Supporting Information for

Direct C–H trifluoromethylation of di- and trisubstituted alkenes by photoredox catalysis

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Experimental procedures and NMR spectra

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Materials and methods

[Ru(bpy)₃](PF₆)₂[1] and fac-Ir(ppy)₃[2] were prepared according to the literature procedures. Umemoto’s reagent (1a) was purchased from Aldrich. Alkenes 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2j, and 2k were prepared by Wittig reactions. (E)-1,2-diphenyl-1-(4-methoxyphenyl)ethylene (2m) prepared according to the literature procedure[3]. Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. All solvents were dried over molecular sieves, degassed and stored under N₂. Thin-layer chromatography was performed on Merck TLC plate with 60 F₂₅₄. Visible light irradiations were performed with a Relyon LED lamp (3 W x 2; λ_max = 425 ± 15 nm). Japan Analytical Industry LC-9201 was utilized for recycling preparative HPLC (GPC). The ¹H NMR was acquired on Bruker AVANCE-400 (400 MHz). NMR chemical shifts were referenced to residual protio impurities in the deuterated solvent. HRMS (ESI-TOF mass spectra) were obtained with a Bruker micrOTOF II.

Reaction apparatus

Irradiation of visible light was performed with a Relyon LED lamp (3 W x 2; λ_max = 425 nm).

Figure S1: The emission spectrum of a Relyon LED lamp.
Synthesis of alkene 2

General procedure for the synthesis of alkenes (2b, 2c, 2d, 2e, 2g, 2h, 2j and 2k) by Wittig reaction

\[ \text{O} \begin{array}{c} \text{R}^1 \end{array} \begin{array}{c} \text{R}^2 \end{array} \xrightarrow{\text{NaHMS, THF}} \begin{array}{c} \text{Ph}^3-\text{CH}^2-\text{R} \end{array} \begin{array}{c} \text{Br} \end{array} \xrightarrow{\text{Et}_2\text{O}} \begin{array}{c} \text{R}^1 \end{array} \begin{array}{c} \text{R}^2 \end{array} \]

Under N\(_2\), a 2-neck 100 mL round-bottom flask was charged with Wittig reagent (6 mmol) and dry THF (25 mL). Then sodium hexamethyldisilazide (1 M THF solution, 6 mL) was added into the solution and stirred at room temperature for 1 h. To the solution, benzophenone derivative (5 mmol) was added and stirred at room temperature overnight. Et\(_2\)O was added into the reaction mixture and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford the product.

The synthesis of \(N-(\text{tert-butoxycarbonyl})-4-(1\text{-phenylvinyl})\text{aniline (2f)}\)

\[ \text{O} \begin{array}{c} \text{Boc}^\text{-O} \end{array} \xrightarrow{\text{dioxane reflux}} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{H} \end{array} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{Boc} \end{array} \xrightarrow{\text{NaHMS, THF}} \begin{array}{c} \text{Ph}^3-\text{P} \end{array} \begin{array}{c} \text{Me} \end{array} \begin{array}{c} \text{Br} \end{array} \xrightarrow{\text{reflux}} \begin{array}{c} \text{N} \end{array} \begin{array}{c} \text{H} \end{array} \begin{array}{c} \text{Boc} \end{array} \]

\(N-(\text{tert-Butoxycarbonyl})\text{-4-benzoylaniline:}\) A 2-neck 100 mL round-bottom flask was charged with 4-aminobenzophenone (1.97 g, 10 mmol), di-\(\text{tert}\)-butyl dicarbonate (2.84 g, 13 mmol), and 1,4-dioxane (30 mL). The solution was refluxed overnight and cooled to room temperature. The reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford \(N-(\text{tert-butoxycarbonyl})\text{-4-benzoylaniline (1.35 g, 46% yield)}\).

\(N-(\text{tert-Butoxycarbonyl})\text{-4-(1-phenylvinyl)aniline (2f):}\) Under N\(_2\), a 2-neck 100 mL round-bottom flask was charged with methyltriphenylphosphonium bromide (1.07 g, 3 mmol) and dry THF (15 mL). Then sodium hexamethyldisilazide (1 M THF solution, 3 mL) was added into the solution and stirred at room temperature for 1 h. To the yellow solution, \(N-(\text{tert-butoxycarbonyl})\text{-4-benzoylaniline (0.53 g, 1.8 mmol)}\) was added and refluxed overnight. After cooling to room temperature, Et\(_2\)O was added into the reaction mixture and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 4:1) to afford \(N-(\text{tert-butoxycarbonyl})\text{-4-(1-phenylvinyl)aniline (0.23 g, 44% yield)}\).

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\), rt): \(\delta 7.34-7.26\) (m, 9 H, Ar), \(6.48\) (brs, 1 H, NH), \(5.41\) (d, \(J = 1.2\) Hz, C=CH\(_2\)), \(5.38\) (d, \(J = 1.2\) Hz, C=CH\(_2\)), \(1.53\) (s, 9 H, C(CH\(_3\))\(_3\)). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\), rt): \(\delta 152.8, 149.6, 141.7, 138.1, 136.4, 129.0, 128.4, 128.3, 127.8, 118.3, 113.6, 80.7,\)
28.5. **HRMS** (ESI-TOF): calculated for \([C_{19}H_{21}NO_2+Na]^+\) requires 318.1465, found 318.1464.

**Typical NMR experimental procedures and NMR spectra**

**NMR experimental procedure (entry 1 in Table 1)**

Under \(N_2\), \(\text{fac-Ir(ppy)}_3\) (0.8 mg, 1.3 \(\mu\)mol), Umemoto’s reagent (1a, 8.5 mg, 25 \(\mu\)mol), \(K_2\text{HPO}_4\) (8.7 mg, 50 \(\mu\)mol), 1,1-diphenylethylene (2a, 4.3 \(\mu\)L, 25 \(\mu\)mol), \(\text{SiEt}_4\) (~1 \(\mu\)L) as an internal standard, and \([D_6]-\text{DMSO}\) (0.5 mL) were added to an NMR tube. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from a blue LED lamp: \(h\nu = 425 \pm 15 \text{ nm}\)).

**NMR experimental procedure (entry 8 in Table 1) and NMR spectra**

Under \(N_2\), \([\text{Ru(bpy)}_3]\text{(PF}_6\text{)}_2\) (1.1 mg, 1.3 \(\mu\)mol), Umemoto’s reagent (1a) (8.5 mg, 25 \(\mu\)mol), 1,1-diphenylethylene (2a) (4.3 \(\mu\)L, 25 \(\mu\)mol), \(\text{SiEt}_4\) (~1 \(\mu\)L) as an internal standard, and \([D_6]-\text{DMSO}\) (0.5 mL) were added to an NMR tube. The reaction was carried out at room temperature (water bath) under irradiation of visible light (placed at a distance of ~3 cm from blue LED lamp: \(h\nu = 425 \pm 15 \text{ nm}\)).
General procedure for the photocatalytic C–H trifluoromethylation of alkenes (Table 2, 3a–e, g–m)

A 20 mL-Schlenk tube was charged with Umemoto’s reagent (1a, 102 mg, 0.3 mmol, 1.2 equiv.), [Ru(bpy)3](PF6)2 (4.3 mg, 2 mol %), alkene 2 (0.25 mmol), and DMSO (2.5 mL) under N2. The tube was irradiated for 2 h at room temperature (water bath) with stirring by 3 W blue LED lamps ($h\nu = 425 \text{ nm} \pm 15 \text{ nm}$) placed at a distance of 2–3 cm. After the reaction, H2O was added. The resulting mixture was extracted with Et2O, washed with H2O, dried (Na2SO4), and filtered. The filtrate was concentrated in vacuo. The product was purified in two ways as described below.

For products 3b, 3e, 3g, 3h, 3k and 3m, the residue was purified by flash column chromatography on silica gel (eluent: hexane and Et2O) to afford the corresponding product 3.

For products 3a, 3c, 3d, 3i, 3j and 3l, the residue was treated by mCPBA (74 mg, ca. 0.3 mmol)
in CH₂Cl₂ to convert the dibenzothiophene to sulfoxide, which was more easily separated from the products. After the solution was stirred at room temperature for 2 h, an aqueous solution of Na₂S₂O₃·5H₂O was added to the solution, which was extracted with CH₂Cl₂. The organic layer was washed with H₂O, dried (Na₂SO₄), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent: hexane) to afford the corresponding product 3. Further purification of 3c and 3d by GPC provided pure 3c and 3d. 3a[4], 3b[5], 3e[5], 3j[6], 3l[7] and 3m[7] were confirmed by published data.

1,1-Bis(4-chlorophenyl)-3,3,3-trifluoropropene (3c)

According to the general procedure, the title compound was synthesized from 1,1-bis(4-chlorophenyl)ethylene (2c, 62 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane) to afford 3c (82%) as a product mixture with bis(trifluoromethyl)alkene 4c (8%). The yields were determined by ¹⁹F NMR using α,α,α-trifluorotoluene as an internal standard. Further purification by GPC provided pure 3c in 53% isolated yield.

¹H NMR (400 MHz, CDCl₃, rt): δ 7.38 (d, J = 8.8 Hz, 2 H, Ar), 7.32 (d, J = 8.8 Hz, 2 H, Ar), 7.16 (d, J = 8.4 Hz, 4 H, Ar), 6.12 (q, J = 8.1 Hz, 1 H, C=CCH₃). ¹³C NMR (100 MHz, CDCl₃, rt): δ 150.4 (q, J = 5.4 Hz), 138.3, 136.1, 135.3, 135.2, 130.6, 129.3, 129.0, 128.7, 122.9 (q, J = 269 Hz), 116.5 (q, J = 33.9 Hz). ¹⁹F NMR (376.5 MHz, CDCl₃, rt): δ -55.76 (d, J = 7.9 Hz, 3 F). HRMS (ESI-TOF): calculated for [C₁₅H₉Cl₂F₃+Na]⁺ requires 338.9926, found 338.9967.

1,1-Bis(4-bromophenyl)-3,3,3-trifluoropropene (3d)

According to the general procedure, the title compound was synthesized from 1,1-bis(4-bromophenyl)ethylene (2d, 85 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane) to afford 3d (84%) as a product mixture with bis(trifluoromethyl)alkene 4d (6%). The yields were determined by ¹⁹F NMR using α,α,α-trifluorotoluene as an internal standard. Further purification by GPC provided pure 3d in
70% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$, rt): $\delta$ 7.54 (d, $J = 8.4$ Hz, 2 H, Ar), 7.47 (d, $J = 8.4$ Hz, 2 H, Ar), 7.10 (d, $J = 8.4$ Hz, 4 H, Ar), 6.12 (q, $J = 8.1$ Hz, 1 H, C=CHCF$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, rt): $\delta$ 150.4 (q, $J = 5.4$ Hz), 138.6, 135.7, 132.0, 131.7, 130.9, 129.6, 124.3, 123.4, 122.9 (q, $J = 269$ Hz), 116.5 (q, $J = 34.0$ Hz). $^{19}$F NMR (376.5 MHz, CDCl$_3$, rt): $\delta$ -55.72 (d, $J = 7.91$ Hz, 3 F).

HRMS (ESI-TOF): calculated for [C$_{15}$H$_9$Br$_2$F$_3$+Na]$^+$ requires 426.8915, found 426.9055.

$N$-(tert-Butoxycarbonyl)-4-(1-phenyl-3,3,3-trifluoropropenyl)aniline (3f)

![Chemical structure](image)

A 20 mL-Schlenk tube was charged with Umemoto’s reagent (1a, 102 mg, 0.3 mmol, 1.2 equiv.), [Ru(bpy)$_3$](PF$_6$)$_2$ (4.3 mg, 2 mol %), $N$-(tert-butoxycarbonyl)-4-(1-phenylvinyl)aniline (2f, 74 mg, 0.25 mmol), 2,6-lutidine (58 $\mu$L, 0.5 mmol, 2 equiv) and DMSO (2.5 mL) under N$_2$. The tube was irradiated for 2 h at room temperature (water bath) with stirring by 3 W blue LED lamps ($h\nu = 425$ nm $\pm 15$ nm) placed at a distance of 2−3 cm. After the reaction, H$_2$O was added. The resulting mixture was extracted with Et$_2$O, washed with H$_2$O, dried (Na$_2$SO$_4$), and filtered. The filtrate was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane→hexane/EtOAc = 9 :1) to afford 3f (60 mg, 59% yield, $E/Z = 91:9$) as a product mixture with bis(trifluoromethyl)alkene 4f (21%). The yields were determined by $^{19}$F NMR using $\alpha,\alpha,\alpha$-trifluorotoluene as an internal standard. Further purification by GPC provided pure 3f in 37% isolated yield. The stereochemistry was confirmed by $^1$H NOESY NMR.

$^1$H NMR (400 MHz, CDCl$_3$, rt): $\delta$ 7.38 (m, 3 H, Ar), 7.32 (d, $J = 8.8$ Hz, 2 H, Ar), 7.22 (m, 2H, Ar), 7.17 (d, $J = 8.4$ Hz, 2 H, Ar), 6.53 (brs, 1 H, NH), 6.08 (q, $J = 8.4$ Hz, 1 H, C=CHCF$_3$ in E-isomer), 6.06 (q, $J = 8.0$ Hz, 1 H, C=CHCF$_3$ in Z-isomer), 1.53 (s, 9 H, C(CH$_3$)$_3$ in Z-isomer), 1.52 (s, 9 H, C(CH$_3$)$_3$ in E-isomer). $^{13}$C NMR (100 MHz, CDCl$_3$, rt): $\delta$ 152.6, 152.0 (q, $J = 5.3$ Hz), 139.8, 137.5, 134.7, 129.3, 128.9, 128.6, 128.1, 123.4 (q, $J = 269$ Hz), 118.32, 114.2 (q, $J = 33.6$ Hz), 81.1, 28.4. $^{19}$F NMR (376.5 MHz, CDCl$_3$, rt): $\delta$ -55.32 (d, $J = 8.28$ Hz, 3 F, E-isomer), -55.56 (d, $J = 9.04$ Hz, 3 F, Z-isomer). HRMS (ESI-TOF): calculated for [C$_{20}$H$_{20}$F$_3$NO$_2$+Na]$^+$ requires 386.1338, found 386.1332.
3,3,3-Trifluoro-1-(4-nitrophenyl)-1-phenylpropene (3g)

According to the general procedure, the title compound was synthesized from 1-(4-nitrophenyl)-1-phenylethylene (2g, 56 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane→hexane/Et₂O = 19:1) to afford 3g (39 mg, 51% yield, E/Z = 17:83). The stereochemistry was confirmed by ¹H NOESY NMR.

¹H NMR (400 MHz, CDCl₃, rt): δ 8.27 (d, J = 8.8 Hz, 2 H, Ar in Z-isomer), 8.19 (d, J = 8.8 Hz, 2 H, Ar in E-isomer), 7.45-7.35 (m, 5 H, Ar), 7.21 (d, J = 8.0 Hz, 2 H, Ar), 6.25 (q, J = 8.1 Hz, 1 H, C=C in Z-isomer), 6.22 (q, J = 8.0 Hz, 1 H, C=C in E-isomer). ¹³C NMR (100 MHz, CDCl₃, rt): δ 150.4 (q, J = 5.4 Hz), 148.5, 148.2, 146.4, 144.1, 138.7, 136.1, 130.3, 130.2, 129.3, 129.1, 129.0, 128.6, 127.9, 123.9, 123.5, 122.8 (q, J = 269 Hz), 118.6 (q, J = 33.8 Hz, E-isomer), 171.7 (q, J = 34.0 Hz, Z-isomer). ¹⁹F NMR (376.5 MHz, CDCl₃, rt): δ -55.72 (d, J = 8.28 Hz, 3 F, Z-isomer), -56.23 (d, J = 8.00 Hz, 3 F, E-isomer). HRMS (ESI-TOF): calculated for [C₁₅H₁₀F₃NO₂+Na]⁺ requires 316.0556, found 316.0553.

3,3,3-Trifluoro-1-phenyl-1-(3-pyridyl)propene (3h)

According to the general procedure, the title compound was synthesized from 1-phenyl-1-(3-pyridyl)ethylene (2h) (45 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane→hexane/Et₂O = 1:1) to afford 3h (48 mg, 78% yield, E/Z = 33:67). The stereochemistry was confirmed by ¹H NOESY NMR.

¹H NMR (400 MHz, CDCl₃, rt): δ 8.66 (dd, J = 4.8, 1.6 Hz, 1H, Ar in Z-isomer), 8.60 (dd, J = 4.8, 1.2 Hz, 1H, Ar in E-isomer), 8.56 (d, J = 2.0 Hz, 1 H, Ar in E-isomer), 8.52 (d, J = 1.6 Hz, 1H, Ar in Z-isomer), 7.57 (d, J = 7.8 Hz, 1 H, Ar in Z-isomer), 7.51 (d, J = 8.1 Hz, 1 H, Ar in E-isomer), 7.42-7.33 (m, 3 H, Ar), 7.28-7.22 (m, 2 H, Ar), 6.23 (q, J = 8.1 Hz, 1 H, C=CHCF₃ in Z-isomer) 6.16 (q, J = 8.0 Hz, 1 H, C=CHCF₃ in E-isomer). ¹³C NMR (100 MHz, CDCl₃, rt): δ 150.5, 149.9, 149.6, 149.1 (q, J = 5.3 Hz), 148.8, 139.3, 136.6, 136.3, 136.0, 135.4, 133.3, 130.0, 129.1, 128.9, 128.5, 128.0, 123.4, 123.1, 122.9 (q, J = 269 Hz, Z-isomer), 122.8 (q, J = 270 Hz, E-isomer), 117.3 (q, J = 33.4 Hz, Z-isomer), 116.9 (q, J = 33.3 Hz, E-isomer). ¹⁹F NMR
(376.5 MHz, CDCl3, rt): δ -55.58 (d, J = 8.28 Hz, 3 F, Z-isomer), -55.99 (d, J = 8.28 Hz, 3 F, E-isomer). **HRMS** (ESI-TOF): calculated for [C14H10F3N+Na]⁺ requires 272.0658, found 272.0657.

1,1,1-Trifluoro-3,5-diphenyl-5-methyl-2-hexene (3i)

According to the general procedure, the title compound was synthesized from 2,4-diphenyl-4-methyl-1-pentene (2i, 59 mg, 0.25 mmol). The product was purified by silica gel flash column chromatography (hexane) to afford 3i (45 mg, 58% yield, E/Z = 88:12). The stereochemistry was confirmed by ¹H NOESY NMR.

**¹H NMR** (400 MHz, CDCl₃, rt): δ 7.21-7.10 (m, 9 H, Ar), 7.06 (t, J = 7.0 Hz, Ar), 5.66 (q, J = 8.8 Hz, 1 H, C=CHCF₃ in E-isomer), 5.37 (q, J = 8.4 Hz, 1 H, C=CHCF₃ in Z-isomer), 3.09 (d, J = 1.2 Hz, 2 H, CCH₂C in E-isomer), 5.66 (q, J = 8.8 Hz, 1 H, C=CHCF₃ in Z-isomer), 1.24 (s, 6 H, CH₃ in Z-isomer), 1.21 (s, 6 H, CH₃ in E-isomer).

**¹³C NMR** (100 MHz, CDCl₃, rt): δ 152.7 (q, J = 5.4 Hz), 149.3, 141.8, 128.3, 128.0, 127.0, 125.8, 125.7, 123.4 (q, J = 269 Hz), 119.6 (q, J = 33.1 Hz), 44.5, 38.4, 28.8. **¹⁹F NMR** (376.5 MHz, CDCl₃, rt): δ -55.87 (d, J = 9.41 Hz, 3 F, E-isomer), -55.96 (d, J = 9.41 Hz, 3 F, E-isomer).

**HRMS** (ESI-TOF): calculated for [C₁₉H₁₉F₃+Na]⁺ requires 327.1331, found 327.1332.

3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-methyl-1-phenylpropene (3k)

According to the general procedure, the title compound was synthesized from 1-methoxyphenyl-1-phenylpropene (2k). The product was purified by silica gel flash column chromatography (hexane→hexane/Et₂O = 29:1) to afford 3k (45 mg, 59% yield, E/Z = 74:26). The stereochemistry was confirmed by ¹H NOESY NMR.

**¹H NMR** (400 MHz, CDCl₃, rt): δ 7.34-7.27 (m, 3 H, Ar), 7.14 (d, J = 9.6 Hz, 2 H, Ar in E-isomer), 7.12 (d, J = 8.4 Hz, 2 H, Ar in Z-isomer), 7.08 (d, J = 8.8 Hz, 2 H, Ar in Z-isomer), 7.05 (d, J = 8.8 Hz, 2 H, Ar in E-isomer), 6.85 (d, J = 8.8 Hz, 2 H, Ar in E-isomer), 6.82 (d, J = 8.8 Hz, 2 H, Ar in Z-isomer), 3.80 (s, 3 H, CH₂O in E-isomer), 3.79 (s, 3 H, CH₂O in Z-isomer), 3.78 (s, 3 H, CH₂O in Z-isomer), 3.78 (s, 3 H, CH₂O in E-isomer), 3.77 (s, 3 H, CH₂O in Z-isomer), 3.76 (s, 3 H, CH₂O in E-isomer), 3.75 (s, 3 H, CH₂O in Z-isomer).
1.96 (s, 3 H, CH₂CCF₃ in E-isomer), 1.90 (s, 3 H, CH₂CCF₃ in Z-isomer). ¹³C NMR (100 MHz, CDCl₃, rt): δ 159.3, 159.3, 147.3, 147.3, 141.8, 141.4, 133.7, 133.4, 130.5, 130.0, 129.0, 128.7, 128.4, 128.0, 127.8, 127.6, 124.8 (q, J = 274 Hz), 123.0 (q, J = 27.9 Hz), 113.8, 113.5, 55.4, 55.3, 16.5. ¹⁹F NMR (376.5 MHz, CDCl₃, rt): δ -59.23 (s, 3 F, E-isomer), -59.36 (s, 3 F, Z-isomer). HRMS (ESI-TOF): calculated for [C₁₇H₁₅F₃O⁺Na]⁺ requires 315.0967, found 315.0963.

Procedures for the photocatalytic double C–H trifluoromethylation of alkenes

2-Trifluoromethyl-3,3,3-trifluoro-1-bis(4-methoxyphenyl)propene (4b)

A 20 mL-Schlenk tube was charged with Umemoto’s reagent (1a, 340 mg, 1.0 mmol, 4 equiv), [Ru(bpy)₃](PF₆)₂ (10.7 mg, 5 mol %), 2b (60 mg, 0.25 mmol), and DMSO (5 mL) under N₂. The tube was irradiated for 3 h at room temperature (water bath) with stirring by 3 W blue LED lamps (hv = 425 nm ± 15 nm) placed at a distance of 2−3 cm. After the reaction, H₂O was added. The resulting mixture was extracted with Et₂O, washed with H₂O, dried (Na₂SO₄), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane→hexane/Et₂O = 29:1) to afford 4b as a product mixture with 3b. Further purification by GPC provided pure 4b in 44% isolated yield. ¹H NMR (400 MHz, CDCl₃, rt): δ 7.09 (d, J = 8.8 Hz, 4 H, Ar), 6.87 (d, J = 8.8 Hz, 4 H, Ar), 3.83 (s, 6 H, CH₃O). ¹³C NMR (100 MHz, CDCl₃, rt): δ 161.3, 160.1, 132.3, 131.2, 122.3, (q, J = 273 Hz), 115.7 (q, J = 30.1 Hz), 113.7, 55.4. ¹⁹F NMR (376.5 MHz, CDCl₃, rt): δ -54.80 (s, 6 F). HRMS (ESI-TOF): calculated for [C₁₈H₁₄F₆O₂⁺Na]⁺ requires 399.0790, found 399.0795.

1-Bis(4-bromophenyl)-2-trifluoromethyl-3,3,3-trifluoropropene (4d)

Two-step reactions were conducted. According to the procedure in Table 2, 2d (85 mg, 0.25 mmol) was converted into the mixture of 3d and a small amount of 4d (90 mg). To the mixture, Umemoto’s reagent (1a, 238 mg), [Ru(bpy)₃](PF₆)₂ (4.3 mg) and DMSO (5 mL) were added under N₂. The solution was placed at a distance of 2−3 cm from the 3 W blue LED lamp (hv =
425 nm ± 15 nm) and stirred at room temperature (water bath) for 2 h. After the reaction, H$_2$O was added. The resulting mixture was extracted with Et$_2$O, washed with H$_2$O, dried (Na$_2$SO$_4$), and filtered. The filtrate was concentrated in vacuo. The residue was treated by mCPBA (0.17 g, ca. 0.7 mmol) in CH$_2$Cl$_2$ to convert the dibenzo thiophene to sulfoxide, which was more easily separated from the products. After the solution was stirred at room temperature for 2 h, an aqueous solution of Na$_2$S$_2$O$_3$·5H$_2$O was added to the solution, which was extracted with CH$_2$Cl$_2$. The organic layer was washed with H$_2$O, dried (Na$_2$SO$_4$), and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel (eluent: hexane) to afford 4d as a product mixture with 3d. Further purification by GPC provided pure 4d in 36% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$, rt): $\delta$ 7.51 (d, $J = 8.4$ Hz, 4 H, Ar), 7.01 (d, $J = 8.4$ Hz, 4 H, Ar).

$^{13}$C NMR (100 MHz, CDCl$_3$, rt): $\delta$ 157.9, 137.7, 131.9, 130.3, 124.9, 121.5 (q, $J = 276$ Hz), 119.4 (q, $J = 31.0$ Hz).

$^{19}$F NMR (376.5 MHz, CDCl$_3$, rt): $\delta$ -55.31 (s, 6 F).

HRMS (ESI-TOF): calculated for [C$_{16}$H$_8$Br$_2$F$_6$+Na]$^+$ requires 474.8950, found 474.8953.
Time profile of the photocatalytic C–H trifluoromethylation of 2a

The trifluoromethylation of 2a was performed with/without visible light irradiation. The time profile is shown in Figure S3. As a result, continuous irradiation of visible light is essential for efficient reaction. Furthermore, the result of this experiment suggests that radical chain propagation is not the main component in this reaction.

Figure S3: Time profile of the photocatalytic C–H trifluoromethylation of 2a
$\text{H, }^{13}\text{C NMR spectra}$

Assignment of stereochemistry of product 3

$^1\text{H NOESY of 3f}$
$^1$H NOESY of 3g
$^1$H NOESY 3h
$^1$H NOESY of 3l
References


$^1$H NMR of

$^{13}$C NMR of
$^1$H NMR of

$^1$C NMR of
$^1$H NMR of

$^{13}$C NMR of
\( ^1H \) NMR of

\[
\text{Boc} \quad \text{CF}_3 \\
\text{3f} \\
\text{E/Z mixture}
\]

\( ^{13}C \) NMR of

\[
\text{Boc} \quad \text{CF}_3 \\
\text{3f} \\
\text{E/Z mixture}
\]
$^1$H NMR of

3g

$EIZ$ mixture

$^{13}$C NMR of

3g

$EIZ$ mixture
$^1$H NMR of

3h

$E/Z$ mixture

$^{13}$C NMR of

3h

$E/Z$ mixture
$^1$H NMR of

E-isomer

$^{13}$C NMR of

E-isomer
$^{1}H$ NMR of

3k
$E/Z$ mixture

$^{13}C$ NMR of

3k
$E/Z$ mixture
$^1$H NMR of

\[ \text{F}_3\text{C}\cdots\text{CF}_3 \]

\[ \begin{array}{c}
\text{MeO} \\
4b \\
\text{OMe}
\end{array} \]

$^{13}$C NMR of

\[ \text{F}_3\text{C}\cdots\text{CF}_3 \]

\[ \begin{array}{c}
\text{MeO} \\
4b \\
\text{OMe}
\end{array} \]