Question 1. NMR Basics. (20 points)

(a) Indicate schematically the magnetic moments of “individual nuclear spins” (at least 10) as arrows for the following situations. Assume as always that the external magnetic field is pointing straight up (z-direction). (8)

<table>
<thead>
<tr>
<th>After the sample is placed in the magnetic field. (But no pulses as yet.)</th>
<th>After one “90° pulse.”</th>
<th>After the experiment and, more precisely, after ten periods of $T_1$ seconds passed.</th>
<th>After one period of $T_2$ seconds passed.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

(b) Schematic of the Zeeman levels for an AX-pair of H-nuclei with $\delta(H_a) << \delta(H_x)$. (6 points)

On the left: Draw the Zeeman levels for $H_a$ and $H_x$ assuming that $J(H_a, H_x) = 0$.

On the right: Draw the Zeeman levels for $H_a$ and $H_x$ assuming that $J(H_a, H_x) \neq 0$.

\[ J(H_a, H_x) = 0 \quad J(H_a, H_x) \neq 0 \]

(c) Solvents (6 points)

Multiplicity depends on the number of equivalent neighbors $n$ and their nuclear spin $I$ and the multiplicity is given by __________. For spin $I = \frac{1}{2}$ nuclei, this formula simplifies to the ________-rule.

**Acetone-d$_6$ (you observe Acetone-d$_-$)**

C couples to $n = ___$ equivalent ___-atom(s) with nuclear spin $I = ____$. Multiplicity of $^{13}$C signal: ________________

**DMSO-d$_6$ (you observe DMSO-d$_-$)**

H couples to $n = ___$ equivalent ___-atom(s) with nuclear spin $I = ____$. Multiplicity of $^1$H signal: ________________
### Question 2. Chemical Shifts & Increment Systems. (20 points)

**1H- and 13C-NMR of Vanillin** (from SDBS, requires the book by Pretsch et al.)

The structure of vanillin is shown and the chemical shift data are taken from the SDBS database. Using the book by Pretsch et al., find the base value for the chemical shift of an aromatic C-atom “Cx”, locate the Zi-values and provide them in the table below. Do the same for the attached H-atom. Make sure to indicate the “i” of the Zi-values (where the underline is shown). Then make the additions to obtain the “calculated” chemical shift, assign the “measured” peaks and enter their chemical shifts in the respective row, and, finally, compute the difference between “calculated” and “measured” values.

<table>
<thead>
<tr>
<th>H-NMR Chemical Shifts (ppm)</th>
<th>Cx</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.959, 6.39, 7.047, 7.42, 7.42, 9.823.</td>
<td>Base =</td>
</tr>
<tr>
<td>C-NMR Chemical Shifts (ppm)</td>
<td>Hx</td>
</tr>
<tr>
<td>191.21, 152.18, 147.50, 129.77, 127.49, 114.75, 109.34, 56.10.</td>
<td>Base =</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cx</th>
<th>Hx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base =</td>
<td>Base =</td>
</tr>
<tr>
<td>Z_(OMe) =</td>
<td>Z_(OMe) =</td>
</tr>
<tr>
<td>Z_(OH) =</td>
<td>Z_(OH) =</td>
</tr>
<tr>
<td>Z_(CHO) =</td>
<td>Z_(CHO) =</td>
</tr>
</tbody>
</table>

Calculated:  
Measured:  
Deviation:

Row 2, 8 points: One point for each base value and each pair of subscript & Z-value.  
Row 3, 4 points: Correct addition.  
Row 4, 6 points: Correct assignments of the measured shifts to Cx and Hx.  
Row 5, 2 points: One point for each correct error calculation.
**Question 3.** Nuclear Overhouser Effect (NOE). (20 points)

This is all about toluene. The numbering of the atoms is shown in the drawing. The $T_1$ and NOE data are taken from the textbook; the intensities are from the toluene spectrum in the SDBS database.

(a) The _________-_________relaxation times $T_1$ are given in column (2). In general, the _________ the relaxation time $T_1$, the higher the signal intensity. In column (3) provide the rankings for the C-peak intensities that you would expect based on $T_1$ alone (from “1” to “5”, “1” highest intensity, “5” lowest intensity). (8 p.)

(b) The NOE factors are given in column (4). The factors specify the amount of the increase of the $^{13}$C-NMR signal that is achieved when the H-nuclei are irradiated. In column (5) provide the rankings for the C-peak intensities that you would expect based on NOE alone (from “1” to “5” as above). (5 points)

(c) Measured intensities with rankings are listed in columns (6) and (8). State whether the intensities are dominated by $T_1$ or by NOE. Provide a very brief explanation as to why this is so; a few good words suffice! (4 p.)

(d) The NOE for the ipso-C is not zero! The NOE effect of the CH$_3$-carbon is much less than 2. The CH-carbons have the best NOEs. Does it matter for a carbon’s NOE how many Hs are attached? Does it matter for a carbon’s NOE whether any H is directly attached? What then is required for a C-atom to show NOE? (3 p.)
Question 4. Valine, (H\textsubscript{3}C)\textsubscript{2}CH–CH(NH\textsubscript{2})COOH. (40 points)

\textsuperscript{1}H-NMR: 89.56 MHz, 0.04 g : 0.5 ml D\textsubscript{2}O

\textsuperscript{13}C-NMR: 25.16 MHz, 0.162 g : 1.5 ml D\textsubscript{2}O
(a) In the spectra of DL-valine (racemic) on previous page, assign as many peaks as you can. (20 points).

(b) State how many signals there are in the $^1$H-NMR spectrum of pure L-valine, state the multiplicity of each of these signals, and state who causes each signal.

(c) State how the $^1$H-NMR spectra of pure L-valine and of pure D-valine differ.

(d) State how many signals there are in the H-decoupled $^{13}$C-NMR spectrum of pure L-valine and explain why.

(e) State how the H-decoupled $^{13}$C-NMR spectra of pure L-valine and of pure D-valine differ and explain.

(f) State how many signals there are in the H-decoupled $^{13}$C-NMR spectrum of 90% $^{15}$N-enriched, enantiomerically pure L-valine, and state the multiplicity of each signal.