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Supporting Information for:

Electronic effects on a one-pot aromatization cascade involving alkynyl-Prins cyclization, Friedel-Crafts alkylation and dehydration to tricyclic benzo[*f*]isochromenes

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General

Materials and Methods. All reactions were carried out under argon gas unless otherwise noted. Dichloromethane was distilled from CaH_2 and THF was purified by a Solv-Tek® alumina drying column. Flash column chromatography was performed using Sorbent Technologies 40-75μm silica gel (200x400 mesh). Thin layer chromatography was conducted using Sorbent Technologies general-purpose silica gel HL TLC plates on glass. Visualization was accomplished with UV light or by heating plates dipped in cerium ammonium molybdate (CAM) or potassium permanganate staining solutions. Fourier transform infrared (FT-IR) spectroscopy was recorded using a DIGILAB FTS 7000 series FTIR spectrophotometer. Single crystal determinations were carried out with a Bruker *SMART Apex II* diffractometer using graphite-monochromated Cu K_α radiation. ^{1}H NMR spectra were recorded on Varian Mercury FTNMR (400 MHz) or Agilent Vnmr J4.1 (400 MHz) spectrometers and are reported in ppm using solvent as an internal standard (tetramethylsilane at 0.00 ppm or $CHCl_3$ at 7.27 ppm). Proton-decoupled ^{13}C-NMR spectra (attached proton test) were recorded on Varian Mercury FTNMR (400 MHz) or Agilent Vnmr J4.1 (400 MHz) spectrometers and are reported in ppm using solvent or TMS as internal standards (77.23 ppm for $CDCl_3$ and 0.00 ppm for TMS). Quaternary carbons (C) are listed as (q), methine carbons (CH) are listed as (t), methylene carbons (CH_2) are listed as (s), and methyl carbons (CH_3) are listed as (p). Gas chromatographic (GC) analyses were conducted using a Varian 3900 spectrometer equipped with an Agilent DB-5MS capillary column (30 m x 0.32 mm i.d., 0.25 μm) and an FID detector using helium as a carrier gas. Gas chromatography–mass spectrometry (GC-MS) analyses were performed using an Agilent Technologies 5973 network mass selective detector and 6890N network GC system. High-performance liquid chromatography (HPLC) was performed using SHIMADZU UFLC with the

following components: DGU-20A 5R degassing unit, LC-20AT liquid chromatograph, SIL-20AC HT auto sampler, CBM-20A communications bus module, SPD-M20A diode array detector and CTO-20A column oven. The type of chiral column used in HPLC analysis was an AD-H (4.6mmΦx250mm, particle size 5μm) from CHIRALPAK. Optical rotations were performed at 20 ^{o}C on a Perkin-Elmer Model 341 digital polarimeter. High Resolution Mass Spectrometry (HRMS) analyses were completed through positive electrospray ionization (FTICR-MS with NaCl) at the Old Dominion University COSMIC center.

General Procedure A for Synthesis of Alkynediols. Synthesis of (±)-1-phenyldec-3-yne-2,6-diol (1f): To a three-neck round bottom flask was added 1-phenyl-3-butyn-2-ol (2.00g, 13.7 mmol)[1] and 15 mL dry THF. The solution was cooled to -78 ^{o}C and *n*-BuLi (2.5M, 10.9 mL, 27 mmol) was added dropwise via syringe. After 1 h, BF_3•Et_2O (2.50 mL, 20.5 mmol) was added dropwise via syringe and the solution stirred 15 min. Hexene oxide (1.65 mL, 13.6 mmol) was the added dropwise at -78°C and the solution stirred for additional 1 h under argon at -78°C. The mixture was then warmed to rt, quenched with saturated NH_4Cl and extracted with Et_2O and EtOAc. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was then purified by flash column chromatography using 60% hexanes, 40% ethyl acetate to obtain alkynediol **1f** (1.06 g , 31%) as a mixture of diastereomers. R_f = 0.48 (50% hexanes, 50% EtOAc). IR (neat): 3345, 2960, 2919, 2858, 1740, 1456, 1243, 1077, 1030, 667. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.35 (m, 5H), 4.59 (t, *J* = 6.0 Hz, 1H), 3.61-3.65 (m, 1H), 2.99 (d, *J* = 6.2 Hz, 2H), 2.38-2.47 (dm, *J* = 16.6 Hz, 1.2 1H, propargylic), 2.29 (ddd, *J* = 16.6, 7.0, 2.0 Hz, 1H, propargylic), 1.42-1.51 (m, 2H), 1.22-1.50 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0 (q), 129.9 (t), 129.0

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(t), 128.6 (t), 127.0 (t), 83.2 (q), 83.0 (q), 70.18 (t), 70.16 (t), 63.53 (t), 63.50 (t), 44.47 (s), 44.45 (s), 36.10 (s), 36.09 (s), 28.0 (s), 27.7 (s), 22.8 (s), 14.2 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{16}H_{22}O_2Na$: 269.1512; found: 269.1512.

(±)-1-(4-chlorophenyl)-6-methylhept-3-yne-2,6-diol (1a): The title compound was prepared according to General Procedure A and purified by flash column chromatography using 40-60% hexanes/EtOAc to afford 35% average yields of diol as a viscous yellow oil: R_f = 0.16 (60% hexanes, 40% ethyl acetate). IR (neat): 3357 (broad), 3056, 2974, 2933, 2879, 2281, 2230, 1896, 1653, 1599, 1493, 1410, 1381, 1265, 1152, 1090, 1037, 905, 808, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.17 (m, 4H), 4.51 (s, 1H), 3.72 (broad s, 1H), 2.93-2.90 (m, 2H), 2.78 (broad s, 1H), 2.31 (d, *J* = 2.0Hz, 2H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7 (q), 132.7 (q), 131.3 (t), 131.2 (t), 128.5 (t), 128.4 (t), 83.4 (q), 83.2 (q), 70.3 (t), 63.1 (t), 43.6 (s), 34.2 (s), 28.8 (p), 28.7 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_{17}ClO_2Na$: 275.0809; found: 275.0813.

(±)-1-(4-methoxyphenyl)-6-methylhept-3-yne-2,6-diol (1b): The compound was prepared using General Procedure A and purified by flash column chromatography using 40-60% hexanes/EtOAc to afford 40% average yields of diol **1b** as a viscous yellow oil: R_f = 0.26 (60% hexanes, 40% ethyl acetate). IR (neat): 3414 (broad), 3038, 2981, 2941, 2886, 2843, 2213, 1671, 1615, 1516, 1302, 1249, 1180, 1035, 906, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.6Hz, 2H), 6.83 (d, *J* = 8.2Hz, 2H), 4.49 (s, 1H), 3.75 (s, 4H), 2.95-2.86 (m, 3H), 2.32 (d, *J* = 1.6Hz, 2H), 1.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4 (q), 130.7 (t), 129.2 (q), 113.8 (t), 83.2 (q), 82.7 (q), 70.1 (q), 63.4 (t), 55.3 (p), 43.5 (s), 34.2 (s), 28.7 (p), 28.6 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{20}O_3Na$: 271.1305; found: 271.1307.

(±)-6-methyl-1-(o-tolyl)hept-3-yne-2,6-diol (1c): This diol was prepared according to General Procedure A and was purified by flash column chromatography using 40-60% hexanes/EtOAc to afford 30% average yield of diol as a viscous yellow oil: R_f = 0.24 (60% hexanes, 40% EtOAc), or R_f = 0.38 (40% hexanes, 60% EtOAc). IR (neat): 3357 (broad), 3065, 3026, 2980, 2931, 2288, 2230, 1495, 1463, 1383, 1156, 1032, 906, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.20 (m, 1H), 7.16-7.12 (m, 3H), 4.60 (t, *J* = 6.8Hz, 1H), 3.34 (broad s, 1H), 3.07 (dd, *J* = 13.7, 7.0Hz, 1H), 3.00 (dd, *J* = 13.7, 7.0Hz, 1H), 2.58 (broad s, 1H), 2.37 (s, 3H), 2.35 (d, *J* = 1.9Hz, 2H), 1.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0 (q), 135.5 (q), 130.6 (t), 130.5 (t), 127.1 (t), 126.0 (t), 83.8 (q), 82.7 (q), 70.1 (q), 62.8 (t), 41.6 (s), 34.4 (s), 28.78 (p), 28.75 (p), 19.9 (p). HRMS (CI): *m/z* $[M+Ma]^+$ calcd for $C_{15}H_{20}O_2Na$: 255.1356; found: 255.1358.

(±)-1-(2,5-dimethylphenyl)-6-methylhept-3-yne-2,6-diol (1d): This compound was synthesized according to General Procedure A and purified by flash column chromatography using 40-60% hexanes-EtOAc to afford 36% average yields as a viscous, yellow oil: R_f = 0.26 (60% hexanes, 40% EtOAc), or R_f = 0.45 (40% hexanes, 60% EtOAc). IR (neat): 3391, 2979, 2933, 2872, 2733, 2233, 1618, 1505, 1460, 1381, 1158, 1036, 906, 809 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.02-6.91 (m, 3H), 4.54 (t, *J* = 6.4Hz, 1H), 3.15 (s, 1H), 2.98 (dd, *J* = 13.7, 7.0Hz, 1H), 2.92 (dd, *J* = 13.7, 7.0Hz, 1H), 2.51 (s, 1H), 2.31 (s, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4 (q), 135.3 (q), 133.7 (q), 131.4 (t), 130.4 (t), 127.7 (t), 83.8 (q), 82.6 (q), 70.1 (q), 62.7 (t), 41.6 (s), 34.4 (s), 28.74 (p), 28.70 (p), 21.1 (p), 19.1 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{16}H_{22}O_2Na$: 269.1512; found: 269.1514.

(±)-1-phenylhept-3-yne-2,6-diol (1e): The compound was prepared *an inseparable mixture of diastereomers* by General Procedure A from 1-phenyl-3-butyn-2-ol (1.0 g, 6.8 mmol) and racemic propylene oxide. The crude diol was purified by flash column chromatography using 40-

60% hexanes-EtOAc to afford 0.95 g (67%) of **1e** as a viscous, yellow oil: R_f = 0.28 (50% hexanes, 50% EtOAc). IR (neat): 3379 (broad), 3091, 3068, 3031, 2973, 2930, 2874, 2234, 1455, 1341, 1094, 1040, 940, 741, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.14-7.03 (m, 5H), 4.39-4.34 (m, 1H), 3.72-3.64 (m, 1H), 2.78 (overlapping d, *J* = 6.4Hz, 2H), 2.80 (broad s, 2H), 2.18 (unresolved dd of m, *J* = 16.6, 4.7Hz, 1H), 2.08 (app ddq, *J* = 16.6, 6.7, 0.9Hz, 1H), 1.02 (d, *J* = 6.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1 (q), 129.9 (t), 128.5 (t), 127.0 (t), 83.20 (q), 83.18 (q), 82.91 (q), 82.88 (q), 66.44 (t), 66.39 (t), 63.43 (t), 63.40 (t), 44.45 (s), 44.43 (s), 29.30 (s), 29.28 (s), 22.39 (p), 22.37 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{16}O_2Na$: 227.1043; found: 227.1045.

(*6S*)-1-phenylhept-3-yne-2,6-diol ((*6S*)-1e): The compound was prepared *an inseparable mixture of diastereomers* in the same manner as **1e** but with *S*-propylene oxide (>99% e.e.). The crude diol was purified by flash column chromatography using 40-60% hexanes-EtOAc to afford (*6S*)-**1e** in 44% yield as a viscous, yellow oil: R_f = 0.28 (50% hexanes, 50% EtOAc). IR (neat): 3379 (broad), 3091, 3068, 3031, 2973, 2930, 2874, 2234, 1455, 1341, 1094, 1040, 940, 741, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.21 (m, 5H), 4.57-4.52 (m, 1H), 3.91-3.82 (m, 1H), 3.26 (broad s, 1H), 2.96 (overlapping d, *J* = 6.6Hz, 2H), 2.81 (broad s, 1H), 2.37 (dddd, *J* = 16.6, 4.7, 1.9, 0.8Hz, 1H), 2.26 (dddd, *J* = 16.6, 7.2, 1.9, 0.8Hz, 1H), 1.18 (d, *J* = 6.3Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1 (q), 129.9 (t), 128.5 (t), 126.9 (t), 83.18 (q), 83.16 (q), 82.89 (q), 82.87 (q), 66.43 (t), 66.37 (t), 63.40 (t), 63.37 (t), 44.4 (s), 29.26 (s), 29.24 (s), 22.37 (p), 22.35 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{13}H_{16}O_2Na$: 227.1043; found: 227.1045.

3.3 SYNTHESIS OF BENZO[f]ISOCHROMENES

General Procedure B for Synthesis of Benzo[*f*]isochromenes. Synthesis of 2,2-dimethyl-9-chloro-4-(p-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aA): To a 13 x 100 mm test tube was added *p*-bromobenzaldehyde (0.103 g, 0.558 mmol, 1.40 equiv) and 3.0 mL dry CH_2Cl_2 under argon gas. The solution was cooled to -78°C and $BF_3{\cdot}Et_2O$ (0.169 g, 1.19 mmol, 3.0 equiv) added dropwise. Then alkynediol **1a** (0.109 g, 0.399 mmol) in 1.0 mL CH_2Cl_2 was added dropwise to the -78°C solution. The mixture was then allowed to slowly warm to rt and stirred under argon gas. After 16 h, the reaction was quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography using 60% hexanes, 40% CH_2Cl_2 to afford **2aA** (0.086 g, 53%) as a viscous, yellow oil: R_f = 0.32 (60% hexanes, 40% CH_2Cl_2). IR (neat): 3050, 2972, 2931, 2897, 2840, 1903, 1732, 1619, 1592, 1501, 1485, 1366, 1264, 1184, 1094, 1069, 1009, 829, 736 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H), 7.71 (d, *J* = 8.6Hz, 1H), 7.52-7.41 (m, 4H), 7.20 (d, *J* = 8.2Hz, 2H), 6.82 (d, *J* = 8.6Hz, 1H), 5.80 (s, 1H), 3.15 (d, *J* = 16.2Hz, 1H), 3.07 (d, *J* = 16.2Hz, 1H), 1.54 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7 (q), 134.6 (q), 133.0 (q), 132.6 (q), 131.9 (t), 130.9 (t), 130.7 (q), 130.3 (t), 127.9 (q), 126.7 (t), 126.0 (t), 124.7 (t), 122.3 (q), 122.3 (t), 75.5 (t), 72.0 (q), 36.4 (s), 31.1 (p), 23.5 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{18}BrClONa$: 423.0122; found: 423.0124.

(±)-9-chloro-2,2-dimethyl-4-(4-nitrophenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aB):

The compound was synthesized from alkynediol **1a** (0.120g, 0.475 mmol) using General Procedure B. Purification by flash column chromatography using 20-80% hexanes-CH_2Cl_2 afforded **2aB (**0.084g, 48%) of as a viscous yellow oil: R_f = 0.55 (40% hexanes, 60% CH_2Cl_2).

IR (neat): 3110, 3079, 3056, 2975, 2931, 2870, 2455, 1927, 1798, 1725, 1609, 1526, 1352, 1270, 1187, 1075, 857, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (dt, *J* = 8.6, 2.1Hz, 2H), 7.98 (d, *J* = 2.0Hz, 1H), 7.73 (d, *J* = 8.6Hz, 1H), 7.54-7.50 (m, 3H), 7.45 (dd, *J* = 8.8, 2.2Hz, 1H), 6.79 (d, *J* = 8.6Hz, 1H), 5.94 (s, 1H), 3.20 (d, *J* = 16.6Hz, 1H), 3.12 (dd, *J* = 16.6, 1.2Hz, 1H), 1.57 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8 (q), 148.0 (q), 133.6 (q), 133.0 (q), 132.9 (q), 130.8 (q), 130.3 (t), 130.0 (t), 128.0 (q), 127.0 (t), 126.4 (t), 124.2 (t), 124.0 (t), 122.4 (t), 75.3 (t), 72.4 (q), 36.4 (s), 31.0 (p), 23.5 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{18}ClNO_3Na$: 390.0867; found: 390.0872.

(±)-9-chloro-2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aC): The title compound was prepared from alkynediol **1a** (0.120g, 0.475 mmol) using General Procedure B. Purification by flash column chromatography using 20-80% hexanes-CH_2Cl_2 gave **2aC** (0.089g, 48%) as a viscous yellow oil: R_f = 0.70 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3054, 2976, 2930, 2871, 2853, 1922, 1737, 1619, 1594, 1502, 1416, 1323, 1164, 1128, 1068, 1019, 989, 838 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 2.0Hz, 1H), 7.68 (d, *J* = 9.0Hz, 1H), 7.56 (d, *J* = 7.8Hz, 2H), 7.49 (d, *J* = 8.6Hz, 1H), 7.42 (d, *J* = 7.0Hz, 2H), 7.40 (dd, *J* = 8.6, 2.0Hz, 1H), 6.79 (d, *J* = 8.6Hz, 1H), 5.87 (s, 1H), 3.16 (d, *J* = 16.4Hz, 1H), 3.07 (dd, *J* = 16.4, 1.2Hz, 1H), 1.55 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6 (q), 134.3 (q), 133.0 (q), 132.7 (q), 130.8 (q), 130.4 (q), 130.3 (t), 129.5 (t), 128.0 (q), 126.8 (t), 126.2 (t), 125.8 (t), 124.3 (CF_3, *J* = 272.1Hz), 124.6 (t), 122.4 (t), 75.6 (t), 72.2 (q), 36.4 (s), 31.0 (p), 23.5 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{18}ClF_3ONa$: 413.0890; found: 413.0895.

(±)-9-chloro-2,2-dimethyl-4-(4-(methyl)phenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aD): The title compound was prepared using General Procedure B from alkynediol **1a** (0.120

g, 0.475 mmol). Purification by flash column chromatography using 30-100% hexanes-CH_2Cl_2 afforded **2aD (**0.107g, 67%) as a light yellow solid: R_f = 0.54 (40% hexanes, 60% CH_2Cl_2); mp = 59 – 61 ^oC. IR (neat ATR, cm^{-1}): 2972 (w), 1620 (w), 1595 (w), 1502 (w), 1365 (w), 1096 (s), 1057 (s), 839 (s), 824 (s), 797 (s); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.96 (s, 1H), 7.70 (*d*, J = 8.6 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 5.80 (s, 1H), 3.15 (d, *J* = 16.4 Hz, 1H), 3.06 (d, *J* =16.4 Hz, 1H), 2.32 (s, 3H), 1.53 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8 (q), 138.0 (q), 135.6 (q), 133.0 (q), 132.5 (q), 130.7 (q), 130.2 (t), 129.5 (t), 129.1 (t), 127.8 (q), 126.4 (t), 125.8 (t), 125.1 (t), 122.3 (t), 75.9 (t), 71.8 (q), 36.6 (s), 31.1 (p), 23.5 (p), 21.4 (p); HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{21}ClONa$: 359.1173; found: 359.1170.

(±)-9-chloro-2,2-dimethyl-4-phenethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aE): The title compound was prepared using General Procedure B from alkynediol **1a** (0.100 g, 0.396 mmol). Purification by flash column chromatography using 20-80% hexanes-CH_2Cl_2 afforded **2aD** (0.052g, 38%) as a viscous yellow oil: R_f = 0.54 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3426, 3063, 3030, 2977, 2930, 2865, 2837, 1944, 1735, 1622, 1595, 1497, 1455, 1094, 838, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 1.5Hz, 1H), 7.59 (d, *J* = 8.7Hz, 1H), 7.49 (d, *J* = 8.7Hz, 1H), 7.25 (dd, *J* = 9.0, 2.0Hz, 1H), 7.13-6.98 (m, 6H), 4.79-4.74 (m, 1H), 2.81 (s, 2H), 2.66-2.58 (m, 1H), 2.39 (ddd, *J* =14.2, 10.0, 4.2Hz, 1H), 2.22-2.13 (m, 1H), 1.99-1.90 (m, 1H), 1.36 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8 (q), 135.6 (q), 133.2 (q), 132.4 (q), 130.6 (q), 130.2 (t), 128.8 (t), 128.47 (q), 128.45 (t), 126.3 (t), 126.1 (t), 125.8 (t), 123.2 (t), 122.3 (t), 70.8 (t), 70.7 (q), 38.1 (s), 36.7 (s), 31.0 (p), 30.9 (s), 23.5 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{23}ClONa$: 373.1330; found: 373.1332.

(±)-4-(*sec*-butyl)-9-chloro-2,2-dimethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aF):

The title compound was prepared from alkynediol **1a** (0.085g, 0.339 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 80-20% *n*-hexane-CH_2Cl_2 and afforded **2aE (**0.036g, 36%) as *a partially-separable pair of diastereomers* in a 2:1 ratio as viscous yellow oil: R_f = 0.53 and 0.59 (70% *n*-hexane, 30% CH_2Cl_2). IR (neat): 3051, 2971, 2934, 2896, 2873, 2833, 2345, 1622, 1596, 1504, 1459, 1369, 1196, 840, 662 cm^{-1}. HRMS (CI): *m/z* $[M+NaO_2]^+$ calcd for $C_{19}H_{23}ClO_3Na$: 357.1228; found: 357.1231.

Diastereomer A. (R_f = 0.53). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.75 (d, *J* = 8.6Hz, 1H), 7.65 (d, *J* = 8.6Hz, 1H), 7.40 (dd, *J* = 8.6, 2.0Hz, 1H), 7.24 (d, *J* = 8.6Hz, 1H), 4.88 (s, 1H), 2.95 (d, *J* = 16.0Hz, 1H), 2.86 (d, *J* = 16.0Hz, 1H), 2.02-1.95 (m, 1H), 1.72-1.60 (m, 1H), 1.51-1.47 (m, 1H), 1.45 (s, 3H), 1.12 (s, 3H), 1.02 (t, *J* = 7.4Hz, 3H), 0.56 (d, *J* = 7.0Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.0 (q), 133.1 (q), 132.2 (q), 130.4 (q), 130.1 (t), 129.0 (q), 126.1 (t), 125.9 (t), 123.3 (t), 122.3 (t), 73.7 (t), 70.0 (q), 40.8 (t), 36.5 (s), 30.9 (p), 27.0 (s), 23.3 (p), 12.9 (p), 12.6 (p).

Diastereomer B. (R_f = 0.58). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.75 (d, *J* = 8.6Hz, 1H), 7.65 (d, *J* = 8.2Hz, 1H), 7.40 (dd, *J* = 8.8, 1.7Hz, 1H), 7.24 (dd, *J* = 8.6, 3.1Hz, 1H), 4.81 (s, 1H), 2.95 (d, *J* = 15.8Hz, 1H), 2.86 (d, *J* = 15.8Hz, 1H), 2.04-1.95 (m, 1H), 1.45 (broad s, 5H), 1.13 (s, 3H), 1.11 (s, 3H), 0.72 (t, *J* = 7.4Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.0 (q), 133.1 (q), 132.2 (q), 130.4 (q), 130.1 (t), 129.0 (q), 126.1 (t), 125.9 (t), 123.3 (t), 122.3 (t), 76.5 (t), 70.2 (q), 40.9 (t), 36.6 (s), 23.3 (p), 22.5 (s), 16.7 (p), 12.9 (p), 12.6 (p).

(±)-9-chloro-4-isopropyl-2,2-dimethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2aG): The title compound was prepared from alkynediol **1a** (0.099 g, 0.339 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2

and afforded **2aF** (0.031g, 27%) as a light yellow solid: R_f = 0.34 (80% hexanes, 20% CH_2Cl_2); mp = 56-58 ºC. IR (neat): 3053, 2973, 2930, 2871, 2827, 1623, 1595, 1504, 1366, 1197, 1048, 841, 630 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 2.0Hz, 1H), 7.72 (d, *J* = 8.7Hz, 1H), 7.62 (d, *J* = 8.6Hz, 1H), 7.38 (dd, *J* = 8.8, 2.1Hz, 1H), 7.22 (d, *J* = 8.2Hz, 1H), 4.74 (d, *J* = 1.6Hz, 1H), 2.93 (dd, *J* = 16.0, 0.8Hz, 1H), 2.83 (d, *J* = 16.0Hz, 1H), 2.27 (sept. of d, *J* = 6.8, 2.4Hz, 1H), 1.44 (s, 3H), 1.13 (d, *J* = 7.0Hz, 3H), 1.09 (s, 3H), 0.57 (d, *J* = 6.7Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9 (q), 133.1 (q), 132.2 (q), 130.5 (q), 130.1 (t), 128.9 (q), 126.1 (t), 125.9 (t), 123.3 (t), 122.3 (t), 75.9 (t), 70.1 (q), 36.6 (s), 34.0 (t), 30.9 (p), 23.4 (p), 20.1 (p), 15.0 (p). HRMS (CI): *m/z* $[M+NaO_2]^+$ calcd for $C_{18}H_{21}ClO_3Na$: 343.1071; found: 343.1074.

(±)-9-chloro-4-ethyl-2,2-dimethyl-1,4-dihydro-2*H*-benzo[*f*]isochromene (2aH): The title compound was prepared from alkynediol **1a** (0.120g, 0.475 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and afforded **2aG** (0.051 g, 39%) as a viscous, yellow oil: R_f = 0.48 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3052, 2972, 2932, 2874, 2831, 1903, 1724, 1623, 1597, 1505, 1367, 1202, 1096, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 2.0Hz, 1H), 7.72 (d, *J* = 8.6Hz, 1H), 7.63 (d, *J* = 8.6Hz, 1H), 7.38 (d, *J* = 8.6Hz, 1H), 7.21 (d, *J* = 8.6Hz, 1H), 4.91-4.88 (m, 1H), 2.92 (unresolved overlapping d, 2H), 2.09-1.99 (m, 1H), 1.90-1.80 (m, 1H), 1.47 (s, 3H), 1.15 (s, 3H), 0.80 (t, *J* = 7.5Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6 (q), 133.1 (q), 132.3 (q), 130.5 (q), 130.2 (t), 128.6 (q), 126.2 (t), 126.0 (t), 123.3 (t), 122.3 (t), 72.3 (t), 70.5 (q), 36.6 (s), 31.0 (p), 29.1 (s), 23.5 (p), 8.7 (p). HRMS (CI): *m/z* $[M+NaO_2]^+$ calcd for $C_{17}H_{19}ClO_3Na$: 329.0915; found: 329.0917.

(±)-4-(4-bromophenyl)-9-methoxy-2,2-dimethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2bA): The title compound was prepared from alkynediol **1b** (0.094g, 0.379 mmol) using

General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and afforded **2bA** (0.048 g, 32%) as a viscous yellow oil: R_f = 0.58 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3054, 2974, 2931, 2836, 1905, 1700, 1626, 1515, 1228, 1071, 1011, 835, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.7Hz, 1H), 7.48 (s, 1H), 7.44 (dd, *J* = 10.7, 2.5Hz, 2H), 7.24-7.19 (m, 3H), 7.16 (dd, *J* = 8.8, 2.5Hz, 1H), 6.68 (d, *J* = 8.2Hz, 1H), 5.81 (s, 1H), 3.97 (s, 3H), 3.15 (d, *J* = 15.9Hz, 1H), 3.05 (d, *J* = 15.9Hz, 1H), 1.55 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4 (q), 142.1 (q), 134.0 (q), 133.3 (q), 131.8 (t), 130.9 (t), 130.3 (t), 127.8 (q), 127.2 (q), 125.9 (t), 122.2 (t), 122.2 (q), 117.9 (t), 102.0(t), 75.6 (t), 72.0 (q), 55.6 (p), 36.7 (s), 31.2 (p), 23.6 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{21}BrO_2Na$: 419.0617; found: 419.0618.

(±)-9-methoxy-2,2-dimethyl-4-(4-nitrophenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2bB): The title compound was prepared from alkynediol **1b** (0.100 g, 0.403 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 0-40% hexanes-CH_2Cl_2 and afforded **2bB** (0.032 g, 22%) as a viscous yellow oil: R_f = 0.61 (100% CH_2Cl_2). IR (neat): 3107, 3078, 3057, 2977, 2933, 2836, 1735, 1626, 1608, 1521, 1459, 1351, 1229, 1065, 837 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 8.6Hz, 2H), 7.70 (d, *J* = 9.0Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7Hz, 1H), 7.24 (d, *J* = 2.4Hz, 1H), 7.18 (dd, *J* = 8.8, 2.5Hz, 1H), 6.65 (d, *J* = 8.6Hz, 1H), 5.95 (s, 1H), 3.98 (s, 3H), 3.18 (d, *J* = 16.3Hz, 1H), 3.09 (d, *J* = 16.3Hz, 1H), 1.57 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.6 (q), 150.3 (q), 147.9 (q), 133.3 (q), 132.9 (q), 130.4 (t), 130.0 (t), 127.9 (q), 127.3 (q), 126.3 (t), 124.0(t), 121.7 (t), 118.2 (t), 102.0 (t), 75.4 (t), 72.4 (q), 55.6 (p), 36.7 (s), 31.1 (p), 23.6 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{21}NO_4Na$: 386.1363; found: 386.1366.

(±)-9-methoxy-2,2-dimethyl-4-(4-(trifluoromethyl)phenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2bC): The title compound was prepared from alkynediol **1b** (0.096 g, 0.387 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and afforded **2bC** (0.038 g, 26%) as a light yellow oil: R_f = 0.33 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3058, 2999, 2980, 2932, 2906, 2836, 1925, 1627, 1516, 1332, 1230, 1168, 1068, 839 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.9Hz, 1H), 7.58 (d, *J* = 8.2Hz, 2H), 7.49 (s, 1H), 7.46 (d, *J* = 8.6Hz, 2H), 7.24 (d, *J* = 2.3Hz, 1H), 7.17 (dd, *J* = 9.0, 2.4Hz, 1H), 6.68 (d, *J* = 8.6Hz, 1H), 5.90(s, 1H), 3.98 (s, 3H), 3.18 (d, *J* = 16.0Hz, 1H), 3.07 (d, *J* = 16.0Hz, 1H), 1.56 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5 (q), 156.3 (CF_3, *J* = 210.6Hz), 147.0(q), 133.6 (q), 133.3 (q), 130.5 (q), 130.3 (t), 129.5 (t), 127.8 (q), 127.3 (q), 126.1 (t), 125.7 (t), 122.1 (t), 118.1 (t), 102.0 (t), 75.8 (t), 72.2 (q), 55.6 (p), 36.8 (s), 31.1 (p), 23.6 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{21}F_3O_2Na$: 409.1386; found: 409.1388.

(±)-9-methoxy-2,2-dimethyl-4-(4-(methyl)phenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2bD): The title compound was prepared using General Procedure B from alkynediol **1b** (0.150 g, 0.604 mmol). Purification by flash column chromatography using 30-100% hexanes-CH_2Cl_2 afforded **2bD** (0.065g, 32%) as an off-white solid: R_f = 0.59 (40% hexanes, 60% CH_2Cl_2); mp = 123-125 ^oC. IR (neat, cm^{-1}) 2972 (w), 1624 (w), 1512 (w), 1225 (m), 1059 (s), 1028 (m), 837 (s); ^1H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 8.6, 1H), 7.18-7.26 (m, 3H), 7.10-7.16 (m, 3H), 6.74 (d, *J* = 8.6 Hz, 1H), 5.81 (s, 1H), 3.97 (s, 3H), 3.15 (d, *J* = 16.1 Hz, 1H), 3.04 (d, *J* = 16.1, 1H), 2.31 (s, 3H), 1.55 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4 (q), 140.2 (q), 137.8 (q), 134.9 (q), 133.3 (q), 130.3 (t), 129.4 (t), 129.1 (t), 127.8 (q), 127.2 (q), 125.8 (t), 122.6 (t), 117.7 (t), 102.1 (t), 76.9 (t), 76.1 (q), 55.6 (p), 36.9 (s),

31.3 (p), 23.6 (p), 21.4 (p); HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{24}O_2Na$: 355.1669; found: 359.1663.

(±)-9-methoxy-2,2-dimethyl-4-phenethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2bE): The title compound was prepared from alkynediol **1b** (0.084 g, 0.337 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 0-40% hexanes-CH_2Cl_2 and afforded **2bD** (0.017 g, 15%) as a viscous yellow oil: R_f = 0.69 (10% hexanes, 90% CH_2Cl_2). IR (neat): 3083, 3060, 3025, 2970, 2927, 2859, 2833, 1738, 1625, 1516, 1458, 1228, 1180, 838, 744 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.6Hz, 1H), 7.46 (d, *J* = 8.2Hz, 1H), 7.11-6.94 (m, 8H), 4.81-4.76 (m, 1H), 3.79 (s, 3H), 2.80 (unresolved overlapping d, 2H), 2.66-2.58 (m , 1H), 2.38 (ddd, *J* = 14.3, 10.2, 4.5Hz, 1H), 2.22-2.13 (m, 1H), 2.00-1.91 (m, 1H), 1.38 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3 (q), 143.0 (q), 134.9 (q), 133.4 (q), 130.2 (t), 128.8 (t), 128.4 (t), 127.8 (q), 127.6 (q), 126.1 (t), 125.8 (t), 120.6 (t), 117.6 (t), 101.9 (t), 70.9 (t), 70.7 (q), 55.6 (p), 38.2 (s), 36.9 (s), 31.1 (p), 30.9 (s), 23.6 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{24}H_{26}O_2Na$: 369.1825; found: 369.1829.

(±)-4-(4-bromophenyl)-2,2,7-trimethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2cA) The title compound was prepared from alkynediol **1c** (0.070 g, 0.301 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and afforded **2cA** ((0.071 g, 62%) as a viscous yellow oil: R_f = 0.60 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3073, 3046, 2991, 2937, 2899, 2871, 2843, 2340, 1906, 1737, 1602, 1488, 1382, 1272, 1187, 1080, 817, 774 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.6Hz, 1H), 7.72 (d, *J* = 9.0Hz, 1H), 7.47-7.43 (m, 3H), 7.33 (d, *J* = 6.6Hz, 1H), 7.20 (d, *J* = 8.2Hz, 2H), 6.86 (d, *J* = 8.6Hz, 1H), 5.82 (s, 1H), 3.18 (unresolved overlapping d, 2H), 2.64 (s, 3H), 1.54 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1 (q), 135.2 (q), 133.1 (q), 132.2 (q),

131.9 (t), 131.6 (q), 130.9 (t), 128.9 (q), 126.8 (t), 126.3 (t), 124.2 (t), 122.3 (t), 122.2 (q), 121.2 (t), 75.5 (t), 72.1 (q), 36.8 (s), 31.1 (p), 23.5 (p), 19.8 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{21}BrONa$: 403.0668; found: 403.0669.

(±)-2,2,7-trimethyl-4-(4-nitrophenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2cB): The title compound was prepared from alkynediol **1c** (0.070 g, 0.301 mmol) using General Procedure B. Purification was accomplished by flash column chromatography on two separate columns using 20-80% hexanes-CH_2Cl_2 and then 70% hexanes, 30% EtOAc to give **2bC** (0.049 g, 47%) as a viscous yellow oil: R_f = 0.34 (40% hexanes, 60% CH_2Cl_2), R_f = 0.69 (70% hexanes, 30% EtOAc). IR (neat): 3071, 2973, 2931, 2893, 2860, 1601, 1520, 1346, 1182, 1072, 846, 798 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 9.0Hz, 2H), 7.87 (d, *J* = 8.2Hz, 1H), 7.73 (d, *J* = 8.6Hz, 1H), 7.52 (d, *J* = 9.0Hz, 2H), 7.47 (t, *J* = 7.8Hz, 1H), 7.34 (d, *J* = 7.0Hz, 1H), 6.82 (d, *J* = 9.0Hz, 1H), 5.96(s, 1H), 3.22 (overlapping d, *J* = 17.6Hz, 2H), 2.64 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3 (q), 147.9 (q), 135.3 (q), 132.2 (q), 132.1 (q), 131.7 (q), 130.0 (t), 129.0 (q), 127.0 (t), 126.5 (t), 124.0 (t), 123.7 (t), 122.7 (t), 121.3 (t), 75.3 (t), 72.4 (q), 36.8 (s), 31.0 (p), 23.6 (p), 19.8 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{22}H_{21}NO_3Na$: 370.1414; found: 370.1415.

(±)-2,2,7-trimethyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2cD): The title compound was prepared from alkynediol **1c** (0.070 g, 0.301 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and gave **2cD** (0.070 g, 74%) as a viscous yellow oil: R_f = 0.61 (40% hexanes, 60% CH_2Cl_2). IR (neat): 3068, 3024, 2987, 2937, 2893, 2864, 2833, 1601, 1509, 1439, 1379, 1301, 1265, 1177, 1068, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.6Hz, 1H), 7.70 (d, *J* = 9.0Hz, 1H), 7.43 (dd, *J* = 8.6, 7.1Hz, 1H), 7.31 (d, *J* = 7.1Hz, 1H), 7.21 (d, *J* = 7.9Hz, 2H), 7.12 (d, *J* =

7.9Hz, 2H), 6.91 (d, *J* = 9.0Hz, 1H), 5.83 (s, 1H), 3.20 (d, *J* = 16.3Hz, 1H), 3.15 (d, *J* = 16.3Hz, 1H), 2.63 (s, 3H), 2.31 (s, 3H), 1.53 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2 (q), 137.8 (q), 135.1 (q), 134.0 (q), 132.2 (q), 131.5 (q), 129.4 (t), 129.1 (t), 128.8 (q), 126.5 (t), 126.1 (t), 124.6 (t), 122.1 (t), 121.3 (t), 75.9 (t), 71.8 (q), 36.9 (s), 31.2 (p), 23.6 (p), 21.4 (p), 19.8 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{24}ONa$: 339.1719; found: 339.1722.

(±)-2,2,7-trimethyl-4-phenethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2cE): The title compound was prepared from alkynediol **1c** (0.070 g, 0.301 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and gave **2cE** (0.057 g, 57%) as a viscous, yellow oil: R_f = 0.61 (40% hexanes, 60% CH_2Cl_2), R_f = 0.45 (50% hexanes, 50% CH_2Cl_2). IR (neat): 3082, 3065, 3025, 2968, 2922, 2861, 1960, 1740, 1694, 1602, 1454, 1379, 1097, 749, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.8Hz, 1H), 7.83 (d, *J* = 8.5Hz, 1H), 7.42 (dd, *J* = 8.4, 6.9Hz, 1H), 7.33-7.13 (m, 7H), 4.99-4.95 (m, 1H), 3.07 (d, *J* = 16.0Hz, 1H), 3.02 (d, *J* = 16.0Hz, 1H), 2.82-2.75 (m, 1H), 2.70 (s, 3H), 2.54 (ddd, *J* = 14.0, 10.1, 4.4Hz, 1H), 2.39-2.31 (m, 1H), 2.18-2.09 (m, 1H), 1.52 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=143.0 (q), 135.1 (q), 134.0(q), 132.4 (q), 131.4 (q), 129.6 (q), 128.8 (t), 128.4 (t), 126.4 (t), 126.0 (t), 125.8 (t), 122.6 (t), 122.4 (t), 121.2 (t), 70.8 (t), 70.8 (q), 38.2 (s), 37.0 (s), 31.1 (p), 30.8 (s), 23.5 (p), 19.9 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{24}H_{26}ONa$: 353.1876; found: 353.1878.

(±)-4-(4-bromophenyl)-2,2,7,10-tetramethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2dA): The title compound was prepared from alkynediol **1d** (0.073 g, 0.296 mmol) and *p*-bromobenzaldehyde (**A**) using General Procedure B. Purification was accomplished by flash

column chromatography using 20-80% hexanes-CH_2Cl_2 and gave **2dA** (0.089 g, 76%) as a light yellow solid: R_f = 0.60 (40% hexanes, 60% CH_2Cl_2); mp = 120-122 ^oC. IR (neat): 3043, 2973, 2928, 2859, 2839, 1906, 1860, 1591, 1579, 1486, 1366, 1184, 1071, 1011, 824 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 9.0Hz, 1H), 7.43 (d, *J* = 8.2Hz, 2H), 7.24-7.15 (m, 4H), 6.86 (d, *J* = 9.0Hz, 1H), 5.83 (s, 1H), 3.57 (d, *J* = 15.8Hz, 1H), 3.33 (d, *J* = 15.8Hz, 1H), 2.90 (s, 3H), 2.57 (s, 3H), 1.49 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.2 (q), 134.1 (q), 133.5 (q), 133.2 (q), 133.1 (q), 133.1 (q), 131.9 (t), 130.8 (t), 130.6 (q), 130.4 (t), 126.5 (t), 124.0 (t), 123.3 (t), 122.1 (q), 76.4 (t), 72.1 (q), 42.2 (s), 31.3 (p), 26.6 (p), 22.9 (p), 20.3 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{23}BrONa$: 417.0824; found: 417.0826.

X-ray crystallography of (±)-4-(4-bromophenyl)-2,2,7,10-tetramethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2dA): A single crystal of the title compound was grown from slow evaporation of a $CDCl_3$ NMR sample at room temperature. The chosen crystal was mounted using an organic epoxy resin and analyzed at 100 K. See pages S92 and S93 for general details of the structure.

(±)-2,2,7,10-tetramethyl-4-(4-nitrophenyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2dB): The title compound was prepared from alkynediol **1d** (0.072 g, 0.292 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using a mixture of 20-80% hexanes in dichloromethane and 80% hexanes-EtOAc to afford **2dB** (0.056 g, 53%) as a viscous yellow oil: R_f = 0.48 (80% hexanes, 20% CH_2Cl_2). IR (neat): 3107, 3078, 3036, 2978, 2935, 2860, 2367, 1738, 1607, 1559, 1526, 1457, 1340 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 9.0Hz, 2H), 7.73 (d, *J* = 9.0Hz, 1H), 7.54 (d, *J* = 9.0Hz, 2H), 7.22 (d, *J* = 7.4Hz, 1H), 7.17 (d, *J* = 7.5Hz, 1H), 6.84 (d, *J* = 9.0Hz, 1H), 5.97 (s, 1H), 3.59 (d, *J* = 16.4, 1H), 3.37 (d, *J* = 16.4Hz, 1H), 2.92 (s, 3H), 2.58 (s, 3H), 1.51 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =

150.4 (q), 147.8 (q), 133.6 (q), 133.3 (q), 133.2 (q), 133.1 (q), 132.1 (q), 130.7 (q), 130.7 (t), 129.9 (t), 126.8 (t), 124.0 (t), 123.7 (t), 123.5 (t), 76.2 (t), 72.5 (q), 42.2 (s), 31.2 (p), 26.6 (p), 23.0 (p), 20.2 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{23}H_{23}NO_3Na$: 384.1570; found: 384.1574.

(±)-2,2,7,10-tetramethyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (2dD): The title compound was prepared from alkynediol **1d** (0.070 g, 0.284 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 and afforded **2dD (**0.080 g, 85%) as light yellow solid: R_f = 0.58 (40% hexane, 60% CH_2Cl_2); mp = 105-107 ^oC. IR (neat): 3024, 2968, 2924, 2860, 2833, 1514, 1452, 1379, 1366, 1300, 1179, 1082, 1058, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.8Hz, 1H), 7.24-7.10 (m, 6H), 6.91 (d, *J* = 8.5Hz, 1H), 5.84 (s, 1H), 3.58 (d, *J* = 16.2Hz, 1H), 3.32 (d, *J* = 16.2Hz, 1H), 2.90 (s, 3H), 2.56 (s, 3H), 2.30 (s, 3H), 1.48 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2 (q), 137.8 (q), 135.0 (q), 133.6 (q), 133.2 (q), 133.1 (q), 133.0 (q), 130.0 (q), 130.3 (t), 129.4 (t), 129.0 (t), 126.3 (t), 124.4 (t), 123.1 (t), 76.8 (t), 71.9 (q), 42.4 (s), 31.4 (p), 26.6 (p), 22.9 (p), 21.4 (p), 20.3 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{24}H_{26}ONa$: 353.1876; found: 353.1877.

(±)-2,2,7,10-tetramethyl-4-phenethyl-1,4-dihydro-*2H*-benzo[*f*]isochromene (2dE): The title compound was prepared from alkynediol **1d** (0.072 g, 0.292 mmol) using General Procedure B. Purification was accomplished by flash column chromatography using 20-80% hexanes-CH_2Cl_2 to afford **2dE (**0.079 g, 78%) as a light yellow solid: R_f = 0.58 (40% hexanes, 60% CH_2Cl_2); mp = 72-74 ^oC. IR (neat): 3086, 3061, 3029, 2978, 2929, 2861, 1736, 1602, 1497, 1454, 1366, 1097, 823, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 9.0Hz, 1H), 7.26-7.12 (m, 8H), 4.98 (dd, *J* = 3.3, 1.8Hz, 1H), 3.40 (d, *J* = 16.0Hz, 1H), 3.19 (dd, *J* = 16.0Hz, 0.9Hz, 1H), 2.85

(s, 3H), 2.83-2.77 (m, 1H), 2.63 (s, 3H), 2.56 (ddd, *J* = 14.5, 10.6, 4.6Hz, 1H), 2.34-2.25 (m, 1H), 2.15-2.06 (m, 1H), 1.48 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9 (q), 135.3 (q), 133.7 (q), 133.1 (q), 133.0 (q), 132.8 (q), 131.3 (q), 130.1 (t), 128.8 (t), 128.4 (t), 126.1 (t), 125.8 (t), 121.3 (t), 122.7 (t), 72.0 (t), 70.9 (q), 42.6 (s), 39.0(s), 31.2 (p), 30.8 (s), 26.5 (p), 22.8 (p), 20.3 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{25}H_{28}ONa$: 367.2032; found: 367.2036.

(*2S*,4R)-2-methyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (*cis*-(±)-2eD) and (*2R,4S*)-2-methyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene ((*2S,4R*)-2eD):** The racemic compound was prepared from alkynediol **1e** (0.206g, 1.01 mmol) according to General Procedure B. Purification by flash column chromatography using 20-80% *n*-hexanes-CH_2Cl_2 afforded a pair of diastereomers in 81% combined yield. The *cis*- diastereomer (0.131 g, 45%) was obtained as a light yellow solid; R_f = 0.43 (50% hexanes, 50% CH_2Cl_2); mp = 113-115 ºC. IR (neat): 3421, 3301, 3052, 3023, 2971, 2926, 2892, 2365, 1916, 1713, 1511, 1456, 1386, 1257, 1118, 948 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.2Hz, 1H), 7.75 (d, *J* = 8.6Hz, 1H), 7.55-7.43 (m, 3H), 7.20 (d, *J* = 8.2Hz, 2H), 7.13 (d, *J* = 8.2Hz, 2H), 6.82 (d, *J* = 8.6Hz, 1H), 5.83 (s, 1H), 4.13-4.05 (m, 1H), 3.21 (unresolved d of m, *J* = 16.1Hz, 1H), 3.05 (app ddd, *J* = 16.1, 10.5, 2.0Hz, 1H), 2.32 (s, 3H), 1.50 (d, *J*= 6.2Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7 (q), 138.0 (q), 135.3 (q), 132.3 (q), 131.8 (q), 129.5 (q), 129.4 (t), 129.1 (t), 128.6 (t), 126.4 (t), 126.1 (t), 125.7 (t), 124.9 (t), 123.1 (t), 81.3 (t), 71.1 (t), 33.4 (s), 22.4 (p), 21.4 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{20}ONa$: 311.1406; found: 311.1409.

X-ray crystallography for (*2S*,4R)-2-methyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo-[*f*]isochromene (*cis*-(±)-2eD):** A single crystal of the title compound was grown from slow evaporation of a $CDCl_3$ NMR sample at room temperature. The chosen crystal was mounted

using an organic epoxy resin and analyzed at 296 K. See pages S94 and S95 for general details of the structure.

Chiral benzo[*f*]isochromenes 2eD: The reaction using (*6S*)-**1e** was accomplished in the same manner as above from 0.155 g (0.76 mmol) of (*6S*)-**1e**. The diastereomers were obtained in 80% combined yield (0.175g) and partially separated for HPLC analysis as well as measurement of optical rotations. The ratios of enantiomers for separated *cis*- and *trans*- compounds were determined using a ChiralPak AD-H column using 1-5% *i*-PrOH in hexanes as eluent. See pp S85-S86 of the Electronic Supporting Information for copies of chromatograms and retention times.

Data for (*2R,4S*)-2-methyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene ((*2S,4R*)-2eD): $[\alpha]_D$ = -152 (c 1.03, CH_2Cl_2). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{20}ONa$: 311.1406; found: 311.1405.

(*2S*,4S)-2-methyl-4-(p-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (*trans*-(±)-2eD)** The *trans*- diastereomer (0.103g, 36%) was isolated as a viscous, colorless oil: R_f = 0.29 (50% *n*-hexanes, 50% CH_2Cl_2). IR (neat): 3052, 2972, 2923, 2892, 1917, 1511, 1446, 1387, 1119, 1062, 817, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J*= 8.6Hz, 1H), 7.84 (dd, *J* = 7.8, 1.6Hz, 1H), 7.64 (d, *J* = 8.6Hz, 1H), 7.57-7.48 (m, 2H), 7.15 (d, *J* = 8.2Hz, 2H), 7.11 (d, *J* = 8.2Hz, 2H), 7.05 (d, *J* = 8.2Hz, 1H), 6.01 (s, 1H), 4.00 (dd of quartets, *J* = 10.2, 6.3, 3.6Hz, 1H), 3.21 (dd, *J* = 16.7, 3.7Hz, 1H), 2.92 (dd, *J* = 16.7, 10.2Hz, 1H), 2.33 (s, 3H), 1.34 (d, *J* = 6.3Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (two aromatic quaternary carbons are overlapped): δ = 139.2 (q), 137.8 (q), 132.7 (q), 132.1 (q), 129.9 (q), 129.7 (t), 129.0 (t), 128.8 (t), 126.5 (t), 126.0 (t), 125.8

(t), 125.5 (t), 123.0 (t), 77.6 (t), 63.8 (t), 32.8 (s), 22.0 (p), 21.36 (p). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{20}ONa$: 311.1406; found: 311.1409.

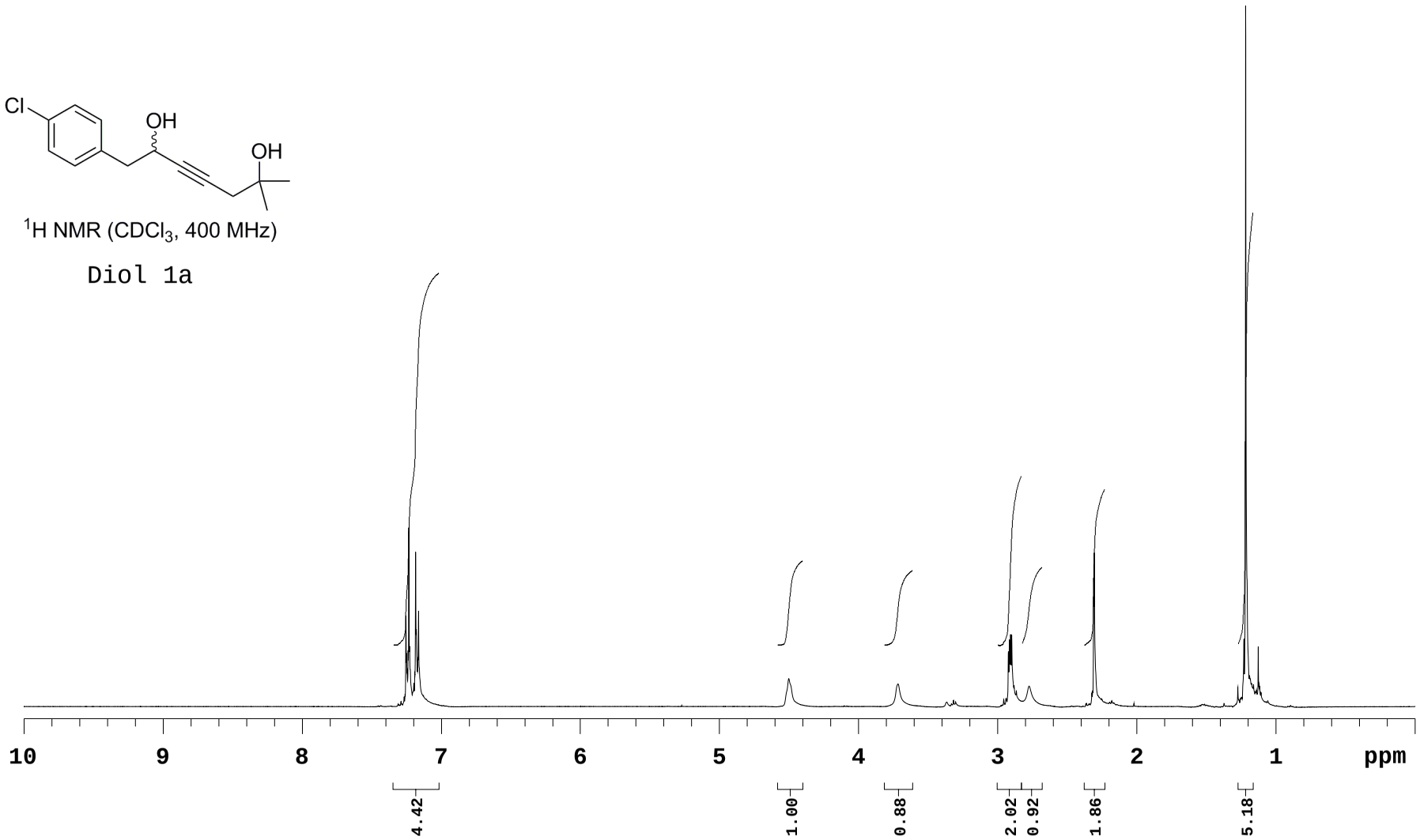
Data For (*2R,4R*)-2-methyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (*2R,4R*)-2eD): $[\alpha]_D$ = +132 (c 1.00, CH_2Cl_2). HRMS (CI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{20}ONa$: 311.1406; found: 311.1404.

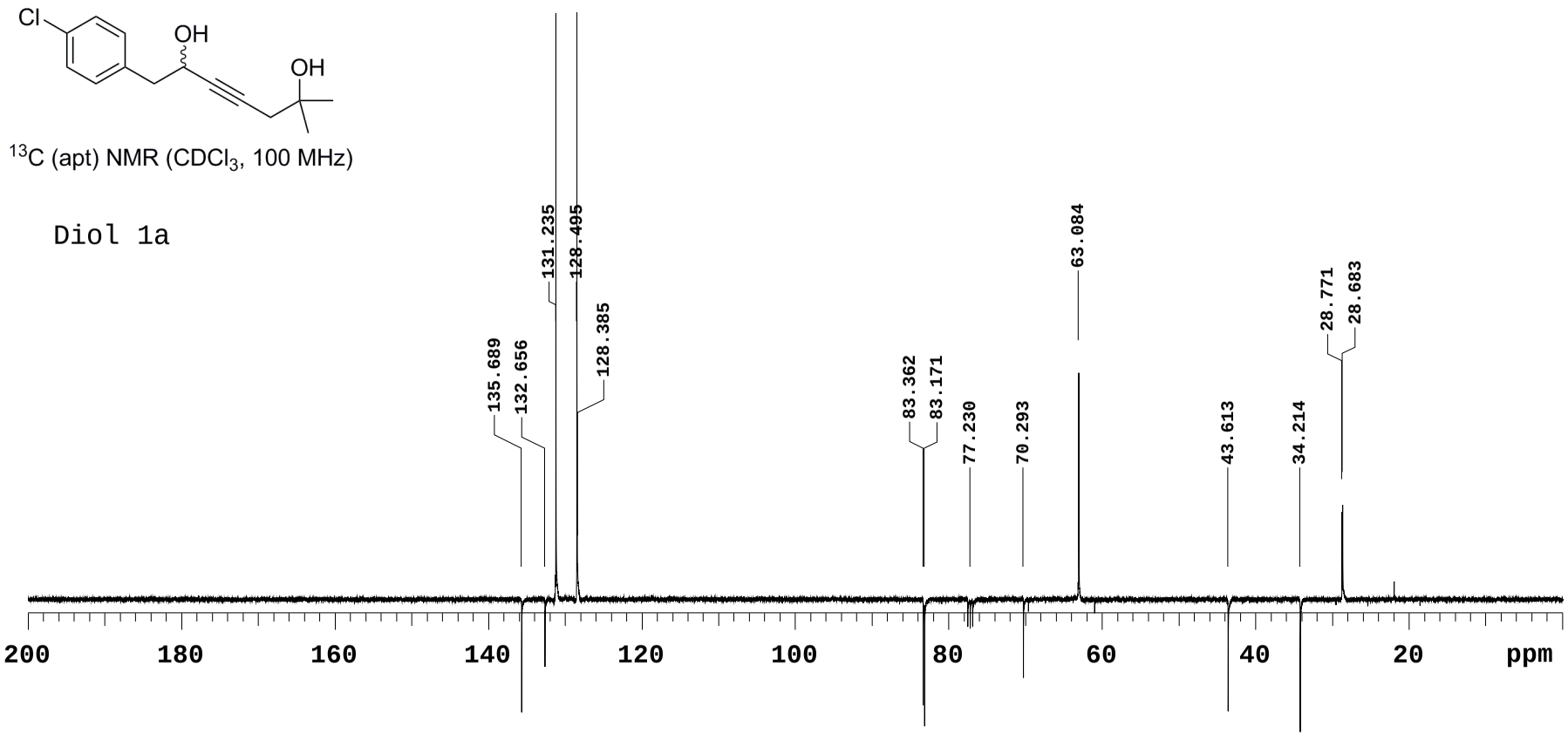
2-butyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (*cis*-(±)-2fD and *trans*-(±)-2fD): The title compounds were prepared from alkynediol **1f** (0.150 g, 0.609 mmol). The crude mixtures contained between 1.4-1.5:1 of *cis-/trans*- diastereomers (^{1}H NMR). The light yellow solid diastereomers were partially separated by flash column chromatography using 95% hexanes, 5% EtOAc to afford ***cis*-(±)-2fD and *trans*-(±)-2fD** (total, combined: 0.141 g, 70%).

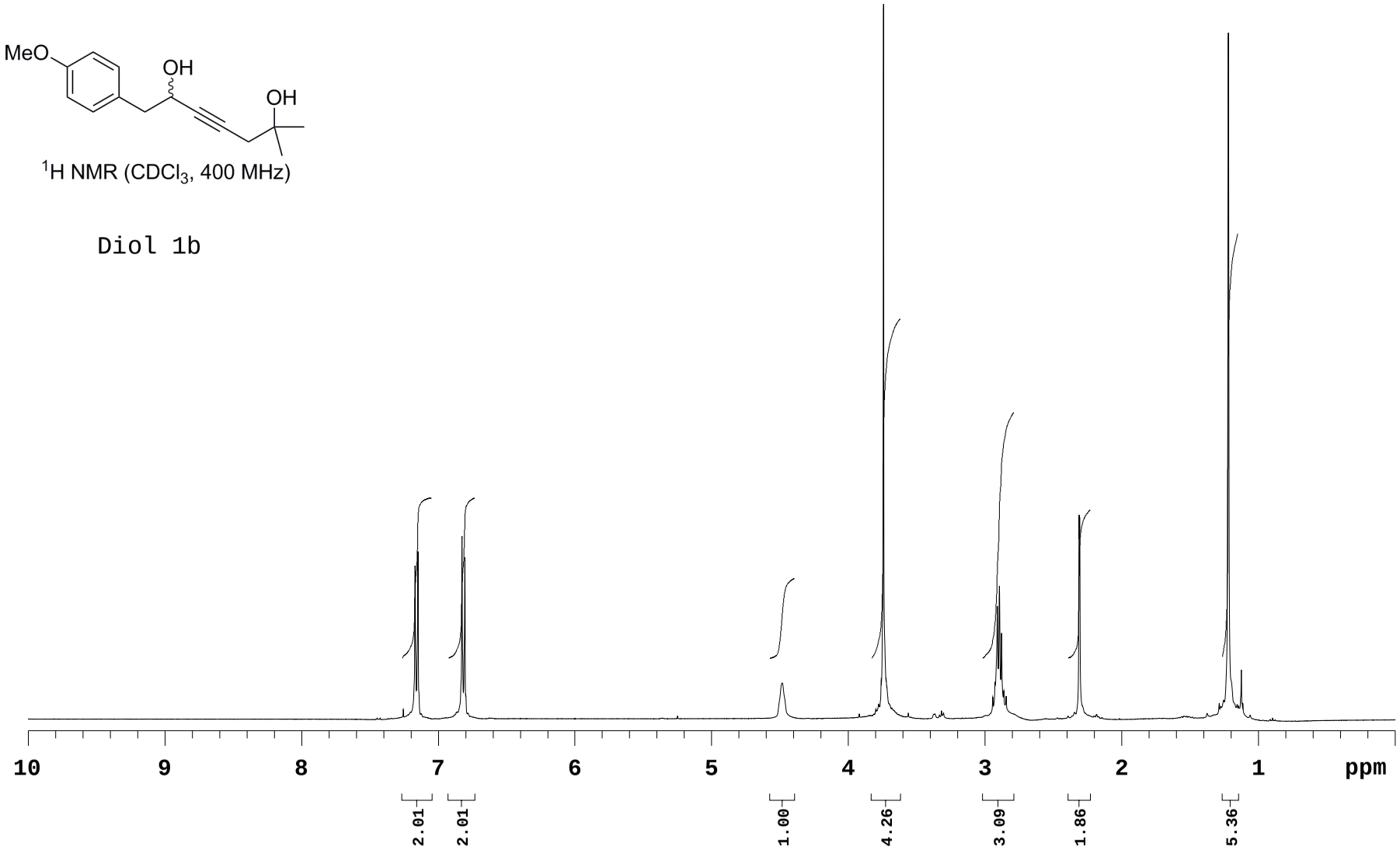
Data for *cis*-(±)-2fD: R_f = 0.46 (95% hexanes, 5% EtOAc); mp = 62-64 ^{o}C. IR (neat): 3055, 2955, 2930, 1602, 1510, 1084, 812, 762 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.44-7.57 (overlapping m, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 5.82 (s, 1H), 3.92 (dddd, *J* = 13.3, 10.1, 6.2, 3.1 Hz, 1H), 3.23 (app d, *J* = 16.1 Hz, 1H), 3.05 (dd, *J* = 16.1, 2.0 Hz, 1H), 2.33 (s, 3H), 1.69-1.95 (m, 2H), 1.44-1.63 (m, 2H), 1.34-1.45 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8 (q), 138.0 (q), 135.6 (q), 132.3 (q), 131.9 (q), 129.7 (q), 129.4 (t), 129.1 (t), 128.6 (t), 126.4 (t), 126.1 (t), 125.7 (t), 124.9 (t), 123.1 (t), 81.4 (t), 75.2 (t), 36.4 (s), 31.7 (s), 28.0 (s), 23.0 (s), 21.4 (p), 14.3 (p). *m/z* $[M+Na]^+$ calcd for $C_{24}H_{26}ONa$: 353.18759; found: 353.18752.

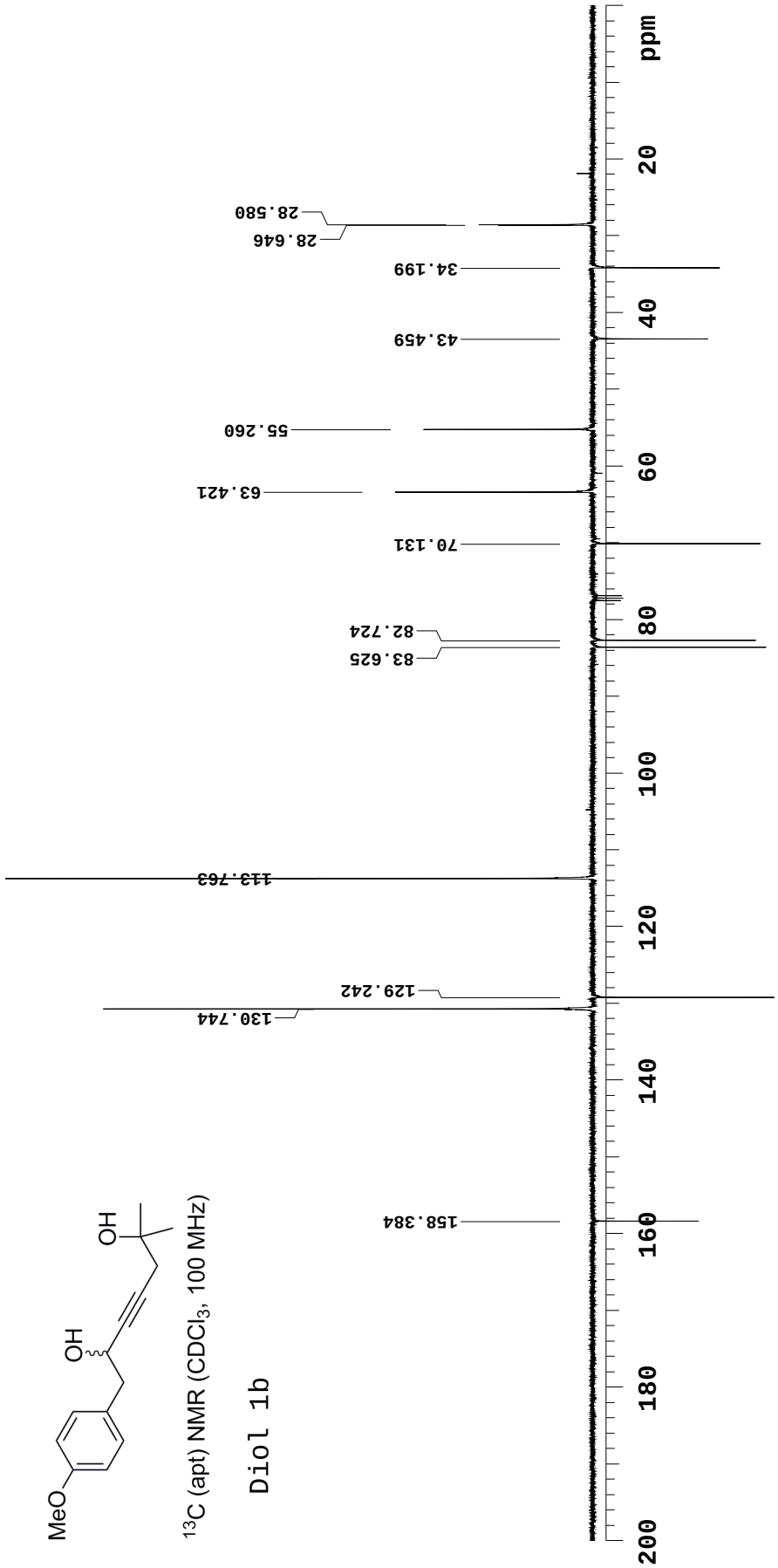
Data for (*2R*,4R)-2-butyl-4-(*p*-tolyl)-1,4-dihydro-*2H*-benzo[*f*]isochromene (*trans*-(±)-2fD):** R_f = 0.43 (95% Hexanes, 5% EtOAc); mp = 84-86 ^{o}C. IR (neat): 2949, 2926, 2897, 1510, 1186,

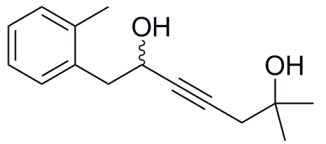
812, 764 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.6 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 1H) 7.48-7.58 (dm, *J* = 1.6 Hz, 2H), 7.09-7.16 (m, 4H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.01 (s, 1H), 3.79 (dddd, *J* = 13.2, 11.2, 8.2, 4.3 Hz, 1H), 3.17 (dd, *J* = 16.6, 3.7 Hz, 1H), 2.93 (dd, *J* = 16.6, 10.4 Hz, 1H), 1.38-1.50 (m, 1H), 1.1.9-1.34 (m, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1 (q), 137.7 (q), 132.9 (q), 132.7 (q), 132.3 (q), 130.1 (q), 129.6 (t), 128.9 (t), 128.8 (t), 126.4 (t), 125.9 (t), 125.8 (t), 126.6 (t), 123.0 (t), 77.4 (t), 67.6 (o), 35.9 (s), 31.3 (s), 27.7 (s), 22.8 (s), 21.3 (p), 14.2 (p). *m/z* $[M+Na]^+$ calcd for $C_{24}H_{26}ONa$: 353.18759; found: 353.18746.


Cl
OH
OH
^{1}H NMR ($CDCl_3$, 400 MHz)
Diol 1a
10
9
8
7
6
5
4
3
2
1
ppm
4.42
1.00
0.88
2.02
0.92
1.86
5.18


Cl
OH
OH
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)
Diol 1a
135.689
132.656
131.235
128.495
128.385
83.362
83.171
77.230
70.293
63.084
43.613
34.214
28.771
28.683
200
180
160
140
120
100
80
60
40
20
ppm

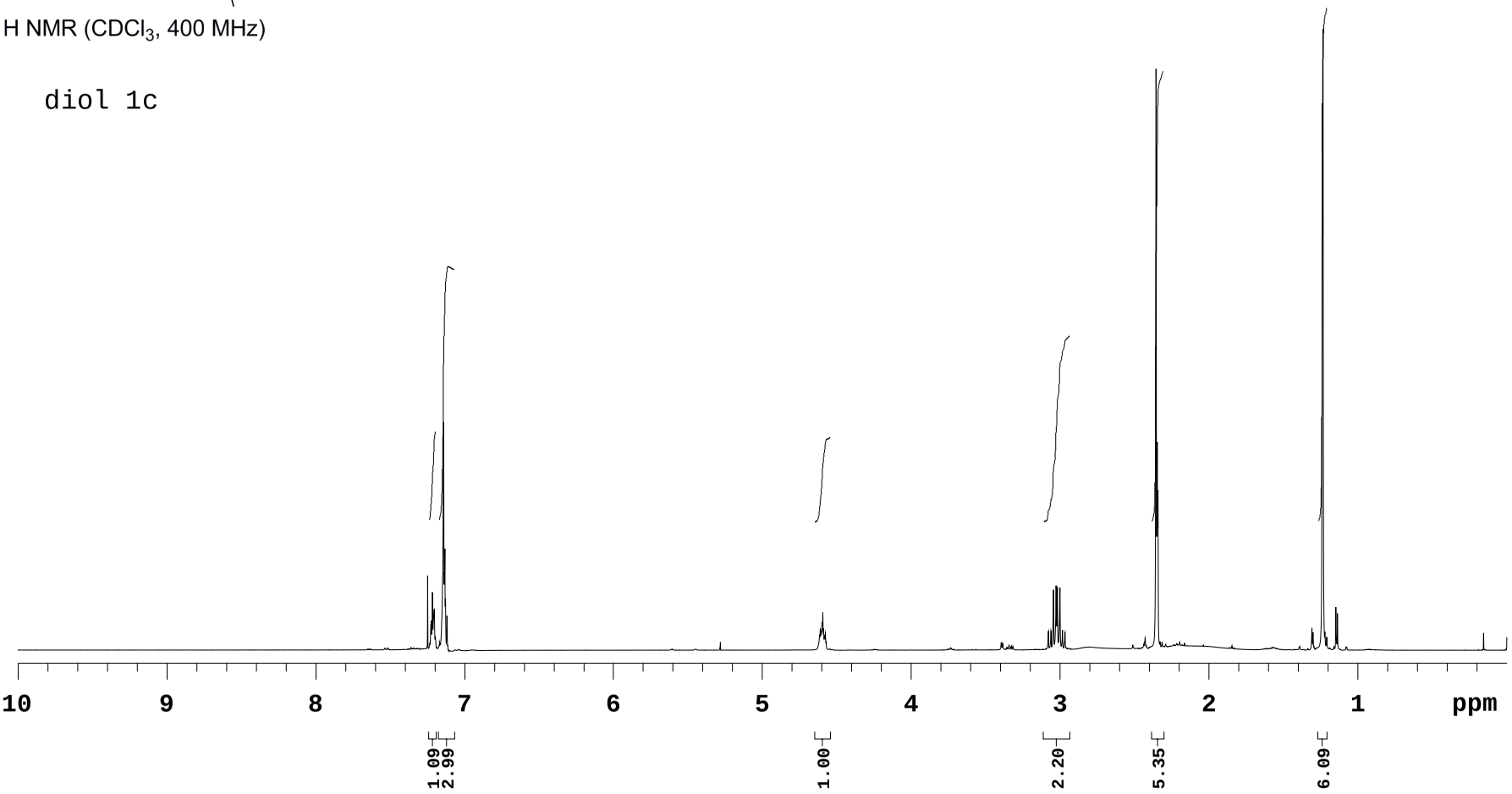

MeO
OH
OH
^{1}H NMR ($CDCl_3$, 400 MHz)
Diol 1b
10
9
8
7
6
5
4
3
2
1
ppm
2.01
2.01
1.00
4.26
3.09
1.86
5.36

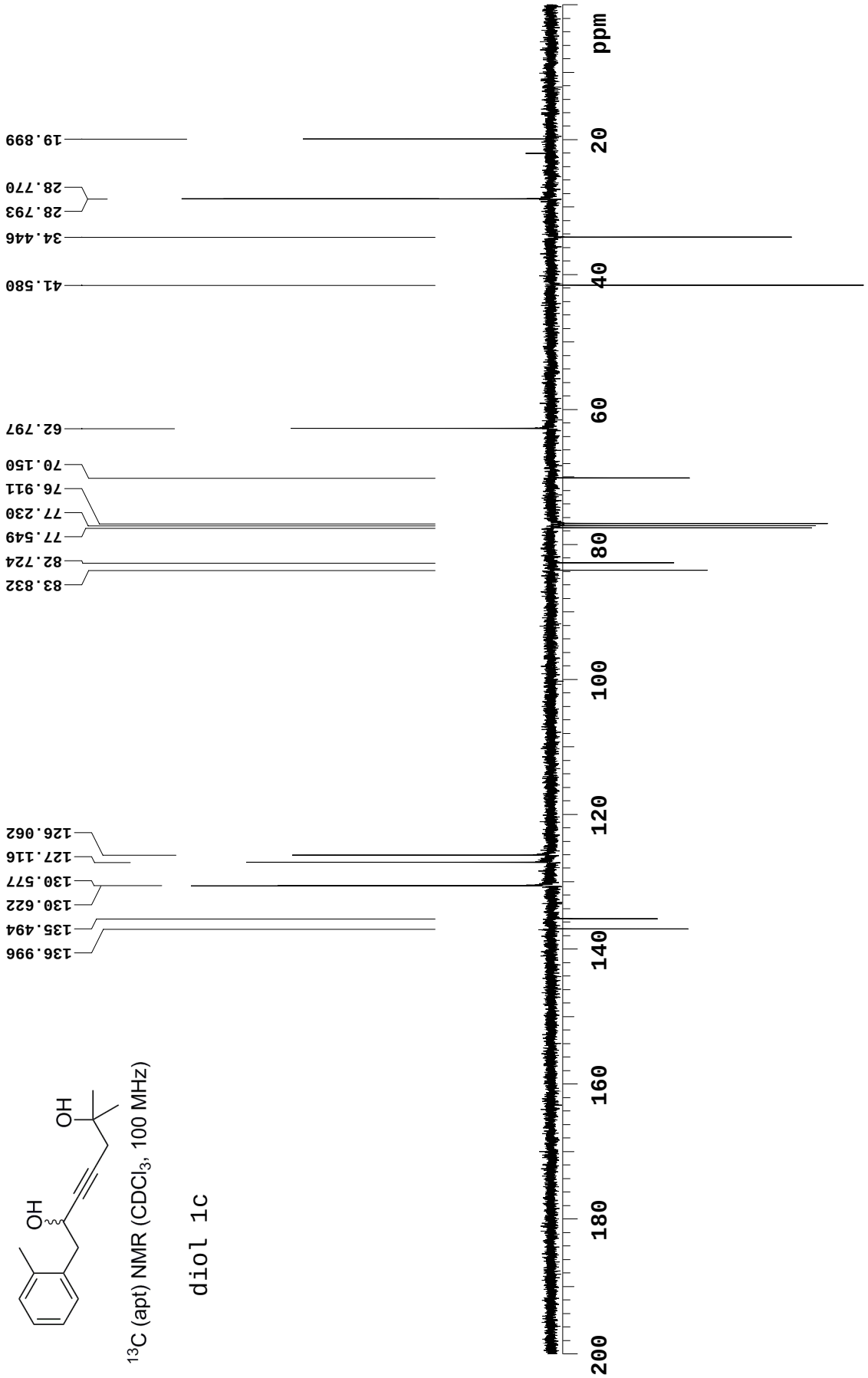

Diol 1b
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)
MeO
OH
OH
158.384
130.744
129.242
113.763
83.625
82.724
70.131
63.421
55.260
43.459
34.199
28.646
28.580
ppm
20
40
60
80
100
120
140
160
180
200

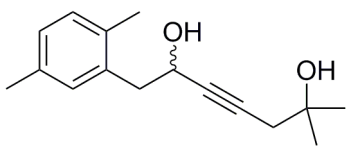


^{1}H NMR ($CDCl_3$, 400 MHz)

diol 1c

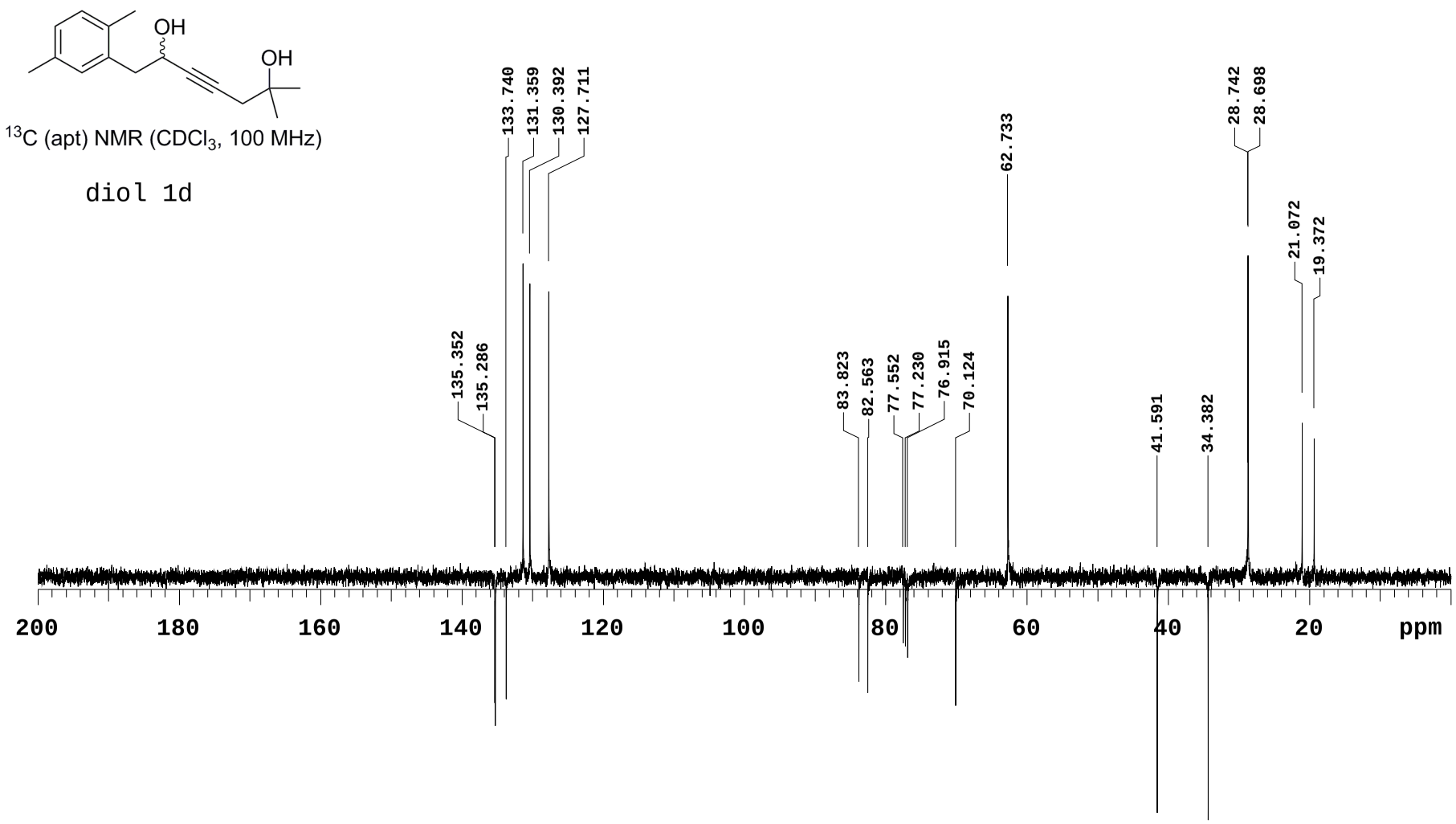


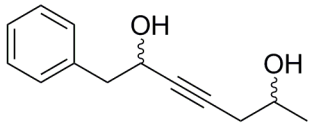

diol 1c
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)
OH
OH
19.899
28.770
28.793
34.446
41.580
62.797
70.150
76.911
77.230
77.549
82.724
83.832
126.062
127.116
130.577
130.622
135.494
136.996
ppm
20
40
60
80
100
120
140
160
180
200



^{1}H NMR ($CDCl_3$, 400 MHz)

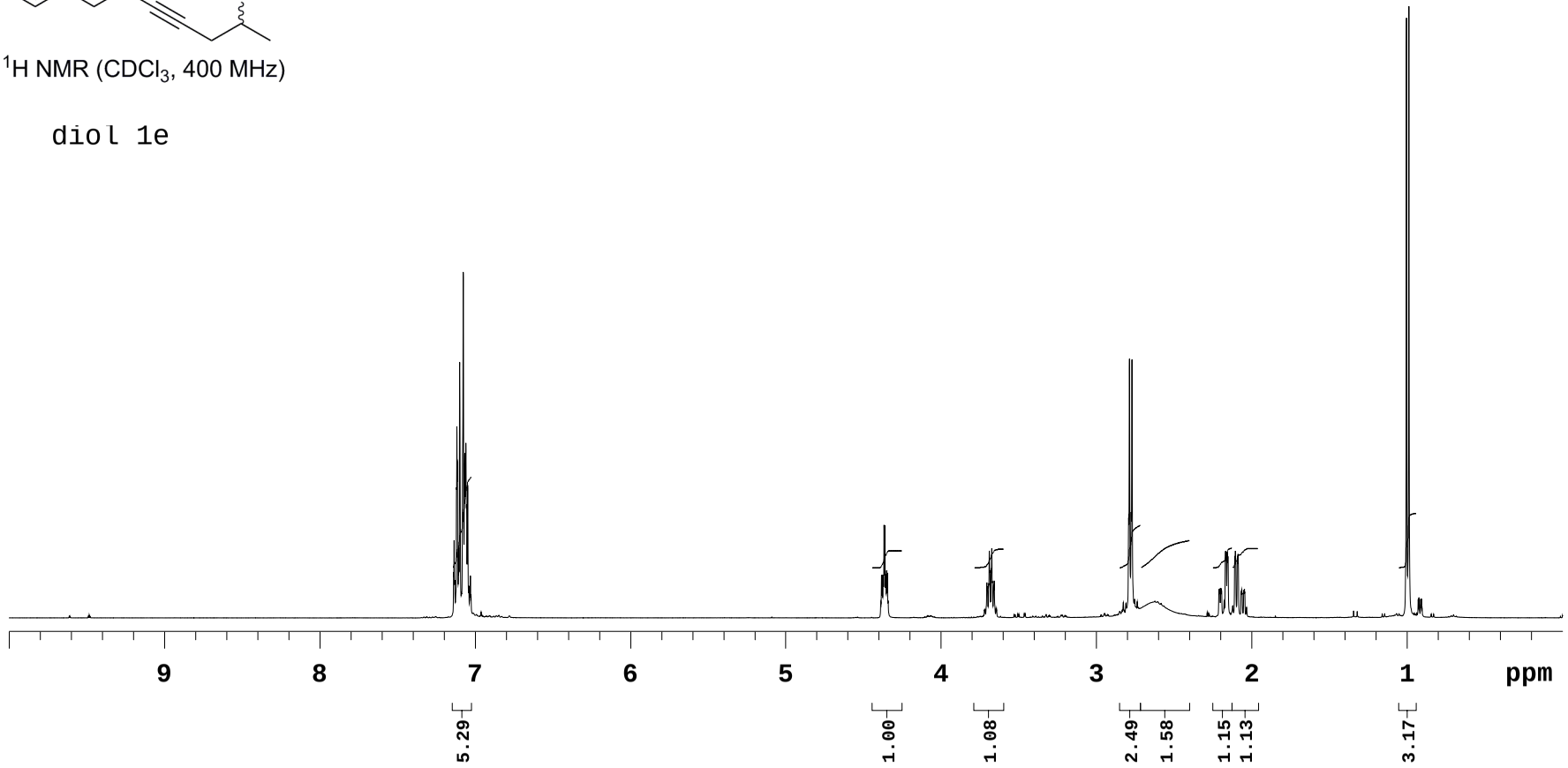
diol 1d

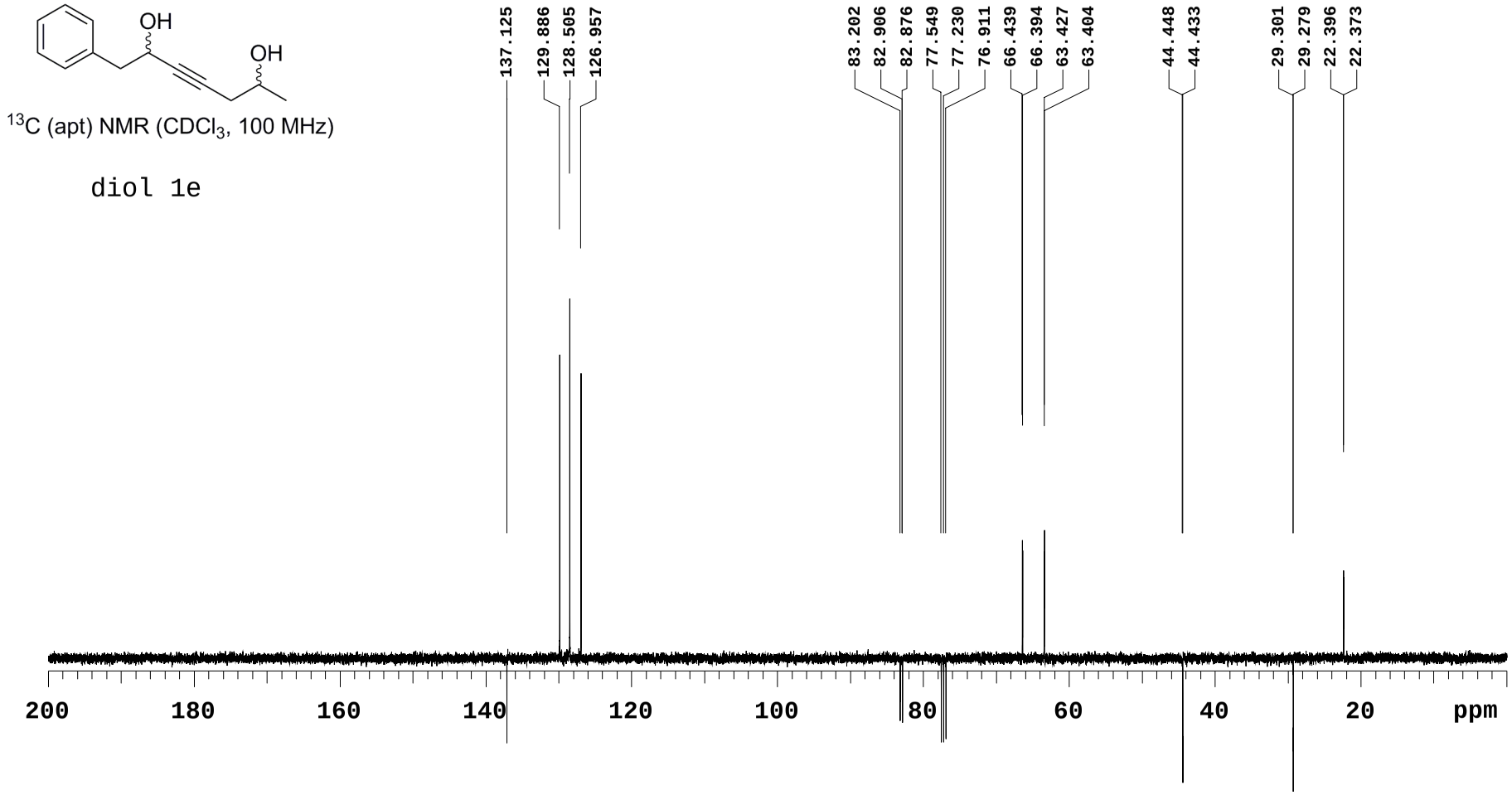

OH
OH
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)
diol 1d
133.740
131.359
130.392
127.711
135.352
135.286
83.823
82.563
77.552
77.230
76.915
70.124
62.733
41.591
34.382
28.742
28.698
21.072
19.372
200
180
160
140
120
100
80
60
40
20
ppm



^{1}H NMR ($CDCl_3$, 400 MHz)

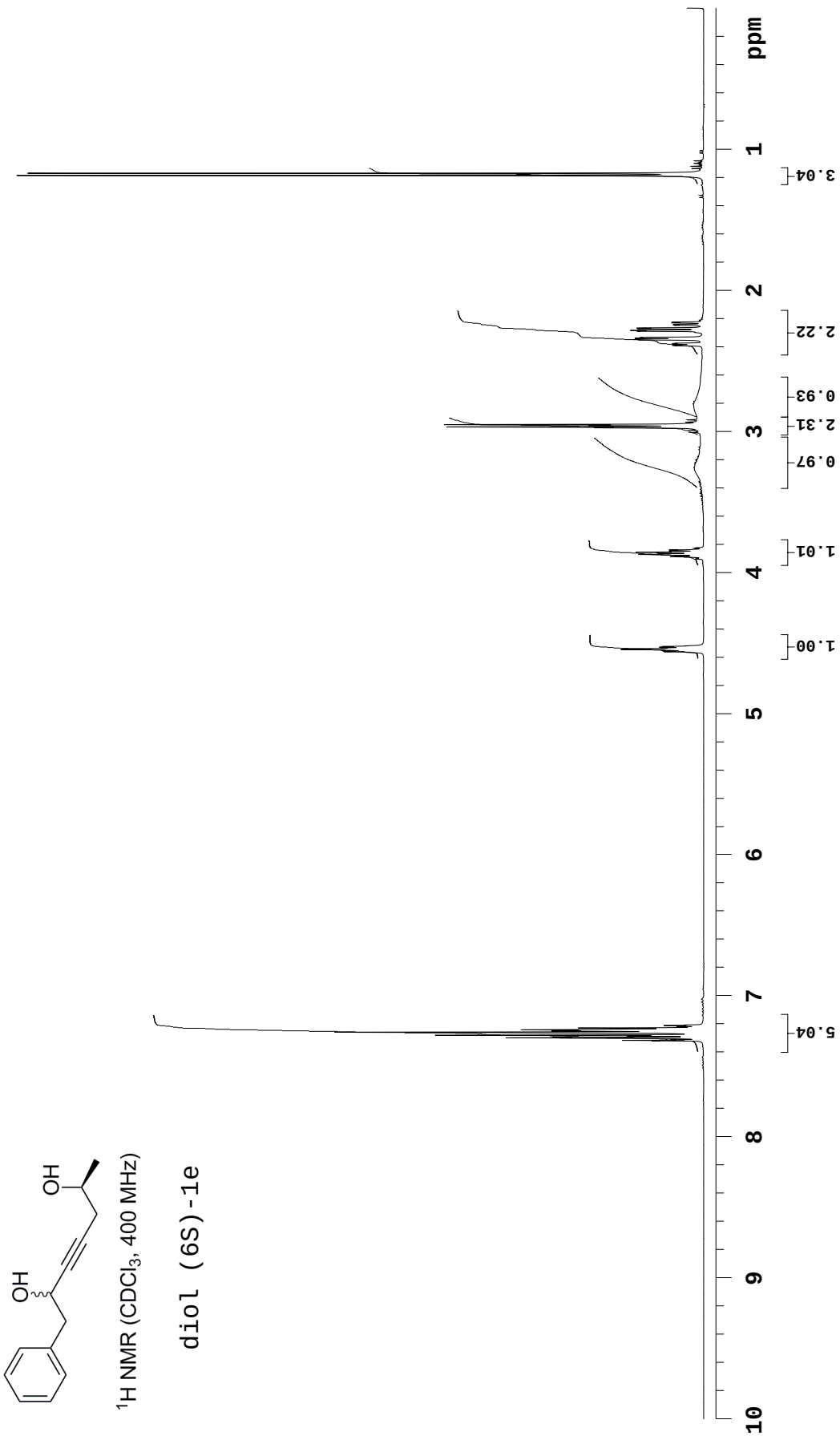
diol 1e

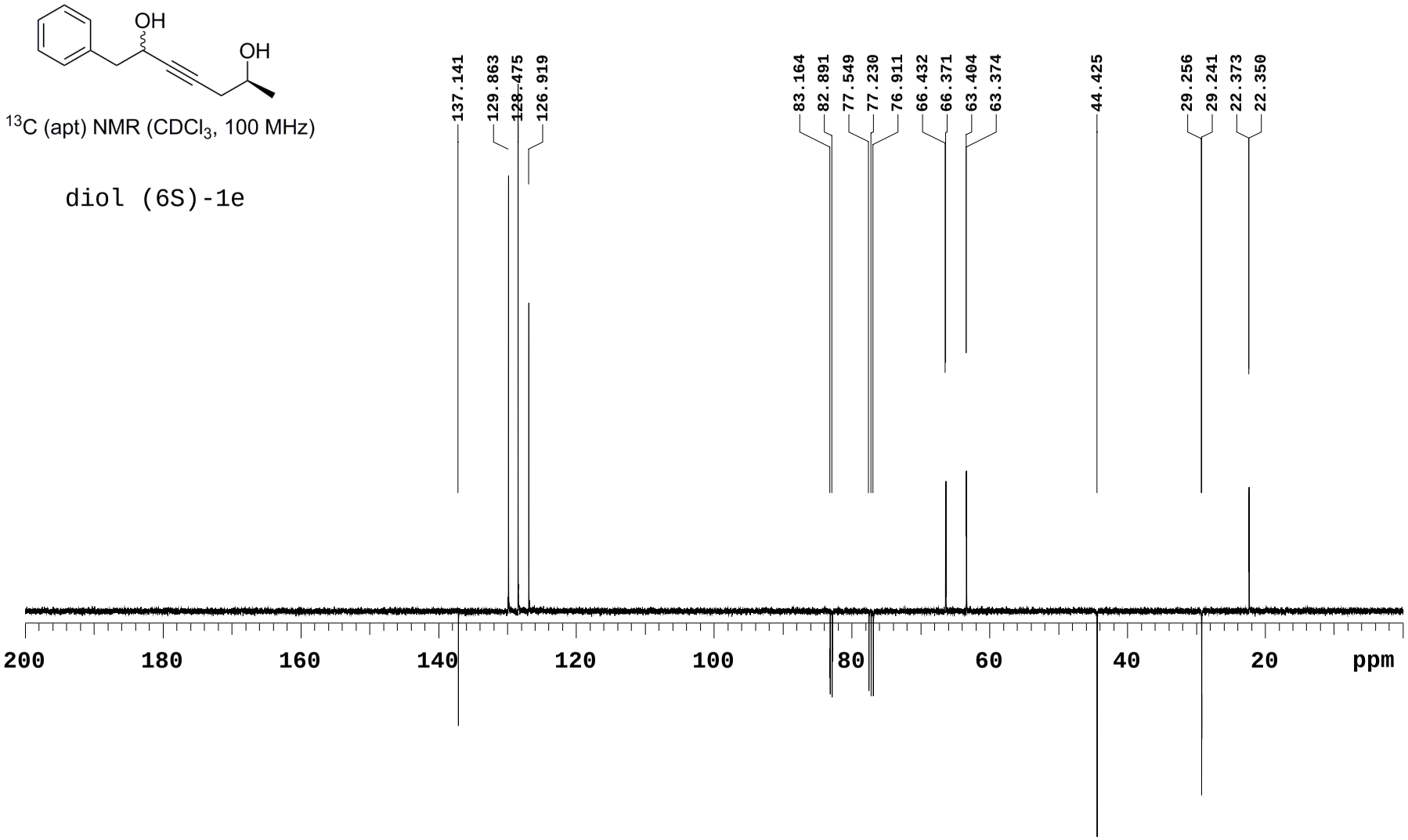


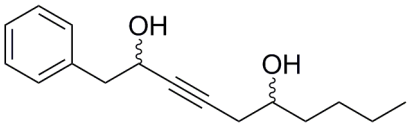


^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

diol 1e

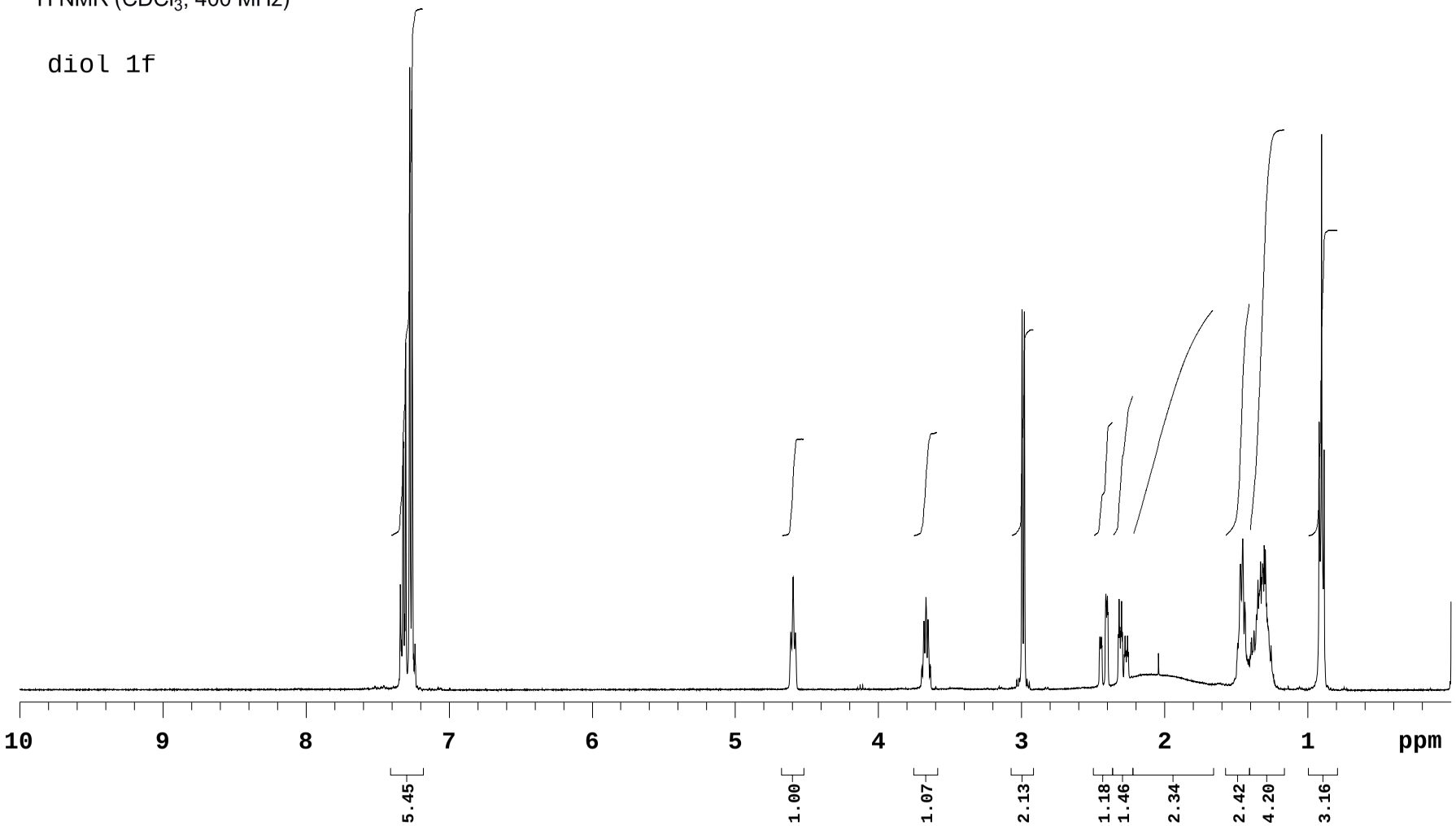

OH
OH
^{1}H NMR ($CDCl_3$, 400 MHz)
diol (6S)-1e
ppm
1
2
3
4
5
6
7
8
9
10
3.04
2.22
0.93
2.31
0.97
1.01
1.00
5.04

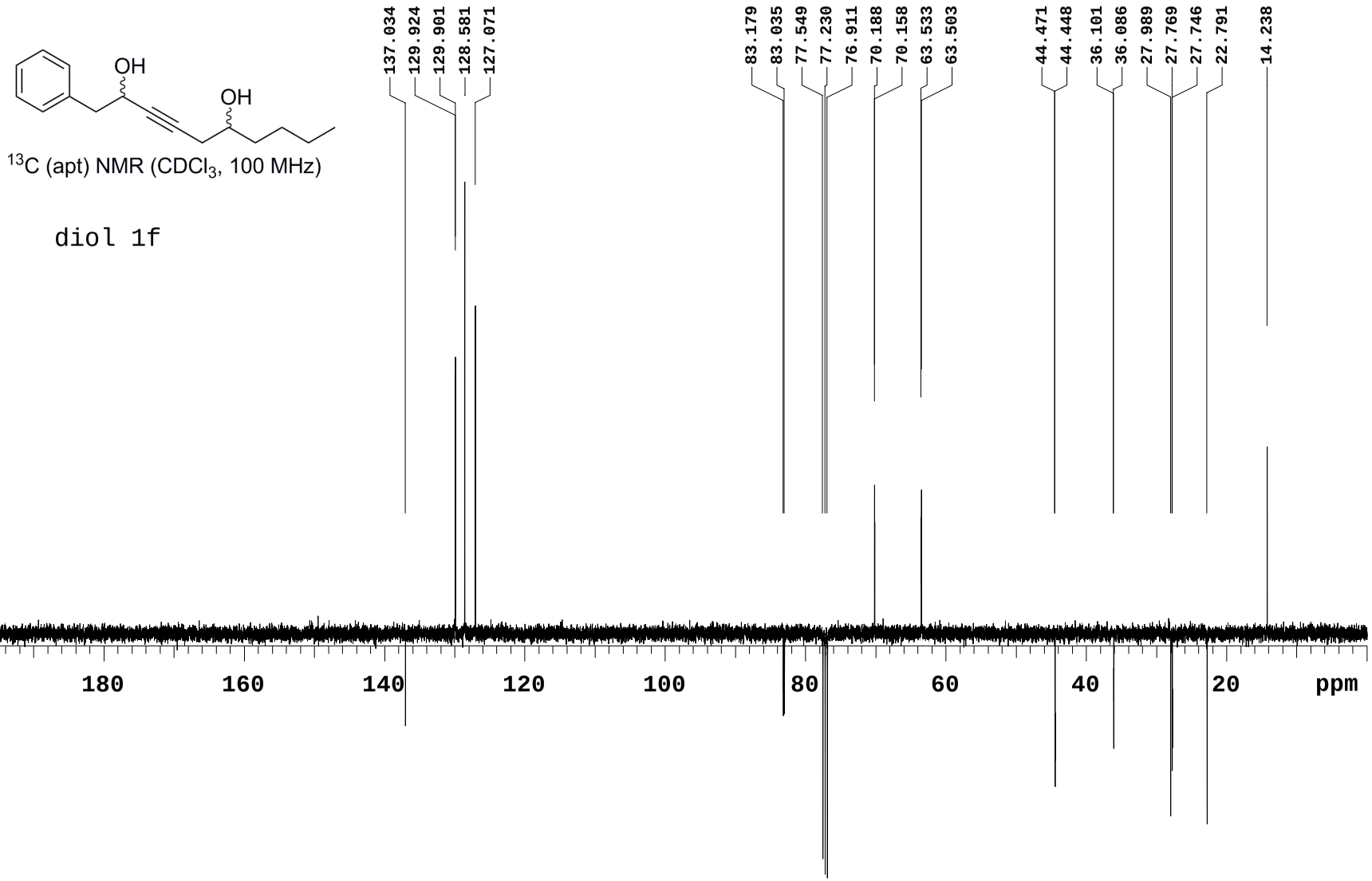

OH
OH
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)
diol (6S)-1e
137.141
129.863
128.475
126.919
83.164
82.891
77.549
77.230
76.911
66.432
66.371
63.404
63.374
44.425
29.256
29.241
22.373
22.350
200
180
160
140
120
100
80
60
40
20
ppm



^{1}H NMR ($CDCl_3$, 400 MHz)

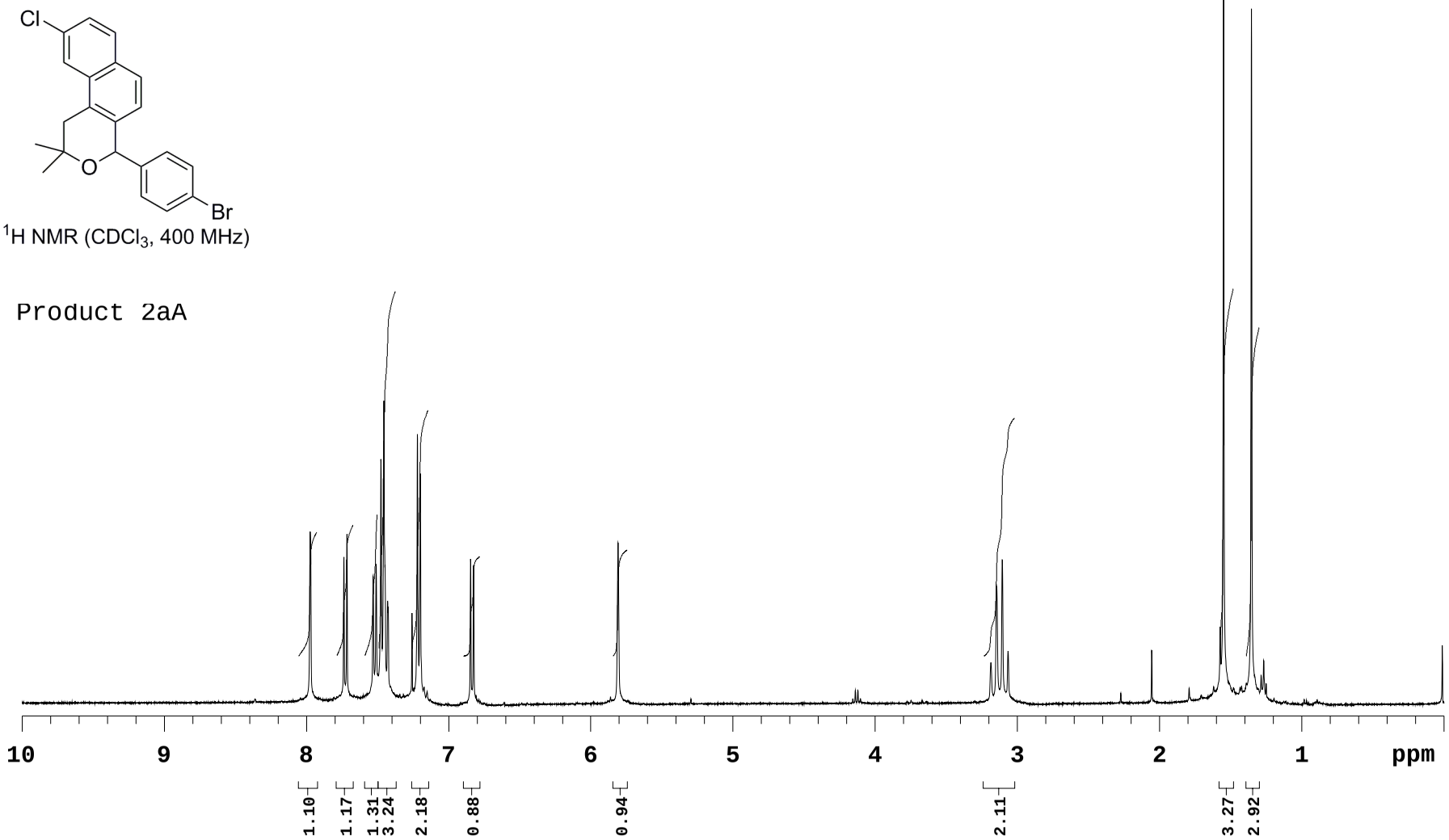
diol 1f

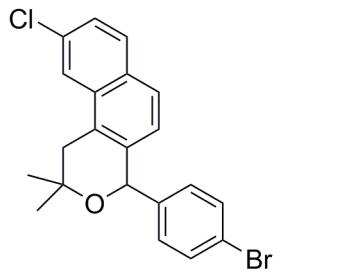




^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

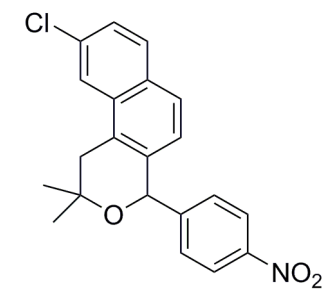
diol 1f


Cl
O
Br
^{1}H NMR ($CDCl_3$, 400 MHz)
Product 2aA
10
9
8
7
6
5
4
3
2
1
ppm
1.10
1.17
1.31
3.24
2.18
0.88
0.94
2.11
3.27
2.92



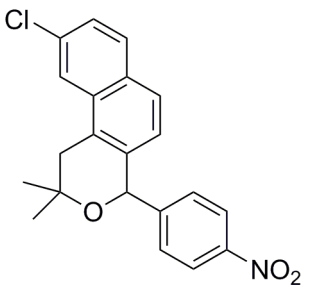
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2aA



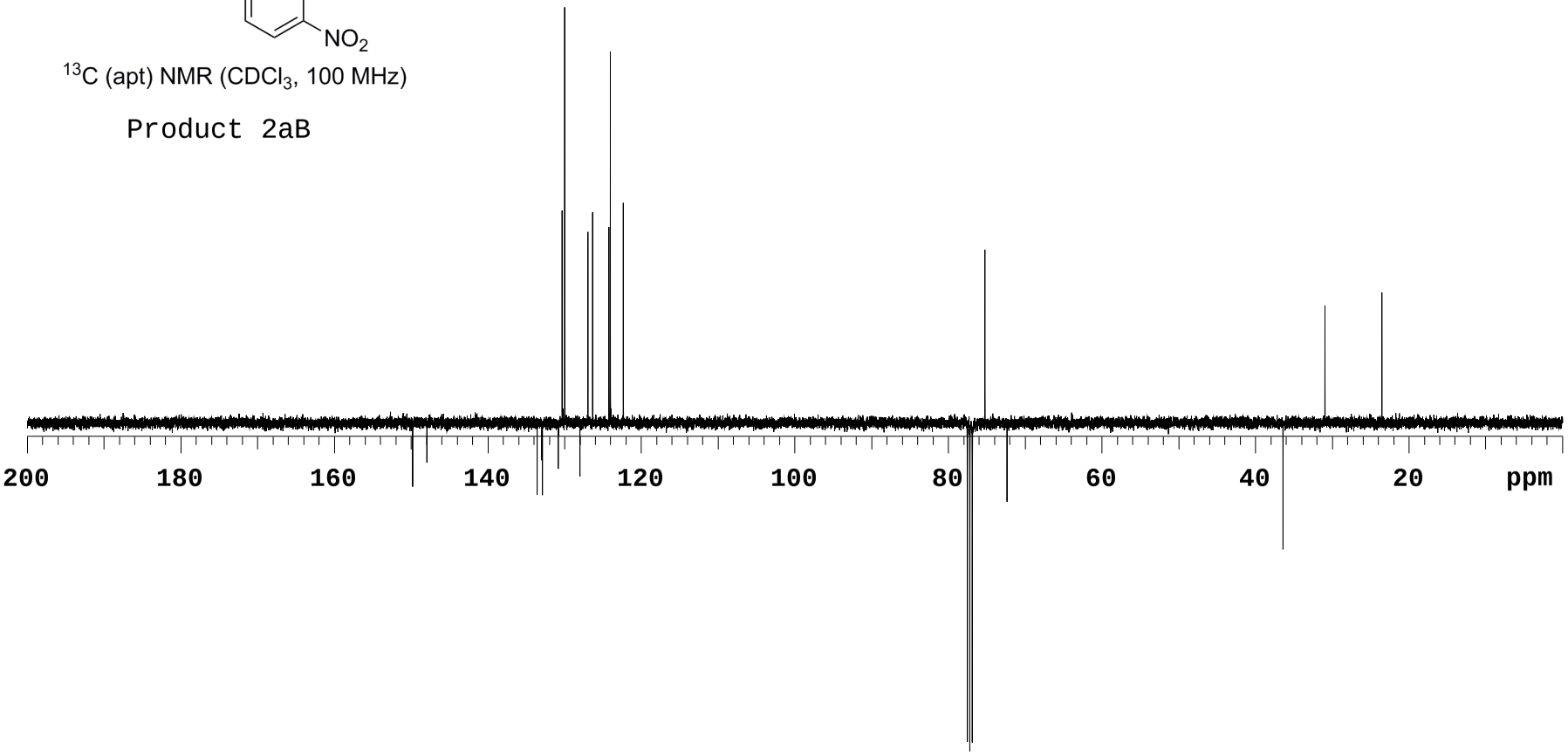
^{1}H NMR ($CDCl_3$, 400 MHz)

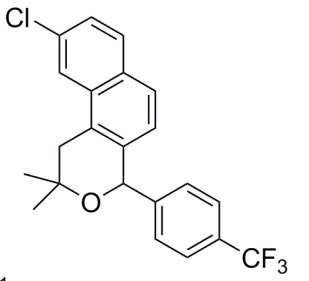
Product 2aB



^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

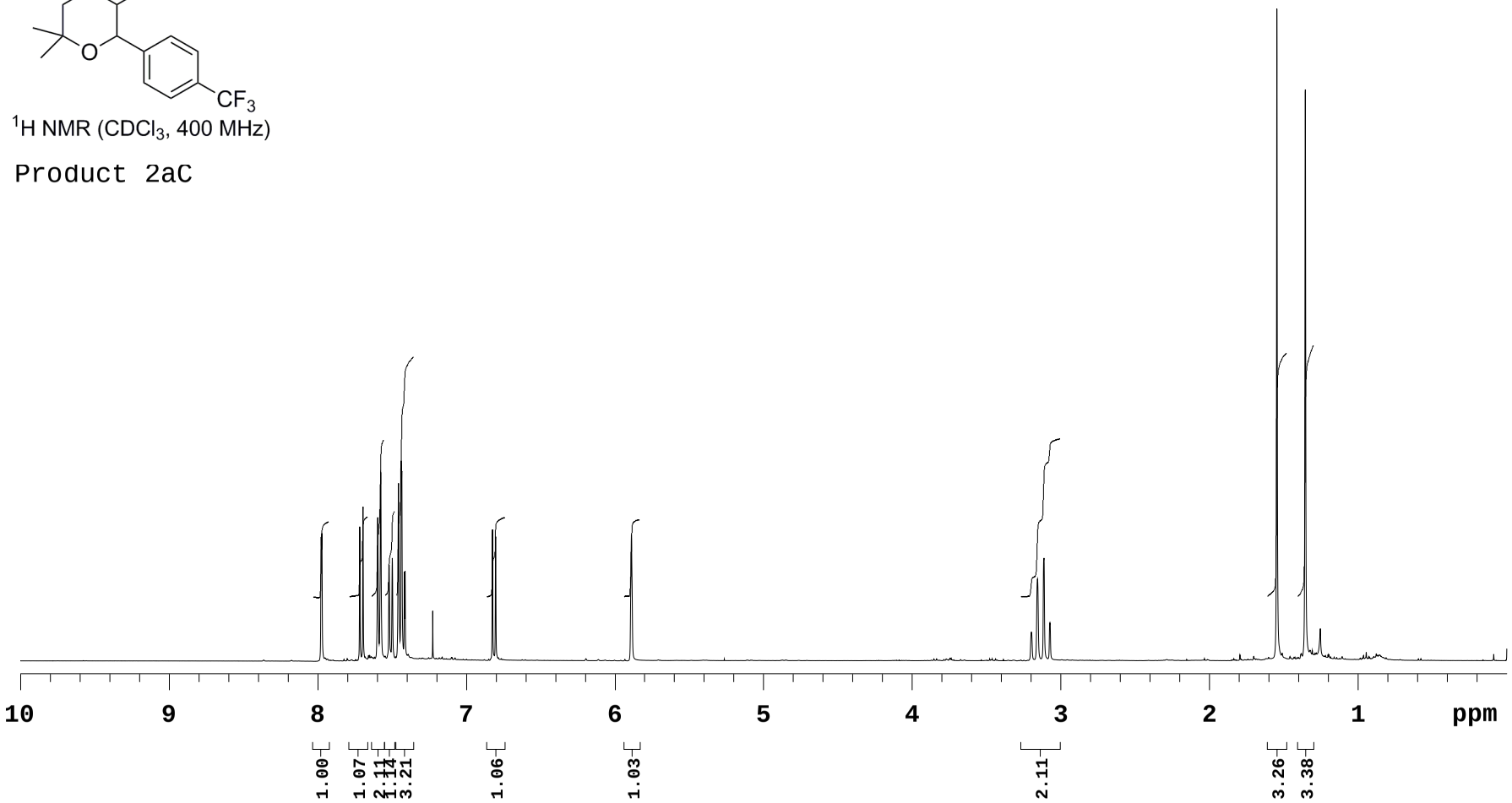
Product 2aB

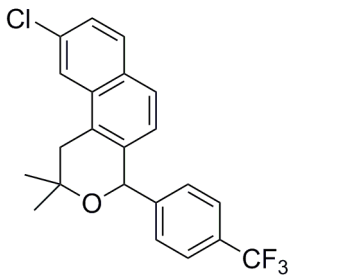




^{1}H NMR ($CDCl_3$, 400 MHz)

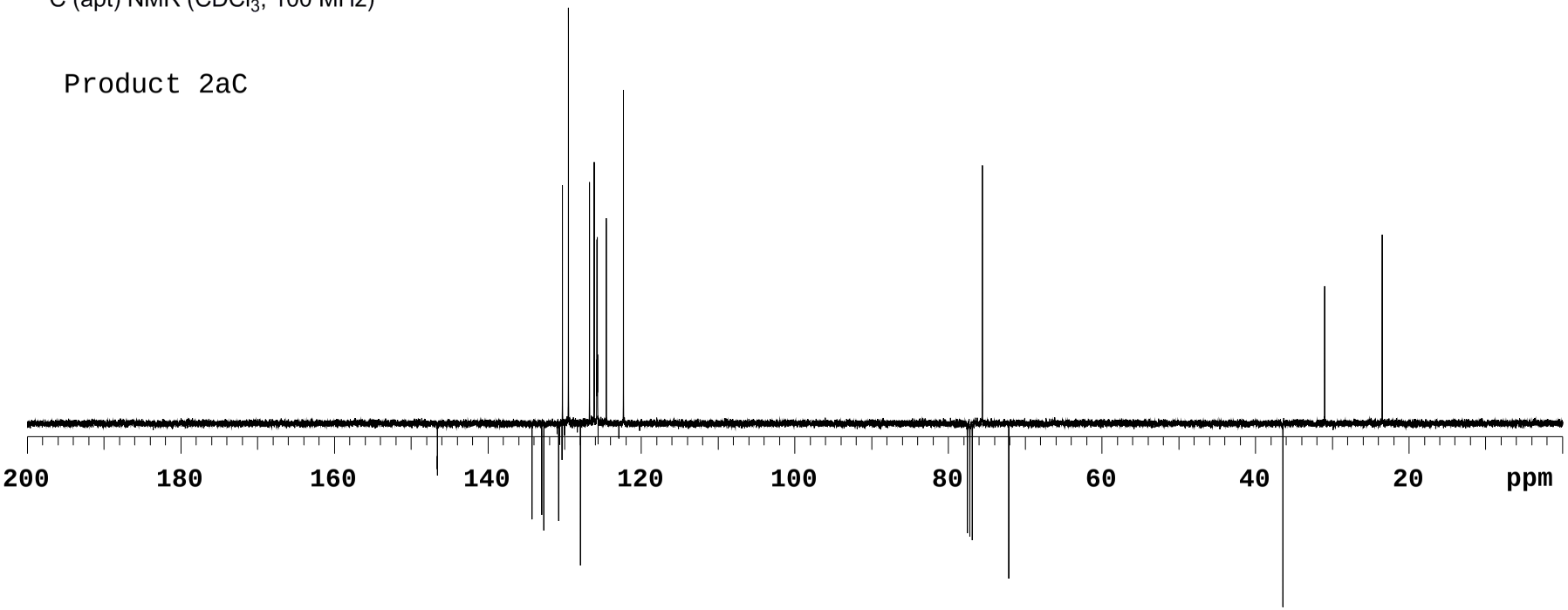
Product 2aC

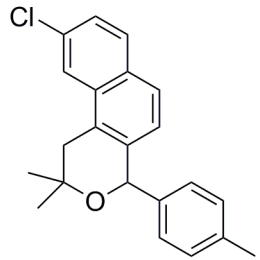




^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

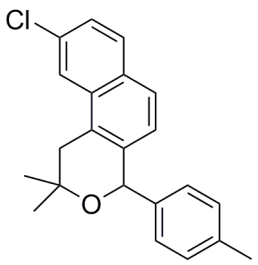
Product 2aC





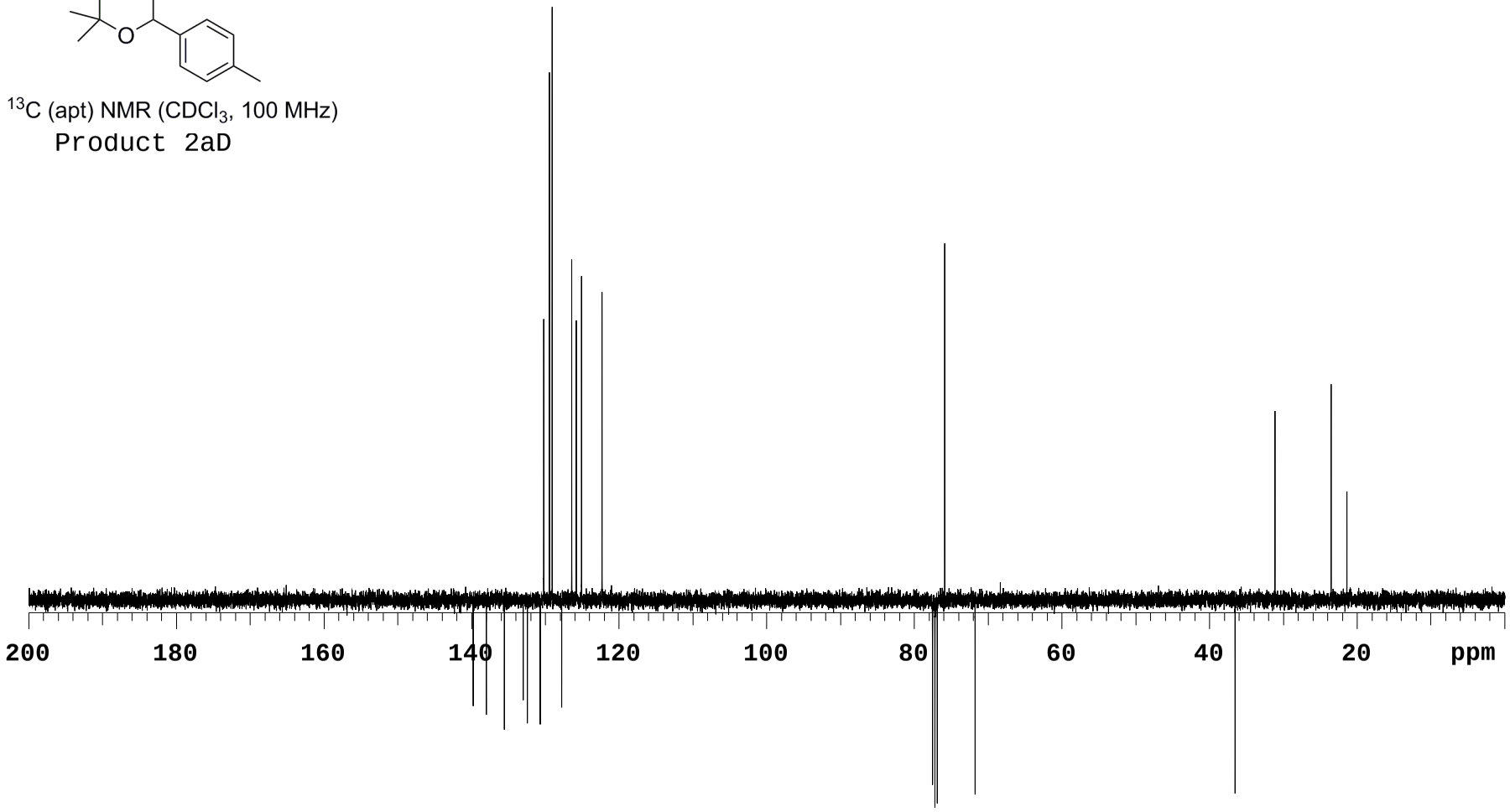
^{1}H NMR ($CDCl_3$, 400 MHz)

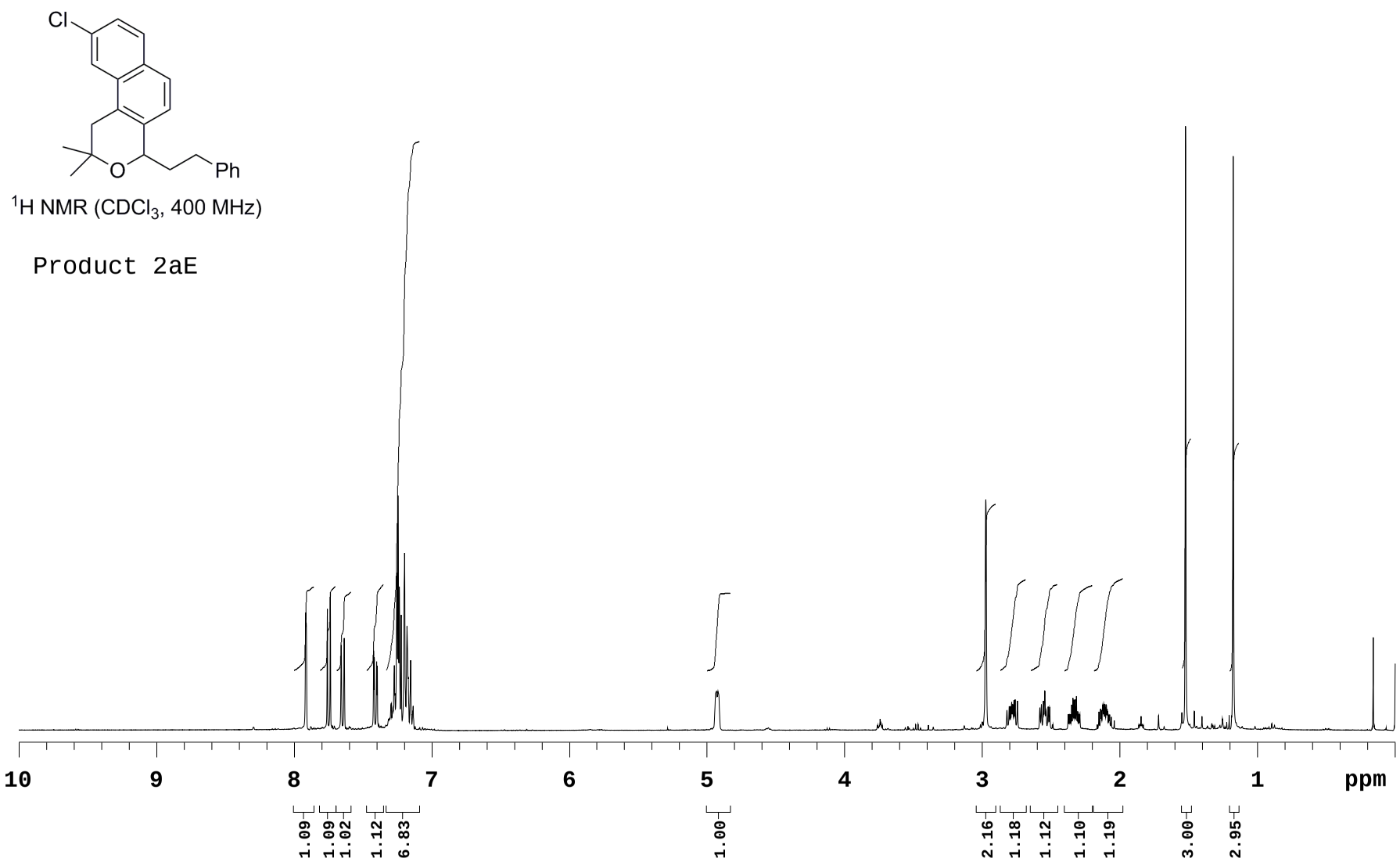
Product 2aD

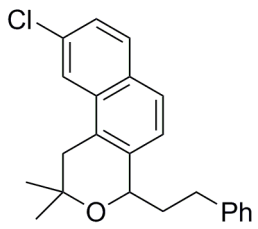


^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2aD

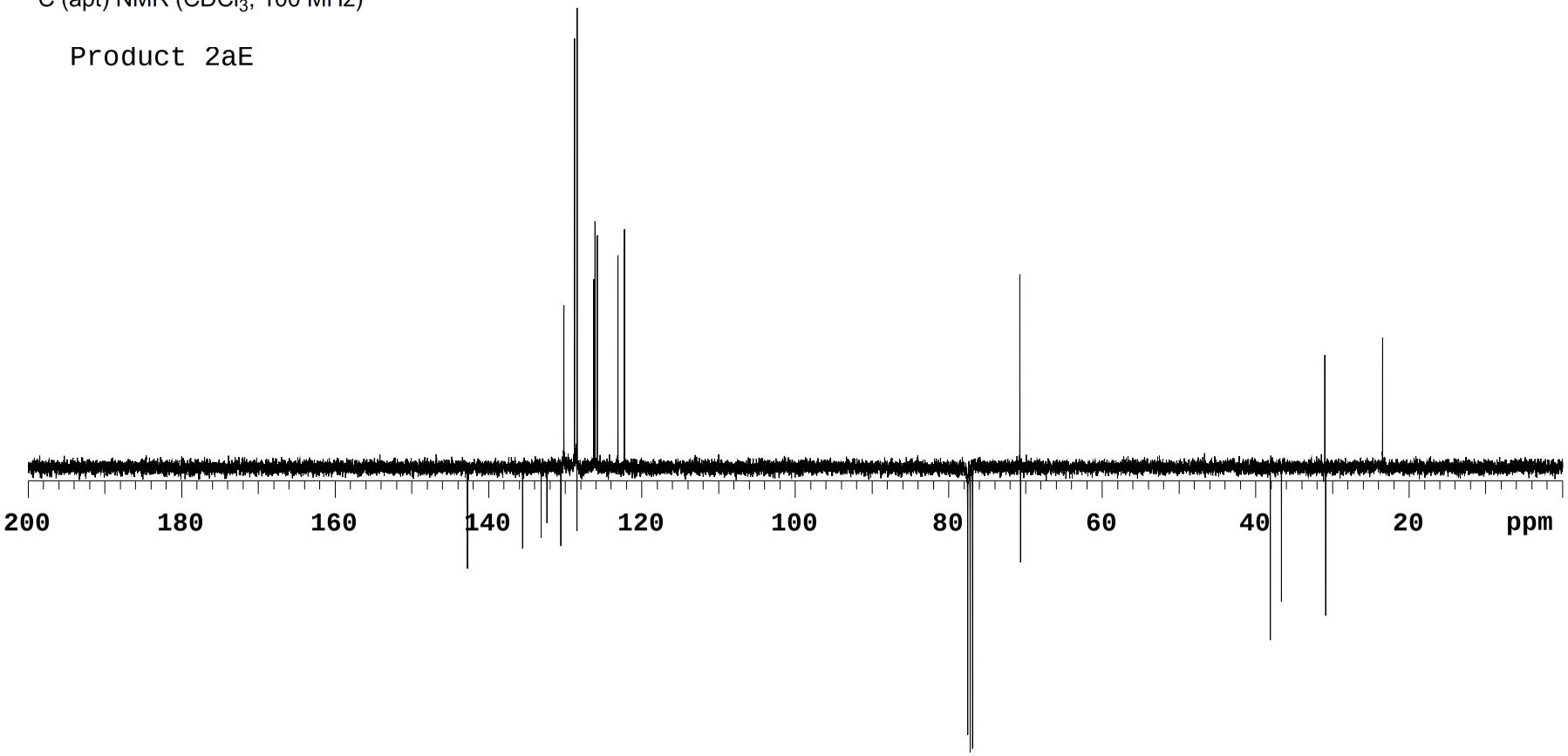


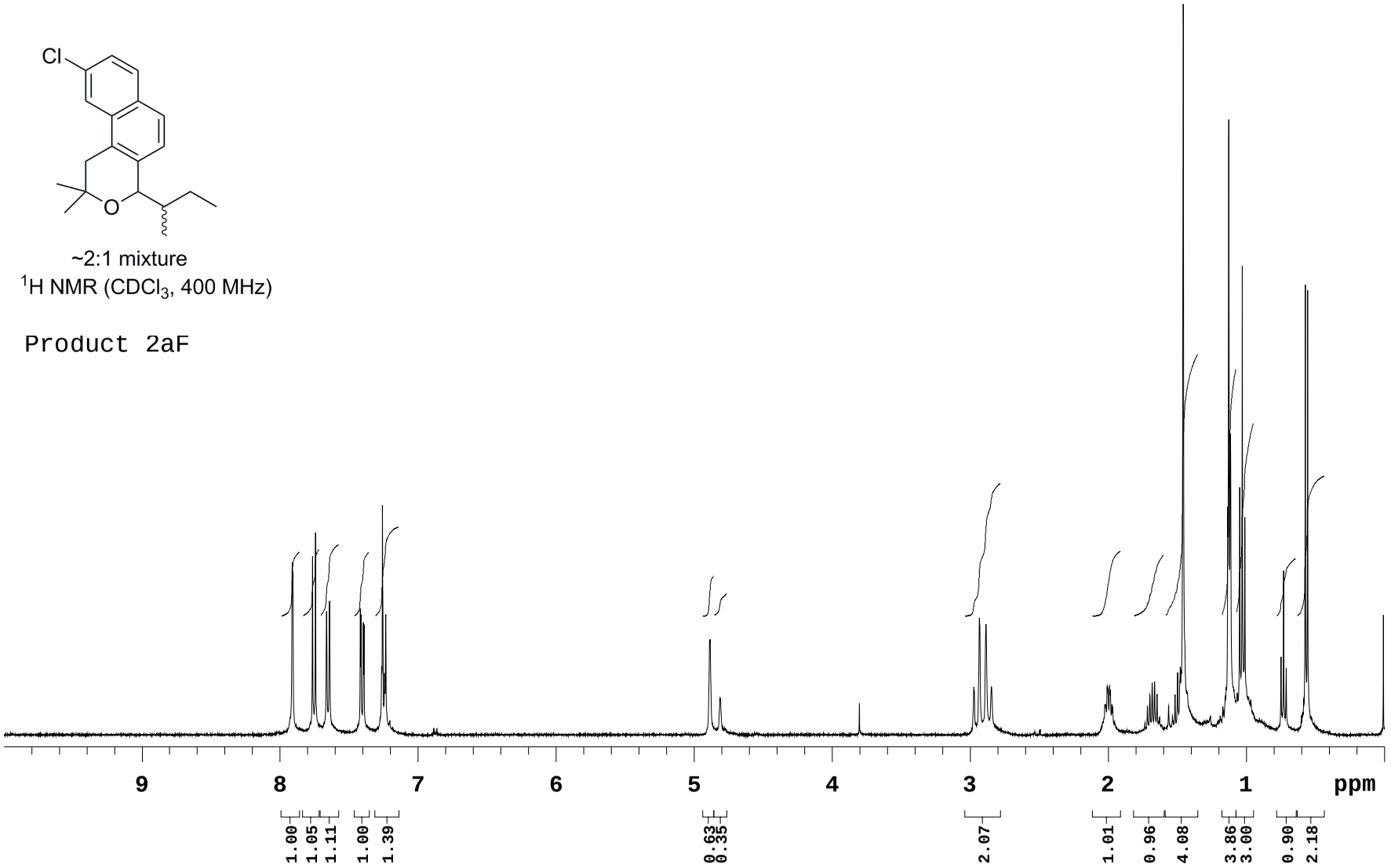

Cl
O
Ph
^{1}H NMR ($CDCl_3$, 400 MHz)
Product 2aE
10
9
8
7
6
5
4
3
2
1
ppm
1.09
1.09
1.02
1.12
6.83
1.00
2.16
1.18
1.12
1.10
1.19
3.00
2.95

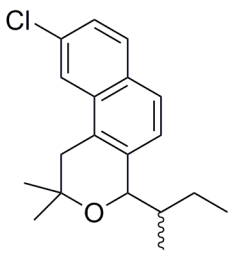


^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2aE



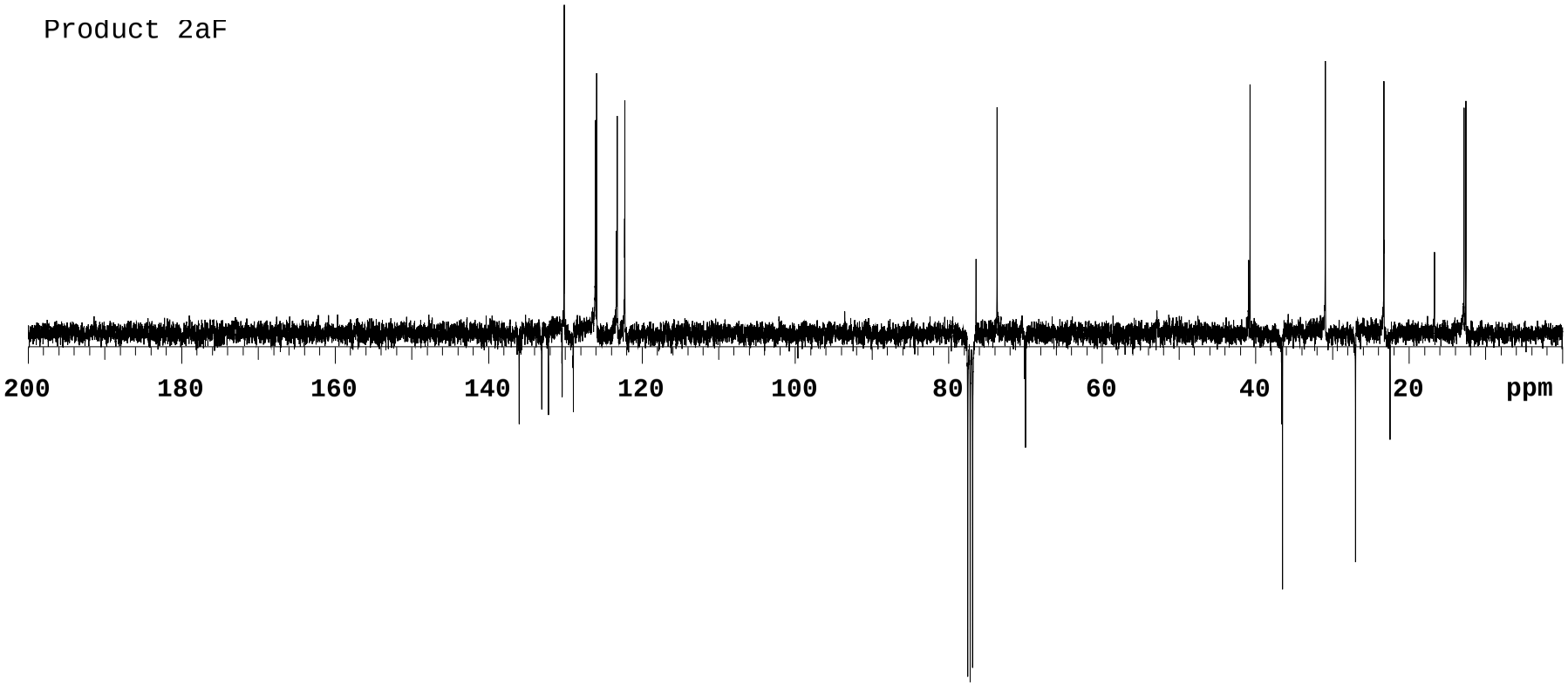

Cl
O
~2:1 mixture
1H NMR (CDCl3, 400 MHz)
Product 2aF
9
8
7
6
5
4
3
2
1
ppm
1.00
1.05
1.11
1.00
1.39
0.63
0.35
2.07
1.01
0.96
4.08
3.86
3.00
0.90
2.18

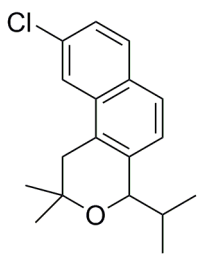


~2:1 mixture

^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

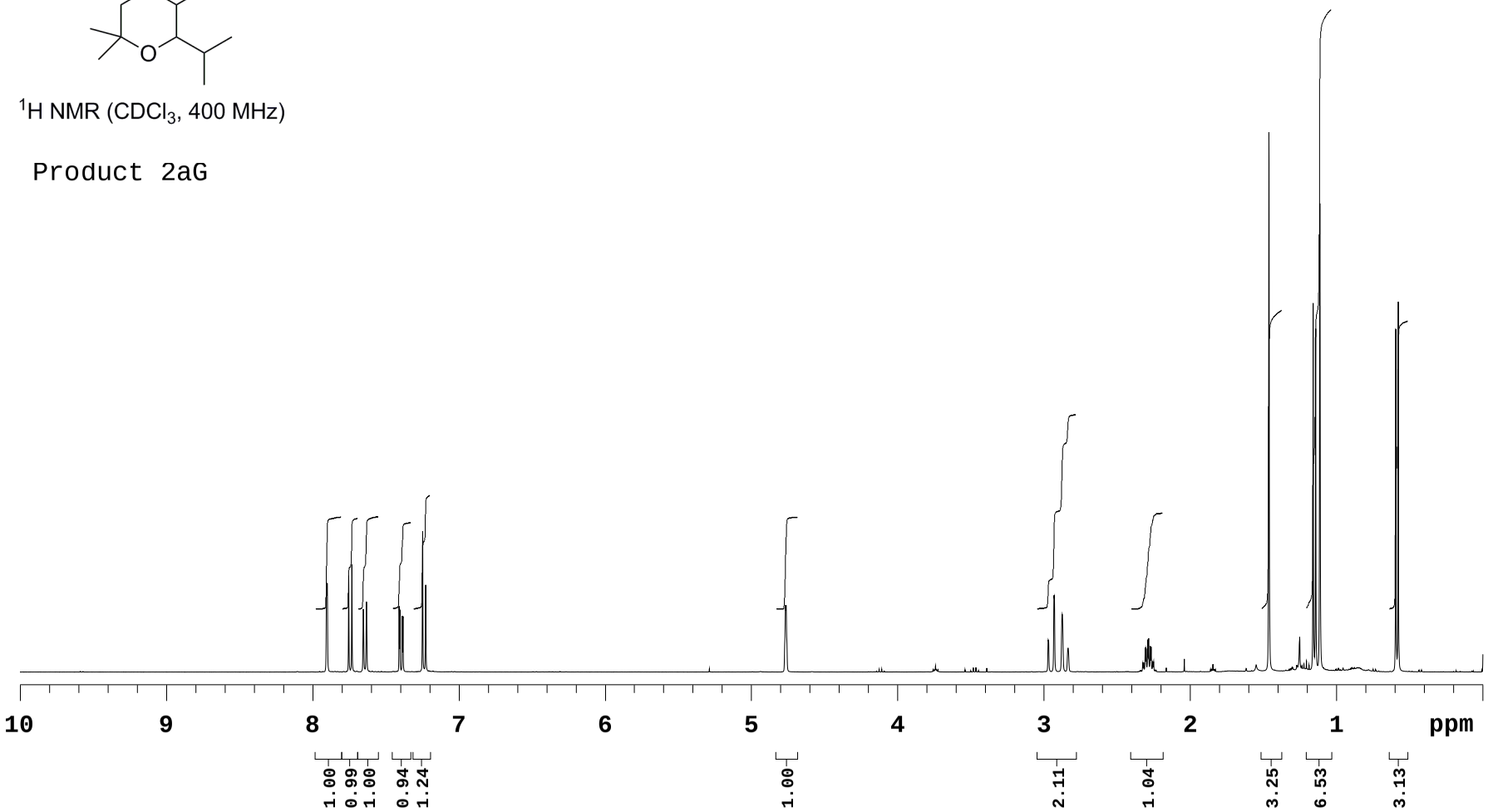
Product 2aF

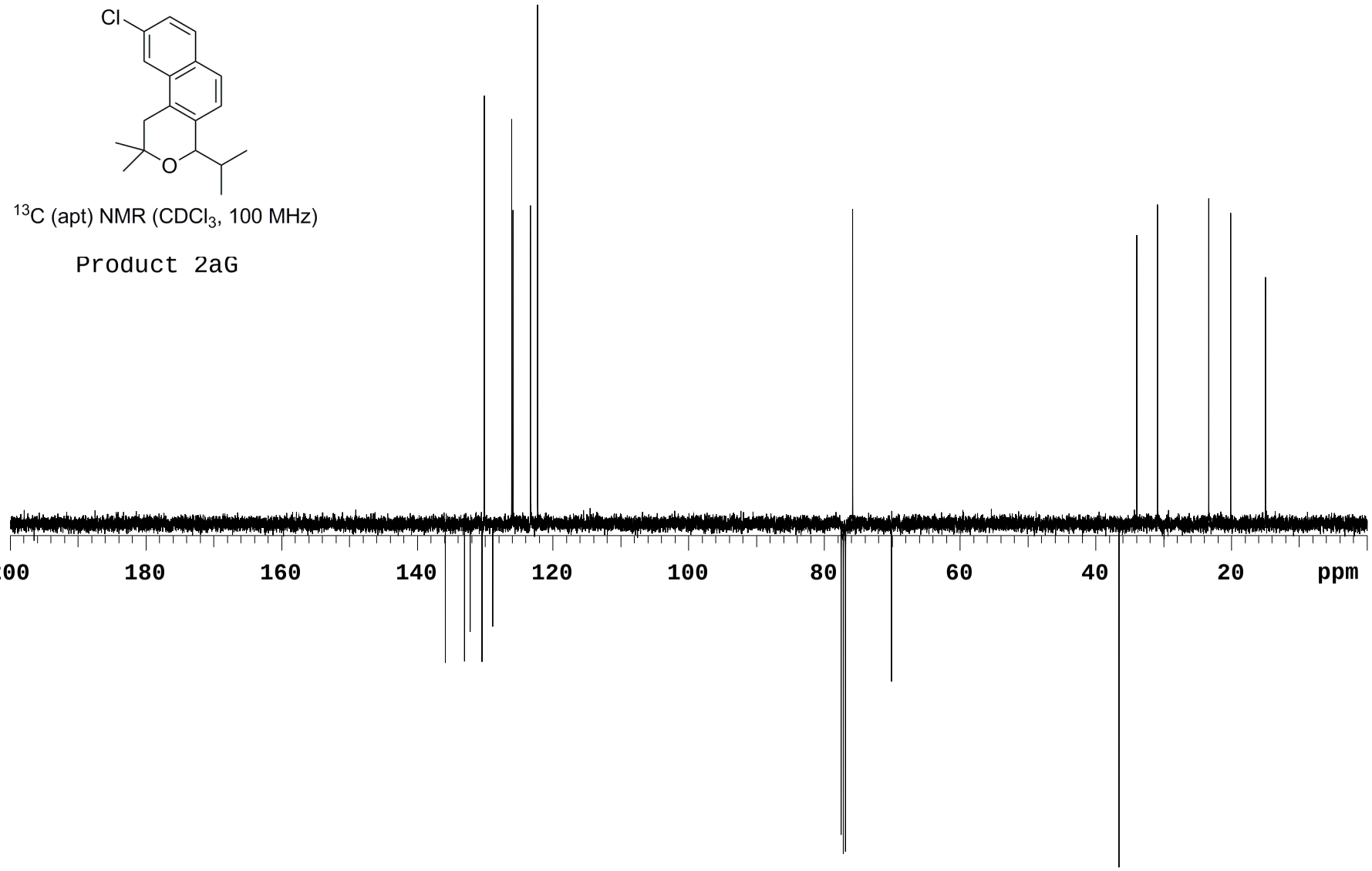


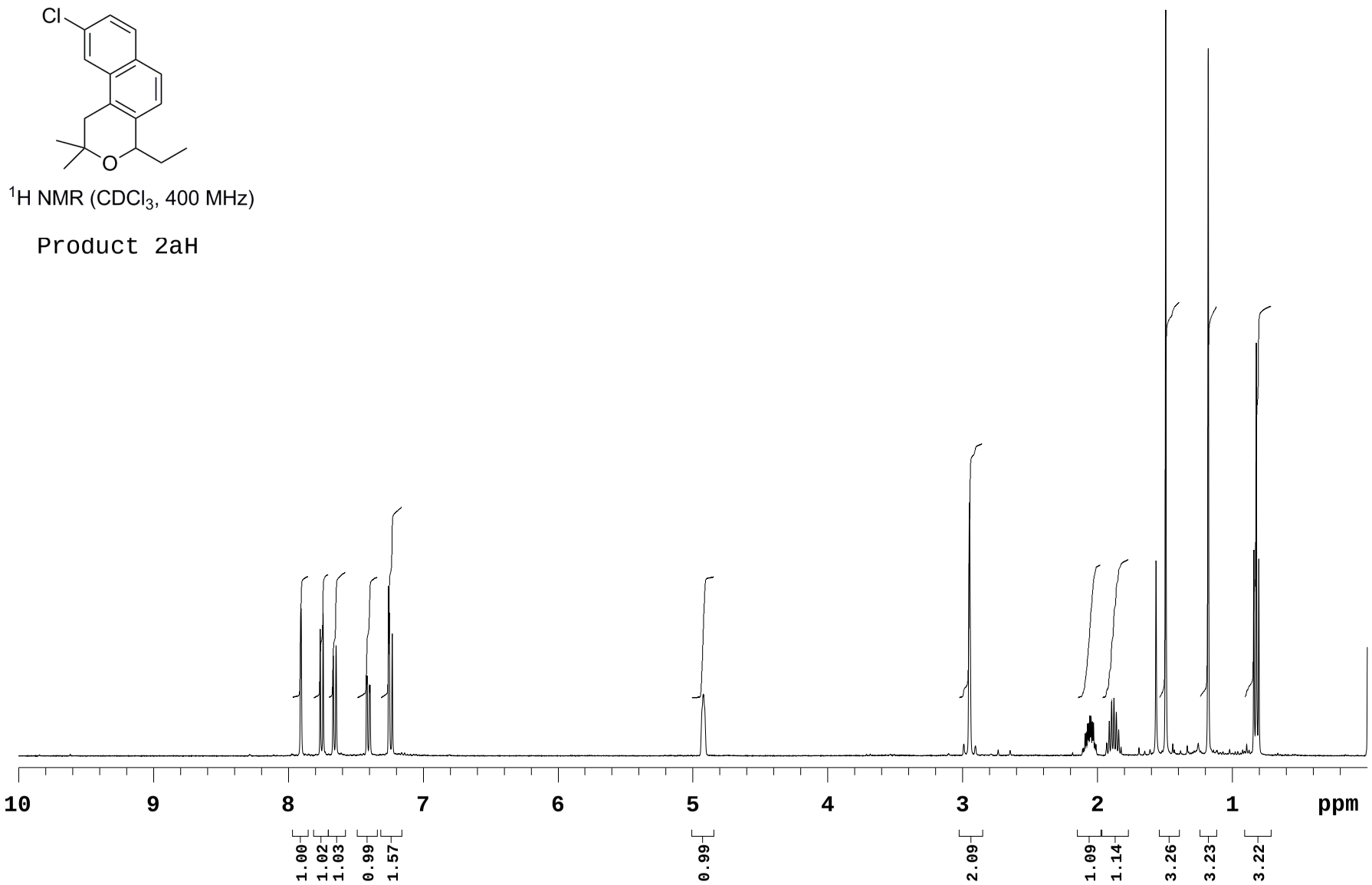


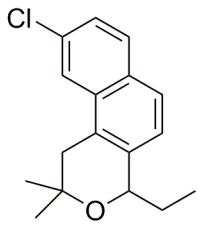
^{1}H NMR ($CDCl_3$, 400 MHz)

Product 2aG



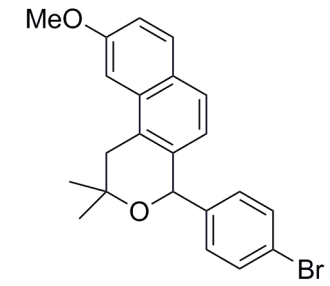

Cl
O
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)
Product 2aG
200
180
160
140
120
100
80
60
40
20
ppm


Cl
O
^{1}H NMR ($CDCl_3$, 400 MHz)
Product 2aH
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.02
1.03
0.99
1.57
0.99
2.09
1.09
1.14
3.26
3.23
3.22



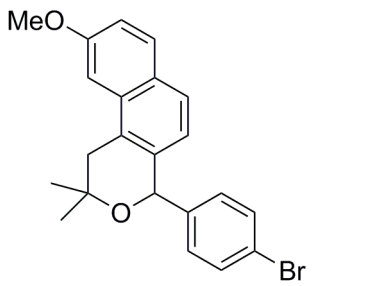
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2aH



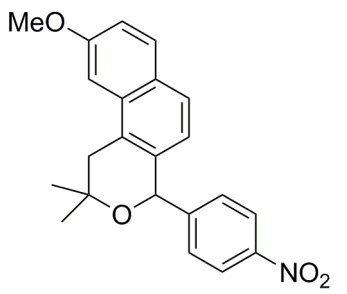
^{1}H NMR ($CDCl_3$, 100 MHz)

Product 2bA



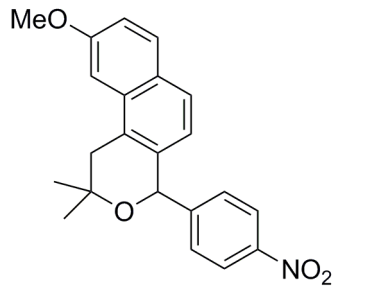
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2bA



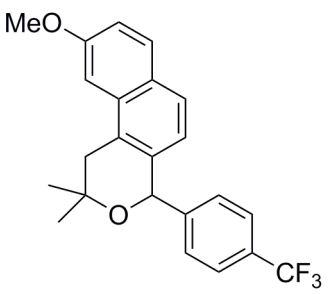
^{1}H NMR ($CDCl_3$, 400 MHz)

Product 2bB



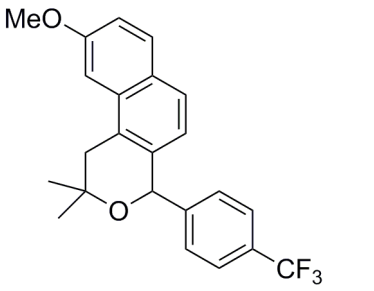
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2bB



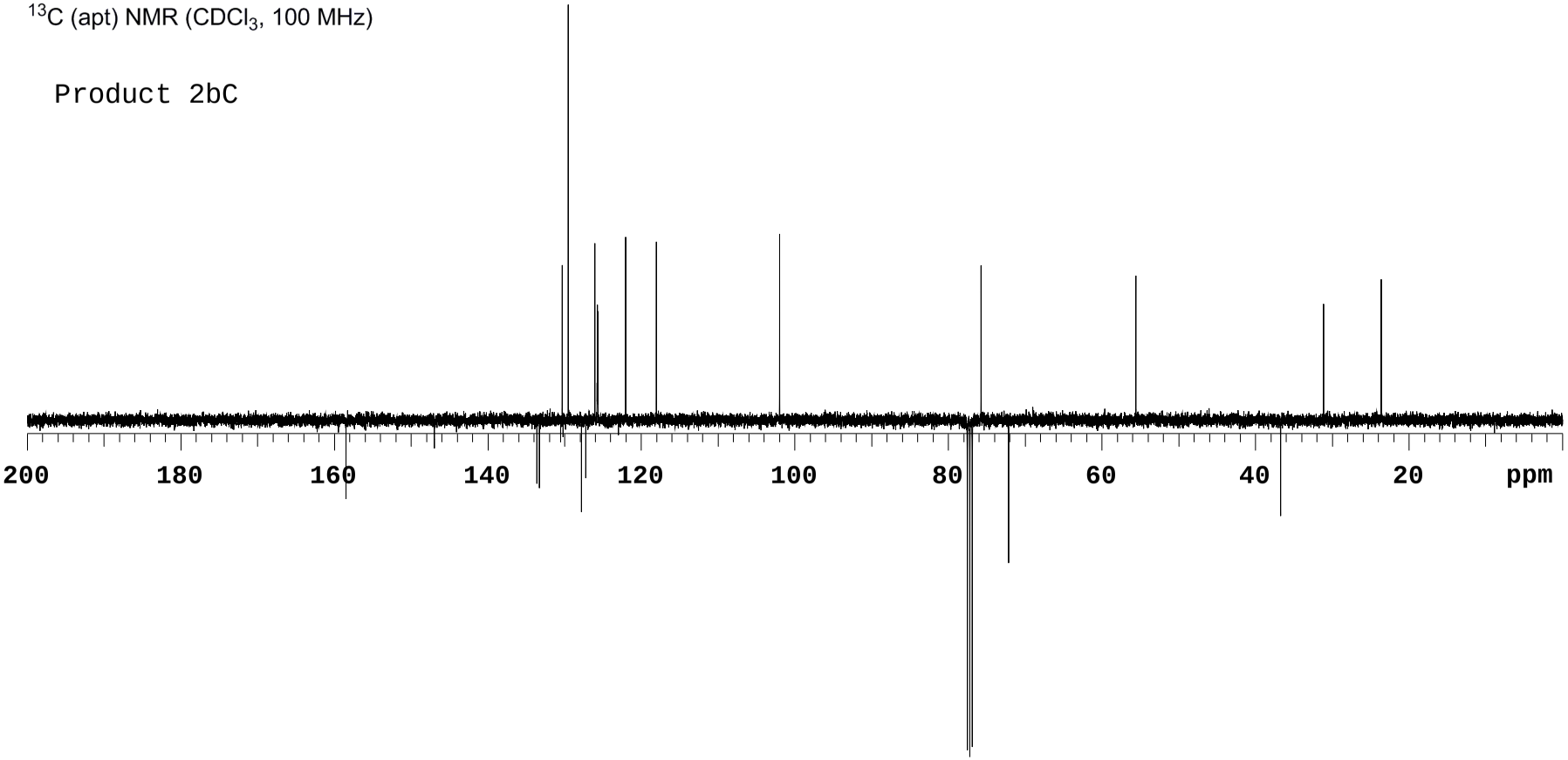
^{1}H NMR ($CDCl_3$, 400 MHz)

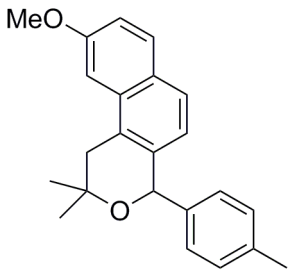
Product 2bC



^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

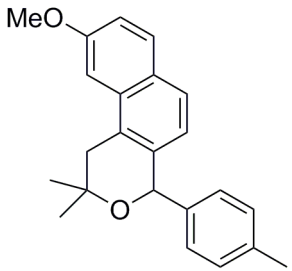
Product 2bC





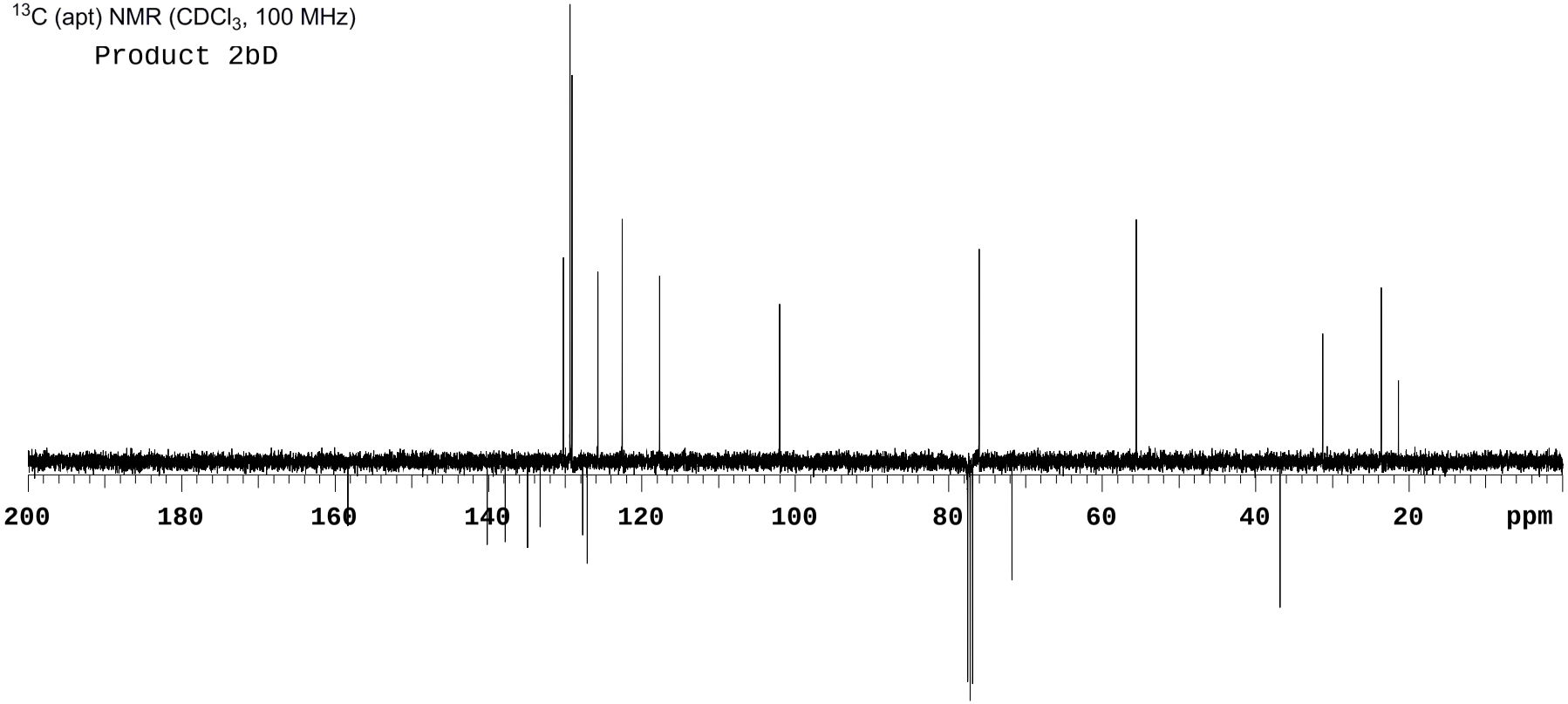
^{1}H NMR ($CDCl_3$, 400 MHz)

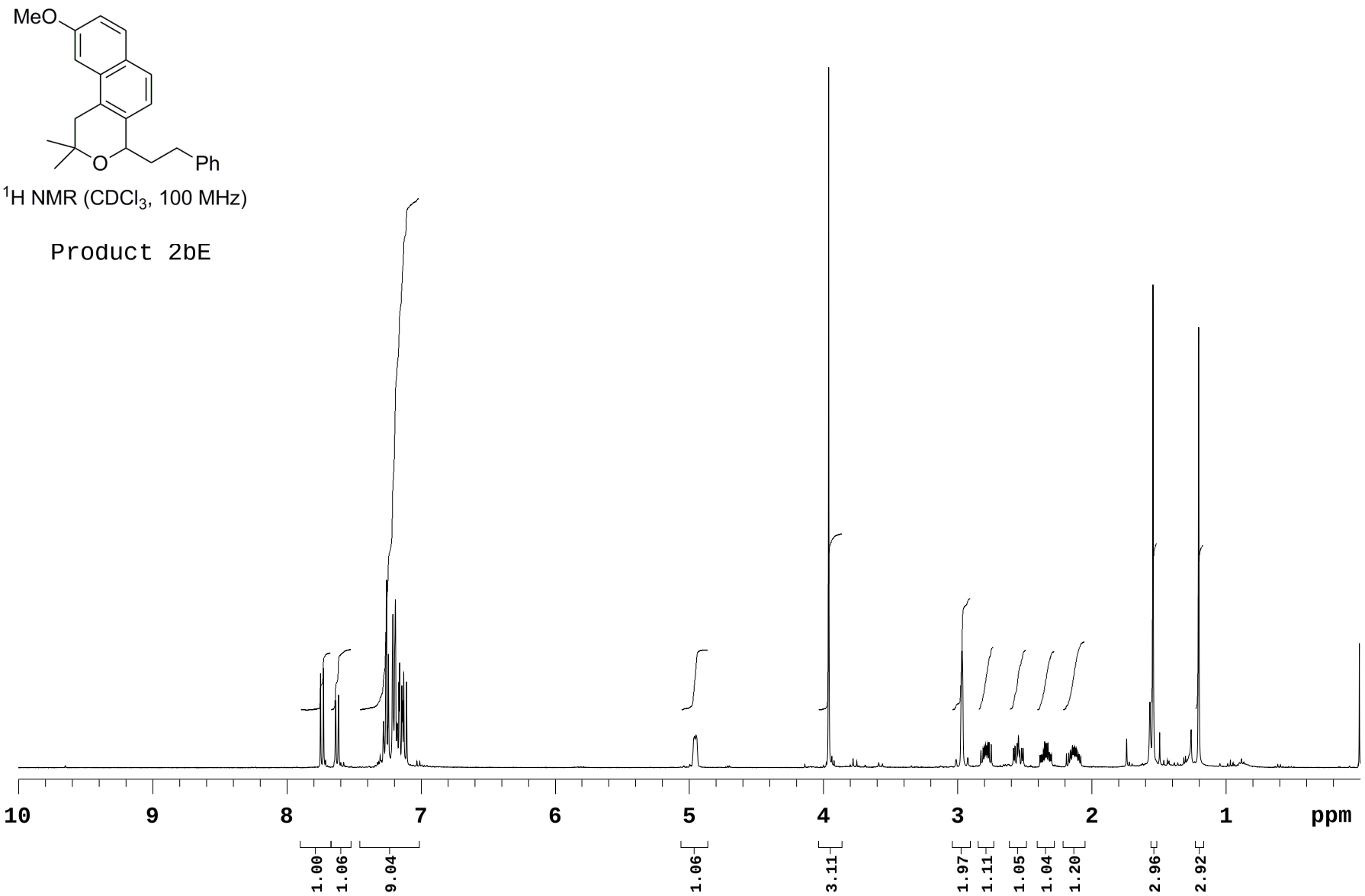
Product 2bD

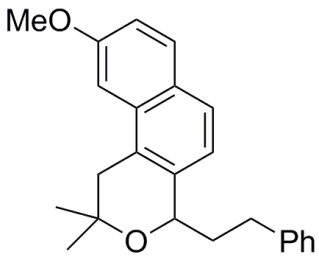


^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2bD

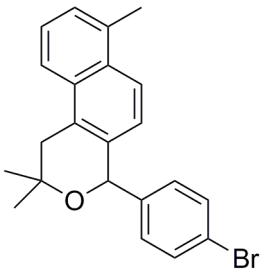



MeO
O
Ph
1H NMR (CDCl3, 100 MHz)
Product 2bE
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.06
9.04
1.06
3.11
1.97
1.11
1.05
1.04
1.20
2.96
2.92



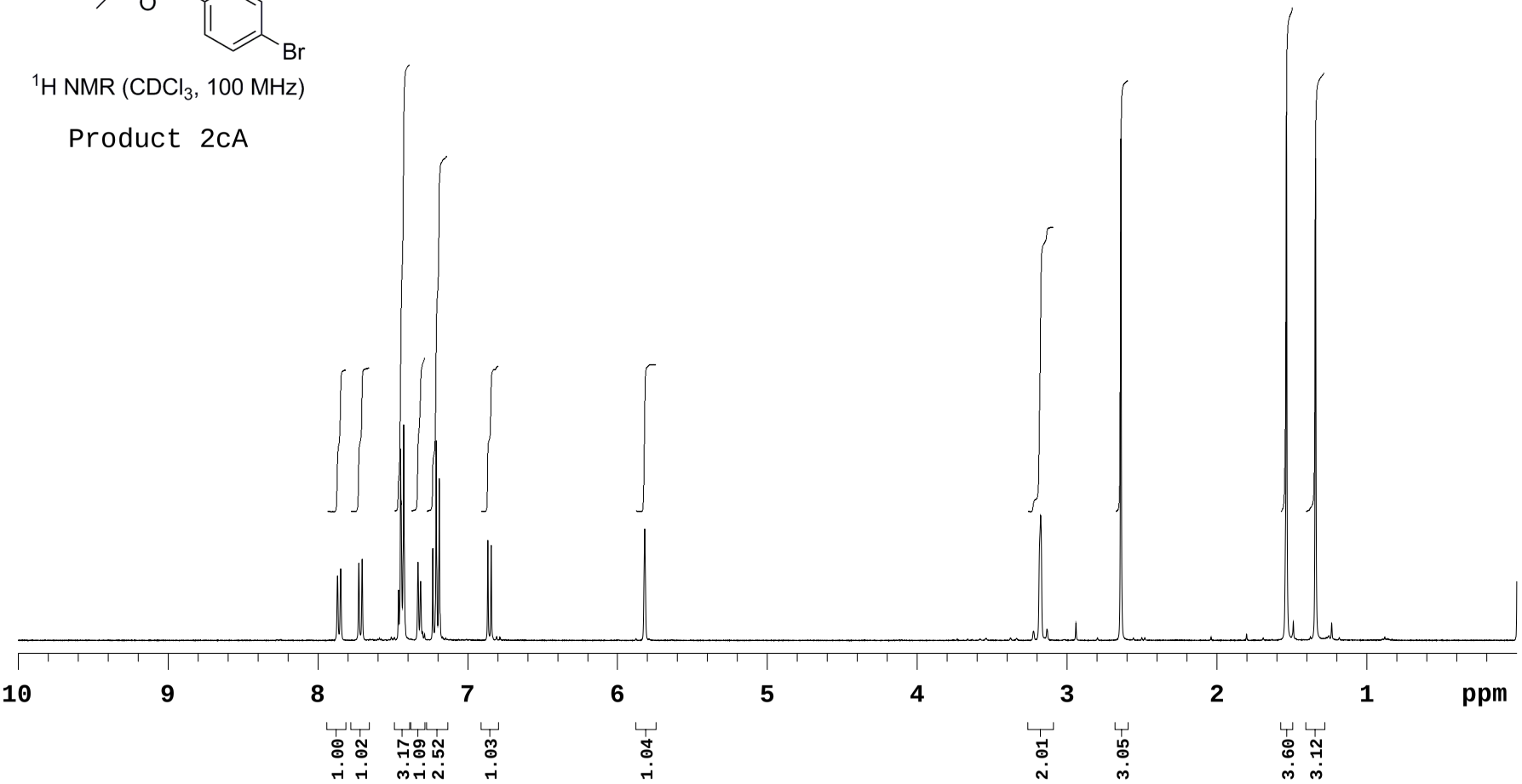
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

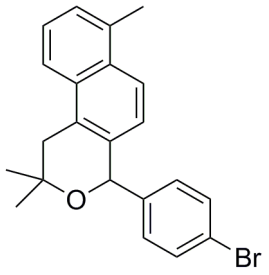
Product 2bE



^{1}H NMR ($CDCl_3$, 100 MHz)

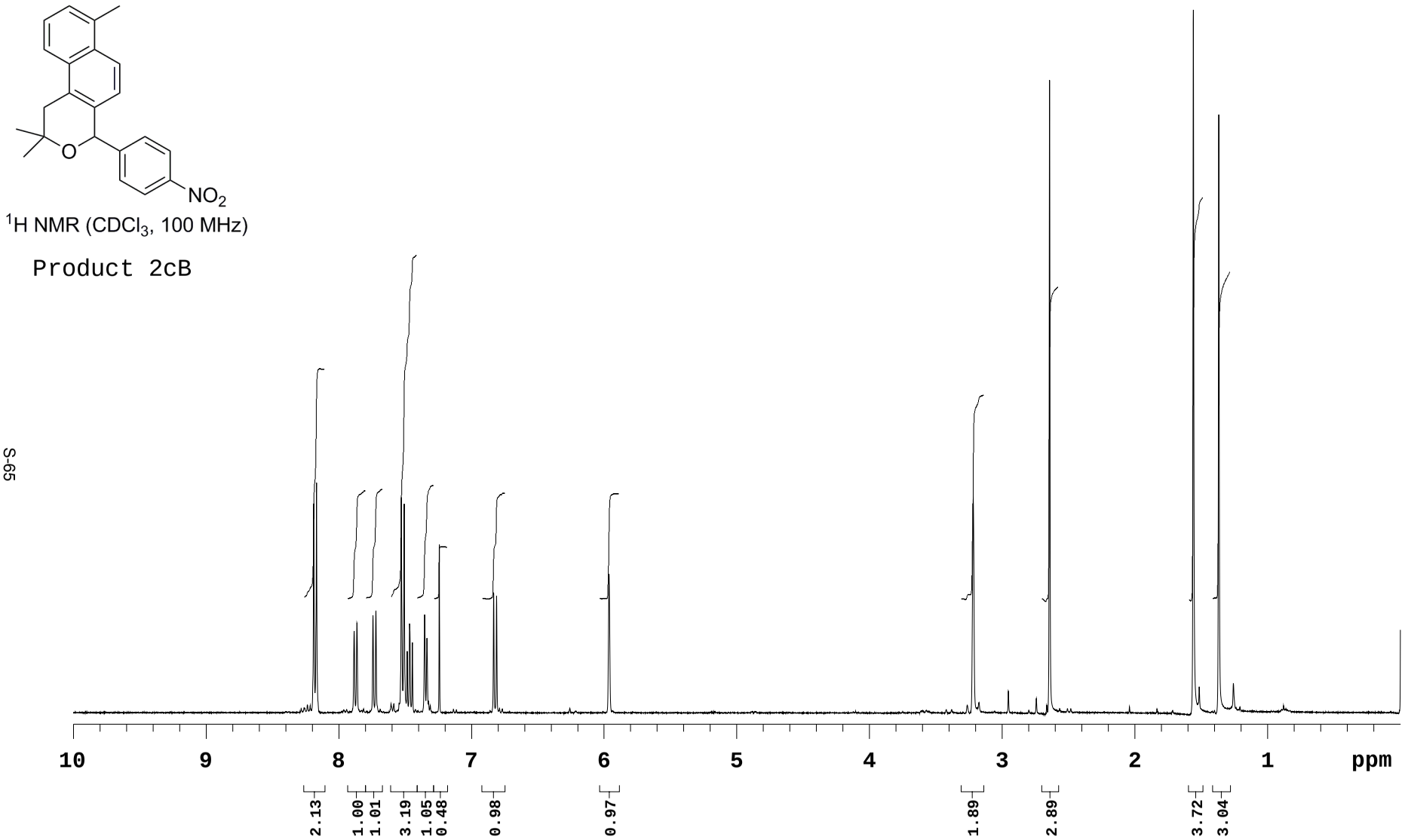
Product 2cA

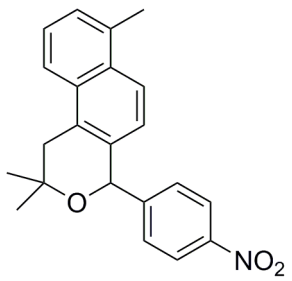




^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

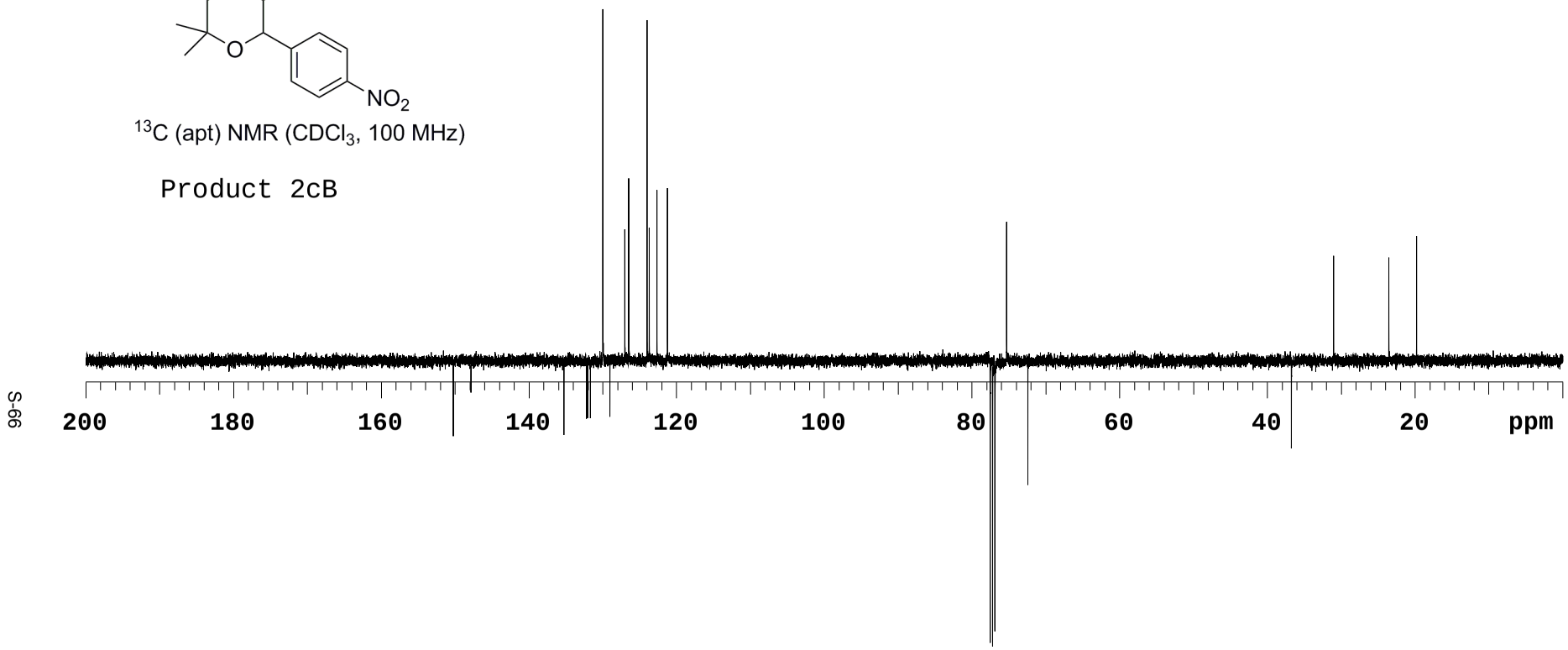
Product 2cA

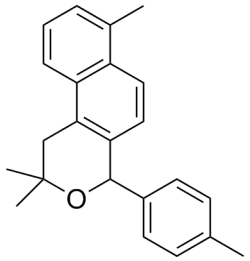

O
NO2
1H NMR (CDCl3, 100 MHz)
Product 2cB
S-65
10
9
8
7
6
5
4
3
2
1
ppm
2.13
1.00
1.01
3.19
1.05
0.48
0.98
0.97
1.89
2.89
3.72
3.04



^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

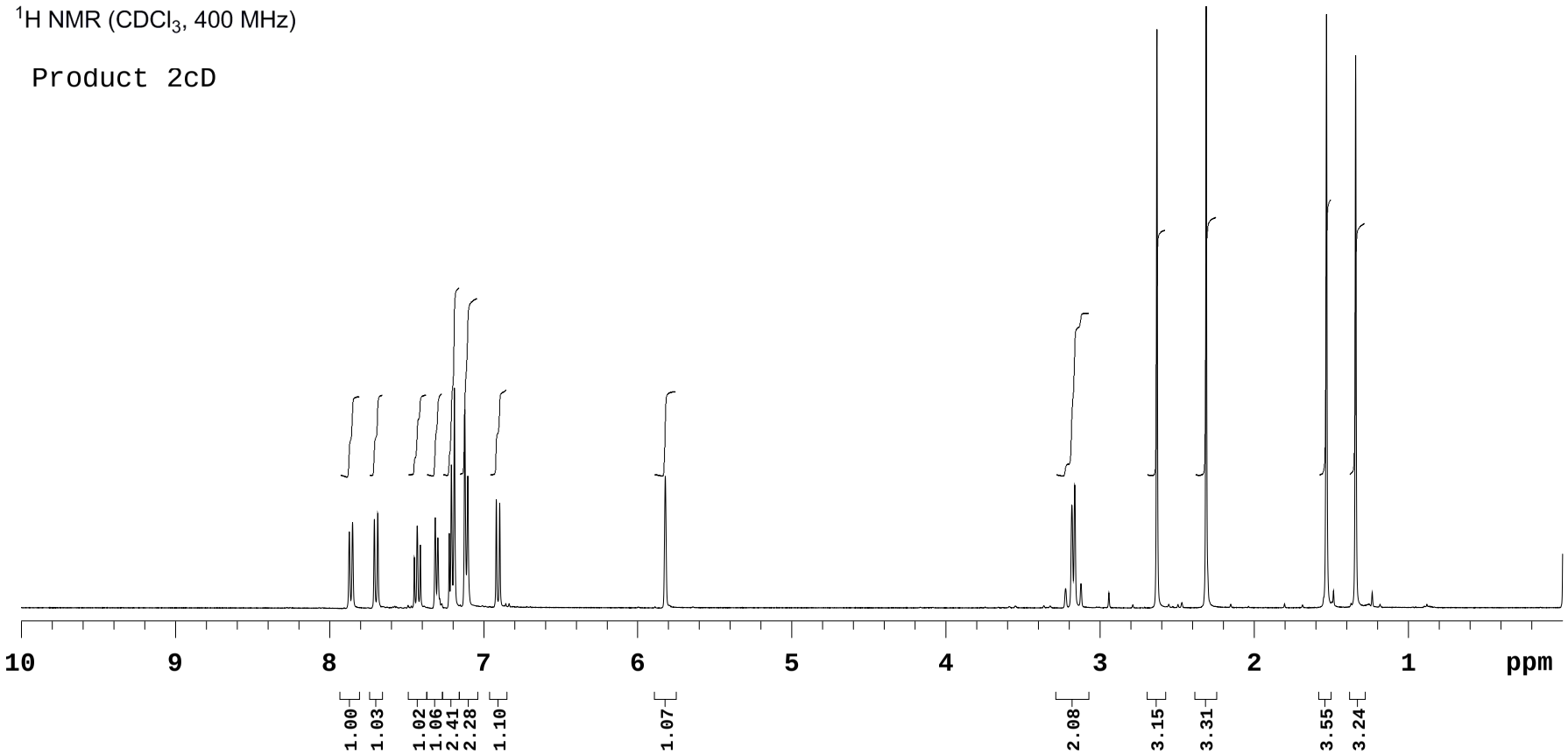
Product 2cB

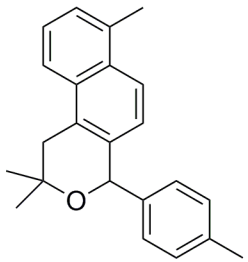




^{1}H NMR ($CDCl_3$, 400 MHz)

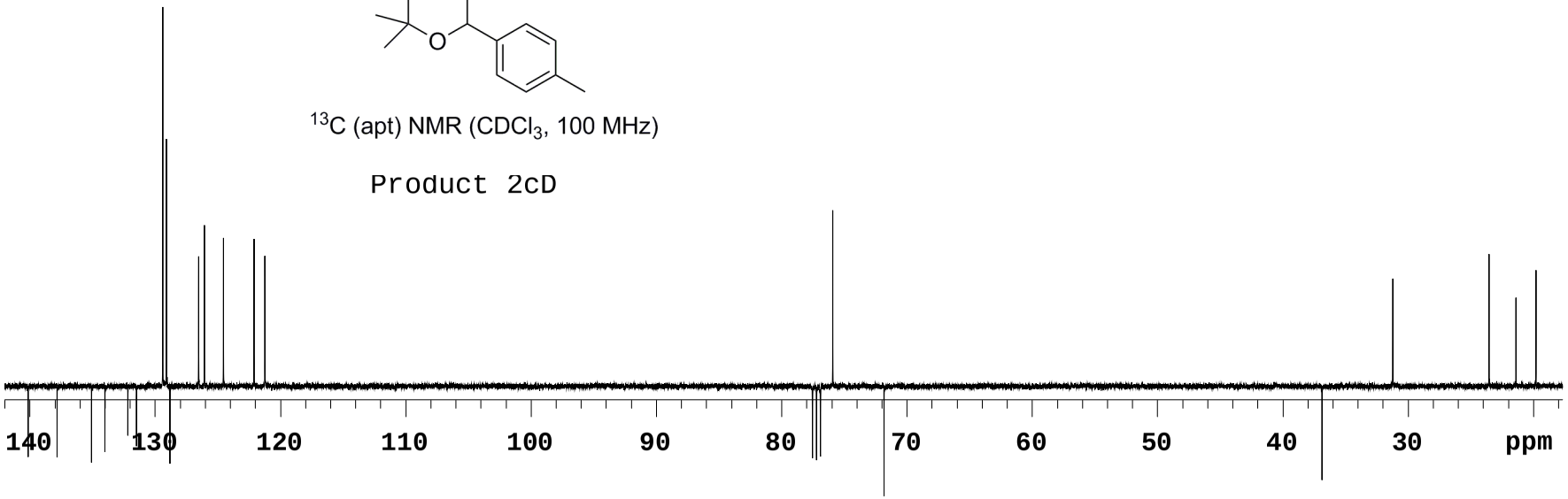
Product 2cD

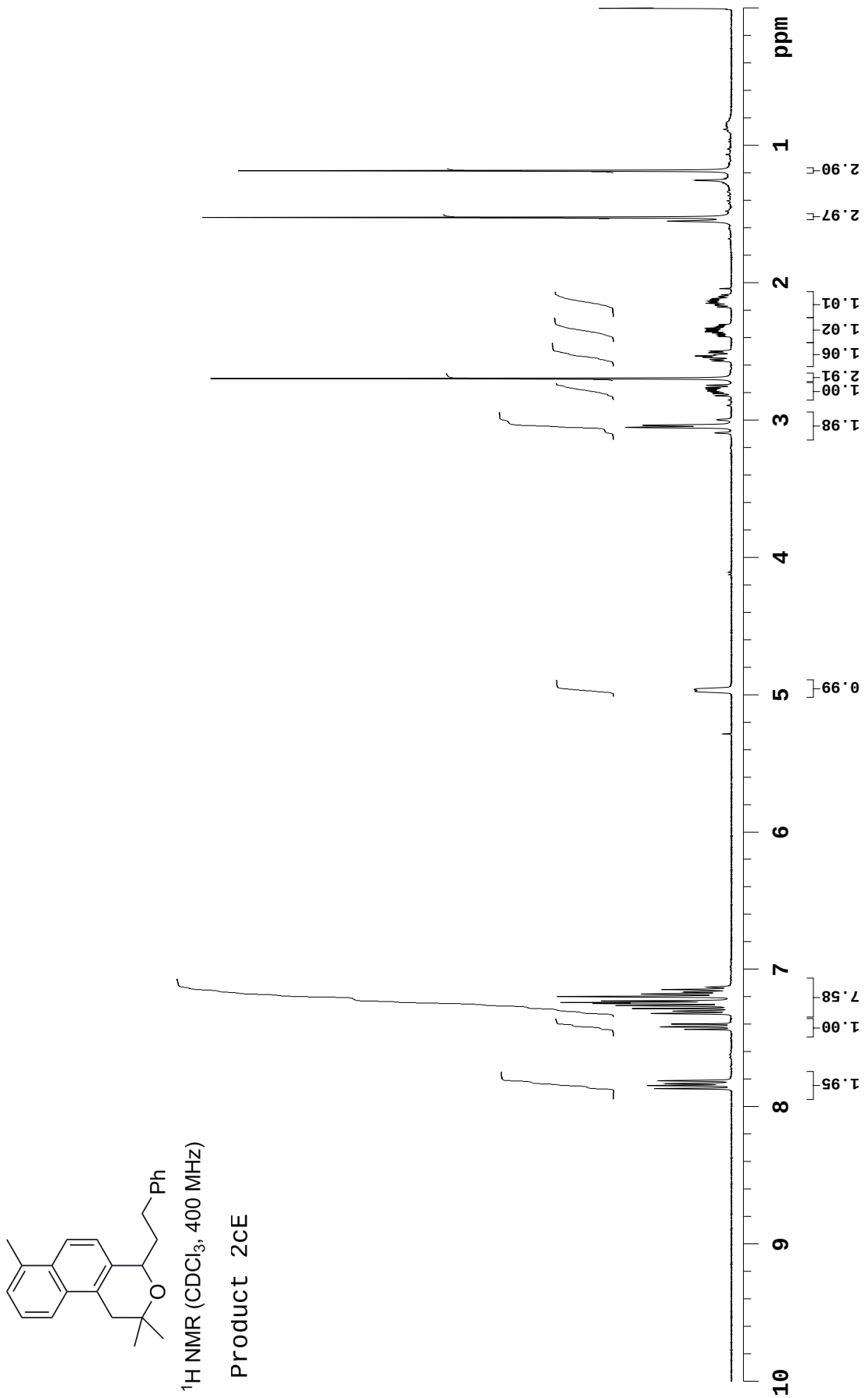


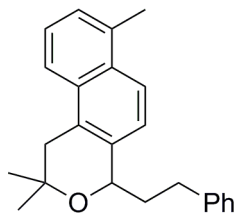


^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2cD

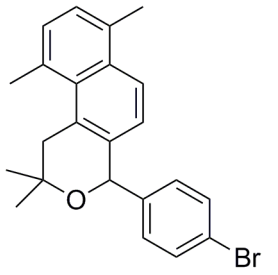



Ph
O
^{1}H NMR ($CDCl_3$, 400 MHz)
Product 2cE
ppm
1
2
3
4
5
6
7
8
9
10
2.90
2.97
1.01
1.02
1.06
2.91
1.00
1.98
0.99
7.58
1.00
1.95



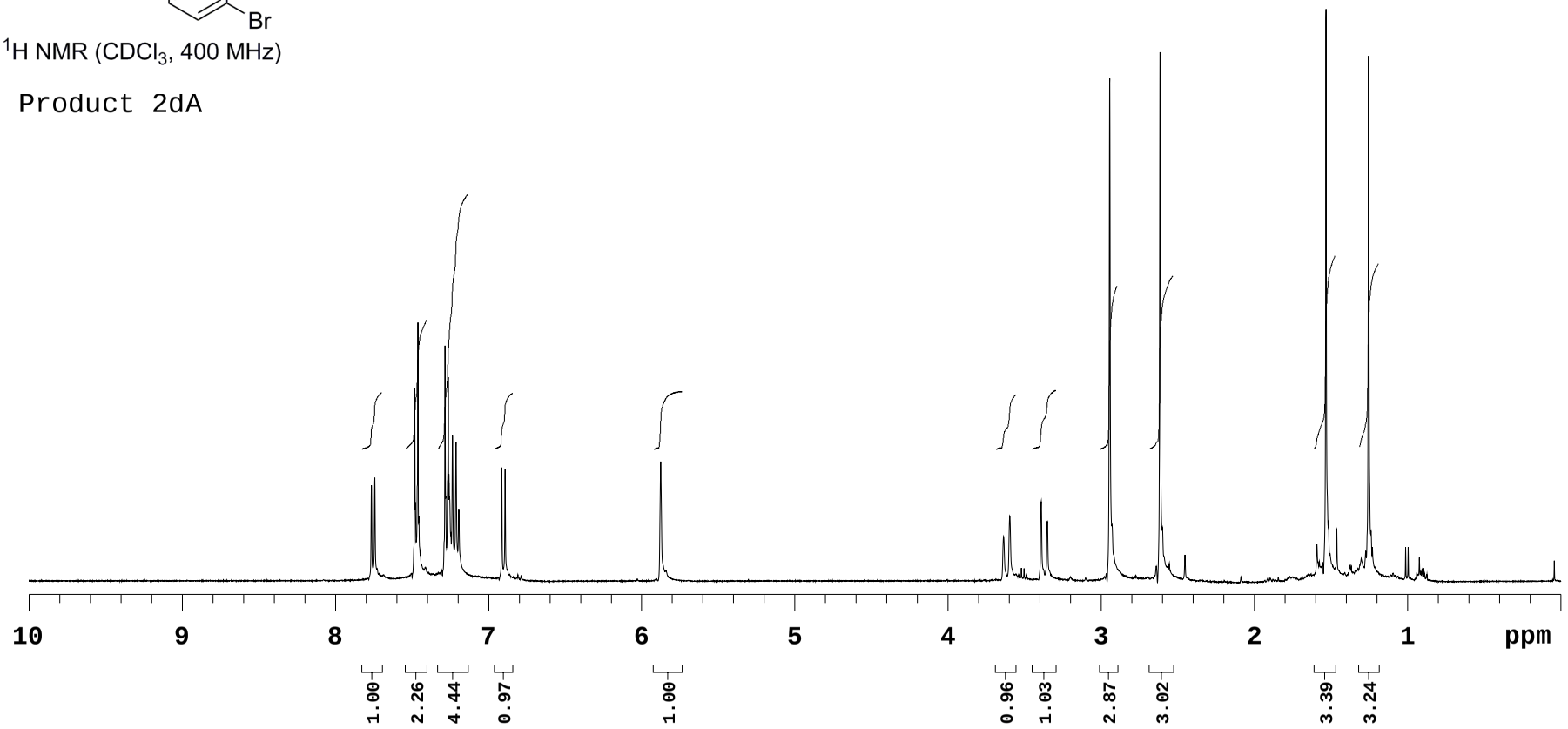
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

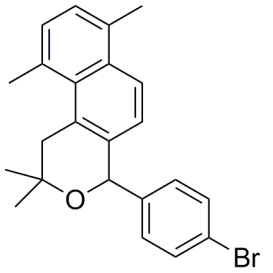
Product 2cE



^{1}H NMR ($CDCl_3$, 400 MHz)

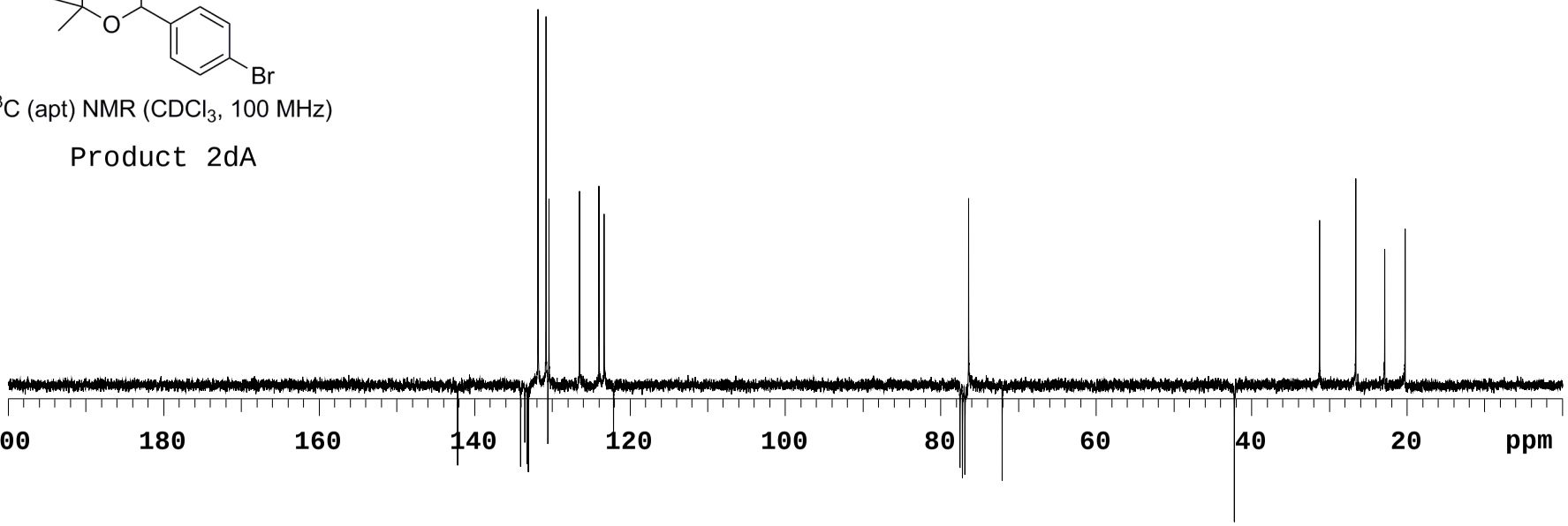
Product 2dA

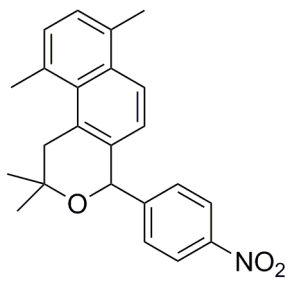




^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

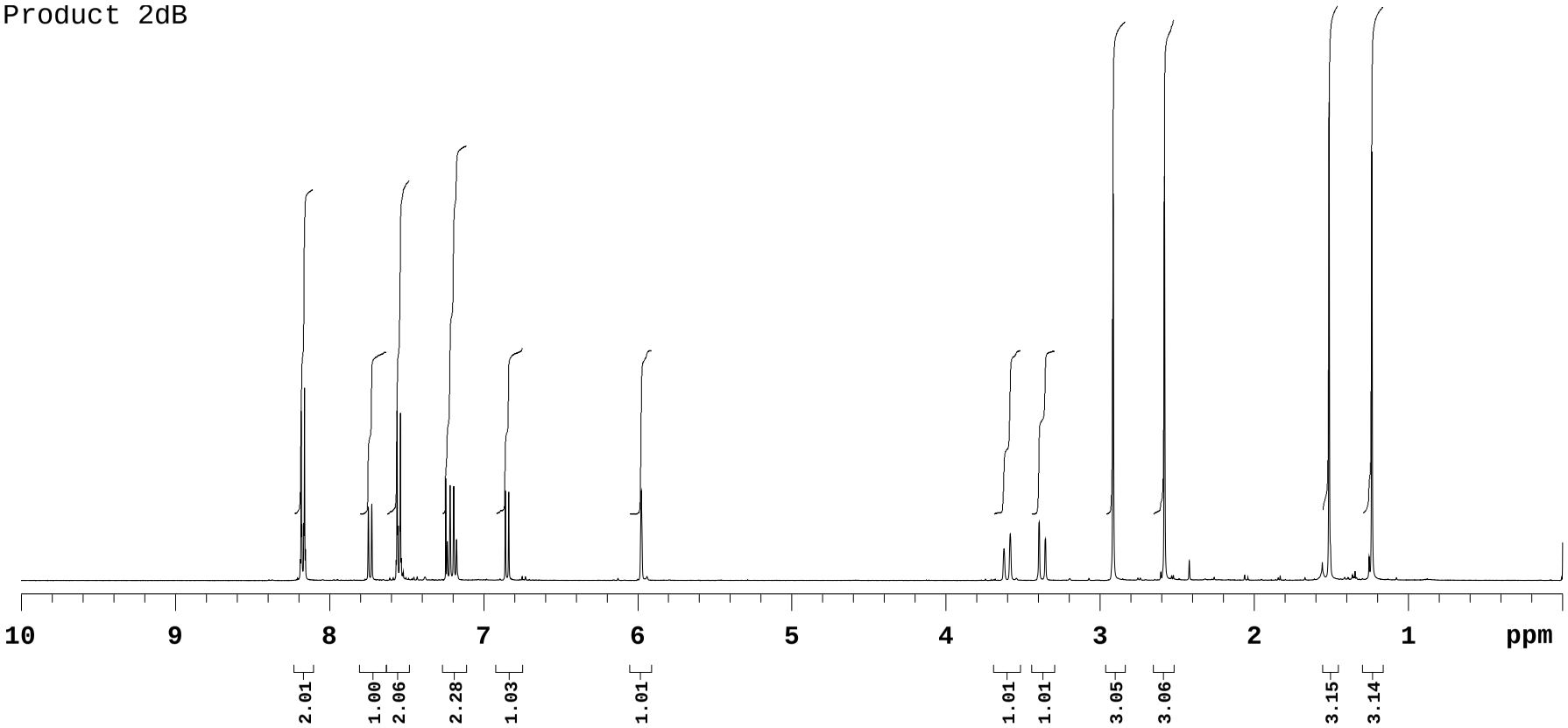
Product 2dA

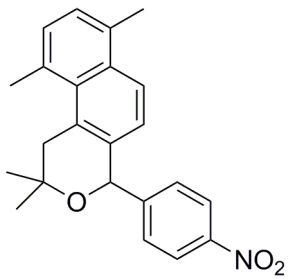




^{1}H NMR ($CDCl_3$, 400 MHz)

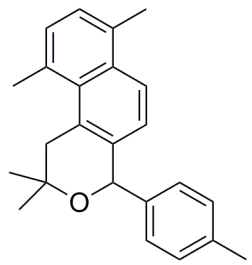
Product 2dB





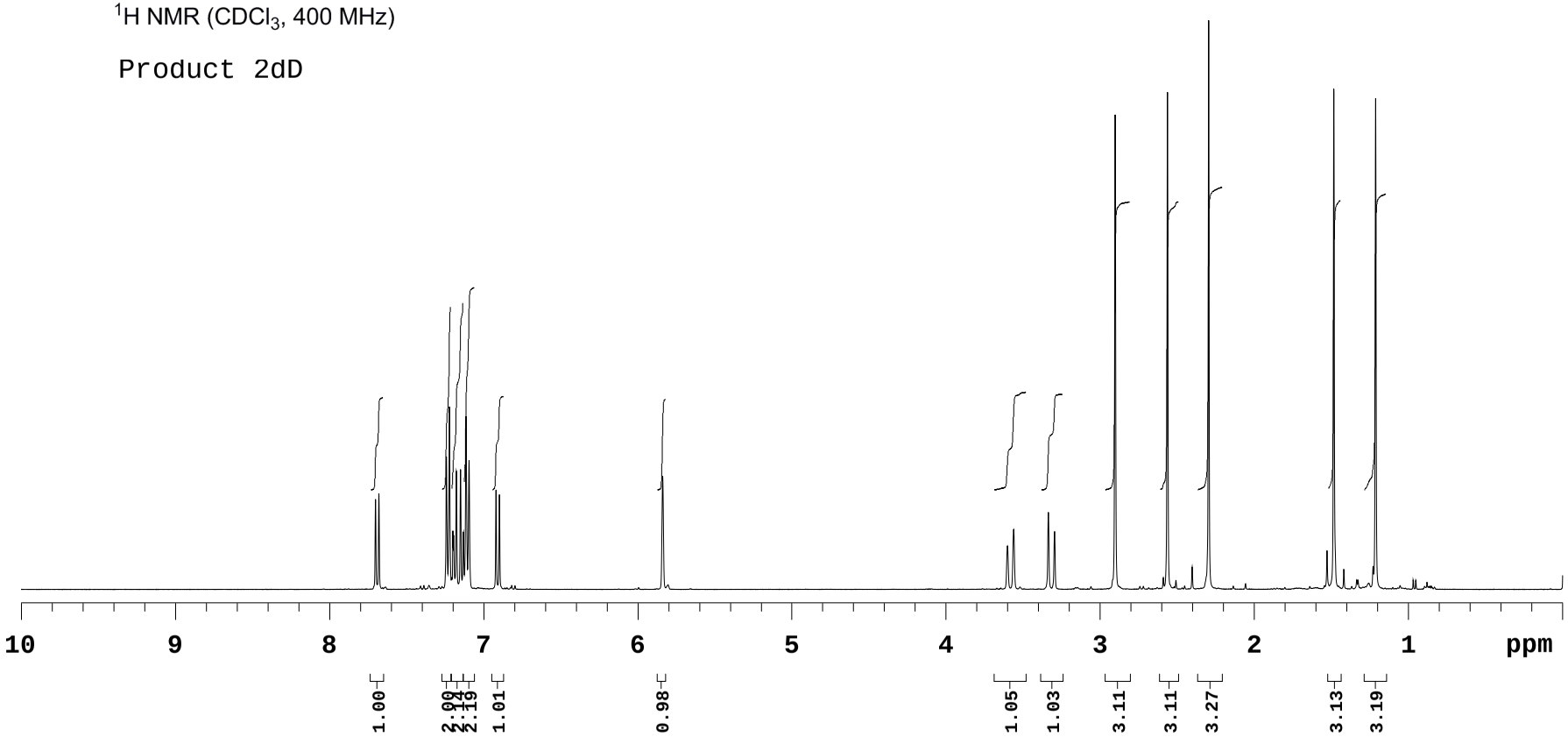
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

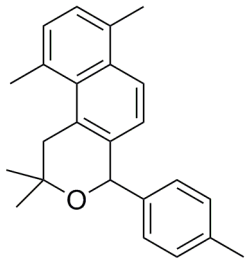
Product 2dB



^{1}H NMR ($CDCl_3$, 400 MHz)

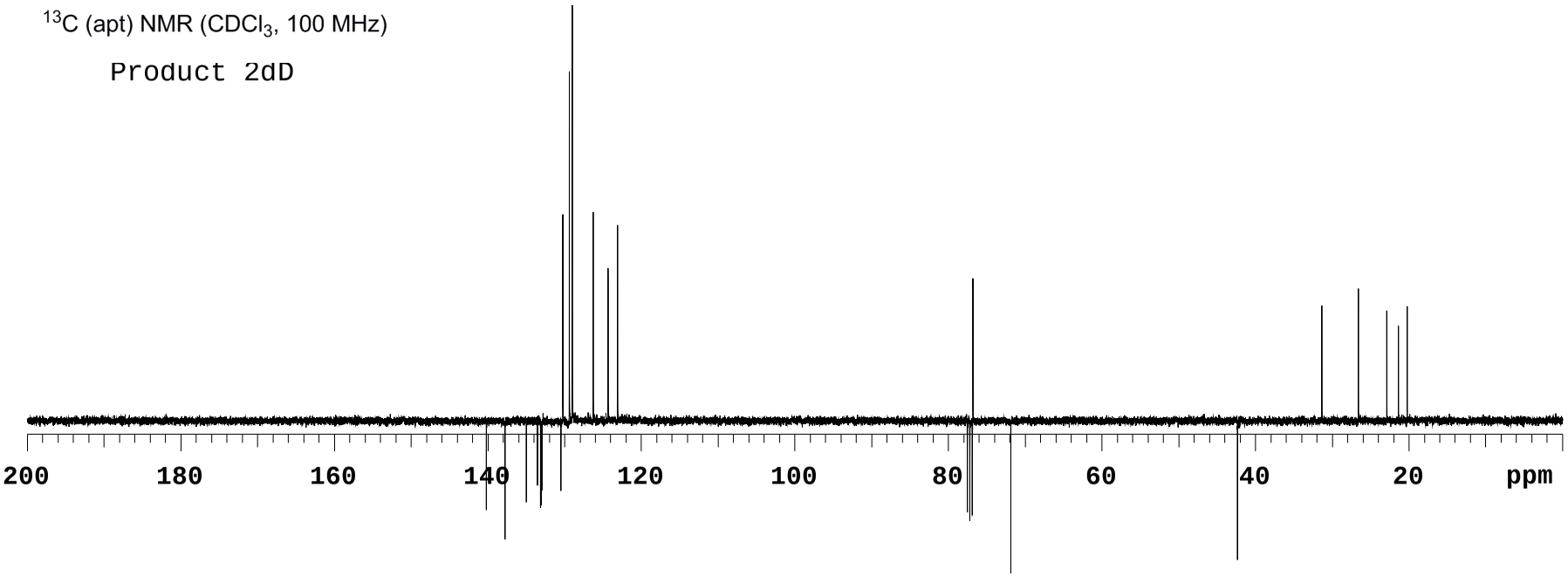
Product 2dD

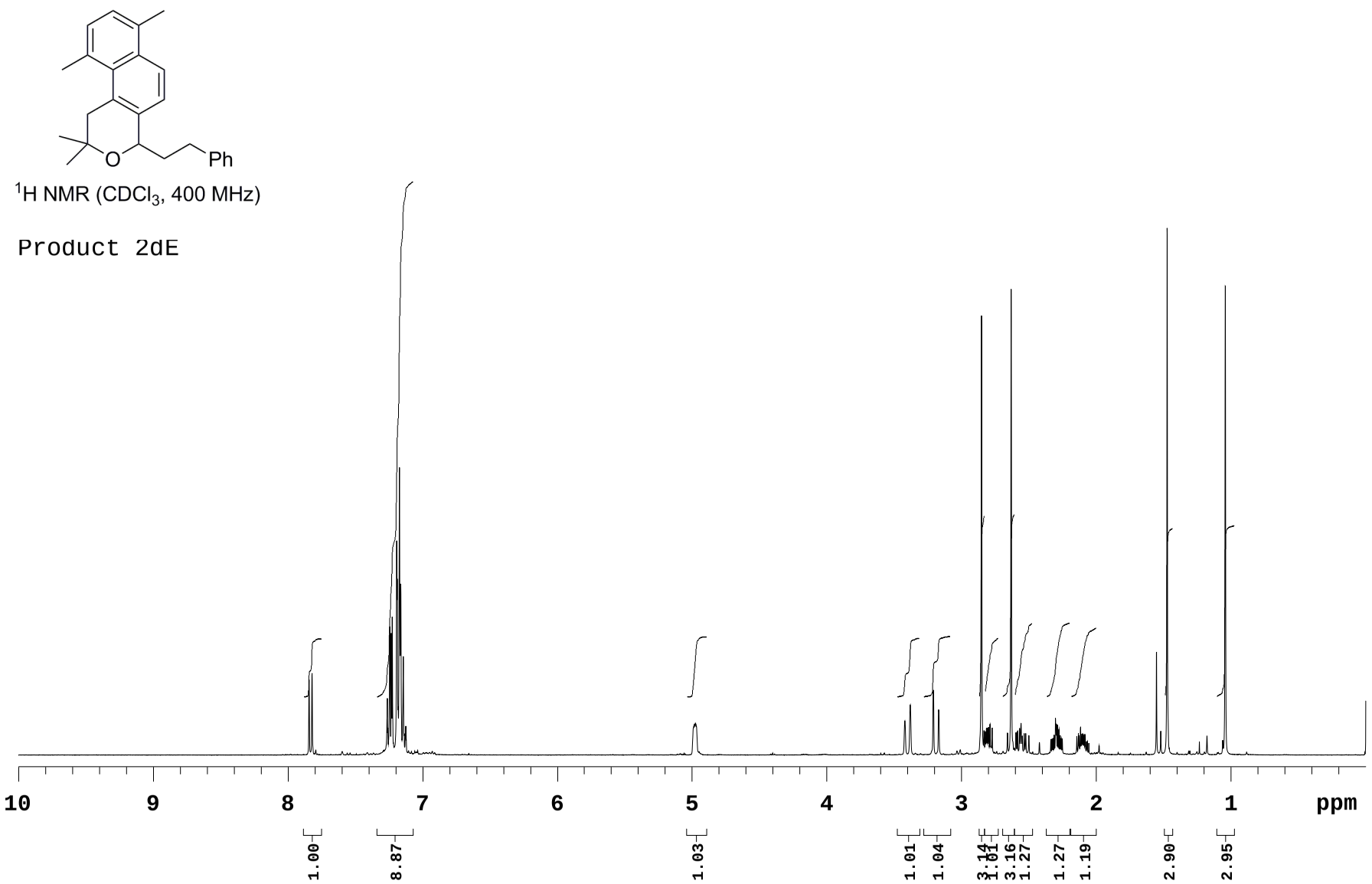


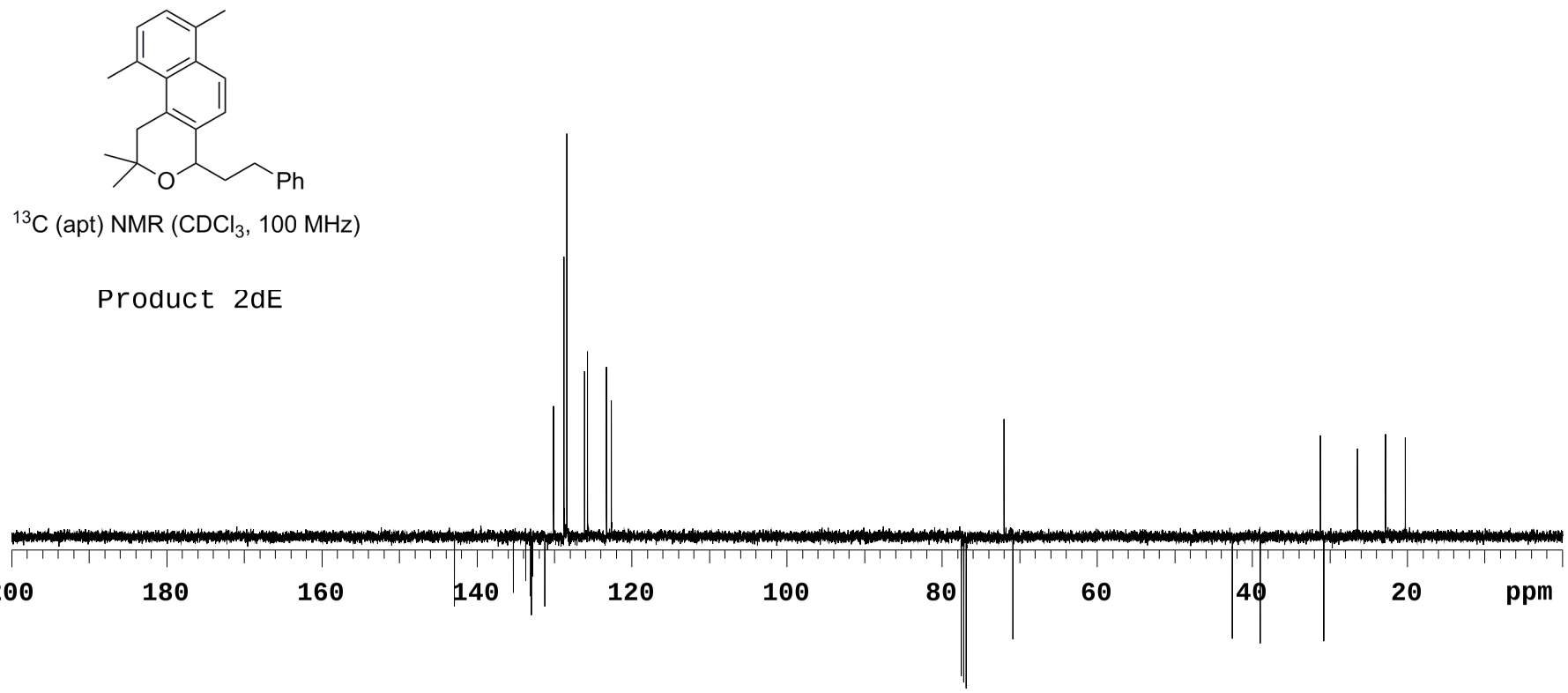


^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2dD

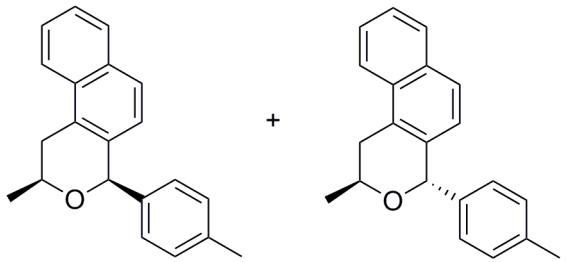



O
Ph
1H NMR (CDCl3, 400 MHz)
Product 2dE
10
9
8
7
6
5
4
3
2
1
ppm
1.00
8.87
1.03
1.01
1.04
3.14
1.01
3.16
1.27
1.27
1.19
2.90
2.95



^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product 2dE

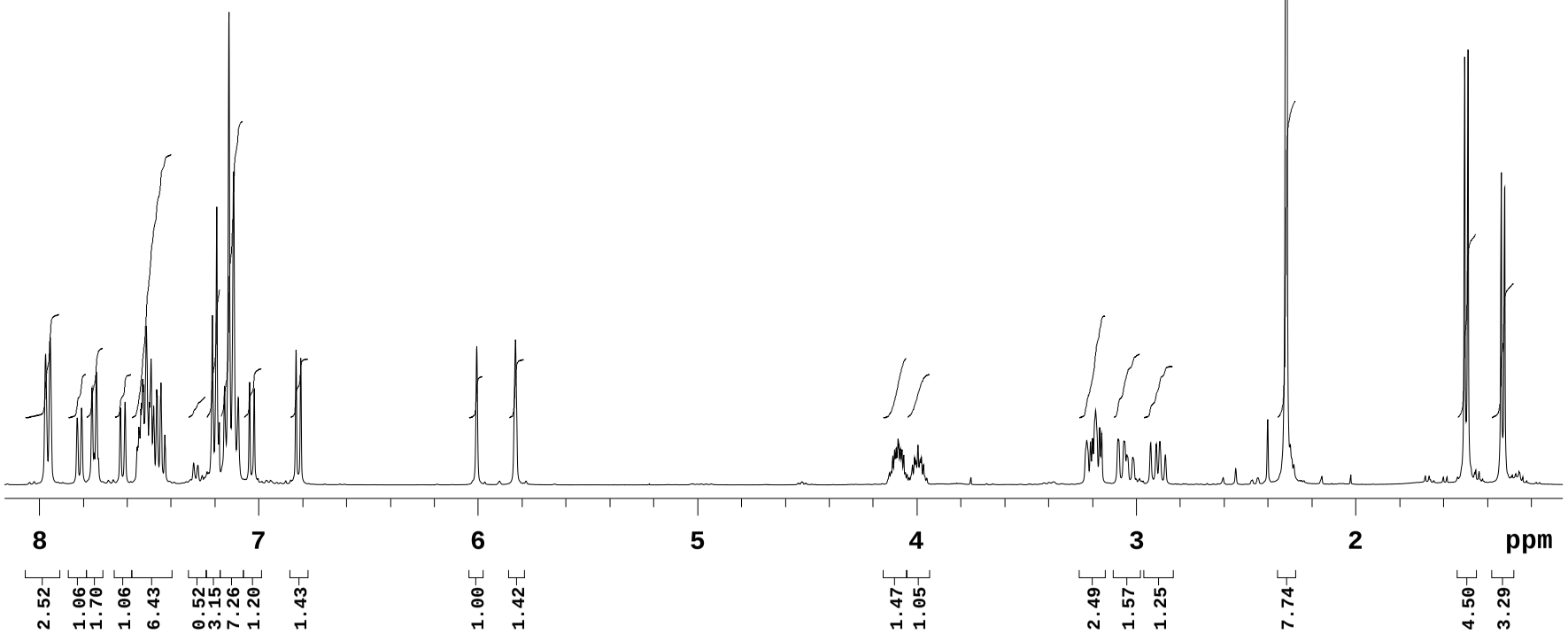


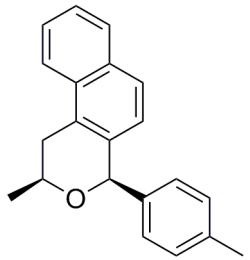
1.4:1

Crude mixture of *cis*- and *trans*- isochromenes

^{1}H NMR ($CDCl_3$, 400 MHz)

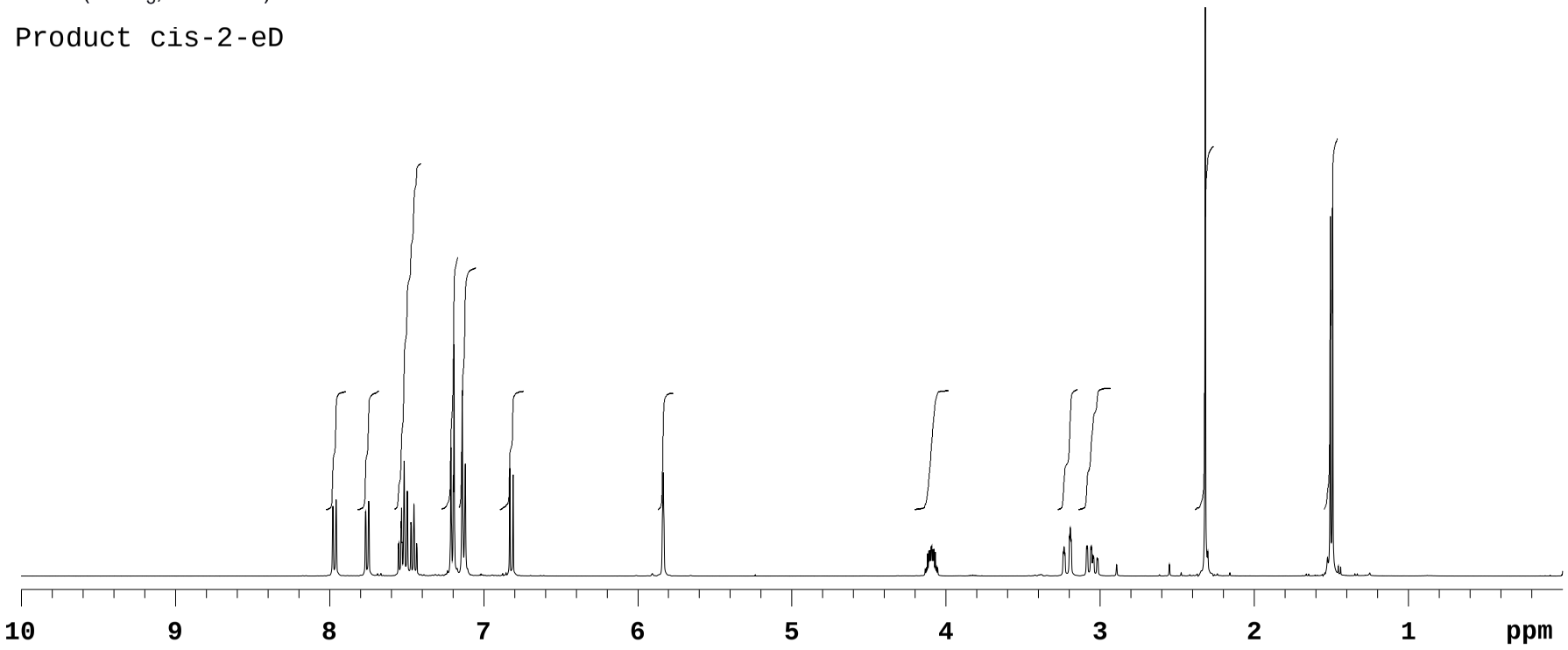
Products cis- and trans-2eD

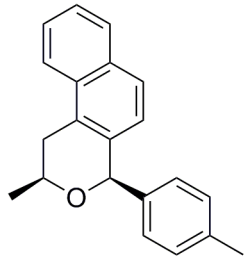




^{1}H NMR ($CDCl_3$, 400 MHz)

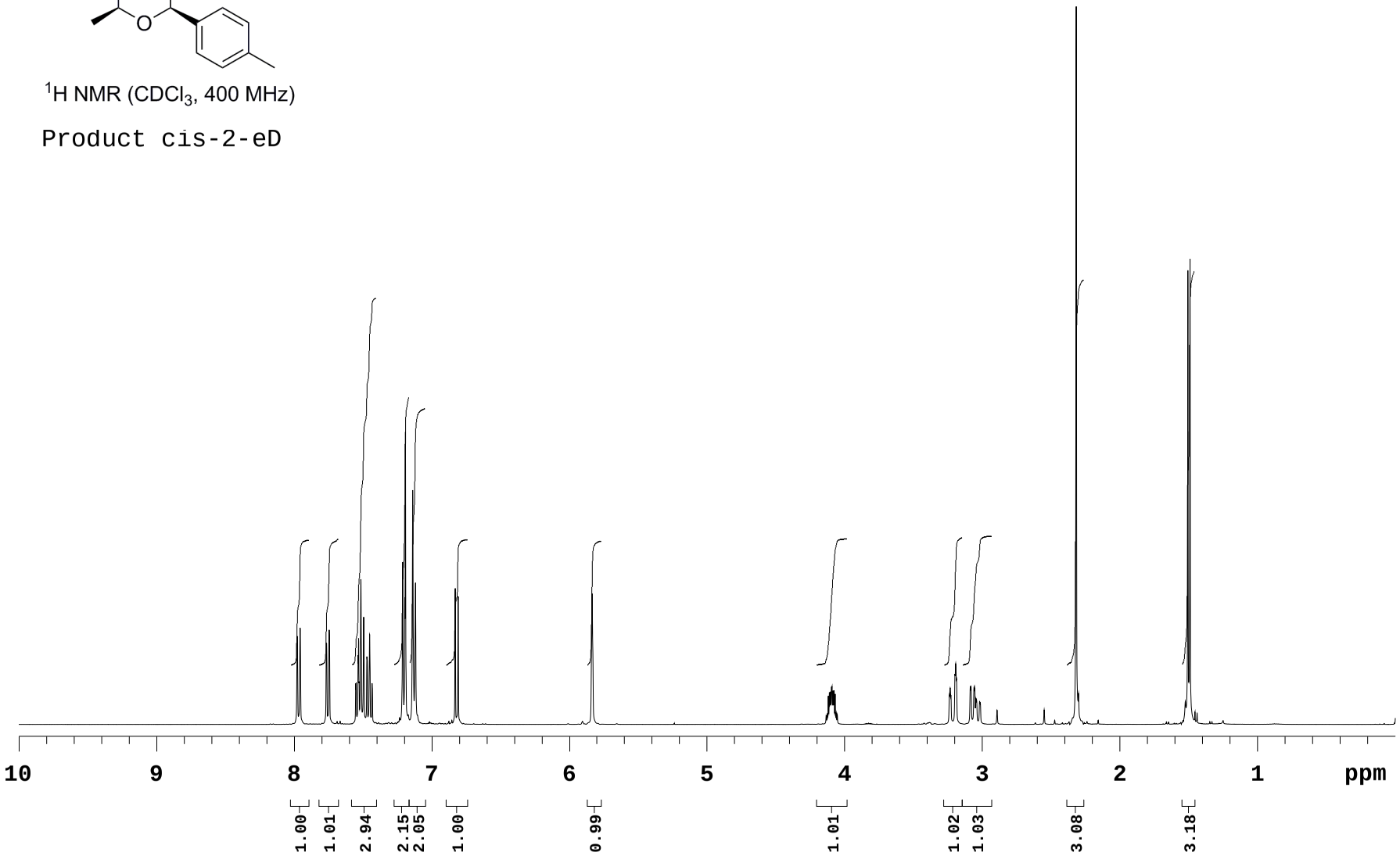
Product cis-2-eD

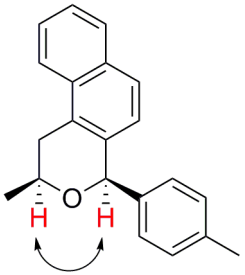




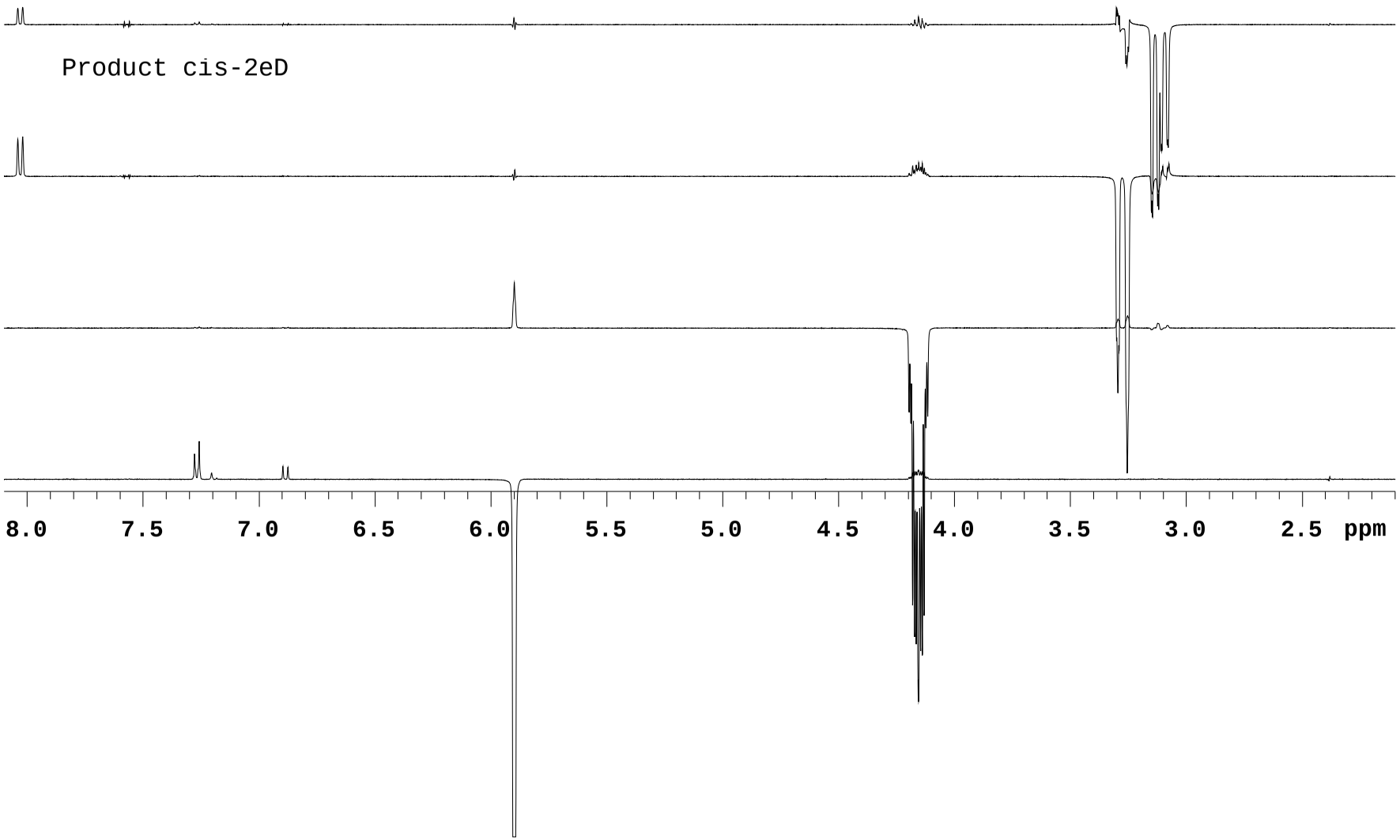
^{1}H NMR ($CDCl_3$, 400 MHz)

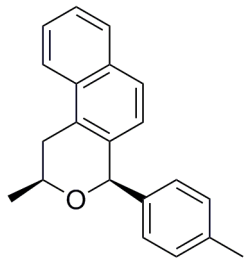
Product cis-2-eD





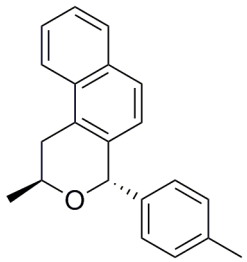
^{1}H Noesy-1D NMR ($CDCl_3$, 400 MHz)





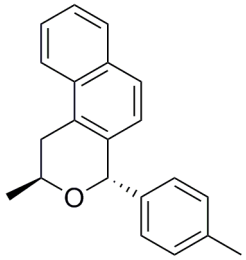
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product cis-2eD



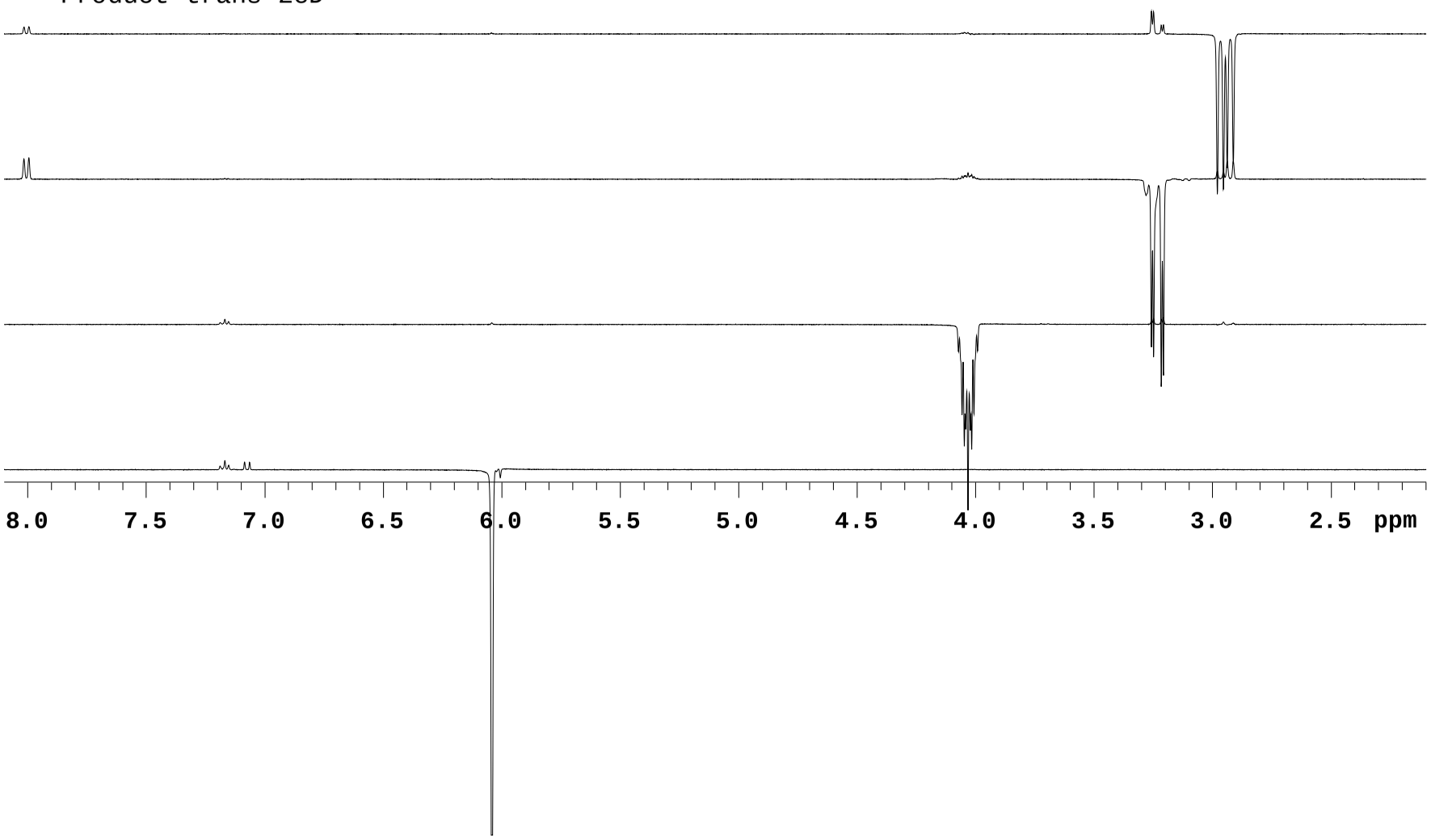
^{1}H NMR ($CDCl_3$, 400 MHz)

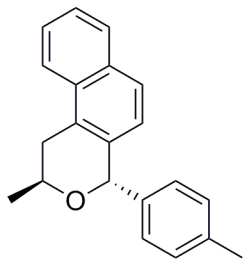
Product trans-2eD



^{1}H Noesy-1D NMR ($CDCl_3$, 400 MHz)

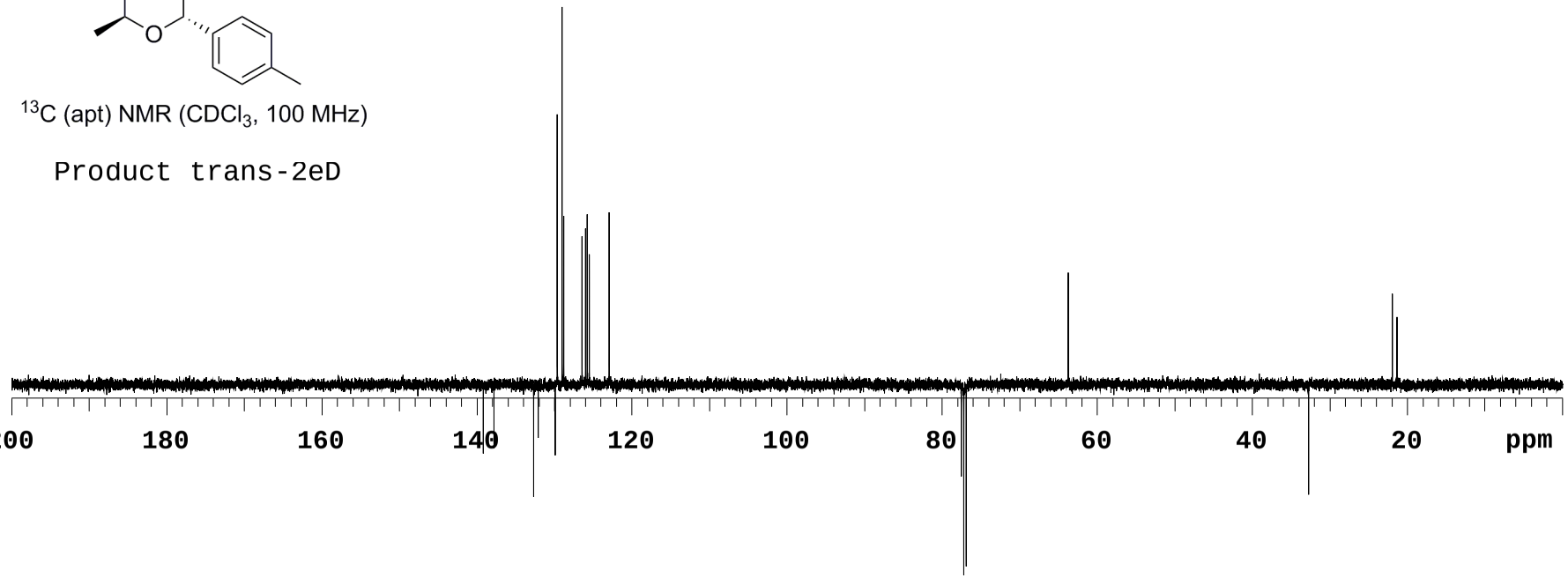
Product trans-2eD





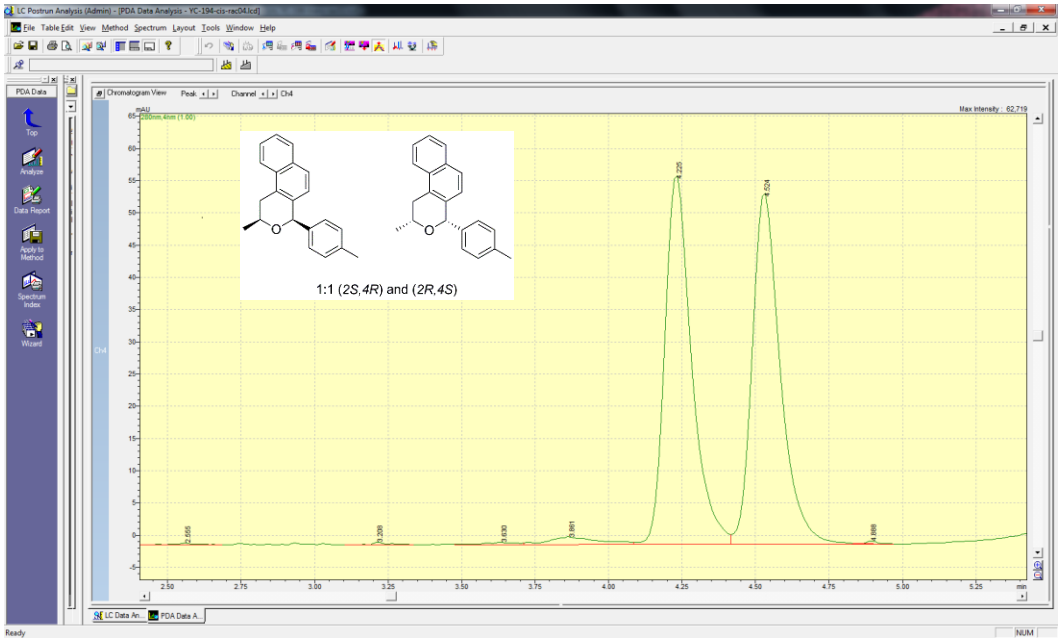
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

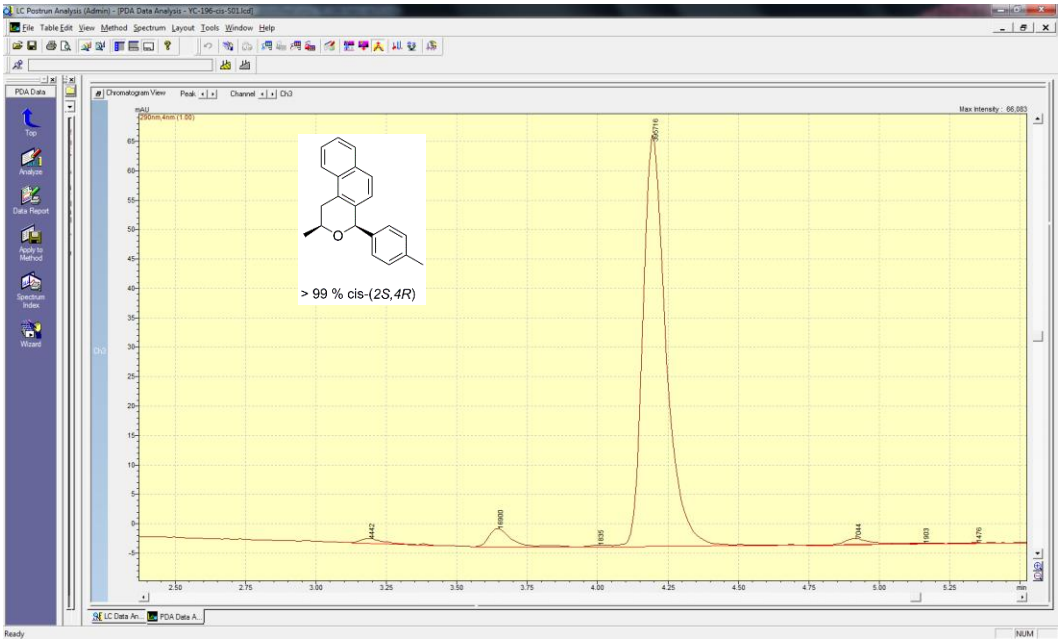
Product trans-2eD



HPLC Traces for *cis*-(±)-**2eD** (top) and *cis*-(*2S*)-**2eD** (bottom).

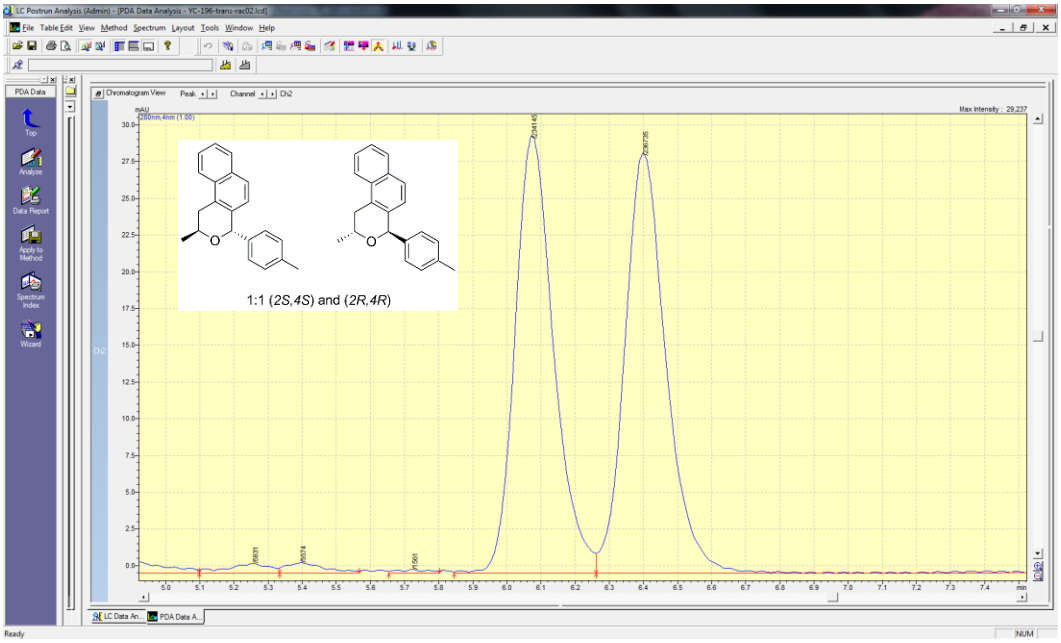
Retention times for enantiomers: 4.23 and 4.53 min

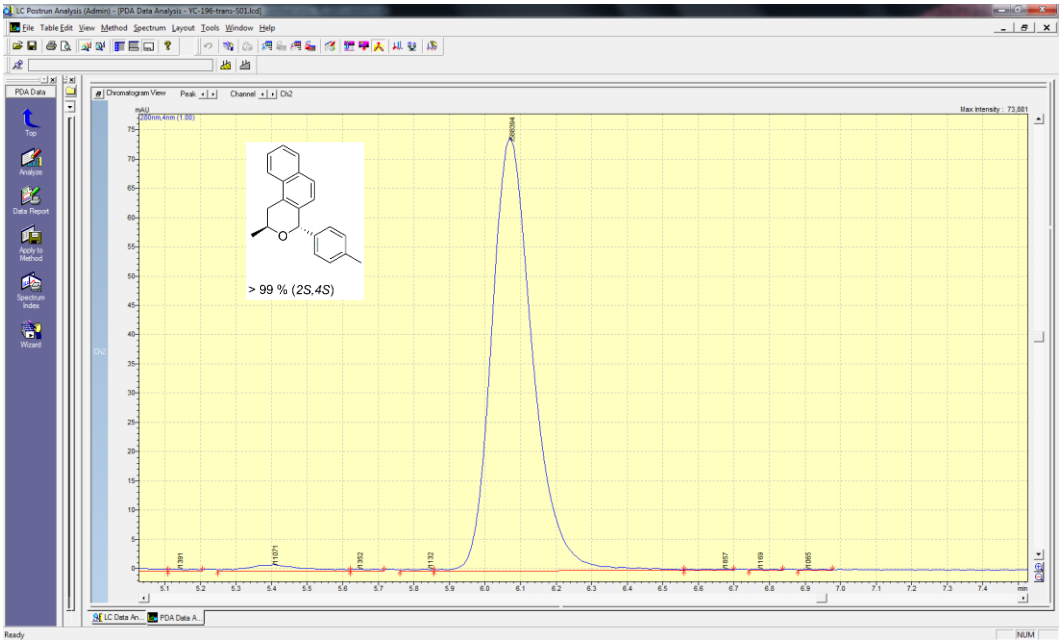


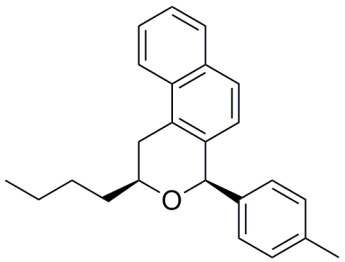


HPLC Traces for *trans*-(±)-**2eD** (top) and *trans*-(*2S*)-**2eD** (bottom).

Retention times for enantiomers: 6.08 and 6.40 min

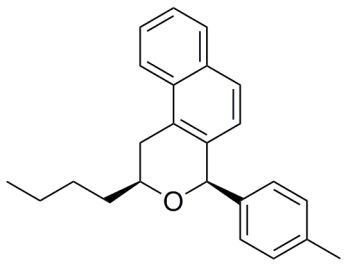






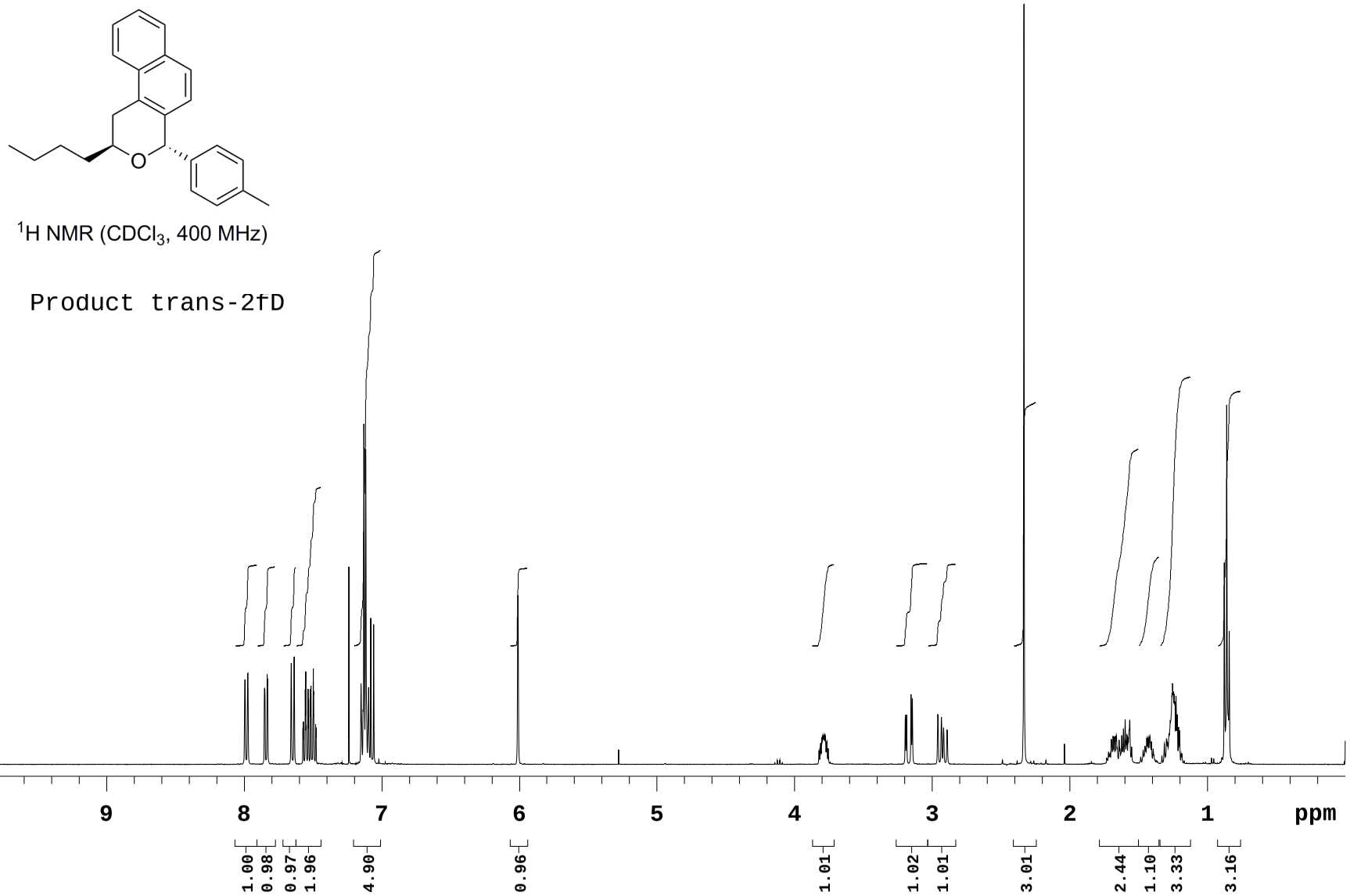
^{1}H NMR ($CDCl_3$, 400 MHz)

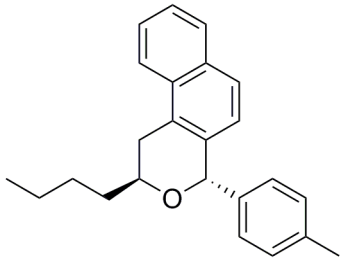
Product cis-2fD



^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

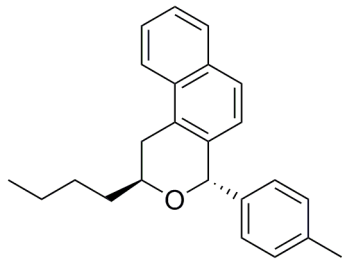
Product cis-2fD


^{1}H NMR ($CDCl_3$, 400 MHz)
Product trans-2fD
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
0.97
1.96
4.90
0.96
1.01
1.02
1.01
3.01
2.44
1.10
3.33
3.16



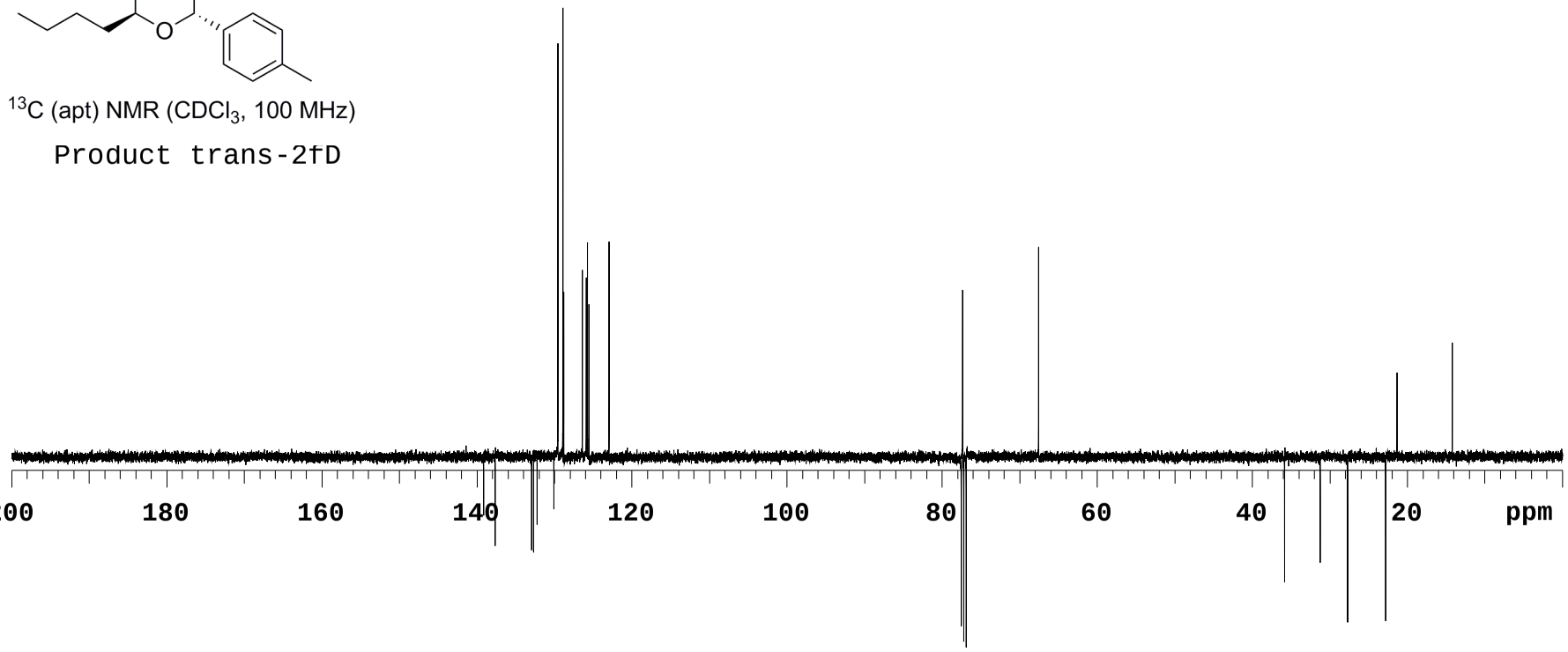
^{1}H Noesy-1D NMR ($CDCl_3$, 400 MHz)

Product trans-2ŧD



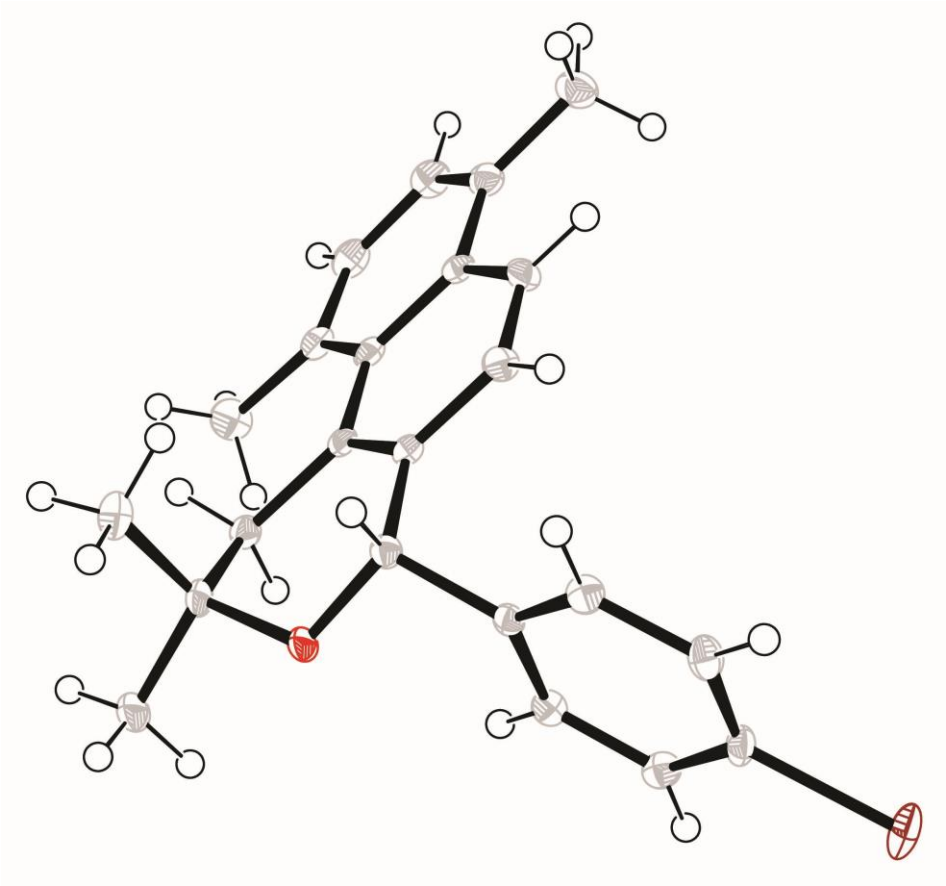
^{13}C (apt) NMR ($CDCl_3$, 100 MHz)

Product trans-2fD

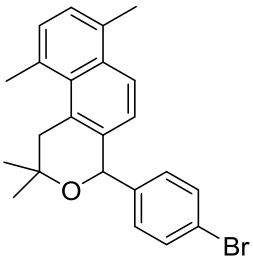


Abbreviated Crystallographic Data For 2dA:

A single crystal was grown from slow evaporation of a $CDCl_3$ NMR sample at room temperature. The chosen crystal was mounted using an organic epoxy resin and analyzed at 100 K. See the following page for general details of the structure.



ORTEP Representation of 1,4-Dihydro-2*H*-Benzo[*f*]isochromene, 2dA. Thermal Elipsoids are shown at the 50% probability level.



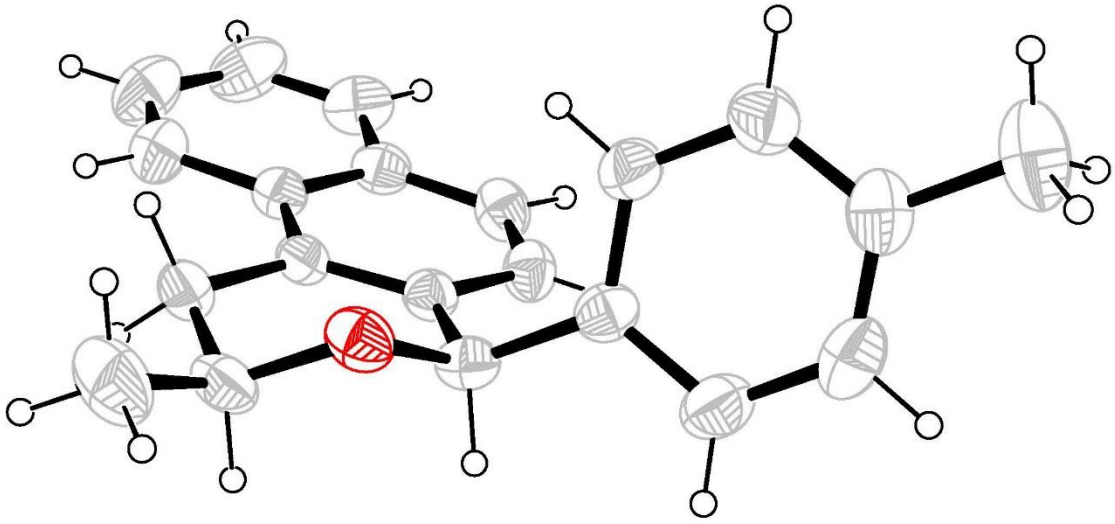
4-(4-bromophenyl)-2,2,7,10-tetramethyl-1,4-dihydro-2*H*-benzo[*f*]isochromene
Chemical Formula: $C_{23}H_{23}BrO$
Exact Mass: 394.09
Molecular Weight: 395.34
m/z: 394.09 (100.0%), 396.09 (97.3%), 397.09 (24.2%), 395.10 (16.2%), 395.10 (8.7%), 398.10 (1.7%), 396.10 (1.6%), 398.10 (1.2%), 396.10 (1.1%)
Elemental Analysis: C, 69.88; H, 5.86; Br, 20.21; O, 4.05

Table 1. Crystal data and structure refinement for 2dA.

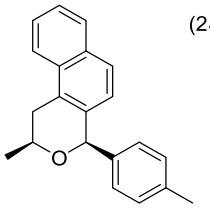
Identification code	P21onn	
Empirical formula	C23 H23 Br O	
Formula weight	395.32	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 17.0425(3) Å	α= 90°.
	b = 6.45510(10) Å	β= 95.9170(6)°.
	c = 17.1404(3) Å	γ = 90°.
Volume	1875.59(5) $Å^3$	
Z	4	
Density (calculated)	1.400 Mg/m^3	
Absorption coefficient	3.026 mm^{-1}	
F(000)	816	
Crystal size	0.555 x 0.248 x 0.189 mm^3	
Theta range for data collection	3.482 to 66.992°.	
Index ranges	-20<=h<=20, -7<=k<=6, -20<=l<=19	
Reflections collected	20549	
Independent reflections	3309 [R(int) = 0.0304]	
Completeness to theta = 67.679°	97.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3309 / 0 / 230	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0654	
R indices (all data)	R1 = 0.0245, wR2 = 0.0656	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.411 and -0.380 $e.Å^{-3}$	

Abbreviated Crystallographic Data For *cis*-2eD:

A single crystal was grown from slow evaporation of a $CDCl_3$ NMR sample at room temperature. The chosen crystal was mounted using an organic epoxy resin and analyzed at 296 K. See the following page for general details of the structure.



ORTEP Representation of Benzo[*f*]isochromene *cis*-2eD. Thermal Elipsoids are shown at the 50% probability level.



(2*S*,4*R*)-2-methyl-4-(*p*-tolyl)-1,4-dihydro-2*H*-benzo[*f*]isochromene

Chemical Formula: $C_{21}H_{20}O$
Exact Mass: 288.15
Molecular Weight: 288.39
m/z: 288.15 (100.0%), 289.15 (22.7%), 290.16 (2.5%)
Elemental Analysis: C, 87.46; H, 6.99; O, 5.55

Table 1. Crystal data and structure refinement for *cis*-2eD.

Identification code	Pbca	
Empirical formula	C21 H20 O	
Formula weight	288.37	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 18.1842(2) Å	α= 90°.
	b = 8.95420(10) Å	β= 90°.
	c = 20.2236(2) Å	γ = 90°.
Volume	3292.91(6) $Å^3$	
Z	8	
Density (calculated)	1.163 Mg/m^3	
Absorption coefficient	0.536 mm^{-1}	
F(000)	1232	
Crystal size	0.450 x 0.170 x 0.100 mm^3	
Theta range for data collection	4.864 to 64.984°.	
Index ranges	-21<=h<=21, -10<=k<=10, -20<=l<=23	
Reflections collected	22603	
Independent reflections	2790 [R(int) = 0.0350]	
Completeness to theta = 67.679°	93.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2790 / 0 / 201	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1157	
R indices (all data)	R1 = 0.0488, wR2 = 0.1246	
Extinction coefficient	0.00126(18)	
Largest diff. peak and hole	0.144 and -0.121 e.$Å^{-3}$	