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NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN ANNULATED DIAZINES UNDER THE ACTION OF 7-AMINOCOUMARINS

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Abstract. To date, 7-aminocoumarin dyes have a huge field of application as active components of optical brighteners, fluorescent and laser dyes and sensors, since they have high quantum yields, large Stokes shifts, and tunable absorption and emission wavelengths [1]. Features of the optical properties of 7-aminocoumarins are determined by the electronic nature of the substituents in 3 or 4 positions of the aminocoumarin framework. Many commercial coumarin dyes contain an azaheterocyclic moiety at position 3, which conjugates with a dialkylamino group at position 7 to form push-pull fluorophores (Fig. 1). Therefore, the purpose of this work is the synthesis of new derivatives of 7-diethylaminocoumarin with diazines.

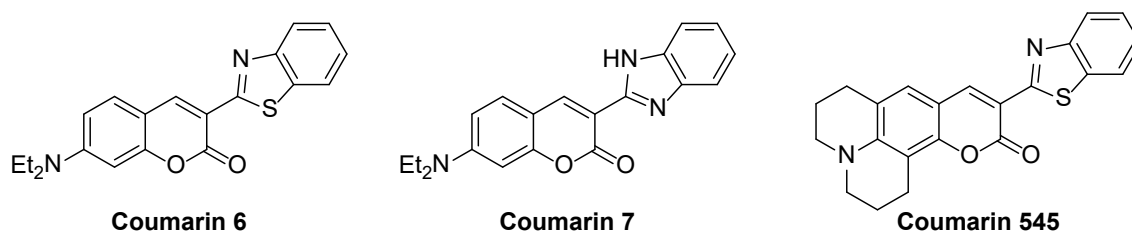
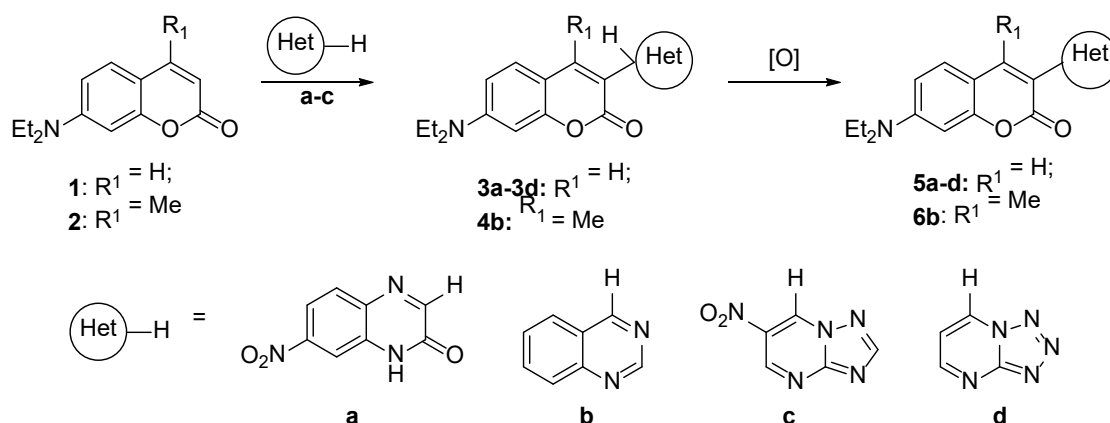


Figure 1. Commercially available 3-substituted 7-aminocoumarins

We have found that the reaction of 7-diethylaminocoumarin **1** with annulated azines **a,c,d** in acetic acid upon activation with 4-equivalents of perfluorobutanoic acid (PFBA) leads to formation of adducts **3a,c,d**. In the case of reaction of 7-diethylaminocoumarins **1,2** with quinazoline **b** in acetic acid, upon activation with 3 equivalents of methanesulfonic acid, adducts **3b, 4b** are obtained. The first stage of obtaining adducts goes with good yields and does not require chromatographic purification. Subsequently, the resulting adducts were oxidized either in dichloroethane (for compound **4b**) or in DMF (for compounds **3a-3d**) with DDQ (1.5 equivalents) at reflux to obtain products of nucleophilic hydrogen substitution **5a-d, 6b**.



References

1. Cao, D. Coumarin-Based Small-Molecule Fluorescent Chemosensors / D. Cao, Z. Liu, P. Verwilt, S. Koo, P. Jangjili, J.S. Kim, W. Lin // *Chem. Rev.* – **2019**. – Vol. 119, Iss. 18. – P. 10403–10519.

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