Successive C-C Coupling of Dienes to Vicinally Dioxygenated Hydrocarbons: Ruthenium Catalyzed [4+2] Cycloaddition across the Diol, Hydroxycarbonyl or Dione Oxidation Levels

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SUPPORTING INFORMATION

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General Comments

All glassware were oven dried at 140 °C overnight and cooled under argon or nitrogen gas before use. All ruthenium catalyzed reactions were carried in sealed pressure tubes (13 x 100 mm). Toluene was purified by distillation from sodium and benzophenone immediately before use. Ruthenium carbonyl [$Ru_3(CO)_{12}$], PCy_3 and BIPHEP were purchased from commercial suppliers and used as received. $Ru(H)_2(CO)(PPh_3)_3$ is commercially available but was synthesized according to a literature procedure for this report.[1] All dienes were distilled in a Hickman still immediately prior to use. Styrene diol **1a** was synthesized according a general procedure.[2] The ^{1}H NMR spectrum of the product was consistent with a literature report.[3] Cycloheptanediol **1g** was prepared according to a literature procedure.[4] All other diols were commercially available and used as received. All dicarbonyl compounds were commercially available and used as received. Hydroxyketones **2a**, **2b**, **2c**, and **2d** were commercially available. 2-Hydroxycyclohexanone **2e** was prepared according to a literature procedure.[5] Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in a *p*-anisaldehyde solution and heating. Purification of reaction products was carried out by flash column chromatography using 40-63 μm silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded with a Varian Gemini spectrometer in $CDCl_3$ solutions unless otherwise noted. ^{13}C NMR spectra were routinely run with broadband decoupling. Chemical shifts for ^{1}H and ^{13}C are reported in parts per million (ppm) down field from TMS, using residual $CDCl_3$ (7.26 ppm and triplet at 77.0 ppm, respectively) or tetramethylsilane as an internal standard. The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Mass spectra (MS) were obtained on a Karatos MS9 and are reported as m/z. Masses are reported for the molecular ion (M-H, M, M+H or M+Na).

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[1] N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.* **1974**, *15*, 45-64.

[2] B. Plietker and M. Niggemann, *Org. Lett.* **2003**, *5*, 3353-3356.

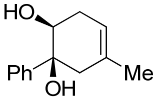
[3] K.C. Nicolaou, S. A. Snyder, D. A. Longbottom, A. Z. Nalbandian, and X. Huang. *Chem. Eur. J.* **2004**, *10*, 5581-5606.

[4] C.A. Horiuchi, G. Dan, M. Sakamoto, K. Suda, S. Usui, O. Sakamoto, S. Kitoh, S. Watanabe, T. Utsukihara, S. Nozaki, *Synthesis* **2005**, *17*, 2861-2864. Spectral data matched literature: C. Yuan, A. Axelrod, M. Varela, L. Danysh, D. Siegel, *Tetrahedron Lett.* **2011**, *52*, 2540-2542.

[5] B. Plietker, *J. Org. Chem.* **2004**, *69*, 8287-8296.

Details for the Syntheses and Characterization of Cycloadducts 5

(1R,2R*)-5-Methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-1,2-diol (5a)*



*From 1-phenylethane-1,2-diol **1a**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) PCy_3 (10.1 mg, 0.036 mmol, 12 mol%) and 1-phenylethane-1,2-diol **1a** (41.4 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **1c** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20% EtOAc:hexane) to provide the cycloadduct **5a** as a colourless solid in 78% yield (63.9 mg, 6:1 rr).

*From 2-hydroxy-1-phenylethanone **2a**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) PCy_3 (10.1 mg, 0.036 mmol, 12 mol%) and 2-hydroxy-1-phenylethanone **2a** (40.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **1c** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20% EtOAc:hexane) to provide the cycloadduct **5a** as a colourless solid 75% yield (51.2 mg, 4:1 rr).

^{1}H NMR (400 MHz, acetone-d_6) δ 7.52 (m, 2H), 7.30 (m, 2H), 7.20 (m, 1H), 5.36-5.32 (m, 0.11H, minor isomer), 5.31-5.27 (m, 0. 82H, major isomer), 4.12 (dd, 0.12H, J^1 = 5.6 Hz, J^2 = 7.4 Hz), 4.06 (dd, 0.82H, J^1 = 5.7 Hz, J^2 = 6.8 Hz), 2.50-2.03 (m, 4H), 1.67 (m, 3H).

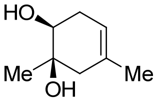
^{13}C NMR (100 MHz, acetone-d_6) δ 146.8, 127.7, 126.4, 125.7, 118.4, 74.8, 71.3, 43.8, 31.2, 22.3.

FTIR (neat): υ 3426, 3056, 2908, 1446, 1047, 877, 699 cm^{-1}.

TLC Rf: 0.21 (3:2 hexanes:ethyl acetate).

MS: Calculated for $C_{13}H_{17}NaO_2$ (M+Na): 227.2; Found: 227.3.

(1R,2R*)-1,5-Dimethyl-cyclohex-4-ene-1,2-diol (5b)*



*From Propane-1,2-diol **1b**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (7.7 mg, 0.012 mmol, 2 mol%) and PCy_3 (20.2 mg, 0.072 mmol, 12 mol%). The pressure tube was purged with argon and toluene (0.30 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.30 mL, 3.0 mmol, 500 mol%) and 1,2-propanediol **1b** (44.0 µL, 0.6 mmol, 100 mol%). The septum was replaced with a screw cap and the reaction was placed in a 150 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 40% EtOAc:hexane) to provide the cycloadduct **5b** as a colourless oil in 60% yield (51.5 mg, 1.6:1 rr).[6]

*From 1-hydroxypropan-2-one **2b**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) PCy_3 (10.1 mg, 0.036 mmol, 12 mol%) and 2-hydroxy-1-phenylethanone **2a** (40.8 mg, 0.3 mmol, 100 mol%) was added. The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 40% EtOAc:hexane) to provide the cycloadduct **5b** as a colourless oil in 75% yield (63.9 mg, 1.6:1 rr).[6]
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^{1}H NMR (400 MHz, DMSO-d_6) δ 5.15-5.13 (m, 3H), 4.43-4.42 (d, *J* = 4.0 Hz, 0.14H), 4.40-4.39 (d, *J* = 4.0 Hz, 0.26H), 4.29-4.27 (d, *J* = 5.0 Hz, 1H), 4.25-4.24 (d, *J* = 5.0 Hz, 1.61H), 4.18 (s, 0.27H), 4.15 (s, 0.14H), 3.95 (m, 1.61H), 3.92 (s, 1H), 3.37-3.35 (m, 1.84H), 2.09-1.99 (m, 8.10H), 1.91-1.81 (m, 3.64H), 1.58-1.56 (m, 9.36H), 1.04 (s, 8.10H), 1.01 (s, 0.82H), 1.00 (s, 0.45H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 130.5, 118.7, 116.9, 72.8, 72.2, 71.4, 70.9, 41.7, 36.9, 36.5, 31.6, 24.7, 24.6, 23.2, 22.9.

FTIR (neat): υ 3376, 2966, 2906, 1438, 1372, 1104, 1072, 1053, 910, 875, 794, 732, 687 cm^{-1}.

TLC Rf: 0.21 (40% ethyl acetate/hexanes).

MS: Calculated for $C_8H_{14}O_2Na$ (M+Na): 165.2; Found: 165.1.

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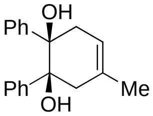
[6] The sample contained approximately 10% of unknown and unidentifiable but related compounds.

(1R,2S*)-4’-Methyl-1’,2’,3’,6’-tetrahydro-[1,1’:2’,1’’-terphenyl]1’,2’-diol (5c)*



From 1,2-diphenyl-1,2-diol (hydrobenzoin) ***1c****:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.1 mg, 0.005 mmol, 2 mol%) BIPHEP (9.5 mg, 0.018 mmol, 6 mol%) and 1,2-diphenyl-1,2-diol (hydrobenzoin) **1c** (64.7 mg, 0.30 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **1c** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 16% EtOAc:hexane) to provide the cycloadduct **5c** as a colourless solid in 90% yield (80.7 mg).

From 2-hydroxy-1,2-diphenylethanone (benzoin) ***2c****:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (4.0 mg, 0.0063 mmol, 2 mol%) BIPHEP (10.7 mg, 0.020 mmol, 6 mol%) and 2-hydroxy-1,2-diphenylethanone (benzoin) **2c** (67.8 mg, 0.32 mmol, 100 mol%) was added. The pressure tube was purged with argon and toluene (0.16 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.16 mL, 1.6 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 16% EtOAc:hexane) to provide the cycloadduct **5c** as a colourless solid in 98% yield (87.8 mg).

From benzil ***3c****:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru(H)_2(CO)(PPh_3)_3$ (16.5 mg, 0.018 mmol, 6 mol%) BIPHEP (9.7 mg, 0.019 mmol, 6 mol%) and 2-benzil **3c** (63.1 mg, 0.30 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%) and >95% formic acid (35 µL, 0.9 mmol, 300 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^oC oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature before slowly opening the reaction vessel to the atmosphere (gas evolution). The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 16% EtOAc:hexane) to provide the cycloadduct **5c** as a colourless solid in 70% yield (58.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (tt, 2H, *J* = 7.2 Hz, 2.4 Hz, 1.2 Hz, 1.2 Hz), 7.14 (t, 4H, *J* = 7.6 Hz), 7.00 (m, 4H), 5.66 (m, 1H), 2.89 (s, 1H), 2.82 (s, 1H), 2.92-2.74 (m, 2H), 2.52 (m, 2H), 1.89 (s, 3H)

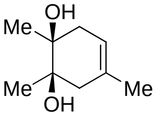
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 142.0, 134.0, 127.2, 127.1, 127.1, 127.0, 126.9, 126.8, 77.3, 44.2, 38.9, 23.2.

FTIR (neat): υ 3423 (br), 3056, 2908, 1446, 1047, 877, 699 cm^{-1}.

TLC Rf: 0.3 (3:1 hexanes:ethyl acetate).

MS: Calculated for $C_{19}H_{20}NaO_2$ (M+Na): 303.14; Found: 303.1.

(1R*,2S*)-1,2,4-Trimethyl-cyclohex-4-ene-1,2-diol (5d)



From butane-2,3-diol ***1d****:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) and BIPHEP (9.4 mg, 0.018 mmol, 6 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by butane-2,3-diol **1d** (27 μL, 0.3 mmol, 100 mol%) and freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5d** as a colourless solid in 84% yield (39.7 mg).

From 3-hydroxybutan-2-one ***2d****:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) and BIPHEP (9.4 mg, 0.018 mmol, 6 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by 3-hydroxybutan-2-one **2d** (27 μL, 0.3 mmol, 100 mol%) and freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5d** as a colourless solid in 84% yield (39.7 mg).

From 2,3-butanedione (biacetyl) ***3d****:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) and BIPHEP (9.4 mg, 0.018 mmol, 6 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by biacetyl **3d** (26 μL, 0.3 mmol, 100 mol%) and freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5d** as a colourless solid in 84% yield (39.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28-5.24 (m, 1H), 2.30-2.03 (m, 6H), 1.66-1.64 (m, 3H), 1.19 (s, 3H), 1.18 (s, 3H).

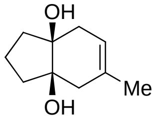
^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1, 118.5, 73.6, 73.1, 43.6, 38.8, 23.1, 22.7, 22.6.

FTIR (neat): υ 3359, 2960, 2914, 1438, 1311, 1091, 1053, 950, 667 cm^{-1}.

TLC Rf: 0.17 (3:2 hexanes:ethyl acetate).

MS: Calculated for $C_9H_{16}NaO_2$ (M+Na): 179.2; Found: 179.3.

(3aR,7aS*)-5-Methyl-2,3,3a,4,7,7a-hexahydro-1H-indene-3a,7a-diol (5e)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *cis*-1,2-cyclopentanediol **1e** (30.4 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5e** as a colourless oil in 93% yield (47.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26-5.23 (m, 1H), 2.31-2.09 (m, 6H), 1.90-1.54 (m, 10H).

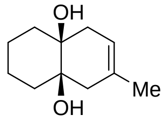
^{13}C NMR (100 MHz, $CDCl_3$) δ 131.2, 117.7, 78.7, 78.0, 40.1, 35.5, 35.1, 34.8, 23.1, 17.4.

FTIR (neat): υ 3405, 2914, 2859, 1399, 1166, 1005, 898 cm^{-1}.

TLC Rf: 0.21 (1.5:1 hexanes:ethyl acetate).

MS: Calculated for $C_{10}H_{16}NaO_2$ ($M+Na^+$): 191.2; Found: 191.1

(4aR,8aS*)-6-Methyl-1,2,3,4,4a,5,8,8a-octahydro-4a,8a-diol (5f)*



*From cyclohexane-1,2-diol **1f**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *trans*-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5f** as a colourless solid in 90% yield (49.9 mg).

*From 2-hydroxycyclohexanone **2f**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and 2-hydroxycyclohexanone **2f**: (34.0032 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **1c** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5a** as a colourless solid in 68% yield (37.5 mg).

*From cyclohexane-1,2-dione **3f**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $RuH_2(CO)(PPh_3)_3$ (16.5 mg, 0.018 mmol, 6 mol%) BIPHEP (9.6 mg, 0.018 mmol, 6 mol%) and cyclohexane-1,2-dione **3f** (33.6 mg, 0.30 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%) and > 95% formic acid (35 µL, 0.9 mmol, 300 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 72 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature before slowly opening reaction tube (gas evolution). The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 1:3 to 2:3 EtOAc:hexane) to provide the cycloadduct **5f** as a colourless solid in 54% yield (32.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27-5.23 (m, 1H), 2.34-2.03 (m, 6H), 1.71-1.61 (m, 7H), 1.51-1.37 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.0, 117.6, 72.5, 72.0, 41.5, 36.6, 34.0, 33.8, 23.1, 21.99, 21.96.

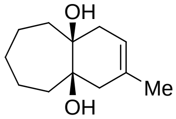
FTIR (neat): υ 3401, 2914, 2859, 1444, 1399, 1005, 898 cm^{-1}.

TLC Rf: 0.33 (1.5:1 hexanes:ethyl acetate).

Melting Point: 77-78 °C.

MS: Calculated for $C_{11}H_{18}NaO_2$ ($M+Na^+$): 205.2; Found: 205.1.

(4aR,9aS*)-2-Methyl-4,4a-5,6,7,8,9,9a-ocahydro-1H-benzo[7]annulene-4a,9a-diol (5g)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *cis*-1,2-cycloheptanediol **1g** (39.1 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20% EtOAc:hexane) to provide the cycloadduct **5g** as a white solid in 80% yield (47.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (s, 1H), 2.29-2.06 (m, 6H), 1.97-1.89 (m, 2H), 1.75-1.71 (m, 3H), 1.66 (s, 3H), 1.55-1.45 (m, 5H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 118.1, 75.4, 74.9, 43.1, 38.3, 35.9, 35.7, 26.2, 23.1, 20.9

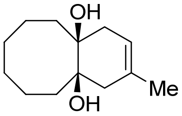
FTIR (neat): υ 3404, 2915, 2862, 1438, 1406, 1321, 1195, 1108, 1091, 1075, 1032, 1020, 959, 931, 894, 885, 860, 796 cm^{-1}.

TLC Rf: 0.23 (20% ethyl acetate/hexanes).

Melting Point: 86-88 °C

MS: Calculated for $C_{12}H_{20}O_2Na$ (M+Na): 219.3; Found: 219.1 (M+Na).

(4aR,10aS*)-2-Methyl-1,4,4a-5,6,7,8,9,10,10a-decahydrobenzo[8]annulene-4a,10a-diol (5h)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *cis*-1,2-cyclooctanediol **1h** (42.3 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20% EtOAc:hexane) to provide the cycloadduct **5h** as a colourless solid in 70% yield (43.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29-2.25 (m, 1H), 2.32-2.04 (m, 6H), 1.98-1.90 (m, 2H), 1.86-1.75 (m, 2H), 1.69-1.41 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 118.1, 75.1, 74.6, 44.8, 40.0, 35.82, 35.75, 28.0, 23.1.

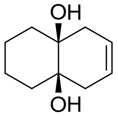
FTIR (neat): υ 3406, 3322, 2923, 2854, 1439, 1147, 1064, 878 cm^{-1}.

TLC Rf: 0.39 (1.5:1 hexanes:ethyl acetate).

Melting Point: 95-96 ^{o}C.

MS: Calculated for $C_{13}H_{22}NaO_2$ ($M+Na^+$): 233.3; Found: 233.2.

(4aR,8aS*)-1,2,3,4,4a,5,8,8a-octahydronaphthlene-4a,8a-diol (5i)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (5.2 mg, 0.0081 mmol, 2 mol%) BIPHEP (12.9 mg, 0.025 mmol, 6 mol%) and cyclohexane-1,2-diol **1a** (47.2 mg, 0.41 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.2 mL, 2.0 M) was added via syringe, followed by 1,3-butadiene (0.2 mL, 2.1 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 2:3 EtOAc:hexanes) to provide the cycloadduct **5i** as a colourless solid in 85% yield (58.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (m, 2H), 2.38-2.16 (m, 6H), 1.66-1.56 (m, 4H), 1.52-1.34 (m, 4H).

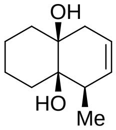
^{13}C NMR (100 MHz, $CDCl_3$) δ 123.8, 72.3, 36.6, 34.0, 22.0.

FTIR (neat): υ 3357, 2959, 2914, 1438, 1311, 1091, 1053, 950, 667 cm^{-1}.

TLC Rf: 0.35 (3:2 hexanes:ethyl acetate).

MS: Calculated for $C_{10}H_{16}NaO_2$ (MNa+): 191.10; Found: 191.1.

(4aR,5R*,8aS*)-5-Methyl-1,2,3,4,4a,5,8,8a-octahydronaphthlalene-4a,8a-diol (5j)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and trans-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled 1,3-pentadiene **4c** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20% EtOAc:hexane) to provide the cycloadduct **5j** as a white solid in 91% yield (49.8 mg, 5:1 dr).

mp: 111-113^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.61-5.55 (m, 1H), 5.35-5.32 (m, 1H), 2.64-2.60 (m, 1H), 2.40-2.33 (m, 1H), 2.17 (s,1H), 2.08-2.02 (m, 1H), 1.77-1.36 (m, 8H), 1.07-1.06 (d, *J*= 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 129.5, 123.6, 74.2, 72.5, 38.1, 34.6, 33.9, 30.0, 22.8, 20.5, 14.2.

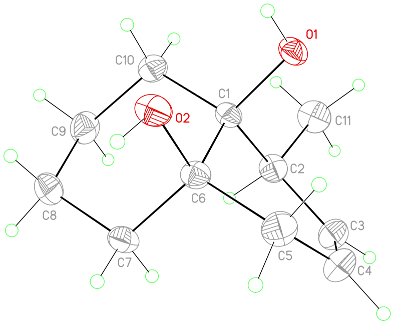
FTIR (neat): υ 3432, 3333, 2950, 2925, 2897, 2861, 1459, 1191, 1158, 1057, 979, 958, 878, 762 cm^{-1}.

TLC Rf: 0.19 (20% ethyl acetate/hexanes).

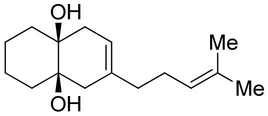
MS: Calculated for $C_{11}H_{18}O_2Na$ (M+Na): 205.2; Found: 205.1 (M+Na).

Relative stereochemistry determined by X-ray crystallography

View of **5j** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



(4aR,8aS*)-6-(4-Methylpent-3-en-1-yl)-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5k)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *trans*-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled myrcene **4d** (0.16 mL, 0.9 mmol, 300 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 10%-40% EtOAc:hexane) to provide the cycloadduct **5k** as a colourless solid in 84% yield (65.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (m, 1H), 5.09-5.03 (m, 1H), 2.34-1.92 (m, 10H), 1.73-1.62 (m, 7H), 1.60 (s, 3H), 1.49-1.36 (m, 4H).

^{13}C NMR (100 MHz, CDC_3) δ 134.7, 131.6, 124.0, 117.3, 72.6, 72.1, 39.7, 36.9, 36.7, 33.9, 33.7, 26.2, 25.7, 22.0, 21.9, 17.7.

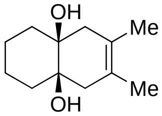
FTIR (neat): υ 3405, 2914, 2859, 1399, 1166, 1005, 898 cm^{-1}.

TLC Rf: 0.33 (1.5:1 hexanes:ethyl acetate).

Melting Point: 84-85 °C.

MS: Calculated for $C_{16}H_{26}NaO_2$ ($M+Na^+$): 273.3; Found: 273.2.

(4aR,8aS*)-6,7-Dimethyl-1,2,3,4,4a,5,8,8a-ocathydronaphthalene-4a,8a-diol (5l)*



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and trans-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled 2,3-dimethylbutadiene **4e** (0.10 mL, 0.9 mmol, 300 mol%). The septum was replaced with a screw cap and the reaction was placed in a 150 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5l** as a colourless solid in 75% yield (44.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25-2.02 (m, 6H), 1.70-1.61 (m, 4H), 1.60 (s, 6H), 1.49-1.36 (m, 4H).

^{13}C NMR (100 MHz, actone-d_6) δ 122.3, 72.6, 42.9, 33.8, 22.0, 18.6.

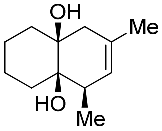
FTIR (neat): υ 3409, 3311, 2918, 1891, 1443, 1403, 1076, 1028, 989, 891 cm^{-1}.

TLC Rf: 0.23 (1.5:1 hexanes:ethyl acetate).

Melting Point: 135-136 ^{o}C.

MS: Calculated for $C_{12}H_{20}NaO_2$ (M+Na$^+$): 219.3; Found: 219.1.

(4aR*,5R*,8aS*)-5,7-Dimethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5m)



To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *trans*-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled 2-methyl-1,3-pentadiene **4f** (0.17 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 150 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20% EtOAc:hexane) to provide the cycloadduct **5m** as a colourless waxy solid in 78% yield (53.8 mg, 1.2:1 dr).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (m, 1H), 5.01 (m, 1.2H), 2.64-2.48 (m, 2H), 2.34-2.15 (m, 4H), 1.98-1.20 (m, 34H), 1.01 (d, 3.6H, *J* = 7.3 Hz), 0.92 (d, 3H, *J* = 6.8 Hz).

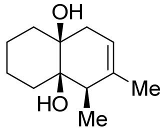
^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4, 131.0, 128.8, 123.5, 73.9, 73.8, 72.92, 72.88, 43.0, 36.5, 35.8, 34.3, 34.0, 30.2, 29.7, 23.1, 22.8, 22.7, 22.3, 21.2, 20.5, 14.5, 14.3.

FTIR (neat): υ 3413, 3322, 2946, 2862, 1447, 1169, 983, 878 cm^{-1}.

TLC Rf: 0.31 (1.5:1 hexanes:ethyl acetate).

MS: Calculated for $C_{12}H_{20}NaO_2$ ($M+Na^+$): 219.3; Found: 219.1.

(4aR,5R*,8aR*)-5,6-Dimethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5n)*



*From 3-methyl-1,3-pentadiene **4g**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *cis*-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled 3-methyl-1,3-pentadiene **4g** (0.17 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5n** as a colourless solid in 82% yield (48.8 mg, >20:1 dr).

*From 3-methyl-1,4-pentadiene **iso-4g**:*
To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *trans*-1,2-cyclohexanediol **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled 3-methyl-1,4-pentadiene **iso-4g** (0.18 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 ^{o}C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide the cycloadduct **5n** as a colourless solid in 91% yield (63.9 mg, >20:1 dr).

^{1}H NMR (400 MHz, acetone-d_6) δ 5.24-5.20 (m, 1H), 3.15-2.99 (m, 1H), 2.34-2.21 (m, 2H), 1.75-1.27 (m, 12H), 1.09 (d, 3H, *J* = 7.2 Hz).

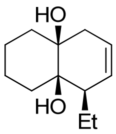
^{13}C NMR (100 MHz, actone-d_6) δ 135.4, 119.1, 74.1, 72.6, 41.0, 37.9, 35.1, 32.9, 23.4, 22.2, 21.9, 13.0.

FTIR (neat): υ 3420, 2942, 2871, 1391, 1160, 976, 884, 838 cm^{-1}.

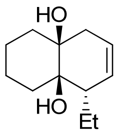
TLC Rf: 0.13 (4:1 hexanes:ethyl acetate).

MS: Calculated for $C_{12}H_{20}NaO_2$ (M+Na$^+$): 219.3; Found: 219.1.

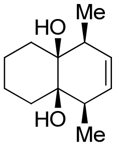
(4aR,5R*,8aS*)-5-Ethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5o)*



5o



***epi*-5o**



***iso*-5o**

To a dry pressure tube sealed with a septum under an argon atmosphere was added $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and *trans*-1,2-cyclohexane **1f** (34.8 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled 2,4-hexadiene **4h** (0.17 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 150 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO_2: 20%-40% EtOAc:hexane) to provide a mixture of cycloadducts **5o** as a colourless oil in 90% yield (53.1 mg). The isomers were separated from each other and characterized independently.

(4aR,5R*,8aS*)-5-Ethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5o)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (m, 2H), 2.36 (m, 1H), 2.27 (m, 1H), 2.14 (br s, 1H), 2.04 (m, 1H), 1.81-1.53 (m, 9H), 1.46-1.18 (m, 4H), 1.03 (t, 3H, J = 7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 126.4, 123.8, 74.7, 72.5, 41.9, 38.0, 33.9, 30.1, 22.9, 21.6, 20.6, 12.9.

MS: Calculated for $C_{12}H_{21}NaO_2$ (M+Na): 219.3; Found: 219.1.

(4aR,5S*,8aS*)-5-Ethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5-epi-5o)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (ddd, 1H, J^1 = 2.5 Hz, J^2 = 4.8 Hz, J^3 = 10 Hz), 5.49-5.43 (m, 1H), 2.58 (br s, 1H), 2.24 (m, 1H), 1.98 (br s, 1H), 1.90-1.16 (m, 14H), 0.91 (t, 3H, J = 7 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 125.6, 74.5, 72.6, 36.6, 36.2, 29.8, 22.3, 21.2, 21.0, 11.7.

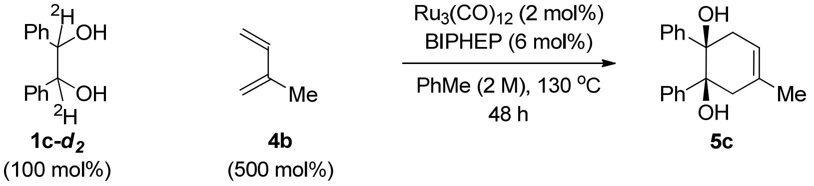
(4aR,5R*,8S,8aS*)-5,8-Dimethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (iso-5o)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (m, 2H), 2.36 (m, 2H), 1.92 (br s, 2H), 1.71-1.52 (m, 7H), 1.45-1.32 (m, 2H), 1.10 (d, 6H, J = 7.4 Hz).

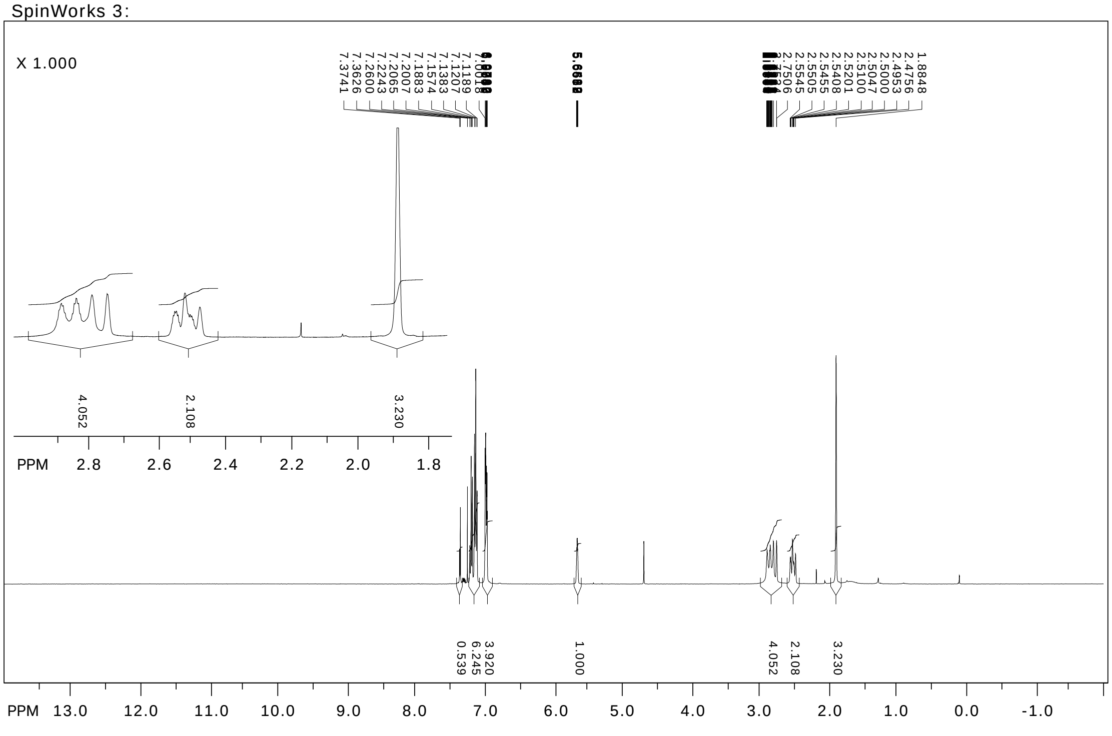
^{13}C NMR (100 MHz, $CDCl_3$) δ 129.1, 74.5, 38.1, 33.3, 21.6, 16.1.

FTIR (neat): υ 3401, 3027, 2940, 2866, 1456, 1365, 1080, 875, 839, 678 cm^{-1}.

Deuterium Labelling Experiment



To a dry pressure tube sealed with a septum under an argon atmosphere was added Ru$_3$(CO)$_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), BIPHEP (9.4 mg, 0.018 mmol, 6 mol%) and d$_2$-hydrobenzoin **1c-d$_2$** (64.9 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly distilled isoprene **4b** (0.15 mL, 1.5 mmol, 500 mol%). The septum was replaced with a screw cap and the reaction was placed in a 130 °C oil bath. After 48 hours, the reaction vessel was removed from the oil bath and was allowed to cool to room temperature. The volatiles were removed under reduced pressure via rotary evaporation and the residue was purified by flash chromatography (SiO$_2$: 5%-20% EtOAc:hexane) to provide the cycloadduct **5c** as a colourless solid in 76% yield (64.4 mg). No ^{2}H incorporation was observed by ^{1}H NMR.



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transmitter freq.: 399.807110 MHz                                          processed size: 65536 complex points
time domain size: 51282 points                                             LB: 0.100   GF: 0.0000
width: 6410.26 Hz = 16.0334 ppm = 0.125000 Hz/pt                           Hz/cm: 256.410    ppm/cm: 0.64133
number of scans: 8
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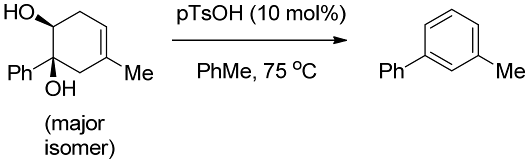
Dehydration and Proof of Regioselectivity

3-Methyl-1,1'-biphenyl

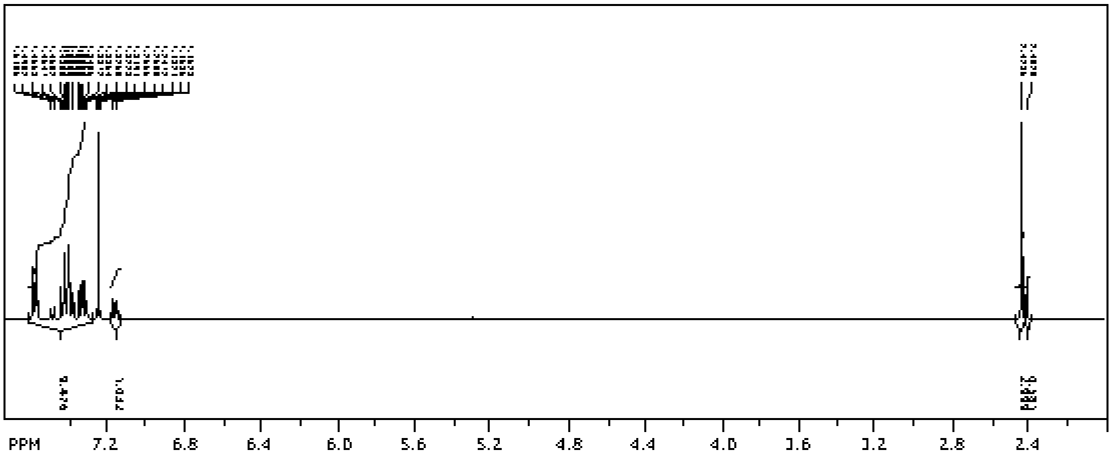


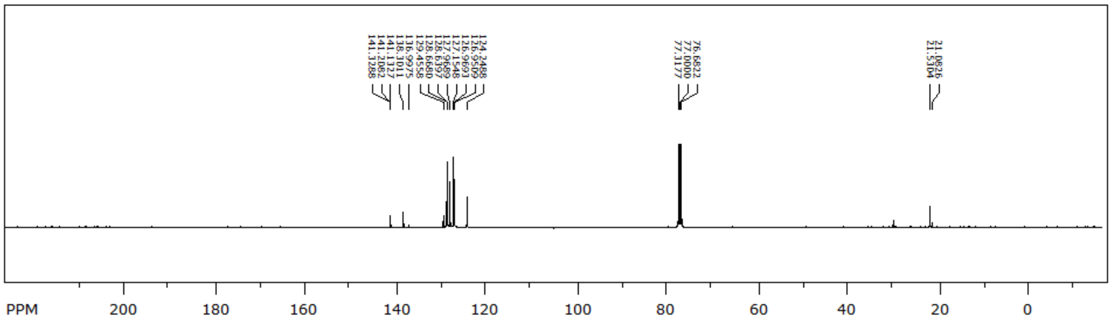
To a round bottomed flask was added cycloadduct **4a** (74.4 mg, 0.36 mmol, 100 mol%) followed by p-toluenesulfonic acid (7 mg, 0.036 mmol, 10 mol%). Toluene was added (5 mL) and the round bottomed flask was fitted with a reflux condenser and the reaction vessel was placed in a 75 °C oil bath. When judged complete by TLC, the reaction vessel was removed from the oil bath and allowed to cool to room temperature. The toluene was removed under reduced pressure via rotary evaporation and the residue was purified via flash chromatography (SiO_2: hexanes) to provide methylbiphenyl as a colourless oil in 65% yield (40.2 mg) as a 5:1 ratio of 3-methylbiphenyl[7] to 4-methylbiphenyl.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.31 (m, 9H), 7.17 (m, 1H), 2.43 (s, 3H), 2.40 (s, 0.6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 141.2, 141.1, 138.3, 137.0, 129.5, 128.7, 129.6, 128.0, 127.2, 126.97, 126.95, 124.2, 21.5 (major), 21.1 (minor).

TLC Rf: 0.68 (3:2 hexanes:ethyl acetate).





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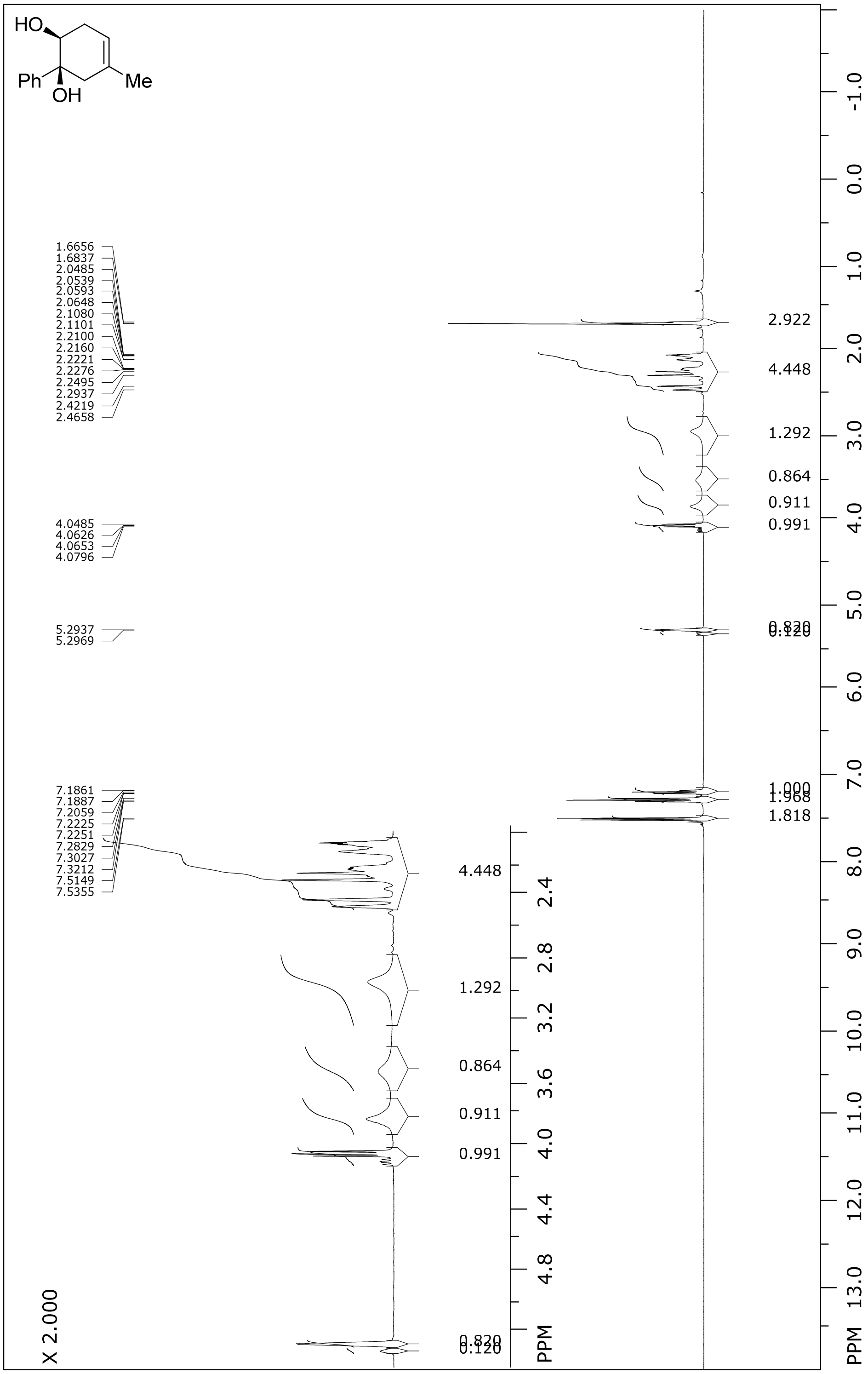
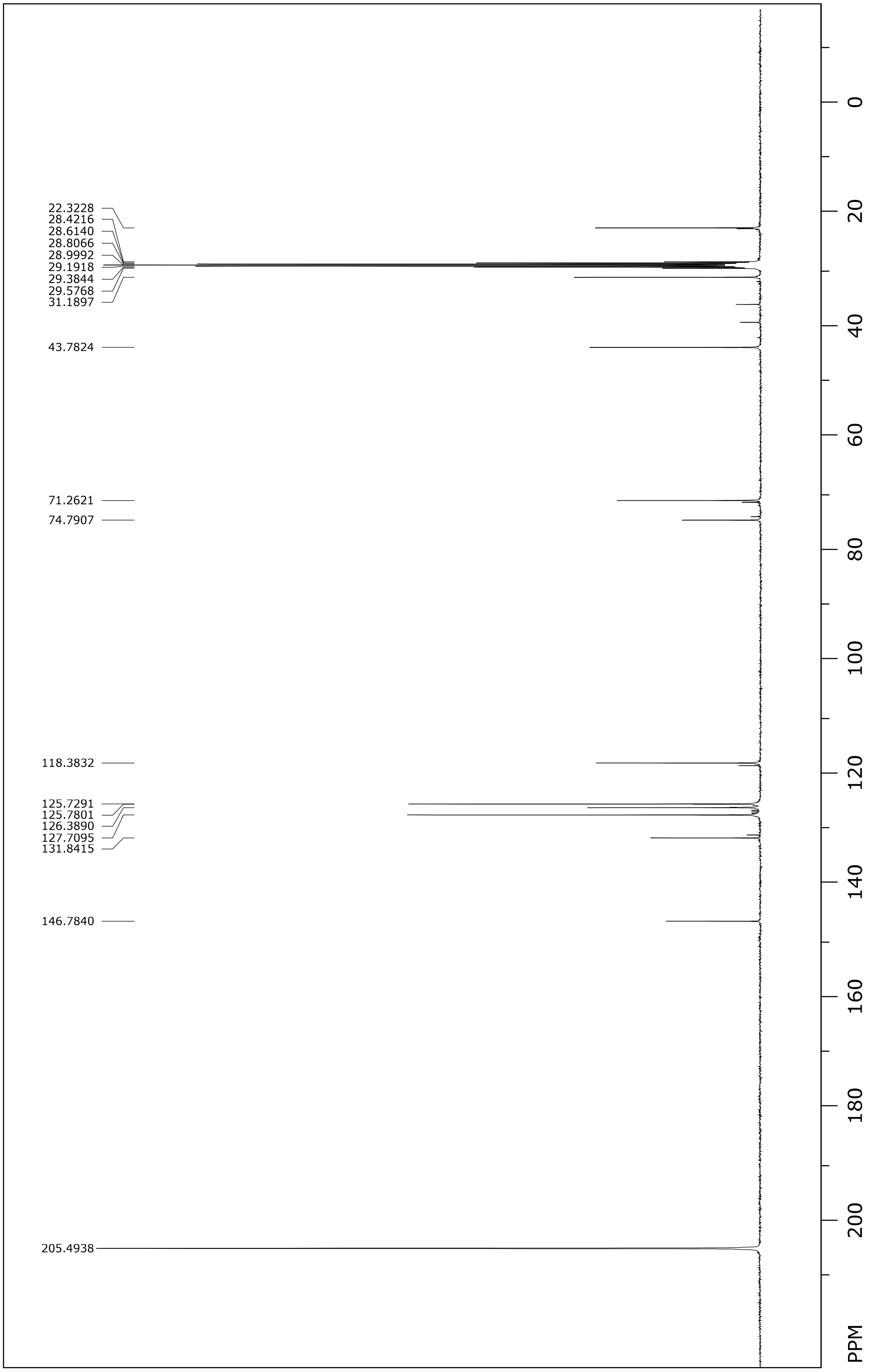
[7] P. D. Stevens, J. Fan, H. M. R. Gardimalla, M. Yen, and Y. Gao *Org. Lett.* **2005**, *7*, 2085-2088.

[8] R. Bandari, T. Höche, A. Prager, K. Dirnberger, M. R. Buchmeiser *Chem. Eur. J.* **2010,** *16*, 4650-4658.

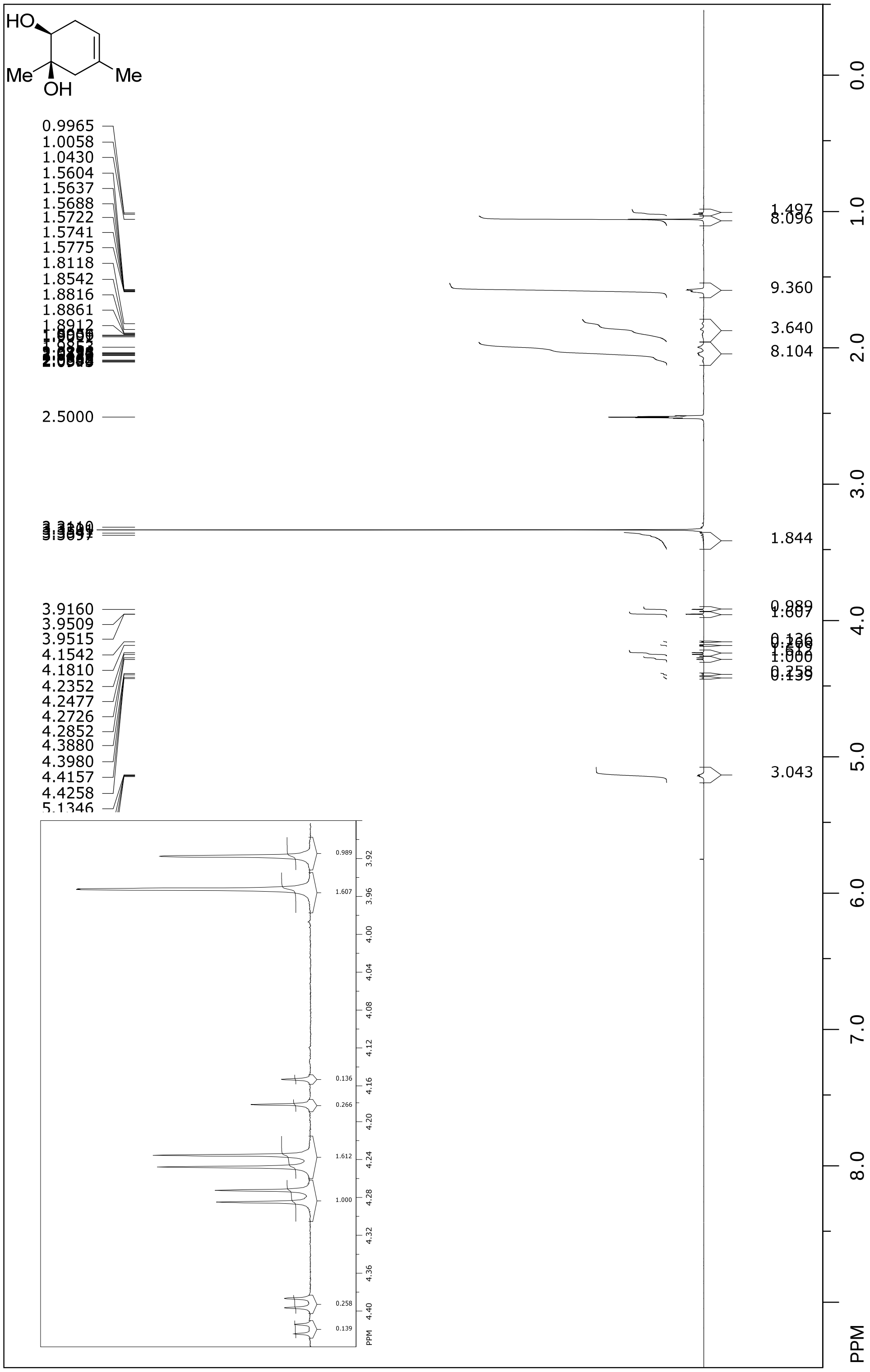
NMR Spectra

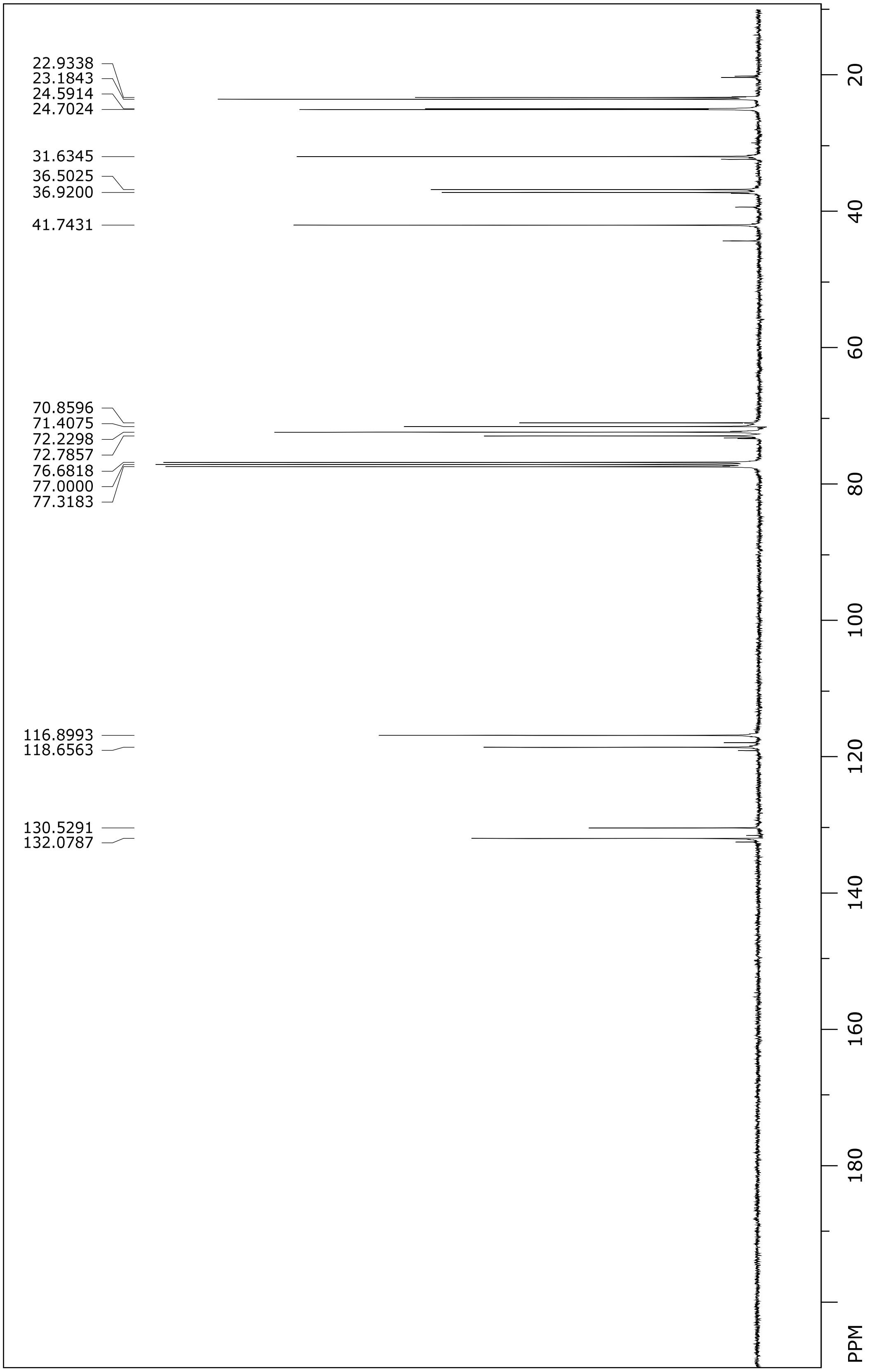
(1R*,2R*)-5-Methyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-1,2-diol (5a)



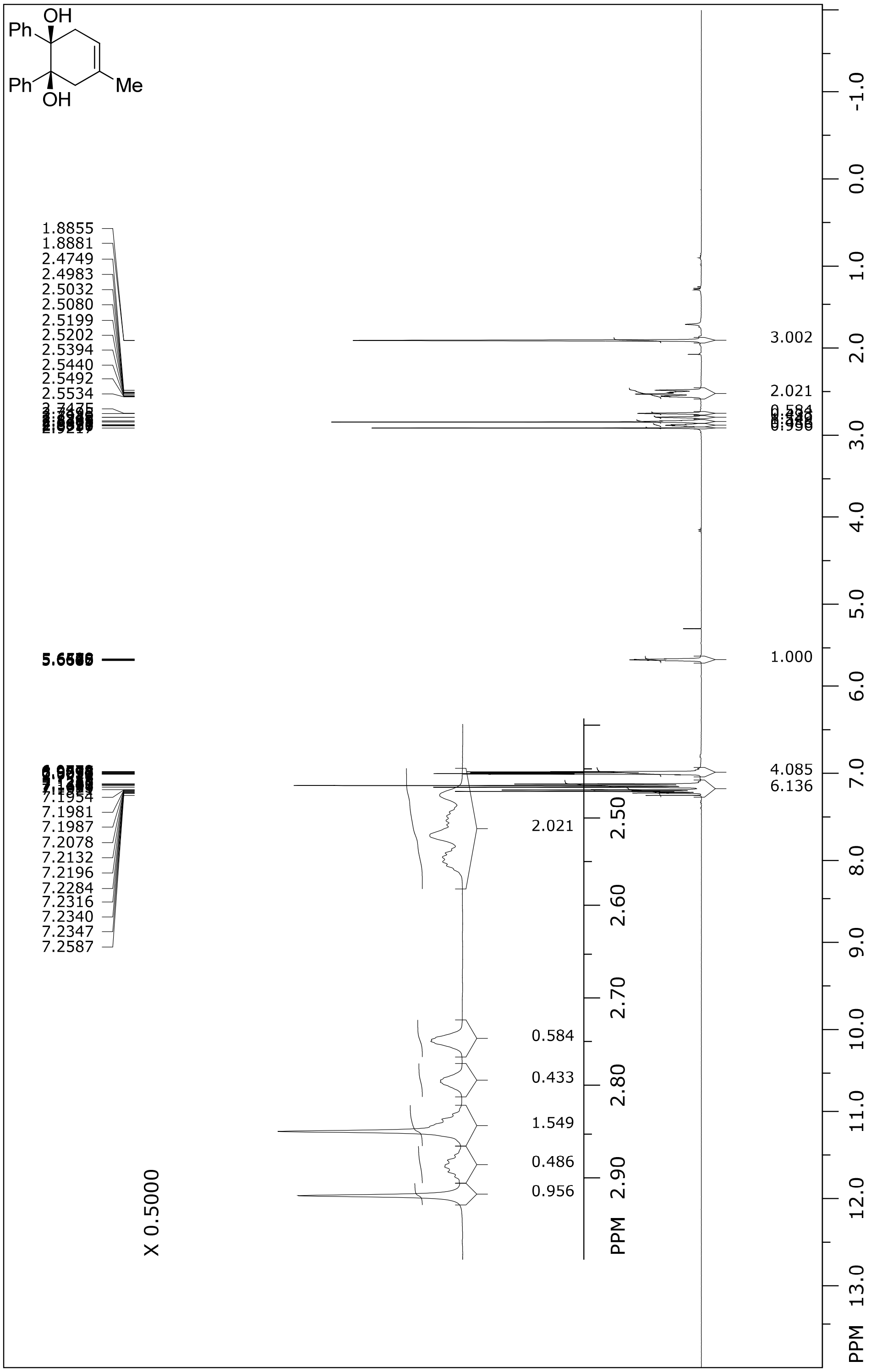

22.3228
28.4216
28.6140
28.8066
28.9992
29.1918
29.3844
29.5768
31.1897
43.7824
71.2621
74.7907
118.3832
125.7291
125.7801
126.3890
127.7095
131.8415
146.7840
205.4938
0
20
40
60
80
100
120
140
160
180
200
PPM

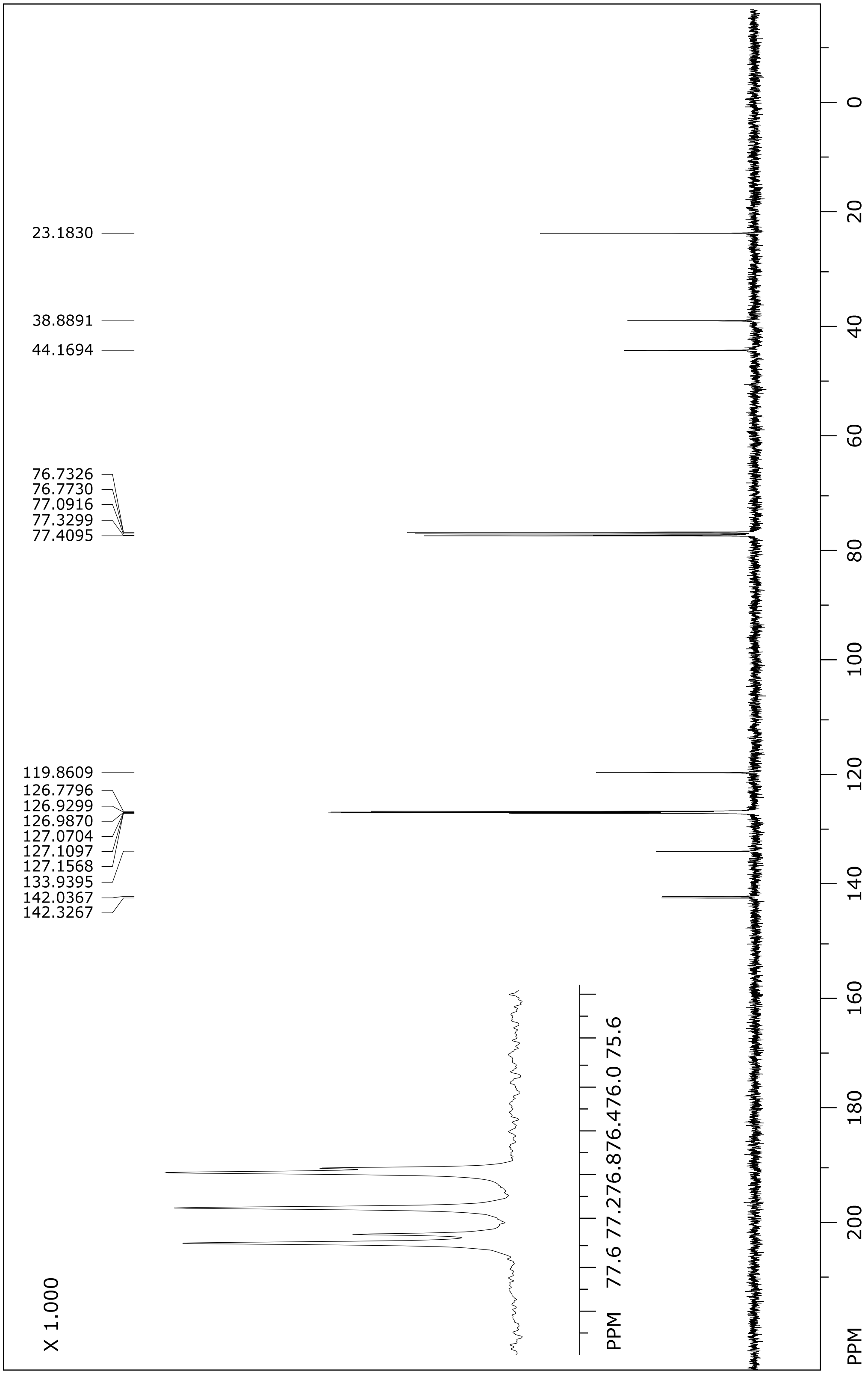
(1R*,2R*)-1,5-Dimethyl-cyclohex-4-ene-1,2-diol (5b)



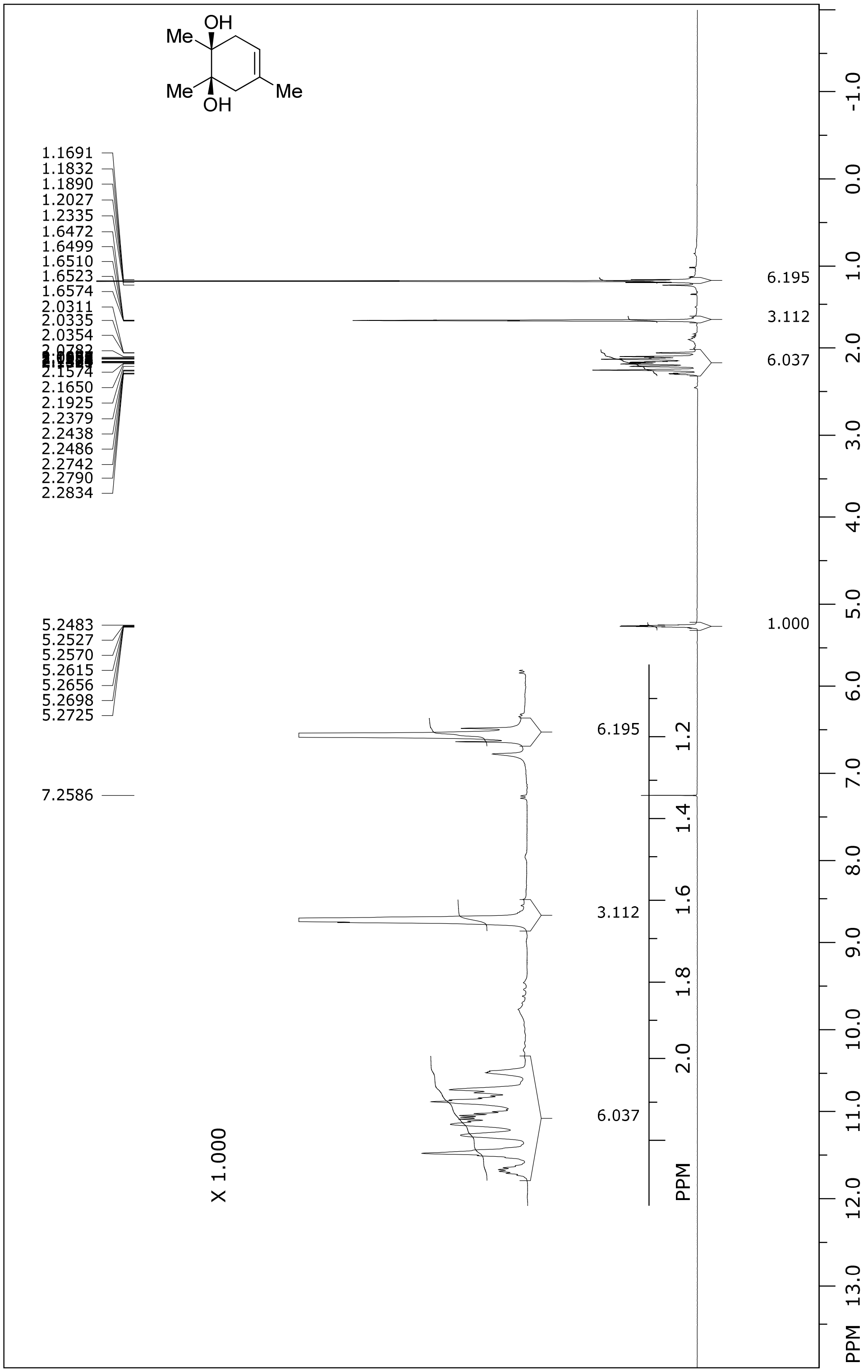

22.9338
23.1843
24.5914
24.7024
31.6345
36.5025
36.9200
41.7431
70.8596
71.4075
72.2298
72.7857
76.6818
77.0000
77.3183
116.8993
118.6563
130.5291
132.0787
20
40
60
80
100
120
140
160
180
PPM

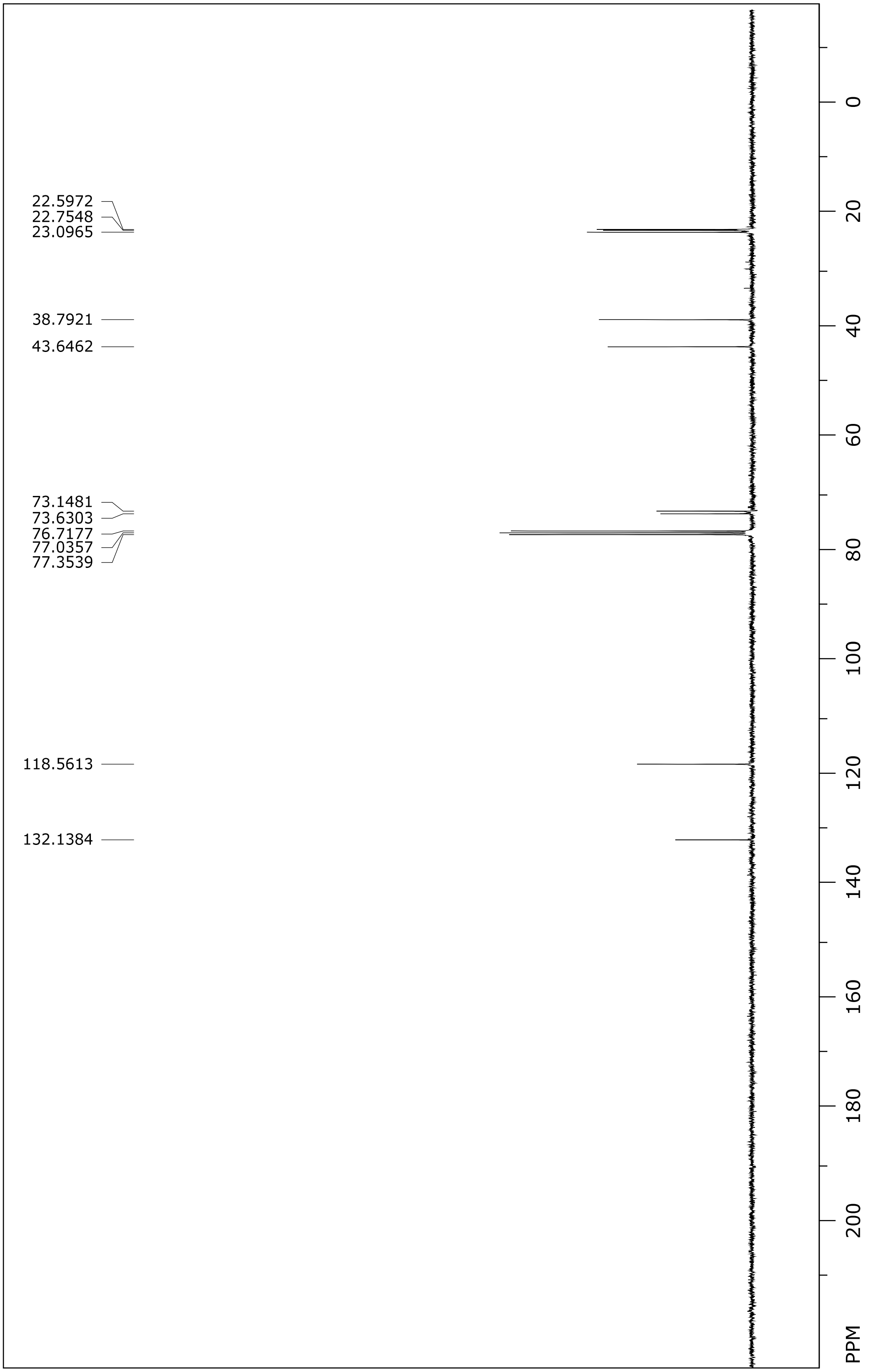
(1R,2S*)-4’-Methyl-1’,2’,3’,6’-tetrahydro-[1,1’:2’,1’’-terphenyl]1’,2’-diol (5c)*



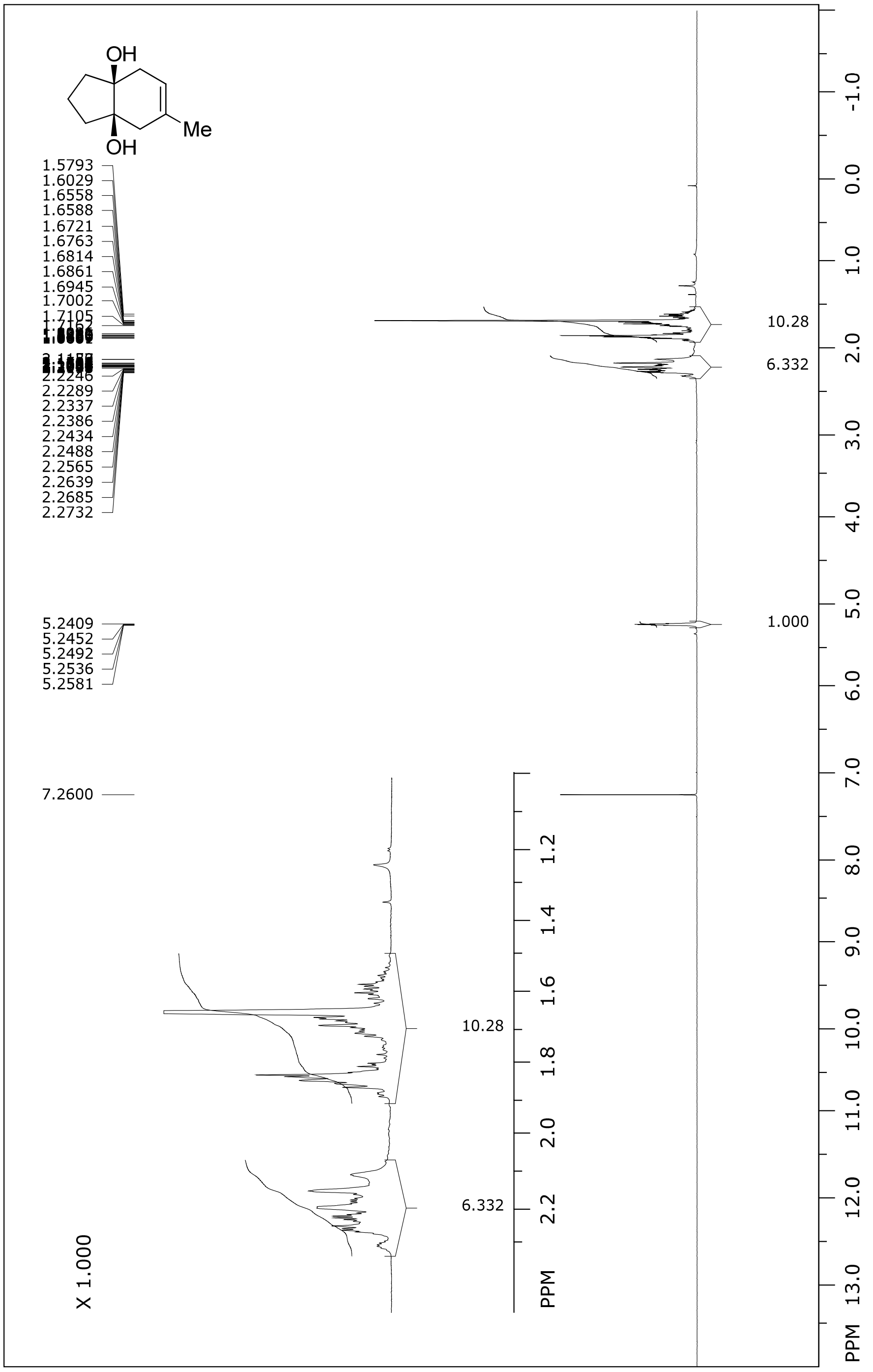

23.1830
38.8891
44.1694
76.7326
76.7730
77.0916
77.3299
77.4095
119.8609
126.7796
126.9299
126.9870
127.0704
127.1097
127.1568
133.9395
142.0367
142.3267
X 1.000
PPM
77.6
77.2
76.8
76.4
76.0
75.6
0
20
40
60
80
100
120
140
160
180
200
PPM

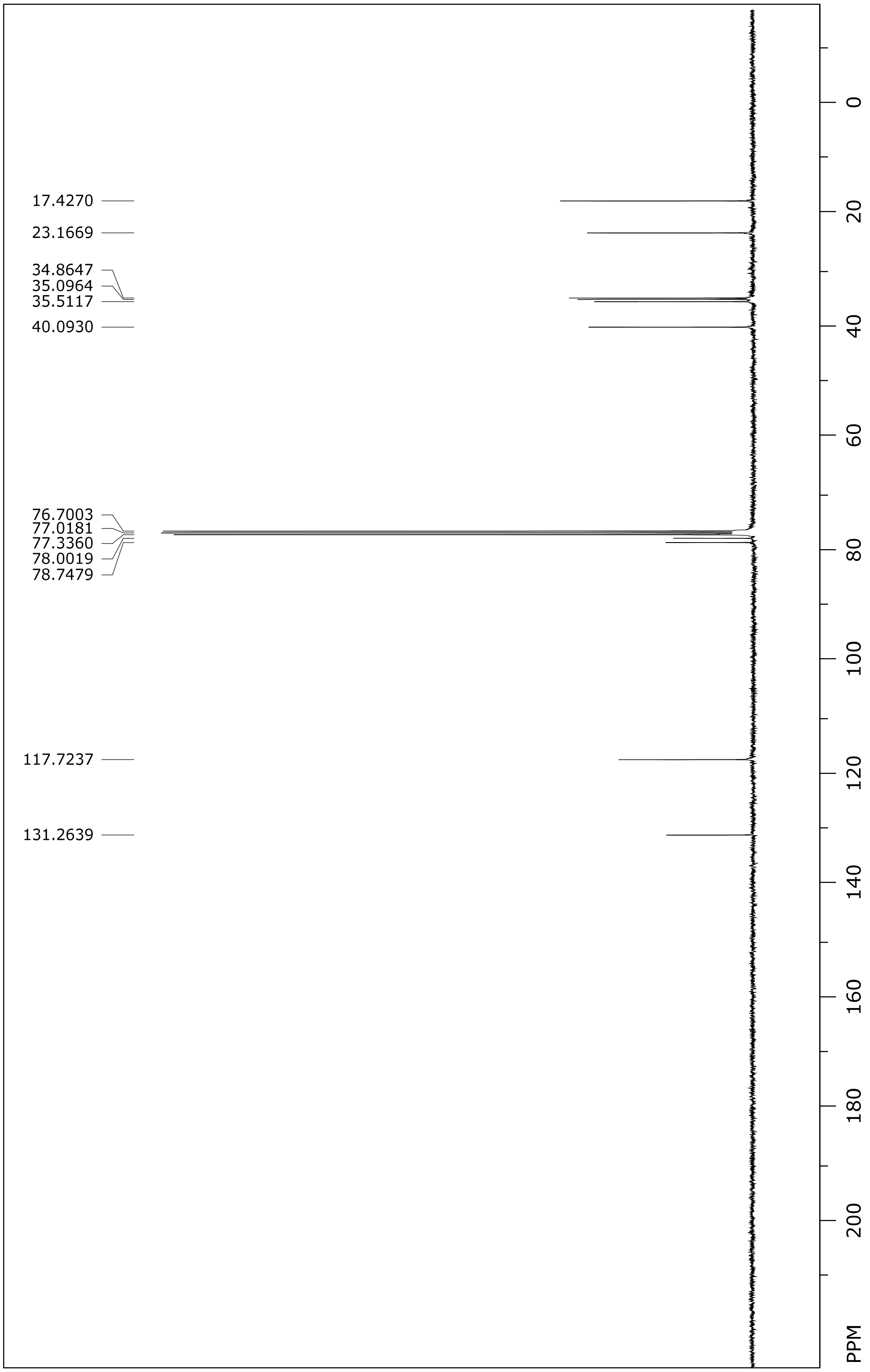
(1R,2S*)-1,2,4-Trimethyl-cyclohex-4-ene-1,2-diol (5d)*



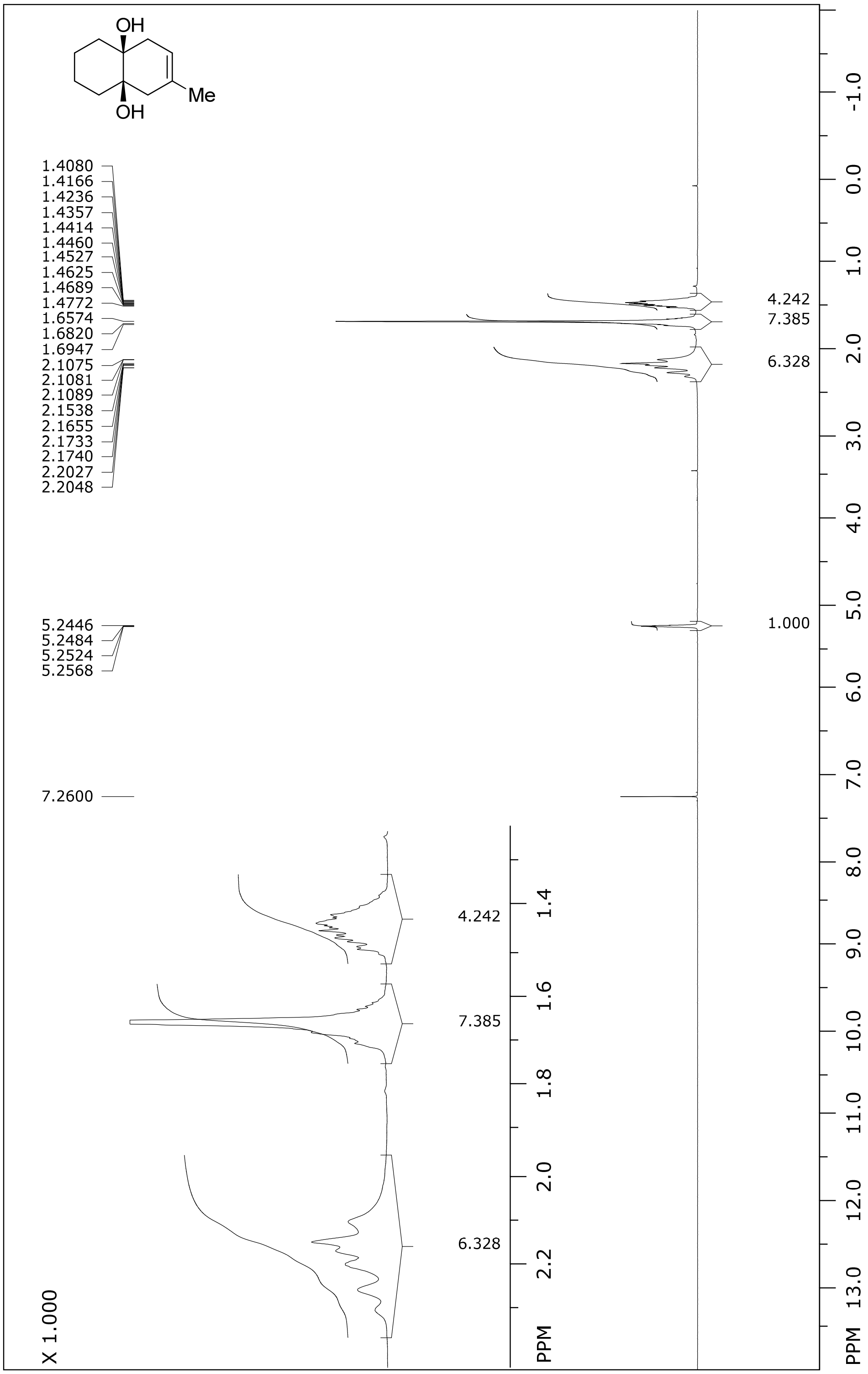

22.5972
22.7548
23.0965
38.7921
43.6462
73.1481
73.6303
76.7177
77.0357
77.3539
118.5613
132.1384
0
20
40
60
80
100
120
140
160
180
200
PPM

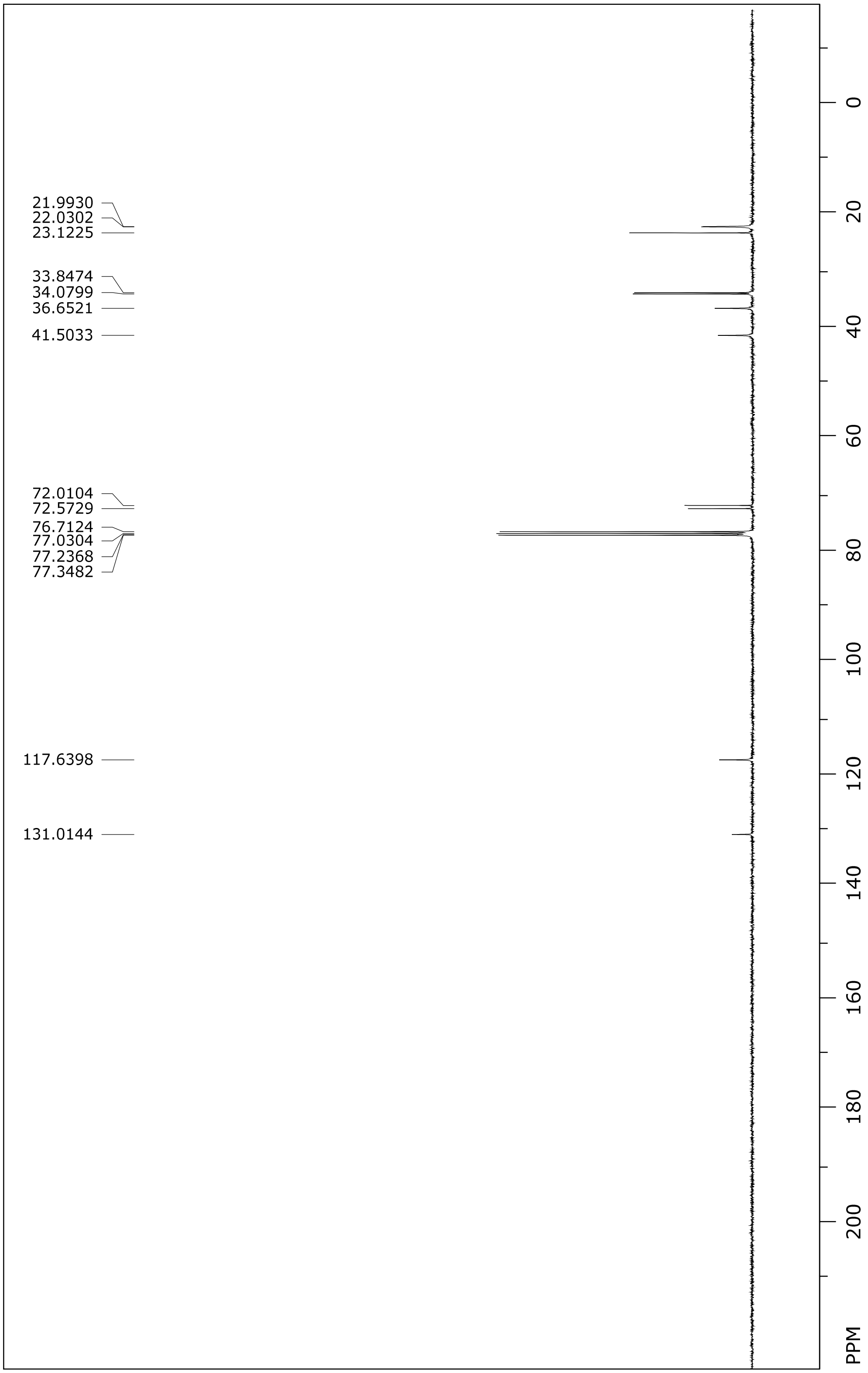
(3aR*,7aS*)-5-Methyl-2,3,3a,4,7,7a-hexahydro-1H-indene-3a,7a-diol (5e)



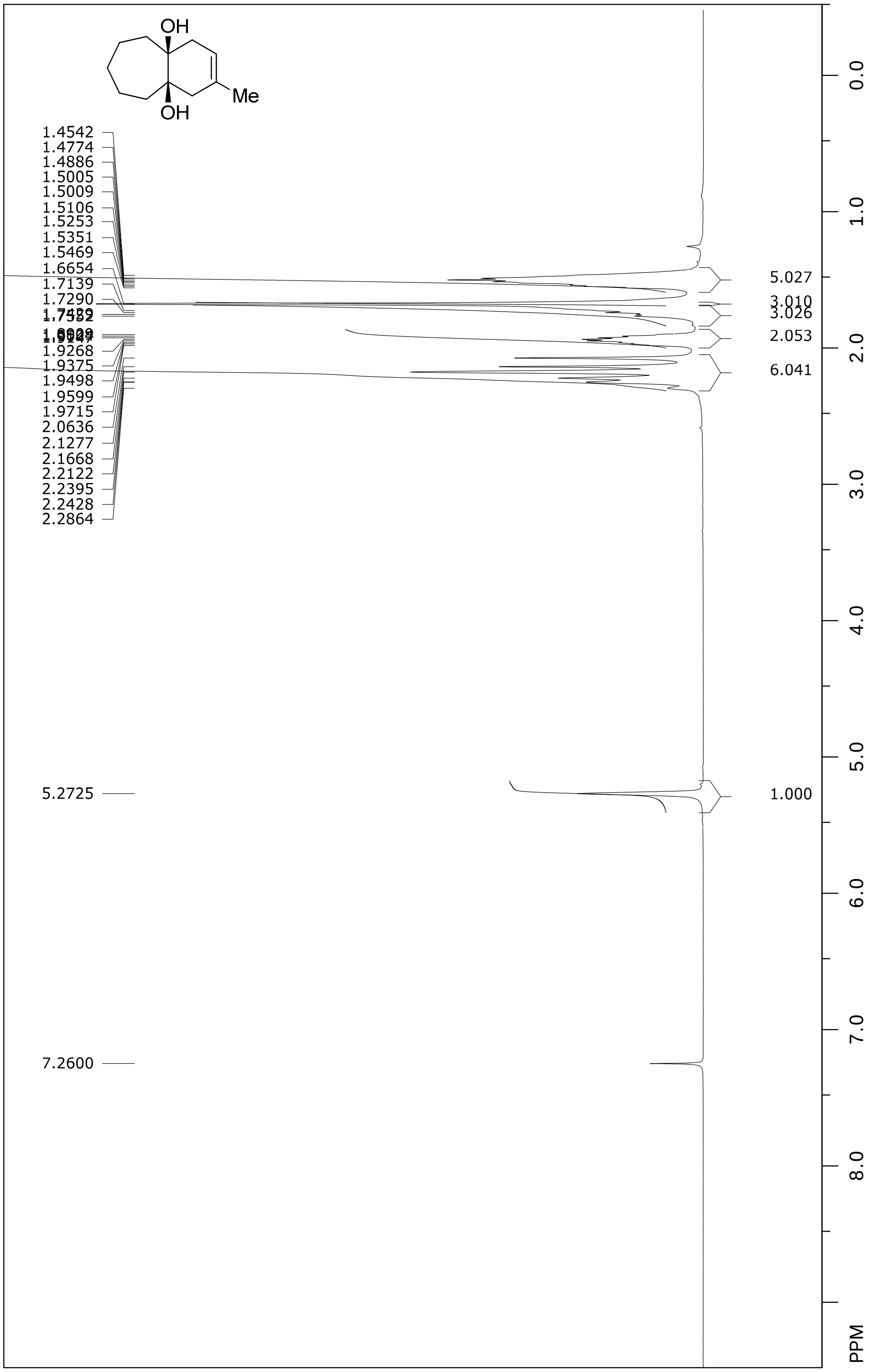

17.4270
23.1669
34.8647
35.0964
35.5117
40.0930
76.7003
77.0181
77.3360
78.0019
78.7479
117.7237
131.2639
0
20
40
60
80
100
120
140
160
180
200
PPM

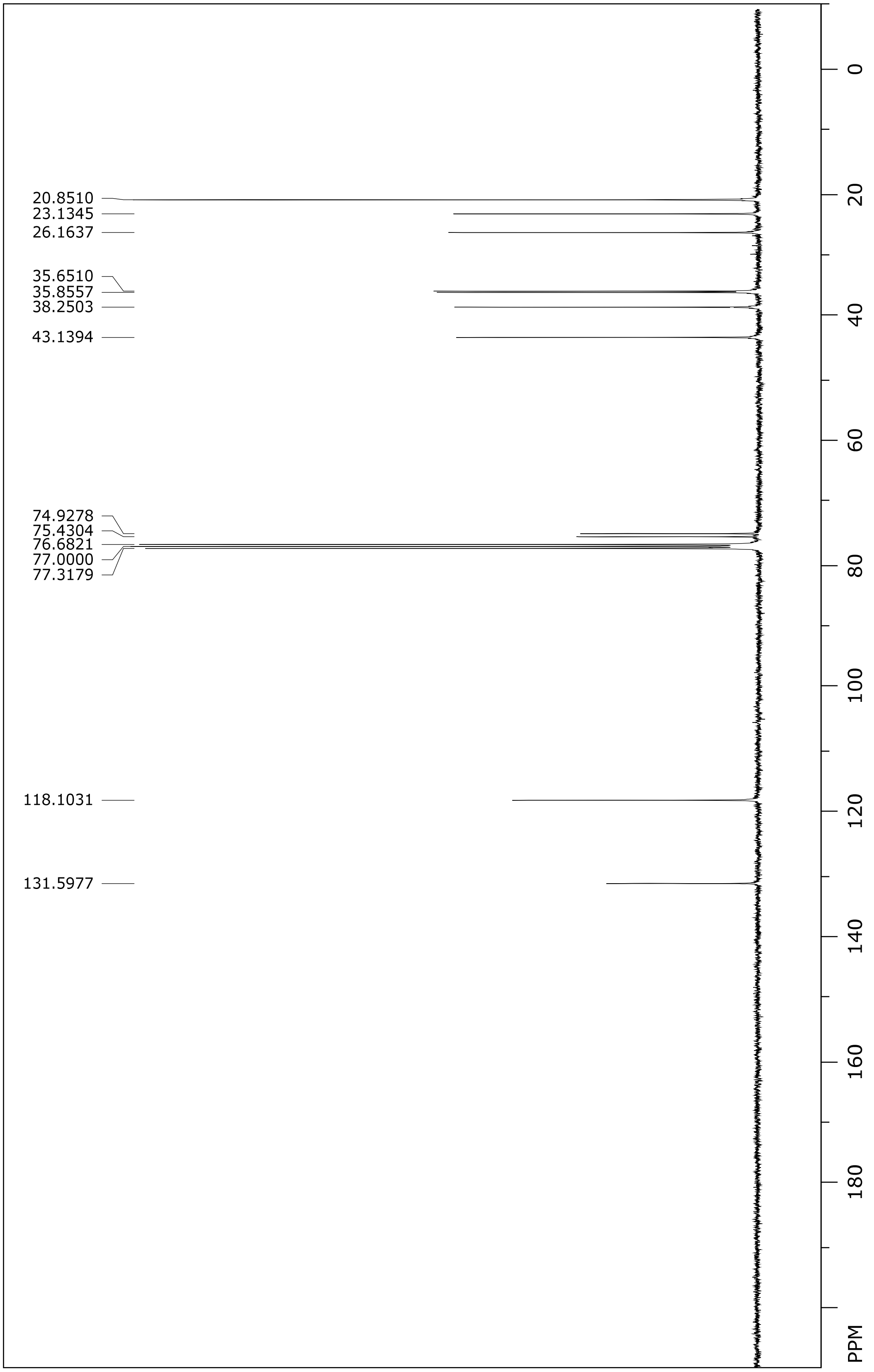
(4aR,8aS*)-6-Methyl-1,2,3,4,4a,5,8,8a-octahydro-4a,8a-diol (5f)*



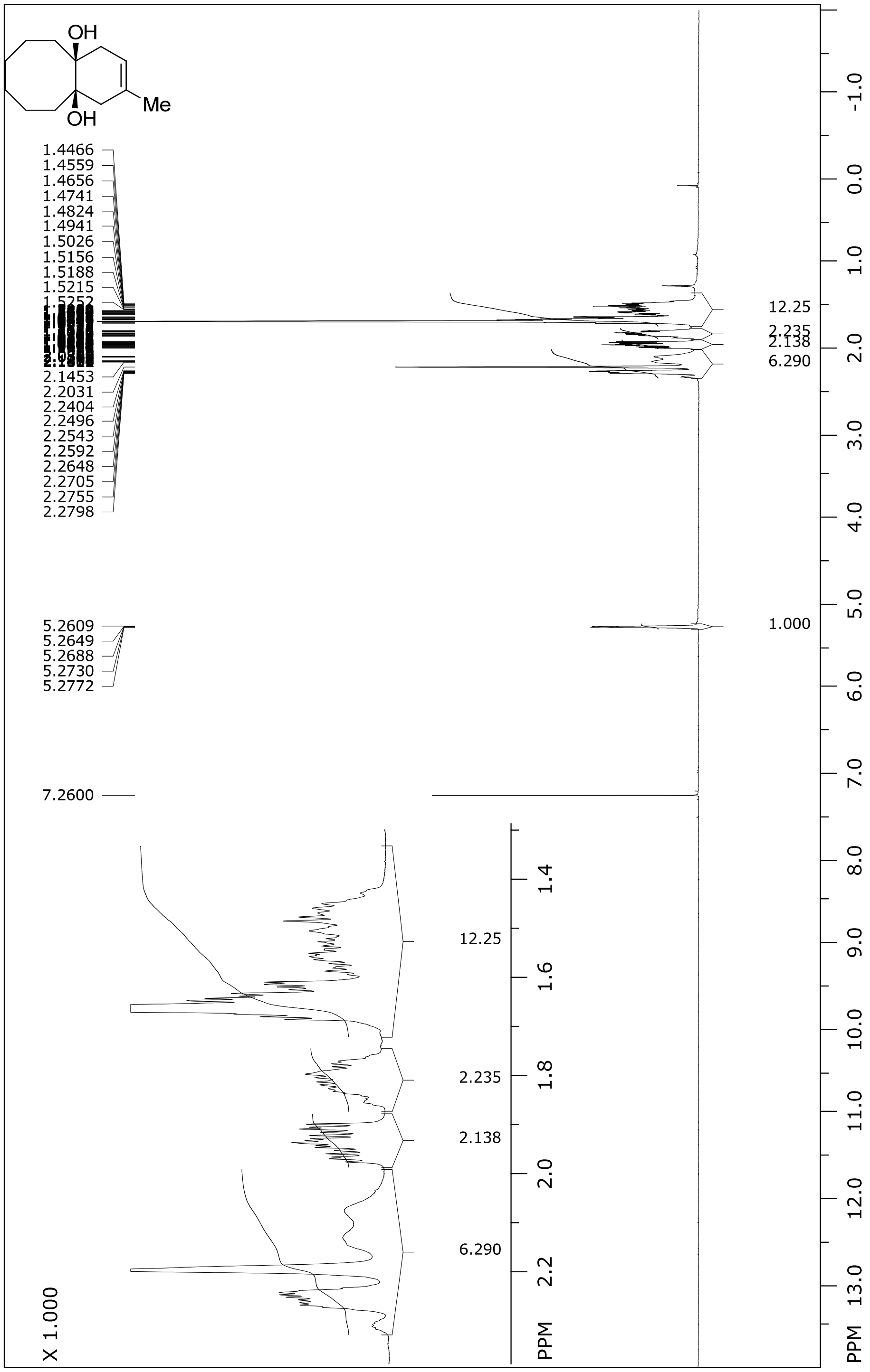

21.9930
22.0302
23.1225
33.8474
34.0799
36.6521
41.5033
72.0104
72.5729
76.7124
77.0304
77.2368
77.3482
117.6398
131.0144
0
20
40
60
80
100
120
140
160
180
200
PPM

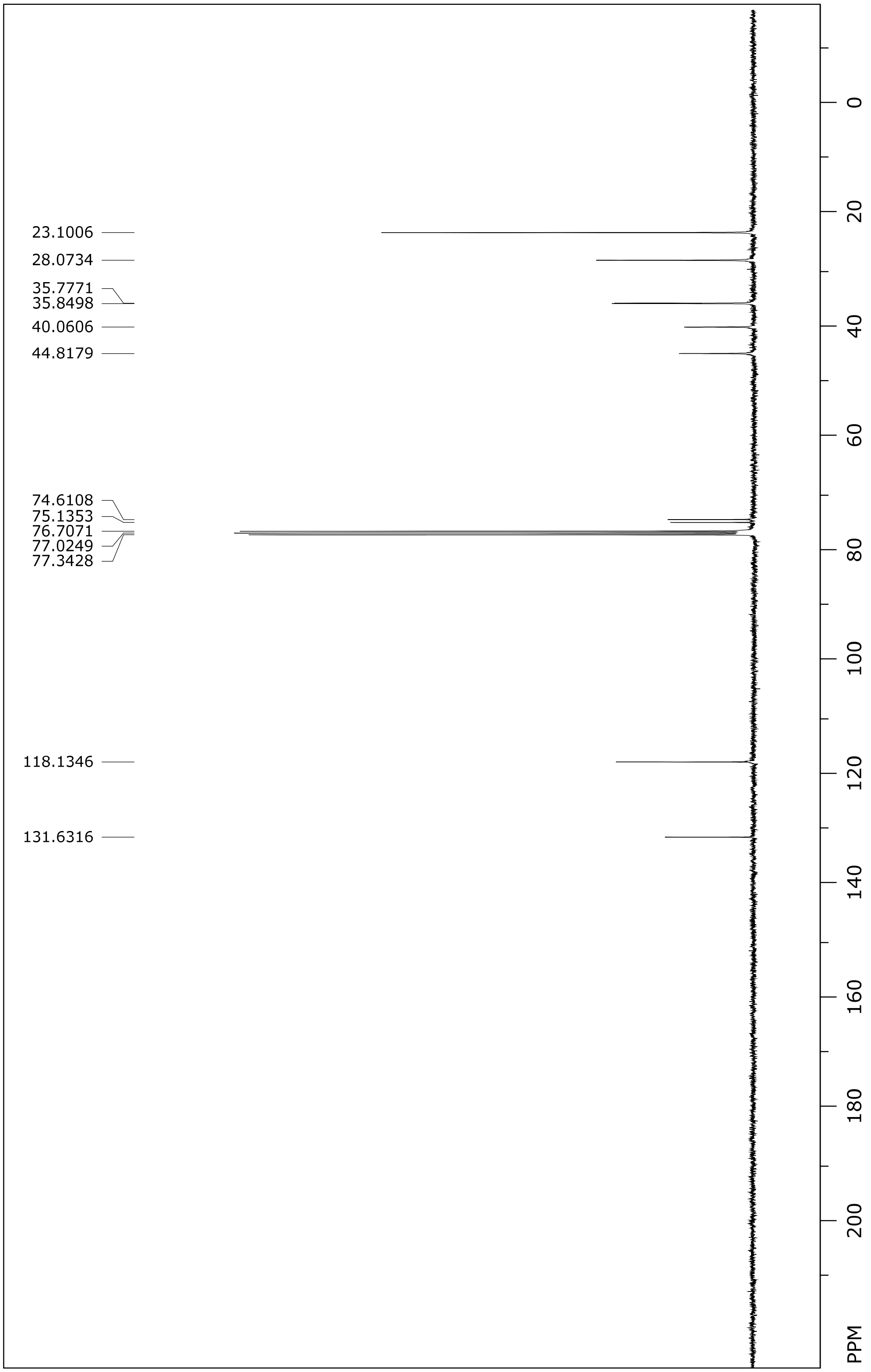
(4aR,9aS*)-2-Methyl-4,4a-5,6,7,8,9,9a-ocahydro-1H-benzo[7]annulene-4a,9a-diol (5g)*



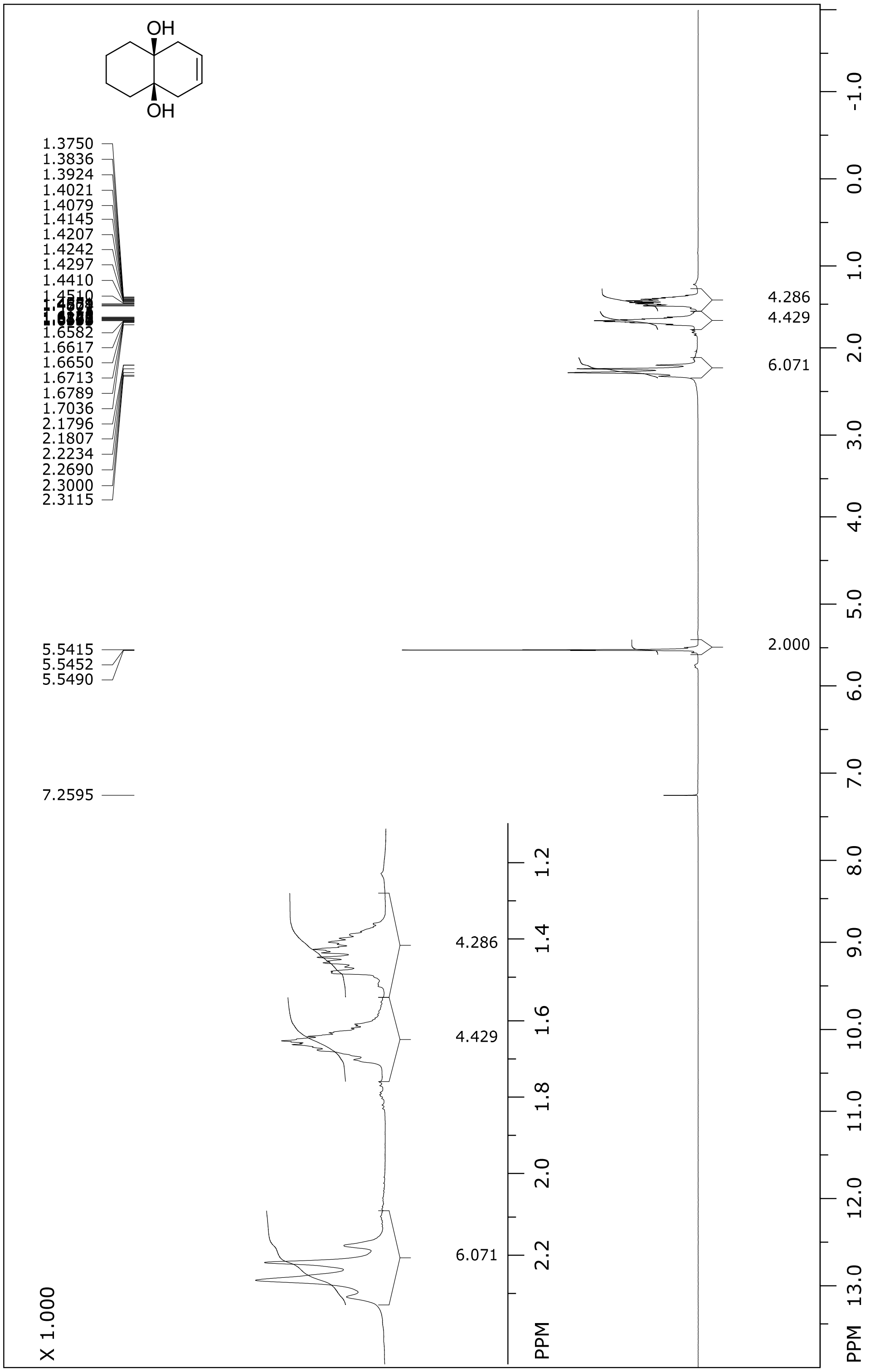

20.8510
23.1345
26.1637
35.6510
35.8557
38.2503
43.1394
74.9278
75.4304
76.6821
77.0000
77.3179
118.1031
131.5977
0
20
40
60
80
100
120
140
160
180
PPM

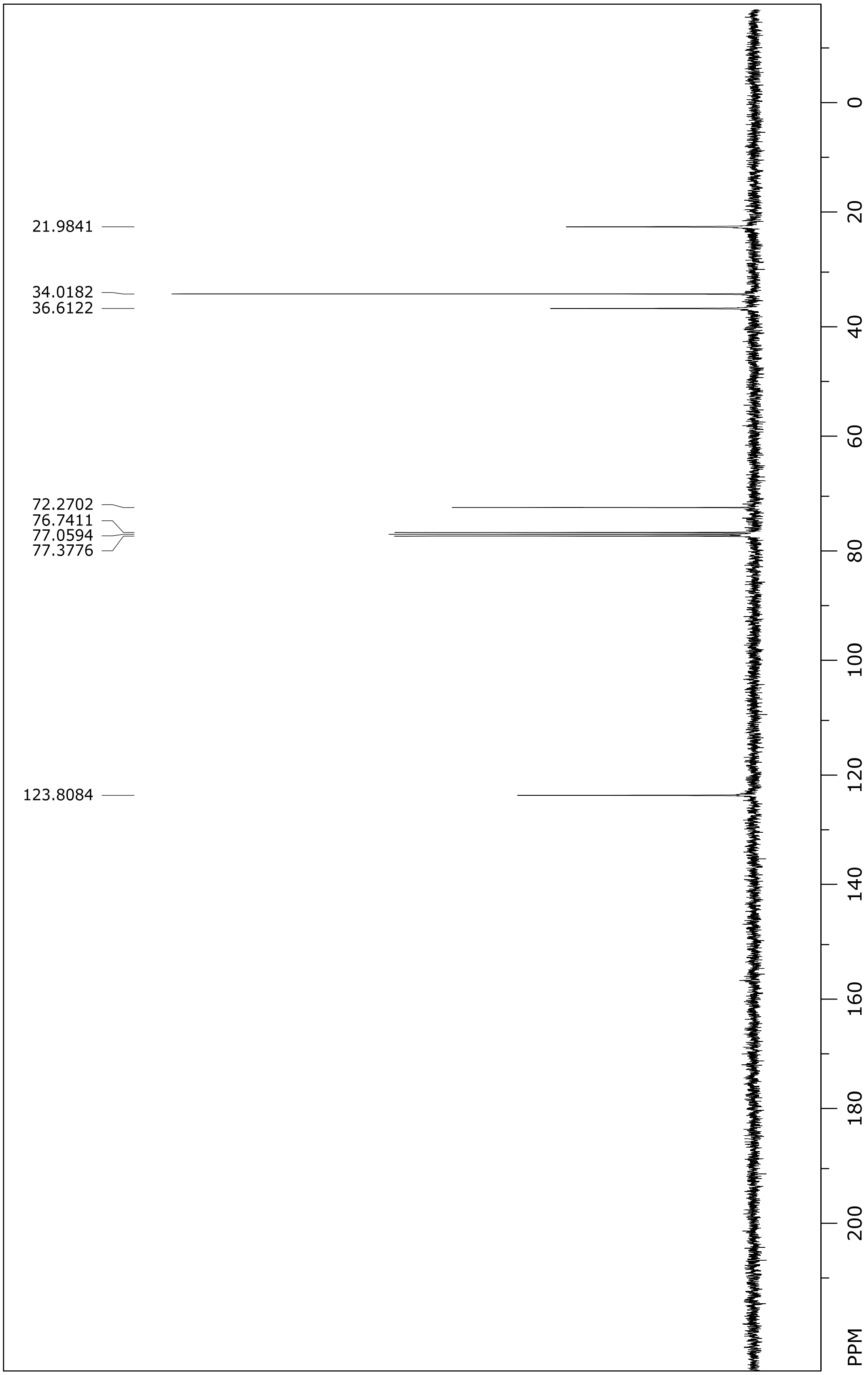
(4aR*,10aS*)-2-Methyl-1,4,4a-5,6,7,8,9,10,10a-decahydrobenzo[8]annulene-4a,10a-diol (5h)



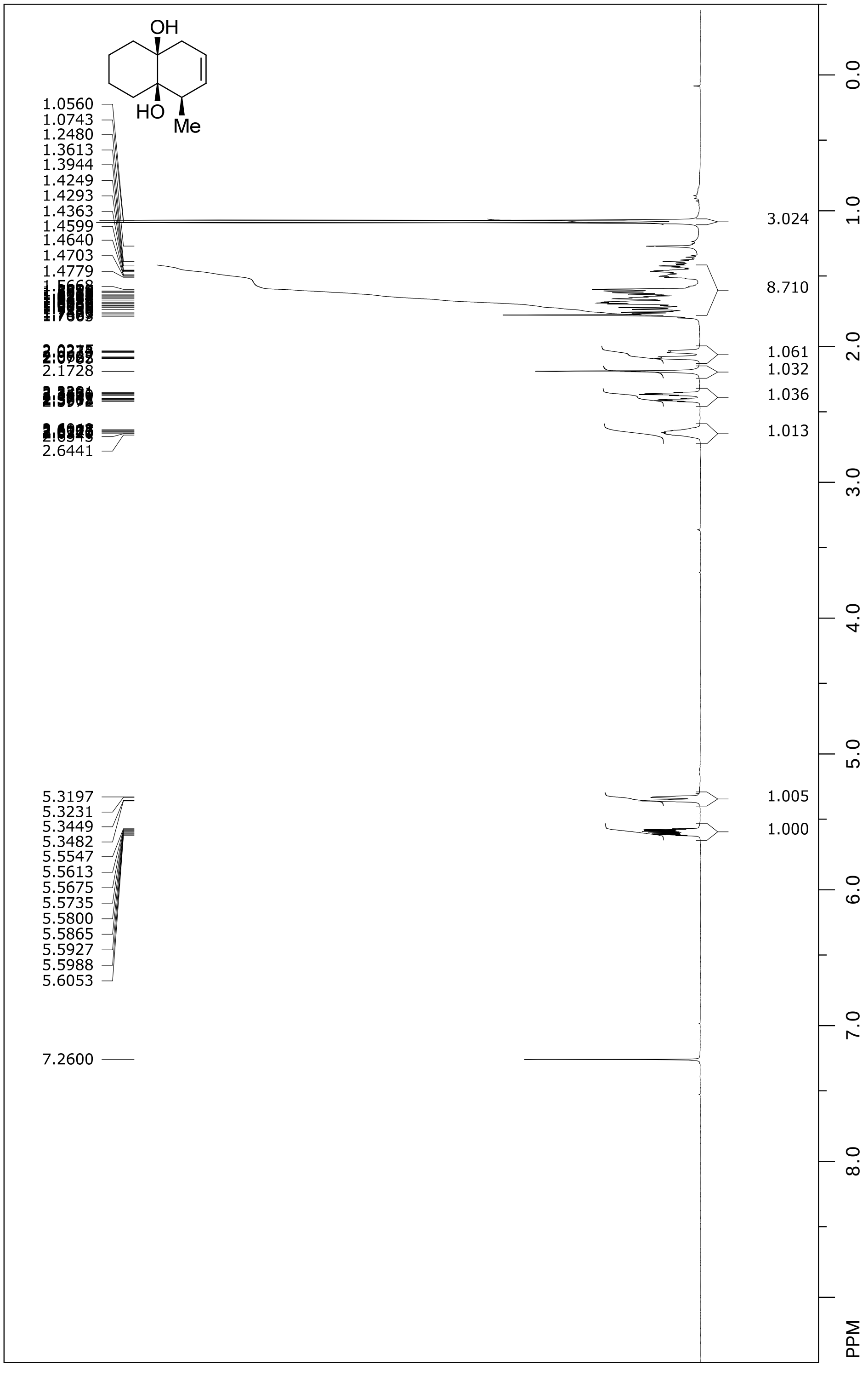

23.1006
28.0734
35.7771
35.8498
40.0606
44.8179
74.6108
75.1353
76.7071
77.0249
77.3428
118.1346
131.6316
0
20
40
60
80
100
120
140
160
180
200
PPM

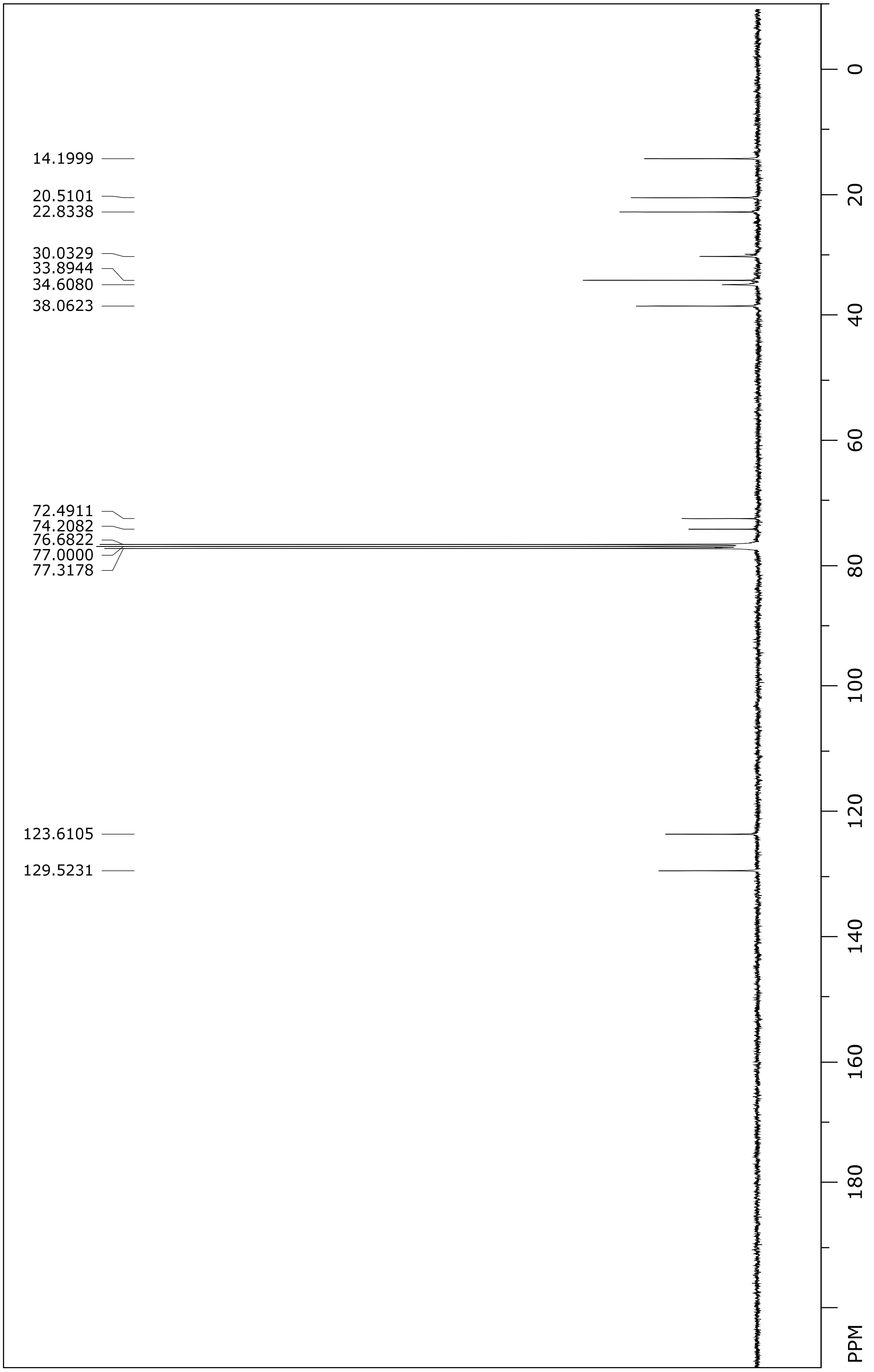
(4aR*,8aS*)-1,2,3,4,4a,5,8,8a-octahydronaphthlene-4a,8a-diol (5i)



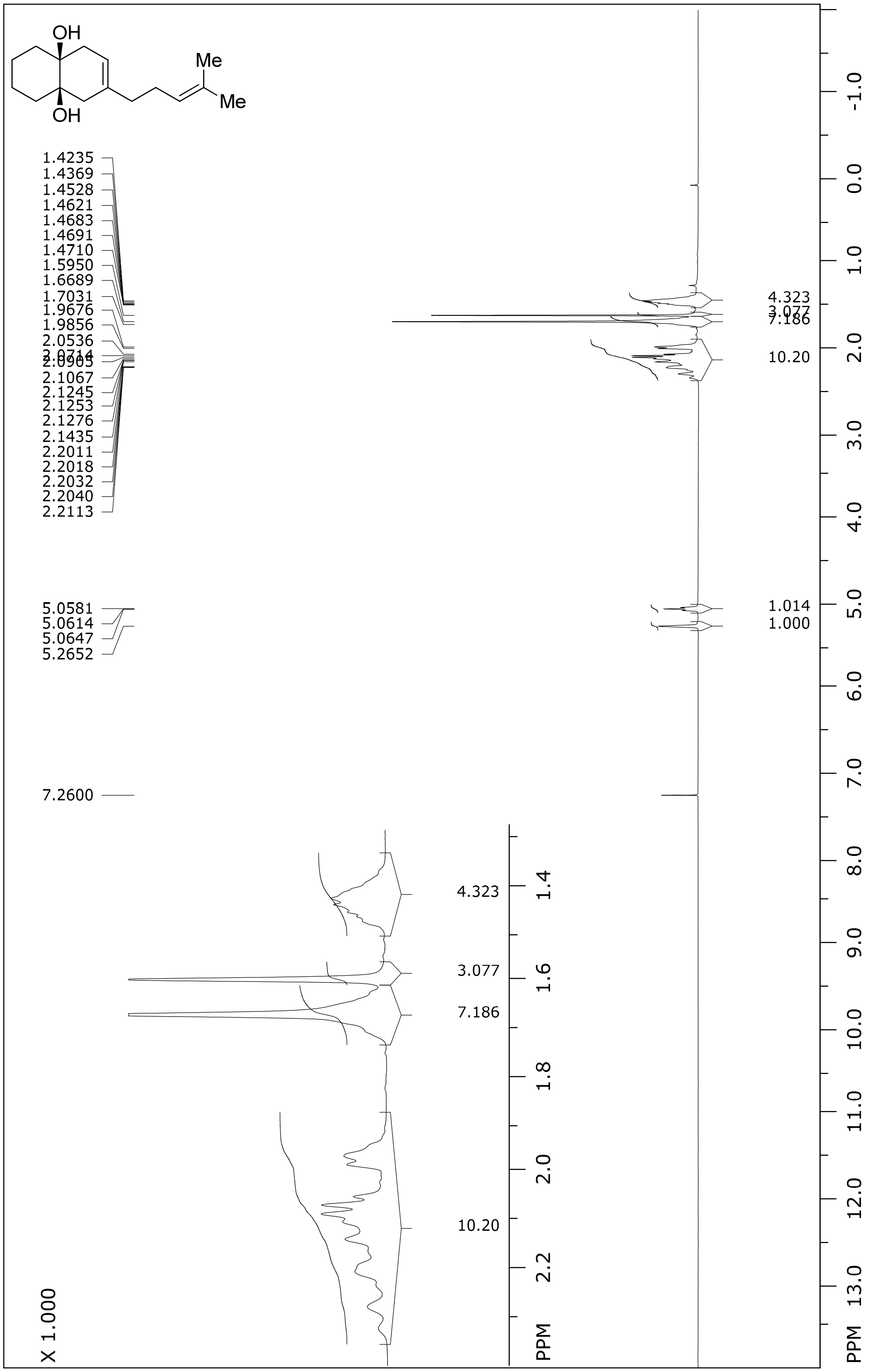

21.9841
34.0182
36.6122
72.2702
76.7411
77.0594
77.3776
123.8084
0
20
40
60
80
100
120
140
160
180
200
PPM

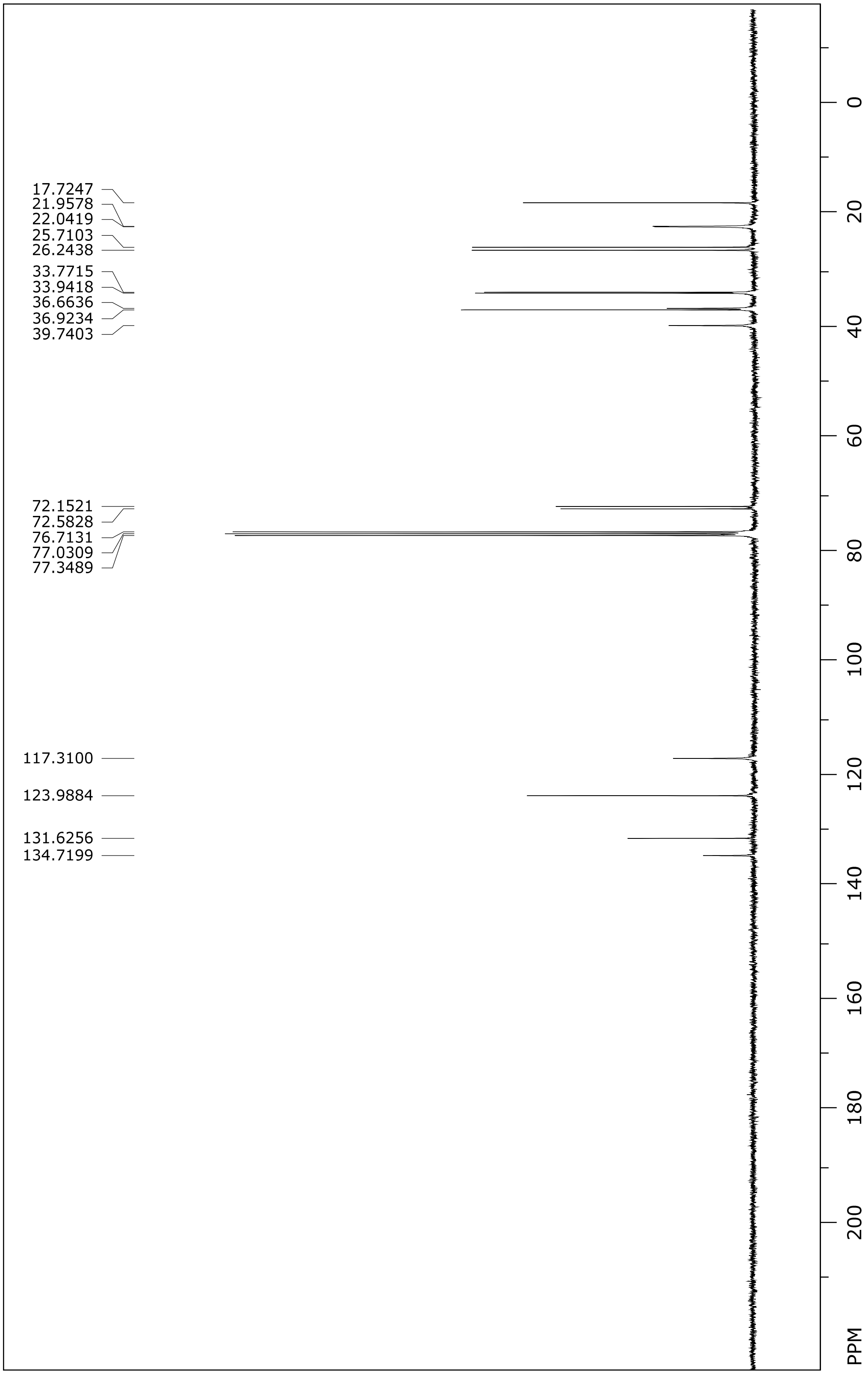
(4aR*,5R*,8aS*)-5-Methyl-1,2,3,4,4a,5,8,8a-octahydronaphthlalene-4a,8a-diol (5j)



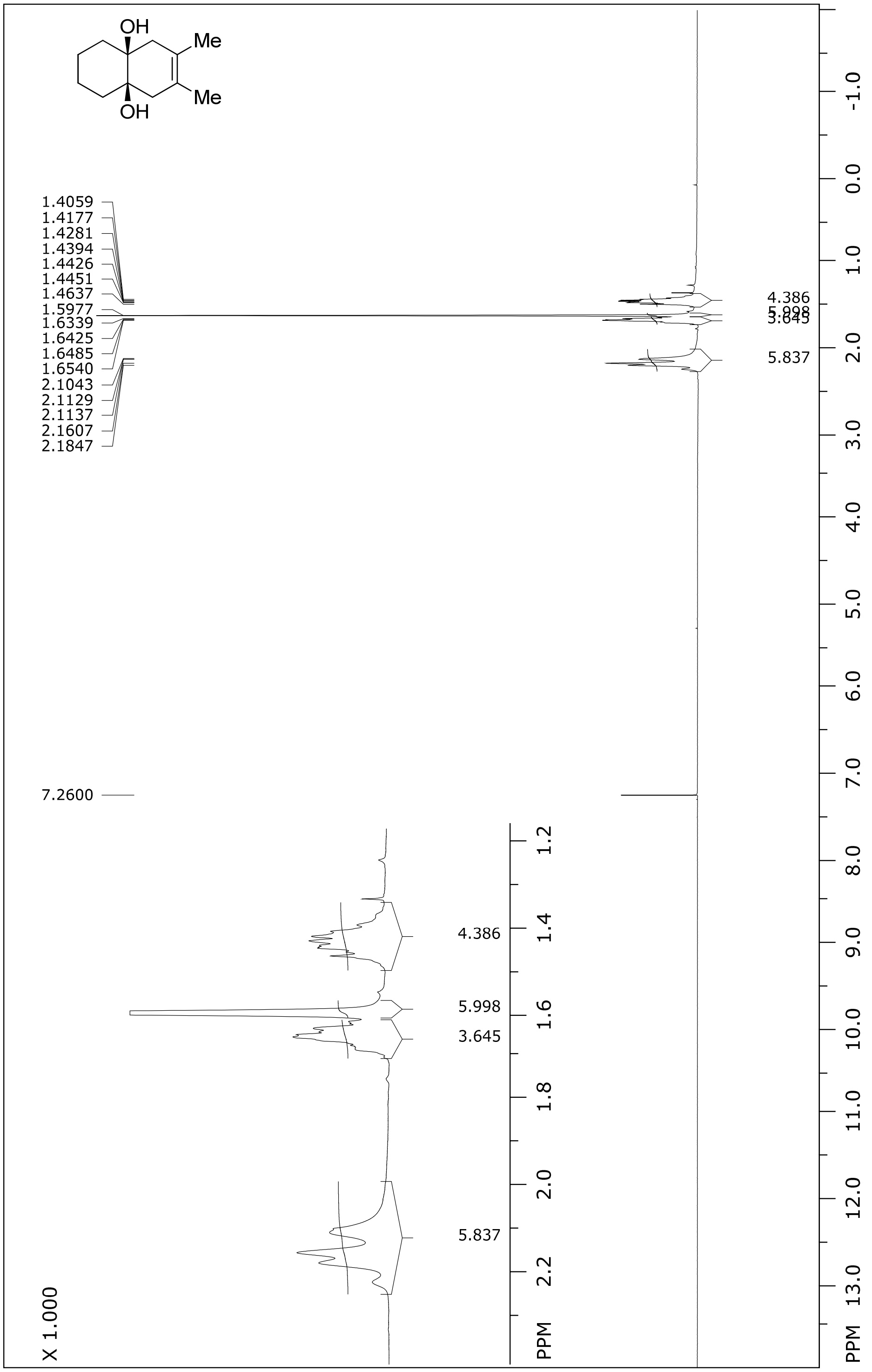

14.1999
20.5101
22.8338
30.0329
33.8944
34.6080
38.0623
72.4911
74.2082
76.6822
77.0000
77.3178
123.6105
129.5231
0
20
40
60
80
100
120
140
160
180
PPM

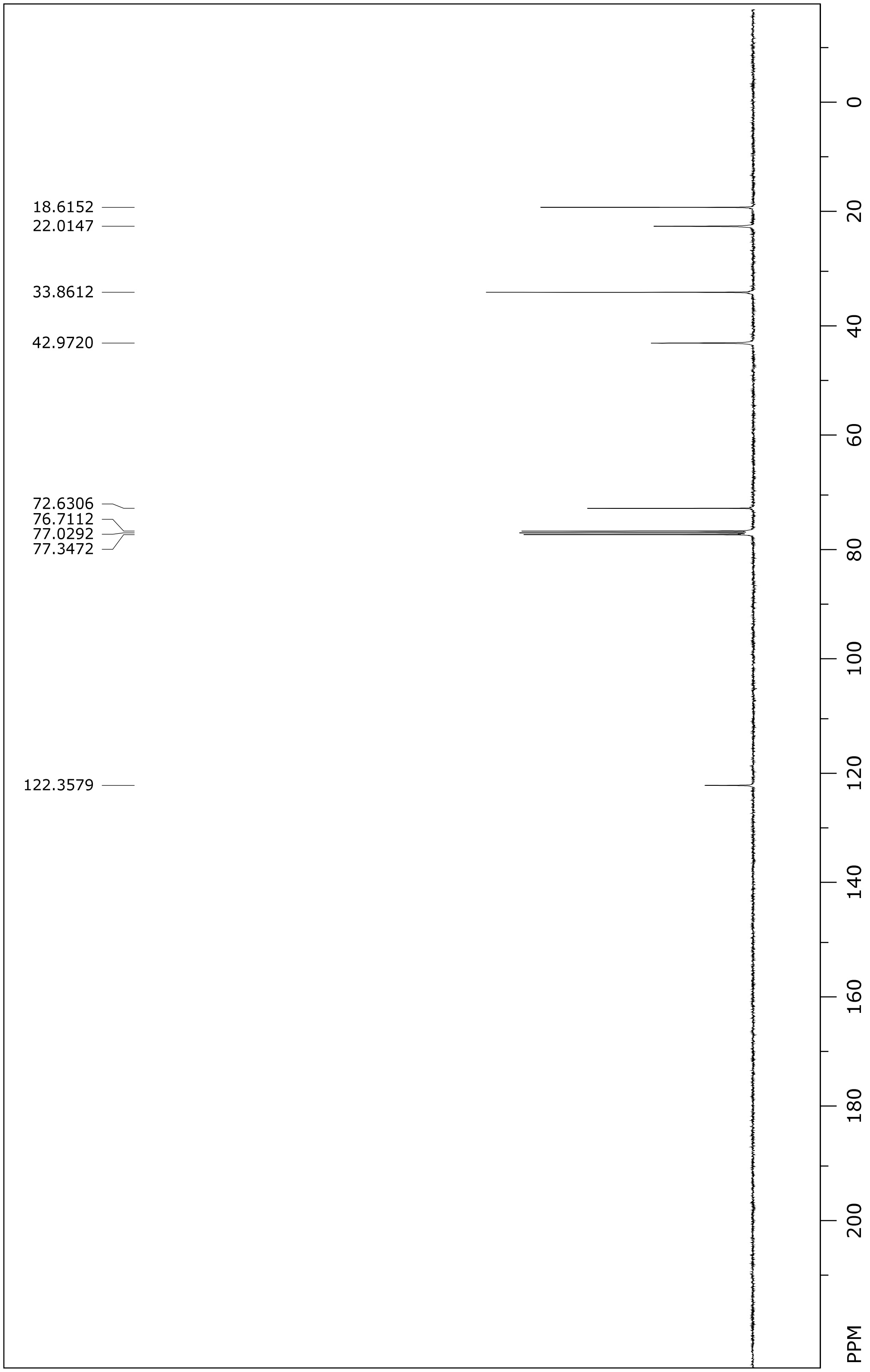
(4aR*,8aS*)-6-(4-Methylpent-3-en-1-yl)-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5k)



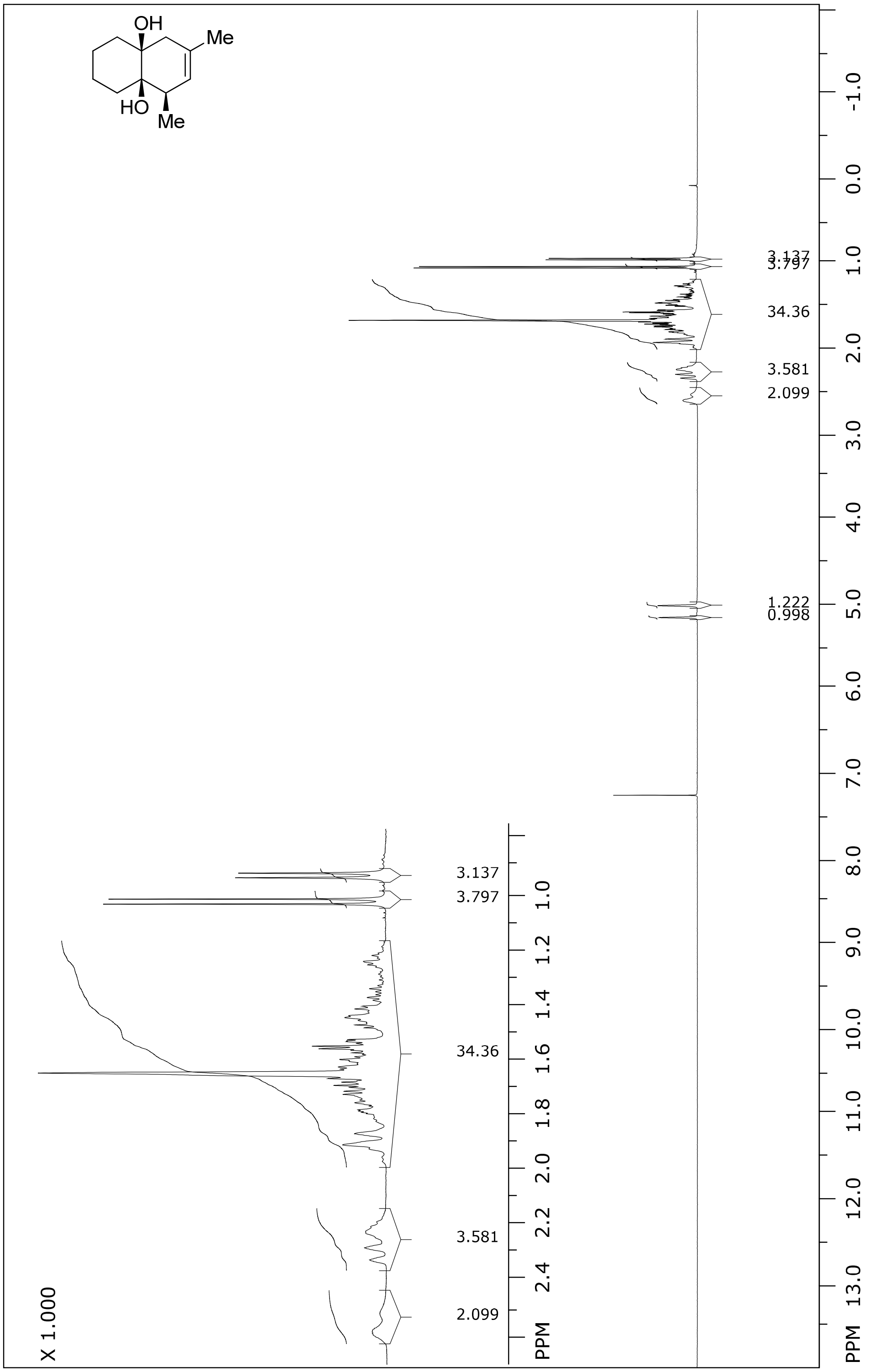

17.7247
21.9578
22.0419
25.7103
26.2438
33.7715
33.9418
36.6636
36.9234
39.7403
72.1521
72.5828
76.7131
77.0309
77.3489
117.3100
123.9884
131.6256
134.7199
0
20
40
60
80
100
120
140
160
180
200
PPM

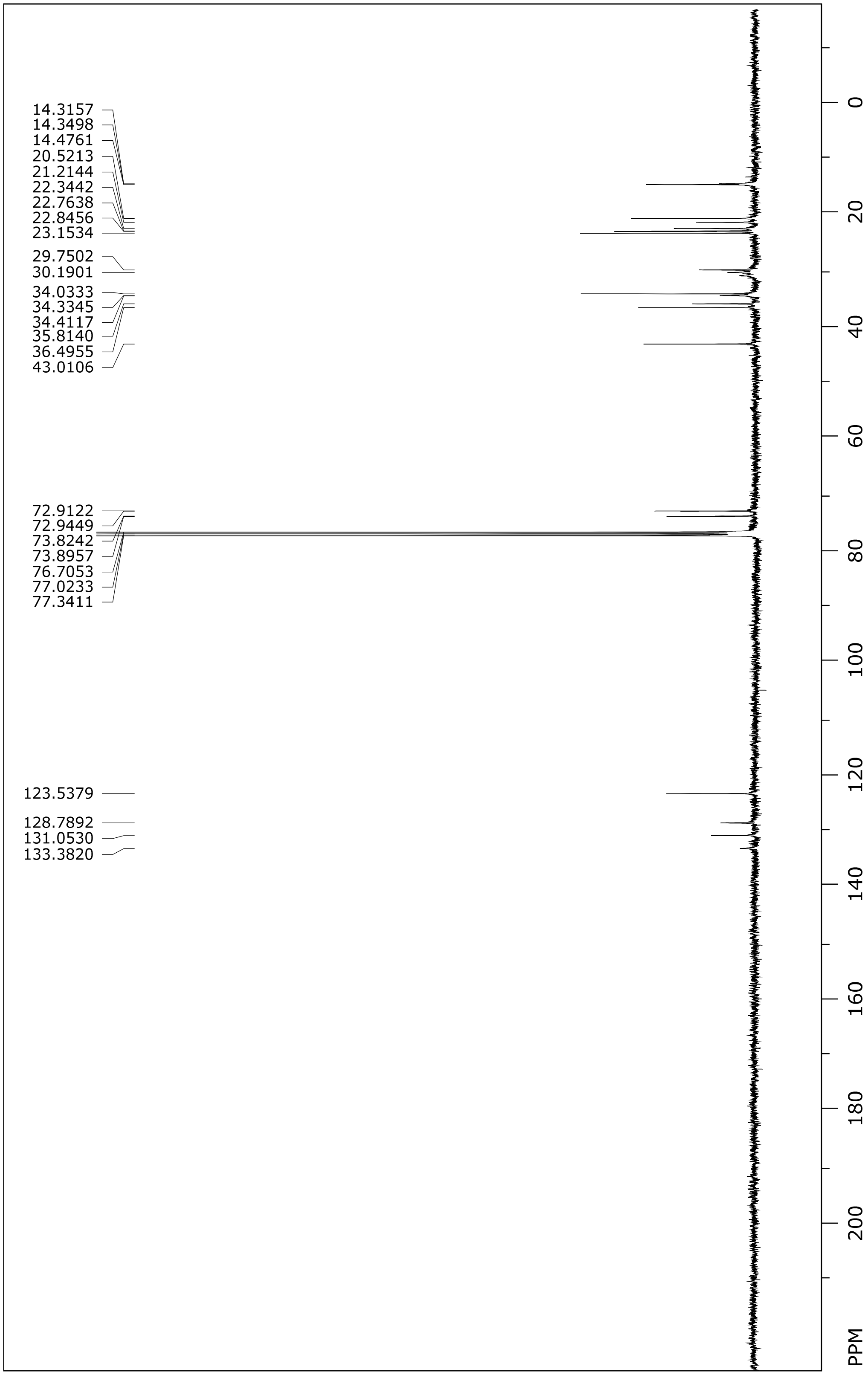
(4aR*,8aS*)-6,7-Dimethyl-1,2,3,4,4a,5,8,8a-ocathydronaphthalene-4a,8a-diol (5l)



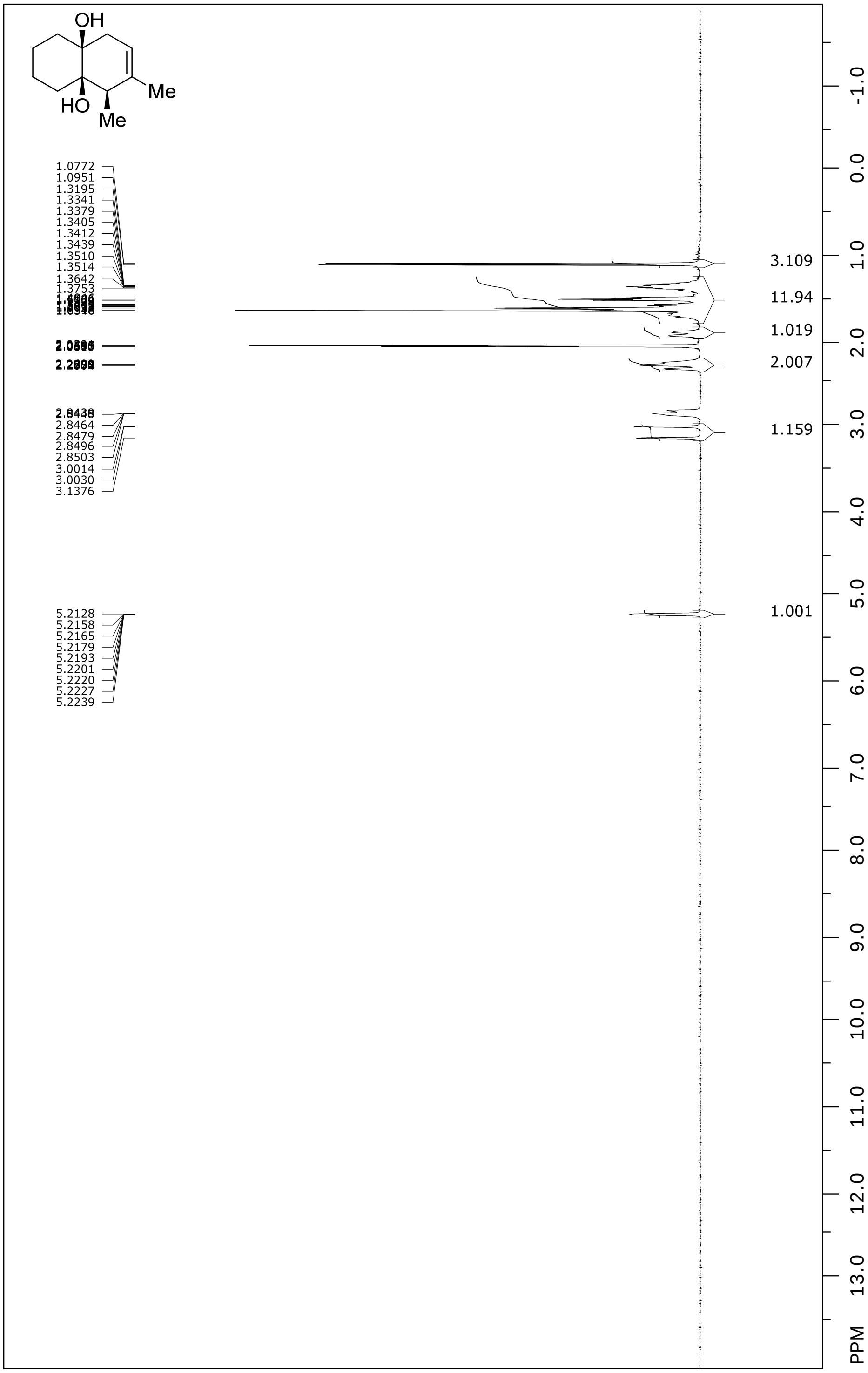

18.6152
22.0147
33.8612
42.9720
72.6306
76.7112
77.0292
77.3472
122.3579
0
20
40
60
80
100
120
140
160
180
200
PPM

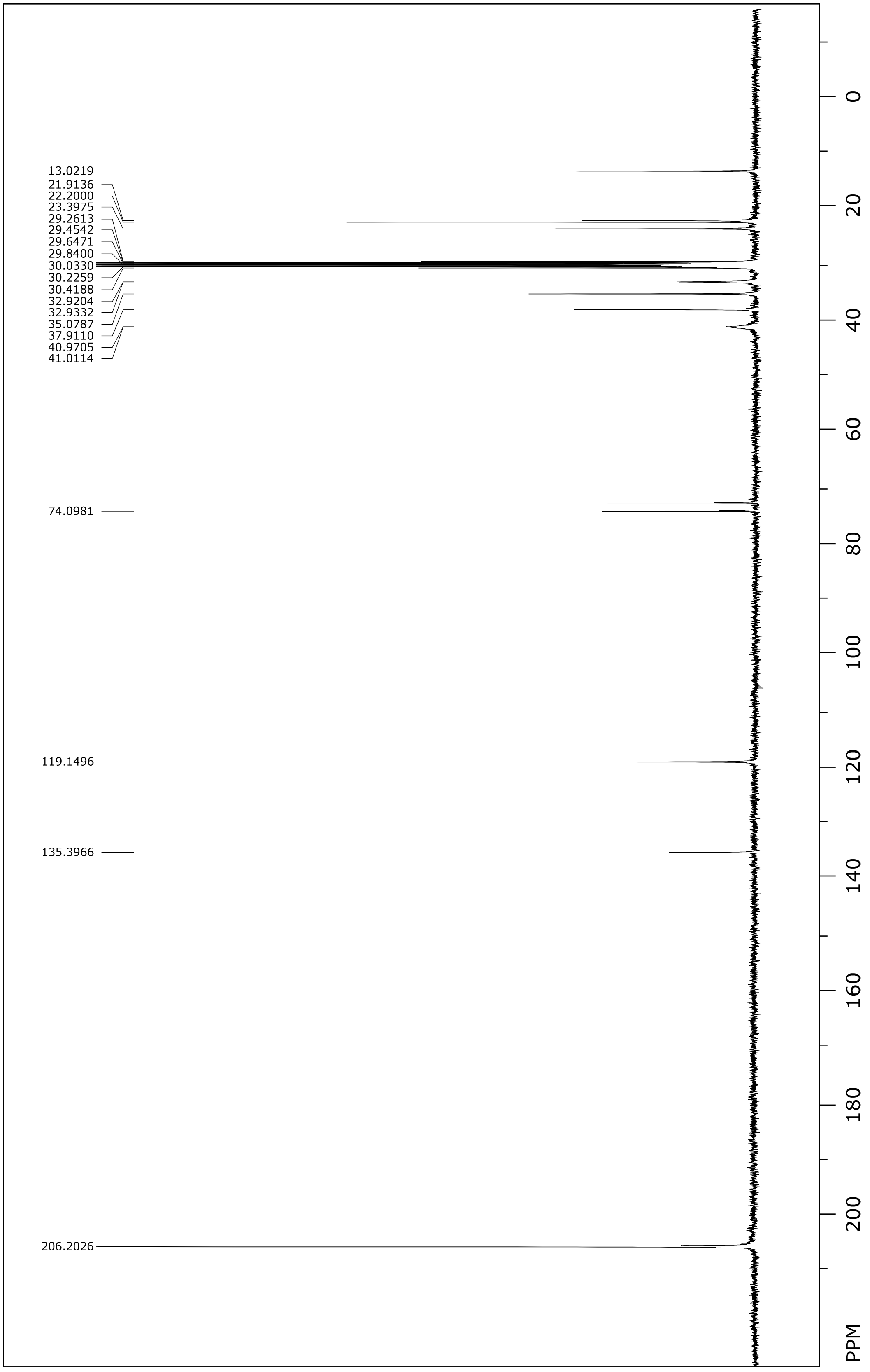
(4aR,5R*,8aS*)-5,7-Dimethyl-1,2,3,4,4a,5,8,8a-ocathydronaphthalene-4a,8a-diol (5m)*



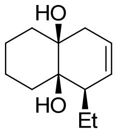

14.3157
14.3498
14.4761
20.5213
21.2144
22.3442
22.7638
22.8456
23.1534
29.7502
30.1901
34.0333
34.3345
34.4117
35.8140
36.4955
43.0106
72.9122
72.9449
73.8242
73.8957
76.7053
77.0233
77.3411
123.5379
128.7892
131.0530
133.3820
0
20
40
60
80
100
120
140
160
180
200
PPM

(4aR*,5R*,8aR*)-5,6-Dimethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5n)

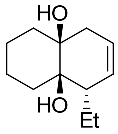



13.0219
21.9136
22.2000
23.3975
29.2613
29.4542
29.6471
29.8400
30.0330
30.2259
30.4188
32.9204
32.9332
35.0787
37.9110
40.9705
41.0114
74.0981
119.1496
135.3966
206.2026
0
20
40
60
80
100
120
140
160
180
200
PPM

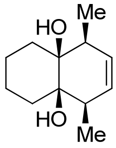
(4aR,5R*,8aS*)-5-Ethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5o)*



2.5

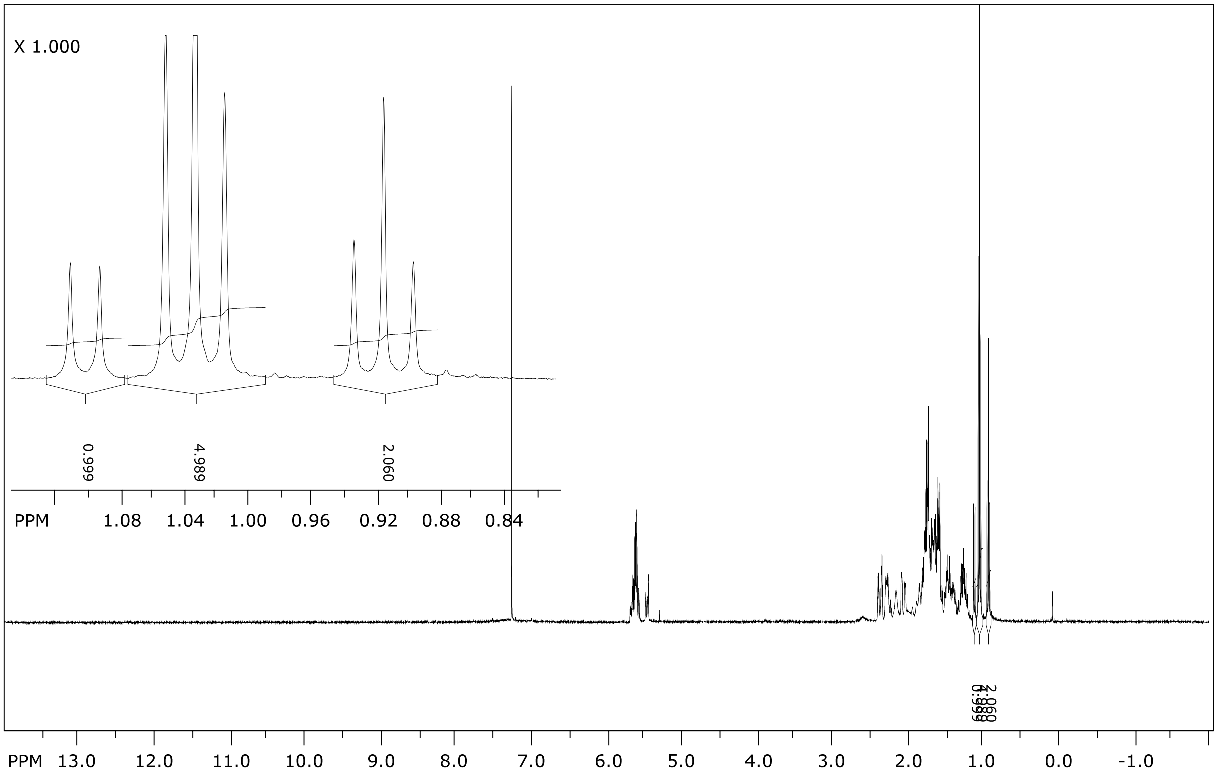


1

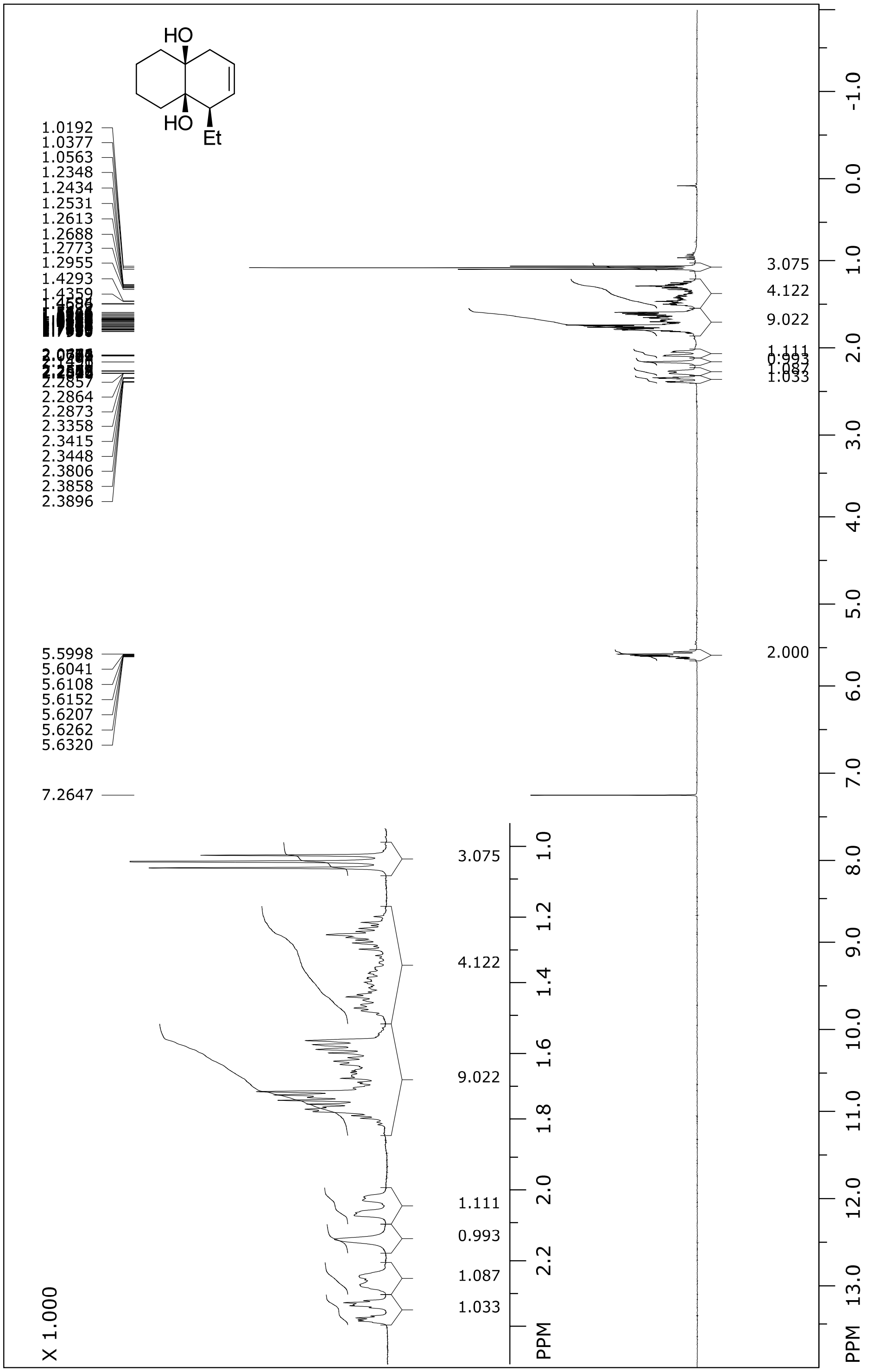


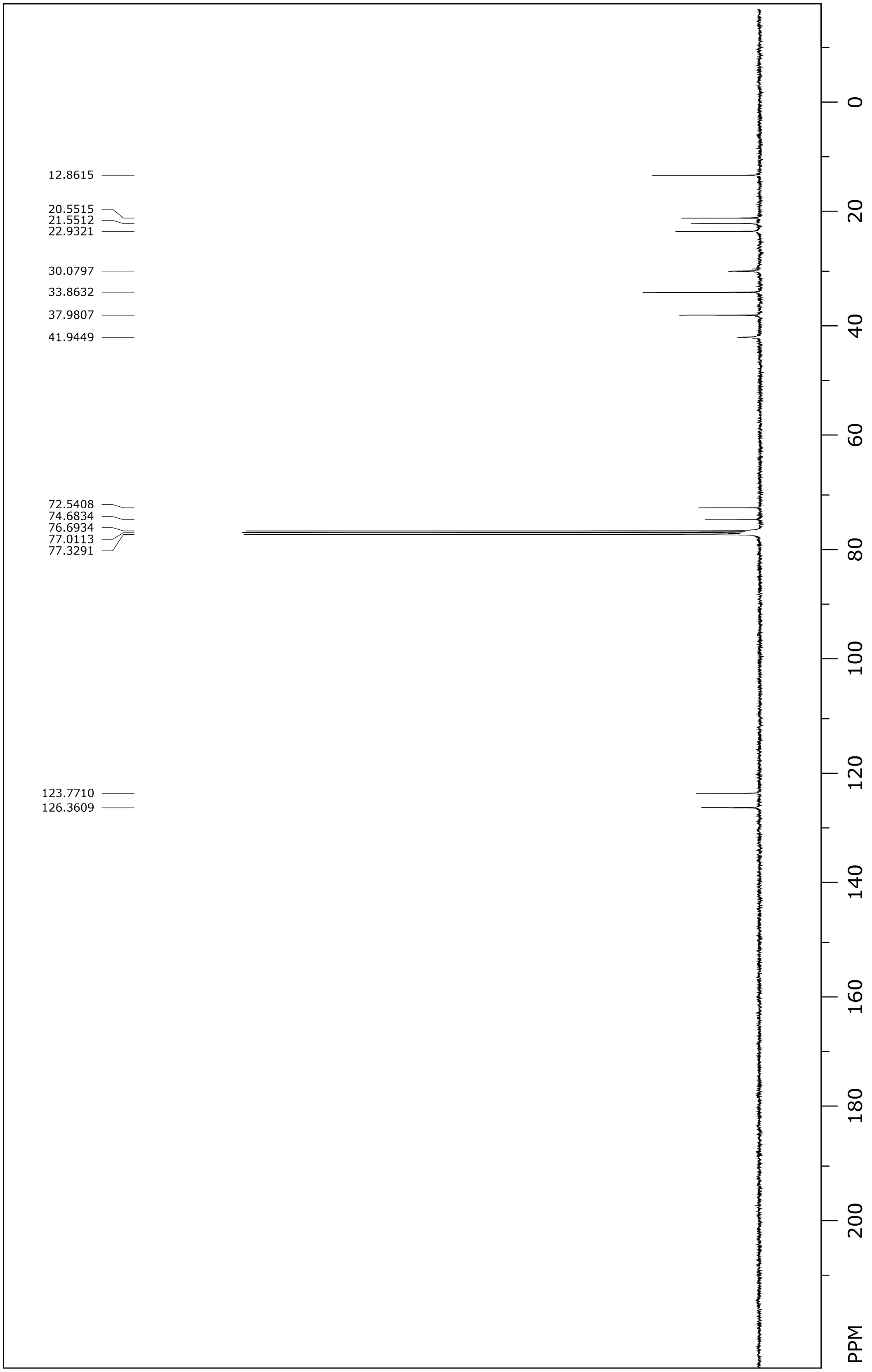
1

Mixture of all three compounds:

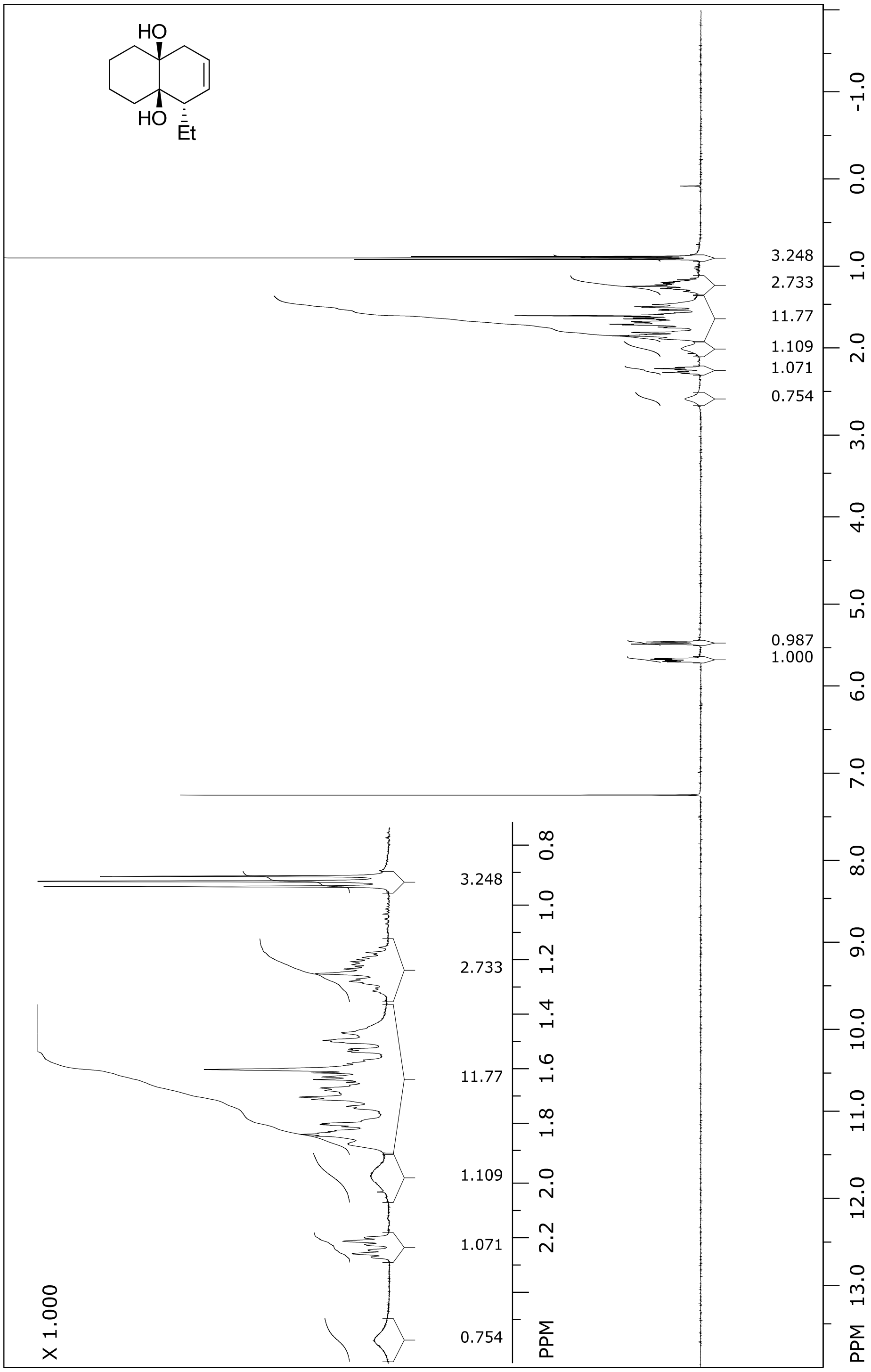


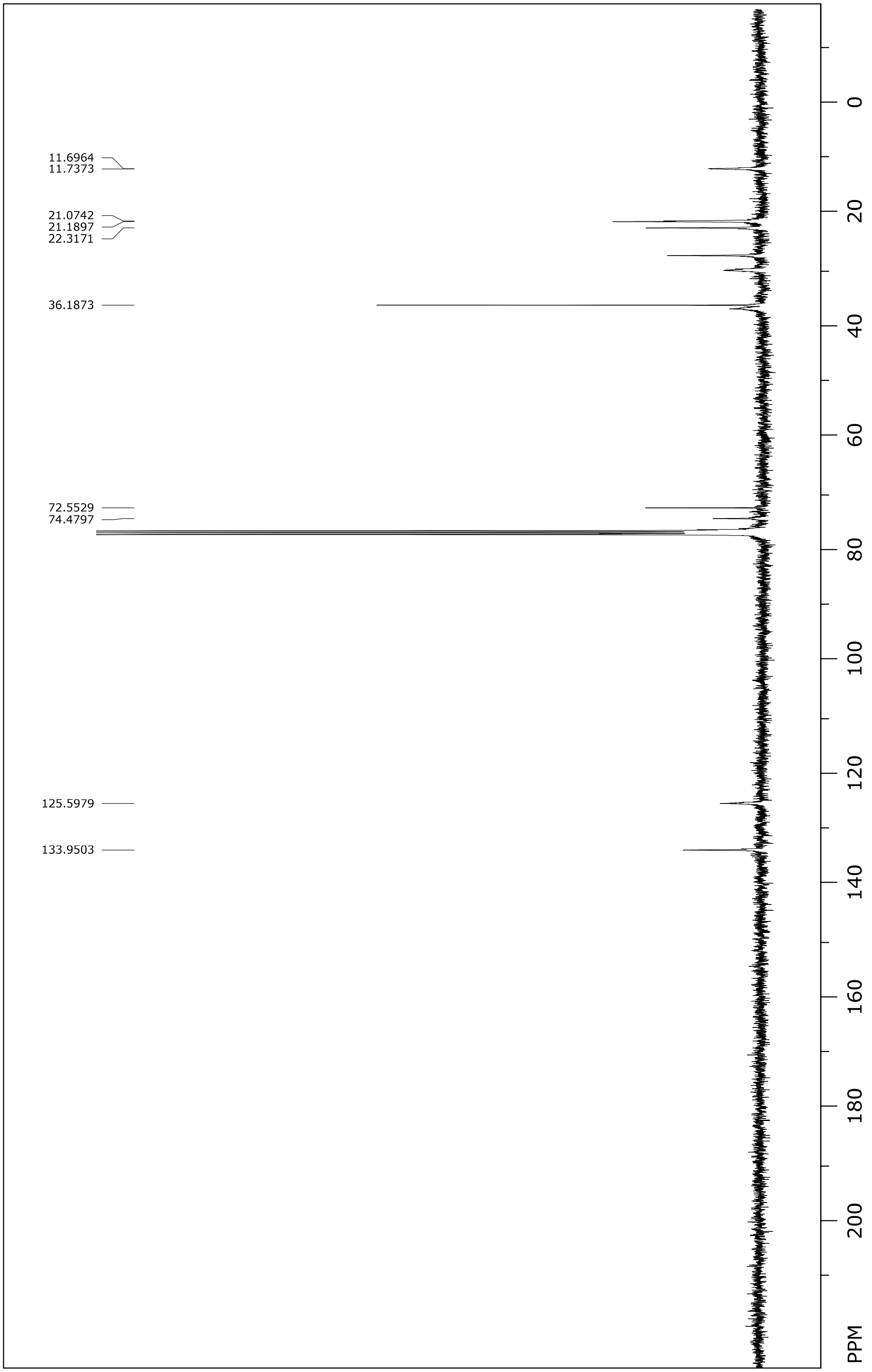
(4aR*,5R*,8aS*)-5-Ethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5o)



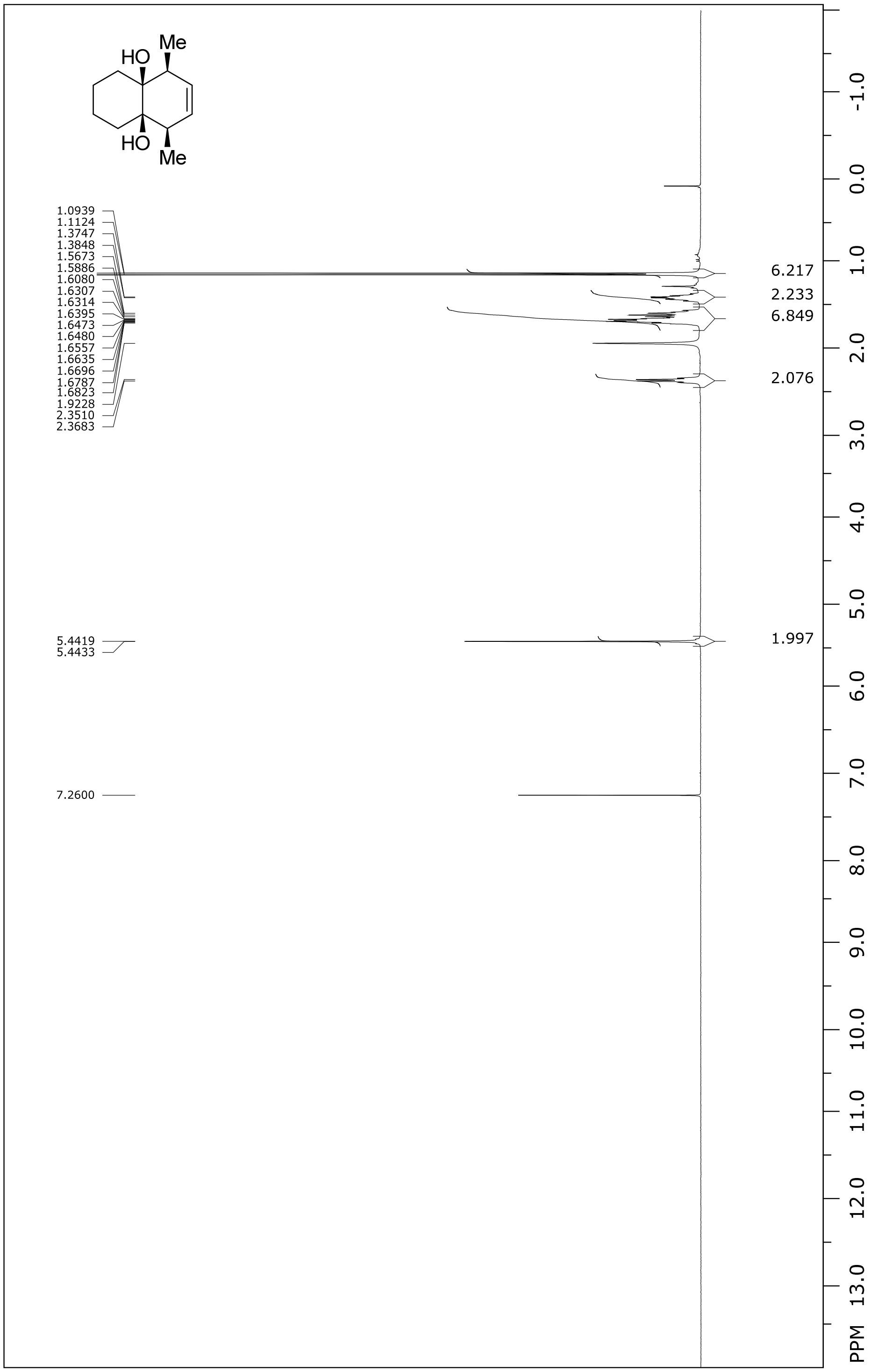

12.8615
20.5515
21.5512
22.9321
30.0797
33.8632
37.9807
41.9449
72.5408
74.6834
76.6934
77.0113
77.3291
123.7710
126.3609
0
20
40
60
80
100
120
140
160
180
200
PPM

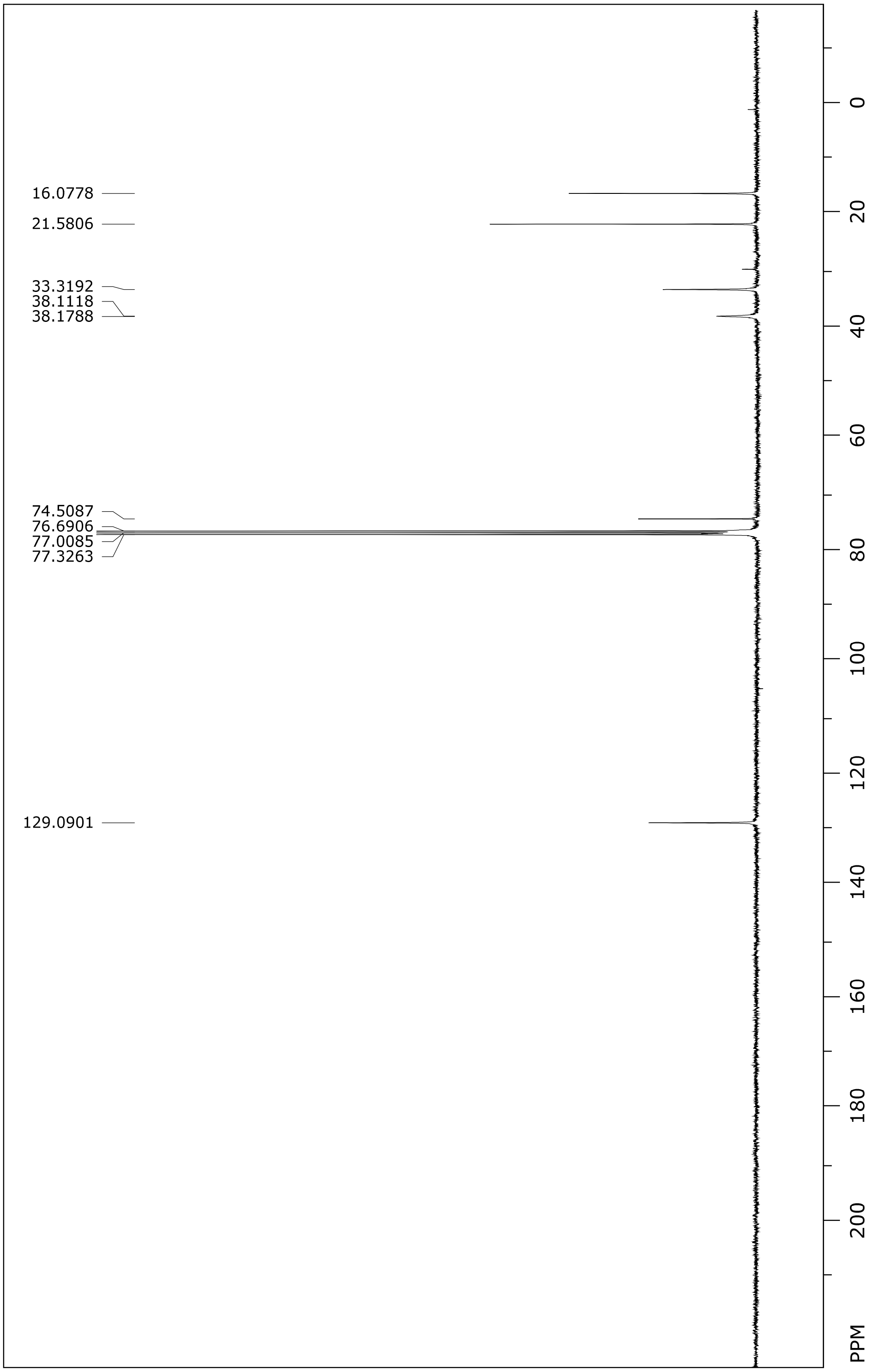
(4aR*,5S*,8aS*)-5-Ethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (5-epi-5o)




11.6964
11.7373
21.0742
21.1897
22.3171
36.1873
72.5529
74.4797
125.5979
133.9503
0
20
40
60
80
100
120
140
160
180
200
PPM

(4aR*,5R*,8S,8aS*)-5,8-Dimethyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene-4a,8a-diol (iso-5o)




16.0778
21.5806
33.3192
38.1118
38.1788
74.5087
76.6906
77.0085
77.3263
129.0901
0
20
40
60
80
100
120
140
160
180
200
PPM