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Difluoromethylation and *gem*-difluorocyclopropanation with difluorocarbene generated by decarboxylation†

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Difluoromethylation of the activated X–H bond (X = N, O and S) and aliphatic thiols, and *gem*-difluorocyclopropanation of alkynes with difluorocarbene generated *in situ* from difluoromethylene phosphobetaine ($\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$) by decarboxylation occurred smoothly without the presence of any base or other additives.

As fluorinated moieties usually show profound effects on the physical, chemical, and biological properties of the target molecules, fluorine has been considered as the “second-favorite heteroatom” after nitrogen in drug design. The number of fluorine-containing pharmaceuticals and agrochemicals has been increasing rapidly in the past decades.¹ Consequently, determined efforts have been devoted to the exploration of applicable protocols for the incorporation of fluorine-containing groups.² Difluorocarbene has proved to be a highly valuable intermediate, not only from the perspective of theoretical investigation, but also from its synthetic utilities as the transformation of difluorocarbene can incorporate the difluoromethylene group into various organic molecules.³ The transformation of difluorocarbene include homocoupling to produce tetrafluoroethylene,⁴ [2+1] cycloaddition with alkenes or alkynes,^{3a} difluoromethylation of the X–H bond (X = N, O, S, *etc.*),^{3a} [¹⁸F]-trifluoromethylation,⁵ and coordination with transition metals.⁶ Although a number of difluorocarbene reagents have been developed to realize a variety of reactions due to the increasing research interest in this chemistry, these reactions usually require the addition of a strong base or additive, and some reagents are volatile or highly hygroscopic.^{7–13} Previously, we have shown that difluoromethylene phosphobetaine ($\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$, PDFA), an efficient phosphonium ylide reagent,¹⁴ can readily generate difluorocarbene simply *via* decarboxylation.¹⁵ We have now investigated the use of this difluorocarbene precursor in the difluoromethylation of the

activated X–H bond (X = N, O and S), difluoromethylation of aliphatic thiols, and *gem*-difluorocyclopropanation of alkynes.

Many difluorocarbene precursors can be successfully applied to the difluoromethylation of the activated X–H bond (X = N, O and S), such as $\text{ClCF}_2\text{CO}_2\text{Na}$,^{12d} $\text{FSO}_2\text{CF}_2\text{CO}_2\text{TMS}$,^{16a} TMSCF_2Br ⁹ and $\text{HCF}_2\text{S}(\text{O})(\text{NTs})\text{Ph}$.¹⁷ However, basic conditions are required in these reactions, limiting their wide applicability. The two exceptions are the *N*-difluoromethylation of imidazoles and benzimidazoles with TMSCF_3 ,^{7c} and *N*-difluoromethylation of *N*-(pyridin-2-yl)acetamide with $\text{ClCF}_2\text{CO}_2\text{Na}$,^{12c} which can proceed under neutral conditions. But the methods suffer from a high reaction temperature, and/or are applicable only to *N*-difluoromethylation. In sharp contrast, we found that all of *N*-, *O*- and *S*-difluoromethylation with PDFA can occur smoothly under mild conditions without the presence of a base.

Although *S*-difluoromethylation with difluorocarbene is a straightforward protocol to incorporate the SCF_2H group, which is a valuable moiety in medicinal chemistry and agrochemistry, it has thus far been limited to isolated examples.^{9,12d,17–19} Especially for the aliphatic S–H difluoromethylation, only two reports have been published. Hu disclosed that both TMSCF_2Br ⁹ and $\text{HCF}_2\text{S}(\text{O})(\text{NTs})\text{Ph}$ ¹⁷ can be used to achieve the difluoromethylation of aliphatic thiols. But in both protocols, strong basic conditions are unavoidable.

The difluorocarbene reagents previously used for *gem*-difluorocyclopropanation to afford *gem*-difluorocyclopropanes, which have received much attention in synthetic chemistry, include $\text{BrCF}_2\text{CO}_2\text{Na}$,¹³ $\text{FSO}_2\text{CF}_2\text{CO}_2\text{TMS}$,^{16b} and $(\text{CF}_3)_2\text{Cd}$.²⁰ Most of these methods still lack generality due to such disadvantages as harsh reaction conditions, the use of highly toxic reagents, low product yields or inconvenient operations. Although TMSCF_3 ,^{7a} TMSCF_2Cl ,⁸ and TMSCF_2Br ⁹ are versatile difluorocarbene precursors and effective for *gem*-difluorocyclopropanation, the reagents are highly volatile and the reaction requires the presence of an initiator for the generation of difluorocarbene.

In this work, PDFA was found to be an efficient difluorocarbene reagent for difluoromethylation and *gem*-difluorocyclopropanation

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Table 1 Screening reaction conditions for the difluoromethylation of the activated X–H bond^a

$\text{Ph}_3\text{PCF}_2\text{COO}^- + \text{MeO}-\text{C}_6\text{H}_4-\text{COOH} \xrightarrow[p\text{-xylene, } 90^\circ\text{C, 2h}]{\text{}} \text{MeO}-\text{C}_6\text{H}_4-\text{COOCF}_2\text{H}$				
Entry	Solvent	Temp. (°C)	Molar ratio (1 : 2a)	Yield ^b (%)
1	Cyclohexane	60	1 : 1	5
2	<i>p</i> -Xylene	60	1 : 1	18
3	DMF	60	1 : 1	7
4	THF	60	1 : 1	11
5	<i>p</i> -Xylene	80	1 : 1	31
6	<i>p</i> -Xylene	90	1 : 1	47
7	<i>p</i> -Xylene	90	2 : 1	84

^a Reaction conditions: 2a (0.6 mmol) and 1 in solvent (3 mL). ^b Determined by ¹⁹F NMR with trifluoromethylbenzene as the internal standard.

via decarboxylation under neutral conditions. The attractive decarboxylative protocol is worthy of attention due to its operational convenience and mild reaction conditions.

In our previous study, it was found that low-polarity solvents such as cyclohexane and *p*-xylene favor the dissociation of PDFA into difluorocarbene.¹⁵ For the difluoromethylation of aromatic carboxylic acids with PDFA, *p*-xylene proved to be a suitable solvent (entries 1–4, Table 1). Elevating the reaction temperature to 90 °C in *p*-xylene improved the yield to 47% (entry 6). The reaction was quite sensitive to the loading of PDFA. Increasing its amount to 2 equiv. led to a significant increase in the yield (entry 7).

With the optimal reaction conditions in hand (entry 7, Table 1), we then investigated the substrate scope for the difluoromethylation of the activated X–H bond (Table 2). For the difluoromethylation of the O–H bond, the hydroxyl group in both carboxylic acids (3a–3c) and phenols (3d–3e) is reactive, and the carboxylic acids seem more reactive compared with phenols. The aromatic thiols can also be converted smoothly into the desired products (3f–3g). N-heterocycles are key structural units prevalent in biological systems. The incorporation of the difluoromethyl group is of great interest in synthetic and medicinal chemistry. Fortunately, the *N*-difluoromethylation of heterocycles with PDFA proceeded very well to afford the products in high yields (3h–3j). It is worth noting that no additive or base is required to generate difluorocarbene from PDFA, and the reaction can occur directly without neutralization of the substrates by base (Table 2).

However, the above reaction conditions (entry 7, Table 1) are not effective for the difluoromethylation of alcohols or aliphatic thiols. We have screened many conditions for the difluoromethylation of alcohols, but no condition can afford the desired product over 30% yield. To our delight, the difluoromethylation of aliphatic thiols seems to be very promising. For the reaction of benzyl thiol 4a with PDFA, 1,4-dioxane was found to be a suitable solvent instead of *p*-xylene. At 60 °C, the reaction furnished the desired product in 44% yield (entry 7, Table 3). Lowering or elevating the reaction temperature cannot increase the yield (entries 8–12). Increasing the loading of PDFA from 1 equiv. to 2 equiv. led to a dramatic improvement in the yield from 44% to 66% (entry 14 vs. entry 7). Further increasing its amount had no effect on the yield (entry 15).

Table 2 Difluoromethylation of the activated X–H bond^a

$\text{Ph}_3\text{PCF}_2\text{COO}^- + \text{R-XH} \xrightarrow[p\text{-xylene, } 90^\circ\text{C, 2h}]{\text{}} \text{R-XCF}_2\text{H}$		
1	2	3
 3a, 84%	 3b, 91%	 3c, 67%
 3d, 64%	 3e, 56%	 3f, 92%
 3g, 65%	 3h, 88%	 3i, 85%
		 3j, 76%

^a Reaction conditions: 2 (0.6 mmol), 1 (1.2 mmol) in *p*-xylene (3 mL) for 2 h at 90 °C.

Table 3 Screening reaction conditions for the difluoromethylation of aliphatic thiols^a

$\text{Ph}_3\text{PCF}_2\text{COO}^- + \text{PhCH}_2\text{SH} \xrightarrow[\text{Temp., 2h}]{\text{solvent}} \text{PhCH}_2\text{SCF}_2\text{H}$				
Entry	Solvent	Temp. (°C)	Molar ratio (1 : 4a)	Yield ^b (%)
1	<i>p</i> -Xylene	60	1 : 1	26
2	Toluene	60	1 : 1	28
3	DMF	60	1 : 1	5
4	DCE	60	1 : 1	Trace
5	Cyanobenzene	60	1 : 1	16
6	THF	60	1 : 1	40
7	1,4-Dioxane	60	1 : 1	44
8	1,4-Dioxane	50	1 : 1	23
9	1,4-Dioxane	70	1 : 1	43
10	1,4-Dioxane	80	1 : 1	43
11	1,4-Dioxane	90	1 : 1	44
12	1,4-Dioxane	100	1 : 1	44
13	1,4-Dioxane	60	1.5 : 1	61
14	1,4-Dioxane	60	2 : 1	66
15	1,4-Dioxane	60	3 : 1	65

^a Reaction conditions: compound 4a (0.6 mmol) and 1 in solvent (3 mL).

^b Determined by ¹⁹F NMR with trifluoromethylbenzene as the internal standard.

The reaction can be applied to a variety of aliphatic thiols (Table 4). In the case of benzyl aliphatic thiol, a low isolated yield was obtained due to the high volatility of the product (5a). Irrespective of whether the aryl group is substituted by an electron-withdrawing or -donating group, the products were obtained in good yields, indicating that the transformation is not sensitive to the electronic effects (5a–5h). The conversion is not only applicable for primary thiols, but also for secondary thiol (5h). Compared with the reported methods,^{9,17} for which strong basic conditions are required, our method seems more attractive.

The successful difluoromethylation prompted us to investigate the *gem*-difluorocyclopropanation. Our initial attempts at the reaction of alkyne 6a with PDFA in *p*-xylene at 80 °C gave the expected products in 63% yield (entry 1, Table 5). The examination of other solvents suggested that *p*-xylene was the suitable solvent for this transformation (entries 2–8 vs. entry 1). Elevating the reaction temperature to 110 °C improved the yield slightly (entries 9 and 10), but higher temperature did not give better results (entries 11–13). Using 2 equiv. of PDFA, the yield was



Table 4 Difluoromethylation of aliphatic thiols^a

$\text{Ph}_3\text{PCF}_2\text{COO}^- + \text{Alkyl-SH}$ 1 4		$\xrightarrow[60^\circ\text{C}, 5\text{h}]{1,4\text{-dioxane}}$ 5
	5a , 43%	
	5b , 54%	
	5c , 60%	
	5d , 56%	
	5e , 61%	
	5f , 58%	
	5g , 61%	
	5h , 59%	

^a Reaction conditions: **4** (0.6 mmol), **1** (1.2 mmol) in *p*-xylene (3 mL) for 5 h at 60 °C.

Table 5 Screening reaction conditions for *gem*-difluorocyclopropanation^a

$\text{Ph}_3\text{PCF}_2\text{COO}^- + \text{MeO-C}_6\text{H}_4\text{-C}\equiv\text{C-R}$ 1 6a		$\xrightarrow[2\text{h}]{\text{solvent}}$ 7a	
Entry	Solvent	Temp. (°C)	Yield ^b (%)
1	<i>p</i> -Xylene	80	63
2	Cyclohexane	80	39
3	Toluene	80	45
4	DMF	80	5
5	DG	80	19
6	Cyanobenzene	80	20
7	THF	80	31
8	1,4-Dioxane	80	39
9	<i>p</i> -Xylene	90	67
10	<i>p</i> -Xylene	110	73
11	<i>p</i> -Xylene	120	70
12	<i>p</i> -Xylene	130	71
13	<i>p</i> -Xylene	140	70
14	<i>p</i> -Xylene	110	96
15 ^c	<i>p</i> -Xylene	110	98

^a Reaction conditions: compound **6a** (0.6 mmol) and **1** in solvent (2 mL). ^b Determined by ¹⁹F NMR with trifluoromethylbenzene as the internal standard. ^c 3 mL of *p*-xylene was used.

increased significantly (entry 14). The concentration of the substrates had no obvious effect on the yield, as evidenced by the observation that the reaction in 3 mL of *p*-xylene instead of 2 mL gave the desired product in almost the same yield (entry 15).

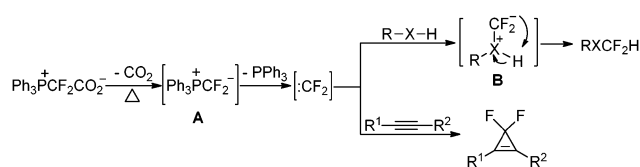
We then explored the substrate scope for the *gem*-difluorocyclopropanation of alkynes with PDFA under these optimal reaction conditions (Table 6). The electronic effects are important for the transformation. The substrates substituted by electron-donating groups on the phenyl ring can be converted well into the expected products in good yields (**7a–7j**), but in the case of substrates substituted by electron-withdrawing groups, low yield was afforded (**7k**). The reaction of aliphatic alkynes was also successful in affording the products in moderate yields (**7l**). Besides terminal alkynes, internal alkynes are also suitable for this conversion (**7m–7n**).

On the basis of the above results and related reports,^{14a,15a} we propose that the reaction mechanism as shown in Scheme 1 is plausible. Decarboxylation of PDFA generates phosphonium ylide **A**,^{14a} the further dissociation of which produces difluorocarbene.^{15a} Difluorocarbene can be readily trapped by the X–H group (X = N, O or S) to give intermediate **B**, which undergoes a 1,2-hydride migration to afford the final difluoromethylation product.

Table 6 *gem*-Difluorocyclopropanation of alkynes^a

$\text{Ph}_3\text{PCF}_2\text{COO}^- + \text{R}^1\text{-C}\equiv\text{C-R}^2$ 1 6		$\xrightarrow[110^\circ\text{C}, 2\text{h}]{p\text{-xylene}}$ 7
	7a , 80%	
	7b , 90%	
	7c , 72%	
	7d , 67%	
	7e , 76%	
	7f , 61%	
	7g , 76%	
	7h , 59%	
	7i , 67%	
	7j , 78%	
	7k , 34% ^b	
	7l , 60%	
	7m , 45%	
	7n , 69%	
	7o , 58%	

^a Reaction conditions: **1** (1.2 mmol) and alkynes (0.6 mmol) in *p*-xylene (3 mL) at 110 °C for 2 h. Isolated yields. ^b Determined by ¹⁹F NMR with trifluoromethylbenzene as the internal standard.



Scheme 1 Proposed reaction mechanism.

For the *gem*-difluorocyclopropanation reaction, the direct cyclization of difluorocarbene with alkyne furnishes the desired product.

In summary, difluoromethylene phosphobetaine ($\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$, PDFA) has been found to be an efficient difluorocarbene precursor in the difluoromethylation of the activated X–H bond (X = N, O, S) and aliphatic thiols, and *gem*-difluorocyclopropanation of alkynes. All of these reactions proceeded smoothly under neutral conditions without the addition of any other additive or base. This decarboxylative protocol represents an efficient method for the transformation of difluorocarbene due to the operational convenience and the high stability of PDFA.

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Notes and references

- (a) P. Kirsch, *Modern fluoroorganic chemistry Synthesis, reactivity, applications*, WILEY-VCH, Weinheim, 2004; (b) K. L. Kirk, *J. Fluorine Chem.*, 2006,



- 127, 1013; (c) A. M. Thayer, *Chem. Eng. News*, 2006, **84**, 15; (d) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320; (e) X.-L. Qiu, X. Yue and F.-L. Qing, in *Chiral Drugs*, ed. G.-Q. Lin, Q.-D. You and J.-F. Cheng, John Wiley & Sons, Inc., Hoboken, New Jersey, 2011, p. 195.
- 2 (a) T. Furuya, A. S. Kamlet and T. Ritter, *Nature*, 2011, **473**, 470; (b) O. A. Tomashenko and V. V. Grushin, *Chem. Rev.*, 2011, **111**, 4475; (c) U. Hennecke, *Angew. Chem., Int. Ed.*, 2012, **51**, 4532; (d) C. Hollingworth and V. Gouverneur, *Chem. Commun.*, 2012, **48**, 2929; (e) A. Studer, *Angew. Chem., Int. Ed.*, 2012, **51**, 8950; (f) X. F. Wu, H. Neumann and M. Beller, *Chem. – Asian J.*, 2012, **7**, 1744; (g) T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem., Int. Ed.*, 2013, **52**, 8214; (h) C.-P. Zhang, Q.-Y. Chen, Y. Guo, J.-C. Xiao and Y.-C. Gu, *Coord. Chem. Rev.*, 2014, **261**, 28.
- 3 For recent reviews, please see: (a) C. Ni and J. Hu, *Synthesis*, 2014, 842; (b) D. Brahms and W. Dailey, *Chem. Rev.*, 1996, **96**, 1585; (c) W. Dolbier and M. Battiste, *Chem. Rev.*, 2003, **103**, 1071. For recent examples, please see: (d) J. M. Lenhardt, M. T. Ong, R. Choe, C. R. Evenhuis, T. J. Martinez and S. L. Craig, *Science*, 2010, **329**, 1057; (e) M. D. Kosobokov, A. D. Dilman, V. V. Levin and M. I. Struchkova, *J. Org. Chem.*, 2012, **77**, 5850; (f) V. V. Levin, A. A. Zemtsov, M. I. Struchkova and A. D. Dilman, *Org. Lett.*, 2013, **15**, 917; (g) G. Liu, X. Wang, X.-H. Xu, X. Lu, E. Tokunaga, S. Tsuzuki and N. Shibata, *Org. Lett.*, 2013, **15**, 1044; (h) G. M. Lee, D. J. Harrison, I. Korobkov and R. T. Baker, *Chem. Commun.*, 2014, **50**, 1128.
- 4 M. Hudlicky and A. E. Pavlath, *Chemistry of Organic Fluorine Compounds II*, American Chemical Society, Washington, DC, 1995.
- 5 For review, please see: (a) A. F. Brooks, J. J. Topczewski, N. Ichiishi, M. S. Sanford and P. J. H. Scott, *Chem. Sci.*, 2014, **5**, 4545. For examples, please see: (b) M. Huiban, M. Tredwell, S. Mizuta, Z. Wan, X. Zhang, T. L. Collier, V. Gouverneur and J. Passchier, *Nat. Chem.*, 2013, **5**, 941; (c) D. Born, C. Sewing, J. D. M. Herscheid, A. D. Windhorst, R. V. A. Orru and D. J. Vugts, *Angew. Chem., Int. Ed.*, 2014, **53**, 11046; (d) P. Ivashkin, G. Lemonnier, J. Cousin, V. Grégoire, D. Labar, P. Jubault and X. Pannecoucke, *Chem. – Eur. J.*, 2014, **20**, 9514; (e) T. Ruhl, W. Rafique, V. T. Lien and P. J. Riss, *Chem. Commun.*, 2014, **50**, 6056.
- 6 (a) D. L. Reger and M. D. Dukes, *J. Organomet. Chem.*, 1978, **153**, 67; (b) G. R. Clark, S. V. Hoskins and W. R. Roper, *J. Organomet. Chem.*, 1982, **234**, C9; (c) G. R. Clark, S. V. Hoskins, T. C. Jones and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1983, 719; (d) G. M. Lee, D. J. Harrison, I. Korobkov and R. T. Baker, *Chem. Commun.*, 2014, **50**, 1128; (e) D. J. Harrison, G. M. Lee, M. C. Leclerc, I. Korobkov and R. T. Baker, *J. Am. Chem. Soc.*, 2013, **135**, 18296.
- 7 (a) F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash and G. A. Olah, *Angew. Chem., Int. Ed.*, 2011, **50**, 7153; (b) P. W. Chia, D. Bello, A. M. Z. Slawin and D. O'Hagan, *Chem. Commun.*, 2013, **49**, 2189; (c) G. K. S. Prakash, S. Krishnamoorthy, S. K. Ganesh, A. Kulkarni, R. Haiges and G. A. Olah, *Org. Lett.*, 2014, **16**, 54.
- 8 F. Wang, W. Zhang, J. Zhu, H. Li, K. Huang and J. Hu, *Chem. Commun.*, 2011, **47**, 2411.
- 9 L. Li, F. Wang, C. Ni and J. Hu, *Angew. Chem., Int. Ed.*, 2013, **52**, 12390.
- 10 D. L. S. Brahms and W. P. Dailey, *Chem. Rev.*, 1996, **96**, 1585.
- 11 (a) D. Seyferth, S. P. Hopper and K. V. Darragh, *J. Am. Chem. Soc.*, 1969, **91**, 6536; (b) I. Nowak, J. F. Cannon and M. J. Robins, *J. Org. Chem.*, 2007, **72**, 532.
- 12 (a) J. M. Birchall, G. W. Cross and R. N. Haszeldine, *Proc. Chem. Soc., London*, 1960, 81; (b) Y. Fujioka and H. Amii, *Org. Lett.*, 2008, **10**, 769; (c) M. Ando, T. Wada and N. Sato, *Org. Lett.*, 2006, **8**, 3805; (d) V. P. Mehta and M. F. Greaney, *Org. Lett.*, 2013, **15**, 5036.
- 13 K. Oshiro, Y. Morimoto and H. Amii, *Synthesis*, 2010, 2080.
- 14 (a) J. Zheng, J. Cai, J.-H. Lin, Y. Guo and J.-C. Xiao, *Chem. Commun.*, 2013, **49**, 7513; (b) V. V. Levin, A. L. Trifonov, A. A. Zemtsov, M. I. Struchkova, D. E. Arkhipov and A. D. Dilman, *Org. Lett.*, 2014, **16**, 6256; (c) Y. Qiao, T. Si, M. Yang and R. A. Altman, *J. Org. Chem.*, 2014, **79**, 7122.
- 15 (a) J. Zheng, J.-H. Lin, J. Cai and J.-C. Xiao, *Chem. – Eur. J.*, 2013, **19**, 15261; (b) X.-Y. Deng, J.-H. Lin, J. Zheng and J.-C. Xiao, *Chin. J. Chem.*, 2014, **32**, 689; (c) J. Zheng, J.-H. Lin, X.-Y. Deng and J.-C. Xiao, *Org. Lett.*, 2015, **17**, 532.
- 16 (a) K. Fuchibe, Y. Koseki, T. Aono, H. Sasagawa and J. Ichikawa, *J. Fluorine Chem.*, 2012, **133**, 52; (b) W. Xu and Q.-Y. Chen, *J. Org. Chem.*, 2002, **67**, 9421.
- 17 W. Zhang, F. Wang and J. Hu, *Org. Lett.*, 2009, **11**, 2109.
- 18 P. S. Fier and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2013, **125**, 2146.
- 19 K. Fuchibe, M. Bando, R. Takayama and J. Ichikawa, *J. Fluorine Chem.*, 2015, **171**, 133.
- 20 R. Eujen and B. Hoge, *J. Organomet. Chem.*, 1995, **503**, C51.

