

FeCl₃-Diorganoyl Dichalcogenides Promoted Cyclization to Fused 4-Substituted selenophenes[2,3-*b*]thiophenes

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INTRODUCTION

The derivatives of fused heterocycles are valued not only for their rich and varied chemistry, but also for many important biological properties.¹ The synthesis of fused heterocycles has also attracted considerable attention because of their use in the synthesis of a variety of functional materials for electronic devices.² Among chalcogenides, fused chalcogenophene derivatives play an important role in organic synthesis because of their excellent electrical properties and environmental stability.³ Thus, during the past years there has been an impressive increasing attention in the development of environmentally benign protocols and the great challenge for chemists is to apply cost-effective, green, mild, and alternative methodologies. In this context, iron has appeared as a versatile alternative, due to its low price, nontoxicity, and environmentally benign properties. Considering these aspects and the large number of methodologies which have successfully used FeCl₃ in the synthesis of interesting heterocycle or carbocycle compounds,⁴ the purpose of this study was to report the convenient one-step synthesis of novel fused heterocyclic ring systems containing selenothiophene moiety **2**, starting from 2-organochalcogen-3-alkynylthiophenes **1** (Figure 1).

RESULTS AND DISCUSSION

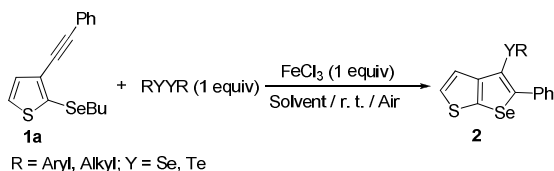


Figure 1. General scheme

Our initial studies on the cyclization have focused on the development of an optimum set of reaction conditions. We have investigated the procedure with respect to five key variables: (1) solvent (CH₂Cl₂, THF, CH₃CN, EtOH and DMSO), (2) diorganoyl diselenide loading (0.55, 1 equiv), (3) iron trichloride loading (0.2, 1 and 1.5 equiv), (4) temperature and (5) atmosphere (inert or ambient atmosphere). In

this way, the optimization process was performed using selenoenyne **1a** and diphenyl diselenide. Thus, careful analysis of the optimized reactions revealed that the optimum condition for the cyclization reaction was found to be **1a** (0.25 mmol), diphenyl diselenide (1 equiv), FeCl₃ (1 equiv) in CH₂Cl₂, at room temperature under ambient atmosphere. The application of the above standardized conditions with different diorganoyl diselenides was studied, and the results are summarized in Figure 2.

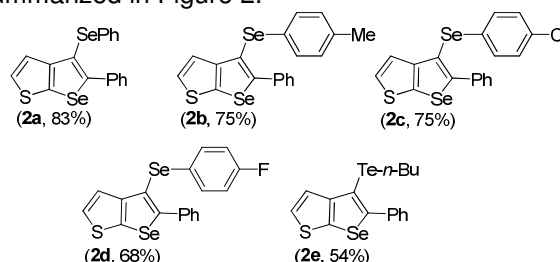


Figure 2. Substituted fused Se(S)-heterocycles prepared

CONCLUSION

In summary, we developed an alternative and efficient method to the synthesis of fused 4-organochalcogen-chalcogenophene derivatives via intramolecular cyclization of 2-organochalcogen-3-alkynylthiophenes. The methodology showed to be highly efficient and was carried out using FeCl₃/RSeSeR at room temperature and under ambient atmosphere which are considered economic and eco-friendly protocol.

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