

Catalytic Deuteration in D₂O as Deuterium Source with H₂ and HCO₂H as Electron Sources

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General considerations

All manipulations were carried out under an argon atmosphere. All aqueous solutions were degassed prior to use. ^1H , ^2H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 spectrometer using sodium 3-(trimethylsilyl)-1-propionic acid- d_4 (TSP- d_4) as an internal standard. Mass spectra were recorded on Waters ZQ2000 (ESI). Elemental analyses were carried out on an Eager 200 instrument. The reaction solution was analyzed by GC (PEG-HT 5%, Uniport HT 60/80, 2 m packed column, 100 °C) or HPLC (Tosoh TSKgel ODS-100V). FT-IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer. The pH values were measured on an Orion Model 290A pH meter with a glass electrode after calibration to standard buffer solutions. The pD values were corrected by adding 0.4 to the observed values ($\text{pD} = \text{pH meter reading} + 0.4$).^{1,2} The complexes **1-3** were prepared according to the literature procedures.³ D_2O (99.9%) and DCO_2D (95wt%) in D_2O were purchased from Isotec. Research grade H_2 (>99.9999%) was used.

Preparation of rhodium and ruthenium catalysts

[Cp* $\text{Rh}(\text{H}_2\text{L})(\text{H}_2\text{O})](\text{SO}_4)$ (4**):** An aqueous solution (50 mL) of $[\text{Cp}^*\text{RhCl}_2]_2$ (250 mg, 0.41 mmol) and Ag_2SO_4 (253 mg, 0.82 mmol) was stirred at 40 °C for 12 h. The reaction mixture was filtered to remove insoluble AgCl_2 . A 4,4'-dihydroxy-2,2'-bipyridine (154 mg, 0.82 mmol) was added to the filtrate. The solution was stirred at 40 °C for 12 h. The solution was filtered and the volume of the filtrate was reduced to ~5 mL in vacuo. The solution was placed in a refrigerator to give a yellow solid **4** (420 mg, 95%). ^1H NMR ($\text{D}_2\text{O}/\text{KOD}$): δ 8.28 (d, $J = 6.6$ Hz, 2H), 7.14 (d, $J = 2.5$ Hz, 2H), 6.69 (dd, $J = 6.6, 2.5$ Hz, 2H), 1.56 (s, 15H); ^{13}C NMR ($\text{D}_2\text{O}/\text{KOD}$): δ 178.83, 159.08, 153.26, 121.52, 115.95, 96.02 (d, $J_{\text{RhH}} = 8.4$ Hz), 10.29; ^1H NMR (D_2O): δ 8.76 (d, $J = 6.4$ Hz, 2H), 7.69 (bs, 2H), 7.24 (dd, $J = 6.4, 2.4$ Hz, 2H), 1.68 (s, 15H); ^{13}C NMR (D_2O): δ 170.34, 159.36, 154.92, 118.92, 114.20, 99.62 (d, $J_{\text{RhC}} = 9.2$ Hz), 10.63; IR (KBr): 1621, 1500, 1450, 1111 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_7\text{SRh} + 2\text{H}_2\text{O}$: C, 41.67; H, 5.07; N, 4.86; S, 5.56. Found: C, 41.75; H, 5.16; N, 4.88; S, 5.60; ESIMS: m/z 425 $[\text{M} - \text{SO}_4 - \text{H}_2\text{O} - \text{H}]^-$.

$[(\text{C}_6\text{Me}_6)\text{Ru}(\text{H}_2\text{L})(\text{H}_2\text{O})](\text{SO}_4)$: An aqueous solution (50 mL) of $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ (250 mg, 0.37 mmol) and Ag_2SO_4 (234 mg, 0.75 mmol) was stirred at 40 °C for 12 h. The reaction mixture was filtered to remove insoluble AgCl_2 . A 4,4'-dihydroxy-2,2'-bipyridine (142 mg, 0.75 mmol) was added to the filtrate. The

solution was stirred at 40 °C for 12 h. The solution was filtered and the volume of the filtrate was reduced to ~5 mL in vacuo. The solution was placed in a refrigerator to give a yellow solid **5** (333 mg, 59%). ¹H NMR (D₂O/KOD): δ 8.19 (d, *J* = 6.6 Hz, 2H), 7.06 (d, *J* = 2.7 Hz, 2H), 6.64 (dd, *J* = 6.6, 2.7 Hz, 2H), 1.95 (s, 18H); ¹³C NMR (D₂O/KOD): δ 178.68, 159.19, 155.10, 121.08, 115.74, 95.27, 17.39; ¹H NMR (D₂O): δ 8.74 (d, *J* = 6.5 Hz, 2H), 7.59 (d, *J* = 2.5 Hz, 2H), 7.18 (dd, *J* = 6.5, 2.6 Hz, 2H), 2.10 (s, 18H); ¹³C NMR (D₂O): δ 159.8, 156.77, 145.26, 119.07, 114.52, 97.59, 17.74; IR (KBr): 1619, 1494, 1452, 1109 cm⁻¹; Anal. Calcd for C₂₂H₂₈N₂O₇SRu: C, 46.72; H, 4.99; N, 4.95; S, 5.67. Found: C, 46.95; H, 5.27; N, 4.71; S, 5.54; ESIMS: *m/z* 451 [M – SO₄ – H₂O – H]⁻.

General procedure for deuteration

A solution of complex in D₂O was added to a solution of substrate in D₂O. The reaction solution was stirred at 50 °C under 1 MPa of H₂. The yield was analyzed by GC (PEG-HT 5%, Uniport HT 60/80, 2 m packed column, 100 °C) or HPLC (Tosoh TSKgel SCX(H⁺)). The ratios of deuterium incorporation were analyzed by ¹H NMR spectroscopy.

Characterization data

1-Deuteriocyclopentanol: ¹H NMR (D₂O): δ 4.26-4.33 (m, 0.08H), 1.85-1.45 (m, 8.00H); ¹³C NMR (D₂O): δ 76.77, 76.39 (t), 36.96, 25.71.

1-Deuteriocyclohexanol: ¹H NMR (D₂O): δ 3.66-3.57 (m, 0.26H), 1.91-1.80 (m, 1.84H), 1.75-1.62 (m, 1.94H), 1.56-1.48 (m, 1.00H), 1.32-1.04 (m, 4.58H); ¹³C NMR (D₂O): δ 69.49, 69.02 (t), 33.32, 24.10, 22.97.

1-Deuteriocycloheptanol: ¹H NMR (CDCl₃): δ 3.89-3.80 (m, 0.14H), 1.98-1.32 (m, 12.00H); ¹³C NMR (CDCl₃): δ 72.82, 72.33 (t), 37.50, 28.14, 22.64.

2-Deuterio-2-propanol: ¹H NMR (D₂O): δ 4.01 (m, 0.09H), 1.15 (bs, 6.00H); ¹³C NMR (D₂O): δ 67.14, 66.75 (t), 26.46.

2-Deuterio-3-methyl-2-butanol: ¹H NMR (D₂O): δ 3.59 (m, 0.14H), 1.62 (m, 0.89H), 1.11 (bs, 3.00H), 0.87 and 0.86 (two d, 6.03H); ¹³C NMR (D₂O): δ 75.77, 75.30 (t), 36.84, 21.17, 20.18, 20.15.

1-Deuterio-1-phenylethanol: ¹H NMR (CDCl₃): δ 7.40-7.23 (bs, 4.80H included CDCl₃), 4.87 (m, 0.27H), 1.49 (bs, 3.00H); ¹³C NMR (CDCl₃): δ 145.75, 128.50, 127.48, 125.39, 70.41, 69.99 (t), 25.00.

1-Deuterio-1-(4-chlorophenyl)ethanol: ¹H NMR (CDCl₃): δ 7.32-7.28 (bs, 3.81H),

4.87 (m, 0.19H), 1.46 (bs, 3.00H); ^{13}C NMR (CDCl_3): δ 144.26, 133.06, 128.59, 126.81, 69.70, 69.29 (t), 25.10.

1-Deuterio-1-(2-chlorophenyl)ethanol: ^1H NMR (CDCl_3): δ 7.60 (dt, $J = 1.6, 7.6$ Hz, 0.98H), 7.34-7.26 (bs, 2.01H), 7.20 (dt, $J = 1.6, 7.5$ Hz, 0.91H), 5.30 (m, 0.13H), 1.49 (bs, 3.00H); ^{13}C NMR (CDCl_3): δ 143.02, 131.63, 129.38, 128.39, 127.20, 126.44, 66.94, 66.57 (t), 23.38.

1. P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, 1960, **64**, 188-190.
2. K. Mikkelsen and S. O. Nielsen, *J. Phys. Chem.*, 1960, **64**, 632-637.
3. Y. Himeda, N. Onozawa-Komatsuzaki, S. Miyazawa, H. Sugihara, T. Hirose and K. Kasuga, *Chem.-Eur. J.*, 2008, **14**, 11076-11081.

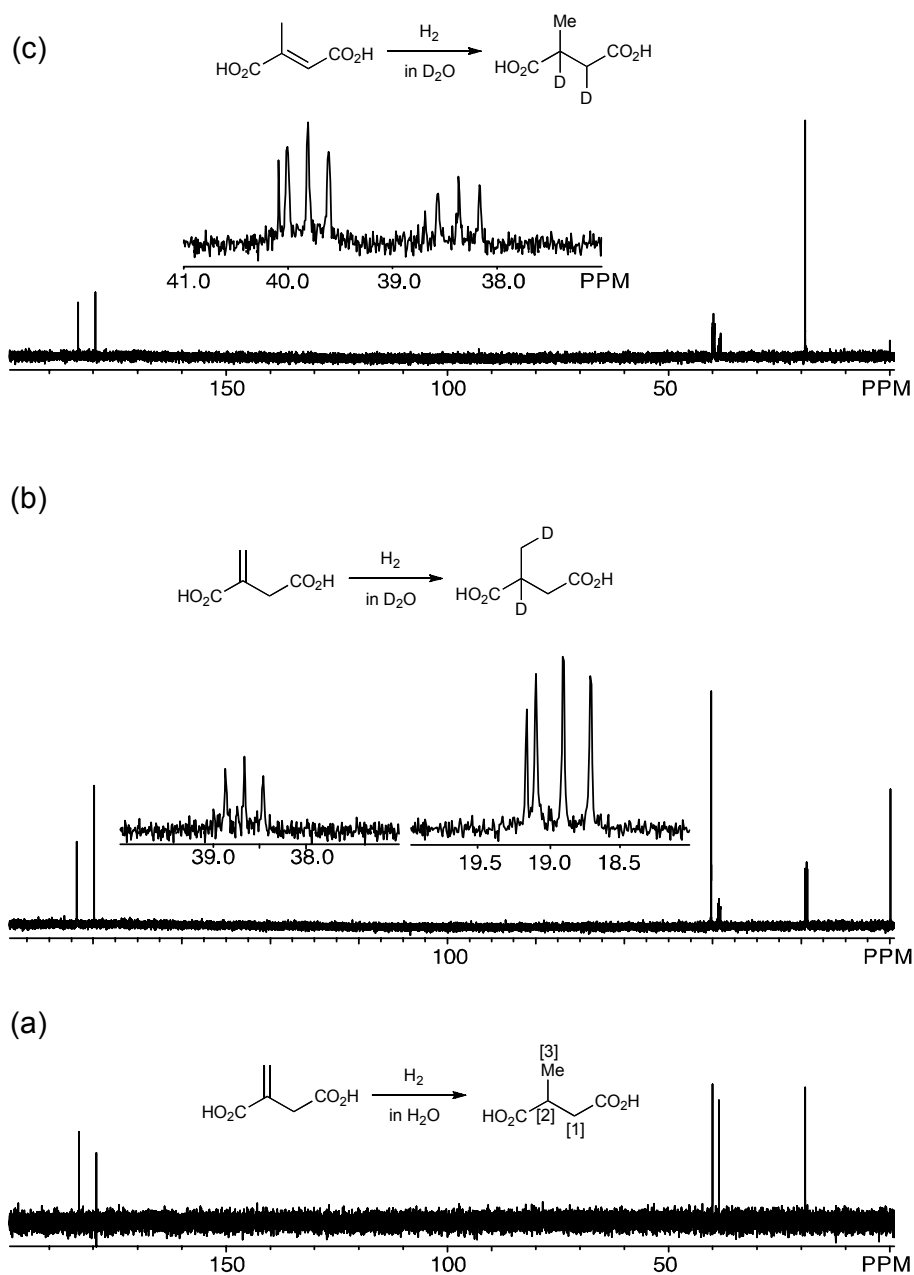


Figure S1. Proton decoupled ^{13}C NMR of methylsuccinic acid from (a) itaconic acid in H_2O , (b) itaconic acid in D_2O , and (c) citraconic acid in D_2O catalyzed by iridium catalyst **1**.

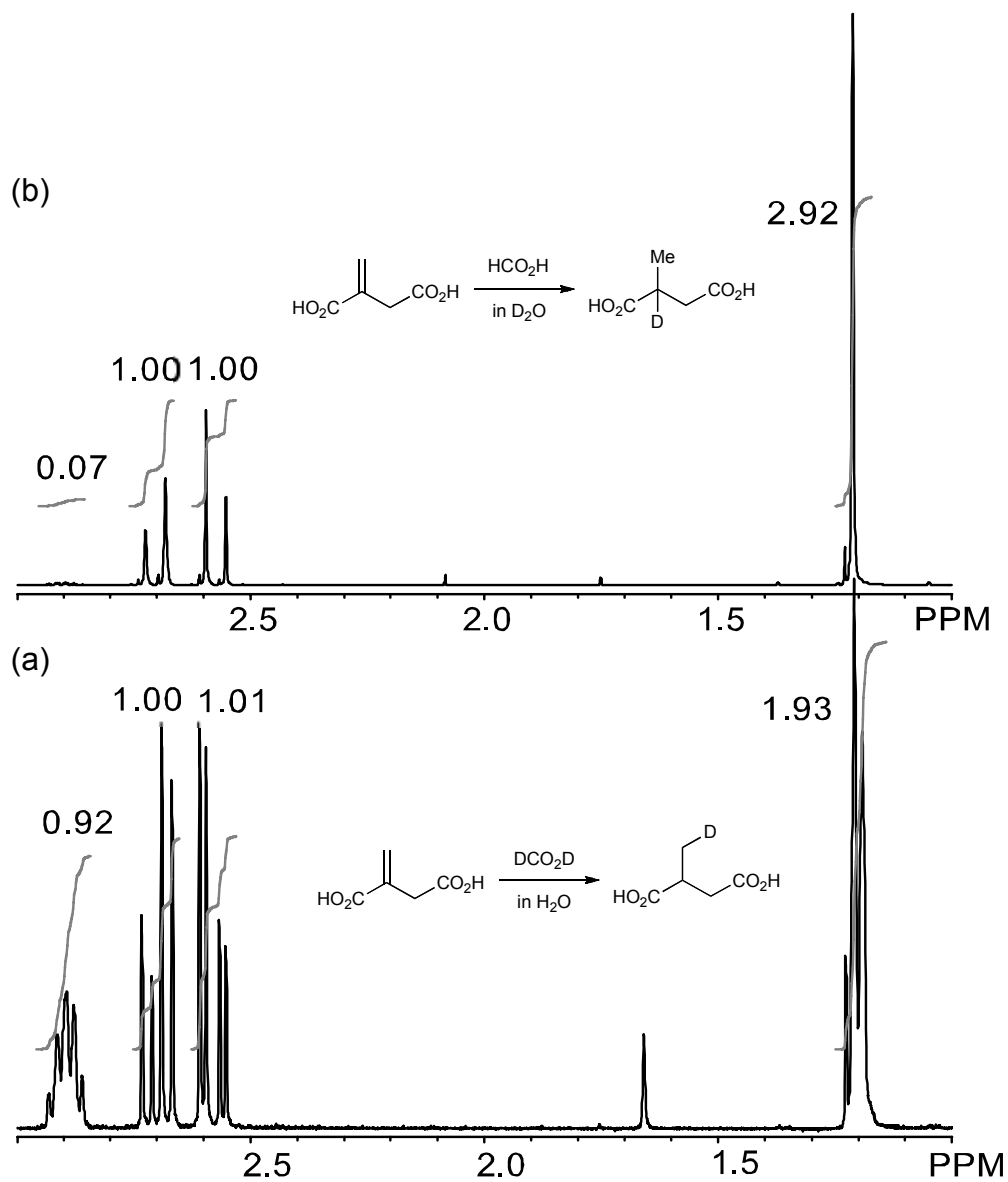
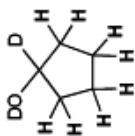
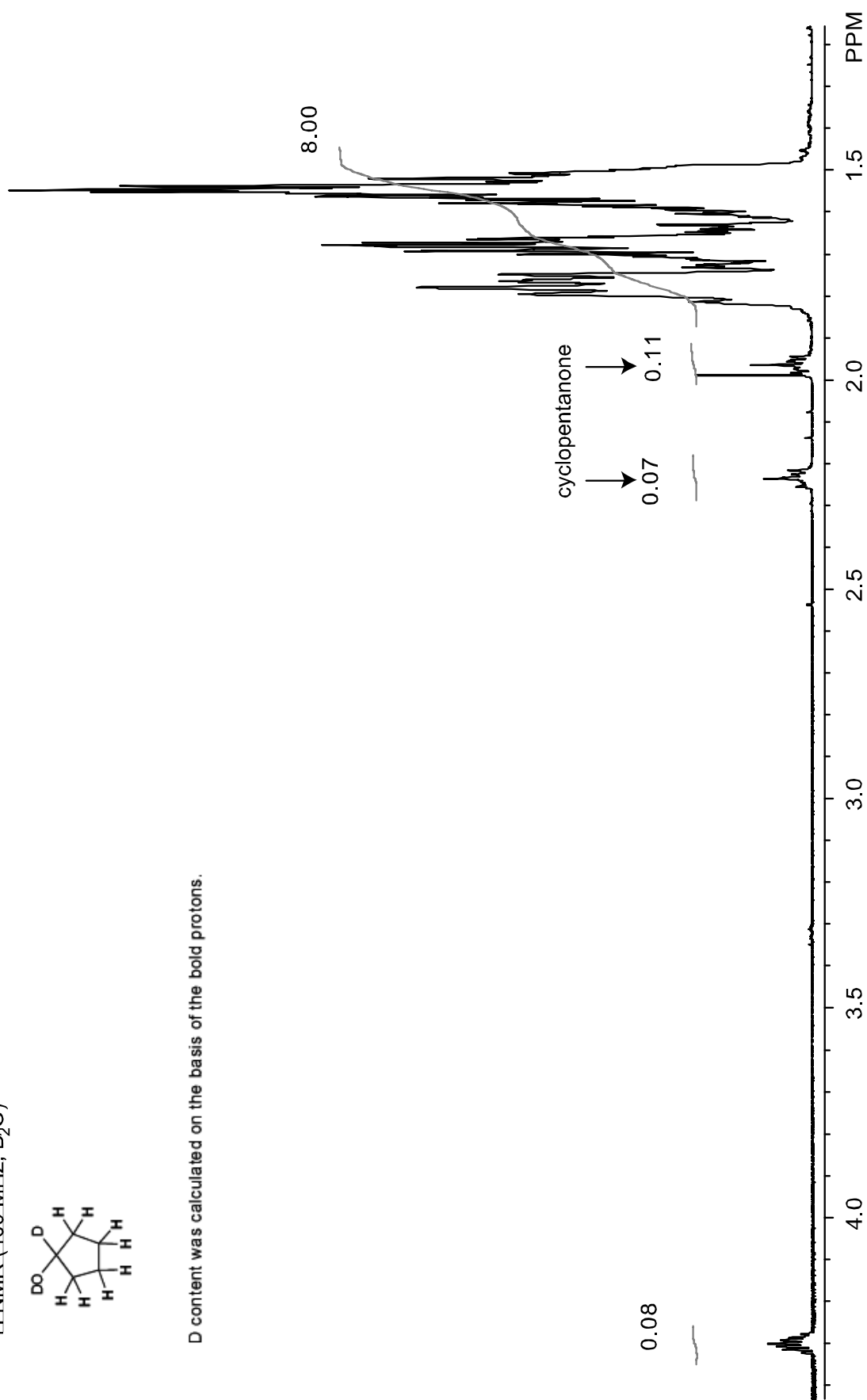


Figure S2. ^1H NMR of methylsuccinic acid from reaction with itaconic acid catalyzed by rhodium catalyst **4** using (a) HCO_2H in D_2O , (b) DCO_2H in H_2O .

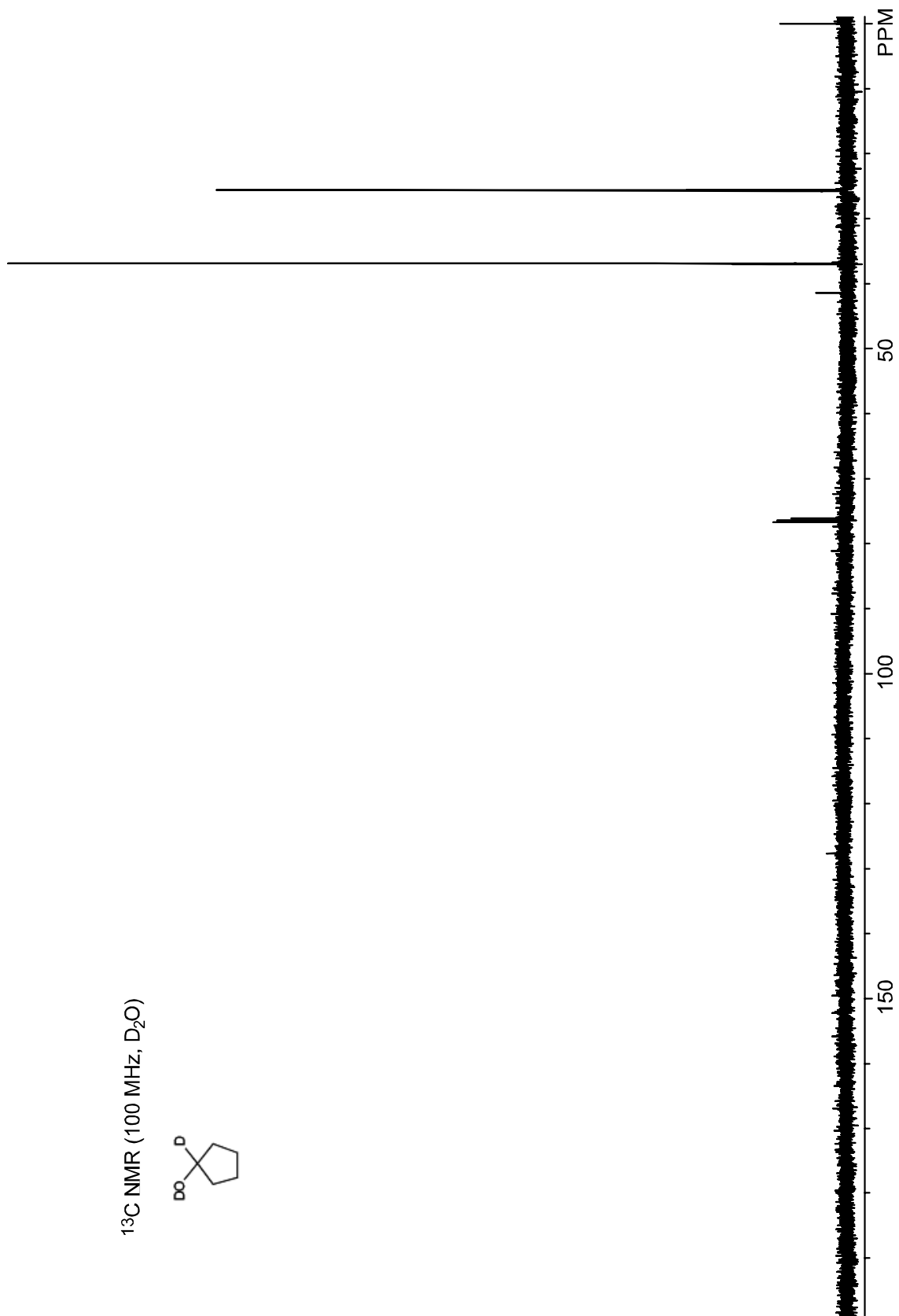
^1H NMR (400 MHz, D_2O)



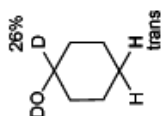
D content was calculated on the basis of the bold protons.



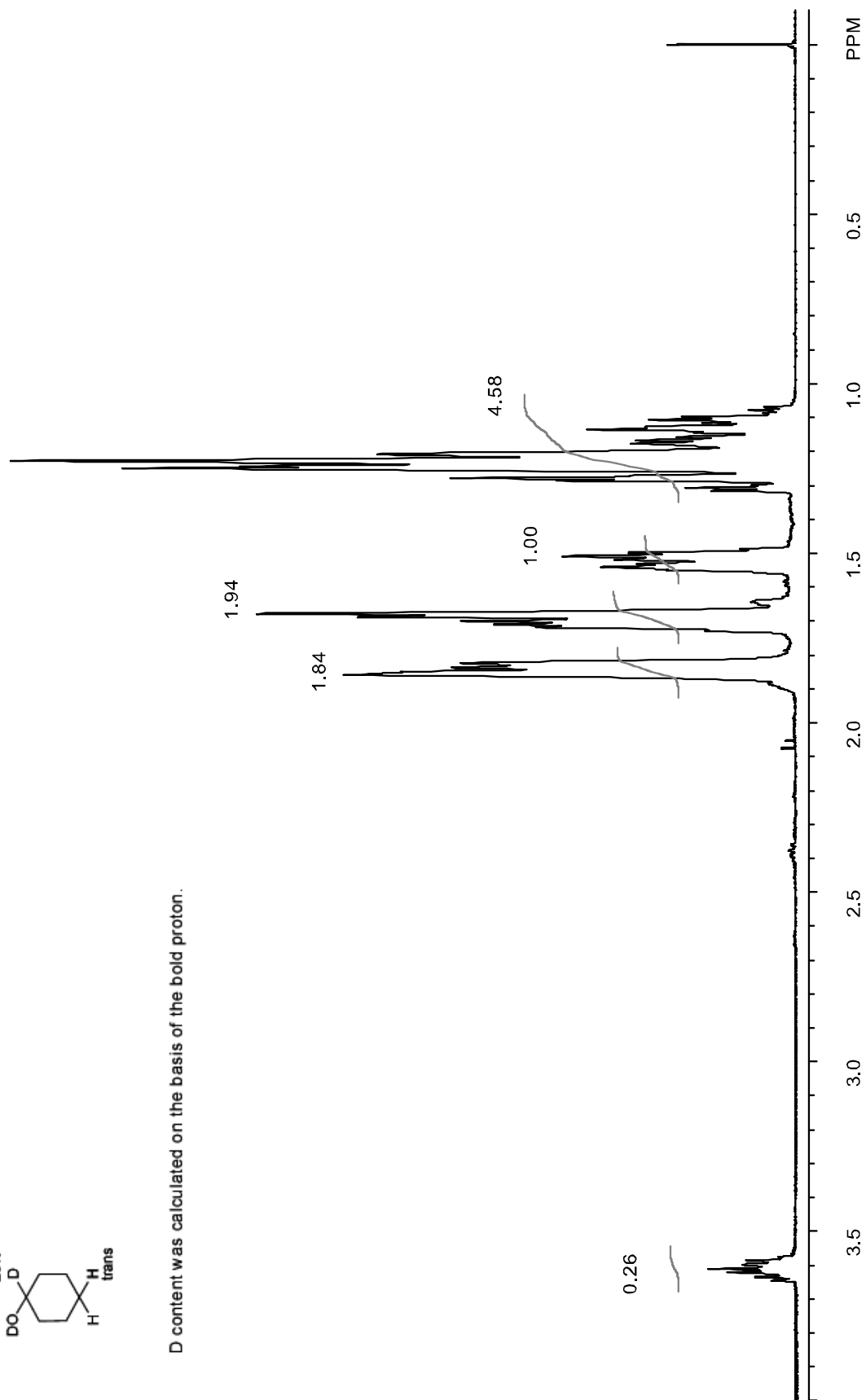
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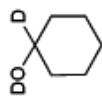
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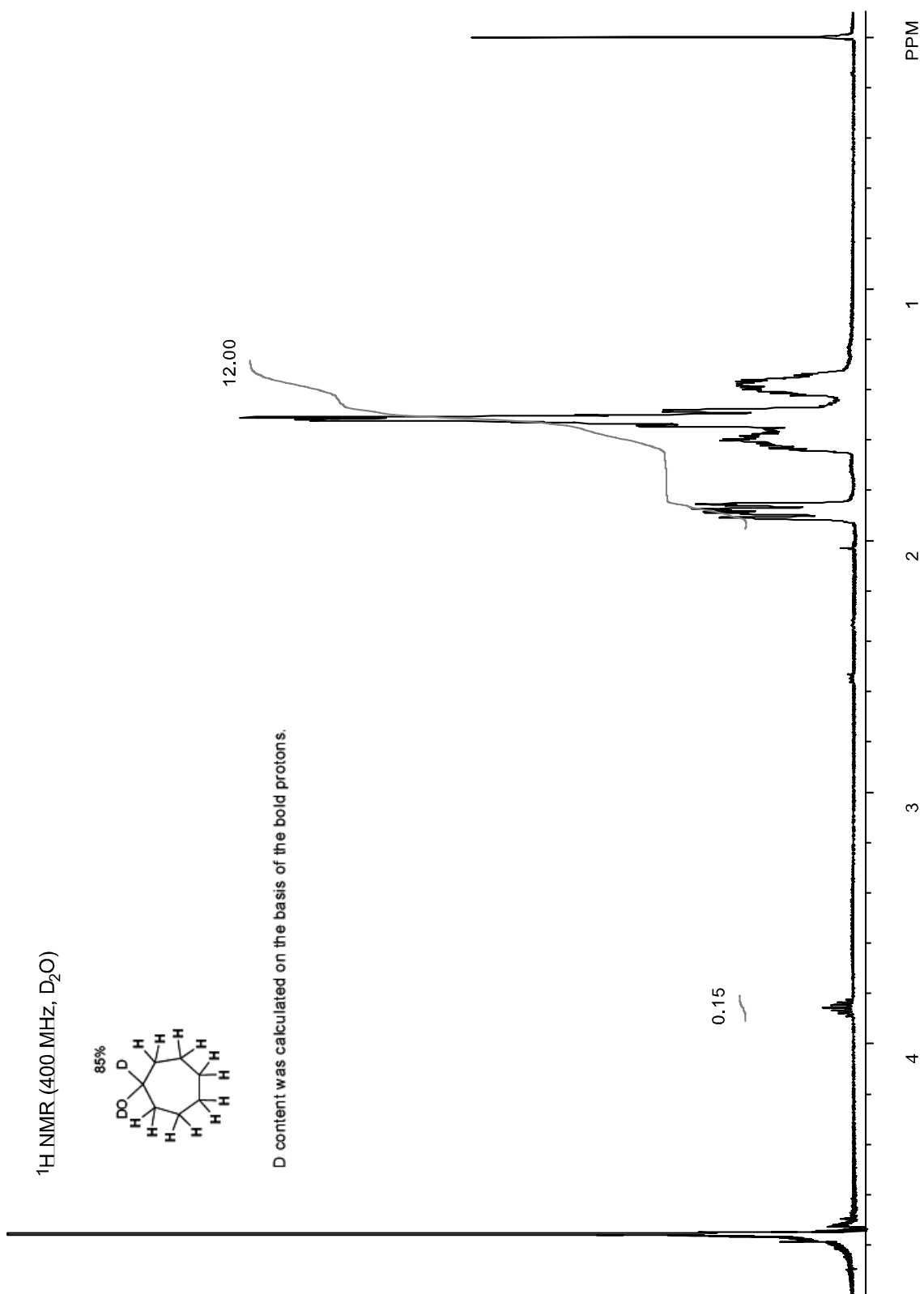


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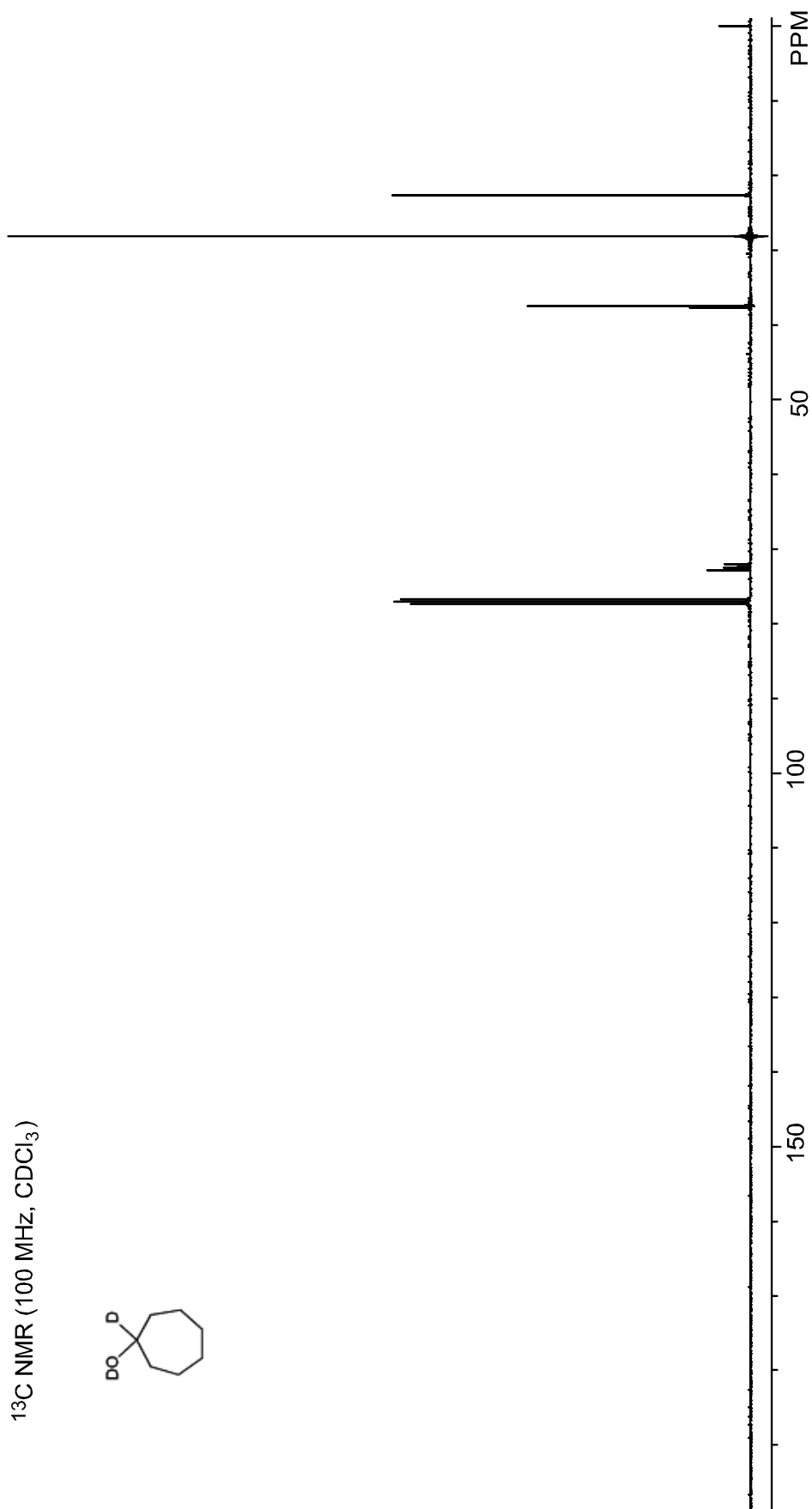
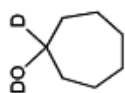


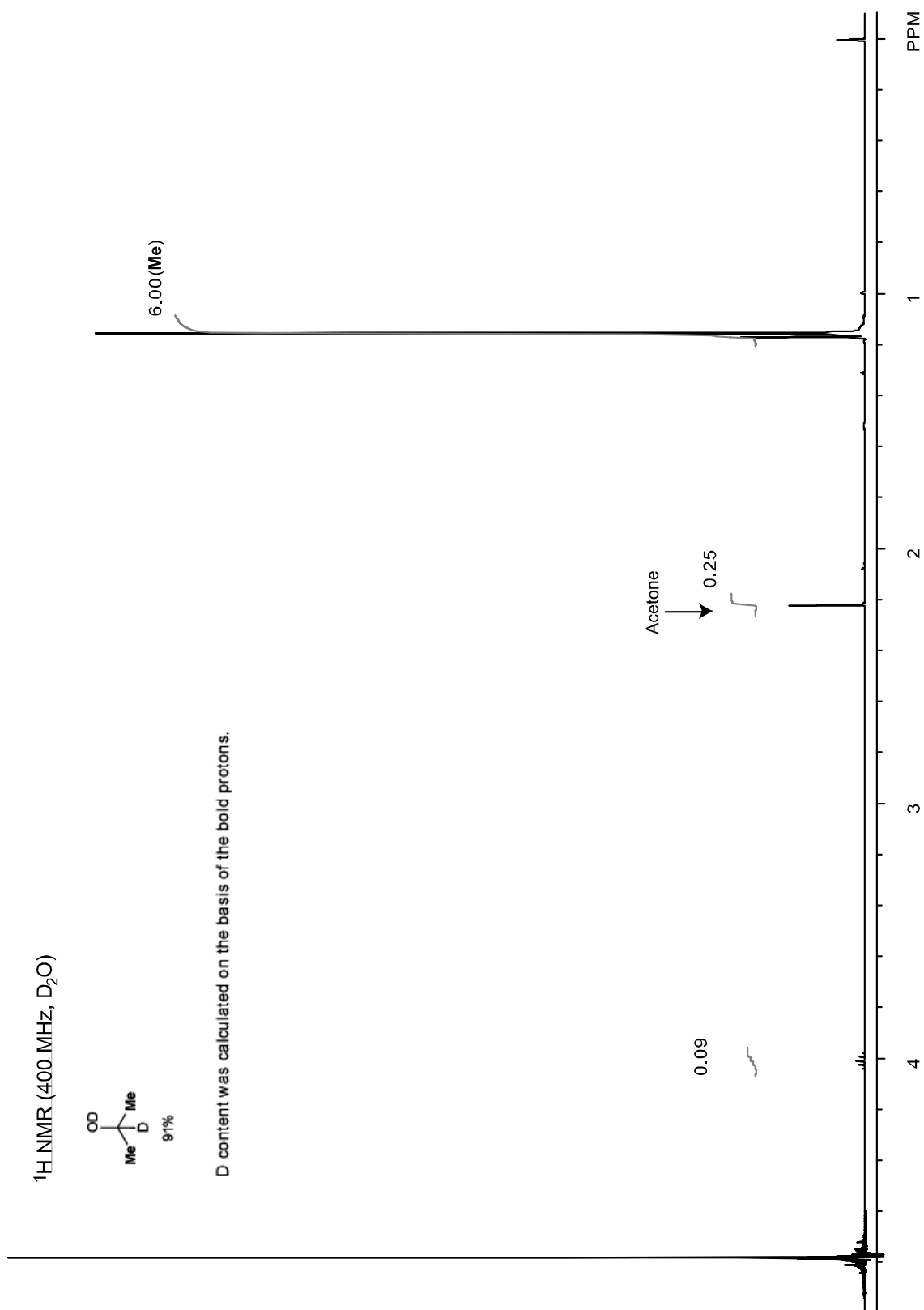
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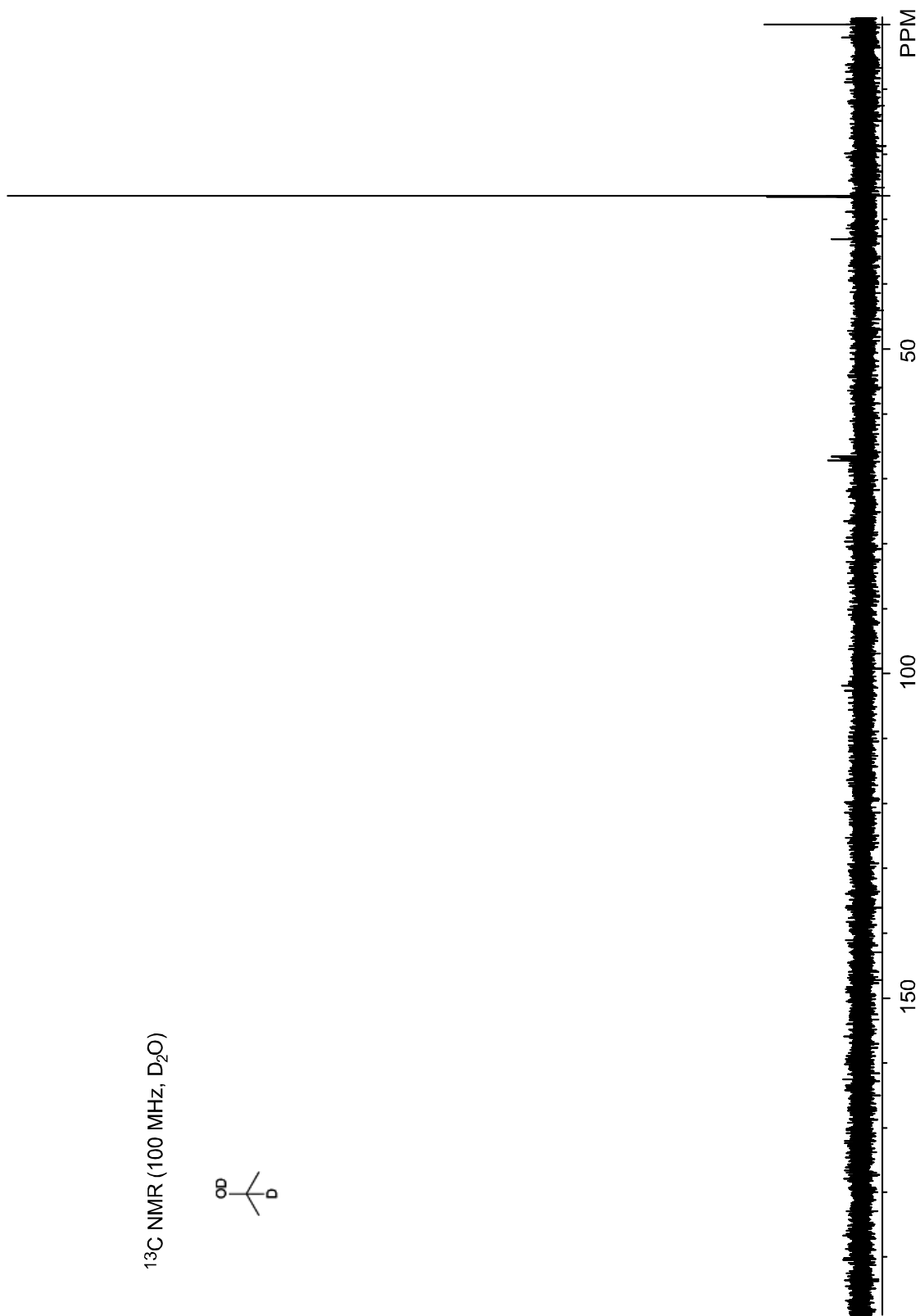


^{13}C NMR (100 MHz, CDCl_3)

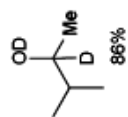




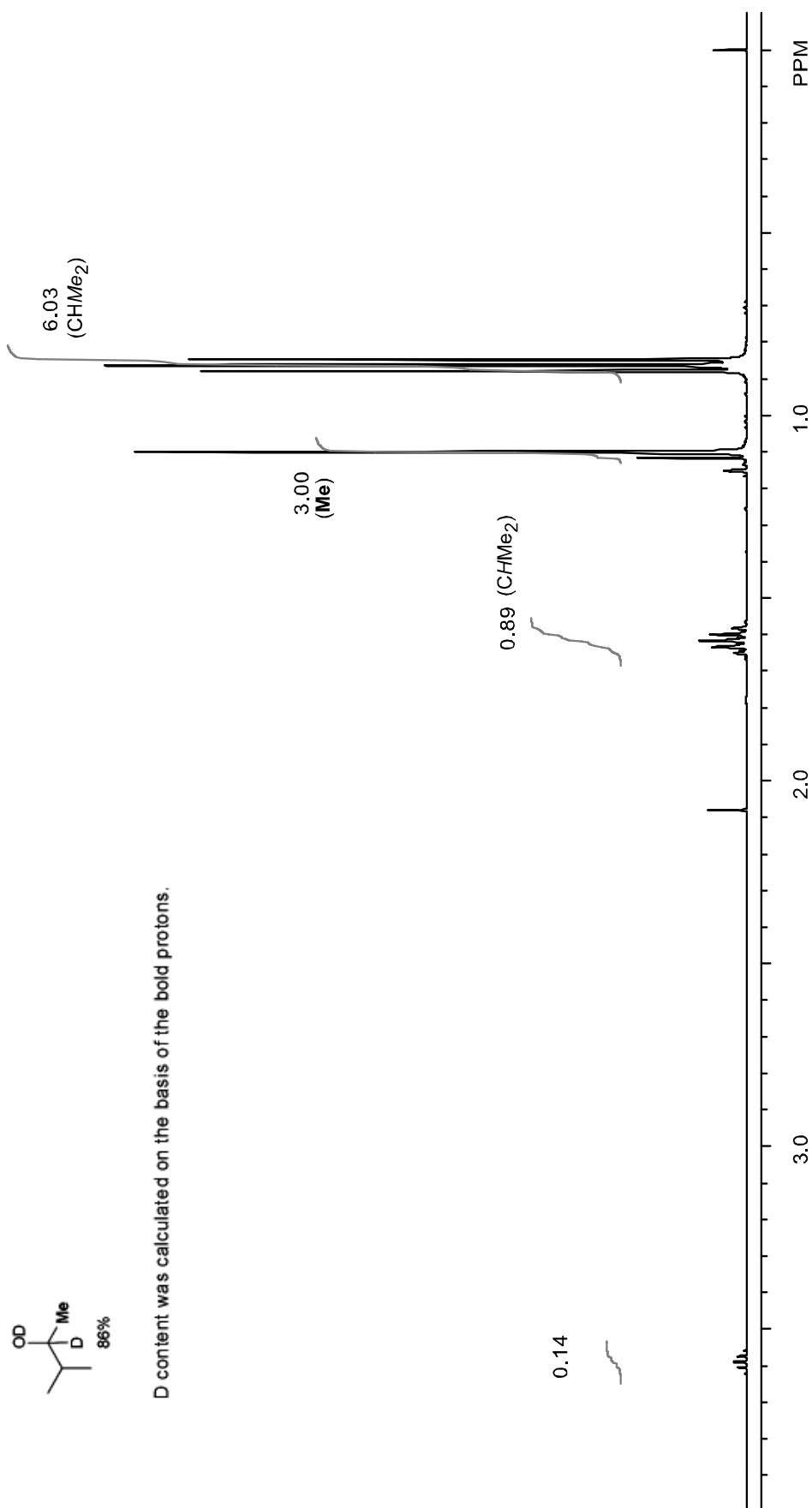
^{13}C NMR (100 MHz, D_2O)



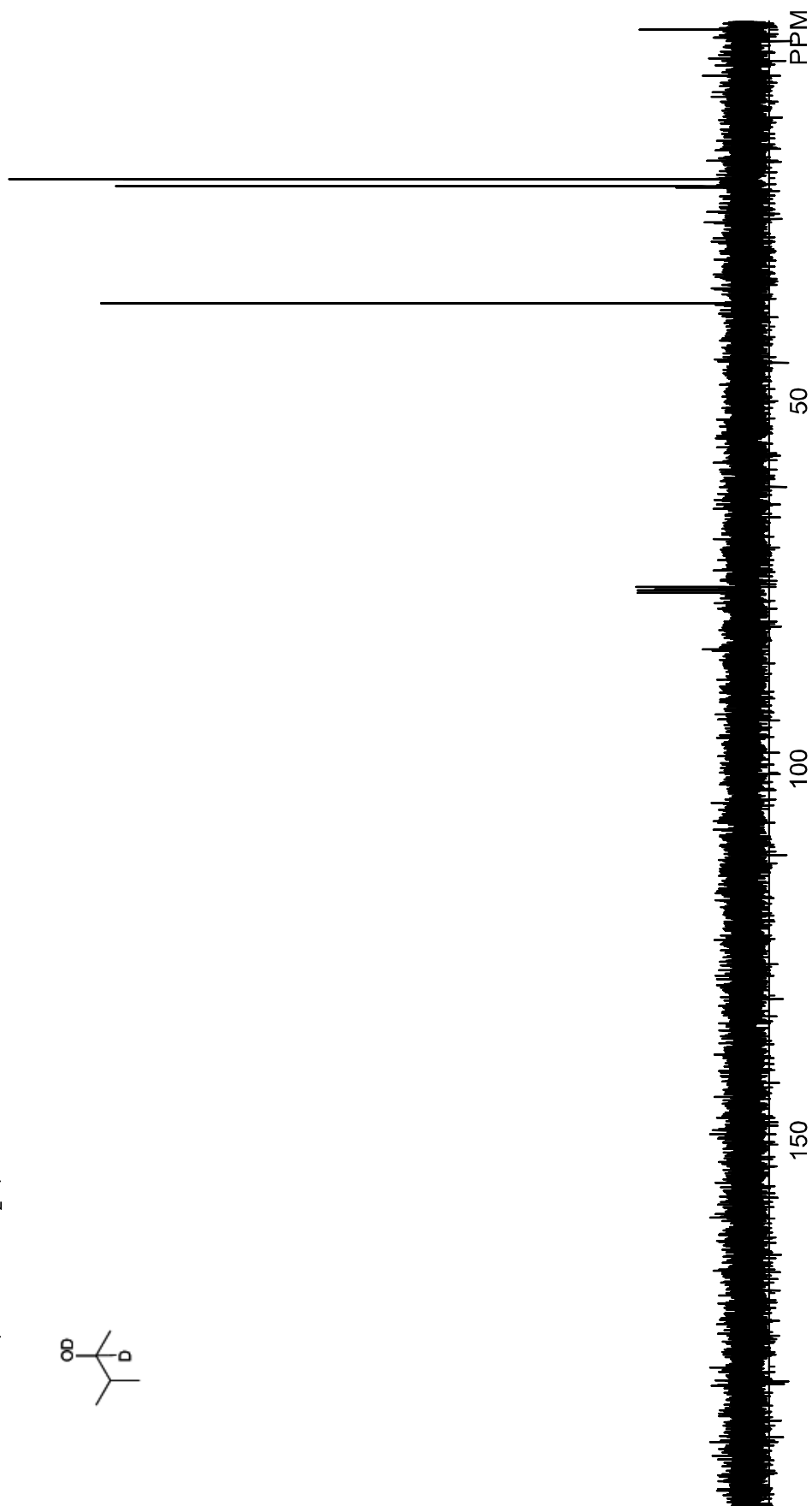
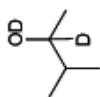
^1H NMR (400 MHz, D_2O)



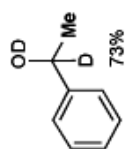
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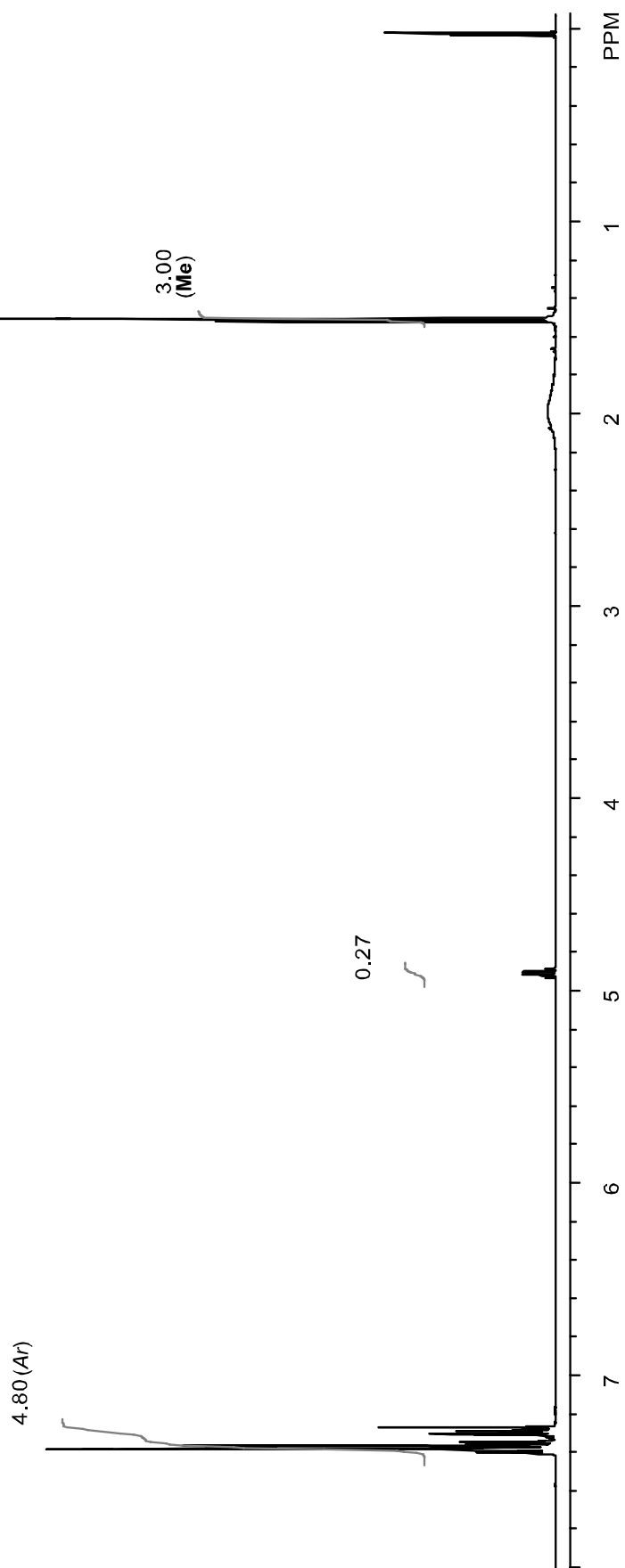
^{13}C NMR (100 MHz, D_2O)

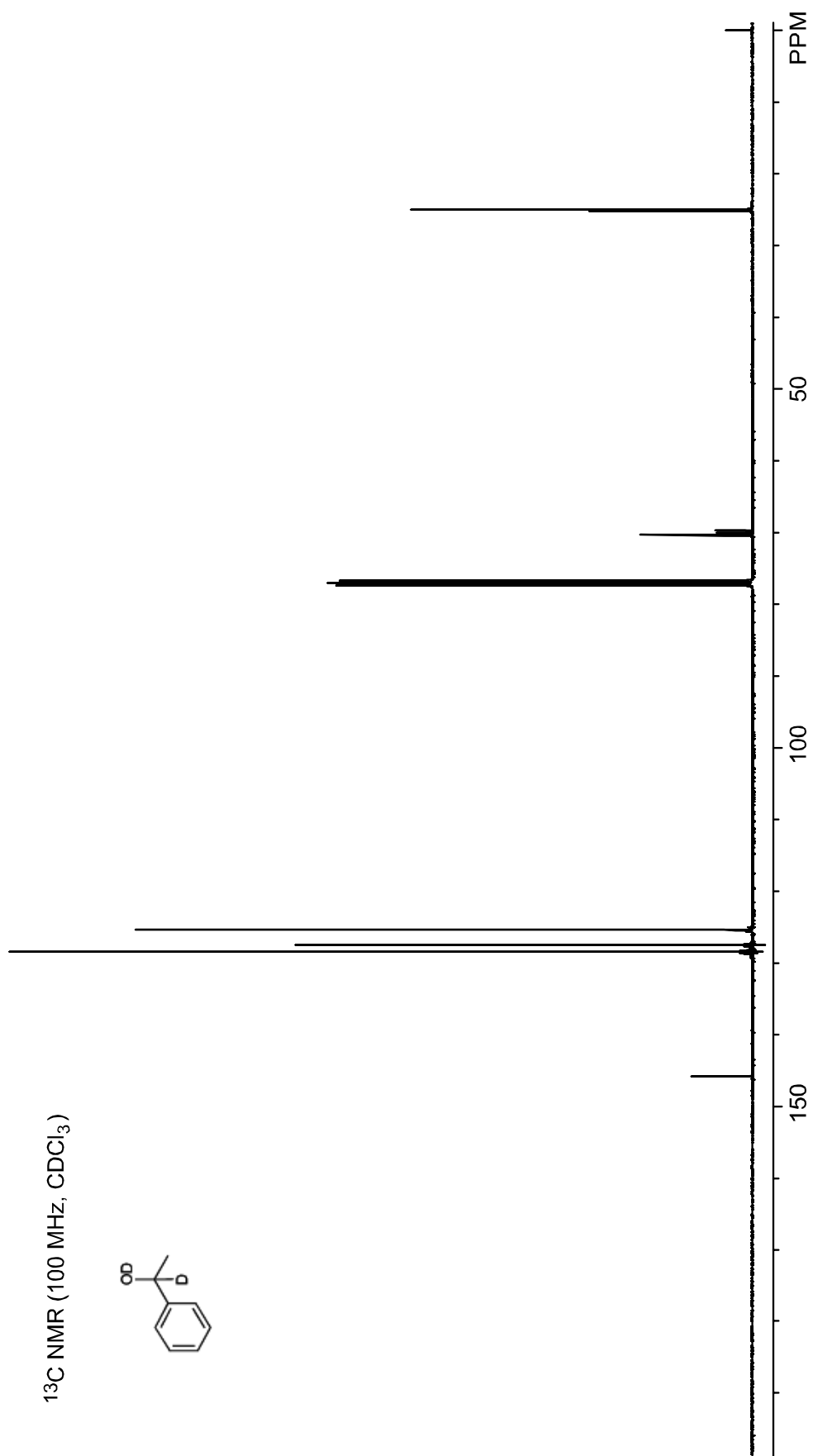


^1H NMR (400 MHz, CDCl_3)

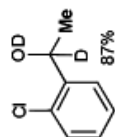


D content was calculated on the basis of the bold protons.

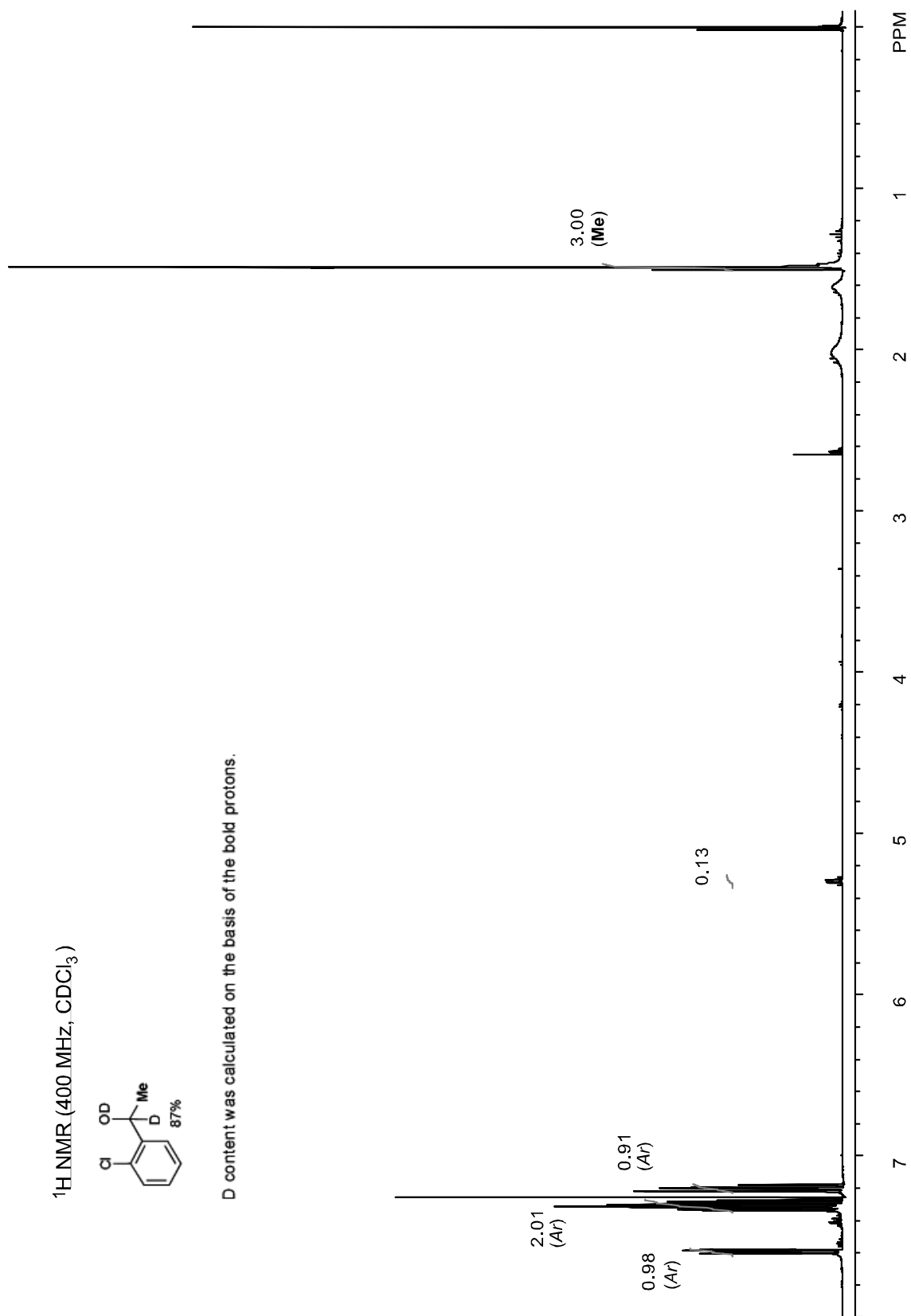




$^1\text{H NMR}$ (400 MHz, CDCl_3)



D content was calculated on the basis of the bold protons.



^{13}C NMR (100 MHz, CDCl_3)

