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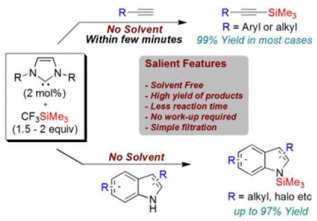
A highly efficient organo-catalytic protocol for the trimethylsilylation of terminal alkynes and *N*-silylation of indoles employing Ruppert's reagent as a trimethylsilyl source have been developed under solvent and fluoride free conditions.



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Cite this: DOI: 10.1039/xoxxoooooox

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Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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An organo-catalytic protocol for the trimethylsilylation of terminal alkynes employing Ruppert's reagent (CF_3SiMe_3) as a trimethylsilyl source has been developed under solvent and fluoride free conditions. This method was found to be very effective as a variety of terminal alkynes bearing aliphatic or aromatic substituents underwent smooth transformation to their corresponding silylated products in excellent yields within few minutes using *N*-heterocyclic carbene as an organo-catalyst. This methodology was also applied to the chemospecific *N*-silylation of indoles.

Alkynylsilicon reagents are considered to be valuable synthons due to their wide spread applications in carbon-carbon bond forming reactions such as metal catalysed cross-coupling reactions,[1] alkynylation reactions[2] and metathesis reactions.[3] Alkynylsilicon compounds also serve as versatile intermediates in the synthesis of some biologically important natural products.[4] Apart from the traditional method for the preparation of alkynylsilicon compounds,[5] which involves deprotonation of terminal acetylene with organolithium or Grignard reagent followed by quenching with a silyl electrophile, some other methods have also been developed which include metallic Zn[6] or Zinc salts mediated[7] and $Zn(OTf)_2$[8] catalysed trimethylsilylation of terminal alkynes with suitable silyl electrophiles. Few Iridium complexes are also known to catalyse silylation of terminal acetylenes.[9] Another fascinating approach to alkynyl silyl compounds encompasses metal catalyzed dehydrogenative coupling of terminal alkynes with silyl hydrides.[10] Apart from the use of conventional silylating agents, Ishizaki's group has demonstrated fluoride catalysed trimethylsilylation of terminal alkynes using an unconventional reagent, CF_3SiMe_3 (Ruppert's reagent), as a silyl source.[11]

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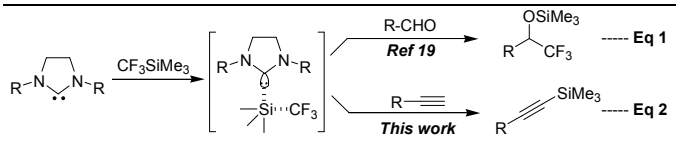
† Electronic supplementary information (ESI) available: Experimental procedures and copies of NMR spectra.

Although most of the above mentioned methods show good functional group compatibility, limitations such as use of metal or a fluoride source and longer reaction times render these methods from practicality. Hence, development of an efficient, metal and fluoride free method for the preparation of alkynylsilyl compounds is highly desired.

Being an integral part of organocatalysis, *N*-heterocyclic carbene (NHC) catalysis is emerging as a powerful tool for carbon-carbon and carbon-heteroatom bond forming reactions.[12,13] It is well documented in the literature that NHC forms a hypervalent complex with silicon compounds.[14] This distinctive reactivity of NHC towards silicon has been explored in fundamental transformations such as cyanosilylation of carbonyl compounds and imines,[15] aziridine ring opening[16] and Mukaiyama aldol reactions.[17] Recently, Song's group reported NHC catalysed trifluoromethylation of aldehydes and ketones,[18] in which the CF_3 anion was utilized as a nucleophile (Eq 1, Scheme 1). While developing NHC catalysed trifluoromethylation of various functional groups with CF_3SiMe_3, we envisioned that CF_3 anion, generated *in situ* during the reaction of NHC with CF_3SiMe_3, could be used as a traceless base to deprotonate acetylenic proton and the resulting acetylide anion could be trapped with electrophilic silicon. Based on this idea, we have developed an efficient and alternative protocol for the preparation of alkynyl trimethylsilanes from terminal acetylenes and CF_3SiMe_3 (Ruppert's reagent)[19] using NHC as a catalyst (Eq 2, Scheme 1).

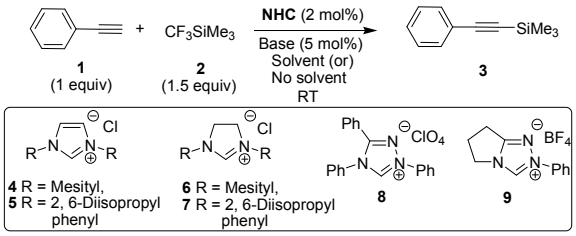


Scheme 1. NHC catalysed trifluoromethylation and trimethylsilylation reactions with CF_3SiMe_3

The optimisation studies were performed using phenyl acetylene (**1**) and CF_3SiMe_3 (**2**). A wide range of NHCs derived from NHC precursors **4** – **9** were utilised for this purpose (Table 1). When the experiment was conducted using 2 mol% of NHC, derived from **5**

and NaH in THF, and **2** as a silyl source the expected product **3** was obtained in 50% yield. Encouraged by this observation, further optimisation experiments were carried out under different conditions with or without solvent (Table 1).

Table 1 Optimisation of reaction conditions



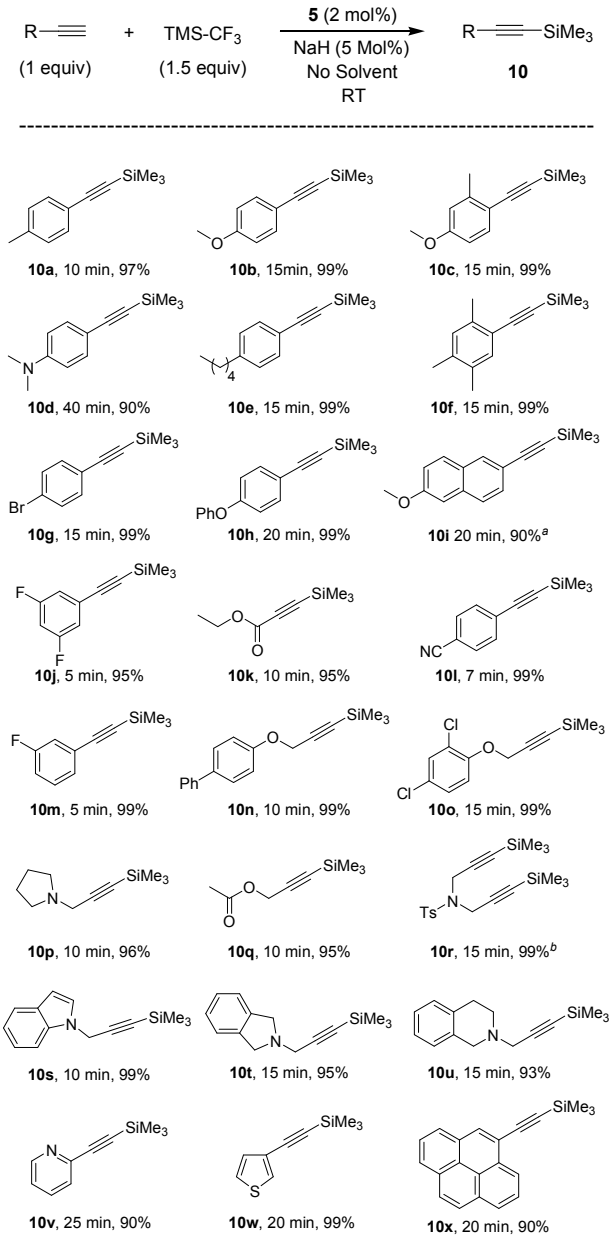
S. No	Catalyst	Base	Solvent	Time [Min]	Yield [%][a]
1	**5**	NaH	THF	20	50
2	**5**	NaH	DCM	20	76
3	**5**	NaH	Et_2O	20	30
4	**5**	**NaH**	**--**	**7**	**98**
5	**5**	DBU	--	360	72
6	**5**	--	--	360	--
7	**4**	NaH	--	60	50
8	**6**	NaH	--	20	81
9	**7**	NaH	--	30	50
10	**8**	NaH	--	120	23
11	**9**	NaH	--	120	7
12	--	NaH	--	360	trace
13	**5**	$NaNH_2$	--	20	85
14	**5**	KO^{t}Bu	--	15	92

[a] Isolated yield; RT = 31 – 33 ^oC

Surprisingly, the reaction rate and the yield of the product **3** were found to be higher when the reaction was performed under solvent free conditions. Out of several conditions screened, the best result was obtained (98% yield in 7 min) using NHC derived from **5** under neat conditions, thus chosen as standard condition (Entry 4). No product or only traces of product was observed if the reaction was conducted without base (Entry 6) or without NHC (Entry 12, Table 1). We also tried the silylation of phenyl acetylene (**1**) with other silyl pro-nucleophiles (See SI for more information) including Et_3SiH[20] using 5 mol% of NHC derived from **5** or **6** as a catalyst under various conditions. Unfortunately, the desired silylated product was not observed in any of the cases.

To generalise this protocol, a variety of terminal alkynes bearing aromatic and aliphatic substituents were subjected to silylation reaction under optimised reaction conditions and the results are summarised in Table 2. It is apparent from Table 2 that, irrespective of the nature of the substituents, most alkynes gave the corresponding trimethylsilylated products in quantitative yields. Almost in all the cases, the reaction was completed within a few minutes. Phenyl acetylenes with electron-withdrawing substituents on the aromatic ring (**10j**–**10m**) reacted at relatively faster rates than the alkynes attached with electron rich aromatic groups (**10a**–**10i**). Alkynes substituted with aliphatic groups also underwent smooth conversion to the corresponding silylated alkynes (**10n**–**10u**) under the standard conditions. This method was found to be efficient for the trimethysilylation of alkynes bearing hetero-aromatic substituents as well (**10v** and **10w**).

Table 2 Substrate Scope

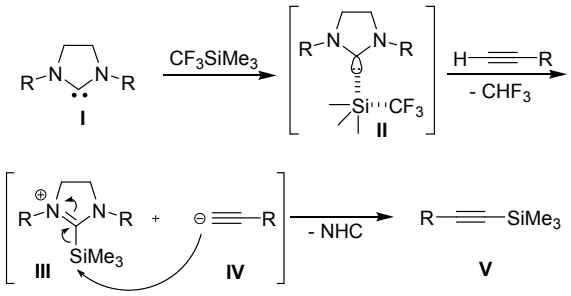


[a] 2 equiv. of CF_3SiMe_3 was used; [b] 3 equiv. of CF_3SiMe_3 was used; RT = 31 – 33 ^oC

At this stage, our attention was shifted towards elucidating a suitable mechanism for this transformation. Careful monitoring of the reaction revealed that the reaction was exothermic and some gas evolution was taking place in the reaction vessel when CF_3SiMe_3 was added to NHC and phenyl acetylene. Since fluoroform is the only by-product possible in this methodology and also it is a gas, we presumed that the evolved gas was CHF_3. To confirm this, the reaction mixture was analyzed by ^{19}F NMR spectroscopy. The spectrum showed a peak at –78.6 ppm (please see SI for ^{19}F

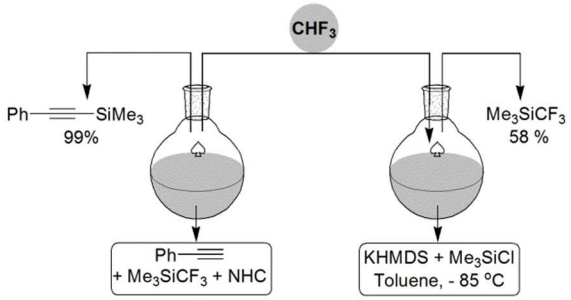
spectrum), which clearly confirms the presence of CHF_3 in the reaction mixture.[21]

Based on the above experimental investigations, a plausible mechanism has been proposed (Scheme 2). We presume that NHC (**I**) reacts with CF_3SiMe_3 and generates a penta co-ordinated silicon complex **II**, which immediately deprotonates the terminal alkyne to give the intermediate **III** along with acetylide anion **IV** and CHF_3. Nucleophillic attack of **IV** on the electrophillic silicon center of **III** gives the silylated product **V** with the expulsion of NHC (Scheme 2).



Scheme 2 Plausible mechanism for silylation of acetylenes

Although Fluoroform is considered to be a potential Green House gas,[22] it has been widely employed as a trifluoromethyl source to introduce CF_3 group in organic molecules.[23,24] Since CHF_3 is the by-product in our methodology, in order to make our process sustainable, we thought of utilising it for the regeneration of CF_3SiMe_3 using a protocol reported by Surya Prakash and co-workers.[24] Scheme 3 portrays the experimental set up adapted for the synthesis of CF_3SiMe_3. The fluoroform (2.1 equiv.) generated during the reaction was purged in to another reaction flask containing KHMDS (1 equiv.) and Me_3SiCl (1 equiv.) in toluene at –85 °C. The reaction proceeded smoothly and the product CF_3SiMe_3 was obtained in 58% yield. It was confirmed by ^{19}F and ^{29}Si NMR spectroscopy. The yield of the product was assigned based on ^{19}F NMR using an internal standard (please refer SI for more details).

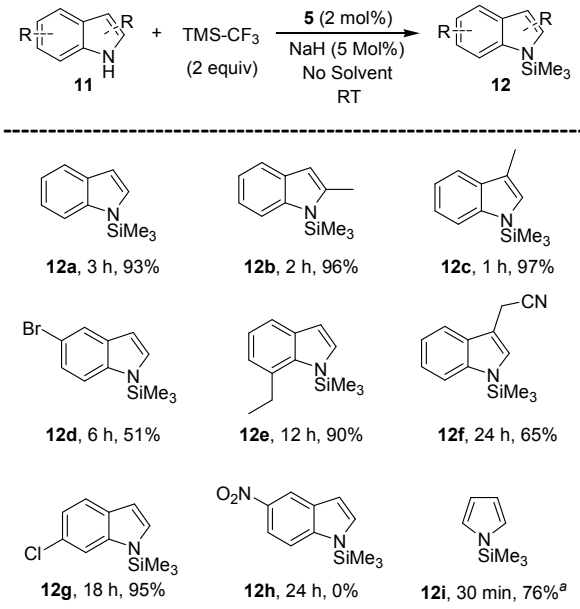


Scheme 3. Regeneration of Me_3SiCF_3 from CHF_3.

While developing the silylation of terminal acetylenes, we were also interested to utilise this methodology for *N*-silylation of indoles, which is considered to be an important transformation, because *N*-silylated indoles serve as prevalent intermediates for the synthesis of indole based natural products.[25] Besides, chemoselective *N*-silylation of indoles still remains as a challenge. The conventional method for the preparation of *N*-silyl indoles involves deprotonation of indole using a bit excess of a strong base followed by treatment with Me_3SiCl.[26] The drawback associated with this method was the formation of equimolar quantities of salt and the requirement of strong base such as ^nBuLi or NaH. In order to over come these issues, few metal catalyzed dehydrogenative Si-N coupling methods have been recently developed.[27] Hartwig's group reported silyl directed site selective borylation of *N*-silyl indoles, where *N*-silyl indoles were prepared *in situ* through Ruthenium catalyzed dehydrogenative silylation.[28] Very recently, Oestreich group has also developed Ruthenium catalysed dehydrogenative Si-N coupling of amines including indoles using hydrosilanes under base free conditions.[29] But, so far, organo-catalytic version for the synthesis of *N*-silylated indoles is not reported in the literature. It is highly preferred to develop an organo-catalytic *N*-silylation of indoles to avoid the use of expensive or toxic metal catalysts.

Since we have demonstrated that the NHC–CF_3SiMe_3 combination was very effective for the silylation of terminal alkynes, we thought of utilising the same recipe for the *N*-silylation of indoles under solvent free conditions. To our surprise, when indole was treated with 2 equiv. of CF_3SiMe_3 and a NHC (2 mol%) derived from **5**, the silylated product **12a** was obtained in 93% isolated yield after 3 h under solvent free condition at room temperature (Entry **12a**, Table 3). A couple of optimisation experiments were carried out using other NHCs, but the yield of the *N*-silylated indole was inferior when compared to the above mentioned condition (Please refer SI for more details). To demostrate the scope of this methodology, a wide range of substituted indoles were subjected to *N*-silylation reaction under the above mentioned reaction conditions and the results are presented in Table 3.

Table 3 NHC catalysed *N*-silylation of indoles



[a] CF_3SiMe_3 was added at 0 °C

It is clear from Table 3 that, most the indoles tried underwent smooth conversion to their corresponding *N*-silylated products in

moderate to good yields at room temperature. Surprisingly, 2- and 3-methyl substituted indoles reacted at faster rate when compared to indole (**12b** and **12c**). In the case of 5-bromo indole (**12d**), the product was obtained in moderate yield. The reaction also worked well in the case of pyrrole and the silylated product **12i** was obtained in 76% yield. Unfortunately, 5-nitroindole failed to give the corresponding silylated product **12h** even after 24 h. The silylation reaction of 5-nitroindole was even tried in the presence of solvents such as THF, DMF and 1,4-dioxane, but in all those cases the product **12h** was not observed. We believe that the mechanism of *N*-silylation reaction is similar to silylation of acetylenes. A general observation in *N*-silylation reactions was that the reaction time was longer when compared to silylation of acetylenes. This could be due to the less nucleophilicity of indole anion (when compared with acetylide anion) towards reaction with NHC-Silicon complex **III** (Scheme 2). This reaction was found to be chemo-specific as no C-3 or C-2 silylated products were observed in any of the cases.

In conclusion, an efficient and metal free process for the synthesis of trimethylsilyl acetylenes has been developed using NHC as a catalyst under solvent free conditions. We have shown that the by-product, fluoroform, can be effectively utilised for the regeneration of CF_3SiMe_3. We have also demonstrated the first organocatalytic *N*-silylation of indoles using NHC as a catalyst. High yield of the products, low catalyst loading (2 mol%), less reaction time and simple work-up procedure are the prominent features of this methodology.

Acknowledgements

The authors sincerely acknowledge the Department of Science and Technology (DST), New Delhi for financial support and IISER Mohali for providing infrastructure. PA and VR thank CSIR for a research fellowship. The NMR and HRMS facilities of IISER Mohali are gratefully acknowledged.

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