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Chemo-, Regio-, and Stereoselective Trifluoromethylation of Styrenes via Visible Light-Driven Single-Electron Transfer (SET) and Triplet−Triplet Energy Transfer (TTET) Processes

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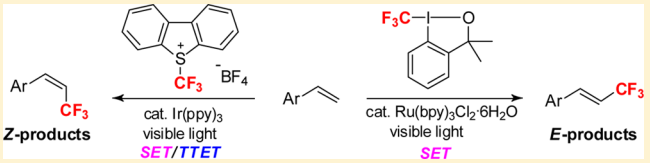
Supporting Information

ABSTRACT: A process for tunable and chemo-, regio-, and stereoselective photocatalytic trifluoromethylation of styrenes was developed. Thermodynamically stable *E*-trifluoromethylated alkenes were prepared using Togni's reagent in the presence of $Ru(bpy)_3Cl_2·6H_2O$ under visible light irradiation, whereas less thermodynamically stable *Z*-trifluoromethylated alkenes were obtained by employing Umemoto's reagent and photocatalyst $Ir(ppy)_3$.

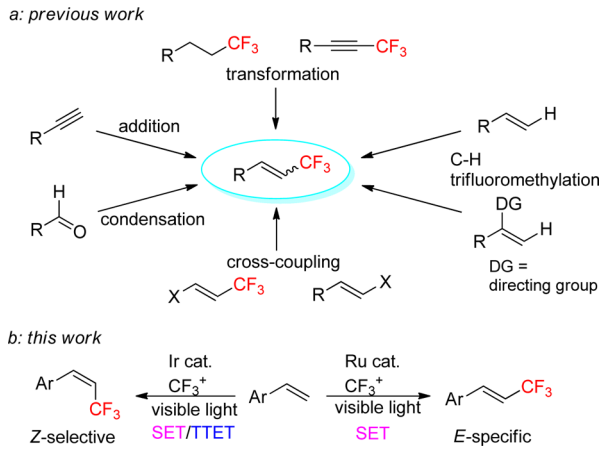


INTRODUCTION

The trifluoromethyl group (CF_3) has received increasing attention in organic synthesis[1] because its incorporation into organic molecules often enhances lipophilicity, metabolic stability, bioavailability, and binding selectivity.[2] Trifluoromethylated alkenes are important structural units that have been widely used in medicinal chemistry[3] and material science.[4] Consequently, a variety of methods have been developed for preparing these compounds (Scheme 1a). The condensation of an aldehyde with a trifluoromethyl-containing building block has been a common synthetic method for developing these alkenes.[5] The addition reaction of trifluoromethylating reagents to alkynes was evaluated as another direct route to trifluoromethylated alkenes.[6] These compounds have also been prepared by indirect approaches, such as transformation from trifluoromethylated alkanes[7] or alkynes.[8] Transition-metal-mediated and -catalyzed cross-coupling reactions of CF_3-substituted alkenes,[9] and trifluoromethylation of prefunctionalized alkenes,[10] have proven to be powerful synthetic strategies. Over the past two years, direct vinyl C—H trifluoromethylation has received increasing attention[11,12] because this method is atom- and step-economical. Despite the significant progress that has been made in the synthesis of trifluoromethylated alkenes, little attention has been paid to the control of *E*/*Z* selectivity of the products. In most cases, thermodynamically stable *E* isomers were formed as the major products. Very few methods have been developed for the stereoselective synthesis of *Z* isomers.[12] The stereoselective synthesis of *Z*- and *E*-trifluoromethylated alkenes, especially from the same substrate, has not been explored and remains a big challenge.

Recently, visible light photoredox catalysis has emerged as an important and ecofriendly synthetic tool,[13] and it has been widely applied for the trifluoromethylation of organic molecules.[14] We wondered if it was possible to selectively synthesize both *Z*- and *E*-trifluoromethylated alkenes from the same substrate via photocatalytic processes. Considering the fact that photoexcited catalysts engage not only in single-electron transfer (SET) but also in triplet−triplet energy transfer (TTET) with organic molecules,[13f] it might be possible to control the configuration of olefinic products by choosing a proper photocatalyst via different processes (SET or SET/

Scheme 1. Different Strategies for the Preparation of Trifluoromethylated Alkenes



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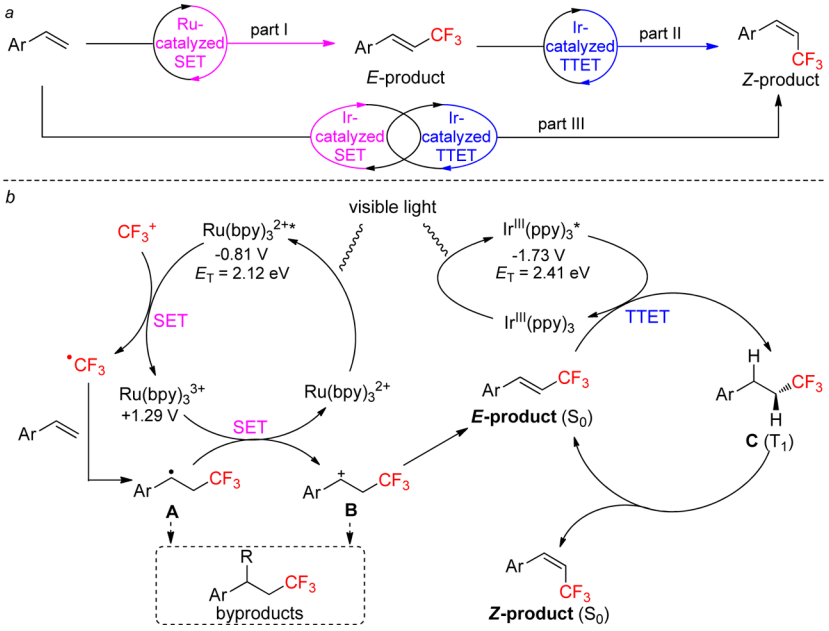
Scheme 2. Visible Light-Induced Trifluoromethylation



TTET). In continuation of our research interest in transition-metal-mediated and -catalyzed trifluoromethylation reactions,[6b,10a,15] we herein report a new type of visible light-induced trifluoromethylation of styrenes using electrophilic trifluoromethylating reagents (Scheme 1b). This protocol accomplished direct C—H trifluoromethylation of styrenes. More importantly, the *E*/*Z* configuration of the trifluoromethylated alkenes could be controlled by choosing specific photocatalysts. To the best of our knowledge, this work is the first example of tunable, stereoselective synthesis of trifluoromethylated alkenes.

Our research plan consisted of three steps (Scheme 2a). The first step was to investigate the chemo-, regio-, and stereoselective synthesis of *E*-trifluoromethylated alkenes via the photocatalytic SET process. In the second step, the TTET process was employed for converting thermodynamically stable *E* isomers into thermodynamically less stable *Z* isomers. The final step focused on a one-pot, tandem SET/TTET reaction for the direct synthesis of less thermodynamically stable *Z*-trifluoromethylated alkenes from styrenes.

The hypothesized reaction process is shown in Scheme 2b. Normally, visible light-induced trifluoromethylation of alkenes using electrophilic trifluoromethylation reagents has been proposed via an oxidative quenching cycle involving SET.[6c,7a,14f,j] First, irradiation with visible light excited ground state $Ru(bpy)_3^{2+}$ into excited state $Ru(bpy)_3^{2+*}$. SET oxidation of $Ru(bpy)_3^{2+*}$ (−0.81 V vs SCE in CH_3CN)[16] by electrophilic trifluoromethylating reagents gave $Ru(bpy)_3^{3+}$ and a trifluoromethyl radical. The resulting trifluoromethyl radical was then added to an alkene to generate radical intermediate **A**. To control the regioselectivity of this addition step, styrene was chosen as the substrate because its neighboring aryl group could stabilize the radical in intermediate **A**. Subsequent oxidation of intermediate **A** by a second SET process produced β-CF_3 carbocation intermediate **B**, which ultimately eliminated the proton to stereoselectively generate the thermodynamically stable *E* product.

Compared to the SET catalytic cycle, the TTET catalytic cycle has been less explored.[13f] In 1973, Wrighton reported that TTET from $Ru(bpy)_3^{2+*}$ could promote olefinic cis−trans isomerization.[17] Inspired by this work, we decided to select a photocatalyst with higher triplet energy, such as $Ir(ppy)_3$ (E_T = 2.41 eV),[18] for additional TTET catalytic cycling. The energy from the triplet excited state of $Ir(ppy)_3$* could promote the transformation of the ground singlet state of *E* alkene into its lowest-energy triplet state **C**(T_1). The decay of intermediate **C** gave a photostationary state mixture of *Z* and *E* alkene. If the *E* alkene could absorb the energy from the triplet excited state of $Ir(ppy)_3$*, the *Z* alkene would be gradually enriched via this catalytic cycle.

RESULTS AND DISCUSSION

We initially examined the photocatalytic trifluoromethylation of styrene **1a** using Togni's reagent **2a**[19] in the presence of $Ru(bpy)_3Cl_2{\cdot}6H_2O$[6c] under visible light irradiation. Unfortunately, the reaction mixture was complex, and the desired product was obtained in low yield. To eliminate the byproducts, which probably formed from intermediates **A** and **B** (Scheme 2b), we decided to introduce an electron-donating group (EDG) into the phenyl ring for chemoselective synthesis of the desired olefinic product. The EDG substituent made intermediate **A** more electron-rich and thus more easily oxidized for the formation of intermediate **B**. Moreover, it was better to attach the EDG substituent at the ortho position to prevent intermolecular nucleophilic attack on the carbocation of intermediate **B**.

On the basis of this consideration, *N*,*N*-dimethyl-2-vinylaniline **1b** was chosen as the substrate for visible light photocatalytic trifluoromethylation (Table 1). To our delight, the desired product **4b** was formed in 81% yield, and no byproduct could be detected from ^{19}F NMR spectroscopy of the crude product (Table 1, entry 1). This result showed that the substituent of an electron-donating group on the phenyl ring was crucial for the formation of trifluoromethylated alkene. Other electrophilic trifluoromethylating reagents **2b**−**d** were then screened. When Togni's reagent **2a** was used as the CF_3^+ source, both of the trifluoromethyl-benzoyloxylated products **3a**[6a] and **4b** were formed in moderate yields (Table 1, entry 2).

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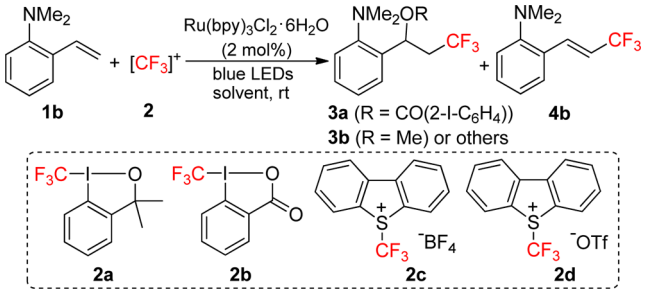
Table 1. Optimization of Reaction Conditions for the Preparation of *E*-Trifluoromethylated Alkenes[a]



entry	2	solvent	time (h)	3/4b yield (%)[b]
1	**2a**	DMF	10	0/81
2	**2b**	DMF	10	44(**3a**)/44
3	**2c**	DMF	10	trace/79
4	**2d**	DMF	10	trace/76
5	**2a**	NMP	10	0/63
6	**2a**	DMSO	10	0/42
7	**2a**	CH_3CN	10	0/72
8	**2a**	$CHCl_3$	10	0/24
9	**2a**	MeOH	10	84(**3b**)/0
10	**2a**	DMF	20	0/86

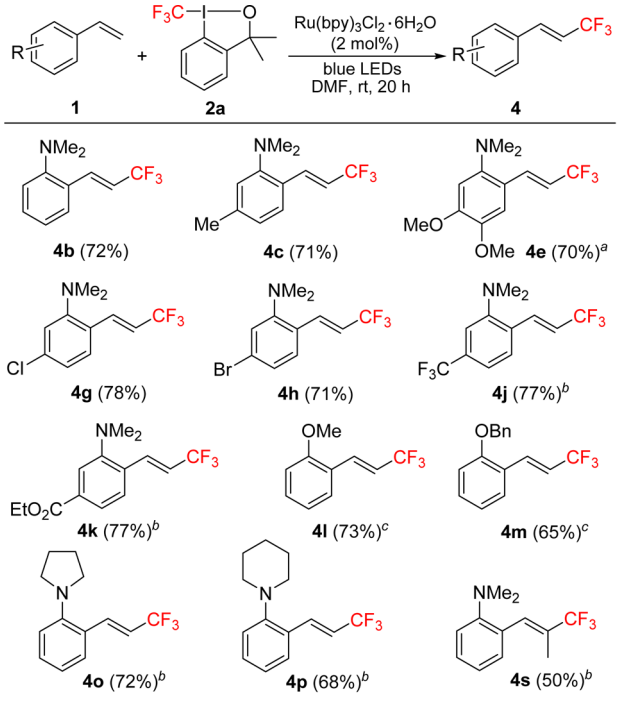
[a]Reaction conditions: **1b** (0.1 mmol), **2** (0.12 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (0.002 mmol), solvent (2.0 mL), visible light, room temperature, and under N_2. [b]Yield determined by ^{19}F NMR spectroscopy using trifluoromethoxybenzene as an internal standard.

Umemoto's reagents **2c** and **2d**[20] also gave **4b** in good yields, along with a trace amount of byproducts (Table 1, entries 3 and 4). The solvent was crucial to the reaction. When the reaction was performed in other polar and less polar solvents, such as NMP, DMSO, CH_3CN, and $CHCl_3$, compound **4b** was formed in lower yields (Table 1, entries 5−8). It is noteworthy that the alkoxytrifluoromethylated product **3b** was produced in 84% yield[7a] when methanol was used as the solvent (Table 1, entry 9). Finally, the yield of **4b** was slightly improved to 86% when the reaction was allowed to proceed for 20 h (Table 1, entry 10).

With the optimized conditions in hand (Table 1, entry 10), the substrate scope of Ru-catalyzed C—H trifluoromethylation of styrenes was investigated (Table 2). In all cases, the *E* isomer of the trifluoromethylated alkenes was formed exclusively. Styrenes bearing halogen atoms on the phenyl ring (Cl and Br) smoothly produced corresponding products **4g** and **4h** in good yields. For substrates with an electron-withdrawing group, more catalyst loading (5 mol %) was needed (**1j** and **1k**). The methoxy and benzoxy substituents at the ortho position of styrenes also promoted the formation of olefinic products **4l** and **4m** in good yields using **2c** as the CF_3^+ source. Both pyrrolidinyl and pyperidinyl substituents proved to be effective electron-donating groups, unlike a dimethylamino group, for photocatalytic trifluoromethylation (**1o** and **1p**). Furthermore, trifluoromethylation of an internal alkene (**1s**) was also successful in giving compound **4s** with excellent regio- and stereoselectivity, although the yield was slightly lower than in terminal alkenes.

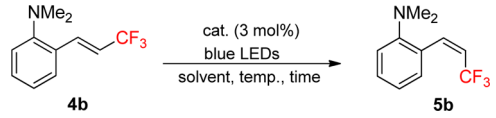
The second step of our research plan focused on the conversion of the *E*-trifluoromethylated alkenes into the thermodynamically less stable *Z* isomers. Optimization of the reaction conditions for *E* to *Z* isomerization is shown in Table 3. No conversion was found in the presence of $Ru(bpy)_3Cl_2·6H_2O$ under visible light irradiation (Table 3, entry 1). All of the Ir catalysts could promote isomerization, and $Ir(ppy)_3$ was found to be optimal by giving the highest *Z* to *E* ratio (Table 3, entries 2−5). This result was similar to Weaver's recent work[21] in which $Ir(ppy)_3$ was used for promoting the isomerization of a thermodynamic *E* alkene to a less stable *Z* isomer. When

Table 2. Substrate Scope of Ru-Catalyzed Trifluoromethylation of Styrenes[d]



[a]**2a** (0.5 mmol). [b]Ru catalyst (0.025 mmol). [c]**2c** (0.6 mmol) was used instead of **2a** (0.6 mmol). [d]Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol), Ru catalyst (0.01 mmol), DMF (10.0 mL), visible light, room temperature, under N_2, 20 h, and isolated yield.

Table 3. Optimization of Reaction Conditions for *E* to *Z* Isomerization[a]



entry	catalyst	solvent	temp	time	4b/5b[b]
1	$Ru(bpy)_3Cl_2·6H_2O$	DMA	rt	2 h	1/0
2	$Ir(ppy)_3$	DMA	rt	2 h	1/8.5
3	$Ir(ppy)_2(dtbbpy)PF_6$	DMA	rt	2 h	1/1.5
4	$Ir[dF(CF_3)ppy]_2(bpy)PF_6$	DMA	rt	2 h	1/2.1
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMA	rt	2 h	1/2.9
6	$Ir(ppy)_3$	NMP	rt	2 h	1/7.5
7	$Ir(ppy)_3$	DMSO	rt	2 h	1/7.8
8	$Ir(ppy)_3$	CH_3CN	rt	2 h	1/8.0
9	$Ir(ppy)_3$	DMA	rt	10 h	1/7.8
10	$Ir(ppy)_3$	DMA	−20 °C	2 h	1/8.3

[a]Reaction conditions: **4b** (0.1 mmol), catalyst (0.003 mmol), solvent (2.0 mL), visible light, and under N_2. [b]*Z*/*E* ratio was determined by ^{19}F NMR spectroscopy of the crude product mixture. Bpy = 2,2′-bipyridyl. Ppy = 2-phenylpyridyl. Dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl.

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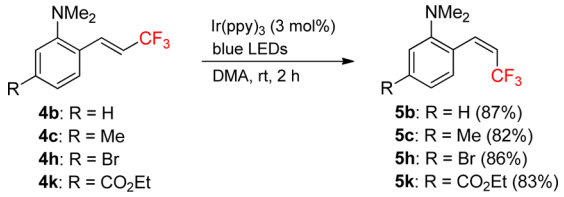
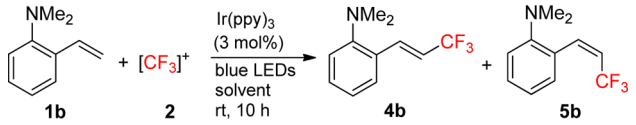
other solvents, such as NMP, DMSO, and CH_3CN, were used, lower *Z* to *E* selectivities were obtained (Table 3, entries 6−8). The reaction conditions were further optimized by prolonging the reaction time or decreasing the reaction temperature (Table 3, entries 9 and 10). However, neither of these alterations gave better results. Then, several *E*-trifluoromethylated alkenes, **4b**, **4c**, **4h**, and **4k**, were investigated for this *E* to *Z* transformation using the optimized conditions (Table 3, entry 2). All of the desired *Z* isomers, **5b**, **5c**, **5h**, and **5k**, were obtained in good yields (Scheme 3). It was noteworthy that *Z*-trifluoromethylated alkene **5b** was not converted into the *E*-trifluoromethyalted alkene **4b** under $Ir(ppy)_3$-catalyzed visible light irradiation.

Scheme 3. Transformation of Compound 4



After the *E*-trifluoromethylated alkenes had been synthesized and transformed from *E* to *Z* isomers, we then attempted one-pot synthesis of *Z*-trifluoromethylated alkenes. The reaction conditions were optimized using **1b** as the model substrate and $Ir(ppy)_3$ as the photocatalyst, which was the optimal catalyst as demonstrated in Table 3. First, different electrophilic trifluoromethylating reagents were screened (Table 4, entries 1−4). When Togni's reagent **2a** was used, the desired product **5b** was formed in 51% yield (Table 4, entry 1). Being the same as the Ru-catalyzed reaction in Table 1, reaction of Togni's reagent **2a** gave trifluoromethyl-benzoyloxylated compound **3a** as the major byproduct (Table 4, entry 2). Umemoto's reagents **2c** and **2d** improved the yield of **5b** to 72% and 64%, respectively (Table 4, entries 3 and 4). Thus, **2c** was chosen as the trifluoromethylating reagent for $Ir(ppy)_3$-catalyzed trifluoromethylation. Then, various solvents were investigated, and DMA was found to be better than other solvents tested (Table 4, entries 5−8). Finally, the additives Li_2CO_3 and DBU were added to the reaction mixture to determine if they could improve yield and *Z*/*E* selectivity; however, no further improvement was obtained (Table 4, entries 9 and 10). This reaction process was monitored by ^{19}F NMR spectroscopy of the reaction mixture. It was found that *E* isomer **4b** was the major product formed at the beginning. As time progressed, **4b** was gradually converted to the *Z* isomer **5b** until reaching a final equilibration between **4b** and **5b**.

Table 4. Optimization of Reaction Conditions for the One-Pot Synthesis of *Z*-Trifluoromethylated Alkenes[a]

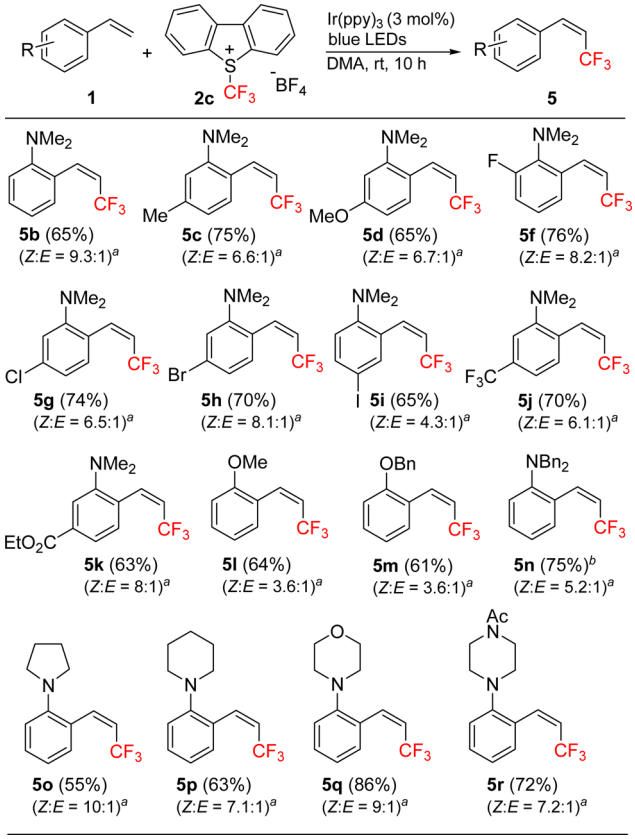


entry	2	solvent	4b/5b yield (%)[b]
1	**2a**	DMF	8/51
2[c]	**2b**	DMF	13/15
3	**2c**	DMF	9/72
4	**2d**	DMF	10/64
5	**2c**	DMSO	5/53
6	**2c**	DCE	3/36
7	**2c**	NMP	4/27
8	**2c**	DMA	8/72
9[d]	**2c**	DMA	13/66
10[e]	**2c**	DMA	12/68

[a]Reaction conditions: **1b** (0.1 mmol), **2** (0.12 mmol), $Ir(ppy)_3$ (0.003 mmol), solvent (2.0 mL), visible light, room temperature, and under N_2. [b]Yields determined by ^{19}F NMR spectroscopy using trifluoromethoxybenzene as an internal standard. [c]**3a** was formed in 35% yield. [d]Li_2CO_3 (0.1 mmol) was added. [e]DBU (0.1 mmol) was added.

The substrate scope of Ir-catalyzed C—H trifluoromethylation of styrenes was then investigated. The *Z*-trifluoromethylated alkenes were obtained in moderate to high yields (Table 5). The trifluoromethylation of styrenes bearing various electron-donating (methyl and methoxy) and electron-withdrawing (ester and trifluoromethyl) substituents at different positions along the phenyl ring proceeded well. All of the halogen atoms (F, Cl, Br, and I) were also compatible; they gave the corresponding products **5f−i** in moderate yields. Other electron-donating groups (e.g., alkoxy and dibenzylamino), unlike a dimethylamino group, could also accelerate the formation of the desired products (**5l−r**). The configuration of

Table 5. Substrate Scope of Ir-Catalyzed Trifluoromethylation of Styrenes[c]



[a]*Z*/*E* ratio was determined by ^{19}F NMR spectroscopy of the crude product mixture. [b]Isolated yields of a mixture of *Z* and *E* isomers. [c]Reaction conditions: **1** (0.5 mmol), **2c** (0.6 mmol), $Ir(ppy)_3$ (0.015 mmol), DMA (10.0 mL), visible light, room temperature, under N_2, and allowed to react for 10 h.

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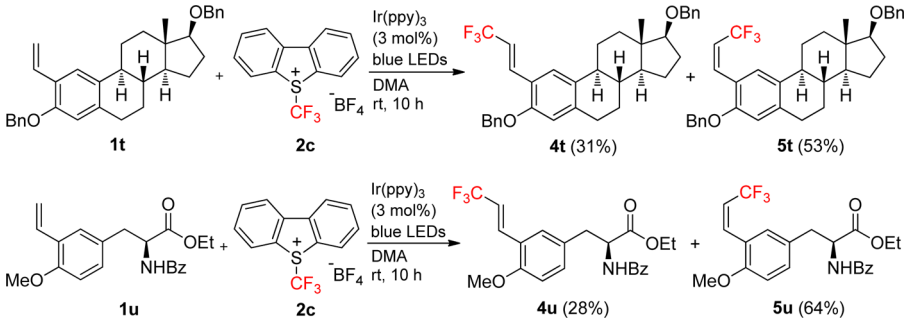
Scheme 4. Photocatalytic C—H Trifluoromethylation of Steroid and Amino Acid Derivatives

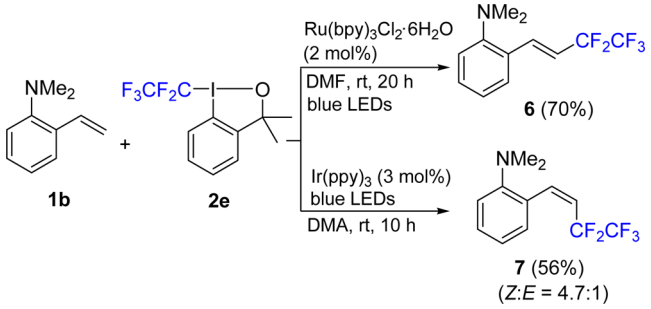


compound **5q** was confirmed by X-ray crystallographic analysis (see Supporting Information).

This photocatalytic protocol could also be applied for direct C—H trifluoromethylation of complex molecules, such as steroid and amino acid derivatives **1t** and **1u** (Scheme 4). The corresponding trifluoromethylated alkenes were isolated in high yields, although the *Z*/*E* selectivities were comparably low. These results showed that this reaction might be applicable to "late-stage trifluoromethylation" of natural products and drugs.

Furthermore, pentafluoroethylating reagent **2e** was synthesized[22] and used for the visible light-induced reaction (Scheme 5). The Ru-catalyzed reaction gave pentafluoroethylated *E* isomer **6** in 70% isolated yield, whereas the Ir-catalyzed reaction produced *Z* isomer **7** in 56% isolated yield. These results showed that this photocatalytic protocol could be extended to perfluoroalkylation reactions.

Scheme 5. Photocatalytic C—H Pentafluoroethylation of 1b

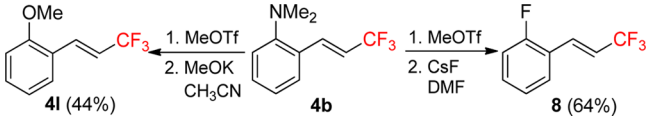


The dimethylamino group could serve as not only an efficient assisting group but also a potential leaving group. For example, treatment of compound **4b** with MeOTf afforded the aryltrimethylammonium triflate intermediate, which then reacted with different nucleophiles, such as methoxide and fluoride anions, to produce the trifluoromethylated alkenes **4l** and **8** (Scheme 6).

CONCLUSION

In summary, we have developed the first example of tunable and chemo-, regio-, and stereoselective synthesis of *Z*- and *E*-trifluoromethylated alkenes by means of visible light catalysis. The thermodynamically stable *E* isomers were prepared by direct C—H trifluoromethylation of styrenes promoted by Ru-catalyzed SET. A one-pot Ir-catalyzed tandem SET/TTET process was developed for the preparation of thermodynamically less stable *Z* isomers. This protocol provides a mild and efficient method for direct C—H trifluoromethylation of various styrenes, including some complex molecules. It could also be extended to other fluoroalkylation reactions, such as pentafluoroethylation.

Scheme 6. Transformation of Compound 4b



EXPERIMENTAL SECTION

General Experimental Methods. ^{1}H NMR (TMS internal standard), ^{19}F NMR ($CFCl_3$ outside standard, low-field positive), and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS spectra using ESI were obtained on an ESI-FTMS mass spectrometer; HRMS spectra using EI were obtained on a GC-TOF mass spectrometer. Unless otherwise noted, all reagents and substrates were obtained commercially and used without further purification. Substrates **1b**–**s**,[23] **1t**,[24] and compound **1u**[25] were prepared according to procedures in the literature. Compounds **1b**,[26a] **1l**,[26b] **1m**,[26c] **1o**,[26d] **1p**,[26e] **1q**,[26e] **1s**,[26f] and **4l**[26g] are all known compounds.

General Procedure for the Synthesis of Styrenes (1). In a sealed tube, 2-fluorobenzaldehyde (5.0 mmol, 1 equiv) was dissolved in DMSO (10.0 mL) and then K_2CO_3 (15.0 mmol, 3 equiv) and dimethylamine hydrochloride (10.0 mmol, 2 equiv) were added, and the reaction mixture was stirred and heated to 100 °C until the reaction was complete. The reaction mixture was then poured into water and extracted with EtOAc (3 × 30 mL/mmol). The organic layers were combined, dried with $MgSO_4$, and concentrated under reduced pressure to get the crude product 2-(*N*,*N*-dimethyl)-benzaldehyde.

Methyl triphenylphosphonium iodide (7.5 mmol, 1.5 equiv) was dissolved in dry diethyl ether (50.0 mL) in a 100 mL round-bottom flask at 0 °C under dry nitrogen. Potassium *tert*-butoxide (10.0 mmol, 2 equiv) was added in one portion, and the mixture was stirred for 10 min. The crude product of aldehyde was added in one portion at 0 °C, and the reaction mixture was stirred for 24 h at rt. The mixture was added to a saturated aqueous NaCl solution (100 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by chromatography on silica gel to afford desired styrene **1**.

*N,N-Dimethyl-2-vinylaniline (**1b**).* Following the general procedure, this product was isolated as a colorless oil (778.1 mg, 96%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, J = 7.6, 1.6 Hz, 1H), 7.33–7.31 (m, 1H), 7.18 (dd, J = 17.6, 11.2 Hz, 1H), 7.13–7.18 (m, 2H), 5.78 (dd, J = 17.6, 1.6 Hz, 1H), 5.35 (dd, J = 10.8, 1.6 Hz, 1H), 2.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 135.1, 131.9, 128.4, 126.9, 122.4, 118.0, 113.1,

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44.6. IR (thin film) ν_{max}: 3083, 2940, 2781, 1625, 1595, 1487, 1316, 948, 906, 756 cm^{-1}. EIMS m/z: M$^+$ 147 (41.8), 132 (100), 117 (62.3). HRMS-EI: calcd for $C_{10}H_{13}N$, 147.1048; found, 147.1046.

*N,N,5-Trimethyl-2-vinylaniline (**1c**).* Following the general procedure, this product was isolated as a colorless oil (687.8 mg, 85%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.0 Hz, 1H), 7.06 (dd, J = 17.6, 10.8 Hz, 1H), 6.85−6.84 (m, 2H), 5.65 (dd, J = 17.6, 1.2 Hz, 1H), 5.22 (dd, J = 10.8, 1.2 Hz, 1H), 2.75 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 138.2, 134.8, 129.0, 126.7, 123.2, 118.8, 112.3, 44.6, 21.5. IR (thin film) ν_{max}: 3082, 2925, 2854, 2779, 1623, 1605, 1498, 1315, 901, 816 cm^{-1}. EIMS m/z: M$^+$ 161 (35.8), 146 (100), 131 (77.3). HRMS-EI: calcd for $C_{11}H_{15}N$, 161.1204; found, 161.1203.

*5-Methoxy-N,N-dimethyl-2-vinylaniline (**1d**).* Following the general procedure, this product was isolated as a colorless oil (747.6 mg, 84%) by flash chromatography in 5:1 petroleum ether/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 1H), 7.00 (dd, J = 18.0, 11.2 Hz, 1H), 6.61−6.57 (m, 2H), 5.60 (d, J = 17.6 Hz, 1H), 5.18 (d, J = 10.8 Hz, 1H), 3.83 (s, 3H), 2.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 153.2, 134.5, 127.9, 124.8, 111.2, 106.8, 104.7, 55.2, 44.5. IR (thin film) ν_{max}: 3080, 2941, 2831, 2782, 1602, 1500, 1320, 1236, 1097 cm^{-1}. EIMS m/z: M$^+$ 177 (35.5), 162 (100), 147 (41.5). HRMS-EI: calcd for $C_{11}H_{15}NO$, 177.1154; found, 177.1153.

*4,5-Dimethoxy-N,N-dimethyl-2-vinylaniline (**1e**).* Following the general procedure, this product was isolated as a pale yellow oil (1.00 g, 97%) by flash chromatography in 10:1 petroleum ether/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (dd, J = 17.6, 11.2 Hz, 1H), 7.00 (s, 1H), 6.62 (s, 1H), 5.54 (d, J = 17.6 Hz, 1H), 5.14 (d, J = 11.2 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.66 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 145.8, 144.9, 133.8, 124.4, 111.3, 109.4, 102.9, 56.2, 55.9, 45.1. IR (thin film) ν_{max}: 3078, 2937, 2827, 2780, 1603, 1510, 1454, 1253, 1216, 997, 820 cm^{-1}. EIMS m/z: M$^+$ 207 (53.7), 192 (100), 161 (29.3). HRMS-EI: calcd for $C_{12}H_{17}NO_2$, 207.1259; found, 207.1263.

*2-Fluoro-N,N-dimethyl-6-vinylaniline (**1f**).* Following the general procedure, this product was isolated as a colorless oil (595.1 mg, 72%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 7.6 Hz, 1H), 7.20 (dd, J = 17.6, 10.8 Hz, 1H), 7.06−7.00 (m, 1H), 6.97−6.92 (m, 1H), 5.69 (dd, J = 18.0, 1.2 Hz, 1H), 5.29 (d, J = 11.2 Hz, 1H), 2.82 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4 (d, J = 247.2 Hz), 138.2 (d, J = 10.2 Hz), 137.7 (d, J = 5.1 Hz), 133.6 (d, J = 2.9 Hz), 124.9 (d, J = 9.5 Hz), 121.3 (d, J = 3.0 Hz), 115.7 (d, J = 21.1 Hz), 114.7, 44.13, 44.09. ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.3 (s, 1F). IR (thin film) ν_{max}: 3081, 2927, 2794, 1571, 1457, 1242, 944, 802, 750 cm^{-1}. EIMS m/z: M$^+$ 165 (58.4), 150 (100), 135 (84.9). HRMS-EI: calcd for $C_{10}H_{12}NF$, 165.0954; found, 165.0950.

*5-Chloro-N,N-dimethyl-2-vinylaniline (**1g**).* Following the general procedure, this product was isolated as a colorless oil (741.8 mg, 82%) by flash chromatography in 10:1 petroleum ether/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.4 Hz, 1H), 7.00−6.93 (m, 3H), 5.66 (dd, J = 17.6, 1.2 Hz, 1H), 5.27 (dd, J = 11.2, 1.2 Hz, 1H), 2.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 134.2, 133.7, 130.2, 128.0, 122.2, 118.4, 113.5, 44.3. IR (thin film) ν_{max}: 3084, 2983, 2944, 2832, 2788, 1624, 1587, 1489, 960, 838, 817 cm^{-1}. EIMS m/z: M$^+$ 181 (34.0), 166 (74.3), 131 (100). HRMS-EI: calcd for $C_{10}H_{12}ClN$, 181.0658; found, 181.0659.

*5-Bromo-N,N-dimethyl-2-vinylaniline (**1h**).* Following the general procedure, this product was isolated as a colorless oil (519.6 mg, 91%) by flash chromatography in 10:1 petroleum ether/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.8 Hz, 1H), 7.13−7.11 (m, 2H), 6.95 (dd, J = 18.0, 10.8 Hz, 1H), 5.62 (d, J = 17.6 Hz, 1H), 5.28 (d, J = 11.2 Hz, 1H), 2.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 134.2, 130.6, 128.3, 125.1, 121.9, 121.4, 113.6, 44.3. IR (thin film) ν_{max}: 3080, 2943, 2832, 2787, 1582, 1485, 954, 822, 696 cm^{-1}. EIMS m/z: M$^+$ 225 (14.2), 212 (16.3), 210 (17.1), 183 (21.3), 131 (100). HRMS-EI: calcd for $C_{10}H_{12}BrN$, 225.0153; found, 225.0148.

*4-Iodo-N,N-dimethyl-2-vinylaniline (**1i**).* Following the general procedure, this product was isolated as a pale yellow oil (764.2 mg, 56%) by flash chromatography in 30:1 petroleum ether/diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 2.4 Hz, 1H), 7.49 (dd, J = 8.4, 2.0 Hz, 1H), 6.91 (dd, J = 17.6, 10.8 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 5.65 (dd, J = 17.6, 1.2 Hz, 1H), 5.28 (dd, J = 10.8, 0.8 Hz, 1H), 2.70 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 136.9, 135.6, 134.2, 133.8, 120.2, 114.2, 85.5, 44.3. IR (thin film) ν_{max}: 3082, 2941, 2830, 2783, 1621, 1578, 1482, 1106, 945, 815 cm^{-1}. EIMS m/z: M$^+$ 273 (64.3), 258 (32.5), 144 (23.8), 131 (100). HRMS-EI: calcd for $C_{10}H_{12}NI$, 273.0015; found, 273.0017.

*N,N-Dimethyl-5-(trifluoromethyl)-2-vinylaniline (**1j**).* Following the general procedure, this product was isolated as a colorless oil (569.7 mg, 55%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 1H), 7.26−7.22 (m, 2H), 7.02 (dd, J = 17.6, 11.2 Hz, 1H), 5.75 (d, J = 18.0 Hz, 1H), 5.36 (d, J = 10.8 Hz, 1H), 2.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 135.0, 134.2, 130.1 (q, J = 31.3 Hz), 127.4, 124.3 (q, J = 270.5 Hz), 118.7 (q, J = 3.7 Hz), 115.1, 114.7 (q, J = 3.6 Hz), 44.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.5 (s, 3F). IR (thin film) ν_{max}: 3087, 2947, 2791, 1337, 1169, 1123, 694 cm^{-1}. EIMS m/z: M$^+$ 215 (52.7), 200 (100). HRMS-EI: calcd for $C_{11}H_{12}NF_3$, 215.0922; found, 215.0926.

*Ethyl 3-(Dimethylamino)-4-vinylbenzoate (**1k**).* Following the general procedure, this product was isolated as a yellow oil (383.5 mg, 35%) by flash chromatography in 5:1 petroleum ether/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 2.0 Hz, 1H), 7.87 (dd, J = 8.8, 2.0 Hz, 1H), 6.94−6.87 (m, 2H), 5.74 (dd, J = 17.6, 1.2 Hz, 1H), 5.29 (dd, J = 11.2, 1.2 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.79 (s, 6H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 155.5, 135.0, 130.4, 129.8, 129.1, 123.2, 116.9, 113.8, 60.6, 43.9, 14.4. IR (thin film) ν_{max}: 3085, 2980, 2836, 2789, 1711, 1601, 1296, 1248, 1113, 757.3 cm^{-1}. EIMS m/z: M$^+$ 219 (90.9), 204 (48.9), 174 (50.6), 131 (100). HRMS-EI: calcd for $C_{13}H_{17}NO_2$, 219.1259; found, 219.1254.

*1-Methoxy-2-vinylbenzene (**1l**).* Following the general procedure, this product was isolated as a colorless oil (496.6 mg, 74%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, J = 7.8, 1.2 Hz, 1H), 7.29−7.25 (m, 1H), 7.10 (dd, J = 17.6, 10.8 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.78 (dd, J = 18.0, 1.2 Hz, 1H), 5.30 (dd, J = 10.8, 1.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 131.7, 128.9, 126.8, 126.6, 120.7, 114.5, 110.9, 55.5. IR (thin film) ν_{max}: 3073, 3002, 2956, 2836, 1624, 1598, 1488, 1463, 1244, 1055, 909, 750 cm^{-1}. EIMS m/z: M$^+$ 134 (40.8), 119 (45.0), 91 (100). HRMS-EI: calcd for $C_9H_{10}O$, 134.0732; found, 134.0728.

*1-(Benzyloxy)-2-vinylbenzene (**1m**).* Following the general procedure, this product was isolated as a colorless oil (657.6 mg, 63%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 1H), 7.49−7.33 (m, 5H), 7.27−7.15 (m, 2H), 7.03−6.95 (m, 2H), 5.82 (dd, J = 17.6, 1.6 Hz, 1H), 5.30 (d, J = 11.2, 1.6 Hz, 1H), 5.13 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 137.2, 131.7, 129.5, 128.9, 128.6, 127.9, 127.5, 127.4, 127.2, 126.6, 121.0, 114.5, 112.5, 70.3. IR (thin film) ν_{max}: 3065, 3032, 2927, 1597, 1487, 1451, 1239, 1014, 910, 749, 696 cm^{-1}. EIMS m/z: M$^+$ 210 (22.6), 91 (100), 65 (15.5). HRMS-EI: calcd for $C_{15}H_{14}O$, 210.1045; found, 210.1042.

*N,N-Dibenzyl-2-vinylaniline (**1n**).* Following the general procedure, this product was isolated as a yellow oil (523.8 mg, 35%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 6.4 Hz, 1H), 7.46 (dd, J = 17.6, 10.8 Hz, 1H), 7.33−7.28 (m, 10H), 7.17 (t, J = 6.8 Hz, 1H), 7.08 (t, J = 6.8 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 5.80 (dd, J = 18.0, 1.2 Hz, 1H), 5.37 (dd, J = 15.2, 1.2 Hz, 1H), 4.19 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 138.2, 134.7, 133.1, 128.8, 128.3, 128.0, 127.0, 126.8, 123.2, 122.1, 113.8, 56.7. IR (thin film) ν_{max}: 3084, 3061, 3027, 2841, 1627, 1595, 1494, 1451, 909, 759, 697 cm^{-1}. EIMS m/z: M$^+$ 299 (5.2), 208 (85.9), 91 (100). HRMS-EI: calcd for $C_{22}H_{21}N$, 299.1674; found, 299.1670.

*1-(2-Vinylphenyl)pyrrolidine (**1o**).* Following the general procedure, this product was isolated as a colorless oil (596.1 mg, 69%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, J = 8.0, 1.6 Hz, 1H), 7.24−7.19 (m, 1H), 7.03 (dd, J = 17.6, 10.8 Hz, 1H), 6.94−6.91 (m, 2H), 5.61 (dd, J = 17.6, 1.6

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Hz, 1H), 5.25 (dd, J = 11.2, 1.6 Hz, 1H), 3.24 (t, J = 6.0 Hz, 4H), 1.97−1.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 136.7, 129.5, 128.2, 128.0, 120.1, 115.6, 112.4, 51.9, 24.9. IR (thin film) ν_{max}: 3083, 2959, 2851, 2819, 1624, 1595, 1484, 1449, 1223, 1117, 934, 758 cm^{-1}. EIMS m/z: M$^+$ 189 (32.3), 144 (21.5), 130 (100). HRMS-EI: calcd for $C_{12}H_{15}NO$, 189.1154; found, 189.1151.

*1-(2-Vinylphenyl)piperidine (**1p**).* Following the general procedure, this product was isolated as a colorless oil (589.2 mg, 63%) by flash chromatography in 5:1 petroleum ether/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 8.0 Hz, 1H), 7.28−7.24 (m, 1H), 7.11 (dd, J = 17.2, 10.8 Hz, 1H), 7.06−7.02 (m, 2H), 5.72 (dd, J = 19.0, 1.2 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 2.92 (t, J = 4.8 Hz, 4H), 1.78−1.72 (m, 4H), 1.63−1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 134.5, 132.2, 128.4, 126.5, 122.5, 118.6, 113.0, 53.8, 26.5, 24.4. IR (thin film) ν_{max}: 3082, 2933, 2851, 2802, 1623, 1595, 1483, 1449, 1227, 905, 755 cm^{-1}. EIMS m/z: M$^+$ 187 (62.3), 172 (32.4), 158 (21.7), 144 (46.1), 130 (100). HRMS-EI: calcd for $C_{13}H_{17}N$, 187.1361; found, 187.1360.

*4-(2-Vinylphenyl)morpholine (**1q**).* Following the general procedure, this product was isolated as a white solid (434.6 mg, 46%, mp 40−41 °C) by flash chromatography in 20:1 petroleum ether/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, J = 8.0, 1.2 Hz, 1H), 7.28−7.24 (m, 1H), 7.11−7.00 (m, 3H), 5.70 (dd, J = 17.6, 1.2 Hz, 1H), 5.25 (dd, J = 10.8, 1.2 Hz, 1H), 3.86 (t, J = 4.8 Hz, 4H), 2.96 (t, J = 4.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 134.2, 132.2, 128.6, 126.9, 123.2, 118.4, 113.8, 67.3, 52.6. IR (thin film) ν_{max}: 3083, 2959, 2851, 2819, 1624, 1595, 1484, 1449, 1223, 1117, 934, 758 cm^{-1}. EIMS m/z: M$^+$ 189 (32.3), 144 (21.5), 130 (100). HRMS-EI: calcd for $C_{12}H_{15}NO$, 189.1154; found, 189.1151.

*1-(4-(2-Vinylphenyl)piperazin-1-yl)ethanone (**1r**).* Following the general procedure, this product was isolated as a pale yellow solid (302.7 mg, 26%, mp 86−88 °C) by flash chromatography in 2:1 dichloromethane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.6 Hz, 1H), 7.26−7.22 (m, 1H), 7.10−7.03 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 5.70 (dd, J = 18.0, 1.2 Hz, 1H), 5.26 (dd, J = 10.8, 1.2 Hz, 1H), 3.75 (t, J = 4.8, 2H), 3.59 (t, J = 4.8, 4H), 2.94−2.89 (m, 4H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 150.0, 133.8, 132.4, 128.6, 126.9, 123.6, 118.7, 114.2, 52.4, 51.9, 46.7, 41.8, 21.4. IR (thin film) ν_{max}: 3056, 3010, 2818, 1648, 1431, 1251, 1225, 997, 760 cm^{-1}. EIMS m/z: M$^+$ 230 (58.1), 215 (11.7), 158 (54.7), 144 (59.3), 130 (100). HRMS-EI: calcd for $C_{14}H_{18}N_2O$, 230.1419; found, 230.1421.

*(E)-N,N-Dimethyl-2-(prop-1-enyl)aniline (**1s**).* Following the general procedure, this product was isolated from the reaction of ethyl triphenylphosphonium iodide and the corresponding aldehyde as a colorless oil (778.3 mg, 96%) by flash chromatography in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 8.4 Hz, 1H), 7.06−7.00 (m, 2H), 6.60 (d, J = 11.2 Hz, 1H), 5.88−5.80 (m, 1H), 2.78 (s, 6H), 1.92 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 130.8, 130.6, 129.1, 127.5, 124.9, 121.2, 117.5, 44.1, 14.7. IR (thin film) ν_{max}: 3061, 3015, 2938, 2827, 2778, 1594, 1488, 1450, 1316, 949, 759, 658 cm^{-1}. EIMS m/z: M$^+$ 161 (75.1), 146 (56.0), 132 (100), 117 (52.4). HRMS-EI: calcd for $C_{11}H_{15}N$, 161.1204; found, 161.1200.

*(8R,9S,13S,14S,17S)-3,17-Bis(benzyloxy)-13-methyl-2-vinyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]-phenanthrene (**1t**).* Following the general procedure, this product was isolated as a white solid (910.2 mg, 38%, mp 118−120 °C) by flash chromatography in 2:1 petroleum ether/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.26 (m, 11H), 7.09 (dd, J = 18.0, 11.2 Hz, 1H), 6.56 (s, 1H), 5.72 (d, J = 18.0 Hz, 1H), 5.20 (d, J = 7.2 Hz, 1H), 5.06 (s, 2H), 4.59 (s, 2H), 3.52 (t, J = 8.4 Hz, 1H), 2.86−2.82 (m, 2H), 2.37−2.34 (m, 1H), 2.21−2.04 (m, 3H), 1.89−1.87 (m, 1H), 1.72−1.58 (m, 2H), 1.47−1.17 (m, 6H), 0.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 139.4, 137.7, 137.4, 132.9, 132.0, 128.5, 128.3, 127.8, 127.34, 127.32, 124.5, 123.6, 113.4, 112.8, 88.4, 50.3, 44.0, 43.4, 38.7, 38.0, 29.9, 28.1, 27.3, 26.5, 23.2, 11.9. IR (thin film) ν_{max}: 3083, 3030, 2927, 2866, 1624, 1607, 1498, 1258, 1117, 895, 735, 696 cm^{-1}. MS-ESI m/z: [M + H]$^+$ 479. HRMS-ESI: [M + H] calcd for $C_{34}H_{39}O_2$, 479.2945; found, 479.2937.

*(S)-Ethyl 2-Benzamido-3-(4-methoxy-3-vinylphenyl)propanoate (**1u**).* Following the general procedure, this product was isolated as a white solid (451.3 mg, 26%, mp 104−105 °C) by flash chromatography in 5:1 petroleum ether/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.2 Hz, 1H), 7.52−7.40 (m, 3H), 7.22 (d, J = 1.6 Hz, 1H), 7.02−6.94 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 7.2 Hz, 1H), 5.60 (dd, J = 17.6, 1.2 Hz, 1H), 5.20 (dd, J = 11.2, 1.2 Hz, 1H), 5.06−5.01 (m, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 3.26−3.16 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 166.8, 156.0, 134.1, 131.8, 131.4, 129.7, 128.6, 127.8, 127.6, 127.0, 126.7, 144.5, 111.0, 61.6, 55.5, 53.6, 37.1, 14.2. IR (thin film) ν_{max}: 3329, 3083, 2980, 2835, 1737, 1642, 1530, 1494, 1251, 1027, 714 cm^{-1}. MS-ESI m/z: [M + H]$^+$ 354. HRMS-ESI: [M + H] calcd for $C_{21}H_{24}O_4N$, 354.1700; found, 354.1695.

General Procedure for the Selective Synthesis of *E*-Trifluoromethylated Alkenes. A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (7.5 mg, 0.01 mmol, 2 mol %), **1** (0.5 mmol, 1.0 equiv), **2a** (198.1 mg, 1.2 equiv, 0.6 mmol), and DMF (10.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 20 h. After the reaction was complete, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography to give *E* product **4**.

*(E)-N,N-Dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**4b**).* Following the general procedure, this product was isolated as a colorless oil (77.1 mg, 72%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.11−7.04 (m, 2H), 6.21 (dq, J = 15.6, 6.8 Hz, 1H), 2.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 135.9 (q, J = 6.8 Hz), 130.5, 127.9, 127.5, 124.0 (q, J = 267.1 Hz), 122.5, 118.5, 115.3 (q, J = 33.5 Hz), 44.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.0 (d, J = 5.6 Hz, 3F). IR (thin film) ν_{max}: 3062, 2926, 2854, 2787, 1658, 1598, 1322, 1127, 988, 761 cm^{-1}. EIMS m/z: M$^+$ 215 (100), 144 (64.4), 132 (81.2). HRMS-EI: calcd for $C_{11}H_{12}NF_3$, 215.0922; found, 215.0924.

*(E)-N,N,5-Trimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**4c**).* Following the general procedure, this product was isolated as a colorless oil (81.6 mg, 71%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, J = 16.4, 2.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 6.89 (s, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.16 (dq, J = 16.4, 6.8 Hz, 1H), 2.74 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 140.8, 135.8 (q, J = 7.0 Hz), 127.7, 124.6, 124.2 (q, J = 266.9 Hz), 123.3, 119.3, 114.2 (q, J = 33.3 Hz), 44.8, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.8 (dd, J = 6.8, 3.0 Hz, 3F). IR (thin film) ν_{max}: 2945, 2788, 1659, 1607, 1321, 1276, 1122, 988, 809, 676 cm^{-1}. EIMS m/z: M$^+$ 229 (94.7), 146 (100), 131 (63.8). HRMS-EI: calcd for $C_{12}H_{14}NF_3$, 229.1078; found, 229.1074.

*(E)-4,5-Dimethoxy-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)-aniline (**4e**).* Following the general procedure, this product was isolated as a colorless oil (97.2 mg, 70%) by flash chromatography in 10:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, J = 16.0, 2.0 Hz, 2H), 6.95 (s, 1H), 6.68 (s, 1H), 6.09 (dq, J = 16.4, 6.4 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 2.71 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 147.9, 145.1, 134.8 (q, J = 7.0 Hz), 124.3 (q, J = 266.9 Hz), 119.9, 113.2 (q, J = 33.3 Hz), 109.9, 103.0, 56.3, 55.9, 45.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.4 (d, J = 4.1 Hz, 3F). IR (thin film) ν_{max}: 2941, 2833, 2785, 1655, 1606, 1513, 1316, 1253, 1100, 943, 938 cm^{-1}. EIMS m/z: M$^+$ 275 (89.8), 260 (100), 232 (32.4). HRMS-EI: calcd for $C_{13}H_{16}NO_2F_3$, 275.1133; found, 275.1137.

*(E)-5-Chloro-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**4g**).* Following the general procedure, this product was isolated as a colorless oil (97.2 mg, 78%) by flash chromatography in 10:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, J = 16.4, 2.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.04−7.01 (m, 2H), 6.18 (dq, J = 16.0, 6.4 Hz, 1H), 2.76 (s, 6H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 154.1, 136.1, 135.1 (q, J = 6.8 Hz), 129.0, 125.7 123.8 (q, J = 267.7 Hz), 122.4, 119.0, 115.5 (q, J = 33.6 Hz), 44.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.1 (d, J = 6.8 Hz, 3F). IR (thin film) ν_{max}: 3087, 2980, 2840, 2794, 1660, 1589, 1321, 1128, 962, 851 cm^{-1}. EIMS m/z: M$^+$ 249 (93.7), 166 (100), 131 (98.9). HRMS-EI: calcd for $C_{11}H_{11}NF_3Cl$, 249.0532; found, 249.0533.

(E)-5-Bromo-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline ***(4h)***. Following the general procedure, this product was isolated as a pale yellow oil (104.3 mg, 71%) by flash chromatography in 10:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dd, J = 16.0, 2.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.16−7.13 (m, 2H), 6.16 (dq, J = 16.4, 6.4 Hz, 1H), 2.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 135.1 (q, J = 6.8 Hz), 129.1, 126.1, 125.3, 124.3, 123.7 (q, J = 268 Hz), 121.9, 115.5 (q, J = 33.6 Hz), 44.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.1 (dd, J = 6.8, 2.6 Hz, 3F). IR (thin film) ν_{max}: 2949, 2840, 2793, 1660, 1584, 1489, 1320, 1275, 1127, 955, 843 cm^{-1}. EIMS m/z: M$^+$ 293 (24.7), 199 (30.0), 131 (100). HRMS-EI: calcd for $C_{11}H_{11}NF_3Br$, 293.0027; found, 293.0032.

(E)-N,N-Dimethyl-5-(trifluoromethyl)-2-(3,3,3-trifluoroprop-1-enyl)aniline ***(4j)***. Following the general procedure, this product was isolated as a colorless oil (109.8 mg, 77%), by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51−7.45 (m, 2H), 7.27−7.25 (m, 2H), 6.25 (dq, J = 16.4, 6.4 Hz, 1H), 2.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 135.0 (q, J = 7.1 Hz), 132.2 (q, J = 32.1 Hz), 130.1, 128.4, 123.9 (q, J = 271.3 Hz), 123.5 (q, J = 267.6 Hz), 118.7 (q, J = 3.7 Hz), 117.2 (q, J = 34.3 Hz), 115.2 (q, J = 3.6 Hz), 44.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.9 (s, 3F), −63.5 (d, J = 6.8 Hz, 3F). IR (thin film) ν_{max}: 2953, 2845, 1665, 1326, 1127, 965 cm^{-1}. EIMS m/z: M$^+$ 283 (100), 212 (75.8), 200 (68.8). HRMS-EI: calcd for $C_{12}H_{11}NF_6$, 283.0796; found, 283.0795.

(E)-Ethyl 3-(Dimethylamino)-4-(3,3,3-trifluoroprop-1-enyl)-benzoate ***(4k)***. Following the general procedure, this product was isolated as a pale yellow oil (103.8 mg, 77%) by flash chromatography in 5:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 2.0 Hz, 1H), 7.96 (dd, J = 8.0, 2.0 Hz, 1H), 7.37 (dd, J = 16.8, 2.0 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 6.25 (dq, J = 16.0, 6.4 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 2.82 (s, 6H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 156.6, 135.9 (q, J = 6.8 Hz), 131.7, 130.0, 125.8, 123.8 (q, J = 267.6 Hz), 123.3, 117.3, 115.8 (q, J = 33.6 Hz), 60.8, 44.1, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.2 (d, J = 6.8 Hz, 3F). IR (thin film) ν_{max}: 2984, 2953, 1716, 1661, 1605, 1250, 1116, 771 cm^{-1}. EIMS m/z: M$^+$ 287 (100), 242 (97.1), 132 (43.6). HRMS-EI: calcd for $C_{14}H_{16}NO_2F_3$, 287.1133; found, 287.1137.

(E)-1-Methoxy-2-(3,3,3-trifluoroprop-1-enyl)benzene ***(4l)***. Following the general procedure, this product was isolated as a colorless oil (73.0 mg, 73%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.42 (m, 2H), 7.40−7.35 (m, 1H), 7.00 (td, J = 7.6, 0.8 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.36 (dq, J = 16.4, 6.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 133.1 (q, J = 7.1 Hz), 131.1, 128.7, 124.0 (q, J = 266.9 Hz), 122.4, 120.7, 116.5 (q, J = 33.1 Hz), 111.1, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.2 (dd, J = 7.1, 3.0 Hz, 3F). IR (thin film) ν_{max}: 2926, 2853, 1661, 1491, 1310, 1248, 1113, 751 cm^{-1}. EIMS m/z: M$^+$ 202 (100), 119 (82.9), 109 (64.3), 91 (76.2). HRMS-EI: calcd for $C_{10}H_9OF_3$, 202.0605; found, 202.0603.

(E)-1-(Benzyloxy)-2-(3,3,3-trifluoroprop-1-enyl)benzene ***(4m)***. Following the general procedure, this product was isolated as a white solid (83.2 mg, 65%, mp 44−46 °C) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.32 (m, 8H), 7.03−6.99 (m, 2H), 6.38 (dq, J = 16.4, 6.6 Hz, 1H), 5.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 136.5, 133.1 (q, J = 7.0 Hz), 131.1, 128.7, 128.2, 128.0, 127.3, 124.0 (q, J = 266.9 Hz), 122.8, 121.1, 116.7 (q, J = 33.3 Hz), 112.8, 70.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.2 (dd, J = 6.8, 3.0 Hz, 3F). IR (thin film) ν_{max}: 3067, 2919, 1660, 1600, 1330, 1111, 750, 696 cm^{-1}. EIMS m/z: M$^+$ 278 (6.7), 91 (100). HRMS-EI: calcd for $C_{16}H_{13}OF_3$, 278.0918; found, 278.0919.

(E)-1-(2-(3,3,3-Trifluoroprop-1-enyl)phenyl)pyrrolidine ***(4o)***. Following the general procedure, this product was isolated as a colorless oil (85.9 mg, 72%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 21.6 Hz, 1H), 7.33 (d, J = 10.0 Hz, 1H), 7.25 (t, J = 10.0 Hz, 1H), 6.91−6.85 (m, 2H), 6.03 (dq, J = 21.2, 8.8 Hz, 1H), 3.21 (t, J = 8.0 Hz, 4H), 1.96−1.91 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 137.7 (q, J = 6.8 Hz), 130.1, 128.6, 124.2, 124.0 (q, J = 267.2 Hz), 119.8, 115.7, 114.1 (q, J = 33.4 Hz), 52.0, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.9 (d, J = 6.8 Hz, 3F). IR (thin film) ν_{max}: 2970, 2875, 2826, 1655, 1598, 1484, 1323, 1123, 988, 752 cm^{-1}. EIMS m/z: M$^+$ 241 (100), 144 (66.8), 130 (75.5). HRMS-EI: calcd for $C_{13}H_{14}NF_3$, 241.1078; found, 241.1075.

(E)-1-(2-(3,3,3-Trifluoroprop-1-enyl)phenyl)piperidine ***(4p)***. Following the general procedure, this product was isolated as a colorless oil (86.3 mg, 68%) by flash chromatography in 5:1 *n*-hexane/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, J = 16.4, 2.0 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.35−7.31 (m, 1H), 7.06−7.02 (m, 2H), 6.20 (dq, J = 16.4, 6.4 Hz, 1H), 2.88 (t, J = 5.2 Hz, 4H), 1.77−1.71 (m, 4H), 1.62−1.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 138.3 (q, J = 7.1 Hz), 130.5, 127.9, 127.5, 124.1 (q, J = 267.1 Hz), 122.6, 119.1, 115.0 (q, J = 33.3 Hz), 54.1, 26.3, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.0 (d, J = 6.8 Hz, 3F). IR (thin film) ν_{max}: 2937, 2854, 2807, 1659, 1597, 1487, 1452, 1320, 1274, 1116, 989, 759, 582 cm^{-1}. EIMS m/z: M$^+$ 255 (100), 172 (97.3), 130 (89.6). HRMS-EI: calcd for $C_{14}H_{16}NF_3$, 255.1235; found, 255.1236.

(E)-N,N-Dimethyl-2-(3,3,3-trifluoro-2-methylprop-1-enyl)aniline ***(4s)***. Following the general procedure, this product was isolated as a colorless oil (57.1 mg, 50%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.25 (m, 2H), 7.19 (s, 1H), 7.08−7.01 (m, 2H), 2.75 (s, 6H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 130.9 (q, J = 6.0 Hz), 130.2, 129.1, 127.6, 124.9 (q, J = 251.0 Hz), 124.5 (q, J = 28.9 Hz), 121.2, 117.7, 44.2, 12.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −69.4 (s, 3F). IR (thin film) ν_{max}: 2925, 2854, 1597, 1162, 1114, 668 cm^{-1}. EIMS m/z: M$^+$ 229 (100), 144 (19.6), 132 (46.8). HRMS-EI: calcd for $C_{12}H_{14}NF_3$, 229.1078; found, 229.1080.

General Procedure for the *E* to *Z* Isomerization. A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with Ir(ppy)$_3$ (3.9 mg, 0.006 mmol, 3 mol %), **4** (0.2 mmol, 1.0 equiv), and DMA (4.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 2 h. The reaction mixture was then diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography to give *Z* product **5**.

(Z)-N,N-Dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline ***(5b)***. Following the general procedure, this product was isolated as a colorless oil (37.6 mg, 87%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 12.4 Hz, 1H), 7.04−6.99 (m, 2H), 5.76 (dq, J = 12.8, 9.2 Hz, 1H), 2.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 138.9 (q, J = 5.6 Hz), 130.5 (q, J = 3.9 Hz), 129.8, 127.9, 123.4 (q, J = 269.9 Hz), 121.6, 117.4, 116.2 (q, J = 33.8 Hz), 44.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 8.3 Hz, 3F). IR (thin film) ν_{max}: 2947, 2836, 2788, 1653, 1598, 1279, 1218, 1180, 1127, 948, 763 cm^{-1}. EIMS m/z: M$^+$ 215 (100), 144 (71.4), 132 (80.8). HRMS-EI: calcd for $C_{11}H_{12}NF_3$, 215.0922; found, 215.0920.

(Z)-N,N,5-Trimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline ***(5c)***. Following the general procedure, this product was isolated as a colorless oil (37.7 mg, 82%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.6 Hz, 1H), 7.07 (d, J = 12.4 Hz, 1H), 6.84−6.82 (m, 2H), 5.71 (dq, J = 12.0, 8.8 Hz, 1H), 2.74 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 140.0, 138.8 (q, J = 5.6 Hz), 130.4 (q, J = 3.9 Hz), 125.0, 123.5 (q, J = 269.8 Hz), 122.4, 118.2, 115.5 (q, J = 34.0 Hz), 44.5, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 8.8 Hz, 3F). IR (thin film) ν_{max}: 2979, 2786, 1651, 1608, 1278, 1181, 1125, 863, 815 cm^{-1}. EIMS m/z: M$^+$ 229 (88.7), 146 (100), 131 (68.4). HRMS-EI: calcd for $C_{12}H_{14}NF_3$, 229.1078; found, 229.1077.

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*(Z)-5-Bromo-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5h**).* Following the general procedure, this product was isolated as a pale yellow oil (50.5 mg, 86%) by flash chromatography in 10:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J = 8.0 Hz, 1H), 7.13−7.11 (m, 2H), 6.96 (d, J = 12.0 Hz, 1H), 5.77 (dq, J = 12.0, 8.4 Hz, 1H), 2.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 137.9 (q, J = 5.8 Hz), 131.7 (q, J = 4.4 Hz), 126.4, 124.5, 123.8, 123.2 (q, J = 269.1 Hz), 120.9, 117.7 (q, J = 34.3 Hz), 44.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.8 (d, J = 7.8 Hz, 3F). IR (thin film) ν_{max}: 2949, 2839, 1654, 1585, 1126, 956, 815 cm^{-1}. EIMS m/z: M$^+$ 293 (18.4), 199 (32.2), 131 (100). HRMS-EI: calcd for $C_{11}H_{11}NF_3Br$, 293.0027; found, 293.0023.

*(Z)-Ethyl 3-(Dimethylamino)-4-(3,3,3-trifluoroprop-1-enyl)-benzoate (**5k**).* Following the general procedure, this product was isolated as a pale yellow oil (47.8 mg, 83%) by flash chromatography in 5:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.95 (dd, J = 8.4, 2.0 Hz, 1H), 6.96 (d, J = 5.6 Hz, 1H), 6.93 (s, 1H), 5.78 (dq, J = 12.4, 8.4 Hz, 1H), 4.34 (q, J = 7.2 Hz, 2H), 2.83 (s, 6H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 156.1, 138.6 (q, J = 5.8 Hz), 132.4 (q, J = 3.9 Hz), 131.2, 127.2, 123.2 (q, J = 269.8 Hz), 122.5, 116.8 (q, J = 33.9 Hz), 116.3, 60.7, 43.8, 14.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.0 (d, J = 8.3 Hz, 3F). IR (thin film) ν_{max}: 2984, 2954, 1713, 1654, 1603, 1501, 1257, 1130, 770 cm^{-1}. EIMS m/z: M$^+$ 287 (99.1), 242 (100), 131 (45.1). HRMS-EI: calcd for $C_{14}H_{16}NO_2F_3$, 287.1133; found, 287.1130.

General Procedure for the Selective Synthesis of *Z*-Trifluoromethylated Alkenes. A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with $Ir(ppy)_3$ (9.8 mg, 0.015 mmol, 3 mol %), **1** (0.5 mmol, 1.0 equiv), **2c** (204.0 mg, 0.6 mmol, 1.2 equiv), and DMA (10.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 10 h. After the reaction was complete, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography to give *Z* product **5**.

*(Z)-N,N-Dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5b**).* **5b** was obtained as a colorless liquid (70.3 mg, 65%).

*(Z)-N,N,5-Trimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5c**).* **5c** was obtained as a colorless liquid (86.3 mg, 75%).

*(Z)-5-Methoxy-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5d**).* Following the general procedure, this product was isolated as a colorless oil (79.3 mg, 65%) by flash chromatography in 5:1 *n*-hexane/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 9.6 Hz, 1H), 7.01 (d, J = 12.4 Hz, 1H), 6.56−6.53 (m, 2H), 5.65 (dq, J = 12.4, 9.2 Hz, 1H), 3.82 (s, 3H), 2.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 154.4, 138.3 (q, J = 5.8 Hz), 131.6 (q, J = 4.1 Hz), 123.6 (q, J = 269.0 Hz), 120.4, 114.5 (q, J = 34.0 Hz), 106.1, 104.2, 55.2, 44.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 9.4 Hz, 3F). IR (thin film) ν_{max}: 2946, 2837, 1649, 1606, 1214, 1125, 1043, 862 cm^{-1}. EIMS m/z: M$^+$ 245 (58.3), 162 (100), 147 (35.6). HRMS-EI: calcd for $C_{12}H_{14}NOF_3$, 245.1027; found, 245.1025.

*(Z)-2-Fluoro-N,N-dimethyl-6-(3,3,3-trifluoroprop-1-enyl)aniline (**5f**).* Following the general procedure, this product was isolated as a colorless oil (88.3 mg, 76%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18−7.15 (m, 2H), 7.07−7.04 (m, 2H), 5.81 (dq, J = 12.4, 8.4 Hz, 1H), 2.83 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (d, J = 247.2 Hz), 139.0 (d, J = 10.3 Hz), 137.9 (dq, J = 5.9, 2.9 Hz), 133.9 (d, J = 5.8 Hz), 125.4 (dq, J = 2.9 Hz), 124.4 (d, J = 8.8 Hz),123.1 (q, J = 269.8 Hz), 117.7 (q, J = 33.5 Hz), 117.3 (d, J = 21.1 Hz), 44.2, 44.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 9.4 Hz, 3F), −121.9 (s, 1F). IR (thin film) ν_{max}: 2926, 2854, 1660, 1202, 1129 cm^{-1}. EIMS m/z: M$^+$ 233 (100), 162 (71.9), 150 (80.1). HRMS-EI: calcd for $C_{11}H_{11}NF_4$, 233.0828; found, 233.0831.

*(Z)-5-Chloro-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5g**).* Following the general procedure, this product was isolated as a colorless oil (91.7 mg, 74%) by flash chromatography in 10:1 *n*-hexane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.0 Hz, 1H), 6.99−6.95 (m, 3H), 5.76 (dq, J = 12.8, 9.2 Hz, 1H), 2.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 137.9 (q, J = 5.9 Hz), 135.5, 131.5 (q, J = 3.6 Hz), 125.9, 123.2 (q, J = 269.8 Hz), 121.5, 117.9, 117.6 (q, J = 33.6 Hz), 44.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.8 (d, J = 9.8 Hz, 3F). IR (thin film) ν_{max}: 2950, 2840, 1654, 1591, 1125, 962, 832 cm^{-1}. EIMS m/z: M$^+$ 249 (67.1), 166 (85.6), 131 (100). HRMS-EI: calcd for $C_{11}H_{11}NF_3Cl$, 249.0532; found, 249.0528.

*(Z)-5-Bromo-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5h**).* **5h** was obtained as a pale yellow liquid (102.8 mg, 70%) .

*(Z)-4-Iodo-N,N-dimethyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5i**).* Following the general procedure, this product was isolated as a pale yellow oil (110.4 mg, 65%) by flash chromatography in 30:1 *n*-hexane/diethyl ether. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.57 (dd, J = 8.4, 2.0 Hz, 1H), 6.94 (d, J = 12.0 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 5.77 (dq, J = 12.4, 8.8 Hz, 1H), 2.71 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 138.7 (q, J = 3.9 Hz), 138.5, 137.4 (q, J = 5.6 Hz), 129.9, 123.1 (q, J = 269.8 Hz), 119.6, 117.2 (q, J = 34.0 Hz), 84.0, 44.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.8 (d, J = 8.3 Hz, 3F). IR (thin film) ν_{max}: 2947, 2789, 1655, 1487, 1178, 1129, 818 cm^{-1}. EIMS m/z: M$^+$ 341 (100), 270 (13.2), 131 (74.2). HRMS-EI: calcd for $C_{11}H_{11}NF_3I$, 340.9888; found, 340.9885.

*(Z)-N,N-Dimethyl-5-(trifluoromethyl)-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5j**).* Following the general procedure, this product was isolated as a colorless oil (99.2 mg, 70%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 1H), 7.24−7.22 (m, 2H), 7.03 (d, J = 12.0 Hz, 1H), 5.85 (dq, J = 12.4, 8.8 Hz, 1H), 2.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 137.8 (q, J = 5.6 Hz), 131.7 (q, J = 31.8 Hz), 131.0 (q, J = 3.6 Hz), 130.9, 124.0 (q, J = 271.3 Hz), 123.1 (q, J = 269.8 Hz), 117.9 (q, J = 3.6 Hz), 117.8 (q, J = 34.3 Hz), 114.1 (q, J = 3.6 Hz), 44.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.9 (d, J = 8.3 Hz, 3F), −62.8 (s, 3F). IR (thin film) ν_{max}: 2952, 2798, 1656, 1614, 1417, 1341, 1174, 1126, 966, 879, 735 cm^{-1}. EIMS m/z: M$^+$ 283 (100), 212 (77.8), 200 (83.4). HRMS-EI: calcd for $C_{12}H_{11}NF_6$, 283.0796; found, 283.0794.

*(Z)-Ethyl 3-(Dimethylamino)-4-(3,3,3-trifluoroprop-1-enyl)-benzoate (**5k**).* **5k** was obtained as a pale yellow liquid (89.7 mg, 63%).

*(Z)-1-Methoxy-2-(3,3,3-trifluoroprop-1-enyl)benzene (**5l**).* Following the general procedure, this product was isolated as a colorless oil (65.4 mg, 64%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 7.2 Hz, 1H), 7.37−7.32 (m, 1H), 7.11 (d, J = 12.4 Hz, 1H), 6.96 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.36 (dq, J = 12.4, 8.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 135.5 (q, J = 5.8 Hz), 130.5, 130.0 (q, J = 3.7 Hz), 123.1 (q, J = 269.8 Hz), 123.0, 120.3, 117.9 (q, J = 34.2 Hz), 110.3, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.9 (d, J = 8.3 Hz, 3F). IR (thin film) ν_{max}: 2927, 1657, 1602, 1128, 754 cm^{-1}. EIMS m/z: M$^+$ 202 (100), 119 (87.8), 109 (67.9), 91 (80.1). HRMS-EI: calcd for $C_{10}H_9OF_3$, 202.0605; found, 202.0604.

*(Z)-1-(Benzyloxy)-2-(3,3,3-trifluoroprop-1-enyl)benzene (**5m**).* Following the general procedure, this product was isolated as a colorless oil (78.3 mg, 61%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.30 (m, 7H), 7.18 (d, J = 12.8 Hz, 1H), 6.99−6.94 (m, 2H), 5.77 (dq, J = 12.4, 8.4 Hz, 1H), 5.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 136.8, 135.6 (q, J = 5.8 Hz), 130.5, 130.1 (q, J = 3.6 Hz), 128.6, 128.0, 127.3, 123.1 (q, J = 269.9 Hz), 123.5, 120.7, 118.0 (q, J = 34.0 Hz), 111.9, 70.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 9.8 Hz, 3F). IR (thin film) ν_{max}: 3036, 2923, 1655, 1601, 1127, 753 cm^{-1}. EIMS m/z: M$^+$ 278 (5.9), 91 (100). HRMS-EI: calcd for $C_{16}H_{13}OF_3$, 278.0918; found, 278.0915.

*(Z)-N,N-Dibenzyl-2-(3,3,3-trifluoroprop-1-enyl)aniline (**5n**).* Following the general procedure, this product was isolated as a colorless oil (138.1 mg, 75%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 12.8 Hz, 1H), 7.34−7.20 (m, 11H), 7.08 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 5.87 (dq, J = 12.4, 8.8 Hz, 1H), 4.15 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 138.9 (q, J = 5.6 Hz), 137.6, 130.6 (q, J = 3.6 Hz), 129.54, 129.47, 128.8, 128.3, 127.2, 123.4 (q, J = 269.8 Hz),

122.8, 121.8, 117.0 (q, J = 34.0 Hz), 56.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.3 (d, J = 8.3 Hz, 3F). IR (thin film) ν_{max}: 3063, 3029, 1653, 1597, 1494, 1452, 1276, 1179, 1124, 766, 698 cm^{-1}. EIMS m/z: M$^+$ 367 (12.4), 276 (10.2), 91 (100). HRMS-EI: calcd for $C_{23}H_{20}NF_3$, 367.1548; found, 367.1547.

*(Z)-1-(2-(3,3,3-Trifluoroprop-1-enyl)phenyl)pyrrolidine (**5o**).* Following the general procedure, this product was isolated as a colorless oil (48.2 mg, 55%) by flash chromatography in *n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.6 Hz, 1H), 7.29−7.25 (m, 1H), 7.06 (d, J = 12.4 Hz, 1H), 6.89−6.86 (m, 2H), 5.73 (dq, J = 12.4, 8.8 Hz, 1H), 3.27 (t, J = 6.6 Hz, 4H), 1.98−1.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 140.5 (q, J = 5.8 Hz), 130.8 (q, J = 3.6 Hz), 129.5, 124.1, 123.4 (q, J = 269.8 Hz), 118.9, 115.2 (q, J = 33.5 Hz), 114.6, 51.8, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.5 (d, J = 9.4 Hz, 3F). IR (thin film) ν_{max}: 2968, 2927, 1650, 1597, 1451, 1176, 1125, 754 cm^{-1}. EIMS m/z: M$^+$ 241 (100), 144 (74.6), 130 (80.0). HRMS-EI: calcd for $C_{13}H_{14}NF_3$, 241.1078; found, 241.1073.

*(Z)-1-(2-(3,3,3-Trifluoroprop-1-enyl)phenyl)piperidine (**5p**).* Following the general procedure, this product was isolated as a colorless oil (80.4 mg, 63%) by flash chromatography in 5:1 *n*-hexane/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.6 Hz, 1H), 7.35−7.31 (m, 1H), 7.13 (d, J = 12.4 Hz, 1H), 7.04−7.01 (m, 2H), 5.73 (dq, J = 12.4, 8.8 Hz, 1H), 2.90 (t, J = 5.4 Hz, 4H), 1.73−1.67 (m, 4H), 1.61−1.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 138.3 (q, J = 5.8 Hz), 130.3 (q, J = 3.9 Hz), 130.0, 128.5, 123.5 (q, J = 269.8 Hz), 121.9, 118.1, 116.0 (q, J = 34.0 Hz), 53.8, 26.5, 24.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.5 (d, J = 8.3 Hz, 3F). IR (thin film) ν_{max}: 2937, 2808, 1652, 1598, 1451, 1278, 1119, 769, 758, 580 cm^{-1}. EIMS m/z: M$^+$ 255 (82.5), 172 (87.5), 130 (100). HRMS-EI: calcd for $C_{14}H_{16}NF_3$, 255.1235; found, 255.1231.

*(Z)-4-(2-(3,3,3-Trifluoroprop-1-enyl)phenyl)morpholine (**5q**).* Following the general procedure, this product was isolated as a white solid (109.8 mg, 86%, mp 97−98 °C) by flash chromatography in 20:1 *n*-hexane/dichloromethane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 1H), 7.38−7.34 (m, 1H), 7.15 (d, J = 12.8 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 5.76 (dq, J = 12.8, 9.2 Hz, 1H), 3.83 (t, J = 4.8 Hz, 4H), 2.96 (t, J = 4.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 138.0 (q, J = 5.6 Hz), 130.6 (q, J = 3.6 Hz), 130.2, 127.3, 123.3 (q, J = 269.8 Hz), 122.8, 118.0, 116.0 (q, J = 34.0 Hz), 67.3, 52.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 8.4 Hz, 3F). IR (thin film) ν_{max}: 2961, 2855, 1650, 1598, 1488, 1350, 1204, 1114, 935, 757, 581 cm^{-1}. EIMS m/z: M$^+$ 257 (46.0), 199 (29.0), 130 (100). HRMS-EI: calcd for $C_{13}H_{14}NOF_3$, 257.1027; found, 257.1023.

*(Z)-1-(4-(2-(3,3,3-Trifluoroprop-1-enyl)phenyl)piperazin-1-yl)-ethanone (**5r**).* Following the general procedure, this product was isolated as a colorless oil (107.3 mg, 72%) by flash chromatography in 2:1 dichloromethane/ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 1H), 7.37−7.32 (m, 1H), 7.14 (d, J = 12.8 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 5.77 (dq, J = 12.4, 8.8 Hz, 1H), 3.74 (t, J = 4.8 Hz, 2H), 3.58 (t, J = 4.8 Hz, 2H), 2.93 (t, J = 4.8 Hz, 4H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 150.9, 137.8 (q, J = 5.8 Hz), 130.6 (q, J = 3.9 Hz), 130.2, 128.8, 123.20, 123.17 (q, J = 269.8 Hz), 118.3, 117.3 (q, J = 34.0 Hz), 52.7, 51.7, 46.7, 41.8, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.6 (d, J = 9.4 Hz, 3F). IR (thin film) ν_{max}: 2920, 2823, 1649, 1597, 1450, 1126, 997, 773 cm^{-1}. EIMS m/z: M$^+$ 298 (31.4), 226 (100), 130 (51.0). HRMS-EI: calcd for $C_{15}H_{17}N_2OF_3$, 298.1293; found, 298.1298.

Trifluoromethylation of Steroid 1t. A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with Ir(ppy)$_3$ (3.9 mg, 0.006 mmol, 3 mol %), **1t** (95.7 mg, 0.2 mmol, 1.0 equiv), **2c** (81.6 mg, 0.24 mmol, 1.2 equiv), and DMA (4.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 10 h. After the reaction was complete, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, *n*-hexane/DCM = 10:1, then 5:1) to give products **4t** (34.1 mg, 31%) and **5t** (58.4 mg, 53%).

*(8R,9S,13S,14S,17S)-3,17-Bis(benzyloxy)-13-methyl-2-((E)-3,3,3-trifluoroprop-1-en-1-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (**4t**).* White solid (mp 122−124 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.32 (m, 11H), 7.30−7.26 (m, 1H), 6.68 (s, 1H), 6.31 (dq, J = 16.0, 6.6 Hz, 1H), 5.10 (s, 2H), 4.58 (s, 2H), 3.51 (t, J = 8.0, Hz, 1H), 2.86−2.82 (m, 2H), 2.34−2.30 (m, 1H), 2.20−2.01 (m, 3H), 1.90−1.86 (m, 1H), 1.73−1.56 (m, 3H), 1.45−1.31 (m, 3H), 1.23−1.16 (m, 2H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 140.4, 139.3, 136.8, 133.4 (q, J = 7.1 Hz), 133.2, 128.7, 128.3, 128.0, 127.33, 127.26, 126.0, 124.1 (q, J = 266.9 Hz), 120.1, 115.5 (q, J = 33.0 Hz), 113.0, 88.3, 71.7, 70.5, 50.2, 43.7, 43.4, 38.5, 37.8, 30.0, 29.7, 28.0, 27.1, 26.4, 23.1, 11.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.0 (s, 3F). IR (thin film) ν_{max}: 2921, 2850, 1657, 1609, 1500, 1313, 1264, 1116, 733, 696 cm^{-1}. EIMS m/z: M$^+$ 546 (6.8), 91 (100). HRMS-EI: calcd for $C_{35}H_{37}O_2F_3$, 546.2746; found, 546.2751.

*(8R,9S,13S,14S,17S)-3,17-Bis(benzyloxy)-13-methyl-2-((Z)-3,3,3-trifluoroprop-1-en-1-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (**5t**).* White solid (mp 88−90 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.26 (m, 11H), 7.17 (d, J = 12.4 Hz, 1H), 6.66 (s, 1H), 5.69 (dq, J = 12.4, 8.8 Hz, 1H), 5.06 (s, 2H), 4.59 (s, 2H), 3.51 (t, J = 8.0 Hz, 1H), 2.88−2.81 (m, 2H), 2.31−2.27 (m, 1H), 2.22−2.01 (m, 3H), 1.90−1.86 (m, 1H), 1.71−1.56 (m, 2H), 1.51−1.29 (m, 5H), 1.23−1.18 (m, 1H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 140.0, 139.4, 137.0, 135.6 (q, J = 5.8 Hz), 132.7, 128.6, 128.3, 128.0, 127.34, 127.31, 127.29, 123.3 (q, J = 269.1 Hz), 120.6, 116.8 (q, J = 34.0 Hz), 112.1, 88.3, 71.7, 70.4, 50.2, 43.9, 43.4, 38.6, 38.0, 30.0, 29.7, 28.1, 27.1, 26.3, 23.1, 11.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.4 (d, J = 9.4 Hz, 3F). IR (thin film) ν_{max}: 2927, 2868, 1654, 1611, 1500, 1210, 1132, 1115, 735, 696 cm^{-1}. EIMS m/z: M$^+$ 546 (4.6), 91 (100). HRMS-EI: calcd for $C_{35}H_{37}O_2F_3$, 546.2746; found, 546.2750.

Trifluoromethylation of Amino Acid Derivatives 1u. A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with Ir(ppy)$_3$ (3.9 mg, 0.006 mmol, 3 mol %), **1u** (70.6 mg, 0.2 mmol, 1.0 equiv), **2c** (81.6 mg, 0.24 mmol, 1.2 equiv), and DMA (4.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 10 h. After the reaction was complete, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 10:1, then 5:1) to give products **4u** (24.2 mg, 28%) and **5u** (64.8 mg, 64%).

*(S,E)-Ethyl 2-Benzamido-3-(4-methoxy-3-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)propanoate (**4u**).* White solid (mp 124−126 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.34 (dd, J = 16.4, 2.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.11 (dd, J = 8.0, 2.0 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 6.8 Hz, 1H), 6.17 (dq, J = 16.4, 6.6 Hz, 1H), 5.03 (q, J = 6.1 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 3.21 (qd, J = 20.0, 6.4 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 166.8, 157.1, 133.9, 132.8 (q, J = 7.1 Hz), 132.0, 131.9, 129.6, 128.7, 128.1, 127.0, 123.8 (q, J = 267.6 Hz), 122.3, 116.6 (q, J = 33.5 Hz), 110.3, 61.8, 55.6, 53.6, 36.9, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.3 (d, J = 5.3 Hz, 3F). IR (thin film) ν_{max}: 3326, 2981, 1739, 1659, 1533, 1501, 1253, 1120, 1028, 713 cm^{-1}. EIMS m/z: M$^+$ 421 (1.7), 300 (100), 215 (37.4). HRMS-EI: calcd for $C_{22}H_{22}NO_4F_3$, 421.1501; found, 421.1502.

*(S,Z)-Ethyl 2-Benzamido-3-(4-methoxy-3-(3,3,3-trifluoroprop-1-en-1-yl)phenyl)propanoate (**5u**).* Colorless semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.13−7.10 (m, 2H), 7.02 (d, J = 12.4 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 6.8 Hz, 1H), 5.72 (dq, J = 12.0, 8.4 Hz, 1H), 5.03 (q, J = 6.1 Hz, 1H), 4.27−4.15 (m, 2H), 3.80

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(s, 3H), 3.21 (qd, J = 14.0, 5.6 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 166.9, 156.3, 135.2 (q, J = 5.8 Hz), 134.0, 131.7, 131.5, 130.8 (q, J = 3.4 Hz), 128.5, 127.6, 127.1, 123.03, 122.96 (q, J = 269.9 Hz), 118.0 (q, J = 34.0 Hz), 110.5, 81.7, 55.6, 53.7, 37.0, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.9 (d, J = 9.4 Hz, 3F). IR (thin film) ν_{max}: 3326, 2982, 1739, 1651, 1531, 1212, 1115, 1028, 716 cm^{-1}. EIMS m/z: M$^+$ 421 (0.5), 300 (100), 215 (45.6). HRMS-EI: calcd for $C_{22}H_{22}NO_4F_3$, 421.1501; found, 421.1499.

1-Pentafluoroethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (2e). A two-necked, 50 mL round-bottom flask equipped with a massive magnetic stirring bar was charged with anhydrous spray-dried potassium fluoride (464.8 mg, 8.0 mmol, 1.6 equiv) and flame-dried with vigorous stirring under high vacuum for 5 min. Then, 1-chloro-3,3-dimethyl-1,2-benziodoxole (1.48 g, 5.0 mmol, 1 equiv) followed by anhydrous MeCN (20 mL) was added. The resulting suspension was vigorously stirred for 12 h and then cooled to −10 °C, and pentafluoroethyltrimethylsilane (1.15 g, 6.0 mmol, 1.2 equiv) was injected in one portion. This resulting suspension was stirred vigorously for 1 h, allowed to warm to rt, and filtered over a 1 cm thick pad of Celite, and the filter cake was washed with a little MeCN. The brown solution was concentrated to dryness in a rotavap. The crystalline, crude residue was redissolved in dry n-pentane (30 mL) at rt, filtered over a pad of activated alumina, and covered by a protective compressed Celite layer into another two-necked, round-bottom flask equipped with a magnetic stirring bar. The filtrate was evaporated by slowly cooling it with stirring under Ar to −78 °C, causing the full precipitation of desired product **2e** (493.7 mg, 26%) as a white solid (mp 121−124 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 1.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 130.0, 130.9−128.6 (m), 129.4, 128.5−126.1 (m), 126.8, 126.4, 115.4, 80.3, 29.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −81.3 (s, 3F), −99.3 (s, 2F). IR (thin film) ν_{max}: 2972, 1461, 1438, 1309, 1199, 1104, 958, 902, 754, 602 cm^{-1}. MS-ESI m/z: [M + H]$^+$ 380.8. HRMS-ESI: [M + H] calcd for $C_{11}H_{11}F_5IO$, 380.9775; found, 380.9769.

(*E*)-*N*,*N*-Dimethyl-2-(3,3,4,4,4-pentafluorobut-1-en-1-yl)-aniline (6). A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with $Ru(bry)_3Cl_2{\cdot}6H_2O$ (3.0 mg, 0.004 mmol, 2 mol %), **1b** (29.4 mg, 0.2 mmol, 1.0 equiv), **2e** (114 mg, 0.3 mmol, 1.5 equiv), and DMF (4.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 20 h. After the reaction was complete, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, n-pentane) to give **6** (37.3 mg, 70%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dt, J = 16.4, 2.2 Hz, 1H), 7.44 (dd, J = 8.0, 1.2 Hz, 1H), 7.35−7.31 (m, 1H), 7.06 (dd, J = 8.0, 0.8 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 5.76 (dtd, J = 16.4, 12.0, 0.8 Hz, 1H), 2.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 138.1 (t, J = 9.5 Hz), 130.6, 127.9, 127.6, 122.3, 118.5, 119.2 (qt, J = 283.7, 38.7 Hz), 113.3 (t, J = 23.3 Hz), 113.1 (tq, J = 249.4, 37.9 Hz), 44.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −85.0 (t, J = 2.8 Hz, 3F), −114.37, −114.41 (m, 2F). IR (thin film) ν_{max}: 2952, 2835, 1654, 1598, 1490, 1456, 1314, 1205, 1107, 1035, 841, 759 cm^{-1}. EIMS m/z: M$^+$ 265 (81.4), 144 (78.0), 132 (100). HRMS-EI: calcd for $C_{12}H_{12}NF_5$, 265.0890; found, 265.0892.

(*Z*)-*N*,*N*-Dimethyl-2-(3,3,4,4,4-pentafluorobut-1-en-1-yl)-aniline (7). A 25 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with $Ir(ppy)_3$ (3.9 mg, 0.006 mmol, 3 mol %), **1b** (29.4 mg, 0.2 mmol, 1.0 equiv), **2e** (114 mg, 0.3 mmol, 1.5 equiv), and DMA (4.0 mL) under a nitrogen atmosphere. The mixture was degassed three times by the freeze−pump−thaw procedure. Then, the vial was placed 2 cm from blue LEDs. The mixture was stirred under a nitrogen atmosphere and irradiated by blue LEDs for 10 h. After the reaction was complete, the reaction mixture was diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, n-pentane) to give **7** (28.8 mg, 56%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 7.35 (td, J = 7.0, 1.2 Hz, 1H), 7.26 (dt, J = 12.4, 3.2 Hz, 1H), 7.06−7.00 (m, 2H), 5.71 (dtd, J = 12.4, 15.6, 0.8 Hz, 1H), 2.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 141.5 (t, J = 4.8 Hz), 130.8 (t, J = 5.6 Hz), 129.9, 128.1, 121.4, 119.3 (qt, J = 284.4, 37.2 Hz), 117.4, 113.2 (t, J = 20.8 Hz), 112.7 (tq, J = 250.9, 37.2 Hz), 44.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −85.4 (t, J = 2.6 Hz, 3F), −109.28, −109.33 (m, 2F). IR (thin film) ν_{max}: 2947, 2836, 2789, 1651, 1598, 1491, 1344, 1201, 1100, 1023, 948, 762 cm^{-1}. EIMS m/z: M$^+$ 265 (3.5), 117 (100). HRMS-EI: calcd for $C_{12}H_{12}NF_5$, 265.0890; found, 265.0888.

(*E*)-1-Methoxy-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (4l). To a dry Schlenk tube were charged **4b** (43.0 mg, 0.2 mmol, 1.0 equiv) and methyl trifluoromethanesulfonate (164.1 mg, 1.0 mmol, 5.0 equiv). The mixture was stirred at 40 °C for 20 h. Excessive methyl trifluoromethanesulfonate was removed. The residue was washed with Et_2O and dried under vacuum. The residue was then dissolved in CH_3CN (2 mL), and MeOK (42.1 mg, 0.6 mmol, 3.0 equiv) was added. The reaction mixture was heated at 120 °C for 3 h and then diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, n-pentane) to give **4l** (17.8 mg, 44%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.42 (m, 2H), 7.40−7.35 (m, 1H), 7.00 (td, J = 7.6, 0.8 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.36 (dq, J = 16.4, 6.4 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 133.1 (q, J = 7.1 Hz), 131.1, 128.7, 124.0 (q, J = 266.9 Hz), 122.4, 120.7, 116.5 (q, J = 33.1 Hz), 111.1, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.2 (dd, J = 7.1, 3.0 Hz, 3F). IR (thin film) ν_{max}: 2926, 2853, 1661, 1491, 1310, 1248, 1113, 751 cm^{-1}. EIMS m/z: M$^+$ 202 (100), 119 (82.9), 109 (64.3), 91 (76.2). HRMS-EI: calcd for $C_{10}H_9OF_3$, 202.0605; found, 202.0603.

(*E*)-1-Fluoro-2-(3,3,3-trifluoroprop-1-en-1-yl)benzene (8). To a dry Schlenk tube were charged **4b** (43.0 mg, 0.2 mmol, 1.0 equiv) and methyl trifluoromethanesulfonate (164.1 mg, 1.0 mmol, 5.0 equiv). The mixture was stirred at 40 °C for 20 h. Excessive methyl trifluoromethanesulfonate was removed. The residue was washed with Et_2O and dried under vacuum. The residue was dissolved in DMF (2 mL), and CsF (91.2 mg, 0.6 mmol, 3.0 equiv) was added. The reaction mixture was heated at 150 °C for 3 h and then diluted with water. The resulting mixture was extracted with diethyl ether, and the combined organic phase was washed with brine and then dried with magnesium sulfate. The solvent was removed under vacuum, and the crude product was purified by column chromatography (silica gel, n-pentane) to give **8** (24.4 mg, 64%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (t, J = 7.4 Hz, 1H), 7.39−7.33 (m, 1H), 7.29−7.25 (m, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.13−7.08 (m, 1H), 6.34 (dq, J = 16.0, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1 (d, J = 250.9 Hz), 131.5 (d, J = 8.7 Hz), 130.7 (qd, J = 7.3, 2.9 Hz), 128.8 (d, J = 2.9 Hz), 124.5 (d, J = 3.7 Hz), 123.4 (q, J = 267.6 Hz), 121.4 (d, J = 11.7 Hz), 118.5 (qd, J = 33.5, 7.3 Hz), 116.2 (d, J = 21.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.9 (d, J = 6.8 Hz, 3F), −115.3 (m, J = 7.2 Hz, 1F). IR (thin film) ν_{max}: 2913, 2844, 1734, 1461, 1073 cm^{-1}. EIMS m/z: M$^+$ 190 (100), 140 (43.1), 101 (21.4). HRMS-EI: calcd for $C_9H_6F_4$, 190.0406; found, 190.0408.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic structure of compound **5q** and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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