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Visible-Light-Induced Trifluoromethylation of Unactivated Alkenes with Tri(9-anthryl)borane as an Organophotocatalyst

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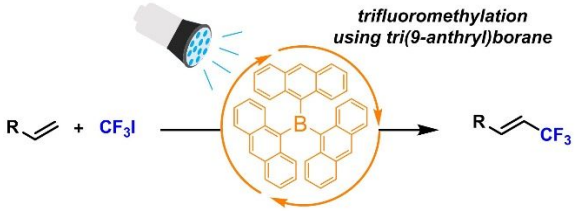
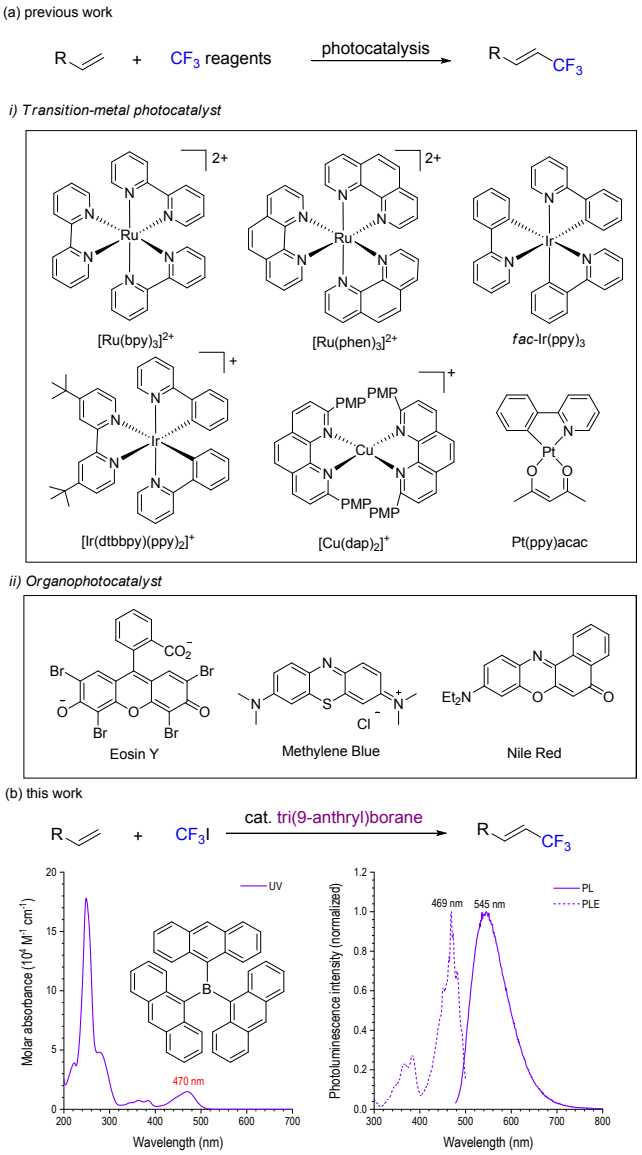


ABSTRACT: Tri(9-anthryl)borane was successfully applied as an organophotocatalyst for the visible-light-induced trifluoromethylation of unactivated alkenes with CF_3I. The mild reaction conditions tolerated a variety of functional groups, and the reaction could be extended to perfluoroalkylations with C_3F_7I and C_4F_9I. Mechanistic studies revealed that the photoredox catalysis involves an oxidative quenching pathway.

Introduction

In the past decades, extensive research efforts have been devoted towards the introduction of fluoroalkyl moieties into target molecules.[1] In general, fluoroalkylated compounds are characterized by improved metabolic stability, bioavailability, lipophilicity, and binding selectivity as compared to their non-fluoroalkylated counterparts.[2] Among the various fluoroalkyl groups available, the trifluoromethyl group is the most prevalent in pharmaceuticals and agrochemicals.[3] For this reason, various trifluoromethylation methods have been developed, including visible-light-induced reactions, which have recently attracted considerable attention due to their environmental compatibility and mechanistic versatility.[3,4] Visible-light-induced trifluoromethylation reactions typically involve the use of polypyridyl-based Ru, Ir and Pt complexes as photosensitizers.[3] Scheme 1 shows the widely used Ru- and Ir-complexes in trifluoromethylations, including $[Ru(bpy)_3]Cl_2$, $[Ru(phen)_3]Cl_2$, $[Ir(dtbbpy)(ppy)_2]PF_6$, and *fac*-$Ir(ppy)_3$. Metal complexes containing Pt and Cu have also been explored as photocatalysts (Scheme 1a-i). Despite synthetic utility, transition-metal photocatalysts have several disadvantages. Some metal complexes are expensive and present toxicity issues associated with metal residues when used in the synthesis of pharmaceuticals. To circumvent these problems, several organic dyes such as Eosin Y, methylene blue, and Nile red (Scheme 1a-ii) have been examined in trifluoromethylations.[5] However, trifluoromethylation reactions in the presence of an organophotocatalyst remain less developed, with only a few reported examples. Herein, we successfully exploited tri(9-anthryl)borane (**1**) as an organophotocatalyst in the trifluoromethylation of unactivated alkenes with CF_3I (Scheme 1b).

Scheme 1. (a) Examples of visible-light photocatalysts used in trifluoromethylation reactions. (b) Left, UV−vis absorption spectrum of 10 μM tri(9-anthryl)borane (Ar-saturated CH_3CN). Right, fluorescence (solid line) and photoluminescence excitation (dotted line) spectra of 10 μM tri(9-anthryl)borane (Ar-saturated CH_3CN). λ_{ex} = 470 nm and λ_{em} = 545 nm.



Result and Discussion

Tri(9-anthryl)borane **1** was developed by the Yamaguchi group for potential applications in organic light-emitting devices (OLEDs).[6,7] However, **1** has not been utilized in synthetic chemistry, although it fulfils the requirements for a visible-light photocatalyst. The strong visible-light absorption ability of this compound was demonstrated by its UV-vis absorption spectrum which contained an intramolecular charge transfer (ICT) transition from the π orbital of the anthryl group to the *p* orbital of borane at 470 nm (ε = 15000 M^{-1} cm^{-1}) (Scheme 1b). The large ε value of **1** is a contrasting advantage over conventional late-transition-metal complexes, which typically display $\varepsilon < 10^4$ M^{-1} cm^{-1} in the metal-to-ligand charge-transfer transition bands in the visible region. The excited-state oxidation potential (E^*_{ox}, −1.12 V vs. SCE; $E^*_{ox} = E_{ox} - E(S_1)$, E_{ox} (1.16 V vs SCE) and $E(S_1)$ (2.28 eV) are the ground-state oxidation potential and the singlet excited-state energy, respectively; see ESI, Figure S1 for the voltammogram of **1**) was more negative than the reduction potential of CF_3I (–0.91 V vs. SCE), suggesting thermodynamic allowance for photoinduced electron transfer from **1** to CF_3I (Figure 1 and Figure S1 in ESI). On the contrary, reductive quenching of the excited-state **1** by DBU, a sacrificial electron donor, was found to be thermodynamically improbable because the excited-state reduction potential (0.73 V vs. SCE) of **1** was less positive than E_{ox} (1.22 V vs. SCE) of DBU.

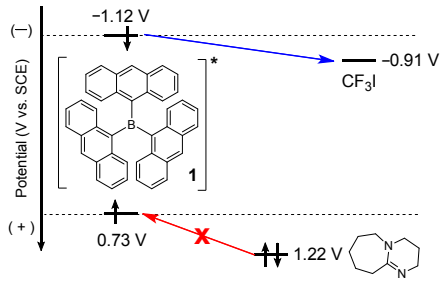


Figure 1. Schematic representations of the electron transfer of the excited-state **1** with DBU or CF_3I.

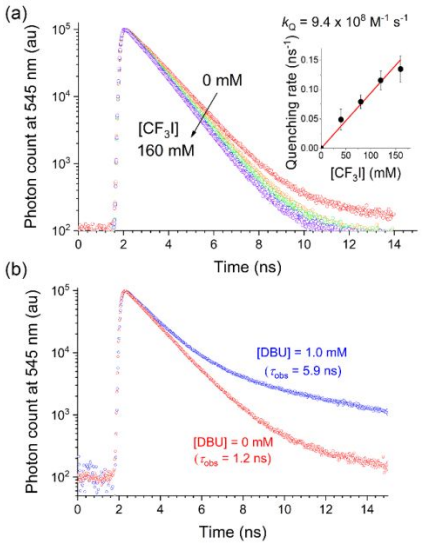
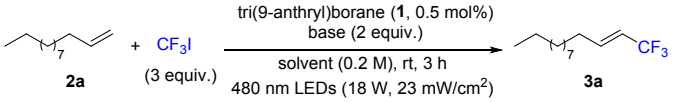


Figure 2. Fluorescence decay traces of 100 μM **1** (Ar-saturated CH_3CN) recorded at an emission wavelength of 545 nm after picosecond pulsed laser excitation at 377 nm (temporal resolution = 0.025 ns) in the presence of (a) increased concentrations of CF_3I (0–160 mM) and (b) 1.0 mM DBU. The inset graph in (a) is a pseudo-first-order plot. The experiments were performed in triplicate using fresh samples. The average and standard deviations were obtained from the three experiments.

Stern–Volmer experiments were performed to examine the excited-state electron transfer from **1** to CF_3I. Fluorescence decay traces of 100 μM **1** were recorded at a wavelength of 545 nm employing time-correlated single-photon-counting techniques, with increasing the concentration of CF_3I. As shown in Figure 2a, the fluorescence lifetime of 100 μM **1** was 1.2 ns in a deaerated CH_3CN solution. The fluorescence lifetime decreased in proportion with the added concentration of CF_3I. On the contrary, the fluorescence lifetime did not decrease in the presence of DBU (Figure 2b). A delayed fluorescence component was rather observed, which was likely due to suppression of non-radiative processes by hydrophobic interactions between **1** and DBU. The

invariance of the lifetime of the prompt fluorescence indicated the absence of reductive quenching of **1** by DBU. A pseudo-first-order plot was constructed with employing the quenching rate of CF_3I which was computed using the relationship, quenching rate = $1/\tau - 1/\tau_0$, where τ and τ_0 are the fluorescence lifetime of **1** in the absence and presence of CF_3I, respectively (the inset graph in Figure 2a). A linear fit of the data returned a rate constant for oxidative quenching of **1** by CF_3I to be as large as 9.4×10^8 M^{-1} s^{-1}. The transient fluorescence studies revealed fast electron transfer from the excited-state **1** to CF_3I.

Table 1. Optimization of trifluoromethylation of alkene **2a**[a]



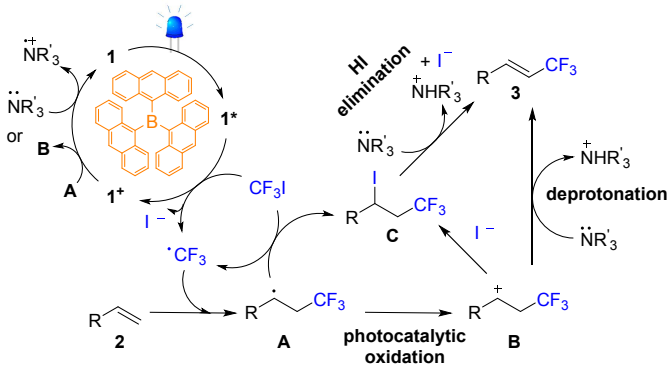
entry	base	solvent	variation	yield[b]
1	TEA	CH_3CN	-	12 (52)[c]
2	TMEDA	CH_3CN	-	43 (16)[c]
3	**DBU**	**CH_3CN**	**-**	**95**
4	-	CH_3CN	-	-
5	K_2CO_3	CH_3CN	-	-
6	Cs_2CO_3	CH_3CN	-	-
7	DBU	CH_3CN	*fac*-Ir(ppy)$_3$	91
8	DBU	CH_3CN	Ru(phen)$_3$Cl$_2$	80 (2)[c]
9	DBU	CH_3CN	Eosin Y	77 (3)[c]
10	DBU	CH_3CN	no hv	5
11	DBU	CH_3CN	no **1**	0
12	DBU	THF	-	62
13	DBU	DCM	-	68
14	DBU	DMF	-	44
15	DBU	1,4-dioxane	-	80
16	DBU	Et_2O	-	67
17	DBU	CH_3CN	CFL (20 W)	82
18	DBU	CH_3CN	520 nm green LEDs (18 W, 10 mW/cm^2)	8 (56)[d]
19	DBU	CH_3CN	no **1,** CFL (20 W)	31 (58)[d]

[a]Reaction scale: **2a** (0.1 mmol); [b]The yield was determined by ^{19}F NMR spectroscopy with trifluorotoluene as an internal standard. [c]Numbers in parentheses indicate yields of the trifluoroalkenyl iodide. [d]Numbers in parentheses indicate yields after 24 h.

We commenced our investigation using 1-dodecene **2a** as the model substrate and CF_3I in the presence of 0.5 mol% **1** as the organophotocatalyst (Table 1). 480 nm LEDs were used to maximize the visible-light absorption ability of **1** (λ_{ex} = 470 nm). Moreover, to obtain the alkenyl-CF_3 compound **3a** as the final product, amine bases were used as additives because an amine in the reaction medium can play multiple roles: a sacrificial electron donor in photoredox catalysis, an elimination base for the dehydrohalogenation of the intermediate, and a Brønsted base for deprotonation.[3d,8] Indeed, the use of amine additives provided the desired **3a** with *E*-selectivity (entries 1-3).[3,9-11] DBU was an optimal additive to give **3a** in 95% yield, while reactions with TEA or TMEDA gave lower yields of **3a** along with a trifluoromethylated iodide product (see **C** in Scheme 2).[12] On the other hand, the reaction in the absence of an amine or the presence of an inorganic base such as K_2CO_3 and Cs_2CO_3 did not provide **3a** (entries 4–6). Additional ^1H NMR experiments showed that there was no Lewis acid-base interaction between **1** and amines, indicating **1** cannot function as a Lewis acid (Figure S2 in ESI). Reactions in the presence of widely used metal- or organo-photocatalysts such as *fac*-Ir(ppy)$_3$, Ru(phen)$_3$Cl$_2$, or Eosin Y provided **3a** in lower yields (entries 3 vs 7-9), probably due to the less efficiency in electron transfer process than **1** under 480 nm-light irradiation.[13]

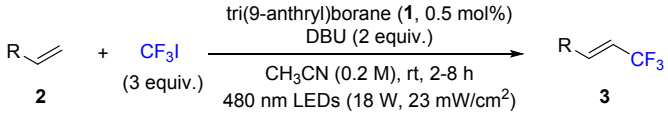
Control experiments showed that the reaction requires both visible-light irradiation and a photocatalyst (entries 10 and 11). CH_3CN was the best solvent system for the transformation (entries 3, 12–16). Further screening of the reaction concentration and stoichiometry of the reagents confirmed that the best reaction conditions that provided **3a** in 95% yield were as follows: 0.5 mol% of **1**, 2–3 equiv of CF_3I, and 2 equiv of DBU in CH_3CN (0.1–0.2 M) (entry 3). The use of CFL or green LEDs as the visible-light source instead of the 480 nm LEDs decreased the reaction efficiency, showing the dependence of the transformation on irradiation wavelength (entries 17 and 18). Notably, the reaction proceeded in the absence of **1**, despite the lower reactivity through halogen bond complex formation between DBU and CF_3I, where visible-light-induced single-electron transfer from DBU to CF_3I generated the $\cdot CF_3$ radical (entry 19).[5c, 14]

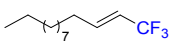
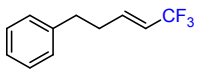
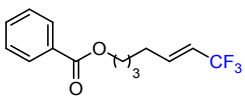
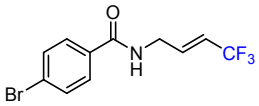
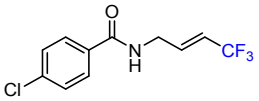
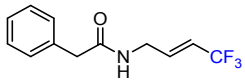
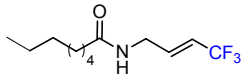
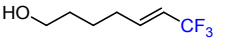
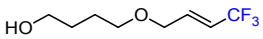
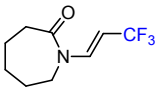
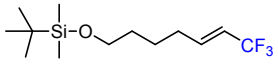
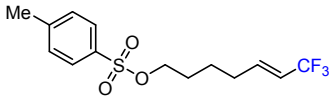
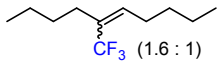
Scheme 2. Proposed mechanism of the alkenyl trifluoromethylation



Based on the aforementioned results, we propose a plausible mechanism for the trifluoromethylation of alkenes (Scheme 2). Initially, **1** is activated by visible light through the anthryl-to-borane charge transfer transition. The photoactivated **1*** is oxidatively quenched by one-electron transfer to CF_3I, producing $[\mathbf{1}]^+$ and the key intermediate, $\cdot CF_3$ radical. Addition of the $\cdot CF_3$ radical to alkene **2** generates trifluoromethylated radical species **A**. Atom-transfer radical addition between **A** and CF_3I can produce iodo-trifluoromethylated product **C**, which after elimination of HI in the presence of DBU, is converted into **3**. Note that this step also yields the $\cdot CF_3$ radical. The radical propagation is beneficial for increased photon economy. A photochemical quantum yield determined using the standard ferrioxialate actinometry was as high as 240% for the trifluoromethylation of **2a** (see ESI for the details). The quantum yield exceeding 100% is a strong indication for the presence of the radical propagation step. Alternatively, **3** can be generated from intermediate **B**, formed by the photocatalytic oxidation of **A**, through DBU-promoted deprotonation. In the photocatalytic cycle, reductive one-electron transfer from DBU or **A** to $[\mathbf{1}]^+$ regenerates **1**.

Table 2. Substrate scope of alkenes[a]



entry		product	yield (%)[b]
1	**3a**		93%
2	**3b**		88%
3	**3c**		88%
4	**3d**		90%
5	**3e**		86%
6	**3f**		88%
7	**3g**		94%
8	**3h**		77%
9	**3i**		72%
10	**3j**		95%
11	**3k**		90%
12	**3l**		96%
13	**3m**		90%

[a]Reaction scale: **2** (0.5 mmol); [b]isolated yield.

Next, we investigated the substrate scope of this transformation by using a variety of terminal alkenes (Table 2). The mild reaction conditions facilitated the trifluoromethylation of alkenes bearing diverse functional groups, including ester (**3c**), aryl halides such as aryl bromide (**3d**) and aryl chloride (**3e**), amide (**3d**, **3e**, **3f**, **3g**), unprotected alcohol (**3h**, **3i**), lactam(**3j**), silyl ether (**3k**), and sulfonates (**3l**). An internal alkene, (*E*)-dec-5-ene, also underwent the transformation smoothly to give the corresponding trifluoromethylated product **3m**, despite the formation of an *E*/*Z* mixture. Unfortunately, aromatic alkenes[15] were not suitable substrates for the transformation, showing very low conversion under the conditions.

The reaction conditions were amenable to a large-scale reaction: **3a** could be prepared on a 10-mmol scale in a yield similar to that of a 0.5-mmol scale reaction (Scheme 3).

Scheme 3. Gram-scale reaction of **2a**

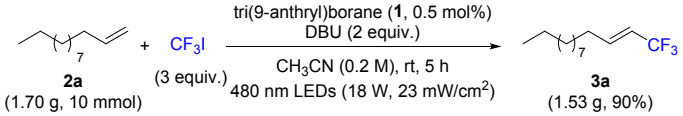
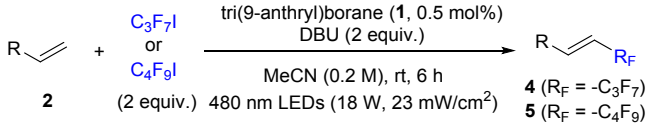
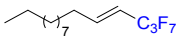
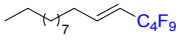
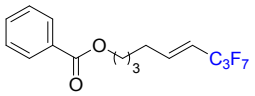
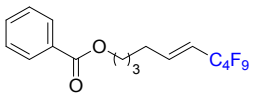
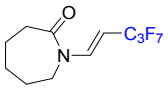
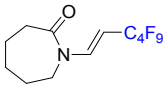


Table 3. Perfluoroalkylations of alkenes[a]

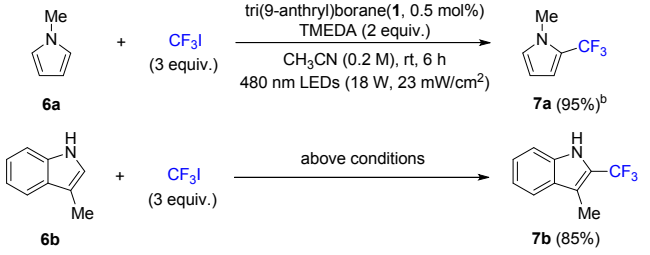


entry		product	yield (%)[b]
1	**4a**		90%
2	**5a**		94%
3	**4c**		93%
4	**5c**		90%
5	**4j**		92%
6	**5j**		93%

[a]Reaction scale: **2** (0.5 mmol); [b]isolated yield.

To further demonstrate the diversity and potential application of the reaction, we attempted to carry out fluoroalkylations using perfluoroalkyl iodides, including heptafluoropropyl iodide (C_3F_7I) and nonafluorobutyl iodide (C_4F_9I) (Table 3). Under the given conditions, the reactions proceeded smoothly to give the corresponding perfluoroalkylated alkenes **4** and **5** in excellent yields.

Scheme 4. Reaction of *N*-heterocycles[a]: [a]Reaction scale: **6** (0.5 mmol); [b]The yield was determined by ^{19}F NMR spectroscopy with trifluorotoluene as an internal standard due to the volatility of **7a**.



N-Heterocycles such as pyrrole and indole were also suitable substrates for the trifluoromethylation. *N*-methylpyrrole **6a** and 3-Methylindole **6b** were converted to the corresponding CF_3 compounds, **7a** and **7b**, respectively (Scheme 4). In the transformation, the use of TMEDA as a base improved the efficiency of the process.

In conclusion, we have employed tri(9-anthryl)borane as an organophotocatalyst in the trifluoromethylation reactions of unactivated alkenes. A wide variety of functional groups were tolerated under the mild reaction conditions, and the reaction could be extended to perfluoroalkylations with C_3F_7I and C_4F_9I. *N*-Heterocycles were also suitable substrates for the transformation. Our mechanistic studies revealed that the photoredox catalysis involves an oxidative quenching pathway. We believe that the photoreactivity of tri(9-anthryl)borane would pave the way for widespread applications in other useful transformations and set a new stage for the development of borane-based organophotocatalysts.

Experimental Section

General Information. Anhydrous CH_3CN was purchased from Sigma-Aldrich chemical company in a Sure-Seal bottle. Commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, or TCI companies. Flash column chromatography was performed using Merck silica gel 60 (70-230 mesh). EvoluChem LED 18 W [blue (480 nm, 23 mW/cm^2)] was used as light sources. The fluoroalkylated alkene products were characterized by ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR, and FT-IR spectroscopy. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^1H NMR, 151 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR). Copies of ^1H NMR, $^{13}C\{^1H\}$ NMR and ^{19}F NMR spectra can be found in the Supporting Information. ^1H NMR experiments are reported in units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^1H decoupling. ^{19}F NMR spectra are reported in ppm, and all were taken composite pulse decoupling (CPD) mode. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Tensor 27 Bruker FT-IR spectrometer. Reactions were monitored by GC-MS using the Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector. Mass spectral data of all unknown compounds were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer.

Experimental Details

1. Synthesis of tri(9-anthryl)borane (**1**).

Tri(9-anthryl)borane was synthesized by following the reported procedure.[6a] A solution of 9-anthryllithium, prepared from 9-bromoanthracene (5.14 g, 20 mmol) and *n*-BuLi (1.6 M hexane solution, 13 mL, 21 mmol) in ether (30 mL), was added to an ether (10 mL) solution of $BF_3{\cdot}OEt_2$ (852 mg, 6 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. The orange precipitates produced were collected by filtration and then washed with Et_2O (5 mL x 2). Benzene was added to the precipitates and the resulting suspension was stirred and then filtered to remove insoluble salts. The filtrate was concentrated under reduced pressure, followed by recrystallization from benzene to afford of compound in 52% yield as orange crystals.

2. Synthesis of trifluoromethylated alkenes (**3a**-**3m**).

A flame-dried tube equipped with a magnetic stirring bar was charged with argon. The substrate (**2**: 0.5 mmol), tri(9-anthryl)borane (0.5 mol%: 2.7 mg), DBU (1.0 mmol, 152.5 uL), and CH_3CN (2.5 mL, 0.2 M) were added to the tube. CF_3I (1.5 mmol, 37.5 mL) was then delivered into the reaction mixture using a gastight syringe. The mixture was stirred at room temperature and irradiated in a distance of 15 cm from 480 nm LEDs (18 W, 23 mW/cm^2). The reaction progress was monitored

by thin layer chromatography or gas chromatography. Upon completion of the reaction, the mixture was diluted with diethyl ether and washed with brine. The layers were separated, and the organic layer was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding trifluoromethylating product **3**.

3. Synthesis of perfluoroalkylated alkenes (**4a**, **5a**, **4c**, **5c**, **4j**, **5j**).

A flame-dried tube equipped with a magnetic stirring bar was charged with argon. The substrate (**2**: 0.5 mmol), tri(9-anthryl)borane (0.5 mol%: 2.7 mg), DBU (1.0 mmol, 152.5 uL), and CH_3CN (2.5 mL, 0.2 M) were added to the tube. Then, the fluoroalkylating reagents (1.0 mmol) was added. The mixture was stirred at room temperature and irradiated in a distance of 15 cm from 480 nm LEDs (18 W, 23 mW/cm^2). The reaction progress was monitored by thin layer chromatography and gas chromatography. Upon completion of the reaction, the mixture was diluted with diethyl ether and washed with brine. The layers were separated, and the organic layer was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding perfluoroalkylating product **4** and **5**.

4. Synthesis of trifluoromethylated heterocycles (**7a, 7b**).

A flame-dried tube equipped with a magnetic stirring bar was charged with argon. The substrate (**6**: 0.5 mmol), tri(9-anthryl)borane (0.5 mol%: 2.7 mg), TMEDA (1.0 mmol, 150 uL), and CH_3CN (2.5 mL, 0.2 M) were added to the tube. CF_3I (1.5 mmol, 37.5 mL) was then delivered into the reaction mixture using a gastight syringe. The mixture was stirred at room temperature and irradiated in a distance of 15 cm from 480 nm LEDs (18 W, 23 mW/cm^2). The reaction progress was monitored by thin layer chromatography and gas chromatography. Upon completion of the reaction, the mixture was diluted with diethyl ether and washed with brine. The layers were separated, and the organic layer was concentrated in vacuo to give a crude residue that was purified by silica gel column chromatography to give the corresponding trifluoromethylating product **7**.

5. Analytical Data for trifluoromethylated alkenes (**3a**-**3m**).

(*E*)-1,1,1-trifluorohept-2-ene (**3a**):[9a] colorless oil (0.5 mmol scale: 109 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.36 (dtq, J = 15.9, 6.9, $^4J_{H\text{-}F}$ = 2.4 Hz, 1H), 5.60 (dqt, J = 15.9, $^3J_{H\text{-}F}$ = 6.4, J = 1.6 Hz, 1H), 2.17–2.12 (m, 2H), 1.45–1.41 (m, 2H), 1.30–1.25 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 141.1 (q, $^3J_{C\text{-}F}$ = 6.5 Hz), 123.4 (q, $^1J_{C\text{-}F}$ = 269.1 Hz), 118.6 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 32.1, 31.7, 29.8, 29.7, 29.6, 29.5, 29.3, 28.2, 22.9, 14.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ −63.91; IR (neat): ν_{max} = 2883, 1623, 1215, 930 cm^{-1}; R_f = 0.95 (only hexanes).

(*E*)-(5,5,5-trifluoropent-3-en-1-yl)benzene (**3b**):[9a] colorless oil (88 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (dd, J = 7.5, 7.4 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 7.5 Hz, 2H), 6.42 (dtq, J = 15.7, 6.7, $^4J_{H\text{-}F}$ = 2.1 Hz, 1H), 5.64 (dqt, J = 15.7, $^3J_{H\text{-}F}$ = 6.4, J = 1.6 Hz, 1H), 2.77 (t, J = 7.5 Hz, 2H), 2.51–2.46 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.7, 139.8 (q, $^3J_{C\text{-}F}$ = 6.6 Hz), 128.7, 128.5, 126.5, 123.2 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 119.1 (q, $^2J_{C\text{-}F}$ = 33.1 Hz), 34.6, 33.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.04; IR (neat): ν_{max} = 2994, 1696, 1239, 1163, 946 cm^{-1}; R_f = 0.74 (only hexanes).

(*E*)-5,5,5-trifluoropent-3-en-1-yl benzoate (**3c**):[9a] colorless oil (121 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 8.0, 7.4 Hz, 2H), 6.39 (dtq, J = 15.7, 6.8, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 5.65 (dqt, J = 15.7, $^3J_{H\text{-}F}$ = 6.4, J = 1.6 Hz, 1H), 4.35 (t, J = 6.5 Hz, 2H), 2.26–2.21 (m, 2H), 1.85–1.77 (m, 2H), 1.65–1.60 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.9, 140.4 (q, $^3J_{C\text{-}F}$ = 6.7 Hz), 133.4, 130.7, 129.9, 128.7, 122.5 (q, $^1J_{C\text{-}F}$ = 269.8 Hz), 119.2 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 64.8, 31.4, 28.6, 24.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.03; IR (neat): ν_{max} = 2883, 1692, 1210, 1186, 944 cm^{-1}; R_f = 0.45 (hex:EtOAc = 8:1).

(*E*)-4-bromo-N-(4,4,4-trifluorobut-2-en-1-yl)benzamide (**3d**):[9a] white solid (138 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 6.47 (dtq, J = 15.9, 7.4, $^4J_{H\text{-}F}$ = 2.1 Hz, 1H), 6.24 (s, 1H), 5.81 (dqt, J = 15.9, $^3J_{H\text{-}F}$ = 6.4, J = 2.0 Hz, 1H), 4.23–4.20 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.7, 136.4 (q, $^3J_{C\text{-}F}$ = 6.3 Hz), 132.7, 132.2, 128.8, 126.9, 122.9 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 120.1 (q, $^2J_{C\text{-}F}$ = 34.2 Hz), 40.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.51; IR (neat): ν_{max} = 3184, 1693, 1578, 1283, 946, 665 cm^{-1}; R_f = 0.34 (hex:EtOAc = 2:1).

(*E*)-4-chloro-N-(4,4,4-trifluorobut-2-en-1-yl)benzamide (**3e**):[9a] white solid (113 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.45 (dtq, J = 15.6, 5.2, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 6.40 (bs, 1H), 5.79 (dqt, J = 15.6, $^3J_{H\text{-}F}$ = 6.4, J = 1.8 Hz, 1H), 4.21−4.18 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.9, 138.7, 136.6 (q, $^3J_{C\text{-}F}$ = 6.4 Hz), 132.5, 129.4, 128.8, 122.2 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 120.3 (q, $^2J_{C\text{-}F}$ = 34.3 Hz), 40.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.50; IR (neat): ν_{max} = 3260, 3046, 1702, 1345, 939, 735 cm^{-1}; R_f = 0.33 (hex:EtOAc = 4:1).

(*E*)-2-phenyl-N-(4,4,4-trifluorobut-2-en-1-yl)acetamide (**3f**):[9a] colorless oil (114 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.6, 7.3 Hz, 2H), 7.32 (d, J = 7.3 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 6.30 (dtq, J = 15.7, 4.9, $^4J_{H\text{-}F}$ = 2.5 Hz, 1H), 5.72 (s, 1H), 5.57 (dq, J = 12.6, $^3J_{H\text{-}F}$ = 6.3 Hz, 1H), 3.97–3.92 (m, 2H), 3.61 (s, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 171.3, 136.5 (q, $^3J_{C\text{-}F}$ = 6.4 Hz), 134.7, 129.4, 127.8, 125.6, 122.1 (q, $^1J_{C\text{-}F}$ = 269.6 Hz), 119.3 (q, $^2J_{C\text{-}F}$ = 34.1 Hz), 43.8, 39.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.21; IR (neat): ν_{max} = 3142, 2961, 1702, 1287, 936 cm^{-1}; R_f = 0.36 (hex:EtOAc = 2:1).

(*E*)-N-(4,4,4-trifluorobut-2-en-1-yl)octanamide (**3g**):[9a] colorless oil (111 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.37 (dtq, J = 15.6, 6.8, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 5.72 (dqt, J = 15.6, $^3J_{H\text{-}F}$ = 6.4, J = 1.8 Hz, 1H), 5.61 (bs, 1H), 4.03−3.99 (m, 2H), 2.21 (t, J = 7.7 Hz, 2H), 1.64 (tt, J = 7.7, 7.4 Hz, 2H), 1.34−1.23 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 173.1, 136.6 (q, $^3J_{C\text{-}F}$ = 6.3 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 119.3 (q, $^2J_{C\text{-}F}$ = 34.1 Hz), 39.4, 36.6, 31.7, 29.3, 29.1, 25.7, 22.6, 14.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.22; IR (neat): ν_{max} = 3143, 3042, 2885, 1699, 1335, 923 cm^{-1}; R_f = 0.38 (hex:EtOAc = 2:1).

(*E*)-7,7,7-trifluorohept-5-en-1-ol (**3h**):[9a] colorless oil (65 mg, 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.35 (dtq, J = 15.6, 6.5, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 5.60 (dqt, J = 15.6, $^3J_{H\text{-}F}$ = 6.3, J = 1.5 Hz, 1H), 3.64 (t, J = 6.3 Hz, 2H), 2.20–2.14 (m, 2H), 1.62–1.48 (m, 5H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.3 (q, $^3J_{C\text{-}F}$ = 6.5 Hz), 122.6 (q, $^1J_{C\text{-}F}$ = 269.9 Hz), 118.7 (q, $^2J_{C\text{-}F}$ = 33.7 Hz), 62.5, 32.0, 31.2, 24.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.01; IR (neat): ν_{max} = 3128, 2963, 1691, 951 cm^{-1}.

(*E*)-4-((4,4,4-trifluorobut-2-en-1-yl)oxy)butan-1-ol (**3i**):[9a] colorless oil (71 mg, 72%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.42 (dtq, J = 15.8, 4.0, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 5.91 (dqt, J = 15.8, $^3J_{H\text{-}F}$ = 6.8, J = 1.8 Hz, 1H), 4.13−4.06 (m, 2H), 3.66 (t, J = 6.0 Hz, 2H), 3.52 (t, J = 6.0 Hz, 2H), 2.04 (s, 1H), 1.75−1.61 (m, 4H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 136.9 (q, $^3J_{C\text{-}F}$ = 6.5 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 270.1 Hz), 118.6 (q, $^2J_{C\text{-}F}$ = 34.2 Hz), 71.3, 68.4, 62.9, 29.7,

26.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ −65.32; IR (neat): ν_{max} = 3382, 2869, 1692, 1321, 1119 cm^{-1}.

(*E*)-1-(3,3,3-trifluoroprop-1-en-1-yl)azepan-2-one (**3j**):[16] white solid (98 mg, 95%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 14.7 Hz, 1H), 5.08 (dq, *J* = 14.7, $^3J_{H\text{-}F}$ = 6.1 Hz, 1H), 3.57 (t, *J* = 4.9 Hz, 2H), 2.69–2.67 (m, 2H), 1.78–1.70 (m, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 175.0, 134.4 (q, $^3J_{C\text{-}F}$ = 7.3 Hz), 125.1 (q, $^1J_{C\text{-}F}$ = 267.8 Hz), 97.0 (q, $^2J_{C\text{-}F}$ = 34.4 Hz), 45.6, 37.2, 29.4, 27.3, 23.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ −59.85; IR (neat): ν_{max} = 2937, 1655, 1343, 969 cm^{-1}; R_f = 0.38 (hex:EtOAc = 4:1).

(*E*)-tert-butyldimethyl((7,7,7-trifluorohept-5-en-1-yl)oxy)silane (**3k**):[9a] colorless oil (127 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.38 (dtq, *J* = 15.6, 6.5, $^4J_{H\text{-}F}$ = 2.0 Hz, 1H), 5.62 (dqt, *J* = 15.6, $^3J_{H\text{-}F}$ = 6.1, *J* = 1.6 Hz, 1H), 3.62 (t, *J* = 6.0 Hz, 2H), 2.21–2.14 (m, 2H), 1.55–1.49 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 140.6 (q, $^3J_{C\text{-}F}$ = 6.3 Hz), 122.9 (q, $^1J_{C\text{-}F}$ = 269.7 Hz), 118.6 (q, $^2J_{C\text{-}F}$ = 32.1 Hz), 62.7, 32.1, 31.2, 25.9, 24.4, 18.4, 5.3; ^{19}F NMR (564 Hz, $CDCl_3$) δ −63.96; IR (neat): ν_{max} = 3002, 2970, 2360, 1738, 1366, 1228 cm^{-1}.

(*E*)-7,7,7-trifluorohept-5-en-1-yl 4-methylbenzenesulfonate (**3l**):[9a] colorless oil (155 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 6.28 (dtq, *J* = 15.7, 6.8, $^4J_{H\text{-}F}$ = 2.1 Hz, 1H), 5.56 (dqt, *J* = 15.7, $^3J_{H\text{-}F}$ = 6.4, *J* = 1.9 Hz, 1H), 4.03 (t, *J* = 6.2 Hz, 2H), 2.44 (s, 3H), 2.10 (dt, *J* = 7.4, 2.5 Hz, 2H), 1.67–1.63 (m, 2H), 1.52–1.43 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 144.8, 139.6 (q, $^3J_{C\text{-}F}$ = 6.5 Hz), 133.0, 129.8, 127.8, 121.9 (q, $^1J_{C\text{-}F}$ = 269.3 Hz), 119.1 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 69.9, 30.6, 28.1, 23.8, 21.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ −64.07; IR (neat): ν_{max} = 2969, 2361, 1738, 1356, 1113, 932 cm^{-1}; R_f = 0.56 (hex:EtOAc = 4:1).

(*E,Z*)-5-(trifluoromethyl)dec-5-ene (**3m**):[9a] colorless oil (94 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.08–6.04 (m, 1H), 2.26–2.20 (m, 3H), 1.45–1.35 (m, 12H), 0.94–0.91 (m, 3H); 5.68–5.65 (m, 1H), 2.16–2.10 (m, 3H), 1.43–1.30 (m, 12H), 0.91–0.89 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 137.7, 32.4, 31.8, 31.4, 31.2, 28.2, 27.2, 25.7, 22.9, 22.6, 22.4, 22.3, 14.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ −59.69; −66.88; IR (neat): ν_{max} = 2970, 2361, 1739, 1366, 1229, 911 cm^{-1}.

6. Analytical Data for perfluoroalkylated alkenes (**4a, 5a, 4c, 5c, 4j, 5j**).

(*E*)-1,1,1,2,2,3,3-heptafluoropentadec-4-ene (**4a**):[17] colorless oil (0.5 mmol scale: 151 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44–6.37 (m, 1H), 5.58 (dt, *J* = 15.3, $^3J_{H\text{-}F}$ = 12.4 Hz, 1H), 2.22–2.16 (m, 2H), 1.47–1.42 (m, 2H), 1.34–1.24 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.2 (t, $J_{C\text{-}F}$ = 9.0 Hz), 116.4 (t, $J_{C\text{-}F}$ = 22.9 Hz), 31.9, 31.8, 29.5, 29.4, 29.3, 29.2, 28.9, 27.9, 22.6, 14.0 (carbon peaks of $-C_3F_7$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -80.46, -112.35, -128.02; IR (neat): ν_{max} = 2970, 2360, 1739, 1228, 904 cm^{-1}; R_f = 0.89 (only hexanes).

(*E*)-1,1,1,2,2,3,3,4,4-nonafluorohexadec-5-ene (**5a**):[17] colorless oil (182 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44–6.38 (m, 1H), 5.59 (dt, *J* = 15.7, $^3J_{H\text{-}F}$ = 12.5 Hz, 1H), 2.23–2.17 (m, 2H), 1.48–1.43 (m, 2H), 1.33–1.24 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.6 (t, $J_{C\text{-}F}$ = 8.6 Hz), 116.9 (t, $J_{C\text{-}F}$ = 22.8 Hz), 32.2, 32.1, 29.9, 29.8, 29.7, 29.6, 29.2, 28.2, 22.9, 14.3 (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -81.21, -111.52, -124.56, -125.85; IR (neat): ν_{max} = 2970, 2361, 1739, 1229, 910 cm^{-1}; R_f = 0.89 (only hexanes).

(*E*)-7,7,8,8,9,9,9-heptafluorononon-5-en-1-yl benzoate (**4c**): colorless oil (174 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 7.7, 7.6 Hz, 2H), 6.46–6.39 (m, 1H), 5.67–5.60 (m, 1H), 4.35 (t, *J* = 6.4 Hz, 2H), 2.32–2.28 (m, 2H), 1.83–1.79 (m, 2H), 1.67–1.61 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.8, 142.6 (t, $J_{C\text{-}F}$ = 8.4 Hz), 133.2, 130.5, 129.7, 128.5, 117.4 (t, $J_{C\text{-}F}$ = 8.4 Hz), 114.1 (t, $J_{C\text{-}F}$ = 29.5 Hz), 113.8, 64.6, 31.7, 28.3, 24.8 (carbon peaks of $-C_3F_7$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -80.40, -112.42, -127.92; IR (neat): ν_{max} = 2970, 2361, 1739, 1366, 1228, 903 cm^{-1}; HRMS m/z (EI) calc. for $C_{16}H_{15}F_7O_2$ [M+] 372.0960, found 372.0958; R_f = 0.70 (hex:EtOAc = 4:1).

(*E*)-7,7,8,8,9,9,10,10,10-nonafluorodecyl benzoate (**5c**): colorless oil (191 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 8.3, 7.8 Hz, 2H), 6.43 (ddt, *J* = 15.8, 6.7, $^3J_{H\text{-}F}$ = 2.1 Hz, 1H), 5.69–5.60 (m, 1H), 4.35 (t, *J* = 6.4 Hz, 2H), 2.32–2.28 (m, 2H), 1.83–1.78 (m, 2H), 1.67–1.61 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 166.6, 142.5 (t, $J_{C\text{-}F}$ = 9.2 Hz), 132.9, 130.3, 129.5, 128.4, 117.4 (t, $J_{C\text{-}F}$ = 22.8 Hz), 64.4, 31.6, 28.2, 24.6 (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -81.14, -111.59, -124.46, -125.81; IR (neat): ν_{max} = 2970, 2360, 1739, 1366, 1264, 911 cm^{-1}; HRMS m/z (EI) calc. for $C_{17}H_{15}F_9O_2$ [M+] 422.0928, found 422.0931; R_f = 0.77 (hex:EtOAc = 4:1).

(*E*)-1-(3,3,4,4,5,5,5-heptafluoropent-1-en-1-yl)azepan-2-one (**4j**): white solid (141 mg, 92%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 14.7 Hz, 1H), 5.02–4.94 (m, 1H), 3.63–3.57 (m, 2H), 2.72–2.66 (m, 2H), 1.82–1.69 (m, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.9, 135.6 (t, $J_{C\text{-}F}$ = 9.9 Hz), 117.3 (q, $J_{C\text{-}F}$ = 32.2 Hz), 115.7 (t, $J_{C\text{-}F}$ = 30.6 Hz), 94.4 (t, $J_{C\text{-}F}$ = 23.5 Hz), 45.6, 37.2, 29.4, 27.3, 23.5 (carbon peaks of $-C_3F_7$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -80.24, -108.83, -127.54; IR (neat): ν_{max} = 2970, 2361, 1739, 1366, 1291, 904 cm^{-1}; HRMS m/z (EI) calc. for $C_{11}H_{12}F_7NO$ [M+] 307.0807, found 307.0805; R_f = 0.42 (hex:EtOAc = 4:1).

(*E*)-1-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)azepan-2-one (**5j**): white solid (161 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 14.7 Hz, 1H), 5.02–4.95 (m, 1H), 3.61 (d, *J* = 4.9 Hz, 2H), 2.71–2.68 (m, 2H), 1.81–1.70 (m, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 174.9, 135.7 (t, $J_{C\text{-}F}$ = 10.5 Hz), 117.4, 115.6, 94.5 (t, $J_{C\text{-}F}$ = 23.9 Hz), 45.6, 37.2, 29.4, 27.3, 23.6 (carbon peaks of $-C_4F_9$ are omitted due to complicated C-F splitting); ^{19}F NMR (564 MHz, $CDCl_3$) δ -81.09, -108.00, -124.02, -125.67; IR (neat): ν_{max} = 2970, 2361, 1739, 1366, 1230, 903 cm^{-1}; HRMS m/z (EI) calc. for $C_{12}H_{12}F_9NO$ [M+] 357.0775, found 357.0778; R_f = 0.41 (hex:EtOAc = 4:1).

7. Analytical Data for trifluoromethylated heterocycles (**7b**).

3-methyl-2-(trifluoromethyl)-1H-indole (**7b**):[18] white solid (0.5 mmol scale: 85 mg, 85%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.20 (dd, *J* = 8.2, 7.8 Hz, 1H), 2.45 (q, $^5J_{H\text{-}F}$ = 1.8 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 135.4, 128.3, 124.9, 122.3 (q, $^1J_{C\text{-}F}$ = 269.6 Hz), 121.7 (q, $^2J_{C\text{-}F}$ = 36.8 Hz), 120.6, 120.3, 114.3 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 111.8, 8.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -58.69; IR (neat): ν_{max} = 3391, 2926, 1593, 903 cm^{-1}; R_f = 0.71 (hex:EtOAc = 10:1).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Additional experiments, analytic data for fluoroalkylated compounds, and NMR spectra (**PDF**)

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Notes

The authors declare no competing financial interest.

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