Questions 1-5 should be solved together.

In the following scheme, find the structural formulas of compounds A-E:

$$\begin{array}{c} \text{excess Br}_2 \\ \text{product}_1 \end{array} \xrightarrow{} C$$

$$product_2 \xrightarrow{H^+} D \xrightarrow{NH_3} E$$

1. Choose the correct structural formula of A.

2. Choose the correct structural formula of B.

HO.

- e.
- 3. Choose the correct structural formula of **C**.

a.

b.

- ÓН
- c.
- $e. \quad CBr_3H$
- 4. Choose the correct structural formula of **D**.

a.

b.



c.

a.

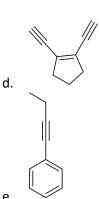
- \_OH
- d. e.

5. Choose the correct structural formula of **E**.

- $NH_2$
- b.

c. 
$$\frac{NH_2}{d}$$

- 6. Hydrocarbon  $C_9H_8$  upon reaction with K gives  $C_9H_7K$  and  $H_2$ , with the excess of  $Br_2 C_9H_8Br_2$ , and with an acidic solution of  $KMnO_4$  carbon dioxide and  $C_8H_6O_4$ . What is the structure of the hydrocarbon?



7. Before the advent of modern physical methods for structure elucidation (NMR, IR, mass spectra), organic chemists relied on a few well-studied chemical processes to break down an unknown compound into smaller known fragments. Examples of such methods include ozonolysis and excessive oxidation with acidic potassium permanganate solution.

1 mole of unknown compound X was subjected to ozonolysis, and the following products were observed:

2 moles of 
$$O$$
, 1 mole of  $O$ , 1 mole of  $O$ , 1 mole of  $O$ 

Unstable  $\mathbf{Y}$  was then subjected to oxidation with acidic potassium permanganate yielding 2 moles of  $CO_2$  and 1 mole of symmetric  $\mathbf{Z}$  (per 1 mole of  $\mathbf{Y}$ ), which, upon heating in acidic conditions, produced 1 mole of acetone and 2 moles of  $CO_2$  (per 1 mole of  $\mathbf{Z}$ ). What is the structural formula of  $\mathbf{X}$ ?

Questions 8-15 should be solved together.

Below is part of the *Gilead Sciences Inc.* synthesis of antiviral drug **oseltamivir** (sold under the brand name *Tamiflu*) from natural product **(-)-shikimic acid**.

# 8. Choose the correct structural formula of A.

- 9. What is the mechanism of synthesis of **A** in this scheme?
  - a.  $S_N 1$
  - $b. \quad S_N 2$
  - c. S<sub>N</sub>2'

- d. E1
- e. E2
- 10. Choose the correct structural formula of **B**.

g. H<sub>3</sub>CO<sub>2</sub>S N COOEt

$$H_3CO_2S$$
 $O_{1}$ 
 $O_{2}$ 
 $O_{2}$ 
 $O_{3}$ 
 $O_{4}$ 
 $O_{2}$ 
 $O_{4}$ 
 $O_{4}$ 
 $O_{5}$ 
 $O_{5}$ 
 $O_{6}$ 
 $O_{7}$ 
 $O_{7}$ 
 $O_{8}$ 
 $O$ 

h.

i. 
$$H_3CO_2S$$
 $N_3$ 
 $N_3$ 

j. H<sub>3</sub>CO<sub>2</sub>S COOEt

### 11. Choose the correct structural formula of **C**.

b. 
$$H_2N$$
 COOEt

$$H_2N$$
e. COOEt

# 12. Choose the correct structural formula of **D**.

a. 
$$H_2N_{1}$$
b.  $H_2N_{2}$ 
COOEt

 $N_3$ 
COOEt

 $N_3$ 
COOEt

d. 
$$H_2N$$
 COOEt  $H_2N$   $N_3$   $N_3$ 

# 13. Choose the correct structural formula of **E**.

COOEt

e. 
$$H_2N$$
 COOEt

- 14. Name the strategy used in this total synthesis to obtain a single enantiomer of the final product.
  - a. kinetic resolution
  - b. chiral catalyst(s)

 $H_2N$ 

d.

- c. chiral pool
- d. chiral auxiliary
- e. chiral reagent(s)
- 15. What is the correct name for the starting material ((-)-shikimic acid) under the IUPAC nomenclature?
  - a. (3R,4S,5R)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid
  - b. (3S,4R,5S)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid
  - c. (3R,4R,5S)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid
  - d. (3S,4S,5S)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid
  - e. (3R,4R,5R)-3,4,5-trihydroxycyclohex-1-ene-1-carboxylic acid
- 16. Choose the correct <sup>1</sup>H NMR spectrum for isooctane
  - a. (1H, d); (2H, t); (6H, t); (9H, s)
  - b. (1H, m); (2H, t); (3H, d); (3H, d); (9H, s)
  - c. (1H, t); (2H, d); (6H, d); (3H, s); (6H; s)
  - d. (1H, m); (1H, d); (1H, d); (6H, d); (9H; s)
  - e. (1H, m); (2H, d); (6H, d); (9H, s)

- 17. The knowledge of the reaction mechanism can be a powerful tool in understanding the reasons for the formation of unexpected products.
  - The mechanism of Hoffmann reaction an important transformation of amides to amines is given below.

Upon studying the reaction of phthalic acid diamide in these conditions, researchers found an unexpected product. Choose the correct structural formula for this product.

Questions 18-22 should be solved together.

In the following scheme, the NMR of compound  $\bf A$  includes 3 signals (singlet, triplet and quartet) and the NMR of compound  $\bf B-4$  signals (2 singlets, triplet and quartet).

A EtONa B 
$$\frac{BrCH_2CN}{EtONa}$$
 C  $\frac{EtONa}{EtOH}$  D  $\frac{B_2H_6}{A}$  E  $\frac{CH_3COCI}{EtOH}$  F NaOH  $H_2O/MeOH$  K  $\frac{1)(CH_3COO)_2Hg}{2)H_3O^+}$  J  $\frac{excess CH_3I}{Ag_2O/H_2O}$  I  $\frac{KOH}{EtOH}$  H  $\frac{Br_2, P}{G}$  G

# 18. Choose the correct structural formula of A.

### 19. Choose the correct structural formula of C.

### 20. Choose the correct structural formula of E.

c. 
$$H_2N$$

21. Choose the correct structural formula of I.

c.

c.

d. 
$$H_2N$$
  $O$   $O$   $O$ 

22. Choose the correct structural formula of K.

23. Choose the correct sequence of reactions to achieve the formation of the product from the starting material in 5 steps:

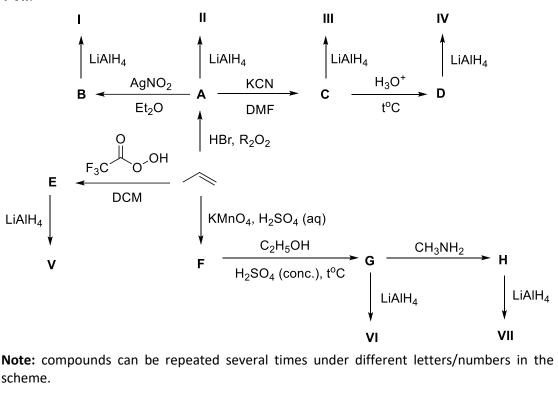
$$HO \longrightarrow OH$$
  $OH$   $OH$ 

- a. 1) MeI; 2) NaBH<sub>4</sub>; 3) HCl, t°C; 4) (COCl)<sub>2</sub>, Et<sub>3</sub>N; 5) CH<sub>2</sub>O, NaH
- b. 1) LiAlH<sub>4</sub>; 2) CH<sub>3</sub>SO<sub>2</sub>Cl; 3) NaCN; 4) H<sub>2</sub>, Pd; 5) KMnO<sub>4</sub>, H<sup>+</sup>;

- c. 1) CH<sub>2</sub>N<sub>2</sub>; 2) MeNH<sub>2</sub>; 3) LiAlH<sub>4</sub>; 4) SOCl<sub>2</sub>; 5) NaBH<sub>4</sub>
- d. 1) MeOH, H<sup>+</sup>; 2) LiAlH<sub>4</sub>; 3) SOCl<sub>2</sub>; 4) NaCN; 5) HCl, t°C
- e. 1) (COCl)<sub>2</sub>, Et<sub>3</sub>N; 2) DIBAL-H; 3) MeMgBr; 4) HCl, t°C; 5) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sup>+</sup>

#### Questions 24-30 should be solved together.

Lithium aluminum hydride is a versatile reagent extensively used in organic synthesis to allow for the formation of numerous functional groups. In the following scheme, find the structural formulas of compounds I-VII:



Note: compounds can be repeated several times under different letters/numbers in the scheme.

#### 24. Choose the correct structural formula of I.

a. 
$$NH_2$$
 d.  $H$  b.  $OH$ 

### 25. Choose the correct structural formula of II.

26. Choose the correct structural formula of III.

a. 
$$\sim$$
 NH<sub>2</sub>

$$h \sim NH_2$$

27. Choose the correct structural formula of IV.

a.

28. Choose the correct structural formula of V.

a.

29. Choose the correct structural formula of VI.

30. Choose the correct structural formula of VII.