

Preparazione per i Giochi della Chimica

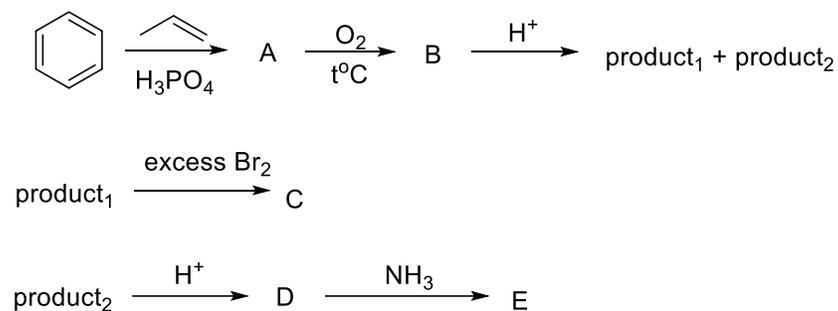
Esercizi di Chimica Organica

Canadian Chemistry Olympiad - Problem Set #4. Organic Chemistry.

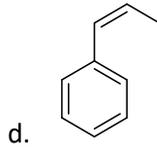
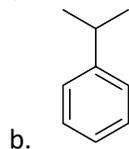
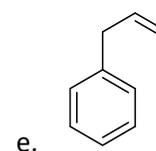
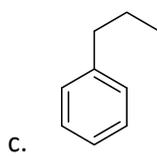
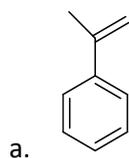
Date: Jan 1, 2025

Le domande 1-5 vanno risolte insieme.

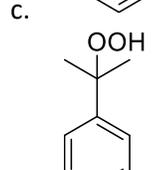
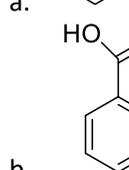
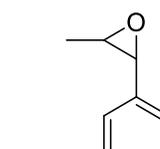
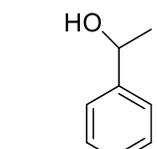
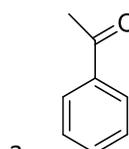
Nel seguente schema, trova le formule di struttura dei composti A-E:



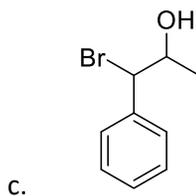
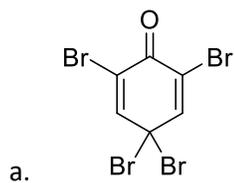
1. Indicare la formula di struttura di **A**.



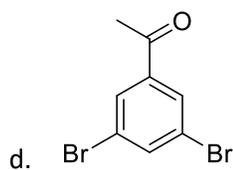
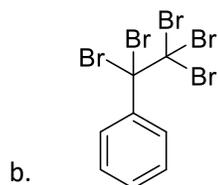
2. Indicare la formula di struttura di **B**.



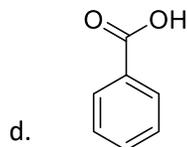
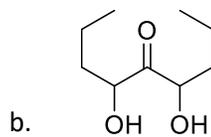
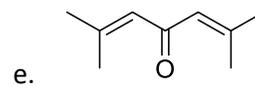
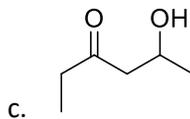
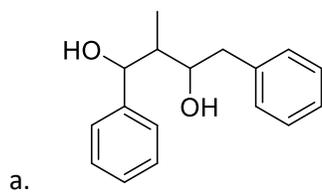
3. Indicare la formula di struttura di C.



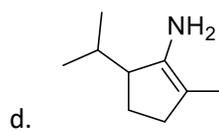
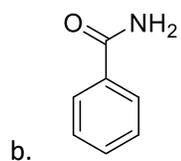
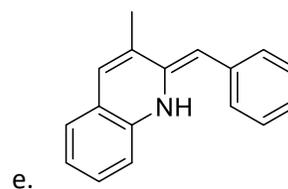
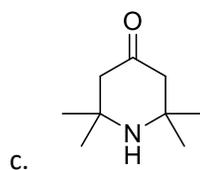
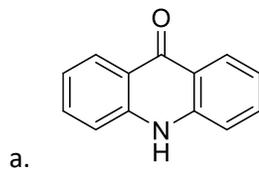
e. CBr_3H



4. Indicare la formula di struttura di D.

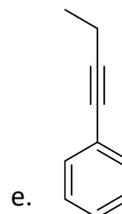
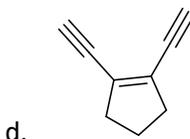
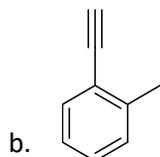
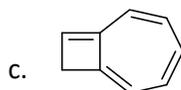
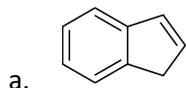


5. Indicare la formula di struttura di E.



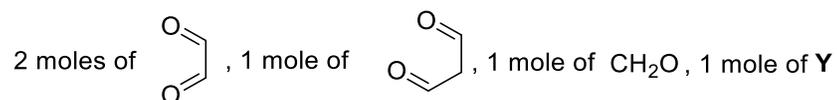
6. L'idrocarburo C_9H_8 per reazione con K forma C_9H_7K e H_2 .
 Con un eccesso di Br_2 forma $C_9H_8Br_2$.
 Per trattamento con una soluzione acida di $KMnO_4$ forma diossido di carbonio e $C_8H_6O_4$.

Indicare la formula di struttura dell'idrocarburo.



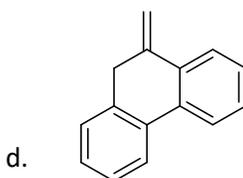
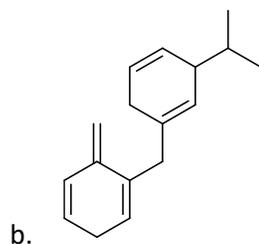
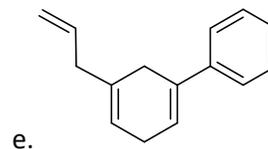
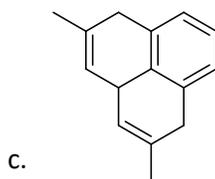
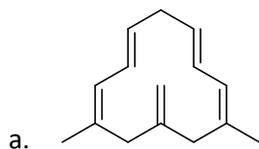
7. Prima dell'avvento dei moderni metodi fisici per la determinazione della struttura molecolari (NMR, IR, spettrometria di massa), i chimici organici si potevano affidare solo a poche e ben note reazioni per rompere un composto incognito in frammenti più piccoli. Esempi di queste tecniche sono l'ozonolisi e l'ossidazione con potassio permanganato in soluzione acida.

1 mole di un composto **X** è stata sottoposta ad ozonolisi, e si sono formati i seguenti prodotti:



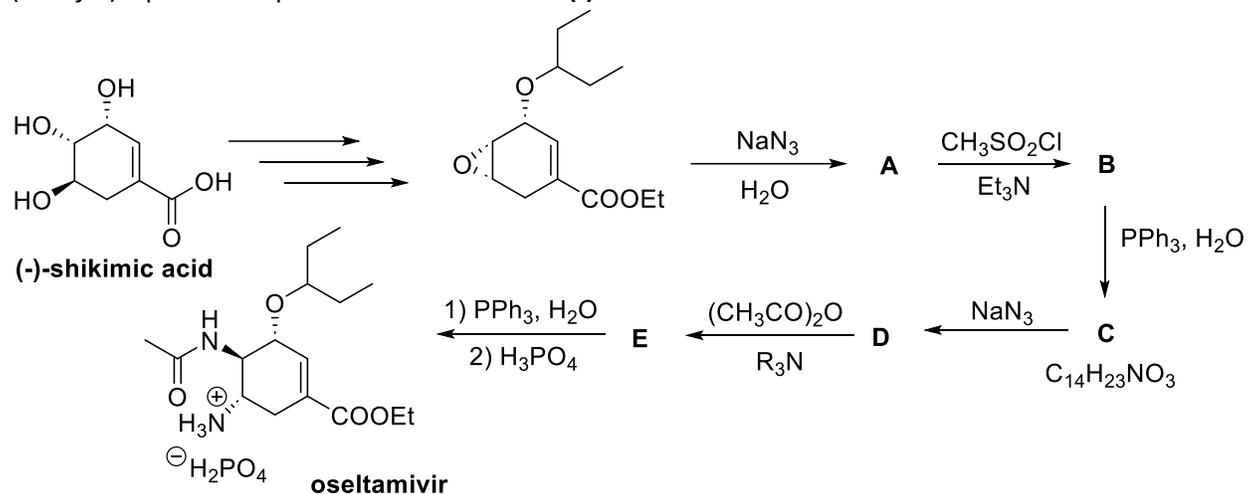
Il composto **Y**, instabile, è stato poi sottoposto ad ossidazione con potassio permanganato in soluzione acida formando 2 moli of CO_2 e 1 mole di un composto simmetrico **Z** (per 1 mole di **Y**), che, per riscaldamento in condizioni acide, ha prodotto 1 mole of acetone e 2 moli di CO_2 (per 1 mole di **Z**).

Indicare la formula di struttura di **X**.

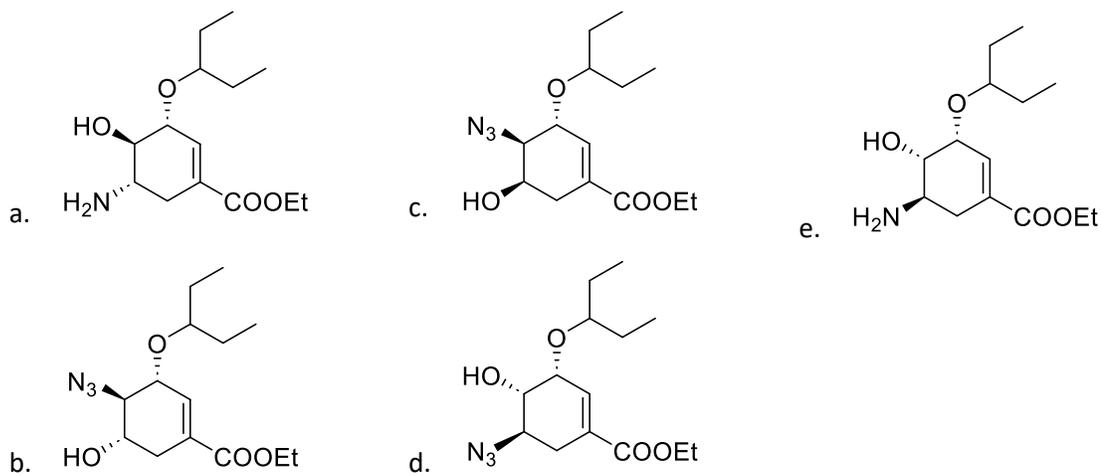


Le domande 8-15 devono essere risolte insieme.

Qui sotto è riportata una parte della sintesi di *Gilead* del farmaco antivirale **oseltamivir** (*Tamiflu*) a partire dal prodotto naturale **acido (-)-shikimico**.



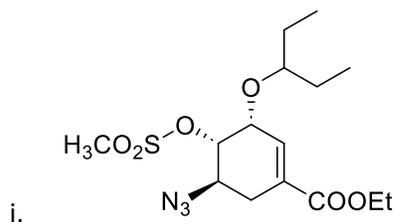
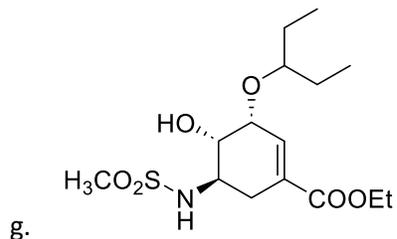
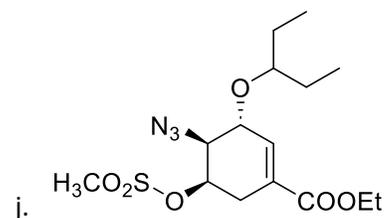
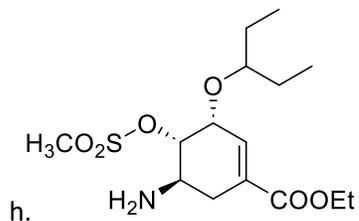
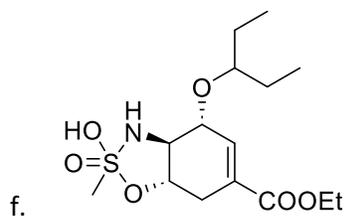
8. Indicare la formula di struttura di **A**.



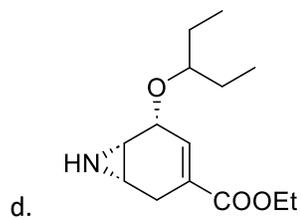
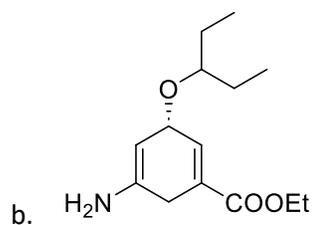
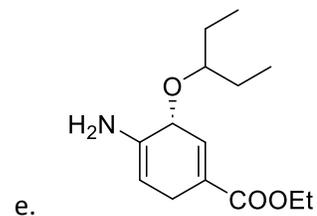
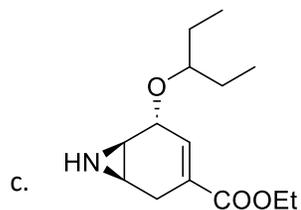
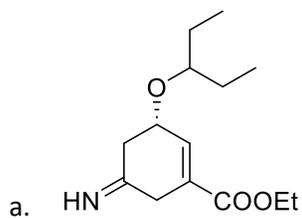
9. Indicare il meccanismo della sintesi di **A** in questo schema.

- | | |
|------------|-------|
| a. S_N1 | d. E1 |
| b. S_N2 | e. E2 |
| c. S_N2' | |

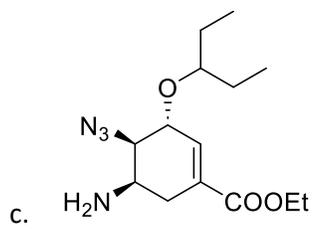
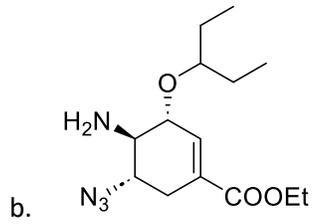
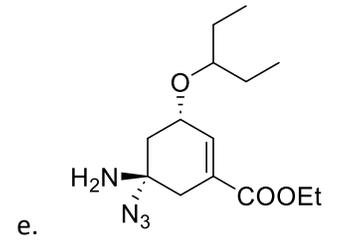
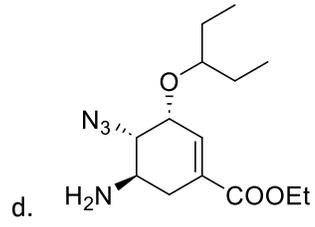
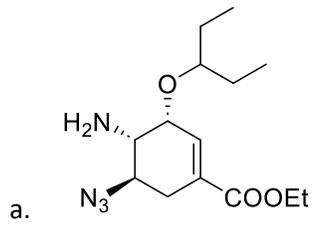
10. Indicare la formula di struttura di **B**.



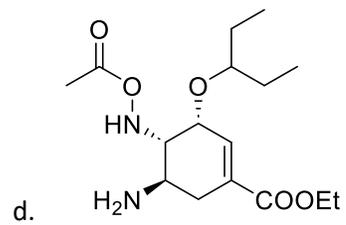
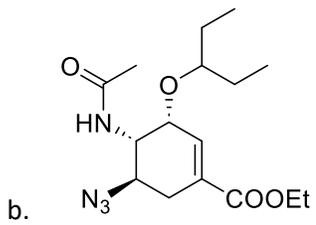
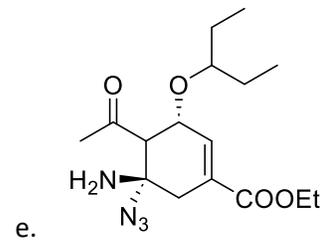
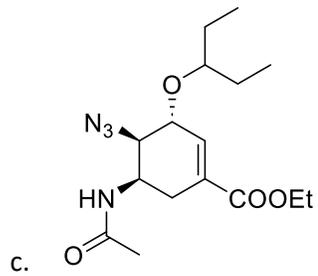
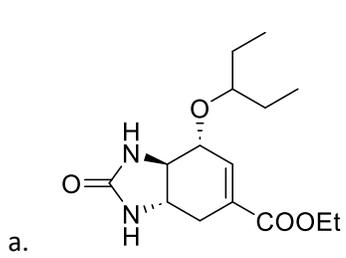
11. Indicare la formula di struttura di **C**.



12. Indicare la formula di struttura di **D**.



13. Indicare la formula di struttura di **E**.



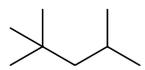
14. Indicare il nome della strategia usata in questa sintesi totale per ottenere un singolo enantiomero del prodotto finale.

- a. risoluzione cinetica
- b. catalizzatori chirali
- c. pool chirale
- d. ausiliari chirali
- e. reagenti chirali

15. Indicare il nome IUPAC della molecola di partenza (acido **(-)-shikimico**).

- a. acido (3*R*,4*S*,5*R*)-3,4,5-triidrossicicloes-1-ene-1-carbossilico
- b. acido (3*S*,4*R*,5*S*)-3,4,5-triidrossicicloes-1-ene-1-carbossilico
- c. acido (3*R*,4*R*,5*S*)-3,4,5-triidrossicicloes-1-ene-1-carbossilico
- d. acido (3*S*,4*S*,5*S*)-3,4,5-triidrossicicloes-1-ene-1-carbossilico
- e. acido (3*R*,4*R*,5*R*)-3,4,5-triidrossicicloes-1-ene-1-carbossilico

16. Indicare i segnali dello spettro ^1H NMR dell'isooottano



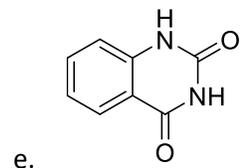
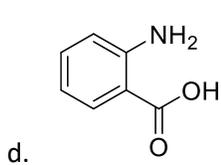
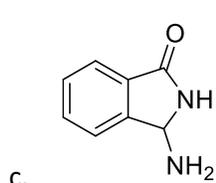
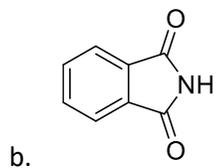
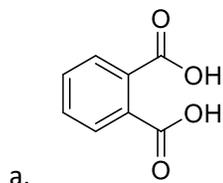
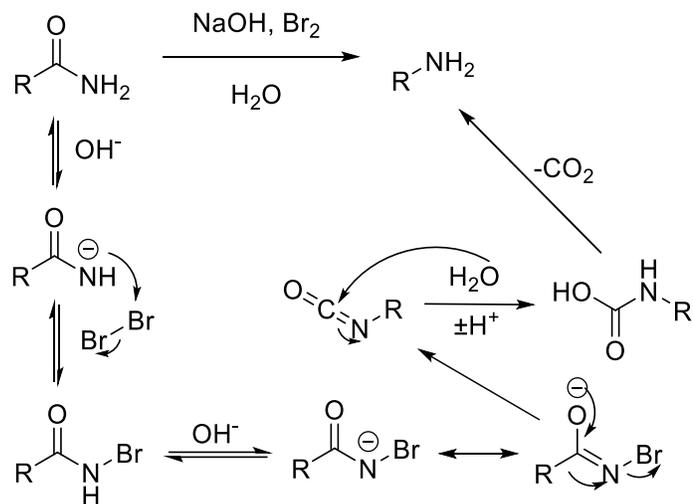
- a. (1H, d); (2H, t); (6H, t); (9H, s)
- b. (1H, m); (2H, t); (3H, d); (3H, d); (9H, s)
- c. (1H, t); (2H, d); (6H, d); (3H, s); (6H, s)
- d. (1H, m); (1H, d); (1H, d); (6H, d); (9H, s)
- e. (1H, m); (2H, d); (6H, d); (9H, s)

17. La conoscenza del meccanismo di reazione è uno strumento potente per capire il motivo della formazione di prodotti inattesi.

Il meccanismo della reazione di Hoffmann – un'importante trasformazione delle ammidi in ammine – è mostrato qui sotto.

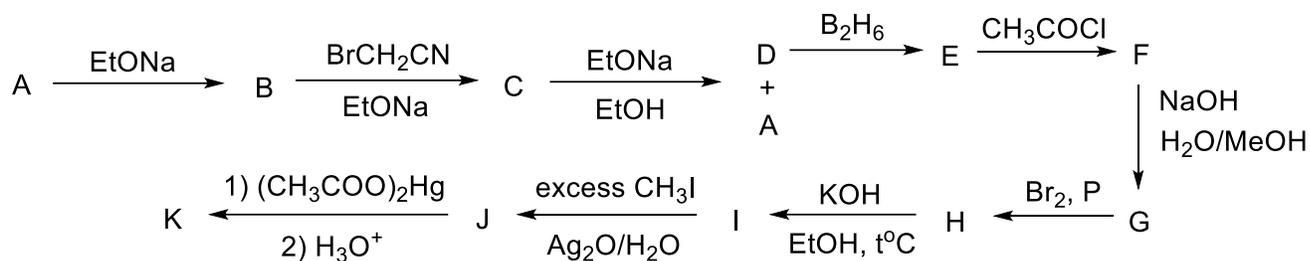
Studiando la reazione della diammide dell'acido ftalico in queste condizioni, i ricercatori hanno trovato un prodotto inatteso.

Indicare la formula di struttura di questo prodotto.

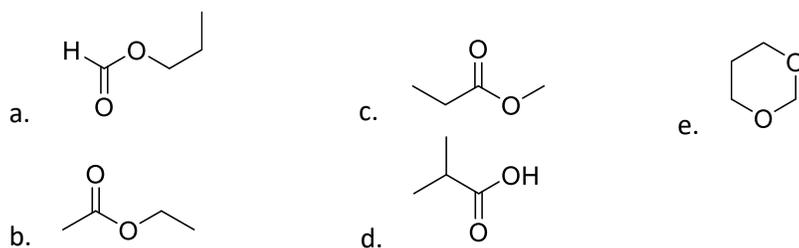


Le domande 18-22 devono essere risolte insieme.

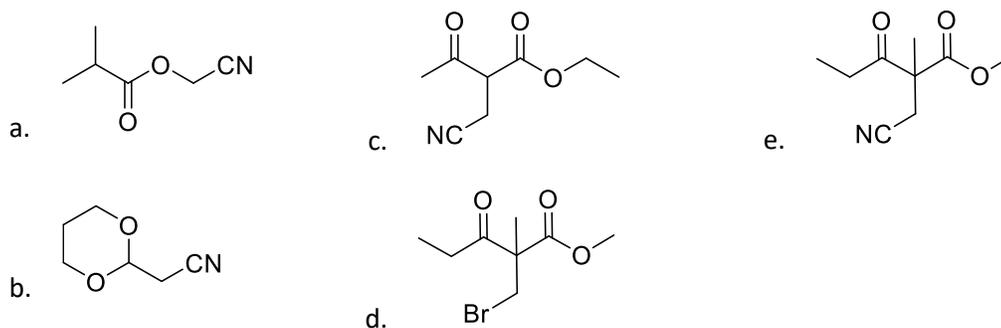
Nello schema seguente, lo spettro NMR del composto **A** mostra 3 segnali (singoletto, tripletto e quartetto) e lo spettro NMR del composto **B** mostra 4 segnali (2 singoletti, tripletto e quartetto).



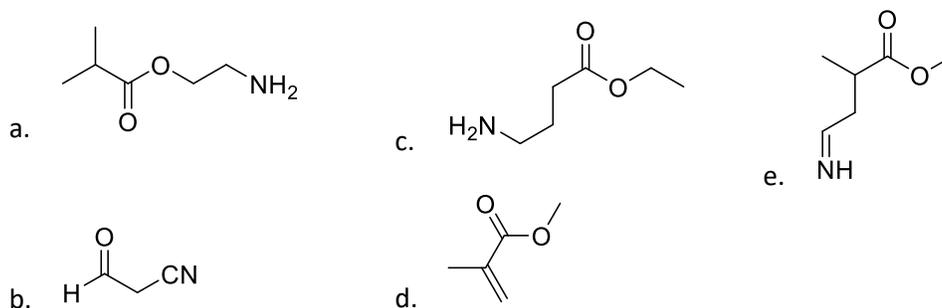
18. Indicare la formula di struttura di **A**.



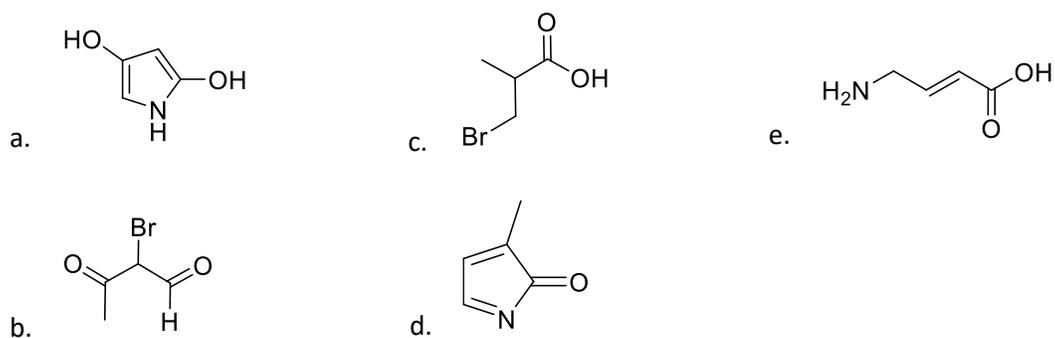
19. Indicare la formula di struttura di **C**.



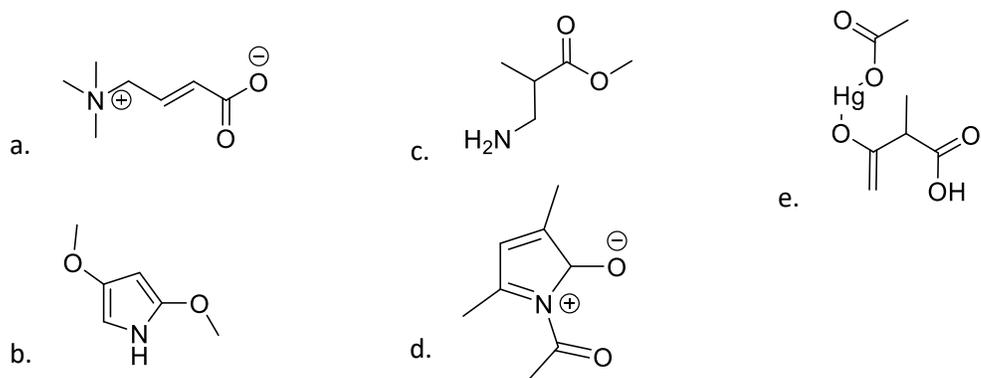
20. Indicare la formula di struttura di **E**.



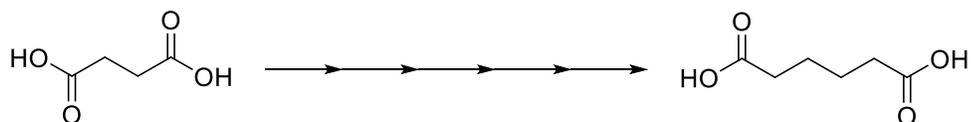
21. Indicare la formula di struttura di I.



22. Indicare la formula di struttura di K.



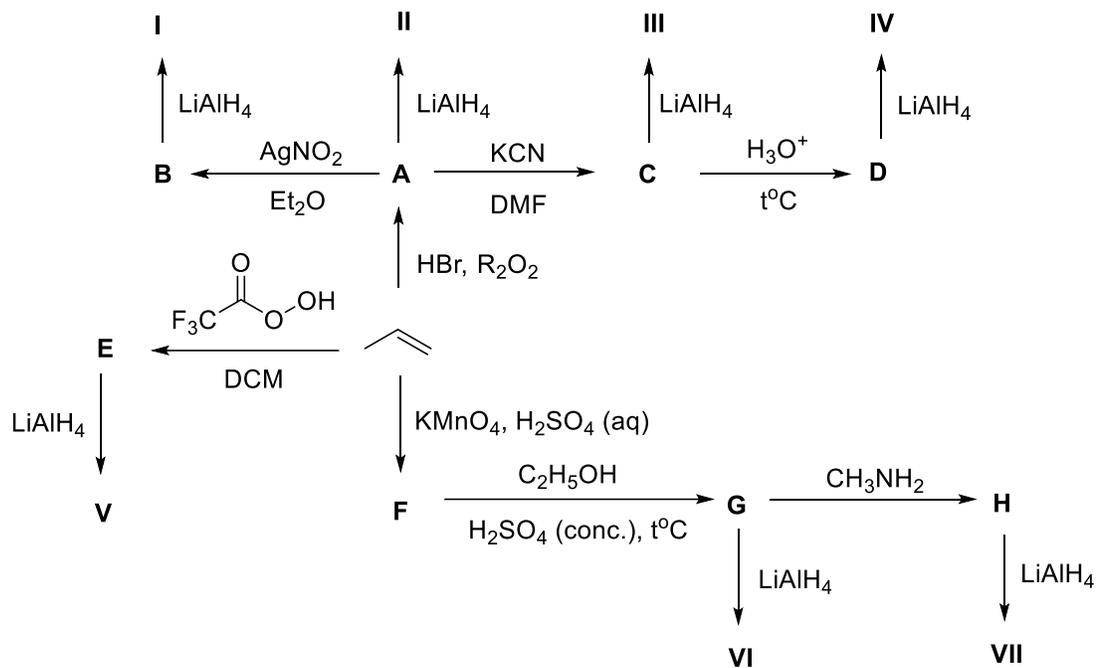
23. Indicare la sequenza di reazioni che permette di ottenere il seguente prodotto dal materiale di partenza n 5 passaggi:



- 1) MeI; 2) NaBH₄; 3) HCl, t°C; 4) (COCl)₂, Et₃N; 5) CH₂O, NaH
- 1) LiAlH₄; 2) CH₃SO₂Cl; 3) NaCN; 4) H₂, Pd; 5) KMnO₄, H⁺;
- 1) CH₂N₂; 2) MeNH₂; 3) LiAlH₄; 4) SOCl₂; 5) NaBH₄
- 1) MeOH, H⁺; 2) LiAlH₄; 3) SOCl₂; 4) NaCN; 5) HCl, t°C
- 1) (COCl)₂, Et₃N; 2) DIBAL-H; 3) MeMgBr; 4) HCl, t°C; 5) K₂Cr₂O₇, H⁺

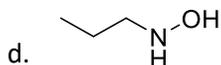
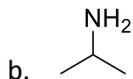
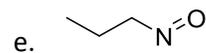
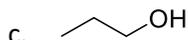
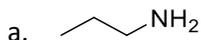
Le domande 24-30 devono essere risolte insieme.

Il litio alluminio idruro è un reagente versatile molto usato nella sintesi organica per ottenere la formazione di numerosi gruppi funzionali. Nel seguente schema, trova la formula di struttura dei composti I-VII:

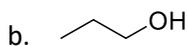
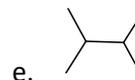
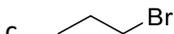
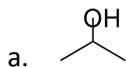


Nota: in questo schema, i composti possono essere ripetuti più volte con lettere o numeri diversi.

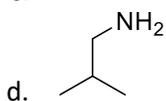
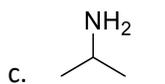
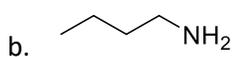
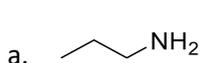
24. Indicare la formula di struttura di I.



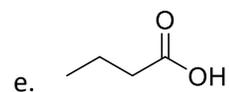
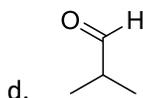
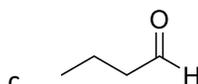
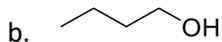
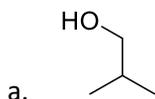
25. Indicare la formula di struttura di II.



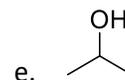
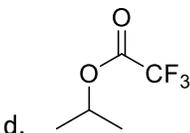
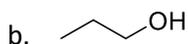
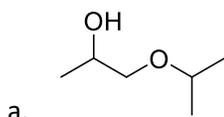
26. Indicare la formula di struttura di **III**.



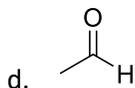
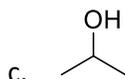
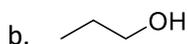
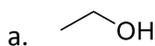
27. Indicare la formula di struttura di **IV**.



28. Indicare la formula di struttura di **V**.



29. Indicare la formula di struttura di **VI**.



30. Indicare la formula di struttura di **VII**.

