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1,3-Oxazoline- and 1,3-oxazolidine-2-thiones as substrates in direct modified Stille and Suzuki cross-coupling

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ABSTRACT

1,3-Oxazoline- (OXT) and 1,3-oxazolidine-2-thiones (OZT) can undergo direct Stille and Suzuki cross-coupling reactions under microwave activation to produce 2-aryloxazoles and 2-aryloxazolines in reasonable to good yields.

As moieties of natural products and medicinal drugs, 1,3-oxazolines and 1,3-oxazoles are widespread heterocycles, which are also considered for their chemical applications, especially in asymmetric synthesis.[1] Numerous methods are available to build up the above molecular motifs, but efficient alternative methods are still needed when addressing selective functionalizations of the heterocycle. Amongst the newly emerging methodologies, transition metal-catalyzed cross-coupling protocols appear as particularly powerful.[2] Those methods that overcome the stability problems of sensitive electrophiles, significantly extend the versatility of the processes.[3] In recent years, heteroaromatic thioethers have been introduced as a new class of electrophiles for their greater stability.[4] The alkylsulfanyl methodology developed by Liebeskind et al., mostly on heteroaromatic templates, can be regarded as a reliable alternative tool in heteroaryl C–C bond formations.[5] The recent publication of a modified desulfurative cross-coupling methodology by Kappe, using direct reaction on thioamides under microwave assistance,[6] prompted us to disclose our own results.[7] 1,3-Oxazolidine-2-thiones (OZTs) and 1,3-oxazoline-2-thiones (OXTs) are parent heterocycles, the chemical properties of which differ greatly. A broad range of applications in chemistry have been reported for OZTs;[8] in sharp contrast, OXTs have been surprisingly far less studied.[9] We have (i) taken advantage of the nucleofugal ability of 2-alkylsulfanyl oxazolines in Pd(0) cross-coupling for Stille and Suzuki reactions[10a] and (ii) more recently successfully explored the potential of a direct Pd(0)-catalyzed cross-coupling reaction making use of the parent thiocarbonyl substrates in a Sonogashira process.[10b] In this Letter, we disclose our recent results on Suzuki and (for the first time) Stille coupling reactions with OXTs and OZTs using microwave and thermal conditions.

The equilibrium between the 1,3-oxazolidine-2-thione and the 2-mercapto-1,3-oxazoline produces a transient analogue of the alkylsulfanyl intermediates (Scheme 1), which is able to undergo the cross-coupling reaction. A similar approach has been exploited by Kappe with thionamide derivatives, to access C–C bond formation through a Suzuki reaction under microwave activation.[6a] We have thus investigated an extension of this direct coupling protocol to the case of complex thionocarbamate derivatives. Three carbohydrate-based OZTs available in our laboratory were selected for a preliminary study: **1** is easily obtained in one step from D-arabinose;[11] **2** is readily prepared through a stereocontrolled sequence starting from D-fructose;[12] **3** (which bears an original hemiaminal structure) is produced from D-xylose.[13] A direct coupling under Suzuki conditions, using *p*-methoxyphenylboronic acid and Cu(I)-thiophene-2-carboxylate (CuTC) in excess, was shown to produce oxazolines **4**–**6** (Table 1, entries 1–3) albeit in moderate yields—47%, 45% and 42%, respectively. Notwithstanding those mediocre

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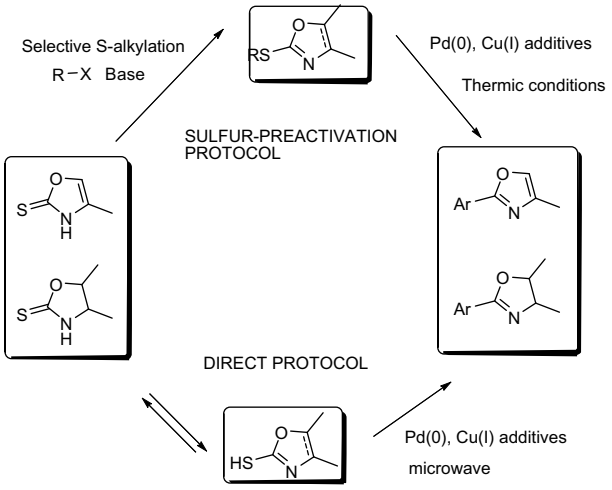
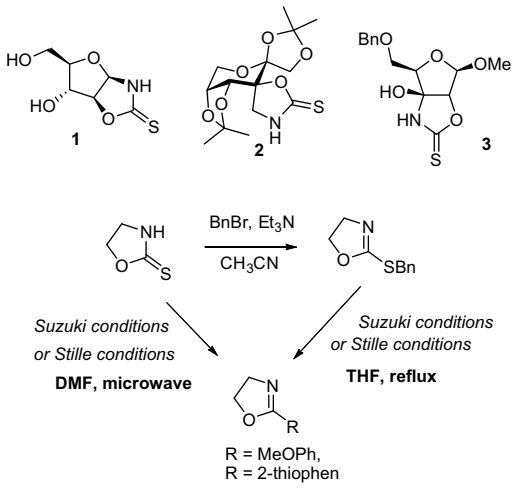


Scheme 1. One-step or two-step approaches to generate 2-aryl-1,3-oxazoles and oxazolines from OXT and OZT.



Scheme 2. Comparison of the reactivities for a two-step and a one-step sequence. *Suzuki conditions*: alkylsulfanyloxazoline or OZT (1 equiv), *p*-methoxyphenylboronic acid (2.2 equiv), CuTC (2.2 equiv), $(Ph_3P)_4Pd$ (0.05 equiv), 24 h thermal conditions or 60 min microwave activation—Stille conditions: alkylsulfanyloxazoline or OZT (1 equiv), arylstannane (2.2 equiv), $CuBr{\cdot}Me_2S$ (2.2 equiv), $(Ph_3P)_4Pd$ (0.05 equiv), 48 h thermal conditions or 60 min microwave activation.

Table 1
Suzuki and Stille cross-coupling reactions on OZTs

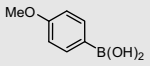
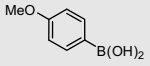
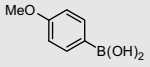
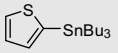
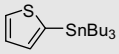
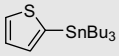
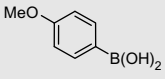
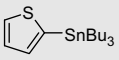
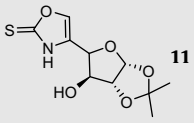
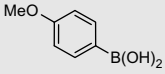
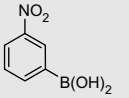
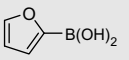
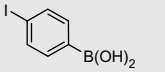
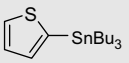
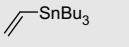
Entry	Starting material	Coupling agent	Product	Direct coupling (%)	Two-step procedure (%)
1	**1**		**4**	47	76
2	**2**		**5**	45	83
3	**3**		**6**	42	80
4	**1**		**7**	72	77
5	**2**		**8**	75	80
6	**3**		**9**	27	67

Table 2
Suzuki and Stille cross-coupling reactions on OXTs

Entry	Starting material	Coupling agent	Product	Yield (%)
1	 **10**		**12**	59
2			**13**	59
3	 **11**		**14**	86
4			**15**	66
5			**16**	61
6			**17**	38
7			**18**	86
8			**19**	72

results for the Suzuki coupling, we were keen on applying for the first time the microwave conditions to a Stille reaction. Therefore, OZTs **1**–**3** were reacted with 2-tributylstannylthiophene using copper bromide as the activating agent. We were pleased to observe that OZTs **1** and **2** afforded the corresponding oxazolines **7** and **8** in 72% and 75% yields, respectively. On the other hand, the reaction with the hemiaminal **3** was much more sluggish: the Stille coupling was not complete, delivering the oxazoline **9** in only 27% yield, whilst OZT **3** was recovered in 44% yield (Scheme 2).

When performed on complex OZTs, the direct cross-coupling procedure patently proved unsatisfactory. For that reason, the two-step procedure was applied with a view to comparing reactivities. All three OZTs were quantitatively converted (BnBr, Et_3N, acetonitrile) into the corresponding 2-benzylsulfanyloxazolines,[10a] which were then submitted to the Pd-catalyzed cross-coupling reaction. On all three selected substrates, the two-step procedures proved much more efficient with overall yields ranging from 67% to 83%. Considering the Suzuki coupling, a general impressive yield increase was observed (entries 1–3); as regards the Stille coupling, a slight improvement could be noted for **7** and **8**, whereas a dramatic effect—yield multiplied by 2.5—was observed for **9**. The two-step procedure therefore appears to be a good alternative to the direct cross-coupling procedure.

However, because of successful precedents,[7] it was also logical to test the reactivity of the aromatic parent OXT structure in Suzuki and Stille direct cross-coupling reactions. Two representative substrates were selected to perform preliminary experiments: the simple 4-methyl-1,3-oxazoline-2-thione **10** was readily prepared

from acetol according to the literature,[9a] and the recently introduced D-xylo-based OXT **11** was synthesized through a regiocontrolled sequence starting from D-glucose.[14]

The OXT **10** was reacted with two coupling reagents, *p*-methoxyphenyl boronic acid and 2-tributylstannylthiophene (Table 2), by which a fair 59% yield of the corresponding 2-substituted oxazoles **12** and **13** was obtained. On the other hand, the carbohydrate-based OXT **11** was reacted with four different boronic acids (entries 3–6) to produce oxazoles in good (**15**, **16**) to excellent (**14**) yields.[15] In the case of *p*-iodophenylboronic acid, however, the outcome was more disappointing with a mediocre 38% yield of derivative **17**, and no clear reason for this drop of the yield could be made out. Finally, both tributylstannyl reagents tested afforded good yields (86% and 72%, respectively) of oxazoles **18** and **19**.

In the case of OXTs, the direct cross-coupling procedure appears to be more favourable than the two-step procedure previously used on OZTs.[16,17] Indeed, all coupling reactions involving the *S*-benzyl derivatives of compounds **10** and **11** proved sluggish and ineffective: no Suzuki-type coupling was detected with 2-benzylsulfanyl-4-methyloxazole (prepared from **10**),[9a] whereas in thermal conditions, the *S*-benzyl derivative of **11** only reacted partially (43% yield recovery of the starting material after 3 days) to produce a 37% yield of oxazole **14**.

This preliminary report about direct Suzuki and Stille cross-couplings on cyclic thionocarbamates has shown interesting reactivity features associated with such small heterocycles. When submitted to modified Stille or Suzuki coupling protocols, the non-aromatic OZTs have shown better results when a two-step procedure involving a S-benzylated intermediate is used rather than a microwave-assisted direct coupling; yet both approaches could compete in the Stille coupling case. In sharp contrast, the aromatic OXTs afford far better results when the direct coupling protocol is applied. In summary, this is a first step towards expanding to Pd-catalyzed cross-coupling reactions to the reactivity study of cyclic thionocarbamates, which have been a long-term research theme in our laboratory.[18]

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14. Silva, S.; Tatibouët, A.; Ortiz-Mellet, C.; Rollin, P.; Rauter, A. P., unpublished results.
15. *Typical protocol for a thermal Suzuki coupling:* The spiro-OZT **2** (0.08 g, 0.24 mmol) in DMF (3 mL) was cooled to 0 °C and reacted with NaH (60%, 10 mg, 0.27 mmol) for 5 min. Then benzyl bromide (0.042 mL, 0.30 mmol) was added and the mixture was allowed to return to room temperature. After 4 h, a large excess of water was added and the solution extracted with EtOAc (4 × 25 mL). The collected organic phases were washed with water and brine, then dried over $MgSO_4$ and evaporated. The resulting crude was purified by chromatography (PE–AcOEt, 4:1) to afford the *S*-benzyl derivative (0.098 g, 0.232 mmol) in 96% yield. The benzylated molecule together with CuMeSal (2.2 equiv) and the boronic acid (2.2 equiv) was diluted under Ar, in THF (5 mL), then $Pd(Ph_3P)_4$ (0.05 equiv) was added. The solution was heated at 60 °C for 20 h, then suspended with a satd Na_2CO_3 solution and extracted with AcOEt (4 × 25 mL). The collected organic phases were washed with water and brine, then dried over $MgSO_4$. After evaporation, the residue was chromatographed over silica gel (EP–AcOEt 7:3) to produce the coupling product **5** (83 mg, 0.205 mmol) in 88% yield. Mp 124–125 °C; $[\alpha]_D$ −112 (c = 1.16, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.35, 1.39, 1.50, 1.54 (4s, 12H, $4CH_3$), 3.84 (s, 3H, OMe), 3.92 (d, 1H, H_{6b}, J_{6b-6a} = 12.9); 3.93 (d, 1H, H_{7a}, J_{7a-7b} = 13.1), 3.98 (d, 1H, H_{1a}, J_{1a-1b} = 9.7), 4.10 (d, 1H, H_{1b}, J_{1b-1a} = 9.7z), 4.22 (d, 1H, H_{7b}, J_{7b-7a} = 13.1), 4.30 (dd, 1H, H_{6b}, J_{6b-6a} = 12.9, J_{6b-5} = 3.1), 4.44 (m, 1H, H_5), 4.58 (d, 1H, H_4, J_{4-5} = 7.3), 6.90 (d, 2H, Ph-H, J = 8.8), 7.86 (d, 2H, Ph-H). ^{13}C NMR (62.89 MHz) δ 24.7, 25.8, 26.0, 26.4 ($4CH_3$), 55.5 (OMe), 59.4 (C-7), 62.9 (C-6), 72.6 (C-1), 73.1 (C-5), 75.2 (C-4), 84.6 (C-3), 105.1 (C-2), 109.9 (CMe_2), 111.4 (CMe_2), 113.8, 119.8, 130.0, 162.8 (C-8). MS (IS): m/z 406.0 $[M+H]^+$. ESI-HRMS calcd for $C_{21}H_{28}NO_7$ $[M+H]^+$: 406.1860, found: 406.1863.
16. *Typical protocol for a direct Suzuki coupling:* In a microwave vial tube, a solution of OXT **11** (100 mg) in THF (5 mL) with a stirring bar was prepared under argon. Following the order, CuTc (2.2 equiv), *p*-$MeOPhB(OH)_2$ (2.2 equiv) and $(Ph_3P)_4Pd$ (0.05 equiv) were added under argon. The tube was sealed and subjected to microwave irradiation at 100 °C with stirring for 60 min. The reaction vessel was allowed to cool to rt, the solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (AcOEt/PE) to afford the oxazole **14** (118 mg, 86% yield) as a yellowish solid, mp 113–114 °C; $[\alpha]_D$ −34 (c = 1, MeOH). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36 and 1.56 (2s, 6H, *i*Prd), 3.84 (s, 3H, OMe), 4.41 (s, 1H, H-3′), 4.69 (d, 1H, $J_{1'-2'}$ = 3.6, H-2′), 4.75 (br s, 1H, OH), 5.18 (d, 1H, $J_{3'-4'}$ = 2.1, H-4′), 6.08 (d, 1H, H-1′), 6.95 (d, 2H, J = 8.8, *ortho*-H-ArOMe), 7.77 (s, 1H, H-5), 7.94 (d, 2H, *meta*-H-ArOMe). ^{13}C NMR (62.89 MHz) δ 26.2 and 26.9 (2 CH_3), 55.5 (OCH_3), 73.5 (C-4′), 76.9 (C-3′), 85.1 (C-2′), 105.2 (C-1′), 111.9 (C_{IV}-*i*Prd), 114.4 (CH *ortho*ArOMe), 119.4, 128.5 (*meta*-CH–ArOMe), 129.5, 136.6 (C-4), 137.6 (C-5 a), 161.9 (C-2). ESI-HRMS calcd for $C_{17}H_{20}NO_6$ $[M+H]^+$: 334.1291, found: 334.1286.
17. *Typical protocol for a direct Stille coupling*: In a microwave vial tube, a solution of OXT **11** (0.100 g) in THF (5 mL) with a stirring bar was prepared under argon. Following the order, $CuBr{\cdot}Me_2S$ (2.2 equiv), 2-tributylstannylthiophene (2.2 equiv) and $(Ph_3P)_4Pd$ (0.05 equiv) were added under argon. The tube was sealed and subjected to microwave irradiation at 100 °C with stirring for 60 min. The reaction vessel was allowed to cool to rt, the solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (AcOEt/PE) to afford the oxazole **18** (103 mg, 86% yield), $[\alpha]_D$ −29 (c = 1, MeOH). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36 and 1.56 (2s, 6H, *i*Prd), 4.25 (d, 1H, $J_{OH-3'}$ = 1.8, OH), 4.43 (s, 1H, H-3′), 4.69 (d, 1H, $J_{1'-2'}$ = 3.6, H-2′), 5.19 (d, 1H,

$J_{3'-4'}$ = 2.5, H-4′), 6.07 (d, 1H, H-1′), 7.11 (dd, 1H, J_{3-4} = 5.1, J_{4-5} = 3.8, H-$4_{thiophenyl}$), 7.45 (dd, 1H, J_{3-5} = 1.1, H-$5_{thiophenyl}$), 7.68 (dd, 1H, H-$3_{thiophenyl}$), 7.75 (s, 1H, H-5). ^{13}C NMR (62.89 MHz) δ 26.2 and 26.9 (2 CH_3), 74.1 (C-4′), 76.6 (C-3′), 85.1 (C-2′), 105.1 (C-1′), 111.9 (C_{IV}-*i*Prd), 128.1 (C-$4_{thiophenyl}$), 128.8 (C-$3_{thiophenyl}$), 129.0 (C-$2_{thiophenyl}$), 129.3 (C-$5_{thiophenyl}$), 136.9 (C-4), 137.5 (C-5), 158.5 (C-2). ESI-HRMS calcd for $C_{14}H_{15}NO_5NaS$ $[M+Na]^+$: 332.0569, found: 332.0577.

18. (a) Gueyrard, D.; Grumel, V.; Leoni, O.; Palmieri, S.; Rollin, P. *Heterocycles* **2000**, *52*, 827–843; (b) Girniene, J.; Gueyrard, D.; Tatibouët, A.; Sackus, A.; Rollin, P. *Tetrahedron Lett.* **2001**, *42*, 2977–2980; (c) Girniene, J.; Apremont, G.; Tatibouët, A.; Sackus, A.; Rollin, P. *Tetrahedron* **2004**, *60*, 2609–2619; (d) Tatibouët, A.; Lawrence, S.; Rollin, P.; Holman, G. D. *Synlett* **2004**, 1945–1948; (e) Girniene, J.; Tardy, S.; Tatibouët, A.; Sackus, A.; Rollin, P. *Tetrahedron Lett.* **2004**, *45*, 6443–6446; (f) Tatibouët, A.; Simao, A. C.; Rollin, P. *Lett. Org. Chem.* **2005**, *2*, 47–50.