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Cu-Catalyzed Multicomponent Reaction of Styrenes, Perfluoroalkyl Halide, Alcohol, and *tert*-Butyl Hydroperoxide: One-Pot Synthesis of (*Z*)-*β*-Alkoxyperfluoroalkenone

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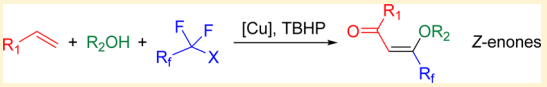
Supporting Information

ABSTRACT: An efficient synthesis of *Z*-perfluoroalkyl-substituted enones by a multicomponent reaction strategy has been described. A variety of elusive perfluoroalkylated enones are furnished under mild reaction conditions in good yields with unique chemo- and stereoselectivity. A sequence of radical-mediated Kornblum−DeLaMare reaction, Michael addition, and HF elimination is proposed for the mechanism.



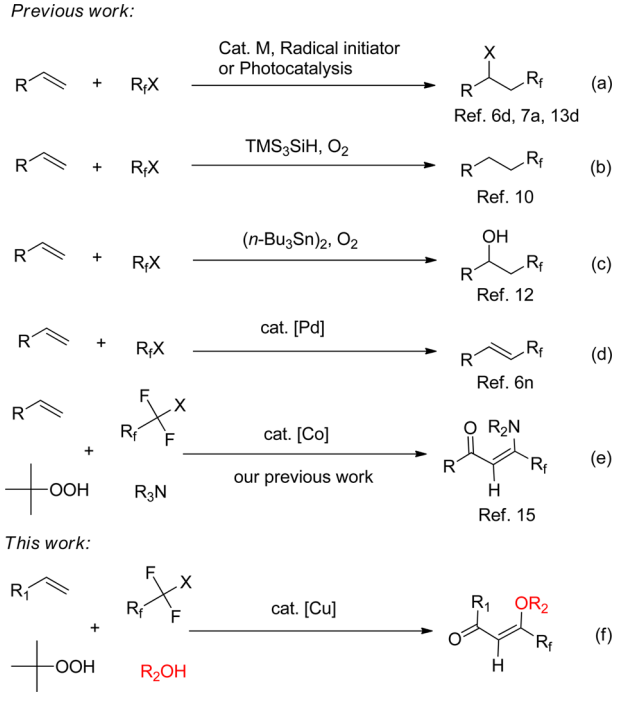
INTRODUCTION

Owing to its particular physical, chemical, and biological properties, perfluoroalkyl has become one of the most prevalent functionalities used in agrochemicals, pharmaceuticals, and materials.[1] As a result, the development of efficient perfluoroalkylation methods is of considerable importance. Although significant progress has been made on the construction of C−R_f bonds, the main efforts employ costly perfluoroalkylation reagents,[2] e.g., Togni reagents,[3] Umemoto reagent,[4] and Ruppert reagent,[5] which might limit the practicality, especially in large-scale reactions. Therefore, the development of a complementary perfluoroalkylation method utilizing routine and inexpensive reagents is still in demand.

The perfluoroalkylation with R_fX has been achieved by means of transition-metal catalysis[6] or radical-mediated transformations by use of peroxide,[7] $Na_2S_2O_4$,[8] AIBN,[9] TMS_3SiH/O_2,[10] BEt_3/O_2,[11] $(n\text{-}Bu_3Sn)_2$,[12] or reductive photocatalysis.[13] The addition of perfluoroalkyl radical to olefins offers a straightforward and powerful perfluoroalkylation method (Scheme 1a−e).[14]

Recently, we reported the efficient synthesis of (*Z*)-*β*-perfluoroalkyl enaminones in the presence of $Co(acac)_2$ and *tert*-butyl hydroperoxide (TBHP) by a multicomponent reaction strategy (Scheme 1e).[15] Inspired by these results, we hypothesized that under similar conditions the reaction among olefin, R_fX, and alcohol might give rise to (*Z*)-perfluoroalkyl-substituted enone (Scheme 1f). Herein, we disclose our new findings in the radical-mediated synthesis of (*Z*)-*β*-alkoxyperfluoroalkyl-substituted enones. A variety of elusive perfluoroalkylated enones have been obtained under mild reaction conditions in good yields with unique chemo- and stereoselectivity. The possible mechanism involves the sequence of radical-mediated Kornblum−DeLaMare reaction, Michael addition, and HF elimination.

Scheme 1. Radical-Mediated Perfluoroalkylation of Olefin



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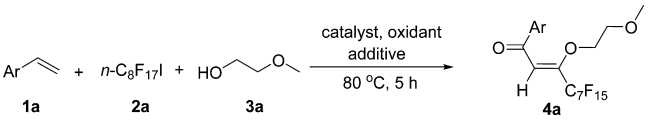
RESULTS AND DISCUSSION

The initial study was conducted with 1-*tert*-butyl-4-vinylbenzene (**1a**), perfluorooctyl iodide (**2a**), and 2-methoxyethanol (**3a**). In the presence of tetrabutylammonium iodide (TBAI) and TBHP,[16] the desired product (*Z*)-*β*-alkoxyperfluoroalkyl enone **4a** was isolated in 44% yield within 5 h at 80 °C (Table 1, entry 1), indicating that the combination of TBAI and TBHP could promote the formation of perfluoroalkyl radical from perfluoroalkyl iodide. The yield of **4a** could be increased to 75% by switching the catalyst to $Co(acac)_2$ (Table 1, entry 2). The similar yield could also be obtained by use of $Cu(acac)_2$ as catalyst (Table 1, entry 3). Later investigation showed that $Cu(acac)_2$, DABCO, and TBHP are all essential for the conversions (Table 1, entries 4–6). Replacement of TBHP by other oxidants such as H_2O_2 or DTBP reduced the chemical yields (Table 1, entries 7–11). The use of other bases such as Cs_2CO_3 or DBU in lieu of DABCO resulted in poor yields (Table 1, entries 12–15).

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	oxidant	additive	% yield[b]
1	TBAI	TBHP	DABCO	44
2	$Co(acac)_2$	TBHP	DABCO	75
3	$Cu(acac)_2$	TBHP	DABCO	75
4		TBHP	DABCO	42
5	$Cu(acac)_2$		DABCO	ND[c]
6	$Cu(acac)_2$	TBHP		trace
7	$Cu(acac)_2$	H_2O_2	DABCO	ND
8	$Cu(acac)_2$	CHP[d]	DABCO	67
9	$Cu(acac)_2$	TBPB[e]	DABCO	ND
10	$Cu(acac)_2$	di-*tert*-peroxide	DABCO	trace
11	$Cu(acac)_2$	oxone	DABCO	trace
12	$Cu(acac)_2$	TBHP	Cs_2CO_3	ND
13	$Cu(acac)_2$	TBHP	NaOAc	19
14	$Cu(acac)_2$	TBHP	DMAP	trace
15	$Cu(acac)_2$	TBHP	DBU	19

[a]Reaction conditions: 1-*tert*-butyl-4-vinylbenzene (**1a**, 0.2 mmol), perfluorooctyl iodide ($C_8F_{17}I$) (**2a**, 0.6 mmol, 3.0 equiv), 2-methoxyethanol (**3a**, 1.0 mmol, 5.0 equiv), catalyst (10 mol %), additive (3.0 equiv), and TBHP (5.0–6.0 M in decane, 3.8 equiv) in 1.0 mL of solvent (THF:PE = 1:4), 80 °C, 5 h (Ar = 4-*t*-Bu-C_6H_4). [b]Isolated yield. [c]Not detected. [d]CHP: cumene hydroperoxide. [e]TBPB: *tert*-butyl peroxybenzoate.

With the optimized reaction conditions in hand, we set out to explore the scope of this perfluoroalkylation reaction. First, a variety of olefins was applied. The protocol exhibited high functional group compatibility, including halide (**4c**–**4g**), alkyl (**4a**, **4h**), ether (**4i**, **4j**), BocNH group (**4k**), CN (**4l**), and CF_3 (**4m**) (Scheme 2). Aliphatic olefins were not tolerated under the reaction conditions. The (*Z*)-configuration of *β*-alkoxyperfluoroalkyl enone was unambiguously assigned by X-ray crystallography of **5** derived from **4d** (Scheme 3).

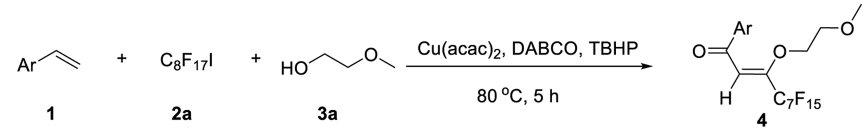
The reaction of styrene **1a** with a variety of perfluoroalkyl halides was then investigated (Scheme 4). A series of perfluoroalkyl iodides with 3–10 carbons reacted smoothly to afford the corresponding products **6a**, **6b**, **6c**, and **6e**. The desired products were also delivered in satisfactory yields while perfluoroalkyl bromides were used (**6d** and **4a**).

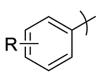
Subsequently, a range of aliphatic alcohols were examined (Scheme 5). The chain length of the alcohols has little impact on the reaction outcome (**7a**–**7d**). The presence of additional functional groups, such as esters and NHBoc, was also tolerated in the reaction, giving the corresponding products in moderate yields (**7i**–**7k**). Notably, the reaction with fluorinated alcohols readily generated the products in good yields (**7l**–**7o**).

A set of experiments was conducted to elucidate the possible mechanism. First, the result of significant suppression by adding radical inhibitors TEMPO to the reaction might suggest that the reaction went through a radical-mediated pathway (Scheme 6a). Trace amounts of byproducts **8** and **9** were observed in the reaction. While the treatment of **8** with alcohol under the standard reaction conditions failed to produce the expected product **4a** (Scheme 6b), the reaction of **9** with alcohol resulted in the desired product **4a** in good yield (Scheme 6c). These results suggested that the compound **9** was a key intermediate in the reaction, but **8** was not.

On the basis of the above results and previous literature, a plausible reaction mechanism is proposed (Scheme 7). Initially, the copper catalyst promotes the decomposition of TBHP to give *t*-BuO radical **A** and *t*-BuOO radical **B** (Scheme 7a).[17] Simultaneously, the copper-catalyzed C–I cleavage of perfluoroalkyl iodide led to the electrophilic perfluoroalkyl radical

Scheme 2. Scope of Substituted Styrenes[a]



Ar: 

4a, Ar = 4-*t*-Bu-C_6H_4, 75%
4b, Ar = Ph, 72%
4c, Ar = 4-F-C_6H_4, 72%
4d, Ar = 4-Cl-C_6H_4, 68%[b]
4e, Ar = 4-Br-C_6H_4, 67%[c]
4f, Ar = 3-F-C_6H_4, 72%
4g, Ar = 3-Br-C_6H_4, 64%
4h, Ar = 4-Me-C_6H_4, 66%
4i, Ar = 4-OMe-C_6H_4, 58%
4j, Ar = 2-OMe-C_6H_4, 48%
4k, Ar = 4-NHBoc-C_6H_4, 58%
4l, Ar = 4-CN-C_6H_4, 42%
4m, Ar = 3-CF_3-C_6H_4, 53%

[a]Reaction conditions: 0.2 mmol of styrene (**1**), 3.0 equiv of perfluorooctyl iodide (**2a**), 5.0 equiv of 2-methoxyethanol (**3a**), 10 mol % $Cu(acac)_2$, 3.0 equiv of DABCO, and 3.8 equiv of TBHP (5.0–6.0 M in decane) in 1.0 mL of solvent (THF:PE = 1:4) were stirred at 80 °C for 5 h. [b]Yield 27% when treated with $Co(acac)_2$. [c]Yield 30% when treated with $Co(acac)_2$.

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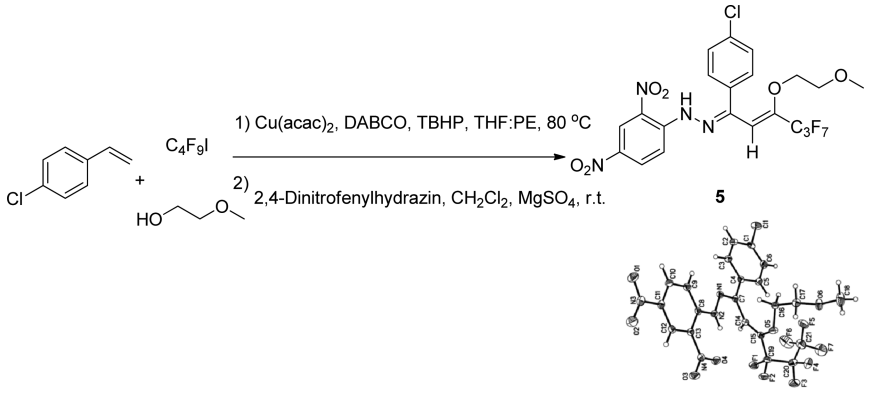
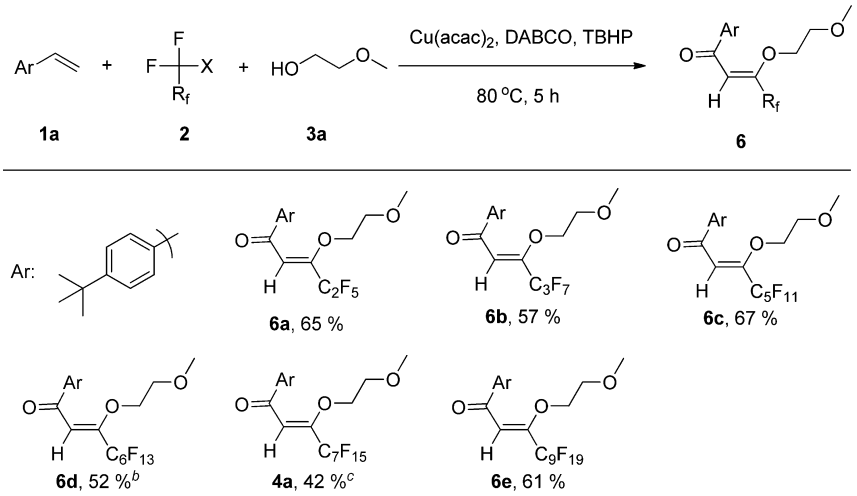
Scheme 3. Configuration Determination of (*Z*)-*β*-Alkoxyperfluoroalkyl Enone



Scheme 4. Scope of Perfluoroalkyl Halides[a]



[a]Reaction conditions: 0.2 mmol of 1-*tert*-butyl-4-vinylbenzene (**1a**), 3.0 equiv of perfluoroalkyl iodide (**2**), 5.0 equiv of 2-methoxyethanol (**3a**), 10 mmol % $Cu(acac)_2$, 3.0 equiv of DABCO, and 3.8 equiv of TBHP (5.0−6.0 M in decane) in 1.0 mL of solvent (THF:PE = 1:4) were stirred at 80 °C for 5 h. [b]$C_7F_{15}Br$ as the perfluoroalkyl source. [c]$C_8F_{17}Br$ as the perfluoroalkyl source.

C (Scheme 7b).[6i,j] The addition of **C** to styrene forms a metastable benzylic radical **D** (Scheme 7c), which reacts with radical **B** to generate the peroxide intermediate **E** (Scheme 7d, path a).[18f] Also, we cannot exclude the possibility of formation of an organo−Cu(III) intermediate via radical recombination and subsequent C−O reductive elimination (Scheme 7d′, path b). The Kornblum−DeLaMare reaction with **E** results in perfluoroalkyl ketone **F** (Scheme 7e),[18] which then undergoes the DABCO-promoted elimination of HF and generates *α*,*β*-unsaturated aryl ketone **G** (Scheme 7f).[19] Michael addition of alcohol to **G** forms the intermediate **H** (Scheme 7g),[12b] which eliminates another HF molecule to eventually generate (*Z*)-*β*-alkoxyperfluoroalkyl-substituted enone (Scheme 7h).

CONCLUSIONS

In summary, an efficient synthesis of *Z*-perfluoroalkyl-substituted enones by multicomponent reaction strategy has been described. A variety of elusive perfluoroalkylated enones are furnished under mild reaction conditions in good yields with unique chemo- and stereoselectivity. A sequence of radical-mediated Kornblum−DeLaMare reaction, Michael addition, and HF elimination is proposed for the mechanism

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under air atmosphere. $Cu(acac)_2$ and TBHP (5.0−6.0 M in decane) were purchased from Sigma-Aldrich. Column chromatography was generally performed on silica gel (300−400 mesh), and reactions were monitored by thin-layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H (400 MHz) and ^{13}C NMR (100 MHz) data were collected with $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^1H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as an internal reference. ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.0 ppm) as internal reference.

General Procedures for the Synthesis of 4a−4m, 6a−6e, and 7a−7o. Styrenes (0.2 mmol), perfluorooctyl iodide (0.6 mmol), 2-methoxyethanol (1.0 mmol), $Cu(acac)_2$ (0.01 mmol), 1,4-diazabicyclo[2.2.2]octane (0.6 mmol), TBHP (0.15 mL, 5.0−6.0 M in decane), 0.2 mL THF, and 0.8 mL petroleum ether were added to a tube that uses an air balloon. The reaction mixture was stirred at 80 °C for 5 h. The reaction mixture was quenched with sodium sulfite anhydrous. The organic solvent was then removed in vacuum, and flash silica gel column chromatographic purification with petroleum ether/ethyl acetate mixtures afforded product.

Procedures for the Synthesis of 5. 1-Chloro-4-vinylbenzene (0.2 mmol), 1,1,1,2,2,3,3,4,4-nonafluoro-4-iodobutane (0.6 mmol), 2-methoxyethanol (1.0 mmol), $Cu(acac)_2$ (0.01 mmol), 1,4-diazabicyclo[2.2.2]octane (0.6 mmol), TBHP (0.15 mL, 5.0−6.0 M

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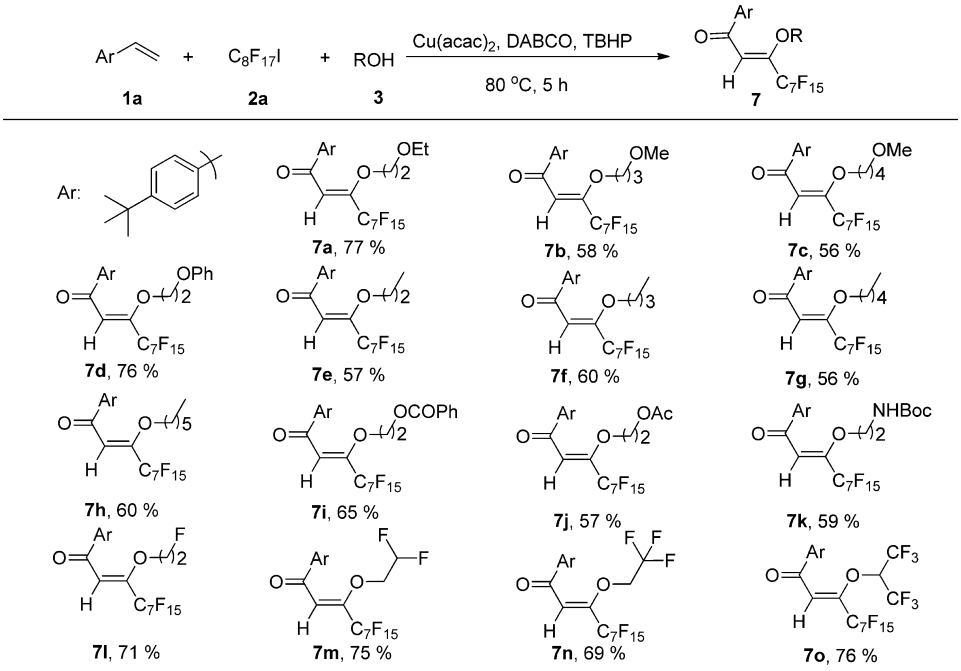
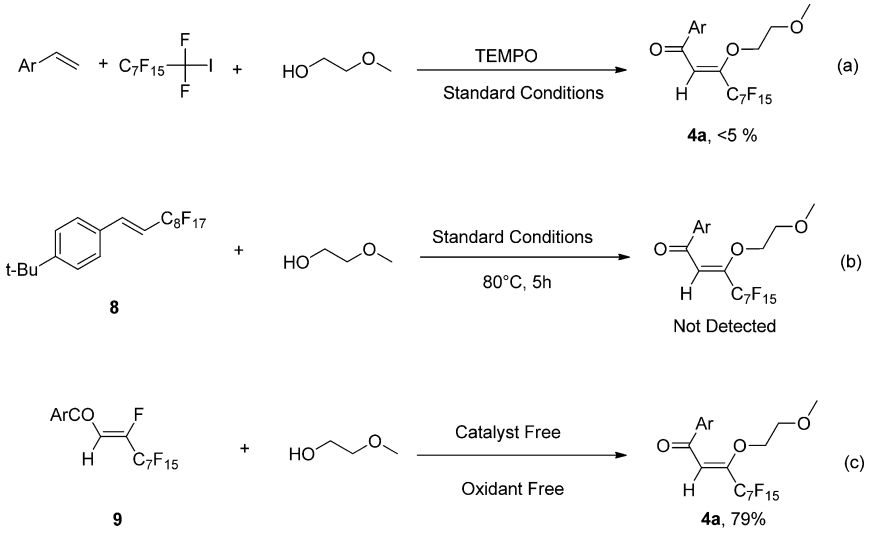
Scheme 5. Scope of Alcohols[a]



[a]Reaction conditions: 0.2 mmol of 1-*tert*-butyl-4-vinylbenzene (**1a**), 3.0 equiv of perfluoroalkyl iodide (**2a**), 5.0 equiv of alcohols (**3**), 10 mmol % $Cu(acac)_2$, 3.0 equiv of additive DABCO, and 3.8 equiv of TBHP (5.0−6.0 M in decane) in 1.0 mL of solvent (THF:PE = 1:4) were stirred at 80 °C for 5 h.

Scheme 6. Investigation on the Mechanism



in decane), 0.2 mL THF, and 0.8 mL petroleum ether were added to a tube that uses an air balloon. The reaction mixture was stirred at 80 °C for 5 h. The reaction mixture was quenched with sodium sulfite anhydrous. Organic solvent was then removed in vacuum, and flash silica gel column chromatographic purification with petroleum ether/ethyl acetate mixtures afforded product. The product was stirred with 2 equiv of (2,4-dinitrophenyl)hydrazine, 2 equiv of TsOH, and 2 equiv of $MgSO_4$ in 2 mL of EtOH refluxed under 80 °C for 1 h. Organic solvent was removed from the reaction mixture in vacuum and flash silica gel column chromatographic purification with petroleum ether/ethyl acetate mixtures afforded product **5**. A single crystal of **5** was obtained in CH_3OH and CH_2Cl_2.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-(2-methoxyethoxy)dec-2-en-1-one (4a). Colorless liquid, 75% yield (91 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 6.50 (s, 1H), 4.15 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 157.7, 152.1 (t, J = 24.5 Hz), 134.7, 128.8, 125.8, 106.7 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 35.2, 31.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.80 (t, J = 10.6 Hz, 3F), −115.72 to −115.87 (m, 2F), −121.62 to −122.06 (m, 6F), −122.73 (s, 2F), −126.05 to −126.23 (m, 2F); HRMS (ESI-TOF) calcd for $C_{23}H_{21}F_{15}O_3$ + H^+ 631.1324, found 631.1331 (M + H^+); IR (KBr, cm^{-1}) ν 1671, 1606, 1237, 1198, 1144, 1130.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-2-(2-methoxyethoxy)-1-phenyldec-2-en-1-one (4b). Colorless liquid, 72% yield (83 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.91 (m, 2H), 7.64−7.58 (m, 1H), 7.54−7.47 (m, 2H), 6.52 (s, 1H), 4.17 (t, J = 4.5 Hz, 2H), 3.59 (t, J = 4.5 Hz, 2H), 3.34 (s, 3H); ^{13}C NMR (100

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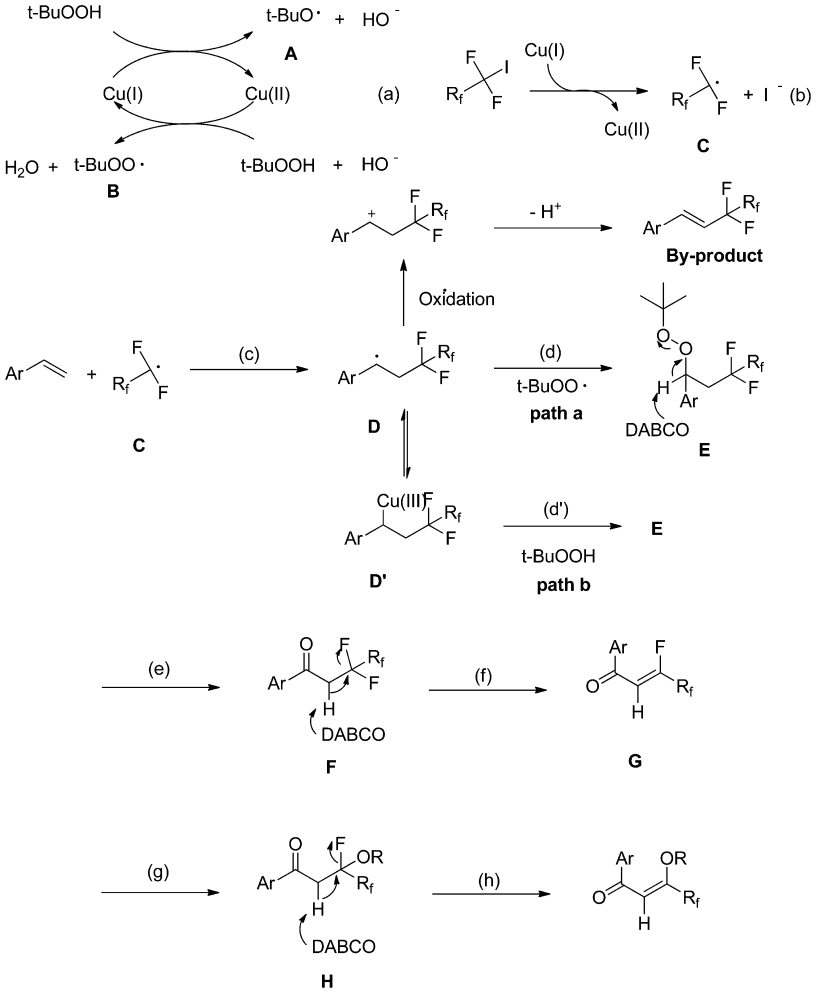
Scheme 7. Proposed Reaction Mechanism



MHz, $CDCl_3$) δ 189.2, 152.7 (t, J = 24.5 Hz), 137.3, 133.7, 128.8, 128.7, 106.5 (t, J = 4.0 Hz), 75.0, 70.7, 58.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.82 (t, J = 10.6 Hz, 3F), −115.71 to −115.85 (m, 2F), −121.63 to −122.06 (m, 6F), −122.74 (s, 2F), −126.05 to −126.25 (m, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{13}F_{15}O_3$ + Na^+ 597.0517, found 597.0538 (M + Na^+); IR (KBr, cm^{-1}) ν 1673, 1624, 1235, 1197, 1143, 1130.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-1-(4-fluorophenyl)-2-(2-methoxyethoxy)dec-2-en-1-one (4c). Colorless liquid, 72% yield (85 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.93 (m, 2H), 7.20−7.14 (m, 2H), 6.48 (s, 1H), 4.16 (t, J = 4.6 Hz, 2H), 3.59 (t, J = 4.6 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 167.4, 164.8, 152.8 (t, J = 24.5 Hz), 133.7, 133.7, 131.5, 131.4, 116.1, 115.9, 106.1 (t, J = 4.5 Hz), 75.0, 70.7, 58.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.83 (t, J = 10.6 Hz, 3F), −103.77 (s, 1F), −115.72 to −115.84 (m, 2F), −121.62 to −122.05 (m, 6F), −122.74 (s, 2F), −126.06 to −126.23 (m, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{12}F_{16}O_3$ + H^+ 593.0598, found 593.0600 (M + H^+); IR (KBr, cm^{-1}) ν 1673, 1599, 1233, 1198, 1146, 1130.

(*Z*)-1-(4-Chlorophenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-(2-methoxyethoxy)dec-2-en-1-one (4d). Colorless liquid, 68% yield (83 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 6.48 (s, 1H), 4.17 (t, J = 4.5 Hz, 2H), 3.60 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 153.2 (t, J = 24.5 Hz), 140.3, 135.6, 130.1, 129.2, 105.9 (t, J = 4.5 Hz), 75.1, 70.7, 58.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.92 (t, J = 10.6 Hz, 3F), −115.81 (t, 2F), −121.66 to −122.13 (m, 6F), −122.80 (s, 2F), −126.11 to −126.34 (m, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{12}{}^{35}ClF_{15}O_3$ + Na^+ 631.0104 and $C_{19}H_{12}{}^{37}ClF_{15}O_3$ + Na^+ 631.0133, found 631.0108 (M + Na^+) and 631.0133 (M + Na^+); IR (KBr, cm^{-1}) ν 1673, 1622, 1236, 1199, 1145, 1130.

(*Z*)-1-(4-Bromophenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-(2-methoxyethoxy)dec-2-en-1-one (4e). Colorless liquid, 67% yield (86 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.6 Hz, 2H), 6.47 (s, 1H), 4.17 (t, J = 4.5 Hz, 2H), 3.60 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 153.2 (t, J = 24.0 Hz), 136.0, 132.2, 130.2, 129.1, 105.8 (t, J = 4.0 Hz), 75.2, 70.7, 59.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.93 (t, J = 10.6 Hz, 3F), −115.76 to −115.89 (m, 2F), −121.65 to −122.12 (m, 6F), −122.81 (s, 2F), −126.13 to −126.32 (m, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{12}{}^{79}BrF_{15}O_3$ + Na^+ 675.9628, $C_{19}H_{12}{}^{81}BrF_{15}O_3$ + Na^+ 677.9608, found 675.9631 (M + Na^+), 677.9650 (M + Na^+); IR (KBr, cm^{-1}) ν 1672, 1620, 1236, 1198, 1143, 1130.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-1-(3-fluorophenyl)-3-(2-methoxyethoxy)dec-2-en-1-one (4f). Colorless liquid, 72% yield (85 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.69 (m, 1H), 7.64−7.60 (m, 1H), 7.52−7.45 (m, 1H), 7.33−7.27 (m, 1H), 6.50 (s, 1H), 4.19 (t, J = 4.5 Hz, 2H), 3.61 (t, J = 4.5 Hz, 2H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 187.7, 164.2, 161.7, 153.5 (t, J = 24.5 Hz), 139.4, 139.4, 130.6, 130.5, 124.6, 124.5, 120.8, 120.6, 115.3, 115.1, 105.7 (t, J = 4.5 Hz), 75.3, 70.7, 58.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.96 (t, J = 10.6 Hz, 3F), −111.36 (s, 1F), −115.87 (m, 2F), −121.66 to −122.13 (m, 6F),

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−122.83 (s, 2F), −126.16 to −126.34 (m, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{12}F_{16}O_3 + H^+$ 593.0604, found 593.0601 (M + H^+); IR (KBr, cm^{-1}) ν 1676, 1609, 1239, 1199, 1145, 1130.

(*Z*)-1-(3-Bromophenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(2-methoxyethoxy)dec-2-en-1-one (4g). Colorless liquid, 64% yield (84 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.05 (m, 1H), 7.85−7.82 (m, 1H), 7.75−7.71 (m, 1H), 7.41−7.35 (m, 1H), 6.48 (s, 1H), 4.18 (t, J = 4.5 Hz, 2H), 3.60 (t, J = 4.5 Hz, 2H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 153.6 (t, J = 24.5 Hz), 139.0, 136.5, 131.6, 130.4, 127.3, 123.2, 105.6 (t, J = 4.5 Hz), 75.3, 70.7, 59.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.95 (t, J = 10.6 Hz, 3F), −115.76 to −115.89 (m, 2F), −121.64 to −122.13 (m, 6F), −122.81 (s, 2F), −126.13 to −126.31 (m, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{12}{}^{79}BrF_{15}O_3 + H^+$ 652.9809 (M + H^+), $C_{19}H_{12}{}^{81}BrF_{15}O_3 + H^+$ 654.9788 (M + H^+), found 652.9786 (M + H^+), 654.9764 (M + H^+); IR (KBr, cm^{-1}) ν 1674, 1621, 1264, 1199, 1144, 1130.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-2-(2-methoxyethoxy)-1-(*p*-tolyl)dec-2-en-1-one (4h). Colorless liquid, 66% yield (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.10 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.50 (s, 1H), 4.15 (t, J = 4.5 Hz, 2H), 3.68 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 152.1 (t, J = 24.5 Hz), 144.8, 134.9, 129.5, 128.9, 106.7 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 21.6, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.99 (t, J = 10.7 Hz, 3F), −115.77 to −115.92 (m, 2F), −121.71 to −122.15 (m, 6F), −122.84 (s, 2F), −126.18 to −126.35 (m, 2F); MS (ESI-TOF) calcd for $C_{20}H_{15}F_{15}O_3 + H^+$ 589.0854, found 589.0848 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1607, 1237, 1199, 1144, 1130.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-(2-methoxyethoxy)-1-(4-methoxyphenyl)dec-2-en-1-one (4i). Colorless liquid, 58% yield (70 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.47 (s, 1H), 4.14 (t, J = 4.5 Hz, 2H), 3.89 (s, 3H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.0, 164.1, 151.6 (t, J = 25.5 Hz), 131.2, 130.4, 114.0, 106.9 (t, J = 4.5 Hz), 74.6, 70.7, 58.9, 55.5, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (600 MHz, $CDCl_3$) δ −80.95 (t, J = 10.4 Hz, 2F), −115.77 to −115.88 (m, 2F), −121.81 (s, 4F), −122.01 (s, 2F), −122.82 (s, 2F), −126.18 to −126.29 (m, 2F); MS (ESI-TOF) calcd for $C_{20}H_{15}F_{15}O_4 + H^+$ 605.0804, found 605.0812 (M + H^+); IR (KBr, cm^{-1}) ν 1668, 1599, 1238, 1198, 1145, 1130.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-(2-methoxyethoxy)-1-(2-methoxyphenyl)dec-2-en-1-one (4j). Colorless liquid, 48% yield (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.73 (m, 1H), 7.54−7.49 (m, 1H), 7.06−6.96 (m, 2H), 6.60 (s, 1H), 4.20 (t, J = 4.7 Hz, 3H), 3.87 (s, 1H), 3.62 (t, J = 4.7 Hz, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 159.0, 150.7 (t, J = 24.0 Hz), 134.5, 130.9, 127.9, 120.8, 112.1 (t, J = 5.0 Hz), 111.7, 74.9, 70.8, 58.9, 55.3, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.83 (t, J = 10.5 Hz, 3F), −115.79 to −115.91 (m, 2F), −121.68 to −122.09 (m, 6F), −122.75 (s, 2F), −125.98 to −126.30 (m, 2F); HRMS (ESI-TOF) calcd for $C_{20}H_{15}F_{15}O_4 + H^+$ 605.0804, found 605.0814 (M + H^+); IR (KBr, cm^{-1}) ν 1665, 1599, 1238, 1198, 1145, 1129.

(*Z*)-*tert*-Butyl (4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-(2-methoxyethoxy)dec-2-enoyl)phenyl)carbamate (4k). Colorless liquid, 58% yield (80 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 7.03 (s, 1H), 6.48 (s, 1H), 4.15 (t, J = 4.5 Hz, 2H), 3.59 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 152.2, 151.9 (t, J = 24.0 Hz), 143.9, 131.6, 130.3, 117.6, 106.7 (t, J = 4.0 Hz), 81.3, 74.6, 70.7, 58.8, 28.1, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.78 (t, J = 10.6 Hz, 3F), −115.65 to −115.82 (m, 2F), −121.60 to −122.04 (m, 6F), −122.71 (s, 2F), −126.03 to −126.20 (m, 2F); HRMS (ESI-TOF) calcd for $C_{24}H_{22}F_{15}NO_5 + H^+$ 690.1331, found 690.1336 (M + H^+); IR (KBr, cm^{-1}) ν 3313, 1734, 1668, 1587, 1230, 1200, 1146.

(*Z*)-4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-(2-methoxyethoxy)dec-2-enoyl)benzonitrile (4l). Colorless liquid, 42% yield (52 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 6.53 (s, 1H), 4.22 (t, J = 4.5 Hz, 2H), 3.62 (t, J = 4.5 Hz, 2H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 154.4 (t, J = 24.0 Hz), 140.2, 132.6, 129.0, 117.7, 116.8, 105.1 (t, J = 4.0 Hz), 75.5, 70.6, 58.8, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.96 (t, J = 10.6, 3F), −115.77 to −115.91 (m, 2F), −121.65 to −122.15 (m, 6F), −122.84 (s, 2F), −126.16 to −126.36 (m, 2F); HRMS (ESI-TOF) calcd for $C_{20}H_{12}F_{15}NO_3 + H^+$ 600.0650, found 600.0661 (M + H^+); IR (KBr, cm^{-1}) ν 2229, 1670, 1606, 1240, 1196, 1145, 1128.

(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-(2-methoxyethoxy)-1-(3-(trifluoromethyl)phenyl)dec-2-en-1-one (4m). Colorless liquid, 53% yield (68 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.12−8.07 (m, 1H), 7.89−7.84 (m, 1H), 7.69−7.63 (m, 1H), 7.26 (s, 1H), 6.52 (s, 1H), 4.19 (t, J = 4.5 Hz, 2H), 3.61 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 154.0 (t, J = 24.5 Hz), 137.9, 132.1, 131.8, 131.5, 131.1, 130.1, 130.0, 130.0, 130.0, 129.5, 127.6, 125.5, 125.5, 125.4, 125.4, 124.9, 122.2, 119.5, 105.5 (t, J = 4.5 Hz), 75.4, 70.7, 58.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −63.27 (s, 3F), −81.11 (t, J = 10.6 Hz, 3F), −115.88 to −116.00 (m, 2F), −121.73 to −122.23 (m, 6F), −122.93 (s, 2F), −126.29 to −126.44 (m, 2F); HRMS (ESI-TOF) calcd for $C_{20}H_{12}F_{18}O_3 + H^+$ 643.0572 (M + H^+), found 643.0576 (M + H^+); IR (KBr, cm^{-1}) ν 1677, 1622, 1296, 1201, 1171, 1128.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,5-pentafluoro-3-(2-methoxyethoxy)pent-2-en-1-one (6a). Colorless liquid, 65% yield (50 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 6.53 (s, 1H), 4.16 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{3}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.7, 151.9 (t, J = 24.0 Hz), 134.7, 128.7, 125.8, 106.3 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 35.2, 31.0, carbons corresponding to the C_2F_5 group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −82.79 (s, 3F), −119.33 to −119.37 (m, 2F); HRMS (ESI-TOF) calcd for $C_{18}H_{21}F_5O_3 + H^+$ 381.1484, found 381.1482 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1264, 1199, 1166, 1126.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,6-heptafluoro-3-(2-methoxyethoxy)hex-2-en-1-one (6b). Colorless liquid, 57% yield (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H), 4.16 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.7, 151.8 (t, J = 24.0 Hz), 134.7, 128.7, 125.8, 106.6 (t, J = 4.5 Hz), 74.7, 70.7, 58.9, 35.2, 31.0, carbons corresponding to the C_3F_7 group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.73 (t, J = 9.61 Hz, 3F), −116.85 to −116.94 (m, 2F), −126.28 (s, 2F); HRMS (ESI-TOF) calcd for $C_{19}H_{21}F_7O_3 + H^+$ 431.1452, found 431.1466 (M + H^+); IR (KBr, cm^{-1}) ν 1671, 1605, 1227, 1187, 1160, 1120.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,8-undecafluoro-3-(2-methoxyethoxy)oct-2-en-1-one (6c). Colorless liquid, 67% yield (71 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 4.16 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.7, 152.1 (t, J = 24.5 Hz), 134.7, 128.8, 125.8, 106.7 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 35.2, 31.0, carbons corresponding to the C_5F_{11} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.91 (t, J = 10.5 Hz, 3F), −115.82 to −115.93 (m, 2F), −121.94 to −122.11 (m, 2F), −122.67 to −122.86 (m, 2F), −126.12 to −126.26 (m, 2F); HRMS (ESI-TOF) calcd for $C_{21}H_{21}F_{11}O_3 + H^+$ 531.1388, found 531.1405 (M + H^+); IR (KBr, cm^{-1}) ν 1671, 1606, 1233, 1196, 1160, 1139.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-Trideca-fluoro-3-(2-methoxyethoxy)non-2-en-1-one (6d). Colorless

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liquid, 52% yield (60 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 4.16 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.8, 152.1 (t, J = 24.5 Hz), 134.7, 128.8, 125.8, 106.8 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 35.2, 31.0, carbons corresponding to the C_6F_{13} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.86 (t, J = 10.6 Hz, 3F), −115.83 (m, 2F), −121.74 to −122.07 (m, 4F), −122.76 (s, 2F), −126.07 to −126.27 (m, 2F); HRMS (ESI-TOF) calcd for $C_{22}H_{21}F_{13}O_3$ + H^+ 581.1356, found 581.1378 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1235, 1196, 1143, 1124.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(2-methoxyethoxy)dec-2-en-1-one (4a). Colorless liquid, 42% yield (53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 4.16 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.7, 152.1(t, J = 24.5 Hz), 134.8, 128.8, 125.8, 106.8 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 35.2, 31.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.92 (t, J = 10.6 Hz, 3F), −115.76 to −115.92 (m, 2F), −121.66 to −122.14 (m, 6F), −122.80 (s, 2F), −126.13 to −126.30 (m, 2F); HRMS (ESI-TOF) calcd for $C_{23}H_{21}F_{15}O_3$ + H^+ 631.1324, found 631.1331 (M + H^+); IR (KBr, cm^{-1}) ν 1671, 1606, 1237, 1198, 1144, 1130.

(*Z*)1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,-8,9,9,10,10,11,11,12,12,12-Nonadecafluoro-3-(2-methoxyethoxy)dodec-2-en-1-one (6e). Colorless liquid, 61% yield (89 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 4.15 (t, J = 4.5 Hz, 2H), 3.58 (t, J = 4.5 Hz, 2H), 3.33 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.7, 152.1 (t, J = 24.0 Hz), 134.8, 128.8, 125.8, 106.7 (t, J = 4.5 Hz), 74.8, 70.7, 58.9, 35.2, 30.9, carbons corresponding to the C_9F_{19} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.80 (t, J = 10.5 Hz, 3F), −115.75 to −115.90 (m, 2F), −121.59 to −122.03 (m, 10F), −122.72 (s, 2F), −126.05 to −126.25 (m, 2F); HRMS (ESI-TOF) calcd for $C_{25}H_{21}F_{19}O_3$ + H^+ 731.1260, found 731.1263 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1237, 1202, 1149, 1130.

(*Z*)-1-(4-*tert*-Butylphenyl)-3-(2-ethoxyethoxy)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodec-2-en-1-one (7a). Colorless liquid, 77% yield (99 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 6.50 (s, 1H), 4.15 (t, J = 4.6 Hz, 2H), 3.62 (t, J = 4.6 Hz, 2H), 3.48 (q, J = 7.0 Hz, 2H), 1.35 (s, 9H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 157.7, 152.2 (t, J = 24.0 Hz), 134.8, 128.8, 125.8, 106.5 (t, J = 4.5 Hz), 75.0, 68.6, 66.6, 35.2, 31.00, 14.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.87 (t, J = 10.6 Hz, 3F), −115.75 to −115.89 (m, 2F), −121.64 to −122.09 (m, 6F), −122.76 (s, 2F), −126.08 to −126.27 (m, 2F); HRMS (ESI-TOF) calcd for $C_{24}H_{23}F_{15}O_3$ + H^+ 645.1480, found 645.1484 (M + H^+); IR (KBr, cm^{-1}) ν 1671, 1606, 1237, 1199, 1144, 1130.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(3-methoxypropoxy)dec-2-en-1-one (7b). Colorless liquid, 58% yield (75 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 6.48 (s, 1H), 4.10 (t, J = 6.1 Hz, 2H), 3.42 (t, J = 6.2 Hz, 2H), 3.28 (s, 3H), 1.90 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 157.7, 152.0 (t, J = 24.0 Hz), 134.8, 128.8, 125.8, 106.5 (t, J = 4.5 Hz), 72.6, 68.3, 58.5, 35.2, 31.0, 29.8, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.80 (t, J = 10.6 Hz, 3F), −115.65 to −115.81 (m, 2F), −121.62 to −122.07 (m, 6F), −122.72 (s, 2F), −126.00 to −126.26 (m, 2F); HRMS (ESI-TOF) calcd for $C_{24}H_{23}F_{15}O_3$ + H^+ 645.1480, found 645.1488 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1237, 1198, 1147, 1128.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(4-methoxybutoxy)dec-2-en-1-one (7c). Colorless liquid, 56% yield (77 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 6.45 (s, 3H), 4.02 (t, J = 6.2 Hz, 2H), 3.35 (t, J = 6.2 Hz, 2H), 3.28 (s, 3H), 1.76−1.67 (m, 2H), 1.66−1.57 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 157.7, 151.9 (t, J = 24.0 Hz), 134.8, 128.8, 125.8, 106.3 (t, J = 4.5 Hz), 75.5, 71.9, 58.3, 35.2, 31.0, 26.2, 25.6, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.82 (t, J = 10.5 Hz, 3F), −115.61 to −115.87 (m, 2F), −121.64 to −122.06 (m, 6F), −122.73 (s, 2F), −126.02 to −126.25 (m, 2F); HRMS (ESI-TOF) calcd for $C_{25}H_{25}F_{15}O_3$ + Na^+ 681.1456, found 681.1486 (M + Na^+); IR (KBr, cm^{-1}) ν 1671, 1606, 1237, 1200, 1147, 1130.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(2-phenoxyethoxy)dec-2-en-1-one (7d). Colorless liquid, 76% yield (105 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.28−7.21 (m, 2H), 6.96−6.90 (m, 1H), 6.86−6.81 (m, 2H), 6.58 (s, 1H), 4.37 (t, J = 4.5 Hz, 2H), 4.15 (t, J = 4.6 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 158.4, 157.9, 152.2 (t, J = 24.5 Hz), 134.7, 129.4, 128.8, 125.9, 121.1, 114.5, 107.0 (t, J = 4.5 Hz), 73.9, 66.0, 35.2, 31.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.78 (t, J = 10.6 Hz, 3F), −115.68 to −115.85 (m, 2F), −121.51 to −122.03 (m, 6F), −122.67 (s, 2F), −125.98 to −126.22 (m, 2F); HRMS (ESI-TOF) calcd for $C_{28}H_{24}O_3F_{15}$ 693.1486, found 693.1508 (M + H^+); IR (KBr, cm^{-1}) ν 1676, 1602, 1236, 1197, 1145, 1128.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-propoxydec-2-en-1-one (7e). Colorless liquid, 57% yield (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.44 (s, 1H), 3.95 (t, J = 6.3 Hz, 2H), 1.71−1.61 (m, 2H), 1.35 (s, 9H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 157.6, 152.2 (t, J = 24.5 Hz), 134.8, 128.8, 125.8, 106.0 (t, J = 4.5 Hz), 77.3, 35.2, 31.0, 22.8, 9.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.81 (t, J = 10.5 Hz, 3F), −115.63 to −115.81 (m, 2F), −121.64 to −122.06 (m, 6F), −122.73 (s, 2F), −126.04 to −126.22 (m, 2F); HRMS (ESI-TOF) calcd for $C_{23}H_{21}F_{15}O_2$ + H^+ 615.1375, found 615.1390 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1237, 1199, 1146, 1131.

(*Z*)-3-Butoxy-1-(4-*tert*-butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodec-2-en-1-one (7f). Colorless liquid, 60% yield (78 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 6.44 (s, 1H), 3.99 (t, J = 6.3 Hz, 2H), 1.65−1.57 (m, 2H), 1.38−1.33 (m, 11H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 157.6, 152.1 (t, J = 24.0 Hz), 134.9, 128.8, 125.8, 106.0 (t, J = 4.0 Hz), 75.5, 35.2, 31.5, 31.0, 18.6, 13.5, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.73 (t, J = 10.6 Hz, 3F), −115.61 to −115.77 (m, 2F), −121.62 to −122.00 (m, 6F), −122.69 (s, 2F), −125.94 to −126.19 (m, 2F); HRMS (ESI-TOF) calcd for $C_{24}H_{23}F_{15}O_2$ + Na^+ 651.1351, found 651.1355 (M + Na^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1237, 1200, 1147, 1131.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(pentyloxy)dec-2-en-1-one (7g). Colorless liquid, 56% yield (72 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 6.43 (s, 1H), 3.98 (t, J = 6.4 Hz, 2H), 1.67−1.58 (m, 2H), 1.35 (s, 9H), 1.32−1.24 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 157.6, 152.1 (t, J = 24.0 Hz), 134.9, 128.8, 125.8, 106.0 (t, J = 4.5 Hz), 75.8, 35.2, 31.0, 29.1, 27.5, 22.2, 13.7, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.85 (t, J = 10.6 Hz, 3F), −115.66 to −115.80 (m, 2F), −121.64 to −122.07 (m, 6F), −122.75 (s, 2F), −126.06 to −126.24 (m, 2F); HRMS (ESI-TOF) calcd for $C_{25}H_{25}O_2F_{15}$ + H^+ 643.1693, found 643.1687 (M + H^+); IR (KBr, cm^{-1}) ν 1671, 1606, 1238, 1200, 1146, 1131.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(hexyloxy)dec-2-en-1-one (7h). Colorless liquid, 60% yield (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 6.44 (s, 1H), 3.99 (t, J = 6.4 Hz, 2H), 1.66−1.58 (m, 2H), 1.35 (s, 9H), 1.32−1.20 (m, 6H), 0.85

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(t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 157.6, 152.1 (t, J = 24.0 Hz), 134.9, 128.8, 125.8, 106.0 (t, J = 4.5 Hz), 75.8, 35.2, 31.3, 31.0, 29.4, 25.0, 22.4, 13.8, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (376 MHz, $CDCl_3$) δ −80.83 (t, J = 10.4 Hz, 3F), −115.63 to −115.80 (m, 2F), −121.65 to −122.07 (m, 6F), −122.74 (s, 2F), −126.05 to −126.24 (m, 2F); HRMS (ESI-TOF) calcd for $C_{26}H_{27}O_2F_{15}$ + H^+ 657.1850, found 657.1848 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1237, 1200, 1147, 1131.

(*Z*)-2-((1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-1-oxodec-2-en-3-yl)oxy)ethyl Benzoate (7i). Colorless liquid, 65% yield (94 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 7.58−7.50 (m, 3H), 7.43−7.38 (m, 2H), 6.60 (s, 1H), 4.53 (t, J = 4.3 Hz, 2H), 4.38 (t, J = 4.3 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 166.3, 157.9, 151.9 (t, J = 24.5 Hz), 134.6, 133.1, 129.6, 128.8, 128.2, 125.9, 107.3 (t, J = 4.5 Hz), 73.3, 62.8, 35.2, 31.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.79 (t, J = 10.5 Hz, 3F), −115.74 to −115.88 (m, 2F), −121.43 to −121.64 (m, 2F), −121.65 to −122.10 (m, 4F), −122.74 (s, 2F), −126.04 to −126.21 (m, 2F); HRMS (ESI-TOF) calcd for $C_{29}H_{23}O_4F_{15}$ + H^+ 721.1435, found 721.1421 (M + H^+); IR (KBr, cm^{-1}) ν 1723, 1671, 1605, 1237, 1201, 1146, 1131.

(*Z*)-2-((1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-1-oxodec-2-en-3-yl)oxy)ethyl Acetate (7j). Colorless liquid, 57% (75 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 6.58 (s, 1H), 4.29−4.21 (m, 4H), 2.02 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 170.7, 157.9, 152.0 (t, J = 24.5 Hz), 134.6, 128.7, 125.9, 107.2 (t, J = 4.0 Hz), 73.3, 62.3, 35.2, 31.0, 20.4, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.79 (t, J = 10.6 Hz, 3F), −115.78 to −115.90 (m, 2F), −121.60 to −122.06 (m, 6F), −122.71 (s, 2F), −126.03 to −126.20 (m, 2F); HRMS (ESI-TOF) calcd for $C_{24}H_{21}O_4F_{15}$ + H^+ 659.1279, found 659.1290 (M + H^+); IR (KBr, cm^{-1}) ν 1747, 1672, 1606, 1232, 1200, 1145, 1110.

(*Z*)-*tert*-Butyl (2-((1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-1-oxodec-2-en-3-yl)oxy)ethyl)carbamate (7k). Colorless liquid, 59% (87 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 6.56 (s, 1H), 4.90 (s, 1H), 4.06 (t, J = 4.8 Hz, 2H), 3.44−3.36 (m, 2H), 1.41 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 157.9, 155.7, 151.6 (t, J = 24.5 Hz), 134.5, 128.8, 125.8, 107.9 (t, J = 4.5 Hz), 79.5, 74.8, 40.1, 35.2, 31.0, 28.2, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.82 (t, J = 10.5 Hz, 3F), −115.61 to −115.85 (m, 2F), −121.59 to −122.02 (m, 6F), −122.71 (s, 2F), −126.02 to −126.22 (m, 2F); HRMS (ESI-TOF) calcd for $C_{27}H_{28}F_{15}NO_4$ + Na^+ 738.1671, found 738.1684 (M + Na^+); IR (KBr, cm^{-1}) ν 3365, 1716, 1672, 1606, 1237, 1201, 1173, 1148.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(2-fluoroethoxy)dec-2-en-1-one (7l). Colorless liquid, 71% (88 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 6.60 (s, 1H), 4.66−4.50 (m, 1H), 4.34−4.22 (m, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 158.0, 152.1 (t, J = 24.5 Hz), 134.7, 128.8, 125.9, 107.2 (t, J = 4.5 Hz), 82.1, 80.4, 74.6, 74.4, 35.2, 31.0, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.81 (t, J = 11.4 Hz, 3F), −115.66 to −116.11 (m, 2F), −121.28 to −122.22 (m, 6F), −122.73 (s, 2F), −125.93 to −126.35 (m, 2F), −224.51 (s, 1F); HRMS (ESI-TOF) calcd for $C_{22}H_{19}F_{16}O_2$ 619.1124, found 619.1137 (M + H^+); IR (KBr, cm^{-1}) ν 1672, 1606, 1237, 1199, 1146, 1110.

(*Z*)-1-(4-*tert*-Butylphenyl)-3-(2,2-difluoroethoxy)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodec-2-en-1-one (7m). Colorless liquid, 75% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 6.71 (s, 1H), 6.11−5.79 (m, 1H), 4.28−4.19 (m, J = 12.8, 4.0 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 158.3, 151.7 (t, J = 25.0 Hz), 134.5, 128.8, 126.0, 115.0, 112.6, 110.2, 108.8 (t, J = 4.5 Hz), 73.6, 73.3, 73.0, 35.3, 30.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.95 (t, J = 10.6 Hz, 3F), −115.94 to −116.09 (m, 2F), −121.72 to −122.13 (m, 6F), −122.81 (s, 2F), −126.15 to −126.32 (m, 2F), −126.57 (s, 2F); HRMS (ESI-TOF) calcd for $C_{22}H_{17}F_{17}O_2$ + H^+ 637.1030, found 637.1032 (M + H^+); IR (KBr, cm^{-1}) ν 1674, 1605, 1238, 1200, 1144, 1130.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-(2,2,2-trifluoroethoxy)dec-2-en-1-one (7n). Colorless liquid, 69% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 6.77 (s, 1H), 4.43 (q, J = 7.9 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 158.5, 151.4 (t, J = 25.0 Hz), 134.3, 128.8, 126.0, 108.9 (t, J = 4.0 Hz), 71.6, 71.2, 70.8, 70.5, 35.3, 30.9, carbons corresponding to the C_7F_{15} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −74.99 (s, 3F), −80.84 (t, J = 10.6 Hz, 3F), −115.79 to −115.96 (m, 2F), −121.65 to −122.05 (m, J = 25.0, 6F), −122.76 (s, 2F), −126.02 to −126.25 (m, 2F); HRMS (ESI-TOF) calcd for $C_{22}H_{16}O_2F_{18}$ + H^+ 655.0941, found 655.0935 (M + H^+); IR (KBr, cm^{-1}) ν 1675, 1605, 1238, 1202, 1167, 1146.

(*Z*)-1-(4-*tert*-Butylphenyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-dec-2-en-1-one (7o). Colorless liquid, 76% (110 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 6.57−6.48 (m, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 159.0, 149.0 (t, J = 25.0 Hz), 134.5, 128.9, 126.1, 108.6 (t, J = 4.5 Hz), 77.8, 77.5, 77.0, 76.8, 76.5, 76.1, 75.8, 35.3, 30.8, carbons corresponding to the C_7F_{15} group and two CF_3 groups cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −73.62 (s, 6F), −81.01 (t, J = 10.6 Hz, 3F), −115.30 to −115.47 (m, 2F), −121.68 to −122.19 (m, 6F), −122.88 (s, 2F), −126.21 to −126.38 (m, 2F); HRMS (ESI-TOF) calcd for $C_{23}H_{15}O_2F_{21}$ + H^+ 723.0815, found 723.0840 (M + H^+); IR (KBr, cm^{-1}) ν 1675, 1605, 1293, 1199, 1146, 1110.

(*E*)-1-*tert*-Butyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodec-1-en-1-yl)benzene (8).[6] Yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 24 Hz, 4H), 7.16−7.12 (m, 1H), 6.17−6.13 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 139.5, 130.8, 127.5, 126.9, 113.4 (t, 3 Hz), 110.4, 34.8, 31.2, carbons corresponding to the C_8F_{17} group cannot be identified due to C−F coupling; ^{19}F NMR (400 MHz, $CDCl_3$) δ −80.8 (t, J = 8.0 Hz, 3F), −110.93 to −110.95 (m, 2F), −121.40 (s, 2F), −121.95 (s, 4F), −122.75 (s, 2H), −123.26 (s, 2F), −126.14 (s, 2F).

(*Z*)-1-(4-*tert*-Butylphenyl)-3,4,4,5,5,6,6,7,7,8,8,9,9,9-tetradecafluorononon-2-en-1-one (9).[15] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 8.0 Hz, 1H), 1.36 (s, 9H).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02664.

Copies of ^{1}H NMR, ^{13}C NMR, and HRMS spectra for all products, and crystallography data for **5** (PDF)

Single-crystal X-ray data for **5** in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Kirsch, P. *Modern Fluoroorgannic Chemistry: Syntheses, Reactivities, Applications*; Wiley-VCH, 2004. (b) Uneyama, K. *Organofluorine Chemistry*; Blackwell, 2006. (c) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (d) Bégué, J.-P.; Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry of Fluorine*; Wiley, 2008. (e) Tomashenko, O. A.; Grushin, V. V. *Chem. Rev.* **2011**, *111*, 4475. (f) Zhang, C.-P.; Chen, Q. Y.; Guo, Y.; Xiao, J.-C.; Gu, Y. C. *Chem. Soc. Rev.* **2012**, *41*, 4536.

(2) Recent reviews on perfluoroalkylation reagent: (a) Zhang, C.-P.; Chen, Q.-Y.; Guo, Y.; Xiao, J.-C.; Gu, Y.-C. *Chem. Soc. Rev.* **2012**, *41*, 4536. (b) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214. (c) Alonso, C.; Martinez de Marigorta, E.; Rubiales, G.; Palacios, F. *Chem. Rev.* **2015**, *115*, 1847. (d) Charpentier, J.; Früh, N.; Togni, A. *Chem. Rev.* **2015**, *115*, 650. (e) Nenajdenko, V. G.; Muzalevskiy, V. M.; Shastin, A. V. *Chem. Rev.* **2015**, *115*, 973. (f) Yang, X.; Wu, T.; Phipps, R. J.; Toste, F. D. *Chem. Rev.* **2015**, *115*, 826.

(3) Some representative examples for the Togni reagent: (a) Kieltsch, I.; Eisenberger, P.; Togni, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 754. (b) Niedermann, K.; Früh, N.; Senn, R.; Czarniecki, B.; Verel, R.; Togni, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 6511. (c) Kong, W.; Casimiro, M.; Merino, E.; Nevado, C. *J. Am. Chem. Soc.* **2013**, *135*, 14480. (d) Wang, Y.; Jiang, M.; Liu, J.-T. *Chem. - Eur. J.* **2014**, *20*, 15315. (e) Xu, P.; Abdukader, A.; Hu, K.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2014**, *50*, 2308. (f) Früh, N.; Togni, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 10813. (g) Kananovich, D. G.; Konik, Y. A.; Zubrytski, D. M.; Järving, I.; Lopp, M. *Chem. Commun.* **2015**, *51*, 8349. (h) Kawamura, S.; Egami, H.; Sodeoka, M. *J. Am. Chem. Soc.* **2015**, *137*, 4865. (i) Yu, P.; Zheng, S.-C.; Yang, N.-Y.; Tan, B.; Liu, X.-Y. *Angew. Chem., Int. Ed.* **2015**, *54*, 4041.

(4) (a) Zhang, C.-P.; Wang, Z. L.; Chen, Q.-Y.; Zhang, C.-T.; Gu, Y.-C.; Xiao, J.-C. *Angew. Chem., Int. Ed.* **2011**, *50*, 1896. (b) Zhang, X.-G.; Dai, H.-X.; Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2012**, *134*, 11948. (c) Mizuta, S.; Verhoog, S.; Engle, K. M.; Khotavivattana, T.; O'Duill, M.; Wheelhouse, K.; Rassias, G.; Medebielle, M.; Gouverneur, V. *J. Am. Chem. Soc.* **2013**, *135*, 2505. (d) Besset, T.; Cahard, D.; Pannecoucke, X. *J. Org. Chem.* **2014**, *79*, 413. (e) Dagousset, G.; Carboni, A.; Magnier, E.; Masson, G. *Org. Lett.* **2014**, *16*, 4340. (f) Yasu, Y.; Arai, Y.; Tomita, R.; Koike, T.; Akita, M. *Org. Lett.* **2014**, *16*, 780.

(5) (a) Ball, N. D.; Gary, J. B.; Ye, Y.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 7577. (b) Chu, L.; Qing, F.-L. *J. Am. Chem. Soc.* **2012**, *134*, 1298. (c) Hu, M.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2012**, *134*, 15257. (d) Mu, X.; Wu, T.; Wang, H. Y.; Guo, L. Y.; Liu, G. *J. Am. Chem. Soc.* **2012**, *134*, 878. (e) Hafner, A.; Bihlmeier, A.; Nieger, M.; Klopper, W.; Bräse, S. *J. Org. Chem.* **2013**, *78*, 7938. (f) Wang, Y.-F.; Lonca, G. H.; Le Runigo, M.; Chiba, M. S. *Org. Lett.* **2014**, *16*, 4272.

(6) (a) Burton, D. J.; Kehoe, L. J. *J. Org. Chem.* **1970**, *35*, 1339. (b) Burton, D. J.; Kehoe, L. J. *J. Org. Chem.* **1971**, *36*, 2596. (c) Hu, C.; Qiu, Y. *J. Org. Chem.* **1992**, *57*, 3339. (d) Zeng, R.; Fu, C.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3888. (e) Baráta-Vallejo, S.; Postigo, A. *Coord. Chem. Rev.* **2013**, *257*, 3051. (f) Xu, T.; Cheung, C.; Hu, X. *Angew. Chem., Int. Ed.* **2014**, *53*, 4910. (g) Zhang, B.; Studer, A. *Org. Lett.* **2014**, *16*, 3990. (h) He, L.; Natte, K.; Rabeah, J.; Taeschler, C.; Neumann, H.; Brückner, A.; Beller, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 4320. (i) Sladojevich, F.; McNeill, E.; Borgel, J.; Zheng, S.; Ritter, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 3712. (j) Kato, H.; Hirano, K.; Kurauchi, D.; Toriumi, N.; Uchiyama, M. *Chem. - Eur. J.* **2015**, *21*, 3895. (k) Feng, Z.; Min, Q.; Zhao, H.; Gu, J.; Zhang, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 1270. (l) Nenajdenko, V. G.; Muzalevskiy, V. M.; Shastin, A. V. *Chem. Rev.* **2015**, *115*, 973.

(7) (a) Brace, N. *J. Org. Chem.* **1962**, *27*, 4491. (b) Bravo, A.; Bjørsvik, H. R.; Fontana, F.; Liguori, L.; Mele, A.; Minisci, F. *J. Org. Chem.* **1997**, *62*, 7128. (c) Antonietti, F.; Gambarotti, C.; Mele, A.; Minisci, F.; Paganelli, R.; Punta, C.; Recupero, F. *Eur. J. Org. Chem.* **2005**, *2005*, 4434.

(8) (a) Bazhin, D. N.; Gorbunova, T. I.; Zapevalov, A. Y.; Saloutin, V. I. *J. Fluorine Chem.* **2009**, *130*, 438. (b) Xiao, Z.-W.; Hu, H.-W.; Ma, J.-L.; Chen, Q.; Guo, Y. *Chin. J. Chem.* **2013**, *31*, 939. (c) Yang, B.; Shi, L.; Wu, J.; Fang, X.; Yang, X.; Wu, F. *Tetrahedron* **2013**, *69*, 3331.

(9) (a) Brace, N. O. *J. Org. Chem.* **1967**, *32*, 430. (b) Naud, C.; Calas, P.; Blancou, H.; Commeyras, A. *J. Fluorine Chem.* **2000**, *104*, 173. (c) Lazzari, D.; Cassani, M. C.; Solinas, G.; Pretto, M. *J. Fluorine Chem.* **2013**, *156*, 34.

(10) Barata-Vallejo, S.; Postigo, A. *J. Org. Chem.* **2010**, *75*, 6141.

(11) (a) Itoh, Y.; Mikami, K. *Org. Lett.* **2005**, *7*, 4883. (b) Yoshioka, E.; Kohtani, S.; Sawai, K.; Kentefu, I.; Tanaka, E.; Miyabe, H. *J. Org. Chem.* **2012**, *77*, 8588.

(12) (a) Yoshida, M.; Ohkoshi, M.; Aoki, N.; Ohnuma, Y.; Iyoda, M. *Tetrahedron Lett.* **1999**, *40*, 5731. (b) Yoshida, M.; Ohkoshi; Muraoka, M.; Matsuyama, T. H.; Iyoda, M. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1833.

(13) (a) Qiu, Z.; Burton, D. *J. Org. Chem.* **1995**, *60*, 3465. (b) Tsuchii, K.; Imura, M.; Kamada, N.; Hirao, T.; Ogawa, A. *J. Org. Chem.* **2004**, *69*, 6658. (c) Nagib, D. A.; Scott, M. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2009**, *131*, 10875. (d) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160. (e) Wallentin, C. J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875. (f) Kim, E.; Choi, S.; Kim, H.; Cho, E. *Chem. - Eur. J.* **2013**, *19*, 6209. (g) Yajima, T.; Yamaguchi, K.; Hirokane, R.; Nogami, E. *J. Fluorine Chem.* **2013**, *150*, 1. (h) Nappi, M.; Bergonzini, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2014**, *53*, 4921. (i) Woźniak, Ł.; Murphy, J.; Melchiorre, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 5678.

(14) For representative examples on radical addition of perfluoroalkyl halides to olefins, see refs 6d−f, 6k, 7a, 8, 9 10, 12, 13d, and 13g.

(15) Liu, C.; Shi, E.; Xu, F.; Luo, Q.; Wang, H.; Chen, J.; Wan, X. *Chem. Commun.* **2015**, *51*, 1214.

(16) Recently, we reported various oxidation reactions using TBHP; see the following: (a) Chen, L.; Shi, E.; Liu, Z.; Chen, S.; Wei, W.; Li, H.; Xu, K.; Wan, X. *Chem. - Eur. J.* **2011**, *17*, 4085. (b) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 3231. (c) Shi, E.; Shao, Y.; Chen, S.; Hu, H.; Liu, Z.; Zhang, J.; Wan, X. *Org. Lett.* **2012**, *14*, 3384. (d) Zhang, F.; Du, P.; Chen, J.; Wang, H.; Luo, Q.; Wan, X. *Org. Lett.* **2014**, *16*, 1932. (e) Du, P.; Li, H.; Wang, Y.; Cheng, J.; Wan, X. *Org. Lett.* **2014**, *16*, 6350. (f) Zhang, J.; Jiang, J.; Xu, D.; Luo, Q.; Wang, H.; Chen, J.; Li, H.; Wang, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 1231.

(17) (a) Lamani, M.; Prabhu, K. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6622. (b) Wu, J.-C.; Song, R.-J.; Wang, Z.-Q.; Huang, X.-C.; Xie, Y.-X.; Li, J.-H. *Angew. Chem., Int. Ed.* **2012**, *51*, 3453. (c) Xia, X.-F.; Zhang, L.-L.; Song, X.-R.; Niu, Y.-N.; Liu, X.-Y.; Liang, Y.-M. *Chem. Commun.* **2013**, *49*, 1410. (d) Xie, Y.-X.; Song, R.-J.; Yang, X. H.; Xiang, J.-N.; Li, J.-H. *Eur. J. Org. Chem.* **2013**, *2013*, 5737. (e) Rout, S. K.; Guin, S.; Gogoi, A.; Majji, G.; Patel, B. K. *Org. Lett.* **2014**, *16*, 1614. (f) Cheng, J.-K.; Loh, T. P. *J. Am. Chem. Soc.* **2015**, *137*, 42.

(18) (a) Kornblum, N.; DeLaMare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 880. (b) Staben, S. T.; Linghu, X.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12658. (c) Nicolaou, K. C.; Totokotsopoulos, S.; Giguère, D.; Sun, Y.-P.; Sarlah, D. *J. Am. Chem. Soc.* **2011**, *133*, 8150. (d) Palframan, M. J.; Kociok-Köhn; Lewis, S. E. *Chem. - Eur. J.* **2012**, *18*, 4766.

(19) (a) Kurykin, M. A.; Vol'pin, I. M.; German, L. S. *J. Fluorine Chem.* **1996**, *80*, 9. (b) Pigeon, X.; Bergeron, M.; Barabe, F.; Dube, P.; Frost, H. N.; Paquin, J. F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1123.

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