Oxidative [3+2]-annulation of nitroalkenes and azolium ylides in the presence of Cu(II): efficient synthesis of [5,5]-annulated *N*-fused heterocycles

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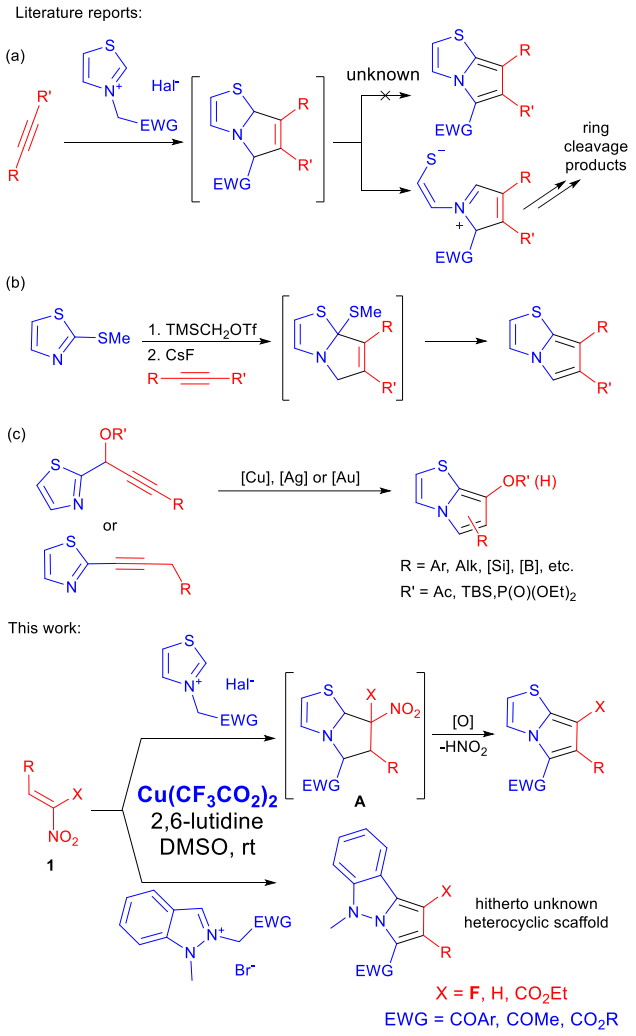
A facile synthesis of [5,5]-annulated *N*-fused heterocycles – pyrrolo[2,1-b]thiazoles and pyrrolo[1,2-b]indazoles via Cu(II)-mediated oxidative [3+2]-annulation between nitroalkenes and azolium ylides was developed. The reaction proceeds in mild conditions with copper (II) trifluoroacetate/2,6-lutidine system as a promoter. The method is applicable to a broad range of nitroalkenes and azolium salts, providing target *N*-fused heterocycles in moderate to good yields. In the case of α-fluoronitroalkenes unique fluorinated derivatives were accessed via this methodology.

Introduction

Fused heterocycles bearing a bridgehead nitrogen atom are of raising interest for organic and medicinal chemistry.[1,2] Thus, indolizines and their aza-analogues are widely explored,[1] although the chemical properties of aromatic [5,5]-annulated heterocycles are much less studied due to limited synthetic routes to access these heterocycles. However, such compounds and in particular pyrrolo[2,1-b]thiazoles are attractive target molecules for organic synthesis[2] due to their anticancer and antitumor activity,[3] with a potency comparable to a commercial anticancer drug Adrucil (5-fluorouracil).[3a] Moreover, antibacterial, antiviral and antifungal biological activities have been explored for pyrrolo[2,1-b]thiazoles,[4] which makes the development of their syntheses a highly important task.

[3+2]-annulation reactions are the most straightforward routes for the construction of five-membered rings.[5] However, reactions of alkynes with azolium ylides fail to give the corresponding [5,5]-annulated heterocycles due to extremely low stability of primary cycloadducts, which easily undergo azole ring cleavage rather than oxidative aromatization (Scheme 1, pathway a).[6] Moreover, comparatively to pyridinium ylides, thiazolium ylides are prone to dimerization and other side reactions due to the presence of active C2 position.[7] Recently it was shown that [3+2]-cycloaddition with alkynes gives pyrrolothiazoles if thiazolium ylides with a leaving group (2-MeS-) are used, though this method requires synthesis of non-stabilized ylides using $TMSCH_2OTf$ (pathway b).[8] Oxidative annulation of azolium ylides with alkenes is rather rare and suffers from limited substrate scope regarding 2π-components and harsh conditions.[3, 9] Nowadays most of the synthetic methods to construct [5,5]-annulated *N*-fused aromatic heterocycles are based on transition metal-catalyzed cycloisomerization reactions of thiazole alkynyl derivatives

(path c).[10] Moreover, highly interesting *N*-fused heterocycles like pyrrolo[1,2-b]indazoles are almost unknown. Only occasional examples of partially saturated derivatives[11a] or more complex analogs such as isoindolo[5,1-a]indazoles[11b-d] currently present in the literature. Therefore, synthesis of [5,5]-annulated nitrogen heterocycles is an important challenge for modern organic chemistry.



Scheme 1 Approaches to [5,5]-annulated heterocycles with a bridgehead nitrogen atom *via* [3+2]-annulation.

We envisioned that aforementioned issues of oxidative [3+2]-annulation can be solved meeting two following requirements. First one is the use of appropriate synthetic equivalents of alkynes. Hereby nitroalkenes **1** are the promising candidates due to the possibility of one pot elimination of HNO_2 from primary cycloadducts of type **A** (Scheme 1, bottom).[12,13] Moreover, nitroalkenes are highly reactive polarized substrates that allow to perform desired transformations in mild conditions and predictable regioselectivity. Use of nitroalkenes is especially interesting concerning synthesis of fluorinated heterocycles - highly attractive compounds for medicinal chemistry.[12b,13,14]

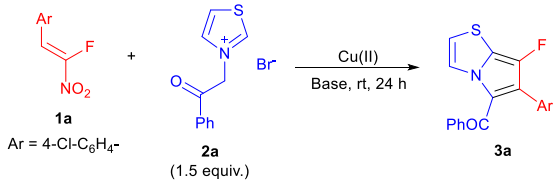
The second requirement for successful annulation is the choice of oxidant. Since partly saturated cycloadducts **A** are prone to decomposition, ring opening and other side reactions (see above) the oxidation (aromatization) step should be accomplished at a fast rate. For this aim we chose Cu(II) species, which are versatile promoters in various oxidative organic transformations,[15] including those with electron-deficient alkenes.[13a-b,15f-h] Moreover, apart from oxidative ability copper salts may act as Lewis acid activators[16] thus also facilitating target reaction.

Herein we report an efficient route for the synthesis of pyrrolo[2,1-a]thiazoles and novel pyrrolo[2,1-b]indazoles *via* copper-mediated oxidative [3+2]-annulation of azolium ylides with nitroalkenes.

Results and discussion

We initiated our study with the attempts to synthesize fluorinated pyrrolo[2,1-a]thiazole via oxidative [3+2]-annulation between fluoronitroalkene **1a** and thiazolium salt **2a** (Table 1). An oxidative system employing copper diacetate and 2,6-lutidine, which was highly efficient for the synthesis of indolizines from nitroalkenes and pyridinium ylides,[13a] was applied. However, the reaction was very poor (**1a** was recovered almost completely) both at room temperature and at the increased temperature up to 80°C if a non-polar solvent DCE was used (entry 1). The nature of solvent can be crucial for annulation reactions, therefore a screening of solvents was performed. Whereas weakly and moderately polar solvents (PhMe and THF) gave poor results (entries 2-3) as well as DCE, conversion could be gradually increased if polar solvents (MeCN, MeOH, DMF, NMP and especially DMSO, entries 4-8) were used. However, even in the case of DMSO the conversion of **1a** was incomplete, which is probably caused by the propensity of thiazolium ylides to side reactions.[7] Increase of the amount of **2a** to 2.5 equiv. was sufficient to achieve complete conversion with a moderate yield of **3a** (entries 9-10). An attempt to switch a mild pyridinium base 2,6-lutidine to a stronger base DMAP was unsuccessful (entry 11). Also, utilization of non-pyridinium bases was completely inefficient (entry 12). This evidence underlines a crucial role of 2,6-lutidine, which can act both as a mild base and a ligand for copper in annulation reactions. Next, variation of different copper salts was also highly important. Anhydrous copper acetate afforded similar result to $Cu(OAc)_2{\cdot}H_2O$ (entry 13). Copper (II) salts of other carboxylic acids than AcOH such as benzoate and pivalate afforded nearly the same result as copper (II) acetate (entries 14-15). More acidic copper triflate afforded better yield if calculated based on recovered **1a**, although with incomplete conversion (entry 16). Finally, copper (II) trifluoroacetate was found to be the optimal copper source, which afforded complete conversion with a better yield (entry 17). Increase of $Cu(CF_3CO_2)_2{\cdot}H_2O$ amount to stoichiometric (2.0 equiv.) allowed reaching good yield of **3a** (70%) (entry 18) in short reaction times (cf. Entries 18-20). Attempts to further increase the copper amount (entry 21) or to switch to a catalytic amount of Cu(II) using oxygen as an external oxidant (entry 22) were unsuccessful.

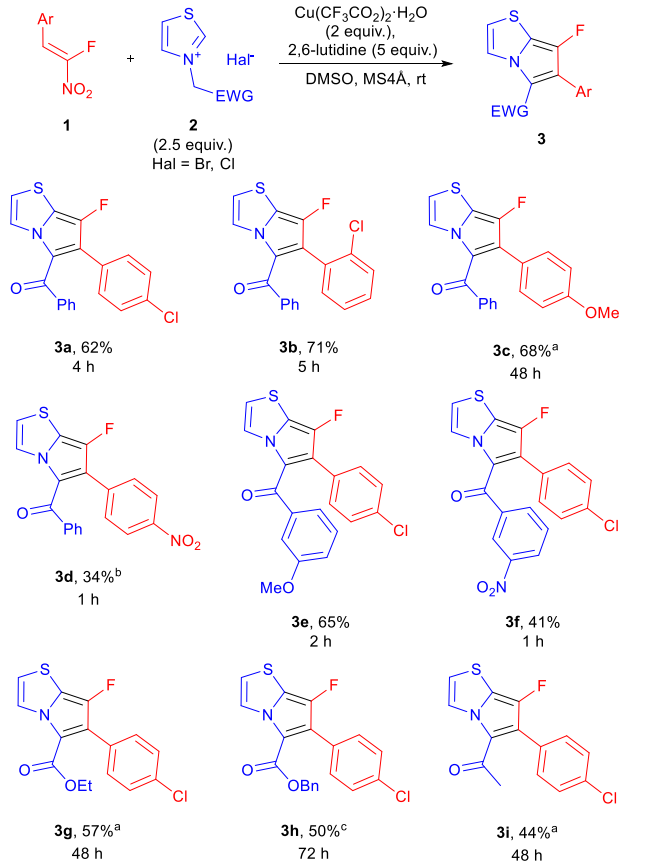
Table 1 Optimization of the reaction conditions.



Entry	Cu(II) (equiv.)	Base (equiv.)	Solvent	Conv. **1a**, %	Yield **3a**[a], %
1[b]	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	DCE	20	trace
2	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	PhMe	<10	trace
3	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	THF	24	11
4	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	MeCN	35	26
5	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	MeOH	41	25
6	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	DMF	55	32
7	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	DMSO	74	42
8	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	NMP	52	30
9[c]	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	DMSO	92	48
10[d]	$Cu(OAc)_2·H_2O$ (1.5)	Lut (5)	DMSO	100	52
11[d]	$Cu(OAc)_2·H_2O$ (1.5)	DMAP (5)	DMSO	100	17
12[d]	$Cu(OAc)_2·H_2O$ (1.5)	other[e]	DMSO	100	trace
13[d]	$Cu(OAc)_2$(1.5)	Lut (5)	DMSO	100	45
14[d]	$Cu(OBz)_2·H_2O$ (1.5)	Lut (5)	DMSO	100	49
15[d]	$Cu(OPiv)_2·H_2O$ (1.5)	Lut (5)	DMSO	100	43
16[d]	$Cu(OTf)_2$ (1.5)	Lut (5)	DMSO	75	42
17[d]	$Cu(CF_3CO_2)_2·H_2O$ (1.5)	Lut (5)	DMSO	100	61
18[d]	$Cu(CF_3CO_2)_2·H_2O$ (2.0)	Lut (5)	DMSO	100	70
19[d,f]	**$Cu(CF_3CO_2)_2·H_2O$ (2.0)**	**Lut (5)**	**DMSO**	**100**	**70**
20[d,g]	$Cu(CF_3CO_2)_2·H_2O$ (2.0)	Lut (5)	DMSO	100	71
21[d]	$Cu(CF_3CO_2)_2·H_2O$ (2.5)	Lut (5)	DMSO	86	52
22[d,h]	$Cu(CF_3CO_2)_2·H_2O$ (0.5)	Lut (5)	DMSO	45	28

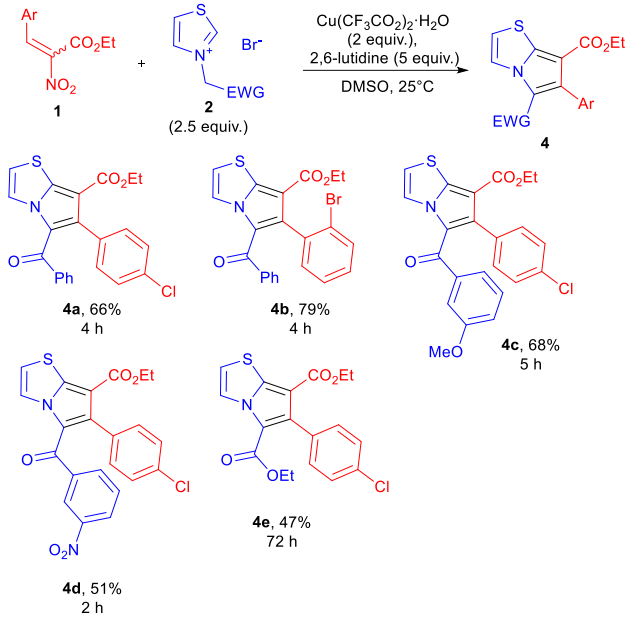
[a] Yields were determined by ^{19}F NMR with $PhCF_3$ as internal standard. Reaction conditions: **1a** (0.05 mmol), **2a** (1.5 equiv. unless noted otherwise), Cu(II) salt, 2,6-lutidine (5 equiv.), MS 4Å (25 mg), dry solvent (0.5 ml), rt. [b] rt or 80°C [c] 2.0 equiv. **2a**, [d] 2.5 equiv. **2a** [e] NaOAc (5 equiv.), K_2CO_3 (2 equiv.), Et_3N (2-5 equiv.) or DBU (2 equiv.) [f] reaction time 4 h; [g] reaction time 3 days; [h] - under O_2 (balloon).

With the optimized reaction conditions in hand (Table 1, entry 19), the scope of pyrrolo[2,1-b]thiazoles was investigated (Scheme 2). First, highly medicinally attractive fluorinated products were prepared from different α-fluoronitroalkenes **1** and thiazolium salts **2** (Scheme 3). Gratifyingly, the reaction was found to be applicable to nitroalkenes with different electronic properties of the aryl ring. In the case of more sterically hindered 2-chlorophenyl- substituted nitroalkene high yield of product **3b** was obtained. Electron-rich 4-methoxyphenyl-substituted nitroalkene also provided the product **3c** in good yield. For the highly electron-deficient 4-nitrophenyl-substituted nitroalkene lower yield was obtained for the compound **3d**, probably, due to increased reactivity of intermediate anionic species resulted in formation of side-products. The rate of the reaction was higher for electron-deficient nitroalkenes and lower for electron-rich nitroalkenes, which is in agreement with previously observed reactivity patterns.[13a-b] Regarding thiazolium salts **2**, phenacyl-substituted salts with methoxy- and nitro-group at the aryl group (products **3e**-**3f**), as well as salts bearing ester groups (**3g**-**3h**) and acetyl group (**3i**) were all found to be applicable for the synthesis of fluorinated pyrrolothiazoles in moderate to good yields. It's worth noting that the reactions with ester-substituted salts required prolonged reaction time, especially in the case of more sterically hindered -CO_2Bn group.

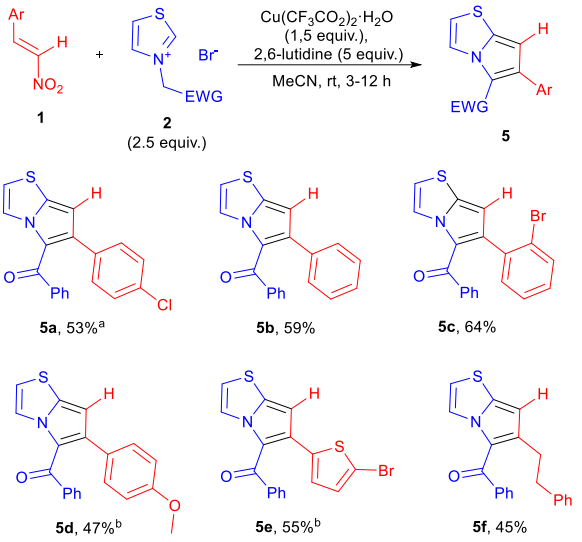


Scheme 2 Synthesis of 7-fluoro-pyrrolo[2,1-b]thiazoles **3** from different fluoronitroalkenes **1** and thiazolium salts **2**. Yields refer to isolated products **3**. [a] 3.0 equiv. of salt **2**, [b] 2.0 equiv. of salt **2**, with 2.5 equiv. of salt **2** product **3d** was obtained in 27% yield; [c] 3.5 equiv. of salt **2**.

To check generality of the method, we studied applicability of $Cu(CF_3CO_2)_2$-mediated annulation to nitroalkenes with different substituents at the α-position. Thus, reactions with highly electron-deficient α-ester-substituted nitroalkenes (nitrocinnamates) were studied (Scheme 3). Presence of the ester group should be useful for further functional group transformations. The method was found to be efficient for the synthesis of ester-substituted pyrrolo[2,1-b]thiazoles **4a-4f** in good yields. Unfortunately, for the reactions of α-methyl- and α-bromosubstituted nitroalkenes with salt **2a** poor conversion was observed.



Scheme 3 Synthesis of 7-ester-substituted pyrrolo[2,1-b]thiazoles **4** from nitrocinnamates **1** and thiazolium salts **2**. Yields refer to isolated products **4**.



Scheme 4 Synthesis of 7-unsubstituted pyrrolo[2,1-a]thiazoles. Yields refer to isolated products **5**. [a] 39% yield was obtained if DMSO was used as a solvent. [b] 3.0 equiv. of salt **2** was used.

The annulation between thiazolium ylides and α-unsubstituted nitroalkenes is of special interest regarding its chemoselectivity. As was observed earlier, oxidative annulation of these nitroalkenes with pyridinium ylide proceeds poorly to afford 1-unsubstituted indolizine in low yield,[13a] while for pyridinium imines a smooth formation of nitro-substituted heterocycle takes place due to excessive oxidation of intermediates.[13b, 17] For the present study the reaction of α-unsubstituted nitroalkene with thiazolium salt **2a** in optimized conditions resulted in formation of 7-unsubstituted pyrrolo[2,1-b]thiazole **5a** and 7-nitro-substituted product in 3:1 ratio according to ^{1}H NMR analysis of the crude mixture. However, the conditions were successfully modified to improve the yield of 7-unsubstituted product **5a**. Reducing the amount of oxidant to 1.5 equiv. and switching to acetonitrile[18] as a solvent was sufficient to improve the chemoselectivity and obtain **5a** in 53% isolated yield, while nitrosubstituted product was observed in trace amounts. In the modified conditions 7-unsubstituted pyrrolo[2,1-b]thiazoles **5** were prepared from α-unsubstituted nitroalkenes (Scheme 4). Pyrrolothiazoles were obtained in moderate yield for phenyl, 4-methoxyphenyl-substituted nitroalkenes (compounds **5b-5c**), and in good yield for 2-bromophenyl-substituted nitroalkene (compound **5d**). Importantly, hetaryl-substituted and aliphatic nitroalkenes were also tolerated to afford products **5e-5f**. In contrast to the chemoselective synthesis of 7-unsubstituted pyrrolothiazoles, variation of the initial conditions (Table 1, entry 19) with α-unsubstituted nitroalkene towards the increase of Cu/lutidine ratio could not facilitate formation of nitro-substituted products.

The structures of all the obtained products were confirmed by ^{1}H and ^{13}C NMR spectra (including 2D) as well as by HRMS data. For the 7-fluoro- and 7-unsubstituted pyrrolo[2,1-b]thiazoles (**3b** and **5a** respectively) a single crystal X-ray analysis was performed (Figure 1).[19]

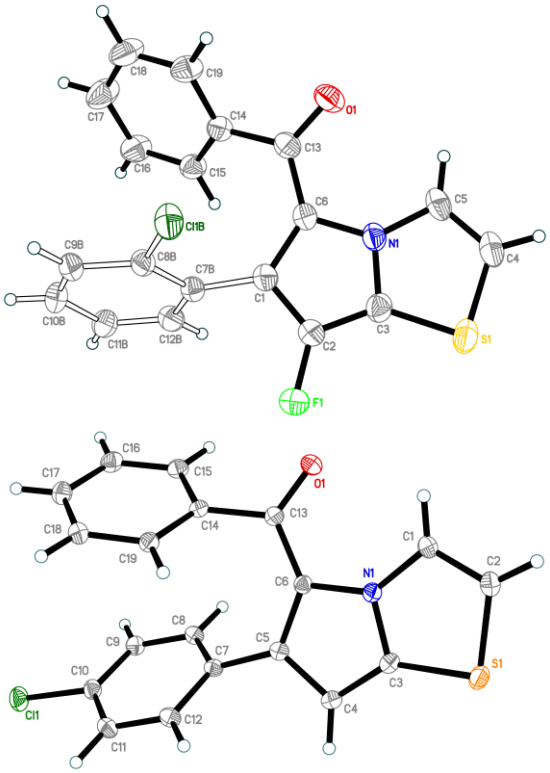
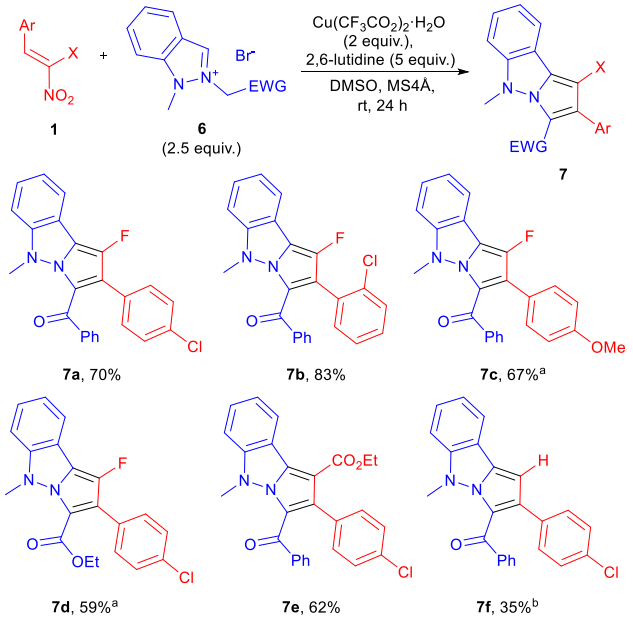


Figure 1 General view of the compounds **3b** and **5a** in representation of atoms *via* thermal ellipsoids at 50% probability level.

Besides thiazolium ylides, copper-mediated [3+2]-annulation with other azolium ylides, including ylides of benzannelated azoles, was attempted. Even though some efficient protocols to access *N*-fused heterocycles from benzimidazolium[20] and benzothiazolium[21] ylides were developed recently, ylides of 1,2-azoles are not common 1,3-dipoles in [3+2]-annulation reactions. For example, oxidative [3+2]-annulation with indazolium and pyrazolium ylides is still unknown due to their propensity to rearrangement via N-N bond cleavage followed by ring expansion to form dihydropyrimidine derivatives.[22] To our delight, application of the present copper-mediated protocol to the indazolium salts **6** afforded novel pyrrolo[1,2-b]indazoles **7** in good yields (Scheme 5). Importantly, in the presence of a mild base 2,6-lutidine rearrangement of the ylide did not take place. To the best of our knowledge, this is the first example of assembly of pyrrolo[1,2-b]indazole heterocyclic core. The reaction was found to proceed in high yields for both fluoro- and ester-substituted nitroalkenes to give products **7a-7e**. For the α-unsubstituted nitroalkene the product **7f** was obtained in 35% yield, probably, due to incomplete chemoselectivity and side-reactions. Indeed, according to ^{1}H (δ_{H1} = 6.50 ppm for **7f**) and ^{13}C NMR shifts of products **7**, the C1 position of pyrrolo[1,2-b]indazole should be even more reactive towards oxidation than C1 position of indolizines.[23]

The structure of the novel pyrrolo[1,2-b]indazole heterocyclic core was additionally confirmed by single crystal X-ray analysis for the fluorinated derivative **7a** (Figure 2).[19]



Scheme 5 Synthesis of pyrrolo[1,2-b]indazoles. Yields refer to isolated products **7**. [a] 3.0 equiv. of salt **6**; reaction time 2 days, [b] MeCN was used as a solvent

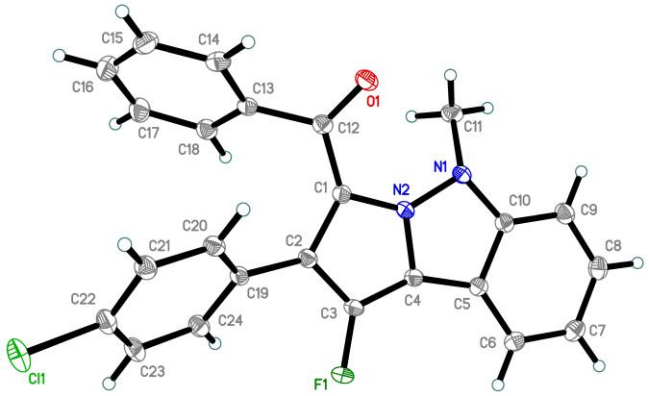
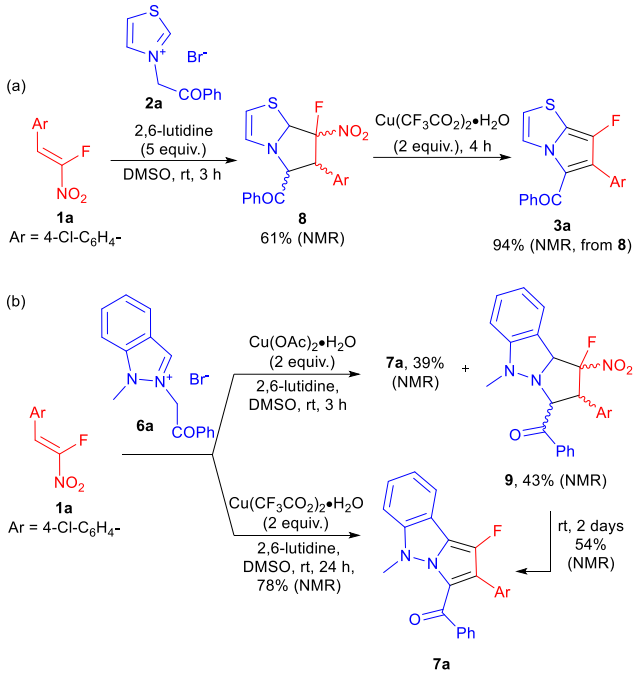


Figure 2 General view of the compound **7a** in representation of atoms *via* thermal ellipsoids at 50% probability level.

To study some mechanistic features of the oxidative annulation with azolium ylides, control experiments were performed. First, the copper-free reaction of fluoronitroalkene **1a** with thiazolium salt **2a** in the presence of lutidine afforded saturated adduct **8** as a mixture of two diastereomers (Scheme 6, a). However, this compound quickly underwent decomposition in the presence of water or silica gel, thus it could not be isolated and purified. Also the intermediate **8** undergoes decomposition upon maintaining the solution at room temperature for several hours. Thus, performing a quick *in situ* oxidation of saturated adduct is the key for the method efficiency. Addition of $Cu(CF_3CO_2)_2{\cdot}H_2O$ to **8** led to nearly quantitative oxidation to pyrrolo[2,1-b]thiazole **3a**. Importantly, the reaction of cycloadduct **8** with $Cu(OAc)_2{\cdot}H_2O$ proceeded much slower and the oxidation was not quantitative. A remarkable difference between these copper carboxylates was observed for annulation of nitroalkene **1a** with indazolium salt **6a** (Scheme 6, b). In the case of copper acetate substrate **1a** was consumed quickly to afford **7a** as well as saturated adduct **9**, which was slowly oxidized further. For the $Cu(CF_3CO_2)_2{\cdot}H_2O$ the reaction proceeded slower, however, **9** was observed in negligible amount. After 24 hours, nitroalkene was consumed to give **7a** in high yield. Therefore, copper trifluoroacetate is beneficial for oxidative annulation due to its higher oxidation potential,[24] which afforded a smooth aromatization of primary cycloadducts in mild conditions.



Scheme 6 Control experiments

Experimental

All reactions were performed in oven-dried (150 °C) glassware. Most of the chemicals were acquired from commercial sources and used as received. For details on the synthesis of substrates see ESI. TLC were performed on silica coated on aluminium with UV254 indicator. Visualization was accomplished with UV. Column chromatography was performed on silica (0.04–0.063 mm, 60 Å). NMR spectra were recorded at the 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), and 282 MHz (^{19}F NMR) frequencies. Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), br (broad). High resolution mass spectra were acquired at TOF spectrometer using electrospray ionization (ESI). Assignment was made on the basis of 2D NMR (COSY, HSQC, HMBC) for compounds **3c**, **5a**, **5b**, **5e**, **5f**, **7f**. For the salts **2** and **6** intensities of CH_2-group signals can be reduced due to their high acidity that causes proton exchange with water in DMSO-d_6. More significant decrease of CH_2-group intensity is attributed to higher acidity (e.g. for compound **2c**).

General procedure 1 for the synthesis of 7-fluoropyrrolo[2,1-b]thiazoles **3**,**4**.

To the solution of thiazolium salt **2** (0.5 mmol, 2.5 equiv.) in dry DMSO (1 ml) powdered 4Å molecular sieves (100 mg) and 2,6-lutidine (107 mg, 1 mmol, 5 equiv.) were added, followed by addition of nitroalkene **1** (0.2 mmol, 1.0 equiv.) and $Cu(OCOCF_3)_2{\cdot}H_2O$ (123 mg, 0.4 mmol, 2.0 equiv.) The mixture was stirred at r. t. for 1 h – 3 d. After the reaction was complete (TLC monitoring), it was quenched with EtOAc/1% aqueous Na_2EDTA solution (30/30 ml). Aqueous layer was extracted with 3*30 ml EtOAc. Combined organic layer was dried over anhydrous Na_2SO_4 and evaporated after addition of silica gel. Crude product was purified by column chromatography using PE/EtOAc as an eluent to give pyrrolo[2,1-b]thiazoles **3**,**4**.

[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-b][1,3]thiazol-5-yl](phenyl)methanone (3a). Pyrrolo[2,1-b]thiazole **3a** was obtained from corresponding α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 5 h). Column chromatography (eluent: 15:1 PE/EtOAc) afforded **3a** (44 mg, 62%) as a yellow solid. R_f = 0.36 (PE/EtOAc, 3:1) (UV) mp = 128-129°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94 (d, *J* = 4.2 Hz, 1H, H2), 6.97-7.03 (m, 4H, CH_{Ar}), 7.06 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.24 (m, 1H, CH_{Ar}), 7.33 – 7.39 (m, 2H, CH_{Ar}), 8.78 (dd, *J* = 4.2, 1.9 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.1 (C2-H), 117.2 (C5), 122.8 (d, $^2J_{CF}$ = 9.1 Hz, C6), 123.9 (C3-H), 124.1 (d, $^2J_{CF}$ = 27.0 Hz, C7a), 127.5 (CH_{Ar}), 127.9 (CH_{Ar}), 129.1 (CH_{Ar}), 129.3 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 131.0 (CH_{Ar}), 131.7 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 133.2 (C_{Ar}-Cl), 138.4 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 242.5 Hz, C7-F), 184.9 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -170.7 (d, *J* = 1.9 Hz). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{11}ClFNOS$ + H^+]: 356.0307, found: 356.0302.

[6-(2-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (3b). Pyrrolo[2,1-b]thiazole **3b** was obtained from corresponding α-fluoronitroalkene **1b** (60.3 mg, 0.25 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 8 h). Column chromatography (eluent: 7:1 PE/EtOAc) afforded **3b** (76 mg, 71%) as a yellow solid. R_f = 0.37 (PE/EtOAc, 3:1) (UV), mp = 167-168°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.83-6.94 (m, 2H, CH_{Ar}), 6.96 (d, *J* = 4.1 Hz, 1H, H2), 6.98-7.05 (m, 3H, CH_{Ar}), 7.11-7.17 (m, 1H, CH_{Ar}), 7.21 (dd, *J* = 8.0, 0.7 Hz, 1H, CH_{Ar}), 7.36-7.43 (m, 2H, CH_{Ar}), 8.81 (dd, *J* = 4.1, 1.8 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.3 (C2-H), 117.6 (C5), 120.8 (d, $^2J_{CF}$ = 10.5 Hz, C6), 123.9 (d, $^2J_{CF}$ = 28.2 Hz, C7a), 124.0 (C3-H), 126.0 (CH_{Ar}), 127.2 (CH_{Ar}), 128.6 (CH_{Ar}), 129.0 (CH_{Ar}), 129.1 (CH_{Ar}), 130.4 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 130.7 (CH_{Ar}), 133.2 (CH_{Ar}), 134.2 (C_{Ar}-Cl), 138.6 (C_{Ar}), 141.5 (d, $^1J_{CF}$ = 243.2 Hz, C7-F), 185.0 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -166.1 (d, *J* = 1.8 Hz). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{11}ClFNOS$ + H^+]: 356.0307, found: 356.0304.

[7-Fluoro-6-(4-methoxyphenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (3c). Pyrrolo[2,1-b]thiazole **3c** was obtained from corresponding α-fluoronitroalkene **1c** (39.4 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 2 days). Column chromatography (eluent: 7:1 to 3:1 PE/EtOAc) afforded **3c** (47.5 mg, 68%) as a yellow solid. R_f = 0.34 (PE/EtOAc, 3:1) (UV), mp = 126-129°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 3.71 (s, 3H, OMe), 6.55-6.61 (m, 2H, CH_{Ar}), 6.90 (d, *J* = 4.1 Hz, 1H, H2), 6.93-7.07 (m, 4H, CH_{Ar}), 7.16-7.22 (m, 1H, CH_{Ar}), 7.36-7.42 (m, 2H, CH_{Ar}), 8.77 (dd, *J* = 4.1, 1.9 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT-135, HSQC, HMBC): δ 55.2 (OMe), 112.5 (C2-H), 113.3 (CH_{Ar}), 117.3 (C5), 123.1 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 124.0 (C3-H), 124.0 (d, $^2J_{CF}$ = 9.1 Hz, C6), 124.1 (d, $^2J_{CF}$ = 28.3 Hz, C7a), 127.4 (CH_{Ar}), 129.2 (CH_{Ar}), 130.7 (CH_{Ar}), 131.7 (d, $^4J_{CF}$ = 0.9 Hz, CH_{Ar}), 138.6 (C_{Ar}), 141.4 (d, $^1J_{CF}$ = 241.0 Hz, C7-F), 158.7 ($\mathbf{C}_{Ar}$-OMe), 185.1 (d, $^4J_{CF}$

= 2.8 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -171.1 (s). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{14}FNO_2S + H^+$]: 352.0802, found: 352.0803.

[7-Fluoro-6-(4-nitrophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (3d). Pyrrolo[2,1-b]thiazole **3d** was obtained from corresponding α-fluoronitroalkene **1d** (42.4 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 3 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3d** (26 mg, 34%) as a bright yellow solid. R_f = 0.30 (PE/EtOAc, 3:1) (UV) mp = 163-164°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (d, *J* = 4.2 Hz, 1H, H2), 7.04 (d, *J* = 7.8 Hz, 2H, CH_{Ar}), 7.17-7.24 (m, 3H, CH_{Ar}), 7.33-7.39 (m, 2H, CH_{Ar}), 7.87-7.92 (m, 2H, CH_{Ar}), 8.79 (dd, *J* = 4.2, 1.9 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1 (C2-H), 117.1 (C5), 121.3 (d, $^2J_{CF}$ = 8.7 Hz, C6), 122.7 (CH_{Ar}), 123.8 (C3-H), 124.2 (d, $^2J_{CF}$ = 28.0 Hz, C7a), 127.7 (CH_{Ar}), 129.1 (CH_{Ar}), 131.2 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 131.4 (CH_{Ar}), 137.8 (d, $^3J_{CF}$ = 2.6 Hz, C_{Ar}), 138.3 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 244.5 Hz, C7-F), 146.4 (C_{Ar}-NO_2), 184.7 (d, $^4J_{CF}$ = 2.7 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -170.1 (m). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{11}FN_2O_3S + H^+$]: 367.0547, found: 367.0550.

[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](3-methoxyphenyl)methanone (3e). Pyrrolo[2,1-b]thiazole **3e** was obtained from corresponding α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2b** (2.5 equiv.) following the general procedure 1 (reaction time 3 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3e** (50 mg, 65%) as an amorphous yellow solid. R_f = 0.31 (PE/EtOAc, 3:1) (UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 3H, OMe), 6.79 (m, 1H, CH_{Ar}), 6.88 (br s, 1H, CH_{Ar}), 6.94 (d, *J* = 4.1 Hz, 1H, H2), 6.96-7.07 (m, 6H, CH_{Ar}), 8.77 (dd, *J* = 4.1, 1.8 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2 (OMe), 113.2 (CH_{Ar}), 114.1 (C2-H), 117.2 (C5, overlapped signal), 117.2 (CH_{Ar}), 121.8 (CH_{Ar}), 122.7 (d, $^2J_{CF}$ = 9.0 Hz, C6), 124.0 (C3-H), 124.2 (d, $^2J_{CF}$ = 28.4 Hz, C7a), 127.8 (CH_{Ar}), 128.7 (CH_{Ar}), 129.4 (d, $^3J_{CF}$ = 2.5 Hz, C_{Ar}), 131.5 (d, $^4J_{CF}$ = 0.9 Hz, CH_{Ar}), 133.2 (C_{Ar}-Cl), 139.7 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 242.5 Hz, C7-F), 158.9 (**C**$_{Ar}$-OMe), 184.6 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -170.6 (s). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{13}ClFNO_2S + H^+$]: 386.0412, found: 386.0411.

[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl](3-nitrophenyl)methanone (3f). Pyrrolo[2,1-b]thiazole **3f** was obtained from corresponding α-fluoronitroalkene **1a** (50.4 mg, 0.25 mmol) and thiazolium salt **2c** (2.5 equiv.) following the general procedure 1 (reaction time 1 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3f** (41 mg, 41%) as a bright yellow solid. R_f = 0.20 (PE/EtOAc, 3:1) (UV), mp = 213-215°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94-7.02 (m, 4H, CH_{Ar}), 7.04 (d, *J* = 4.1 Hz, 1H, H2), 7.32 (dd, *J* = 8.7, 7.7 Hz, 1H, CH_{Ar}), 7.75 (d, *J* = 7.7 Hz, 1H, CH_{Ar}), 8.05-8.14 (m, 2H, CH_{Ar}), 8.82 (dd, *J* = 4.1, 1.8 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1 (C2-H), 116.7 (C5), 123.1 (d, $^2J_{CF}$ = 9.6 Hz, C6), 124.0 (C3-H), 124.5 (CH_{Ar}), 125.1 (CH_{Ar}), 125.9 (d, $^2J_{CF}$ = 28.0 Hz, C7a), 128.1 (CH_{Ar}), 128.6 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 128.9 (CH_{Ar}), 131.8 (br s, CH_{Ar}), 133.9 (C_{Ar}-Cl), 134.4 (CH_{Ar}), 139.9 (C_{Ar}), 141.4 (d, $^1J_{CF}$ = 243.8 Hz, C7-F), 147.0 (C_{Ar}-NO_2), 181.5 (d, $^4J_{CF}$ = 3.0 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -169.5 (s). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{10}ClFN_2O_3S + H^+$]: 401.0157, found: 401.0149.

Ethyl 6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazole-5-carboxylate (3g). Pyrrolo[2,1-b]thiazole **3g** was obtained from corresponding α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2d** (3.0 equiv.) following the general procedure 1 (reaction time 2 days). Column chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **3g** (36 mg, 57%) as a white solid. R_f = 0.47 (PE/EtOAc, 3:1) (UV), mp = 102-103°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.1 Hz, 3H, CH_3), 4.22 (q, *J* = 7.1 Hz, 2H, CH_2), 6.84 (d, *J* = 4.2 Hz, 1H, H2), 7.36-7.45 (m, 4H, CH_{Ar}), 8.43 (dd, *J* = 4.2, 1.9 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1 (CH_3), 60.1 (CH_2), 108.0 (d, $^3J_{CF}$ = 1.5 Hz, C5), 112.3 (C2-H), 121.1 (d, $^2J_{CF}$ = 28.1 Hz, C7a), 121.8 (d, $^2J_{CF}$ = 10.0 Hz, C6), 123.3 (C3-H), 127.8 (CH_{Ar}), 129.4 (d, $^3J_{CF}$ = 2.4 Hz, C_{Ar}), 131.9 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 133.6 (C_{Ar}-Cl), 141.2 (d, $^1J_{CF}$ = 240.3 Hz, C7-F), 160.7 (d, $^4J_{CF}$ = 2.7 Hz, **C**O_2Et). ^{19}F NMR (282 MHz, $CDCl_3$): δ -171.1 (br s). HRMS (ESI): *m/z* calcd. for [$C_{15}H_{11}ClFNO_2S + Na^+$]: 346.0075, found: 346.0069.

Benzyl 6-(4-chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazole-5-carboxylate (3h). Pyrrolo[2,1-b]thiazole **3h** was obtained from corresponding α-fluoronitroalkene **1a** (30.3 mg, 0.15 mmol) and thiazolium salt **2e** (3.5 equiv.) following the general procedure 1 (reaction time 3 days). Column chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **3h** (28.5 mg, 50%) as a white solid. R_f = 0.65 (PE/EtOAc, 3:1) (UV), mp = 101-103°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.18 (s, 2H, CH_2), 6.84 (d, *J* = 4.2 Hz, 1H, H2), 7.08 (dd, *J* = 6.5, 2.9 Hz, 2H, CH_{Ar}), 7.26-7.32 (m, 5H, CH_{Ar}), 7.36 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 8.44 (dd, *J* = 4.2, 1.9 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.9 (CH_2), 107.8 (d, $^3J_{CF}$ = 1.7 Hz, C5), 112.5 (C2-H), 121.6 (d, $^2J_{CF}$ = 28.1 Hz, C7a), 122.1 (d, $^2J_{CF}$ = 10.6 Hz, C6), 123.3 (C3-H), 127.9 (CH_{Ar}), 128.0 (CH_{Ar}), 128.1 (CH_{Ar}), 128.4 (CH_{Ar}), 129.3 (d, $^3J_{CF}$ = 2.2 Hz, C_{Ar}), 131.9 (d, $^4J_{CF}$ = 0.9 Hz, CH_{Ar}), 133.7 (C_{Ar}-Cl), 135.5 (C_{Ar}), 141.2 (d, $^1J_{CF}$ = 240.4 Hz, C7-F), 160.5 (d, $^4J_{CF}$ = 2.9 Hz, **C**O_2Et). ^{19}F NMR (282 MHz, $CDCl_3$): δ -171.4 (br s). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{13}ClFNO_2S + H^+$]: 386.0412, found: 386.0418.

1-[6-(4-Chlorophenyl)-7-fluoropyrrolo[2,1-*b*][1,3]thiazol-5-yl]ethan-1-one (3i). Pyrrolo[2,1-b]thiazole **3i** was obtained from corresponding α-fluoronitroalkene **1a** (40.3 mg, 0.2 mmol) and thiazolium salt **2f** (3.0 equiv.) following the general procedure 1 (reaction time 48 h). Column chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **3i** (26.5 mg, 44%) as a colorless oil, which solidifies upon storage in a refrigerator. R_f = 0.35 (PE/EtOAc, 3:1) (UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H, Me), 6.89 (d, *J* = 4.1 Hz, 1H, H2), 7.36-7.39 (m, 2H, CH_{Ar}), 7.45-7.48 (m, 2H, CH_{Ar}), 8.82 (dd, *J* = 4.1, 1.8 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.3 (Me), 112.9 (C2-H), 118.3 (C5), 122.0 (d, $^2J_{CF}$ = 10.3 Hz, C6), 123.3 (d, $^2J_{CF}$ = 28.1 Hz, C7a), 124.3 (C3-H), 128.8 (CH_{Ar}), 129.8 (d, $^3J_{CF}$ = 1.9 Hz, C_{Ar}), 131.8 (br s, CH_{Ar}), 134.7 (C_{Ar}-Cl), 141.5 (d, $^1J_{CF}$ = 241.0 Hz, C7-F), 186.2 (d, $^4J_{CF}$ = 2.8 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -171.0 (d, *J* = 1.8 Hz). HRMS (ESI): *m/z* calcd. for [$C_{14}H_9ClFNOS + H^+$]: 293.0072, found: 293.0068.

Ethyl 5-benzoyl-6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate (4a). Pyrrolo[2,1-b]thiazole **4a** was obtained from corresponding nitroalkene **1e** (37 mg, 0.145 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 10 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **3k** (39 mg, 66%) as a slightly yellow solid. R_f = 0.33 (PE/EtOAc, 3:1) (UV), mp = 158-161°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 4.24 (q, *J* = 7.1 Hz, 2H, CH_2), 6.92-6.98 (m, 2H, CH_{Ar}), 6.99-7.07 (m, 4H, CH_{Ar}), 7.13 (d, *J* = 4.2 Hz, 1H, H2), 7.20-7.32 (m, 3H, CH_{Ar}), 8.74 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (CH_3), 60.3 (CH_2), 105.3 (C7), 115.4 (C2-H), 123.9 (C_q), 124.3 (C3-H), 127.0 (CH_{Ar}), 127.5 (CH_{Ar}), 128.8 (CH_{Ar}), 130.9 (CH_{Ar}), 131.4 (C_q), 132.5 (CH_{Ar}), 133.5 (C_q), 138.0 (C_q), 138.1 (C_q), 144.7 (C_q), 162.9 (**C**O_2Et), 186.8 (**C**OPh). HRMS (ESI): *m/z* calcd. for [$C_{22}H_{16}ClNO_3S$ + H^+]: 410.0612, found: 410.0604.

Ethyl 5-benzoyl-6-(2-bromophenyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate (4b). Pyrrolo[2,1-b]thiazole **4b** was obtained from corresponding nitroalkene **1f** (60 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 1 (reaction time 5 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **4b** (72 mg, 79%) as a slightly yellow solid. R_f = 0.35 (PE/EtOAc, 3:1) (UV), mp = 123-126°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (t, *J* = 7.1 Hz, 3H, CH_3), 4.06-4.28 (m, 2H, CH_2), 6.89-6.91 (m, 3H, CH_{Ar}), 7.03 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 4.2 Hz, 1H, H2), 7.12-7.18 (m, 1H, CH_{Ar}), 7.32-7.36 (m, 1H, CH_{Ar}), 7.40-7.44 (m, 2H, CH_{Ar}), 8.77 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0 (CH_3), 60.2 (CH_2), 106.3 (C7), 115.3 (C2-H), 123.7 (C_q), 124.4 (C3-H), 125.1 (C_{Ar}-Br), 126.0 (CH_{Ar}), 127.2 (CH_{Ar}), 128.2 (CH_{Ar}), 128.8 (CH_{Ar}), 130.8 (CH_{Ar}), 131.7 (CH_{Ar}), 132.4 (CH_{Ar}), 134.9 (C_q), 137.1 (C_q), 138.5 (C_q), 144.3 (C_q), 162.9 (**C**O_2Et), 186.6 (**C**OPh). HRMS (ESI): *m/z* calcd. for [$C_{22}H_{16}BrNO_3S$ + H^+]: 454.0107, found: 454.0098.

Ethyl 6-(4-chlorophenyl)-5-(3-methoxybenzoyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate (4c). Pyrrolo[2,1-b]thiazole **4c** was obtained from corresponding nitroalkene **1e** (35 mg, 0.137 mmol) and thiazolium salt **2b** (2.5 equiv.) following the general procedure 1 (reaction time 4 h). Column chromatography (eluent: 4:1 PE/EtOAc) afforded **4c** (41 mg, 68%) as an amorphous slightly yellow solid.R_f = 0.26 (PE/EtOAc, 3:1) (UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 3H, CH_3), 3.69 (s, 3H, OMe), 4.23 (q, *J* = 7.1 Hz, 2H, CH_2), 6.74-6.80 (m, 1H, CH_{Ar}), 6.89 (dt, *J* = 7.5, 1.2 Hz, 1H, CH_{Ar}), 6.93-7.06 (m, 5H, CH_{Ar}), 7.12 (d, *J* = 4.2 Hz, 1H, H2), 8.73 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3), 55.2 (OMe), 60.3 (CH_2), 105.3 (C7), 114.0 (CH_{Ar}), 115.4 (C2-H), 116.7 (CH_{Ar}), 121.3 (CH_{Ar}), 123.8 (C_q), 124.3 (C3-H), 127.0 (CH_{Ar}), 128.8 (CH_{Ar}), 131.5 (C_q), 132.2 (CH_{Ar}), 133.4 (C_q), 138.1 (C_q), 139.5 (C_q), 144.7 (C_q), 158.6 (**C**$_{Ar}$-OMe), 162.9 (**C**O_2Et), 186.4 (**C**OPh). HRMS (ESI): *m/z* calcd. for [$C_{23}H_{18}ClNO_4S$ + H^+]: 410.0612, found: 410.0604.

Ethyl 6-(4-chlorophenyl)-5-(3-nitrobenzoyl)pyrrolo[2,1-*b*][1,3]thiazole-7-carboxylate (4d). Pyrrolo[2,1-b]thiazole **4d** was obtained from corresponding nitroalkene **1e** (44 mg, 0.172 mmol) and thiazolium salt **2c** (2.5 equiv.) following the general procedure 1 (reaction time 2 h). Column chromatography (eluent: 4:1 PE/EtOAc) afforded **4d** (36.5 mg, 51%) as a dark yellow solid. R_f = 0.19 (PE/EtOAc, 3:1) (UV), mp = 172-175°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, *J* = 7.1 Hz, 3H, CH_3), 4.23 (q, *J* = 7.1 Hz, 2H, CH_2), 6.94 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 7.00-7.06 (m, 2H, CH_{Ar}), 7.20 (d, *J* = 4.2 Hz, 1H, H2), 7.32 (t, *J* = 7.9 Hz, 1H, CH_{Ar}), 7.70 (d, *J* = 7.6 Hz, 1H, CH_{Ar}), 7.99 (t, *J* = 1.8 Hz, 1H, CH_{Ar}), 8.05-8.11 (m, 1H, CH_{Ar}), 8.78 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3), 60.5 (CH_2), 106.1 (C7), 116.1 (C2-H), 123.3 (C_q), 124.1 (CH), 124.3 (CH), 125.0 (CH), 127.2 (CH_{Ar}), 128.9 (CH_{Ar}), 131.1 (C_q), 132.4 (CH_{Ar}), 133.9 (C_q), 134.0 (CH_{Ar}), 138.7 (C_q), 139.7 (C_q), 145.5 (C_q), 146.9 (C_{Ar}-NO_2), 162.6 (**C**O_2Et), 183.5 (**C**OPh). HRMS (ESI): *m/z* calcd. for [$C_{22}H_{15}ClN_2O_5S$ + H^+]: 455.0463, found: 455.0454.

Diethyl 6-(4-chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazole-5,7-dicarboxylate (4e). Pyrrolo[2,1-b]thiazole **4e** was obtained from corresponding nitroalkene **1e** (51.6 mg, 0.2 mmol) and thiazolium salt **2d** (3.0 equiv.) following the general procedure 1 (reaction time 2 days). Column chromatography (eluent: 19:1 to 5:1 PE/EtOAc) afforded **4e** (37.5 mg, 47%) as a white solid. R_f = 0.38 (PE/EtOAc, 3:1) (UV), mp = 114-115°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (t, *J* = 7.1 Hz, 3H, CH_3), 1.20 (t, *J* = 7.1 Hz, 3H, CH_3), 4.13 (q, *J* = 7.1 Hz, 2H, CH_2), 4.19 (q, *J* = 7.1 Hz, 2H, CH_2), 7.05 (d, *J* = 4.2 Hz, 1H, H2), 7.27-7.38 (m, 4H, CH_{Ar}), 8.48 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8 (CH_3), 14.2 (CH_3), 60.1 (CH_2), 60.3 (CH_2), 105.7 (C7), 114.9 (C2-H), 115.0 (C_q), 123.6 (C3-H), 127.1 (CH_{Ar}), 131.4 (CH_{Ar}), 132.7 (C_q), 133.3 (C_q), 137.0 (C_q), 142.6 (C_q), 160.7 (**C**O_2Et), 163.0 (**C**O_2Et). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{16}ClNO_4S$ + H^+]: 378.0561, found: 378.0560.

General procedure 2 for the synthesis of 7-unsubstituted pyrrolo[2,1-b]thiazoles **5**

To the solution of thiazolium salt **2** (0.5 mmol, 2.5 equiv.) in dry MeCN (1 ml) powdered 4Å molecular sieves (100 mg) and 2,6-lutidine (107 mg, 1 mmol, 5 equiv.) were added, followed by addition of nitroalkene **1** (0.2 mmol, 1.0 equiv.) and $Cu(OCOCF_3)_2{\cdot}H_2O$ (92 mg, 0.3 mmol, 1.5 equiv.) The mixture was stirred at r. t. for 5-24 hours. After the reaction was complete (TLC monitoring), it was evaporated after addition of silica gel. Crude product was purified by column chromatography using PE/EtOAc as an eluent to give pyrrolo[2,1-b]thiazoles **5**.

[6-(4-Chlorophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (5a). Pyrrolo[2,1-b]thiazole **5a** was obtained from corresponding nitroalkene **1g** (37 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 2 (reaction time 5 h). Column chromatography (eluent: 15:1 to 5:1 PE/EtOAc) afforded **5a** (32 mg, 53%) as a slightly yellow solid. R_f = 0.41 (PE/EtOAc, 3:1) (UV), mp = 141-142°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 6.42 (s, 1H, H7), 6.93-6.98 (m, 5H, CH_{Ar}, H2), 7.02-7.08 (m, 2H, CH_{Ar}), 7.20-7.27 (m, 1H, CH_{Ar}), 7.37-7.41 (m, 2H, CH_{Ar}), 8.75 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ 101.7 (C7-H), 113.1 (C2-H), 121.4 (C6), 124.0 (C3-H), 127.5 (CH_{Ar}), 127.7 (CH_{Ar}), 129.2 (CH_{Ar}), 130.8 (CH_{Ar}), 130.9 (CH_{Ar}), 132.7 (C_{Ar}-Cl), 134.2 (C_{Ar}), 138.9 (C_q), 139.0 (C_q), 139.1 (C_q), 185.1 (C=O).

HRMS (ESI): *m/z* calcd. for [$C_{19}H_{12}ClNOS + H^+$]: 338.0401, found: 338.0396.

Phenyl(6-phenylpyrrolo[2,1-*b*][1,3]thiazol-5-yl)methanone (5b). Pyrrolo[2,1-b]thiazole **5b** was obtained from corresponding nitroalkene **1h** (37 mg, 0.25 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 2 (reaction time 5 h). Column chromatography (eluent: 15:1 to 7:1 PE/EtOAc) afforded **5b** (44 mg, 59%) as a slightly yellow solid. R_f = 0.46 (PE/EtOAc, 3:1) (UV), mp = 106-109°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46 (s, 1H, H7), 6.93 (d, *J* = 4.2 Hz, 1H, H2), 6.98-7.07 (m, 7H, CH_{Ar}), 7.12-7.20 (m, 1H, CH_{Ar}), 7.38-7.44 (m, 2H, CH_{Ar}), 8.77 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$, HSQC, HMBC): δ 101.8 (C7-H), 112.8 (C2-H), 121.4 (C6), 124.0 (C3-H), 126.6 (CH_{Ar}), 127.3 (CH_{Ar}), 127.5 (CH_{Ar}), 129.3 (CH_{Ar}), 129.8 (CH_{Ar}), 130.6 (CH_{Ar}), 135.6 (C_{Ar}), 139.0 (C_q), 139.1 (C_q), 140.4 (C_q), 185.3 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{13}NOS + H^+$]: 304.0791, found: 304.0802.

[6-(2-Bromophenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (5c). Pyrrolo[2,1-b]thiazole **5c** was obtained from corresponding nitroalkene **1j** (45.6 mg, 0.2 mmol) and thiazolium salt **2b** (2.5 equiv.) following the general procedure 2 (reaction time 6 h). Column chromatography (eluent: 15:1 to 7:1 PE/EtOAc) afforded **5c** (49 mg, 64%) as a slightly yellow oil, which solidifies upon storage in a refrigerator. R_f = 0.38 (PE/EtOAc, 3:1) (UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.44 (s, 1H, H7), 6.86-7.04 (m, 6H, CH_{Ar}), 7.10-7.16 (m, 1H, CH_{Ar}), 7.34 (dd, *J* = 6.9, 1.7 Hz, CH_{Ar}), 7.42 (d, *J* = 7.3 Hz, 2H), 8.79 (d, *J* = 4.1 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 103.0 (C7-H), 113.2 (C2-H), 122.0 (C6), 123.8 (C_{Ar}-Br), 124.0 (C3-H), 126.3 (CH_{Ar}), 127.1 (CH_{Ar}), 128.5 (CH_{Ar}), 128.7 (CH_{Ar}), 130.4 (CH_{Ar}), 132.3 (CH_{Ar}), 132.8 (CH_{Ar}), 136.7 (C_{Ar}), 137.9 (C_q), 138.9 (C_q), 139.0 (C_q), 185.0 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{12}BrNOS + H^+$]: 381.9896, found: 381.9894.

[6-(4-Methoxyphenyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (5d). Pyrrolo[2,1-b]thiazole **5d** was obtained from corresponding nitroalkene **1i** (35 mg, 0.2 mmol) and thiazolium salt **2a** (3.0 equiv.) following the general procedure 2 (reaction time 24 h). Column chromatography (eluent: 5:1 PE/EtOAc) afforded **5d** (31 mg, 47%) as an amorphous yellow solid. R_f = 0.34 (PE/EtOAc, 3:1) (UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 3H, OMe), 6.41 (s, 1H, H7), 6.50-6.61 (m, 2H, CH_{Ar}), 6.91 (d, *J* = 4.2 Hz, 1H, H2), 6.93-6.98 (m,2H, CH_{Ar}), 7.03 (t, *J* = 7.6 Hz, 2H), 7.15-7.21 (m, 1H, CH_{Ar}), 7.38-7.43 (m, 2H, CH_{Ar}), 8.75 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2 (OMe), 101.7 (C7-H), 112.5 (C2-H), 113.1 (CH_{Ar}), 121.4 (C6), 124.0 (C3-H), 127.3 (CH_{Ar}), 128.1 (C_{Ar}), 129.3 (CH_{Ar}), 130.5 (CH_{Ar}), 130.9 (CH_{Ar}), 139.0 (C_q), 139.1 (C_q), 140.2 (C_q), 158.5 (**C_{Ar}**-OMe), 185.2 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{15}NO_2S + H^+$]: 334.0896, found: 334.0900.

[6-(5-Bromothiophen-2-yl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl](phenyl)methanone (5e). Pyrrolo[2,1-b]thiazole **5e** was obtained from corresponding nitroalkene **1k** (46.8 mg, 0.2 mmol) and thiazolium salt **2a** (3.0 equiv.) following the general procedure 2 (reaction time 24h). Column chromatography (eluent: 9:1 PE/EtOAc) afforded **5e** (43 mg, 55%) as a slightly yellow solid. R_f = 0.44 (PE/EtOAc, 3:1) (UV), mp = 119-123°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 6.21 (d, *J* = 3.8 Hz, 1H, thiophene), 6.44 (s, 1H, H7), 6.57 (d, *J* = 3.8 Hz, 1H, thiophene), 6.95 (d, *J* = 4.2 Hz, 1H, H2), 7.19 (t, *J* = 7.6 Hz, 2H, CH_{Ar}), 7.30-7.37 (m, 1H, CH_{Ar}), 7.50-7.55 (m, 2H, CH_{Ar}), 8.68 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$, HSQC): δ 102.3 (C7-H), 112.1 (C(thiophene)-Br), 113.5 (C2-H), 121.5 (C6), 123.8 (C3-H), 127.8 (CH_{Ph}), 128.2 (CH(thiophene)), 128.9 (CH_{Ph}), 129.5 (CH(thiophene), 130.6 (C_q(thiophene)), 131.1 (CH_{Ph}), 138.5 (C_q), 139.0 (C_q), 139.1 (C_q), 185.0 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{17}H_{10}BrNOS_2 + H^+$]: 387.9460, found: 387.9468.

Phenyl[6-(2-phenylethyl)pyrrolo[2,1-*b*][1,3]thiazol-5-yl]methanone (5f). Pyrrolo[2,1-b]thiazole **5f** was obtained from corresponding nitroalkene **1l** (35.4 mg, 0.2 mmol) and thiazolium salt **2a** (2.5 equiv.) following the general procedure 2 (reaction time 24 h). Column chromatography (eluent: 9:1 PE/EtOAc) afforded **5f** (30.5 mg, 45%) as a slightly yellow oil, which solidifies upon storage in a refrigerator. R_f = 0.34 (PE/EtOAc, 3:1) (UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54-2.73 (m, 4H, 2*CH_2), 6.27 (s, 1H, H7), 6.82 (d, *J* = 6.4 Hz, 2H, CH_{Ar}), 6.85 (d, *J* = 4.3 Hz, 1H, H2), 7.09-7.21 (m, 3H, CH_{Ar}), 7.42-7.55 (m, 3H, CH_{Ar}), 7.61-7.66 (m, 2H, CH_{Ar}), 8.59 (d, *J* = 4.2 Hz, 1H, H3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.6 (CH_2), 37.9 (CH_2), 101.7 (C7-H), 112.1 (C2-H), 122.5 (C6), 124.1 (C3-H), 125.8 (CH_{Ar}), 128.0 (CH_{Ar}), 128.2 (CH_{Ar}), 128.4 (CH_{Ar}), 130.7 (CH_{Ar}), 139.6 (C_q), 140.1 (2*C_q), 141.1 (C_q), 141.2 (C_q), 184.9 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{21}H_{17}NOS + H^+$]: 332.1104, found: 332.1102.

General procedure 3 for the synthesis of pyrrolo[1,2-b]indazoles **7**.

To the solution of indazolium salt **6** (0.25 mmol, 2.5 equiv.) in dry DMSO (0.5 ml) powdered 4Å molecular sieves (100 mg) and 2,6-lutidine (54 mg, 0.5 mmol, 5 equiv.) were added, followed by addition of nitroalkene **1** (0.1 mmol, 1.0 equiv.) and $Cu(OCOCF_3)_2 \cdot H_2O$ (62 mg, 0.2 mmol, 2.0 equiv.) The mixture was stirred at r. t. for 24 hours (for **7c** and **7f** – 3 days). After the reaction was complete (TLC monitoring), it was quenched with EtOAc/1% aqueous Na_2EDTA solution (20+20 ml). Aqueous layer was extracted by EtOAc (3*20 ml). Combined organic layer was dried over anhydrous Na_2SO_4 and evaporated after addition of silica gel. Crude product was purified by column chromatography using PE/EtOAc as an eluent to give pyrrolo[1,2-b]indazoles **7**.

[2-(4-Chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone (7a). Pyrrolo[1,2-b]indazole **7a** was obtained from corresponding α-fluoronitroalkene **1a** (20 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3. Column chromatography (eluent: 19:1 to 7:1 PE/EtOAc) afforded **7a** (28 mg, 70%) as a bright yellow solid. R_f = 0.53 (PE/EtOAc, 3:1) (UV), mp = 178-179°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, 3H, N-Me), 7.02 (s, 4H, CH_{Ar}), 7.10 (t, *J* = 7.7 Hz, 2H), 7.26-7.35 (m, 3H, CH_{Ar}), 7.44-7.50 (m, 1H, CH_{Ar}), 7.51-7.56 (m, 2H, CH_{Ar}), 7.84 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.8 (N-Me), 111.5 (CH), 115.6 (C3), 116.8 (d, $^3J_{CF}$ = 2.9 Hz, C9a), 119.3 (d, $^2J_{CF}$ = 9.4 Hz, C2), 120.4 (C9-H), 121.2 (d, $^2J_{CF}$ = 28.5 Hz, C9b), 123.4 (CH), 127.6 (CH),

127.7 (CH_{Ar}), 127.8 (CH_{Ar}), 129.6 (CH_{Ar}), 129.7 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 131.6 (CH_{Ar}), 131.9 (d, $^4J_{CF}$ = 0.7 Hz, CH_{Ar}), 132.8 (C_{Ar}-Cl), 137.5 (d, $^1J_{CF}$ = 242.8 Hz, C1-F), 138.8 (C_{Ph}), 149.0 (C5a), 183.8 (d, $^4J_{CF}$ = 2.4 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -172.4 (s). HRMS (ESI): *m/z* calcd. for [$C_{24}H_{16}ClFN_2O$ + H^+]: 403.1008, found: 403.0998.

[2-(2-Chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone (7b). Pyrrolo[1,2-b]indazole **7b** was obtained from corresponding α-fluoronitroalkene **1b** (20 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3. Column chromatography (eluent: 19:1 to 7:1 PE/EtOAc) afforded **7b** (33 mg, 83%) as a bright yellow solid. R_f = 0.40 (PE/EtOAc, 3:1) (UV), mp = 176-177°C ($CHCl_3$).^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, N-Me), 6.85-6.92 (m, 1H, CH_{Ar}), 6.96-7.11 (m, 4H, CH_{Ar}), 7.15-7.22 (m, 2H, CH_{Ar}), 7.29-7.33 (m, 1H, CH_{Ar}), 7.35 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.48 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H, CH_{Ar}), 7.53-7.56 (m, 2H, CH_{Ar}), 7.85 (d, *J* = 7.7 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.3 (N-Me), 111.2 (CH), 115.7 (d, $^3J_{CF}$ = 0.9 Hz, C3), 116.8 (d, $^3J_{CF}$ = 2.9 Hz, C9a), 117.3 (d, $^2J_{CF}$ = 10.8 Hz, C2), 120.4 (C9-H), 121.1 (d, $^2J_{CF}$ = 28.6 Hz, C9b), 123.3 (CH), 125.8 (CH), 127.3 (CH), 127.6 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 130.8 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 131.3 (CH), 133.5 (CH), 134.5 (C_{Ar}-Cl), 137.8 (d, $^1J_{CF}$ = 243.5 Hz, C1-F), 139.0 (C_{Ph}), 148.7 (C5a), 183.7 (d, $^4J_{CF}$ = 2.5 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -167.9 (s). HRMS (ESI): *m/z* calcd. for [$C_{24}H_{16}ClFN_2O$ + H^+]: 403.1008, found: 403.1006.

[1-Fluoro-2-(4-methoxyphenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone (7c). Pyrrolo[1,2-b]indazole **7c** was obtained from corresponding α-fluoronitroalkene **1c** (20 mg, 0.1 mmol) and indazolium salt **6a** (3.0 equiv.) following the general procedure 3 (reaction time 3 days). Column chromatography (eluent: 19:1 to 5:1 PE/EtOAc) afforded **7c** (26.5 mg, 67%) as a bright yellow solid. R_f = 0.29 (PE/EtOAc, 3:1) (UV), mp = 173-176°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71 (s, 3H, OMe), 3.74 (s, 3H, N-Me), 6.60 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.01 (d, *J* = 8.4 Hz, 2H, CH_{Ar}), 7.08 (t, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.20-7.35 (m, 3H, CH_{Ar}), 7.42-7.49 (m, 1H, CH_{Ar}), 7.54 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.83 (d, *J* = 7.7 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.9 (N-Me), 55.1 (OMe), 111.5 (CH), 113.2 (CH_{Ar}), 115.7 (C3), 117.1 (d, $^3J_{CF}$ = 3.0 Hz, C9a), 120.3 (d, $^4J_{CF}$ = 0.7 Hz, C9-H), 120.5 (d, $^2J_{CF}$ = 9.6 Hz, C2), 121.2 (d, $^2J_{CF}$ = 28.8 Hz, C9b), 123.3 (CH), 123.5 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 127.4 (CH), 127.5 (CH_{Ar}), 129.6 (CH_{Ar}), 131.3 (CH_{Ar}), 131.8 (br s, CH_{Ar}), 137.7 (d, $^1J_{CF}$ = 241.4 Hz, C1-F), 138.9 (C_{Ph}), 149.2 (C5a), 158.4 (**C_{Ar}**-OMe), 184.0 (d, $^4J_{CF}$ = 2.4 Hz, **C**=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ -172.4 (s). HRMS (ESI): *m/z* calcd. for [$C_{25}H_{19}FN_2O_3$ + H^+]: 399.1503, found: 399.1494.

Ethyl 2-(4-chlorophenyl)-1-fluoro-5-methyl-5*H*-pyrrolo[1,2-*b*]indazole-3-carboxylate (7d). Pyrrolo[1,2-b]indazole **7d** was obtained from corresponding α-fluoronitroalkene **1a** (20 mg, 0.1 mmol) and indazolium salt **6b** (3.0 equiv.) following the general procedure 3 (reaction time 3 days). Column chromatography (eluent: 19:1 to 7:1 PE/EtOAc) afforded **7b** (22 mg, 59%) as a white solid. R_f = 0.50 (PE/EtOAc, 3:1) (UV), mp = 108-110°C ($CHCl_3$).^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (t, *J* = 7.1 Hz, 3H, CH_3), 3.76 (s, 3H, N-Me), 4.18 (q, *J* = 7.1 Hz, 1H, CH_2),7.26-7.33 (m, 2H, CH_{Ar}), 7.36-7.45 (m, 5H, CH_{Ar}), 7.76 (d, *J* = 7.7 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9 (CH_3), 43.6 (N-Me), 60.2 (CH_2), 107.6 (d, $^3J_{CF}$ = 1.3 Hz, C3), 112.3 (CH), 117.8 (d, $^4J_{CF}$ = 2.9 Hz, C9a), 119.1 (d, $^2J_{CF}$ = 9.9 Hz, C2), 120.1 (d, $^4J_{CF}$ = 1.1 Hz, C9-H), 120.6 (d, $^2J_{CF}$ = 28.1 Hz, C9b), 123.7 (CH), 127.1 (CH), 127.7 (CH_{Ar}), 130.1 (d, $^3J_{CF}$ = 2.3 Hz, C_{Ar}), 132.1 (d, $^4J_{CF}$ = 1.0 Hz, CH_{Ar}), 133.2 (C_{Ar}-Cl), 137.6 (d, $^1J_{CF}$ = 241.4 Hz, C1-F), 150.3 (**C**5a-NMe), 159.9 (d, $^4J_{CF}$ = 2.3 Hz, **C**O_2Et). ^{19}F NMR (282 MHz, $CDCl_3$): δ -173.0 (s). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{16}ClFN_2O_2$ + H^+]: 371.0957, found: 371.0951.

Ethyl 3-benzoyl-2-(4-chlorophenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazole-1-carboxylate (7e). Pyrrolo[1,2-b]indazole **7e** was obtained from corresponding nitroalkene **1e** (25.5 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3. Column chromatography (eluent: 19:1 to 5:1 PE/EtOAc) afforded **7e** (28.5 mg, 62%) as a slightly yellow solid. R_f = 0.39 (PE/EtOAc, 3:1) (UV), mp = 189-191°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (t, *J* = 7.1 Hz, 3H, CH_3), 3.73 (s, 3H, N-Me), 4.26 (q, *J* = 7.1 Hz, 2H, CH_2), 6.97 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 7.04 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 7.11 (t, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.27-7.42 (m, 3H, CH_{Ar}), 7.49 (d, *J* = 7.7 Hz, 1H, CH_{Ar}), 7.53-7.60 (m, 1H, CH_{Ar}), 8.57 (d, *J* = 7.9 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3 (CH_3), 40.3 (N-Me), 59.9 (CH_2), 102.0 (C1), 110.6 (CH), 117.2 (C_q), 122.9 (CH), 123.9 (CH), 126.9 (CH_{Ar}), 127.7 (CH_{Ar}), 128.6 (CH), 128.7 (C_q), 129.4 (CH_{Ar}), 131.8 (CH_{Ar}), 132.5 (CH_{Ar}), 132.7 (C_q), 132.9 (C_q), 135.2 (C_q), 135.6 (C_q), 138.5 (C_{Ph}), 148.9 (C5a), 164.1 (**C**O_2Et), 185.6 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{27}H_{21}ClN_2O_3$ + H^+]: 457.1313, found: 457.1312.

[2-(4-Chlorophenyl)-5-methyl-5*H*-pyrrolo[1,2-*b*]indazol-3-yl](phenyl)methanone (7f). Pyrrolo[1,2-b]indazole **7f** was obtained from corresponding nitroalkene **1g** (18.4 mg, 0.1 mmol) and indazolium salt **6a** (2.5 equiv.) following the general procedure 3 using MeCN as a solvent. Column chromatography (eluent: 19:1 to 9:1 PE/EtOAc) afforded **7f** (13.5 mg, 35%) as a slightly yellow solid. R_f = 0.43 (PE/EtOAc, 3:1) (UV), mp = 168-170°C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 3.79 (s, 3H, N-Me), 6.50 (s, 1H, C1-H), 6.98-7.05 (m, 4H, CH_{Ar}), 7.13 (t, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.27-7.34 (m, 2H, CH_{Ar}), 7.39 (d, *J* = 8.3 Hz, 1H, CH_{Ar}), 7.49 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H, CH_{Ar}), 7.58 (dd, *J* = 8.2, 1.2 Hz, 2H, CH_{Ar}), 7.81 (d, *J* = 7.7 Hz, 1H, CH_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$, HSQC): δ 41.5 (N-Me), 97.2 (C1-H), 111.7 (CH), 118.1 (C_q), 120.1 (C9-H), 123.0 (CH), 127.5 (CH), 127.59 (CH_{Ar}), 127.63 (CH_{Ar}), 129.7 (CH_{Ar}), 131.1 (CH_{Ar}), 131.5 (CH_{Ar}), 132.3 (C_{Ar}-Cl), 134.0 (C_q), 135.1 (C_q), 135.7 (C_q), 139.3 (C_{Ph}), 149.7 (C5a), 184.4 (**C**=O). HRMS (ESI): *m/z* calcd. for [$C_{24}H_{17}ClN_2O$ + H^+]: 385.1102, found: 385.1092.

Conclusions

In conclusion, an efficient method for the preparation of rare [5,5]-annulated aromatic heterocycles - pyrrolo[2,1-b]thiazoles and pyrrolo[1,2-b]indazoles via copper (II) trifluoroacetate-mediated annulation of nitroalkenes with azolium ylides was developed. In particular, highly pharmaceutically attractive novel fluorinated heterocycles were accessed from α-fluoronitroalkenes. Assembly of

pyrrolo[1,2-b]indazole ring represents synthesis of a novel heterocyclic core. Detailed investigation of reactivity and transformations as well as biological studies of these peculiar compounds (in particular, for anticancer properties) are promising future tasks for organic and medicinal chemistry.

Conflicts of interest

There are no conflicts to declare.

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