

Cite this: *Chem. Sci.*, 2020, **11**, 276

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 6th October 2019
Accepted 9th November 2019DOI: 10.1039/c9sc05018c
rsc.li/chemical-science

Controllable double CF₂-insertion into sp² C–Cu bond using TMSCF₃: a facile access to tetrafluoroethylene-bridged structures†

Qiqiang Xie, Ziyue Zhu, Lingchun Li, Chuanfa Ni and Jinbo Hu *

A highly efficient method for controllable double CF₂-insertion into pentafluorophenylcopper species using TMSCF₃ as difluoromethylene source has been developed. The newly generated fluoroalkylcopper(I) species, C₆F₅CF₂CF₂Cu, shows good reactivity towards a myriad of structurally diverse aryl, heteroaryl and alkenyl iodides. This protocol is easy to handle, ready to scale up and applicable for the synthesis of relative complex molecules, thus providing a convenient method for facile access to tetrafluoroethylene-bridged structures.

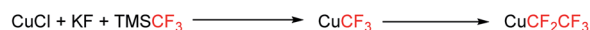
Introduction

Due to the unique physical, chemical and biological properties of organofluorine compounds, the introduction of fluorine atom(s) or fluorinated moieties into organic molecules has become a routine strategy in drug design and advanced material development.^{1–4} Among various fluorinated functionalities, the tetrafluoroethylene motif (–CF₂CF₂–) has attracted considerable attention because of its applications in agrochemicals⁵ and liquid-crystalline materials.^{6–8} Moreover, the introduction of –CF₂CF₂– group into liquid crystals often results in highly advantageous properties such as high clearing temperature, broad nematic phase range, low rotational viscosity and high dielectric anisotropy.^{6–8} Therefore, it is of strong demand to access tetrafluoroethylene-bridged molecules.

Current methods for the syntheses of tetrafluoroethylene-bridged structures are mainly based on (1) deoxofluorination of 1,2-dicarbonyl compounds with SF₄ and DeoxoFluor;^{9–11} (2) fluorination of C–C triple bonds using F₂;^{12–14} (3) 1,2-difunctionalization of tetrafluoroethylene (TFE);^{15–23} (4) difluoromethylene insertion using CF₂Br₂ as the CF₂ source;^{24,25} and (5) using RCF₂CF₂Br as the build block.⁵ However, these methods suffer from several drawbacks such as (1) using toxic, highly reactive or hazardous reagents; (2) low functional group tolerance and/or (3) using explosive gaseous reagents or ozone-depleting substances (ODS). As such, developing a new method to incorporate –CF₂CF₂– structure motif into organic

molecules with readily available, easy to handle and environmentally benign reagents under mild conditions is highly desired.

(Trifluoromethyl)trimethylsilane (TMSCF₃), often called Ruppert–Prakash reagent, is arguably the most widely used trifluoromethylating agent.^{26–30} In 2011, our group, in collaboration with the Prakash group, revealed that TMSCF₃ is a good difluorocarbene precursor, which can be used in the [2 + 1] cycloaddition reaction with alkenes and alkynes.³¹ Recently, our group reported that difluorocarbene generated from TMSCF₃ could undergo dimerization to give tetrafluoroethene (TFE),^{32,33} which can be used for a variety of transformations.³³ Very recently, our group demonstrated that, by using TMSCF₃ as the difluoromethylene source, controllable CF₂-insertion into CuCF₃ to generate CuCF₂CF₃ could be realized.³⁴ Inspired by this C₁ to C₂ process, we envisioned that it might be possible to insert CF₂ into other C–M bonds. Herein, we report our latest progress in the fluorocarbon homologation reaction using TMSCF₃ as the difluoromethylene source. By carefully tuning the reaction conditions, controllable double insertion of CF₂ into C₆F₅–Cu gives rise to C₆F₅CF₂CF₂Cu, which can be applied to the preparation of a diverse range of tetrafluoroethylene-bridged compounds (Scheme 1).

a) Previous work: single CF₂ insertion into CF₃Cu with TMSCF₃b) **This work:** double CF₂ insertion into C₆F₅Cu with TMSCF₃

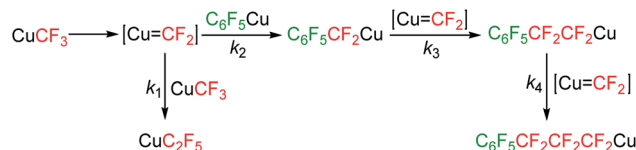
Scheme 1 Fluorocarbon homologation with TMSCF₃. TMS = trimethylsilyl.

Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. E-mail: jinbohu@sioc.ac.cn

† Electronic supplementary information (ESI) available. CCDC 1957757. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc05018c

Results and discussion

Our investigation commenced with the preparation of $\text{C}_6\text{F}_5\text{-CF}_2\text{CF}_2\text{Cu}$ from TMSC_6F_5 and TMSCF_3 . Initially, we used 1 equivalent of TMSC_6F_5 as the $\text{C}_6\text{F}_5\text{Cu}$ precursor, 1 equivalent of TMSCF_3 as the difluorocarbene precursor, 2 equivalents of KF as the desilylating reagent and 2.5 equivalents of CuCl as the copper source. All these components were added simultaneously with DMF as the solvent, and the resulting mixture was stirred at room temperature for 12 hours. Analysis of the mixture by ^{19}F NMR spectroscopy revealed that $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ (21%), $\text{C}_6\text{F}_5\text{Cu}$ (57%) and CuCF_3 (37%) were formed; no single CF_2 -insertion product $\text{C}_6\text{F}_5\text{CF}_2\text{Cu}$ could be detected (Table 1, entry 1). When adding 2 equivalents of difluorocarbene source TMSCF_3 , we found that the desired product $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was formed in 79% yield, in conjunction with $\text{C}_6\text{F}_5\text{Cu}$ (3%), CuCF_3 (10%) and CuC_2F_5 (5%) (entry 2).³⁵ If 3 equivalents of TMSCF_3 was used, $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was formed in 83% yield, along with CuCF_3 (16%) and CuC_2F_5 (12%) being formed; neither $\text{C}_6\text{F}_5\text{Cu}$ nor triple CF_2 -insertion product $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{CF}_2\text{Cu}$ could be detected (entry 3). These results (entries 1–3) clearly indicate that the TMSCF_3 -derived difluorocoppercarbene ($\text{Cu}=\text{CF}_2$) species³⁴ could selectively undergo double CF_2 -insertion into $\text{C}_6\text{F}_5\text{Cu}$, regardless of the amount of TMSCF_3 used. This behaviour is in accord with previous reports.²⁴ The high selectivity may be attributed to the intrinsic reactivity of different fluoroalkylcopper species toward $\text{Cu}=\text{CF}_2$ (Scheme 2). As to the possible intermediate, $\text{C}_6\text{F}_5\text{CF}_2\text{Cu}$, its benzylic C–Cu bond is highly reactive and tended to insert another CF_2 unit to give $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$;^{24,25} the resulting $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ has lower reactivity than CuCF_3 because of its longer fluoroalkyl chain.^{24,25} Therefore, even in the presence of excess of TMSCF_3 , triple CF_2 -



Scheme 2 Proposed reaction mechanism.

insertion into $\text{C}_6\text{F}_5\text{Cu}$ could not be observed; in that case, the CF_2 -insertion into CuCF_3 to generate CuC_2F_5 would be favoured. Altogether, the relative reaction rate of each step is $k_3 > k_2 > k_1 > k_4$.

With this understanding in mind, we went on to optimize the reaction conditions in order to increase the yield of $\text{C}_6\text{F}_5\text{-CF}_2\text{CF}_2\text{Cu}$ and minimize those of CuCF_3 and CuC_2F_5 . By using 2 equivalents of TMSCF_3 and prolonging reaction time to 20 hours, $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was formed in 87% yield (entry 4). When we decreased the amount of CuCl from 4 equivalents to 3 equivalents, only trace of $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was observed, with >80% $\text{C}_6\text{F}_5\text{Cu}$ and CuCF_3 being recovered (entry 5). This result revealed that the presence of excess amount of CuCl is crucial for the $\text{Cu}=\text{CF}_2$ generation, which is consistent with our previous report.³⁴ As CuCF_3 was always observed, we tried to speed up the decomposition of CuCF_3 at elevated temperatures. However, when the reaction was carried out at 50 °C, although no CuCF_3 was observed, a larger amount of CuC_2F_5 was detected, and $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was obtained in relatively lower yield (entry 6 vs. entry 4). Next, we attempted to add TMSCF_3 into the reaction mixture after the preparation of $\text{C}_6\text{F}_5\text{Cu}$. Gratifyingly, the yield of $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was increased slightly (entry 7). In light of the decomposition of CuCF_3 to $\text{Cu}=\text{CF}_2$ would release

Table 1 Optimization of reaction conditions for the double CF_2 insertion into $\text{C}_6\text{F}_5\text{Cu}$ with TMSCF_3 ^a

$\text{TMSC}_6\text{F}_5 + \text{CuCl} + \text{KF} \xrightarrow[\text{RT, 0.5 h}]{\text{DMF}} \text{C}_6\text{F}_5\text{Cu} \xrightarrow[\text{t, T}]{\text{TMSCF}_3} \text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$					
Entry	$\text{TMSC}_6\text{F}_5 : \text{CuCl} : \text{KF} : \text{TMSCF}_3$	t (h)	T (°C)	Yield (%)	
				$\text{C}_6\text{F}_5\text{C}_2\text{F}_4\text{Cu}$	$\text{C}_6\text{F}_5\text{Cu}/\text{CuCF}_3/\text{CuC}_2\text{F}_5$
1 ^b	1 : 2.5 : 2 : 1	12	rt	21	57/37/n.d.
2 ^b	1 : 4 : 3 : 2	12	rt	79	3/10/5
3 ^b	1 : 5.5 : 4 : 3	12	rt	83	n.d./16/12
4 ^b	1 : 4 : 3 : 2	20	rt	87	4/2/4
5 ^b	1 : 3 : 3 : 2	20	rt	1	87/82/n.d.
6 ^b	1 : 4 : 3 : 2	10	50	75	1/n.d./23
7	1 : 4 : 3 : 2	28	rt	91	<1/<1/4
8	1 : 4 : 2 : 2	28	rt	76	n.d./2/5
9 ^c	1 : 4 : 3 : 2	28	rt	91	n.d./6/2
10 ^d	1 : 4 : 3 : 2	28	rt	93	n.d./8/2
11 ^e	1 : 4 : 3 : 1.9	28	rt	92	2/4/2
12 ^e	1 : 4 : 3 : 1.9	36	rt	86	3/4/2
13 ^{e,f}	1 : 4 : 3 : 1.9	28	rt	89	n.d./1/2

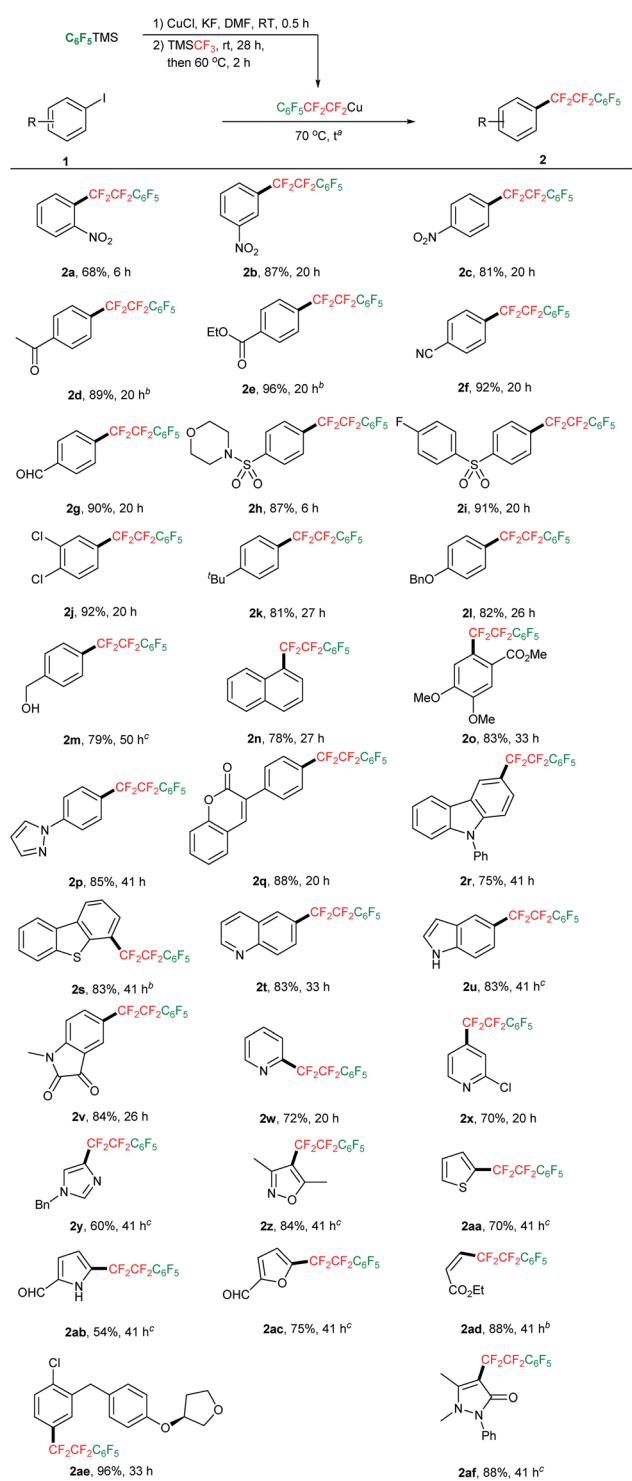
^a Reactions were performed on 0.2 mmol TMSC_6F_5 (1.0 equiv.) scale. Yields were determined by ^{19}F NMR spectroscopy using PhOCF_3 as an internal standard. n.d. = not detected. ^b TMSC_6F_5 and TMSCF_3 were added simultaneously without the pre-preparation of $\text{C}_6\text{F}_5\text{Cu}$. ^c TMSCF_3 was added in three portions for every 4 hours. ^d TMSCF_3 was added in three portions for every 6 hours. ^e TMSCF_3 was added in two portions for every 6 hours. ^f After reacted at rt for 28 hours, the reaction mixture was stirred at 60 °C for another 2 hours.



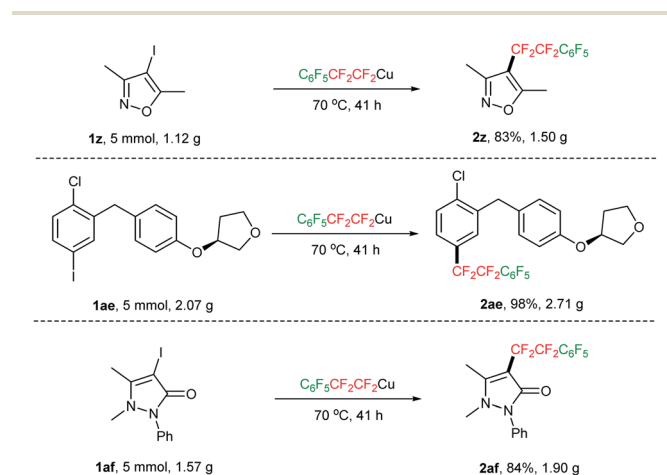
fluoride ions, we surmised that the amount of externally added KF could be reduced. However, lowering down KF to 2 equivalents gave inferior result (entry 8). To further decrease the yield

of CuC_2F_5 , we envisaged that adding TMSCF_3 in batches to decrease the concentration of CuCF_3 might be helpful. After some brief optimizations and decreasing the amount of TMSCF_3 to 1.9 equivalents (entries 9–11), $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ was formed in 92% yield, together with 2% of $\text{C}_6\text{F}_5\text{Cu}$ and 4% of CuCF_3 being formed (entry 11). Prolonging the reaction time to 36 hours did not have any beneficial effect (entry 12). Finally, when the reaction was conducted at room temperature for 28 hours, then stirred at 60°C for 2 hours, no $\text{C}_6\text{F}_5\text{Cu}$ and little amounts of CuCF_3 (1%) and CuC_2F_5 (2%) could be detected, with $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ being formed in 89% yield (entry 13).

With the optimized conditions (Table 1, entry 13) in hand, the reactivity of this TMSCF_3 -derived $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ towards aryl iodides was studied. A variety of structurally diverse (hetero)aryl and alkenyl iodides are all viable substrate, giving the desired tetrafluoroethylene-bridged products in moderate to good yields (Scheme 3). The electronic character of aryl iodides do not have obvious influence on the reaction efficiency, and both electron-deficient (**2a–i**) and electron-rich (**2k–p**, **2r–s**) substrates were readily transformed to the desired products in good yields. Common functional groups such as nitro (**2a–c**, in *ortho*, *meta* and *para* positions), acetyl (**2d**), ester (**2e**), cyano (**2f**), sulfonamide (**2h**) and sulfone (**2i**) were compatible with the reaction conditions, and good yields of products were observed. Notably, because of the mildness of the reaction conditions, some sensitive functionalities including aldehyde (**2g**, **2ab–ac**), alcohol (**2m**) and unprotected NH group (**2u**, **2ab**), were also tolerated. Heterocycles, such as pyrazole (**2p**), coumarin (**2q**), carbazole (**2r**), benzothiophene (**2s**), quinoline (**2t**) and indole (**2u**) were competent under the reaction conditions, as demonstrated by the formation of tetrafluoroethylene-bridged products in high yields. Moreover, heteroaryl iodides, including iodopyridine (**2w–x**), iodoimidazole (**2y**), iodoisoxazole (**2z**), iodothiophene (**2aa**), iodopyrrole (**2ab**) and iodofuran (**2ac**), participated in this per-fluorophenylethylation to afford corresponding products in moderate to good yields (54–84%). Iodoalkene **1ad** also showed good reactivity towards $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$, furnishing the desired product **2ad** in 88% yield. This protocol is also



Scheme 3 Perfluorophenylethylation of (hetero)aryl iodides with TMSCF_3 -derived $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$. ^a Unless otherwise noted, reactions were performed on 0.5 mmol of **1** (1.0 equiv.) scale, and TMSCF_3 was added in two portions every 6 h; 1.5 equivalents of TMSCF_3 was used; the molar ratio of TMSCF_3 : CuCl : KF : TMSCF_3 = 1 : 4 : 3 : 1.9. ^b 1.6 equivalent of TMSCF_3 was used. ^c 1.8 equivalent of TMSCF_3 was used.



Scheme 4 Gram-scale synthesis.



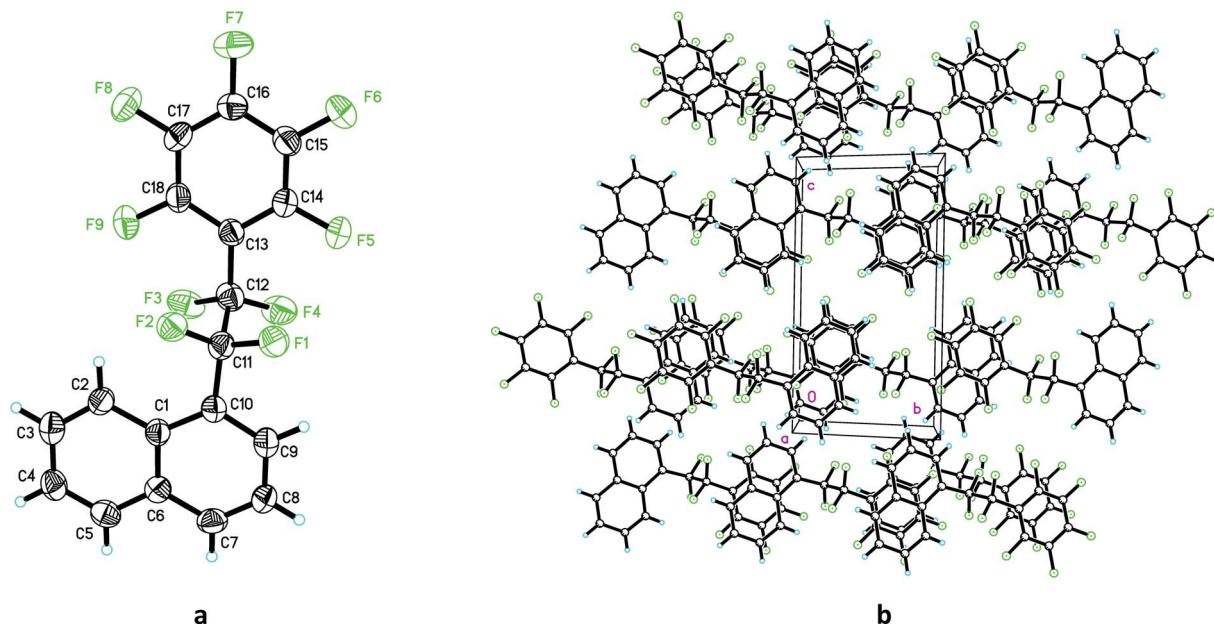


Fig. 1 (a) The single crystal structure and (b) packing diagram of **2n**.³⁶

effective for the perfluorophenylethylation of relatively complex compounds and pharmaceutical intermediates **1ae** and **1af**, giving the corresponding products **2ae** and **2af** in 96% and 88% yields, respectively. The broad scope of this reaction underscores the great potential of its application in the synthesis of a raft of valuable $-\text{CF}_2\text{CF}_2-$ bridged molecules.

The inherent value of our controllable double CF_2 -insertion strategy with TMSCF_3 for the introduction of tetrafluoroethylene bridge is further demonstrated by its applicability to gram-scale synthesis. For example, when iodoisoxazole **1z** was scaled up to 5 mmol (1.12 g), the desired product **2z** was obtained in 83% yield (1.50 g). Analogously, pharmaceutical intermediates **1ae** and **1af** were also successfully scaled up to 5 mmol, with the yields comparable to that on 0.5 mmol scale (Scheme 4).

It is worthwhile to note that the tetrafluoroethylene-bridged product **2n** possesses interesting conformation and intermolecular interaction. As shown in Fig. 1,³⁶ the single crystal structure of product **2n** shows that the dihedral angle of C10–C11–C12–C13 is 174.1° , and two aromatic (the naphthalenyl and pentafluorophenyl) rings in **2n** are almost parallel to each other (see Fig. 1a, also see ESI†). The packing diagram shows there are extensive intermolecular π – π stackings between naphthalenyl and pentafluorophenyl rings of **2n** (Fig. 1b), which might find useful applications in crystal engineering and materials science.

Conclusions

In conclusion, a controllable double CF_2 -insertion into $\text{C}_6\text{F}_5\text{Cu}$ was realized using TMSCF_3 as the difluoromethylene source. The resulting $\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$ species showed high reactivity towards various (hetero)aryl iodides and alkenyl iodides,

providing an easy access to a variety of $-\text{CF}_2\text{CF}_2-$ bridged molecules. Compared with previous methods for the construction of $-\text{CF}_2\text{CF}_2-$ unit, this approach owns several merits such as utilizing commercially available and environmentally benign reagents as the CF_2 source, easy to handle, broad substrate scope and mild conditions. This double CF_2 -insertion strategy represents the second generation of fluorocarbon homologation reactions *via* difluoromethylene insertion using TMSCF_3 (the first generation is single CF_2 -insertion into CuCF_3). Further efforts to seek after novel CF_2 -insertion reactions using TMSCF_3 are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Basic Research Program of China (No. 2015CB931900, 2016YFB0101200), the National Natural Science Foundation of China (No. 21632009, 21421002), the Key Programs of the Chinese Academy of Sciences (No. KGZD-EW-T08), the Key Research Program of Frontier Sciences of CAS (No. QYZDJ-SSW-SLH049), and Shanghai Science and Technology Program (No. 18JC1410601).

Notes and references

- 1 K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, 2006.
- 2 P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis. Reactivity, Applications*, Wiley-WCH, Weinheim, 2nd edn, 2013.



- 3 I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology*, Wiley-Blackwell, Chichester, U.K., 2009.
- 4 R. Berger, G. Resnati, P. Metrangolo, E. Weber and J. Hulliger, *Chem. Soc. Rev.*, 2011, **40**, 3496–3508.
- 5 J. Zhu, C. Ni, B. Gao and J. Hu, *J. Fluorine Chem.*, 2015, **171**, 139–147.
- 6 P. Kirsch and M. Bremer, *ChemPhysChem*, 2010, **11**, 357–360.
- 7 P. Kirsch, F. Huber, M. Lenges and A. Taugerbeck, *J. Fluorine Chem.*, 2001, **112**, 69–72.
- 8 P. Kirsch, M. Bremer, F. Huber, H. Lannert, A. Ruhl, M. Lieb and T. Wallmichrath, *J. Am. Chem. Soc.*, 2001, **123**, 5414–5417.
- 9 Y. Chang, A. Tewari, A.-I. Adi and C. Bae, *Tetrahedron*, 2008, **64**, 9837–9842.
- 10 R. P. Singh, U. Majumder and J. n. M. Shreeve, *J. Org. Chem.*, 2001, **66**, 6263–6267.
- 11 W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, 1960, **82**, 543–551.
- 12 J. Gateno and S. Rozen, *J. Fluorine Chem.*, 2009, **130**, 332–335.
- 13 C. York, G. K. S. Prakash and G. A. Olah, *J. Org. Chem.*, 1994, **59**, 6493–6494.
- 14 M. Zupan and A. Pollak, *J. Org. Chem.*, 1974, **39**, 2646–2647.
- 15 H. Shirataki, T. Ono, M. Ohashi and S. Ogoshi, *Org. Lett.*, 2019, **21**, 851–856.
- 16 T. Kawashima, M. Ohashi and S. Ogoshi, *J. Am. Chem. Soc.*, 2018, **140**, 17423–17427.
- 17 H. Shirataki, M. Ohashi and S. Ogoshi, *Eur. J. Org. Chem.*, 2019, 1883–1887.
- 18 T. Kawashima, M. Ohashi and S. Ogoshi, *J. Am. Chem. Soc.*, 2017, **139**, 17795–17798.
- 19 M. Ohashi, N. Ishida, K. Ando, Y. Hashimoto, A. Shigaki, K. Kikushima and S. Ogoshi, *Chem. –Eur. J.*, 2018, **24**, 9794–9798.
- 20 M. Ohashi, T. Adachi, N. Ishida, K. Kikushima and S. Ogoshi, *Angew. Chem., Int. Ed.*, 2017, **56**, 11911–11915.
- 21 M. Ohashi, H. Shirataki, K. Kikushima and S. Ogoshi, *J. Am. Chem. Soc.*, 2015, **137**, 6496–6499.
- 22 H. Saijo, M. Ohashi and S. Ogoshi, *J. Am. Chem. Soc.*, 2014, **136**, 15158–15161.
- 23 L. Li, C. Ni, Q. Xie, M. Hu, F. Wang and J. Hu, *Angew. Chem., Int. Ed.*, 2017, **56**, 9971–9975.
- 24 Z.-Y. Yang, D. M. Wiemers and D. J. Burton, *J. Am. Chem. Soc.*, 1992, **114**, 4402–4403.
- 25 Z.-Y. Yang and D. J. Burton, *J. Fluorine Chem.*, 2000, **102**, 89–103.
- 26 X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2015, **115**, 683–730.
- 27 S. Roy, B. T. Gregg, G. W. Gribble, V.-D. Le and S. Roy, *Tetrahedron*, 2011, **67**, 2161–2195.
- 28 R. P. Singh and J. n. M. Shreeve, *Tetrahedron*, 2000, **56**, 7613–7632.
- 29 J.-A. Ma and D. Cahard, *J. Fluorine Chem.*, 2007, **128**, 975–996.
- 30 G. K. Prakash and A. K. Yudin, *Chem. Rev.*, 1997, **97**, 757–786.
- 31 F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. Prakash and G. A. Olah, *Angew. Chem., Int. Ed.*, 2011, **50**, 7153–7157.
- 32 G. M. Lee, D. J. Harrison, I. Korobkov and R. T. Baker, *Chem. Commun.*, 2014, **50**, 1128–1130.
- 33 L. Li, C. Ni, Q. Xie, M. Hu, F. Wang and J. Hu, *Angew. Chem., Int. Ed.*, 2017, **56**, 9971–9975.
- 34 Q. Xie, L. Li, Z. Zhu, R. Zhang, C. Ni and J. Hu, *Angew. Chem., Int. Ed.*, 2018, **57**, 13211–13215.
- 35 The chemical shifts of these fluoroalkylcopper/fluoroarylcopper species were assigned as follows (in ppm): C₆F₅CF₂CF₂Cu, –101.1 (t, 2F), –106.6 (s, 2F), –139.4 (m, 2F), –153.1 (t, 1F), –163.9 (t, 2F); C₆F₅Cu, –111.0 (d, 2F), –163.3 (t, 1F), –164.3 (t, 2F); CuCF₃, –26.7 (s, 3F); CuC₂F₅, –84.0 (s, 3F), –112.4 (s, 2F).
- 36 CCDC 1957757† contains the supplementary crystallographic data for compound **2n**.

