1. (32 points) Circle the letter on the right which corresponds to the answer to each question. There is only one correct answer for each question.

(i) Which of the following best describes the mechanism of an acyl substitution reaction?

- A. Addition followed by elimination
- B. Bimolecular nucleophilic substitution
- C. Elimination followed by addition
- D. Substitution followed by elimination

(ii) Which of the following is the least reactive toward acyl substitution?

- E. CH₃OCH₃
- F. CH₃NH₂
- G. CF₃O
- H. ClO

(iii) Arrange the following in order of increasing basicity (weakest base < strongest base).

- I. 2 < 1 < 3 < 4
- J. 3 < 2 < 4 < 1
- K. 3 < 4 < 1 < 2
- L. 4 < 3 < 1 < 2

(iv) Which of the following types of amine can produced by reduction of an amide with LiAlH₄?

- M. only primary amines
- N. only primary or secondary amines
- O. only secondary amines
- P. primary, secondary or tertiary amines

(v) Which of the following is not a resonance structure of protonated propanoic acid?

- Q.
- R.
- S.
- T.

(vi) Which of the following will efficiently produce butanamine (CH₃CH₂CH₂CH₂NH₂) from bromobutane?

- U. Reaction with ammonia and H₂/Pt
- V. Reaction with cyanide, followed by reduction with LiAlH₄
- W. Reaction with sodium azide, followed by reduction with LiAlH₄
- X. Reaction with one equivalent of ammonia

(vii) Which of the following is not an acyl substitution reaction?

- Y. Treatment of a nitrile with LiAlH₄ to provide an amine
- Z. Treatment of an acid chloride with a sodium carboxylate to provide an acid anhydride
- AA. Treatment of an acid anhydride with an alcohol to provide an ester
- BB. Treatment of an ester with an amine to provide an amide

(viii) Which of the following best describes the geometry around the nitrogen of a tertiary amine?

- CC. Planar
- DD. Trigonal pyramidal
- EE. Linear
- FF. Cubic
2. (30 pts) Provide the organic product(s) of the following reactions. Your answers should include all of the carbon atoms in the starting materials and reagents.

\[ \text{HO N(CH}_3\text{)}_3 \quad 150 \degree C \]

\[ \text{OOC} \quad \text{H}_2\text{N} \quad \text{NaN}_3 \quad \text{then heat} \]

\[ \text{CH}_2\text{Cl} \quad \text{SOCl}_2 \quad \text{EtOH} \]

\[ \text{CH}_2\text{OH} \quad \text{SOCl}_2 \quad \text{EtOH} \]

\[ \text{CH}_2\text{Cl} \quad \text{H}_2\text{NEt} \quad \text{i) LAiH}_4 \quad \text{ii) H}_2\text{O} \]

\[ \text{NH} \quad \text{KOH} \quad \text{CH}_2\text{Br} \quad \text{H}_2\text{NNH}_2 \]

3. (8 pts) Provide a brief explanation of the origin of the following observations.

(i) Ammonia undergoes polyalkylation, even in the presence of only one mole equivalent of an alkyl halide.

(ii) Phthalimide does not undergo polyalkylation in the Gabriel synthesis of amines.
4. (20 points) The following transformations cannot be completed in a single step. Provide a sequence of reactions to perform each transformation, showing the reagents and structures of all isolated synthetic intermediates. The synthesis must use the given starting materials; you may also use any other starting materials with 3 or fewer carbon atoms. You may use any reagents but all carbon atoms in the products must be obtained from the given starting material. Do not show mechanisms or the structures of reactive intermediates. Shorter, more efficient syntheses are preferred; overly long or inefficient sequences will lose some credit.
4. (10 points) The mechanism for the Hoffmann rearrangement begins with the conversion of an amide to an isocyanate (shown on the right). Provide a neatly drawn and detailed stepwise mechanism for this process, showing all intermediates [Use curved arrows to show the movement of electrons; all structures should be valid Lewis structures]. (The isocyanate undergoes further reaction to generate an amine and CO₂; do not provide a mechanism for this subsequent conversion).