doi.org/10.1002/adsc.202200053

Advanced Synthesis & Catalysis

Divergent Synthesis of C5-Heteroatom Substituted Oxazoles

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Manuscript received: January 19, 2022; Revised manuscript received: April 4, 2022;
Version of record online: April 28, 2022

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.202200053

Abstract: 5-Oxazoyl-sulfamates have been profiled as versatile building blocks for modifications of oxazoles with various nucleophiles. The unified approach provides a diversification platform to directly access 5-amino-oxazoles, 5-oxazolyl-sulfides, and 5-oxazoyl-aryl ethers from a single precursor.

Keywords: N-heterocycles; Oxazoles; Conjugate Addition; Diversification

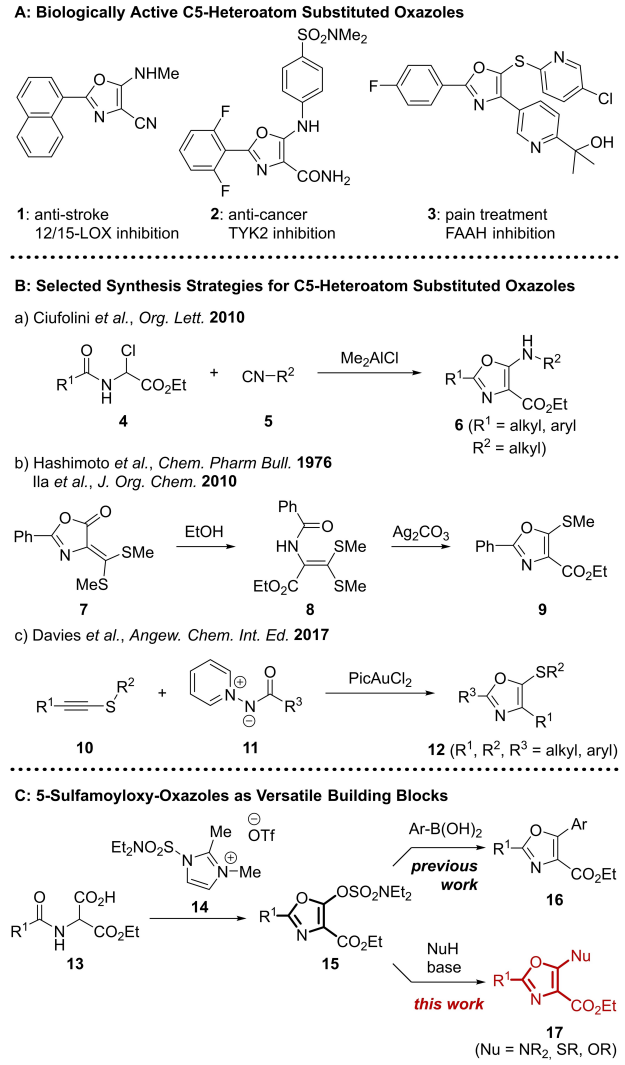
Oxazoles are a common scaffold in natural products[1] as well as in medicinal chemistry.[2] In natural products, oxazoles emerge from serine and threonine residues by cyclodehydration and oxidation, to provide oxazoles with C5-H or C5-Me substitution.[3] Natural products featuring 5-indolyl-oxazole and 5-phenyl-oxazole are biosynthesized from tryptophan and phenylalanine.[4] Oxazoles with more diverse substitution patterns have been studied in drug discovery and have been frequently reported to show important bioactivities.[5] The development of new and improved synthetic methods for the *de novo* synthesis of highly substituted oxazoles hence enjoys continued interest.[6,7] Notably, the incorporation of heteroatom-based substituents has been reported to result in pharmacologically active small molecules (Scheme 1, A).[8]

Several synthetic methods for the formation of C5-NR_2 and SR-substituted oxazoles have been described (Scheme 1, B).[9] For example, Ciufolini *et al.* used α-chloroglycinates **4** and alkyl isonitriles **5** catalyzed by dimethylaluminium chloride to assemble 5-amino-oxazoles.[10] Related approaches use α-methoxyglycinates and react them with isonitriles.[11] Although these methods provide good yields,[12] they are limited to the formation of secondary amines **6**. Tertiary 5-aminooxazoles have therefore been prepared instead by Cornforth rearrangement of 5-ethoxy-oxazole-4-amides.[13]

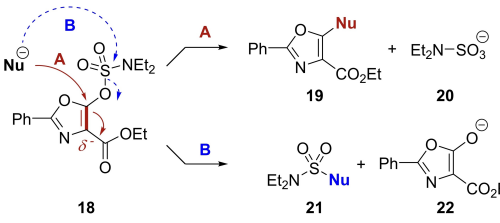
The synthesis of C5-SMe substituted oxazoles **9** has been reported early on by Ag(I)-mediated cyclization of 3,3-bis(methylthio)acrylates **8** (Scheme 1, B).[14] This chemistry has been extended to different C4-substituents.[15] Alkynyl thioethers **10** were combined with nucleophilic nitrenoids **11** in a Au(III)-catalyzed formal [3+2] dipolar cycloaddition, to assemble 2,4,5-trisubstituted oxazoles **12** with C5-thioether substituents (Scheme 1, B).[16] By using alkynyl amines and *N*-(pivaloyloxy)amides with Co(III)-catalysis, this chemistry was expanded to prepare 5-amino-oxazoles.[17]

Although a considerable variety of options to produce substituted oxazoles exists, individual substituent choice remains limited. During our studies on Suzuki-Miyaura reactions of peptide-integrated sulfamoyloxy-oxazoles **15** that are easily accessible from α-carboxy amides **13**,[18] we speculated that nucleophilic attack at the C5-atom of the oxazole scaffold might directly lead to C5-heteroatom substituted oxazole **17** (Scheme 1, C). This S_NAr-like reactivity should be guided by preferential stabilization of the putative anionic intermediate (cf. **18**) and subsequent elimination of sulfamate (**20**, Scheme 2, A). However, depending on the nucleophile, the S(VI)-atom of the sulfamate functionality may be alternatively attacked to yield sulfamide **21** upon loss of an oxazolone (cf. **22**, Scheme 2, B).

To investigate these possibilities, 2-phenyl-5-sulfamoyloxy-oxazole **18**[18] was selected for a feasibility study with morpholine as a moderately reactive nucleophile (table 1). These studies revealed the desired reaction mode (A) to be operative, independent



Scheme 1. Bioactive oxazoles featuring C5-heteroatom substituents (**A**), selected synthetic access to C5-heteroatom substituted oxazoles (**B**), and oxazolyl-sulfamates for the C5-modification of oxazoles (**C**).



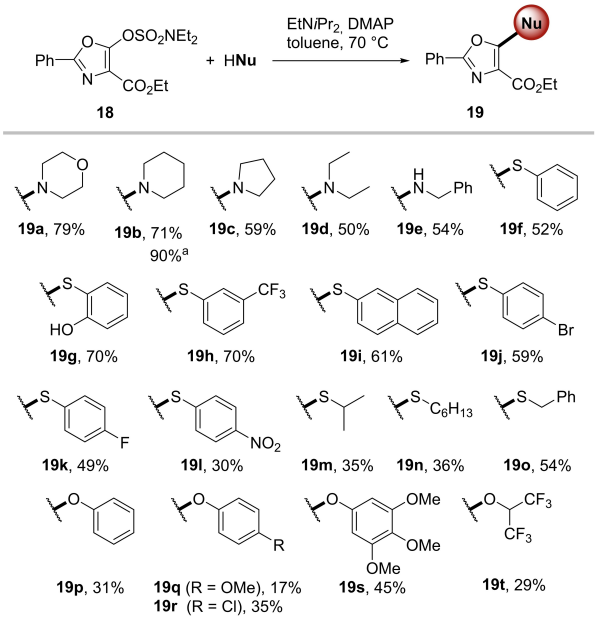
Scheme 2. Putative reaction pathways of 5-sulfamoyloxy-oxazoles with a nucleophile. The nucleophilic attack can occur at the C5-atom of the oxazole (**A**) leading to the desired product upon sulfamate elimination, or at the S(VI)-atom (**B**).

of solvent (entries 1–3). Reactions with limiting amine did not run to completion, but additional non-nucleophilic base and adjusted reaction temperature were helpful (entries 4–9). The addition of DMAP was found to improve the reaction rate, to identify conditions that allowed for the synthesis of oxazolyl-morpholine **19a** in 79% yield (table 1, entry 10).

We then investigated the scope of the conjugate additions by using 2-phenyl-5-oxazolyl-sulfamate **18** and different *N*-, *S*-, and *O*-nucleophiles (Scheme 3). Dialkylamines such as morpholine, piperidine, pyrrolidine, or diethylamine smoothly gave the corresponding 5-amino-oxazoles **19a–e** (50–90% yield). Piperidyl-oxazole **19b** was obtained in 90% yield in a gram scale synthesis experiment, signifying the general utility of the method.

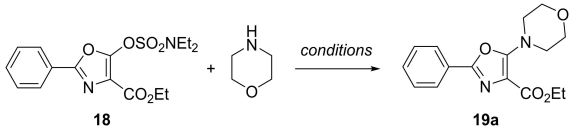
To our delight, thiophenols offered a direct access to pharmacologically interesting oxazolyl-thioethers. Thiophenol could be introduced in 52% yield (**19f**) while both, the electron-rich 2-hydroxythiophenol and electron-poor 3-trifluoromethylthiophenol provided 70% yield (**19g**, **h**). 2-Naphthalenethiol has been found to be a competent nucleophilic coupling partner (**19i**, 61%). Halogenated thiophenols gave the oxazolyl-sulfides **19j** and **19k** in 59% and 49%, respectively. A nitro substituent rendered the substitution slightly less productive (**19l**, 30%).

To further investigate the reaction's scope, alkyl mercaptans were additionally studied. 2-Thiopropane and 1-thiohexane could be coupled by using the standard conditions, but with reduced efficacy, to give alkyl-thioethers **19m** and **19n** in 35% and 36% yield, respectively. Benzyl mercaptan produced the respective thioether in 54% yield (**19o**).



Scheme 3. Conjugate additions of *N*-, *S*-, and *O*-nucleophiles and 2-phenyl-5-sulfamoyloxyoxazole **18**. [a]reaction performed on 1 g scale.

Table 1. Optimization of the reaction conditions for the conjugate addition of morpholine and oxazolyl-sulfamate **18** as the electrophilic reactant.



18 **19a**

entry	HNR_2 (equiv.)	solvent	$EtNiPr_2$ (equiv.)	temp. (°C)	yield (%)
1	3	MeCN	0	50	43[a]
2	3	DCE	0	50	50[a]
3	3	toluene	0	50	69[a]
4	3	toluene	0	r.t.	65[a]
5	3	toluene	0	70	76[a]
6	3	toluene	0	100	48[a]
7	1.2	toluene	0	70	39[a]
8	1.2	toluene	2	70	74[a]
9	2	toluene	3	70	75[a]
10	2	toluene	3	70	79[b]

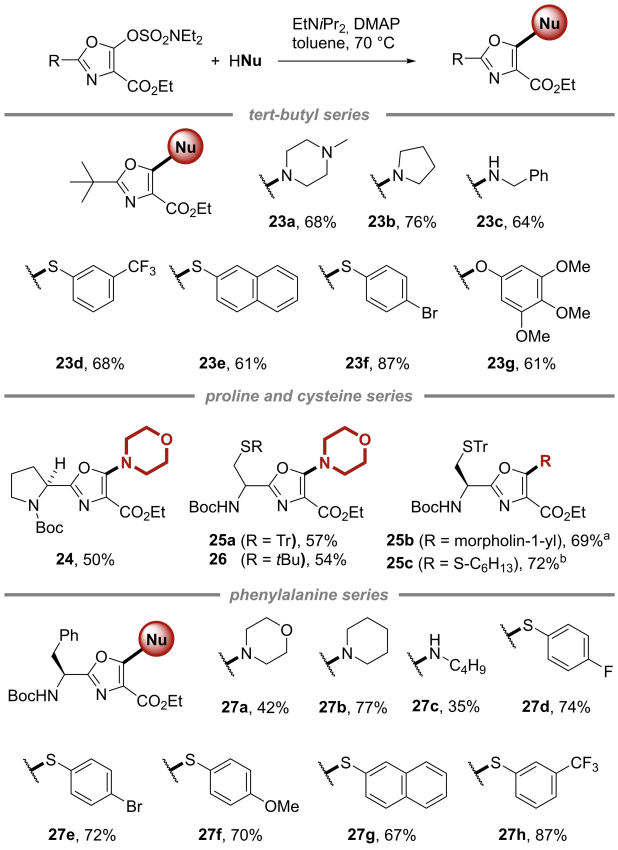
[a] 24 h reaction time,
[b] additional DMAP (0.4 equiv.) was used, 6 h reaction time. DCE = 1,2-dichloroethane.

As only few synthetic methods have been reported yet to access oxazolyl-aryl ethers,[19] we explored phenols as well. The obtained yields were found similar to those for alkyl mercaptans ranging from 17% with 4-methoxyphenol to 45% in the case of 3,4,5-trimethoxyphenol (**19 p–s**). Less acidic primary alcohols such as methanol or 1-hexanol were not productive and gave complex reaction mixtures. However, hexafluoro-2-propanol gave the ether **19 t** in 29% yield, likely because of its lower pK_a value.

These initial investigations using 2-phenyl-5-sulfamoyloxy-oxazole **18** set the stage to investigate the relevance of the C2 substituent of the oxazole scaffold for this reactivity (Scheme 4). The phenyl group was initially replaced by a *tert*-butyl group, in order to evaluate the influence of conjugation at C2. Gratifyingly, substitutions by secondary amines proceeded again cleanly to provide oxazolyl-piperazine **23 a**, oxazolyl-pyrrolidine **23 b**, and the secondary amino-oxazole **23 c**, in 68%, 76%, and 64% yield respectively.

Thiophenols were confirmed as suitable nucleophiles. For them, yields of up to 87% were obtained (**23 d–f**). By using 3,4,5-trimethoxyphenol, the diaryl-ether **23 g** was formed in 61% yield. Compared to the results observed for the 2-phenyloxazolyl-sulfamate, similar or even better yields for the conjugate additions with the *tert*-butyl substituent were obtained, suggesting that C2-conjugation was not a guiding factor for the S_NAr-like reactivity.

Hence chiral amino acid derived C2-substituents were studied next. Proline- as well as cysteine-derived oxazolyl-sulfamates could be substituted with morpholine to yield the amino-oxazoles **24**, **25**, and **26 a** in yields up to 57%. For cysteinyl oxazoles **25 a** and **26**,



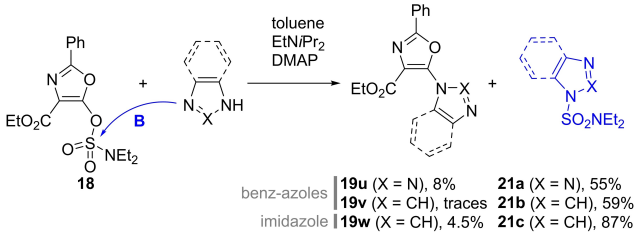
Scheme 4. Substrate scope of the conjugated additions with varying substituents at the C2-position. [a]Reaction conditions: morpholine, $EtNiPr_2$, toluene, 70 °C; [b]reaction conditions: $C_6H_{13}SH$, K_2CO_3, DMF, r.t.

racemization was evident from chiral HPLC and optical rotation measurements (see S.I.) when DMAP was applied, but could be suppressed without using it (**25 b**, **c**; see S.I.). A phenylalanine-derived oxazolyl-sulfamate was investigated in more detail. While coupling with morpholine provided the 5-amino-oxazole in 42% yield (**27 a**), piperidine reacted more cleanly (77% yield, **27 b**).

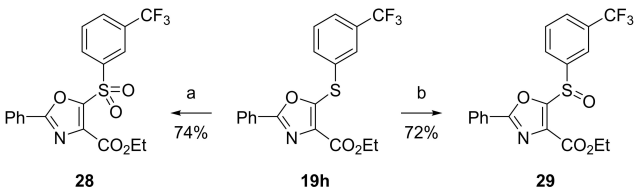
Primary amines could be introduced, but less effectively, as exemplified for butylamine (35%, **27 c**). As before, excellent yields were obtained for the substitution by different thiophenols (**27 d**–**h**, 70–87%). Phenylalanine-derived oxazoles were not sensitive to racemization, as specifically shown by the synthesis of the L- and D-stereoisomers of oxazoles **27 b** and **27 g**, and by their comparison using chiral HPLC and optical rotation (see S.I.).

Unfortunately, while primary and secondary alkyl amines were suitable nucleophiles for substitution, anilines, pyrrole, indole, phthalimide, and *α*-amino acids were found to be unproductive under the conditions investigated. Benzotriazole, benzimidazole, and imidazole preferentially reacted at the S(VI)-atom to produce the heterocyclic sulfamates **21 a**–**c** (Scheme 5). The desired biheteroaryls **19 u**–**w** were detected by LCMS, but were only isolated in minor amounts.

Further diversification of the obtained oxazoles may be easily achieved. As an example, the oxidation of thioether **19 h** was accomplished to cleanly provide sulfone **28** and racemic sulfoxide **29** in 74% and 72% yield, respectively (Scheme 6). Overoxidation at the oxazole core was not observed. Notably, despite the



Scheme 5. Reactivity of oxazolyl-sulfamates and five-membered N-heteroarenes.



Scheme 6. Synthesis of sulfone **28** and sulfoxide **29** by oxidation of sulfide **19 h**. Reagents and conditions: [a]*meta*-chloroperoxybenzoic acid (10 equiv.), CH_2Cl_2, r.t.; [b]*meta*-chloroperoxybenzoic acid (1.1 equiv.), CH_2Cl_2, r.t.

increased leaving group character of the sulfur substituent, these materials were stable to isolation and manipulation.

In summary, we have shown that 5-sulfamoyloxy-oxazoles can serve as versatile building blocks that allow for the diversification of the oxazole scaffold by the conjugate addition of different *N*-, *S*-, and *O*-centered nucleophiles. Compared to existing methodology, a single sulfamoyloxy-substituted precursor now allows to incorporate different C5-substituents, both heteroatom as well as carbon-based.[18] The acceleration of the transformation by substoichiometric amounts of DMAP may suggest potential for nucleophilic catalysis. This chemistry is hence expected to be highly useful for diversifying oxazole-based libraries in medicinal and materials chemistry research.

Experimental Section

Sample procedure: Ethyl-2-*tert*-butyl-5-(*N*,*N*-diethyl-sulfamoyloxy)-oxazole-4-carboxylate **30** (37.9 mg, 109 µmol), pyrrolidine (17.9 µL, 218 µmol), EtN*i*Pr$_2$ (55.9 µL, 326 µmol), and DMAP (2.7 mg, 21.8 µmol) were stirred in toluene (1 mL) at 70 °C for 3 h. Flash chromatography (5 g silica, CH_2Cl_2/petrol ether/EtOAc 50:50:5) afforded ethyl-2-*tert*-butyl-5-(pyrrolidin-1'-yl)-oxazole-4-carboxylate (**23 b**) as a colorless solid (22.0 mg, 82.6 µmol, 76%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 297 K): $\delta = 4.28$ (q, $J = 7.1$ Hz, 2H), 3.63 (dd, $J = 7.9$, 5.6 Hz, 4H), 1.98–1.91 (m, 4H), 1.37–1.31 (m, 12H) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.5 MHz, 297 K): $\delta = 163.1$, 159.0, 158.1, 103.5, 60.0, 49.9, 33.5, 28.3, 25.6, 14.7 ppm. HRMS (ESI-TOF) calculated for $C_{14}H_{22}N_2O_3$ $[M+H]^+$ 267.1703; found 267.1704. IR (ATR): $\tilde{\nu} = 2970$ (m), 2937 (w), 2874 (m), 1748 (m), 1690 (s), 1628 (s), 1578 (s), 1481 (m), 1443 (m), 1384 (w), 1339 (m), 1304 (w), 1238 (s), 1130 (s), 1077 (s), 972 (w), 934 (w), 914 (w), 856 (w), 822 (w), 772 (m), 725 (m), 617 (m), 575 (w), 455 (m) cm^{-1}. m.p.: 66–68 °C.

Acknowledgements

Support by the Carl-Zeiss-Foundation is gratefully acknowledged (PhD fellowship to A.O.). This work benefitted from an equipment grant of the DFG (INST 275/442-1 FUGG). Open access funding enabled and organized by Projekt DEAL.

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