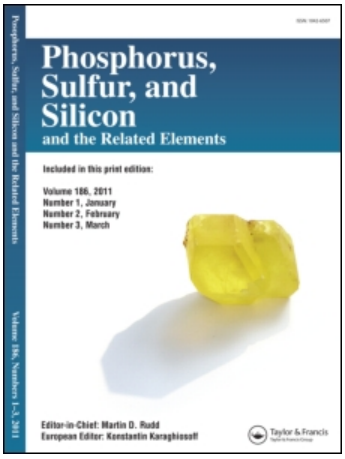

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New Synthetic Uses of 2,3-Dihydro-3-Oxobenzo[B]Thiophene

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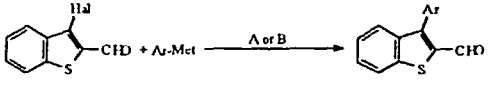
Synthesis of benzo[b]thiophenes functionalized in the position 3 and new polycyclic systems are discussed.

Keywords: Vilsmeier-Haack-Arnold; palladium-catalysed coupling; Pomeranz-Fritsch

The 2-carboxaldehyde-3-halogeno derivatives **2(a-b)** are conveniently obtained by Vilsmeier-Haack-Arnold reaction [1] applied to the 2,3-dihydro-3-oxobenzo[b]thiophene **1**. Compounds **2(a-b)** are reacted either under Stille conditions[2] (with an organostannane) or under Suzuki conditions[3] (with an organoboronic acid). The results are summarized in table **I**.

Table I : Stille and Suzuki cross-coupling reactions of compounds **2(a-b)**



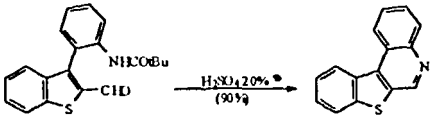
A : Ar-$SnBu_3$,$Pd(PPh_3)_4$ (0.02 mol%), toluene, reflux
B : Ar-$B(OH)_2$, $Pd(PPh_3)_4$ (0.02 mol%), K_2CO_3 2N (2 eq.), DME, reflux

Compound	Hal	Ar-Met	Yield (%)
3a	Cl	Ph-$SnBu_3$	39
3a	Br	Ph-$SnBu_3$	92
3b	Cl	Ph-$B(OH)_2$	5
3b	Br	Ph-$B(OH)_2$	82

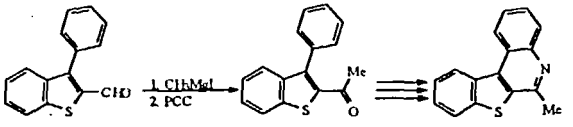
A variety of organoboronic acids, including 2-thienyl boronic acid and 2-furyl bronic acid were coupled with the 3-bromo-2-carboxaldehyde benzo[b]thiophene in very good yields.

The 2-carboxaldehyde-3-phenylbenzo[b]thiophene is a useful starting material for the synthesis of benzothieno[2,3-c]quinoline (**Scheme 1**) and 6-methylbenzothieno[2,3-c]quinoline (**Scheme 2**).

Scheme 1 : Access to benzothieno[2,3-c]quinoline

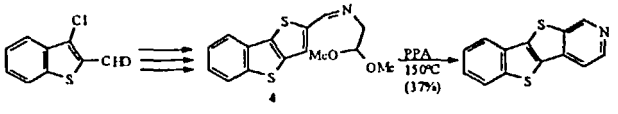


Scheme 2 : Access to 6-methylbenzothieno[2,3-c]quinoline



Analogues of pyridocarbazoles were synthesized from 2-carboxaldehyde-3-chlorobenzo[b]thiophene by a procedure involving a Pomeranz-Fritsch cyclisation[4] of Schiff's base 4 (**Scheme 3**) or by a Bischler-Napieralski cyclisation of amide 5 (**Scheme 4**).

Scheme 3 : Synthesis of benzothieno[2,3-f]thieno[2,3-c]pyridine



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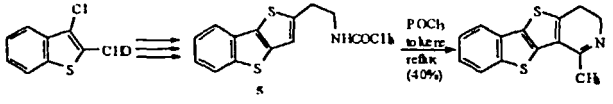
Scheme 4:Synthesis of 1-methyl-3,4-dihydro-benzothieno[3,2-g] thieno[3,2-c]pyridine



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