Electronic Supplementary Material (ESI) for ChemComm.

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1. General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F254 aluminium plates (Merck) and/or gas chromatography-mass spectrometry (GCMS). Visualization of compounds on TLC was accomplished by irradiation with UV light at 254 nm and/or vanillin stain. GCMS Analysis was performed with 'Agilent 7820A' gas chromatograph equipped with 'Agilent 5975' quadrupole mass selective detector, using Agilent HP-5MS capillary column (30 m, 0.25 mm, 0.25 μm film).

Column chromatography was performed using silica gel 60 (particle size 0.040 - 0.063 mm) purchased from Sigma-Aldrich.

Proton and carbon NMR spectra were recorded on Varian Mercury 300 MHz or Varian Mercury 500 MHz spectrometer in deuterated solvent. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm). ^{13}C chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constants (Hz). High resolution mass spectra were determined on a Thermo Scientific LTQ Orbitrap XL (FTMS).

Infrared (IR) spectra were recorded on a Thermo Fischer Scientific NICOLET iS10 spectrometer.

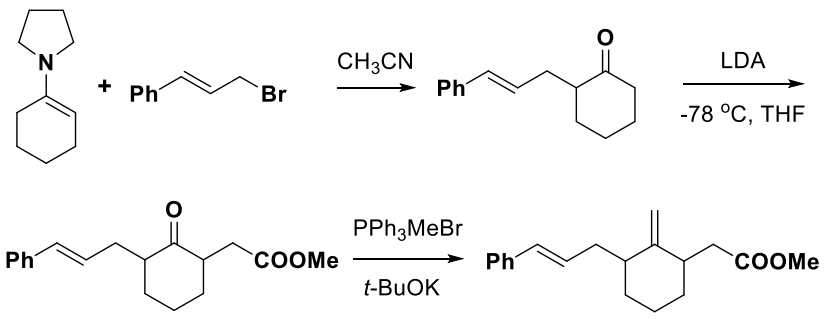
Unless otherwise noted, the diastereomeric ratios were calculated from GCMS analysis of the crude reaction mixture. All NMR spectra of tricyclic lactones, their corresponding substrates and bicyclic compound 31 show the mixture of diastereomers.

2. Synthesis of Cyclic Precursors:

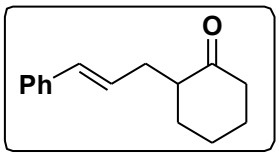
2.1. Synthesis of α,α'-dialkylated cycloalkyl methylene compounds:

Cycloalkyl substrates were synthesized from double alkylation of cyclic ketones followed by Wittig olefination to obtain the desired diene carboxylic esters.[1]

2.2. Synthesis of methyl 2-(3-cinnamyl-2-methylenecyclohexyl)acetate:

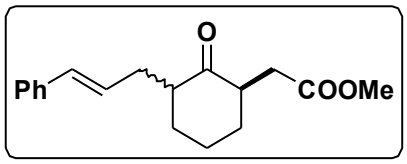


2-Cinnamylcyclohexan-1-one



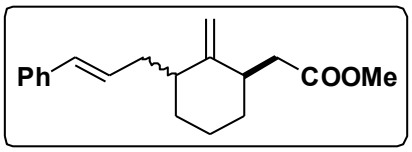
By following a literature procedure[1], 1-(cyclohex-1-en-1-yl)pyrrolidine was freshly prepared by refluxing cyclohexanone (15 mmol, 1.0 equiv.) and pyrrolidine (45 mmol, 3.0 equiv.) in dry toluene (1 M), in the presence of catalytic amount of *p*TSA, till all water was distilled by Dean-Stark apparatus. After removal of toluene and traces of pyrrolidine by vacuum evaporation, to the crude compound was added dry CH_3CN (20 mL) followed by cinnamyl bromide (15 mmol, 1.0 equiv.) dropwise. The mixture was stirred for 1 h at room temperature. The reaction was quenched with water and refluxed for 1 h. After cooling to room temperature, the solution was diluted with diethyl ether and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, 5% Et_2O/hexanes) to yield 2-cinnamylcyclohexan-1-one in 39% yield (1.25 g) as yellow liquid.

Methyl 2-(3-cinnamyl-2-oxocyclohexyl)acetate



By following a literature procedure[1], to a flask under nitrogen atmosphere was added diisopropyl amine (1.0 mL, 1.2 equiv.) in 15 mL of THF. At -20 ^oC, *n*-BuLi was added slowly and the mixture was allowed to stir for 15 min at rt. LDA was added dropwise to the solution of 2-cinnamylcyclohexan-1-one (5.8 mmol, 1.0 equiv.) in 6 mL THF at -78 ^oC and allowed to stir for 2 h at -10 ^oC. Methyl 2-bromoacetate (6.96 mmol, 1.2 equiv.) was added slowly and the resulting mixture was stirred overnight at rt. The reaction was quenched with saturated NH_4Cl solution and extracted with ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, 5% Et_2O/hexanes) to yield methyl 2-(3-cinnamyl-2-oxocyclohexyl)acetate in 51% yield (0.85 g) as a yellow liquid.

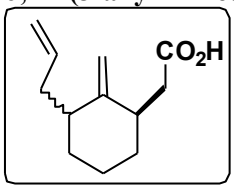
Methyl 2-(3-cinnamyl-2-methylenecyclohexyl)acetate ***I***



This compound was synthesized by following the literature procedure,[1] using methyl 2-(3-cinnamyl-2-oxocyclohexyl)acetate (0.80 g, 3 mmol, 1 equiv.), methyltriphenylphosphonium bromide (2.0 equiv.) and potassium *tert*-butoxide (3.0 equiv.) in THF (0.1 M). The crude product was purified by column chromatography (SiO_2, 2% Et_2O/hexanes) to afford methyl 2-(3-cinnamyl-2-methylenecyclohexyl)acetate (0.36 g, 42%, dr 86:14).

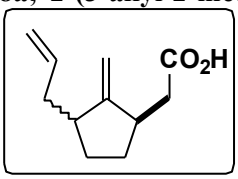
2.3. General procedure A; Hydrolysis of diene carboxylic ester to corresponding acids (6, 8a-i, 19a-b and 24): This reaction was performed by following the literature procedure.[2] Ester (1.0 mmol, 1.0 equiv.) was dissolved in THF (8 mL) and 2 M aq. NaOH (6.0 equiv.) or 2 M aq. KOH (15.0 equiv.) was added. The solution was stirred at 60 ºC for 3 h. The reaction mixture was concentrated under vacuum and the residue was quenched with water. The aqueous solution was extracted with ether, acidified with conc. HCl to pH = 1, and extracted again with ethyl acetate. The combined organic extracts was dried over Na_2SO_4, filtered, and evaporated, to yield the desired acid as a mixture of diastereoisomers.

6; 2-(3-allyl-2-methylenecyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (2.7 g, 13.0 mmol) and KOH. Purification of the residue by flash column chromatography (60% ethyl acetate in hexane) yielded pure 2-(3-allyl-2-methylenecyclohexyl)acetic acid (2.4 g, 95% yield, pale yellow oil, dr 89:11).



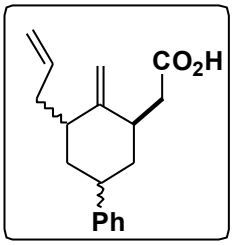
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.86-5.75 (m, 1H), 5.07-4.99 (m, 2H), 4.70-4.61 (m, 2H), 2.70-2.63 (m, 1H), 2.47-2.30 (m, 3H), 2.05-1.91 (m, 4H), 1.82-1.75 (m, 1H), 1.56-1.50 (m, 1H) and 1.14-0.91 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.9, 154.5, 137.5, 115.8, 102.1, 43.5, 40.7, 38.0, 37.1, 35.3, 34.6 and 25.9. **IR** (neat): 2923, 2853, 1705, 1640, 1414, 1293, 910, 887 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{12}H_{19}O_2$ ($[M+H]^+$): 195.1385; found: 195.1378.

8a; 2-(3-allyl-2-methylenecyclopentyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (780 mg, 4.02 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (20% diethyl ether in hexane) yielded pure 2-(3-allyl-2-methylenecyclopentyl)acetic acid (550 mg, 78% yield, pale yellow oil, dr 84:16).



^{1}H NMR (300 MHz, $CDCl_3$): δ 10.86 (br s, 1H), 5.84-5.75 (m, 1H), 5.06-4.98 (m, 2H), 4.93-4.89 (m, 2H), 2.91-2.68 (m, 1H), 2.65-2.50 (m, 2H), 2.36-2.25 (m, 2H), 2.13-1.71 (m, 3H), 1.66-1.23 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.6, 157.9, 157.7, 137.2, 137.0, 115.8, 115.7, 105.3, 105.0, 43.5, 43.2, 40.5, 40.4, 39.4, 39.2, 39.1_2, 39.1_0, 31.4, 30.4, 30.2 and 29.2. **IR** (neat): 2953, 2840, 1705, 1640, 1414, 1277, 992, 910, 884 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{16}O_2Na$ ($[M+Na]^+$): 203.1048; found: 203.1044.

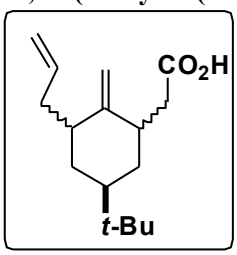
8b; 2-(3-allyl-2-methylene-5-phenylcyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (273 mg, 0.96 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (30% ethyl acetate in hexane) yielded pure 2-(3-allyl-2-methylene-5-phenylcyclohexyl)acetic acid (226 mg, 87% yield, pale yellow oil, dr 48:41:11).



^{1}H NMR (300 MHz, $CDCl_3$): δ 10.89 (br s, 1H), 7.35-7.20 (m, 5H), 5.89-5.74 (m, 1H), 5.11-5.02 (m, 2H), 4.84-4.66 (m, 2H), 3.16-1.65 (m, 10H) and 1.46-1.18 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.7, 179.5, 179.2, 152.2, 152.1, 145.9,

145.7, 144.9, 137.3, 13.2, 137.0, 128.4, 127.1, 126.8, 126.2, 125.9, 116.2, 116.1, 115.7, 109.9, 108.0, 106.5, 102.8, 45.1, 44.0, 43.1, 42.4, 41.9, 41.6, 41.6, 41.3, 40.8, 40.3, 39.1, 38.5, 38.4, 38.2, 37.8, 37.6, 37.4, 37.1, 36.9, 36.8, 34.7 and 34.6. **IR** (neat): 2921, 2852, 1766, 1664, 1601, 1493, 1455, 1278, 1189, 1149, 1125, 1013, 958, 908, 886 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{18}H_{22}O_2Na$ ($[M+Na]^+$): 293.1517; found: 293.1512.

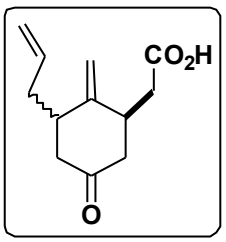
8c; 2-(3-allyl-5-(*tert*-butyl)-2-methylenecyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (2.1 g, 8.0 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (50% diethyl ether in hexane) yielded pure 2-(3-allyl-5-(tert-butyl)-2-methylenecyclo hexyl)acetic acid (1.58 g, 80% yield, pale yellow solid, dr 56:24:20).



M.p.: 53-54 °C

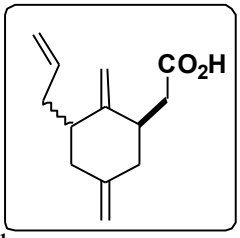
^{1}H NMR (300 MHz, $CDCl_3$): δ 11.42 (br s, 1H), 5.87-5.68 (m, 1H), 5.08-4.95 (m, 2H), 4.84-4.54 (m, 2H), 2.73-2.62 (m, 1H), 2.53-2.20 (m, 4H), 2.10-1.76 (m, 4H), 1.51-1.21 (m, 2H), 0.87-0.79 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.5, 154.5, 153.3, 137.6, 137.3, 115.8, 115.5, 101.7, 47.4, 44.8, 42.9, 42.2, 41.6, 40.2, 38.1, 37.3, 37.1, 36.5, 36.4, 35.7, 35.5, 34.9, 32.4, 32.3, 32.2, 27.6 and 27.4. **IR** (neat): 2961, 2865, 1706, 1641, 1415, 1365, 1283, 1220, 980, 908, 894 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{16}H_{26}O_2Na$ ($[M+Na]^+$): 273.1830; found: 273.1825.

8d; 2-(3-allyl-2-methylene-5-oxocyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (830 mg, 3.70 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (40% ethyl acetate in hexane) yielded pure 2-(3-allyl-2-methylene-5-oxocyclohexyl)acetic acid (395 mg, 47% yield, pale yellow oil, dr 91:9).



^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (br s, 1H), 5.77-5.65 (m, 1H), 5.07-4.93 (m, 4H), 2.90-2.86 (m, 1H), 2.78-2.70 (m, 1H), 2.65-2.56 (m, 2H), 2.53-2.37 (m, 3H) and 2.18-1.98 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 209.0, 177.2, 149.6, 135.5, 117.2, 106.6, 47.5, 47.3, 40.9, 38.2, 37.4 and 37.0. **IR** (neat): 2950, 2918, 1706, 1643, 1416, 1281, 1218, 1160, 1052, 994, 906 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{12}H_{16}O_3Na$ ($[M+Na]^+$): 231.0997; found: 231.0992.

8e; 2 2-(3-allyl-2,5-dimethylenecyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (130 mg, 0.60 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (30% ethyl acetate in hexane) yielded pure 2-(3-allyl-2,5-dimethylenecyclohexyl)acetic acid (117 mg, 95% yield, pale yellow solid, dr 90:10).

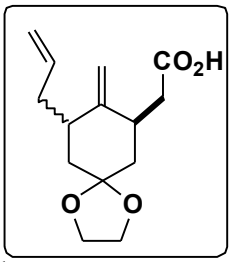


M.p.: 59-60 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.75 (br s, 1H), 5.86-5.74 (m, 1H), 5.09-5.02 (m, 2H), 4.79-4.74 (2 br s, 4H), 2.74-2.63(m, 1H), 2.60-2.36 (m, 5H), 2.15-2.01z (m, 2H), 1.85 and 1.72 (2 t, *J* = 11.8 Hz and 11.7 Hz respectively, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.3, 152.7, 145.8, 144.1, 137.0, 116.2, 116.0, 111.1, 109.5, 107.4, 104.2, 43.6, 42.6, 42.2, 41.9, 41.5, 40.7, 38.3, 37.8, 37.6, 37.1 and 36.7. **IR** (neat): 2929, 1707, 1688, 1643,

1433, 1416, 1269, 1231, 1204, 1167, 949, 902, 850 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{13}H_{18}O_2Na$ ($[M+Na]^+$): 229.1204; found: 229.1204.

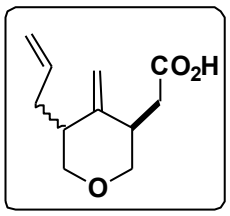
8f; 2-(9-allyl-8-methylene-1,4-dioxaspiro[4.5]decan-7-yl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (260 mg, 0.98 mmol) and aq. KOH. Purification of the residue by flash column chromatography (30% ethyl acetate in hexane) yielded pure 2-(9-allyl-8-methylene-1,4-dioxaspiro[4.5]decan-7-yl)acetic acid (176 mg, 71% yield, white solid, dr 92:8).



M.p.: 116-117 ^oC

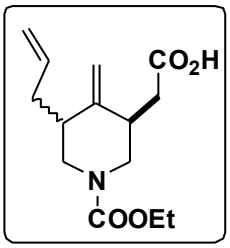
^{1}H NMR (300 MHz, $CDCl_3$): δ 10.14 (br s, 1H), 5.84-5.74 (m, 1H), 5.08-5.02 (m, 2H), 4.80-4.72 (m, 2H), 3.99-3.93 (m, 4H), 2.81-2.66 (m, 2H), 2.50-2.43 (m, 1H), 2.38-2.30 (m, 2H), 2.07-1.92 (m, 3H) and 1.40-1.19 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.5, 152.3, 137.1, 136.8, 116.4, 116.1, 108.3, 103.7, 64.4_3, 64.4_2, 42.6, 42.2, 40.3, 40.2, 39.4, 38.0, 37.3, 37.0, 36.9 and 36.5. **IR** (neat): 2912, 1690, 1644, 1419, 1306, 1272, 1172, 1143, 1057, 1053, 944, 903 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{14}H_{20}O_4Na$ ($[M+Na]^+$): 275.1259; found: 275.1253.

8g; 2-(5-allyl-4-methylenetetrahydro-2H-pyran-3-yl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (1.14 g, 5.40 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (5% ethyl acetate in hexane) yielded 2-(5-allyl-4-methylenetetrahydro-2H-pyran-3-yl)acetic acid (0.92 g, 87% yield, pale yellow oil, dr 92:8).



^{1}H NMR (300 MHz, $CDCl_3$): δ 10.26 (br s, 1H), 5.80-5.69 (m, 1H), 5.07-5.01 (m, 2H), 4.79 and 4.74 (2 br s, 2H), 4.02-3.95 (m, 2H), 3.15-3.02 (m, 2H), 2.78-2.73 (m, 1H), 2.61-2.53 (m, 1H), 2.39-2.25 (m, 3H), 2.04-1.97 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.8, 149.6, 136.0, 116.6, 104.9, 73.6, 73.4, 42.4, 39.7, 33.6 and 33.0. **IR** (neat): 2977, 2908, 2842, 1708, 1642, 1407, 1262, 1166, 1107, 1067, 993, 948, 894 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{16}O_3Na$ ($[M+Na]^+$): 219.0997; found: 219.0990.

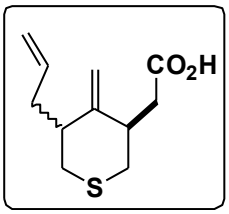
8h; 2-(5-allyl-1-(ethoxycarbonyl)-4-methylenepiperidin-3-yl)acetic acid: General procedure A was adopted using the corresponding methyl ester of diene carboxylic acid (400 mg, 1.42 mmol) and 2.3 mL of 10% NaOH (4.0 equiv.). This reaction was performed at room temperature for 4 h. Purification of the residue by flash column chromatography (30% ethyl acetate in hexane) yielded pure 2-(5-allyl-1-(ethoxycarbonyl)-4-methylenepiperidin-3-yl)acetic acid (253 mg, 68% yield, white solid, dr 91:9).



M.p.: 66-67 ^oC

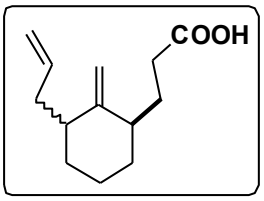
^{1}H NMR (300 MHz, $CDCl_3$): δ 10.38 (br s, 1H), 5.85-5.73 (m, 1H), 5.11-5.05 (m, 2H), 4.84-4.80 (m, 2H), 4.18-4.11 (m, 4H), 2.70-2.56 (m, 4H), 2.44-2.33 (m, 2H), 2.21-2.16 (m, 1H), 2.11-2.03 (m, 1H) and 1.26 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.8, 155.5, 149.9, 149.0, 135.8, 116.7, 106.1, 61.6, 50.0, 49.8, 42.0, 39.1, 35.0, 34.4 and 14.5. **IR** (neat): 2983, 2905, 2857, 1741, 1674, 1637, 1485, 1444, 1418, 1310, 1272, 1240, 1156, 1130, 1011, 923, 900 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{14}H_{21}NO_4Na$ ($[M+Na]^+$): 290.1368; found: 290.1361.

8i; 2-(5-allyl-4-methylenetetrahydro-2H-thiopyran-3-yl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (190 mg, 0.84 mmol) and aq. KOH. Purification of the residue by flash column chromatography (30% ethyl acetate in hexane) yielded pure 2-(5-allyl-4-methylenetetrahydro-2H-thiopyran-3-yl)acetic acid (166 mg, 93% yield, pale yellow oil, dr 82:18).

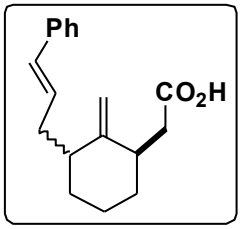


^{1}H NMR (300 MHz, $CDCl_3$): δ 10.27 (br s, 1H), 5.81-5.69 (m, 1H), 5.09-5.04 (m, 2H), 4.78 and 4.76 (2 br s, 2H), 2.90-2.84 (m, 1H), 2.80-2.75 (m, 2H), 2.70-2.54 (m, 2H), 2.53-2.31 (m, 4H) and 2.23-2.15 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.7, 151.6, 150.6, 136.3, 136.1, 116.9, 116.7, 108.9, 106.7, 45.2, 42.2, 42.1, 39.1, 37.8, 37.3, 36.8, 36.1, 35.9, 35.4, 35.3 and 34.9. **IR** (neat): 2905, 1704, 1639, 1416, 1291, 1218, 1137, 992, 900 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{16}O_2SNa$ ($[M+Na]^+$): 235.0769; found: 235.0768.

19a; 3-(3-allyl-2-methylenecyclohexyl)propanoic acid: This compound was prepared by following the reported procedure.[1]

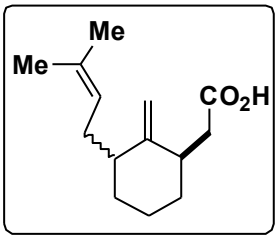


19b; 2-(2-methylene-3-(3-phenylallyl)cyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid **I** (360 mg, 1.27 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (20% diethyl ether in hexane) yielded pure 2-(2-methylene-3-(3-phenylallyl)cyclohexyl)acetic acid (255 mg, 74% yield, pale yellow oil, dr 86:14)



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.17 (m, 5H), 6.44 and 6.39 (2 br s, 1H), 5.02-4.65 (m, 2H), 2.73-2.55 (m, 2H), 2.49-2.32 (m, 2H), 2.21-1.92 (m, 4H), 1.82 and 1.78 (2 br s, 1H), 1.60-1.51 (m, 1H), 1.13-0.97 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.9, 154.5, 137.7, 131.2, 129.5, 128.5, 126.9, 125.9, 102.3, 44.0, 40.7, 37.9, 36.3, 35.4, 34.7 and 26.0. **IR** (neat): 2923, 2852, 1738, 1706, 1642, 1445, 1412, 1373, 1238, 1170, 1045, 964, 889 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{18}H_{22}O_2Na$ ($[M+Na]^+$): 293.1517; found: 293.1513.

24; 2-(3-(3-methylbut-2-en-1-yl)-2-methylenecyclohexyl)acetic acid: General procedure A was applied using the corresponding methyl ester of diene carboxylic acid (950 mg, 4.03 mmol) and aq. NaOH. Purification of the residue by flash column chromatography (5% ethyl acetate in hexane) yielded pure 2-(3-(3-methylbut-2-en-1-yl)-2-methylenecyclohexyl)acetic acid (740 mg, 84% yield, pale yellow oil, dr 92:8).



^{1}H NMR (300 MHz, $CDCl_3$): δ 11.50 (br s, 1H), 5.16-5.10 (m, 1H), 4.68-4.61 (m, 2H), 2.71-2.64 (m, 1H), 2.45-2.21 (m, 3H), 2.10-1.88 (m, 4H), 1.81-1.75 (m, 1H), 1.71 (s, 3H), 1.61 (s, 3H), 1.55-1.49 (m, 1H), 1.10-0.90 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.9, 154.9, 132.1, 123.3, 102.0, 44.4, 40.7, 38.1, 35.4, 34.7, 31.2,

26.1, 25.8 and 17.9. **IR** (neat): 2921, 2852, 1705, 1641, 1441, 1413, 1294, 1224, 887, 843 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{14}H_{22}O_2Na$ ($[M+Na]^+$): 245.1517; found: 245.1513.

3. Synthesis of Acyclic Precursors:

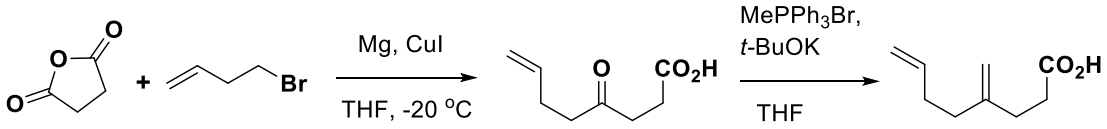
3.1. General procedure B; Grignard reaction with succinic anhydride:

This reaction was performed by following the literature procedure.[3] To a suspension of magnesium turnings (4.0 equiv.) in dry THF (30 mL) was slowly added a solution of homoallyl bromide (2.0 equiv.) in dry THF (20 mL) using syringe pump over a period of 30 min at room temperature. The reaction mixture was stirred at room temperature for 2 h. The resulting Grignard reagent was then added dropwise over a period of 30 min to a suspension of succinic anhydride (1.0 equiv., 15 mmol) and copper iodide (15 mol %) in dry THF (20 mL) at –20 °C. The reaction mixture was stirred at –20 °C and then warmed to 0 °C for 3 h. The reaction mixture was quenched with HCl (2 M, 20 mL) at 0 °C and extracted with EtOAc (4 × 50 mL). The combined organic phases were washed with brine (50 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography using SiO_2 to afford the difunctionalized ketone.

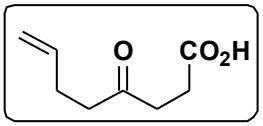
3.2. General procedure C; Wittig olefination:

This reaction was performed by following the literature procedure.[4] To a suspension of methyltriphenylphosphonium bromide (2.0 equiv.) in THF (0.1 M) was added potassium *tert*-butoxide (3.0 equiv.) at 0 °C. The mixture was then stirred for 30 minutes. Difunctionalized ketone (1.0 equiv., 10 mmol) was added to the reaction mixture at 0 °C. The mixture was allowed to warm to room temperature and the resukting mixture was stirred for 16 h. The solvent was evaporated and the crude was treated with 10% NaOH (50 mL). The solution was washed with CH_2Cl_2 (40 mL) and the organic layer was separated. The aqueous layer was acidified (pH ~ 1) with 3 N HCl and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with a saturated solution of NaCl (50 mL), dried over Na_2SO_4, and evaporated in vacuo. The crude product was purified by column chromatography using SiO_2 to afford the desired methenylated carboxylic acid.

3.3. Synthesis of 4-methyleneoct-7-enoic acid (26a):

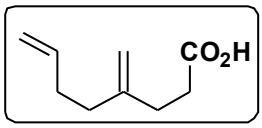


4-oxooct-7-enoic acid



This compound was prepared by following general procedure B, using magnesium turnings (1.44 g, 60 mmol), homoallyl bromide (3.03 mL, 30 mmol), succinic anhydride (1.5 g, 15 mmol) and copper iodide (0.412 g, 2.25 mmol) in dry THF. The crude product was purified by column chromatography (SiO_2, 30% EtOAc/hexanes) to afford 4-oxooct-7-enoic acid (1.39 g, 30%) as a pale yellow viscous oil.

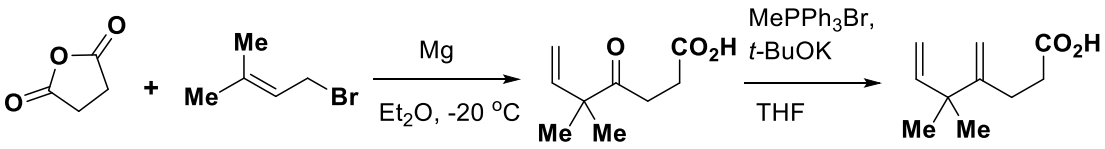
26a; *4-methyleneoct-7-enoic acid*



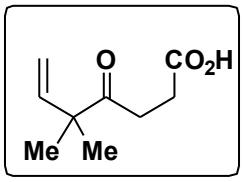
This compound was prepared by following the general procedure C by using 4-oxooct-7-enoic acid (8.9 mmol), methyltriphenylphosphonium bromide (6.35 g, 17.8 mmol) and , potassium *tert*-butoxide (2.99 g, 26.7 mmol) in THF. The crude was purified by column chromatography with 15% EtOAc/ hexanes as eluent to afford 4-methyleneoct-7-enoic acid (0.60 g, 43%) as a pale yellow viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.90 (br s, 1H), 5.87-5.74 (m, 1H), 5.05-4.94 (m, 2H), 4.79-4.76 (2 br s, 2H), 2.54-2.46 (m, 2H), 2.39-2.29 (m, 2H), 2.25-2.15 (m, 2H) and 2.15-2.07 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 180.0, 146.9, 138.0, 114.7, 109.7, 35.5, 32.4, 31.8 and 30.4. **IR** (neat): 2952, 2919, 1707, 1642, 1287, 1211, 995, 891 cm^{-1}. **HRMS** (*m/z*) calcd for $C_9H_{14}O_2Na$ ($[M+Na]^+$): 177.0891; found: 177.0889.

3.4. Synthesis of 5,5-dimethyl-4-methylenehept-6-enoic acid (29b):

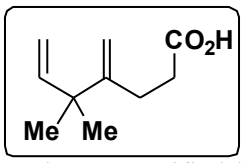


5,5-dimethyl-4-oxohept-6-enoic acid



This compound was prepared by adopting general procedure B, using prenyl magnesium bromide[5] [which was prepared by using prenyl bromide (2 mL, 17 mmol) in dry Et_2O (17 mL) and magnesium turnings (2.04 g, 85 mmol) in dry Et_2O (10 mL)], succinic anhydride (1.0 g, 10.0 mmol), and copper iodide (0.28 g, 1.50 mmol) in dry THF. The crude product was purified by column chromatography (SiO_2, 30% EtOAc/hexanes), to afford 5,5-dimethyl-4-oxohept-6-enoic acid (1.16 g, 68%) as a yellow viscous oil.

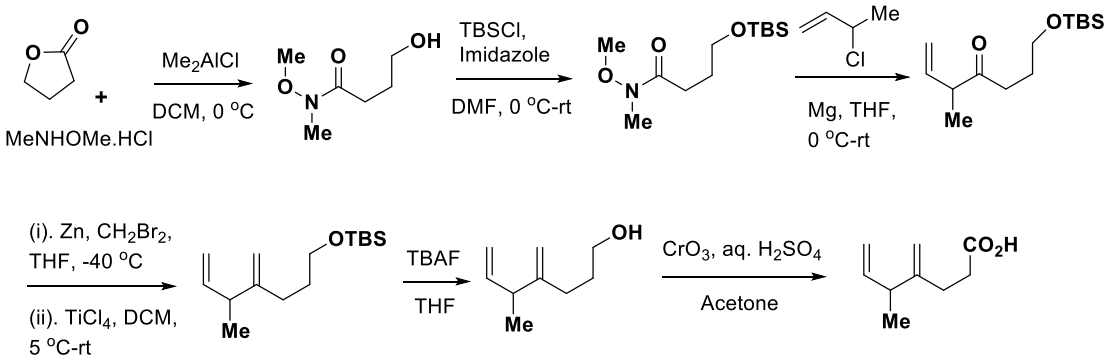
29b*; 5,5-dimethyl-4-methylenehept-6-enoic acid*



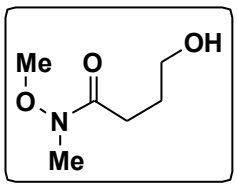
This compound was prepared by following general procedure C, using 5,5-dimethyl-4-oxohept-6-enoic acid (0.94 g, 5.5 mmol), methyltriphenylphosphonium bromide (3.93 g, 11.0 mmol), and potassium *tert*-butoxide (1.85 g, 16.5 mmol) in THF (55 mL). The crude was purified by column chromatography with 30% EtOAc/hexanes as eluent, to afford 5,5-dimethyl-4-methylenehept-6-enoic acid (0.67 g, 72%) as a yellow viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.7 (br s, 1H), 5.81-5.72 (m, 1H), 5.02-4.97 (m, 3H), 4.76 (s, 1H), 2.54-2.49 (m, 2H), 2.36-2.30 (m, 2H) and 1.16 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 180.2, 153.7, 146.7, 111.5, 108.0, 42.6, 33.4, 26.2 and 26.1. **IR** (neat): 2969, 2835, 1708, 1634, 1412, 1286, 1265, 911, 895 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{10}H_{16}O_2Na$ ($[M+Na]^+$): 191.1048; found: 191.1048.

3.5. Synthesis of 5-methyl-4-methylenehept-6-enoic acid:

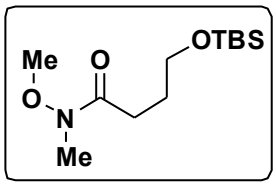


4-hydroxy-N-methoxy-N-methylbutanamide



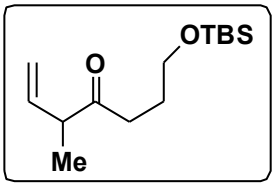
This compound was prepared by following the reported procedure.[6] N,O-Dimethylhydroxylamine hydrochloride (3 g, 31 mmol, 1.10 equiv) was dissolved in CH_2Cl_2 (150 mL) and cooled to 0 °C. Dimethylaluminum chloride 1.0 M in hexane (31 mL, 31 mmol, 1.10 equiv) was added dropwise via cannula over 40 min and the resulting mixture was stirred at this temperature for 1 h. γ-Butyrolactone (2.2 mL, 28 mmol, 1.0 equiv) was added slowly over 15 min and the mixture was allowed to warm up to rt. After 30 h of stirring, the reaction was quenched by slow addition of water (30 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic extracts were dried over Na_2SO_4. Filtration and concentration under reduced pressure yielded 4-hydroxy-N-methoxy-N-methylbutanamide (3.46 g, 84%) as a clear colorless oil. An analytically pure sample of 4-hydroxy-N-methoxy-N-methylbutanamide could be obtained by column chromatography (hexane/EtOAc 3:1).

4-((tert-butyldimethylsilyl)oxy)-N-methoxy-N-methylbutanamide



This compound was prepared by following the reported procedure.[7] To a solution of 4-hydroxy-N-methoxy-N-methylbutanamide (2.1 g, 14.3 mmol) and imidazole (2.9 g, 42.9 mmol) in DMF (100 mL) was added TBSCl (3.2 g, 21.5 mmol) at 0 °C. The mixture was stirred at rt for 3 h. The mixture was then quenched by addition of H_2O, and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by silica gel chromatography (20% EtOAc/hexane) to yield (3.45 g, 92%) as a colorless oil.

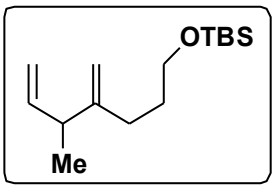
7-((tert-butyldimethylsilyl)oxy)-3-methylhept-1-en-4-one



This compound was prepared by following the reported procedure.[8] The Grignard reagent was prepared by dropwise addition of 3-chloro-1-butene (0.6 mL, 6 mmol) in dry THF (4 mL) to a stirred suspension of magnesium turnings (145 mg, 6 mmol) and a catalytic amount of iodine in dry THF (1.0 mL) at room temperature. After the addition of 3-chloro-1-butene was completed, the reaction

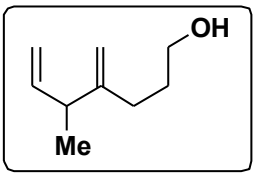
was allowed to stir for another 30 min. A solution of N-methoxy-N-methylamide (1.3 g, 5 mmo1) in dry THF (5 mL) was added dropwise at 0 °C to the freshly prepared solution of Grignard reagent. The mixture was allowed to warm to room temperature, and stirred for 3 h at rt. The reaction mixture was quenched with HCl (2 M, 10 mL) at 0 °C and extracted with EtOAc (4 × 25 mL). The combined organic phases were washed with brine (50 mL) and dried with anhydrous Na_2SO_4. The crude product was used for the next step without further purification.

tert-butyldimethyl((5-methyl-4-methylenehept-6-en-1-yl)oxy)silane



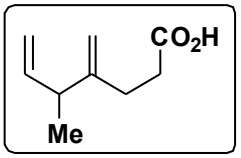
This compound was prepared by following the reported procedure.[9] To a flask equipped with a magnetic stirrer and connected to a nitrogen was added 28.75 g (0.44 mol) of activated zinc powder, 10.1 mL (0.144 mol) of dibromomethane in 250 mL of dry THF. The mixture was stirred and cooled with a dry ice–acetone cooling bath at −40 °C. To the stirred mixture was added 11.5 mL (0.103 mol) of titanium tetrachloride dropwise over 15 min. The cooling bath was removed and the mixture was stirred at 5 °C (cold room) for 3 days under a nitrogen atmosphere. The dark-gray slurry was cooled with an ice–water bath and 50 mL of dry DCM was added. The crude product of 7-((*tert*-butyldimethylsilyl)oxy)-3-methylhept-1-en-4-one in 50 mL of DCM was slowly added to the stirred mixture. The reaction mixture is stirred at room temperature for 1.5 h. Pentane (300 mL) was added, followed by the addition of a slurry of 150 g of $NaHCO_3$ in 80 mL of water over 1 h. The organic layer was separated and the residue was washed with pentane (3 × 50 mL). The combined extracts were dried over Na_2SO_4: $NaHCO_3$ (5:1). The solvent was removed under vacuum and the crude product was used for the next step without further purification.

5-methyl-4-methylenehept-6-en-1-ol



This compound was prepared by following the reported procedure.[10] A solution of silyl ether (630 mg, 2.48 mmol) in THF (1.0 mL) was treated with 1 M TBAF (10 mL, 10 mmol). After stirring for 4 h under nitrogen at rt, the reaction mixture was diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (20% Et_2O/hexane) to yield (0.24 g, 68%) 5-methyl-4-methylenehept-6-enoic acid as a pale yellow oil.

29a; *5-methyl-4-methylenehept-6-enoic acid*

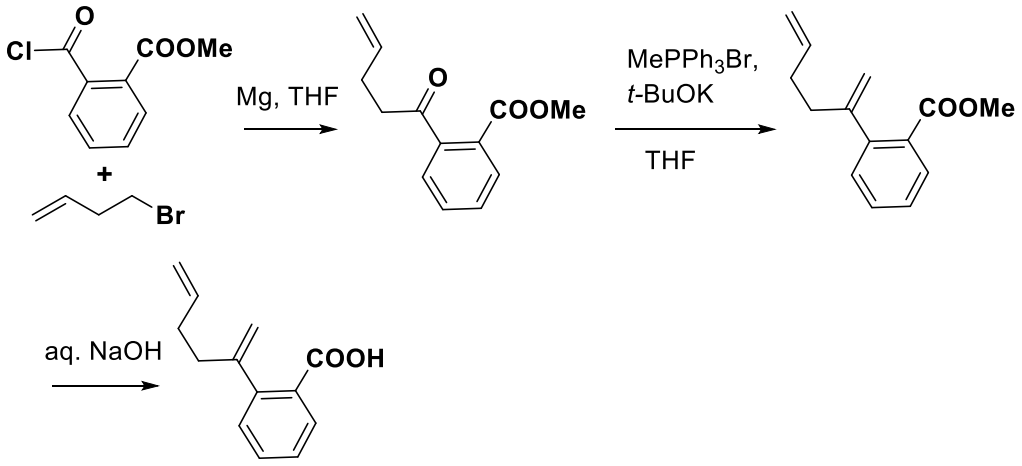


This compound was prepared by following the reported procedure.[11] To a vial equipped with a stirring bar were added 220 mg (1.6 mmol, 1.0 equiv.) of 5-methyl-4-methylenehept-6-en-1-ol and 7.2 mL of acetone. The solution was cooled to 0 ^oC and an 8 N solution of Jones reagent (12.0 mmol, 5.0 equiv.) was added dropwise. The reaction was allowed to stir for 1 h at 0 ^oC. Water was added and the aqueous layer was extracted three times with Et_2O. The combined extracts were washed with saturated aq. $NaHCO_3$. The aqueous layer was carefully acidified with 1 M HCl before extracting three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and

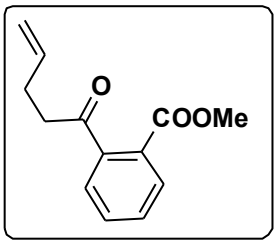
concentrated. The residue was purified by silica gel chromatography (30% Et_2O/hexane) to yield (84 mg, 34%) 5-methyl-4-methylenehept-6-enoic acid as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.49 (br s, 1H), 5. 80-5.69 (m, 1H), 5.07-4.98 (m, 2H), 4.86 and 4.78 (2 br s, 2H), 2.86-2.77 (m, 1H), 2.55-2.50 (m, 2H), 2.38-2.32 (m, 2H) and 1.15 (d, J = 6.9 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 179.7, 150.8, 142.2, 113.8, 108.8, 43.9, 32.6, 28.7 and 18.5 **IR** (neat): 2967, 2927, 1708, 1635, 1413, 1369, 1284, 1215, 1165, 993, 911, 894 cm^{-1}.

3.6. Synthesis of 2-(hexa-1,5-dien-2-yl)benzoic acid (26b):

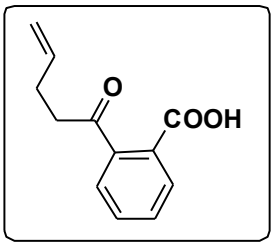


Methyl 2-(pent-4-enoyl)benzoate



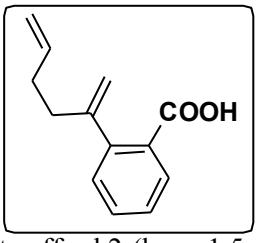
This compound was synthesized by following a reported procedure,[12] using 4-bromobutene (1.02 mL, 10 mmol, 1.0 equiv.), Mg (0.250 g, 10.2 mmol, 1.02 equiv.), CuI (0.095 g, 0.5 mmol, 0.05 equiv.), and acid chloride[13] (2.0 g, 10.0 mmol, 1.0 equiv.) in THF (25 mL). The crude product was purified by column chromatography (SiO_2, 10% EtOAc/hexane) to afford methyl 2-(pent-4-enoyl)benzoate (2.07 g, 95% yield).

2-(Pent-4-enoyl)benzoic acid



General procedure A was applied to synthesize this compound by using methyl 2-(pent-4-enoyl)benzoate (1.75 g, 8.0 mmol, 1.0 equiv.) in THF (64 mL) and NaOH (1.92 g in 24 mL of water, 48.0 mmol, 6.0 equiv.). The crude product was purified by column chromatography (SiO_2, 30% EtOAc/Hexane) to afford 2-(pent-4-enoyl)benzoic acid (1.47 g, 90% yield).

26b; *2-(Hexa-1,5-dien-2-yl)benzoic acid*



General procedure C was applied to synthesize this compound by using 2-(pent-4-enoyl)benzoic acid (1.22 g, 6.0 mmol, 1.0 equiv.), methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 2.0 equiv.), and potassium *tert*-butoxide (2.02 g, 18.0 mmol, 3.0 equiv.) in THF (60 mL). The crude product was purified by column chromatography (SiO_2, 30% EtOAc/hexane) to afford 2-(hexa-1,5-dien-2-yl)benzoic acid (0.87 g, 72% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 11.21 (br s, 1H), 8.01(d, *J*=7.8, 1H), 7.51 (t, *J*=7.5, 1H), 7.37 (t, *J*=7.6, 1H), 7.25 (d, *J*=7.6, 1H), 5.90-5.81 (m, 1H), 5.17-5.16 (m, 1H), 5.07-4.95 (m, 3H), 2.57-2.52 (m, 2H) and 2.25-2.18 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 173.3, 150.2, 145.5, 138.2, 132.4, 130.8, 130.4, 128.1, 127.1, 114.7, 113.0, 36.8 and 32.2. **IR** (neat): 2978, 2925, 2650, 1689, 1638, 1590, 1569, 1484, 1405, 1296, 1264, 1138, 1071, 996, 897 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{13}H_{14}O_2Na$ ($[M+Na]^+$): 225.0891; found: 225.0888.

4. General Procedure D; Pd-catalyzed cascade cyclization

*Screening conditions of **6** leading to tricyclic lactone **7** with different solvents:*

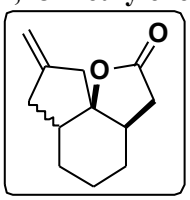
Entry	Catalyst (15mol %), Oxidant	Temp °C	Solvent (0.1M)	Yield (%)[a]
1	$Pd(OAc)_2$, AgOAc (2.2 eq.)	100	DMF	12
2	$Pd(OAc)_2$, AgOAc (2.2 eq.)	80	ACN	53
3	$Pd(OAc)_2$, AgOAc (2.2 eq.)	80	THF	22
4	$Pd(OAc)_2$, AgOAc (2.2 eq.)	100	Toluene	13
5	$Pd(OAc)_2$, AgOAc (2.2 eq.)	100	Dioxane	22
6	$Pd(OAc)_2$, AgOAc (2.2 eq.)	100	Pyridine	27

[a] Yields are determined by gc

Synthesis of spiranoid lactones (7, 10-18, 21-23, 27-28 and 31-32):

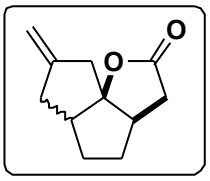
Diene carboxylic acid (1.0 equiv, 0.5 mmol), $Pd(OAc)_2$ (0.15 equiv, 0.075 mmol, 17 mg), AgOAc (2.2 equiv, 1.1 mmol, 184 mg) were weighed into an oven-dried sealed tube. The tube was then evacuated and back-filled with nitrogen. After addition of dry DMSO (0.1 M, 5 mL), the reaction mixture was stirred in a preheated oil bath at 100 °C for 16 h. At the end of this time, the flask was allowed to cool to room temperature, and the contents were diluted with water and extracted with EtOAc. The solution was then concentrated under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/EtOAc, diethyl ether) to afford the desired spiranoid lactone.

7; 8-methyleneoctahydroindeno[3a,4-b]furan-2(3H)-one: General procedure D was adopted using diene carboxylic acid **6** (97 mg, 0.5 mmol). Purification of the residue by flash column chromatography (30% diethyl ether in hexane) yielded pure 8-methyleneoctahydroindeno[3a,4-b]furan-2(3H)-one (70 mg, 73% yield, colorless oil, dr 90:10) as a mixture of diastereomers.



^{1}H NMR (300 MHz, $CDCl_3$): δ 5.04-4.92 (m, 2H), 2.78-2.70 (m, 1H), 2.60-2.55 (m, 1H), 2.49-2.23 (m, 4H), 2.17-2.12 (m, 1H), 1.88-1.66 (m, 4H) and 1.46-1.11 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.7, 145.8, 108.5, 93.6, 45.4, 44.0, 38.5, 37.8, 35.8, 28.8, 23.9 and 23.1. **IR** (neat): 2930, 2858, 2859, 1767, 1640, 1447, 1446, 1423, 1352, 1276, 1176, 930, 912, 883 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{12}H_{16}O_2Na$ ($[M+Na]^+$): 215.1048; found: 215.1041.

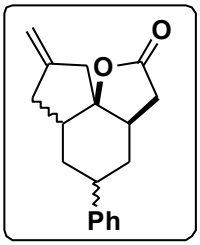
10; 7-methyleneoctahydro-2H-pentaleno[6a,1-b]furan-2-one: General procedure D was applied using the diene carboxylic acid **8a** (90 mg). Purification of the residue by flash column chromatography (30% diethyl ether in hexane) yielded pure 7-methyleneoctahydro-2H-pentaleno[6a,1-b]furan-2-one (38 mg, 43% yield, white solid, dr 75:25) as a mixture of diastereomers.



M.p.: 113-114 ^oC

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.01-4.95 (m, 2H), 2.85-2.76 (m, 1H), 2.56-2.49 (m, 2H), 2.43-2.33 (m, 5H), 2.22-2.09 (m, 1H), 1.78-1.66 (m, 2H), 1.55-1.46 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.5, 152.5, 109.4, 106.4, 54.5, 38.9, 38.0, 37.7, 36.0, 31.8 and 24.0. **IR** (neat): 2957, 2877, 1759, 1651, 1453, 1415, 1327, 1287, 1237, 1162, 1032, 922, 856 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{14}O_2Na$ ($[M+Na]^+$): 201.0891; found: 201.0883.

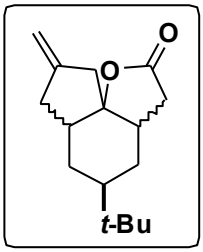
11; 8-methylene-5-phenyloctahydroindeno[3a,4-b]furan-2(3H)-one: General procedure D was adopted using diene carboxylic acid **8b** (135 mg, 05. mmol), $Pd(OAc)_2$ (0.15 equiv.) and AgOAc (3.00 equiv.). Purification of the residue by flash column chromatography (30% diethyl ether in hexane) yielded pure 8-methylene-5-phenyloctahydroindeno[3a,4-b]furan-2(3H)-one (85 mg, 63% yield, yellow solid, dr 63:20:12:5) as a mixture of diastereomers.



M.p.: 97-98 ^oC

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.18 (m, 5H), 5.04-4.93 (m, 2H), 2.85-2.61 (m, 3H), 2.57-2.32 (m, 4H), 2.23-2.16 (m, 1H), 2.10-1.68 (m, 4H) and 1.41-1.22(m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.5, 146.4, 146.0, 145.7, 145.3, 128.5, 126.9, 126.8, 126.5, 126.2, 109.0, 108.8, 108.4, 94.4, 93.0, 92.5, 46.3, 44.8, 43.8, 43.5, 43.0, 40.4, 38.8, 38.6, 38.3, 38.2, 37.5, 37.3, 36.8, 36.5, 36.0, 35.5, 35.3, 34.0 and 30.3. **IR** (neat): 2921, 2852, 1766, 1664, 1601, 1493, 1455, 1346, 1278, 1189, 1149, 908 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{18}H_{20}O_2Na$ ($[M+Na]^+$): 291.1361; found: 291.1353.

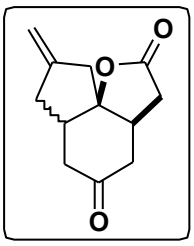
12; 5-(*tert*-butyl)-8-methyleneoctahydroindeno[3a,4-b]furan-2(3H)-one: General procedure D was adopted using diene carboxylic acid **8c** (250 mg, 1.0 mmol). Purification of the residue by flash column chromatography (10% diethyl ether in hexane) yielded pure 5-(*tert*-butyl)-8-methyleneoctahydroindeno[3a,4-b]furan-2(3H)-one (197 mg, 79% white solid, dr 80:14:4:2) as a mixture of diastereomers.



M.p.: 127-128 ^{o}C

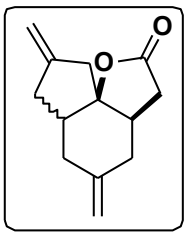
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.99-4.86 (m, 2H), 2.98-2.03 (m, 7H), 1.89-1.11 (m, 6H), 0.85-0.81 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.2, 176.8, 147.3, 146.1, 145.1, 108.7, 108.4, 107.9, 93.4, 90.2, 46.9, 46.6, 45.2, 44.6, 44.0, 43.5, 41.3, 40.4, 40.0, 39.9, 39.2, 38.7, 38.5, 38.2, 38.0_4, 38.0_0, 37.8, 37.1, 36.9, 36.3, 35.7, 35.6, 34.6, 33.9, 32.4, 32.0, 30.8, 30.4, 30.3, 28.8, 27.6, 27.5, 27.4, 27.3, 26.7, 25.3, 25.1, 24.4 and 24.0. **IR** (neat): 2945, 2866, 1771, 1662, 1470, 1432, 1365, 1234, 1181, 1156, 996, 917, 906, 883 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{16}H_{25}O_2$ ($[M+H]^+$): 249.1855; found: 249.1845.

13; 8-methylenehexahydroindeno[3a,4-b]furan-2,5(3H,6H)-dione: General procedure D was applied using diene carboxylic acid **8d** (104 mg). Purification of the residue by flash column chromatography (60% diethyl ether in hexane) yielded pure 8-methylenehexahydroindeno[3a,4-b]furan-2,5(3H,6H)-dione (59 mg, 57% yield, pale yellow oil, dr 91:9) as a mixture of diastereomers.



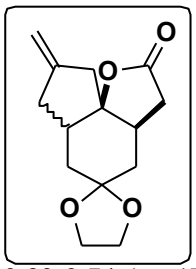
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.11-4.99 (m, 2H), 2.98-2.90 (m, 2H), 2.83-2.75 (m, 2H), 2.70-2.30 (m, 7H), 2.21-2.15 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 209.0, 174.7, 145.6, 109.3, 92.7, 44.2, 43.8, 42.9, 38.9, 37.3, 36.8 and 36.1. **IR** (neat): 2945, 2832, 1762, 1712, 1640, 1421, 1282, 1250, 1195, 1174, 1020, 923, 891 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{12}H_{14}O_3Na$ ($[M+Na]^+$): 229.0841; found: 229.0833.

14; 5,8-dimethyleneoctahydroindeno[3a,4-b]furan-2(3H)-one: General procedure D was adopted using diene carboxylic acid **8e** (93 mg, 0.45 mmol). Purification of the residue by flash column chromatography (90% DCM in hexane) yielded pure 5,8-dimethyleneoctahydroindeno[3a,4-b]furan-2(3H)-one (55 mg, 60% yield, pale yellow oil, *dr* 89:11) as a mixture of diastereomers.



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.99 and 4.93 (2 br s, 2H), 4.82-4.80 (2 br s, 2H), 2.86-2.78 (m, 1H), 2.67-2.32 (m, 7H), 2.28-2.09 (m, 3H) and 1.94-1.85 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.4, 146.4, 143.2, 111.4, 108.6, 94.2, 44.3, 44.1, 37.9, 37.5, 37.4, 35.9 and 31.4. **IR** (neat): 2990, 2937, 2850, 1770, 1651, 1421, 1277, 1226, 1186, 1150, 1118, 966, 921, 881 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{13}H_{16}O_2Na$ ($[M+Na]^+$): 227.1048; found: 227.1040.

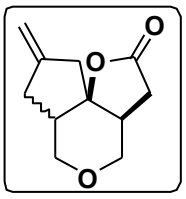
15; 8-methylenehexahydro-6H-spiro[indeno[3a,4-b]furan-5,2'-[1,3]dioxolan]-2(3H)-one: General procedure D was applied using diene carboxylic acid **8f** (126 mg). Purification of the residue by flash column chromatography (50% diethyl ether in hexane) yielded pure 8-methylenehexahydro-6H-spiro[indeno[3a,4-b]furan-5,2'-[1,3]dioxolan]-2(3H)-one (91 mg, 73% yield, white solid, dr 89:11) as a mixture of diastereomers.



M.p.: 118-119 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.00-4.95 (m, 2H), 3.95-3.94 (m, 4H), 2.82-2.74 (m, 1H), 2.61-2.18 (m, 7H), 1.95-1.87 (m, 1H), 1.77-1.74 (m, 2H), 1.46-1.37 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.2, 145.8, 109.0, 108.4, 92.7, 64.5, 64.4, 43.1, 42.8, 38.2, 37.4, 36.4, 35.0 and 33.0. **IR** (neat): 2953, 2923, 2865, 1751, 1665, 1451, 1310, 1194, 1125, 1065, 944, 911, cm^{-1}. **HRMS** (*m/z*) calcd for $C_{14}H_{18}O_4Na$ ($[M+Na]^+$): 273.1103; found: 273.1094.

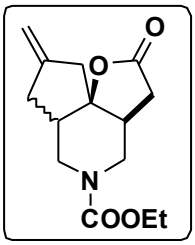
16; 8-methylenehexahydro-6H-cyclopenta[c]furo[2,3-d]pyran-2(3H)-one: General procedure D was applied using diene carboxylic acid **8g** (98 mg). Purification of the residue by flash column chromatography (40% ethyl acetate in hexane) yielded pure 8-methylenehexahydro-6H-cyclopenta[c]furo[2,3-d]pyran-2(3H)-one (67 mg, 70% yield, white solid, dr 92:8) as a mixture of diastereomers.



M.p.: 86-87 ^{o}C

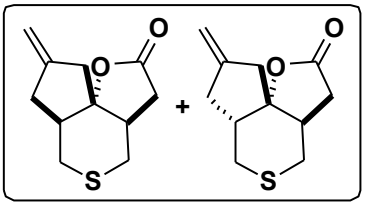
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.07-5.02 (m, 2H), 4.02-3.92 (m, 2H), 3.59-3.52 (m, 1H), 3.17-3.10 (m, 1H), 2.80-2.54 (m, 3H) and 2.52-2.06 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 175.5, 144.4, 109.7, 91.3, 67.2, 65.6, 43.4, 43.4, 37.8, 34.2 and 31.8. **IR** (neat): 2950, 2921, 2851, 1768, 1640, 1447, 1423, 1363, 1272, 1156, 1073, 915 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{14}O_3Na$ ($[M+Na]^+$): 217.0841; found: 217.0833.

17; Ethyl 8-methylene-2-oxooctahydrocyclopenta[c]furo[2,3-d]pyridine-5(6H)-carboxylate: General procedure D was applied using diene carboxylic acid **8h** (133 mg). Purification of the residue by flash column chromatography (40% diethyl ether in hexane) yielded pure ethyl 8-methylene-2-oxooctahydrocyclopenta[c]furo[2,3-d]pyridine-5(6H)-carboxylate (91 mg, 70% yield, pale yellow oil, dr 92:8) as mixture of diastereomers.



^{1}H NMR (300 MHz, $CDCl_3$): δ 5.01 and 4.95 (2 br s, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.66-3.20 (m, 4H), 2.89-2.80 (m, 1H), 2.70-2.20 (m, 7H) and 1.22 (t, *J* = 3.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 175.2, 169.4, 145.1, 109.4, 92.3, 61.7, 44.5, 44.2, 43.9, 42.7, 41.9, 37.1, 34.8, 33.6, 28.6, 28.2, 24.4, 24.3, 23.8 and 14.6. **IR** (neat): 2960, 2923, 2850, 1768, 1690, 1466, 1421, 1353, 1310, 1272, 1207, 1163, 1120, 1027, 972, 921, 885 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{14}H_{19}NO_4Na$ ($[M+Na]^+$): 288.1212; found: 288.1202.

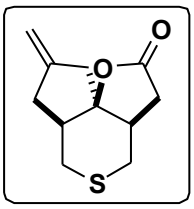
18(a-c); (6aR)-8-methylenehexahydro-6H-cyclopenta[4,5]thiopyrano[4,3-b]furan-2(3H)-one: General procedure D was adopted using diene carboxylic acid **8i** (96 mg, 0.44 mmol). Purification of the residue by flash column chromatography (30% ethylacetate in hexane) yielded the mixture of (6aR)-8-methylenehexahydro-6H-



cyclopenta[4,5]thiopyrano[4,3-b]furan-2(3H)-one (**18a** + **18c**; 55 mg, 59% yield, gummy liquid) and pure (3aR,6aS,9aR)-8-methylenehexahydro-6H-cyclopenta[4,5]thiopyrano [4,3-b]furan-2(3H)-one **18b** (19 mg, 21% yield, white needles).

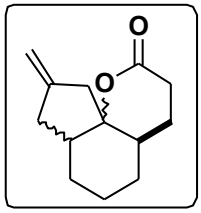
18a+18c [**18a-c**; dr 48:33:19]: **^{1}H NMR** (300 MHz, $CDCl_3$): Mixture of diastereomers: δ 2.97-2.41 (m, 18H), 2.38-2.24 (m, 4H), 2.23-2.09 (m, 2H); major diastereoisomer: δ 5.07 (d, *J* = 14.0 Hz, 2H); minor diastereomer: δ 4.98 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): major diastereoisomer: δ 174.3, 144.5, 110.9, 94.6, 44.3, 44.0, 37.7, 35.2, 34.8, 30.6 and 27.0; minor diastereoisomer, characteristic signals: δ 110.0, 109.1, 43.5, 37.4, 32.8, 30.9 and 28.3. **IR** (neat): 2984, 2900, 1784, 1735, 1650 (w), 1446, 1372, 1230, 1177, 1136, 1044, 1014, 938, 915 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{14}O_2SNa$ ($[M+Na]^+$): 233.0612; found: 233.0604.

18b [**18a-c**; dr 48:33:19]: **M.p.:** 94-95 ^{o}C.



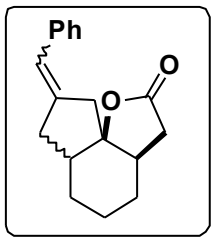
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.01-4.96 (m, 2H), 2.97-2.85 (m, 2H), 2.75-2.66 (m, 2H), 2.75-2.66 (m, 4H), 2.62-2.49 (m, 2H), 2.44-2.31 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 175.6, 144.0, 108.9, 91.8, 45.4, 42.6, 38.4, 36.6, 36.5, 29.1 and 24.5. **IR** (neat): 2919, 2810, 1761, 1640, 1428, 1319, 1273, 1213, 1154, 1114, 912, 881 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{11}H_{14}O_2SNa$ ($[M+Na]^+$): 233.0612; found: 233.0605.

21; 9-methylenedecahydro-2H-cyclopenta[i]chromen-2-one: General procedure D was applied using diene carboxylic acid **19a** (104 mg). Purification of the residue by flash column chromatography (90% DCM in hexane) yielded pure 9-methylenedecahydro-2H-cyclopenta[i]chromen-2-one (68 mg, 66% yield, colorless oil, dr 46:37:17) as a mixture of diastereomers.



^{1}H NMR (300 MHz, $CDCl_3$): δ 5.01-4.92 (m, 2H), 2.95-2.73 (m, 1H), 2.69-2.21 (m, 5H), 2.16-1.99 (m, 1H), 1.87-1.69 (m, 4H), 1.62-1.30 (m, 4H) and 1.15-0.94 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.3, 172.0, 171.7, 147.0, 146.3, 109.3, 108.6, 108.3, 93.7, 91.8, 90.5, 48.0, 45.2, 44.6, 43.8, 42.9, 38.7, 37.5, 36.8, 36.5, 35.2_0, 35.1_6, 32.4, 30.0, 29.4, 29.1, 28.0, 27.6, 26.7, 25.9, 25.8, 25.1, 24.5, 24.0, 23.7, 22.7, 22.5 and 19.5. **IR** (neat): 2927, 2856, 1723, 1620, 1447, 1350, 1277, 1233, 1168, 1026, 981, 880 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{13}H_{18}O_2Na$ ($[M+Na]^+$): 229.1204; found: 229.1195.

22; 8-benzylideneoctahydroindeno[3a,4-b]furan-2(3H)-one: General procedure D was applied using diene carboxylic acid **19b** (135 mg). Purification of the residue by flash column chromatography (10% ethyl acetate in hexane) yielded pure 8-benzylideneoctahydroindeno[3a,4-b]furan-2(3H)-one (107 mg, 80% yield, white solid, dr 98:2) as a mixture of diastereomers.

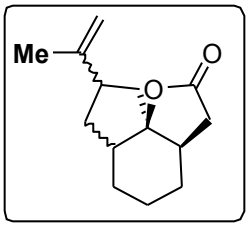


M.p.: 123-124 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.18 (m, 5H), 6.36 (s, 1H), 2.85-2.74 (m, 3H), 2.64-2.52 (m, 2H), 2.36-2.28 (m, 1H), 2.25-2.16 (2 br s, 1H), 1.92-1.71 (m, 4H), 1.56-1.41 (m, 1H) and 1.38-1.15 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.9, 139.4, 138.02, 128.2, 128.0, 126.2, 124.2, 92.7, 45.9, 45.7, 38.6, 37.6, 34.9, 28.9, 24.1 and 23.3. **IR** (neat): 2938, 2859, 1764, 1620, 1560, 1490, 1447, 1422, 1274, 1235,

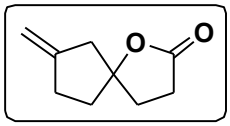
1179, 1139, 992, 935, 903, 880 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{18}H_{20}O_2Na$ ($[M+Na]^+$): 291.1361; found: 291.1359.

23; 8-(prop-1-en-2-yl)octahydroindeno[3a,4-b]furan-2(3H)-one: General procedure D was applied using diene carboxylic acid **24** (111 mg). Purification of the residue by flash column chromatography (30% diethyl ether in hexane) yielded pure 8-(prop-1-en-2-yl)octahydroindeno[3a,4-b]furan-2(3H)-one (72 mg, 65% yield, pale yellow oil, dr 57:19:11:13) as a mixture of diastereomers.



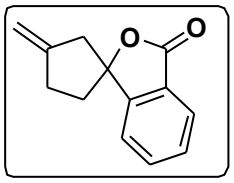
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.74-4.66 (m, 2H), 2.81-2.47 (m, 2H), 2.24-2.10 (m, 2H), 1.93-1.78 (m, 3H), 1.71 (br s, 4H), 1.63-1.56 (m, 3H), 1.41-1.24 (m, 3H), 1.14-1.07 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 177.1, 177.0, 147.7, 109.6, 108.4, 94.2, 46.2, 45.2, 44.6, 43.2, 42.7, 41.9, 41.5, 41.2, 40.9, 38.7, 38.6, 38.5, 37.8, 35.2, 34.6, 34.2, 33.7, 32.7, 31.1, 28.9_4, 28.9_1, 28.8, 27.4, 25.2, 24.2, 24.1, 24.0, 23.6, 23.3, 23.0, 20.9, 20.5 and 20.1. **IR** (neat): 2931, , 2857, 1766, 1643, 1445, 1424, 1352, 1235, 1180, 1152, 934, 907, 883 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{14}H_{20}O_2Na$ ($[M+Na]^+$): 243.1361; found: 243.1353.

27; 7-methylene-1-oxaspiro[4.4]nonan-2-one: General procedure D was applied using diene carboxylic acid **26a** (77 mg). Purification of the residue by flash column chromatography (30% diethyl ether in hexane) yielded pure 7-methylene-1-oxaspiro[4.4]nonan-2-one (62 mg, 82% yield, pale yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.90-4.93 (m, 2H), 2.73-2.43 (m, 6H), 2.21-2.14 (m, 2H), 2.09-2.02 (m, 1H), 1.86-1.78 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.5, 147.5, 107.7, 93.3, 44.8, 38.0, 31.7, 30.6 and 29.5. **IR** (neat): 2948, 1764, 1661, 1419, 1339, 1271, 1161, 1022 930, 879 cm^{-1}. **HRMS** (*m/z*) calcd for $C_9H_{12}O_2Na$ ($[M+Na]^+$): 175.0735; found: 175.0728.

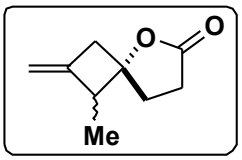
28; 3-methylene-3'H-spiro[cyclopentane-1,1'-isobenzofuran]-3'-one: General procedure D was applied using diene carboxylic acid **26b** (101 mg). Purification of the residue by flash column chromatography (15% diethyl ether in hexane) yielded pure 3-methylene-3'H-spiro [cyclopentane-1,1'-isobenzofuran]-3'-one (76 mg, 76% yield, white solid).



M.p.: 89-90 ^oC

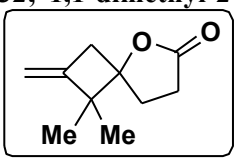
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85(d, *J*=7.6, 1H), 7.67 (t, *J*=7.5, 1H), 7.51 (t, *J*=7.5, 1H), 7.42 (d, *J*=7.6, 1H), 5.05 and 5.00 (2 br s, 2H), 2.92-2.62 (m, 4H), 2.29-2.10 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.6, 151.7, 147.7, 134.2, 129.2, 126.1, 125.5, 121.0, 108.1, 93.9, 45.4, 39.2 and 31.5. **IR** (neat): 2927, 1754, 1662, 1598, 1465, 1416, 1281, 1244, 1191, 1092, 1012, 993, 910, 885, 759 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{13}H_{12}O_2Na$ ($[M+Na]^+$): 223.0735; found: 223.0727.

31; 1-methyl-2-methylene-5-oxaspiro[3.4]octan-6-one: General procedure D was applied using diene carboxylic acid **29a** (77 mg). Purification of the residue by flash column chromatography (60% DCM in hexane) yielded 1-methyl-2-methylene-5-oxaspiro[3.4]octan-6-one (20 mg, 26% yield, colorless volatile oil, dr 50:50) as an inseparable mixture of two diastereomers and reduced product (~10%; confirmed by GCMS analysis).



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.94-4.91 (m, 2H), 3.16-3.07 (m, 1H), 2.87-2.66 (m, 1H), 2.58-2.48 (m, 2H), 2.36-2.25 (m, 2H), 2.19-1.95 (m, 1H), 1.17 and 1.09 (2 d, 3H, *J* = 7.2 Hz and 6.9 Hz respectively). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.4, 145.9, 143.8, 106.7, 105.6, 84.8, 84.3, 49.7, 48.0, 43.8, 42.6, 33.5, 29.0, 28.8, 27.3, 13.3 and 11.7. **IR** (neat): 2963, 2926, 1772, 1682, 1452, 1420, 1275, 1180, 1141, 1077, 912, 877 cm^{-1}. **HRMS** (*m/z*) calcd for $C_9H_{12}O_2Na$ ($[M+Na]^+$): 175.0735; found: 175.0732.

32; 1,1-dimethyl-2-methylene-5-oxaspiro[3.4]octan-6-one: General procedure D was applied using diene carboxylic acid **29b** (84 mg). Purification of the residue by flash column chromatography (30% ethyl acetate in hexane) yielded pure 1,1-dimethyl-2-methylene-5-oxaspiro [3.4]octan-6-one (66 mg, 79% yield, pale yellow oil).



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.94-4.91 (m, 2H), 3.13-3.07 (m, 1H), 2.87-2.66 (m, 1H), 2.58-2.49 (m, 2H), 2.36-2.25 (m, 2H), 2.05-2.02 (m, 1H), 1.17 and 1.09 (2 d, 3H, *J* = 7.2 Hz and 6.9 Hz respectively). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.6, 176.4, 145.9, 143.8, 106.7, 105.6, 84.8, 84.3, 49.7, 48.0, 43.8, 42.6, 33.5, 29.0, 28.8, 27.3, 13.3 and 11.7. **IR** (neat): 2963, 2930, 2850, 1771, 1650, 1461, 1421, 1266, 1166, 1133, 1032, 911, 881 cm^{-1}. **HRMS** (*m/z*) calcd for $C_{10}H_{14}O_2Na$ ($[M+Na]^+$): 189.0891; found: 189.0886.

5. References:

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6. X-Ray Crystallography:

X-ray Crystal Structure for 18b (CCDC. 1437227)

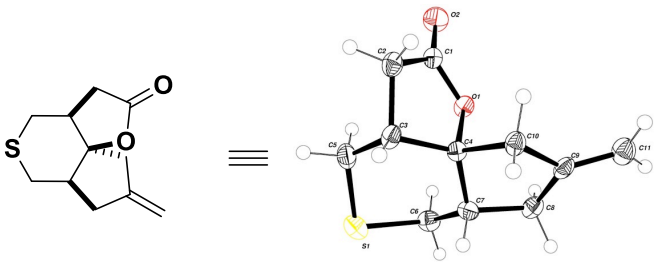
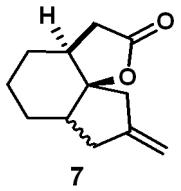


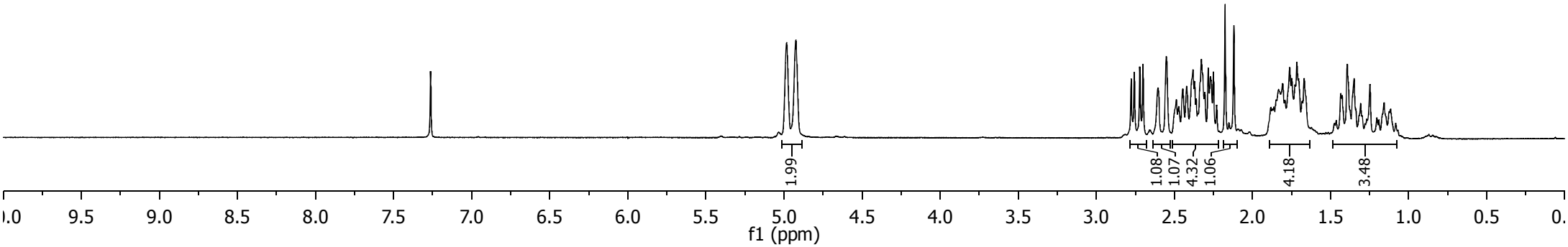
Table 1. Crystal data and structure refinement for **18b**

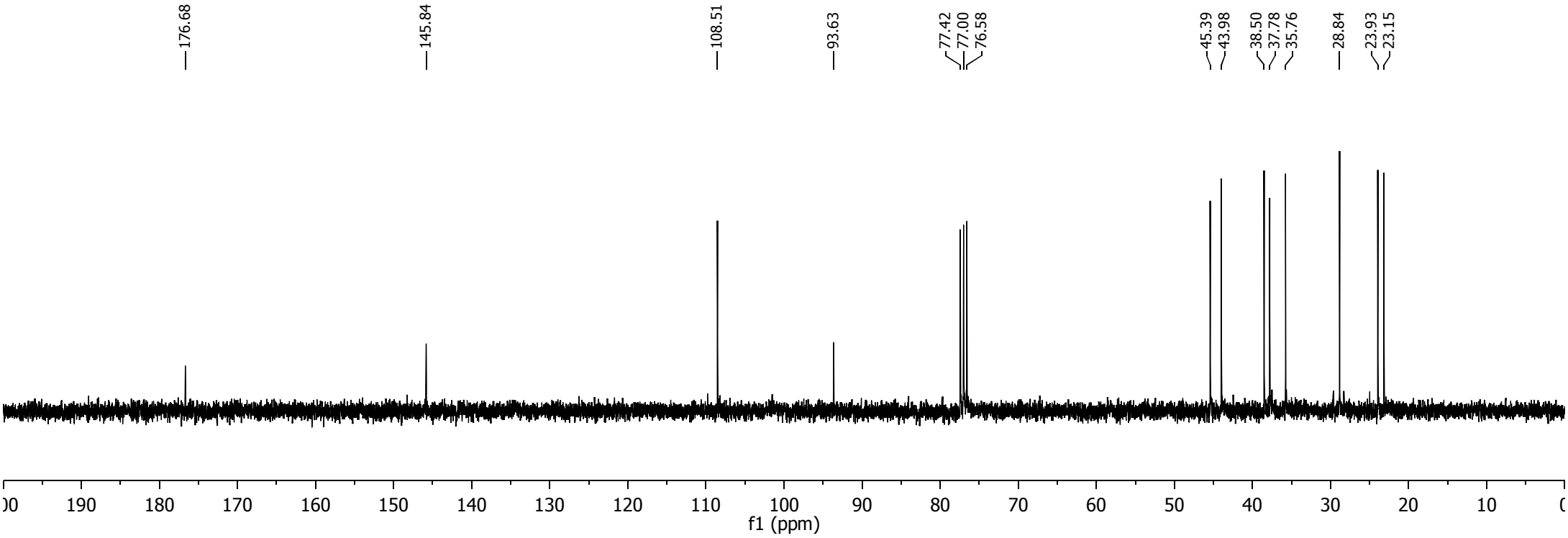
Empirical formula	C11 H14 O2 S	
Formula weight	210.28	
Temperature	173(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 23.952(5) Å	α= 90°.
	b = 5.752(1) Å	β= 100.445(4)°.
	c = 14.804(3) Å	γ= 90°.
Volume	2005.8(7) $Å^3$	
Z	8	
Density (calculated)	1.393 Mg/m^3	
Absorption coefficient	0.292 mm^{-1}	
F(000)	896	
Crystal size	0.43 x 0.07 x 0.07 mm^3	
Theta range for data collection	2.59 to 27.00°.	
Index ranges	-30<=h<=30, -7<=k<=7, -18<=l<=18	
Reflections collected	21059	
Independent reflections	4367 [R(int) = 0.0863]	
Completeness to theta = 27.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9798 and 0.8847	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4367 / 0 / 253	
Goodness-of-fit on F^2	1.194	
Final R indices [I>2sigma(I)]	R1 = 0.0918, wR2 = 0.1685	
R indices (all data)	R1 = 0.1249, wR2 = 0.1804	
Largest diff. peak and hole	0.794 and -0.324 $e.Å^{-3}$	

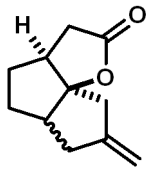


7

Mixture of 2 diastereoisomers

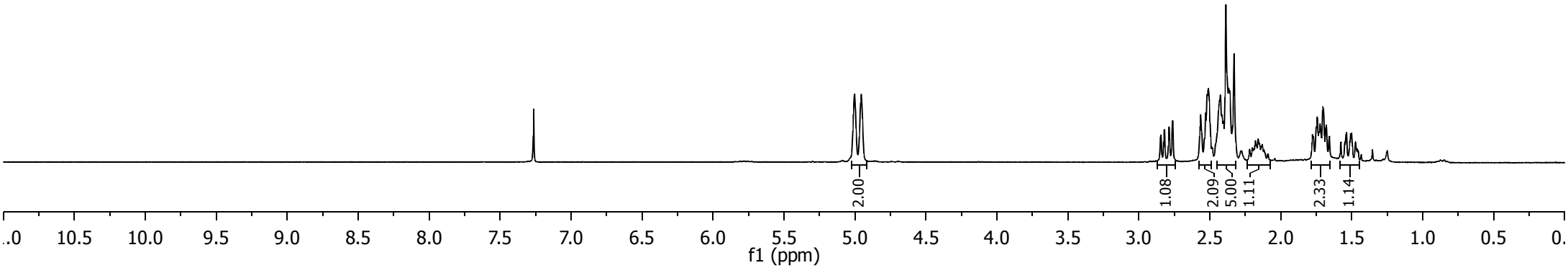


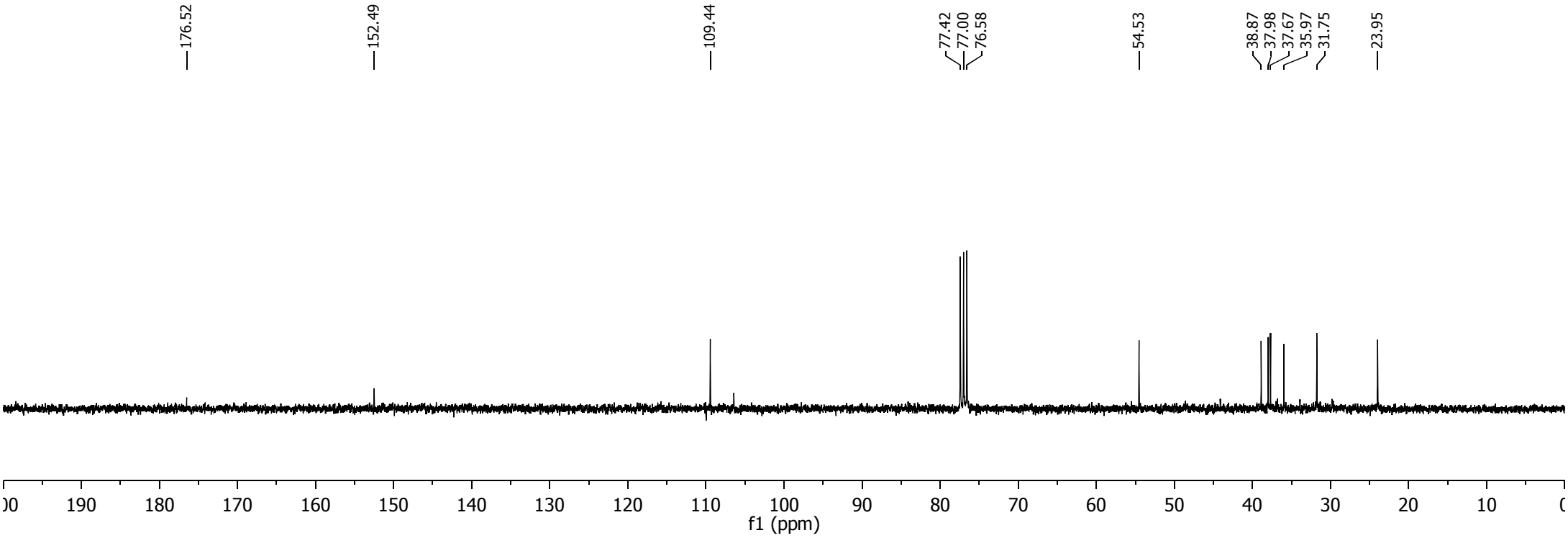


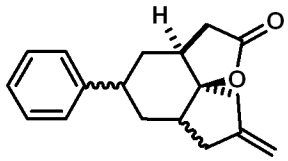


10

Mixture of 2 diastereoisomers

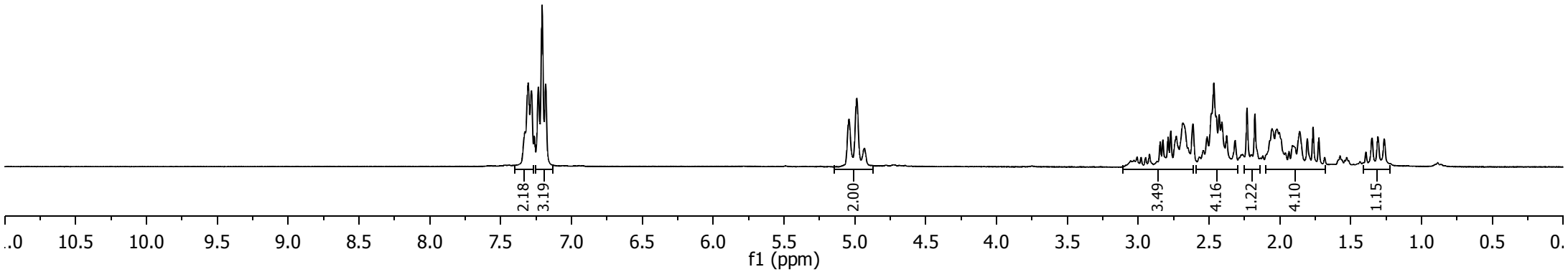


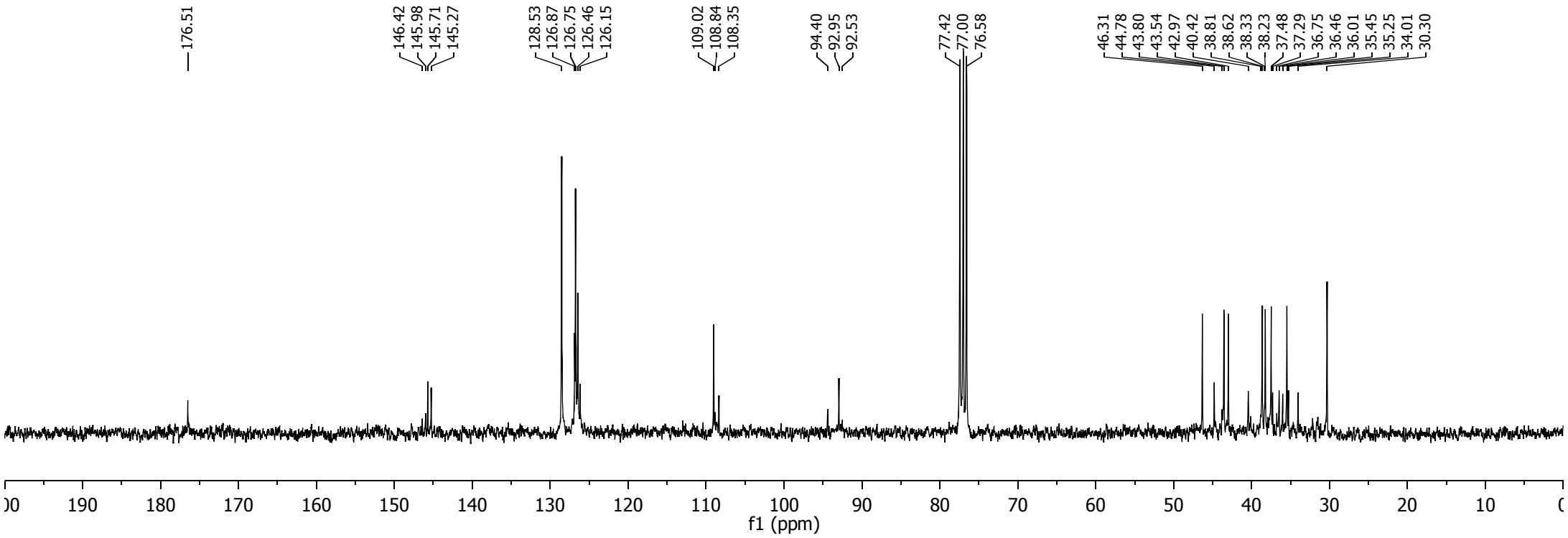


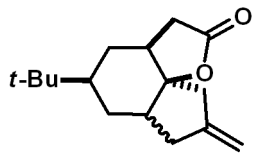


11

Mixture of 4 diastereoisomers

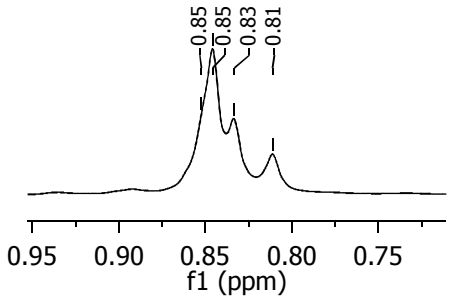


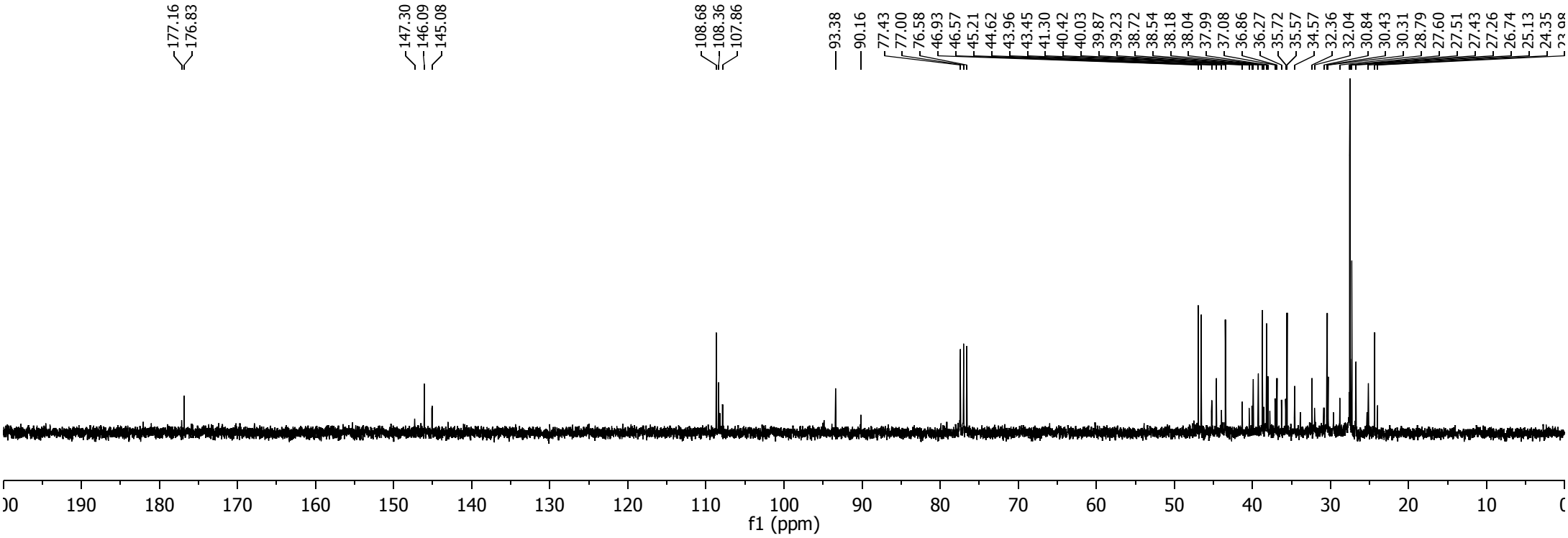


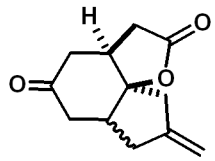


12

Mixture of 4 diastereoisomers

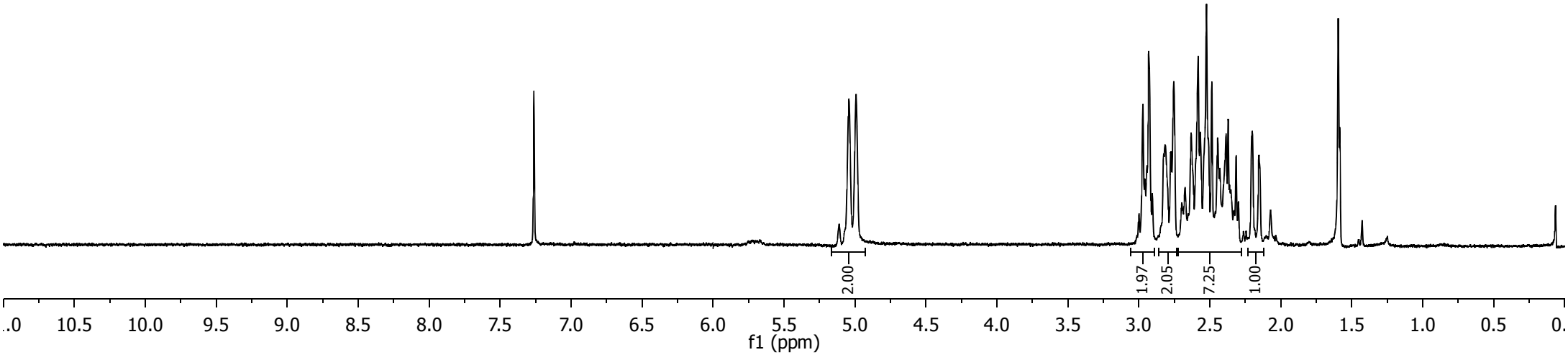


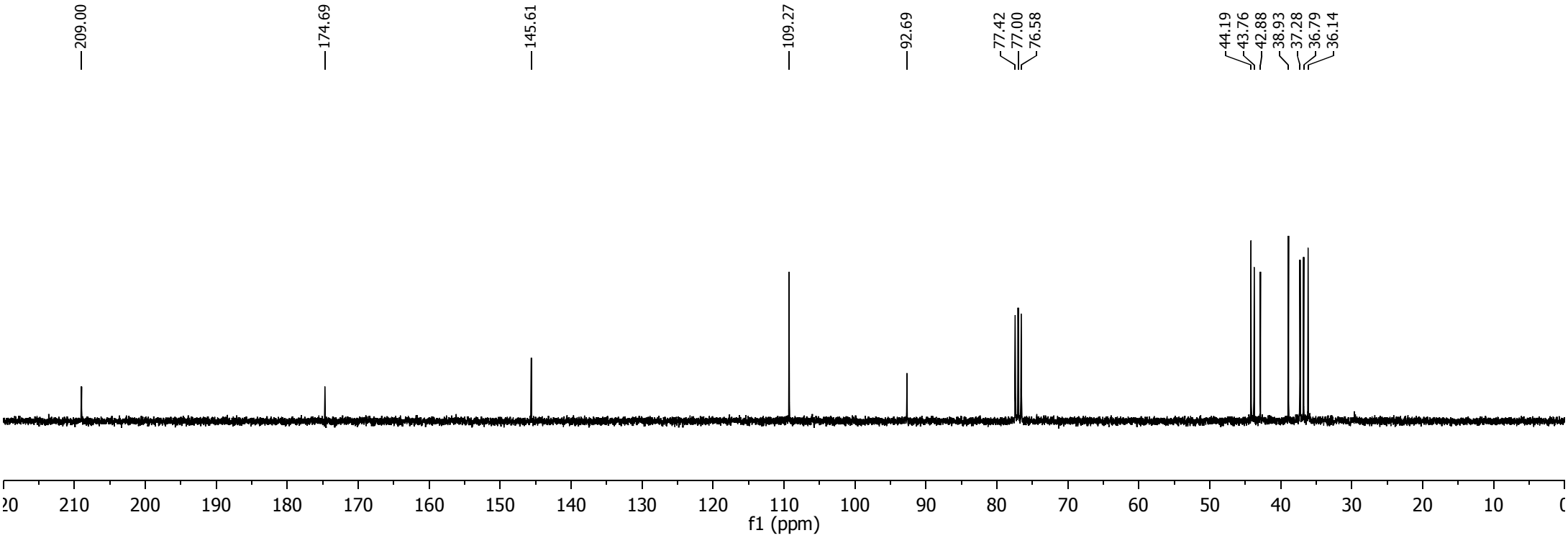


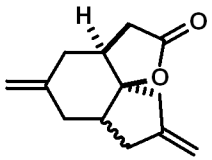


Mixture of 2 diastereoisomers

13

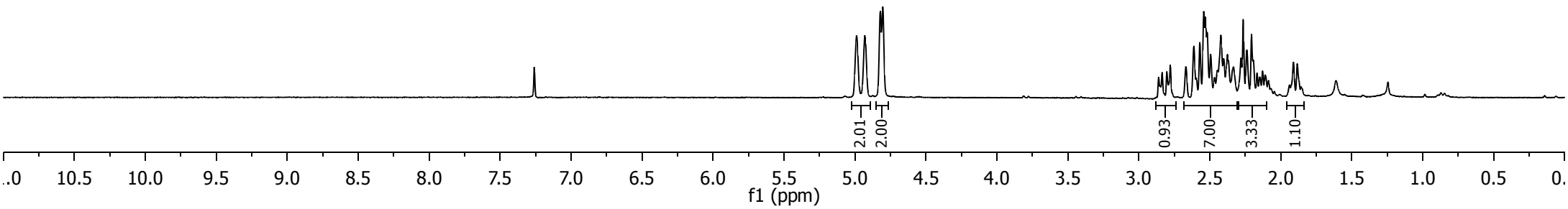


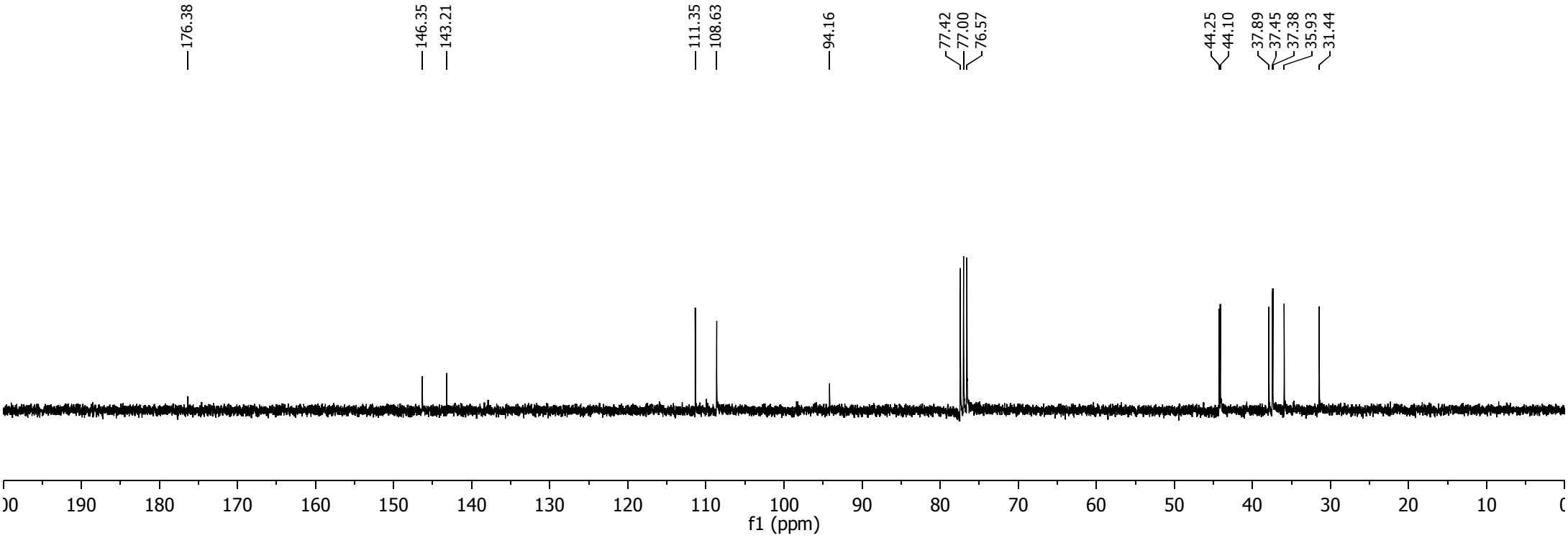


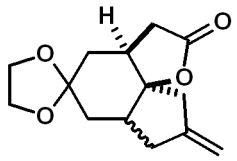


14

Mixture of 2 diastereoisomers

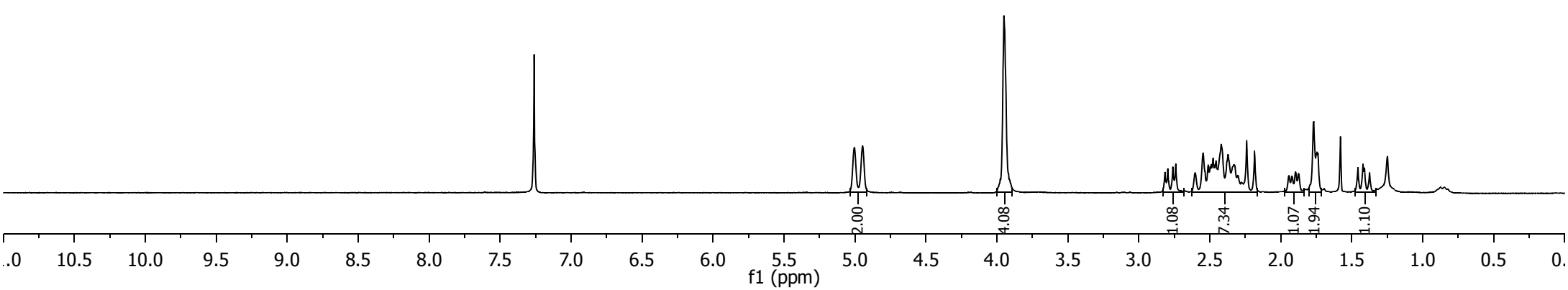


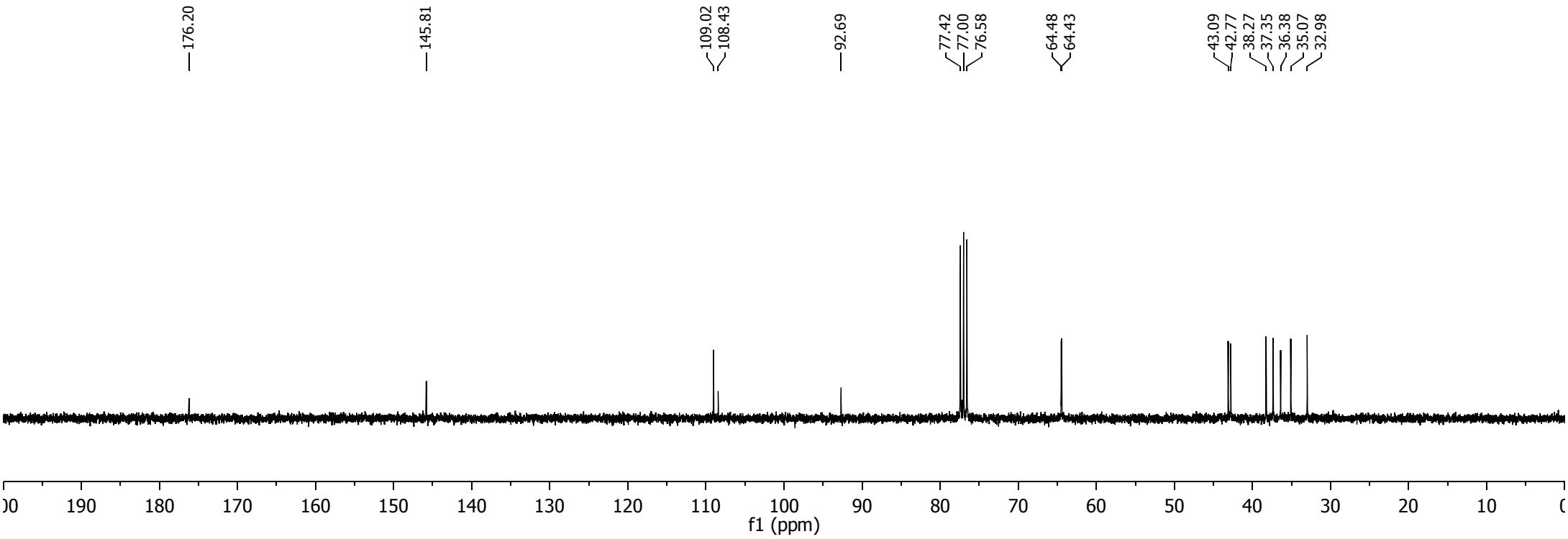


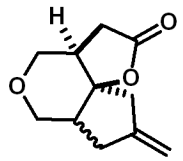


Mixture of 2 diastereoisomers

15

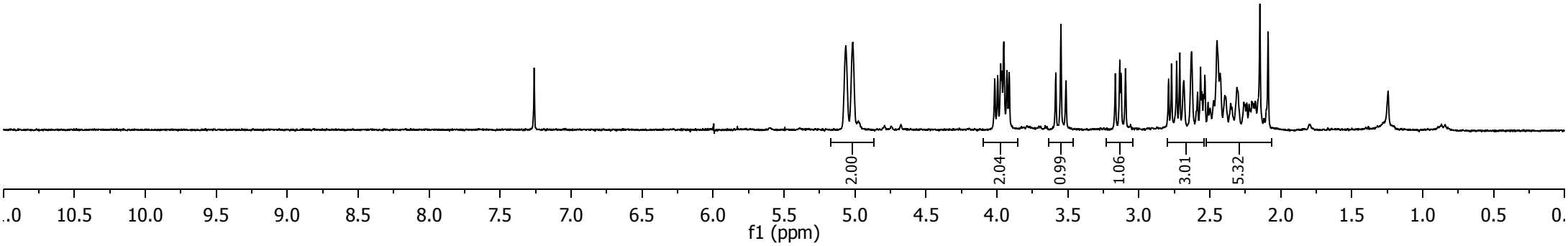


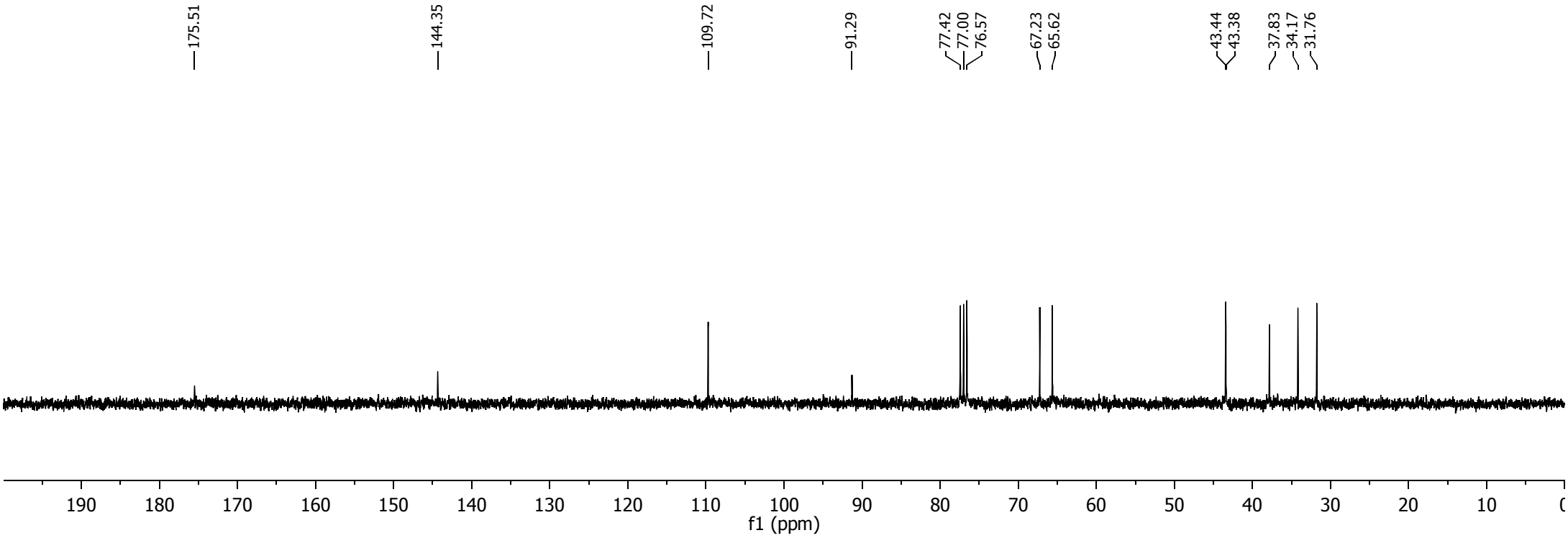


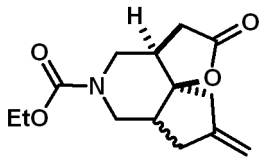


16

Mixture of 2 diastereoisomers

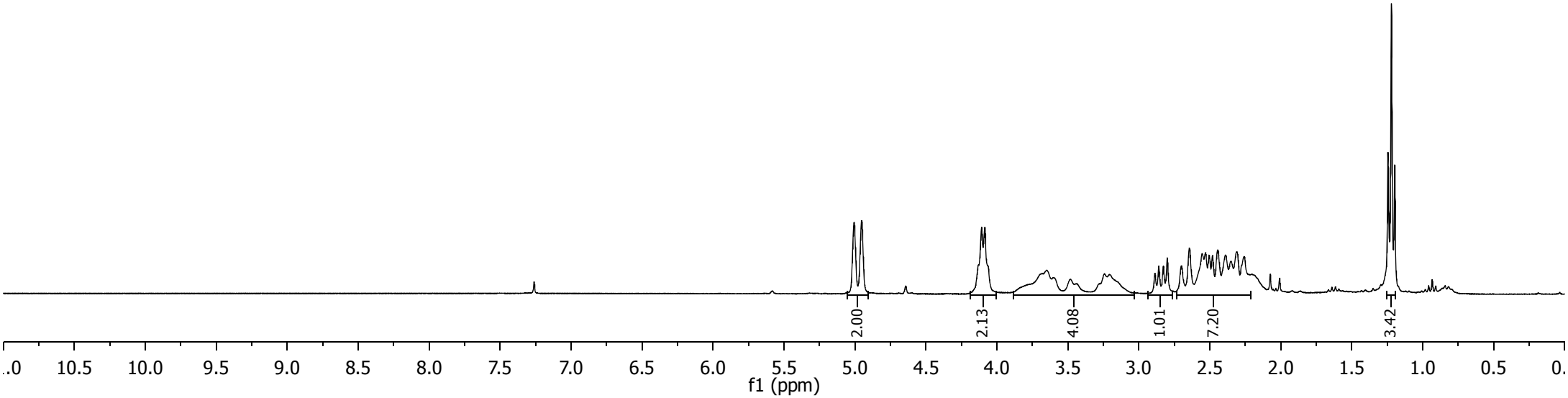


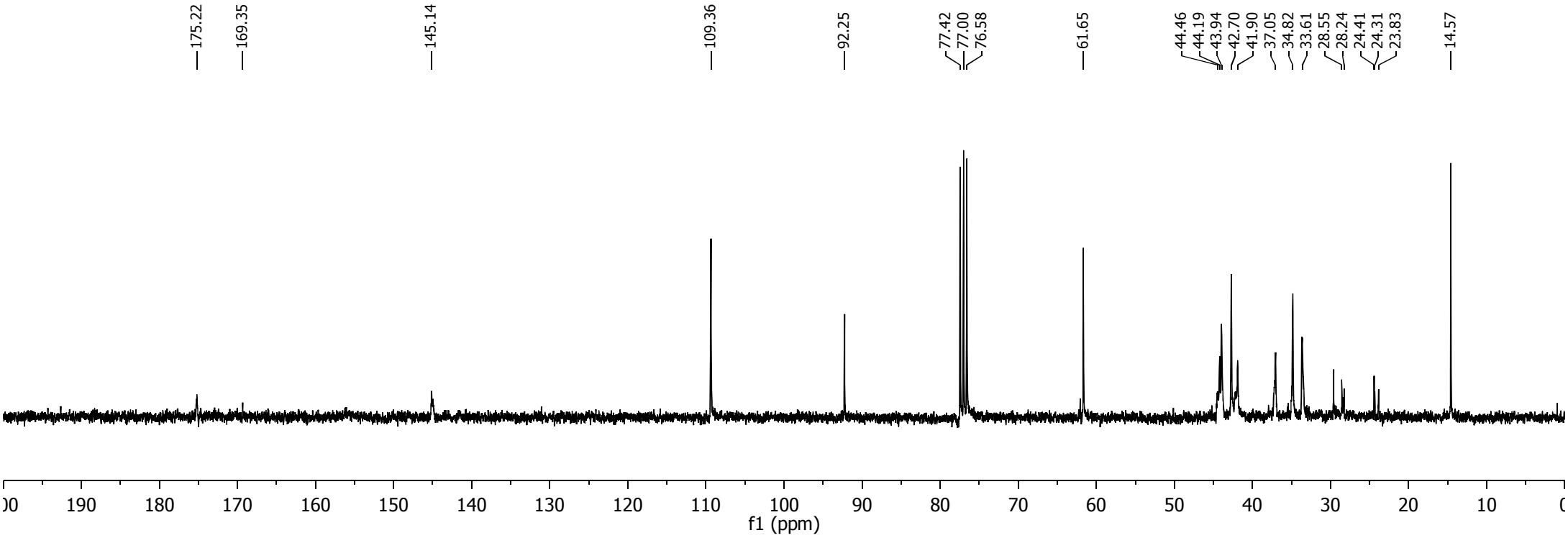


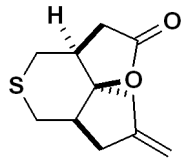


17

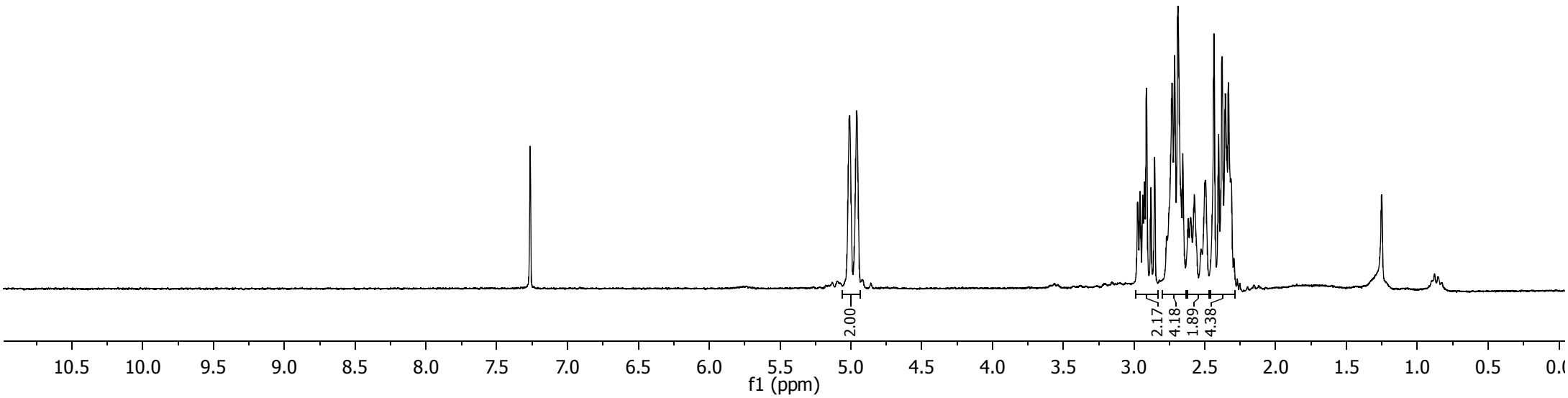
Mixture of 2 diastereoisomers

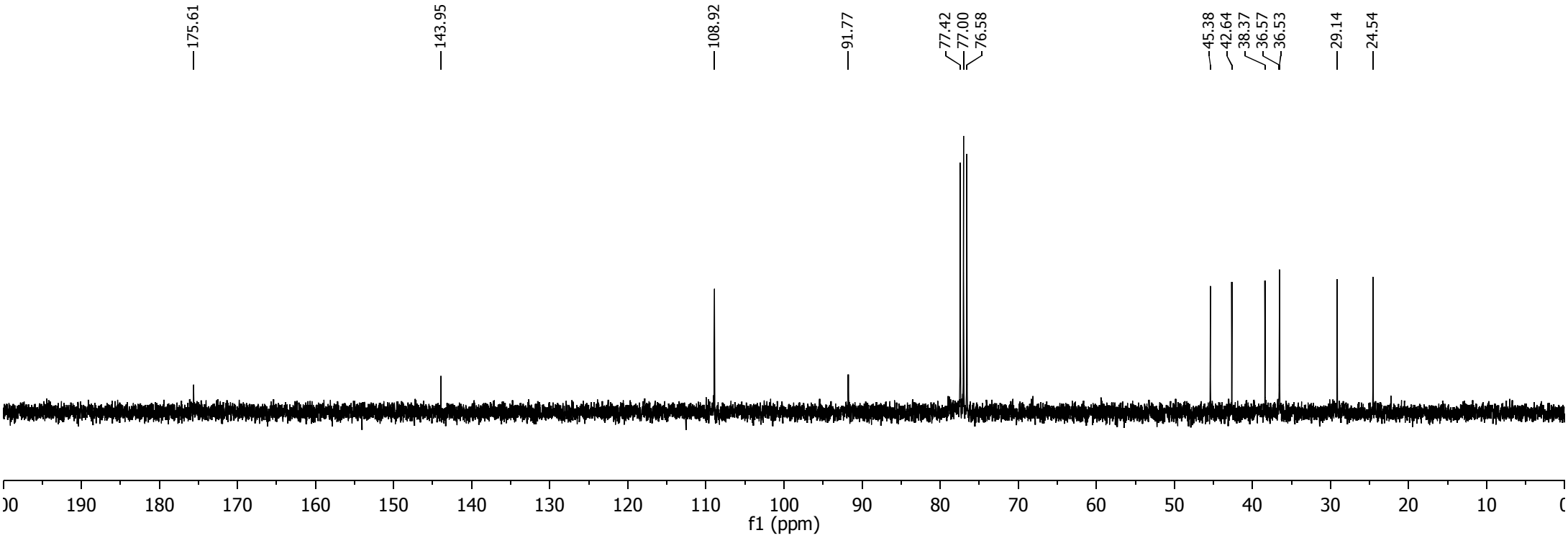


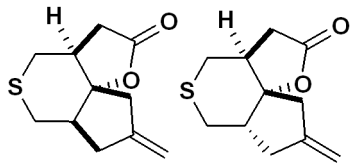



H
O
S
O

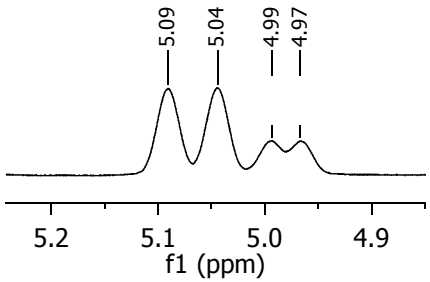
18b

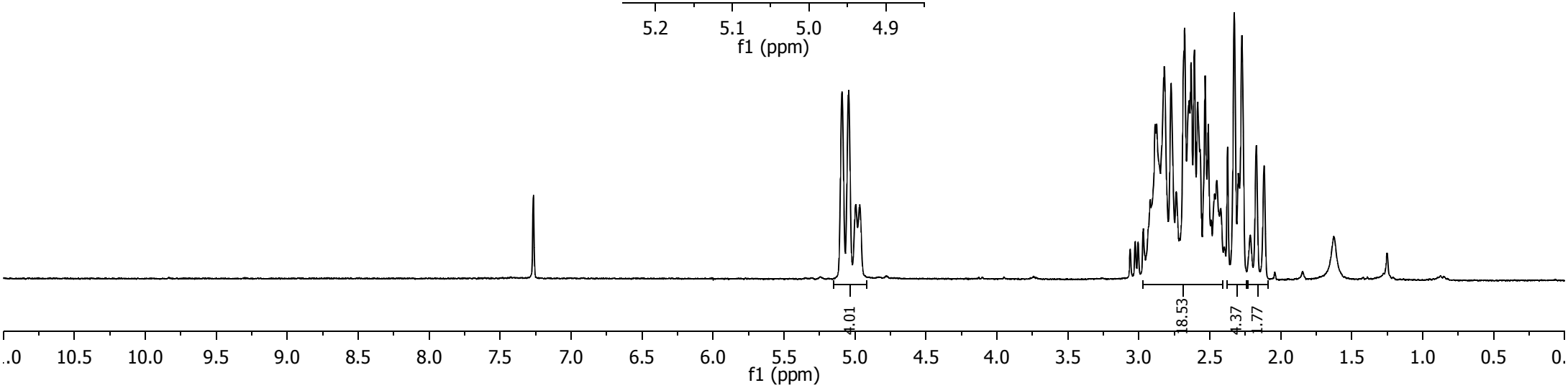

2.00
2.17
4.18
1.89
4.38
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

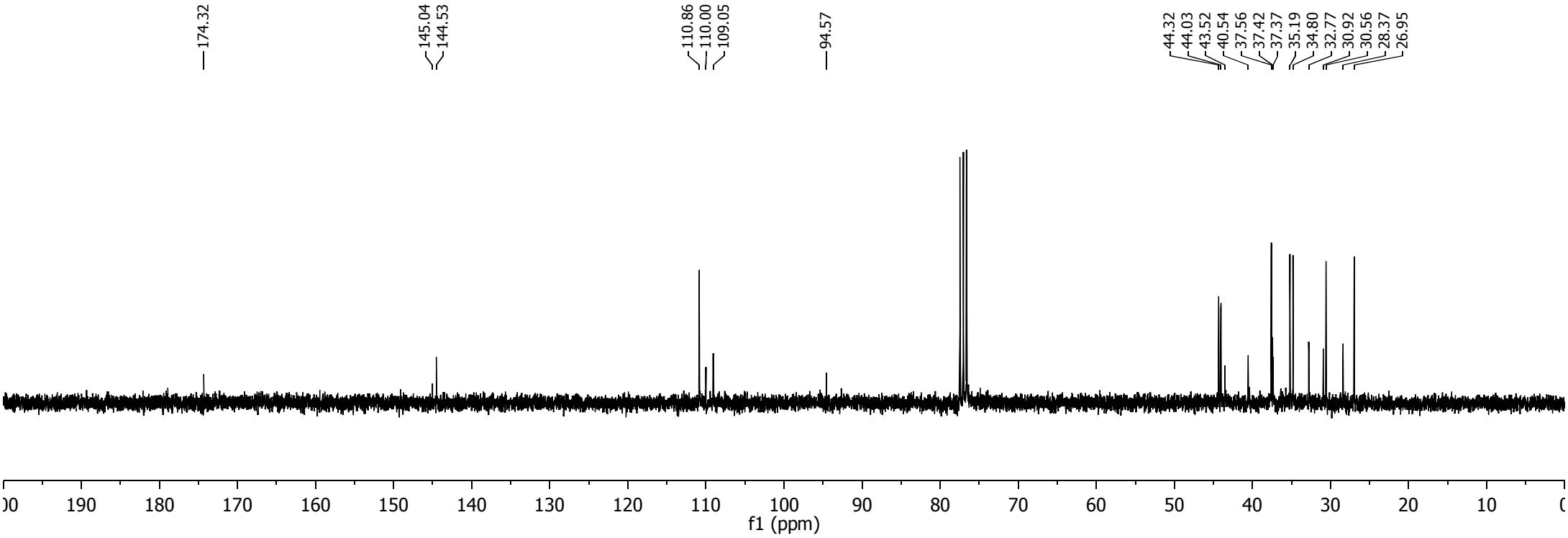

175.61
143.95
108.92
91.77
77.42
77.00
76.58
45.38
42.64
38.37
36.57
36.53
29.14
24.54
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

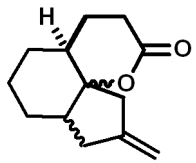

H
O
S
O
H
O
S
O

18a+c


5.09
5.04
4.99
4.97
5.2
5.1
5.0
4.9
f1 (ppm)

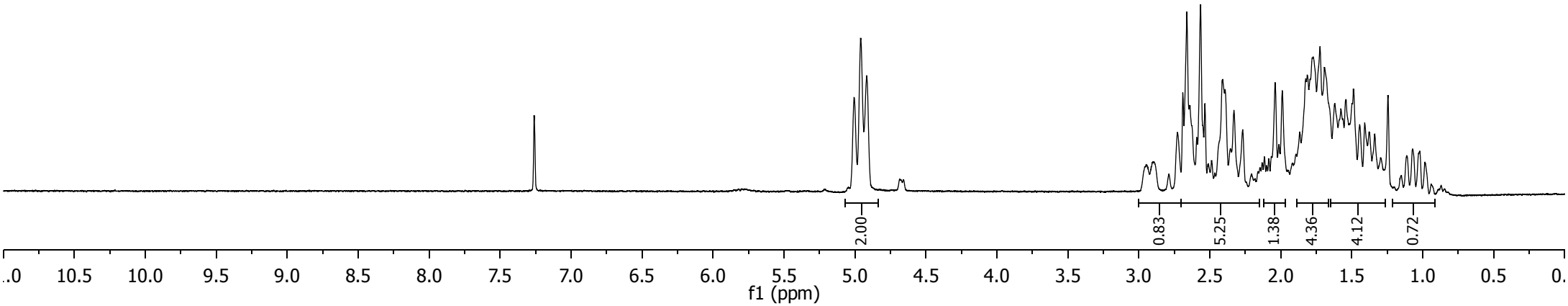

4.01
18.53
4.37
1.77
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

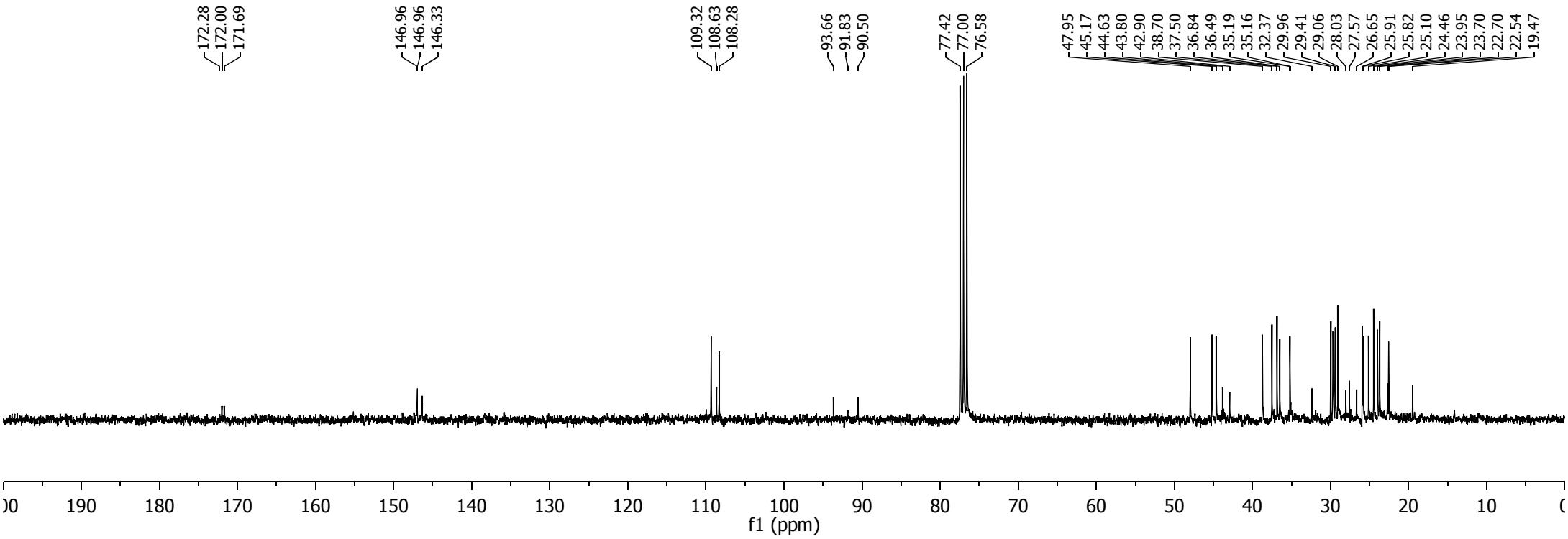

174.32
145.04
144.53
110.86
110.00
109.05
94.57
44.32
44.03
43.52
40.54
37.56
37.42
37.37
35.19
34.80
32.77
30.92
30.56
28.37
26.95
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

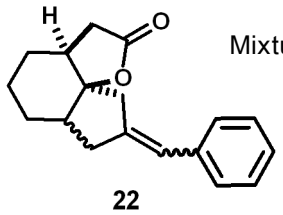


Mixture of 3 diastereoisomers

21

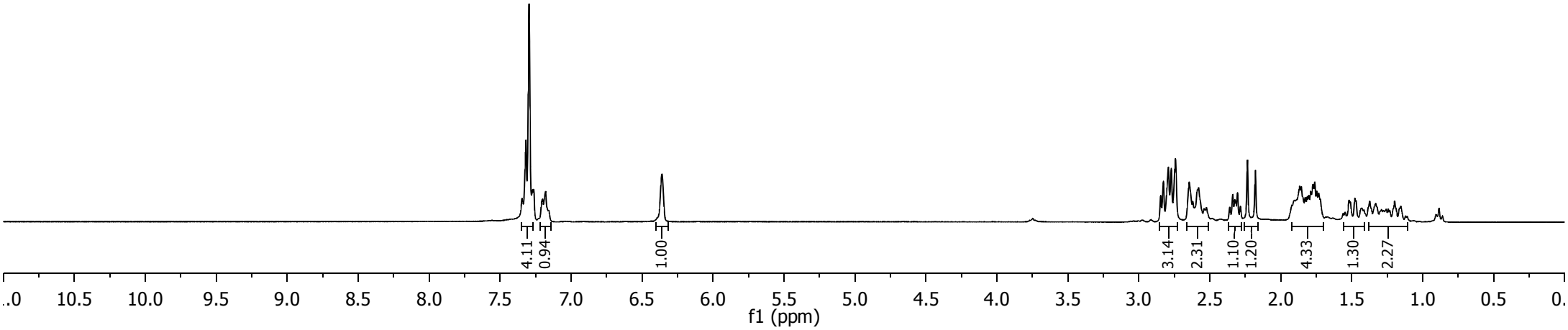


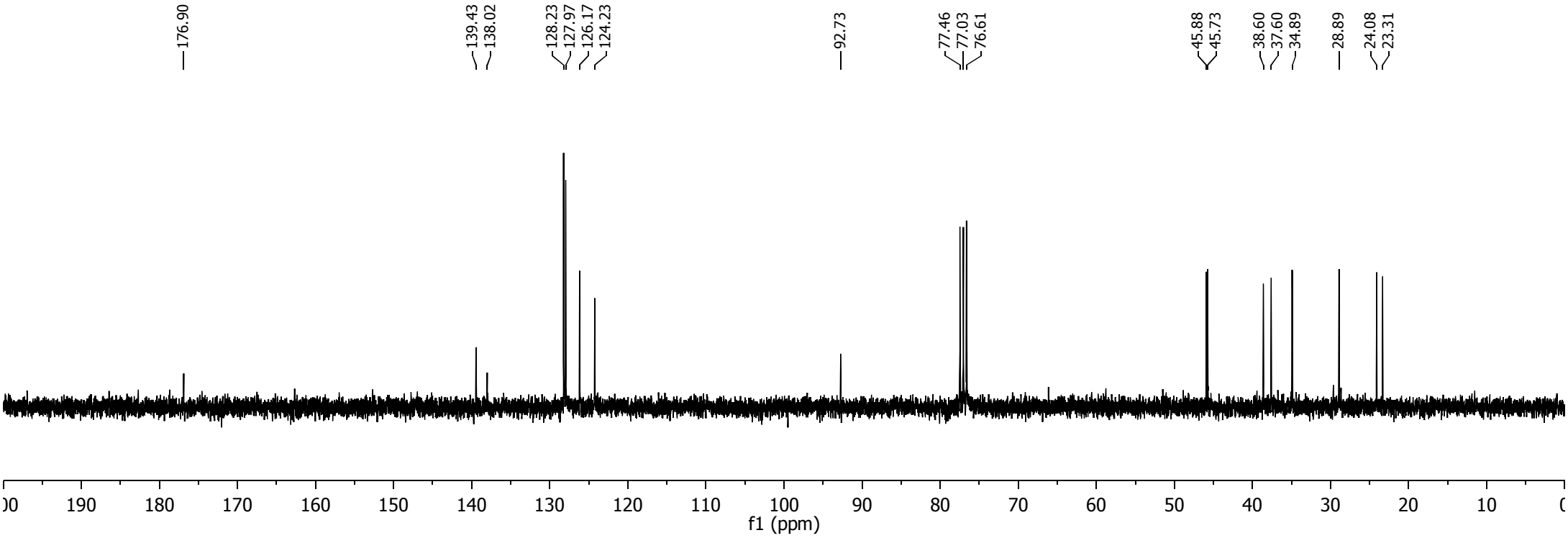


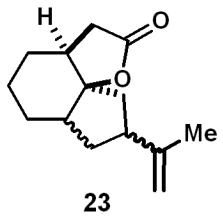


22

Mixture of 2 diastereoisomers

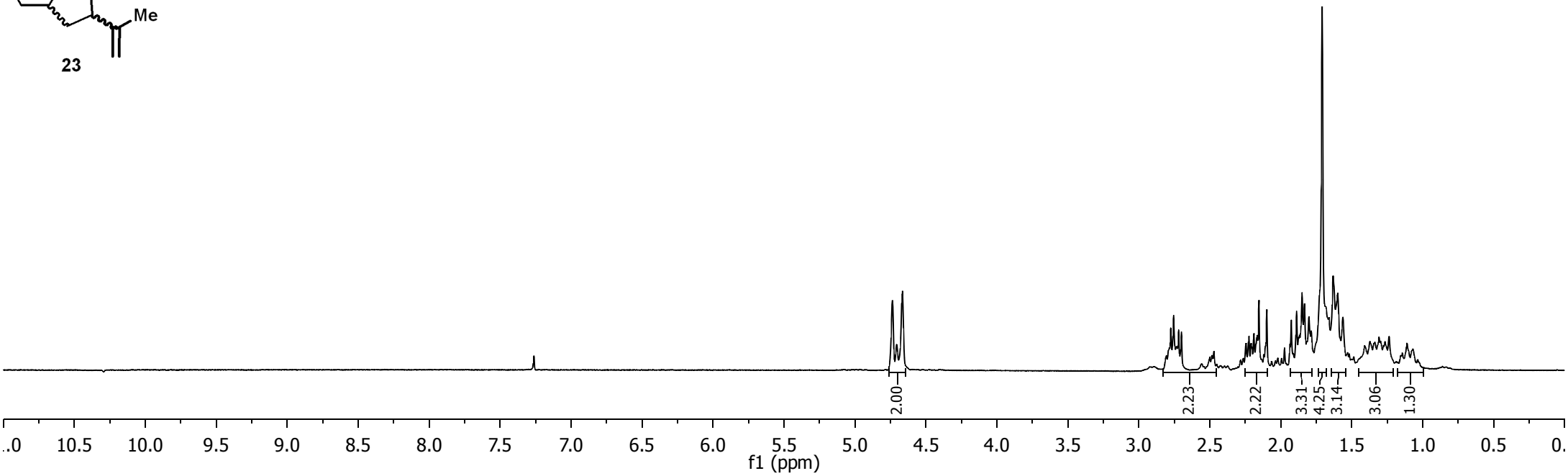


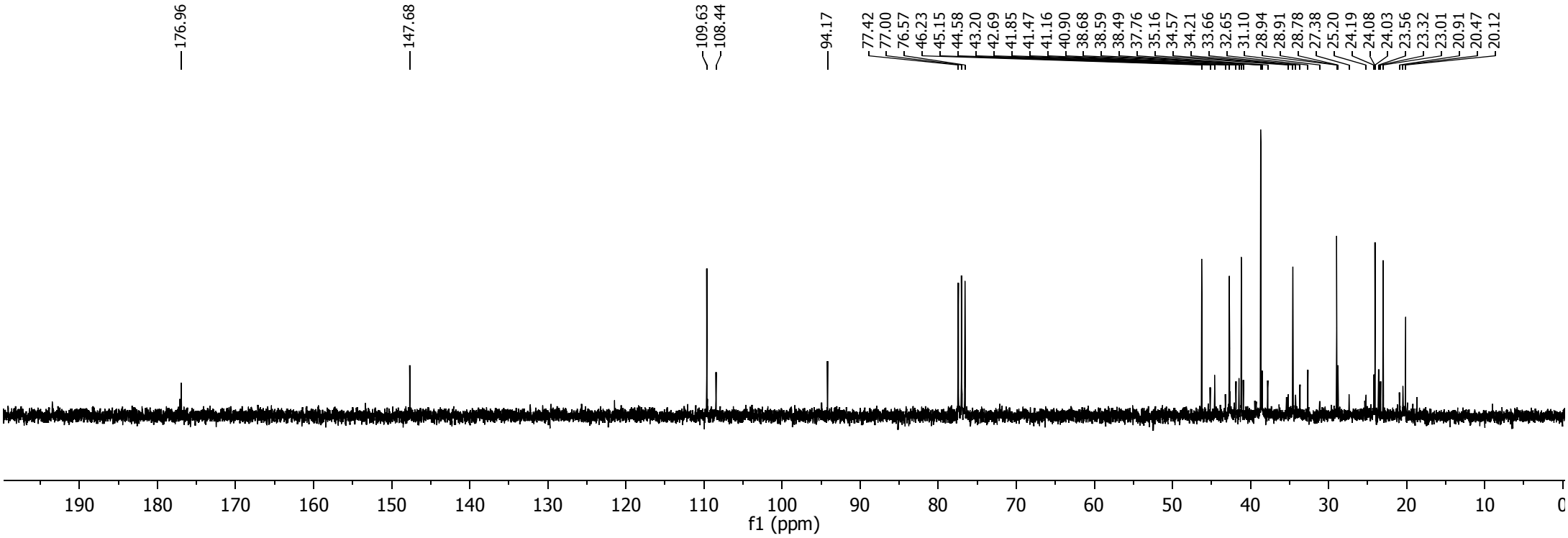


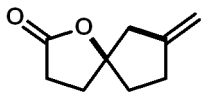


23

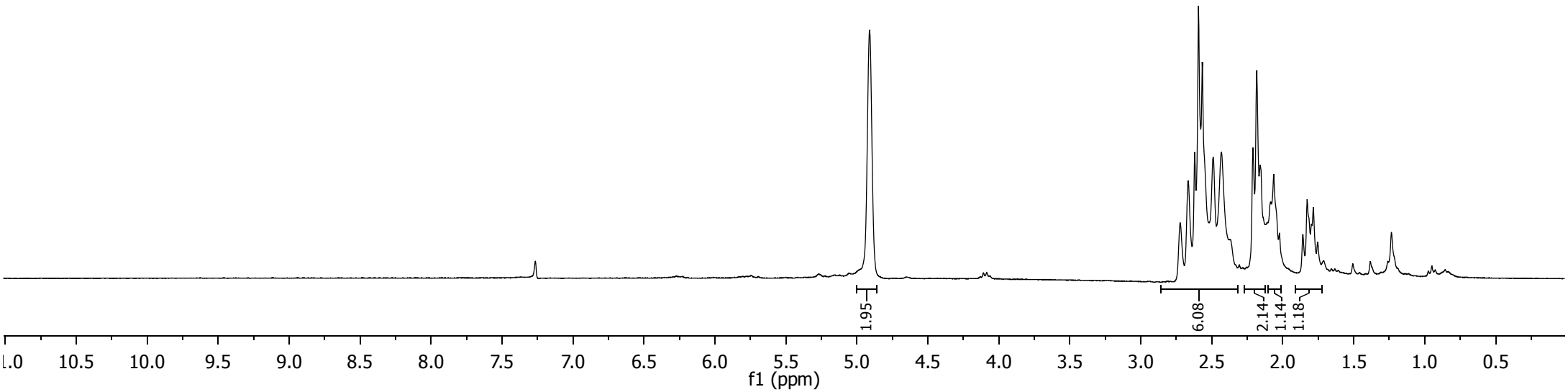
Mixture of 4 diastereoisomers

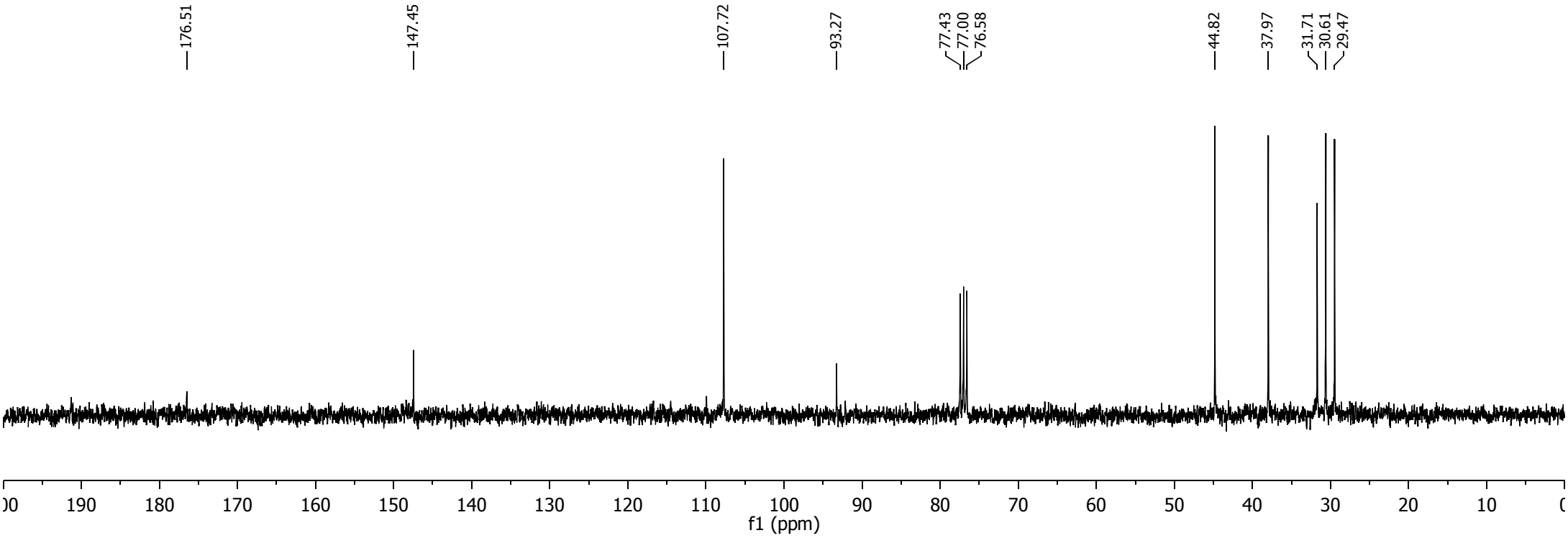


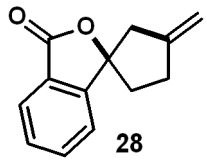




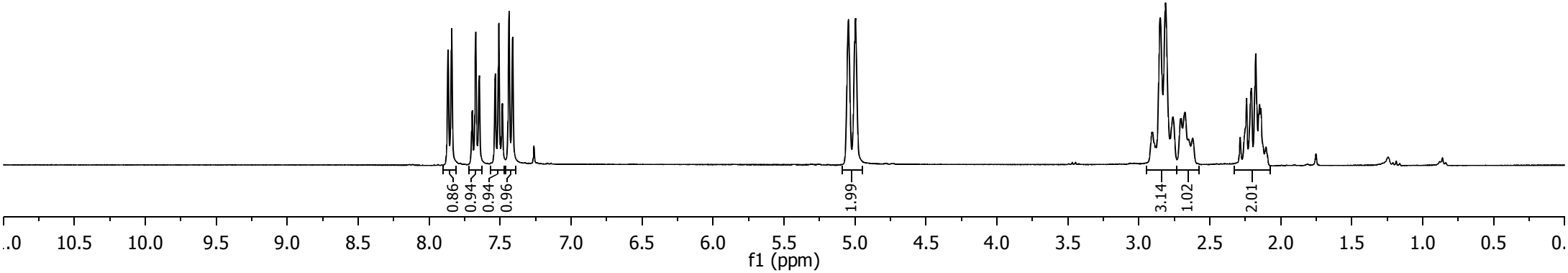
27

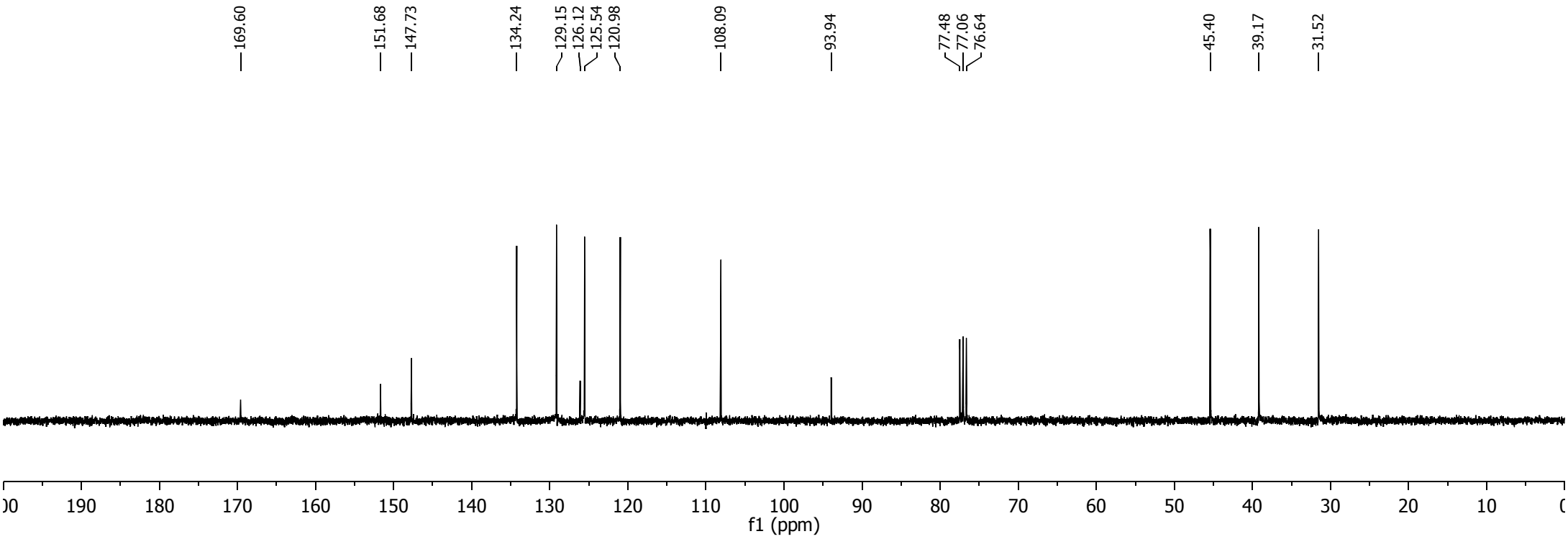

1.95
6.08
2.14
1.14
1.18
f1 (ppm)

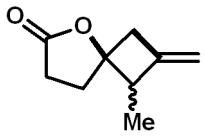

176.51
147.45
107.72
93.27
77.43
77.00
76.58
44.82
37.97
31.71
30.61
29.47
f1 (ppm)



28

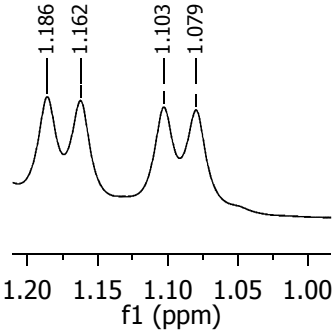

0.86
0.94
0.94
0.96
1.99
3.14
1.02
2.01
f1 (ppm)

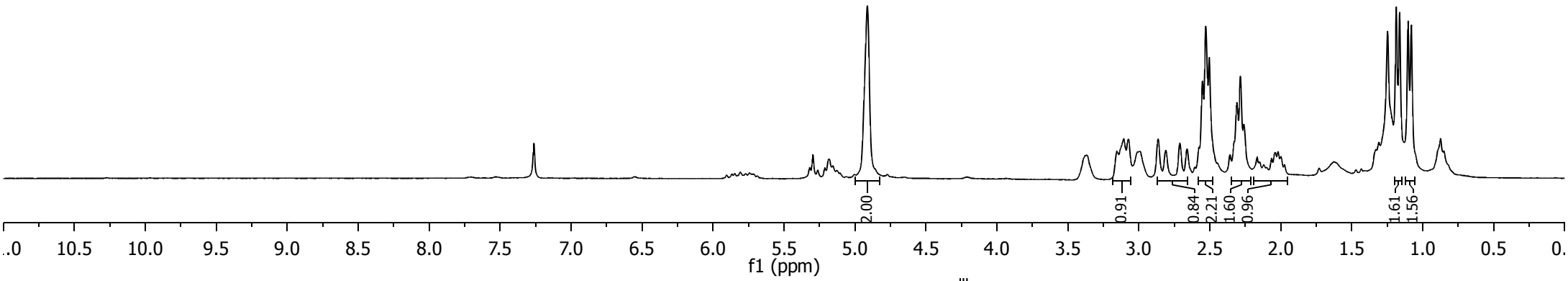

169.60
151.68
147.73
134.24
129.15
126.12
125.54
120.98
108.09
93.94
77.48
77.06
76.64
45.40
39.17
31.52
f1 (ppm)

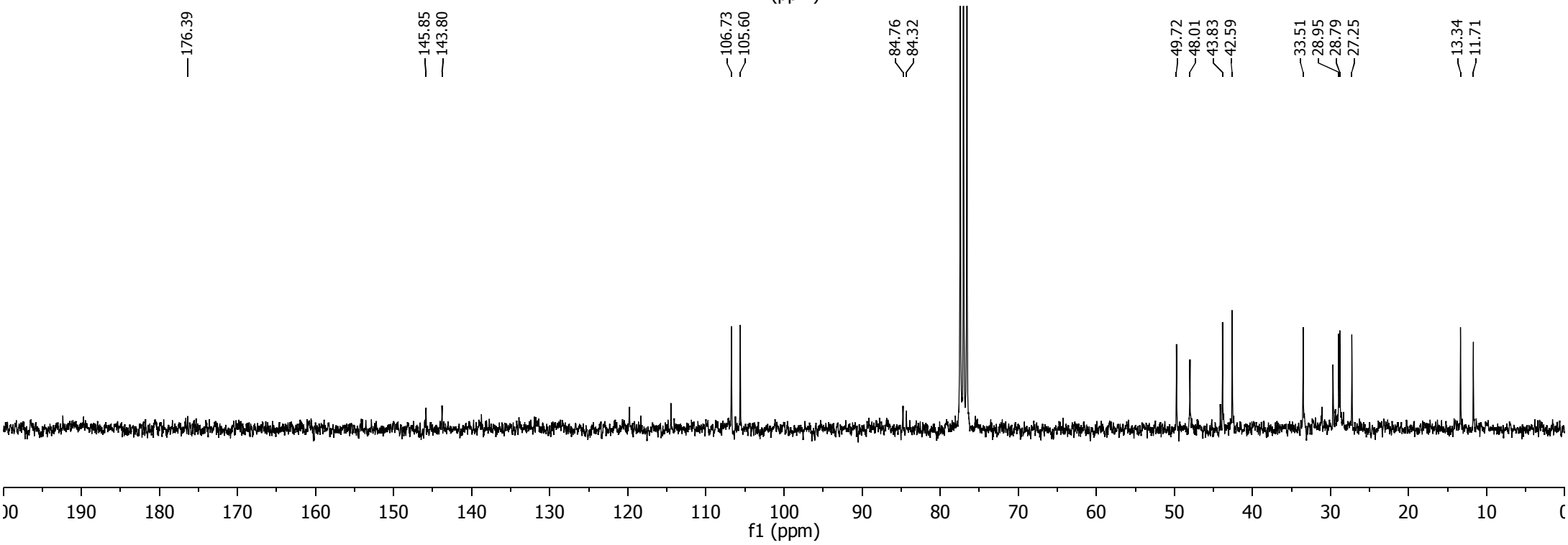


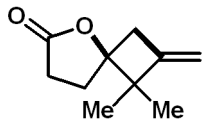
31

Inseparable mixture of 2 diastereoisomers
and reduced product (~10%)

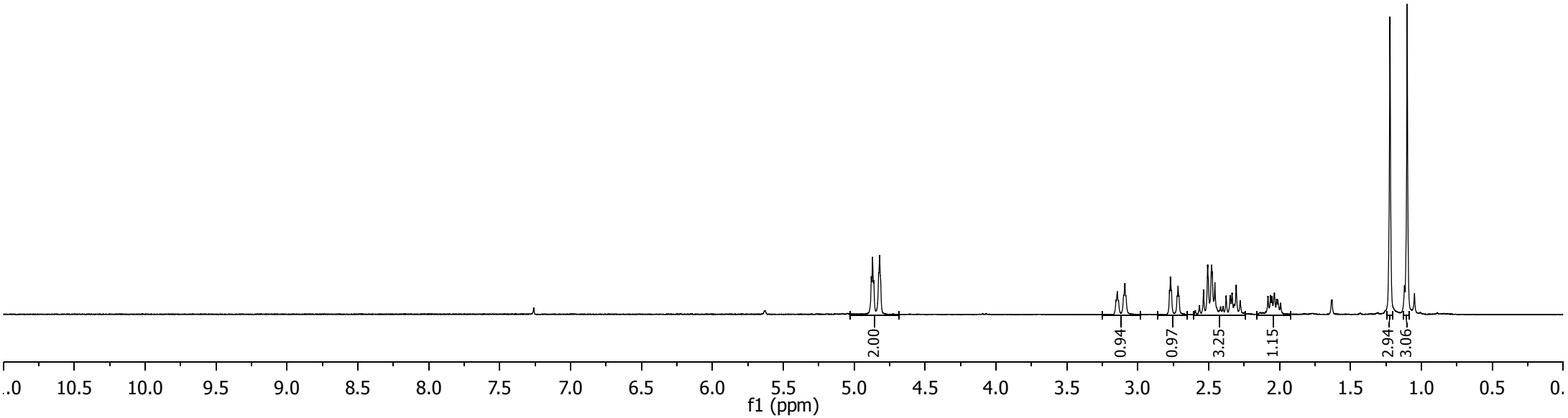


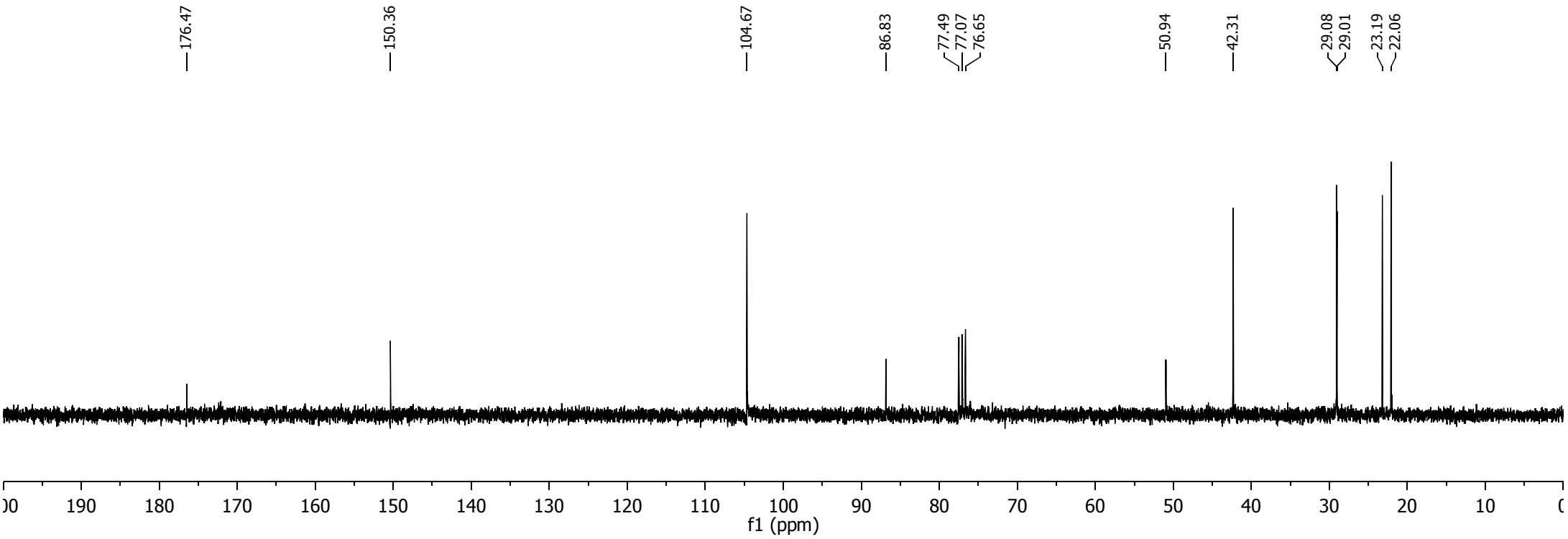


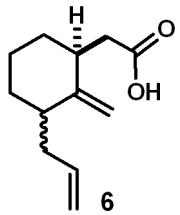



O
O
Me
Me

32

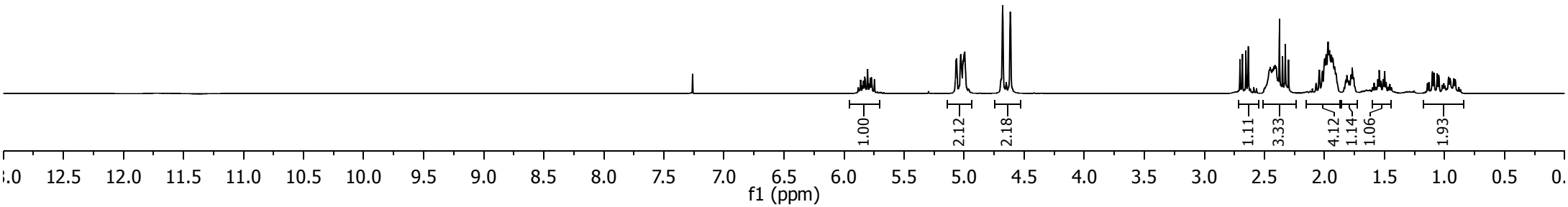

2.00
0.94
0.97
3.25
1.15
2.94
3.06
f1 (ppm)

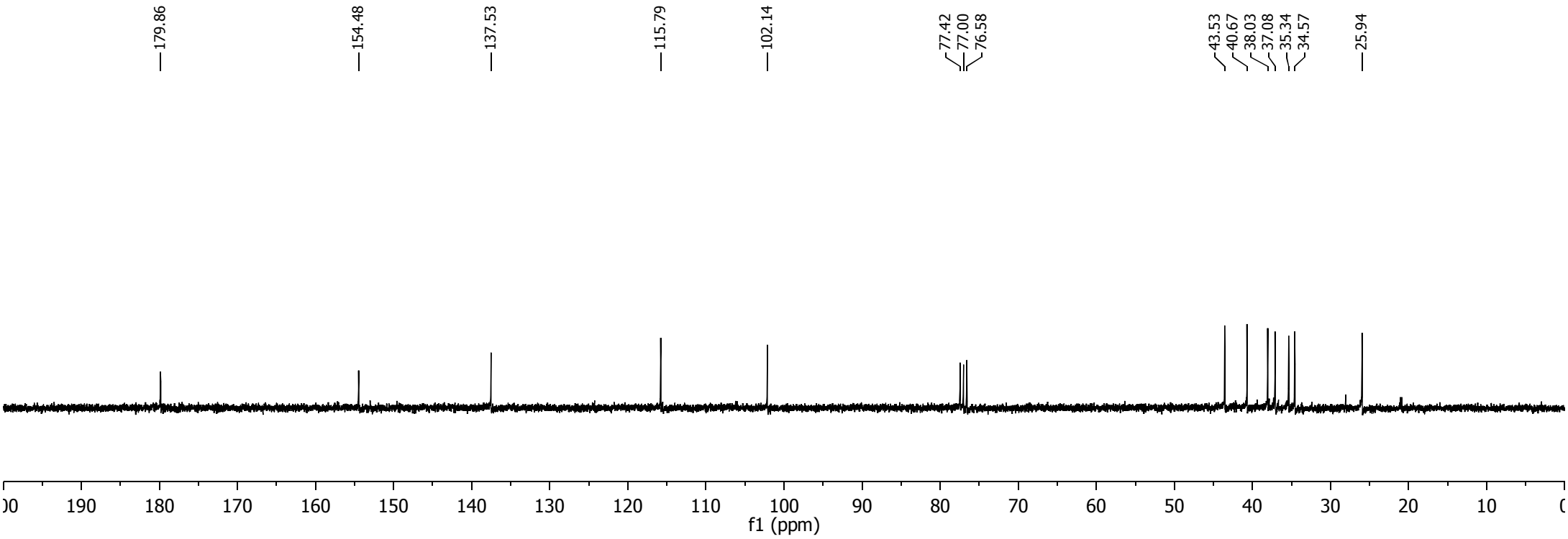

176.47
150.36
104.67
86.83
77.49
77.07
76.65
50.94
42.31
29.08
29.01
23.19
22.06
f1 (ppm)

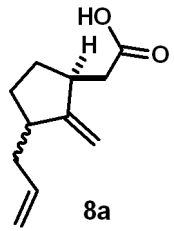


6

Mixture of 2 diastereoisomers

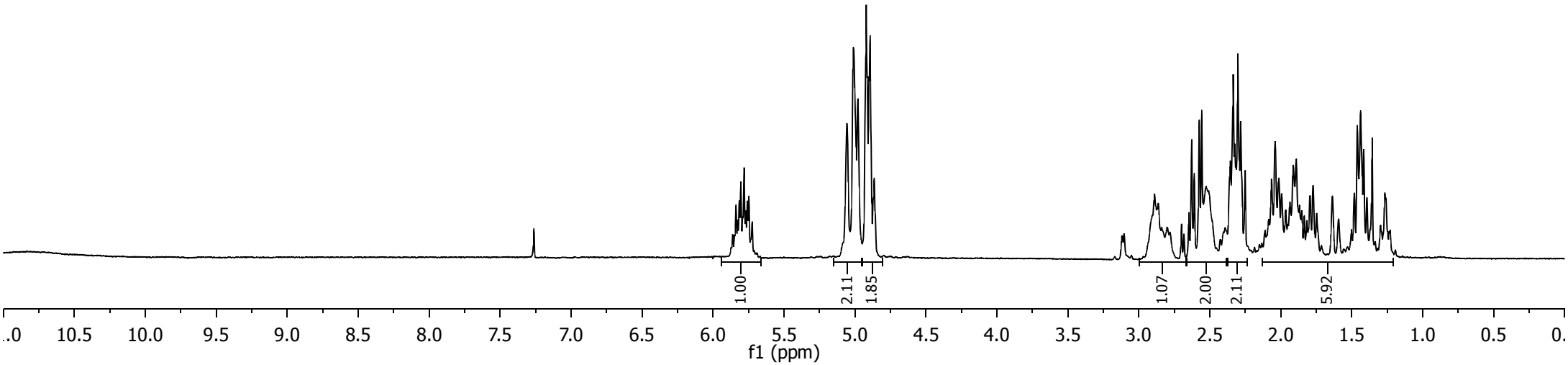


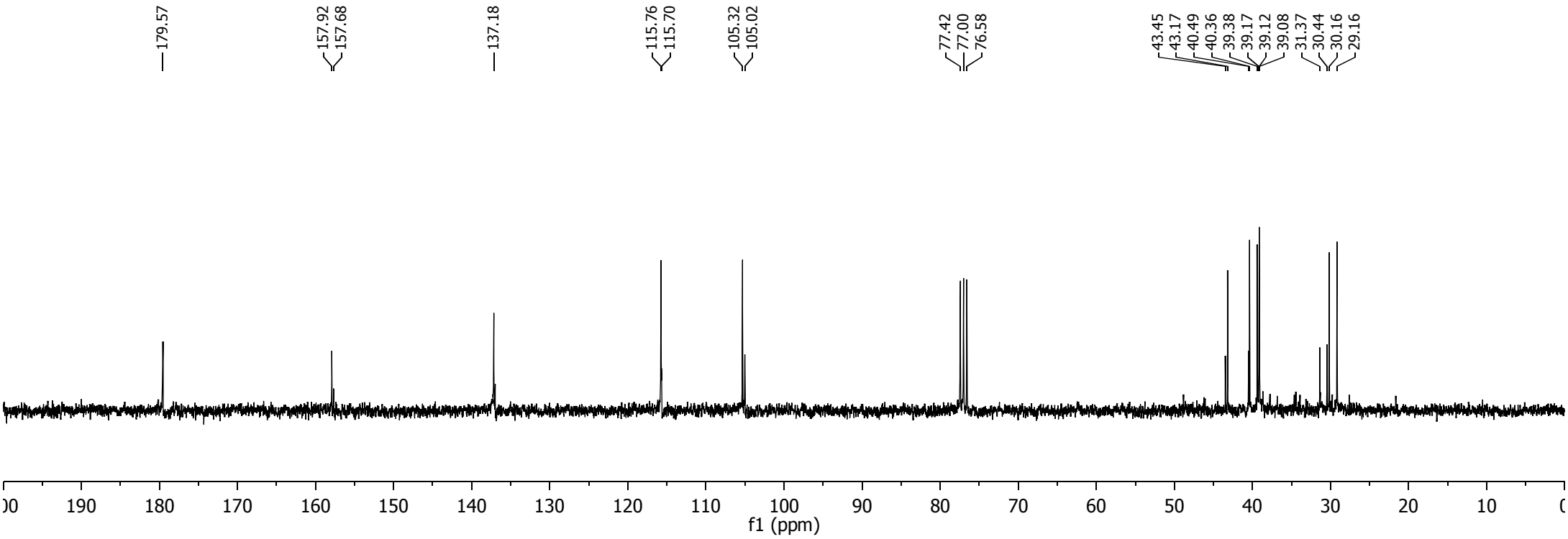


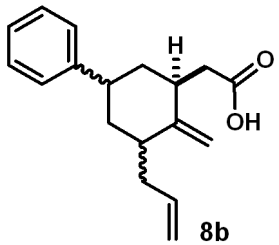


8a

Mixture of 2 diastereoisomers

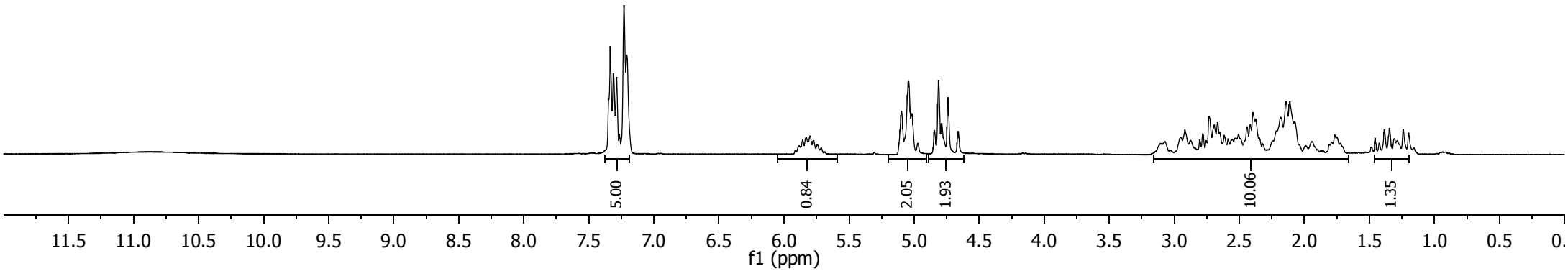


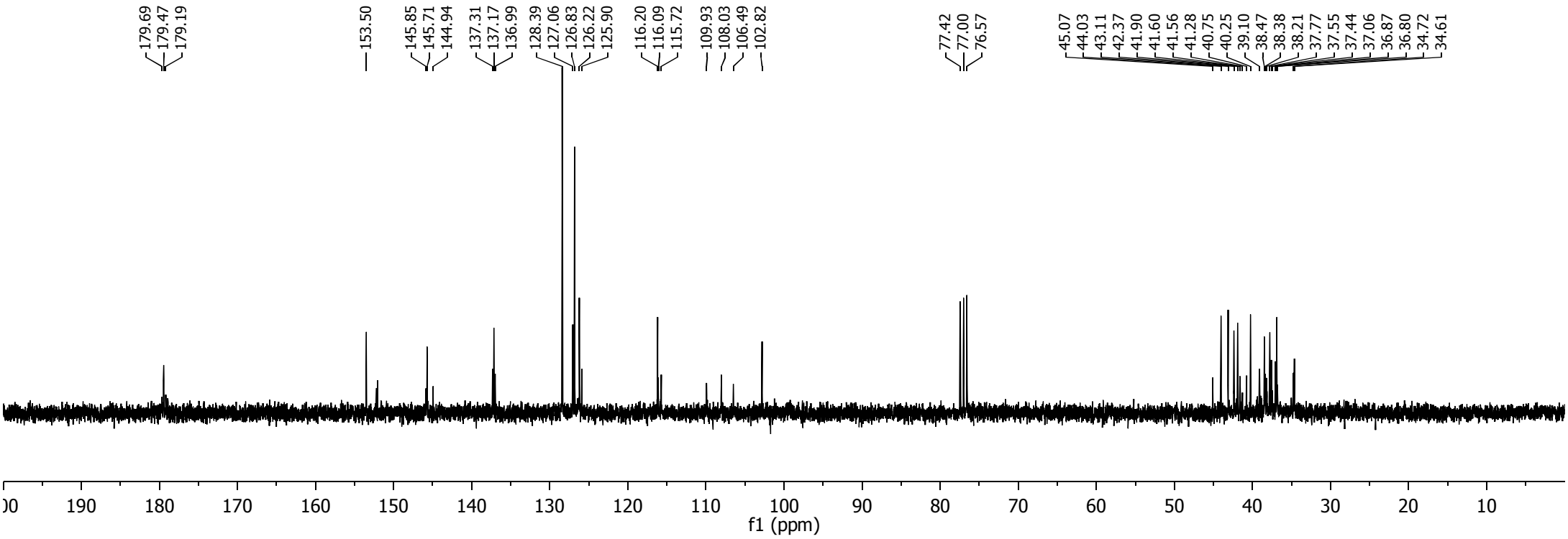


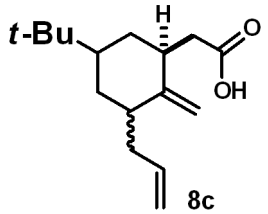


8b

Mixture of 4 diastereoisomers

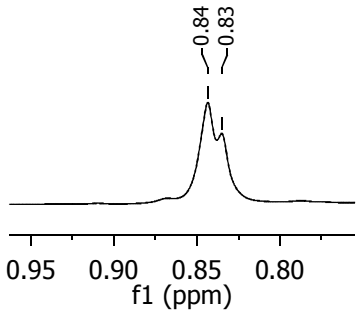


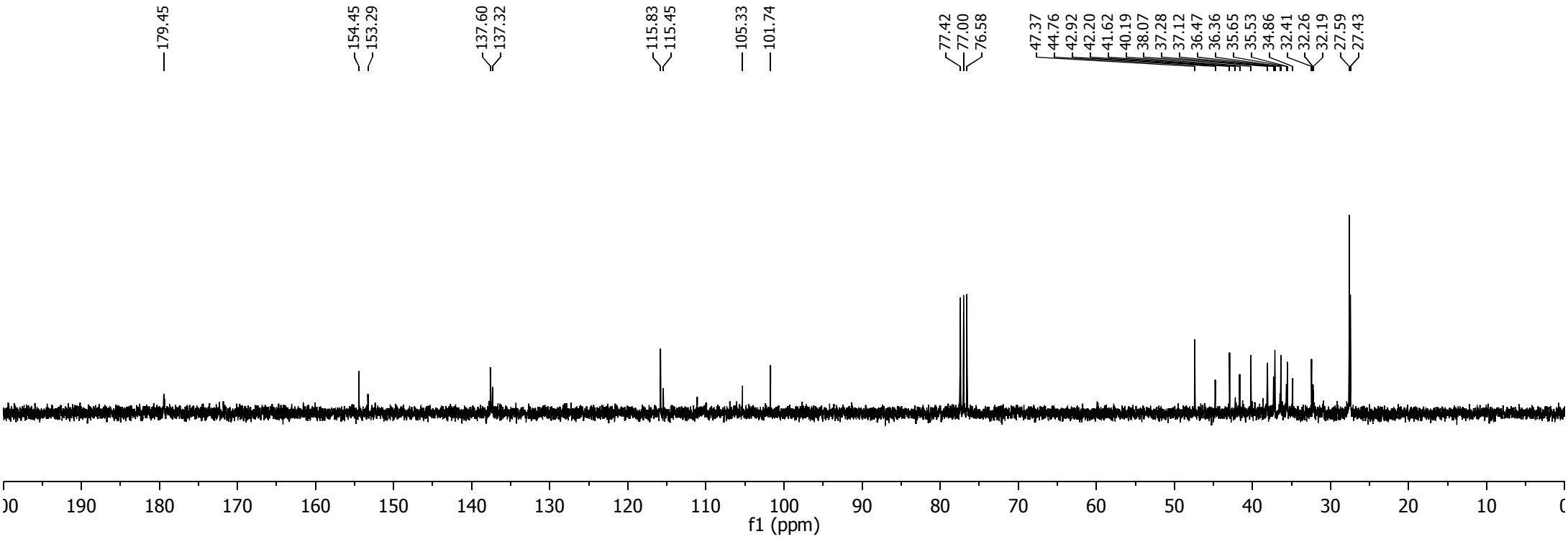


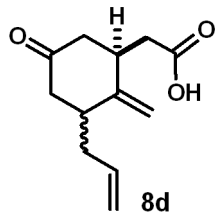


8c

Mixture of 2 diastereoisomers

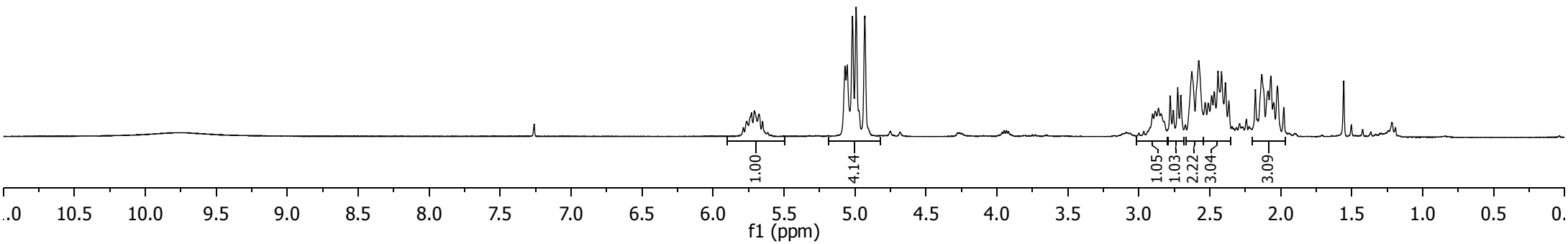


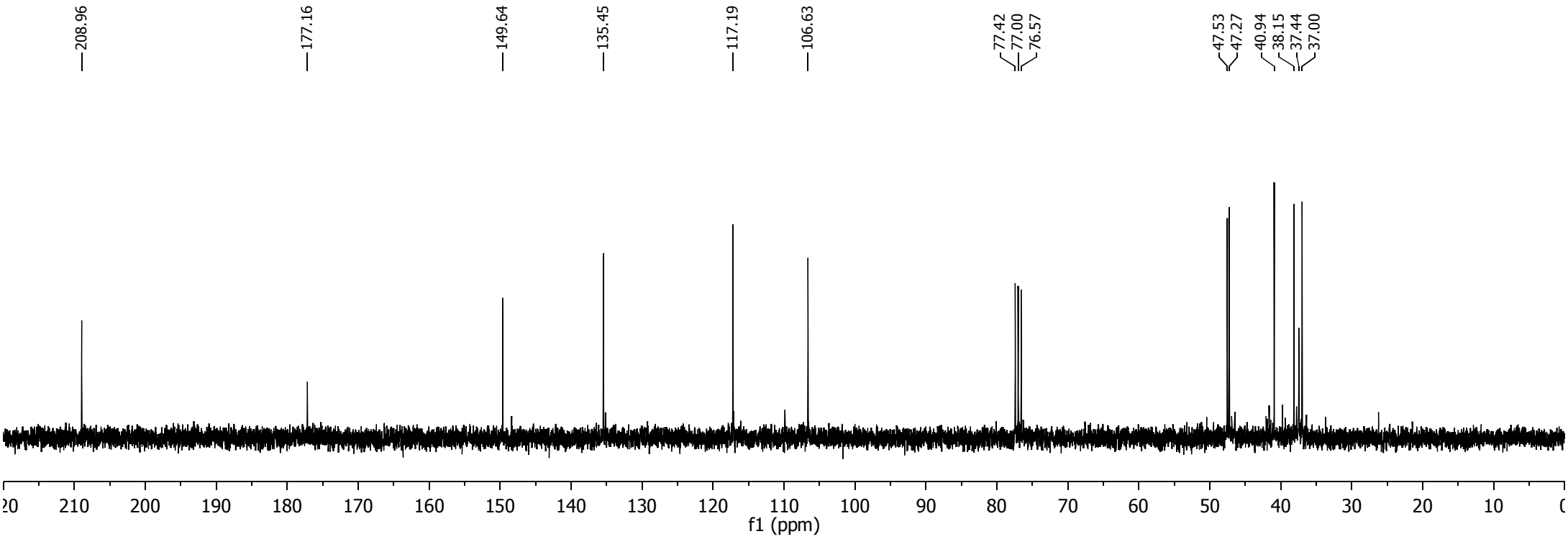


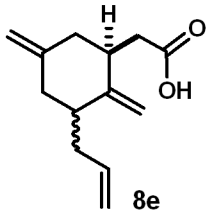


8d

Mixture of 2 diastereoisomers

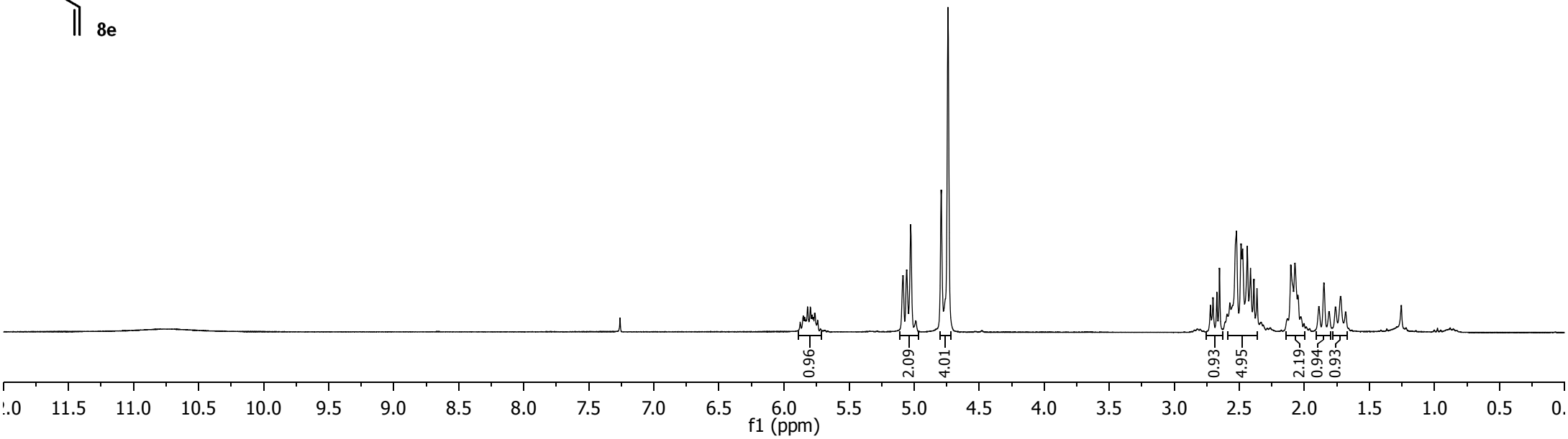


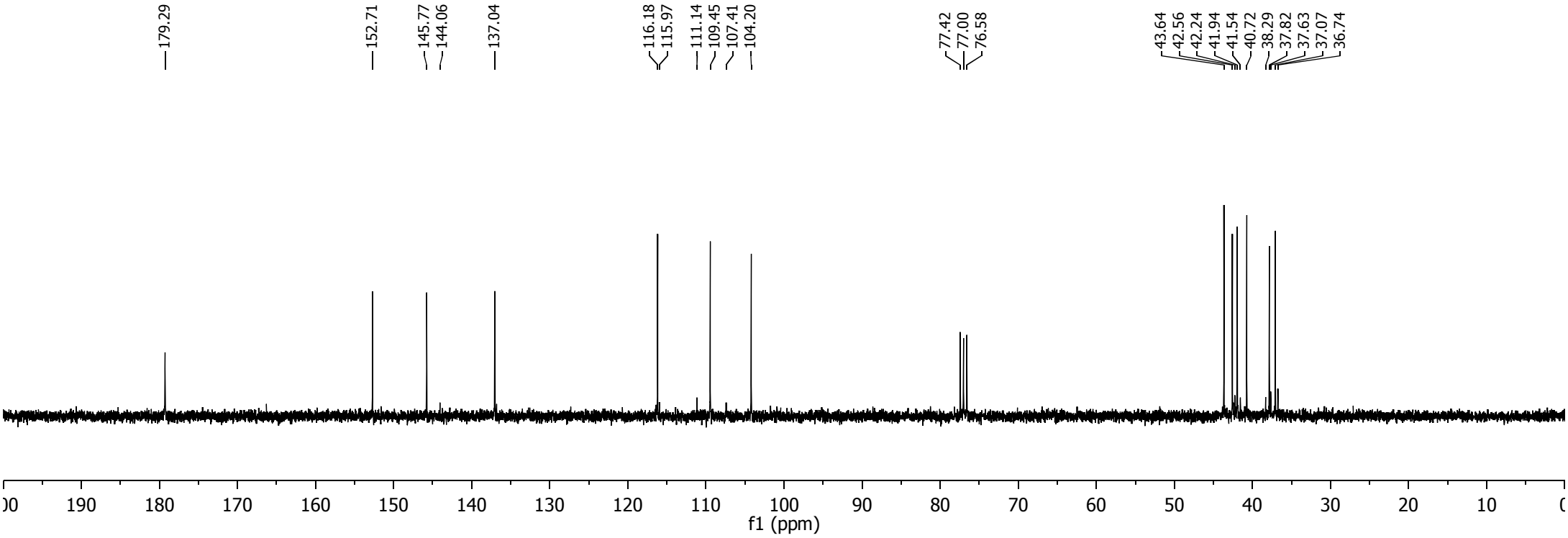


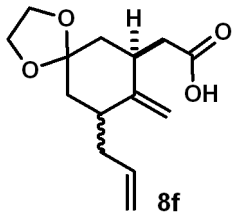


8e

Mixture of 2 diastereoisomers

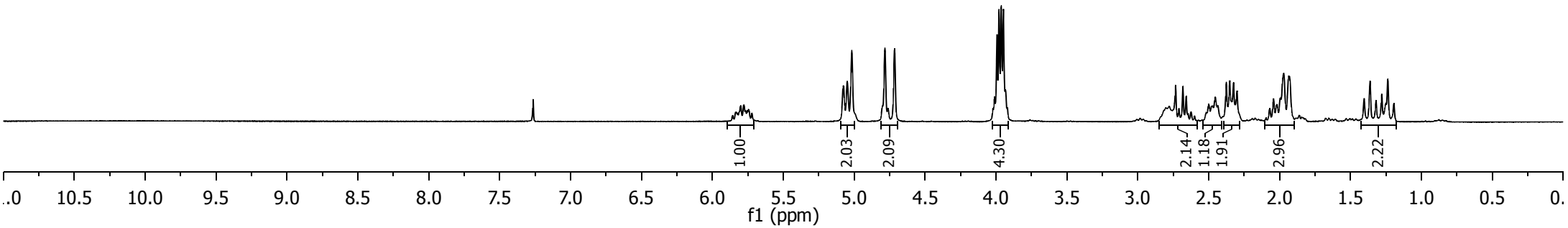


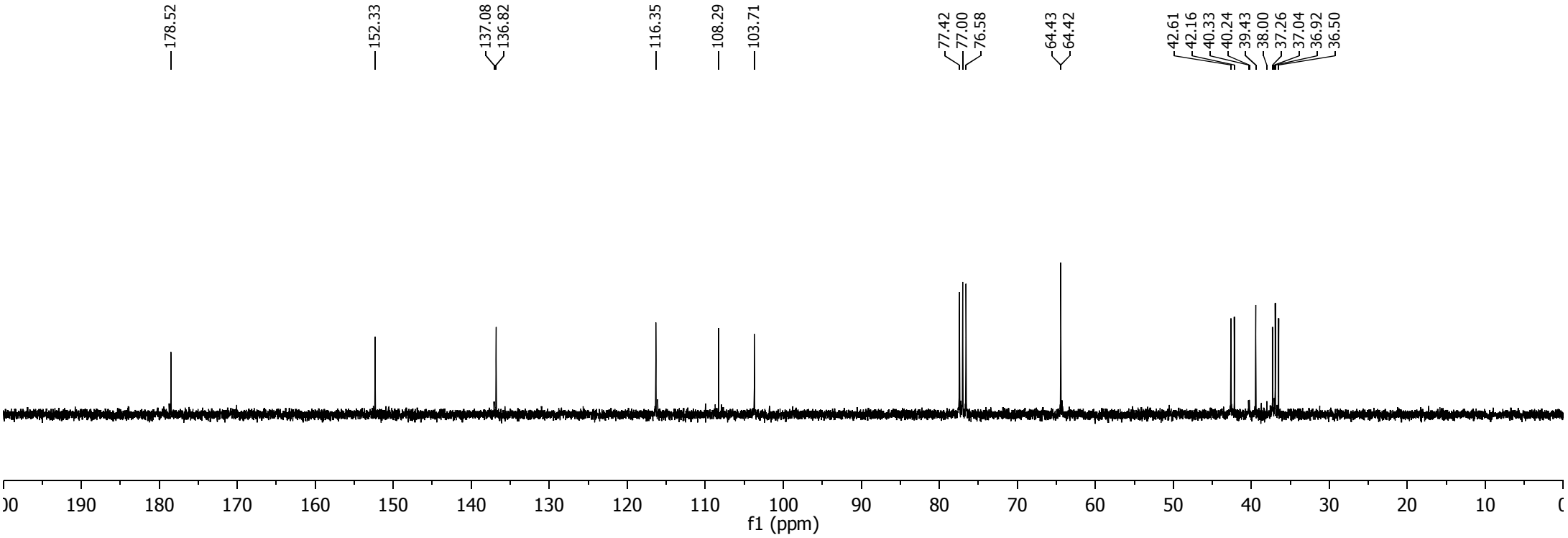


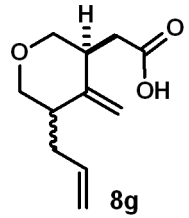


8f

Mixture of 2 diastereoisomers

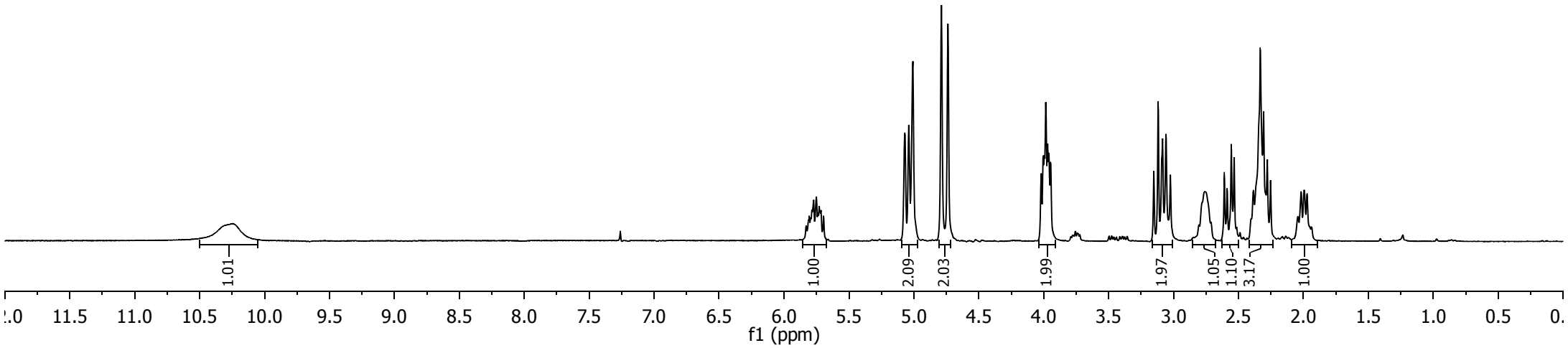


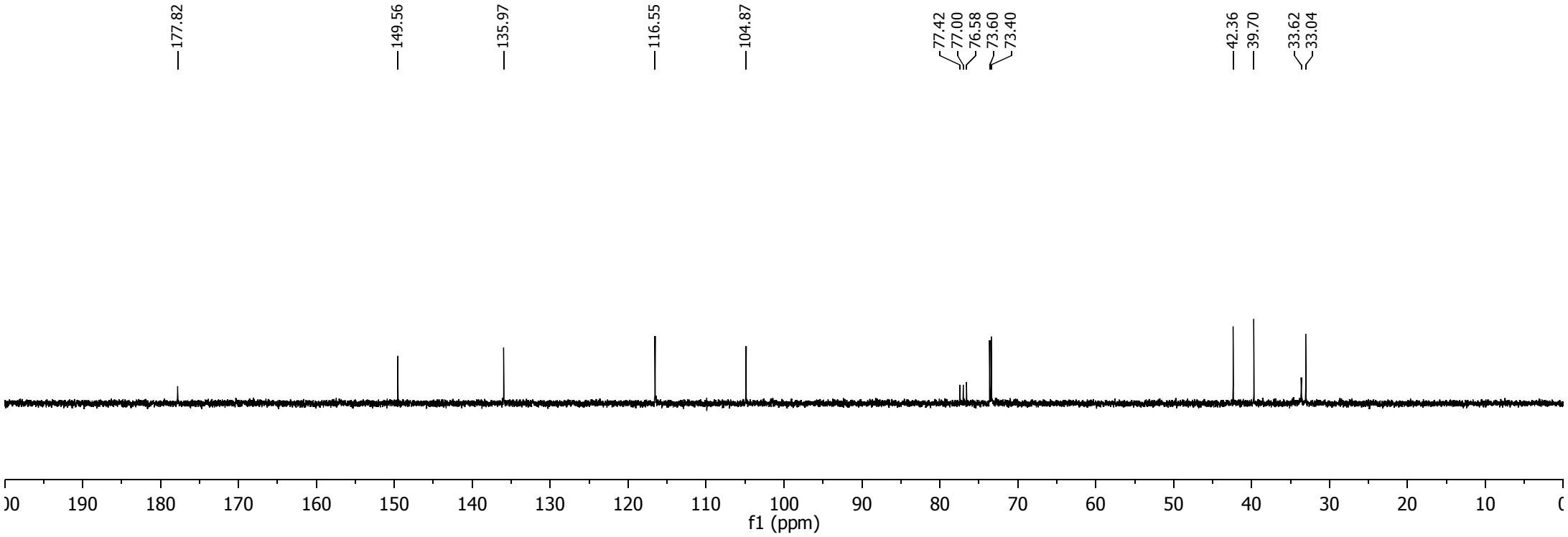


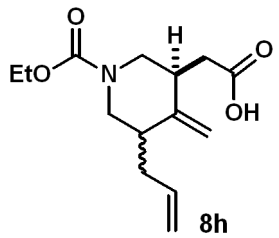


8g

Mixture of 2 diastereoisomers

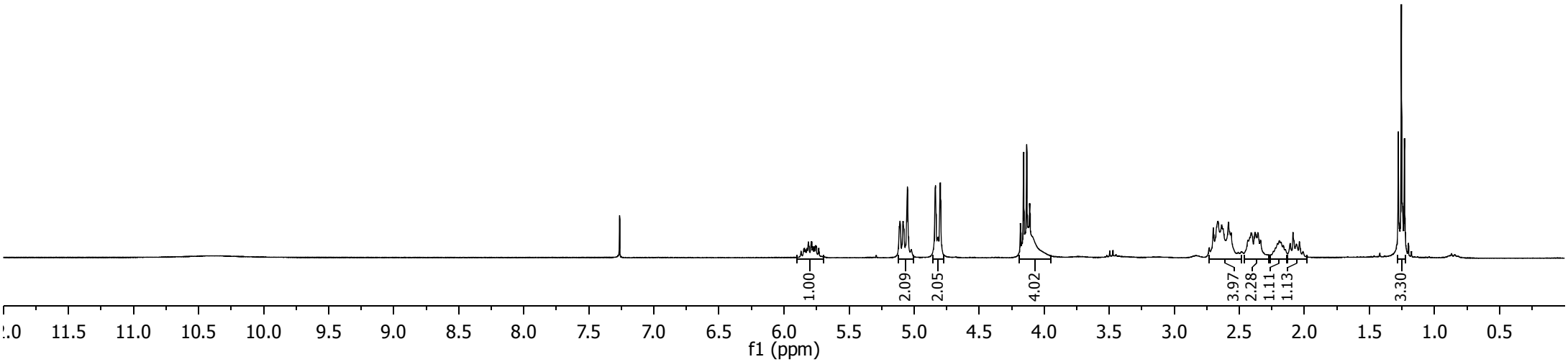


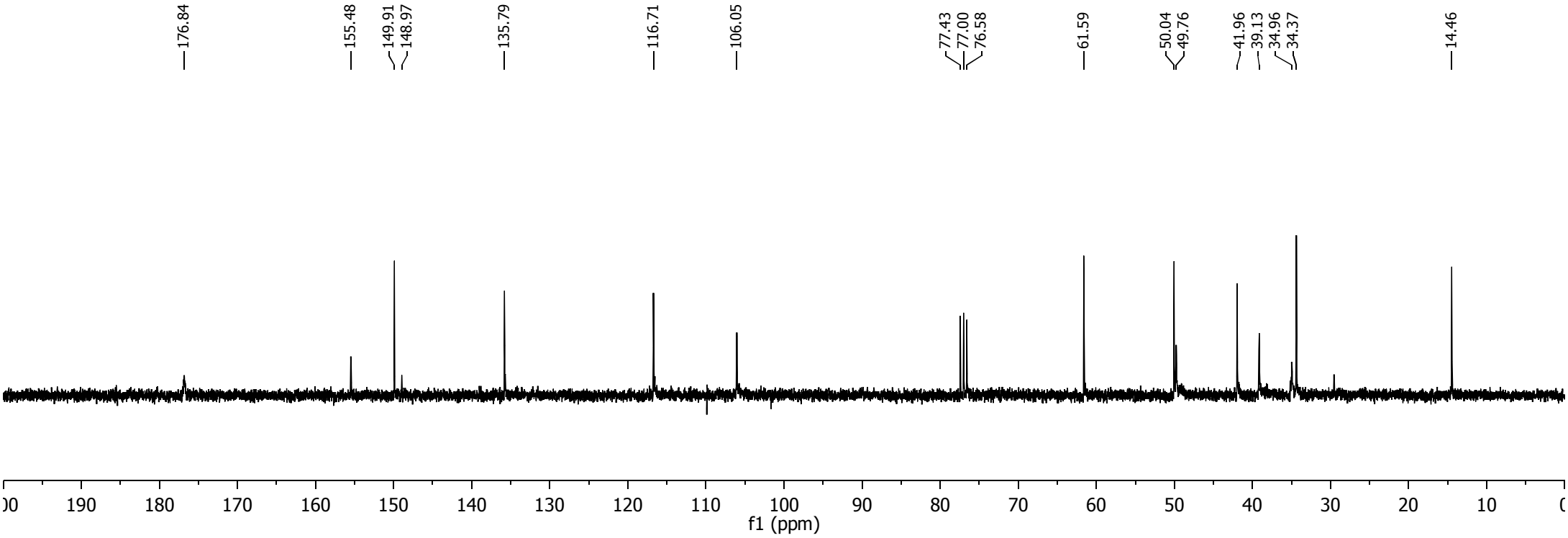


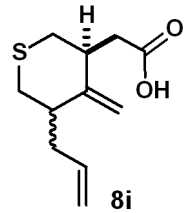


8h

Mixture of 2 diastereoisomers

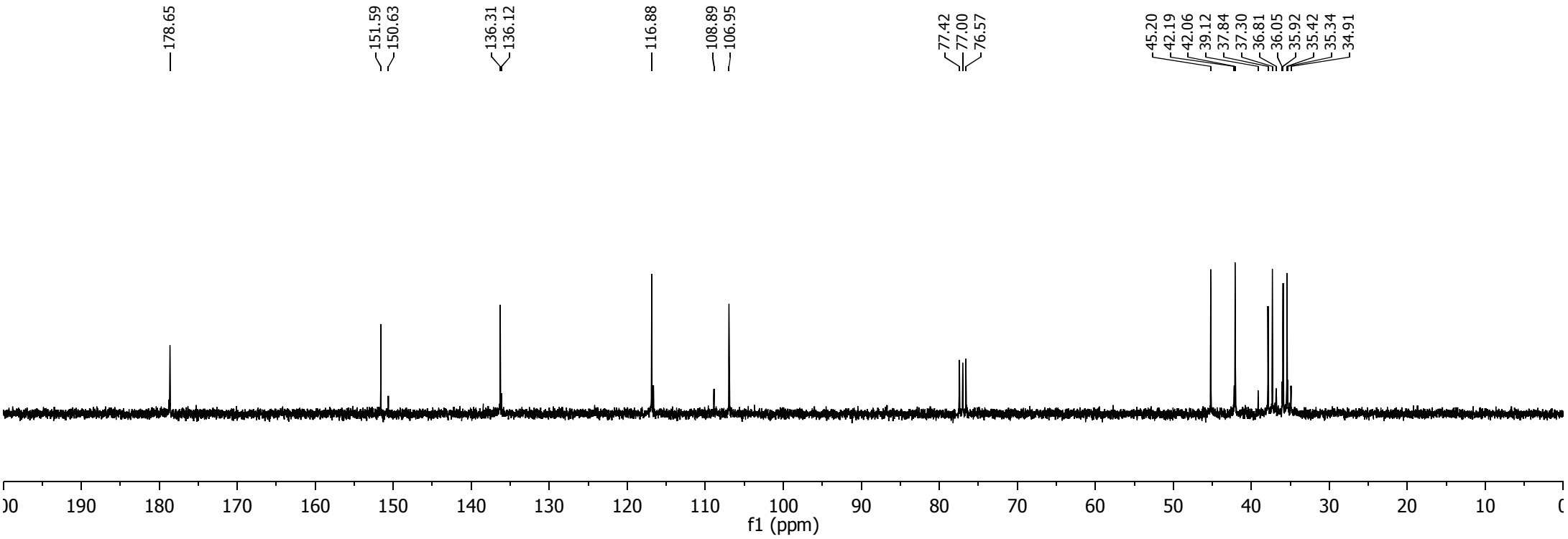


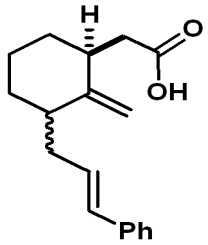




8i

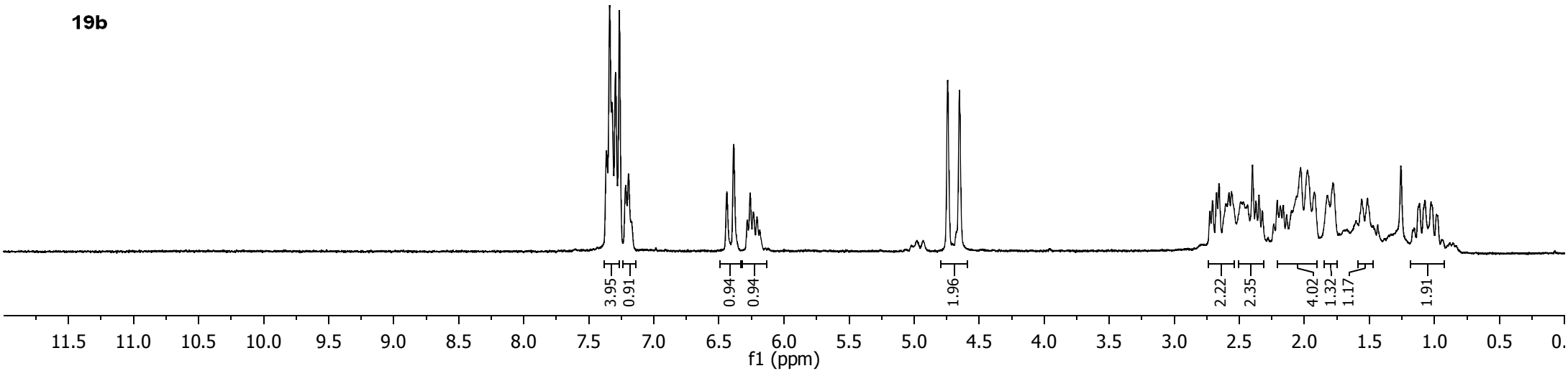
Mixture of 2 diastereoisomers

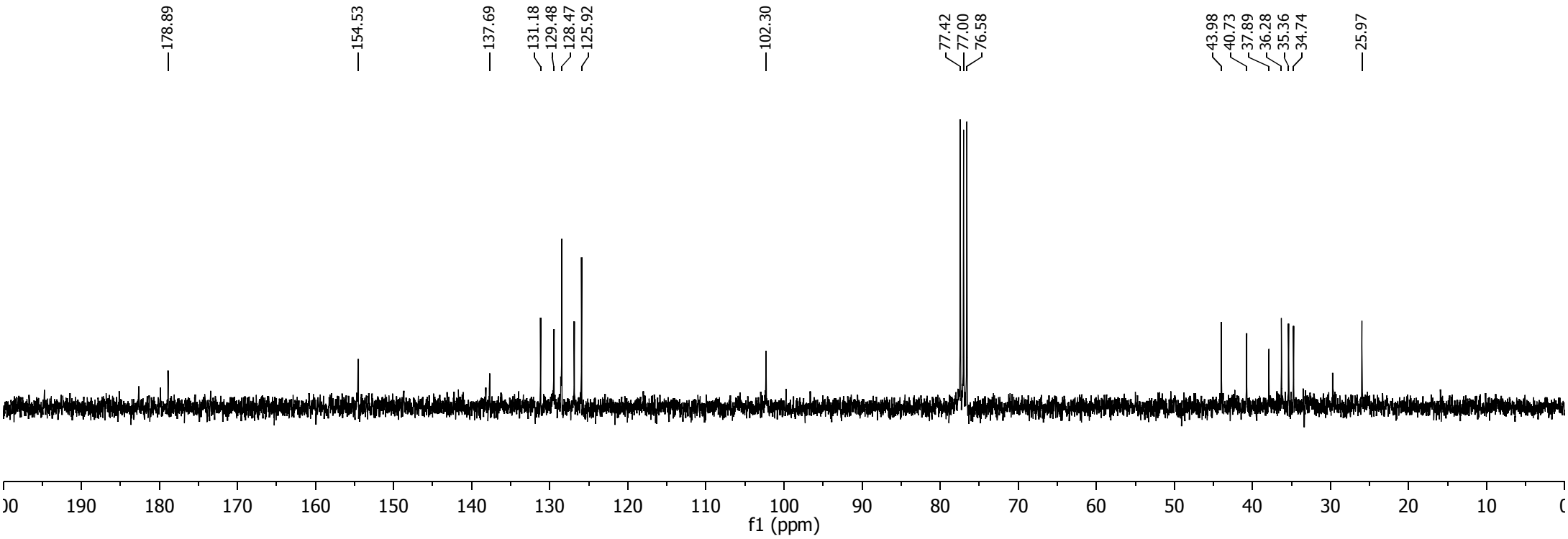


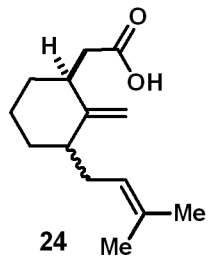


Mixture of 2 diastereoisomers

19b

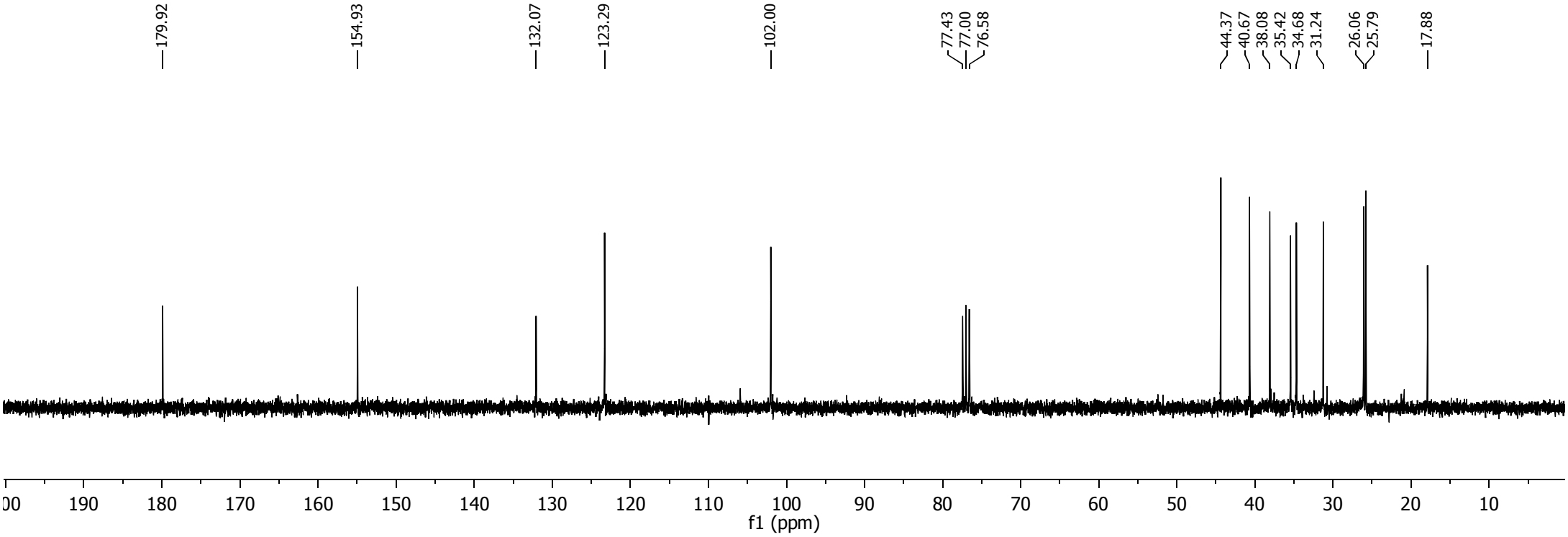


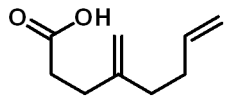




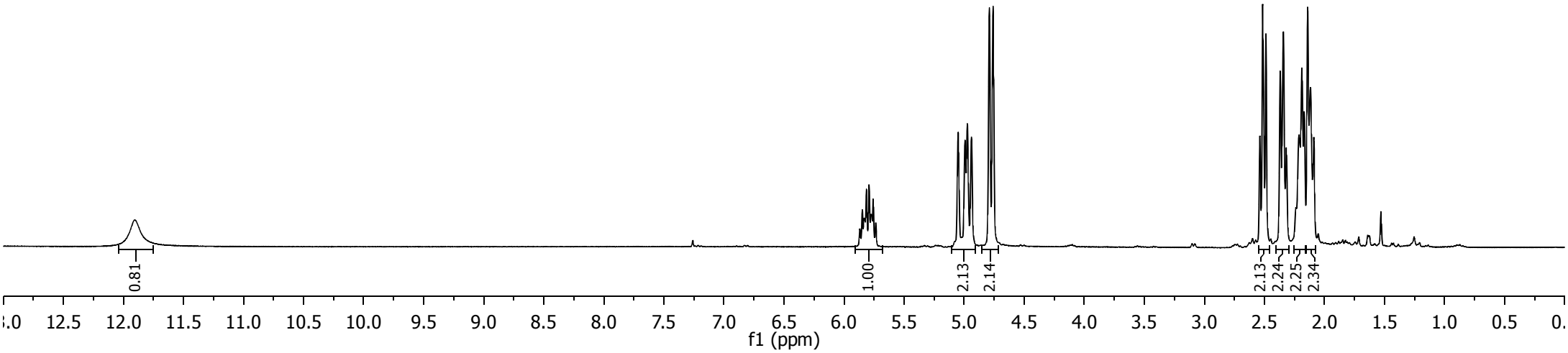
24

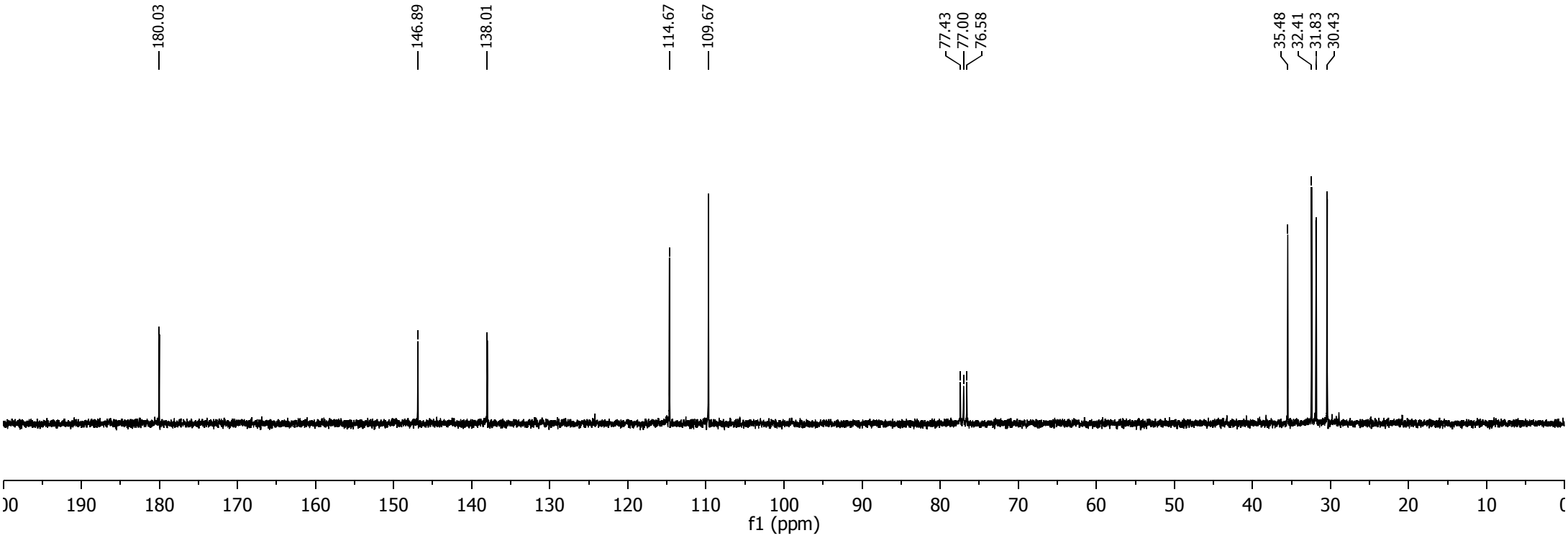
Mixture of 2 diastereoisomers

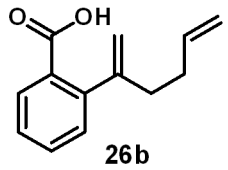



O
OH

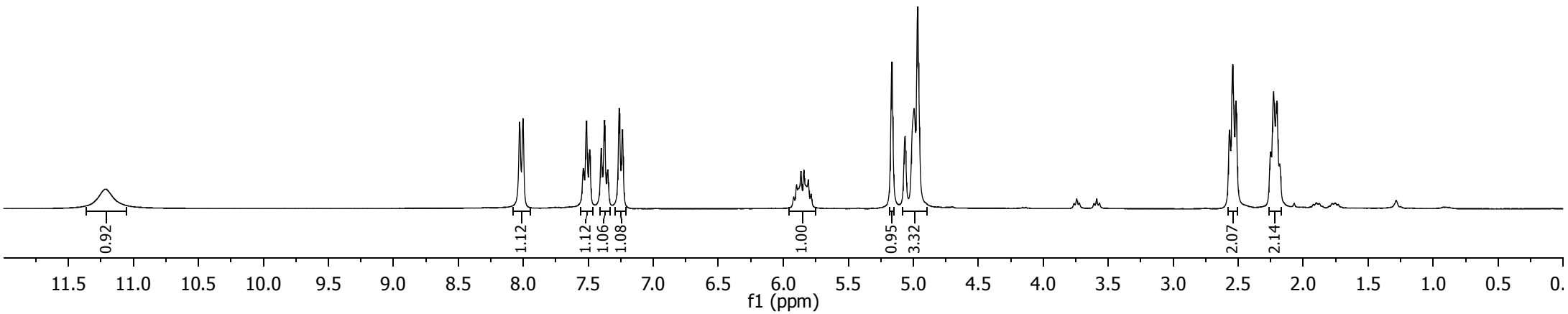
26a

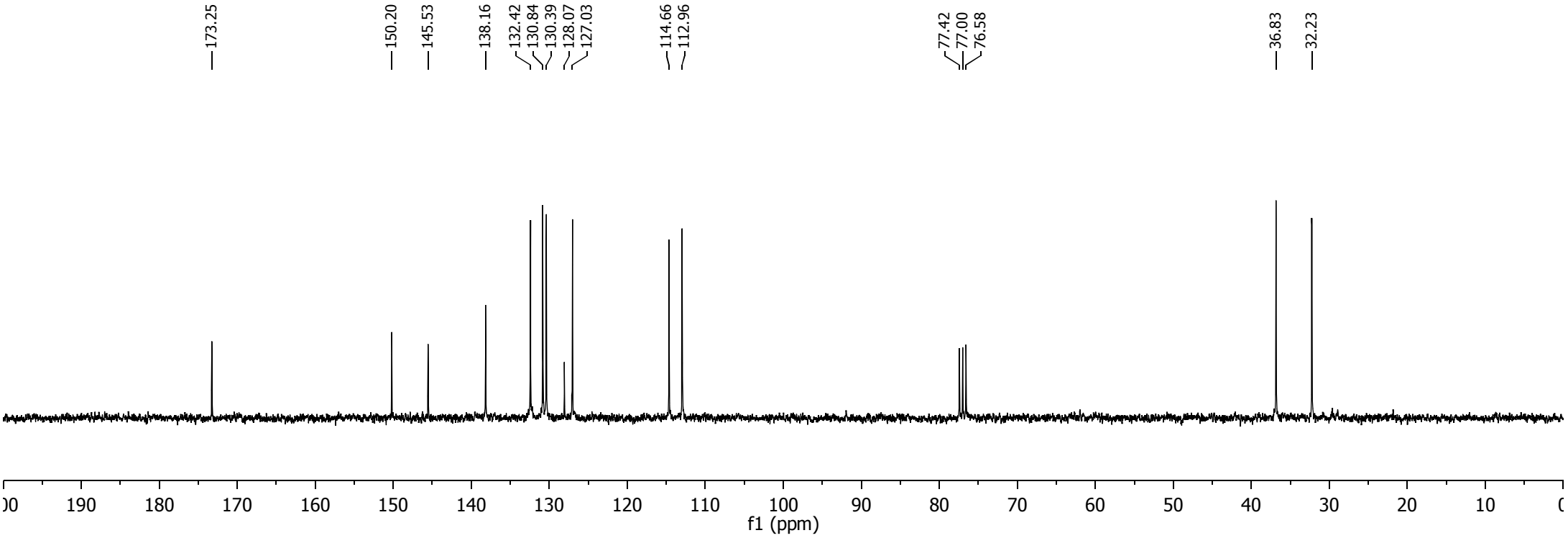

0.81
1.00
2.13
2.14
2.13
2.24
2.25
2.34
f1 (ppm)

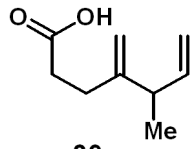

180.03
146.89
138.01
114.67
109.67
77.43
77.00
76.58
35.48
32.41
31.83
30.43
f1 (ppm)


O
OH

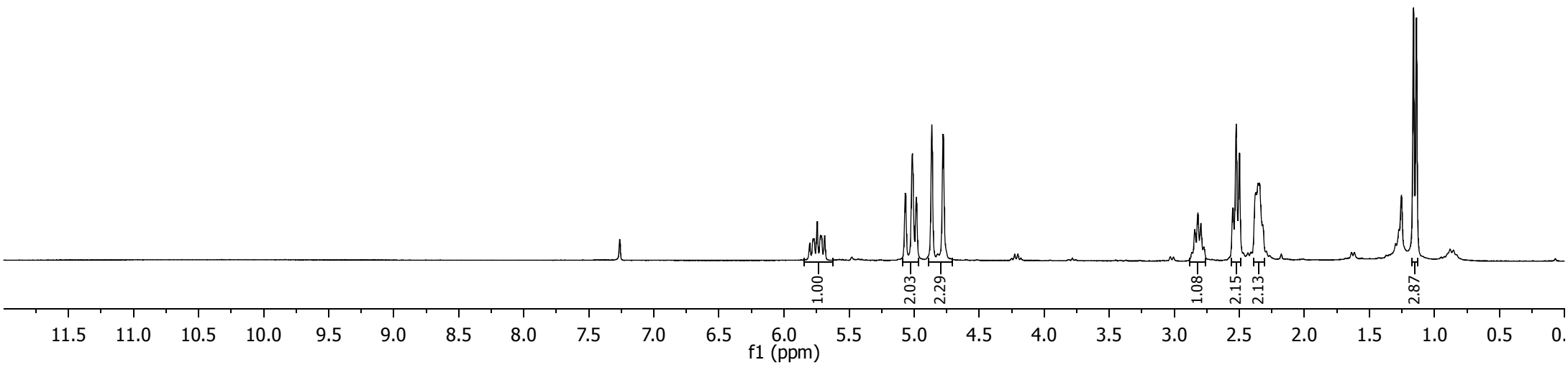
26b

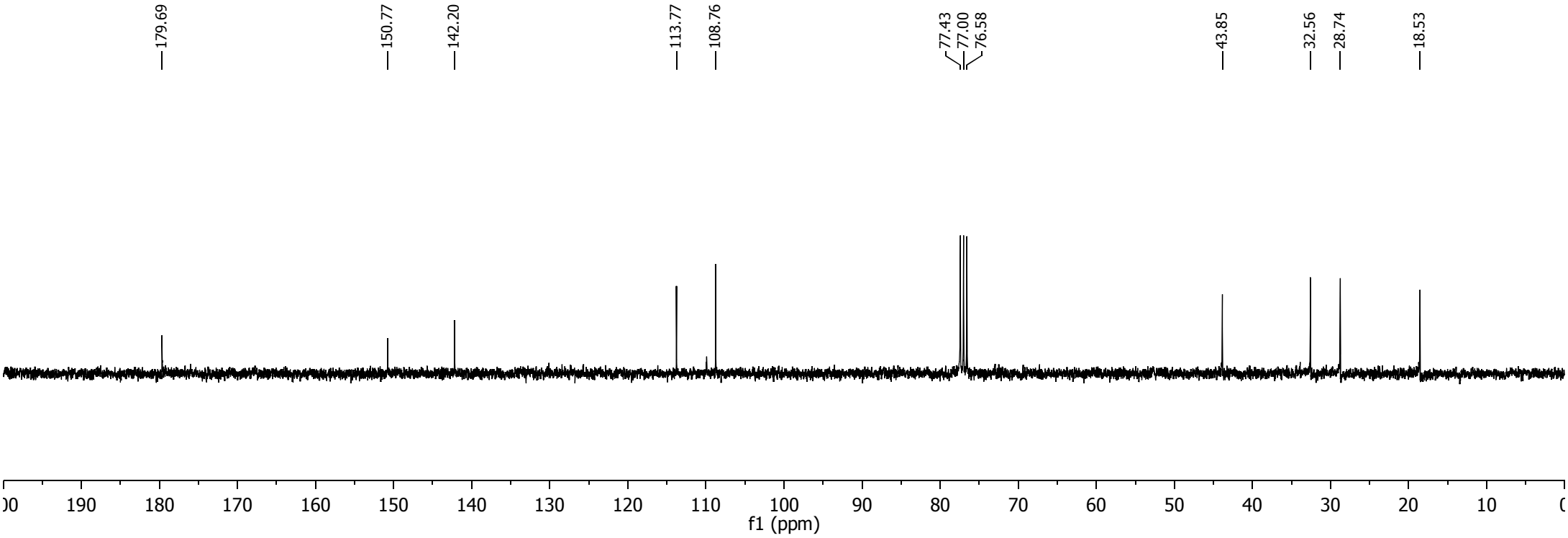

0.92
1.12
1.12
1.06
1.08
1.00
0.95
3.32
2.07
2.14
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

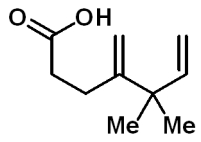

173.25
150.20
145.53
138.16
132.42
130.84
130.39
128.07
127.03
114.66
112.96
77.42
77.00
76.58
36.83
32.23
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
OH
Me

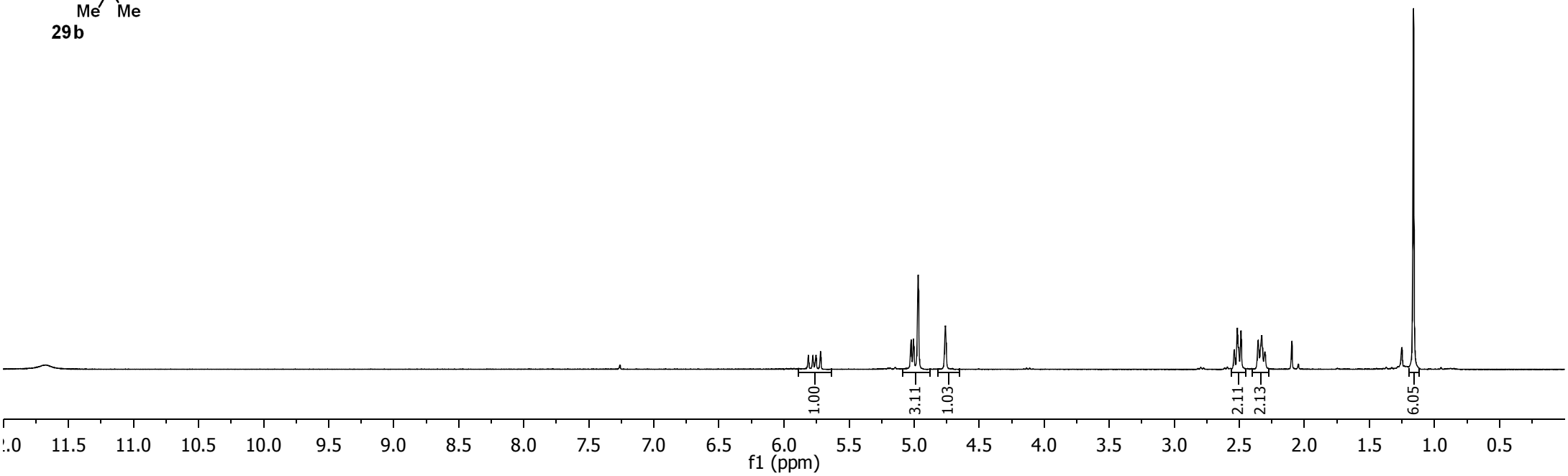
29a

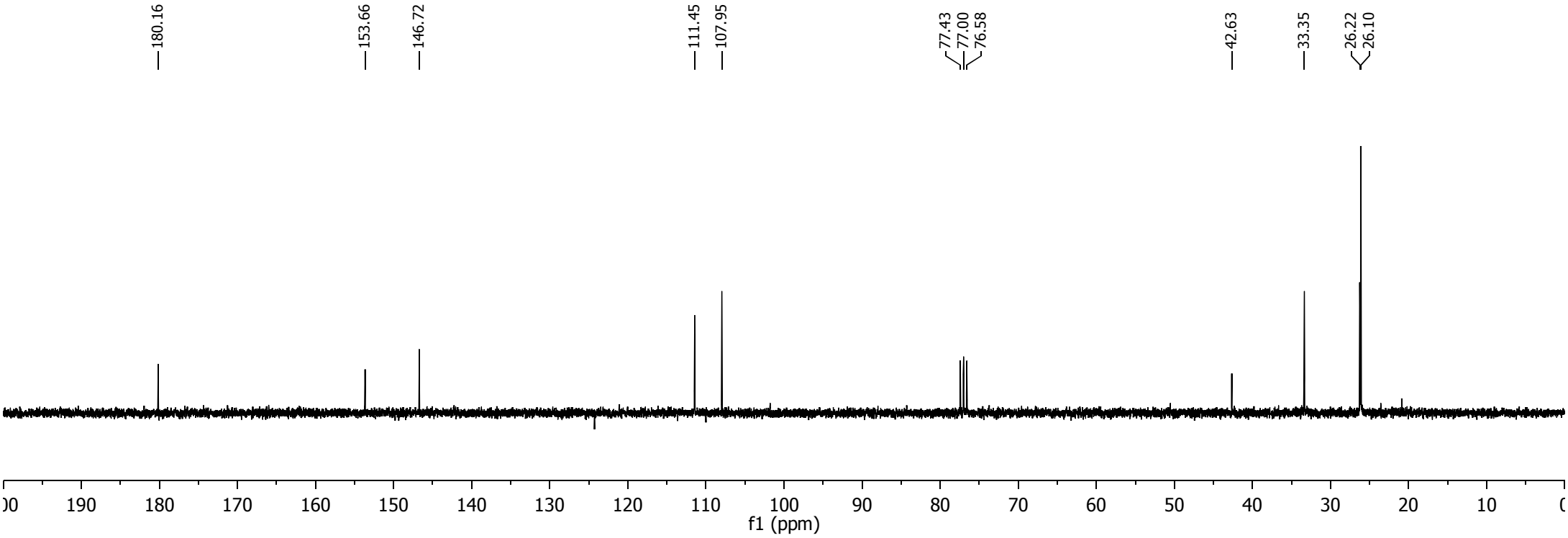

1.00
2.03
2.29
1.08
2.15
2.13
2.87
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


179.69
150.77
142.20
113.77
108.76
77.43
77.00
76.58
43.85
32.56
28.74
18.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
OH
Me
Me

29b


1.00
3.11
1.03
2.11
2.13
6.05
f1 (ppm)


180.16
153.66
146.72
111.45
107.95
77.43
77.00
76.58
42.63
33.35
26.22
26.10
f1 (ppm)