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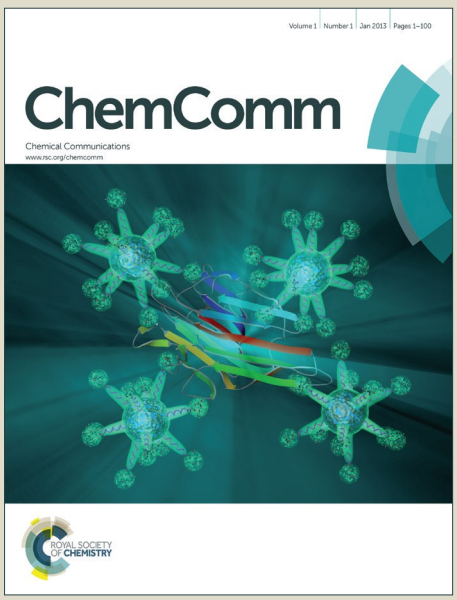

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Synthesis of Quaternary α-Perfluoroalkyl Lactams via Electrophilic Perfluoroalkylation†

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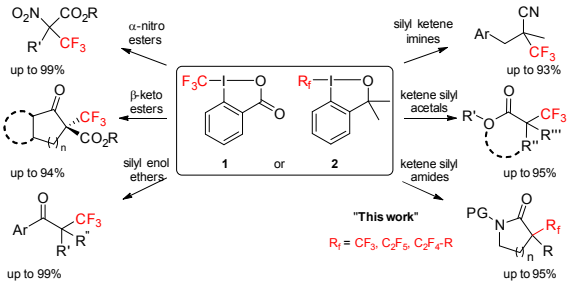
Efficient protocols enabling the rapid installation of trifluoromethyl, as well as further functionalized fluoroalkyl groups by an electrophilic perfluoroalkylation of lactam-derived ketene silyl amides (KSAs) using hypervalent iodine reagents 1 and 2 have been developed.

The selective introduction of a single fluorine atom, a trifluoromethyl or perfluoroalkyl group into an organic molecule is an important process for the development of new materials,[1] pharmaceuticals[2] and crop protection chemicals,[3] and has attracted much attention in recent years. The presence of fluorine atoms for example in drugs can potentially improve their biological activity as a consequence of a number of parameters such as e.g. increased lipophilicity, binding selectivity, or improved metabolic stability. α-Fluoroalkylated cyclic amides are particularly important as core structures present in bioactive compounds[4] and as precursors for the synthesis, for instance, of α-fluoroalkylated amides[5] and β-fluoroalkylated alkylamine derivatives.[4c,6] It has also been demonstrated that quaternary α-trifluoromethylated γ-lactams and their reduced form, β-trifluoromethylated pyrrolidines, exhibit excellent insecticidal efficacy and may be used as pesticides in agrochemistry or in the field of veterinary medicine.[6b] Thus, the development of new synthetic methods to generate a fluoroalkylated quaternary carbon next to a carbonyl center has emerged as a central objective in organofluorine chemistry. To this goal, important advances have been recently achieved. These include a series of fluoroalkylations of nucleophilic enolates or enolate equivalents promoted and/or initiated by radical initiators,[7]



Scheme 1 Application of hypervalent iodine(III)-R_f reagents **1** and **2** in the formation of a quaternary carbon center.

visible-light photocatalysts[8] or transition-metal catalysts.[9] Alternatively, over the last decade, methods for electrophilic trifluoromethylation, especially those using hypervalent iodine reagents **1** and **2a** (R_f = CF_3), have found an extremely broad application in organic synthesis.[10] These reagents are easily accessible from commercially available 2-iodobenzoic acid as air-stable crystalline solids.[11] However, only a few methods for the construction of a quaternary carbon center using reagents **1** and **2a** have been reported so far. As outlined in Scheme 1, substrates, such as α-CF_3-α-nitro esters,[12] α-CF_3-β-keto esters,[11b,12b,12d,13] α-CF_3-aryl ketones[9a,12a,b,13] and α-CF_3-nitriles[14] can be prepared via direct trifluoromethylation or from the corresponding metal enolates or their equivalents under mild reaction conditions in good to excellent yields. Recently, our laboratory introduced an efficient protocol for the trifluoromethylation of ketene silyl acetals employing reagents **1** and **2a**, which proceeds under trimethylsilyl triflimide catalysis ($TMSNTf_2$, up to 2.5 mol %), providing direct access to a variety of substituted α-trifluoromethyl esters and lactones.[15]

Thus, based on these general considerations and inspired by previously developed methods, we turned our attention to lactams, an important class of compounds. However, first attempts to directly trifluoromethylate in-situ generated lithium enolate of lactam **3a** using reagents **1** or **2a** were unsuccessful, leading to product formation only in trace amounts with concomitant decomposition of the reagents.

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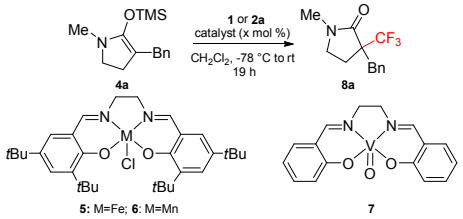
Table 1 Optimization of reaction conditions for the catalytic trifluoromethylation of KSA **4a**



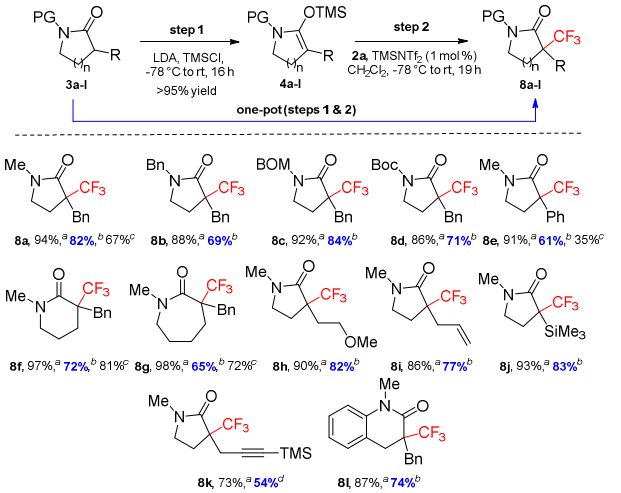
entry[a]	reagent	catalyst	mol %	yield (%)[b]
1	**1**	-	-	42
2	**2a**	-	-	67
3	**2a**	$Zn(NTf_2)_2$	1	79
4	**2a**	$LiNTf_2$	1	68
5	**2a**	$AgNTf_2$	1	62
6	**2a**	$CuNTf_2$	1	71
7	**2a**	$TMSNTf_2$	1	96(94)[c]
8	**2a**	$TMSNTf_2$	2.5	86
9	**2a**	$TMSNTf_2$	3	83
10	**2a**	$[V(acac)_2O]$	1	74
11	**2a**	**5**	1	74
12	**2a**	**6**	1	91
13	**2a**	**7**	1	93

[a]Reaction conditions: **4a** (0.3 mmol, 0.5 M in CH_2Cl_2), **1** or **2a** (0.23 mmol), catalyst (1-3 mol %), Ar atmosphere, 19 h. [b]Yields were determined by ^{19}F NMR using benzotrifluoride as an internal standard. [c]Isolated yield. TMS-trimethylsilyl.

To overcome this problem, we envisaged that the conversion of substrates to the corresponding ketene silyl amides (KSAs) might be beneficial to control the reactivity of these species towards hypervalent iodine-CF_3 reagents. Hence, we report herein a mild, operationally simple and highly efficient method for the α-trifluoromethylation and α-perfluoroalkylation of lactam-derived KSAs by the use of reagents **1** and **2a** in the presence of catalytic amounts of $TMSNTf_2$ (1 mol %) or even under catalyst-free conditions. Additionally, we describe a direct one-pot protocol enabling these transformations without the isolation of intermediate KSAs.

To probe the viability of this transformation, we investigated the reaction between KSA **4a** and reagents **1** and **2a** under various conditions (Table 1). It turned out that the direct trifluoromethylation of **4a** using either **1** or **2a** in CH_2Cl_2 at low temperature (–78 °C) gave after 19 h the corresponding product **8a** in only moderate yields, whereby reagent **2a** exhibited a slightly better reactivity (entries 1–2). Based on our experience with the activation of reagents **1** and **2a**, we next tested various Lewis acids such as triflimides[16] and metal complexes as catalysts (entries 3–7, 10–12). Among them, trimethylsilyl triflimide displayed excellent catalytic properties, leading to the desired product in 96% ^{19}F NMR yield (entry 6). Notably, 1 mol % of Mn and Fe catalysts with salen-type ligands also efficiently catalyzed the reaction (entries 12–13). Surprisingly, however, catalyst loadings higher than 1 mol % significantly lowered product yields (entries 8–9).

Having found an effective catalyst system for the trifluoromethylation of KSAs, we next examined the reaction scope with various substituted KSAs, which were prepared by lithiation of the corresponding lactams followed by trapping with TMSCl. It is important to highlight that their synthesis was straightforward, as the isolated crude compounds were pure by elemental analysis and were directly used in the next



Reaction conditions: [a]**4a–l** (1.3 mmol, 1.3 M in DCM), **2a** (1.0 mmol), $TMSNTf_2$ (1 mol %), –78 °C to rt, 19 h. [b]One-pot procedure: LDA (1.4 mmol), **3a–l** (1.3 mmol), TMSCl (2.2 mmol), THF, –78 °C to rt, 19 h; **2a** (1.0 mmol), $TMSNTf_2$ (1 mol %), –78 °C to rt, 19 h. [c]In the absence of $TMSNTf_2$. [d]One-pot procedure: LDA (2.8 mmol), **3k** (1.3 mmol), TMSCl (4.4 mmol), THF, –78 °C to rt, 19 h; **2a** (1.0 mmol), $TMSNTf_2$ (1 mol %), –78 °C to rt, 19 h.

Scheme 2 α-Trifluoromethylation of KSAs and direct, one-pot α-trifluoromethylation of carbonyl compounds: lactam scope.

trifluoromethylation step.[†] As summarized in Scheme 2, a broad range of KSAs exhibiting diverse steric and electronic properties readily participate in this transformation. First experiments showed that lactam-derived KSAs undergo trifluoromethylation with reagent **2a** even without the $TMSNTf_2$ catalyst giving the corresponding α-trifluoromethylated products in moderate to good yields (**8a**, **8e**, **8f**, **8g**). We believe that the level of efficiency observed under catalyst-free conditions is the result of both low steric requirements of the substrates and their high electron density. The addition of 1 mol % of the catalyst ($TMSNTf_2$) considerably improved the reactivity as shown in Scheme 2. The reaction tolerates different N-protecting groups, albeit benzyl (Bn), benzyloxymethyl (BOM), and *tert*-butyloxycarbonyl (Boc) derivatives formed the corresponding products in lower yields relative to N-Me derivatives (**8b–d**). The ring size of KSAs had minimal impact on the yield of the corresponding products (**8f–g**). KSAs derived from γ-lactam with a variety of α-substituents such as benzyl (**4a**), phenyl (**4e**), methoxyethyl (**4h**) and trimethysilyl (**4j**) featured excellent reactivity delivering the corresponding products in high yields. Functional α-substituents such as allyl (**4i**) and 3-TMS-propargyl (**4k**) are fully compatible with this method as well. Notably, KSA **4l** derived from substituted 3,4-dihydroquinolin-2-one was successfully triflurometylated forming product **8l** in 87% isolated yield. The latter substructure is present in many nitrogen heterocyclic compounds with a potential activity as plant disease control agents.[17]

Having demonstrated that both reaction steps, silylation of lactams and their subsequent trifluoromethylation, give excellent yields, we further optimised the synthetic applicability of this method and devised a one-pot, two-step protocol for the direct α-trifluoromethylation of lactams (Scheme 2). Thus, the chosen KSA is first formed in situ,

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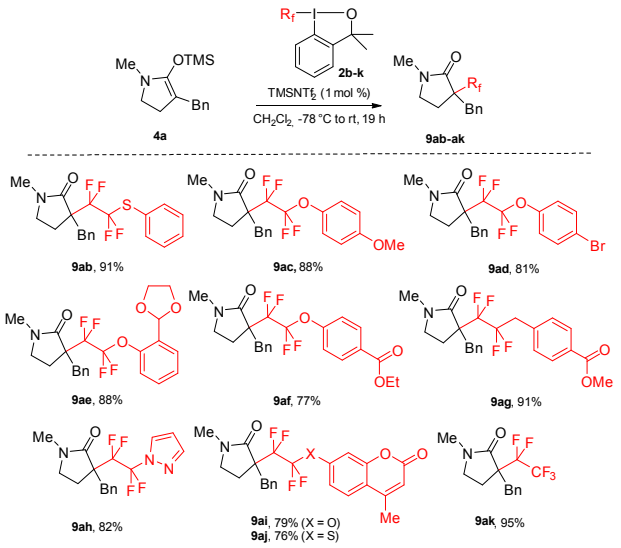


Reaction conditions: **4a** (0.78 mmol, 0.78 M in DCM), **2b–k** (0.6 mmol), $TMSNTf_2$ (1 mol %), –78 °C to rt, 19 h.

Scheme 3 α-Perfluoroalkylation of KSA **4a**.

followed by the addition of reagent and catalyst to affect the targeted α-trifluoromethylation. This simple and straightforward procedure is applicable to various α-substituted lactams as shown in Scheme 2, affording the desired products with high overall efficiency. Interestingly, in the case of α-propargyl substituted NMP (**3k**) silylation of the terminal alkyne takes place in addition to α-trifluorormethylation.

Recently, our group developed a series of new hypervalent iodine(III)-R_f reagents based on the 1,3-dihydro-3,3-dimethyl-1,2-benziodoxole scaffold, able to transfer a functionalised tetrafluoroethyl unit.[18] These reagents demonstrated very similar reactivity in a number of transformations compared to their established CF_3 analogues **1** and **2a** providing access to tetrafluoroethylated compounds. We therefore examined the applicability of previously developed (**2b–d**, **2f**, **2h**) and newly synthesised (**2e**, **2g**, **2i–k**) fluoroalkyl hypervalent iodine(III)-R_f reagents in the α-perfluoroalkylation of lactams. KSA **4a** was chosen as a model substrate for these transformations, and the results are summarized in Scheme 3. We were thus pleased to find that all tested reagents displayed excellent levels of reactivity towards KSA **4a** giving the corresponding α-fluoroalkylated products in moderate to high yields. The obtained products contain tetrafluoroethyl moieties bearing S-Ar (**9ab**), O-Ar (**9ac–af**), CH_2-Ar (**9ag**), and N-heterocyclic (**9ah**) substituents and can be used for further functionalizations. Products **9ai** and **9aj** are particularly interesting due to the presence of a fluorescent moiety based on coumarin, which can serve for the labelling of biological targets.

Finally, crystalline α-perfluoroethyl lactam **9ak** was obtained in high (95%) yield from reagent **2k** and was characterised by X-ray analysis (Figure 1). X-Ray crystal structures of acyclic and cyclic all-carbon-substituted α-perfluoroethyl carbonyl compounds have not been reported previously, as confirmed by a CCDC database search. In the solid state compound **9ak** displays value of bond lengths and angles in the expected ranges.

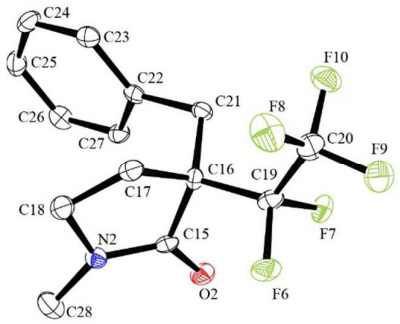
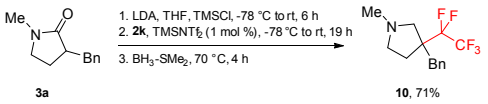


Figure 1 ORTEP view of the X-ray structure of compound **9ak**. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level. Only one of the two independent molecules in the asymmetric unit is shown. Selected bond lengths [Å] and bond angles [°]: C16-C19 1.523(5), C16-C21 1.553(5), C16-C17 1.545(5), C16-C15 1.548(5), F8-C20 1.326(5), F6-C19 1.369(4); C19-C16-C21 110.8(3), C19-C16-C17 112.2(3), C19-C16-C15 108.4(3), C17-C16-C21 113.6(3). CCDC 1442867.

α-Fluoroalkylated lactams are expected to be valuable intermediates in the synthesis of a wide range of organofluorine compounds. To illustrate the practical applicability of our methods, we designed a one-pot, multi-step procedure towards the synthesis of fluorinated pyrrolidine derivatives, compounds of potential interest in the life sciences.[6] As shown in Scheme 4, lactam **3a** was successfully transformed to the corresponding 3-perfluoroethyl-substituted pyrrolidine **10** in overall 71% isolated yield via a straightforward three-step protocol including in situ silylation, α-fluoroalkylation and reduction steps.



Scheme 4 Synthesis of (perfluoroethyl)pyrrolidine **10** via one-pot, multi-step transformation of lactam **3a**.

At the present stage we assume that the perfluoroalkylation step proceeds via a similar mechanistic scenario as we suggested in our recent work on the α-trifluoromethylation of ketene silyl acetals derived from esters and lactones.[15] In the case of these Lewis acid-catalyzed processes, $TMSNTf_2$ activates the reagent to form a cationic (iodonium) species, which should be able to engage a first substrate molecule in a SET process, thus leading to the formation of CF_3 radicals.[19] If this indeed happens, CF_3 radicals are then rapidly trapped by a second substrate molecule subsequently taking part in a second SET with reagent **2** pre-activated by the catalyst. The thereby formed silyloxycarbenium intermediate generates the desired product in the presence of the triflimide anion (NTf_2^-) via desilylation and concomitant regeneration of the catalyst. Additionally, one should also take into account the silylating properties of electron-rich lactam-derived KSAs, and hence their ability to

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transfer the silyl group to reagent **2**. The latter assumption can explain the background reaction in the non-catalyzed process.

In conclusion, we have developed a method allowing facile α-fluoroalkylation of lactam-derived KSAs by hypervalent iodine reagents, which proceeds with high efficiency in the presence of 1 mol % of $TMSNTf_2$ as the catalyst or with moderate performance under catalyst-free reaction conditions. Moreover, we have devised a one-pot protocol that allows the installation of the trifluoromethyl group directly onto a variety of lactams, requiring no isolation or purification steps of the intermediates. Given the simplicity, efficiency and the broad scope of this protocol, we envisage that it will be extensively used by synthetic chemists working in the fields of medicinal chemistry, agrochemistry and material sciences.

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