Supporting Information

Novel Pd/C-Catalyzed Redox Reactions between Aliphatic Secondary Alcohols and Ketones under Hydrogenation Conditions: Application to H-D Exchange Reaction and the Mechanistic Study

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Experimental Procedure

General Procedure for the H-D Exchange Reaction using Pd/C-H_2-D_2O System.

Method A: A mixture of substrate (2 mmol) and 10% Pd/C (10 wt % of the substrate) in D_2O in a Dimroth-type condenser was heated at reflux under *ca*. 1 atm H_2 pressure. After 24 h the mixture was cooled to room temperature, diluted with diethyl ether (10 mL), and passed through a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtered catalyst was washed with diethyl ether (2 × 10 mL). The combined filtrates were washed with H_2O (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the deuterated substrate and corresponding alcohol or ketone.

Method B: A mixture of substrate (2 mmol) and 10% Pd/C (10 wt % of the substrate) in D_2O (4 mL) in a sealed tube was stirred at 160 ºC under H_2 atmosphere. After 24 h the mixture was cooled to room temperature, diluted with diethyl ether (10 mL), and passed through a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtered catalyst was washed with diethyl ether (2 × 10 mL). The combined filtrates were washed with H_2O (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the deuterated substrate and corresponding alcohol or ketone.

Determination Method of Deuteratium-Content of Labelled Products

The crude deuterated products were purified by flash column chromatography, weighed ca. 10 mg with accuracy and transferred to a NMR tube (5 mm in diameter) together with CD_3OD as a solvent. An equimolar of *p*-anisic acid was used as an internal standard of ^{1}H NMR. The deuterium-content was determined from the integrations against the internal standard.

Synthesis of Substrate

1-Phenyl-3-heptanol. To a solution of 3-phenylpropionaldehyde (671 mg, 5 mmol) in diethyl ether (20 mL) was added a solution of butylmagnesium chloride (5 mL, 2M solution in diethyl ether, 10 mmol) at 0 ºC and the mixture was stirred at room temperature. After 2 h the reaction mixture was cooled to 0 ºC and saturated aqueous NH_4Cl solution (20 mL) and H_2O (20 mL) were successively added dropwise. After stirring for 10 min, the two phases were separated. The aqueous phase was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ether = 50:1) to afford 1-phenyl-3-heptanol (783 mg, 81%). ^{1}H NHR (CD_3OD) δ 7.16-7.01 (m, 5H), 3.42-3.40 (m, 1H), 2.67-2.49 (m, 2H), 1.65-1.54 (m, 2H), 1.35-1.19 (m, 6H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CD_3OD) δ 143.4, 129.0, 128.9, 126.3, 71.4, 40.1, 37.8, 32.7, 28.7, 23.4, 14.0; MS (EI) *m/z* (%) 192 (6), 174 (54), 117 (52), 104 (78), 91 (100); HRMS: calcd for $C_{13}H_{20}O$: 192.15142; found: 192.15072.

2-Methoxydecane. A suspension of 2-decanol (1.58 g, 10 mmol) and sodium hydride (*ca*. 60% in oil: 600 mg, 15 mmol) in THF (20 mL) was stirred under argon atmosphere (balloon) at 0 ºC for 30 min and at room temperature for 1 h. The reaction mixture was cooled to 0 ºC and methyl iodide (2.13 g, 15 mmol) was

added. The mixture was stirred at 0 ºC for 1 h and then at room temperature for 6 h. Methanol (10 mL) and triethylamine (5 mL) were then added. The reaction mixture was diluted with diethyl ether (50 mL) and washed with H_2O (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ether = 40:1) to afford 2-methoxydecane (1.30 g, 75%). ^{1}H NMR ($CDCl_3$) δ 3.35-3.20 (m, 1H), 3.29 (s, 3H), 1.53-1.46 (m, 1H), 1.41-1.25 (m, 12H), 1.10 (d, J = 6.3 Hz, 3H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 76.9, 55.9, 36.3, 31.9, 29.8, 29.6, 29.3, 25.4, 22.7, 19.0, 14.1.

2-*tert*-Butyldimethylsilyloxydecane. To a solution of 2-decanol (475 mg, 3 mmol) and imidazole (495 mg, 7.2 mmol) in DMF (2 mL) was added *tert*-butyldimethylchlorosilane (3.6 mmol). The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (10 mL) and washed with H_2O (2 × 10 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane) to afford 2-*tert*-butyldimethylsilyloxydecane (797 mg, 97%). ^{1}H NMR (CD_3OD) δ 3.78-3.74 (m, 1H), 1.33-1.24 (m, 14H), 1.06 (d, J = 6.3 Hz, 3H), 0.84 (s, 12H), 0.00 (s, 6H); ^{13}C NMR (CD_3OD) δ 69.8, 40.8, 33.0, 30.7, 30.7, 30.3, 26.8, 26.3, 24.2, 23.6, 18.9, 14.4, -4.2, -4.6.

Characterization Data

Scheme 1. Method A.

4-Phenyl-2-butanol-d_n (1-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 7.17-7.02 (m, 4.03H), 3.64-3.62 (m, 0.23H), 2.59 (s, 0.05H), 2.51 (s, 0.05H), 1.60 (s, 0.04H), 1.55 (m, 0.05H), 1.10-1.05 (m, 1.03H); ^{2}H NMR (CH_3OH) δ 7.25 (br s), 7.15 (br s), 3.47 (br s), 2.66 (br s), 2.57 (br s), 1.66 (br s), 1.62 (br s).

4-Phenyl-2-butanone-d_n (2-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 7.17-7.14 (m, 1.31H), 7.10-7.04 (m, 2.43H), 2.72 (s, 0.11H), 2.65 (s, 0.09H), 2.02-1.98 (m, 0.20H); ^{2}H NMR (CH_3OH) δ 7.27 (br s), 7.18 (br s), 2.78 (br s), 2.73 (br s), 2.06 (br s).

Scheme 2. Method A.

4-Phenyl-2-butanone-d_n (2-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 7.16-7.12 (m, 1.69H), 7.09-7.02 (m, 2.48H), 2.71 (s, 0.15H), 2.64 (s, 0.16H), 2.01-1.97 (m, 0.46H); ^{2}H NMR (CH_3OH) δ 7.26 (br s), 2.78 (br s), 2.72 (br s), 2.06 (br s).

4-Phenyl-2-butanol-d_n (1-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 7.25-7.10 (m, 4.54H), 3.69 (s, 0.10H), 2.67 (s, 0.07H), 2.58 (s, 0.07H), 1.68 (s, 0.19H), 1.63 (s, 0.11H), 1.21-1.12 (m, 1.01H); ^{2}H NMR (CH_3OH) δ 3.66 (br s), 2.63 (br s), 2.55 (br s), 1.63 (br s), 1.09 (br s).

Table 1, entry 1. Method B.

2-Decanol-d_n (3-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.71-3.66 (m, 0.34H), 1.39-1.21 (m, 4.22H), 1.15-1.08 (m, 1.02H), 0.90-0.83 (m, 0.94H); ^{2}H NMR (CH_3OH) δ 3.66 (br s), 1.23 (br s), 1.08 (br s), 0.82 (br s).

2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.36-2.31 (m, 0.16H), 2.05-1.97 (m, 0.25H), 1.38 (s, 0.15), 1.18-1.14 (m, 0.88H), 0.81-0.73 (m, 0.28H); ^{2}H NMR (CH_3OH) δ 2.36 (br s), 2.03 (br s), 1.43 (br s), 1.18 (br s), 0.77 (br s).

Table 1, entry 2. Method B.

2-Decanol-d_n (3-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.59 (s, 0.15H), 1.32-1.17 (m, 4.23H), 1.05-1.01 (m, 0.46H), 0.83-0.76 (m, 1.36H); ^{2}H NMR (CH_3OH) δ 3.65 (br s), 1.31-1.22 (m), 1.07 (br s), 0.82 (br s).

2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.41 (s, 0.13H), 2.09-2.08 (m, 0.21H), 1.48 (s, 0.27H), 1.27-1.17 (m, 2.28H), 0.90-0.83 (m, 0.96H); ^{2}H NMR (CH_3OH) δ 2.36 (br s), 2.03 (br s), 1.43 (br s), 1.17 (br s), 0.78 (br s).

Table 1, entry 3. Method B.

3-Decanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.43-3.34 (m, 0.55H), 1.50-1.29 (m, 6.35H), 0.94-0.87 (m, 3.39H); ^{2}H NMR (CH_3OH) δ 3.39 (br s), 1.37-1.23 (m), 0.86 (br s), 0.83 (br s).

3-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.37-2.29 (m, 0.32H), 1.44-1.38 (m, 0.30H), 1.24-1.08 (m, 1.37H), 0.93-0.86 (m, 0.57H), 0.81-0.74 (m, 1.17H); ^{2}H NMR (CH_3OH) δ 2.38 (br s), 1.46 (br s), 1.20 (br s), 0.94 (br s), 0.82 (br s).

Table 1, entry 4. Method B.

3-Decanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.31 (s, 0.09H), 1.51-1.20 (m, 5.97H), 0.85-0.78 (m, 2.84H); ^{2}H NMR (CH_3OH) δ 3.39 (br s), 1.36-1.23 (m), 0.86 (br s), 0.82 (br s).

3-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.32-2.29 (m, 0.18H), 1.44-1.18 (m, 3.72H), 0.91-0.74 (m, 2.03H); ^{2}H NMR (CH_3OH) δ 2.40 (br s), 1.46 (br s), 1.22-1.20 (m), 0.94 (br s), 0.82 (br s).

Table 1, entry 5. Method B.

4-Decanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.41 (s, 0.20H), 1.32-1.18 (m, 2.54H), 0.84-0.78 (m, 1.09H); ^{2}H NMR (CH_3OH) δ 3.48 (br s), 1.35-1.24 (m), 0.85 (br s).

4-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.32-2.28 (m, 0.40H), 1.41-1.35 (m, 0.39H), 1.22-1.13 (m, 0.77H), 0.81-0.74 (m, 0.78H).

Table 1, entry 6. Method B.

4-Decanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.41 (s, 0.19H), 1.36-1.15 (m, 2.17H), 0.85-0.76 (m, 1.25H); ^{2}H NMR (CH_3OH) δ 3.48 (br s), 1.33-1.23 (m), 0.84 (br s).

4-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.29 (s, 0.26H), 1.43-1.36 (m, 0.29H), 1.24-1.14 (m, 1.12H), 0.83-0.76 (m, 1.12H); ^{2}H NMR (CH_3OH) δ 2.37 (br s), 1.49 (br s), 1.46 (br s), 1.20 (br s), 0.83 (br s).

Table 1, entry 7. Method B.

Cyclooctanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.69-3.66 (m, 0.56H), 1.74-1.39 (m, 6.54H); ^{2}H NMR (CH_3OH) δ 3.72 (br s), 1.73-1.39 (m).

Cyclooctanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.37 (s, 0.37H), 1.87-1.82 (m, 0.65H), 1.58-1.50 (m, 1.15H), 1.39-1.28 (m, 0.94H); ^{2}H NMR (CH_3OH) δ 2.37 (br s), 1.81 (br s), 1.49 (br s), 1.28 (br s).

Table 1, entry 8. Method B.

Cyclooctanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.29 (s, 0.37H), 1.74 (s, 0.37H), 1.41 (s, 0.38H), 1.21 (s, 0.37H); ^{2}H NMR (CH_3OH) δ 2.36 (br s), 1.81 (br s), 1.48 (br s), 1.27 (br s).

Table 1, entry 9. Method B.

4-Methyl-3-heptanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.48-3.29 (m, 2.15H), 1.48-1.28 (m, 4.36H), 0.96-0.84 (m, 5.47H); ^{2}H NMR (CH_3OH) δ 3.22 (br s), 1.40-1.03 (m), 0.87-0.79 (m).

4-Methyl-3-heptanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.48-2.35 (m, 0.35H), 1.46 (s, 0.05H), 1.25-1.20 (m, 2.54H), 0.96-0.76 (m, 2.90H); ^{2}H NMR (CH_3OH) δ2.55-2.43 (m), 1.54 (br s), 1.23 (br s), 1.17 (br s), 0.98-0.94 (m), 0.94 (br s), 0.83 (br s).

Table 1, entry 10. Method B.

1-Phenyl-3-heptanol-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 7.16-6.99 (m, 3.12H), 3.63-3.57 (m, 0.12H), 2.69-2.41 (m, 0.17H), 1.58-1.06 (m, 3.84H), 0.84-0.78 (m, 2.33H); ^{2}H NMR (CH_3OH) δ 3.48 (br s), 2.70 (br s), 2.58 (br s), 1.66 (br s), 1.38 (br s), 1.25 (br s), 0.84 (br s).

1-Phenyl-3-heptanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 7.25-7.21 (m, 1.33H), 7.17-7.11 (m, 2.45H), 2.80 (s, 0.12H), 2.70 (0.12H), 2.35 (s, 0.13H), 1.48-1.43 (m, 0.60H), 1.30-1.21 (m, 0.71H), 0.88-0.81 (m, 1.68H); ^{2}H NMR (CH_3OH) δ 7.26 (br s), 7.18 (br s), 2.79 (br s), 2.70 (br s), 2.35 (br s), 1.42 (br s), 1.18 (br s), 0.81 (br s).

Table 2, entry 2. Method B. 10% Rh/C was used instead of 10% Pd/C.

2-Decanol-d_n (3-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.62-3.57 (m, 0.28H), 1.30-1.19 (m, 8.36H), 1.09-0.99 (m, 1.00H), 0.81-0.76 (m, 2.34H); ^{2}H NMR (CH_3OH) δ 3.66 (br s), 1.37-1.23 (m), 1.08 (br s), 0.82 (br s).

2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.38-2.32 (m, 0.12H), 2.02-1.98 (m, 0.19H), 1.42-1.41 (m, 0.30H), 1.30-1.19 (m, 5.56H), 0.81-0.76 (m, 2.01H); ^{2}H NMR (CH_3OH) δ 2.40 (br s), 2.08 (br s), 1.46 (br s), 1.21 (br s), 0.82 (br s).

Table 2, entry 3. Method B. 10% Pt/C was used instead of 10% Pd/C.

2-Decanol-d_n (3-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.59 (s, 0.19H), 1.31-1.16 (m, 1.31H), 1.00 (s, 0.26H), 0.81-0.75 (m, 0.35H); ^{2}H NMR (CH_3OH) δ 3.65 (br s), 1.33-1.22 (m), 1.07 (br s), 0.82 (br s).

2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.33 (s, 0.12H), 2.03-1.99 (m, 0.19H), 1.40-1.36 (m, 0.15H), 1.24-1.16 (m, 1.63H), 0.83-0.75 (m, 0.63H); ^{2}H NMR (CH_3OH) δ 2.40 (br s), 2.08 (br s), 1.47 (br s), 1.22 (br s), 0.82 (br s).

Table 3, entry 2. Method B. 10% Rh/C was used instead of 10% Pd/C.
2-Decanol-d_n (3-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.66 (s, 0.10H), 1.39-1.28 (m, 5.03H), 1.13-1.04 (m, 5.03H), 0.90-0.87 (m, 1.46H); ^{2}H NMR (CH_3OH) δ 3.55 (br s), 1.25 (br s), 0.96 (br s), 0.74 (br s).
2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.31 (s, 0.05H), 2.01-1.97 (m, 0.09H), 1.42-1.35 (m, 0.60H), 1.30-1.06 (m, 6.15H), 0.79 (t, J = 6.8 Hz, 1.95H); ^{2}H NMR (CH_3OH) δ 2.03 (br s), 1.40 (br s), 1.22 (br s), 0.84 (br s).

Table 3, entry 3. Method B. 10% Pt/C was used instead of 10% Pd/C.
2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.34-2.32 (m, 0.12H), 2.01-1.97 (m, 0.17H), 1.39 (s, 0.13H), 1.30-1.06 (m, 1.58H), 0.81-0.74 (m, 0.57H); ^{2}H NMR (CH_3OH) δ 2.40 (br s), 2.07 (br s), 1.46 (br s), 1.21 (br s), 0.82 (br s).

Scheme 3, 24 h. Method B.
2-Decanol-d_n [(*R*/*S*)-3-d_n]: $[\alpha]_D$ -5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.64-3.61 (m, 0.87H), 1.32-1.22 (m, 12.9H), 1.11-1.04 (m, 2.87H), 0.84-0.79 (m, 2.77H); ^{2}H NMR (CH_3OH) δ 3.64 (br s), 1.39-1.22 (m), 1.08 (br s), 0.82 (br s).
2-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ.2.39-2.33 (s, 0.12H), 2.03-1.99 (m, 0.24H), 1.44-1.36 (m, 1.27H), 1.31-1.07 (m, 4.13H), 0.83-0.75 (m, 1.56H); ^{2}H NMR (CH_3OH) δ 2.40 (br s), 2.07 (br s), 1.47 (br s), 1.22 (br s), 0.82 (br s).

Scheme 3, 7 days. Method B. The reaction was run for 7 days.
2-Decanol-d_n [(*R*/*S*)-3-d_n]: $[\alpha]_D$ 0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.57 (s, 0.09H), 1.30-1.15 (m, 1.06H), 1.03-0.99 (m, 0.24H), 0.80-0.74 (m, 0.20H); ^{2}H NMR (CH_3OH) δ 3.65 (br s), 1.37-1.22 (m), 1.07 (br s), 0.82 (br s).
2-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.34-2.31 (m, 0.17H), 2.05-1.97 (m, 0.45H), 1.38 (s, 0.13H), 1.18-1.14 (m, 0.85H), 0.80-0.73 (m, 0.28H); ^{2}H NMR (CH_3OH) δ 2.41 (br s), 2.08 (br s), 1.47 (br s), 1.23 (br s), 0.83 (br s).

Table 8, entry 2. Method B. The reaction was performed under argon atmosphere.
2-Decanone-d_n (4-d_n): ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.47-2.40 (m, 0.09H), 2.11-2.06 (m, 0.16H), 1.51-1.48 (m, 077H), 1.33-1.28 (m, 5.83H), 0.90-0.84 (m, 2.20H); ^{2}H NMR (CH_3OH) δ 2.40 (br s), 2.07 (br s), 1.46 (br s), 1.21 (br s), 0.82 (br s).

Table 8, entry 5. Method B. The reaction was performed under argon atmosphere.

2-Decanone-d_n: ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.47-2.40 (m, 0.36H), 2.11-2.07 (m, 0.47H), 1.53-1.51 (m, 1.90H), 1.30-1.19 (m, 9.78H), 0.88 (t, J = 6.8 Hz, 2.80H); ^{2}H NMR (CH_3OH) δ 2.42 (br s), 2.08 (br s).

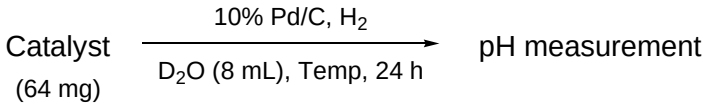
Table 8, entry 6. A mixture of 2-decanone (**3**, 313 mg, 2 mmol) and 10% Pd/C (31.3 mg, 10 wt % of the substrate) in D_2O (4 mL) in a test tube was stirred at room temperature under H_2 atmosphere. After 24 h the mixture was diluted with methanol (20 mL), and passed through a membrane filter (Millipore Millex®-LH, 0.45 μm) to remove the catalyst. The filtered catalyst was washed with diethyl ether (2 × 10 mL). The combined filtrates were washed with H_2O (2 × 30 mL) and brine (30 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ether = 40:1) to afford the 2-decanone-d_n (**4-d_n**, 128 mg) and 2-decanol-d_n (**3-d_n**, 9.2 mg).

2-decanol-d_n (3-d_n). ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 3.69-3.64 (m, 0.12H), 1.39-1.29 (m, 9.06H), 1.14-1.08 (m, 0.99H), 0.89 (t, J = 6.8 Hz, 3.00H).

2-decanone-d_n (4-d_n). ^{1}H NMR (CD_3OD, *p*-anisic acid as an internal standard) δ 2.35-2.34 (m, 0.03H), 2.01-1.98 (m, 0.11H), 1.44-1.43 (m, 1.93H), 1.19 (br s, 9.98H), 0.83-0.78 (m, 2.94H); ^{2}H NMR (CH_3OH) δ 2.41 (br s), 2.07 (br s).

Comparison of the Acidity of catalysts

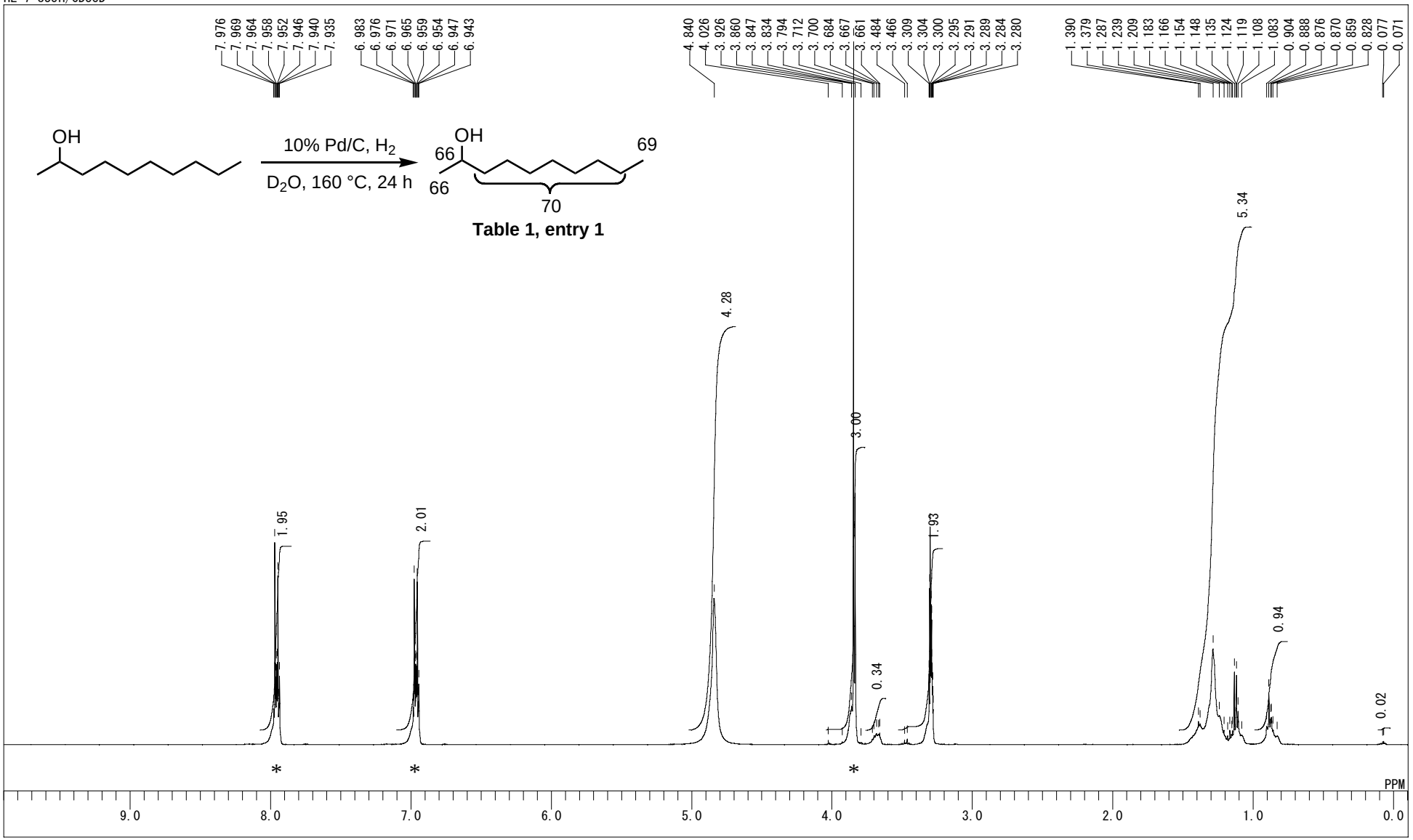
A suspension of catalyst (64 mg) and H_2O (8 mL, Wako HPLC grade) was stirred at room temperature in a flask or at 160 ºC in a sealed tube under H_2 atmosphere for 24 h and the catalyst was filtered through a membrane filter (Millipore, Millex®-LH, 0.45 μm). The pH of filtrate was measured using a Horida D-21 pH meter.



entry	Catalyst	Temp.[a]	pH	Temp.[b]
1	10% Pd/C (Aldrich)	rt	6.25	23.2 ºC
2		160 ºC	5.91	24.3 ºC
3	10% Rh/C (N.E. Chemcat)	rt	4.02	21.1 ºC
4		160 ºC	4.85	21.1 ºC
5	10% Pt/C (N.E. Chemcat)	rt	5.65	21.1 ºC
6		160 ºC	5.74	20.8 ºC

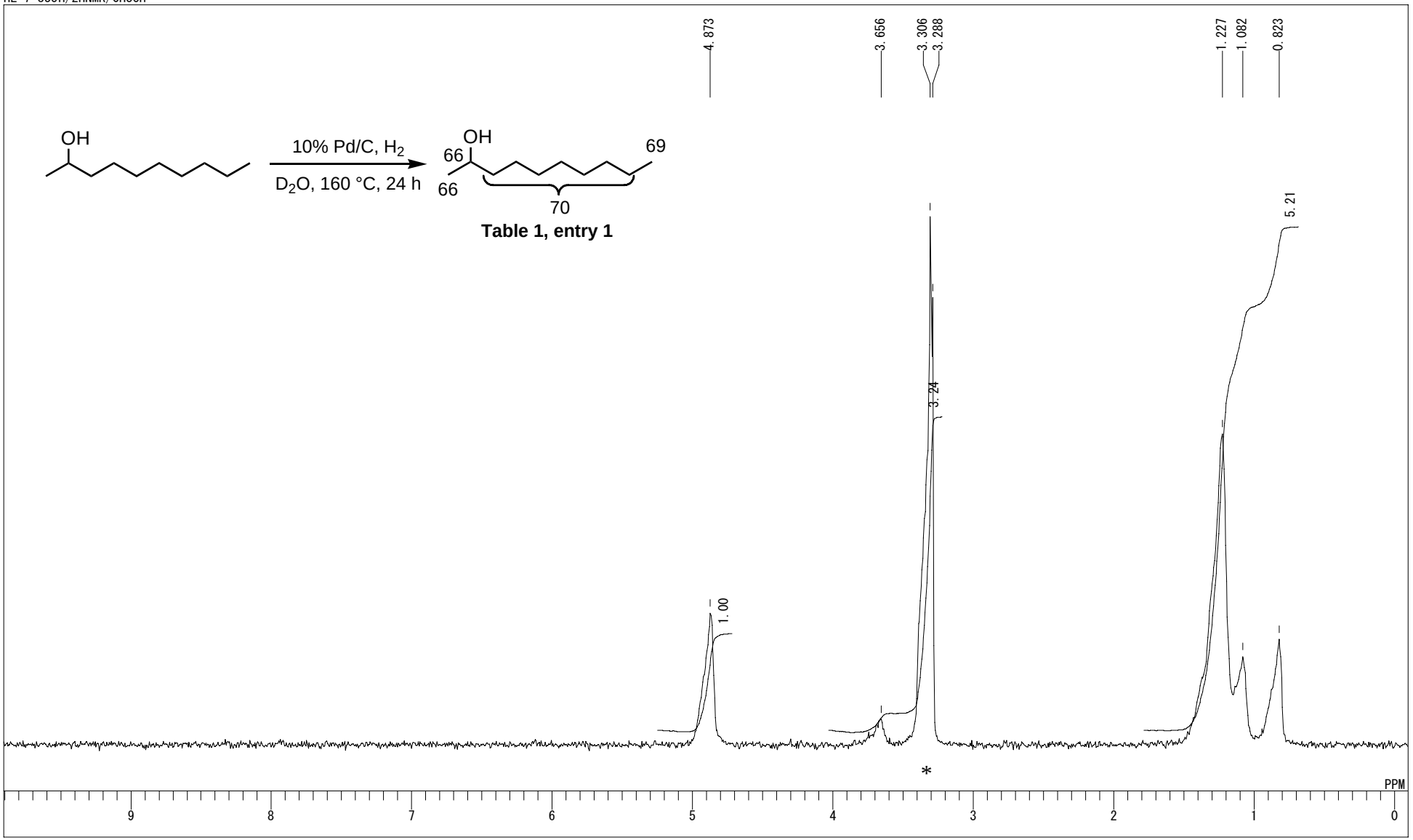
[a] Stirring temperature. [b] Sample temperature.

* *p*-anisic acid as an internal standard

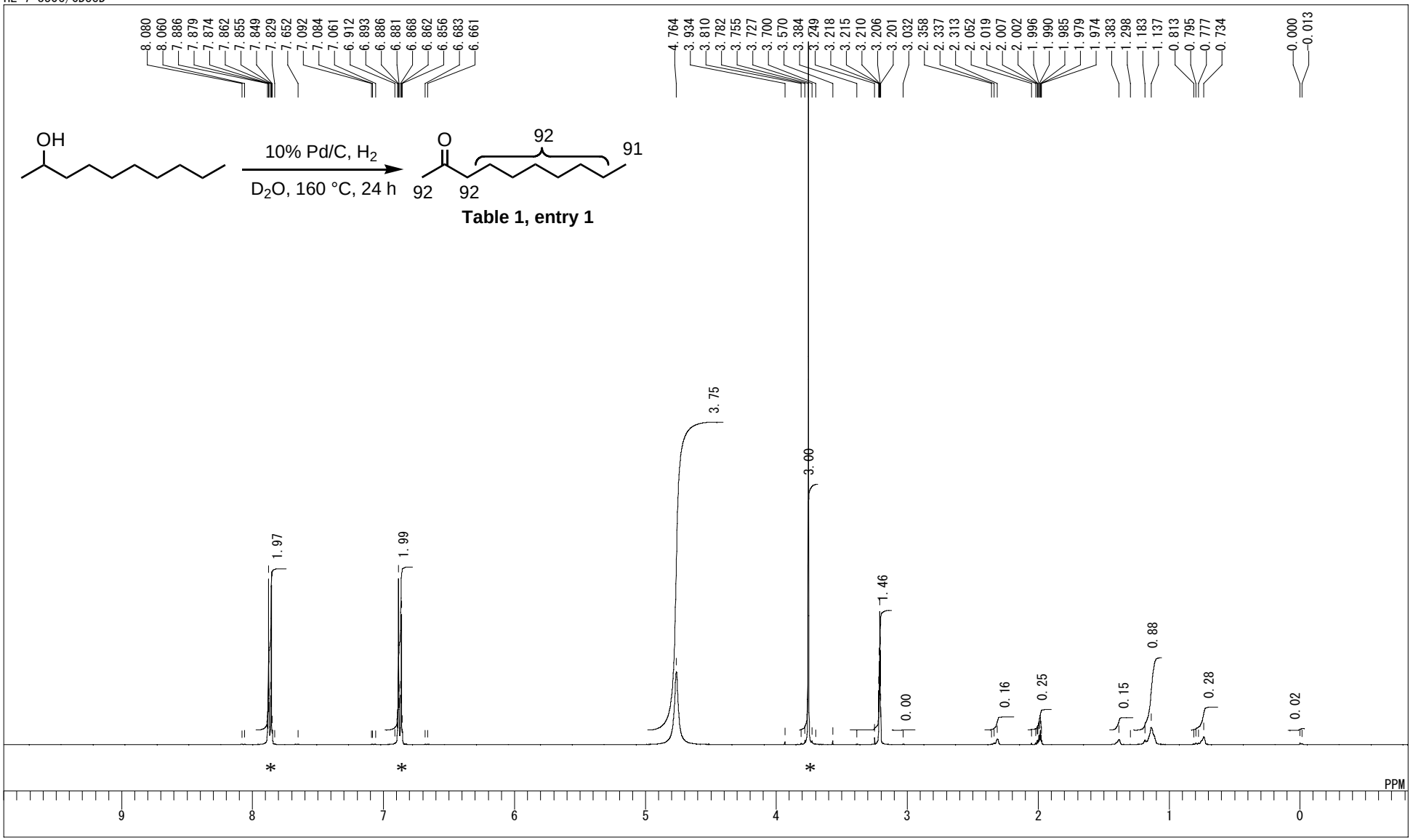


HE-7-83OH/2HNMR/CH3OH

* CD_3OD as an internal standard

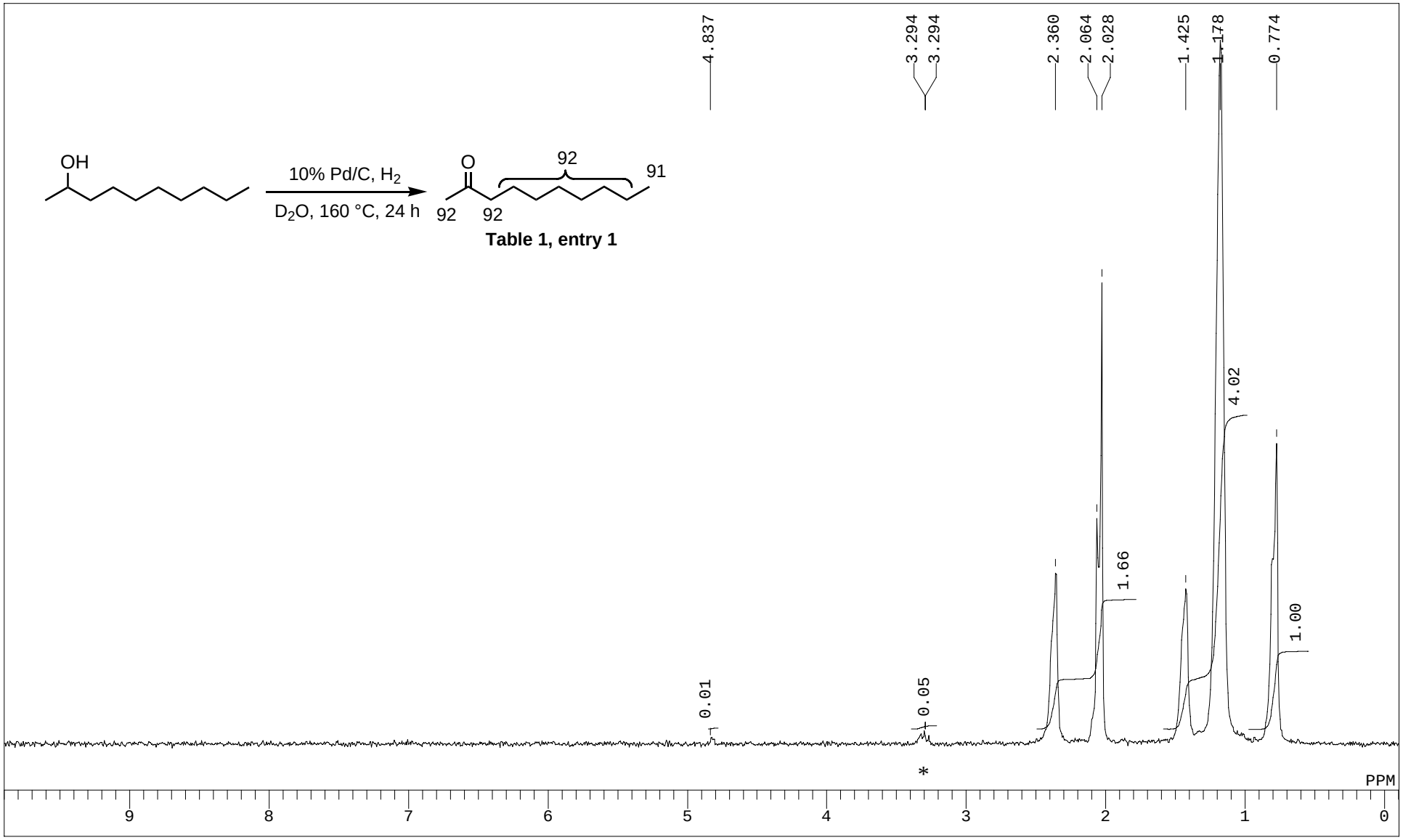


* *p*-anisic acid as an internal standard

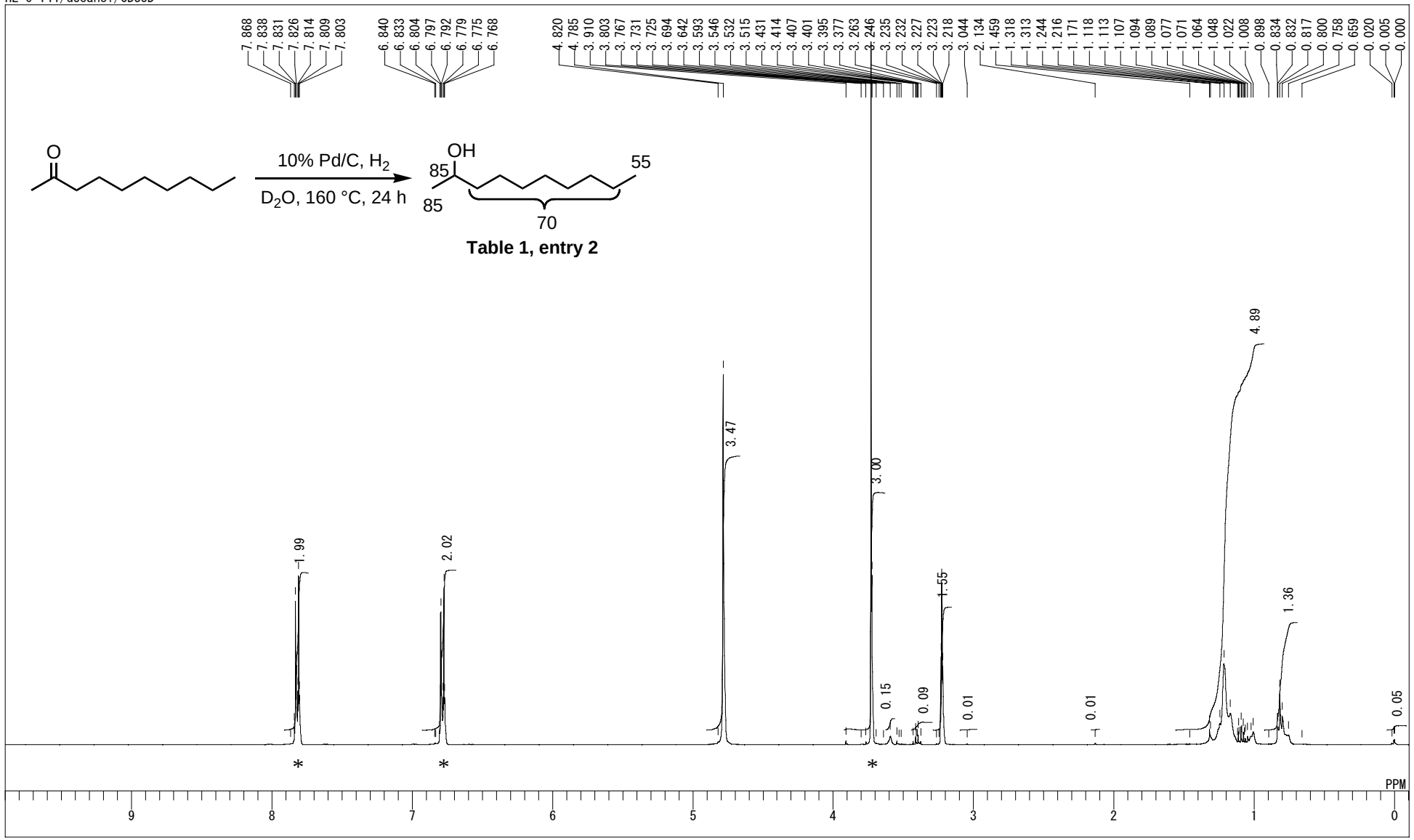


HE-7-83CO/2HNMR/CH3OH

* CD_3OD as an internal standard

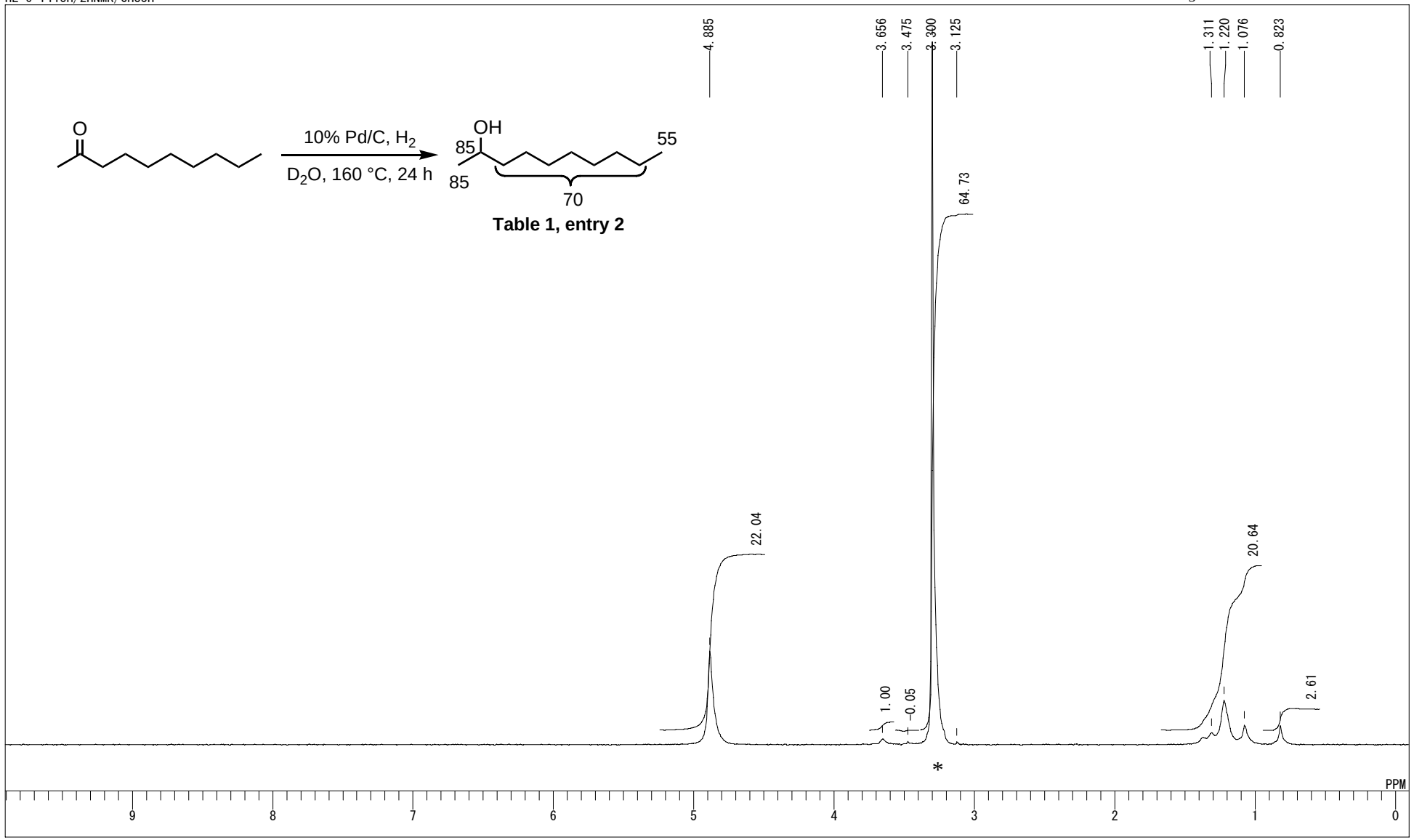


* *p*-anisic acid as an internal standard



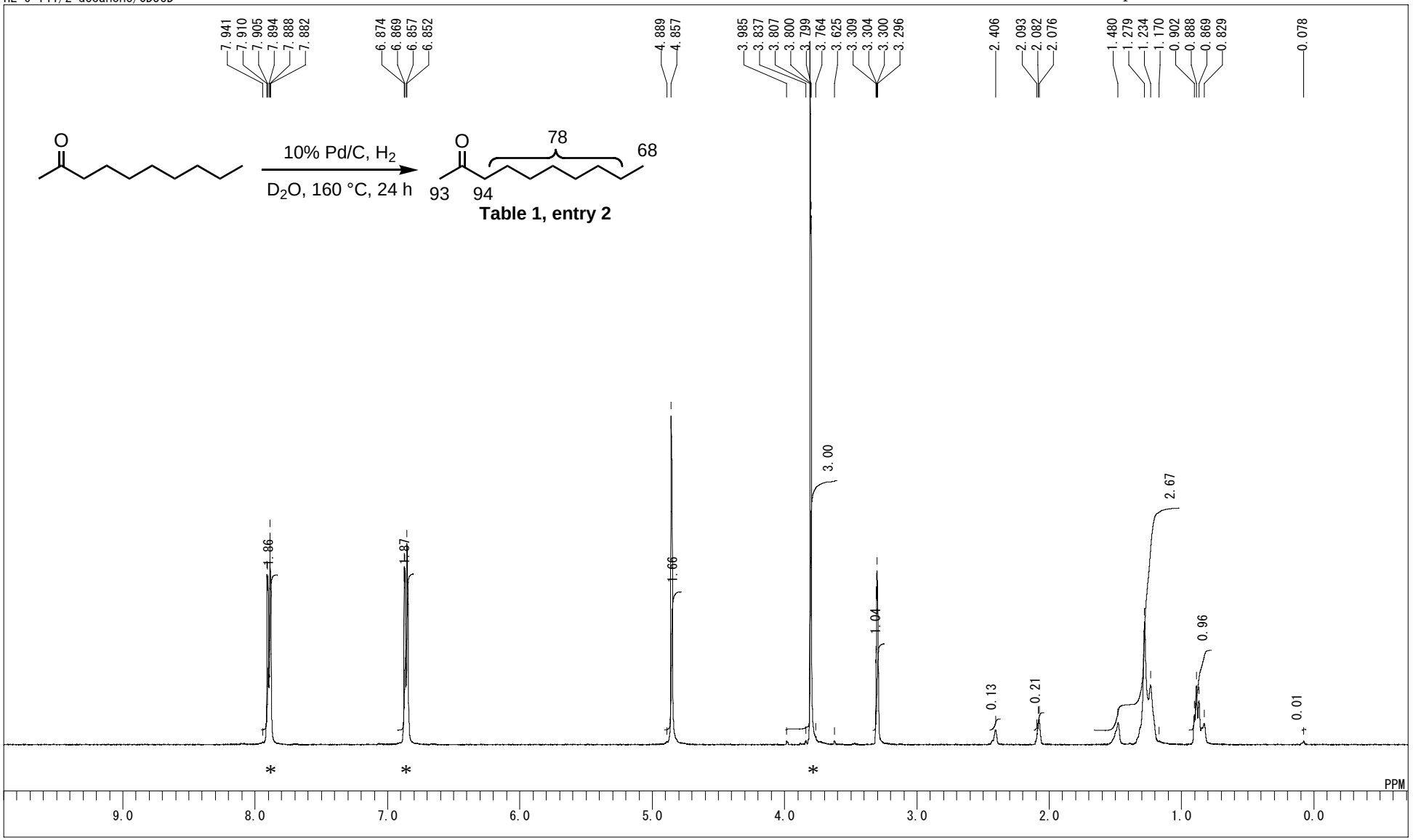
HE-6-1440H/2HNMR/CH3OH

* CD_3OD as an internal standard



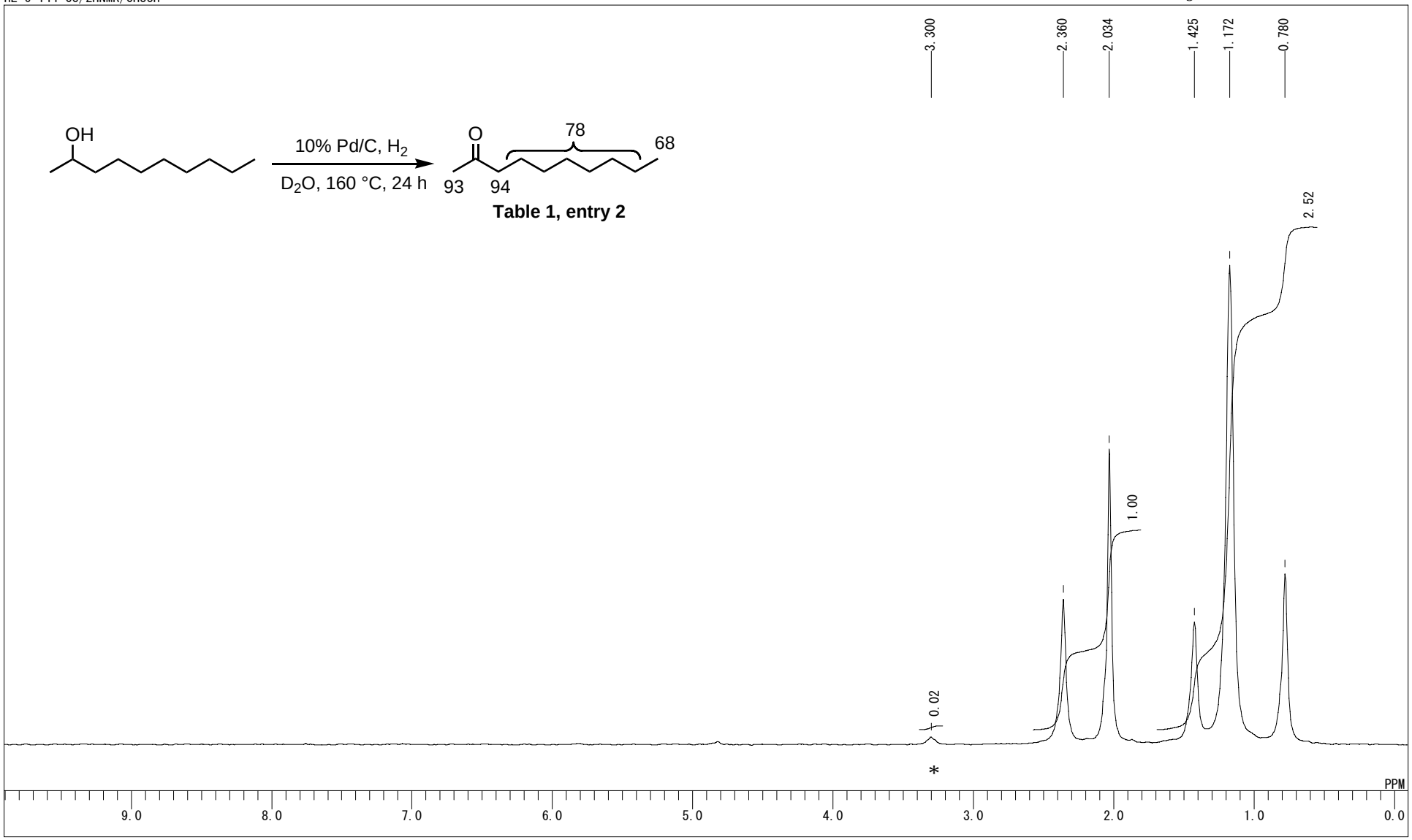
HE-6-144/2-decanone/CD3OD

* *p*-anisic acid as an internal standard

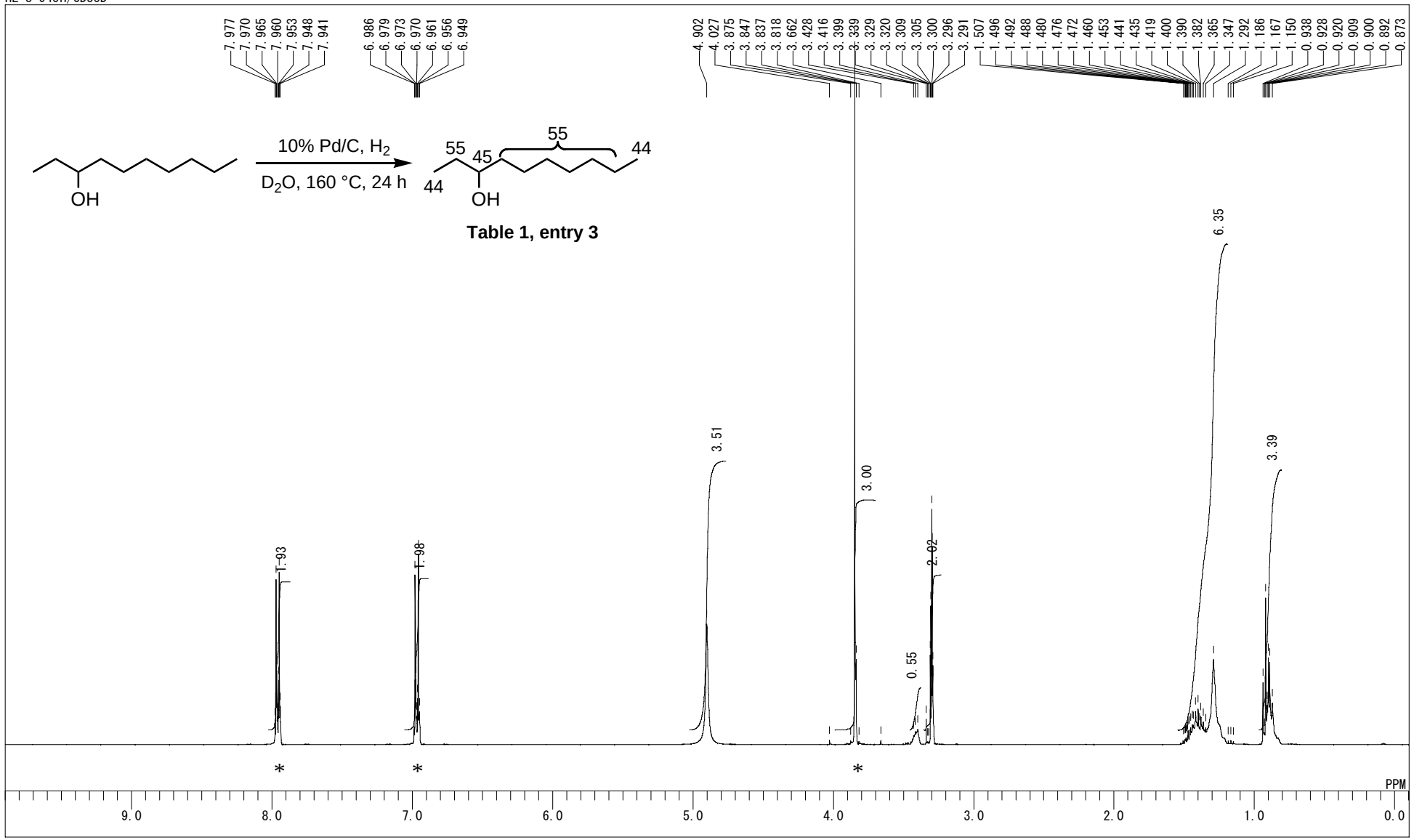


HE-6-144-CO/2HNMR/CH3OH

* CD_3OD as an internal standard



* *p*-anisic acid as an internal standard



HE-8-94OH/2HNMR/CH3OH

* CD_3OD as an internal standard

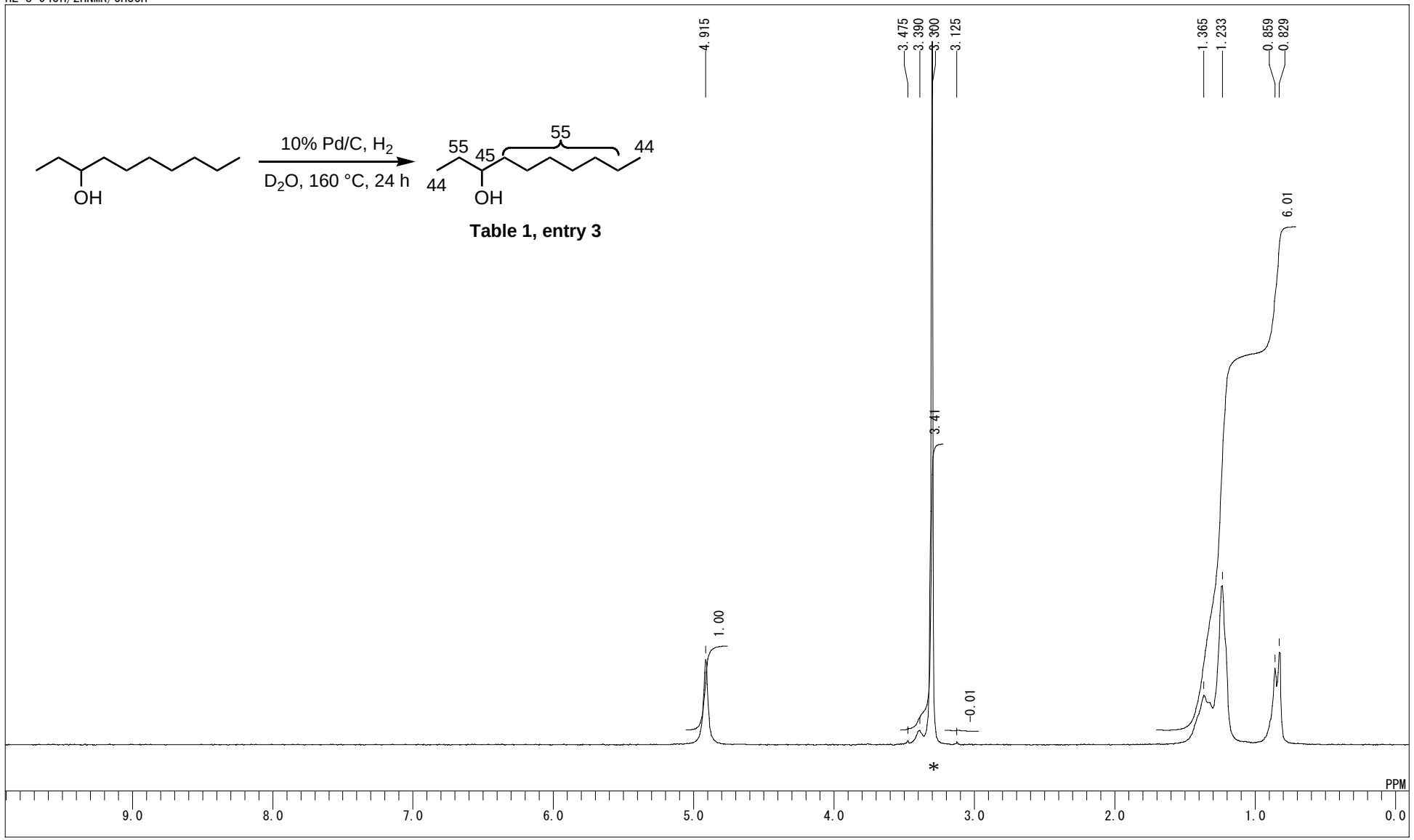
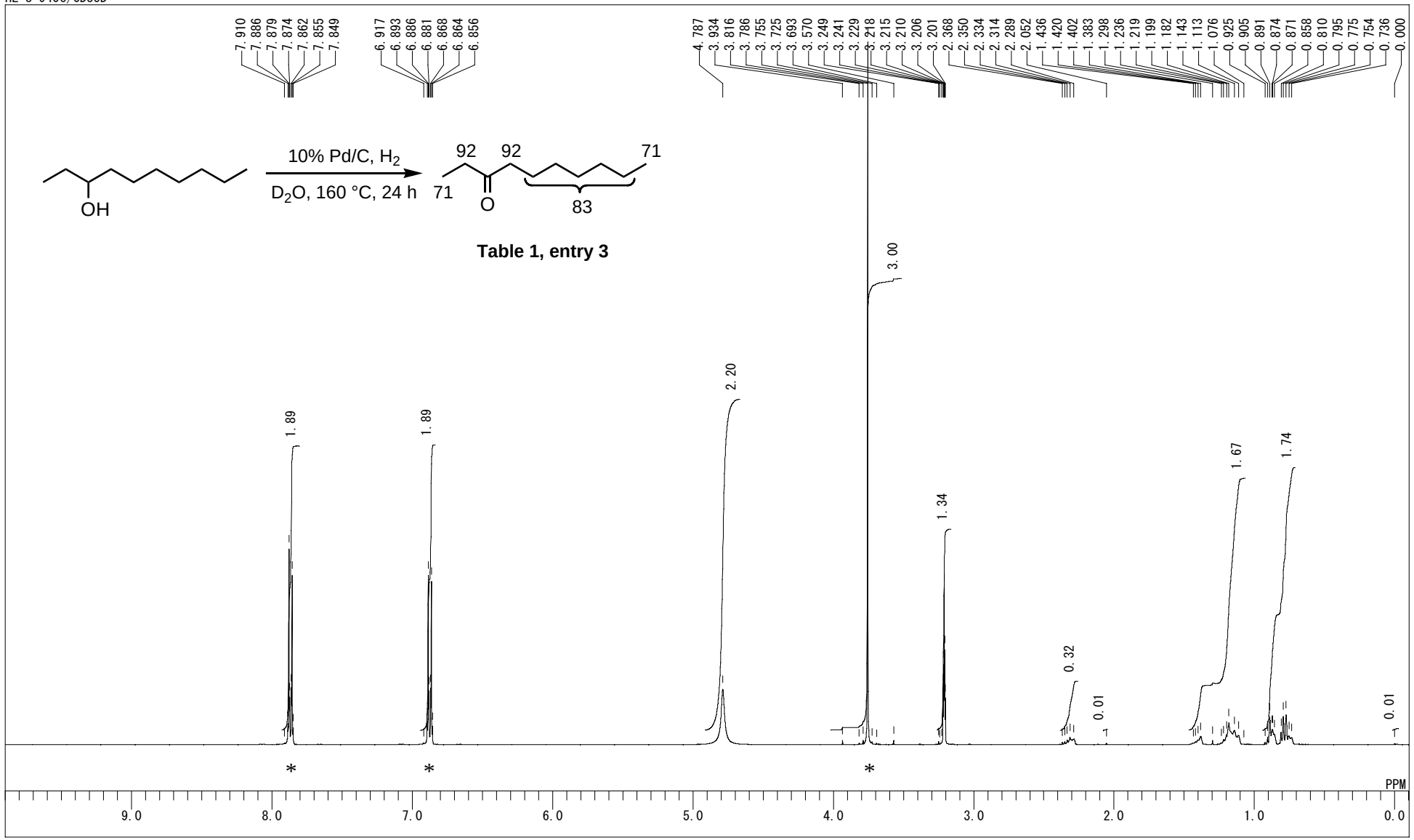


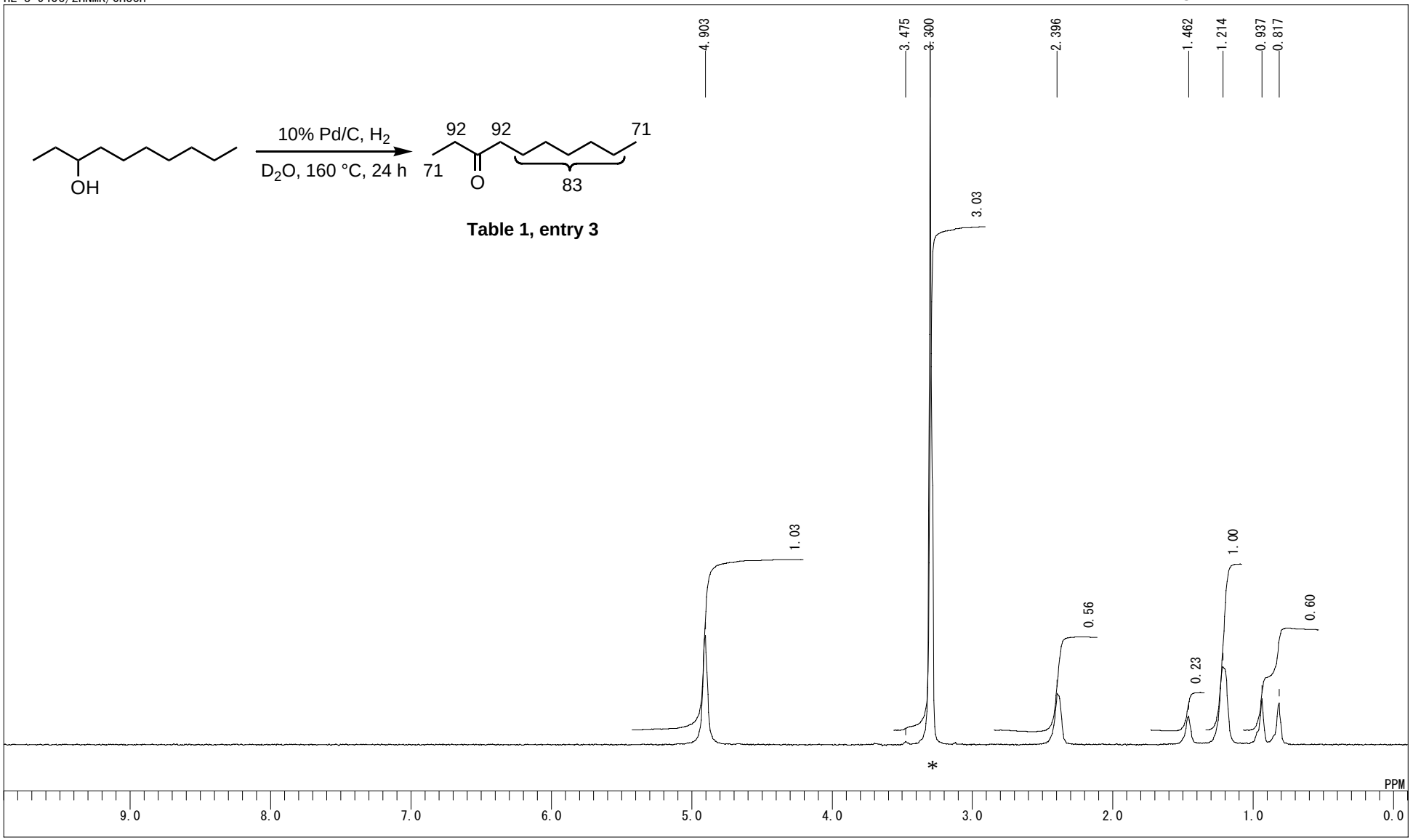
Table 1, entry 3

* *p*-anisic acid as an internal standard



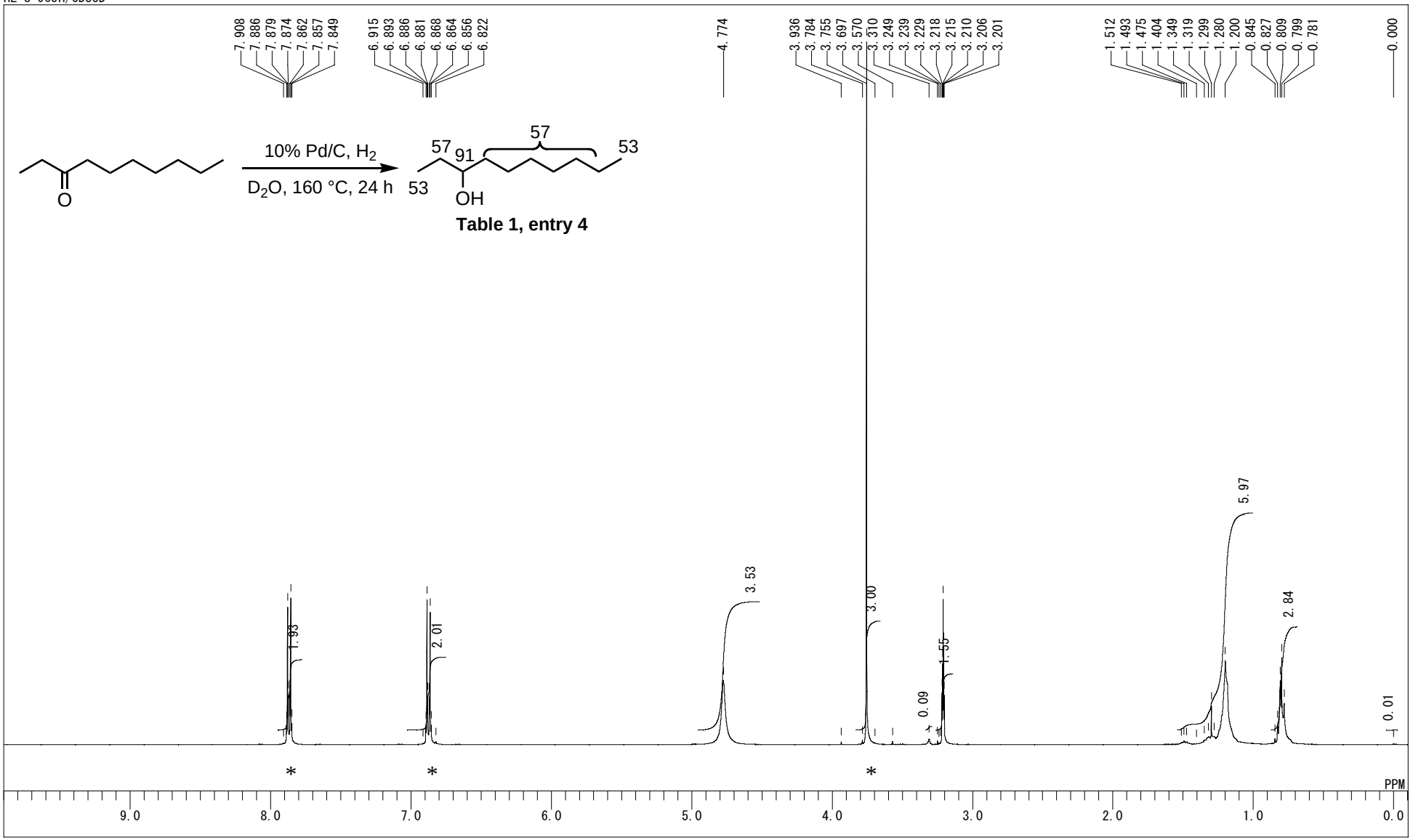
HE-8-94CO/2HNMR/CH3OH

* CD_3OD as an internal standard



HE-8-96OH/CD3OD

* *p*-anisic acid as an internal standard



HE-8-96OH/2HNMR/CH3OH

* CD_3OD as an internal standard

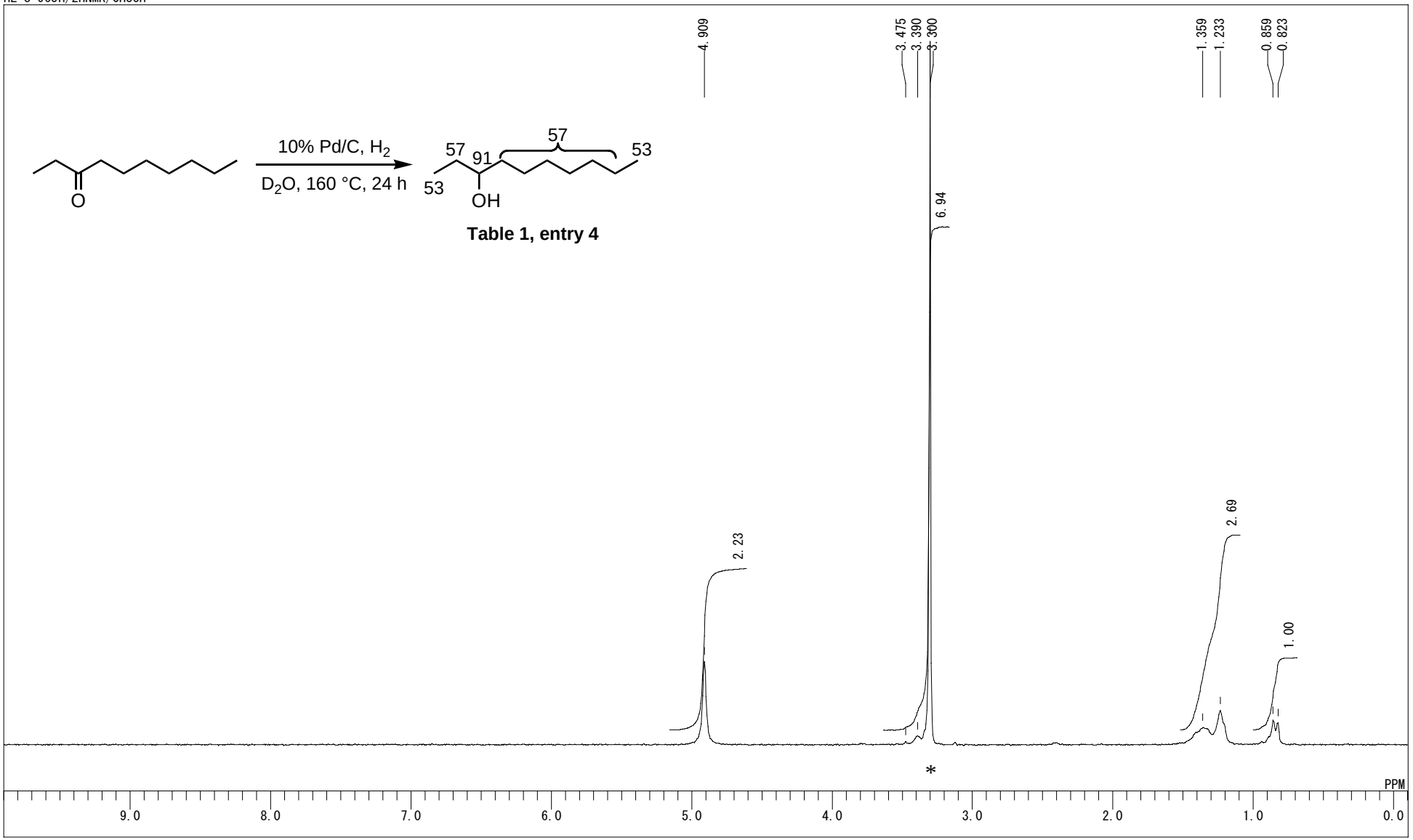
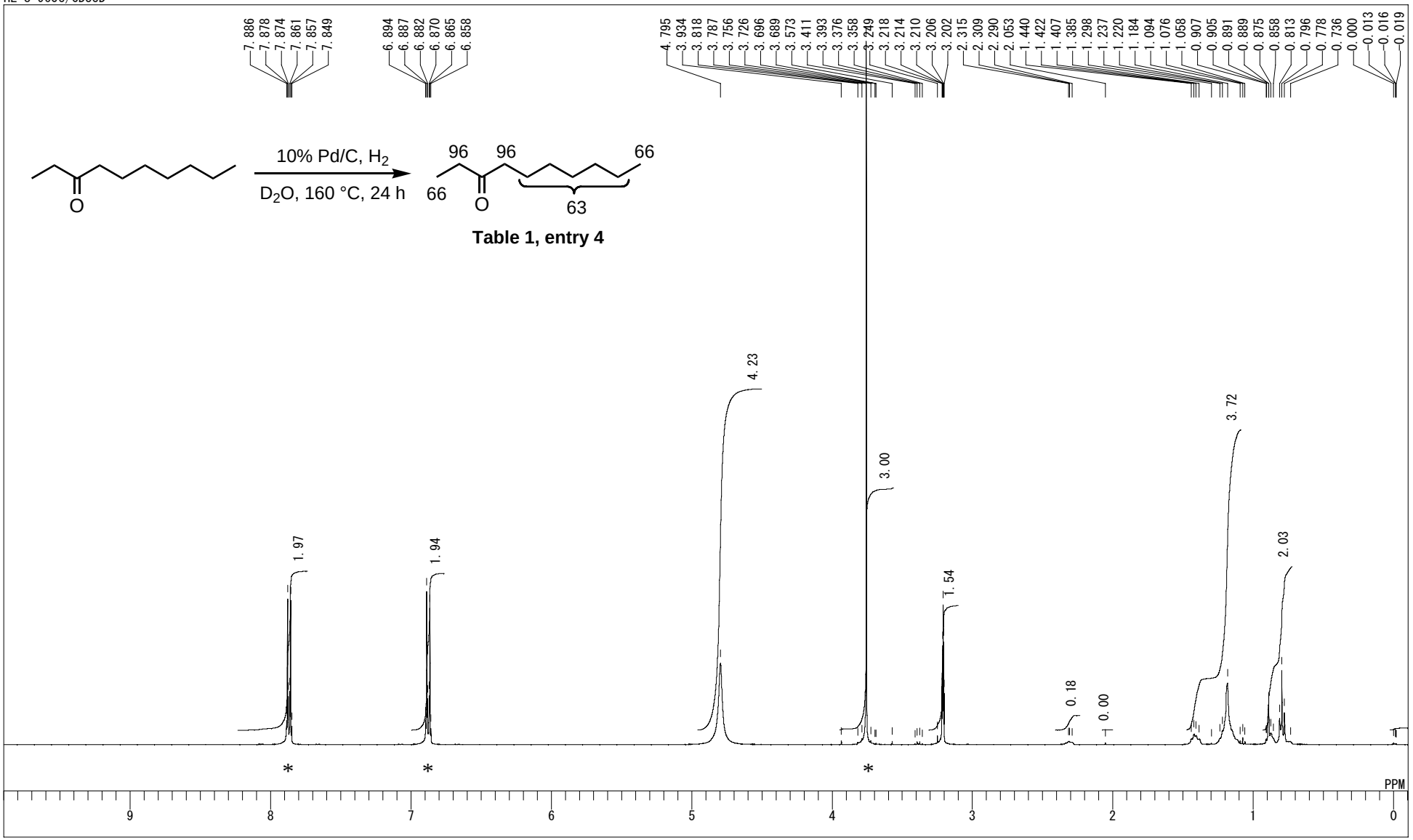


Table 1, entry 4

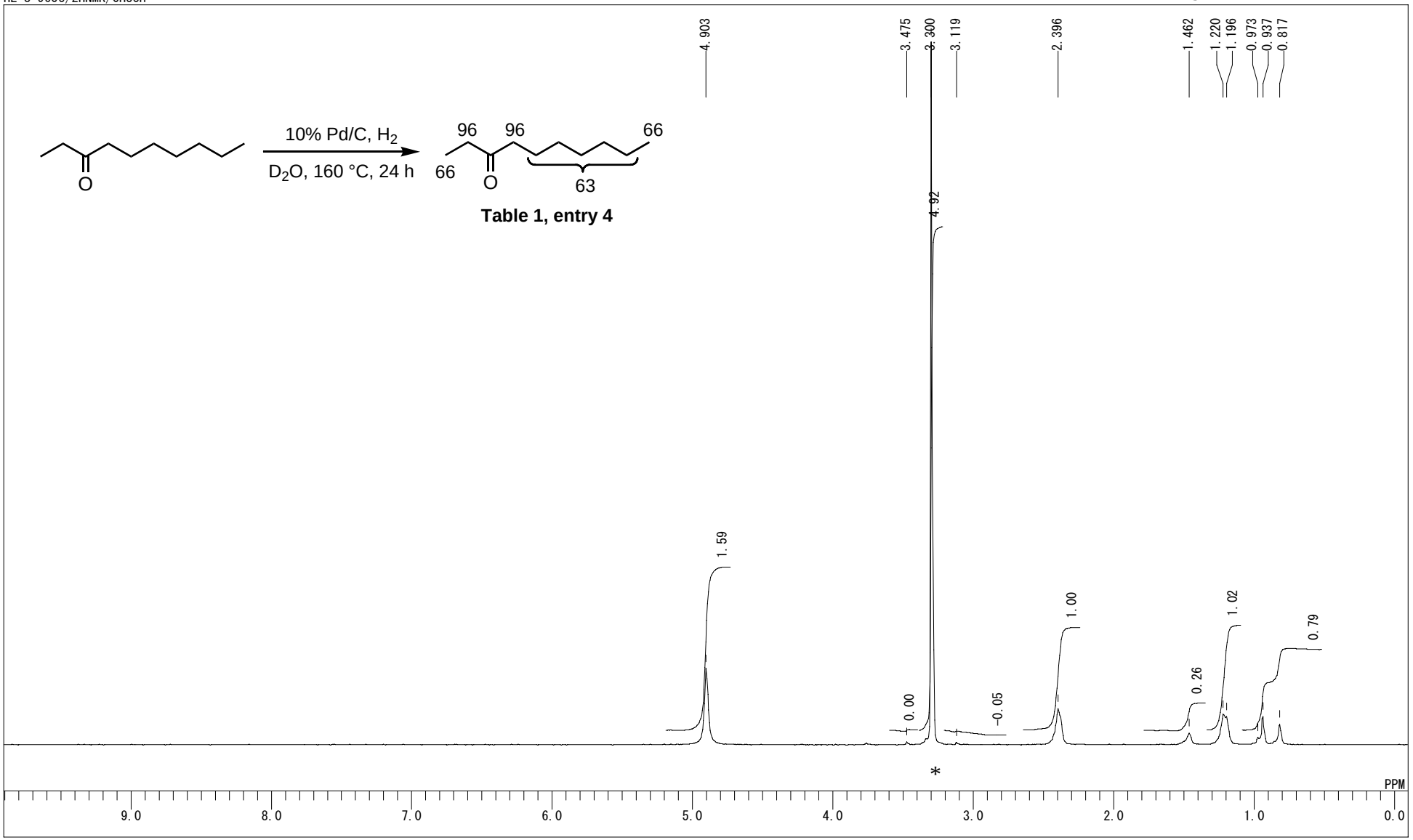
HE-8-96CO/CD3OD

* *p*-anisic acid as an internal standard



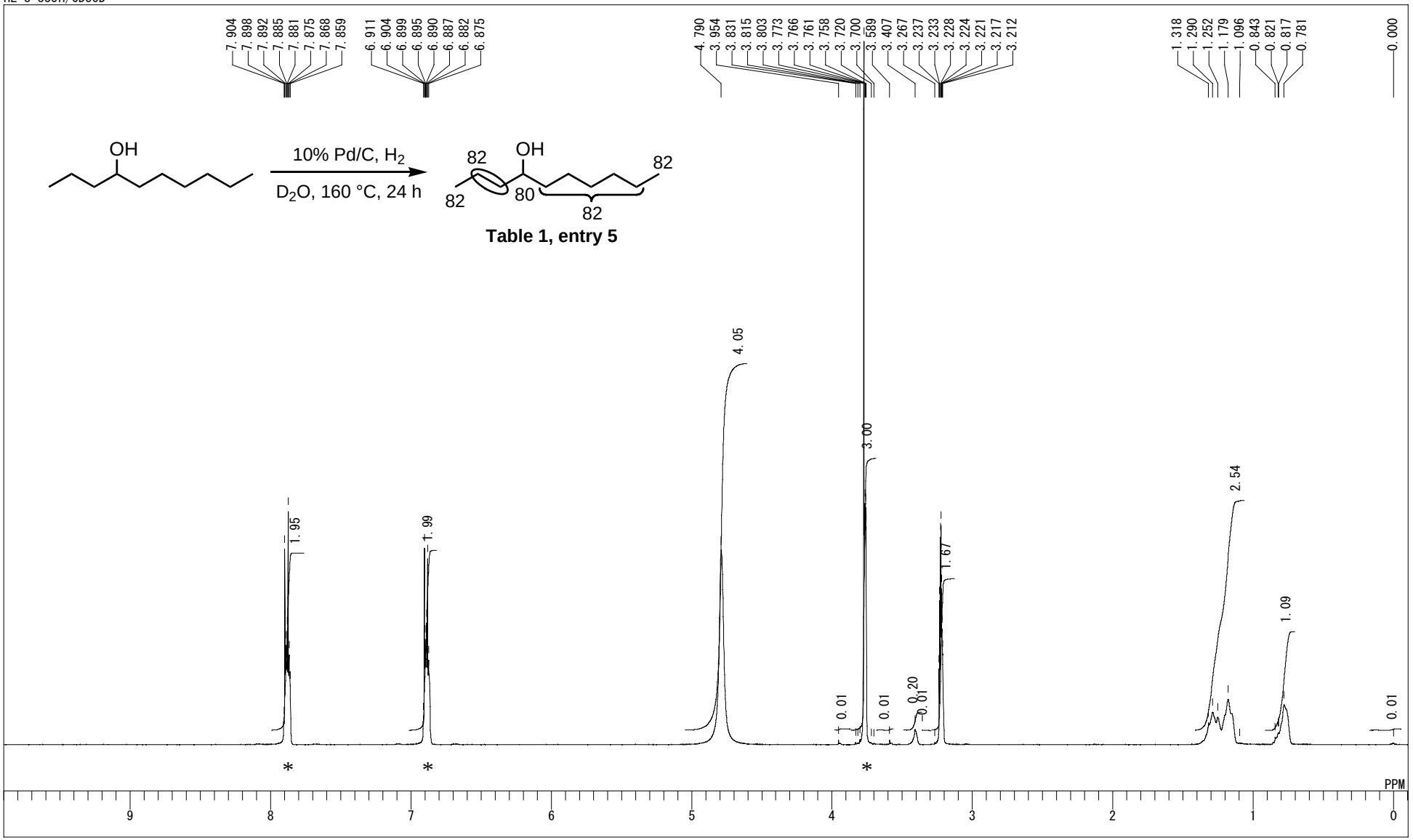
HE-8-96CO/2HNMR/CH3OH

* CD_3OD as an internal standard



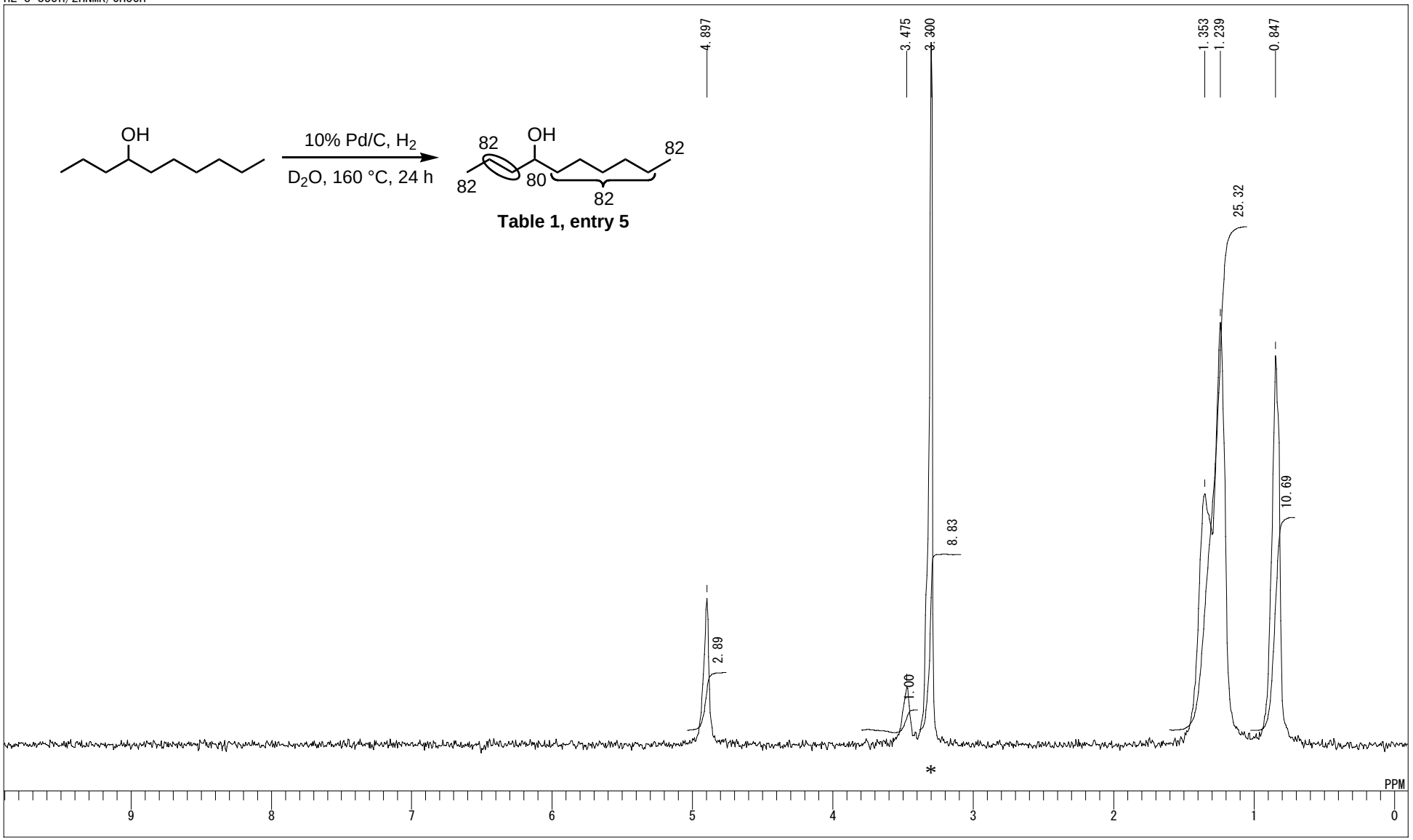
HE-8-830H/CD3OD

* *p*-anisic acid as an internal standard



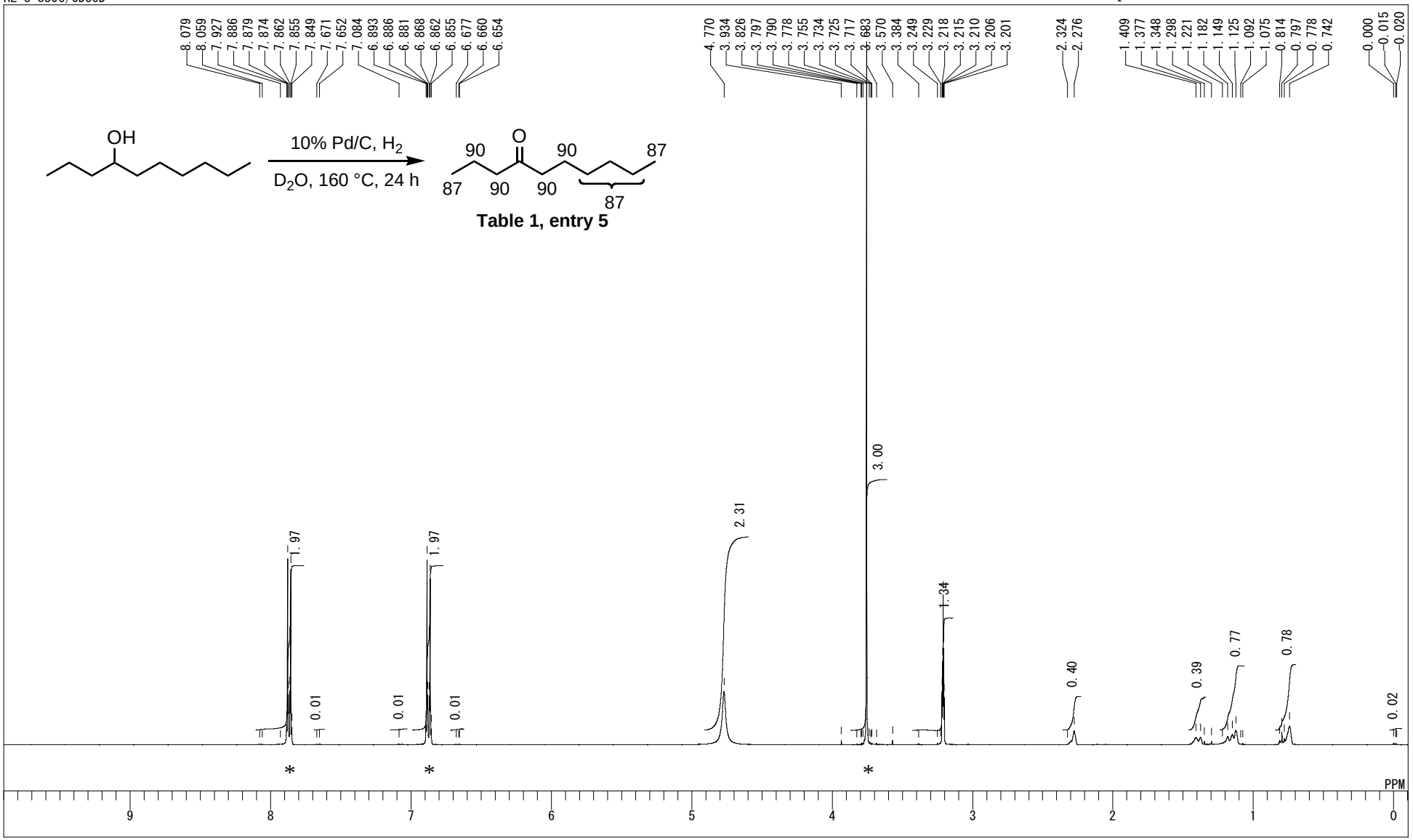
HE-8-83OH/2HNMR/CH3OH

* CD_3OD as an internal standard



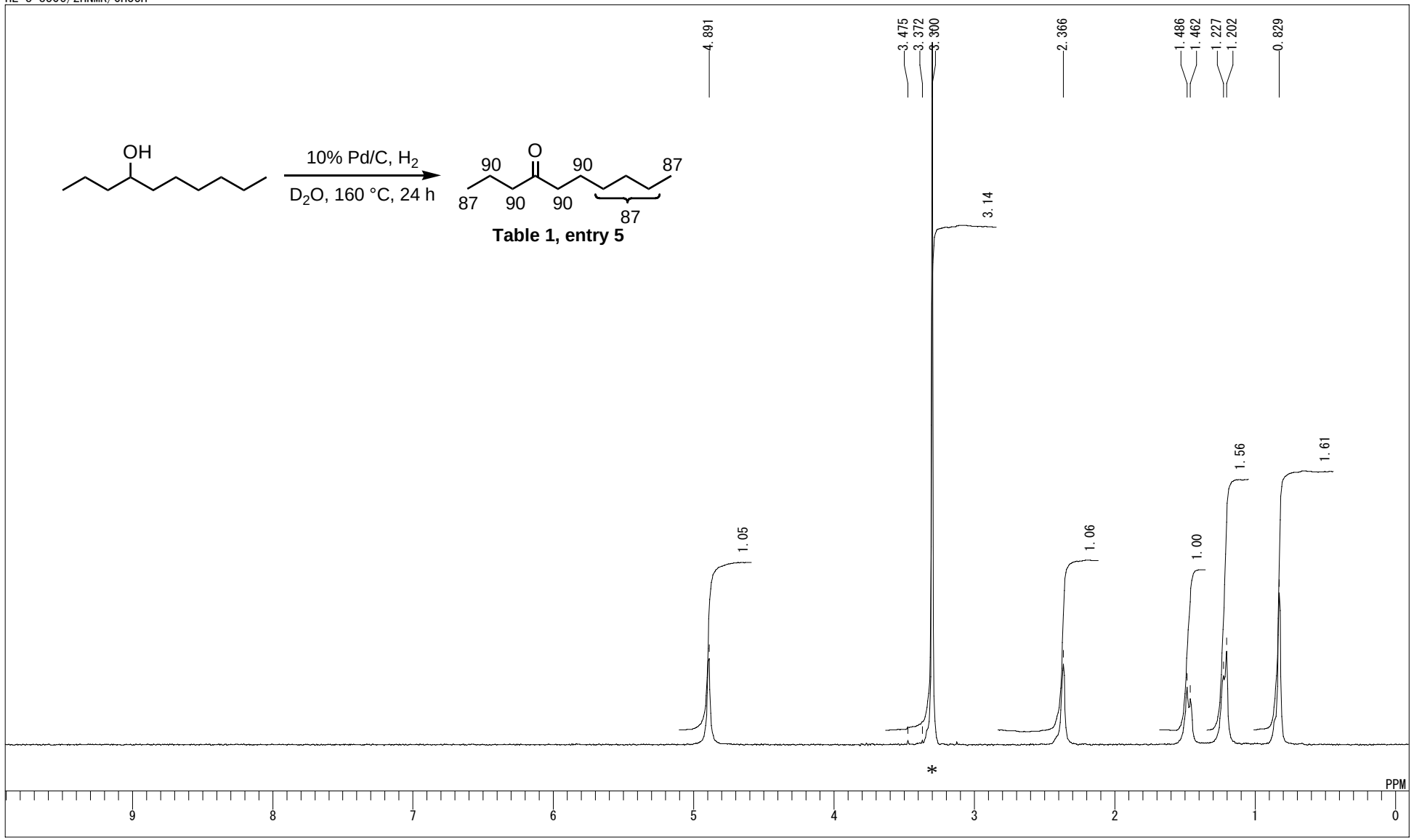
HE-8-83CO/CD3OD

* *p*-anisic acid as an internal standard



HE-8-83CO/2HNMR/CH3OH

* CD_3OD as an internal standard



HE-6-146/decanol/CD3OD

* *p*-anisic acid as an internal standard

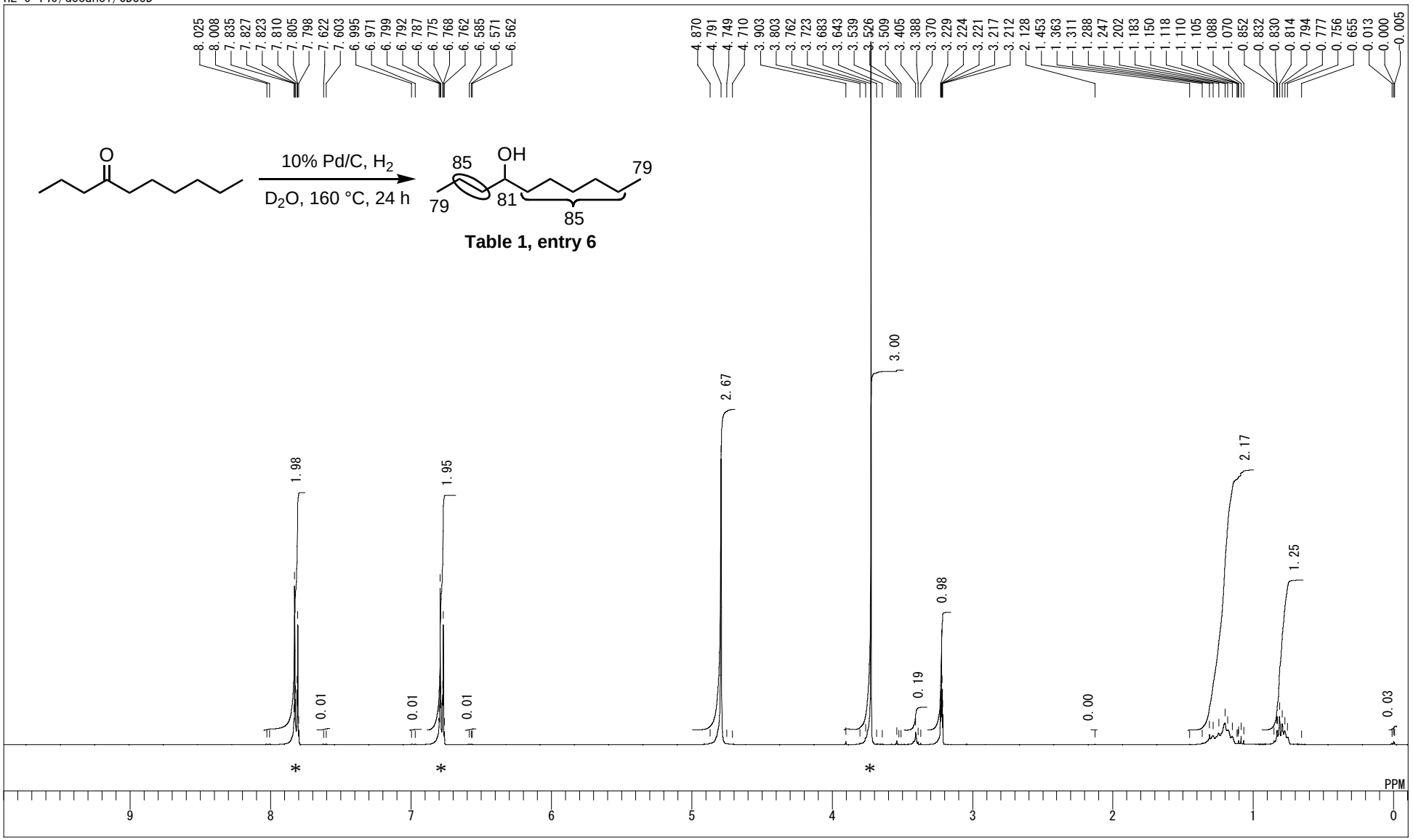
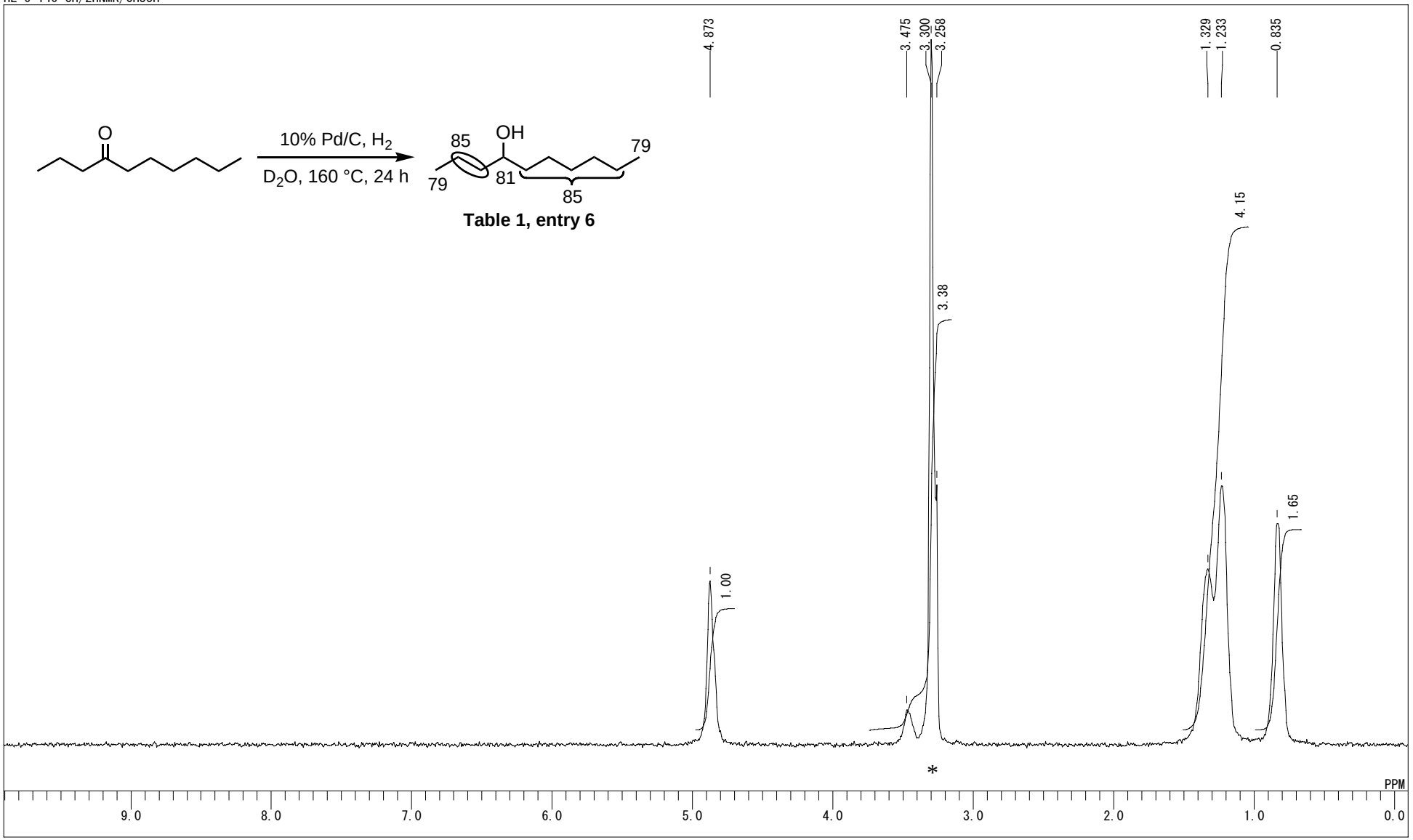


Table 1, entry 6

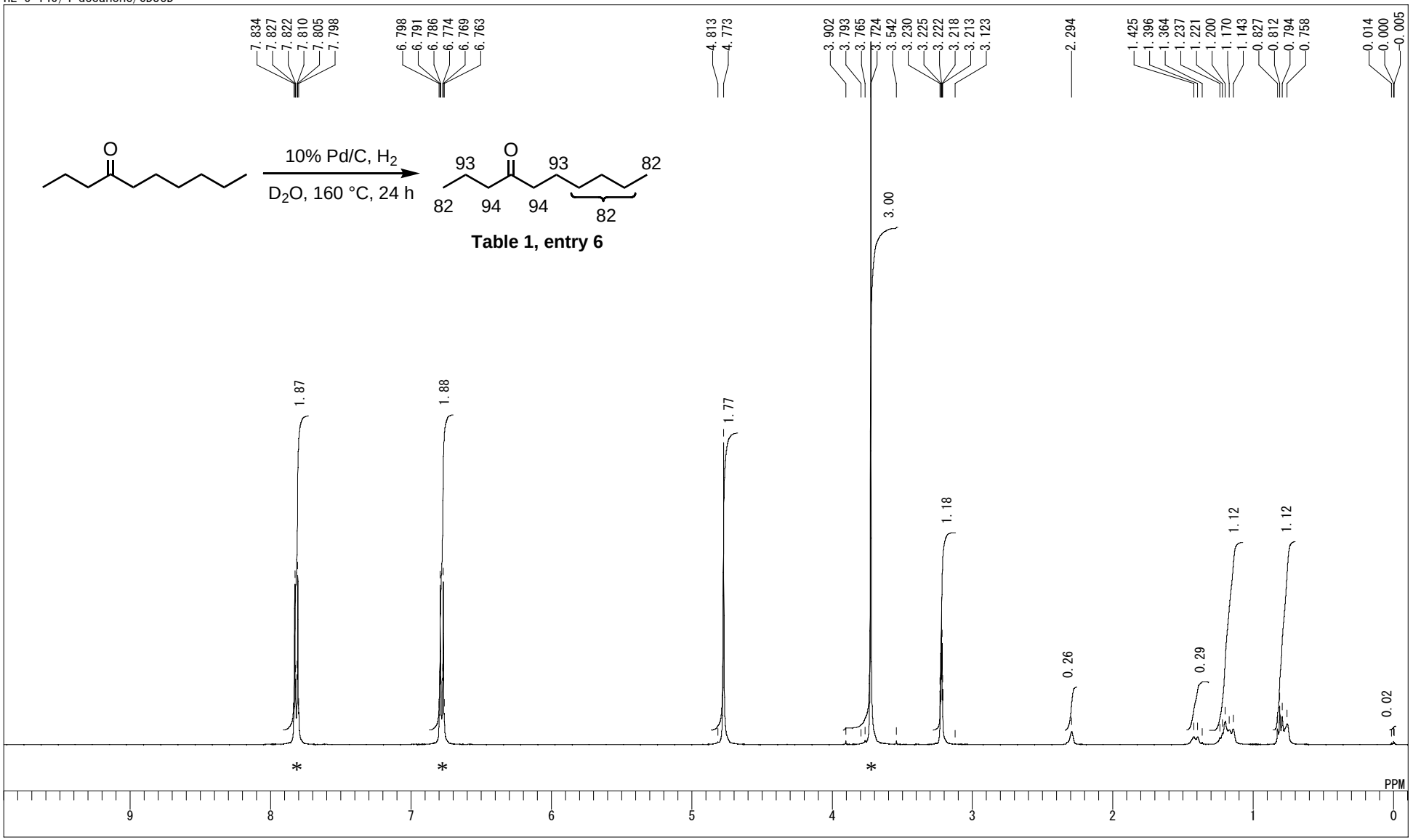
HE-6-146-OH/2HNMR/CH3OH

* CD_3OD as an internal standard



HE-6-146/4-decanone/CD3OD

* *p*-anisic acid as an internal standard



HE-6-146-CO/2HNMR/CH3OH

* CD_3OD as an internal standard

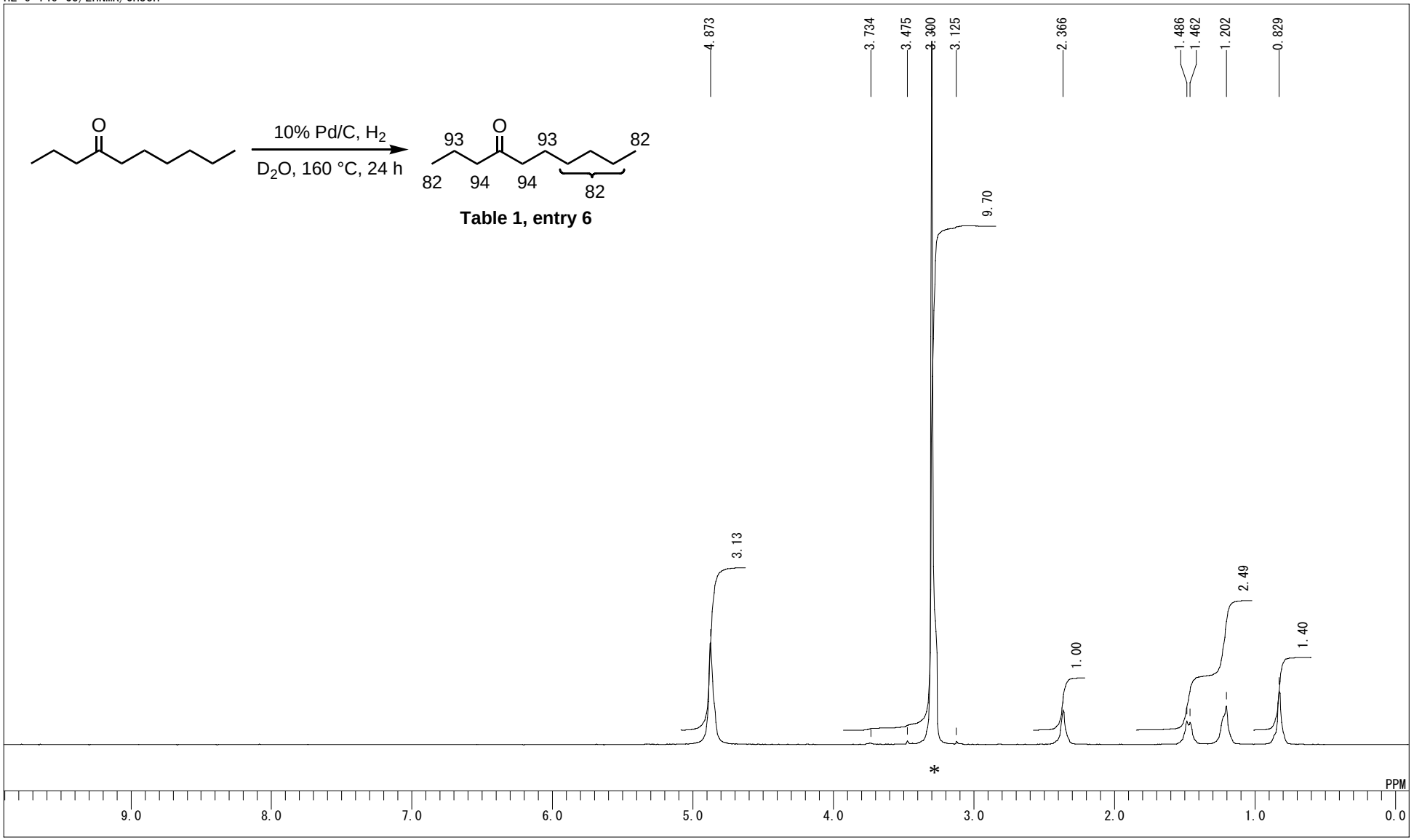
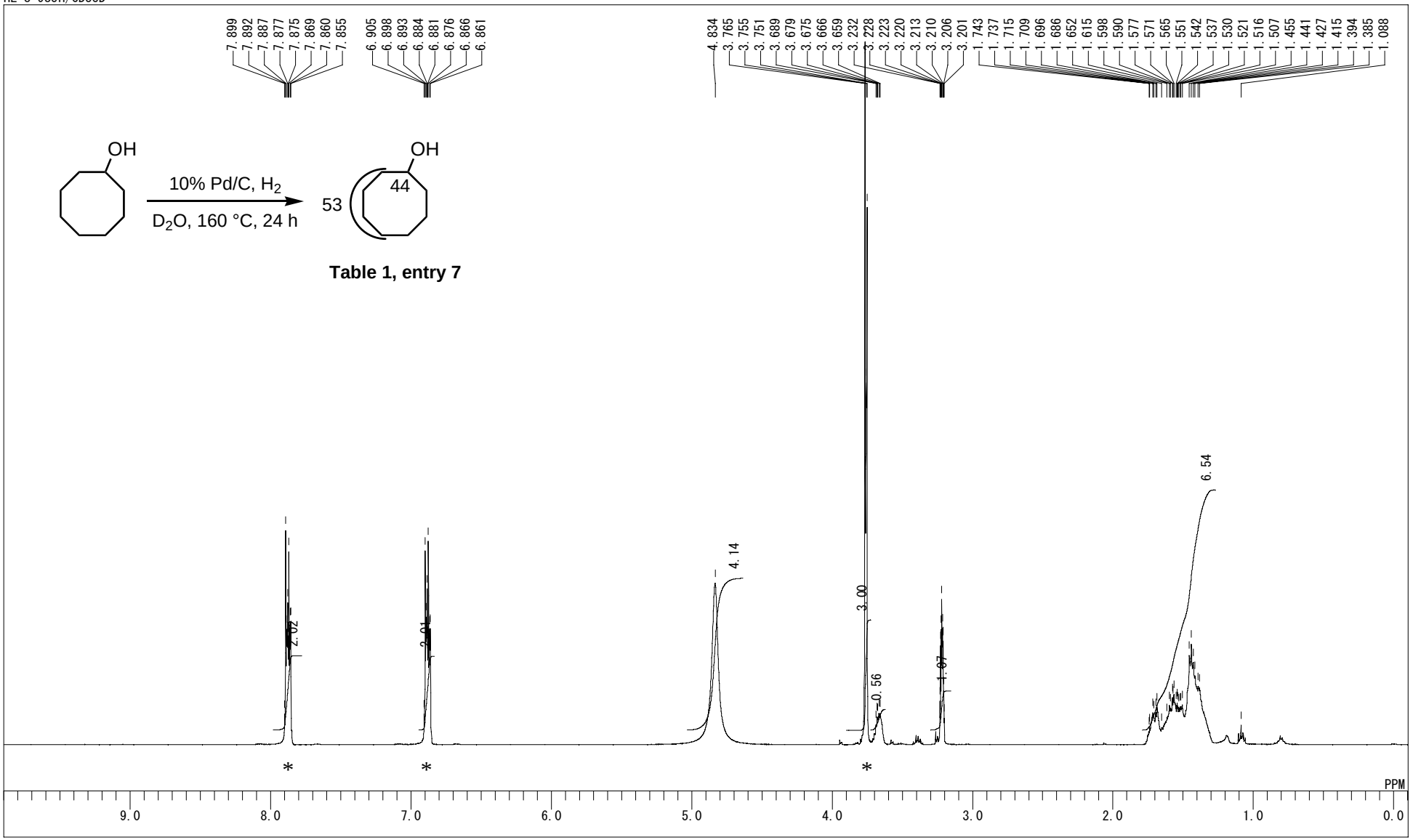


Table 1, entry 6

HE-8-98OH/CD3OD

* *p*-anisic acid as an internal standard



* CD_3OD as an internal standard

HE-8-98OH/2HNMR/CH3OH

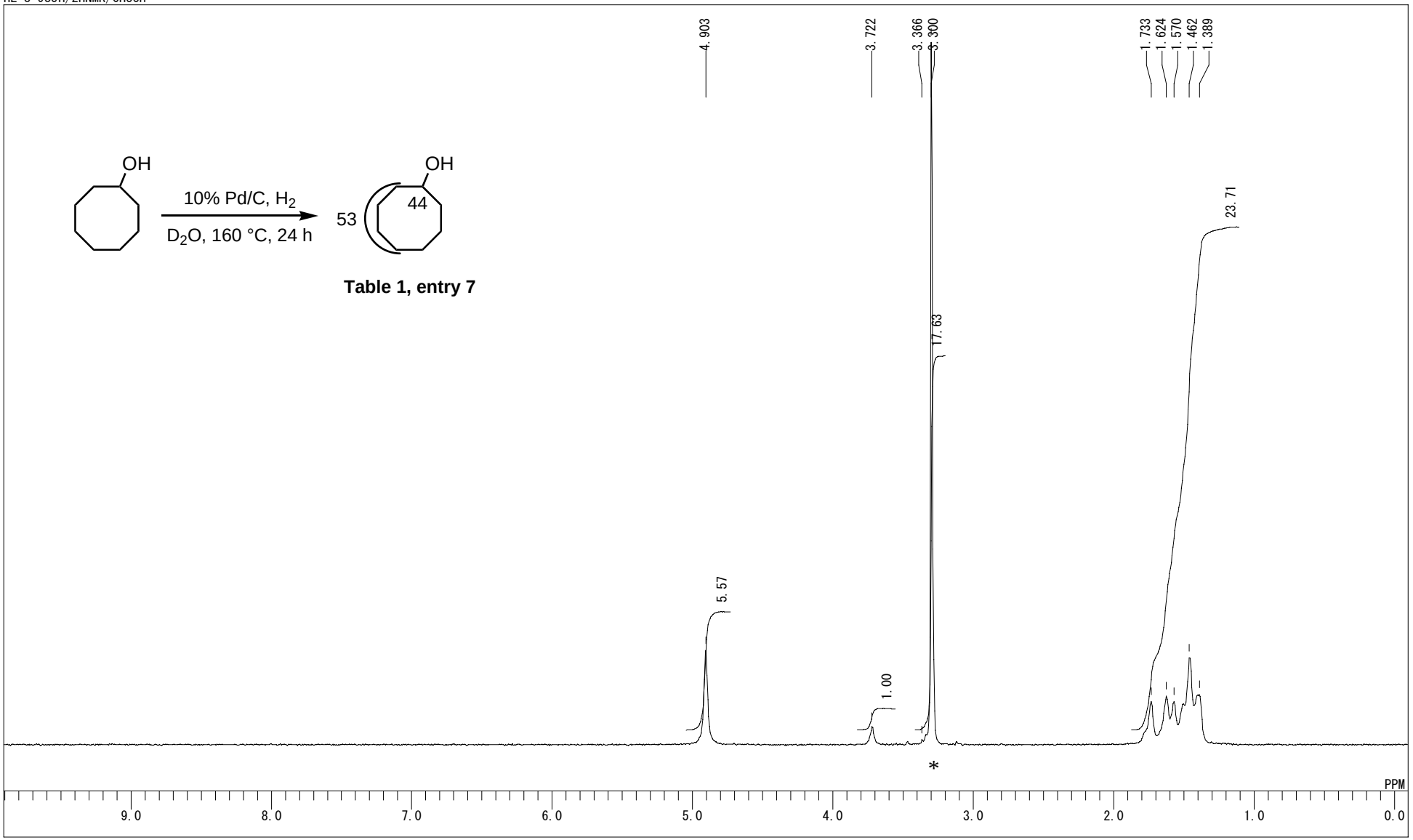
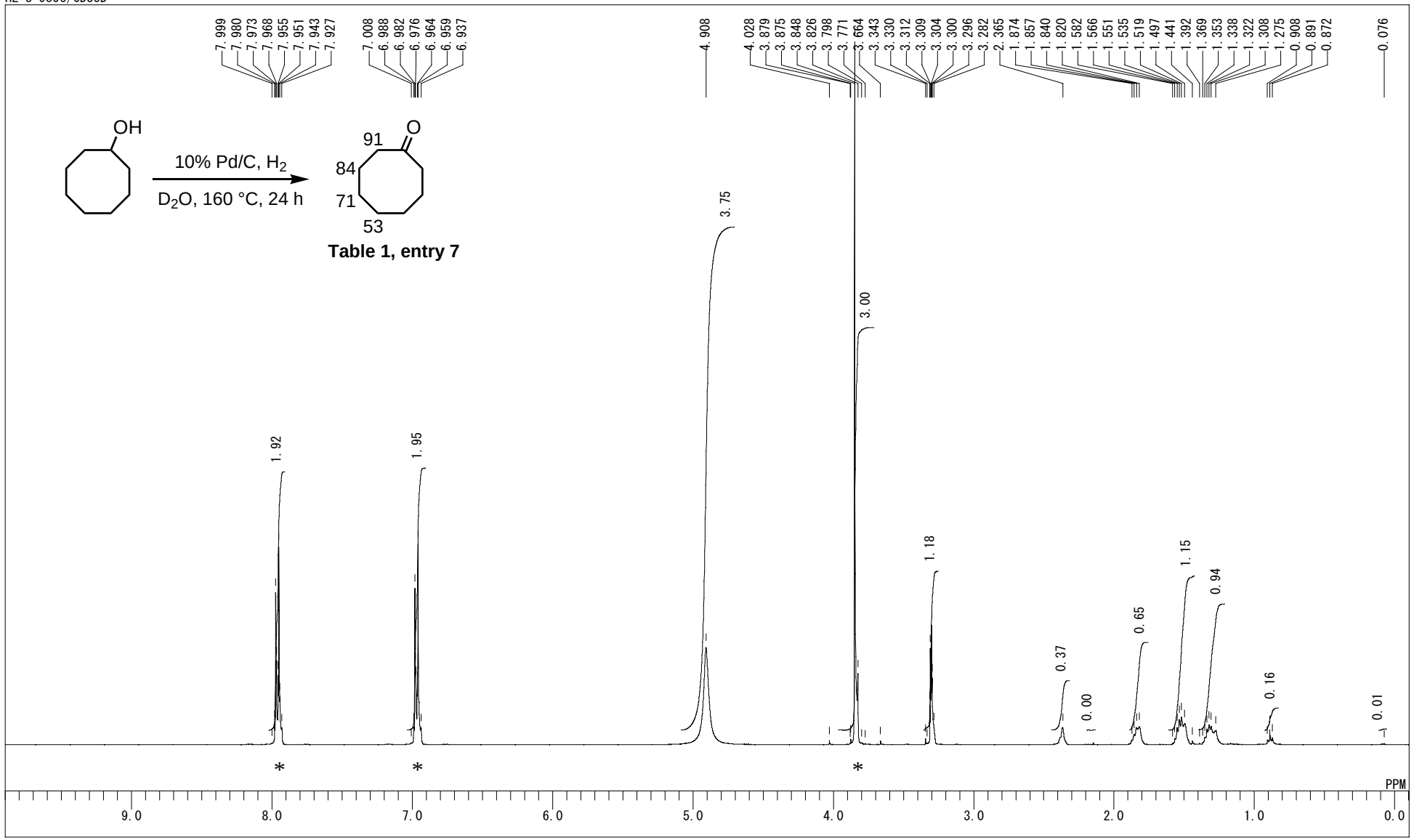


Table 1, entry 7

HE-8-98CO/CD3OD

* *p*-anisic acid as an internal standard



HE-8-98CO/2HNMR/CH3OH

* CD_3OD as an internal standard

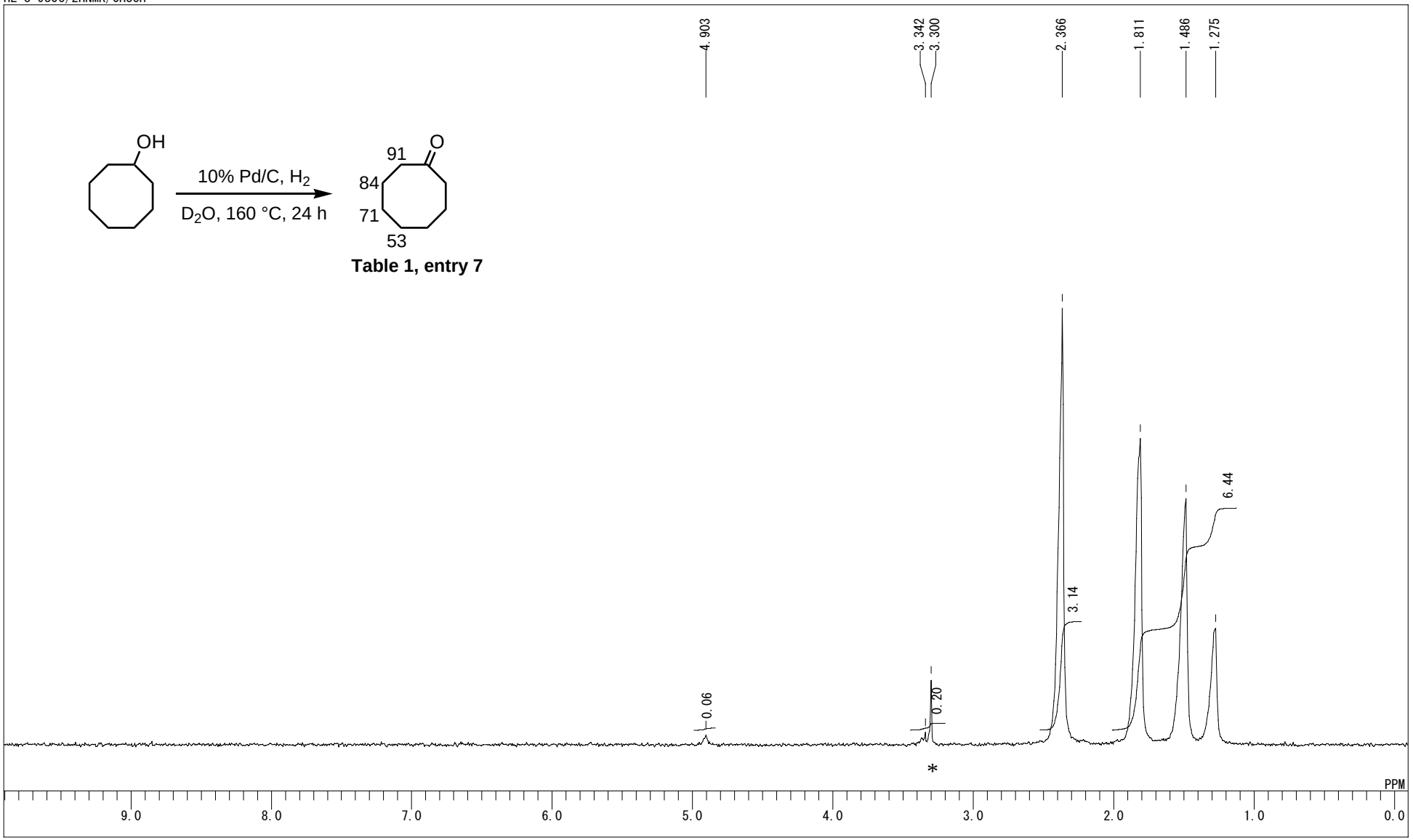
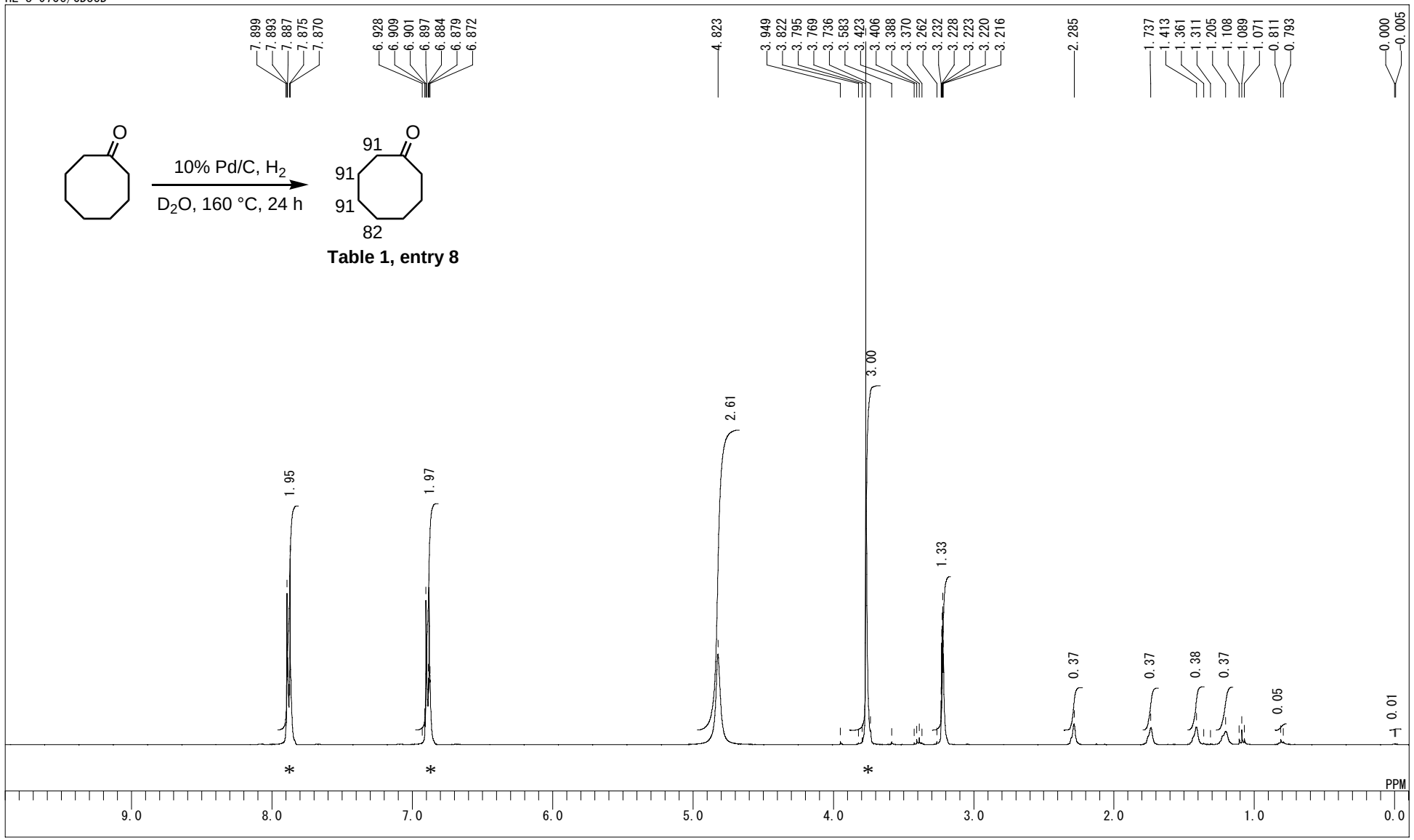


Table 1, entry 7

HE-8-97CO/CD3OD

* *p*-anisic acid as an internal standard



HE-8-97CO/2HNMR/CH3OH

* CD_3OD as an internal standard

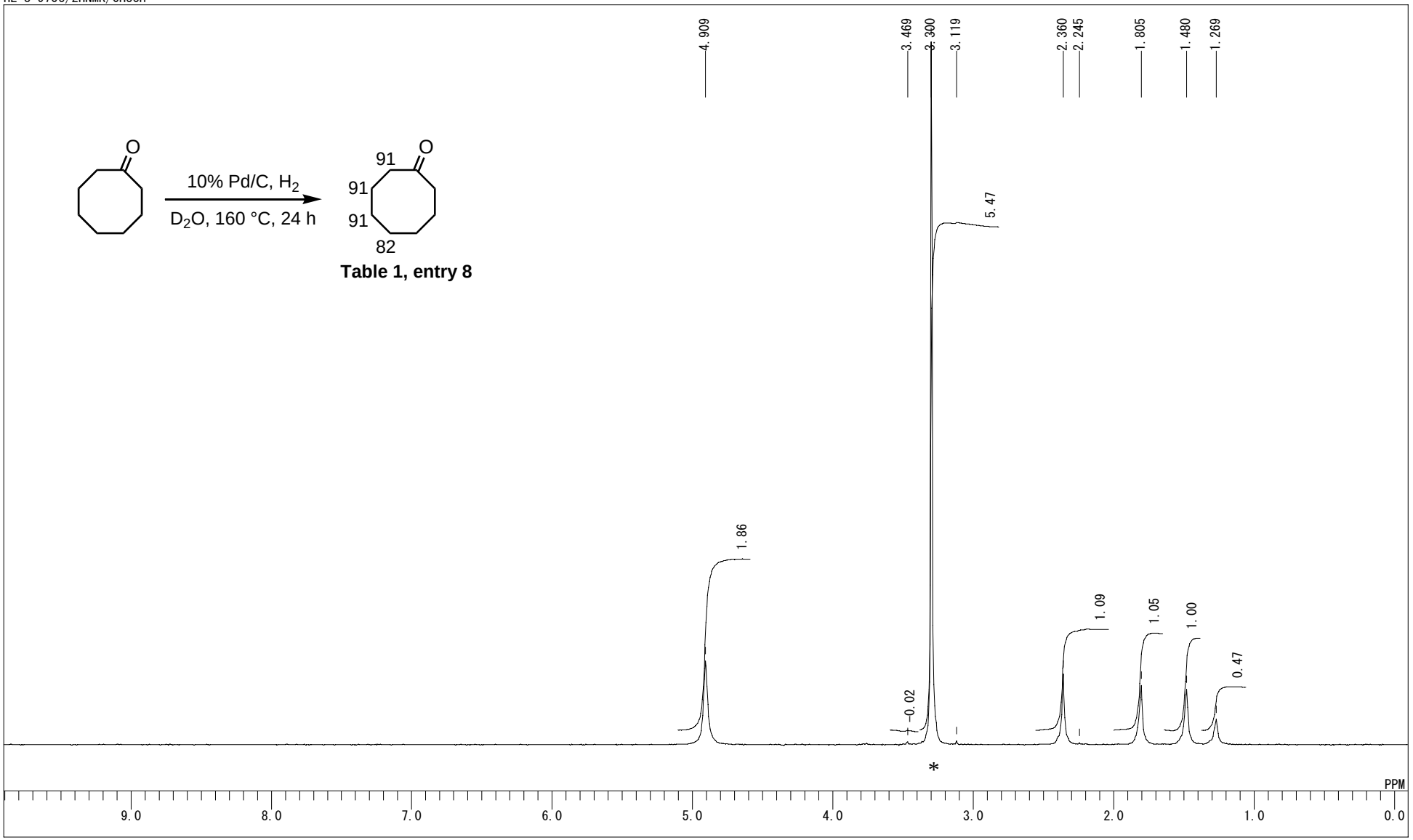


Table 1, entry 8

HE-8-1090H/CD3OD

* *p*-anisic acid as an internal standard

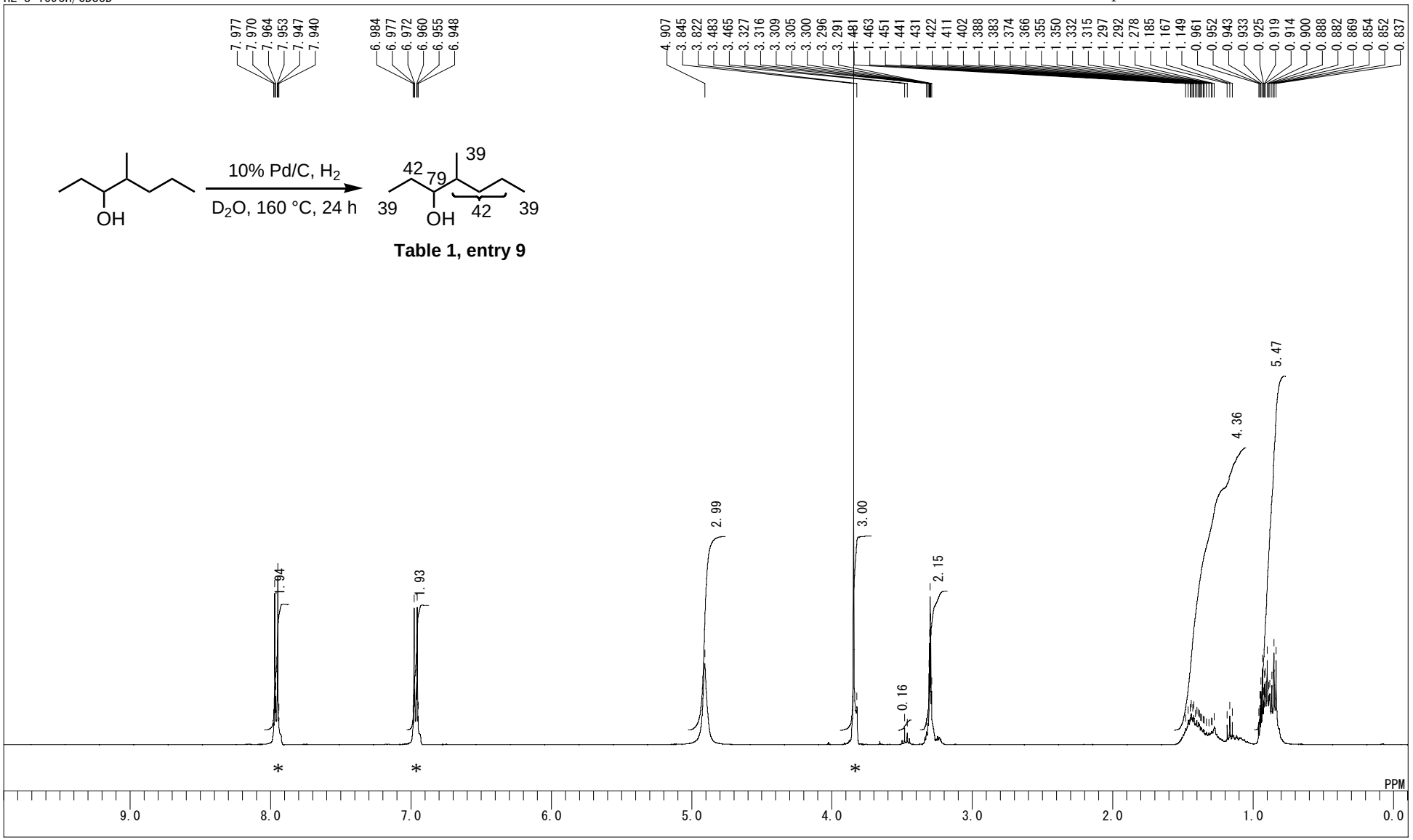
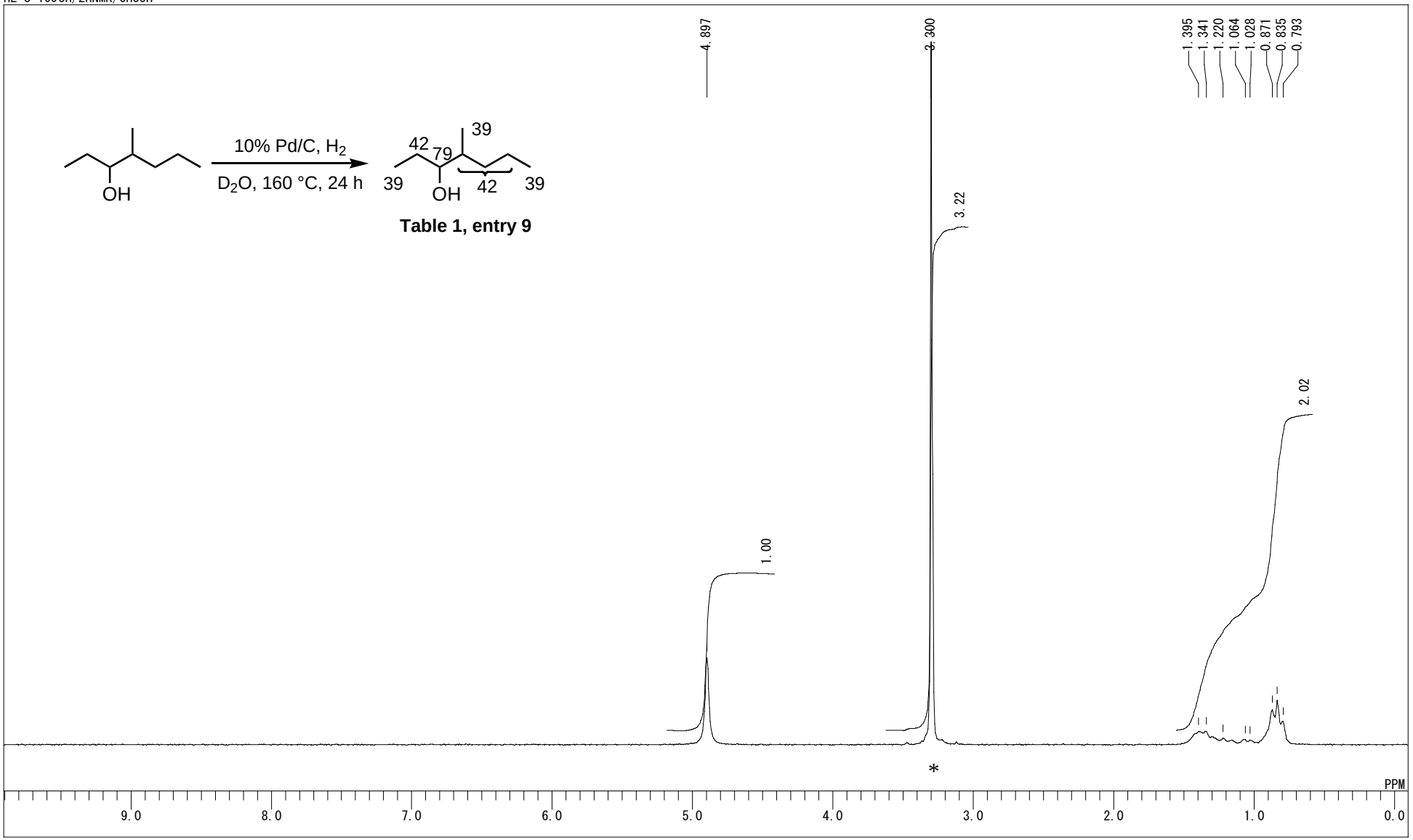


Table 1, entry 9

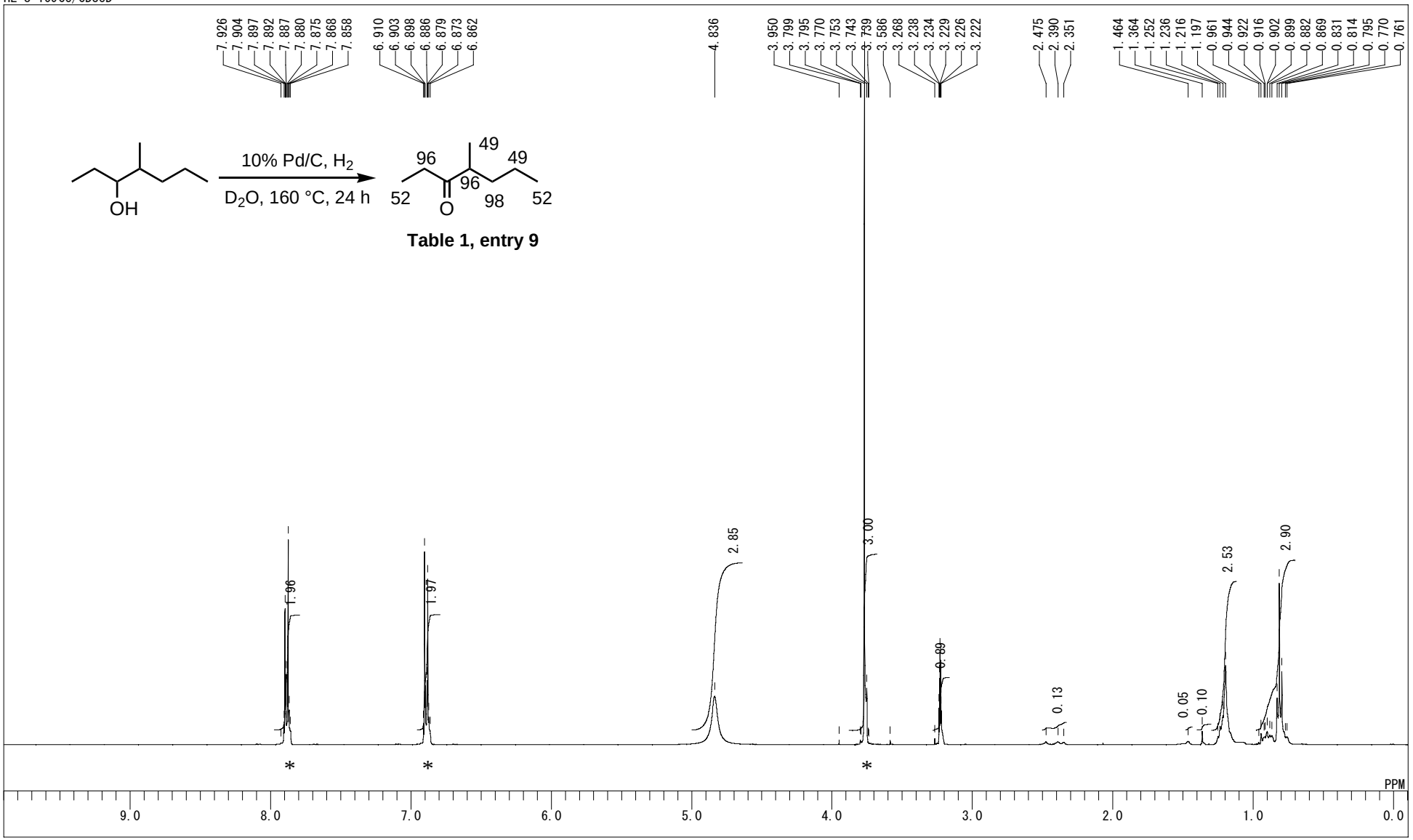
HE-8-109OH/2HNMR/CH3OH

* CD_3OD as an internal standard



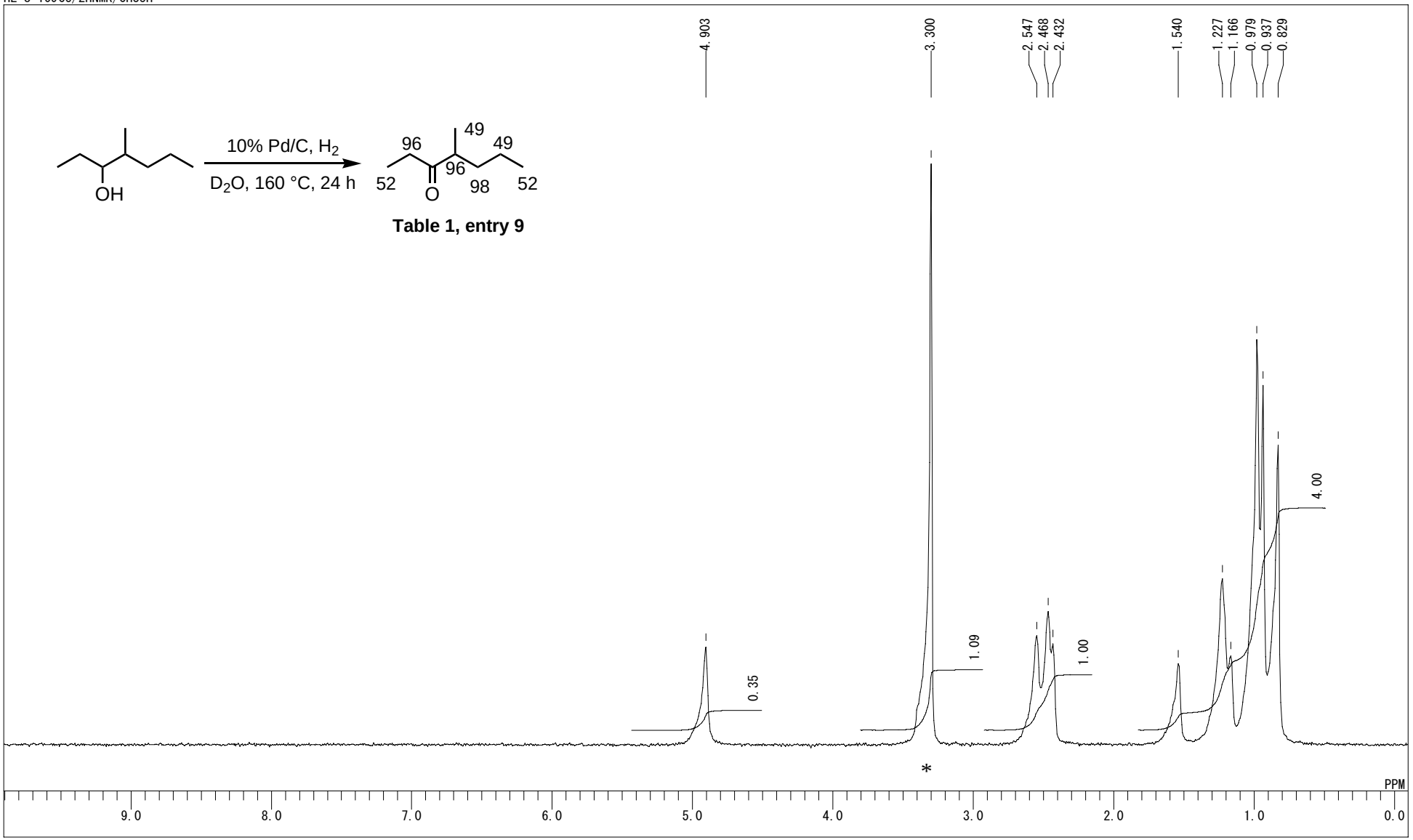
HE-8-109CO/CD3OD

* *p*-anisic acid as an internal standard



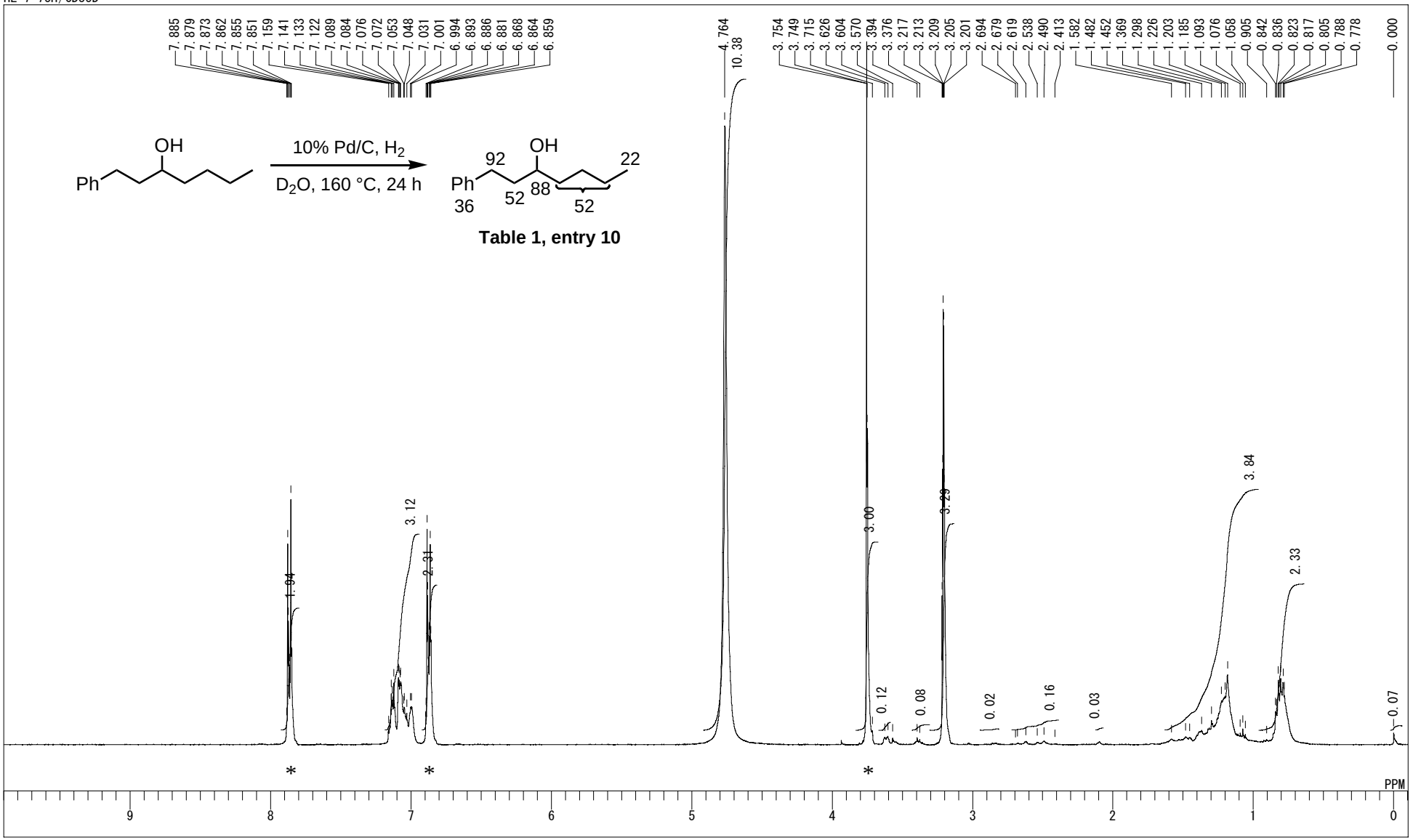
HE-8-109CO/2HNMR/CH3OH

* CD_3OD as an internal standard



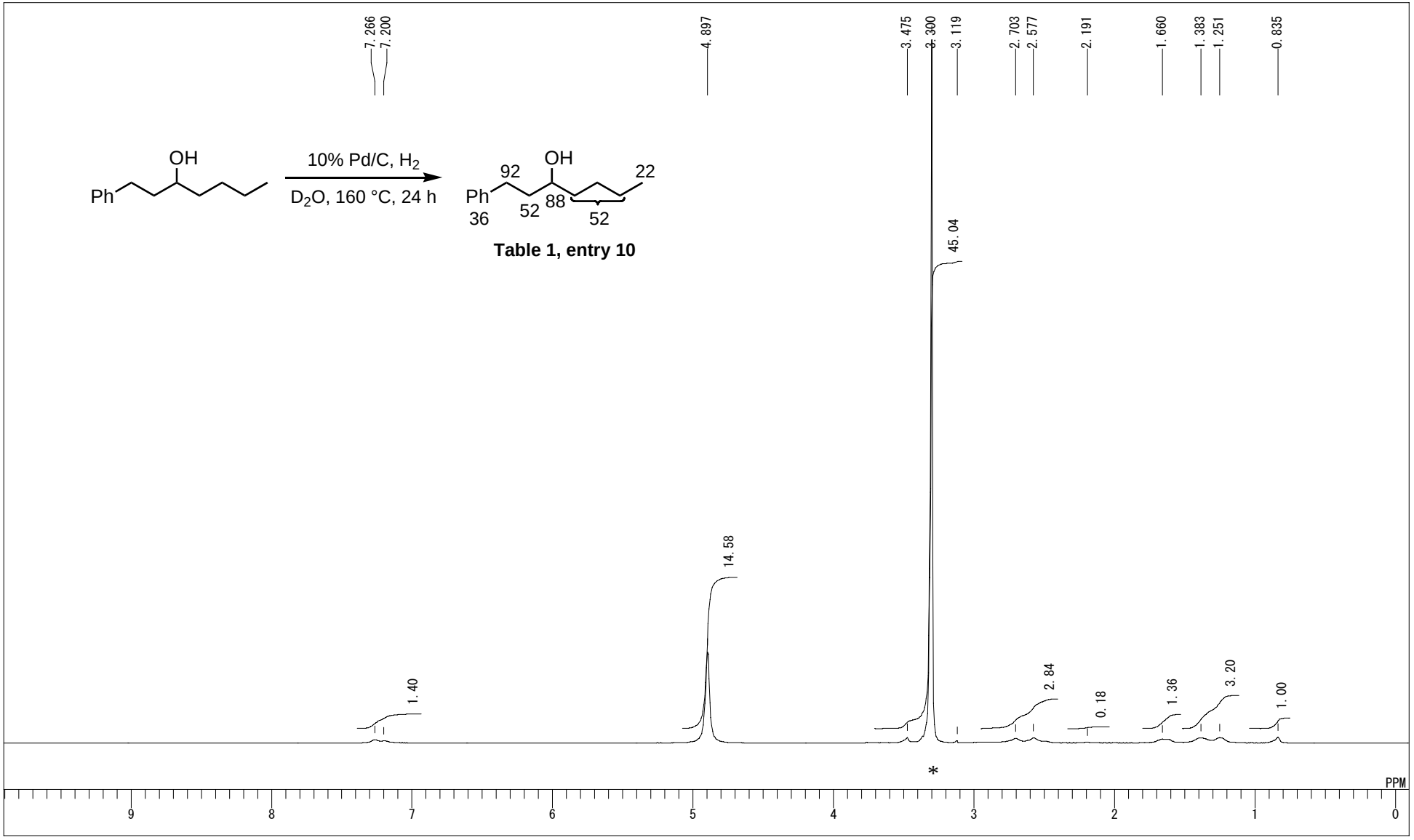
HE-7-7OH/CD3OD

* *p*-anisic acid as an internal standard

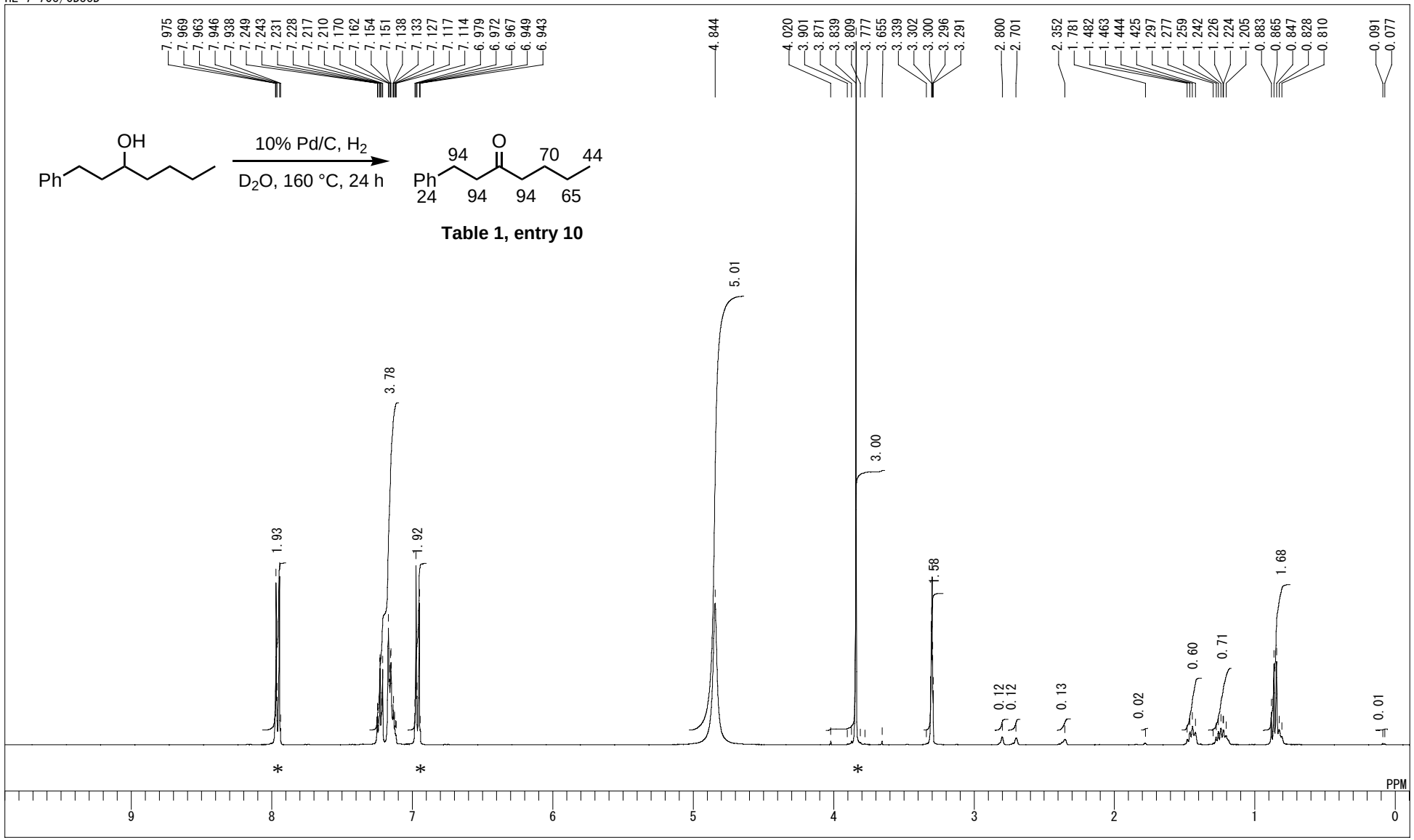


HE-7-7OH-2HNMR

* CD_3OD as an internal standard



* CD_3OD as an internal standard



* *p*-anisic acid as an internal standard

HE-7-7CO/2HNMR/CH3OH

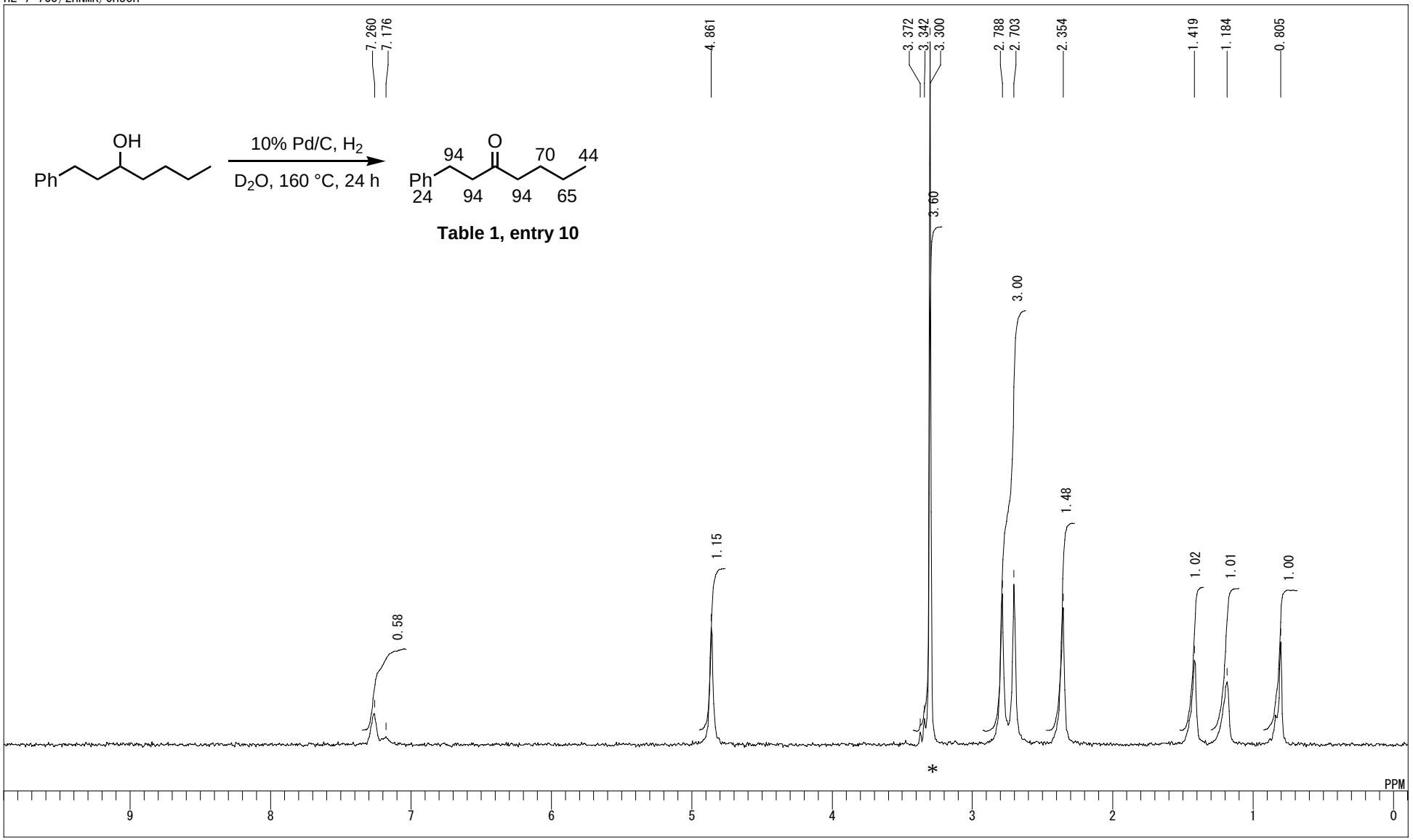


Table 1, entry 10