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Pd-Catalyzed Carbonylative Carboperfluoroalkylation of Alkynes. Through-Space $^{13}C-^{19}F$ Coupling as a Probe for Configuration Assignment of Fluoroalkyl-Substituted Olefins

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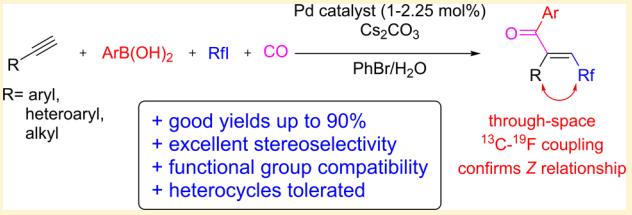
Supporting Information

ABSTRACT: A four-component Pd-catalyzed protocol for direct synthesis of perfluoroalkyl-substituted enones is reported. Under mild conditions and low catalyst loading, alkynes, iodoperfluoroalkanes, (hetero)arylboronic acids, and carbon monoxide are assembled into highly elaborate products with good yields and excellent regio- and stereoselectivities. The configuration of the products was confirmed by the observation of through-space $^{13}C-^{19}F$ couplings, accessible through the analysis of routine ^{13}C NMR spectra.

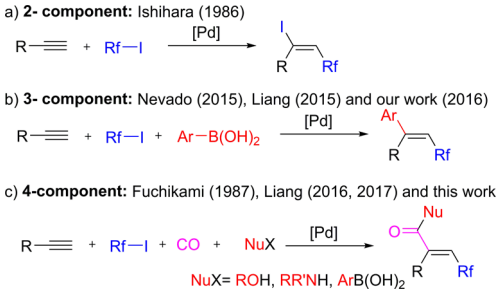


INTRODUCTION

Fluorinated organic molecules exhibit a range of remarkable chemical, physical, and biological properties of immense significance to various branches of science, including medicinal chemistry.[1] However, their synthesis is challenging and often requires harsh conditions, the use of an excess of elaborate reagents, or both. For instance, the vast majority of methodologies developed for the direct synthesis of perfluoroalkyl-substituted olefins from alkynes is based on the application of expensive trifluoromethylating agents, e.g., Togni or Umemoto reagents.[2] Conversely, the alternative approach, based on cross-coupling chemistry, requires the prior synthesis of appropriate vinyl halides, vinylborates, or vinylstannanes.[3] A more attractive and atom-economic approach, based on the utilization of readily accessible and inexpensive haloperfluoroalkanes or related compounds (e.g., halodifluoroacetates) for double functionalization of alkynes, has recently gained significant momentum.[4−9] Nevertheless, the field is still severely underdeveloped.

In the mid-1950s, Haszeldine published a seminal report describing the radical iodoperfluoroalkylation of alkynes.[10] Since then, several methods for the addition of iodoperfluoroalkanes across acetylenes, based on various radical initiators[11] or transition-metal catalysts,[12,13] have been reported. In particular, three decades ago, Ishihara showed that Pd complexes can be competent catalysts for this process (Scheme 1a).[13] The resulting perfluoroalkyl-substituted vinyl iodides are valuable building blocks, which could be further functionalized by taking advantage of cross-coupling chemistry. A one-pot procedure for the sequential iodoperfluoroalkylation and Sonogashira coupling has also been reported.[14] More recently, Nevado,[4] Liang,[5] and our group[6] have independently developed tandem Pd-catalyzed protocols for three-component carboperfluoroalkylation of alkynes with iodoperfluoroalkynes (iododifluoroacetate in Liang's methodology) and arylboronic acids

Scheme 1. Pd-Catalyzed Perfluoroalkylative Functionalization of Alkynes



(Scheme 1b). A related method for the synthesis of acrylonitriles via the copper powder-mediated double functionalization of alkynes with ethyl difluoroiodoacetate and trimethylsilyl cyanide has also been demonstrated.[15] In the late 1980s, shortly after the first Pd-catalyzed iodoperfluoroalkylation of alkynes had been developed, Fuchikami reported a tandem procedure for the perfluoroalkylation-alkoxycarbonylation of acetylenes (Scheme 1c).[16] Interestingly, this atom-economic four-component strategy witnessed little, if any, attention for almost three decades. Very recently, a similar approach involving the initial addition of a perfluoroalkyl radical to alkynes has been introduced for the synthesis of fluoroalkyl-substituted α,β-unsaturated esters, amides, and ketones via tandem Pd-catalyzed reactions.[7−9] This strategy, still severely underdeveloped, fits into a broad field encompassing carbonylative transformations involving a C-(sp^3)−halogen bond, including tandem processes benefiting from the interplay of plausible radical intermediates (initially

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formed from alkyl halide or resulting from subsequent carbonylation and the addition to C−C multiple bonds) and Pd catalysis responsible for further productive transformation of the intermediate radical species.[17]

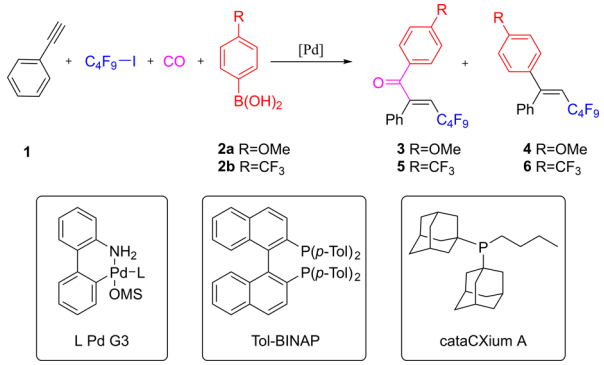
RESULTS AND DISCUSSION

We began this work with an investigation of the recently developed carboperfluoroalkylation of alkynes[6] in a carbon monoxide atmosphere. The benchmark reaction of phenylacetylene (**1**) with perfluorobutyl iodide and *p*-methoxyphenylboronic acid (**2a**) proceeded smoothly in an atmosphere of carbon monoxide (balloon) when catalyzed by only 1 mol % of a Pd/BINAP catalyst. The formation of the mixture of the desired ketone **3** along with the substituted alkene **4** was observed. A series of Pd catalysts and a range of reaction variables were examined to identify satisfactory reaction conditions.[18] Buchwald-type third generation Pd precatalysts were used as a platform for testing catalysts due to their insensitivity to air and moisture, as well as fast and clean activation under basic conditions.[19] The application of the more sterically demanding Tol-BINAP ligand improved the selectivity toward enone **3** (Table 1, entry 2). A further increase in steric hindrance of the catalyst (3,5-xylyl-BINAP) was counterproductive (Table 1, entry 3). From among the solvents and bases examined, the combination of aqueous Cs_2CO_3 and bromobenzene performed best (Table 1, entry 4). A further improvement of chemoselectivity was noticed when pyridine (2 equiv in respect to the catalyst) was added to the reaction mixture (Table 1, entry 5).

Unfortunately, the developed protocol proved to be unproductive for reactions involving electron-deficient arylboronic acids, e.g., **2b** (Table 1, entries 6−8). The formation of only small amounts of simple carboperfluoroalkylation product **6** were observed. The application of a catalyst based on a hindered electron-rich phosphine ligand (cataCXium A, i.e., di(1-adamantyl)-*n*-butylphosphine) opened the carbonylative pathway again, although the conversion of the alkyne was incomplete even under higher catalyst loadings (Table 1, entry 9). This obstacle was surmounted by the application of a combination of catalysts based on Tol-BINAP and cataCXium A ligands (Table 1, entry 10). It could be speculated that the reaction involving electron-deficient boronic acids in the presence of carbon monoxide suffers from sluggish transmetalation with the palladium species. Although the details of the interaction of the two palladium species ligated by different phosphine ligands are not fully understood, a Pd complex bonded to an electron-rich phosphine (which is normally ineffective in the discussed functionalization of alkynes) could efficiently mediate the transfer of the aryl group from the boronic acid and then either relay it to the other, catalytically active Tol-BINAP complex or promote carbonylative coupling by itself.[18]

Having developed satisfactory conditions for the model reactions, the scope in respect to alkynes (Table 2), (hetero)arylboronic acids (Table 3), and iodofluoroalkanes (Table 4) was investigated. Two base protocols were taken into account: one employing 1 mol % Tol-BINAP Pd G3 as a

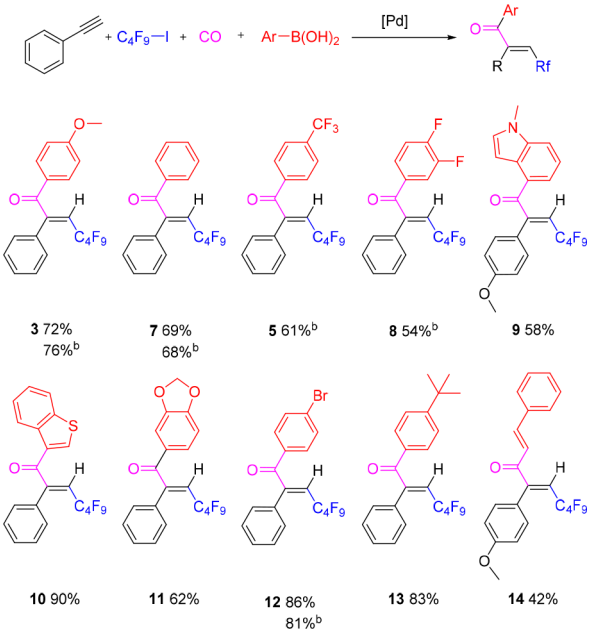
Table 1. Search for the Optimal Reaction Conditions[a]



entry	R	conditions	% yield (**3** or **5**)[b]	% yield (**4** or **6**)[b]
1	OMe	BINAP Pd G3, DCE	47	35
2	OMe	Tol-BINAP Pd G3, DCE	62	38
3	OMe	3,5-xylyl-BINAP Pd G3, DCE	15	10
4	OMe	Tol-BINAP Pd G3, PhBr	73	21
5	OMe	Tol-BINAP Pd G3, PhBr, pyridine 2 mol %	82	14
6	CF_3	BINAP Pd G3, DCE	0	12
7	CF_3	Tol-BINAP Pd G3, DCE	0	10
8	CF_3	Tol-BINAP Pd G3, PhBr, pyridine 2 mol %	0	<5
9	CF_3	cataCXium A Pd G3, PhBr	17	<5
10	CF_3	Tol-BINAP/cataCXium A Pd G3 (1.25/0.75 mol%), PhBr	64	18

[a]Reaction conditions: alkyne (0.125 mmol), arylboronic acid (0.175 mmol), C_4F_9I (0.375 mmol), catalyst (1 mol%), solvent, additive, 2 M aqueous Cs_2CO_3 (0.125 mL), CO pressure of 1 atm, 50 °C, 4 h. [b]Determined by GC with dodecane as an internal standard.

Table 2. Substrate Scope: Boronic Acids[a]



[a]Method A: phenylacetylene (0.250 mmol), arylboronic acid (0.350 mmol), iodoperfluorobutane (0.75 mmol), Tol-BINAP Pd G3 (1 mol %), pyridine (2 mol %), bromobenzene (1.2 mL), 2 M aqueous Cs_2CO_3 (0.25 mL), H_2O (0.1 mL), CO pressure of 1 atm, 50 °C, 4 h. [b]Method B: phenylacetylene (0.250 mmol), arylboronic acid (0.350 mmol), iodoperfluorobutane (0.75 mmol), cataCXium A/Tol-BINAP Pd G3 (1.25 mol %/0.75 mol %), bromobenzene (1.2 mL), 2 M aqueous Cs_2CO_3 (0.25 mL), H_2O (0.1 mL), CO pressure of 1 atm, 50 °C, 4 h.

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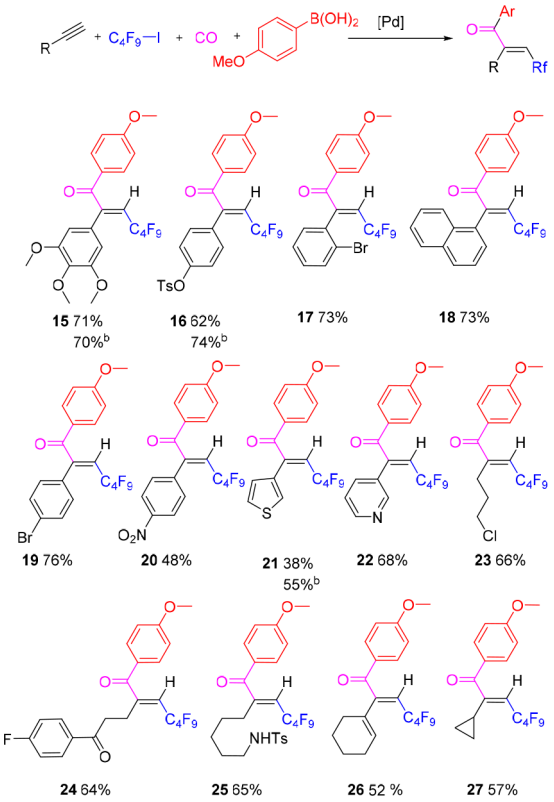
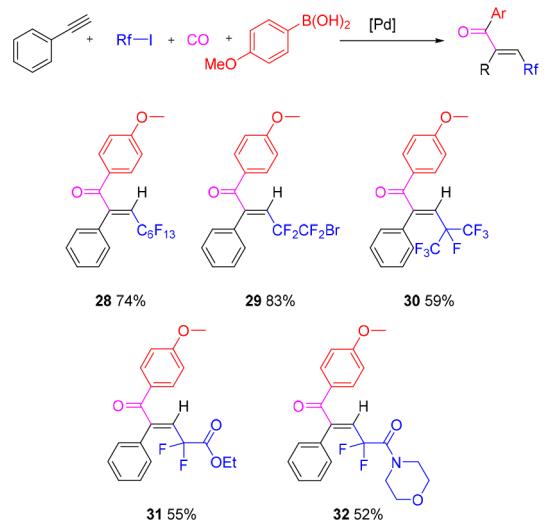
Table 3. Substrate Scope: Alkynes[a]



[a]Method A: alkyne (0.250 mmol), 4-methoxyphenylboronic acid (0.350 mmol), iodoperfluorobutane (0.75 mmol), Tol-BINAP Pd G3 (1 mol %), pyridine (2 mol %), bromobenzene (1.2 mL), 2 M aqueous Cs_2CO_3 (0.25 mL), H_2O (0.1 mL), CO pressure of 1 atm, 50 °C, 4 h. [b]Method B: alkyne (0.250 mmol), 4-methoxyphenylboronic acid (0.350 mmol), iodoperfluorobutane (0.75 mmol), cataCXium A/Tol-BINAP Pd G3 (1.25 mol %/0.75 mol %), bromobenzene (1.2 mL), 2 M aqueous Cs_2CO_3 (0.25 mL), H_2O (0.1 mL), CO pressure of 1 atm, 50 °C, 4 h.

Table 4. Substrate Scope: Perfluoroalkyl Iodides[a]



[a]Method A: phenylacetylene (0.250 mmol), 4-methoxyphenylboronic acid (0.350 mmol), RfI (0.75 mmol), Tol-BINAP Pd G3 (1 mol %), pyridine (2 mol %), bromobenzene (1.2 mL), 2 M aqueous Cs_2CO_3 (0.25 mL), H_2O (0.1 mL), CO pressure of 1 atm, 50 °C, 4 h.

precatalyst with the addition of 2 mol % pyridine (method A) and another using a mixture of precatalysts based on cataCXium A (1.5 mol %) and Tol-BINAP (0.75 mol %) ligands (method B). Method B is generally applicable to reactions involving electron-rich and electron-poor boronic acids. In contrast, method A completely failed for electron-deficient arylboronic acids, while for electron-rich and neutral substrates it is superior in terms of catalyst loading. In all cases, the reactions proceeded with complete regioselectivity and excellent stereoselectivity (typically E/Z >95:5) toward the antiaddition product, isolated in good to very good yields.

A range of aryl- and heteroarylboronic acids were evaluated in the reaction of phenylacetylene and iodoperfluorobutane (**3**, **5**, **7**−**14**) (Table 2). The desired products were isolated in very good yields, for both electron-rich and electron-deficient arylboronic acids as substrates. For the latter (**5**, **8**), only method B provided satisfactory results. Additionally, heteroaryl- (**9**−**11**) and vinylboronic acids (**14**) were also well tolerated.

In the next step, various acetylenes were investigated in the reaction with *p*-methoxyphenylboronic acid and iodoperfluorobutane (Table 3). Alkynes bearing variously substituted arenes (**14**−**20**) as well as heteroaryl moieties, such as thiophene (**21**) or pyridine (**22**), performed similarly to simple phenylacetylene. Alkyl-substituted alkynes were also accepted, leading to desired products with good yields (**23**−**25**). Interestingly, vinyl- or cyclopropyl-substituted acetylenes proved to be compatible with the reaction conditions as well (**26**, **27**). Unfortunately, internal alkynes proved to be incompatible with the developed protocol. Only small amounts of the desired product were observed in the reaction of 1-phenylpropyne under many reaction conditions tested, probably due to the higher temperature, necessary for the efficiency of the noncarbonylative variant of the reaction,[6] being detrimental to the carbonylative transformation.

Finally, perfluoroalkyl iodides other than iodoperfluorobutane were investigated as reaction partners (Table 4) (**28**−**32**). In all cases, even for sterically demanding 2-iodoperfluoropropane (**30**), products were isolated in yields similar to or slightly lower than that of those obtained with the model substrate. Also, iododifluoroacetyl esters and amides are compatible with the reaction conditions, leading to the expected products with moderate yields (**31** and **32**).

Furthermore, the applicability of the methodology was demonstrated on substrates containing biologically relevant moieties in their structures (Scheme 2). Alkynes tethered to phenylglycine *N*-acetate **33** and cholesterol **35** easily entered into the reaction with iodoperfluorobutane and *p*-methoxyboronic acid. The corresponding products **34** and **36** were isolated as single isomers in acceptable yields.

To demonstrate the scalability of the procedure, the reactions of phenylacetylene and iodoperfluorobutane with *p*-methoxy- and *p*-trifluoromethylphenylboronic acids were performed on a 2 mmol scale (Scheme 3). Enones **3** and **5** were isolated in 70 and 58% yields, respectively. The obtained results were comparable or only slightly inferior to the corresponding reactions presented in Table 1, which were run on an 8 times smaller scale.

All of the reactions presented above proceeded with excellent stereoselectivity resulting from the *anti*-addition of iodoperfluoroalkanes across the triple bond of alkynes. The configuration of the isolated products was confirmed by the comparison to literature data,[8] by independent synthesis from corresponding vinyl iodides of known configuration, or by

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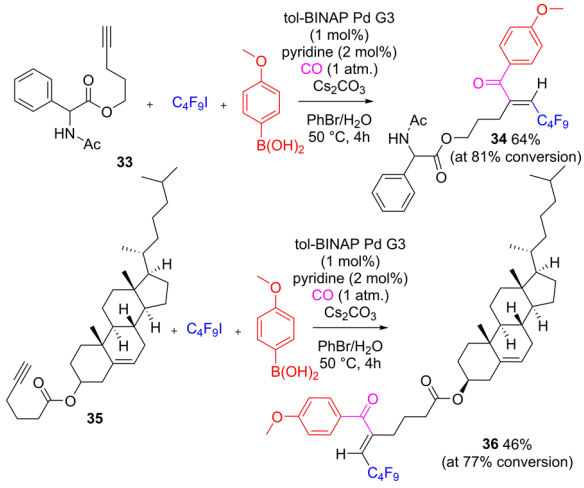
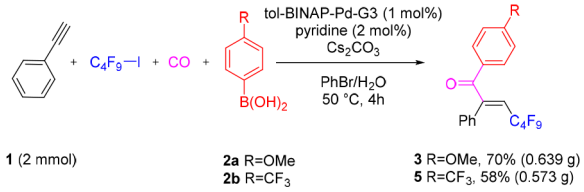
Scheme 2. Reactions Involving Biologically Relevant Substrates

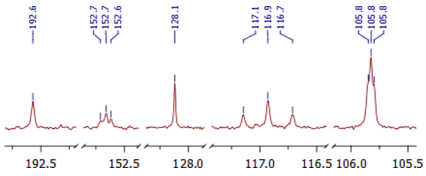


Scheme 3. Scale-Up of Model Reactions



NMR experiments.[18] Careful analysis of the ^{13}C NMR spectra revealed that the signals corresponding to nuclei at the homoallylic position located *Z* to the fluoroalkyl chain exhibit pronounced multiplet structures. It is very unlikely that through-bond $^{5}J_{CF}$ are measurable. Thus, this observation could be attributed to through-space coupling.[20] Table 5

Table 5. C−F Through-Space Coupling as a Probe for Configuration Assignment

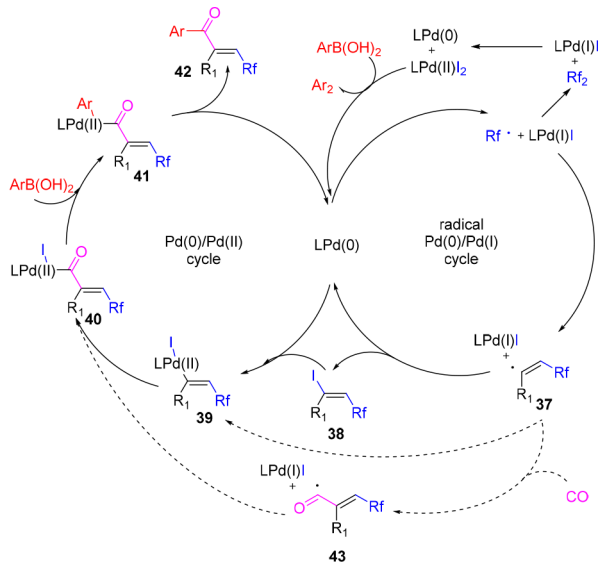


entry	C atom	δ (ppm)	*J* (Hz)	type of *J*
1	1	116.9	21.8 (t)	$^{2}J_{CF}$
2	2	152.7	4.6 (t)	$^{3}J_{CF}$
3	3	128.1		$^{4}J_{CF}$
4	3′	192.6		$^{4}J_{CF}$
5	4	105.8	2.5 (t)	through-space

summarizes C−F couplings for compound **15**. As expected, $^{2}J_{CF}$ and $^{3}J_{CF}$ are equal to 21.8 and 4.6 Hz, respectively, while longer range through-bond $^{4}J_{CF}$ were not measurable. In contrast, the through-space coupling between the CF_2 group and one of the C nuclei of the arene ring at the *Z* position (formally $^{5}J_{CF}$) is well visible (2.5 Hz). This phenomenon was observed for all obtained enones.[18] Although the information is available from routine ^{13}C spectra, the existence of C−F through-space couplings is very seldom noticed explicitly.[20,21] Taking advantage of the C−F through space coupling, which is easily accessible from routine 1D NMR spectra, constitutes a powerful tool for structure and configuration assignment. It could be beneficial especially when classic methods, e.g., crystallography or NOESY experiments, fail.

Due to the ability of palladium complexes to enter a variety of mechanistically distinct reaction pathways (both radical and "classic" 2e), multiple scenarios for the presented reaction involving four components, including carbon monoxide, could be envisioned. Plausible reaction manifolds are depicted in Scheme 4. One of the envisioned mechanistic pictures of the

Scheme 4. Plausible Reaction Mechanism



transformation is composed of two independent catalytic cycles (radical and 2e$^-$), linked by a common reaction intermediate (vinyl iodide **38**) and the Pd(0) form of the catalyst.[6] Alternatively, the formation of acyl radical **43** via direct carbonylation of vinyl radical **37** (without the aid of the Pd catalyst) could be postulated as a crucial step, followed by the recombination of **43** with the Pd(I) species and further coupling with the boronic acid. Such direct, metal-free carbonylation of the radical intermediate is widely accepted for Pd-catalyzed carbonylative reactions of alkyl halides.[17,22] It is well documented that Pd-catalyzed reactions involving the addition of perfluoroalkyl iodides to C−C multiple bonds are radical in nature.[4−8,22,23] There is, however, some controversy concerning the fate of the vinyl radical intermediate. Although the recombination of vinyl radical **37** with the Pd(I) species to directly form **39** or the addition of **37** to CO followed by the recombination of intermediate **43** with the Pd(I) species leading to **40**, implying a single catalytic cycle for the whole reaction (Scheme 2, dashed arrow), could not be unambiguously ruled out, experimental data supports the involvement of two separate catalytic cycles. We have recently reported that Pd-catalyzed iodoperfluoroalkylation of alkynes is more efficient in the presence of an arylboronic acid.[18] Thus, it could be assumed that the vinyl iodide could be a plausible intermediate rather than a side product, which could further undergo classic or carbonylative Suzuki coupling[24] under the reaction conditions. This hypothesis is strongly supported by the observation of the formation of considerable amounts of vinyl iodide **38** (up to 16%) during the reaction progress, which disappeared upon reaching full conversion of the acetylene. For instance, after 1 h the amounts of intermediate **38** and final

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product **42** are comparable (12 and 13%, respectively),[18] illustrating effective formation of **38** under the reaction conditions in the Pd-catalyzed atom transfer radical addition process (ATRA). As expected, independently prepared **38** underwent the carbonylative coupling under typical reaction conditions, providing a similar ratio of the desired enone **3** and noncarbonylative coupling product **4** as was obtained in the tandem four-component process. These observations strongly point toward the engagement of vinyl iodide **38** as a highly probable intermediate and, as a consequence, the involvement of two separate catalytic cycles in the overall process.

CONCLUSION

In conclusion, we developed a tandem four-component procedure for the Pd-catalyzed carbonylative carboperfluoroalkylation of alkynes. The reaction proceeded smoothly under mild conditions and with low catalyst loading, enabling the assembly of alkyne, perfluoroalkyl iodide, (hetero)arylboronic acid, and carbon monoxide into perfluoroalkyl-substituted enones with good yields and excellent regio- and stereoselectivities. A reaction mechanism involving two independent catalytic cycles, Pd(0)/Pd(I) and Pd(0)/Pd(II), was proposed. $^{13}C-^{19}F$ through-space couplings, accessible from routine 1D ^{13}C NMR experiments, were employed for the configuration assignment of the products.

EXPERIMENTAL SECTION

General Information. All manipulations were performed in a nitrogen-filled glovebox or under an argon atmosphere using Schlenk techniques, unless mentioned otherwise. Flash chromatography was performed using Merck silica gel 60 (230−400 mesh). TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates and visualized with a cerium molybdate stain (Hanessian's stain). ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded with a Bruker AV 400 spectrometer. ^1H and ^{13}C chemical shifts were given in ppm relative to TMS. Residual solvent signals were used as references ($CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.0 ppm), and the chemical shifts were converted to the TMS scale. Coupling constants (J) are reported in hertz, and the following abbreviations were used to denote multiplets: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet (denotes a complex pattern), dd = doublet of doublets, dt = doublet of triplets, and br = broad signal. Infrared spectra were recorded with a Jasco FTIR-6200 spectrometer. Electron ionization high-resolution mass spectra (EI-HR) were recorded with an Autospec Premier (Waters Inc.) mass spectrometer using the narrow-range high-voltage scan technique with low-boiling perfluorokerosene (PFK) as the internal standard. Samples were introduced by using a heated direct insertion probe. Electrospray ionization high-resolution mass spectra (ESI-HR) were recorded with a MALDISynapt G2-S HDMS (Waters Inc.) mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer. ESI-MS spectra were recorded in the positive ion mode (source parameters: capillary voltage 3.15 kV, sampling cone 25 V, source temperature 120 °C, desolvation temperature 150 °C). Unless otherwise noted, all commercially available compounds (ABCR, Acros, Fluorochem, TCI, Sigma-Aldrich, Strem) were used as received. Phosphine ligands were purchased from Sigma-Aldrich or Fluorochem, and $Pd(OAc)_2$ was purchased from Strem. Tol-BINAP Pd G3 precatalyst was prepared by following Buchwald's procedure.[19]

General Procedure for the Carbonylative Carboperfluoroalkylation of Alkynes. Caution: The sequence of the addition of the reagents is important and guarantees the reproducibility of results. The quality and purity of the reagents play an important role in the efficiency of the reaction. In most cases, iodoperfluoroalkanes were received as colorless transparent liquids and were used without purification. Otherwise the reagent was purified by washing with an aqueous solution of sodium dithionite and filtration through a short pad of silica gel under an inert atmosphere (in a drybox).

Conditions A (for the Reaction of Terminal Alkyne with Iodoperfluoroalkane, Electron-Rich Boronic Acid). In a glovebox, to a 4 mL screw-capped vial containing Tol-BINAP Pd G3 (2.62 mg, 2.5 μmol) was sequentially added the following reagents: iodoperfluoroalkane (0.75 mmol), bromobenzene (1 mL), acetylene (0.25 mmol), boronic acid (0.35 mmol), 2 M aq Cs_2CO_3 (0.25 mL, 0.5 mmol), and pyridine (2 mol %, 5 μmol, 200 μL of 25 mM solution in bromobenzene). Then, a magnetic stirring bar was placed in the reaction mixture, and the vial was sealed with a cap fitted with a rubber septum. Carbon monoxide was delivered to the reaction by a needle inserted into the rubber septum (1 atm). The reaction mixture was stirred at 50 °C for 4 h and then cooled to room temperature. The mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated, and the crude product was purified by column chromatography on silica gel using hexanes/EtOAc as the eluent.

Conditions B (for the Reaction of Internal Alkyne with Iodoperfluoroalkane, Electron-Deficient Boronic Acid). In a glovebox, to a 4 mL screw-capped vial containing Tol-BINAP Pd G3 (1.96 mg, 1.875 μmol) and CataCXium A Pd G3 (3.15 mg, 4.375 μmol) was sequentially added the following reagents: iodoperfluoroalkane (0.75 mmol), bromobenzene (1.2 mL), acetylene (0.25 mmol), boronic acid (0.35 mmol), and 2 M aq Cs_2CO_3 (0.25 mL, 0.5 mmol). Then, a magnetic stirring bar was placed in the reaction mixture, and the vial was sealed with a cap fitted with a rubber septum. Carbon monoxide was delivered to the reaction by a needle inserted into the rubber septum (1 atm). The reaction mixture was stirred at 50 °C for 4 h and then cooled to room temperature. The mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated, and the crude product was purified by column chromatography on silica gel using hexanes/EtOAc as the eluent.

Procedure for Reaction Run at a 2 mmol Scale. In a 50 mL Schlenk tube containing Tol-BINAP Pd G3 (20.96 mg, 20 μmol) (for 4-methoxyphenylboronic acid) or Tol-BINAP Pd G3 (15.68 mg, 15 μmol) and CataCXium A Pd G3 (25.2 mg, 35 μmol) (for 4-(trifluoromethyl)phenylboronic acid), evacuated and backfilled with CO three times, the following reagents were sequentially added: iodoperfluoroalkane (6 mmol), bromobenzene (6.4 mL), acetylene (2 mmol), a solution of boronic acid (2.8 mmol in 3.2 mL of bromobenzene), 2 M aq Cs_2CO_3 (2 mL, 4 mmol), and pyridine (for the reaction with 4-methoxyphenylboronic acid; 2 mol %, 40 μmol, 1.6 mL of 25 mM solution in bromobenzene). The reaction mixture (protected from light with aluminum foil) was stirred at 50 °C for 4 h and then cooled to room temperature. The mixture was quenched with water (30 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated, and the crude product was purified by column chromatography on silica gel using hexanes/EtOAc as the eluent.

Analytical Data of Isolated Compounds. *(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-2-phenylhept-2-en-1-one (**3**).* Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (82 mg, 0.18 mmol, yield 72%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 7.50−7.27 (m, 5H), 6.96 (d, J = 8.9 Hz, 2H), 5.99 (t, J = 14.3 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 164.4, 152.8 (t, J = 4.5 Hz), 133.1, 132.6, 129.0, 128.2, 128.1 (t, J = 2.6 Hz), 127.6, 117.6, 114.2, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.7 (m, 3F), −106.4 (m, 2F), −124.5 (m, 2F), −127.2 (m, 2F); IR (CH_2Cl_2) 3060, 2939, 2844, 1666, 1600, 1575, 1511, 1354, 1234, 1134, 1021, 881, 869, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{20}H_{13}F_9O_2Na$ 479.0664, found 479.0659.

*(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1,2-diphenylhept-2-en-1-one (**7**).* Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with perfluorobutyl iodide and phenylboronic acid under Conditions A (76 mg, 0.18 mmol, yield 72%). The title compound was isolated as a

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colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.88 (m, 2H), 7.67−7.55 (m, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.43−7.33 (m, 5H), 6.06 (t, J = 14.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 152.4 (t, J = 4.3 Hz), 135.0, 134.0, 132.8 130.1, 129.1, 128.8, 128.3, 128.2, 118.8 (t, J = 22.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.5 (m, 3F), −106.6 (m, 2F), −125.0 (m, 2F), −128.1 (m, 2F); IR (CH_2Cl_2) 3062, 2926, 2855, 1675, 1598, 1448, 1353, 1234, 1134, 1021, 881, 741, 698, 589, 528 (cm^{-1}); MS (EI) m/z 426.1 (14, M$^+$), 407.1 (33), 321.1 (9), 182.1 (11), 151.1 (13), 105.2 (100), 102.2 (17), 77.3 (47), 51.4 (16); HRMS (EI/magnetic sector) m/z M$^+$ calcd for $C_{19}H_{11}F_9O$ 426.0666, found 426.0674.

(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-2-phenyl-1-(4-(trifluoromethyl)-phenyl)hept-2-en-1-one (**5**). Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with perfluorobutyl iodide and (4-(trifluoromethyl)phenyl)boronic acid under Conditions B (76 mg, 0.153 mmol, yield 61%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/toluene 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.38 (bm, 5H), 6.13 (t, J = 14.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.97 (s), 151.83 (t, J = 4.5 Hz), 137.85 (s), 132.27 (s), 130.22 (s), 129.69 (s), 129.46 (s, J = 6.5 Hz), 129.38 (s), 128.38 (s), 128.26 (t, J = 2.6 Hz), 125.98−125.73 (m), 120.03 (t, J = 22.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.8 (m, 3F), −83.9 (m, 3F), −106.5 (m, 2F), −121.0 (m, 2F), −124.2 (m, 2F); IR (CH_2Cl_2) 3064, 2927, 1685, 1327, 1235, 1174, 1134, 1068, 1015, 854, 698; MS (EI) m/z 494.1 (22, M$^+$), 475.1 (10), 321.1 (14), 182.1 (11), 174.1 (18), 173.1 (100), 151.1 (14), 145.1 (41), 102.2 (19); HRMS (EI/magnetic sector) m/z M$^+$ calcd for $C_{20}H_{10}F_{12}O$ 494.0540, found 494.0542.

(E)-1-(3,4-Difluorophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylhept-2-en-1-one (**8**). Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with (3,4-difluorophenyl)boronic acid and perfluorohexyl iodide under Conditions B (60 mg, 0.13 mmol, yield 52%). The title compound was isolated as a dark brown oil after chromatography on silica gel (17 g column, hexane/toluene 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.32 (m, 7H), 7.18 (bm, J = 8.1, 4.4, 1.5 Hz, 1H), 6.23 (t, J = 14.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 152.6 (t, J = 4.4 Hz), 133.4, 131.5, 129.2, 129.0, 128.7 (t, J = 2.4 Hz), 128.7, 128.1, 127.9, 127.2, 125.5 (d, J = 3.6 Hz), 124.9−124.5 (m), 121.8 (d, J = 16.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.9 (m, 3F), −106.7 (m, 2F), −123.6 (m, 2F), −125.8 (m, 2F), −134.9 (d, J = 22.2 Hz, 1F), −136.28 (d, J = 21.6 Hz, 1F); IR (CH_2Cl_2) 3062, 2925, 2854, 2197, 1680, 1645, 1484, 1353, 1236, 1134, 1030, 883, 757, 700, 532 (cm^{-1}); HRMS (EI/magnetic sector) m/z M$^+$ calcd for $C_{19}H_9F_{11}O$ 462.0478, found 462.0482.

(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-4-yl)hept-2-en-1-one (**9**). Prepared in the reaction of 4-methoxyphenylacetylene (33 mg, 0.250 mmol) with perfluorobutyl iodide and (1-methyl-1*H*-indol-4-yl)boronic acid under Conditions A (74 mg, 0.145 mmol, yield 58%). The title compound was isolated as a dark yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 1.4 Hz, 1H), 7.88 (dd, J = 8.7, 1.6 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.7 Hz, 1H), 7.13 (d, J = 3.2 Hz, 1H), 6.88 (d, J = 8.9 Hz, 2H), 6.62 (dd, J = 3.2, 0.5 Hz, 1H), 5.95 (t, J = 14.5 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 160.2, 153.3 (t, J = 4.0 Hz), 139.6, 130.9, 129.8 (t, J = 2.8 Hz), 128.1, 126.8, 125.8, 125.7, 123.4, 116.0 (t, J = 21.8 Hz), 113.7, 109.5, 103.4, 55.2, 33.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.9 (m, 3F), −104.8 (m, 2F), −121.9 (m, 2F), −125.2 (m, 2F); IR (CH_2Cl_2) 3103, 3061, 2929, 1659, 1606, 1567, 1512, 1452, 1345, 1307, 1249, 1235, 1197, 1181, 1133, 1104, 1033, 888, 816, 754, 723, 582, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + H]$^+$ calcd for $C_{23}H_{17}F_9NO_2$ 510.1110, found 510.1118.

(E)-1-(Benzo[b]thiophen-3-yl)-4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylhept-2-en-1-one (**10**). Prepared in the reaction of phenylacetylene (25.8 mg, 0.253 mmol) with perfluorobutyl iodide and 3-benzothiopheneboronic acid under Conditions A (110 mg, 0.228 mmol, yield 90%). The title compound was isolated as a brown oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 7.9 Hz, 1H), 8.25 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.53−7.35 (m, 7H), 6.21 (t, J = 14.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.1, 153.2 (t, J = 4.4 Hz), 141.1, 140.0, 136.6, 133.1, 129.2, 128.3, 128.2 (t, J = 2.6 Hz), 126.3, 126.1, 125.6, 122.4, 122.34, 118.6 (t, J = 22.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.5 (m, 3F), −106.9 (m, 2F), −124.7 (m, 2F), −128.5 (m, 2F); IR (CH_2Cl_2) 3100, 3063, 3033, 2927, 2854, 2196, 1652, 1594, 1491, 1460, 1422, 1354, 1235, 1203, 1134, 1114, 1059, 1031, 931, 883, 767, 742, 699, 596, 525, 478 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{21}H_{11}F_9OSNa$ 505.0279, found 505.0266.

(E)-1-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylhept-2-en-1-one (**11**). Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with perfluorobutyl iodide and benzo[*d*][1,3]dioxol-5-ylboronic acid under Conditions A (73 mg, 0.155 mmol, yield 62%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 8.2, 1.7 Hz, 1H), 7.42 (d, J = 1.7 Hz, 1H), 7.41−7.34 (m, 5H), 6.87 (d, J = 8.2 Hz, 1H), 6.06 (s, 2H), 5.97 (t, J = 14.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 152.9, 152.7 (t, J = 3.8 Hz), 148.6, 133.0, 129.5, 129.1, 128.2, 128.1 (t, J = 2.6 Hz), 127.5, 117.7 (t, J = 22.1 Hz), 109.1, 108.1, 102.2; ^{19}F NMR (376 MHz, $CDCl_3$) −81.2 (m, 3F), −106.9 (m, 2F), −124.6 (m, 2F), −128.7 (m, 2F); IR (CH_2Cl_2) 3062, 2910, 1663, 1603, 1505, 1488, 1444, 1354, 1237, 1134, 1111, 1038, 932, 885, 741, 698, 588, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{11}F_9O_3Na$ 493.0457, found 493.0458.

(E)-1-(4-Bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylhept-2-en-1-one (**12**). Prepared in the reaction of phenylacetylene (25.8 mg, 0.253 mmol) with perfluorobutyl iodide and 4-bromophenylboronic acid under Conditions A (110 mg, 0.217 mmol, yield 86%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.38 (m, 5H), 6.07 (t, J = 14.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 152.1 (t, J = 4.8 Hz), 133.7, 132.5, 132.2, 131.8, 131.4, 129.3, 128.3, 128.2 (t, J = 2.6 Hz), 119.1 (t, J = 22.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.2 (m, 3F), −104.8 (m, 2F), −121.3 (m, 2F), −125.1 (m, 2F); IR (CH_2Cl_2) 3060, 3033, 2928, 2854, 2198, 1675, 1586, 1484, 1445, 1397, 1353, 1303, 1234, 1174, 1134, 1071, 1032, 1011, 925, 881, 842, 741, 700, 590, 513 (cm^{-1}); MS (EI) m/z 503.9 (13, M$^+$), 183.0 (100), 155.0 (27), 105.2 (15), 102.2 (22), 75.3 (19); HRMS (EI/magnetic sector) m/z M$^+$ calcd for $C_{19}H_{10}BrF_9O$ 503.9771, found 503.9776.

(E)-1-(4-(tert-Butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylhept-2-en-1-one (**13**). Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with perfluorobutyl iodide and (4-(*tert*-butyl)phenyl)boronic acid under Conditions A (99 mg, 0.205 mmol, yield 82%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/toluene 8:2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.43−7.33 (m, 5H), 6.01 (t, J = 14.2 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 158.2, 152.6 (t, J = 4.8 Hz), 133.0, 132.2, 130.2, 129.0, 128.2, 126.7 (t, J = 1.1 Hz), 125.9, 118.1 (t, J = 22.2 Hz), 35.3, 31.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.6 (m, 3F), −104.8 (m, 2F), −121.8 (m, 2F), −125.7 (m, 2F); IR (CH_2Cl_2) 3065, 2930, 1685, 1330, 1238, 1175, 1133, 1070, 1017, 857, 698 (cm^{-1}); MS (EI) m/z 482.1 (12, M$^+$), 243.1 (17), 158.2 (100), 102.2 (18); HRMS (EI/magnetic sector) m/z M$^+$ calcd for $C_{23}H_{19}F_9O$ 482.1292, found 482.1295.

(1E,4E)-6,6,7,7,8,8,9,9,9-Nonafluoro-1,4-diphenylnona-1,4-dien-3-one (**14**). Prepared in the reaction of 4-methoxyphenylacetylene (34.3 mg, 0.260 mmol) with perfluorobutyl iodide and (*E*)-styrylboronic acid under Conditions A (54 mg, 0.112 mmol, yield 43%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 15.8 Hz, 1H), 7.44 (dd, J = 7.7, 1.6 Hz, 2H), 7.37 (dd, J = 6.5, 4.5 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 15.8 Hz, 1H), 6.55 (t, J = 14.7 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1,

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160.2, 151.6 (t, J = 4.2 Hz), 146.5, 134.2, 131.1, 130.0 (t, J = 2.5 Hz), 129.0, 128.76−128.28 (m), 125.2, 122.3, 120.3 (t, J = 21.5 Hz), 113.9, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −78.62 (m, 3F), −105.50 (m, 2F), −122.00 (m, 2F), −124.32 (m, 2F); IR (CH_2Cl_2) 3062, 3030, 2958, 2932, 2842, 1663, 1605, 1575, 1512, 1450, 1354, 1293, 1236, 1178, 1133, 1106, 1032, 979, 883, 831, 748, 689, 562, 529 (cm^{-1}); MS (EI) m/z 482.1 (24, M^+), 351.1 (18), 131.1 (100), 103.2 (354), 77.3 (21); HRMS (EI/magnetic sector) m/z M^+ calcd for $C_{22}H_{15}F_9O_2$ 482.0928, found 482.0929.

*(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-2-(3,4,5-trimethoxyphenyl)hept-2-en-1-one (**15**).* Prepared in the reaction of 5-ethynyl-1,2,3-trimethoxybenzene (48.0 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (97 mg, 0.178 mmol, yield 71%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 6.63 (s, 2H), 5.92 (t, J = 14.3 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.83 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 164.5, 153.0, 152.7 (t, J = 4.6 Hz), 138.9, 132.5, 128.1, 127.6, 116.9 (t, J = 21.8 Hz), 114.2, 105.8 (t, J = 2.5 Hz), 60.8, 56.2, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.9 (m, 3F), −106.4 (m, 2F), −124.4 (m, 2F), −127.40 (m, 2F); IR (CH_2Cl_2) 3005, 2941, 2843, 2588, 1665, 1599, 1581, 1509, 1466, 1415, 1353, 1314, 1237, 1170, 1132, 1028, 954, 884, 844, 773, 737, 708, 586, 527 (cm^{-1}); HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{23}H_{19}F_9O_5Na$ 569.0981, found 569.0978.

*(E)-4-(4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-1-oxohept-2-en-2-yl)phenyl 4-Methylbenzenesulfonate (**16**).* Prepared in the reaction of 4-ethynylphenyl 4-methylbenzenesulfonate (68 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (115.8 mg, 0.185 mmol, yield 74%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.02−6.94 (m, 4H), 5.99 (t, J = 14.1 Hz, 1H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 164.6, 151.3 (t, J = 4.2 Hz), 150.1, 145.6, 132.6, 132.0, 132.0, 129.7, 129.5 (t, J = 2.5 Hz), 128.5, 127.3, 122.2, 118.7 (t, J = 22.2 Hz), 114.3, 55.6, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −81.5 (m, 3F), −106.9 (m, 2F), −124.6 (m, 2F), −128.5 (m, 2F); IR (CH_2Cl_2) 3500, 3068, 2925, 2851, 1664, 1599, 1574, 1502, 1462, 1378, 1355, 1235, 1179, 1134, 1049, 1023, 865, 844, 768, 749, 709, 686, 584, 553 (cm^{-1}); HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{27}H_{19}F_9O_5SNa$ 649.0707, found 649.0698.

*(E)-2-(2-Bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)hept-2-en-1-one (**17**).* Prepared in the reaction of 2-bromophenylacetylene (45.8 mg, 0.253 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (101 mg, 0.182 mmol, yield 72%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.9 Hz, 2H), 7.56 (d, J = 7.9 Hz, 1H), 7.42−7.33 (m, 2H), 7.30−7.23 (m, 1H), 6.99 (d, J = 8.9 Hz, 2H), 6.35 (t, J = 13.8 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 164.1, 150.2 (t, J = 3.9 Hz), 135.0, 132.9, 132.3, 131.9 (t, J = 2.9 Hz), 130.3, 128.2, 126.8, 123.8 (t, J = 21.8 Hz), 121.6 (t, J = 1.9 Hz), 114.0, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.7 (m, 3F), −108.0 (m, 2F), −121.4 (m, 2F), −125.1 (m, 2F); IR (CH_2Cl_2) 3303, 3064, 3010, 2965, 2937, 2843, 1660, 1600, 1574, 1509, 1469, 1437, 1421, 1353, 1314, 1232, 1171, 1134, 1026, 929, 883, 844, 734, 589, 530 (cm^{-1}); HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{20}H_{12}BrF_9O_2Na$ 556.9769; found 556.9761.

*(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-2-(naphthalen-1-yl)hept-2-en-1-one (**18**).* Prepared in the reaction of 1-ethynylnaphthalene (38.3 mg, 0.252 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (93 mg, 0.184 mmol, yield 73%). The title compound was isolated as a yellow oil solid after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.9 Hz, 2H), 7.97 (t, J = 7.6 Hz, 1H), 7.88−7.82 (m, 2H), 7.55−7.44 (m, 4H), 6.97 (d, J = 8.9 Hz, 2H), 6.45 (t, J = 13.8 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 164.3, 151.3 (t, J = 4.5 Hz), 133.4, 132.5, 131.3 (t, J = 4.5 Hz), 131.1, 129.7, 129.3, 128.32, 128.2, 127.8, 126.7, 125.6, 124.7, 122.2 (t, J = 21.8 Hz), 114.2, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.8 (m, 3F), −106.9 (s, 2F), −123.2 (m, 2F), −124.7 (m, 2F); IR (CH_2Cl_2) 3061, 2936, 2843, 1661, 1600, 1509, 1236, 1171, 1134, 1031, 845, 781; HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{24}H_{15}F_9O_2Na$ 529.0826, found 529.0826.

*(E)-2-(4-Bromophenyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)hept-2-en-1-one (**19**).* Prepared in the reaction of 4-bromophenylacetylene (45.3 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (102 mg, 0.190 mmol, yield 76%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 6.02 (t, J = 14.1 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 164.6, 151.5 (t, J = 4.8 Hz), 132.6, 132.0, 131.4, 129.7 (t, J = 2.6 Hz), 127.4, 123.5, 118.4 (t, J = 22.3 Hz), 114.3, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.5 (m, 3F), −106.9 (m, 2F), −124.7 (m, 2F), −128.5 (m, 2F); IR (CH_2Cl_2) 3062, 2936, 2844, 1664, 1599, 1575, 1509, 1488, 1353, 1235, 1169, 1134, 1027, 1013, 881, 845, 714, 528 (cm^{-1}); MS (EI) m/z 533.9 (5, M^+), 135.1 (100), 107.2 (10), 92.2 (15), 77.3 (15); HRMS (EI/magnetic sector) m/z M^+ calcd for $C_{20}H_{12}BrF_9O_2$ 533.9877, found 533.9884.

*(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-2-(4-nitrophenyl)hept-2-en-1-one (**20**).* Prepared in the reaction of with 4-nitrophenylacetylene (36.9 mg, 0.251 mmol) with perfluorobutyl iodide and 4-methoxyphenyl boronic acid under Conditions B (60 mg, 0.120 mmol, yield 48%). The title compound was isolated as a dark yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.9 Hz, 2H), 7.93 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.9 Hz, 2H), 6.13 (t, J = 13.9 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 164.9, 150.1 (t, J = 5.2 Hz), 148.1, 139.7, 132.6, 129.2 (t, J = 2.5 Hz), 127.0, 123.3, 120.2 (t, J = 22.5 Hz), 114.5, 55.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.3 (m, 3F), −105.6 (m, 2F), −122.7 (m, 2F), −124.4 (m, 2F); IR (CH_2Cl_2) 3077, 2925, 1729, 1664, 1599, 1524, 1463, 1348, 1233, 1169, 1134, 1025, 883, 846, 707, 529 (cm^{-1}); MS (EI) m/z 501.0 (5, M^+), 135.1 (100), 107.2 (12), 92.2 (14), 77.3 (19); HRMS (EI/magnetic sector) m/z M^+ calcd for $C_{20}H_{12}F_9NO_4$ 501.0623, found 501.0625.

*(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-2-(thiophen-3-yl)hept-2-en-1-one (**21**).* Prepared in the reaction of 3-ethynylthiophene (27.0 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (44 mg, 0.095 mmol, yield 38%) or under Conditions B (64 mg, 0.138 mmol, yield 55%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.9 Hz, 2H), 7.48 (dd, J = 2.8, 1.0 Hz, 1H), 7.31 (dd, J = 5.1, 3.0 Hz, 1H), 7.19 (dd, J = 5.0, 0.9 Hz, 1H), 6.95 (d, J = 8.9 Hz, 2H), 5.89 (t, J = 14.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 164.5, 148.0 (t, J = 4.6 Hz), 132.6, 132.5, 127.9 (t, J = 3.4 Hz), 127.6, 126.7 (t, J = 3.6 Hz), 125.8, 116.0 (t, J = 22.6 Hz), 114.2, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.8 (m, 3F), −105.0 (m, 2F), −121.4 (m, 2F), −124.4 (m, 2F); IR (CH_2Cl_2) 3316, 3111, 2962, 2937, 2844, 2583, 1666, 1600, 1575, 1511, 1463, 1422, 1353, 1318, 1243, 1170, 1133, 1113, 1026, 938, 886, 847, 798, 766, 750, 711, 615, 526 (cm^{-1}); HRMS (ESI/Q-TOF) m/z $[M + Na]^+$ calcd for $C_{18}H_{11}F_9O_2SNa$ 485.0228, found 485.0222.

*(E)-4,4,5,5,6,6,7,7,7-Nonafluoro-1-(4-methoxyphenyl)-2-(pyridin-3-yl)hept-2-en-1-one (**22**).* Prepared in the reaction of 3-ethynylpyridine (25.4 mg, 0.246 mmol) with 4-methoxyphenylboronic acid and perfluorohexyl iodide under Conditions A (72 mg, 0.157 mmol, yield 64%). The title compound was isolated as a dark yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 8:2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 1.3 Hz, 1H), 8.59 (dd, J = 4.9, 1.5 Hz, 1H), 7.92 (d, J = 8.9 Hz, 2H), 7.78−7.68 (m, 1H), 7.36−7.27 (m, 1H), 6.98 (d, J = 8.9 Hz, 2H), 6.11 (t, J = 14.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.81, 164.71, 150.0, 148.9 (t, J

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= 4.3 Hz), 148.3 (t, J = 2.8 Hz), 135.6 (t, J = 2.1 Hz), 132.6, 129.8, 127.2, 122.9, 120.2 (t, J = 22.3 Hz), 114.4, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.3 (m, 3F), −104.9 (m, 2F), −120.3 (m, 2F), −124.6 (m, 2F); IR (CH_2Cl_2) 3304, 3054, 3034, 3012, 2967, 2939, 2844, 2586, 1663, 1600, 1574, 1511, 1476, 1418, 1353, 1318, 1234, 1170, 1134, 1026, 931, 883, 846, 713, 617, 589, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + H]$^+$ calcd for $C_{19}H_{12}F_9NO_2$ 458.0803, found 458.0791.

(E)-2-(3-Chloropropyl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)hept-2-en-1-one (**23**). Prepared in the reaction of 5-chloropent-1-yne (25.6 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (75 mg, 0.165 mmol, yield 66%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 5.84 (t, J = 14.9 Hz, 1H), 3.89 (s, 3H), 3.53 (t, J = 6.6 Hz, 2H), 2.92−2.74 (m, 2H), 2.04−1.84 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 164.4, 152.8 (t, J = 4.6 Hz), 132.2, 128.1, 120.08 (t, J = 23.9 Hz), 114.2, 55.6, 44.0, 31.2, 27.2 (t, J = 2.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.2 (m, 3F), −106.2 (m, 2F), −121.6 (m, 2F), −124.9 (m, 2F); IR (CH_2Cl_2) 2962, 2844, 1661, 1600, 1510, 1462, 1313, 1233, 1168, 1134, 1029, 884, 844, 740, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{17}H_{14}ClF_9O_2Na$ 479.0431, found 479.0428.

(E)-5-(4-Fluorophenyl)-1-(4-methoxyphenyl)-2-(2,2,3,3,4,4,5,5,5-nonafluoropentylidene)pentane-1,5-dione (**24**). Prepared in the reaction of 1-(4-fluorophenyl)pent-4-yn-1-one (44.9 mg, 0.255 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (86.5 mg, 0.163 mmol, yield 64%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.88 (m, 2H), 7.88−7.79 (m, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 5.87 (t, J = 15.0 Hz, 1H), 3.88 (s, 3H), 3.20 (dd, J = 8.1, 6.3 Hz, 2H), 3.08 (t, J = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 194.7, 167.1, 164.3 (s, J = 22.3 Hz), 153.0 (t, J = 4.5 Hz), 132.8 (d, J = 3.0 Hz), 132.4, 130.7 (d, J = 9.3 Hz), 127.9, 120.2 (t, J = 23.7 Hz), 115.7 (d, J = 21.9 Hz), 114.1, 55.6, 37.0, 24.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.9 (m, 3F), −105.4 (s, 1F), −106.5 (m, 2F), −121.7 (m, 2F), −124.9 (m, 2F); IR (CH_2Cl_2) 3360, 3302, 3075, 3010, 2938, 2844, 2582, 1688, 1659, 1599, 1575, 1509, 1462, 1419, 1354, 1308, 1232, 1170, 1134, 1031, 980, 884, 844, 793, 595, 565, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{23}H_{16}F_{10}O_3Na$ 553.0832, found 553.0828.

(E)-4-Methyl-N-(8,8,9,9,10,10,11,11,11-nonafluoro-6-(4-methoxybenzoyl)undec-6-en-1-yl)benzenesulfonamide (**25**). Prepared in the reaction of *N*-(hex-5-yn-1-yl)-4-methylbenzenesulfonamide (66.3 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (101 mg, 0.163 mmol, yield 65%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 8:2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.9 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 5.73 (t, J = 15.0 Hz, 1H), 4.64 (t, J = 6.1 Hz, 1H), 3.88 (s, 3H), 2.87 (dd, J = 13.3, 6.7 Hz, 2H), 2.61 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 1.44−1.38 (m, 2H), 1.30−1.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 164.3, 154.2 (t, J = 4.4 Hz), 143.3, 137.0, 132.2, 129.6, 128.2, 127.0, 118.9 (t, J = 23.7 Hz), 114.1, 55.6, 42.9, 29.3 (t, J = 2.5 Hz), 29.1, 27.6, 26.4, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.6 (m, 3F), −105.9 (m, 2F), −123.5 (m, 2F), −124.9 (m, 2F); IR (CH_2Cl_2) 3288, 2936, 2864, 1659, 1599, 1509, 1324, 1233, 1165, 1134, 1095, 1029, 883, 845, 815, 664, 552 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{26}H_{26}F_9NO_4SNa$ 642.1331, found 642.1328.

(E)-2-(Cyclohex-1-en-1-yl)-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)hept-2-en-1-one (**26**). Prepared in the reaction of 1-ethynylcyclohex-1-ene (26.5 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (60 mg, 0.130 mmol, yield 52%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 5.84 (br s, 1H), 5.64 (t, J = 14.3 Hz, 1H), 3.89 (s, 3H), 2.12 (m, J = 5.8, 3.8 Hz, 4H), 1.68−1.55 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 164.3, 155.4 (t, J = 4.2 Hz), 132.4, 131.6, 129.5 (t, J = 3.2 Hz), 128.1, 116.3 (t, J = 21.8 Hz), 114.0, 55.6, 28.2 (t, J = 1.9 Hz), 25.3, 22.3, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.9 (m, 3F), −105.9 (m, 2F), −121.7 (m, 2F), −125.8 (m, 2F); IR (CH_2Cl_2) 2936, 2861, 2843, 1665, 1600, 1575, 1510, 1462, 1422, 1353, 1311, 1234, 1170, 1133, 1105, 1032, 925, 881, 845, 743, 713, 610, 529 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{17}F_9O_2Na$ 483.0977, found 483.0974.

(E)-2-Cyclopropyl-4,4,5,5,6,6,7,7,7-nonafluoro-1-(4-methoxyphenyl)hept-2-en-1-one (**27**). Prepared in the reaction of ethynylcyclopropane (16.7 mg, 0.253 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (55 mg, 0.132 mmol, yield 52%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 5.49 (t, J = 15.1 Hz, 1H), 3.89 (s, 3H), 2.25−2.13 (m, 1H), 0.98−0.88 (m, 2H), 0.77−0.69 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 164.6, 156.3 (t, J = 5.0 Hz), 132.3, 128.3, 114.8 (t, J = 24.4 Hz), 114.1, 55.6, 11.2 (t, J = 3.8 Hz), 8.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.8 (m, 3F), −105.7 (m, 2F), −122.3 (m, 2F), −125.8 (m, 2F); IR (CH_2Cl_2) 3079, 3015, 2939, 2845, 1666, 1600, 1575, 1509, 1464, 1423, 1314, 1232, 1167, 1134, 1106, 1032, 938, 7, 876, 847, 737, 718, 528 (cm^{-1}); MS (EI) m/z 420.1 (25, M$^+$), 389.1 (15), 201.1 (11), 135.1 (100), 107.2 (13), 92.2 (22), 77.3 (23); HRMS (EI/magnetic sector) m/z M$^+$ calcd for $C_{17}H_{13}F_9O_2$ 420.0772, found 420.0769.

(E)-4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-(4-methoxyphenyl)-2-phenylnon-2-en-1-one (**28**). Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with perfluorohexyl iodide and 4-methoxyphenylboronic acid under Conditions A (103 mg, 0.185 mmol, yield 74%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 7.43−7.39 (m, 2H), 7.38−7.32 (m, 3H), 6.96 (d, J = 8.9 Hz, 2H), 5.99 (t, J = 14.2 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 164.4, 152.8 (t, J = 4.6 Hz), 133.6, 132.6, 129.0, 128.2 (s, J = 5.4 Hz), 128.1 (t, J = 2.7 Hz), 127.7, 117.7 (t, J = 22.2 Hz), 114.2, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.1 (m, 3F), −104.3 (m, 2F), −121.3 (m, 2F), −122.8 (m, 2F), −122.4 (m, 2F), −125.9 (m, 2F); IR (CH_2Cl_2) 3060, 2938, 2844, 1665, 1601, 1575, 1510, 1317, 1241, 1203, 1170, 1145, 1121, 1031, 846, 744, 699, 528 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{22}H_{13}F_{13}O_2Na$ 579.0600, found 579.0591.

(E)-5-Bromo-4,4,5,5-tetrafluoro-1-(4-methoxyphenyl)-2-phenylpent-2-en-1-one (**29**). Prepared in the reaction of phenylacetylene (26.0 mg, 0.255 mmol) with 1-bromo-1,1,2,2-tetrafluoro-2-iodoethane and 4-methoxyphenylboronic acid under Conditions A (88 mg, 0.212 mmol, yield 83%). The title compound was isolated as a colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 7.45−7.39 (m, 2H), 7.39−7.33 (m, 3H), 6.96 (d, J = 8.9 Hz, 2H), 6.02 (t, J = 13.8 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 164.4, 152.5 (t, J = 4.0 Hz), 133.3, 132.6, 128.9, 128.2 (t, J = 2.7 Hz), 128.1, 127.8, 118.0 (t, J = 22.7 Hz), 114.1, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.5 (t, J = 7.0 Hz, 2F), −103.5 (t, J = 7.0 Hz, 2F); IR (CH_2Cl_2) 3060, 3022, 2960, 2936, 2843, 1663, 1599, 1574, 1510, 1461, 1443, 1421, 1316, 1262, 1244, 1168, 1148, 1115, 1084, 1027, 915, 845, 793, 762, 702, 602, 565, 536 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{18}H_{13}BrF_4O_2Na$ 438.9927, found 438.9917.

(E)-4,5,5,5-Tetrafluoro-1-(4-methoxyphenyl)-2-phenyl-4-(trifluoromethyl)pent-2-en-1-one (**30**). Prepared in the reaction of phenylacetylene (26.4 mg, 0.259 mmol) with 1,1,1,2,3,3,3-heptafluoro-2-iodopropane and 4-methoxyphenylboronic acid under Conditions A (62 mg, 0.153 mmol, yield 59%). The title compound was isolated as colorless oil after chromatography on silica gel (17 g column, hexane/AcOEt 95:5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 7.40−7.30 (m, 5H), 7.01 (d, J = 8.9 Hz, 2H), 5.89 (d, J = 25.8 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 164.4, 152.0, 133.3 (d, J = 2.5 Hz), 132.5, 128.5, 127.9, 127.9, 127.7, 115.8 (d, J = 14.5 Hz), 114.2, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −76.4

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(d, J = 7.9 Hz, 6F), −182.8 (m, 1F); IR (CH_2Cl_2) 3060, 2928, 1665, 1601, 1575, 1510, 1462, 1444, 1421, 1308, 1259, 1228, 1207, 1170, 1081, 1034, 980, 847, 716, 702, 608, 593, 522 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{13}F_7O_2Na$ 429.0696, found 429.0693.

*(E)-Ethyl 2,2-Difluoro-5-(4-methoxyphenyl)-5-oxo-4-phenylpent-3-enoate (**31**).* Prepared in the reaction of phenylacetylene (25.5 mg, 0.250 mmol) with ethyl 2,2-difluoro-2-iodoacetate and 4-methoxyphenylboronic acid under Conditions A (52 mg, 0.145 mmol, yield 58%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 9:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.35 (m, J = 6.7, 3.6 Hz, 5H), 6.95 (d, J = 8.8 Hz, 2H), 6.17 (t, J = 11.4 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 164.2, 149.1 (t, J = 8.4 Hz), 132.7, 132.2, 129.1, 128.8 (t, J = 2.0 Hz), 128.3, 125.0 (t, J = 28.6 Hz), 114.0, 113.5, 63.1, 55.5, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −93.7 (s, 2F); IR (CH_2Cl_2) 3058, 2982, 2937, 2842, 1772, 1659, 1600, 1574, 1510, 1444, 1308, 1257, 1170, 1108, 1091, 1044, 1027, 848, 771, 701, 615 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{18}F_2O_4Na$ 383.1065, found 383.1064.

*(E)-4,4-Difluoro-1-(4-methoxyphenyl)-5-morpholino-2-phenylpent-2-ene-1,5-dione (**32**).* Prepared in the reaction of phenylacetylene (25.3 mg, 0.248 mmol) with 2,2-difluoro-2-iodo-1-morpholinoethanone and 4-methoxyphenylboronic acid under Conditions A (52 mg, 0.129 mmol, yield 52%). The title compound was isolated as a yellow oil after chromatography on silica gel (17 g column, hexane/AcOEt 8:2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 9.0 Hz, 2H), 7.46−7.39 (m, 2H), 7.38−7.29 (m, 3H), 6.91 (d, J = 9.0 Hz, 2H), 6.21 (t, J = 11.9 Hz, 1H), 3.84 (s, 3H), 3.63−3.58 (m, 2H), 3.58−3.52 (m, 2H), 3.52−3.47 (m, 2H), 3.39−3.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 164.2, 160.9 (t, J = 29.6 Hz), 148.1, 133.1, 132.7, 129.1, 128.6 (t, J = 1.9 Hz), 128.2, 128.0, 124.7 (t, J = 27.5 Hz), 114.0, 66.35 (d, J = 5.1 Hz), 55.5, 46.6 (t, J = 3.8 Hz), 43.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −89.1 (s), −120.9 (s); IR (CH_2Cl_2) 3057, 2966, 2924, 2857, 1664, 1599, 1574, 1510, 1443, 1257, 1121, 1170, 1116, 1069, 1022, 843, 758, 703, 597 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{22}H_{21}F_2NO_4Na$ 424.1331, found 424.1326.

(E)-(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 7,7,8,8,9,9,10,10,10-Nonafluoro-5-(4-methoxybenzoyl)dec-5-enoate. Prepared in the reaction of (8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl hex-5-ynoate (123.5 mg, 0.250 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (100 mg, 0.115 mmol, yield 46%, 77% conversion). The title compound was isolated as a colorless oil after chromatography on silica gel (25 g column, hexane/AcOEt 9:1): $[\alpha]_D^{22.1}$ = −31.826 (*c* 1.01 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 5.76 (t, J = 14.9 Hz, 1H), 5.33 (d, J = 4.1 Hz, 1H), 4.56 (ddd, J = 11.2, 10.5, 4.4 Hz, 1H), 3.88 (s, 3H), 2.70 (t, J = 7.6 Hz, 2H), 2.25 (m, J = 7.2 Hz, 4H), 2.05−1.91 (m, 3H), 1.88−1.73 (m, 4H), 1.66 (dt, J = 15.1, 7.4 Hz, 3H), 1.50 (m, J = 17.3, 15.7, 8.0 Hz, 8H), 1.39−1.21 (m, 6H), 1.21−1.04 (m, 8H), 0.99 (s, 6H), 0.92 (s, 3H), 0.86 (m, J = 6.6, 1.5 Hz, 6H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 172.5, 164.3, 154.0 (t, J = 4.0 Hz), 139.6, 132.2, 128.3, 122.6, 119.1 (t, J = 23.8 Hz), 114.1, 73.8, 56.7, 56.2, 55.5, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.6, 36.2, 35.8, 34.2, 31.9, 31.9, 29.3 (t, J = 2.5 Hz), 28.2, 28.0, 27.7, 27.7, 25.0, 24.3, 23.8, 22.8, 22.5, 21.0, 19.2, 18.7, 11.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.3 (m, 3F), −105.9 (m, 2F), −122.3 (m, 2F), −124.9 (m, 2F); IR (CH_2Cl_2) 2939, 2869, 2851, 1733, 1664, 1600, 1575, 1509, 1466, 1353, 1308, 1235, 1169, 1134, 1030, 883, 844, 740, 529 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{46}H_{61}F_9O_4Na$ 871.4320, found 871.4324.

(E)-6,6,7,7,8,8,9,9,9-Nonafluoro-4-(4-methoxybenzoyl)non-4-en-1-yl 2-Acetamido-2-phenylacetate. Prepared in the reaction of pent-4-yn-1-yl 2-acetamido-2-phenylacetate (66.5 mg, 0.257 mmol) with perfluorobutyl iodide and 4-methoxyphenylboronic acid under Conditions A (101 mg, 0.165 mmol, yield 64%, 81% conversion). The title compound was isolated as a pink oil after chromatography on silica gel (25 g column, hexane/acetone 8:2): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.9 Hz, 2H), 7.36−7.29 (m, 5H), 6.96 (d, J = 8.9 Hz, 2H), 6.52 (d, J = 7.2 Hz, 1H), 5.79 (t, J = 14.9 Hz, 1H), 5.56 (d, J = 7.3 Hz, 1H), 4.19−4.07 (m, 2H), 3.89 (s, 3H), 2.70−2.57 (m, 2H), 2.02 (s, 3H), 1.76 (m, J = 12.5, 6.3 Hz, 2H); ^{3}C NMR (101 MHz, $CDCl_3$) δ 194.5, 170.8, 169.3, 164.4, 152.8 (t, J = 4.0 Hz), 136.5, 132.2, 128.9, 128.5, 128.0, 127.1, 120.0 (t, J = 23.7 Hz), 114.2, 64.9, 56.5, 55.6, 27.2, 26.0 (t, J = 2.4 Hz), 23.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.9 (m, 3F), −106.3 (m, 2F), −123.1 (m, 2F), −124.8 (m, 2F); IR (CH_2Cl_2) 3301, 3064, 3035, 2960, 2844, 1745, 1659, 1599, 1512, 1457, 1372, 1315, 1235, 1172, 1133, 1030, 884, 844, 738, 699, 526 (cm^{-1}); HRMS (ESI/Q-TOF) m/z [M + Na]$^+$ calcd for $C_{27}H_{24}F_9NO_5Na$ 636.1403, found 636.1401.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01236.

Evaluation of reaction conditions, assignment of the structure of products, details of optimization and control experiments, list of the through-space ^{13}C−^{19}F couplings for all compounds, and copies of ^{1}H and ^{13}C NMR spectra of all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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