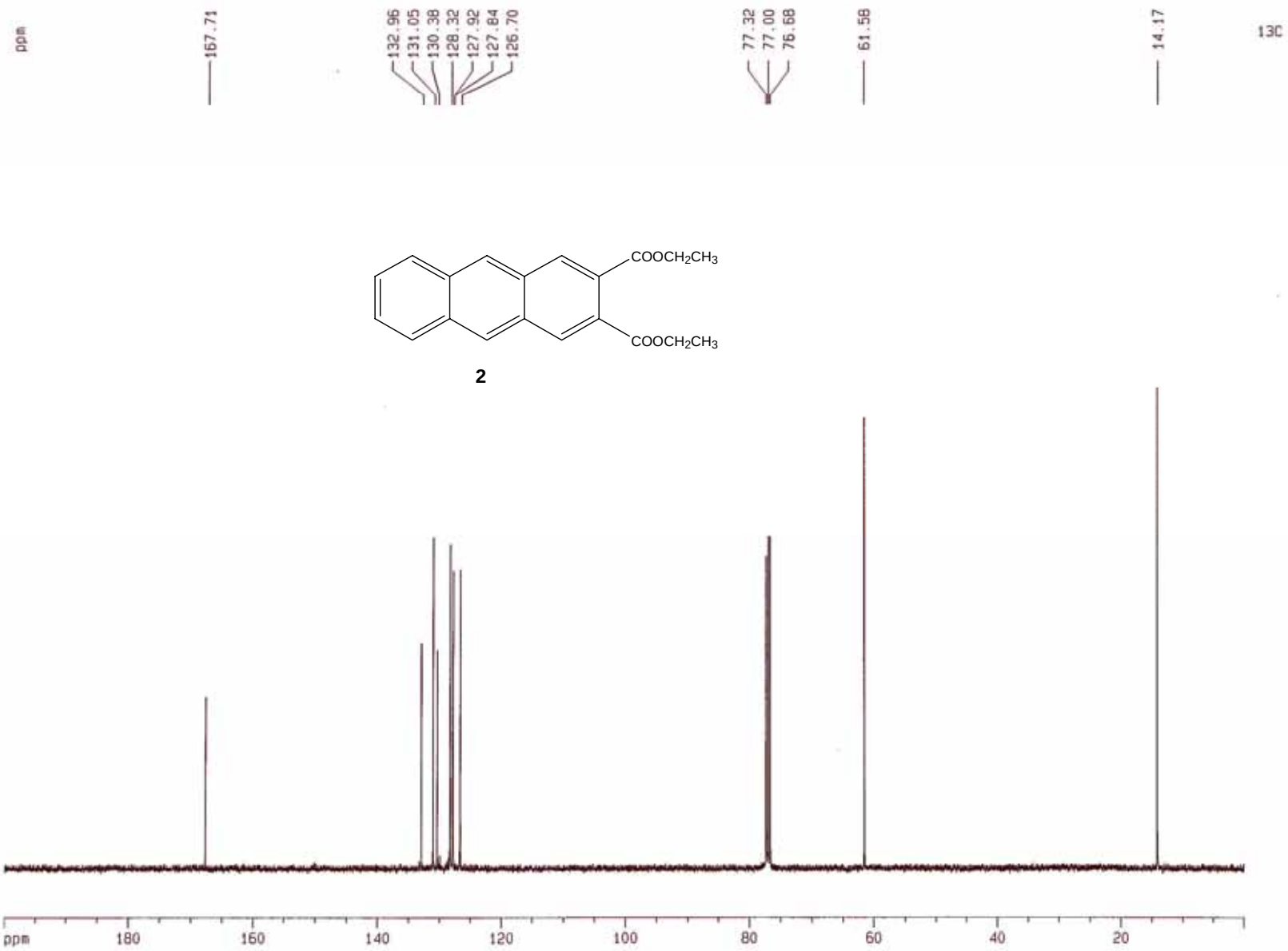
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



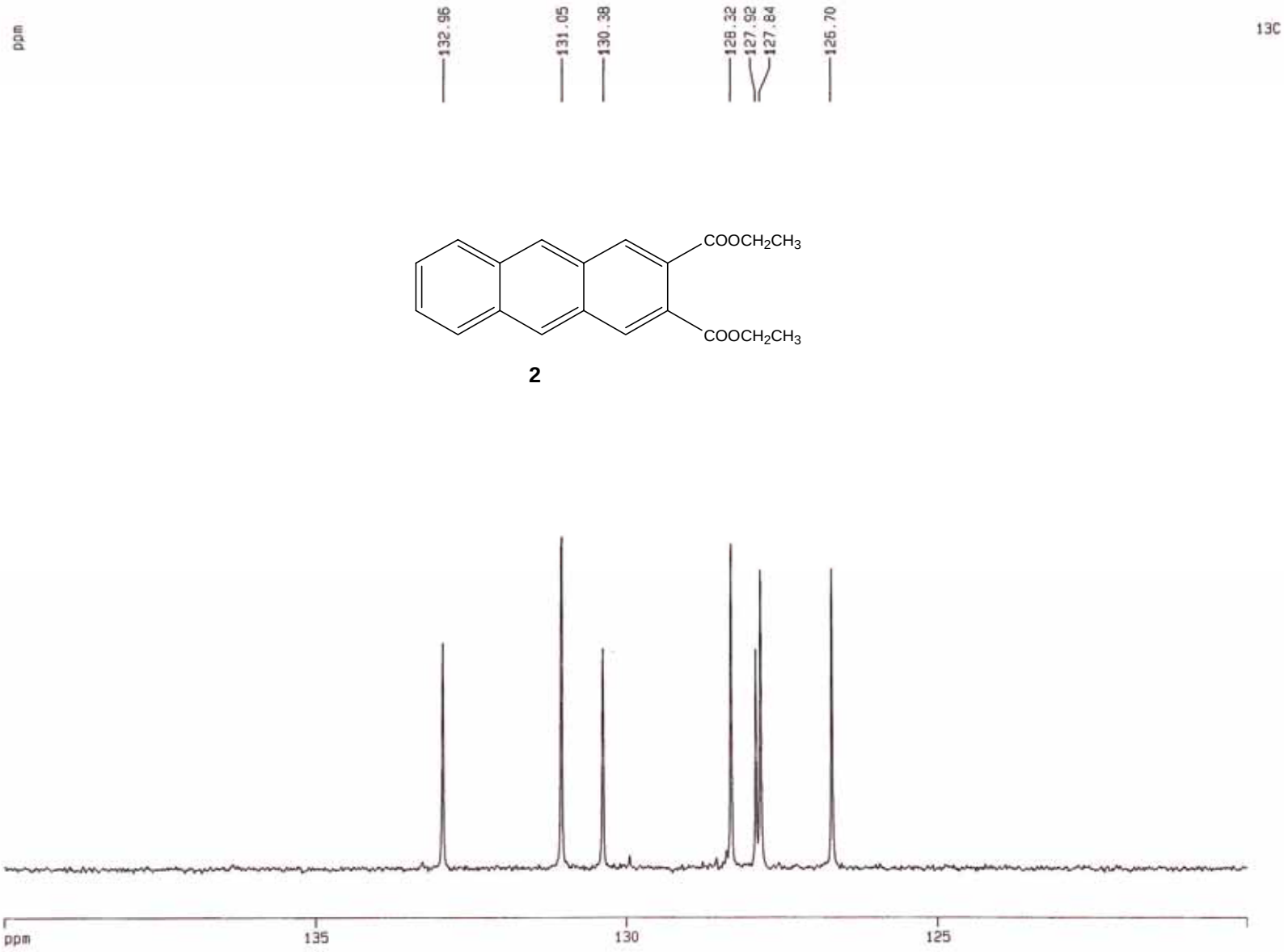
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



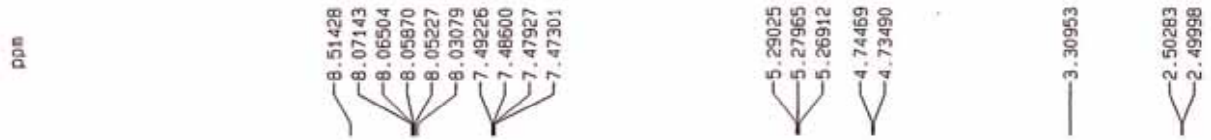
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

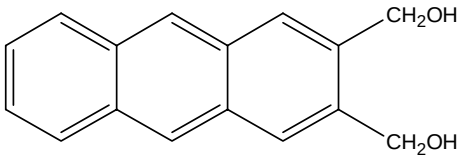


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

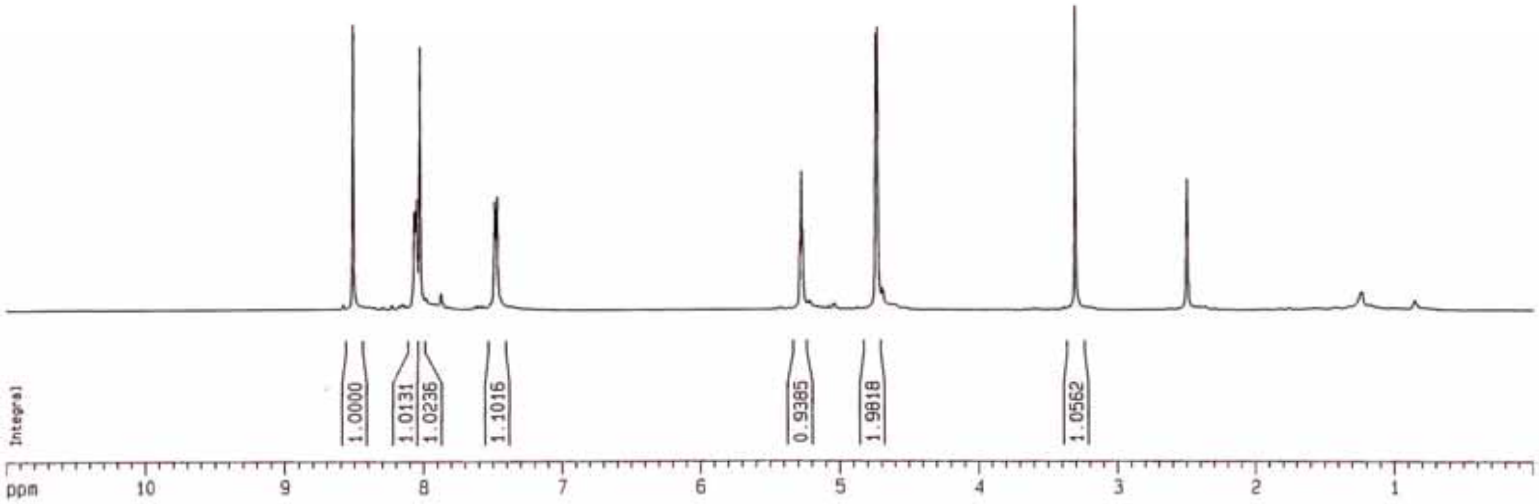


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



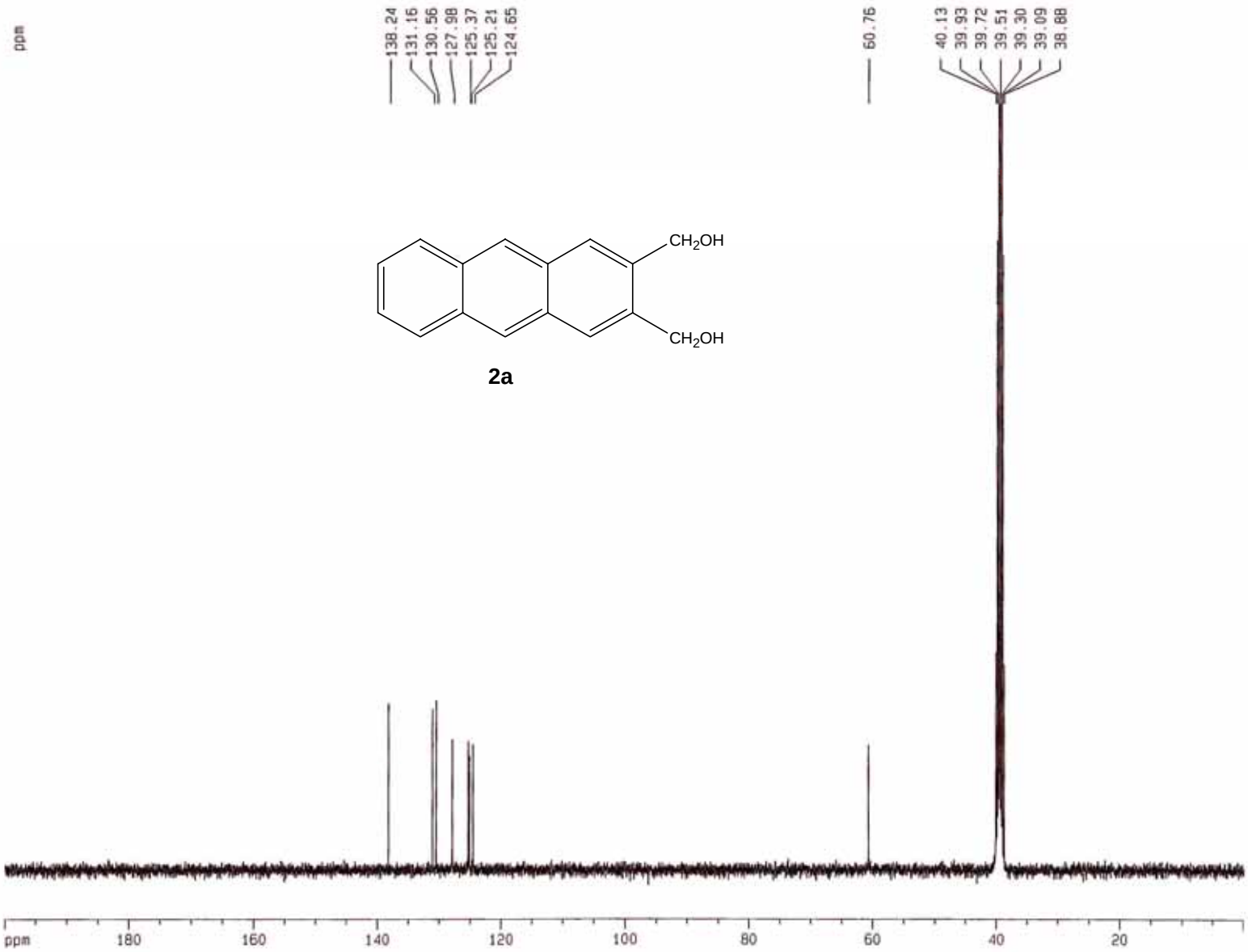


2a

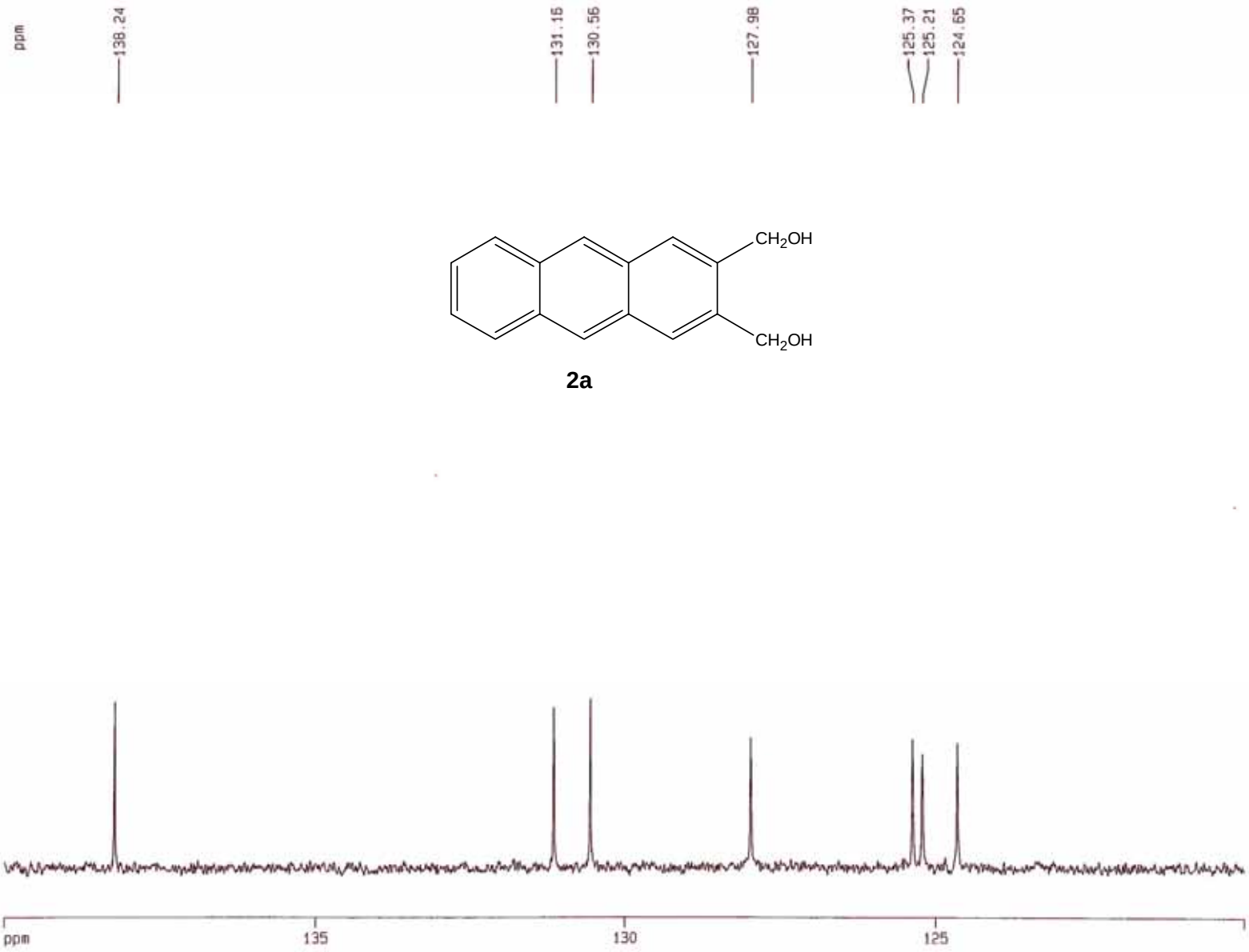


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

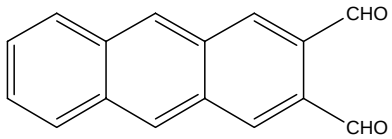
This journal is © The Royal Society of Chemistry 2009



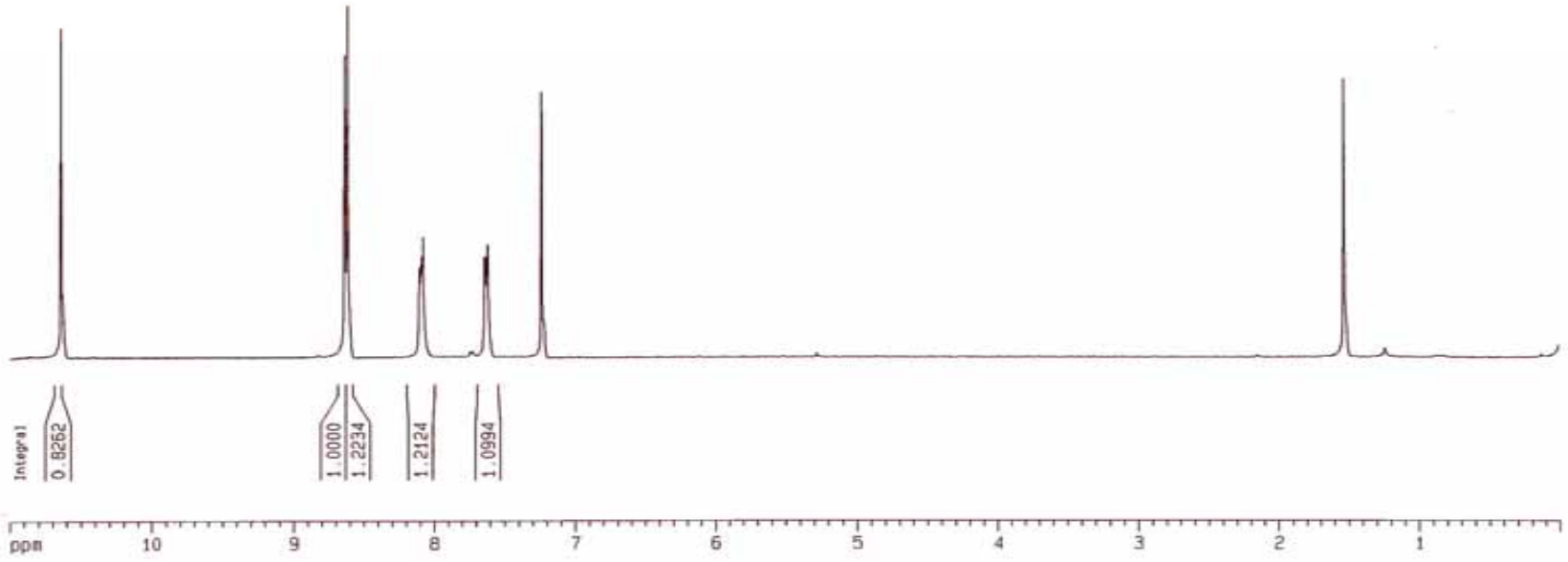
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



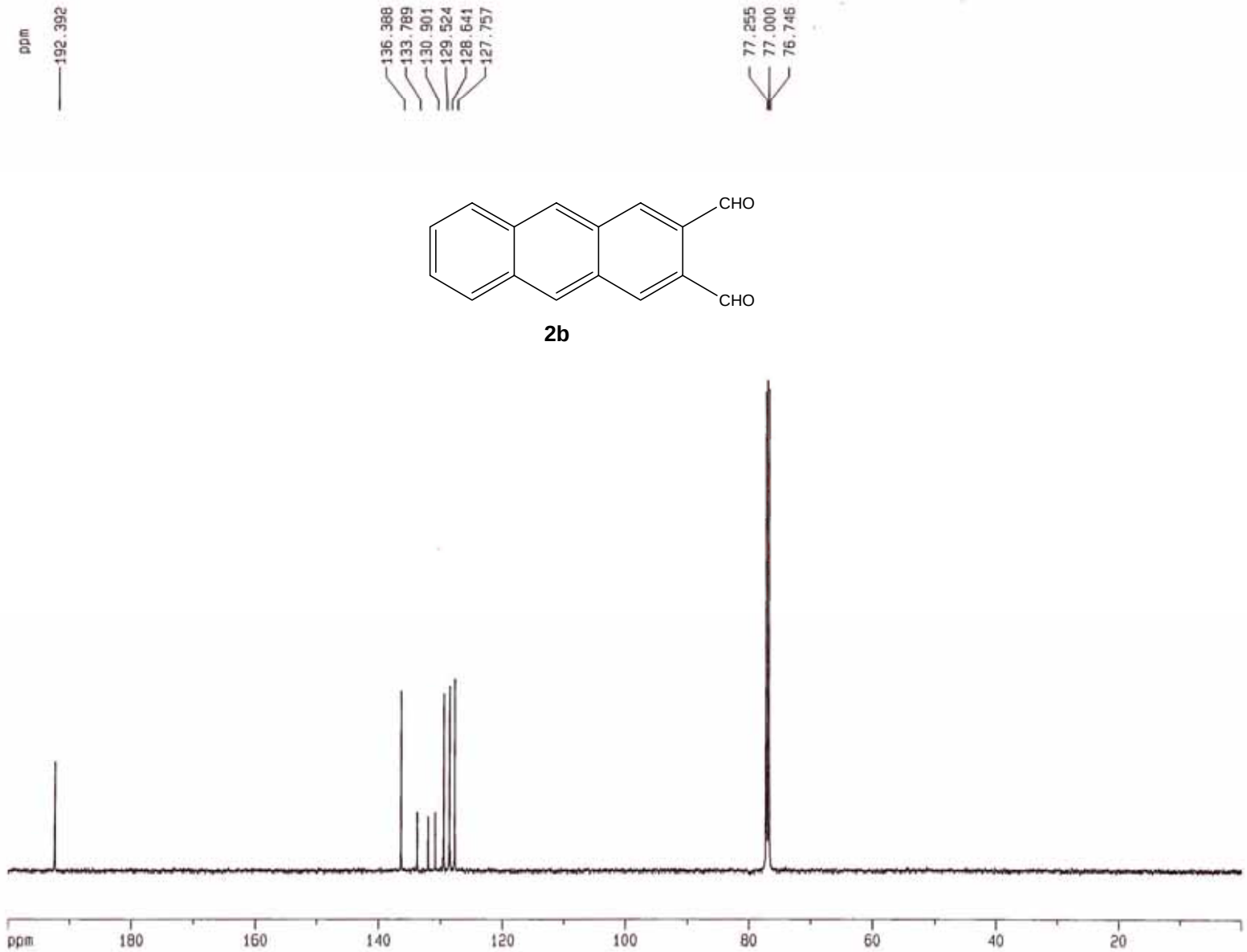
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



2b

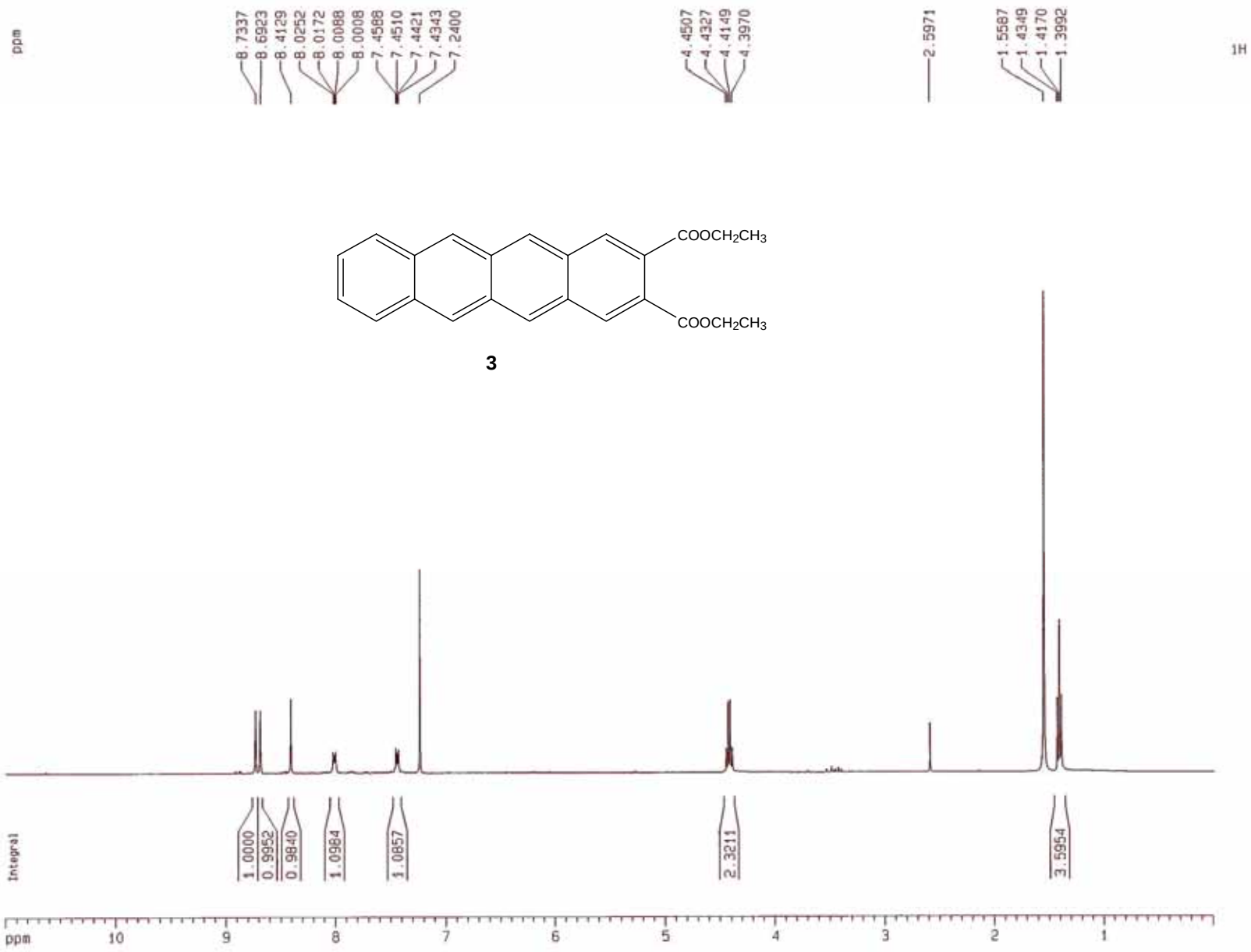


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

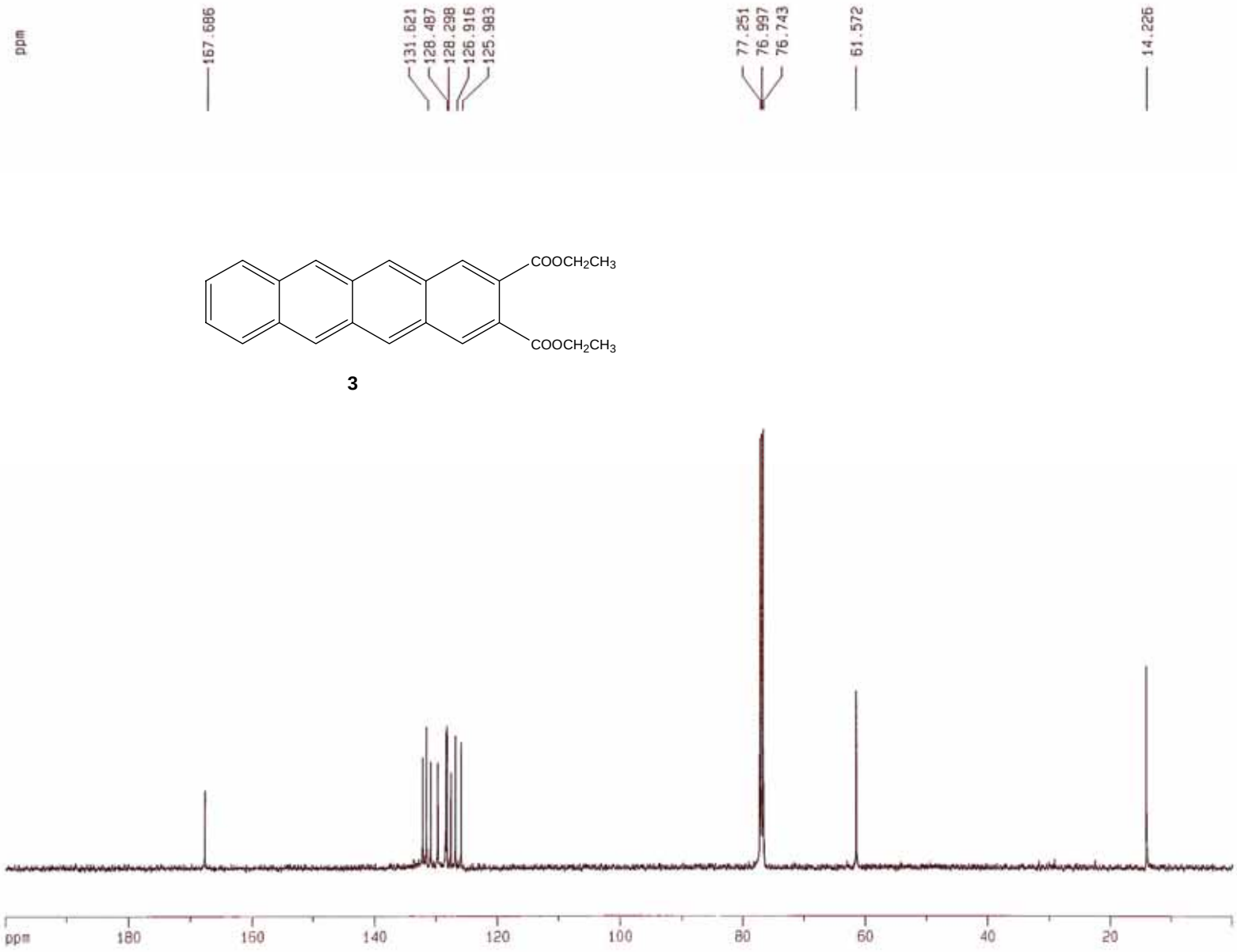


2b

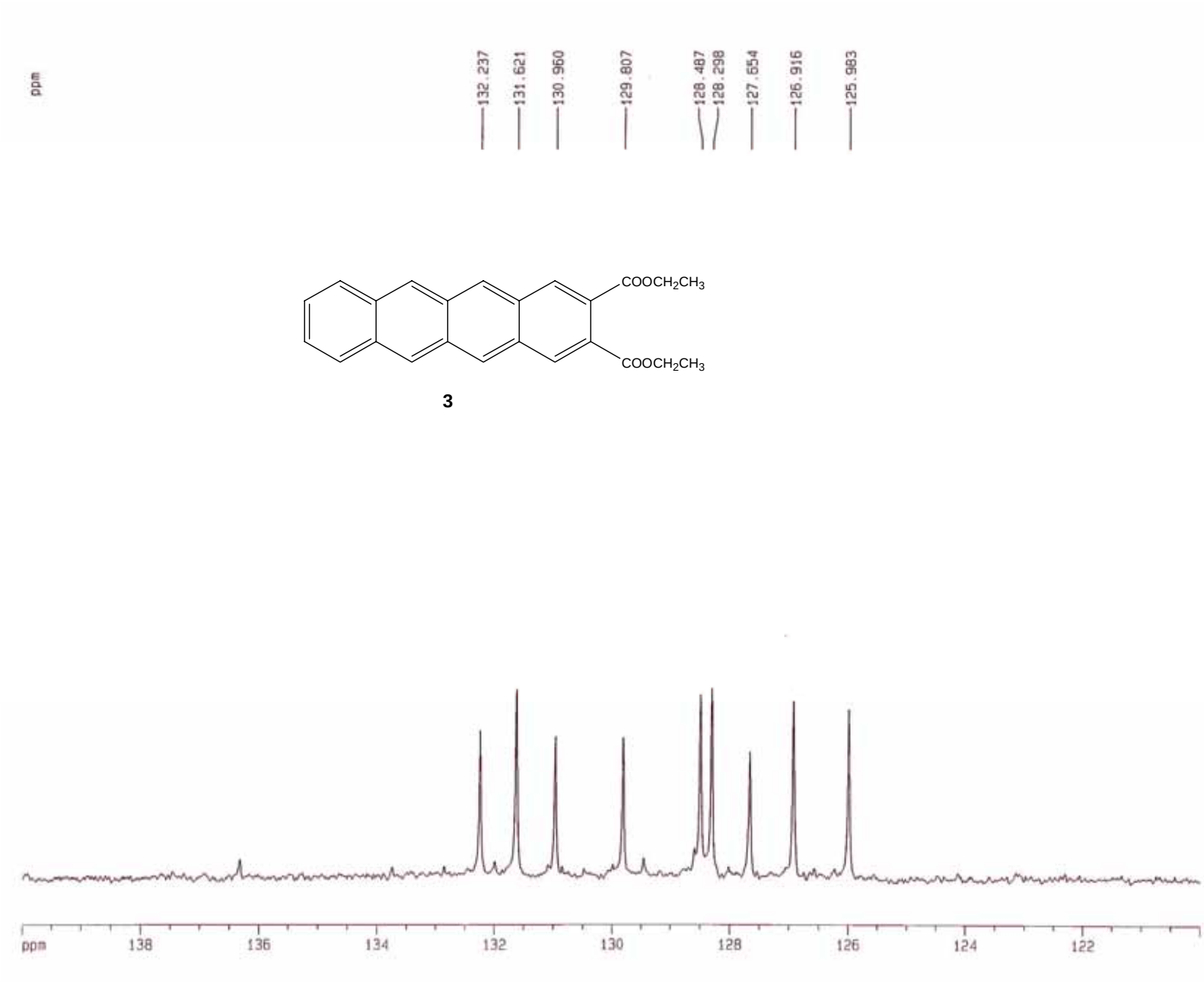
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



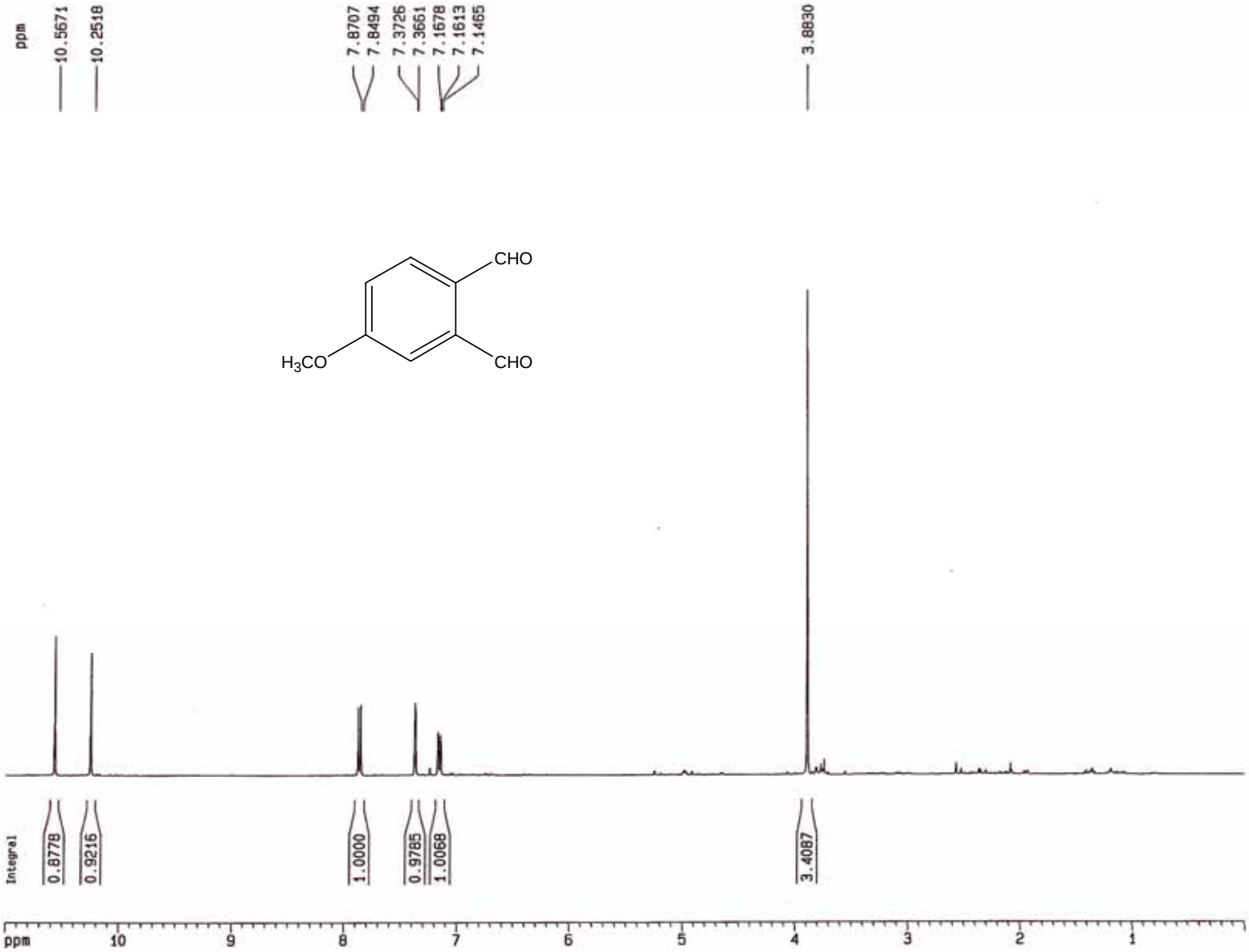
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



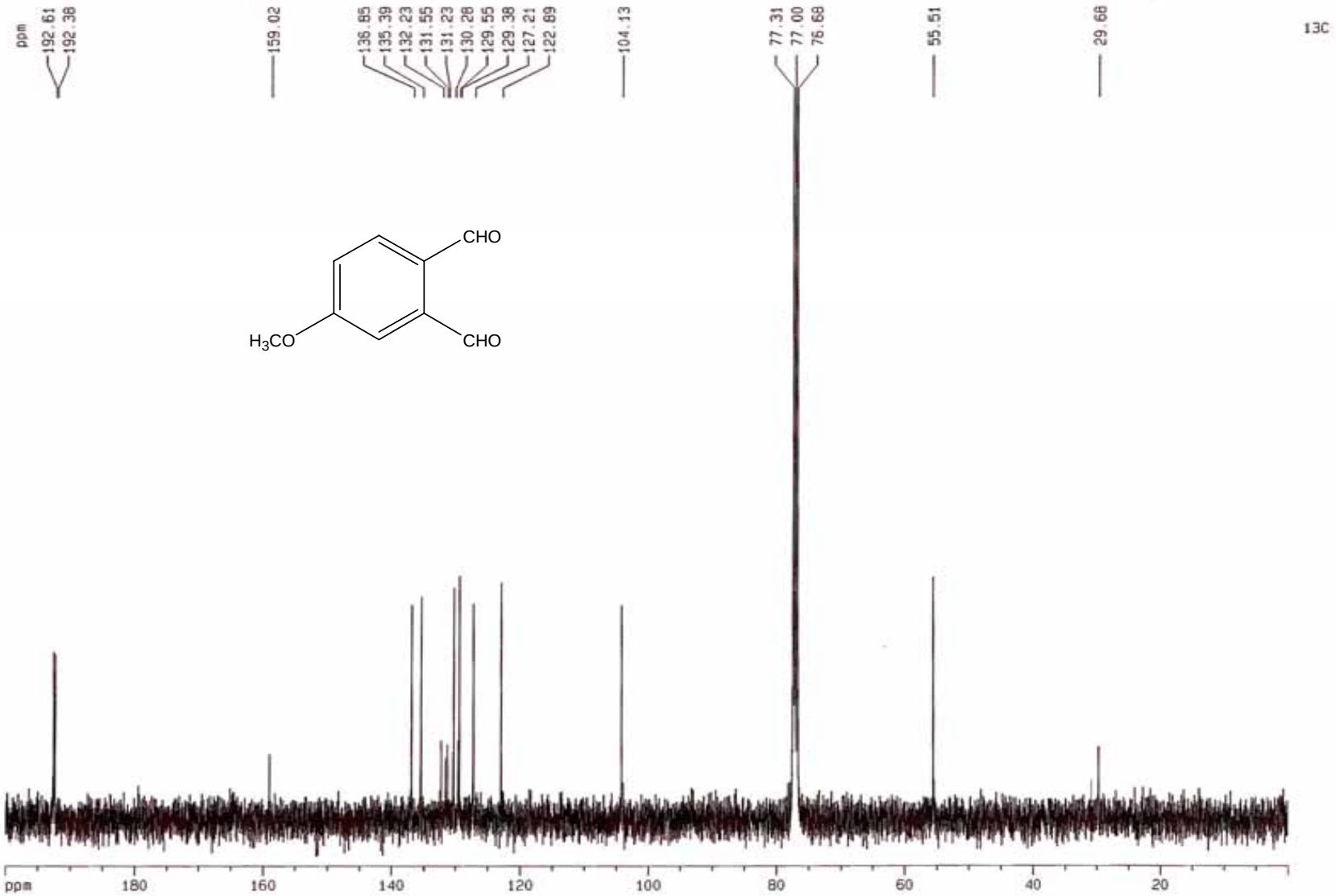
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



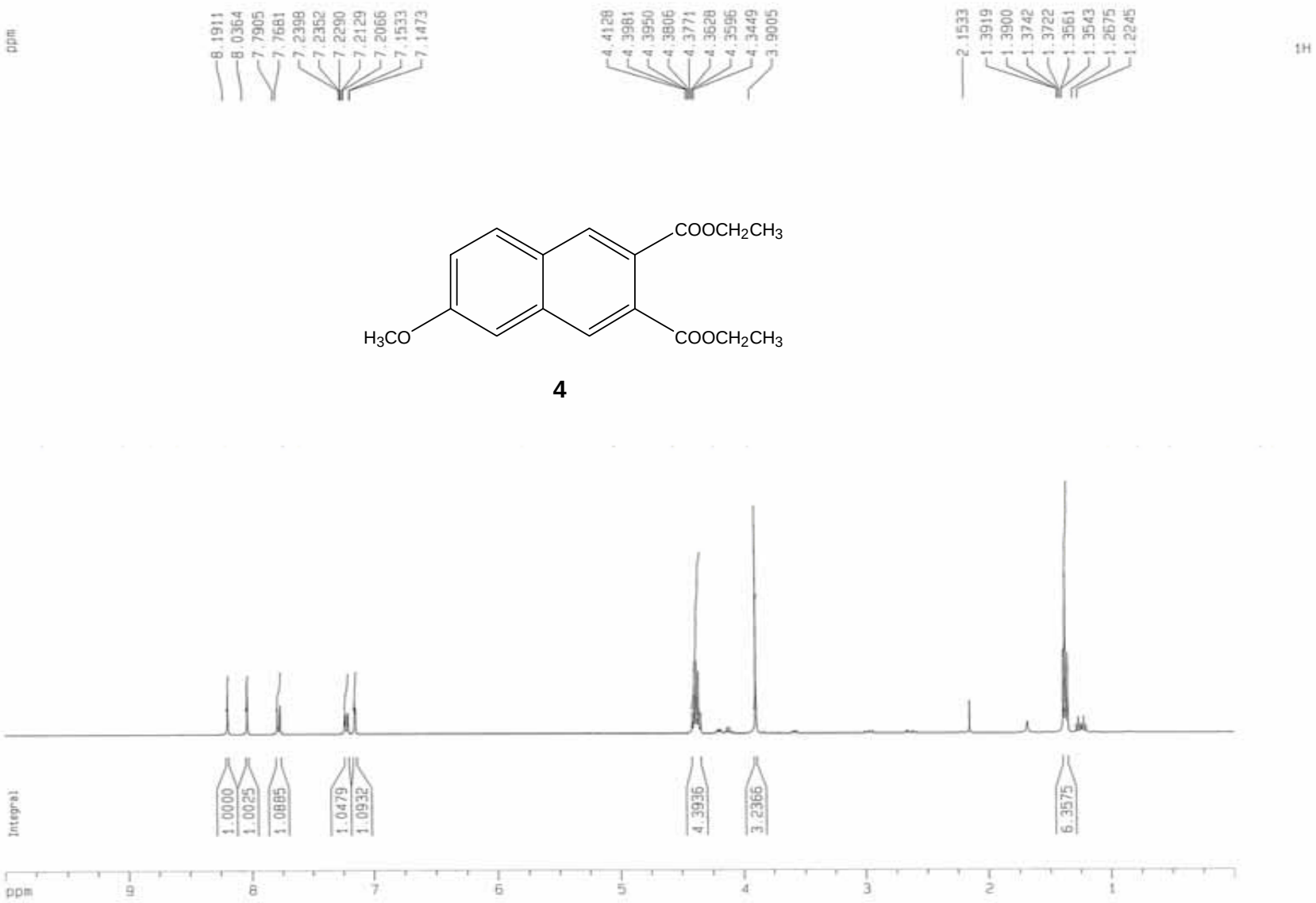
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



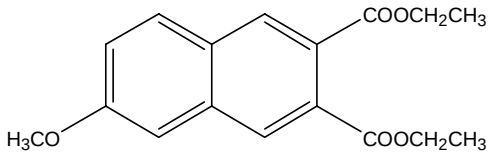
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



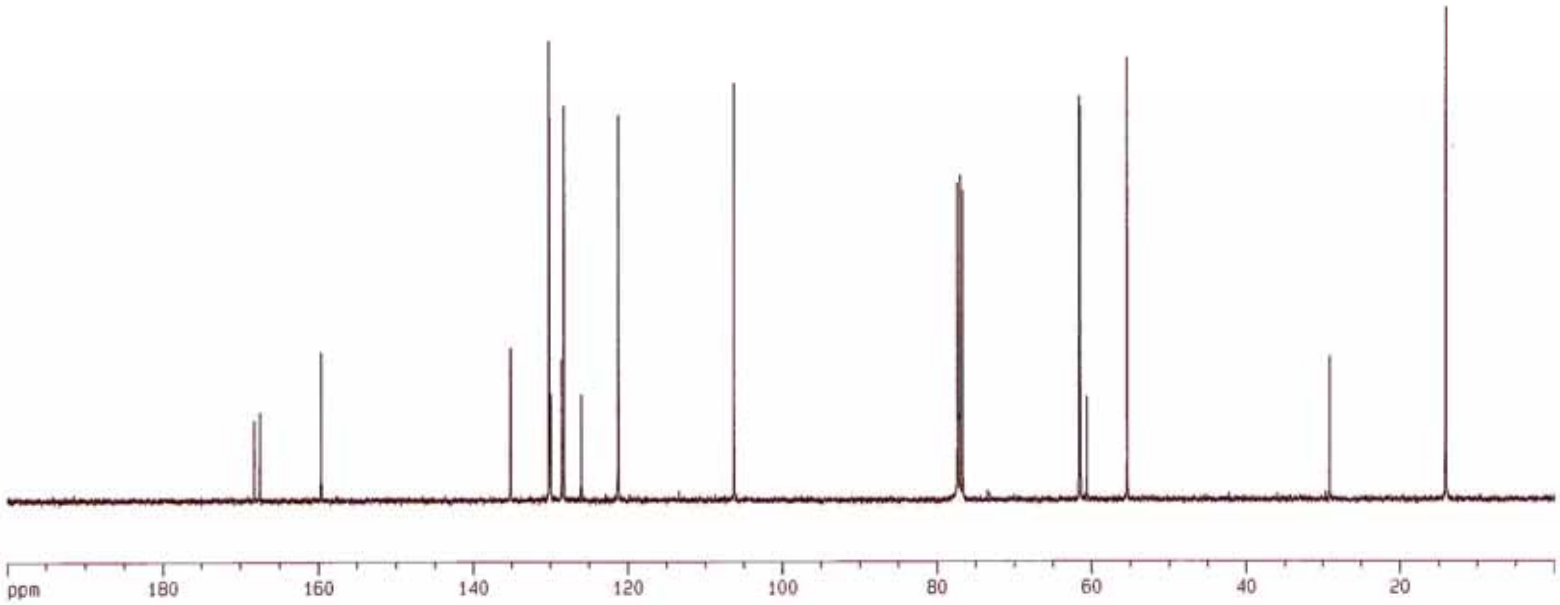
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



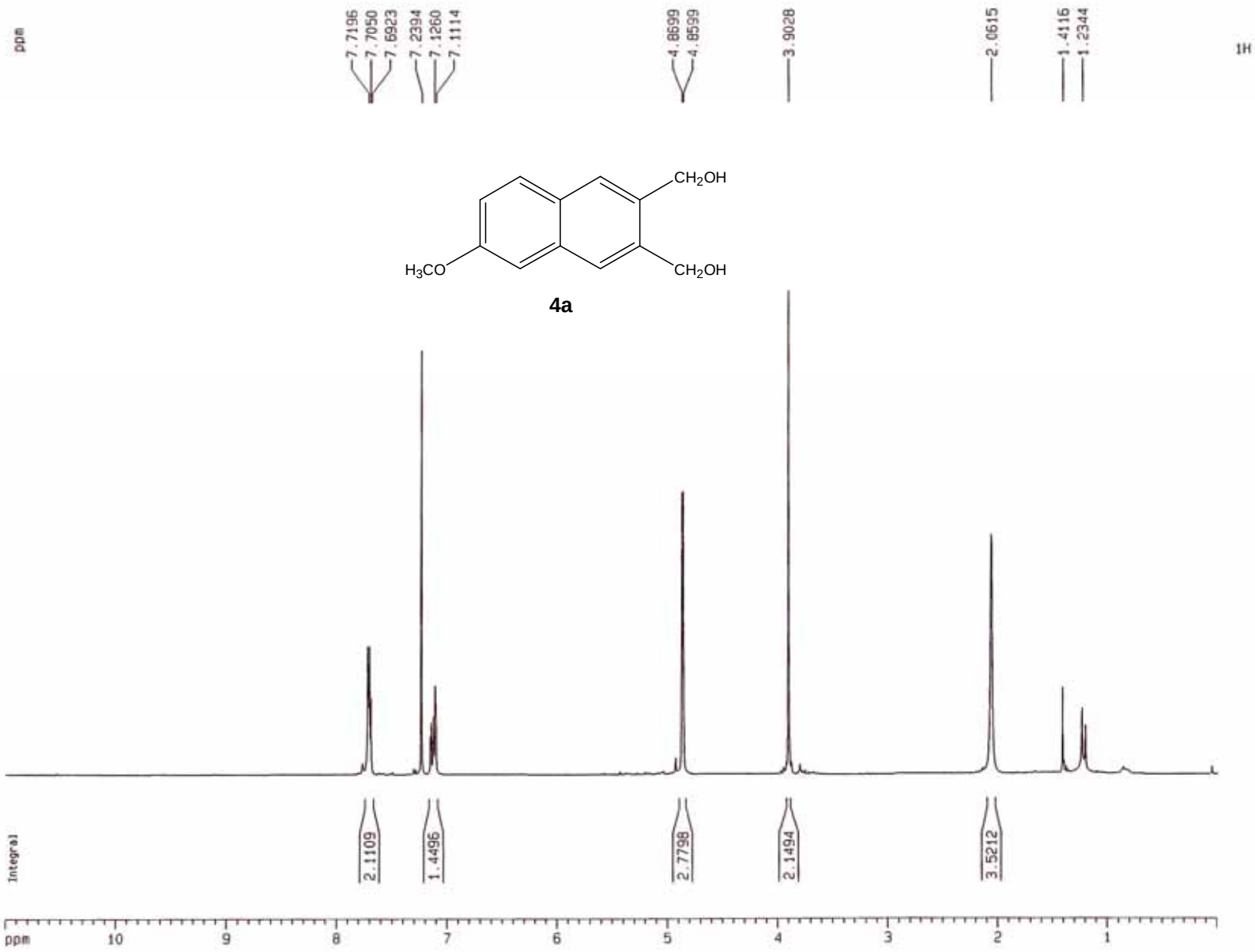
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



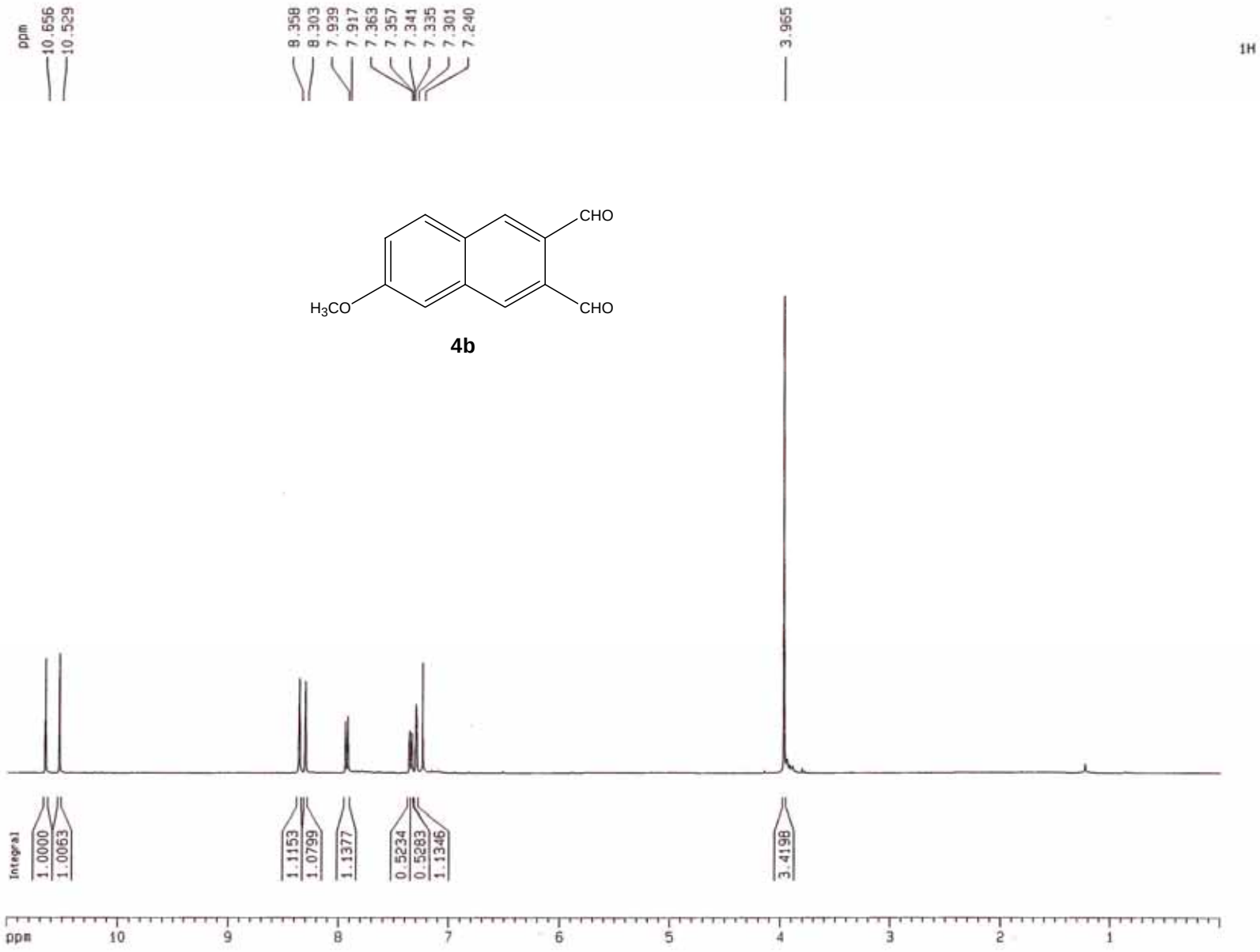
4



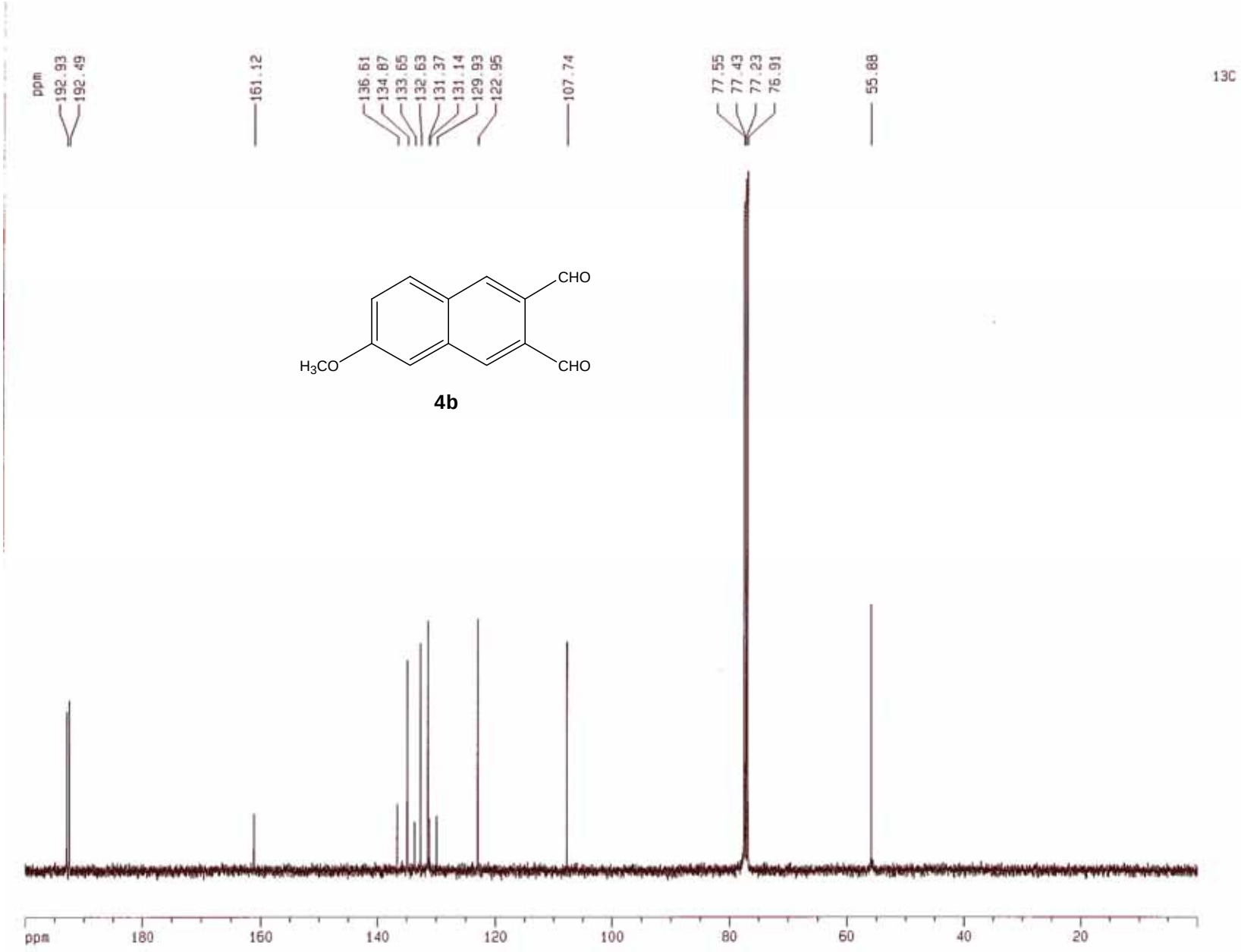
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



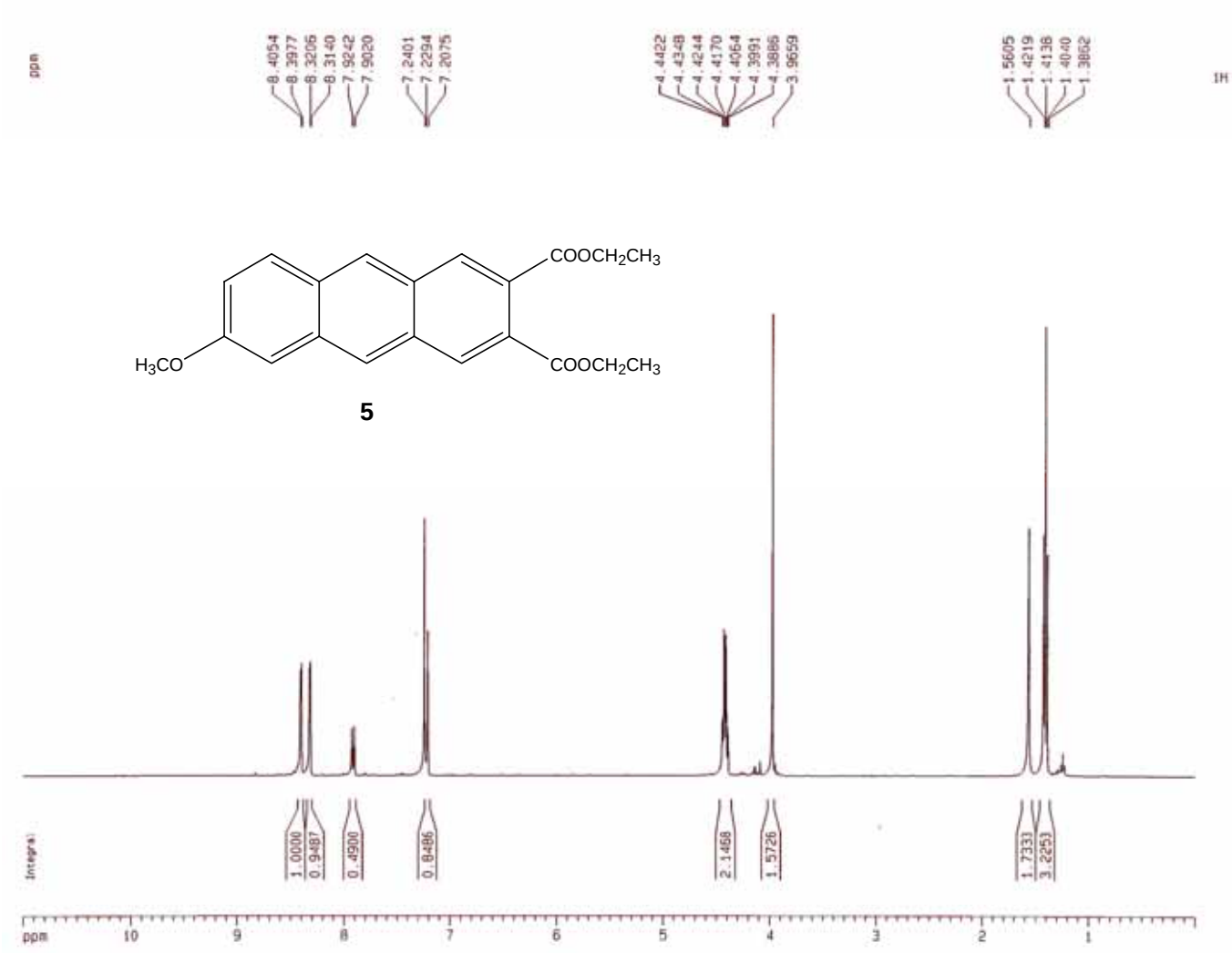
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



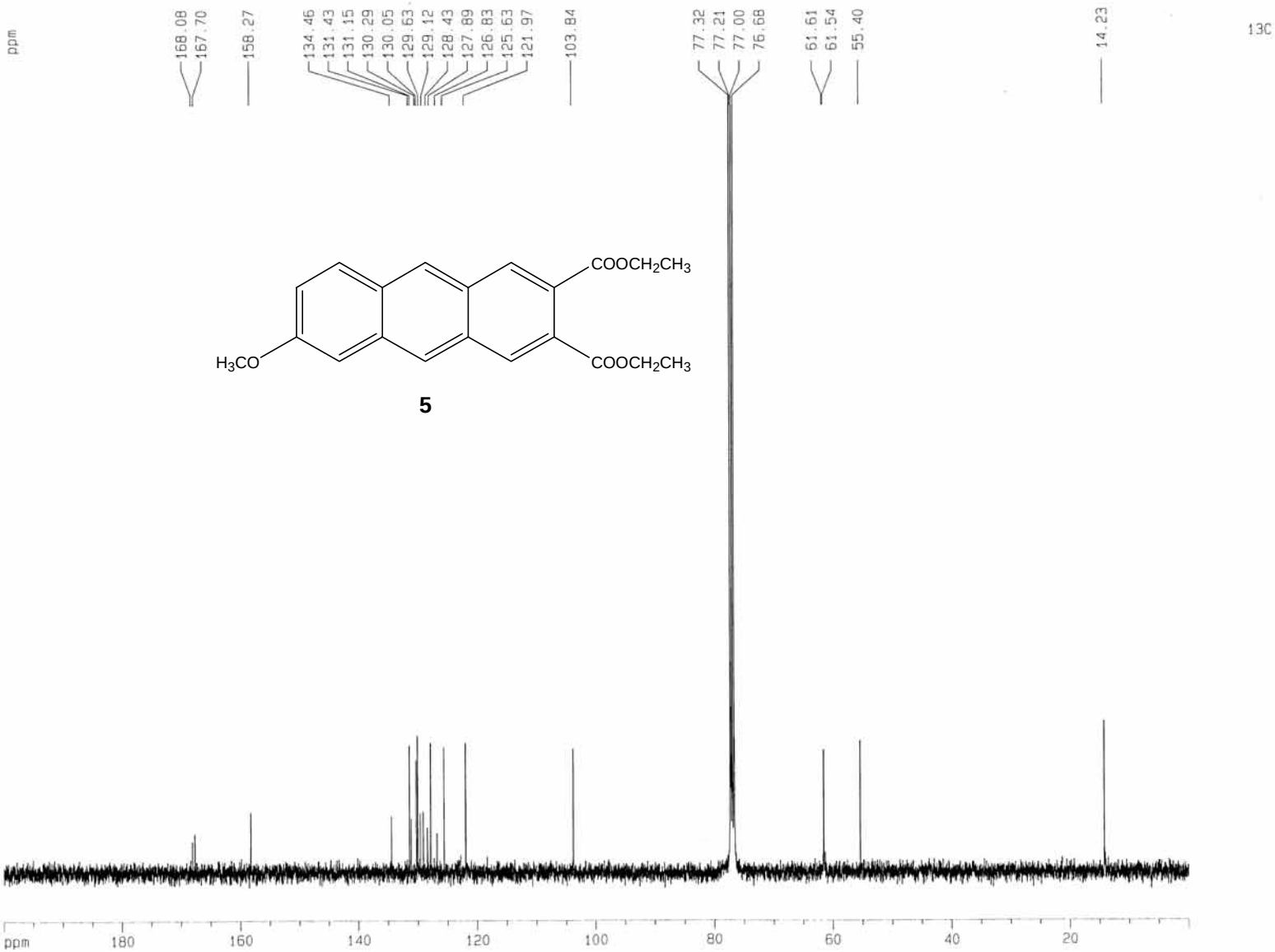
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



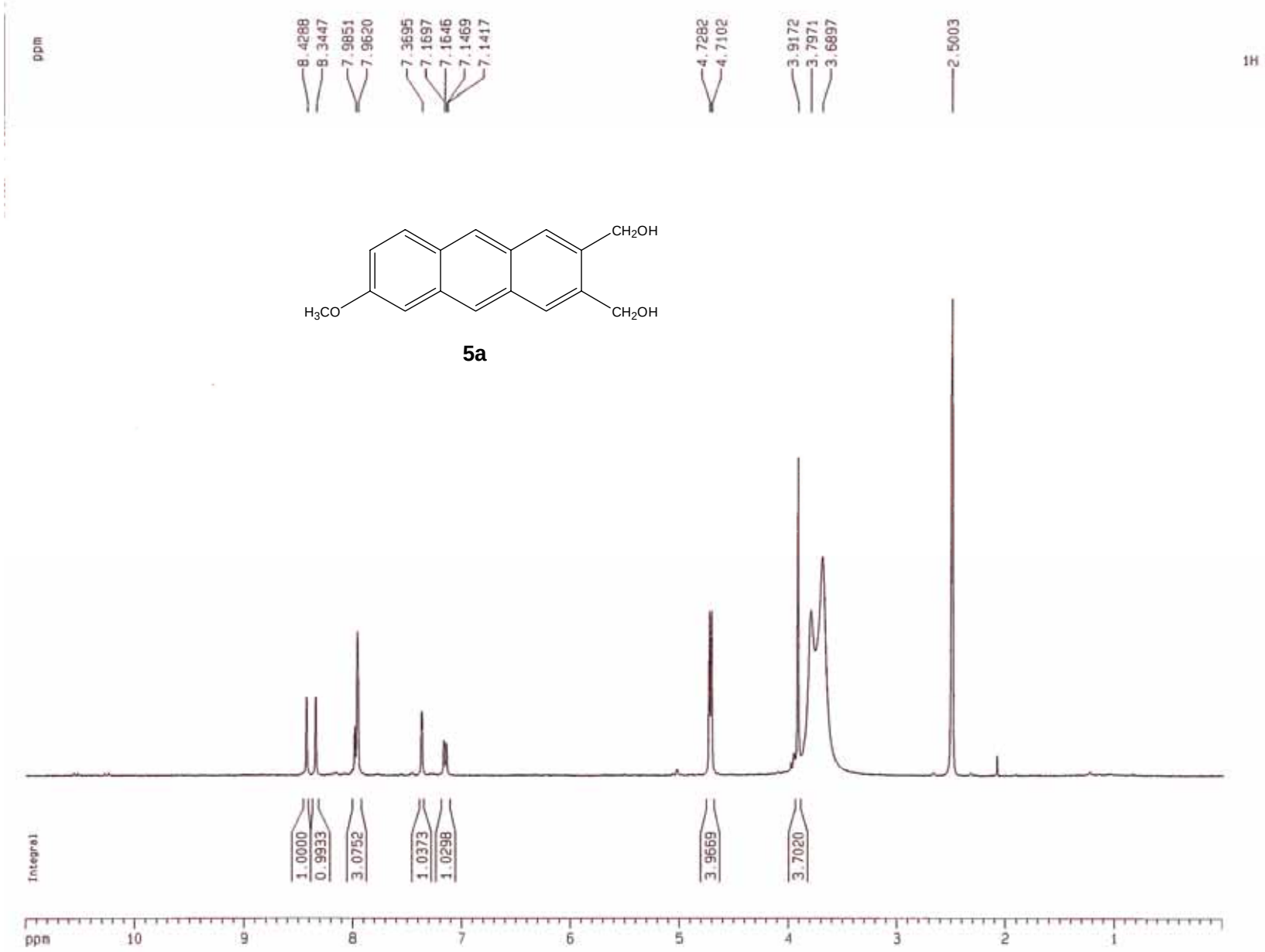
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



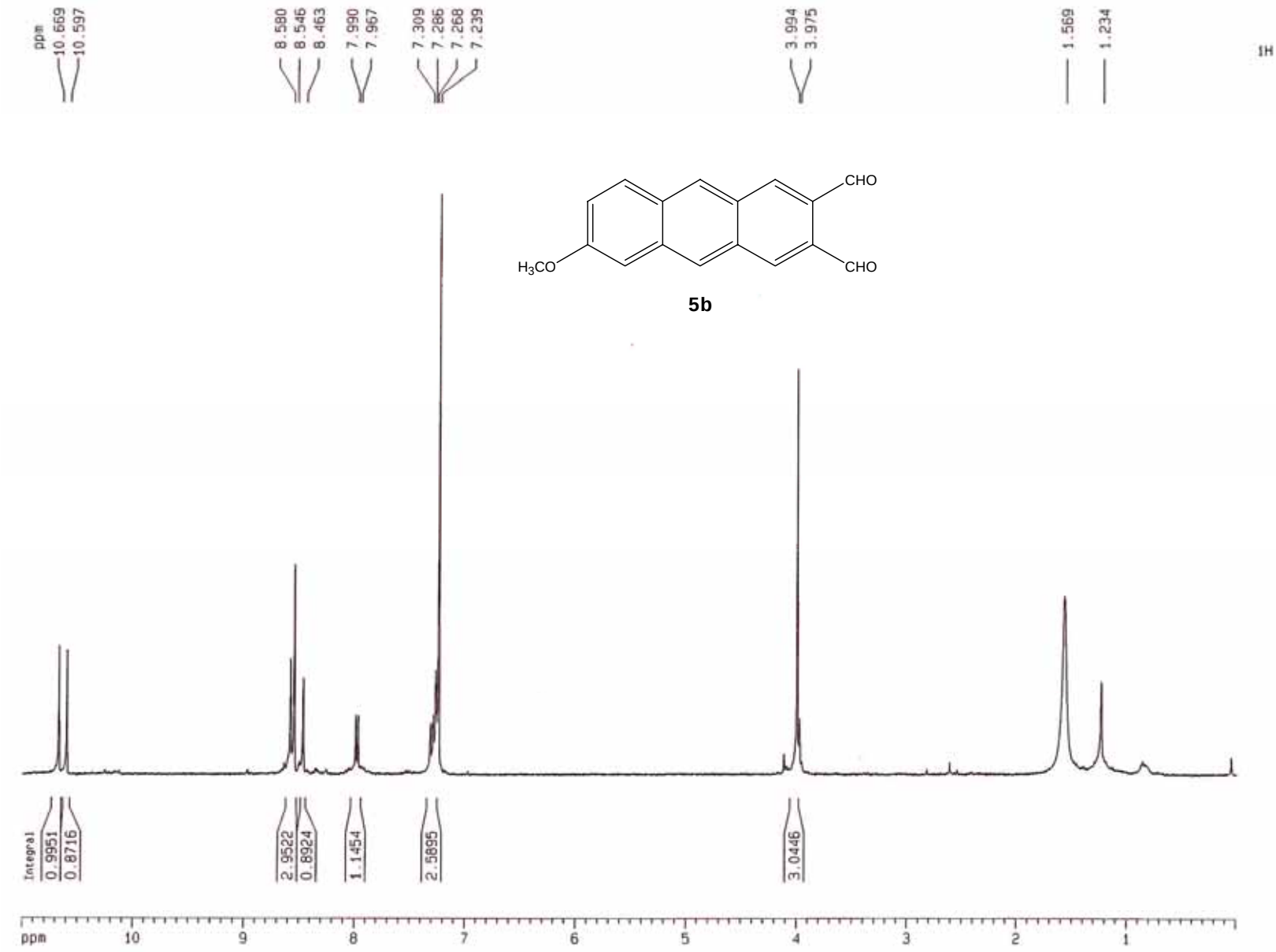
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



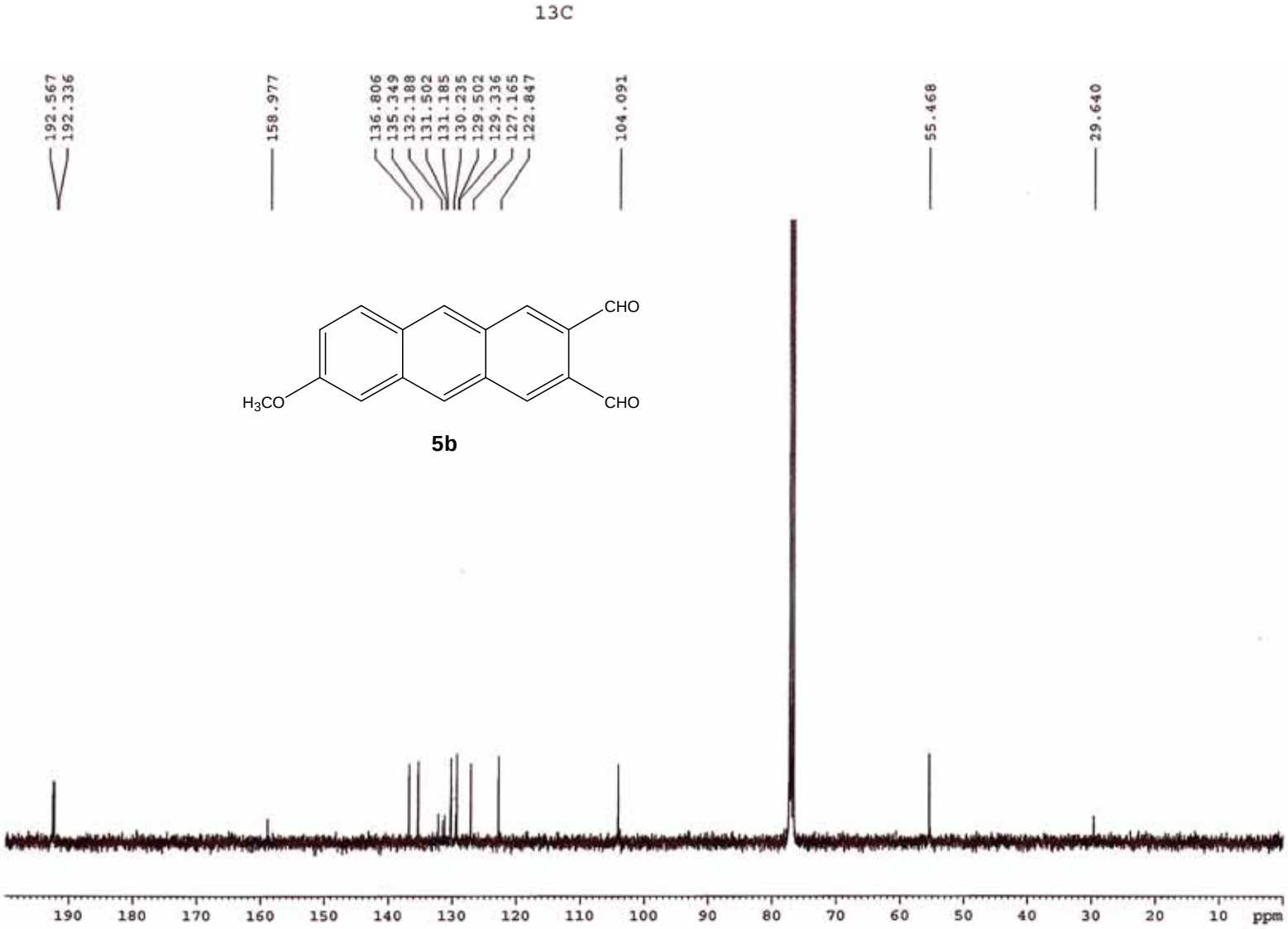
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



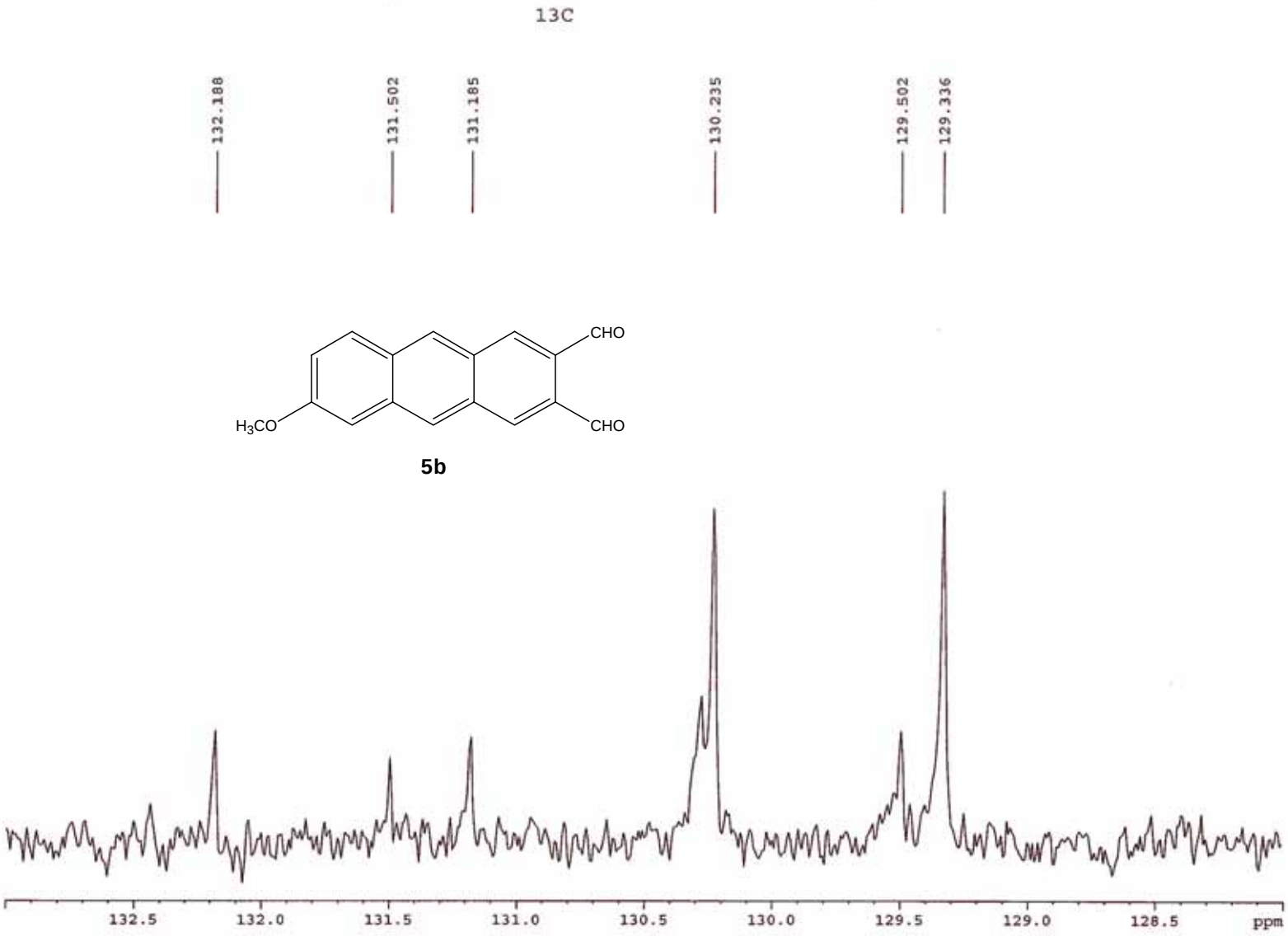
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



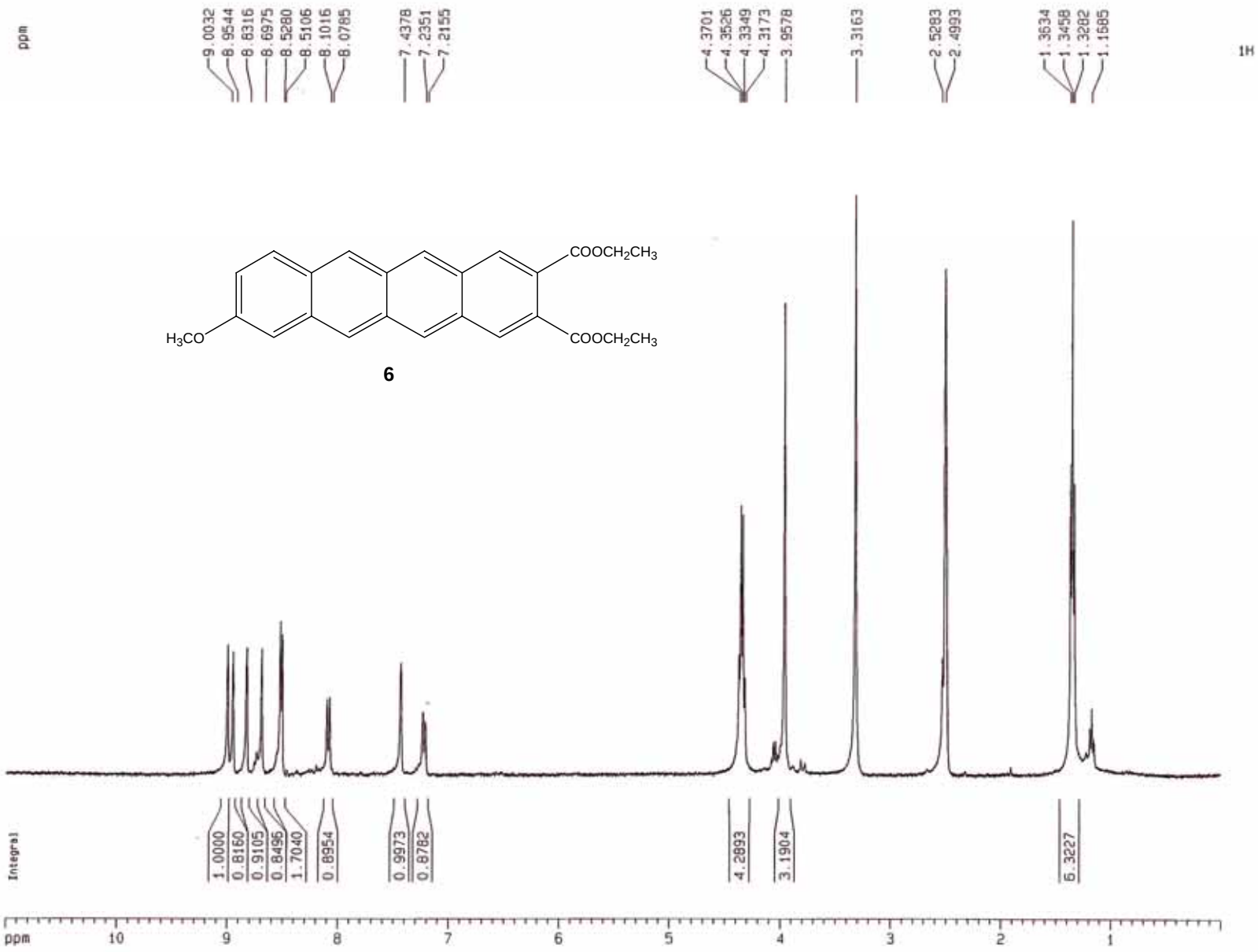
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



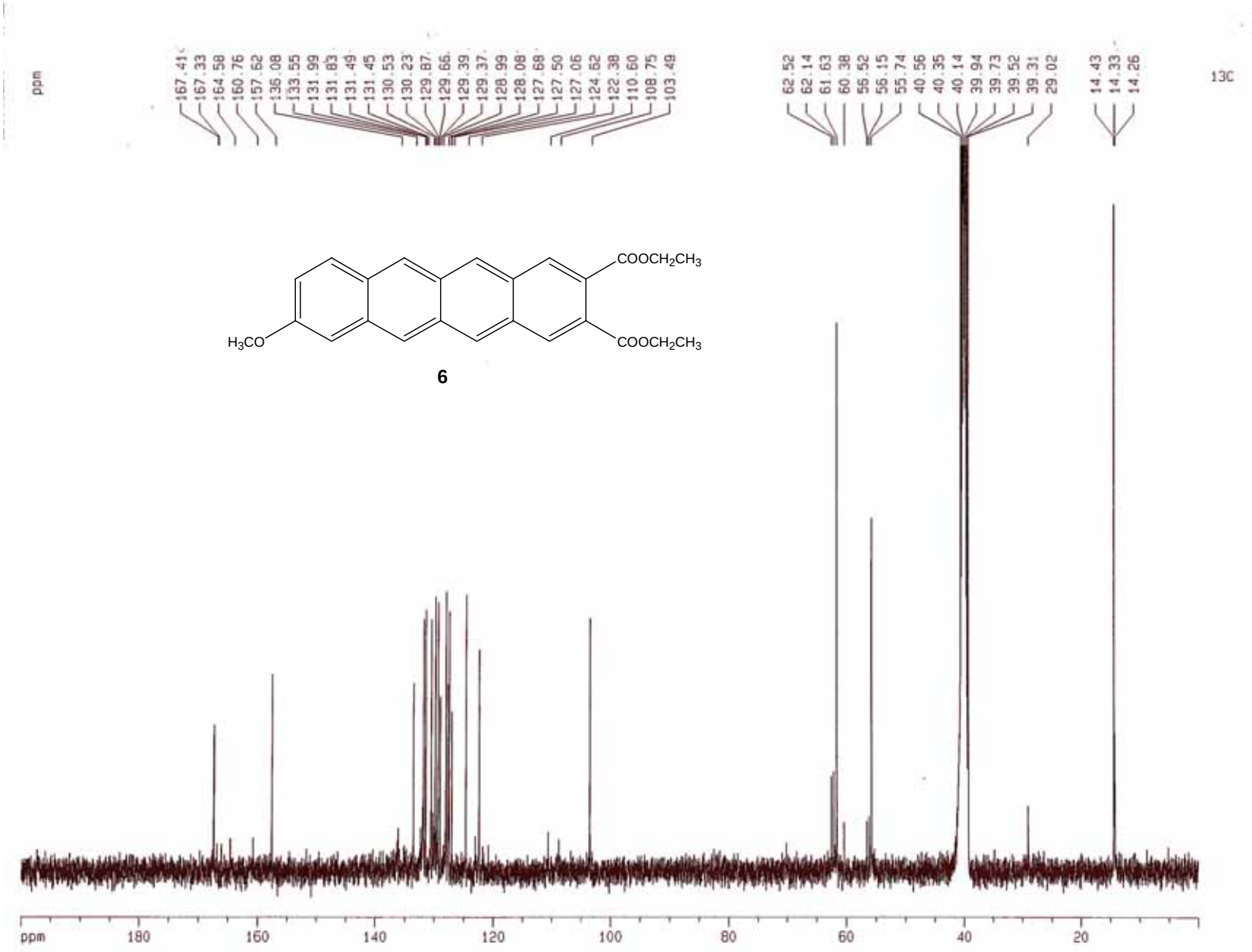
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



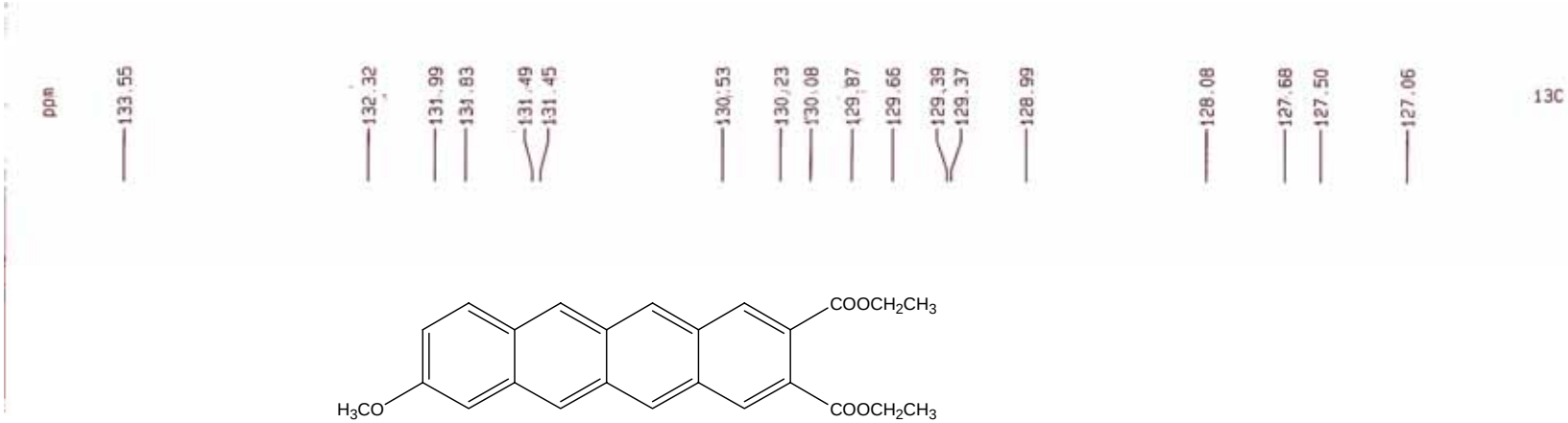
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



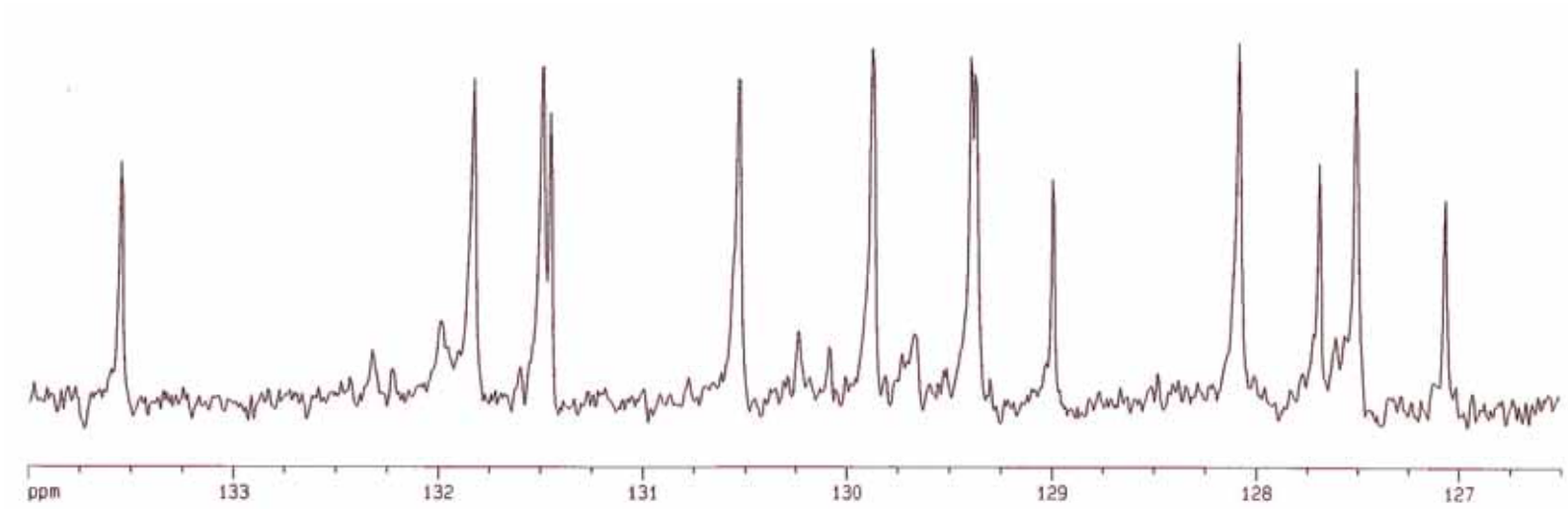
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



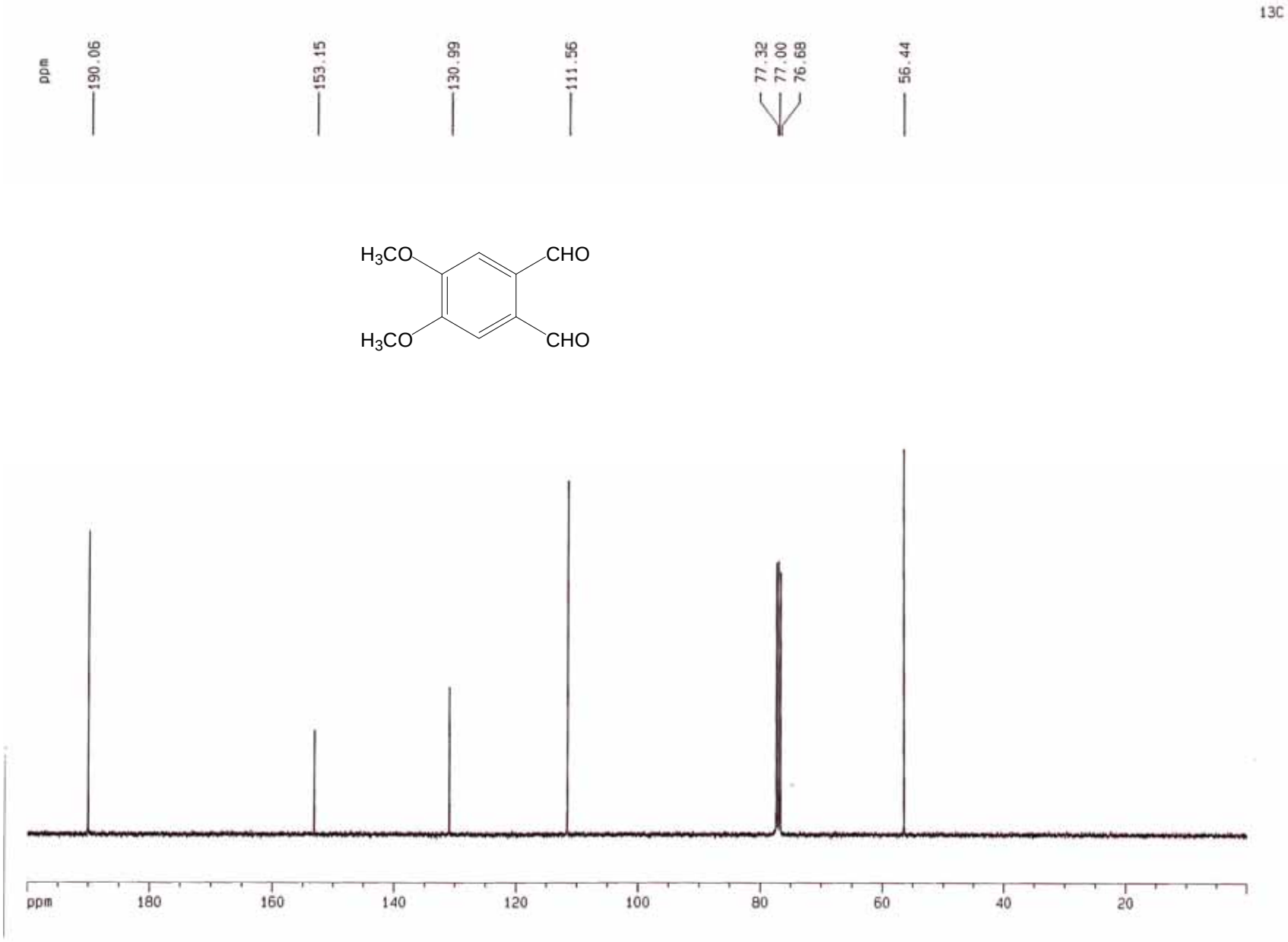
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



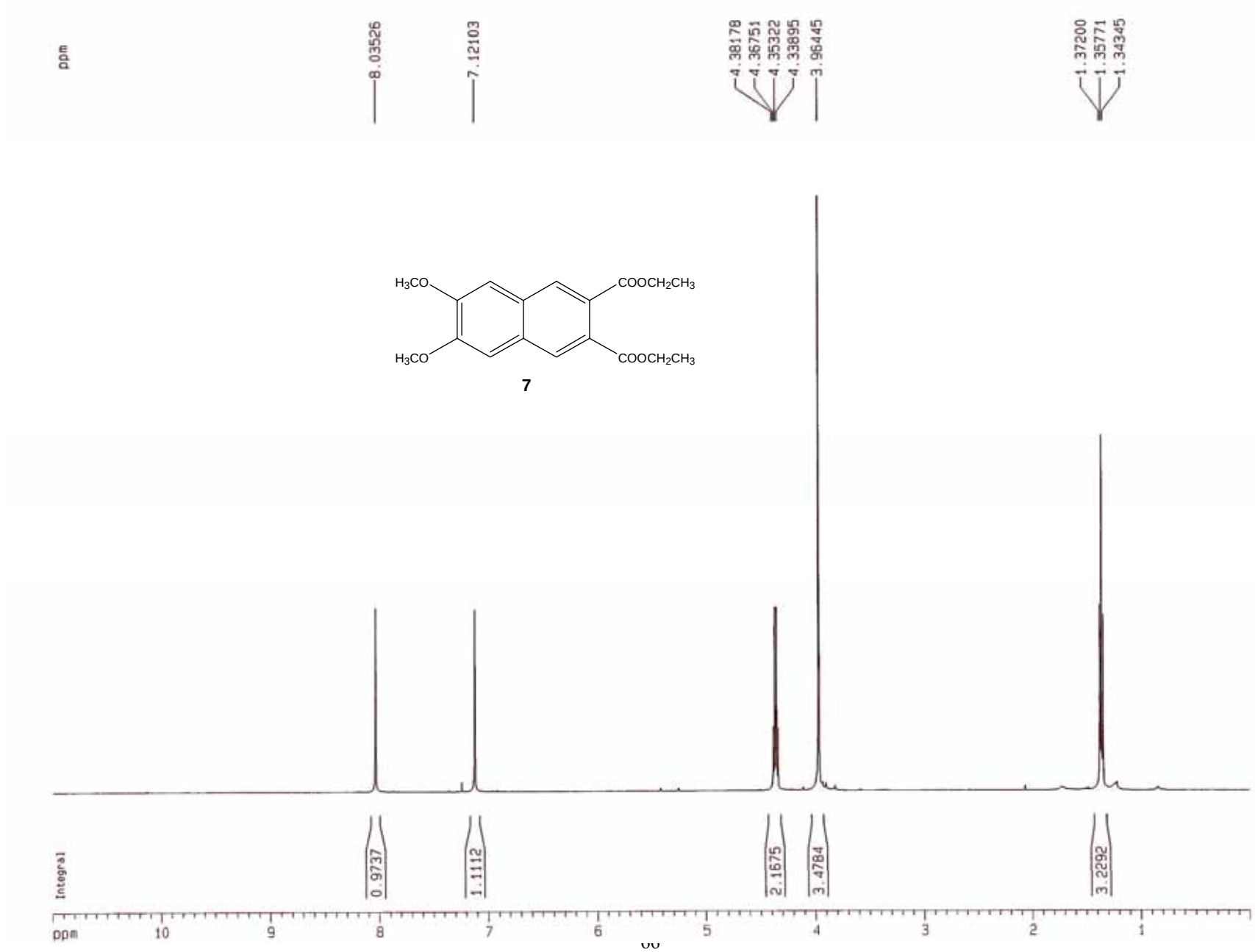
6



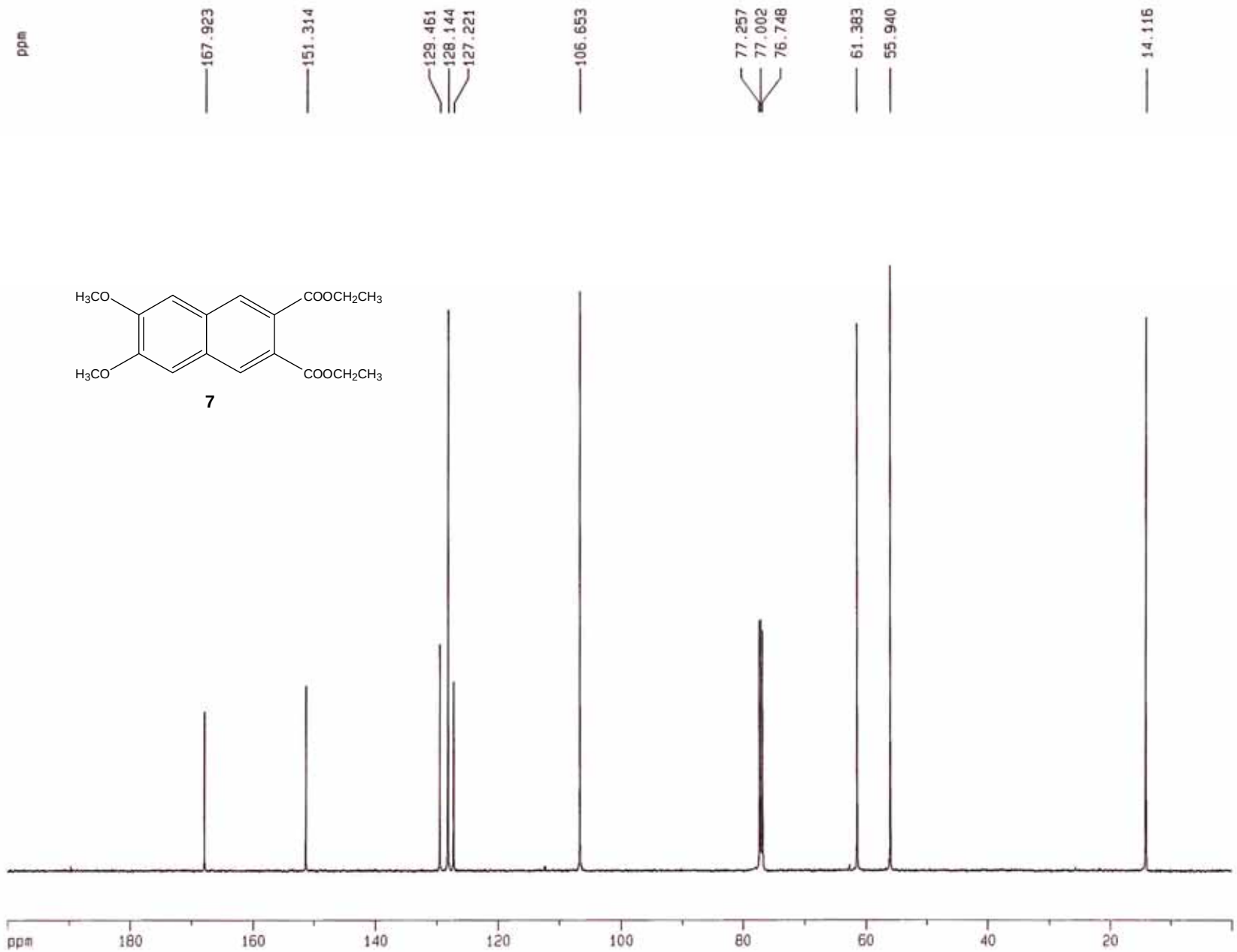
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



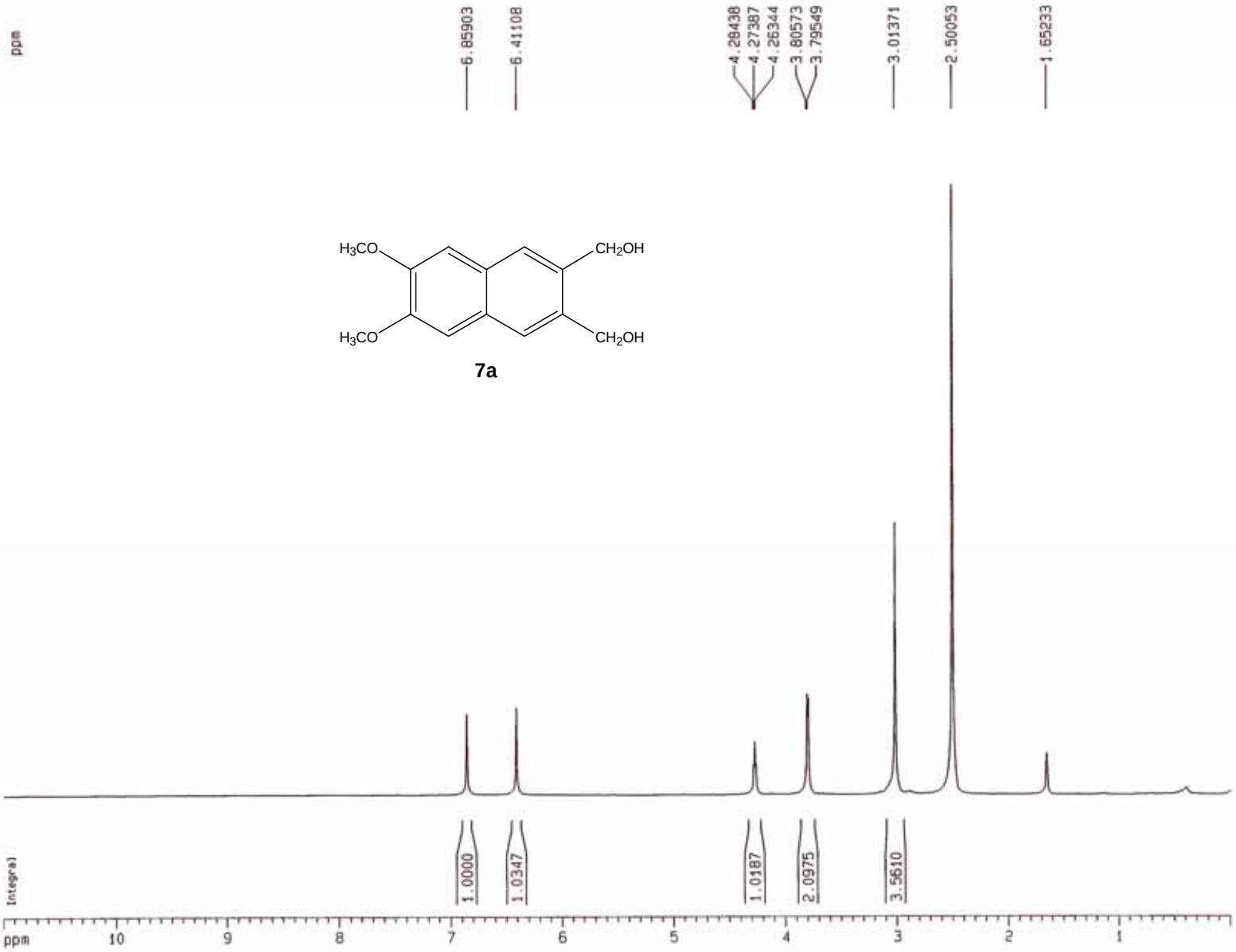
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



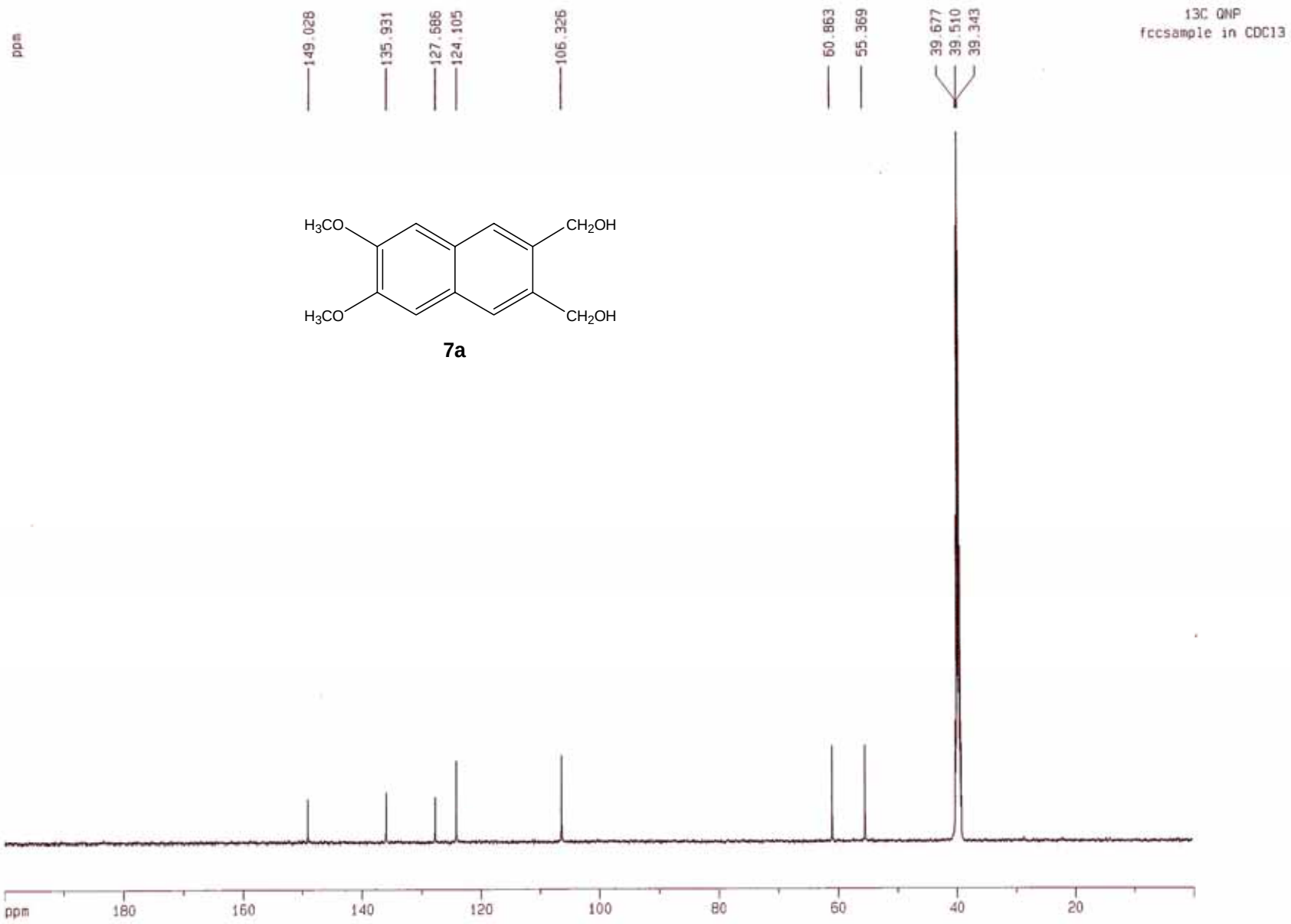
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



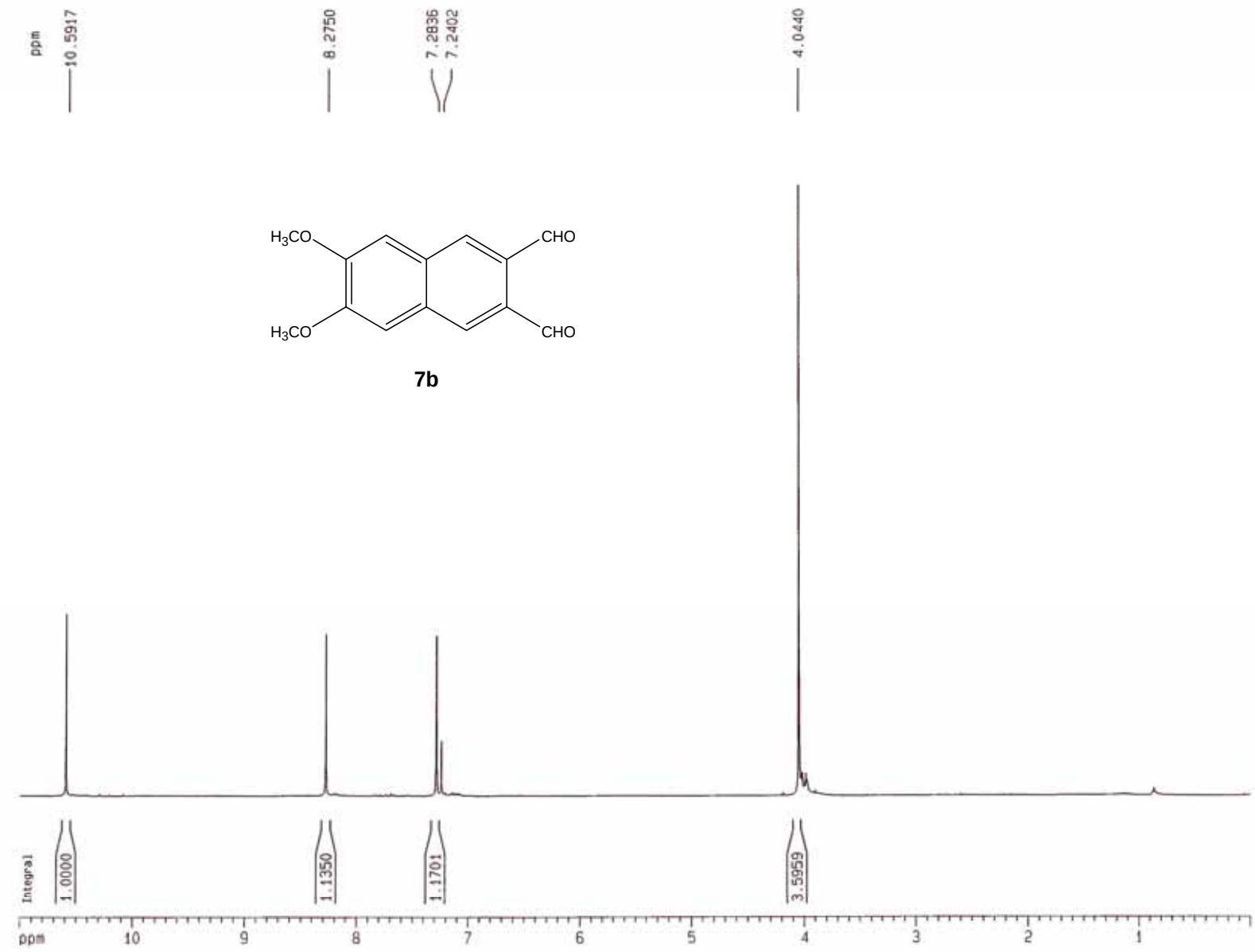
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



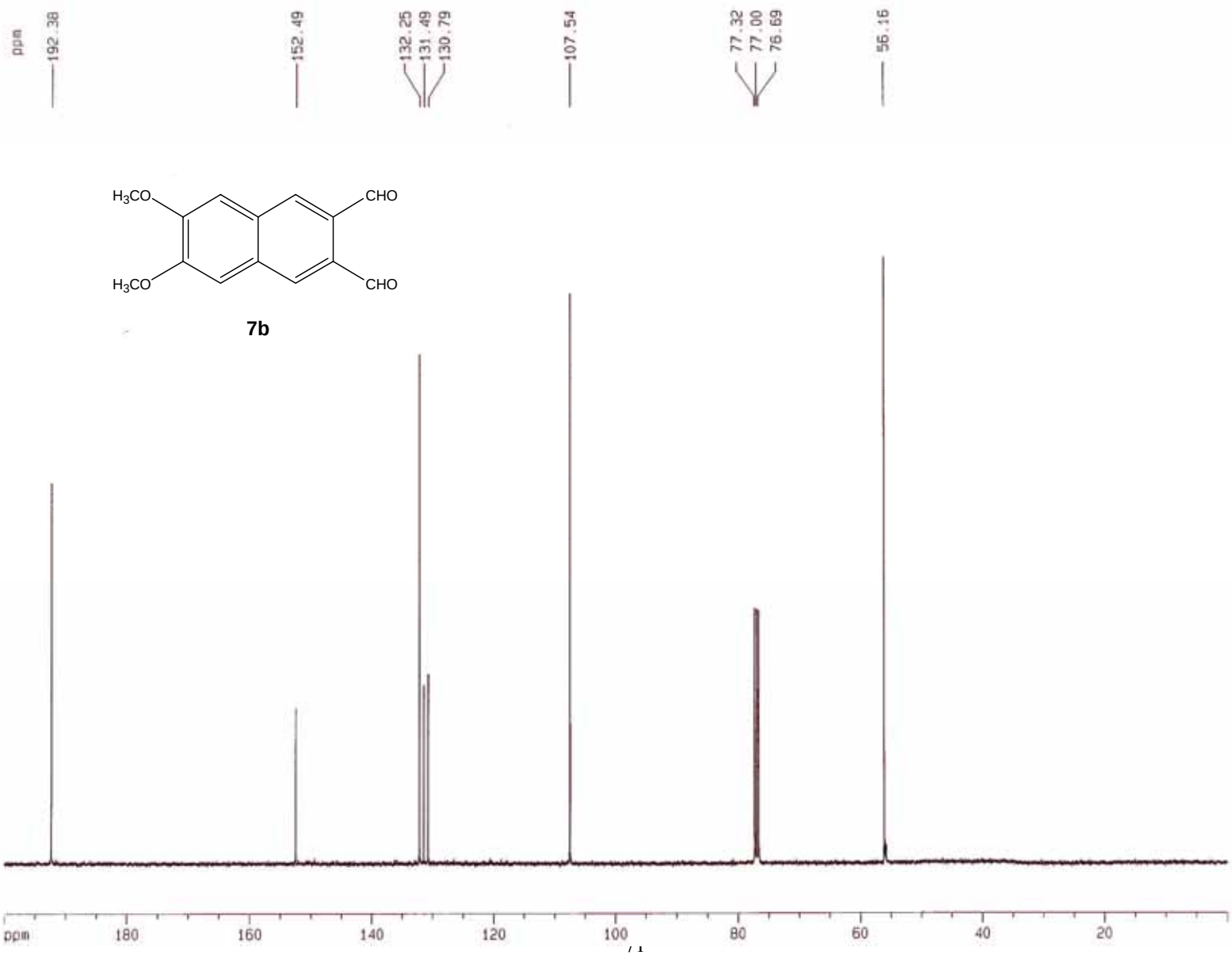
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

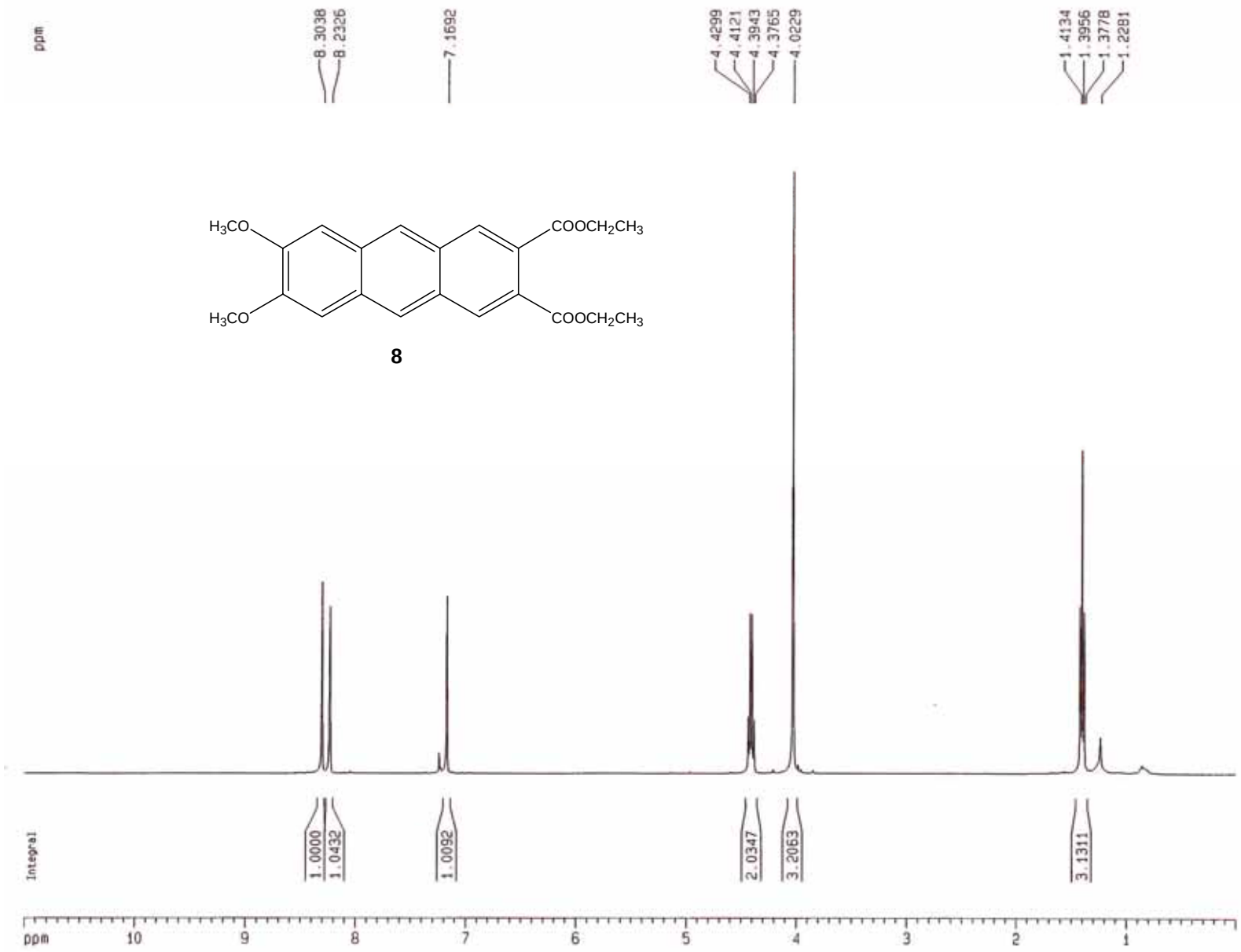


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

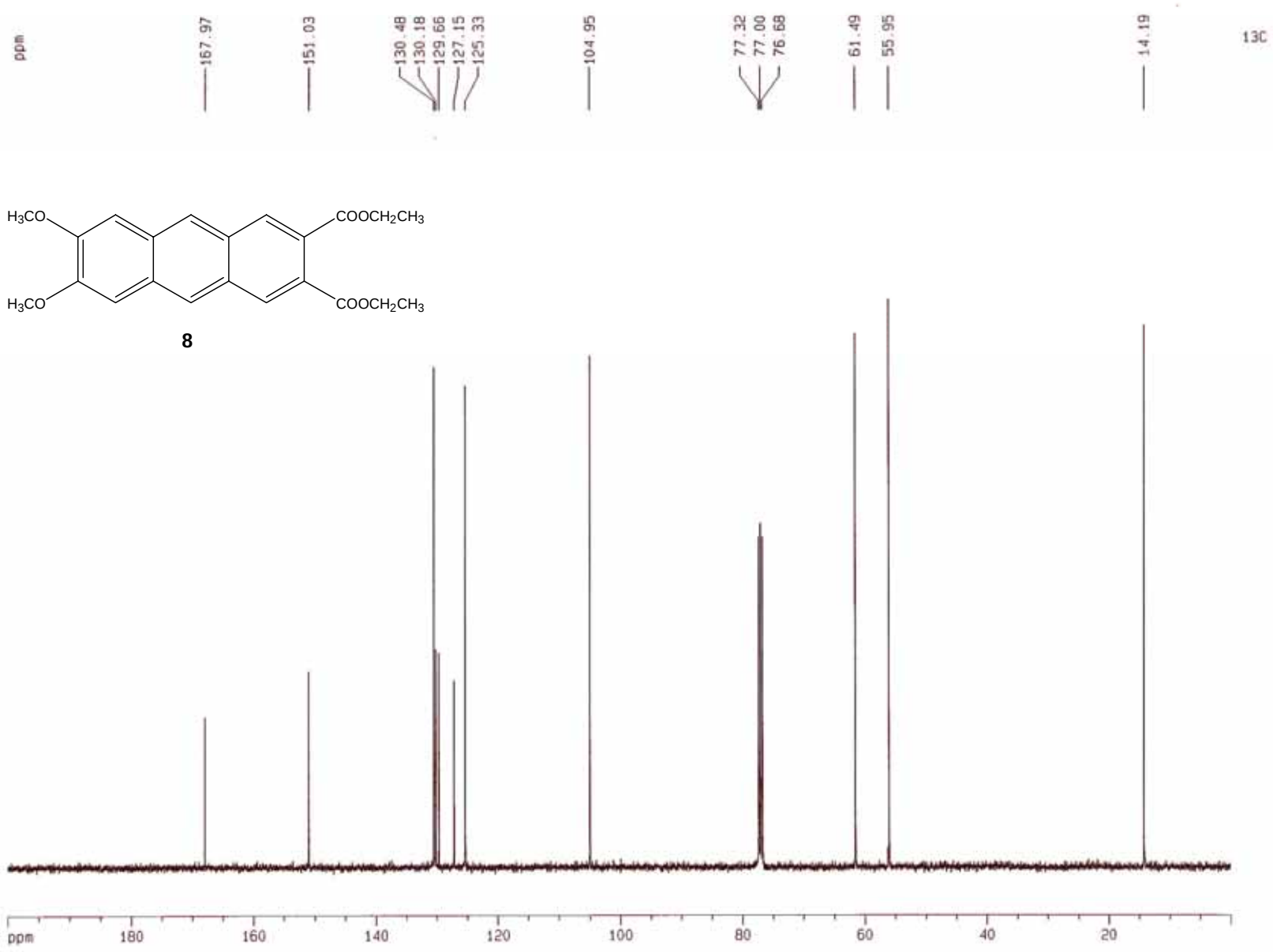


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

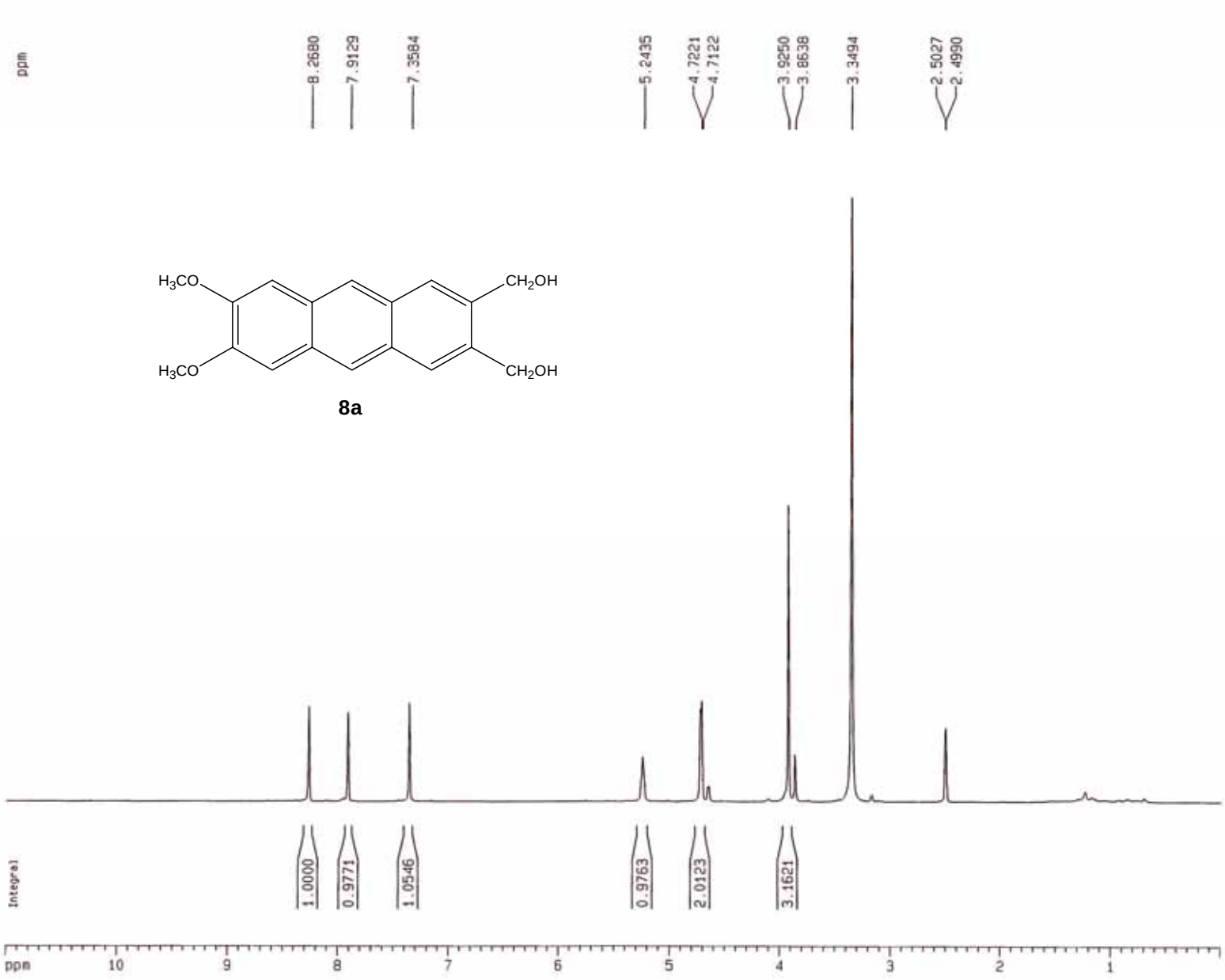

ppm
192.38
152.49
132.25
131.49
130.79
107.54
77.32
77.00
76.69
56.16
H3CO
CHO
H3CO
CHO
7b
ppm
180
160
140
120
100
80
60
40
20



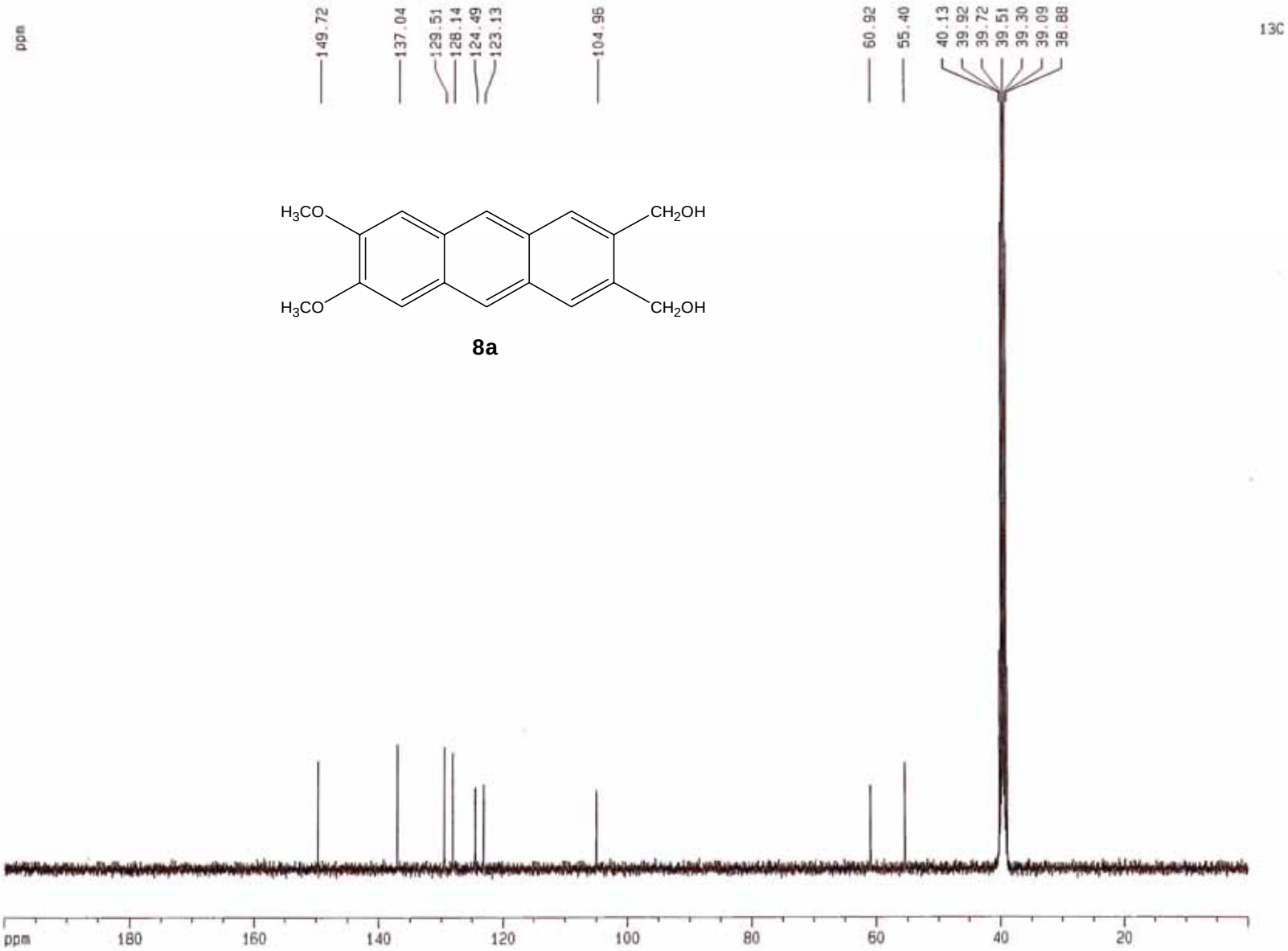
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



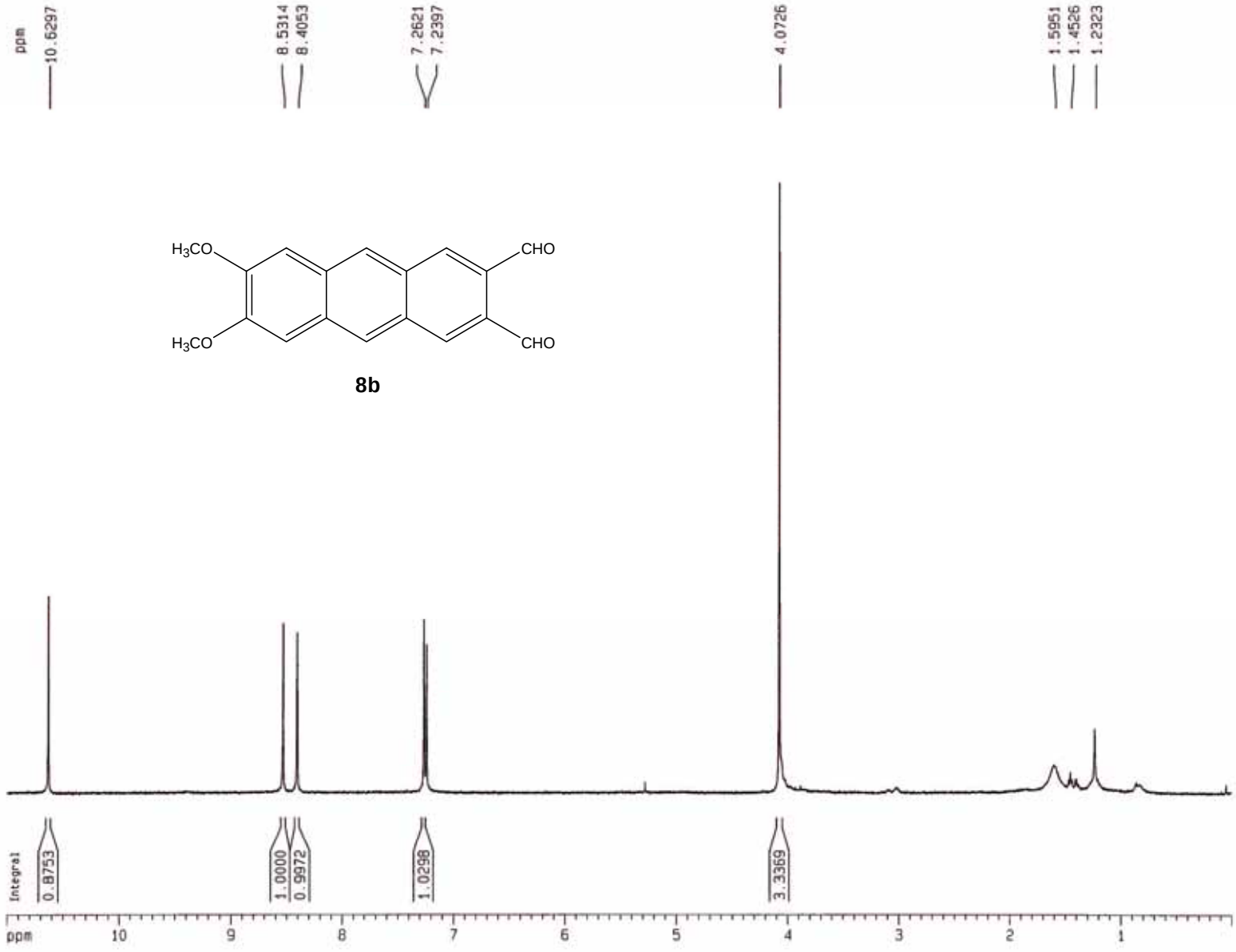
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



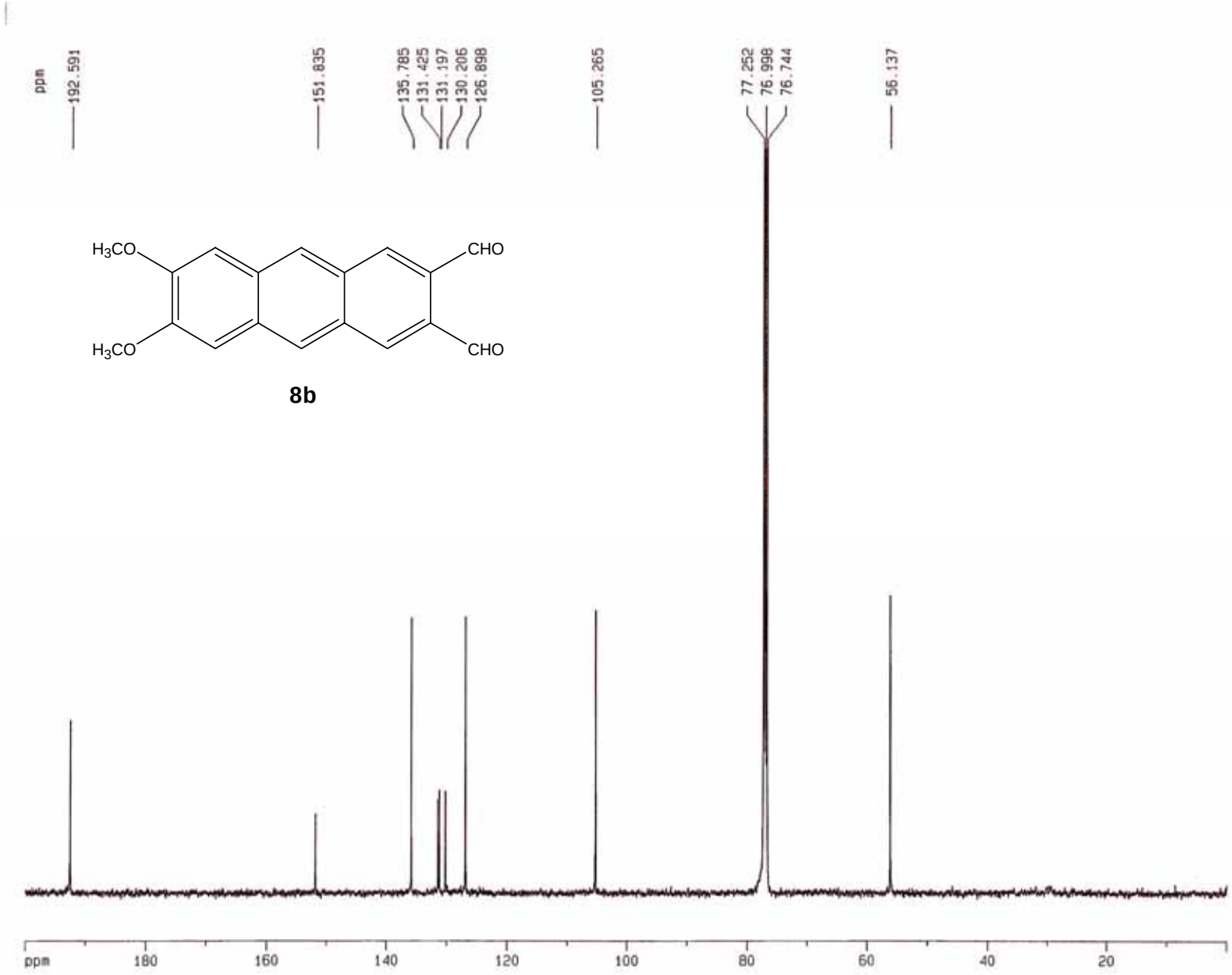
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



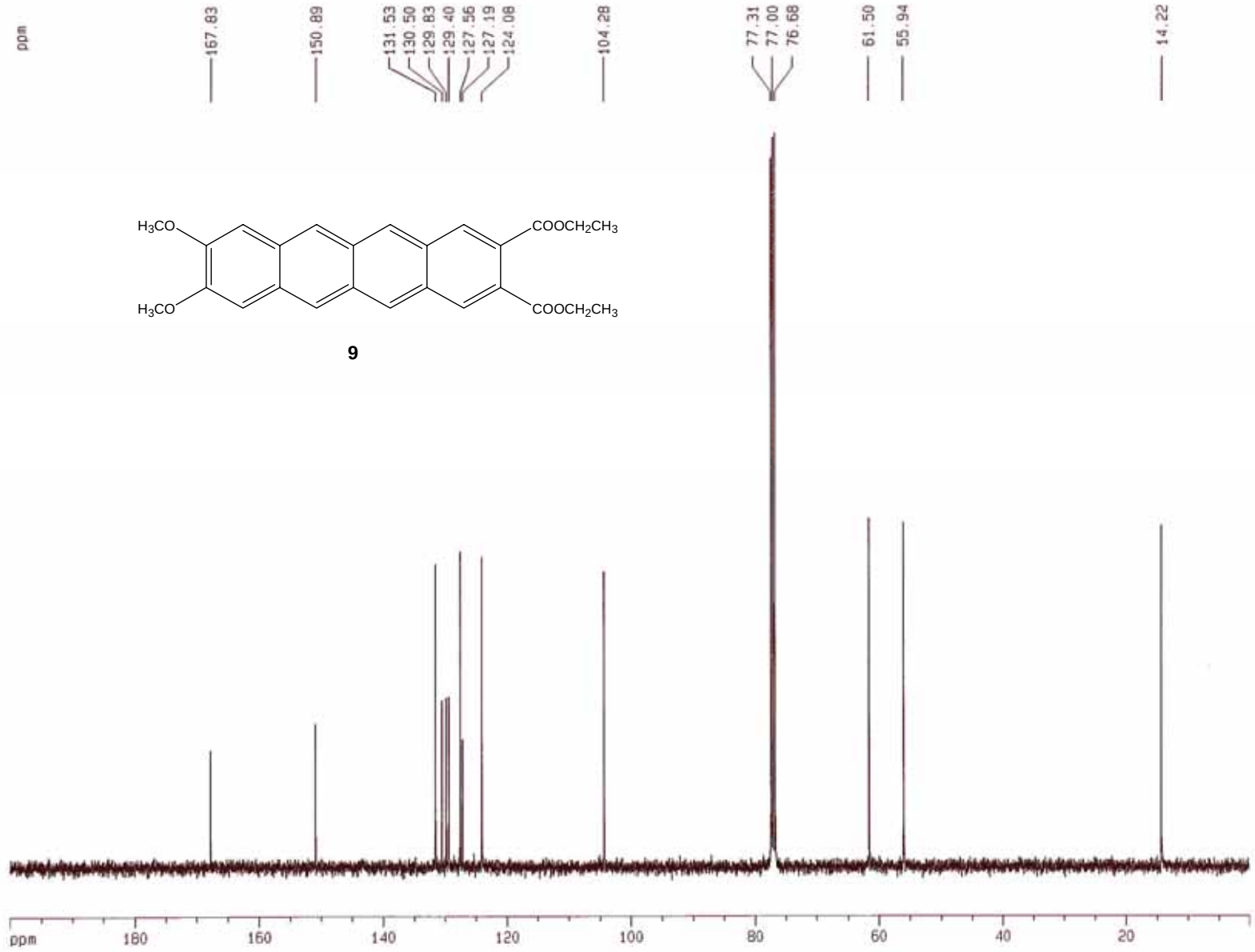
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



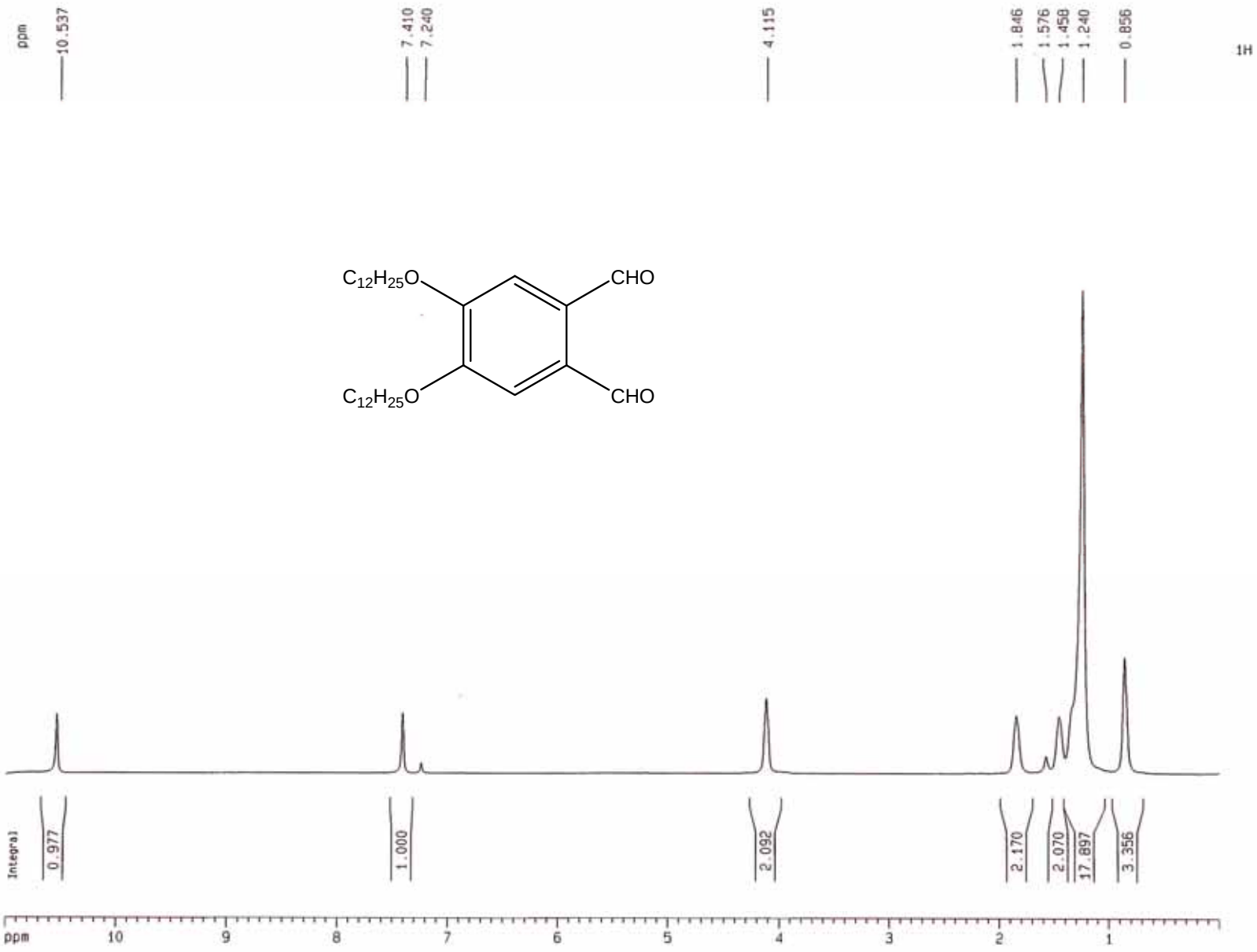
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY


ppm
192.591
151.835
135.785
131.425
131.197
130.206
126.898
105.265
77.252
76.998
76.744
56.137
H3CO
CHO
H3CO
CHO
8b
ppm
180
160
140
120
100
80
60
40
20

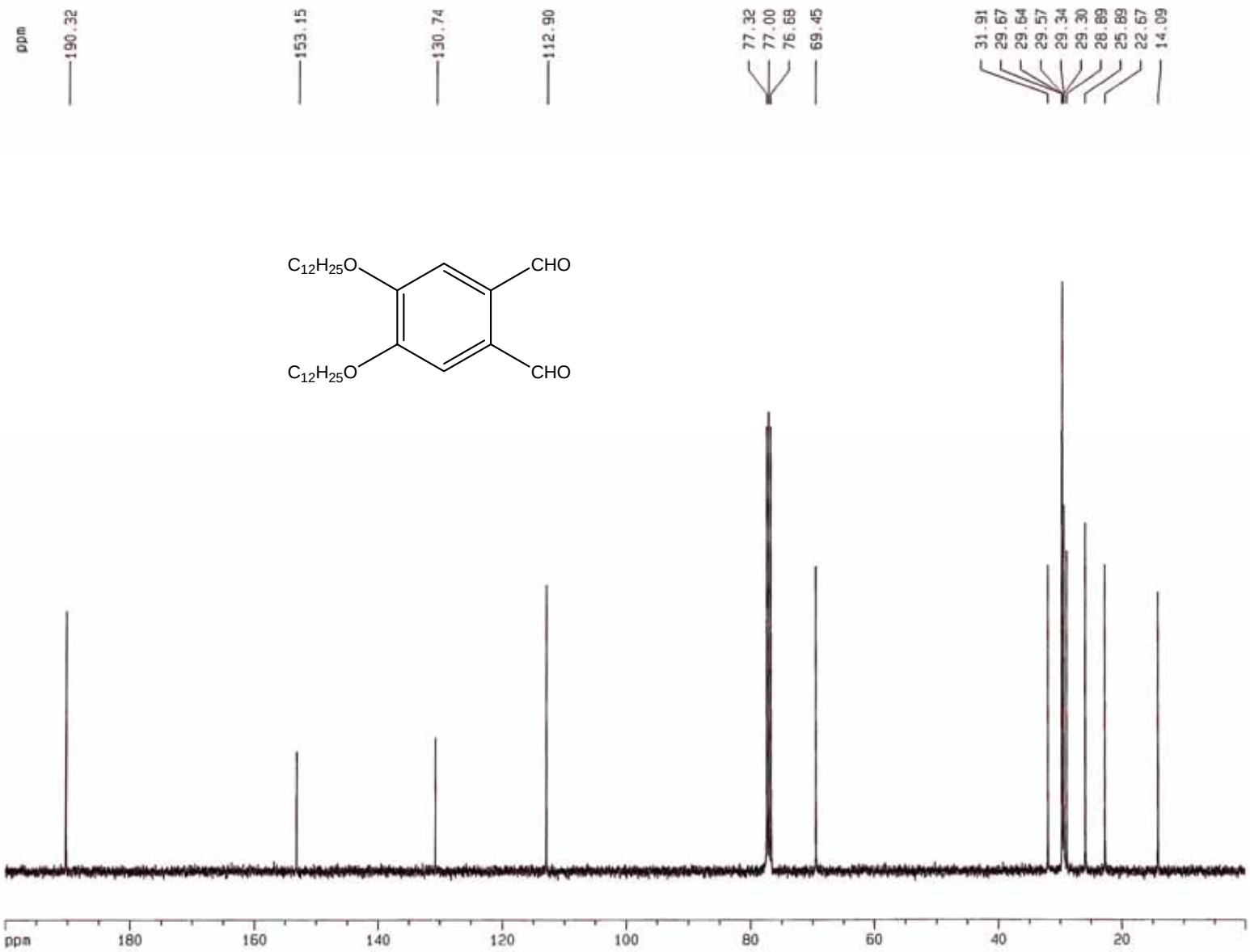
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



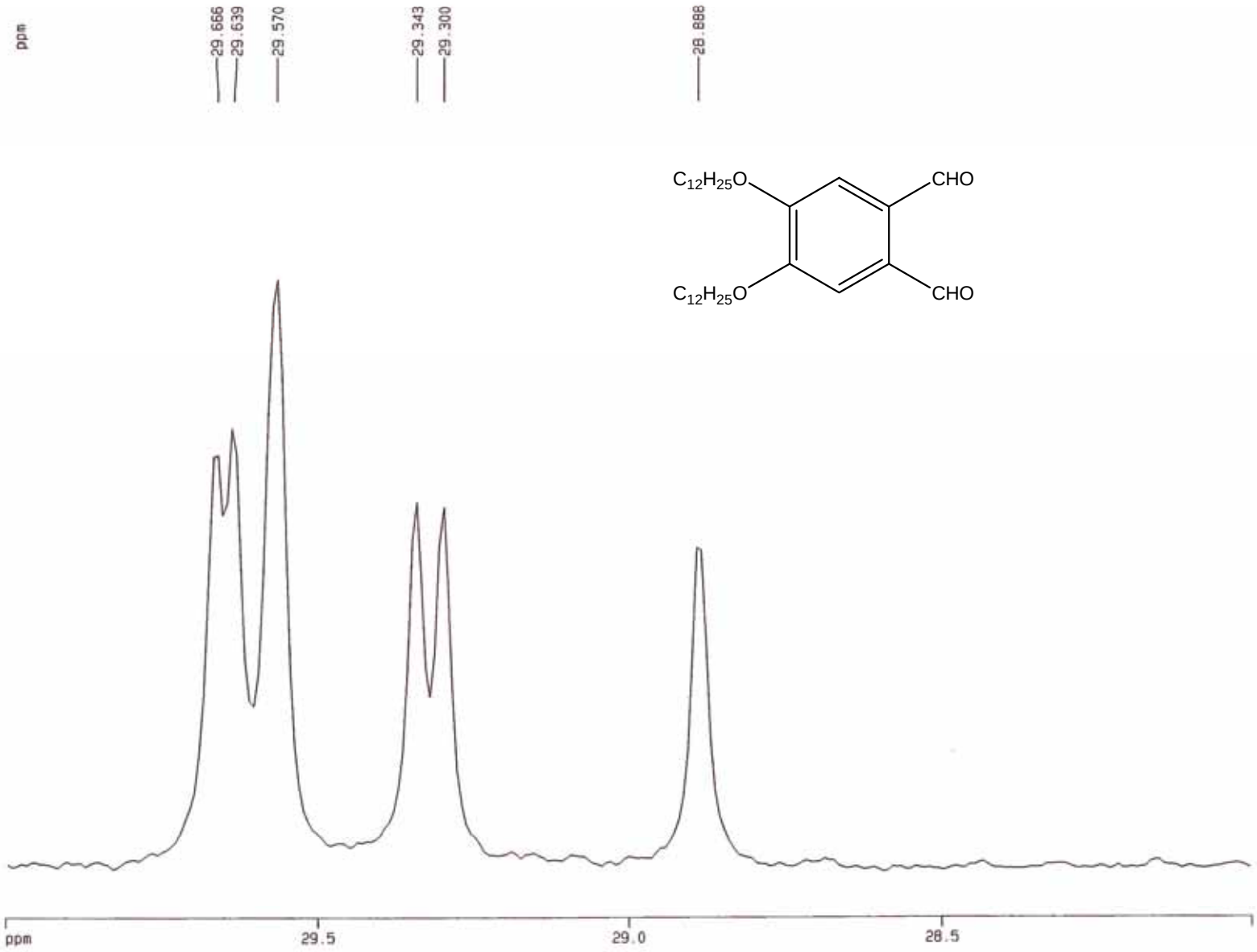
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

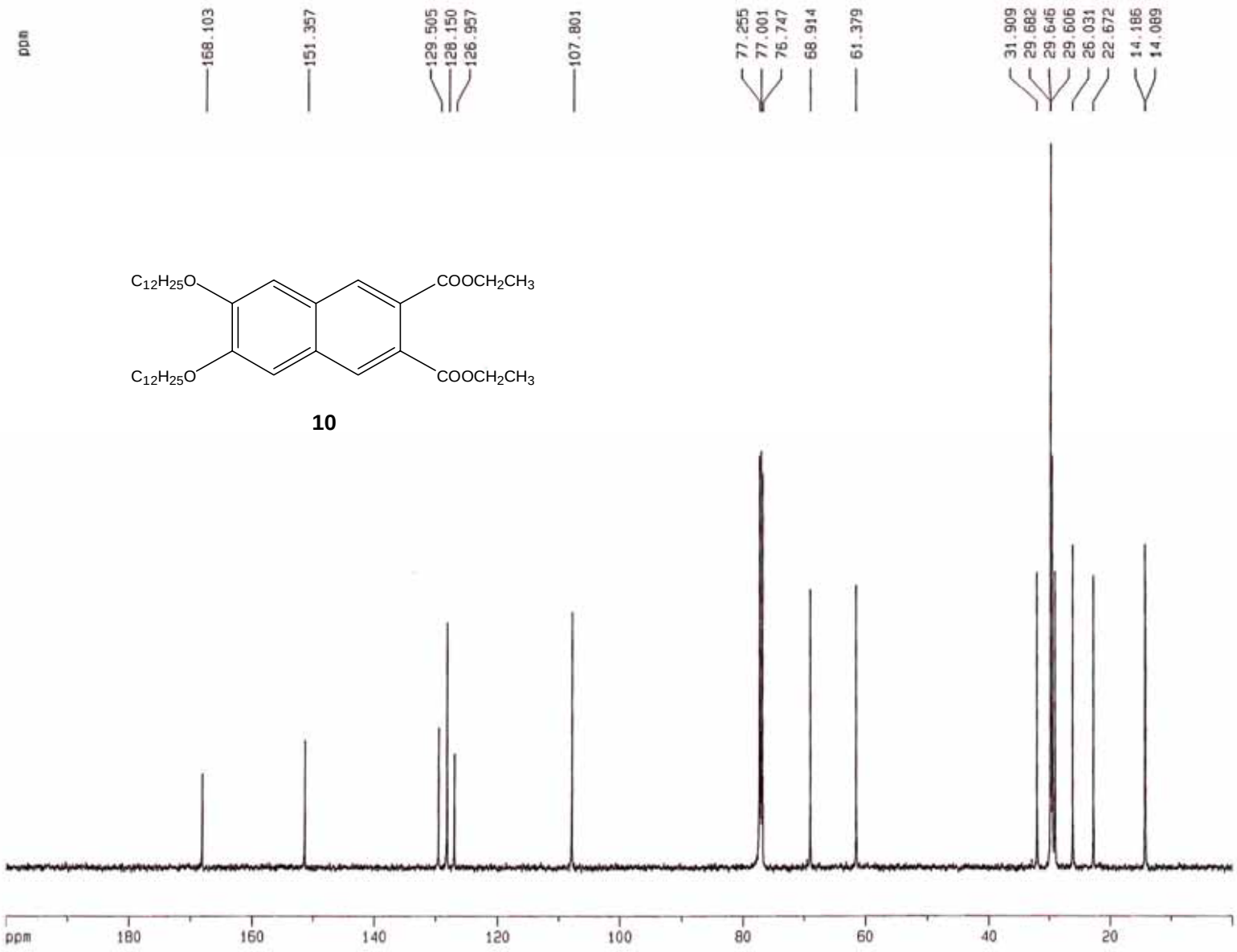


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

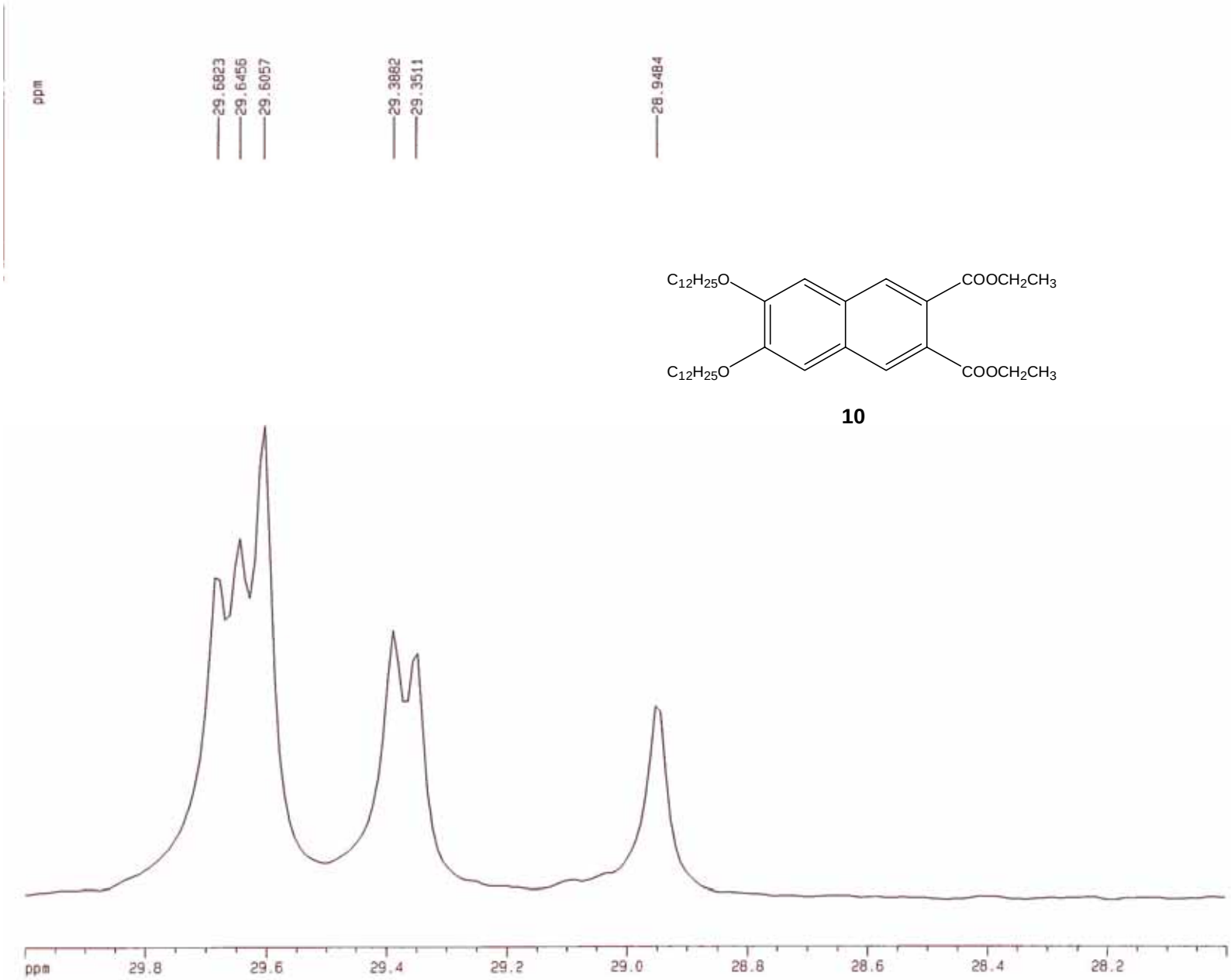


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

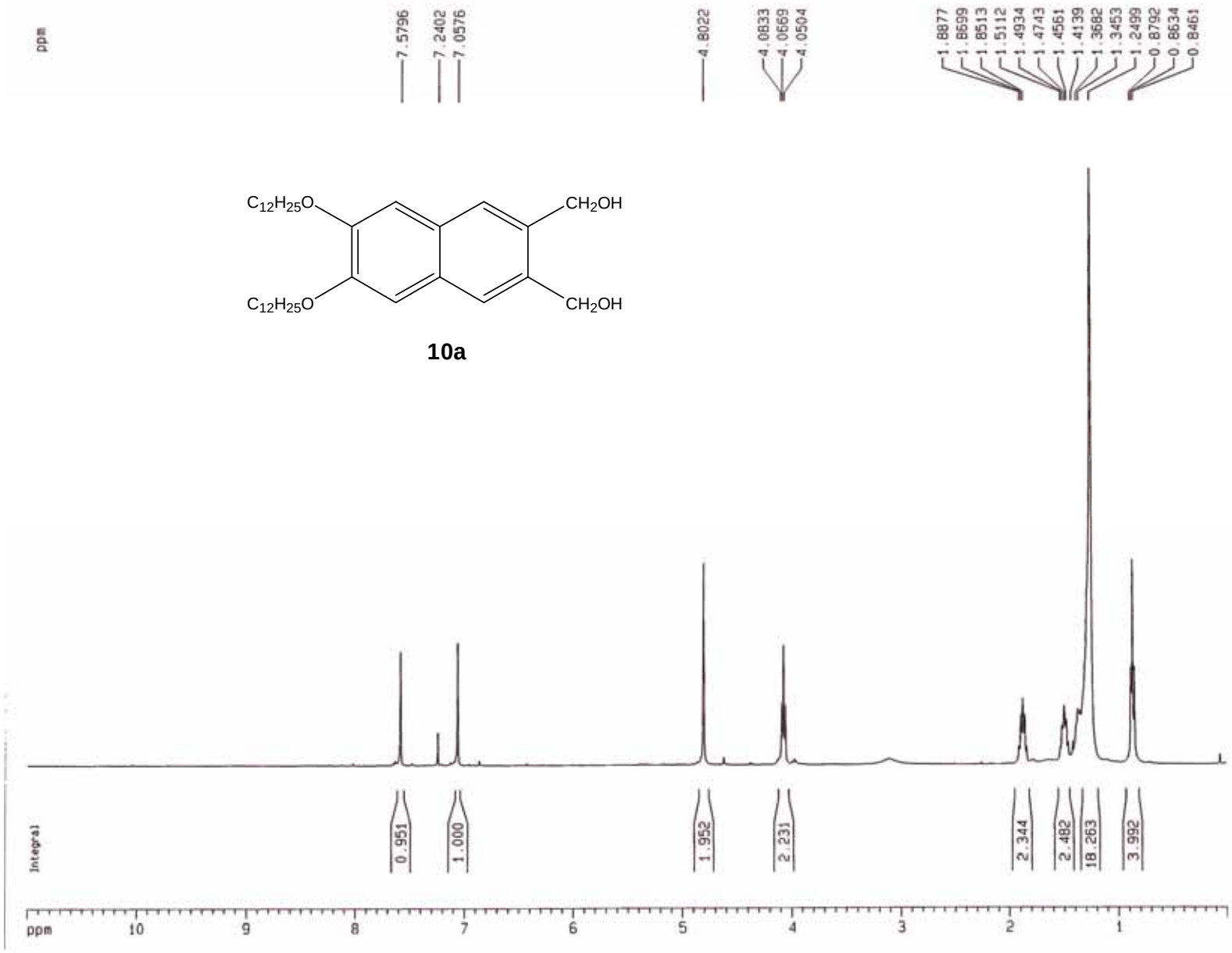


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

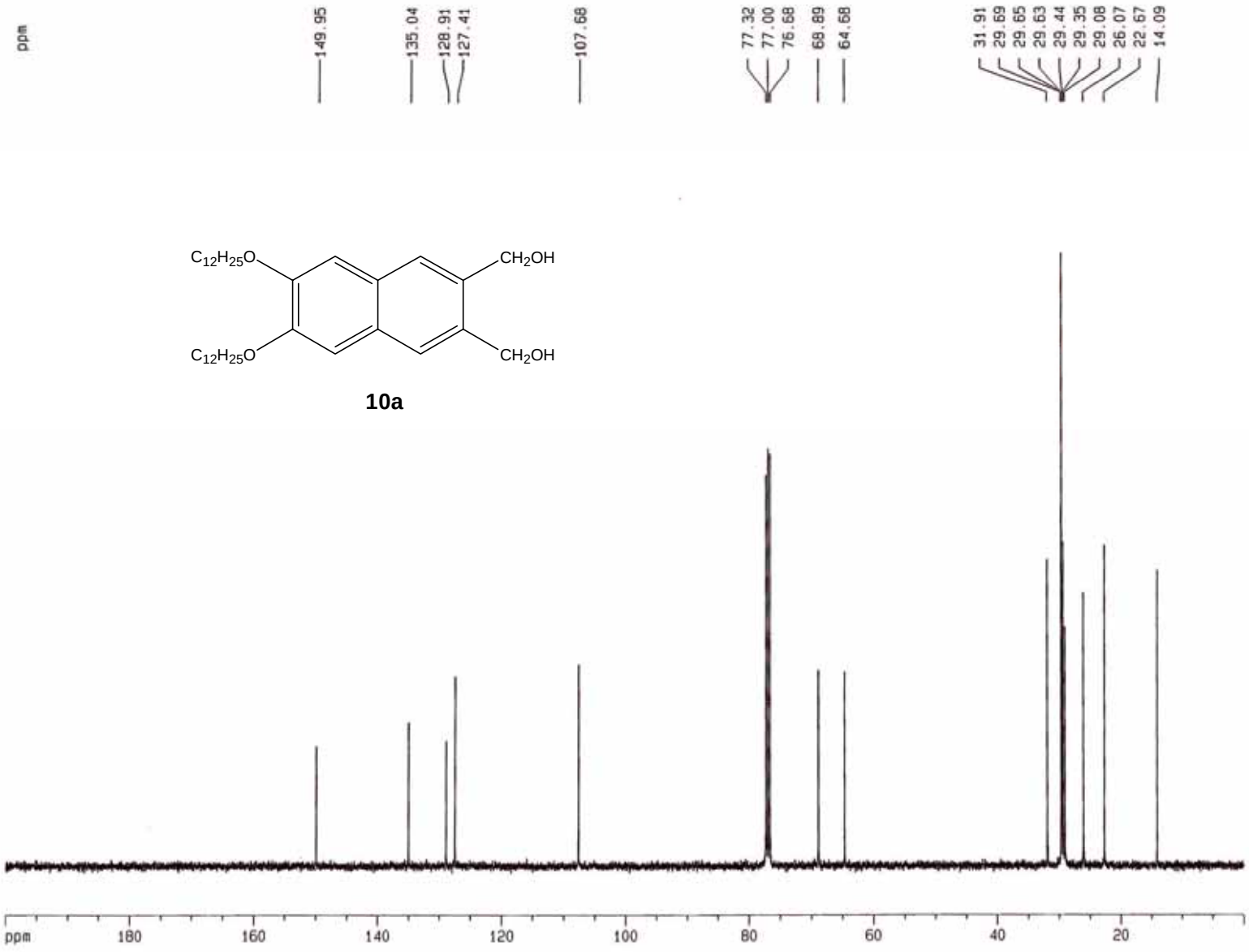


10

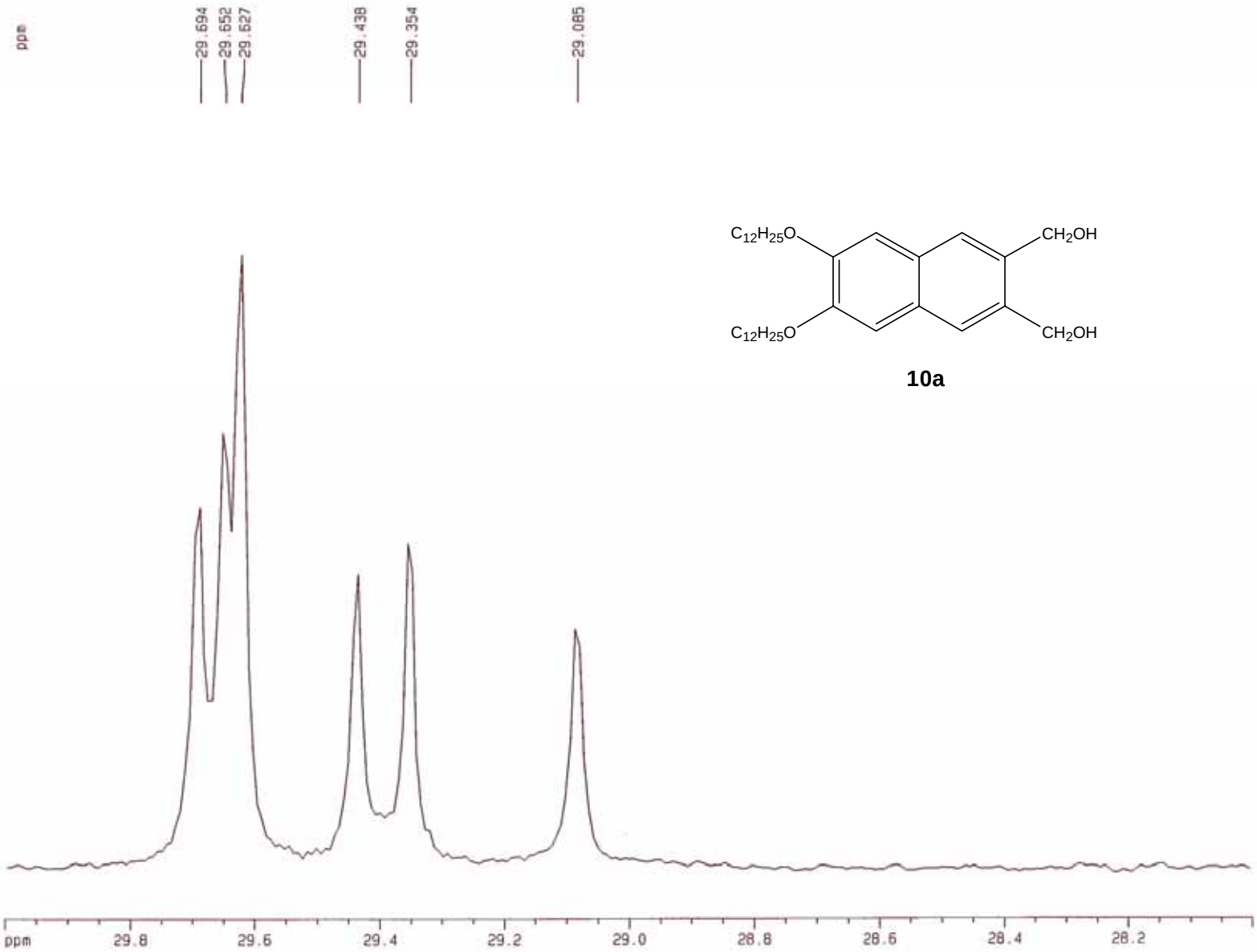
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

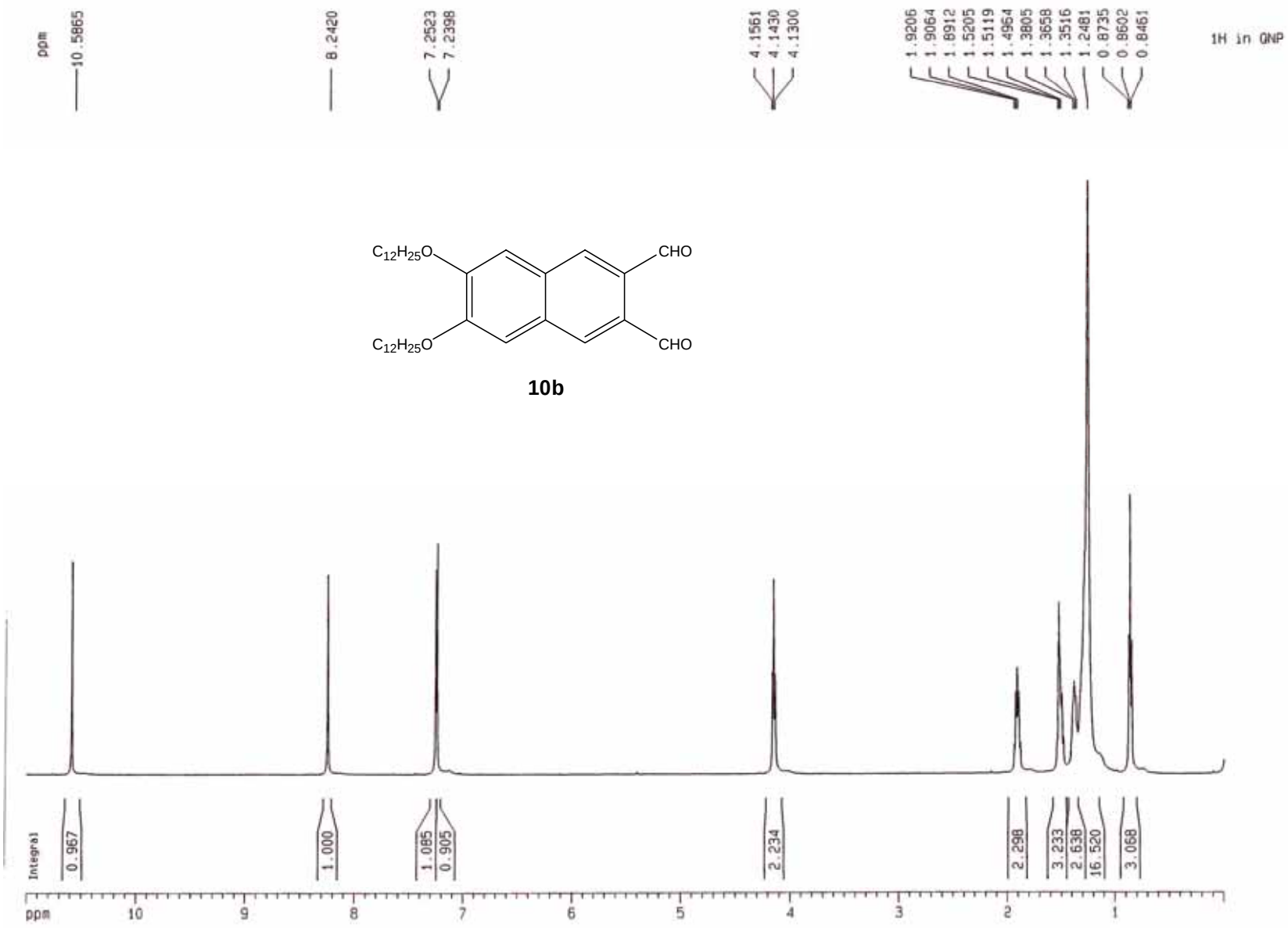


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

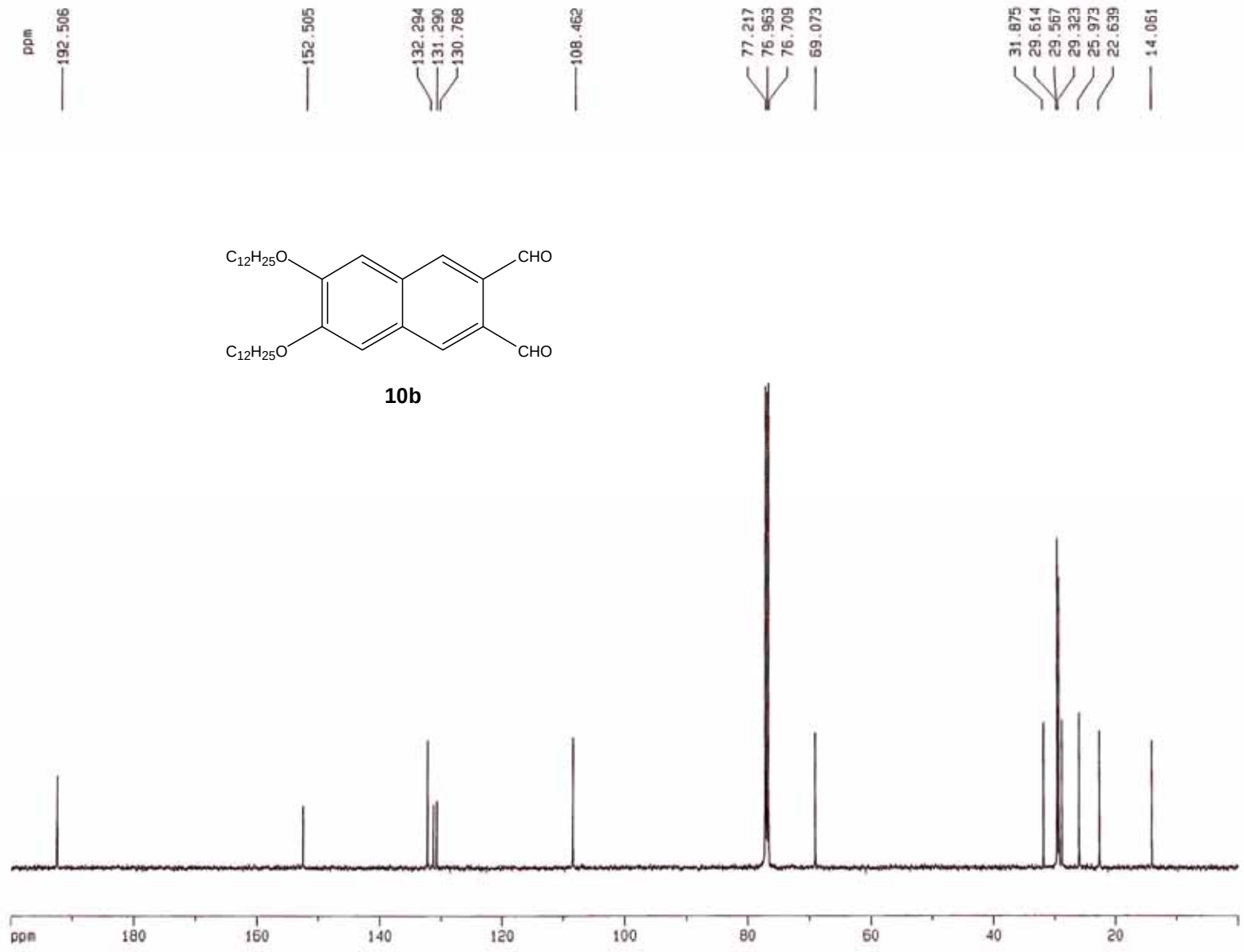


10a

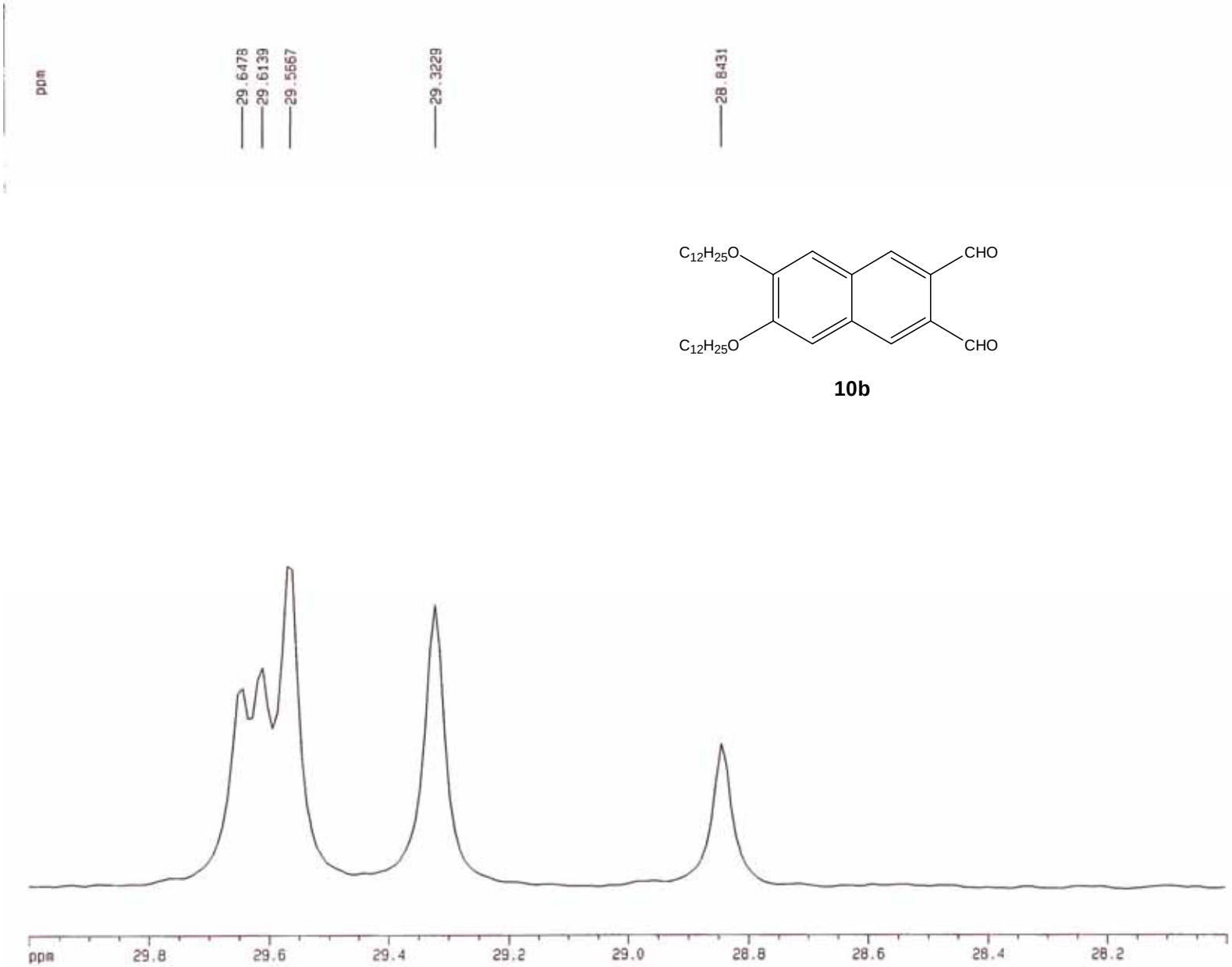
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

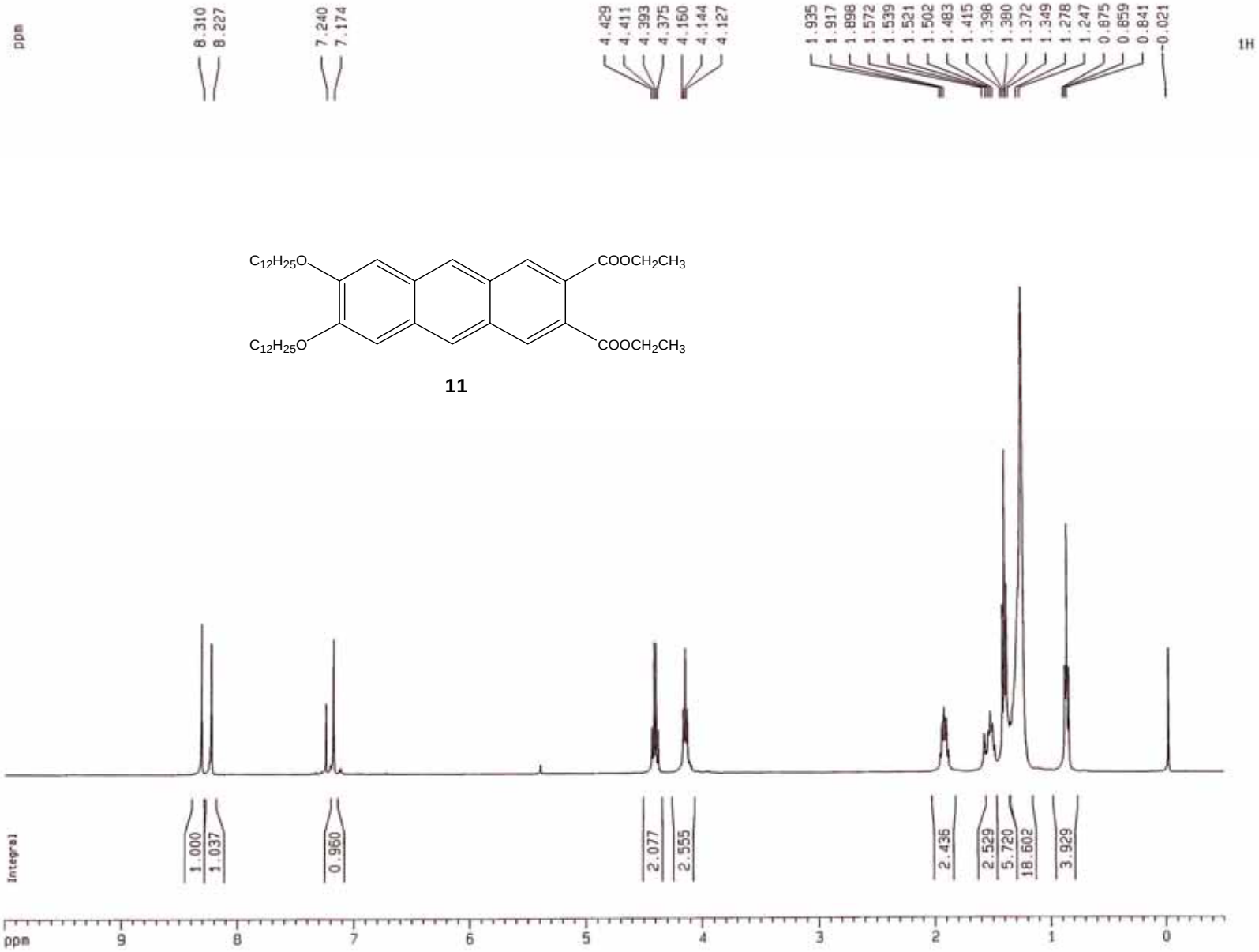


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

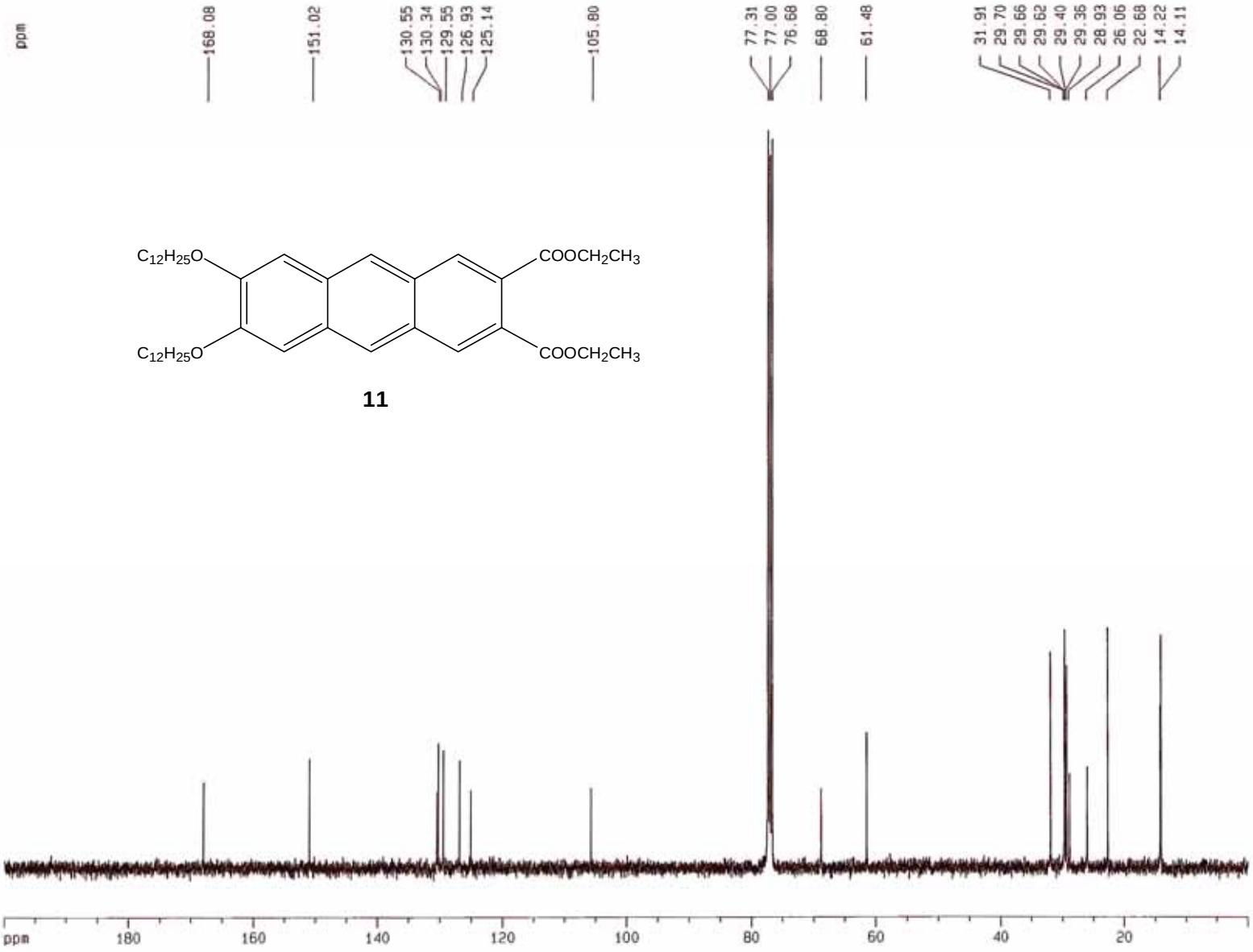


10b

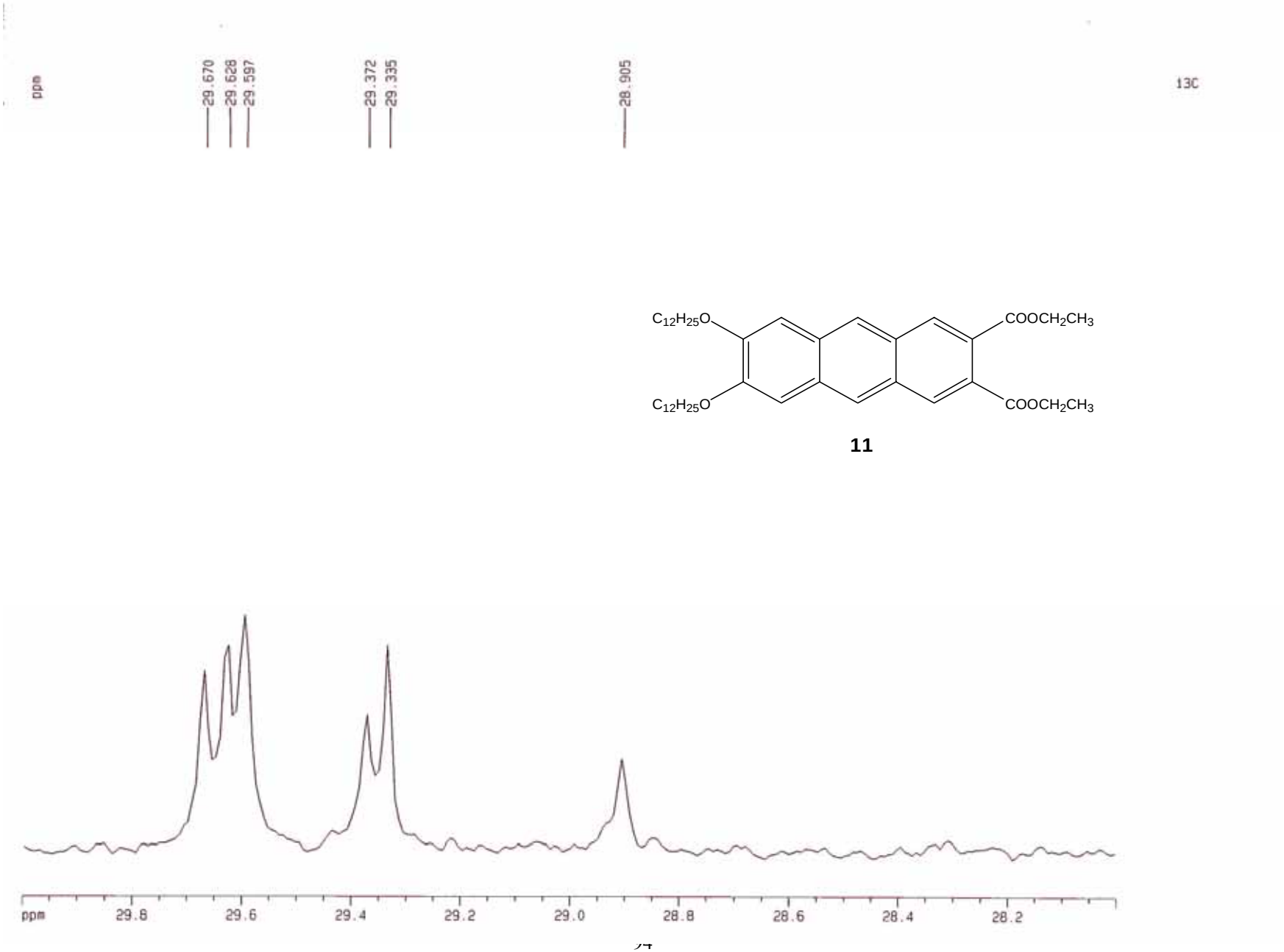
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

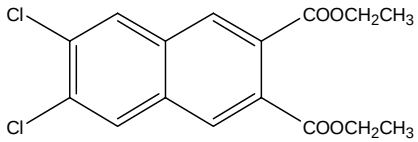


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

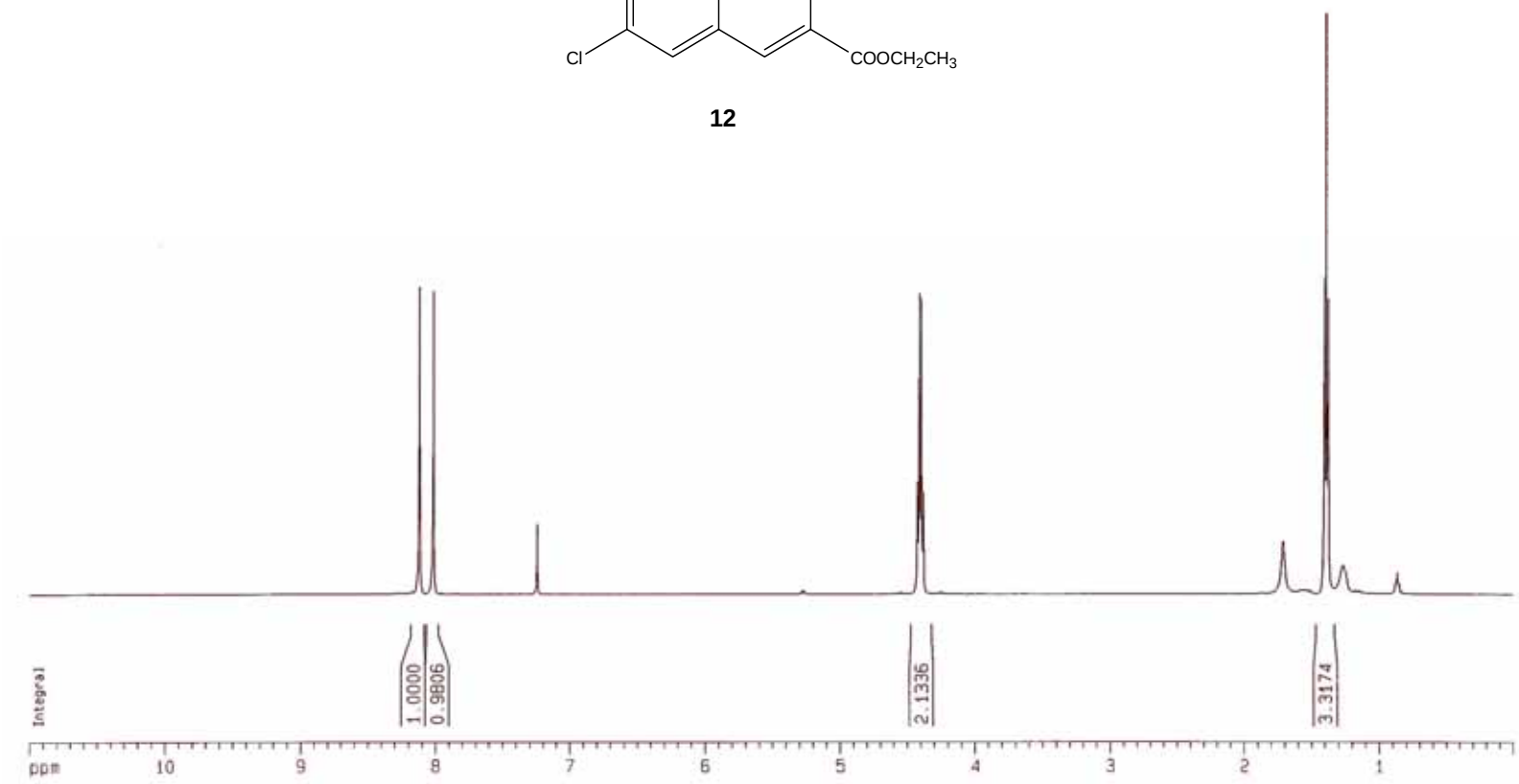


11

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

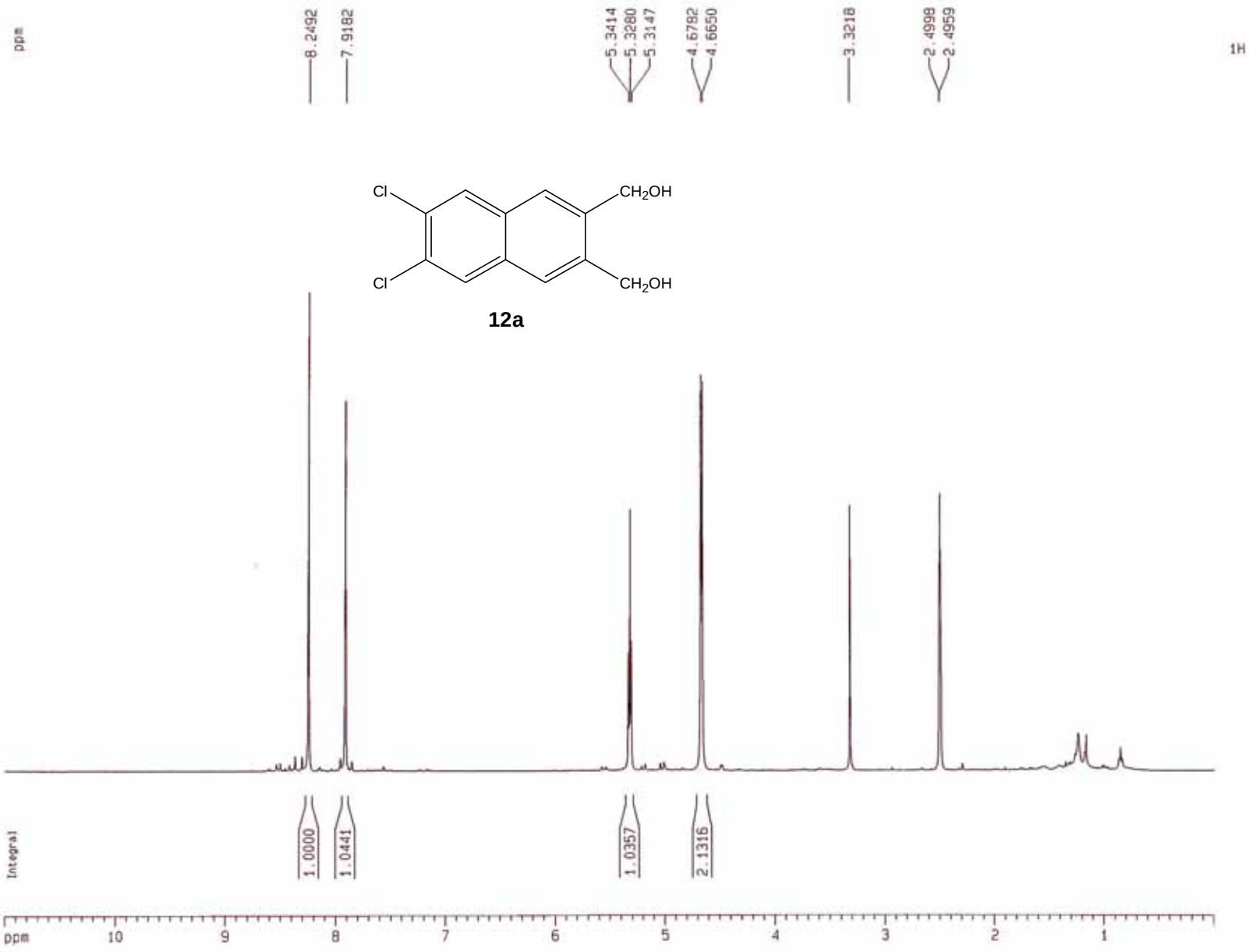


12

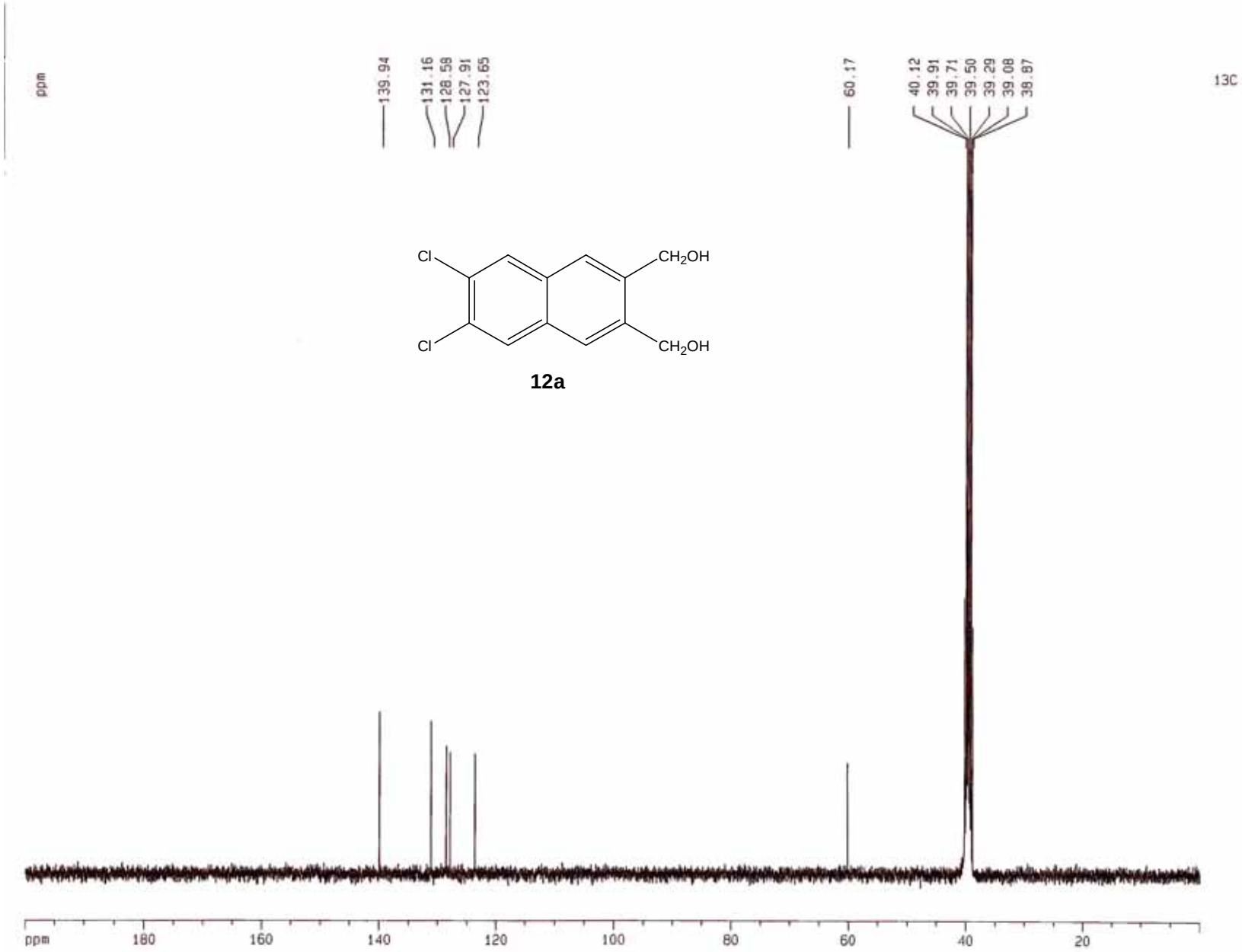


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

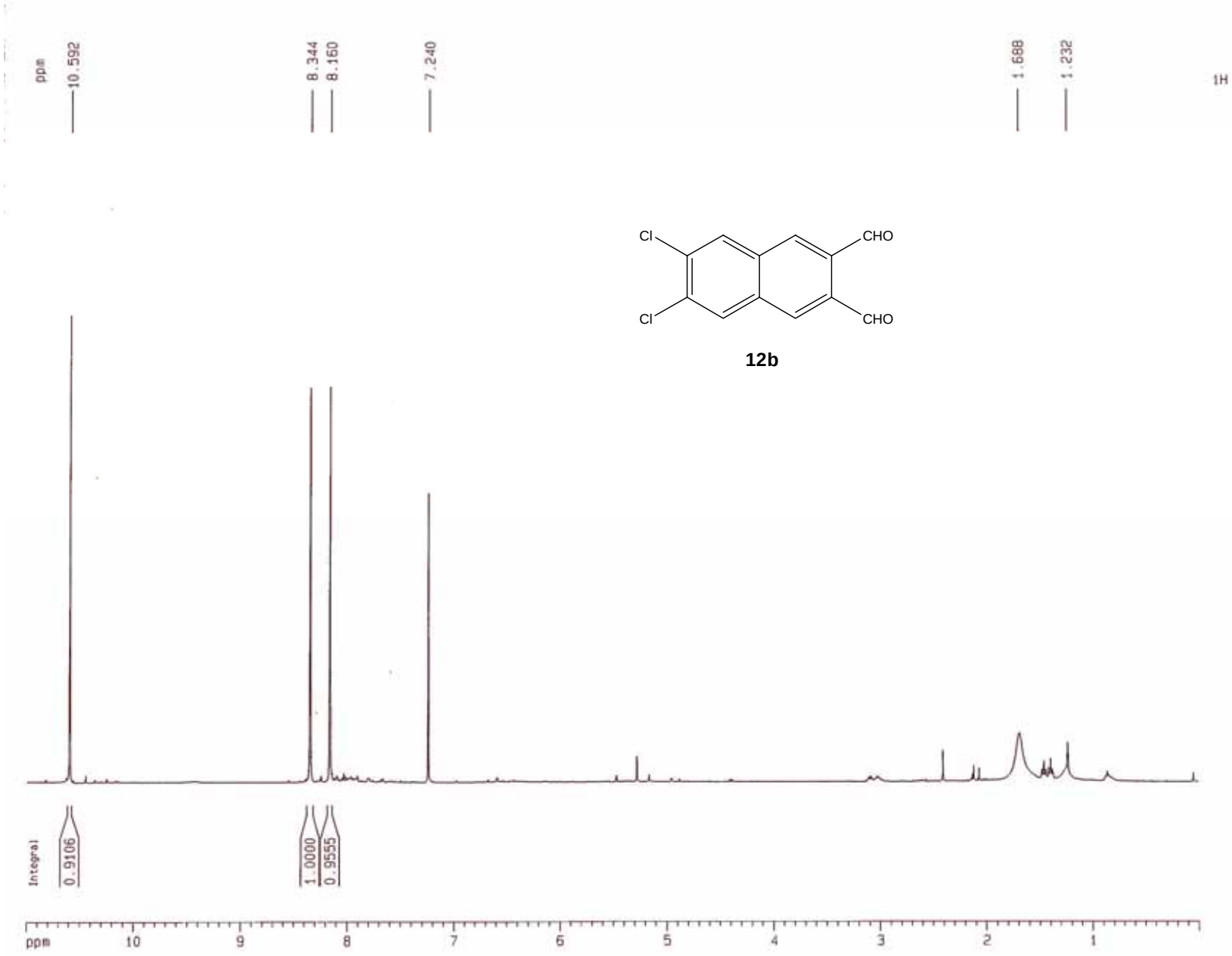
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

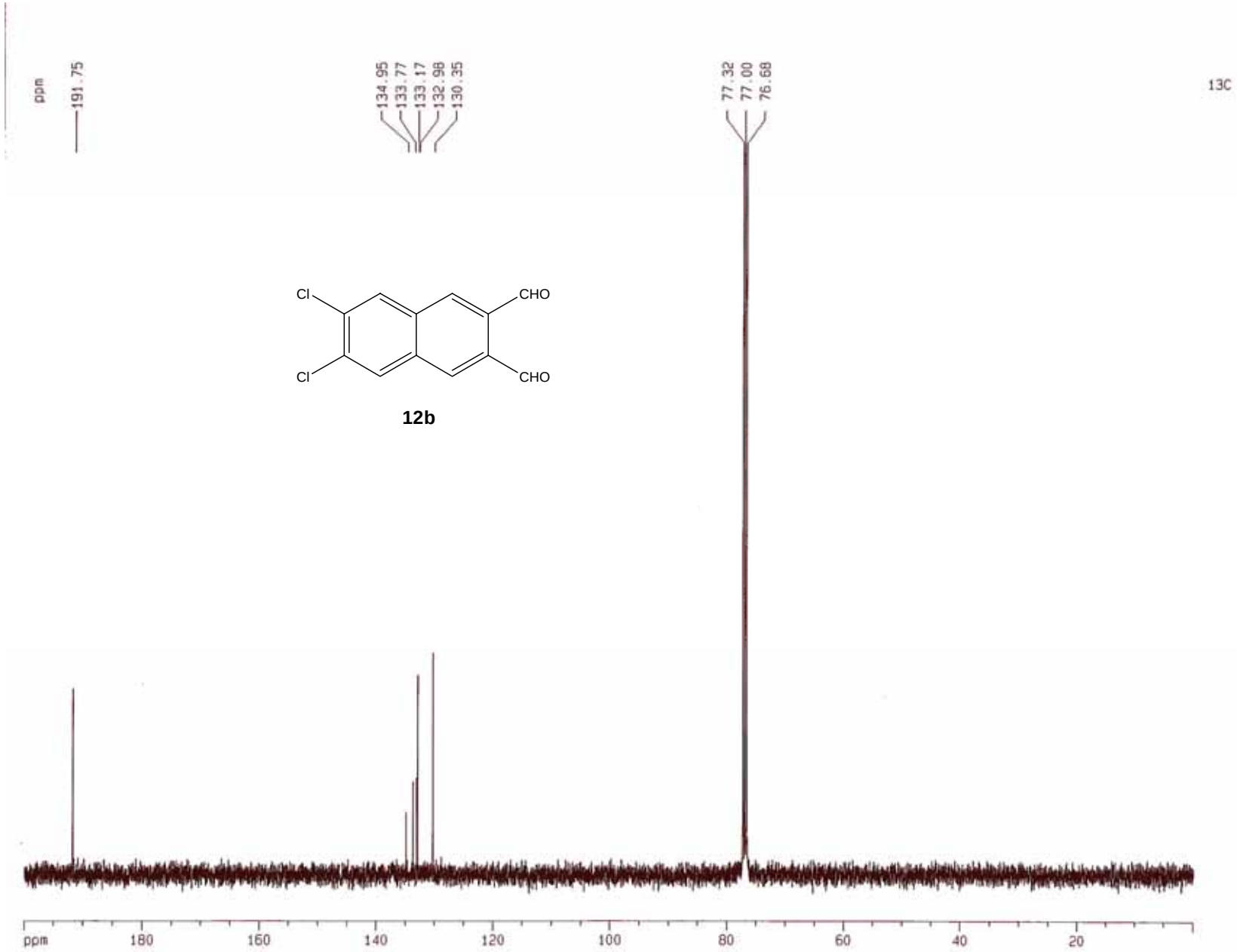


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

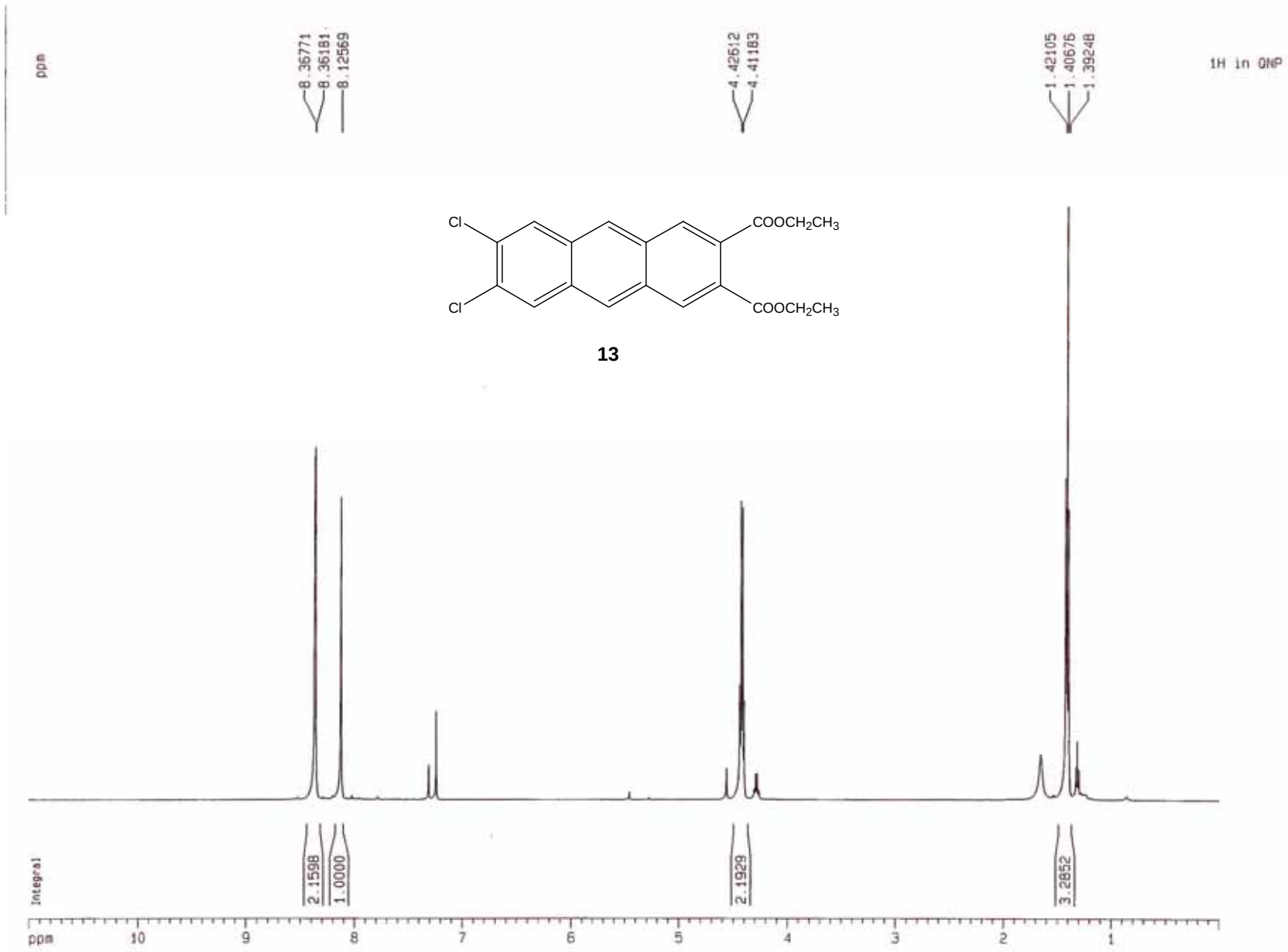


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

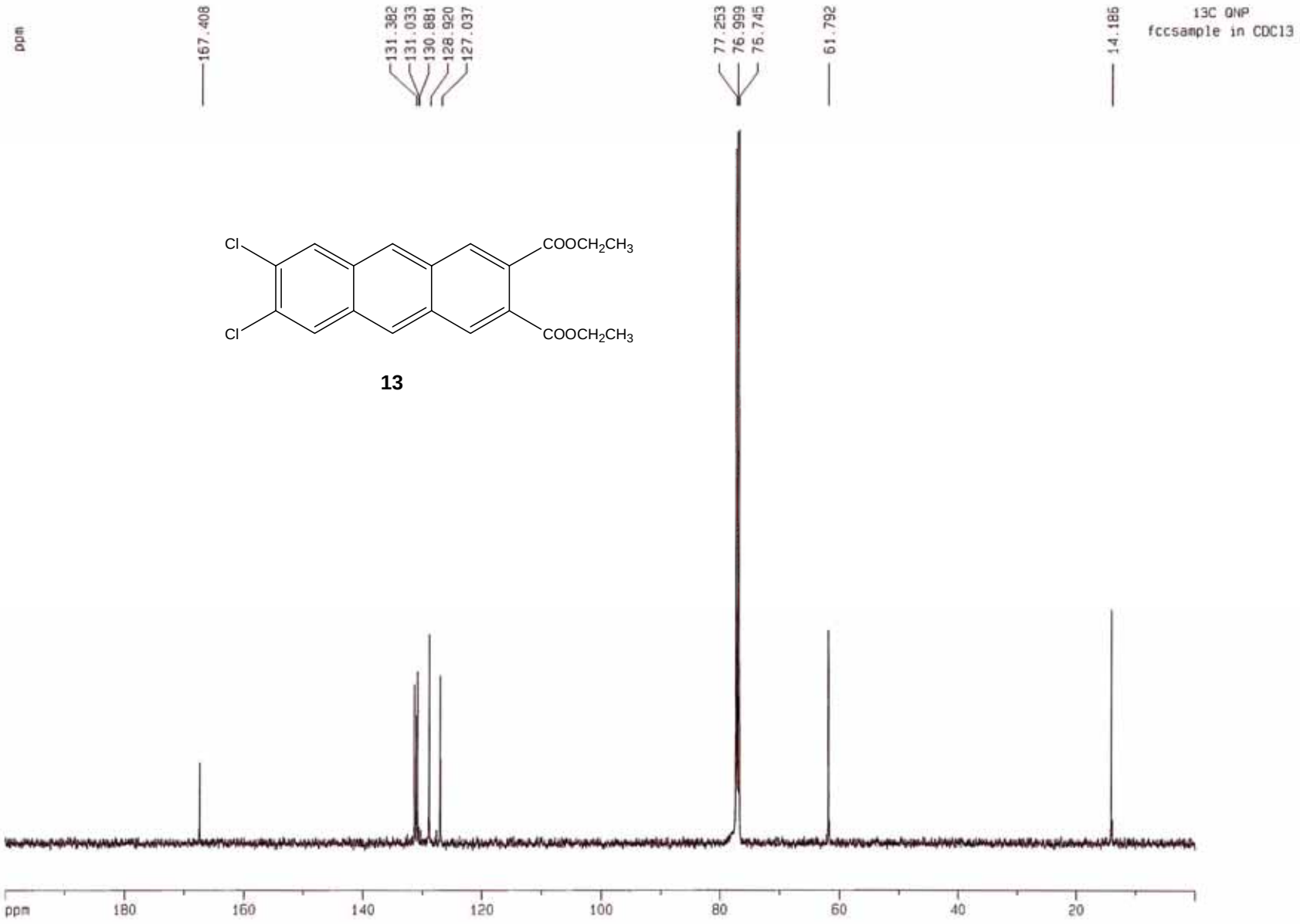

ppm
10.592
8.344
8.160
7.240
1.688
1.232
1H
Cl
CHO
Cl
CHO
12b
Integral
0.9106
1.0000
0.9555
ppm
10
9
8
7
6
5
4
3
2
1



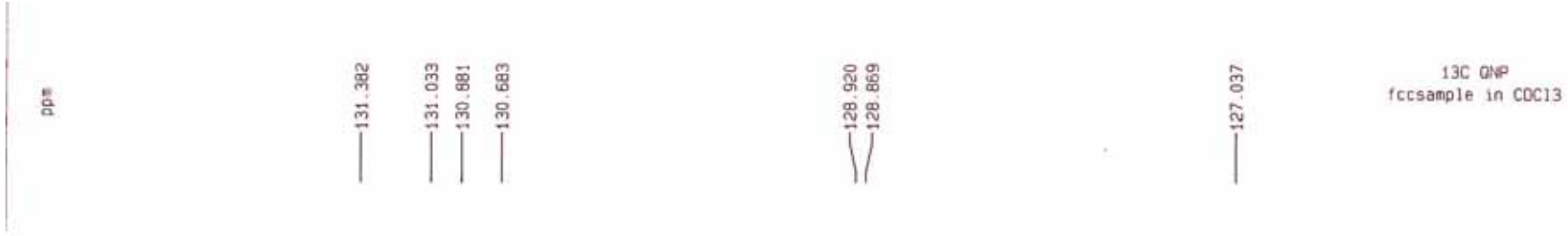
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

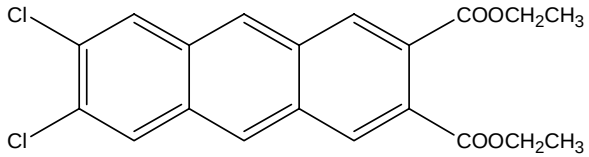


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

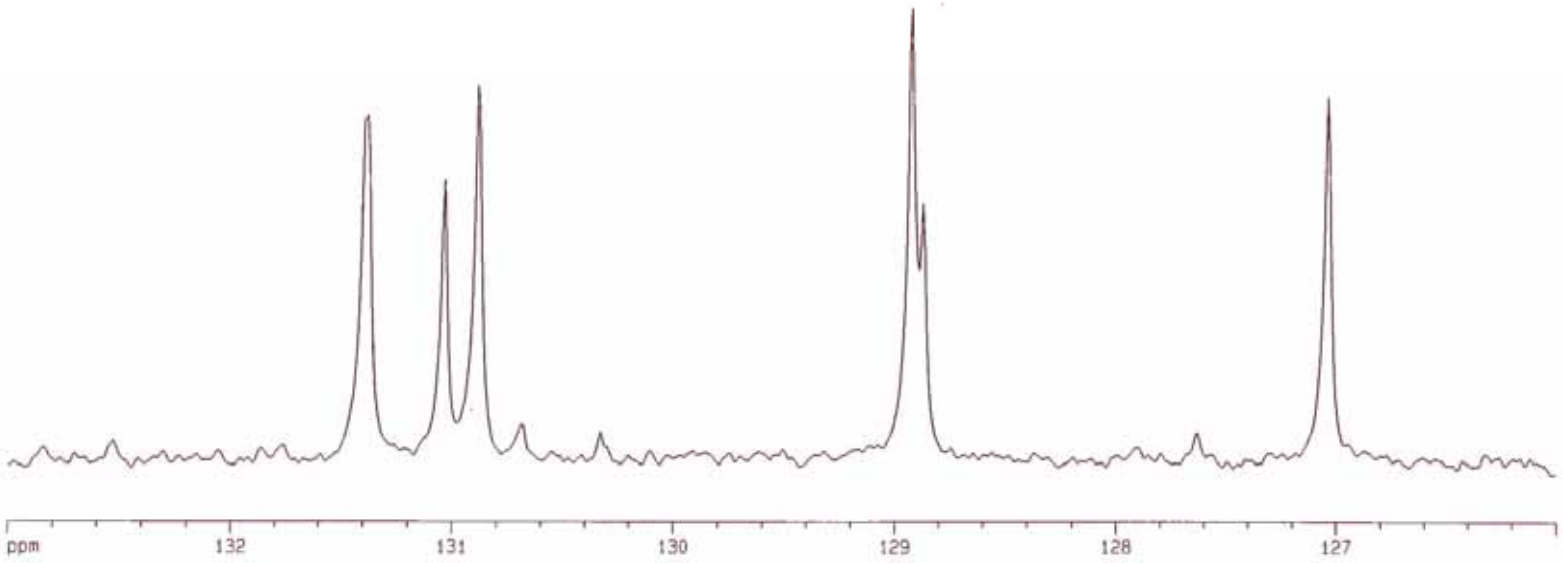


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

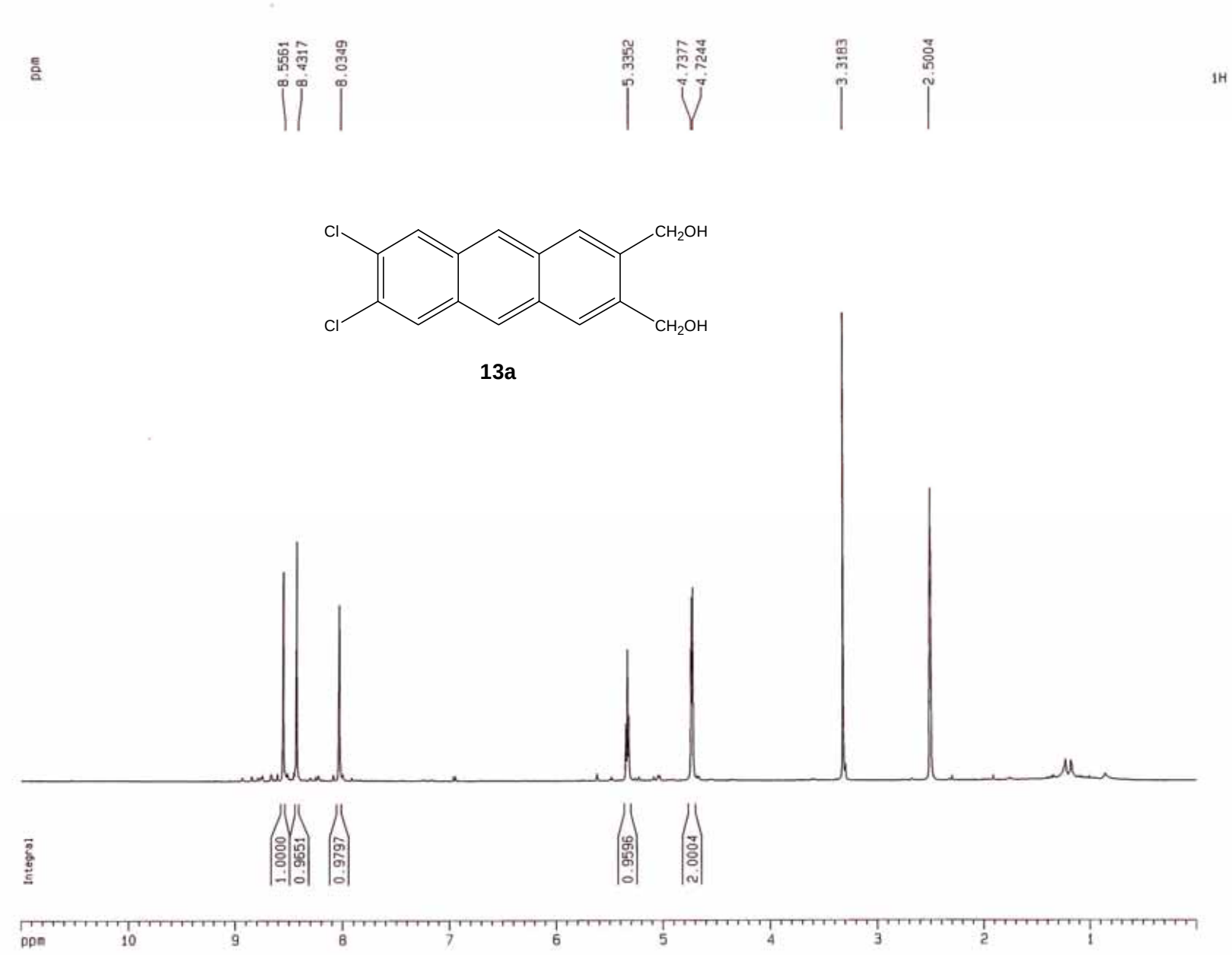




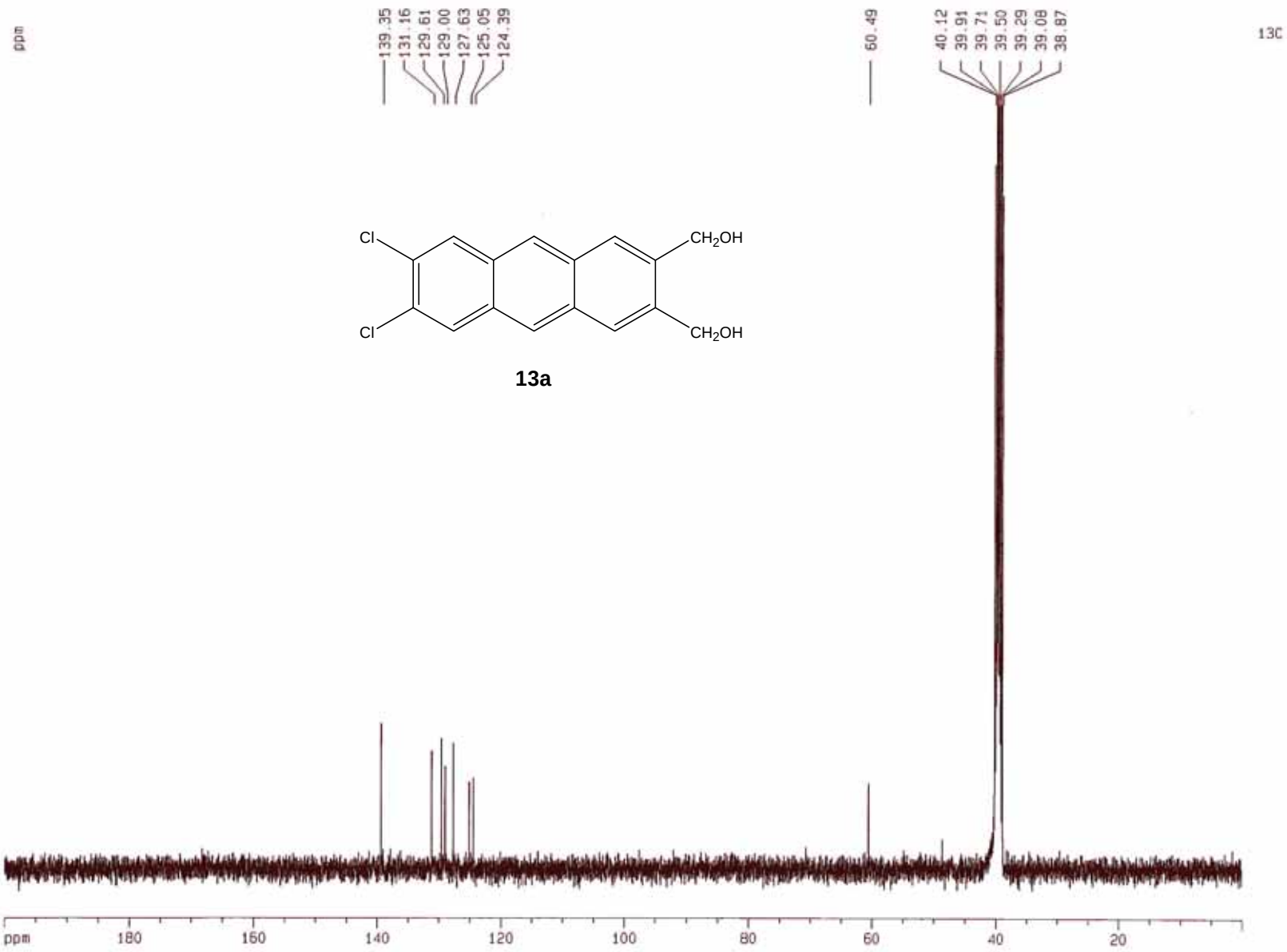
13



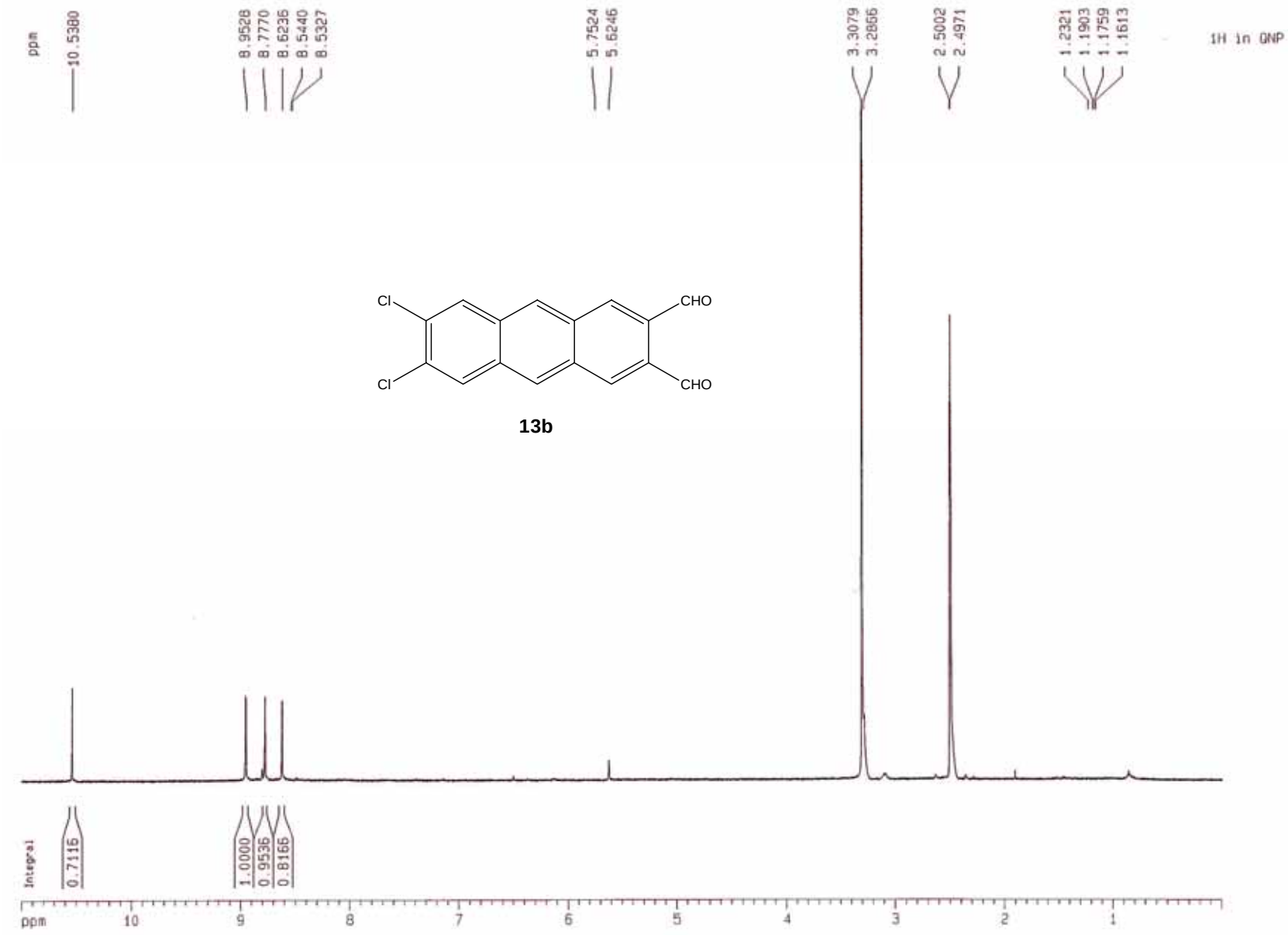
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



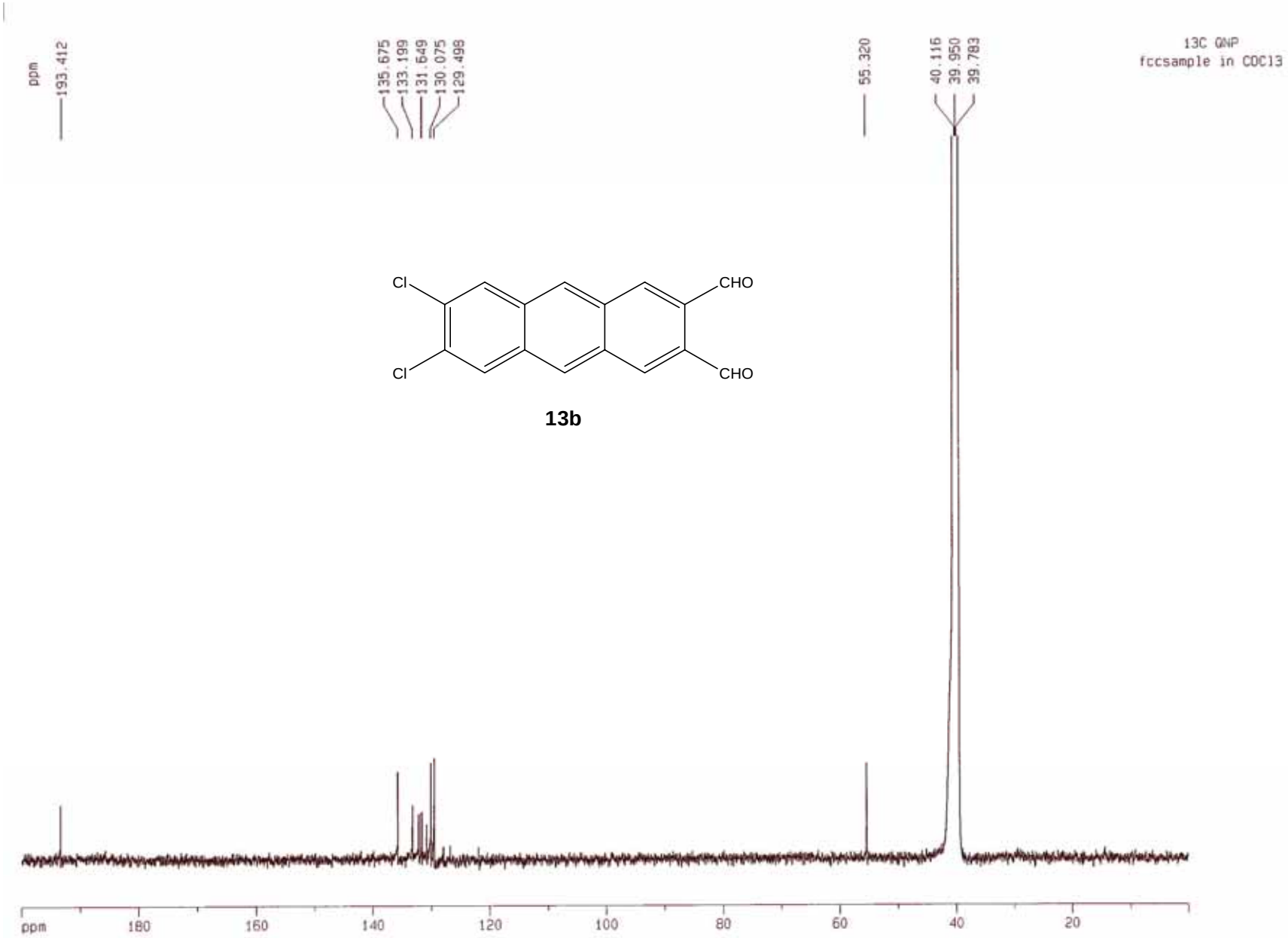
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



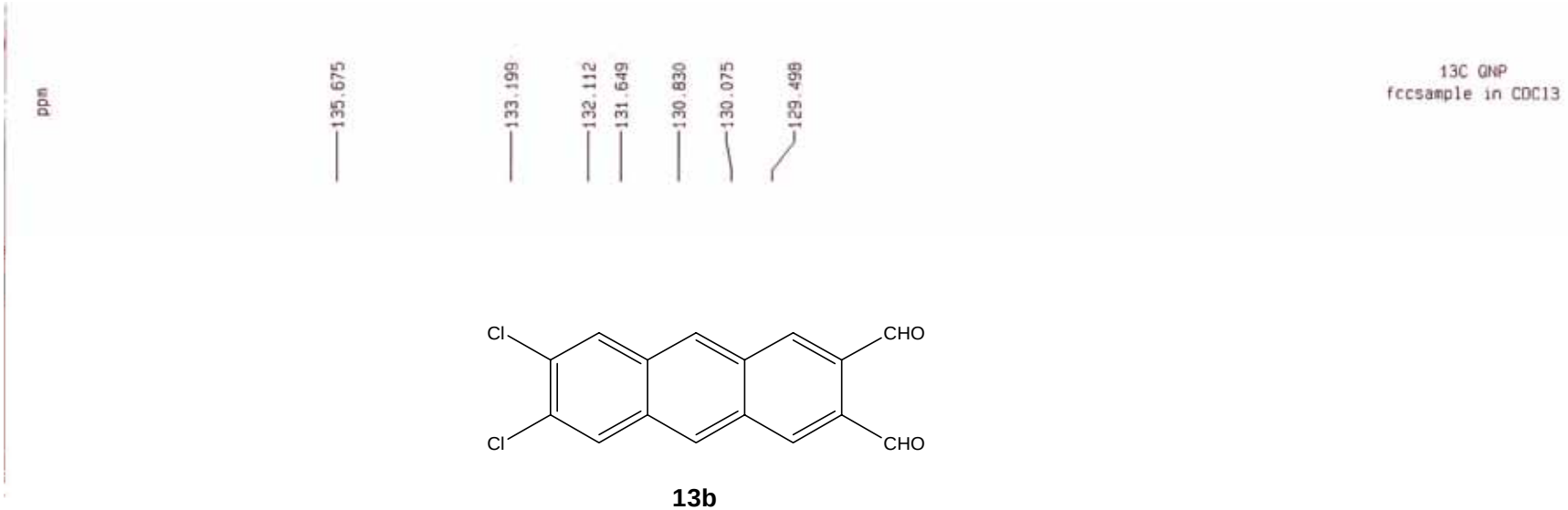
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



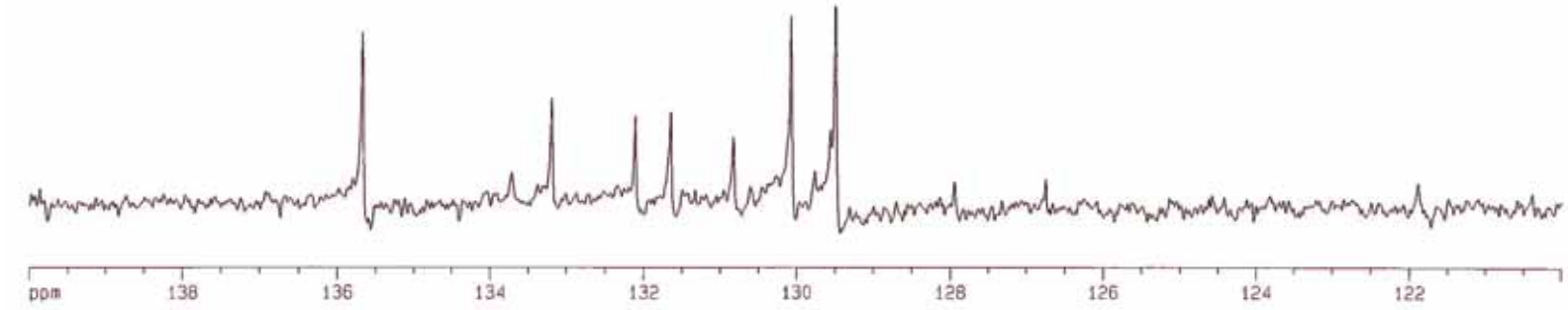
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



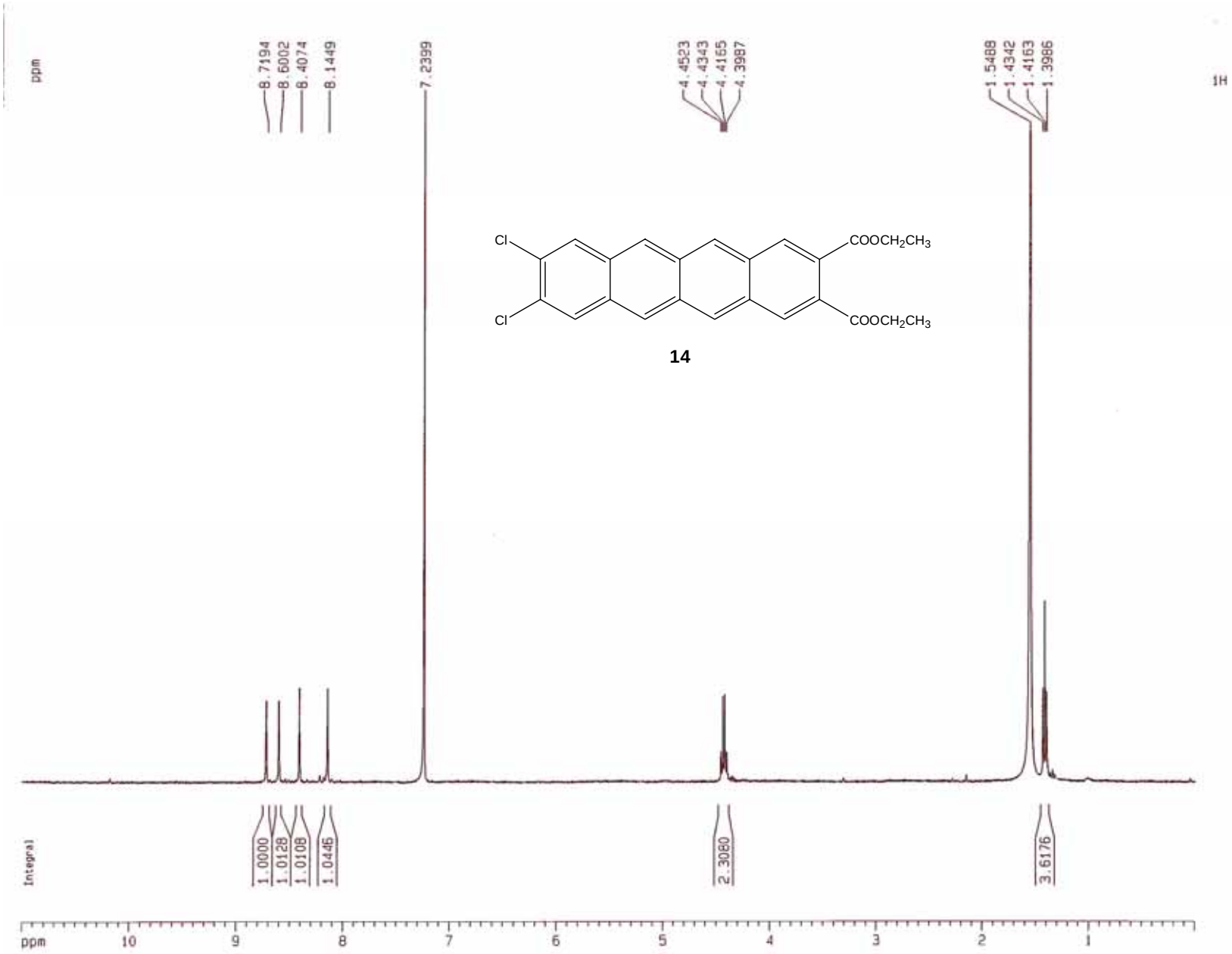
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



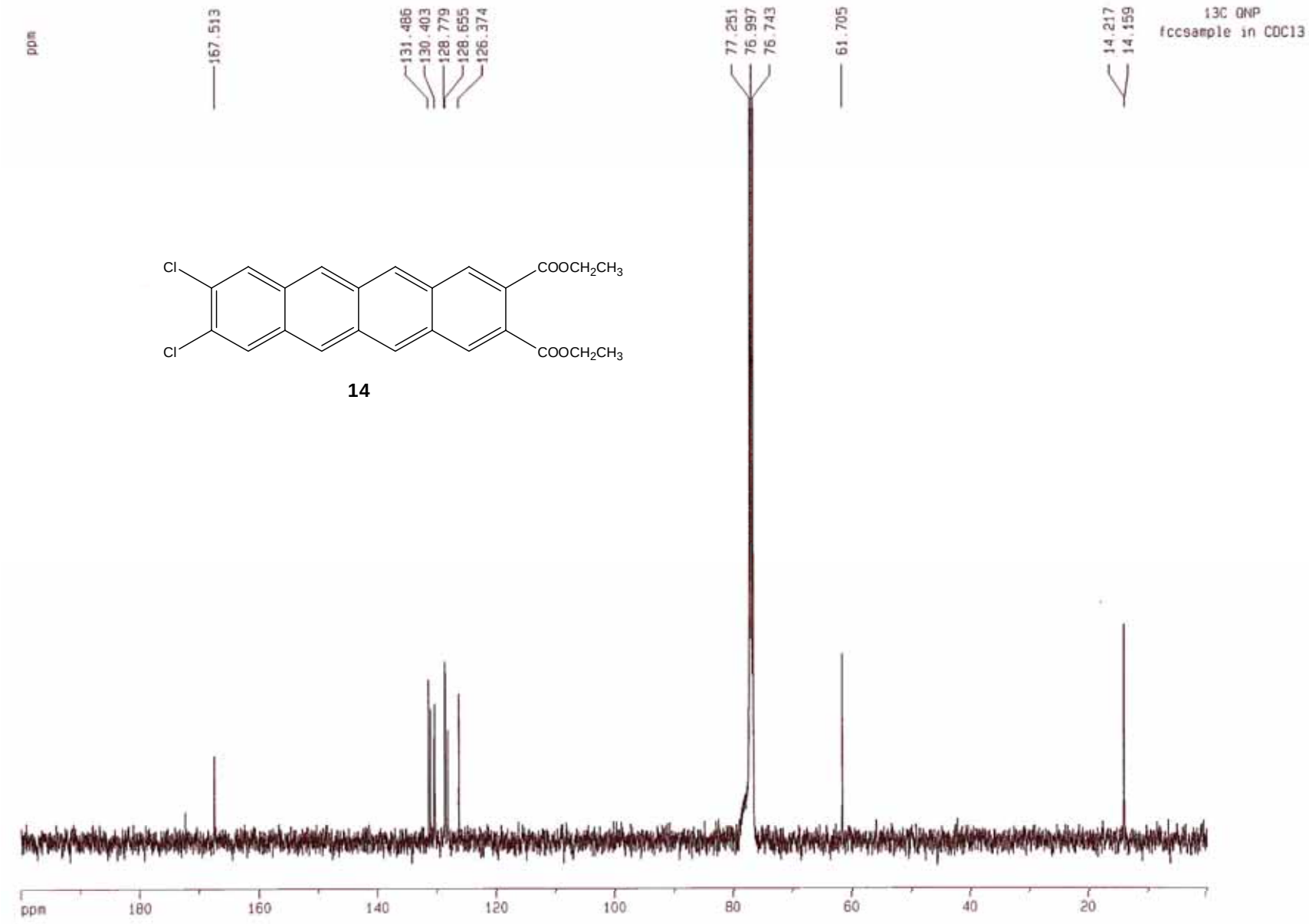
13b



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

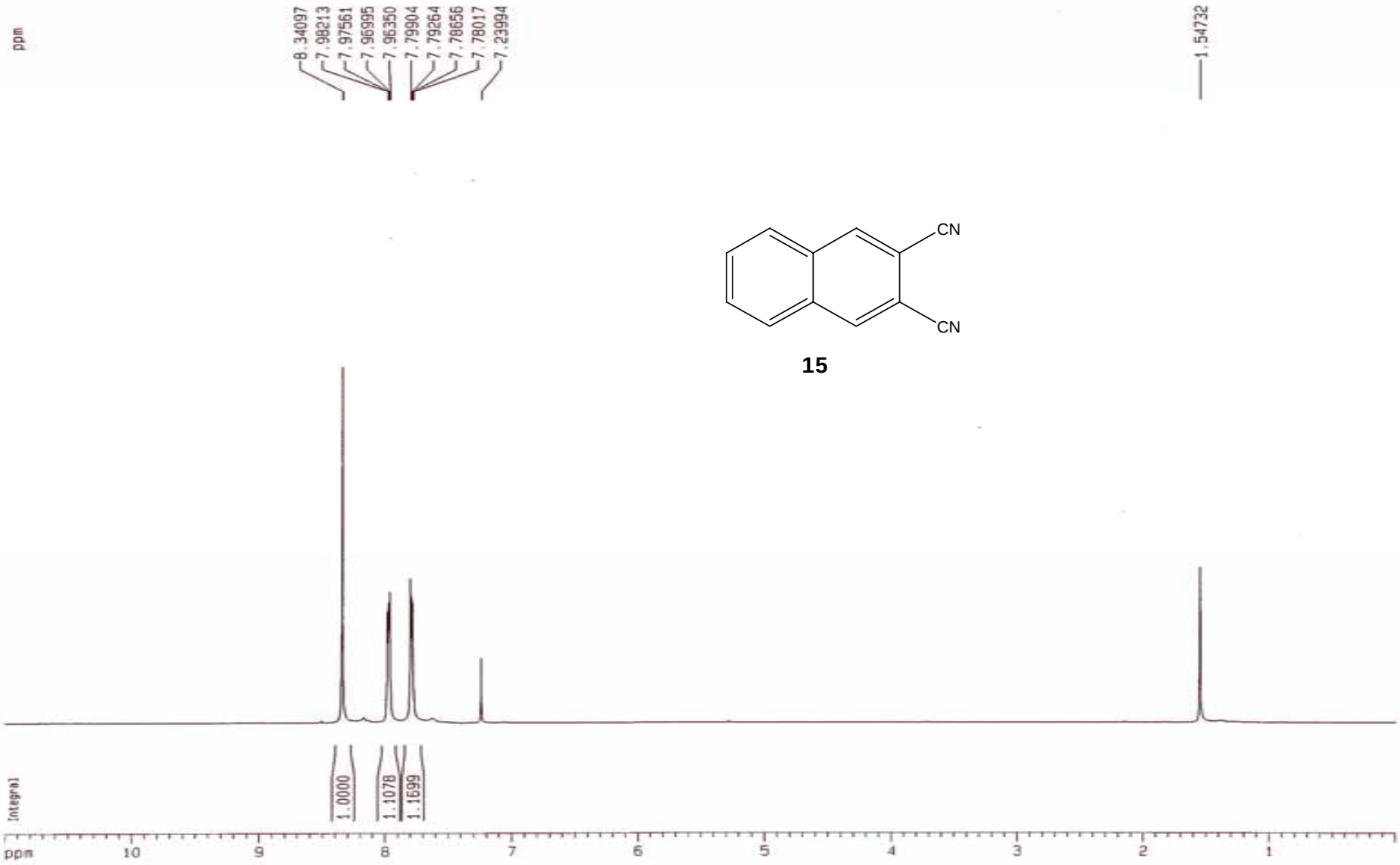


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

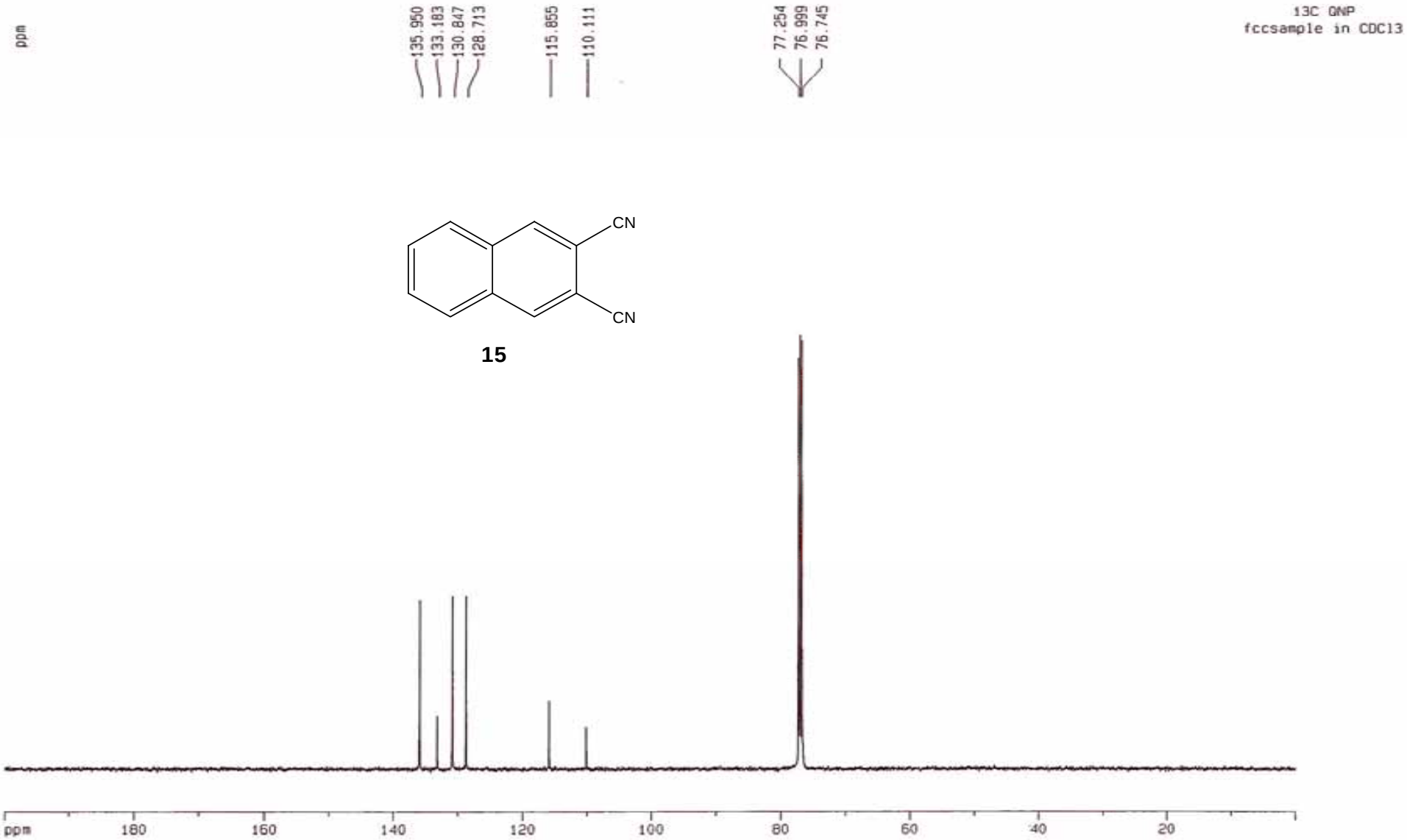


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

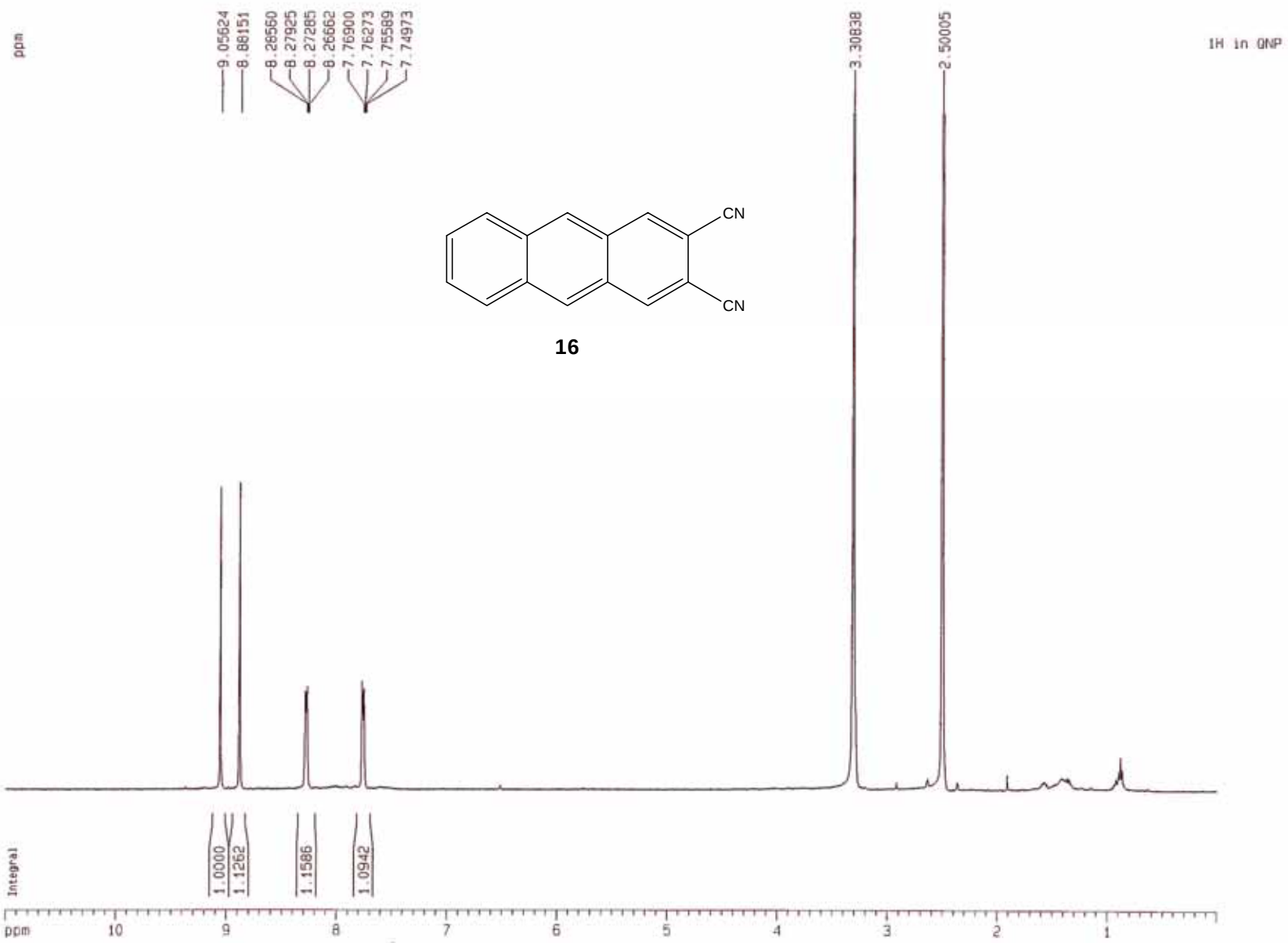
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



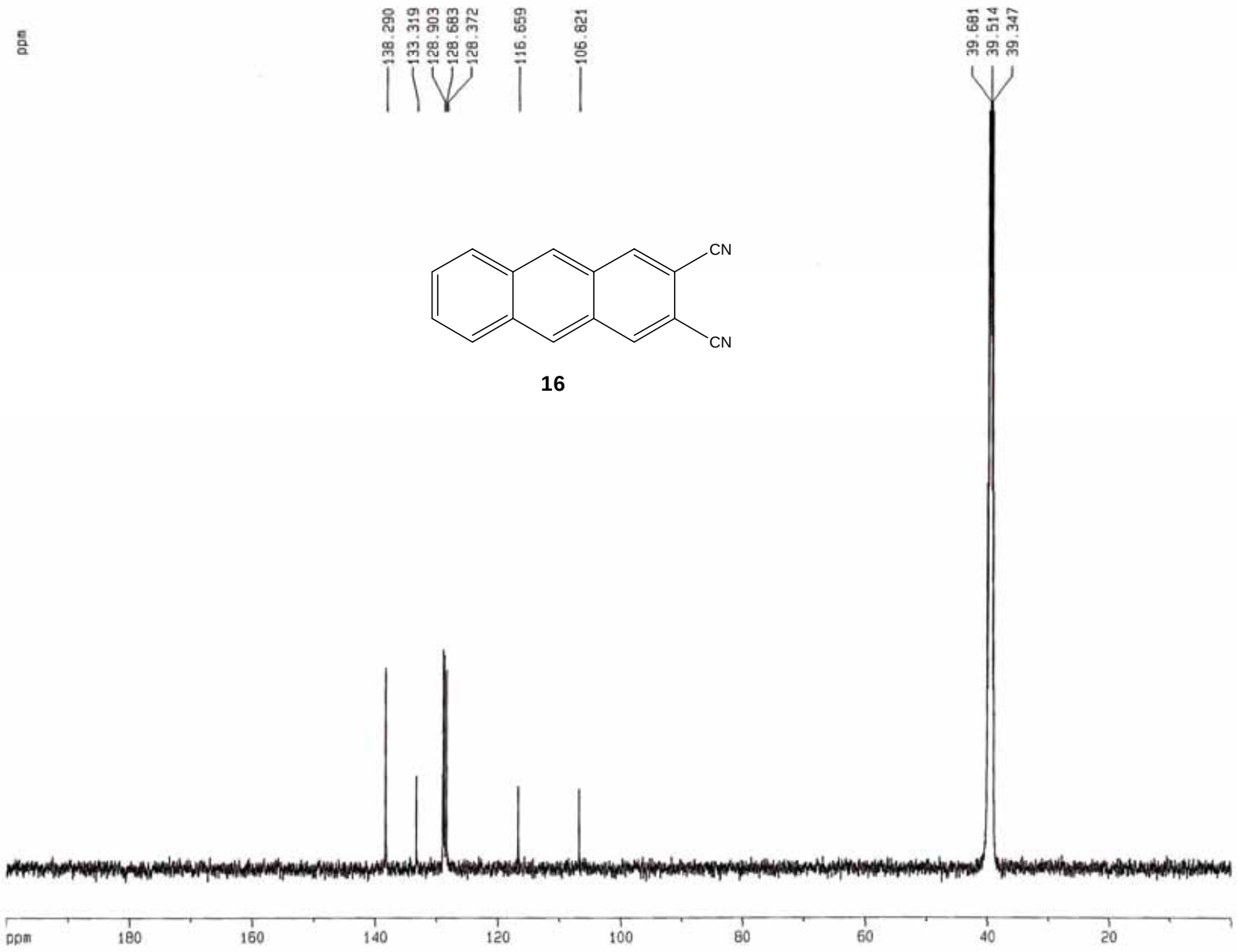
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



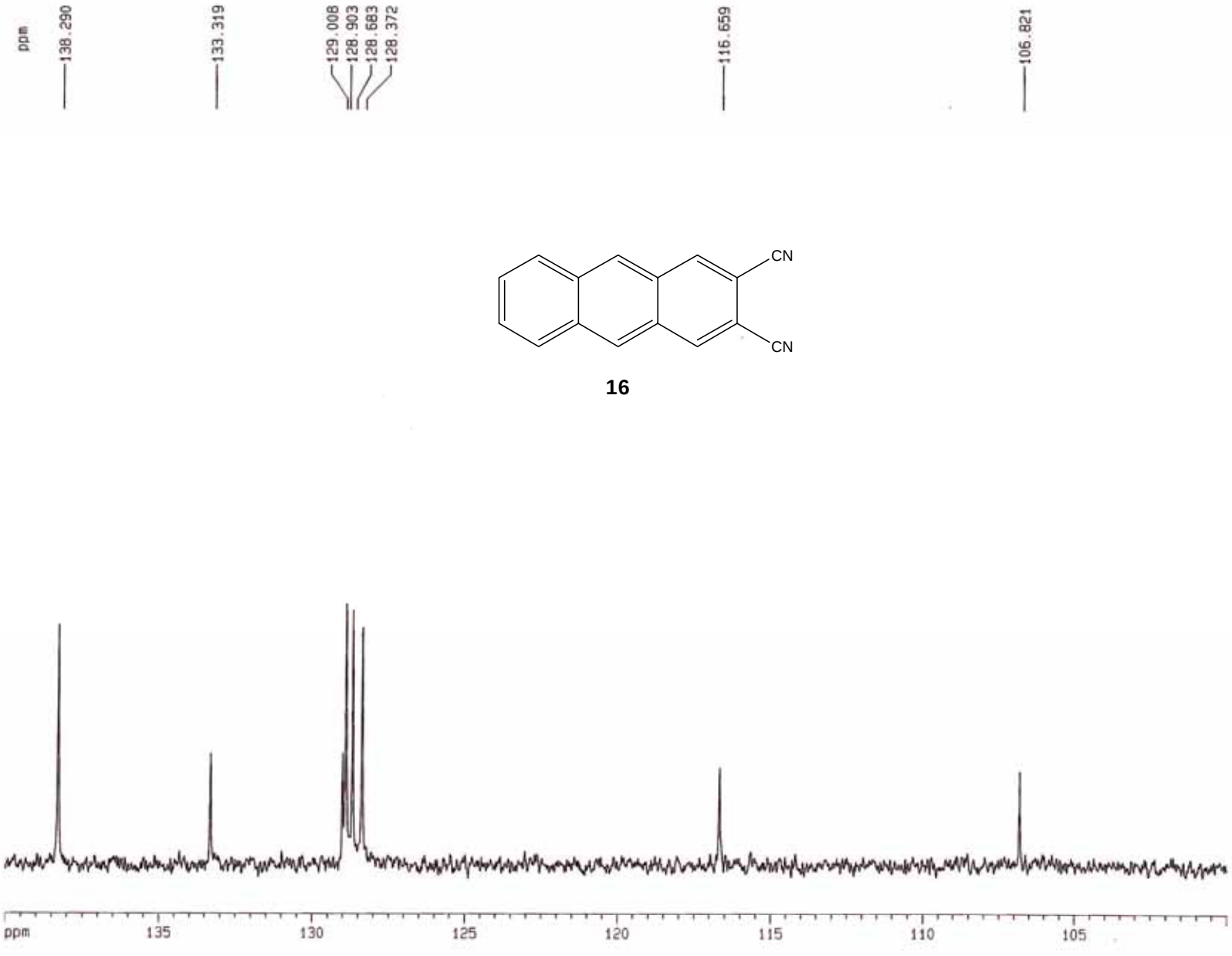
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



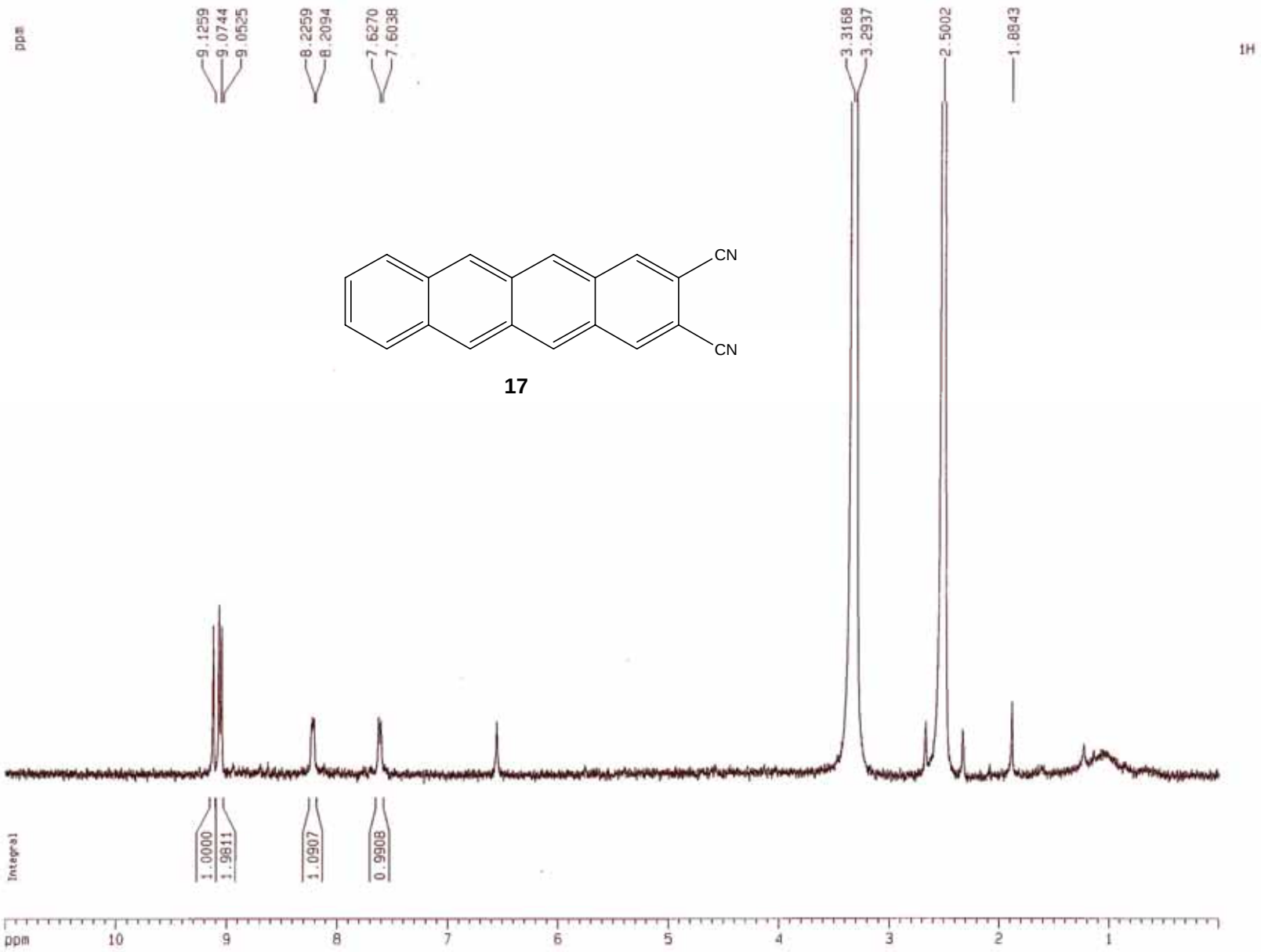
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



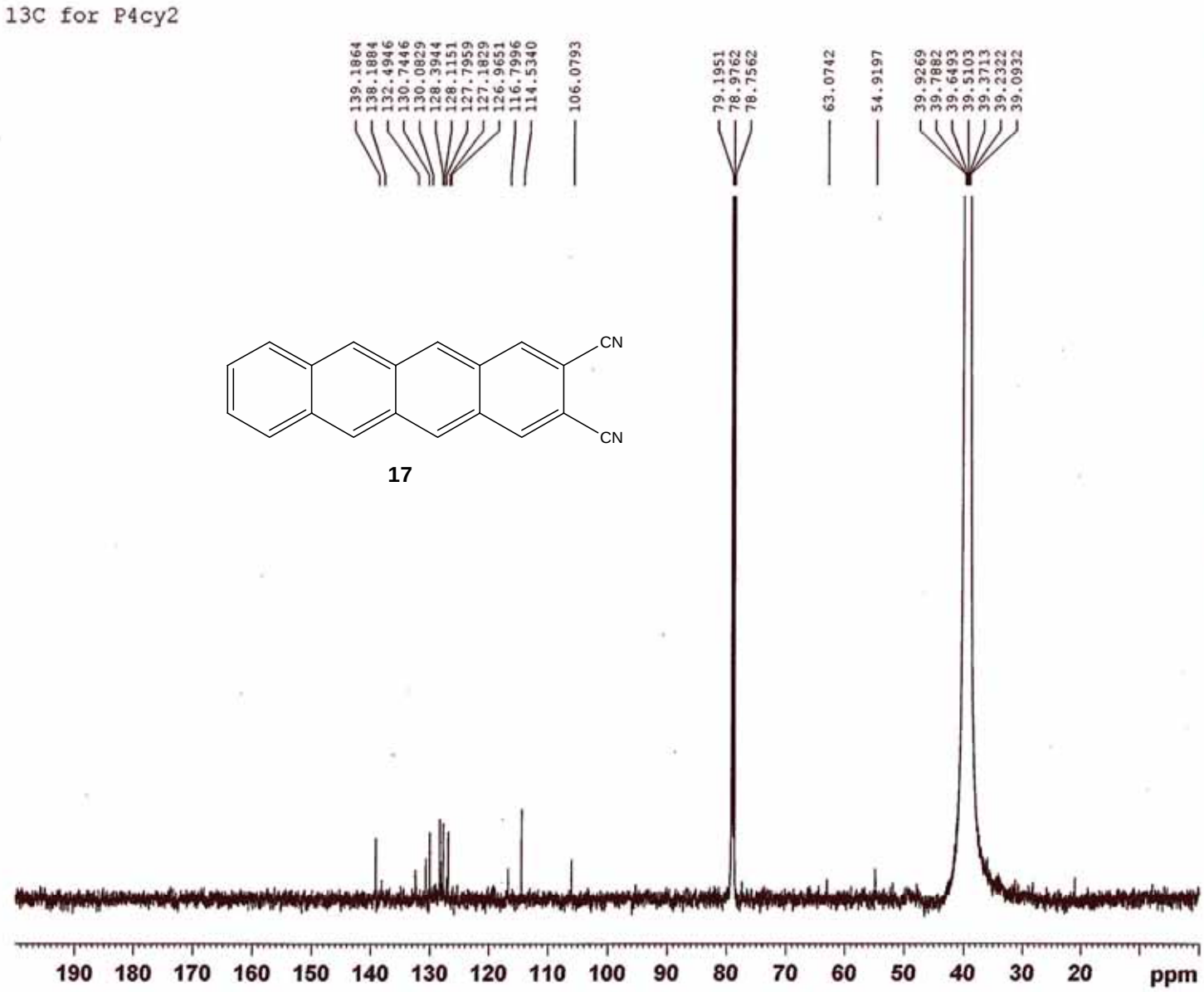
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



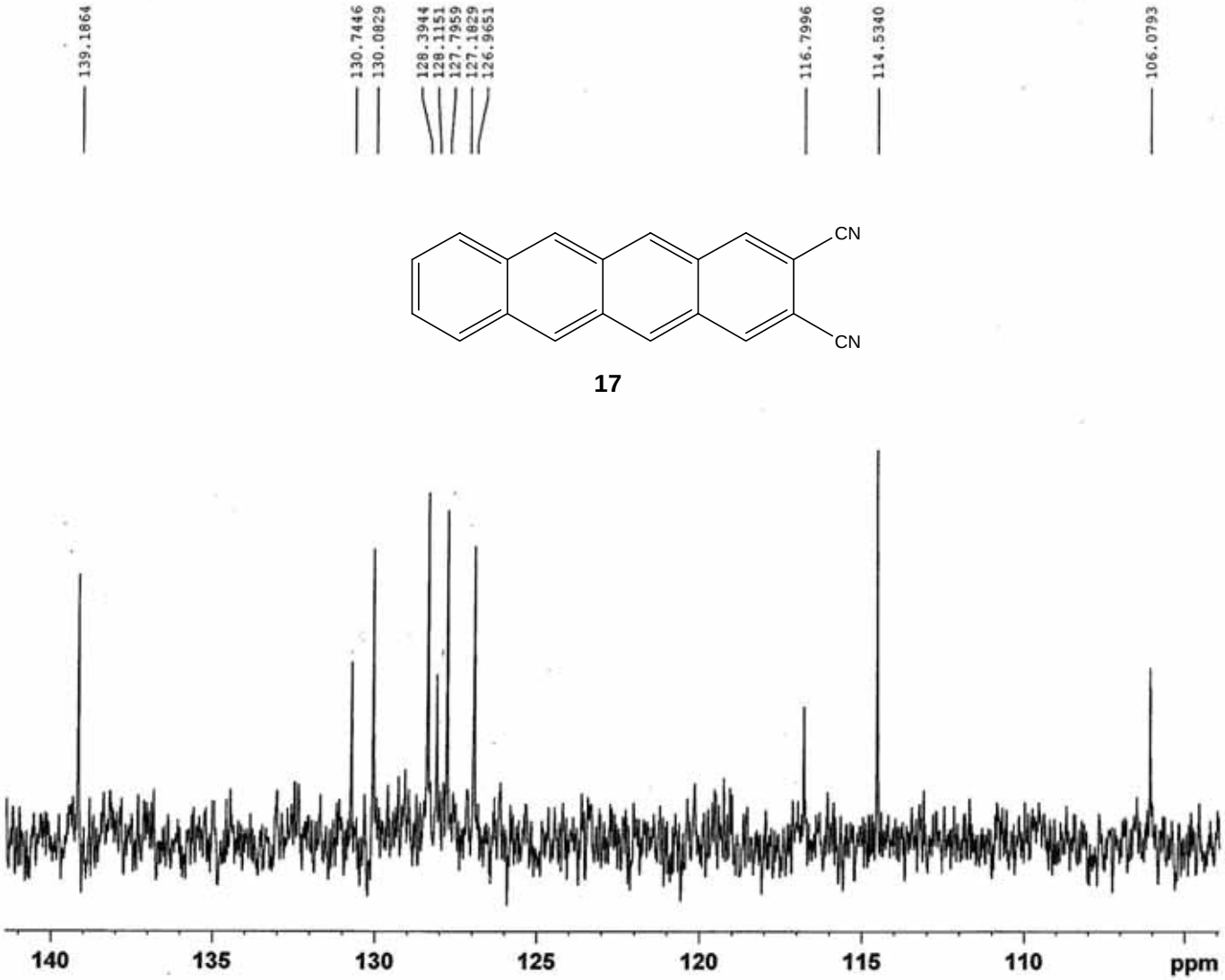
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY




```
Current Data Parameters
NAME                  P4cy2
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20060622
Time                  18.38
INSTRUM               spect
PROBHD   5 mm CPDCH 13C
PULPROG             zgpg30
TD                  131072
SOLVENT               DMSO
NS                    28044
DS                        0
SWH              39370.078 Hz
FIDRES            0.300370 Hz
AQ               1.6646771 sec
RG                     3640
DW                   12.700 usec
DE                     6.00 usec
TE                    295.1 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.25 usec
PL1                    4.70 dB
SFO1           150.9251924 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    0.33 dB
PL12                  18.50 dB
PL13                  21.50 dB
SFO2           600.1539010 MHz

F2 - Processing parameters
SI                    65536
SF             150.9079086 MHz
WDW                      EM
SSB                       0
LB                     3.00 Hz
GB                        0
PC                     0.00
```

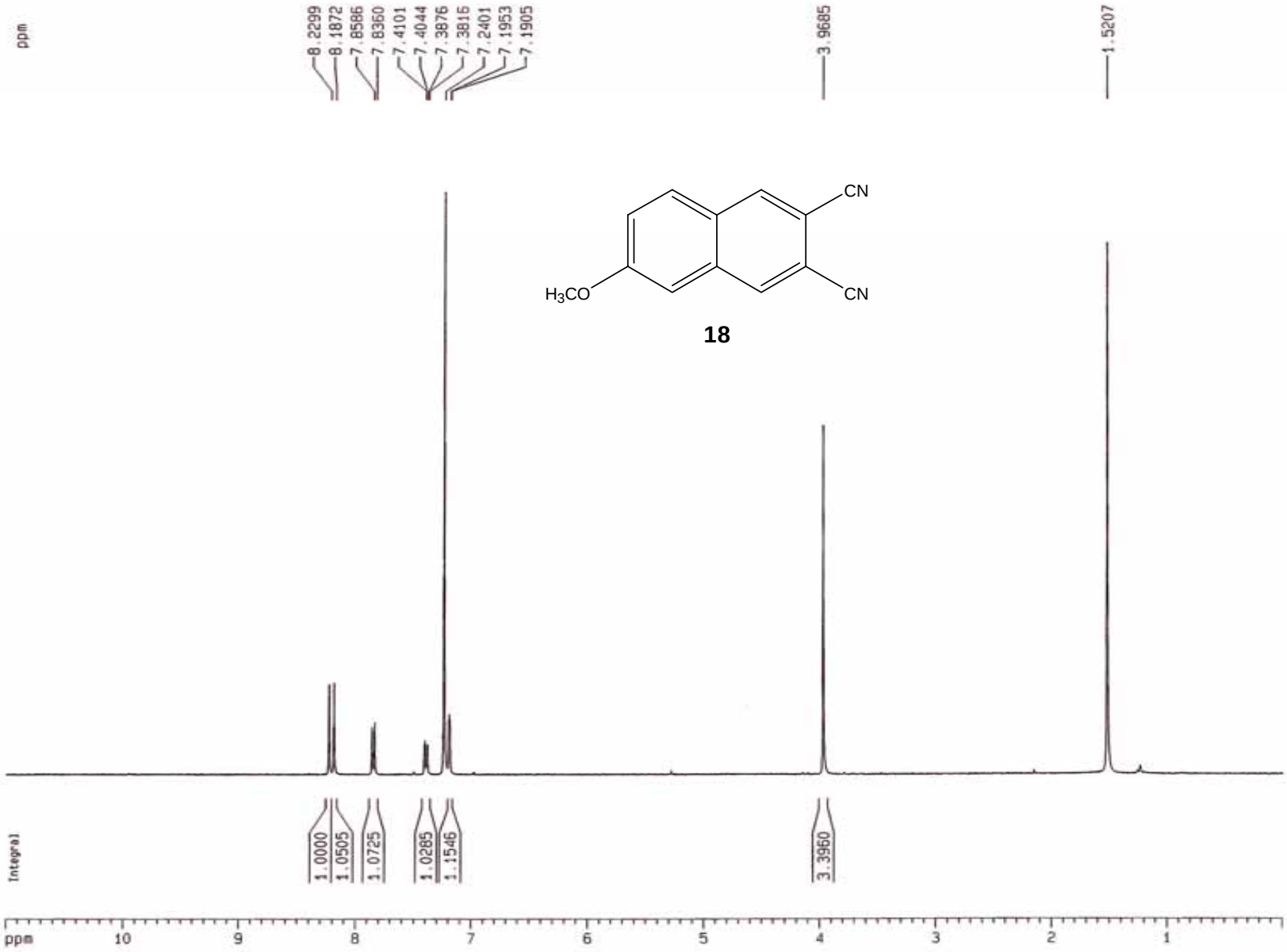

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

13C for P4cy2

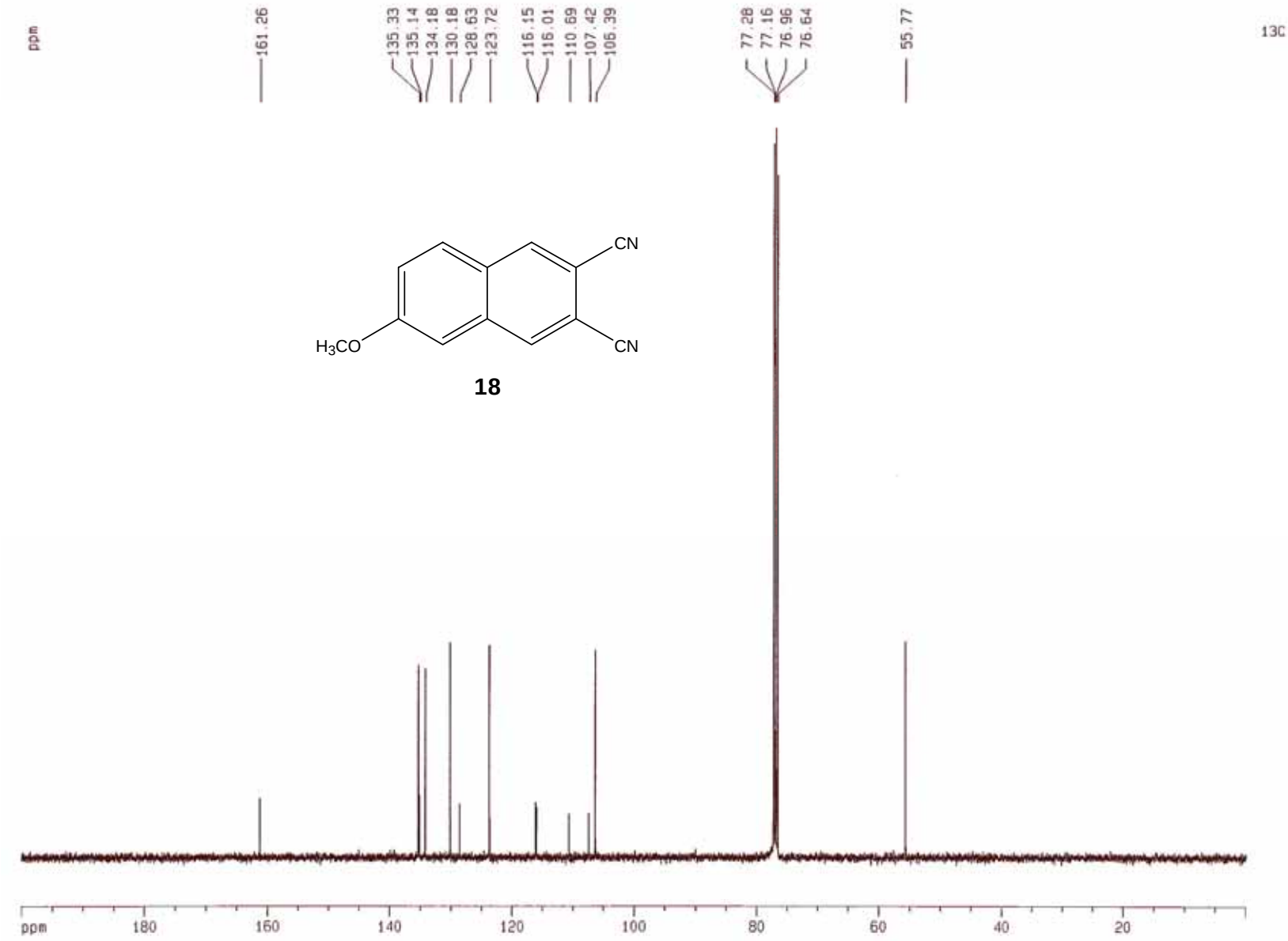



```
Current Data Parameters
NAME                P4cy2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060622
Time                18.38
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                131072
SOLVENT              DMSO
NS                   28044
DS                       0
SWH            39370.078 Hz
FIDRES          0.300370 Hz
AQ             1.6646771 sec
RG                    3640
DW                  12.700 usec
DE                    6.00 usec
TE                   295.1 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.25 usec
PL1                   4.70 dB
SFO1          150.9251924 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.33 dB
PL12                 18.50 dB
PL13                 21.50 dB
SFO2          600.1539010 MHz

F2 - Processing parameters
SI                   65536
SF            150.9079086 MHz
WDW                     EM
SSB                      0
LB                    3.00 Hz
GB                       0
PC                    0.00
```

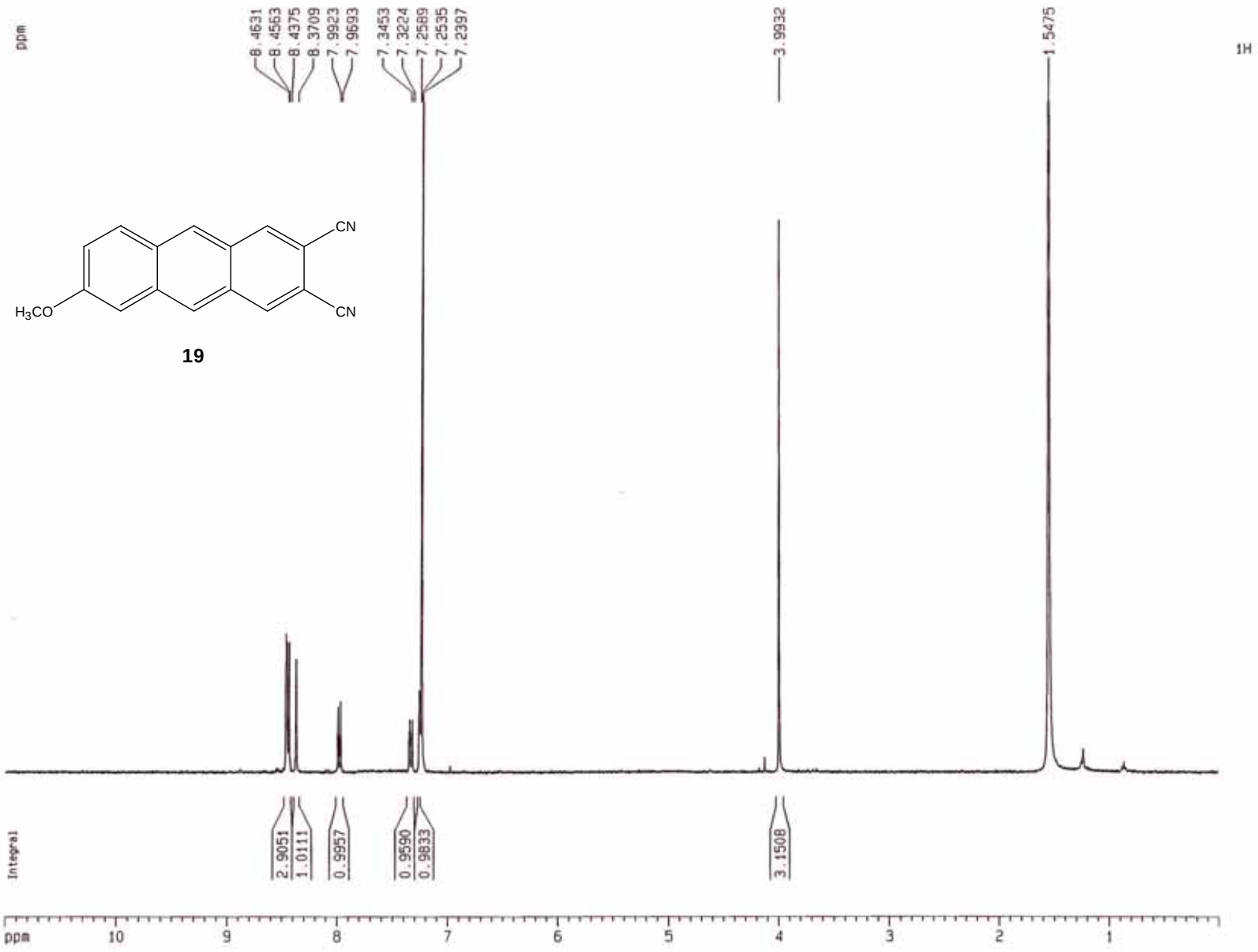

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



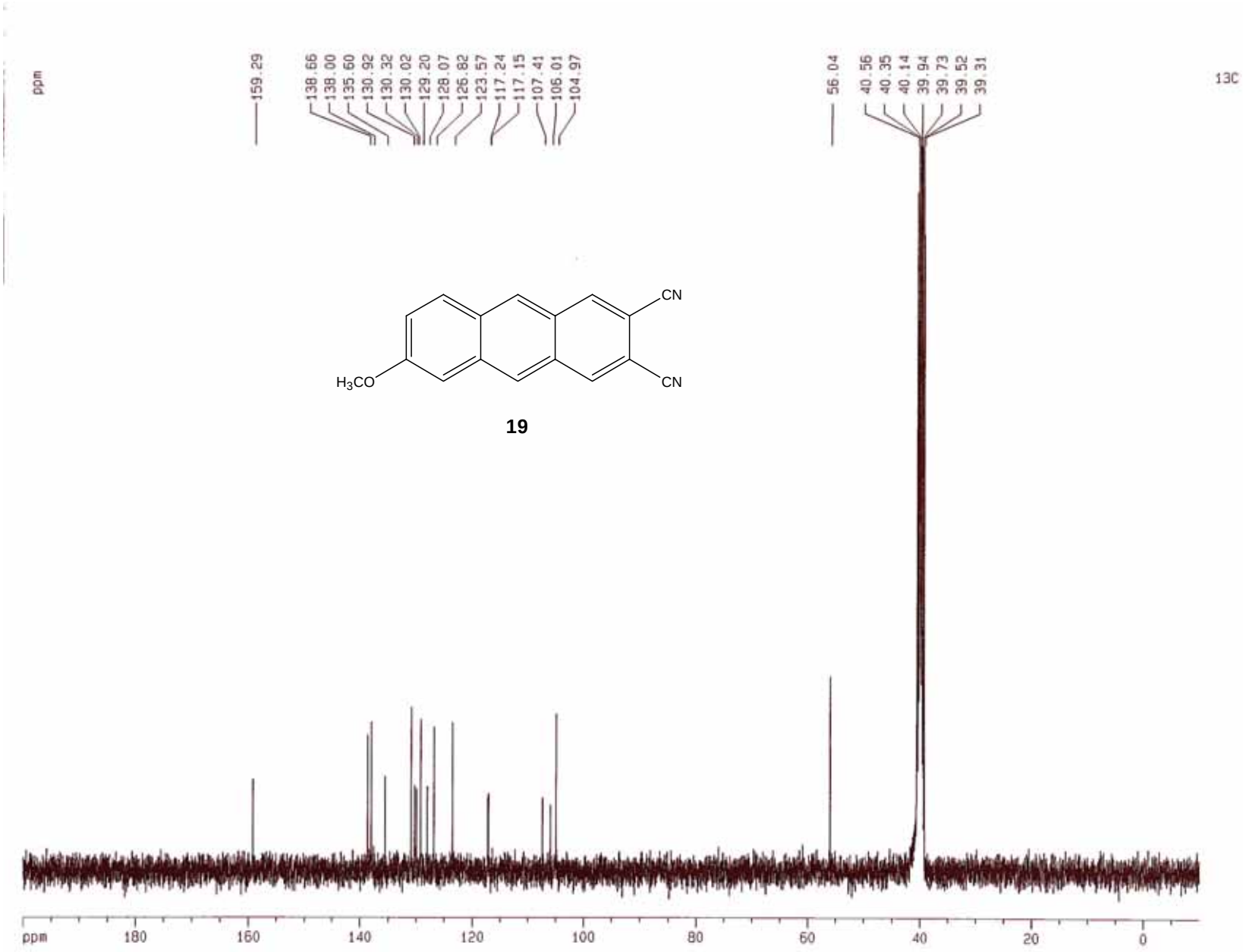
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



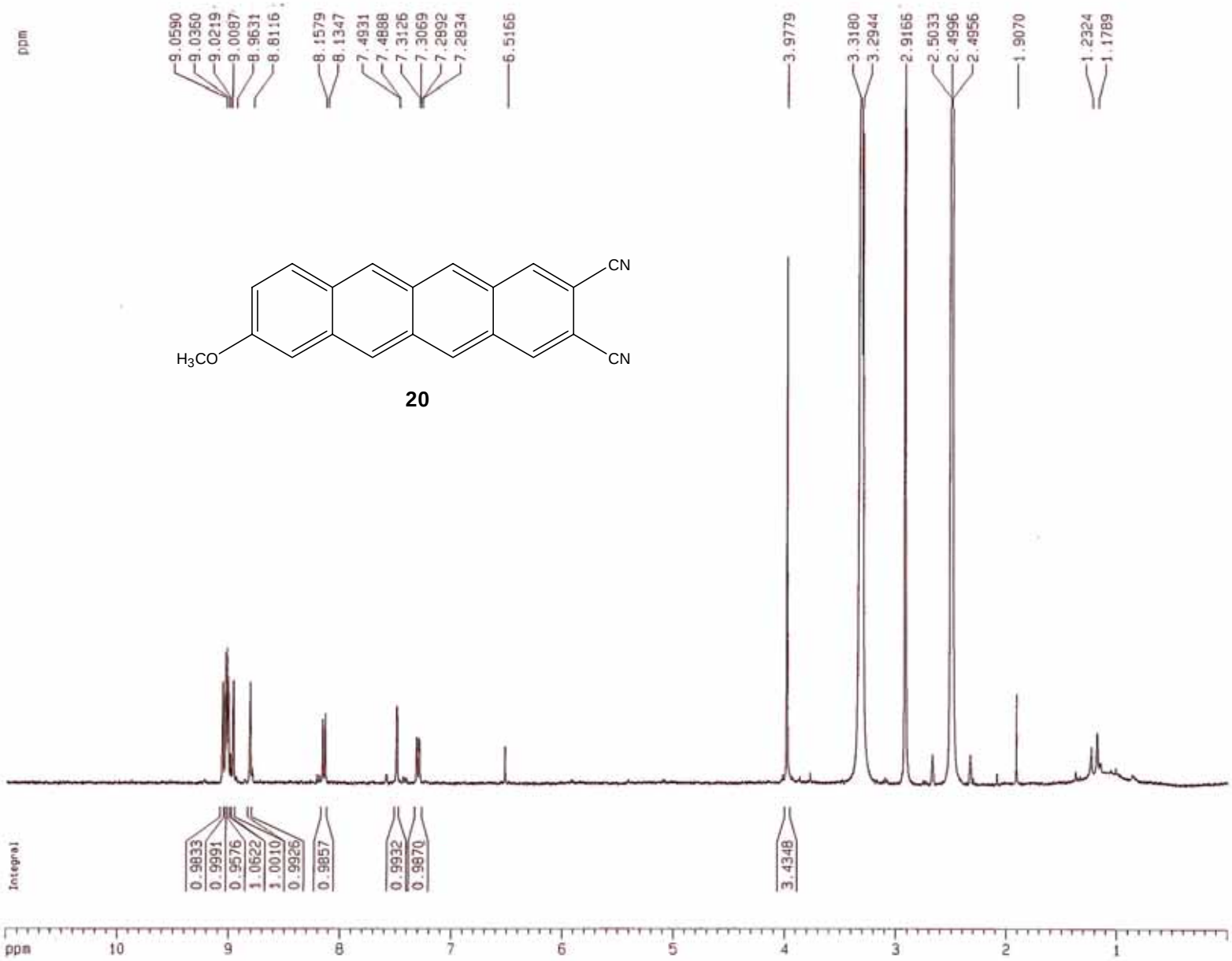
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



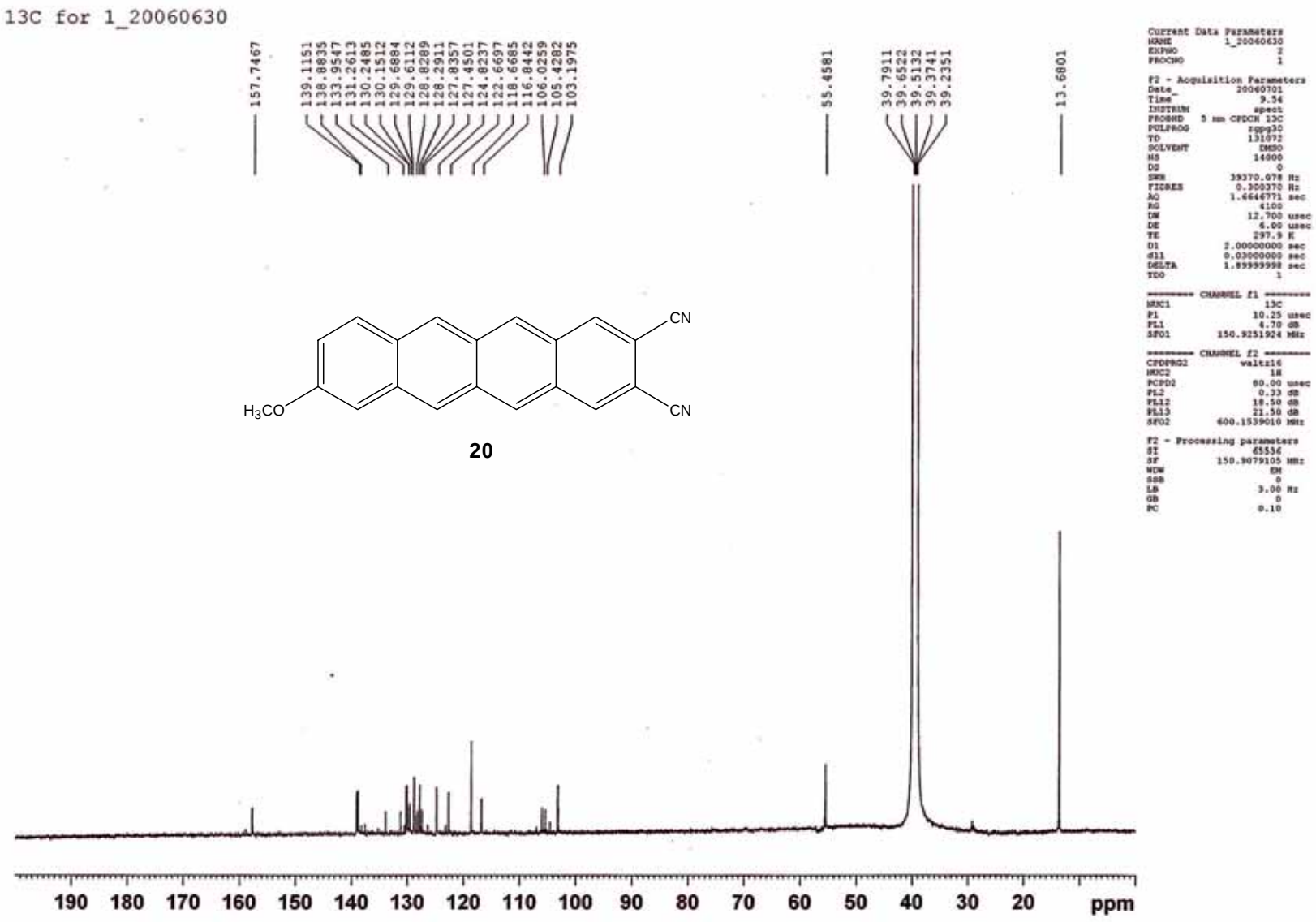
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



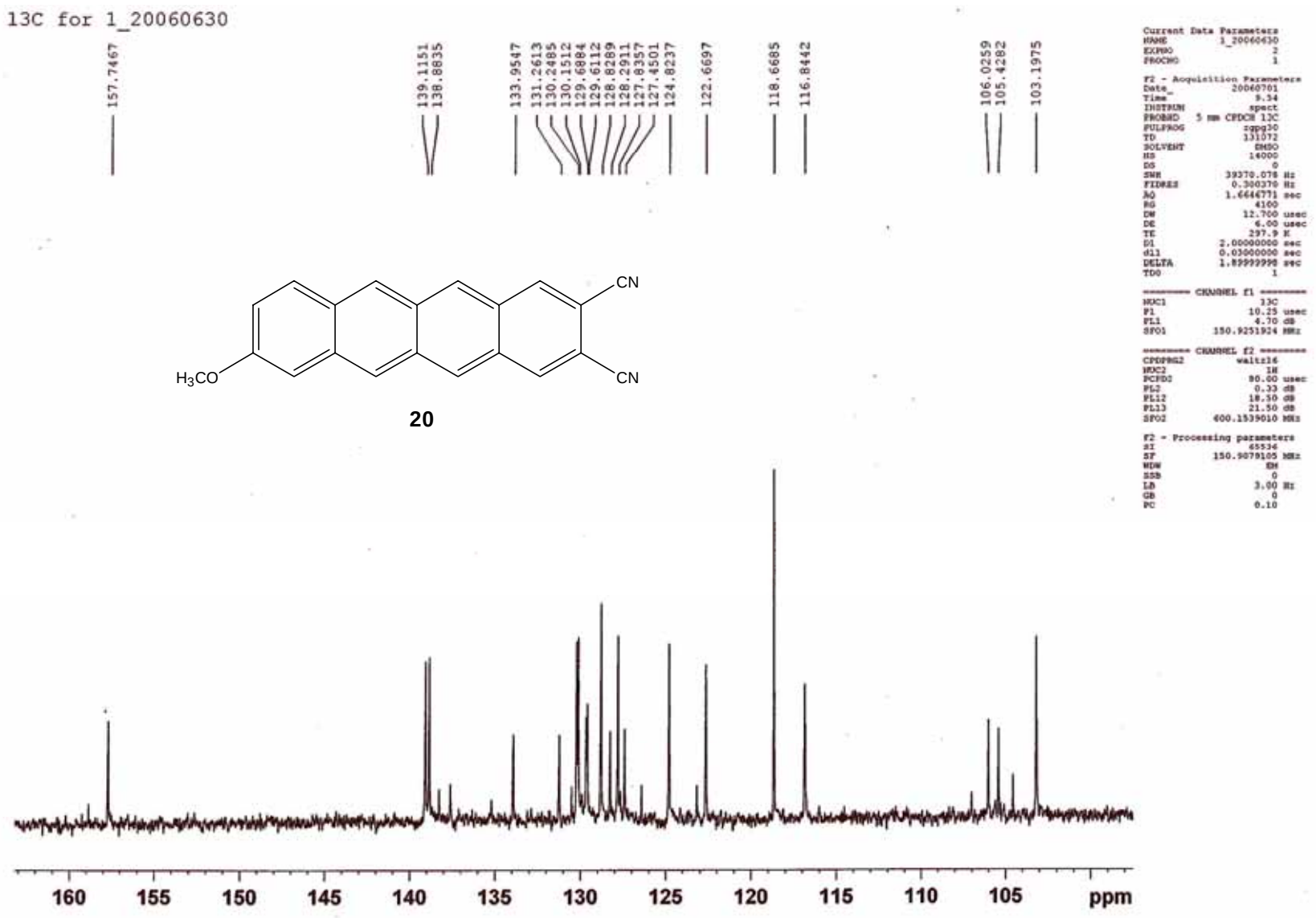
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



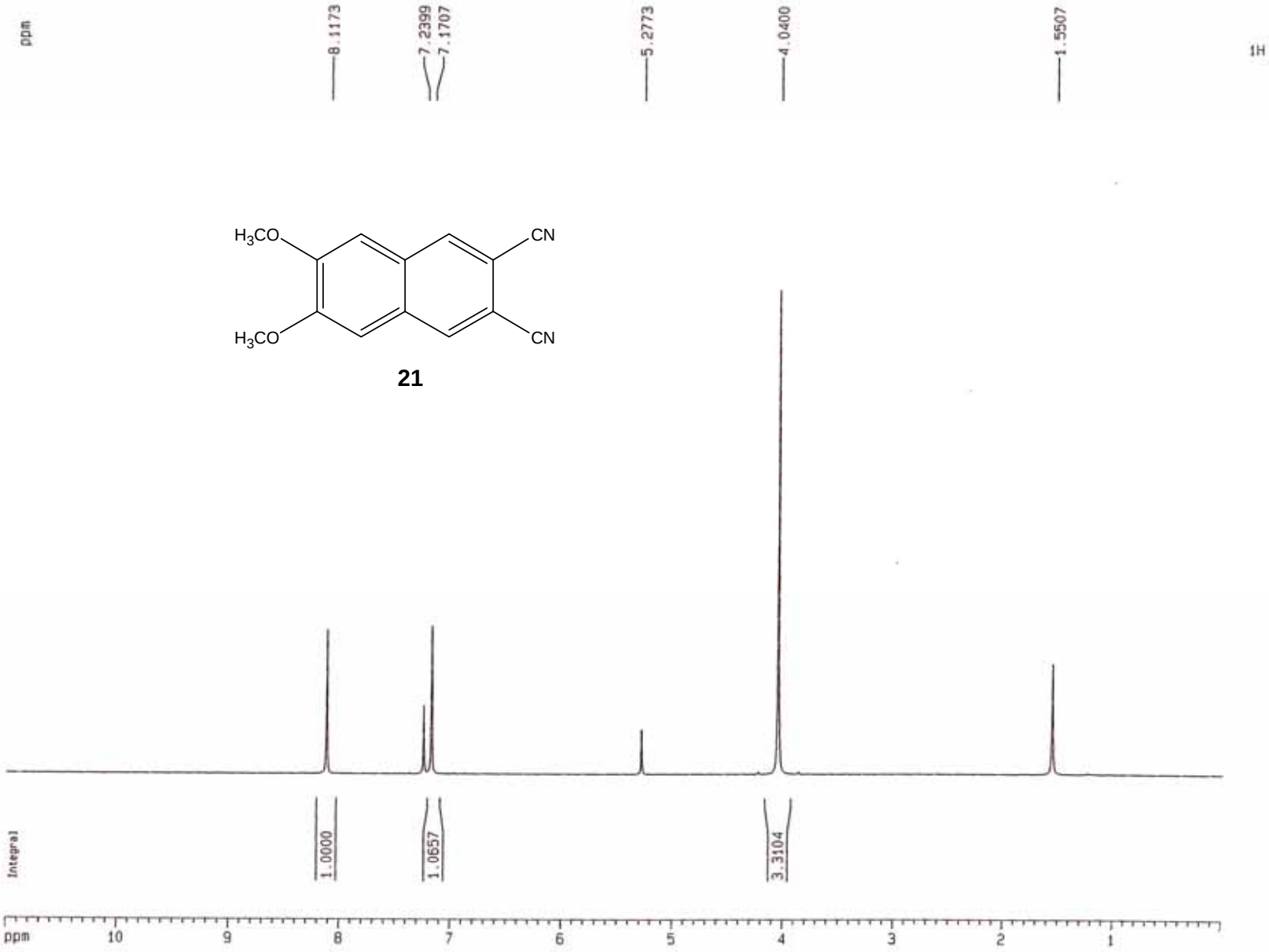
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



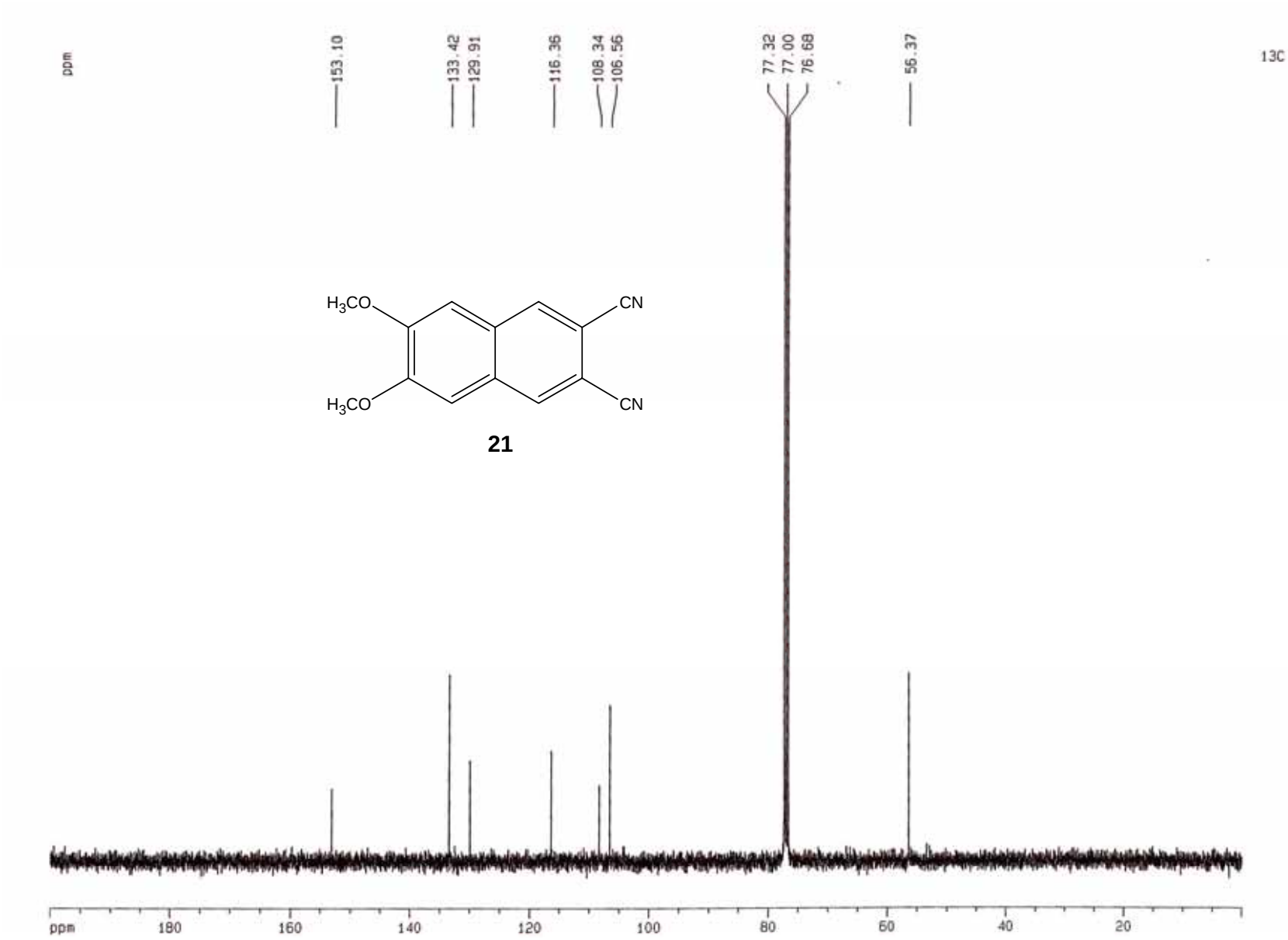
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



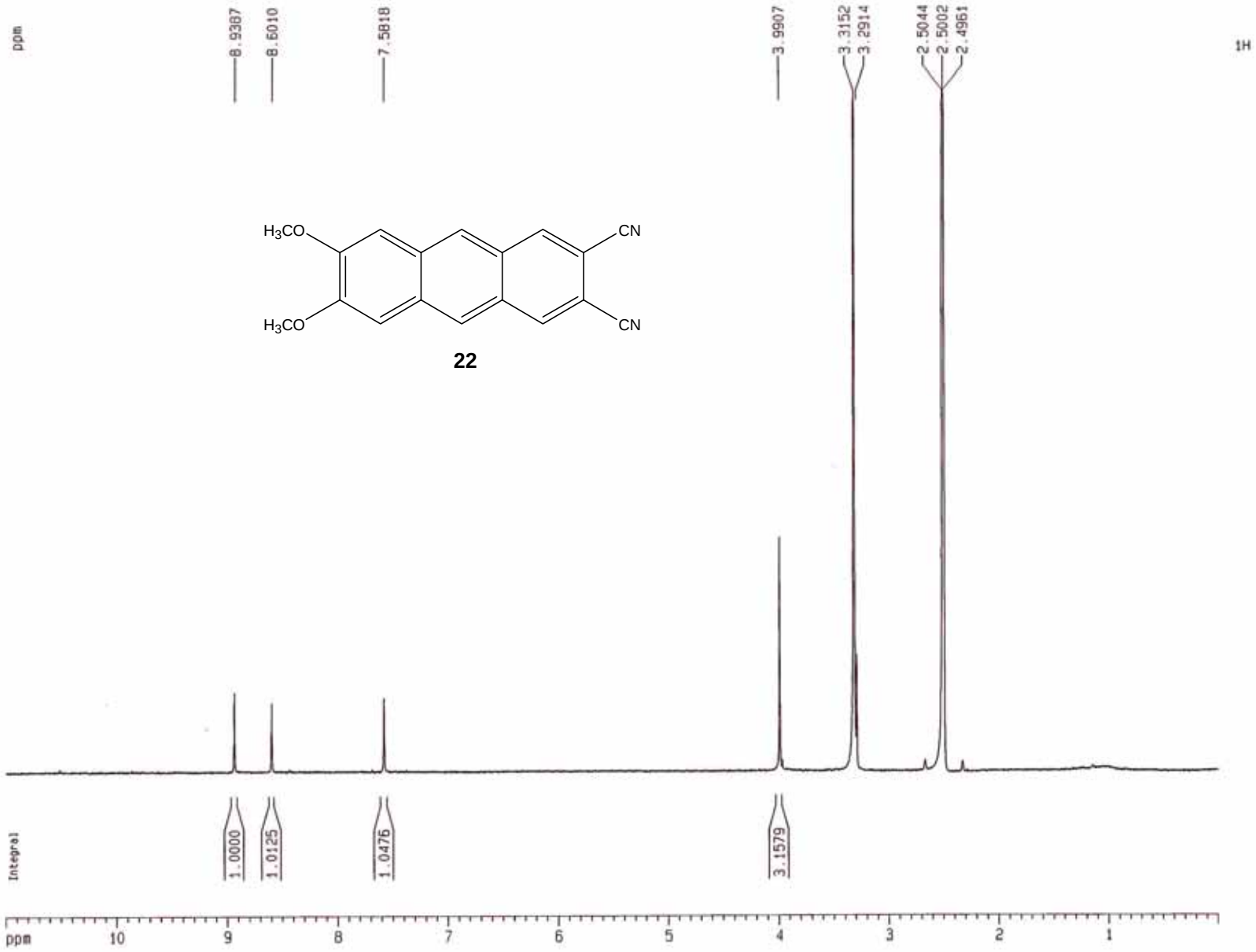
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



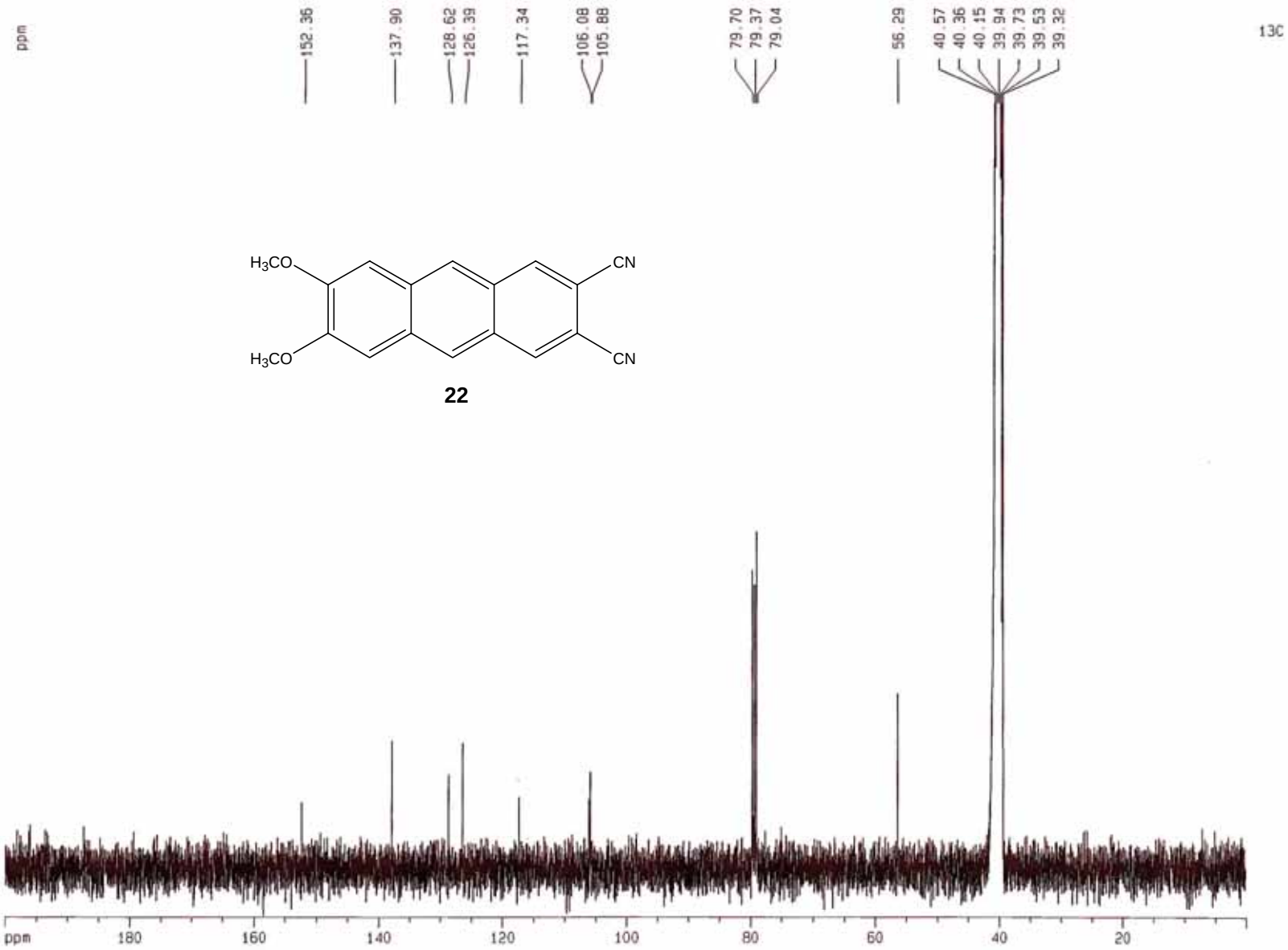
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



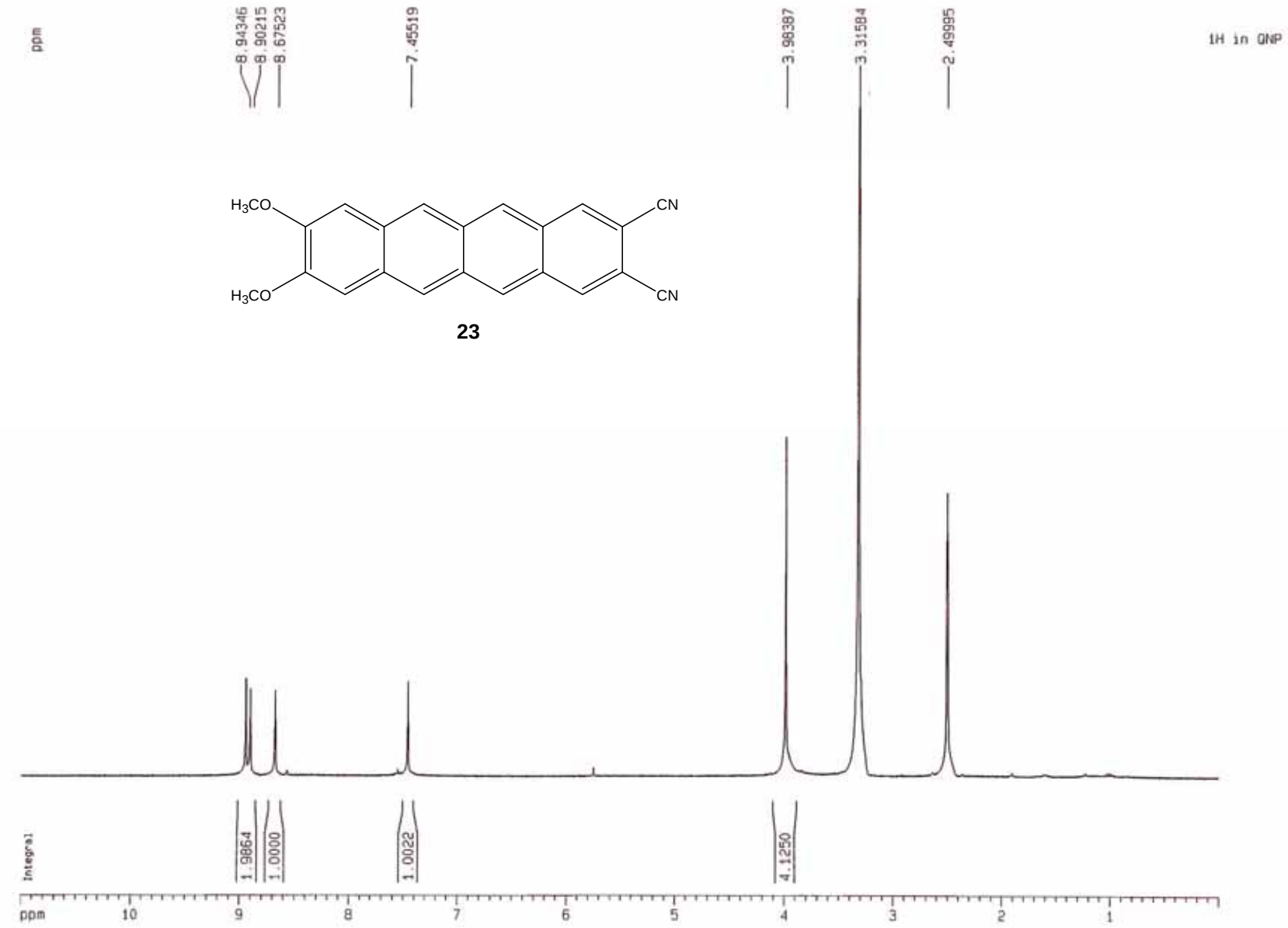
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



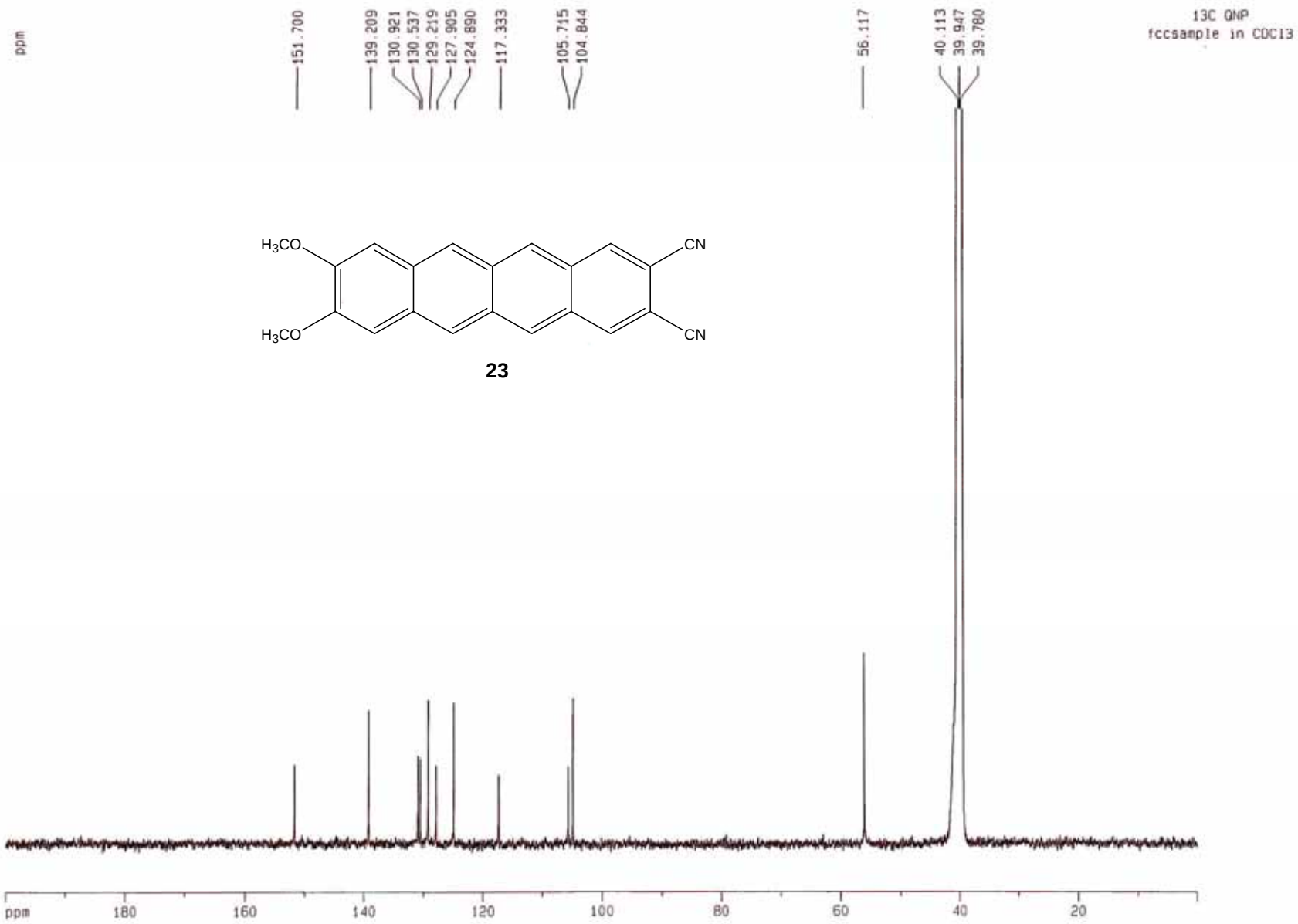
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



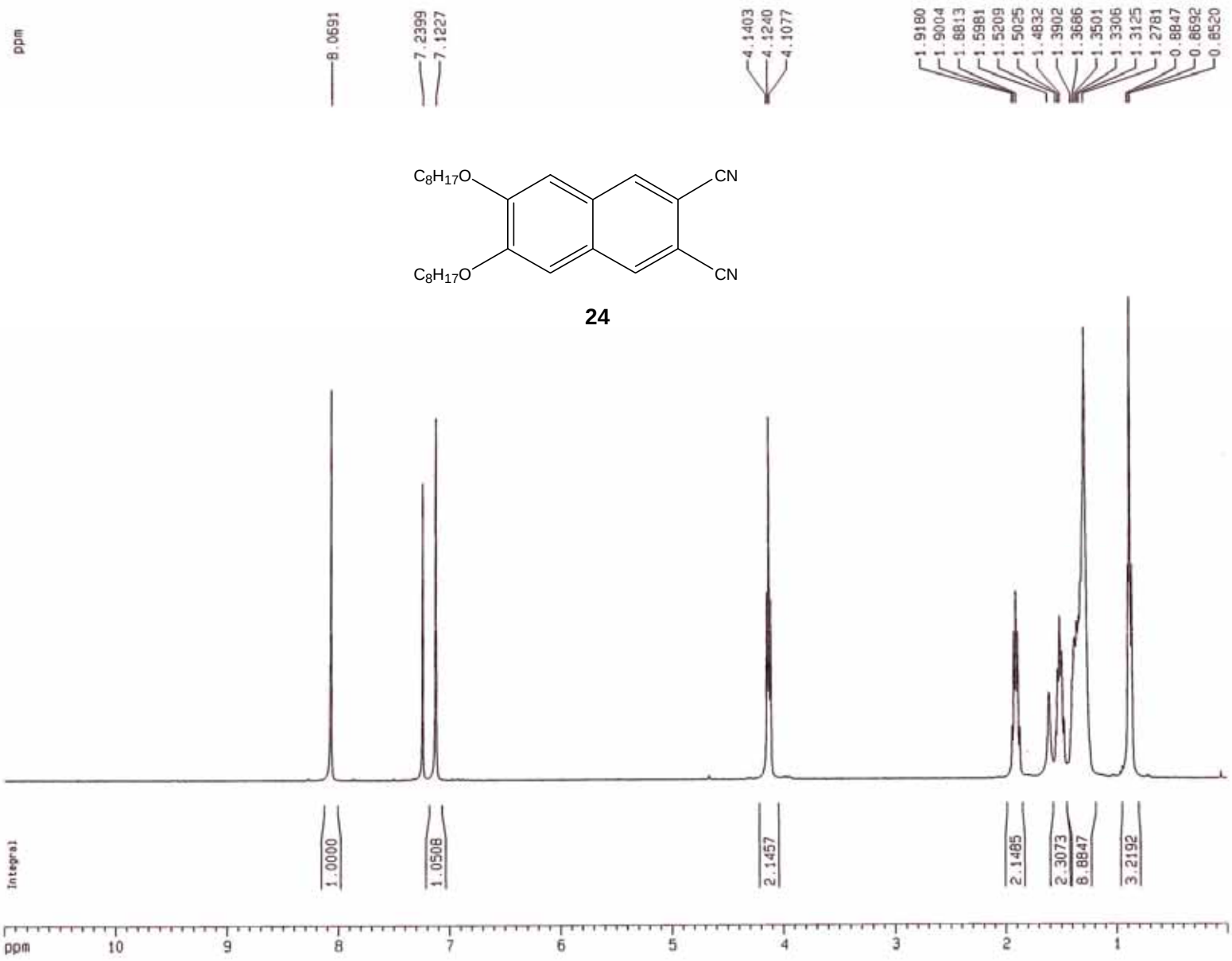
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



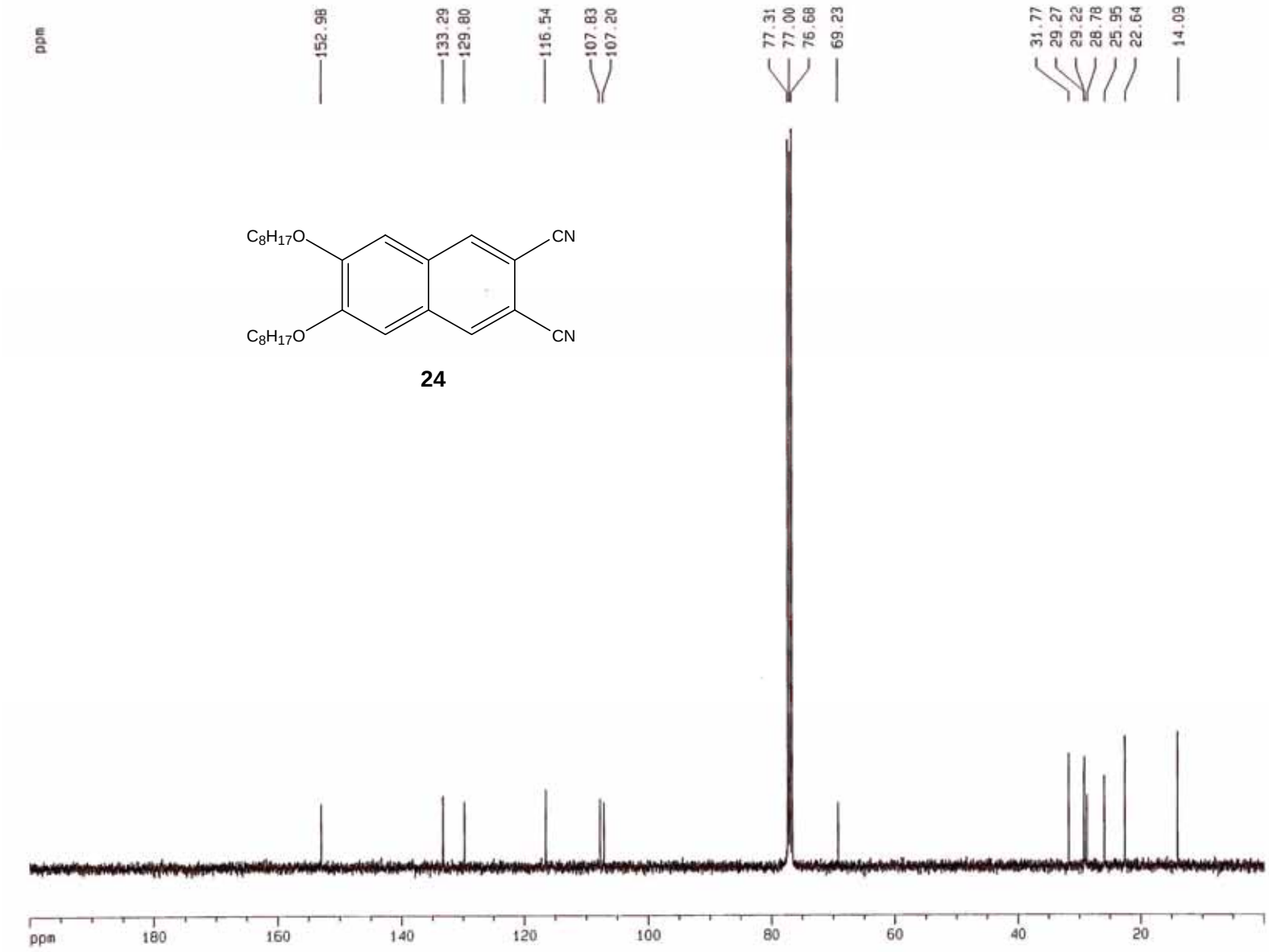
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



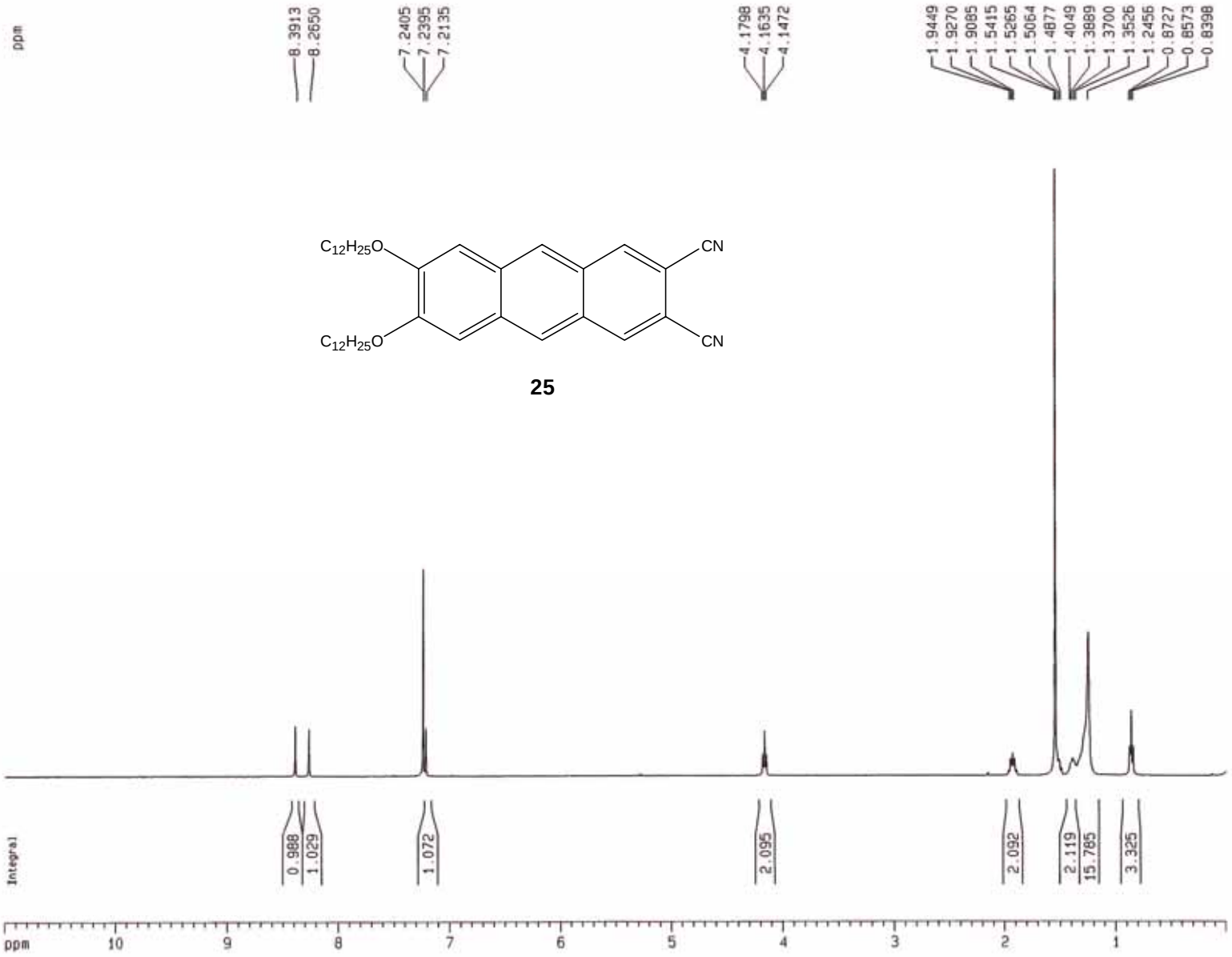
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



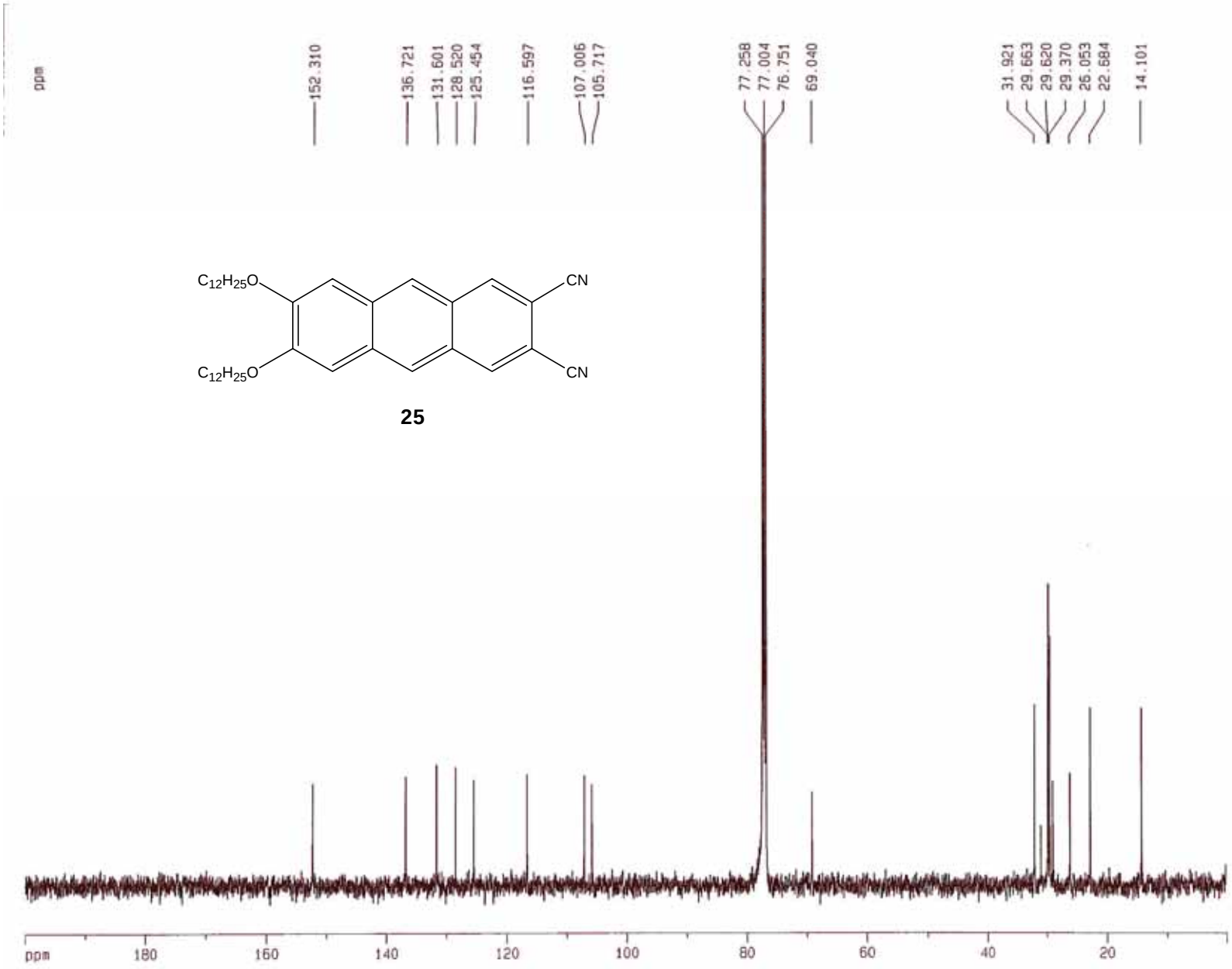
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



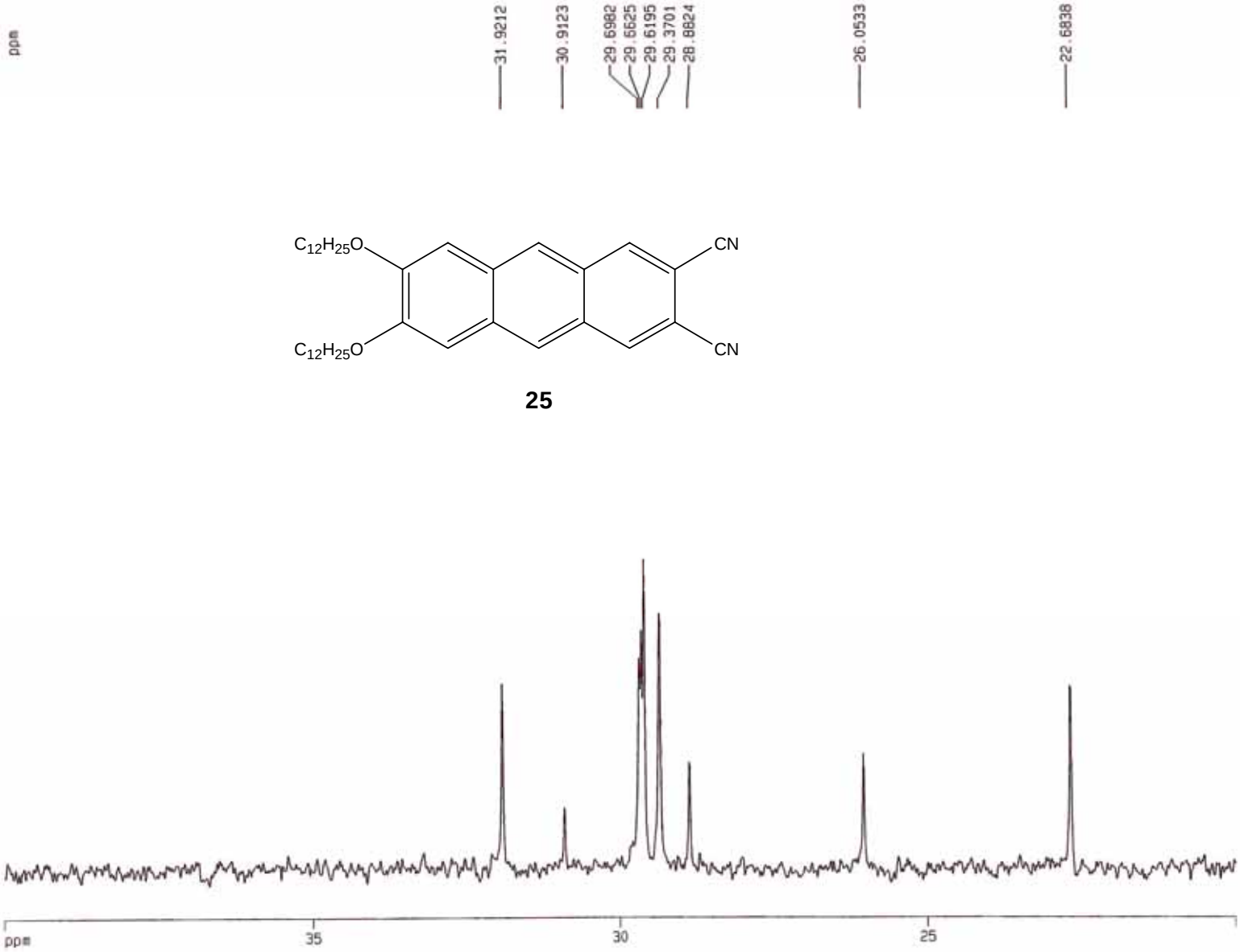
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

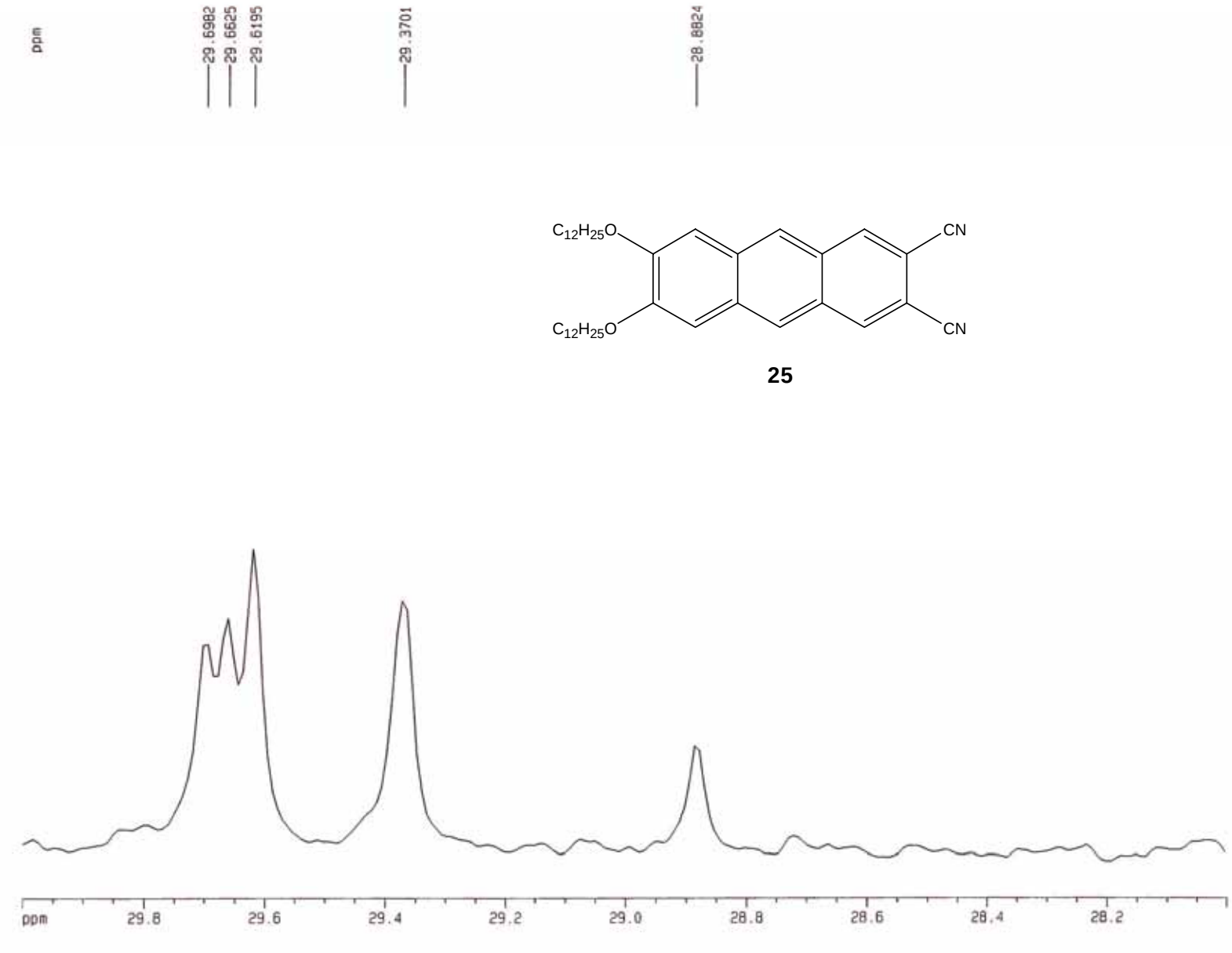


PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



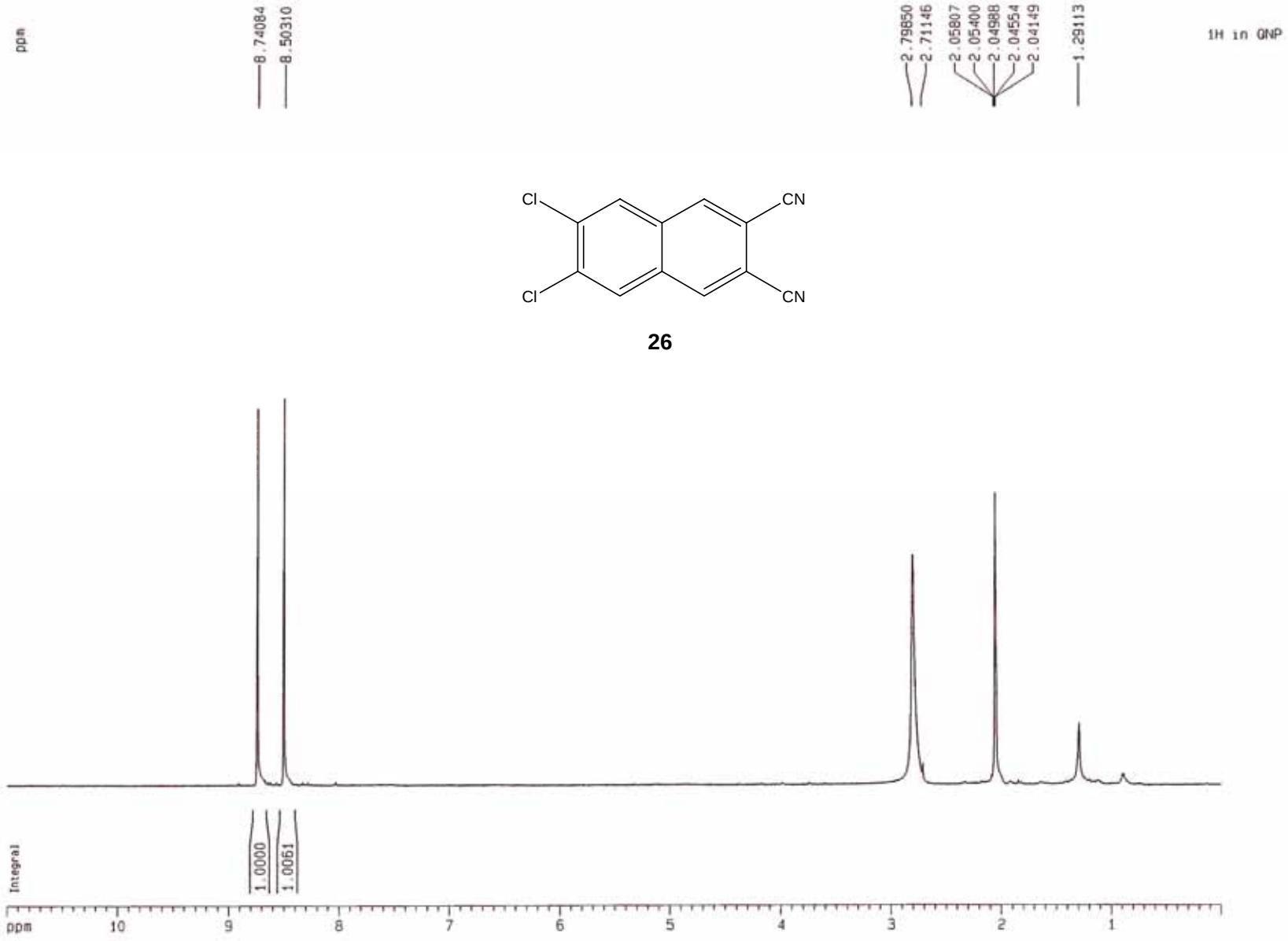
25

PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

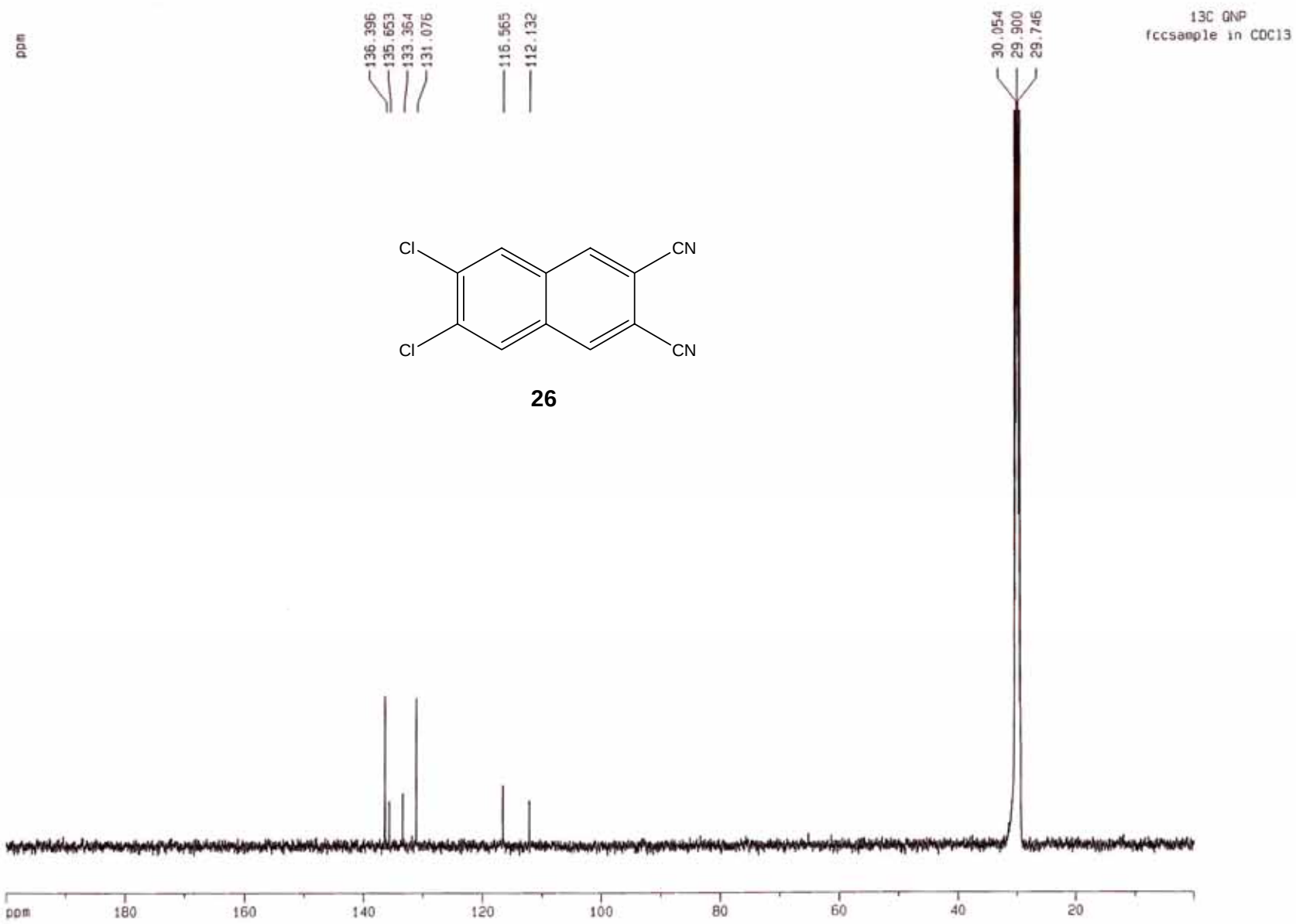


25

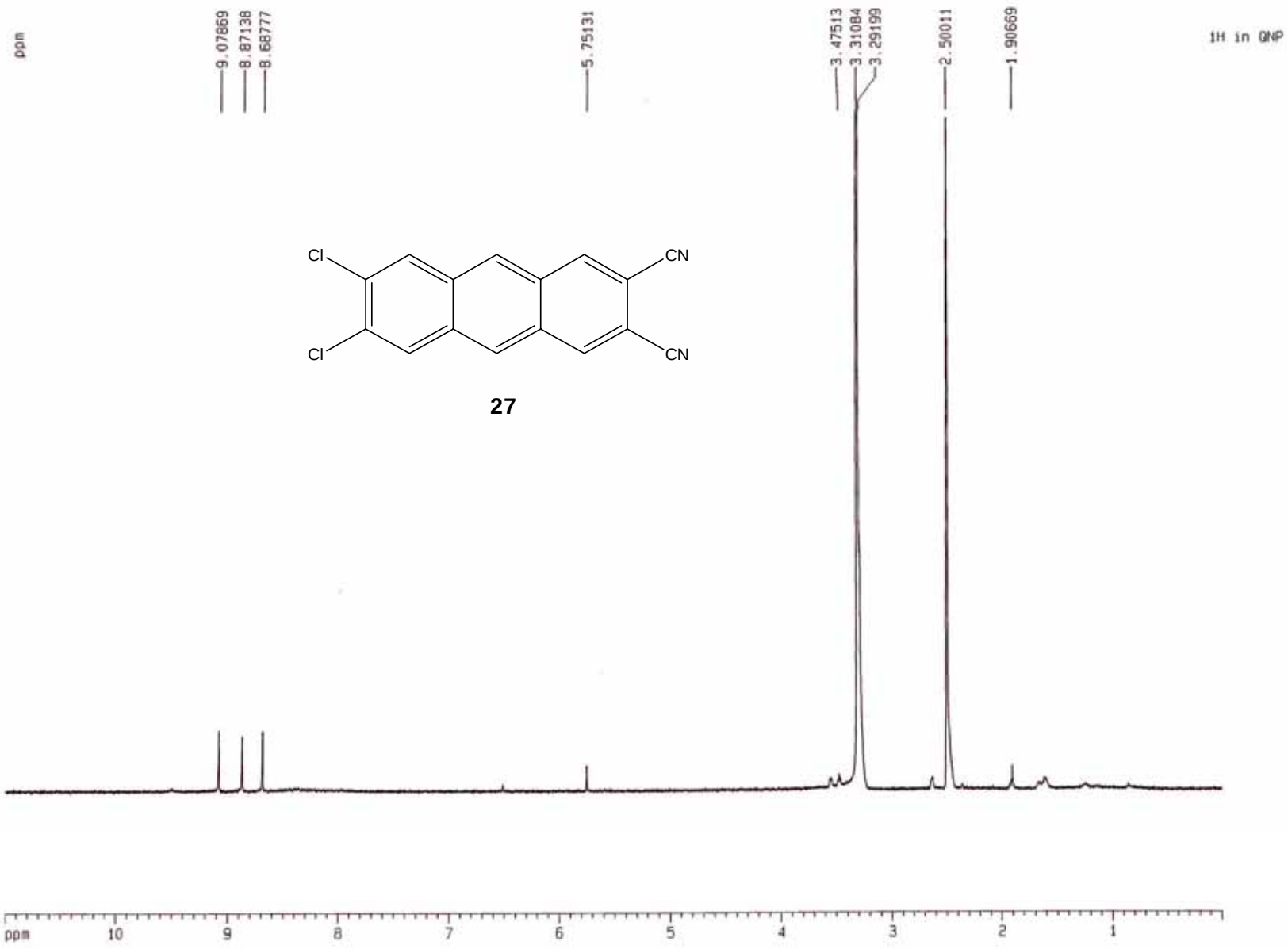
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



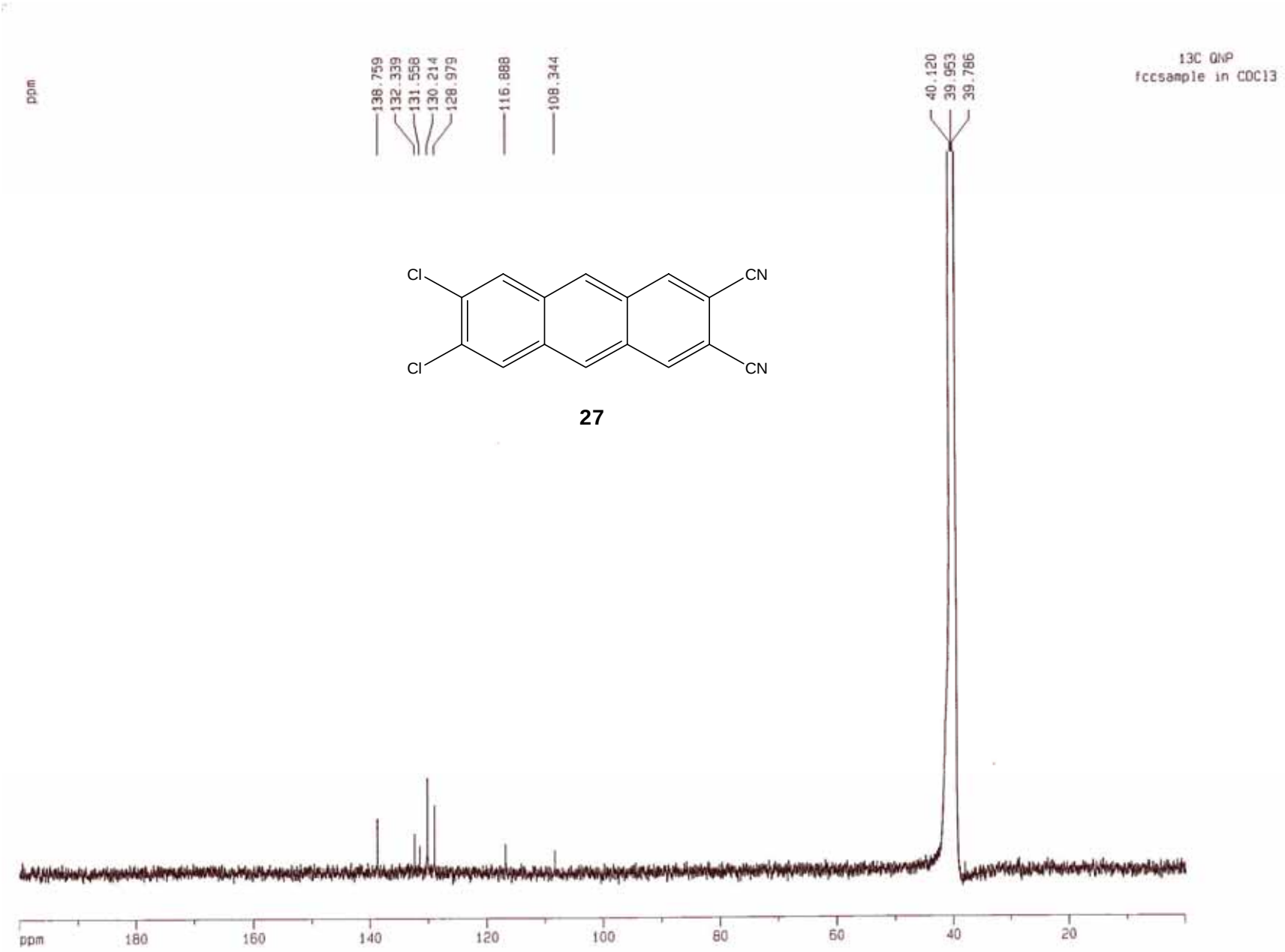
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



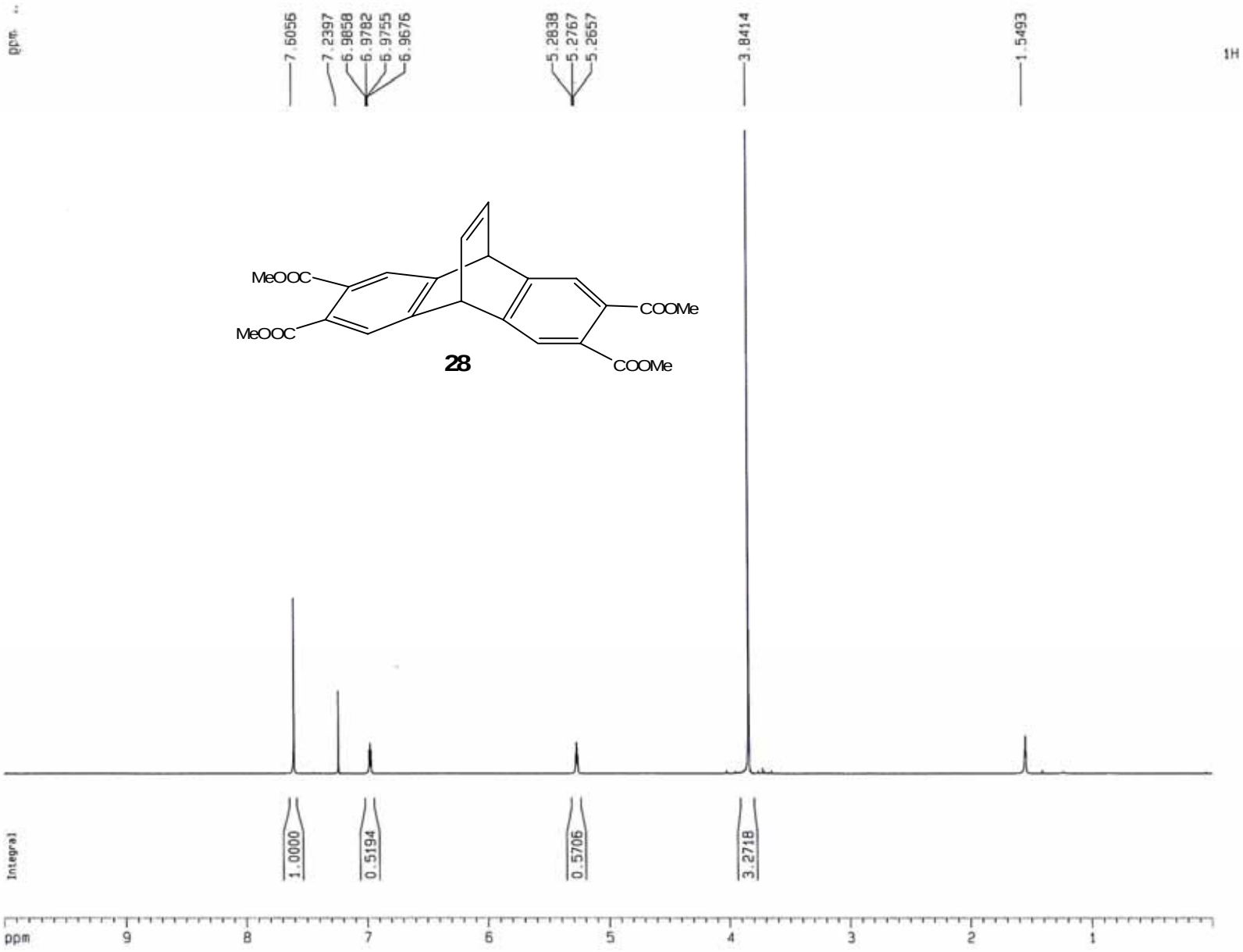
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



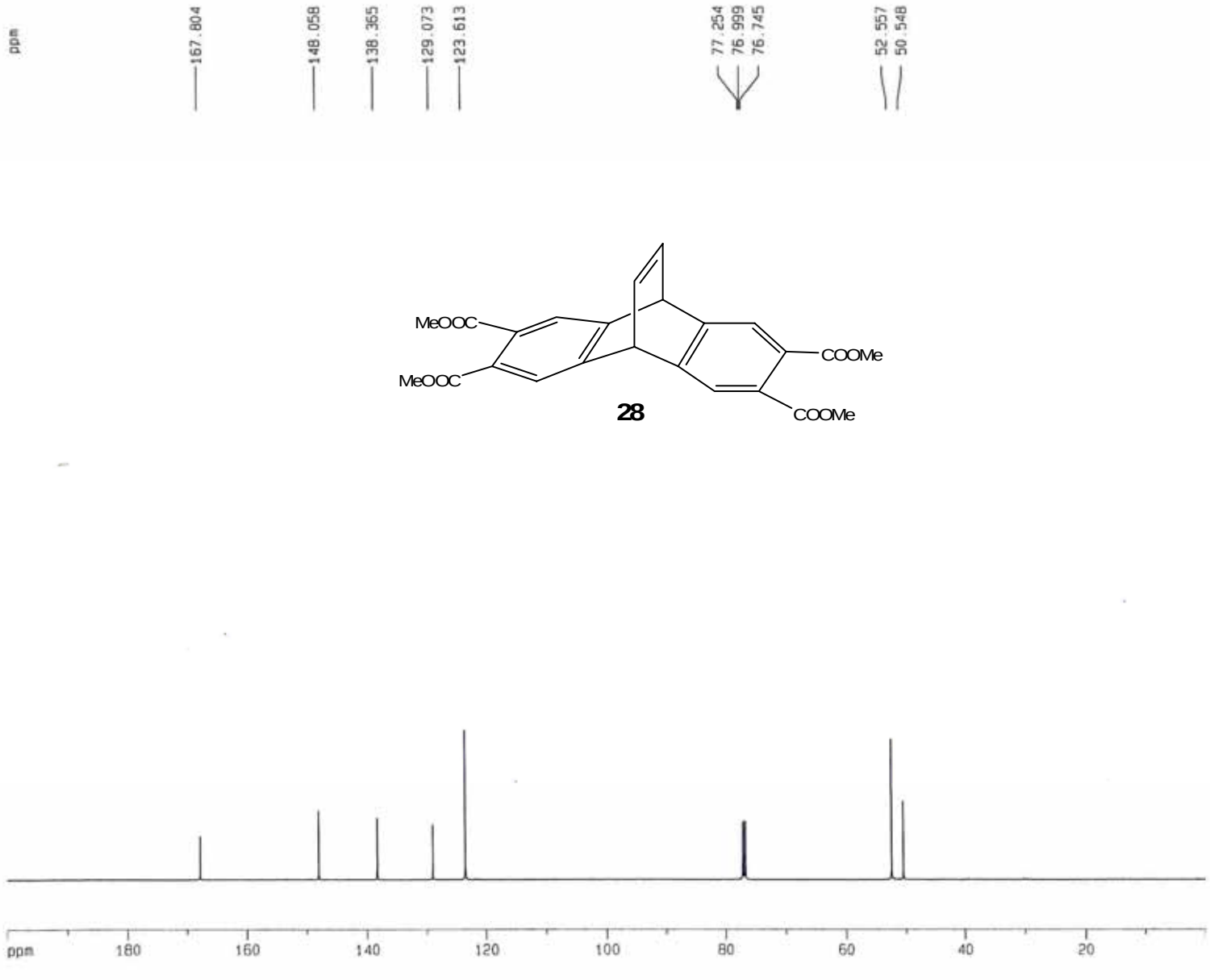
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



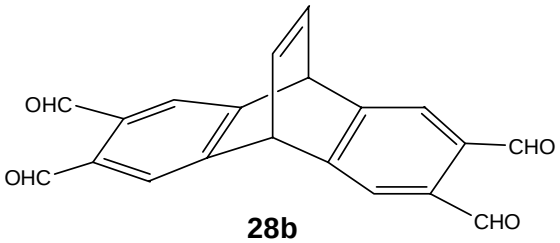
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



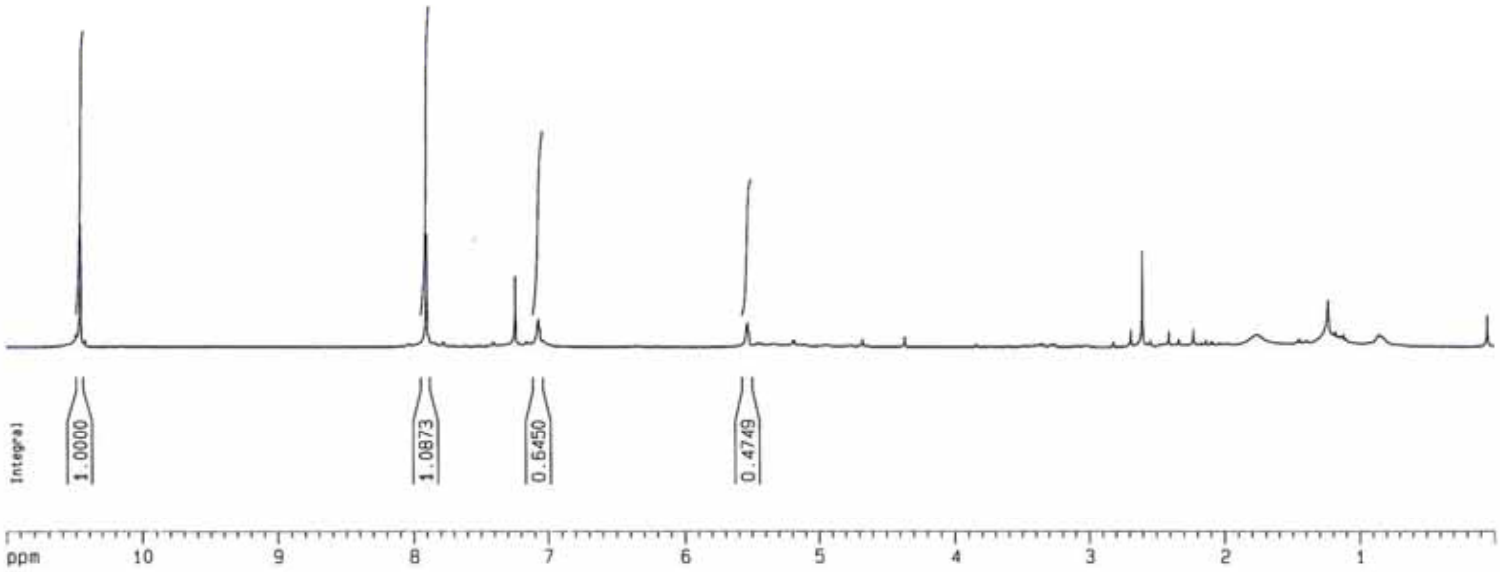
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



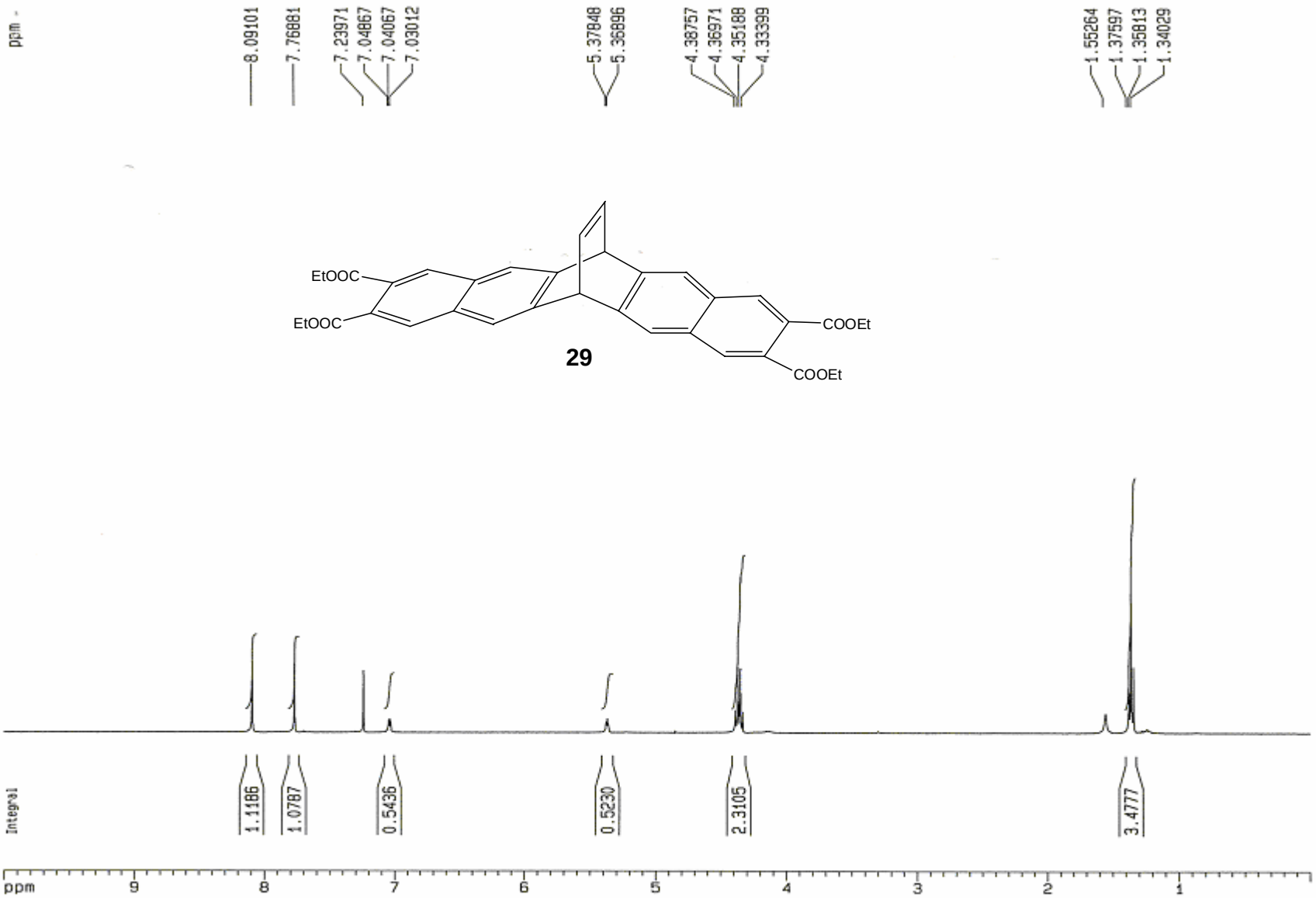
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



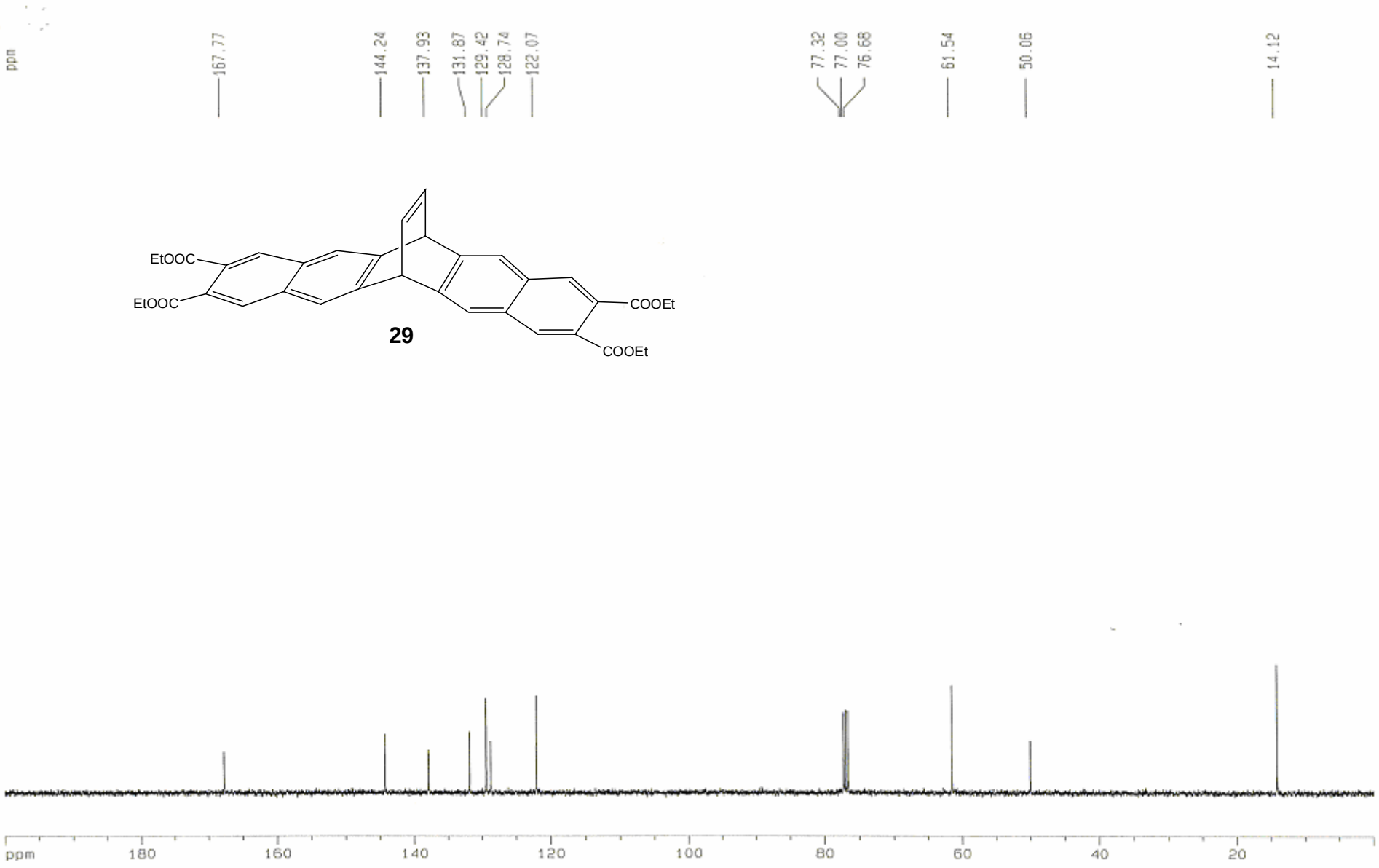
28b



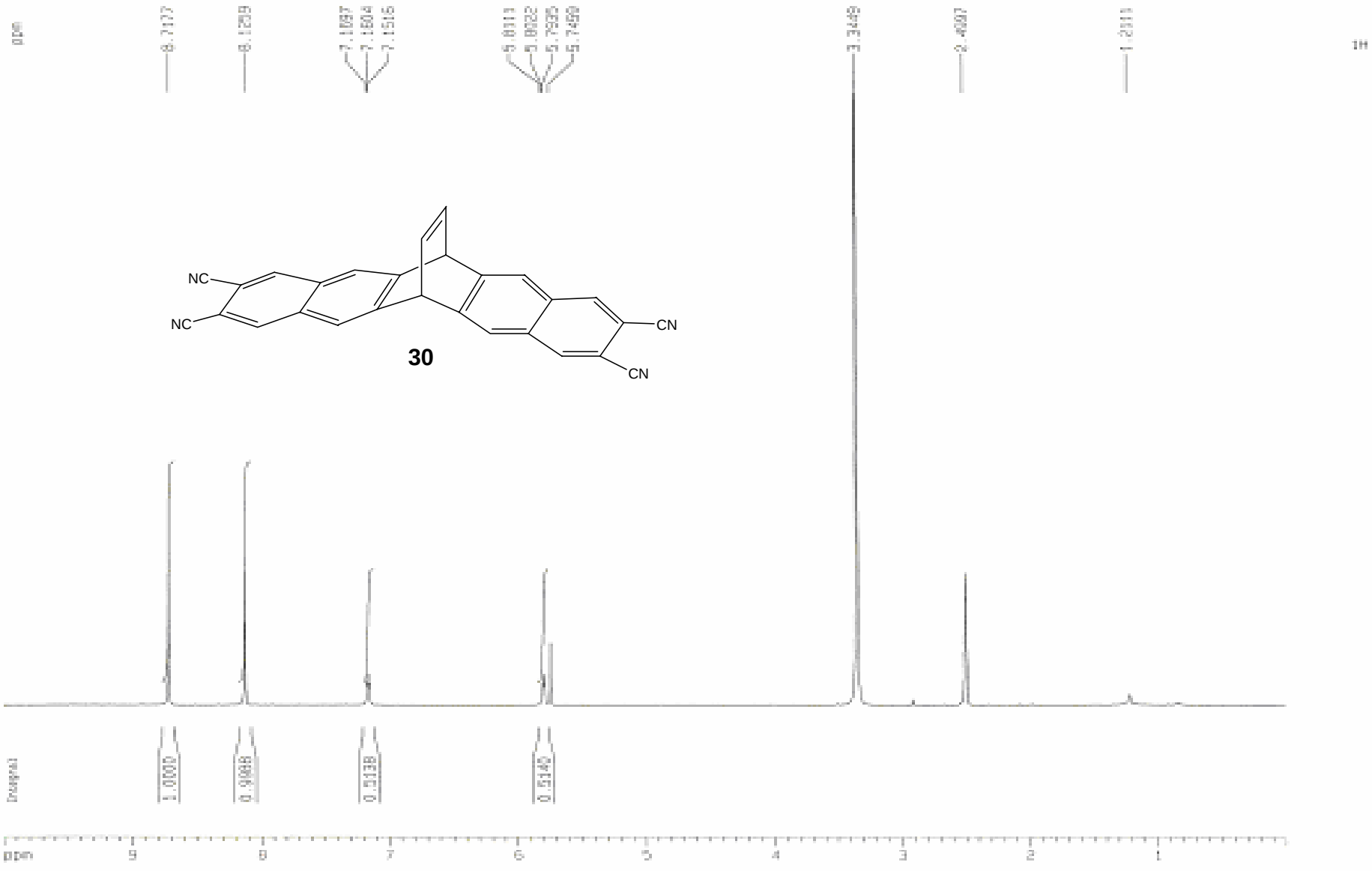
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



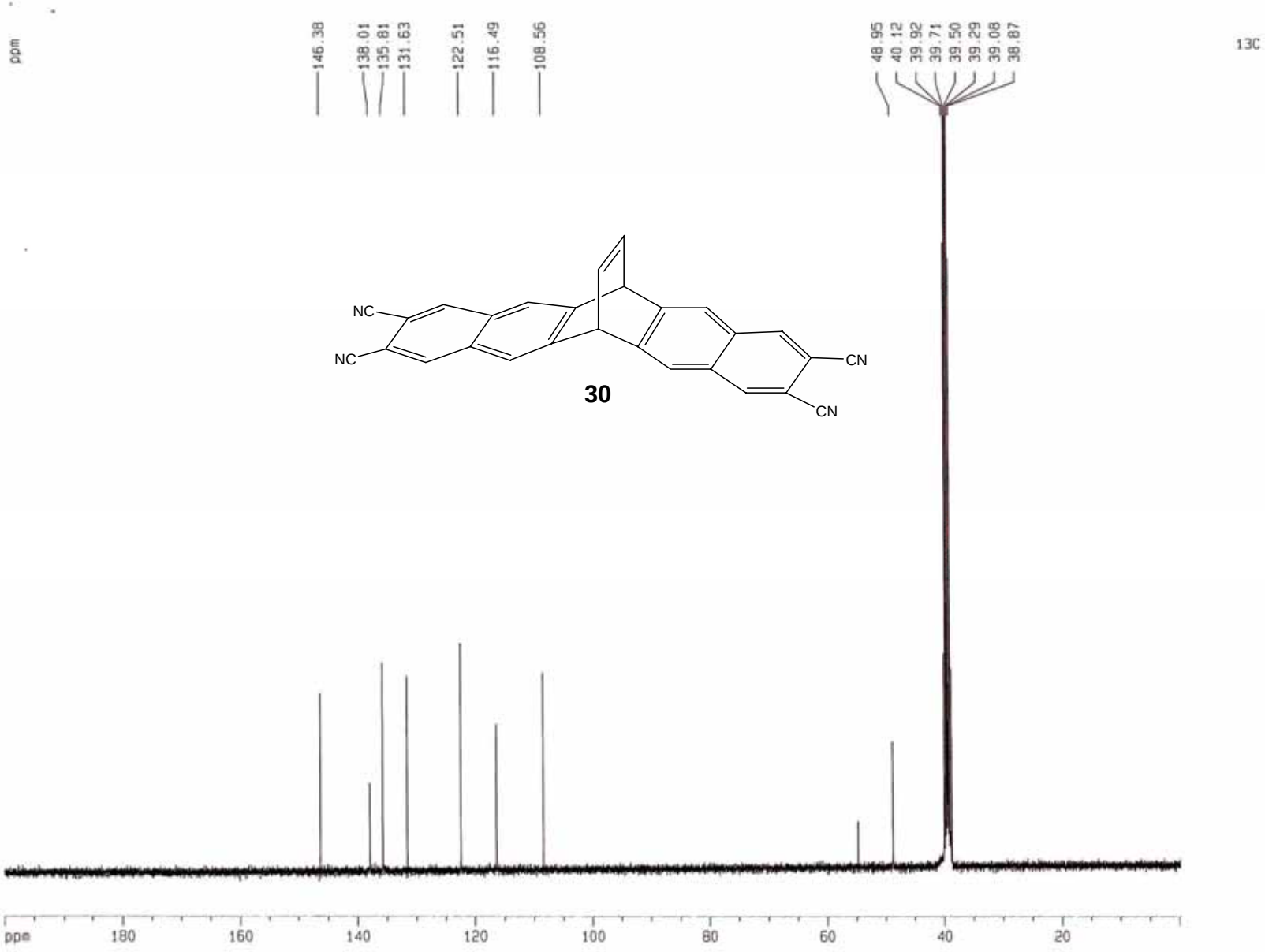
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



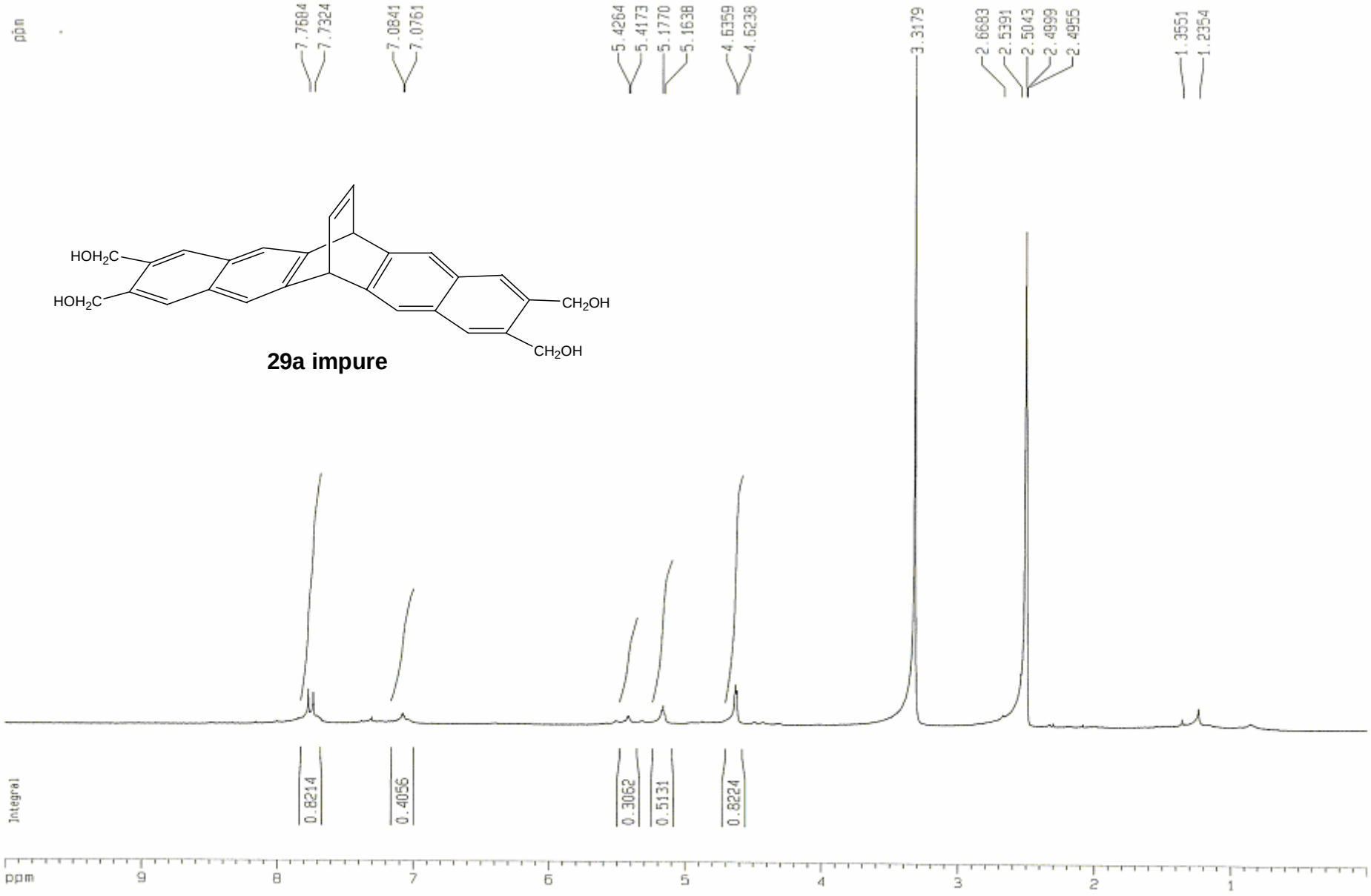
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



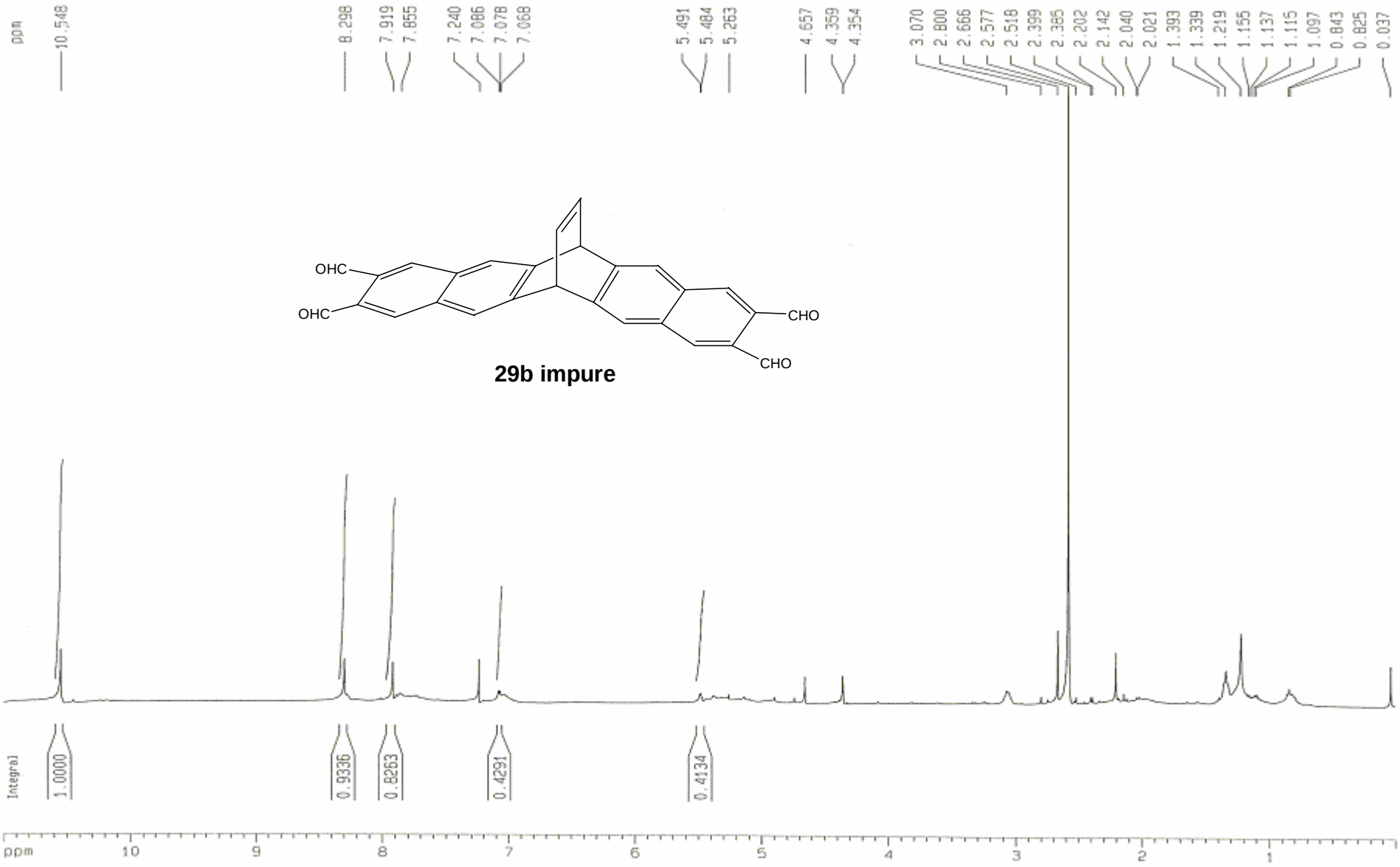
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



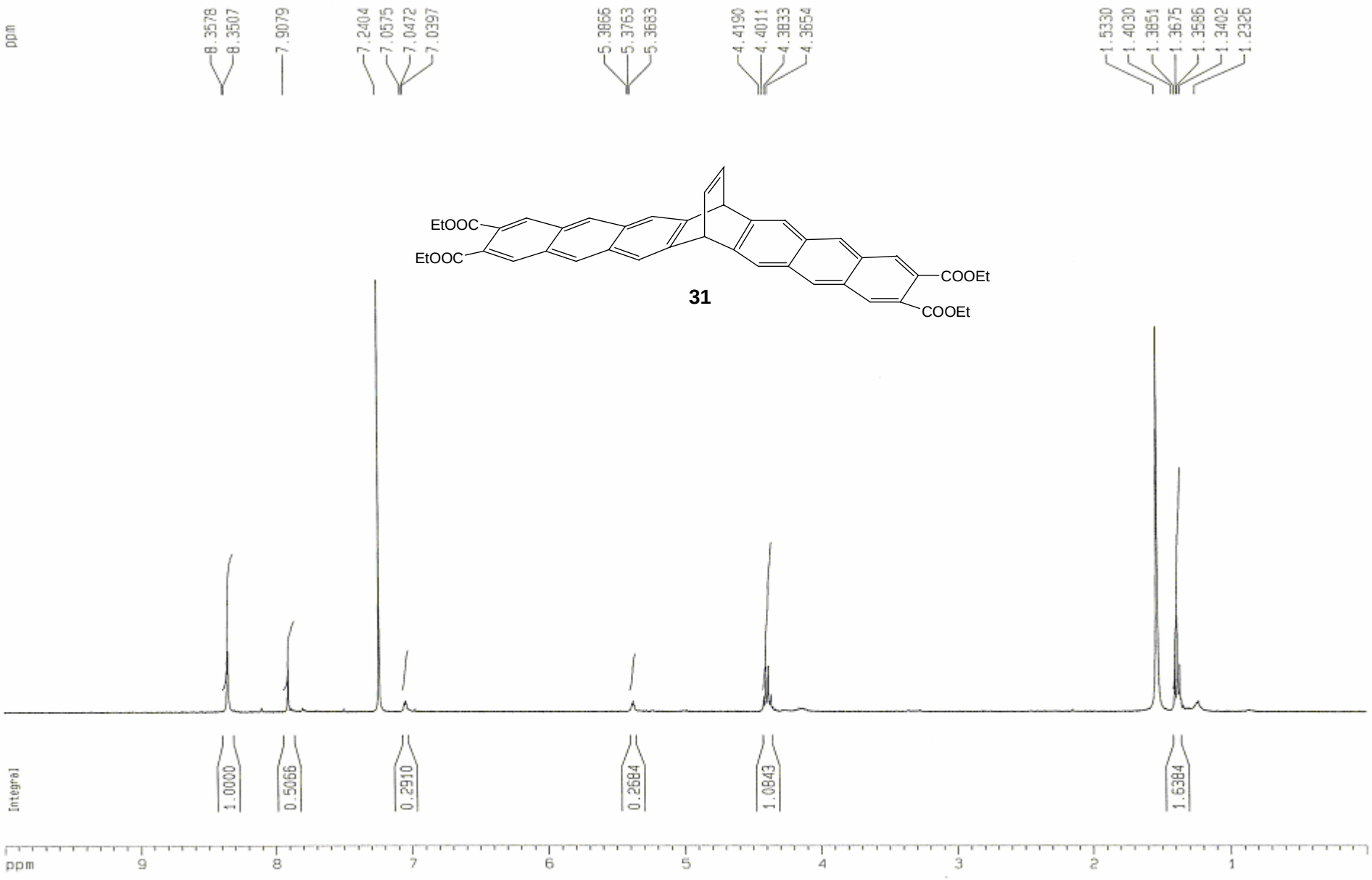
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



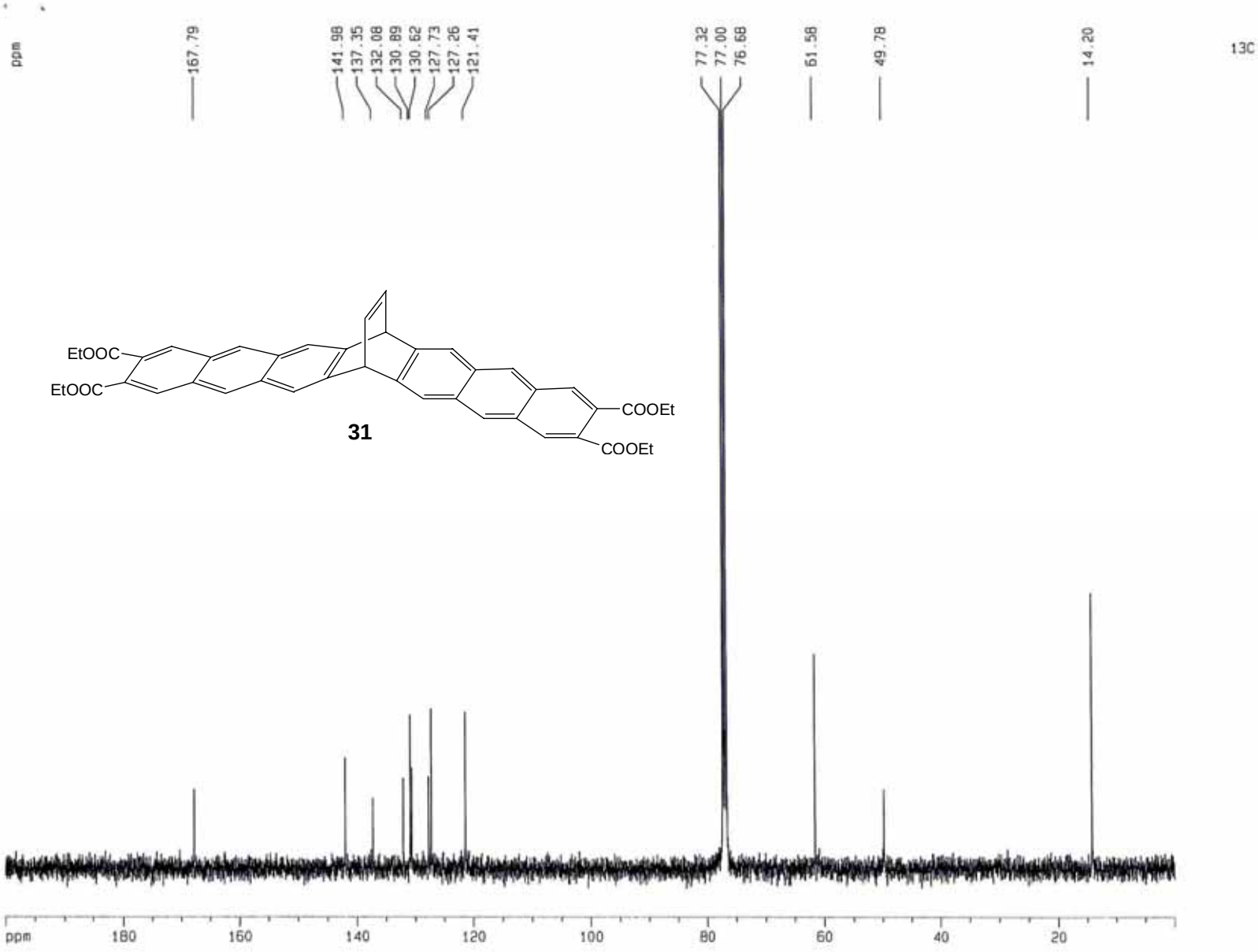
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



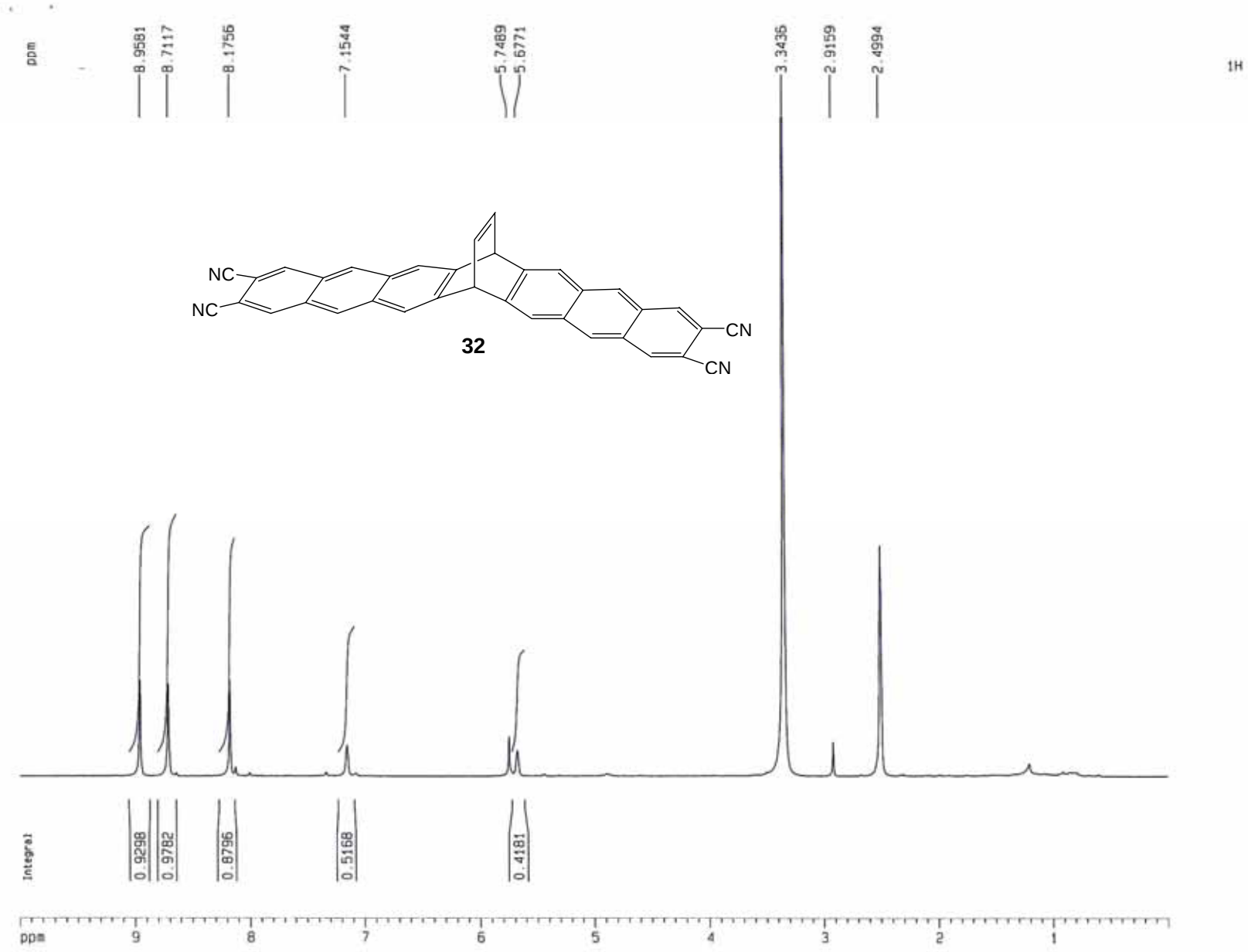
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



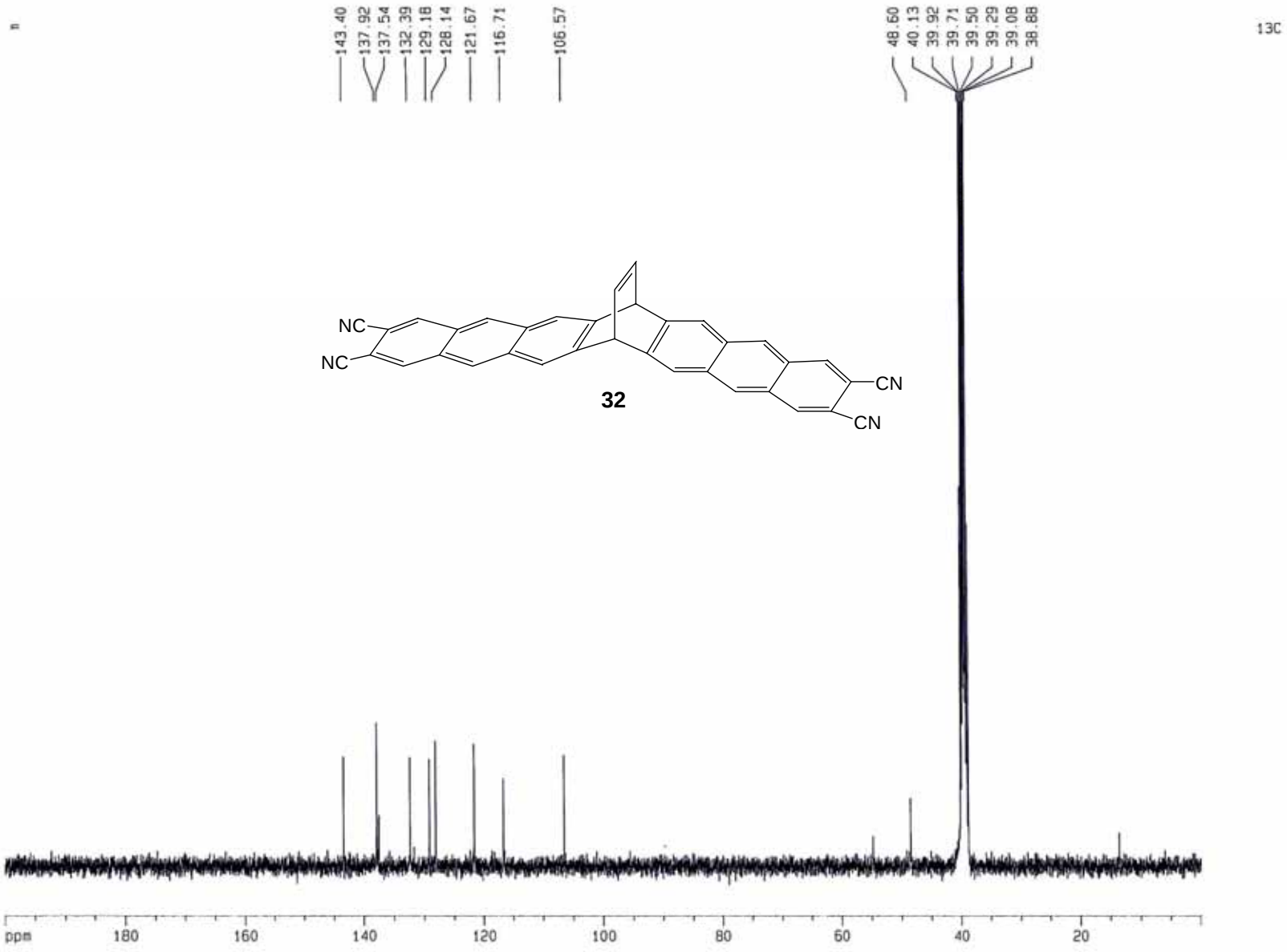
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



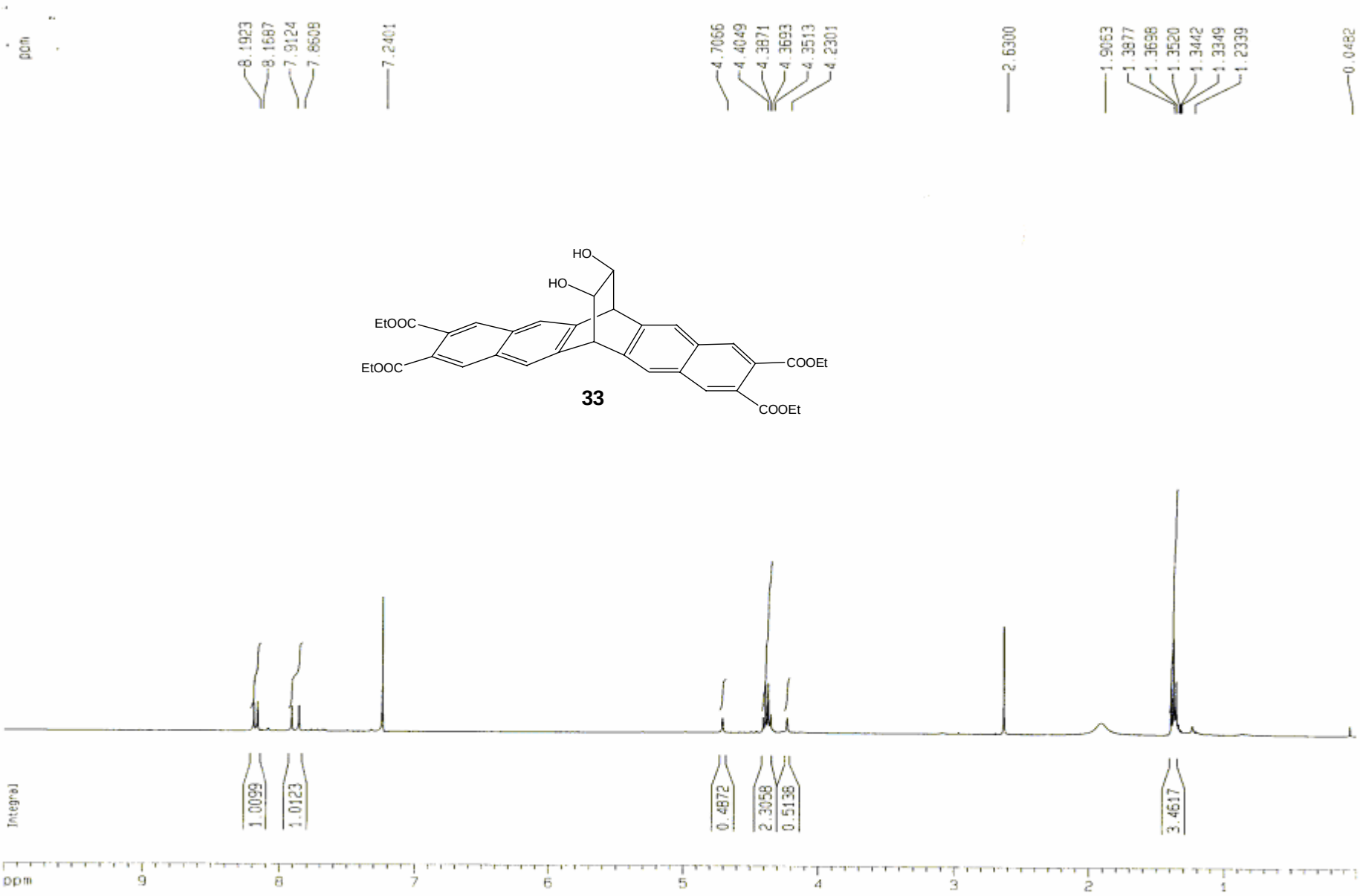
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



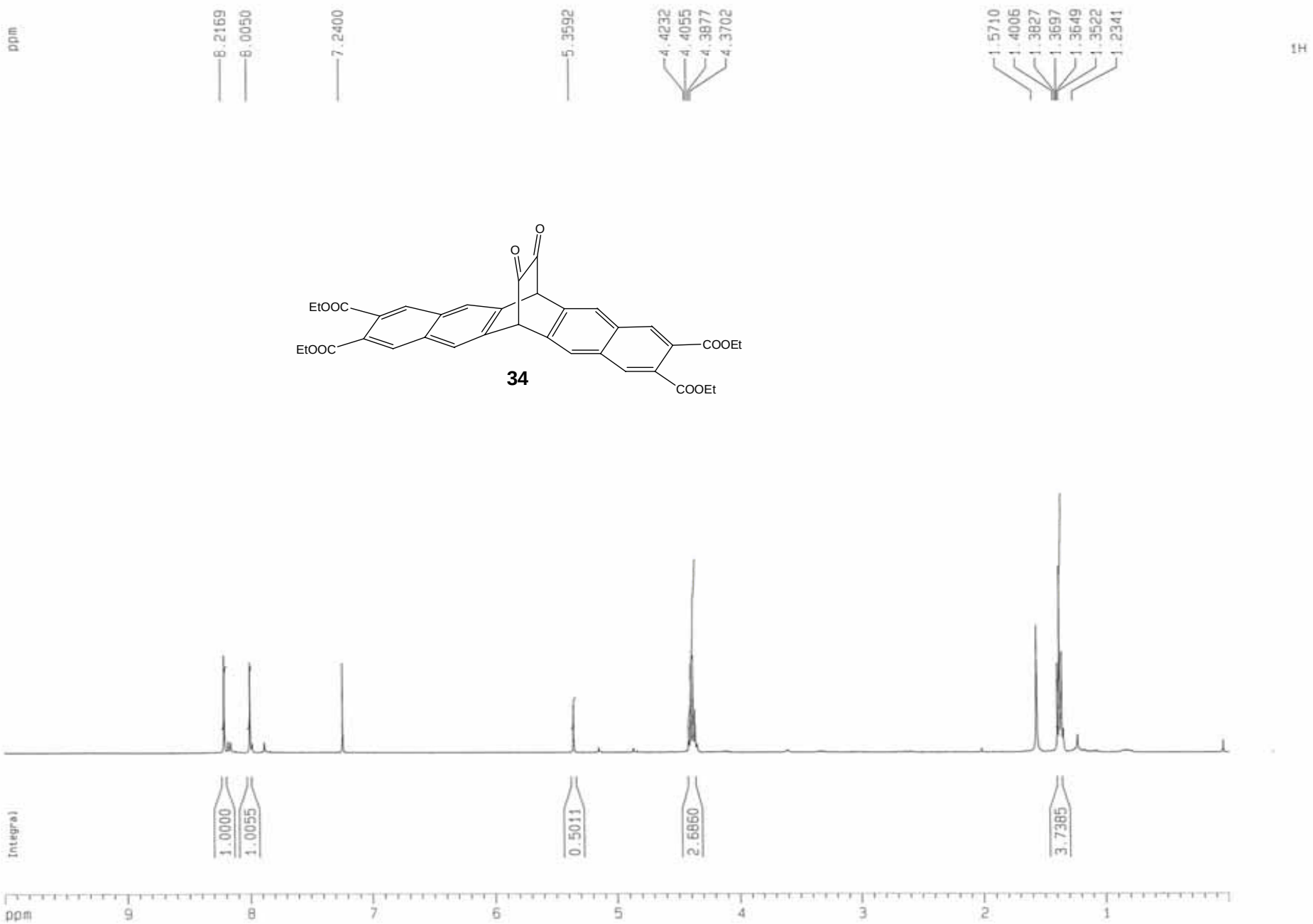
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY

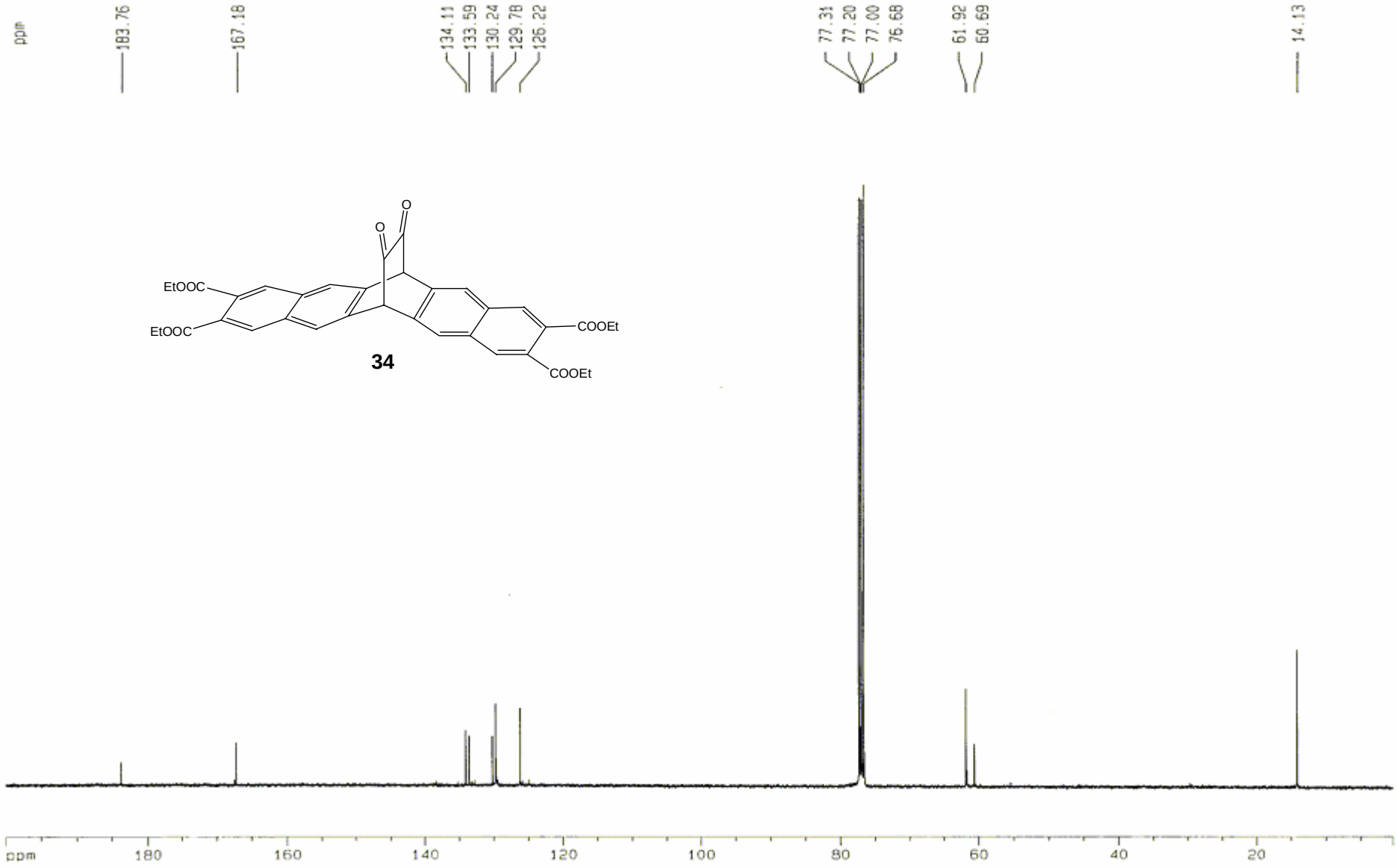


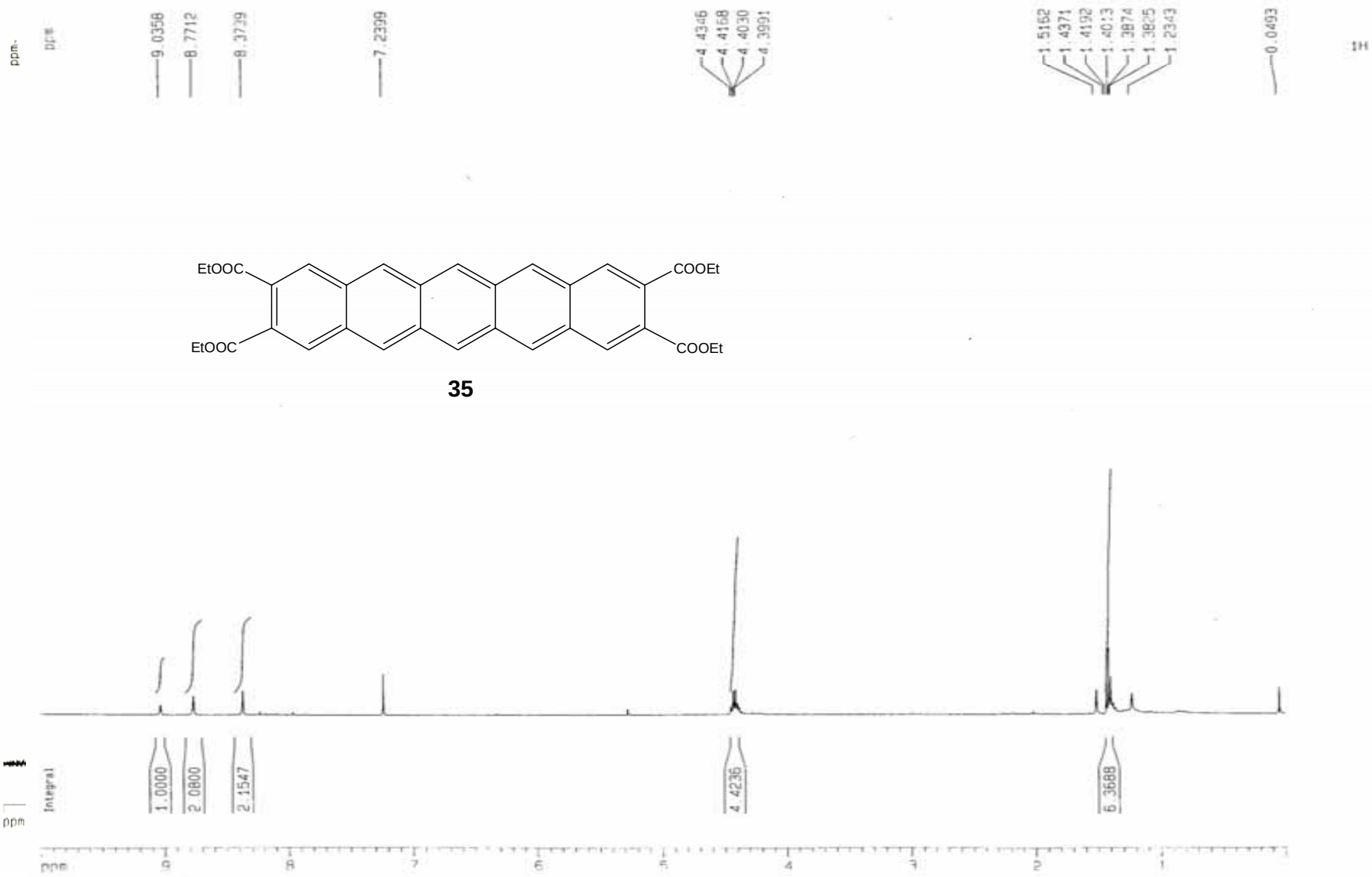
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



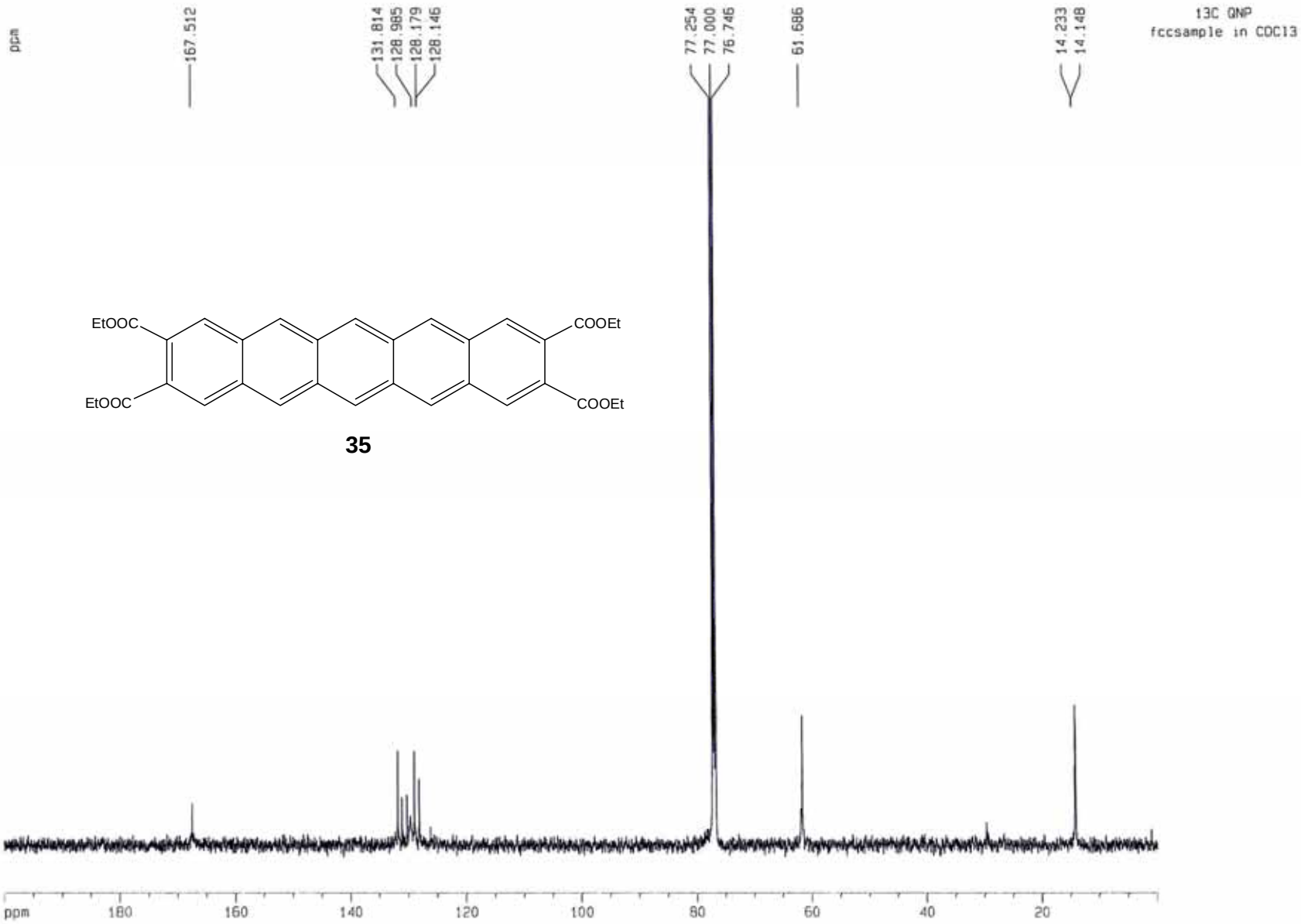
PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY


ppm
8.2169
8.0050
7.2400
5.3592
4.4232
4.4055
4.3877
4.3702
1.5710
1.4006
1.3827
1.3697
1.3649
1.3522
1.2341
1H
O
O
EtOOC
EtOOC
COOEt
COOEt
34
Integral
1.0000
1.0055
0.5011
2.6860
3.7385
ppm
9
8
7
6
5
4
3
2
1

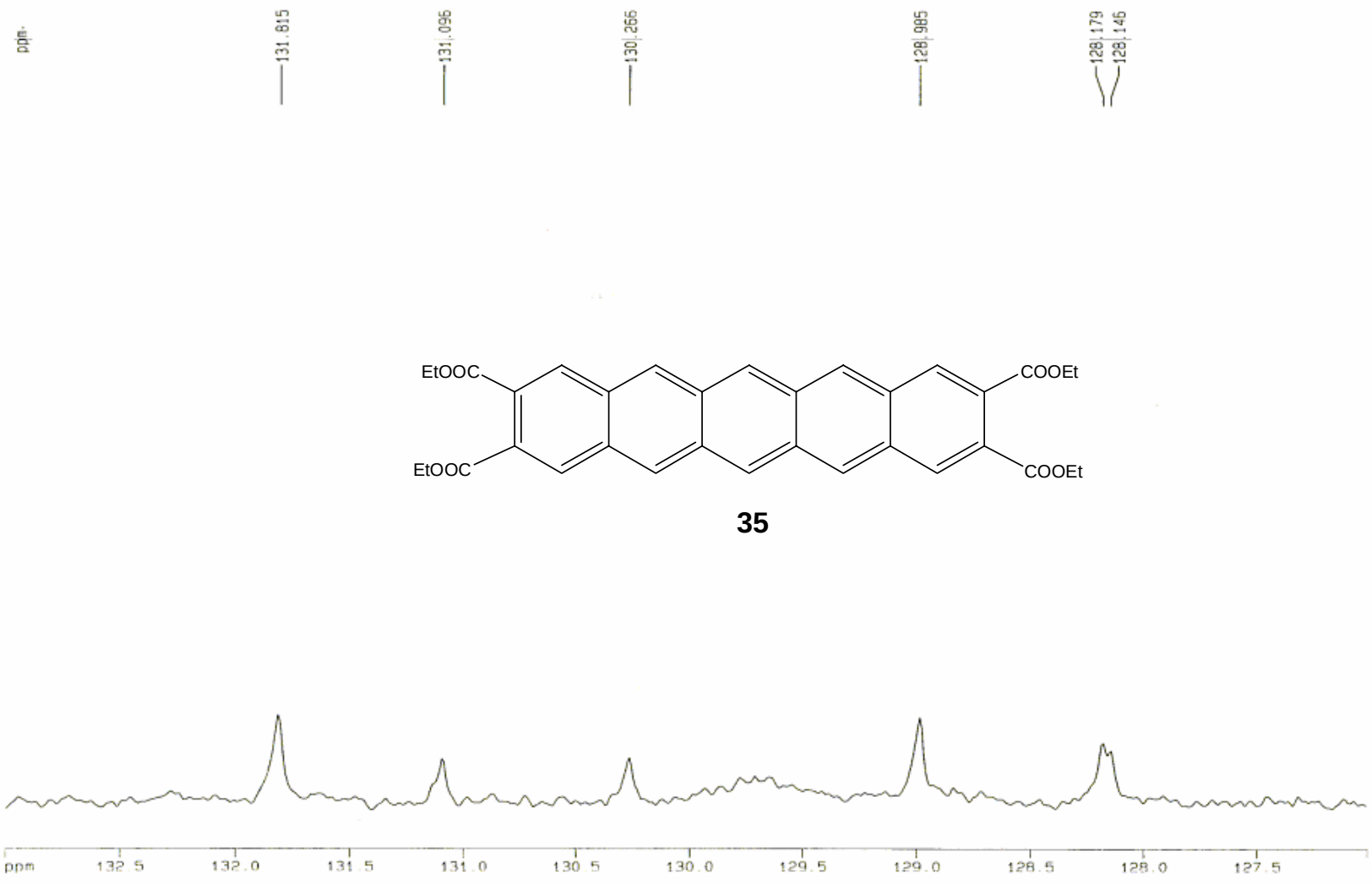

ppm
183.76
167.18
134.11
133.59
130.24
129.78
126.22
77.31
77.20
77.00
76.68
61.92
60.69
14.13
O
O
EtOOC
EtOOC
COOEt
COOEt
34
ppm
180
160
140
120
100
80
60
40
20



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY



PRIVILEGED DOCUMENT FOR REVIEW PURPOSES ONLY