

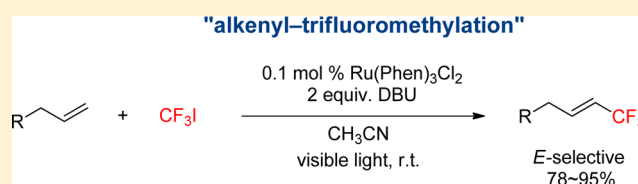
# Trifluoromethylation of Alkenes by Visible Light Photoredox Catalysis

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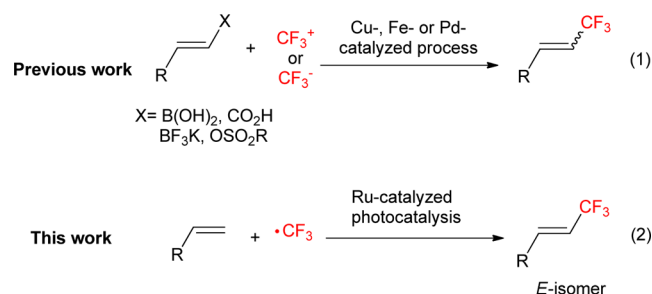
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**S** Supporting Information

**ABSTRACT:** A method for trifluoromethylation of alkenes has been developed employing visible light photoredox catalysis with  $\text{CF}_3\text{I}$ ,  $\text{Ru}(\text{Phen})_3\text{Cl}_2$ , and DBU. This process works especially well for terminal alkenes to give alkenyl- $\text{CF}_3$  products with only *E*-stereochemistry. The mild reaction conditions enable the trifluoromethylation of a range of alkenes that bear various functional groups.



The trifluoromethylation of organic molecules is of vital importance in the fields of pharmaceuticals and agrochemicals since inclusion of a  $\text{CF}_3$  moiety into organic molecules can result in enhanced lipophilicity, metabolic stability, bioavailability, and binding selectivity.<sup>1</sup> A variety of nucleophilic, electrophilic, and radical processes for  $\text{C}-\text{CF}_3$  bond formation have been reported,<sup>1d,2</sup> including several transition-metal-catalyzed methods<sup>3,4</sup> that directly form  $\text{Csp}^2-\text{CF}_3$  bonds. However, these methods are mainly limited to the formation of aryl- $\text{CF}_3$  bonds. Only a limited number of processes for the construction of alkenyl- $\text{CF}_3$  bonds are currently available (Figure 1 (1)).<sup>5</sup> In addition, the known



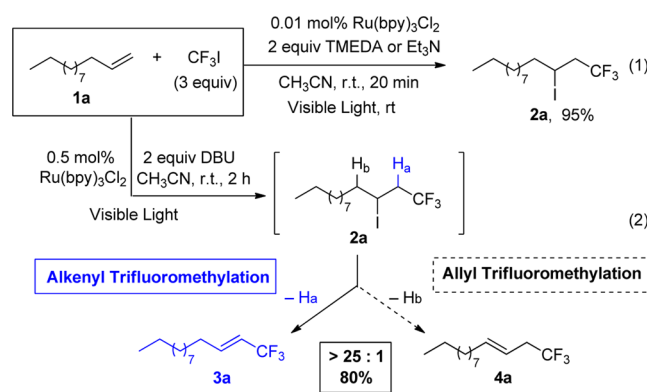
**Figure 1.** Alkenyl trifluoromethylations.

alkenyl trifluoromethylation methods have some limitations. They not only have a narrow scope but also require prefunctionalized substrates. The lack of *E/Z* selectivity is another shortcoming with some of these methods. Herein, we report a radical-based trifluoromethylation of unactivated alkenes via visible light photoredox catalysis<sup>6,7</sup> that shows a broad substrate scope and high *E/Z* selectivity (Figure 1 (2)).

Radical-based halotrifluoromethylations of alkenes using  $\text{CF}_3\text{I}$  or  $\text{CF}_3\text{SO}_2\text{Cl}$  as the  $\text{CF}_3$  radical sources had been developed by several groups.<sup>8</sup> More recently, Stephenson and co-workers provided trifluoroalkylated alkyl iodides by visible light-induced photocatalysis, using 1 mol % of  $[\text{Ir}(\text{dF}(\text{CF}_3)-$

$\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$  in  $\text{DMF}/\text{H}_2\text{O}$  with 48 h reaction time or 1 mol % of  $\text{Ru}(\text{bpy})_3\text{Cl}_2/0.35$  equiv of Na ascorbate in  $\text{CH}_3\text{CN}/\text{MeOH}$  with 48 h reaction time as useful examples of atom-transfer radical additions.<sup>9</sup> On the basis of these iodotrifluoromethylations and our previously reported trifluoromethylation of heterocycles<sup>10</sup> of the photocatalysis, we commenced our investigation with 1-dodecene as a model compound employing our previous reductive quenching pathway conditions. With  $\text{CF}_3\text{I}$ , TMEDA (or TEA), and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  in  $\text{CH}_3\text{CN}$ , trifluoromethylated alkyl iodide was obtained in excellent yield within 20 min with merely 0.01 mol % of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  under a 14 W household lamp (Scheme 1 (1)). Based on this encouraging result, we hypothesized that alkenyl- $\text{CF}_3$  products can be generated by employing a base that can potentially act both as a reductive quencher for the photocatalysis and as a base<sup>11</sup> for the hydrogen iodide elimination from **2a**. For the elimination,  $\text{H}_a$  could be selectively eliminated over  $\text{H}_b$  due to

## Scheme 1. Trifluoromethylation via Visible Light Photocatalysis



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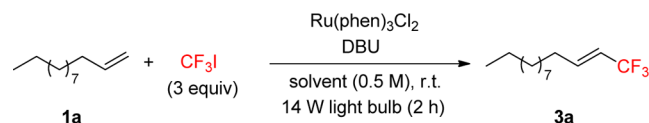
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its lower  $pK_a$  resulting from a highly electron-withdrawing nature of the trifluoromethyl group.<sup>12</sup> Several bases including DIPEA and DBU were examined, and the use of DBU in the reaction of 1-dodecene **1a** generated alkenyl- $CF_3$  product **3a** in good yield and excellent regio- and  $E/Z$  selectivity (Scheme 1 (2)). Allyl- $CF_3$  product **4a**<sup>13</sup> from the  $H_b$  elimination was barely formed (2–3%). No detectable amounts of  $Z$ -isomers of both **3a** and **4a** were observed in the reaction.

With these promising initial results, we further optimized the reaction conditions. First, various Ru and Ir photocatalysts were evaluated. We found that besides  $Ru(bpy)_3Cl_2$ , a range of Ru or Ir photocatalysts such as  $Ir(ppy)_3$ ,  $Ir(ppy)_2(dtbbpy)PF_6$ , and  $Ru(phen)_3Cl_2$  were also effective for the reaction. Among them,  $Ru(phen)_3Cl_2$ <sup>14a</sup> was chosen for further studies because of its lower cost and cleaner reaction profile. In addition, control experiments showed that both the photocatalyst and visible light are required for the transformation.

Next, we examined the effect of other parameters on the reaction, including solvents, concentration, and the stoichiometry of reagents (Table 1).  $CH_3CN$  was found to be the most

**Table 1. Optimization Studies for the Trifluoromethylation of 1-Dodecene<sup>a</sup>**



entry	$Ru(phen)_3Cl_2$ (mol %)	DBU (equiv)	solvent	product yield <sup>b</sup> (%)
1	0.5	2.0	$CH_2Cl_2$	80
2	0.5	2.0	DMF	76
3	0.5	2.0	$CH_3CN$	96
4	0.5	1.0	$CH_3CN$	80
5	0.5	1.5	$CH_3CN$	89
6	0.1	2.0	$CH_3CN$	96
7 <sup>c</sup>	0.01	2.0	$CH_3CN$	90

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol),  $CF_3I$  (0.6 mmol),  $Ru(phen)_3Cl_2$ , DBU, solvent (0.4 mL). <sup>b</sup>The yield was determined by <sup>19</sup>F NMR spectroscopy with 4-fluorotoluene as an internal standard. <sup>c</sup>4 h reaction time.

effective solvent, although the reaction could be carried out in other solvents such as  $CH_2Cl_2$  and DMF (entries 1–3). Reaction concentration also affected the efficiency, and 0.5 M in  $CH_3CN$  afforded the best result. An excess amount (2 equiv) of DBU was required for the maximum yield, and inferior results were obtained with less than 2 equiv of DBU despite a full conversion (entries 3–5). The use of at least 2 equiv of  $CF_3I$  was also required for reproducible results. Notably, an extremely low photocatalyst loading (0.01 mol %) was enough for full conversion and high product yields (entries 3, 6, and 7), showing the efficacy of this catalytic process.

With the optimized conditions in hand, the reactions of a variety of terminal alkenes were explored (Table 2). The mild reaction conditions allowed trifluoromethylation of alkenes containing a range of functional groups, including unprotected alcohol (**3b**, **3m**), aldehyde (**3c**), ketone (**3d**), ester (**3e**, **3f**), carbamate (**3g**), amide (**3h**, **3i**, **3j**), silyl ether (**3k**), sulfonates (**3l**), and aryl halides such as aryl bromide (**3i**) and aryl chloride (**3j**). Notably, aromatic systems appeared to be inactive under the reaction conditions.<sup>15</sup> In most cases, a trace amount (2–4%) of allyl- $CF_3$  products were produced. In

**Table 2. Scope of the Trifluoromethylation of Terminal Alkenes<sup>a</sup>**

entry	1	product	yield (%) <sup>b</sup>
1	<b>3a</b>		95
2	<b>3b</b>		80
3	<b>3c</b>		78
4	<b>3d</b>		81
5	<b>3e</b>		80
6	<b>3f</b>		93
7	<b>3g</b>		80
8	<b>3h</b>		85
9	<b>3i</b>		83
10	<b>3j</b>		79
11	<b>3k</b>		89
12	<b>3l</b>		90
13	<b>3m</b>		84 <sup>c</sup>
14	<b>3n</b>		90

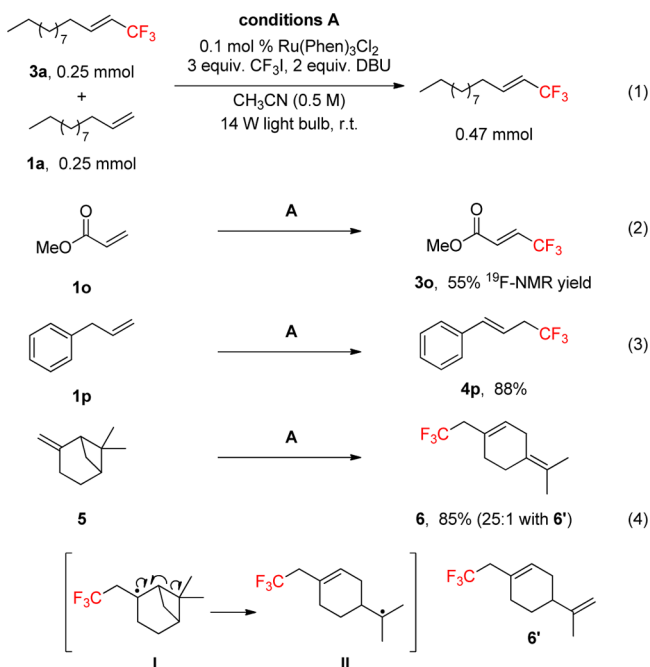
<sup>a</sup>Reaction conditions: **1** (1.0 mmol),  $CF_3I$  (2.0–3.0 mmol),  $Ru(phen)_3Cl_2$  (0.001 mmol), DBU (2.0 mmol),  $CH_3CN$  (2 mL), 2–10 h. <sup>b</sup>Isolated yield based on an average of two runs. <sup>c</sup>17:1 ratio with the allyl- $CF_3$  product.

addition to allyl- $CF_3$  products, to a minor extent (<5%) trifluoromethylated alkyl iodides (such as **2a** shown in Scheme 1) or bis-trifluoromethylation products from further reactions of alkenyl- $CF_3$  products were also observed. The current reaction conditions were amenable to a large scale reaction such

that alkenyl-CF<sub>3</sub> product **3a** was prepared on a 5 mmol scale with yield similar to that of a 1 mmol scale reaction.

Besides high regio- and stereoselectivity, another salient feature of this transformation is the lower reactivity of the trifluoromethylated alkene toward the second trifluoromethylation, resulting in the monotrifluoromethylation. In the reaction of a mixture of **1a** and isolated **3a**, only **1a** selectively participated in the transformation (Scheme 2 (1)). The

### Scheme 2. Trifluoromethylation of Alkenes

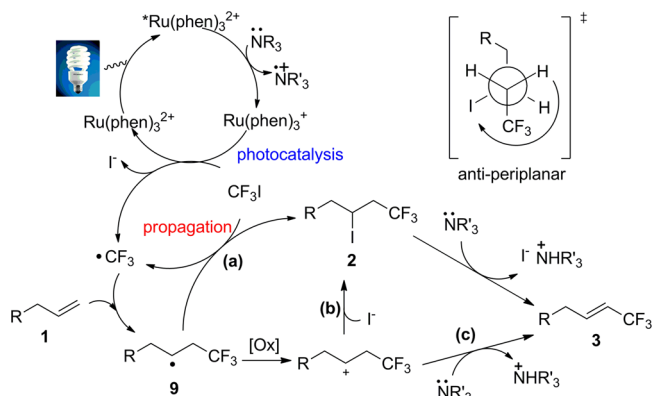
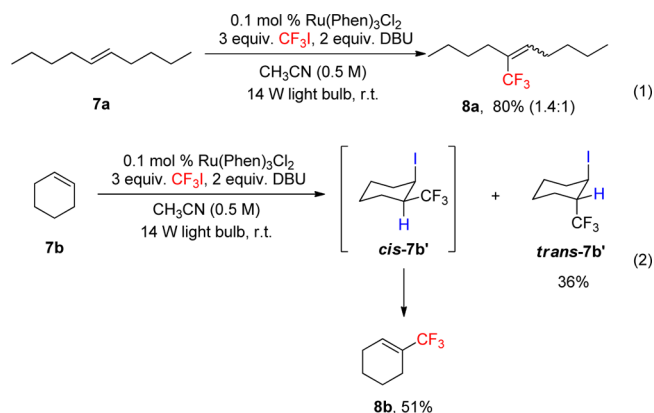


reaction of methyl acrylate **1o** also supported that electron-deficient alkenes are less reactive toward the trifluoromethylation, providing significantly lower yield of **3o** (55%) (Scheme 2 (2)).<sup>16</sup> Interestingly, the reaction of allylbenzene **1p** provided allyl-CF<sub>3</sub> product **4p** by selective elimination of benzylic hydrogen (Scheme 2 (3)). The formation of a conjugated system is likely the driving force for this allyl trifluoromethylation. The reaction of  $\beta$ -pinene **5** gave a ring-opened diene **6** as the major product through the radical rearrangement from **I** to **II** after the addition of <sup>\*</sup>CF<sub>3</sub> radical to the alkene as shown in Scheme 2 (4).

Although the reactions of terminal alkenes are regio- and stereoselective, those of internal alkenes generated a mixture of isomers. The reaction of a symmetrical alkene, *trans*-5-decene **7a**, provided a mixture of *E*- and *Z*-isomers in 80% yield (Scheme 3 (1)). With cyclic alkene **7b**, the reaction provided a mixture of the desired alkenyl-CF<sub>3</sub> product **8b** and trifluoromethylated alkyl iodide *trans*-**7b'** due to a limited C–C bond rotation in the cyclic system (Scheme 3 (2)).<sup>16</sup>

Based on these results, we propose a plausible mechanism of the transformation in Figure 2. We assume that the excitation of Ru(phen)<sub>3</sub><sup>2+</sup> by visible light provides Ru(phen)<sub>3</sub><sup>2+\*</sup>, which is then reductively quenched by DBU to produce Ru(phen)<sub>3</sub><sup>+</sup> and the ammonium radical cation. The Ru(phen)<sub>3</sub><sup>+</sup> (E<sub>oxi</sub> [Ru(phen)<sub>3</sub><sup>+</sup>/Ru(phen)<sub>3</sub><sup>2+</sup>] = +1.41 V vs SCE in CH<sub>3</sub>CN)<sup>14a</sup> in turn performs a single-electron reduction of the F<sub>3</sub>C–I (1.22 V vs SCE in CH<sub>3</sub>CN)<sup>14b</sup> bond, regenerating Ru(phen)<sub>3</sub><sup>2+</sup> and forming a carbon-centered <sup>\*</sup>CF<sub>3</sub> radical. Addition of this electron-deficient radical species with an alkene generates the

### Scheme 3. Trifluoromethylation of Internal Alkenes



**Figure 2.** Proposed mechanism of the alkenyl trifluoromethylation.

trifluoromethylated secondary carbon radical **9**. The reaction of this radical can proceed to generate alkenyl-CF<sub>3</sub> products by three possible pathways:<sup>17</sup> (a) radical propagation, (b) oxidation<sup>18</sup> followed by nucleophilic iodide attack, or (c) oxidation followed by H<sub>a</sub> abstraction by a base. Pathway c would be less likely because *E*-alkenes seems to be predominantly generated via E2 elimination of HI from trifluoromethylated alkyl iodide intermediates as shown in Figure 2.

In conclusion, we have developed a visible light-induced trifluoromethylation for alkenes, providing a direct method to access trifluoromethylated alkenes without prefunctionalization. This process works especially well for terminal alkenes to give alkenyl-CF<sub>3</sub> over allyl-CF<sub>3</sub> products with only *E*-stereochemistry. Mild reaction conditions enable the trifluoromethylation of a broad range of alkenes bearing various functional groups.

## EXPERIMENTAL SECTION

**Experimental Procedure for the Iodotrifluoromethylation of 1a.** An oven-dried resealable test tube equipped with a magnetic stir bar was charged with 1-dodecene **1a** (1.0 mmol), sealed with a silicone septa screw cap, and degassed by alternating vacuum evacuation and argon backfill. A solution of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (0.01 mol %, 0.0001 mmol) in CH<sub>3</sub>CN (4.0 mL, 0.25 M) and TMEDA (2.0 mmol) were then added to the tube under argon. CF<sub>3</sub>I (3.0 mmol) was then bubbled into the reaction mixture using a gastight syringe. The test tube was placed under a 14 W household light bulb at room temperature. The reaction was allowed to proceed for 20 min, and reaction progress was checked by TLC. The reaction mixture was then diluted with diethyl ether and washed with water and brine. The organic layers were dried

over MgSO<sub>4</sub>, concentrated in vacuo, and purified by flash column chromatography (hexanes/Et<sub>2</sub>O) to give 1,1,1-trifluoro-3-iodotridecane **2a** as a colorless oil in 95% (346 mg): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.24–4.16 (m, 1H), 2.98–2.70 (m, 2H), 1.85–1.68 (m, 2H), 1.59–1.47 (m, 1H), 1.45–1.22 (m, 15H), 0.89 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 125.8 (q, *J* = 279.8 Hz), 45.2 (q, *J* = 28.2 Hz), 39.9, 32.1, 29.8, 29.8, 29.7, 29.6, 29.6, 28.8, 22.9, 22.0 (q, *J* = 2.7 Hz), 14.3; IR (neat)  $\nu_{\max}$  = 2926, 2856, 1256, 1149 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>13</sub>H<sub>24</sub>F<sub>3</sub>I 364.0875, found 364.0877; *R*<sub>f</sub> 0.90 (only hexanes).

**General Experimental Procedure for the Trifluoromethylation of Alkenes.** An oven-dried resealable test tube equipped with a magnetic stir bar was charged with an alkene (1.0 mmol), sealed with a silicone septa screw cap, and degassed by alternating vacuum evacuation and argon backfill. A solution of Ru(phen)<sub>3</sub>Cl<sub>2</sub>·xH<sub>2</sub>O (0.1 mol %, 0.001 mmol) in CH<sub>3</sub>CN (2.0 mL, 0.5 M) and DBU (2.0 mmol) were then added to the tube under argon. CF<sub>3</sub>I (2.0 mmol·3.0 mmol) was then bubbled into the reaction mixture using a gastight syringe. The test tube was placed under a 14 W household light bulb at room temperature. The reaction was allowed to proceed for 2–10 h, and reaction progress was checked by TLC or gas chromatography. The reaction mixture was then diluted with diethyl ether and washed with water and brine. The organic layers were dried over MgSO<sub>4</sub>, concentrated in vacuo, and purified by flash column chromatography (hexanes/EtOAc or hexanes/Et<sub>2</sub>O) to give the trifluoromethylated alkene.

**Analytic Data for Trifluoromethylated Alkenes.** (*E*)-1,1,1-Trifluorotridec-2-ene (**3a**): colorless oil (224 mg, 95%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.38 (dtq, *J* = 15.8, 6.8, 2.0 Hz, 1H), 5.60 (dqt, *J* = 15.8, 6.4, 1.6 Hz, 1H), 2.19–2.10 (m, 2H), 1.47–1.39 (m, 2H), 1.33–1.24 (m, 14H), 0.88 (t, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.0 (q, *J* = 6.4 Hz), 123.4 (q, *J* = 270.0 Hz), 118.6 (q, *J* = 33.2 Hz), 32.2, 31.7, 29.9, 29.8, 29.7, 29.6, 29.3, 28.3, 23.0, 14.3; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.27; IR (neat)  $\nu_{\max}$  = 2928, 2857, 1273, 1122 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>13</sub>H<sub>23</sub>F<sub>3</sub> 236.1752, found 236.1750; *R*<sub>f</sub> 0.95 (only hexanes).

(*E*)-7,7,7-Trifluorohept-5-en-1-ol (**3b**): colorless oil (135 mg, 80%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.36 (dtq, *J* = 16.0, 6.8, 2.0 Hz, 1H), 5.61 (dqt, *J* = 16.0, 6.4, 1.6 Hz, 1H), 3.37 (t, *J* = 6 Hz, 2H), 2.22–2.15 (m, 2H), 1.92 (bs, 1H), 1.61–1.47 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.5 (q, *J* = 6.6 Hz), 123.2 (q, *J* = 269.9 Hz), 118.8 (q, *J* = 33.3 Hz), 62.5, 32.1, 31.3, 24.4; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -60.34; IR (neat)  $\nu_{\max}$  = 3347, 2939, 1681, 1275, 1121 cm<sup>-1</sup>.

(*E*)-12,12,12-Trifluorododec-10-enal (**3c**): colorless oil (184 mg, 78%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (t, *J* = 1.8 Hz, 1H), 6.37 (dtq, *J* = 15.6, 6.8, 2.0 Hz, 1H), 5.60 (dqt, *J* = 15.6, 6.4, 1.8 Hz, 1H), 2.42 (td, *J* = 7.4, 1.8 Hz, 2H), 2.19–2.08 (m, 2H), 1.67–1.58 (m, 2H), 1.47–1.37 (m, 2H), 1.36–1.26 (m, 8H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 203.1, 140.9 (q, *J* = 6.5 Hz), 123.3 (q, *J* = 270.2 Hz), 118.6 (q, *J* = 33.2 Hz), 44.1, 31.6, 29.4, 29.3, 29.3, 29.1, 28.1, 22.2; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -63.89; IR (neat)  $\nu_{\max}$  = 2931, 2858, 1727, 1681, 1274, 1119 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>12</sub>H<sub>19</sub>F<sub>3</sub>O 236.1388, found 236.1390; *R*<sub>f</sub> 0.53 (hex/EtOAc, 8/1).

(*E*)-13,13,13-Trifluorotridec-11-en-2-one (**3d**): colorless oil (203 mg, 81%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.37 (dtq, *J* = 15.6, 6.8, 2.0 Hz, 1H), 5.60 (dqt, *J* = 15.6, 6.4, 1.8 Hz, 1H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.19–2.10 (m, 2H), 2.14 (s, 3H), 1.62–1.52 (m, 2H), 1.48–1.38 (m, 2H), 1.34–1.24 (m, 8H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 209.5, 141.0 (q, *J* = 6.5 Hz), 123.3 (q, *J* = 270.1 Hz), 118.5 (q, *J* = 33.2 Hz), 43.9, 31.6, 30.0, 29.4, 29.34, 29.29, 29.1, 28.1, 24.0; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -63.89; IR (neat)  $\nu_{\max}$  = 2932, 2858, 1718, 1119 cm<sup>-1</sup>; HRMS (FAB) calcd for C<sub>13</sub>H<sub>22</sub>F<sub>3</sub>O 251.1623, found 251.1620; *R*<sub>f</sub> 0.43 (hex/EtOAc, 8/1).

(*E*)-7,7,7-Trifluorohept-5-en-1-yl octanoate (**3e**): colorless oil (236 mg, 80%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.35 (dtq, *J* = 15.6, 6.8, 2.0 Hz, 1H), 5.61 (dqt, *J* = 15.6, 6.4, 1.2 Hz, 1H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 2.22–2.13 (m, 2H), 1.68–1.55 (m, 4H), 1.55–1.46 (m, 2H), 1.34–1.20 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 140.2 (q, *J* = 6.6 Hz), 123.2 (q, *J* = 269.9 Hz), 119.0 (q, *J* = 33.5 Hz), 63.9, 34.5, 31.9, 31.2, 29.3, 29.1,

28.2, 25.2, 24.6, 22.8, 14.2; IR (neat):  $\nu_{\max}$  = 2932, 2859, 1737, 1682, 1274, 1121 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>15</sub>H<sub>25</sub>F<sub>3</sub>O<sub>2</sub> 294.1807, found 294.1805; *R*<sub>f</sub> 0.58 (hex/EtOAc, 8/1).

(*E*)-7,7,7-Trifluorohept-5-en-1-yl benzoate (**3f**): colorless oil (253 mg, 93%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41–8.07 (m, 5H), 6.39 (dtq, *J* = 16.0, 6.8, 2.0 Hz, 1H), 5.64 (dqt, *J* = 16.0, 6.4, 1.6 Hz, 1H), 2.27–2.18 (m, 2H), 1.84–1.76 (m, 2H), 1.65–1.57 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.8, 140.4 (q, *J* = 6.5 Hz), 133.1, 130.5, 129.7, 128.6, 123.2 (q, *J* = 270.0 Hz), 119.0 (q, *J* = 33.3 Hz), 64.6, 31.2, 28.3, 24.7; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -63.97; IR (neat):  $\nu_{\max}$  = 2946, 1720, 1681, 1275, 1117 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>14</sub>H<sub>15</sub>F<sub>3</sub>O<sub>2</sub> 272.1024, found 272.1026; *R*<sub>f</sub> 0.50 (hex/EtOAc, 8/1).

(*E*)-7,7,7-Trifluorohept-5-en-1-yl dimethylcarbamate (**3g**): colorless oil (192 mg, 80%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.35 (dtq, *J* = 16.0, 6.8, 1.6 Hz, 1H), 5.61 (dqt, *J* = 16.0, 6.4, 1.6 Hz, 1H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.89 (s, 6H), 2.23–2.13 (m, 2H), 1.69–1.61 (m, 2H), 1.56–1.46 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.9, 140.4 (q, *J* = 6.5 Hz), 123.2 (q, *J* = 269.9 Hz), 118.9 (q, *J* = 33.3 Hz), 65.0, 36.5, 36.0, 31.2, 28.7, 24.6; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.00; IR (neat)  $\nu_{\max}$  = 2940, 1704, 1403, 1188, 1117 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>10</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>2</sub> 239.1133, found 239.1135; *R*<sub>f</sub> 0.28 (hex/EtOAc, 8/1).

(*E*)-N-(4,4,4-Trifluorobut-2-en-1-yl)octanamide (**3h**): colorless oil (214 mg, 85%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.35 (dtq, *J* = 15.6, 6.8, 2.0 Hz, 1H), 6.14 (bs, 1H), 5.70 (dqt, *J* = 15.6, 6.4, 1.8 Hz, 1H), 4.01–3.94 (m, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.62 (tt, *J* = 7.6, 7.6 Hz, 2H), 1.34–1.20 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.6, 136.9 (q, *J* = 6.3 Hz), 123.0 (q, *J* = 270.28 Hz), 119.3 (q, *J* = 34.14 Hz), 39.5, 36.7, 31.8, 29.4, 29.2, 25.9, 22.8, 14.2; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.21; IR (neat):  $\nu_{\max}$  = 3289, 2930, 2859, 1651, 1547, 1124 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>12</sub>H<sub>20</sub>F<sub>3</sub>NO 251.1497, found 251.1500; *R*<sub>f</sub> 0.28 (hex/EtOAc, 2/1).

(*E*)-4-Bromo-N-(4,4,4-trifluorobut-2-en-1-yl)benzamide (**3i**): white solid (256 mg, 83%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 6.78 (bs, 1H), 6.42 (dtq, *J* = 15.6, 5.2, 2.0 Hz, 1H), 5.76 (dqt, *J* = 15.6, 6.0, 1.8 Hz, 1H), 4.18–4.12 (bs, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.9, 136.4 (q, *J* = 6.3 Hz), 132.7, 132.1, 128.8, 126.9, 122.9 (q, *J* = 270.5 Hz), 119.8 (q, *J* = 34.2 Hz), 40.2; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.14; IR (neat)  $\nu_{\max}$  = 3317, 1651, 1541, 1302, 1275, 1111 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>11</sub>H<sub>9</sub>BrF<sub>3</sub>NO 306.9820, found 306.9816; *R*<sub>f</sub> 0.35 (hex/EtOAc, 2/1).

(*E*)-4-Chloro-N-(4,4,4-trifluorobut-2-en-1-yl)benzamide (**3j**): white solid (208 mg, 79%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.79 (bs, 1H), 6.42 (dtq, *J* = 15.8, 5.2, 2.0 Hz, 1H), 5.76 (dqt, *J* = 15.8, 6.4, 1.8 Hz, 1H), 4.18–4.12 (bs, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.8, 138.5, 136.4 (q, *J* = 6.4 Hz), 132.3, 129.2, 128.6, 122.9 (q, *J* = 270.4 Hz), 119.9 (q, *J* = 34.3 Hz), 40.2; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.32; IR (neat)  $\nu_{\max}$  = 3327, 3074, 1640, 1550, 1326, 1116 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>11</sub>H<sub>9</sub>ClF<sub>3</sub>NO 263.0325, found 263.0328; *R*<sub>f</sub> 0.40 (hex/EtOAc, 2/1).

(*E*)-tert-Butyldimethyl((7,7,7-trifluorohept-5-en-1-yl)oxy)silane (**3k**): colorless oil (251 mg, 89%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.39 (dtq, *J* = 16.0, 6.8, 1.8 Hz, 1H), 5.61 (dqt, *J* = 16.0, 6.4, 1.6 Hz, 1H), 3.62 (t, *J* = 6.0 Hz, 2H), 2.24–2.14 (m, 2H), 1.58–1.46 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.8 (q, *J* = 6.6 Hz), 123.3 (q, *J* = 269.9 Hz), 118.7 (q, *J* = 33.3 Hz), 62.9, 32.3, 31.4, 26.2, 24.6, 18.6, -5.1; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -62.92; IR (neat)  $\nu_{\max}$  = 2932, 2860, 1682, 1257, 1123 cm<sup>-1</sup>; HRMS (FAB) calcd for C<sub>13</sub>H<sub>26</sub>F<sub>3</sub>OSi 283.1705, found 283.1702.

(*E*)-7,7,7-Trifluorohept-5-en-1-yl benzenesulfonate (**3l**): colorless oil (278 mg, 90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92–7.53 (m, 5H), 6.28 (dtq, *J* = 16.0, 6.8, 2.2 Hz, 1H), 5.56 (dqt, *J* = 16.0, 6.4, 1.6 Hz, 1H), 4.06 (t, 6.4 Hz, 2H), 2.16–2.07 (m, 2H), 1.71–1.62 (m, 2H), 1.52–1.42 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.8 (q, *J* = 6.5 Hz), 136.2, 134.0, 129.5, 128.0, 123.1 (q, *J* = 270.2 Hz), 119.2 (q, *J* = 33.5 Hz), 70.4, 30.8, 28.3, 24.0; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.59; IR (neat)  $\nu_{\max}$  = 2940, 1680, 1361, 1188, 1097 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>13</sub>H<sub>15</sub>F<sub>3</sub>O<sub>3</sub>S 308.0694, found 308.0698; *R*<sub>f</sub> 0.40 (hex/EtOAc, 4/1).

(*E*)-4-((4,4,4-Trifluorobut-2-en-1-yl)oxy)butan-1-ol (**3m**): colorless oil (167 mg, 84%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.40 (dtq, *J* = 15.8, 4.0, 2.0 Hz, 1H), 5.89 (dqt, *J* = 15.8, 6.8, 1.8 Hz, 1H), 4.11–4.05 (m, 2H), 3.65 (t, *J* = 6.0 Hz, 2H), 3.51 (t, *J* = 6.0 Hz, 2H), 2.03 (bs, 1H), 1.74–1.61 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.8 (q, *J* = 6.5 Hz), 123.3 (q, *J* = 270.1 Hz), 118.8 (q, *J* = 34.2 Hz), 71.3, 68.7, 62.8, 29.9, 26.5; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ –64.28; IR (neat)  $\nu_{\max}$  = 3384, 2871, 1687, 1312, 1120 cm<sup>-1</sup>; HRMS (FAB) calcd for C<sub>8</sub>H<sub>14</sub>F<sub>3</sub>O<sub>2</sub> 199.0946, found 199.0945; *R*<sub>f</sub> 0.30 (hex/EtOAc, 2/1).

(*E*)-(5,5,5-Trifluoropent-3-en-1-yl)benzene (**3n**): colorless oil (180 mg, 90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38–7.17 (m, 5H), 6.44 (dtq, *J* = 15.6, 6.8, 2.0 Hz, 1H), 5.65 (dqt, *J* = 15.6, 6.4, 1.2 Hz, 1H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.54–2.44 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.1, 139.9 (q, *J* = 6.5 Hz), 128.7, 128.6, 126.5, 123.3 (q, *J* = 270.3 Hz), 119.2 (q, *J* = 33.5 Hz), 34.5, 33.8; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ –62.40; IR (neat)  $\nu_{\max}$  = 2930, 1681, 1604, 1328, 1277, 1123 cm<sup>-1</sup>; HRMS (EI) Calcd for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub> 200.0813, Found 200.0814; *R*<sub>f</sub> 0.75 (only hexanes).

(*E*)-(4,4,4-trifluorobut-1-en-1-yl)benzene (**4p**): colorless oil (164 mg, 88%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35–7.40 (m, 5H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.10 (dt, *J* = 16.0, 7.2 Hz, 1H), 3.04–2.93 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.9, 136.4, 128.9, 128.3, 126.7, 126.1 (q, *J* = 277.8 Hz), 117.4 (q, *J* = 3.5 Hz), 37.9 (q, *J* = 29.3 Hz); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ –66.21; IR (neat)  $\nu_{\max}$  = 2930, 1369, 1251, 1138 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub> 186.0656, found 186.0654; *R*<sub>f</sub> 0.53 (only hexanes).

4-(Propan-2-ylidene)-1-(2,2,2-trifluoroethyl)cyclohex-1-ene (**6**): colorless oil (174 mg, 85%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.66 (s, 1H), 2.81 (m, 2H), 2.73 (q, *J* = 11.2 Hz, 2H), 2.33 (t, *J* = 2.4 Hz, 2H), 2.12 (m, 2H), 1.70 (s, 3H), 1.66 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 129.0, 128.0 (q, *J* = 2.63 Hz), 126.5 (q, *J* = 278.66 Hz), 42.0 (q, *J* = 28.79 Hz), 30.2, 29.9, 26.6, 20.4, 20.0; <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ –63.44; IR (neat)  $\nu_{\max}$  = 2979, 2928, 1357, 1253, 1132 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>11</sub>H<sub>15</sub>F<sub>3</sub> 204.1126, found 204.1128; *R*<sub>f</sub> 0.83 (only hexanes).

## ASSOCIATED CONTENT

### Supporting Information

Characterization and spectral data of 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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