SYNTHESIS OF 2,4-DISUBSTITUTED 9,9'-SPIROBIFLUORENES AND FLUORO DISPIROINDENO[2,1-C]FLUORENES THROUGH CATALYTIC [2+2+2] CYCLOTRIMERIZATION

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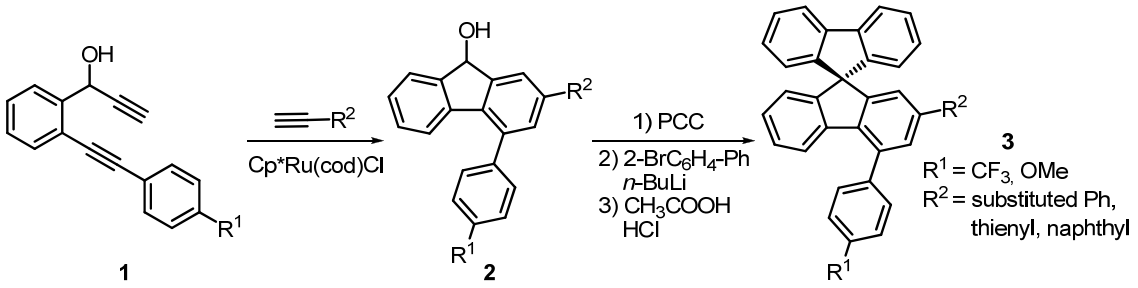
Recently, we have shown that Rh-catalyzed [2+2+2] cyclotrimerization of appropriately substituted diynes and alkynes can be a straightforward method for the synthesis of various 1,2,3,4-tetrasubstituted fluorenols (precursors for spirobifluorenes) [1, 2]. Herein, we would like to demonstrate that Ru-catalyzed [2+2+2] cyclotrimerization is a suitable method for regioselective synthesis of 2,4-disubtituted fluorenols. The Cp*RuCl(cod) catalyzed cyclotrimerization between monosubstituted diynes **1** and various terminal alkynes provided fluorenols **2** with a good regioselectivity for the *meta*-regioisomer (*meta/ortho* = 3-10:1). The fluorenols were then converted in the corresponding spirobifluorenes **3**. Measurement of photophysical properties of **3** revealed that fluorescence emission maxima depend on the substitution pattern. Further attention was also payed to synthesis of variously fluorinated spirobifluorenes and their congeners (e.g. dispiroindeno[2,1-c]fluorenes).



[1] Kaiser, R. P.; Hessler, F.; Mosinger, J.; Císařová, I.; Kotora, M. *Chem. Eur. J.*, **2015**, *21*, 13577.

[2] Kaiser, R. P.; Mosinger, J.; Císařová, I.; Kotora, M. *Org. Biomol. Chem.*, **2017**, *15*, 6913.