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Palladium-catalyzed amination of 2,3,3-trifluoroallyl esters: synthesis of trifluoromethylenamines *via* an intramolecular fluorine shift and CF_3 group construction†

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The palladium-catalyzed reaction of 2,3,3-trifluoroallyl esters with several types of amines afforded trifluoromethylenamines, which were formed by the addition of a nitrogen nucleophile at the C-2 position and the intramolecular construction of the trifluoromethyl group *via* the fluorine atom shift from the C-2 to the C-3 position.

The palladium-catalyzed reaction of allylic compounds with nucleophiles generally provides allylic substituted products through the attack of the nucleophile on the terminal carbon atom of the π-allyl group.[1,2] As an alternative reaction process, the formation of cyclopropane derivatives is known and the reaction proceeds by the attack of the nucleophile on the central carbon atom of the π-allyl unit.[3] Furthermore, there is an exceptional reaction process during the palladium-catalyzed reaction of 2-haloallyl compounds with nucleophiles, and such a reaction provides a doubly-substituted product through the palladacyclobutane intermediate.[4–7] On the other hand, the study of the transformation of fluorine-containing organic compounds has recently attracted much attention,[8] and we have also reported several types of transition-metal catalyzed reactions.[9] For example, we previously reported that the palladium-catalyzed reaction of 1-aryl-2,3,3-trifluoroallyl acetates with carbon nucleophiles afforded branch-type allylic alkylated products,[9a] and during the course of that study, we further found that the reaction of 2,3,3-trifluoroallyl esters with amines provided trifluoromethylenamines[10] as the major products. We now report the synthesis of trifluoromethylenamines using the palladium-catalyzed reaction of 2,3,3-trifluoroallyl esters with amines, which includes the attack of the nitrogen nucleophile on the C-2 carbon of the π-allyl moiety and intramolecular construction of a trifluoromethyl group through a fluorine atom shift *via* C–F bond activation.[11–13]

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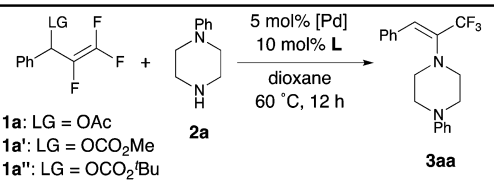
Based on our previous study of the palladium-catalyzed branch selective allylic alkylation of 2,3,3-trifluoroallyl acetates (**1a**) with carbon nucleophiles,[9a] we initially conducted the reaction with 1-phenylpiperazine (**2a**) using a $Pd(OAc)_2$/xantphos (Pd/L = 1/2) catalyst in dioxane at 60 °C. However, the reaction did not produce the intended allylic aminated product, and we confirmed that the reaction provided the unexpected trifluoromethyl group possessing the enamine **3aa**,[14,15] which was formed by the addition of the amine nucleophile at the C-2 position and the fluorine atom shift from the C-2 to the C-3 position, in low yield (Table 1, entry 2). Based on this finding, we attempted to obtain **3aa** in a high yield using a palladium catalyst. To increase the formation of **3aa**, we examined the reaction by $Pd(OAc)_2$ using several phosphine ligands, such as PPh_3, DPPE, BINAP, and DPPF, and found that a good yield (73%) was obtained when DPPF was used as the ligand (Table 1, entries 3–6). Changing the leaving group of the 2,3,3-trifluoroallyl substrates from acetate to methyl or *tert*-butyl carbonate was also effective in increasing the

Table 1 Palladium-catalyzed amination of **1** with **2a**[a]



1a: LG = OAc
1a': LG = OCO_2Me
1a'': LG = $OCO_2{}^tBu$

2a

3aa

Entry	1	L	Yield[b] (%)
1[c]	**1a**	—	0
2	**1a**	Xantphos	21
3	**1a**	PPh_3[d]	0
4	**1a**	DPPE	0
5	**1a**	BINAP	34
6[c]	**1a**	DPPF	73
7	**1a'**	DPPF	77
8	**1a''**	DPPF	92 (88)[e]

[a] Reaction conditions: **1** (0.17 mmol), **2a** (0.24 mmol), 5 mol% of $Pd(OAc)_2$, and 10 mol% of **L** in dioxane (1 mL). [b] NMR yields. [c] The reaction was conducted without the palladium catalyst and the ligand. [d] 20 or 40 mol% of PPh_3 was used. [e] Isolated yields in parentheses.

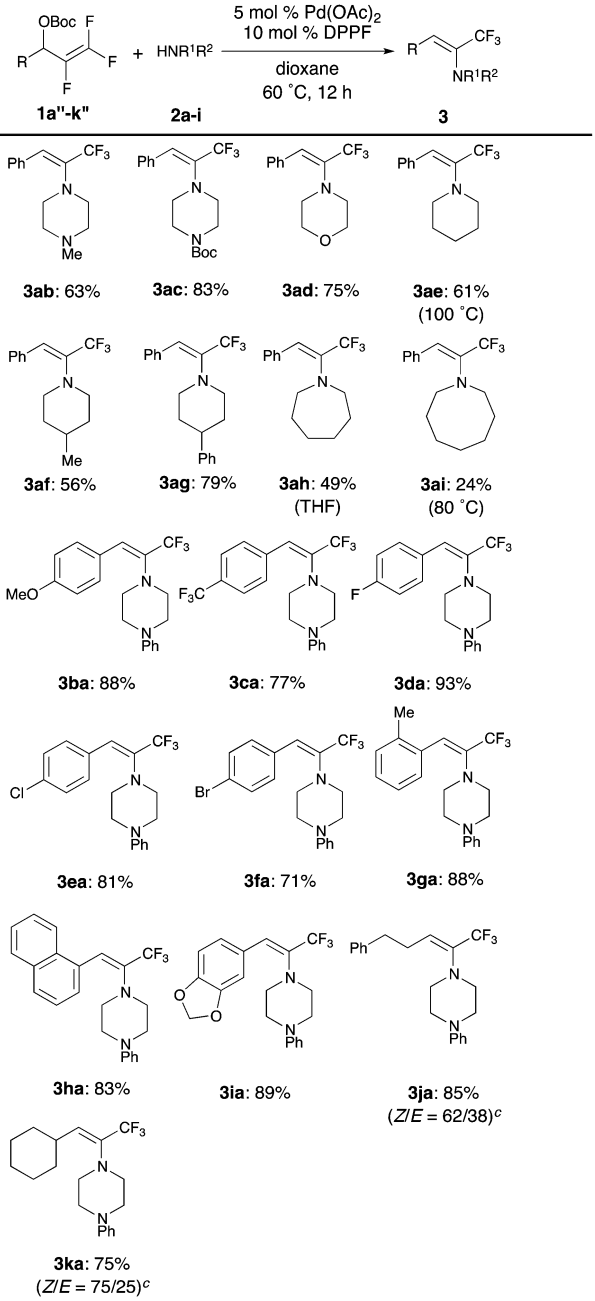
yield (entries 7 and 8), and the reaction of **1a″** using the $Pd(OAc)_2$/DPPF catalyst realized the highest yield (92% NMR yield, 88% isolated yield) (entry 8).

With the optimal conditions in hand, we examined the palladium-catalyzed reaction of the 2,3,3-trifluoroallyl substrates **1a″–k″** with several cyclic amines **2a–i** (Table 2). Although the reaction with **2e** required a higher reaction temperature (100 °C) for obtaining the desired product, most reactions of **1a″** with six-membered aliphatic amines, such as **2b–g**, afforded the intended trifluoromethyl group possessing enamines **3ab–ag** in 56–83% isolated yields. Both reactions with seven- or eight-membered amines (**2h** or **2i**) also provided the intended product but their yields were slightly lower. We further demonstrated the reactions of other 2,3,3-trifluoroallyl esters **1b″–f″**, which contained an electron-donating or withdrawing group at the *para*-position of the phenyl group, and confirmed that all the reactions proceeded smoothly in good to high yields. Allyl substrates **3g″** and **3h″**, which have *o*-tolyl or 1-naphthyl groups located at the C-1 position, also gave the desired products **3ga** and **3ha** in 88% and 83% isolated yields, respectively. Furthermore, although the *Z*/*E* ratio was low, we confirmed that the intended reaction also proceeded for the alkyl group-substituted allyl substrates **1j″** and **1k″**.

To extend the scope of this reaction, we next examined the reaction of **1a″** with several aromatic amines **4a–i**. As shown in Table 3, the *N*-methyl aniline analogues **4a–c** provided the trifluoromethylenamines **5aa–ac** using the $Pd(OAc)_2$/DPPF catalyst at elevated temperatures. The reactions with 1,2,3,4-tetrahydroquinoline (**4d**) or indoline (**4e**) also proceeded smoothly and afforded **5ad** (84% at 100 °C) and **5ae** (81%), respectively. Furthermore, the reactions with the aniline derivatives **4f–i** afforded the intended products **5af–ai** in 45–84% yields.

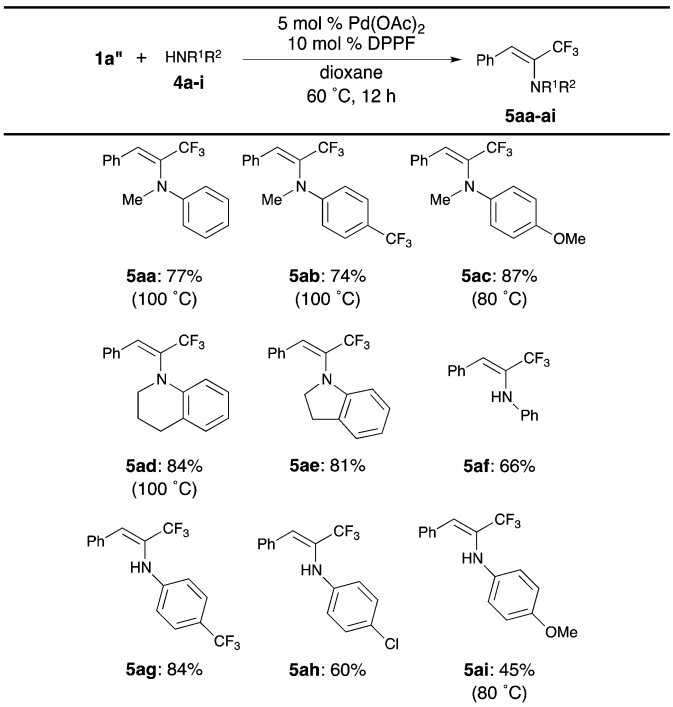
We further examined the reaction of the 2,3,3-trifluoroallyl esters with acyclic secondary aliphatic amines, such as **6a**, but unfortunately, the reaction using the optimized $Pd(OAc)_2$/DPPF catalyst did not provide any desired product (Table 4, entry 1). Therefore, we reinvestigated a suitable palladium catalyst which realized the desired reaction of **1a″** with **6a**. Although

Table 2 Products of the $Pd(OAc)_2$/DPPF-catalyzed amination of **1a″–k″** with cyclic amines[a,b]



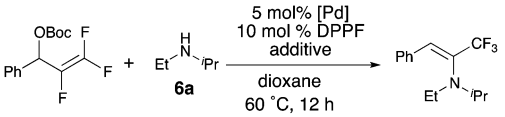
[a] All reactions were carried out with **1** (0.17 mmol), **2** (0.24 mmol), 5 mol% of $Pd(OAc)_2$, 10 mol% of DPPF in dioxane (1.0 mL) at 60 °C for 12 h unless otherwise noted. [b] Isolated yields after chromatography are shown. [c] Ratios were determined by ^1H and ^{19}F NMR analyses of crude materials.

Table 3 Products of the amination of **1a″** with aromatic amines[a,b]



[a] All reactions were carried out with **1a″** (0.17 mmol), **4** (0.24 mmol), 5 mol% of $Pd(OAc)_2$, and 10 mol% of DPPF in dioxane (1.0 mL) at 60 °C for 12 h unless otherwise noted. [b] Isolated yields after chromatography are shown.

Table 4 Palladium-catalyzed amination of **1a″** with **6a**[a]



1a" 7aa

Entry	[Pd]	Additive	Yield[b] (%)
1	$Pd(OAc)_2$	—	0
2[c]	$Pd_2(dba)_3$	—	14
3[c]	$[Pd(C_3H_5)Cl]_2$	—	<2
4	$[Pd(C_3H_5)(cod)]BF_4$	—	25
5	$[Pd(PhC_3H_4)(cod)]BF_4$	—	24
6[d]	$[Pd(C_3H_5)(cod)]BF_4$	$AgBF_4$	65
7[d]	$[Pd(PhC_3H_4)(cod)]BF_4$	$AgBF_4$	75
8[d,e]	$[Pd(C_3H_5)(cod)]BF_4$	$AgBF_4$	68
9[d,e]	$[Pd(PhC_3H_4)(cod)]BF_4$	$AgBF_4$	83 (65)[f]

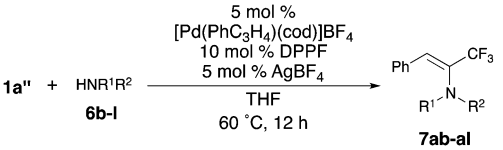
[a] Reaction conditions: **1a″** (0.17 mmol), **6a** (0.24 mmol), 5 mol% of [Pd], and 10 mol% of DPPF in dioxane (1.0 mL). [b] NMR yields. [c] 2.5 mol% of $Pd_2(dba)_3$ or $[Pd(C_3H_5)Cl]_2$ was used. [d] 5 mol% of $AgBF_4$ was added. [e] THF was used as the solvent. [f] Isolated yields in parentheses.

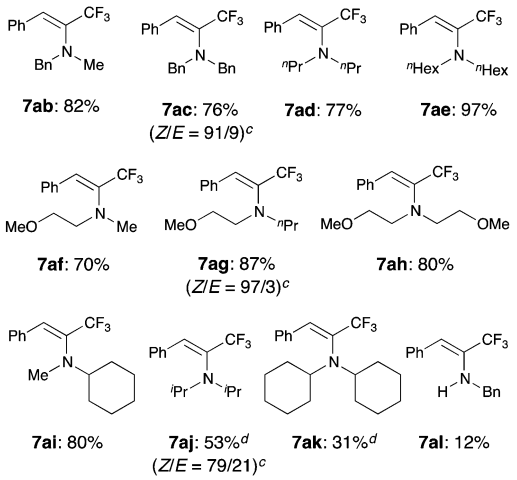
the catalyst activity of $Pd_2(dba)_3$ or $[Pd(C_3H_5)Cl]_2$ with DPPF was low (entries 2 and 3), we found that the $[Pd(C_3H_5)(cod)]BF_4$ or $[Pd(PhC_3H_4)(cod)]BF_4$ with DPPF exhibited slightly better results (entries 4 and 5). We further confirmed that the yields increased upon the addition of $AgBF_4$, and the desired product **7aa** was obtained in 65% (using $[Pd(C_3H_5)(cod)]BF_4$) or 75% yield (using $[Pd(PhC_3H_4)(cod)]BF_4$) (entries 6 and 7). Furthermore, changing the solvent from dioxane to THF in the reaction and using $[Pd(PhC_3H_4)(cod)]BF_4$/DPPF/$AgBF_4$ afforded the highest yield (83% NMR yield) (entry 9). Based on these results, we concluded that $[Pd(PhC_3H_4)(cod)]BF_4$/DPPF/$AgBF_4$ in THF is a suitable catalyst for the reaction with acyclic secondary aliphatic amines.

We next demonstrated the reaction of **1a″** with several acyclic secondary aliphatic amines **6b–l** using $[Pd(PhC_3H_4)(cod)]BF_4$/DPPF/$AgBF_4$ in THF at 60 °C (Table 5). Reactions with several dialkylamines, such as **6b–h**, successfully provided the corresponding trifluoromethylenamines **7ab–ah** in 70–97% isolated yields. We also examined the reaction with some sterically-hindered substituents possessing amines. For example, the reaction with *N*-methylcyclohexanamine (**6i**) proceeded smoothly and provided the intended product **7ai** in 80% yield, but the reaction with diisopropylamine (**6j**) required 10 mol% of the palladium catalyst, and the reaction with dicyclohexylamine resulted in a low yield (31%). These results indicated that the reaction with acyclic secondary aliphatic amines proceeded, but the reactions are very sensitive to the steric factors of amines. Unfortunately, we confirmed that the aliphatic primary amines, such as benzylamine (**6l**), gave a very poor yield (12%).

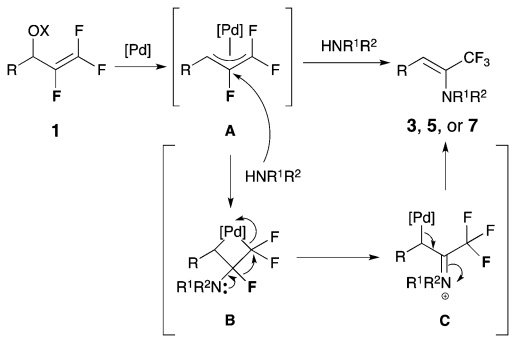
Although the mechanistic details of the present unusual reaction, especially the mechanism of the intramolecular fluorine atom shift, are unclear, we outlined one possible reaction pathway in Scheme 1. The trifluoroallyl substrate **1** forms a fluorine-containing π-allylpalladium complex **A**, then palladacyclobutane **B** was obtained *via* the attack of the nitrogen nucleophile on the central carbon atom of the π-allyl moiety.[4–7] In complex **B**, which might be unstable, the formation of an iminium cation and the following intramolecular fluorine atom shift occurred immediately and afforded the trifluoromethylenamine **3**. On the other hand, we also examined the

Table 5 Products of the $[Pd(PhC_3H_4)(cod)]BF_4$/DPPF/$AgBF_4$-catalyzed amination of **1a″** with **6b–l**[a,b]





[a] All reactions were carried out with **1a″** (0.17 mmol), **6b–l** (0.24 mmol), 5 mol% of $[Pd(PhC_3H_4)(cod)]BF_4$, 10 mol% of DPPF, and 5 mol% of $AgBF_4$ in THF (1.0 mL) at 60 °C for 12 h unless otherwise noted. [b] Isolated yields after chromatography are shown. [c] Ratios were determined by ^1H and ^{19}F NMR analyses of crude materials. [d] The reaction was conducted by 10 mol% of $[Pd(PhC_3H_4)(cod)]BF_4$, 20 mol% of DPPF, and 10 mol% of $AgBF_4$.



Scheme 1 A possible reaction mechanism.

reaction of difluoroallyl ester **8**, and observed that the reaction provided the branch-type allylic aminated product **9** in low yield (eqn (1)). These results suggest that the fluorine atom at the C-2 position is essential to realize the attack of the nitrogen nucleophile on the C-2 carbon and formation of trifluoromethylenamines. Further studies to reveal the details of the reaction mechanism will be the subject of a future study.

(1)

In conclusion, we have demonstrated the palladium-catalyzed reaction of 2,3,3-trifluoroallyl esters with amines and successfully obtained trifluoromethylenamines. Although the exact reaction pathway and mechanism are unclear, the product was formed *via* the attack of nitrogen nucleophiles at the C-2 position and the fluorine atom shift from the C-2 to the C-3 position. The study of the mechanistic details and development of related reactions with other types of nucleophiles are currently underway in our group.

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14 The structure was confirmed by X-ray crystallographic analysis (CCDC-1037126). Please see the ESI† for details.

15 The olefin geometry of other major products was estimated by comparison with that of **3aa**.

