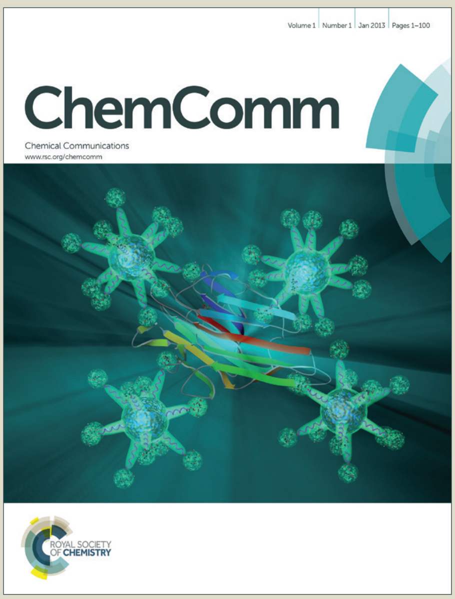
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Efficient Direct 2,2,2-Trifluoroethylation of Indoles via C-H Functionalization[§†]

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A novel highly C3 selective metal free trifluoroethylation of indoles using 2,2,2-trifuoroethyl(mesityl)-iodonium triflate was developed. The methodology enables the introduction of the trifluoroethyl group in a fast and efficient reaction under mild conditions with high functional group tolerance. Beyond the synthetic developments, quantumchemical calculations provide deeper understanding of the transformation.

The presence of fluorine in organic molecules often provides advantageous properties to the molecules, as fluorinated functional groups can beneficially modify electronic properties of the compounds, improve their metabolic stability, and enhance their lypophilicity. Therefore the development of new synthetic methods for the installation of the fluorine and fluorous functional groups is an emerging field of synthetic organic chemistry.[1]

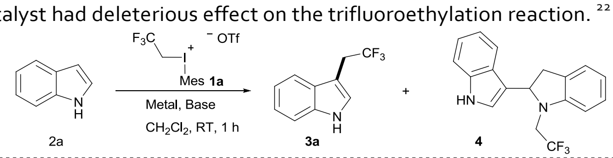
Modification of lead compounds with fluorous functional groups to fine tune their biological activity is one of the most frequently used strategies in medicinal chemistry. Aside from the simple fluorine atom and CF_3 group, the presence of other related small fluorous functional groups such as trifluoromethoxy,[2] trifluoromethylthio[3] or structurally similar trifluoroethyl[4] groups on an aromatic core structure has also gained exceptional attention from the fields of synthetic organic and medicinal chemistry.

Due to the importance of the indole framework in the structure of drug candidates much attention has been focused on the synthesis of fluoroalkylated indole derivatives. In general, trifluoroethylated indoles are accessible through indole core functionalization via multistep syntheses (3-6 synthetic steps)[5] or ring constructions such as a novel radical Fisher indole type synthesis developed by Antonchik.[6] Compared to trifluoromethylation, the synthetic transformations to access trifluoroethylated compounds via C-C bond formation are underdeveloped. The main, but still uncommon methods for the construction of trifluoroethyl group involve the trifluoromethylation of a benzylic position,[7] the addition of trifluoromethyl group onto alkenes,[8] and the utilization of gaseous trifluoromethyl diazomethane.[9] Although, the unique electronic properties of the CF_3CH_2X (X= Br, I, OTf) compounds limit their use as simple electrophiles,[10] recently several cross-coupling approaches were developed for the introduction of trifluoroethyl group into aromatic systems.[11] The direct C-H functionalization with trifluoroethyl group is seldom explored. Very recently Ackermann described the first nickel catalyzed trifluoroethylation process utilizing an 8-aminoquinoline directing group and trifluoroethyliodide as alkyl source.[12] A Catellani type palladium catalyzed cascade trifluoroethylation was developed by Liu for the synthesis of olefinated trifluoroethyl arenes.[13] A unique example for transition metal catalyst free direct trifluoroethylation of heterocycles is Baran's radical alkylation strategy using zinc sulfinate salts.[14]

In our work, we aimed to develop a new alkylation methodology for the direct trifluoroethylation of indoles with the aid of a electrophilic trifluoroethyl synthon originated from hypervalent iodonium salts. Introduction of hypervalent iodonium salts as useful reagents in organic chemistry[15] opens new possibilities for the formation of carbon-heteroatom and carbon-carbon bonds via C-H activation.[16] Besides numerous synthetic applications,[15a,17] the use of $\lambda 3$ iodo compounds provides an emerging transition metal catalyzed strategy for the direct functionalization of indoles.[18] The pioneering work of Umemoto in the field of fluoroalkyliodonium salts[19] inspired us to use hypervalent iodine reagents for the trifluoroethylation of indoles. These reagents were used mostly for the fluoroalkylation of heteroatom[20] and soft carbon[21] nucleophiles to build C-N, C-O, C-S and C(sp3)-C(sp3) bonds.

For the realization of the desired transformation we synthesized 2,2,2-trifuoroethyl(mesityl)-iodonium triflate salt **(1a)** as a new reagent from bis(trifluoroacetatoxy)(2,2,2-trifluoroethyl)iodide and mesitylene in 94 % isolated yield on multigram scale. We strategically chose the mesityl group (Mes) as a frequently used aromatic system for the synthesis of aryliodonium salts with high stability and activity. However, two additional trifluoroethylaryliodonium salts were prepared, but the phenyl **(1b)** and 4-tolyl **(1c)** derivatives were obtained with lower efficiency (68% and 83% respectively).

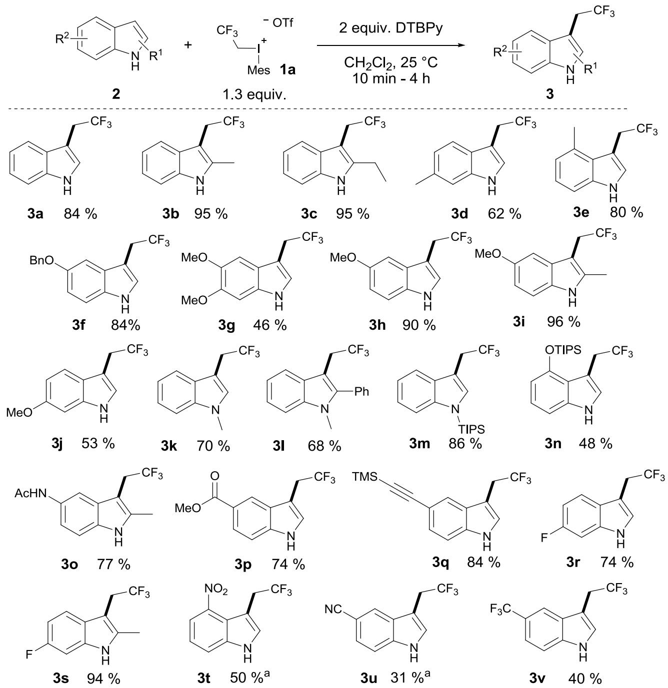
After having the designed reagents in hand, we turned our attention to the possible C-H functionalization of unprotected indoles to develop a powerful synthetic methodology to enable C-C bond formation without the necessity of protecting groups. First, we studied the trifluoroethylation reaction of indole **(2a)** with 1a in dichloromethane (CH_2Cl_2) at 25 °C with or without transition metal catalyst (Cu(II), Pd(II), Ag(I) salts). To our delight the reaction of unsubstituted indole provided the desired C3 trifluoroethylated product **3a** (Scheme 1.). In contrast with the known iodonium salt based transition metal catalyzed indole functionalization methodologies, we found that the presence of transition metal catalyst had deleterious effect on the trifluoroethylation reaction. [22]



Catalyst	Base[a]	Yield[b]	3a:4 ratio[c]
Pd(II), Cu(II), Ag(I) cat.	-	13-38 %	
no metal	-	70 %	2:1
no metal	Na_2CO_3	61 %	10:1
no metal	TEA	0 %	-
no metal	DTBPy	78 %, 84 %[d]	100:1

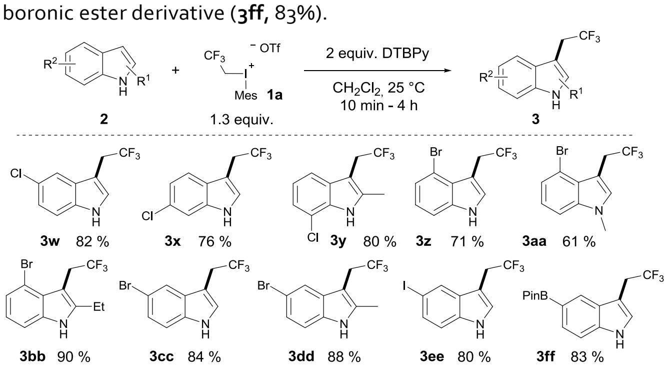
Scheme 1. Adjustment of reactivity by different bases. [a] 2 Equivalents of base, 1 equivalent of **1a** reagent. [b] Isolated yield of the mixture. [c] Determined by ^{19}F NMR measurements. [d] 1.3 Equivalent of iodonium salt (**1a**) was used

Despite of the high reactivity of the polyfluoroalkyl λ3 iodonium compounds toward heteroatom nucleophiles[20a,20b] trifluoroethylation did not occur on the indole nitrogen due to its lower nucleophilicity. Besides these beneficial features, we observed the formation of significant amount of N-trifluoroethylated indolino-indole derivative **(4)**. The presence of trifluoromethanesulfonic acid, generated in the reaction, accelerates the dimerization of indole, and the formed indoline moiety undergoes straightforward N-trifluoroethylation.[22] It was anticipated, that the amount of this side product could be decreased by adding an appropriate base such as 2,6-di-tert-butylpyridine (DTBPy) and target compound **3a** was isolated in 84 % yield.[22] Next, we explored the synthetic utility of this reaction by examining the substrate scope in CH_2Cl_2 at 25 °C.[22] Indole and alkyl indoles reacted smoothly with **1a** under our conditions to provide trifluoroethyl indoles **3a-3e** in 10 minutes reaction time (Scheme 2.). In case of 3-methylindole, formation of any trifluoroethylated product were not observed (not shown). More electron rich alkoxyindoles were also successfully functionalized in a rapid reaction (10-60 minutes) and the desired compounds **(3f-j)** could also be isolated in good to excellent yields (46-96%). Although, the indole nitrogen does not require protection, the tested N-methyl and N-TIPS derivatives were also successfully trifluoroethylated **(3k-m)**. Nucleophilic functional groups connected to the indole frame such as free hydroxyl, amino and carboxyl functions could be masked with different protecting groups for the efficient trifluoroethylation **(3n-p)** of indole in position 3 to obtain valuable heterocyclic building blocks. Indole containing TMS protected alkyne was also converted to its corresponding trifluoroethylated compound **(3q)** in 84 % yield, opening the way for further synthetic transformations through the acetylene part. To further explore the real synthetic power of the method we examined



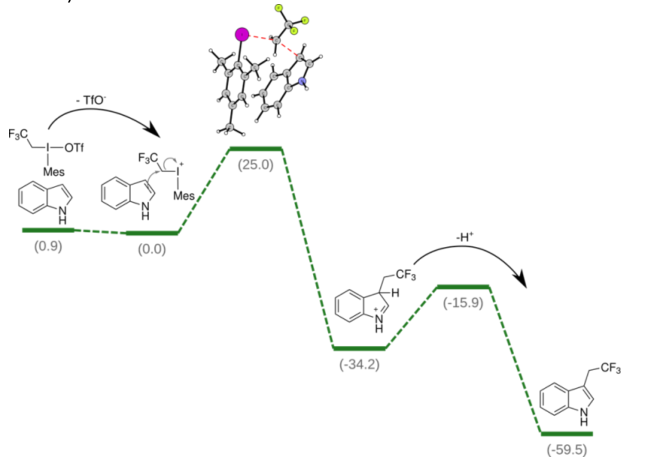
Scheme 2. Substrate scope of the transformation. [a] without base, 2 equiv. of iodonium salt

the scope with electron withdrawing groups on the indole skeleton. To our delight the presence of fluorine, nitro, cyano and trifluoromethyl group on the indole core were well tolerated, and the desired products **(3r-v)** were isolated in 31-94 % yield after 1.5 - 4 hours reaction time. Demonstrating the power of the methodology we examined the trifluoroethylation of indoles bearing functional groups suitable for cross coupling chemistry (Cl, Br, I, boronic ester; Scheme 3.). Each halogen substituted indoles gave the desired products **(3w-3ee)** in good to excellent yields (61-90 %), as well as the boronic ester derivative (**3ff**, 83%).



Scheme 3. Trifluorethylated indoles for cross-coupling chemistry.

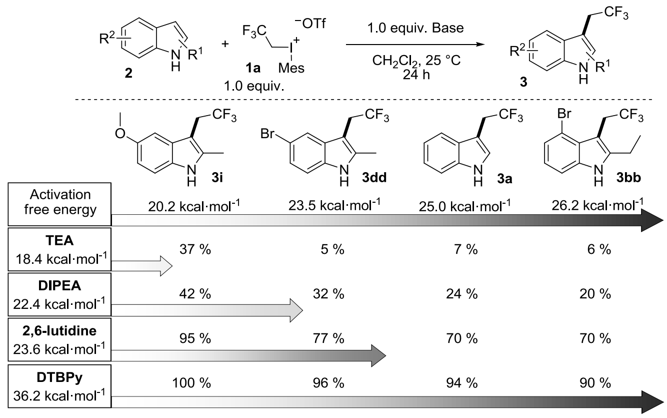
We employed DFT calculations to understand the mechanism and the selectivity of the present reaction. First we considered the reaction between indole **(2a)** and 2,2,2-trifluoroethyl(mesityl)-iodonium triflate **(1)** (Scheme 4.). The dissociation of the triflate anion proved to be slightly exergonic (-0.9 kcal·mol^{-1}) suggesting a dissociated resting state. The rate-determining step is the trifluoroethylation of the indole-ring. The next step is the deprotonation of the σ-complex by the basis with a 18.3 kcal·mol^{-1} barrier. Both steps are highly exergonic indicating irreversible transformations. Formation of 1- and 2-substituted indoles is much less favourable which explains that they could not be observed in experiment.[22] We have also calculated the free energy barrier heights for the all the substrates indicated in Schemes 2 and 3.[22] Within the expected accuracy the calculations nicely correlate with experiment providing confidence in the conclusion. The formation of 3-indolyl-trifluorethyl-mesityl-iodonium salt from **1a** and **2a** as another possible intermediate of the reaction and subsequent product formation through reductive elimination have been also taken into consideration. This reaction pathway has been safely excluded on the basis of the prohibitively high barrier (52 kcal·mol^{-1}) for the formation of the key intermediate from **1a** and **2**.



Scheme 4. Free energy profile in kcal·mol^{-1} of the transformation based on DFT calculation

To explain the special efficiency of DTBPy as base in the reaction we have also calculated the activation barriers of the alkylations of different amine bases such as TEA, DIPEA, 2,6-lutidine and DTBPy. It was found that the activation energies of the N-trifluoroethylation of these bases with **1a** were 18.4 kcal·mol^{-1}, 22.4 kcal·mol^{-1} and 23.6 kcal·mol^{-1} respectively which are in the same range as the barriers of the C alkylations of the studied indoles. However, computation results showed that the N-trifluoroethylation of DTBPy required extremely high activation energy (36.2 kcal·mol^{-1}) due to the significant steric repulsion.[22] These results indicate that variations in the barrier heights of trifluoroethylations can strongly influence the outcome of the reaction, which is important from a synthetic standpoint. Additional experiments have convincingly confirmed this prediction as shown in Scheme 5. In this scheme we collected the conversions of four indole derivatives in the presence of different bases. From left to right the reactivity (TS barriers of trifluoroethylation) of the indole derivatives are tuned by varying their substituents. Going down in the columns, the barriers of the N-alkylation increase. The trends obtained for the all possible combinations of indole-base pairs demonstrate that the efficiency of a substrate-base combination is determined by the activation barrier differences of the competing N- and C-alkylations. Clearly, alkylations of the bases and substrates are competitive reactions, and the yields support the postulated kinetic control.

In conclusion we have developed a transition metal free direct C-H trifluoroethylation reaction, which enables the selective trifluoroethylation of a heterocyclic system for the first time resulting in C(sp2)-C(sp3) bond formation.



Scheme 5. GC Conversion of trifluoroethyl indole derivatives obtained from reactions carried out in the presences of different amines. Activation energies of trifluoroethylation of indole derivatives and bases are indicated.

The readily accessible new 2,2,2-trifluoroethyl(mesityl)-iodonium triflate reagent ensures the straightforward trifluoroethylation of indoles in position 3 under very mild conditions in a rapid reaction (10-240 minutes reaction time). The excellent functional group tolerance of the developed transformation enables the access of chemically diverse compound classes with potential medicinal interest. Additionally, with the aid of DFT studies we revealed the mechanistic steps of the reaction, and explained the important role of basic additives in the transformation. Beyond these mechanistic studies and the synthesis of 3-trifluoroethyl indoles with high versatility the developed methodology opens new doors to the synthesis of other trifluoroethylated aromatic and heterocyclic compounds via C-H functionalization or transition metal catalyzed C-H activation. The study of these synthetic possibilities currently undergoes in our laboratory.

Notes and references

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§ This paper is dedicated to Prof. József Rábai on the occasion of his 65th birthday

† Electronic Supplementary Information (ESI) available: [detailed experimental procedures, characterization of products and the details of DFT calculations]. See DOI: 10.1039/b000000x/

‡ Both authors contributed equally to this work

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22 For further data and detailed optimization results see ESI