/20

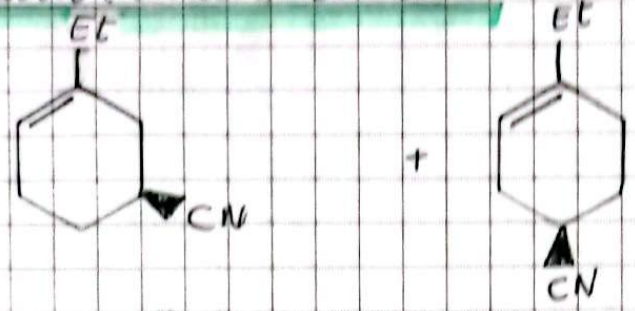
TMCO3 - TD - Corrigé

* Uniquement s'il s'agit d'un examen.

Application directe du cours

Ex 1

1.



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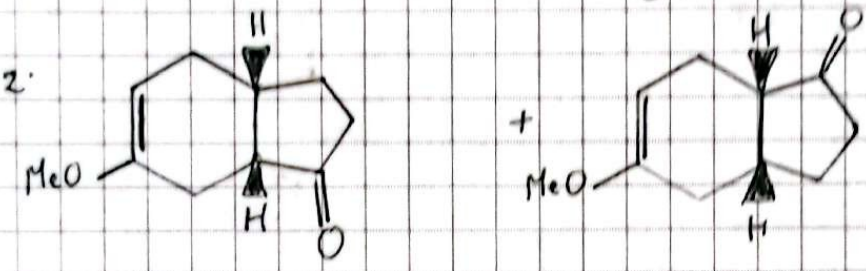

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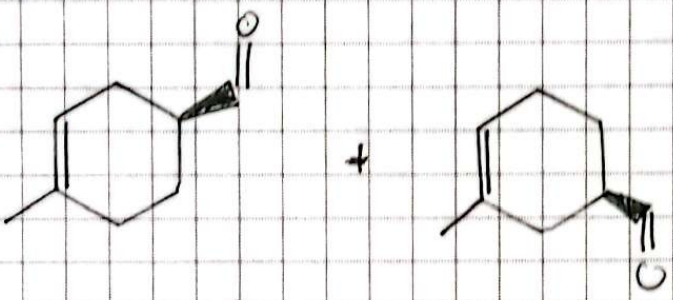

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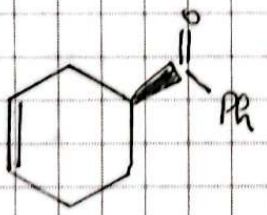

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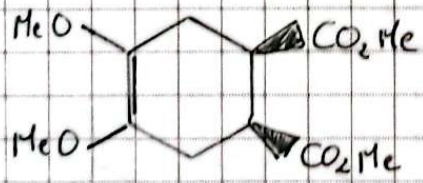

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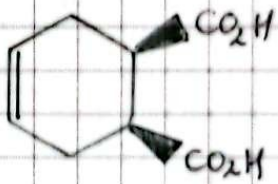

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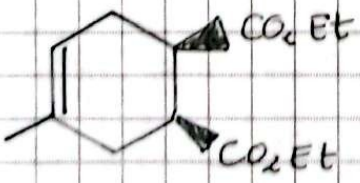

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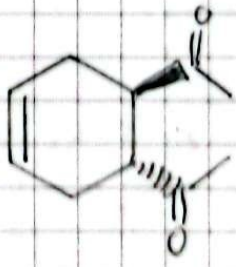

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Ex 2

1.

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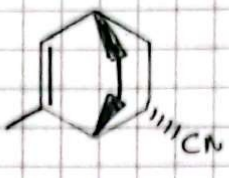

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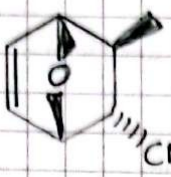

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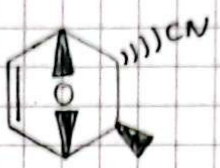

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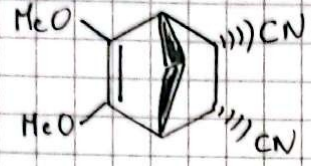

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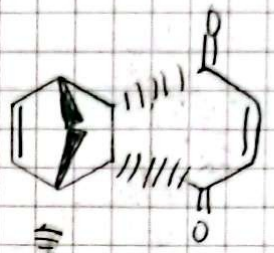

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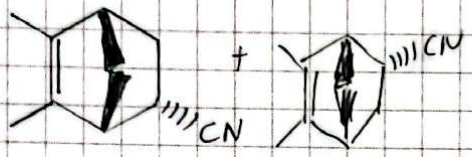

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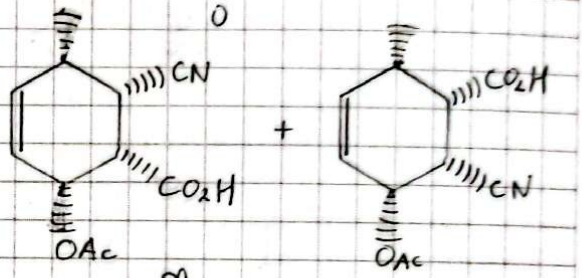

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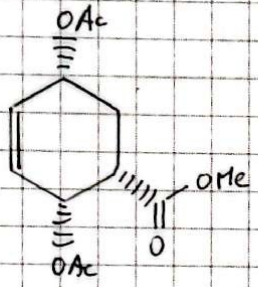

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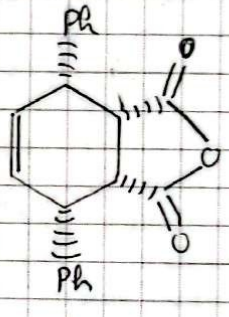

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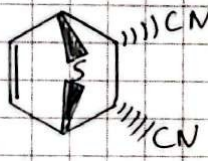

Ex 3

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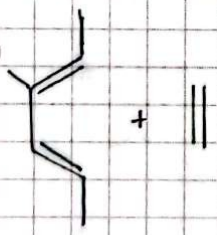

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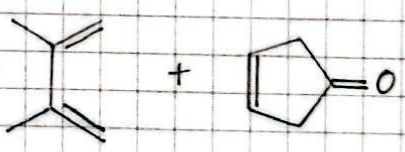

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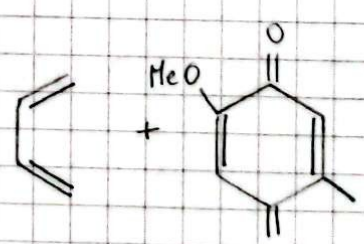

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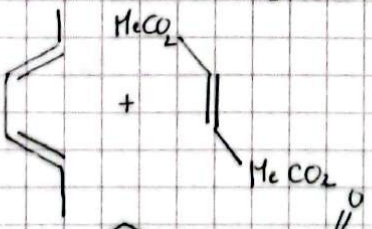

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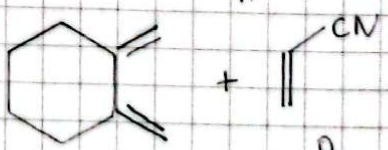

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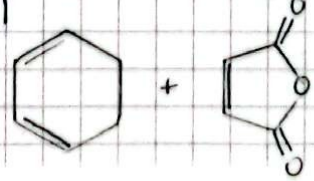

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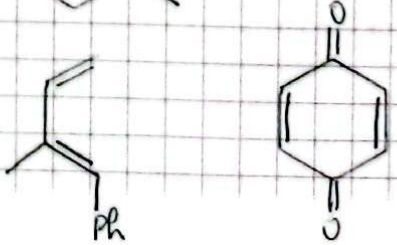

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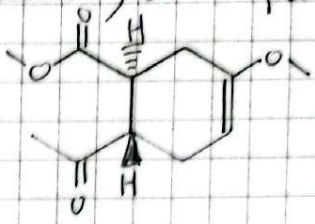
Ex4

1. 2 Carbones asymétriques → 4 stéréoisomères

Comme Diels-Alder est une syn addition, on ne peut obtenir que C et son énantiomère



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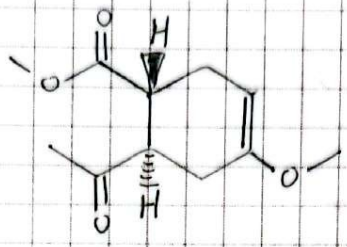

3. Pour A : $HO = \psi_6$ et $BV = \psi_7$ ($12e^- \pi$)

Pour B : $HO = \psi'_4$ et $BV = \psi'_5$ ($8e^- \pi$)

$\psi'_5 - \psi_6 = \alpha - 0{,}65\beta - \alpha - \beta = -1{,}65\beta$

$\psi_7 - \psi'_4 = \alpha - 0{,}09\beta - \alpha - 0{,}54\beta = -0{,}63\beta$

⇒ interaction prépondérante entre ψ_7 et ψ'_4 ⇒ BV_A et HO_B

or A est un dienophile appauvri (2 groupt ester – M) et que B est un diène enrichi (groupt + M) ⇒ la réaction suit la règle d'Alder.

4. Ds ψ_7, C_1 a le plus gros coefficient

Ds ψ'_4, $C_{1'}$ " " " " " "

donc 1 recouvre 1' donc C est bien le regioisomère majoritaire

Ex5

1.

2. Le plus petit écart HO-BV est entre 2 buta-1,3-diène (9,9 eV)

⇒ réaction privilégiée

3. Le ΔE entre B et E est supérieur à $\Delta E_{B\text{-}B}$ → formé + rapidement

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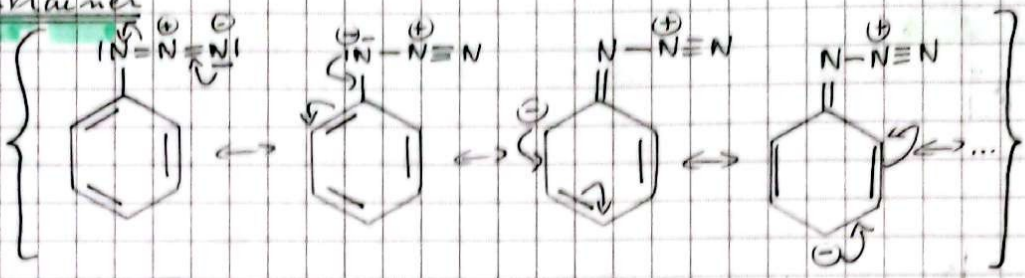
S'entraîner

Ex 1

1.



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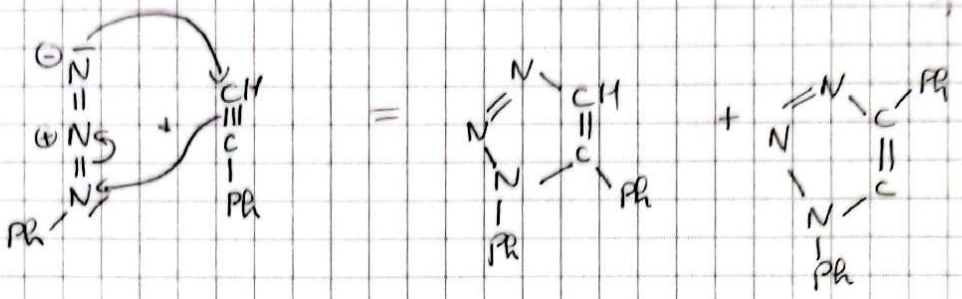
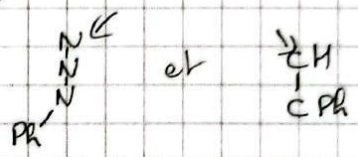
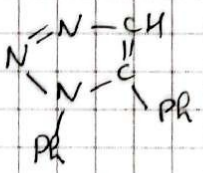


3. Interaction entre BV_A et HO_B (ΔE minimal)

→ interaction entre les 2 + gros lobes



=> C :



ne rien écrire dans la partie barrée

Note : /20

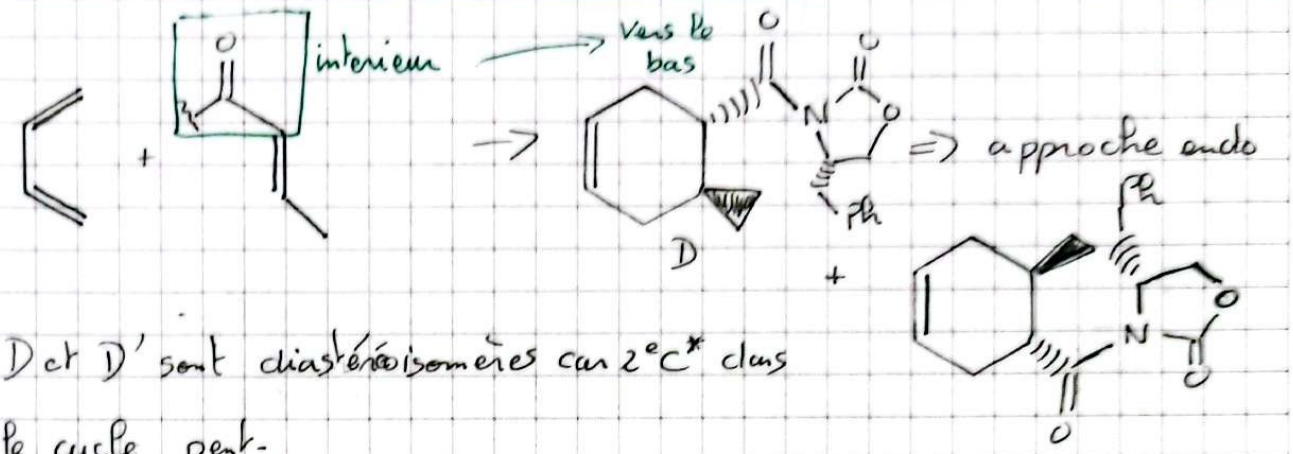
Appréciation du correcteur (uniquement s'il s'agit d'un examen) :

IMCO3 - TD - Corrigé

* Uniquement s'il s'agit d'un examen.

Ex 2

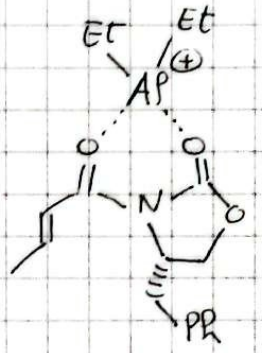
1.



⇒ approche endo

D et D' sont diastéréoisomères car 2 C^* dans le cycle pent.

2.

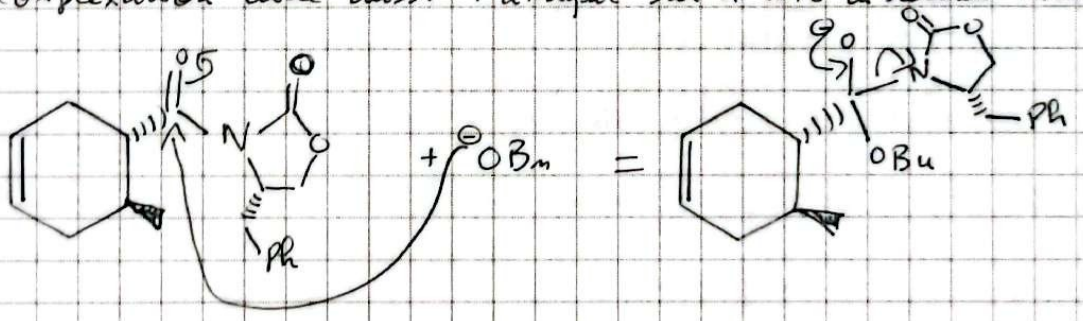


3. Dans D, le butadiène approche en étant moins gêné par CH_2-Ph (pas convaincu)

4. Complexation affaibli les liaisons ⇒ diénophile appauvri en e^-
⇒ réagit + vite

Complexation aide aussi l'attaque sur 1 coté en rendant la molécule plane

5



6. La réaction du butadiène et de F conduit bien à E mais aucune approche n'est privilégiée ⇒ mélange racémique

La stratégie permet une synthèse asymétrique

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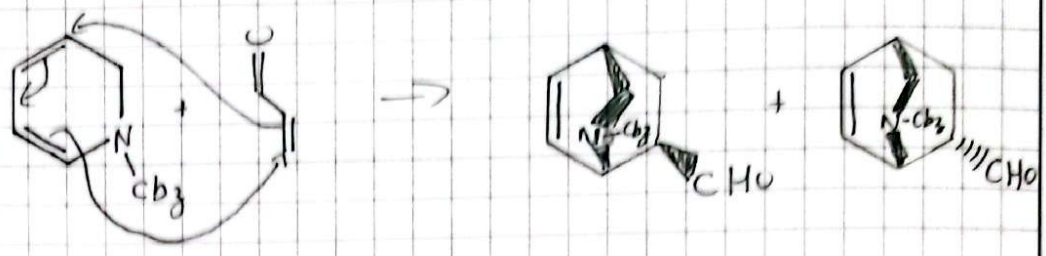
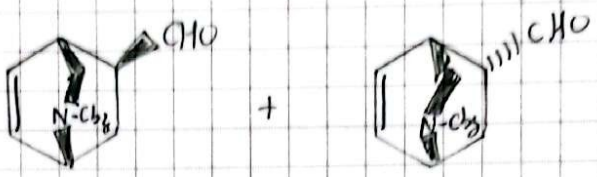
Ex3

1. 

2 

3. Pour A : HO : ψ_2 BV : ψ_3 ($4e^- \pi$)

pour B : HO = ψ_3 BV = ψ_4 ($4e^- \pi$ + doublet nl)

$\Delta E_1 = E_{HO_B} - E_{BV_A} = -7,12 + 0,14 = -6,98$

$\Delta E_2 = E_{BV_B} - E_{HO_A} = 4,06 + 11,01 = 15,07$

⇒ interaction entre BV_A et HO_B

⇒ meilleur recouvrement : C_{1A} et C_{5B}

⇒ 1 isomère C plutôt que D

4. Approche endo dit que CHO passe en dessous ⇒ C_1 plutôt que C_2

5. Technique de RMN par exemple.

Ex4

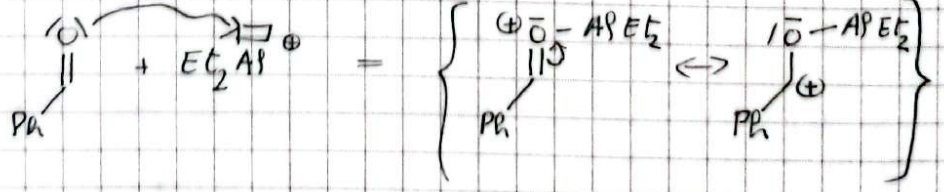
1. $\Delta E_1 = E_{BV_A} - E_{HO_B} = 14,99$ eV

$\Delta E_2 = E_{BV_B} - E_{HO_A} = 11,37$ eV

⇒ interaction entre HO de A et BV de B

Sur A, le plus gros lobe est sur C_4 mais plus délocalisé sur B

⇒ données insuffisantes

2. 

⇒ fragilise C=O, abaisse Pa BV du diénophile ⇒ accelère Pa réaction

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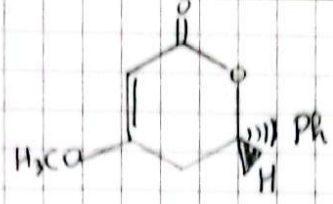
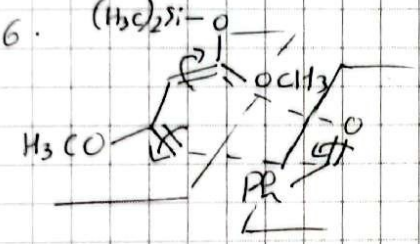
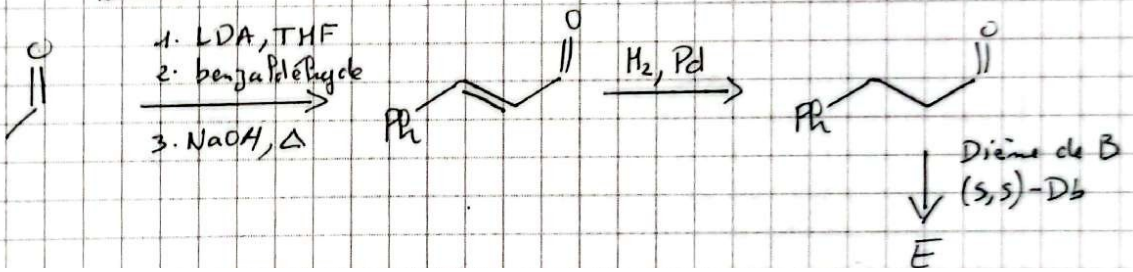
3. 

composé 5

4. Paramètres qui augmente l'énantiosélectivité
   - Encombrement du catalyseur (1 vs 2-3-4)
   - Pa faible T (3 vs 2)
   - Pa proportion de catalyseur (3 vs 4)
   - Le positionnement du groupe Dxc (3 vs 5)

5. Le H le plus accessible est celui le ⊕ à droite de la figure

6. 

7. 

Ex 5.

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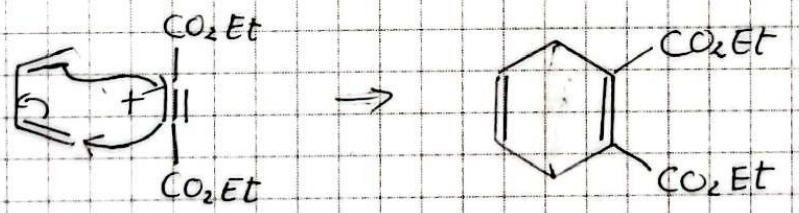

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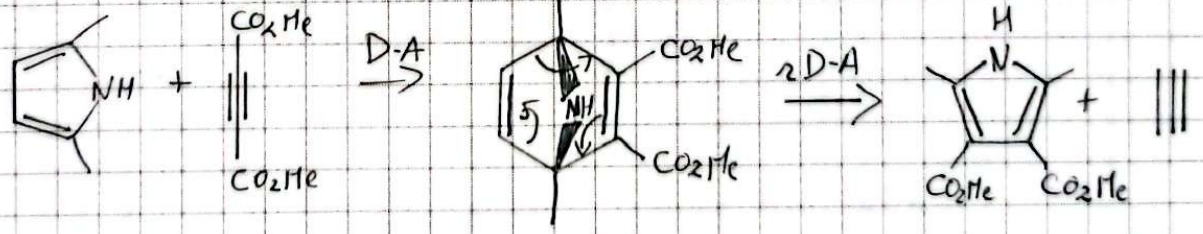

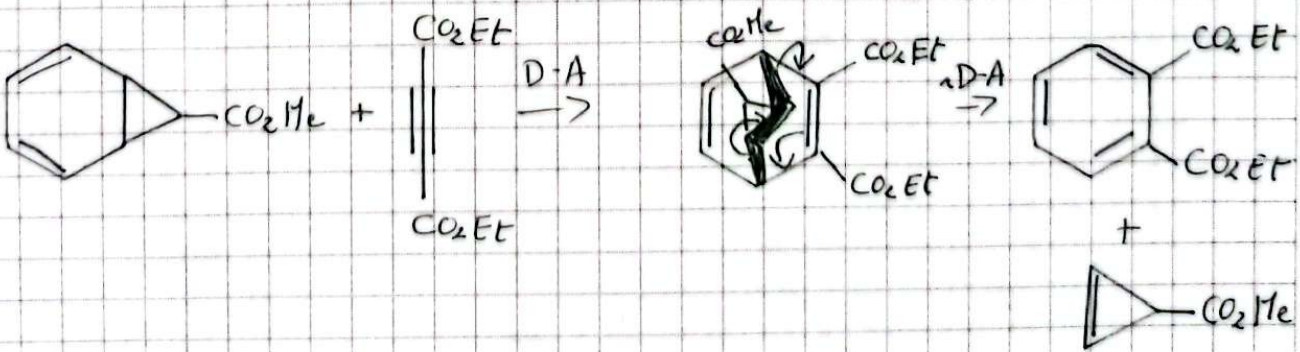

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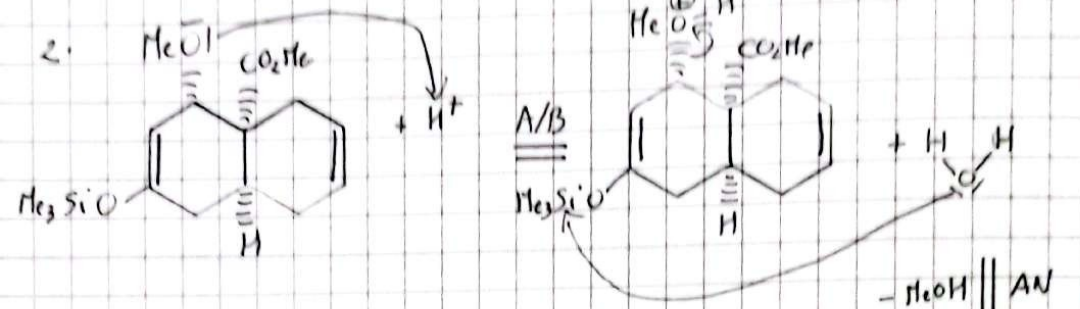
Il est interdit aux candidats de signer leur composition ou d'y mettre un signe quelconque pouvant indiquer sa provenance.

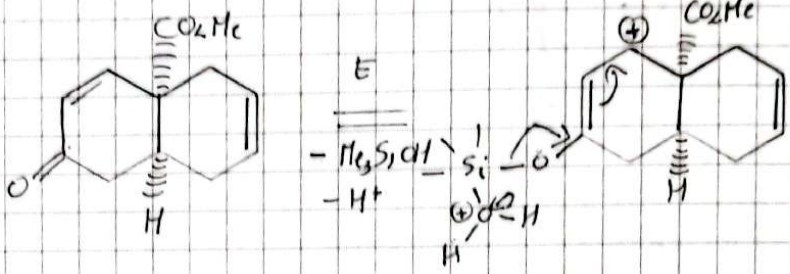
Approfondis

Ex 1

1. Approche endo.

2.





Ex 2

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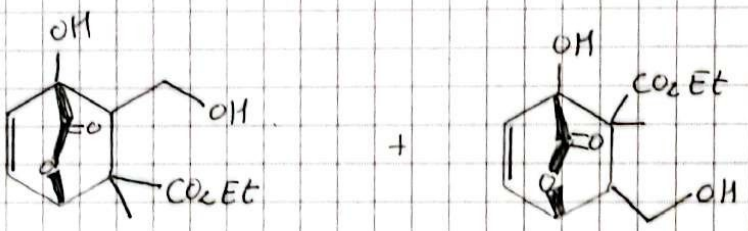
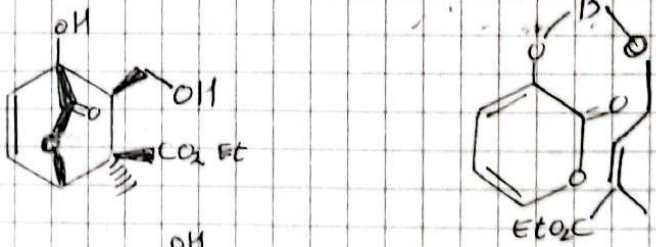
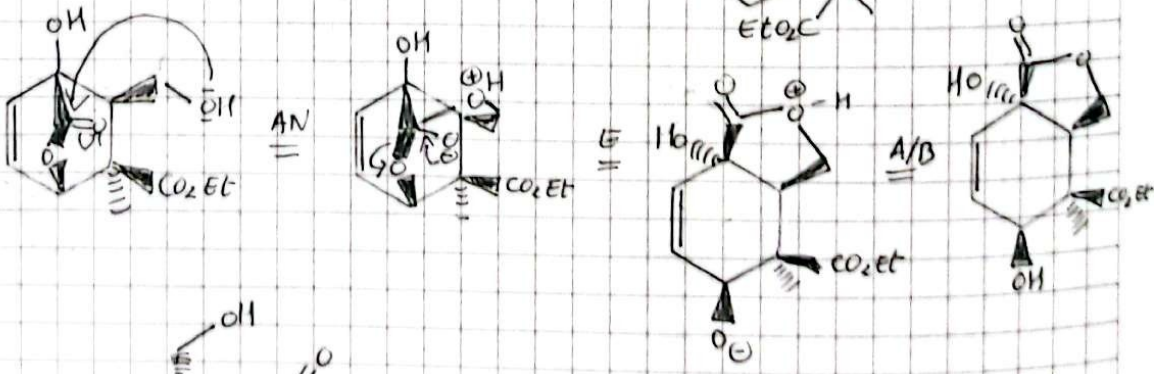


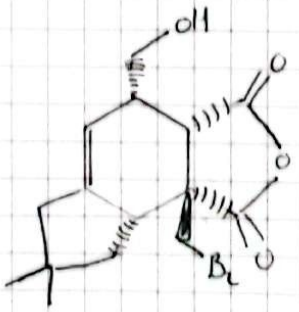
2. Diels-Alder intramoléculaire



3.



4. F



par approche endo.

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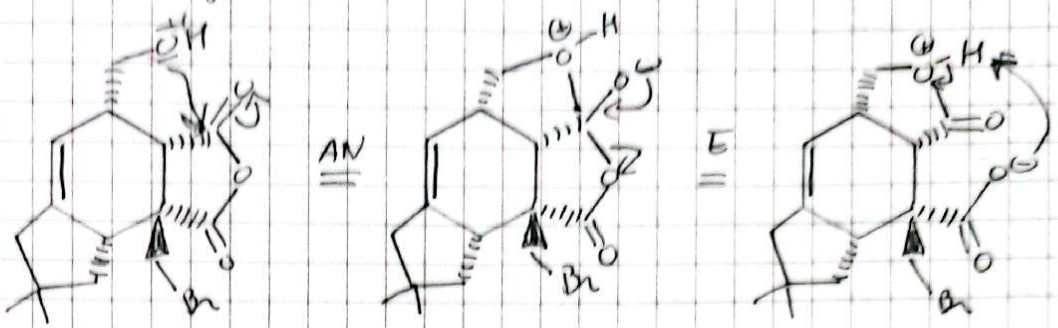
.../...

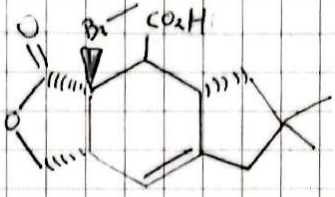
5. Transesterification



II A/B

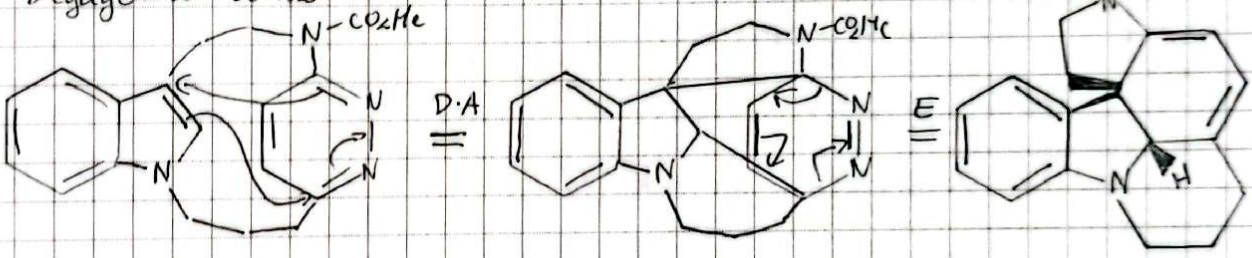
G

6.

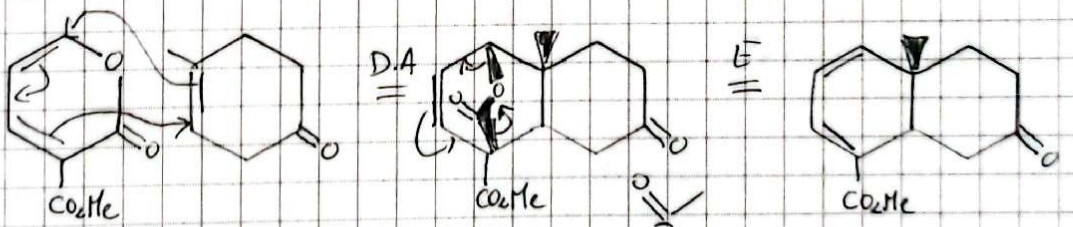


EX3

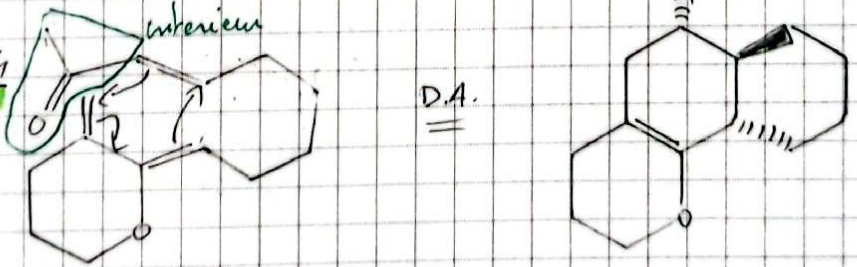
1 Dégagement de N_2



2.

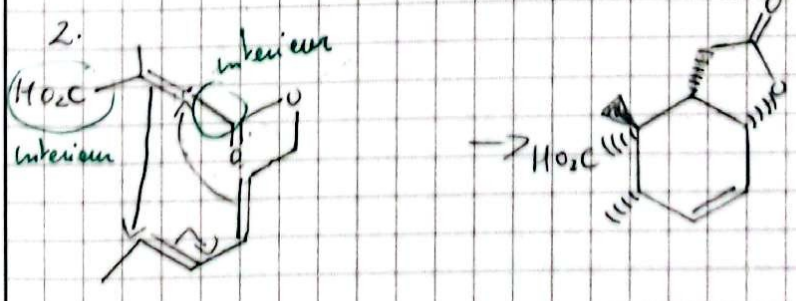


EX4



1.

2.



N°

.../...