Using (+)-Carvone to Access Novel Derivatives of (+)-*ent*-Cannabidiol (CBD): The First Asymmetric Syntheses of (+)-*ent*-CBDP and (+)-*ent*-CBDV

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Supporting Information

Unless otherwise noted, reactions were performed in flame-dried glassware under an atmosphere of dry nitrogen. Reaction solvents (CH_2Cl_2, THF, and Et_2O) were purified before use in a Glass Contour Solvent Purification System under a flow of dry nitrogen. All other solvents and reagents were purchased from Sigma-Aldrich and used as received, unless otherwise specified. Thin-layer chromatography (TLC) was performed using plates precoated with silica gel 60 Å F- 254 (250 μm) purchased from Silicycle and visualized by UV light, $KMnO_4$ or anisaldehyde stains, followed by heating. Silicycle SilicaFlash ® P60 silica gel (particle size 40-63 μm) or Silicycle Brand disposable columns were used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 (operating at 500 MHz and 125 MHz, respectively), and are reported relative to residual solvent peak (δ 7.26 for ^1H and δ 77.0 for ^{13}C in $CDCl_3$). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) [multiplicity, coupling constant (Hz), integration]. Spectra obtained are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. IR spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrometer and samples were prepared by evaporation from $CHCl_3$ or CH_2Cl_2 on NaCl plates. High-resolution mass spectra were obtained through positive electrospray ionization on a Q-Tof Micromass Spectrometer coupled with a Waters Acquity Ultra Performance LC.

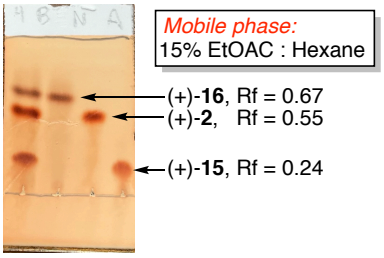
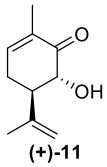


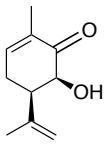
Figure ESI 1. Representative TLC Plate showing the difference in Rf values

Experimental Procedures and Characterization Data



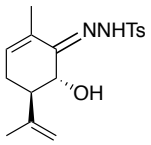
(+)-11

5*R*,6*R*-α-Hydroxy Carvone [(+)-**11**]. Was prepared according to the procedure found in *J. Med. Chem*. **2011**, *54*, 3866–3874. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.75 (d, *J* = 6 *Hz*, 1H), 4.94 (s, 1H), 4.92 (s, 1H), 4.15 (d, *J* = 13 *Hz*, 1H), 2.70 (dt, *J* = 5, 11 *Hz*, 1H), 2.51-2.45 (m, 1H), 2.40-2.34 (m, 1H), 1.84 (s, 6H). All other data matches known literature values (*Chem. Eur. J.* **2019** *25* 2983–2988).



(–)-13

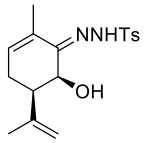
5*R*,6*S*-α-Hydroxy Carvone [(–)-**13**]. Was prepared according to the procedure found in *J. Med. Chem*. **2011**, *54*, 3866–3874. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.66-6.67 (m, 1H), 4.86 (s, 1H), 4.70 (s, 1H), 4.43 (d, *J* = 6 *Hz*, 1H), 3.18-3.20 (m, 1H), 2.76-2.71 (m, 1H), 2.55-2.50 (m, 1H), 1.83 (s, 3H), 1.69 (s, 3H). All other data matches known literature values (*Chem. Eur. J.* **2019** *25* 2983–2988).



(–)-12

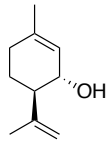
Tosylhydrazone (–)-**12**. Hydroxycarvone (+)-**11** (0.743 g, 4.47 mmol, 1.0 equiv.) was added to a 250 mL round bottom flask and dissolved in CH_2Cl_2 (55 mL). To this solution, tosylhydrazide (0.998 g, 5.36 mmol, 1.2 equiv.) was added in a single portion followed by the drop wise addition of acetic acid (0.17 mL, 3.13 mmol, 0.7 equiv.) and concentrated hydrochloric acid (0.1 mL, 4.08 mmol, 0.9 equiv.). The solution was then heated to reflux (40 °C) and allowed to stir for 48h. After the disappearance of starting material was noted *via* TLC analysis, the reaction mixture was quenched by the addition of a 1N aqueous solution of HCl (50 mL) and transferred to a separatory funnel where the aqueous layer was washed with CH_2Cl_2 (ca. 3x 50 mL). The combined organic layers were then washed with a saturated aqueous solution of $NaHCO_3$ (ca. 50 mL), followed by brine (ca. 50 mL) before being dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified *via* flash column chromatography (15% EtOAc / 85% Hexanes to 30% EtOAc / 70% Hexanes) to

afford the desired product (–)-**12** (1.100 g, 74% yield) as a thick yellow foam: $[\alpha]_D^{23}$ = -90.9 (c = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.30 (br. s, 1H), 7.84 (d, *J* = 8z *Hz*, 2H), 7.29 (d, *J* = 8 *Hz*), 5.97 (br. d, 1H), 5.02 (s, 1H), 4.91 (s, 1H), 4.44 (d, *J* = 11 *Hz*, 1H), 2.43-2.51 (m, 1H), 2.42 (s, 3H), 2.13-2.17 (m, 2H), 1.79 (s, 3H), 1.72 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) 149.5, 143.6, 143.3, 135.8, 133.1, 131.0, 129.4, 127.9, 115.5, 70.5, 51.1, 28.3, 21.6, 18.8, 18.1 ; IR (neat, thin film) 3470, 3194, 2922, 2857, 1646, 1597, 1450, 1328, 1169, 1030 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{17}H_{22}O_3N_2SNa$ 357.1248; found 357.1241 m/z.



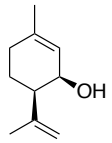
(+)-14

Tosylhydrazone (+)-**14**. Was prepared in a similar manner to tosylhydrazone (–)-**12**. The crude product was purified via flash column chromatography (15% EtOAc / 85% Hexanes to 30% EtOAc / 70% Hexanes) to afford the desired product (+)-**14** (70% yield) as a thick yellow foam: $[\alpha]_D^{23}$ = +52.7 (c = 2.0, $CHCl_3$) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.40 (br., 1H), 7.85 (d, *J* = 8 *Hz*, 2H), 7.29 (d, *J* = 8 *Hz*, 2H), 6.08-6.11 (m, 1H), 5.11 (s, 1H), 4.86 (s, 1H), 4.64 (s, 1H), 2.41 (s, 3H), 2.31-2.37 (m, 1H), 2.00-2.05 (m, 2H), 1.83 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 153.8, 143.9, 143.3, 135.1, 134.0,131.0, 129.3, 128.0, 113.6, 62.2, 45.6, 23.9, 22.3, 21.5, 17.4 ; IR (neat, thin film) 3463 (br.), 3187 (br.), 2975, 2922, 1643, 1598, 1165, 1030 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{17}H_{22}O_3N_2SNa$ 357.1248; found 357.1235 m/z..



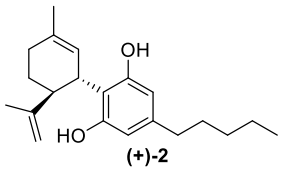
(–)-8

1*S*-(–)-Isopiperitenol [(–)-**8**]. Tosylhydrazone (–)-**12** (0.053 g, 0.158 mmol, 1.0 equiv.) was added to a flame dried 25 mL round bottom flask and dissolved in CH_2Cl_2 (3 mL). To this solution at 0 °C was added catecholborane (0.037 mL, 0.347 mmol, 2.2 equiv.) drop wise over the course of 2 min. After the addition was complete, the reaction mixture was allowed to stir for 1 h before NaOAc•XH_2O (0.078 g, 0.573 mmol, 3.6 equiv.) was added in a single portion. After an additional 1 h of stirring, a reflux condenser was attached and the mixture was heated to reflux (40 °C) overnight. After the disappearance of starting material was noted *via* TLC analysis, the reaction mixture was passed over a pad a celite and concentrated *in vacuo*. The crude product was purified *via* flash column chromatography (5% EtOAc / 95% Hexanes to 15% EtOAc / 85% Hexanes) to afford the desired product (–)-**8** (0.021 g, 88% yield) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.44 (s, 1H), 4.89 (s, 1H), 4.85 (s, 1H), 4.11 (d, *J* = 8.5 *Hz*, 1H), 2.05-2.09 (m, 2H), 1.93 (dd, *J* = 4.5, 17.5 *Hz*, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.56-1.64 (ddd, *J* = 5.5, 12, 24.5 *Hz*, 2H). All other data matches known literature values (*J. Nat. Prod*. **2018** *81*, 1546–1552).



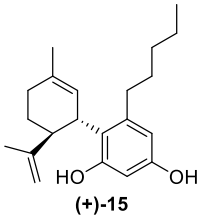
(–)-9

1*R*-(+)-Isopiperitenol [(–)-**9**]. Was prepared in a similar manner to (–)-**8**. The crude product was purified via flash column chromatography (15% EtOAc / 85% Hexanes) to afford the desired product (–)-**9** (65% yield) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.67-5.68 (m, 1H), 5.00 (s, 1H), 4.81 (s, 1H), 4.13 (br. s, 1H), 2.09-2.12 (m, 1H), 2.01-2.05 (m, 2H), 1.83 (s, 3H), 1.78-1.75 (m, 1H), 1.72 (s, 3H), 1.60-1.55 (m, 1H), 1.48 (d, *J* = 3.5 *Hz*, 1H). All other data matches known literature values (*J. Nat. Prod*. **2018** *81*, 1546–1552).



(+)-2

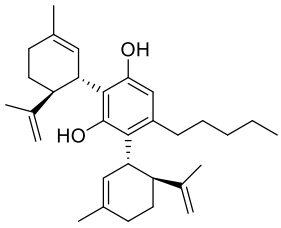
(+)-*ent*-CBD [(+)-**2**]. Basic alumina (0.920 g, 9.032 mmol, 25.0 equiv.) was added to a flame dried 10 mL roundbottom flask and suspended with CH_2Cl_2 (1.5 mL). A reflux condenser was attached to the flask before BF_3•OEt_2 (0.133 mL, 1.083 mmol, 3.0 equiv.) was added drop wise through the top of the condenser. After being allowed to stir 15 min, the flask was lowered into a pre-heated oil bath and the contents of the flask were boiled for ca. 1 min. To this solution, was added a solution of olivetol (**10**, 0.078 g, 0.433 mmol, 1.2 equiv.) and 1*S*-(–)-Isopiperitenol [(–)-**8**, 0.055 g, 0.361 mmol, 1.0 equiv.) in CH_2Cl_2 (1.5 mL) as quickly as possible *via* cannula. After 10 sec, the reaction was quenched by the addition of 2 mL of a saturated aqueous solution of $NaHCO_3$. After cooling to room temperature, the contents of the flask were passed over a pad of celite before being added to a separatory funnel and extracted using CH_2Cl_2 (ca. 10 mL). The combined organic layers were then washed with brine (ca. 20 mL) before being dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified *via* flash column chromatography (10% EtOAc / 90% Hexanes to 30% EtOAc / 70% Hexanes) to afford the desired product (+)-**2** (0.0245 g, 22% yield) as an amorphous white solid. Characterization data for (+)-**2** (known): $[\alpha]_D^{23}$ = +93.4 (c = 0.5, EtOH), {lit. $[\alpha]_D^{23}$ = +90 (c = 3, EtOH)} ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.27 (br. s, 1H), 6.17 (br. s, 1H), 5.97 (br. s, 1H), 5.57 (s, 1H), 4.69 (br. s, 1H), 4.66 (s, 1H), 4.56 (s, 1H), 3.85 (br. d, *J* = 8.5 *Hz*), 2.44 (t, *J* = 8 *Hz*, 2H), 2.40 (dt, *J* = 3, 11 *Hz*, 1H), 2.20-2.26 (m, 1H), 2.07-2.12 (m, 1H), 1.79 (s, 3H), 1.76-1.84 (m, 2H), 1.65 (s, 3H), 1.53-1.59 (m, 2H), 1.25-1.32 (m, 4H), 0.88 (t, *J* = 7 *Hz*, 3H). All other data matches known literature values (*Org. Biomol. Chem.* **2005**, *3*, 1116–1123).



(+)-15

Isolated as a by-product from the reaction of (–)-**8** and **10** shown above was the abnormal regioisomer (+)-**15** (0.0145 g, 13% yield) as an amorphous white solid. Characterization data for (+)-**15** : $[\alpha]_D^{23}$ = +68.76 (c = 0.40 $CHCl_3$) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 6.19 (s, 1H), 6.05 (br. s, 1H), 5.52 (s, 1H), 4.64 (s, 1H), 4.45 (s, 1H), 3.52 (br. d, *J* = 8.5 *Hz*, 1H), 2.55-2.61 (m, 1H), 2.44-2.49 (m, 1H), 2.21-2.28 (m, 2H), 2.06-2.11 (m, 1H), 1.72-1.86 (m, 2H), 1.78 (s, 3H), 1.53 (s, 3H), 1.44-1.48 (m, 2H), 1.25-1.34 (m, 4H), 0.89 (t, *J* = 7 *Hz*, 3H) ; ^{13}C NMR (125

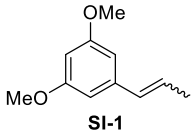
MHz, $CDCl_3$) δ = 156.6, 154.6, 147.7, 144.1, 139.9, 124.8, 120.1, 111.5, 108.6, 102.2, 45.1, 40.1, 34.1, 32.0, 31.2, 30.4, 28.2, 23.8, 22.7, 21.4, 14.2 ; IR (neat, thin film) 3429 (br.), 2857-2957, 1620, 1596, 1448, 1133, 1149, 1009, 894, 842 cm^{-1} ; HRMS (ESI) m/z: $[M+H]^+$ calc'd for $C_{21}H_{31}O_2$ 315.2326; found 315.2336 m/z.



(+)-16

Isolated as a by-product from the reaction of (–)-**8** and **10** shown above was the *bis*-CBD isomer (+)-**16** as an amorphous white solid**.** Characterization data for (+)-*bis*-CBD (0.0079g, 5% yield) $[\alpha]_D^{23} = +131.5$ (c = 0.04 $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 5.92 (s, 1H), 5.78 (s, 1H), 5.58 (s, 1H), 5.48 (s, 1H), 4.59 (s, 1H), 4.49 (s, 1H), 4.44 (s, 1H), 4.42 (s, 1H), 4.00 (br. d, J = 6.5 Hz, 1H), 3.49 (br. d, J = 7.5 Hz, 1H), 2.50-2.56 (m, 1H), 2.41-2.46 (m, 2H), 2.18-2.23 (m, 3H), 2.04-2.10 (m, 2H), 1.78 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.50-1.65 (m, 2H), 1.49 (s, 3H), 1.43-1.47 (m, 2H), 1.22-1.33 (m, 6H), 0.88 (t, *J* = 7 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.4, 154.7, 147.6, 143.9, 139.7, 132.1, 131.9, 128.5, 128.4, 124.7, 119.8, 115.2, 111.3, 108.5, 102.1, 44.9, 40.0, 33.9, 33.9, 31.9, 31.8, 31.1, 30.4, 30.2, 29.6, 28.1, 23.6, 23.6, 22.5, 21.4, 21.3, 14.0 ; IR (neat, thin film) 3438 (br.), 2854-2959, 1645, 1578-1617, 1435, 1378, 1261, 887 cm^{-1} ; HRMS (ESI) m/z: $[M+H]^+$ calc'd for $C_{31}H_{45}O_2$ 449.3421; found 449.3420 m/z.

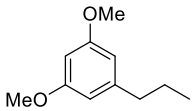
Note: By using this same procedure, substituting 1*S*-(–)-isopiperitenol with 1*R*-(–)-isopiperitenol (–)-**9** (0.050 g, 0.328 mmol), one can also obtain (+)-*ent*-CBD (+)-**2** (0.024 g, 23% yield), (+)-*abn*-CBD (+)-**15** (0.009 g, 9% yield) and (+)-*bis*-CBD (+)-**16** (0.008 g, 5% yield).



SI-1

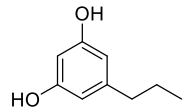
1,3-dimethoxy-5-(prop-1-en-1-yl)benzene (**SI-1**). Ethyltriphenylphosphonium bromide (1.00 g, 2.69 mmol, 1.00 equiv., Sigma Aldrich) was added to a flame dried 100 mL round bottom flask and suspended in THF (20 mL). To this suspension at 0 °C was added *n*-Butyl lithium (1.38 mL, 2.96 mmol, 2.14 M in hexanes, 1.1 equiv.) drop wise over the course of ca. 2 min. After the addition was complete, the orange / red ylide solution was allowed to stir for an additional 30 min at 0 °C before 3,5-dimethoxybenzaldehyde (0.49 g, 2.96 mmol, 1.1 equiv.) in THF (5 mL) was added drop wise *via* cannula. The reaction mixture was then allowed to warm to rt and stir overnight before being quenched with brine (ca. 25 mL), added to a separatory funnel and extracted using EtOAc (ca. 3x 25 mL). The combined organic layers were then concentrated *in vacuo*, dissolved in hexanes (ca. 25 mL) and filtered over a pad of celite to remove the triphenylphosphine oxide byproduct (*note*: it may be advantageous to repeat this operation several times to remove most of the $Ph_3P=O$). After

concentration, the crude product was purified *via* flash column chromatography (10% EtOAc / 90% Hexanes to 20% EtOAc / 80% Hexanes) to afford the desired product **SI-1** (0.3944 g, 82% yield) as an 1:1 inseparable mixture of alkene isomers that was taken directly on to the next step without extensive characterization. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.47 (d, *J* = 19.5 *Hz*, 2H), 6.37 (d, *J* = 13.5 *Hz*, 1H), 6.32-6.34 (m, 1H), *Z* alkene proton 6.25 (dq, *J* = 6.5 15.5 *Hz*, 1H) or E proton alkene 5.81 (dq, *J* = 7, 11.5 *Hz*, 1H), 3.79 (s, 6H), 1.89 (dd, *J* = 7, 16 *Hz*, 3H). All other data matches known literature values (*Tetrahedron Lett.*, **2015**, *56*, 5106–5111).



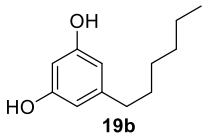
SI-2

1,3-dimethoxy-5-propylbenzene (**SI-2**). An 10 mL round bottom flask was charged with alkene isomers **SI-1** (0.745 g, 4.179 mmol, 1.0 equiv.), EtOAc (5 mL), and 5% palladium on carbon (ca. 0.100 g). A fresh septum was placed over the flask, which was then evacuated using a vacuum pump, replacing the inner atmosphere with a blanket of H_2 using a balloon (*note*: this step was repeated several times to ensure all of the air had been replaced by H_2). After being allowed to stir 2 h, the crude product was passed over a bed of celite and concentrated *in vacuo* to afford the desired product **SI-2** (0.736 g, 98% yield) as a slight yellow oil in sufficient enough purity to use in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.34 (s, 2H), 6.30 (s, 1H), 3.78 (s, 6H), 2.53 (t, *J* = 7.5 *Hz*, 2H), 1.63 (q, *J* = 7.5 *Hz*, 2H), 0.94 (t, *J* = 7 *Hz*, 3H). All other data matches known literature values (*J. Org. Chem.* **1997**, *62*, 417–421).



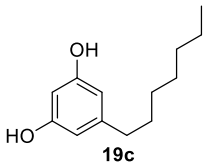
19a

5-propylbenzene-1,3-diol (**19a**). In a 100 mL round bottom flask, open to the atmosphere was added the crude product **SI-2** (0.736 g, 4.08 mmol, 1.0 equiv.) and a 1:1 mixture of glacial acetic acid (20 mL, 349.7 mmol, 17.4 M) and hydrobromic acid (48% in H_2O, 20 mL, 368.3 mmol, 18.4 M). The reaction mixture was refluxed at 125 °C for 3 hours while stirring, or until the starting material was consumed via TLC analysis. At this point, the reaction was allowed to cool to room temperature and quenched by the addition of DI H_2O. The biphasic solution was added to a separatory funnel, wherein the organic portion was extracted Et_2O (ca. 3x 20 mL). The organic layers were then combined, neutralized with a concentrated sodium bicarbonate solution (ca. 30 mL), washed with a saturated brine solution (ca. 50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the final product without purification (0.609 g, 99% yield) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.24 (s, 2H), 6.17 (s, 1H), 4.63 (br. s, 2H), 2.47 (t, *J* = 7.5 *Hz*, 2H), 1.60 (q, *J* = 7.5 *Hz*, 2H), 0.93 (t, *J* = 7.5 *Hz*, 3H). All other data matches known literature values (*J. Org. Chem.* **1997**, *62*, 417–421).



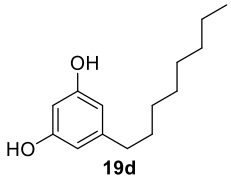
19b

5-hexylbenzene-1,3-diol (**19b**). Was prepared in a similar manner to **19a** by substituting ethyltriphenylphosphonium bromide with pentyltriphenylphosphonium bromide (0.153 g, 0.372 mmol, 1.0 equiv.). After three steps, the crude product was purified *via* flash column chromatography (15% EtOAc / 85% Hexanes) to afford the desired product **19b** (0.0617 g, 85% yield) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.24 (s, 2H), 6.18 (s, 1H), 4.70 (br. s, 2H), 2.44 (t, *J* = 7.5 *Hz*, 2H), 1.50-1.54 (m, 2H), 1.24-1.31 (m, 6H), 0.86 (t, *J* = 7 *Hz*, 3H). All other data matches known literature values (*Chem. Pharm. Bull.* **1989**, *37*, 2431–2434).



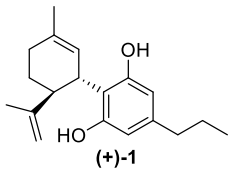
19c

5-heptylbenzene-1,3-diol (**19c**). Was prepared in a similar manner to **19a** by substituting ethyltriphenylphosphonium bromide with hexyltriphenylphosphonium bromide (2.00 g, 4.68 mmol, 1.0 equiv.). After three steps, the crude product was purified *via* flash column chromatography (15% EtOAc / 85% Hexanes) to afford the desired product **19c** (0.386 g, 96% yield) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.24 (s, 2H), 6.17 (s, 1H), 4.64 (br. s, 2H), 2.48 (t, *J* = 8 *Hz*, 2H), 1.20-1.30 (m, 10H), 0.88 (t, *J* = 6.5 *Hz*, 3H). All other data matches known literature values (*Chem. Pharm. Bull.* **1989**, *37*, 2431–2434)..



19d

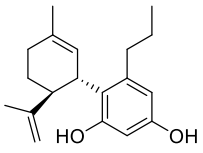
5-octylbenzene-1,3-diol (**19d**). Was prepared in a similar manner to **19a** by substituting ethyltriphenylphosphonium bromide with heptyltriphenylphosphonium bromide (0.132 g, 0.299 mmol, 1.0 equiv.). After three steps, the crude product was purified *via* flash column chromatography (15% EtOAc / 85% Hexanes) to afford the desired product **19d** (0.0385 g, 58% yield) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.24 (s, 2H), 6.17 (s, 1H), 2.48 (t, *J* = 8 *Hz*, 2H), 1.24-1.31 (m, 12H), 0.88 (t, *J* = 7 *Hz*, 3H). All other data matches known literature values (*J. Exp. Bot.* **2007***, 58,* 3262–3272).



(+)-1

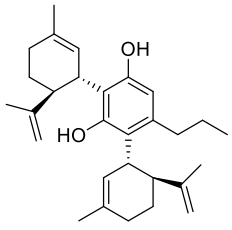
(+)-*ent*-CBDV [(+)-**1**]. Was prepared in a similar manner to (+)-*ent*-CBD [(+)-**2**] by substituting olivetol (**10**) with 5-propylbenzene-1,3-diol (**19a**, 0.059 g, 0.394 mmol, 1.2 equiv.). The crude product was purified *via* flash column chromatography (10% EtOAc / 90% Hexanes to 30% EtOAc / 70% Hexanes) to afford the desired product (+)-**1** (0.0349 g, 37% yield) as an amorphous white solid. Characterization data for (+)-**1**: $[\alpha]_D^{23}$ = +64.0 (c = 1.9, $CHCl_3$) {lit. for (–)-CBDV: $[\alpha]_D^{23}$ = –139.5 (c = 0.4, $CHCl_3$) *Tetrahedron Lett*. **1969**, (*3*), 145–147} ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.28 (br. s, 1H), 6.16 (br. s, 1H), 5.99 (br. s, 1H), 5.57 (s, 1H), 4.72 (br. s, 1H), 4.65

(s, 1H), 4.55 (s, 1H), 3.85 (br. d, *J* = 10 *Hz*, 1H), 2.42 (t, *J* = 7.5 *Hz*, 2H), 2.36-2.38 (m, 1H), 2.10-2.26 (m, 1H), 2.07-2.11 (m, 1H), 1.79 (s, 3H), 1.73-1.83 (m, 2H), 1.65 (s, 3H), 1.58 (q, J = 7.5 Hz, 2H), 0.90 (t, *J* = 7 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.5, 142.8, 140.2, 124.2, 123.8, 113.9, 110.9, 107.7, 46.2, 37.7, 37.3, 30.5, 28.5, 24.1, 23.8, 20.6, 13.9 ; IR (neat, thin film) 3435 (br.), 2865-2965, 1629, 1582, 1448 cm^{-1} ; HRMS (ESI) m/z: $[M+K]^+$ calc'd for $C_{19}H_{26}O_2K$ 325.2916; found 325.1598 m/z.



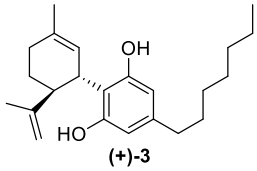
SI-3

Isolated as a by-product from the reaction of (–)-**8** and **19a** shown above was the abnormal regioisomer (+)-*abn*-CBDV (**SI-3**, 0.0169 g, 18% yield) as an amorphous white solid. Characterization data for (+)-**SI-3**: $[\alpha]_D^{23}$ = +82.2 (c = 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 6.19 (s, 1H), 6.04 (s, 1H), 5.52 (s, 1H), 4.64 (s, 1H), 4.45 (s, 1H), 3.53 (d, *J* = 8.5 *Hz*, 1H), 2.52-2.61 (m, 1H), 2.45-2.50 (m, 1H), 2.21-2.27 (m, 2H), 2.06-2.11 (m, 1H), 1.78 (s, 3H), 1.74-1.85 (m, 2H), 1.53 (s, 3H), 1.44-1.51 (m, 2H), 0.92 (t, *J* = 7 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.6, 154.6, 147.7, 143.8, 139.9, 124.8, 120.1, 111.5, 108.7, 102.2, 45.1, 40.1, 36.2, 30.4, 28.2, 24.6, 23.8, 21.4, 14.3 ; IR (neat, thin film) 3414 (br.), 2870-2963, 1625, 1596, 1448, 1150, 1002, 887, 844 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{19}H_{26}O_2Na$ 309.1830; found 309.1824 m/z.



SI-4

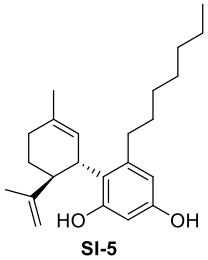
Isolated as a by-product from the reaction of (–)-**8** and **19a** shown above was the *bis* isomer **SI-4** as an amorphous white solid. Characterization data for (+)-*bis*-CBDV (**SI-4**, 0.0172g, 12% yield) $[\alpha]_D^{23}$ = +101.07 (c = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 5.91 (s, 1H), 5.77 (s, 1H), 5.58 (s, 1H), 5.48 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 4.45 (s, 1H), 4.42 (s, 1H), 4.00 (br d, *J* = 9 *Hz*, 1H), 3.50 (br d, *J* = 8 *Hz*, 1H), 2.50-2.56 (m, 1H), 2.40-2.48 (m, 2H), 2.05-2.25 (m, 7H), 1.78 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.63-1.67 (m, 2H), 1.52-1.56 (m, 2H), 1.49 (s, 3H), 0.91 (t, *J* = 7.5 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) 154.1, 153.8, 148.0, 147.7, 141.1, 139.8, 139.2, 125.1, 125.0, 119.2, 115.4, 111.5, 111.4, 109.6, 46.7, 44.5, 40.6, 36.2, 35.8, 30.6, 30.5, 28.6, 28.5, 24.6, 23.7, 23.6, 21.6, 19.0, 14.4 ; IR (neat, thin film) 3441 (br.), 2832-2962, 1645, 1622, 1581, 1432 cm^{-1} ; HRMS (ESI) m/z: $[M]^+$ calc'd for $C_{29}H_{41}O_2$ 421.3108; found 421.3116 m/z.



(+)-3

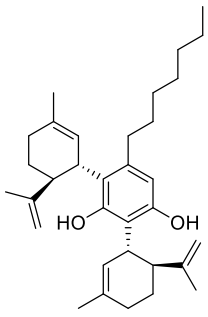
(+)-*ent*-CBDP [(+)-**3**]. Was prepared in a similar manner to (+)-*ent*-CBD [(+)-**2**] by substituting olivetol (**10**) with 5-heptylbenzene-1,3-diol (**19c**, 0.0782 g, 0.375 mmol, 1.2 equiv.). The crude product was purified *via* flash column chromatography (10% EtOAc / 90% Hexanes to 30% EtOAc / 70%

Hexanes) to afford the desired product (+)-**3** (0.0232 g, 22% yield) as an amorphous white solid. Characterization data for (+)-**3**: $[\alpha]_D^{23}$ = +126.0 (c = 0.02, MeCN) {lit. for (–)-CBDP: $[\alpha]_D^{23}$ = –146.0 (c = 1.0, MeCN) *Scientific Reports,* **2019**, *9*, 20335} ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.28 (br. s, 1H), 6.16 (br. s, 1H), 5.97 (br. s, 1H), 5.56 (s, 1H), 4.66 (s, 1H), 4.59 (br. s, 1H), 4.55 (s, 1H), 3.84 (br. d, *J* = 8.5 *Hz*, 1H), 2.43 (t, *J* = 8 *Hz*, 2H), 2.39 (dt, *J* = 5, 10.5 *Hz*, 1H), 2.19-2.26 (m, 1H), 2.06-2.12 (m, 1H), 1.79 (s, 3H), 1.72-1.83 (m, 2H), 1.65 (s, 3H), 1.52-1.57 (m, 3H), 1.24-1.29 (m, 7H), 0.87 (t, *J* = 7 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.2, 153.9, 149.5, 143.1, 140.2, 124.2, 113.8, 110.9, 109.9, 108.1, 46.2, 37.4, 35.6, 31.9, 31.1, 30.5, 29.4, 29.3, 28.5, 23.8, 22.8, 20.6, 14.2 ; IR (neat, thin film) 3433 (br.), 2855-2958, 1629, 1584, 1443 cm^{-1} ; HRMS (ESI) m/z: $[M]^+$ calc'd for $C_{23}H_{35}O_2$ 343.2639; found 343.2639 m/z.



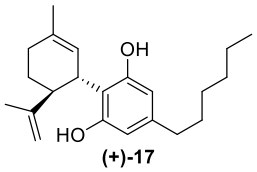
SI-5

Isolated as a by-product from the reaction of (–)-**8** and **19c** shown above was the abnormal regioisomer (+)-*abn*-CBDP (**SI-5**, 0.0066 g, 6% yield) as an amorphous white solid. Characterization data for (+)-**SI-5**: $[\alpha]_D^{23}$ = +81.7 (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 6.19 (s, 1H), 6.04 (s, 1H), 5.52 (s, 1H), 4.64 (s, 1H), 4.45 (s, 1H), 3.52 (br. d, *J* = 10 *Hz*, 1H), 2.55-2.61 (m, 1H), 2.44-2.49 (m, 1H), 2.19-2.28 (m, 2H), 2.06-2.12 (m,1H), 1.78 (s, 3H), 1.72-1.85 (m, 2H), 1.53 (s, 3H), 1.43-1.48 (m, 2H), 1.25-1.30 (m, 8H), 0.88 (t, *J* = 7.5 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.6, 154.6, 147.7, 144.1, 139.9, 124.8, 120.1, 111.5, 108.6, 102.2, 45.1, 40.1, 34.1, 31.9, 31.5, 30.4, 29.8, 29.3, 28.2, 23.8, 22.8, 21.4, 14.2 ; IR (neat, thin film) 3439 (br.), 2855-2959, 1628, 1590, 1443, 1149, 1133 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{23}H_{34}O_2Na$ 365.2456; found 365.2459 m/z.



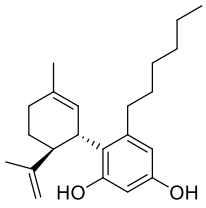
SI-6

Isolated as a by-product from the reaction of (–)-**8** and **19c** shown above was the *bis* isomer **SI-6** as an amorphous white solid**.** Characterization data for (+)-*bis*-CBDP (**SI-6**, 0.0162 g, 11% yield): $[\alpha]_D^{23}$ = +95.68 (c = 0.2, $CHCl_3$) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 5.92 (s, 1H), 5.77 (s, 1H), 5.58 (s, 1H), 5.48 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 4.45 (s, 1H), 4.42 (s, 1H), 4.00 (br. d, *J* = 7 *Hz*, 1H), 3.49 (br. d, *J* = 9 *Hz*, 1H), 2.53 (quint., *J* = 8 *Hz*, 1H), 2.39-2.47 (m, 2H), 2.18-2.25 (m, 3H), 2.04-2.10 (m, 2H), 1.78 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.49 (s, 3H), 1.42-1.56 (m, 5H), 1.23-1.30 (m, 9H), 0.87 (t, *J* = 7 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.1, 153.8, 148.0, 147.7, 141.3, 139.8, 139.2, 125.1, 124.9, 119.1, 115.4, 111.4, 111.3, 109.5, 46.7, 44.4, 40.6, 35.8, 34.1, 31.9, 31.6, 30.6, 30.5, 29.9, 29.3, 28.6, 28.5, 23.8, 23.7, 22.8, 21.6, 19.0, 14.2 ; IR (neat, thin film) 3441 (br.), 3073, 2830-2962, 1624, 1577, 1434, 1376, 1260, 888 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{33}H_{48}O_2Na$ 499.3551; found 499.3536 m/z.



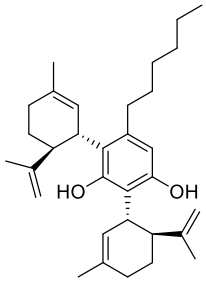
(+)-17

(+)-*ent*-CBD-Hex [(+)-**17**]. Was prepared in a similar manner to (+)-*ent*-CBD [(+)-**2**] by substituting olivetol (**10**) with 5-hexylbenzene-1,3-diol (**19b**, 0.061 g, 0.313 mmol, 1.0 equiv.). The crude product was purified *via* flash column chromatography (10% EtOAc / 90% Hexanes to 30% EtOAc / 70% Hexanes) to afford the desired product (+)-**17** (0.036 g, 35% yield) as an amorphous white solid. Characterization data for (+)-**17**: $[\alpha]_D^{23} = +66.86$ (c = 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.28 (br. s, 1H), 6.16 (br. s, 1H), 5.98 (br. s, 1H), 5.57 (s, 1H), 4.69 (br. s, 1H), 4.66 (s, 1H), 4.55 (s, 1H), 3.85 (br. d, *J* = 10 *Hz*, 1H), 2.43 (t, *J* = 8 *Hz*, 2H), 2.36-2.40 (m, 1H), 2.07-2.26 (m, 2H), 1.79 (s, 3H), 1.71-1.82 (m, 2H), 1.65 (s, 3H), 1.53-1.57 (m, 2H), 1.25-1.30 (m, 6H), 0.86-0.89 (m, 3H), ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.7, 154.1, 149.4, 143.0, 140.0, 124.1, 113.7, 110.8, 110.0, 107.5, 46.1, 37.2, 35.5, 31.7, 30.9, 30.4, 28.9, 28.4, 23.7, 22.6, 20.5, 14.1 ; IR (neat, thin film) 3444 (br.), 2853-2961, 1629, 1582, 1446, 1028 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{22}H_{32}O_2Na$ 351.2288 m/z .



SI-7

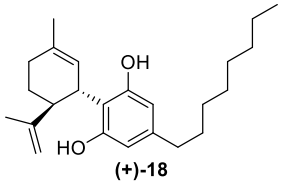
Isolated as a by-product from the reaction of (–)-**8** and **19b** shown above was the abnormal regioisomer (+)-*abn*-CBDH (**SI-7**, 0.0133 g, 13% yield) as an amorphous white solid. Characterization data for (+)-**SI-7**: $[\alpha]_D^{23} = +123.73$ (c = 0.06, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.19 (s, 1H), 6.20 (s, 1H), 6.04 (s, 1H), 5.52 (s, 1H), 4.64 (s, 1H), 4.45 (s, 1H), 3.49-3.55 (m, 1H), 2.55-2.61 (m, 1H), 2.44-2.49 (m, 1H), 2.19-2.28 (m, 2H), 2.07-2.11 (m, 1H), 1.79 (s, 3H), 1.74-1.83 (m, 2H), 1.53 (s, 3H), 1.44-1.47 (m, 2H), 1.27-1.31 (m, 6H), 0.86-0.90 (m, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.4, 154.6, 147.7, 144.1, 139.9, 124.8, 120.1, 111.5, 108.6, 102.2, 45.1, 40.1, 34.1, 31.8, 31.5, 30.4, 29.5, 28.2, 23.8, 22.7, 21.4, 14.2 ; IR (neat, thin film) 3433 (br.), 2853-2958, 1594-1622, 1453, 1149, 1135 cm^{-1} ; HRMS (ESI) m/z: $[M]^+$ calc'd for $C_{22}H_{24}O_2$ 329.2482; found 329.2480 m/z.



SI-8

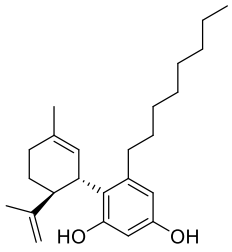
Isolated as a by-product from the reaction of (–)-**8** and **19b** shown above was the *bis* isomer **SI-8** as an amorphous white solid. Characterization data for (+)-*bis*-CBDH (**SI-8**, 0.0306 g, 21% yield) $[\alpha]_D^{23} = +103.87$ (c = 0.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 5.92 (s, 1H), 5.77 (s, 1H), 5.58 (s, 1H), 5.48 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 4.44 (s, 1H), 4.42 (s, 1H), 4.00 (br. d, *J* = 8.5 *Hz*, 1H), 3.48-3.50 (m, 1H), 2.53 (quint., *J* = 7.5 *Hz*, 1H), 2.41-2.47 (m, 2H), 2.18-2.24 (m, 3H), 2.04-2.10 (m, 2H), 1.78 (s, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.53-1.67 (m, 4H), 1.49 (s, 3H), 1.39-1.46 (m, 2H), 1.25-1.31 (m, 6H), 0.85-0.90 (m, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.1, 153.8, 148.0, 147.7, 141.3, 139.8, 139.2, 125.1, 124.9, 119.1, 115.4, 111.4, 111.3, 109.5, 46.7, 44.4, 40.6, 35.8, 34.1,

31.9, 31.6, 30.6, 30.5, 29.6, 28.6, 28.4, 23.8, 23.7, 22.8, 21.6, 19.0, 14.2 ; IR (neat, thin film) 3440 (br.), 3073, 2832-2968, 1644, 1620, 1579, 1434, 1376, 1257, 890 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{32}H_{46}O_2Na$ 485.3395; found 485.3393 m/z.



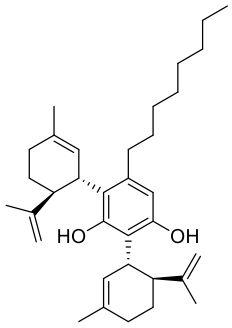
(+)-18

(+)-*ent*-CBD-Oct [(+)-**18**]. Was prepared in a similar manner to (+)-*ent*-CBD [(+)-**2**] by substituting olivetol (**10**) with 5-octylbenzene-1,3-diol (**19d**, 0.086 g, 0.394 mmol, 1.2 equiv.). The crude product was purified *via* flash column chromatography (10% EtOAc / 90% Hexanes to 30% EtOAc / 70% Hexanes) to afford the desired product (+)-**18** (0.0324 g, 28% yield) as an amorphous white solid. Characterization data for (+)-**18**: $[\alpha]_D^{23} = +71.64$ (c = 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.27 (br. s, 1H), 6.15 (br. s, 1H), 5.97 (br. s, 1H), 5.56 (s, 1H), 4.65 (s, 1H), 4.55 (s, 1H), 3.84 (br. d, *J* = 8.5 *Hz*, 1H), 2.43 (t, *J* = 8 *Hz*, 2H), 2.39 (dt, *J* = 2.5, 11 *Hz*, 1H), 2.20-2.25 (m, 1H), 2.06-2.12 (m, 1H), 1.79 (s, 3H), 1.75-1.83 (m, 2H), 1.65 (s, 3H), 1.20-1.60 (m, 12H), 0.87 (t, *J* = 6.5 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.2, 154.0, 149.5, 143.1, 140.2, 124.2, 113.8, 100.9, 109.9, 108.0, 46.2, 37.4, 35.6, 32.0, 31.1, 30.5, 29.6, 29.4, 29.4, 28.5, 23.8, 22.8, 20.6, 14.2 ; IR (neat, thin film) 3443 (br.), 2855-2955, 1628, 1581, 1445 cm^{-1} ; HRMS (ESI) m/z: $[M]^+$ calc'd for $C_{24}H_{37}O_2$ 357.2795; found 357.2785 m/z.



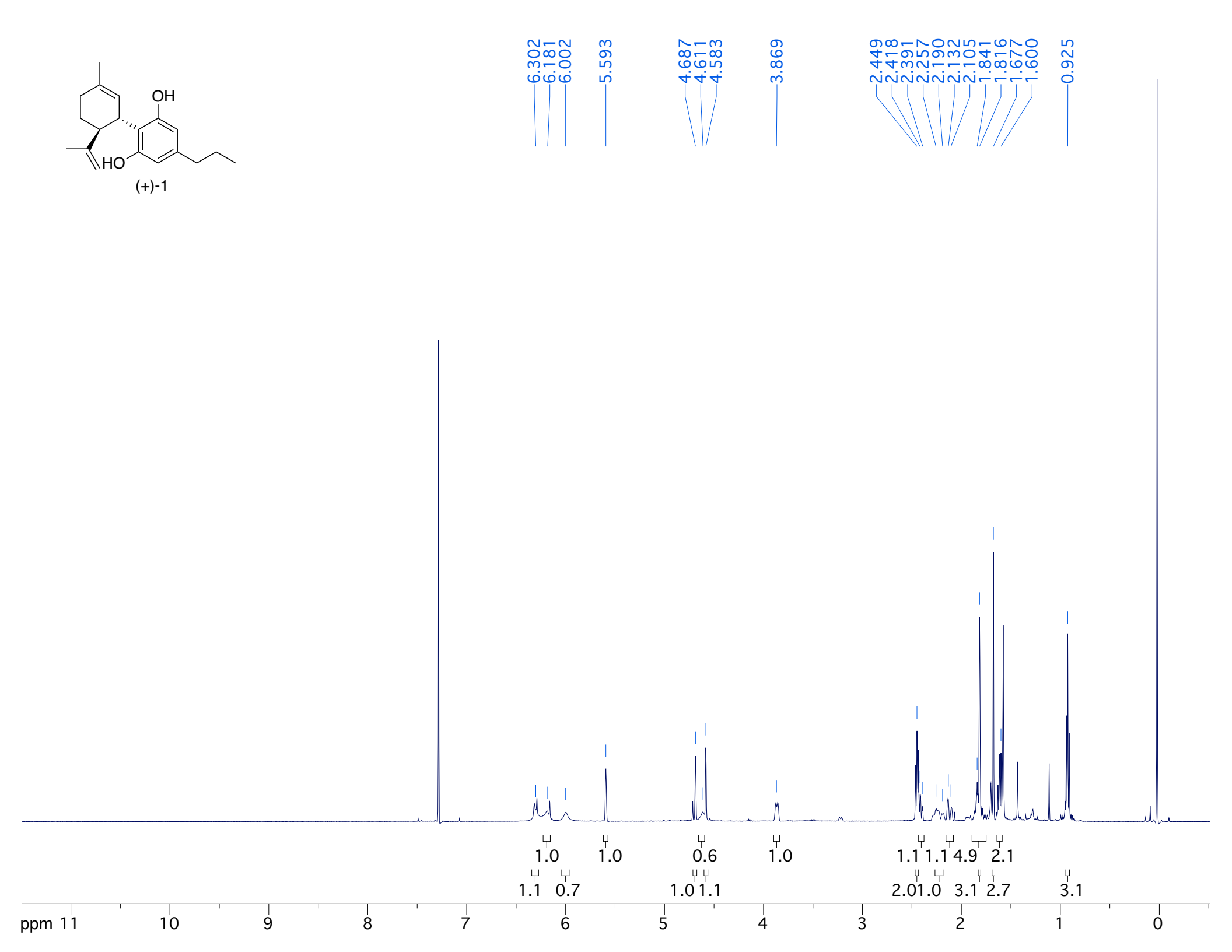
SI-9

Isolated as a by-product from the reaction of (–)-**8** and **19d** shown above was the abnormal regioisomer (+)-*abn*-CBD-Oct (**SI-9**, 0.0179 g, 15% yield) as an amorphous white solid. Characterization data for (+)-**SI-9**: $[\alpha]_D^{23} = +84.5$ (c = 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 6.19 (s, 1H), 6.04 (s, 1H), 5.52 (s, 1H), 4.64 (s, 1H), 4.45 (s, 1H), 3.52 (br. d, *J* = 8 *Hz*, 1H), 2.58 (quint., *J* = 7 *Hz*, 1H), 2.47 (app. t, *J* = 9.5 *Hz*, 1H), 2.19-2.28 (m, 2H), 2.06-2.12 (m, 1H), 1.78 (s, 3H), 1.75-1.86 (m, 2H), 1.53 (s, 3H), 1.40-1.50 (m, 2H), 1.20-1.33 (m, 10H), 0.88 (t, *J* = 6.5 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 156.6, 154.6, 147.7, 144.1, 139.9, 124.8, 120.0, 111.5, 108.6, 102.2, 45.0, 40.1, 34.1, 32.0, 31.5, 30.4, 29.8, 29.6, 29.4, 28.2, 23.8, 22.8, 21.4, 14.2 ; IR (neat, thin film) 3439 (br.), 2852-2952, 1632, 1592, 1449, 1149, 1133 cm^{-1} ; HRMS (ESI) m/z: $[M]^+$ calc'd for $C_{24}H_{37}O_2$ 357.2795; found 357.2803 m/z.



SI-10

Isolated as a by-product from the reaction of (–)-**8** and **19d** shown above was the *bis* isomer **SI-10** as an amorphous white solid. Characterization data for (+)-*bis*-CBD-Oct (**SI-10**, 0.033 g, 21% yield): $[\alpha]_D^{23} = +95.08$ (c = 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ = 6.20 (s, 1H), 5.92 (s, 1H), 5.78 (br. s, 1H), 5.58 (s, 1H), 5.49 (s, 1H), 4.60 (s, 1H), 4.50 (s, 1H), 4.45 (s, 1H), 4.42 (s, 1H), 4.00 (br. d, *J* = 8.5 *Hz*, 1H), 3.48-3.50 (m, 1H), 2.53 (quint. , *J* = 7.5 *Hz*, 1H), 2.40-2.47 (m, 2H), 2.18-2.30 (m, 3H), 2.03-2.11 (m, 2H), 1.78 (s, 3H), 1.76 (s, 3H), 1.75-1.83 (m, 4H), 1.70 (s, 3H), 1.49 (s, 3H), 1.25-1.30 (m, 12H), 0.87 (t, *J* = 6.5 *Hz*, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.1, 153.8, 148.0, 147.7, 141.3, 139.8, 139.2, 125.1, 124.9, 119.1, 115.4, 111.4, 111.3, 109.5, 46.7, 44.4, 40.6, 35.8, 34.1, 32.0, 31.6, 30.5, 30.5, 29.9, 29.6, 29.6, 28.6, 28.5, 23.8, 23.7, 22.8, 21.6, 19.0, 14.2 ; IR (neat, thin film) 3441 (br.), 3075, 2857-2962, 1646, 1624, 1577, 1432, 1376, 1258, 885 cm^{-1} ; HRMS (ESI) m/z: $[M+Na]^+$ calc'd for $C_{34}H_{50}O_2Na$ 513.3708; found 513.3689 m/z .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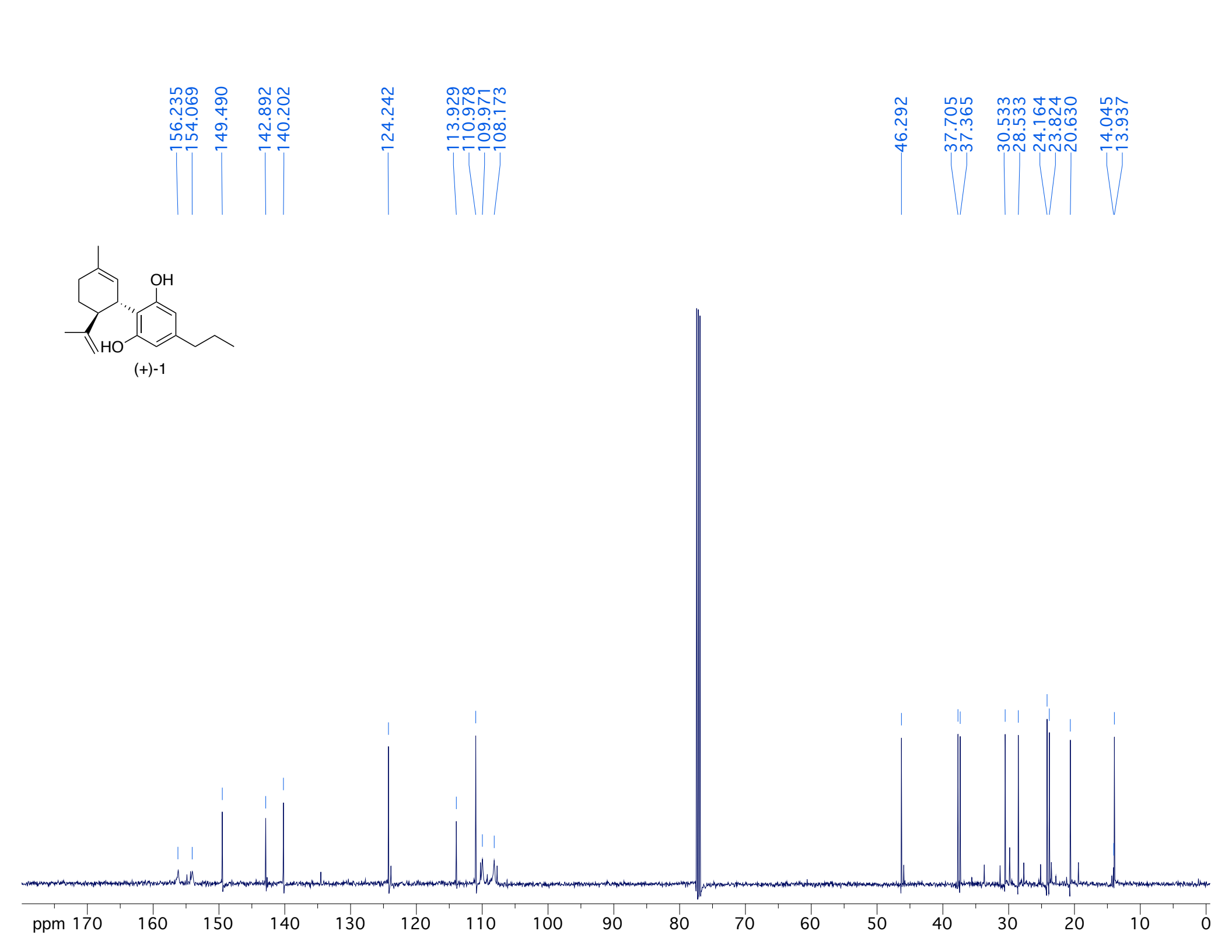
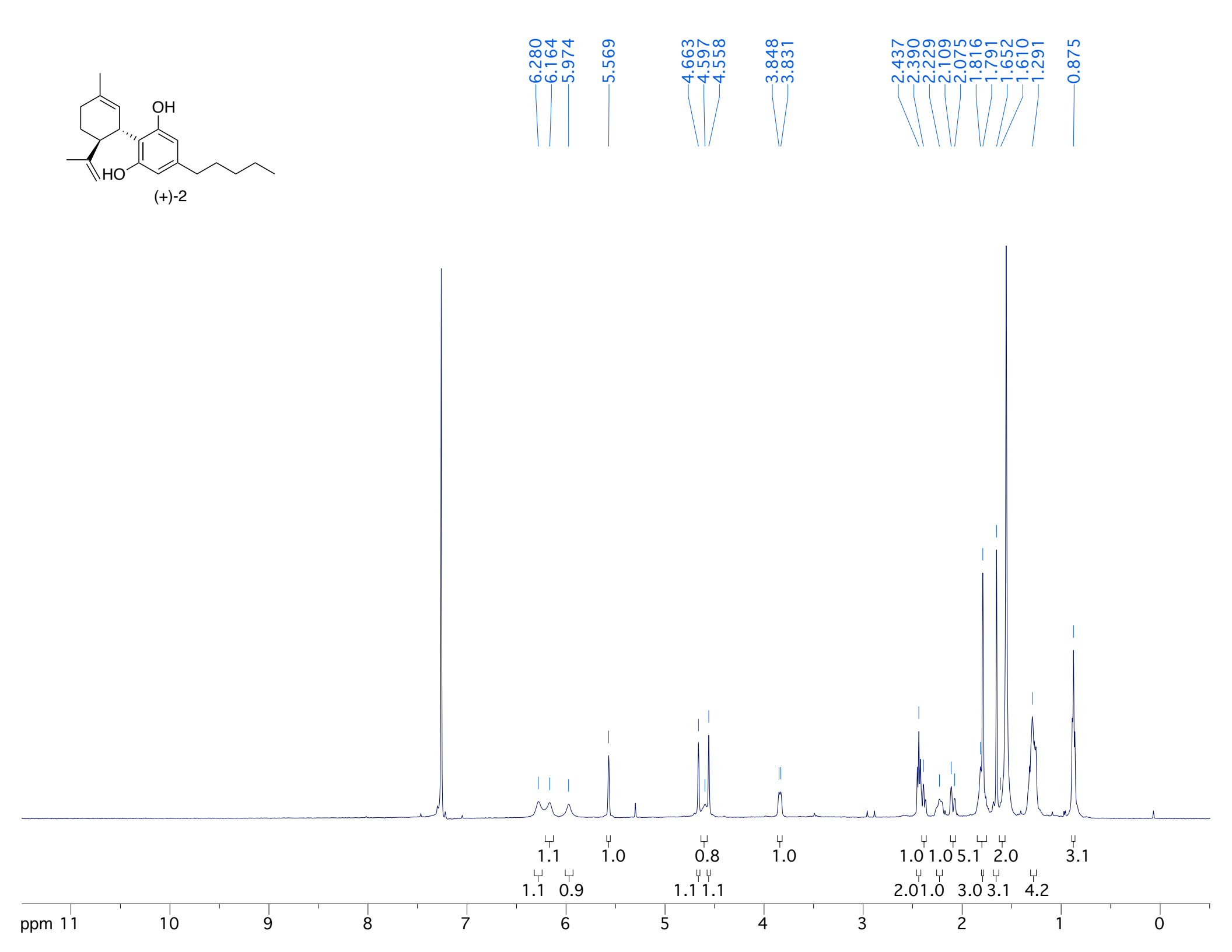
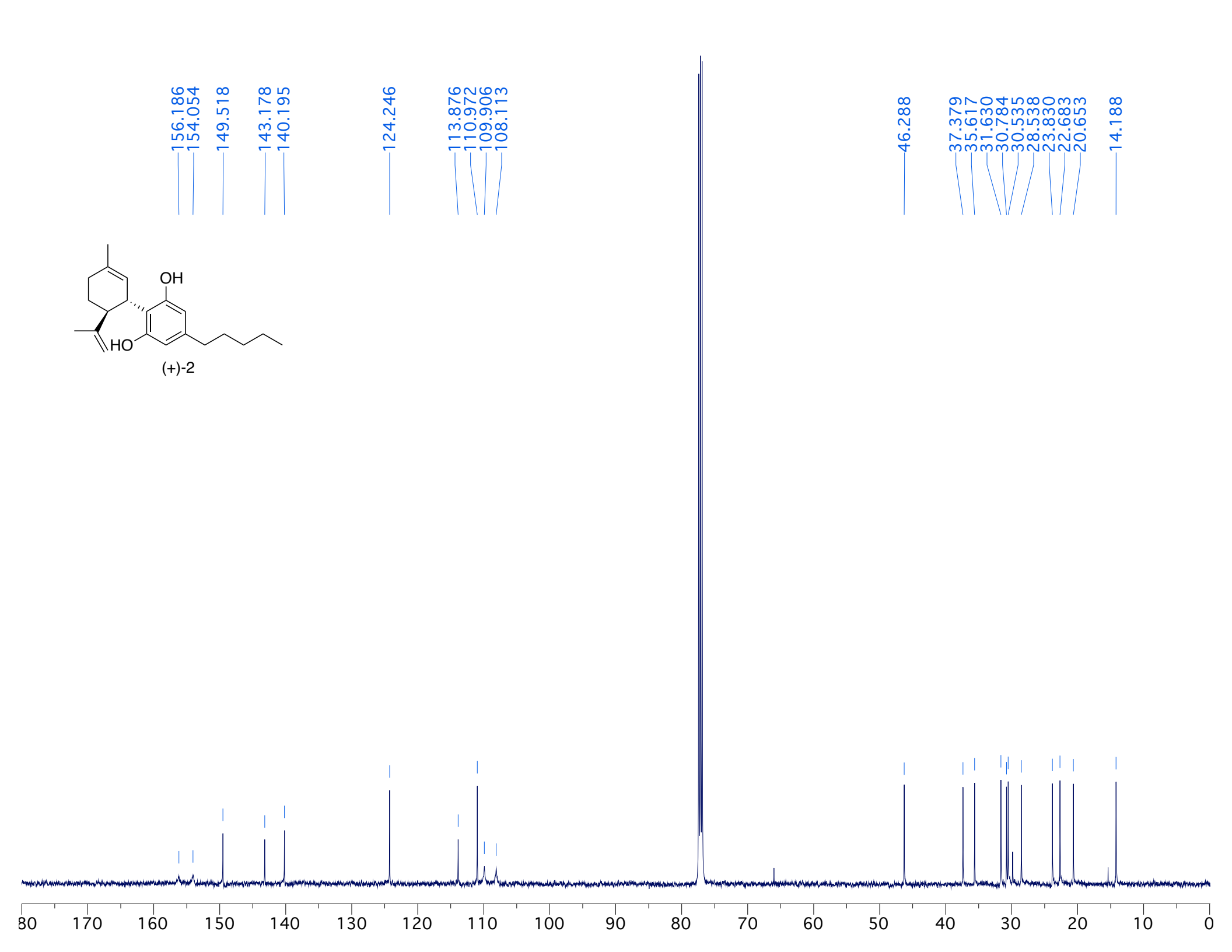
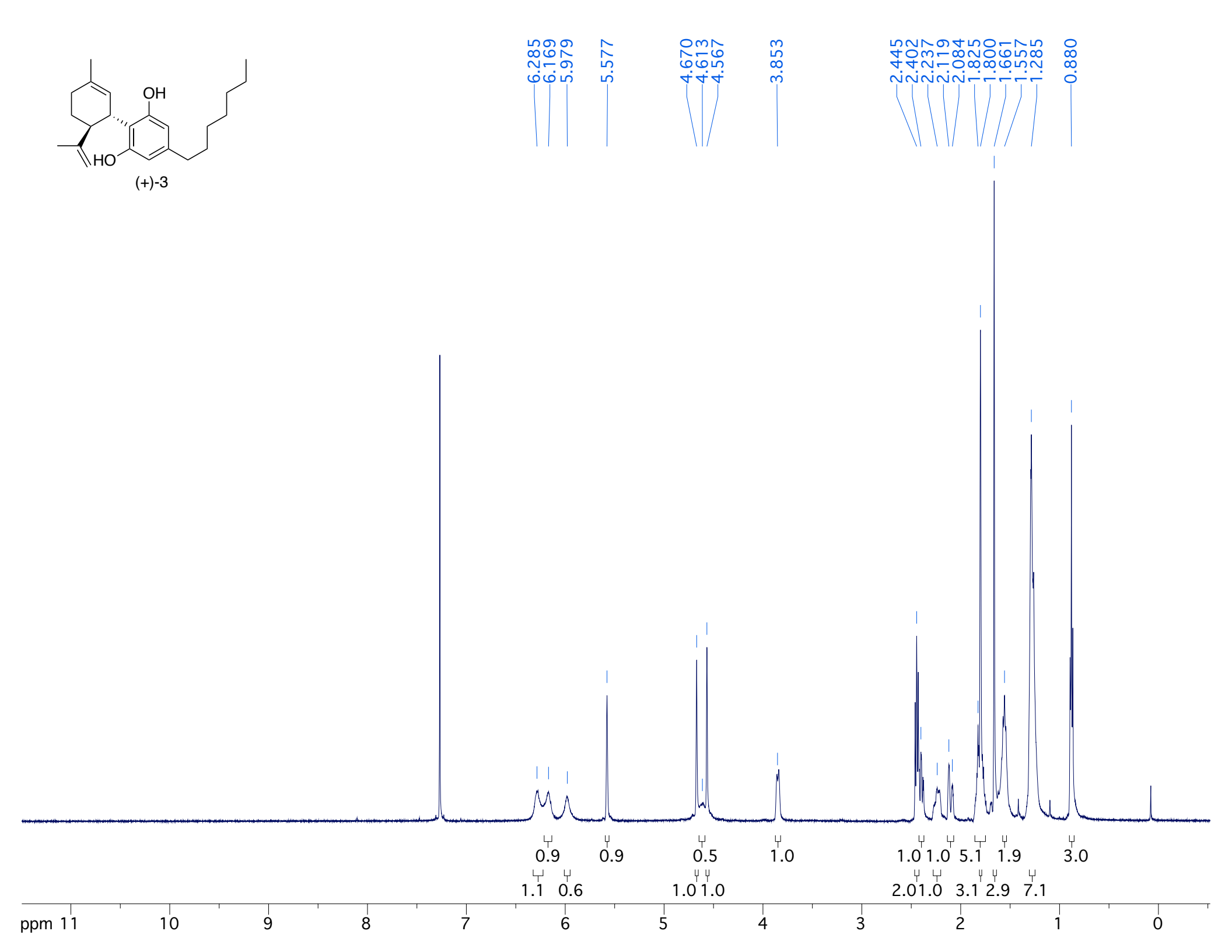
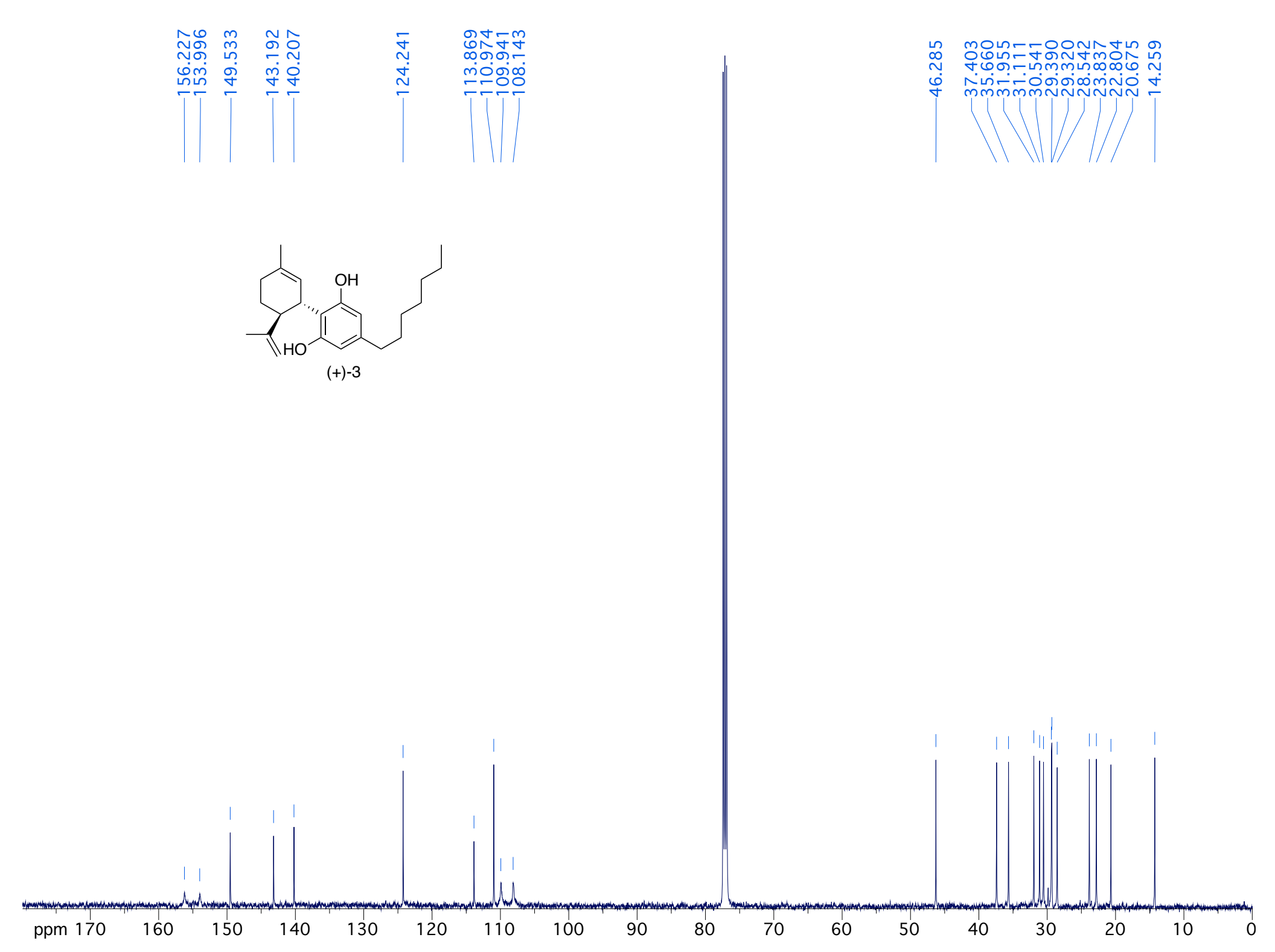
HO
(+)-1
6.302
6.181
6.002
5.593
4.687
4.611
4.583
3.869
2.449
2.418
2.391
2.257
2.190
2.132
2.105
1.841
1.816
1.677
1.600
0.925
1.0
1.0
0.6
1.0
1.1
1.1
4.9
2.1
1.1
0.7
1.0
1.1
2.0
1.0
3.1
2.7
3.1
ppm 11
10
9
8
7
6
5
4
3
2
1
0

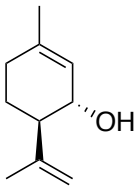

156.235
154.069
149.490
142.892
140.202
124.242
113.929
110.978
109.971
108.173
46.292
37.705
37.365
30.533
28.533
24.164
23.824
20.630
14.045
13.937
OH
HO
(+)-1
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
HO
(+)-2
6.280
6.164
5.974
5.569
4.663
4.597
4.558
3.848
3.831
2.437
2.390
2.229
2.109
2.075
1.816
1.791
1.652
1.610
1.291
0.875
1.1
1.0
0.8
1.0
1.0
1.0
5.1
2.0
3.1
1.1
0.9
1.1
1.1
2.0
1.0
3.0
3.1
4.2
ppm 11
10
9
8
7
6
5
4
3
2
1
0


156.186
154.054
149.518
143.178
140.195
124.246
113.876
110.972
109.906
108.113
46.288
37.379
35.617
31.630
30.784
30.535
28.538
23.830
22.683
20.653
14.188
OH
HO
(+)-2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

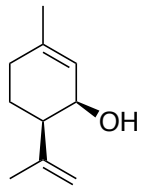

OH
HO
(+)-3
6.285
6.169
5.979
5.577
4.670
4.613
4.567
3.853
2.445
2.402
2.237
2.119
2.084
1.825
1.800
1.661
1.557
1.285
0.880
0.9
0.9
0.5
1.0
1.0
1.0
5.1
1.9
3.0
1.1
0.6
1.0
1.0
2.0
1.0
3.1
2.9
7.1
ppm 11
10
9
8
7
6
5
4
3
2
1
0


156.227
153.996
149.533
143.192
140.207
124.241
113.869
110.974
109.941
108.143
46.285
37.403
35.660
31.955
31.111
30.541
29.390
29.320
28.542
23.837
22.804
20.675
14.259
OH
HO
(+)-3
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH

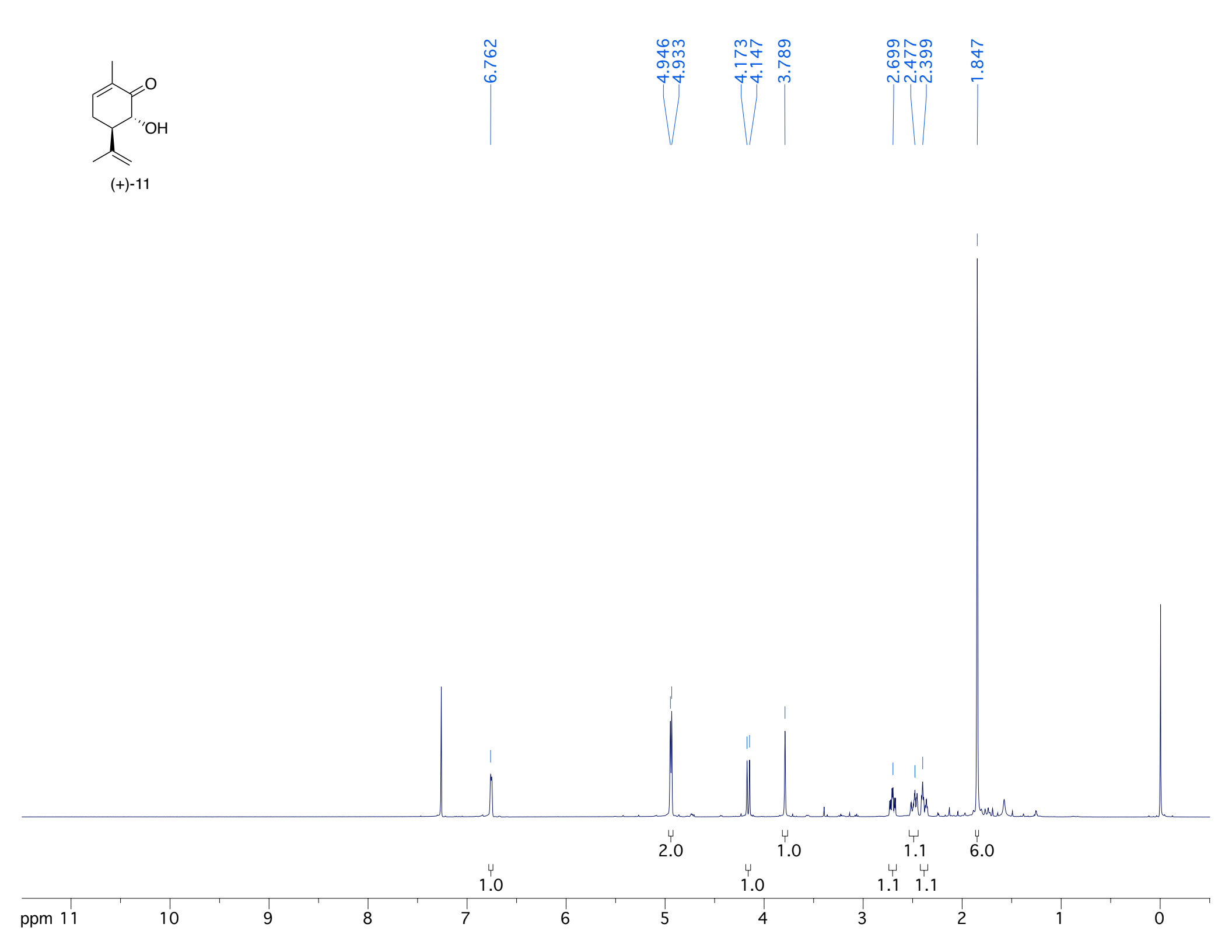
(–)-8

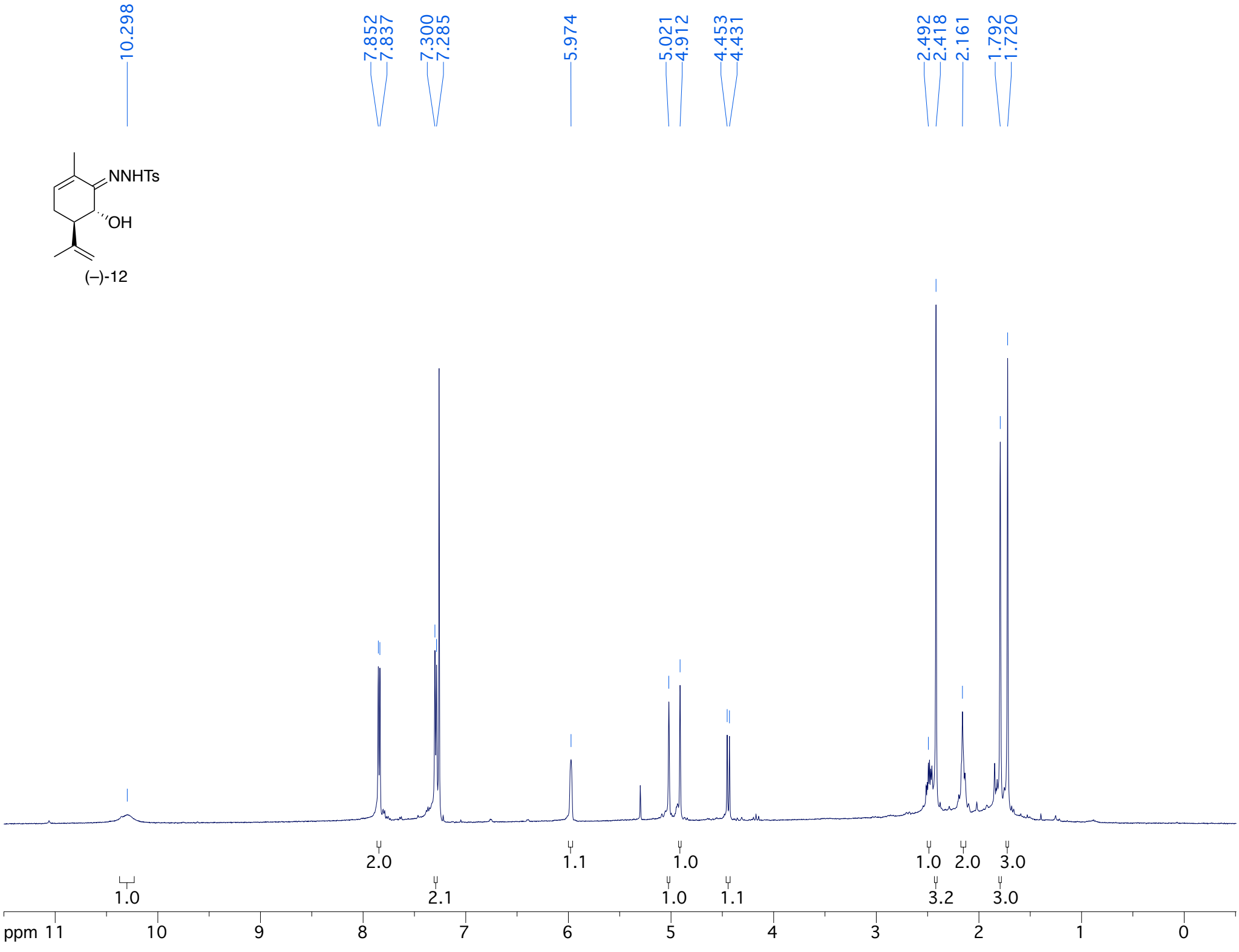
5.445
4.891
4.851
4.124
4.107
2.094
2.072
2.052
1.951
1.942
1.916
1.907
1.730
1.694
1.645
1.634
1.621
1.610
1.596
1.585
1.571
1.560
1.1
1.1
1.2
4.4
1.0
1.1
2.2
4.0
2.2
ppm 11
10
9
8
7
6
5
4
3
2
1
0

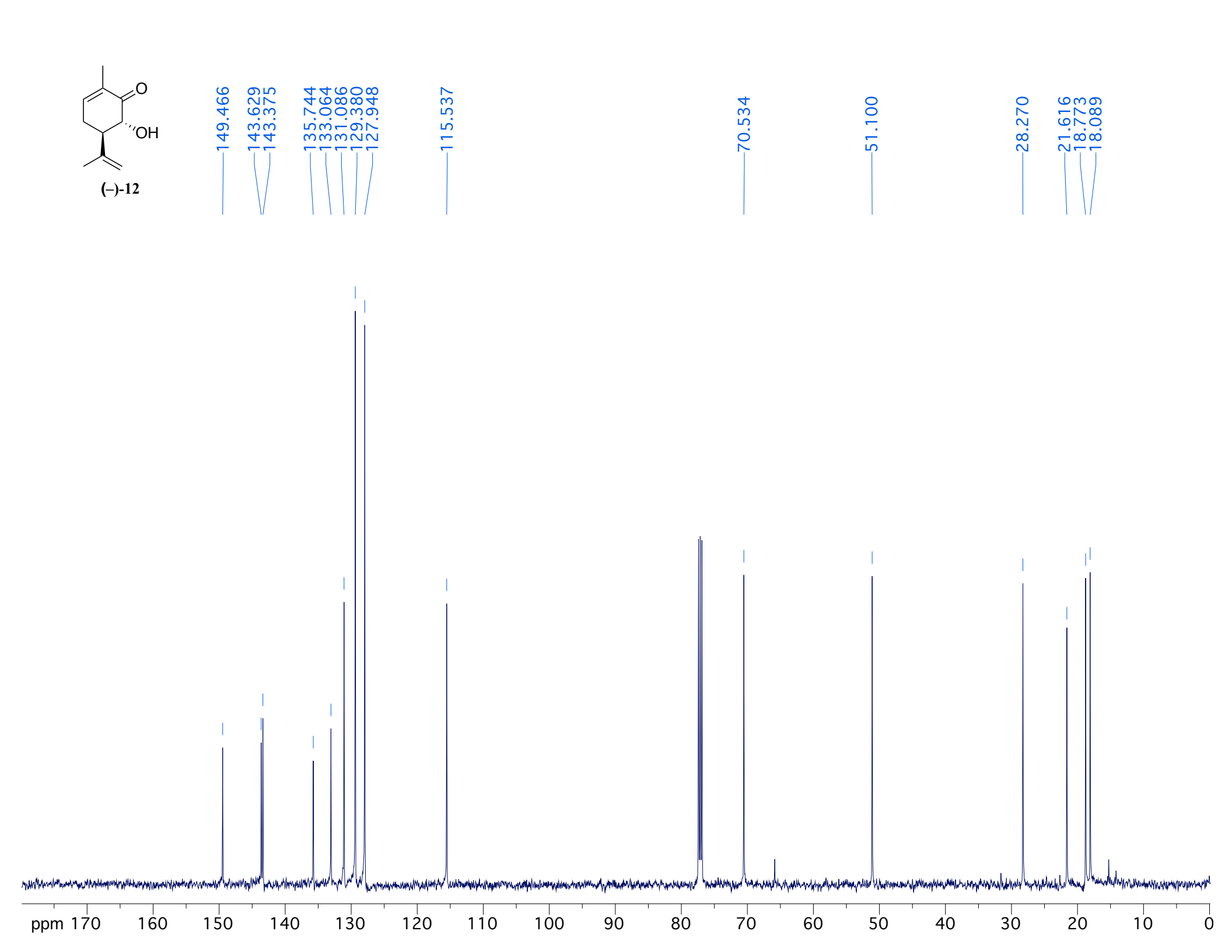

OH

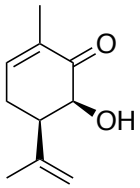
(–)-9

5.683
5.677
5.003
4.812
4.130
2.124
2.098
2.045
1.830
1.787
1.752
1.724
1.605
1.556
1.490
1.483
1.0
1.0
1.0
1.8
1.0
1.0
1.0
1.0
1.1
3.3
3.2
1.1
ppm 11
10
9
8
7
6
5
4
3
2
1
0


O
OH
(+)-11
6.762
4.946
4.933
4.173
4.147
3.789
2.699
2.477
2.399
1.847
2.0
1.0
1.1
6.0
1.0
1.0
1.1
1.1
ppm 11
10
9
8
7
6
5
4
3
2
1
0

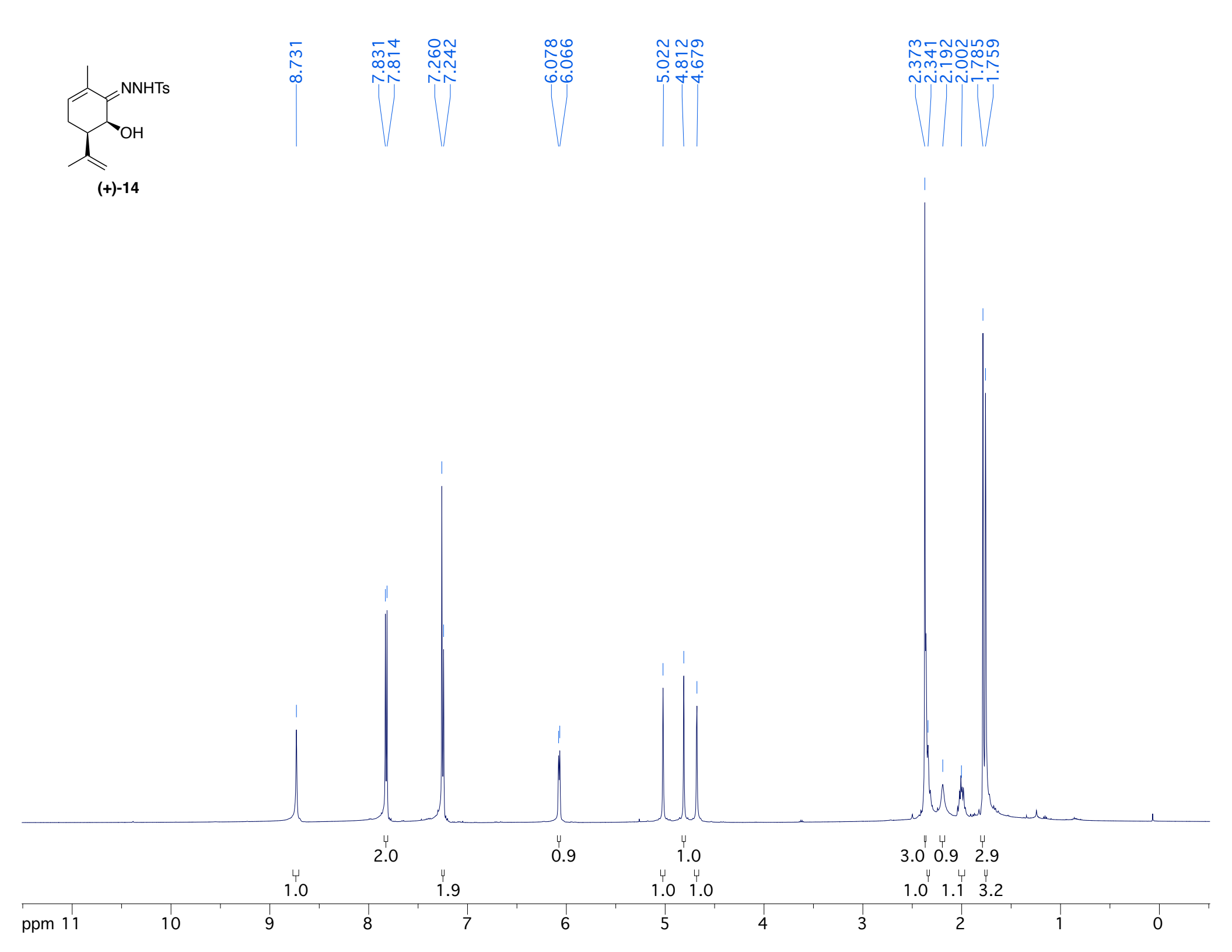

10.298
7.852
7.837
7.300
7.285
5.974
5.021
4.912
4.453
4.431
2.492
2.418
2.161
1.792
1.720
NNHTs
OH
(–)-12
2.0
1.1
1.0
1.0
2.0
3.0
1.0
2.1
1.0
1.1
3.2
3.0
ppm 11
10
9
8
7
6
5
4
3
2
1
0

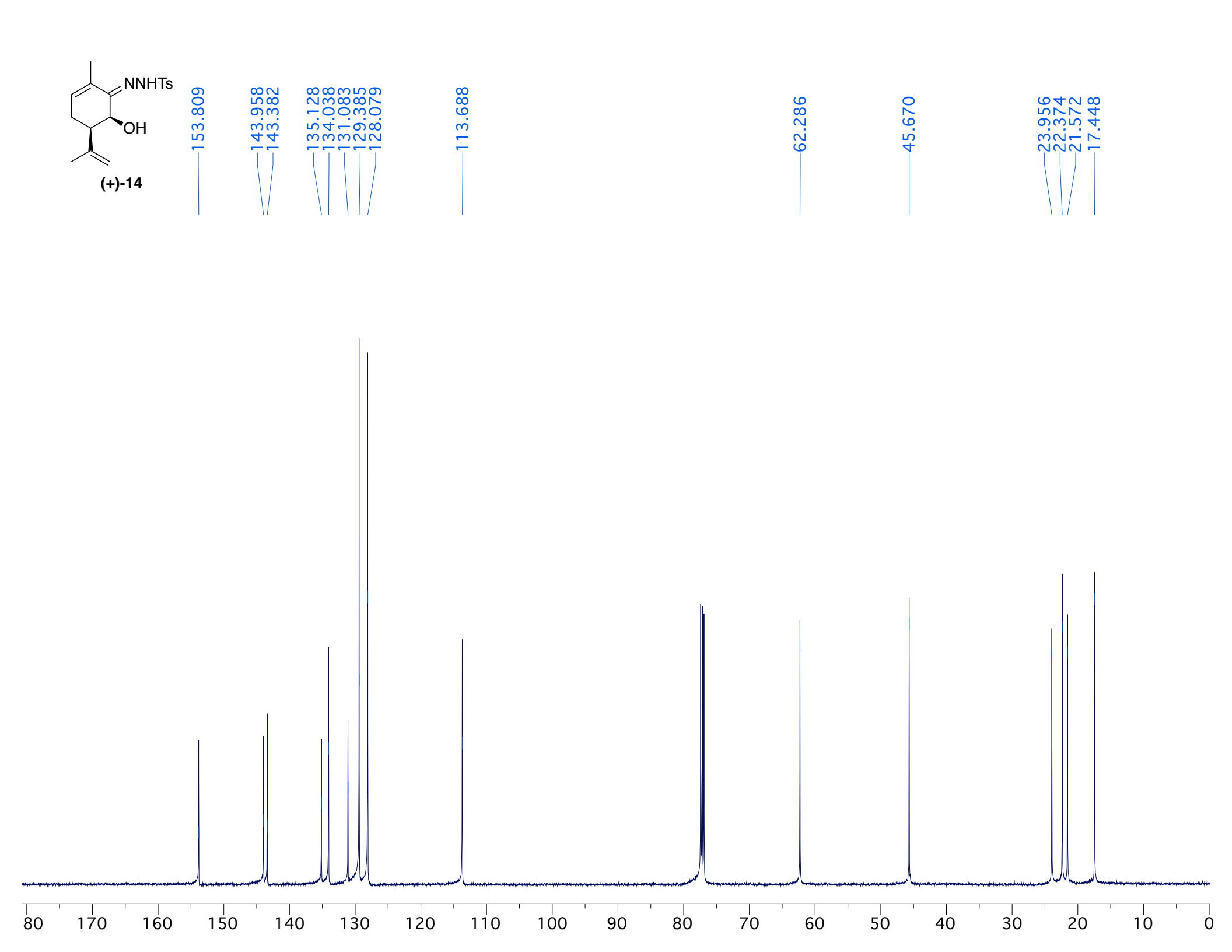

O
OH
(–)-12
149.466
143.629
143.375
135.744
133.064
131.086
129.380
127.948
115.537
70.534
51.100
28.270
21.616
18.773
18.089
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

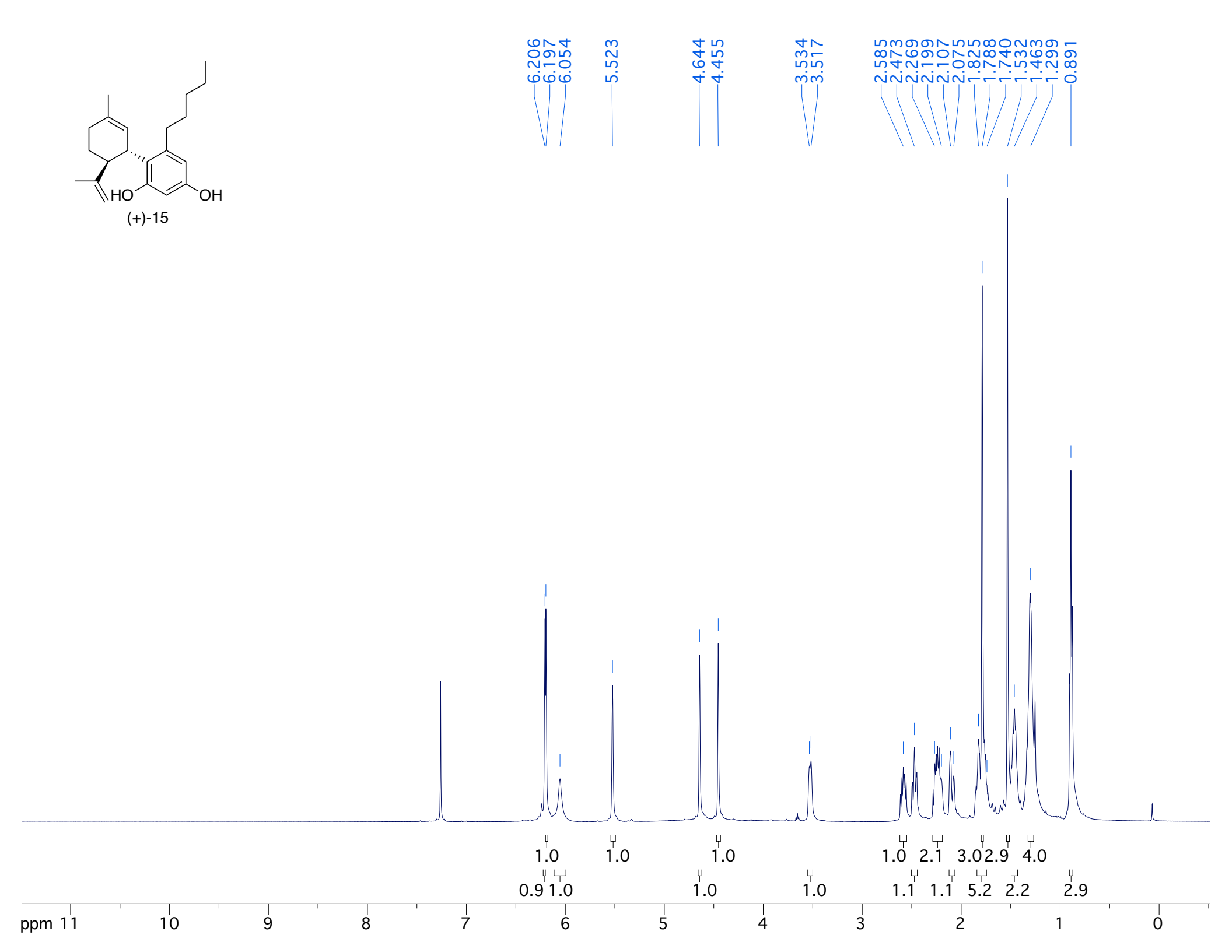

O
OH

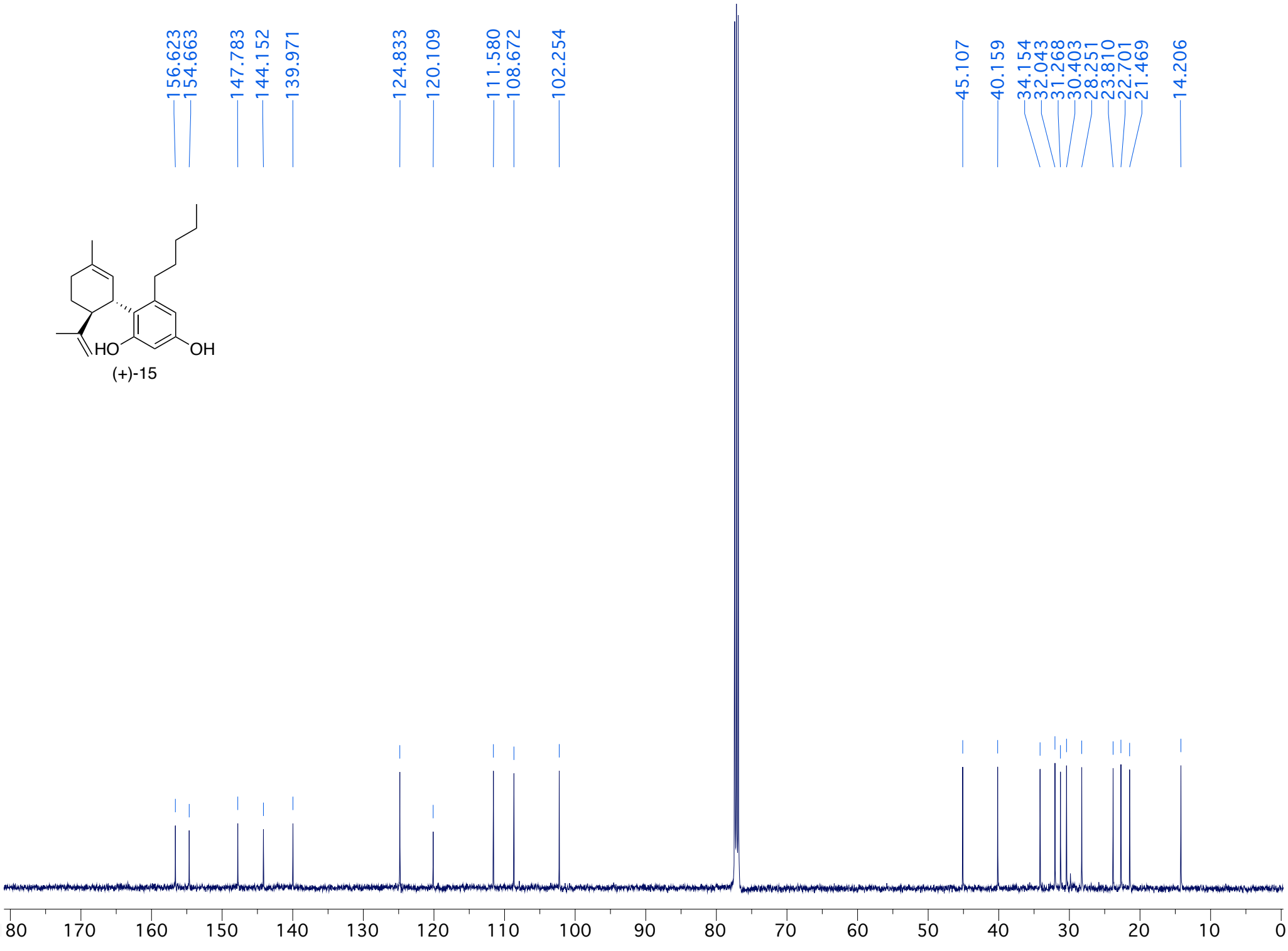
(–)-13

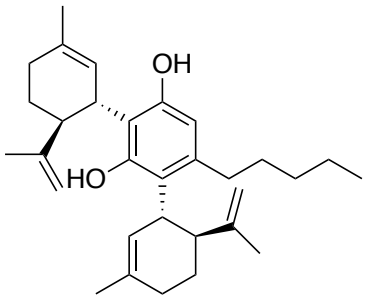
6.671
4.859
4.707
4.436
4.424
3.195
2.758
2.716
2.555
2.511
1.834
1.691
0.9
0.9
0.9
1.0
2.8
0.9
0.9
0.9
1.0
2.8
ppm 11
10
9
8
7
6
5
4
3
2
1
0


NNHTs
OH
(+)-14
8.731
7.831
7.814
7.260
7.242
6.078
6.066
5.022
4.812
4.679
2.373
2.341
2.192
2.002
1.785
1.759
2.0
0.9
1.0
3.0
0.9
2.9
1.0
1.9
1.0
1.0
1.0
1.1
3.2
ppm 11
10
9
8
7
6
5
4
3
2
1
0


NNHTs
OH
(+)-14
153.809
143.958
143.382
135.128
134.038
131.083
129.385
128.079
113.688
62.286
45.670
23.956
22.374
21.572
17.448
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

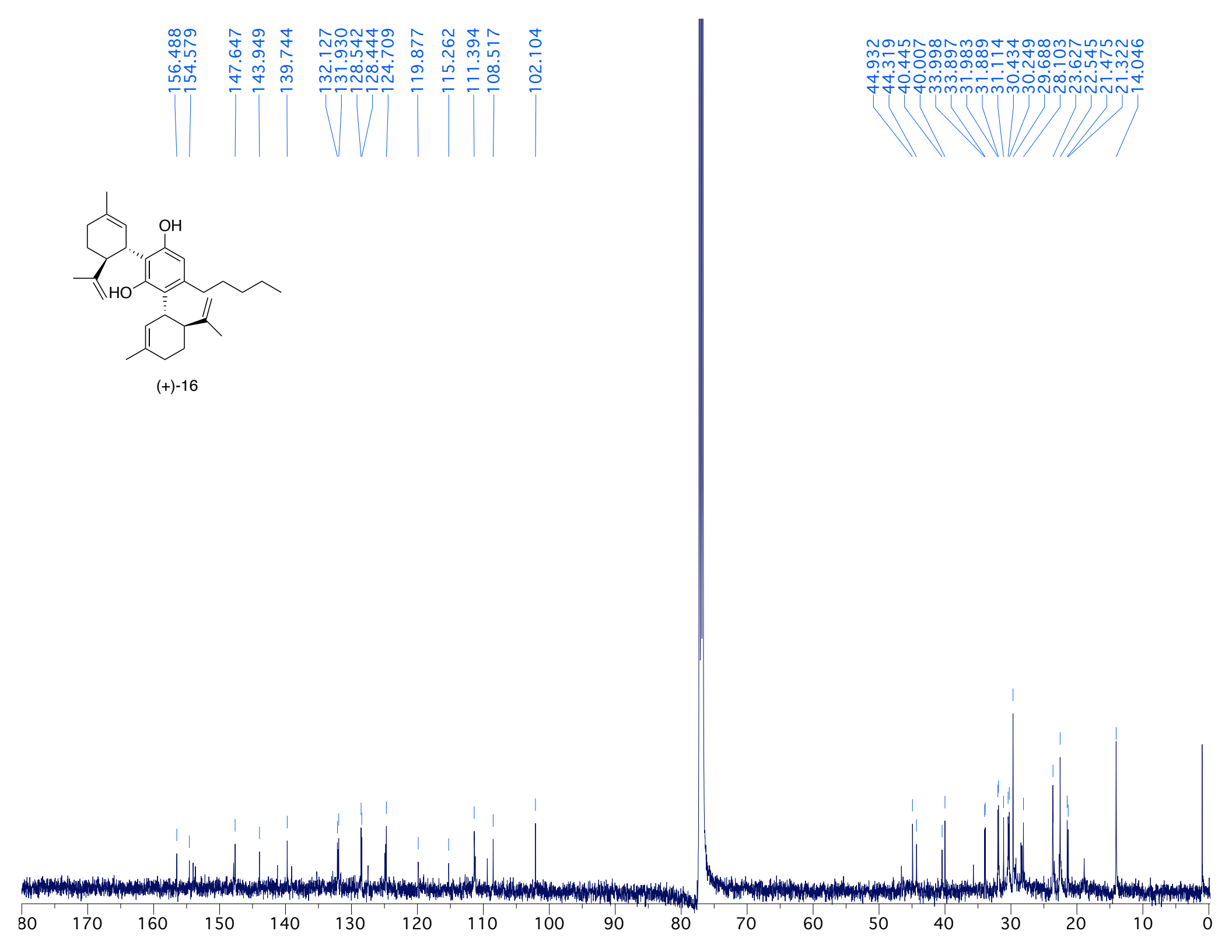

HO
OH
(+)-15
6.206
6.197
6.054
5.523
4.644
4.455
3.534
3.517
2.585
2.473
2.269
2.199
2.107
2.075
1.825
1.788
1.740
1.532
1.463
1.299
0.891
1.0
1.0
1.0
1.0
2.1
3.0
2.9
4.0
0.9
1.0
1.0
1.0
1.1
1.1
5.2
2.2
2.9
ppm
11
10
9
8
7
6
5
4
3
2
1
0

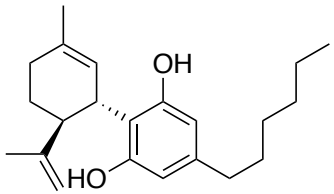

156.623
154.663
147.783
144.152
139.971
124.833
120.109
111.580
108.672
102.254
45.107
40.159
34.154
32.043
31.268
30.403
28.251
23.810
22.701
21.469
14.206
HO
OH
(+)-15
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
HO

(+)-16

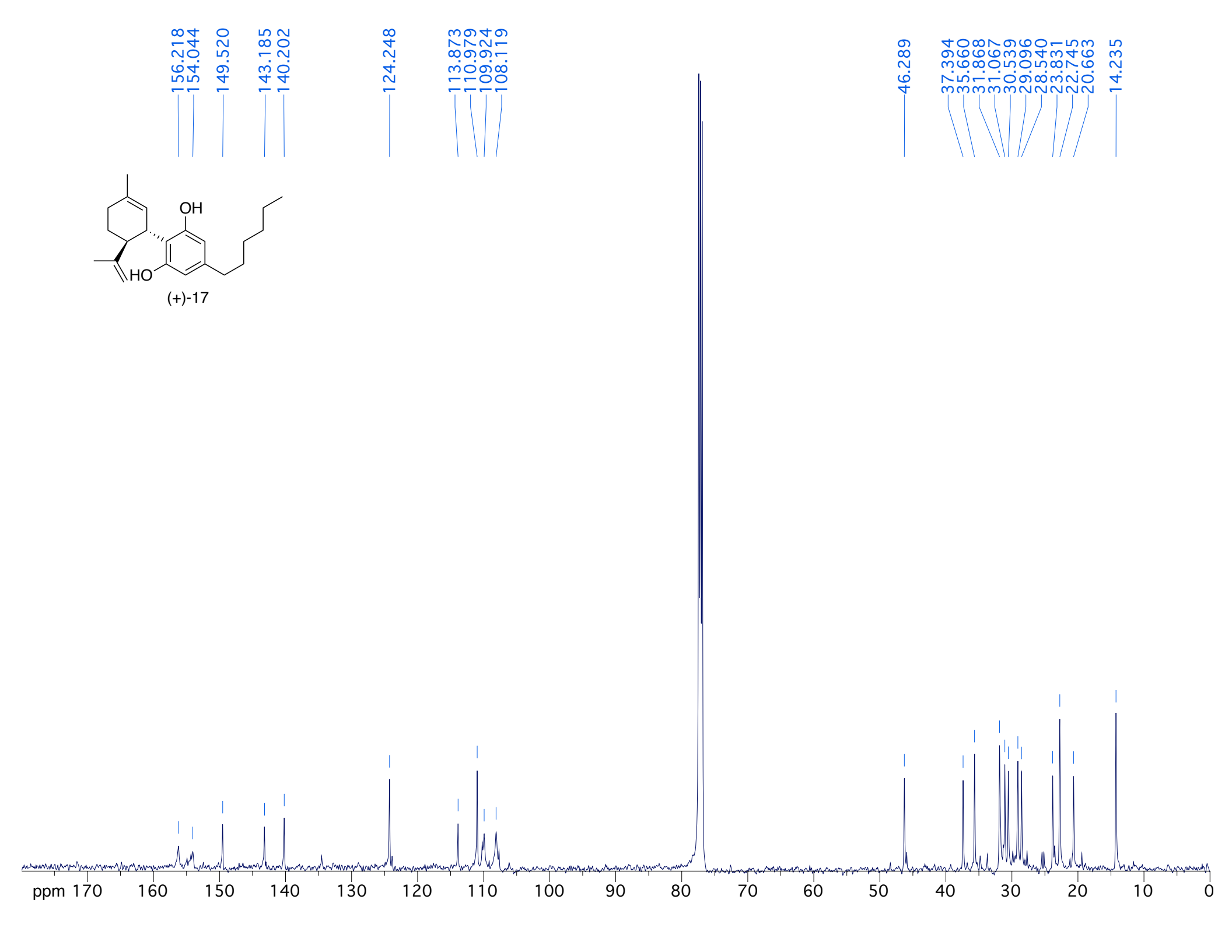
6.202
5.922
5.778
5.579
5.487
4.600
4.500
4.447
4.421
3.997
3.499
2.533
2.431
2.208
2.089
1.781
1.763
1.700
1.493
1.454
1.302
0.886
1.0 1.1
1.1 0.9 1.0
1.0 3.2 2.0 2.9 6.0
1.0 1.0 1.1
1.1 1.0
1.1
2.0 2.1 3.3 3.1 2.2 3.1
ppm 11 10 9 8 7 6 5 4 3 2 1 0

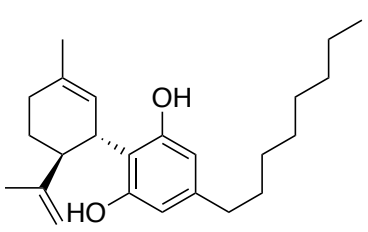

156.488
154.579
147.647
143.949
139.744
132.127
131.930
128.542
128.444
124.709
119.877
115.262
111.394
108.517
102.104
44.932
44.319
40.445
40.007
33.998
33.897
31.983
31.889
31.114
30.434
30.249
29.688
28.103
23.627
22.545
21.475
21.322
14.046
OH
HO
(+)-16
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
HO

(+)-17

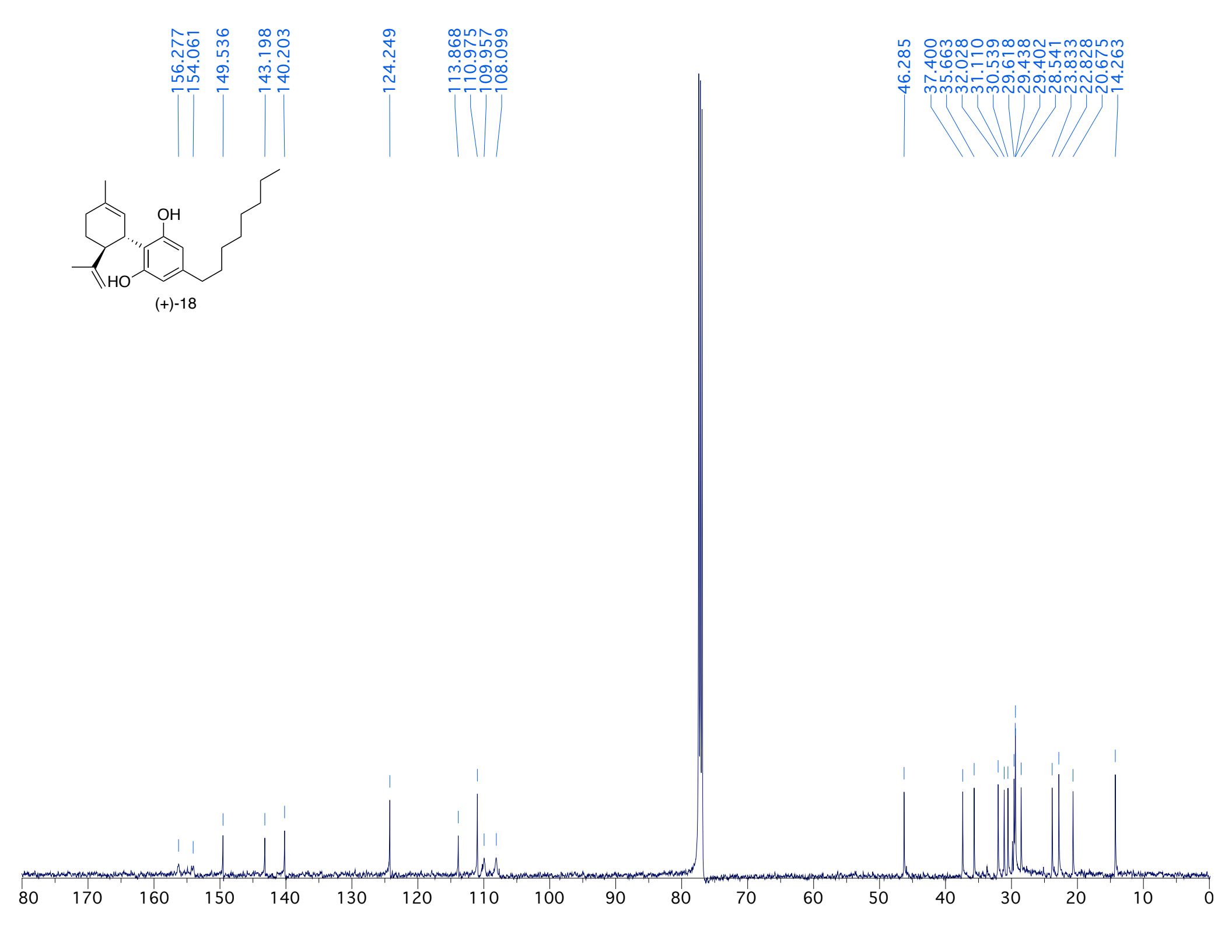
6.283
6.165
5.984
5.572
4.696
4.662
4.559
3.860
3.840
2.439
2.399
2.373
2.256
2.076
1.820
1.794
1.719
1.657
1.550
1.278
0.873
1.0
1.0
1.9
1.0
1.0
3.0
3.0
6.3
1.0
0.8
1.0
1.0
2.1
2.3
5.1
2.2
3.1
ppm
11
10
9
8
7
6
5
4
3
2
1
0

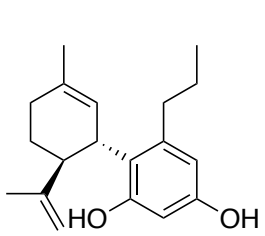

156.218
154.044
149.520
143.185
140.202
124.248
113.873
110.979
109.924
108.119
46.289
37.394
35.660
31.868
31.067
30.539
29.096
28.540
23.831
22.745
20.663
14.235
OH
HO
(+)-17
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
HO

(+)-18

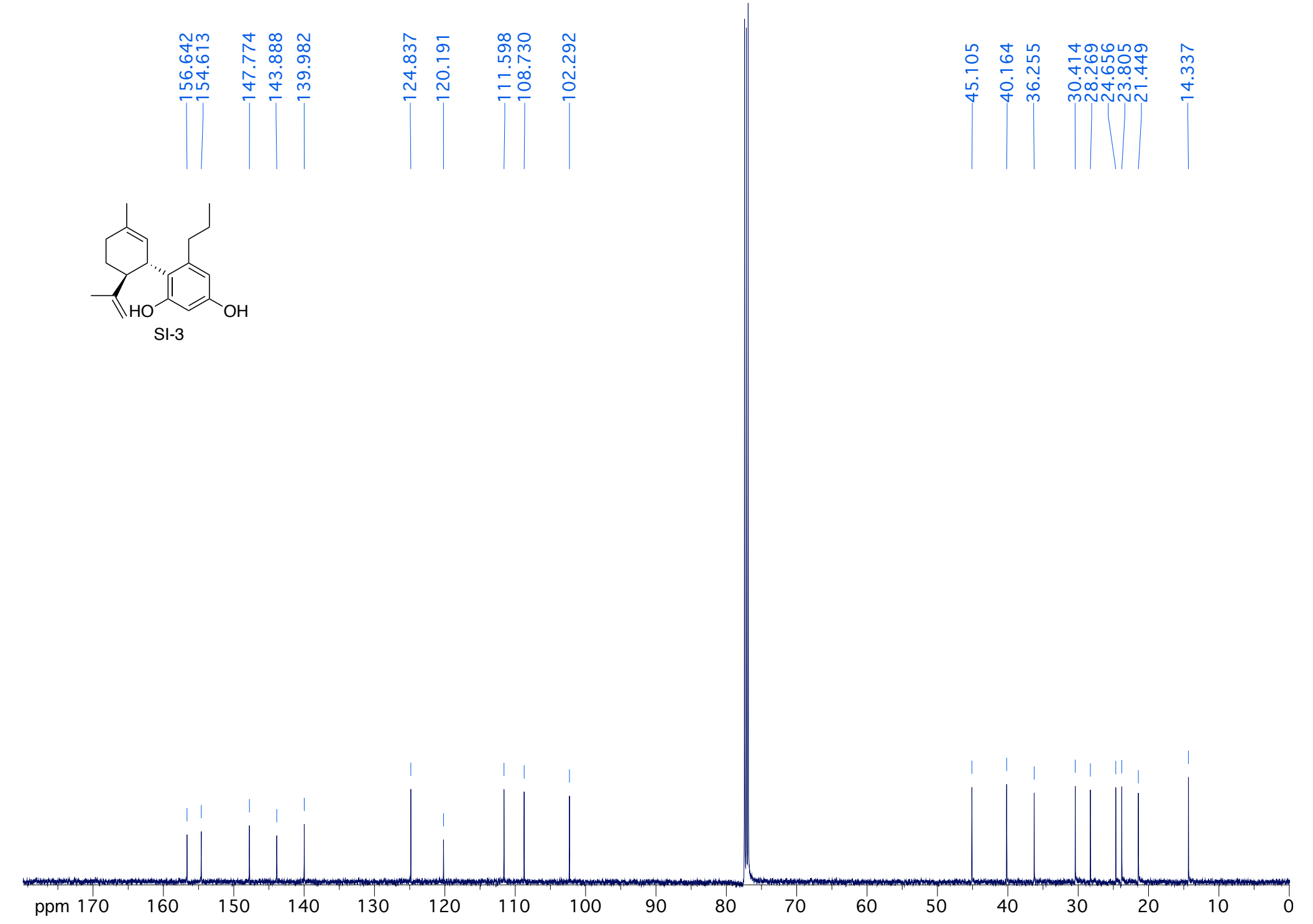
6.276
6.166
5.974
5.569
4.660
4.557
3.851
3.834
2.435
2.389
2.226
2.116
2.070
1.816
1.792
1.746
1.653
1.579
1.277
0.873
1.0
0.8
0.9
1.8
1.1
2.7
2.8
7.5
1.1
0.9
1.8
1.0
0.9
1.0
4.7
3.7
2.8
ppm
11
10
9
8
7
6
5
4
3
2
1
0

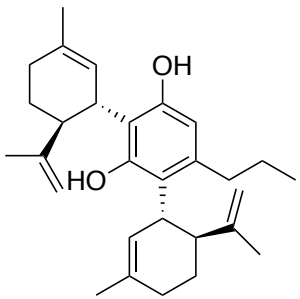

156.277
154.061
149.536
143.198
140.203
124.249
113.868
110.975
109.957
108.099
46.285
37.400
35.663
32.028
31.110
30.539
29.618
29.438
29.402
28.541
23.833
22.828
20.675
14.263
OH
HO
(+)-18
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
OH

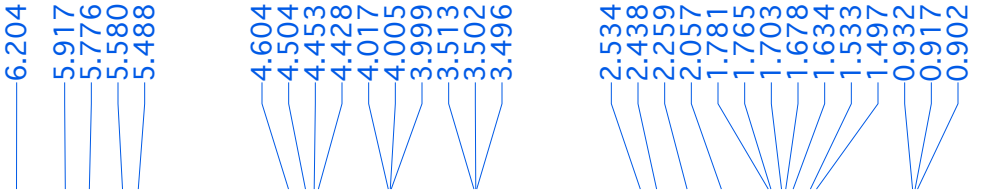
SI-3

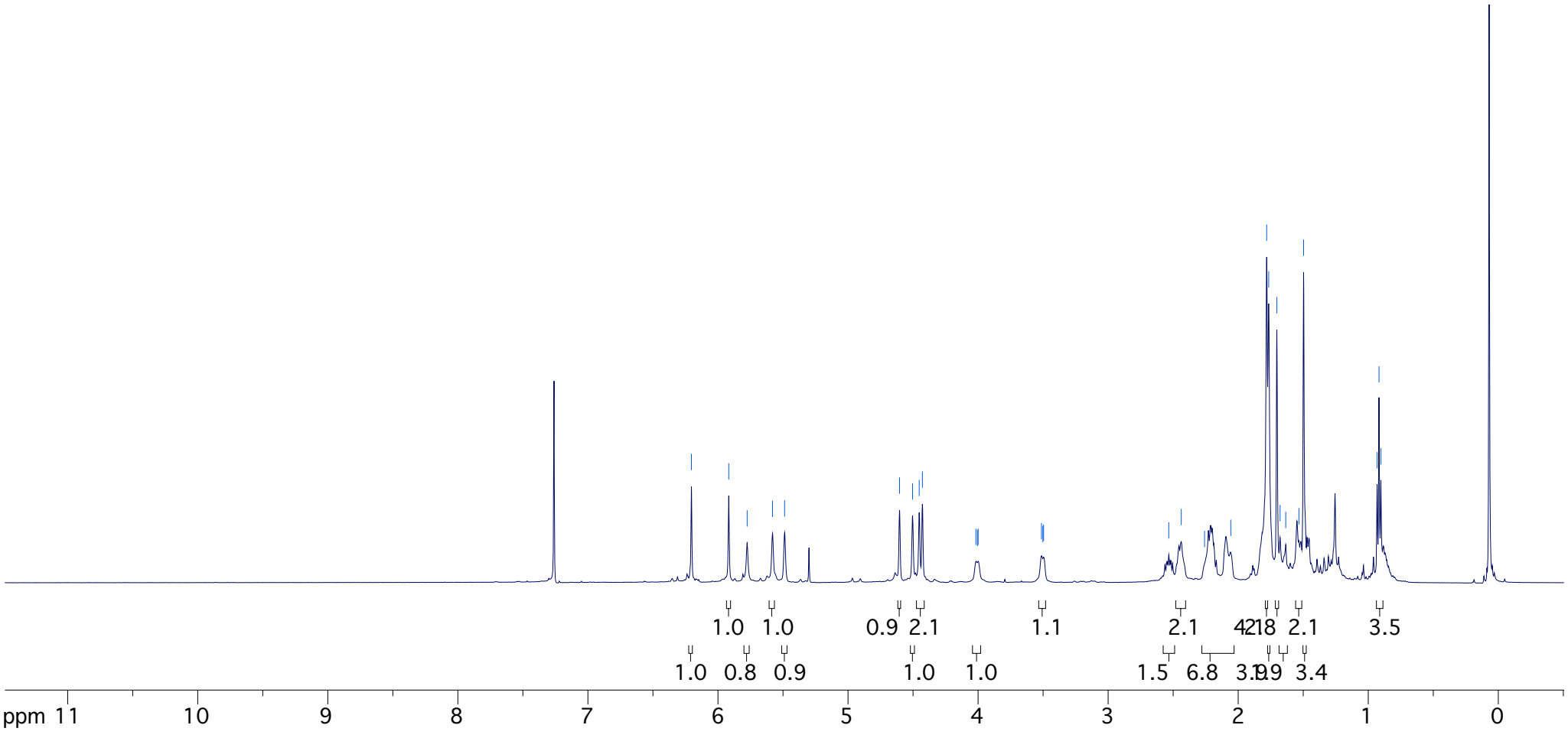
6.211
6.197
6.048
5.524
4.648
4.460
3.542
3.525
2.615
2.556
2.504
2.455
2.272
2.212
2.111
2.080
1.855
1.789
1.744
1.537
1.519
1.449
0.941
0.926
0.912
0.9
1.0
1.0
1.0
1.1
5.0
2.0
1.8
0.9
1.0
1.0
2.0
2.7
2.5
2.8
ppm 11
10
9
8
7
6
5
4
3
2
1
0

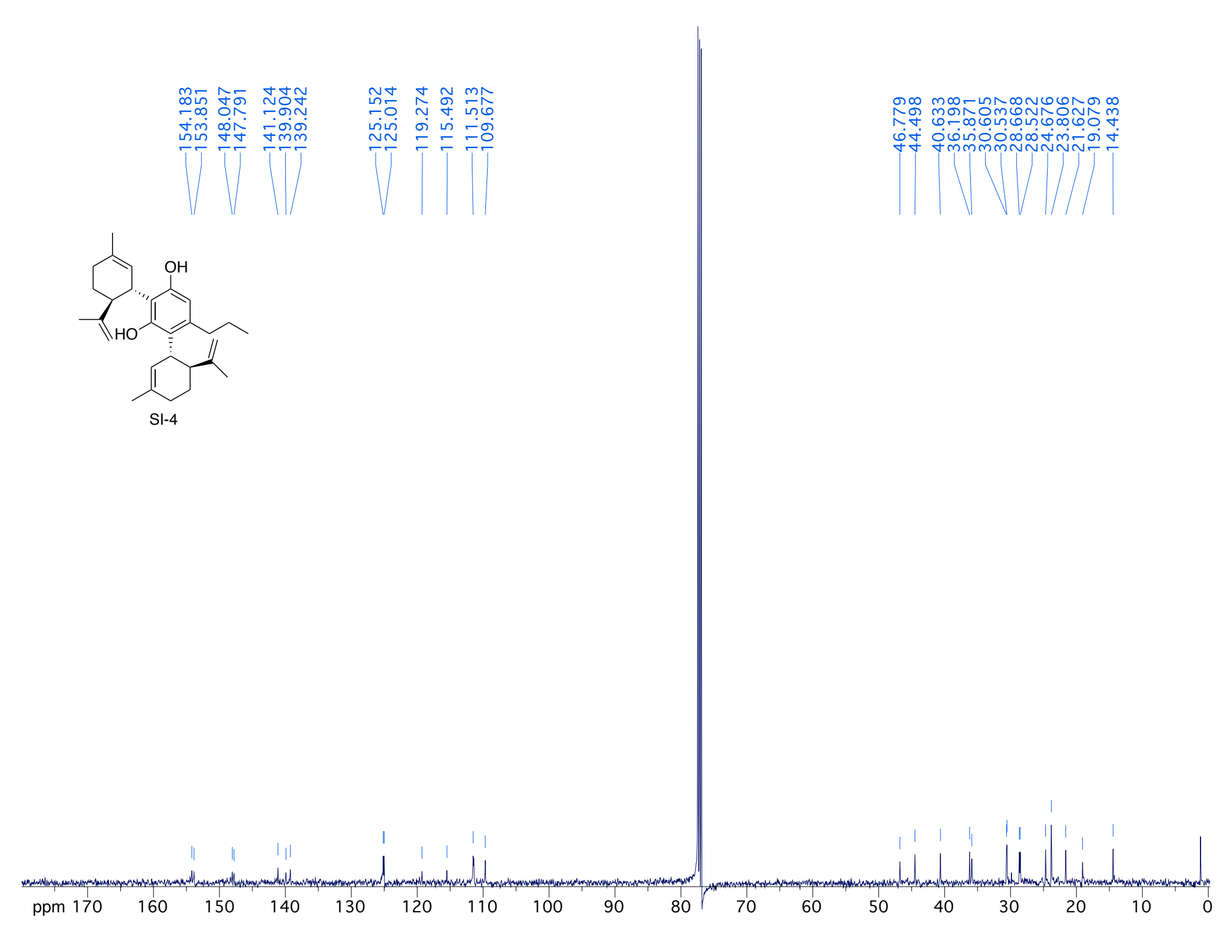

156.642
154.613
147.774
143.888
139.982
124.837
120.191
111.598
108.730
102.292
45.105
40.164
36.255
30.414
28.269
24.656
23.805
21.449
14.337
HO
OH
SI-3
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

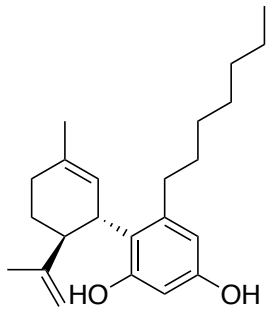

OH
HO

SI-4


6.204
5.917
5.776
5.580
5.488
4.604
4.504
4.453
4.428
4.017
4.005
3.999
3.513
3.502
3.496
2.534
2.438
2.259
2.057
1.781
1.765
1.703
1.678
1.634
1.533
1.497
0.932
0.917
0.902

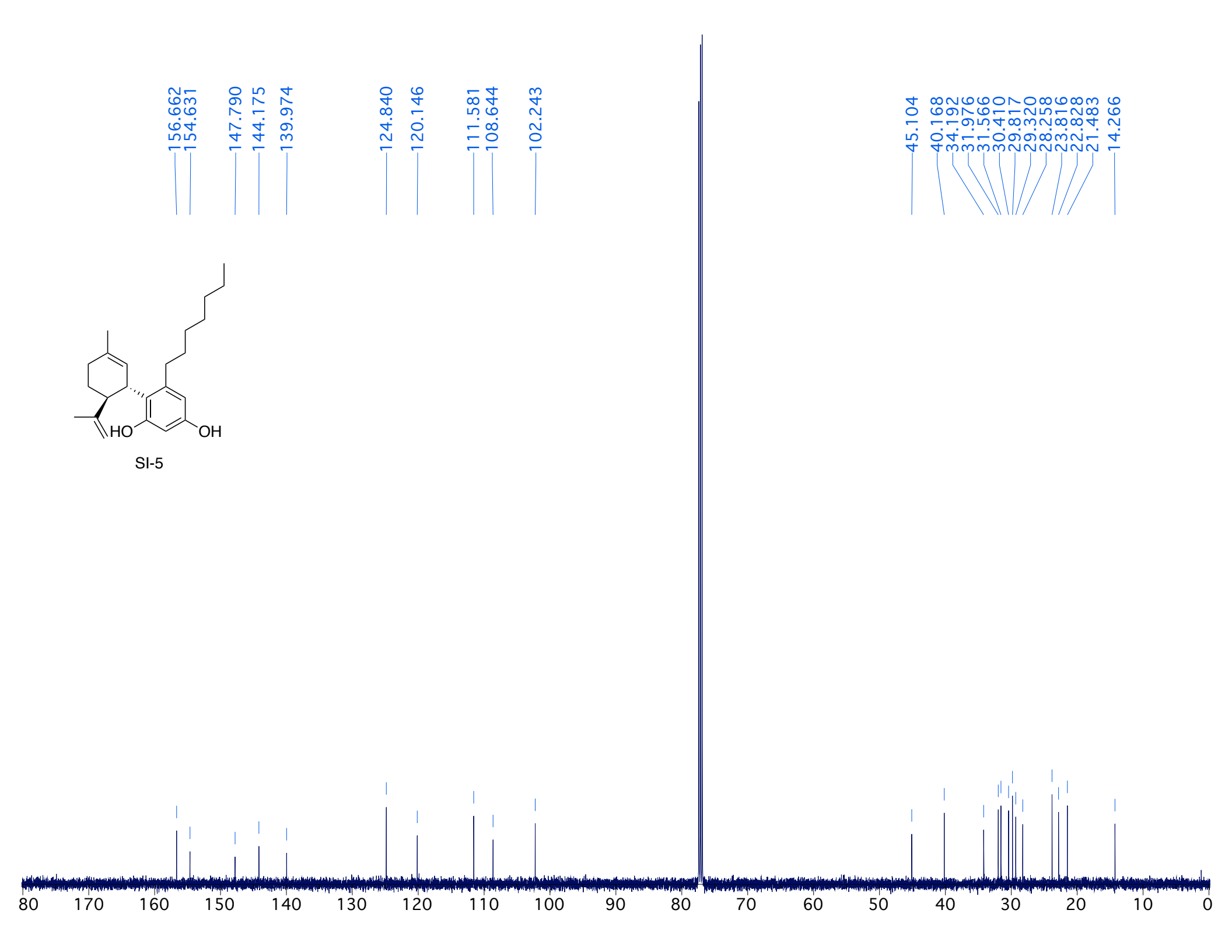

1.0
1.0
0.9
2.1
1.1
2.1
4
2
1
8
2.1
3.5
1.0
0.8
0.9
1.0
1.0
1.5
6.8
3.1
0.9
3.4
ppm
11
10
9
8
7
6
5
4
3
2
1
0

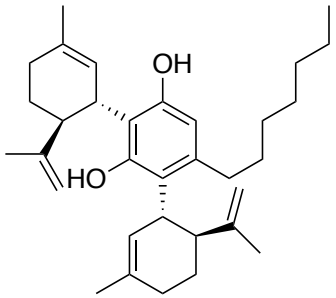

154.183
153.851
148.047
147.791
141.124
139.904
139.242
125.152
125.014
119.274
115.492
111.513
109.677
46.779
44.498
40.633
36.198
35.871
30.605
30.537
28.668
28.522
24.676
23.806
21.627
19.079
14.438
OH
HO
SI-4
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
OH

SI-5

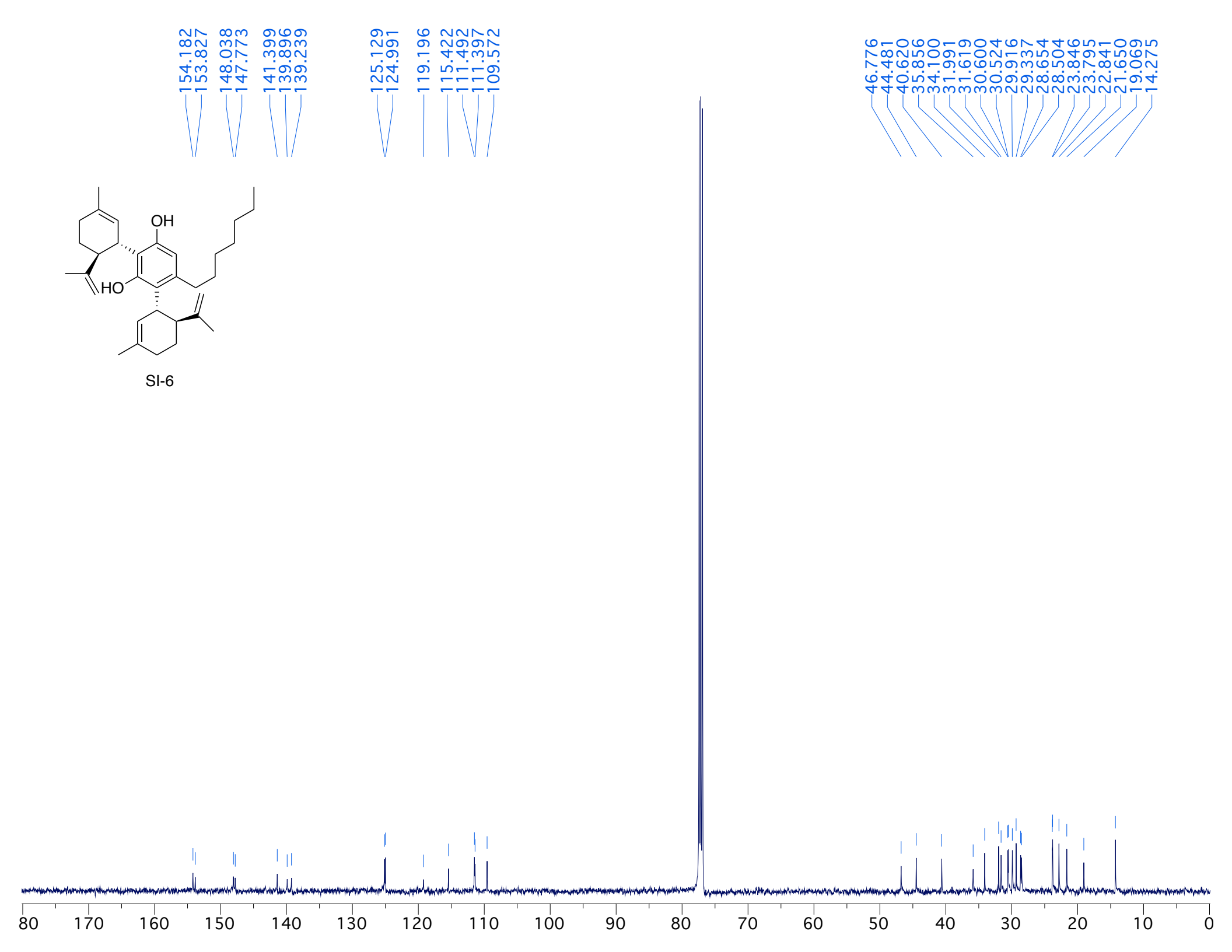
6.203
6.193
6.046
5.524
4.645
4.456
3.529
2.586
2.473
2.242
2.109
1.839
1.791
1.756
1.533
1.458
1.291
0.883
1.0
1.0
0.9
1.0
2.1
3.1
2.9
8.1
1.0
1.0
1.0
1.1
1.1
1.2
5.2
2.0
2.9
ppm 11
10
9
8
7
6
5
4
3
2
1
0

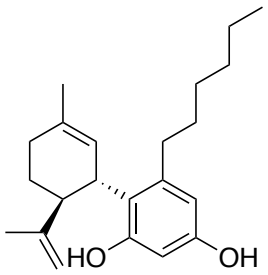

156.662
154.631
147.790
144.175
139.974
124.840
120.146
111.581
108.644
102.243
45.104
40.168
34.192
31.976
31.566
30.410
29.817
29.320
28.258
23.816
22.828
21.483
14.266
HO
OH
SI-5
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
HO

SI-6

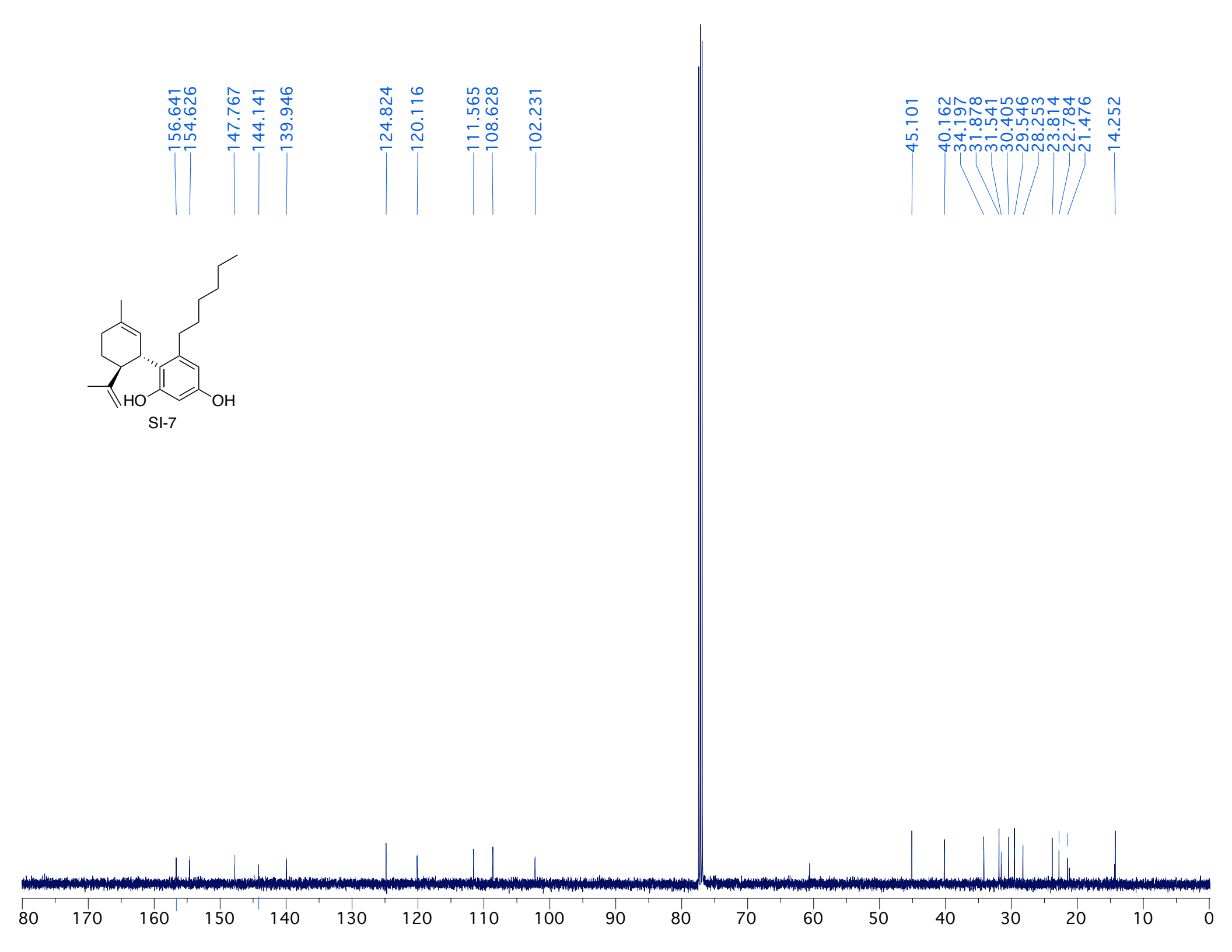
6.204
5.922
5.779
5.581
5.488
4.603
4.503
4.450
4.424
4.011
3.997
3.492
2.535
2.434
2.212
2.080
1.785
1.766
1.703
1.563
1.495
1.451
1.287
0.879
1.0 1.0 1.0 1.0 1.1 1.0 3.1 3218 8.1 3.0
1.0 1.0 0.9 1.11.0 1.0 2.0 2.2 3.1 2.8 9.0
ppm 11 10 9 8 7 6 5 4 3 2 1 0

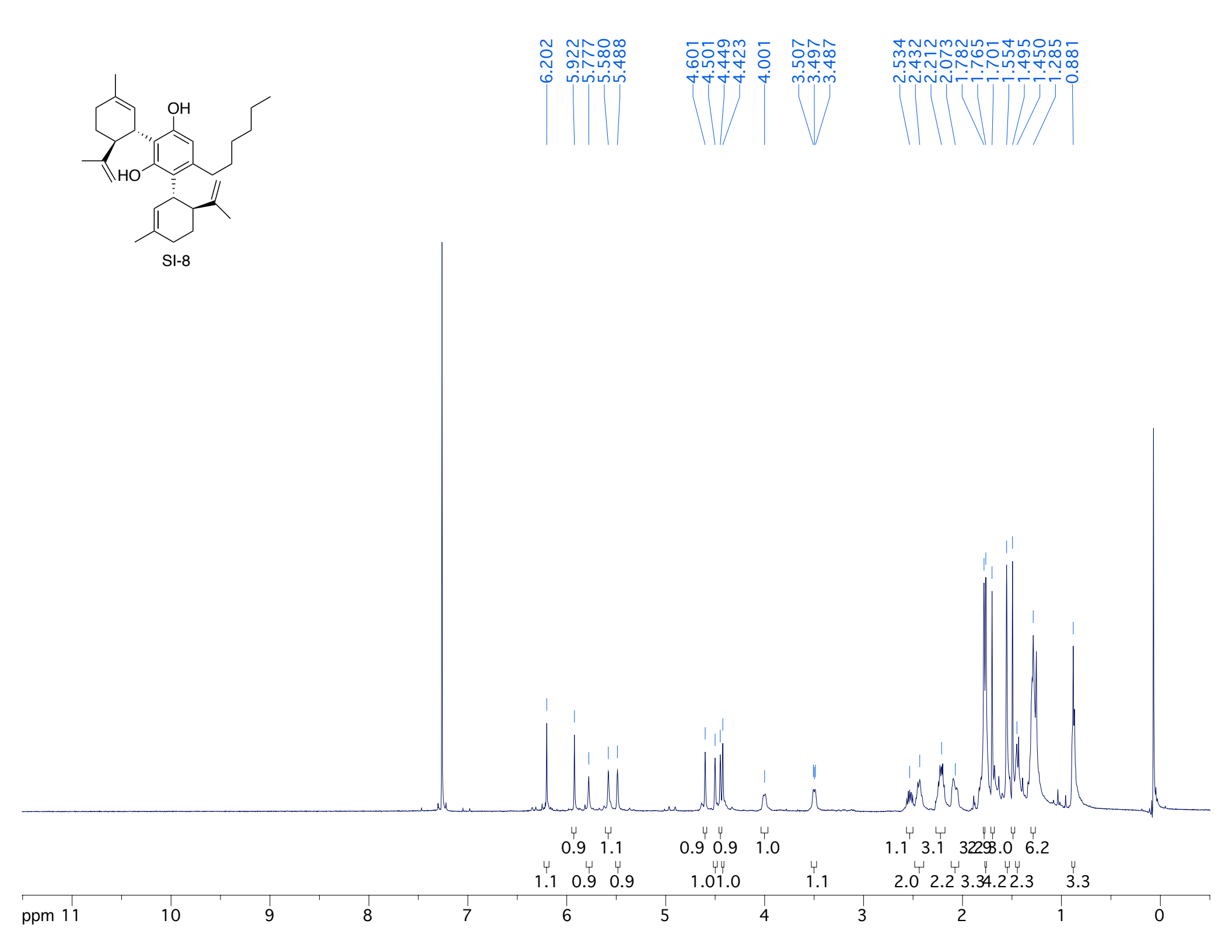

154.182
153.827
148.038
147.773
141.399
139.896
139.239
125.129
124.991
119.196
115.422
111.492
111.397
109.572
46.776
44.481
40.620
35.856
34.100
31.991
31.619
30.600
30.524
29.916
29.337
28.654
28.504
23.846
23.795
22.841
21.650
19.069
14.275
OH
HO
SI-6
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

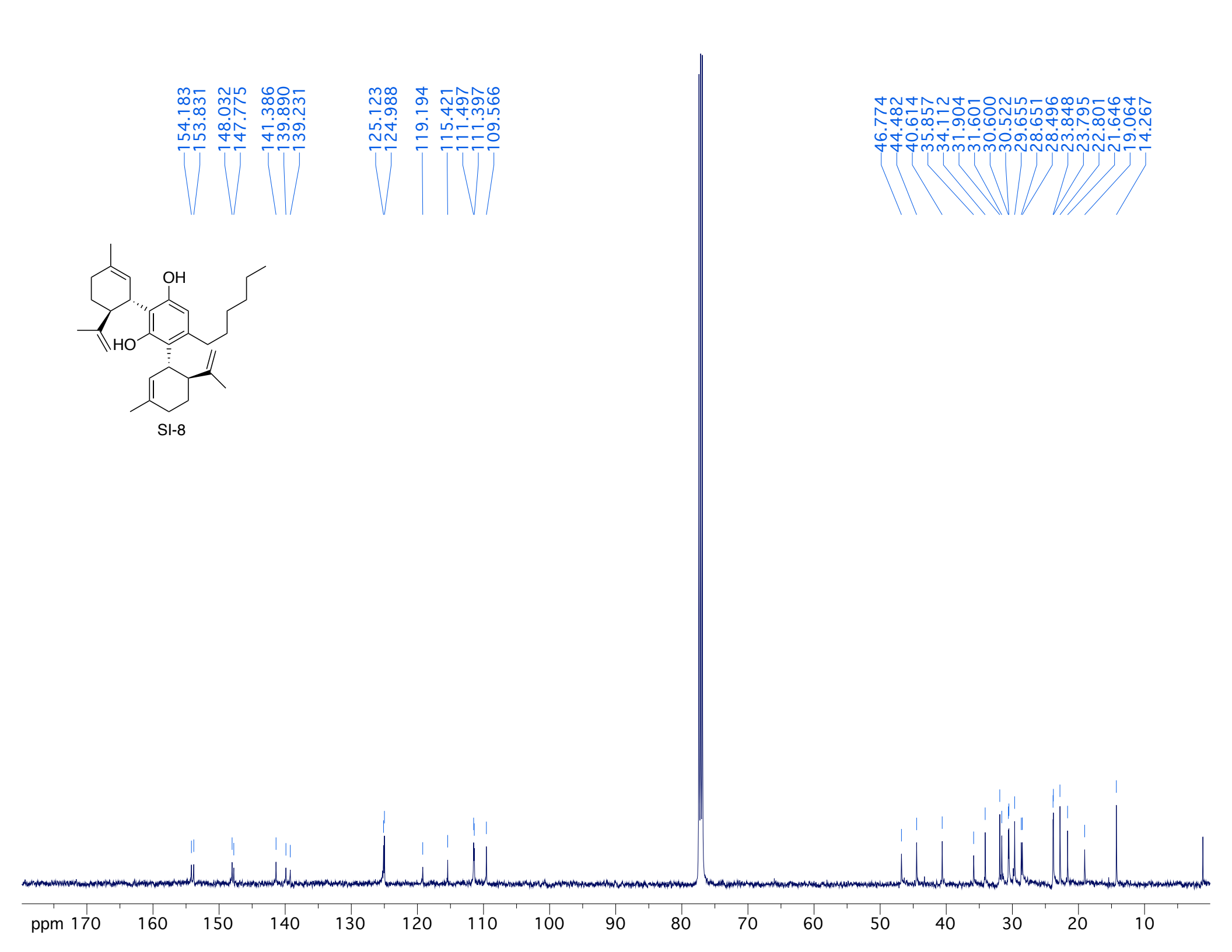

HO
OH

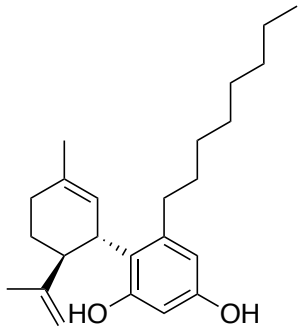
SI-7

6.201
6.191
6.045
5.522
4.644
4.455
3.522
2.585
2.472
2.254
2.112
2.077
1.831
1.789
1.533
1.457
1.290
0.884
0.9
1.0
1.2
1.1
2.0
3.0
3.1
6.0
0.9
0.9
1.1
1.0
1.2
1.1
5.1
2.0
3.2
ppm 11
10
9
8
7
6
5
4
3
2
1
0


156.641
154.626
147.767
144.141
139.946
124.824
120.116
111.565
108.628
102.231
45.101
40.162
34.197
31.878
31.541
30.405
29.546
28.253
23.814
22.784
21.476
14.252
HO
OH
SI-7
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

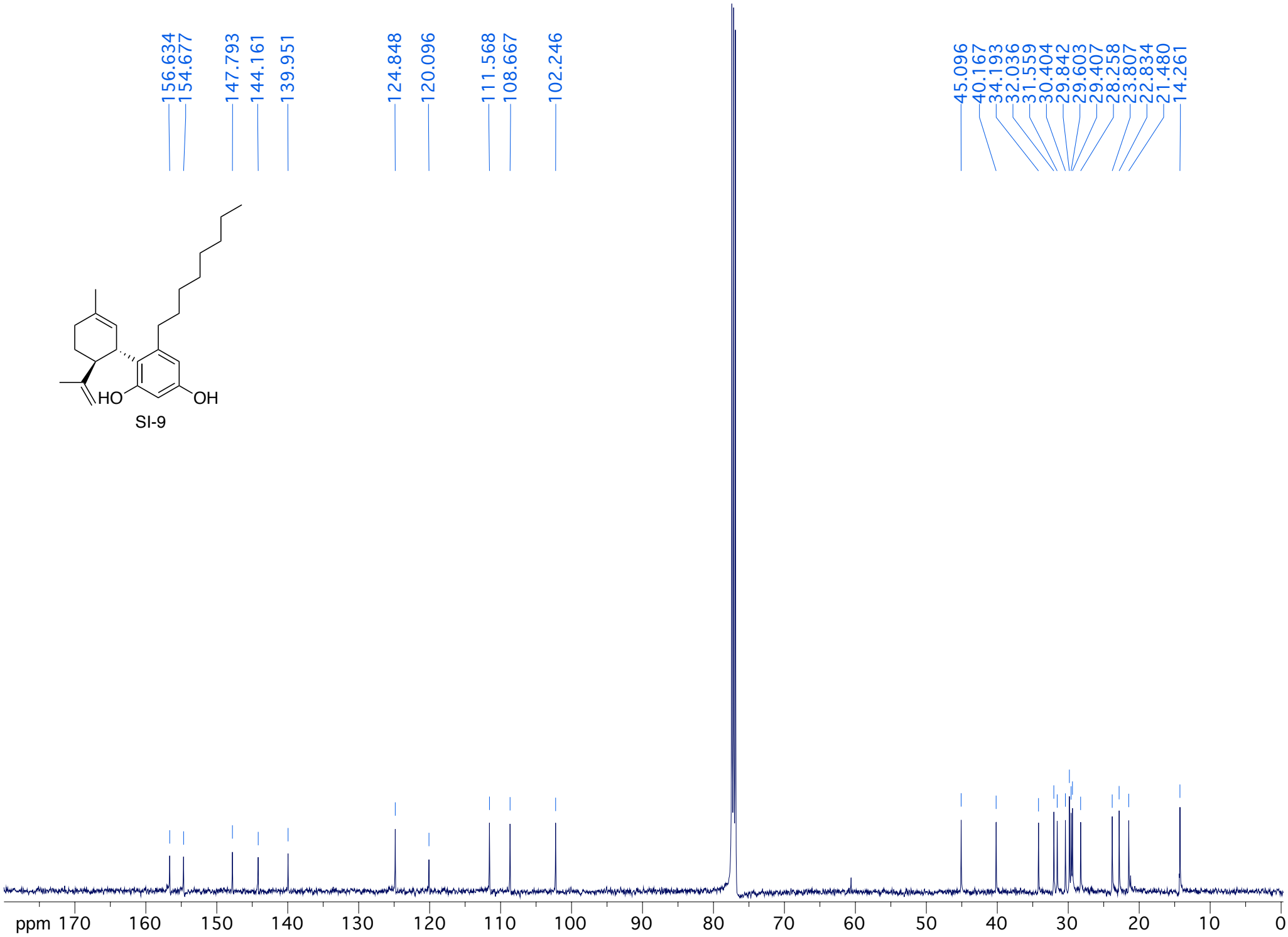

OH
HO
SI-8
6.202
5.922
5.777
5.580
5.488
4.601
4.501
4.449
4.423
4.001
3.507
3.497
3.487
2.534
2.432
2.212
2.073
1.782
1.765
1.701
1.554
1.495
1.450
1.285
0.881
0.9 1.1 0.9 0.9 1.0 1.1 3.1 3.2 2.9 3.0 6.2
1.1 0.9 0.9 1.0 1.0 1.1 2.0 2.2 3.3 4.2 2.3 3.3
ppm 11 10 9 8 7 6 5 4 3 2 1 0

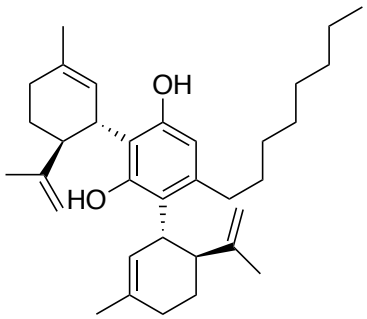

154.183
153.831
148.032
147.775
141.386
139.890
139.231
125.123
124.988
119.194
115.421
111.497
111.397
109.566
46.774
44.482
40.614
35.857
34.112
31.904
31.601
30.600
30.522
29.655
28.651
28.496
23.848
23.795
22.801
21.646
19.064
14.267
OH
HO
SI-8
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HO
OH

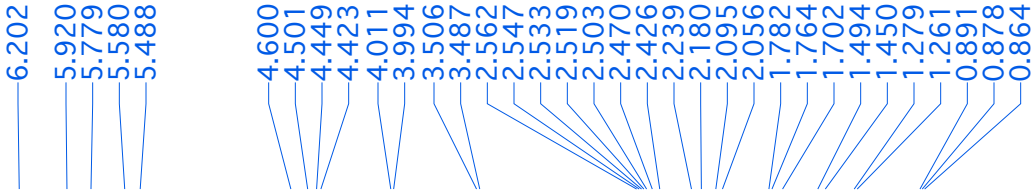
SI-9

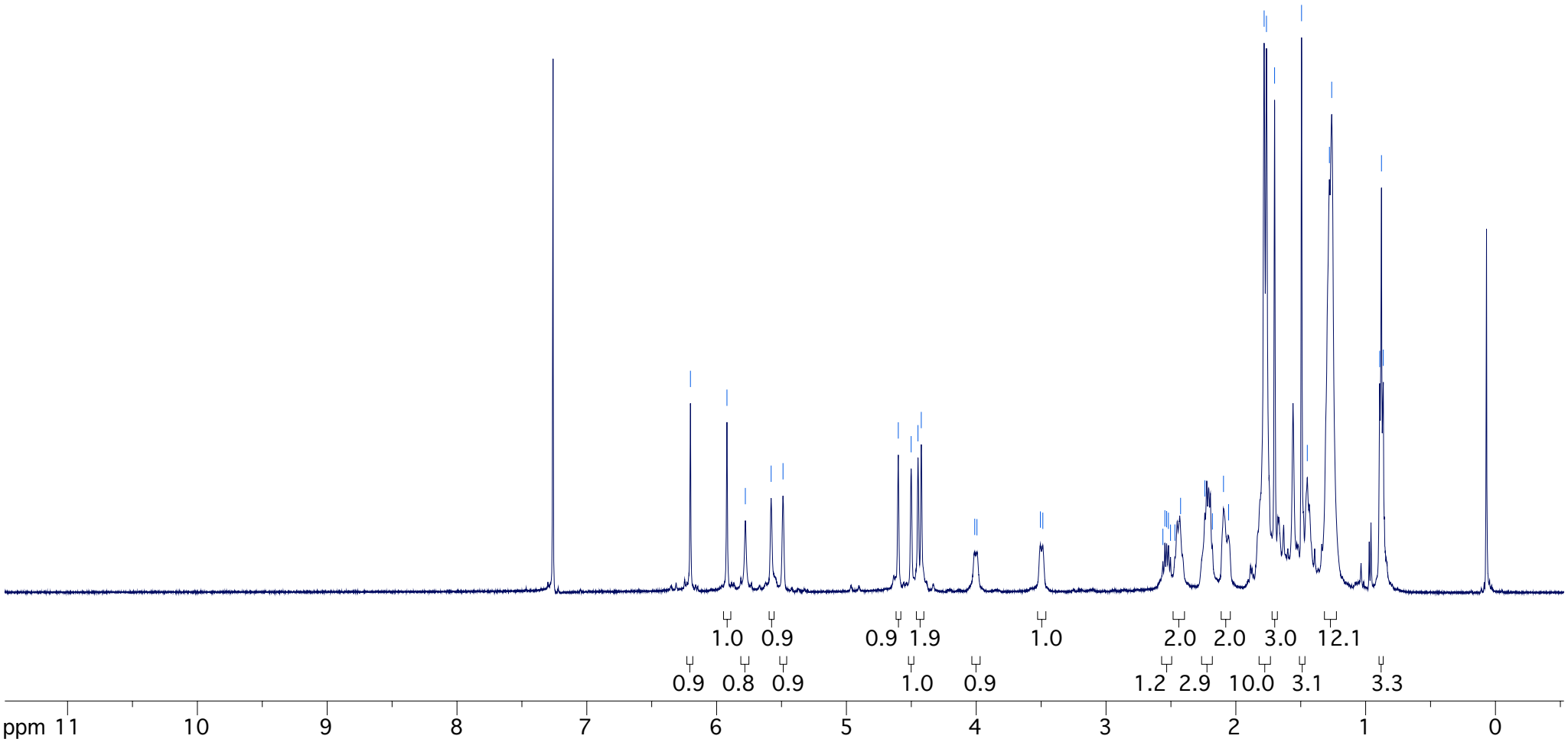
6.200
6.190
6.041
5.523
4.643
4.455
3.522
2.585
2.471
2.239
2.112
2.075
1.851
1.788
1.755
1.532
1.455
1.277
0.880
1.0
1.0
1.2
1.1
2.0
3.1
3.1
10.3
0.9
0.9
1.0
1.1
1.1
1.1
5.2
2.1
3.2
ppm 11
10
9
8
7
6
5
4
3
2
1
0

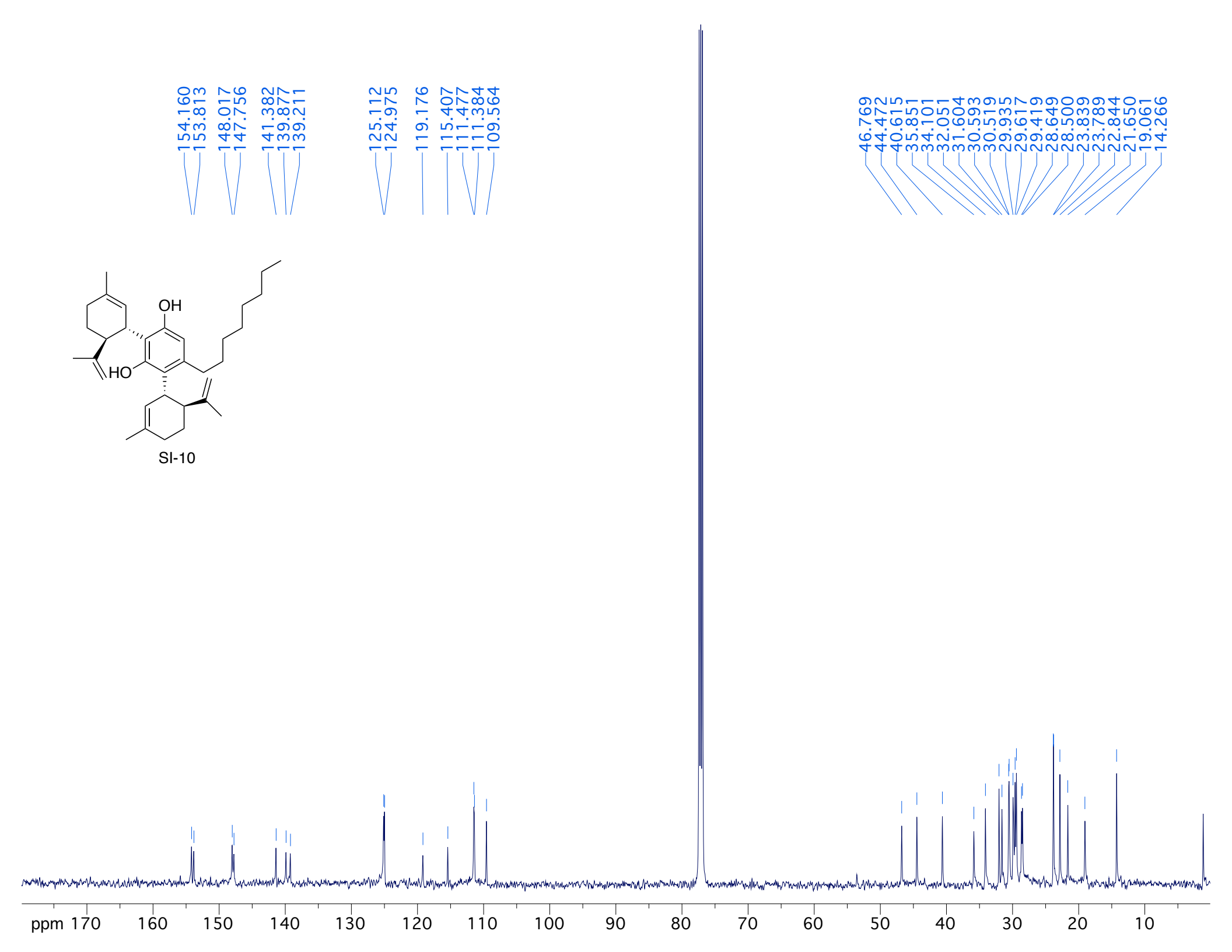

156.634
154.677
147.793
144.161
139.951
124.848
120.096
111.568
108.667
102.246
45.096
40.167
34.193
32.036
31.559
30.404
29.842
29.603
29.407
28.258
23.807
22.834
21.480
14.261
HO
OH
SI-9
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


OH
HO

SI-10


6.202
5.920
5.779
5.580
5.488
4.600
4.501
4.449
4.423
4.011
3.994
3.506
3.487
2.562
2.547
2.533
2.519
2.503
2.470
2.426
2.239
2.180
2.095
2.056
1.782
1.764
1.702
1.494
1.450
1.279
1.261
0.891
0.878
0.864


1.0
0.9
0.9
1.9
1.0
2.0
2.0
3.0
12.1
0.9
0.8
0.9
1.0
0.9
1.2
2.9
10.0
3.1
3.3
ppm 11
10
9
8
7
6
5
4
3
2
1
0


154.160
153.813
148.017
147.756
141.382
139.877
139.211
125.112
124.975
119.176
115.407
111.477
111.384
109.564
46.769
44.472
40.615
35.851
34.101
32.051
31.604
30.593
30.519
29.935
29.617
29.419
28.649
28.500
23.839
23.789
22.844
21.650
19.061
14.266
OH
HO
SI-10
ppm 170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10