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ARTICLE

Fluoroalkenylation of boronic acids via oxidative Heck reaction

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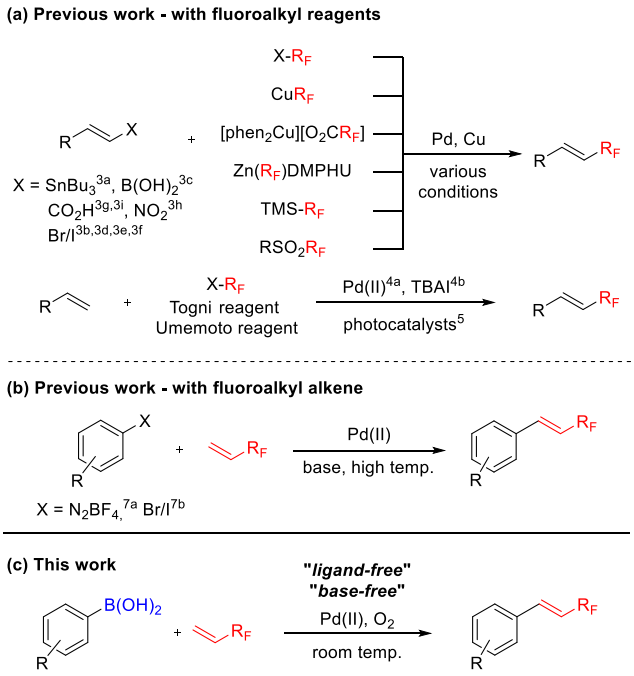
A fluoroalkenylation of boronic acids with fluoroalkyl alkenes has been developed. The Pd-catalyzed oxidative Heck coupling reaction proceeds under oxygen atmosphere at room temperature, in the absence of base and/or ligand, showing excellent practicality of the process. This simple transformation is highly stereoselective to provide only *E*-isomers. In addition to the general approach using alkenes with functionalized fluoroalkyl reagents, this method, transferring aromatic system into the electron-deficient fluoroalkyl alkene, provides an efficient alternative way to yield valuable organofluorines.

Introduction

Fluoroalkylated compounds possess unique characteristics such as high lipophilicity, bioavailability, and metabolic stability compared to their non-fluoroalkylated analogues.[1] Therefore, a wide range of fluoroalkylation reactions have been developed. The synthesis of fluoroalkylated alkenes, in particular, has been of great interest.[2] The fluoroalkenyl motif is present in a variety of functional molecules, including pharmaceuticals. Fluoroalkenyl molecules also serve as versatile synthetic building blocks owing to the high reactivity of the unsaturated alkenyl moiety towards a variety of organic transformations.

Synthesis of fluoroalkylated alkenes has been reported through many methods. Pd- or Cu-catalyzed traditional coupling reactions utilized functionalized alkenyl precursors such as organotin compounds or carboxylic acids with fluoroalkyl reagents to generate fluoroalkylated alkene complexes (Scheme 1a).[3] Likewise, synthetic protocols for the reaction of unfunctionalized, simple alkenes with fluoroalkyl halides have also been developed.[4] However, these reactions require high temperature and use of base or/and ligand additives. Recent advances in visible light photocatalysis of unactivated alkenes in the presence of metal- or organo-photosensitizers enabled the reactions to be carried out under much milder conditions. However, many of these processes still require the use of additives such as sacrificial electron donors or acceptors.[5,6]

In this regard, the approach using fluoroalkyl alkene (R_F-alkene) instead of activated fluoroalkyl reagent under the mild conditions is an efficient alternative. There are Pd-catalyzed reactions using aryl halide or diarylazonium salt as the coupling partner (Scheme 1b).[7] However, these reactions also require base additives and high temperature. In this backdrop, herein, we report a mild and efficient fluoroalkenylation reaction of arylboronic acid with R_F-alkene using the oxidative Heck coupling process[8] (Scheme 1c). This reaction has several advantages over the previous methods. It uses molecular oxygen as the oxidant[9] and easily available arylboronic acids as the precursor,[10] and can be carried out at room temperature under ligand-, and base-free conditions. In addition, the process is highly stereoselective, leading to the formation of only the *E*-isomer.



Scheme 1. Synthesis of fluoroalkylated alkenes with (a) various fluoroalkyl reagent and (b) fluoroalkyl alkene, and (c) our strategy.

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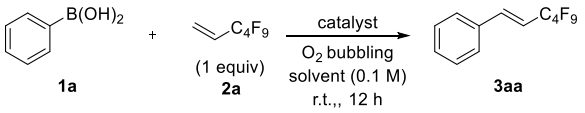
Electronic Supplementary Information (ESI) available: Experimental Procedure, Characterization data, and NMR spectra (^{1}H, ^{13}C, ^{19}F) of the synthesized compounds. See DOI: 10.1039/x0xx00000x

Results and discussion

We began the investigation for the synthesis of fluoroalkenylated compound using phenylboronic acid (**1a**) and nonafluorobutyl ethylene (**2a**) as model substrates (Table 1). The use of $Pd(OAc)_2$ provided the desired *E*-selective **3aa** in oxygen-saturated *N*,*N*-dimethylacetamide (DMA) solution in 71% yield (entry 1). The oxidative Heck coupling gave significantly better reactivity with Pd(II) catalyst (entry 1) than Pd(0) and other transition-metal complexes such as $Cu(OAc)_2$, which showed very low reactivity, or $Ni(OAc)_2$ which did not show any reactivity (entries 2–4). Interestingly, the use of the ligands, 2,2'-bipyridine and 1,10-phenanthroline (entries 5 & 6), and increased reaction temperature (entry 7) considerably lowered the reactivity. A control experiment under argon atmosphere after freeze-pump-thaw degassing process, clearly demonstrated the role of molecular oxygen as an oxidant for the reaction (entry 8). Subsequently, different solvents such as *N*,*N*-dimethylforamide (DMF), acetonitrile (CH_3CN), dimethylsulfoxide (DMSO), dichloromethane (DCM) and 2,2,2-trifluoroethanol (TFE) were screened (entries 9-13). However, none of them showed better reactivity than DMA. Further screening was performed which showed the best reactivity at 0.1 M concentration (entries 14 & 15) and the stoichiometry of **2a** and $Pd(OAc)_2$ was optimized to 1.2 equiv and 5 mol%, respectively (entries 16-21). Notably, the optimized reaction conditions showed that the process is highly practical and mild, using only molecular oxygen in the presence of $Pd(OAc)_2$, at room temperature.

Table 1. Optimization for fluoroalkenylation of boronic acids[a]



1a 2a 3aa

Entry	Catalyst (3 mol%)	Solvent	Variations	Yield(%)[b]
1	$Pd(OAc)_2$	DMA	-	71%
2	$Pd_2(dba)_3$	DMA	-	7%
3	$Cu(OAc)_2$	DMA	-	2%
4	$Ni(OAc)_2$	DMA	-	0%
5	$Pd(OAc)_2$	DMA	3 mol% 2,2'-bipyridine	9%
6	$Pd(OAc)_2$	DMA	3 mol% 1,10-phenanthroline	4%
7	$Pd(OAc)_2$	DMA	80 ^{0}C	25%
8	$Pd(OAc)_2$	DMA	no O_2[c]	trace
9	$Pd(OAc)_2$	DMF	-	55%
10	$Pd(OAc)_2$	MeCN	-	44%
11	$Pd(OAc)_2$	DMSO	-	trace
12	$Pd(OAc)_2$	DCM	-	0%
13	$Pd(OAc)_2$	TFE	-	0%
14	$Pd(OAc)_2$	DMA (0.05 M)	-	40%
15	$Pd(OAc)_2$	DMA (0.2 M)	-	57%
16	$Pd(OAc)_2$	DMA	**2a** (0.5 equiv)	44%
17	$Pd(OAc)_2$	DMA	**2a** (1.2 equiv)	78%
18	$Pd(OAc)_2$	DMA	**2a** (1.5 equiv)	78%
19	$Pd(OAc)_2$ (2 mol%)	DMA	**2a** (1.2 equiv)	67%
20	**$Pd(OAc)_2$ (5 mol%)**	**DMA**	**2a (1.2 equiv)**	**87%**
21	$Pd(OAc)_2$ (6 mol%)	DMA	**2a** (1.2 equiv)	87%

[a]All the reactions were carried out on a 0.1 mmol scale. [b]Yields were determined by ^{19}F NMR spectrometry using α,α,α -trifluorotoluene as the internal standard. [c]Degassed by freeze-pump-thaw cycling.

With the optimized conditions in hand, we investigated the substrate scope of the transformation using different boronic acid derivatives (**1**) and R_F-alkenes (**2**) to synthesize a variety of fluoroalkenylated compounds (**3**) (Table 2). Regardless of the electron-density on boronic acids, the reactions showed similar reactivity. Use of substrates with both electron-donating substituents such as *p*-tert-butyl (**1b**), *o*-methoxy (**1c**), *p*-methoxy (**1d**), and 3,5-dimethyl (**1e**) groups and electron-withdrawing substituents such as *p*-nitro (**1f**), *m*-chloro (**1g**), *p*-chloro (**1h**), and acetyl (**1i**) groups led to the formation of the corresponding coupled products (**3**) in moderate to good yields. Polycyclic aromatic derivatives such as naphthyl (**1j**), phenanthrenyl (**1k**), and pyrenyl (**1l**) were also suitable substrates, but the reaction in these cases required the use of a ligand and higher temperature to improve the reaction efficiency. In general, along with the desired cross-coupled compound **3**, diaryl compound, formed by homo-coupling of the boronic acid, was also produced as a side product. In addition, benzene derivatives, generated from the boronic acid substrate, were also detected as minor side products. With regards to the fluoroalkyl alkene partner, C_6F_{13}- (**2b**) and C_8F_{17}- (**2c**) alkenes worked as well as C_4F_9-ethylene (**2a**).[11] Moreover, the transformation was amenable to gram-scale synthesis under the optimized reaction conditions, where product **3aa** was prepared on a 10 mmol scale with a yield similar to that of the 0.7 mmol scale reaction (Scheme 2).

The reaction was selective with unsubstituted perfluoroalkylated alkenes. Resubjection of isolated **3aa** did not provide the second Heck product and gave only homocoupling product of **1a** with mostly recovered **3aa** (Scheme 3).

Difluoroalkenylation of 1,4-benzenediboronic acid (**1m**), which has two reaction sites, was also tried, but it furnished the di-coupled product (**3ma**) in only 15% yield along with several side products (Scheme 4a). On the other hand, the reaction of 4-bromo-3,3,4,4-tetrafluoro-1-butene (**2d**), which has two different functional reaction sites (alkenyl vs bromide), afforded the Heck product (**3ad**) in 43% yield without formation of the Suzuki product (**3ad'**), indicating that the Heck coupling preferentially proceed over Suzuki coupling under the conditions (Scheme 4b).

Vinyl boronic acid derivatives were not suitable substrates for the transformation. Reactions of (*E*)-styrylboronic acid (**1n**) and 1-phenylvinyl boronic acid (**1o**) did not proceed well under the conditions to give homo-coupled products, **6** and **7**, respectively, along with trace amount of the Heck product (Scheme 5).

The use of the boronic acid moiety was found to be essential for this transformation; consequently, the transformation did

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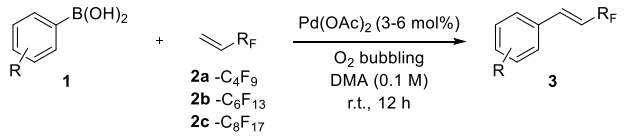
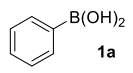
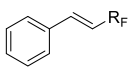
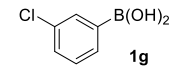
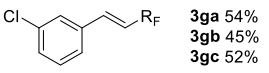
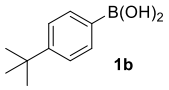
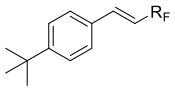
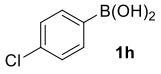
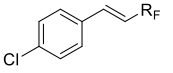
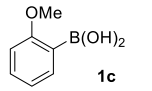
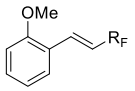
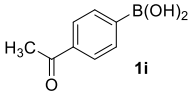
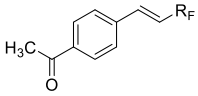
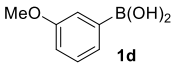
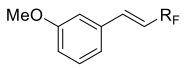
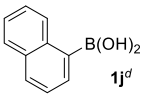
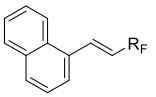
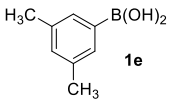
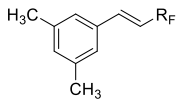
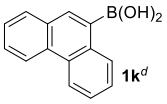
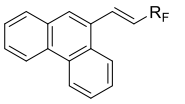
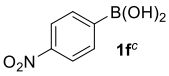
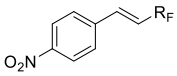
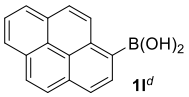
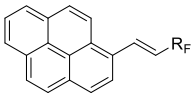
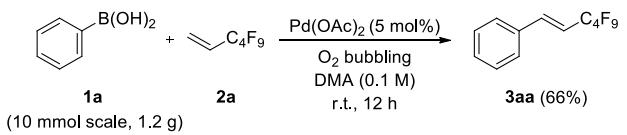
Table 2. Substrate scope for fluoroalkenylation of boronic acids.[a]

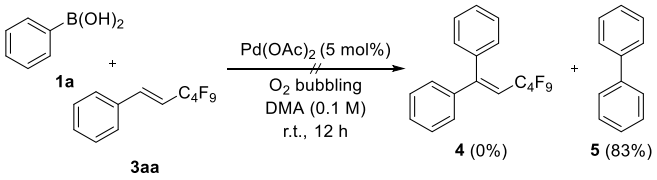


Entry	Boronic acid (1)	Alkene (2)	Product (3)	yield (%)[b]	Entry	Boronic acid (1)	Alkene (2)	Product (3)	yield (%)[b]
1 2 3	 1a	2a 2b 2c		3aa 67% 3ab 67% 3ac 61%	14 15 16	 1g	2a 2b 2c		3ga 54% 3gb 45% 3gc 52%
4 5 6	 1b	2a 2b 2c		3ba 59% 3bb 48% 3bc 55%	17 18	 1h	2a 2b		3ha 52% 3hb 47%
7	 1c	2a		3ca 50%	19 20	 1i	2a 2b		3ia 67% 3ib 45%
8 9	 1d	2a 2b		3da 53% 3db 54%	21 22 23	 1j[d]	2a 2b 2c		3ja 42% 3jb 49% 3jc 44%
10 11 12	 1e	2a 2b 2c		3ea 61% 3eb 60% 3ec 60%	24 25	 1k[d]	2a 2b		3ka 43% 3kb 43%
13	 1f[c]	2a		3fa 51%	26 27	 1l[d]	2a 2b		3la 40% 3lb 44%

[a] All reactions were carried out on a 0.7 mmol scale. [b] Isolated yield or ^{19}F NMR yields (using α,α,α-trifluorotoluene as the internal standard) owing to the volatility of the products. [c]The reaction of **1f** was conducted in the presence of 3 mol% 2,2'-bipyridine at 80 °C. [d]The reactions of **1j**, **1k**, and **1l** were conducted in the presence of 3 mol% 1,10-phenanthroline at 80 °C.



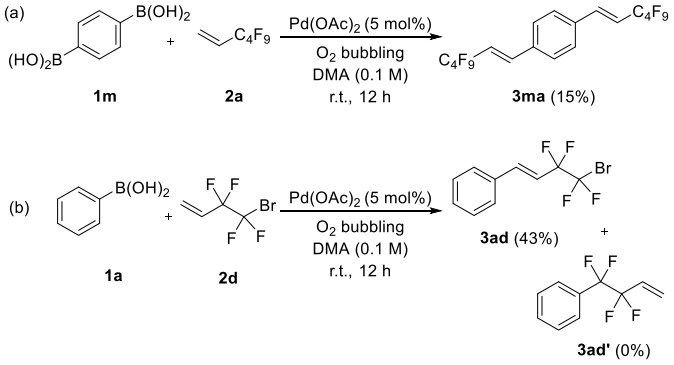
Scheme 2. Gram-scale reaction of **1a** and **2a**.



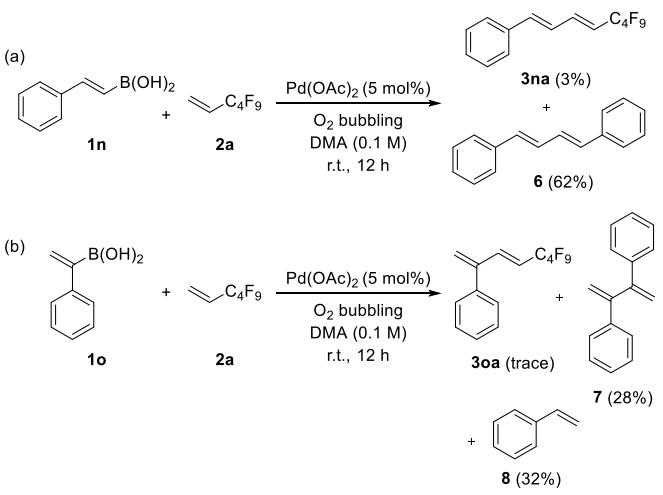
Scheme 3. Reaction of **3aa** for the second Heck reaction.

not proceed when the less Lewis acidic phenylboronic ester (**9**) was used.[12] In addition, the reactions of chloro- (**10**), bromo- (**11**), and iodobenzene (**12**) did not provide the cross-coupled product **3aa,** which further proved that halogens are not suitable precursors for this transformation (Scheme 6).[7b]

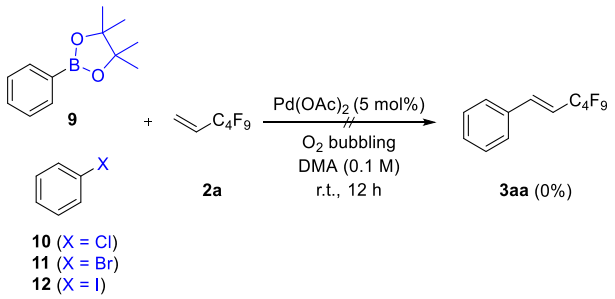
The proposed mechanism for the fluoroalkenylation of arylboronic acids with fluoroalkyl alkenes is shown in Scheme 7. The cycle begins with transmetalation between boronic acid **1** and $Pd(OAc)_2$. The Pd complex then forms a π-complex with alkene **2** and the alkene inserts itself in the Pd-C bond, in the *syn* orientation, to produce the reaction intermediate **B**, in a stereoselective manner. Subsequent *β*-hydride elimination in **B** results in the desired *E*-stereoselective fluoroalkenylated compound **3** and the Pd(II) hydride complex **C**. Reductive elimination of **C** generates Pd(0), which is oxidized by molecular oxygen[9] to regenerate Pd(II) species. Hydrogen peroxide is formed during the oxidation, which was proved by using hydrogen peroxide determination strip.



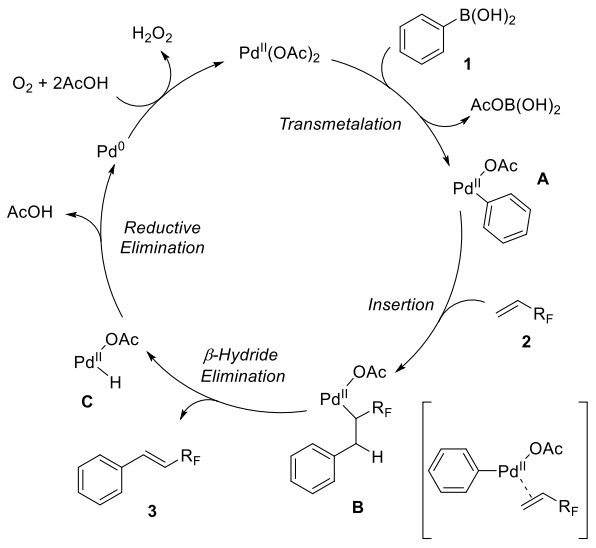
Scheme 4. Reactions of (a) 1,4-benzenediboronic acid (**1m**) and (b) 4-bromo-3,3,4,4-tetrafluoro-1-butene (**2d**).



Scheme 5. Reactions with vinylboronic acids



Scheme 6. Unsuccessful fluoroalkenylation with other precursors



Scheme 7. Proposed mechanism.

Conclusions

In summary, we developed a mild and efficient method for fluoroalkenylation of arylboronic acid derivatives through a Pd-catalyzed oxidative Heck reaction, which proceeds at room temperature under ligand- and base-free conditions. In addition, the reaction is highly stereoselective to provide only *E*-isomers.

Experimental

General reagent information

Palladium acetate and *N*,*N*-dimethylacetamide (DMA) were purchased from Sigma-Aldrich chemical company. Fluoroalkyl ethylenes and commercially available boronic acid derivatives were purchased from Sigma-Aldrich, Alfa Aesar, TCI, Combi-Blocks, or Ark pharm companies. Flash column chromatography was performed using ZEOCHEM ZEOprep silicagel 60 (60-200 mesh).

General analytical information

The synthesized fluoroalkenylated compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR). Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra can be found at the end of the Supporting Information. ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) or acetone (2.09 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm) or deuterated acetone (205.87 ppm), and all were obtained with ^{1}H decoupling. ^{19}F NMR spectra are reported in ppm, and all were taken composite pulse decoupling (CPD) mode. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet 6700 Thermo Scientific FT-IR spectrometer. Reactions were monitored by ^{19}F NMR spectrometry and thin layer chromatography. Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.

Experimental Procedure

Synthesis of Fluoroalkenylated Compound (3)

An oven-dried reaction flask equipped with a magnetic stir bar was charged with boronic acid derivative **1** (0.7 mmol) and 3–6 mol% of $Pd(OAc)_2$ in DMA (7 mL). Molecular oxygen was bubbled through the reaction mixture for 2 min, and then fluoroalkyl alkene **2** (0.84 mmol) was added, and it was allowed to stir for 12–15 h at room temperature. The reaction progress was monitored by thin layer chromatography or ^{19}F NMR spectroscopy. After completion, the mixture solution was concentrated using a rotary evaporator (carefully evaporated using a vacuum controller owing to the volatility of the fluoroalkenylated product) and purified using silica gel flash column chromatography using petroleum ether as the eluent to afford the corresponding fluoroalkenylated compound **3**.

Analytic Data for Fluoroalkenylated Compound (3)

(*E*)-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3aa**[3i]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.50 – 7.46 (m, 2H), 7.44 – 7.38 (m, 3H), 7.18 (dt, *J* = 16.1, 2.3 Hz, 1H), 6.21 (dt, *J* = 16.1, 12.3 Hz, 1H).; **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.01 (t, *J* = 10.1 Hz), 133.77, 130.42, 129.19, 127.87, 114.48 (t, *J* = 23.0 Hz). (carbon peaks of –C_4F_9 are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.06 (3F), -111.35 (2F), -124.14 (2F), -125.73 (2F); **IR (neat)**: ν_{max} = 2969, 1677, 1239, 1204, 973 cm^{-1}; ***R$_f$*** 0.42 (Petroleum ether).

(*E*)-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)benzene, **3ab**[3i]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.51 - 7.47 (m, 2H), 7.44 - 7.39 (m, 3H), 7.19 (dt, *J* = 16.1, 2.1 Hz, 1H), 6.22 (dt, *J* = 16.1, 12.4 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.00 (t, *J* = 9.6 Hz), 133.84, 130.42, 129.20, 127.88, 114.63 (t, *J* = 23.1 Hz) (carbon peaks of –C_6F_{13} are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.99 (3F), -111.22 (2F), -121.69 (2F), -122.95 (2F), -123.33 (2F), -126.28 (2F); **IR (neat)**: ν_{max} = 3034, 1658, 1240, 1200, 973 cm^{-1}; ***R$_f$*** 0.38 (Petroleum ether).

(*E*)-(10,10,10,10,10,10,10,10,10,10,10,10,10-tridecafluoro-10λ^{16}-deca-1-en-3,5,7,9-tetrayn-1-yl)benzene, **3ac**[3i]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.51 – 7.46 (m, 2H), 7.44 – 7.38 (m, 3H), 7.19 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 16.0, 12.3 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 139.97 (t, *J* = 9.3 Hz), 133.82, 130.41, 129.19, 127.87, 114.63 (t, *J* = 23.1 Hz) (carbon peaks of –C_8F_{17} are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.93 (3F), -111.19 (2F), -121.45 (2F), -122.00 (m, 4F), -122.81 (2F), -123.26 (2F), -126.22 (m, 2F); **IR (neat)**: ν_{max} = 3035, 1659, 1243, 1205, 973 cm^{-1}; ***R$_f$*** 0.69 (Petroleum ether).

(*E*)-1-(tert-butyl)-4-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3ba**: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.47 -7.43 (m, 4H), 7.18 (dt, *J* = 16.1, 2.3 Hz, 1H), 6.19 (dt, *J* = 16.1, 12.3 Hz, 1H), 1.36 (s, 9H).; **^{13}C NMR (151 MHz, CDCl$_3$)** δ 153.99, 139.79 (t, *J* = 9.5 Hz), 131.07, 127.71, 126.16, 13.57 (t, *J* = 23.0 Hz), 35.09, 31.37 (carbon peaks of –C_4F_9 are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.15 (3F), -111.18 (2F), -124.18 (2F), -125.75 (2F); **IR (neat)**: ν_{max} = 2967, 2872, 1657, 1214, 975, 733 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{16}H_{15}F_9$ [M+] 378.1030, found 378.1033; ***R$_f$*** 0.70 (Petroleum ether).

(*E*)-1-(tert-butyl)-4-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)benzene, **3bb**[4a]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.49 - 7.45 (m, 4H), 7.21 (dt, *J* = 16.1, 2.1 Hz, 1H), 6.22 (dt, *J* = 16.1, 12.4 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 154.04, 139.80 (t, *J* = 9.5 Hz), 131.17, 127.75, 126.19, 113.75 (t, *J* = 23.1 Hz), 35.09, 31.34 (carbon peaks of –C_6F_{13} are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.12 (3F), -111.09 (2F), -121.71 (2F), -123.01 (2F), -123.41 (2F), -126.33 (2F); **IR (neat)**: ν_{max} = 3035, 2967, 1657, 1240, 975, 832 cm^{-1}; ***R$_f$*** 0.69 (Petroleum ether).

(*E*)-1-(tert-butyl)-4-(10,10,10,10,10,10,10,10,10,10,10,10,10-tridecafluoro-10λ^{16}-deca-1-en-3,5,7,9-tetrayn-1-yl)benzene, **3bc**: off-white solid; **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.45 - 7.41 (m, 4H), 7.16 (d, *J* = 16.0 1H), 6.17 (dt, *J* = 16.0, 12.3 Hz, 1H), 1.34 (s, 9H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 153.97, 139.73 (t, *J* = 9.3 Hz), 131.07, 127.70, 126.16, 113.68 (t, *J* = 22.9 Hz), 35.09, 31.37 (carbon peaks of –C_8F_{17} are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.89 (3F), -110.98 (2F), -121.42 (2F), -121.98 (m, 4F), -122.77 (2F), -123.29 (2F), -126.19 (2F); **IR (neat)**: ν_{max} = 3035, 2968, 1657, 1241, 1209, 974, 816 cm^{-1}; ***R$_f$*** 0.73 (Petroleum ether).

(*E*)-1-methoxy-2-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3ca**[13]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.47 - 7.44 (m, 2H), 7.36 (dd, *J* = 7.6, 7.5 Hz, 1H), 6.98 (dd, *J* = 8.3, 7.6 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.33 (dt, *J* = 16.1, 12.6 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.21, 135.40 (t, *J* = 9.4 Hz), 131.53, 128.98, 122.74, 120.96, 114.95 (t, *J* = 23.1 Hz), 111.41, 55.73 (carbon peaks of –C_4F_9 are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.06 (3F), -111.19 (2F), -124.12 (2F), -125.70 (2F); **IR (neat)**: ν_{max} = 2925, 1620, 1234, 913, 745 cm^{-1}; ***R$_f$*** 0.71 (Petroleum ether/Ether, 8/1).

(*E*)-1-methoxy-3-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3da**[13]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.32 (dd, *J* = 8.1, 7.7 Hz, 1H), 7.15 (d, *J* = 16.1 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.99 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.19 (dt, *J* = 16.1, 12.3 Hz, 1H), 3.84 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 160.23, 139.96 (t, *J* = 9.5 Hz), 135.12, 130.22, 120.43, 116.09, 114.78 (t, *J* = 23.1 Hz), 113.10, 55.57 (carbon peaks of –C_4F_9 are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.06 (3F), -111.34 (2F), -124.12 (2F), -125.72 (2F); **IR (neat)**: ν_{max} = 3008, 2961, 1659, 1234, 974, 748 cm^{-1}; ***R$_f$*** 0.86 (Petroleum ether/Ether, 8/1).

(*E*)-1-methoxy-3-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)benzene, **3db**: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.32 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.15 (d, *J* = 16.1 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.99 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.19 (dt, *J* = 16.1, 12.3 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 160.26, 139.95 (t, *J* = 9.5 Hz), 135.15, 130.25, 120.46, 116.12, 114.91 (t, *J* = 22.9 Hz), 113.14, 55.60 (carbon peaks of –C_6F_{13} are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.82 (3F), -111.13 (2F), -121.61 (2F), -122.87 (2F), -123.23 (2F), -126.15 (2F); **IR (neat)**: ν_{max} = 2987, 2901, 1604, 1230, 1066, 1053, 974 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{15}H_9F_{13}O$ [M+] 452.0446, found 452.0443; ***R$_f$*** 0.77 (Petroleum ether/Ether, 8/1).

(*E*)-1,3-dimethyl-5-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3ea**: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.14 - 7.08 (m, 3H), 7.04 (s, 1H), 6.17 (dt, *J* = 15.9, 12.8 Hz, 1H), 2.34 (s, 6H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.23 (t, *J* = 9.7 Hz), 138.78, 133.68, 132.12, 125.73, 113.96 (t, *J* = 22.8 Hz), 21.37 (carbon peaks of –C_4F_9 are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.09 (3F), -111.25 (2F), -124.19 (2F), -125.73 (2F); **IR (neat)**: ν_{max} = 3188, 2929, 1589, 1309, 1146, 936 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{14}H_{11}F_9$ [M+] 350.0717, found 350.0714; ***R$_f$*** 0.68 (Petroleum ether).

(*E*)-1,3-dimethyl-5-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)benzene, **3eb**: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.15 - 7.10 (m, 3H), 7.05 (s, 1H), 6.19 (dt, *J* = 16.0, 12.3 Hz, 1H), 2.36 (s, 6H); **^{13}C NMR (151 MHz,**

$CDCl_3$) δ 140.23 (t, *J* = 9.6 Hz), 138.81, 133.74, 132.14, 125.75, 114.09 (t, *J* = 23.1 Hz), 21.33 (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.96 (3F), -111.07 (2F), -121.66 (2F), -122.94 (2F), -123.34 (2F), -126.26 (2F); **IR (neat)**: ν_{max} = 2924, 1657, 1605, 1237, 1199, 974 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{16}H_{11}F_{13}$ [M+] 450.0653, found 450.0651; ***R_f*** 0.73 (Petroleum ether).

(*E*)-1-(10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10-heptadecafluoro-10λ^{20}-deca-1-en-3,5,7,9-tetrayn-1-yl)-3,5-dimethylbenzene, **3ec**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.15 - 7.10 (m, 3H), 7.05 (s, 1H), 6.19 (dt, *J* = 16.0, 12.4 Hz, 1H), 2.35 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 140.22 (t, *J* = 9.4 Hz), 138.81, 133.77, 132.13, 125.75, 114.13 (t, *J* = 23.0 Hz), 21.30 (carbon peaks of $-C_8F_{17}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.05 (3F), -111.12 (2F), -121.48 (2F), -122.04 (m, 4F), -122.86 (2F), -123.33 (2F), -126.29 (2F); **IR (neat)**: ν_{max} = 2924, 1657, 1241, 1211, 973, 728 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_{11}F_{17}$ [M+] 550.0589, found 550.0593; ***R_f*** 0.68 (Petroleum ether).

(*E*)-1-nitro-4-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3fa**[3f]: off-white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.28 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 15.9 Hz, 1H), 6.37 (dt, *J* = 15.9, 11.7 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 148.88, 139.64, 137.74 (t, *J* = 9.3 Hz), 128.64, 124.50, 118.95 (t, *J* = 23.6 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.00 (3F), -112.02 (2F), -123.95 (2F), -125.70 (2F); **IR (neat)**: ν_{max} = 2916, 1608, 1535, 1349, 1237, 913 cm^{-1}; ***R_f*** 0.56 (Petroleum ether/Ether, 8/1).

(*E*)-1-chloro-3-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3ga**[3f]: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47 (s, 1H), 7.40 – 7.32 (m, 3H), 7.12 (dt, *J* = 16.0, 2.2 Hz, 1H), 6.22 (dt, *J* = 16.0, 12.1 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.66 (t, *J* = 9.5 Hz), 135.51, 135.31, 130.45, 130.39, 127.72, 126.10, 116.07 (t, *J* = 23.3 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.06 (3F), -111.63 (2F), -124.09 (2F), -125.73 (2F); **IR (neat)**: ν_{max} = 3068, 2971, 1661, 1234, 970, 785 cm^{-1}; ***R_f*** 0.67 (Petroleum ether).

(*E*)-1-chloro-3-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)benzene, **3gb**: colorless oil; **^{1}H NMR (300 MHz,$CDCl_3$)** δ 7.47 (s, 1H), 7.39 – 7.32 (m, 3H), 7.13 (dt, *J* = 16.1, 2.1 Hz, 1H), 6.22 (dt, *J* = 16.1, 12.0 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.63 (t, *J* = 9.7 Hz), 135.53, 135.31, 130.45, 130.39, 127.72, 126.11, 116.17 (t, *J* = 23.4 Hz) (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.84 (3F), -111.43 (2F), -121.62 (2F), -122.88 (2F), -123.21 (2F), -126.18 (2F); **IR (neat)**: ν_{max} = 2932, 1661, 1240, 971, 781, 725 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{14}H_6ClF_{13}$ [M+] 455.9950, found 455.9950; ***R_f*** 0.71 (Petroleum ether).

(*E*)-1-chloro-3-(10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10-heptadecafluoro-10λ^{20}-deca-1-en-3,5,7,9-tetrayn-1-yl)benzene, **3gc**: colorless oil**; ^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.47 (s, 1H), 7.39 – 7.32 (m, 3H), 7.12 (d, *J* = 16.1 Hz, 1H), 6.22 (dt, *J* = 16.1, 12.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.62 (t, *J* = 9.5 Hz), 135.59, 135.36, 130.43, 130.39, 127.74, 126.08, 116.23 (t, *J* = 23.1 Hz) (carbon peaks of $-C_8F_{17}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.08 (3F), -111.58 (2F), -121.52 (2F), -122.07 (m, 4F), -122.89 (2F), -123.26 (2F), -126.33 (2F); **IR (neat)**: ν_{max} = 2974, 1661, 1200, 971, 779, 732 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{16}H_6ClF_{17}$ [M+] 555.9887, found 555.9889; ***R_f*** 0.71 (Petroleum ether).

(*E*)-1-chloro-4-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)benzene, **3ha**[3i]: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.13 (dt, *J* = 16.2, 2.2 Hz, 1H), 6.18 (dt, *J* = 16.2, 12.0 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.74 (t, *J* = 9.6 Hz), 136.44, 132.21, 129.48, 129.07, 115.10 (t, *J* = 23.3 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.04 (3F), -111.47 (2F), -124.09 (2F), -125.72 (2F); **IR (neat)**: ν_{max} = 3044, 2927, 1660, 1236, 1206, 974 cm^{-1}; ***R_f*** 0.62 (Petroleum ether).

(*E*)-1-chloro-4-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)benzene, **3hb**[3i]: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 16.2 Hz, 1H), 6.18 (dt, *J* = 16.2, 12.0 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.71 (t, *J* = 9.2 Hz), 136.45, 132.22, 129.48, 129.08, 115.21 (t, *J* = 22.9 Hz) (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.83 (3F), -111.25 (2F), -121.64 (2F), -122.86 (2F), -123.20 (2F), -126.16 (2F); **IR (neat)**: ν_{max} = 2927, 1660, 1240, 1197, 974 cm^{-1}; ***R_f*** 0.79 (Petroleum ether).

(*E*)-1-(4-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)phenyl)ethan-1-one, **3ia**: colorless oil; **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 16.1 Hz, 1H), 6.30 (dt, *J* = 16.1, 12.0 Hz, 1H), 2.60 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 197.30, 138.83 (t, *J* = 9.6 Hz), 138.33, 137.90, 129.09, 127.99, 116.99 (t, *J* = 23.1 Hz), 26.77 (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -81.24 (3F), -111.87 (2F), -124.17 (2F), -125.87 (2F); **IR (neat)**: ν_{max} = 3033, 2987, 1685, 1235, 1207, 974, 816 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{14}H_9F_9O$ [M+] 364.0510, found 364.0508; ***R_f*** 0.67 (Petroleum ether/Ether, 8/1).

(*E*)-1-(4-(8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)phenyl)ethan-1-one, **3ib**[7b]: off-white solid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 16.1 Hz, 1H), 6.31 (dt, *J* = 16.1, 12.0 Hz, 1H), 2.61 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 197.36, 138.81 (t, *J* = 9.5 Hz), 138.35, 137.95, 129.13, 128.03, 117.15 (t, *J* = 23.3 Hz), 26.83 (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.95 (3F), -111.58 (2F), -121.67 (2F), -122.93 (2F), -123.21 (2F), -126.25 (2F); **IR (neat)**: ν_{max} = 3044, 2966, 1725, 1688, 1240, 975 cm^{-1}; ***R_f*** 0.50 (Petroleum ether/Ether, 8/1).

(*E*)-1-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)naphthalene, **3ja**[13]: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 15.9 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 7.1 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.61 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.57 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.51 (dd, *J* = 8.0, 7.7 Hz, 1H), 6.31 (dt, *J* = 15.9, 12.3 Hz, 1H).; **^{13}C NMR (151 MHz, $CDCl_3$)** δ 137.75 (t, *J* = 9.6 Hz), 133.85, 131.52,

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131.35, 130.61, 129.00, 127.21, 126.57, 125.65, 125.18, 123.37, 117.59 (t, *J* = 22.9 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.06 (3F), -111.28 (2F), -124.10 (2F), -125.63 (2F); **IR (neat)**: ν_{max} = 3066, 2957, 1654, 1236, 886 cm^{-1}; ***R$_f$*** 0.54 (Petroleum ether).

(*E*)-1-(8,8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)naphthalene, **3jb**: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.07 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 15.6 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.61 (dd, *J* = 7.7, 7.0 Hz, 1H), 7.56 (dd, *J* = 7.7, 7.2 Hz, 1H), 7.51 (dd, *J* = 7.9, 7.7 Hz, 1H), 6.30 (dt, *J* = 15.6, 12.2 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.72 (t, *J* = 9.4 Hz), 133.86, 131.53, 131.37, 130.61, 129.00, 127.21, 126.57, 125.65, 125.18, 123.37, 117.69 (t, *J* = 22.9 Hz) (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.92 (3F), -111.09 (2F), -121.55 (2F), -122.87 (2F), -123.23 (2F), -126.20 (2F); **IR (neat)**: ν_{max} = 3065, 2987, 1653, 1239, 1201, 972 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{18}H_9F_{13}$ [M+] 472.0497, found 472.0495; ***R$_f$*** 0.59 (Petroleum ether).

(*E*)-1-(10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10,10-heptadecafluoro-10λ^{20}-deca-1-en-3,5,7,9-tetrayn-1-yl)naphthalene, **3jc**: off-white solid; m. p. 40-42 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 15.9 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.59 (dd, *J* = 7.4, 7.0 Hz, 1H), 7.55 (dd, *J* = 8.2, 7.4 Hz, 1H), 7.50 (dd, *J* = 8.1, 8.0 Hz, 1H), 6.28 (dt, *J* = 15.9, 12.1 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.69 (t, *J* = 9.5 Hz), 133.82, 131.51, 131.33, 130.61, 129.00, 127.22, 126.58, 125.66, 125.19, 123.37, 117.70 (t, *J* = 23.7 Hz) (carbon peaks of $-C_8F_{17}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.78 (3F), -111.02 (2F), -121.28 (2F), -121.88 (m, 4F), -122.70 (2F), -123.14 (2F), -126.10 (2F); **IR (neat)**: ν_{max} = 3081, 2987, 1661, 1242, 1152, 972 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_9F_{17}$ [M+] 572.0433, found 572.0436; ***R$_f$*** 0.54 (Petroleum ether).

(*E*)-9-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)phenanthrene, **3ka**: off-white oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.76 (d, *J* = 8.1 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 15.6 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.89 (s, 1H), 7.75 – 7.67 (m, 3H), 7.64 (dd, *J* = 7.8, 7.1 Hz, 1H), 6.37 (dt, *J* = 15.6, 12.3 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.56 (t, *J* = 9.3 Hz), 131.31, 131.25, 130.71, 130.65, 130.03, 129.34, 127.92, 127.41, 127.36, 127.33, 126.67, 124.38, 123.52, 122.87, 118.16 (t, *J* = 22.5 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.96 (3F), -111.26 (2F), -124.02 (2F), -125.57 (2F); **IR (neat)**: ν_{max} = 2953, 2922, 2852, 1656, 1235, 970 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{20}H_{11}F_9$ [M+] 422.0717, found 422.0719; ***R$_f$*** 0.58 (Petroleum ether).

(*E*)-9-(8,8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)phenanthrene, **3kb**: off-white solid; m. p. 68-70 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.75 (d, *J* = 8.0 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 15.5 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 1H), 7.88 (s, 1H), 7.71 (m, 3H), 7.71 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.36 (dt, *J* = 15.5, 12.0 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.53 (t, *J* = 9.4 Hz), 131.31, 131.24, 130.70, 130.65, 130.03, 129.34, 127.92, 127.40, 127.35, 127.32, 126.65, 124.37, 123.51, 122.87, 118.23 (t, *J* = 22.9 Hz) (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.77 (3F), -111.02 (2F), -121.47 (2F), -122.79 (2F), -123.08 (2F), -126.09 (2F); **IR (neat)**: ν_{max} = 2971, 2923, 1655, 1241, 1202, 971 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{11}F_{13}$ [M+] 522.0653, found 522.0652; ***R$_f$*** 0.47 (Petroleum ether).

(*E*)-1-(8,8,8,8,8,8,8,8,8,8,8,8,8-tridecafluoro-8λ^{16}-octa-1-en-3,5,7-triyn-1-yl)pyrene, **3la**: pale-green oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.35 (d, *J* = 9.2 Hz, 1H), 8.29 (d, *J* = 15.9 Hz, 1H), 8.25 - 8.24 (m, 2H), 8.20 - 8.17 (m, 3H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.08 - 8.05 (m, 2H), 6.45 (dt, *J* = 15.9, 12.2 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.33 (t, *J* = 9.4 Hz), 132.81, 131.56, 130.91, 129.51, 129.00, 128.80, 127.61, 127.52, 126.59, 126.30, 126.07, 125.29, 125.08, 124.84, 124.42, 122.40, 117.10 (t, *J* = 22.4 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.95, -110.88, -123.91, -125.55; **IR (neat)**: ν_{max} = 2987, 2901, 1650, 1240, 903, 723 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{22}H_{11}F_9$ [M+] 446.0717, found 446.0715; ***R$_f$*** 0.40 (Petroleum ether).

(*E*)-1-(6,6,6,6,6,6,6,6,6-nonafluoro-6λ^{12}-hexa-1-en-3,5-diyn-1-yl)pyrene, **3lb**: pale-green solid; m. p. 82-85 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.34 (d, *J* = 9.2 Hz, 1H), 8.29 (d, *J* = 15.8 Hz, 1H), 8.26 - 8.23 (m, 2H), 8.21 - 8.18 (m, 3H), 8.13 (d, *J* = 8.9 Hz, 1H), 8.09 - 8.04 (m, 2H), 6.45 (dt, *J* = 15.8, 12.1 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.32 (t, *J* = 9.2 Hz), 132.81, 131.56, 130.91, 129.51, 128.98, 128.79, 127.78, 127.51, 126.59, 126.29, 126.07, 125.28, 125.08, 124.84, 124.40, 122.39, 117.09 (t, *J* = 22.5 Hz) (carbon peaks of $-C_6F_{13}$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -80.76 (3F), -110.64 (2F), -121.45 (2F), -122.77 (2F), -122.98 (2F), -126.07 (2F); **IR (neat)**: ν_{max} = 2987, 2901, 1653, 1241, 903, 723 cm^{-1}; **HRMS** m/z (EI) calc. for $C_{24}H_{11}F_{13}$ [M+] 546.0653, found 546.0656; ***R$_f$*** 0.40 (Petroleum ether).

Analytic Data for Side Products

1,1'-biphenyl, **5**: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.61 (d, *J* = 7.8 Hz, 4H), 7.46 (dd, *J* = 7.8, 7.6 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 141.46, 128.96, 127.46, 127.38.

1-((*E*)-3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)-4-((*E*)-3,3,4,4,5,5,6,6,6-octafluoro-5-methylhex-1-en-1-yl)benzene, **3ma**: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** 7.52 (s, 4H), 7.18 (d, *J* = 16.1 Hz, 2H), 6.25 (dt, *J* = 16.1, 12.1 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 138.94 (t, *J* = 10.0 Hz), 135.40, 128.43, 115.81 (t, *J* = 23.3 Hz) (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -81.04 (3F), -111.51 (2F), -124.04 (2F), -125.72 (2F).

(*E*)-(4-bromo-3,3,4,4-tetrafluorobut-1-en-1-yl)benzene, **3ad**[14]: colorless oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.49 (m, 2H), 7.41 (m, 3H), 7.20 (d, *J* = 16.1 Hz, 1H), 6.25 (dt, *J* = 16.1, 11.8 Hz, 1H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 140.02 (t, *J* = 8.6 Hz), 133.93, 130.30, 129.16, 127.82, 114.56 (t, *J* = 23.9 Hz) (carbon peaks of $-C_2F_5$ are omitted due to complicated C-F splitting); **^{19}F NMR (564 MHz, CDCl$_3$)** δ -65.65 (2F), -109.04 (2F).

(1*E*,3*E*)-1,4-diphenylbuta-1,3-diene, **6**[15]: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.45 (d, *J* = 7.7 Hz, 4H), 7.34 (dd, *J* = 7.7, 7.4

Hz, 4H), 7.24 (t, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 11.9 Hz, 2H), 6.69 (d, *J* = 11.9 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 137.58, 133.04, 129.47, 128.87, 127.78, 126.60.

buta-1,3-diene-2,3-diyldibenzene, **7**[16]: white solid; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.39 (d, *J* = 7.7 Hz, 4H), 7.27 (dd, *J* = 7.7, 7.4 Hz, 4H), 7.22 (t, *J* = 7.4 Hz, 2H), 5.54 (d, *J* = 1.6 Hz, 2H), 5.3 (d, *J* = 1.6 Hz, 2H); **^{1}H NMR (600 MHz, (CD$_3$)$_2$CO)** δ 7.44 (d, *J* = 7.6 Hz, 4H), 7.31 (dd, *J* = 7.6, 7.2 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 2H), 5.64 (d, *J* = 1.7 Hz, 2H), 5.37 (d, *J* = 1.7 Hz, 2H); **^{13}C NMR (151 MHz, CDCl$_3$)** δ 150.06, 140.42, 128.38, 127.71, 116.57, 110.24. **^{13}C NMR (151 MHz, (CD$_3$)$_2$CO)** δ 150.86, 140.57, 128.88, 128.26, 127.94, 116.20.

styrene, **8**: colorless liquid; **^{1}H NMR (600 MHz, (CD$_3$)$_2$CO)** δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.39 (dd, *J* = 7.6 , 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 17.7, 10.9 Hz, 1H), 5.86 (d, *J* = 17.7 Hz, 1H), 5.29 (d, *J* = 10.9 Hz, 1H); **^{13}C NMR (151 MHz, (CD$_3$)$_2$CO)** δ 138.38, 137.76, 129.28, 128.57, 126.92, 114.01.

Conflicts of interest

There are no conflicts to declare.

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