

BÖLÜM 9

PROBLEMLER II

HETEROATOMLAR VE HETEROSİKLIK BİLEŞİKLER

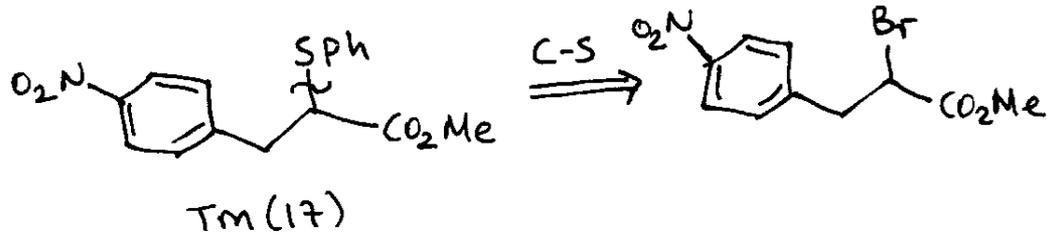
4. PROBLEMLER

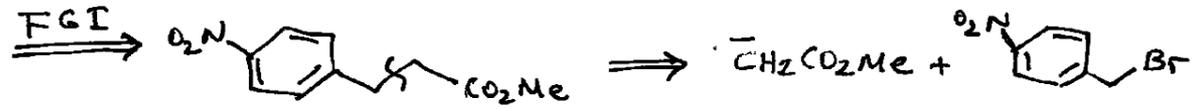
Heterosiklikler ve heteroatomlar ile ilgili bilgileri pekiştirmek için üç problem hazırlanmıştır. Bunlardan ilk ikisi kükürt içermektedir. Kükürt atomu, oksijen atomu gibi düşünülebilir.

Problem 1: Tm(17) bileşiğinin sentez tasarımını

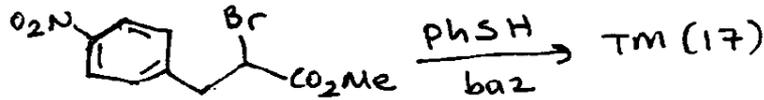
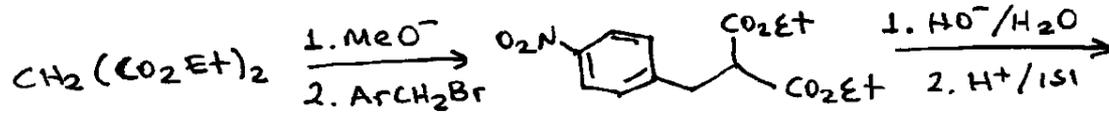
yapınız.

Analizi:



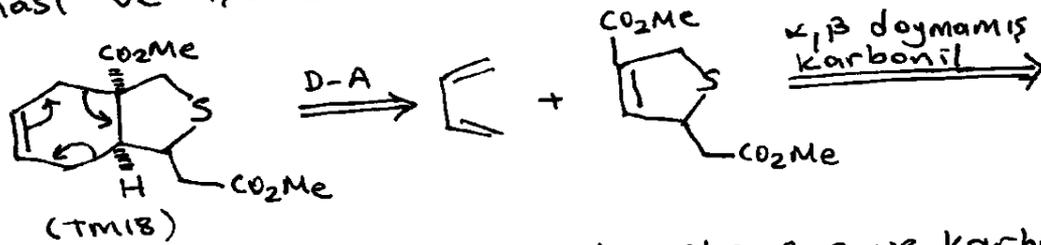


Sentezi: pHSH kolayca hazırlanabilir.

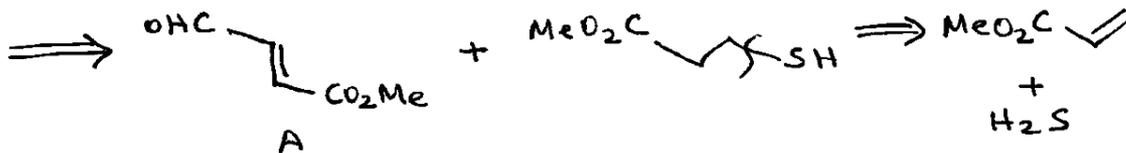


Problem 2: (TM 18) bileşiğinin sentez tasarımını yapınız.

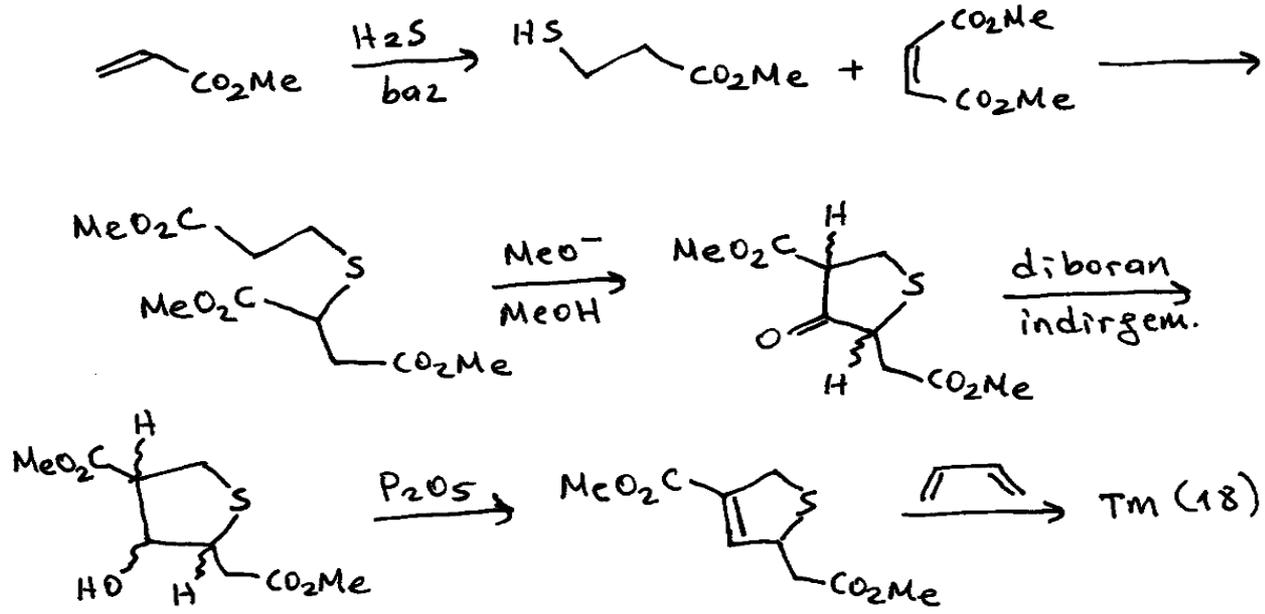
Analizi: Bazı C-S bağları için Diels-Alder parçalanması ve 1,6-dikarbonil bağıntısı kullanılabilir.



Burada, her iki C-S ve karbonil C-C bağları ters Michael reaksiyonu ile sıra ile parçalanır.

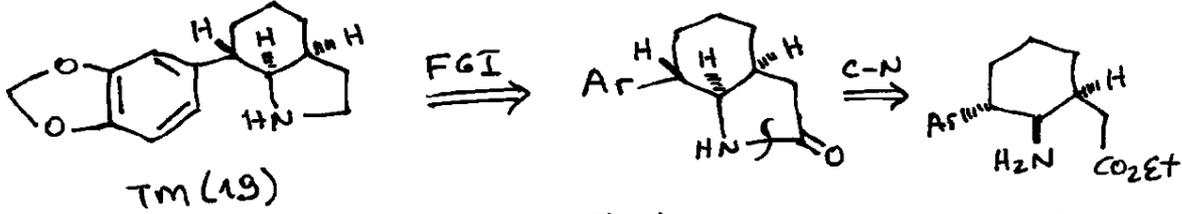


Sentezi: öncelikle A reaktifinden (synthon) senteze başlamak oldukça zor olacaktır. Bunu kolaylaştırmak için diester'e dönüştürmek gerekecektir. Bu bileşiğin gerçek sentezi Stork tarafından yapılmıştır (J. Amer. Chem. Soc., 1969, 91, 7780).



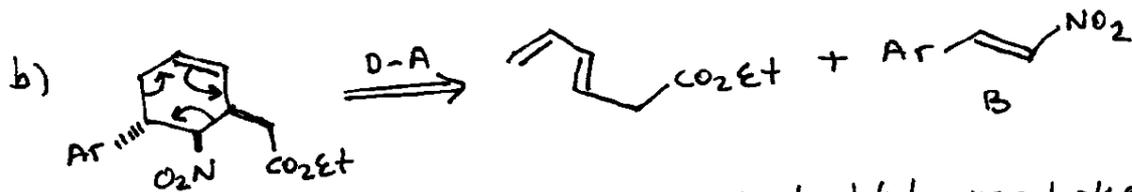
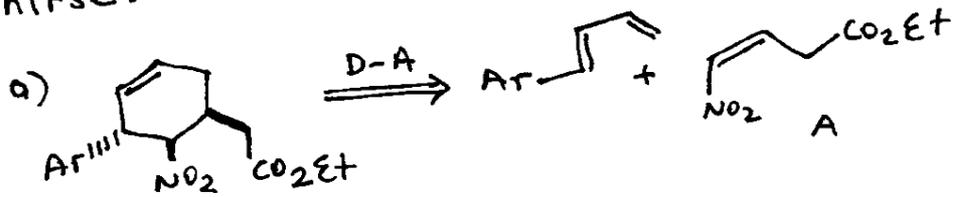
Problem 3: Aşağıdaki bileşiği (TM 19) analiz ederek sentezini yapınız.

Analizi: Belkide şimdiye kadar görülen soruların en zoru. Bir çok çözüm yolu öngörülebilir ve burada yalnızca biri verilecektir.



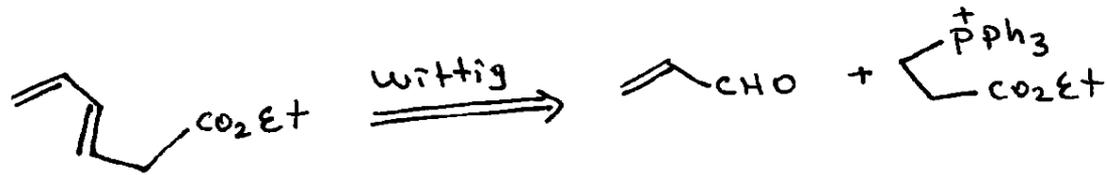
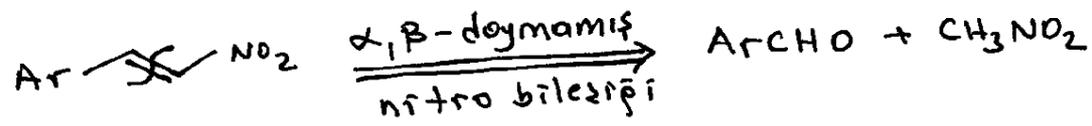
TM(19)'da N atomuna bağlı bir CH_2 - grubu olduğundan, genel amin sentezinde olduğu gibi karbonil grubu yerleştirilir (FGI).

ikinci aşamada, altılı halkada parçalanma yapılmalıdır. Bunun için Diels-Alder reaksiyonu düşünülmelidir. Yerleştirilecek çift bağın yeri için iki alternatif yol vardır, eğer NH_2 grubunu ihtiyacı duyulan alternatifleştirici bir gruba dönüştürmek istenirse:

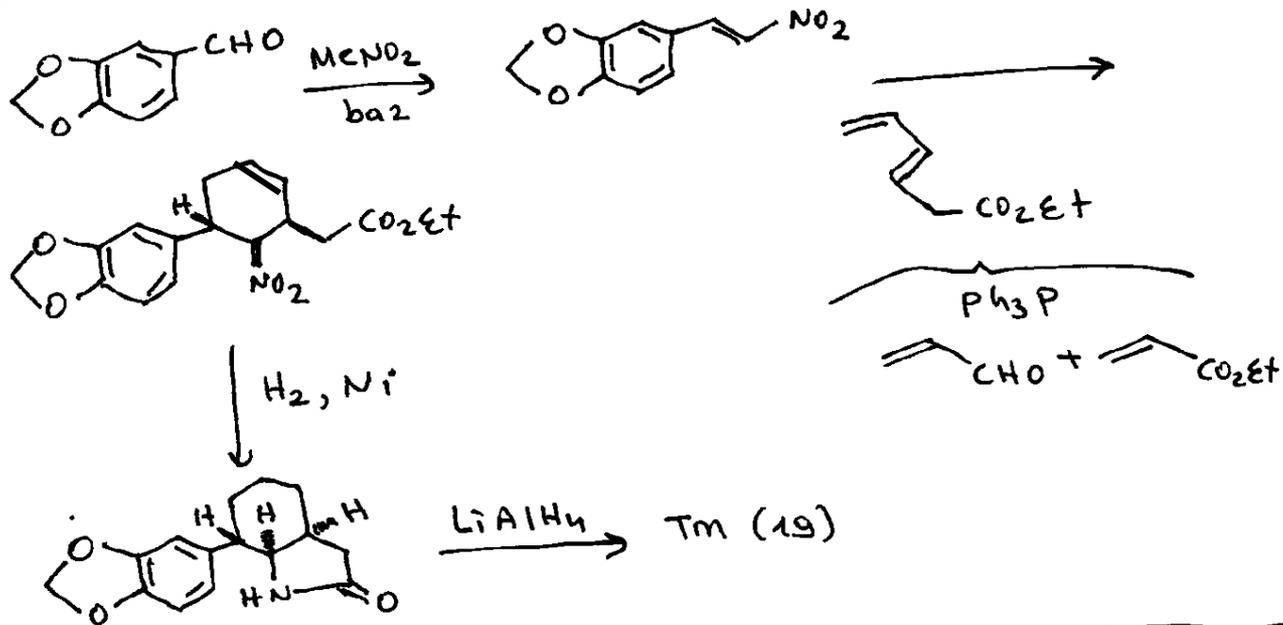


(b) yoluyla trans-nitro-alken kolaylıkla yapılırken (a) yoluyla elde edilen cis-nitroalken (A) sentezi zor olacaktır.

şimdi (b) yoluna göre analizini düşünelim:

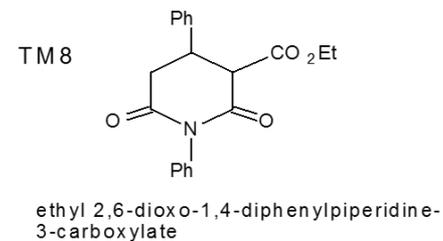
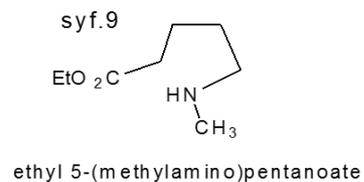
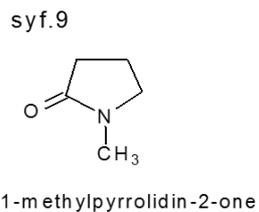
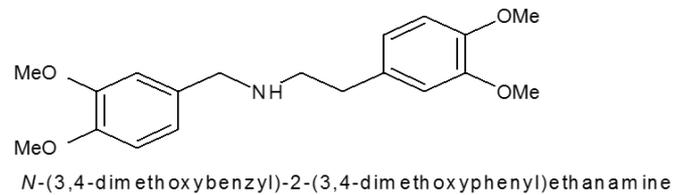
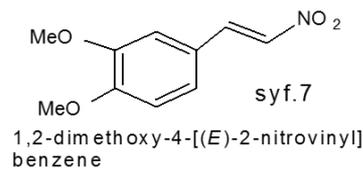
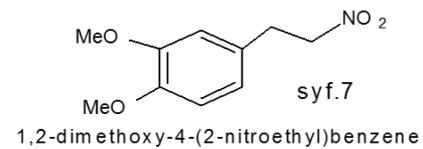
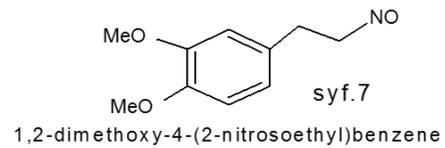
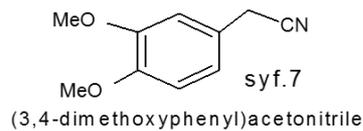
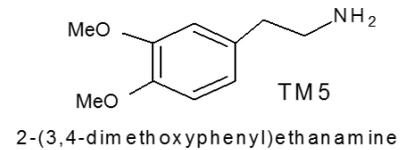
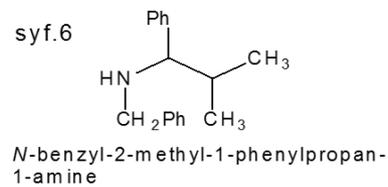
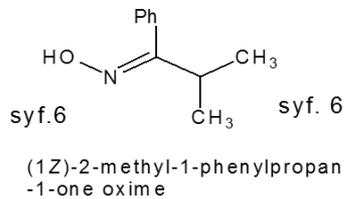
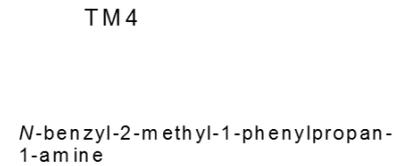
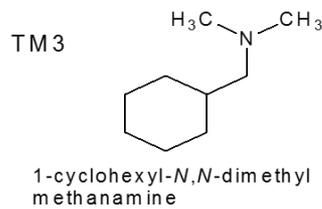


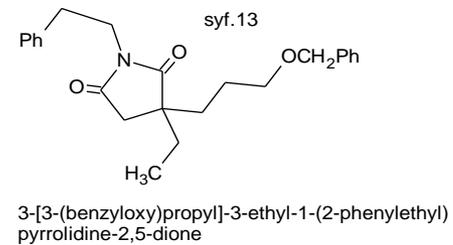
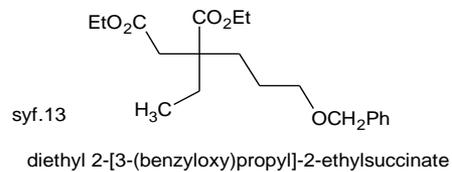
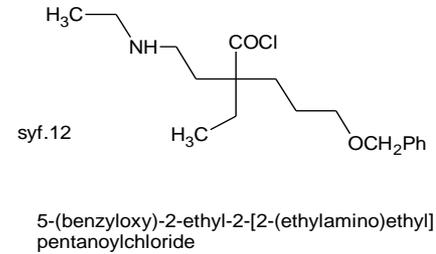
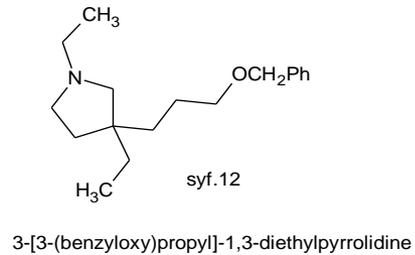
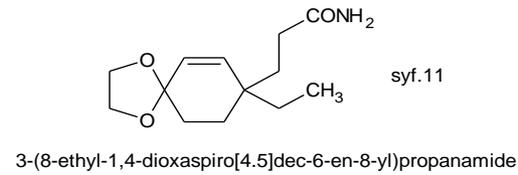
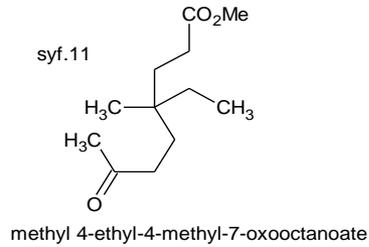
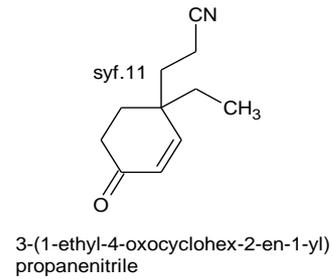
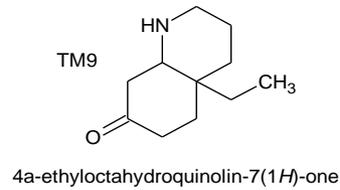
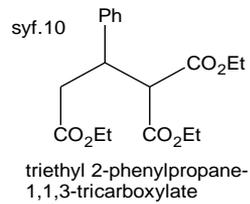
Sentezi: Sentezi, α -lycorane sentezinde kullanılan yöntemi içerir (J. Amer. Chem. Soc., 1962, 84, 4951).



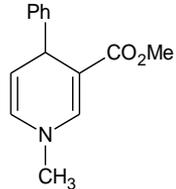
BÖLÜM SONU

Bölüm 7 : Bileşiklerin adlandırılması

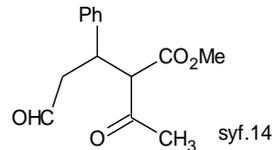




syf. 14

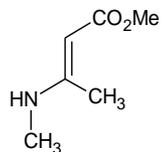


Methyl 1-methyl-4-phenyl-1,4-dihydropyridine-3-carboxylate



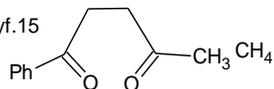
methyl 2-acetyl-5-oxo-3-phenylpentanoate

syf. 14



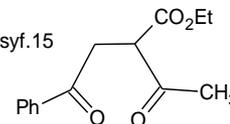
methyl (2E)-3-(methylamino)but-2-enoate

syf. 15



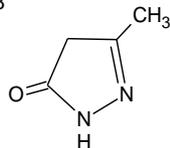
1-phenylpentane-1,4-dione

syf. 15

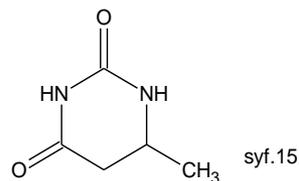


ethyl 2-acetyl-4-oxo-4-phenylbutanoate

TM13



5-methyl-2,4-dihydro-3H-pyrazol-3-one

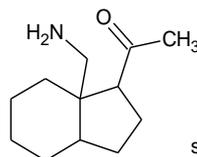


6-methyldihydropyrimidine-2,4(1H,3H)-dione

TM15

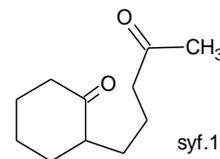


2,4,5,5a,6,7,8,9-octahydro-1H-indeno[1,7a-c]pyrrole



syf. 17

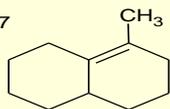
1-[7a-(aminomethyl)octahydro-1H-inden-1-yl]ethanone



syf. 17

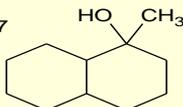
2-(4-oxopentyl)cyclohexanone

syf.17



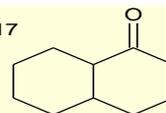
8-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalene

syf.17



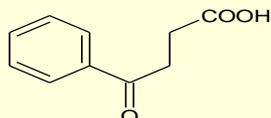
1-methyldecahydronaphthalen-1-ol

syf.17



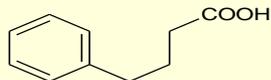
octahydronaphthalen-1(2H)-one

syf.18

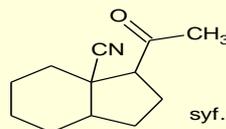


4-oxo-4-phenylbutanoic acid

syf.18

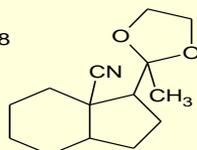


4-phenylbutanoic acid

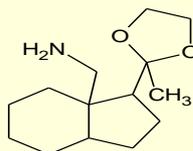


3-acetyloctahydro-3aH-indene-3a-carbonitrile

syf.18

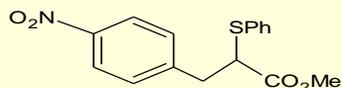


3-(2-methyl-1,3-dioxolan-2-yl)octahydro-3aH-indene-3a-carbonitrile



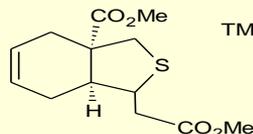
1-[3-(2-methyl-1,3-dioxolan-2-yl)octahydro-3aH-inden-3a-yl]methanamine

TM (17)



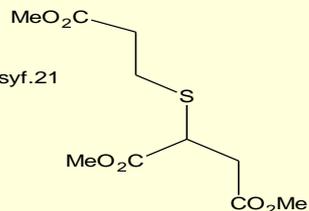
methyl 3-(4-nitrophenyl)-2-(phenylthio)propanoate

TM (18)

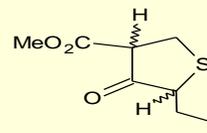


methyl (3aR,7aS)-1-(2-methoxy-2-oxoethyl)-1,4,7,7a-tetrahydro-2-benzothiophene-3a(3H)-carboxylate

syf.21

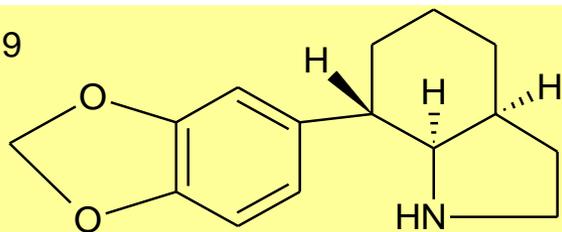


dimethyl 2-[(3-methoxy-3-oxopropyl)thio]succinate



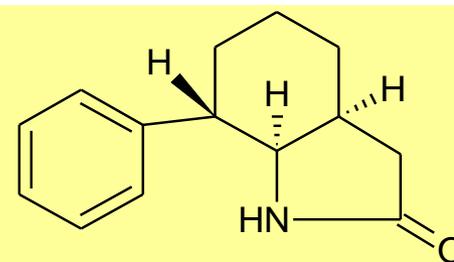
methyl 5-(2-methoxy-2-oxoethyl)-4-oxotetrahydrothiophene-3-carboxylate

TM19



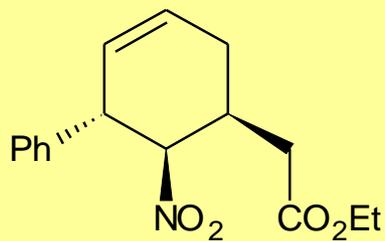
(3a*S*,7*S*,7a*R*)-7-(1,3-benzodioxol-5-yl)
octahydro-1*H*-indole

syf.22

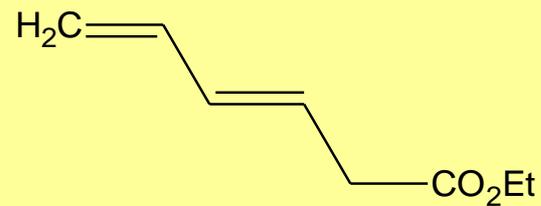


(3a*S*,7*S*,7a*R*)-7-phenyloctahydro-2*H*-indol-2-one

syf.22



ethyl [(1*S*,5*S*,6*R*)-6-nitro-5-phenylcyclohex-
3-en-1-yl]acetate



ethyl (3*E*)-hexa-3,5-dienoate