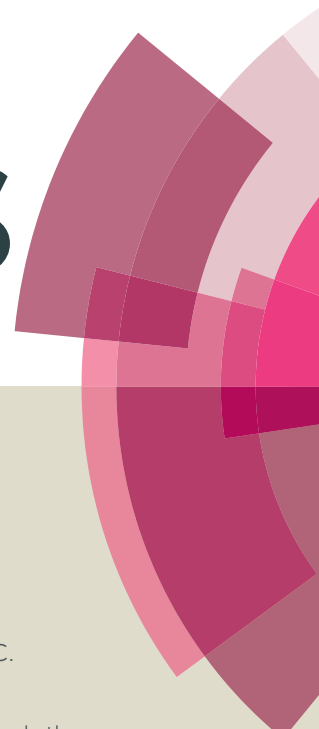


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COMMUNICATION

N-Heterocyclic Carbene-Catalysed Pentafluorophenylation of Aldehydes

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N-Heterocyclic carbenes have been utilized as highly efficient organocatalysts to catalyse multifluorophenylation of aldehydes with pentafluorophenyltrimethylsilane or bis(trimethylsilyl)tetrafluorobenzene to afford the corresponding fluorinated adducts in 49-99% yields.

The last decade has witnessed an explosive growth in N-heterocyclic carbenes (NHCs) catalysis.¹ As an important type of organocatalyst, NHCs have been utilized widely in organic synthesis. Aside from the classical benzoin reaction² and Stetter reaction,³ a large number of NHCs catalysed transformations, such as homoenolate reaction of enals,⁴ redox reaction of functional aldehydes,⁵ cycloaddition of ketenes,⁶ transesterification,⁷ Michael addition⁸ and other reactions⁹ have been studied. To date, three different activation modes based on the corresponding ambiphilicity, nucleophilicity and basicity of NHCs have been established.^{1d} More interestingly, NHCs exhibit extremely high reactivity toward the activation of silicon-based nucleophiles.¹⁰ For example, Song and co-workers reported that only 0.01 mol% of NHC was enough to efficiently catalyse the cyanosilylation reaction of TMSCN and aldehydes.¹¹ Based on this nucleophilic activation strategy, several NHC catalysed reactions such as trifluoromethylation reaction,^{12a} Mukaiyama aldol reaction,^{12b-d} ring opening reaction,^{12e} silyl-Reformasky reaction,^{12f, 12g} group-transfer polymerization¹³ and ring-opening polymerization¹⁴ have been developed recently. Despite remarkable progress made in this research field, NHC catalysed activation of Ar-Si bonds remains elusive.

Organofluorine compounds are widely applied in pharmaceutical and agricultural chemistry as well as material science.¹⁵ Owing to the special electronic properties of fluorine, the incorporation of fluorinated moieties can modify the biological and physiological

properties of a known molecule significantly, which has become a routine strategy in new drug discovery. Therefore, the development of efficient methods for the introduction of fluorinated groups into organic molecules has attracted considerable research interest.

Among different fluorinated moieties, pentafluorophenyl group is an important subset, and compounds containing this moiety are widely utilized in pharmaceuticals, functional material and other fields.¹⁶ The nucleophilic addition of pentafluorophenyllithium or the Grignard reagent to carbonyl compounds is the most straightforward approach¹⁷ for the construction of these vital fluorinated molecules. However, many sensitive functional groups can't be well tolerated and the reaction suffers from harsh reaction conditions. Therefore, the development of mild and highly efficient pentafluorophenylation reaction is highly desirable.

The commercially available pentafluorophenyltrimethylsilane **1a** can serve as precursor of pentafluorophenyl carbanion to react with carbonyl compounds. TASF and the toxic KCN can catalyse the addition reactions,¹⁸ but with very limited substrate scope. Recently, Lam and co-workers reported¹⁹ that transition metal catalyst Cu(OAc)₂·dppe can catalyse pentafluorophenylation of aldehydes and active ketones. However, some heteroaromatic aldehydes are not suitable for the reaction. We have developed NHCs-catalysed vinylogous Mukaiyama aldol reaction, phospho-aldol reaction and silyl-Reformasky reaction via nucleophilic activation of silylated nucleophiles.¹² We envisioned that NHCs can activate Ar-Si bonds to catalyse pentafluorophenylation reaction of aldehydes. Herein, we would like to disclose this result.

Our studies commenced with the reaction of pentafluorophenyltrimethylsilane **1a** and 4-

chlorobenzaldehyde **2a**. To our delight, under the catalysis of 5 mol% NHC **4** (1,3-bis (2,6-diisopropylphenyl)imidazol-2-ylidene, IPr),²⁰ the reaction proceeded smoothly in THF to produce the desired product **3a** in 66% yield (Table 1, entry 1). Encouraged by this result, other common NHCs were next examined. NHCs generated *in situ* from imidazolium, imidazolinium and different bases can catalyse the reaction efficiently (Table 1, entries 2-5). Whereas NHCs derived from thiazolium and triazolium showed very low efficiency (Table 1, entries 6-8). A brief screening of reaction media indicated that the polar solvents of acetonitrile and formdimethylamide (DMF) can give high yields (Table 1, entries 9-12). Reduction of catalyst loading to 1 mol% led to decrease of reaction rate, but with high yield maintained (Table 1, entry 13).

Table 1 Screening of reaction conditions ^a

Ar = 2, 6-(i-Pr)₂C₆H₃ Ar = 2, 4, 6-Me₃C₆H₂ Ar = 2, 6-(i-Pr)₂C₆H₃			
7a: R = Bn, X = Cl 7b: R = Me, X = I			
Entry	Conditions	Time (h)	Yield ^b (%)
1	4 , THF	2	66%
2	5 , ^t BuOK, THF	2	64%
3	6 , ^t BuOK, THF	3	47%
4	5 , DBU, THF	2	63%
5	5 , Cs ₂ CO ₃ , THF	2	55%
6	7a , DBU, THF	6	18%
7	7b , DBU, THF	6	14%
8	8 , DBU, THF	6	< 10%
9	4 , PhCH ₃	2	67%
10	4 , CH ₂ Cl ₂	2	45%
11	4 , CH ₃ CN	2	88%
12	4 , DMF	2	84%
13 ^c	4 , CH ₃ CN	12	85%

^a **1a** (1.5 eq.), **2a** (1.0 eq.). ^b Isolated yield. ^c Using 1 mol% NHC **4**.

With the optimal reaction conditions in hand, the generality of the reaction was next investigated and the results are summarized in Table 2. Both aromatic and aliphatic aldehydes can undergo the addition smoothly to produce the corresponding products. Aromatic aldehydes with electron-withdrawing (entries 1-5), -neutral (entries 6-9), and donating groups (entries 9 and 10) can participate in the reaction smoothly to afford the corresponding products in excellent yields. Meanwhile, different

positions of the substituents showed no obvious impact on the reaction yields (entries 11-17). Interestingly, heteroaromatic aldehydes and cinnamaldehyde were proved to be good candidates for the addition, releasing the desired adducts in excellent yields (entries 18-20). The experiment results indicate that aliphatic aldehydes underwent smooth reaction to produce the corresponding products in moderate to high yields (entries 21-23). It is noteworthy that these pentafluorophenylation reactions of aldehydes can be conveniently conducted on gram-scale without sacrificing reaction yield (entry 24).

Table 2 Evaluation of aldehydes ^a

Entry	1a R	Time (h)	Product	Yield ^b (%)
1		2	3a	88
2		1	3b	96
3		2	3c	93
4		1	3d	92
5		1	3e	94
6		2	3f	99
7		2	3g	94
8		2	3h	91
9		2	3i	88
10		4	3j	95
11		3	3k	81
12		1	3l	91
13		2	3m	93
14		1	3n	92

15		1	3o	98
16		1	3p	99
17		3	3p	93
18		2	3q	92
19		2	3r	90
20		2	3s	92
21		2	3t	49
22		2	3u	69
23		2	3v	86
24 ^c		12	3a	92

[a] Reaction conditions: 5 mol% of NHC **4**, 1.5 equiv of **1a**, 0.3 mol L⁻¹ of **2**, room temperature for 1-3 h. [b] Isolated yield. [c] **1a** (18 mmol), **2a** (15 mmol), using 1 mol% of NHC **4**, anhydrous acetonitrile 10.0 mL, room temperature for 12 h.

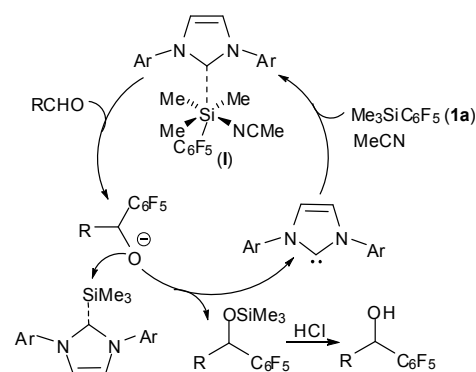
We also found that NHCs can facilitate tetrafluorophenylation of aldehydes efficiently (Table 3). Under the optimized reaction conditions, 1,4-bis(trimethylsilyl)tetrafluorobenzene **1b** served as a synthon of tetrafluorobenzene dianion to undergo dual addition with two equiv. of aldehydes to produce tetrafluorophenylation adducts **9** in moderated to good yields.

Table 3 NHCs-catalysed dual tetrafluorophenylation of aldehydes^a

Entry	R	Time (h)	Product	Yield ^b (%)
1		2	9a	74
2 ^c		12	9a	72
3		2	9b	71
4		3	9c	51
5		2	9d	68

[a] Reaction conditions: 5 mol% of NHC **4**, 2.0 equiv of **2**, 0.3 mol L⁻¹ of **1b**, room temperature for 2-3 h. [b] Isolated yield. [c] Using 1 mol% of NHC **4**.

Based on the pioneering work of NHCs-catalysed nucleophilic addition of silylated reagents with carbonyl compounds,¹¹⁻¹² a plausible mechanism is speculated and illustrated in Scheme 1. NHC attacks the trimethylsilyl group of **1a** to form a reactive hexavalent silicon species²¹ (**I**), which might initiate the following addition to aldehyde and produce the desired product after acidic work up.



Scheme 1 Proposed Reaction Mechanism

Conclusions

In summary, NHC-catalysed pentafluorophenylation and dual tetrafluorophenylation of aldehydes have been developed. The extremely mild reaction conditions, simple procedure and high yields provide a novel and efficient organocatalytic protocol for the incorporation of multifluorophenyl groups into aldehydes. Further exploration of NHCs-catalysed introduction of other fluorinated moieties are on-going in our laboratory.

Notes and references

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Graphical Abstract

N-heterocyclic carbene-catalysed pentafluorophenylation of aldehydes.

