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Oxidative Sonogasihira cross-coupling reactions of (*E*)-trimethyl(3,3,3-trifluoroprop-1-enyl)silane with arylacetylene were achieved using silver fluoride and a palladium catalyst, to afford high yields of various 1,3-enynes with a CF_3 group on the terminal sp² carbon. Silver fluoride promoted C-Si bond dissociation and oxidation of palladium, enabling catalytic use of palladium.

terminal arylacetylene.

Introduction

Conjugated 1,3-envne structures are important motifs in organic chemistry, and they are found in many compounds such as natural products¹ and functionalized materials². In organic synthesis, the 1,3-envne motif plays a pivotal role as a versatile building block for constructing numerous compounds such as substituted naphthalenes³ and heterocycles⁴⁻⁷. Additionally, they are present in a wide range of bioactive compounds with promising biological properties, including terbinafine⁸, which is used to treat fungal infections, and NNC 61-4655⁹, which is a peroxisome proliferator-activated receptor agonist and is used to reduce blood lipids. Much effort has been made to develop convenient methods for preparing 1,3-envne motifs, such as dehydration of propargyl alcohol¹⁰, Wittig reactions of propargyl aldehyde¹¹, and Sonogashira cross-coupling reactions¹². A wide range of Sonogashira cross-coupling reactions have been reported and they provide a powerful and direct method for constructing such structures.¹³⁻¹⁹ Despite the great success of Sonogashira cross-coupling reactions in organic synthesis, synthesy approaches to conjugated 1,3-envne structures containing a trifluoromethyl (CF₃) group on the terminal sp^2 carbon remain scarce. 20,21 It is difficult to prepare 1,3-enynes with a CF3 group because of the thermodynamic instability of the structures.

We have shown that (E)-trimethyl(3,3,3-trifluoroprop-1useful reagent for 3,3,3enyl)silane (**1**) is а trifluoropropenylation of aryl iodides to give βtrifluoromethylstyrenes in good yields through Hiyama crosscoupling reaction.²² In this report, we confirmed that the reagent (1) has an obvious advantage in practical operation compared with (E)-1-bromo-3,3,3-trifluoroprop1-ene²³, which

carbon.

been used successfully in many organic syntheses. In 2010, Qing et al. developed the first copper-mediated oxidative trifluoromethylation of terminal alkynes using $CuCF_3^{24}$, which was prepared from (trifluoromethyl)trimethylsilane (Ruppert-Prakash reagent, Me₃SiCF₃) and copper iodide, to afford trifluoromethylated acetylenes in high yields (Scheme 2, condition 1).²⁵ At almost the same time, Zhang et al. reported a similar reaction, performed using Ag₂CO₃, for the

Scheme 1: Oxidative Sonogashira cross-coupling reaction of 1 with

is gaseous material under the atmospheric condition. The

higher boiling point of 1 makes it easy to use for several

reactions. We hypothesized that the trifluoromethylated 1,3-

enyne structure could be effectively constructed via an

oxidative Sonogashira cross-coupling reaction of 1 with

terminal arylacetylene groups (Scheme 1). The Sonogashira

cross-coupling reaction of 1 with phenylacetylene was

performed using silver fluoride (AgF) in the presence of a

palladium catalyst to give the desired product in 93% yield.

Here, we describe in detail our method for the construction of

conjugated 1,3-enynes with a CF_3 group on the terminal sp^2

The Sonogashira cross-coupling reaction, which is one of the

$$\mathsf{R} \longrightarrow \mathsf{H} \quad \mathsf{Me}_3\mathsf{SiCF}_3 \xrightarrow[]{\begin{array}{c} \mathsf{condition A} \\ \mathsf{Cul / phen, KF, DMF} \\ 100^\circ\mathsf{C}, \mathsf{O}_2(\mathsf{air}) \\ \hline \\ \mathsf{condition B} \\ \mathsf{CuCl, phen, 'BuOK} \\ \mathsf{Ag}_2\mathsf{CO}_3, \mathsf{DMF} \end{array}} \quad \mathsf{R} \longrightarrow \mathsf{CF}_3$$

Scheme 2: Current approaches to trifluoromethylation of arylacetylenes using Sonogashira cross-coupling reaction.



-CF₂

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Sonogashira cross-coupling of Me_3SiCF_3 with arylacetylenes (Scheme 2, condition 2).²⁶ These reactions are classified as oxidative Sonogashira cross- coupling reactions, and they enable C-C bond formation between nucleophilic partners in contrast to usual Sonogashira cross-coupling reactions. On the basis of these reports, we expected that oxidative Sonogashira cross-coupling reactions with **1** instead of Me_3SiCF_3 would provide 1,3-enyne structures containing a CF_3 group on the terminal sp² carbon.

Results and discussion

First, we examined the Sonogashira cross-coupling reaction of 1 with phenylacetylene (2a) using AgF, which acted as both a source of fluoride anions and a palladium oxidant (Table 1). The reaction conducted using AgF and NaHCO₃ in the presence of Pd(OAc)₂ proceeded quickly to give homocoupling product of 2a in good yield (Table 1, entry 1). Even when the reaction temperature was lowered to 0 °C, and a longer time was used, the reaction resulted in predominant formation of the homocoupling product of 2a (Table 1, entry 2). When a mixture of 1 and 2a dissolved in CH₃CN was added dropwise to the reaction during 1 h, the desired cross-coupling product (3a) was obtained in 14% yield, along with a large amount of homocoupling product (Table 1, entry 3). This result indicated that the desired reaction was possible, and encouraged us to investigate other reaction conditions. We explored the use of different bases such as Et₃N and K₂CO₃ to increase the yield of 3a, but they were not effective in the reaction (Table 1, entries 4 and 5). To investigate the role of the fluoride anion, CuF_2 , CsF_2

Table 1: Investigation of reaction condition."								
				F anion	, Pd cat. (5 mol?	%)		\sim
()		Ĭ	+ TMS	base, solv., time, rt		Ţ		
	\sim	2a		1		\sim		3a
	entry	1 (eq) ^b	F anion(eq) ^b	Pd cat.	base (eq) ^b	solv.	time (h)	yield (%
	1 ^{<i>d</i>}	2	AgF (2)	Pd(OAc) ₂	NaHCO ₃ (1)	CH ₃ CN	1	0
	2 ^{<i>d,e</i>}	2	AgF (2)	Pd(OAc) ₂	NaHCO ₃ (1)	CH ₃ CN	2	0
	3	2	AgF (2)	Pd(OAc) ₂	NaHCO ₃ (1)	CH ₃ CN	2	14
	4	2	AgF (2)	Pd(OAc) ₂	Et ₃ N (1)	CH ₃ CN	2	trace
	5	2	AgF (2)	Pd(OAc) ₂	K ₂ CO ₃ (1)	CH ₃ CN	2	0
	6	2	CuF ₂ (3)	Pd(OAc) ₂	Ag ₂ CO ₃ (3)	CH ₃ CN	3	0
	7	2	CsF (3)	Pd(OAc) ₂	Ag ₂ CO ₃ (3)	CH ₃ CN	3	0
	8	2	ZnF ₂ (3)	Pd(OAc) ₂	Ag ₂ CO ₃ (3)	CH ₃ CN	3	0
	9	2	AgF (3)	Pd(OAc) ₂	-	CH ₃ CN	2	21
	10	2	AgF (3)	Pd(OAc) ₂	-	DMF	1	0
	11	2	AgF (3)	Pd(OAc) ₂	-	DMA	1	trace
	12	2	AgF (3)	Pd(OAc) ₂	-	THF	1	0
	13	2	AgF (3)	PdCl ₂	-	CH ₃ CN	3	12
	14	2	AgF (3)	Pd(PPh ₃) ₂ Cl ₂	-	CH ₃ CN	3	2
	15	2	AgF (3)	Pd(dppe) ₂ Cl ₂	-	CH ₃ CN	3	2
	16	2	AgF (3)	Pd(dppf) ₂ Cl ₂	-	CH_3CN	3	1
	17 ^f	4	AgF (4)	Pd(OAc) ₂	-	CH ₃ CN	5	72
	18 ^f	5	AgF (5)	Pd(OAc) ₂	-	CH ₂ CN	5	101

^{*a*}The reaction was carried out with **2a** (0.16 mmol) in CH₃CN at room temperature. ^{*b*}The number of equivalents with respect to **2a** (0.16 mmol). ^{*c*}NMR yields of **3a**, which were calculated by integration of the ¹⁹F NMR signals of **3a** relative to an ethyl trifluoroacetate standard. ^{*d*}The reaction was carried out without dropwise addition of **1** and **2a**. ^{*e*}The reaction was performed at 0 °C. ^{*f*}The reaction was performed at a 0.2M concentration. ^{*g*}Isolated yields.

CH₃CN

102(93)^g

Pd(OAc)₂

and ZnF₂ were used, with Ag₂CO₃ as a silver source; however, the desired product was not obtained (Table 12,3 entries 16.38). These results indicated that AgF was a better reagent for accomplishing the reaction. The yield of **3a** was increased by increasing the amounts of AgF (Table 1, entry 9). Other solvents such as DMF, DMA, and THF were not suitable, and resulted in the decomposition of **2a** (Table 1, entries 10-12). Other palladium catalysts such as PdCl₂ and Pd(PPh₃)₂Cl₂, were tested, but gave poor yields of **3a** compared with Pd(OAc)₂ (Table 1, entries 13-16). When increasing both the amounts of AgF and **1** to 5 equivalents, the reaction was proceeded effectively to obtain **3a** in high yield (Table 1, entry 18). Finally, we found that the amounts of **1** could be decrease to 4 equivalents without the loss of the yield of **3a**; therefore, the reaction condition shown in entry 19 was found to be the best.

With the optimal reaction conditions in hand, we investigated the scope and limitations of this Sonogashira



^aThe reactions were carried out with **1** (0.64 mmol), **2** (0.16 mmol), AgF (0.8 mmol), and Pd(OAc)₂ (5 mol%) in CH₃CN (0.8 mL) at room temperature for 5 h. ^bIsolated yields. ^cNMR yields of **3**, which were calculated by integration of the ¹⁹F NMR signals of **3** relative to that of an internal standard, ethyl trifluoroacetate.

AgF (5)

19^f

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^aThe reactions were carried out with 2a (0.16 mmol) in CH₃CN (0.8 mL) at room temperature for 5h.



Scheme 3: Plausible reaction mechanism for oxidative Sonogashira cross-coupling reaction.

cross-coupling reaction, using terminal alkynes with different electronic and steric properties as substrates (Table 2). Substrates with electron-donating groups (**2b-d**) showed good reactivities and gave good yields of **3b-d** (Table 2, entries 1-3). In contrast, arylacetylenes with electron-withdrawing substituents (**2e-g**) gave more moderate yields (Table 2, entries 4-6). Extension of the reaction time did not improve the product yield. An arylacetylene with steric hindrance at *ortho* position was tolerated in the reaction, and afforded **3h** in 99% yield (Table 2, entry 7). Unfortunately, nitrogencontaining arylacetylenes **2j** and **2k** were not tolerated and decomposed under these reaction conditions.

Further control experiments were conducted to investigate the mechanism of this Sonogashira cross-coupling reaction (Table 3). When the reaction was performed without a silver salt, the desired product (**3a**) was not formed and phenylacetylene (**2a**) remained in the reaction mixture (Table 3, entry 1). Additionally, the reaction with oxygen as the oxidant instead of a silver salt gave the homocoupling product of **2a** (Table 3, entry 2). These results suggest that AgF plays a key role in this coupling reaction and acts as an oxidant for palladium catalyst. In the absence of a palladium catalyst, **2a** decomposed, and a complex mixture was obtained (Table 3, entry 3). This result indicates that a palladium catalyst is needed for the catalytic cycle.

Details of the proposed mechanism are outlined in Scheme 3. The catalytic cycle begins with generation of intermediate 4 by exchange of X for a $CH=CHCF_3$ group on the palladium catalyst. Then intermediate 5 is formed by transmetallation of X with the alkyne group in 4. Reductive elimination of 5 provides both the desired product **3** and palladium (0), which is subsequently oxidized by the silver salt to generate palladium ($\frac{10}{10}$ palladiu

Conclusions

We have demonstrated an effective and convenient method for preparing conjugated 1,3-enynes with a CF_3 group on the terminal sp^2 carbon via an oxidative Sonogashira crosscoupling of **1** with arylacetylenes in the presence of AgF under palladium-catalyzed conditions. Various arylacetylenes participated in the reaction to give the desired 1,3-enynes in good yields. Further studies are ongoing to clarify the reaction mechanism.

Experimental

General information

All experiments were carried out under an argon atmosphere in flame-dried glassware and used standard inert techniques for introducing reagents and solvents unless otherwise noted. All commercially available reagents were used as received without further purification. In solvents, acetonitrile (CH₃CN), *N,N*-dimethylformamide N,N-dimethylacetamide (DMF), (DMA) and dimethoxyethane (DME) were distilled over calcium hydride and stored in a bottle with activated molecular sieves (4Å). Tetrahydrofuran (THF) was distilled over benzophenone ketyl sodium just before use. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at room temperature on JNM-GX400 spectrometers. ¹⁹F NMR spectrum was recorded at room temperature on Hitachi FT-NMR R-90H spectrometer. Chemical shifts of ¹H NMR and ¹³C NMR are reported in parts per million (ppm) from an internal standard, tetramethylsilane (TMS, 0.00 pm) and CHCl₃ (77.0 ppm), respectively. Chemical shifts of ¹⁹F NMR are reported in ppm from CFCl₃ (0.00 ppm) as an internal standard. All data are reported as follow; chemical shifts relative integration value, number of equivalent nuclei, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants J (Hz). High-resolution mass spectroscopy (HRMS) experiments were performed with a double-focusing mass spectrometer with EI ionization on JEOL JMS-700T spectrometer. Melting points were measured on Yanagimoto micro melting point apparatus MP-S3.

Typical procedure for Sonogashira cross-coupling reaction

Under argon atmosphere, AgF (101 mg, 0.8 mmol) and palladium acetate (1.8 mg, 5 mol%) were placed in a glassware and dissolved in anhydrous CH₃CN (0.4 mL). To the mixture was added the solution of **1** (108 mg, 0.64 mmol) and arylacetylenes (0.16 mmol) dissolved in CH₃CN (0.4 mL) over 1 hour at room temperature. After the reaction mixture was stirred for another 5 hours, it was poured into water to quench the reaction. The resulting mixture was filtered off to remove the silver salt, and the filtrate was extracted with Et₂O, and the organic layer was dried over anhydrous MgSO₄. After filtration

of the solid, the solvent was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the title compound **3**.

(E)-(5,5,5-Trifluoropent-3-en-1-ynyl)benzene 3a

The title product (**3a**) was obtained as a colorless oil (29.1 mg, 93%) after column chromatography (hexane 100%). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 6.15 (1H, qd, *J* 6.8, 15.9 Hz), 6.49 (1H, qd, *J* 2.1, 16.1 Hz), 7.32-7.38 (3H, m), 7.46-7.48 (2H, m); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 84.1, 96.3, 118.9 (q, *J* 8.1 Hz), 121.8, 122.5 (q, *J* 268.8 Hz), 127.2 (q, *J* 33.9 Hz), 128.4, 129.3, 131.8; $\delta_{\rm F}$ (CDCl₃, 90 MHz) - 65.45 (3F, d, *J* 6.0 Hz); *m/z* (EI) 196.498 (M⁺. C₁₁H₇F₃ requires 196.0500).

(E)-1-tert-Butyl-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene 3b

The title product (**3b**) was obtained as a light yellow solid (39.9 mg, 99%) after column chromatography (hexane 100%). mp 66-67 °C; $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.32 (9H, s), 6.13 (1H, qd, *J* 6. 8, 15.9 Hz), 6.49 (1H, qd, *J* 2.2, 15.9 Hz), 7.37 (2H, d, *J* 8.3 Hz), 7.41 (2H, d, *J* 8.8 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 31.2, 35.0, 83.6, 96.7, 118. 8, 119.1 (q, *J* 7.8 Hz), 122.6 (q, *J* 268.8 Hz), 125.5, 126.8 (q, *J* 33.6 Hz), 131.6, 152.7; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -66.34 (3F, d, *J* 7.0 Hz); m/z (EI) 252.129 (M⁺. $C_{15}H_{15}F_{3}$ requires 252.1126).

(E)-1-Ethyl-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene 3c

The title product (**3c**) was obtained as a colorless oil (33.9 mg, 95%) after column chromatography (hexane 100%). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.24 (3H, t, J 7.6 Hz), 2.66 (2H, q, J 7.7 Hz), 6.12 (1H, qd, J 6.8, 15.9 Hz), 6.49 (1H, qd, J 2.3, 15.9 Hz), 7.18 (2H, d, J 7.8 Hz), 7.39 (2H, d, J 7.8 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 15.3, 29.0, 83.6, 96.7, 119.0 (q, J 7.8 Hz), 122.4 (q, J 269.3 Hz), 126.7 (q, J 33.6 Hz), 128.0, 131.8, 145.1; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.34 (3F, d, J 6.4 Hz); m/z (EI) 224.0816 (M⁺. C₁₃H₁₁F₃ requires 224.0813).

(E)-1-Methoxy-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene 3d

The title product (**3d**) was obtained as a colorless oil (32.9 mg, 91%) after column chromatography (hexane 100%). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 3.82 (3H, s), 6.10 (1H, qd, *J* 6.8, 16.0 Hz), 6.48 (1H, qd, *J* 2.3, 15.9 Hz), 6.87 (2H, d, *J* 8.7 Hz), 7.41 (2H, d, *J* 8.8 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 55.5, 83.2, 96.7, 113.9, 114.1, 119.1 (q, *J* 7.8 Hz), 122.7 (q, *J* 268.8 Hz), 126.2 (q, *J* 32.6 Hz), 133.4, 160.4; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.23 (3F, d, *J* 6.4 Hz); *m/z* (EI) 226.0607 (M⁺. C₁₂H₉F₃O requires 226.0605).

(E)-1-Fluoro-4-(5,5,5-trifluoropent-3-en-1-ynyl)benzene 3e

The title product (**3e**) was obtained as a colorless oil (23.0 mg, 60%) after column chromatography (hexane 100%). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 6.14 (1H, qd, *J* 6.8, 15.9 Hz), 6.47 (1H, qd, *J* 2.3, 15.8 Hz), 7.05 (2H, dd, *J* 8.8, 8.8 Hz), 7.46 (2H, dd, *J* 8.6, 8.8 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 83.9 (q, *J* 1.7 Hz), 95.2 (q, *J* 1.6 Hz), 115.8 (d, *J* 21.6 Hz), 117.9 (d, *J* 3.3 Hz), 18.7 (d, *J* 7.8 Hz), 122.5 (q, *J* 268.8 Hz), 127.3 (q, *J* 33.4 Hz), 133.8 (d, *J* 8.4 Hz), 163.0 (d, *J* 24.1 Hz); $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.46 (3F, d, *J* 6.0 Hz), 40.30-40.05 (1F, m); m/z (EI) 241.0407 (M⁺. C₁₁H₄F₄ requires 214.0406).

(E)-1-(4-(5,5,5-Trifluoropent-3-en-1-ynyl)phenyl)ethanone 3f

The title product (**3f**) was obtained as a colorless oil (24.7 mg, 65%) after column chromatography (CH₂Cl₂ : hexane = 30:70). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 2.61 (3H, s), 6.21 (1H, qd, *J* 6.7, 16.1 Hz), 6.51 (1H, qd, *J* 2.7, 16.1 Hz), 7.67 (2H, d, *J* 8.3 Hz), 7.94 (2H, d, *J* 8.8 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 26.7, 86.8, 95.1, 118.4 (q, *J* 7.8 Hz), 122.3 (q, *J* 268.9 Hz), 126.5, 128.2, 128.2 (q, *J* 33.9 Hz), 131.9, 137.0, 197.0; δ_F (CDCl₃, 90 MHz) -65.60 (3F, d, J_{Λ} , A_{Λ} , $A_$

(E)-Ethyl 4-(5,5,5-trifluoropent-3-en-1-ynyl)benzoate 3g

The title product (**3g**) was obtained as a colorless oil (23.6 mg, 61%) after column chromatography (CH₂Cl₂ : hexane = 30:70). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.40 (3H, t, J 7.1 Hz), 4.39 (2H, q, J 7.0 Hz), 6.20 (1H, qd, J 6.6, 15.9 Hz), 6.50 (1H, qd, J 2.2, 15.9 Hz), 7.5 (2H, d, J 8.3 Hz), 8.03 (2H, d, J 8.3 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 14.4, 61.3, 86.4, 95.3, 118.5 (q, J 8.3 Hz), 122.4 (q, J 269.1 Hz), 126.2, 128.2 (q, J 34.2 Hz), 129.5, 131.0, 131.7, 165.6; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.61 (3F, d, J 6.0 Hz); *m/z* (EI) 268.073 (M⁺. C₁₄H₁₁F₃O₂ requires 268.0711).

(E)-1-Methoxy-2-(5,5,5-trifluoropent-3-en-1-ynyl)benzene 3h

The title product (**3h**) was obtained as a colorless oil (35.9 mg, 99%) after column chromatography (hexane 100%). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 3.89 (3H, s), 6.16 (1H, qd, J 6.8, 16.0 Hz), 6.55 (1H, qd, J 2.4, 15.9 Hz), 6.89-6.95 (2H, m), 7.32-7.37 (1H, m), 7.41-7.43 (1H, m); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 55.8, 88.0, 93.0, 110.7, 111.0, 119.1 (q, J 7.8 Hz), 120.5, 122.6 (q, J 268.8 Hz), 126.7 (q, J 33.6 Hz), 130.9, 133.7, 160.1; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.33 (3F, d, J 6.4 Hz); m/z (EI) 226.0605 (M⁺. $C_{12}H_9F_3O$ requires 226.0605).

(E)-1-(5,5,5-Trifluoropent-3-en-1-ynyl)naphthalene 3i

The title product (**3i**) was obtained as a colorless oil (37.6 mg, 95%) after column chromatography (hexane 100%). $\delta_{\rm H}$ (CDCl₃, 400 MHz) 6.27 (1H, qd, *J* 6.8, 16.1 Hz), 6.66 (1H, qd, *J* 2.4, 15.9 Hz), 7.44-7.48 (1H, m), 7.53-7.63 (2H, m), 7.71-7.73 (1H, m), 7.87-7.90 (2H, m), 8.23 (1H, d, *J* 8.3 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 88.6, 94.5, 118.9 (q, *J* 8.1 Hz), 119.4, 122.6 (q, *J* 268.3 Hz), 125.1, 125.4, 126.0, 127.1, 127.2 (q, *J* 33.6 Hz), 128.4, 129.9, 131.2, 133.0, 133.1; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.35 (3F, d, *J* 6.0Hz); *m/z* (EI) 246.0650 (M⁺. C₁₅H₉F₃ requires 246.0656).

(E)-2-(5,5,5-Trifluoropent-3-en-1-ynyl)benzenamine 3j

The title product (**3***j*) was obtained as a yellow solid after column chromatography (CH₂Cl₂ : hexane = 30 : 70). mp 31-33 $^{\circ}$ C; δ_{H} (CDCl₃, 400 MHz) 4.22 (2H, br s), 6.13 (1H, qd, *J* 6.8, 15.7 Hz), 6.54 (1H, qd, *J* 2.4, 15.7 Hz), 6.69-6.72 (2H, m), 7.15-7.19 (1H, m), 7.28-7.30 (1H, m); δ_{C} (CDCl₃, 400 MHz) 89.5, 93.8, 106.3, 114.5, 118.0, 118.6 (q, *J* 8.1 Hz), 122.6 (q, *J* 269.8 Hz), 126.4 (q, *J* 33.6 Hz), 130.9, 132.5, 148.2; δ_{F} (CDCl₃, 90 MHz) - 65.26 (3F, d, *J* 6.0 Hz); *m/z* (EI) 211.0610 (M⁺. C₁₁H₈F₃N requires 211.0609).

(E)-6-(5,5,5-Trifluoropent-3-en-1-ynyl)quinolone 3k

The title product (**3k**) was obtained as a light yellow solid after column chromatography (AcOEt : hexane = 70 : 30). mp 62-63 °C; $\delta_{\rm H}$ (CDCl₃, 400 MHz) 6.22 (1H, qd, *J* 6.7, 15.8 Hz), 6.55 (1H, qd, *J* 2.3, 15.9 Hz), 7.44 (1H, dd, *J* 3.9, 8.3 Hz), 7.73 (1H, dd, *J* 1.4, 8.8 Hz), 7.97-7.98 (1H, m), 8.07-8.14 (2H, m), 8.94 (1H, dd, *J* 1.5, 4.4 Hz); $\delta_{\rm C}$ (CDCl₃, 400 MHz) 85.1, 95.7, 118.6 (q, *J* 7.8 Hz), 120.1, 121.9, 122.4 (q, *J* 269.1 Hz), 127.8 (q, *J* 34.2 Hz), 127.8, 129.9, 131.7, 131.9, 135.8, 148.0, 151.4; $\delta_{\rm F}$ (CDCl₃, 90 MHz) -65.46 (3F, d, *J* 6.0 Hz); *m/z* (EI) 247.0611 (M⁺. C₁₁H₈F₃N requires 247.0609).

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