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Supporting Information

Efficient and Convenient Heterogeneous Palladium-Catalyzed Regioselective Deuteration at the Benzylic Position

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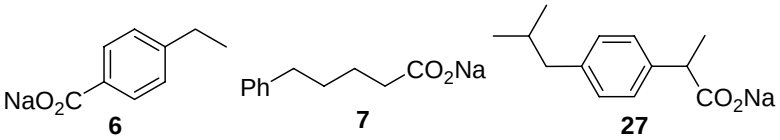
General

The 10% Pd/C was purchased from Aldrich Chemical Co. (product number; 20569-9, 50 g, Lot. 0581713C) and the 5% Pd/C(en) was obtained from Wako Pure Chemical Industries, Ltd. (product number; 169-21443, 5g, Lot. 12021716). D_2O (>99.9 % D atom) was obtained from Cambridge Isotope Laboratories, Inc. or Spectra Gases, Inc. All other reagents were purchased from commercial sources and used without further purification. Analytical thin-layer chromatography (TLC) was carried out on pre-coated Silica Gel 60 F_{254} plates (Merck, Art 5715) and visualized with UV light and/or stain (10% phosphomolybdic acid in EtOH). Flash column chromatography was accomplished using a Silica Gel 60 (Merck; 230–400 mesh) or Silica Gel 60N (Kanto Chemical Co., Inc.; 63–210 μm, spherical, neutral). The ^{1}H, ^{2}H and ^{13}C NMR spectra were recorded by a JEOL AL 400 spectrometer or a JEOL EX 400 spectrometer (400 MHz for ^{1}H NMR, 60.7 MHz for ^{2}H NMR, 100 MHz for ^{13}C NMR). The chemical shifts (δ) are expressed in ppm and are internally referenced to trimethylsilane or residual solvents (4.75 ppm/H_2O, 7.26 ppm/$CHCl_3$, 3.30 ppm/MeOH and 3.58 ppm/THF for ^{2}H NMR). Elemental analyses were performed using a YANACO CHN CORDER MT-5 instrument. The EI and FAB mass spectra were taken by a JEOL JMS-SX102A instrument at the Mass Spectrometry Laboratory of the Gifu Pharmaceutical University. In Mass spectra data, M(d_2) indicates the molecular ion peak of deuterated substrate with two deuterium atoms, and M(d_0) indicates the peak of non-deuterated substrate. Heating reactions were carried out using a personal organic synthesizer, ChemiStation™ (Tokyo Rikakikai Co., Ltd.) or Chemist Plaza (Shibata Science Technology, Ltd.). Unless otherwise noted, the deuterium content (D content) was determined by ^{1}H NMR on the basis of the integration of the aromatic protons.

Synthesis of Substrates

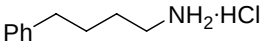
Carboxylic acid sodium salts (6, 7 and 27)



6 **7** **27**

4-Ethylbenzoic acid sodium salt (**6**), 5-phenyl-*n*-valeric acid sodium salt (**7**) and ibuprofen sodium salt (**27**) were prepared from the corresponding carboxylic acid as follows: carboxylic acid (5 mmol) and sodium hydroxide (0.18 g, 4.5 mmol) were each added to H_2O (10 mL) and the reaction mixture was stirred at room temperature for 6 h, washed with ethyl acetate (2 × 10 mL), and then concentrated in vacuo to give the corresponding carboxylic acid sodium salt in quantitative yield.

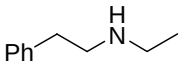
4-Phenylbutylamine hydrochloride (11)



11

4-Phenylbutylamine (1.49 g, 10.0 mmol) was added to conc. hydrochloric acid (10 mL) and the mixture was stirred at room temperature for 10 min, concentrated in vacuo, and then dried under reduced pressure with sodium hydroxide tube to give 4-phenylbutylamine hydrochloride (1.85 g, 100%) as a colorless solid: ^{1}H NMR (D_2O) δ 1.56–1.58 (m, 4H), 2.55–2.58 (t, J = 6.4 Hz, 2H), 2.88 (m, 2H), 7.15–7.29 (m, 5H, Ph); MS (EI) m/z (%): 149 (16) [M^+–HCl], 91 (100); Anal. calcd for $C_{10}H_{16}ClN$: C 64.68, H 8.68; found C 64.40, H 8.80.

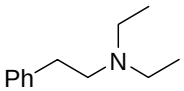
***N*-Ethyl phenethylamine (12)**



12

2-Chloroethylbenzene (1.41 g, 10.0 mmol) was added to ethylamine (1.60 mL, 25.0 mmol). The reaction mixture was stirred at room temperature for 24 h and then concentrated in vacuo. The residue was partitioned between $CHCl_3$ (50 mL) and 10% Na_2CO_3 aqueous solution (25 mL), and the organic layer was dried over Mg_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography ($CHCl_3$: MeOH = 100 : 1) to give *N*-ethyl phenethylamine (0.283 g, 19%): ^{1}H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.2 Hz, 3H), 2.66 (q, *J* = 7.2 Hz, 2H), 2.77–2.91 (m, 4H), 7.19–7.31 (m, 5H, Ph); MS (Gly, FAB) m/z (%): 150 (27) [M^++H], 105 (5). ^{1}H NMR spectrum was identical with that in the literature.[1]

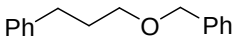
***N,N*-Diethylphenethylamine (13)**



13

N,N-Diethylphenethylamine (**13**) was synthesized according to the literature.[2] After vacuum/H_2 cycles to replace air in the reaction flask with hydrogen, the stirred mixture of diethylamine (0.731 g, 10.0 mmol), 10% Pd/C (146 mg, 10 wt % of the amine) and phenylacetonitrile (3.51 g, 30.0 mmol) in MeOH (10 mL) was hydrogenated at ordinary pressure (balloon) and room temperature for 24 h. The reaction mixture was filtered using celite and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane : Et_2O = 1 : 3) to give **13** (0.284 g, 16%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ1.06 (t, *J* = 7.2 Hz, 6H), 2.61 (q, *J* = 7.2 Hz, 4H), 2.67–2.76 (m, 4H), 7.17–7.30 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ 11.8, 33.5, 46.9, 55.0, 125.9, 128.4, 128.7, 140.8; MS (NBA, FAB) m/z (%): 178 (100) [M^++H]. ^{1}H NMR spectrum was identical with that in the literature.[3]

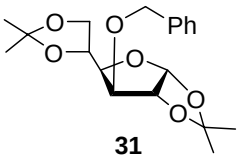
1-Benzyloxy-3-phenylpropane (29)



29

A suspension of 3-phenyl-1-propanol (1.36 g, 10.0 mmol) and NaH (60% W/W in mineral oil, 480 mg, 12.0 mmol) in DMF (20 mL) was stirred at 0 ˚C for 2 h. To the reaction mixture was added benzyl bromide (1.31 mL, 11.0 mmol) and the mixture was stirred at room temperature for 9 h and then concentrated in vacuo. The residue was partitioned between Et_2O (100 mL) and water (100 mL). The ethereal layer was washed with water (100 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : Et_2O = 20 : 1) to give 1-benzyloxy-3-phenylpropane (2.11 g, 93%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 1.88 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 3.46 (t, *J* = 6.3 Hz, 2H), 4.47 (s, 2H, -OC$\underline{H_2}$Ph), 7.11–7.33 (m, 10H, Ph); ^{13}C NMR (CD_3OD) δ 33.5, 34.2, 71.4, 74.8, 127.7, 129.6, 129.8, 130.2, 130.3, 130.4, 140.7, 144.1; MS (NBA, FAB) m/z (%): 227 (4.2) [M^++H], 91 (69); HRMS (NBA, FAB): m/z: calcd for $C_{16}H_{19}O$: 227.1436, found 227.1428 [M^++H]. ^{1}H NMR spectrum was identical with that in the literature.[4]

3-*O*-Benzyl-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (31)

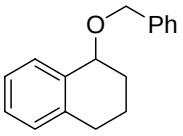


31

3-*O*-Benzyl-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (**31**) was synthesized according to the literature.[5] To a solution of 1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (3.50 g, 10.0 mmol) in THF (20 mL) were added successively powdered potassium hydroxide (1.01 g, 18.0 mmol), 18-crown-6 (106 mg, 0.400 mmol) and benzyl bromide (1.31 mL, 11.0 mmol). The reaction mixture was stirred at room temperature for 3 h and then concentrated in vacuo. The residue was partitioned between Et_2O (100 mL) and water (100 mL). The ethereal layer was washed with water (100 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : Et_2O = 5 : 1) to **31** (4.01 g, 85%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 1.29 (s, 3H), 1.33 (s, 3H), 1.38 (s, 3H), 1.44 (s, 3H), 3.91 (dd, *J* = 8.5, 6.0 Hz, 1H, H-6), 3.97 (d, *J* = 3.1 Hz, 1H, H-3), 4.04 (dd, *J* = 8.5, 6.3 Hz, 1H, H-6'), 4.13 (dd, *J* = 7.0, 3.1 Hz, 1H, H-4), 4.33 (m, 1H, H-5), 4.57 (d, *J* = 11.6 Hz, 1H, -OC$\underline{H_2}$Ph), 4.66 (d, *J* = 3.6 Hz, 1H, H-2), 4.68 (d, *J* = 11.6 Hz, 1H, -OC$\underline{H_2}$Ph), 5.86 (d, *J* = 3.6 Hz, 1H, H-1), 7.27–7.36 (m, 5H, Ph); ^{13}C NMR (CD_3OD) δ 25.4, 26.2, 26.8, 26.9, 67.7, 73.0, 73.9, 82.2, 82.8,

83.4, 106.4, 109.8, 112.6, 128.6, 128.7, 129.1, 138.9; MS (NBA, FAB) m/z (%): 351 (9) [M^++H], 91 (52); HRMS (NBA, FAB): m/z: calcd for $C_{19}H_{26}O_6$: 351.1808, found 351.1815 [M^++H]. ^{1}H NMR spectrum was identical with that in the literature.[5]

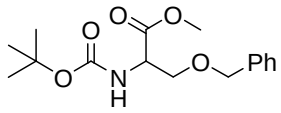
1-Benzyloxy-1,2,3,4-tetrahydronaphthalene (34)



34

A suspension of 1,2,3,4-tetrahydronaphthol (2.96 g, 20.0 mmol) and NaH (60% W/W in mineral oil, 960 mg, 24.0 mmol) in DMF (20 mL) was stirred at 0 ˚C for 1 h. To the reaction mixture was added benzyl bromide (2.61 mL, 22.0 mmol) and the mixture was stirred at room temperature for 12 h and then concentrated in vacuo. The residue was partitioned between ethyl acetate (100 mL) and water (200 mL). The organic layer was washed with water (200 mL) and brine (100 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : ethyl acetate = 100 : 1) to give 1-benzyloxy-1,2,3,4-tetrahydronaphthalene (1.69 g, 35%) as a yellow oil: ^{1}H NMR (CD_3OD) δ 1.64 (m, 1H), 1.80–1.97 (m, 3H), 2.61 (m, 1H), 2.71 (m, 1H), 4.42 (t, *J* = 4.6 Hz, 1H), 4.48 (d, *J* = 11.6 Hz, 1H, -OC<u>H</u>$_2$Ph), 4.57 (d, *J* = 11.6 Hz, 1H, -OC<u>H</u>$_2$Ph), 6.96–7.29 (m, 9H, Ph); ^{13}C NMR (CD_3OD) δ 20.0, 29.2, 30.2, 71.7, 76.3, 126.8, 128.8, 129.3, 129.5, 130.0, 130.7, 137.9, 139.0, 140.3; MS (EI) m/z (%): 147 (66) [M–Bn]$^+$, 131 (59), 91 (100); Anal. calcd for $C_{17}H_{18}O$·0.28 H_2O: C 83.90, H 7.69; found C 83.93, H 7.46.

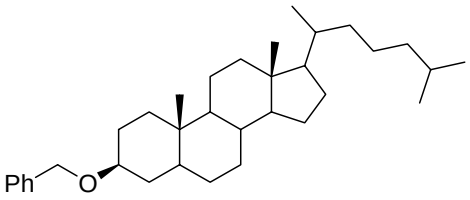
***N*-Boc-*O*-benzyl-L-serine methyl ester (35)**



35

To a solution of *N*-Boc-*O*-benzyl-L-serine (1.48 g, 5.00 mmol) in DMF (5 mL) were added *N*,*N*-dimethylformamide dimethylacetal (3.30 mL, 25.0 mmol). The reaction mixture was stirred at room temperature for 61 h and then concentrated in vacuo. The residue was partitioned between Et_2O (50 mL) and water (50 mL). The ethereal layer was washed with water (50 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : Et_2O = 1 : 1) to give *N*-Boc-*O*-benzyl-L-serine methyl ester (1.13 g, 73%) as a yellow oil: ^{1}H NMR (CD_3OD) δ 1.43 (s, 9H), 3.68 (dd, *J* = 9.5, 3.9 Hz, 1H), 3.70 (s, 3H), 3.78 (dd, *J* = 9.5, 4.9 Hz, 1H), 4.36 (m, 1H), 4.47 (d, *J* = 12.2 Hz, 1H, -OC$\underline{H}_2$Ph), 4.53 (d, *J* = 12.2 Hz, 1H, -OC$\underline{H}_2$Ph), 7.24–7.34 (m, 5H, Ph); ^{13}C NMR (CD_3OD) δ 29.2, 55.3, 55.9, 71.2, 74.6, 81.4, 129.3, 129.4, 129.9, 139.7, 158.4, 173.2; MS (NBA, FAB) m/z (%): 310 (19) [M^++H], 254 (37), 210(25), 91 (53); HRMS (NBA, FAB): m/z: calcd for $C_{16}H_{24}NO_5$: 310.1654, found 310.1671 [M^++H]. ^{1}H and ^{13}C NMR spectra were identical with those in the literature.[6]

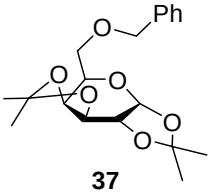
3β-Benzyloxycholestane (36) (containing a small amount of 3α-benzyloxycholestane)



36

To a solution of β-cholestanol (containing a small amount of α-cholestanol) (1.94 g, 5.00 mmol) in THF (30 mL) were added successively powdered potassium hydroxide (0.500 g, 9.00 mmol), 18-crown-6 (52.9 mg, 0.200 mmol) and benzyl bromide (0.650 mL, 5.50 mmol). The reaction mixture was stirred at room temperature for 22 h and then concentrated in vacuo. The residue was partitioned between Et_2O (100 mL) and water (100 mL). The organic layer was washed with water (100 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : Et_2O = 60 : 1) to give 3-benzyloxycholestane (1.34 g, 56%) as a diastereomixture at the 3-position (3α : 3β = 1 : 2) as a colorless solid: ^{1}H NMR (THF-d_8, 3β-isomer) δ 0.69 (s, 3H, H-18), 0.84 (s, 3H, H-19), 0.88 (d, *J* = 6.8 Hz, 3H, H-26 or 27), 0.88 (d, *J* = 6.3 Hz, 3H, H-26 or 27), 0.94 (d, *J* = 6.8 Hz, 3H, H-21), 3.31 (m, 1H, H-3), 4.49 (d, *J* = 12.1 Hz, 1H, -OC$\underline{H}_2$Ph), 4.52 (d, *J* = 12.1 Hz, 1H, -OC$\underline{H}_2$Ph), 7.16–7.34 (m, 5H, Ph) (The existence of 3α-isomer was confirmed by the peak of 4.53 ppm which corresponds to the benzylic signal.); ^{13}C NMR (THF-d_8, 3α/3β-mixture) δ 11.6, 11.6, 11.8, 11.8, 18.3, 21.2, 22.1, 22.3, 23.9, 24.2, 28.1, 28.2, 28.3, 28.9, 32.2, 35.0, 35.6, 35.7, 35.9, 36.2, 37.1, 39.5, 40.2, 42.6, 44.9, 54.7, 56.5, 56.6, 69.3, 69.3, 69.3, 71.8, 71.8, 71.8, 77.8, 77.8, 126.8, 127.0, 127.1, 127.3, 127.9, 128.0, 138.9, 139.9; MS (EI) m/z (%): 478 (4) [M^+], 387 (100), 355 (10), 91 (31); HRMS (EI): m/z: calcd for $C_{34}H_{54}O$: 478.4175, found 478.4168 [M^+]; Anal. calcd for $C_{34}H_{54}O$: C 85.29, H 11.37; found C 85.08, H 11.17. ^{1}H NMR spectrum was identical with that in the literature.[7]

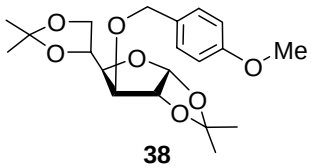
6-*O*-Benzyl-1,2:3,4-di-*O*-isopropyridene-α-galactopyranose (37)



37

6-*O*-Benzyl-1,2:3,4-di-*O*-isopropyridene-α-galactopyranose (**37**) was synthesized according to the literature.[5] To a solution of 1,2:3,4-di-*O*-isopropyridene-α-galactopyranose (1.30 g, 5.00 mmol) in THF (20 mL) were added successively powdered potassium hydroxide (0.500 g, 9.00 mmol), 18-crown-6 (52.9 mg, 0.200 mmol) and benzyl bromide (0.650 mL, 5.50 mmol). The reaction mixture was stirred at room temperature for 40 min and then concentrated in vacuo. The residue was partitioned between ethyl acetate (50 mL) and water (50 mL). The organic layer was washed with water (50 mL) and brine (25 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : ethyl acetate = 10 : 1) to give **36** (1.12 g, 69%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 1.32 (s, 3H), 1.32 (s, 3H), 1.38 (s, 3H), 1.50 (s, 3H), 3.57 (dd, *J* = 10.4, 7.1 Hz, 1H, H-6), 3.65 (dd, *J* = 10.4, 5.1 Hz, 1H, H-6'), 4.02 (m, 1H, H-5), 4.25 (dd, *J* = 7.9, 2.2 Hz, 1H, H-4), 4.34 (dd, *J* = 5.0, 2.2 Hz, 1H, H-2), 4.52 (d, *J* = 12.0 Hz, 1H, -OC$\underline{H}_2$Ph), 4.56 (d, *J* = 12.0 Hz, 1H, -C$\underline{H}_2$Ph), 4.61 (dd, *J* = 7.9, 2.2 Hz, 1H, H-3), 5.48 (d, *J* = 5.0, 1H, H-1), 7.26–7.35 (m, 5H, Ph); ^{13}C NMR (CD_3OD) δ 24.6, 25.1, 26.3, 26.3, 68.3, 70.3, 72.0, 72.0, 72.6, 74.3, 97.8, 109.8, 110.4, 128.7, 128.9, 129.3, 139.6; MS (NBA, FAB) m/z (%): 351 (26) [M^++H], 91 (100); HRMS (NBA, FAB): m/z: calcd for $C_{19}H_{27}O_6$: 351.1808, found 351.1816 [M^++H]; Anal. calcd for $C_{19}H_{26}O_6$: C 65.13, H 7.48; found C 65.02, H 7.43.

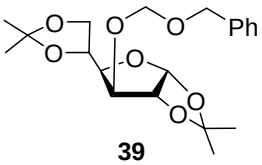
3-*O*-(*p*-Methoxybenzyl)-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (38)



38

3-*O*-(*p*-Methoxybenzyl)-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (**38**) was synthesized according to the literature.[8] 18-crown-6 (10.0 mg, 0.0378 mmol) was added to a suspension of NaH (60% W/W in mineral oil, 0.400 g, 10.0 mmol) and tetrabutylammonium iodide (92.3 mg, 0.250 mmol) in THF (25 mL) and the suspension was stirred for 10 min. To the mixture at 0 ºC was added a solution of 1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (1.30 g, 5.00 mmol) in THF (5 mL) dropwise. The mixture was stirred at room temperature for 1 h and then cooled to 0 ˚C. *p*-Methoxybenzyl chloride (0.610 mL, 4.50 mmol) was added and the reaction mixture was stirred for a further 87 h at 50 ˚C before being poured slowly into water (100 mL) and extracted with ethyl acetate (2 × 50 mL). The organic layers were washed with brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : ethyl acetate = 10 : 1) to give **38** (0.760 g, 44%) as a yellow oil: ^{1}H NMR (CD_3OD) δ 1.19 (s, 3H), 1.24 (s, 3H), 1.28 (s, 3H), 1.34 (s, 3H), 3.68 (s, 3H, -O<u>Me</u>), 3.81 (dd, *J* = 8.7, 6.3 Hz, 1H, H-6), 3.85 (d, *J* = 2.9 Hz, 1H, H-3), 3.93 (dd, *J* = 8.5, 6.3 Hz, 1H, H-6'), 4.03 (dd, *J* = 7.0, 2.9 Hz, 1H, H-4), 4.21 (m, 1H, H-5), 4.40 (d, *J* = 11.1 Hz, 1H, -OC<u>H</u>$_2$Ph), 4.50 (d, *J* = 11.1 Hz, 1H, -OC<u>H</u>$_2$Ph), 4.53 (d, *J* = 3.7 Hz, 1H, H-2), 5.74 (d, *J* = 3.7 Hz, 1H, H-1), 6.79 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (CD_3OD) δ 25.6, 26.4, 27.0, 27.1, 55.7, 67.9, 73.0, 74.2, 82.4, 82.7, 83.7, 106.7, 110.0, 112.9, 114.8, 130.6, 131.1, 161.0; MS (EI) m/z (%): 380 (2) [M^+], 121 (100); HRMS (EI): m/z: calcd for $C_{20}H_{28}O_7$: 380.1835, found 380.1829 [M^+]; Anal. calcd for $C_{20}H_{28}O_7$: C 63.14, H 7.42; found C 63.27, H 7.29. ^{1}H and ^{13}C NMR spectra were identical with those in the literature.[8]

3-*O*-Benzyloxymethyl-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (39)



39

18-Crown-6 (10.0 mg, 0.0378 mmol) was added to a suspension of NaH (60% W/W in mineral oil, 0.400 g, 10.0 mmol) in THF (25 mL) and the suspension was stirred for 10 min. To the mixture at 0 ºC was added a solution of 1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (1.30 g, 5.00 mmol) in THF (4 mL) dropwise. The mixture was stirred at room temperature for 1 h and then cooled to 0 ˚C. Benzyloxymethyl chloride (0.890 mL, 6.50 mmol) was added and the reaction mixture was stirred for a further 42 h at room temperature before being poured slowly into water (100 mL) and extracted with ethyl acetate (2 × 50 mL). The organic layers were washed with brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : ethyl acetate = 20 : 1 → 10 : 1) to give 3-*O*-benzyloxymethyl-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose (1.66 g, 87%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 1.27 (s, 3H), 1.27 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 3.92 (dd, *J* = 8.5, 5.6 Hz, 1H, H-6), 4.06–4.11 (m, 3H, H-4, H-6'), 4.24 (d, *J* = 2.9 Hz, 1H, H-3), 4.30 (m, 1H, H-5), 4.56 (d, *J* = 11.6 Hz, 1H, -OC<u>H</u>$_2$Ph), 4.59 (d, *J* = 3.7 Hz, 1H, H-2), 4.76 (d, *J* = 11.6 Hz, 1H, -OC<u>H</u>$_2$Ph), 4.81 (d, *J* = 7.2, 1H, -OC<u>H</u>$_2$OPh), 4.86 (d, *J* = 7.2, 1H, -OC<u>H</u>$_2$OPh), 5.82 (d, *J* = 3.7 Hz, 1H, H-1), 7.27–7.35 (m, 5H, Ph); ^{13}C NMR (CD_3OD) δ 26.1, 27.0, 27.7, 27.7, 68.8, 71.4, 74.4, 80.6, 82.9, 84.7, 95.3, 107.2, 110.8, 113.6, 129.3, 129.6, 130.0, 139.9; MS (FAB, NBA) m/z (%): 381 (10) [M^++H], 91 (53); HRMS (FAB, NBA): m/z: calcd for $C_{20}H_{29}O_7$: 381.1913, found 381.1907 [M^++H]; Anal. calcd for $C_{20}H_{28}O_7$: C 63.14, H 7.42; found C 62.99, H 7.27.

Typical procedure for Benzylic Site Selective H–D Exchange Reaction Using Pd/C–D_2O–H_2 System

A suspension of the substrate (1.00 mmol) and 10% Pd/C (10 wt % of the substrate) in D_2O (0.5 mL) was stirred for at room temperature or 50 °C in a sealed test tube filled with hydrogen gas. After the appropriate time, the mixture was diluted with Et_2O (10 mL), and then filtered using a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtrate was partitioned between ethereal and aqueous layers. The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined ethereal layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give the corresponding deuterated substrate at the benzylic site.

Typical Procedures for Benzylic Site Selective Deuteration of *O*-Benzyl Protective Group Using Pd/C–D_2O–H_2 System

A suspension of substrate possessing the *O*-benzyl protective group (0.250 mmol) and 5% Pd/C(en) (20 wt % of the substrate) in D_2O (1 mL) was stirred at 50 ˚C in a sealed test tube filled with hydrogen. After the appropriate time, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and then filtered using a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtrate was partitioned between ethyl acetate and aqueous layers. The aqueous layer was then extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate) to give the corresponding deuterated substrate at the benzylic site.

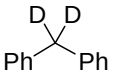
Method for Determining Deuterium Content of Labeled Molecules

Unless otherwise noted, deuterium content was determined on the basis of the integration of the aromatic protons in the ^1H NMR spectrum.

Characterization Data

Diphenylmethane-d_2 (1-d, Table 6, Entry 1)

(92% D)

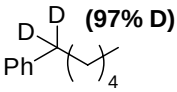


1-d

^{1}H NMR (CD_3OD) δ 3.88 (s, 0.17H), 7.10–7.23 (m, 10H); ^{2}H NMR (60.7 MHz, CH_3OH) δ 3.87 (br s); MS (EI) m/z (%): 170 (100) $[M(d_2)]^+$, 169 (93) $[M(d_1)]^+$, 168 (30) $[M(d_0)]^+$.

***n*-Hexylbenzene-d_2 (2-d, Table 3, Entry 2)**

(97% D)

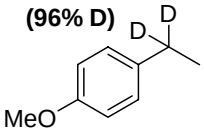


2-d

^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 6.8 Hz, 3H), 1.30–1.65 (m, 6H), 2.62 (s, 0.053H), 7.20–7.35 (m, 5H); MS (EI) m/z (%): 164 (33) $[M(d_2)]^+$, 163 (4) $[M(d_1)]^+$, 162 (0) $[M(d_0)]^+$, 93 (100).

4-Ethylanisole-d_2 (3-d, Table 3, Entry 3)

(96% D)

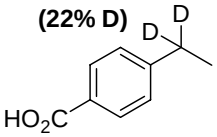


3-d

^{1}H NMR ($CDCl_3$) δ 1.32 (m, 3H), 2.73 (m, 0.083H), 3.92 (s, 3H), 6.97 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H); MS (EI) m/z (%): 138 (28) $[M(d_2)]^+$, 137 (4) $[M(d_1)]^+$, 136 (1) $[M(d_0)]^+$, 123 (100).

4-Ethylbenzoic acid-d_2 (4-d, Table 3, Entry 4)

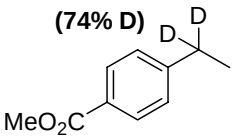
(22% D)



4-d

^{1}H NMR (CD_3OD) δ 1.23 (t, J = 7.7 Hz, 3H), 2.68 (q, J = 7.7 Hz, 1.57H), 7.28 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H); ^{2}H NMR (CH_3OH) δ 2.63 (br s); MS (EI) m/z (%): 152 (23) $[M(d_2)]^+$, 151 (12) $[M(d_1)]^+$, 150 (79) $[M(d_0)]^+$, 135 (67), 105 (100).

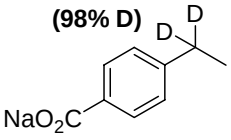
4-Ethylbenzoic acid methyl ester-d_2 (5-d, Table 3, Entry 5)



5-d

^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.6 Hz, 3H), 2.70 (m, 0.521H), 3.90 (s, 3H), 7.27 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H); MS (EI) m/z (%): 166 (37) $[M(d_2)]^+$, 165 (27) $[M(d_1)]^+$, 164 (6) $[M(d_0)]^+$, 135 (100), 134 (67).

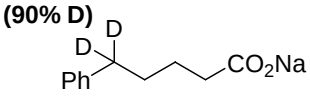
4-Ethylbenzoic acid sodium salt-d_2 (6-d, Table 3, Entry 6)



6-d

^{1}H NMR (D_2O) δ 1.02 (m, 3H), 2.47 (m, 0.032H), 7.13 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H).

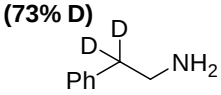
5-Phenyl-*n*-valeric acid sodium salt-d_2 (7-d, Table 3, Entry 7)



7-d

^{1}H NMR (D_2O) δ 1.60 (m, 4H), 2.21 (t, J = 6.6 Hz, 2H), 2.64 (m, 0.148H), 7.24–7.39 (m, 5H).

Phenethylamine-d_2 (8-d, Table 6, Entry 2)

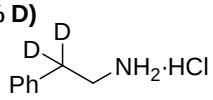


8-d

^{1}H NMR (CD_3OD) δ 2.63 (t, J = 7.0 Hz, 0.54H), 2.75 (m, 2H), 7.06–7.20 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.78 (br s); MS (EI) m/z (%): 123 (12) $[M(d_2)]^+$, 122 (12) $[M(d_1)]^+$, 121 (5) $[M(d_0)]^+$, 105 (100), 93 (36).

Phenethylamine hydrochloride-d_2 (9-d, Table 6, Entry 3)

(77% D)

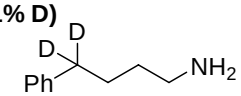


9-d

^{1}H NMR (CD_3OD) δ 2.94 (m, 0.46H), 3.16 (m, 2H), 7.23–7.36 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.92 (br s); MS (EI) m/z (%): 123 (49) $[M(d_2)–HCl]^+$, 122 (14) $[M(d_1)–HCl]^+$, 121 (5) $[M(d_0)–HCl]^+$, 93 (100).

4-Phenylbutylamine-d_2 (10-d, Table 6, Entry 4)

(91% D)

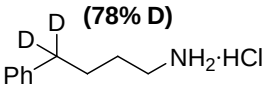


10-d

^{1}H NMR (CD_3OD) δ 1.38 (m, 2H), 1.52 (t, J = 7.5 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H) 2.52 (m, 0.19H), 7.01–7.15 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.56 (br s); MS (EI) m/z (%): 151 (100) $[M(d_2)]^+$, 150 (53) $[M(d_1)]^+$, 149 (8) $[M(d_0)]^+$, 93 (78).

4-Phenylbutylamine hydrochloride-d_2 (11-d, Table 3, Entry 11)

(78% D)

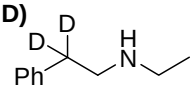


11-d

^{1}H NMR (D_2O) δ 1.56 (m, 4H), 2.56 (m, 0.436H), 2.86 (m, 2H), 7.15–7.27 (m, 5H); MS (EI) m/z (%): 151 (100) $[M(d_2)–HCl]^+$, 150 (40) $[M(d_1)–HCl]^+$, 149 (6) $[M(d_0)–HCl]^+$, 105 (63), 93 (70).

***N*-Ethyl-phenethylamine-d_2 (9-d, Table 3, Entry 12)**

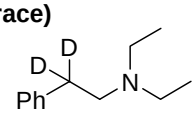
(0% D)



12-d

***N,N*-Diethylphenethylamine-d_2 (13-d, Table 3, Entry 13)TK7-153**

(trace)

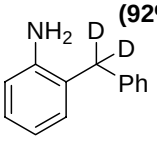


13-d

^{1}H NMR (CD_3OD) δ 0.98 (t, J = 7.2 Hz, 6H), 2.54 (q, J = 7.2 Hz, 4H), 2.58–2.67 (m, 4H), 7.04–7.18 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.72 (br s); MS (NBA, FAB) m/z (%): 180 (2) $[M(d_2)+H]^+$, 179 (16) $[M(d_1)+H]^+$, 178 (96) $[M(d_0)+H]^+$.

2-Benzylanline-d_2 (14-d, Table 6, Entry 5)

(92% D)

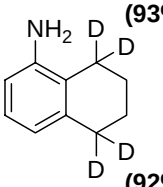


14-d

^{1}H NMR (CD_3OD) δ 3.83 (m, 0.16H), 6.66 (td, J = 7.5, 1.1 Hz, 1H), 6.70 (dd, J = 7.5, 1.1 Hz, 1H), 6.93 (dd, J = 7.5, 1.7 Hz, 1H), 7.00 (td, J = 7.5, 1.7 Hz, 1H), 7.13–7.25 (m, 5H); ^{2}H NMR (CH_3OH) δ 3.82 (br s); MS (EI) m/z (%): 185 (100) $[M(d_2)]^+$, 184 (54) $[M(d_1)]^+$, 183 (15) $[M(d_0)]^+$.

5,6,7,8-Tetrahydro-1-naphthylamine-d_3 (15-d, Table 6, Entry 6)

(93% D)



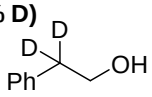
(92% D)

15-d

^{1}H NMR (CD_3OD) δ 1.70 (t, J = 5.6 Hz, 2H), 1.80 (t, J = 5.6 Hz, 2H), 2.43 (m, 0.15H), 2.65 (m, 0.16H), 6.44 (dd, J = 7.6, 1.2 Hz, 1H), 6.52 (dd, J = 7.6, 1.2 Hz, 1H), 6.81–6.84 (m, 1H); ^{2}H NMR (CH_3OH) δ 2.41 (br s), 2.62 (br s); MS (EI) m/z (%): 151 (83) $[M(d_4)]^+$, 150 (48) $[M(d_3)]^+$, 149 (26) $[M(d_2)]^+$, 148 (16) $[M(d_1)]^+$, 147 (11) $[M(d_0)]^+$.

Phenethyl alcohol-d_2 (16-d, Table 6, Entry 7)

(5% D)

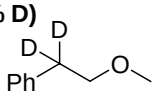


16-d

^{1}H NMR (CD_3OD) δ 2.70 (t, J = 7.0 Hz, 1.90H), 3.63 (t, J = 7.0 Hz, 2H), 7.04–7.17 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.77 (br s); MS (EI) m/z (%): 124 (1) $[M(d_2)]^+$, 123 (9) $[M(d_1)]^+$, 122 (36) $[M(d_0)]^+$, 93 (36), 92 (74), 91 (100).

Phenylethyl methyl ether-d_2 (17-d, Table 6, Entry 8)

(1% D)

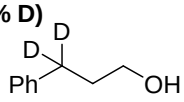


17-d

^{1}H NMR (CD_3OD) δ 2.73 (t, J = 7.0 Hz, 2H), 3.21 (s, 3H), 3.48 (t, J = 7.0 Hz, 2H), 7.06–7.17 (m, 5H); ^{2}H NMR (CH_3OH) δ no peak; MS (EI) m/z (%): 136 (48) $[M(d_0)]^+$, 91 (70).

3-Phenyl-1-propanol-d_2 (18-d, Table 6, Entry 9)

(93% D)

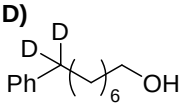


18-d

^{1}H NMR (CD_3OD) δ 1.80 (t, J = 6.5 Hz, 2H), 2.64 (m, 0.14H), 3.55 (t, J = 6.5 Hz, 2H), 7.11–7.25 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.61 (br s); MS (EI) m/z (%): 138 (41) $[M(d_2)]^+$, 137 (5) $[M(d_1)]^+$, 136 (2) $[M(d_0)]^+$, 118 (83), 93 (100).

7-Phenyl-1-octanol-d_2 (19-d, Table 6, Entry 10)

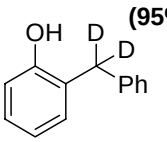
(95% D)



19-d

^{1}H NMR (CD_3OD) δ 1.19–1.25 (m, 8H), 1.47–1.59 (m, 4H), 2.56 (m, 0.10H), 3.52 (t, J = 6.6 Hz, 2H), 7.09–7.15 (m, 3H), 7.20–7.24 (m, 2H); ^{2}H NMR (CH_3OH) δ 2.53 (br s); MS (EI) m/z (%): 208 (37) $[M(d_2)]^+$, 207 (5) $[M(d_1)]^+$, 206 (1) $[M(d_0)]^+$, 105 (64), 93 (100).

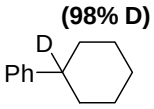
2-Benzylphenol-d_2 (20-d, Table 6, Entry 11)



20-d

^{1}H NMR (CD_3OD) δ 3.90 (br s, 0.11H), 6.71 (td, J = 7.4, 1.1 Hz, 1H), 6.79 (dd, J = 8.2, 1.1 Hz, 1H), 6.98 (m, 1H), 7.10 (m, 1H), 7.16–7.19 (m, 5H); ^{2}H NMR (CH_3OH) δ 3.88 (br s); MS (EI) m/z (%): 186 (100) $[M(d_2)]^+$, 185 (38) $[M(d_1)]^+$, 184 (7) $[M(d_0)]^+$.

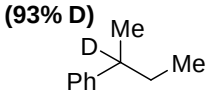
Phenylcyclohexane-d_2 (21-d, Table 6, Entry 12)



21-d

^{1}H NMR (CD_3OD) δ 1.21–1.34 (m, 5H), 1.72–1.82 (m, 5H), 2.46 (m, 0.05H), 7.08–7.24 (m, 5H); ^{2}H NMR (CH_3OH) δ 2.45 (br s); MS (EI) m/z (%): 161 (100) $[M(d_1)]^+$, 160 (6) $[M(d_0)]^+$, 118 (72), 105 (73), 92 (38).

***sec*-Butylbenzene-d_2 (22-d, Table 3, Entry 22)**

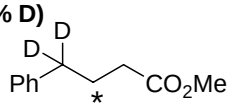


22-d

^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7.3 Hz, 3H), 1.23 (s, 3H), 1.59 (q, J = 7.3 Hz, 2H), 2.59 (m, 0.14H), 7.15–7.31 (m, 5H); MS (EI) m/z (%): 135 (23) $[M(d_1)]^+$, 134 (3) $[M(d_0)]^+$, 106 (100), 84 (45).

4-Phenylbutyric acid methyl ester-d_2 (converted 23-d into the corresponding methyl ester, Table 4, Entry 4)

(95% D)



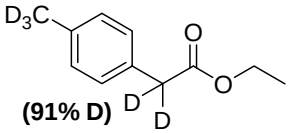
Methyl ester of 23-d

* The deuteration slightly proceeded.

^{1}H NMR (CD_3OD) δ 1.87 (t, J = 7.4 Hz, 2H), 2.29 (t, J = 7.4 Hz, 2H), 2.58 (m, 0.10H), 3.62 (s, 3H), 7.12–7.16 (m, 3H), 7.22–7.26 (m, 2H); ^{2}H NMR (CH_3OH) δ 1.85 (br s), 2.56 (br s); MS (EI) m/z (%): 180 (25) $[M(d_2)]^+$, 179 (4) $[M(d_1)]^+$, 178 (2) $[M(d_0)]^+$, 105 (100) 93 (70).

***p*-Tolylacetic acid ethyl ester-d_3 (24-d, Table 7, Entry 3)**

(93% D)



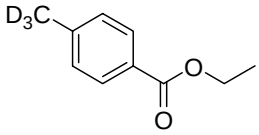
(91% D)

24-d

^{1}H NMR (CD_3OD) δ 1.12 (t, J = 7.2 Hz, 3H), 2.17 (m, 0.26H), 3.44 (m, 0.14H), 4.01 (q, J = 7.2 Hz, 2H), 6.99–7.05 (m, 4H); ^{2}H NMR (CH_3OH) δ 2.20 (m), 3.46 (br s); MS (EI) m/z (%): 183 (29) $[M(d_5)]^+$, 182 (16) $[M(d_4)]^+$, 181 (3) $[M(d_3)]^+$, 179 (1) $[M(d_2)]^+$, 179 (0) $[M(d_1)]^+$, 178 (0) $[M(d_0)]^+$, 110 (100).

***p*-Toluic acid ethyl ester-d_3 (25-d, Table 7, Entry 5)**

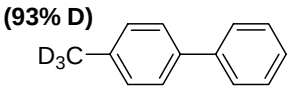
(90% D)



25-d

^{1}H NMR (CD_3OD) δ 1.28 (t, J = 7.1 Hz, 3H), 2.27 (m, 0.21H), 4.24 (q, J = 7.1 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H); ^{2}H NMR (CH_3OH) δ 2.34 (m); MS (EI) m/z (%): 167 (24) $[M(d_3)]^+$, 166 (8) $[M(d_2)]^+$, 165 (1) $[M(d_1)]^+$, 164 (0) $[M(d_0)]^+$, 139 (23), 122 (100), 94 (28).

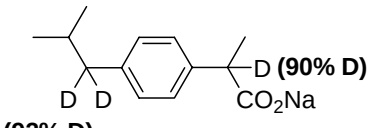
4-Phenyltoluene-d_3 (26-d, Table 7, Entry 8)



26-d

^{1}H NMR (CD_3OD) δ 2.20 (m, 0.22H), 7.10 (dt, J = 8.2, 2.0 Hz, 2H), 7.17 (m, 1H), 7.27 (m, 2H), 7.35 (dt, J = 8.2, 2.0 Hz, 2H), 7.44 (m, 2H); ^{2}H NMR (CH_3OH) δ 2.76 (br s); MS (EI) m/z (%): 171 (100) $[M(d_3)]^+$, 170 (864) $[M(d_2)]^+$, 169 (29) $[M(d_1)]^+$, 168 (13) $[M(d_0)]^+$.

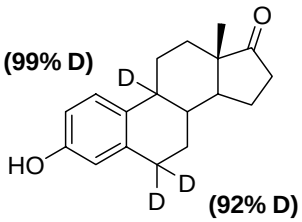
Ibuprofen sodium salt-d_3 (27-d, Table 8, Entry 3)



27-d

^{1}H NMR (D_2O) δ 0.72 (m, 3H), 0.74 (m, 3H), 1.25 (d, J = 6.8 Hz, 3H), 1.68 (m, 1H), 2.31 (m, 0.16H), 3.47 (m, 0.10H), 7.07 (dd, J = 8.0, 1.7 Hz, 2H), 7.13 (dd, J = 8.0, 1.7 Hz, 2H); ^{2}H NMR (H_2O) δ 2.41 (br s), 3.56 (br s); MS (EI) m/z (%): 209 (50) $[M(\text{Ibprofen-}d_3)]^+$, 208 (14) $[M(\text{Ibprofen-}d_2)]^+$, 207 (1) $[M(\text{Ibprofen-}d_1)]^+$, 206 (0) $[M(\text{Ibprofen-}d_0)]^+$, 164 (100), 122 (41), 93 (37).

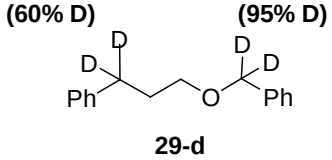
Estrone-d_3 (28-d, Table 8, Entry 7)



28-d

^{1}H NMR ($CDCl_3$) δ 0.91 (s, 3H), 1.38–1.68 (m, 6H), 1.92–2.19 (m, 4H), 2.33 (m, 0.01H), 2.37 (m, 1H), 2.51 (m, 1H), 2.85 (m, 0.16H), 6.59 (d, J = 2.8 Hz, 1H), 6.64 (dd, J = 8.4, 2.8 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H); ^{2}H NMR ($CHCl_3$) δ 2.16 (br s), 2.78 (br s); MS (EI) m/z (%): 273 (100) $[M(d_3)]^+$, 272 (22) $[M(d_2)]^+$, 271 (2) $[M(d_1)]^+$, 270 (1) $[M(d_0)]^+$.

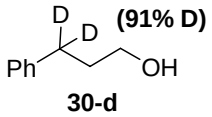
1-Benzyloxy-3-phenylpropane-d_4 (29-d, Table 9, Entry 2)



29-d

^{1}H NMR (CD_3OD) δ 1.83 (m, 2H), 2.62 (m, 0.81H), 3.41 (t, J = 6.3 Hz, 2H), 4.40 (br s, 0.10H, -OC$\underline{H}_2$Ph), 7.09–7.30 (m, 10H, Ph); ^{2}H NMR (CH_3OH) δ 2.62 (br s), 4.43 (br s); MS (NBA, FAB) m/z (%): 231 (10) $[M(d_4)+H]^+$, 230 (9) $[M(d_3)+H]^+$, 229 (5) $[M(d_2)+H]^+$, 228 (7) $[M(d_1)+H]^+$, 227 (4) $[M(d_0)+H]^+$, 93 (84) $[Bn(d_2)]$.

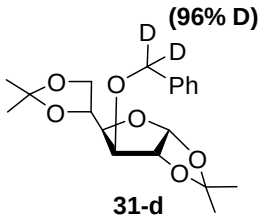
3-Phenyl-1-propanol-d_2 (30-d, Table 9, Entry 5)



30-d

^{1}H NMR (CD_3OD) δ 1.76 (t, J = 6.4 Hz, 2H), 2.60 (m, 0.19H), 3.51 (t, J = 6.4 Hz, 2H), 7.07–7.22 (m, 5H, Ph); ^{2}H NMR (CH_3OH) δ 2.64 (br s); MS (EI) m/z (%): 138 (40) $[M(d_2)]^+$, 137 (9) $[M(d_1)]^+$, 136 (2) $[M(d_0)]^+$, 119 (62), 118 (83), 93 (100) $[Bn(d_2)]$.

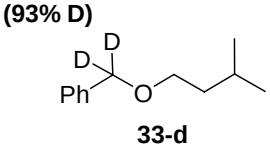
3-*O*-Benzyl-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose-d_2 (31-d, Table 10, Entry 2)



31-d

^{1}H NMR (CD_3OD) δ 1.20 (s, 3H), 1.24 (s, 3H), 1.29 (s, 3H), 1.34 (s, 3H), 3.82 (dd, J = 8.5, 6.0 Hz, 1H, H-6), 3.87 (d, J = 3.2 Hz, 1H, H-3), 3.94 (dd, J = 8.5, 6.3 Hz, 1H, H-6'), 4.04 (dd, J = 7.2, 3.2 Hz, 1H, H-4), 4.23 (m, 1H, H-5), 4.46 (bs, J = 12.0 Hz, 0.04H, -OC$\underline{H}_2$Ph), 4.56 (d, J = 3.7 Hz, 1H, H-2), 4.56 (d, J = 12.0 Hz, 0.04H, -OC$\underline{H}_2$Ph), 5.76 (d, J = 3.7 Hz, 1H, H-1), 7.18–7.25 (m, 5H, Ph); ^{2}H NMR (CH_3OH) δ 4.54 (br s), 4.64 (br s); MS (NBA, FAB) m/z (%): 353 (14) $[M(d_2)+H]^+$, 352 (2) $[M(d_1)+H]^+$, 351 (3) $[M(d_0)+H]^+$, 93 (100) $[Bn(d_2)]$.

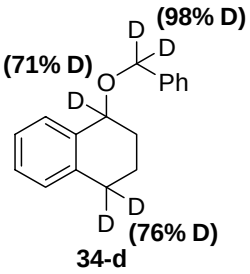
Benzyl isoamyl ether-d_2 (33-d, Table 11, entry 4)



33-d

^{1}H NMR (CD_3OD) δ 0.78 (s, 3H), 0.79 (s, 3H), 1.37 (q, J = 6.7 Hz, 2H), 1.61 (m, 1H), 3.38 (t, J = 6.7 Hz, 2H), 4.33 (m, 0.14H, -OC$\underline{H_2}$Ph), 7.12–7.21 (m, 5H, Ph); ^{2}H NMR (CH_3OH) δ 4.43 (s); MS (EI) m/z (%): 93 (100) [Bn(d_2)], 92 (12) [Bn(d_1)], 91 (8) [Bn(d_0)].

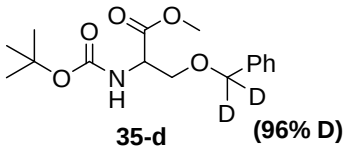
1-Benzyloxy-1,2,3,4-tetrahydronaphthalene-d_n (34-d, Table 12, Entry 1)



34-d

^{1}H NMR (CD_3OD) δ 1.58 (m, 1H), 1.72–1.95 (m, 3H), 2.54 (m, 0.02H), 2.65 (m, 0.46H), 4.38 (t, J = 4.6 Hz, 0.29H), 4.43 (s, 0.01H, -OC$\underline{H_2}$Ph), 4.51 (s, 0.02H, -OC$\underline{H_2}$Ph), 6.94–7.28 (m, 9H, Ph); ^{2}H NMR (CH_3OH) δ 2.63 (br s), 2.74 (br s), 4.47 (br s), 4.52 (br s), 4.61 (br s); MS (EI) m/z (%): 151 (2) [M(d_4)–Bn]$^+$, 150 (21) [M(d_3)–Bn]$^+$, 149 (51) [M(d_2)–Bn]$^+$, 148 (33) [M(d_1)–Bn]$^+$, 147 (2) [M(d_0)–Bn]$^+$, 93 (100) [Bn(d_2)].

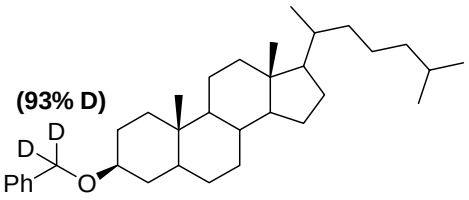
***N*-Boc-*O*-benzyl-L-serine methyl ester-d_2 (35-d, Table 12, Entry 3)**



35-d

^{1}H NMR (CD_3OD) δ 1.34 (s, 9H), 3.58 (dd, J = 9.7, 3.9 Hz, 1H), 3.60 (s, 3H), 3.67 (dd, J = 9.7, 4.8 Hz, 1H), 4.26 (m, 1H), 4.36 (br s, 0.03H, -OC$\underline{H_2}$Ph), 4.42 (br s, 0.05H, -OC$\underline{H_2}$Ph), 7.14–7.24 (m, 5H, Ph); ^{2}H NMR (CH_3OH) δ 4.48 (br s); MS (NBA, FAB) m/z (%): 312 (23) [M(d_2)+H]$^+$, 311 (2) [M(d_1)+H]$^+$, 310 (1) [M(d_0)+H]$^+$, 93 (34) [Bn(d_2)].

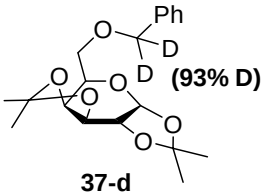
3β-Benzyloxycholestane-d_2 (36-d, Table 12, Entry 6)



36-d

^{1}H NMR (THF-d_8) δ 0.64 (s, 3H, H-18), 0.79 (s, 3H, H-19), 0.82 (d, J = 6.6 Hz, 3H, H-26 or 27), 0.83 (d, J = 6.6 Hz, 3H, H-26 or 27), 0.88 (d, J = 6.6 Hz, 3H, H-21), 3.25 (m, 1H, H-3), 4.43 (br s, 0.075H, -OC<u>H</u>$_2$Ph), 4.45 (br s, 0.075H, -OC<u>H</u>$_2$Ph), 7.11–7.29 (m, 5H, Ph); ^{2}H NMR (THF) δ 4.49 (br s); MS (NBA, FAB) m/z (%): 480 (5) [M(d_2)+H]$^+$, 479 (1) [M(d_1)+H]$^+$, 478 (1) [M(d_0)+H]$^+$, 93 (34) [Bn(d_2)].

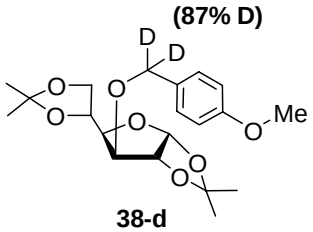
6-*O*-Benzyl-1,2:3,4-di-*O*-isopropyridene-α-galactopyranose-d_2 (37-d, Table 12, Entry 9)



37-d

^{1}H NMR (CD_3OD) δ 1.21 (s, 3H), 1.22 (s, 3H), 1.28 (s, 3H), 1.40 (s, 3H), 3.47 (dd, J = 10.4, 7.0 Hz, 1H, H-6), 3.55 (dd, J = 10.4, 5.1 Hz, 1H, H-6'), 3.92 (m, 1H, H-5), 4.15 (dd, J = 7.7, 1.9 Hz, 1H, H-4), 4.24 (dd, J = 4.8, 2.4 Hz, 1H, H-2), 4.41 (br s, 0.07H, -OC<u>H</u>$_2$Ph), 4.44 (br s, 0.07H, -C<u>H</u>$_2$Ph), 4.51 (dd, J = 7.7, 2.4 Hz, 1H, H-3), 5.38 (d, J = 4.8 Hz, 1H, H-1), 7.14–7.25 (m, 5H, Ph); ^{2}H NMR (CH_3OH) δ 4.51 (br s); MS (NBA, FAB) m/z (%): 353 (17) [M(d_2)+H]$^+$, 352 (4) [M(d_1)+H]$^+$, 351 (2) [M(d_0)+H]$^+$, 93 (54) [Bn(d_2)].

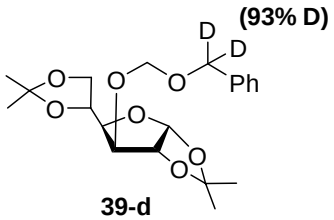
3-*O*-(*p*-Methoxybenzyl)-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose-d_2 (38-d, Table 12, Entry 11)



38-d

^{1}H NMR (CD_3OD) δ 1.19 (s, 3H), 1.24 (s, 3H), 1.28 (s, 3H), 1.34 (s, 3H), 3.68 (s, 3H, -O<u>Me</u>), 3.91 (dd, *J* = 8.5, 6.0 Hz, 1H, H-6), 3.97 (d, *J* = 3.0 Hz, 1H, H-3), 4.04 (dd, *J* = 8.5, 6.3 Hz, 1H, H-6'), 4.13 (dd, *J* = 6.8, 3.0 Hz, 1H, H-4), 4.33 (m, 1H, H-5), 4.39 (d, *J* = 12.6 Hz, 0.10H, -OC<u>H</u>$_2$Ph), 4.49 (d, *J* = 12.6 Hz, 0.16H, -OC<u>H</u>$_2$Ph), 4.53 (d, *J* = 3.7 Hz, 1H, H-2), 5.74 (d, *J* = 3.7 Hz, 1H, H-1), 6.79 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H); ^{2}H NMR (CH_3OH) δ 4.46 (br s), 4.56 (br s); MS (EI) m/z (%): 382 (2) [M(d_2)]$^+$, 381 (1) [M(d_1)]$^+$, 380 (0) [M(d_0)]$^+$, 123 (100) [PMB(d_2)], 122 (37) [PMB(d_1)], 121 (5) [PMB(d_0)].

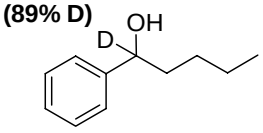
3-*O*-Benzyloxymethyl-1,2:5,6-di-*O*-isopropyridene-α-gulcofuranose-d_2 (39-d, Table 12, Entry 12)



39-d

^{1}H NMR (CD_3OD) δ 1.18 (s, 3H), 1.18 (s, 3H), 1.27 (s, 3H), 1.35 (s, 3H), 3.82 (dd, *J* = 8.6, 5.3 Hz, 1H, H-6), 3.96–4.00 (m, 3H, H-4, H-6'), 4.15 (d, *J* = 2.9 Hz, 1H, H-3), 4.21 (m, 1H, H-5), 4.45 (br s, 0.06H, -OC<u>H</u>$_2$Ph), 4.50 (d, *J* = 3.7 Hz, 1H, H-2), 4.64 (br s, 0.08H, -OC<u>H</u>$_2$Ph), 4.72 (d, *J* = 7.0 Hz, 1H, -OC<u>H</u>$_2$OPh), 4.76 (d, *J* = 7.0 Hz, 1H, -OC<u>H</u>$_2$OPh), 5.72 (d, *J* = 3.7 Hz, 1H, H-1), 7.17–7.28 (m, 5H, Ph); ^{2}H NMR (CH_3OH) δ 4.53 (br s), 4.72 (br s, 1H); MS (NBA, FAB) m/z (%): 383 (10) [M(d_2)+H]$^+$, 382 (2) [M(d_1)+H]$^+$, 381 (1) [M(d_0)+H]$^+$, 93 (54) [Bn(d_2)].

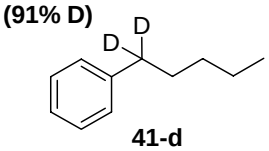
1-Phenyl-1-pentanol-d_1 (40-d, Scheme 1)



40-d

A suspension of 1-phenyl-1-pentanol (82.1mg, 0.500 mmol) and 5% Pd/C(en) (16.4 mg, 20 wt % of the substrate) in D_2O (3 mL) in a 50 mL flask filled with hydrogen (75 mL) was stirred for at 50 ˚C. After 72 h, the mixture was cooled to room temperature, diluted with Et_2O (10 mL), and then passed through a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtrate was partitioned between ethereal and aqueous layers. The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined ethereal layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : Et_2O = 15 : 1) to give 1-phenyl-1-pentanol-d_1 (63.6 mg, 77%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 0.88 (t, , J = 7.2 Hz, 3H), 1.17–1.40 (m, 4H), 1.70 (m, 2H), 4.57 (t, J = 6.7 Hz, 0.11H), 7.19–7.33 (m, 5H); ^{2}H NMR (CH_3OH) δ 4.56 (br s); MS (EI) m/z (%): 165 (8) $[M(d_1)]^+$, 164 (1) $[M(d_0)]^+$, 108 (100), 80 (32).

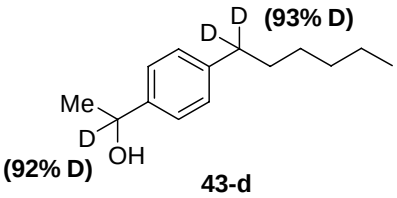
Amylbenzene-d_2 (41-d, Scheme 1)



41-d

A suspension of 1-phenyl-1-pentanol (164 mg, 1.00 mmol) and 5% Pd/C (32.9 mg, 20 wt % of the substrate) in D_2O (3 mL) in a 100 mL flask filled with hydrogen (160 mL) was stirred for at 50 ˚C. After 24 h, the mixture was cooled to room temperature, diluted with Et_2O (10 mL), and then passed through a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtrate was partitioned between ethereal and aqueous layers. The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined ethereal layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by a preparative TLC (hexane) to give amylbenzene-d_2 (104 mg, 70%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 0.89 (t, , J = 7.0 Hz, 3H), 1.25–1.39 (m, 4H), 1.58 (t, J = 7.0 Hz, 2H), 2.55 (m, 0.18H), 7.09–7.15 (m, 3H), 7.22 (m, 2H),; ^{2}H NMR (CH_3OH) δ 2.54 (br s); MS (EI) m/z (%): 150 (41) $[M(d_2)]^+$, 149 (9) $[M(d_1)]^+$, 148 (1) $[M(d_0)]^+$, 93 (100), 92 (28).

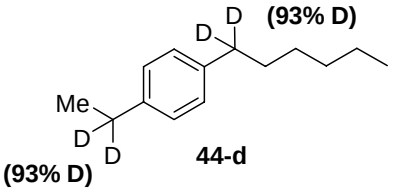
1-(4-Hexylphenyl)ethanol-d_3 (43-d, Scheme 2)



43-d

A suspension of *p*-hexylacetophenone (102 mg, 0.500 mmol) and 5% Pd/C(en) (20.4 mg, 20 wt % of the substrate) in D_2O (3 mL) in a test tube filled with hydrogen (125 mL) was stirred for at 50 ˚C. After 24 h, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and then passed through a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtrate was partitioned between ethyl acetate and aqueous layers. The aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane : ethyl acetate = 10 : 1) to give 1-(4-hexylphenyl)ethanol-d_3 (92.0 mg, 89%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 0.88 (m, 3H), 1.30–1.34 (m, 6H), 1.41 (m, 3H), 1.57 (m, 2H), 2.55 (t, J = 7.7 Hz, 0.15H), 4.77 (q, J = 6.3 Hz, 0.16H), 7.12 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H); ^{2}H NMR (CH_3OH) δ 1.39 (br s), 2.53 (br s), 4.75 (br s); MS (EI) m/z (%): 209 (18) $[M(d_3)]^+$, 208 (4) $[M(d_2)]^+$, 207 (1) $[M(d_1)]^+$, 206 (1) $[M(d_0)]^+$, 194 (100).

1-Ethyl-4-hexylbenzene-d_4 (44-d, Scheme 2)



44-d

A suspension of *p*-hexylacetophenone (102 mg, 0.500 mmol) and 5% Pd/C (20.4 mg, 20 wt % of the substrate) in D_2O (3 mL) in a test tube filled with hydrogen (125 mL) was stirred for at 50 ˚C. After 24 h, the mixture was cooled to room temperature, diluted with ethyl acetate (10 mL), and then filtered using a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtrate was partitioned between ethyl acetate and aqueous layers. The aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane) to give 1-ethyl-4-hexylbenzene-d_4 (91.5 mg, 96%) as a colorless oil: ^{1}H NMR (CD_3OD) δ 0.79 (t, J = 6.5 Hz, 3H), 1.07 (m, 2H), 1.20–1.23 (m, 7H), 1.46 (m, 2H), 2.40–2.47 (m, 0.27H), 6.93–7.00 (m, 4H); ^{2}H NMR (CH_3OH) δ 0.80 (br s), 1.12 (br s), 1.52 (br s), 2.51 (br s); MS (EI) m/z (%): 194 (32) $[M(d_4)]^+$, 193 (12) $[M(d_3)]^+$, 192 (6) $[M(d_2)]^+$, 191 (4) $[M(d_1)]^+$, 190 (2) $[M(d_0)]^+$, 123 (100).

References

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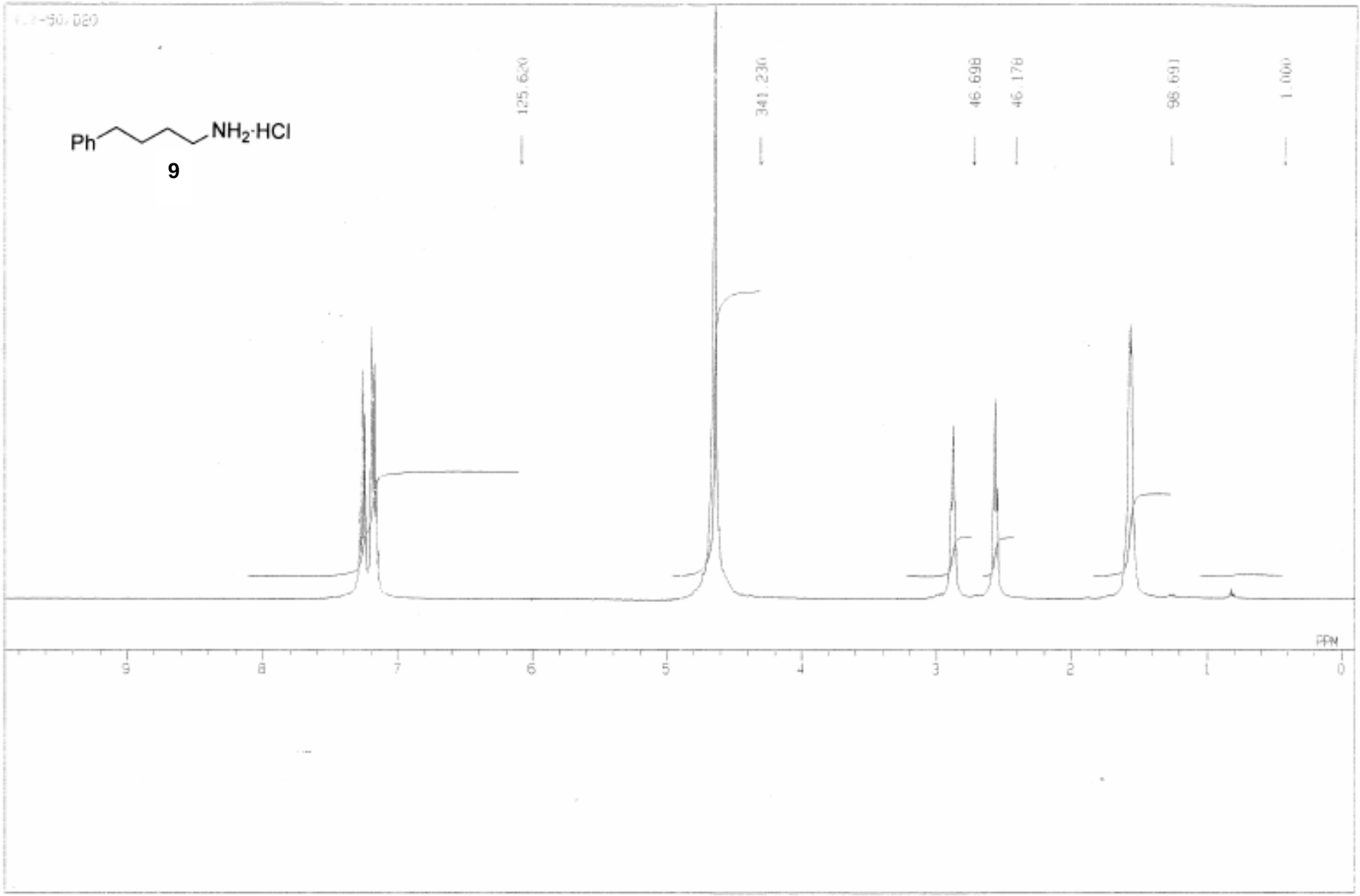
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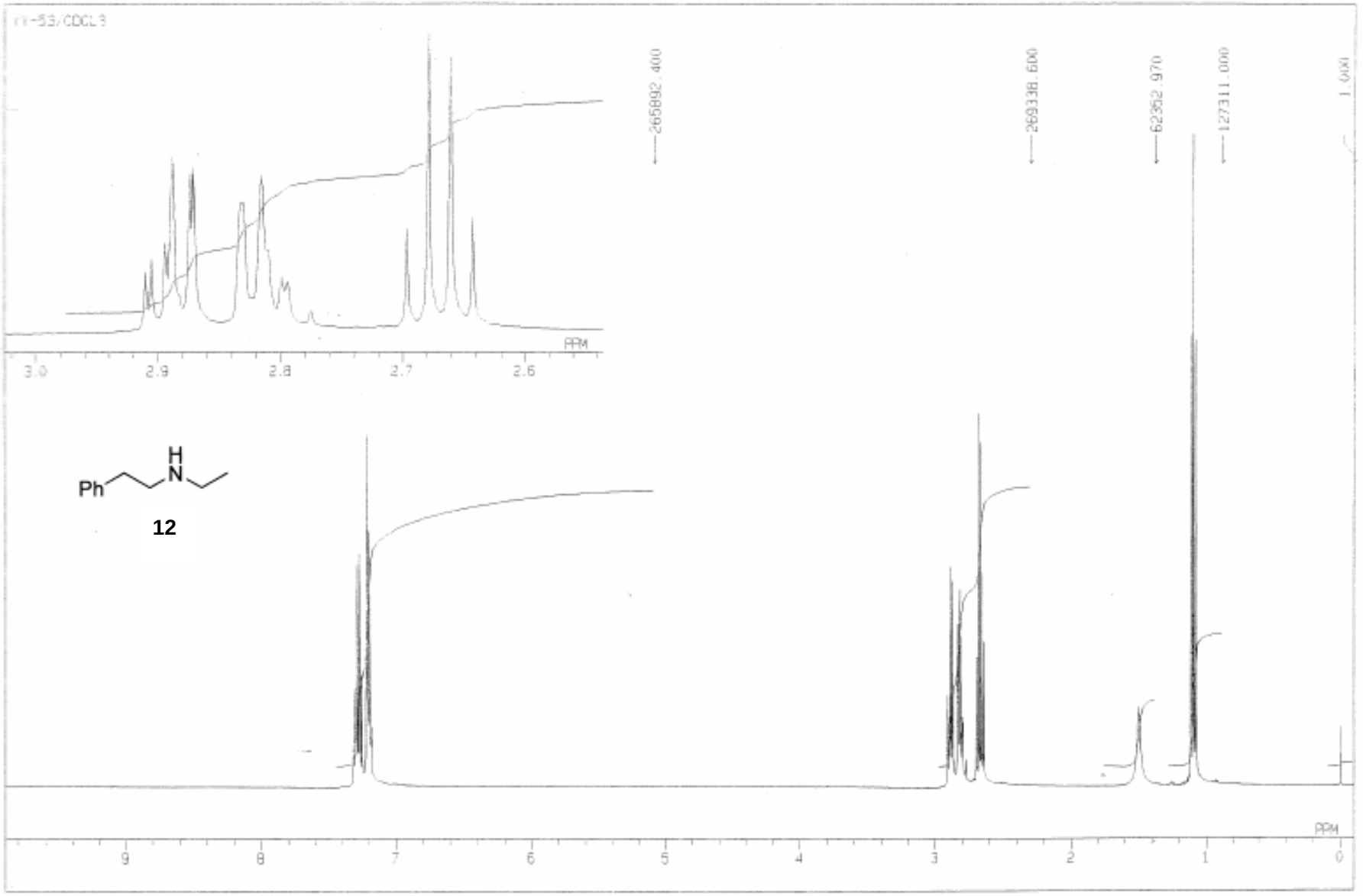
NH2·HCl
9
125.620
341.230
46.698
46.178
98.691
1.000
PPM
9
8
7
6
5
4
3
2
1
0


Ph
H
N
12
PPM
PPM

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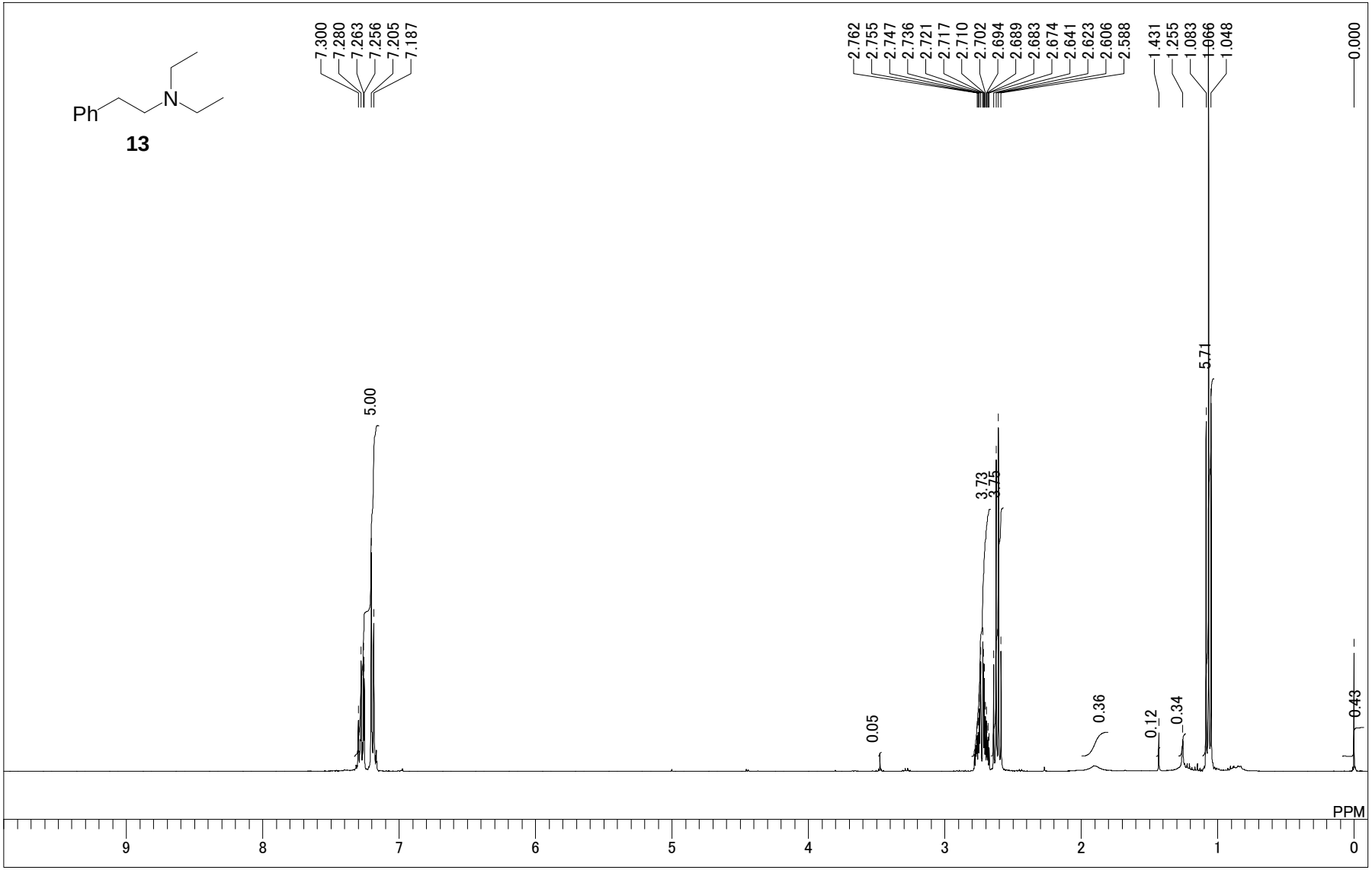
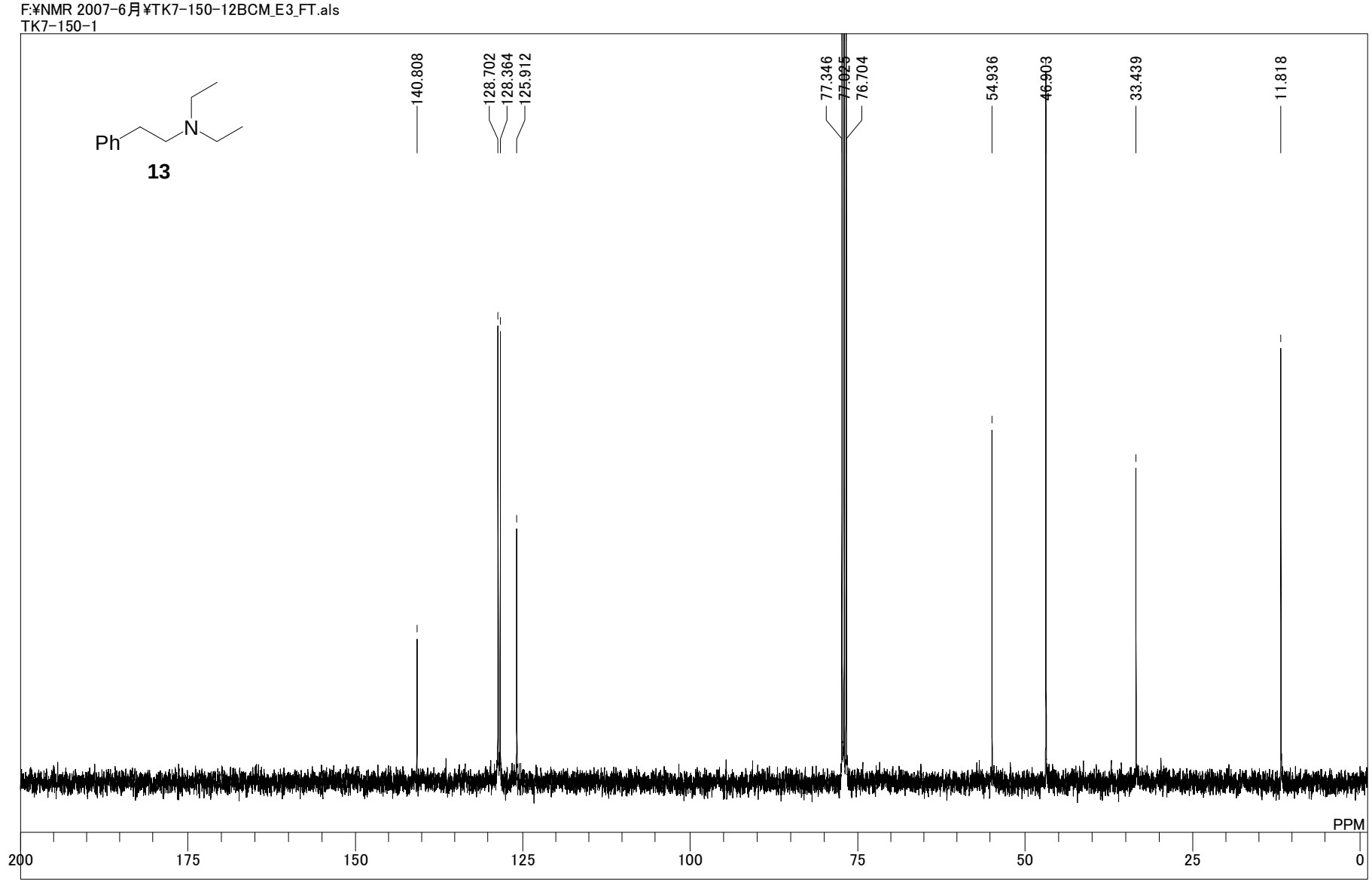
TK7-150-1

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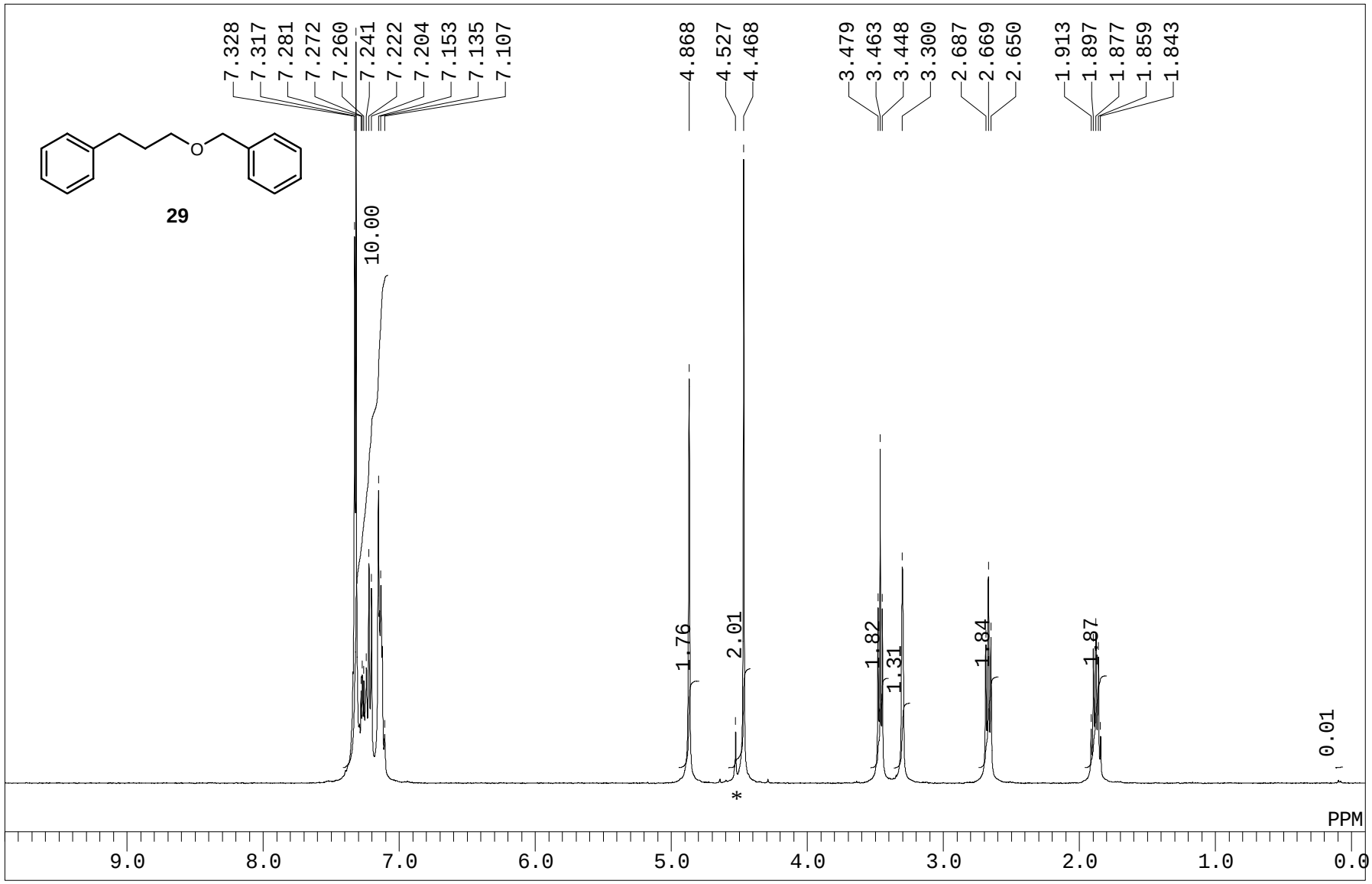
TK7-150-1
Ph
N
13
140.808
128.702
128.364
125.912
77.346
77.025
76.704
54.936
46.903
33.439
11.818
PPM
200
175
150
125
100
75
50
25
0

J:\1-16\TK5-79-FT.als
TK5-79



* dibenzyl ether (diagnostic singlet: 4.53 ppm, 4H)

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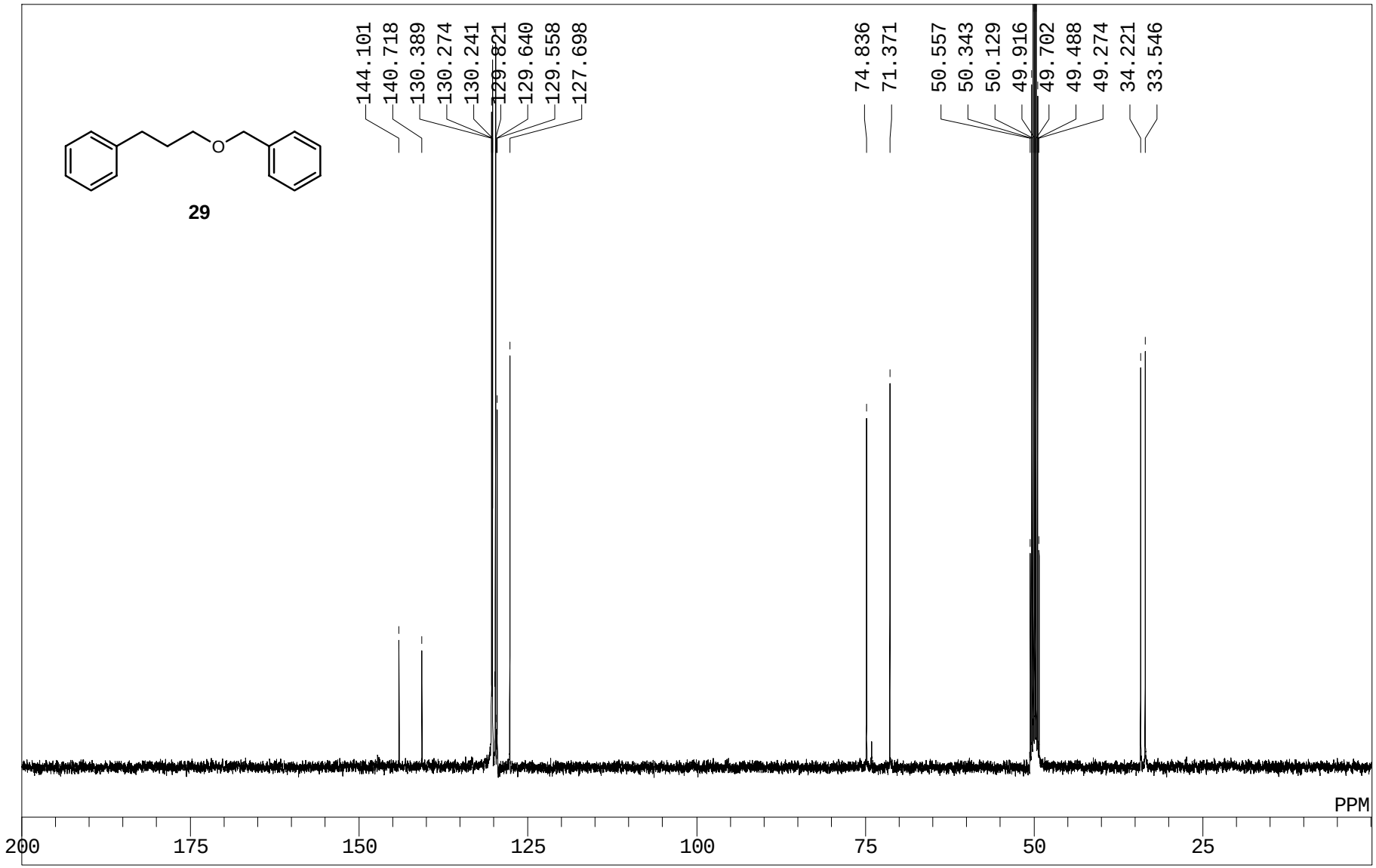
TK5-79



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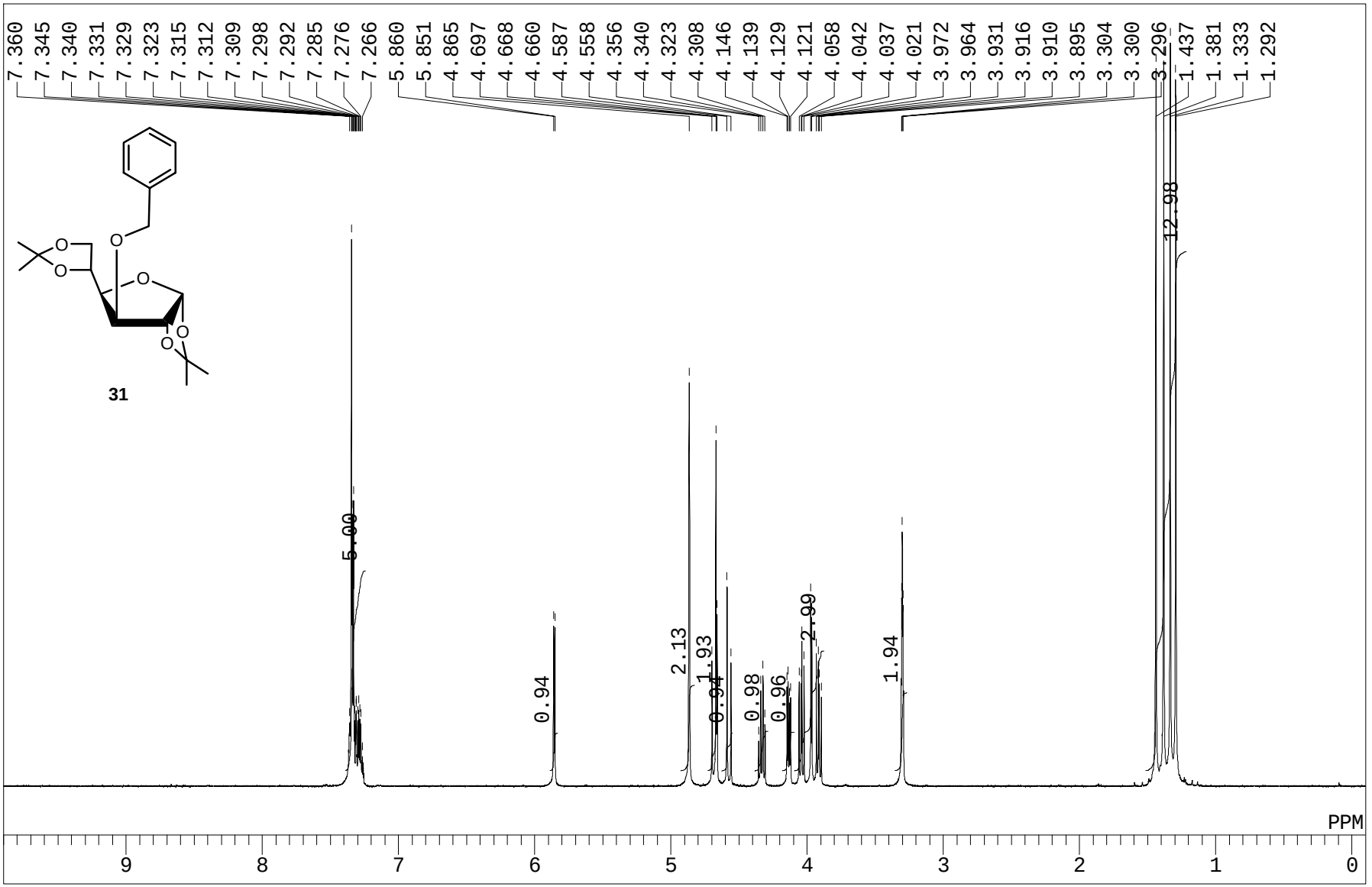
TK5-80



31

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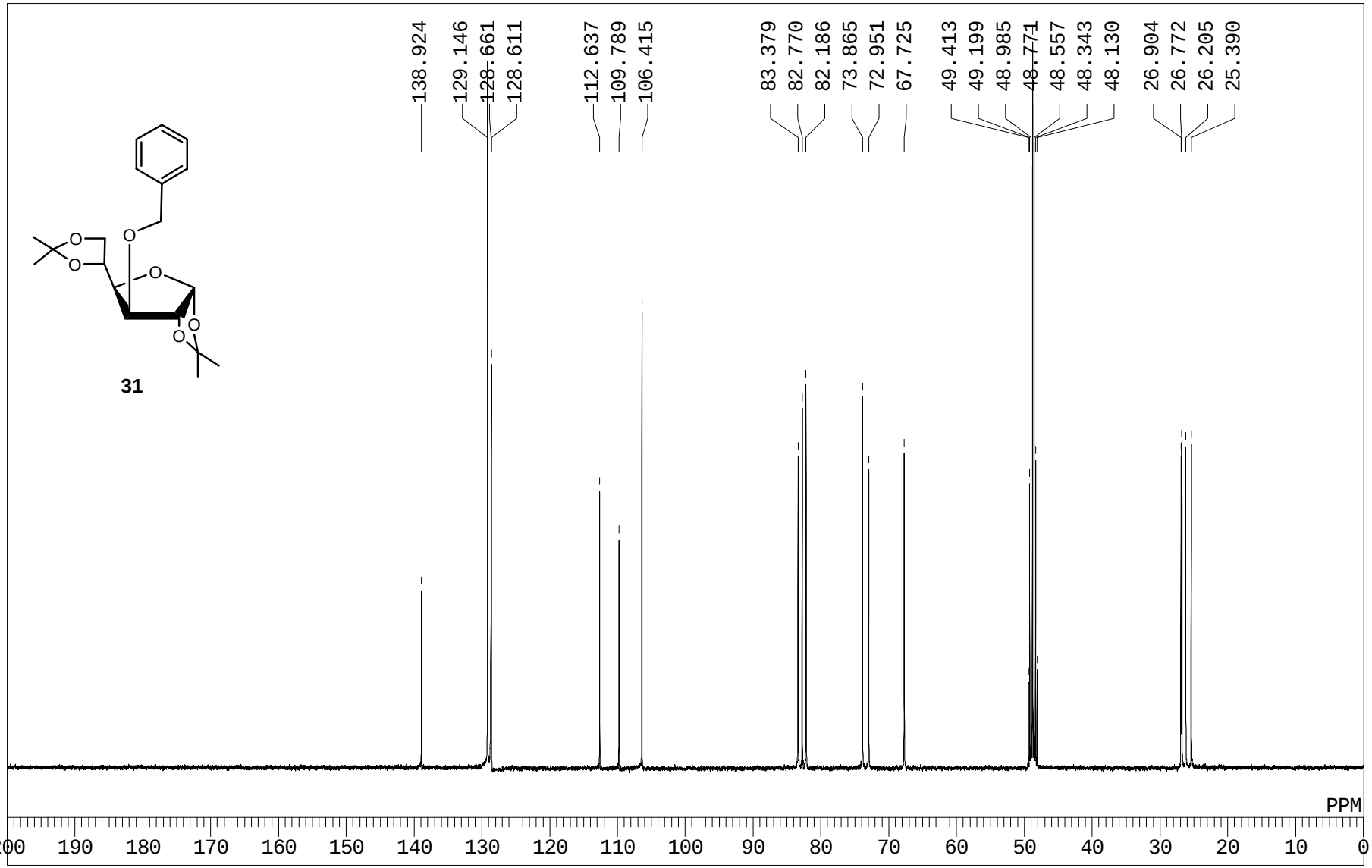
TK5-80-13C NMR



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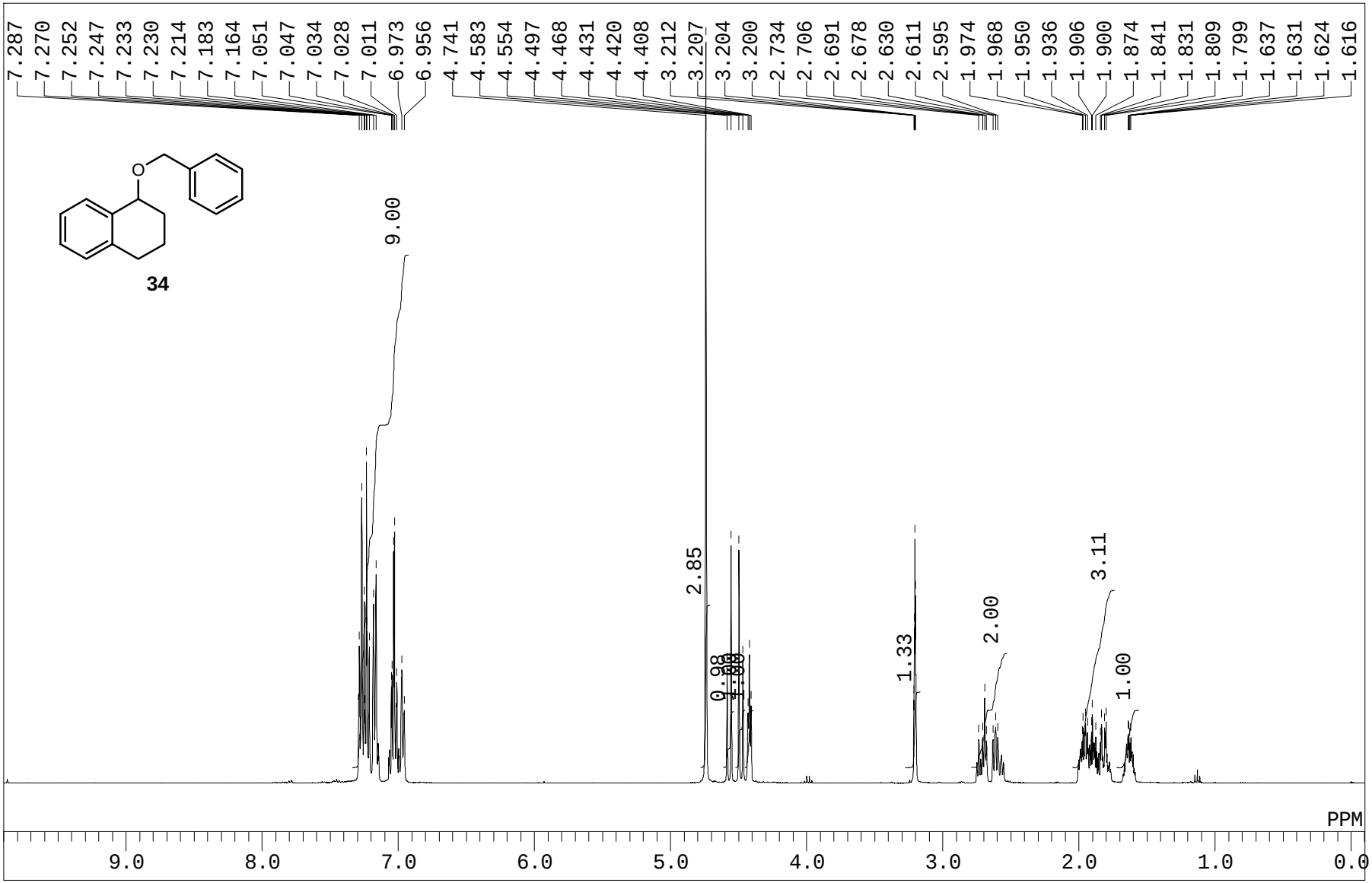
TK6-2



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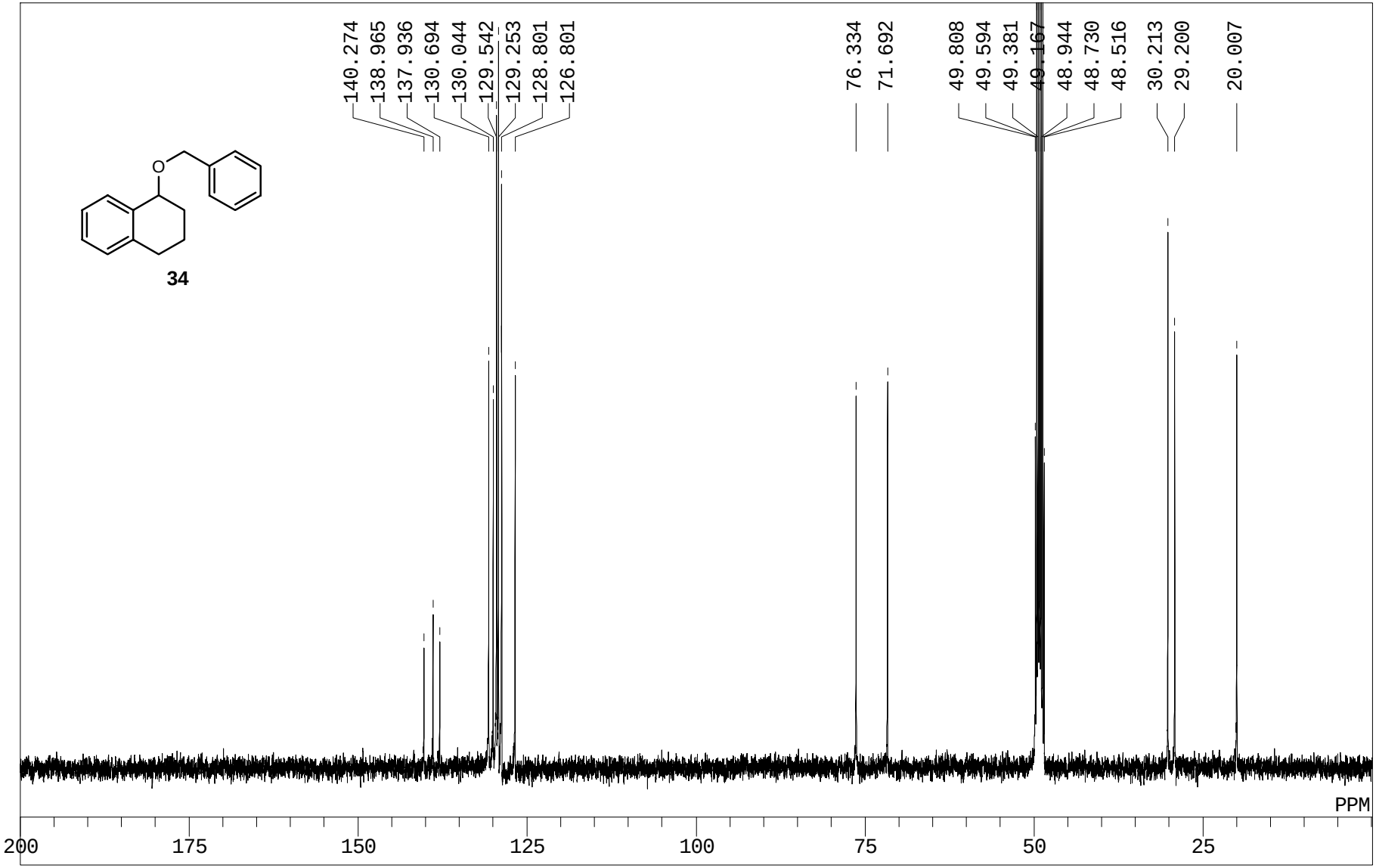
TK6-2



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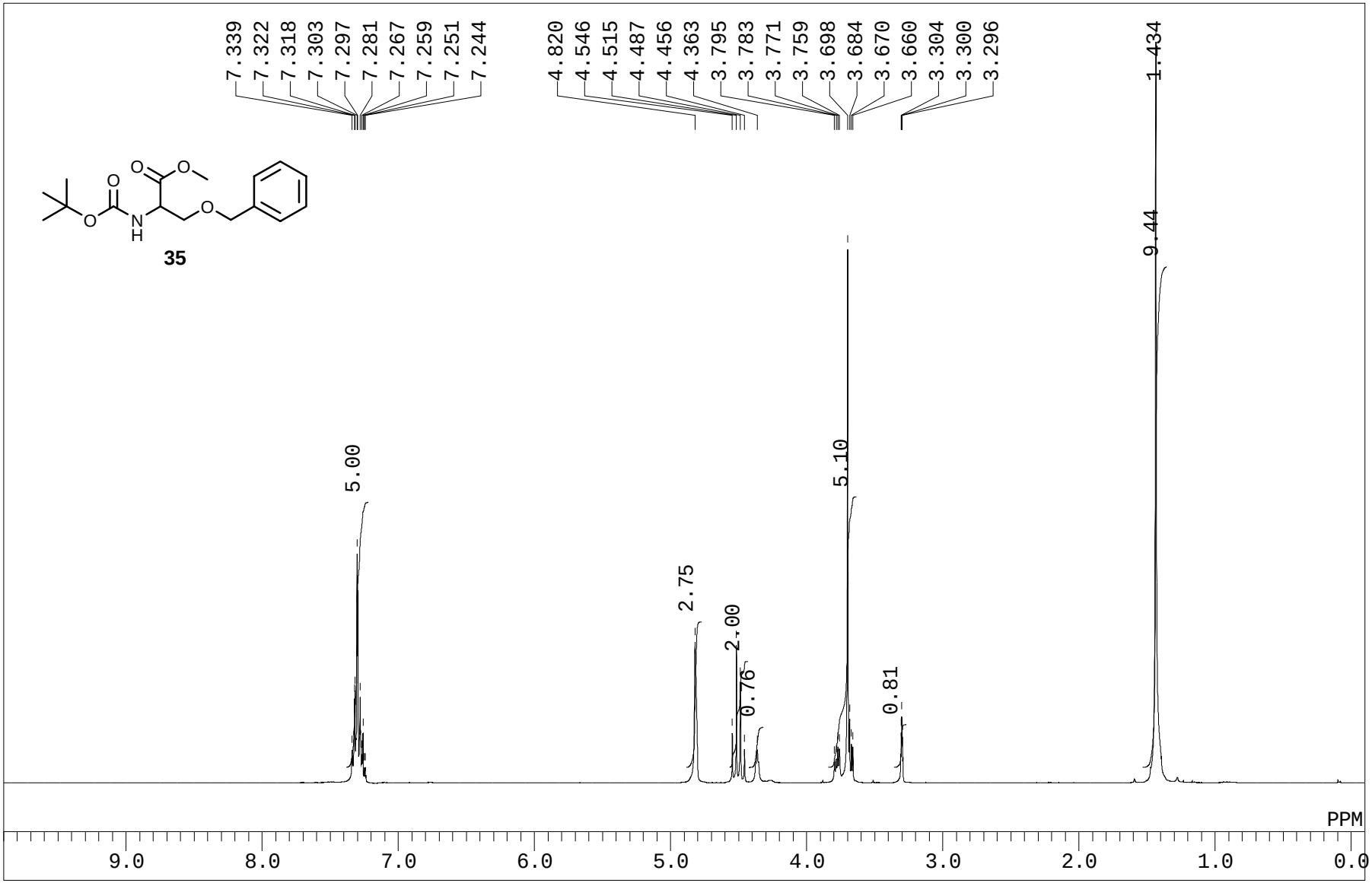

35

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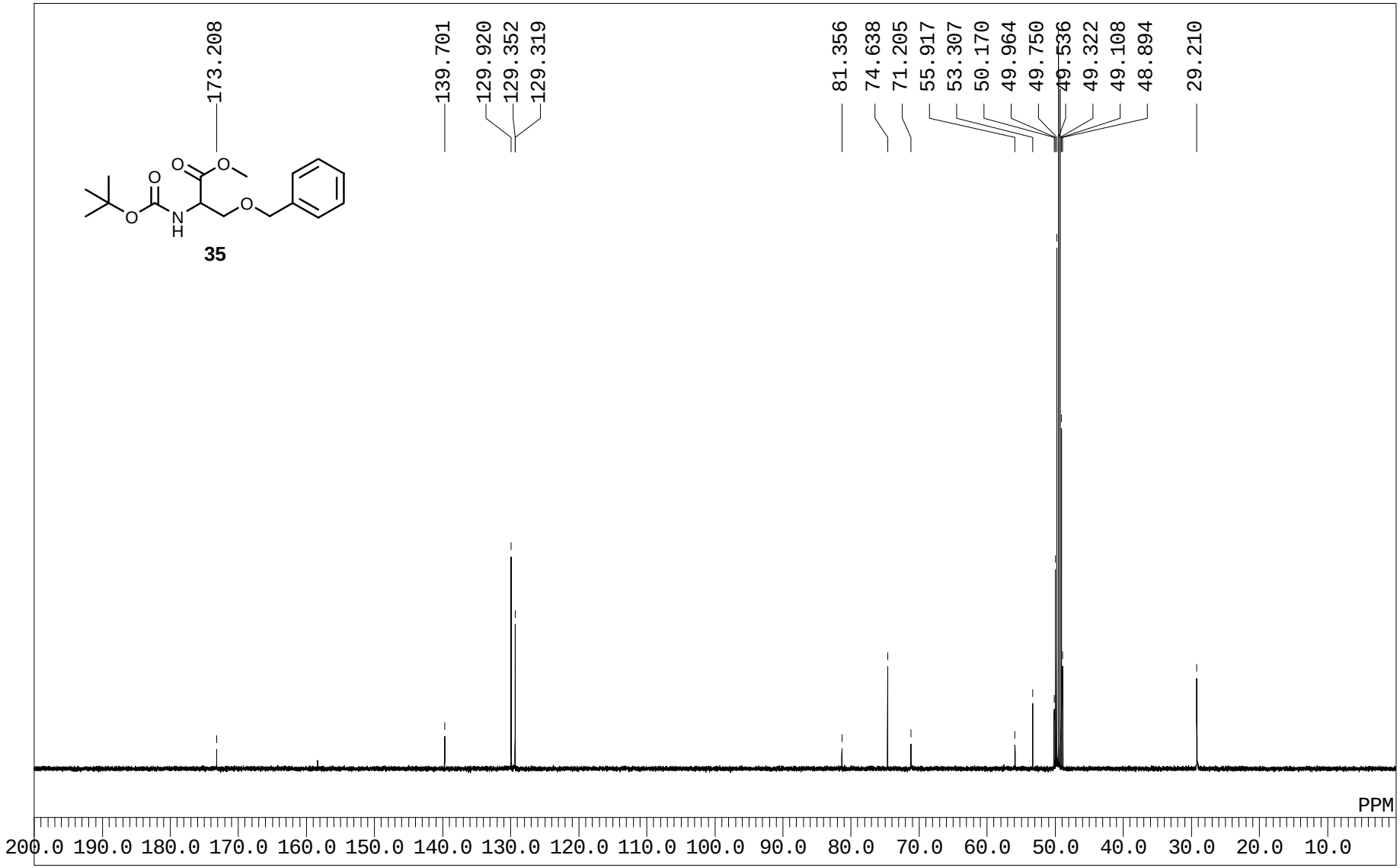
TK5-54-13C NMR



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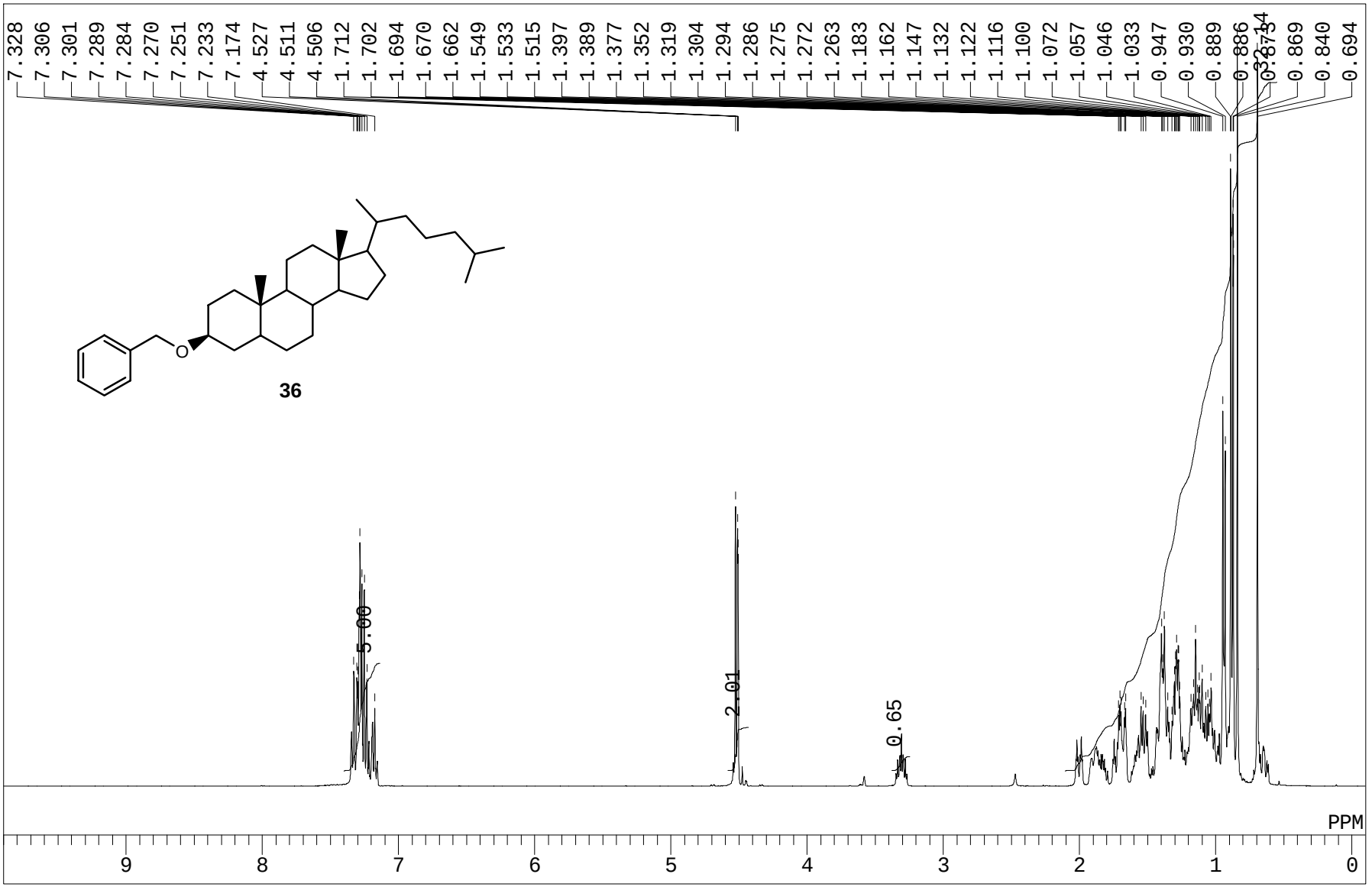
TK6-51



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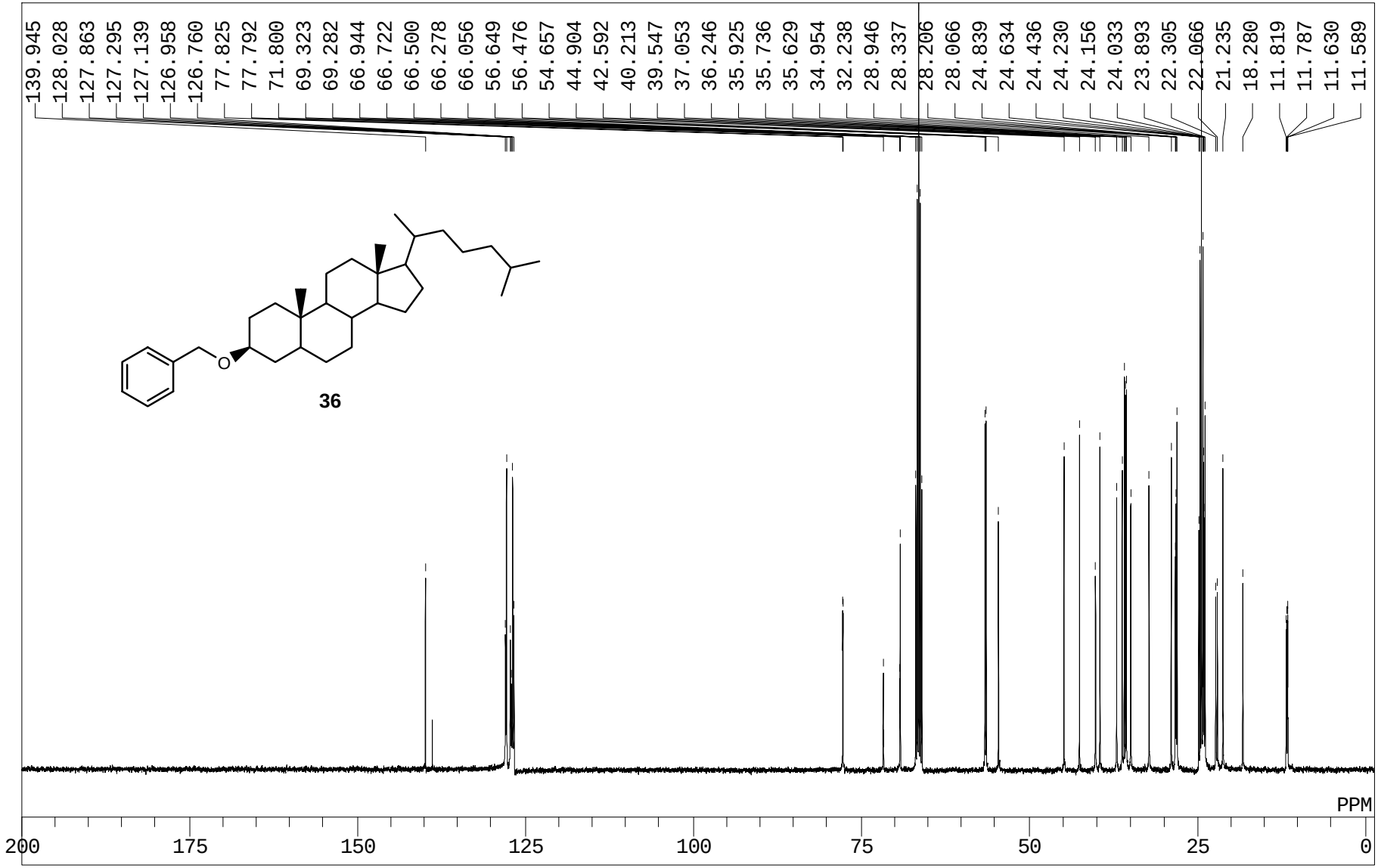

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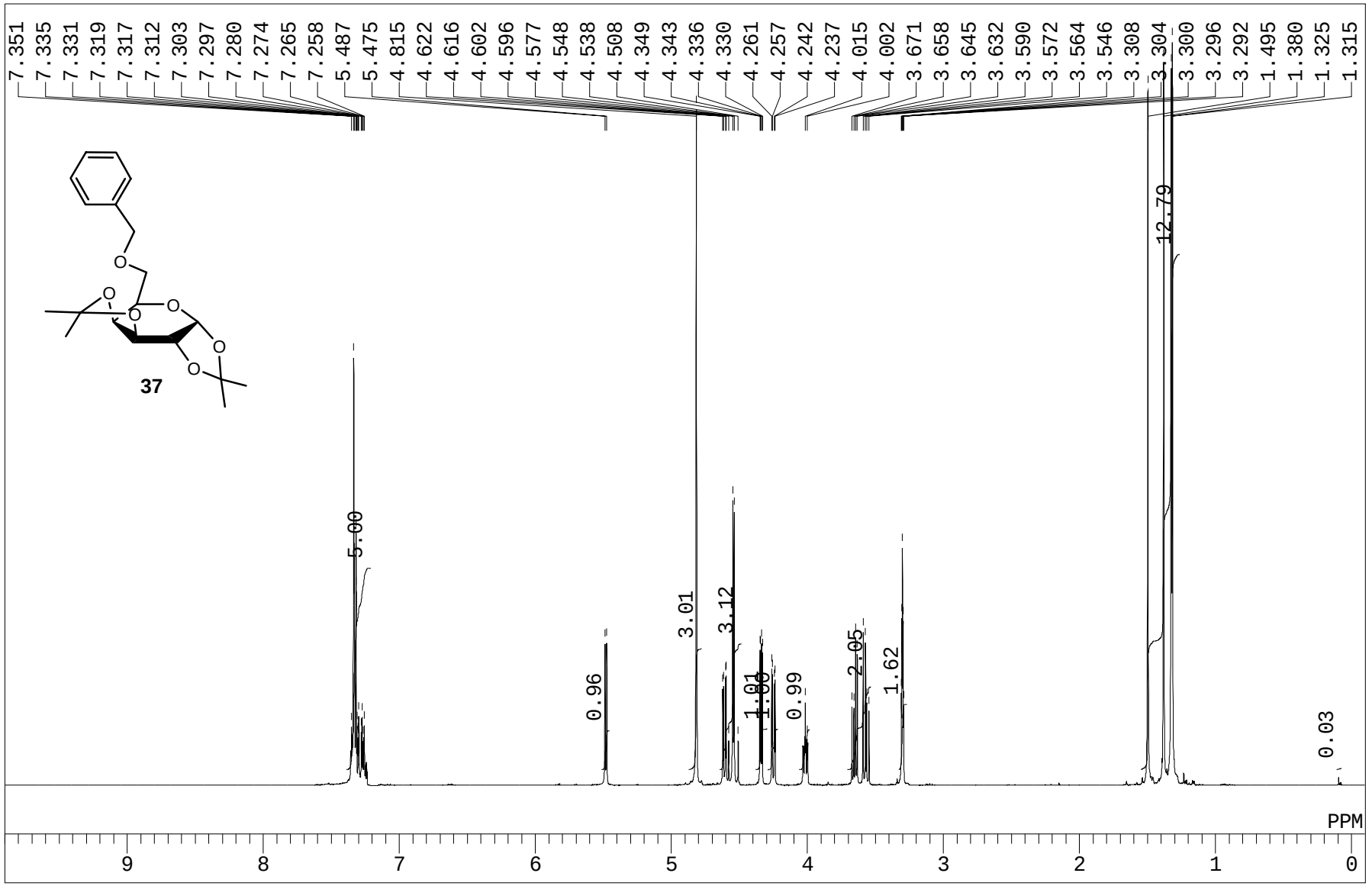
TK6-3



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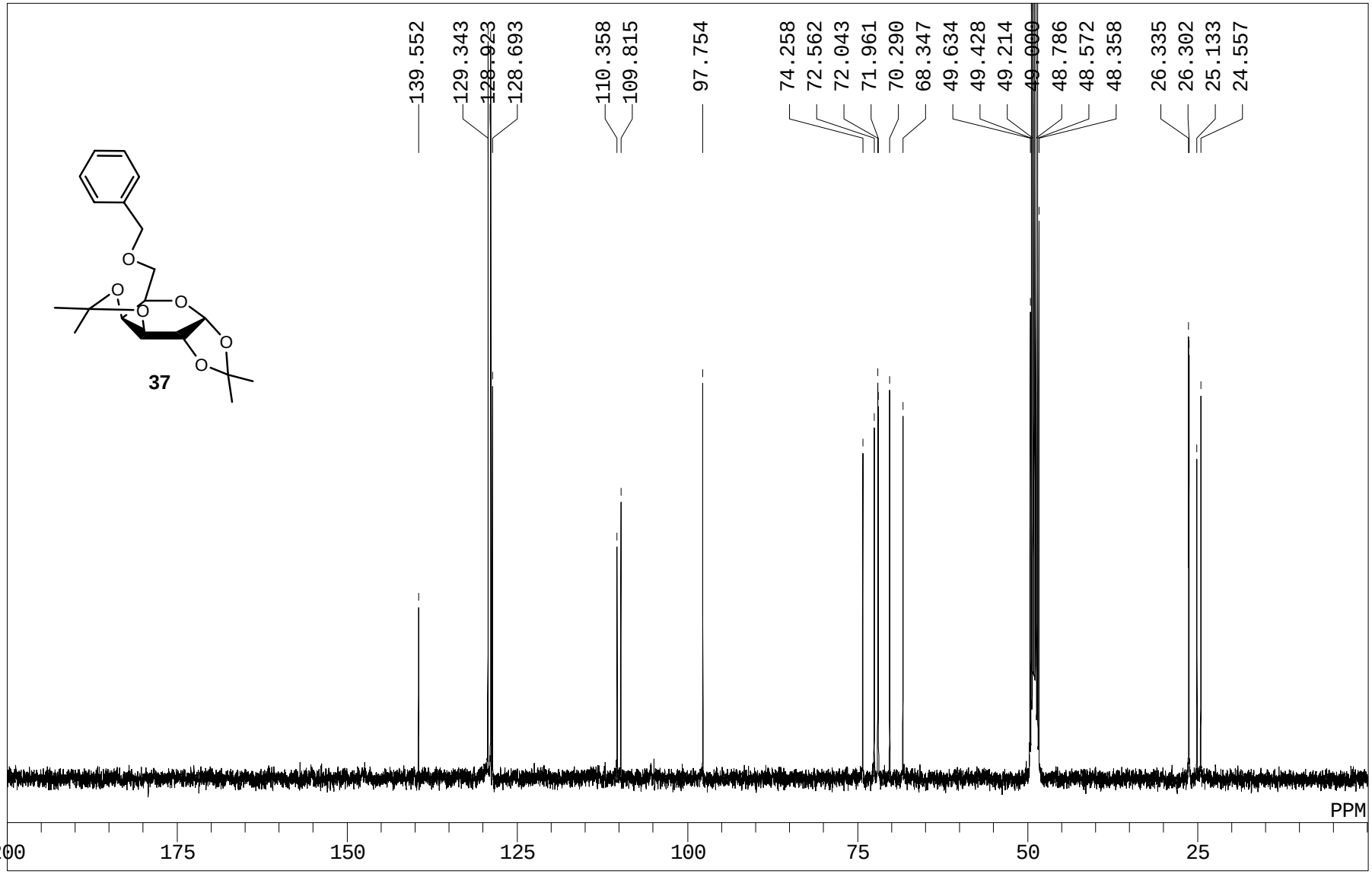
TK6-3-13C NMR



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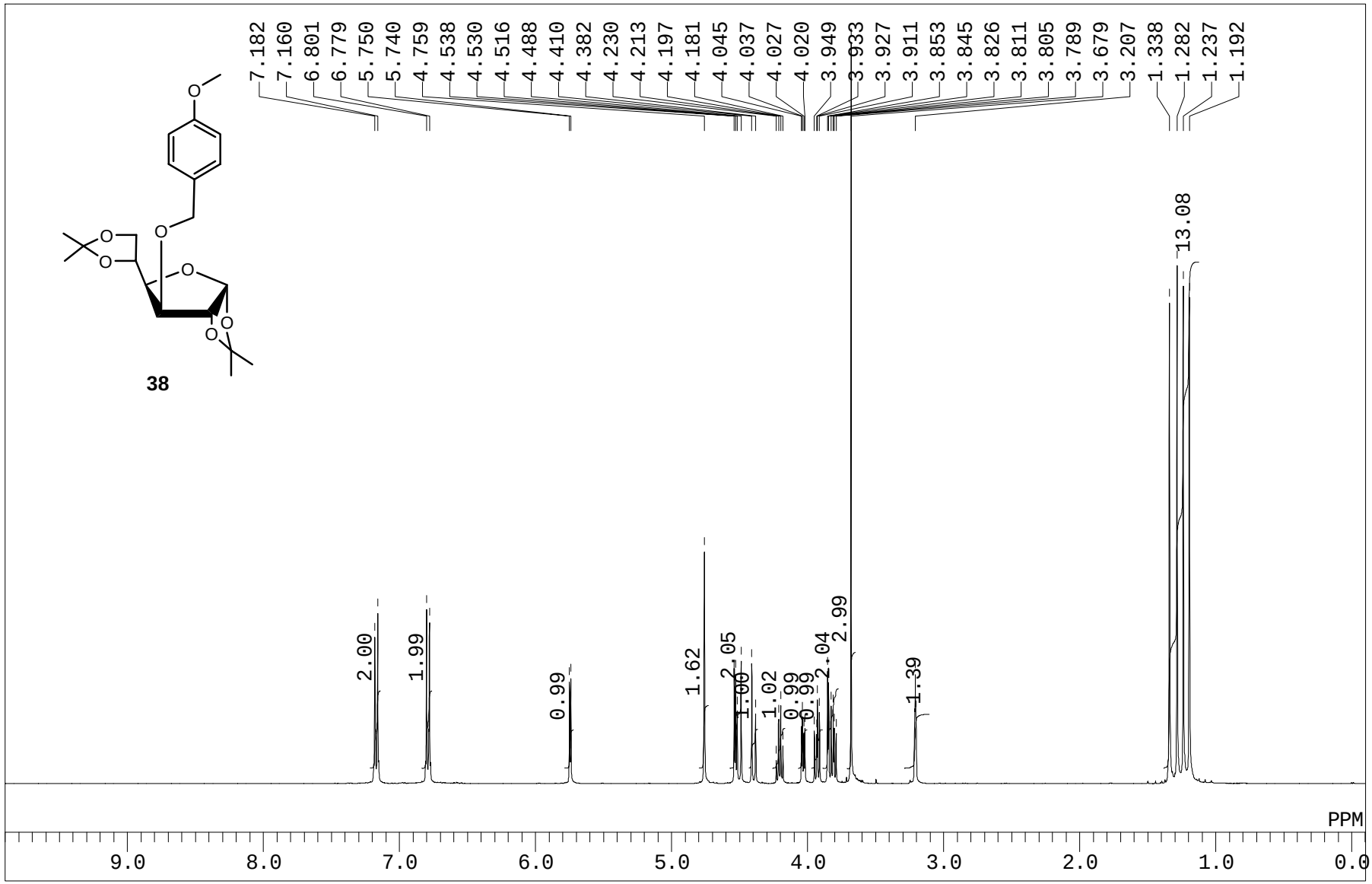

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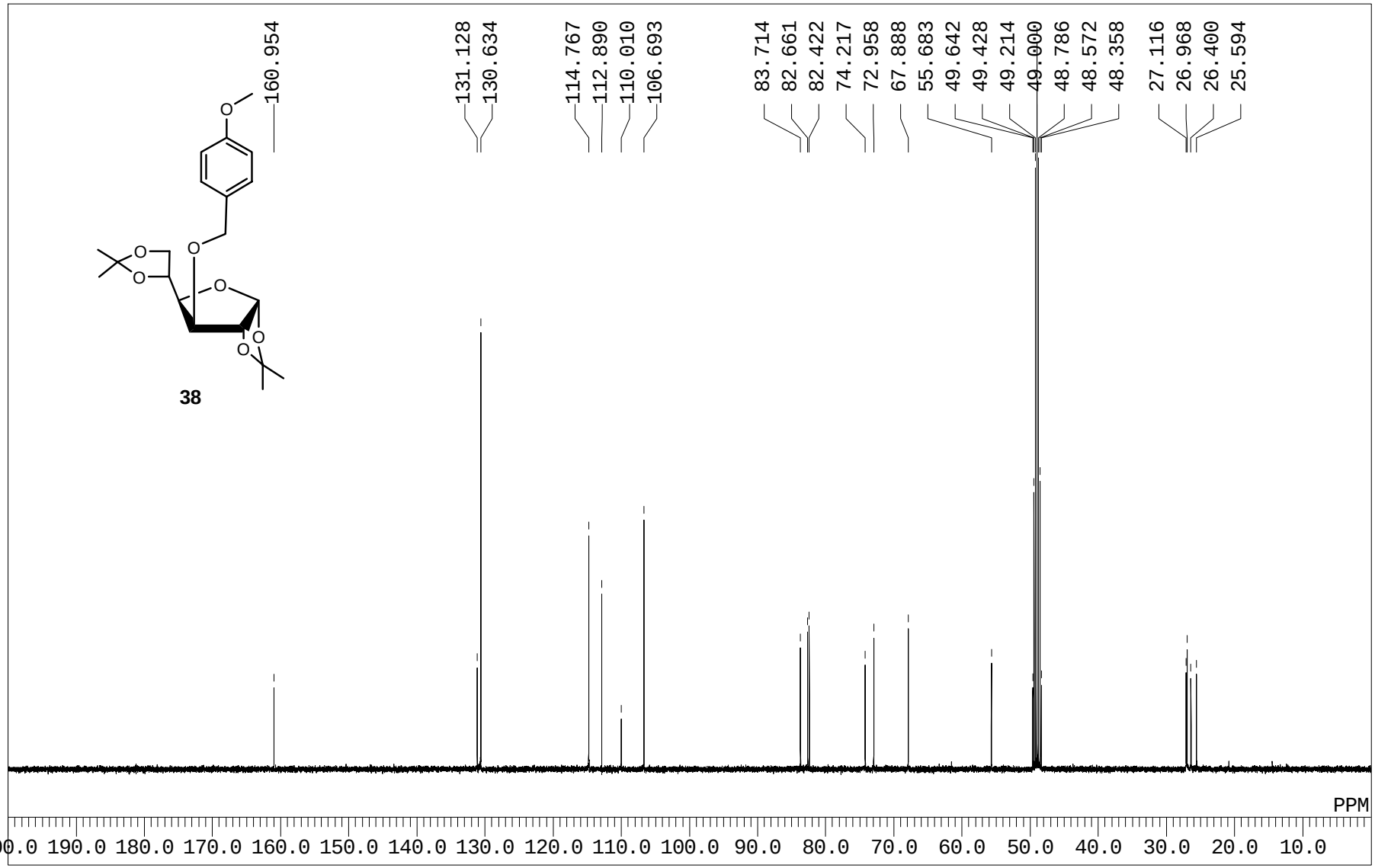

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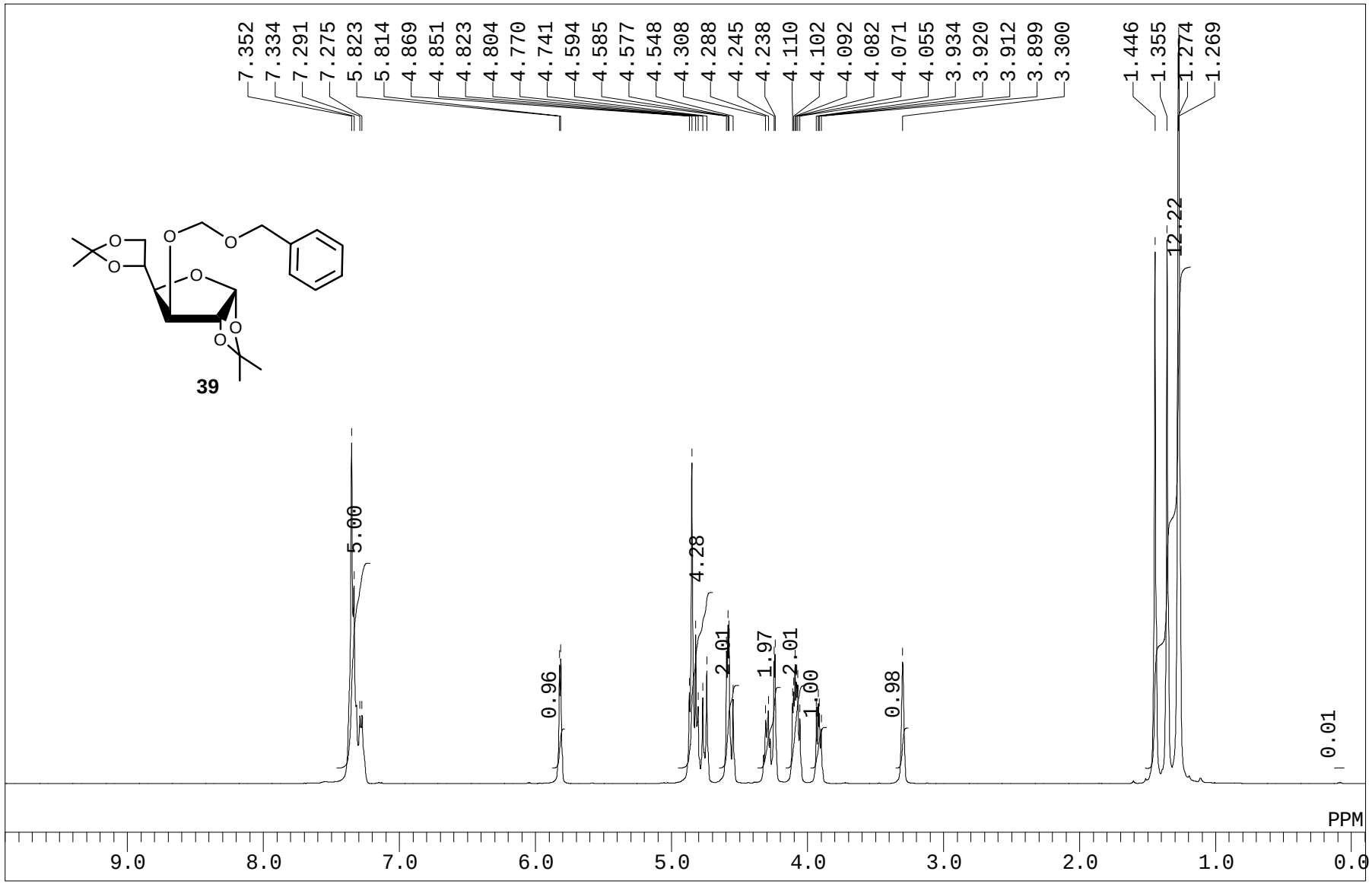

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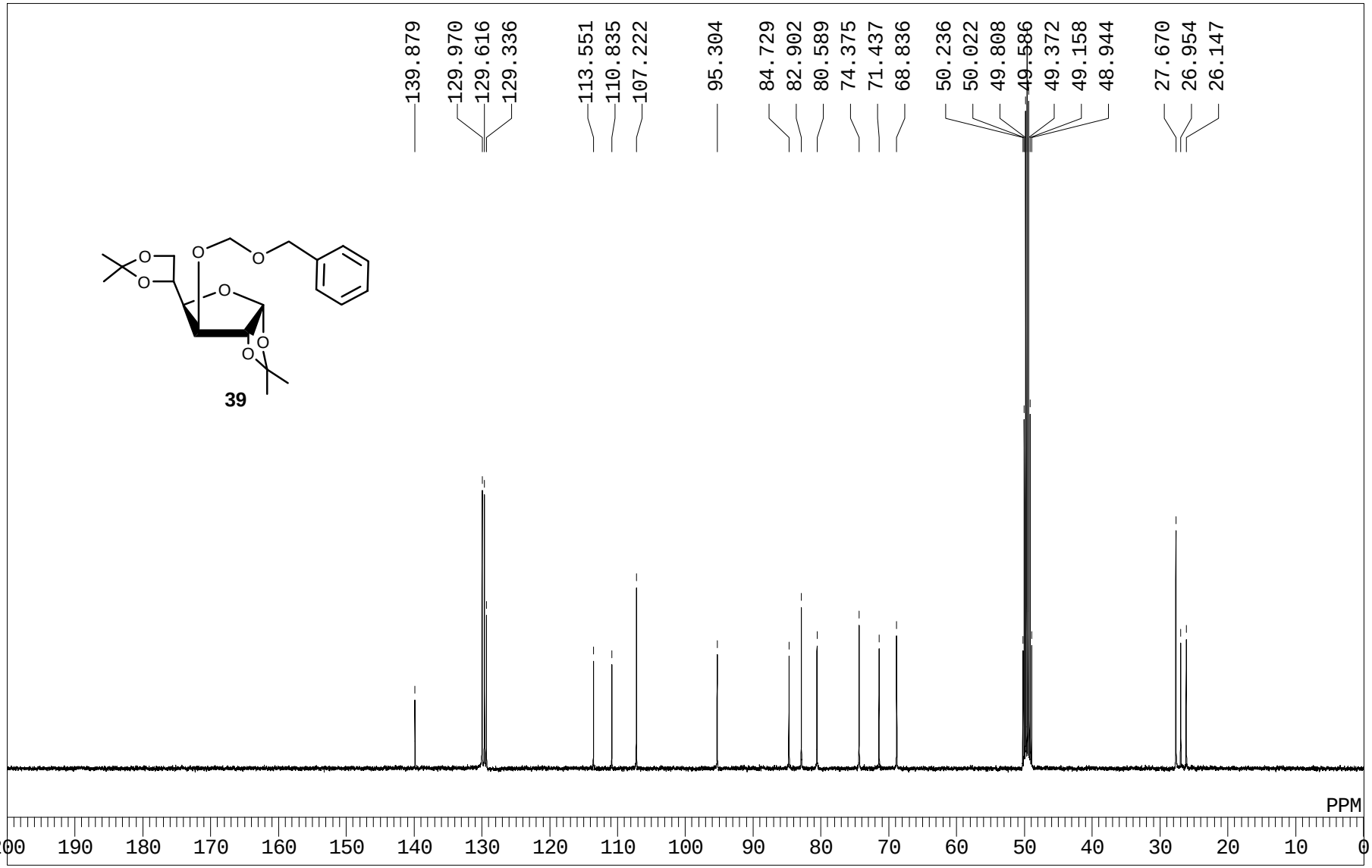
TK6-127-13C NMR



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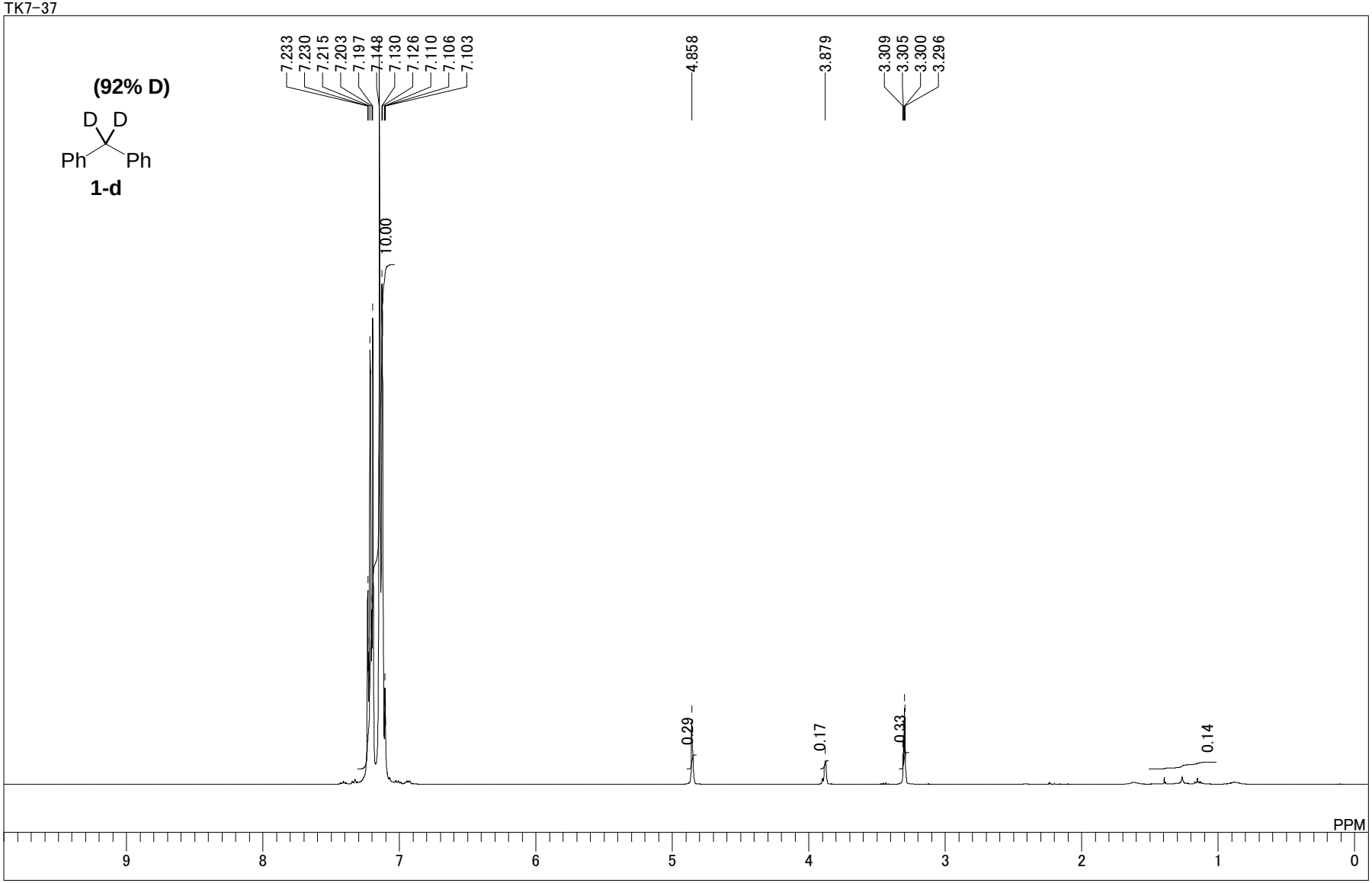
TK7-37



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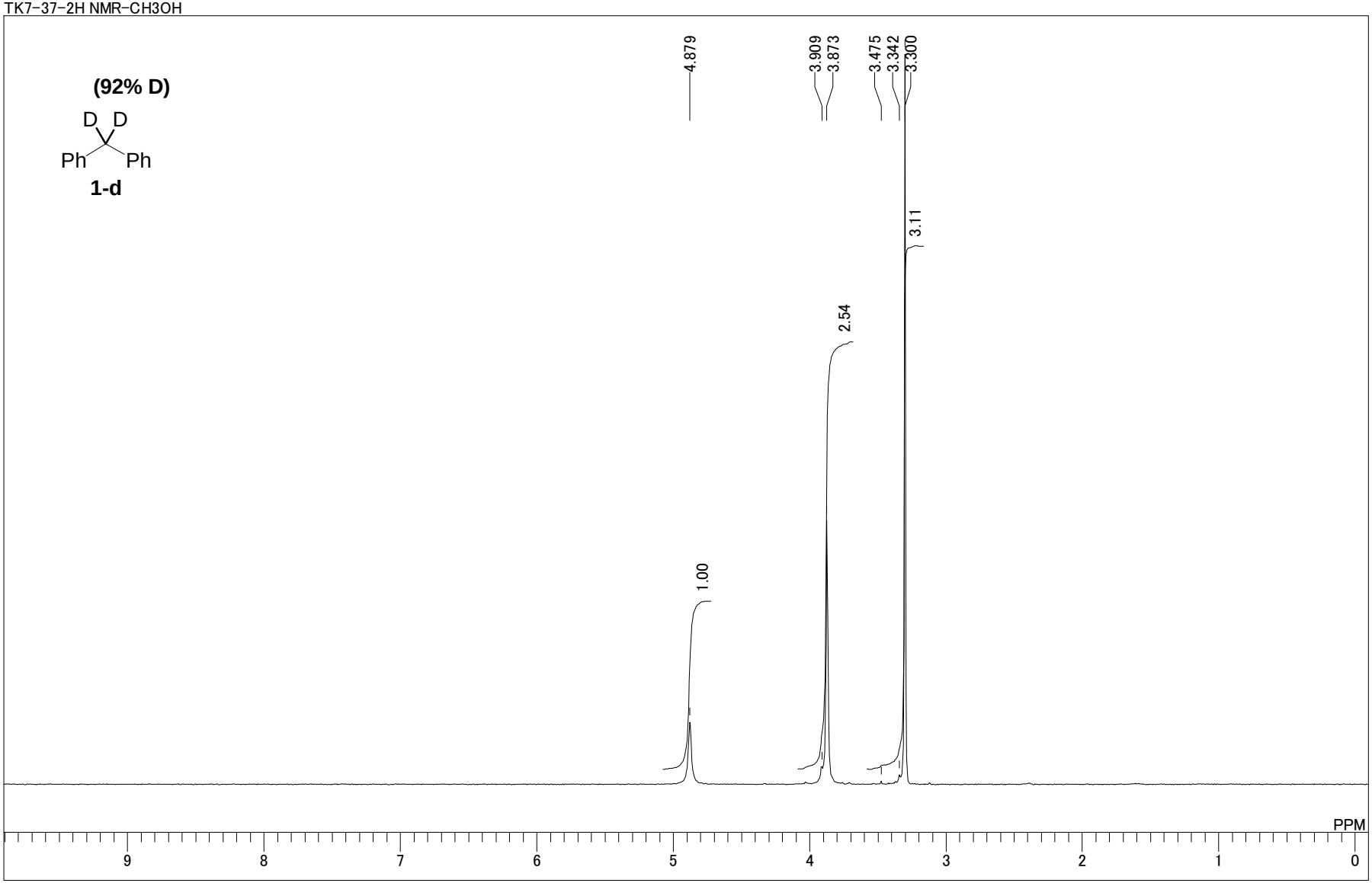
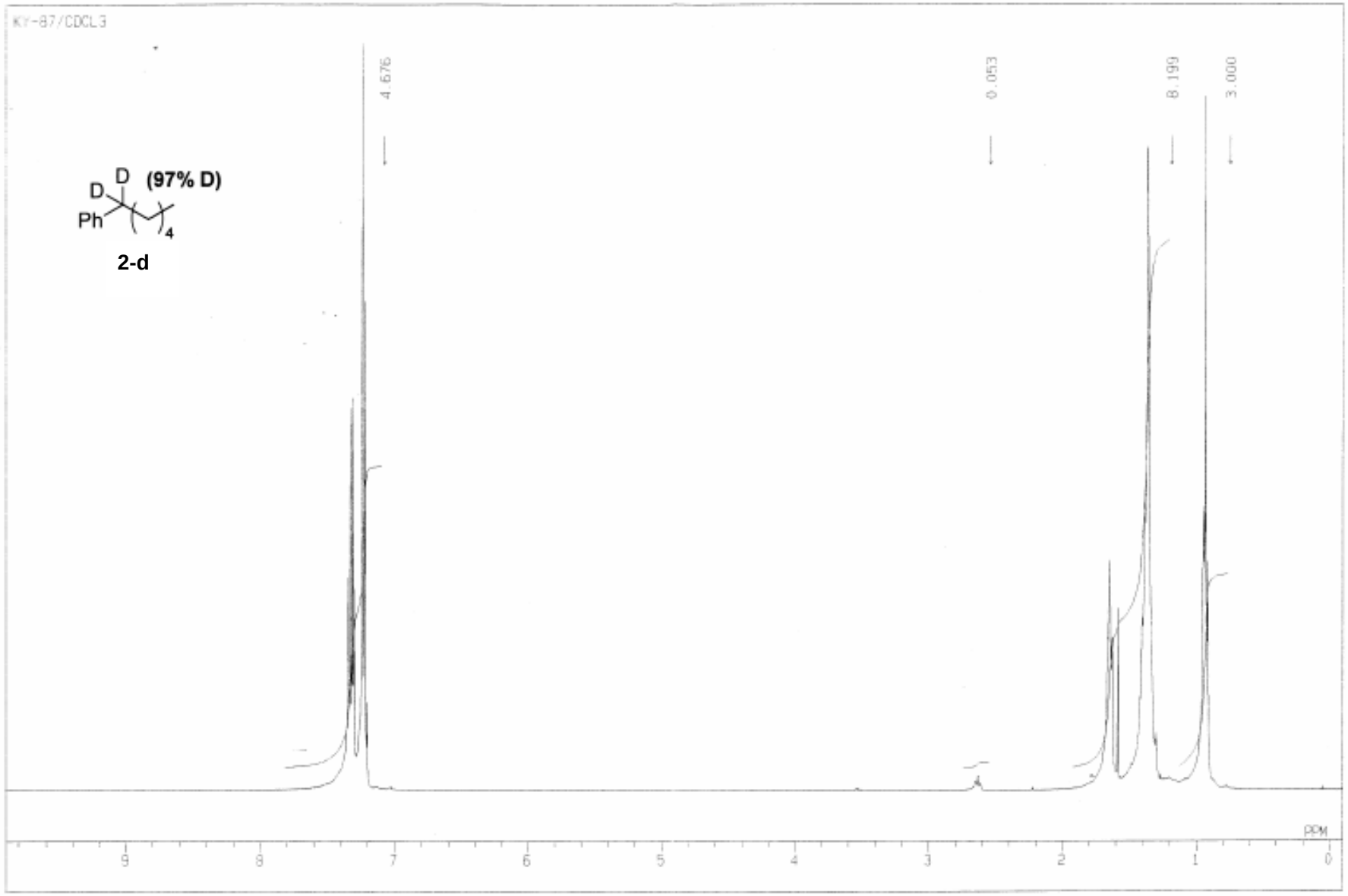
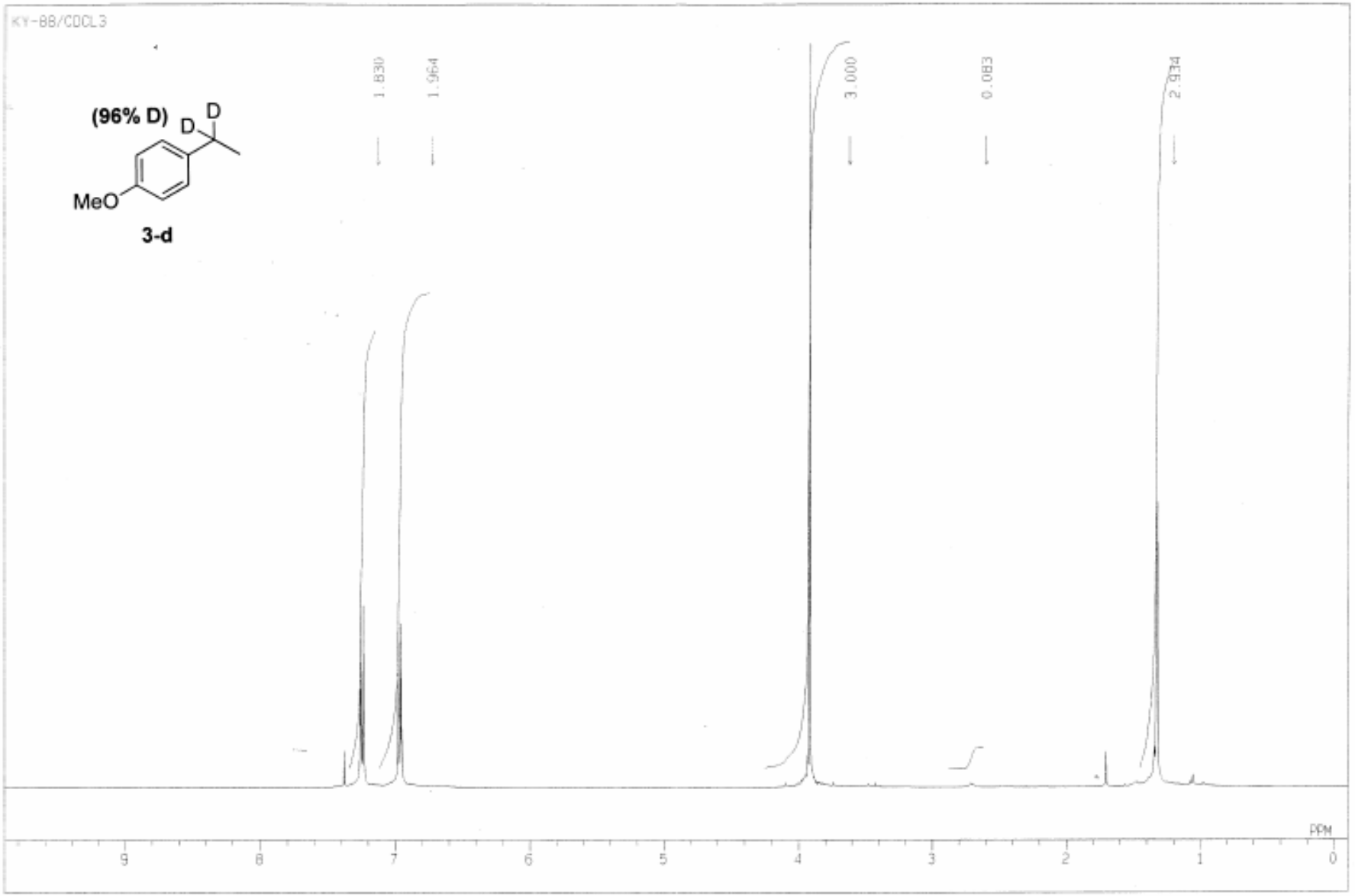
TK7-37-2H NMR-CH3OH




KY-87/CDCL3
4.676
0.053
8.199
3.000
D
D
Ph
4
(97% D)
2-d
PPM
9
8
7
6
5
4
3
2
1
0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D
D
MeO
3-d
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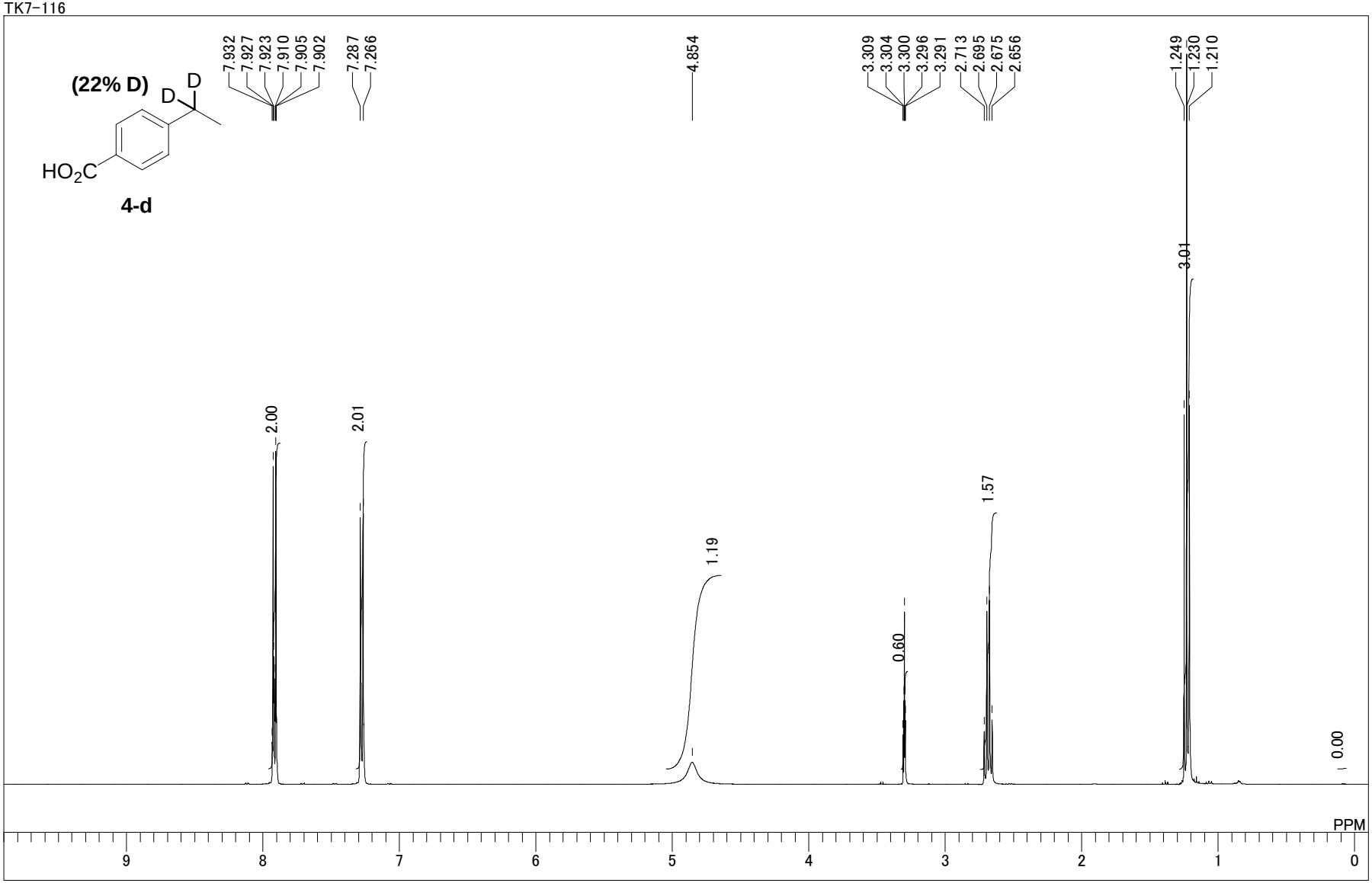
1.964
3.000
0.083
2.934
PPM
9
8
7
6
5
4
3
2
1
0

F:¥NMR 2007-5月¥TK7-1161NON_E2_FT.als
TK7-116



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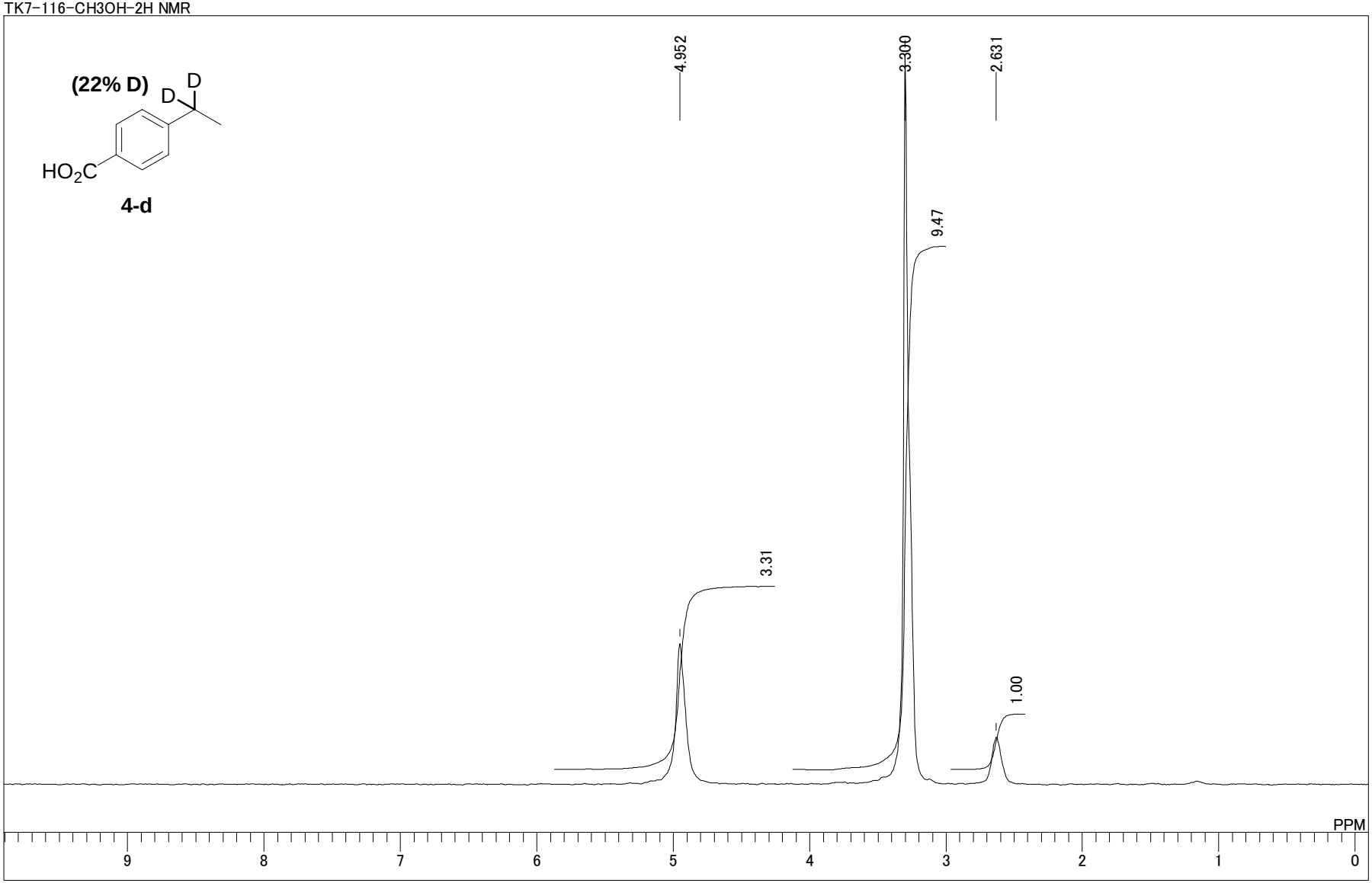
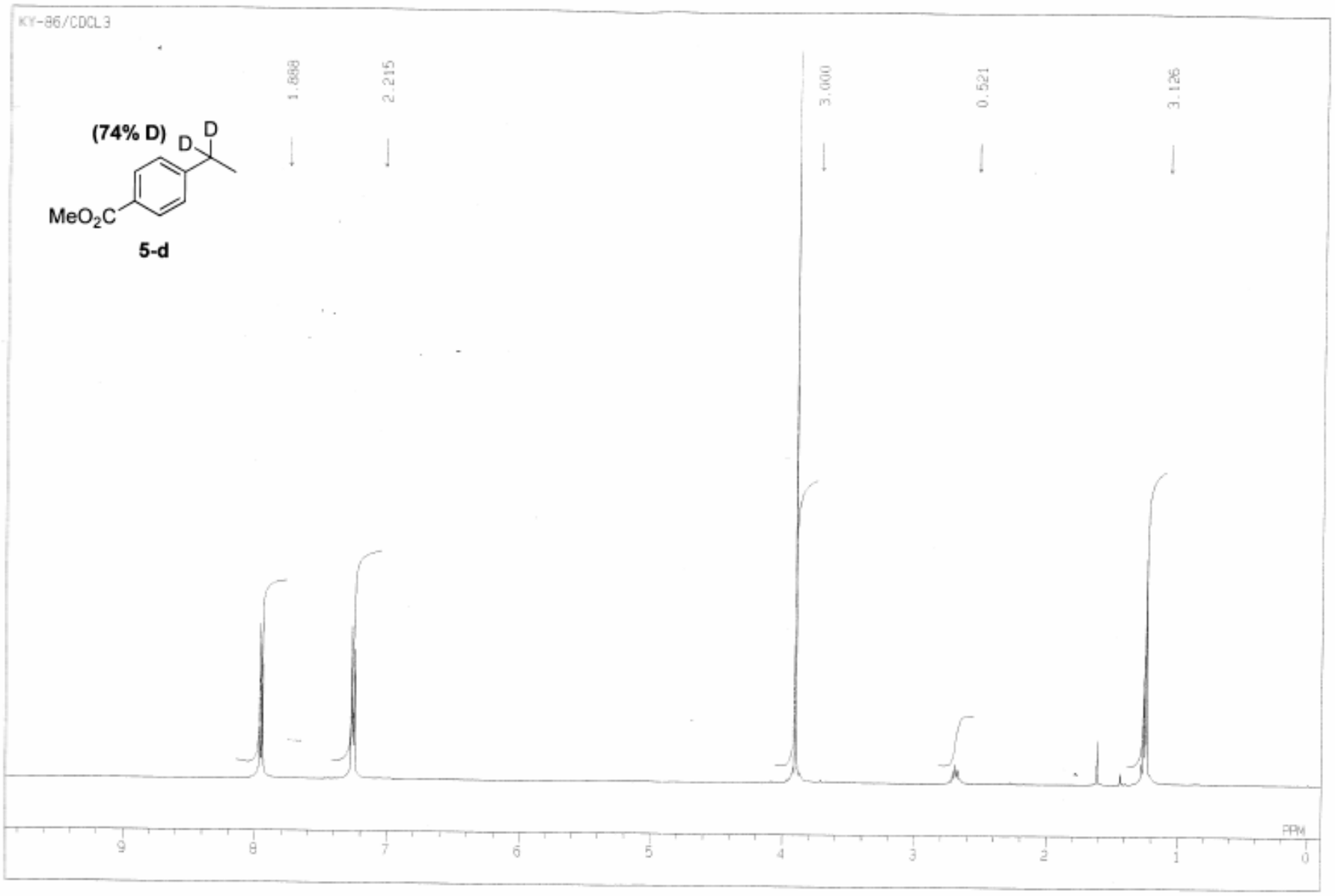
TK7-116-CH3OH-2H NMR

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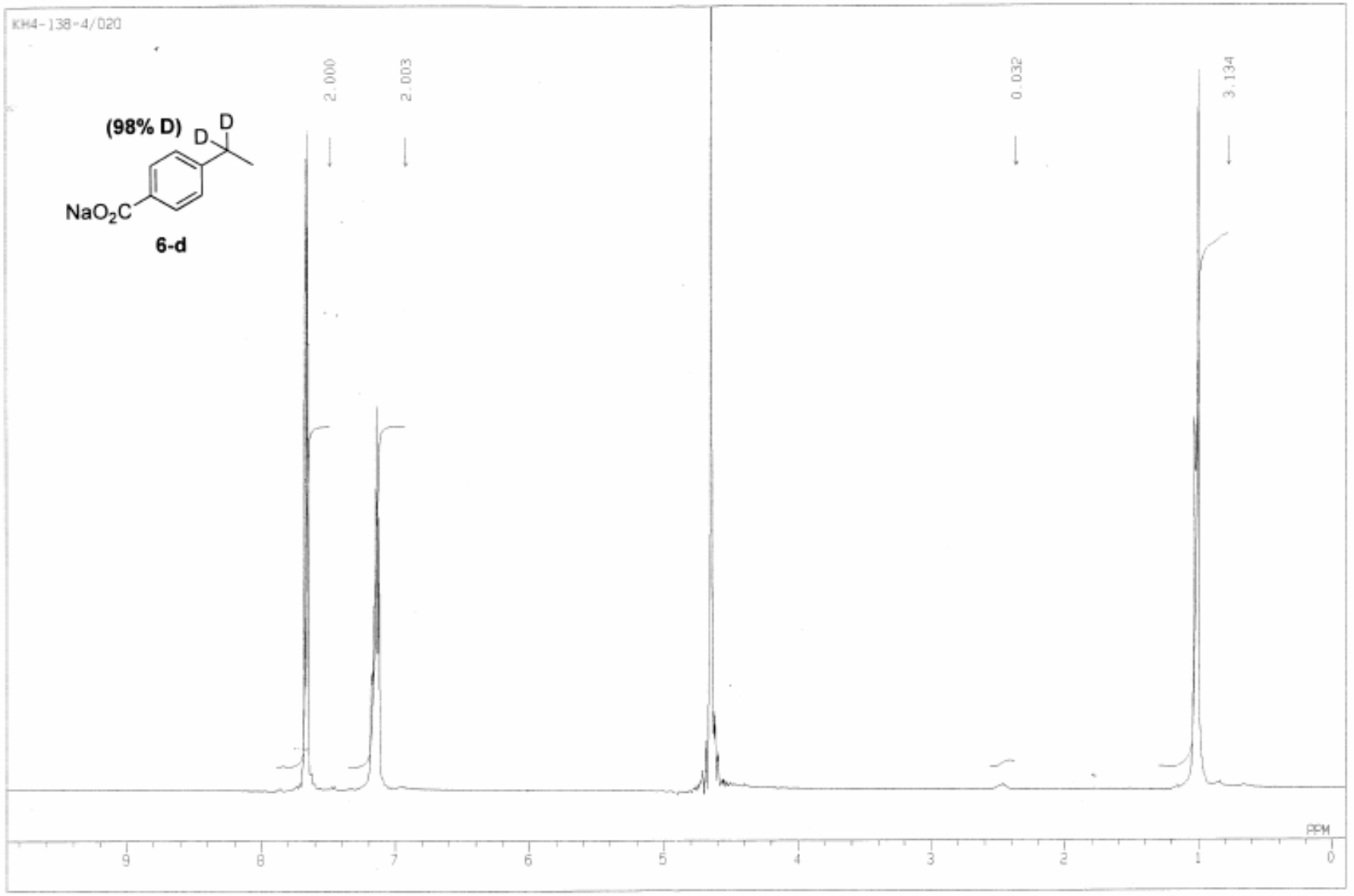
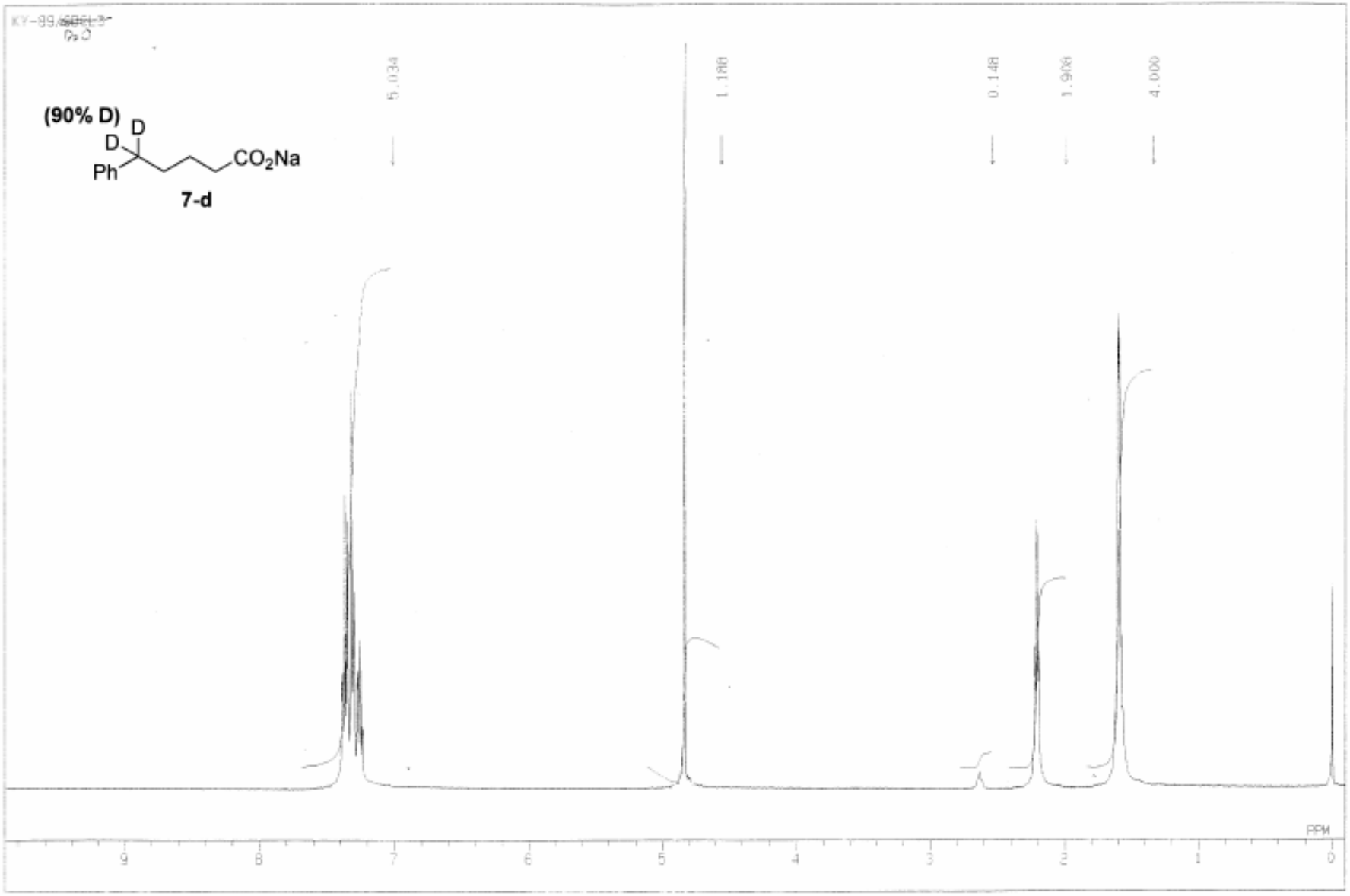
2.215
3.000
0.521
3.126
(74% D)
D
D
MeO2C
5-d
PPM
9
8
7
6
5
4
3
2
1
0


KH4-138-4/020
(98% D)
D
D
NaO2C
6-d
2.000
2.003
0.032
3.134
PPM
9
8
7
6
5
4
3
2
1
0


(90% D)
D
D
Ph
CO2Na
7-d
5.134
1.188
0.148
1.906
4.000
PPM

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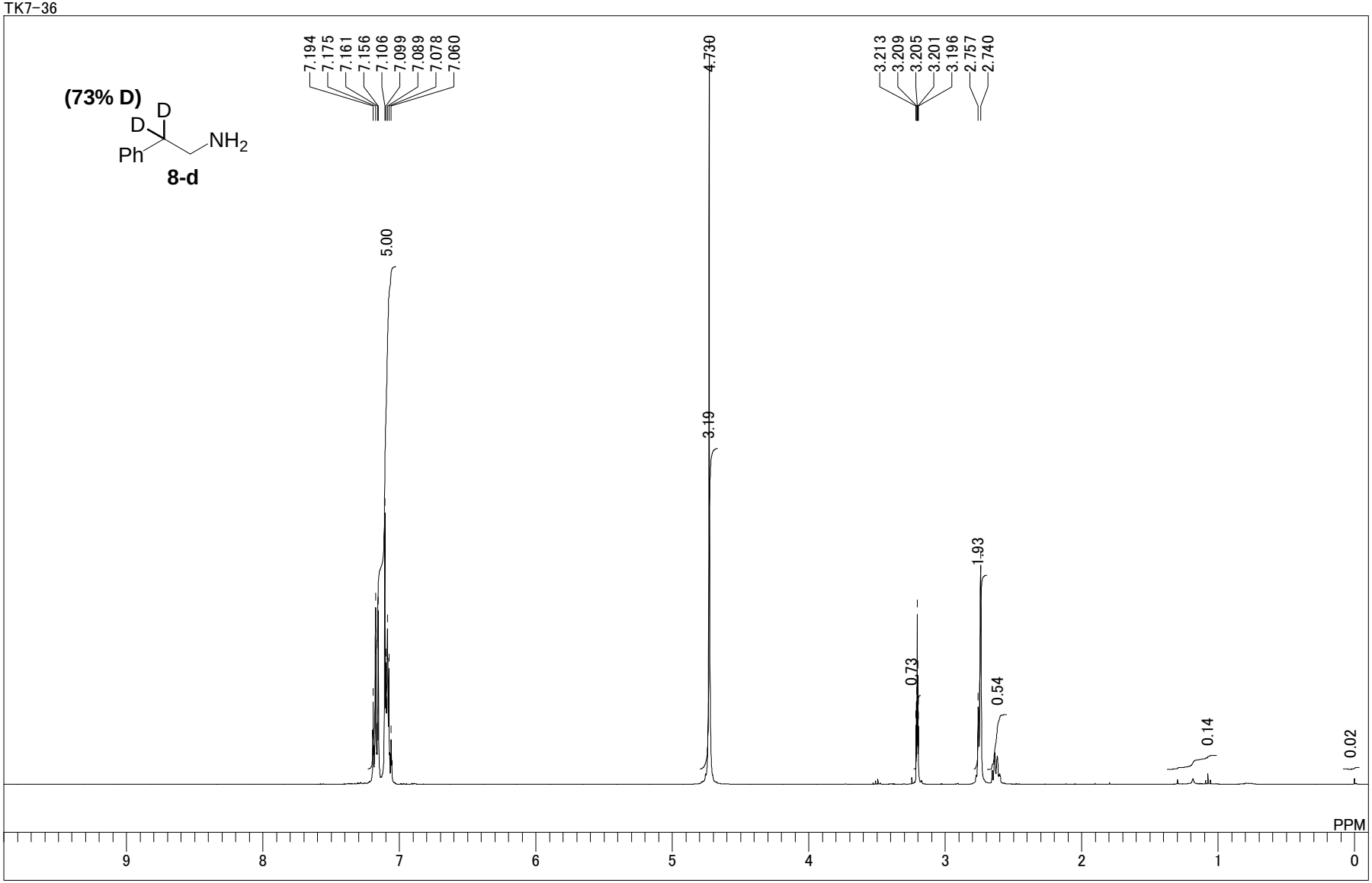
TK7-36



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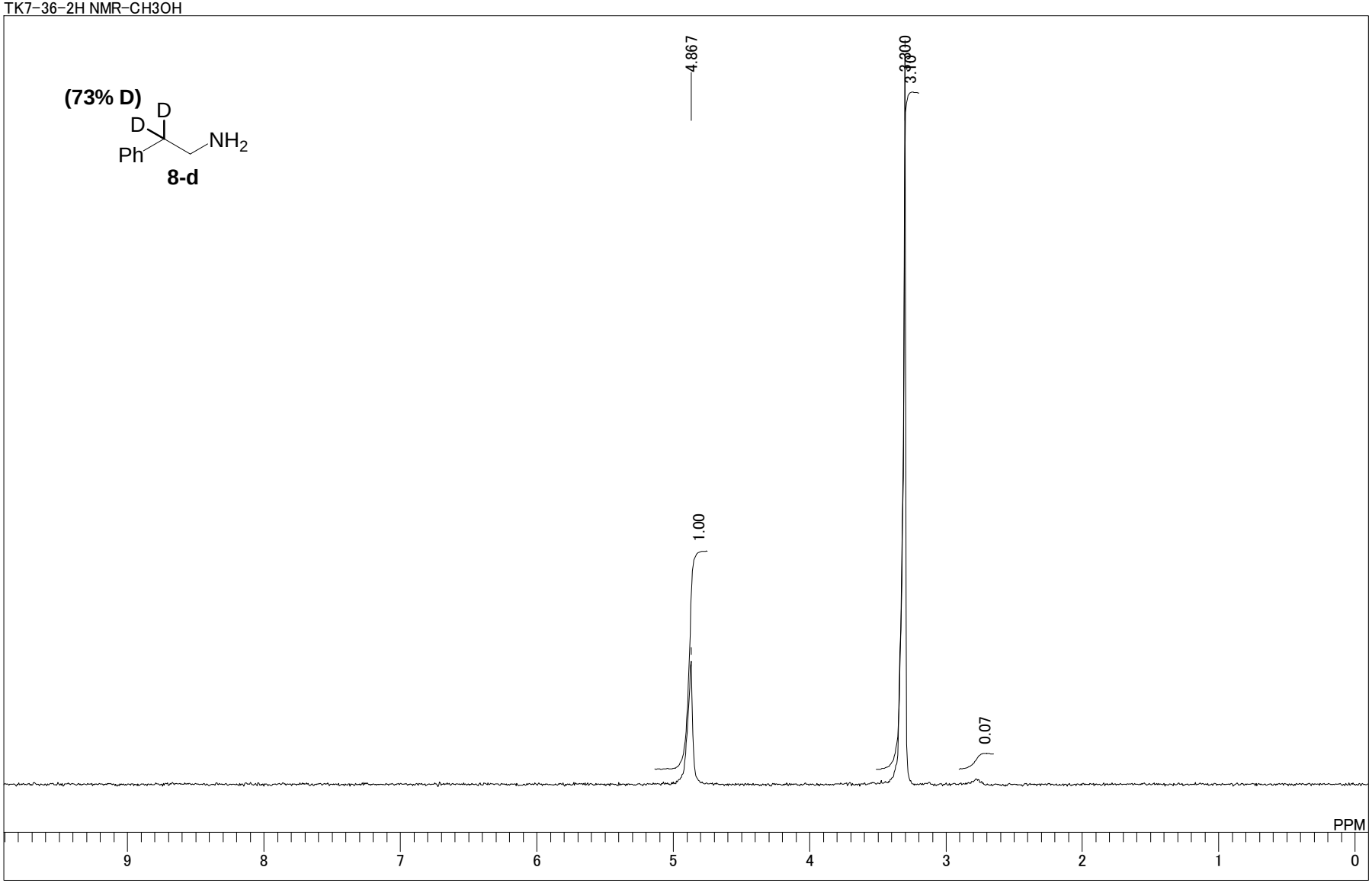
TK7-36-2H NMR-CH3OH



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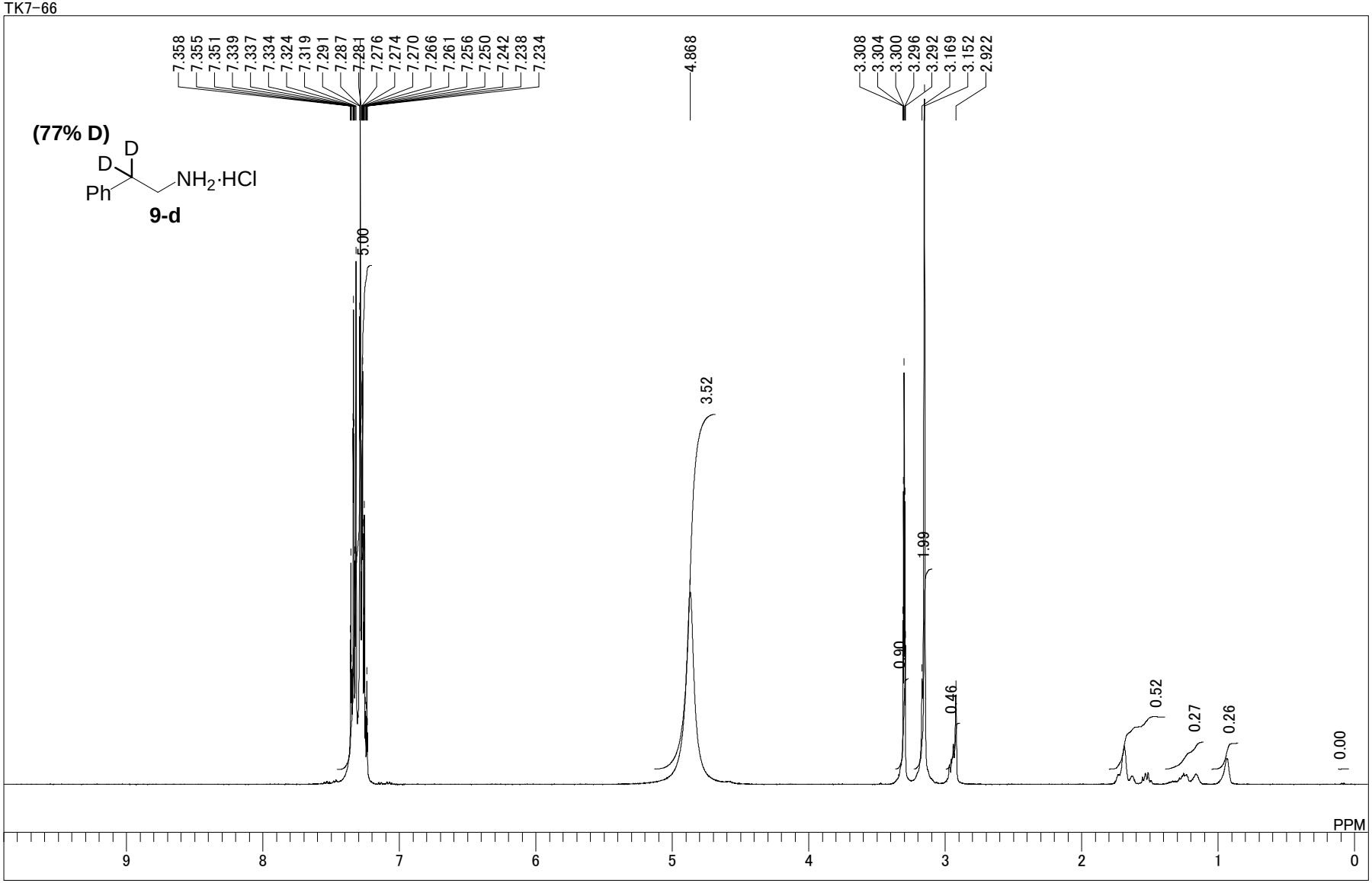
TK7-66



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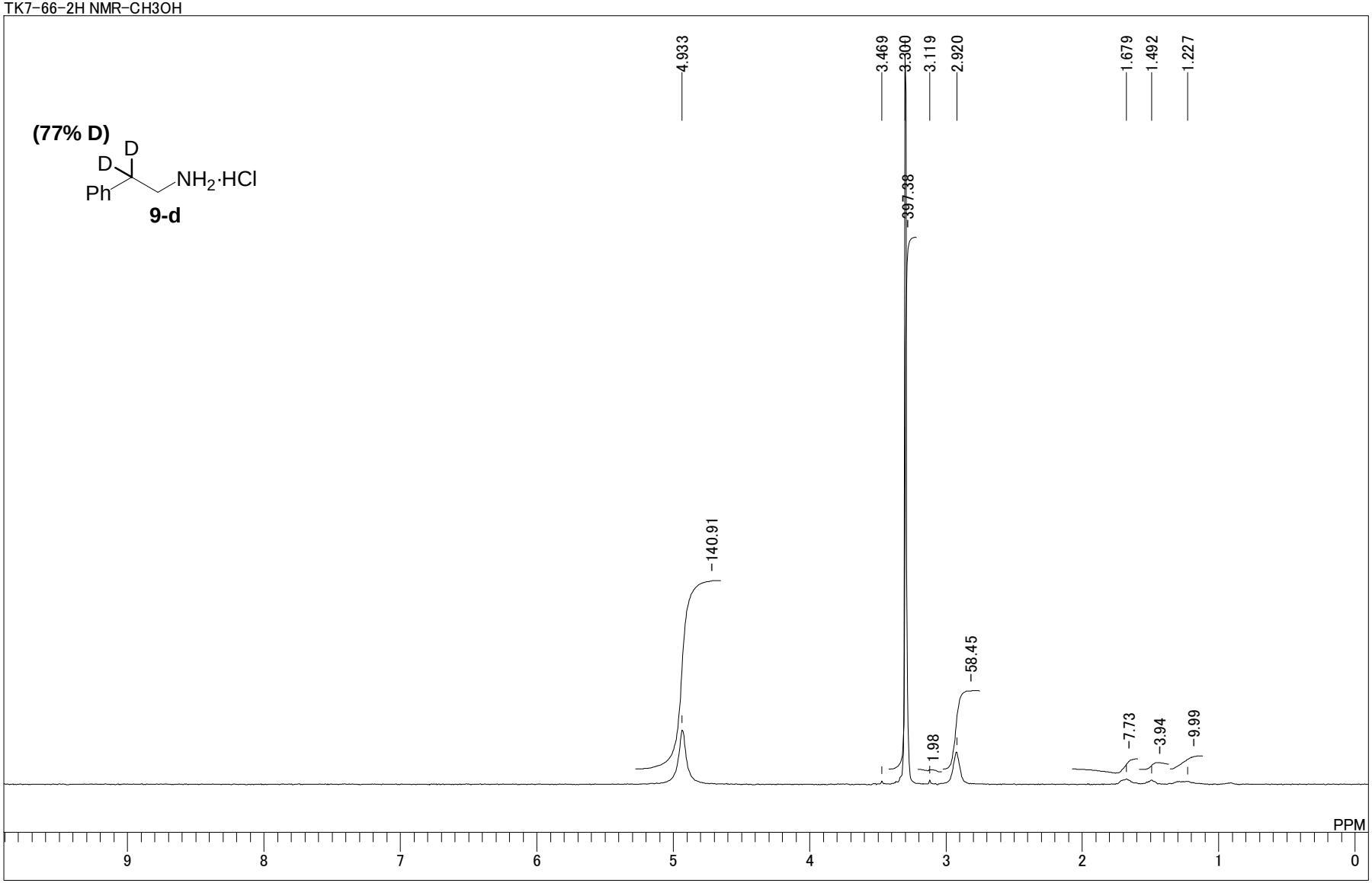
TK7-66-2H NMR-CH3OH



(77% D)

9-d

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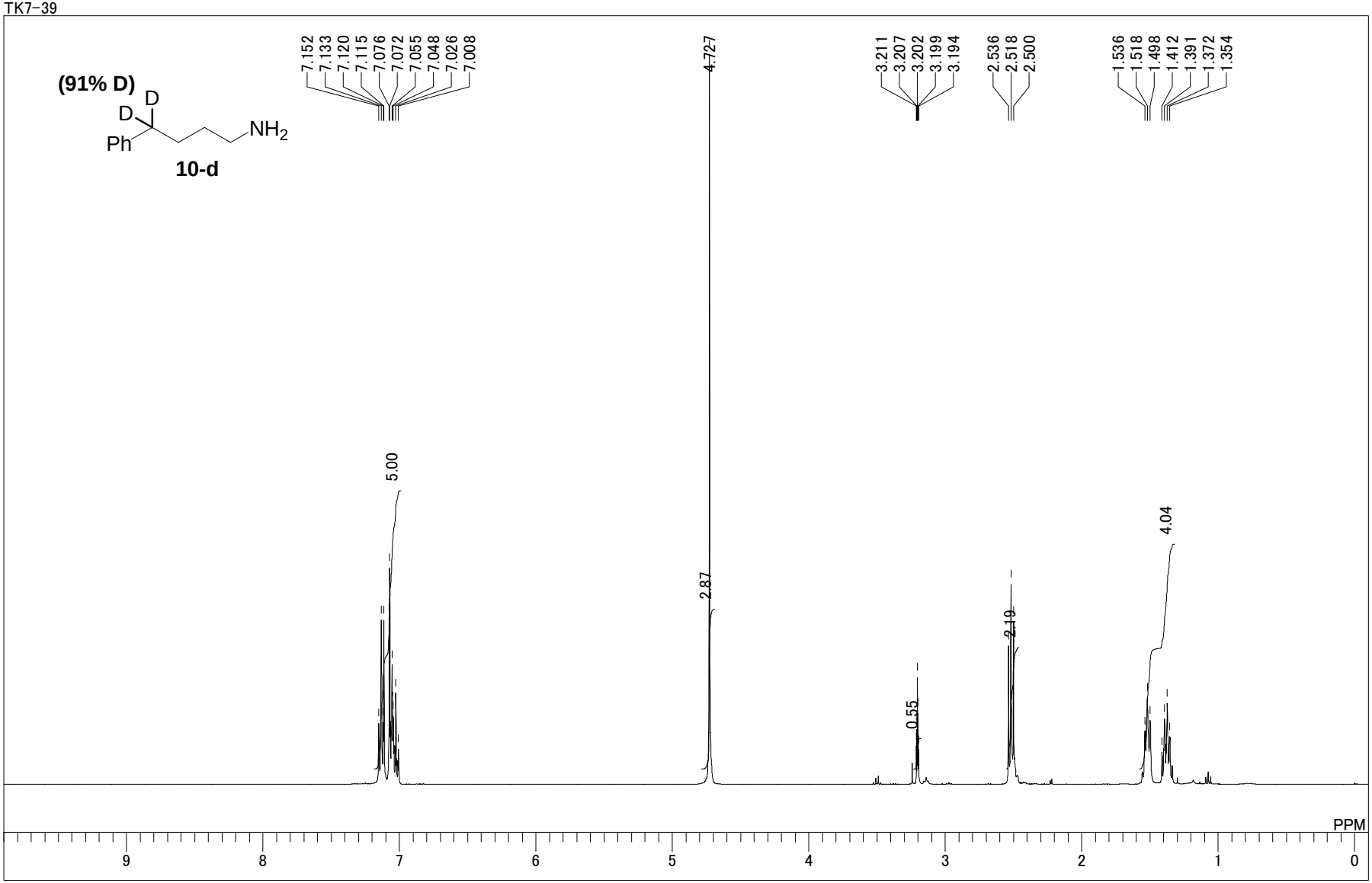
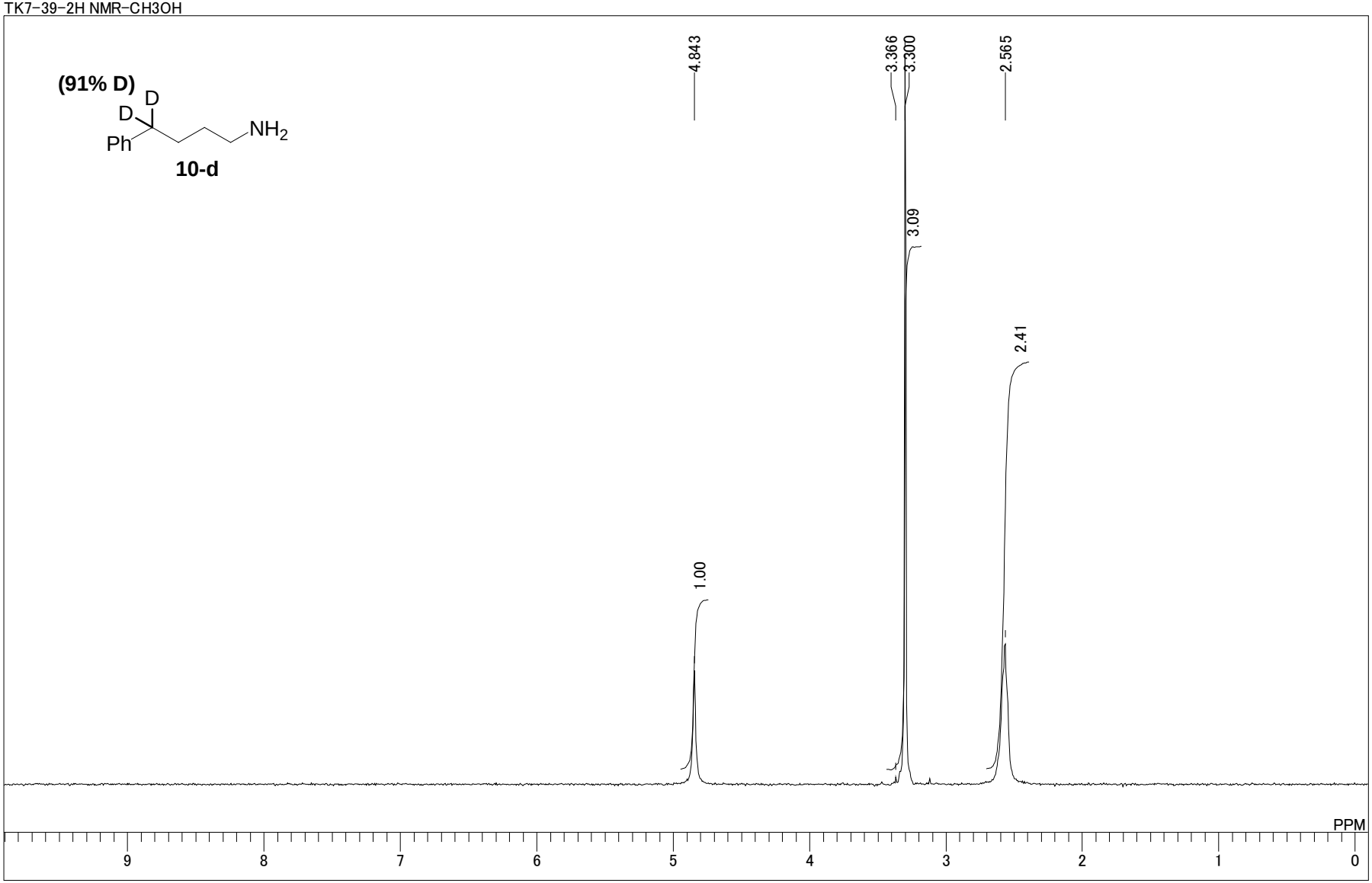
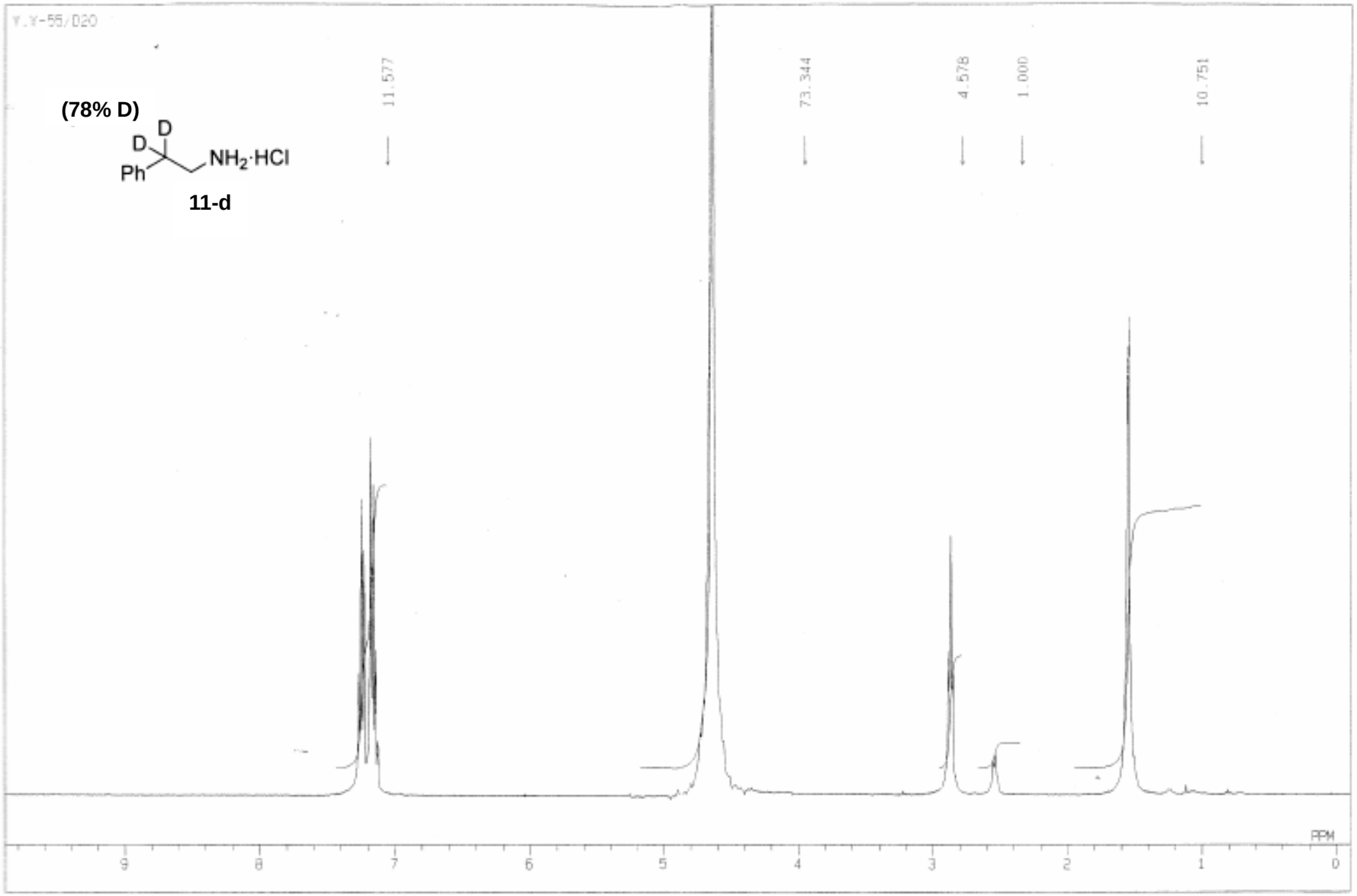
TK7-39



D:¥Data¥NMR 2007年¥NMR 2007-4月¥2H NMR 4-15¥TK7-39-2H NMR-CH3OH-FT.als
TK7-39-2H NMR-CH3OH




Y.Y-55/D2O
(78% D)
D
D
Ph
NH2·HCl
11-d
11.577
73.344
4.578
1.000
10.751
PPM
9
8
7
6
5
4
3
2
1
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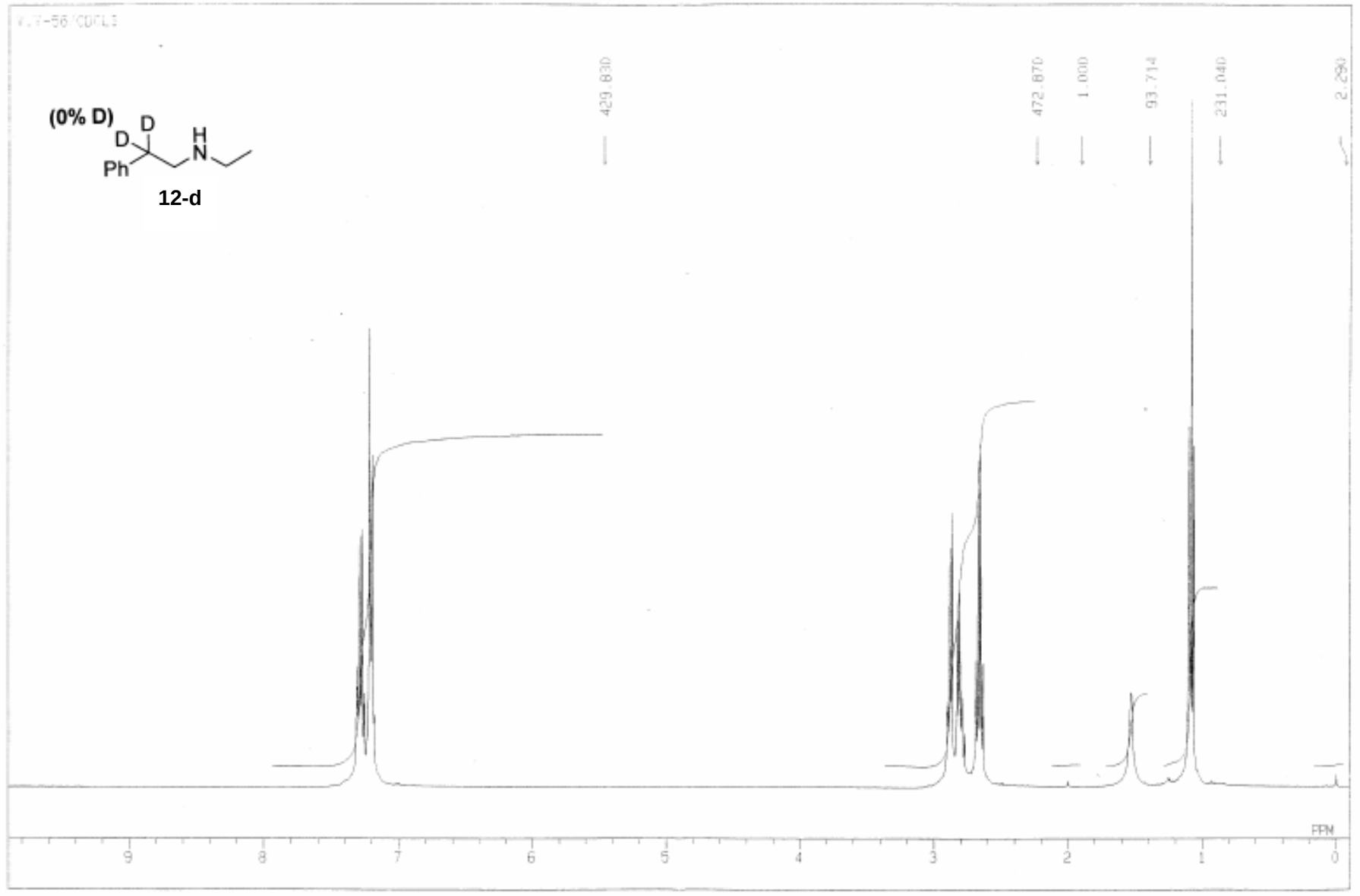
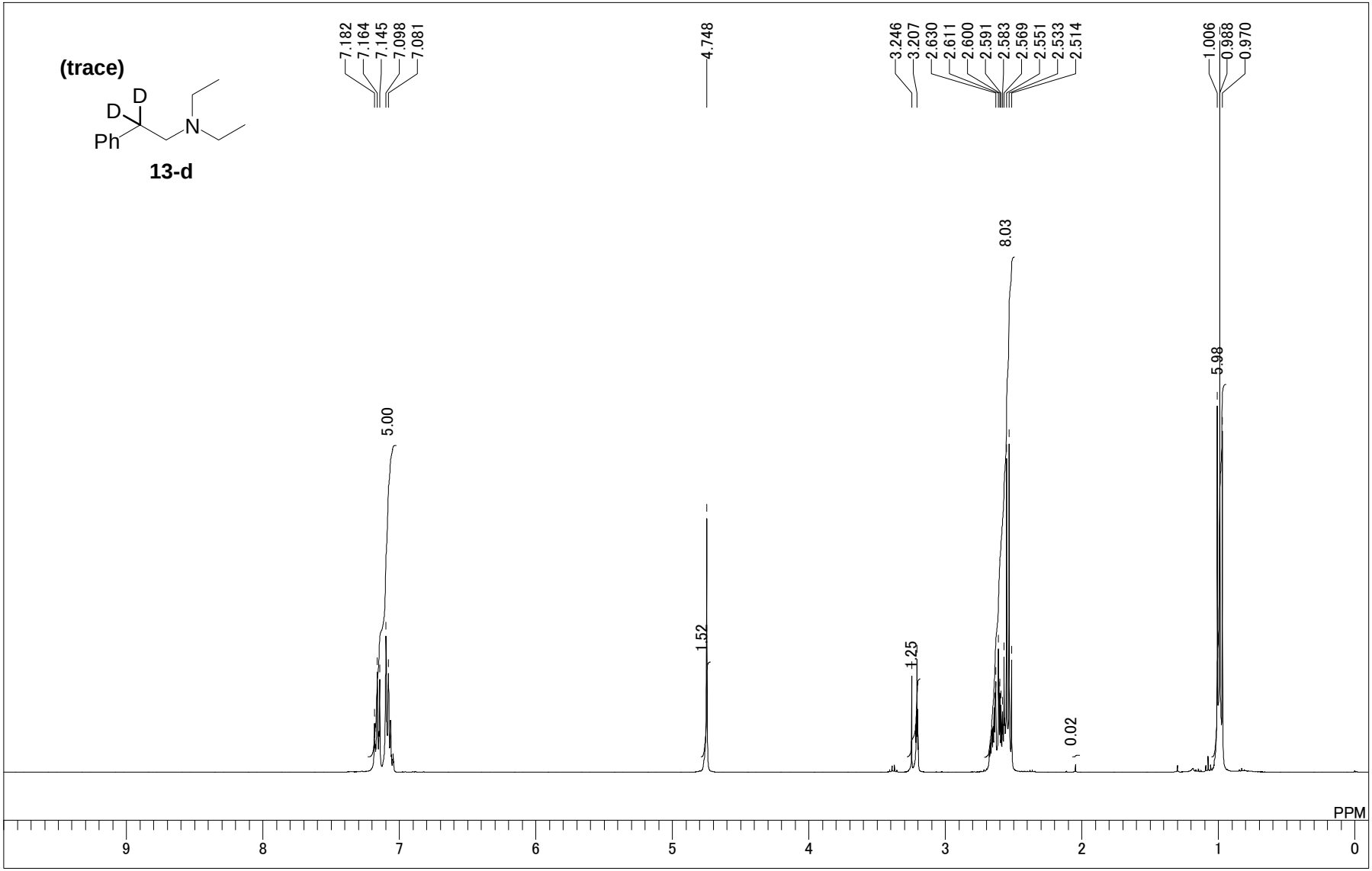
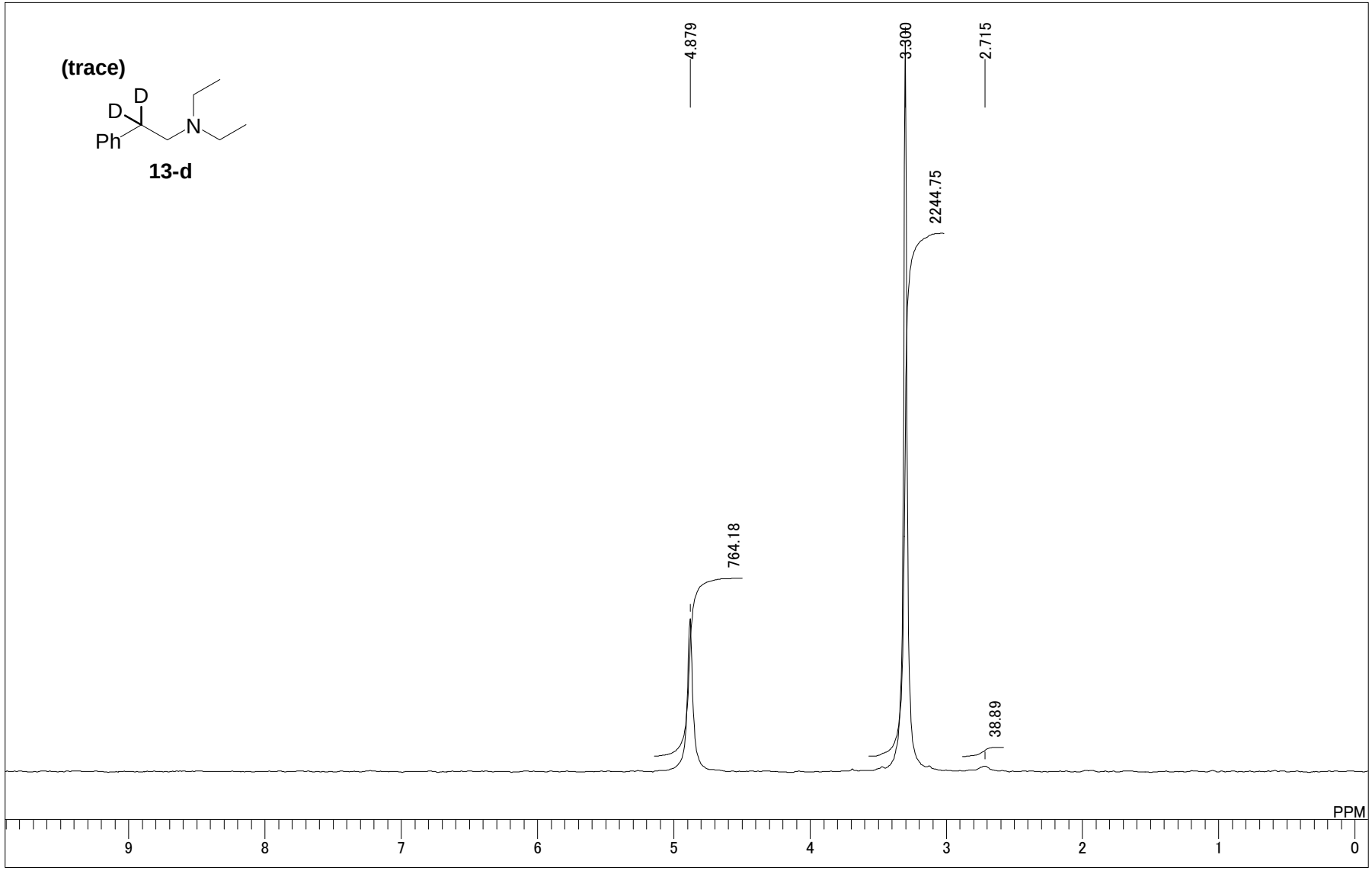

(0% D)
D
D
Ph
H
N
12-d
429.830
472.870
1.000
93.714
231.040
2.290
PPM
9
8
7
6
5
4
3
2
1
0

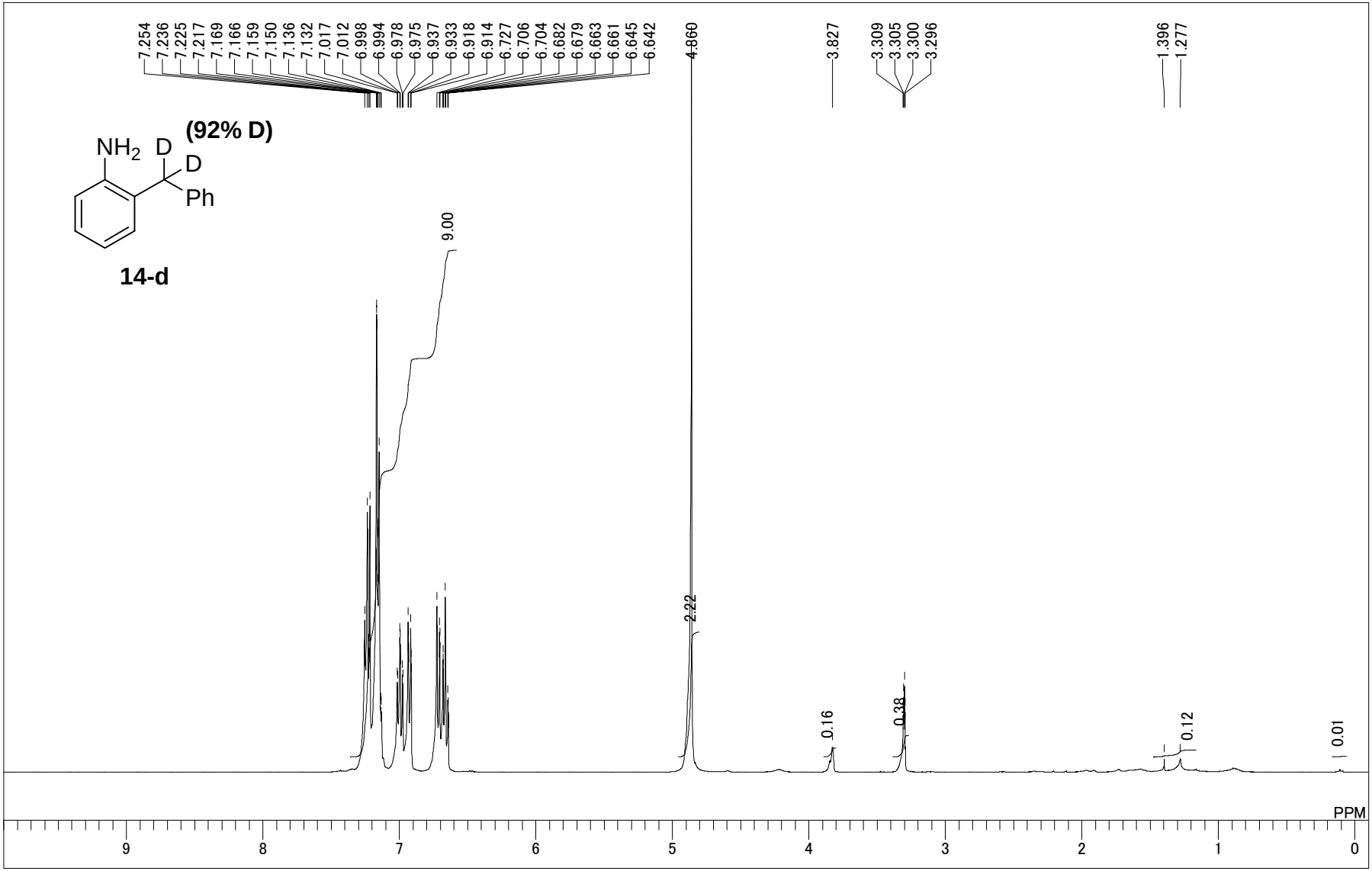
F:¥TK7-1531NON_E2_FT.als
TK7-153



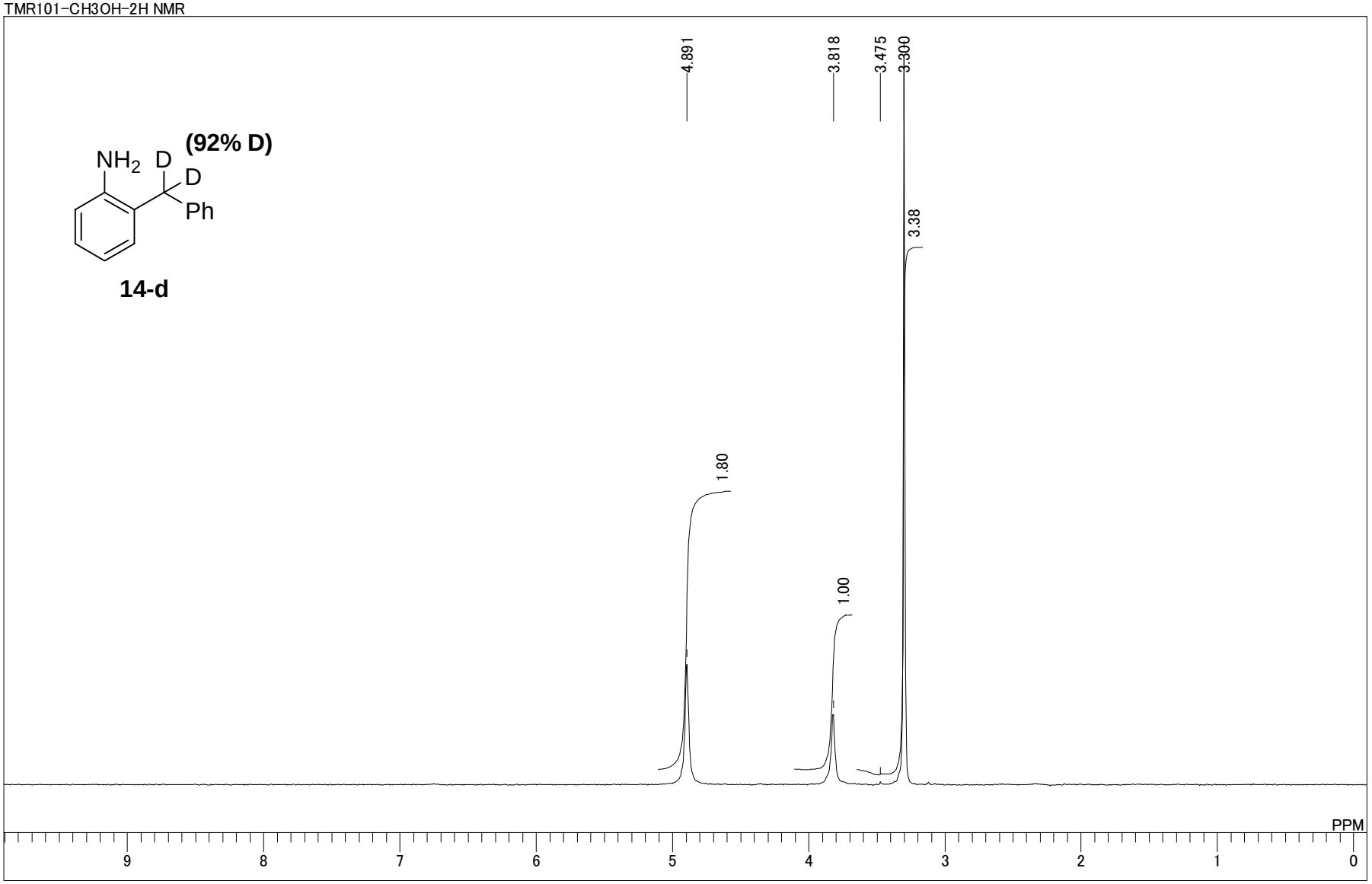
F:¥NMR 2007-6月¥TK7-153-2H NMR-CH3OH-FT.als
TK7-153-2H NMR-CH3OH



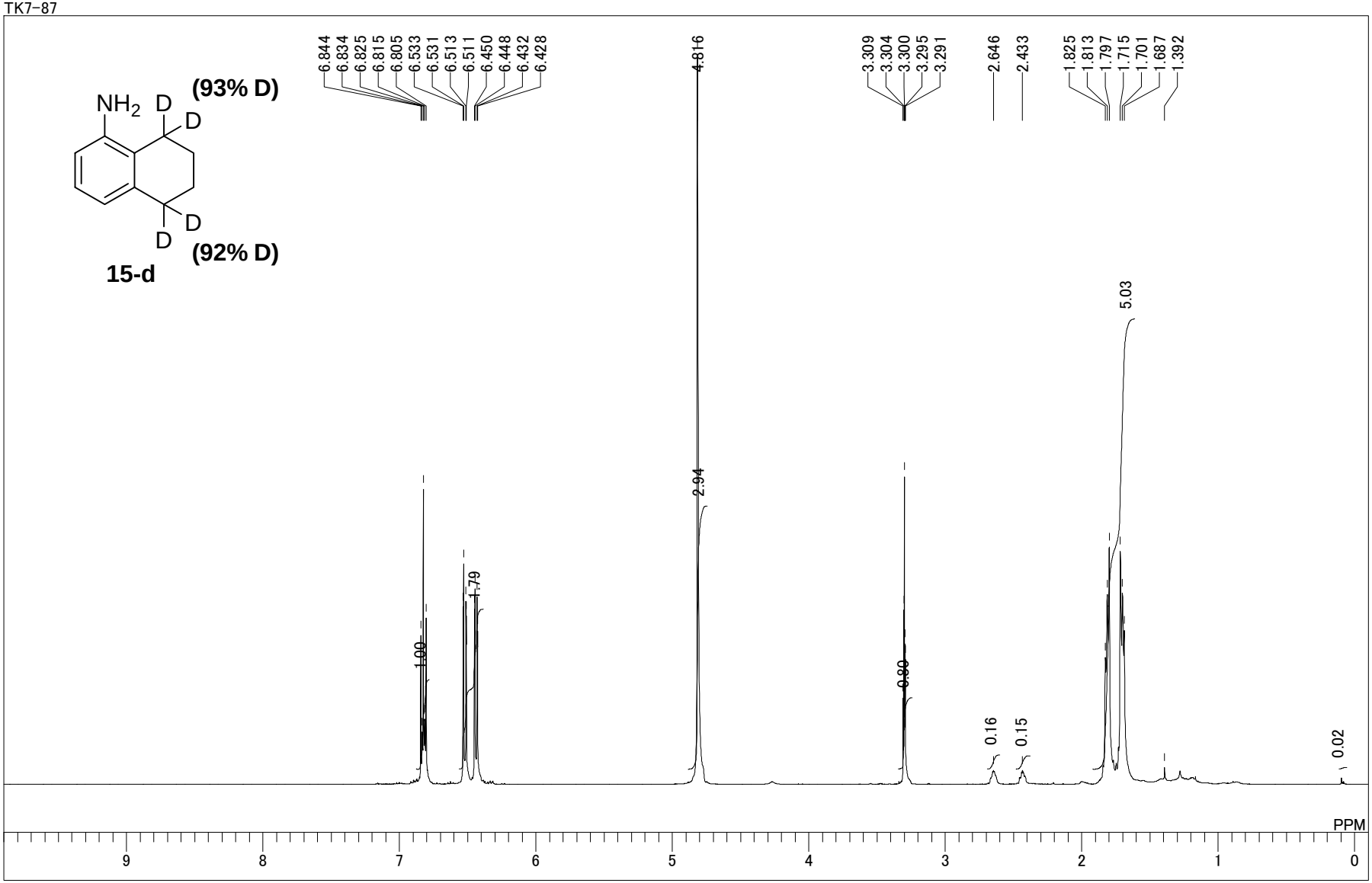
D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR1011NON_E2-FT.als
TMR101



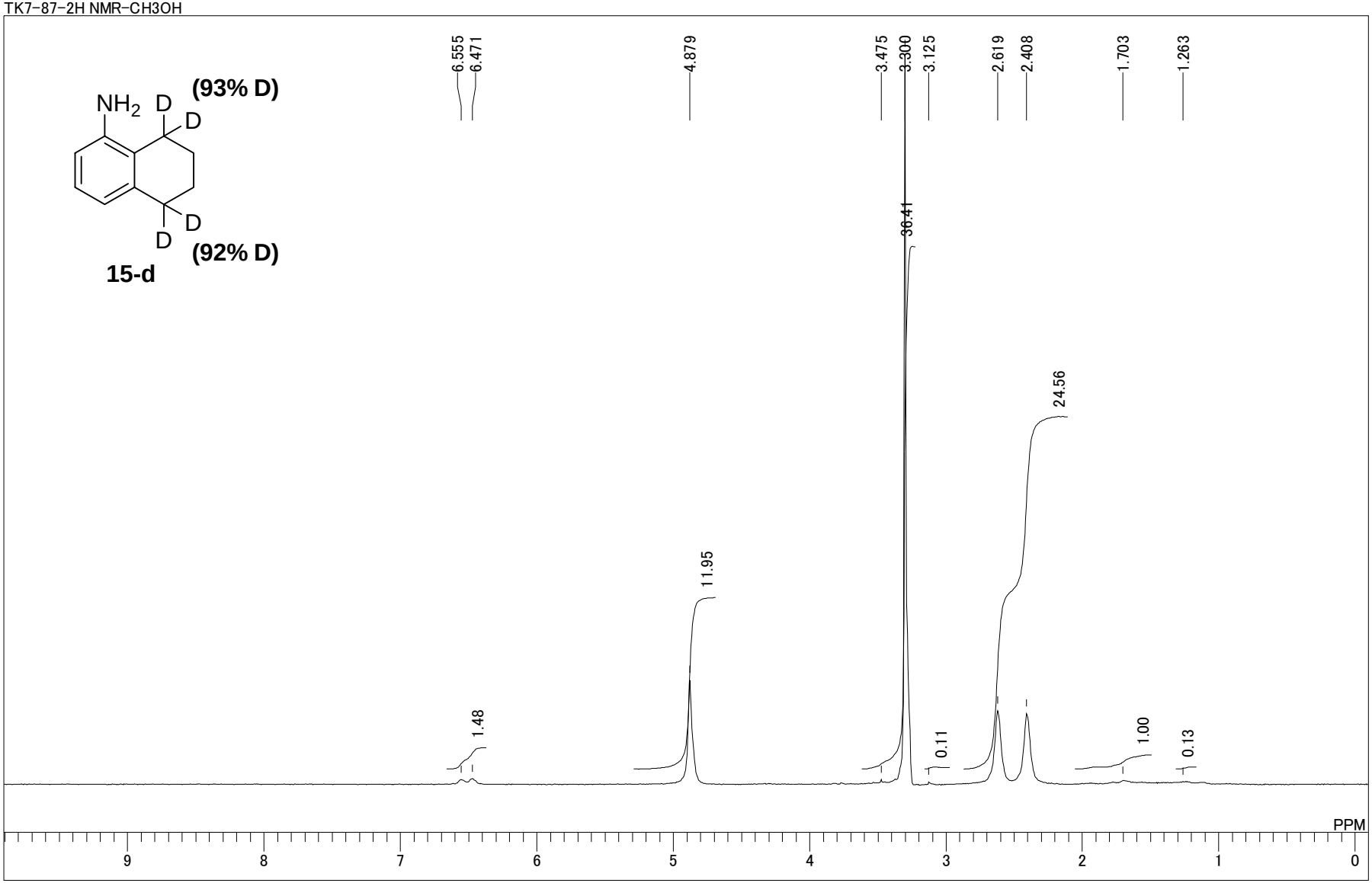
D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR101-CH3OH-2H NMR-FT.als
TMR101-CH3OH-2H NMR



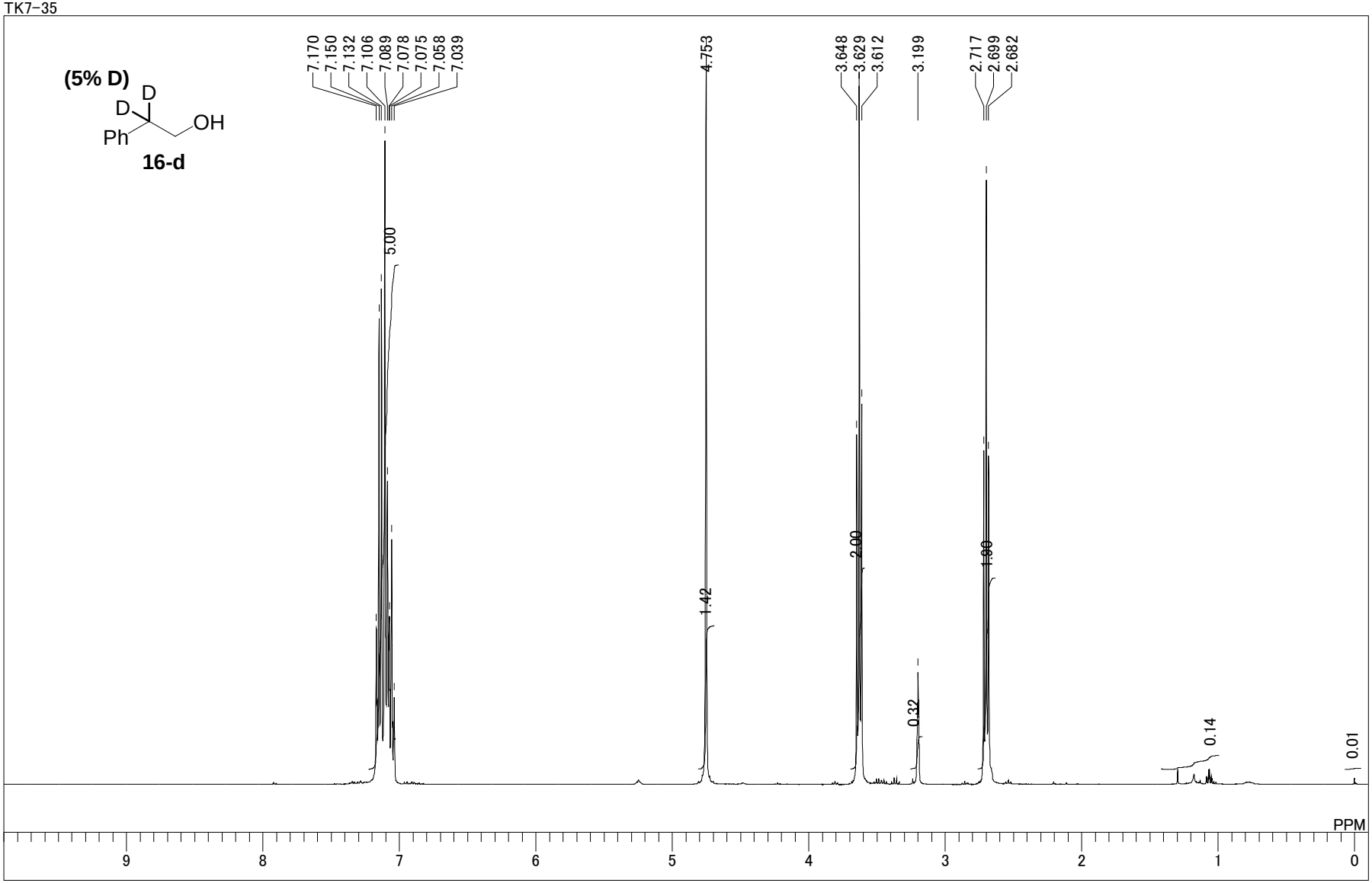
D:¥Data¥NMR 2007年¥NMR 2007-4月¥TK7-871NON_E1_FT.als
TK7-87



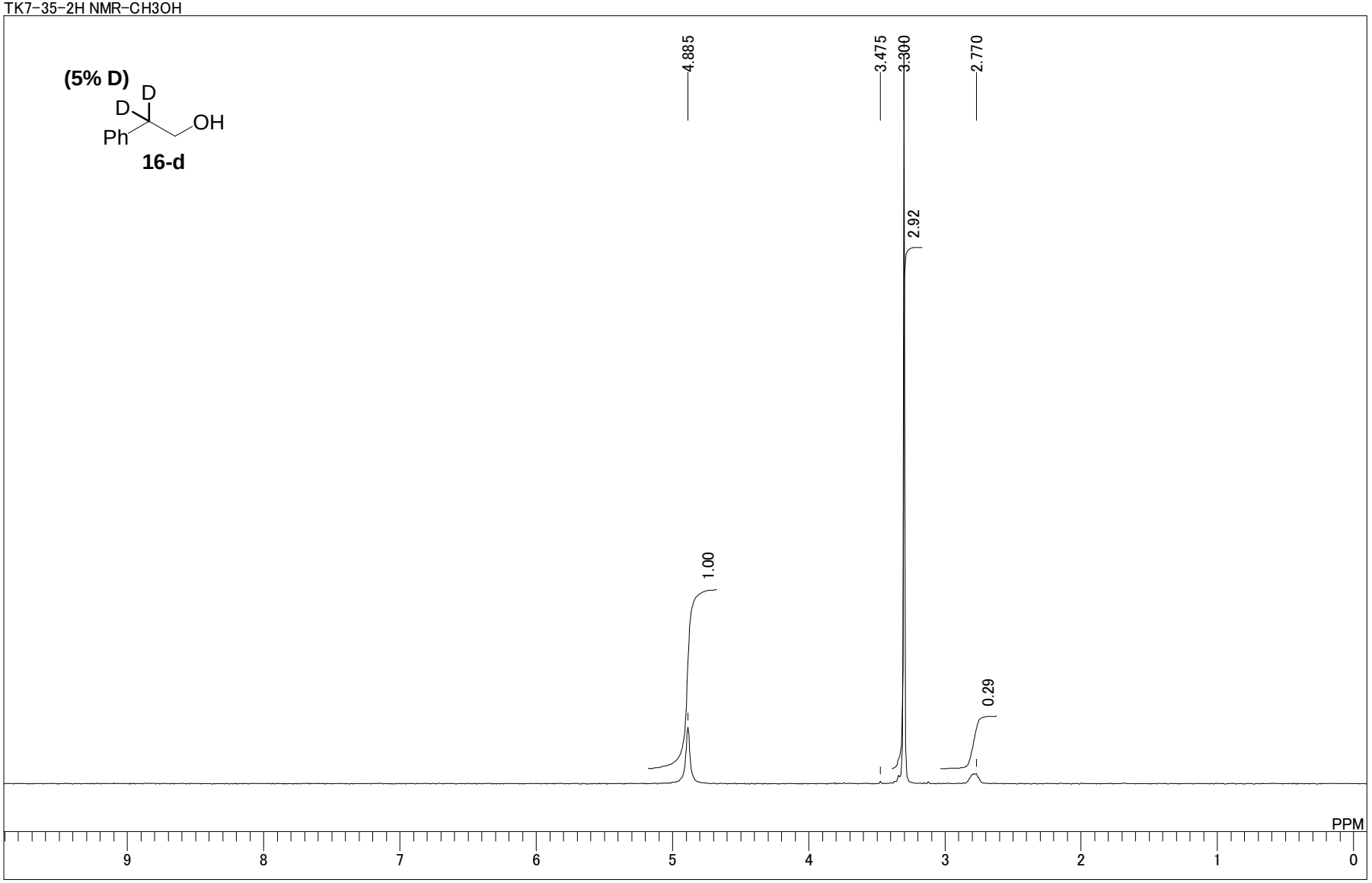
F:¥NMR 2007-5月¥2H NMR, 5-13¥TK7-87-2H NMR-CH3OH-FT.als
TK7-87-2H NMR-CH3OH



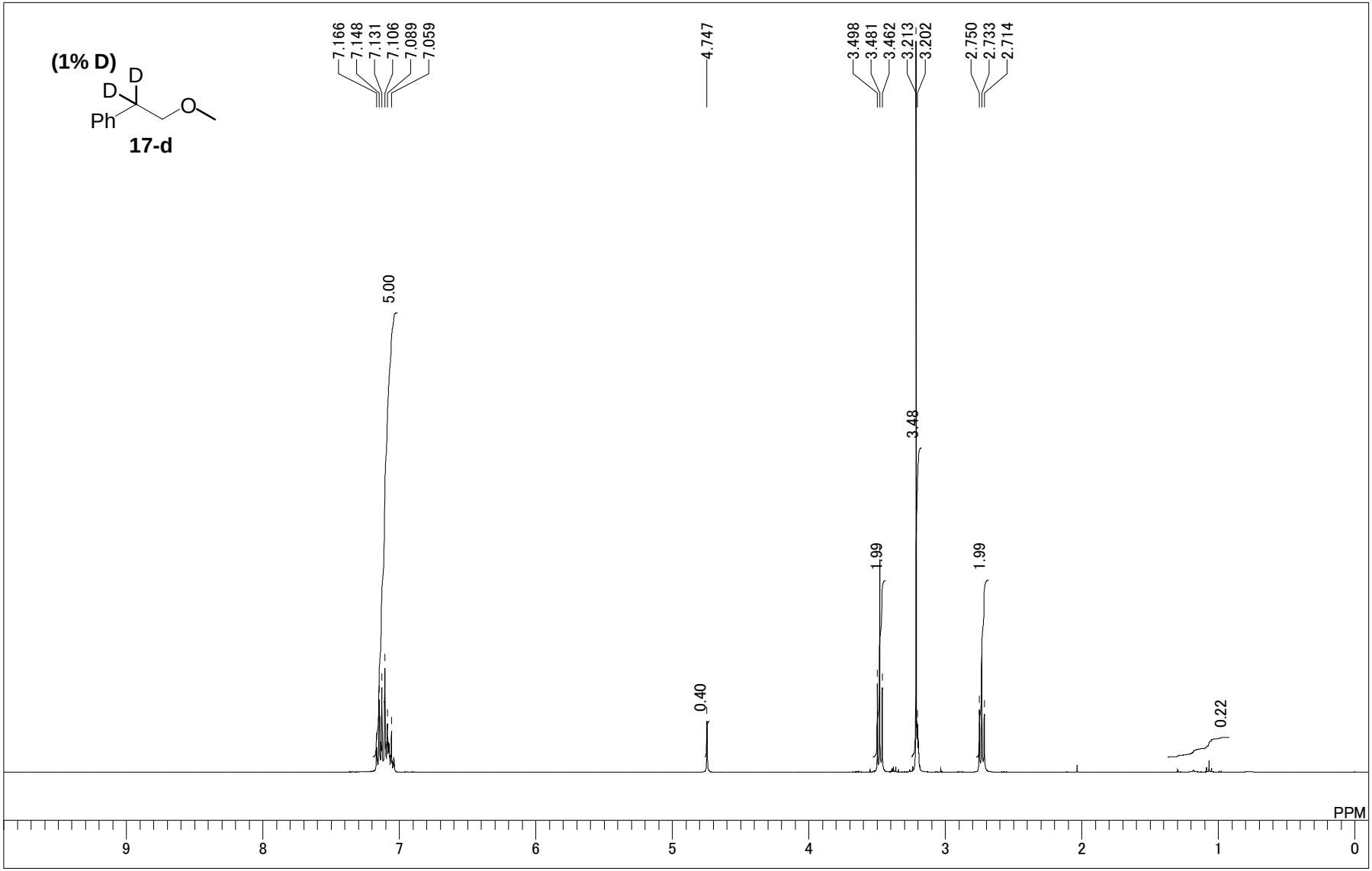
D:¥Data¥NMR 2007年¥NMR 2007-4月¥TK7-351NON_E1_FT.als
TK7-35



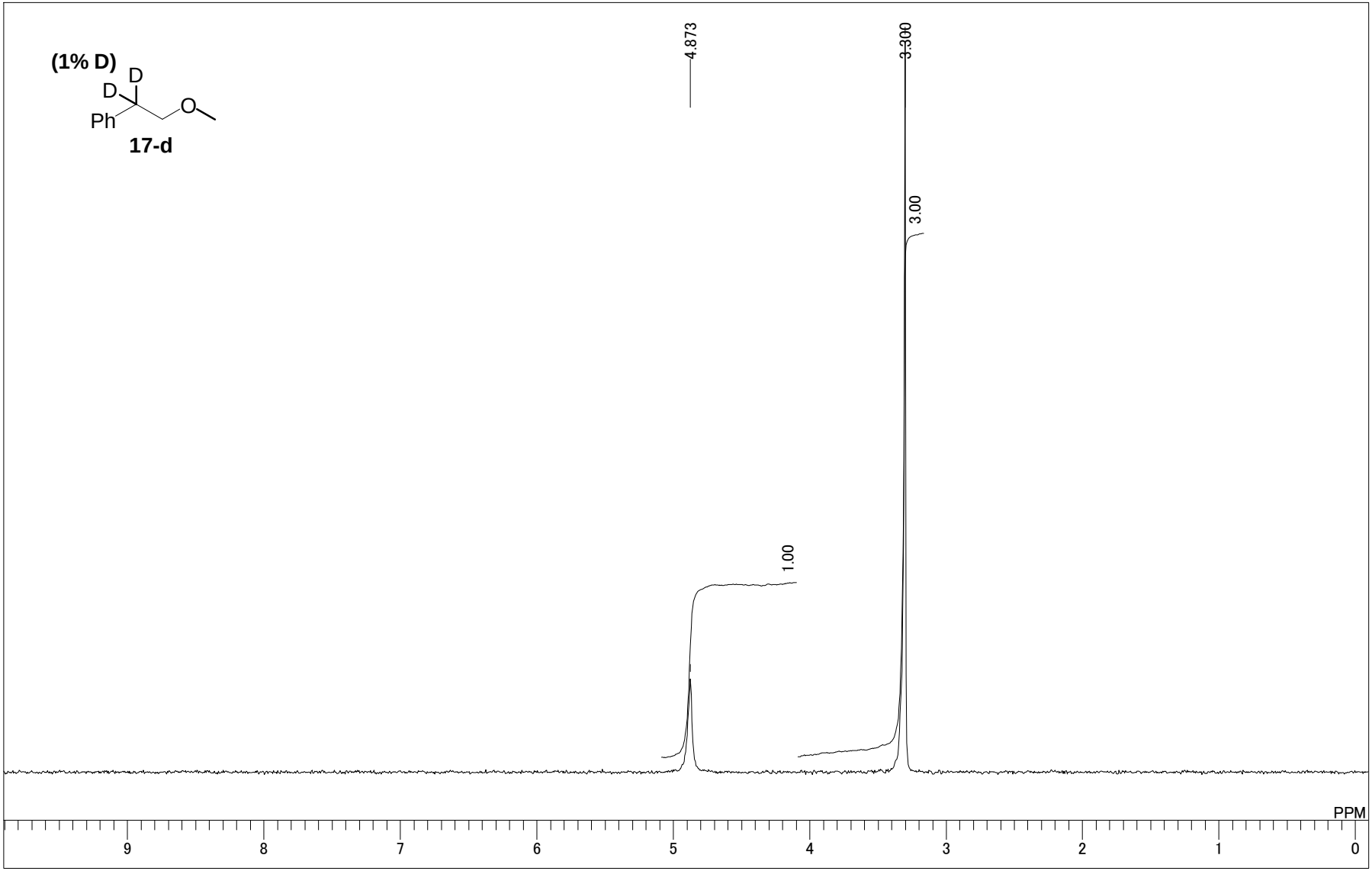
D:¥Data¥NMR 2007年¥NMR 2007-4月¥2H NMR 4-15¥TK7-35-2H NMR-CH3OH-FT.als
TK7-35-2H NMR-CH3OH



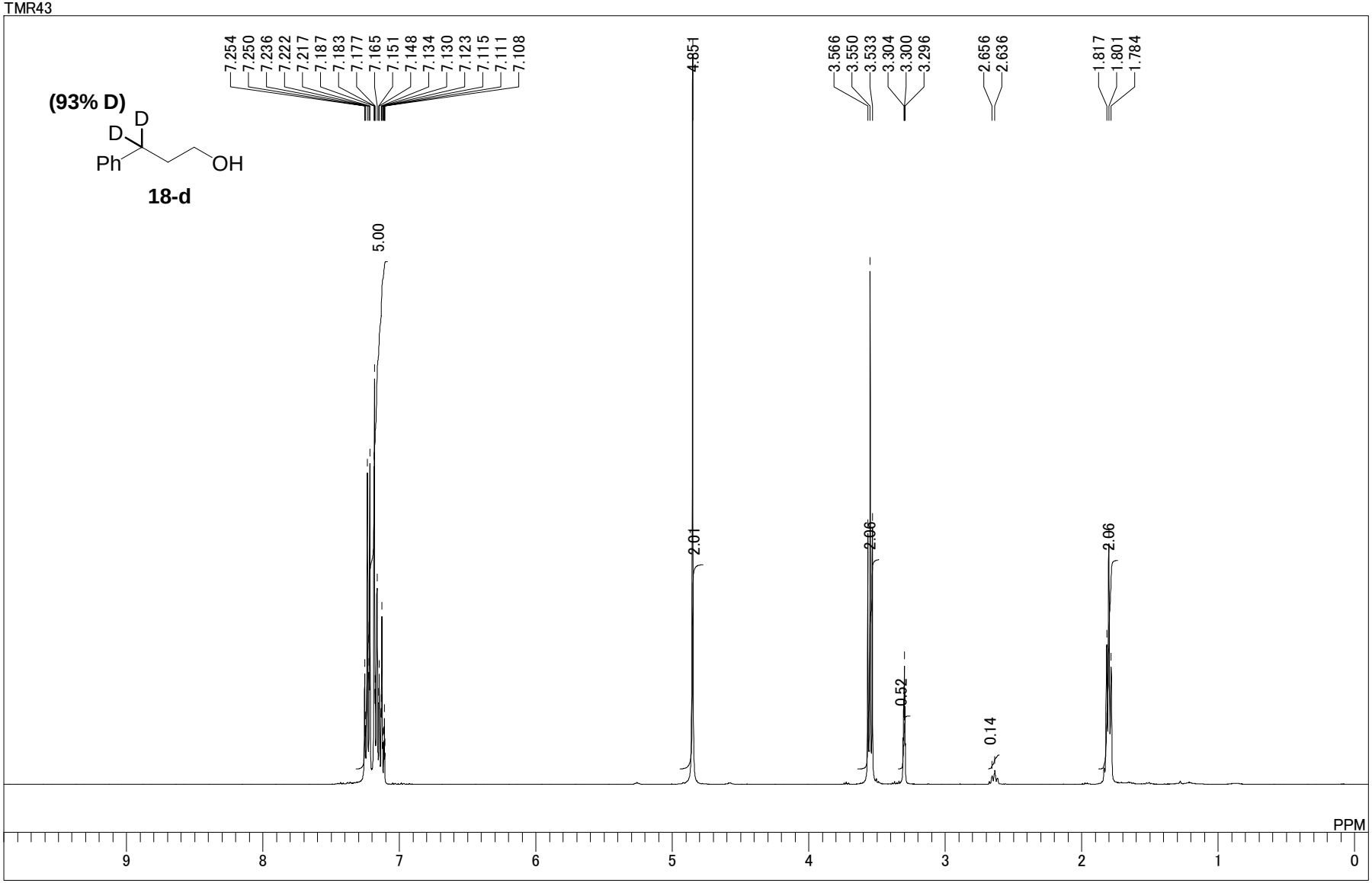
D:¥Data¥NMR 2007年¥NMR 2007-4月¥TK7-411NON_E4_FT.als
TK7-41



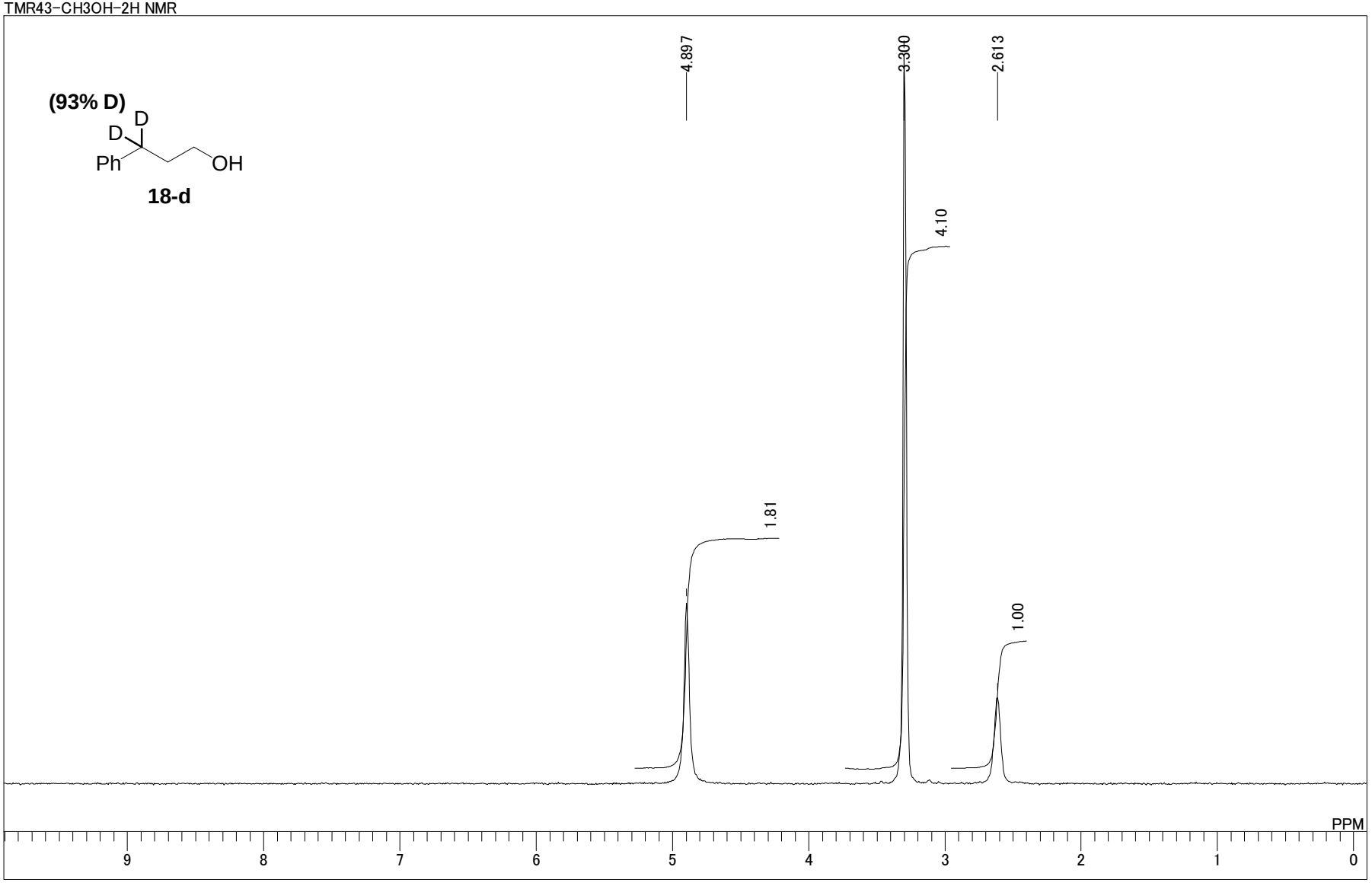
D:¥Data¥NMR 2007年¥NMR 2007-4月¥2H NMR 4-15¥TK7-41-2H NMR-CH3OH-FT.als
TK7-41-2H NMR-CH3OH



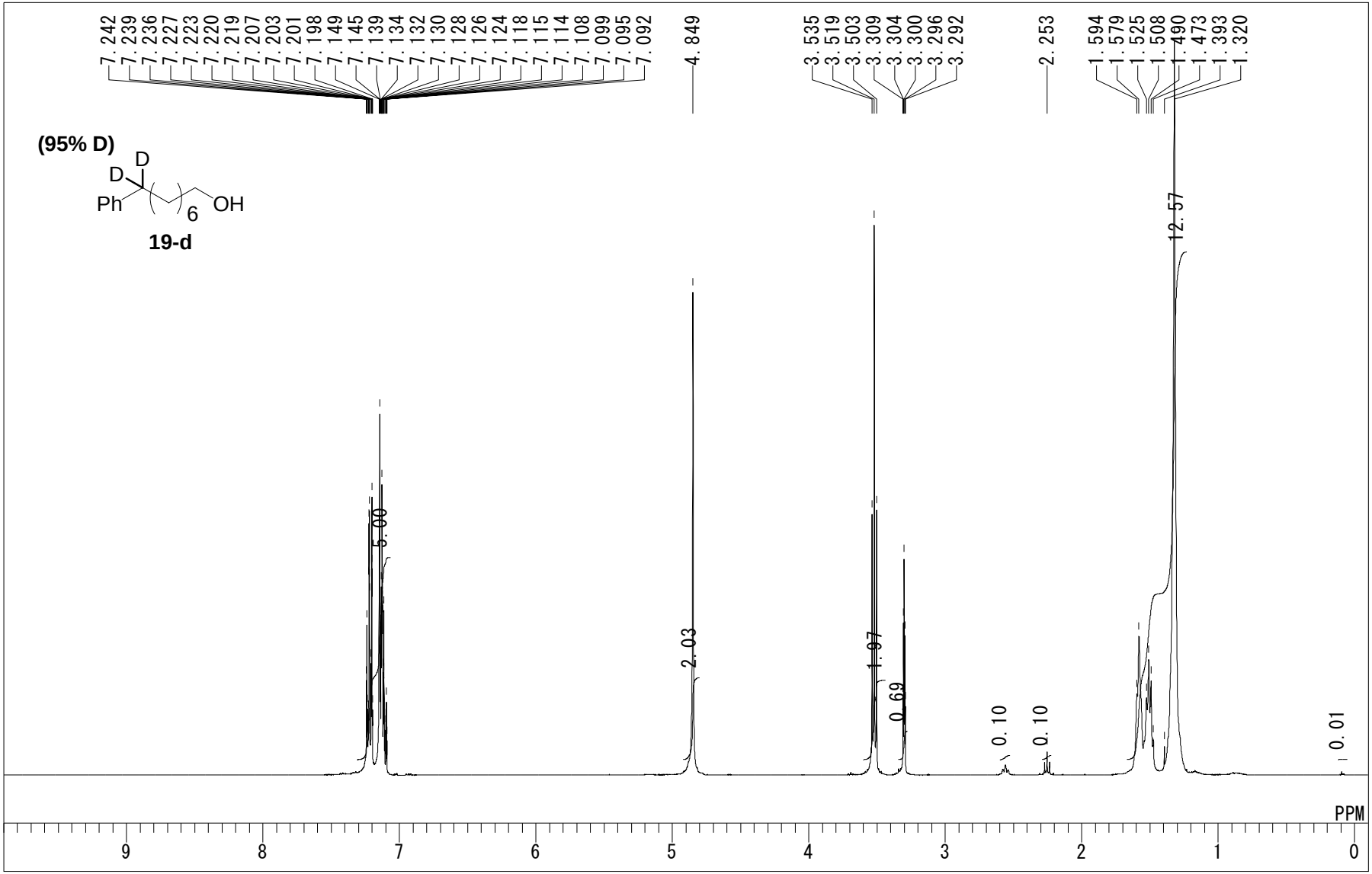
D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR431NON_E3-FT.als
TMR43



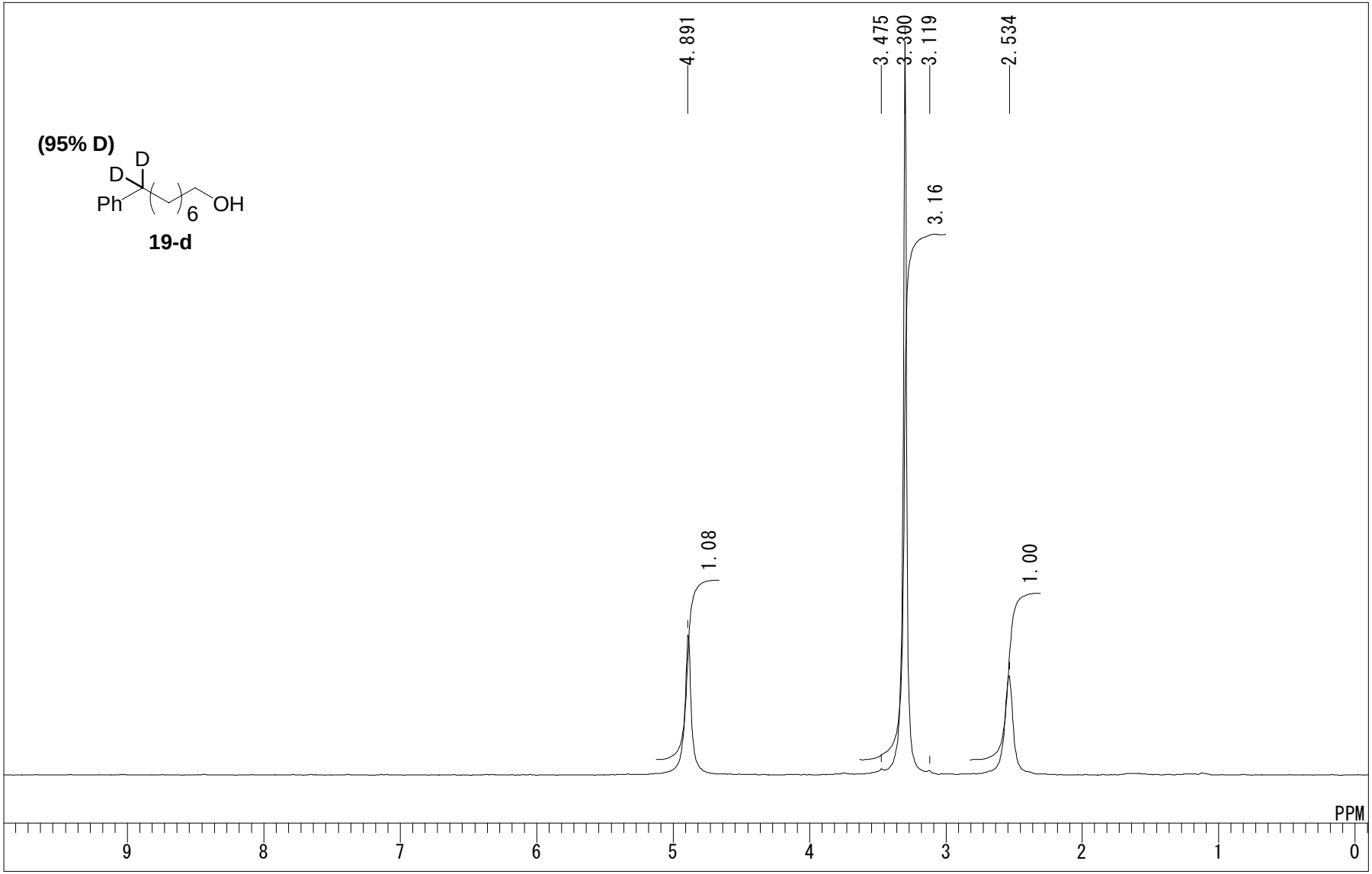
D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR43-CH3OH-2H NMR-FT.als
TMR43-CH3OH-2H NMR



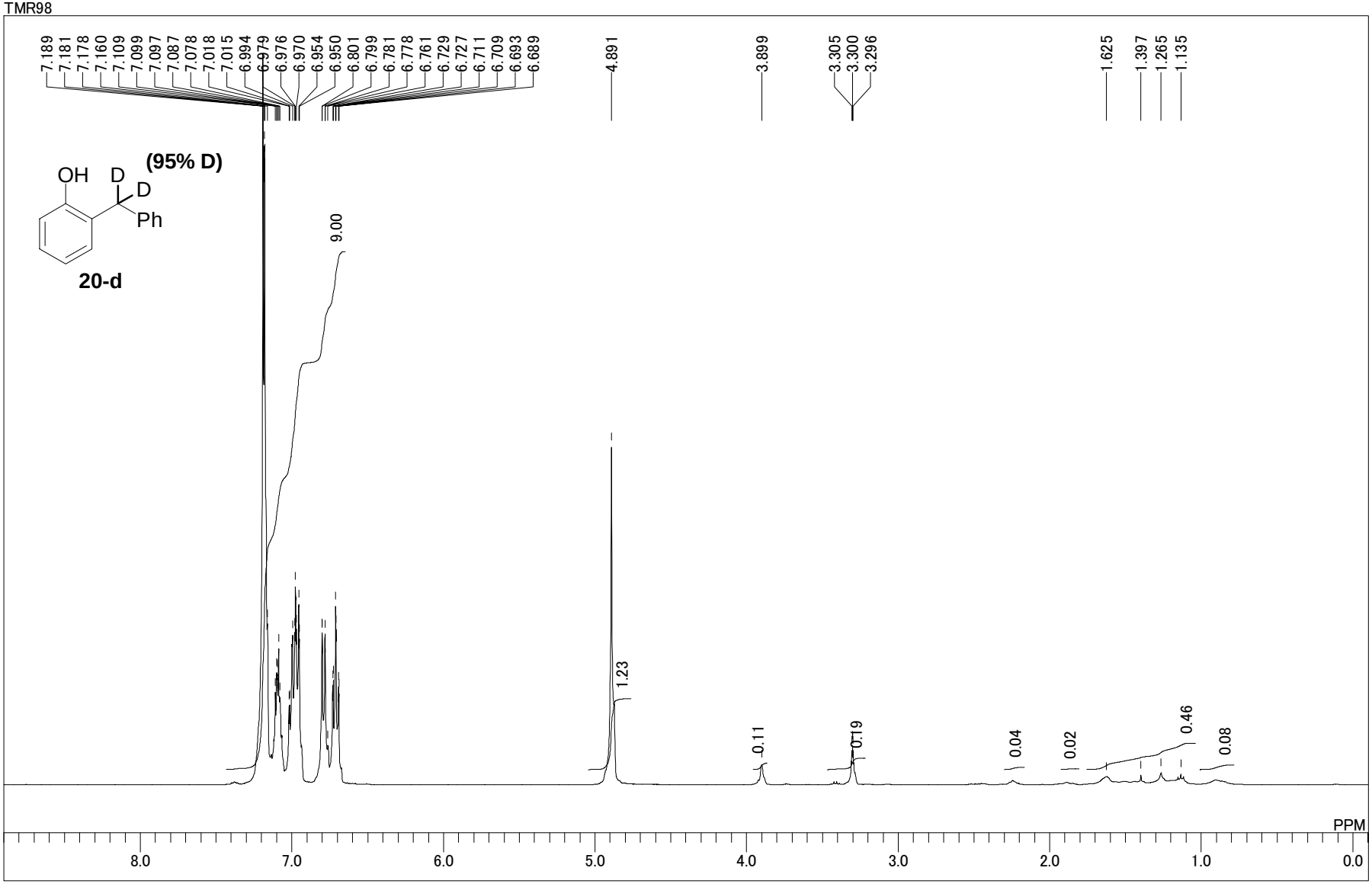
F:¥NMR 2007-7月¥TK7-167-11NON_E1_FT.als
TK7-167-1



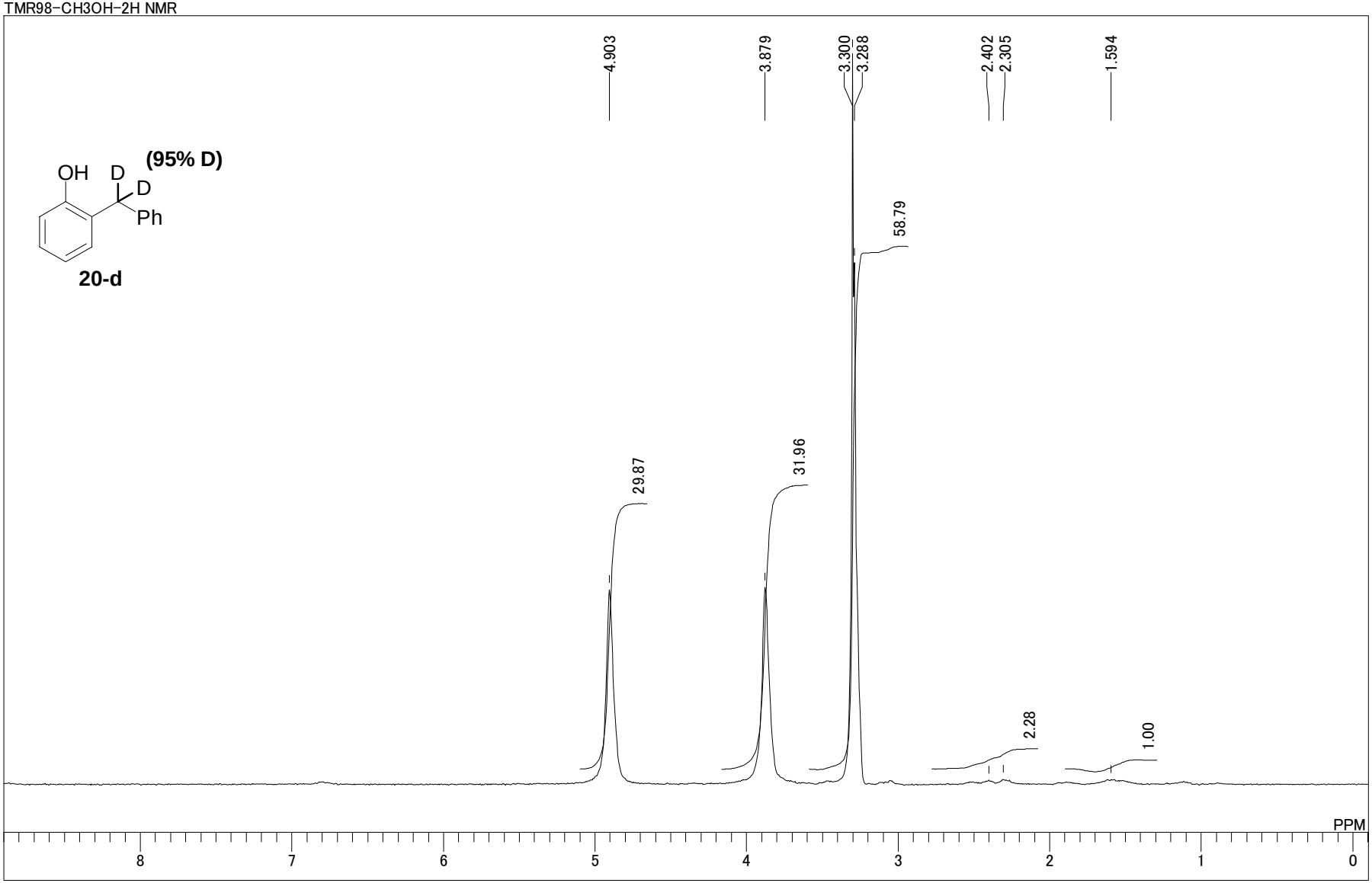
F:¥NMR 2007-7月¥TK7-167-1-CH3OH-2H NMR-FT.als
TK7-167-1-CH3OH-2H NMR



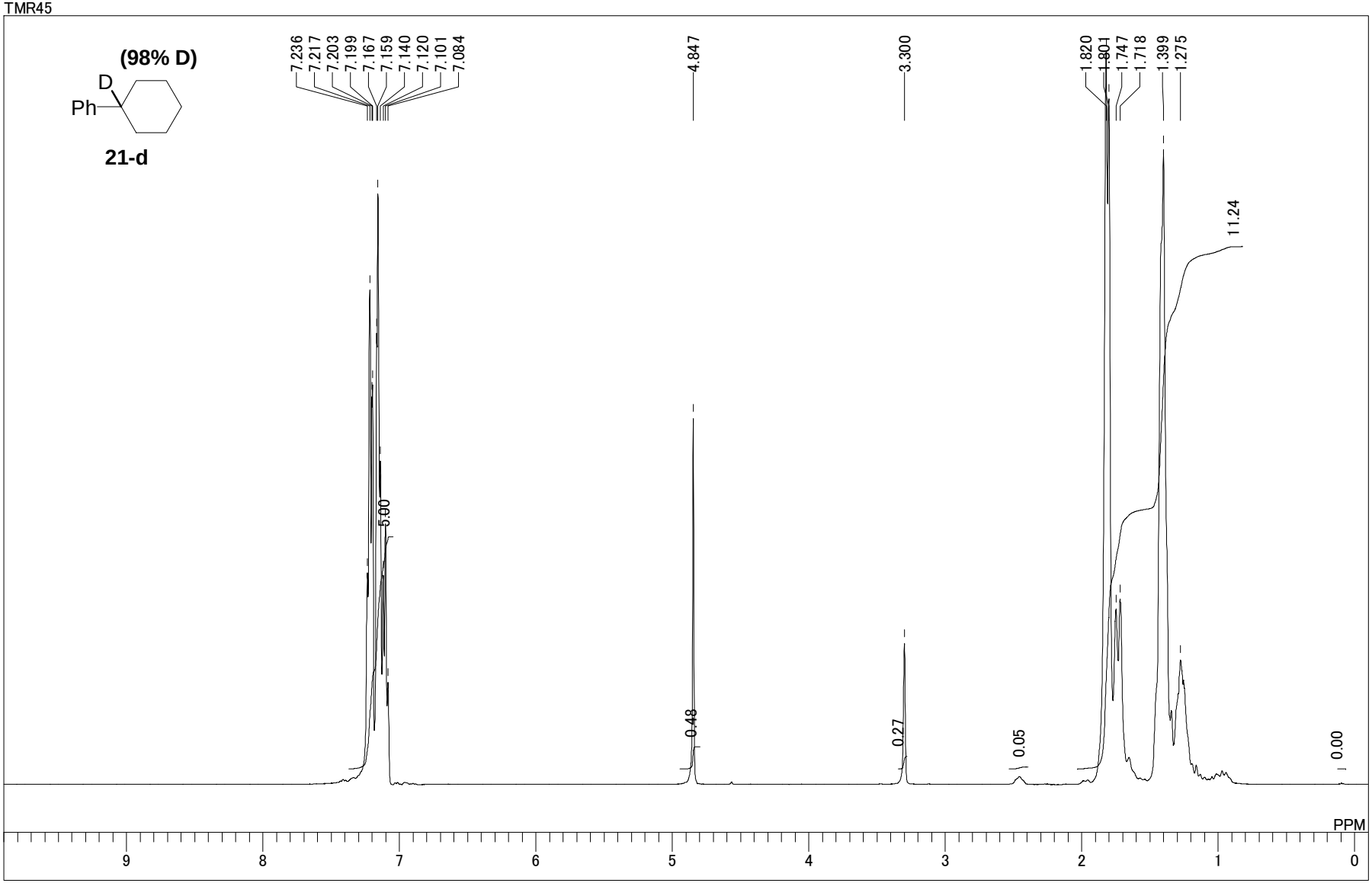
D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR981NON_E1-FT.als
TMR98



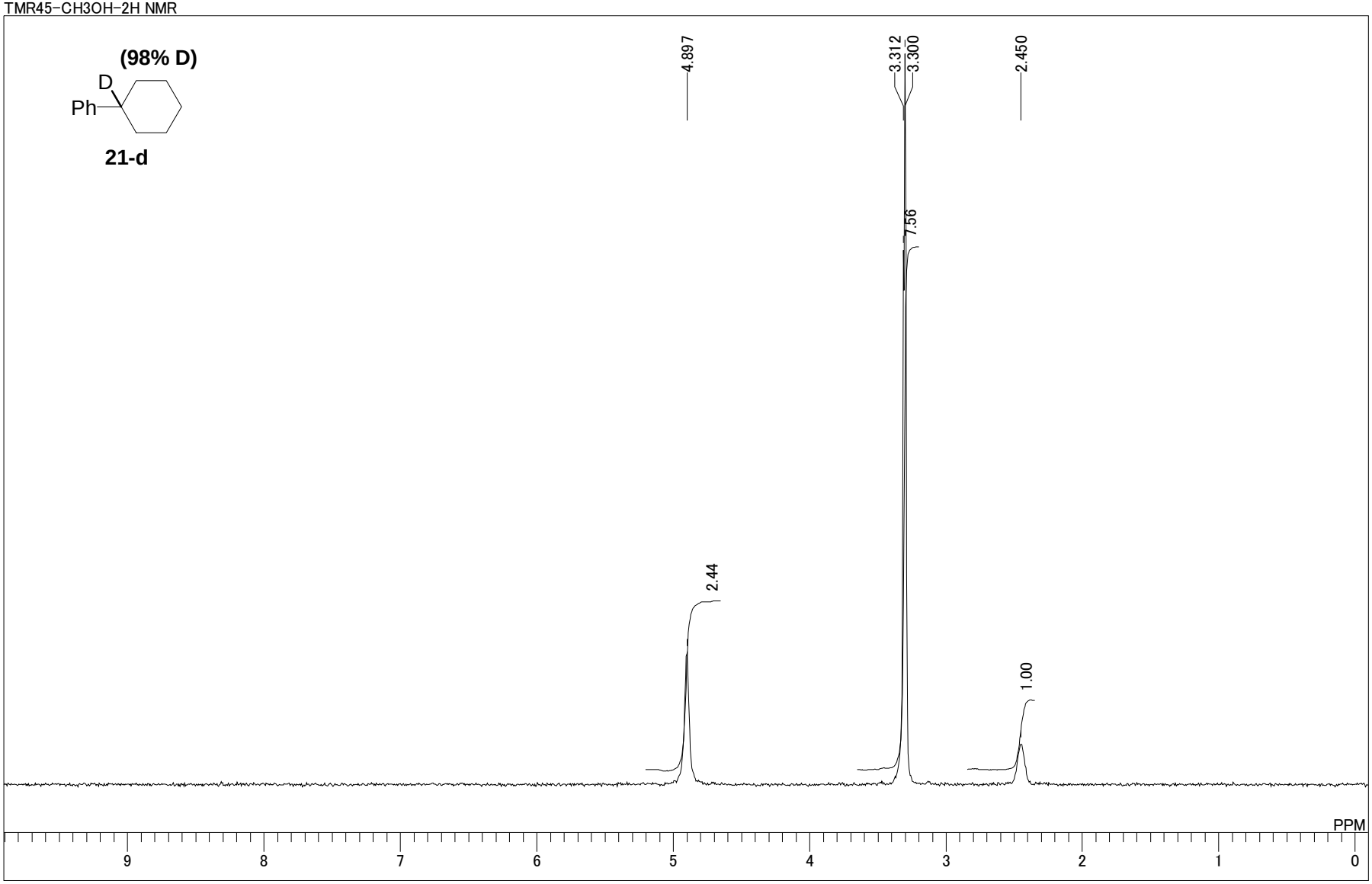
D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR98-CH3OH-2H NMR-FT.als
TMR98-CH3OH-2H NMR

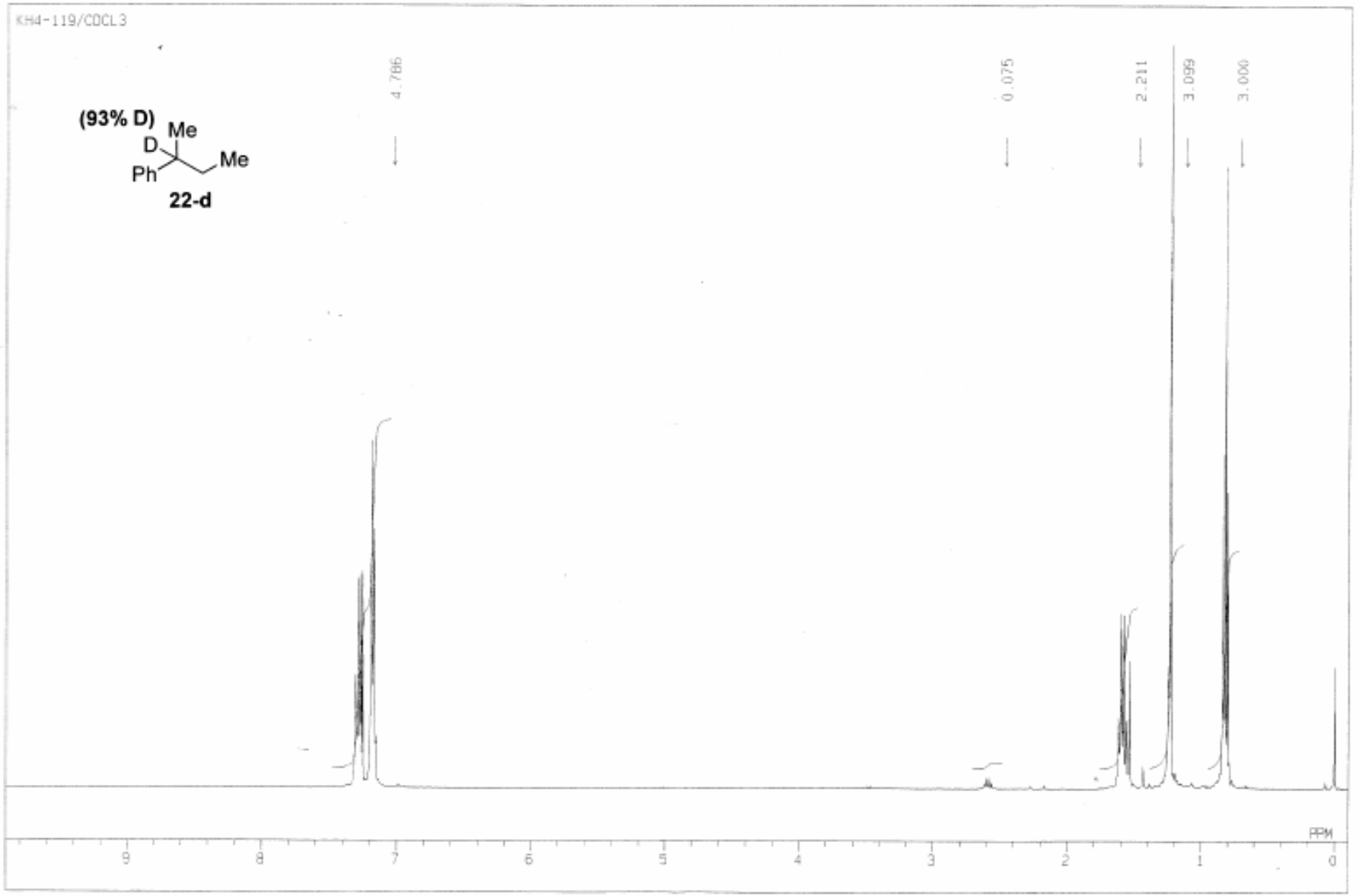


D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR451NON_E2-FT.als
TMR45

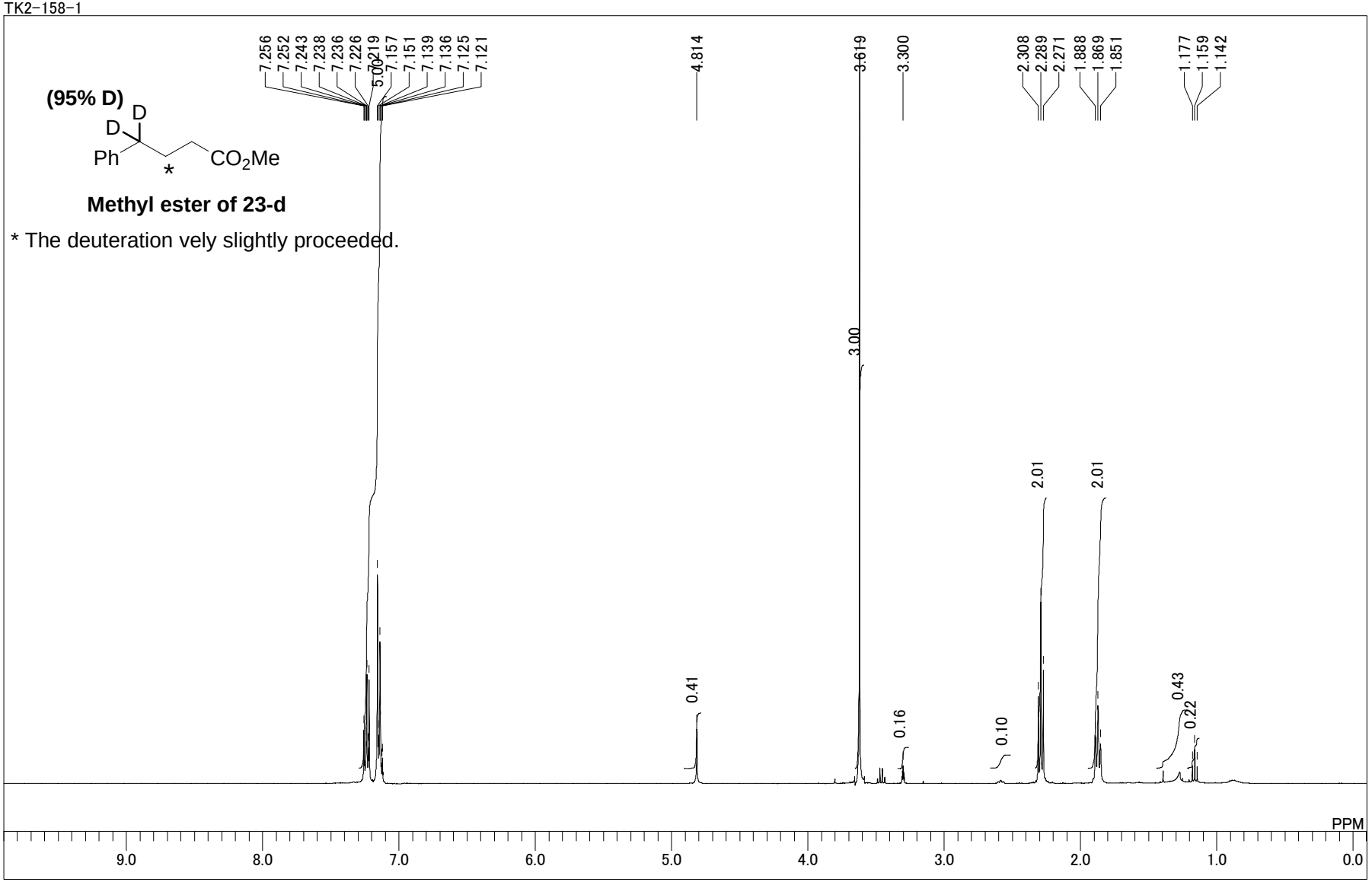


D:¥Data¥水本¥TMR NMR Data (ベンジル位論文用)¥TMR45-CH3OH-2H NMR-FT.als
TMR45-CH3OH-2H NMR




KH4-119/CDCL3
(93% D)
Me
D
Ph
Me
22-d
4.786
0.075
2.211
3.099
3.000
PPM
9
8
7
6
5
4
3
2
1
0

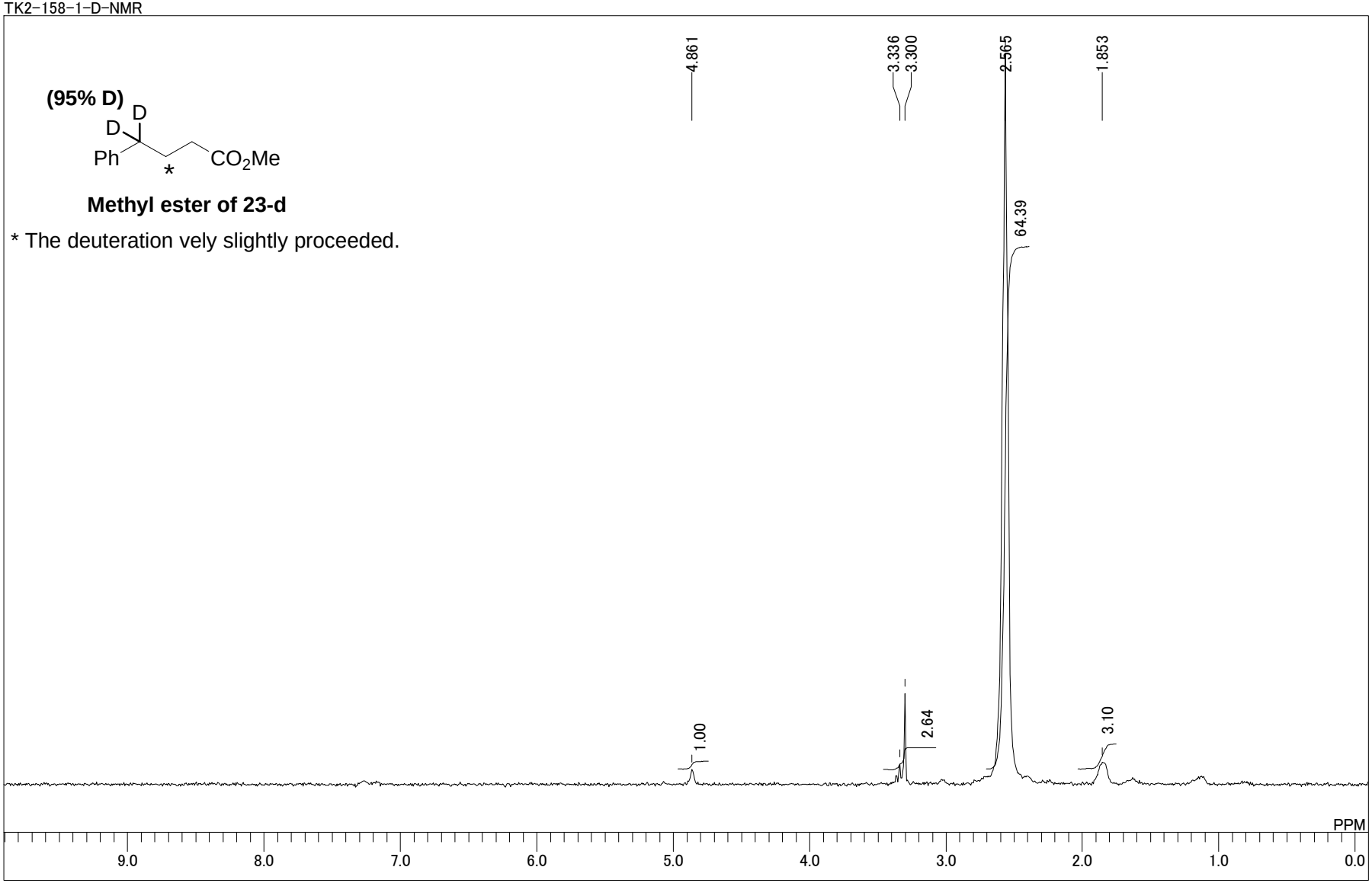
D:¥Data¥保存版 My Document¥NMR DATA¥NMR 2004-2005年¥NMR1¥TK2-158-1-FT.als
TK2-158-1



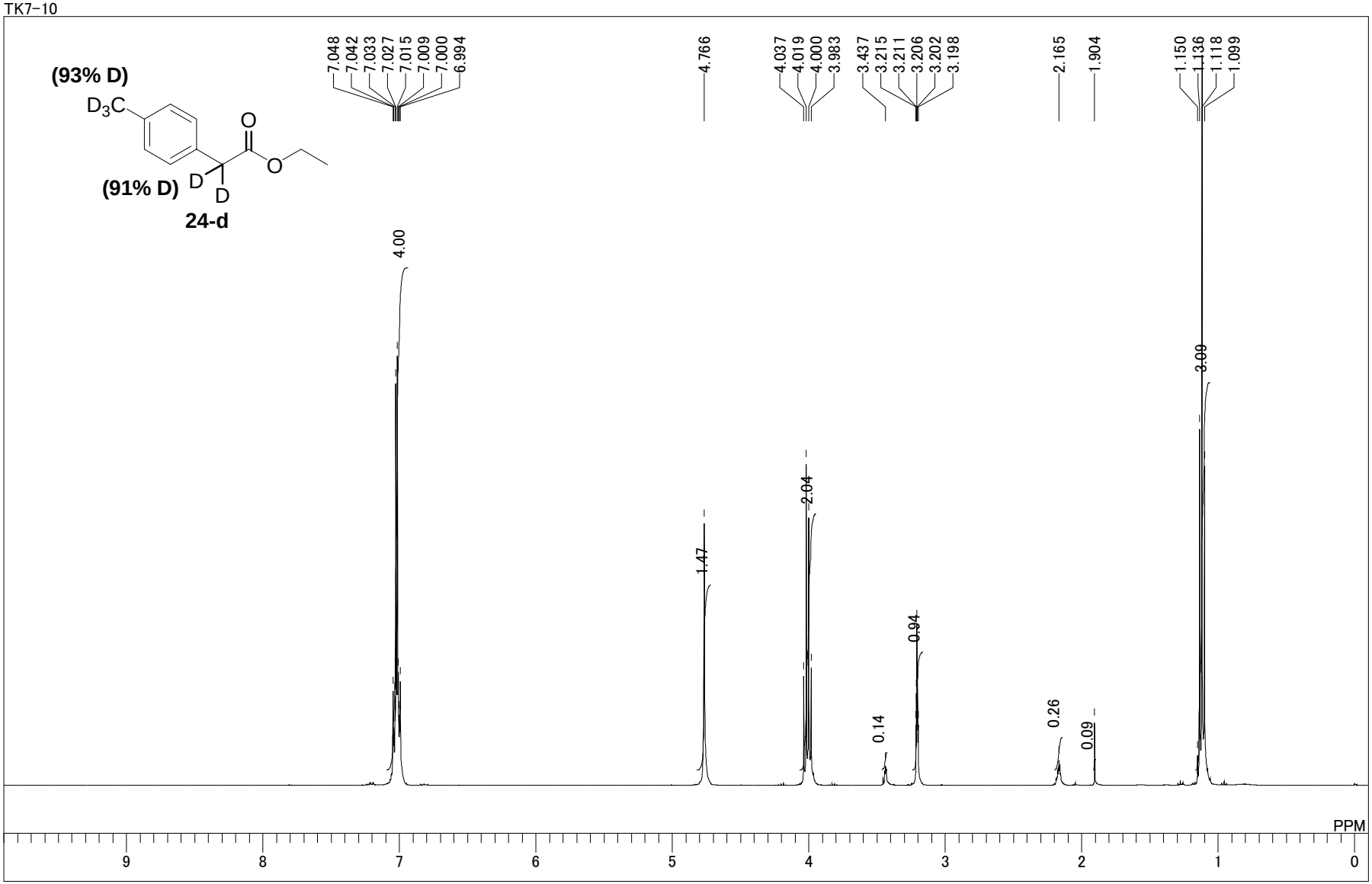
Methyl ester of 23-d

* The deuteration vely slightly proceeded.

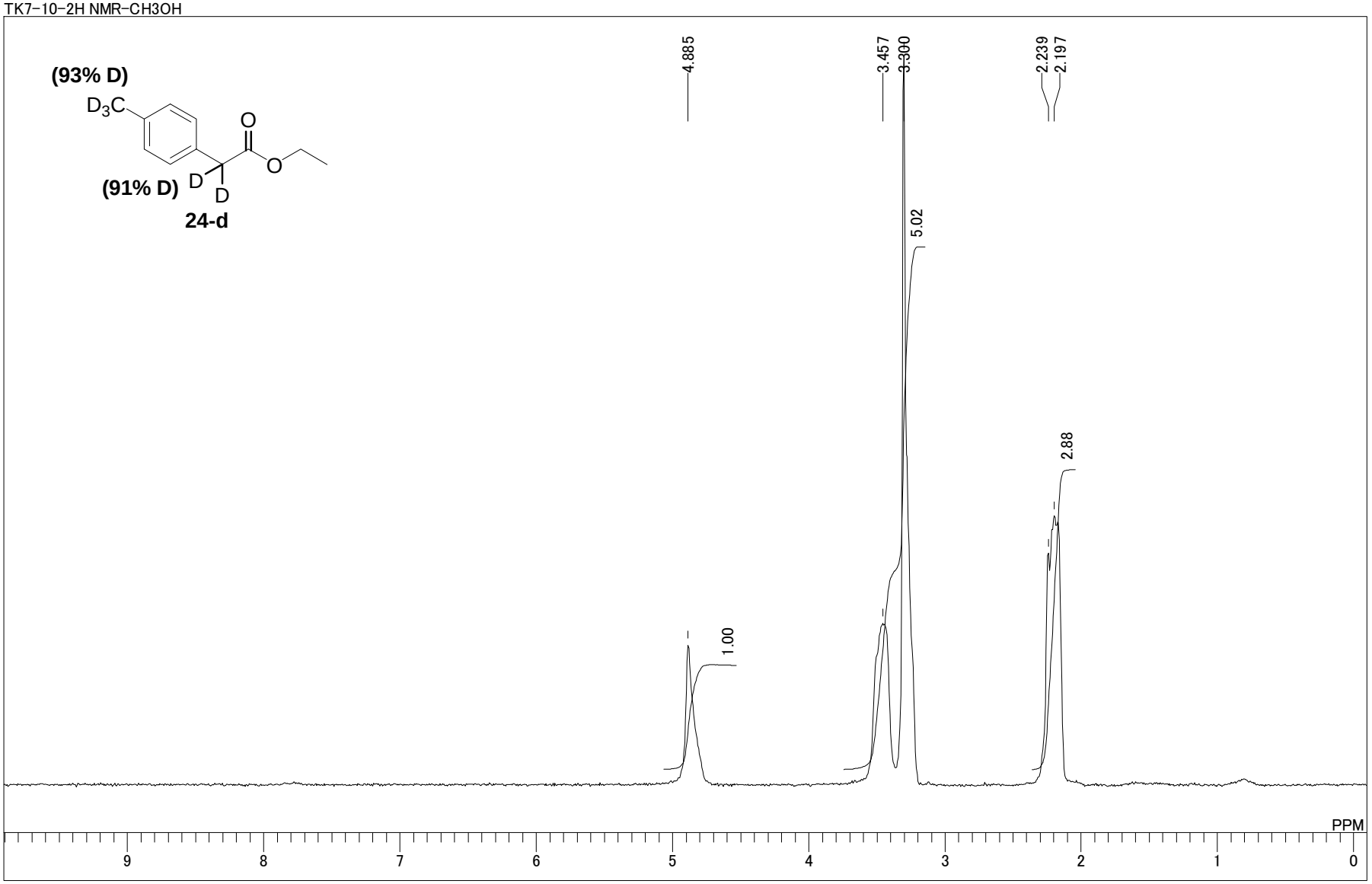
D:¥Data¥保存版 My Document¥NMR DATA¥NMR 2004-2005年¥NMR1¥TK2-158-1-D-NMR-FT.als
TK2-158-1-D-NMR



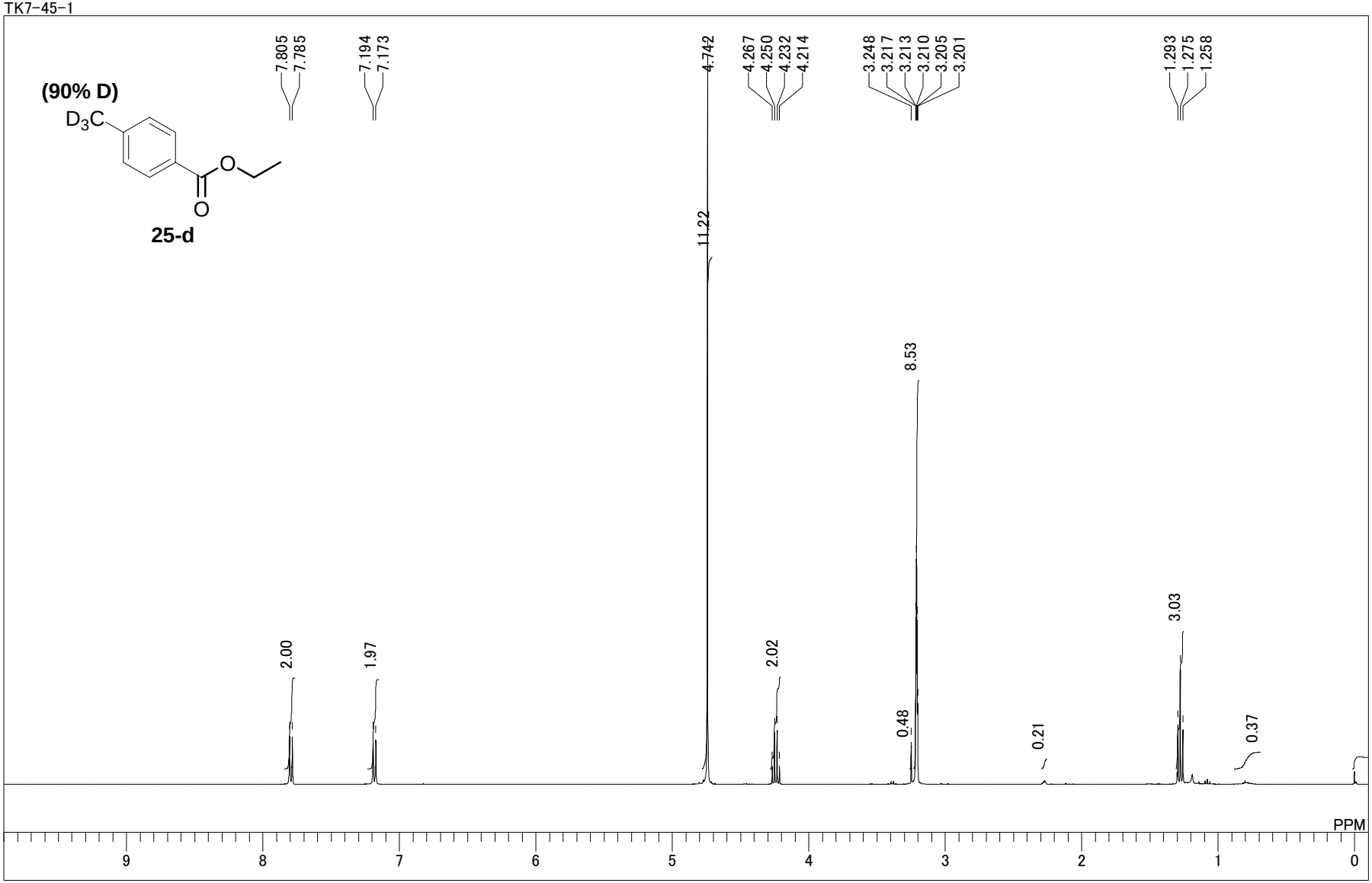
D:¥Data¥NMR 2007年¥NMR 2007-3月¥TK7-101NON_E5_FT.als
TK7-10



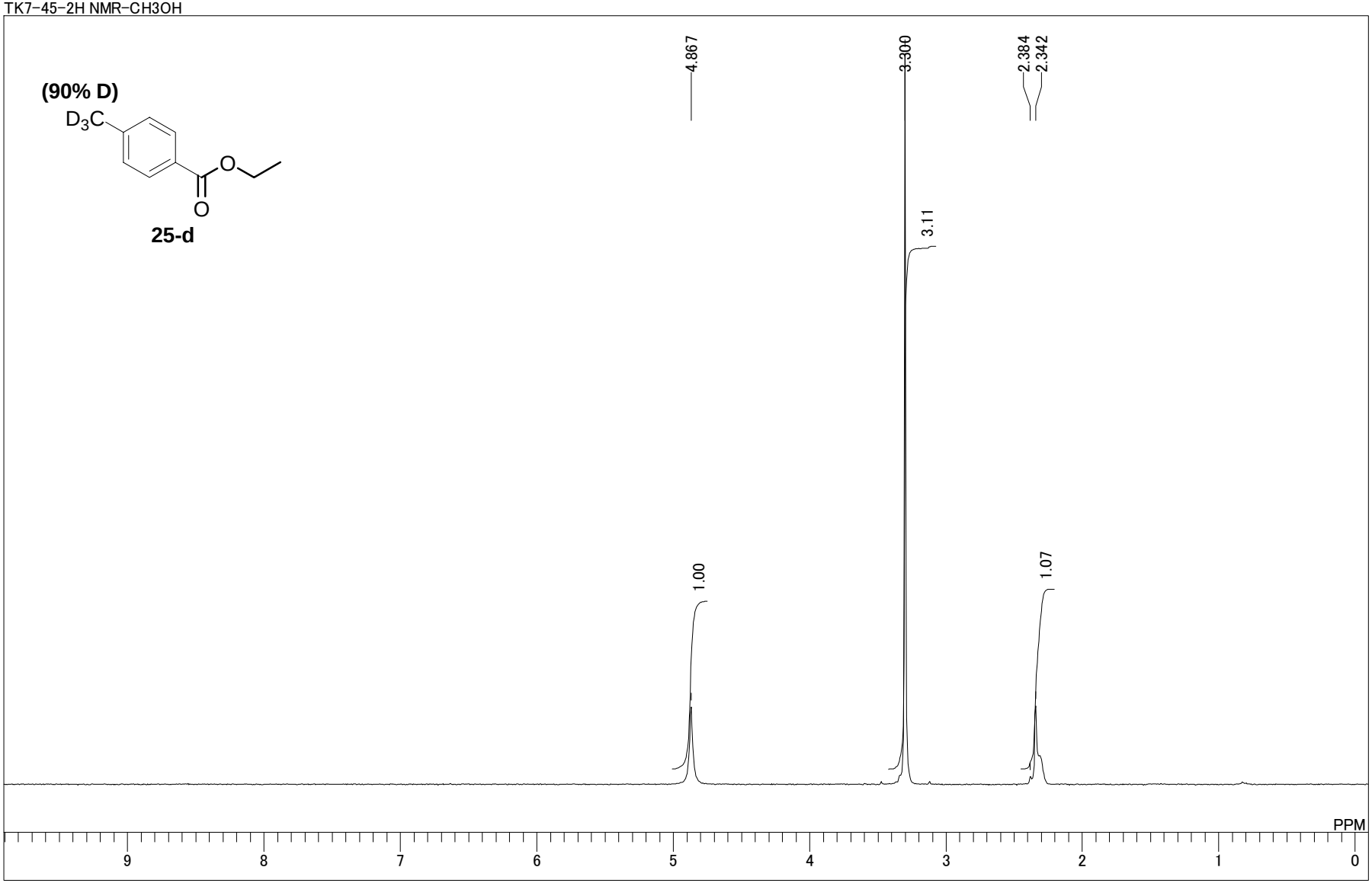
D:¥Data¥NMR 2007年¥NMR 2007-4月¥2H NMR 4-3¥TK7-10-2H NMR-CH3OH-FT.als
TK7-10-2H NMR-CH3OH



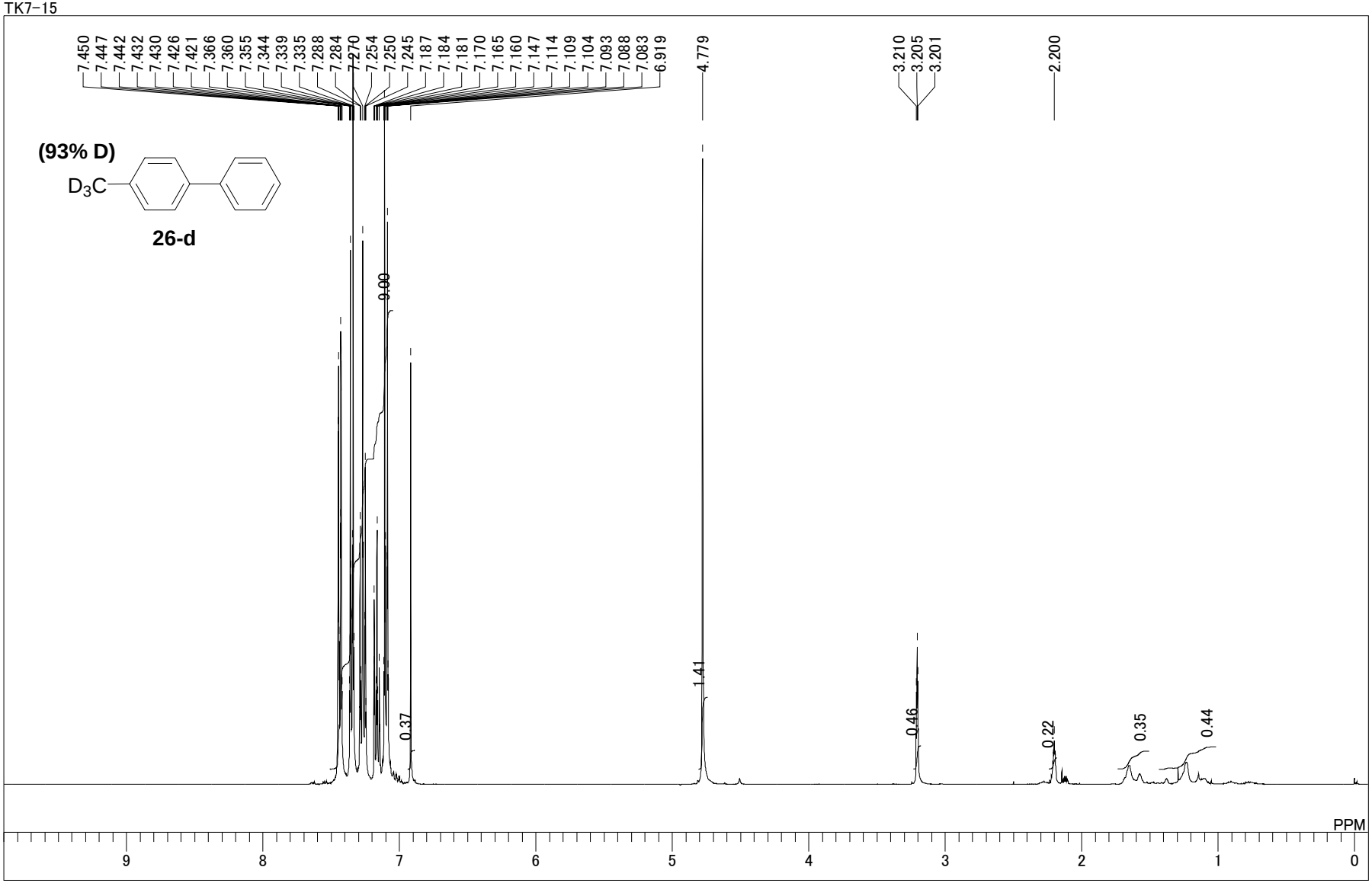
D:¥Data¥NMR 2007年¥NMR 2007-4月¥TK7-45-11NON_E1_FT.als
TK7-45-1



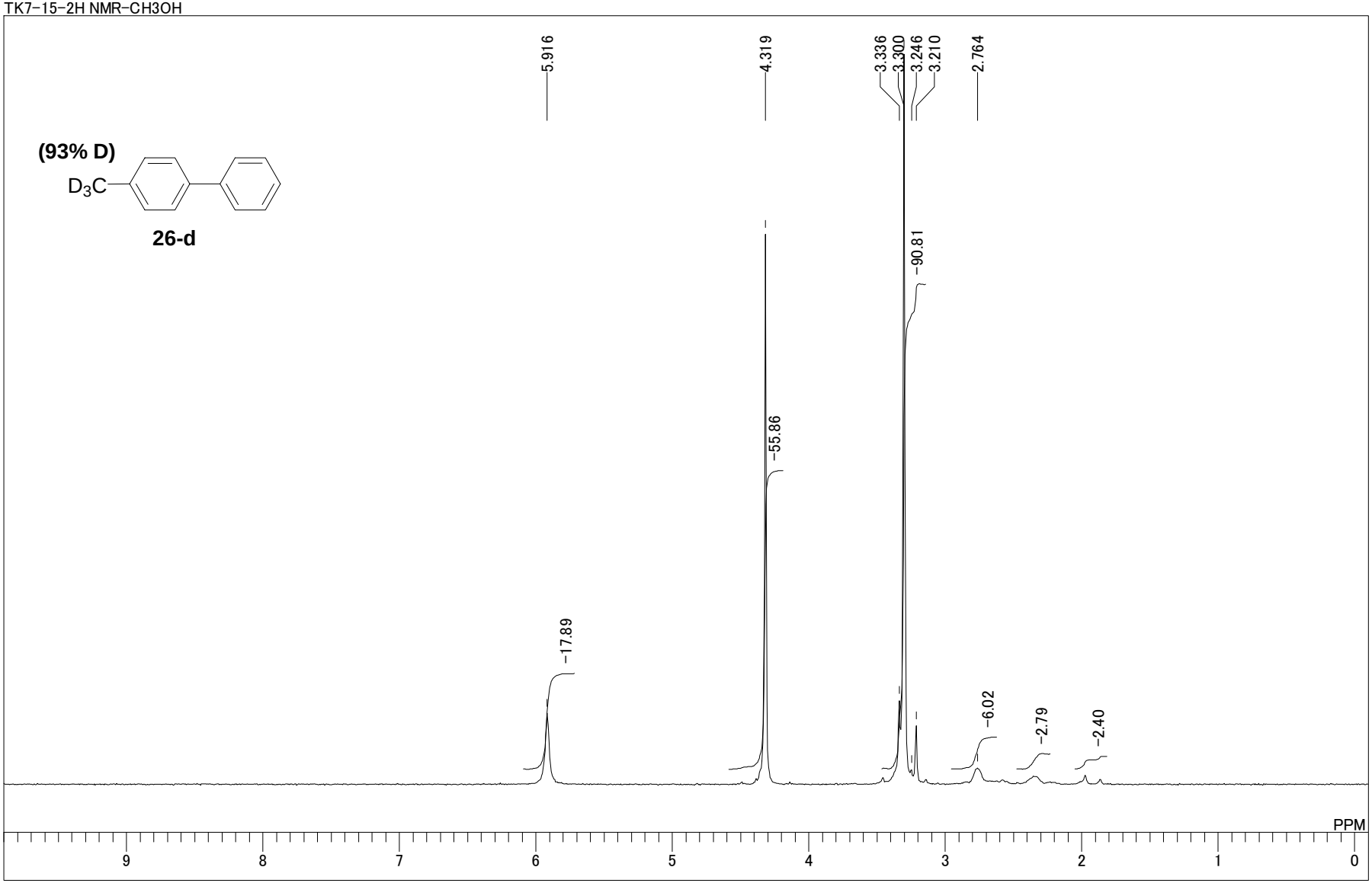
D:¥Data¥NMR 2007年¥NMR 2007-4月¥2H NMR 4-15¥TK7-45-2H NMR-CH3OH-FT.als
TK7-45-2H NMR-CH3OH



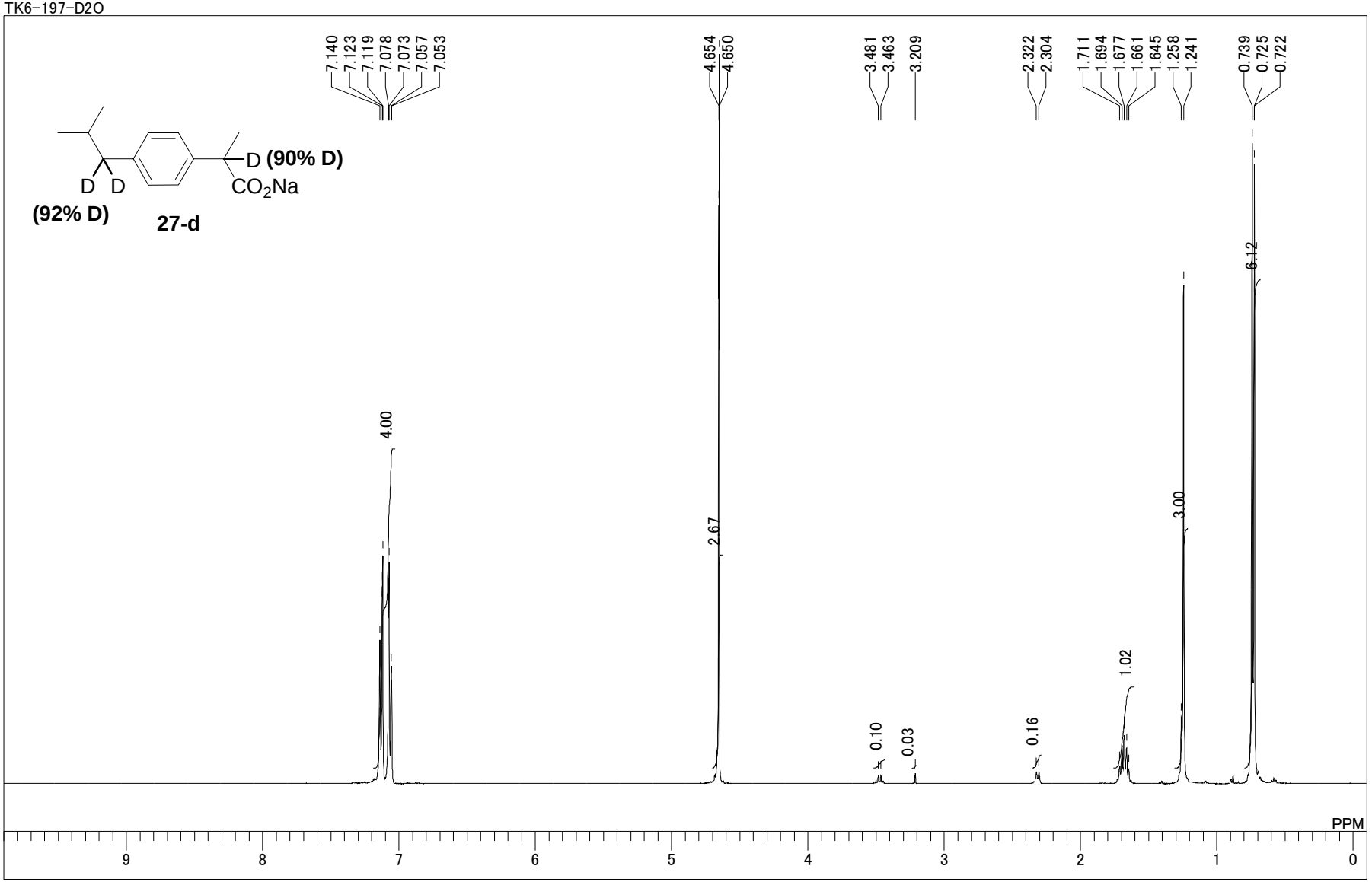
D:¥Data¥NMR 2007年¥NMR 2007-3月¥TK7-151NON_E1_FT.als
TK7-15



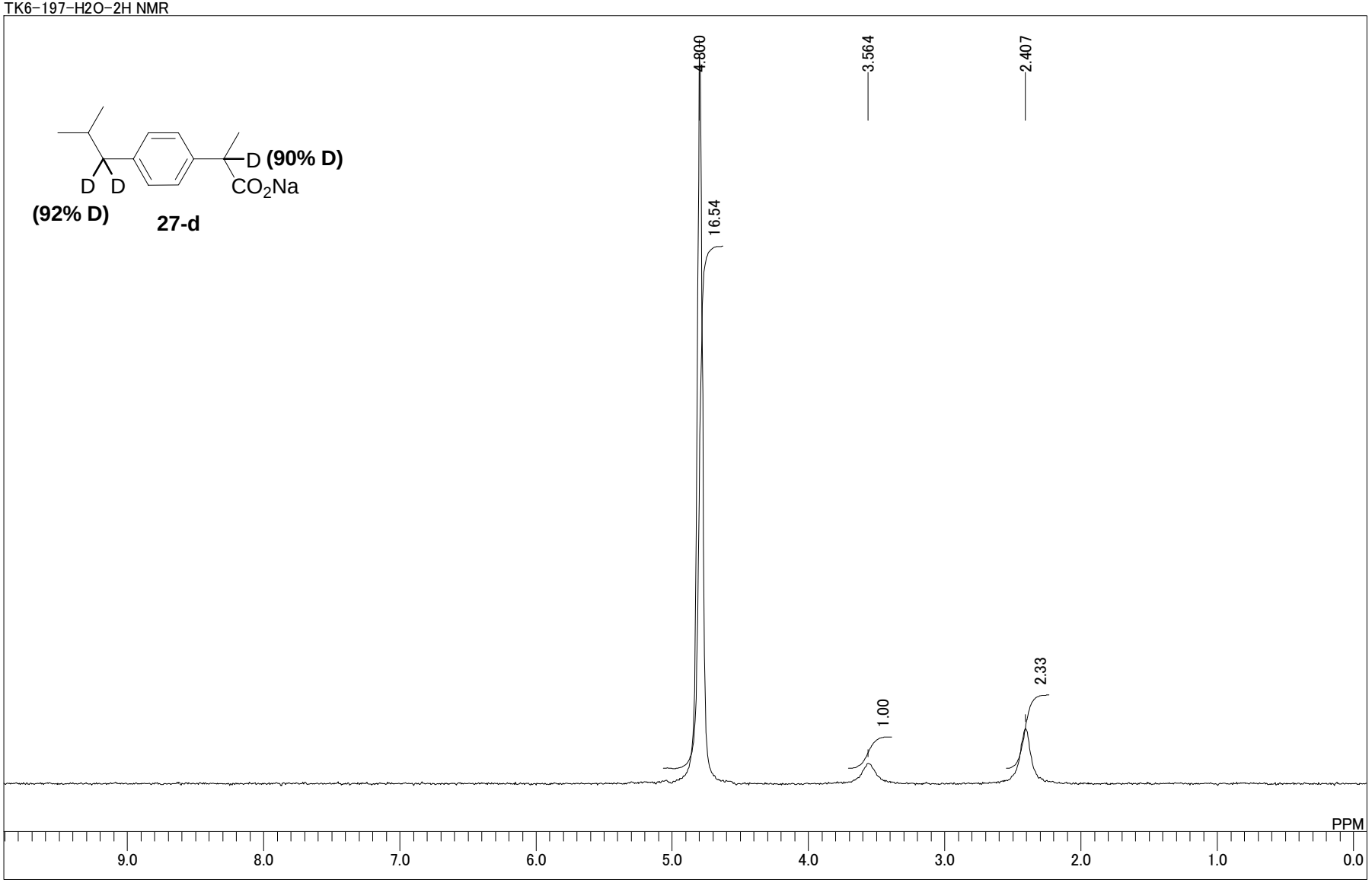
D:¥Data¥NMR 2007年¥NMR 2007-4月¥2H NMR 4-3¥TK7-15-2H NMR-CH3OH-FT.als
TK7-15-2H NMR-CH3OH



D:¥Data¥NMR 2007年¥NMR 2007-2月¥TK6-197-D2O-FT.als
TK6-197-D2O



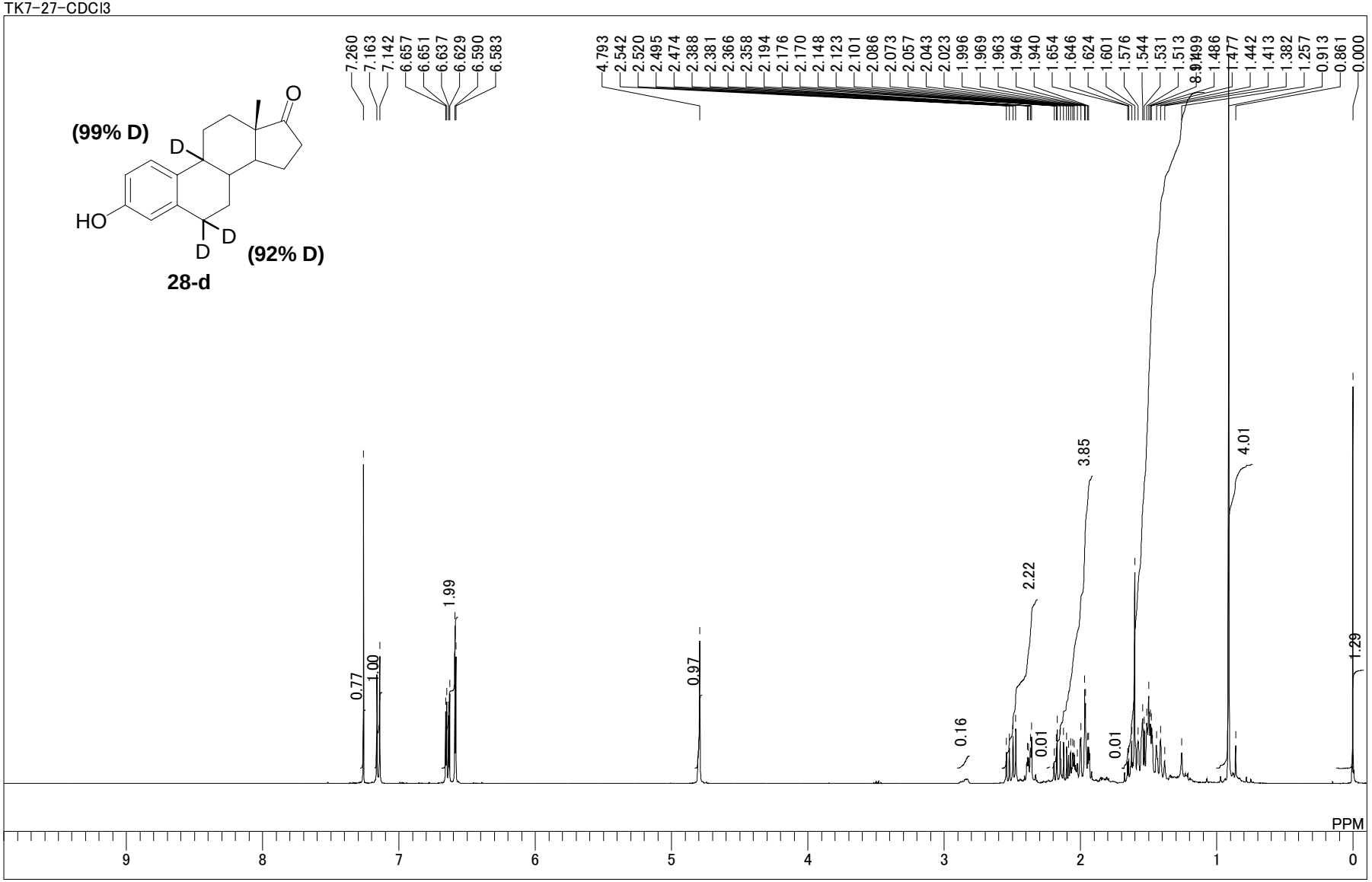
D:¥Data¥NMR 2007年¥NMR 2007-2月¥2H 2-21¥TK6-197-H2O-2H NMR-FT.als
TK6-197-H2O-2H NMR



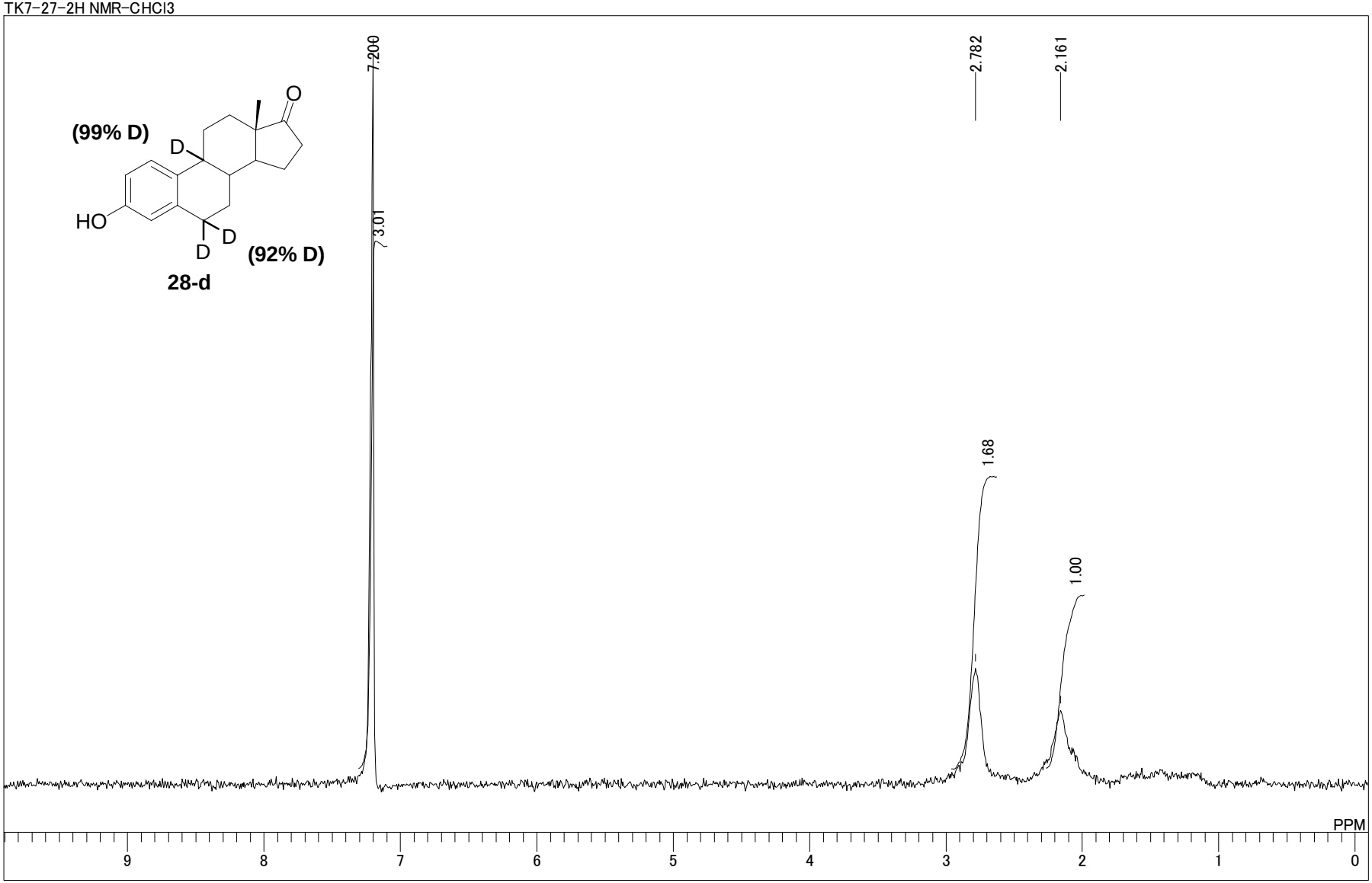
(92% D)

27-d

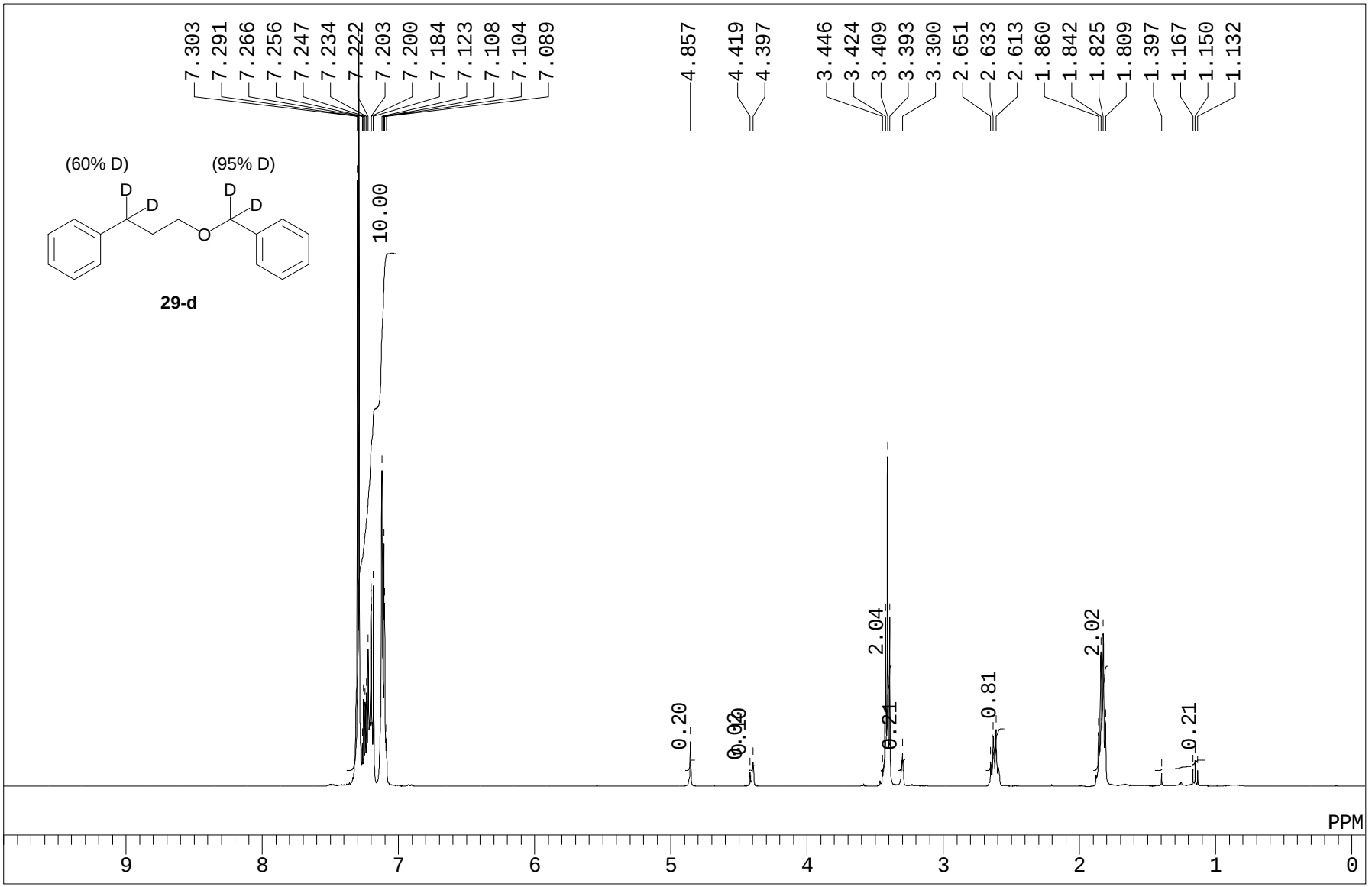
D:¥Data¥NMR 2007年¥NMR 2007-4月¥TK7-27-CDCl31NON_E1_FT.als
TK7-27-CDCl3



F:¥NMR 2007-5月¥2H NMR 5-19¥TK7-27-2H NMR-CHCl3-FT.als
TK7-27-2H NMR-CHCl3



D:\My Documents\•U‘¶”A My Document\NMR DATA\NMR 2006”N\NMR 2006.1\TK4-1971NON_E2_FT.als
TK4-197



* dibenzyl ether (diagnostic singlet: 4.42 ppm, 4H)

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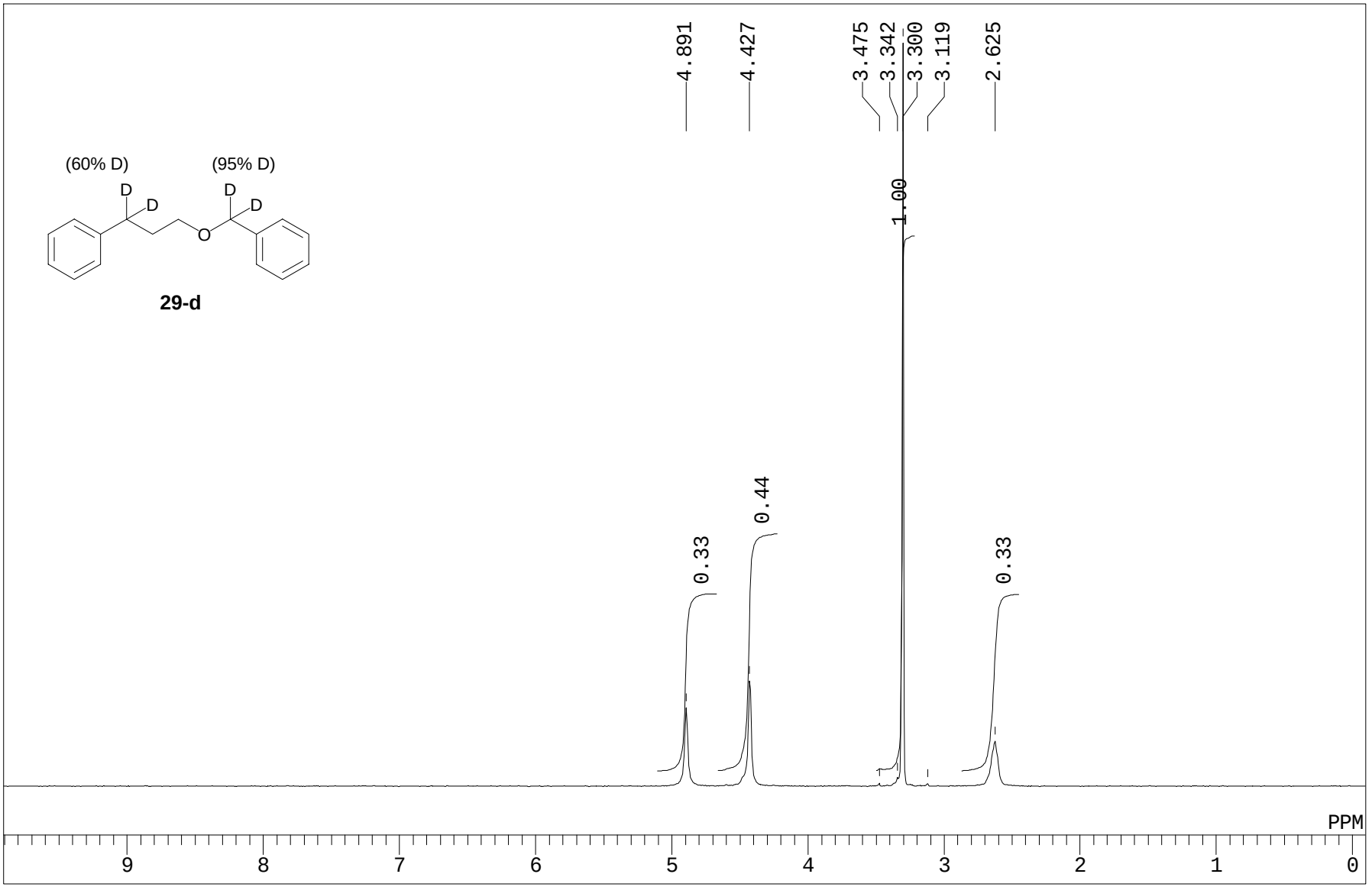
TK4-197-2H NMR



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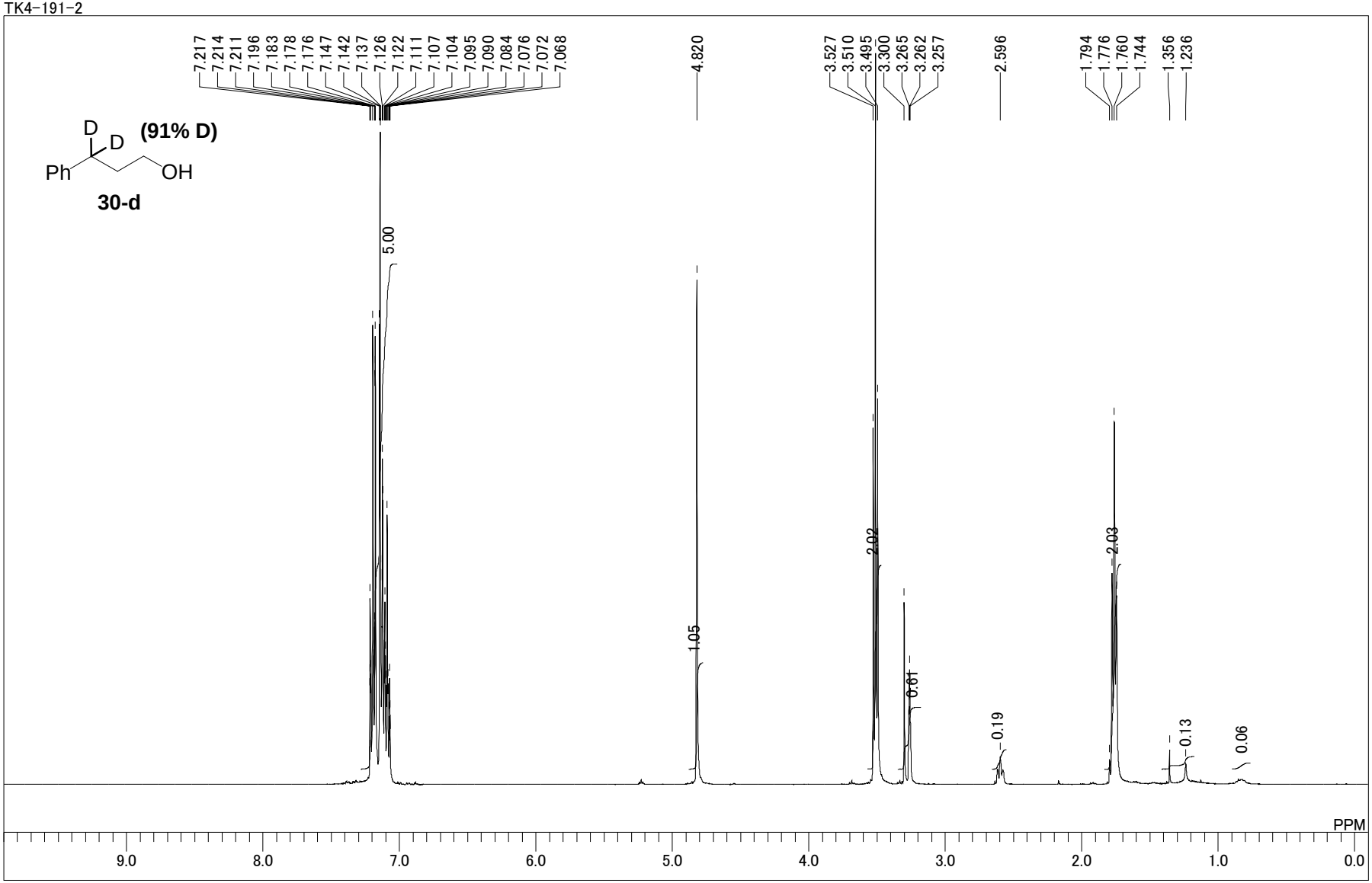
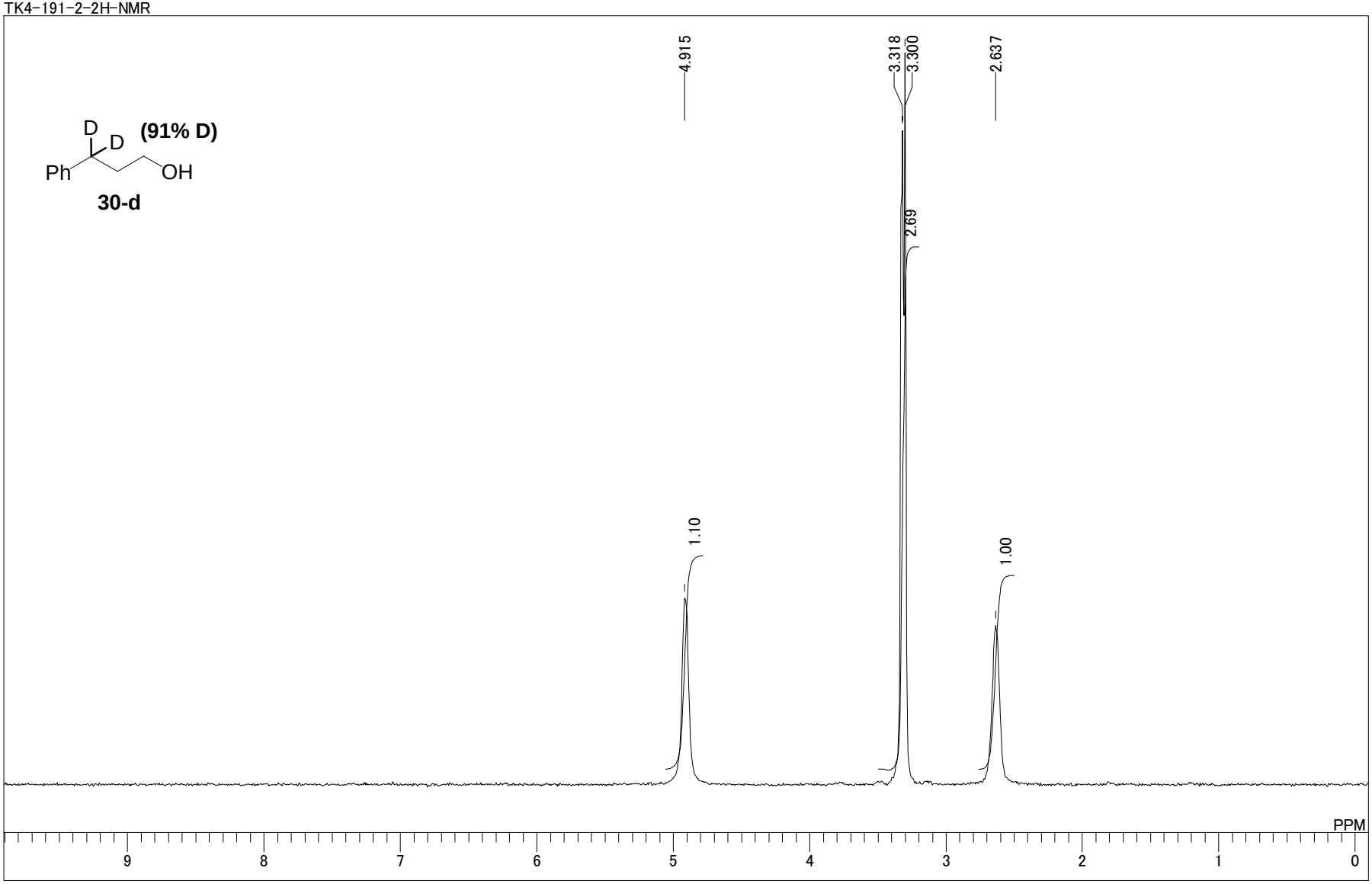
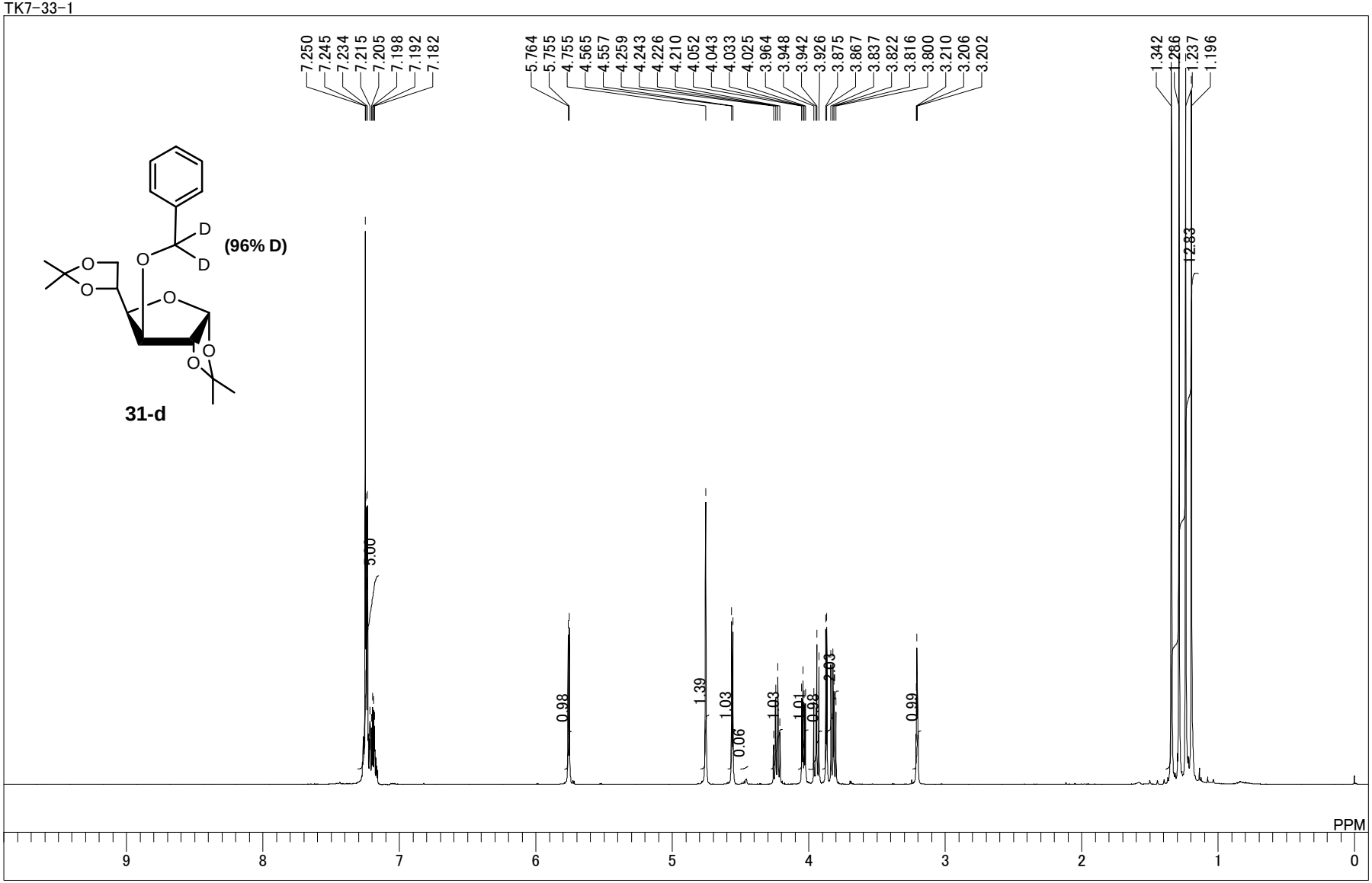
TK4-191-2



D:¥Data¥保存版 My Document¥NMR DATA¥NMR 2004-2005年¥NMR 2005.12¥TK4-191-2-2H-NMR-FT.als
TK4-191-2-2H-NMR



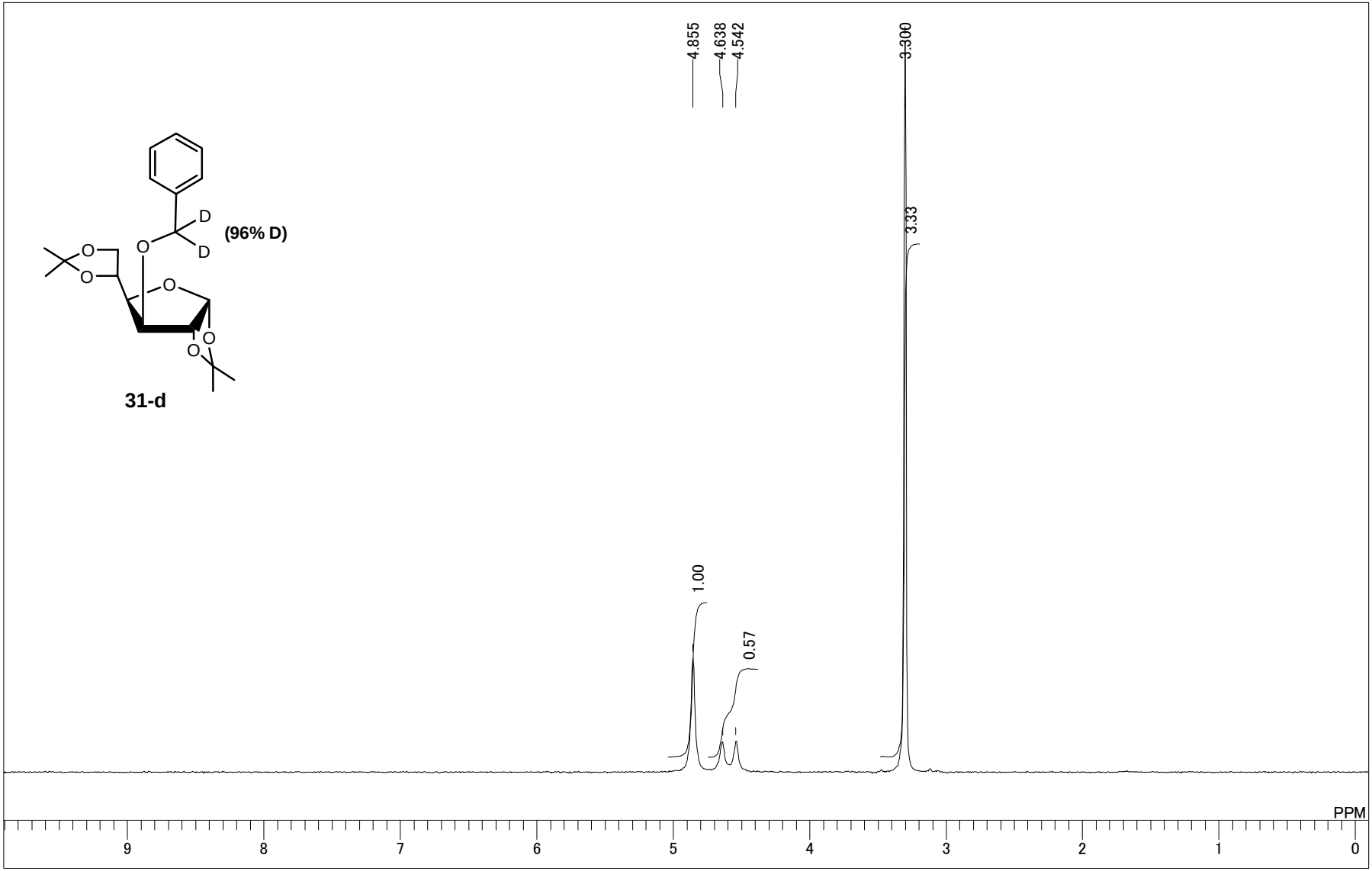
F:¥NMR 2007-4月¥TK7-33-11NON_E3_FT.als
TK7-33-1



(96% D)

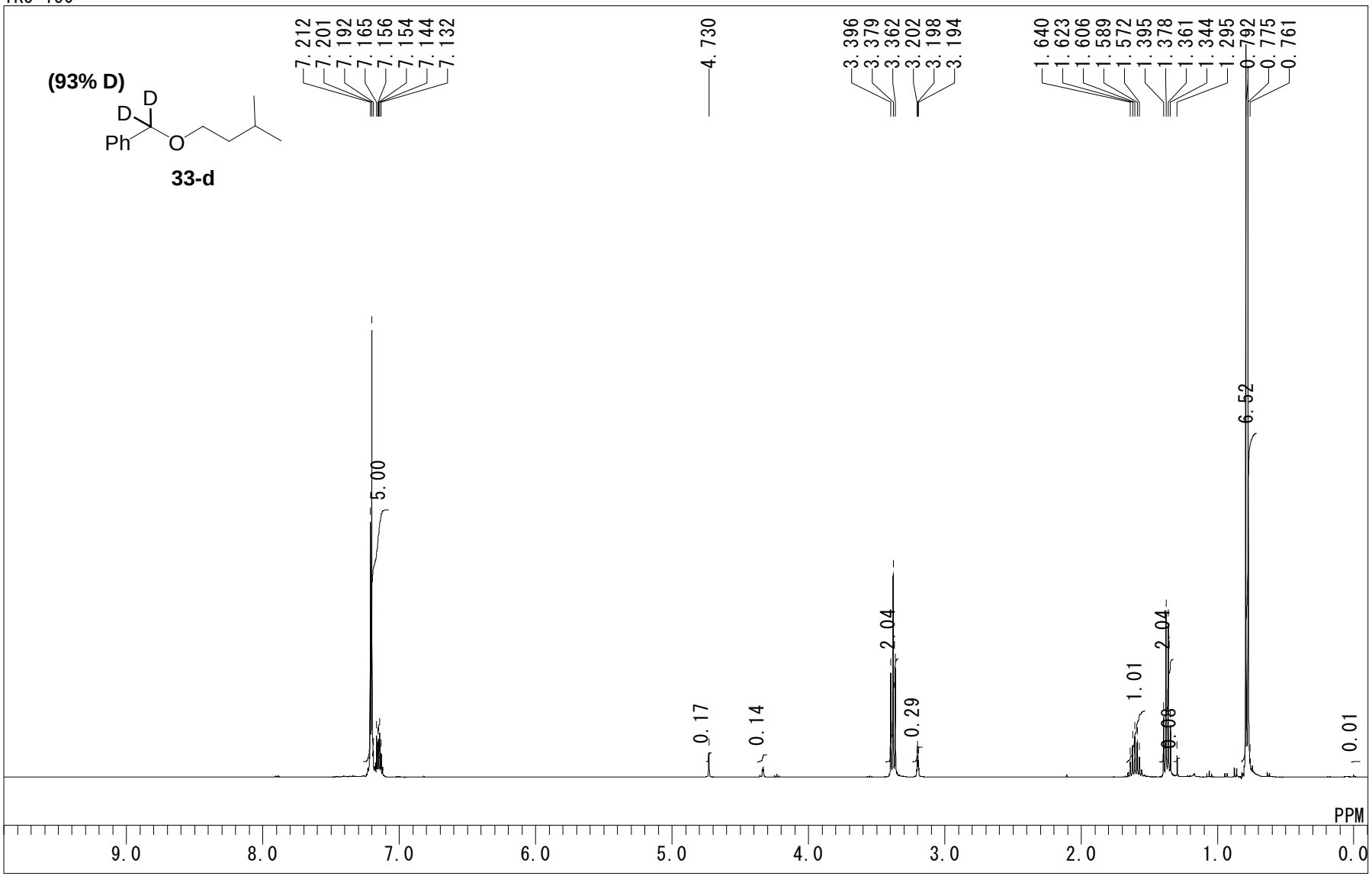
31-d

F:¥2H NMR 4-15¥TK7-33-1-2H NMR-CH3OH-FT.als
TK7-33-1-2H NMR-CH3OH

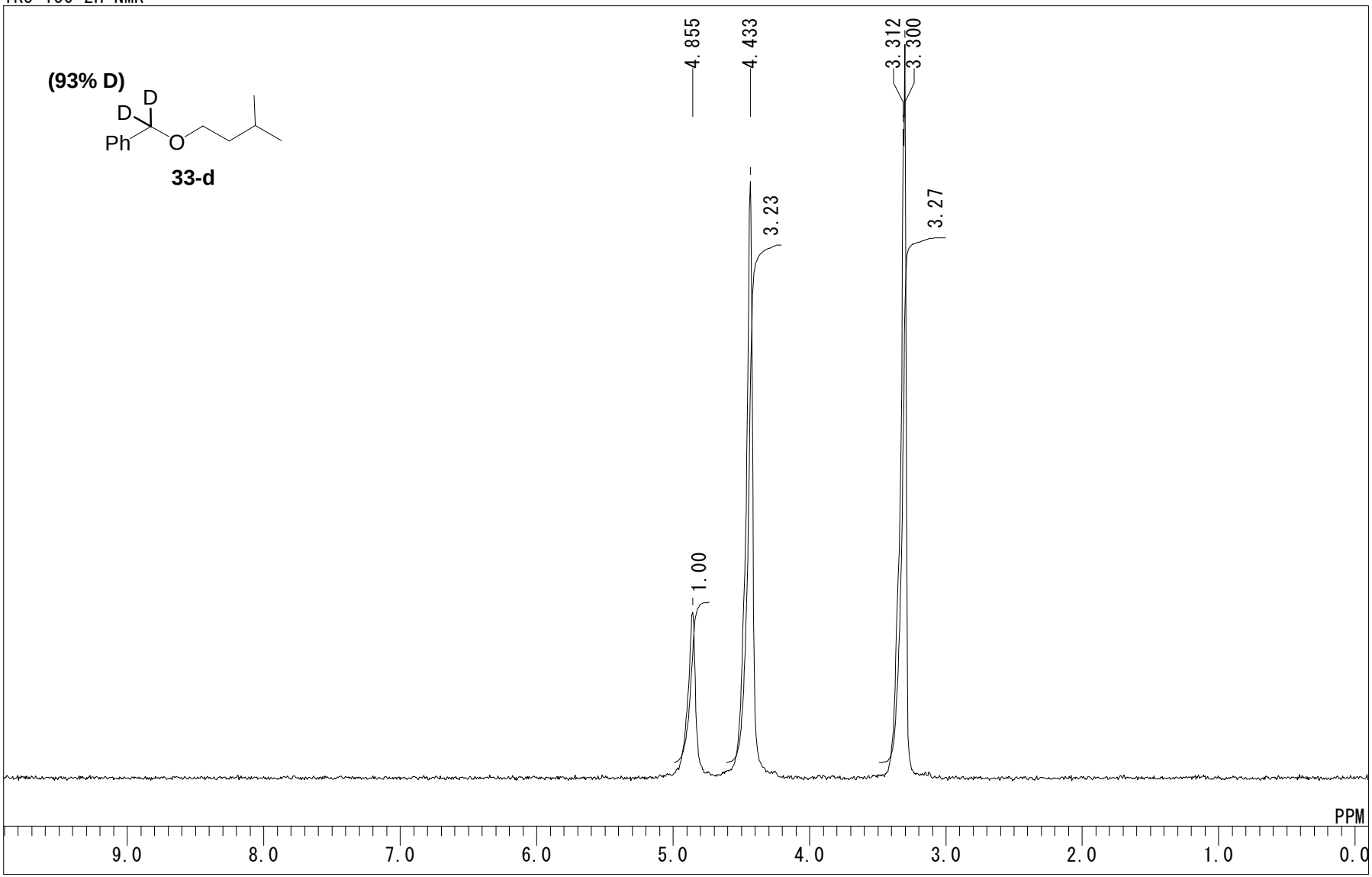


31-d

D:¥Data¥保存版 My Document¥NMR DATA¥NMR 2006年¥NMR 2006.6¥TK5-150-FT.als
TK5-150



D:¥Data¥保存版 My Document¥NMR DATA¥NMR 2006年¥NMR 2006.6¥TK5-150-2H-NMR-FT.als
TK5-150-2H-NMR



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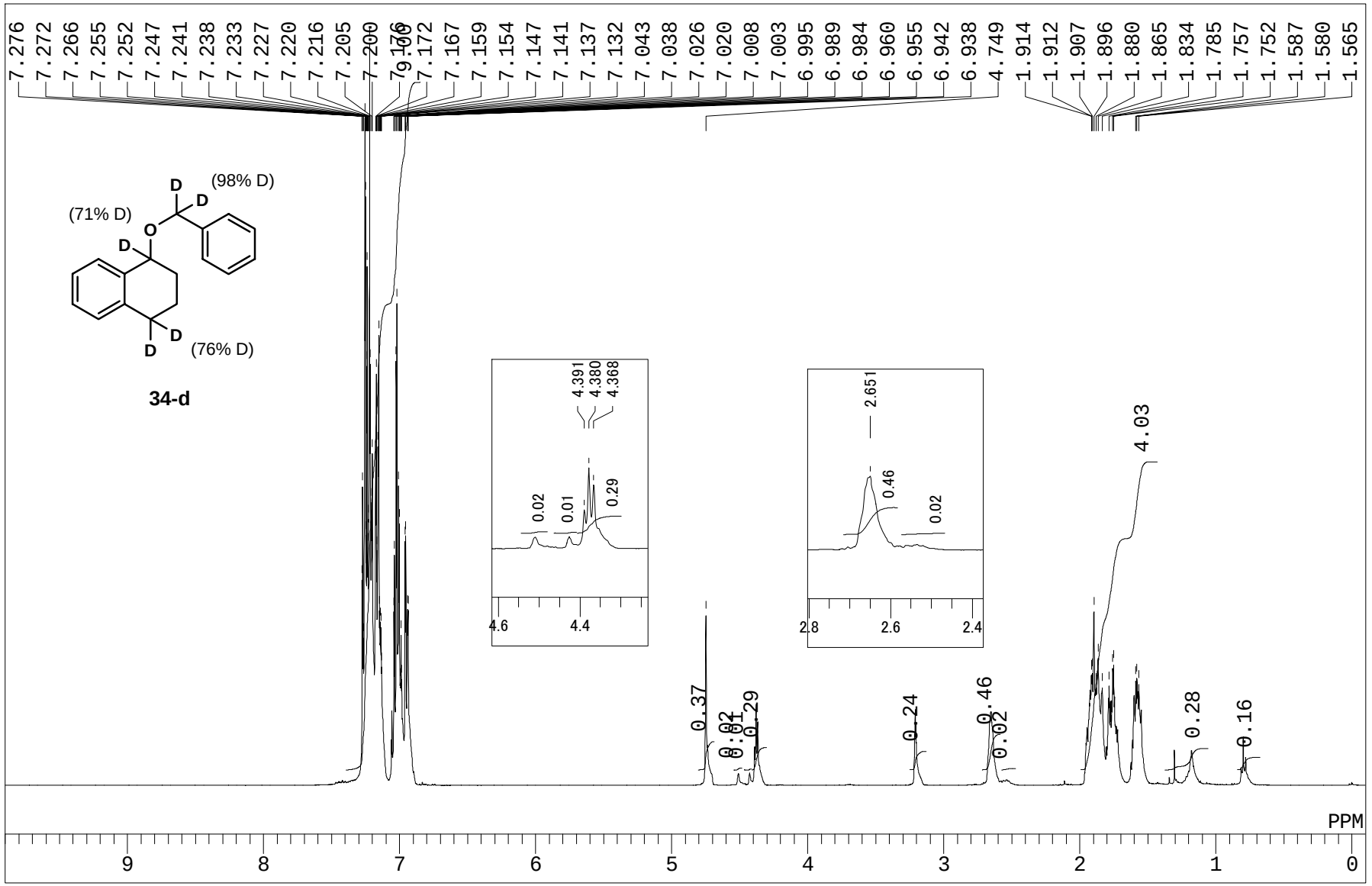
TK4-104-1



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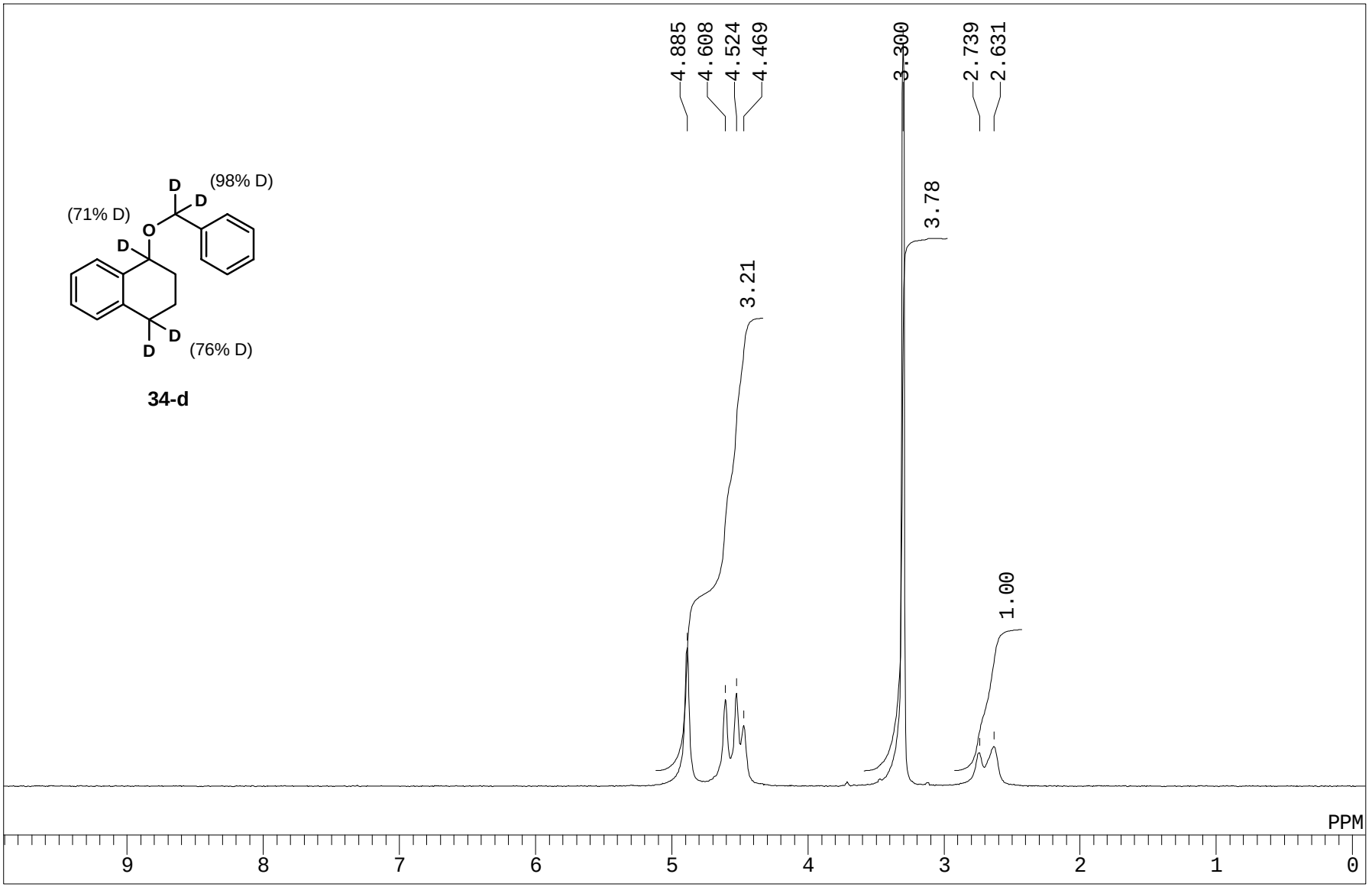
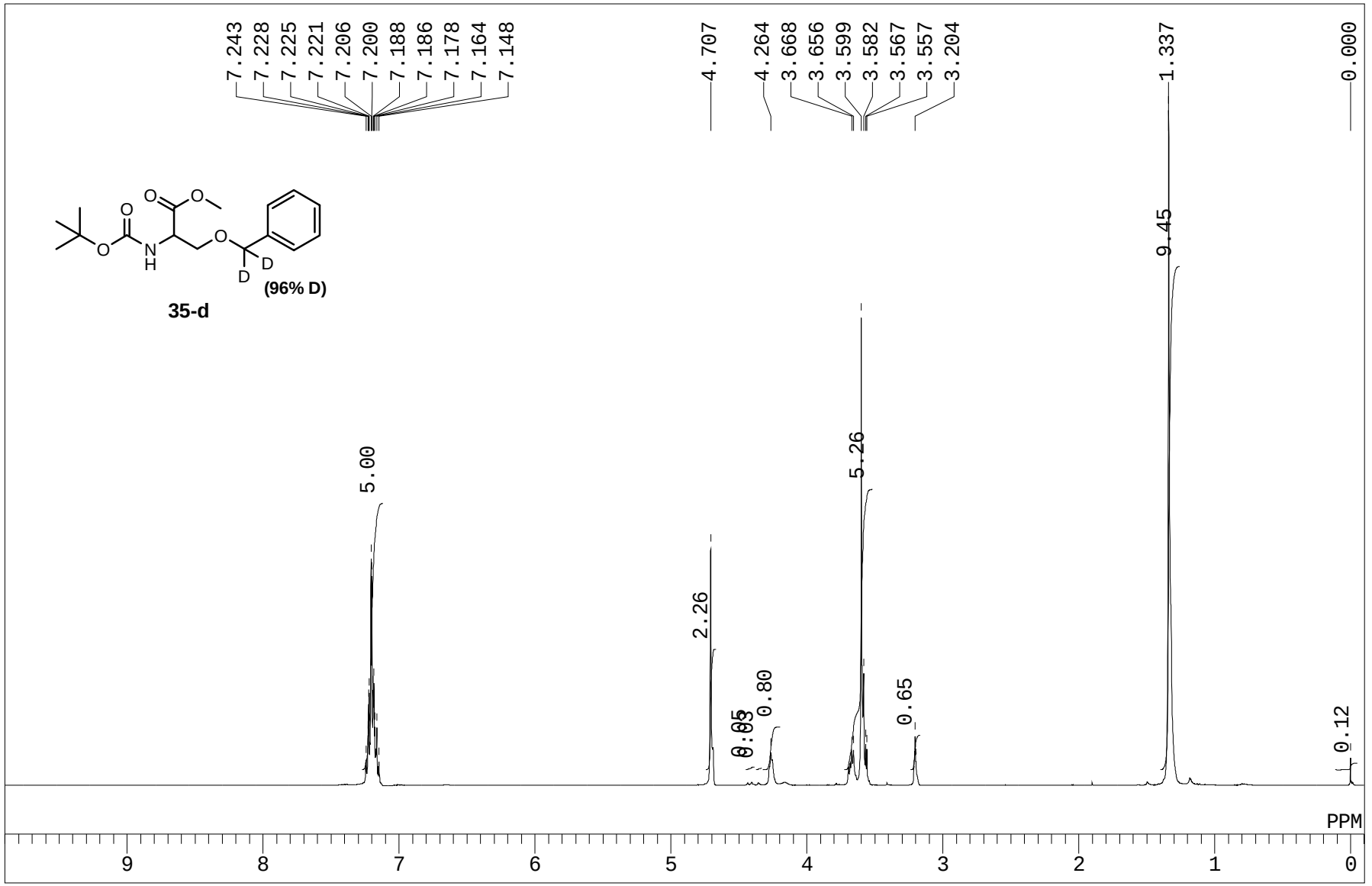
TK4-104-1-2H-NMR



34-d

D:\My Documents\•U‘¶”A My Document\NMR DATA\NMR 2006”N\NMR 2006.8\TK6-231NON_E3_FT.als
TK6-23



35-d **(96% D)**

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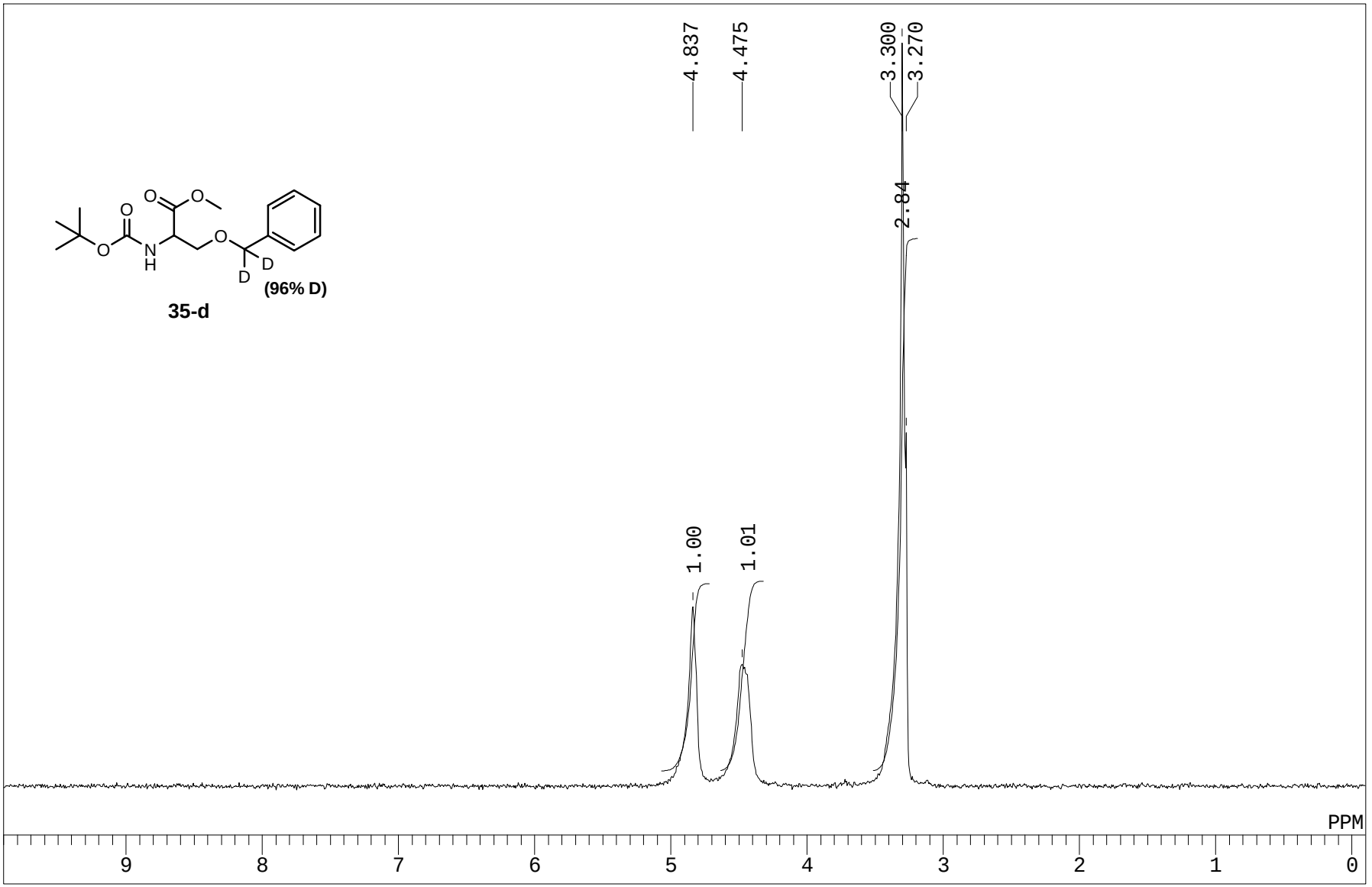
TK6-23-2H NMR



35-d **(96% D)**

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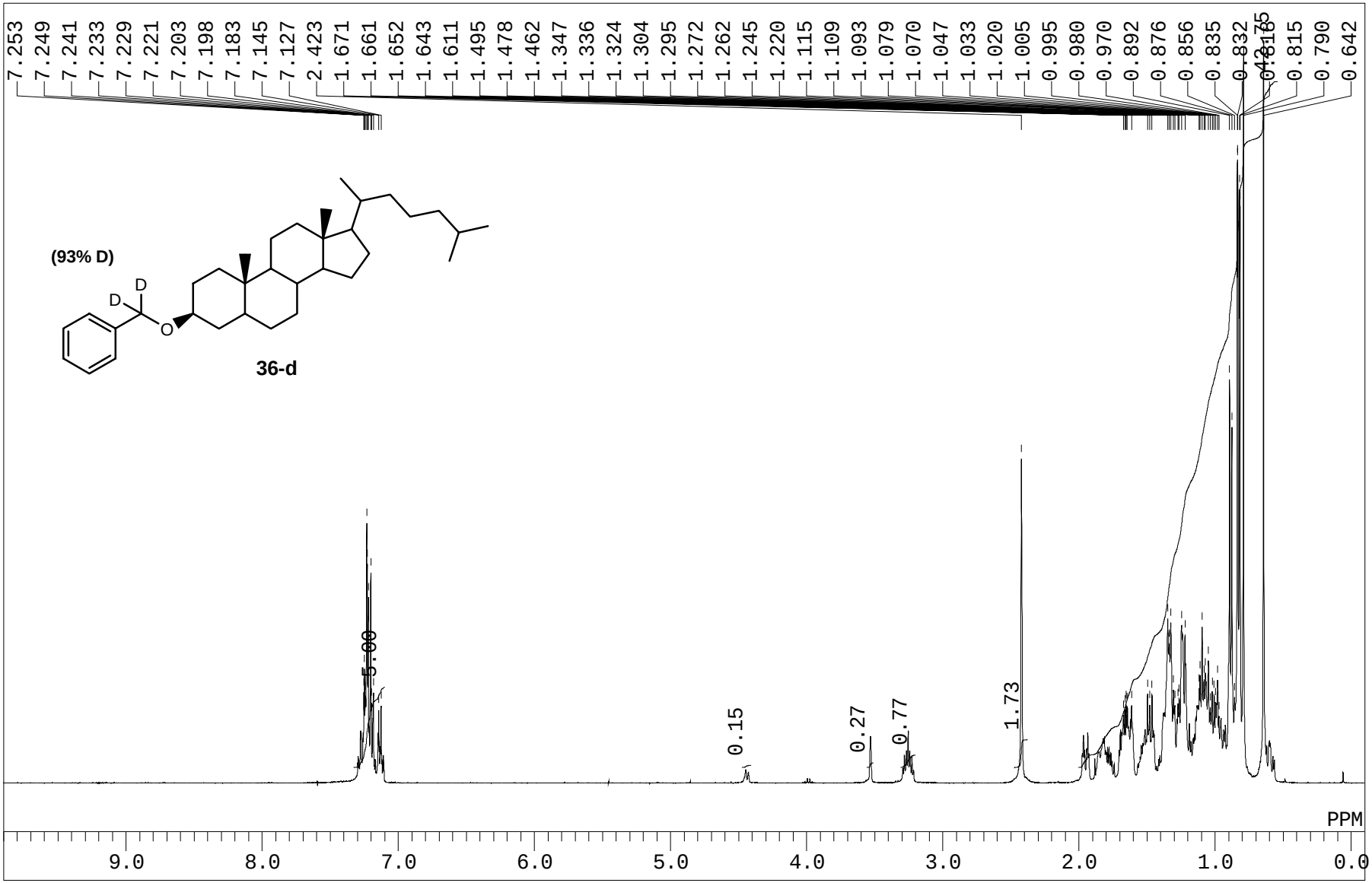
TK6-108



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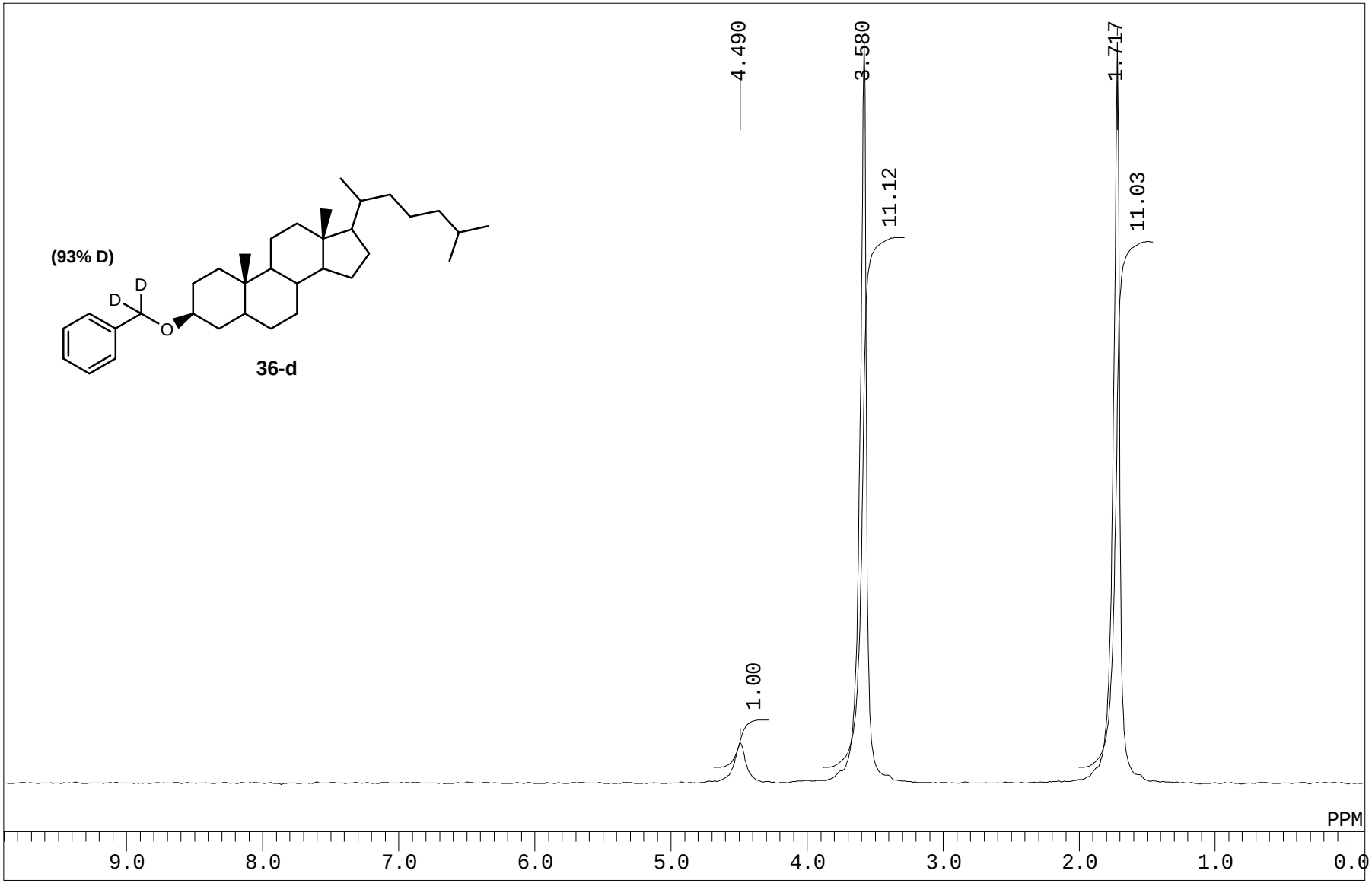

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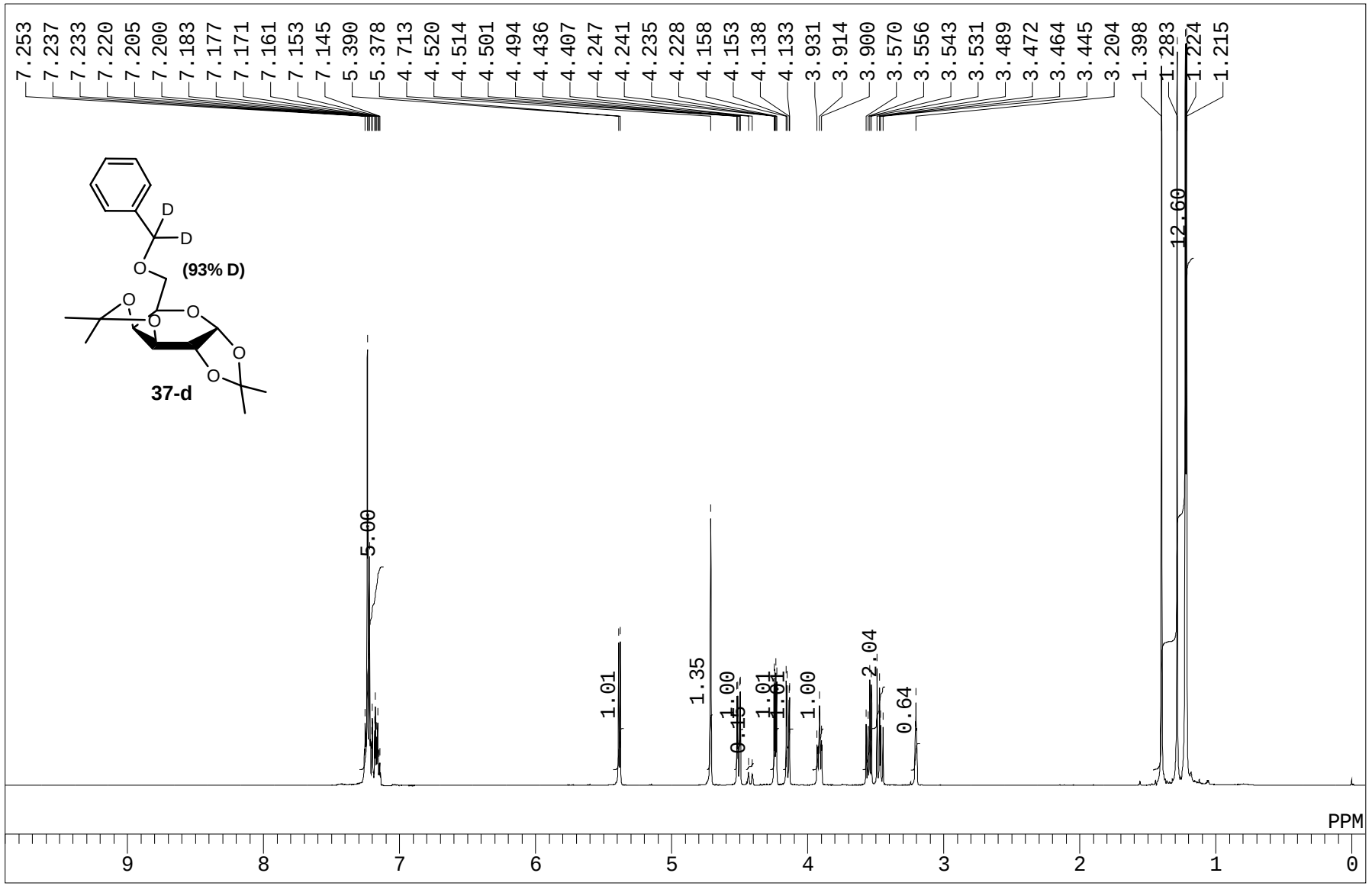

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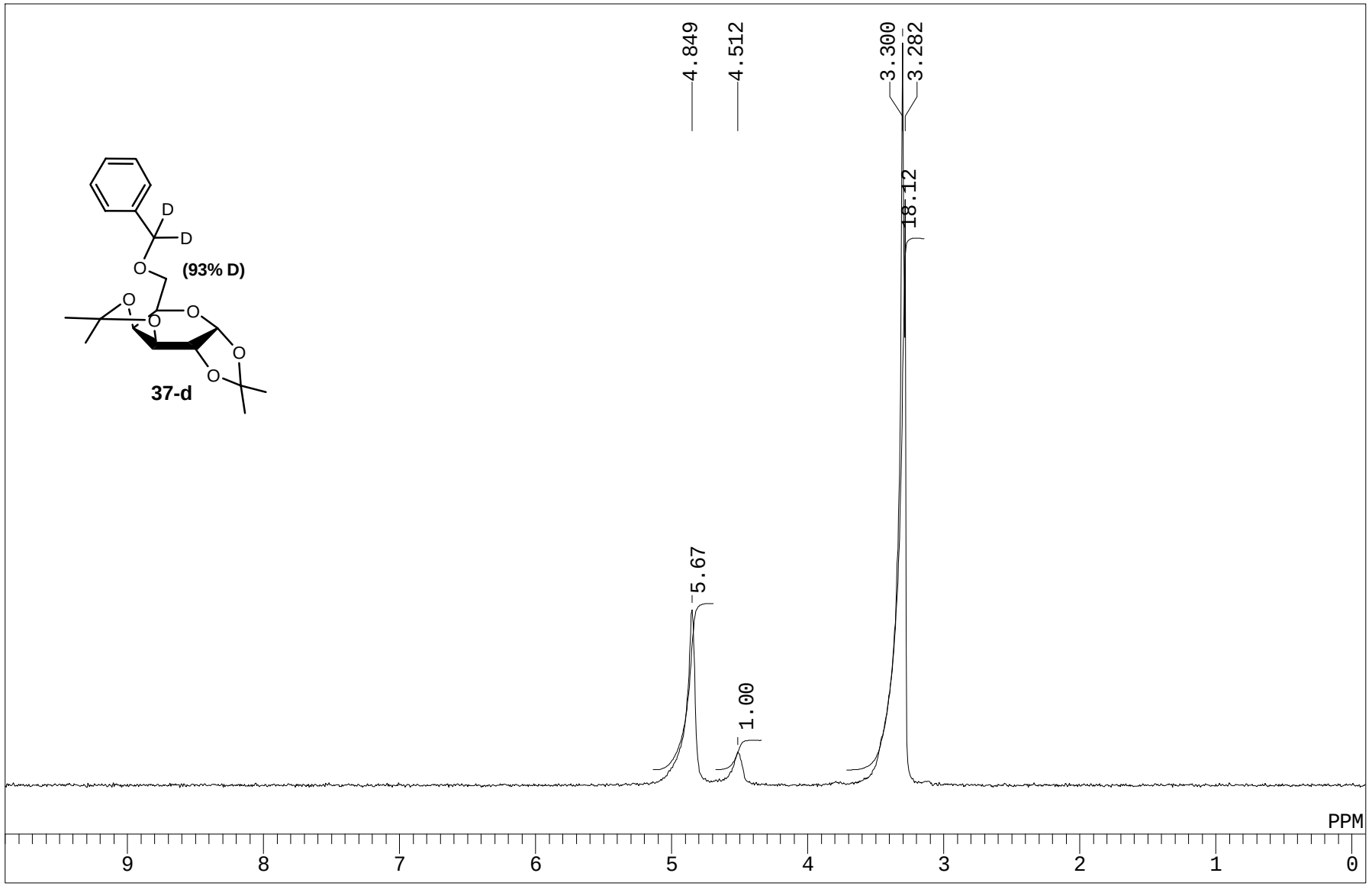

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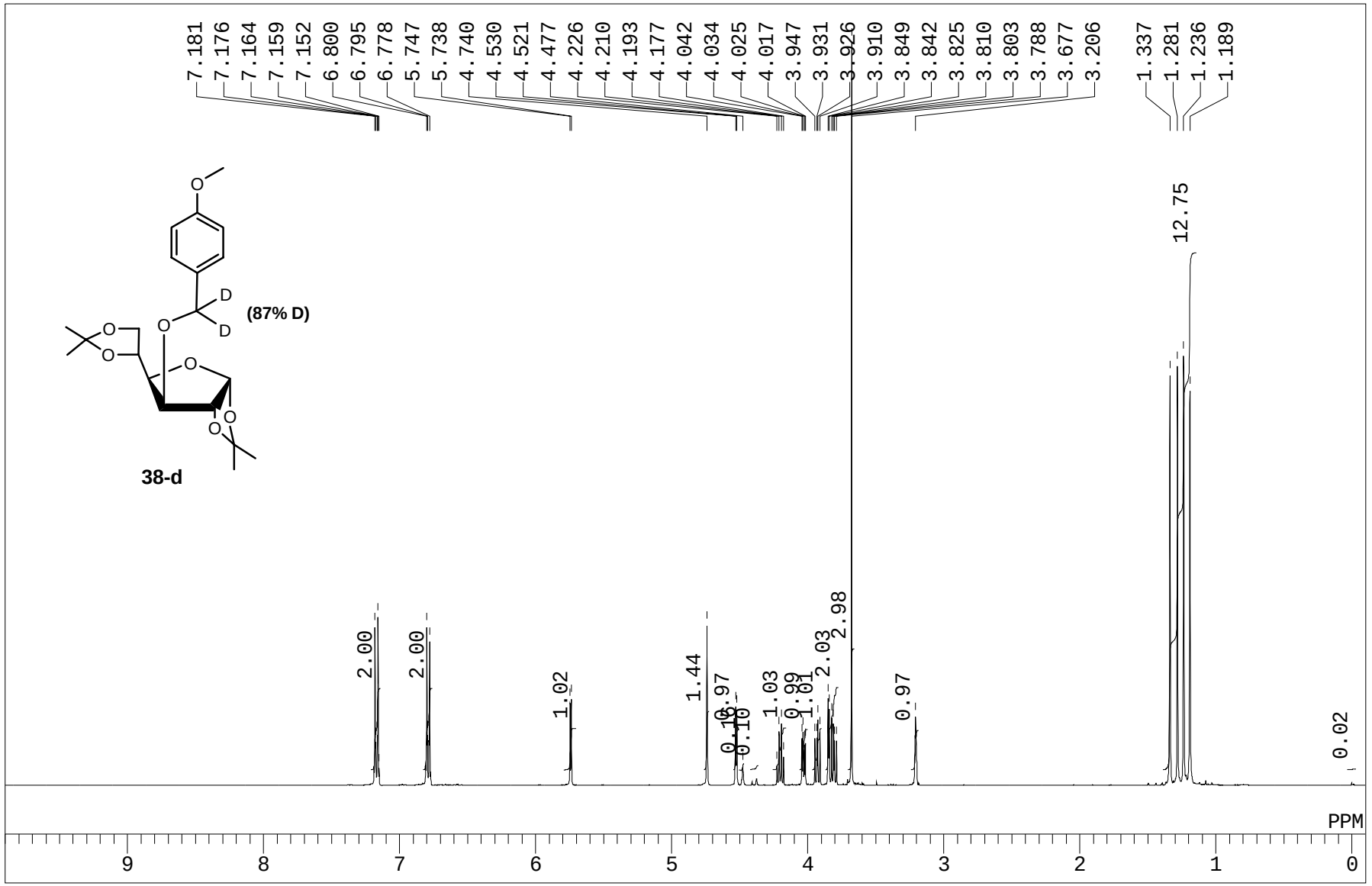

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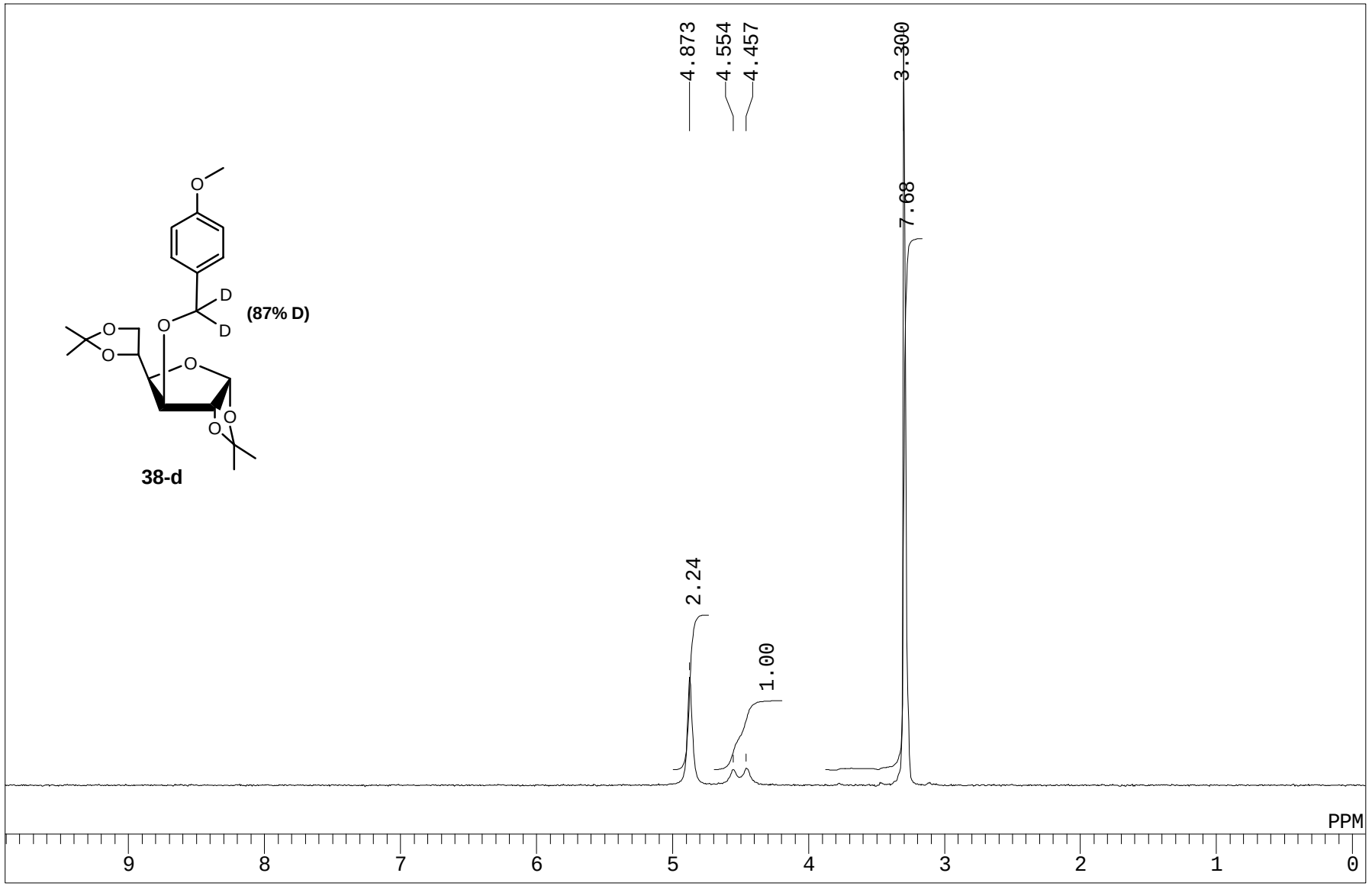

38-d

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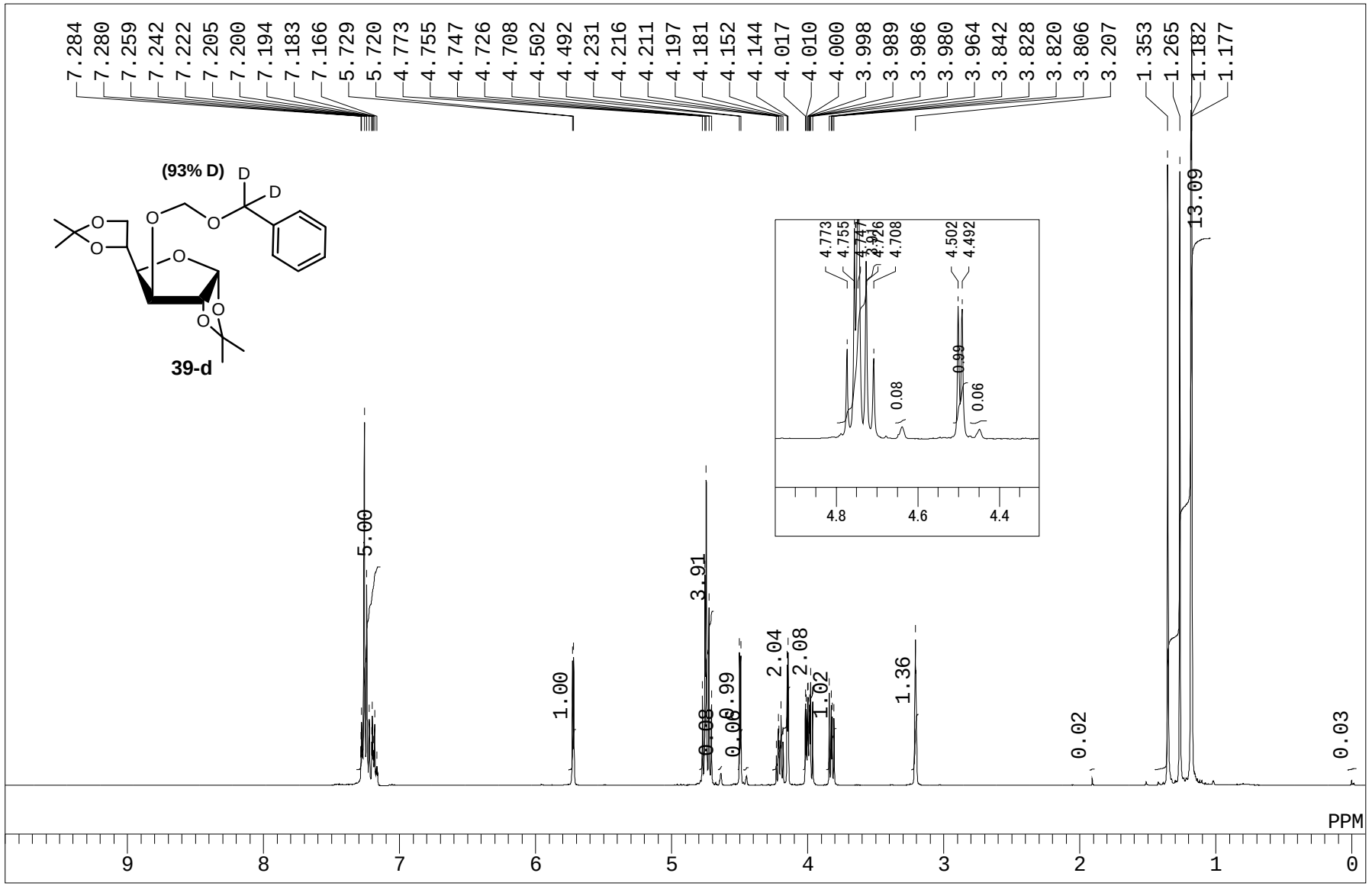

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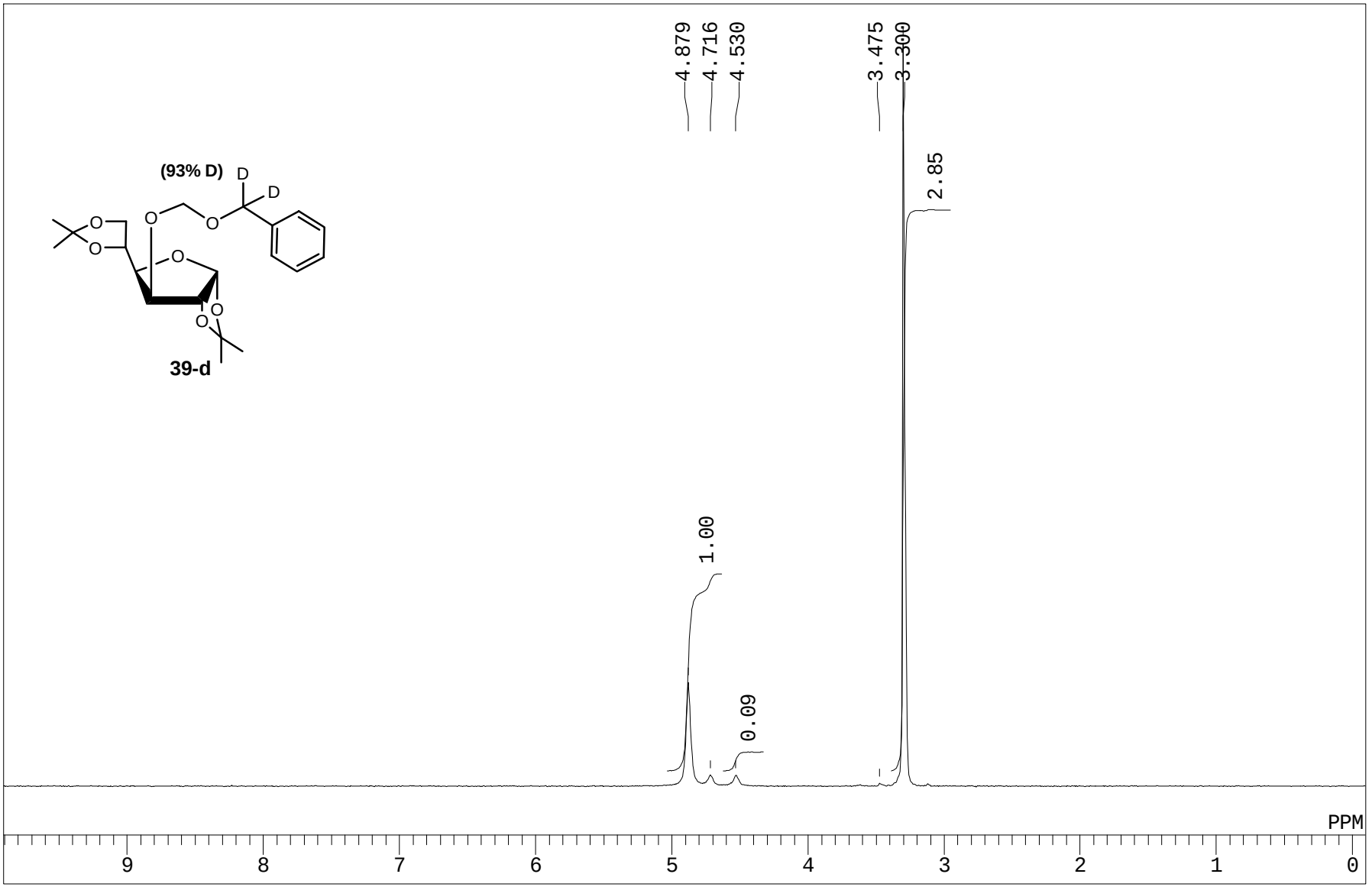

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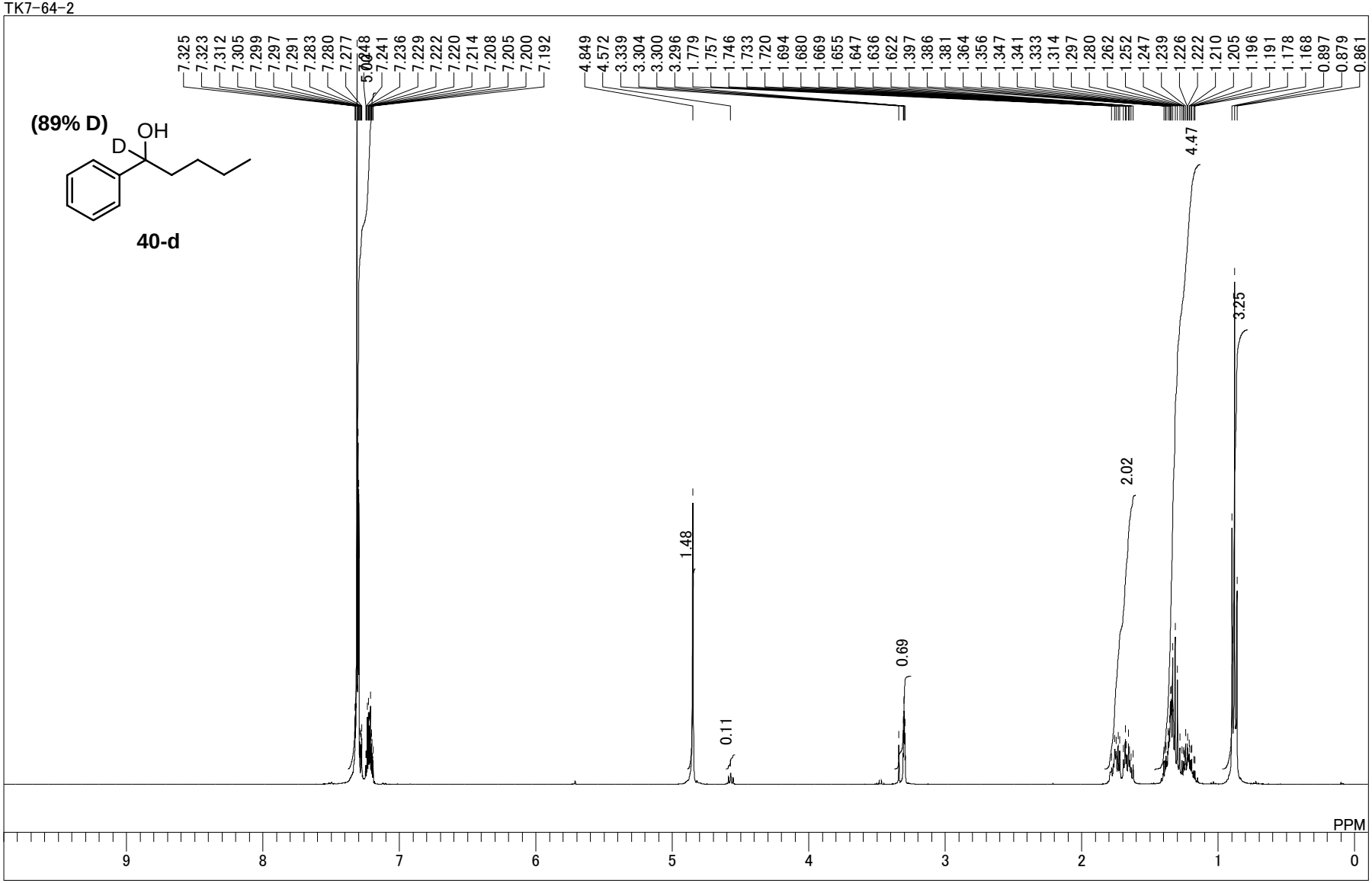

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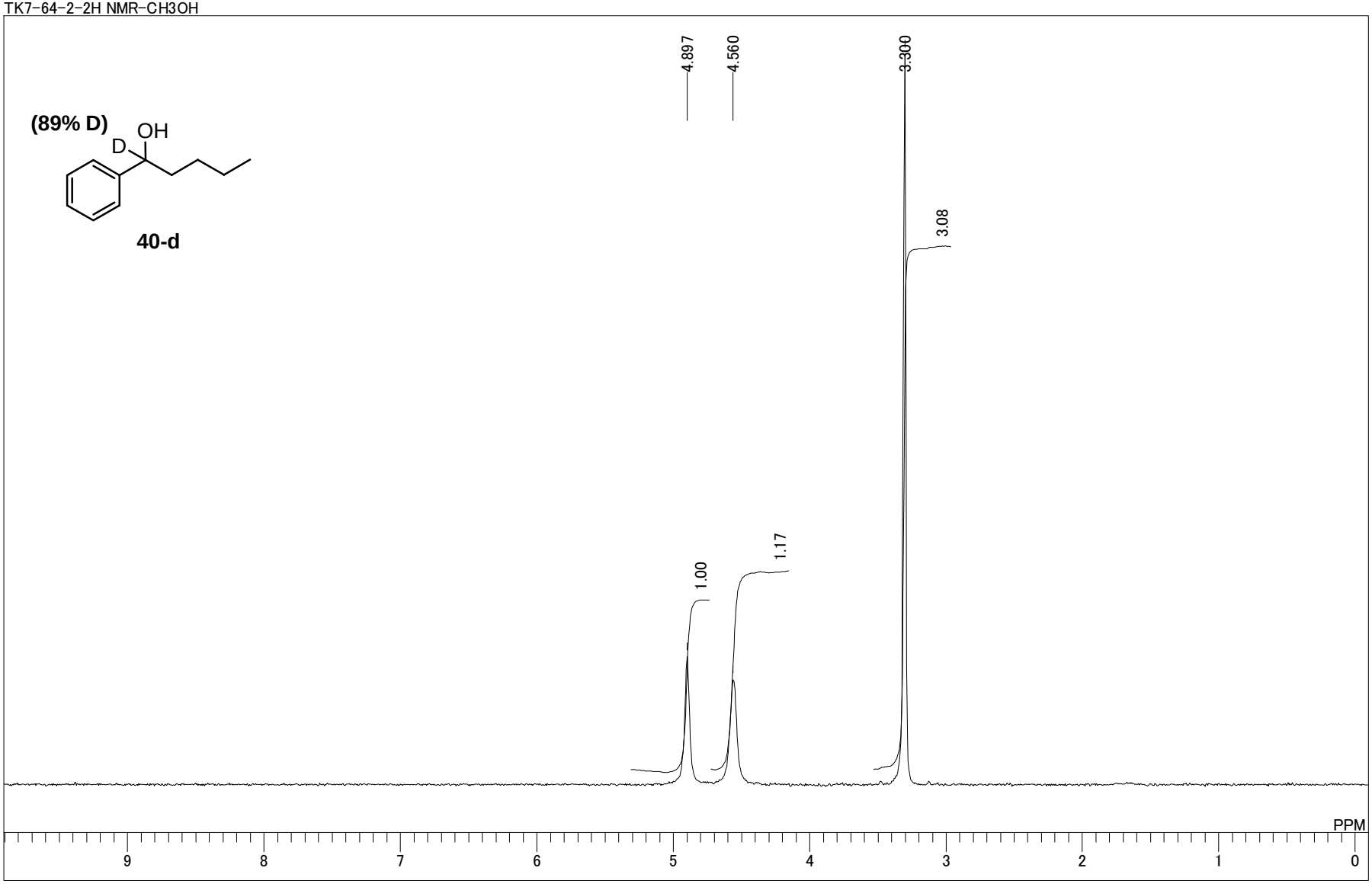

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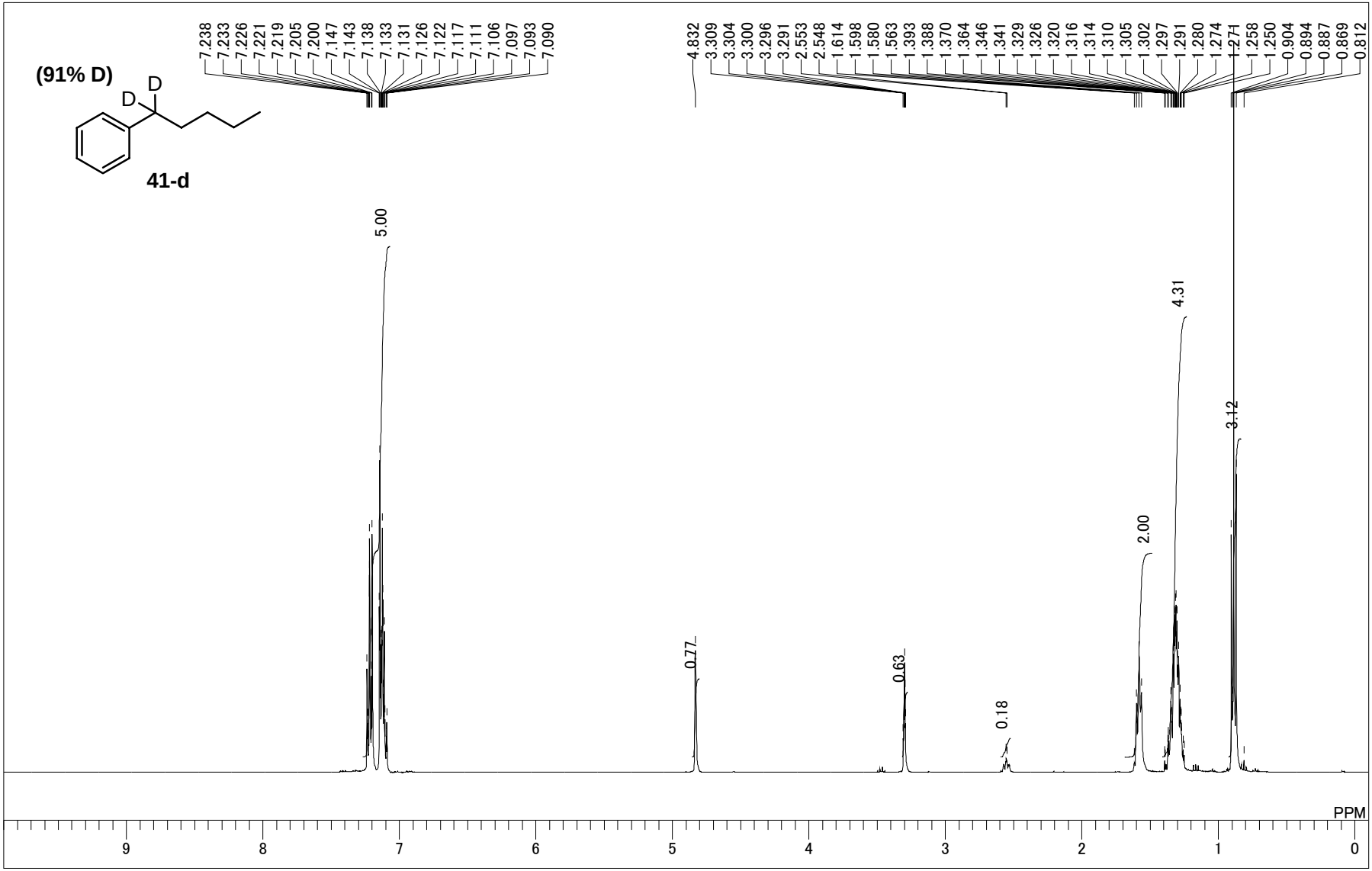

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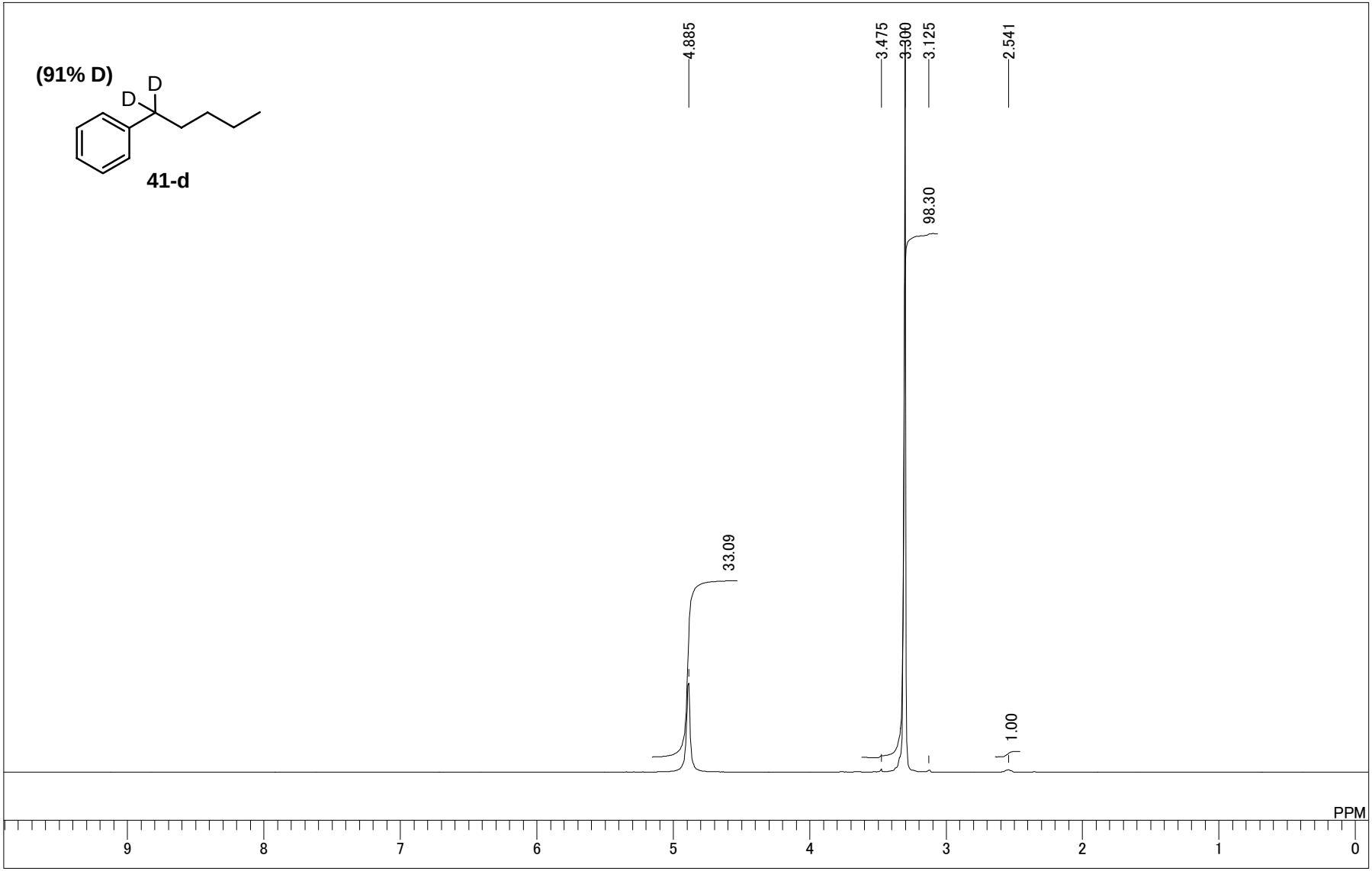

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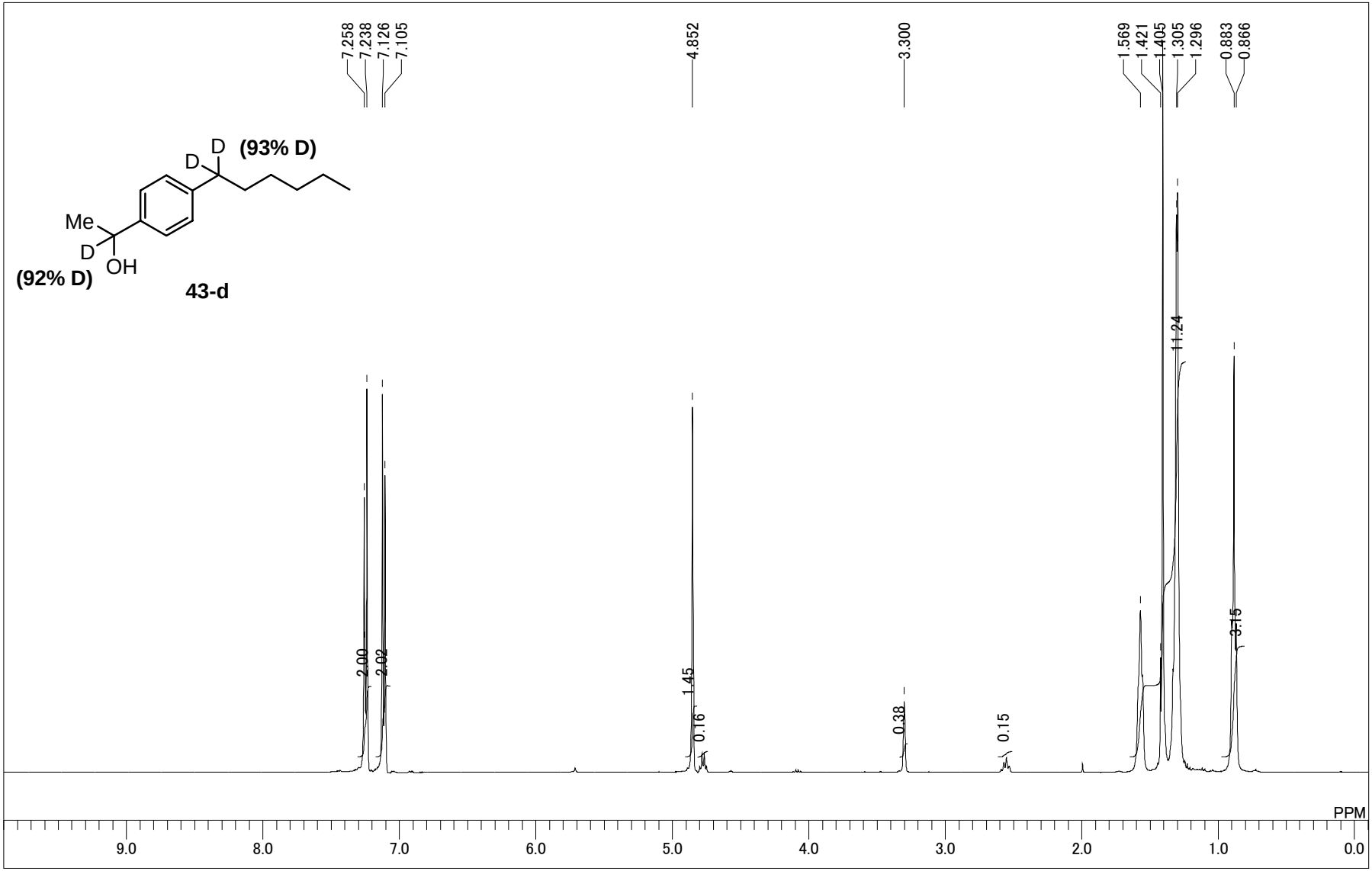

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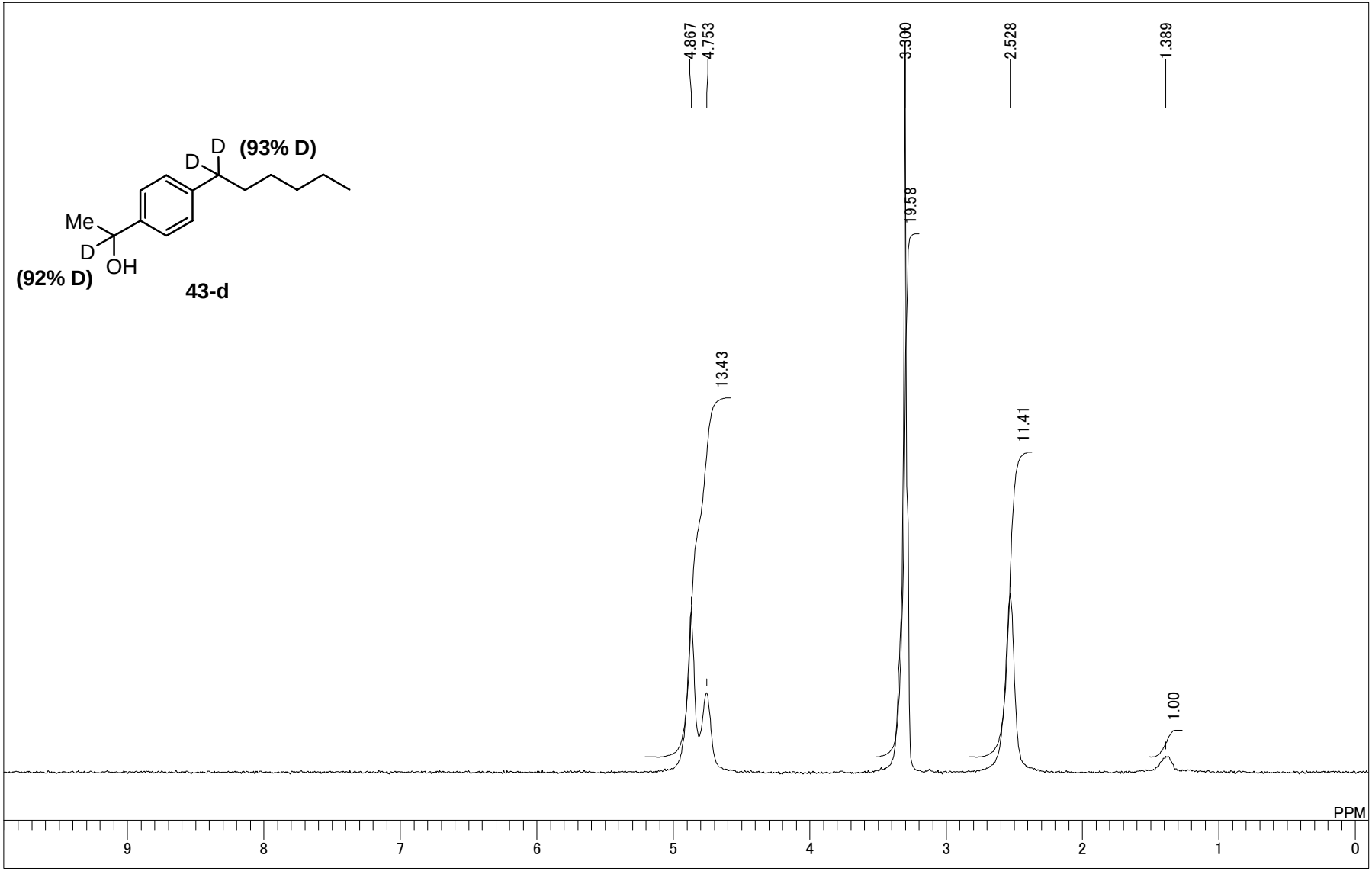

43-d

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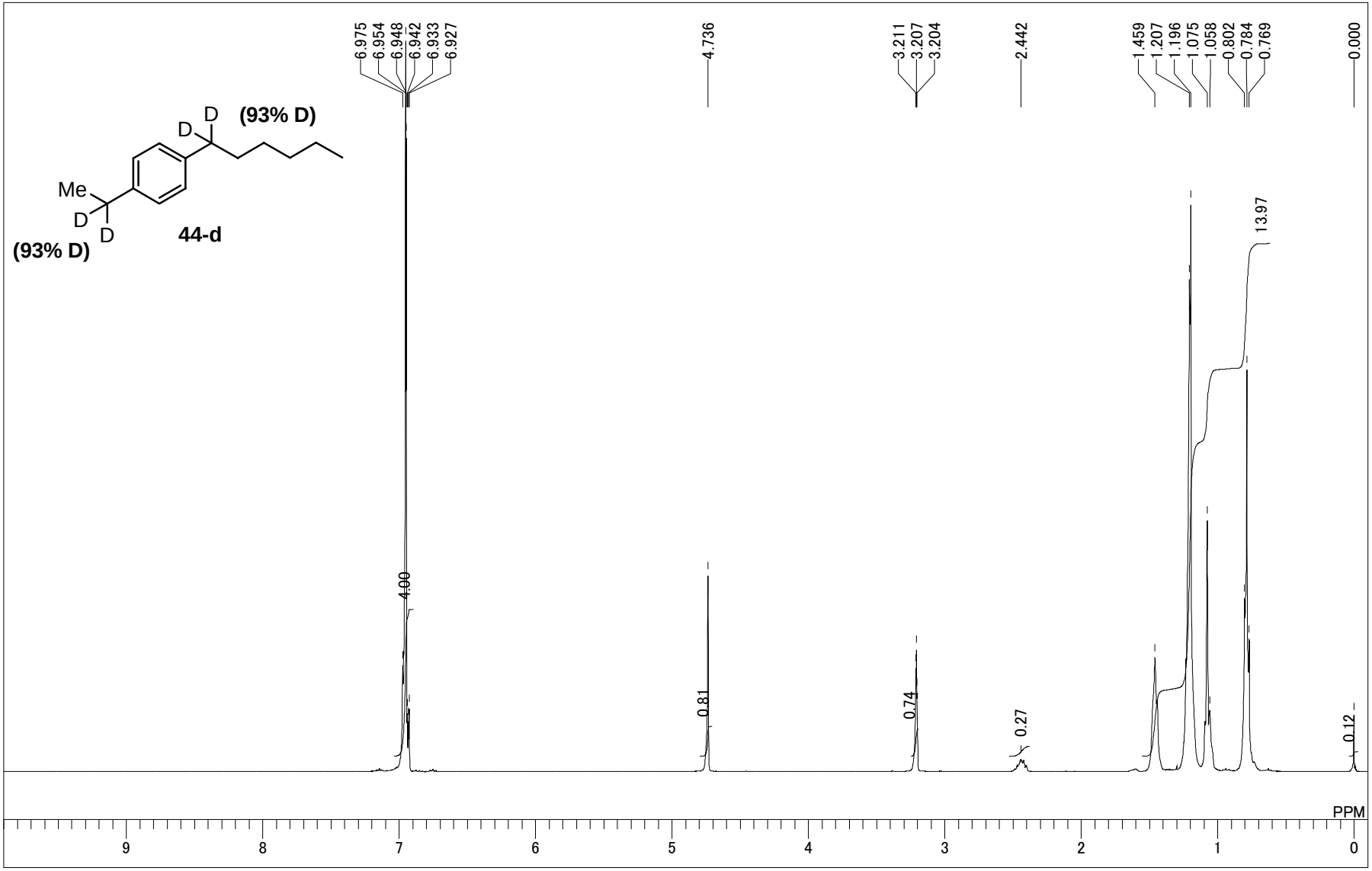
TK6-17



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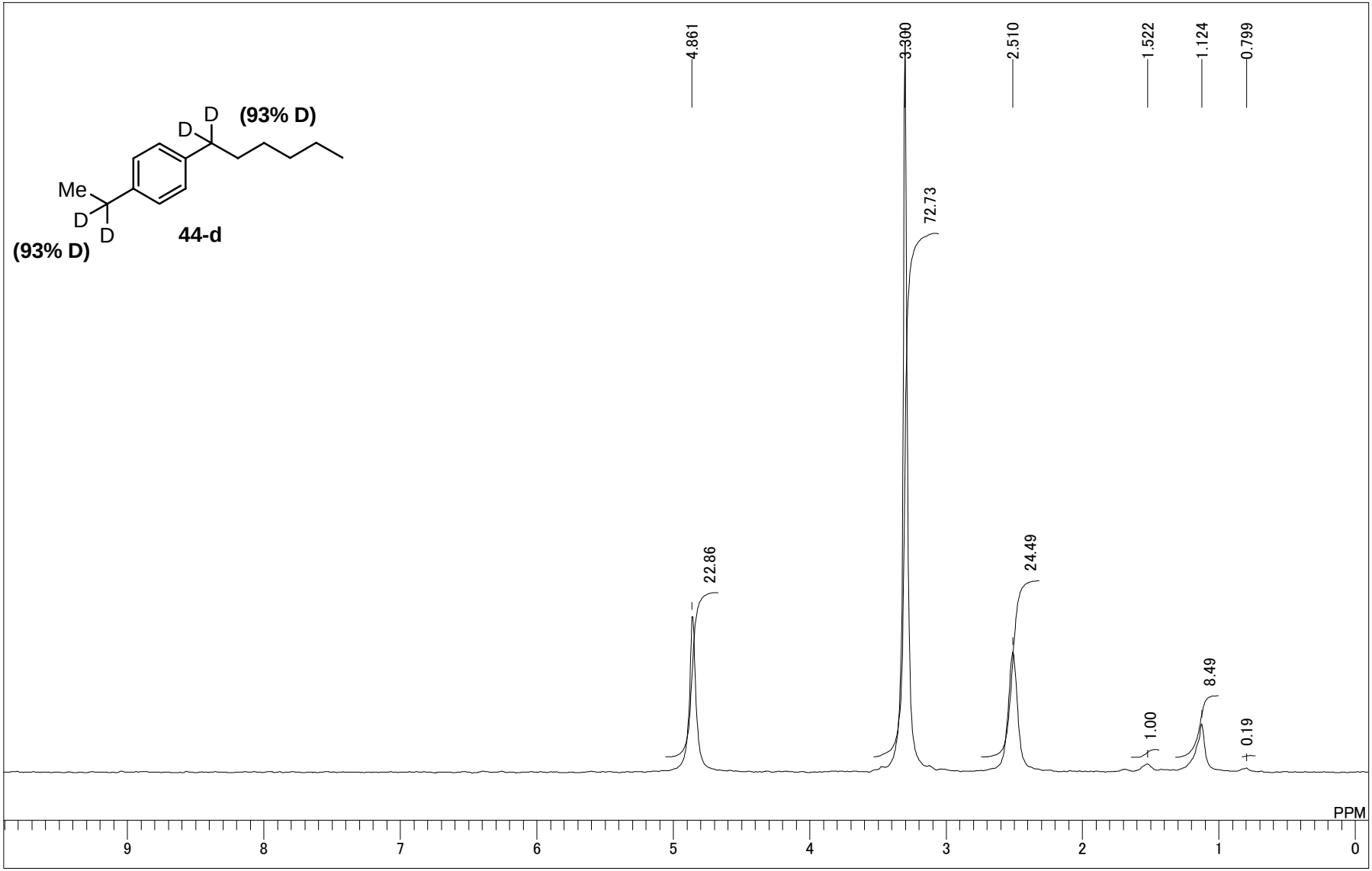

44-d