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

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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 <sup>[11]</sup> applied to the 2,3-dihydro-3-oxobenzo[b]thiophene 1. Compounds 2(a-b) are reacted either under Stille conditions<sup>[21]</sup> (with an organostannane) or under Suzuki conditions<sup>[3]</sup> (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<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 mol%), toluene, reflux

B : Ar-B(OH)2, Pd(PPh3)4 (0.02 mol%), K2CO3 2N (2 eq.), DME, reflux

Compound	Hal	Ar-Met	Yield (%)
3a	Cl	Ph-SnBu <sub>3</sub>	39
3a	Br	Ph-SnBu <sub>3</sub>	92
3b	Cl	Ph-B(OH) <sub>2</sub>	5
3b	Br	Ph-B(OH) <sub>2</sub>	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-3chlorobenzo[b]thiophene by a procedure involving a Pomeranz-Fritsch cyclisation<sup>[4]</sup> 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



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



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