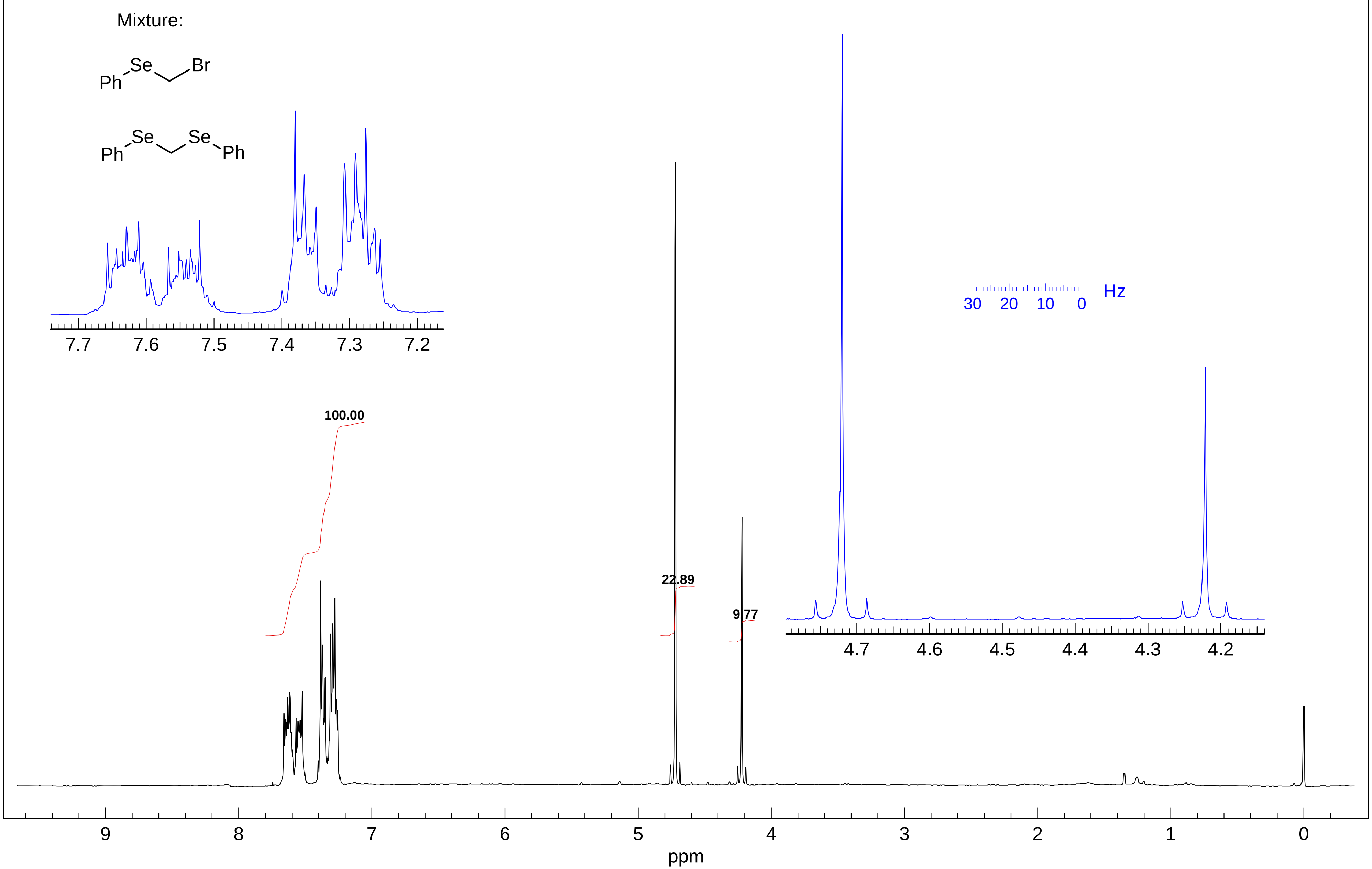
Problem R-09S (C_7H_7BrSe, $C_{13}H_{12}Se_2$)
200 MHz ^1H NMR spectrum in $CDCl_3$.
Source: R. D. Dykstra/Reich (digitized hard copy) g



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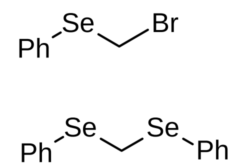
Problem R-09S. The 200 MHz ^{1}H NMR spectrum of a mixture of two selenides (approx a 2:1 ratio) is shown below. The compounds are bis(phenylseleno)methane and bromo(phenylseleno)methane.

(a) Identify all of the peaks in the region δ 4 to δ 5. Give chemical shifts and any couplings you have identified.

Mixture:



(b) Identify **two** distinct features of the spectrum which allow you to unambiguously assign which signal corresponds to which compound.

Method 1:

Method 2:

10

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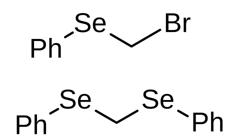

2 δ 4.22, with Se satellites $^2J_{H\text{-}Se}$ = 12 Hz - CH_2 of $PhSeCH_2SePh$

2 δ 4.72, with Se satellites $^2J_{H\text{-}Se}$ = 14 Hz - CH_2 of $PhSeCH_2Br$

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3 Method 1:

Size of the ^{77}Se satellites. The δ 4.22 signal has double-intensity ^{77}Se satellites, thus this signal must be $PhSeCH_2SePh$

3 Method 2:

Integrations: Because the two ortho protons at δ 7.54 and δ 7.64 are present in a ca 1:1 ratio, the compounds must be present in a 2:1 ratio, with twice as much $PhSeCH_2Br$ as $PhSeCH_2SePh$, thus the larger CH_2 peak must be $PhSeCH_2Br$

Method 3:

Chemical shift calculations:

	$PhSeCH_2Br$	$PhSeCH_2SePh$
	1.20	1.20
	2.15 α-Br	1.55 α-PhSe
	1.55 α-PhSe	1.55 α-PhSe
Calculated:	4.90	4.30
Observed:	**4.72**	**4.22**

Method 4:

The integration of the aromatic vs the CH_2 protons defines which must be the major isomer: if Br is major then Ar = 5 + 10/2 = 10, CH_2 = 2 + 2/2 = 3, hence 3.33/1. If PhSe is major then ArH = 10 + 5/2 = 12.5, CH_2 = 2 + 2/2 = 3, hence 12.5/3 = 4.1. Observed is 100/33.66 = 3.06, much closer to Br being the major isomer.

Method 5:

The chemical shift of $PhSeCH_2SePh$ is in the handouts!!

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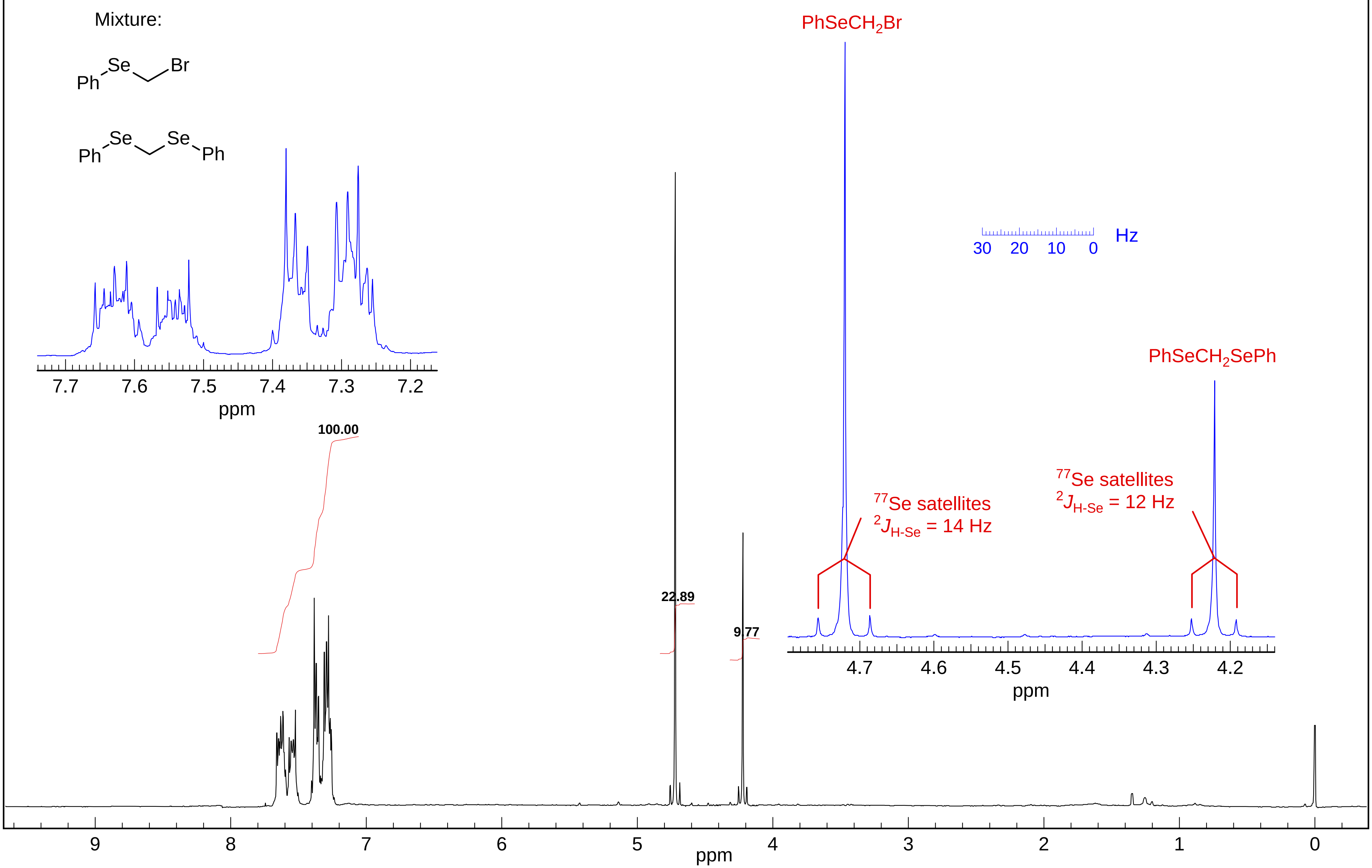

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