

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

N-Heterocyclic Carbene-Catalysed Pentafluorophenylation of Aldehydes

Cite this: DOI: 10.1039/x0xx00000x

Guang-Fen Du,^{a,b} Fen Xing,^b Cheng-Zhi Gu,^{*b} Bin Dai^{*b} and Lin He^bReceived 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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, imidazolium 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

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	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.

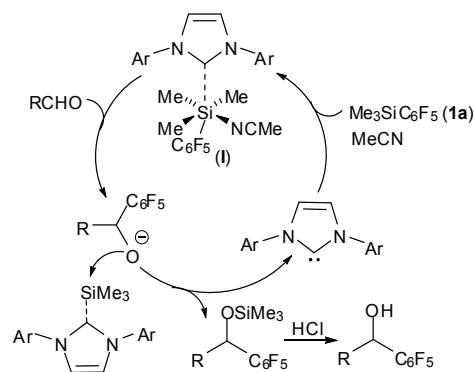
We also found that NHCs can facilitate tetrafluorophenylation of aldehydes efficiently (Table 3). Under the optimized reaction conditions, 1,4-bis(trimethylsilyl)tetrafluorobenzene **1b** served as a synthon of tetrafluorobenzene dianion to undergo dual addition with two equiv. of aldehydes to produce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

^a School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, P. R. of China

^b School of Chemistry and Chemical Engineering, Shihezi University, Xinjiang Uygur Autonomous Region, 832000, China. Fax: (+86) 993-2057270

E-mail: gcz_tea@shzu.edu.cn; db_tea@shzu.edu.cn

This work was supported by the National Natural Science Foundation of China (No. 21262027) and the Natural Science Foundation of Shihezi university (No. 2011ZRKJTD-04, 2012ZRKXJQ06)

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

- (a) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, 107, 5606; (b) A. T. Biju, N. Kuhl and F. Glorius, *Acc. Chem. Res.*, 2011, 44, 1182; (c) J. Mahatthanachai and J. W. Bode, *Chem. Sci.*, 2012, 3, 192–197; (d) A. Grossmann and D. Enders, *Angew. Chem. Int. Ed.*, 2012, 51, 314; (e) N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, 510, 485–496.
- (a) Enders, D.; Kallfass, U. *Angew. Chem., Int. Ed.* 2002, 41, 1743. (b) Hachisu, Y.; Bode, J. W.; Suzuki, K. *J. Am. Chem. Soc.* 2003, 125, 8432. (c) Enders, D.; Niemeier, O.; Balensiefer, T. *Angew. Chem., Int. Ed.* 2006, 45, 1463. (d) Takikawa, H.; Hachisu, Y.; Bode, J. W.; Suzuki, K. *Angew. Chem., Int. Ed.* 2006, 45, 3492. (e) L. H. Sun; Z. Q. Liang; W. Q. Jia; S. Ye, *Angew. Chem., Int. Ed.* 2013, 52, 5803–5806 (f) K. J. Wu; G. Q. Li; Y. Li; L. X. Dai; S. L. You, *Chem. Commun.*, 2011, 47, 493–495; (g) G. Q. Li; L. X. Dai; S. L. You, *Chem. Commun.*, 2007, 852–854.
- (a) Stetter, H.; Schreckenberger, M. *Angew. Chem., Int. Ed.* 1973, 12, 81. (b) Kerr, M. S.; Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* 2002, 124, 10298. (c) Kerr, M. S.; Rovis, T. *J. Am. Chem. Soc.* 2004, 126, 8876. (d) Read de Alaniz, J.; Rovis, T. *J. Am. Chem. Soc.* 2005, 127, 6284. (e) Mattson, A. E.; Zuhl, A. M.; Reynolds, T. E.; Scheidt, K. A. *J. Am. Chem. Soc.* 2006, 128, 4932; (f) Q. Liu; S. Perreault; T. Rovis, *J. Am. Chem. Soc.*, 2008, 130, 14066–14067; (g) D. Enders; J. W. Han; A. Henseler, *Chem. Commun.*, 2008, 3989–3991 (h) DiRocco, D. A.; Oberg, K. M.; Dalton, D. M.; Rovis, T. *J. Am. Chem. Soc.* 2009, 131, 10872. (i) K. Hirano; A. T. Biju; I. Piel; F. Glorius, *J. Am. Chem. Soc.*, 2009, 131, 14190–14191. (j) DiRocco, D. A.; Rovis, T. *J. Am. Chem. Soc.* 2011, 133, 10402.
- For an excellent review, see: (a) V. Nair, R. S. Menon, A. T. Biju, C. R. Sinu, R. Paul, A. Jose, V. Sreekumar, *Chem. Soc. Rev.*, 2011, 40, 5336. For selected examples, see: (b) C. Burstein and F. Glorius, *Angew. Chem. Int. Ed.*, 2004, 43, 6205; (c) S. S. Sohn, E. L. Rosen and J. W. Bode, *J. Am. Chem. Soc.*, 2004, 126, 14370; (d) V. Nair, S. Vellalath, M. Poonoth and E. Suresh, *J. Am. Chem. Soc.*, 2006, 128, 8736–8737; (e) J. Izquierdo and K. A. Scheidt, *J. Am. Chem. Soc.* 2013, 135, 10634. (f) X. Chen; X. Fang; Y. R. Chi, *Chem. Sci.*, 2013, 4, 2613–2618; (g) S. Bera; R. C. Samanta; C. G. Daniliuc; A. Studer, *Angew. Chem. Int. Ed.*, 2014, 53, 9622–9626; (h) H. Lv, W.-Q. Jia, L. H. Sun, S. Ye, *Angew. Chem. Int. Ed.*, 2013, 52, 8607–8610; (i) Nicholas A. White and Tomislav Rovis, *J. Am. Chem. Soc.*, 2014, 136, 14674–14677; (j) C. Guo, B. Sahoo, C. G. Daniliuc, F. Glorius, *J. Am. Chem. Soc.*, 2014, 136 (50), 17402–17405.
- For an excellent review, see: (a) H. U. Vora, P. Wheeler and T. Rovis, *Adv. Synth. Catal.*, 2012, 354, 1617; for selected examples, see: (b) N. T. Reynolds, J. R. D. Alaniz and T. Rovis, *J. Am. Chem. Soc.*, 2004, 126, 9518; (c) K. Y.-K. Chow and J. W. Bode, *J. Am. Chem. Soc.*, 2004, 126, 8126; (d) H. U. Vora and T. Rovis, *J. Am. Chem. Soc.*, 2007, 129, 13796; (e) J. W. Bode and S. S. Sohn, *J. Am. Chem. Soc.*, 2007, 129, 13798; (f) G.-Q. Li, Y. Li, L.-X. Dai and S.-L. You, *Org. Lett.*, 2007, 9, 3519; (g) J. Mo, X. Chen and Y. R. Chi, *J. Am. Chem. Soc.* 2012, 134, 8810; (h) Q. Ni, H. Zhang, A. Grossmann, C. C. J. Loh, C. Merckens, D. Enders, *Angew. Chem. Int. Ed.* 2013, 52, 13562–13566. (i) J. Izquierdo and K. A. Scheidt, *J. Am. Chem. Soc.* 2013, 135, 10634; (k) L. Candish, A. Levens and D. W. Lupton, *Chem. Sci.*, 2015, DOI: 10.1039/C4SC03726J.
- (a) For an excellent review, see: X.-Y. Chen, S. Ye, *Synlett*, 2013, 24, 1614–1622; for selected examples, see: (b) Zhang, Y. R.; He, L.; Wu, X.; Shao, P. L.; Ye, S. *Org. Lett.* 2008, 10, 277. (c) Duguet, N.; Campbell, C. D.; Slawin, A. M. Z.; Smith, A. D. *Org. Biomol. Chem.* 2008, 6, 1108; (d) Huang, X.-L.; He, L.; Shao, P.-L.; Ye, S. *Angew. Chem. Int. Ed.* 2009, 48, 192. (e) Jian, T. Y.; He, L.; Tang, C.; Ye, S. *Angew. Chem. Int. Ed.* 2011, 50, 9104; (f) P.-L. Shao, X.-Y. Chen, S. Ye. *Angew. Chem. Int. Ed.* 2010, 49, 8412; (g) T. Y. Jian, X. Y. Chen, L. H. Sun, Y. Song, *Chem. Commun.* 2013, 11, 158–163. (h) J. Douglas, J. E. Taylor, G. Churchill, A. M. Z. Slawin, A. D. Smith, *J. Org. Chem.*, 2013, 78, 3925; (i) H.-M. Zhang, Z.-H. Gao, S. Ye, *Org. Lett.*, 2014, 16, 3079–3081.
- (a) G. A. Grasa, R. M. Kissling and S. P. Nolan, *Org. Lett.*, 2002, 4, 3583; (b) G. W. Nycy, J. A. Lamboy, E. F. Connor, R. M. Waymouth and J. L. Hedrick, *Org. Lett.*, 2002, 4, 3587. (c) G. A. Grasa, T. Güveli, R. Singh and S. P. Nolan, *J. Org. Chem.*, 2003, 68, 2812; (d) R. Singh, R. M. Kissling, M.-A. Letellier and S. P. Nolan, *J. Org. Chem.*, 2004, 69, 209; (e) T. Kano, K. Sasaki and K. Maruoka, *Org. Lett.*, 2005, 7, 1347.
- (a) T. Boddaert, Y. Coquerel and J. Rodriguez, *Adv. Synth. Catal.*, 2009, 351, 1744–1748. (b) T. Boddaert, Y. Coquerel and J. Rodriguez, *Chem. Eur. J.*, 2011, 17, 2266–2271. (c) E. M. Phillips, M. Riedrich, K. A. Scheidt, *J. Am. Chem. Soc.*, 2010, 132, 13179. (d) Q. Kang and Y. Zhang, *Org. Biomol. Chem.*, 2011, 9, 6715; (e) M. Hans, L. Delaude, J. Rodriguez and Y. Coquerel, *J. Org. Chem.*, 2014, 79, 2758–2764; (f) Y. Z. Li, Y. Wang, G. F. Du, H. Y. Zhang, H. L. Yang, L. he, *Asian. J. Org. Chem.*, 2015, doi: 10.1002/ajoc.201402241.
- For selected examples, see: (a) L. He, H. Guo, Y. Z. Li, G. F. Du and B. Dai, *Chem. Commun.* 2014, 50, 3719; (b) Fu, Z.; Xu, J.; Zhu, T.; Leong, W. W. Y.; Chi, Y. R. *Nat. Chem.* 2013, 5, 835.; (c) Chauhan, P.; Enders, D. *Angew. Chem. Int. Ed.* 2014, 53, 1485.; (d) X. Bugaut, F. Liu, and F. Glorius, *J. Am. Chem. Soc.*, 2011, 133, 8130–8133; (e) M. T. Hovey, C. T. Check, A. F. Sipher and K. A. Scheidt, *Angew. Chem. Int. Ed.*, 2014, 53, 9603–9607; (f) X. Chen, Z. Gao, C. Song, C. Zhang, Z. Wang and S. Ye, *Angew. Chem. Int. Ed.*, 2014, 53, 11611; (g) F. Li, Z. Wu and J. Wang, *Angew. Chem. Int. Ed.*, 2015, 54, 656; (h) X. Dong, W. Yang, W. Hu, J. Sun, *Angew. Chem. Int. Ed.*, 2015, 54, 660; (i) Z. Wu, F. Li and J. Wang, *Angew. Chem. Int. Ed.*, 2015, 54, 1629.
- For reviews see: (a) Fuchter, M. J. *Chem. Eur. J.* 2010, 16, 12286; (b) L. He, H. Guo, Y. Wang, G.-F. Du, B. Dai, *Tetrahedron Lett.* 2015, 56, 972.

11. For NHCs-catalysed cyanation reactions, see: (a) Fukuda, Y.; Maeda, Y.; Ishii, S.; Kondo, K.; Aoyama, T. *Synthesis* 2006, 2006, 589; (b) Song, J. J.; Gallou, F.; Reeves, J. T.; Tan, Z.; Yee, N. K.; Senanayake, C. H. *J. Org. Chem.* 2006, 71, 1273. (c) Suzuki, Y.; Bakar, M.; Muramatsu, K.; Sato, M. *Tetrahedron* 2006, 62, 4227. (d) Tan, M.; Zhang, Y.; Ying, J. Y. *Adv. Synth. Catal.* 2009, 351, 1390.
12. (a) Song, J. J.; Tan, Z.; Reeves, J. T.; Gallou, F.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* 2005, 7, 2193. (b) Song, J. J.; Tan, Z.; Reeves, J. T.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* 2007, 9, 1013; (c) Du, G. F.; He, L.; Gu, C. Z.; Dai, B. *Synlett*, 2010, 16, 2513; (d) Cai, Z. H.; Du, G. F.; He, L.; Gu, C. Z.; Dai, B. *Synthesis*, 2011, 2011, 2073; (e) Wu, J.; Sun, X.; Ye, S.; Sun, W. *Tetrahedron Lett.* 2006, 47, 4813; (f) Zou, X. L.; Du, G. F.; Sun, W. F.; He, L.; Ma, X. W.; Gu, C. Z.; Dai, B. *Tetrahedron* 2013, 69, 607.; (g) Fan, Y. C.; Du, G. F.; Sun, W. F.; Kang, W.; He, L. *Tetrahedron Lett.* 2012, 53, 2231.
13. (a) Raynaud, J.; Ciolino, A.; Baceiredo, A.; Destarac, M.; Bonnette, F.; Kato, T.; Gnanou, Y.; Taton, D. *Angew. Chem. Int. Ed.* 2008, 47, 5390; (b) Raynaud, J.; Liu, N.; Gnanou, Y.; Taton, D. *Macromolecules* 2010, 43, 8853; (c) Raynaud, J.; Liu, N.; Fèvre, M.; Gnanou, Y.; Taton, D. *Polym. Chem.* 2011, 2, 1706.
14. (a) Lohmeijer, B. G.; Dubois, G.; Leibfarth, F.; Pratt, R. C.; Nederberg, F.; Nelson, A.; Waymouth, R. M.; Wade, C.; Hedrick, J. L. *Org. Lett.* 2006, 8, 4683; (b) Brown, H. A.; Chang, Y. A.; Waymouth, R. M. *J. Am. Chem. Soc.* 2013, 135, 18738.
15. (a) J. Wang, M. Sánchez-Roselló, J. Luis Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, 114, 2432–2506. (b) P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications*, Wiley-VCH, Weinheim, 2nd edn, 2013; (c) I. Ojima, *J. Org. Chem.* 2013, 78, 6358; (d) K. Uneyama, *J. Fluorine Chem.* 2008, 129, 550–576; (e) K. Müller, C. Faeh and F. Diederich, *Science*, 2007, 317, 1881–1886; (f) *Fluorinated Materials for Energy Conversion*, ed. T. Nakajima and H. Groult, Elsevier, 2005; (g) M. Pagliaro and R. Ciriminna, *J. Mater. Chem.*, 2005, 15, 4981–4991.
16. (a) Zahn, A.; Brotschi, C.; Leumann, C. J. *Chem. Eur. J.* 2005, 11, 2125; (b) J. S. Reddy, V. G. Anand, *J. Am. Chem. Soc.* 2008, 130, 3718–3719; (c) Montes, V. A.; Li, G.; Pohl, R.; Shinar, J.; Anzenbacher, P. *Adv. Mater.* 2004, 16, 2001. (d) Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Tokito, S.; Taga, Y. *J. Am. Chem. Soc.* 2000, 122, 1832; (e) Matsui, M.; Shirai, K.; Tanaka, N.; Funabiki, K.; Muramatsu, H.; Shibata, K.; Abe, Y.; Ohgomori, Y. *J. Mater. Chem.* 1999, 9, 2755; (f) Clarke, M. L. *J. Organomet. Chem.* 2003, 665, 65.
17. (a) Jung, M. E.; Jung, Y. H.; Miyazawa, Y. *Tetrahedron Lett.* 1990, 31, 6983; (b) Gupta, H. K.; Stradiotto, M.; Hughes, D. W.; McGlinchey, M. J. *J. Org. Chem.* 2000, 65, 3652; (c) Elshani, S.; Du, H.; Laintz, K. E.; Natale, N. R.; Wai, C. M.; Elkarim, N. S. A.; Bartsch, R. A. *Tetrahedron* 2000, 56, 4651.
18. (a) Fujita, M.; Obayashi, M.; Hiyama, T. *Tetrahedron* 1988, 44, 4135; (b) Gostevskii, B. A.; Kruglaya, O. A.; Albanov, A. I.; Vyazankin, N. S. *J. Organomet. Chem.* 1980, 187, 157; (c) Webb, A. F.; Sethi, D. S.; Gilman, H. J. *Organomet. Chem.* 1970, 21, P61.
19. S. Brogan, N. B. Carter, H. W. Lam, *Synlett*, 2010, 4, 615–617.
20. Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* 1999, 55, 14523.
21. For recent study of penta- and hexacoordinate silicon-NHC complexes see: R. S. Ghadwal, S. S. Sen, H. W. Roesky, G. Tavcar, S. Merkel, D. Stalke, *Organometallics*, 2009, 28, 6374.

Graphical Abstract

N-heterocyclic carbene-catalysed pentafluorophenylation of aldehydes.

