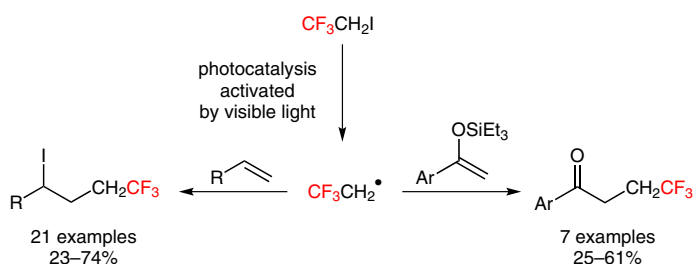


Visible-Light-Induced Photocatalysis of 1,1,1-Trifluoro-2-iodoethane with Alkylalkenes and Silyl Enol Ethers

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Abstract Reactions of 1,1,1-trifluoro-2-iodoethane with alkylalkenes and silyl enol ethers were performed in the presence of a catalytic amount of *fac*-Ir(ppy)₃ and an excessive amount of Hünig's base in acetonitrile irradiated by a 24 W fluorescent lamp under nitrogen atmosphere for 48 hours. The visible-light-induced photoredox reactions introduce simultaneously a 2,2,2-trifluoroethyl group and an iodine atom to both sides of the double bond of ordinary alkenes via an atom-transfer radical addition (ATRA). The same reaction with silyl enol ethers generates β-trifluoromethyl ketones, which are typically a challenge to synthesize. The reactions proved to be tolerant of a variety of functionalities.

Key words trifluoromethyl, radical, photochemical, visible light, alkene

Introduction of fluorine is essential in agrochemicals, pharmaceuticals, and various materials because of the significant influence of fluorine atoms on the acidity, dipole, rigidity, metabolic stability, lipophilicity, and bioavailability of the respective products.^{1,2} In recent years, in order to meet the increasing demand of new fluorinated compounds, various methods for the introduction of fluorine into organic molecules have been developed.^{3–6} The 2,2,2-trifluoroethyl group has attracted the attention of synthetic chemists as an important fluorinated functionality. Compounds bearing a CF₃CH₂ group can be constructed from activated halides and their analogues (e.g., trifluoroacetate) using nucleophilic or electrophilic trifluoromethylation reagents such as the Chen reagent (FO₂SCF₂CO₂Me), Ruppert-Prakash reagent (Me₃SiCF₃), Togni reagent [1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one and trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole], and Umemoto reagent [S-(trifluoromethyl)dibenzothiophenium salts].^{7,8} Metal-catalyzed trifluoromethylation reactions of alkenes

and allylsilanes can provide 2,2,2-trifluoroethylated alkenes by using electrophilic trifluoromethylation reagents.⁹ The copper-catalyzed oxidative trifluoromethylation of alkenes bearing allylic protons by using Me₃SiCF₃ has also been reported.¹⁰ Another common technique is based on the introduction of the 2,2,2-trifluoroethyl group directly from C-2 fluorinated substrates.^{11–16} 1,1,1-Trifluoro-2-iodoethane (**1**) is a useful 2,2,2-trifluoroethylation reagent and has been used in radical reactions. We have reported earlier the sulfinate-dehalogenation reaction of **1** with alkenes and alkynes to form addition products.^{13a}

Visible-light photoredox catalysis with transition metal complexes has been widely applied in organic synthesis.¹⁷ Because of the electron-withdrawing ability of fluorine, fluorinated substrates are good precursors for the generation of fluorinated radicals in photochemical reactions. The cobalt-catalyzed photochemical synthesis of 2,2,2-trifluoroethylated alkenes from styrene derivatives using **1** has

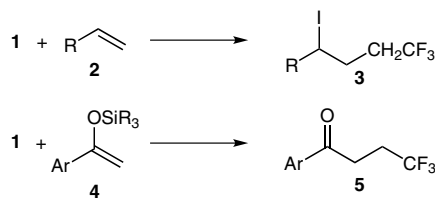
previous work:

Co-catalyzed photoredox reaction of styrenes



this work:

Ir-catalyzed photoredox reaction of alkenes and silyl enol ethers



Scheme 1 Previous work on arylated alkenes and our design of visible-light-induced photoredox reaction of alkenes and silyl enol ethers using **1**

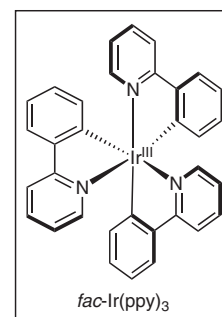
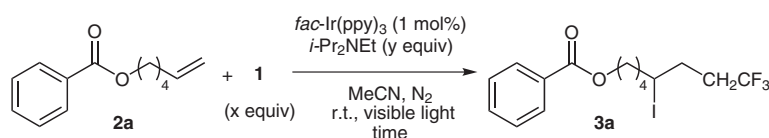
been described by Carreira et al. in 2013 (Scheme 1).¹⁴ Inspired by our interest in the reactions at neighboring positions of the CF₃ group,¹⁸ we speculated that in the reaction of alkenes with **1**, an atom-transfer radical addition (ATRA) to alkenes will occur instead of the generation of the alkene product reported by Carreira et al. (Scheme 1). A general synthetic strategy for β -trifluoromethylated ketones is lacking.¹⁹ Interestingly, the application of the photoredox system to silyl enol ethers will induce desilylation instead of iodination, generating the corresponding β -trifluoromethylated ketones (Scheme 1).

We initially investigated the reaction of alkene **2a** with **1** in the presence of various amounts of Hünig's base. In

these screenings, a mixture of alkene **2a**, 3 equivalents of **1**, and 1 mol% of *fac*-Ir(ppy)₃ complex in acetonitrile was irradiated by a 24 W fluorescent lamp at room temperature under nitrogen atmosphere for 48 hours in the presence of 1–6 equivalents of Hünig's base (Table 1, entries 1–6). When 2 equivalents of amine were employed, the yield reached 44%.

By increasing the amount of **1** to 6 equivalents and that of amine to 5 equivalents, the best yield of the ATRA product (70%) was obtained (Table 1, entry 8). During these investigations (entries 7–11), we found that, in order to achieve high yields of the desired product, the amount of amine must be slightly lower than that of **1**. Further in-

Table 1 Screening of Conditions for Iodotrifluoroethylation of **2a** with **1**^a



Entry	Time (h)	x (equiv)	y (equiv)	Yield of 3a (%) ^b
1	48	3	1	34
2	48	3	2	44
3	48	3	3	27
4	48	3	4	27
5	48	3	5	19
6	48	3	6	4
7	48	6	6	52
8	48	6	5	70
9	48	6	4	55
10	48	6	3	38
11	48	6	2	26
12	48	7	6	52
13	48	8	6	59
14	48	9	6	59
15	48	10	6	61
16	3	6	5	24
17	6	6	5	27
18	12	6	5	40
19	24	6	5	48

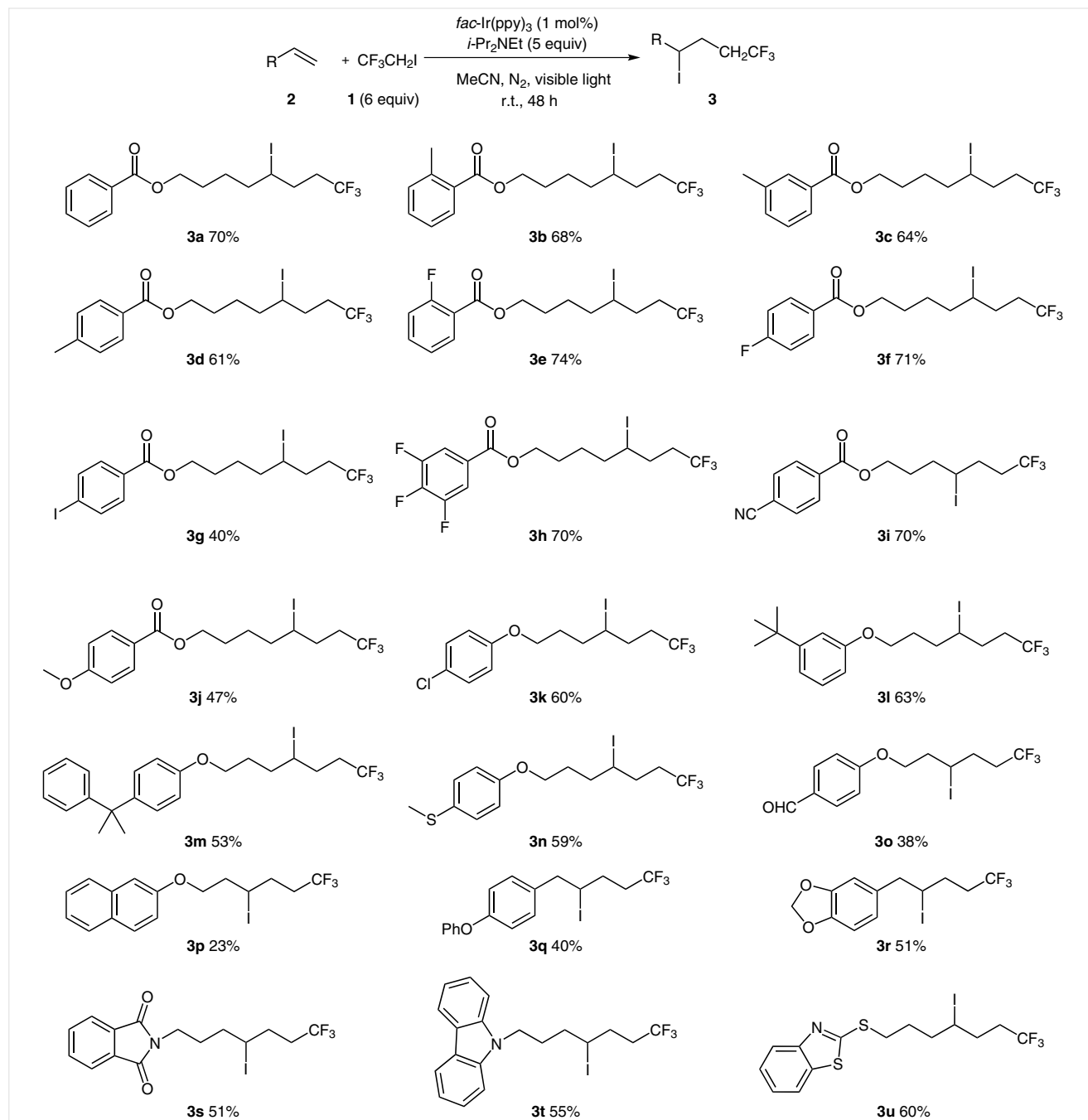
^a The reactions were carried out with **1** (0.2 mmol), **2a** (x equiv), *i*-Pr₂NEt (y equiv), and *fac*-Ir(ppy)₃ (0.002 mmol, 1 mol%) in MeCN (2 mL) irradiated by a 24 W fluorescent lamp at r.t. under N₂ atmosphere.

^b Isolated yields.

creasing the amount of **1** did not improve the yield significantly (entries 12–15). The reaction time was also carefully examined, and the yield was found to increase with increasing time (entries 8, 16–19).

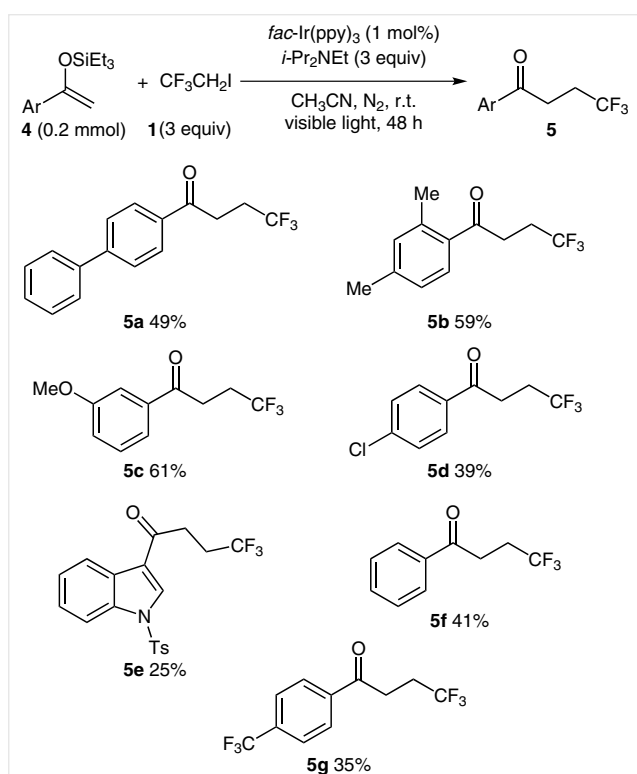
Thus, using the conditions of entry 8 in Table 1, the substrate scope of alkenes was examined by performing the atom-transfer reaction of **1** with various olefins (Scheme 2). Several functional groups, including ester, aryl ether, thio-

ether, aryl iodide, aryl aldehyde, and aryl nitrile are well tolerated under the reaction conditions. In addition, various nitrogen and sulfur-containing heterocycles are compatible with the protocol. The alkene reactants were found to be fully converted within 48 hours although the yields of desired products were only low to moderate, and the products can be easily isolated by column chromatography on silica gel.



Scheme 2 Visible-light-induced photoredox iodotrifluoroethylation of alkenes with **1**

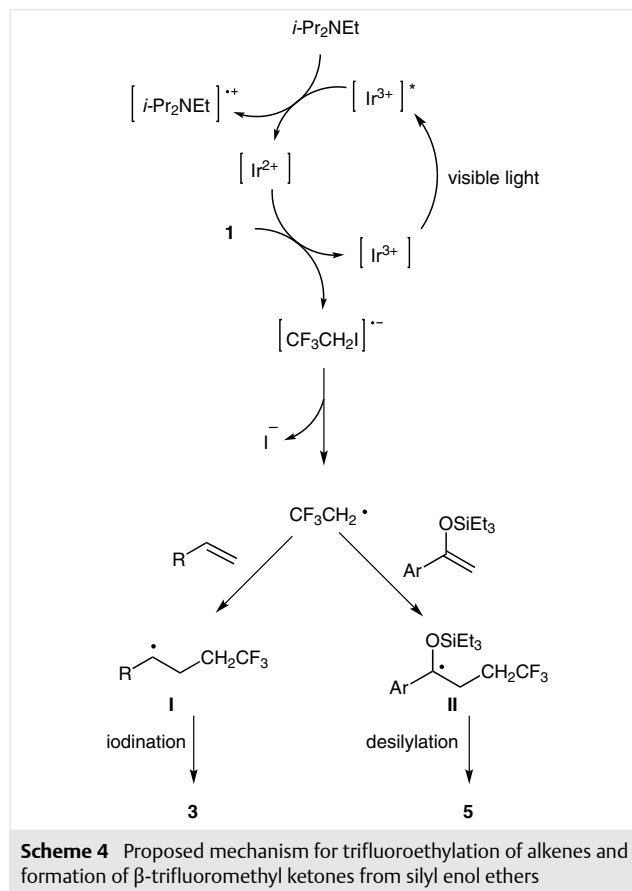
Next, the more electron-rich silyl enol ethers were tested, using fewer equivalents of **1** and Hünig's base compared with those used in the reaction of ordinary olefins, in the presence of 1 mol% *fac*-Ir(ppy)₃ activated by visible light under nitrogen atmosphere. The corresponding β-CF₃-substituted aryl ketones were obtained (Scheme 3). Silyl enol ethers **5a–c** bearing an electron-donating substituent on the aromatic ring yield the target products in moderate yields. Electron-withdrawing and neutral substituents on the aromatic ring (**5d,f,g**) were also tolerated, although lower yields were observed. In addition, silyl enol ether with a protected indole moiety affords the target ketone **5e**.



Scheme 3 Visible-light-induced photoredox reaction of silyl enol ethers with **1**

We propose that the trifluoroethylation of alkenes proceeds via the mechanism shown in Scheme 4. First, irradiated by visible light, *fac*-Ir(III)(ppy)₃ undergoes a metal-to-ligand transfer (MLCT) that produces a redox-active photoexcited state, *fac*-Ir³⁺(III)(ppy)₃. The active *fac*-Ir³⁺(III)(ppy)₃ complex readily accepts an electron from a reductive quencher (Hünig's base) to generate the low-valent species *fac*-Ir²⁺(II)(ppy)₃ with a high reducing ability. Next, the single-electron reduction of CF₃CH₂I by *fac*-Ir²⁺(II)(ppy)₃ generates a radical anion and then a 2,2,2-trifluoroethyl radical (CF₃CH₂•). When the reaction is carried out with ordinary alkenes, addition of the 2,2,2-trifluoroethyl radical gives radical intermediate **I**. Iodine atom-transfer to **I** yields prod-

ucts **3**. In the case of silyl enol ethers, addition of the 2,2,2-trifluoroethyl radical generates radical intermediate **II**, which yields ketone products **5** by instant desilylation.



Scheme 4 Proposed mechanism for trifluoroethylation of alkenes and formation of β-trifluoromethyl ketones from silyl enol ethers

In summary, iodotrifluoroethylation of alkylalkenes with 2,2,2-trifluoro-1-iodoethane can be realized using photoredox catalysis and activation by visible light. The visible-light-induced system can be extended to silyl enol ethers, thus producing β-trifluoromethyl ketones. This method provides a new path to trifluoromethyl-substituted organic compounds and will find applications in biological, medical, and materials sciences.

NMR spectra were obtained on 400 MHz spectrometers and recorded at 25 °C. Chemical shifts for ¹H NMR spectra are reported in ppm downfield from TMS, and for ¹³C NMR spectra in ppm relative to residual CHCl₃ (δ = 77.0 for ¹³C). The chemical shifts for ¹⁹F NMR are reported in ppm downfield from CFCl₃. Coupling constants (*J*) are reported in hertz. Standard abbreviations are used to denote the signal multiplicities. ¹³C NMR was broad-band decoupled from hydrogen nuclei. Absorbance frequencies in IR spectra are given at maximum intensity in cm⁻¹. The mass analyzer type used for the HRMS is time-of-flight mass spectrometry (TOF-MS) or Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). Column chromatography was performed using silica gel (mesh 300–400). All reactions

were carried out under N₂. MeCN was purified by distillation over CaH₂. Petroleum ether (PE) used refers to the hydrocarbon mixture with a boiling range of 60–90 °C. The alkenes **2** were prepared based on the literature procedure.²⁰ The preparation, and the analytical and spectral data of the new products **2b–e,g,h,j,m,n** are given below. The silyl enol ethers **4** were prepared following the literature procedure.²¹

Alkenes **2b–e,g,h,j**; General Procedure

To a 100 mL flask charged with hex-5-en-1-ol (0.50 g, 5.0 mmol), Et₃N (1.8 g, 18.0 mmol), and CH₂Cl₂ (25 mL) was added the appropriate acyl chloride (6 mmol) in CH₂Cl₂ (ca. 5 mL) at 0 °C. The reaction mixture was vigorously stirred overnight at r.t. Sat. aq NaHCO₃ (20 mL) was added and the mixture was stirred at r.t. for 20 min. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel (eluent: PE–EtOAc, 15 to 10:1 v/v) to provide the corresponding product.

Hex-5-en-1-yl 2-Methylbenzoate (**2b**)

Yield: 1.0 g (91%); colorless oil.

IR (neat): 3076, 3033, 2860, 1719, 1641, 1603, 1577, 1457, 1259, 1143, 994, 912, 737, 696 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.50–1.58 (m, 2 H), 1.73–1.80 (m, 2 H), 2.07–2.16 (m, 2 H), 2.59 (s, 3 H), 4.29 (t, *J* = 8.0 Hz, 2 H), 4.95–5.05 (m, 2 H), 5.75–5.86 (m, 1 H), 7.21–7.24 (m, 2 H), 7.35–7.39 (m, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 25.3, 28.1, 33.2, 64.6, 114.8, 125.6, 129.8, 130.4, 131.77, 131.8, 138.3, 140.0, 167.7.

HRMS (EI): *m/z* (M⁺) calcd for C₁₄H₁₈O₂: 218.1307; found: 218.1311.

Hex-5-en-1-yl 3-Methylbenzoate (**2c**)

Yield: 1.0 g (91%); colorless oil.

IR (neat): 2936, 2861, 1719, 1640, 1608, 1591, 1457, 1299, 1278, 1200, 1109, 995, 911, 745, 683 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.50–1.58 (m, 2 H), 1.73–1.80 (m, 2 H), 2.09–2.14 (m, 2 H), 2.59 (s, 3 H), 4.29 (t, *J* = 8.0 Hz, 2 H), 4.95–5.05 (m, 2 H), 5.75–5.85 (m, 1 H), 7.27–7.34 (m, 2 H), 7.83 (d, *J* = 8.0 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 25.2, 28.1, 33.2, 64.7, 114.8, 126.5, 128.1, 130.0, 130.3, 133.5, 138.0, 138.2, 166.7.

HRMS (EI): *m/z* (M⁺) calcd for C₁₄H₁₈O₂: 218.1307; found: 218.1301.

Hex-5-en-1-yl 4-Methylbenzoate (**2d**)

Yield: 1.0 g (91%); colorless oil.

IR (neat): 2936, 2860, 1717, 1613, 1508, 1457, 1310, 1274, 1208, 1178, 1109, 994, 912, 841, 754 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.49–1.57 (m, 2 H), 1.73–1.80 (m, 2 H), 2.08–2.14 (m, 2 H), 2.39 (s, 3 H), 4.29 (t, *J* = 8.0 Hz, 2 H), 4.94–5.04 (m, 2 H), 5.75–5.85 (m, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 25.3, 28.2, 33.3, 64.7, 114.8, 127.7, 129.0, 129.5, 138.4, 143.4, 166.7.

HRMS (EI): *m/z* (M⁺) calcd for C₁₄H₁₈O₂: 218.1307; found: 218.1311.

Hex-5-en-1-yl 2-Fluorobenzoate (**2e**)

Yield: 0.94 g (85%); colorless oil.

IR (neat): 3078, 2937, 2861, 1717, 1640, 1614, 1585, 1489, 1457, 1299, 1250, 1158, 1128, 994, 913, 757, 692 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.52–1.60 (m, 2 H), 1.75–1.82 (m, 2 H), 2.10–2.16 (m, 2 H), 4.34 (t, *J* = 8.0 Hz, 2 H), 4.95–5.04 (m, 2 H), 5.75–5.85 (m, 1 H), 7.11–7.22 (m, 2 H), 7.49–7.54 (m, 1 H), 7.93 (d, *J* = 4.0 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 28.1, 33.2, 65.2, 114.9, 117.0 (d, *J*_{C,F} = 23 Hz), 119.0 (d, *J*_{C,F} = 10 Hz), 123.9 (d, *J*_{C,F} = 4 Hz), 132.1, 134.3 (d, *J*_{C,F} = 10 Hz), 138.4, 162.0 (d, *J*_{C,F} = 270 Hz), 163.3, 164.5 (d, *J*_{C,F} = 4 Hz).

¹⁹F NMR (376 MHz, CDCl₃): δ = –109.5 to –109.6 (m).

HRMS (EI): *m/z* (M⁺) calcd for C₁₃H₁₅FO₂: 222.1056; found: 222.1052.

Hex-5-en-1-yl 4-Iodobenzoate (**2g**)

Yield: 1.4 g (83%); colorless oil.

IR (neat): 3076, 2935, 2858, 1720, 1640, 1587, 1481, 1457, 1393, 1269, 1177, 1115, 1103, 1008, 1056, 912, 845, 754 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.48–1.50 (m, 2 H), 1.72–1.79 (m, 2 H), 2.07–2.13 (m, 2 H), 4.29 (t, *J* = 8.0 Hz, 2 H), 4.94–5.03 (m, 2 H), 5.74–5.84 (m, 1 H), 7.70–7.78 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 25.3, 28.1, 33.3, 65.2, 100.6, 115.0, 129.9, 131.0, 137.7, 138.3, 166.1.

HRMS (EI): *m/z* (M⁺) calcd for C₁₃H₁₅I O₂: 330.0117; found: 330.0125.

Hex-5-en-1-yl 3,4,5-Trifluorobenzoate (**2h**)

Yield: 1.1 g (86%); colorless oil.

IR (neat): 3028, 2938, 2862, 1731, 1653, 1641, 1625, 1529, 1441, 1354, 1251, 1225, 1086, 1049, 994, 914, 889 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.49–1.56 (m, 2 H), 1.72–1.80 (m, 2 H), 2.08–2.13 (m, 2 H), 4.31 (t, *J* = 8.0 Hz, 2 H), 4.95–5.04 (m, 2 H), 5.74–5.84 (m, 1 H), 7.66 (t, *J* = 8.0 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 33.2, 66.9, 114.1 (m), 115.1, 126.4 (m), 138.1, 143.1 (t, *J*_{C,F} = 258, 15 Hz), 151.0 (ddd, *J*_{C,F} = 250, 10, 3.5 Hz), 163.8 (m).

¹⁹F NMR (376 MHz, CDCl₃): δ = –132.7 to –132.9 (m, 2 F), –152.9 (tt, *J* = 22.0, 6.7 Hz, 1 F).

HRMS (EI): *m/z* (M⁺) calcd for C₁₃H₁₃F₃O₂: 258.0868; found: 258.0862.

Hex-5-en-1-yl 4-Methoxybenzoate (**2j**)

Yield: 1.0 g (85%); colorless oil.

IR (neat): 3077, 2937, 2841, 1716, 1640, 1559, 1582, 1458, 1420, 1386, 1258, 1168, 1103, 1031, 995, 913, 848, 771, 697, 613 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.47–1.56 (m, 2 H), 1.70–1.77 (m, 2 H), 2.07–2.12 (m, 2 H), 3.81 (s, 3 H), 4.26 (t, *J* = 8.0 Hz, 2 H), 4.93–5.02 (m, 2 H), 5.73–5.84 (m, 1 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 7.96 (d, *J* = 8.0 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 25.3, 28.2, 30.4, 56.4, 64.6, 113.6, 114.8, 122.9, 131.5, 138.4, 163.2, 166.4.

HRMS (EI): *m/z* (M⁺) calcd for C₁₃H₁₅O₂: 234.1256; found: 234.1258.

Alkenes **2m** and **2n**; General Procedure

A 50 mL flask was charged with the respective aromatic alcohol (5.0 mmol), K₂CO₃ (2.1 g, 15.0 mmol), 5-bromopent-1-ene (1.5 g, 10.0 mmol), and MeCN (10 mL) and the mixture was refluxed for 12 h. It was then cooled to 25 °C and the solvent was removed under vacuum. EtOAc and H₂O were added and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 × 20 mL). The combined

organic extracts were washed with brine, dried (Na_2SO_4), and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel (eluent: hexane– CH_2Cl_2 , 10:1 v/v) to provide the corresponding alkene.

1-(Pent-4-en-1-yloxy)-4-(2-phenylpropan-2-yl)benzene (2m)

Yield: 1.2 g (87%); colorless oil.

IR (neat): 3032, 2968, 2871, 1640, 1609, 1509, 1458, 1446, 1385, 1250, 1183, 1013, 934, 914, 829, 764, 700 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.66 (s, 6 H), 1.85–1.90 (m, 2 H), 2.20–2.25 (m, 2 H), 3.94 (t, J = 8.0 Hz, 2 H), 4.98–5.07 (m, 2 H), 5.80–5.90 (m, 1 H), 6.80 (d, J = 12.0 Hz, 2 H), 7.12–7.28 (m, 7 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 28.5, 30.2, 30.9, 42.3, 67.1, 113.9, 115.1, 125.5, 126.8, 127.8, 128.0, 137.9, 142.8, 151.0, 156.9.

HRMS (EI): m/z (M^+) calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: 280.1827; found: 280.1826.

Methyl [4-(Pent-4-en-1-yloxy)phenyl] Sulfide (2n)

Yield: 1.0 g (93%); colorless oil.

IR (neat): 3076, 2976, 2920, 2807, 1640, 1653, 1595, 1570, 1494, 1472, 1437, 1280, 1243, 1175, 1106, 994, 914, 822, 662 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.82–1.89 (m, 2 H), 2.13–2.24 (m, 2 H), 2.42 (s, 3 H), 3.93 (t, J = 8.0 Hz, 2 H), 4.97–5.06 (m, 2 H), 5.78–5.88 (m, 1 H), 6.82 (d, J = 8.0 Hz, 2 H), 7.24 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 18.1, 28.4, 30.1, 67.3, 115.2, 128.6, 130.2, 133.1, 137.7, 157.7.

HRMS (EI): m/z (M^+) calcd for $\text{C}_{12}\text{H}_{16}\text{OS}$: 208.0922; found: 280.0918.

Photoredox ATRA of 2,2,2-Trifluoro-1-iodoethane (1) to Alkenes 2; General Procedure

A 10 mL Schlenk tube was charged with **2** (0.2 mmol) and *fac*-Ir(ppy)₃ (1.3 mg, 0.002 mmol). The tube was then evacuated and backfilled with N_2 (3 times). 1,1,1-Trifluoro-2-iodoethane (**1**; 190 mg, 1.2 mmol), *i*-Pr₂NEt (129 mg, 1.0 mmol), and anhydrous MeCN (2 mL) were added to the Schlenk tube subsequently under N_2 . The reaction was irradiated by a 24 W fluorescence lamp for 24 h at r.t. The mixture was evaporated under vacuum and the residue was separated by column chromatography on silica gel (PE–EtOAc, 10:1 v/v) to afford the desired product.

8,8,8-Trifluoro-5-iodooctyl Benzoate (3a)

Yield: 57.9 mg (70%); yellow oil.

IR (neat): 3064, 3034, 2950, 2864, 1717, 1602, 1585, 1492, 1451, 1275, 1171, 1027, 963, 842, 806, 712, 687 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.56–2.45 (m, 10 H), 4.05 (m, 1 H), 4.33 (t, J = 6.0 Hz, 2 H), 7.43 (m, 2 H), 7.55 (m, 1 H), 8.03 (d, J = 6.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 27.9, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.0, 40.1, 64.5, 126.7 (q, $J_{\text{C,F}}$ = 274 Hz), 128.4, 129.6, 130.8, 133.0, 166.6.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz).

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{IO}_2$: C, 43.50; H, 4.38. Found: C, 43.60; H, 4.42.

8,8,8-Trifluoro-5-iodooctyl 2-Methylbenzoate (3b)

Yield: 58.2 mg (68%); yellow oil.

IR (neat): 2951, 2864, 1717, 1603, 1577, 1449, 1393, 1293, 1255, 1144, 1083, 1053, 793, 696, 429 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.58–2.44 (m, 10 H), 2.60 (s, 3 H), 4.02–4.08 (m, 1 H), 4.30 (t, J = 6.0 Hz, 2 H), 7.21 (2 H), 7.38 (t, J = 8.0 Hz, 1 H), 7.89 (d, J = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.8, 26.2, 27.9, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 40.2, 64.3, 125.7, 126.9 (q, $J_{\text{C,F}}$ = 275 Hz), 129.7, 130.5, 131.7, 132.0, 140.1, 167.6.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz, 3 F).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{IO}_2$: 428.0460; found: 428.0459.

8,8,8-Trifluoro-5-iodooctyl 3-Methylbenzoate (3c)

Yield: 54.8 mg (64%); yellow oil.

IR (neat): 2950, 2865, 1719, 1604, 1508, 1449, 1393, 1276, 1197, 1153, 1118, 1091, 1015, 963, 855, 768, 688, 503 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.54–2.40 (m, 13 H), 4.02–4.09 (m, 1 H), 4.31 (t, J = 6.0 Hz, 2 H), 7.24–7.36 (m, 2 H), 7.81–7.84 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.3, 26.1, 27.8, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 40.1, 64.4, 126.7, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 128.3, 130.7, 130.2, 133.7, 138.1, 166.8.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{IO}_2$: 428.0460; found: 428.0465.

8,8,8-Trifluoro-5-iodooctyl 4-Methylbenzoate (3d)

Yield: 52.2 mg (61%); yellow oil.

IR (neat): 2950, 2864, 1717, 1612, 1508, 1449, 1393, 1275, 1110, 1076, 1021, 842, 755 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.55–2.43 (m, 13 H), 4.02–4.08 (m, 1 H), 4.30 (t, J = 6.0 Hz, 2 H), 7.22 (t, J = 8.0 Hz, 2 H), 7.91 (t, J = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.6, 26.1, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 40.1, 64.3, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 127.5, 129.1, 129.6, 143.6, 166.7.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{15}\text{H}_{20}\text{F}_3\text{IO}_2$: 428.0460; found: 428.0457.

8,8,8-Trifluoro-5-iodooctyl 2-Fluorobenzoate (3e)

Yield: 63.9 mg (74%); yellow oil.

IR (neat): 2950, 2865, 1728, 1614, 1585, 1489, 1457, 1393, 1299, 1253, 1197, 1130, 1085, 963, 692, 657 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.57–2.44 (m, 10 H), 4.03–4.08 (m, 1 H), 4.34 (t, J = 6.0 Hz, 2 H), 7.09–7.21 (m, 2 H), 7.48–7.53 (m, 1 H), 7.90–7.94 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 27.7, 32.7 (q, $J_{\text{C,F}}$ = 2.9 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 40.1, 64.8, 116.7 (d, $J_{\text{C,F}}$ = 23 Hz), 118.8 (d, $J_{\text{C,F}}$ = 10 Hz), 123.9 (d, $J_{\text{C,F}}$ = 5 Hz), 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 132.1, 134.4 (d, $J_{\text{C,F}}$ = 9 Hz), 161.9 (d, $J_{\text{C,F}}$ = 258 Hz), 164.5 (d, $J_{\text{C,F}}$ = 3 Hz).

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz, 3 F), –109.9 to –109.4 (m, 1 F).

Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{F}_4\text{IO}_2$: C, 41.69; H, 3.96. Found: C, 41.71; H, 3.93.

8,8,8-Trifluoro-5-iodooctyl 4-Fluorobenzoate (3f)

Yield: 61.3 mg (71%); yellow oil.

IR (neat): 2950, 2865, 1717, 1608, 1590, 1449, 1393, 1297, 1253, 1201, 1111, 1083, 963, 746, 684 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.55–2.46 (m, 10 H), 4.02–4.08 (m, 1 H), 4.31 (t, J = 6.0 Hz, 2 H), 7.07–7.12 (m, 2 H), 8.02–8.06 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 27.3, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 40.1, 64.6, 115.5 (d, $J_{\text{C,F}}$ = 22 Hz), 126.5 (d, $J_{\text{C,F}}$ = 3 Hz), 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 132.1 (d, $J_{\text{C,F}}$ = 7 Hz), 165.6, 165.8 (d, $J_{\text{C,F}}$ = 253 Hz).

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz, 3 F), –105.7 to –105.8 (m, 1 F).

Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{F}_4\text{O}_2$: C, 41.69; H, 3.96. Found: C, 41.90; H, 4.14.

8,8,8-Trifluoro-5-iodooctyl 4-Iodobenzoate (3g)

Yield: 42.3 mg (40%); yellow oil.

IR (neat): 2949, 1719, 1587, 1473, 1449, 1393, 1269, 1143, 1117, 1110, 1008, 846, 754 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.58–2.44 (m, 10 H), 4.01–4.07 (m, 1 H), 4.31 (t, J = 8.0 Hz, 2 H), 7.71–7.80 (m, 4 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 27.8, 32.8 (q, $J_{\text{C,F}}$ = 2.9 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 40.1, 64.7, 100.7, 126.6 (q, $J_{\text{C,F}}$ = 274 Hz), 129.8, 130.8, 137.8, 166.1.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{15}\text{H}_{17}\text{F}_3\text{I}_2\text{O}_2$: 539.9270; found: 539.9273.

8,8,8-Trifluoro-5-iodooctyl 3,4,5-Trifluorobenzoate (3h)

Yield: 65.5 mg (70%); yellow oil.

IR (neat): 3086, 2951, 2865, 1731, 1625, 1529, 1353, 1254, 1225, 1145, 1049, 889, 767 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.54–2.44 (m, 10 H), 4.02–4.08 (m, 1 H), 4.31 (t, J = 6.0 Hz, 2 H), 7.07–7.12 (m, 2 H), 8.02–8.06 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 26.0, 27.7, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 34.9, 40.0, 65.4, 114.0–114.3 (m), 126.1–126.3 (m), 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 144.6 (dt, J = 258, 15.3 Hz), 151.0 (ddd, J = 251, 10.2, 3.4 Hz), 163.8.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz, 3 F), –132.7 (m, 2 F), –152.6 to –152.7 (tt, J = 20.0, 7.5 Hz, 1 F).

Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{F}_6\text{IO}_2$: C, 38.48; H, 3.23. Found: C, 38.70; H, 3.31.

7,7,7-Trifluoro-4-iodoheptyl 4-Cyanobenzoate (3i)

Yield: 59.5 mg (70%); yellow oil.

IR (neat): 3079, 2957, 2854, 2232, 1724, 1641, 1610, 1570, 1449, 1394, 1276, 1108, 1073, 861, 546 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.84–2.46 (m, 8 H), 4.04–4.10 (m, 1 H), 4.38 (t, J = 8.0 Hz, 2 H), 7.74 (d, J = 8.0 Hz, 2 H), 8.12 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 28.8, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 37.2, 66.6, 116.6, 117.9, 126.6 (q, $J_{\text{C,F}}$ = 276 Hz), 130.1, 132.9, 133.9, 164.9.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z ($\text{M} - \text{I}$)⁺ calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NO}_2$: 298.1055; found: 298.1048.

8,8,8-Trifluoro-5-iodooctyl 4-Methoxybenzoate (3j)

Yield: 41.7 mg (47%); yellow oil.

IR (neat): 2952, 2841, 1712, 1607, 1581, 1511, 1257, 1168, 1143, 1031, 848, 771, 697, 613 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.53–2.43 (m, 10 H), 3.84 (s, 1 H), 4.02–4.08 (m, 1 H), 4.29 (t, J = 8.0 Hz, 2 H), 6.90 (d, J = 8.0 Hz, 2 H), 7.98 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 27.9, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.2, 40.1, 55.4, 64.1, 113.6, 126.7 (q, $J_{\text{C,F}}$ = 274 Hz), 122.7, 131.5, 163.4, 166.3.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{IO}_3$: 444.0409; found: 444.0407.

1-Chloro-4-[(7,7,7-trifluoro-4-iodoheptyloxy)benzene (3k)

Yield: 48.8 mg (60%); yellow oil.

IR (neat): 2949, 2873, 1581, 1597, 1492, 1473, 1247, 1006, 825, 668, 509 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.84–2.46 (m, 8 H), 3.94 (t, J = 6.0 Hz, 2 H), 4.02–4.06 (m, 1 H), 6.79 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 29.3, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 34.9, 37.3, 67.0, 115.7, 125.7, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 129.4, 157.4.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{13}\text{H}_{15}\text{ClF}_3\text{IO}$: 405.9808; found: 405.9805.

1-(tert-Butyl)-3-[(7,7,7-trifluoro-4-iodoheptyloxy)benzene (3l)

Yield: 53.9 mg (63%); yellow oil.

IR (neat): 2962, 2870, 1607, 1581, 1488, 1253, 1145, 1070, 972, 777, 701 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.29 (s, 9 H), 1.84–2.41 (m, 8 H), 3.98 (t, J = 6.0 Hz, 2 H), 4.08–4.15 (m, 1 H), 6.68 (d, J = 4.0 Hz, 1 H), 6.67–6.69 (m, 1 H), 6.97–6.99 (m, 1 H), 7.18–7.22 (m, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 29.4, 31.3, 32.9 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 34.8, 35.1, 37.4, 66.6, 110.5, 112.5, 118.1, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 129.0, 153.1, 158.6.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 9.4 Hz, 3 F).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{17}\text{H}_{24}\text{F}_3\text{IO}$: 428.0824; found: 428.0822.

1-(2-Phenylpropan-2-yl)-4-[(7,7,7-trifluoro-4-iodoheptyloxy)benzene (3m)

Yield: 51.9 mg (53%); yellow oil.

IR (neat): 3057, 2967, 2871, 1609, 1581, 1510, 1495, 1252, 1183, 1144, 1072, 830, 764, 771, 551 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.66 (s, 6 H), 1.86–2.47 (m, 8 H), 3.96 (q, 2 H), 4.08–4.13 (m, 1 H), 6.78 (d, J = 4.0 Hz, 2 H), 7.12–7.27 (m, 7 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 29.4, 30.9, 32.9 (q, $J_{\text{C,F}}$ = 2.9 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 35.1, 37.3, 42.3, 66.6, 113.8, 125.5, 126.69 (q, $J_{\text{C,F}}$ = 274 Hz), 126.70, 127.8, 127.9, 143.1, 150.9, 156.6.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{22}\text{H}_{26}\text{F}_3\text{IO}$: 490.0980; found: 490.0979.

Methyl {4-[(7,7,7-Trifluoro-4-iodoheptyloxy)phenyl] Sulfide (3n)

Yield: 49.3 mg (59%); yellow oil.

IR (neat): 2921, 2870, 1595, 1570, 1494, 1473, 1143, 1072, 822, 661, 515 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.84–2.46 (m, 11 H), 3.95 (t, J = 4.0 Hz, 2 H), 4.06–4.13 (m, 1 H), 6.81 (d, J = 4.0 Hz, 2 H), 7.24 (d, J = 4.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 18.0, 29.3, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 34.9, 37.3, 66.9, 115.2, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 128.1, 130.1, 157.4.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{IOS}$: 418.0075; found: 418.0074.

4-[(6,6,6-Trifluoro-3-iodohexyl)oxy]benzaldehyde (3o)

Yield: 29.3 mg (38%); yellow oil.

IR (neat): 2936, 2829, 2740, 1694, 1601, 1578, 1509, 1254, 1160, 1110, 1074, 1025, 832, 515 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.10–2.50 (m, 6 H), 4.21–4.32 (m, 3 H), 7.01 (d, J = 8.0 Hz, 2 H), 7.85 (d, J = 8.0 Hz, 2 H), 9.89 (s, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 29.4, 33.0 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 39.7, 67.5, 114.8, 126.6 (q, $J_{\text{C,F}}$ = 275 Hz), 130.3, 132.0, 163.5, 190.7.

^{19}F NMR (CDCl_3 , 376 MHz): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{IO}_2$: 385.9991; found: 385.9987.

2-[(6,6,6-Trifluoro-3-iodohexyl)oxy]naphthalene (3p)

Yield: 18.8 mg (23%); yellow solid; mp 74.0–78.8 °C.

IR (KBr): 3058, 2932, 2860, 1629, 1600, 1511, 1464, 1448, 1394, 1339, 1257, 1217, 1141, 1028, 840, 747, 719, 580 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 2.21–2.52 (m, 6 H), 4.18–4.41 (m, 3 H), 7.09–7.17 (m, 2 H), 7.33 (t, J = 7.4 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.69–7.78 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 31.1, 33.0 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.2 (q, $J_{\text{C,F}}$ = 29 Hz), 39.9, 67.1, 106.9, 118.7, 123.8, 126.5, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 126.8, 128.1, 129.1, 129.5, 134.5, 156.4.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{16}\text{H}_{16}\text{F}_3\text{IO}_2$: 408.0198; found: 408.0192.

1-Phenoxy-4-(5,5,5-trifluoro-2-iodopentyl)benzene (3q)

Yield: 33.6 mg (40%); yellow oil.

IR (neat): 3038, 2923, 2857, 1590, 1507, 1489, 1394, 1241, 1137, 1033, 966, 872, 843, 750, 692 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.93–2.04 (m, 2 H), 2.05–2.26 (m, 1 H), 2.38–2.51 (m, 1 H), 3.10–3.15 (m, 1 H), 3.25–3.22 (m, 1 H), 4.15–4.23 (m, 1 H), 6.94–7.02 (m, 4 H), 7.02–7.14 (m, 3 H), 7.31–7.35 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 31.6 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.3 (q, $J_{\text{C,F}}$ = 29 Hz), 34.7, 46.6, 118.8, 119.0, 123.4, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 129.8, 130.2, 133.7, 156.4, 157.0.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.8 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{IO}$: 420.1098; found: 420.1095.

4-(5,5,5-Trifluoro-2-iodopentyl)benzo[d][1,3]dioxole (3r)

Yield: 37.9 mg (51%); yellow oil.

IR (neat): 2895, 2778, 1609, 1505, 1490, 1445, 1393, 1251, 1139, 1041, 810, 735, 569 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.92–2.49 (m, 4 H), 3.02–3.08 (m, 1 H), 3.20–3.25 (m, 1 H), 4.09–4.20 (m, 1 H), 5.94 (s, 2 H), 6.61–6.65 (m, 2 H), 6.74–6.75 (m, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 31.5 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.6 (q, $J_{\text{C,F}}$ = 29 Hz), 34.9, 47.1, 101.1, 108.4, 109.1, 122.1, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 132.1, 146.7, 147.8.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.8 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{12}\text{H}_{12}\text{F}_3\text{IO}_2$: 371.9834; found: 371.9828.

N-(8,8,8-Trifluoro-5-iodoheptyl)phthalimide (3s)

Yield: 43.3 mg (51%); yellow oil.

IR (neat): 3064, 2938, 2859, 1772, 1709, 1640, 1616, 1438, 1397, 1142, 1074, 794, 720, 657, 530 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.69–2.43 (m, 8 H), 3.71 (t, J = 4.0 Hz, 2 H), 4.04–4.11 (m, 1 H), 7.69–7.73 (m, 2 H), 7.81–7.86 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 28.7, 32.9 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.23 (q, $J_{\text{C,F}}$ = 29 Hz), 34.25, 36.8, 37.6, 123.3, 126.7 (q, $J_{\text{C,F}}$ = 274 Hz), 132.0, 134.1, 168.4.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{INO}_2$: 425.0100; found: 425.0103.

9-(7,7,7-Trifluoro-4-iodoheptyl)-9H-carbazole (3t)

Yield: 48.9 mg (55%); yellow solid; mp 52.0–54.6 °C.

IR (KBr): 3050, 2951, 2900, 2853, 1626, 1594, 1483, 1463, 1089, 1144, 754, 558 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.68–2.36 (m, 10 H), 3.91–3.97 (m, 1 H), 3.71 (t, J = 8.0 Hz, 2 H), 7.21–7.28 (m, 2 H), 7.36–7.42 (m, 2 H), 7.43–7.51 (m, 2 H), 8.11 (d, J = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 29.0, 32.8 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.1 (q, $J_{\text{C,F}}$ = 29 Hz), 34.7, 38.0, 41.9, 108.5, 119.0, 120.4, 122.9, 125.8, 126.6 (q, $J_{\text{C,F}}$ = 274 Hz), 140.2.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 9.4 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{IN}$: 445.0514; found: 445.0520.

2-[(7,7,7-Trifluoro-4-iodoheptyl)thio]benzo[d]thiazole (3u)

Yield: 53.4 mg (60%); yellow oil.

IR (neat): 2920, 2850, 1559, 1457, 1428, 1394, 1310, 1096, 1075, 1018, 995, 757, 727 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 1.89–2.44 (m, 8 H), 3.38 (t, J = 8.0 Hz, 2 H), 4.05–4.11 (m, 1 H), 7.26–7.30 (m, 1 H), 7.38–7.42 (m, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.85 (d, J = 12.0 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 29.3, 32.3, 32.6 (q, $J_{\text{C,F}}$ = 2.7 Hz), 34.1 (q, $J_{\text{C,F}}$ = 29 Hz), 34.4, 39.3, 121.0, 121.5, 124.3, 126.1, 126.7 (q, $J_{\text{C,F}}$ = 275 Hz), 135.2, 153.2, 166.4.

^{19}F NMR (376 MHz, CDCl_3): δ = –65.9 (t, J = 11.3 Hz).

HRMS (EI): m/z (M^+) calcd for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{INS}_2$: 444.9643; found: 444.9640.

Radical Addition of 2,2,2-Trifluoro-1-iodoethane (1) to Silyl Enol Ethers 4; General Procedure

A 10 mL Schlenk tube was charged with the appropriate silyl enol ether **4** (0.2 mmol) and *fac*-Ir(ppy)₃ (1.3 mg, 0.002 mmol). The tube was then evacuated and backfilled with N₂ (3 times). 1,1,1-Trifluoro-2-iodoethane (**1**; 126 mg, 0.6 mmol) and *i*-Pr₂NEt (77 mg, 0.6 mmol) were added to the Schlenk tube subsequently under N₂ atmosphere. The reaction was irradiated by a 24 W fluorescence lamp for 48 h at r.t. The mixture was evaporated under vacuum. The residue was separated by column chromatography on silica gel (PE-CH₂Cl₂, 5:1 v/v) to afford the desired product.

1-([1,1'-Biphenyl]-4-yl)-4,4,4-trifluorobutan-1-one (5a)

Yield: 27.2 mg (49%); white solid; mp 121.3–123.4 °C.

IR (KBr): 3036, 2917, 1682, 1440, 1263, 1139, 759 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.57–2.64 (m, 2 H), 3.28 (t, *J* = 7.8 Hz, 2 H), 7.38–7.49 (m, 3 H), 7.61–7.63 (m, 2 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 8.03 (d, *J* = 8.4 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 28.4 (q, *J* = 30 Hz), 31.3 (q, *J* = 2.6 Hz), 127.2 (q, *J* = 276 Hz), 127.3, 127.4, 128.4, 128.6, 129.0, 134.8, 139.7, 146.3, 195.9.

¹⁹F NMR (376 MHz, CDCl₃): δ = -66.4 (t, *J* = 10.9 Hz).

HRMS (EI): *m/z* (M⁺) calcd for C₁₆H₁₃F₃O: 278.0918; found: 278.0921.

1-(2,4-Dimethylphenyl)-4,4,4-trifluorobutan-1-one (5b)

Yield: 27.2 mg (59%); pale yellow oil.

IR (neat): 2964, 1686, 1442, 1259, 1135, 820 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.35 (s, 3 H), 2.49 (s, 3 H), 2.50–2.60 (m, 2 H), 3.16 (t, *J* = 7.6 Hz, 2 H), 7.07 (s, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.4, 21.7, 28.6 (q, *J* = 29 Hz), 33.3 (q, *J* = 2.6 Hz), 126.5, 127.3 (q, *J* = 276 Hz), 129.2, 133.2, 133.7, 139.3, 142.7, 199.0.

¹⁹F NMR (376 MHz, CDCl₃): δ = -66.4 (t, *J* = 10.9 Hz).

HRMS (EI): *m/z* (M⁺) calcd for C₁₂H₁₃F₃O: 230.0918; found: 230.0914.

4,4,4-Trifluoro-1-(3-methoxyphenyl)butan-1-one (5c)

Yield: 28.3 mg (61%); pale yellow oil.

IR (KBr): 2962, 1690, 1432, 1253, 1138, 821 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.51–2.63 (m, 2 H), 3.23 (t, *J* = 7.8 Hz, 2 H), 3.84 (s, 3 H), 7.12 (d, *J* = 8.2 Hz, 1 H), 7.38 (t, *J* = 7.8 Hz, 1 H), 7.47 (s, 1 H), 7.53 (d, *J* = 7.5 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 28.4 (q, *J* = 30 Hz), 31.3 (q, *J* = 2.6 Hz), 55.5, 112.3, 120.4, 120.6, 127.1 (q, *J* = 276 Hz), 129.8, 137.5, 160.0, 196.2.

¹⁹F NMR (376 MHz, CDCl₃): δ = -66.5 (t, *J* = 10.9 Hz).

HRMS (EI): *m/z* (M⁺) calcd for C₁₁H₁₁F₃O₂: 232.0711; found: 232.0709.

1-(4-Chlorophenyl)-4,4,4-trifluorobutan-1-one (5d)

Yield: 18.5 mg (39%); pale yellow solid; mp 62.5–64.2 °C.

IR (KBr): 2966, 1686, 1440, 1258, 1136, 826 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.53–2.61 (m, 2 H), 3.21 (t, *J* = 7.6 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 7.90 (d, *J* = 8.6 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 28.3 (q, *J* = 30 Hz), 31.2 (q, *J* = 2.7 Hz), 127.1 (q, *J* = 276 Hz), 129.1, 129.4, 134.4, 140.1, 195.1.

¹⁹F NMR (376 MHz, CDCl₃): δ = -66.5 (t, *J* = 10.9 Hz).

HRMS (EI): *m/z* (M⁺) calcd for C₁₀H₈ClF₃O: 236.0216; found: 236.0217.

4,4,4-Trifluoro-1-(1-tosyl-1*H*-indol-3-yl)butan-1-one (5e)

Yield: 19.8 mg (25%); pale yellow solid; mp 148.7–151.6 °C.

IR (KBr): 2955, 1678, 1448, 1279, 1131, 750 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.36 (s, 3 H), 2.54–2.66 (m, 2 H), 3.18 (t, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.31–7.39 (m, 2 H), 7.83 (d, *J* = 8.2 Hz, 2 H), 7.92 (d, *J* = 7.5 Hz, 1 H), 8.24 (s, 1 H), 8.28 (d, *J* = 7.5 Hz, 1 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 28.1 (q, *J* = 30 Hz), 31.3 (q, *J* = 2.6 Hz), 113.2, 120.5, 123.0, 125.0, 126.0, 127.1 (q, *J* = 276 Hz), 127.2, 127.4, 130.3, 131.8, 134.5, 134.9, 146.1, 191.8.

¹⁹F NMR (376 MHz, CDCl₃): δ = -66.4 (t, *J* = 10.9 Hz).

HRMS (EI): *m/z* (M⁺) calcd for C₁₉H₁₆F₃NO₃S: 395.0803; found: 395.0805.

4,4,4-Trifluoro-1-phenylbutan-1-one (5f)

Yield: 16.6 mg (41%); pale yellow solid; mp 54.6–56.2 °C.

IR (KBr): 2964, 1686, 1450, 1262, 1127, 750 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.54–2.64 (m, 2 H), 3.25 (t, *J* = 7.6 Hz, 2 H), 7.45–7.49 (m, 2 H), 7.56–7.80 (m, 1 H), 7.96 (d, *J* = 7.8 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 28.4 (q, *J* = 30 Hz), 31.2 (q, *J* = 2.6 Hz), 127.1 (q, *J* = 276 Hz), 128.0, 128.8, 133.6, 136.1, 196.3.

¹⁹F NMR (376 MHz, CDCl₃): δ = -66.5 (t, *J* = 10.9 Hz).

HRMS (EI): *m/z* (M⁺) calcd for C₁₀H₉F₃O: 202.0605; found: 202.0608.

4,4,4-Trifluoro-1-[4-(trifluoromethyl)phenyl]butan-1-one (5g)

Yield: 18.9 mg (35%); pale yellow solid; mp 57.5–59.6 °C.

IR (KBr): 2931, 1690, 1446, 1260, 1140, 840 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.55–2.63 (m, 2 H), 3.27 (t, *J* = 7.8 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 8.06 (d, *J* = 8.2 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 28.2 (q, *J* = 30 Hz), 31.6 (q, *J* = 2.6 Hz), 123.4 (q, *J* = 272 Hz), 125.9 (q, *J* = 3.7 Hz), 126.9 (q, *J* = 276 Hz), 128.4, 135.0 (q, *J* = 33 Hz), 138.7, 195.4.

¹⁹F NMR (376 MHz, CDCl₃): δ = -63.2 (s, 3 F), -66.5 (t, *J* = 10.9 Hz, 3 F).

HRMS (EI): *m/z* (M⁺) calcd for C₁₁H₈F₆O: 270.0479; found: 270.0481.

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Supporting Information

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