Lecture:

Development of chemistry of imidazoline nitroxides on the way to the synthesis of mesogenic paramagnetic molecules

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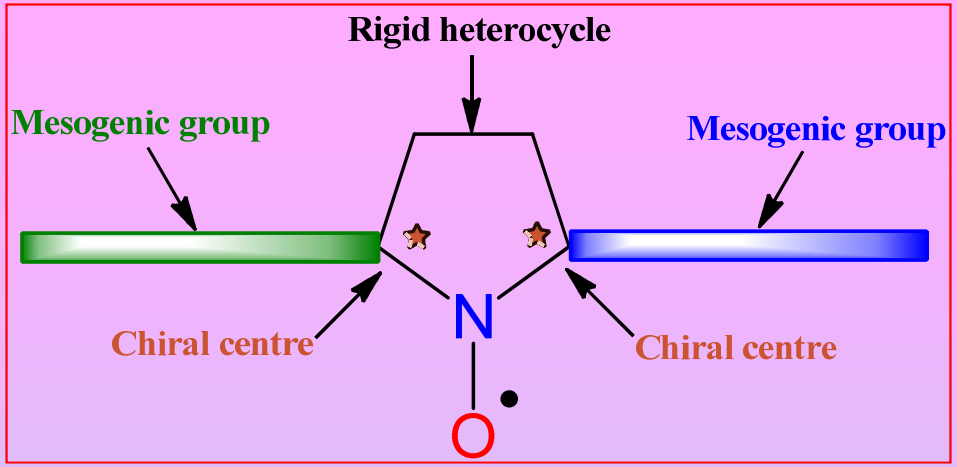
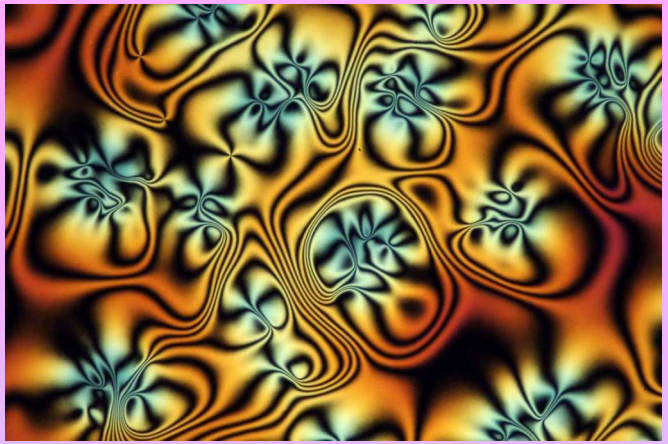
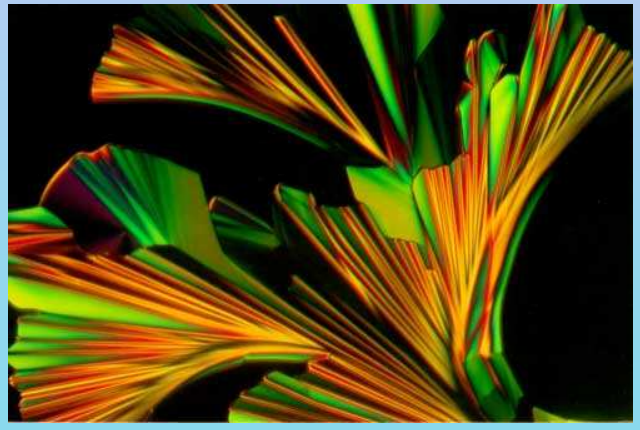
- *Novosibirsk State University, 630090 Novosibirsk, Russia*

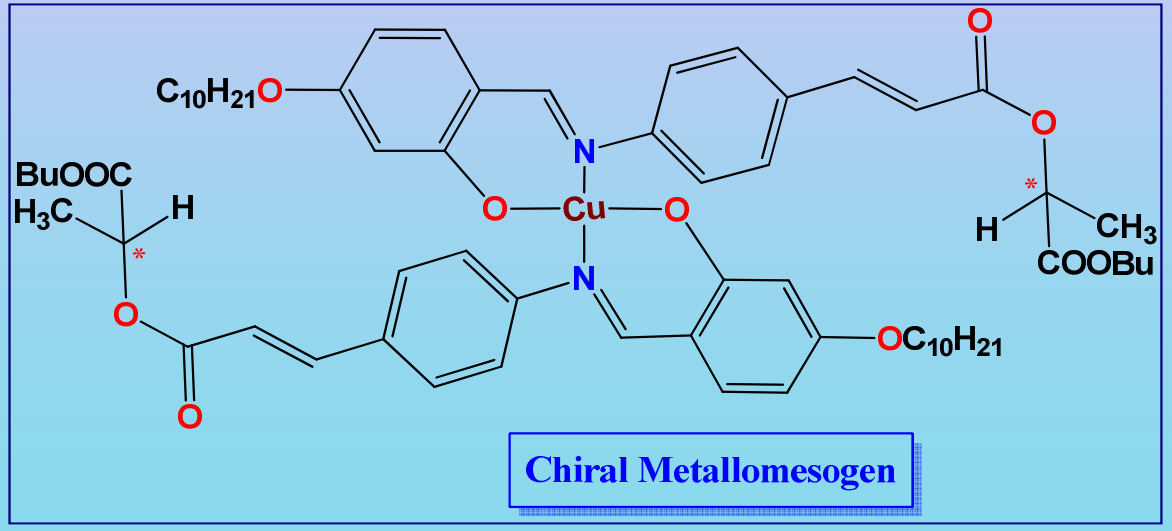
TYPICAL PARAMAGNETIC LIQUID CRYSTALLINE MOLECULES



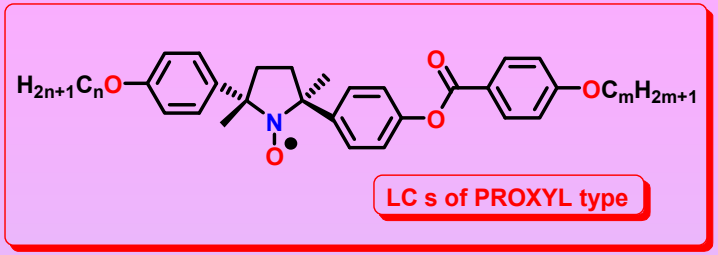


Tamura, R., Uchida, Y., Ikuma, N., *J. Mater. Chem.*, **2008**, *18*, 2872-2876.
Ikuma, N.; Tamura, R.; Shimono, S., *Angew. Chem. Int. Ed.*, **2004**, *43*, 3677-3682.
Ikuma, N.; Tamura, R.; Shimono, S., *Adv. Mater.*, **2006**, *18*, 477-480.
Uchida, Y.; Suzuki, K.; Tamura, R., *J. Amer. Chem. Soc.*, **2010**, *132*, 9746-9752.

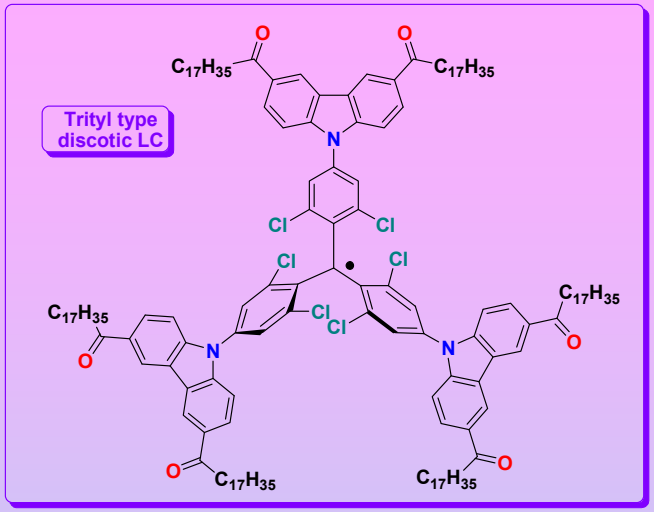




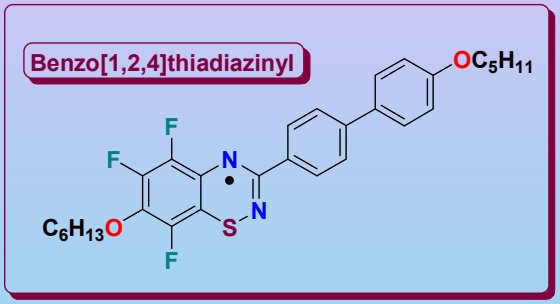
Examples of Fully Organic Paramagnetic Liquid Crystals (PLCs) with Different Source of Radical Centre



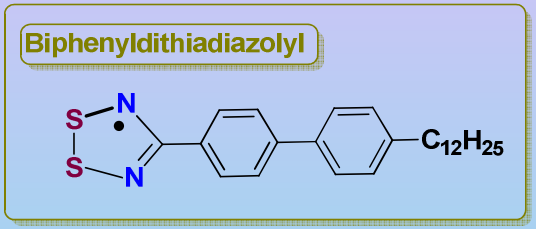
N. Ikuma, R. Tamura *et al*. *Angew. Chem. Int. Ed.*, **2004**, *43*, 3677.



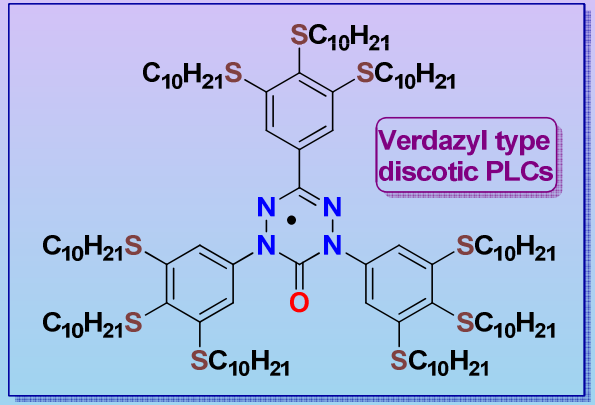
S. Castellanos, F. Lopez-Calahorra *et al. Angew. Chem. Int. Ed.*, **2009**, *48*, 6516



J. Zienkiewicz, P. Kaszynski *et al. J. Org. Chem.*, **2007**, *72*, 3510.



Rawson, J. M.; Clarke, C. S.; Bruce, D. W. Magn. Reson. Chem. **2009**, 47, 3.

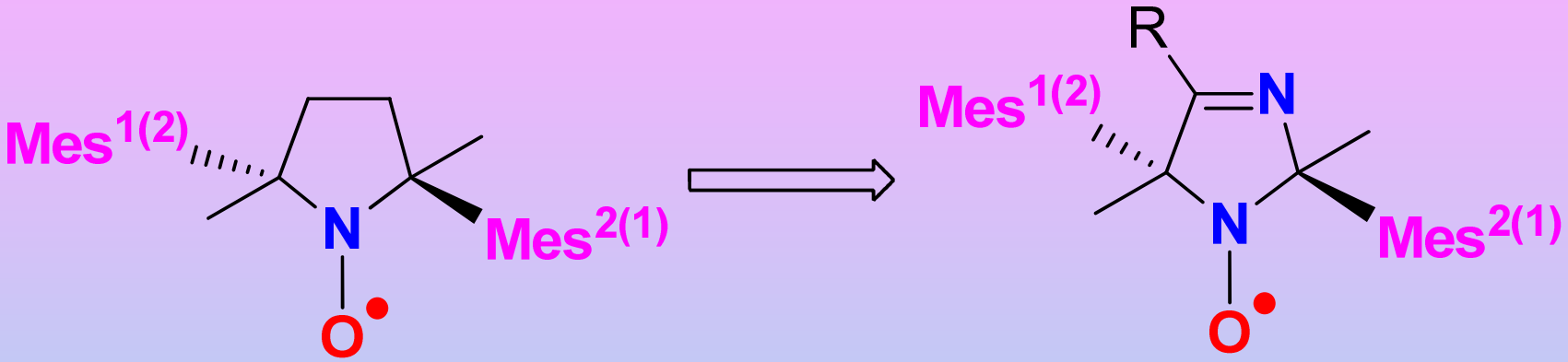


A. Jankowiak, D. Pociecha, P. Kaszynski *et al. J. Am. Chem. Soc.*, **2012**, *134*, 2465.

Paramagnetic calamitic LCs, based on pyrrolidine type nitroxide radicals (PROXYLs), possess considerable paramagnetic anisotropy and can to respond quickly under applied magnetic field unlike LCs based on metallomesogens and another types of fully organic PLCs.

Searching of new heterocyclic cores in the family of PLCs

Why imidazoline?

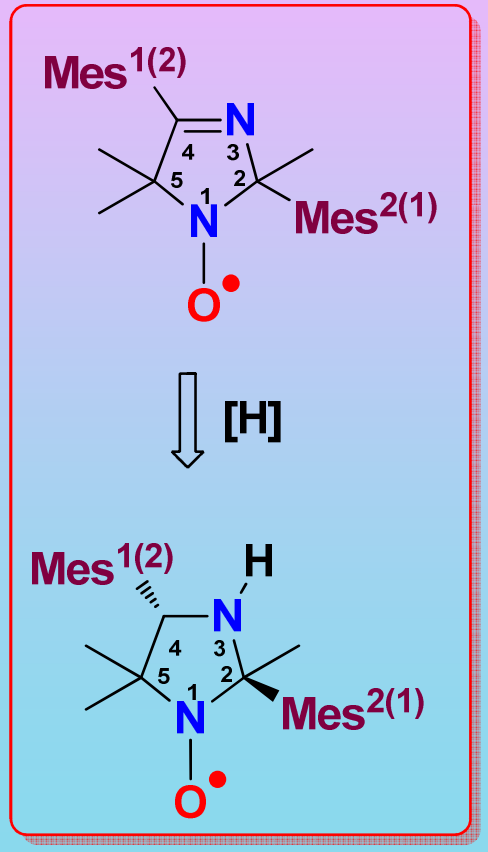


- *More robust and more planar*
- *Additional nitrogen atom provides additional capabilities*

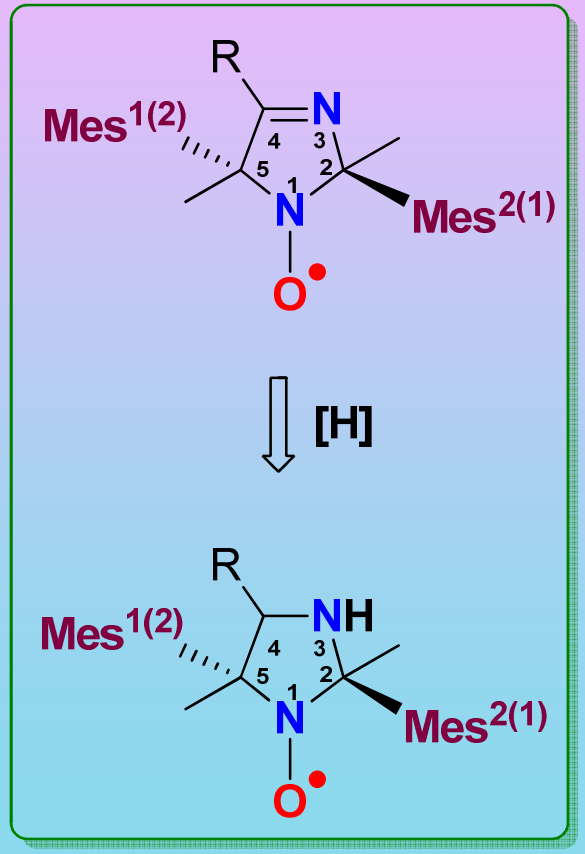
Transition from PLCs monoazoles to 1,3-diazoles

Different variants of arrangement of mesogenic substituents in imidazoline and imidazolidine nucleus

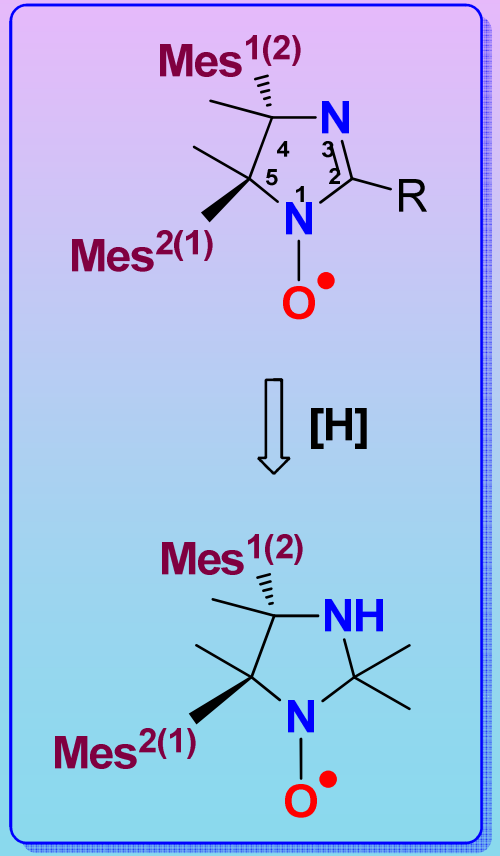
A) 2,4



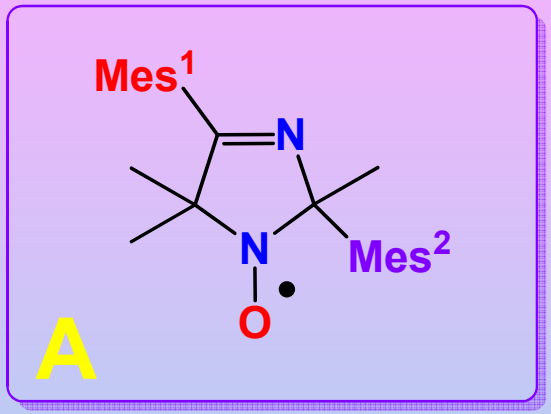
B) 2,5

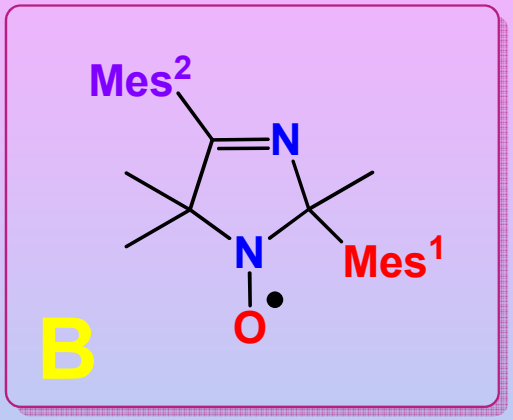


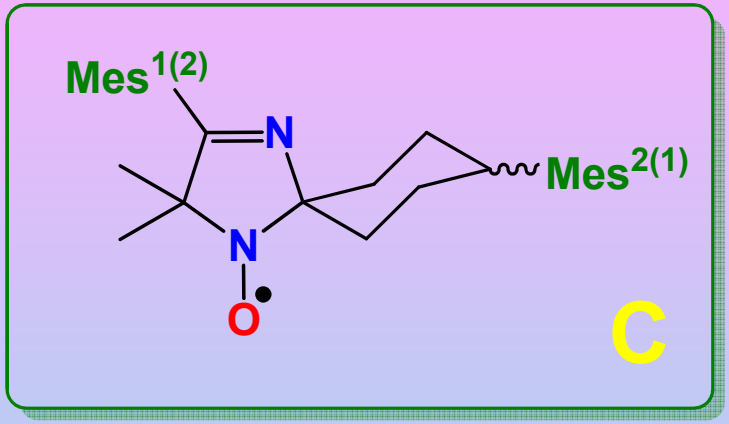
C) 4,5

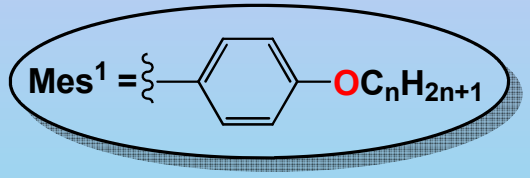


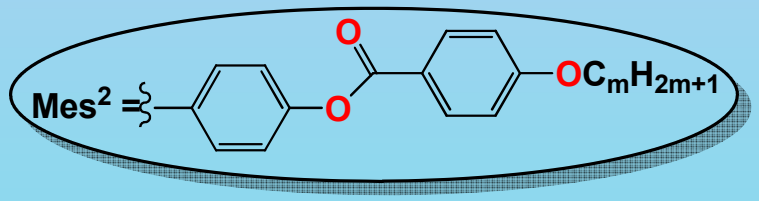
The Purpose of Our Work: Design and synthesis of novel *imidazoline mono- and binitroxides* possessing with one or two different mesogenic residues at 2(4) position of heterocycle

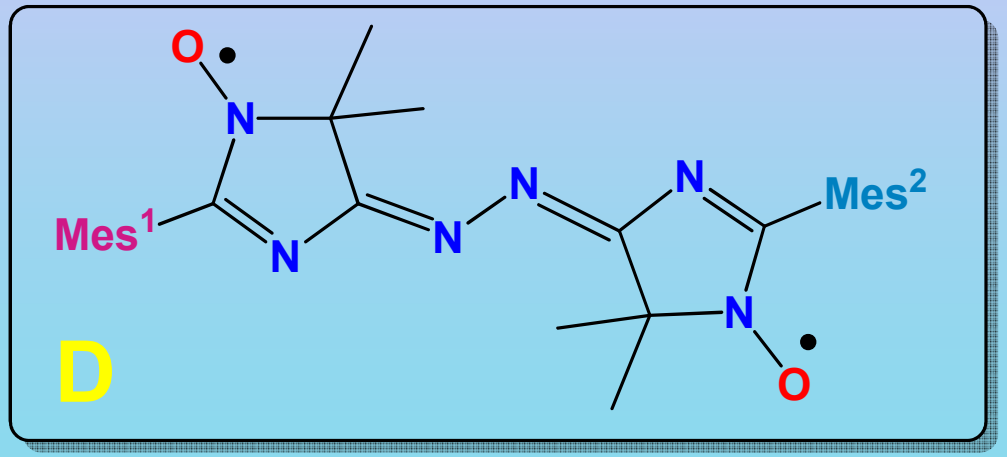




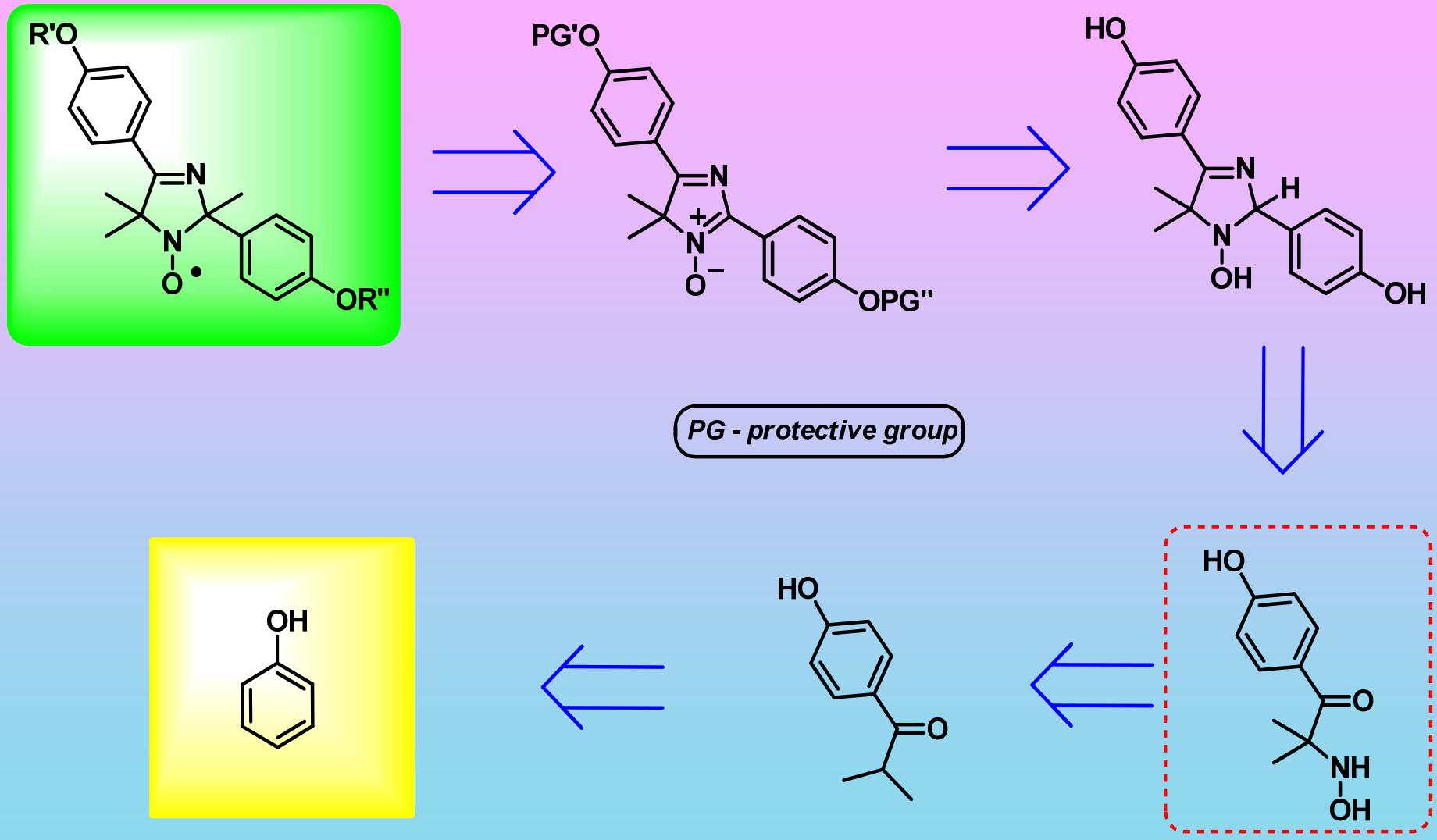




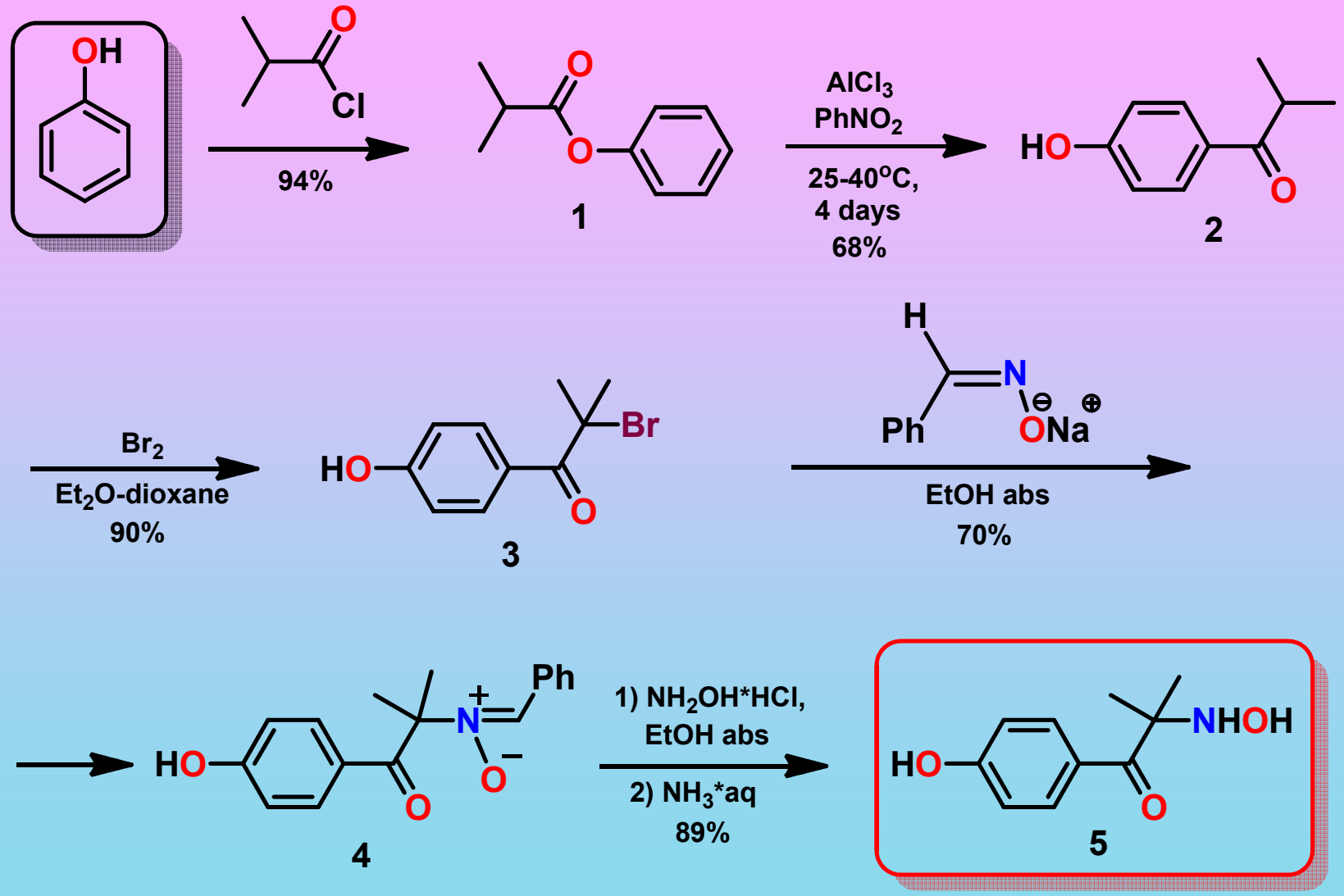




Part A: Retrosynthetic Disconnection of Target Molecule A

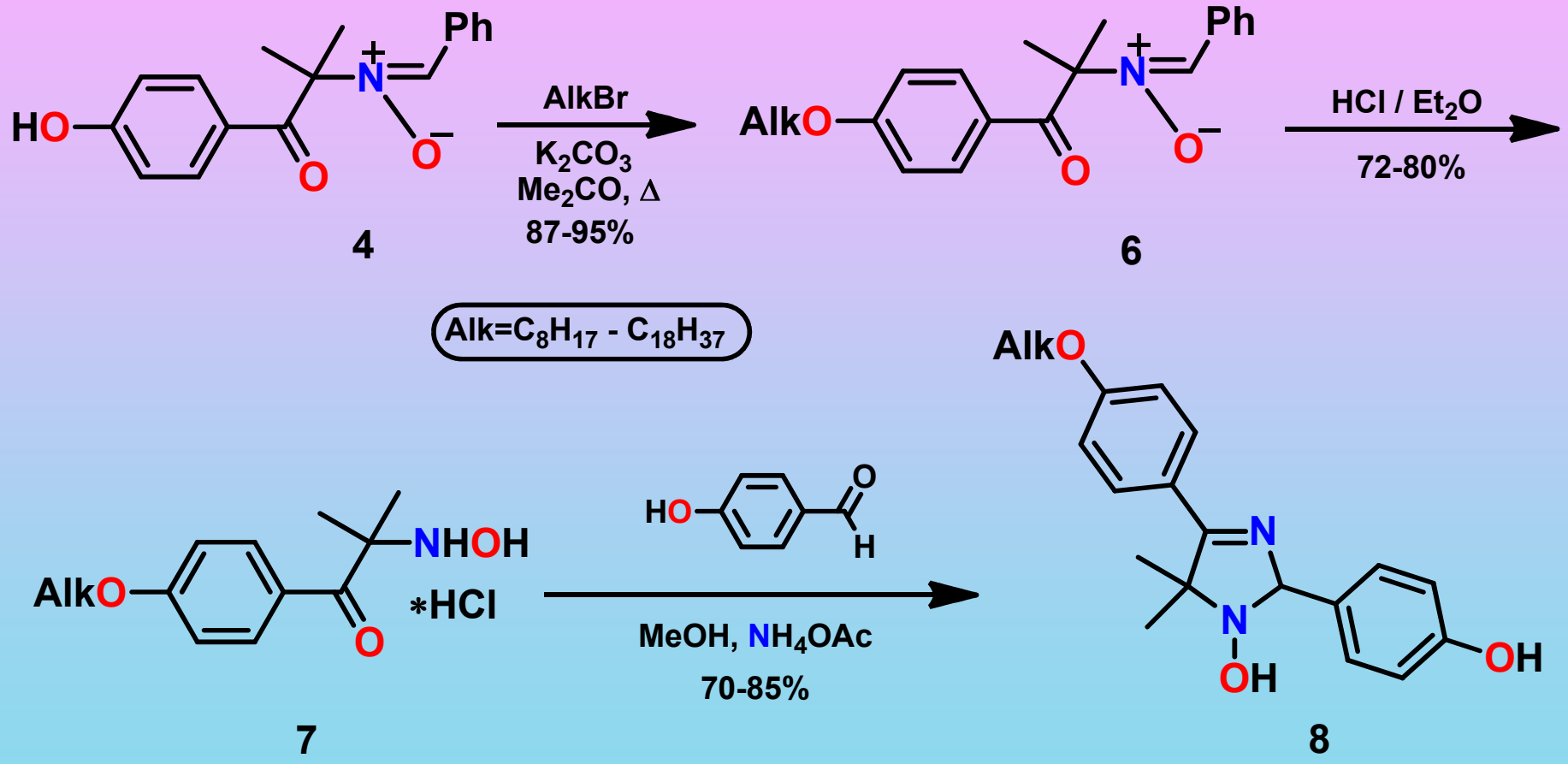


Synthesis of Key Initial Compound – *p*-Hydroxyaryl Substituted 1,2-Hydroxyaminoketone



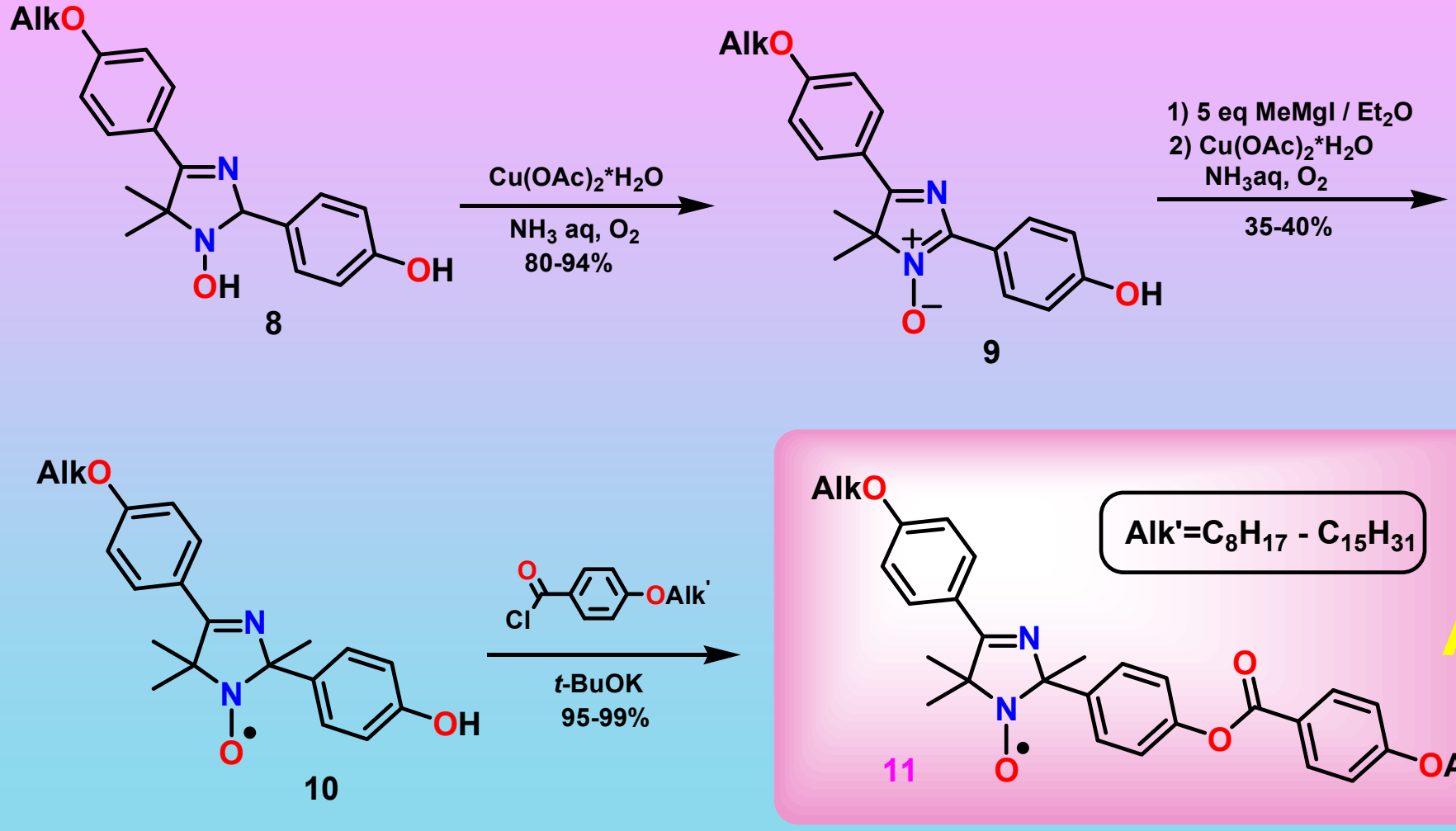
Synthesis of 3-Imidazoline NRs Bearing Two Different Mesogenic Fragments

The first approach



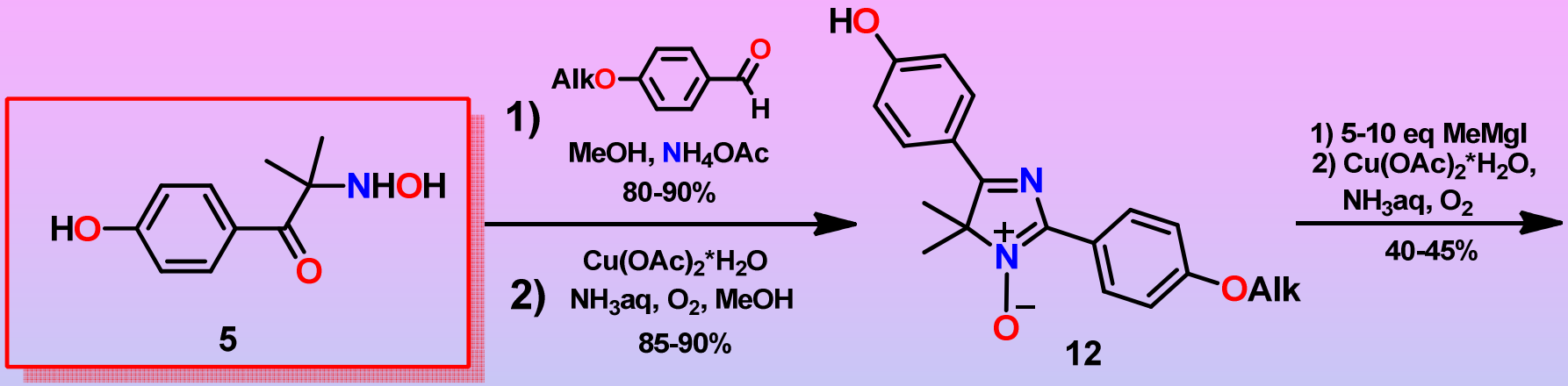
Synthesis of 3-imidazoline NRs bearing two different mesogenic fragments

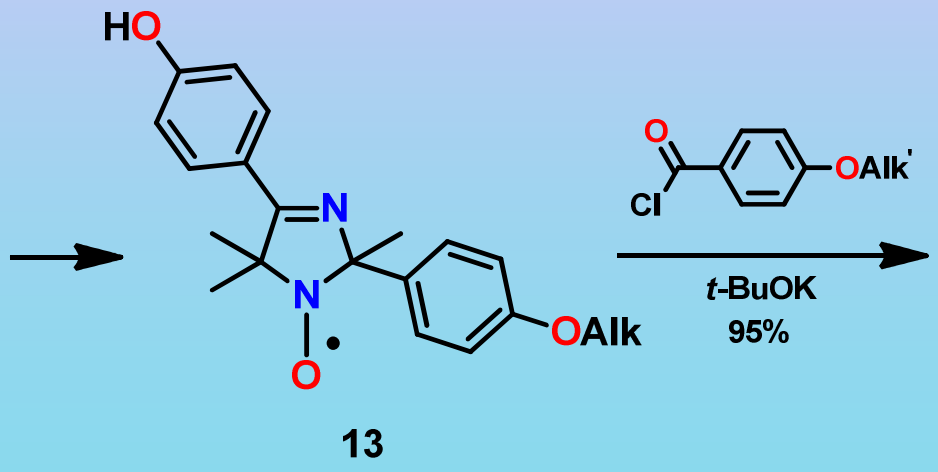
The first approach

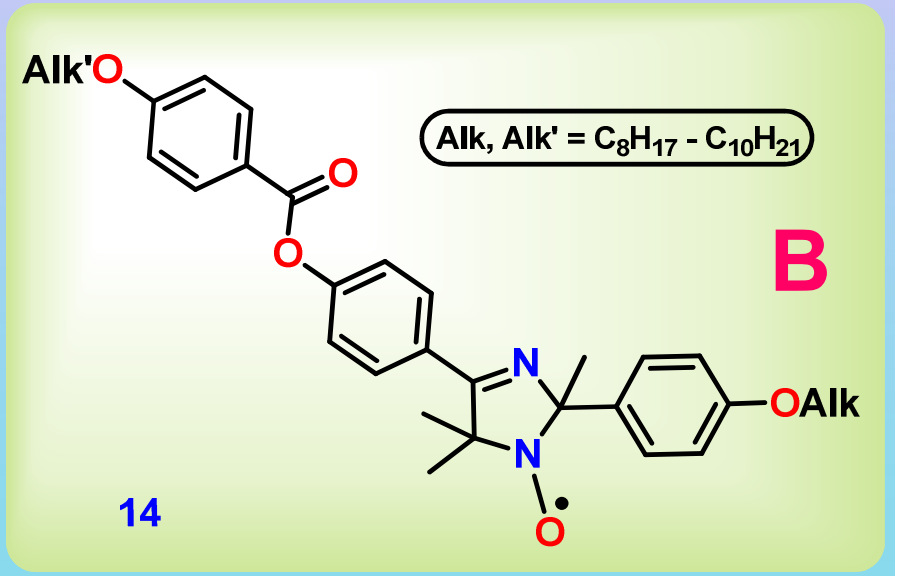


Synthesis of 3-Imidazoline NRs Bearing Two Different Mesogenic Fragments

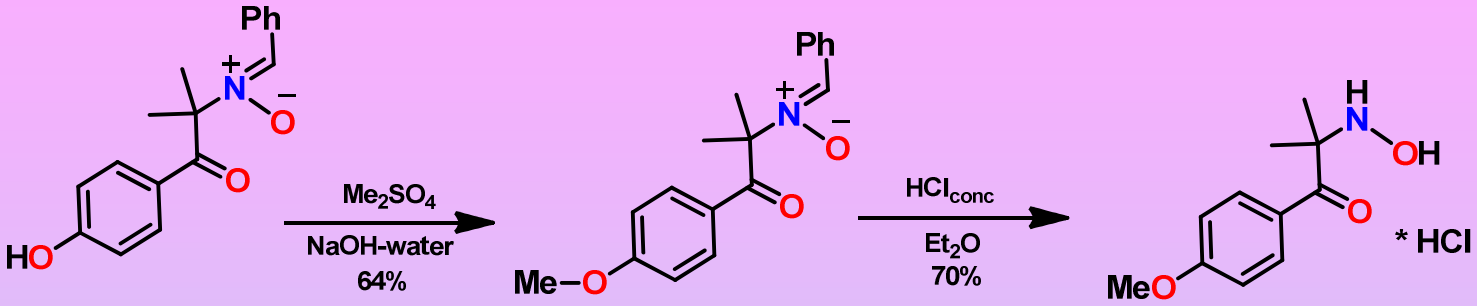
The second approach

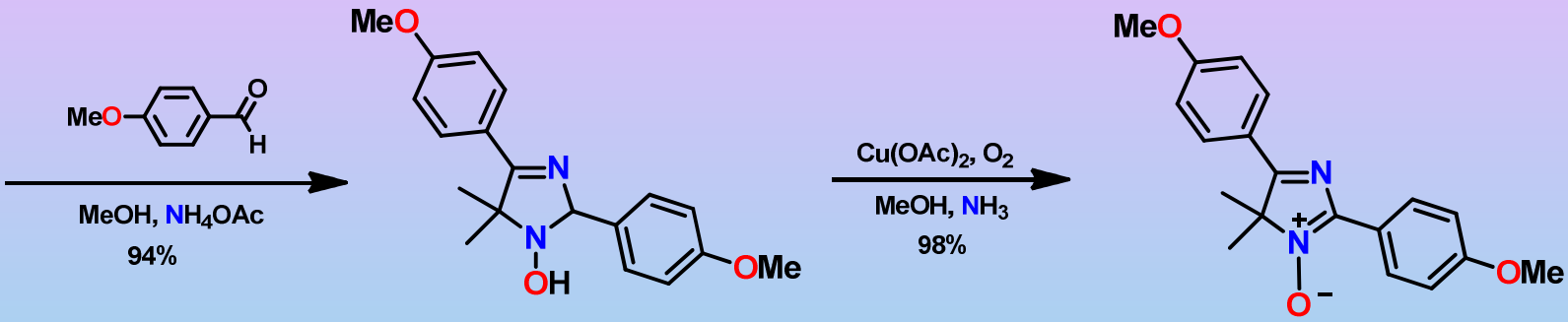


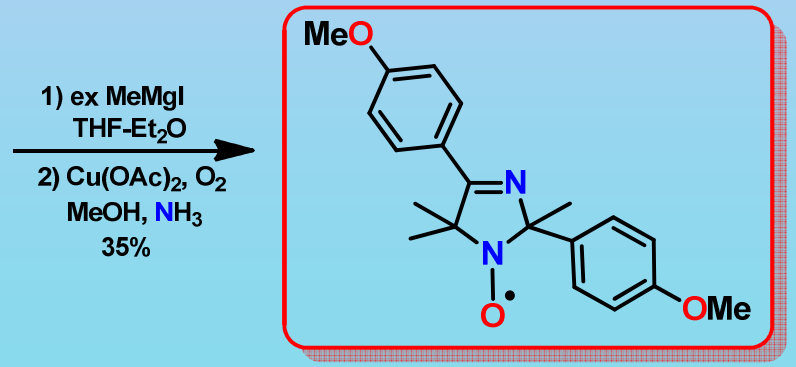




Could 3-imidazoline nitroxides possessing aromatic substituents in the positions of 2- and 4- heterocycle adopt linear or bent-core conformation?



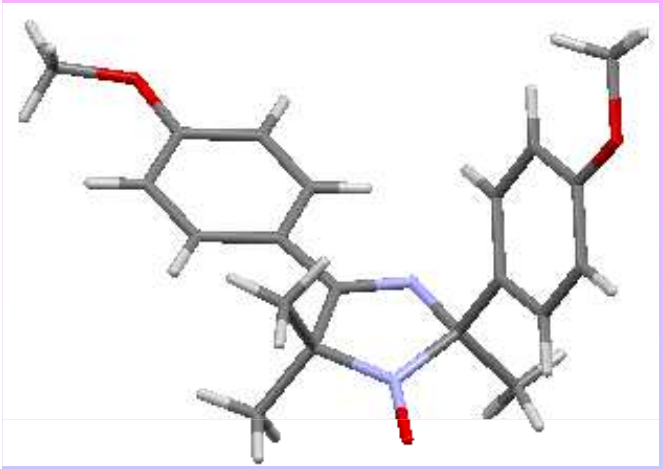


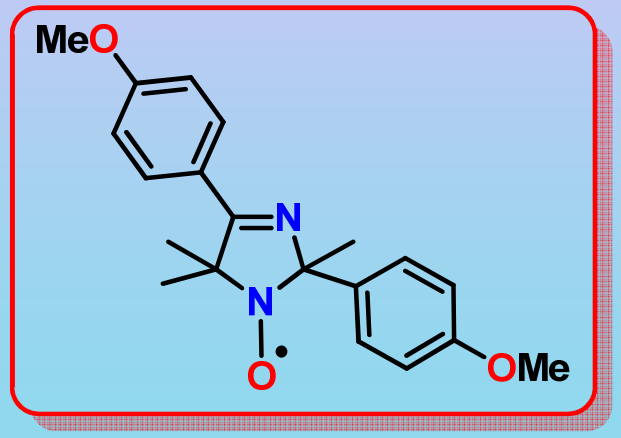


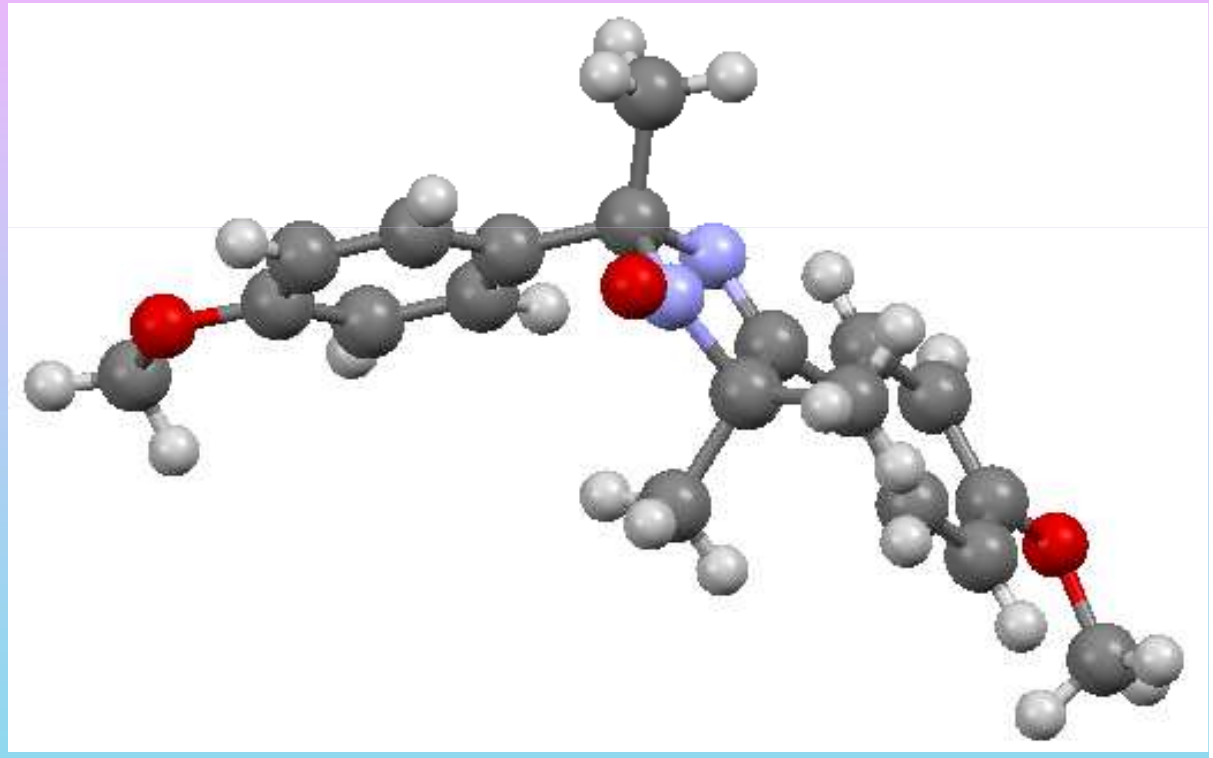
Good quality crystals were grown by slow evaporation of an ether solution

M.p. 128°C

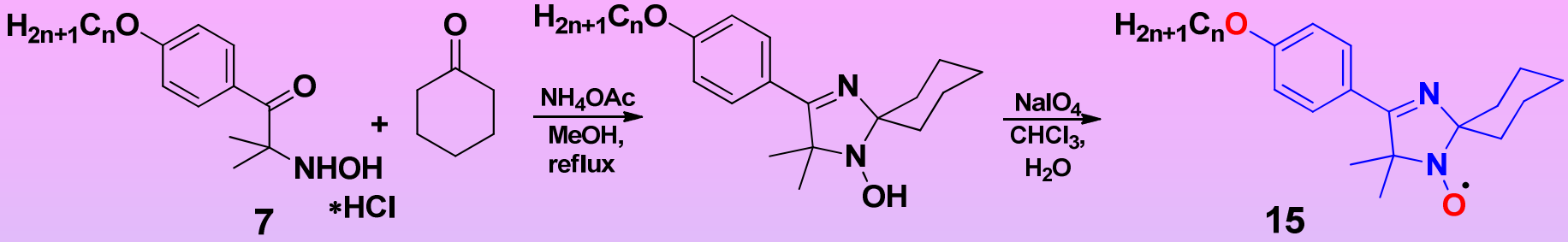
X-ray Diffraction Analysis of Synthesized Nitroxide







Synthesis of Spirocyclic Nitroxides C



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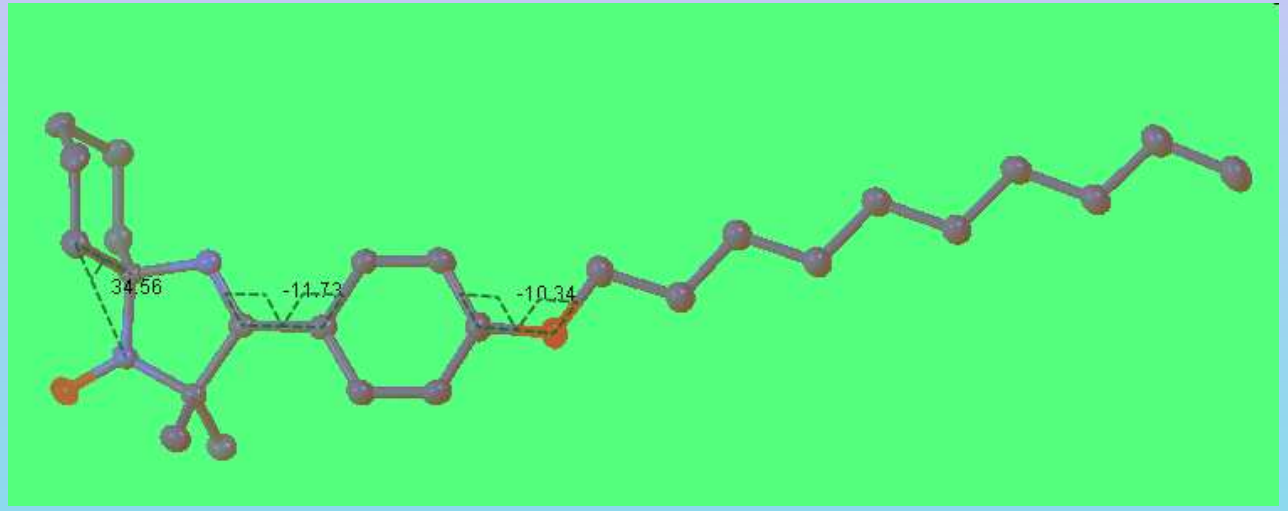
a, n=8
b, n=10
c, n=12
d, n=16

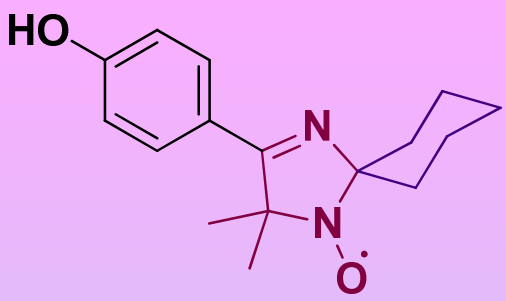
15

a, n=8
b, n=10
c, n=12
d, n=16

X-Ray of spirocyclic compound 15b



Synthesis of Spirocyclic Nitroxides C



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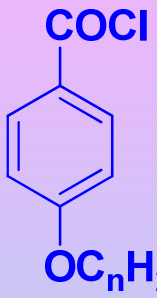
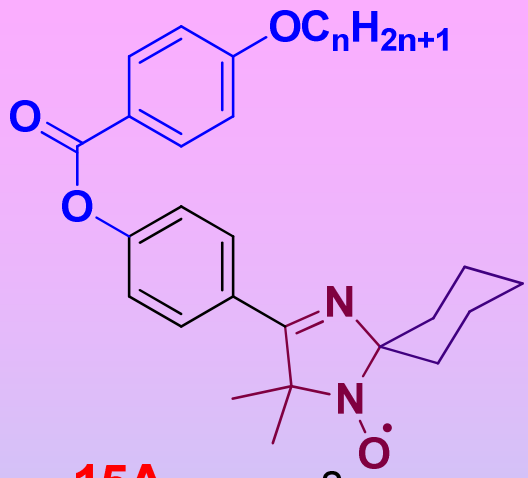
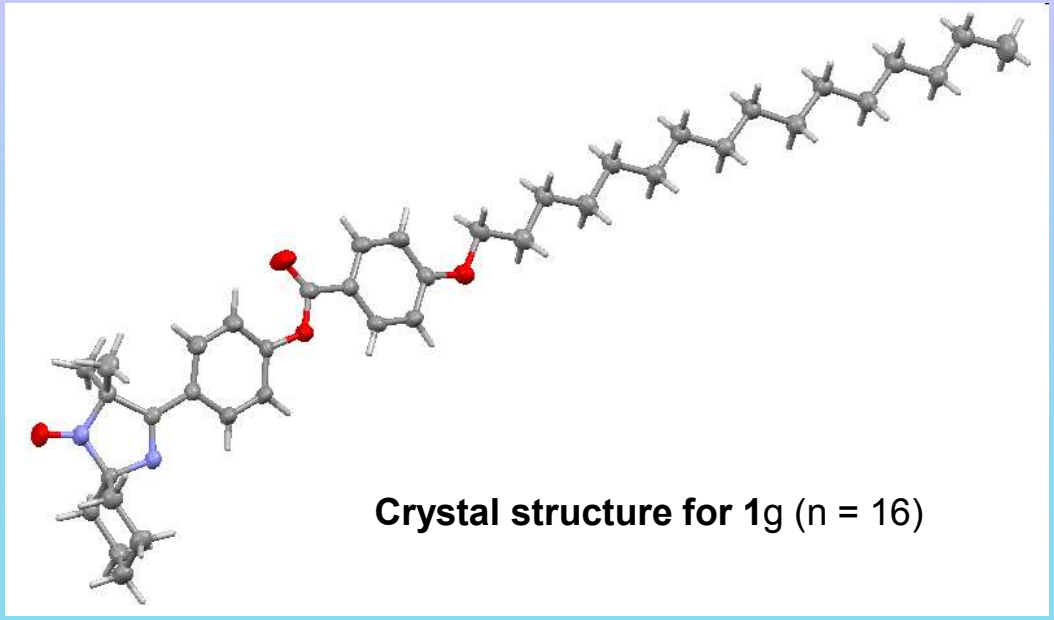
2. 

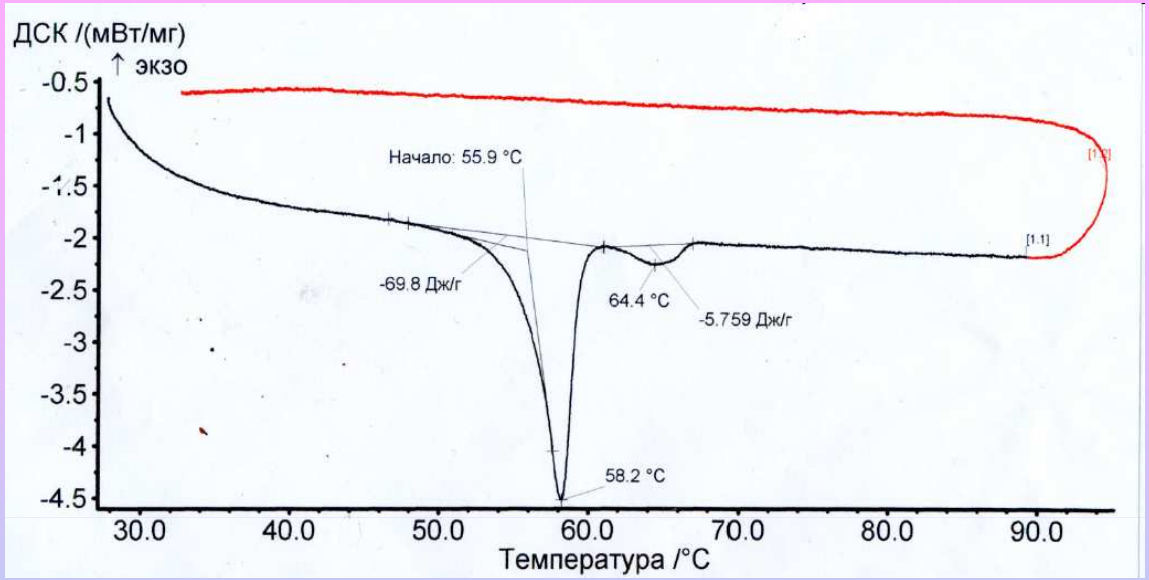


15A a: n = 8,
b: n = 9,
c: n = 10,
d: n = 11,
e: n = 12,
f: n = 14,
g: n = 16

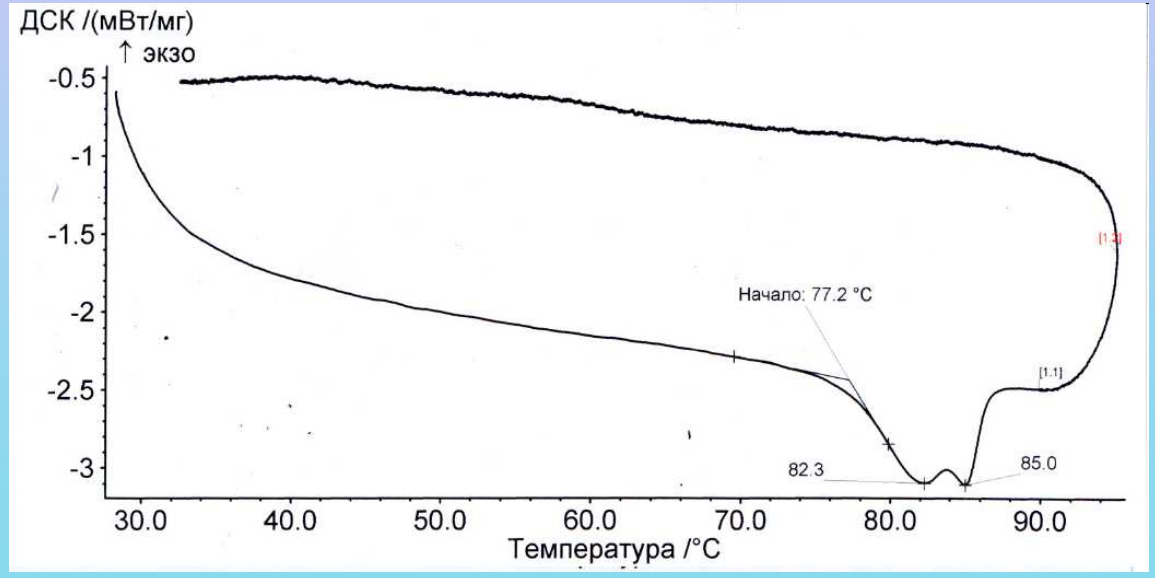


Crystal structure for 1g (n = 16)

DSC analysis data for 15A

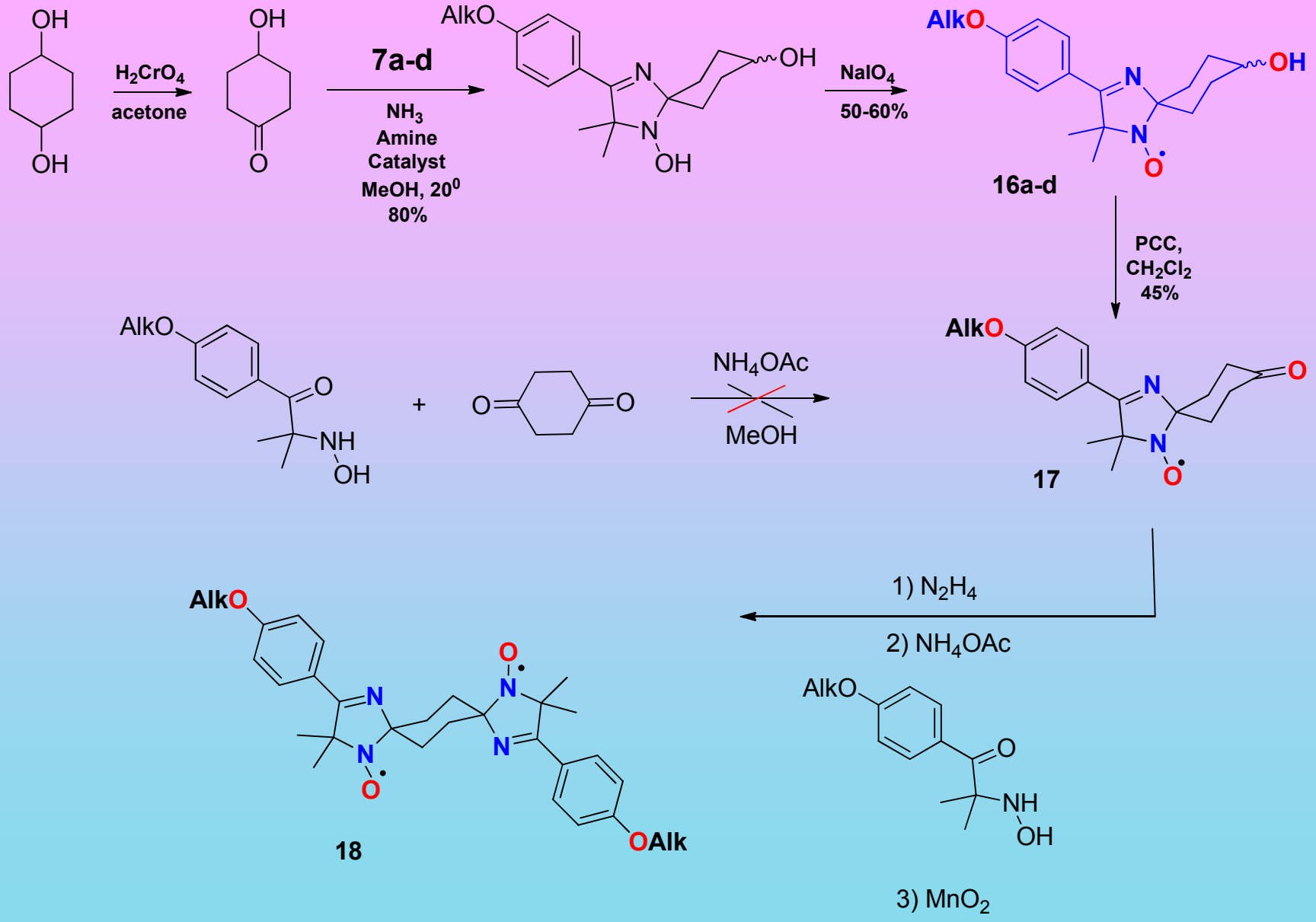


15A a (n = 8)

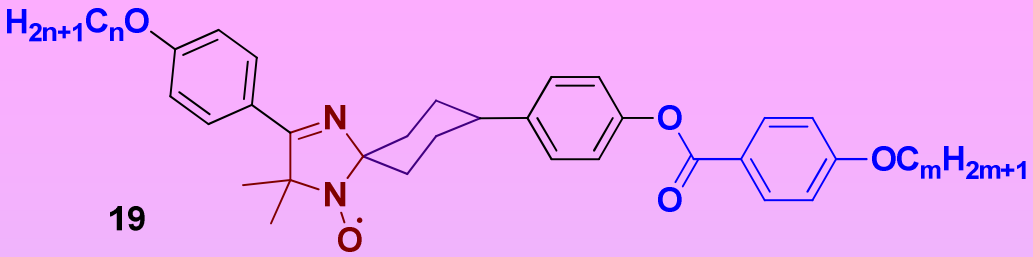


15A f (n = 14)

Synthesis of Spirocyclic Nitroxides



The next goal of our investigation



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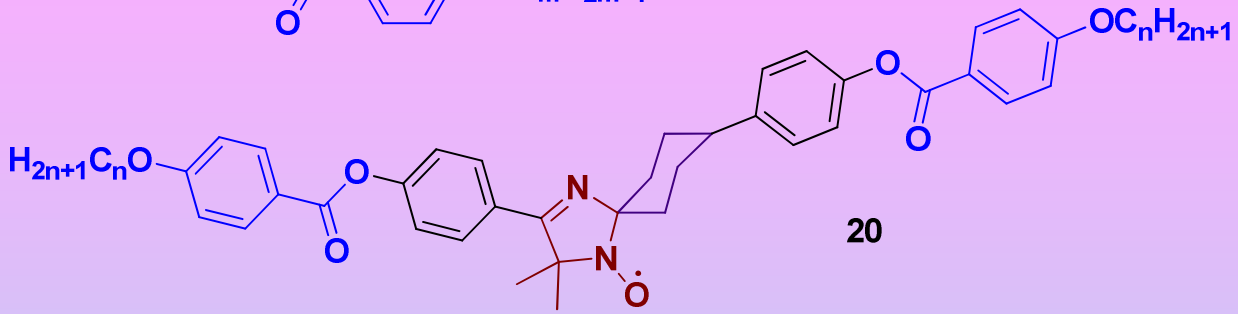

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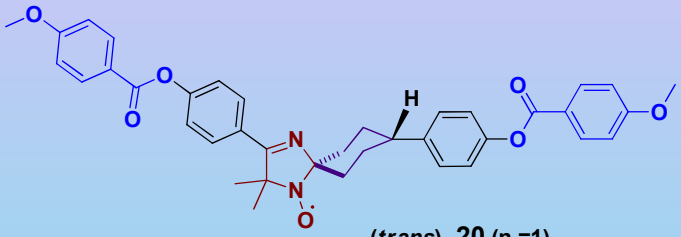
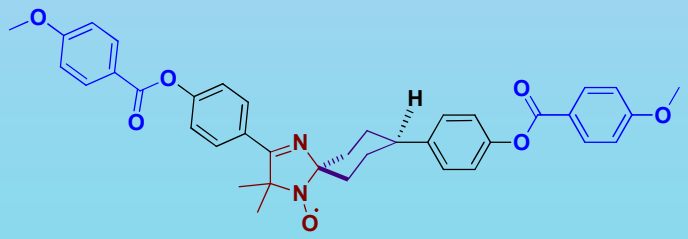
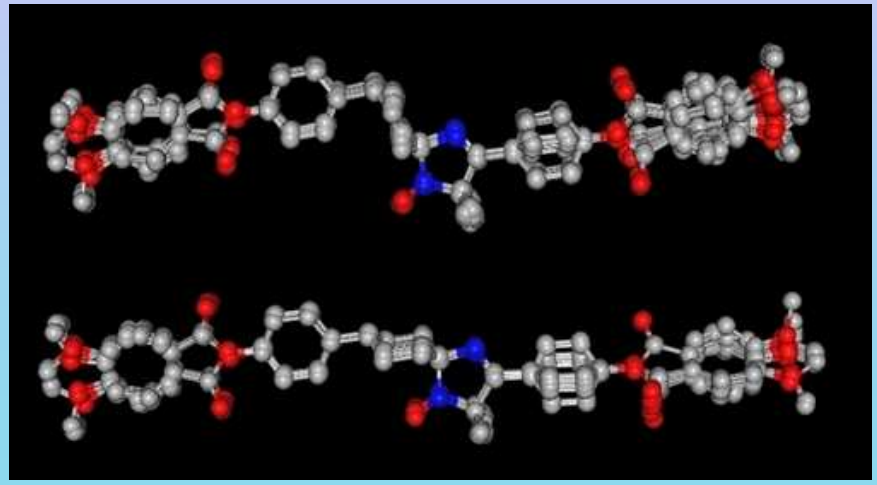
Conformational analysis data



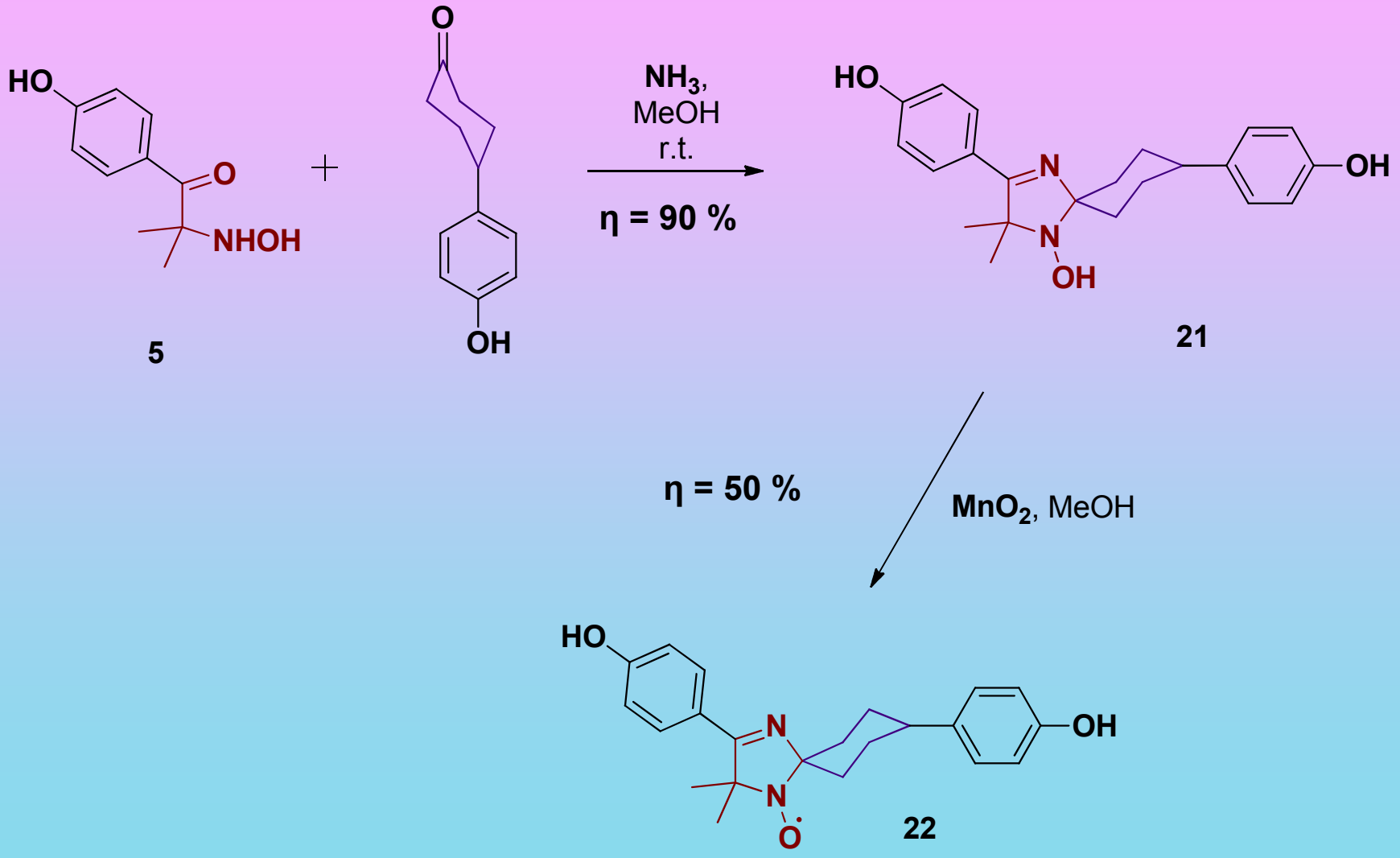
(*trans*)- **20** (n =1)



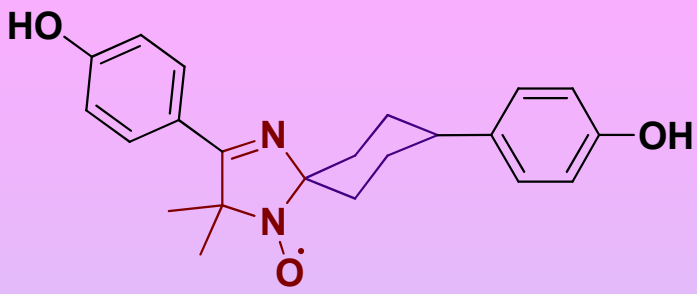
(*cis*)- **20** (n =1)



Synthesis of spirocyclic nitroxides containing 4-hydroxyphenyl substituent at 4-th position of cyclohexane



Synthesis of spirocyclic nitroxide with two acyl groups



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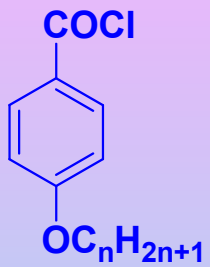
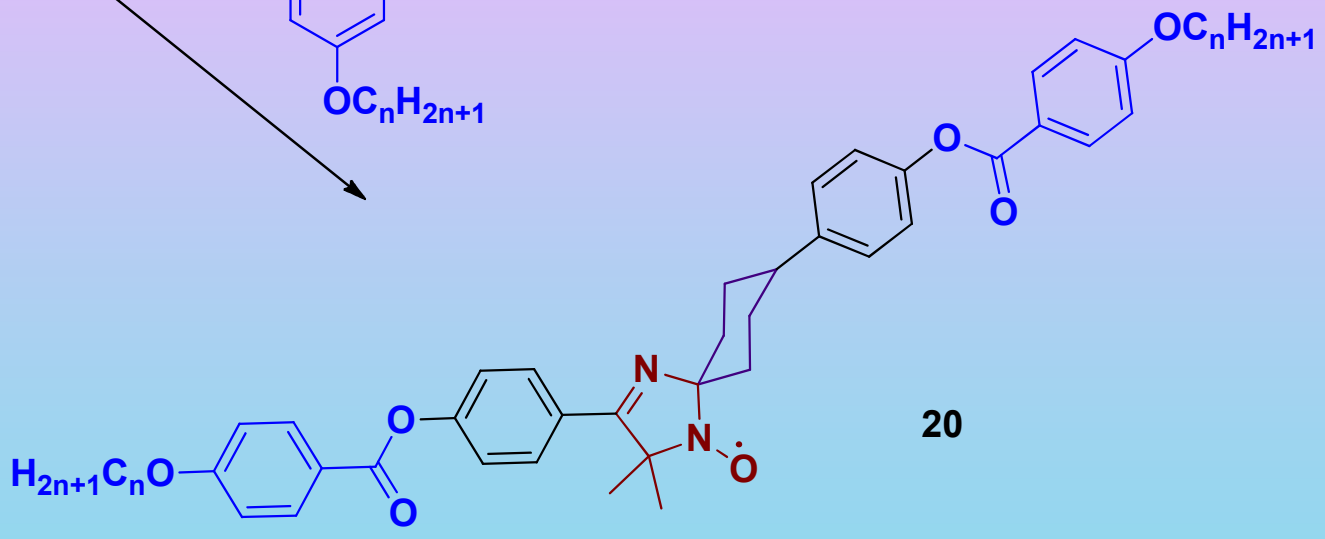
1. **tBuOK**, THF
2.



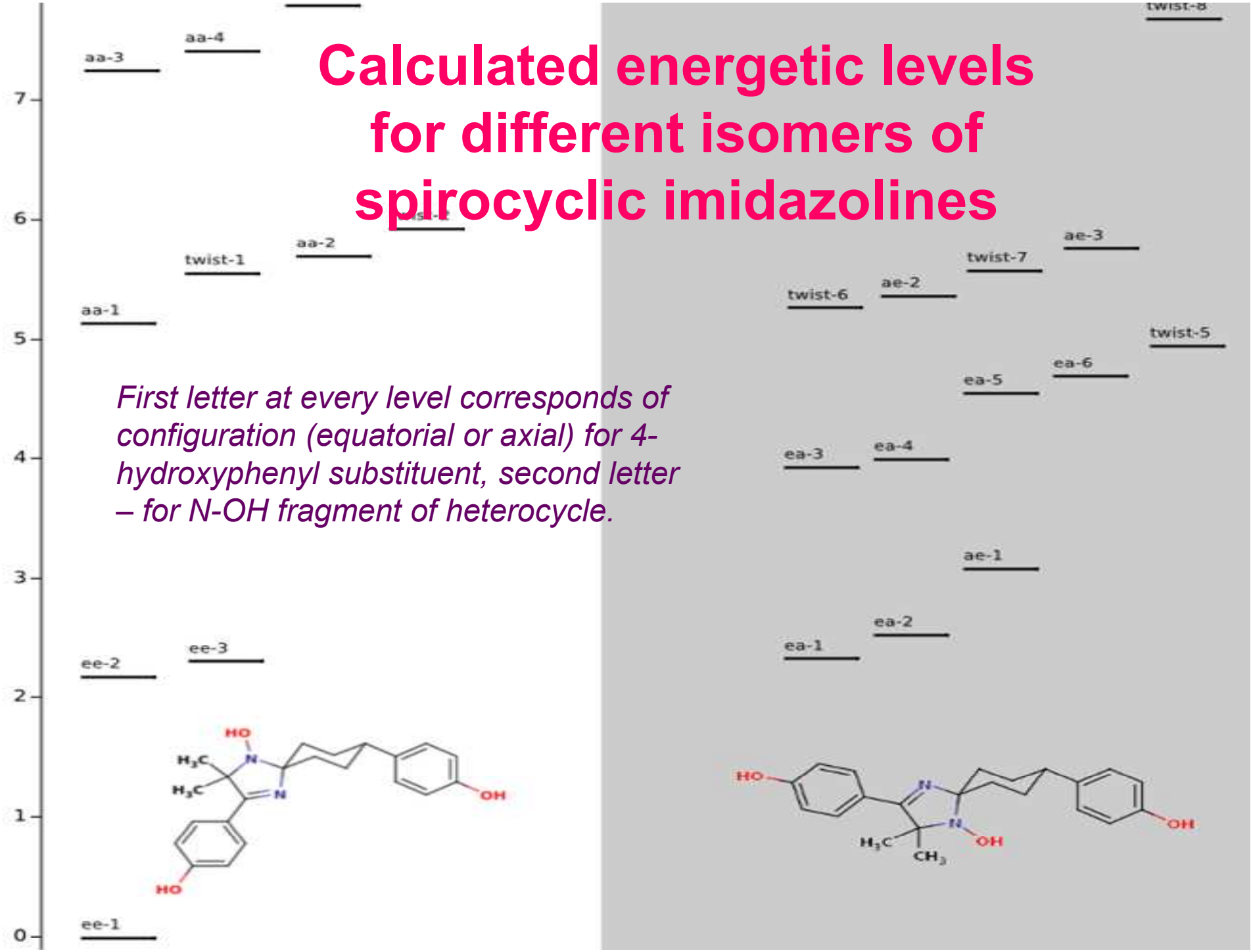


20

3 **a: n = 8**
b: n = 9
c: n = 10
d: n = 11
e: n = 12
f: n = 14
g: n = 16

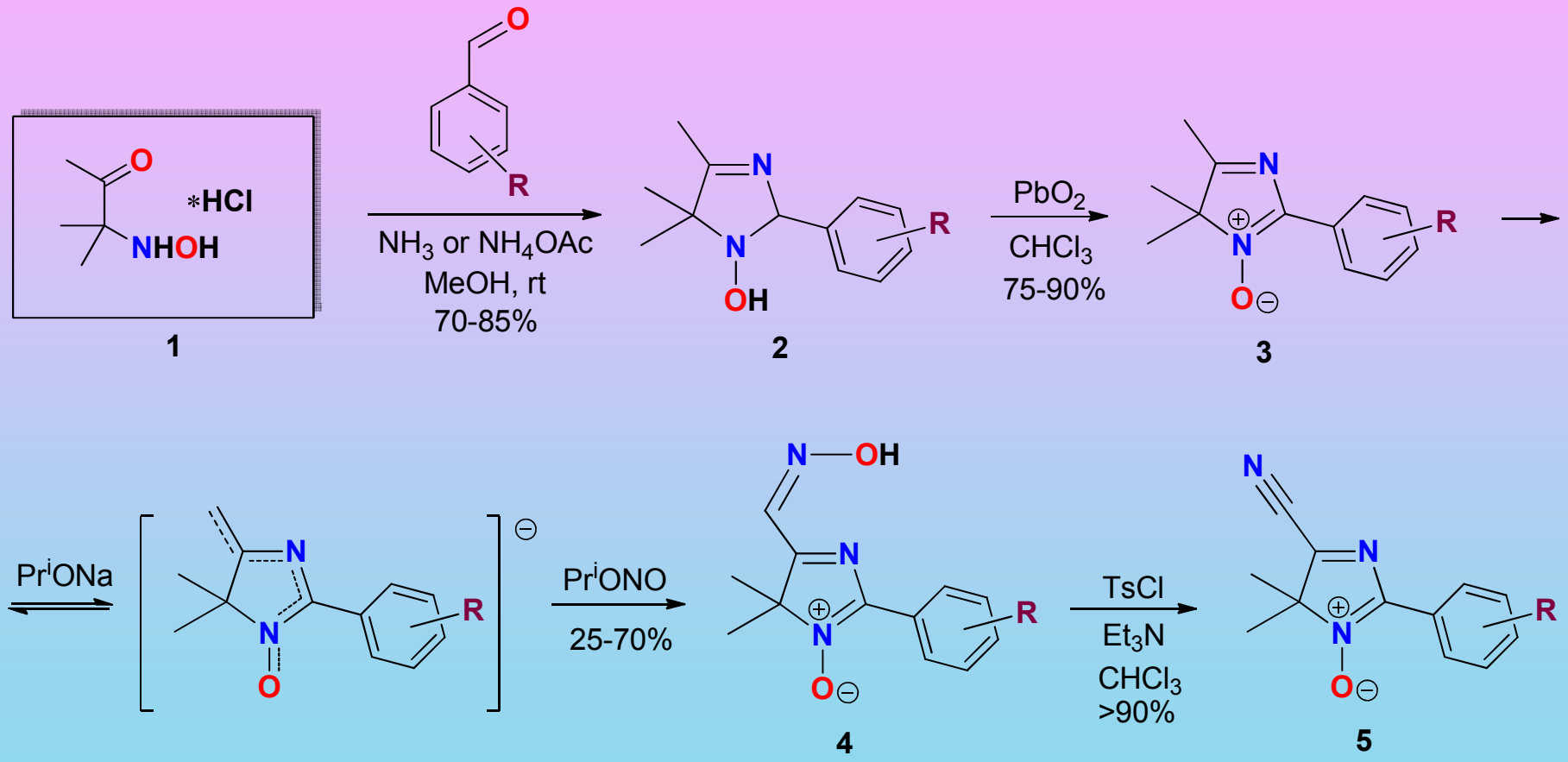
Calculated energetic levels for different isomers of spirocyclic imidazolines

First letter at every level corresponds of configuration (equatorial or axial) for 4-hydroxyphenyl substituent, second letter – for N-OH fragment of heterocycle.

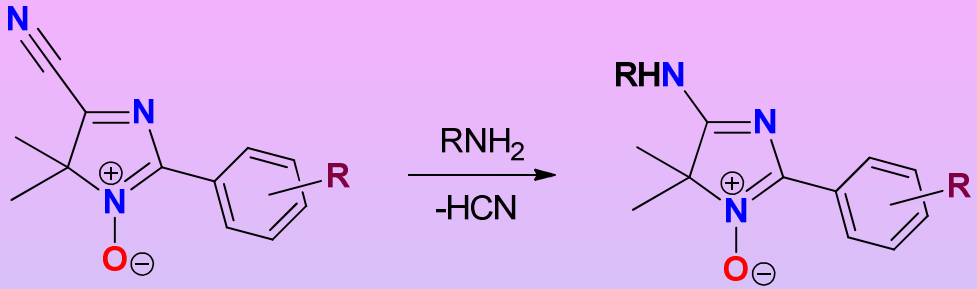


Part B: Development of synthetic approach to the imidazoline conjugated biradicals D

Preparation of key compound

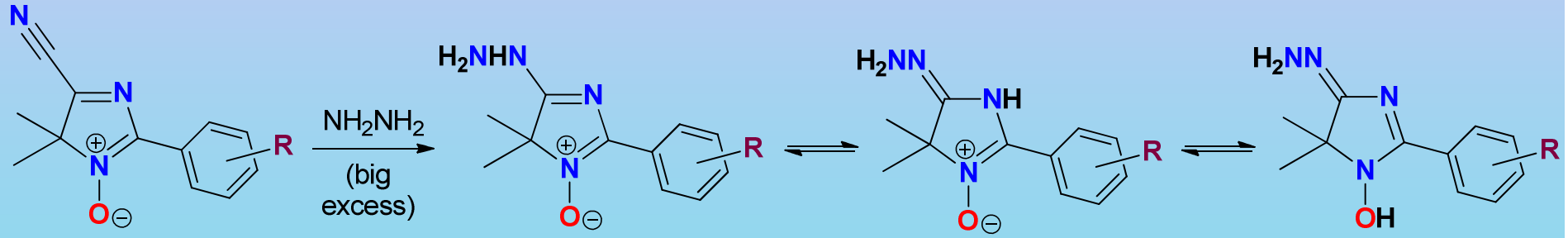


Development of synthetic approach to the mesogenic biradicals: selection of optimal conditions



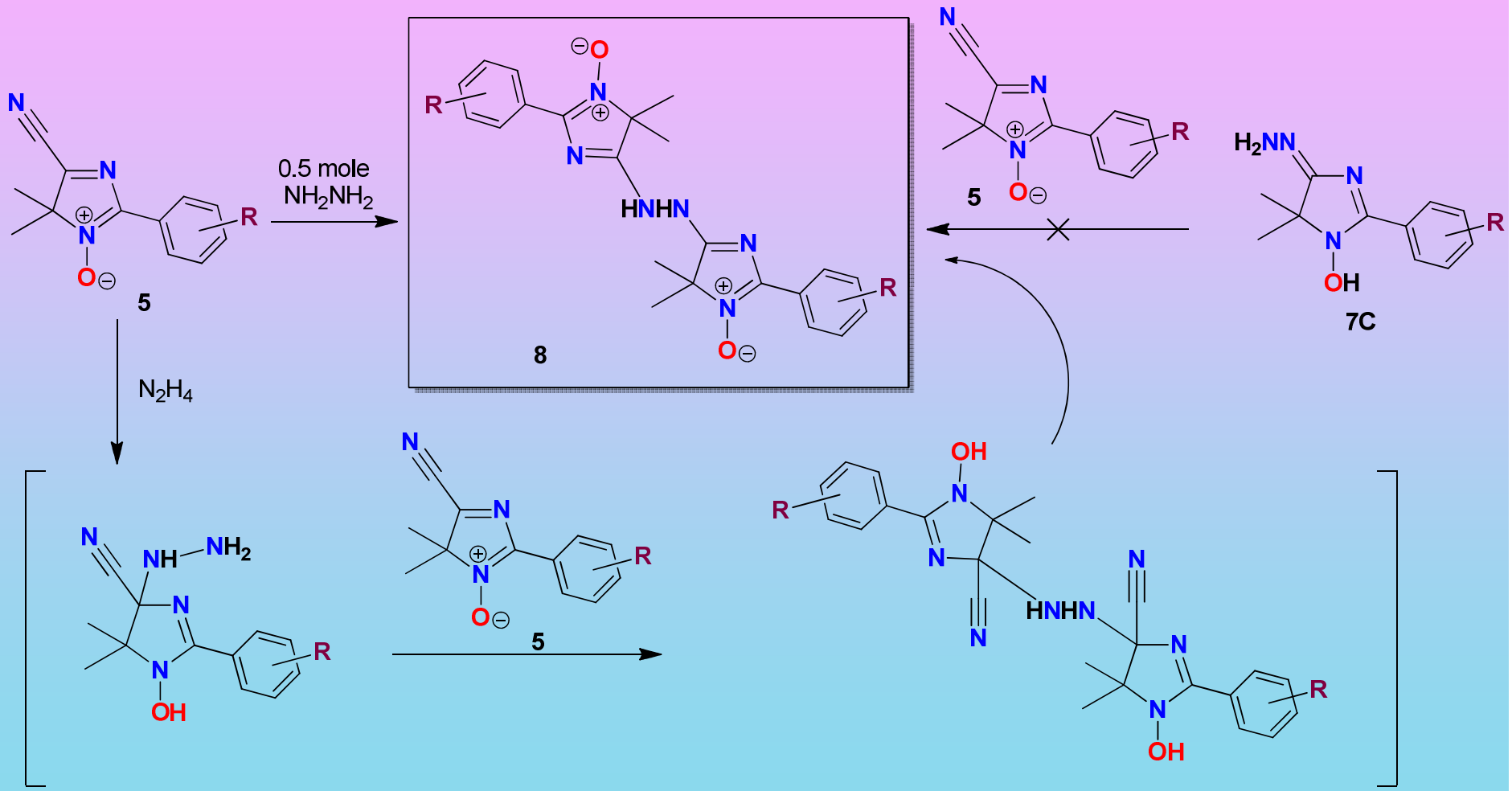
5 6

Kirilyuk, I.A.; Shevelev, T.G.; Morozov, D.A. et al. *Synthesis*, 2003, 871.
Kirilyuk, I.A.; Bobko, A.A.; Khramtsov, V.V. et al. *Org. Biomol. Chem.,* 2005, 1269

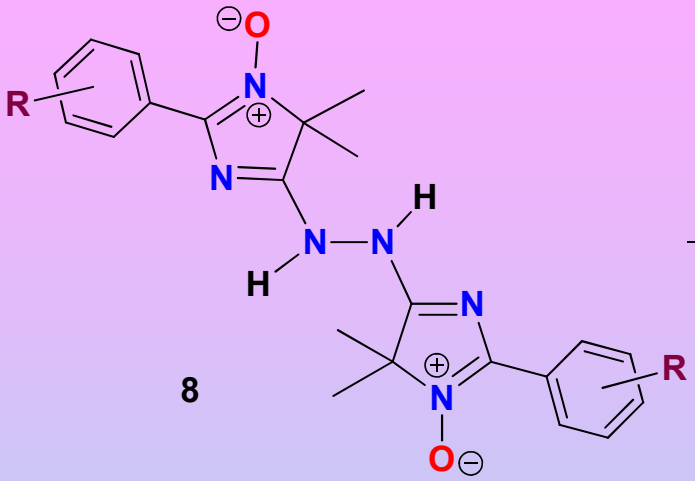


5 7A 7B 7C

Development of synthetic approach to the mesogenic biradicals: selection of optimal conditions



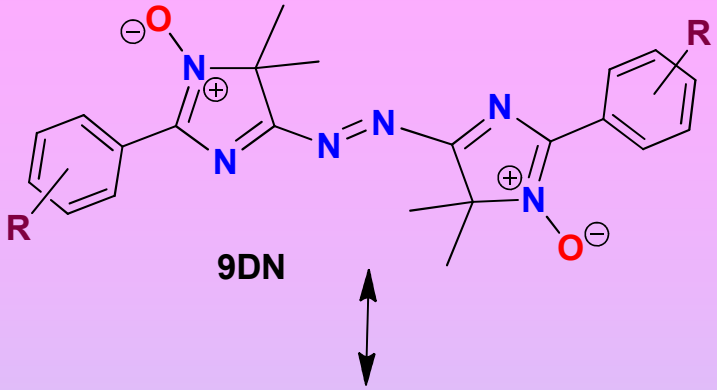
Final oxidation to biradical



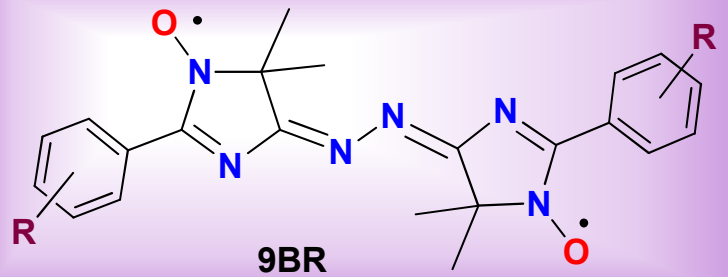
8

$NaNO_2$ / AcOH

or PbO_2

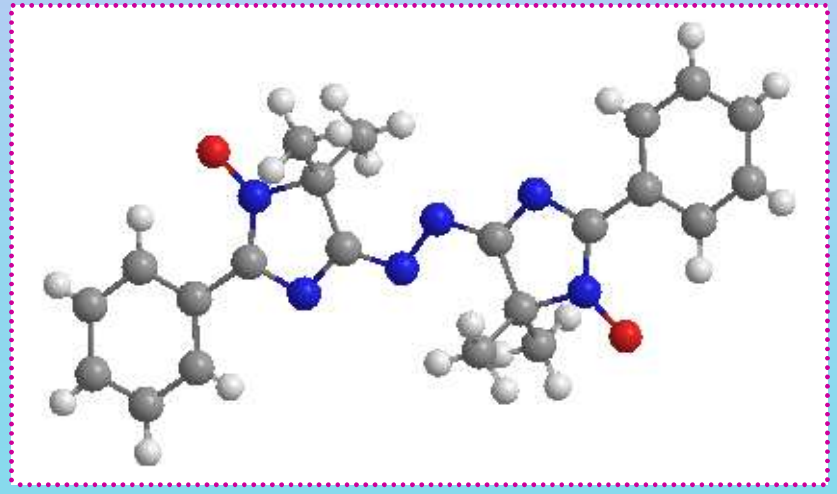


9DN



9BR

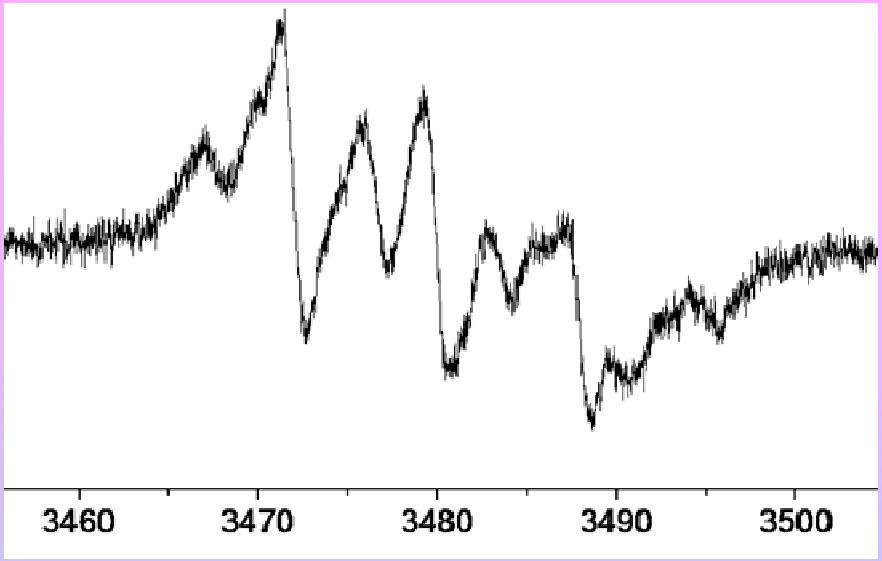
R = H, 4-OBn, 4-$OCH_2COOAlk$, 2-OMe, 4-NO_2, 4-Pyridyl, 4-NMe_2, etc



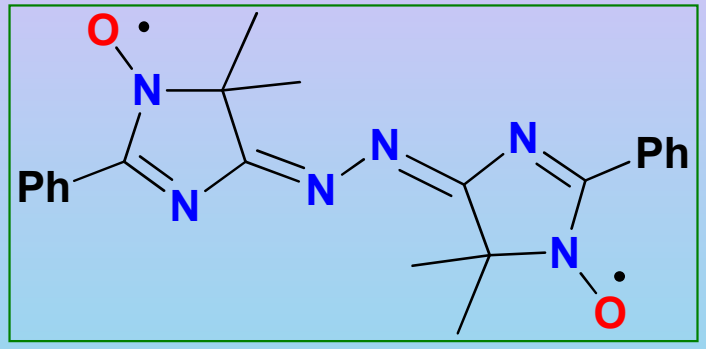
Crystalline solids with distinctive metallic luster

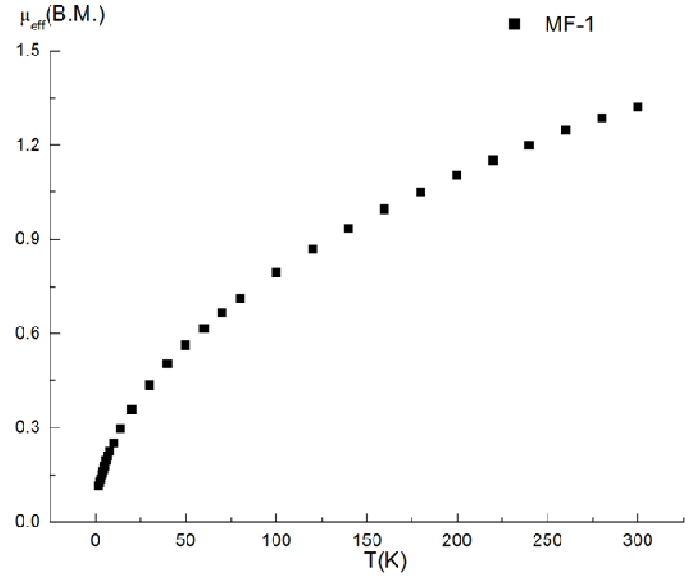
X-Ray structure of 9BR, R=H

EPR-spectrum and magnetic properties of biradical



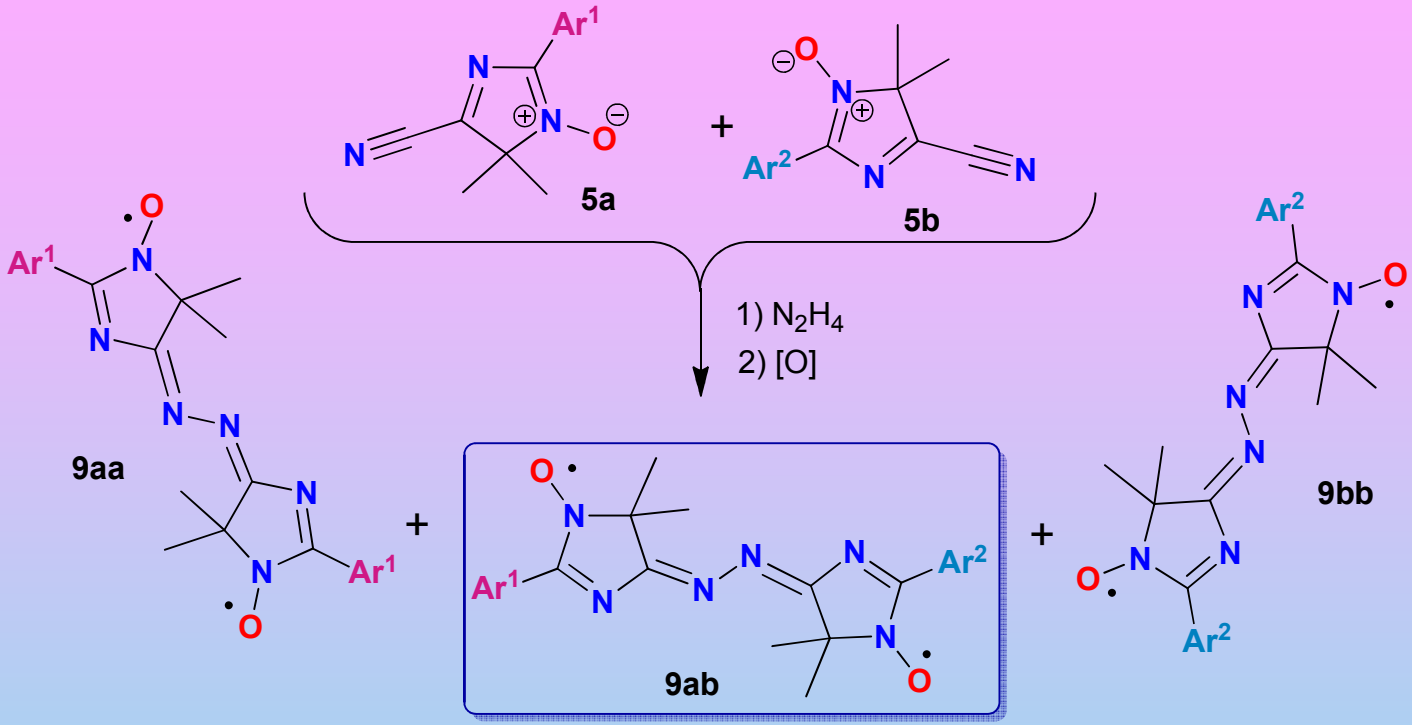
Spectrum of biradical in diluted solution

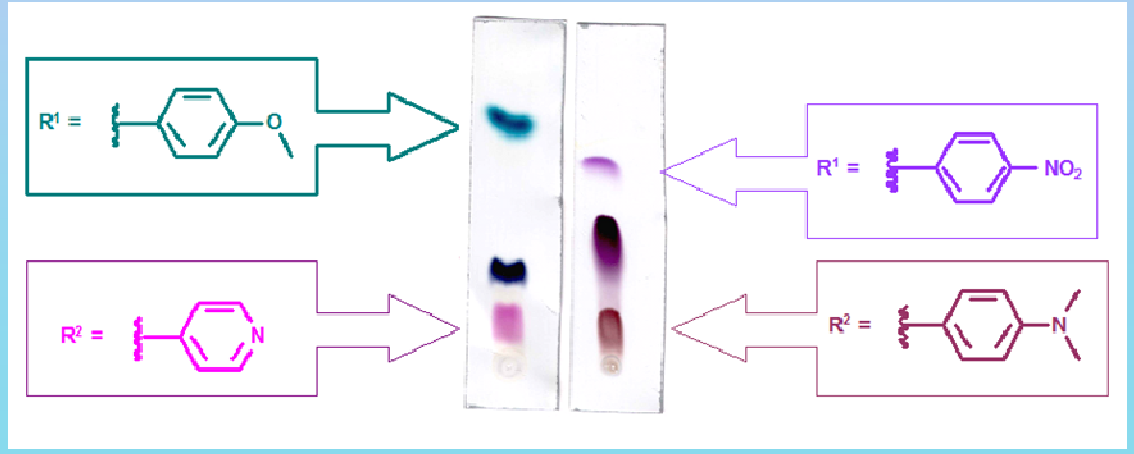




Effective magnetic moment depends on the temperature, under normal conditions, its value corresponds to ~ 30% of the content of the biradical form

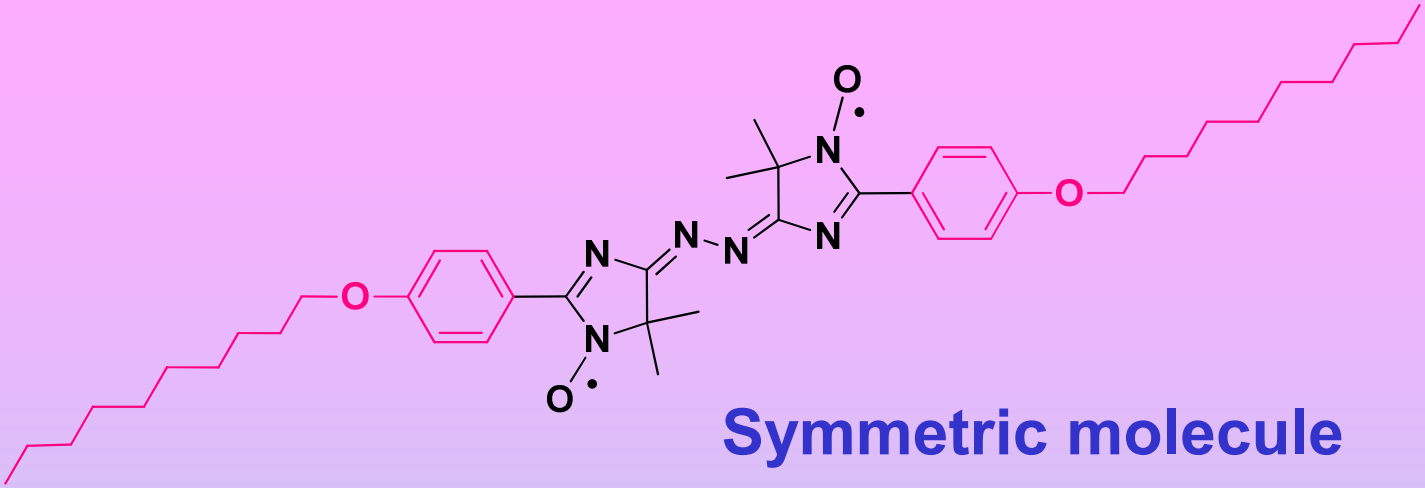
One-pot cross-reaction for the synthesis of asymmetric biradicals



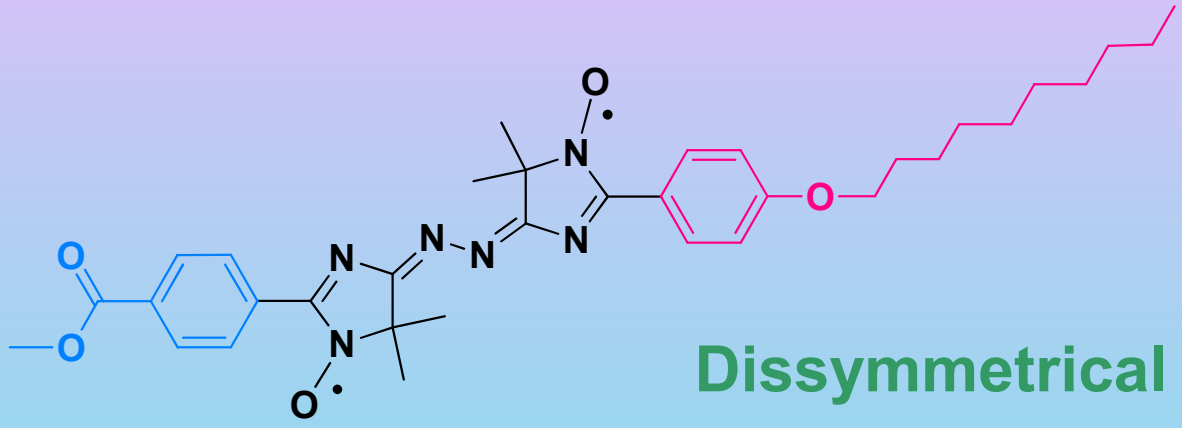


Previously synthesized adducts

Newly prepared structures of imidazoline biradicals



Symmetric molecule



Dissymmetrical molecule

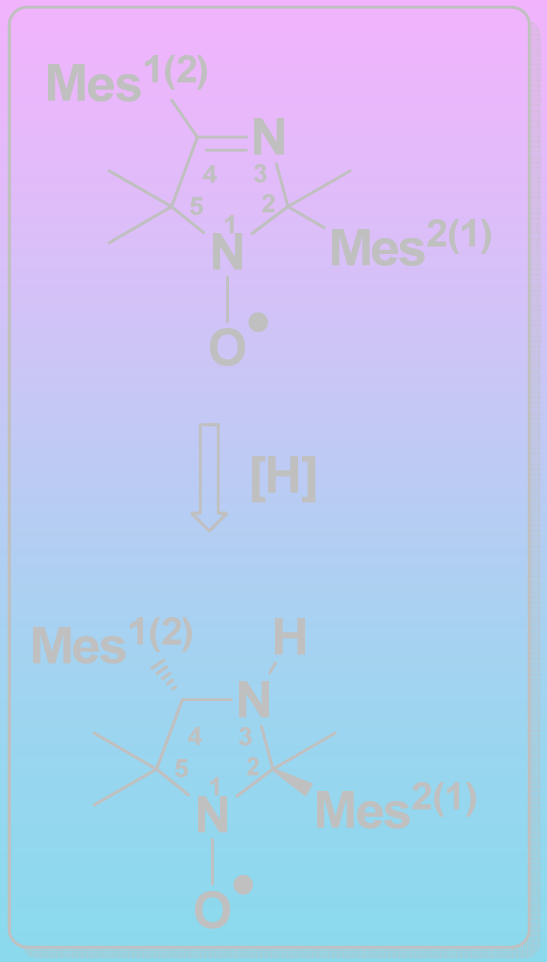
Both substances have very high melting points (~195–210°C), followed by decomposition, resulting in the loss of color and splitting of oxygen molecule, liquid crystalline phases was not observed upon heating

Resume

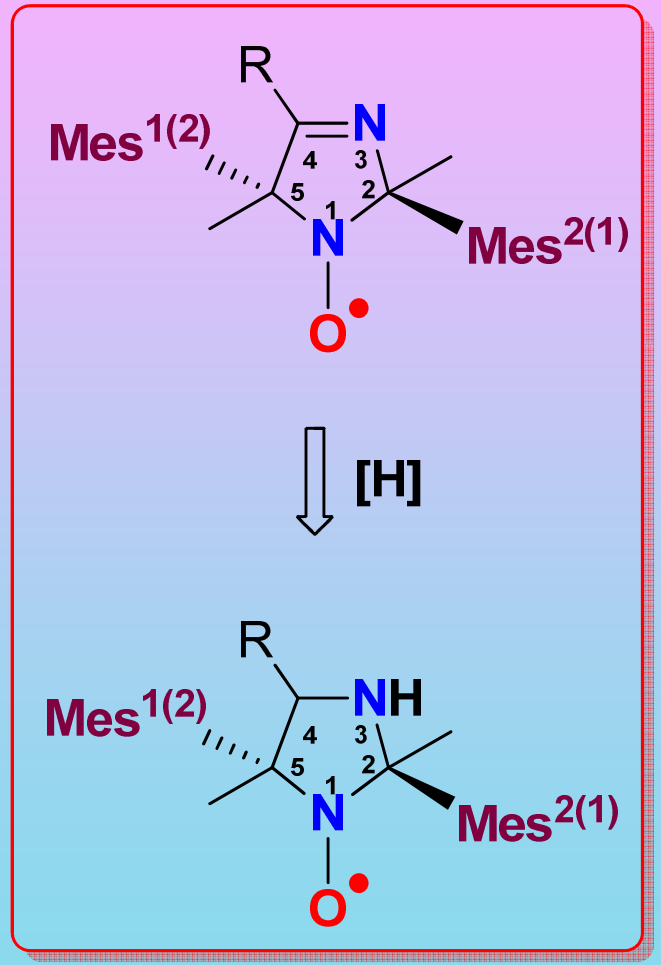
- *Two approaches for synthesis of 3-imidazoline nitroxide radicals bearing two different mesogenic groups at C-2 and C-4 carbon atoms were elaborated;*
- *Spirocyclic nitroxides – useful intermediates for synthesis of functionalized mono- and biradicals were obtained;*
- *Strategy for synthesis of asymmetric biradicals 2-imidazoline type linked with each other an azo-group was developed*

Near Future Planes

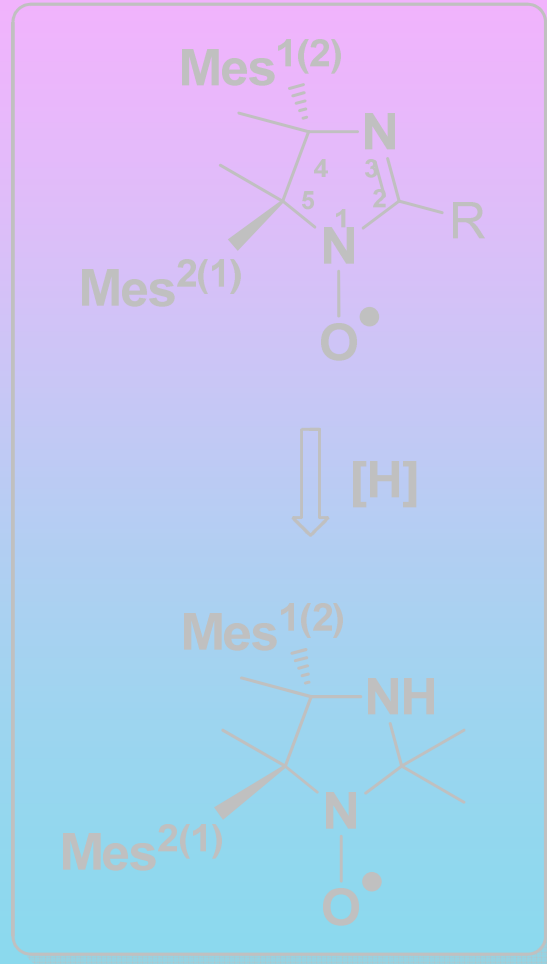
A) 2,4



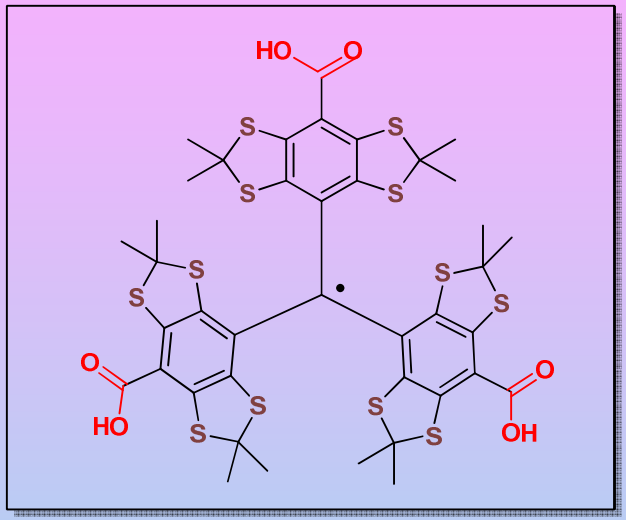
B) 2,5



C) 4,5



Investigations of transformations of superstable trityl radicals for creation of paramagnetic discotic liquid crystals



Finland Trityl