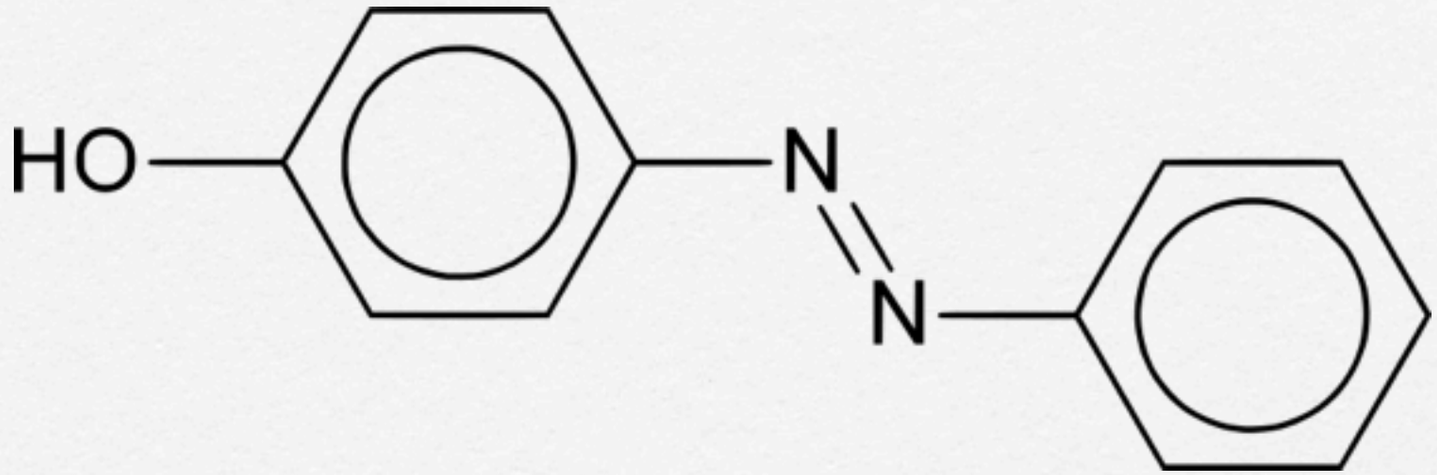
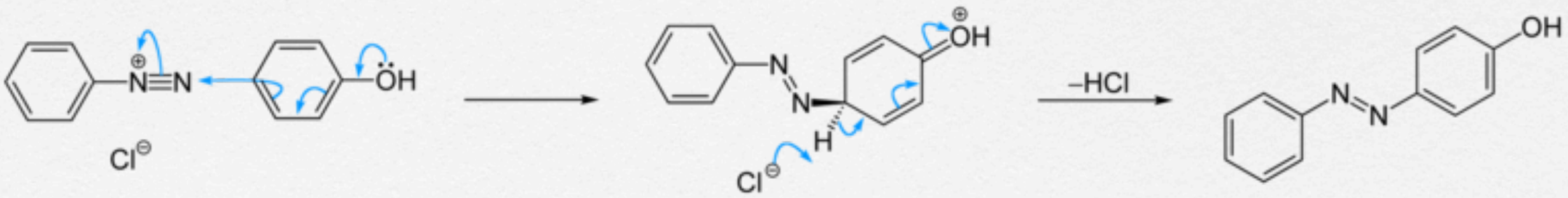
organic dyes

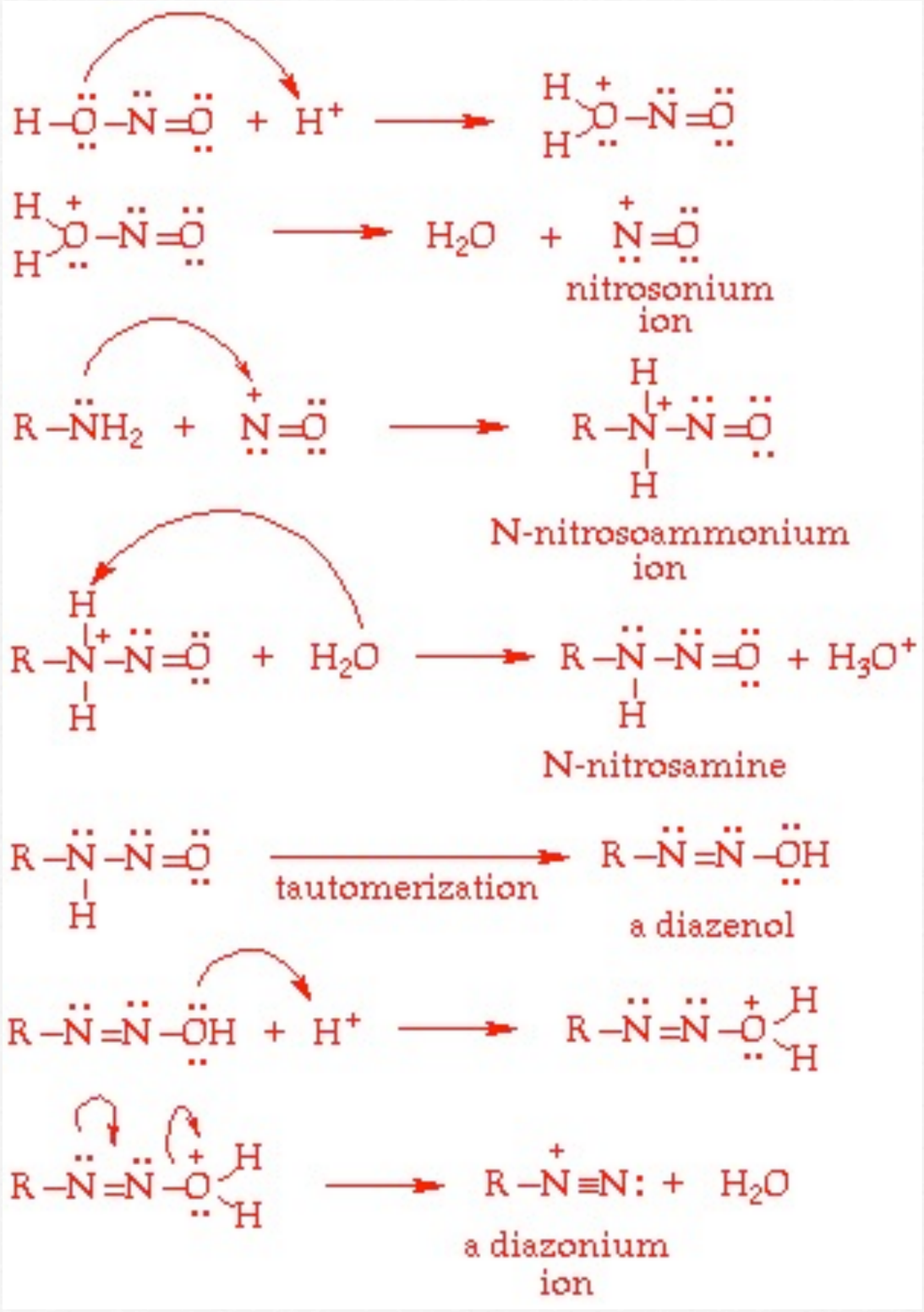
a short introduction

azo dyes

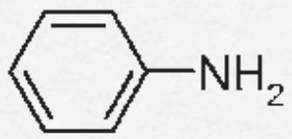




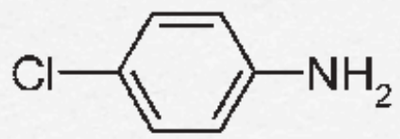
formation of diazonium ion



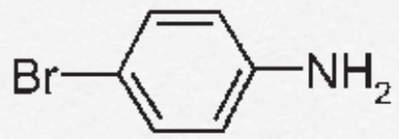
anilines & phenols



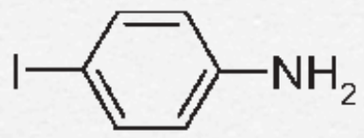
1a



1b



1c



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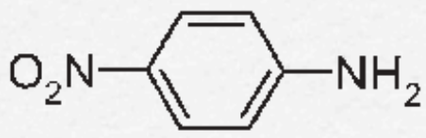

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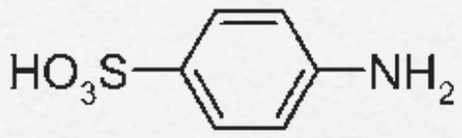
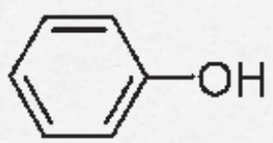
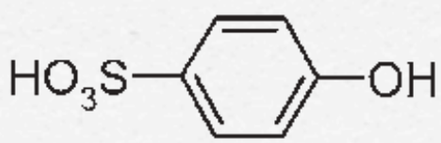


1f



4a



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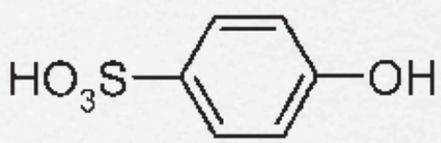

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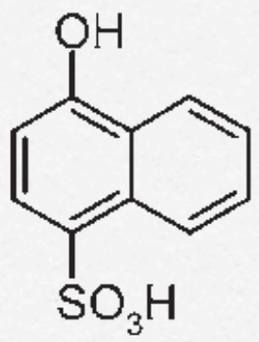
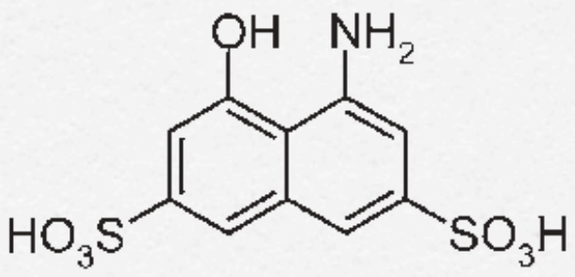


4d



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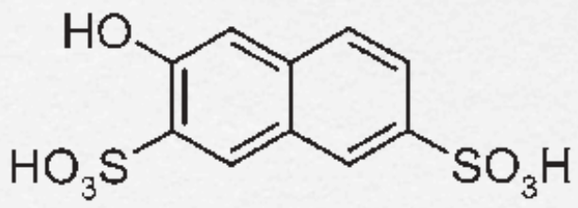
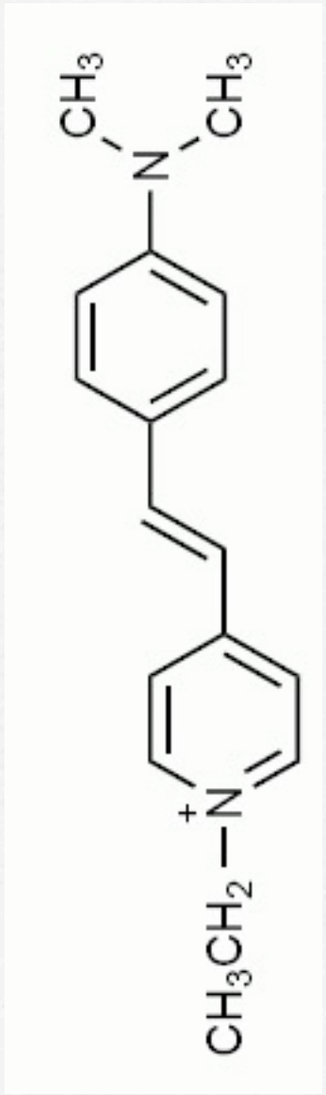
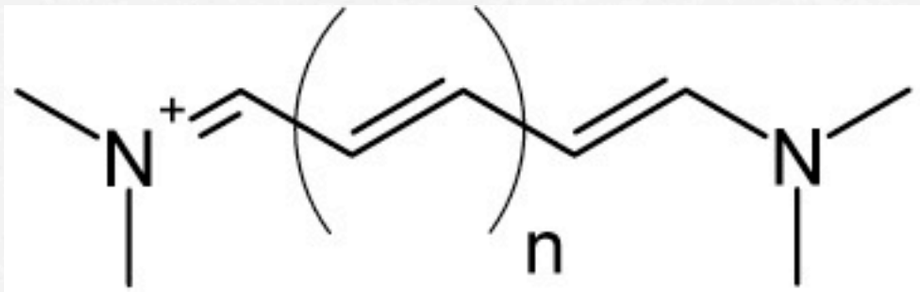


4f

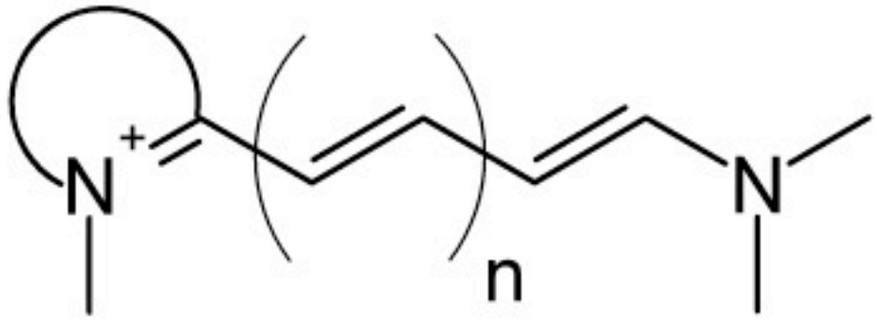
cyanine dyes

two nitrogens are joined by a polymethine chain

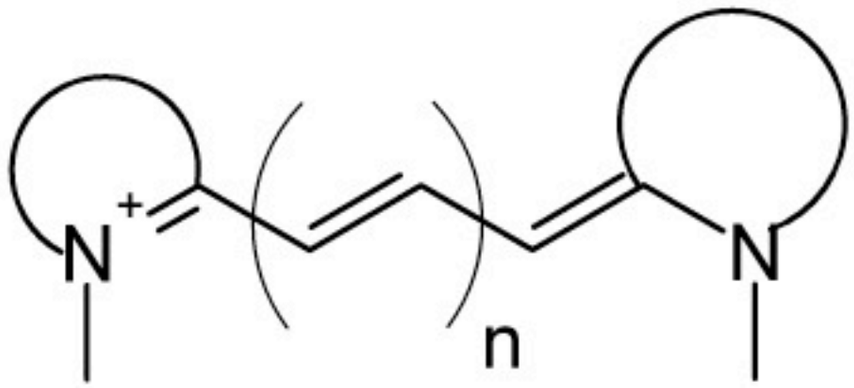




I = Streptocyanines

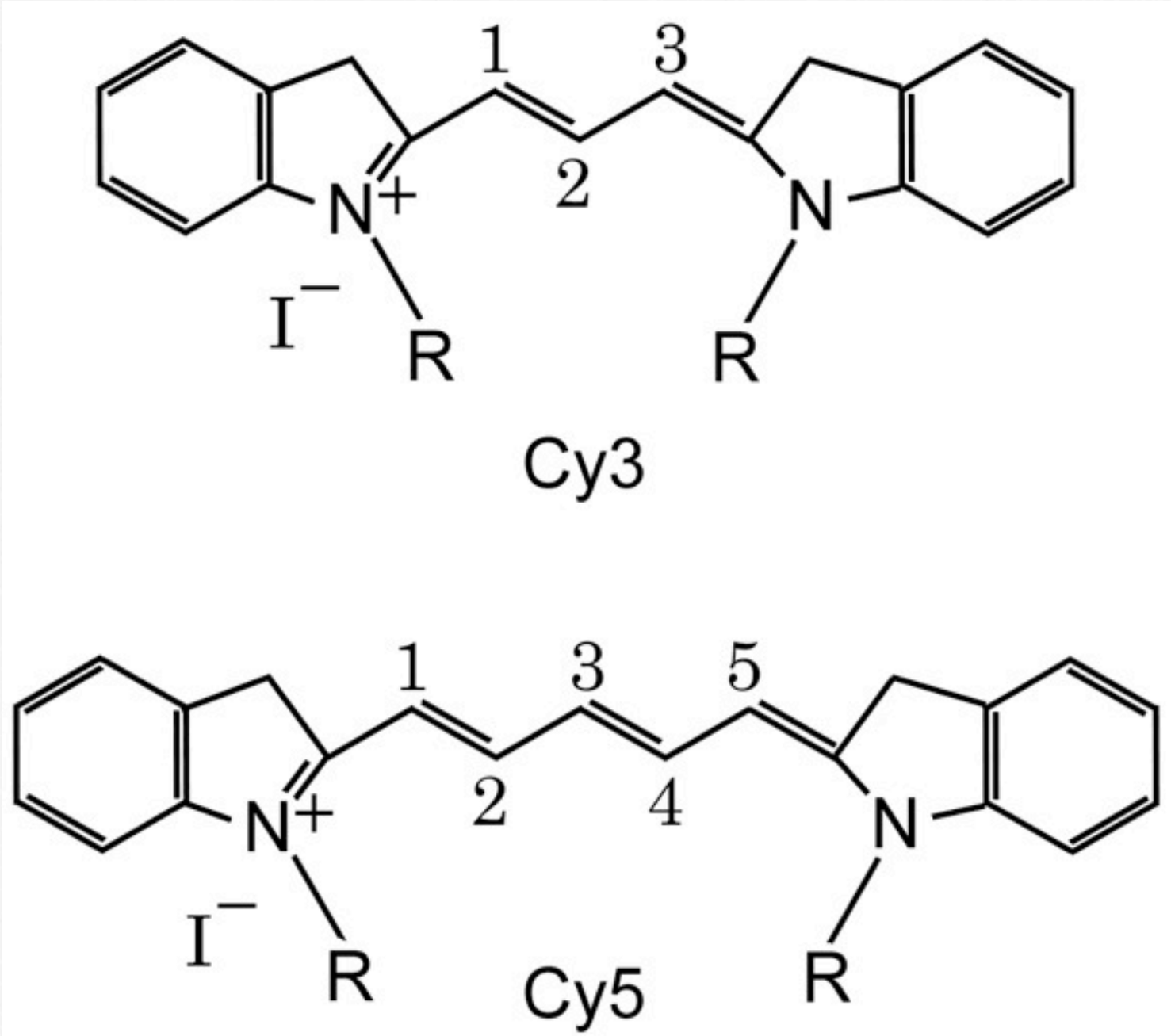


II = Hemicyanines



III = Closed cyanine

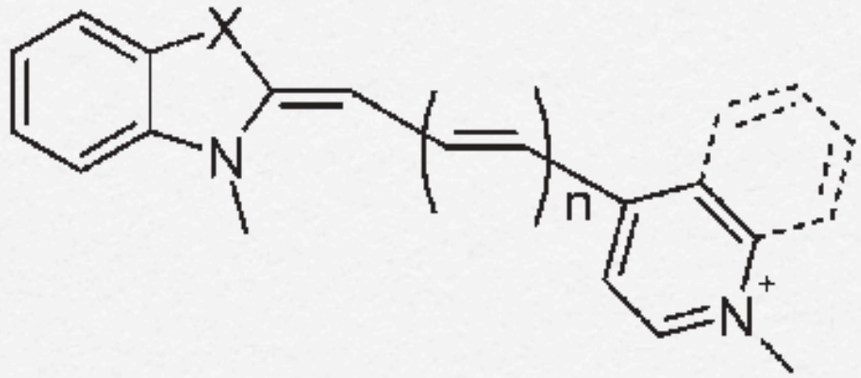
cyanine dyes: the famous ones



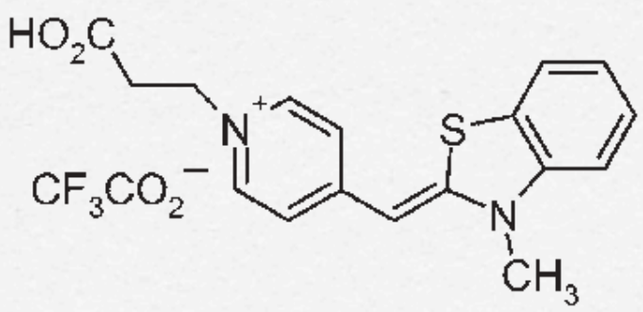
Cy3

Cy5

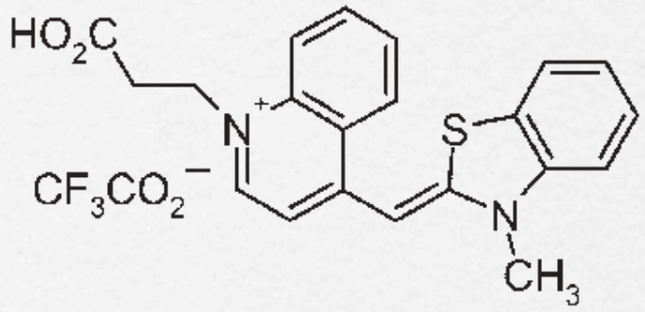
asymmetric cyanine dyes



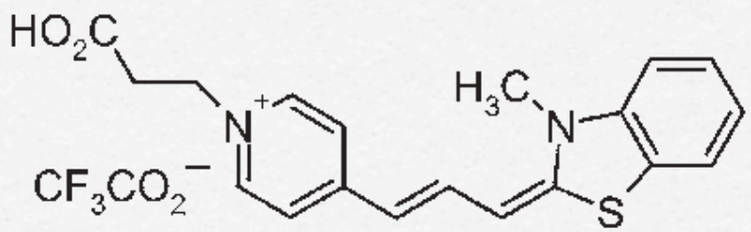
n = 0, 1, 2, etc.
X = S, O, NH, CRR'



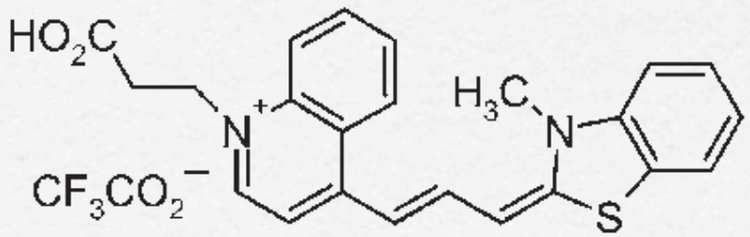
8a (yellow)



8b (orange)

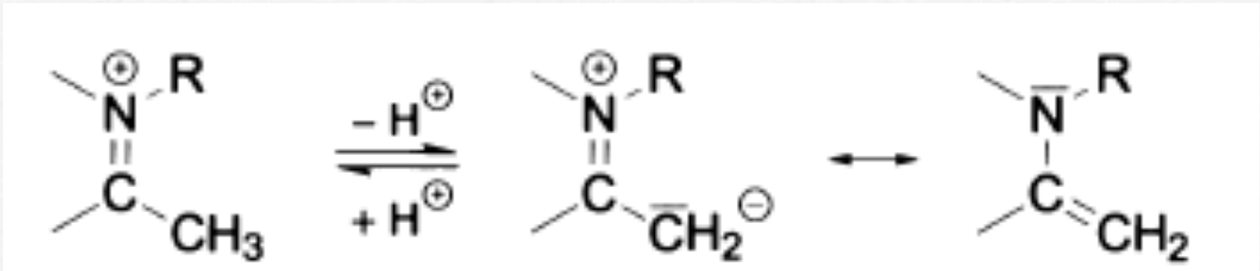


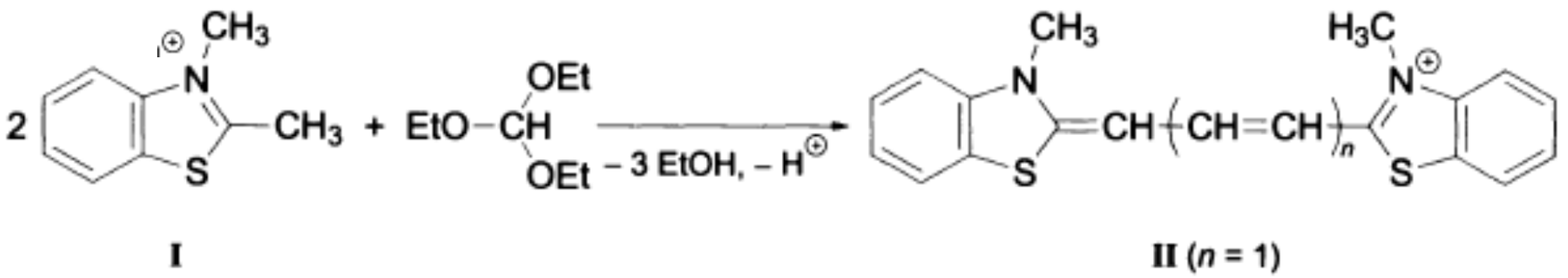
8c (purple)



8d (blue)

polymethine synthesis

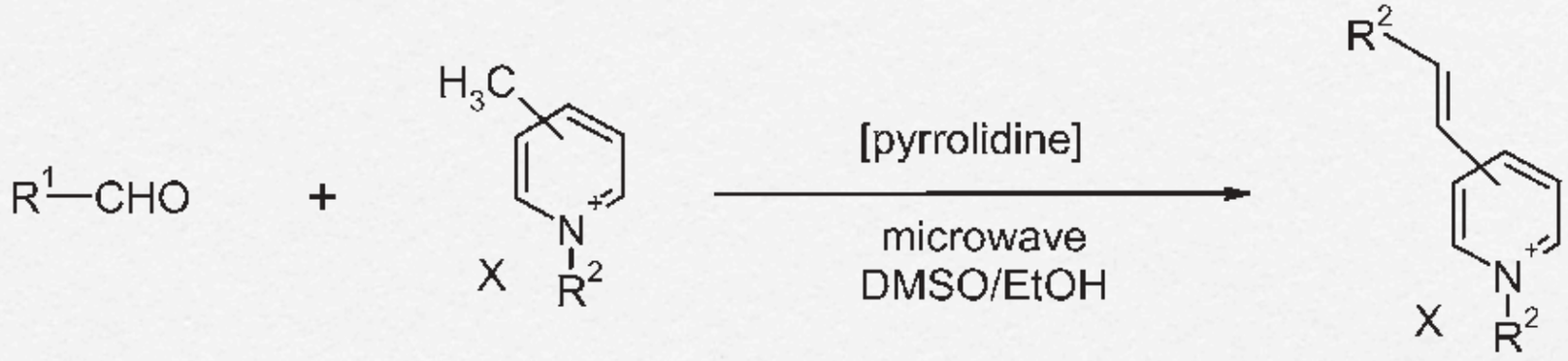




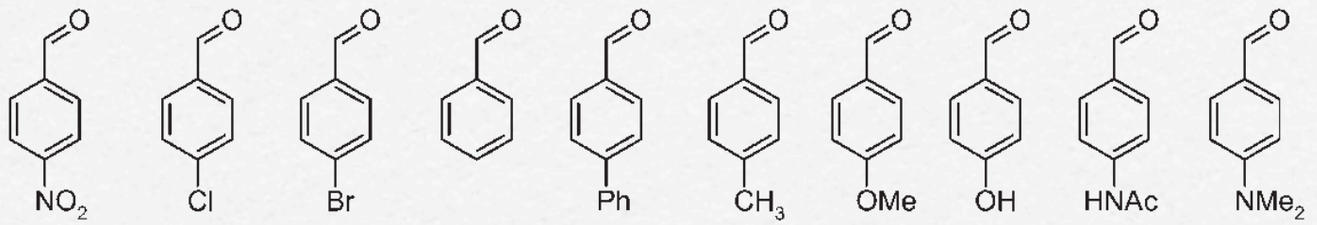
I

II (*n* = 1)

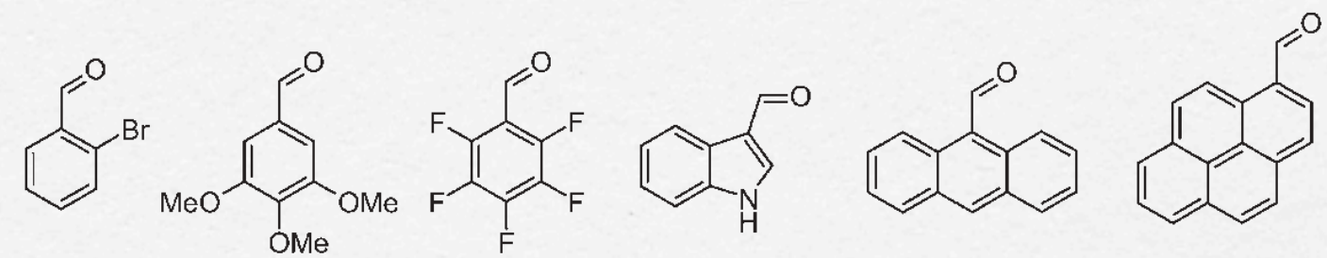
stilbazolium dyes



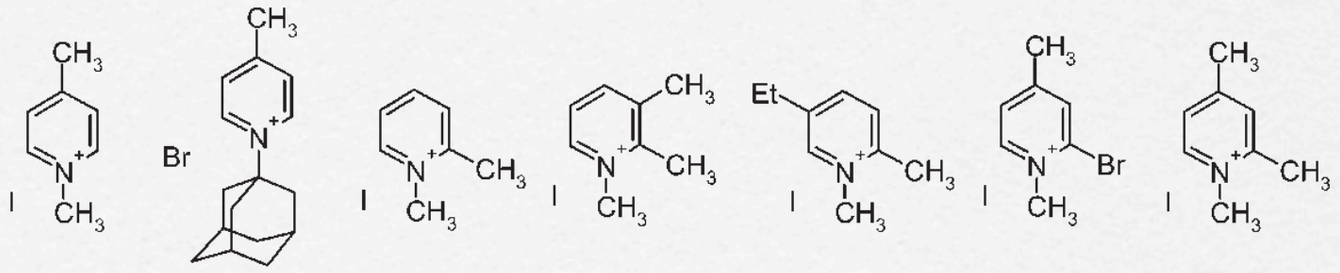
stilbazolium dyes



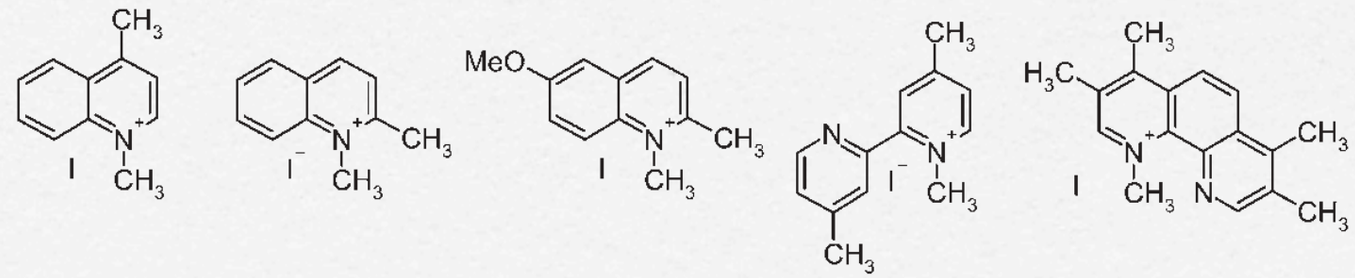
9a **9b** **9c** **9d** **9e** **9f** **9g** **9h** **9i** **9j**



9k **9l** **9m** **9n** **9o** **9p**

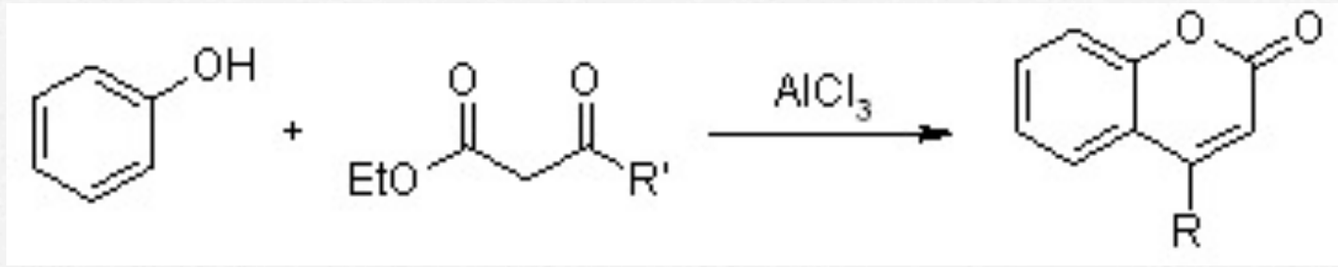


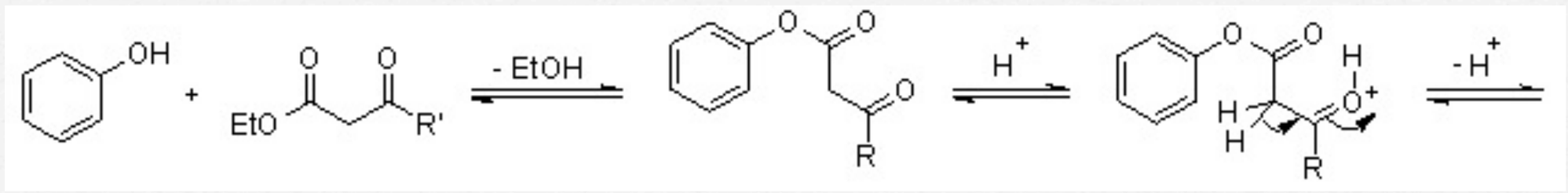
10a **10b** **10c** **10d** **10e** **10f** **10g**

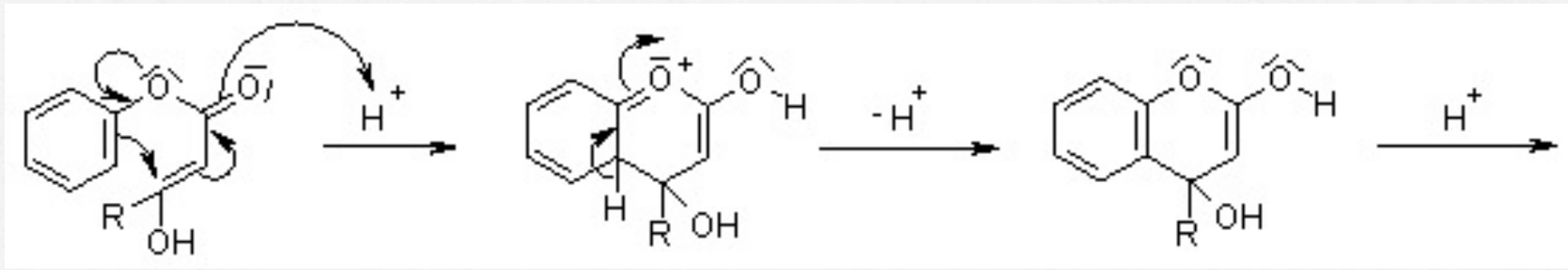


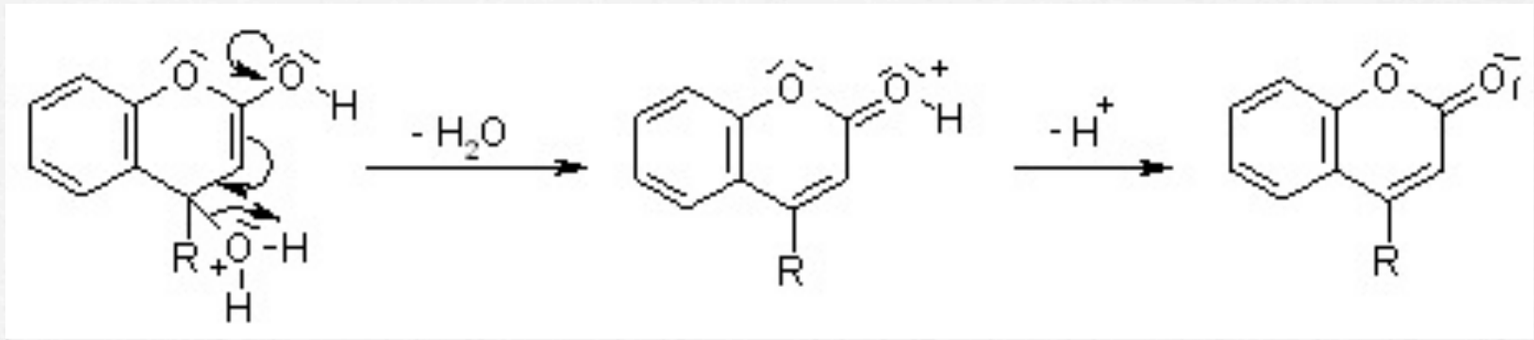
10h **10i** **10i** **10k** **10l**

coumarin dye synthesis



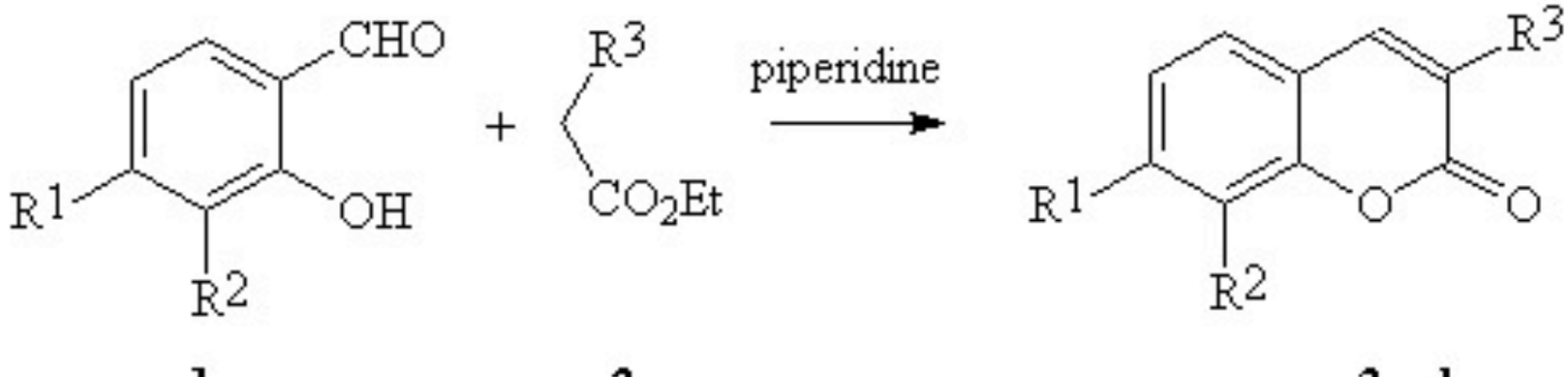






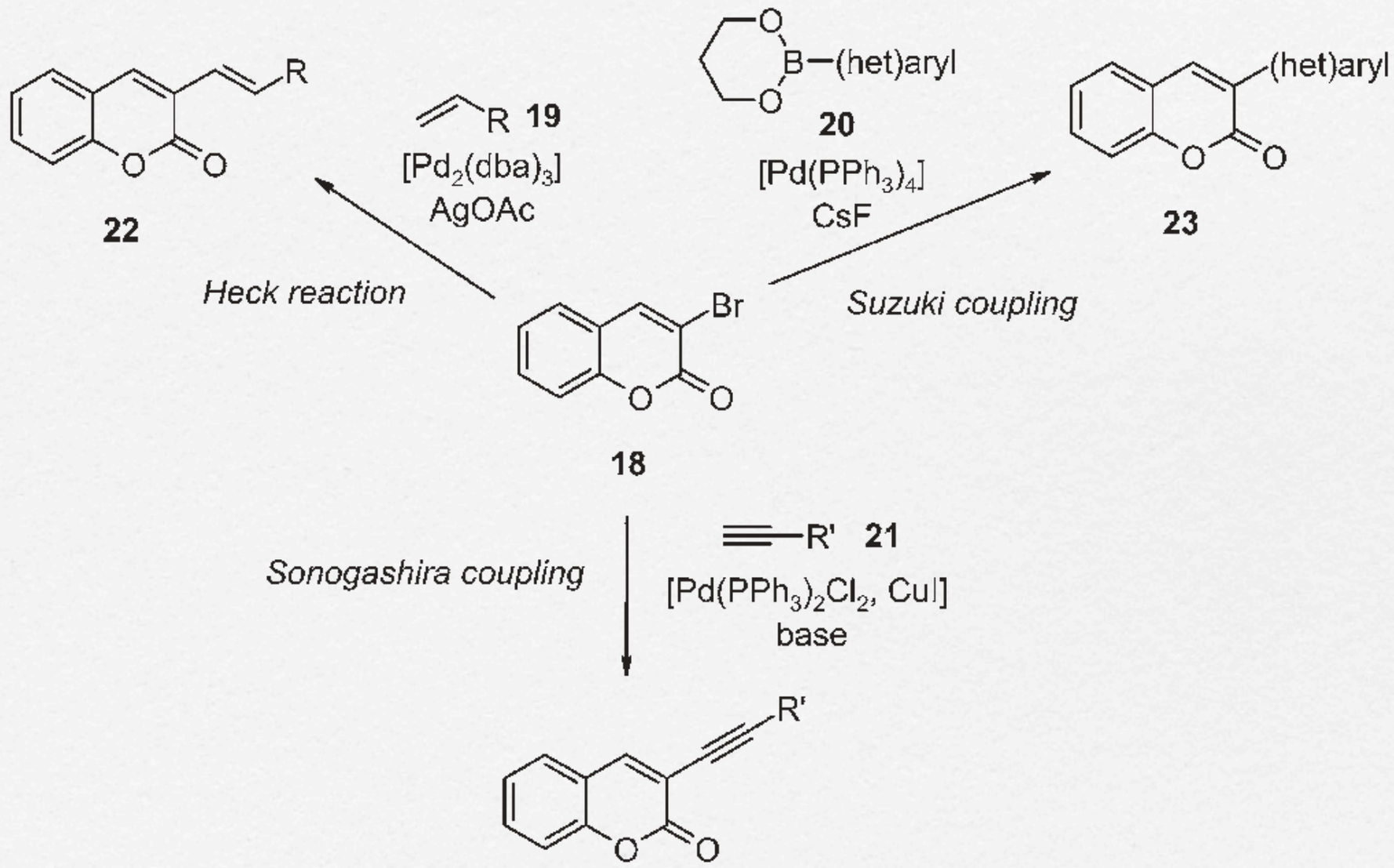
Pechmann-condensation

coumarin dye synthesis

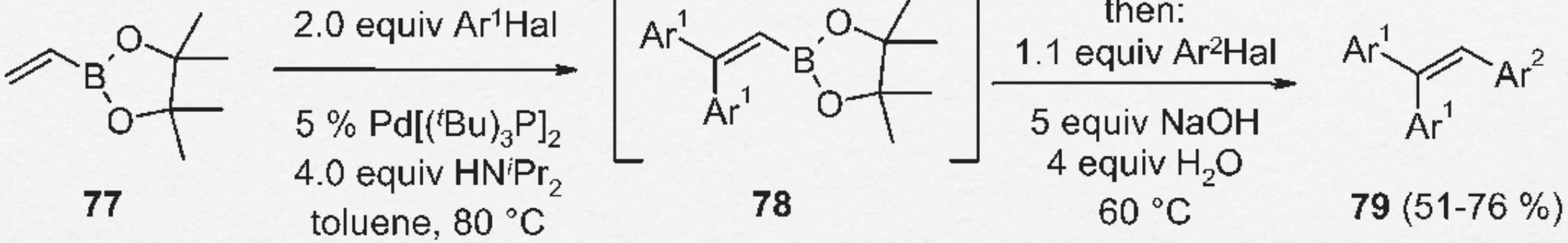


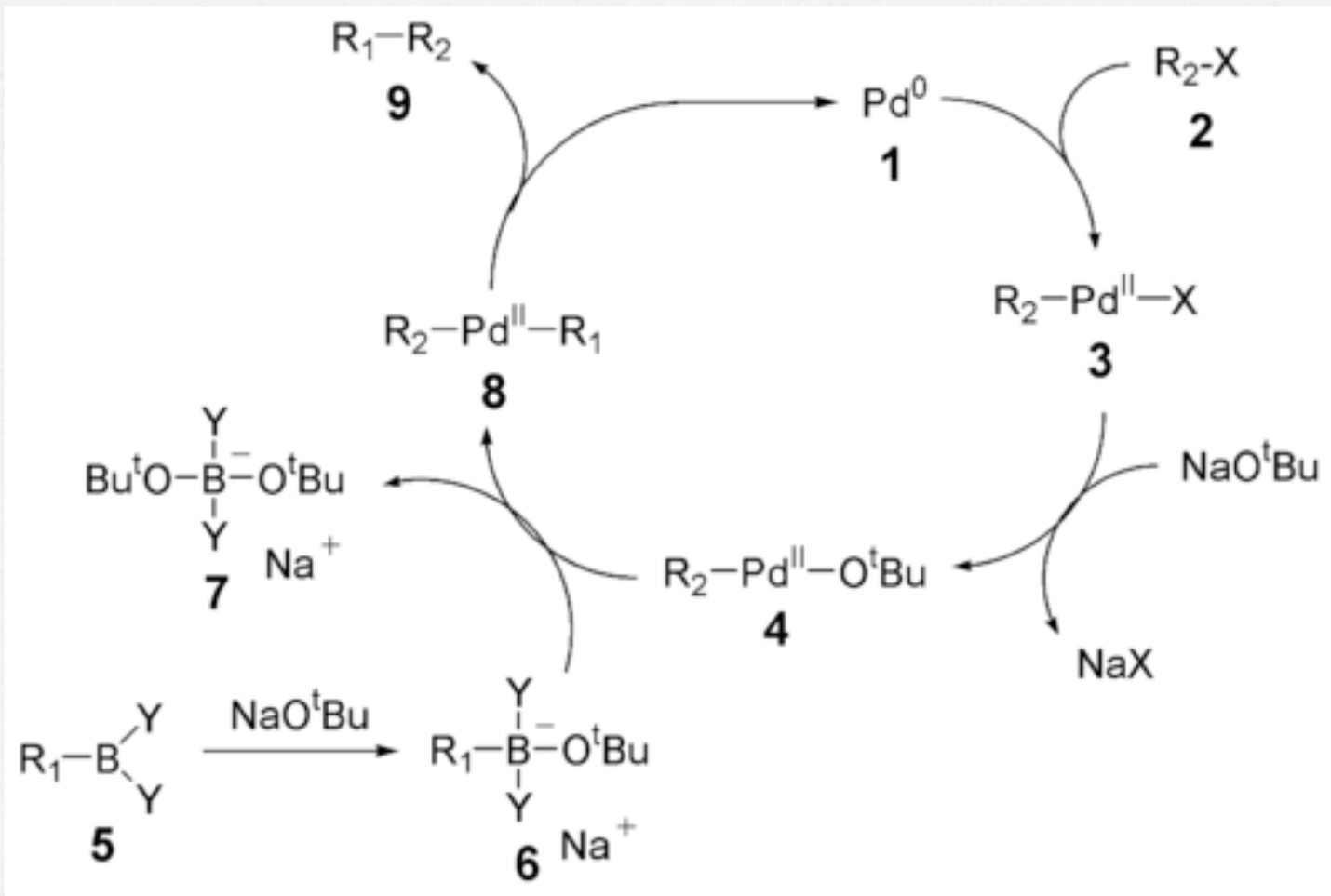
1 **2** **3 a-l**

coumarin dyes



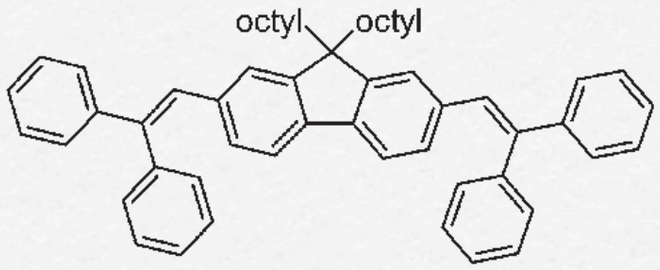
Suzuki coupling



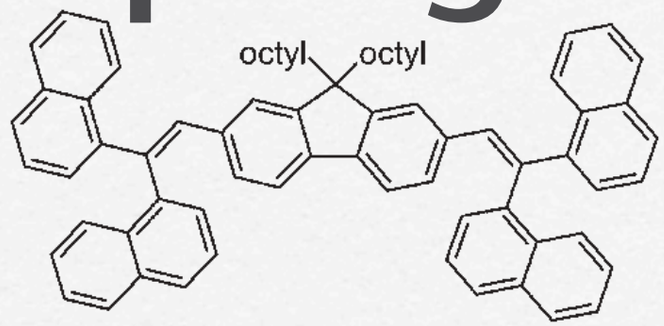


boronic acid must be activated, for example with base

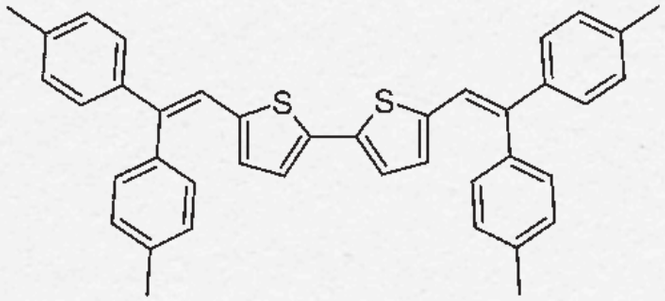
Suzuki coupling



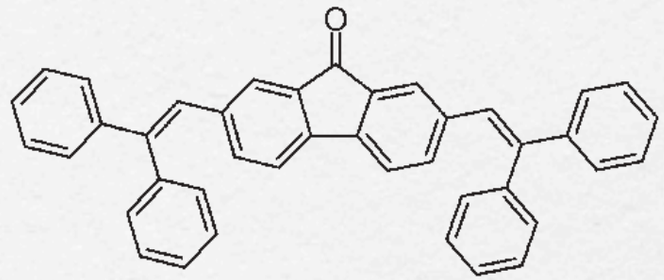
80c (98 %)



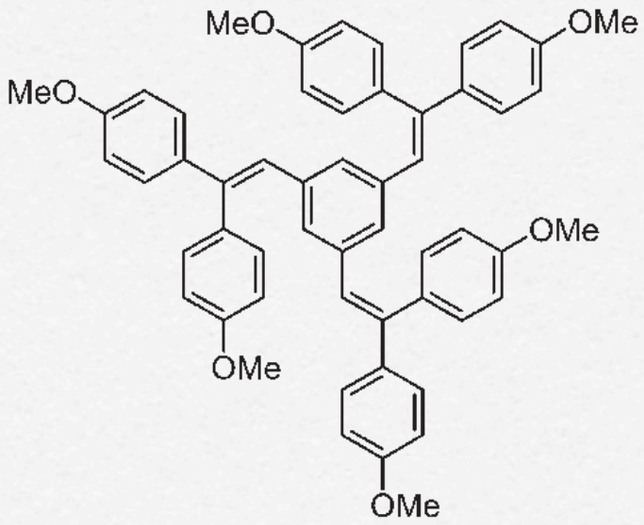
80d (53 %)



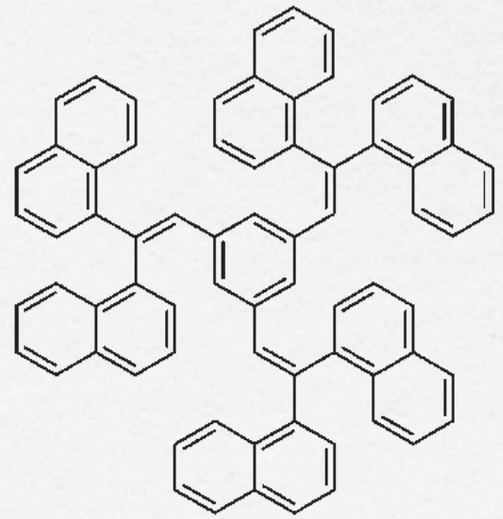
80e (58 %)



80f (67 %)

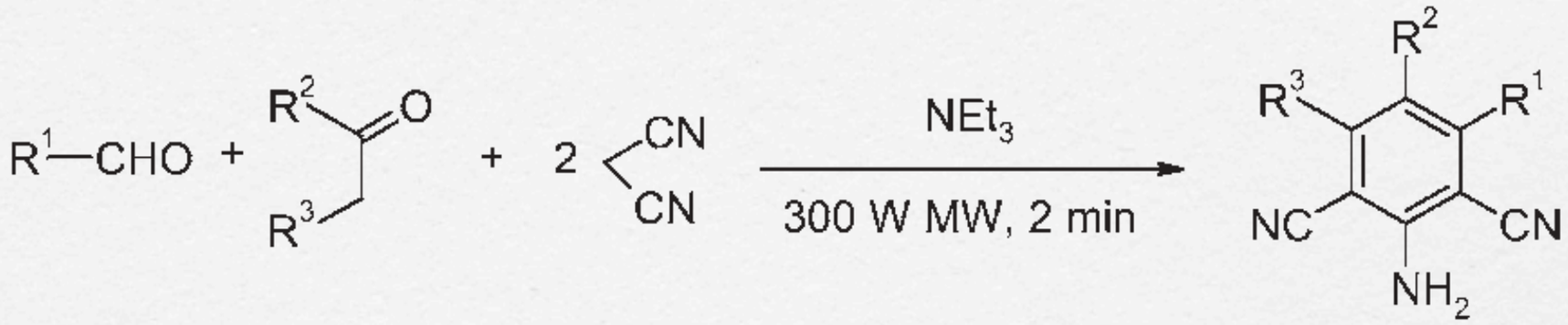


81a (50 %)



81b (59 %)

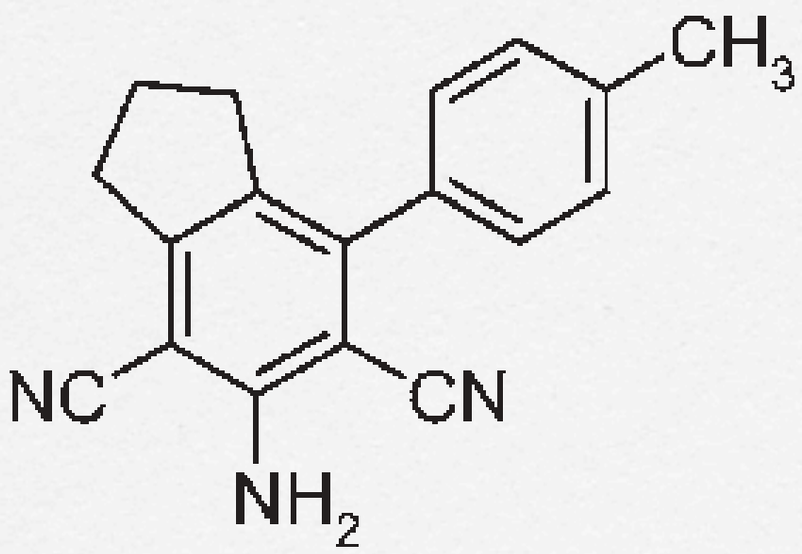
2,6-dicyanoanilines: A-D-A



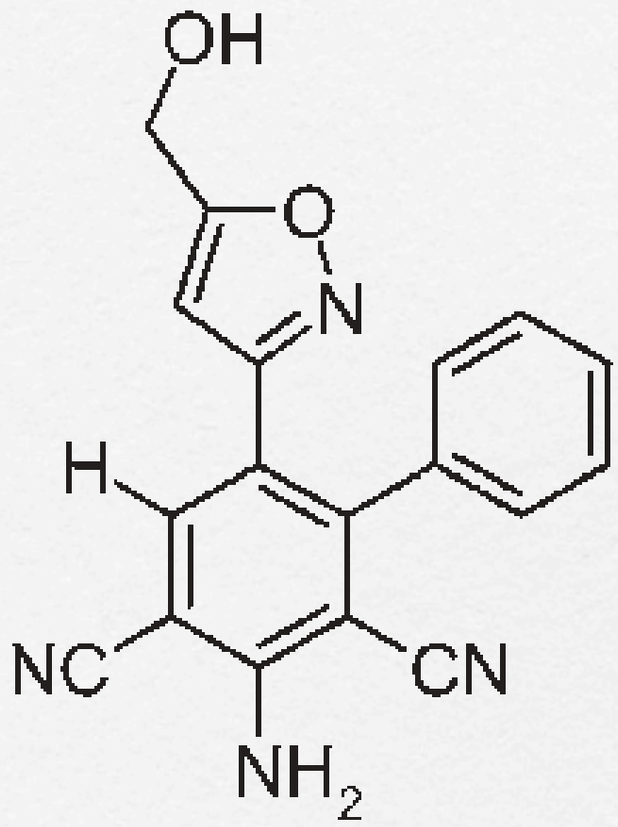
63 **64** **62** (51-63 %)

R^1 = (hetero)aryl
R^2, R^3= alkyl, (hetero)aryl, $(CH_2)_{3\text{-}4}$

2,6-dicyanoanilines: A-D-A



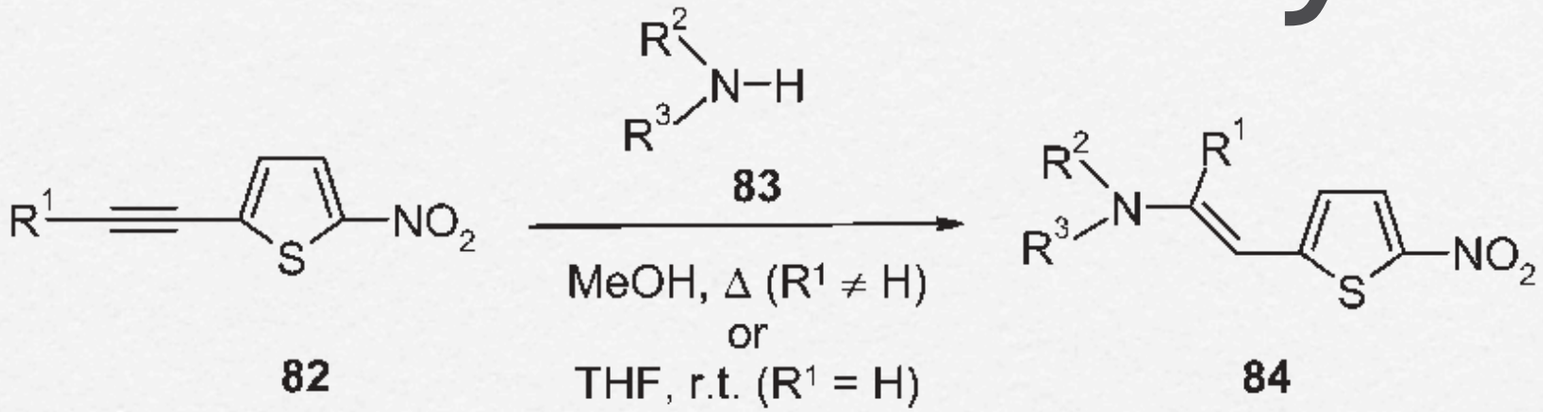
62a



62b

Fig. 5.20 Strongly fluorescent 2,6-dicyanoanilines **62a** and **62b**.

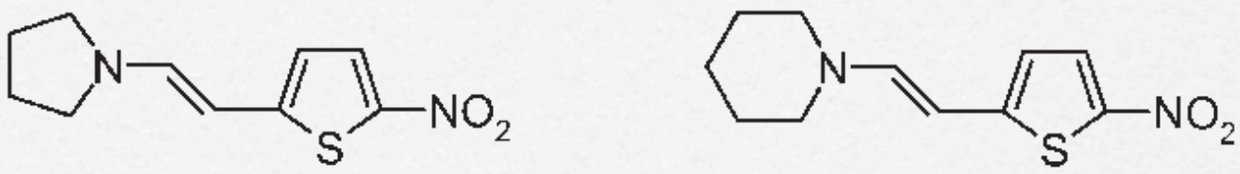
solvochromicity



82 84

R^1 = H, aryl, ferrocenyl

Scheme 5.18 Michael-type addition of secondary amines to nitrothienyl-substituted alkynes.



84a

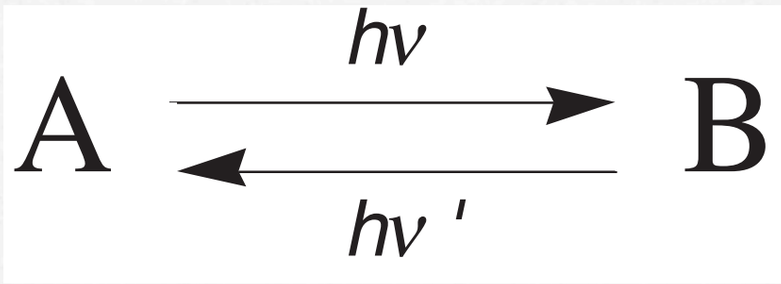
λ_{max} (pentane) = 450 nm
λ_{max} ($CHCl_3$) = 520 nm
$\beta^0 = 31 \times 10^{-30}$ esu
$\beta^0\mu/M_w = 1.34$

84b

λ_{max} (pentane) = 443 nm
λ_{max} ($CHCl_3$) = 513 nm
$\beta^0 = 29 \times 10^{-30}$ esu
$\beta^0\mu/M_w = 1.23$

Fig. 5.23 Solvochromicity and NLO properties of selected β-aminovinylnitrothiophenes **84**.

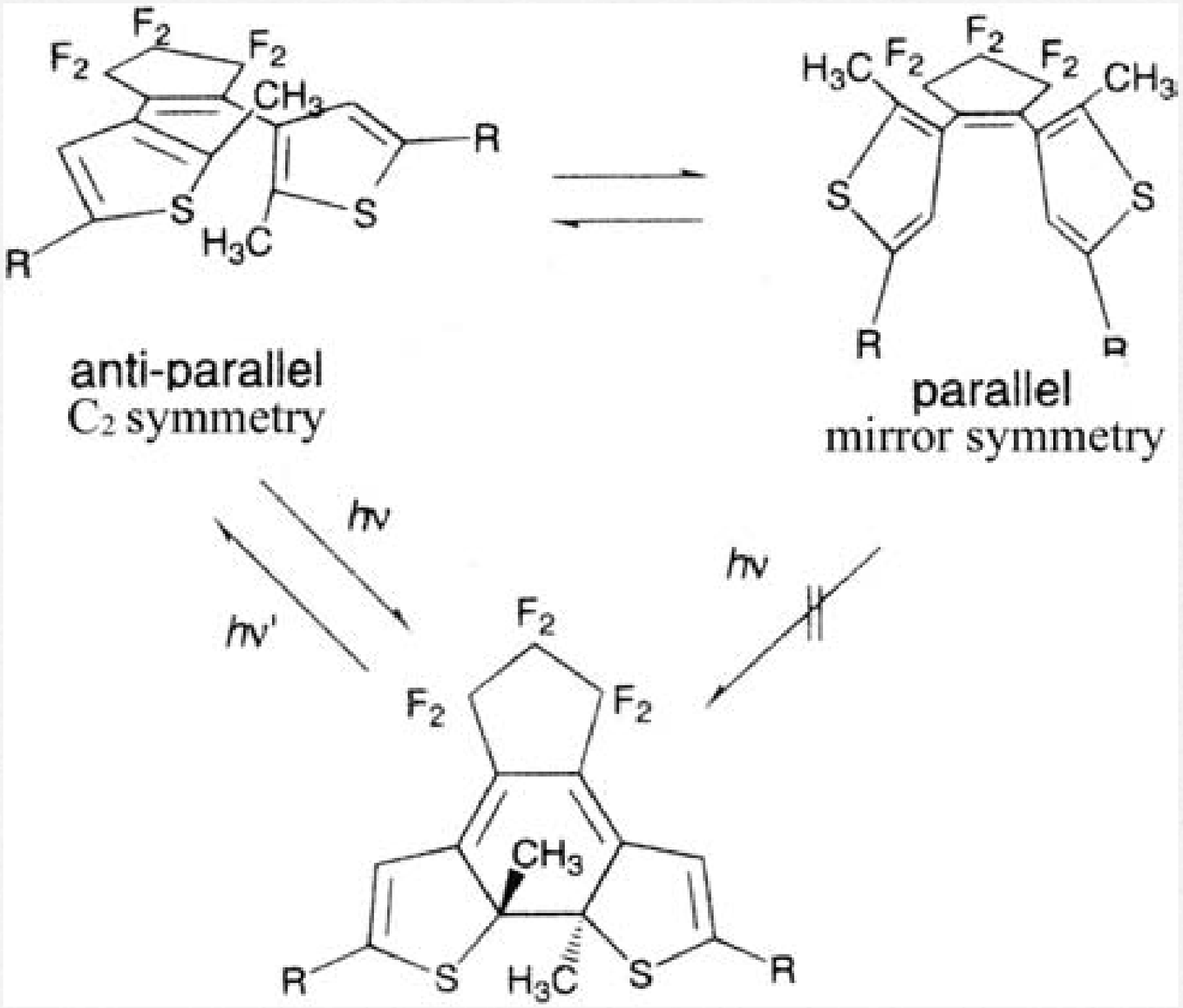
photoswitches



Light-induced reversible transformation between two isomers having different absorption spectra is referred to as photochromism.

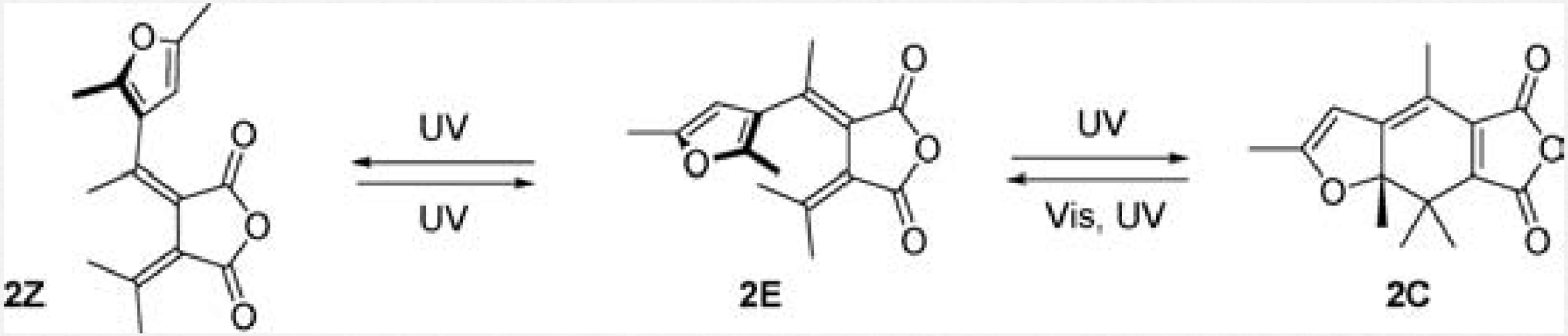
photoswitches

diarylethene derivatives.



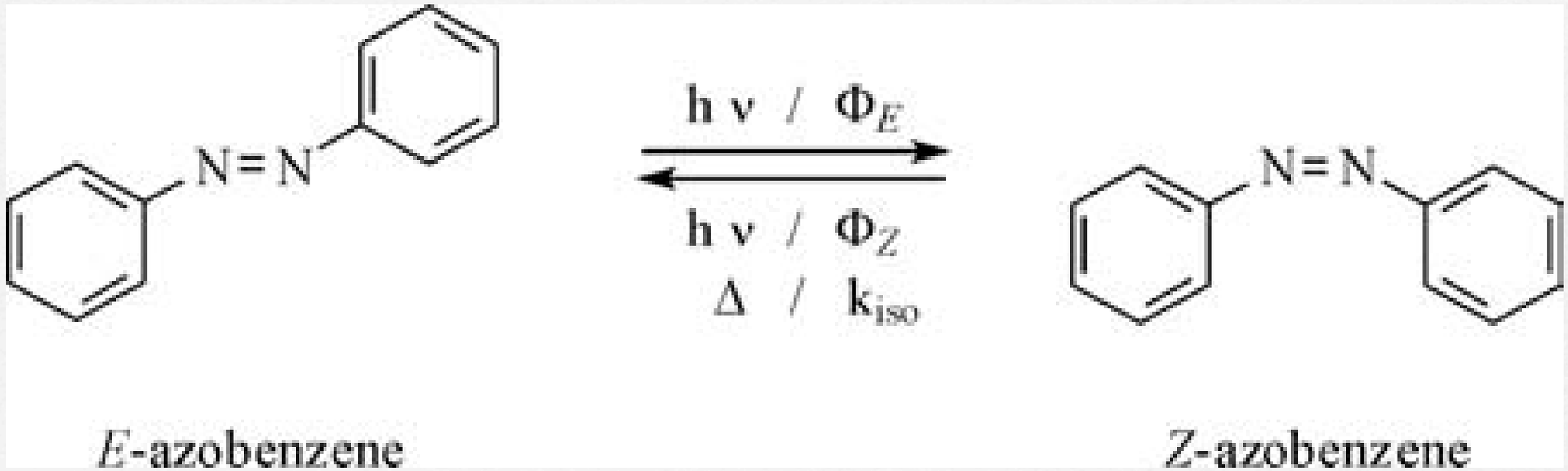
photoswitches

fulgide



photoswitches

azobenzene

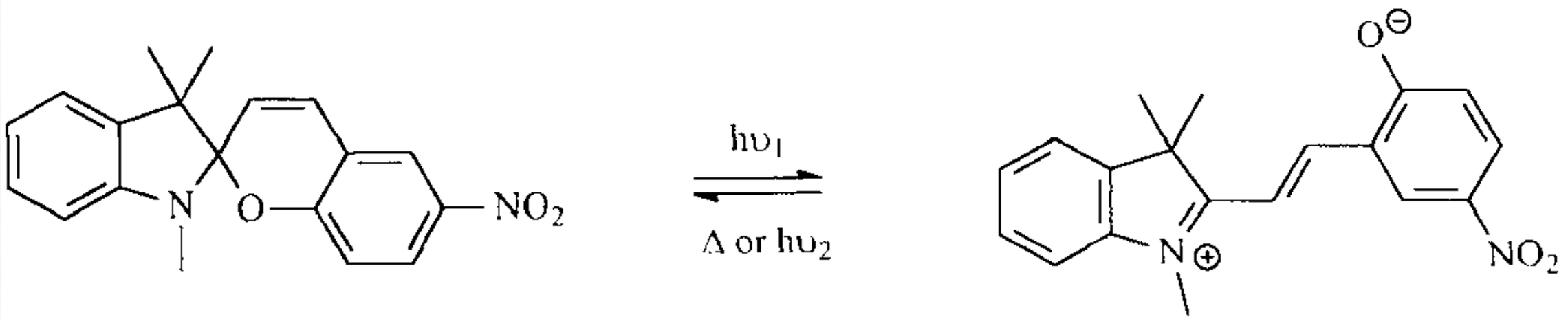


E-azobenzene

Z-azobenzene

photoswitches

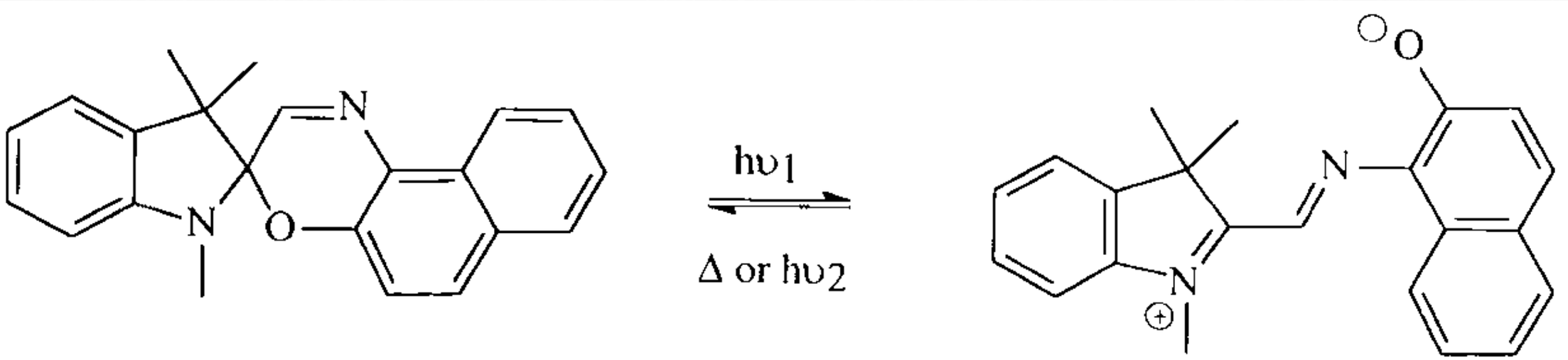
Spiropyrans



1

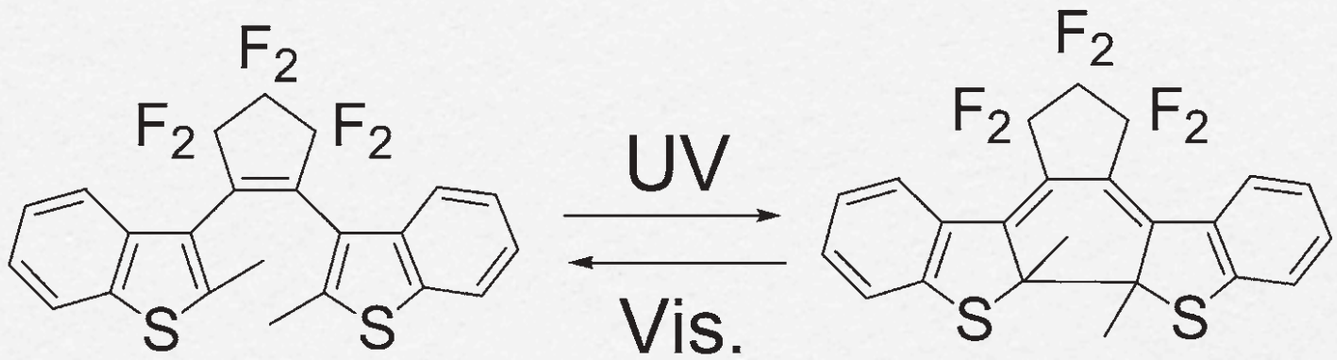
photoswitches

Spirooxazines

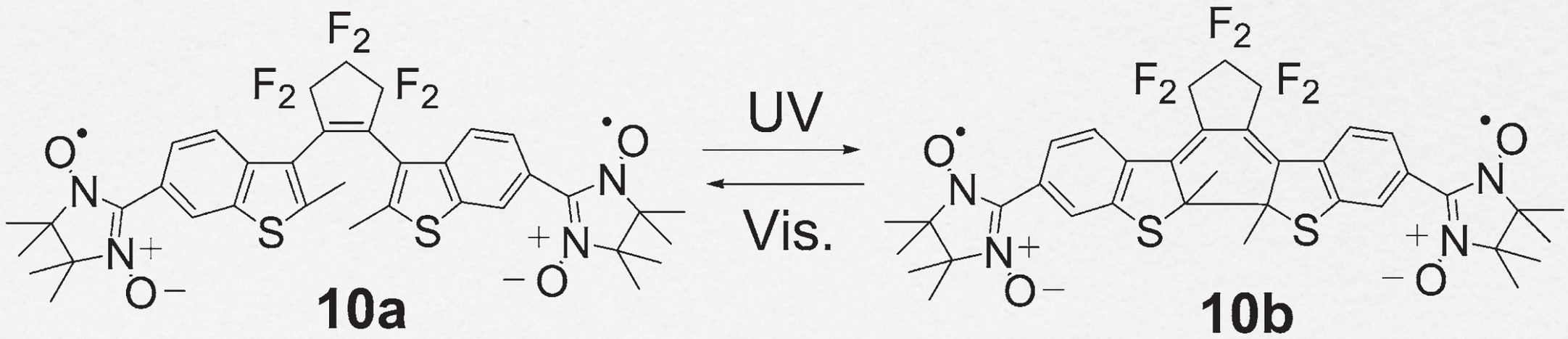


2

photoswitches: diarylethene

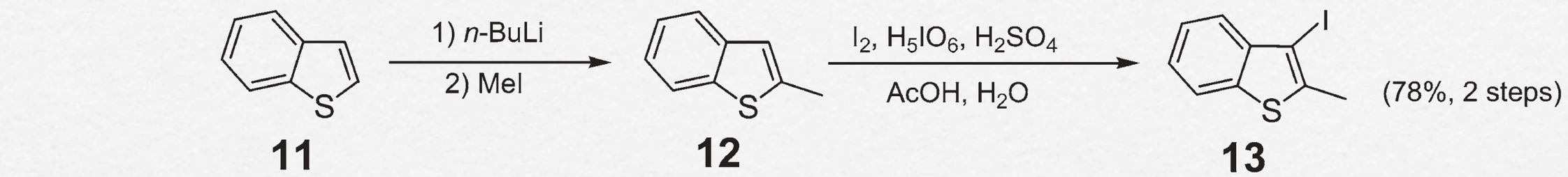


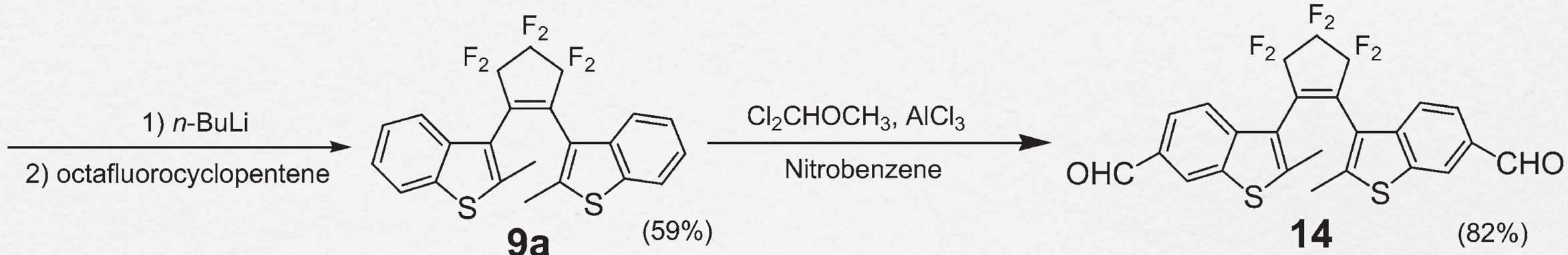
9a **9b**

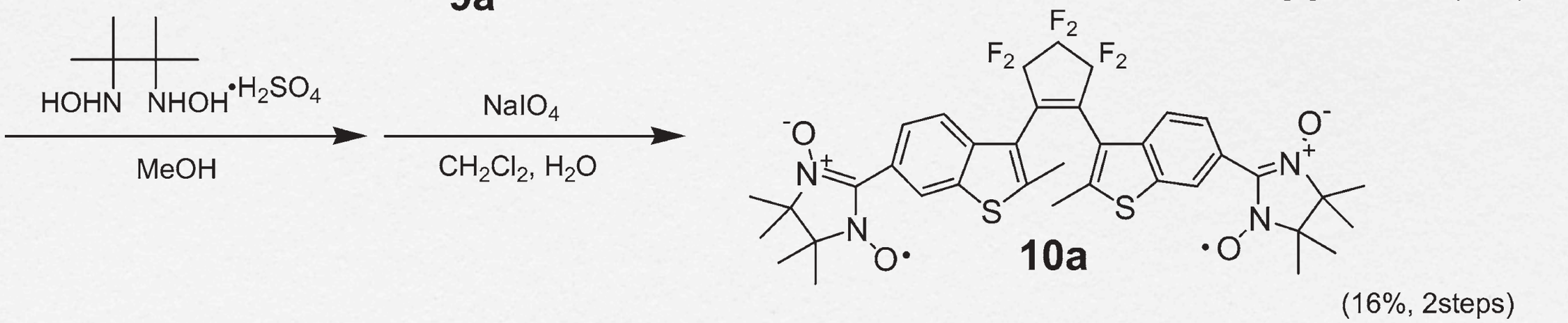


10a **10b**

photoswitches







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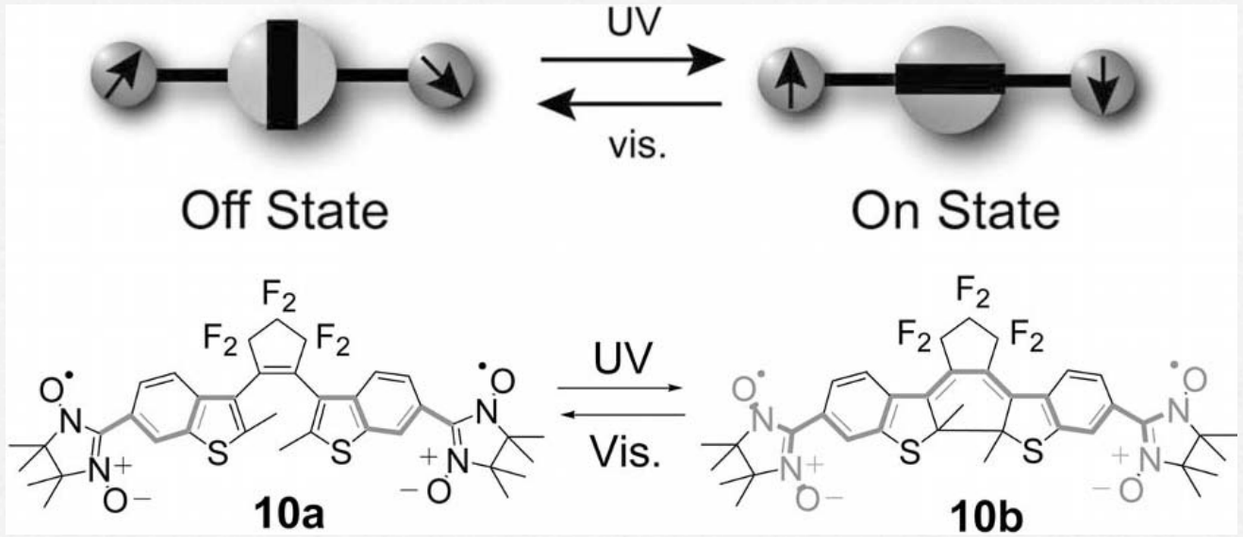
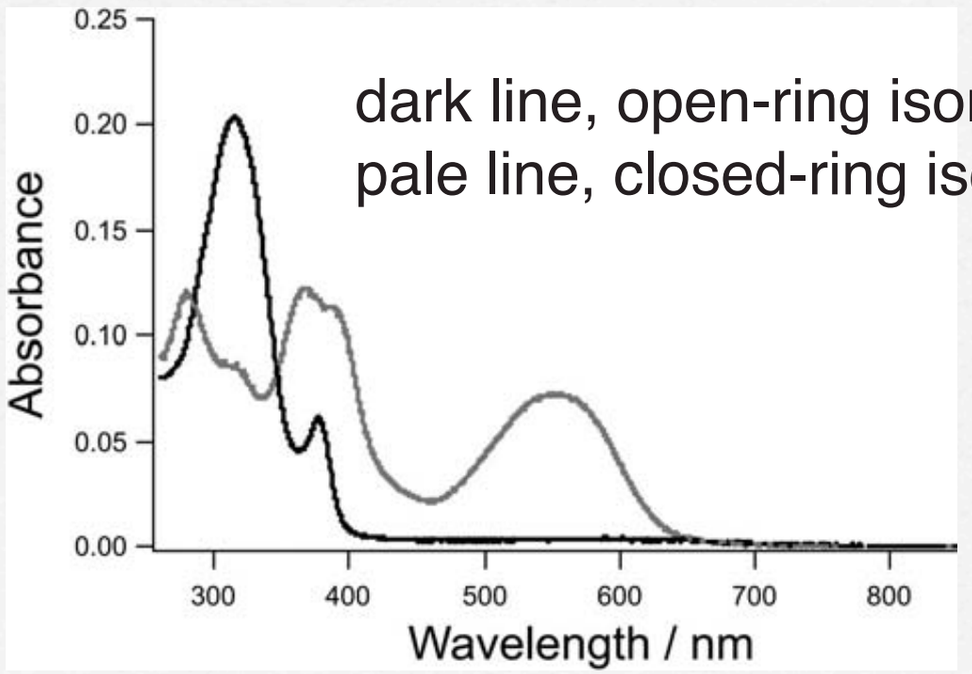
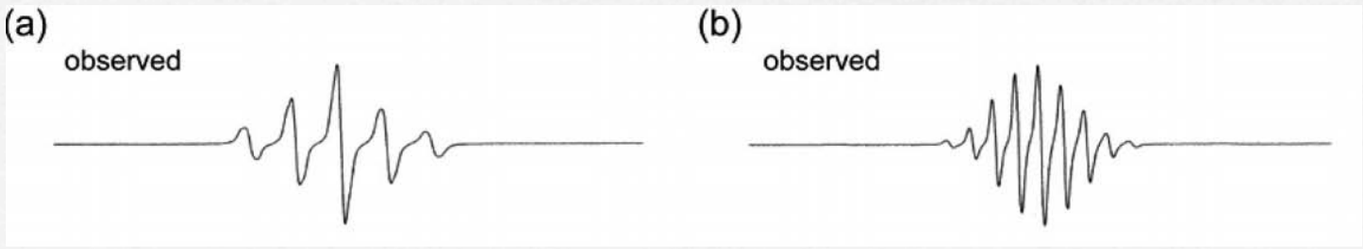
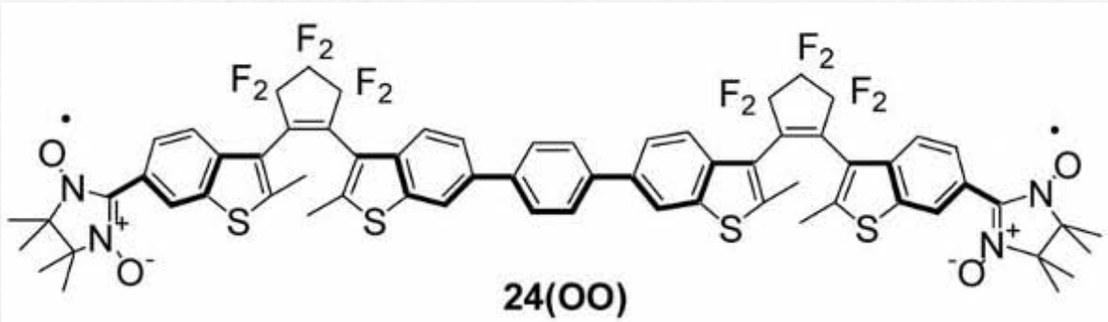


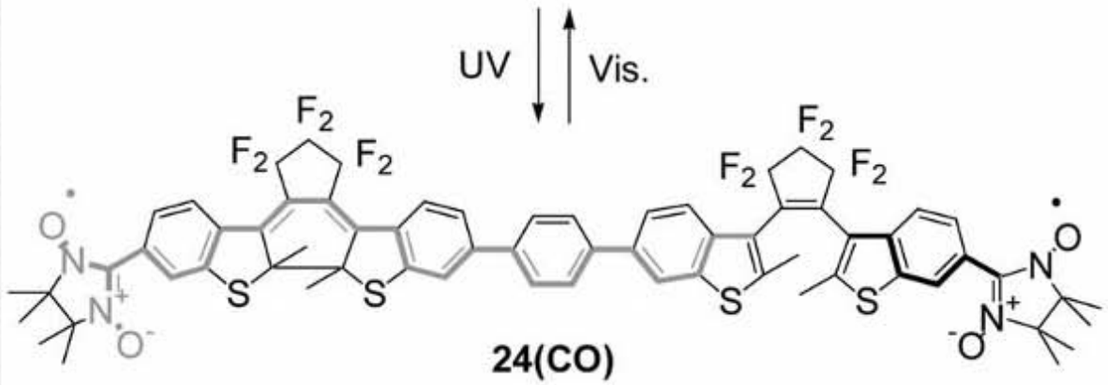


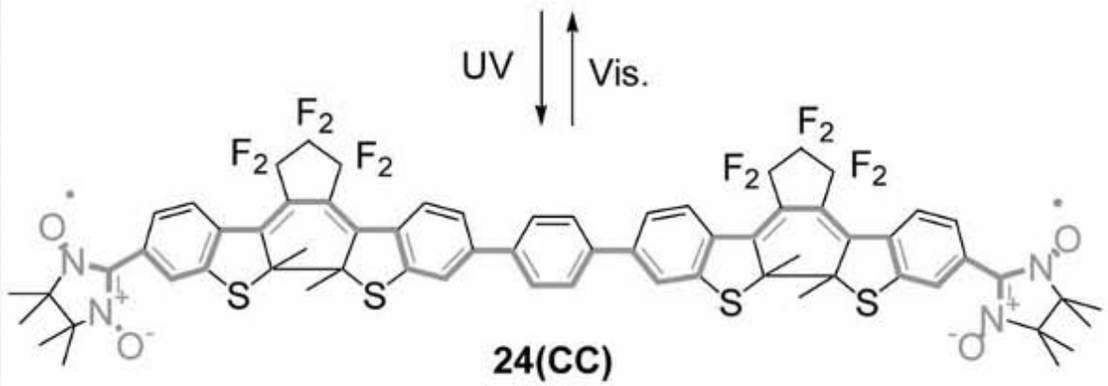


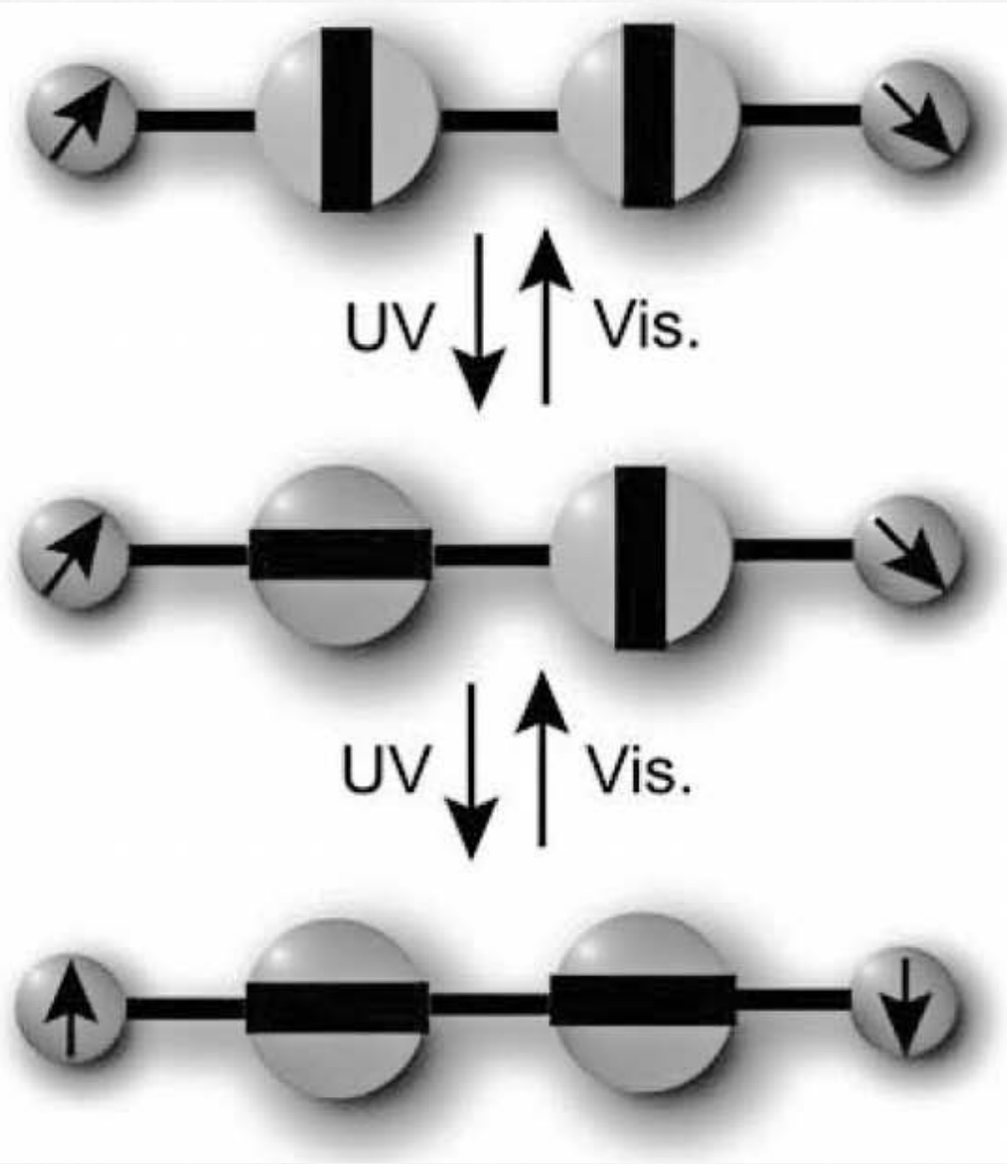
(a) Open-ring isomer 19a; (b) closed-ring isomer 19b.

photoswitches









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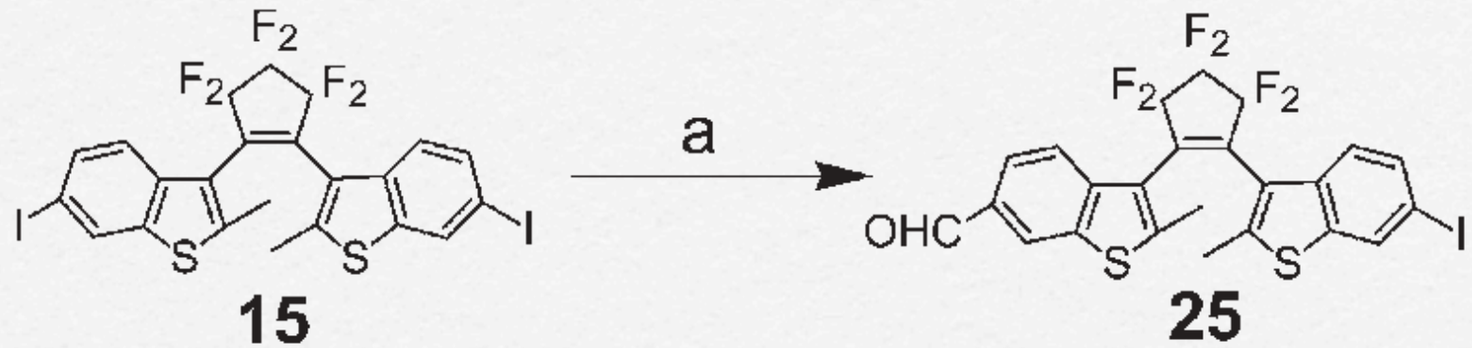

Reagents and conditions: (a) n-BuLi, THF then DMF; (b) p-phenylenediboronic acid, Pd(PPh3)4, Na2CO3, THF, H2O; (c) 2,3-dimethyl-2,3-bis(hydroxyamino)butane sulfate, methanol then NaIO4, CH2Cl2, (4.7 %, in three steps).

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