4.14   Spectra of Solvents and Reference Compounds

4.14.1 ^{13}C NMR Spectra of Common Deuterated Solvents *(125 MHz, δ in ppm)*
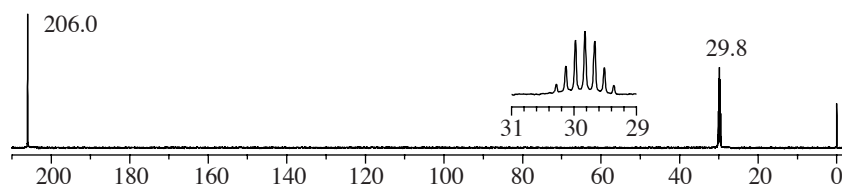
Acetone-d_6

Acetonitrile-d_3
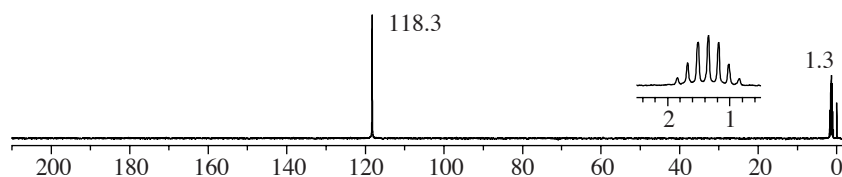
Benzene-d_6
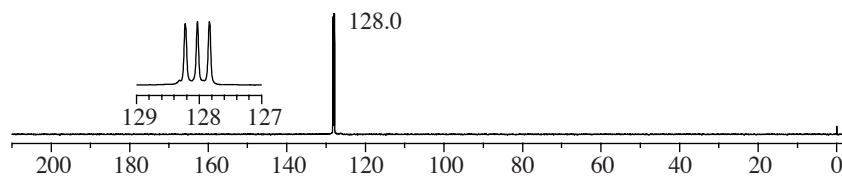
Bromoform-d
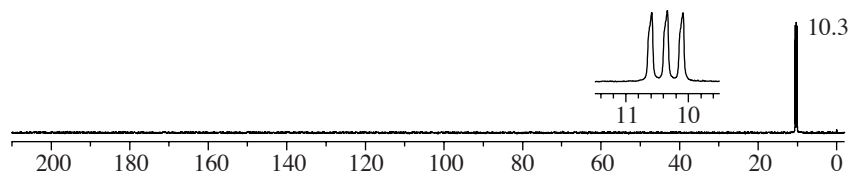
Chloroform-d
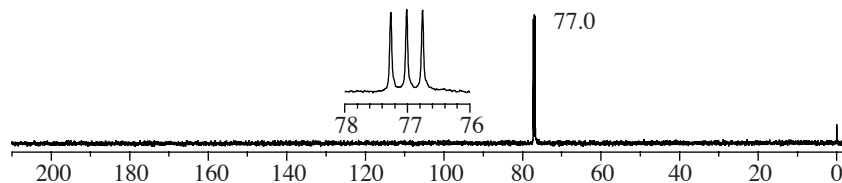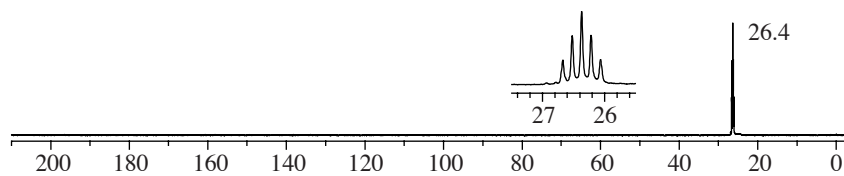
Solvents

Cyclohexane-d_{12}

26.4

27 26

200 180 160 140 120 100 80 60 40 20 0

Dimethyl sulfoxide-d_6

39.5

40 39

200 180 160 140 120 100 80 60 40 20 0

Methanol-d_1

49.9

51 50 49

200 180 160 140 120 100 80 60 40 20 0

Methanol-d_4

49.0

50 49 48

200 180 160 140 120 100 80 60 40 20 0

Pyridine-d_5

149.9

135.5

123.5

151 150 149

136.0 135.0

124.0 123.0

200 180 160 140 120 100 80 60 40 20 0

Tetrahydrofuran-d_8

67.4

25.3

68 67

26 25

Solvents

200 180 160 140 120 100 80 60 40 20 0
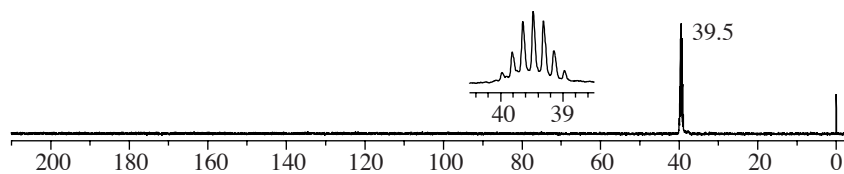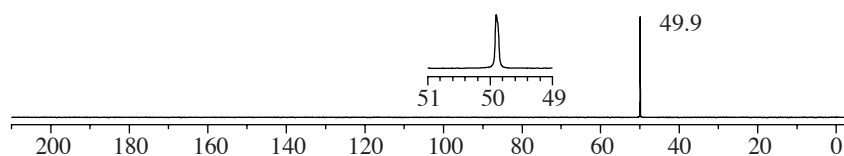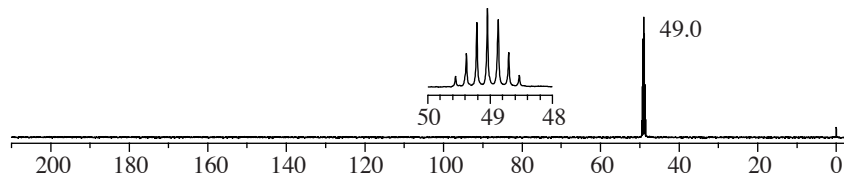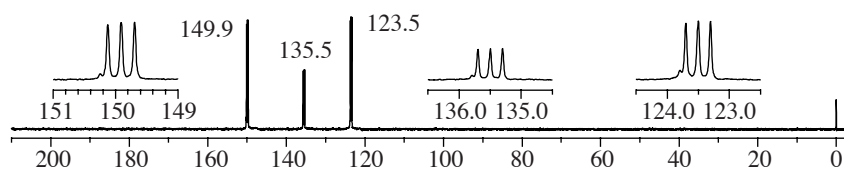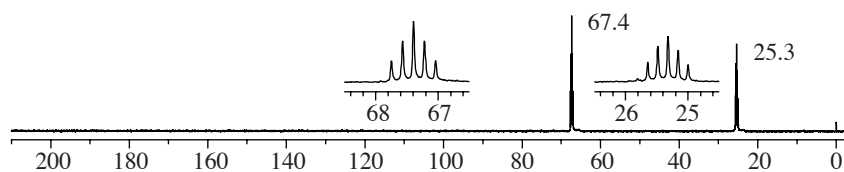
4.14.2 ¹³C NMR Spectra of Secondary Reference Compounds

Chemical shifts in ^{13}C NMR spectra are usually reported relative to the peak position of tetramethylsilane (TMS), which is added as an internal reference. If TMS is not sufficiently soluble in the sample, the use of a capillary with TMS as external reference is recommended. In this case, owing to the difference in volume susceptibilities, the local magnetic fields in the solvent and reference are different. Therefore, the position of the reference must be corrected. For a D_2O solution in a cylindrical sample with TMS in a capillary, the correction amounts to +0.68 and -0.34 ppm for superconducting and electromagnets, respectively. These values must be subtracted from the ^{13}C chemical shifts relative to the external TMS signal if its position is set to 0.00 ppm. Alternatively, secondary references with $(CH_3)_3SiCH_2$ groups may be used. The following spectra of two secondary reference compounds in D_2O were measured at 125 MHz with a superconducting magnet and TMS as external reference. Chemical shifts are reported in ppm relative to TMS upon correction for the difference in the volume susceptibilities of D_2O. As a result, the peak for the external TMS appears at 0.68 ppm.

3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (sodium 4,4-dimethyl-4-silapentane-1-sulfonate; DSS)
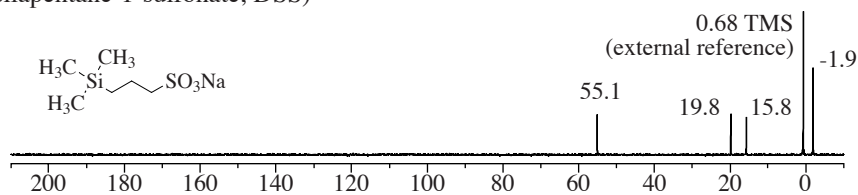
2,2,3,3-D₄-3-(Trimethylsilyl)-propionic acid sodium salt
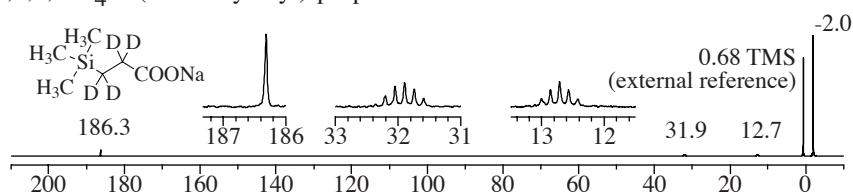
Solvents

4.14.3 ^{13}C NMR Spectrum of a Mixture of Common Nondeuterated Solvents

The broad-band-decoupled ^{13}C NMR spectrum (125 MHz, δ in ppm relative to TMS) of a CDCl$_3$ sample with 20 common solvents (0.05–0.4 vol%) shown below serves as a guide to identify possible solvent impurities. Chemical shifts of signals marked with an asterisk (*) may change up to a few ppm if the sample contains solutes having functional groups that can form hydrogen bonds.

DMF: dimethyl formamide; THF: tetrahydrofuran; EGDME: ethylene glycol dimethyl ether.

149.9* pyridine

ethyl acetate 171.1   DMF 162.5

206.8* acetone   192.6 CS$_2$

210 205 200 195 190 185 180 175 170 165 160 155 150 145 140

pyridine 136.0   129.1 toluene   128.4, 128.3 toluene, benzene   125.3 toluene   123.8 pyridine   116.3* acetonitrile   96.2* CCl$_4$ CDCl$_3$ 77.1* CHCl$_3$ 77.3*   (top part of signal not drawn)

toluene 137.9

140 135 130 125 120 115 110 105 100 95 90 85 80 75

53.4 CH$_2$Cl$_2$

71.9 EGDME   67.1 dioxane   60.4 ethyl acetate   59.1* ethanol   58.4 EGDME   methanol 50.7*

THF 68.0   65.9 diethyl ether

75 70 65 60 55 50

DMF 31.3   27.0 cyclohexane   30.9 acetone

dimethyl sulfoxide 41.1   hexane 31.6   25.6 THF

DMF 36.4

50 45 40 35 30 25

22.7 hexane   15.3 diethyl ether   1.8 acetonitrile
21.4 toluene   14.2 ethyl acetate   TMS
21.0 ethyl acetate   14.1 hexane
18.5 ethanol

25 20 15 10 5 0