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Photoinduced Synthesis of *P*-Perfluoroalkylated Phosphines from Triarylphosphines and Their Application in the Copper-Free Cross-Coupling of Acid Chlorides and Terminal Alkynes

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Abstract: A practical synthesis yielding *P*-perfluoroalkylated phosphines from triarylphosphines and perfluoroalkyl iodides has been developed. The photoinduced reaction involves the substitution of aryl groups on the phosphorus atom with perfluoroalkyl groups to successfully afford *P*-perfluoroalkylated phosphines. In addition, the *P*-perfluoroalkylated phosphines were found to promote the Cu-free cross-coupling reaction of acid chlorides with terminal alkynes.

Keywords: cleavage reactions; cross-coupling; fluorinated ligands; palladium; phosphanes

Introduction

Phosphines bearing fluorous tags are functional ligands that can aid in the recycling of metal catalysts *via* extraction with a fluorous biphasic system (FBS). This concept was first proposed by Horváth and Rábai in 1994,[1] and numerous studies regarding FBS were subsequently reported.[2] A number of ligands and metal catalysts suitable for FBS have been developed;[3] however, *P*-perfluoroalkylated phosphines, in which a perfluoroalkyl group is directly bonded to the phosphine, have received little attention as ligands,[4] because the electron-withdrawing perfluoroalkyl groups presumably influence the coordination of the phosphine ligands to metal catalysts. However, our research group recently revealed that *P*-perfluoroalkylated phosphine **1** (Figure 1) could form a complex with palladium; common coupling reactions such as Suzuki–Miyaura coupling, Sonogashira coupling, and the Heck reaction proceed successfully in the presence of the complex.[5] Specifically, we found that, when used as a ligand, phosphine **1** had a positive effect on Pd-catalyzed coupling reactions between acid chlorides and terminal alkynes, affording the corresponding ynones under Cu-free conditions.

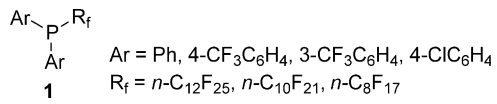

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Figure 1. Directly fluorinated phosphines.

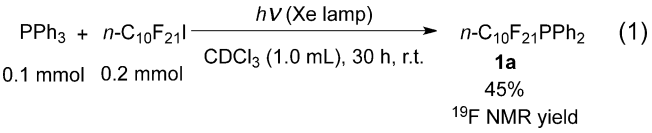
Ynones serve as excellent electrophiles in Michael addition reactions,[6] versatile components in the synthesis of heterocycles,[7] and valuable intermediates in the total synthesis of natural products.[8] The generation of ynones *via* the coupling reaction of acid chlorides with terminal alkynes is one of the most efficient routes towards ynones, and palladium catalysts in the presence of copper salts are typically employed in their synthesis.[9] However, copper salts occasionally induce the Glaser reaction,[10] and therefore, it is desirable to develop Cu-free coupling reactions.[11,12] Moreover, the possibility of catalyst recycling is an advantage in the use of perfluoroalkylated phosphine ligands. Additionally, directly perfluoroalkylated phosphines can be synthesized relatively easily. Our research group previously reported that perfluoroalkylphosphines could be formed by a photoinduced reaction between diphosphines and perfluoroalkyl iodides.[5] However, diphosphines are difficult to handle and synthesize their derivatives. We thus investigated readily available phosphorus sources in order to synthesize perfluoroalkylphosphines. Notably, when triphenylphosphine was used as a starting material,

a photoinduced perfluoroalkylation reaction was observed. Triphenylphosphine is one of the most commonly used phosphine compounds. Although substitution reactions on the phosphorus atom of triarylphosphines are synthetically useful, this type of reaction is still limited,[13] except for the reaction of PAr_3 with alkali metals.[14] Therefore, in this paper, we report a novel synthesis of *P*-perfluoroalkylated phosphines *via* the photoinduced reaction of triarylphosphines with perfluoroalkyl iodides and their application as ligands in the Cu-free Pd-catalyzed coupling reactions between acid chlorides and terminal alkynes.

Results and Discussion

Photoinduced Reaction of Triarylphosphines with Perfluoroalkyl Iodides

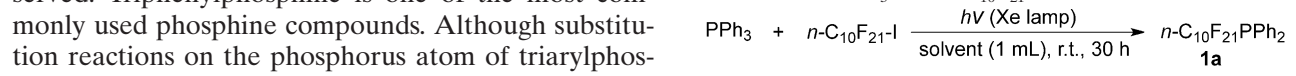
First, we examined the reaction between PPh_3 (0.1 mmol) and *n*-$C_{10}F_{21}$-I (0.2 mmol) under photoirradiation by a xenon lamp (500 W) in a sealed Pyrex NMR tube in $CDCl_3$ [Eq. (1)]. Interestingly, *n*-$C_{10}F_{21}$-PPh_2 (**1a**) was formed in a moderate yield after irradiation for 30 h.



Based on this positive result, the reaction conditions were optimized (Table 1). First, we examined the molar ratio of PPh_3/*n*-$C_{10}F_{21}$-I (entries 1–5). Notably, 0.3/0.1 mmol afforded the highest yield (entry 3). When the solvent was varied, benzotrifluoride (BTF)[15] (entries 6–8) gave the desired product in decent yields. However, when BTF was used, phenylated BTF and perfluoroalkylated BTF were also observed (~5% of both). Conducting the reaction in a sealed quartz tube and irradiation with a tungsten lamp or super-high pressure mercury lamp did not improve the yield (entries 10–12).

Next, the scope and limitations of the photoinduced reaction between triarylphosphines and perfluoroalkyl iodides were investigated (Table 2). Several triarylphosphines such as $(4\text{-}CF_3C_6H_4)_3P$, $(3\text{-}CF_3C_6H_4)_3P$, and $(4\text{-}ClC_6H_4)_3P$ gave the corresponding perfluoroalkylated phosphines in moderate to good yields (entries 2–4). On the other hand, the electron-deficient phosphine $(3,4,5\text{-}F_3C_6H_2)_3P$, and electron-rich phosphines $(4\text{-}CH_3C_6H_4)_3P$ and $(4\text{-}CH_3OC_6H_4)_3P$ did not afford the corresponding perfluoroalkylated phosphines (entries 5–7). The perfluoroalkylation reaction proceeded when both long-chain, *n*-$C_{12}F_{25}I$, and short chain, *n*-$C_8F_{17}I$, perfluoroalkyl iodides were employed,

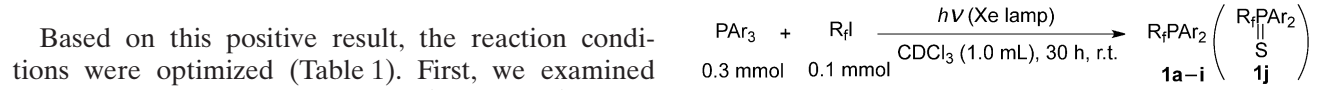
Table 1. Optimization of the reaction conditions in the reaction between PPh_3 and *n*-$C_{10}F_{21}$-I.



Entry	PPh_3 (mmol)	*n*-$C_{10}F_{21}$-I (mmol)	Solvent	Yield (%)[a]
1	0.1	0.1	$CDCl_3$	13
2	0.2	0.1	$CDCl_3$	45
3	0.3	0.1	$CDCl_3$	81 (79)
4	0.4	0.1	$CDCl_3$	71
5	0.6	0.1	$CDCl_3$	43
6	0.3	0.1	CD_3CN	10
7	0.3	0.1	C_6D_6	10
8	0.3	0.1	BTF	62
9	0.1	0.2	BTF	76
10[b]	0.1	0.2	BTF	59
11[c]	0.3	0.1	$CDCl_3$	0
12[d]	0.3	0.1	$CDCl_3$	40

[a] Determined by ^{19}F NMR. Isolated yield is shown in parentheses.
[b] The reaction was conducted in a sealed quartz NMR tube.
[c] Irradiation with a tungsten lamp (450 W).
[d] Irradiation with a super-high pressure mercury lamp (250 W).

Table 2. Scope and limitations of reaction between triarylphosphines and perfluoroalkyl iodides under photoirradiation.



Entry	Ar	R_fI	Product	Yield[a]
1	Ph	*n*-$C_{10}F_{21}I$	**1a**	79%
2	$4\text{-}CF_3C_6H_4$	*n*-$C_{10}F_{21}I$	**1b**	84%
3	$3\text{-}CF_3C_6H_4$	*n*-$C_{10}F_{21}I$	**1c**	84%
4	$4\text{-}ClC_6H_4$	*n*-$C_{10}F_{21}I$	**1d**	73%
5	$3,4,5\text{-}F_3C_6H_2$	*n*-$C_{10}F_{21}I$	**1e**	0%
6	$4\text{-}CH_3C_6H_4$	*n*-$C_{10}F_{21}I$	**1f**	0%
7	$4\text{-}CH_3OC_6H_4$	*n*-$C_{10}F_{21}I$	**1g**	0%
8	$4\text{-}CF_3C_6H_4$	*n*-$C_{12}F_{25}I$	**1h**	71%
9	$4\text{-}CF_3C_6H_4$	*n*-$C_8F_{17}I$	**1i**	83%
10[b]	Ph	*i*-$C_5F_{11}I$	**1j**	39%

[a] Isolated yield.
[b] The product was isolated as a phosphine sulfide.

(entries 8 and 9). The branched perfluoroalkyl iodide *i*-$C_5F_{11}I$ gave the corresponding fluorinated phosphines in moderate yields (entries 10). Because of the low fluorine content of this fluorinated phosphine, it could not be extracted *via* FBS. Therefore, its isola-

tion was carried out *via* silica gel column chromatography as the corresponding phosphine sulfide (**1j**), after treatment with sulfur.

Moreover, in order to elucidate the tolerance of this reaction, trialkylphosphines were examined. When $(n\text{-Bu})_3P$ and $(n\text{-octyl})_3P$ were used, the corresponding *P*-perfluoroalkylated phosphines (**1k** and **1l**) were obtained rapidly in good yields [Eq. (2)]. Overall, the present reaction was tolerant to several triaryl- or trialkylphosphines and perfluoroalkyl iodides and successfully afforded the corresponding *P*-perfluoroalkylated phosphines.

$$\underset{0.3\ \text{mmol}}{PR_3} + \underset{0.1\ \text{mmol}}{n\text{-}C_{10}F_{21}I} \xrightarrow[CDCl_3\ (0.5\ \text{mL}),\ 0.5\ \text{h, r.t.}]{h\nu\ (\text{Xe lamp})} \underset{\mathbf{1}}{n\text{-}C_{10}F_{21}PR_2} \quad (2)$$

R = *n*-Bu, **1k**: 79%
= *n*-octyl, **1l**: 77%
Isolated yield

To obtain insight into the reaction pathway, the perfluoroalkylation reactions were conducted under several conditions [Eq. (3)]. When a mixture of PPh_3 and

$$\underset{0.3\ \text{mmol}}{PPh_3} + \underset{0.1\ \text{mmol}}{n\text{-}C_{10}F_{21}I} \xrightarrow{\text{conditions}} \underset{\mathbf{1a}}{n\text{-}C_{10}F_{21}PPh_2} \quad (3)$$

BTF (2.0 mL), test tube, reflux, dark, 24 h	0%
BTF (2.0 mL), two-necked flask AIBN (0.1 mmol), reflux, dark, 8 h	0%
BTF (1.0 mL), Pyrex NMR tube filter (>350 nm), 30 h	0%

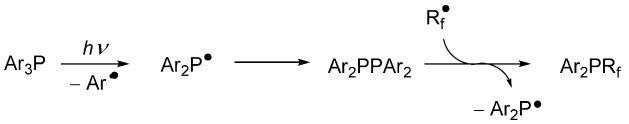
$n\text{-}C_{10}F_{21}\text{-I}$ was heated without irradiation, the desired perfluoroalkylphosphine was not obtained. Heating in the presence of the radical initiator AIBN[16] did not facilitate the perfluoroalkylation reaction. Photoirradiation through a filter (>350 nm) also prevented the reaction. As heating of R_f-I with AIBN and irradiation of R_f-I[17] around 350 nm can cause homolytic cleavage of R_f-I and generate perfluoroalkyl radicals ($R_f^{\bullet}$), these results suggested that $R_f^{\bullet}$ did not trigger the perfluoroalkylation reaction on the phosphorus atom.

Next, photoirradiation of Ar_3P was performed in the absence of R_f-I [Eq. (4)]. Irradiation of PPh_3 and

$$\underset{0.3\ \text{mmol}}{PAr_3} \xrightarrow[BTF\ (1\ \text{mL}),\ \text{r.t.},\ 30\ \text{h}]{\text{Xe lamp}} Ar_2P\text{-}PAr_2 \quad (4)$$

Ar:	yield (%)[a]
C_6H_5	24
3,4,5-$F_3C_6H_2$	0
4-$CF_3C_6H_4$	30

[a] Determined by ^{31}P NMR.



Scheme 1. A proposed reaction pathway for the photoinduced reaction between PAr_3 with R_f-I.

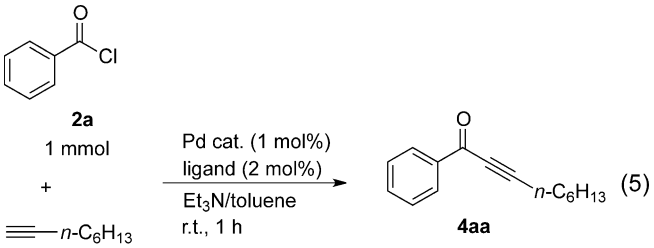
$(4\text{-}CF_3C_6H_4)_3P$ afforded diphosphines,[18] but $(3,4,5\text{-}F_3C_6H_2)_3P$ did not afford the corresponding diphosphine. Triarylphosphines that could give the corresponding diphosphines were required for the perfluoroalkylation reaction.

A proposed reaction pathway for the photoinduced reaction between PAr_3 with R_f-I is illustrated in Scheme 1. It was previously reported that PAr_3 could be excited with a UV laser flash to generate diarylphosphino radicals ($Ar_2P^{\bullet}$).[18,19] In the present reaction, we assumed that $Ar_2P\cdot$ was also generated *via* the cleavage of the C–P bond of PAr_3 upon irradiation with the Xe lamp. The generated $Ar_2P^{\bullet}$ forms diphosphine $Ar_2P\text{-}PAr_2$. Photoirradiation of R_f-I also generated perfluoroalkyl radicals ($R_f^{\bullet}$),[17] and the generated $R_f^{\bullet}$ could attack $Ar_2P\text{-}PAr_2$ to afford the product (Ar_2PR_f). The S_H2 reaction between the phosphorus atom of Ar_3P and the perfluoroalkyl radical does not proceed, because there is no leaving group. However, the formation of $Ar_2P\text{-}PAr_2$ facilitates the attack by the radical and $Ar_2P^{\bullet}$ serves as the leaving group.

Overall, by using triarylphosphines, a practical synthesis of *P*-perfluoroalkylated phosphines **1** has been developed. Next, we investigated the utility of the synthesized *P*-perfluoroalkylated phosphines as ligands.

Cu-Free Pd-Catalyzed Coupling Reaction between Acid Chlorides and Terminal Alkynes Using Perfluoroalkylated Phosphines as Ligands

We previously reported that $n\text{-}C_{10}F_{21}PPh_2$ reacted with $PdCl_2(PhCN)_2$ to form the palladium complex $PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2$.[5] Therefore, reactions using $PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2$ as a catalyst were examined. When the coupling reaction between benzoyl chloride (**2a**) and 1-octyne (**3a**) was conducted in the presence of $PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2$ under Cu-free conditions, surprisingly, the coupling product (1-phenylnon-2-yn-1-one, **4aa**) was obtained in quantitative yield [Eq. (5)]. As a control, the coupling reaction was conducted in the absence of the *P*-perfluoroalkylated phosphine ligand and the desired product was obtained in a low yield. With $Pd(OAc)_2$ alone, the desired product was also obtained in a low yield. In contrast, the use of $Pd(OAc)_2$ with ligand **1a** afforded the product in excellent yield. These results showed that perfluoroal-



Pd catalyst	ligand	NMR yield
$PdCl_2(PhCN)_2$	**1a**	99%
$PdCl_2(PhCN)_2$	none	20%
$Pd(OAc)_2$	**1a**	94%
$Pd(OAc)_2$	none	10%

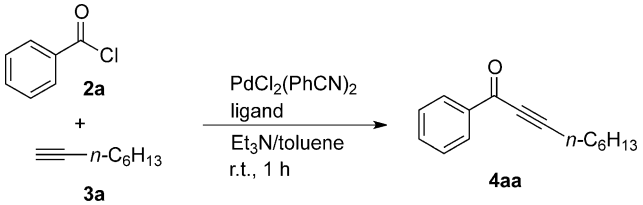
kylphosphine ligand **1a** had a positive effect on the coupling reaction.

Therefore, the effect of phosphine ligand **1** on the coupling reaction between acid chlorides and terminal alkynes was investigated. We first investigated the effects of the electronic properties of the phosphine ligands on the coupling reaction, because a characteristic feature of *P*-perfluoroalkylated phosphines is the electron deficiency (Table 3). The $^{31}P,^{77}Se$ coupling constant ($^1J_{P,Se}$) is known to correlate with the electronic properties of phosphines.[20] Specifically, a large $^1J_{P,Se}$ indicates that the phosphine ligand has a poor electron-donating ability. As such, these values are included in Table 3. When electron-poor phosphines (as compared to PPh_3) such as $(4\text{-}CF_3C_6H_4)_2P(n\text{-}C_{10}F_{21})$, $(4\text{-}CF_3C_6H_4)_3P$, and $(3,4,5\text{-}F_3C_6H_2)_3P$ were used, the coupling reaction proceeded to give **4aa** in excellent yield (entries 2, 7 and 8). In contrast, upon addition of relatively electron-rich phosphines such as $(4\text{-}CH_3C_6H_4)_3P$, $(4\text{-}CH_3OC_6H_4)_3P$, and $(2\text{-}CH_3C_6H_4)_3P$, the coupling reaction did not occur (entries 4–6). These results suggested that electron-deficient ligands were favorable for this coupling reaction.

The tolerance of the base and solvent for the coupling reaction was investigated (Table 4). As expected, the coupling reaction did not proceed in the absence of a base (entry 2). Other organic and inorganic bases were examined in place of Et_3N; however, the coupling reaction did not proceed (entries 3–6). The coupling reaction proceeded well using THF, $CHCl_3$, CH_3CN, and BTF as the solvent (entries 8–11). Decreasing the amount of toluene was also tolerated in the coupling reaction and the use of toluene together with Et_3N represented the optimal conditions for the coupling reaction (entry 12).

With the optimal conditions in hand, the scope of the Cu-free coupling reaction was investigated (Table 5). When several benzoyl chlorides such as *p*-

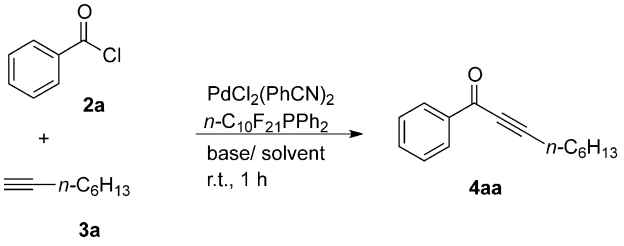
Table 3. Effect of ligands on coupling reaction of benzoyl chloride with 1-octyne.[a]



Entry	Ligand		Yield [%][b]	$^1J_{P,Se}$ [Hz]
	$n\text{-}C_{10}F_{21}PAr_2$			
1	Ar = Ph	**1a**	99	824[c]
2	$4\text{-}CF_3C_6H_4$	**1b**	99	847
	PAr_3			
3	Ar = Ph		trace	729[c]
4	$4\text{-}CH_3C_6H_4$		0	719
5	$4\text{-}CH_3OC_6H_4$		0	712
6	$2\text{-}CH_3C_6H_4$		0	704
7	$4\text{-}CF_3C_6H_4$		92	766[c]
8	$3,4,5\text{-}F_3C_6H_2$		99	792

[a] *Reaction conditions:* benzoyl chloride (0.6 mmol), 1-octyne (0.5 mmol), $PdCl_2(PhCN)_2$ (1 mol%), ligand (2 mol%), Et_3N (0.2 mL), toluene (0.5 mL), room temperature.
[b] Determined by ^1H NMR.
[c] The data are from ref.[5]

Table 4. Influence of base and solvent on the coupling reaction between benzoyl chloride and 1-octyne.[a]

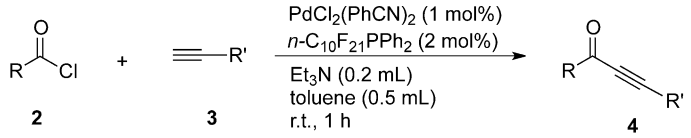


Entry	Base	Solvent	Yield [%][b]
1	Et_3N	toluene	99
2	-	toluene	0
3	$EtN(i\text{-}Pr)_2$	toluene	16
4	pyridine	toluene	0
5	K_2CO_3	toluene	trace
6	KO-*t*-Bu	toluene	7
7	Et_3N	dioxane	57
8	Et_3N	THF	98
9	Et_3N	$CHCl_3$	99
10	Et_3N	CH_3CN	76
11	Et_3N	BTF	82
12[c]	Et_3N	toluene	99 (85)

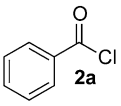
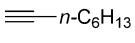
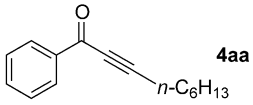
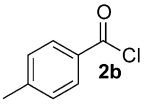
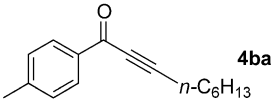
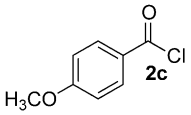
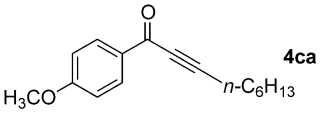
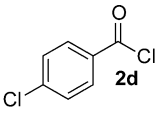
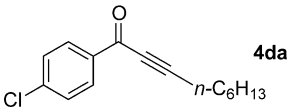
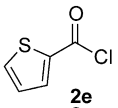
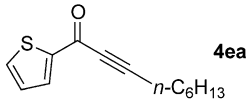
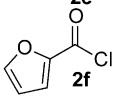
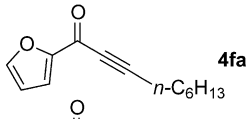
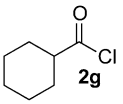
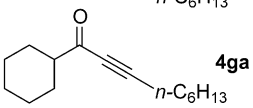
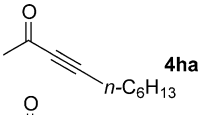
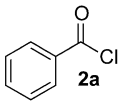
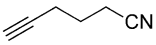
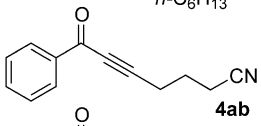
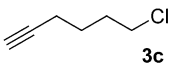
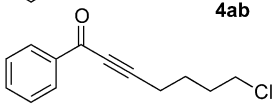
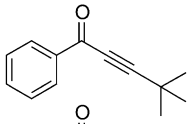
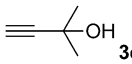
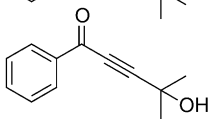
[a] *Reaction conditions:* benzoyl chloride (0.6 mmol), 1-octyne (0.5 mmol), $PdCl_2(PhCN)_2$ (1 mol%), ligand (2 mol%), Et_3N (0.2 mL), toluene (1.5 mL).
[b] Determined by ^1H NMR (isolated yield).
[c] Solvent (0.5 mL).

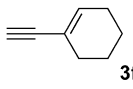
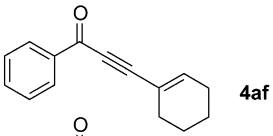
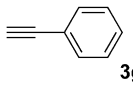
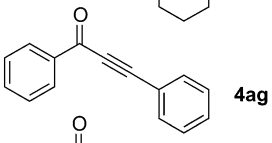
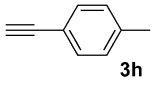
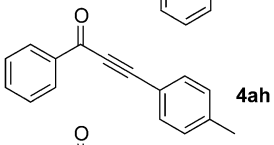
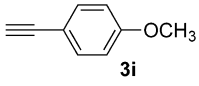
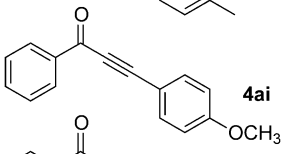
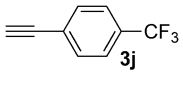
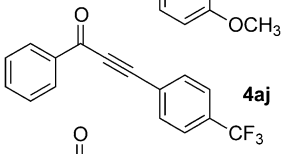
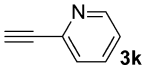
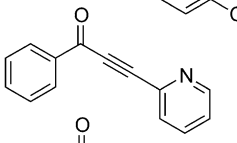
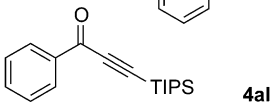
methylbenzoyl chloride, *p*-methoxybenzoyl chloride, and *p*-chlorobenzoyl chloride were coupled with 1-octyne, the corresponding 1-arylnon-2-yn-1-ones were obtained in moderate to good yields (entries 2–4). The use of heteroaromatic acid chlorides also gave the desired products in good yields (entries 5 and 6). Furthermore, an aliphatic acid chloride, cyclohexanecarbonyl chloride, afforded the corresponding ynone successfully and in a good yield (entry 7). On the other hand, with acetyl chloride, the desired coupling

Table 5. Scope and limitations of Cu-free coupling reaction between acid chlorides and terminal alkynes.[a]



2 3 4

Entry	2	3	Product, 4	Yield [%][b]
1	 **2a**	 **3a**	 **4aa**	85
2	 **2b**	**3a**	 **4ba**	76
3	 **2c**	**3a**	 **4ca**	86
4	 **2d**	**3a**	 **4da**	87
5	 **2e**	**3a**	 **4ea**	89
6	 **2f**	**3a**	 **4fa**	85
7	 **2g**	**3a**	 **4ga**	78
8	 **2h**	**3a**	 **4ha**	0
9	 **2a**	 **3b**	 **4ab**	86
10	**2a**	 **3c**	 **4ac**	92
11	**2a**	 **3d**	 **4ad**	86
12	**2a**	 **3e**	 **4ae**	43

Entry	2	3	Product, 4	Yield [%][b]
13	2a	 3f	 4af	83
14	2a	 3g	 4ag	94
15	2a	 3h	 4ah	95
16	2a	 3i	 4ai	87
17	2a	 3j	 4aj	97
18	2a	 3k	 4ak	0
19	2a	 TIPS 3l	 TIPS 4al	97[c]

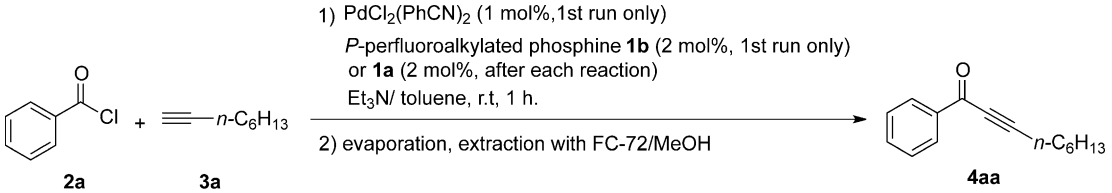
[a] *Reaction conditions:* benzoyl chloride (0.6 mmol), 1-octyne (0.5 mmol), $PdCl_2(PhCN)_2$ (1 mol%), ligand (2 mol%), Et_3N (0.2 mL), toluene (0.5 mL), room temperature.
[b] Isolated yield.
[c] The reaction was conducted at 40 °C for 1.5 h.

product was not obtained (entry 8). When several aliphatic terminal alkynes such as hex-5-ynenitrile, 6-chlorohex-1-yne, and 3,3-dimethylbut-1-yne were employed, the coupling reactions proceeded efficiently (entries 9–11). Although the reaction between acid chlorides and alcohols generally produces esters, the reaction between benzoyl chloride and 2-methylbut-3-yn-2-ol gave the desired coupling product in moderate yield (entry 12). The coupling reactions with conjugated and aromatic alkynes also proceeded efficiently (entries 13–17). However, the use of an alkyne bearing a pyridyl group prevented the coupling reaction (entry 18). Finally, although the coupling reaction that employed triisopropylsilylacetylene required a longer reaction time and higher temperature, the coupling product was obtained in excellent yield (entry 19). As shown in Table 5, the $PdCl_2(n\text{-}C_{10}F_{21}PPh_2)_2$-catalyzed coupling reaction had a relatively high tolerance for a wide range of acid chlorides and terminal alkynes.

Finally, we attempted to recycle the Pd catalyst in the coupling reaction (Scheme 2). In the presence of a catalytic amount of $PdCl_2(PhCN)_2$ and ligand **1b**,[21] the reaction between acid chloride **2a** and alkyne **3a** was examined. After the reaction, the crude product and palladium catalyst were separated *via* FBS and isolated in their respective layers. Next, the reaction between **2a** with **3a** was conducted with the recovered catalyst from the fluorous layer. The palladium catalyst could be reused at least twice[22] to afford the desired coupling product **4aa** in good yields (entry 1). Additionally, we conducted the recycling reaction with addition of a *P*-perfluoroalkylated phosphine ligand **2a** after every coupling reaction. As the result, the coupling products were obtained in higher yields than those without addition of the *P*-perfluoroalkylated phosphine ligand after every reaction (entry 2).

Conclusions

We have developed a facile photoinduced reaction between triarylphosphines and perfluoroalkyl iodides to afford *P*-perfluoroalkylated phosphines. The utility of triarylphosphines as a phosphorus source was highlighted. The synthesized *P*-perfluoroalkylated phosphines can form a complex with palladium, which catalyzes the coupling reaction between acid chlorides and terminal alkynes in the absence of copper iodide. Electron-deficient phosphine ligands had a positive effect on the coupling reaction. This palladium–*P*-per-



	yield of **4aa**[a]			
	1st run	1st recycle	2nd recycle	3rd recycle
entry 1[b]	96%	81%	76% (75%)	-
entry 2[c]	97%	97%	87%	85% (79%)

[a] ^{1}H NMR yield (isolated yield).
[b] *P*-Perfluoroalkylated phosphine (**1b**) was added before first run only.
[c] *P*-Perfluoroalkylated phosphine (**1a**) was added before first run and after every reaction.

Scheme 2. Effects of recycling the palladium catalyst on the coupling reaction between acid chlorides and alkynes.

fluoroalkylated phosphine complex-catalyzed coupling reaction has a tolerance for various aromatic acid chlorides and terminal alkynes. The recyclability of the complex was also demonstrated. Because of the facile synthesis of *P*-perfluoroalkylated phosphines, investigations regarding their potential synthetic applications as well as those of their palladium complexes are ongoing in our laboratory.

Experimental Section

General Comments

$(4\text{-}CF_3C_6H_4)_3P$,[23] $(3\text{-}CF_3C_6H_4)_3P$,[24] $(4\text{-}ClC_6H_4)_3P$,[25] and $(3,4,5\text{-}F_3C_6H_2)_3P$[26] were synthesized according to the literature. Other materials were obtained from commercial suppliers. All liquids were purified by distillation before use except deuterated solvents and alkynes.

General Procedure for the Photoinduced Reaction of Triarylphosphines with Perfluoroalkyl Iodides

PAr_3 (0.3 mmol), perfluoroalkyl iodide (R_f-I, 0.1 mmol), and $CDCl_3$ (1 mL) were placed in a sealed Pyrex glass NMR tube under an argon atmosphere. The mixture was stirred for 30 s and was then irradiated with a xenon lamp (500 W) at room temperature for 30 h. After the reaction, the generation of Ar_2PR_f was confirmed by ^{19}F NMR analysis. The crude mixture was poured into a 30-mL Schlenk flask and evaporated. MeOH (2 mL) was added to the flask, and the product was extracted with FC-72 (3 mL×5). The obtained product was sufficiently pure without further purification The spectral and analytical data of **1a** are shown in ref.[5]

(Perfluorodecyl)bis[4-(trifluoromethyl)phenyl]phosphine (1b): white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.70 (d, J=7.9 Hz, 4H), 7.78 (t, $J_{H,H}=J_{H,P}$=8.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=123.6 (d, $J_{C,P}$=272.8 Hz), 125.7 (dq, $J_{C,F}=J_{C,P}$=3.8 Hz), 132.8 (q, $J_{C,F}$=15.3 Hz), 133.1 (q, $J_{C,F}$=33.4 Hz), 135.3 (d, $J_{C,P}$=22.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ=0.4–1.2 (m); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−126.2 (2F), −122.7 (2F), −121.9 (2F), −121.7 (6F), −121.3 (2F), −117.3 (d, $J_{F,P}$=28.3 Hz, 2F), −108.2 (dt, $J_{F,P}$=57.0 Hz, J=14.3 Hz, 2F), −80.7 (t, J=9.9 Hz, 3F), −63.3 (6F); HR-MS (FAB): m/z=841.0031, calcd. for $C_{24}H_9F_{27}P$ $[M+H]^+$: 841.0011.

(Perfluorodecyl)bis[3-(trifluoromethyl)phenyl]phosphine (1c): white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54 (dd, $J_{H,H}$=7.7, $J_{H,P}$=8.6 Hz, 2H), 7.70 (d, J=7.7 Hz, 2H) 7.78 (dd, $J_{H,H}$=7.7, $J_{H,P}$=7.3 Hz, 2H), 7.85 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=123.9 (q, $J_{C,F}$=272.6 Hz), 128.0 (q, $J_{C,F}$=2.9 Hz), 129.5 (d, $J_{C,P}$=7.7 Hz), 131.7 (q, $J_{C,F}$=24.4 Hz), 131.8 (dq, $J_{C,P}$=20.1 Hz, $J_{C,F}$=3.8 Hz), 138 (d, $J_{C,P}$=20.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ=0.3–1.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.0 (2F), −122.7 (2F), −121.8 (2F), −121.7 (6F), −121.2 (2F) −117.4 (2F), −108.3 (dt, $J_{F,P}$=56.9 Hz, $J_{F,P}$=11.4 Hz, 2F), −80.7 (t, J=11.4 Hz, 3F), 62.9 (6F); HR-MS (FAB): m/z=878.9791, calcd. for $C_{22}H_8F_{27}PONa$ $[M+Na]^+$: 878.9776.

Bis(4-chlorophenyl)(perfluorodecyl)phosphine (1d): white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.41 (d, J=8.8 Hz, 4H), 7.58 (t, $J_{H,H}=J_{H,P}$=8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=129.0 (d, $J_{C,P}$=7.7 Hz), 134.8 (d, $J_{C,P}$=20.0 Hz), 135.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ=−0.7- −0.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−126.1 (2F), −123.6 (2F), −121.2 (8F), −120.8 (2F), −117.8 (d, $J_{F,P}$=21.3 Hz, 2F), −108.8 (dt, $J_{F,P}$=51.5 Hz, J=14.3 Hz, 2F), −80.6 (t, J=11.2 Hz, 3F); HR-MS (FAB): m/z=788.9436, calcd. for $C_{22}H_9Cl_2F_{21}OP$ $[M+H]^+$: 788.9433.

(Perfluorododecyl)bis[4-(trifluoromethyl)phenyl]phosphine (1h): white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.71 (d, J=7.6 Hz, 4H), 7.78 (t, $J_{H,H}=J_{H,P}$=8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=123.8 (q, $J_{C,F}$=271.6 Hz), 125.6 (q, $J_{C,F}$=2.9 Hz), 131.5 (q, $J_{C,F}$=16.7 Hz), 134.0 (d, $J_{C,P}$=20.0 Hz); ^{31}P NM R (162 MHz, $CDCl_3$): δ=0.1–1.0

(m); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -126.0$ (2F), −121.8 (4F), −121.6 (10F), −121.2 (2F), −117.2 (d, $J_{F,P} = 28.5$ Hz, 2F), −108.4 (dt, $J_{F,P} = 56.9$ Hz, $J = 11.4$ Hz, 2F), −80.6 (t, $J = 11.4$ Hz, 3F), −63.2 (6F): HRMS (FAB): $m/z = 955.9811$, calcd. for $C_{26}H_8F_{31}PO$ $[M]^+$: 955.9818.

(Perfluorooctyl)bis[4-(trifluoromethyl)phenyl]phosphine (1i): white solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.71$ (d, $J = 8.2$ Hz, 4H), 7.78 (t, $J_{H,H} = J_{H,P} = 8.2$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 123.6$ (q, $J_{C,F} = 273.7$ Hz), 125.7 (q, $J_{C,F} = 3.8$ Hz), 132.8 (q, $J_{C,F} = 14.3$ Hz), 135.3 (d, $J_{C,P} = 22.9$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 0.26$–1.1 (m); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -126.1$ (2F), −122.7 (2F), −121.9 (2F), −121.8 (2F), −121.3 (2F), −117.6 (d, $J_{F,P} = 19.9$ Hz, 2F), −108.2 (dt, $J_{F,P} = 56.9$ Hz, $J = 11.4$ Hz, 2F), −80.8 (t, $J = 11.4$ Hz, 3F), −63.5 (6F); HR-MS (FAB): $m/z = 757.0009$, calcd. for $C_{22}H_9F_{23}PO$ $[M+H]^+$: 757.0023.

In the case of product **1j**: after the reaction of Ph_3P with R_f-I, the generation of Ph_2PR_f was confirmed by ^{31}P NMR analysis. Sulfur (28.8 mg, 0.9 mmol) was added to the tube, and then the tube was heated at 60 °C after which it was shaken for 30 seconds. The crude mixture was purified by preparative TLC on silica gel.

(Perfluoroisopentyl)diphenylphosphine sulfide (1j): white solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$–7.57 (m, 4H), 7.62–7.64 (m, 2H), (dd, $J_{H,H} = 8.0$ Hz, $J_{H,P} = 13.5$. Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 126.3$ (d, $J_{C,P} = 83.4$ Hz), 129.0 (d, $J_{C,P} = 13.8$ Hz), 133.0 (d, $J_{C,P} = 10.5$ Hz), 133.3 (d, $J_{C,P} = 3.1$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 46.3$ (t, $J_{P,F} = 67.2$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -185.4$ (1F), −113.6 (d, $J = 80.1$ Hz, 2F), −110.6 (d, $J = 80.1$ Hz, 2F), −71.8 (t, $J = 11.5$ Hz, 6F); HR-MS (FAB): $m/z = 487.0131$, calcd. for $C_{17}H_{11}F_{11}PS$ $[M+H]^+$: 487.0143.

Dibutyl(perfluorodecyl)phosphine (1k): colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.93$ (d, $J = 7.5$ Hz, 6H), 1.40–1.53 (m, 8H), 1.57–1.63 (m, 2H), 1.80–1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.6$, 21.6 (d, $J_{C,P} = 15.2$ Hz), 24.2 (d, $J_{C,P} = 13.3$ Hz), 28.0 (d, $J_{C,P} = 16.2$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -3.4$ to −2.6 (m); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -126.1$ (2F), −122.7 (2F), −121.8 (2F), −121.5 (8F), −119.2 (2F), −114.5 (dt, $J_{F,P} = 45.4$ Hz, $J = 11.4$ Hz, 2F), −80.8 (t, $J = 11.2$ Hz, 3F); HR-MS (FAB): $m/z = 681.0850$, calcd. for $C_{18}H_{19}F_{21}PO$ $[M+H]^+$: 681.0838.

Dioctyl(perfluorodecyl)phosphine (1l): colorless oil; H NMR (400 MHz, $CDCl_3$): $\delta = 0.81$ (t, $J = 6.3$ Hz, 6H), 1.21–1.52 (m, 26H), 1.71–1.79 (m, 2H); ^{13}C N MR (100 MHz, $CDCl_3$): $\delta = 14.0$, 21.8 (d, $J_{C,P} = 5.7$ Hz), 22.0 (d, $J_{C,P} = 4.8$ Hz) 22.7, 25.9 (d, $J_{C,P} = 16.8$ Hz), 29.1, 31.1 (d, $J_{C,P} = 12.4$ Hz), 31.8; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -3.6$ to −2.7 (m); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -126.1$ (2F), −122.7 (2F), −121.7 (8F), −121.5 (2F), −119.2 (2F), −114.5 (dt, $J_{F,P} = 45.6$ Hz, $J = 11.4$ Hz, 2F), −80.8 (t, $J = 11.2$ Hz, 3F); HR-MS (FAB): $m/z = 777.2156$, calcd. for $C_{26}H_{35}F_{21}P$ $[M+H]^+$: 777.2141.

Experimental Procedures for the Measurement of ^{31}P,^{77}Se Coupling Constants of Several Phosphine Selenides

Preparation of phosphine selenide: Under inert atmosphere, phosphine (0.1 mmol), selenium powder (23.7 mg, 0.3 mmol), and $CHCl_3$ or toluene were added into a 20-mL two-necked round-bottomed flask equipped with a condenser. The mixture was heated at 100 °C for 48 hours. Then unreacted selenium powder was removed by filtration. Purification of phosphine selenide was performed by preparative TLC on silica gel using AcOEt and hexane as eluent to give pure phosphine selenide. The phosphine selenides (n-$C_{10}F_{21}$)Ph_2P=Se,[5] Ph_3P=Se,[27] (4-$CH_3C_6H_4)_3P$=Se,[27] (4-$CH_3OC_6H_4)_3P$=Se,[27] (2-$CH_3C_6H_4)_3P$=Se,[27] and (4-$CF_3C_6H_4)_3P$=Se[27] are described in the literature.

(Perfluorodecyl)bis[4-(trifluoromethyl)phenyl]phosphine selenide: white solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$ (dd, $J_{H,H} = 8.2$ Hz, $J_{H,F} = 2.7$ Hz, 4H), 8.17 (dd, $J_{H,P} = 13.6$ Hz, $J_{H,H} = 8.2$ Hz, 4H); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 38.1$ (t, $J_{P,F} = 67.1$ Hz, $J_{P,Se} = 847$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -126.1$ (2F), −122.7 (2F), −121.8 (2F), −121.7 (6F), −121.3 (2F), −114.4 (2F), −108.5 (dt, $J_{F,P} = 65.5$ Hz, $J = 14.2$ Hz, 2F), −80.7 (t, $J_{F,P} = 9.9$ Hz, 3F), −63.4 (6F).

Tris(3,4,5-trifluorophenyl)phosphine selenide: white solid; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$ (dt, $J = 14.0$ Hz, 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 117.2$ (m), 126.5 (dd, $J = 80.1$, 4.8 Hz), 142.8 (dt, $J = 264.2$, 15.3 Hz), 151.4 (dqd, $J = 258.0$, 10.5, 2.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 35.3$ (m, $J_{P,Se} = 795$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -128.6$ (d, $J = 22.8$ Hz, 6F), −150.8 (t, $J = 22.8$ Hz, 3F); ^{77}Se NMR (76 MHz, $CDCl_3$): $\delta = -260.0$ (d, $J_{P,Se} = 794$ Hz).

Experimental Procedure for Catalyst Recycling in the Cu-Free Cross Coupling Reactions between Acid Chlorides and Terminal Alkynes Using *P*-Perfluoroalkylated Phosphines

Under an inert atmosphere, $PdCl_2(PhCN)_2$ (1.9 mg, 0.005 mmol), (n-$C_{10}F_{21}$)P(4-$CF_3C_6H_4)_2$ (8.4 mg, 0.010 mmol), toluene (0.5 mL), acid chloride (0.60 mmol), terminal alkyne (0.50 mmol), and Et_3N (0.20 mL, 1.7 mmol) were added into a 20-mL two-necked round-bottomed flask in this order. After the mixture was stirred at room temperature for 1 h, solvents were removed under vacuum. After MeOH (5 mL) was added, the mixture was extracted with FC-72 (5 mL × 5). After the fluorous layer was poured into a 20-mL two-necked round-bottomed flask, the solvent was removed under vacuum. Under an inert atmosphere, toluene (0.5 mL), acid chloride (0.60 mmol), terminal alkyne (0.50 mmol), and Et_3N (0.20 mL, 1.7 mmol) were added to the flask. The second reaction was conducted in a similar fashion. In the recycled reaction, purification was performed *via* preparative TLC on silica gel using AcOEt and hexane (=1:30 in the case of **4aa**) as the eluents to give the coupling product. Structural identification was conducted using ^{1}H NMR, ^{13}C NMR, and GC-MS (EI).

1-Phenyl-2-nonyn-1-one (4aa):[11a] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3H), 1.29–1.35 (m, 4H), 1.43–1.51 (m, 2H), 1.67 (quint, $J = 7.3$ Hz, 2H), 2.49 (t, $J = 7.3$ Hz, 2H), 7.46 (dd, $J = 7.8$, 7.8 Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 1H), 8.18 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 13.9$, 19.1, 22.4, 27.7, 28.5, 31.1, 79.6, 96.8, 128.4, 129.4, 133.7, 136.8, 178.1; MS (EI): $m/z = 214$ (M^+).

1-(4-Methylphenyl)-2-nonyn-1-one (4ba):[11a] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, $J = 6.9$ Hz, 3H), 1.28–1.38 (m, 4H), 1.43–1.52 (m, 2H), 1.67 (quint, $J =$

7.3 Hz, 2H), 2.43 (s, 3H), 2.49 (t, J=7.3 Hz, 2H), 7.26 (d, J=8.2 Hz, 2H), 8.02 (d, J=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.2, 19.4, 21.9, 22.6, 27.9, 28.8, 31.4, 79.9, 96.5, 129.3, 129.8, 134.8, 145.0, 178.1; MS (EI): m/z=228 (M^+).

1-(4-Methoxyphenyl)-2-nonyn-1-one (4ca):[11a] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91 (t, J=6.8 Hz, 3H), 1.29–1.35 (m, 4H), 1.44–1.51 (m, 2H), 1.63–1.71 (m, 2H), 2.49 (t, J=7.3 Hz, 2H), 3.89 (s, 3H), 6.95 (dd, J=6.8, 2.3 Hz, 2H), 8.10 (d, J=6.8, 2.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.2, 19.4, 22.6, 28.0, 28.8, 31.4, 55.7, 79.8, 96.1, 113.9, 130.5, 132.0, 164.4, 177.1; MS (EI): m/z=244 (M^+).

1-(4-Chlorophenyl)-2-nonyn-1-one (4da):[11a] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91 (t, J=7.1 Hz, 3H), 1.30–1.35 (m, 4H), 1.44–1.51 (m, 2H), 1.68 (quint, J=7.3 Hz, 2H), 2.50 (t, J=7.1 Hz, 2H), 7.45 (dt, J=8.7, 2.0 Hz, 2H), 8.07 (dt, J=8.7, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1, 19.4, 22.6, 27.9, 28.8, 31.4, 79.5, 97.7, 129.0, 131.0, 135.5, 140.6, 177.0; MS (EI): m/z=248, 250 (M^+).

1-(2-Thienyl)-2-nonyn-1-one (4ea):[27] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.91 (t, J=7.0 Hz, 3H), 1.30–1.34 (m, 4H), 1.43–1.51 (m, 2H), 1.62–1.70 (m, 2H), 2.47 (t, J=7.0 Hz, 2H), 7.14 (dd, J=5.0, 3.6 Hz, 1H), 7.68 (dd, J=5.0, 1.4 Hz, 1H), 7.89 (dd, J=4.1, 1.4 Hz, 1H); ^{13}C NM R (100 MHz, $CDCl_3$): δ=14.1, 19.2, 22.6, 27.8, 28.7, 31.3, 79.4, 95.5, 128.3, 134.91, 134.94, 145.1, 170.1; MS (EI): m/z=220 (M^+).

1-(2-Furyl)-2-nonyn-1-one (4fa):[28] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.90 (t, J=7.0 Hz, 3H), 1.30–1.34 (m, 4H), 1.42–1.50 (m, 2H), 1.61–1.68 (m, 2H), 2.46 (t, J=7.3 Hz, 2H), 6.57 (dd, J=3.6, 1.8 Hz, 1H), 7.32 (dd, J=3.6, 0.9 Hz, 1H), 7.65 (dd, J=1.8, 0.9 Hz, 1H); ^{13}C NM R (100 MHz, $CDCl_3$): δ=14.1, 19.2, 22.6, 27.7, 28.6, 31.3, 79.1, 95.8, 112.6, 120.7, 147.8, 153.3, 165.1; MS (EI): m/z=204 (M^+).

1-Cyclohexyl-2-nonyn-1-one (4ga):[11a] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.90 (t, J=7.0 Hz, 3H), 1.19–1.35 (m, 6H), 1.36–1.46 (m, 4H), 1.55–1.68 (m, 3H), 1.78 (dt, J=12.2, 7.3 Hz, 2H), 1.97 (dd, J=13.1, 3.2 Hz, 2H), 2.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.2, 19.1, 22.6, 25.6, 26.0, 27.9, 28.4, 28.7, 31.3, 52.4, 80.3, 95.2, 191.9; MS (EI): m/z=220 (M^+).

7-Oxo-7-phenylhept-5-ynenitrile (4ab):[11a] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.04 (quint, J=7.0 Hz, 2H), 2.58 (t, J=7.0 Hz, 2H), 2.71 (t, J=7.0 Hz, 2H), 7.49 (t, J=7.5 Hz, 2H), 7.62 (tt, J=7.3, 1.4 Hz, 1H), 8.11 (dd, J=7.9, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=16.4, 18.2, 23.8, 80.8, 92.7, 118.7, 128.7, 129.5, 134.3, 136.5, 177.8; MS (EI): m/z=197 (M^+).

1-Phenyl-7-chlorohept-2-yn-1-one (4ac): pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.80–1.88 (m, 2H), 1.93–2.00 (m, 2H), 2.55 (t, J=6.8 Hz, 2H), 3.60 (t, J=6.3 Hz, 2H), 7.48 (t, J=7.7 Hz, 2H), 7.60 (tt, J=7.5, 1.4 Hz, 1H), 8.13 (dd, J=7.3, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=18.6, 25.1, 31.5, 44.3, 80.0, 95.5, 128.6, 129.5, 134.0, 136.8, 178.1; MS (EI): m/z=220, 222 (M^+); HR-MS (ESI): m/z=243.0553, calcd. for $C_{13}H_{13}ClONa$ $[M+Na]^+$: 243.0553.

1-Phenyl-4,4-dimethylpent-2-yn-1-one (4ad):[12b] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.39 (s, 9H), 7.47 (t, J=7.7 Hz, 2H), 7.59 (tt, J=7.4, 1.4 Hz, 1H), 8.12 (dd, J=8.6, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=28.1, 30.2, 78.2, 104.0, 128.5, 129.6, 133.9, 137.1, 178.4; MS (EI): m/z=186 (M^+).

1-Phenyl-4-hydroxy-4-methylpent-2-yn-1-one (4ae):[11a] pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.68 (s, 6H), 7.48 (t, J=7.7 Hz, 2H), 7.61 (tt, J=7.5, 1.4 Hz, 1H), 8.12 (dd, J=8.4, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=30.8, 65.4, 80.0, 98.3, 128.7, 129.7, 134.4, 136.6, 178.1; MS (EI): m/z=188 (M^+).

1-Phenyl-3-(1-cyclohexenyl)prop-2-yn-1-one (4af):[11a] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.62–1.74 (m, 2H), 2.18–2.24 (m, 1H), 2.27–2.31 (m, 1H), 6.58–6.60 (m, 1H), 7.48 (t, J=7.7 Hz, 2H), 7.60 (tt, J=7.7, 1.4 Hz, 1H), 8.14 (dd, J=7.7, 0.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.2, 22.1, 26.3, 28.5, 85.4, 95.9, 119.3, 128.6, 129.6, 133.9, 137.2, 142.8, 178.3; MS (EI): m/z=210 (M^+).

1,3-Diphenylprop-2-yn-1-one (4ag):[11a] pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.42 (tt, J=7.3, 1.6 Hz, 2H), 7.46–7.54 (m, 3H), 7.63 (tt, J=7.5, 1.4 Hz, 1H), 7.70 (dd, J=8.4, 1.4 Hz, 2H), 8.23 (dd, J=8.6, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=87.0, 93.2, 120.2, 128.7, 128.8, 129.7, 130.9, 133.2, 134.2, 137.0, 178.1; MS (EI): m/z=206 (M^+).

3-(4-Methylphenyl)-1-phenylprop-2-yn-1-one (4ah):[11a] pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.40 (s, 3H), 7.22 (d, J=7.7 Hz, 2H), 7.51 (t, J=7.7 Hz, 2H), 7.58 (d, J=8.2 Hz, 2H), 7.62 (tt, J=7.5, 1.4 Hz, 1H), 8.22 (dd, J=8.2, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=21.9, 86.9, 93.6, 117.1, 128.7, 129.6, 129.7, 133.2, 134.1, 137.0, 141.7, 178.2; MS (EI): m/z=220 (M^+).

3-(4-Methoxyphenyl)-1-phenylprop-2-yn-1-one (4ai):[11a] yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.86 (s, 3H), 6.94 (d, J=8.2 Hz, 2H), 7.52 (t, J=7.7 Hz, 2H), 7.60–7.66 (m, 3H), 8.20 (d, J=7.7, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.6, 87.0, 94.4, 112.1, 114.6, 128.7, 129.6, 134.0, 135.3, 137.2, 161.9, 178.2; MS (EI): m/z=236 (M^+).

1-Phenyl-3-(4-trifluoromethylphenyl)prop-2-yn-1-one (4aj):[11a] pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.54 (dd, J=7.7, 7.3 Hz, 2H), 7.66 (tt, J=7.7, 1.4 Hz, 1H), 7.69 (d, J=8.6 Hz, 2H), 7.79 (d, J=8.2 Hz, 2H), 8.22 (dd, J=8.4, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=88.2, 90.6, 123.7 (q, $J_{C,F}$=272.8 Hz), 124.0, 125.9 (q, $J_{C,F}$=3.8 Hz), 128.9, 129.8, 132.4 (q, $J_{C,F}$=33.4 Hz), 133.3, 134.6, 136.7, 177.8; ^{19}F NMR (373 MHz, $CDCl_3$): δ=−63.0; MS (EI): m/z=274 (M^+).

1-Phenyl-3-(triisopropylsilyl)prop-2-yl-1-one (4al):[11a] yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.12–1.26 (m, 21H), 7.49 (t, J=7.5 Hz, 2H), 7.61 (tt, J=7.3, 1.4 Hz, 1H), 8.18 (dd, J=7.9, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.2, 18.7, 98.1, 103.2, 128.7, 129.6, 134.2, 136.9, 177.6; MS (EI): m/z=286 (M^+).

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[22] There are some considerable reasons for the low recyclability of the catalyst. Among them, we assume that the oxidation of *P*-perfluoroalkylated phosphine ligand during the coupling reaction causes the low recyclability of the catalyst, because we detected a certain amount of *P*-perfluoroalkylated phosphine oxide after the reaction. Therefore, we conducted the recycling re-

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