Supporting Information

Multiple Deuteration of Alkanes Synergistically-Catalyzed by Platinum and Rhodium on Carbon as a Mixed Catalytic System

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1. General

10% Pt/C catalyst was obtained from N.E. Chemcat Corporation, Japan. 5% Rh/C catalyst was purchased from the Aldrich Chemical Co. D_2O (>99.9% D atom) was purchased from Spectra Gases, Inc. *i*-PrOD-d_8 (>99.5% D atom) was purchased from the Aldrich Chemical Co. All other reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{2}H NMR spectra were recorded by a JEOL AL-400, EX-400 (^{1}H: 400 MHz) or ECA-500 spectrometer (^{1}H: 500 MHz, ^{2}H: 61 MHz). Chemical shifts (δ) are expressed in ppm and are internally referenced (7.26 ppm for $CDCl_3$ for ^{1}H and ^{2}H NMR or 7.16 ppm for benzene-d_6 for ^{1}H and ^{2}H NMR). All H-D exchange reactions were carried out using a 6 mL stainless-steel sealed tube. The deuterium contents were determined by the ^{1}H NMR using 1,4-dioxane as the internal standard as a value of integral. The deuterium incorporation was also assigned by the ^{2}H NMR.

2. Procedures for Pt/C and Rh/C-catalyzed multi-deuteration of alkanes

2-1. Typical procedure for Pt/C and Rh/C-catalyzed multi-deuteration of alkanes (Table 1 and Table 2, entries 1-2, 4-7 and 9)

A suspension of an alkane (0.25mmol), 10% Pt/C (15 mol%) and 5% Rh/C (15 mol%) in *i*-PrOD-d_8 (0.5 mL) and D_2O (2 mL) in a 6 mL stainless-steel sealed tube was stirred at 120 °C under atmospheric conditions. After stirring for 24 h, the mixture was cooled to room temperature and filtered by a membrane filter (Milipore, Millex®-LH, 0.2 μm) to remove the catalysts. The filtrate was extracted with Et_2O (20 mL) and H_2O (20 mL), and then the aqueous layer was further extracted with Et_2O (10 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtrated and concentrated in vacuo to give the deuterated product.

2-2. Procedure for Pt/C and Rh/C-catalyzed multi-deuteration of alkane (Table 2. entry 3)

A suspension of an alkane (0.125 mmol), 10% Pt/C (30 mol%) and 5% Rh/C (30 mol%) in *i*-PrOD-d_8 (0.5 mL) and D_2O (2 mL) in a 6 mL stainless-steel sealed tube was stirred at 120 °C under atmospheric conditions. After stirring for 24 h, the mixture was cooled to room temperature and filtered by a membrane filter (Milipore, Millex®-LH, 0.2 μm) to remove the catalysts. The filtrate was extracted with hexane (20 mL) and H_2O (20 mL), and then the aqueous layer was further extracted with hexane (10 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtrated and concentrated in vacuo to give the deuterated product.

2-3. Procedure for Pt/C and Rh/C-catalyzed multi-deuteration of alkane (Table 2. entry 8)

A suspension of an alkane (0.125 mmol), 10% Pt/C (30 mol%) and 5% Rh/C (30 mol%) in *i*-PrOD-d_8 (0.5 mL), D_2O (2 mL) and cyclohexane (0.1 mL) in a 6 mL stainless-steel sealed tube was stirred at 120 °C under atmospheric conditions. After stirring for 24 h, the mixture was cooled to room temperature and filtered by a membrane filter (Milipore, Millex®-LH, 0.2 μm) to remove the catalysts. The filtrate was extracted with hexane (20 mL : Table 2, entries 3 and 9) and H_2O (20 mL), and then the aqueous layer was further extracted with hexane (10 mL x 3). The combined organic layers were dried over anhydrous $MgSO_4$, filtrated and concentrated in vacuo to give the deuterated product.

3. Spectroscopic data of multi-deuterated alkanes

***n*-Dodecane-d_{26} (Table 1, entry 5)** : 100% (49.1 mg, 250 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24–1.18 (m, 1.26H), 0.80 (m, 0.27H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.20 (brs), 0.83 (brs).

***n*-Pentadecane-d_{32} (Table 2, entry 1)** : 92% (56.9 mg, 230 μmol) as a colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24–1.17 (m, 1.52H), 0.81 (m, 0.15H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.20 (brs), 0.83 (brs).

***n*-Eicosane-d_{42} (Table 2, entry 2)** : 95% (77.4 mg, 238 μmol) as a colorless oil, ^{1}H NMR (500 MHz, Benzene-d_6): δ 1.28–1.50 (m, 1.17H), 0.86 (m, 0.32H); ^{2}H NMR (61 MHz, Benzene): δ 1.20 (brs), 0.82 (brs).

***n*-Hexatriacontane-d_{74} (Table 2, entry 3)** : 69% (49.3 mg, 86 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19–1.25 (m, 6.66H), 0.86 (m, 1.35H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.20 (brs), 0.83 (brs).

***n*-Hexatriacontane-d_{74} (Table 2, entry 3[c])** : 69% (62.6 mg, 86 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19–1.25 (m, 8.26H), 0.82–0.89 (m, 0.68H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.19 (brs), 0.82 (brs).

2,2,4,4,6,8,8,-Heptamethylnonane-d_{34} (Table 2, entry 4) : 100% (62.2 mg, 250 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59 (m, 0.47H), 1.03–1.27 (m, 4.97H), 0.85–0.97 (m, 10.21H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.57 (brs), 1.22 (brs), 0.87–0.94 (brd).

2,2,4,4,6,8,8,-Heptamethylnonane-d_{34} (Table 2, entry 4[c]) : 100% (60.1 mg, 250 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.59 (m, 0.56H), 1.04–1.24 (m, 5.08H), 0.85–0.97 (m, 7.03H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.54 (brs), 1.18–1.20 (brs), 0.84–0.91 (brd).

Bicyclohexyl-d_{22} (Table 2, entry 5) : 86% (39.7 mg, 215 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.62–1.64 (m, 2.14H), 0.88–1.24 (m, 3.00H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.65 (m), 0.90–1.13 (m).

***trans*-Decaline-d_{18} (Table 2, entry 6)** : 85% (32.1 mg, 213 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (m, 0.12H), 1.41 (m, 0.18H), 1.23 (m, 0.44H),

0.86 (m, 0.32H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.61 (brs), 1.49 (brs), 1.17 (brs), 0.87 (brs).

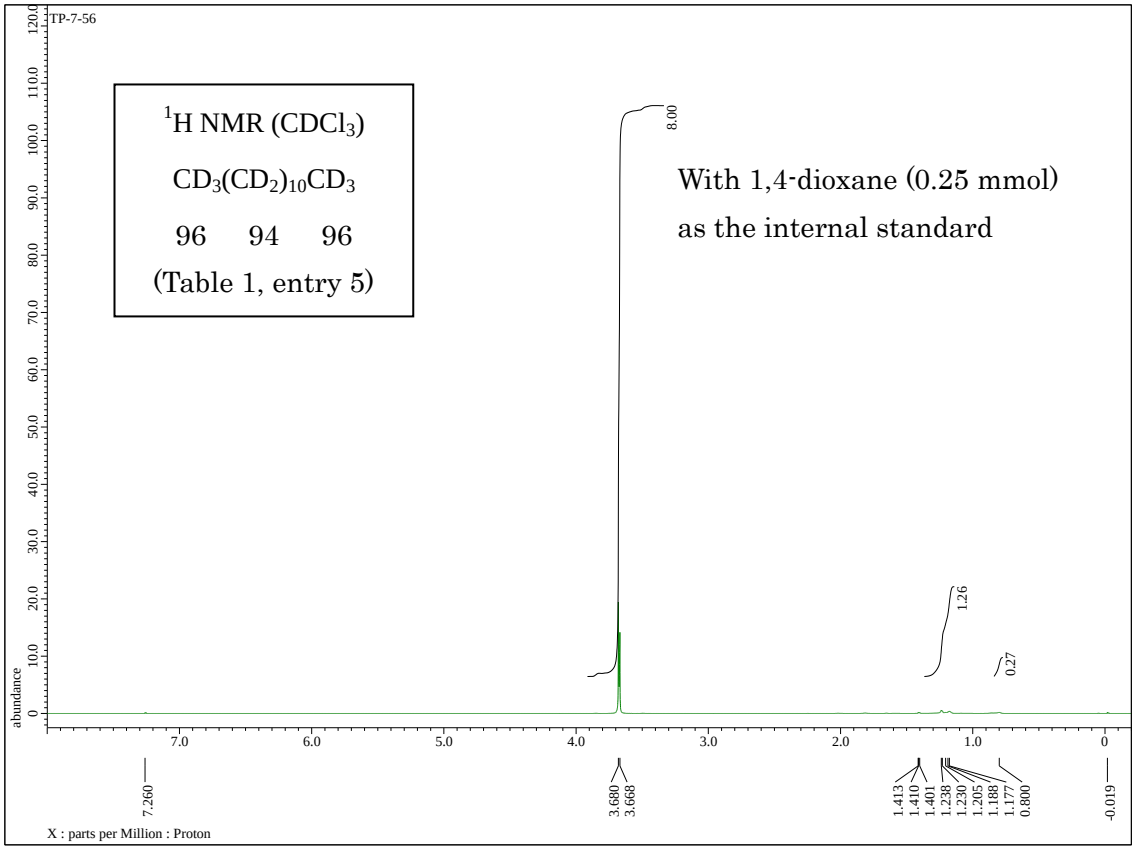
Adamantane-d_{16} (Table 2, entry 7) : 99% (34.6 mg, 248 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.85 (m, 2.60H), 1.75 (brd, 7.20H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.81 (brs), 1.69 (brs).

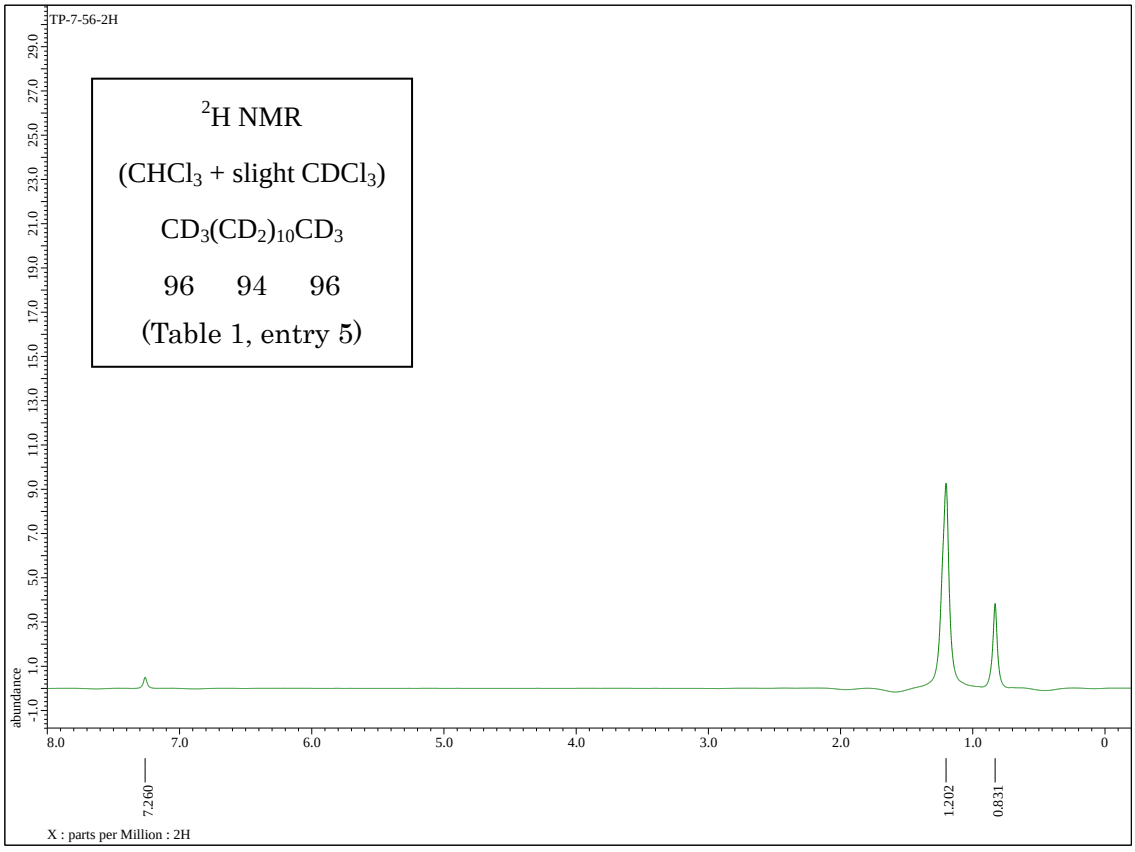
α-Cholestane-d_{48} (Table 2, entry 8[c]) : 82% (38.1 mg, 112.5 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.63–1.95 (m, 33.84H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 0.92–1.16 (m).

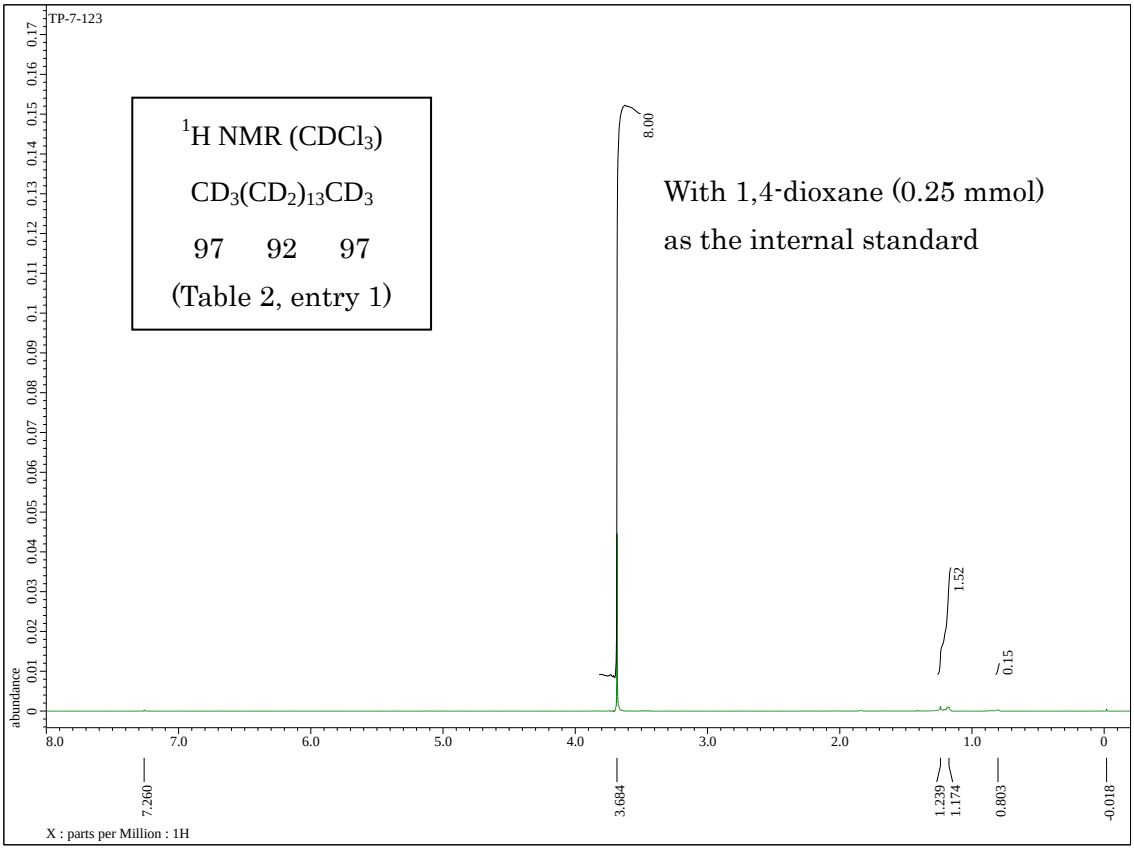
α-Cholestane-d_{48} (Table 2, entry 8[d]) : 90% (44.7 mg, 112.5 μmol) as a colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.63–1.93 (m, 26.67H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 0.82–1.78 (m).

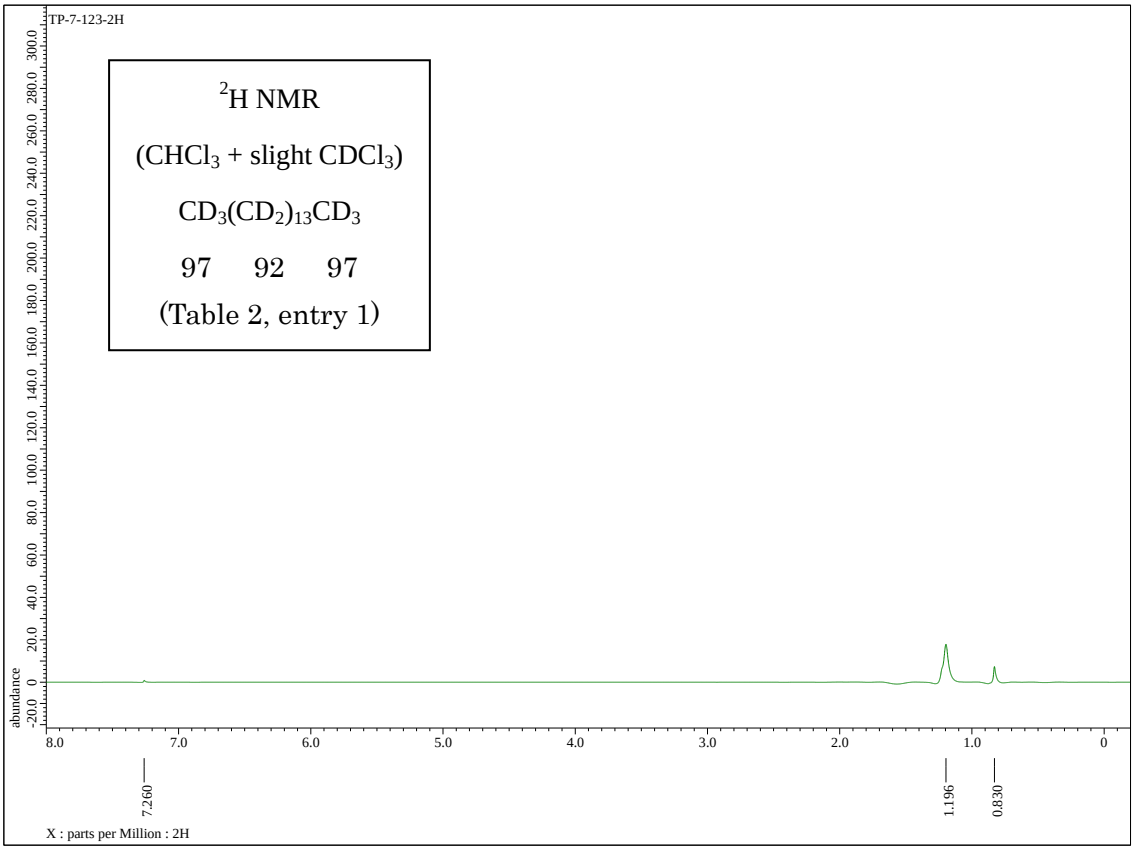
Cyclopentadecane-d_{30} (Table 2, entry 9) : 99% (59.7 mg, 248 μmol) as a colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 0.91H); ^{2}H NMR (61 MHz, $CHCl_3$): δ 1.27 (brs).

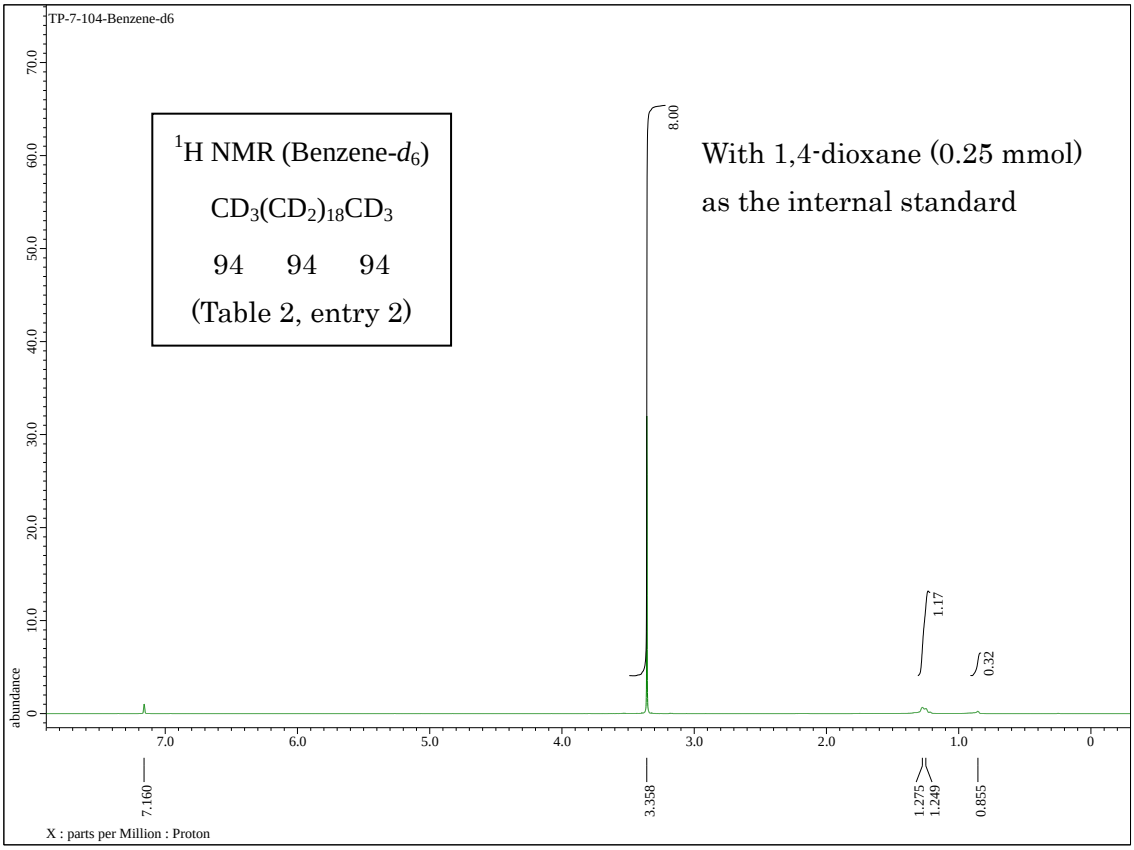
4. ^{1}H and ^{2}H NMR spectra of multi-deuterated alkanes

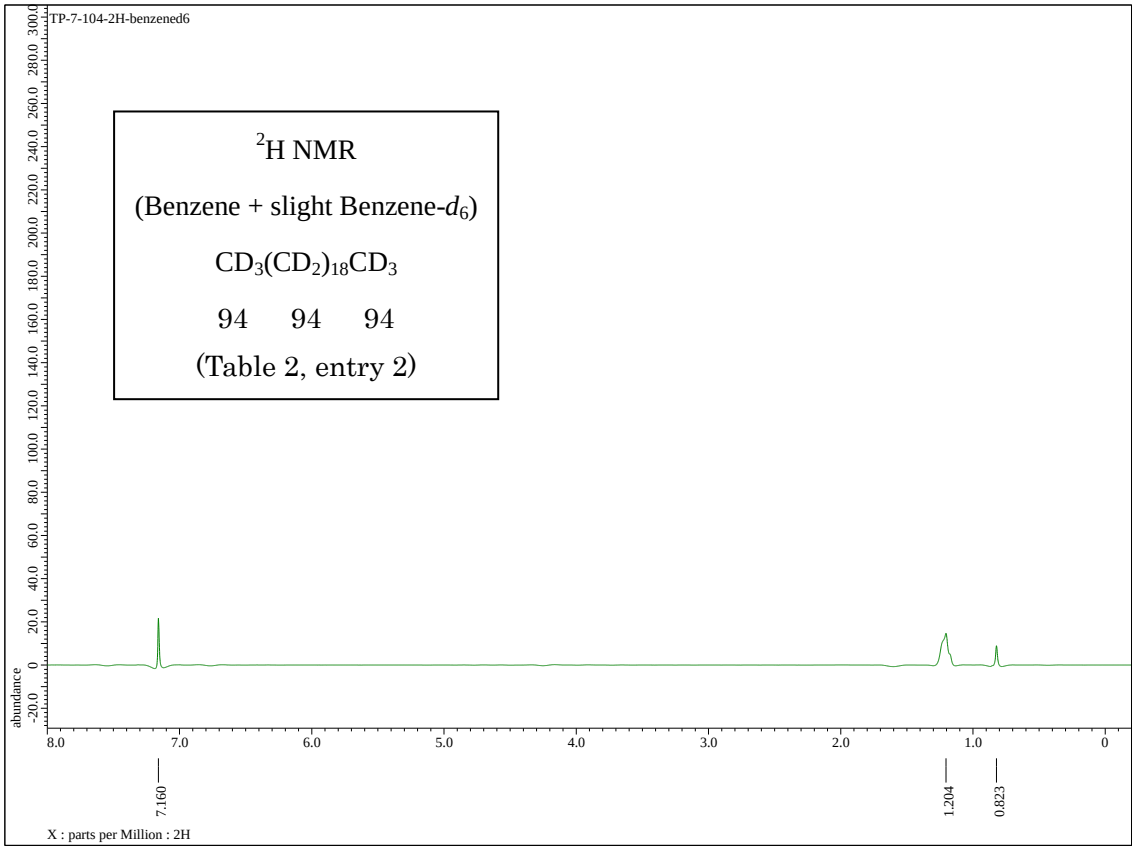

TP-7-56
^{1}H NMR ($CDCl_3$)
$CD_3(CD_2)_{10}CD_3$
96 94 96
(Table 1, entry 5)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
1.26
0.27
abundance
7.260
3.680
3.668
1.413
1.410
1.401
1.238
1.230
1.205
1.188
1.177
0.800
-0.019
X : parts per Million : Proton

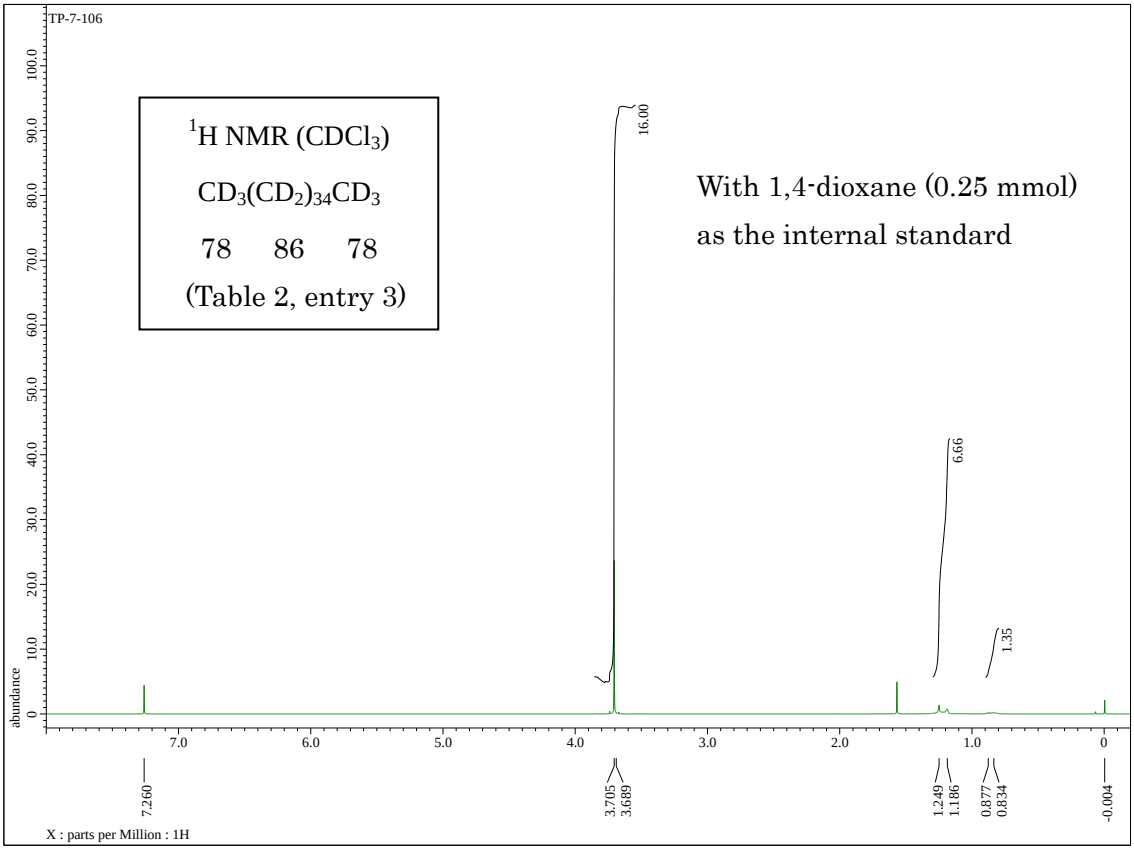

TP-7-56-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
$CD_3(CD_2)_{10}CD_3$
96 94 96
(Table 1, entry 5)
abundance
7.260
1.202
0.831
X : parts per Million : 2H

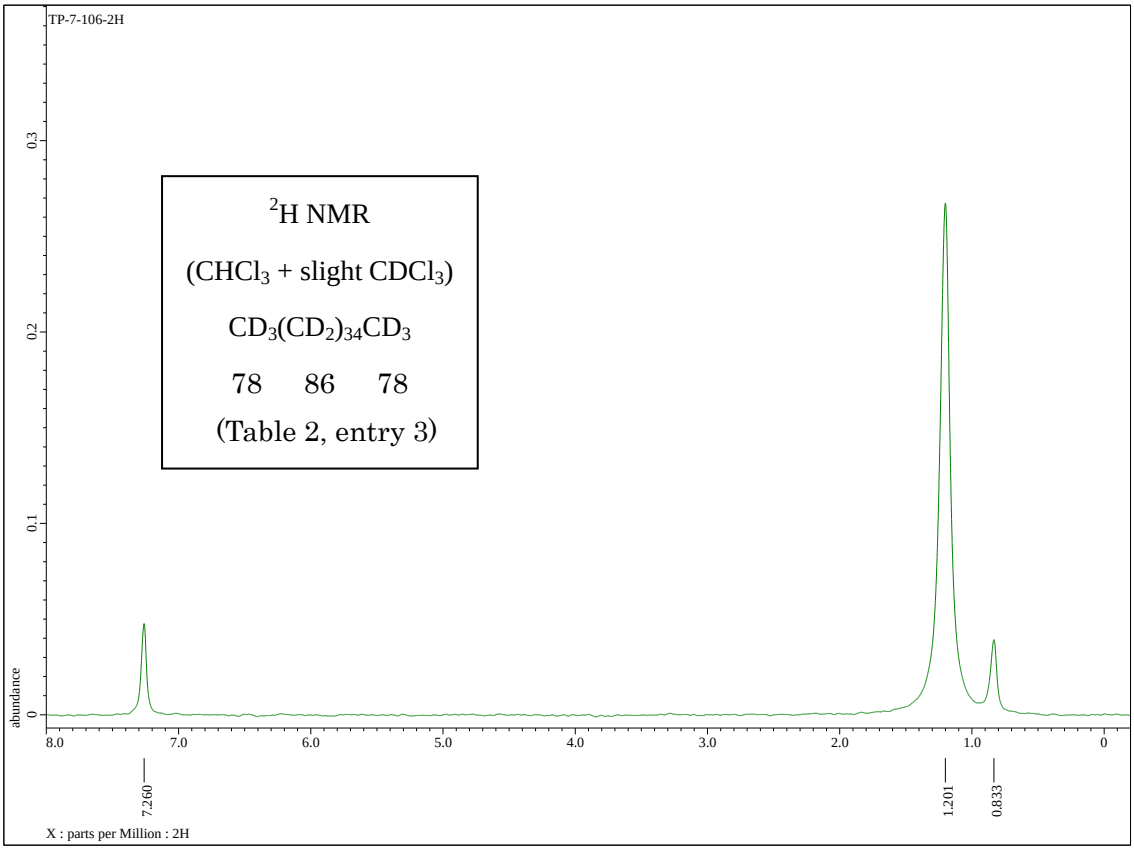

TP-7-123
^{1}H NMR ($CDCl_3$)
$CD_3(CD_2)_{13}CD_3$
97 92 97
(Table 2, entry 1)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
1.52
0.15
abundance
X : parts per Million : 1H
7.260
3.684
1.239
1.174
0.803
-0.018

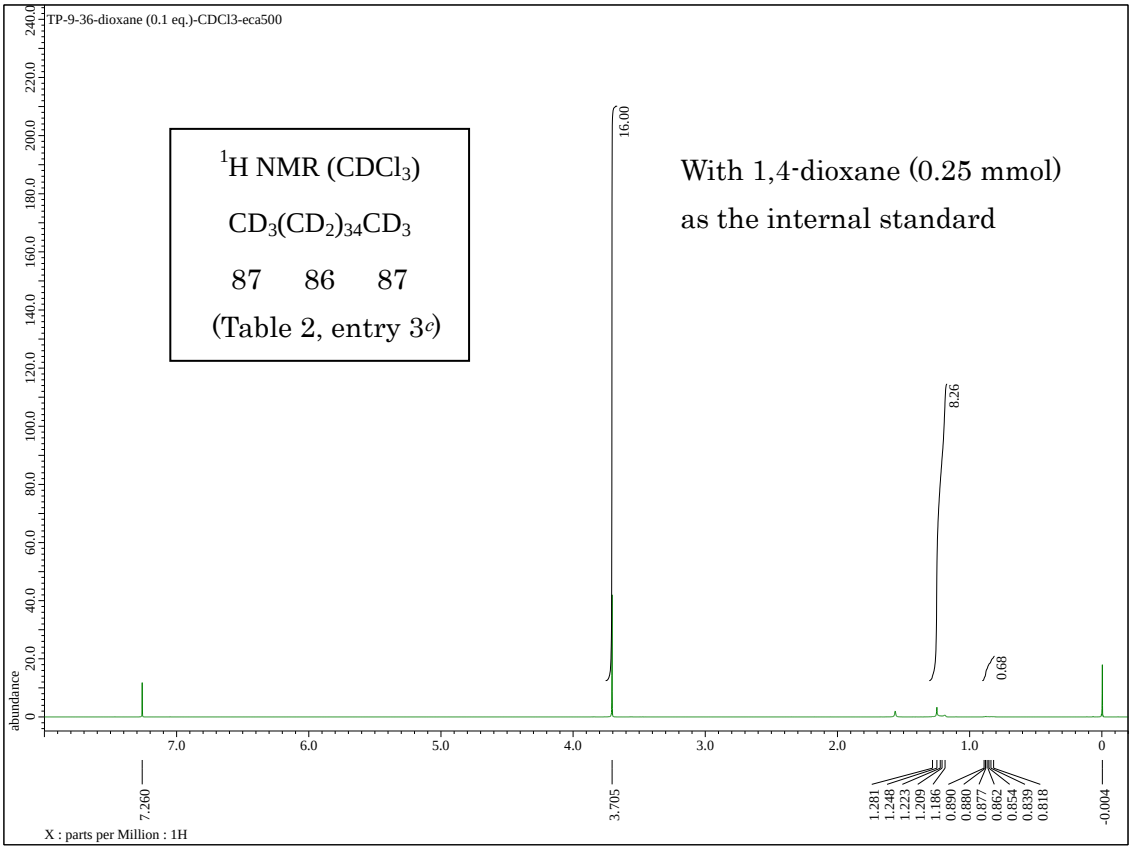

TP-7-123-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
$CD_3(CD_2)_{13}CD_3$
97 92 97
(Table 2, entry 1)
abundance
X : parts per Million : 2H
7.260
1.196
0.830

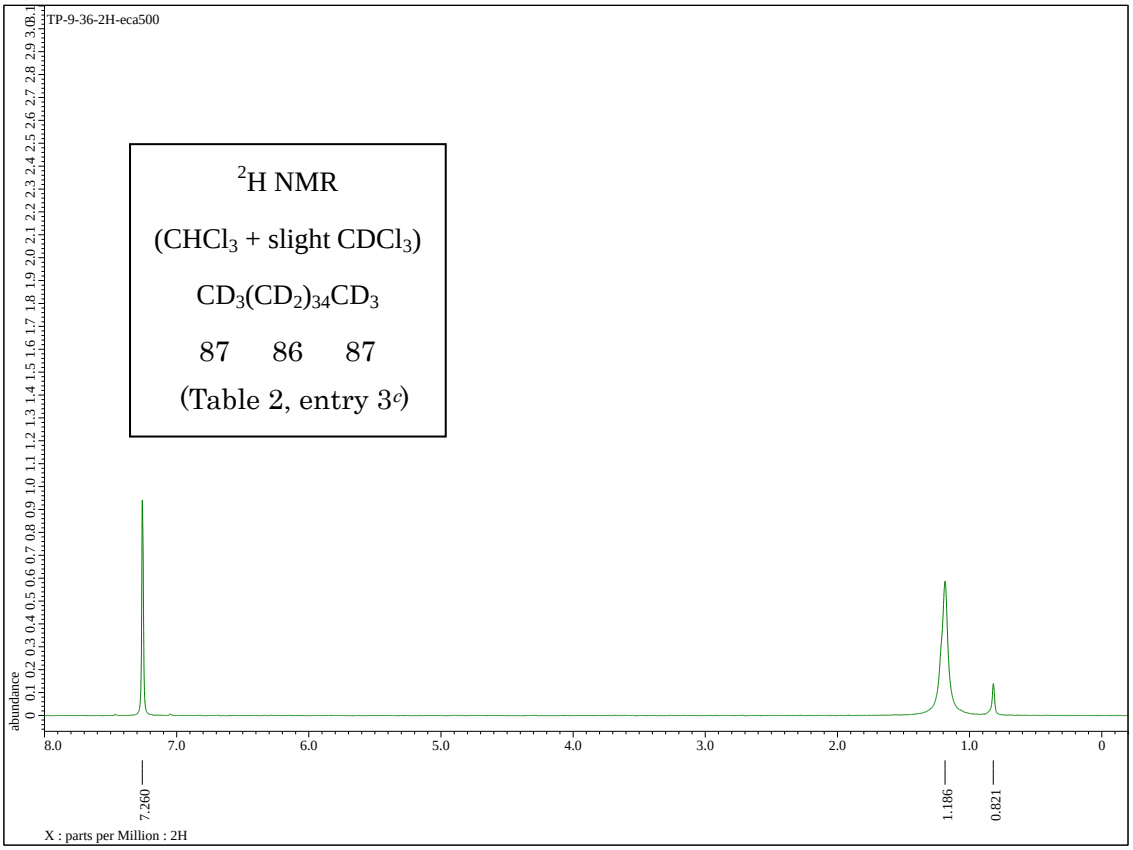

TP-7-104-Benzene-d6
^{1}H NMR (Benzene-d_6)
$CD_3(CD_2)_{18}CD_3$
94 94 94
(Table 2, entry 2)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
1.17
0.32
abundance
7.160
3.358
1.275
1.249
0.855
X : parts per Million : Proton

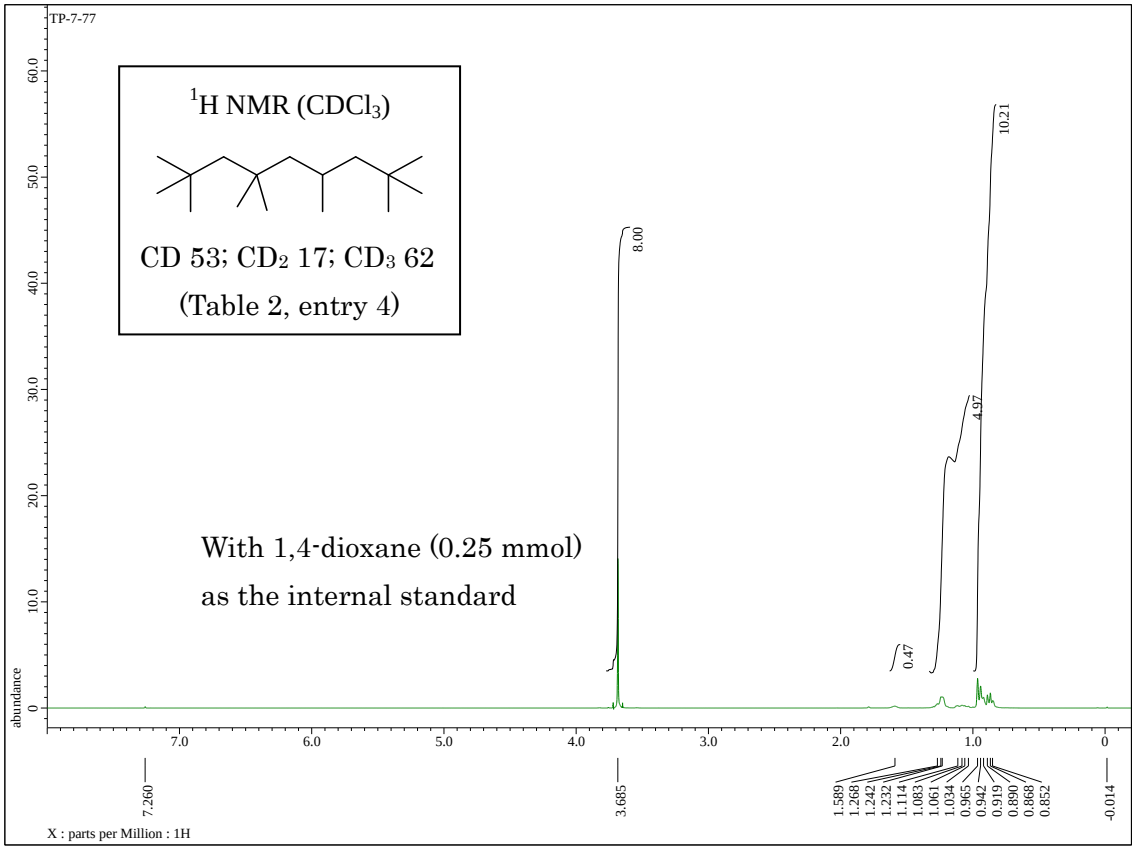

TP-7-104-2H-benzened6
^{2}H NMR
(Benzene + slight Benzene-d_6)
$CD_3(CD_2)_{18}CD_3$
94 94 94
(Table 2, entry 2)
abundance
7.160
1.204
0.823
X : parts per Million : 2H

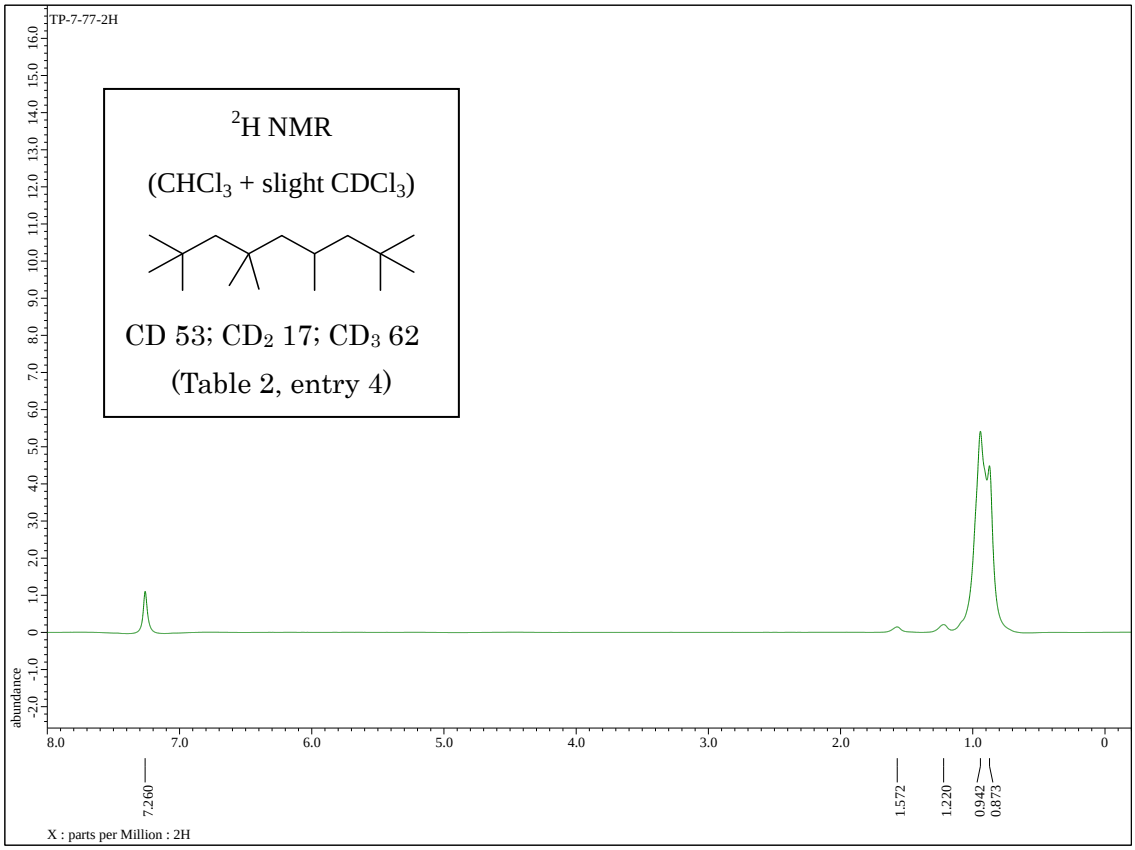

TP-7-106
^{1}H NMR ($CDCl_3$)
$CD_3(CD_2)_{34}CD_3$
78 86 78
(Table 2, entry 3)
With 1,4-dioxane (0.25 mmol)
as the internal standard
16.00
6.66
1.35
abundance
7.260
3.705
3.689
1.249
1.186
0.877
0.834
-0.004
X : parts per Million : 1H

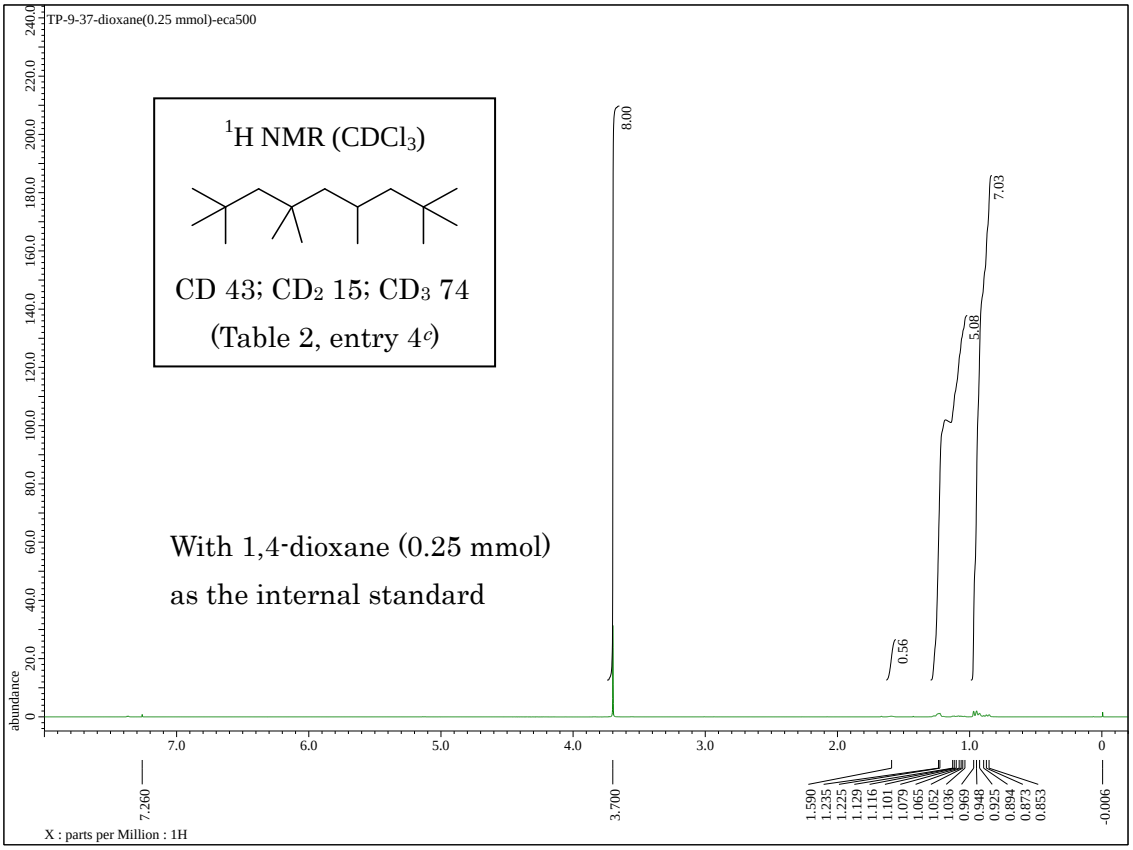

TP-7-106-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
$CD_3(CD_2)_{34}CD_3$
78 86 78
(Table 2, entry 3)
abundance
7.260
1.201
0.833
X : parts per Million : 2H

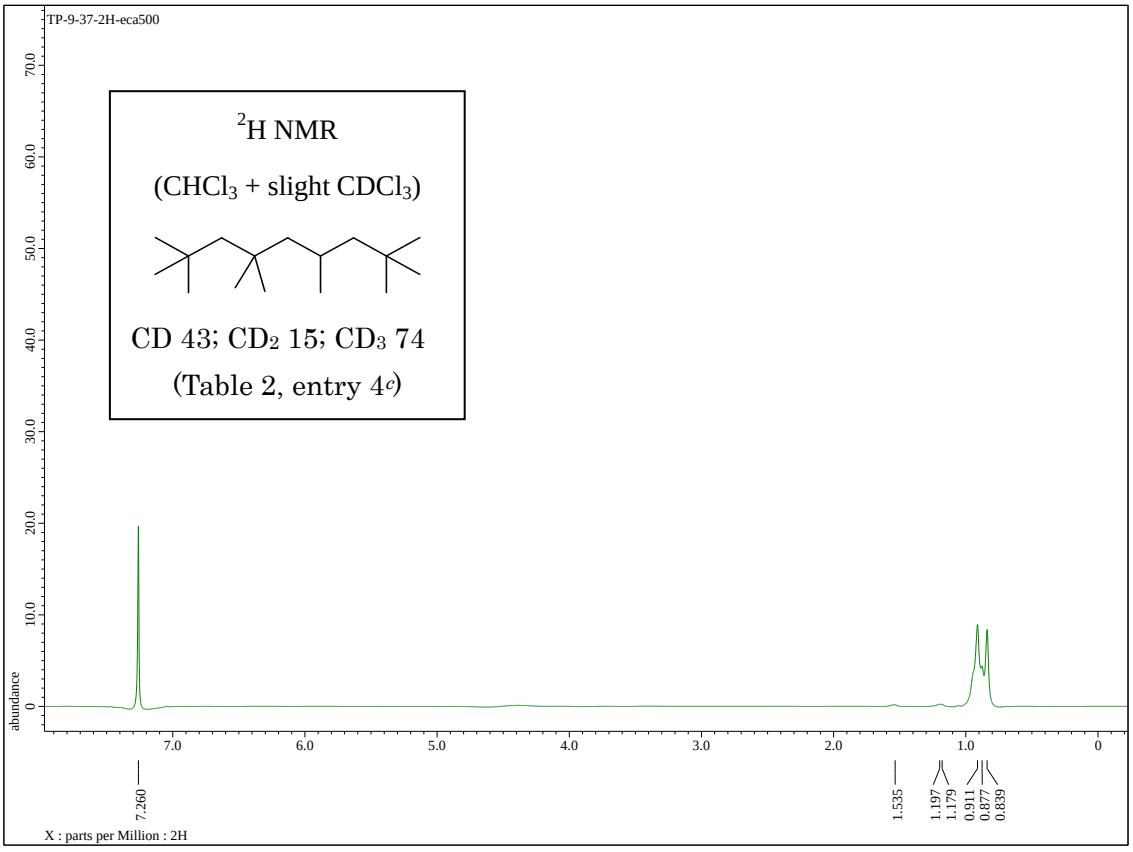

TP-9-36-dioxane (0.1 eq.)-CDCl3-eca500
^{1}H NMR ($CDCl_3$)
$CD_3(CD_2)_{34}CD_3$
87 86 87
(Table 2, entry 3^c)
With 1,4-dioxane (0.25 mmol)
as the internal standard
16.00
8.26
0.68
abundance
7.260
3.705
1.281
1.248
1.223
1.209
1.186
0.890
0.880
0.877
0.862
0.854
0.839
0.818
-0.004
X : parts per Million : 1H

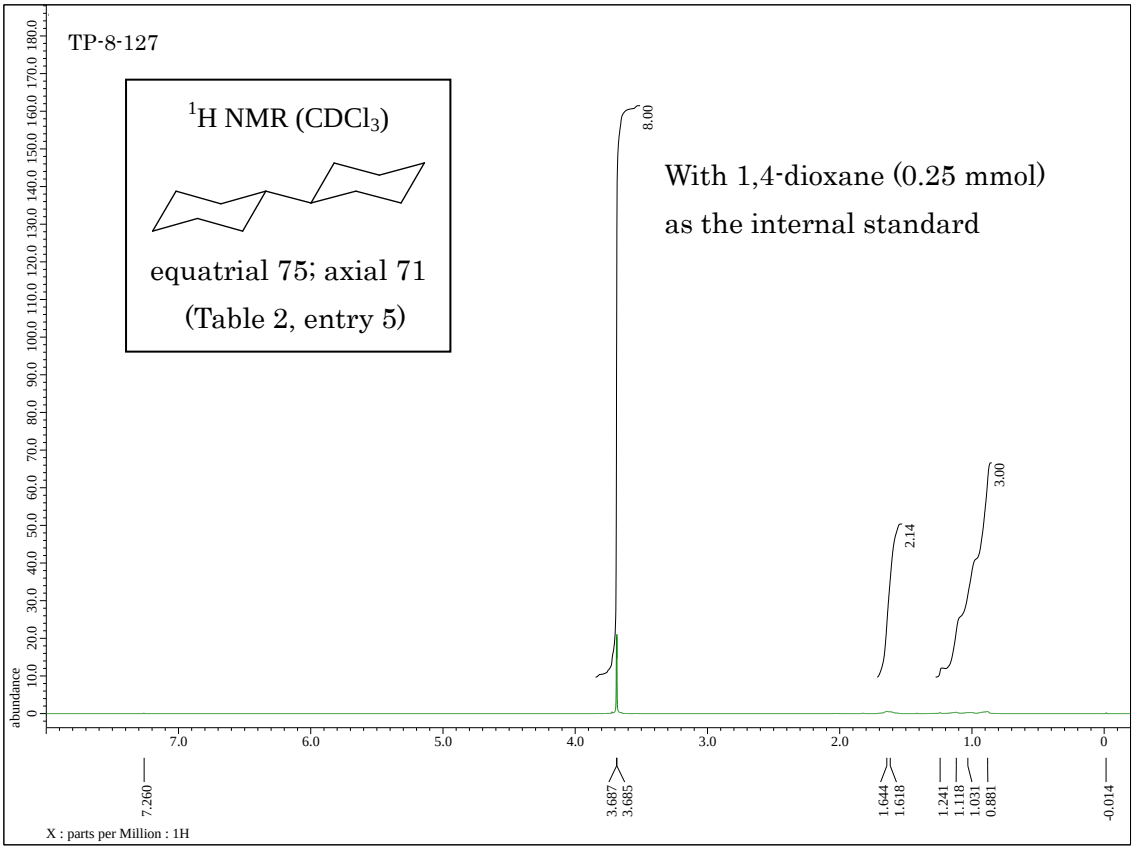

TP-9-36-2H-eca500
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
$CD_3(CD_2)_{34}CD_3$
87 86 87
(Table 2, entry 3^c)
abundance
7.260
1.186
0.821
X : parts per Million : 2H

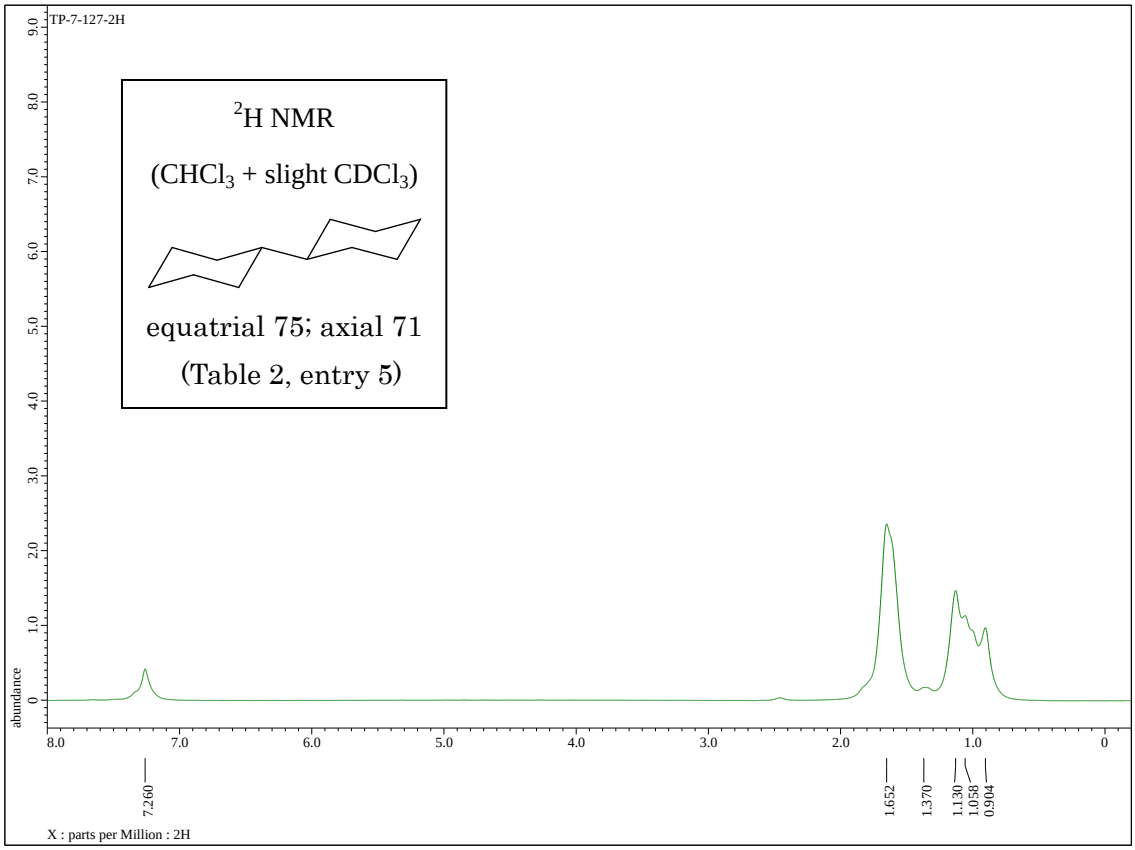

TP-7-77
^{1}H NMR ($CDCl_3$)
CD 53; CD_2 17; CD_3 62
(Table 2, entry 4)
With 1,4-dioxane (0.25 mmol)
as the internal standard
abundance
X : parts per Million : 1H
7.260
3.685
-0.014

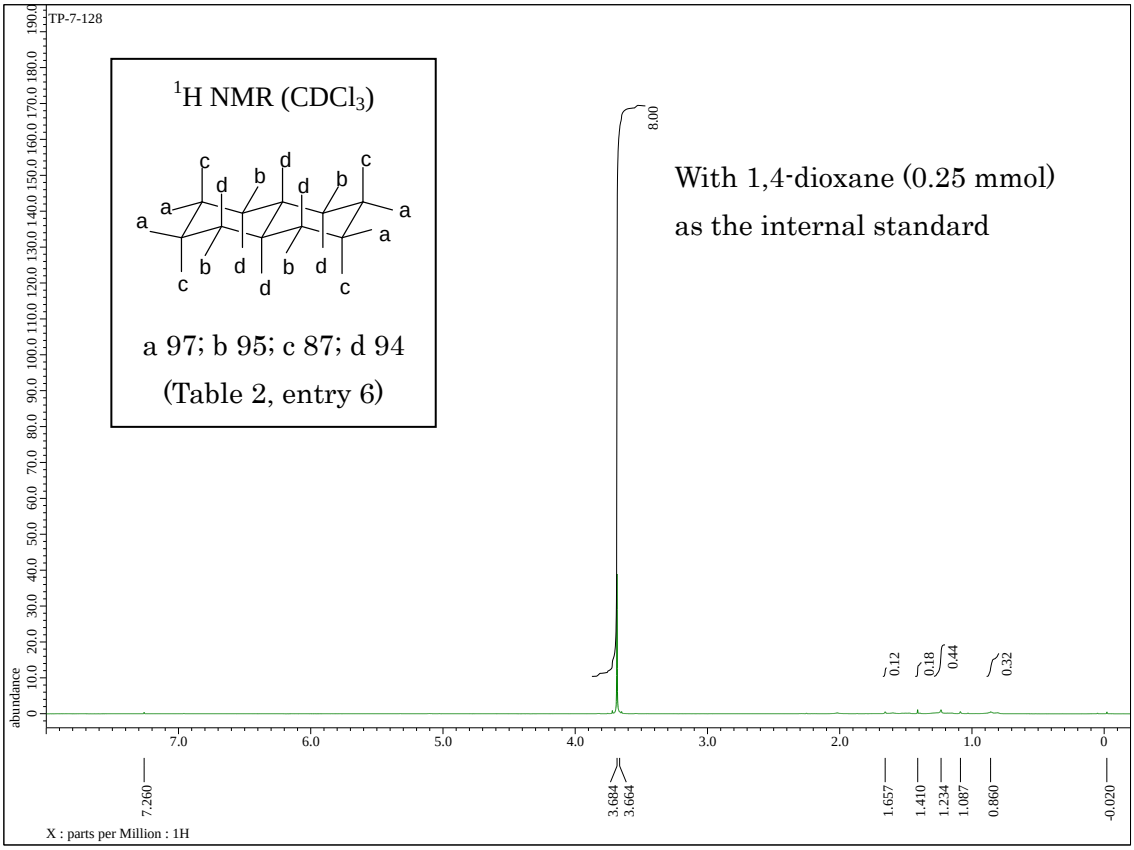

TP-7-77-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
CD 53; CD_2 17; CD_3 62
(Table 2, entry 4)
abundance
X : parts per Million : 2H
7.260
1.572
1.220
0.942
0.873

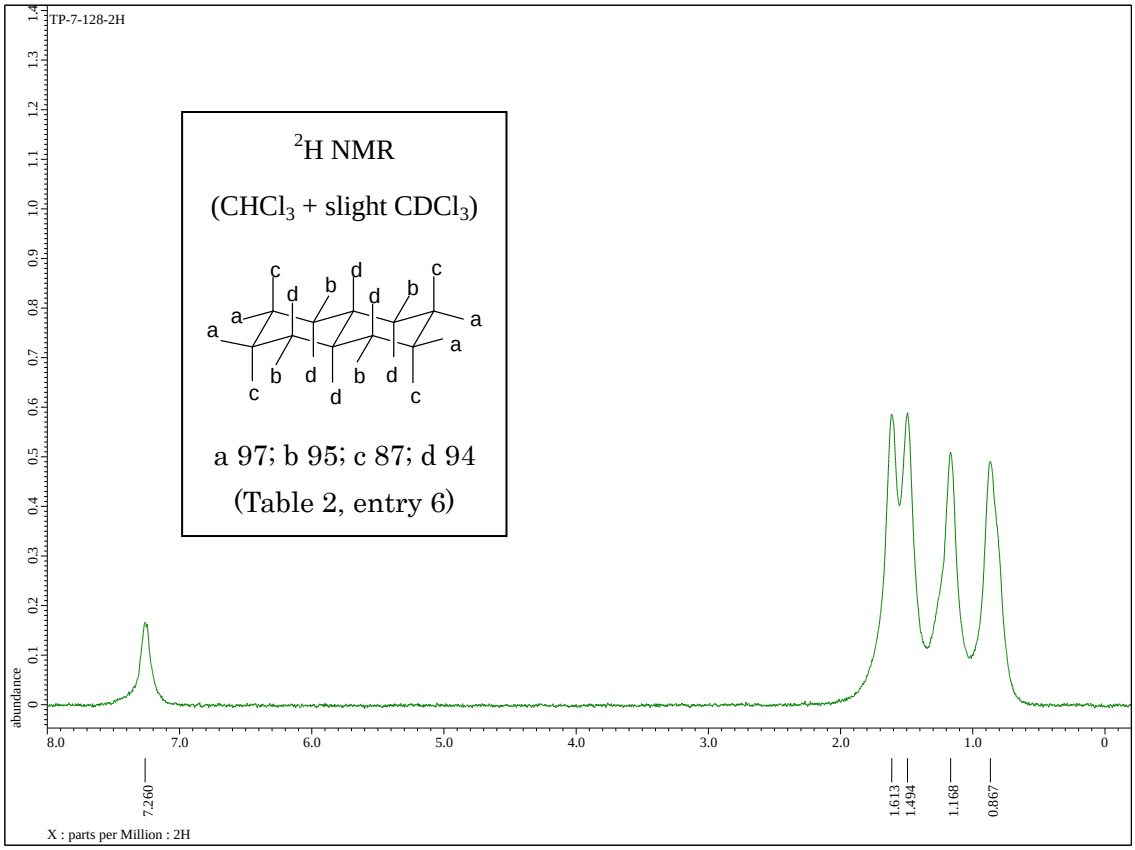

TP-9-37-dioxane(0.25 mmol)-eca500
^{1}H NMR ($CDCl_3$)
CD 43; CD_2 15; CD_3 74
(Table 2, entry 4c)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
7.03
5.08
0.56
abundance
X : parts per Million : 1H
7.260
3.700
1.590
1.235
1.225
1.129
1.116
1.101
1.079
1.065
1.052
1.036
0.969
0.948
0.925
0.894
0.873
0.853
-0.006

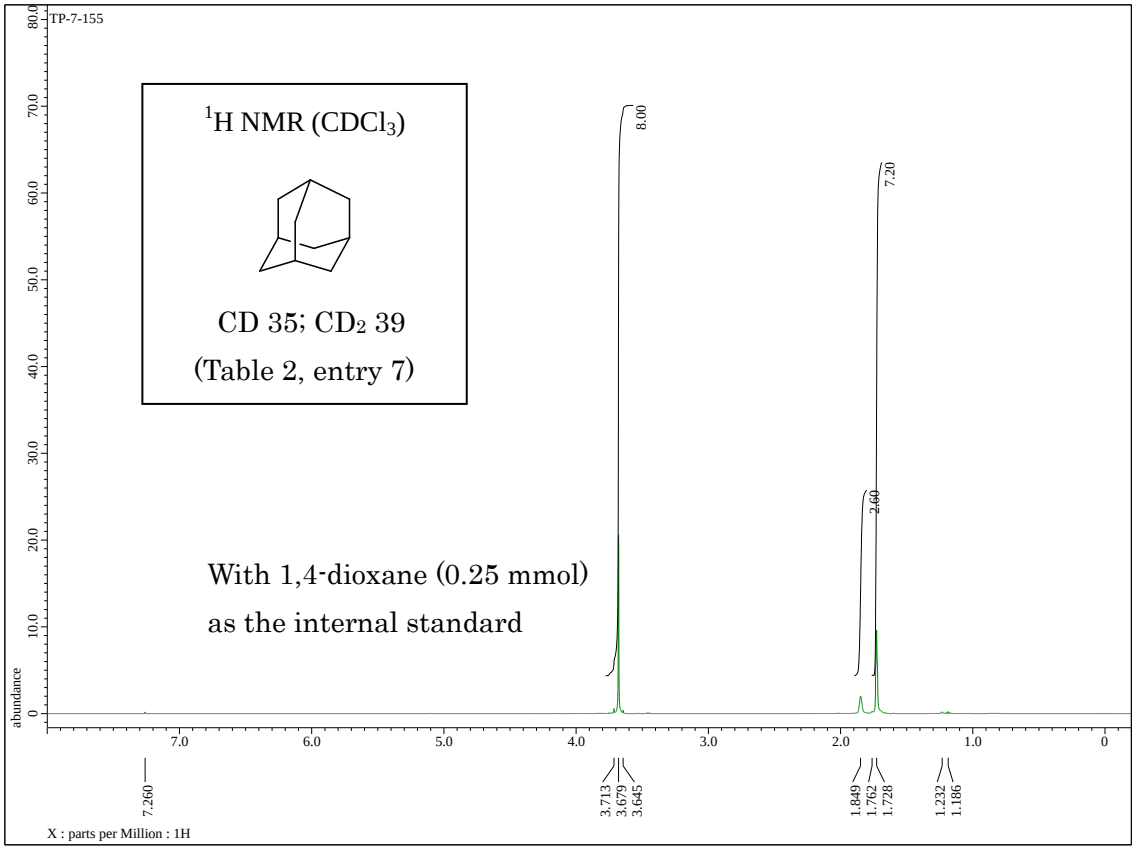

TP-9-37-2H-eca500
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
CD 43; CD_2 15; CD_3 74
(Table 2, entry 4c)
abundance
X : parts per Million : 2H
7.260
1.535
1.197
1.179
0.911
0.877
0.839

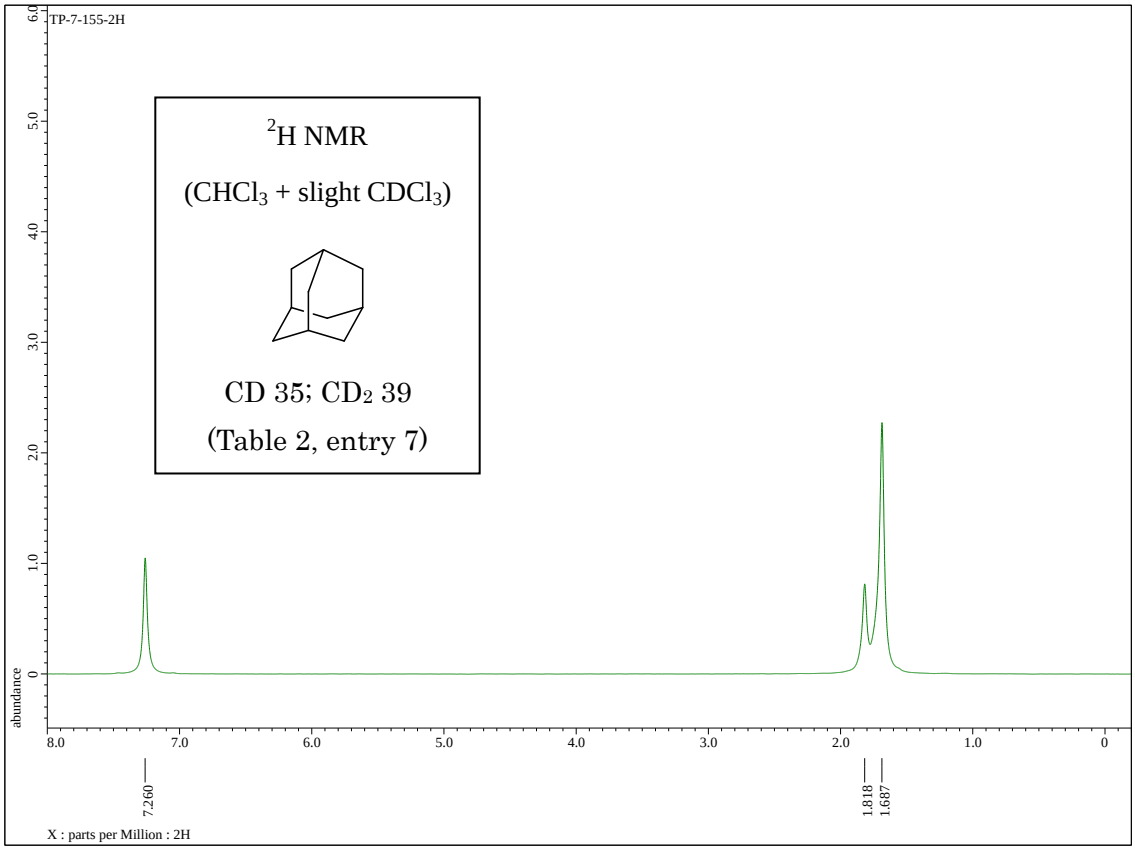

TP-8-127
^{1}H NMR ($CDCl_3$)
equatrial 75; axial 71
(Table 2, entry 5)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
2.14
3.00
abundance
7.260
3.687
3.685
1.644
1.618
1.241
1.118
1.031
0.881
-0.014
X : parts per Million : 1H

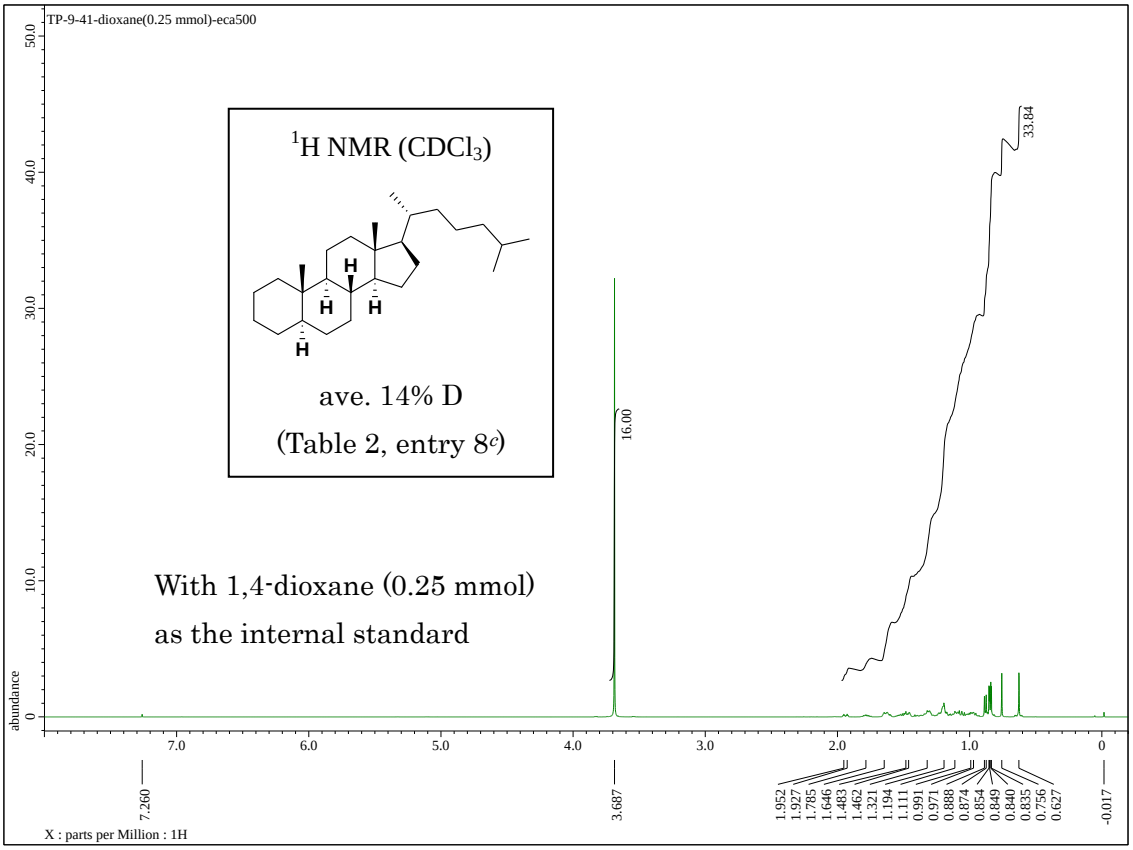

TP-7-127-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
equatrial 75; axial 71
(Table 2, entry 5)
abundance
7.260
1.652
1.370
1.130
1.058
0.904
X : parts per Million : 2H

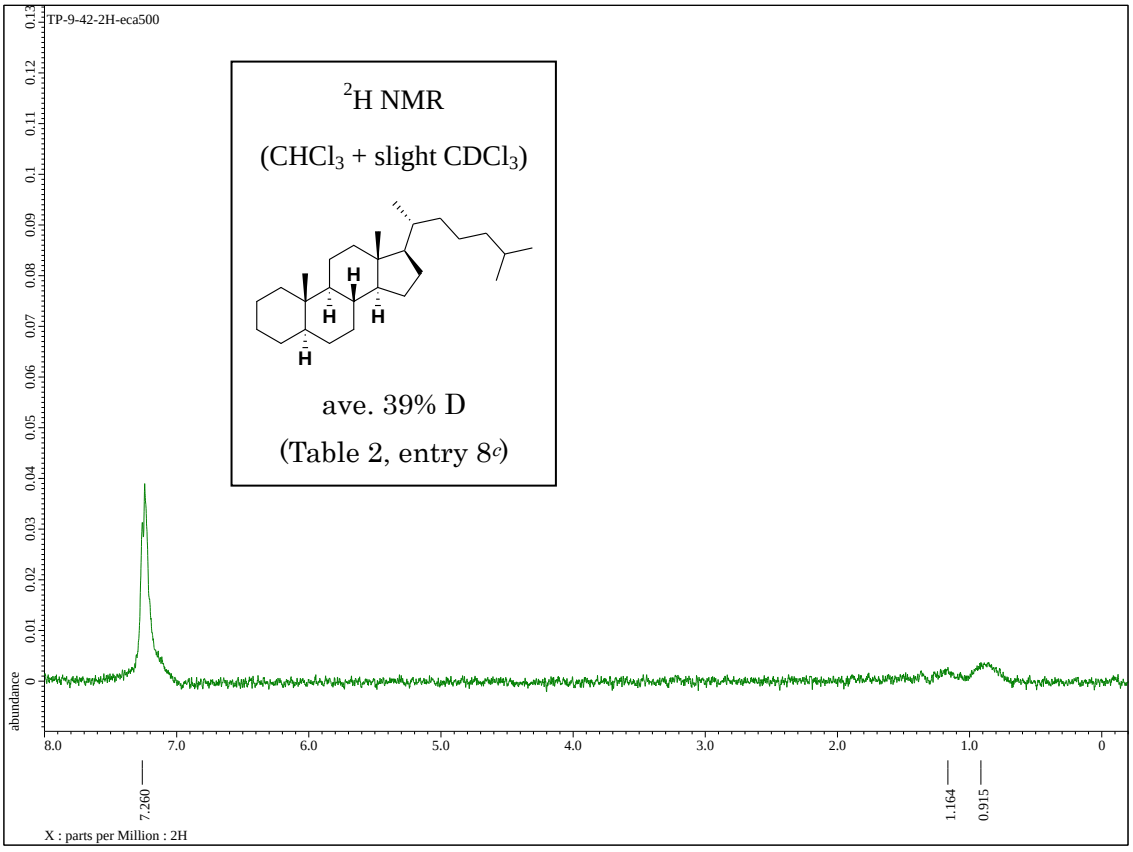

TP-7-128
^{1}H NMR ($CDCl_3$)
a 97; b 95; c 87; d 94
(Table 2, entry 6)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
0.12
0.18
0.44
0.32
abundance
7.260
3.684
3.664
1.657
1.410
1.234
1.087
0.860
-0.020
X : parts per Million : 1H

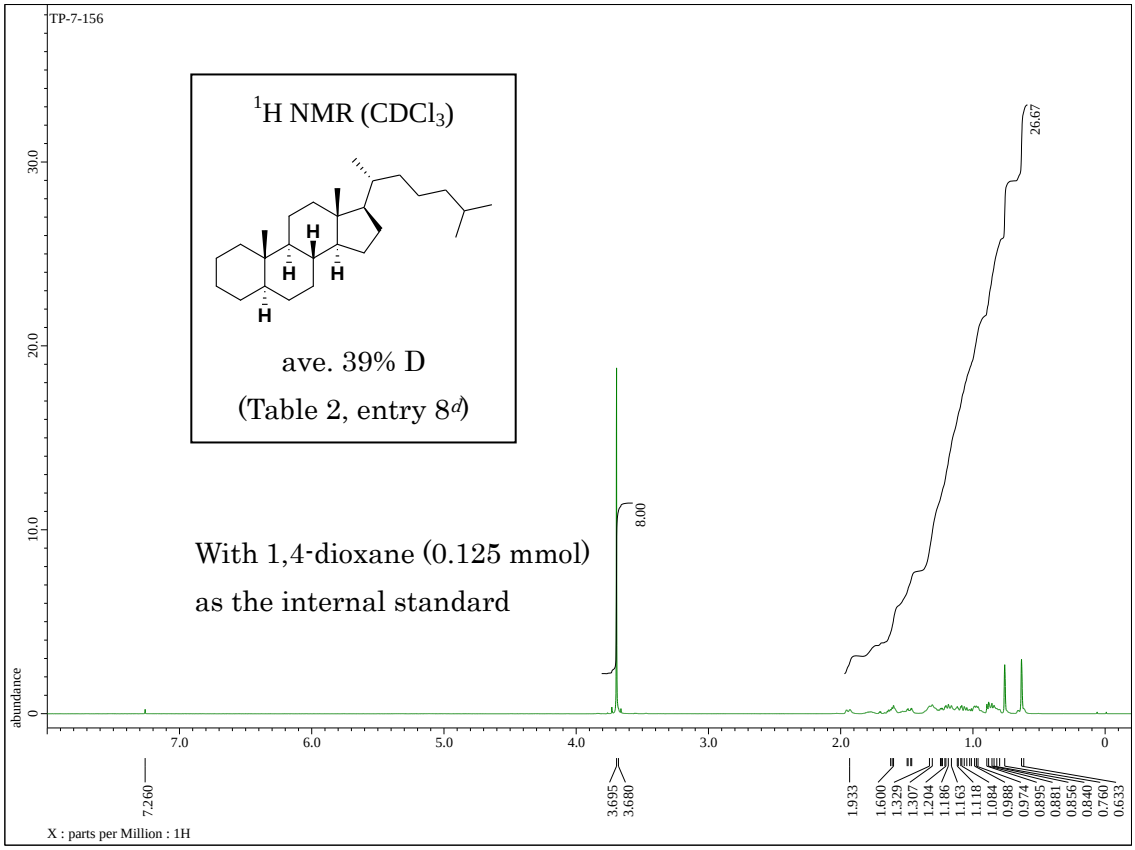

TP-7-128-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
a 97; b 95; c 87; d 94
(Table 2, entry 6)
abundance
7.260
1.613
1.494
1.168
0.867
X : parts per Million : 2H

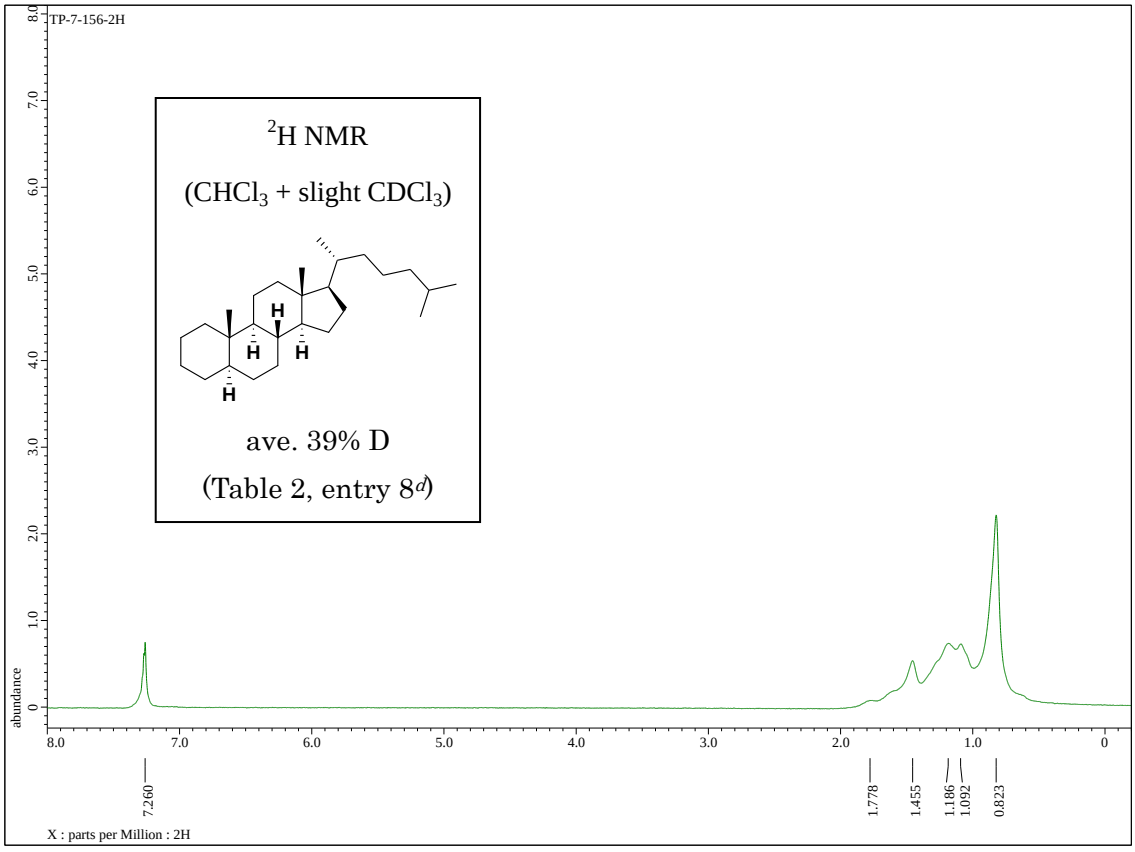

TP-7-155
^{1}H NMR ($CDCl_3$)
CD 35; CD_2 39
(Table 2, entry 7)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
7.20
2.60
abundance
7.260
3.713
3.679
3.645
1.849
1.762
1.728
1.232
1.186
X : parts per Million : 1H

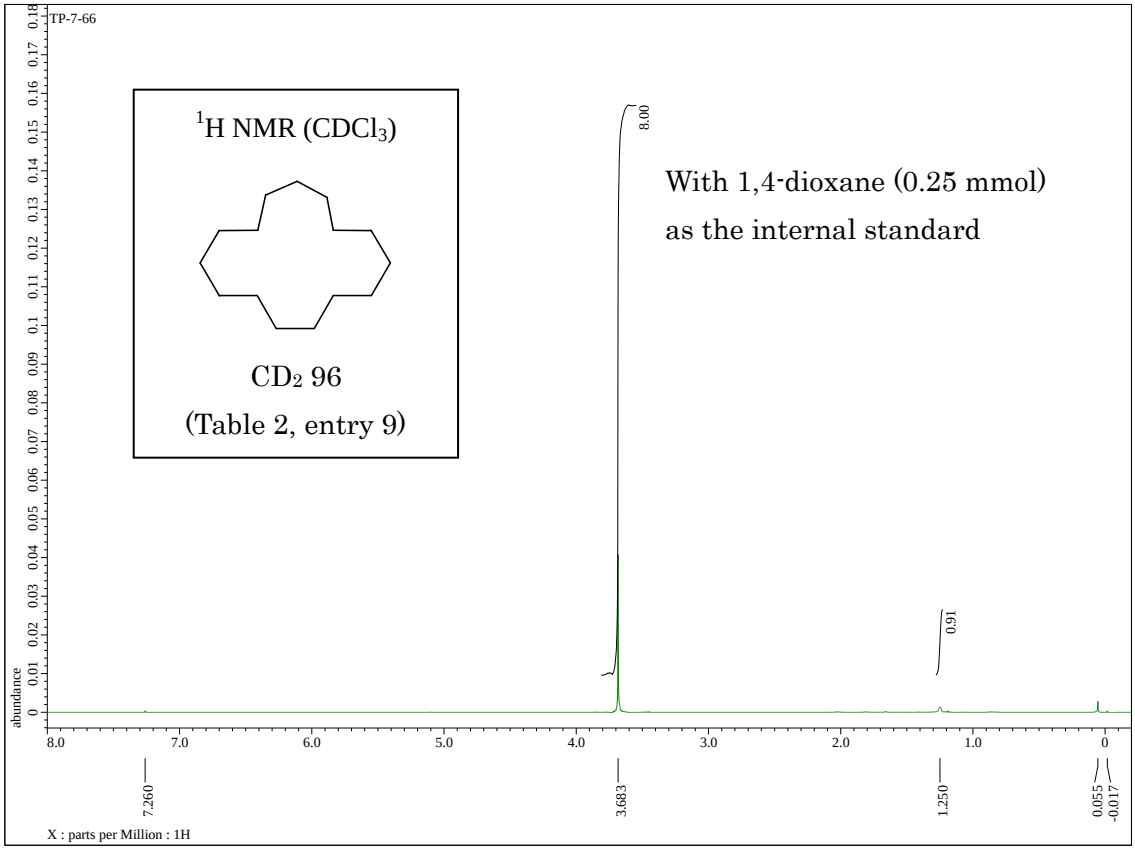

TP-7-155-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
CD 35; CD_2 39
(Table 2, entry 7)
abundance
7.260
1.818
1.687
X : parts per Million : 2H

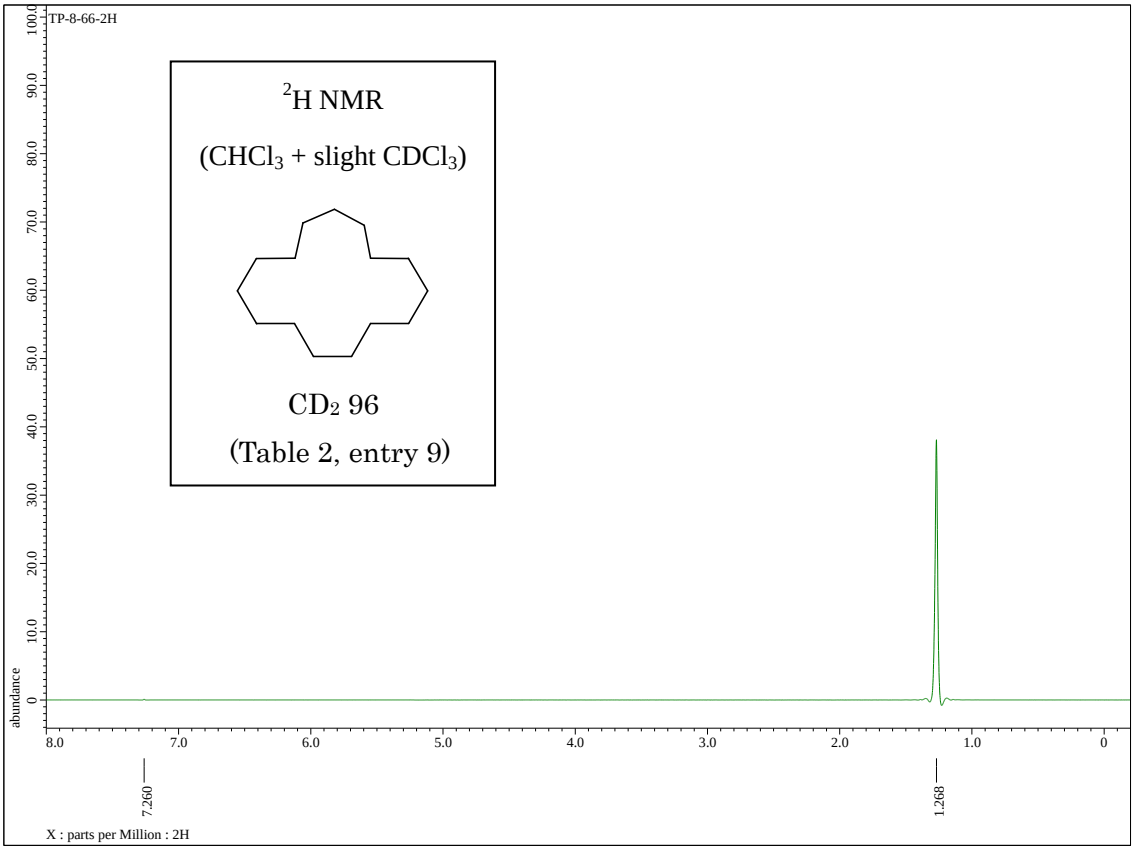

TP-9-41-dioxane(0.25 mmol)-eca500
^{1}H NMR ($CDCl_3$)
ave. 14% D
(Table 2, entry 8^c)
With 1,4-dioxane (0.25 mmol)
as the internal standard
16.00
33.84
abundance
X : parts per Million : 1H


TP-9-42-2H-eca500
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
ave. 39% D
(Table 2, entry 8^c)
abundance
X : parts per Million : 2H


TP-7-156
^{1}H NMR ($CDCl_3$)
ave. 39% D
(Table 2, entry 8[d])
With 1,4-dioxane (0.125 mmol)
as the internal standard
8.00
26.67
abundance
7.260
3.695
3.680
1.933
1.600
1.329
1.307
1.204
1.186
1.163
1.118
1.084
0.988
0.974
0.895
0.881
0.856
0.840
0.760
0.633
X : parts per Million : 1H


TP-7-156-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
ave. 39% D
(Table 2, entry 8[d])
abundance
7.260
1.778
1.455
1.186
1.092
0.823
X : parts per Million : 2H


TP-7-66
^{1}H NMR ($CDCl_3$)
CD_2 96
(Table 2, entry 9)
With 1,4-dioxane (0.25 mmol)
as the internal standard
8.00
0.91
abundance
7.260
3.683
1.250
0.055
-0.017
X : parts per Million : 1H


TP-8-66-2H
^{2}H NMR
($CHCl_3$ + slight $CDCl_3$)
CD_2 96
(Table 2, entry 9)
abundance
7.260
1.268
X : parts per Million : 2H