$Sc(OTf)_3$触媒を用いた芳香族チオールとジオールの直接的環化反応によるチオピラン誘導体合成

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$Sc(OTf)_3$-Catalyzed Direct Cyclization of Aromatic Thiols with Diols for Preparation of Thiopyran Derivatives

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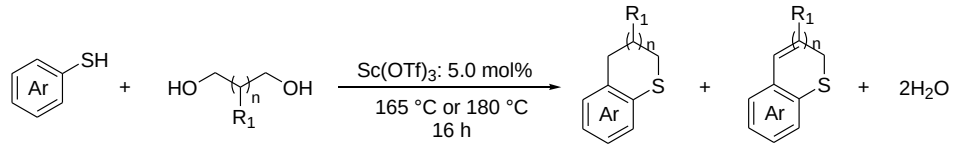
Carbon-Sulfur(C-S) bond formations are important reactions in organic synthesis for the preparation of biologically active compounds and organic electronic materials. The conventional strategies for the direct catalytic formation of C-S bonds usually requires thiols with alkene, alkyne and/or halides as starting materials. Previously, the direct cyclization of aromatic amine with diols was described to give the corresponding *N*-heterocycles.[1] Here, we report a $Sc(OTf)_3$-catalyzed direct cyclization of aromatic thiols with diols to afford the corresponding *S*-heterocycles via catalytic C-S bond and C-C bond formations. The direct cyclization of 2-napthalenethiol (**1a**) with 1,3-propanediol (**2a**) in the presence of $Sc(OTf)_3$ (5.0 mol%) gave **3aa** in 68% yield (Scheme 1). The reaction of various aromatic thiols with diols also proceeded under similar reaction conditions led to the corresponding thiopyran derivatives.

Keywords: $Sc(OTf)_3$; Aromatic Thiols; Diols; Direct Cyclization; Thiopyran Derivative

炭素-硫黄(C-S)結合形成は，生体活性物質や有機電子材料の合成において重要である．触媒的 C-S 結合形成は，チオールとハロゲン化物やアルケンまたは，アルキンを原料とする．当研究室では，芳香族アミンとジオールを用いた含窒素環化合物の触媒合成に成功した.[1] 本研究では，スカンジウム触媒を用いた芳香族チオール類とジオール類の直接的環化反応を検討した．触媒として $Sc(OTf)_3$ (5.0 mol%)存在下，2-naphthalenethiol (**1a**)と 1,3-propanediol (**2a**)の反応において，含硫黄ヘテロ環化合物 **3aa** を 68%の収率で得た(Scheme 1). 同様の触媒反応条件下，様々な芳香族チオールとジオールで対応するチオピラン誘導体を得た.



1 **2** **3** **4**

Ar=**1a**: 2-naphthyl
Ar=**1b**: 1-naphthyl
Ar=**1c**: 4-$OMeC_6H_4$
Ar=**1d**: 4-MeC_6H_4
Ar=**1e**: 4-EtC_6H_4
Ar=**1f**: 4-$^{i}PrC_6H_4$
Ar=**1g**: 4-$^{t}BuC_6H_4$
Ar=**1h**: C_6H_5
Ar=**1i**: 4-ClC_6H_4

2a: R_1=H, n=1
2b: R_1=CH_3, n=1
2c: R_1=H, n=0

1a–i+2a
3aa: 68%, **3ba**: 24%,
3ca+4ca: 50% (**3ca+4ca**=96:4), **3da+4da**: 71% (**3da+4da**=72:28),
3ea+4ea: 67% (**3ea+4ea**=84:16), **3fa+4fa**: 53% (**3fa+4fa**=85:15),
3ga+4ga: 53% (**3ga+4ga**=84:16), **3ha+4ha**: 35% (**3ha+4ha**=50:50),
3ia+4ia: 7% (**3ia+4ia**=10:90)

1a+2b
3ab: 93%

1a+2c
4ac: 55%

Scheme 1. $Sc(OTf)_3$-Catalyzed Direct Cyclization of Aromatic Thiols with Diols.

1) Minakawa, M.; Watanabe, K.; Toyoda, S.; Uozumi, Y. *Synlett*, **2018**, *29*, 2385.

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